ACID PROMOTED ONE-POT PROCESSES: EFFICIENT SYNTHESIS OF INDANONES, INDENONES, SPIRO TETRACYCLIC INDANONES, INDENES AND INDANES

Bokka Venkat Ramulu

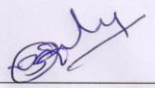
A Dissertation Submitted to
Indian Institute of Technology Hyderabad
In Partial Fulfillment of the Requirements for
The Degree of Doctor of Philosophy

Department of Chemistry

August, 2015

Declaration

I declare that this written submission represents my ideas in my own words, and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.



(Signature)

(Bokka Venkat Ramulu)

(cy10p005)

Approval Sheet

This thesis entitled **Acid Promoted One-Pot Processes: Efficient Synthesis of Indanones, Indenones, Spiro Tetracyclic Indanones and Indenes** by Bokka Venkat Ramulu is approved for the degree of Doctor of Philosophy from IIT Hyderabad.

Dec 11, 2015
Sambasivarao Kotha
Professor
Examiner

11/12/15
Dr. D. S. Sharada
Assistant Professor
Examiner

11-12-15
Dr. G. Satyanarayana
Associate Professor
Adviser

11-12-15
Dr. J. Suryanarayana
Assistant Professor
Chairman

Acknowledgements

It gives me immense pleasure to express my profound gratitude to my research supervisor **Dr. G. Satyanarayana**, for giving me an opportunity to work under his supervision in his research group. I thank him all the time for his valuable guidance, encouragement and constant motivation during my stay in the lab. I will always remain grateful to him and consider myself privileged to be associated with him.

I sincerely thank:

- Head of the Department (Prof. F. A. Khan) and other faculties of the Department of chemistry IIT Hyderabad.
- Late Prof. A. Srikrishna.
- Prof. K. R. Prasad, Prof. Martin E Maier, Dr. Dattatraya H. Dethe, Dr. Santosh J Gharpure and Dr. P. C. Ravi Kumar towards their valuable suggestions.
- Faculties during my master degree Prof. P. S. N. Reddy and Dr. Sarbani Pal,
- My B. Sc. teachers Dr. T. Veeraiah Sir, shiva Prakash Sir and Ramachandraiah Sir
- Dr. A. Gopi Krishna Reddy and Mr. Md. Samiuddin and K. Ramesh for recording NMR spectra.
- Mr. L. Mahendar (IR, HR-MS) and Mr. Md. Samiuddin (HR-MS) for recording the spectras.
- Dr. K. Ravi Kumar, Mr. Kishor Sudhir Naktode, Mr. A. Srinivas, Mr. K. Srinivas, Mr. J. Raju for X-Ray difractometer measurements and analysis of single crystal samples.
- My lab collegues Mr. Ravi Kumar, Mr. Suchand Basuli, Mr. L. Mahendar, Dr. A. Gopi Krishna Reddy, Dr. J Krishna, Mr. K. Ramesh, Ms. Niharika, Mr. Mritunjoy, Ms. Madhurima, Mr. Debyendu Das, Mr. Akash, Ms. Amrita, Ms. Jyoti and Mr. Kailash for their support, co-operation and the friendly lab environment for providing congenial atmosphere.

- Mr. Ravi Kumar and Mr. Suchand Basuli for their help during the preparation of thesis.
- My Ph.D. batchmates Dr. K. Raveendra babu, Dr. P. Suresh, Dr. V. Laxmaiah, Dr. K. Ravi Kumar, Mrs. Dr. Md. Unnisa, Mrs. Dr. Dayamani, Mrs. Dr. Remya and Mr. L. Mahendar for the memorable moments.
- All other departmental friends Mr. K. Krishna Murthy, Dr. Manoj Reddy, Dr. A. Baskar, Dr. Rambabu, Mr. Naresh, Dr. Linga Reddy, Dr. B. Narasimha Reddy, Mrs. Sranvanthi, Mr. Narendar, Dr. H. Surendar, Dr. B. M. Basavraj, Dr. A. Satyanarayana, Mr. Ch. Nagababu, Mr. K. Srinivas, Mr. K. Ramesh, Mr. Kishor, Mr. A. Srinivas, Mr. Shinde vidya charan, Mr. Anand H. Shinde, Mr. Sagar Arepally, Ms. Srilaxmi and Mr. Harinath for their help and company.
- Friends of other departments of IIT-Hyderabad Mr. Dr. V. Nageswara Rao, Y. Sudhakar Reddy, Mr. Jadav Ganesh, Mr. Seenu Seenaiah and Mr. Lokesh.
- Friends of my villages Mr. G. Srinivas, Mr. Ch. Chennaiah (Teacher), Mr. E. Narsimulu, Mr. E. Srinivas, Mr. K. Narsimulu, Mr. G. Srinivas (Teacher), Mr. B. Venkataiah, Mr. G. Ravi Kumar, Dr. D. Sai Reddy, Dr. J. Ananthaiah, Mr. K. Yellaiah (Teacher), Mr. D. Ramulu (Teacher), Mr. D. Gopal (News reporter).
- Indian Institute of Technology Hyderabad for providing facilities and the Council of Scientific and Industrial Research (CSIR) for the financial support.
- My Sir family (Dr. G. Satyanarayana, Vasantha and Varshitha)
- My dearest parents (Bheemamma and Bichaiah), My wife and daughter (Vandhana and Sai Pranavi), My brother family (Anantharamulu, Balamani, Srilatha, Srinivas and Srilekha), My sister family (Mangamma, Narsimulu and Harun Kumar), My uncle familys (B. Hanmanthu, Mogulamma and Narsamma), (B. Laxmaiah, Sain Prabha, Anuradha, Balakrishna and Ramakrishna), (K. Chandraiah, Ramulamma, Anjilaiah, Anusha and Bhagyalaxmi), (K. Venkataiah, Chennamma, Ramachandraiah, Venkatalaxmi, Hanmanthu, Manasa), My grand mothers (B. Karremma, Balaiah and K chukkamma and Hanmaiah) all of my relatives for their love and affection. Without their support, I wouldn't have been what I am today.

Dedicated to

My beloved

Parents

And

My Vandhana

Abstract

One-pot synthetic processes are considered as convenient methods to synthesize organic molecules with high degree of complexity, without isolating intermediates. These processes proved to have several advantages over step-wise operations, as it avoids the isolation of intermediate species, thereby considerably reducing the waste generation, increasing efficiency, minimizing the use of solvents, reagents, time and energy. Moreover, it was also found that in most cases the overall yields in one-pot processes are usually higher than those obtained from the corresponding step-wise operations. Herein, we have developed efficient one-pot synthetic strategies for the synthesis of 1-indanones, indenones, novel spiro-tetracyclic indanones, indenes and indanes.

The synthesis of benzocyclic ketones with varied substituents in both the aromatic and aliphatic rings of the bicyclic system remains a challenge and truly no mild and general approaches yet exist. When compared to the formation of other carbocyclic ketones, formation of 1-indanones is of particular challenge and their formation is the main focus of the research presented in this thesis. Common benzocyclic ketones containing carbonyl group at benzylic position are as shown in Figure 1.

Common benzocyclic ketones:

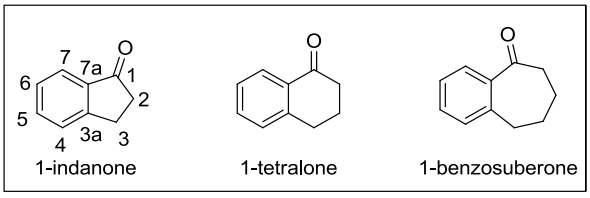


Figure 1

Both the aromatic ring and carbonyl functionalities of this diverse class of compounds can be readily exploited for synthetic manipulation. As a result, these structural motifs have proven utility in the synthesis of numerous biologically active

natural products and play a major role in medicinal chemistry and in the development of pharmaceuticals. As illustrated in Figure 2, the anti-hypertensive drug (+)-indacrinone, the sesquiditerpenoid natural product taiwaniaquinol B and the acetylcholinesterase inhibitor donepezil hydrochloride (Aricept®) are used for the treatment of Alzheimer's disease, indanones which belong to the family of pterosins are known for their cytotoxic and antibacterial activities, pauciflorol **F** also contains the 1-indanone core.

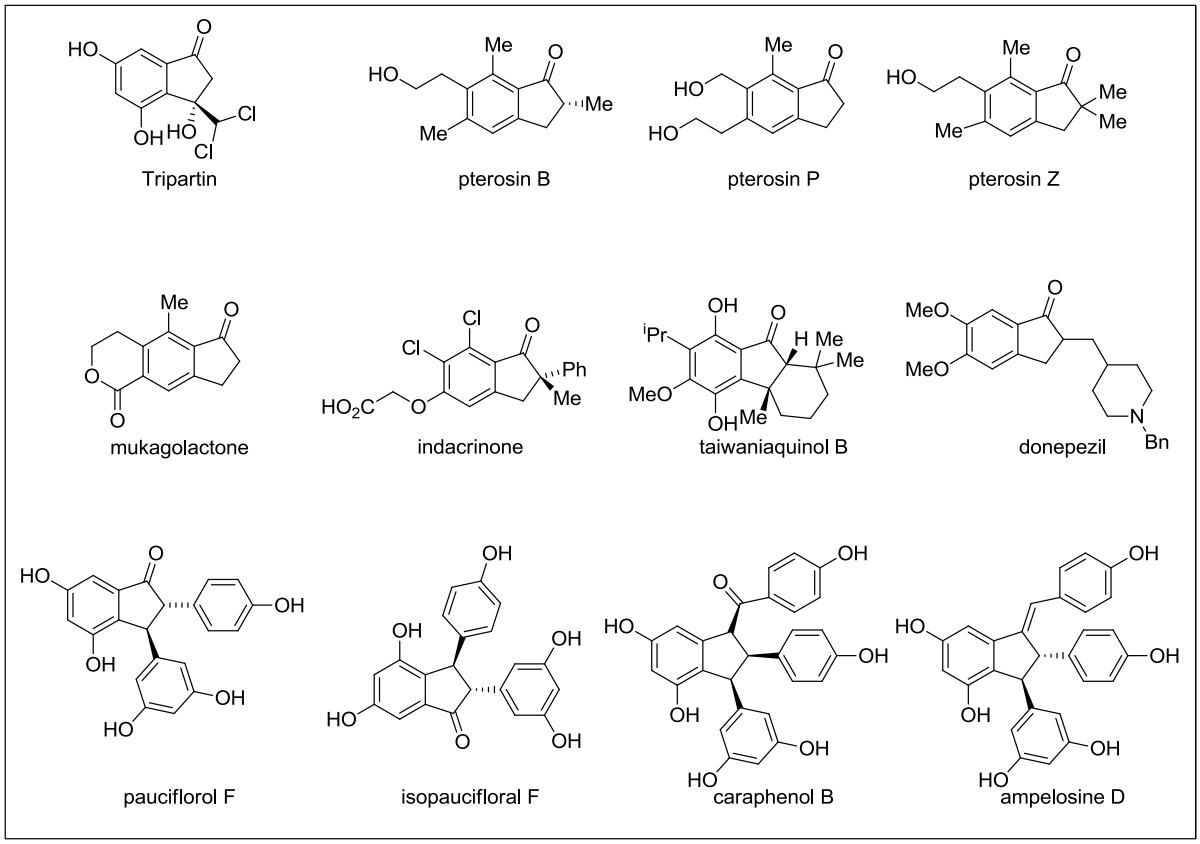


Figure 2: Naturally occurring indanones and pharmaceutically important indanone scaffolds.

Indanones in particular, constitute the structurally simple and important group of compounds in organic chemistry as their basic core is found in a variety of drugs and natural products exhibiting a broad range of biological activities. The biological

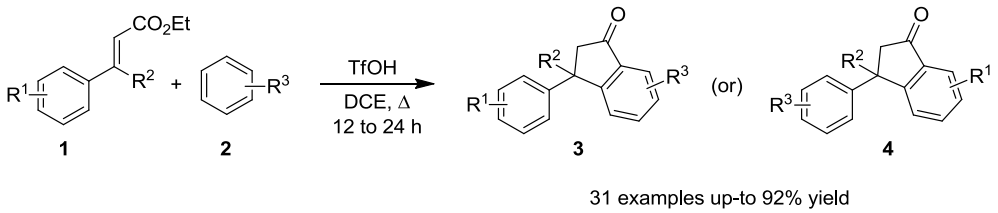
qualities of this moiety have encouraged the study of designing novel synthetic routes for its synthesis.

Usually, acid chlorides and acids were used for the Friedel-Crafts acylation reactions. To the best of our knowledge, except Meldrum's acid derivatives (activated esters) or by the use of external agents to activate esters (in case of simple esters) for acylation, there are no reports on the direct use of esters under Friedel-Crafts acylation conditions. This would be due to the relatively more inert nature of ester moiety and thus may require forceful conditions. However, unlike previous reports, we presume that the sufficiently strong acidic conditions could drive the esters to Friedel-Crafts acylation. Gratifyingly, we were quite successful in accomplishing the synthesis of various carbocyclic ketones in domino one-pot fashion under superacid promoted conditions. Majority of this thesis work (chapters 1 and 2) is focused on the Brønsted acid (superacid) mediated synthesis of indanones, indanones, novel spiro-tetracyclic indanones and indenes, starting from simple cinnamic acid derivatives. While chapter 3 of the thesis deals with the temperature dependent dimerization of styrenes to give 2,4-diaryl-4-methylpent-2-ene and cyclization of indanes under Lewis acidic conditions.

Synthesis of 1-Indanones:

With the interest in develop synthetic techniques based on acid mediated reactions, we wish to develop one-pot synthesis of indanones. Herein we have developed a simple and a practical method for the synthesis of 3-substituted indan-1-ones **3** and **4**, based on a hitherto unexplored superacid (triflic acid) mediated dual C–C bond formation, starting from simple cinnamic acid esters **1** (Scheme 1). It was observed that the reaction proceeds via initial intermolecular Friedel-Crafts alkylation (Michael addition type) and then intramolecular acylation sequence. Therefore, relatively more electron rich arene is involved in the acylation step (Scheme 1). In addition, it was proved that the reaction was smooth irrespective of the geometry of the enoate double bond, because the double bond was totally consumed by the reaction. In

addition to the spectroscopic evidence towards structural confirmation of indanones **3** and **4**, it was further unambiguously confirmed by the single crystal X-ray diffraction analysis (Figure 3).



Scheme 1

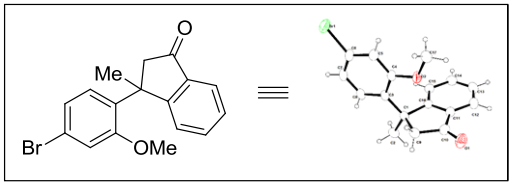
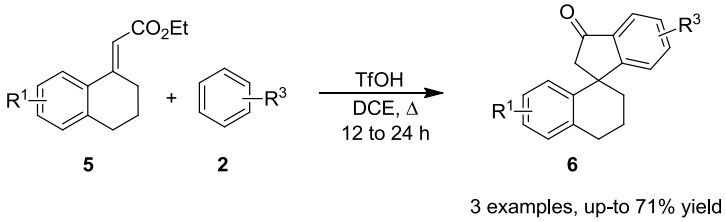


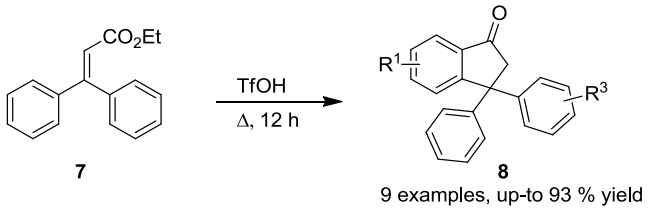
Figure 3: X-ray crystal structure of product **4**. Thermal ellipsoids are drawn at 50% probability level.

Furthermore, to check the scope and applicability of the method, the reaction was explored on cyclic equivalent of cinnamic acid ester **5**, for the synthesis of novel spirotetracyclic systems. Therefore, the enoate **5** was treated with toluene **2** as well as veratrol **2**. Delightfully, the reaction was successful at slightly lower temperature and furnished the expected novel spirotetracyclic systems **6** (Scheme 2).



Scheme 2

In addition, to check the scope and generality of the method, we focused on β-diaryl acrylate **7**. In this case, we presumed that the reactivity of the ester **7** would be high, as the double bond is more active due to β-diaryl substituents. The reaction was unsuccessful under standard reaction conditions. However, the reaction was quite successful when benzene **2** was used as the solvent as well as the external arene and gave the indanone **8** in excellent yield.



Scheme 3

Synthesis of indenones and indanones:

Among the classical reactions, for the creation of C-C bond, the Friedel-Crafts reaction turned to be one of the powerful techniques towards aromatic electrophilic substitutions. Notably, for the past few decades there have been numerous applications of this reaction under different acids (Brønsted/Lewis). Particularly, the intramolecular acylation of this protocol was found to be ideal as it constructs the carbocyclic systems, because many natural products or drugs are cyclic compounds. In this regards, indanones and indenones are essential carbocyclic compounds as they constitute natural as well as in pharmaceutical products. Some of the biologically important natural and unnatural indenones are shown in Figure 4.

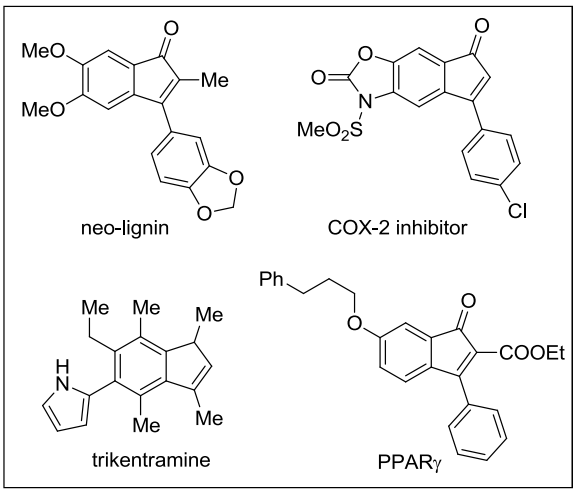
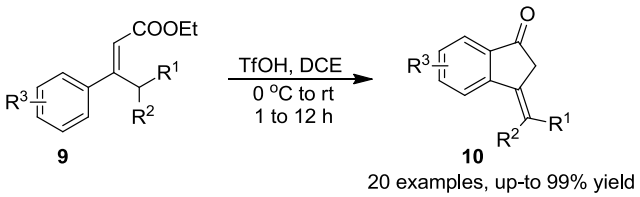


Figure 4: Naturally occurring and pharmaceutically important indenones.

The successful one-pot accomplishment of indanones encouraged us to further develop on this concept. Therefore, we thought that direct treatment of the cinnamic acid esters in the presence of superacid would furnish indenones. Interestingly, as anticipated, the reaction of esters **9** with TfOH, gave indenone products. Surprisingly, in all resulting indenones, the olefin bond is rearranged to *exo* position of the five membered rings. Notably, this phenomenon was further supported by the previous reports of indenone synthesis (Scheme 4). In addition to the spectroscopic data for their structure confirmation, the X-ray diffraction analysis unambiguously confirmed the skeletal structure and also the geometry of the double bond (Figure 5).



Scheme 4

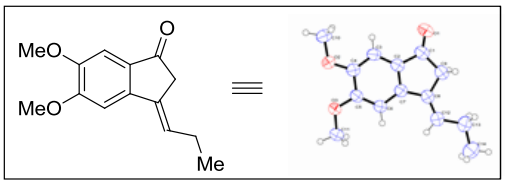
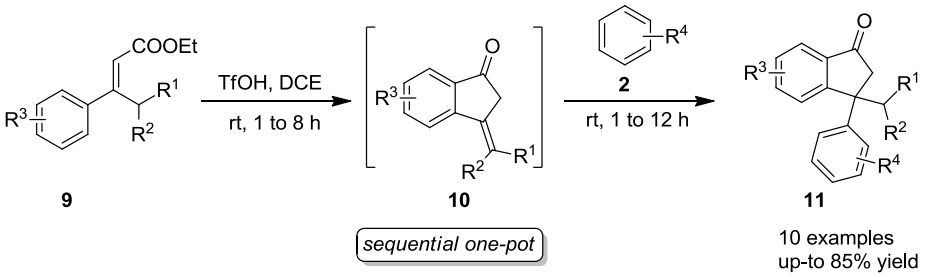


Figure 5: X-ray crystal structure of product **10**. Thermal ellipsoids are drawn at 50% probability level.

After the successful synthesis of indenones **10**, to further extend the method, the synthesis of substituted indanones containing quaternary carbon atom was planned in a sequential one-pot manner. It was anticipated that treatment of in-situ generated indenone **10** with an external arene would deliver indanones in a complimentary mode to our previous method for the synthesis of indanones. Gratifyingly, the sequential one-pot reaction was amenable to the synthesis of indanones **11** (Scheme 5). Significantly, this sequential one-pot method, unlike our previous report, enabled us to achieve indanones **11**, wherein, the external arene was limited only to the Friedel-Crafts alkylation irrespective of its electron poor or rich nature.



Scheme 5

Synthesis of spiro tetra cyclic indanones and indenes:

In continuation with the development of one-pot protocols, we have also developed the superacid mediated synthesis of novel spiro-tetracyclic indanones, ubiquitous core structures of alkaloid natural product-like systems, especially,

spiroindanone scaffolds, which are known for their anti-mycobacterial properties (Figure 6). Notably, many of them have shown comparable or even better activities than some of the fist-line tuberculosis drugs. The spiro[indene-1,1′-indane]-5,5′-diol as a new framework for estrogen receptor ligands. Due to their interesting biological activities, we tried to combine the indanone frameworks in the form of novel spiro-tetracyclic scaffolds.

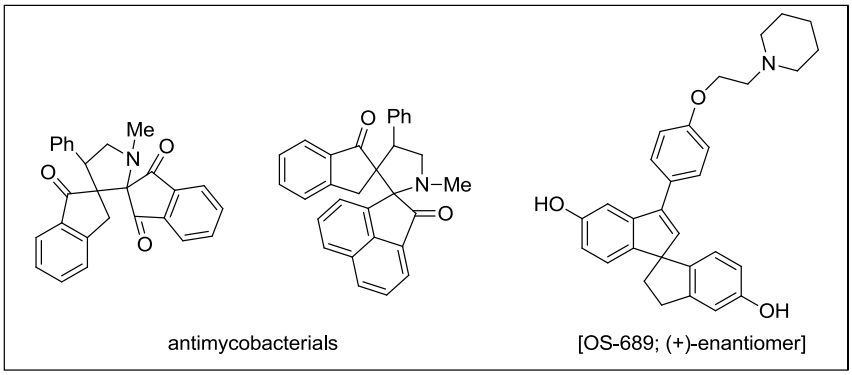
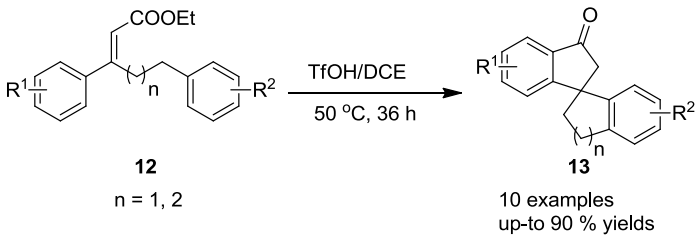


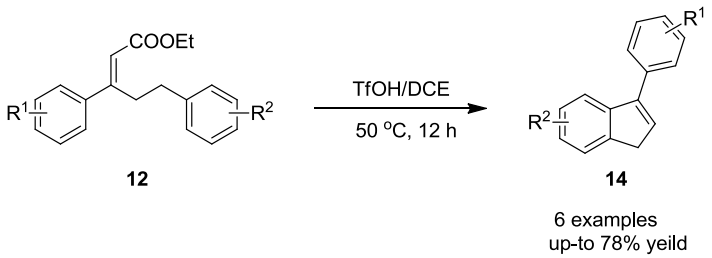
Figure 6: Naturally occurring and pharmaceutically important spiro-cyclic indanones/indenes.

Our plan for the construction of spiro-cyclic indanone structures was based on intramolecular Friedel-Crafts alkylation/acylation strategy. When the ester moiety has pendant aryl groups, they may have the capability of undergoing a second cyclization, leading to spiro-cyclic indanones. To our delight, the reaction of the esters **12**, smoothly furnished the respective spirocyclic products **13** (Scheme 6).



Scheme 6

Surprisingly, when β-aryl group has electron deactivating groups such as fluoro, chloro and bromo substituent, the reaction took different mechanistic path and gave aryl-indenes **14** as the final products (Scheme 7). This may be due to the low reactivity of the β-aryl moiety that would not prefer acylation, rather allowing the fragmentation of the ester group followed by internal rearrangement.



Scheme 7

Synthesis of indanes and dimerization alkenes:

The indane ring system is an attractive scaffold for biologically active compounds due to the combination of aromatic and aliphatic properties fused together in one rigid system. This bicyclic structure provides a wide range of possibilities to incorporate specific substituents in different directionalities, thus being an attractive scaffold for medicinal chemists. Notably, many indane-based compounds are being used in the clinic to treat various diseases, such as indinavir, an HIV-1 protease inhibitor; indantadol, a potent MAO-inhibitor; the amine uptake inhibitor indatraline, and the ultra–long–acting β-adrenoreceptor agonist indacaterol (Figure 7). Given the diversity of targets these drugs act on, one could argue that the indane ring system is a privileged substructure, just like indole, the nitrogen atom containing unsaturated version of it.

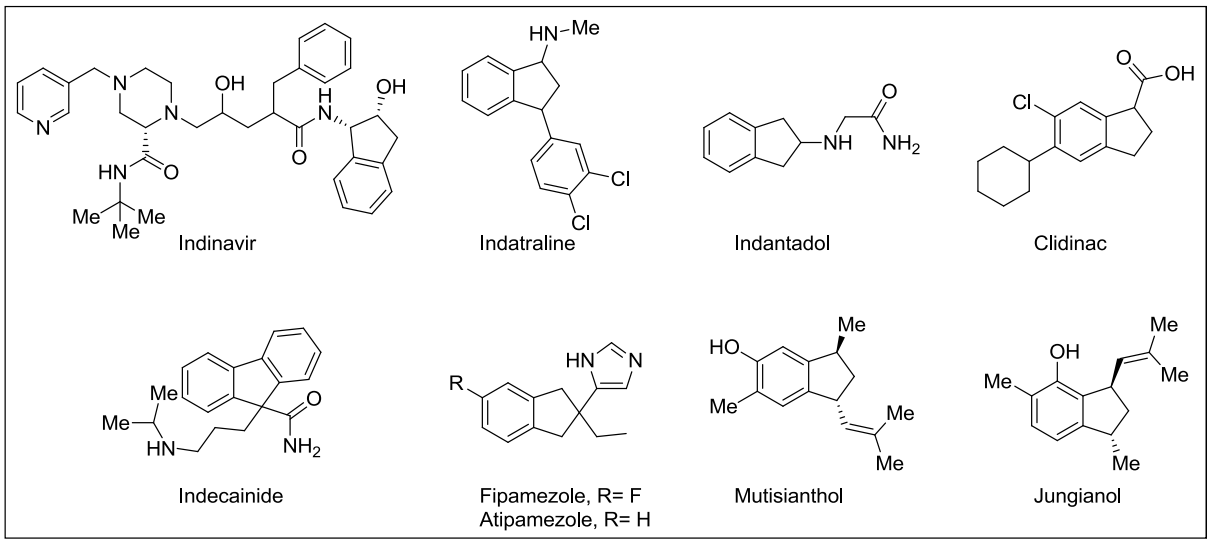
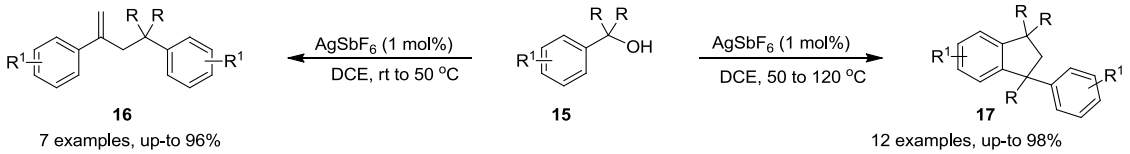


Figure 7: Naturally occurring indanes and pharmaceutically important indane scaffolds.

Several Lewis acids, including $FeCl_3$, $AlCl_3$, $BiCl_3$, $RuCl_3$ and also Brønsted acids have been reported to catalyze this reaction for the synthesis of indanes. Though there were good number of protocols for the synthesis of indanes, starting from either styrenes or from tertiary benzyl alcohols, most of them were carried out under strong acidic or harsh conditions. This ultimately limits the applicability of the method, particularly when the arene is electron rich. Therefore, a mild and selective method is always preferred for wide applicability of the method. In this regard, we have developed a mild approach for the selective formation of 2,4-diaryl-4-methylpent-2-enes and indanes. The reaction proceeds with Markovnikov selectivity in both C–C bond-forming steps. Unsaturated dimer is an important chain transfer reagent in the production of polymers. Due to the importance of being able to generate the dimerization product selectively, a chemoselective reaction pathway to generate either dimerized olefin product **16** or cyclized indane **17** has been developed at the temperature at which the reaction was performed (Scheme 8). However, the reaction outcome was dependent on the temperature. When the reaction was run at RT to 50 ^{o}C, the dimeric products **16** were formed exclusively in near quantitative yields. When the reaction was performed at 50 ^{o}C to 120 ^{o}C, indanes **17** were obtained in excellent yields. The fact that the reaction was impeded after the dimerization at lower

temperatures implies that these are kinetic products **16** and the indanes **17** are the thermodynamic products. This mild Lewis acidic method allows the formation of indanes even from electron rich aromatic rings that may otherwise be impossible or difficult to achieve.



16
7 examples, up-to 96%

15

17
12 examples, up-to 98%

Scheme 8

LIST OF ABBREVIATIONS

Ac	:	acetyl
Anal	:	analysis
Anhy	:	anhydrous
APCI	:	atmospheric pressure chemical ionization
Ar	:	aryl
aq	:	aqueous
Bn	:	benzyl
br. s	:	broad singlet
calcd	:	calculated
cm	:	centi meter
cy	:	cyclohexyl
CPD	:	carbon proton decoupling
DCE	:	dichloro ethane
DCM	:	dichloro methane
dd	:	doublet of doublet
ddd	:	doublet of doublet of doublet
dt	:	doublet of triplet
DIPA	:	N,N-diisopropyl amine
DMA	:	N,N-Dimethyl acetamide
DMF	:	N,N-dimethyl formamide
DMSO	:	dimethyl sulfoxide
equiv	:	equivalents
Et	:	ethyl
ESI	:	electron spray ionization
Fig.	:	figure
g	:	gram(s)

h	:	hour(s)
HR-MS	:	high resolution mass spectrum
Hz	:	Hertz
^{i}pr	:	iso propyl
IR	:	infrared
Liq	:	liquid
Lit.	:	literature
m	:	multiplet
Me	:	methyl
mg	:	milli gram(s)
MHz	:	mega hertz
min	:	minute(s)
mL	:	milli liter(s)
mmol	:	milli mole(s)
M.P	:	melting point
MS	:	molecular seives
NMR	:	Nuclear Magnetic Resonance
ph	:	phenyl
q	:	quartet
R_f	:	Retention factor
rt	:	room temperature
sept	:	septet
t	:	triplet
TEBAC	:	triethylbenzylammonium chloride
TEPA	:	triethyl phospano acetate
^{t}Bu	:	tertiary butyl
tert	:	tertiary
TFA	:	trifluoroacetic acid
TfOH	:	trifluoromethanesulfonic acid

THF	:	tetrahydrofuran
TLC	:	thin layer chromatography
UV	:	ultra violet

Contents

CHAPTER I

Superacid Promoted Dual C-C Bond Formation by Friedel-Crafts Alkylation/Acylation of Cinnamate Esters: Synthesis of Indanones

I.1 INTRODUCTION:

One-pot synthetic methods are considered to be the most useful procedures in organic synthesis, since they allow construction of more than one bond in a single operation without the need to isolate intermediates.[1] These processes proved to have several advantages over step-wise operations, as it avoids the isolation of intermediate species, thereby considerably reducing the waste generation, increasing efficiency, minimizing the use of solvents, reagents and saving time and energy. Moreover, it was also found that in most cases the overall yields in one-pot processes are usually higher than those obtained from the corresponding step-wise operations. Therefore, the development of such one-pot processes which involve formation of multiple C–C bonds, particularly to construct cyclic structures, are of great interest because many cyclic structures are identified as core structures of several biologically active natural products.

In this context, the Friedel-Crafts reaction is considered as one of the most classical and powerful methods for forming C–C bond through alkylation or acylation reactions invented by Friedel and Crafts in 1877.[2] Notably, in the last few decades this reaction has been enormously

exploited using various acids (Brønsted and Lewis).[3-5] Significantly, the synthesis of cyclic systems via single or multiple C–C bond formation illustrates the power of the Friedel-Crafts reaction.[6] Friedel-Crafts alkylation has been widely exploited in terms of the variations in the catalysts leading to the reshaping of classical conditions. Some of the commonly used Lewis acids are $AlCl_3$, $FeCl_3$, BF_3•OEt_2, $TiCl_4$ and $SnCl_4$. Afterwards, implementation of superelectrophiles came into light by Olah's research work in the seventies.[7] made use of superelectrophiles and dicationic electrophiles to construct ring systems efficiently, because they are more reactive were followed by the implementation of triflates of the rare earth metals and other protic acids. Gold and iron Lewis acid catalysts have also been extensively implemented in the enhancement of the feasibility of Friedel-Crafts reaction. Olah et al. introduced the superelectrophiles after which the superelectrophiles and dicationic electrophiles were widely applied for synthesis of ring systems. Recently, the research group of Hashmi et al.[8] reported the use of gold Lewis acid catalysts in the Friedel-Crafts reaction. Later, D. A. Klumpp et al.[9] showed the potency of triflic acid in performing multiple cyclizations. Since then triflic acid and triflates have drawn extreme focus in cyclization reactions. Common benzocyclic ketones containing the carbonyl group at benzylic position are as shown in Figure I.1.[10]

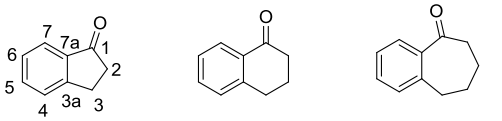


Figure I.1

The implementation of the Friedel-Crafts reaction for the formation of cyclic compounds has often gained recognition and has led to the formation of various biologically important moieties like the indanones and indenes. Particularly, indanones constitute the structurally simple and important group of compounds in organic chemistry, as their basic core is found in a variety of drugs and natural products exhibiting a broad range of biological activities. The biological properties of this moiety have encouraged the study of designing novel synthetic routes for its synthesis.

Both the aromatic ring and carbonyl functionalities of this diverse class of compounds can be readily exploited for synthetic manipulation. As a result, these structural motifs have

proven utility in the synthesis of numerous biologically active natural products and play a major role in medicinal chemistry and in the development of pharmaceuticals. As illustrated in Figure I.2,[11] the anti-hypertensive drug (+)-indacrinone, the sesquiditerpenoid natural product taiwaniaquinol B, and the acetylcholinesterase inhibitor donepezil hydrochloride (Aricept®) used for the treatment of Alzheimer's disease, indanones which belong to the family of pterosins, known for their cytotoxic and antibacterial activities all contain a 1-indanone core.

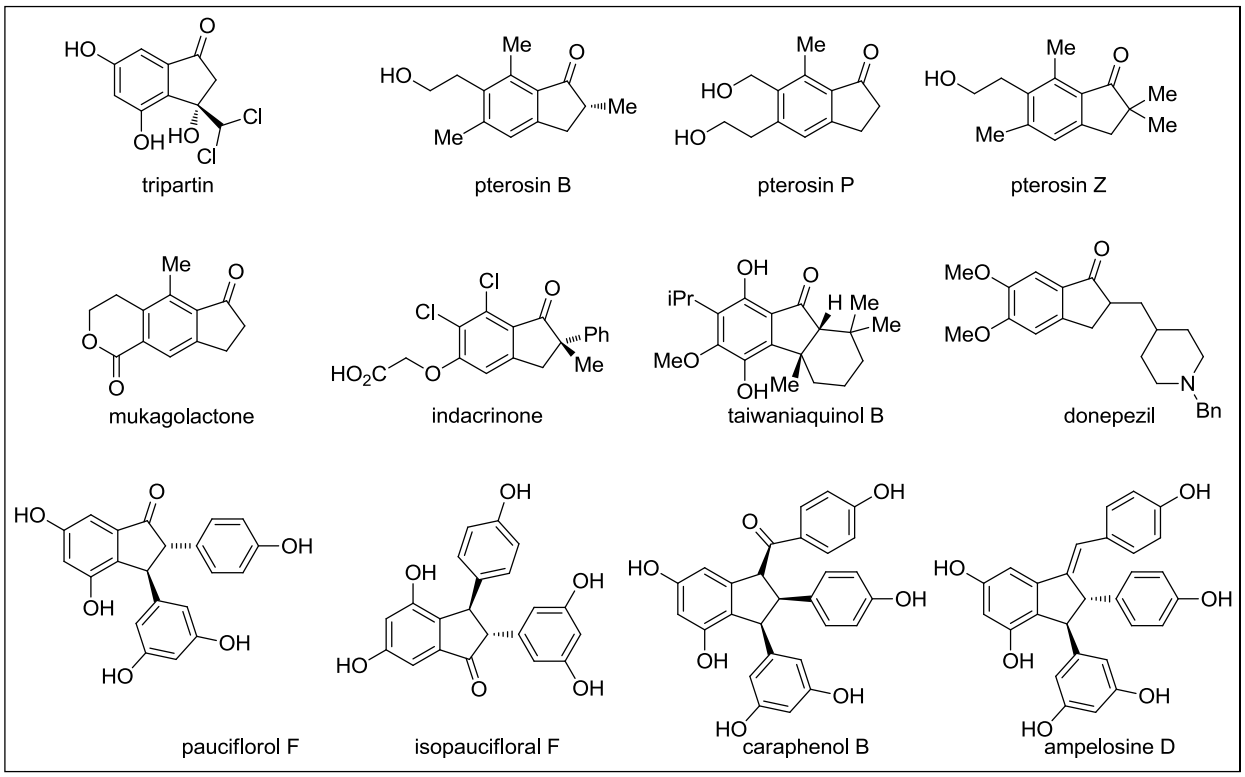


Figure I.2: Naturally occurring indanones and pharmaceutically important indanone scaffolds.

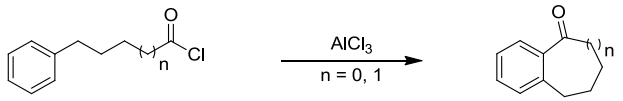
The synthesis of benzocyclic ketones with varied substituents in both the aromatic and aliphatic rings of the bicyclic system remains a challenge and no truly mild and general approach yet exists. 1-Indanones are a particular challenge and their formation is the main focus of the research presented in this thesis. Thus far, there are a number of unique approaches that have been explored, for the synthesis of indanones.

I.2 BACKGROUND:

Due to the relative abundance of the indanone core in natural products having interesting biological activities, number of synthetic approaches has been reported for the synthesis of the 1-indanone ring system. Majority of the methods for the synthesis of 1-indanones are based on Friedel-Crafts reaction. The classical intramolecular Friedel-Crafts acylation involves the reaction of an acyl halide or carboxylic acid with a tethered arene promoted by either Lewis or Brønsted acids. Reacting aromatic ring with an acyl chloride in combination with strong Lewis acids such as $AlCl_3$, $FeCl_3$, $TiCl_4$ and $SnCl_4$ etc. is one of the most common acylation procedures.

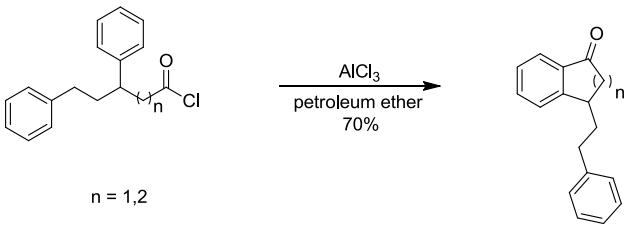
I.2.1 Intramolecular Friedel–Crafts acylations mediated by Lewis acid(s):

In 1926 the research group of J. Braun and G. Manz reported an efficient method for the synthesis of tetralone and benzsuberone employing intramolecular Friedel-Crafts acylation using $AlCl_3$ (Scheme I.1).[12]



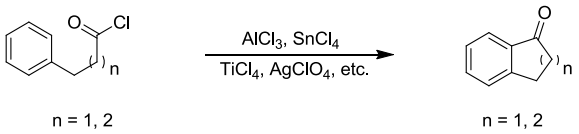
Scheme I.1

In 1965, R. M. Robery et al.[13] presented an efficient method for the synthesis of indanones and tetralones. The reaction proceeds through preferential formation of indanones over benzsuberone via Friedel-Crafts acylation (Scheme I.2).



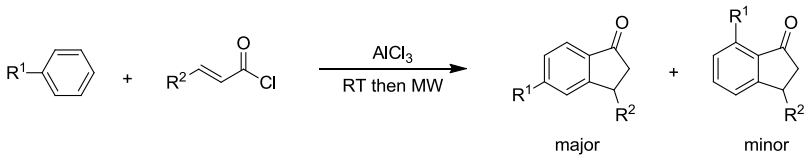
Scheme I.2

Intramolecular Friedel-Crafts acylation of carboxylic acid chloride derivatives in the presence of a strong Lewis acid such as $AlCl_3$, $TiCl_4$, $SnCl_4$ and $AgClO_4$ is one of the most common acylation procedures, for the synthesis of indanones and tetralones (Scheme I.3).[14]



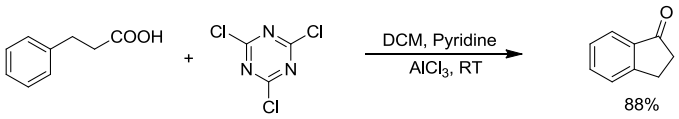
Scheme I.3

The research group of Yuan Ma in 2006 disclosed a tandem Friedel-Crafts acylation and Nazarov cyclization of arenes and α, β-unsaturated acyl chlorides promoted by aluminum chloride, a series of 1-indanones were synthesized in good yields (Scheme I.4).[15]



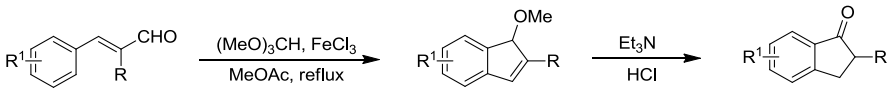
Scheme I.4

C. O. Kangani et al.[16] reported a mild method for Friedel-Crafts acylation with aromatic and aliphatic carboxylic acids using cyanuric chloride, pyridine, and $AlCl_3$ was developed. Both inter and intramolecular acylations were accomplished at room temperature in high yields and in very short reaction times (Scheme I.5).



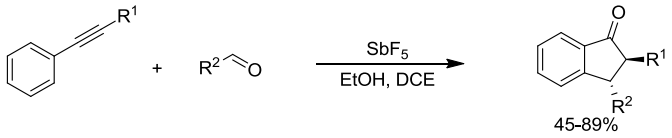
Scheme I.5

In 2007 Gary B. Womack developed the conversion of 2-alkylcinnamaldehydes to 2-alkylindanones via catalytic intramolecular Friedel-Crafts reaction (Scheme I.6).[17]



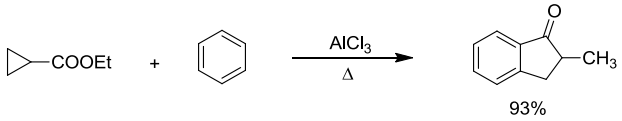
Scheme I.6

Akio Saito et al.[18] reported a novel one-pot approach for the synthesis of indanones through Sb(V)-catalyzed reaction of phenylalkynes with aldehydes. Notably, this reaction stereoselectively afforded the corresponding 2,3-disubstituted indanones as a single *trans*-isomer (Scheme I.7).



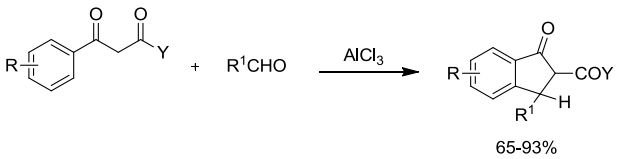
Scheme I.7

The reaction of ethyl cyclopropanecarboxylate with benzene in the presence of aluminum chloride, gave 2-methyl-1-indanone in excellent yield (Scheme I.8).[19]



Scheme I.8

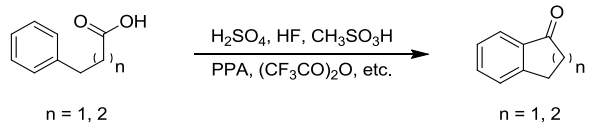
Aryl substituted 1,3-dicarbonyl compounds react with non-enolizable aldehydes in the presence of C_2H_5MgBr or $AlCl_3$ affording 2-carbethoxy and 2-acetyl-1-indanones via tandem Knoevenagel condensation-cycloalkylation process (Scheme I.9).[20]



Scheme I.9

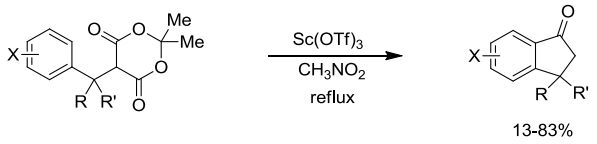
I.2.2 Intramolecular Friedel-Crafts acylations mediated by Brønsted acid(s):

The Friedel-Crafts dehydrative acylation with carboxylic acids has been promoted by polyphosphoric acid, methanesulfonic acid, HF, dehydrating agent P_2O_5, trifluoroacetic anhydride and trifluoromethanesulfonic anhydride, which is one of the most common acylation procedures for synthesis of indanones and tetralones (Scheme I.10).[21]



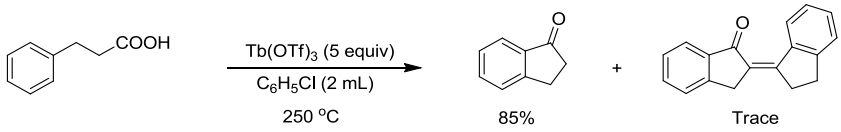
Scheme I.10

Eric Fillion in 2003 showed the synthesis of indanones employing intramolecular Friedel−Crafts acylation of benzyl Meldrum's acids using catalytic amount of $Sc(OTf)_3$ under mild reaction conditions. This protocol enabled the synthesis of various polysubstituted 1-indanones (Scheme I.11).[22]



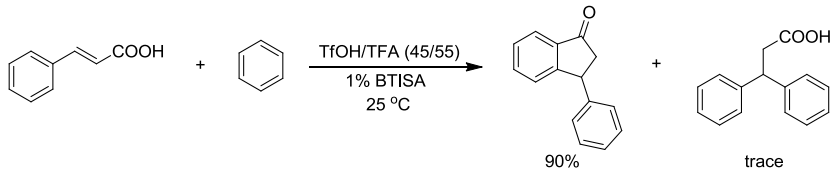
Scheme I.11

Shigeru Shimada et al. in 2004, presented intramolecular Friedel–Crafts acylation reaction of 3-arylpropionic acids catalyzed by $Tb(OTf)_3$ at 25 ^oC, for the preparation of indanones. Significantly, this protocol was also successful for even deactivated 3-arylpropionic acids with halogen atoms on the aromatic ring (Scheme I.12).[23]



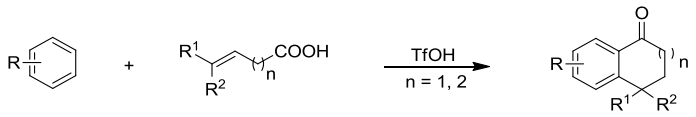
Scheme I.12

The Friedel-Crafts bimolecular cyclizations of cinnamic acid or cinnamoyl chloride with aromatic compounds under strong and superstrong acids along with 1 mol% BTISA, furnished indanones (Scheme I.13).[24]



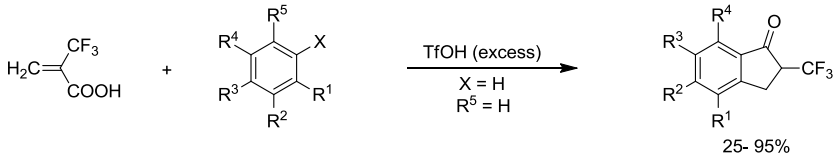
Scheme I.13

In 2003 George A. Olah reported superacid (trifluoromethanesulfonic acid) induced synthesis of 1-indanone and 1-tetralone derivatives through Friedel-Crafts alkylation/cycloacylation of aromatics with unsaturated carboxylic acids. Depending on the reactants used, different substituted indanones and tetralones were obtained, in moderate to good yields (Scheme I.14).[25]



Scheme I.14

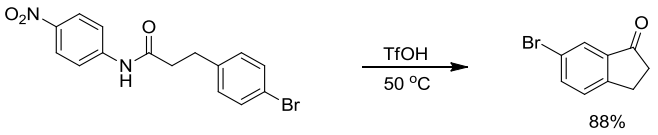
The same research group reported an efficient one-pot synthesis of indanones and dihydrocoumarins through Friedel-Crafts alkylation or tandem Friedel-Crafts alkylation/cycloacylation of arenes with 2-(trifluoromethyl) acrylic acid under superacidic conditions using trifluoromethanesulfonic acid (Scheme I.15).[26]



Scheme I.15

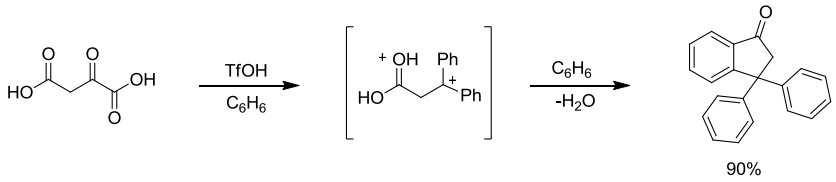
The Friedel-Crafts acylation is usually performed with carboxylic acid chlorides or anhydrides, while amides are generally not useful substrates in these reactions. Despite being the

least reactive carboxylic acid derivative, Douglas A. Klumpp and colleagues found a series of amides capable of providing indanones in good yields involving diminished C–N resonance through superelectrophilic activation and subsequent cleavage to acyl cations (Scheme I.16).[27]



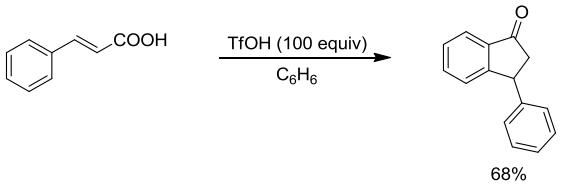
Scheme I.16

The electrophilic chemistry of α-ketosuccinic acid was also examined. When α-ketosuccinic is reacted with C_6H_6 in TfOH, indanone was obtained as the major product (Scheme I.17).[28]



Scheme I.17

Klumpp et al. achieved the synthesis of indanones in 2003 by the Friedel-Crafts alkylation/cycloacylation of cinnamic acids. However, the reaction made use of large excess of super acid (100 equiv) (Scheme I.18).[29]

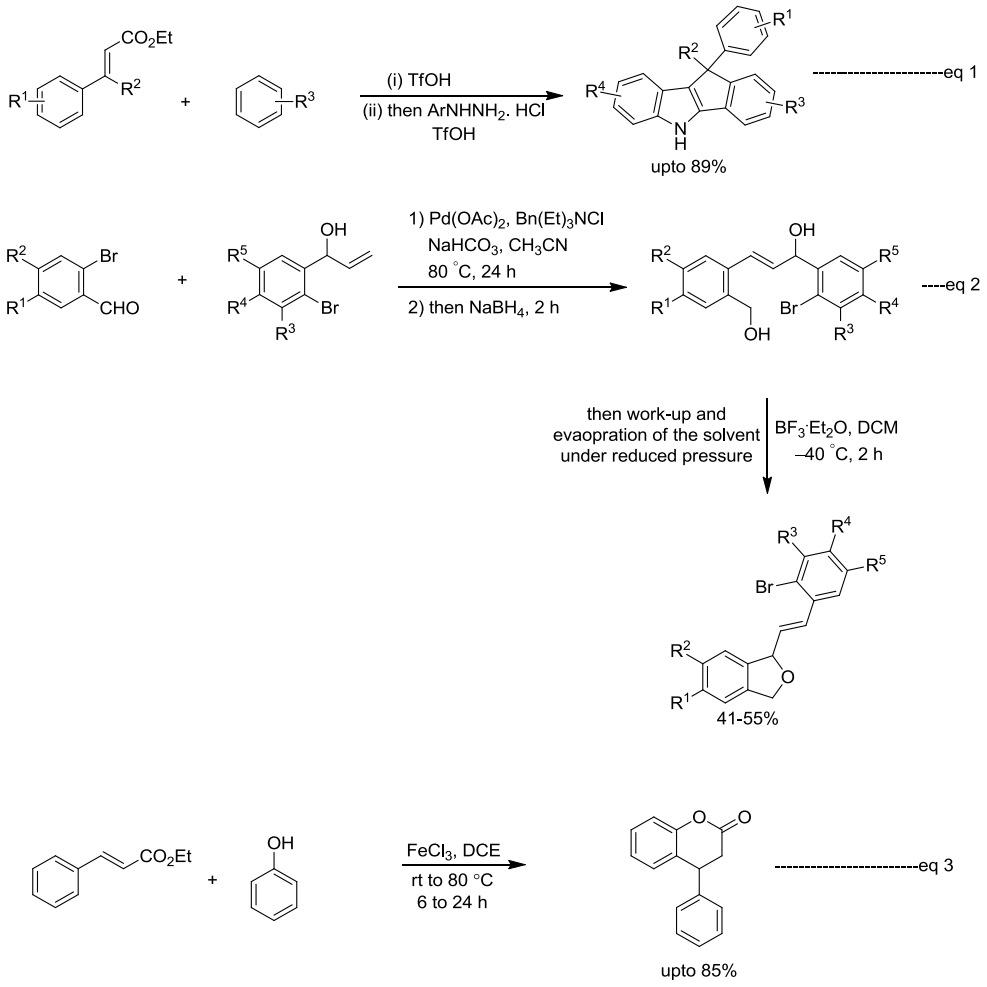


Scheme I.18

Recently, from our research group, we also have disclosed acid catalyzed efficient domino protocols for the synthesis of complex molecules in domino one-pot or sequencial domino one-pot

operations. Notabaly, these one-pot processes enabled the efficient synthesis of structurally novel heterocyclic compounds (Scheme I.19, equations 1 to 3).[30]

Acid catalysis:

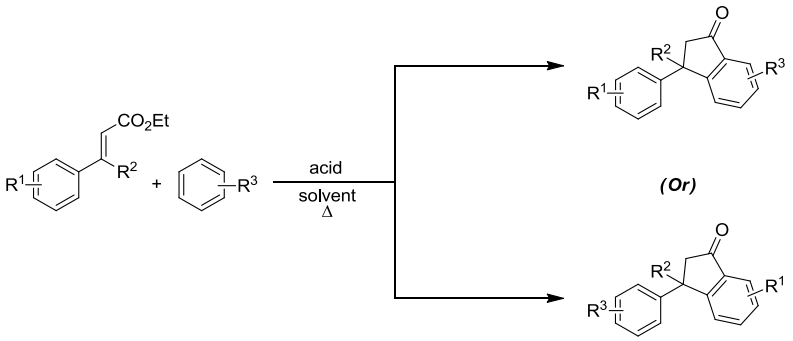


Scheme I.19

I.3. RESULTS AND DISCUSSION:

I.3.1 Synthesis of indanones via acid mediated catalysis:

With this background and based on our research interest on domino/sequential one-pot domino processes, we became interested to explore the acid promoted reaction of β-alkyl cinnamic acid esters. The inspiration behind this study is to accomplish one-pot synthesis of indanones from simple β-alkyl cinnamic acid esters, in the presence of external arene, under acidic conditions. The anticipated reaction path for the formation of dual C–C bond via intermolecular Friedel–Crafts alkylation (Michael addition type)/intramolecular Friedel–Crafts cycloacylation. Certainly, Friedel–Crafts alkylation take place by the external arene, while the cycloacylation step is dependent on the electronic nature of both the aromatic rings. Presumably, relatively more electron rich arene would preferably participate in the cycloacylation reaction (Scheme I.20).

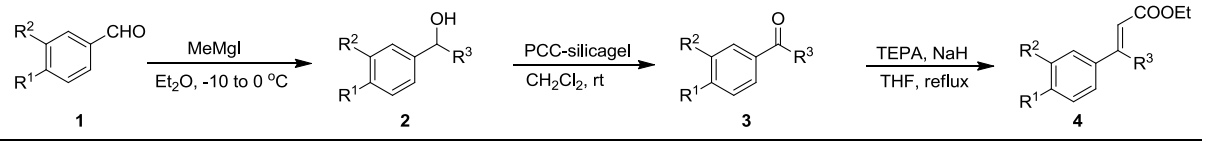


Scheme I.20

Thus, the synthetic study was initiated with the preparation of cinnamic acid esters **4** from benzaldehydes **1** and alkyl-aryl ketones **3**. Initially the synthesis of alkyl-aryl ketones **3** was aimed at. Hence, addition of alkyl (ethyl or methyl) Grignard reagent to benzaldehydes **1**, gave the corresponding secondary alcohols **2** (82-98%, Table I.1). Oxidation of the resulting secondary alcohols **2** with PCC-silica gel, furnished the ketones **3** in good to excellent yields (73-97%, Table I.1). The required cinnamic acid esters **4** were prepared from benzaldehydes **1** or

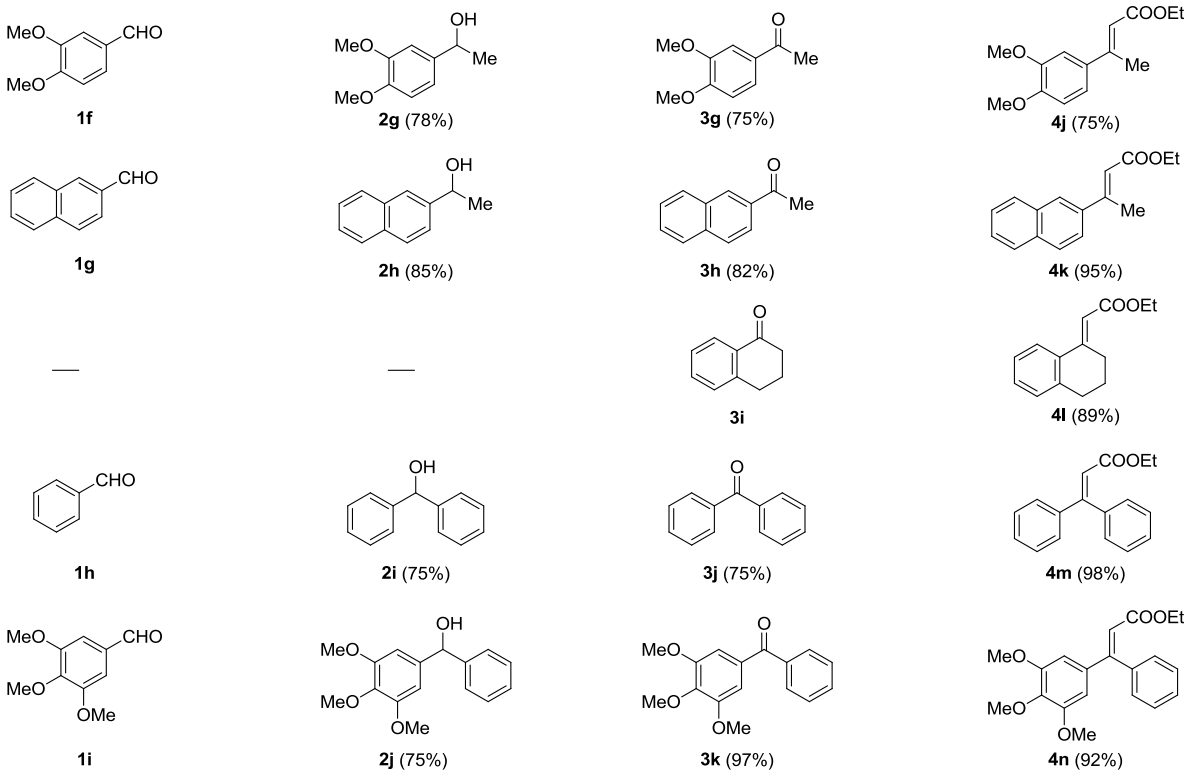
alkyl aryl ketones **3** using standard Wittig–Horner–Wadsworth–Emmons reaction, in good to excellent yields (73-98%, Table I.1).

Table I.1: Synthesis of cinnamic acid ester **4a**-**4n** from corresponding benzaldehydes **1a-1i** and alkyl aryl ketones **3a-3k**.[a]



1 **2** **3** **4**

1a	—	—	**4a** (89%)
1b	—	—	**4b** (86%)
1c	—	—	**4c** (90%)
1a	**2a** (96%)	**3a** (95%)	**4d** (92%)
1a	**2b** (92%)	**3b** (90%)	**4e** (88%)
1b	**2c** (84%)	**3c** (82%)	**4f** (88%)
1b	**2d** (98%)	**3d** (97%)	**4g** (90%)
1d	**2e** (93%)	**3e** (91%)	**4h** (87%)
1e	**2f** (85%)	**3f** (84%)	**4i** (90%)



[a]Yields in the parentheses are isolated yields of chromatographically pure products.

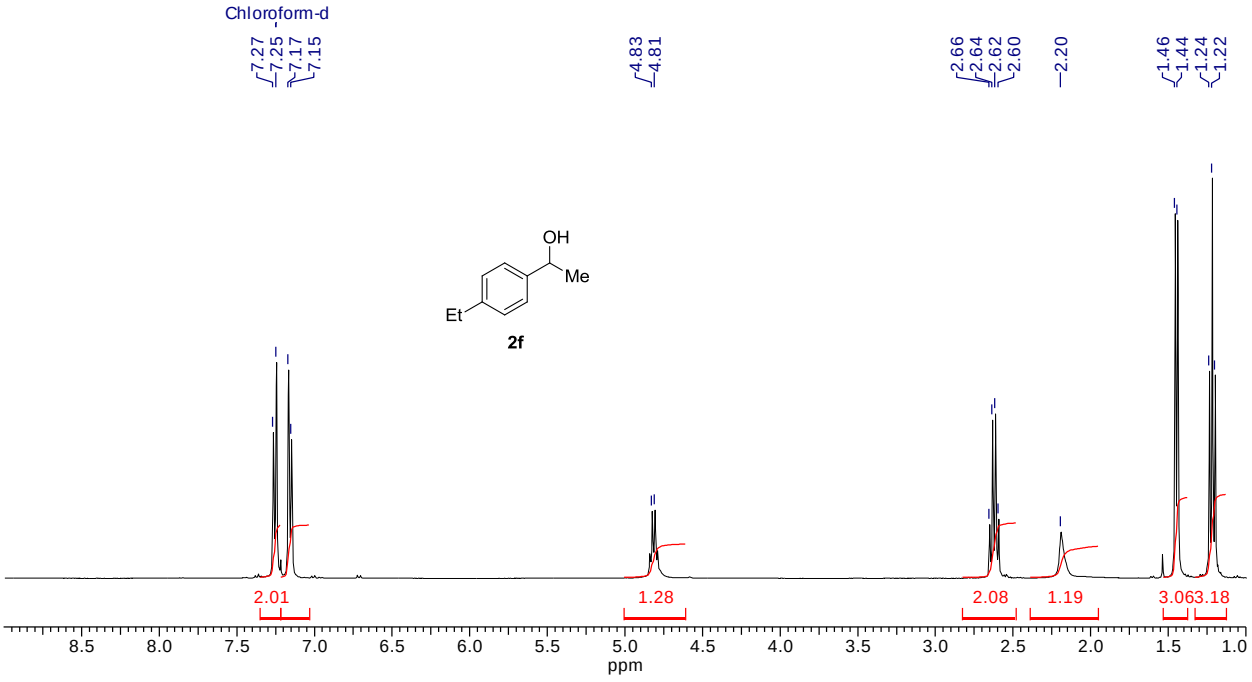


Figure I.3: ^{1}H-NMR (400 MHz) spectrum of **2f** in $CDCl_3$

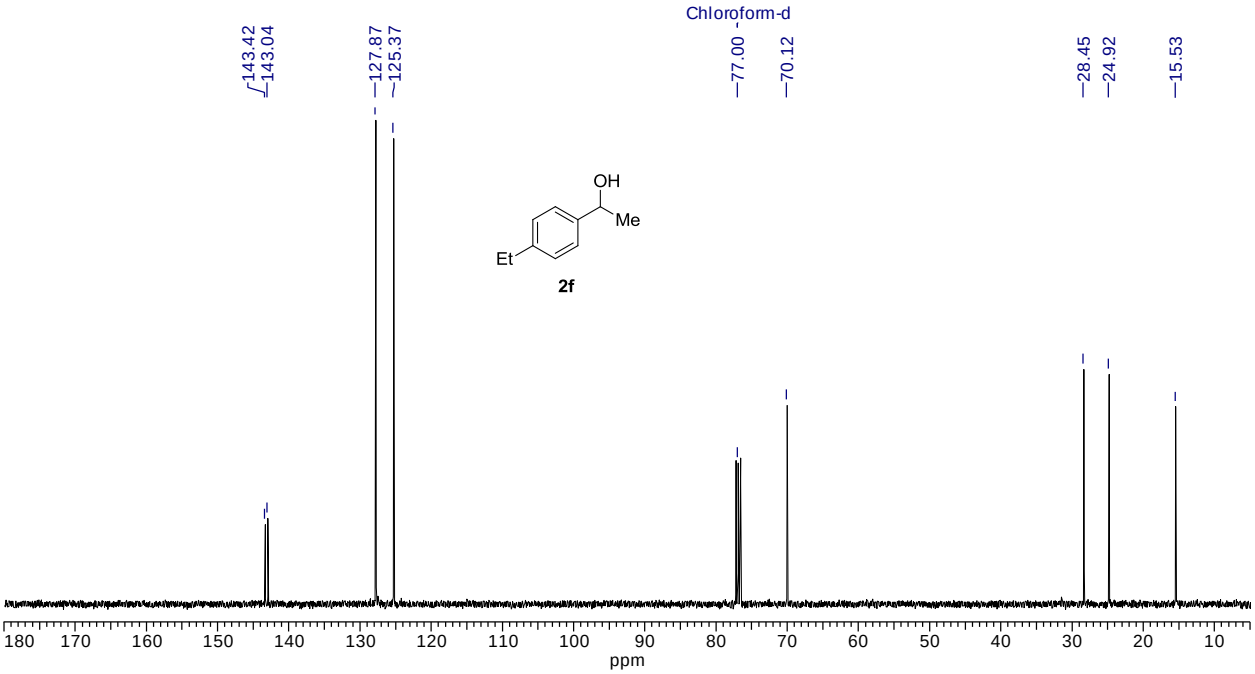


Figure I.4: ^{13}C-NMR (100 MHz) spectrum of **2f** in $CDCl_3$

The structure of 1-(4-ethylphenyl) ethanol **2f** was confirmed from its spectral data. IR spectra show the absence of the absorption band due to carbonyl stretching of aldehyde group and presence of broad absorption band due to OH stretching at 3351 cm^{-1}. In the ^{1}H-NMR spectrum (Figure I.3), presence of two doublets at δ 7.27 (*J*=7.8 Hz) and δ 7.17 (*J*=7.8 Hz) due to four aromatic protons, presence of one quartate at δ 4.83 (*J*=6.4 Hz) due to one benzylic methine proton, presence of one quartate at δ 2.64 (*J*=7.8 Hz) due to one methylene protons of ethyl group, presence of one broad singlet at δ 2.20 due to one hydroxyl group, presence of one doublet at δ 1.46 (*J*=6.4 Hz) due to three protons of methyl group, presence of one triplet at δ 1.22 (*J*=7.8 Hz) due to methyl protons of ethyl group, established the structure of alcohol **2f**. In 8 lines ^{13}C-NMR spectrum (Figure I.4), presence of two quaternary carbons at δ 143.4 and 143.0 due to aromatic carbons, four aromatic methine carbons at δ 127.9 (2C) and 125.4 (2C), one benzylic methine carbon at δ 70.1, one methylene carbon at δ 28.5, presence of two methyl carbons at δ 24.9 and 15.5 ppm, confirmed the structure of alcohol **2f**.

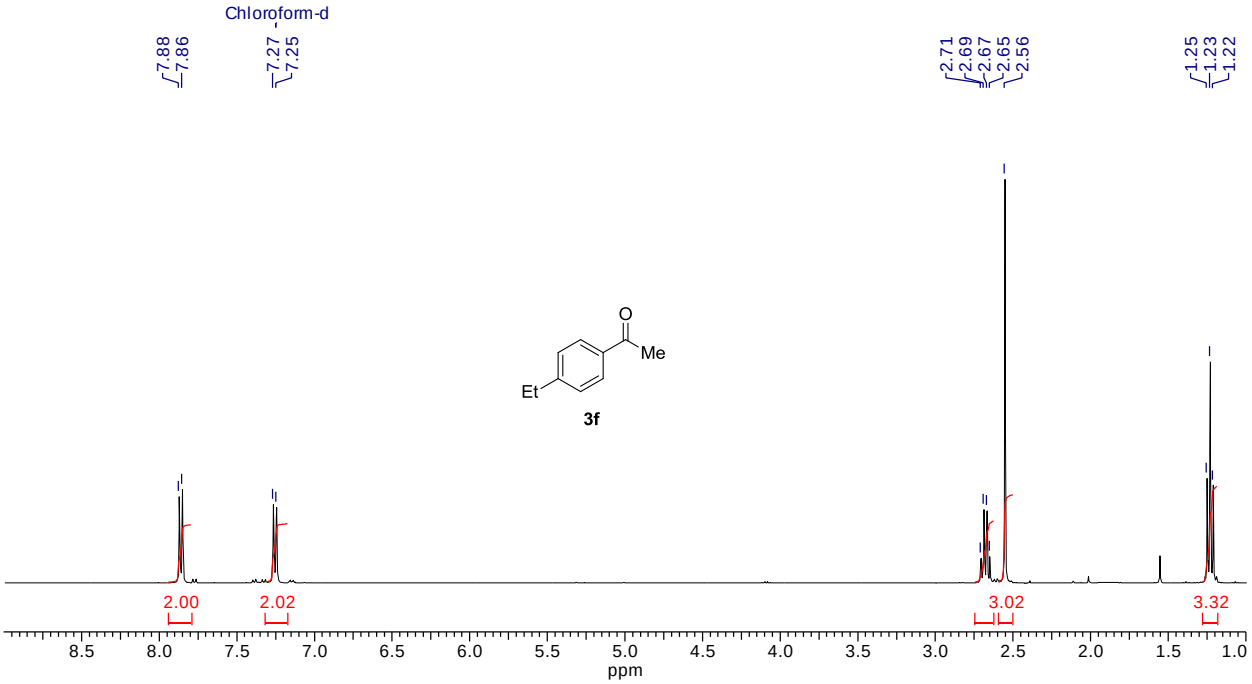


Figure I.5: ^{1}H-NMR (400 MHz) spectrum of **3f** in $CDCl_3$

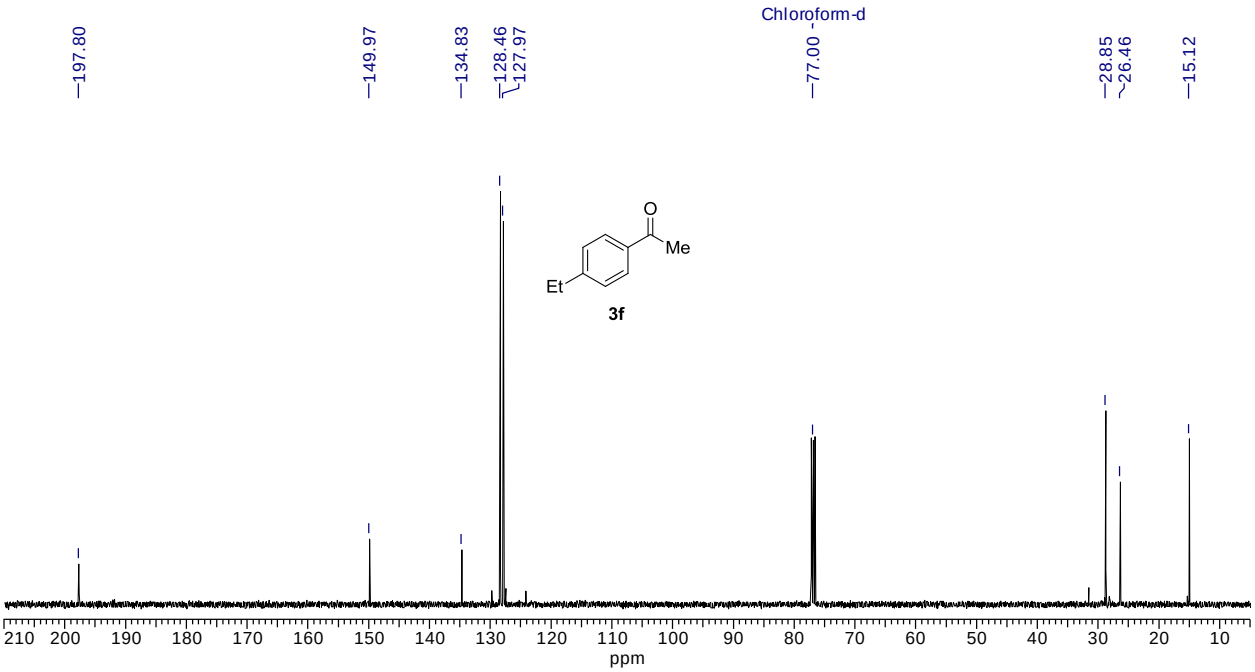


Figure I.6: ^{13}C-NMR (100 MHz) spectrum of **3f** in $CDCl_3$

The structure of 1-(4-ethylphenyl)ethanone **3f** was confirmed from its spectral data. IR spectra shows the absence of broad absorption band due to OH and presence of C=O stretching

at 1679 cm^{-1}. In the ^{1}H-NMR spectrum (Figure I.5), presence of two doublets δ 7.88 (*J*=8.3 Hz) and δ 7.27 (*J*=8.3 Hz) due to four aromatic protons, presence of one quartet at δ 2.69 (*J*=7.8 Hz) due to two protons of methylene group of ethyl moiety, presence of one singlet at δ 2.56 due to three protons of methyl group, presence of one triplet at δ 1.23 (*J*=7.8 Hz) for three protons due to methyl group of ethyl moiety, established the structure of ketone **3f**. In 8 lines ^{13}C-NMR spectrum (Figure I.6), presence of one quaternary carbon resonance at δ 197.8 indicates the C=O group, presence of two quaternary carbons resonances at δ 150.0 and 134.8 due to aromatic carbons, four aromatic methine carbons at δ 128.5 (2C) and 128.0 (2C), methylene carbon at δ 28.9, presence of two methyl carbons at δ 26.5 and 15.1 ppm, confirmed the structure of ketone **3f**.

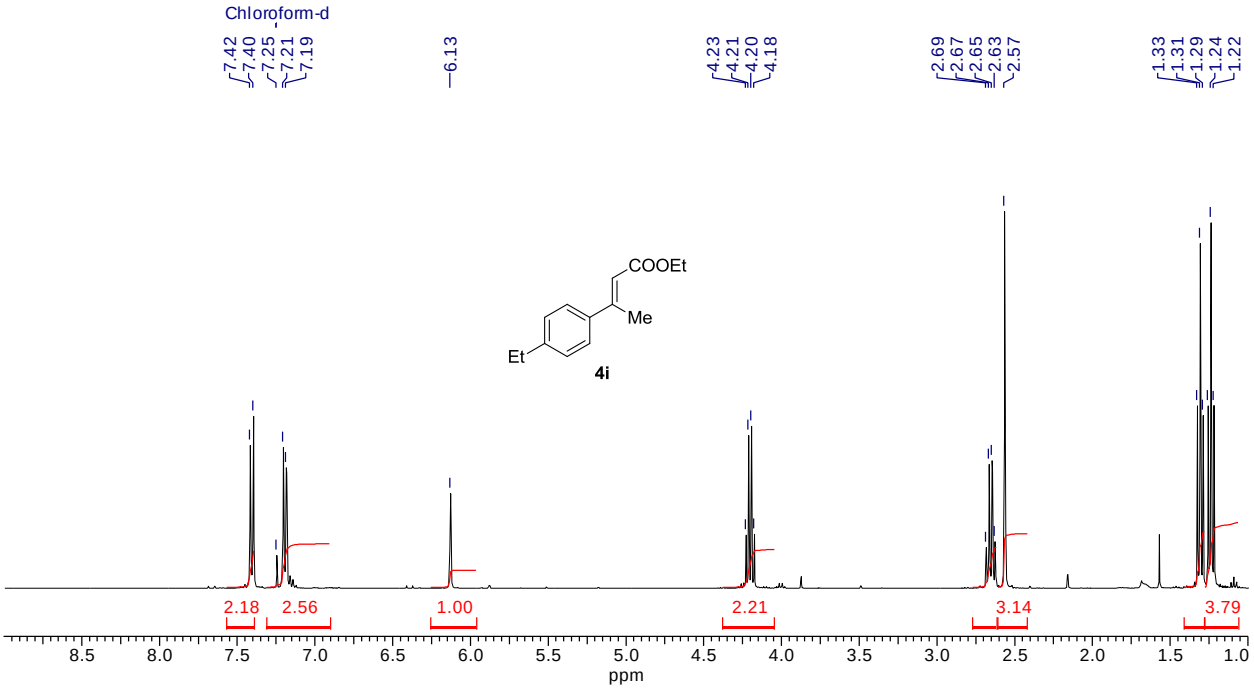


Figure I.7: ^{1}H-NMR (400 MHz) spectrum of **4i** in $CDCl_3$

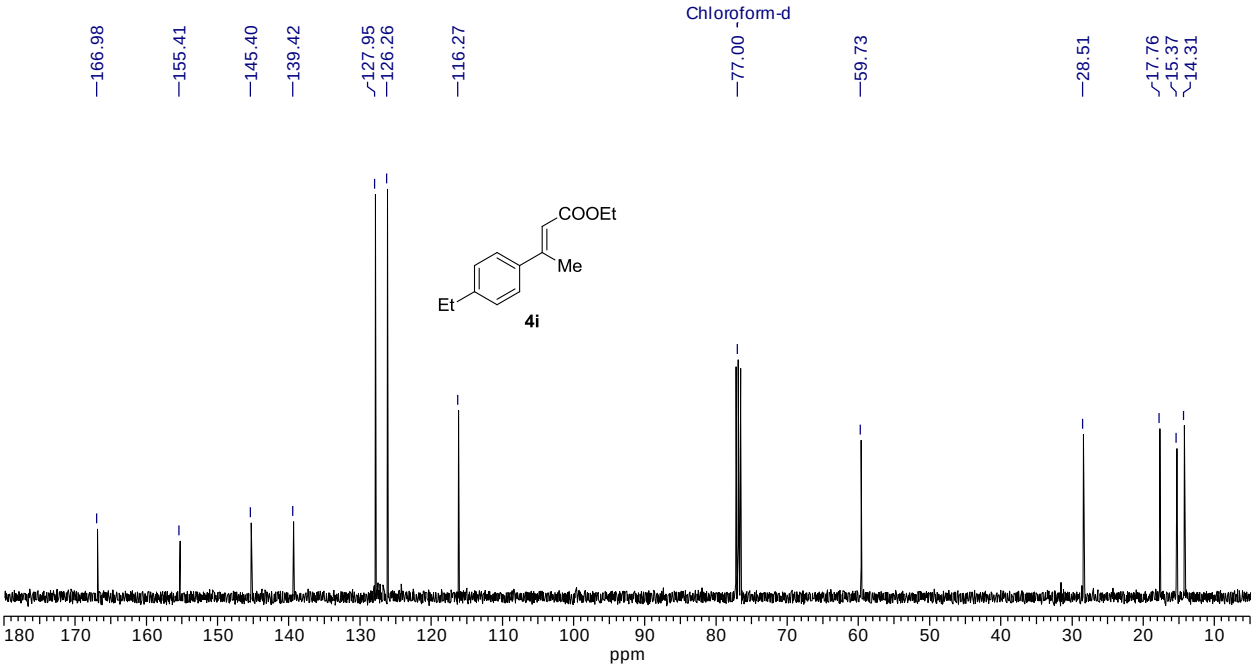
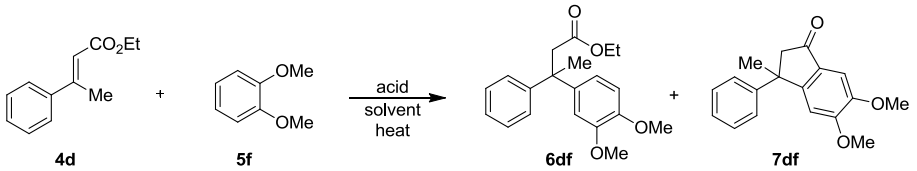


Figure I.8: ^{13}C-NMR (100 MHz) spectrum of **4i** in $CDCl_3$

The structure of ethyl (2*E*)-3-(4-ethylphenyl)but-2-enoate **4i** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1710 cm^{-1} due to C=O stretching of ester moiety. In the ^{1}H-NMR spectrum (Figure I.7), presence of two doublets at δ 7.42 (*J*=8.3 Hz) and δ 7.21 (*J*=8.3 Hz) due to four aromatic protons, presence of one singlet at δ 6.13 due to olefinic proton, presence of one quartet at δ 4.21 (*J*=7.3 Hz) due to two methylene protons of ethyl group of ester moiety, presence of one quartet at δ 2.67 (*J*=7.8 Hz) due to two protons of methylene group of ethyl moiety, presence of one singlet at δ 2.57 due to three protons of methyl group, presence of two triplets at δ 1.31 (*J*=7.3 Hz) and 1.24 (*J*=7.8 Hz) due to six protons of two methyl groups of ethyl moieties, established the structure of ester **4i**. In 12 lines ^{13}C-NMR spectrum (Figure I.8), presence of one quaternary carbon resonance at δ 167.0 indicates the C=O group, presence of three quaternary carbons resonances at δ 155.4, 145.4 and 139.4 due to aromatic and olefinic carbons, four aromatic methine carbons at δ 127.9 (2C) and 126.3 (2C), one olefinic carbon at δ 116.3, two methylene carbons resonances at δ 59.7 and δ 28.5, presence of three methyl carbons at δ 26.5, 15.4 and 14.3 ppm, confirmed the structure of ester **4i**.

With the required β-alkyl cinnamic acid esters **4** in hand, the reaction was explored to sort out the best optimized reaction conditions under various acids and the results are summarized in Table I.2. Thus, the β-alkyl cinnamic acid ester **4** [i.e. the major (*E*)-isomer] was chosen as the model system for this study and treated with the external arene **5** in the presence of different acids (Brønsted or Lewis), as shown in Table I.2. Initially, the reaction was neither successful with protic acid (*p*-TSA) nor with Lewis acid ($TiCl_4$) to deliver the required product **7** (Table I.2, entries 1 to 3). However, the reaction with $FeCl_3$ at room temperature, selectively furnished the alkylated product **6**, albeit in poor yield (Table I.2 entry 4). The selective formation of **6** clearly indicates that the intermolecular Friedel-Crafts alkylation (Michael addition type) is preferred over the intermolecular Friedel-Crafts acylation. Interestingly, the yield of **6** increased in parallel with the increase in acid quantity (Table I.2, entry 5). Subsequently, increased quantity of $FeCl_3$ at elevated temperature, either in DCE or in $CHCl_3$, promoted the reaction towards the cyclized product **7** in fair yield (Table I.2, entries 6 to 10). Gratifyingly, the reaction in the presence of [superacid TfOH (3 equiv)], furnished the target indanone **7** as an exclusive product, in very good yield (84%, Table I.2, entry 11). In contrast, the reactions with gold Lewis acid catalysts were unable to drive the reaction towards the product **7** (Table I.2, entries 12 & 13).

Table I.2: Optimization conditions for the synthesis of indanone **7**.



[a]Entry	Acid (equiv)	Solvent (mL)	Temp (^oC)	Time (h)	Yield (%)[b]	
					6df	**7df**
1	*p*-TSA (0.2)	toluene (3)	120	24	0[c]	0[c]
2	*p*-TSA (0.3)	DMF (2)	140	24	0[c]	0[c]
3	$TiCl_4$ (0.3)	CH_2Cl_2 (2)	Rt	96	0[c]	0[c]
4	$FeCl_3$ (0.3)	CH_2Cl_2 (2)	rt	12	30	0[d]
5	$FeCl_3$ (0.7)	CH_2Cl_2 (2)	rt	12	69	0[d]
6	$FeCl_3$ (0.7)	DCE (2)	80	12	18	43
7	$FeCl_3$ (3)	$CHCl_3$ (2)	60	12	12	54
8	$FeCl_3$ (1.5)	DCE (2)	80	12	0	42
9	$FeCl_3$ (2)	DCE (2)	80	12	0[e]	44
10	$FeCl_3$ (3)	DCE (2)	80	12	0[e]	62
11	**TfOH (3)**	**DCE (2)**	**80**	**12**	**0[e]**	**84**
12	TfOH (0.2)	DCE (2)	80	12	0[f]	0[f]
13	$(PPh_3)_3AuCl$ (0.05)	DCE (2)	80	12	0	0
14	30% $AuCl_3$ in dil. HCl (0.1)	DCE (2)	100	20	9	0

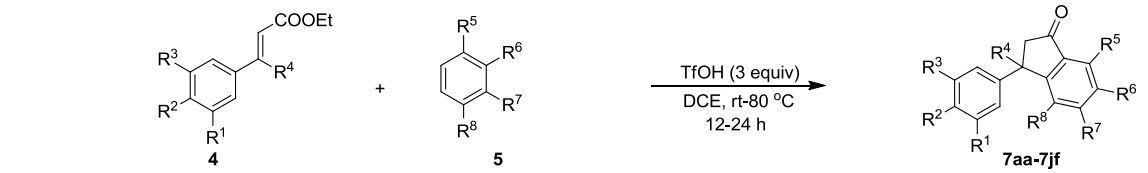
[a]All reactions were carried out on 95 mg (0.5 mmol) scale of **4d** (*E*-isomer) and 103 mg (0.75 mmol) of **5f**. [b]yields of chromatographically pure products. [c]Neither **6df** nor **7df** were observed, [d]No **6df** was formed. [e]No **7df** was identified, [f]only starting material **4d** was recovered .

To further establish the scope and limitations of the method, we have applied the above optimized conditions (Table I.2, entry 11) to other β-alkyl cinnamic acid esters **4a-4k** [i.e. major (*E*)-isomers] in the presence of external arenes **5a-5g** (Table I.3). The method was quite successful and amenable for the systems having electron withdrawing and donating substituents on the aromatic rings and gave the corresponding indanones **7aa-7kd** with tertiary and quaternary carbon atoms, in very good to excellent yields (Table I.3). It is worth mentioning that in the indanones **7aa-7jf**, the aromatic moiety of all β-alkyl cinnamic acid esters **4a-4j** is

relatively electron deficient than that of the external arenes **5a-5g** employed. Therefore, it was observed that the external arenes **5a-5g** were exclusively involved in the formation of both the new C-C bonds with the β-alkyl cinnamic acid esters **4a-4j** (Table I.3).

Notably, the reaction between **4a** and *ortho*-xylene **5c**, gave a regioisomeric mixture of products **7ac** and **7ac'**, which were separated by column chromatography and fully characterized by the spectral data and the structures were also further confirmed by the 2-D NMR analysis. Notably, the same trend was noticed in the reaction of the same external arene **5c** with the cinnamic acid ester **4b** and furnished a mixture of indanones **7bc** and **7bc'**. It is important to mention that in all the above successful examples, the reaction was performed exclusively on pure *E*-isomer of β-alkyl cinnamic acid esters **4**.

Table I.3: Scope of super acid mediated one-pot formation of indanones **7** from various esters **4**.[a,b,c]



4

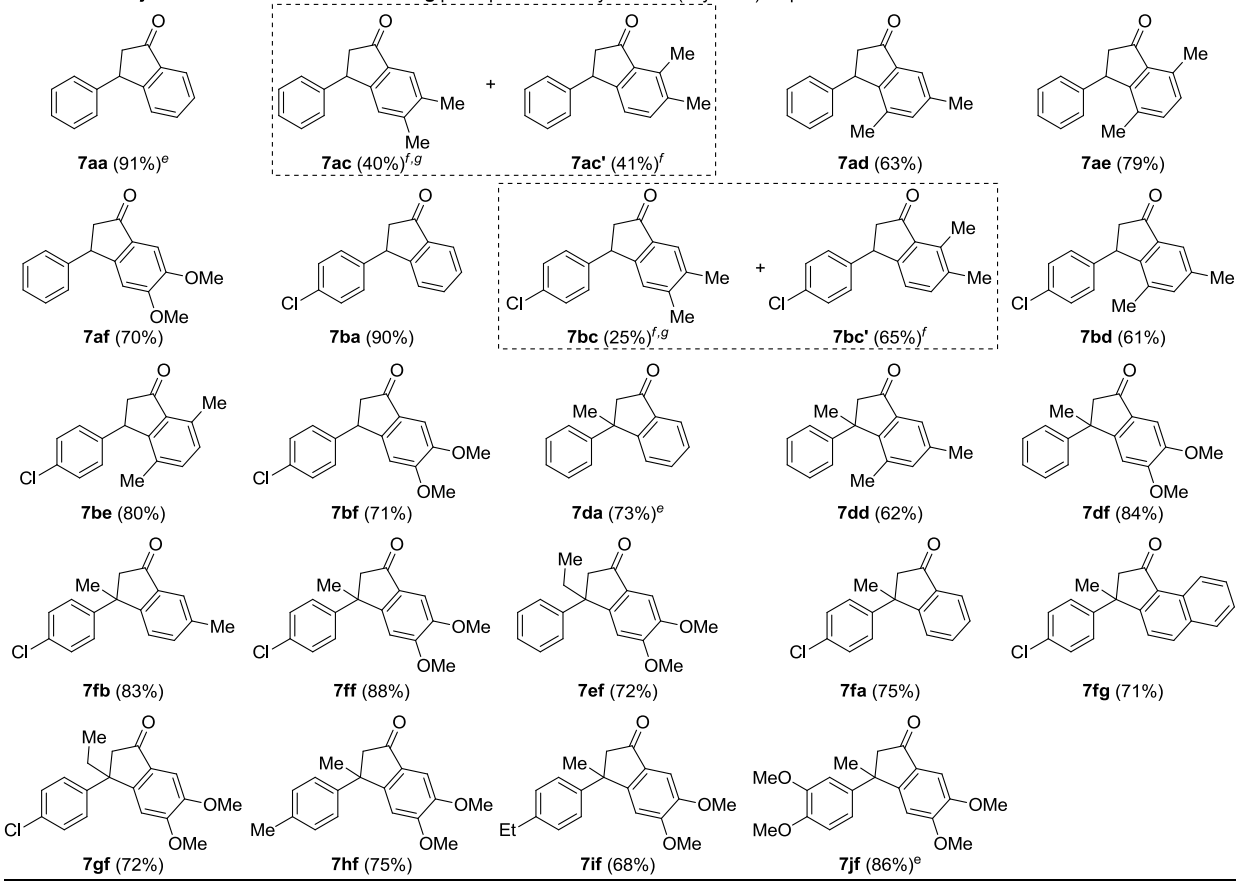
4a: R^1=H, R^2=H, R^3=H, R^4=H
4b: R^1=H, R^2=Cl, R^3=H, R^4=H
4d: R^1=H, R^2=H, R^3=H, R^4=Me
4e: R^1=H, R^2=H, R^3=H, R^4=Et
4f: R^1=H, R^2=Cl, R^3=H, R^4=Me
4g: R^1=H, R^2=Cl, R^3=H, R^4=Et
4h: R^1=H, R^2=Me, R^3=H, R^4=Me
4i: R^1=H, R^2=Et, R^3=H, R^4=Me
4j: R^1=H, R^2=OMe, R^3=OMe, R^4=Me

5

5a: R^5=H, R^6=H, R^7=H, R^8=H
5b: R^5=CH_3 , R^6=H, R^7=H, R^8=H
5c: R^5=CH_3, R^6=CH_3, R^7=H, R^8=H
5d: R^5=H, R^6=CH_3, R^7=H, R^8=CH_3
5e: R^5=CH_3, R^6=H, R^7=H, R^8=CH_3
5f: R^5=H, R^6=OMe, R^7=OMe, R^8=H
5g: naphthalene

7aa-7jf

Indanones **7aa-7jf** in which the external arenes **5a-5g** participated in the cyclization (acylation) step:[d]



7aa (91%)[e] | **7ac** (40%)[f,g] + **7ac'** (41%)[f] | **7ad** (63%) | **7ae** (79%)

7af (70%) | **7ba** (90%) | **7bc** (25%)[f,g] + **7bc'** (65%)[f] | **7bd** (61%)

7be (80%) | **7bf** (71%) | **7da** (73%)[e] | **7dd** (62%) | **7df** (84%)

7fb (83%) | **7ff** (88%) | **7ef** (72%) | **7fa** (75%) | **7fg** (71%)

7gf (72%) | **7hf** (75%) | **7if** (68%) | **7jf** (86%)[e]

[a]One-pot reaction conditions for the formation of indanones **7**: cinnamic acid ester **4** (0.5 mmol), arene **5** (6.0 mmol for **5a**, **5b**, **5c**, **5d** & **5e** and for **5f** and **5g** (0.75 mmol), DCE (2 mL), triflic acid (1.5 mmol), 80 ºC, 24 h for **7aa**, **7af**, **7ba**, **7bf**, **7da**, **7df**, **7ef**, **7fa**, **7fb**, **7ff** and **7gf**. [b]Yields in the parentheses are isolated yields of chromatographically pure products. [c]For indanones **7aa-7kd**; first alphabet stands for the cinnamate ester **4a-4k**, whereas the second alphabet represents the external arene **5a-5g**. [d]Indanones resulted due to the involvement of relatively electron rich external arenes **5a-5g** in the cyclization (acylation) step. [e]Either the external arene **5a** or parent arene of the cinnamate **4a/4d** might be involved in cyclization (acylation) step. [f]Regioisomeric indanones [(**7ac** & **7ac'**) and **7bc** & **7bc**')] formed with the cinnamic acid esters **4a** and **4b** respectively with the external arene **5c**. [g]The compound was formed as a mixture with another inseperable isomer.

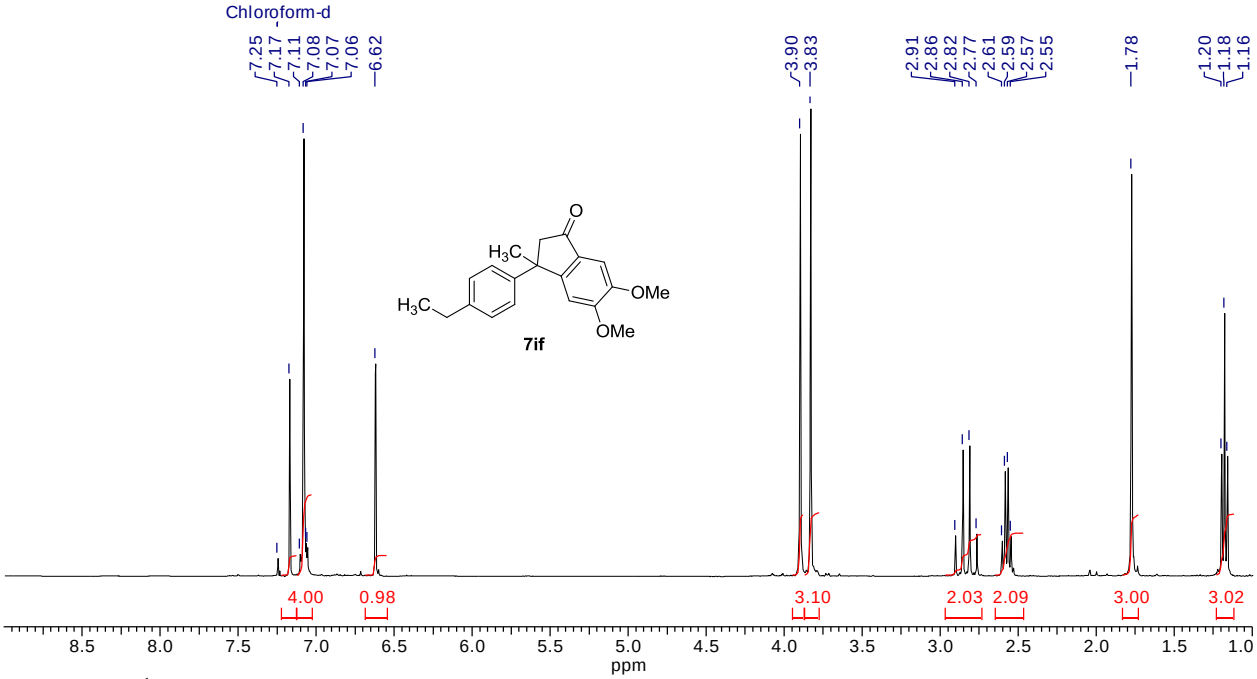


Figure I.9: ^{1}H-NMR (400 MHz) spectrum of **7if** in $CDCl_3$

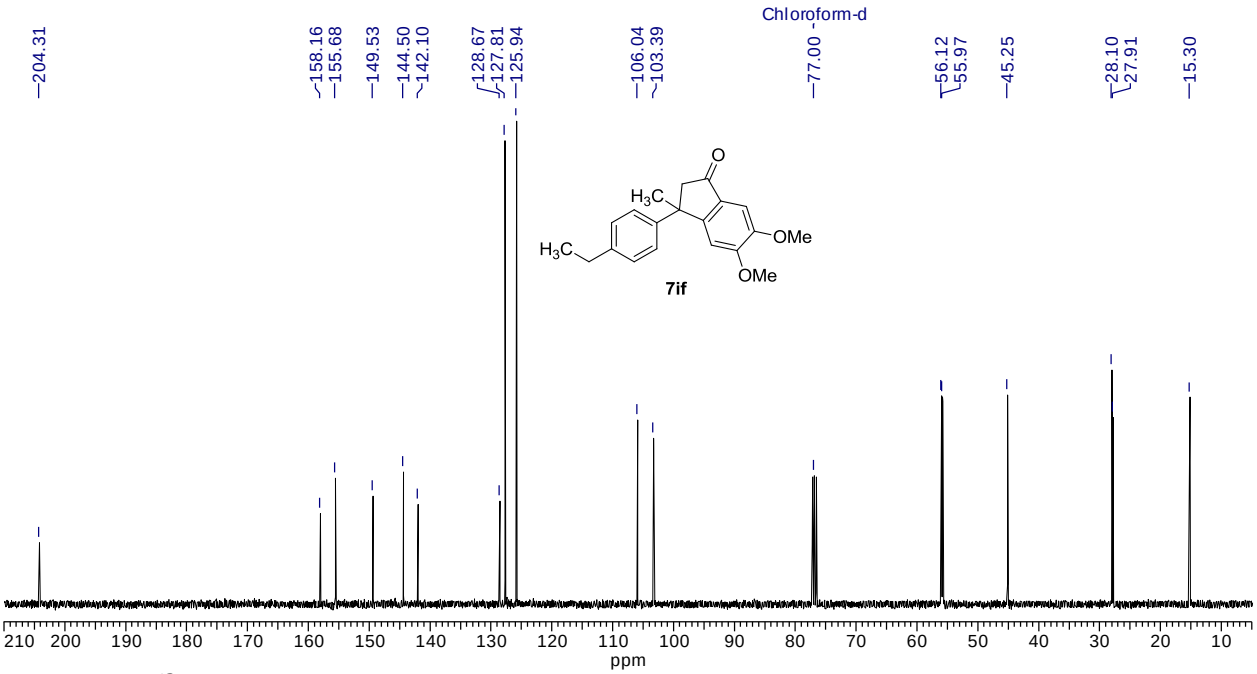
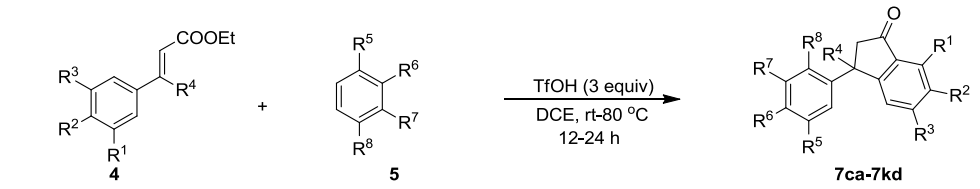


Figure I.10: ^{13}C-NMR (100 MHz) spectrum of **7if** in $CDCl_3$

The structure of 3-(4-ethylphenyl)-5,6-dimethoxy-3-methylindan-1-one **7if** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1709 cm^{-1} due to C=O stretching of cyclic ketone. In the ^{1}H-NMR spectrum (Figure I.9), presence of two singlets at δ 7.17 and δ 6.62 due to two aromatic protons, one multiplet at δ 7.13–7.02 (*J*=9.8 and 9.3 Hz) due to four aromatic protons, two singlets at δ 3.90 and δ 3.83 due to six protons of two aromatic methoxy groups, presence of two doublets at δ 2.86 (*J*=18.6 Hz) and δ 2.82 (*J*=18.6 Hz) due to two protons of a methylene group, presence of a quartet at δ 2.57 (*J*=7.3 Hz) due to to two protons of a methylene group of ethyl moiety, presence of one singlet at δ 1.78 due to three protons of methyl group, presence of one triplet at δ 1.18 (*J*=7.3 Hz) due to three protons of ethyl group, established the structure of indanone **7if**. In 18 lines ^{13}C-NMR spectrum (Figure I.10), presence of one quaternary carbon resonances at δ 204.3 indicates the C=O group, six quaternary carbons resonances at δ 158.2, 155.7, 149.5, 144.5, 142.1 and 128.7 due to aromatic carbons, six aromatic methine carbons at δ 127.8 (2C), 125.9 (2C), 106.0 and 103.4, two methoxy carbons at δ 56.1 and δ 56.0, methylene carbon at δ 55.9, quaternary carbon at δ 45.2, methylene carbon at δ 28.1, presence of two methyl carbons at δ 27.9 and 15.3 ppm, confirmed the structure of indanone **7if**. Presence of the $[M+H]^{+}$ peak at m/z $[C_{20}H_{23}O_3]^{+}$=311.1643 in the mass spectrum further established the structure of indanone **7if**.

In the above study, always the external arenes **5a-5g** were relatively electron rich than that from cinnamic acid esters **4a-4j**. Thus, external arenes **5a-5g** were exclusively involved in forming both the C-C bonds (Table I.3). However, in the case of external arenes **5a**, **5d** and **5e**, which are electron deficient than the aromatic ring of the β-alkyl cinnamic acid esters **4c**, **4h**, **4j** and **4k**. As anticipated, the aromatic moiety of the β-alkyl cinnamic acid esters **4c**, **4h**, **4j** and **4k**, ultimately participated in the acylation step after the formation of Friedel-Crafts alkylation C-C bond with the external arenes **5a**, **5d** and **5e**, and furnished the indanones **7ca**, **7cd**, **7ha**, **7ja**, **7jd**, **7je** and **7kd** (Table I.4).

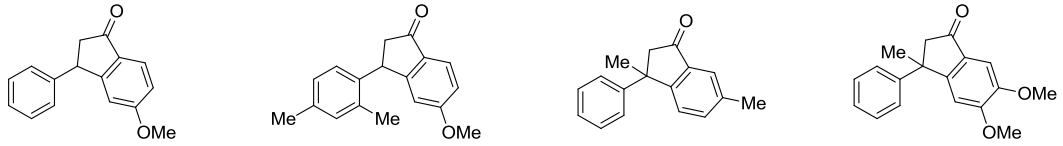
Table I.4: Scope of super acid mediated one-pot formation of indanones **7** from various esters **4**.[a,b,c,d]



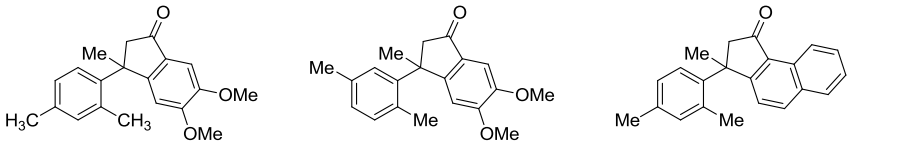
4c: R^1=H, R^2=H, R^3=OMe, R^4=H
4h: R^1=H, R^2=Me, R^3=H, R^4=Me
4j: R^1=H, R^2=OMe, R^3=OMe, R^4=Me
4k: naphthalene ester

5a: R^5=H, R^6=H, R^7=H, R^8=H
5d: R^5=H, R^6=CH_3, R^7=H, R^8=CH_3
5e: R^5=CH_3, R^6=H, R^7=H, R^8=CH_3

Indanones **7ca-7kd** in which the cinnamate arenes (**4c**, **4h**, **4j** & **4k**) were involved in the cyclization (acylation) step:[d]



7ca (46%) **7cd** (40%) **7ha** (75%) **7ja** (72%)



7jd (80%) **7je** (77%) **7kd** (77%)

[a]One-pot reaction conditions for the formation of indanones **7**: cinnamic acid ester **4** (0.5 mmol), arene **5** (6.0 mmol for **5a**, **5d** & **5e** (0.75 mmol), DCE (2 mL), triflic acid (1.5 mmol), 50 °C, 12-24 h for **7ca**, **7cd**, **7ha**, **7ja**, **7jd**, **7je** and **7kd**. [b]Yields in the parentheses are isolated yields of chromatographically pure products. [c]For indanones **7ca-7kd**; first alphabet stands for the cinnamate ester **4a-4k**, whereas the second alphabet represents the external arene **5a-5j**. [d]Indanones resulted due to the involvement of relatively electron rich parent arene of the cinnamic acid esters **4c**,**4h**,**4j** & **4k** were involved in cyclization (acylation) step.

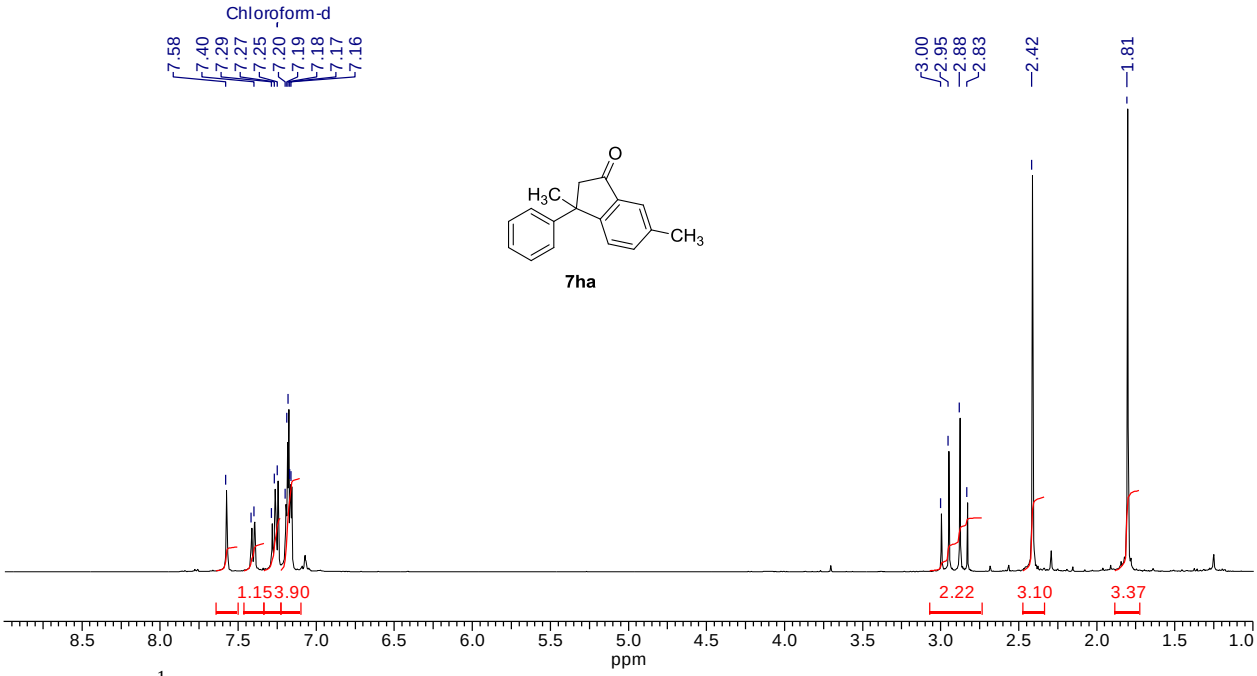


Figure I.11: ^{1}H-NMR (400 MHz) spectrum of **7ha** in $CDCl_3$

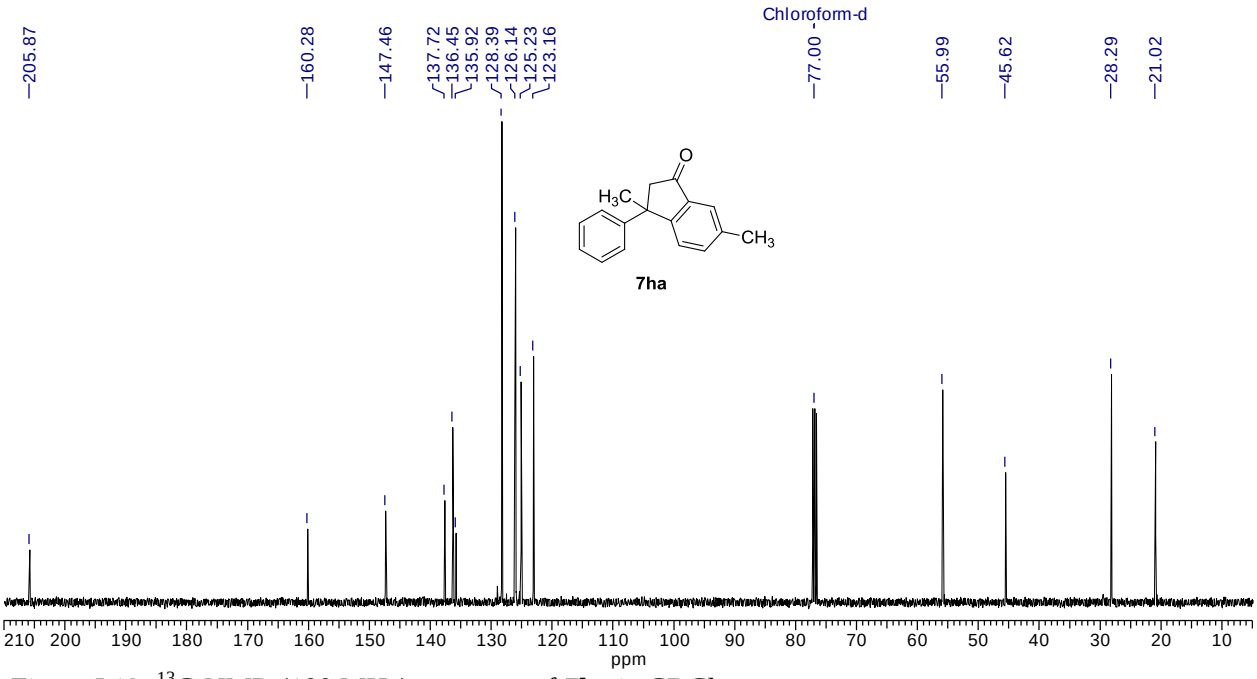


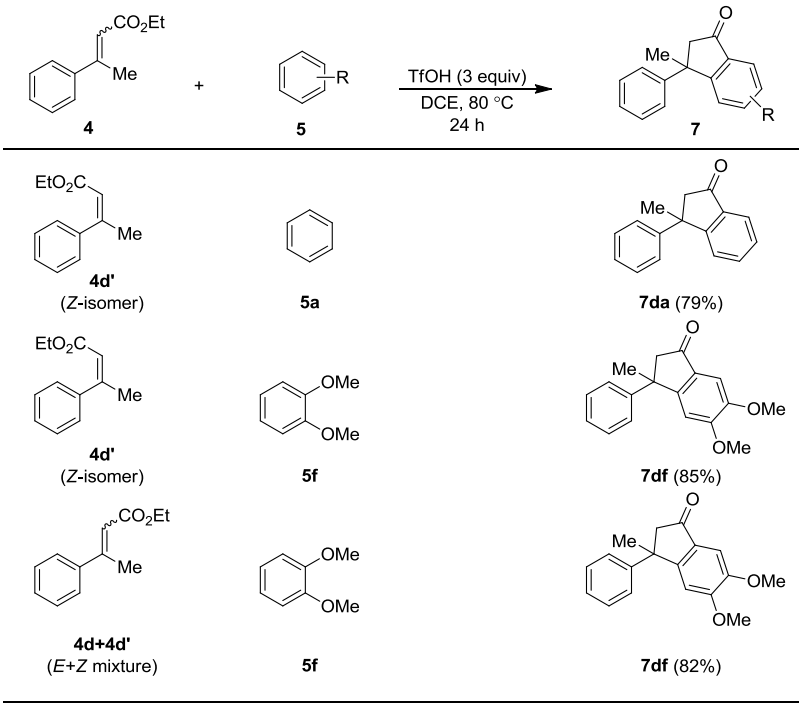
Figure I.12: ^{13}C-NMR (100 MHz) spectrum of **7ha** in $CDCl_3$

The structure of 3,6-dimethyl-3-phenylindan-1-one **7ha** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1708 cm^{-1} due to C=O stretching

of cyclic ketone. In the ^{1}H-NMR spectrum (Figure I.11), presence of one doublet at δ 7.58 (*J*=1.5 Hz) due to one aromatic proton, two doublet of doublets at δ 7.42 (*J*=7.8 and 1.5 Hz) and δ 7.27 (*J*=7.8 and 1.5 Hz) due to three aromatic protons, one multiplet at δ 7.22–7.14 due to four aromatic protons, presence of two doublets at δ 2.95 (*J*=19.1 Hz) and δ 2.88 (*J*=19.1 Hz) due to two protons of methylene group, presence of one singlet at δ 2.42 due to three protons of aromatic methyl group, presence of one singlet at δ 1.81 due to three protons of methyl group, established the structure of indanone **7ha**. In 15 lines ^{13}C-NMR spectrum (Figure I.12), presence of one quaternary carbon resonances at δ 205.9 indicates the C=O group, four quaternary carbons resonances at δ 160.3, 147.5, 137.7 and 135.9 due to aromatic carbons, eight aromatic methine carbons at δ 136.5, 128.4 (2C), 126.3, 126.1(2C), 125.2 and 123.2, methylene carbon at δ 56.0, quaternary carbon resonances at δ 45.6, presence of two methyl carbons at δ 28.3 and δ 21.0 ppm, confirmed the structure of indanone **7ha**. Presence of the $[M+H]^{+}$ peak at m/z $[C_{17}H_{17}O]^{+}$=237.1250 in the mass spectrum further established the structure of indanone **7ha**.

Since, the double bond of ethyl cinnamic acid ester was totally consumed in the reaction; irrespective of *E*- or *Z*-isomer used, both would result in the same indanone product. Therefore, to further investigate the authenticity of the reaction, the reaction was also performed with *Z*-isomer **4d'** in the presence of external arenes **5f** and **5a** (Table I.5). As anticipated, the same indanones **7df** and **7da** were obtained in comparable yields to that of *E*-isomer. To further confirm that both the *E*- and *Z*-isomers follow the same mechanistic path, the reaction was conducted on a mixture of *E*- and *Z*-isomers of β-alkyl cinnamic acid esters (**4d**+**4d'** in 4:1 ratio) with the external arene **5f** (Table I.5). As expected, the product **7df** was obtained in comparable yield (Table I.5).

Table I.5: Superacid promoted synthesis of indanones **7da** and **7df** from the *Z*-isomer **4d'** and (*E*+*Z*)-isomers of **4d**.[a, b]



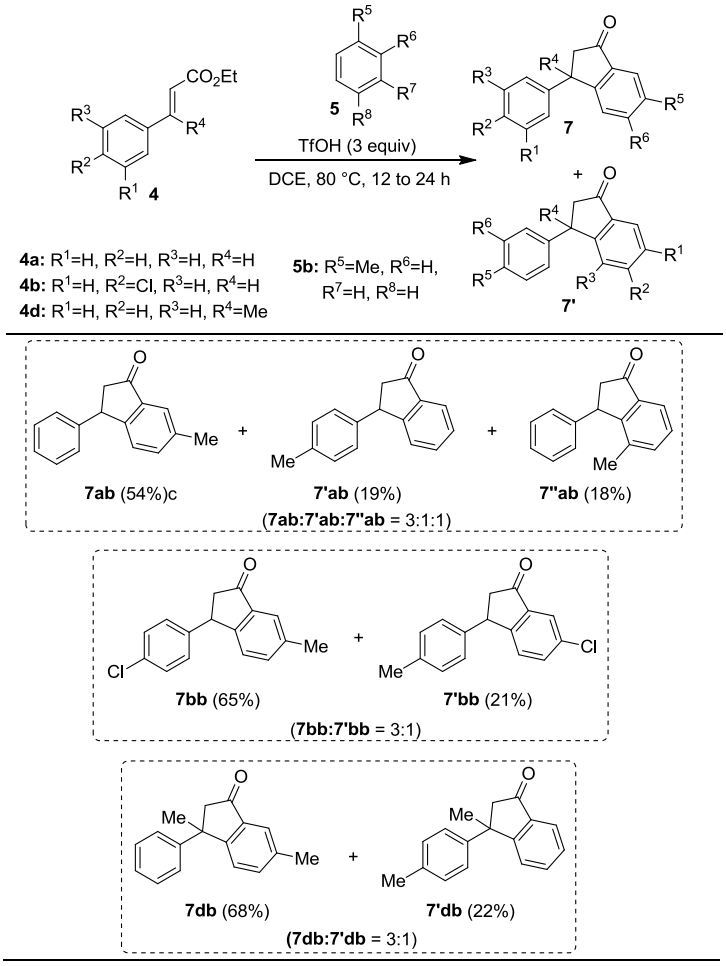
[a]Reaction conditions for the formation of indanones **7**: ester **4d** (0.5 mmol), arene **5** (6.0 mmol **5a** and 0.75 mmol **5f**), DCE (2 mL), triflic acid (1.5 mmol), 80 ºC for 12-24 h for indanones **7da** & **7df**. [b]Yields in the parentheses are isolated yields of chromatographically pure products.

We experienced that the *E* and *Z* isomers can be identified using TLC based on the RF difference. For all these compounds, the *E*-isomer found as slightly less polar than the *Z*-isomer. Though the RF difference between then is small, but still they are separable. This is true for each and every system. On the basis of ^{1}H-NMR studies, in *E*-isomer olefinic proton observed at 6.14 ppm whereas *Z*- isomer olefinic proton observed at 6.12 ppm (i.e. the chemical shift value for *E*-isomer is slightly down field than the *Z*-isomer). In case of *E*-isomer there is not much steric hindrance between the large substituents, as they positioned "*trans*" to each other with regards to the olefinic double bond. Therefore, in *E*-isomer both the double bonds (i.e. olefinic double bond and carbonyl double bond) are co-planar to each other and has better conjugation. Whereas, in the case of *Z*-isomer, steric hindrance between the adjacent bulky groups of the olefin bond can be seen as they are placed "*cis*" to each other and hence the planarity will be disturbed to some extent between both double bonds. Thus, the β-carbon atom of the double bond of the *E*-isomer is somewhat more deshielded than that of the *Z*-isomer. As a result, the proton connected to the

β-carbon of *E*-isomer appears at relatively higher chemical shift (δ) than that of the *Z*-isomer on the NMR scale. The coupling constants (*J*) of ^{1}H-NMR spectra also helps to distinguish *E*- and *Z*-isomers. Usually the *J* values of *E*-isomer are more (10-16 Hz) than the *Z*-isomer (6-10 Hz). The same concept can be extended based on the conjugation between the double bonds using IR spectroscopy to distinguish *E*- and *Z*-isomers. Since there is a better conjugation in *E*-isomer, the carbonyl double bond stretching frequency (1709 cm^{-1}) is lower than that of the *Z*-isomer (1718 cm^{-1}).

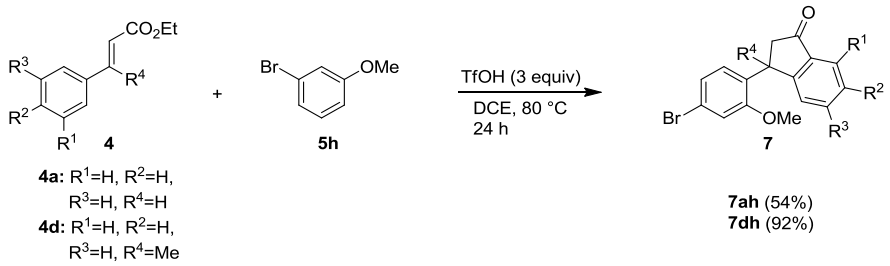
Interestingly, in the cases of β-alkyl cinnamic acid esters **4a**, **4b** and **4d**, and the external arene **5b**, both arene moieties have more or less equal reactivity and may compete with each other for the final intramolecular acylation step, after the initial Friedel-Crafts alkylation and hence would furnish mixture of indanones **7**+**7'**. So, β-alkyl cinnamic acid esters **4a**, **4b** and **4d** were reacted with the arene **5b**. As expected, the reaction furnished an inseparable mixture of two possible products [(**7ab**+**7'ab**), (**7bb**+**7'bb**) & (**7db**+**7'db**)], as shown in the Table I.6. Relatively more reactive aromatic ring involved readily in the acylation step and furnished the corresponding indanones **7ab**, **7bb** and **7db** as the major products (Table I.6). It is worth mentioning that in the reaction of **4a** with **5b**, the careful analysis of the ^{1}H-NMR spectrum revealed an additional isomeric product, which might probably be **7''ab**.

Table I.6: Formation of inseparable mixture of indanones **7**.[a, b]



[a]Reaction conditions for the formation of indanones **7**: ester **4** (0.5 mmol), toluene **5b** (6.0 mmol) and DCE (2 mL), triflic acid (1.5 mmol) at 80 ºC for 24 h for indanones [(**7ab**+**7'ab**), (**7bb**+**7'bb**) & (**7db**+**7'db**)]. [b]Yields in the parentheses are based on ^{1}H-NMR analysis. [c]Reaction between **4a** and **5b** resulted in three (**7ab**+**7'ab**+**7''ab**) isomers.

Notably, when the esters **4a** and **4d** [i.e. major (*E*)-isomers] were subjected to reaction with 3-bromoanisole **5h**, under standard conditions, furnished the indanone products **7ah** and **7dh**, in which simple benzene ring of ester **4** was reacted in intramolecular Friedel-Crafts acylation step, after the initial Friedel-Crafts alkylation by 3-bromoanisole **5h** (Scheme I.21). This might be either due to a weakly deactivating negative inductive effect of *meta*-Br and *meta*-OMe groups or might as well be due to the protonation of the methoxy group resulting in deactivation of the arene to affect cyclization.



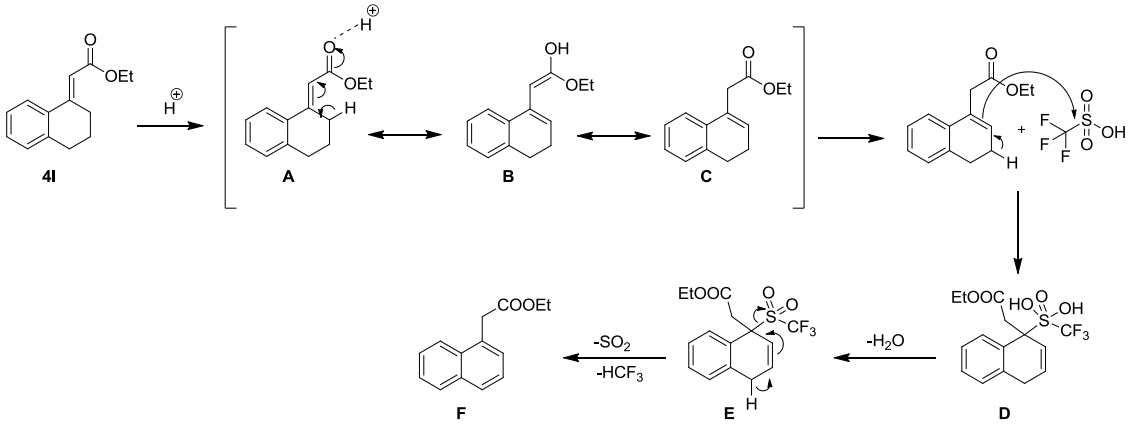
Scheme I.21

Superacid promoted synthesis of indanones **7ah** & **7dh**. In addition to the spectroscopic confirmation of the indanone products **7**, the structure of **7dh** was unambiguously confirmed from the single crystal X-ray diffraction analysis (Figure I.13).

Figure I.13: X-ray crystal structure of **7dh** (CCDC 1025163). Thermal ellipsoids are drawn at 50% probability level.

Further, to check the applicability and limitations of the method, we turned our interest to explore the reaction of ester **4l** derived from tetralone, anticipating the formation of novel spiro-tetracyclic systems. The serious concern in this particular case is the self-aromatization of **4l** under strong acidic conditions. However, we thought that it would be possible to push the reaction towards the spiro-tetracyclic product either by using excess amount of the acid or by increasing the amount of the external arene. Nevertheless, under a variety of conditions with many external arenes, the reaction was unsuccessful to furnish the target spiro-system, instead, led to the isolation of self-aromatized product solely.[31]

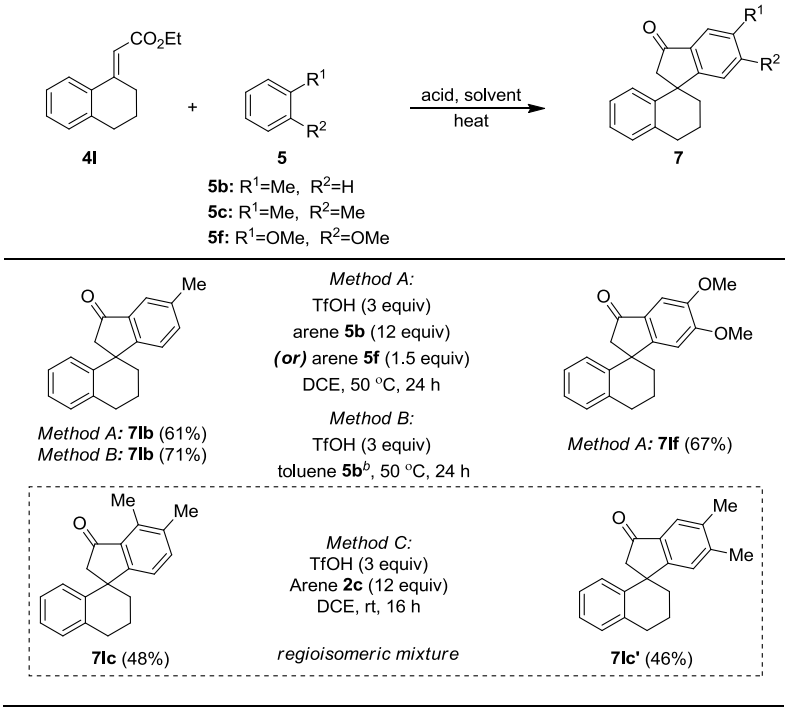
A plausible mechanism for the self-aromatization of tetralone ester is as shown in Scheme I.22. Initially, the proton attacks the carbonyl oxygen atom of the ester moiety and might yield the double bond isomerised equilibrating intermediates **A** to **C**. The intermediate **C** could combine with the triflic acid and furnishes the quaternary carbon intermediate **D**. Dehydration of **D**, gives the intermediate **E**. Finally, the intermediate **E** undergoes elimination to give the aromatized bi-product **F**.



Scheme I.22

However, delightfully, out of all the attempts, we were successful in obtaining few spiro-tetracyclic products **7** (Table I.7). Particularly, it was observed that at slightly lower temperature than the usual condition, was found to be suitable and furnished the expected novel spiro-tetracyclic systems **7lb** and **4lf**. Also, it was noticed that toluene **5b** played a dual role both as a solvent and external arene unlike with veratrole **5f**. This may due to electron rich nature of veratrole **5f** that makes it react quickly with electrophilic cinnamic acid ester **4l**. However, when *ortho*-xylene **2c** was used as external arene, it furnished a mixture of regioisomeric products **7lc** and **7lc'** (Table I.7). This is in good agreement with that observed in the earlier studies for the formation of a mixture of indanones with *ortho*-xylene **2c** [i.e. (**7ac**+**7ac'**) and (**7bc**+**7bc'**) of Table I.3].

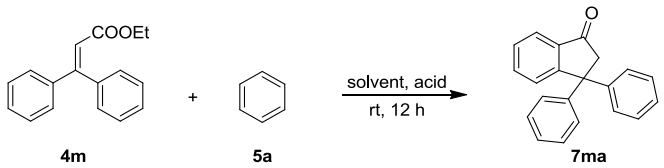
Table I.7: Synthesis of spiro-tetracyclic indanones **7**.[a]



[a]Yields in the parentheses are isolated yields of chromatographically pure products. [b]Toluene (**5b**) was used as the solvent as well as external arene.

Furthermore, to check the scope and applicability of the method, we focused on the ethyl β-diaryl acrylates **4m** and **4n**. In this case the reactivity may be highly enhanced in the cyclization step due to an extra aromatic ring. Initially, the reaction was explored using benzene as the external arene **5a** with the ethyl β-diaryl acrylate **4m** under standard reaction conditions (Table I.8). However, the reaction was unsuccessful in furnishing indanone **7ma**, even after several attempts under established as well as varying conditions (Table I.8, entries 1 to 10). Gratifyingly, the reaction was quite successful when benzene **5a** was used as the solvent as well as the external arene and gave the indanone **7ma** in excellent yield (91%, Table I.8, entry 11).

Table I.8: Optimization conditions for the synthesis of indanone **7ma** from benzophenone ester **4m.**



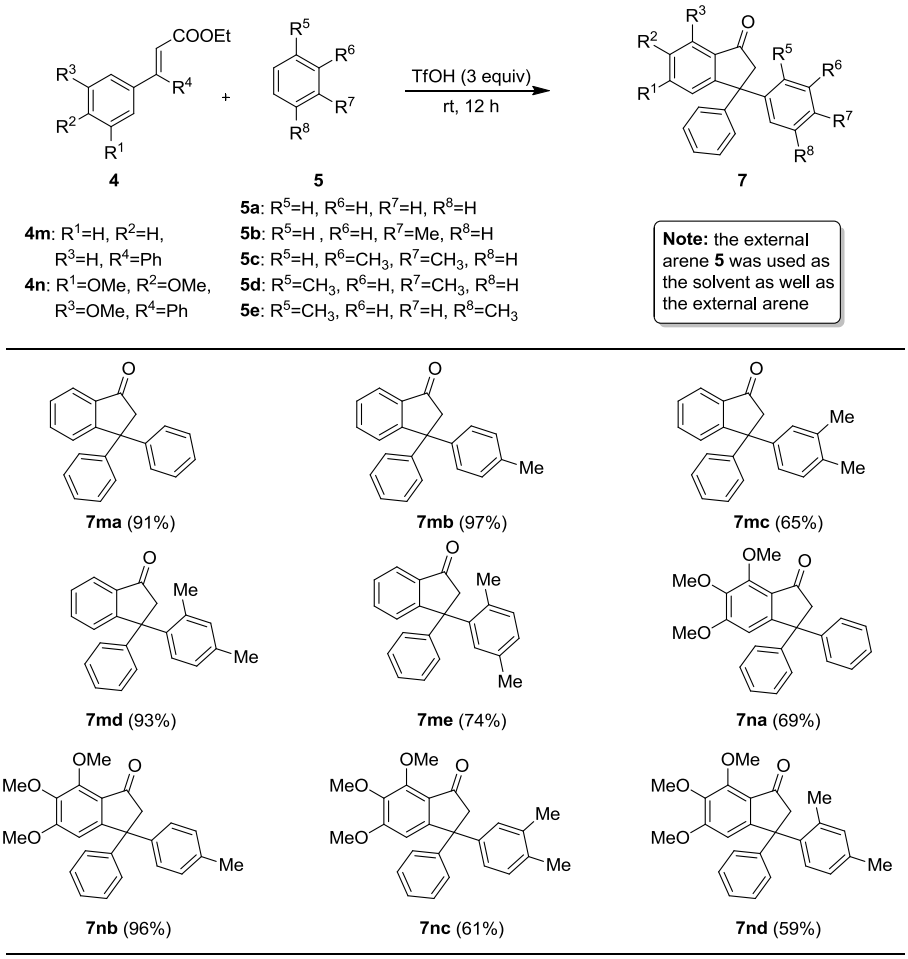
Entry[a]	External arene (equiv)	Solvent (2mL)	Acid (equiv)	Temp (^oC)	Yield (%)[b] **7ma**
1	benzene (12)	DCE	TfOH (3)	80	0[c]
2	benzene (12)	DCE	TfOH (3)	0-rt	0[d]
3	benzene (12)	DCM	TfOH (3)	0-rt	0[d]
4	benzene (12)	$CHCl_3$	TfOH (3)	0-rt	0[d]
5	benzene (12)	DCE	TfOH (3)	50	0[c]
6	benzene (12)	$CHCl_3$	TfOH (3)	50	0[c]
7	benzene (12)	DCE	$FeCl_3$ (3)	rt	0[d]
8	benzene (12)	DCE	$FeCl_3$ (3)	50	0[c]
9	benzene (12)	DCE	TfOH (6)	rt	0[e]
10	benzene (12)	DCE	TfOH (10)	rt	0[e]
11	**benzene (2mL)**	**-**	**TfOH (3)**	**rt**	**91%**[f]

[a]All reactions were carried out on 126.15 mg (0.5 mmol) scale of **4m**. [b]Isolated yields of chromatographically pure products. [c]No clean spot seen on TLC, drag of mixture of spots was visible. [d]No product was observed, only starting material was recovered. [e]No **7ma** was identified. [f]Benzene was used as the solvent as well as external arene **5a**.

These optimized conditions were then applied to the other systems. Interestingly, the reaction was quite successful with other systems as well and furnished the corresponding indanone products **7ma-7nd** in good to excellent yields (Table I.9). Quite surprisingly, ethyl β-diaryl acrylates **4m** and **4n** behaved differently than those with β-alkyl cinnamic acid esters **4a-4l**. In contrast to the β-alkyl cinnamic acid esters **4a-4l**, the reaction of β-diaryl acrylates **4m** and **4n** with slightly more electron rich external arenes such as toluene **5b** and xylenes **5c-5e**, gave the products **4mb-4me**, in which toluene **5b** and xylenes **5c-5e** were not involved in the cyclization (acylation) step, instead, the simple phenyl group of β-diaryl acrylates **4m** and **4n** was involved in cyclization step. This might be due to the reason that these esters **4m** and **4n** are highly reactive and hence, in the presence of acid would prefer quick intramolecular cyclization

than intermolecular Friedel-Crafts reaction unlike the case with β-alkyl cinnamates **4a-4l**. In an analogous way, the more electron rich trimethoxy phenyl group of cinnamate **4n** participated in cyclization and furnished the corresponding products **7na-7nd** (Table I.9). However, the reaction with more electron rich external arene such as veratrole **5f** was inconclusive.

Table I.9: Synthesis of indanones **7** from esters **4**.[a, b]



[a]Reaction conditions for the formation of indanones **7**: benzophenone esters **4** (0.5 mmol), arene **5** (2mL), TfOH (1.5 mmol, 3 equiv.) and at room temperature for 12 h for the formation of indanones **7ma-7nd**. [b]Yields in the parentheses are isolated yields of chromatographically pure products.

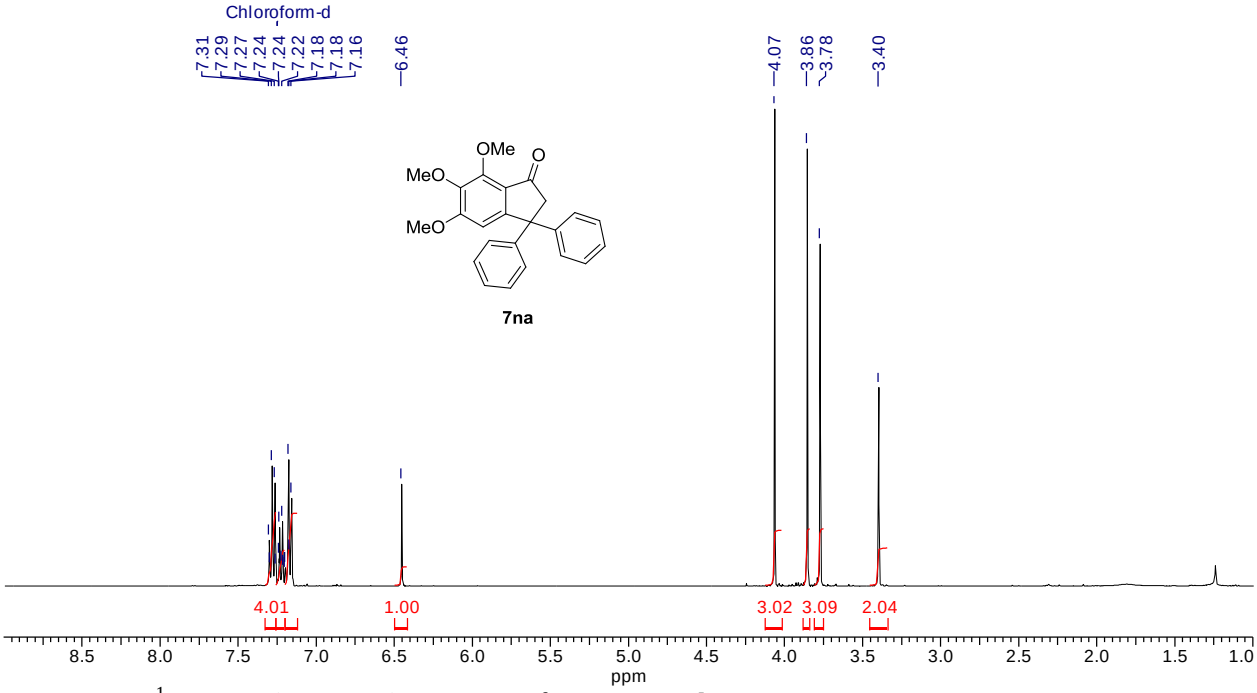


Figure I.14: ^{1}H-NMR (400 MHz) spectrum of **7na** in $CDCl_3$

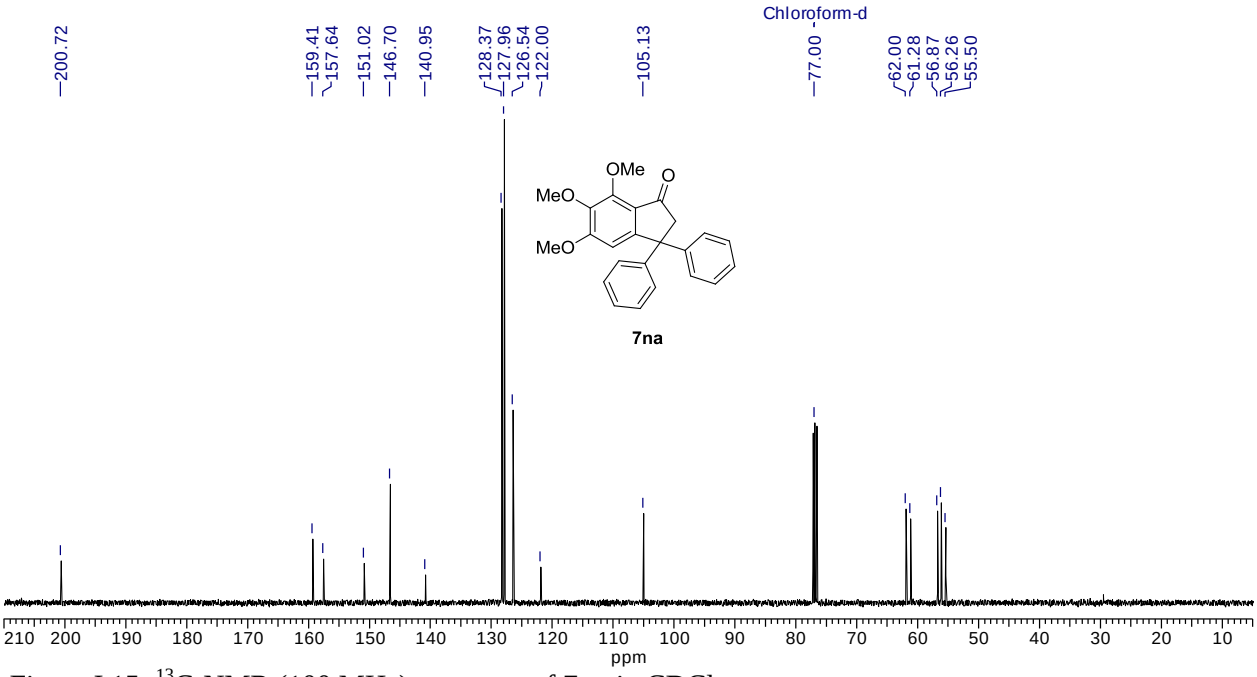
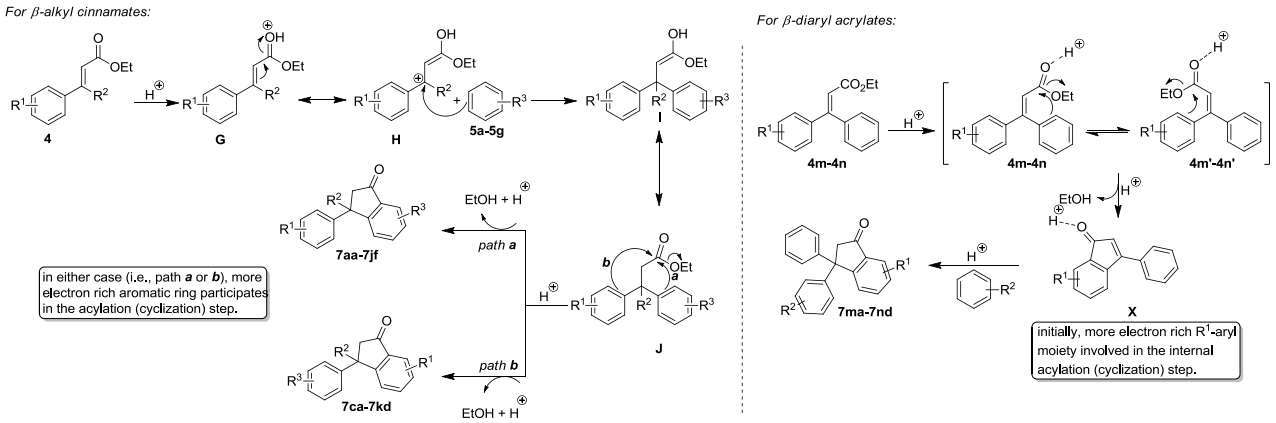


Figure I.15: ^{13}C-NMR (100 MHz) spectrum of **7na** in $CDCl_3$

The structure of 5,6,7-trimethoxy-3,3-diphenylindan-1-one **7na** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1700 cm^{-1} due to C=O stretching of cyclic ketone. In the ^{1}H-NMR spectrum (Figure I.14), presence of three multiplets at δ 7.32–7.35, 7.25–7.19 and δ 7.20–7.15 due to ten aromatic protons, one singlet at δ 6.46 due to one aromatic proton, three singlets at δ 4.07, 3.86 and δ 3.78 due to nine protons of three aromatic methoxy groups, presence of one singlet at δ 3.40 due to two protons of methylene group, established the structure of indanone **7na**. In 16 lines ^{13}C-NMR spectrum (Figure I.15), presence of one quaternary carbon resonances at δ 200.7 indicates the C=O group, seven quaternary carbons resonances at δ 159.4, 157.6, 151.0, 146.7 (2C), 141.0 and 122.0 due to aromatic carbons, eleven aromatic methine carbons at δ 128.4 (3C), 128.0 (4C), 126.5 (3C) and 105.1, three aromatic methoxy carbons at δ 62.0, 61.3 and 56.3, methylene carbon at δ 56.9 ppm, presence of one quaternary carbon at δ 55.5, confirmed the structure of indanone **7na**. Presence of the $[M+H]^{+}$ peak at m/z $[C_{24}H_{23}O_4]^{+}$=375.1591 in the mass spectrum further established the structure of indanone **7na**.

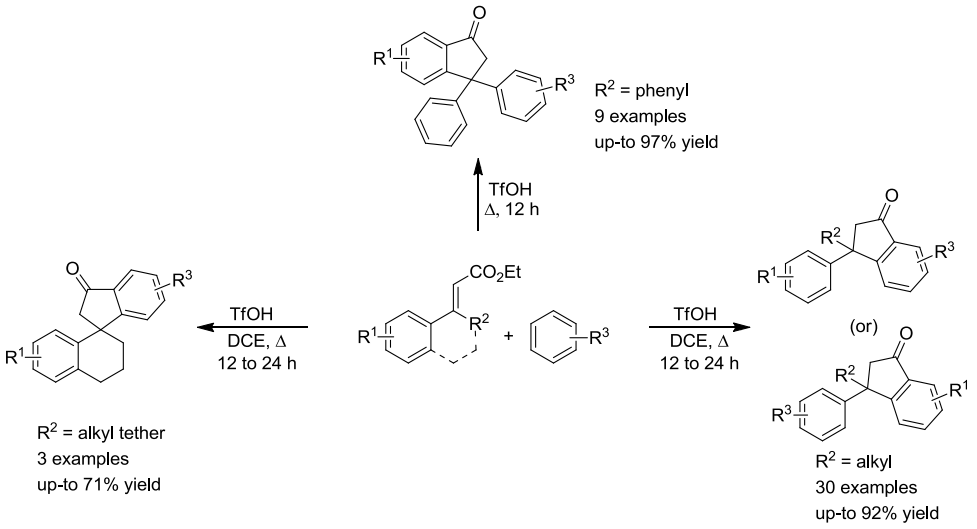
A plausible reaction mechanism for the formation of indanones **7aa-7jf** and **7ca-7kd** is depicted in Scheme I.23. In the case of β-alkyl cinnamic acid esters **4a-4k**, acid could activate the ketone group of the esters to yield the equilibrium of structures **G** and **H,** subsequent attack of the external arenes **5a-5g** at the β-carbon of the enoate double bond leads to the adduct intermediates **I**, **I** equilibrium with **J**. At this stage, a selective intramolecular acylation of **J** by more electron rich aromatic moiety gives the final products **7aa-7jf** (compounds **7ah** & **7dh** also fall into this category) and **7ca-7kd** (compounds **7lb**, **7lf**, **7lc & 7lc'** also fit into this category) as shown in Scheme I.23. On the other hand, more sensitive ethyl β-diaryl acrylates **4m-4n**, in the presence of acid, would tend to be in rapid equilibrium with **7m'-7n'**. Now, intramolecular acylation by electron rich aromatic ring would furnish the indenones **X**. Finally, intermolecular addition of the external arenes **5a-5e** across the double bond of **X** gives the final products **7ma-7nd** (Scheme I.23).



Scheme I.23: Plausible mechanism for the formation of indanones **7aa-7jf, 7ca-7kd** and **7ma-7nd**.

I.4. CONCLUSIONS:

We have developed an efficient method for the construction of dual C-C bond, for the efficient synthesis of indanones promoted by superacid. The scope and the limitations of the method have been studied extensively by performing the reaction between many cinnamic acid esters and external arenes. Also, the electronic factors affecting the acylation step in a selective manner has been studied systematically.



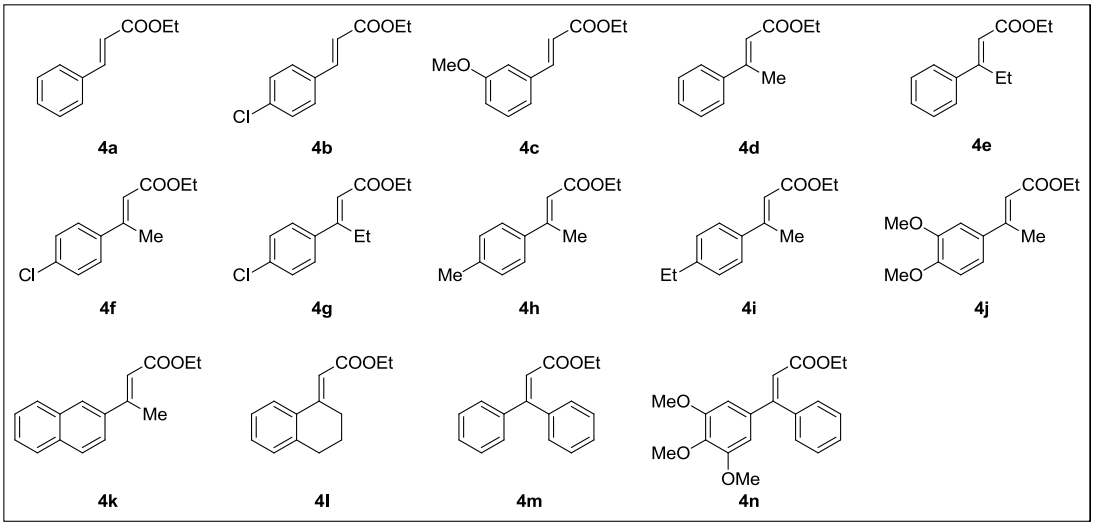
Scheme I.24

I.5 EXPERIMENTAL SECTION:

General:

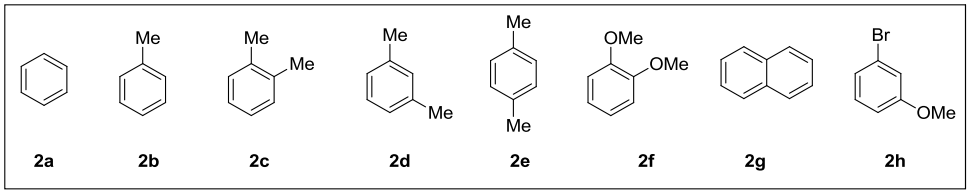
IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H-NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H =0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C-NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C-NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C carbon proton decoupled (CPD) and distortionless enhancement polarization transfer (DEPT) spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small scale dry reactions were carried out using Schlenk tubes under inert atmosphere. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. Dichloroethane (DCE) was dried over CaH_2 and absolute ethanol was purchased from local sources, used as received. Trifluoromethanesulfonic acid (triflic acid) was purchased from Spectrochem pvt. Ltd. And used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

The following ethyl cinnamic acid esters **4a-4n** are known in the literature.

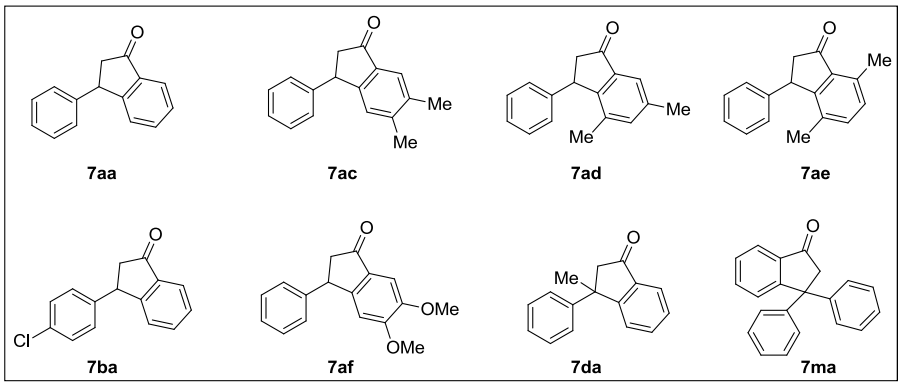


Compound **4a** is commercially available; compounds (**4b**, **4d**, **4e**, **4f**, **4g**, **4l**),[32] **4c**,[33] **4i**,[34] **4j**,[35] **4k**,[36] **4m**[37] and **4n**[38] are known in the literature.

The arenes **2** used for the reaction were obtained commercially and have been represented

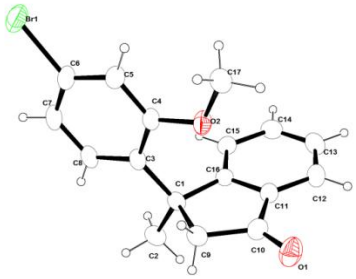


The literature reported indanones **7** are shown.



Compounds **7aa**,[39] **(7ac, 7ad**, **7ae**),[40] **7af**,[41] & (**7ba, 7da, 7ma)**[29] reported in the literature

X-Ray crystal structure data for **7dg**: (CCDC 1025163):



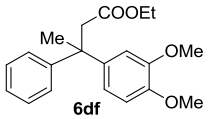
Operator	**K. Ravikumar**
Instrument	**Oxford SuperNova**
Identification code	exp_1653
Empirical formula	$C_{17}H_{15}BrO_2$
Formula weight	331.19
Temperature/K	150.00(10)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.0011(15)
b/Å	10.9288(7)
c/Å	13.0605(14)
α/°	90.00
β/°	116.233(14)
γ/°	90.00
Volume/$Å^3$	1664.6(3)
Z	8
$\rho_{calc}mg/mm^3$	2.509
m/mm^{-1}	1.412
F(000)	1344.0
Crystal size/mm^3	0.20 ×0.16 × 0.12
2Θ range for data collection	11.08 to 141.62°
Index ranges	$-14 \leq h \leq 9$, $-9 \leq k \leq 13$, $-11 \leq l \leq 16$
Reflections collected	3843
Independent reflections	2462[R(int) = 0.0156]
Data/restraints/parameters	2462/0/211
Goodness-of-fit on F^2	1.190
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1446
Final R indexes [all data]	R_1 = 0.0481, wR_2 = 0.1512
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.19

GP-1 (General Procedure for Friedel-Crafts Alkylation and Acylation of Ethyl Cinnamates):

To an oven dried Schlenk tube, under nitrogen atmosphere, were added ester **1** (0.5 mmol), arene **5** (in case of benzene, toluene and xylene 6.0 mmol and for other electron rich arenes 0.75 mmol were used for 0.5 mmol of the ester **4**) and DCE (2 mL), followed by the addition of triflic acid (0.13 mL, 1.5 mmol). The resultant reaction mixture was stirred at 50–80 °C for 12–24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indanone **7** (40–92%).

GP-2 (General Procedure for indanone formation with benzophenones):

To an oven dried Schlenk tube, under nitrogen atmosphere, were added ester **4** (0.5 mmol), arene **5** (2 mL) followed by the addition of triflic acid (0.13 mL, 1.5 mmol). The resultant reaction mixture was stirred at rt for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indanone **7** (59–97%).



6df

Procedure for Micheal Addition on Ethyl Cinnamate:

Ethyl 3-(3,4-dimethoxyphenyl)-3-phenylbutanoate hydrate (6df):

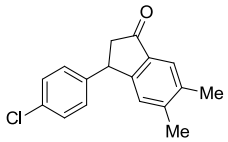
To an oven dried Schlenk tube under nitrogen atmosphere, were added ester **4d** (100 mg, 0.52 mmol), varatrole **5f** (108.8 mg, 0.78 mmol) and $FeCl_3$ (224.0 mg, 1.5 mmol), followed by addition of dry DCM (4 mL). The resulted reaction mixture was stirred at RT for 12 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate

95:5 to 85:15) furnished the arylated ester **6df** (120 mg, 69%) as pale yellow oil. [TLC control R_f(**4d**)=0.80, R_f(**6df**)=0.30, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2975, 2937, 1730 (C=O), 1595, 1457, 1409, 1370, 1329, 1255, 1149, 1073, 1029, 954, 853, 766, 701 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.32–7.22 (m, 2H, ArH), 7.23–7.10 (m, 3H, ArH), 6.79 (d, 1H, *J*=8.3 Hz, ArH), 6.77 (d, 1H, *J*=8.3 Hz, ArH), 6.66 (s, 1H, ArH), 3.88 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.85 (s, 3H, ArOCH$_3$), 3.75 (s, 3H, ArOCH$_3$), 3.10 (s, 2H, CH$_2$COOEt), 1.86 [s, 3H, ArC(CH$_2$)C*H*$_3$], 0.99 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=171.3 (s, C=O), 148.5 (s, ArC), 148.3 (s, ArC), 147.2 (s, ArC), 140.8 (s, ArC),127.9 (d, 2C, ArCH), 126.9 (d, 2C, ArCH), 126.0 (d, ArCH), 119.0 (d, ArCH), 111.1 (d, ArCH), 110.3 (d, ArCH), 60.0 (t, O*C*H$_2$CH$_3$), 55.8 (q, ArOCH$_3$), 55.7 (q, ArOCH$_3$), 46.7 (t, *C*H$_2$COOEt), 45.1 [s, Ar*C*(CH$_2$)CH$_3$], 28.4 (q, ArC(CH$_2$)*C*H$_3$), 13.9 [q, OCH$_2$*C*H$_3$] ppm.



7bc

3-(4-Chlorophenyl)-5, 6-dimethylindan-1-one (7bc):

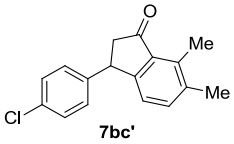
GP-1 was carried out and the indanone **7bc** (34 mg, 25%) was furnished as a yellow highly viscous liquid [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4b**)=0.65, R_f(**7bc**)=0.50, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 1704(C=O), 1614, 1453, 1284, 1168, 876, 730, 699 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.60 (s, 1H, ArH), 7.30 (d, 2H, *J*=8.3 Hz, ArH), 7.08 (d, 2H, *J*=8.3 Hz, ArH), 7.03 (s, 1H, ArH), 4.50 (dd, 1H, *J*=7.8 and 3.9 Hz, ArC*H*CH$_2$CO), 3.22 (dd, 1H, *J*=19.1 and 7.8 Hz, ArCHC*H*$_a$H$_b$CO), 2.62 (dd, 1H, *J*=19.1 and 3.9 Hz, ArCHCH$_a$*H*$_b$CO), 2.35 (s, 3H, ArCH$_3$), 2.31 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=205.4 (s, C=O), 155.6 (s, ArC), 145.6 (s, ArC), 142.5 (s, ArC), 137.1 (s, ArC), 134.8 (s, ArC), 132.5 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 128.8 (d, 2C, 2 × ArCH), 127.2 (d, ArCH), 123.7 (d, ArCH), 46.9 (t, ArCH*C*H$_2$CO), 43.3 (d, Ar*C*HCH$_2$CO), 20.7 (q, ArCH$_3$), 19.7 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{15}ClONa]^+=[M+Na]^+$: 293.0704; found: 293.0700.



7bc'

3-(4-Chlorophenyl)-6,7-dimethylindan-1-one (7bc'):

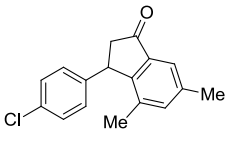
GP-1 was carried out and the indanone **7bc'** (87.8 mg, 65%) was furnished as a yellow highly viscous liquid [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4b**)=0.65, R_f(**7bc'**)=0.50, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=1699, 1600 (C=O), 1581, 1493, 1250, 907, 727 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.31 (d, 1H, J=7.8 Hz, ArH), 7.26 (d, 2H, J=8.3 Hz, ArH), 7.05 (d, 2H, J=8.3 Hz, ArH), 6.93 (d, 1H, J=7.8 Hz, ArH), 4.52 (dd, 1H, J=7.8 and 3.9 Hz, ArC*H*CH_2CO), 3.18 (dd, 1H, J=18.6 and 8.3 Hz, ArCHCH_aH_bCO), 2.64 (s, 3H, $ArCH_3$), 2.60 (dd, 1H, J=18.6 and 3.9 Hz, ArCHCH_aH_bCO), 2.31 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=206.7 (s, C=O), 156.0 (s, ArC), 142.9 (s, ArC), 137.0 (s, ArC), 136.9 (s, ArC), 136.2 (d, ArCH), 133.9 (s, ArC), 132.5 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 128.8 (d, 2C, 2 × ArCH), 123.5 (d, ArCH), 47.6 (t, ArCH*C*H_2CO), 42.5 (d, Ar*C*HCH_2CO), 19.0 (q, $ArCH_3$), 13.6 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{16}ClO]^+=[M+H]^+$: 271.0884; found: 271.0883.



7bd

3-(4-Chlorophenyl)-4, 6-dimethylindan-1-one (7bd):

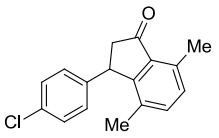
GP-1 was carried out and the indanone **7bd** (82.0 mg, 61%) was furnished as a highly viscous yellow liquid [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4b**)=0.65, R_f(**7bd**)=0.45, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=1705, 1615, 1601, 1480, 1453, 1304, 863, 760, 700, 609 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.48 (s, 1H, ArH), 7.26–7.19 (m, 3H, ArH), 6.96 (d, 2H, *J*=8.3 Hz, ArH), 4.52 (dd, 1H, *J*=8.3 and 2.4 Hz, ArC*H*CH_2CO), 3.22 (dd, 1H, *J*=19.1 and 8.3 Hz, ArCHCH_aH_bCO), 2.53 (dd, 1H, *J*=19.1 and 2.4 Hz, ArCHCH_aH_bCO), 2.40 (s, 3H, $ArCH_3$), 1.98 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=206.1 (s, C=O), 152.5 (s, ArC), 142.4 (s, ArC), 138.6 (s, ArC), 137.8 (d, ArCH), 137.3 (s, ArC), 136.2 (s, ArC), 132.3 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 128.6 (d, 2C, 2 × ArCH), 121.0 (d, ArCH), 47.7 (t, ArCH*C*H_2CO), 42.8 (d, Ar*C*HCH_2CO), 21.0 (q, $ArCH_3$), 18.2 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{16}ClO]^+$=$[M+H]^+$: 271.0884; found: 271.0882.



7be

3-(4-Chlorophenyl)-4,7-dimethylindan-1-one (7be):

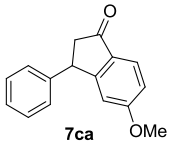
GP-1 was carried out and the indanone **7be** (108.4 mg, 80%) was furnished as a yellow highly viscous liquid [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4b**)=0.65, R_f(**7be**)=0.40, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=1698, 1600, 1581, 1493, 1250, 907, 727, 699, 604 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.25–7.17 (m, 3H, ArH), 7.09 (d, 1H, *J*=7.8 Hz, ArH), 6.94 (d, 2H, *J*=8.8 Hz, ArH), 4.48 (dd, 1H, *J*=8.3 and 2.4 Hz, ArC*H*CH_2CO), 3.17 (dd, 1H, *J*=19.1 and 8.3 Hz, ArCHCH_aH_bCO), 2.65 (s, 3H, $ArCH_3$), 2.49 (dd, 1H, *J*=19.1 and 2.4 Hz, ArCHCH_aH_bCO), 1.95 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=207.0 (s, C=O), 155.5 (s, ArC), 142.6 (s, ArC), 135.9 (s, ArC), 135.8 (d, ArCH), 134.4 (s, ArC), 133.5 (s, ArC), 132.3 (s, ArC), 130.4 (d, ArCH), 128.9 (d, 2C, 2 × ArCH), 128.6 (d, 2C, 2 × ArCH), 47.8 (t, ArCH*C*H_2CO), 42.6 (d, Ar*C*HCH_2CO), 18.0 (2 × q, 2C, 2 × $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{16}ClO]^+=[M+H]^+$: 271.0884; found: 271.0883.



7ca

5-Methoxy-3-phenylindan-1-one (7ca):

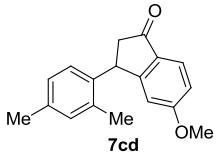
GP-1 was carried out and the indanone **7ca** (55 mg, 46%) was furnished as a yellow highly viscous liquid [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**4c**)=0.60, R_f(**7ca**)=0.50, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2852, 1701(C=O), 1593, 1488, 1454, 1285, 1246, 1085, 827, 700 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.74 (d, 1H, *J*=7.8 Hz, ArH), 7.31 (dd, 2H, *J*=8.3 and 7.3 Hz, ArH), 7.25 (t, 1H, *J*=7.3 Hz, ArH), 7.13 (d, 2H, *J*=8.3 Hz, ArH), 6.94 (dd, 1H, *J*=8.3 and 1.9 Hz, ArH), 6.85 (d, 1H, *J*=1.9 Hz, ArH), 4.49 (dd, 1H, *J*=8.3 and 3.4 Hz, ArC*H*CH_2CO), 3.78 (s, 3H, $ArOCH_3$), 3.19 (dd, 1H, *J*=19.1 and 8.3 Hz, ArCHC$H_a$$H_b$CO), 2.65 (dd, 1H, *J*=19.1 and 3.4 Hz, ArCHC$H_a$$H_b$CO) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.1 (s, C=O), 165.6 (s, ArC), 160.9 (s, ArC), 143.6 (s, ArC), 130.1 (s, ArC), 128.9 (d, 2C, 2 × ArCH), 127.6 (d, 2C, 2 × ArCH), 126.9 (d, ArCH), 125.0 (d, ArCH), 116.0 (d, ArCH), 109.7 (d, ArCH), 55.6 (q, $ArOCH_3$), 47.0 (t, ArCH*C*H_2CO), 44.4 (d, Ar*C*HCH_2CO) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{15}O_2]^+=[M+H]^+$: 239.1067; found: 239.1065.



7cd

3-(2,4-Dimethylphenyl)-5-methoxyindan-1-one (7cd):

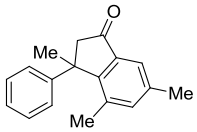
GP-1 was carried out and the indanone **7cd** (53.2 mg, 40%) was furnished as a yellow highly viscous liquid [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**4c**)=0.60, R_f(**7cd**)=0.55, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2852, 1701 (C=O), 1593, 1488, 1454, 1285, 1246, 1085, 827, 700 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.74 (d, 1H, *J*=8.3 Hz, ArH), 7.03 (s, 1H, ArH), 6.94 (dd, 1H, *J*=8.3 and 1.9 Hz, ArH), 6.90 (d, 1H, *J*=7.3 Hz, ArH), 6.69 (d, 1H, *J*=7.3 Hz, ArH), 6.68 (d, 1H, *J*=1.9 Hz, ArH), 4.71 (dd, 1H, *J*=8.3 and 3.4 Hz, ArC*H*CH_2CO), 3.80 (s, 3H, $ArOCH_3$), 3.19 (dd, 1H, *J*=19.1 and 8.3 Hz, ArCHCH_aH_bCO), 2.51 (dd, 1H, *J*=19.1 and 3.4 Hz, ArCHCH_aH_bCO), 2.37 (br. s, 3H, $ArCH_3$), 2.29 (s, 3H, $ArOCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.3 (s, C=O), 165.5 (s, 2C, 2 × ArC), 161.0 (s, ArC), 136.3 (s, ArC), 135.7 (s, ArC), 130.7 (s, ArC), 127.2 (d, ArCH), 125.1 (d, 2C, 2 × ArCH), 115.9 (d, 2C, 2 × ArCH), 109.7 (d, ArCH), 55.6 (q, $ArOCH_3$), 46.2 (t, ArCH*C*H_2CO), 44.4 (d, Ar*C*HCH_2CO), 20.8 (q, $ArCH_3$), 19.7 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{19}O_2]^+$=$[M+H]^+$: 267.1380; found: 267.1379.



7dd

3,4,6-trimethyl-3-phenylindan-1-one (7dd):

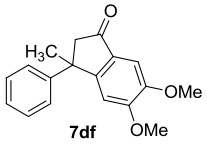
GP-1 was carried out and the indanone **7dd** (74.5 mg, 62%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4d**)=0.80, R_f(**7dd**)=0.60, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2966, 2921, 1702 (C=O), 1612, 1494, 1445, 1374, 1292, 1251, 1194, 1027, 878, 764, 730, 698, 646 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.50 (s, 1H, ArH), 7.23 (ddd, 2H, *J*=8.3, 7.3 and 1.0 Hz, ArH), 7.15 (ddd, 3H, *J*=8.3, 6.8 and 1.0 Hz, ArH), 6.98 (s, 1H, ArH), 2.88 (d, 1H, *J*=19.1 Hz, C$H_a$$H_b$CO), 2.80 (d, 1H, *J*=19.1 Hz, C$H_a$$H_b$CO), 2.27 (s, 3H, $ArCH_3$), 2.24 (s, 3H, $ArCH_3$), 1.75 [s, 3H, Ar-C(CH_2CO)CH_3] ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=205.7 (s, C=O), 161.1 (s, ArC), 147.6 (s, ArC), 145.5 (s, ArC), 136.8 (s, ArC), 134.0 (s, ArC), 128.4 (d, 2C, ArCH), 126.2 (d, 2C, ArCH), 126.1 (d, 2C, ArCH), 123.6 (d, ArCH), 56.0 (t, *C*H_2CO), 45.6 [s, Ar-*C*(CH_2CO)CH_3], 28.2 [q, Ar-C(CH_2CO)*C*H_3], 20.9 (q, $ArCH_3$), 19.7 (q, $ArCH_3$) ppm.

HR-MS (APCI+): (APCI+) m/z calculated for $[C_{16}H_{14}ClO]^+$=$[M+H]^+$: 257.0728; found: 257.0724.



7df

5,6-Dimethoxy-3-methyl-3-phenylindan-1-one (7df):

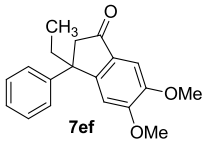
GP-1 was carried out with ester **4d** (100 mg, 0.52 mmol), veratrole **2f** (108.9 mg, 0.79 mmol), DCE (2 mL) triflic acid (0.1 mL, 1.57 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indanone **7df** (125 mg, 84%) as colorless viscous liquid. [TLC control R_f(**4d**)=0.80, R_f(**7df**)=0.40, (petroleum ether/ethyl acetate 85:15, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2962, 2930, 2836, 1696 (C=O), 1592, 1496, 1442, 1295, 1212, 1125, 1029, 821, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.36–7.28 (m, 2H, ArH), 7.27–7.18 (m, 4H, ArH), 6.65 (s, 1H, ArH), 3.96 (s, 3H, $ArOCH_3$), 3.89 (s, 3H, $ArOCH_3$), 2.93 (d, 1H, J=19.1 Hz, CH_aH$_b$CO), 2.89 (d, 1H, J=19.1 Hz, CHH_bCO), 1.85 [s, 3H, Ar-C(CH_2CO)CH_3] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=204.3 (s, C=O), 158.1 (s, ArC), 155.8 (s, ArC), 149.7 (s, ArC), 147.3 (s, ArC), 128.8 (s, ArC), 128.5 (d, 2C, ArCH), 126.3 (d, ArCH), 126.1 (d, 2C, ArCH), 106.1 (d, ArCH), 103.5 (d, ArCH), 56.2 (q, $ArOCH_3$), 56.1 (q, $ArOCH_3$), 55.9 (t, CH_2CO), 45.6 [s, Ar-C(CH_2CO)CH_3], 27.9 [q, Ar-C(CH_2CO)CH_3] ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{19}O_3]^+$=$[M+H]^+$: 283.1329; found: 283.1324.



7ef

3-Ethyl-5,6-dimethoxy-3-phenylindan-1-one (7ef):

GP-1 was carried out with ester **4d** (100 mg, 0.49 mmol), veratrole **2f** (92.1 mg, 0.67 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.46 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Purification of the residue by silica gel column chromatography

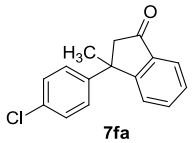
(petroleum ether/ethyl acetate 95:5 to 85:15) furnished indanone **7ef** (105 mg, 72%) as pale yellow viscous liquid. [TLC control R_f(**4d**)=0.80, R_f(**7ef**)=0.30, (petroleum ether/ethyl acetate 85:15, UV detection)].

IR (neat; MIR–ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2921, 2851, 1696 (C=O), 1592, 1496, 1462, 1302, 1276, 1213, 1039, 861, 766, 701 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.33–7.24 (m, 2H, ArH), 7.24–7.14 (m, 4H, ArH), 6.62 (s, 1H, ArH), 3.92 (s, 3H, ArOCH$_3$), 3.86 (s, 3H, ArOCH$_3$), 2.86 (d, 1H, *J*=19.1 Hz, CH_aH$_b$CO), 2.82 (d, 1H, *J*=19.1 Hz, CH$_a$$H_b$CO), 2.42–2.26 (m, 1H, C$H_aH_bCH_3$), 2.24–2.08 (m, 1H, CH$_a$$H_bCH_3$), 0.73 (t, 3H, *J*=7.3 Hz, CH$_2$CH_3) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=204.4 (s, C=O), 155.6 (s, ArC), 155.5 (s, ArC), 149.6 (s, ArC), 147.2 (s, ArC), 130.2 (s, ArC), 128.5 (d, 2C, ArCH), 126.4 (d, 2C, ArCH), 126.3 (d, ArCH), 106.6 (d, ArCH), 103.5 (d, ArCH), 56.3 (q, ArO*C*H$_3$), 56.1 (q, ArO*C*H$_3$), 52.5 (t, *C*H$_2$CO), 49.8 [s, Ar-*C*(CH$_2$CO)CH$_2$CH$_3$], 31.8 (t, *C*H$_2$CH$_3$), 9.1 (q, CH$_2$*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{19}$H$_{21}$O$_3$]$^+$=[M+H]$^+$: 297.1485; found: 297.1501.



7fa

3-(4-Chlorophenyl)-3-methylindan-1-one (7fa):

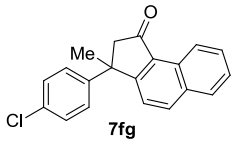
GP-1 was carried out with ester **4f** (100 mg, 0.44 mmol), benzene **5a** (416.6 mg, 5.34 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.33 mmol). The resulted reaction mixture was stirred at 80 °C for 24 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished indanone **7fa** (86 mg, 75%) as colorless oil. [TLC control R_f(**4f**)=0.80, R_f(**7fa**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2966, 2930, 1710 (C=O), 1602, 1491, 1462, 1288, 1234, 1151, 1093, 1012, 828, 762 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.78 (d, 1H, *J*=7.3 Hz, ArH), 7.60 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 7.43 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 7.25 (d, 1H, *J*=7.8 Hz, ArH), 7.24 (ddd, 2H, *J*=8.8, 2.4 and 2.4 Hz, ArH), 7.10 (ddd, 2H, *J*=8.8, 2.4 and 2.4 Hz, ArH), 2.91 (d, 1H, *J*=19.1 Hz, CH_aH$_b$CO), 2.88 (d, 1H, *J*=19.1 Hz, CH$_a$$H_b$CO), 1.81 [s, 3H, Ar-C(CH$_2$CO)CH_3] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=205.3 (s, C=O), 162.3 (s, ArC), 145.8 (s, ArC), 135.6 (s, ArC), 135.4 (d, ArCH), 132.3 (s, ArC), 128.5 (d, 2C, ArCH), 128.0 (d, ArCH), 127.7 (d, 2C, ArCH), 125.4 (d, ArCH), 123.4 (d, ArCH), 55.5 (t, *C*H_2CO), 45.6 [s, Ar-*C*(CH_2CO)CH_3], 28.3 [q, Ar-C(CH_2CO)*C*H_3] ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{14}ClO]^+$=$[M+H]^+$: 257.0728; found: 257.0724.



7fg

1-(4-Chlorophenyl)-1-methyl-1,2-dihydro-3*H*-cyclopenta[*a*]naphthalen-3-one (4fg):

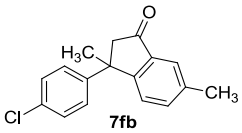
GP-1 was carried out and indanone **7fg** (106.6 mg, 71%) was furnished as brown color liquid. [TLC control R_f(**4f**)=0.60, R_f(**7fg**)=0.40, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 1698 (C=O), 1572, 1492, 1374, 1226, 1187, 1095, 827, 756, 528 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=9.20 (d, 1H, *J*=8.3 Hz, ArH), 8.03 (d, 1H, *J*=8.8 Hz, ArH), 7.89 (d, 1H, *J*=8.3 Hz, ArH), 7.70 (ddd, 1H, *J*=8.3, 6.8 and 1.0 Hz, ArH), 7.58 (ddd, 1H, *J*=8.3, 6.8 and 1.0 Hz, ArH), 7.23 (dd, 3H, *J*=8.3 and 1.5 Hz, ArH), 7.13 (dd, 2H, *J*=8.8 and 2.4 Hz, ArH), 3.00 (d, 1H, *J*=18.6 Hz, C$H_a$$H_b$CO), 2.98 (d, 1H, *J*=18.6 Hz, C$H_a$$H_b$CO), 1.85 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=205.9 (s, C=O), 164.8 (s, ArC), 145.5 (s, ArC), 136.6 (d, ArCH), 132.7 (s, ArC), 132.4 (s, ArC), 129.5 (s, ArC), 129.3 (d, ArCH), 128.9 (s, ArC), 128.6 (d, 2C, ArCH), 128.1 (d, ArCH), 127.8 (d, 2C, ArCH), 127.0 (d, ArCH), 124.4 (d, ArCH), 122.3 (d, ArCH), 56.1 (t, *C*H_2CO), 45.2 [s, Ar-*C*(CH_2CO)CH_3], 27.6 [q, Ar-C(CH_2CO)*C*H_3] ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{16}ClO]^+$=$[M+H]^+$: 307.0884; found: 307.0883.



7fb

3-(4-Chlorophenyl)-3,6-dimethylindan-1-one (7fb):

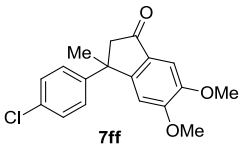
GP-1 was carried out with ester **4f** (100 mg, 0.44 mmol), toluene **5b** (492.0 mg, 5.34 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.33 mmol). The resulted reaction mixture was stirred at 80 °C for 24 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished indanone **7fb** (100 mg, 83%) as colorless viscous liquid. [TLC control R_f(**4f**)=0.80, R_f(**7fb**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2964, 2851, 1705 (C=O), 1581, 1488, 1399, 1282, 1244, 1151, 1160, 1093, 826, 724, 665, 588 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.57 (s, 1H, ArH), 7.42 (d, 1H, J=7.8 Hz, ArH), 7.22 (ddd, 2H, J=8.8, 2.4 and 2.4 Hz, ArH), 7.14 (d, 1H, J=7.8 Hz, ArH), 7.10 (ddd, 2H, J=8.8, 2.4 and 2.4 Hz, ArH), 2.89 (d, 1H, J=19.1 Hz, CH_aH$_b$CO), 2.87 (d, 1H, J=19.1 Hz, CH$_a$$H_b$CO), 2.42 (s, 3H, ArCH$_3$), 1.78 [s, 3H, Ar-C(CH$_2$CO)$CH_3$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=205.4 (s, C=O), 159.7 (s, ArC), 146.1 (s, ArC), 138.0 (s, ArC), 136.6 (d, ArCH), 135.9 (s, ArC), 132.2 (s, ArC), 128.5 (d, 2C, ArCH), 127.6 (d, 2C, ArCH), 125.1 (d, ArCH), 123.3 (d, ArCH), 55.8 (t, CH$_2$CO), 45.3 [s, Ar-C(CH$_2$CO)CH$_3$], 28.3 [q, Ar-C(CH$_2$CO)CH$_3$], 21.1 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [$C_{17}H_{16}ClO$]$^+$=[M+H]$^+$: 271.0884; found: 271.0880.



7ff

3-(4-Chlorophenyl)-5,6-dimethoxy-3-methylindan-1-one (7ff):

GP-1 was carried out with ester **4f** (100 mg, 0.44 mmol), veratrole **5f** (92.1 mg, 0.67 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.33 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished indanone **7ff** (125 mg, 88%) as brown

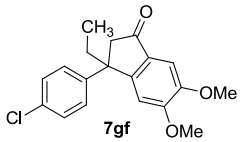
viscous liquid. [TLC control R_f(**4f**)=0.8, R_f(**7ff**)=0.30, (petroleum ether/ethyl acetate 85:15, UV detection)].

IR (neat; MIR–ATR, 4000–600 cm^{-1}): ν_{max}=2966, 2930, 1710 (C=O), 1602, 1491, 1462, 1234, 1093, 1011, 828, 761 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.21 (ddd, 2H, *J*=8.8, 2.4 and 2.4 Hz, ArH), 7.16 (s, 1H, ArH), 7.08 (ddd, 2H, *J*=8.8, 2.4 and 2.4 Hz, ArH), 6.56 (s, 1H, ArH), 3.90 (s, 3H, ArOCH$_3$), 3.84 (s, 3H, ArOCH$_3$), 2.81 (d, 1H, *J*=19.1 Hz, C*H*$_a$H$_b$CO), 2.80 (d, 1H, *J*=19.1 Hz, CH$_a$*H*$_b$CO), 1.77 [s, 3H, Ar-C(CH$_2$CO)C*H*$_3$] ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=203.7 (s, C=O), 157.5 (s, ArC), 155.9 (s, ArC), 149.8 (s, ArC), 145.9 (s, ArC), 132.2 (s, ArC), 128.7 (s, ArC), 128.5 (d, 2C, ArCH), 127.6 (d, 2C, ArCH), 105.8 (d, ArCH), 103.5 (d, ArCH), 56.2 (q, ArOCH$_3$), 56.1 (q, ArOCH$_3$), 55.7 (t, *C*H$_2$CO), 45.2 [s, Ar-*C*(CH$_2$CO)CH$_3$], 27.8 [q, Ar-C(CH$_2$CO)*C*H$_3$] ppm.

HR-MS (APCI+): m/z calculated for [C$_{18}$H$_{18}$ ClO$_3$]$^+$=[M+H]$^+$: 317.0939; found: 317.0946.



7gf

3-(4-Chlorophenyl)-3-ethyl-5,6-dimethoxyindan-1-one (4gf):

GP-1 was carried out with ester **4g** (100 mg, 0.42 mmol), veratrole **5f** (86.7 mg, 0.63 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.25 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished the indanone **4gf** (101 mg, 73%) as pale brown viscous liquid. [TLC control R_f(**4g**)=0.80, R_f(**7gf**)=0.30, (petroleum ether/ethyl acetate 85:15, UV detection)].

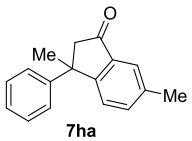
IR (neat; MIR–ATR, 4000–600 cm^{-1}): ν_{max}=2964, 2922, 2851, 1698 (C=O), 1592, 1498, 1464, 1302, 1278, 1214, 1094, 1040, 826, 802 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.24 (ddd, 2H, *J*=8.8, 2.4 and 2.4 Hz, ArH), 7.18 (s, 1H, ArH) 7.12 (ddd, 2H, *J*=8.8, 2.4 and 2.4 Hz, ArH), 6.57 (s, 1H, ArH), 3.92 (s, 3H, ArOCH$_3$), 3.86 (s, 3H, ArOCH$_3$), 2.84 (d, 1H, *J*=19.1 Hz, C*H*$_a$H$_b$CO), 2.75 (d, 1H, *J*=19.1 Hz, CH$_a$*H*$_b$CO), 2.38–

2.22 (m, 1H, CH_aH$_b$CH$_3$), 2.20–2.05 (m, 1H, CH$_a$$H_bCH_3$), 0.71 (t, 3H, *J*=7.3 Hz, ArC-CH$_2$CH_3) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=203.9 (s, C=O), 155.7 (s, ArC), 155.0 (s, ArC), 149.7 (s, ArC), 145.8 (s, ArC), 132.1 (s, ArC), 130.1 (s, ArC), 128.6 (d, 2C, ArCH), 127.9 (d, 2C, ArCH), 106.3 (d, ArCH), 103.5 (d, ArCH), 56.3 (q, ArOCH$_3$), 56.1 (q, ArOCH$_3$), 52.3 (t, *C*H$_2$CO), 49.4 [s, Ar-*C*(Et)CO], 31.7 (t, *C*H$_2$CH$_3$), 9.1 (q, CH$_2$*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{19}$H$_{20}$ClO$_3$]$^+$=[M+H]$^+$: 331.1095; found: 331.1099.



7ha

3,6-Dimethyl-3-phenylindan-1-one (7ha):

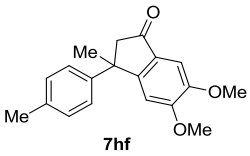
GP-1 was carried out and the indanone **7ha** (88 mg, 75%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4h**)=0.65, R_f(**7ha**)=0.45, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2963, 2923, 1708(C=O), 1614, 1582, 1445, 1406, 1376, 1282, 1245, 1161, 1067, 1028, 828, 768, 700, 607 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.58 (s, 1H, ArH), 7.42 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 7.27 (dd, 2H, *J*=7.3 and 1.5 Hz, ArH), 7.22–7.14 (m, 4H, ArH), 2.95 (d, 1H, *J*=19.1 Hz, CH_aH$_b$CO), 2.88 (d, 1H, *J*=19.1 Hz, CH$_a$$H_b$CO), 2.42 (s, 3H, ArCH$_3$), 1.81 [s, 3H, Ar-C(CH$_2$CO)C$H_3$] ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=205.9 (s, C=O), 160.3 (s, ArC), 147.5 (s, ArC), 137.5 (s, ArC), 137.7 (s, ArC), 136.4 (d, ArCH), 135.9 (s, ArC), 128.4 (d, 2C, ArCH), 126.2 (d, ArCH), 126.1 (d, ArCH), 125.2 (d, ArCH), 123.2 (d, ArCH), 56.0 (t, *C*H$_2$CO), 45.6 [s, Ar-*C*(CH$_2$CO)CH$_3$], 28.3 [q, Ar-C(CH$_2$CO)*C*H$_3$], 21.0 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{17}$H$_{16}$NaO] $^+$=[M+Na]$^+$: 259.1093; found: 259.1098.



7hf

5,6-Dimethoxy-3-methyl-3-(4-methylphenyl)indan-1-one (7hf):

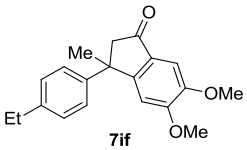
GP-1 was carried out and the indanone **7hf** (111.12 mg, 75%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4h**)=0.80, R_f(**7hf**)=0.60, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2962, 2925, 1694(C=O), 1591, 1496, 1463, 1360, 1295, 1211, 1113, 1031, 861, 818, 726, 589 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.18 (s, 1H, ArH), 7.08 (dd, 4H, J=8.8 and 2.9 Hz, ArH), 6.61 (s, 1H, ArH), 3.92 (s, 3H, $ArOCH_3$), 3.85 (s, 3H, $ArOCH_3$), 2.86 (d, 1H, J=18.5 Hz, CH_aH_bCO), 2.83 (d, 1H, J=18.5 Hz, CH_aH_bCO), 2.30 (s, 3H, $ArCH_3$), 1.78 [s, 3H, Ar-$C(CH_2CO)CH_3$] ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.5 (s, C=O), 158.3 (s, ArC), 155.8 (s, ArC), 149.6 (s, ArC), 144.4 (s, ArC), 135.9 (s, ArC), 129.1 (d, 2C, ArCH), 128.8 (s, ArC), 126.0 (d, 2C, ArCH), 106.1 (d, ArCH), 103.5 (d, ArCH), 56.2 (q, $ArOCH_3$), 56.1 (q, $ArOCH_3$), 56.0 (t, CH_2CO), 45.3 [s, Ar-$C(CH_2CO)CH_3$], 28.0 [q, Ar-$C(CH_2CO)CH_3$], 20.8 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{19}H_{21}O_3]^+$=$[M+H]^+$: 297.1485; found: 297.1498.



7if

3-(4-Ethylphenyl)-5,6-dimethoxy-3-methylindan-1-one (7if):

GP-1 was carried out and the indanone **7if** (105.4 mg, 68%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4i**)=0.80, R_f(**7if**)=0.60, (petroleum ether/ethyl acetate 98:2, UV detection)].

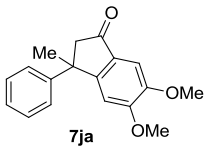
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2934, 1709 (C=O), 1578, 1453, 1412, 1368, 1239, 1211, 1151, 1125, 1005, 834, 736 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.17 (s, 1H, ArH), 7.08 (dd, 4H, J=9.8 and 3.4 Hz, ArH), 6.62 (s, 1H, ArH), 3.90 (s, 3H, $ArOCH_3$), 3.83 (s, 3H, $ArOCH_3$), 2.86 (d, 1H, J=18.6 Hz,

C*H*$_a$H$_b$CO), 2.82 (d, 1H, *J*=18.6 Hz, CH$_a$*H*$_b$CO), 2.57 (q, 3H, *J*=15.2 and 7.3 Hz, Ar*C*H$_2$CH$_3$), 1.78 [s, 3H, Ar-C(CH$_2$CO)C*H*$_3$], 1.18 (t, 3H, *J*=7.3 Hz, ArCH$_2$*C*H$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): *δ*=204.3 (s, C=O), 158.2 (s, ArC), 155.7 (s, ArC), 149.5 (s, ArC), 144.5 (s, ArC), 142.1 (s, ArC), 128.7 (s, ArC), 127.8 (d, 2C, ArCH), 125.9 (d, 2C, ArCH), 106.0 (d, ArCH), 103.4 (d, ArCH), 56.1 (q, ArOCH$_3$), 56.0 (q, ArOCH$_3$), 55.9 (t, *C*H$_2$CO), 45.2 [s, Ar-*C*(CH$_2$CO)CH$_3$], 28.1 [q, Ar-C(CH$_2$CO)*C*H$_3$], 27.9 (t, Ar*C*H$_2$CH$_3$), 15.3 (q, ArCH$_2$*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{20}$H$_{23}$O$_3$]$^+$=[M+H]$^+$: 311.1642; found: 311.1643.



7ja

5,6-Dimethoxy-3-methyl-3-phenylindan-1-one (7ja):

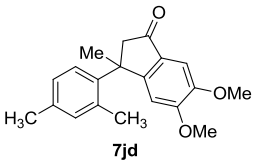
GP-1 was carried out and the indanone **7ja** (101.5 mg, 72%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4j**)=0.50, R_f(**7ja**)=0.40, (petroleum ether/ethyl acetate 88:12, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2962, 2924, 1696 (C=O), 1592, 1496, 1463, 1442, 1361, 1295, 1212, 1126, 1029, 861, 822, 769, 701 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): *δ*=7.32 (dd, 2H, *J*=8.3 and 7.3 Hz, ArH), 7.23 (s, 1H, ArH), 7.21 (d, 3H, *J*=8.3 Hz, ArH), 6.66 (s, 1H, ArH), 3.96 (s, 3H, ArOCH$_3$), 3.89 (s, 3H, ArOCH$_3$), 2.93 (d, 1H, *J*=18.6 Hz, C*H*$_a$H$_b$CO), 2.89 (d, 1H, *J*=18.6 Hz, CH$_a$*H*$_b$CO), 1.85 [s, 3H, Ar-C(CH$_2$CO)C*H*$_3$] ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): *δ*=204.3 (s, C=O), 158.1 (s, ArC), 155.8 (s, ArC), 149.7 (s, ArC), 147.4 (s, ArC), 128.8 (s, ArC), 128.5 (d, 2C, ArCH), 126.3 (d, ArCH), 126.1 (d, 2C, ArCH), 106.1 (d, ArCH), 103.5 (d, ArCH), 56.2 (q, ArOCH$_3$), 56.1 (q, ArOCH$_3$), 55.9 (t, -CH$_2$CO), 45.6 [s, Ar-*C*(CH$_2$CO)CH$_3$], 27.9 [q, Ar-C(CH$_2$CO)*C*H$_3$] ppm.

HR-MS (APCI+): m/z calculated for [C$_{18}$H$_{19}$O$_3$]$^+$=[M+H]$^+$: 283.1329; found: 283.1321.



7jd

3-(2,4-Dimethylphenyl)-5,6-dimethoxy-3-methylindan-1-one (7jd):

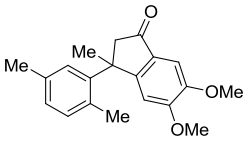
GP-1 was carried out and indanone **7jd** (124 mg, 80%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4j**)=0.60, R_f(**7jd**)=0.35, (petroleum ether/ethyl acetate 88:12, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2961, 2925, 1693 (C=O), 1591, 1495, 1462, 1300, 1287, 1210, 1029, 861, 810, 734 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.36 (d, 1H, J=7.8 Hz, ArH), 7.18 (s, 1H, ArH), 7.01 (d, 1H, J=7.8 Hz, ArH), 6.91 (s, 1H, ArH), 6.54 (s, 1H, ArH), 3.91 (s, 3H, $ArOCH_3$), 3.82 (s, 3H, $ArOCH_3$), 3.05 (d, 1H, J=19.1 Hz, CH_aH_bCO), 2.78 (d, 1H, J=19.1 Hz, CH_aH_bCO), 2.28 [s, 3H, Ar-$C(CH_2CO)CH_3$], 1.78 (s, 3H, $ArCH_3$), 1.74 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.3 (s, C=O), 159.4 (s, ArC), 155.8 (s, ArC), 149.4 (s, ArC), 140.1 (s, ArC), 136.5 (s, ArC), 136.3 (d, ArCH), 133.6 (d, ArCH), 128.4 (s, ArC), 126.9 (d, ArCH), 126.2 (d, ArCH), 105.7 (d, ArCH), 103.9 (d, ArCH), 56.3 (q, $ArOCH_3$), 56.0 (q, $ArOCH_3$), 53.3 (t, CH_2CO), 45.5 [s, Ar-$C(CH_2CO)CH_3$], 31.3 [q, Ar-$C(CH_2CO)CH_3$], 21.1 (q, $ArCH_3$), 20.6 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{22}NaO]^+$=$[M+Na]^+$: 333.1461; found: 333.1460.



7je

3-(2,5-Dimethylphenyl)-5,6-dimethoxy-3-methylindan-1-one (7je):

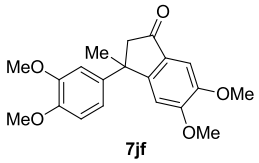
GP-1 was carried out and the indanone **7je** (119.3 mg, 77%) was furnished as colorless liquid. [TLC control R_f(**4j**)=0.60, R_f(**7je**)=0.40, (petroleum ether/ethyl acetate 88:12, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2923, 1696 (C=O), 1591, 1497, 1463, 1301, 1289, 1212, 1127, 1029, 862, 810 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.29 (s, 1H, ArH), 7.19 (s, 1H, ArH), 6.98 (dd, 2H, *J*=9.3 and 7.8 Hz, ArH), 6.55 (s, 1H, ArH), 3.93 (s, 3H, $ArOCH_3$), 3.83 (s, 3H, $ArOCH_3$), 3.07 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 2.78 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 2.35 [s, 3H, Ar-$C(CH_2CO)CH_3$], 1.76 (s, 6H, 2 × $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.3 (s, C=O), 159.4 (s, ArC), 155.8 (s, ArC), 149.4 (s, ArC), 142.8 (s, ArC), 135.0 (s, ArC), 133.4 (s, ArC), 132.8 (d, ArCH), 128.5 (s, ArC), 127.8 (d, ArCH), 127.6 (d, ArCH), 105.8 (d, ArCH), 104.0 (d, ArCH), 56.3 (q, $ArOCH_3$), 56.1 (q, $ArOCH_3$), 53.4 (t, CH_2CO), 45.8 [s, Ar-$C(CH_2CO)CH_3$], 31.4 [q, Ar-$C(CH_2CO)CH_3$], 21.2 (q, $ArCH_3$), 20.8 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_3]^+$=$[M+H]^+$: 311.1642; found: 311.1630.



7jf

3-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-3-methylindan-1-one (7jf):

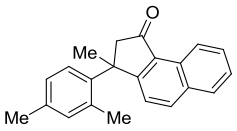
GP-1 was carried out and the indanone **7jf** (147 mg, 86%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4j**)=0.55, R_f(**7jf**)=0.30, (petroleum ether/ethyl acetate 70:30, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2961, 2935, 1692 (C=O), 1591, 1496, 1462, 1361, 1294, 1250, 1127, 1026, 859, 811, 730 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.17 (s, 1H, ArH), 6.75 (dd, 2H, *J*=10.3 and 8.3 Hz, ArH), 6.60 (s, 2H, ArH), 3.91 (s, 3H, $ArOCH_3$), 3.84 (s, 3H, $ArOCH_3$), 3.82 (s, 3H, $ArOCH_3$), 3.73 (s, 3H, $ArOCH_3$), 2.86 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 2.82 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 1.76 [s, 3H, Ar-$C(CH_2CO)CH_3$] ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.3 (s, C=O), 158.2 (s, ArC), 155.8 (s, ArC), 149.6 (s, ArC), 148.8 (s, ArC), 147.5 (s, ArC), 139.9 (s, ArC), 128.7 (s, ArC), 118.2 (d, ArCH), 110.8 (d, ArCH), 109.8 (d, ArCH), 106.0 (d, ArCH), 103.5 (d, ArCH), 56.2 (q, $ArOCH_3$), 56.0 (q, $ArOCH_3$), 55.9 (t, CH_2CO), 55.8 (q, $ArOCH_3$), 55.7 (q, $ArOCH_3$), 45.3 [s, Ar-$C(CH_2CO)CH_3$], 28.2 [q, Ar-$C(CH_2CO)CH_3$] ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_5]^+$=$[M+H]^+$: 343.1540; found: 343.1539.



7kd

3,4,6-Trimethyl-3-(2-naphthyl)indan-1-one (7kd):

GP-1 was carried out and the indanone **7kd** (115.5 mg, 77%) was furnished as white solid, [TLC control R_f(**4k**)=0.60, R_f(**7kd**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

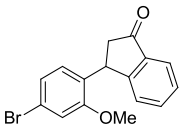
M.p.:108-110 ^{o}C

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 1697 (C=O), 1511, 1461, 1374, 1225, 1103, 1042, 828, 755 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=9.21 (d, 1H, *J*=8.3 Hz, ArH), 8.03 (d, 1H, *J*=8.8 Hz, ArH), 7.89 (d, 1H, *J*=7.8 Hz, ArH), 7.71 (ddd, 1H, *J*=8.3, 7.3 and 1.5 Hz, ArH), 7.58 (ddd, 1H, *J*=8.3, 7.3 and 1.5 Hz, ArH), 7.38 (d, 1H, *J*=8.3 Hz, ArH), 7.27 (d, 1H, *J*=8.3 Hz, ArH), 7.04 (1H, *J*=7.8 Hz, ArH), 6.93 (s, 1H, ArH), 3.21 (d, 1H, *J*=18.6 Hz, CH_aH$_b$CO), 2.96 (d, 1H, *J*=18.6 Hz, CH$_a$$H_b$CO), 2.31 (s, 3H, ArC$H_3$), 1.84 (s, 3H, ArC$H_3$), 1.79 [s, 3H, Ar-C(C$H_2$CO)C$H_3$] ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=206.4 (s, C=O), 166.8 (s, ArC), 139.8 (s, ArC), 136.8 (s, ArC), 136.3 (s, ArC), 136.3 (d, ArCH), 133.7 (d, ArCH) 132.6 (s, ArC), 129.2 (d, 2C, ArCH), 128.1 (d, ArCH), 127.2 (d, ArCH), 126.7 (d, 2C, ArCH), 126.4 (d, ArCH), 124.3 (d, ArCH), 122.4 (d, ArCH), 53.7 (t, *C*H$_2$CO), 45.6 [s, Ar-*C*(CH$_2$CO)CH$_3$], 31.2 [q, Ar-C(CH$_2$CO)*C*H$_3$], 21.31 (q, ArCH$_3$), 20.6 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{22}H_{21}O]^+$=$[M+H]^+$: 301.1587; found: 301.1589.



7ah

3-(4-Bromo-2-methoxyphenyl)indan-1-one (7ah):

GP-1 was carried out with ester **4a** (100 mg, 0.57 mmol), 3-bromoanisole **5h** (159.2 mg, 0.85 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.70 mmol). The resultant reaction mixture was stirred at 80 °C for 24 h Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished the indanone **7ah** (111.3 mg, 54%) as

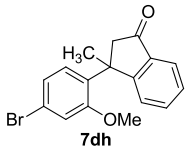
pale yellow viscous liquid. [TLC control R_f(**4a**)=0.70, R_f(**7ah**)=0.35, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2938, 1710 (C=O), 1603, 1589, 1488, 1462, 1397, 1243, 1028, 840, 761 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.78 (d, 1H, *J*=7.3 Hz, ArH), 7.55 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 7.39 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 7.26 (d, 1H, *J*=7.8 Hz, ArH), 7.00 (s, 1H, ArH), 6.99 (d, 1H, *J*=8.3 Hz, ArH), 6.79 (d, 1H, *J*=8.3 Hz, ArH), 4.81 (dd, 1H, *J*=7.8 and 3.4 Hz, ArC*H*CH$_2$), 3.73 (s, 3H, ArOCH$_3$), 3.14 (dd, 1H, *J*=19.1 and 7.8 Hz, ArCHC*H$_a$*H$_b$), 2.61 (dd, 1H, *J*=19.1 and 3.4 Hz, ArCHCH$_a$*H$_b$*) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=206.3 (s, C=O), 157.8 (s, ArC), 157.1 (s, ArC), 137.0 (s, ArC), 134.8 (d, ArCH), 130.7 (s, ArC), 129.5 (d, ArCH), 127.6 (d, ArCH), 126.4 (d, ArCH), 123.6 (d, ArCH), 123.3 (d, ArCH), 121.2 (s, ArC), 114.4 (d, ArCH), 55.6 (q, ArOCH$_3$), 44.9 (t, ArCH*C*H$_2$), 38.6 (d, Ar*C*HCH$_2$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{14}BrO_2]^+$=$[M+H]^+$: 317.0172; found: 317.0186.



7dh

3-(2-Bromo-4-methoxyphenyl)-3-methylindan-1-one (7dh):

GP-1 was carried out with ester **4d** (100 mg, 0.52 mmol), 3-bromoanisole **5h** (147.7 mg, 0.78 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.57 mmol). The resulted reaction mixture was stirred at 80 °C for 24 hrs. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished indanone **7dh** (160.0 mg, 92%) as white solid, recrystallized the solid, [TLC control R_f(**4d**)=0.80, R_f(**7dh**)=0.40, (petroleum ether/ethyl acetate 85:15, UV detection)].

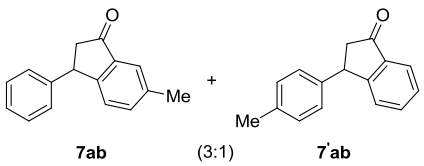
M.p.: 120–124 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2965, 2934, 1711 (C=O), 1602, 1486, 1462, 1392, 1287, 1237, 1157, 1068, 1026, 858, 758, 583 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.74 (d, 1H, *J*=7.3 Hz, ArH), 7.50 (dd, 1H, *J*=7.8 and *J*=7.3 Hz, ArH), 7.35 (dd, 1H, *J*=7.8 and *J*=7.8 Hz, ArH), 7.27 (d, 1H, *J*=8.3 Hz, ArH), 7.13 (d, 1H, *J*=7.8 Hz, ArH), 7.08 (dd, 1H, *J*=8.3 and 1.9 Hz, ArH), 6.88 (d, 1H, *J*=1.9 Hz, ArH), 3.40 (s, 3H, $ArOCH_3$), 3.11 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 2.63 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 1.71 [s, 3H, $ArC(CH_2CO)CH_3$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=206.3 (s, C=O), 162.4 (s, ArC), 157.9 (s, ArC), 135.8 (s, ArC), 134.5 (d, ArCH), 133.3 (s, ArC), 128.2 (d, ArCH), 127.2 (d, ArCH), 124.2 (d, ArCH), 123.2 (d, ArCH), 123.0 (d, ArCH), 121.5 (s, ArC), 115.3 (d, ArCH), 55.2 (q, $ArOCH_3$), 52.4 (t, CH_2CO), 44.1 [s, Ar-$C(CH_2CO)CH_3$], 29.0 [q, Ar-$C(CH_2CO)CH_3$] ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{16}BrO_2]^+$=$[M+H]^+$: 331.0328; found: 331.0343.



6-Methyl-3-phenylindan-1-one (7ab) and 3-(4-Methylphenyl) indan-1-one (7'ab):

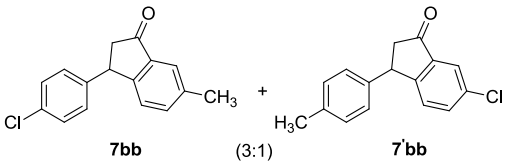
GP-1 was carried out, to an oven dried Schlenk tube under nitrogen atmosphere, were added ester **4a** (100 mg, 0.57 mmol), toluene **5b** (626.5 mg, 6.81mmol) and DCE (2 mL), followed by the addition of triflic acid (0.15 mL, 1.70 mmol). The resultant reaction mixture was stirred at 80 °C for 24 h. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished as an inseparable mixture of indanones **(7ab+7'ab)** (114.8 mg, 91%) in 3:1 ratio as a pale yellow viscous liquid. [TLC control R_f(**4a**)=0.65, R_f(**7ab+7'ab**)=0.40, (petroleum ether/ethyl acetate 95:5, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2955, 1709 (C=O), 1602, 1584, 1488, 1454, 1280, 1157, 1046, 822, 758, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): (data for the major isomer **7ab**) δ=7.52 (s, 1H, ArH), 7.30 (d, 2H, *J*=7.8 Hz, ArH), 7.26–7.10 (m, 3H, ArH), 7.07 (d, 1H, *J*=7.8 Hz, ArH), 6.94 (m, 1H, ArH), 4.44 (dd, 1H, *J*=7.8 and 3.9 Hz, $ArCHCH_2$), 2.58 (dd, 1H, *J*=19.1 and 7.8 Hz, $ArCHCH_aH_b$), 2.58 (dd, 1H, *J*=19.1 and 3.9 Hz, $ArCHCH_aH_b$), 2.33 (s, 3H, $ArCH_3$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): (data for the major isomer **7ab**) δ=206.1 (s, C=O), 155.4 (s, ArC), 143.9 (s, ArC), 137.8 (d, ArCH), 136.3 (d, ArCH), 129.5 (s, ArC), 128.8 (d, 2C, ArCH), 127.5 (d, 2C, ArCH), 126.8 (d, ArCH), 126.5 (d, ArCH), 123.2 (s, ArC), 47.1 (t, ArCH*C*H_2), 44.0 (d, Ar*C*HCH$_2$), 21.1 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{15}O]^+$=$[M+H]^+$: 223.1117; found: 223.1108 (for the mixture of **7ab+7'ab**).



3-(4-Chlorophenyl)-6-methyl indan-1-one (7bb) and 6-Chloro-3-(4-methylphenyl) indan-1-one (7'bb):

GP-1 was carried out with ester **4b** (100 mg, 0.47 mmol), toluene **5b** (524.1 mg, 5.70 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.42 mmol). The resulted reaction mixture was stirred at 80 °C for 24 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 94:6) furnished an inseparable mixture of indanones **7bb** +**7'bb** (105 mg, 86%) as brown solid, [TLC control R_f(**4b**)=0.80, R_f(**7bb+7'bb**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

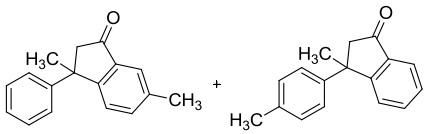
M.p.:110–115 °C

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2854, 1707 (C=O), 1611, 1487, 1405, 1278, 1242, 1156, 1089, 1048, 935, 822, 783, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): (data for the major isomer **7bb**) δ=7.48 (s, 1H, ArH), 7.28 (d, 1H, *J*=7.8 Hz, ArH), 7.14 (ddd, 2H, *J*=8.3, 2.4 and 2.4 Hz, ArH), 7.01 (d, 1H, *J*=7.8 Hz, ArH), 6.93 (ddd, 2H, *J*=8.3, 2.4 and 2.4 Hz, ArH), 4.39 (dd, 1H, *J*=7.8 and 3.4 Hz, C*H*CH$_2$CO), 3.09 (dd, 1H, *J*=19.1 and 7.8 Hz, CHCH_aH$_b$CO), 2.48 (dd, 1H, *J*=19.1 and 3.4 Hz, CHCH$_a$$H_b$CO), 2.30 (s, 3H, ArCH$_3$) ppm.

^{13}CNMR ($CDCl_3$, 100 MHz): (data for the major isomer **7bb**) δ=205.6 (s, C=O), 154.7 (s, ArC), 142.4 (s, ArC), 138.1 (s, ArC), 136.4 (d, ArCH), 132.6 (s, ArC), 129.0 (s, ArC), 128.9 (d, 2C, ArCH), 128.8 (d, 2C, ArCH) 126.3 (d, ArCH), 123.3 (d, ArCH), 47.0 (t, CH*C*H$_2$CO), 43.4 (d, *C*HCH$_2$CO), 21.1 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{14}ClO]^+=[M+H]^+$: 257.0728 found: 257.0714 (for mixture of **7bb+7'bb)**.



7db (3:1) **7'db**

3,6-Dimethyl-3-phenyl indan-1-one(7db) and 3-Methyl-3-(4-methylphenyl) indan-1-one (7' db):

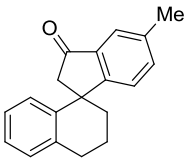
GP-1 was carried out with ester **4d** (100 mg, 0.52 mmol), toluene **5b** (581.1 mg, 6.30 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.57 mmol). The resulted reaction mixture was stirred at 80 °C for 24 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 94:6) furnished an inseparable mixture of indanones **7db+7'db** (112 mg, 90%). [TLC control R_f(**4d**)=0.80, R_f(**7db+7'db**)=0.40 (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2963, 2920, 2850, 1706 (C=O), 1614, 1488, 1282, 1243, 1094, 1011, 826, 734, 710, 665 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): (data for the major isomer **7db+7'db**) δ=7.63 (s, 1H, ArH), 7.46 (d, 1H, *J*=8.3 Hz, ArH), 7.32 (dd, 2H, *J*=7.8 and 1.5 Hz, ArH), 7.29–7.17 (m, 4H, ArH), 3.02 (d, 1H, *J*=19.1 Hz, CH_aH$_b$CO), 2.91 (d, 1H, *J*=19.1 Hz, CH$_a$$H_b$CO), 2.47 (s, 3H, ArCH$_3$), 1.86 [s, 3H, Ar-C(CH$_2$CO)C$H_3$] ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): (data for the major isomer **7db+7'db**) δ=205.9 (s, C=O), 160.3 (s, ArC), 147.5 (s, ArC), 137.7 (s, ArC), 136.5 (d, ArCH), 135.2 (s, ArC), 129.1 (d, ArCH), 128.4 (d, 2C, ArCH), 126.1 (d, 2C, ArCH), 125.2 (d, ArCH), 123.1 (d, ArCH), 56.0 (t, CH$_2$CO), 45.6 [s, Ar-*C*(CH$_2$CO)CH$_3$], 28.3 (q, ArCH$_3$), 21.0 [q, Ar-C(CH$_2$CO)*C*H$_3$] ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{17}O]^+=[M+H]^+$: 237.1274; found: 237.1273 (for mixture of **7db+7'db).**



7lb

5-Methyl-3',4'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-3(2*H*)-one (7lb):

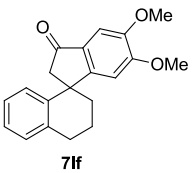
To an oven dried Schlenk tube under nitrogen atmosphere, were added ester **4l** (100 mg, 0.52 mmol), toluene **5b** (581.1 mg, 6.30 mmol) and DCE (2 mL) followed by the addition of triflic acid (0.1 mL, 1.57 mmol). The resultant reaction mixture was stirred at 50 °C for 24 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished the spiro-tetracyclic ketone **7lb** (74.1 mg, 61%) as yellow viscous liquid. [TLC control R_f(**4l**)=0.55, R_f(**7lb**)=0.40, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2926, 1711(C=O), 1581, 1487, 1448, 1281, 1243, 1160, 1050, 1026, 763, 732 cm^{-1}**.**

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.58 (s, 1H, ArH), 7.40 (d, 1H, *J*=7.3 Hz, ArH), 7.13 (d, 1H, *J*=7.3 Hz, ArH), 7.11 (d, 1H, *J*=7.8 Hz, ArH), 7.10 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 7.00 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 6.61 (d, 1H, *J*=7.8 Hz, ArH), 3.05–2.88 (m, 3H, ArCH_2CH$_2$CH$_2$ and CH_aH$_b$CO), 2.85 (d, 1H, *J*=19.1 Hz, CH$_a$$H_b$CO), 2.42 (s, 3H, ArCH$_3$), 2.16–2.00 (m, 2H, ArCH$_2$CH_2CH$_2$), 1.96–1.80 (m, 2H, ArCH$_2$CH$_2$CH_2) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=206.2 (s, C=O), 161.4 (s, ArC), 142.2 (s, ArC), 137.7 (s, ArC), 136.7 (s, ArC), 136.6 (s, ArC), 136.6 (d, ArCH), 129.0 (d, ArCH), 128.1 (d, ArCH), 126.4 (d, ArCH), 126.2 (d, ArCH), 125.4 (d, ArCH), 122.9 (d, ArCH), 56.0 (t, *C*H$_2$CO), 46.3 [s, (CO)*C*CH$_2$CH$_2$CH$_2$], 39.5 (t, Ar*C*H$_2$CH$_2$CH$_2$), 29.8 (t, CH$_2$), 21.1 (q and t, 2C, ArCH$_3$ and CH$_2$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{19}$H$_{19}$O]$^+$=[M+H]$^+$: 263.1430; found: 263.1436.



7lf

5,6-dimethoxy-3',4'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-3(2*H*)-one (7lf):

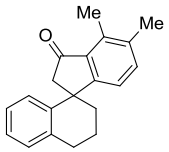
To an oven dried Schlenk tube under nitrogen atmosphere, were added ester **4l** (100 mg, 0.46 mmol), veratrole **5f** (95.8 mg, 0.69 mmol) and DCE (2 mL) followed by the addition of triflic acid (0.12 mL, 1.70 mmol). The resultant reaction mixture was stirred at 50 °C for 24 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished spiro-tetracyclic ketone **7lf** (98.4 mg, 67%) as pale yellow semi-solid. [TLC control R_f(**4l**)=0.75, R_f(**7lf**)=0.40, (petroleum ether/ethyl acetate 75:25, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2933, 1693 (C=O), 1592, 1496, 1464, 1453, 1290, 1049, 1025, 803, 729, 701 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.20 (s, 1H, ArH), 7.12 (d, 1H, *J*=7.3 Hz, ArH), 7.10 (dd, 1H, *J*=7.8 and 7.3 Hz, ArH), 7.01 (dd, 1H, *J*=7.8 and 7.8 Hz, ArH), 6.62 (d, 1H, *J*=7.8 Hz, ArH), 6.58 (s, 1H, ArH), 3.93 (s, 3H, ArOCH_3), 3.83 (s, 3H, ArOCH_3), 2.95 (dd, 2H, *J*=11.2 and 5.4 Hz, ArCH_2CH$_2$CH$_2$), 2.88 (d, 1H, *J*=19.1 Hz, CH_aH$_b$CO), 2.78 (d, 1H, *J*=19.1 Hz, CH$_a$H$_b$CO), 2.16–2.00 (m, 2H, ArCH$_2$CH_2CH$_2$), 1.96–1.76 (m, 2H, ArCH$_2$CH$_2$CH_2) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=204.6 (s, C=O), 159.0 (s, ArC), 155.9 (s, ArC), 149.7 (s, ArC), 142.1 (s, ArC), 136.6 (s, ArC), 129.6 (s, ArC), 129.0 (d, ArCH), 128.0 (s, ArC), 126.6 (d, ArCH), 126.3 (d, ArCH), 106.2 (d, ArCH), 103.3 (d, ArCH), 56.3 (q, ArOCH$_3$), 56.1 (q, ArOCH$_3$), 55.9 (t, *C*H$_2$CO), 46.4 [s, (CO)*C*CH$_2$CH$_2$CH$_2$], 39.2 (t, Ar*C*H$_2$CH$_2$CH$_2$), 29.7 (t, CH$_2$), 21.2 (t, CH$_2$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{20}$H$_{21}$O$_3$]$^+$=[M+H]$^+$: 309.1485; found: 309.1463.



7lc

5,6-Dimethyl-3',4'-dihydro-*2'H*-spiro[indene-1,1'-naphthalen]-3(*2H*)-one (7lc):

GP-1 was carried out and the indanone **7lc** (66.2 mg, 48%) was furnished as a white solid [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**4l**)=0.60, R_f(**7lc**)=0.4, UV detection].

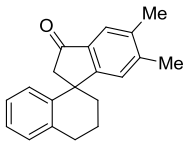
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2858, 1703 (C=O), 1612, 1578, 1448, 1246, 882, 762, 730 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.55 (s, 1H, ArH), 7.15–7.05 (m, 2H, ArH), 7.04–6.95 (m, 2H, ArH), 6.62 (d, 1H, *J*=7.8 Hz, ArH), 3.02–2.85 (m, 3H, CH$_2$ and CH_aH$_b$CO), 2.79 (d, 1H,

J=18.6 Hz, CH_aH_bCO), 2.32 (s, 3H, $ArCH_3$), 2.27 (s, 3H, $ArCH_3$), 2.17–1.98 (m, 2H, CH_2), 1.95–1.78 (m, 2H, CH_2) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=205.9 (s, C=O), 162.2 (s, ArC), 145.6 (s, ArC), 142.4 (s, ArC), 136.8 (s, ArC), 136.7 (s, ArC), 134.7 (s, ArC), 129.0 (d, ArCH), 128.2 (d, ArCH), 126.5 (d, ArCH), 126.3 (d, ArCH), 126.2 (d, ArCH), 123.4 (d, ArCH), 56.1 (t, ArCH_2CO), 46.3 (s, Ar-*C*-CH_2CO), 39.5 (t, $ArCH_2$), 29.8 (t, $ArCH_2$), 21.1 (t, $ArCH_2$), 20.8 (q, $ArCH_3$), 19.7 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{21}O]^+$=$[M+H]^+$: 277.1587; found: 277.1584.



7Ic'

4,5-Dimethyl-3',4'-dihydro-*2'H*-spiro[indene-1,1'-naphthalen]-3(*2H*)-one(7'Ic):

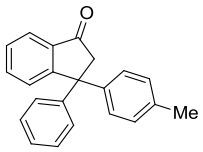
GP-1 was carried out and the indanone **7'Ic** (63.5 mg, 46%) was furnished as a yellow highly viscous liquid [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**4l**)=0.60, R_f(**7'Ic**)=0.50, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2920, 2857, 1699 (C=O), 1608, 1575, 1440, 1246, 830, 725, 647 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.32 (d, 1H, *J*=7.8 Hz, ArH), 7.20–7.05 (m, 2H, ArH), 7.00 (dd, 1H, *J*=8.3 and 8.3 Hz, ArH), 6.93 (d, 1H, *J*=7.8 Hz, ArH), 6.65 (d, 1H, *J*=8.3 Hz, ArH), 3.02–2.85 (m, 3H, CH_2 and CH_aH_bCO), 2.81 (d, 1H, *J*=18.6 Hz, CH_aH_bCO), 2.66 (s, 3H, $ArCH_3$), 2.32 (s, 3H, $ArCH_3$), 2.15–1.98 (m, 2H, CH_2), 1.95–1.78 (m, 2H, CH_2) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=207.3 (s, C=O), 162.8 (s, ArC), 142.6 (s, ArC), 136.8 (s, ArC), 136.5 (s, ArC), 136.4 (s, ArC), 136.3 (d, ArCH), 133.8 (s, ArC), 128.9 (d, ArCH), 128.2 (d, ArCH), 126.4 (d, ArCH), 126.1 (d, ArCH), 122.6 (d, ArCH), 56.7 (t, ArCH_2CO), 45.1 (s, Ar-*C*-CH_2CO), 39.8 (t, $ArCH_2$), 29.8 (t, $ArCH_2$), 21.0 (t, $ArCH_2$), 19.0 (q, $ArCH_3$), 13.4 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{21}O]^+$=$[M+H]^+$: 277.1587; found: 277.1585.



7mb

3-(4-Methylphenyl)-3-phenylindan-1-one (7mb):

GP-2 was carried out and the indanone **7mb** (144.72 mg, 97%) was furnished as yellow colour solid, [TLC control R_f(**4m**)=0.60, R_f(**7mb**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

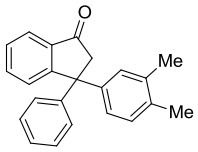
M.p.: 70-72 ^{o}C

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3024, 2921, 1711 (C=O), 1599, 1493, 1460, 1286, 1232, 1059, 815, 761, 700 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.81 (d, 1H, *J*=7.8 Hz, ArH), 7.58 (ddd, 1H, *J*=8.3, 7.3 and 1.0 Hz, ArH), 7.41 (dd, 1H, *J*=8.3 and 7.3 Hz, ArH), 7.38 (d, 1H, *J*=7.8 Hz, ArH), 7.28 (ddd, 2H, *J*=7.8, 6.8 and 2.0 Hz, ArH), 7.24 (d, 1H, *J*=8.3 and 7.3 Hz, ArH), 7.18 (dd, 2H, *J*=7.3 and 1.5 Hz, ArH), 7.07 (dd, 4H, *J*=8.3 and 7.8 Hz, ArH) 3.48 (d, 1H, *J*=19.1 Hz, CH_aH$_b$CO), 3.47 (d, 1H, *J*=19.1 Hz, CH$_a$$H_b$CO), 2.32 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=205.1 (s, C=O), 160.1 (s, ArC), 146.9 (s, ArC), 143.7 (s, ArC), 136.2 (s, ArC), 135.7 (s, ArC), 134.7 (d, ArCH), 129.1 (d, 3C, ArCH), 128.3 (d, 3C, ArCH), 128.0 (d, 2C, ArCH), 127.8 (d, 2C, ArCH), 126.5 (d, ArCH), 123.6 (d, ArCH), 56.1 (t, *C*H$_2$CO), 55.8 [s, Ar-*C*(CH$_2$CO)CH$_3$], 20.8 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{22}$H$_{18}$NaO]$^+$=[M+Na]$^+$: 321.1250; found: 321.1236.



7mc

3-(3,4-Dimethylphenyl)-3-phenylindan-1-one(7mc):

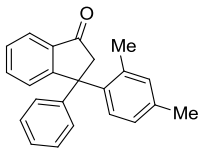
GP-2 was carried out and the indanone **7mc** (101.4 mg, 65%) was furnished as a yellow highly viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4m**)=0.60, R_f(**7mc**)=0.45, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2920, 2851, 1714 (C=O), 1600, 1459, 1445, 1229, 760, 700 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.79 (d, 1H, *J*=7.8 Hz, ArH), 7.58 (dd, 1H, *J*=7.8 and 7.8 Hz, ArH), 7.41 (dd, 1H, *J*=8.3 and 7.8 Hz, ArH), 7.37 (d, 1H, *J*=8.3 Hz, ArH), 7.32–7.11 (m, 5H, ArH), 7.03 (d, 1H, *J*=7.8 Hz, ArH), 6.92 (s, 1H, ArH), 6.86 (dd, 1H, *J*=7.8 and 2.4 Hz, ArH), 3.47 (d, 1H, *J*=19.1 Hz, C*H*$_a$H$_b$CO), 3.45 (d, 1H, *J*=19.1 Hz, CH$_a$*H*$_b$CO), 2.22 (s, 3H, ArCH$_3$), 2.18 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=205.3 (s, C=O), 160.2 (s, ArC), 147.0 (s, ArC), 144.2 (s, ArC), 136.6 (s, ArC), 135.7 (s, ArC), 134.9 (s, ArC), 134.7 (d, ArCH), 129.6 (d, ArCH), 129.1 (d, ArCH), 128.3 (d, 2C, 2 × ArCH), 128.0 (d, 3C, 3 × ArCH), 127.8 (d, ArCH), 126.5 (d, ArCH), 125.4 (d, ArCH), 123.6 (d, ArCH), 56.1 (t, *C*H$_2$CO), 55.8 (s, Ar-*C*-CH$_2$CO), 20.0 (q, ArCH$_3$), 19.2 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{23}H_{21}O]^+$=$[M+H]^+$: 313.1587; found: 313.1585.



7md

5,7-Dimethyl-3,3-diphenylindan-1-one (7md):

GP-2 was carried out and the indanone **7md** (145 mg, 93%) was furnished as colorless viscous liquid. [TLC control R_f(**4m**)=0.60, R_f(**7md**)=0.40, (petroleum ether/ethyl acetate 98:2, UV detection)].

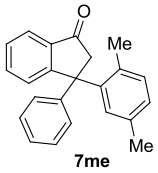
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3029, 2922, 1711 (C=O), 1600, 1493, 1460, 1445, 1287, 1233, 1059, 818, 759, 700 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.80 (d, 1H, *J*=7.3 Hz, ArH), 7.53 (ddd, 1H, *J*=8.3, 7.3 and 1.0 Hz, ArH), 7.37 (ddd, 1H, *J*=8.3, 7.3 and 1.0 Hz, ArH), 7.22 (ddd, 3H, *J*=9.8, 7.3 and 1.0 Hz, ArH), 7.14 (dd, 1H, *J*=8.3 and 1.5 Hz, ArH), 7.11 (dd, 1H, *J*=8.8 and 1.5 Hz, ArH), 7.04 (s, 2H, ArH), 6.82 (dd, 2H, *J*=9.8 and 8.3 Hz, ArH), 3.84 (d, 1H, *J*=19.1 Hz, C*H*$_a$H$_b$CO), 3.16 (d, 1H, *J*=19.1 Hz, CH$_a$*H*$_b$CO), 2.29 (s, 3H, ArCH$_3$), 1.93 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=205.4 (s, C=O), 160.8 (s, ArC), 146.5 (s, ArC), 141.5 (s, ArC), 136.7 (s, ArC), 136.6 (s, ArC), 135.3 (s, ArC), 134.6 (d, ArCH), 133.5 (d, ArCH),

129.2 (d, 2C, ArCH), 128.7 (d, 3C, ArCH), 127.8 (d, ArCH), 127.7 (d, ArCH), 126.2 (d, ArCH), 125.8 (d, ArCH), 123.6 (d, ArCH), 55.5 [s, Ar-*C*(CH_2CO)CH_3], 53.7 (t, *C*H_2CO), 21.8 (q, $ArCH_3$), 20.7 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{23}H_{20}NaO]^+$=$[M+Na]^+$: 335.1406; found: 335.1395.



7me

3-(2,5-Dimethylphenyl)-3-phenylindan-1-one(7me):

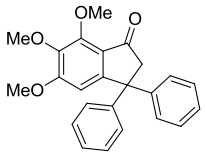
GP-2 was carried out and the indanone **7me** (115.4 mg, 74%) was furnished as a white semi solid [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**4m**)=0.60, R_f(**7me**)=0.40, UV detection].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2853, 1712 (C=O), 1600, 1493, 1460, 1287, 1229, 815, 760 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.80 (d, 1H, *J*=7.8 Hz, ArH), 7.54 (dd, 1H, *J*=8.3 and 7.8 Hz, ArH), 7.38 (dd, 1H, *J*=7.8 and 7.8 Hz, ArH), 7.26 (d, 1H, *J*=8.3 Hz, ArH), 7.24–7.05 (m, 6H, ArH), 7.01 (d, 1H, *J*=7.8 Hz, ArH), 6.75 (s, 1H, ArH), 3.87 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 3.15 (d, 1H, *J*=19.1 Hz, CH_aH_bCO), 2.18 (s, 3H, $ArCH_3$), 1.91 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=205.2 (s, C=O), 160.7 (s, ArC), 146.5 (s, ArC), 144.2 (s, ArC), 135.3 (s, ArC), 134.7 (s, ArC), 134.6 (d, ArCH), 133.7 (s, ArC), 132.5 (d, ArCH), 129.3 (d, ArCH), 128.7 (d, ArCH), 128.6 (d, 2C, 2 × ArCH), 127.7 (d, ArCH), 127.6 (d, ArCH), 126.2 (d, ArCH), 126.0 (d, 2C, 2 × ArCH), 123.6 (d, ArCH), 55.7 (s, Ar-*C*-CH_2CO), 53.6 (t, *C*H_2CO), 21.5 (q, $ArCH_3$), 21.1 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{23}H_{21}O]^+$=$[M+H]^+$: 313.1587; found: 313.1585.



7na

5,6,7-Trimethoxy-3,3-diphenylindan-1-one (7na):

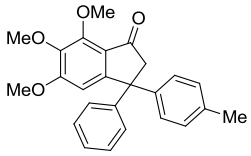
GP-2 was carried out and the indanone **7na** (129.0 mg, 69%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4n**)=0.60, R_f(**7na**)=0.40, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2851, 1700 (C=O), 1587, 1463, 1328, 1257, 1129, 1013, 838 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.29 (ddd, 4H, *J*=8.3, 7.8 and 1.5 Hz, ArH), 7.22 (ddd, 2H, *J*=8.8, 7.3 and 1.5 Hz, ArH), 7.18 (dd, 4H, *J*=8.8 and 2.0 Hz, ArH), 6.46 (s, 1H, ArH), 4.07 (s, ArOMe), 3.86 (s, ArOMe), 3.78 (s, ArOMe), 3.40 (s, 2H, CH_2CO) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=200.7 (s, C=O), 159.4 (s, ArC), 157.6 (s, ArC), 151.0 (s, ArC), 146.7 (s, 2C, ArC), 140.9 (s, ArC), 128.4 (d, 3C, ArCH), 128.0 (d, 4C, ArCH), 126.5 (d, 3C, ArCH), 122.0 (s, ArC), 105.1 (d, ArCH), 62.0 (q, ArOMe), 61.3 (q, ArOMe), 56.9 (t, CH_2CO), 56.3 (q, ArOMe), 55.5 [s, Ar-$C(CH_2CO)CH_3$] ppm.

HR-MS (APCI+): m/z calculated for $[C_{24}H_{23}O_4]^+$=$[M+H]^+$: 375.1591; found: 375.1579.



7nb

5,6,7-Trimethoxy-3-(4-methylphenyl)-3-phenylindan-1-one (7nb):

GP-2 was carried out and the indanone **7nb** (156.0 mg, 96%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4n**)=0.60, R_f(**7nb**)=0.40, (petroleum ether/ethyl acetate 84:16, UV detection)].

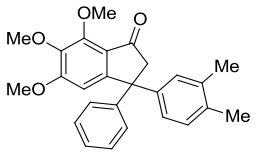
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2928, 1708 (C=O), 1603, 1512, 1251, 1159, 1033, 830 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.32 (ddd, 3H, *J*=7.8, 6.8 and 1.5 Hz, ArH), 7.27 (dd, 1H, *J*=6.8 and 1.5 Hz, ArH), 7.21 (dd, 1H, *J*=6.8 and 1.5 Hz, ArH), 7.10 (dd, 4H, *J*=8.3 and 6.8

Hz, ArH), 6.49 (s, 1H, ArH), 4.10 (s, 3H, ArOMe), 3.89 (s, 3H, ArOMe), 3.81 (s, 3H, ArOMe), 3.42 (d, 1H, *J*=18.6 Hz, C$H_a$$H_b$CO), 3.41 (d, 1H, *J*=18.6 Hz, CH$_a$$H_b$CO), 2.35 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=200.8 (s, C=O), 159.4 (s, ArC), 157.9 (s, ArC), 151.0 (s, ArC), 146.9 (s, ArC), 143.7 (s, ArC), 140.9 (s, ArC), 136.2 (s, ArC), 129.1 (d, 2C, ArCH), 128.3 (d, 2C, ArCH), 128.0 (d, 2C, ArCH), 127.9 (d, 2C, ArCH), 126.5 (d, ArCH), 122.0 (s, ArC), 105.1 (d, ArCH), 62.0 (q, ArOMe), 61.3 (q, ArOMe), 56.9 (t, *C*H$_2$CO), 56.3 (q, ArOMe), 55.2 [s, Ar-*C*(CH$_2$CO)CH$_3$], 20.8 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{25}$H$_{25}$O$_4$] $^+$=[M+H]$^+$: 389.1747; found: 389.1742.



7nc

5,6,7-Trimethoxy-3-(4-methylphenyl)-3-phenylindan-1-one (7nc):

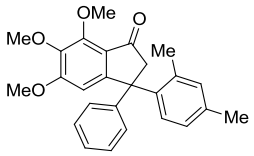
GP-2 was carried out and the indanone **7nc** (123.0 mg, 61%) was furnished as pale yellow viscous liquid. [TLC control R_f(**4n**)=0.60, R_f(**7nc**)=0.40, (petroleum ether/ethyl acetate 84:16, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 1736 (C=O), 1703, 1586, 1480, 1238, 1101, 1045, 706, 654 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.28 (ddd, 3H, *J*=7.8, 6.8 and 1.5 Hz, ArH), 7.24 (dd, 1H, *J*=6.8 and 1.5 Hz, ArH), 7.18 (dd, 1H, *J*=6.8 and 1.5 Hz, ArH), 7.05 (d, 1H, *J*=8.3 Hz, ArH), 6.94 (s, 1H, ArH), 6.89 (dd, 1H, *J*=7.8 and 2.0 Hz, ArH), 6.48 (s, 1H, ArH), 4.07 (s, 3H, ArOMe), 3.86 (s, 3H, ArOMe), 3.78 (s, 3H, ArOMe), 3.39 (d, 1H, *J*=18.6 Hz, C$H_a$$H_b$CO), 3.36 (d, 1H, *J*=18.6 Hz, CH$_a$$H_b$CO), 2.22 (s, 3H, ArCH$_3$), 2.19 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=201.0 (s, C=O), 159.4 (s, ArC), 158.0 (s, ArC), 151.0 (s, ArC), 147.0 (s, ArC), 144.1 (s, ArC), 141.0 (s, ArC), 136.6 (s, ArC), 134.9 (s, ArC), 129.5 (d, ArCH), 129.1 (d, ArCH), 128.3 (d, 2C, ArCH), 128.0 (d, 2C, ArCH), 126.4 (d, ArCH), 125.4 (d, ArCH), 122.0 (s, ArC), 105.1 (d, ArCH), 62.0 (q, ArOMe), 61.3 (q, ArOMe), 56.9 (t, *C*H$_2$CO), 56.3 (q, ArOMe), 55.1 [s, Ar-*C*(CH$_2$CO)CH$_3$], 20.0 (q,ArCH$_3$), 19.2 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{26}$H$_{27}$O$_4$] $^+$=[M+H]$^+$: 403.1904; found: 403.1872.



7nd

5,6,7-Trimethoxy-3-(4-methylphenyl)-3-phenylindan-1-one (7nd):

GP-2 was carried out and the indanone **7nd** (119.0 mg, 59%) was furnished as white solid, [TLC control R_f(**4n**)=0.60, R_f(**7nd**)=0.40, (petroleum ether/ethyl acetate 84:16, UV detection)].

M.p.: 192-194 ^{o}C

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2982, 1736 (C=O), 1702, 1586, 1481, 1373, 1238, 1045, 735, 707, 654 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.24 (dd, 2H, *J*=7.3 and 3.0 Hz, ArH), 7.18 (d, 2H, *J*=7.3 Hz, ArH), 7.12 (d, 1H, *J*=5.9 Hz, ArH), 7.04 (s, 1H, ArH), 6.89 (s, 2H, ArH), 6.34 (s, 1H, ArH), 4.07 (s, 3H, ArOMe), 3.86 (s, 3H, ArOMe), 3.78 (d, 1H, *J*=18.6 Hz, CH_aH$_b$CO), 3.73 (s, 3H, ArOMe), 3.10 (d, 1H, *J*=18.6 Hz, CH$_a$$H_b$CO), 2.30 (s, 3H, ArCH$_3$), 1.90 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=201.0 (s, C=O), 159.2 (s, ArC), 158.5 (s, ArC), 150.9 (s, ArC), 146.5 (d, ArCH), 141.7 (s, ArC), 140.7 (s, ArC), 136.8 (s, ArC), 136.6 (s, ArC), 133.5 (d, 2C, ArCH), 128.7 (s, ArC), 127.7 (d, 2C, ArCH), 126.2 (d, 2C, ArCH), 125.8 (d, ArCH), 121.7 (s, ArC), 106.2 (d, ArCH), 62.0 (q, ArOMe), 61.3 (q, ArOMe), 56.1(q, ArOMe), 54.8 [s, Ar-*C*(CH$_2$CO)CH$_3$], 54.6 (t, *C*H$_2$CO), 21.8 (q, ArCH$_3$), 20.7 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [$C_{26}H_{27}O_4$] $^{+}$ =[M+H]$^{+}$: 403.1904; found: 403.1869.

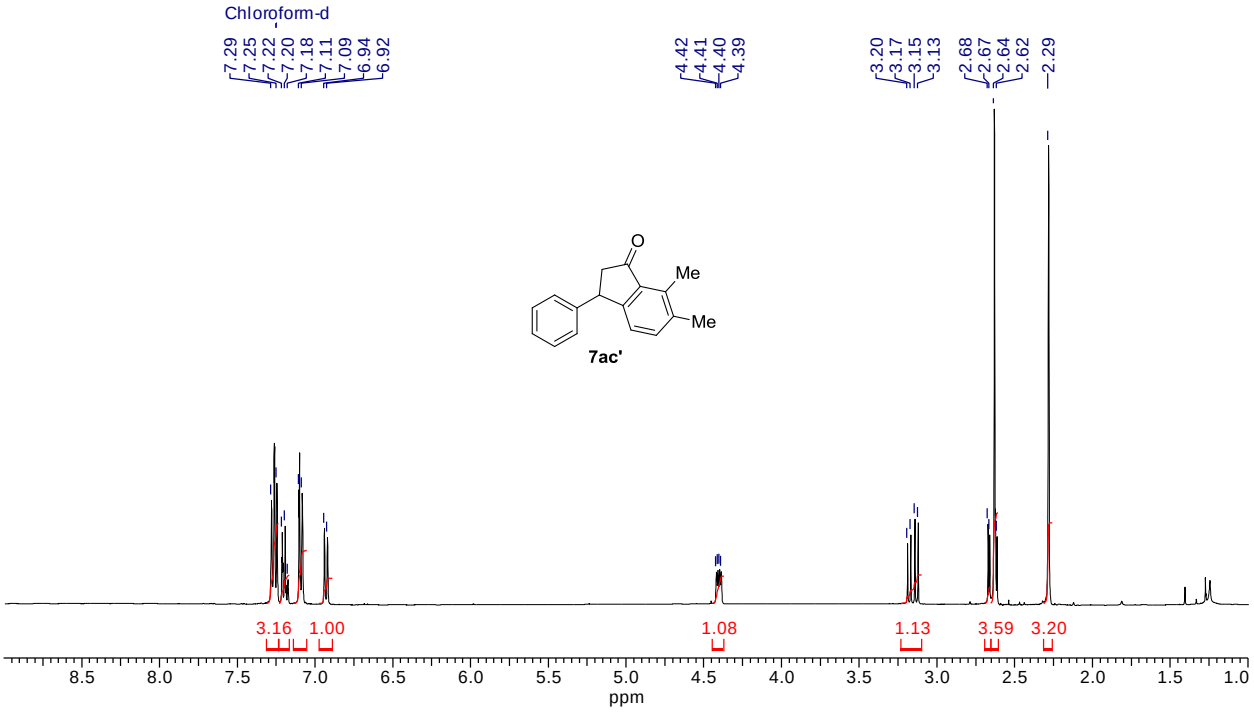


Figure I.16: ^{1}H-NMR (400 MHz) spectrum of **7ac'** in $CDCl_3$

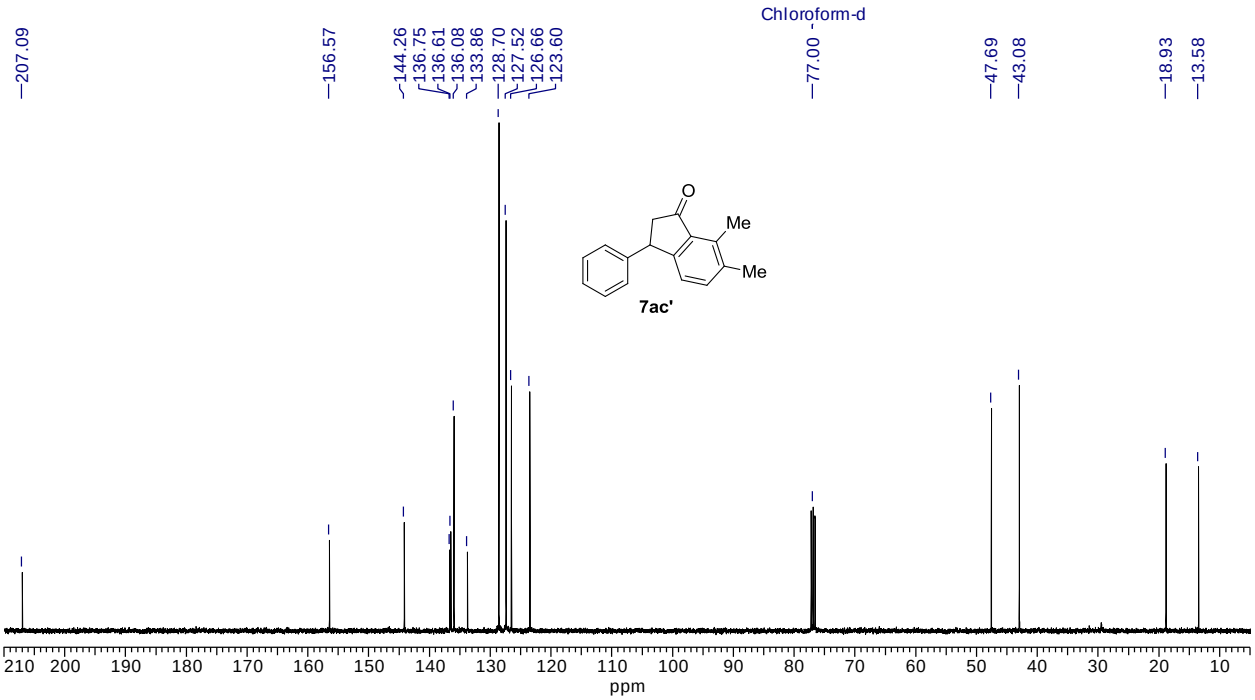


Figure I.17: ^{13}C-NMR (100 MHz) spectrum of **7ac'** in $CDCl_3$

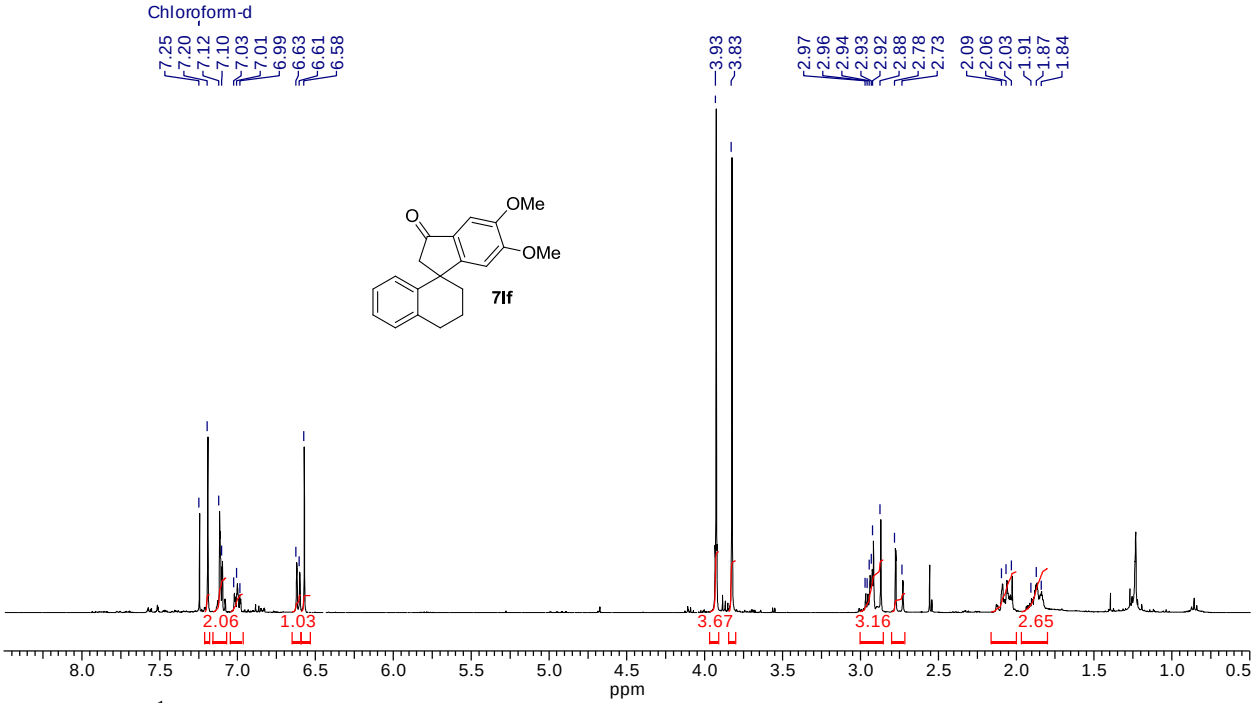


Figure I.18: ^{1}H-NMR (400 MHz) spectrum of **7lf** in $CDCl_3$

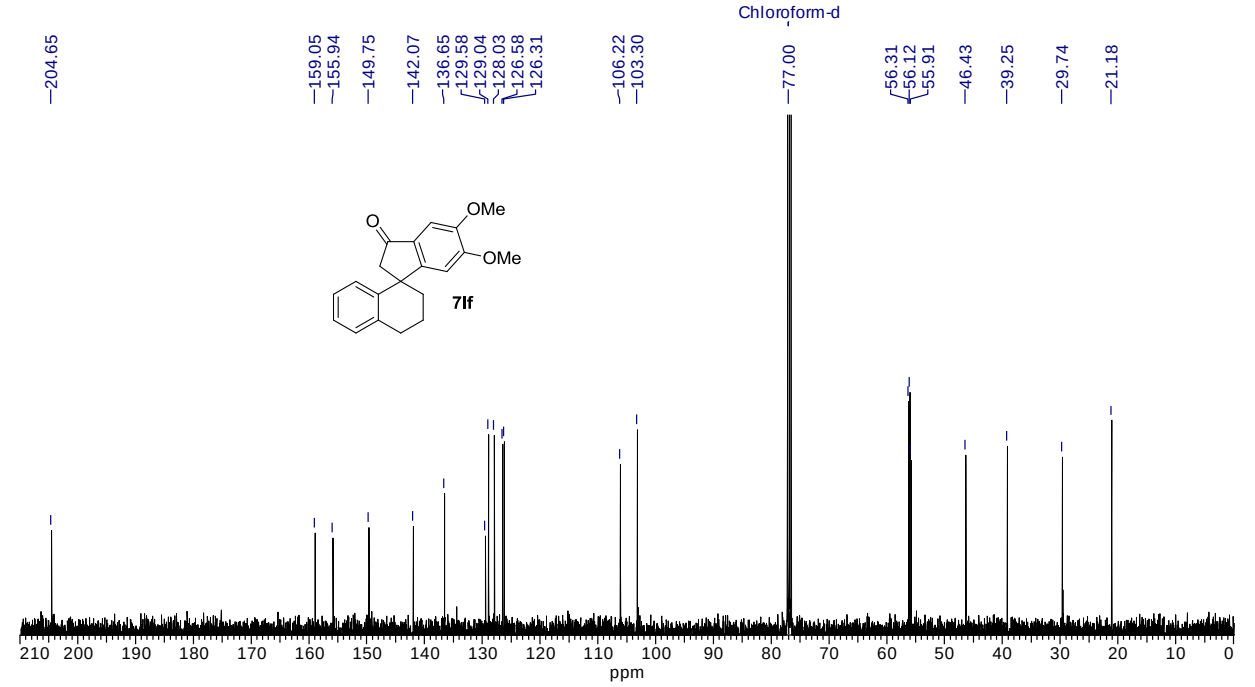


Figure I.19: ^{13}C-NMR (100 MHz) spectrum of **7lf** in $CDCl_3$

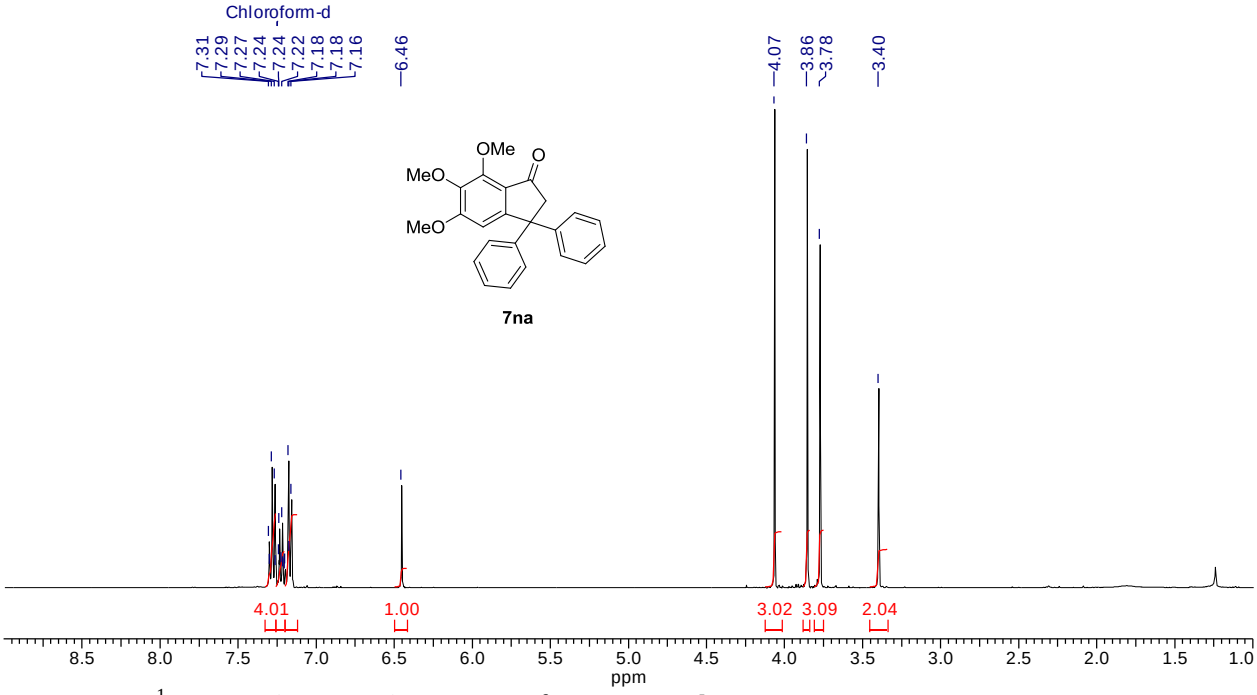


Figure I.20: ^{1}H-NMR (400 MHz) spectrum of **7na** in $CDCl_3$

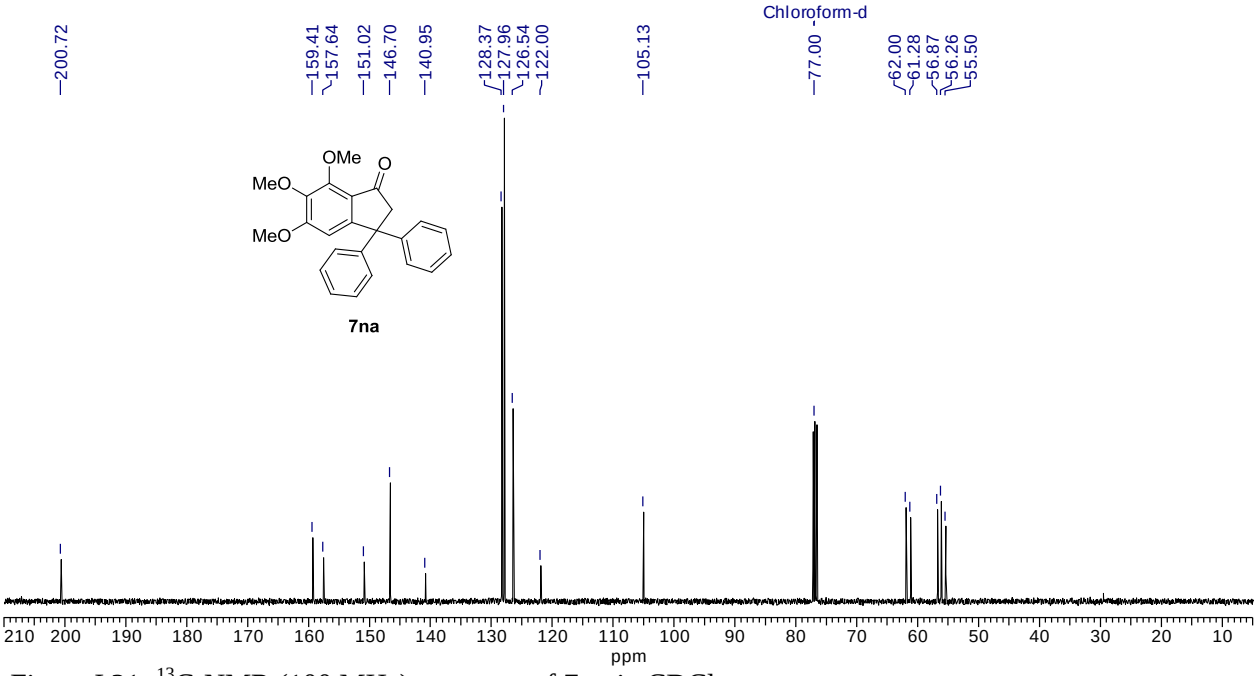


Figure I.21: ^{13}C-NMR (100 MHz) spectrum of **7na** in $CDCl_3$

Notes and references:

1) (a) Ulaczyk-Lesanko, A.; Hall, D. G. *Curr. Opin. Chem. Biol.* **2005**, *9*, 266. (b) Parsons, P. J.; Penkett, C. S.; Shell, A. J. *Chem. Rev.* **1996**, *96*, 195. (c) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115. (d) Domling, A. *Chem. Rev.* **2006**, *106*, 17. (e) Toure, B. B.; Hall, D. G. *Chem. Rev.* **2009**, *109*, 4439.
2) Friedel, C.; Crafts, J. M. *C. R. Hebd. Seances Acad. Sci.* **1877**, *84*, 1450.
3) For reviews, see: Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227. (b) Poulsen, T. B.; Jorgensen, K. A. *Chem. Rev.* **2008**, *108*, 2903. (c) Sartori, G.; Maggi, R. *Chem. Rev.* **2011**, *111*, 181. (d) Rueping, M.; Nachtsheim, B. J. *Beils. J. Org. Chem.* **2010**, *6*, 6. (e) Shi, M.; Lu, J.-M.; Wei, Y.; Shao, L.-X. *Acc. Chem. Res.* **2012**, *45*, 641.
4) (a) Gore, P. H. In *Friedel–Crafts and Related Reactions*; Olah, G. A. Ed. John Wiley & Sons Inc.; London, **1964**, Vol. *III*, Part I, p 1. (b) Olah, G. A.; Klumpp, D. A. *Superelectrophiles and Their Chemistry*; Wiley: New York, 2008.
5) a) Sai, K. K. S.; Tokarz, M. J.; Malunchuk, A. P.; Zheng, C.; Gilbert, T. M.; Klumpp, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 14388. (b) Zhang, Y.; Sheets, M. R.; Raja, E. K.; Boblak, K. N.; Klumpp, D. A. *J. Am. Chem. Soc.* **2011**, *133*, 8467. (c) Evans, D. A.; Fandrick, K. R. *Org. Lett.* **2006**, *8*, 2249. (d) Rose, M. D.; Cassidy, M. P.; Rashatasakhon, P.; Padwa, A. *J. Org. Chem.* **2007**, *72*, 538. (e) Wu, Y.-C.; Liu, L.; Liu, Y.-L.; Wang, D.; Chen, Y.-J. *J. Org. Chem.* **2007**, *72*, 9383.
6) (a) Suzuki, T.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1997**, *119*, 6774. (b) Suzuki, T.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1998**, *120*, 4629. (c) Kurouchi, H.; Sugimoto, H.; Otani, Y.; Ohwada, T. *J. Am. Chem. Soc.* **2010**, *132*, 807. (d) Colquhoun, H. M.; Lewis, D. F.; Williams, D. J. *Org. Lett.* **2001**, *3*, 2337. (e) Fillion, E.; Fishlock, D. *Org. Lett.* **2003**, *5*, 4653. (f) Wang, Q.; Padwa, A. *Org. Lett.* **2006**, *8*, 601. (g) Chassaing, S.; Kumarraja, M.; Pale, P.; Sommer, J. *Org. Lett.* **2007**, *9*, 3889. (h) Saito, A.; Umakoshi, M.; Yagyu, N.; Hanzawa, Y. *Org. Lett.* **2008**, *10*, 1783. (i) Tang, S.; Xu, Y.; He, J.; He, Y.; Zheng, J.; Pan, X.; She, X. *Org. Lett.* **2008**, *10*, 1855. (j) Kangani, C. O.; Day, B. W. *Org. Lett.* **2008**, *10*, 2645. (k) Kim, K.; Kim, I. *Org. Lett.* **2010**, *12*, 5314. (l) Chinnagolla, R. K.;

Jeganmohan, M. *Org. Lett*. **2012**, *14*, 5246. (m) Eom, D.; Park, S.; Park, Y.; Ryu, T.; Lee, P. H. *Org. Lett*. **2012**, *14*, 5392.

7) Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. A. *J. Am. Chem. Soc*. **1975**, *97*, 2928.

8) (a) Hashmi, A. S. K.; Schwarz, L.; Choi, J.-H. *Angew. Chem*. **2000**, *112*, 2382. *Angew. Chem. Int. Ed*. **2000**, *39*, 2285. (b) Gerald Dyker, G.; Muth, E.; Hashmi, A. S. K.; Ding, L. *Adv. Synth. Catal*. **2003**, *345*, 1247. (c) Hashmi, A. S. K.; Schwarz, L.; Rubenbauer, P.; Blanco, M. C.; *Adv. Synth. Catal*. **2006**, *348*, 705.

9) (a) Boblak, K. N.; Klumpp, D. A. *J. Org. Chem*. **2014**, *79*, 5852. (b) Klumpp, D. A.; Baek, D. N.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem*. **1997**, *62*, 6666. (c) Sai, K. K. S.; Esteves, P. M.; Penha, E. T. D.; Klumpp, D. A. *J. Org. Chem*. **2008**, *73*, 6506.

10) TenBrink, R. E.; McCall, J. M. J. *Heterocycl. Chem*. **1981**, *18*, 821.

11) (a) Kim, S. H.; Kwon, S. H.; Park, S. H.; Lee, J. K.; Bang, H. S.; Nam, S. J.; Kwon, H. C.; Shin, J.; Tripartin, D. C. *Org. Lett*. **2013**, *15*, 1834. (b) Dolling, U.-H.; Davis, P.; Grabowski, E. J. J. *J. Am. Chem. Soc*. **1984**, *106*, 446. (b) Solms, S. J.; Woltersdorf, O. W. J.; Cragoe, E. J. J. *J. Med. Chem*. **1978**, *21*, 437.

12) Braun, J. V.; Manz, G. *Justus Liebigs Ann. Chem*. **1929**, *468*, 258.

13) Khalaf, A. A.; Roberry, R. M. *New Fridel-Crafts chemistry*, **1966**, *31*, 89.

14) Olah, G. Friedel-Crafts Chemistry; Wiley-Interscience: New York, 1973; (b) Heaney, H. In Comprehensive Organic Synthesis; Trost, B. M.; Flemming, I. Eds.; Pergamon Press: Oxford, **1991**, *2*, 733 and 753.

15) (a) Yin, W.; Ma, Y.; Xu, J.; Zhao, Y. *J. Org. Chem*. **2006**, *71*, 4312. (b) Lawrence, N. J.; Armitage, E. M. S.; Greedy, B.; Cook, D.; Ducki, S.; McGown, A. T.; *Tetrahedron Lett*. **2006**, *47*, 1637.

16) Kangani, C. O.; Day, B. W.; *Org. Lett*. **2008**, *10*, 13.

17) Womack, G. B.; Angeles, J. G.; Fanelli, V. E.; Heyer, C. A. *J. Org. Chem*. **2007**, *72*, 7046.

18) Saito, A.; Umakoshi, M.; Yagyu, N.; Hanzawa, Y. *Org. Lett*. **2008**, *10*, 1783.

19) Pinnick, H. W.; Brown, S. P.; McLean, E. A.; Zoller, L. W. *J. Org. Chem*. **1981**, *46*, 3758.

20) Sartori, G.; Maggi, R.; Bigi, F.; Porta, C.; Taob, X.; Bernardi, G. L.; Ianelli, S.; Nardelli, M. *Tetrahedron* **1995**, *51*, 12179.

21) Olah, G. Friedel-Crafts Chemistry; Wiley-Interscience: New York, 1973; (b) Heaney, H. In Comprehensive Organic Synthesis; Trost, B. M.; Flemming, I. Eds.; Pergamon Press: Oxford, **1991**, *2*, 733 and 753.

22) Fillion, E.; Fishlock, D. *Org. Lett.* **2003**, *5*, 4653.

23) Cui, D.-M.; Zhang, C.; Kawamura, M.; Shimada, S. *Tetrahedron Letters* **2004**, *45*, 1741.

24) Posternak, A. G.; Garlyauskayte, R. Y.; Yagupolskii, L. M.; Posternak, A. G. *J. Fluorine Chem.* **2010**, *131*, 274.

25) Surya Prakash, G. K.; Torok, P. Y. B.; Olah, G. A. *Catalysis Letters* **2003**, *87*, 109.

26) Surya Prakash, G. K.; Paknia, F.; Vaghoo, H.; Rasul, G.; Mathew, T.; Olah, G. A. *J. Org. Chem.* **2010**, *75*, 2219.

27) Raja, E. K.; DeSchepper, D. J.; Lill, S. O. N.; Klumpp, D. A. *J. Org. Chem.* **2012**, *77*, 5788.

28) Klumpp, D. A.; Lau Manuel Garza, S.; Schick, B.; Kantardjieff, K. *J. Org. Chem.* **1999**, *64*, 7635.

29) Rendy, R.; Zhang, Y.; McElrea, A.; Gomez, A.; Klumpp, D. A. *J. Org. Chem.* **2004**, *69*, 2340.

30) (a) Reddy, A. G. K.; Satyanarayana, G. Synthesis, **2015**, *47*, 1269. (b) Krishna, J.; Niharika, P.; Satyanarayana, G. *RSC Adv.*, **2015**, *5*, 26749. (c) Pedireddi, N.; Ramulu, B. V.; Satyanarayana, G. *Org. Biomol. Chem.*, **2014**, *12*, 4347.

31) Wang, F.; Tong, Z. *RSC Adv.*, **2014**, *4*, 6314.

32) Ramulu, B. V.; Reddy, A. G. K.; Satyanarayana, G. *Synlett* **2013**, *24*, 868.

33) Chintareddy, V. R.; Ellern, A.; Verkade, J. G. *J. Org. Chem.* **2010**, *75*, 7166.

34) Srikrishna, A.; Reddy, T.; Kumar, J.; Praveen, P.; Vijaykumar, D. *Synlett* **1996**, *1*, 67.

35) Tolochko, A. F.; Dombrovskii, A. V. *Ukr. Khim. Zh.* (*Russ. Ed.*). **1965**, *31*, 220.

36) Reddy, A. G. K.; Mahendar, L.; Satyanarayana, G. *Synth. Commun.* **2014**, *44*, 2076.

37) Srikrishna, A.; Rao, M. S.; Gharpure, J. S.; Chandrasekhar, N. B. *Synlett* **2001**, *12*, 1986.

38) Groundwater, P. W.; Garnett, I.; Morton, A. J.; Sharif, T.; Coles, S. J.; Hursthouse, B. M.; Anderson, M. J.; Bendell, D.; McKillop, A.; Zhang, W. *J. Chem. Soc. Perkin Trans.* **2001**, *1*, 2781.

39) Raja, E. K.; DeSchepper, D. J.; Lill, S. O. N.; Klumpp, D. A. *J. Org. Chem.* **2012**, *77*, 5788.

40) Granger, R.; Orzalesi, H.; Favier, J. C.; Muratelle, A. *Compt. rend.* **1961**, *252*, 3271.

41) Bradshaw, D. P.; Jones, D. W.; Nongrum, F. M. *J. Chem. Soc. Perkin Trans.* **1991**, *1*, 19.

CHAPTER-II

Superacid Mediated Intramolecular Condensation: Facile Synthesis of Indenones, Indanones, Spiro tetracyclic indanones and Indenes

II.1 INTRODUCTION:

Among the classical reactions for the creation of C–C bond, the Friedel-Crafts reaction turned to be one of the powerful techniques towards aromatic electrophilic substitutions.[1] In particular, for the past few decades there have been numerous applications of this reaction using different acids (Brønsted/Lewis).[2-4] Particularly, the intramolecular acylation of this protocol was found to be ideal as it constructs the carbocyclic systems, because many natural products or drug candidates are cyclic compounds. In this regards, indanones and indenones are essential carbocyclic compounds as they constitute in natural as well as in pharmaceutical products. Indenes are an important class of compounds, naturally occurring indenes display a broad spectrum of biological properties (e.g. antimicrobial, antiviral, antifungal and anticancer activities), and have numerous applications in medicine. Substituted indene derivatives are useful

compounds that serve as building blocks for functional materials. Some of the biologically important natural and unnatural indanones/indenones are shown in Figure II.1. The spiro-cyclicindanone scaffolds are also known for their anti-mycobacterial properties, many of them have shown comparable or even better activities than some of the first-line tuberculosis drugs. The spiro[indene-1,1′-indane]-5,5′-diol as a new framework for estrogen receptor ligands (Figure II.1).[5]

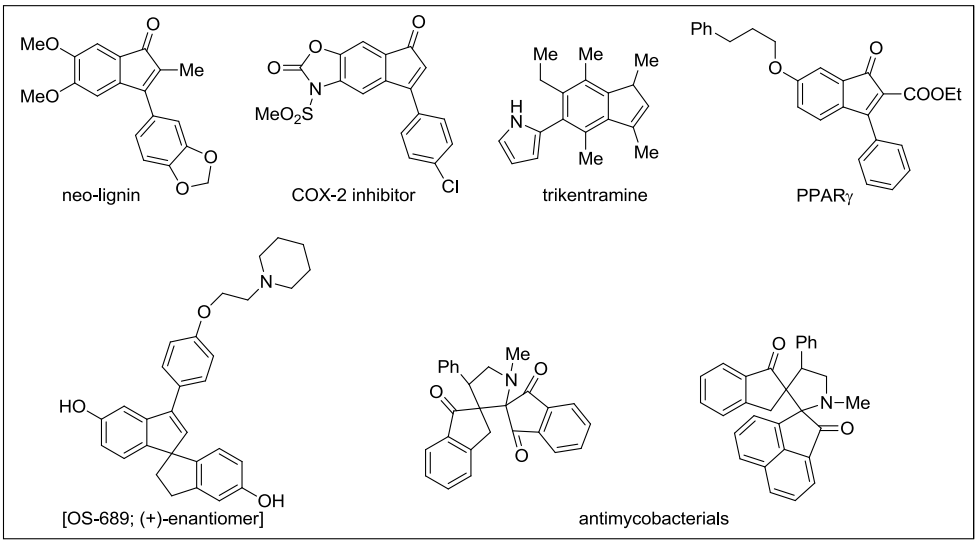


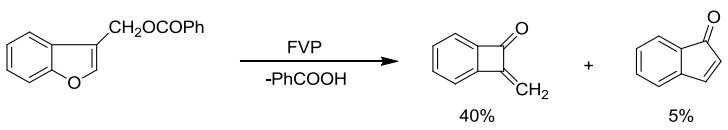
Figure II.1: Naturally occurring and pharmaceutically important indanones/indene/indenones.

II.2 BACKGROUND:

Their interesting biological activities prompted organic chemists to develop new synthetic methods for their synthesis. Of late, many methods have been developed for the synthesis of indanones/indenones. For example, indanones were synthesized using the Friedel-Crafts, [Rh]-catalysis[6] and Nazarov cyclizations.[7] Also, indenones were prepared by employing the Friedel-Crafts and metal-mediated reactions.[8] Some notable [Pd]-catalyzed annulations for the synthesis of indenones have been accomplished by the research groups of Larock,[9] Chiusoli,[10] Buchwald[11] and Li.[12] The research group of Nagao[13] reported the formation of indenones from allenyl aryl ketones upon treatment with BF_3•OEt_2. Liang and co-workers disclosed the synthesis of indenones under gold catalyzed tandem rearrangement.[14] While, the

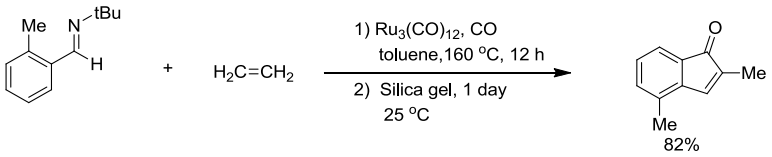
research group of Ohwada reported triflic acid promoted cyclization for the synthesis of indenes and dihydro naphthalenes.[15] Womack disclosed synthesis of indanones and indenols from 2-alkylcinnamaldehydes via intramolecular Friedel-Crafts reaction using $FeCl_3$.[16] On the other hand, Klumpp[17] et al. and Fillion[18] et al. reported the synthesis of indanones under Friedel-Crafts acylation conditions. Normally, the classical intramolecular Friedel-Crafts acylation works between an acyl halide or carboxylic acid or anhydride with an aromatic ring under acid promoter (Lewis or Brønsted). Lewis acid promoted intramolecular Friedel-Crafts acylation of acyl halides are not familiar. Whereas, intramolecular acylation protocols by direct use of carboxylic acids as carbocation equivalents suffer due to the poor leaving nature of the hydroxyl group, hence require forceful conditions. For Meldrum's acids, competition studies for the rate of intramolecular acylation is determined to be tetralone>benzosuberone>indanone. Therefore, synthesis of five-membered ketones (1-indanones) might be feasible under harsh conditions. In addition, direct synthesis of indanones starting from esters using intramolecular Friedel-Crafts acylation are not familiar. However, use of Meldrum's acid for the synthesis of carbocylic ketones under mild Friedel-Crafts conditions is very good alternative. In 2008, the research group of Baba reported[19] acylation of arenes with esters by dimethylchlorosilane and indium tribromide. As part of our ongoing research interests in domino or sequential domino one-pot process, very recently, we have developed a super acid promoted synthesis of indanones starting from simple cinnamic acid esters using.[20] The generality and scope of this method has been well studied by synthesizing numerous compounds. We also developed a practical method for the direct synthesis of highly substituted indanones from very simple aryl isopropyl ketones and benzaldehydes promoted by super acid.[21] Some of the notable approaches have been discussed below.

Flash vacuum pyrolyses (FVP) of benzoic 3-methyl-2-benzofurancarboxylic anhydride at 550 °C and ca. 10^{-2} torr, gave methylenebenzocyclobutenone and indenone as major and minor products, respectively (Scheme II.1).[22]



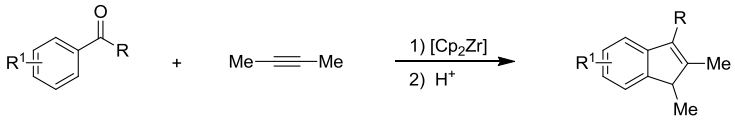
Scheme II.1

Shinji Murai et al. in 1997 reported the preparation of indenones by the $Ru_3(CO)_{12}$-catalyzed reaction of aromatic imines with CO and olefins (Scheme II.2).[23]



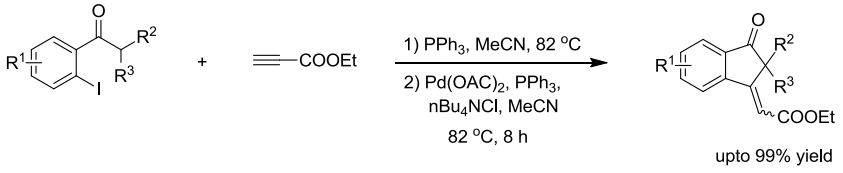
Scheme II.2

Zhenfeng Xi et al. reported in 2003 one-pot formation of indene derivatives from aryl ketones and alkynes (Scheme II.3).[24]



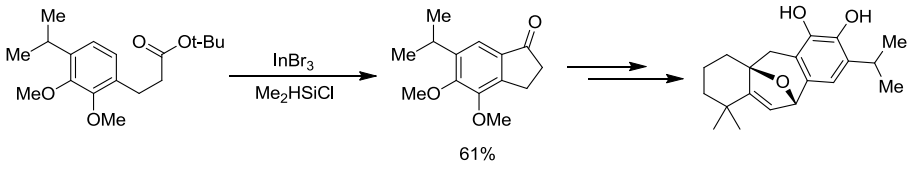
Scheme II.3

Ohyun Kwon reported a simple and rapid method that grants access to various functionalized indanes and indanones from readily accessible 2-iodobenzylmalonates and 2-iodobenzoylacetates and electron-poor alkynes (Scheme II.4).[25]



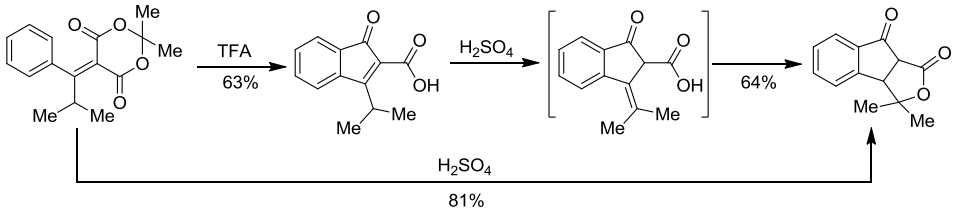
Scheme II.4

Akio Baba in 2008 reported Friedel-Crafts reaction system accommodating esters as acylation reagents, in which Me_2HSiCl and 5-10 mol% of $InBr_3$ combination was used to promote the acylation of various arenes (Scheme II.5).[19]



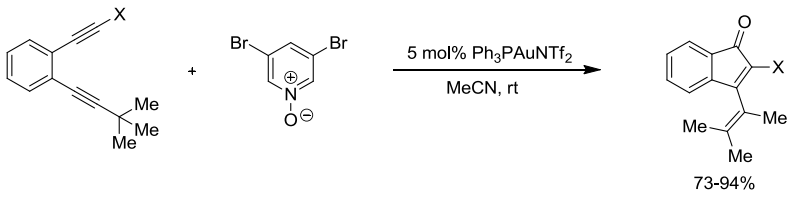
Scheme II.5

Campaigne and Frierson reported that isopropylidene phenyl Meldrum's acid could form 3-isopropylindenone-2-carbonylic acid after stirring in trifluoroacetic acid. Subsequent treatment with concentrated sulfuric acid provided fused indanone-lactone. The exclusive use of H_2SO_4 without TFA, furnished the fused indanone-lactone directly (Scheme II.6).[26]



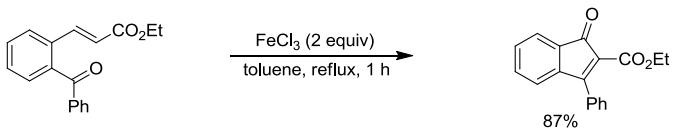
Scheme II.6

Stephen K. Hashmi in 2013 reported in the presence of a gold catalyst an unprecedented oxidative cyclization of diynes. The reaction cascade is initiated by an oxygen transfer from N-oxide onto a gold-activated alkyne. The formed α-oxo carbene is transferred across the second alkyne yielding a stabilized vinyl carbene/cation. Alkyl migration or sp^3-CH insertion then terminates the catalytic cycle by formation of highly substituted functionalized indanones (Scheme II.7).[27]



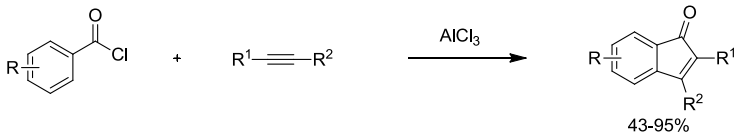
Scheme II.7

Dattatraya H. Dethe in 2015 presented a novel $FeCl_3$ mediated formal [2+2] cycloaddition/ring opening cascade of *ortho*-keto-cinnamic acid esters developed for the synthesis of indanones (Scheme II.8).[28]



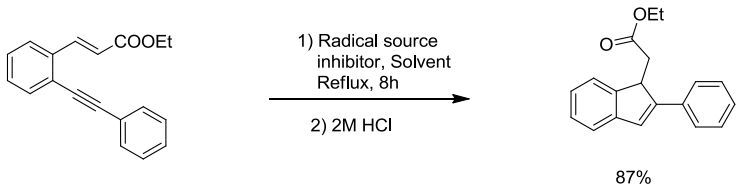
Scheme II.8

P. Galatsis et al. in 1994 disclosed the synthesis of indanones under aluminum chloride catalyzed addition of substituted benzoyl chlorides to acetylenic compounds (Scheme II.9).[29]



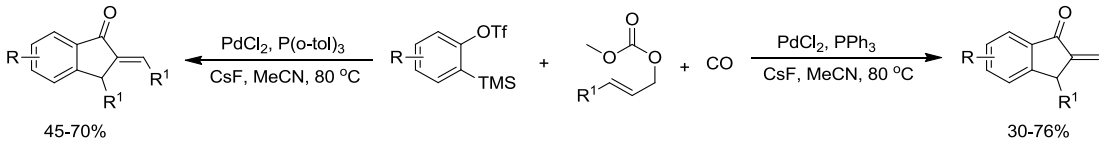
Scheme II.9

I. V. Alabugin et al. in 2013 reported the intermolecular radical addition to the triple bond, followed by intramolecular 5-*exo*-trig closure of the vinyl radical onto the tethered alkene. This reaction provides a convenient approach to Bu_3Sn-functionalized indenes (Scheme II.10).[30]



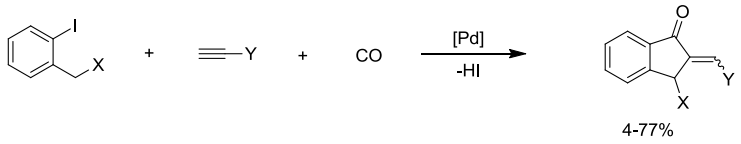
Scheme II.10

Jin-Heng Li in 2010 disclosed a selective protocol for the synthesis of 2-methylene-3-substituted-2,3-dihydro-1*H*-inden-1-ones and 2-benzylidene-2,3-dihydro-1*H*-inden-1-ones via [Pd]-catalyzed cyclocarbonylation reactions of arynes with allyl carbonates and carbon monoxide (CO) (Scheme II.11).[12]



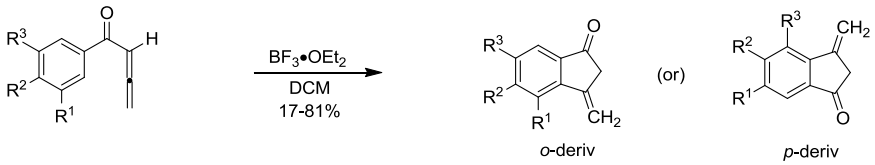
Scheme II.11

G. P. Chiusoli in 1992 reported sequential oxidative additions of *ortho*-alkoxycarbonylmethylene or alkylamidomethylene-substituted aryl iodides, carbon monoxide insertion, reductive coupling with terminal alkynes, nucleophilic attack by the activated methylene group, and protonation with metal elimination afford the title compounds in a one-pot catalytic process (Scheme II.12).[10]



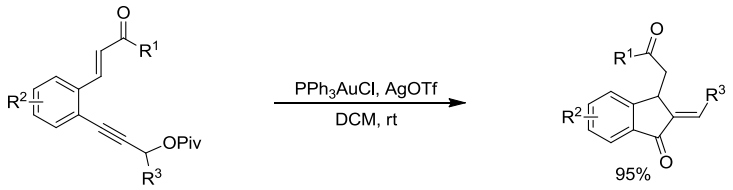
Scheme II.12

In 1994 Y. Nagao, presented that the treatment of allenyl aryl ketones with BF_3•OEt_2, gave methylenebenzocyclopentenones via a new 5-*endo*-mode cyclization (Scheme II.13).[13]



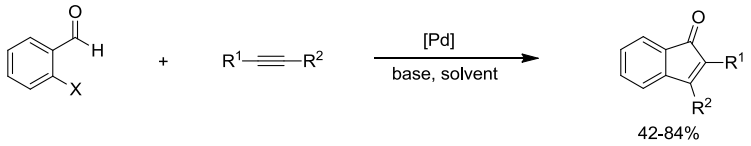
Scheme II.13

Yong-Min Liang in 2014 developed an efficient method for the synthesis of (*E*)-1(*H*)-inden-1-ones using gold-catalyzed tandem [3,3]-propargyl ester rearrangement followed by Michael addition under mild reaction conditions (Scheme II.14).[14]



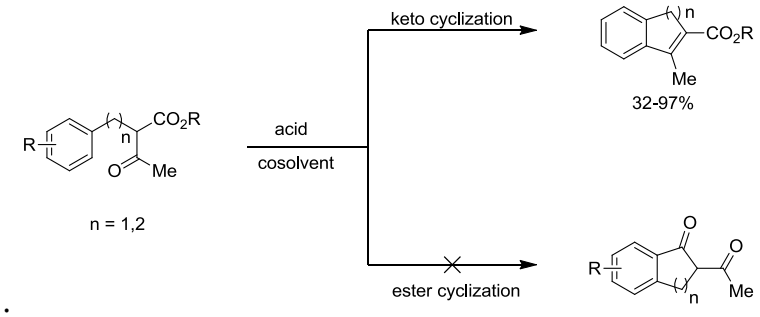
Scheme II.14

The research group of R. C. Larock in 1993 a number of 2,3-disubstituted 1-indenones have been prepared in fair to good yields by treating *ortho*-iodo or *ortho*-bromobenzaldehyde with various internal alkynes in the presence of a [Pd]-catalyst (Scheme II.15).[9]



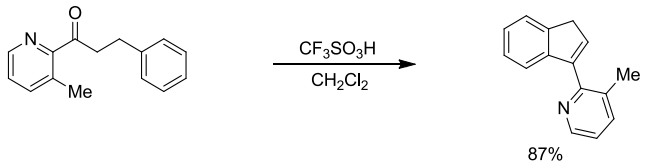
Scheme II.15

Tomohiko Ohwada in 2010 reported cyclization of arylacetoacetates to chemoselective cyclization indene and dihydronaphthalene derivatives in strong acids (Scheme II.16).[15]



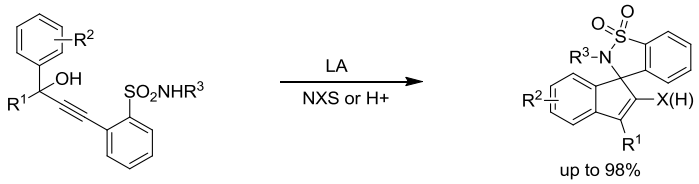
Scheme II.16

Douglas A. Klumpp in 2014 described superacid-promoted cyclodehydrations leading to functionalized indenes from ketones. The product indenes are synthesized having N-heterocyclic substituents (Scheme II.17).[17]



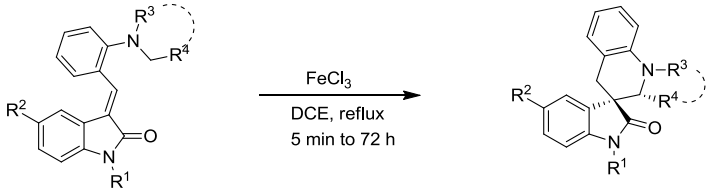
Scheme II.17

Yanguang Wang in 2014 presented a highly efficient and convenient construction of the spiro[indene-benzosultam] skeleton from propargylic alcohols. The reaction proceeded in a Lewis acid catalyzed cascade process, including the trapping of allene carbocation with sulfonamide, electrophilic cyclization, and intramolecular Friedel−Crafts alkylation. In the presence of NIS or NBS, iodo/bromo-substituted spiro[indenebenzosultam]s could be prepared in excellent yields (Scheme II.18).[31]



Scheme II.18

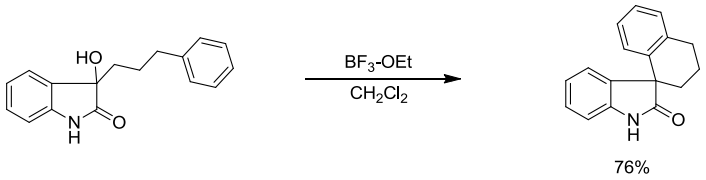
Wei-Cheng Yuan in 2012 an efficient $FeCl_3$-catalyzed stereoselective intramolecular tandem 1,5-hydride transfer/ring closure reaction was developed. The method allowed the formation of structurally diverse spirooxindole tetrahydroquinolines in high yields with good to excellent diastereoselectivity (Scheme II.19).[32]



Scheme II.19

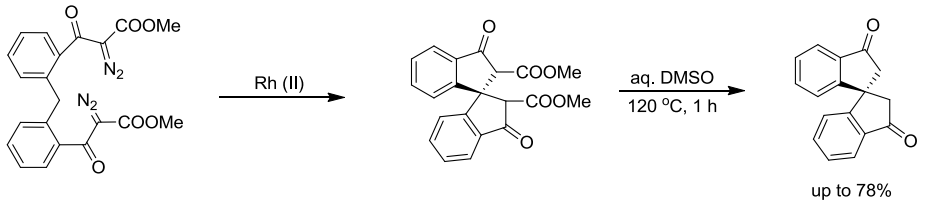
Albert Padwa in 2007 reported the synthesis of quasi-antiaromatic 2*H*-indol-2-one ring system by treating a 3-hydroxy-substituted 1,3-dihydroindol-2-one with a Lewis acid. The

cyclization was also carried out in an intramolecular fashion to give spiro-substituted oxindoles in good yield (Scheme II.20).[33]



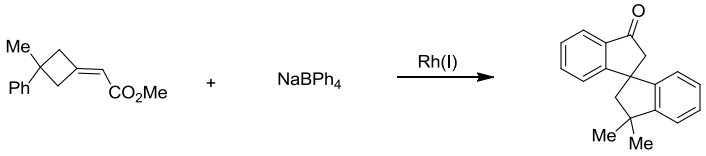
Scheme II.20

Shunichi Hashimoto in the year of 2001 a highly efficient one-pot construction of optically active 1,1'-spirobi[indan-3,3'-dione] derivative (up to 80% ee) has been achieved by exploiting the double intramolecular C–H insertion reaction of dimethyl 2,2'-methylenebis(α-diazo-β-oxobenzenepropanoate) under the influence of dirhodium(II) tetrakis[N-phthaloyl-(*R* or *S*)-*tert*-leucinate] as a catalyst (Scheme II.21).[34]



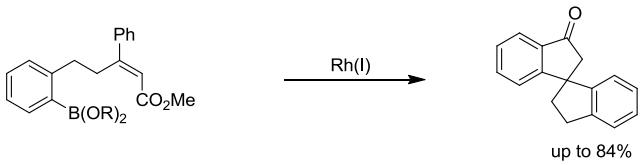
Scheme II.21

Takanori Matsuda in 2012 reported 1,4-Rhodium migration that occurs twice during the course of the rhodium-catalyzed arylative ring-opening/spirocyclization reaction of (3-arylcyclobutylidene)acetates with sodium tetraarylborates to afford ketones possessing a 1,10-spirobiindane skeleton (Scheme II.22).[35]



Scheme II.22

The same group reported in 2015 a spirocyclization reaction synthesizing spirocyclic 1-indanones from phenylboronic esters, containing a pendant β-phenyl α,β-unsaturated ester moiety. The rhodium(I)-catalyzed reaction involved, in sequence, transmetallation, intramolecular addition to a C=C bond, 1,4-rhodium migration, intramolecular addition to a C=O bond, and β-oxygen elimination (Scheme II.23).[36]

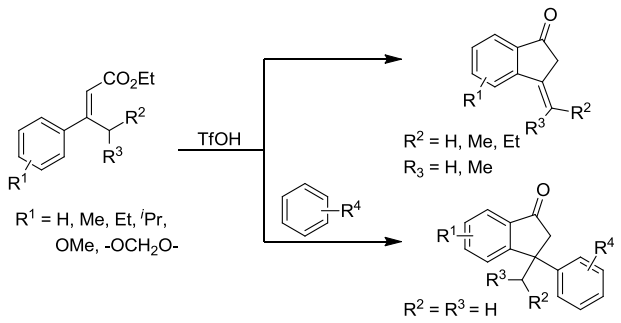


Scheme II.23

II.3 RESULTS AND DISCUSSION:

II.3.1 Synthesis of indenones and indanones via acid mediated catalysis:

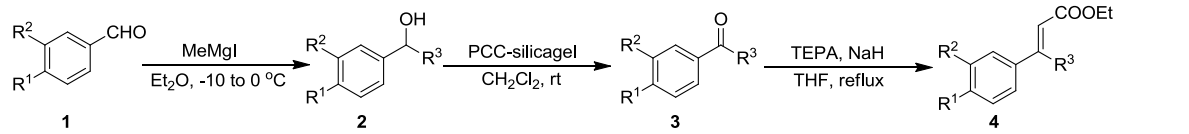
With this background, we were fascinated for the synthesis of indenones by the direct treatment of simple cinnamic acid esters. Herein, we describe an efficient and practical method for the synthesis of indenones using triflic acid as the promoter under Friedel-Crafts acylation conditions. Also, unlike our previous report, the present method was applied for the synthesis of indanones in a sequential one-pot manner. In the earlier report, for synthesis of indanones, relatively more electron rich aromatic ring was involved in acylation step, whereas, the present sequential strategy allows the acylation exclusively by the ring that is derived from cinnamic acid ester, thereby limiting the external arene only to alkylation step irrespective of its reactive nature **(**Scheme II.24).

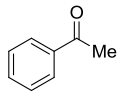
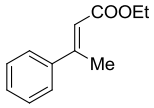
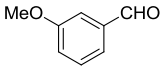
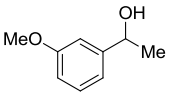
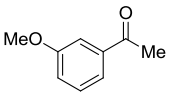
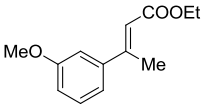
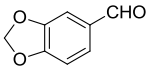
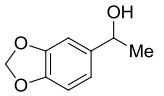
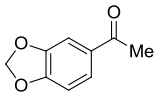
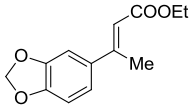
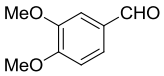
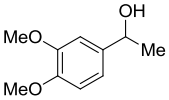
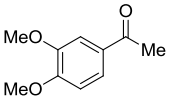
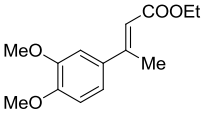
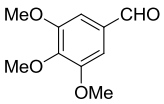
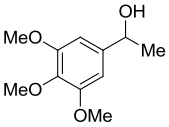
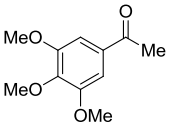
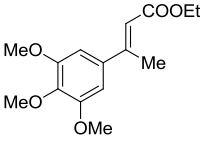
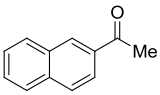
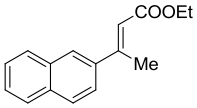
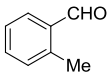
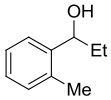
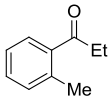
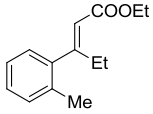
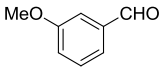
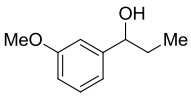
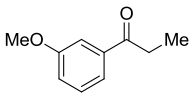
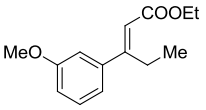
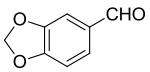
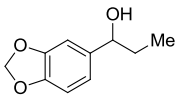
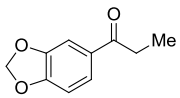
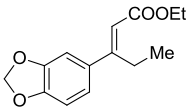


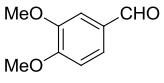
Scheme II.24

To initiate the synthetic study, the required β-alkyl cinnamic acid ester **4** were readily synthesized from the corresponding carbonyl compounds (benzaldehydes or corresponding ketones) under standard Wittig-Horner-Wadsworth-Emmons conditions.

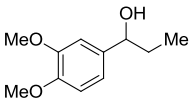
Table II.1: Synthesis of cinnamic acid ester **4a-4t** from corresponding benzaldehydes **1a-1h** and alkyl aryl ketones **3a-3t**.[a]



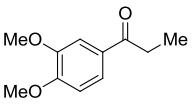
1	2	3	4
—	—	 **3a**	 **4a** (86%)
 **1a**	 **2a** (83%)	 **3b** (92%)	 **4b** (80%)
 **1b**	 **2b** (96%)	 **3c** (98%)	 **4c** (92%)
 **1c**	 **2c**(92%)	 **3d** (96%)	 **4d** (86%)
 **1d**	 **2d** (97%)	 **3e** (96%)	 **4e** (88%)
—	—	 **3f**	 **4f** (86%)
 **1e**	 **2e** (88%)	 **3g** (86%)	 **4g** (85%)
 **1a**	 **2f** (92%)	 **3h** (83%)	 **4h** (85%)
 **1b**	 **2g** (86%)	 **3i** (92%)	 **4i** (92%)



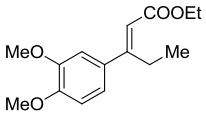
1c



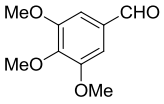
2h (90%)



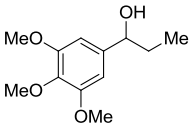
3j (98%)



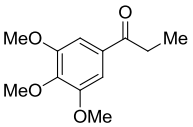
4j (89%)



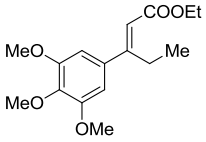
1d



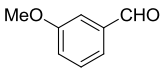
2i (89%)



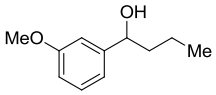
3k (91%)



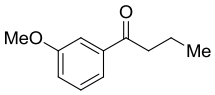
4k (92%)



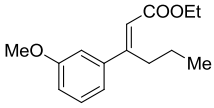
1a



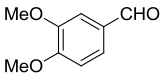
2g (89%)



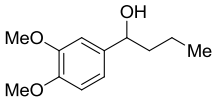
3l (97%)



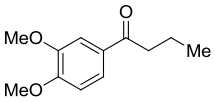
4l (89%)



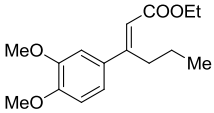
1c



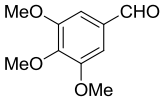
2h (92%)



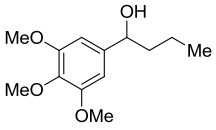
3m (96%)



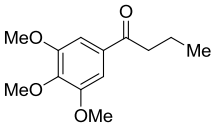
4m (91%)



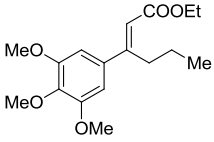
1d



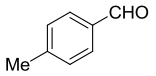
2i (90%)



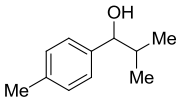
3n (90%)



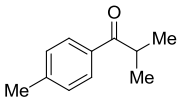
4n (88%)



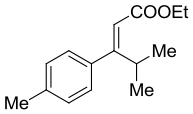
1f



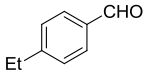
2j (87%)



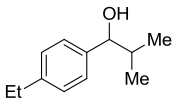
3o (85%)



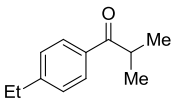
4o (96%)



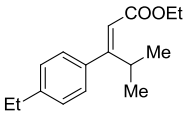
1g



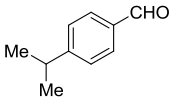
2k (87%)



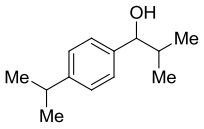
3p (85%)



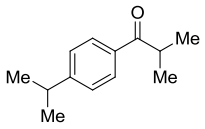
4p (96%)



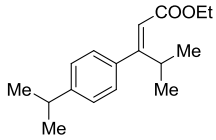
1h



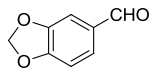
2l (80%)



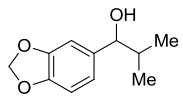
3q (92%)



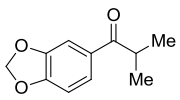
4q (93%)



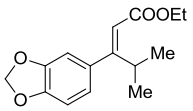
1b



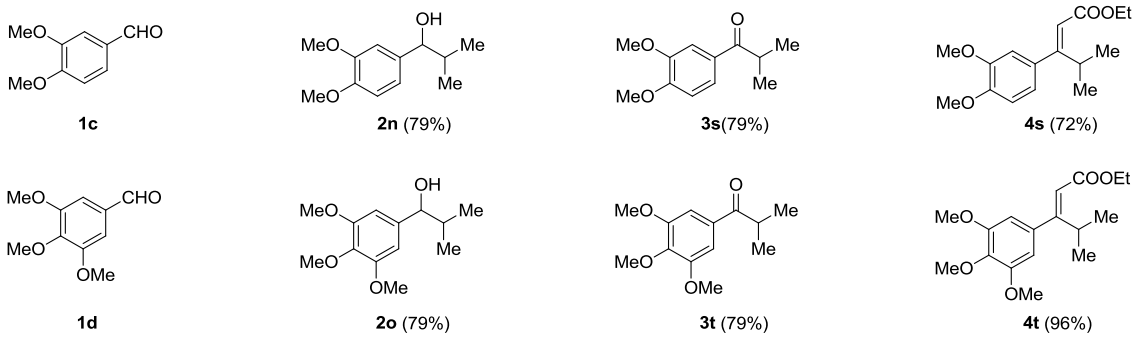
2m (87%)



3r (97%)



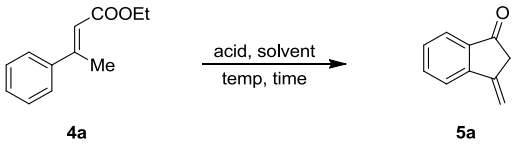
4r (92%)



[a]Yields in the parentheses are isolated yields of chromatographically pure products.

As a model study, the β-methyl cinnamic acid ester **4a** was explored under different acids to sort out optimized conditions and the results are as summarized in Table II.2. Therefore, initially our previously established conditions for the synthesis of indanones were applied on β-methyl cinnamic acid ester **4a**. However, no progress was seen and led to recovery of the starting material **4a** (Table II.2, entry 1). Almost same trend has been noticed with $CHCl_3$ and Lewis acids ($FeCl_3$ and BF_3•OEt_2) as well (Table II.2, entries 2 to 4). Neither the product **5a** nor the starting material **4a** was isolated when H_2SO_4 and $AlCl_3$ were used (Table II.2, entries 5 to 6). Interestingly, the expected product **5a** was observed but with the double bond isomerization to *exo*-cyclic position of the five membered ketone by increasing the amount of TfOH (Table II.2, entry 7). Interestingly, further increase of TfOH (20 equiv), gave the indenone **5a** in fair yield (Table II.2, entry 8). Gratifyingly, the reaction with 24 equiv of TfOH, furnished the indenone **5a** in very good yield (87%, Table II.2, entry 9). However, no progress was noticed with more equivalents of mild Lewis acid BF_3•OEt_2 (Table II.2, entry 10). Significantly, the preference of rearranged olefin bond to the *exo* position to ring reveals its unusual stability over the *endo* double bond isomer. This present study is further supported by the previous reports for the synthesis of indenones under various conditions, wherein the olefin bond is placed at *exo* position of the ring as well.[10-14]

Table II.2: Optimizing conditions for the formation of indenone **5a** starting from **4a**.



4a **5a**

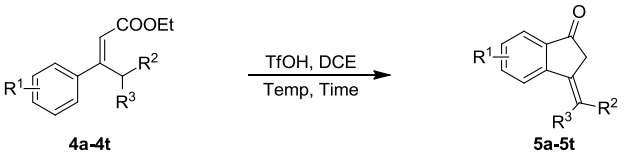
[a]Entry	Acid (equiv)	Solvent (mL)	Temp ([o]C)	Time (h)	Yield (%)[b]
					5a
1	TfOH (3)	DCE (2)	80	12	0[c]
2	TfOH (3)	$CHCl_3$ (2)	80	12	0[c]
3	$FeCl_3$ (3)	DCE (2)	80	12	0[c]
4	BF_3•OEt_2 (3)	DCE (2)	80	12	0[c]
5	H_2SO_4 (3)	DCE (2)	80	12	–[d]
6	$AlCl_3$ (3)	DCE (2)	80	12	–[d]
7	TfOH (10)	DCE (2)	RT	12	50%[e]
8	TfOH (20)	DCE (2)	RT	12	72%
9	**TfOH (24)**	**DCE (2)**	**RT**	**8**	**87%**
10	BF_3•OEt_2 (20)	DCE (2)	80	12	0[c]

[a]All reactions were carried out on 95 mg (0.5 mmol) scale of **4a**. [b]Yields of chromatographically pure products. [c]Only starting material 1a was recovered. [d]Neither the product **5a** nor the starting material **4a** was recovered. [e]Starting material **4a** was also recovered.

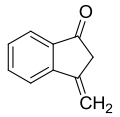
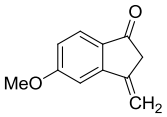
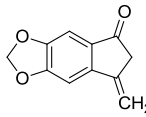
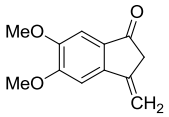
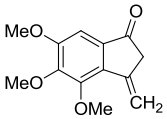
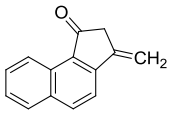
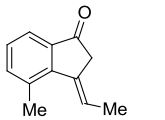
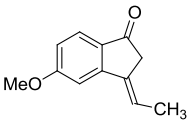
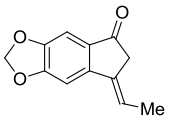
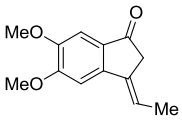
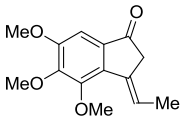
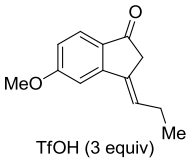
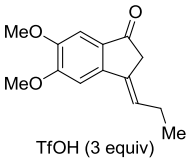
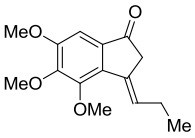
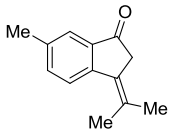
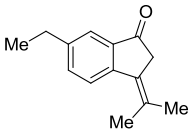
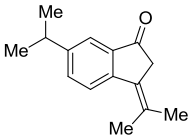
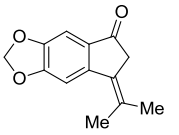
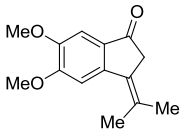
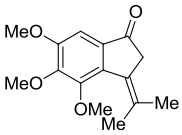
To check the scope and generality of the method, we have applied the above established conditions (Table II.2, entry 9) to other β-alkyl cinnamic acid esters **4b-4t** and the results are as summarized in Table II.3. Delightfully, the protocol was quite successful and amenable for the systems with different substituents and gave the corresponding indenones **5a-5t** with di-, tri- and tetra-substituted *exo*-cyclic olefins, in very good to excellent yields (Table II.3). It is worth mentioning that in the case of similar aromatic systems such as phenyl/naphthyl/alkyl substituent on the ring (**5a**, **5f**, **5g**, **5o**, **5p** & **5q**), the reaction was quite successful under established conditions [i.e. TfOH 24 (equiv), 8 to 12 h, RT]. On the other hand, usually, the reaction with electron rich aromatic rings (**5b-5e**, **5h-5n** & **5r-5t**) completed quickly even with low amount of triflic acid (3 equiv). Notably, the substrate scope has been well studied with simple to electron rich aromatic rings and with different β-alkyl substituents (methyl, ethyl, *n*-propyl & isopropyl) as well. Unless otherwise noted, for each system, the reaction was explored at least two to four

times, under varying amount of the acid and time, and the best conditions are presented in Table II.3.

Table II.3: Synthesis of indenones **5** via intramolecular acylation from cinnamic acid esters **4**.[a,b]



4a-4t **5a-5t**

 TfOH (24 equiv) RT, 8 h (**5a**, 87%)	 TfOH (24 equiv) RT, 6 h (**5b**, 77%)	 TfOH (24 equiv) 0 °C, 30 min (**5c**, 76%)	 TfOH (24 equiv) RT, 1 h (**5d**, 75%)	 TfOH (24 equiv) RT, 1 h (**5e**, 72%)
 TfOH (24 equiv) RT, 8 h (**5f**, 66%)	 TfOH (24 equiv) RT, 12 h (**5g**, 79%)	 TfOH (3 equiv) RT, 5 h (**5h**, 80%)	 TfOH (3 equiv) 0 °C to RT, 2 h (**5i**, 56%)	 TfOH (3 equiv) RT, 1 h (**5j**, 98%)
 TfOH (3 equiv) RT, 1 h (**5k**, 95%)	 TfOH (3 equiv) RT, 4 h (**5l**, 86%)	 TfOH (3 equiv) RT, 4 h (**5m**, 98%)	 TfOH (3 equiv) RT, 4 h (**5n**, 99%)	 TfOH (24 equiv) RT, 12 h (**5o**, 81%)
 TfOH (24 equiv) RT, 12 h (**5p**, 60%)	 TfOH (24 equiv) RT, 12 h (**5q**, 68%)	 TfOH (3 equiv) 0 °C to RT, 1 h (**5r**, 78%)	 TfOH (3 equiv) RT, 1 h (**5s**, 91%)	 TfOH (3 equiv) RT, 1 h (**5t**, 98%)

[a]All reactions were carried out on 0.5 mmol scale of **4**. [b]Yields of chromatographically pure products.

In addition to the spectroscopic evidence for structural elucidation of indenones **5**, the stereochemistry of the *exo*-cyclic olefin is unambiguously confirmed from the single crystal X-ray diffraction analysis of **5m**.

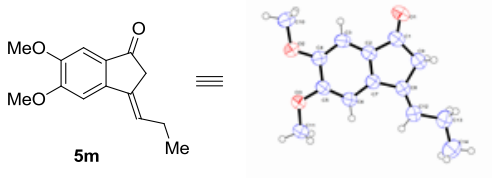


Figure II.2: X-ray crystal structure of product **5m**. Thermal ellipsoids are drawn at 50% probability level.

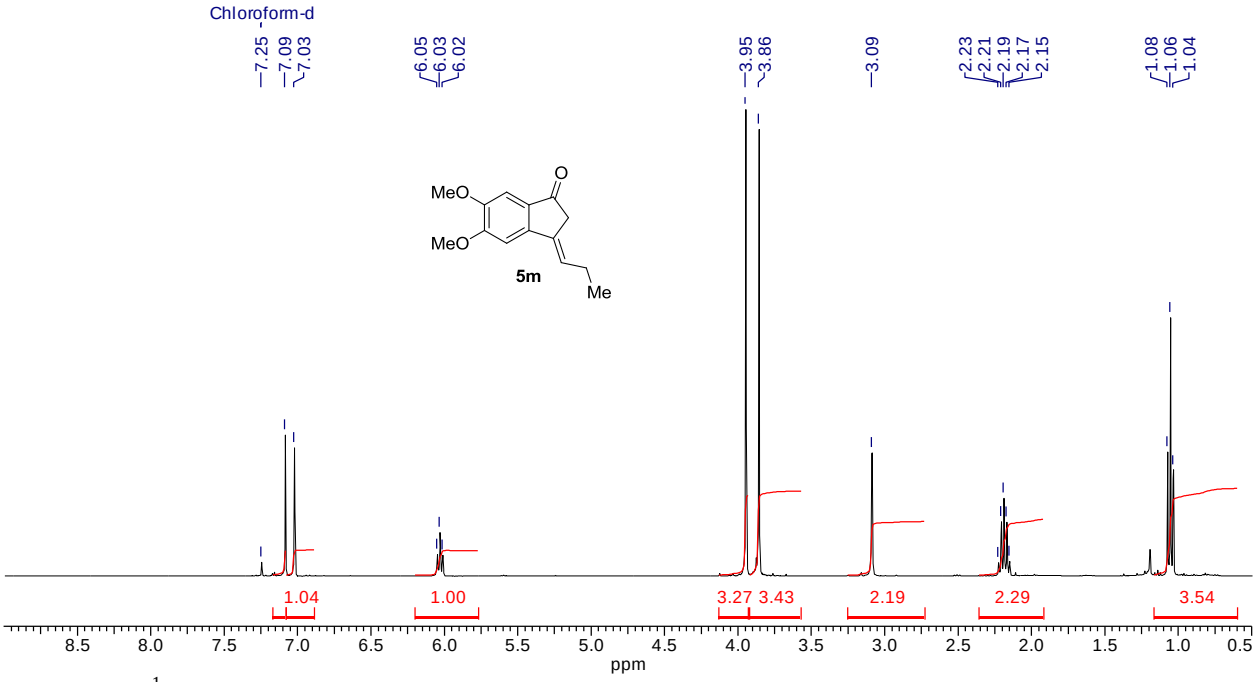


Figure II.3: ^{1}H-NMR (400 MHz) spectrum of **5m** in $CDCl_3$

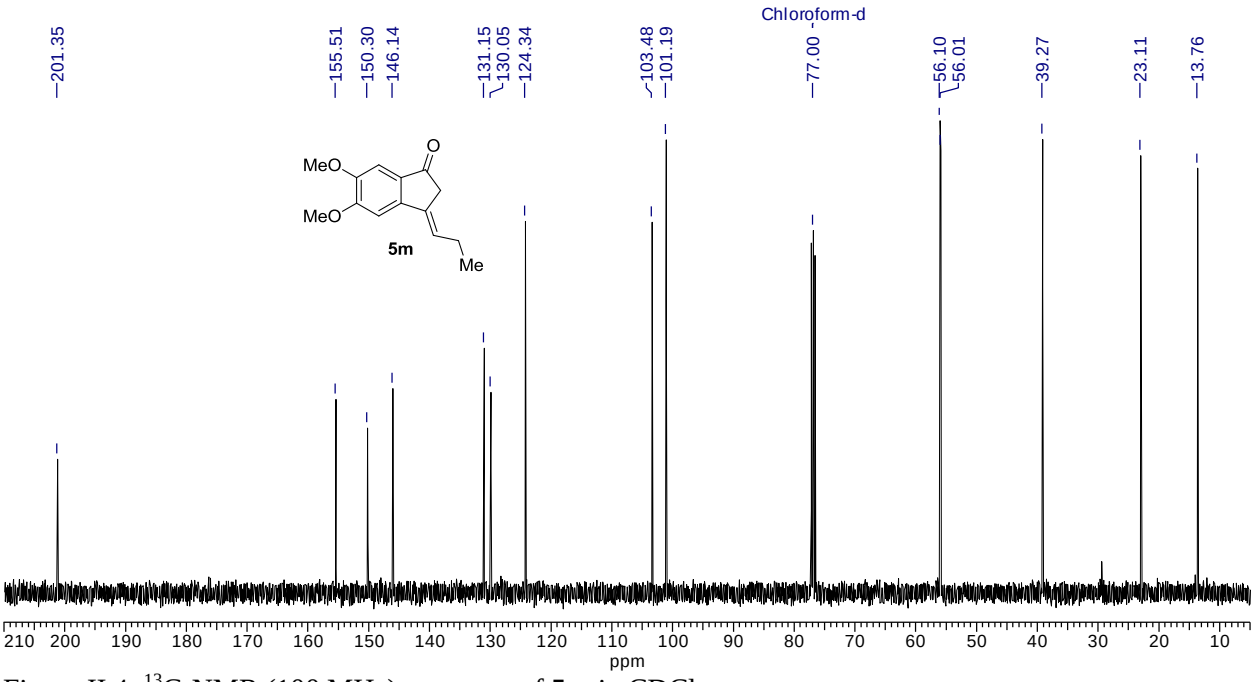


Figure II.4: ^{13}C-NMR (100 MHz) spectrum of **5m** in $CDCl_3$

The structure of (3*E*)-5,6-dimethoxy-3-propylideneindan-1-one **5m** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1695 cm^{-1} due to

C=O stretching. In the ^{1}H-NMR spectrum (Figure II.3), presence of two singlets at δ 7.09 and 7.03 due to two aromatic protons, one triplet at δ 6.03 (*J*=7.3 Hz) due to one olefinic proton, two singlets at δ 3.95 and δ 3.86 due to six protons of two aromatic methoxy groups, presence of one singlet at δ 3.09 due to methylene protons, one multiplet at δ 2.24–2.14 due to two protons of methylene moiety of ethyl group, presence of one triplet at δ 1.06 (*J*=7.3 Hz) due to three protons of methyl moiety of ethyl group, established the structure of indenone **5m**. In 14 lines ^{13}C-NMR spectrum (Figure II.4), presence of one quaternary carbon resonance at δ 201.4 indicates the C=O group, five quaternary carbons resonances at δ 155.5, 150.3, 146.1, 131.2 and 130.1 due to four aromatic and one olefinic carbons, three methine carbons at δ 124.3, 103.5 and 101.2 due to two aromatic and one olefinic carbons, two aromatic methoxy carbons at δ 56.1 and 56.0, two methylene carbons at δ 39.3 and 23.1, presence of one methyl carbon at δ 13.8 ppm, confirmed the structure of indenone **5m**. Presence of the $[M+H]^{+}$ peak at m/z $[C_{14}H_{17}O_3]^{+}$=233.1170 in the mass spectrum further established the structure of indanone **5m**.

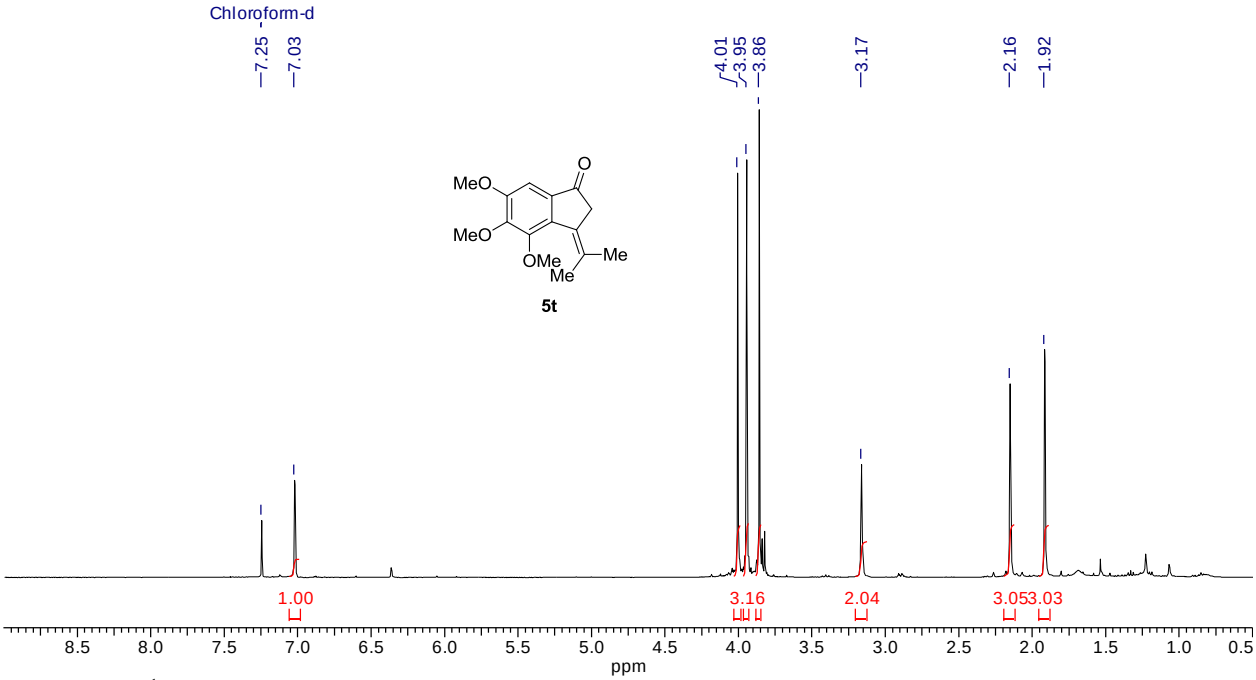


Figure II.5: ^{1}H-NMR (400 MHz) spectrum of **5t** in $CDCl_3$

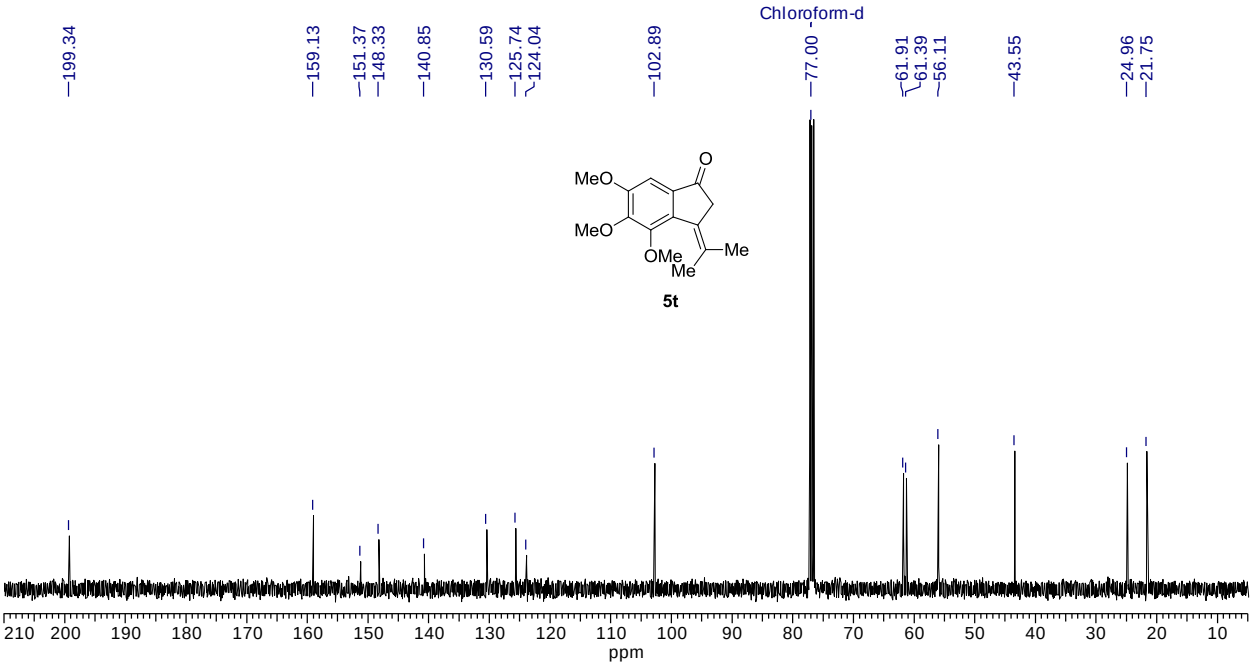
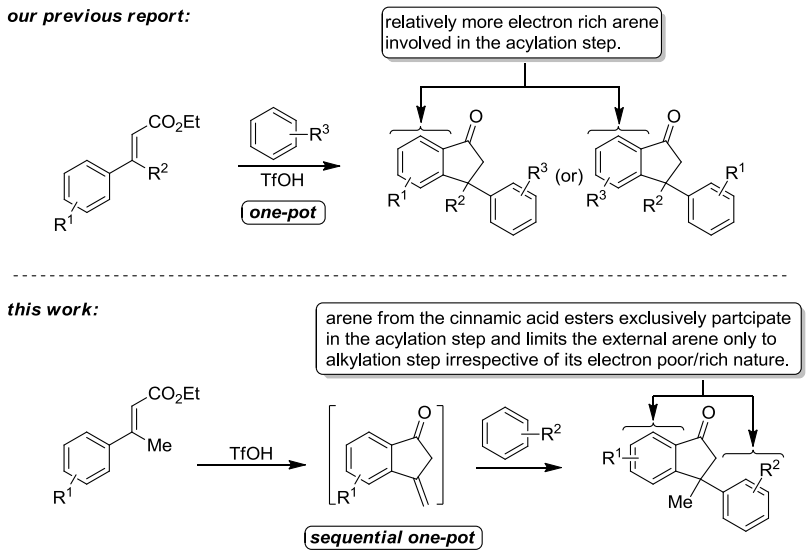


Figure II.6: ^{13}C-NMR (100 MHz) spectrum of **5t** in $CDCl_3$

The structure of 4,5,6-trimethoxy-3-(1-methylethylidene)indan-1-one **5t** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1769 cm^{-1} due to C=O stretching. In the ^{1}H-NMR spectrum (Figure II.5), presence of one singlet at δ 7.03 due

to one aromatic proton, three singlets at δ 4.01, 3.95 and 3.86 due to nine protons of three aromatic methoxy groups, presence of one singlet at δ 3.17 due to two protons of a methylene group, presence of two singlets at δ 2.16 and 1.92 due to six protons of two methyl groups, established the structure of indenone **5t**. In 15 lines ^{13}C-NMR spectrum (Figure II.6), presence of one quaternary carbon resonance at δ 199.3 indicates the C=O group, seven quaternary carbons resonances at δ 159.1, 151.4, 148.3, 140.9, 130.6, 125.7 and 124.0 due to six aromatic and one olefinic carbons, one aromatic methine carbon at δ 102.9, three aromatic methoxy carbons at δ 61.9, 61.4 and 56.1, one methylene carbon at δ 43.6, presence of two methyl carbons at δ 25.0 and 21.8 ppm, confirmed the structure of indenone **5t**. Presence of the $[M+H]^+$ peak at m/z $[C_{15}H_{19}O_4]^+$=263.1275 in the mass spectrum further established the structure of indanone **5t**.

Furthermore, to extend the method, the synthesis of substituted indanones containing quaternary carbon atom was planned, in a sequential one-pot manner. It was anticipated that treatment of in-situ generated indenone with an external arene would deliver indanones in a complimentary mode to our previous method for the synthesis of indanones (Scheme II.25).

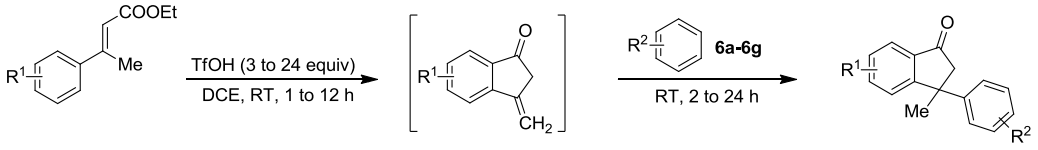


Scheme II.25 Comparing the technical differences between the present and previous results.

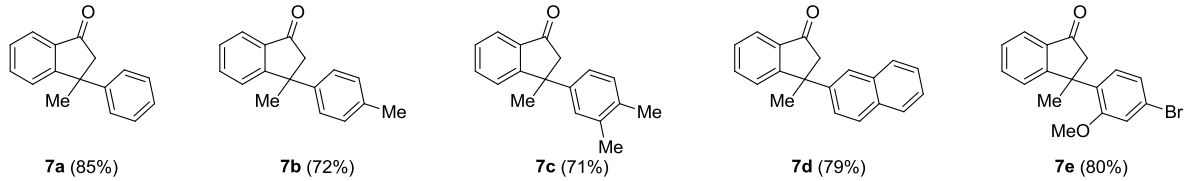
Gratifyingly, as expected, the sequential one-pot protocol was found successful and furnished the corresponding indanones **7a-7j** (Table II.4). Significantly, unlike our previous method for the synthesis of indanones (in which the relatively more electron rich aromatic ring

selectively participated in the Friedel-Crafts acylation step), the present method limits the external arene to only Friedel-Crafts alkylation irrespective of its electron poor/rich nature. However, the reaction was smooth for simple acetophenone derived cinnamic acid esters, but in case of higher β-alkyl cinnamic acid esters, the reaction was not successful. This may be due to more thermodynamic stability of more substituted double bond of the intermediate indenone **5**. On the other hand, forceful conditions led to the decomposition of the reaction mixture.

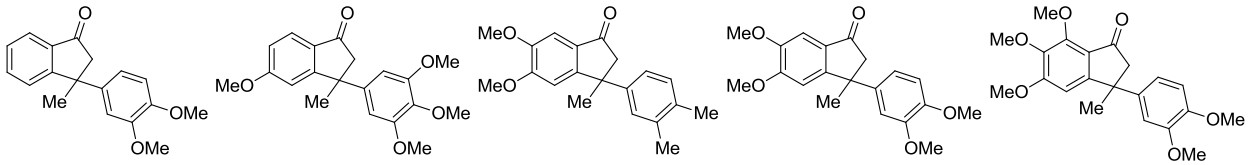
Table II.4: Synthesis of indanones **5** from cinnamic acid esters **4** via intramolecular acylation and intermolecular arylation.[a,b]



4a, **4b**, **4d** & **4e** | **5a**, **5b**, **5d** & **5e** | **7a-7j**



7a (85%) | **7b** (72%) | **7c** (71%) | **7d** (79%) | **7e** (80%)



7f (77%) | **7g** (70%) | **7h** (81%) | **7i** (70%) | **7j** (80%)

[a]All reactions were carried out on 0.5 mmol scale of **4**. [b]Yields of chromatographically pure products **7**.

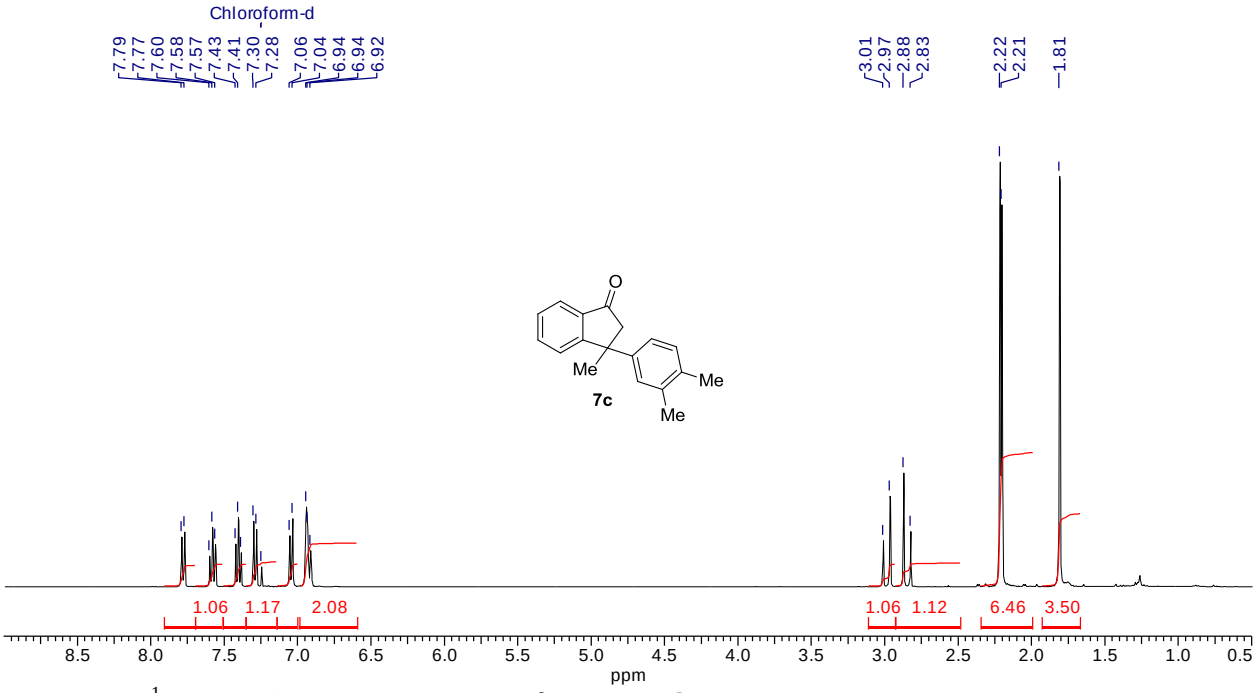


Figure II.7: ^{1}H-NMR (400 MHz) spectrum of **7c** in $CDCl_3$

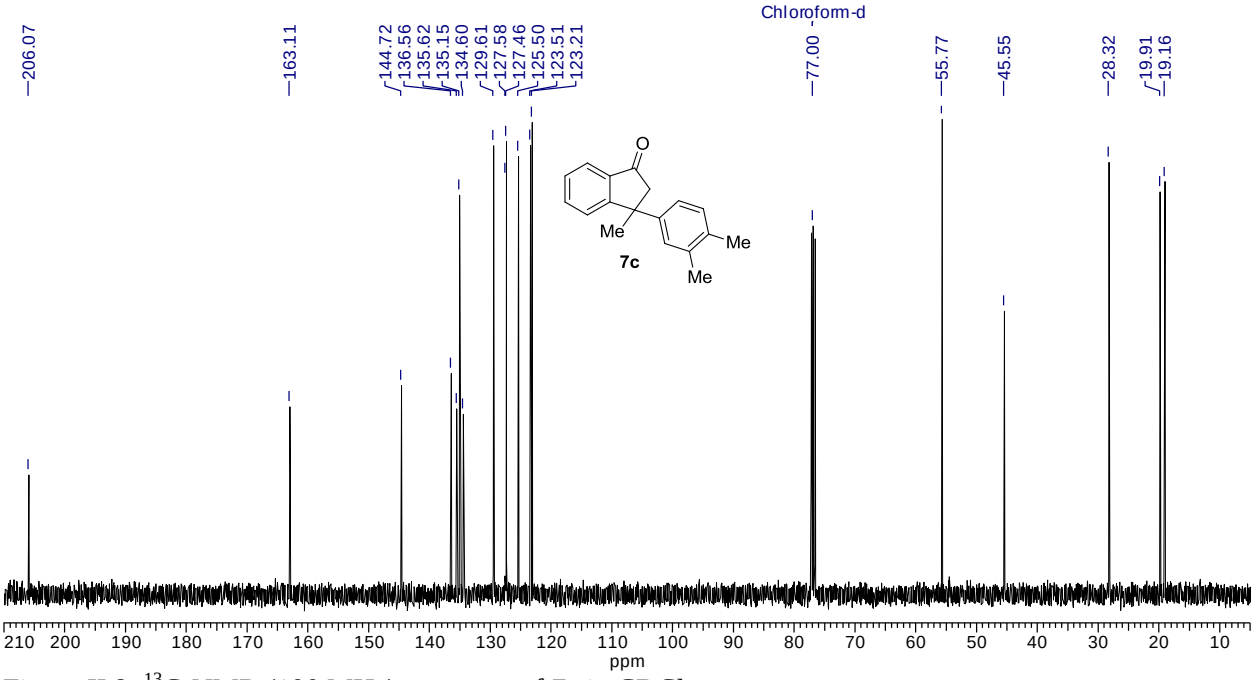
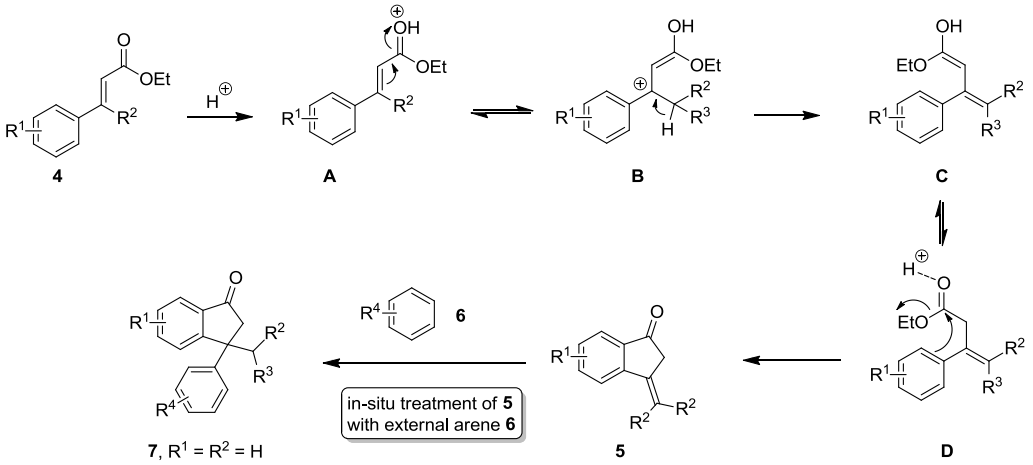


Figure II.8: ^{13}C-NMR (100 MHz) spectrum of **7c** in $CDCl_3$

The structure of 3-(3,4-dimethylphenyl)-3-methylindan-1-one **7c** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1712 cm^{-1} due to C=O stretching. In the ^{1}H-NMR spectrum (Figure II.7), presence of one doublet at δ 7.79 (*J*=7.8 Hz)

due to one aromatic proton, one doublet of doublet of doublets at δ 7.58 (*J*=7.8, 7.3 and 1.5 Hz) due to one aromatic proton, one doublet of doublets at δ 7.41 (*J*=7.3 and 7.3 Hz) due to one aromatic proton, presence of two doublets at δ 7.30 (*J*=7.8 Hz) and 7.06 (*J*=7.8 Hz) due to two aromatic protons, one doublet of doublets at 6.94 (*J*=8.3 and 3.0 Hz) due to two aromatic protons, presence of two doublets at δ 3.01 (*J*=18.6 Hz) and δ 2.88 (*J*=18.6 Hz) due to two protons of methylene group, presence of three singlets at δ 2.22, 2,21 and 1.8 due to nine protons of three methyl groups, established the structure of indanone **7c**. In 18 lines ^{13}C-NMR spectrum (Figure II.8), presence of one quaternary carbon resonances at δ 206.1 indicates the C=O group, five quaternary carbons resonances at δ 163.1, 144.7, 136.6, 135.6 and 134.6 due to aromatic carbons, seven aromatic methine carbons at δ 135.2, 129.6, 127.6, 127.5, 125.5, 123.5 and 123.2, one methylene carbon at δ 55.8, quaternary carbon at δ 45.6, presence of three methyl carbons at δ 28.3, 19.9 and δ 19.2.0 ppm, confirmed the structure of indanone **7c**. Presence of the $[M+H]^+$ peak at m/z $[C_{18}H_{19}O]^+$=251.1429 in the mass spectrum further established the structure of indanone **7c**.

A plausible reaction mechanism for the formation of indenones **5** and indanones **7** is shown in Scheme II.26. Initially, the protic acid could activate and isomerize the ketone group of the ester **4** to yield the equilibrating structures **A, B**, deprotanation of intermediate **B** would be form resonance structures **C** and **D.** Intramolecular acylation of **D** and rearomatization leads to the indenone **5**. Further, in-situ treatment of indenone **5** with an external arene **6** affords indanone **7**.

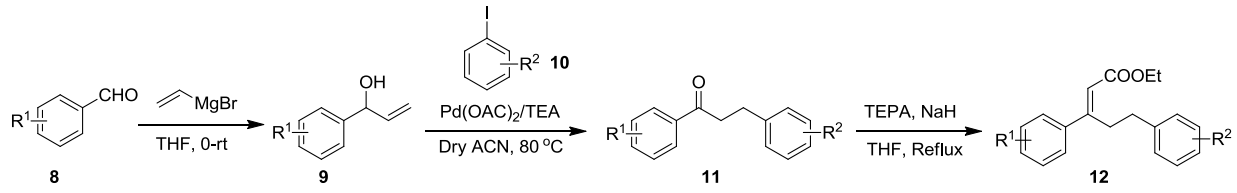


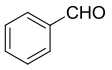
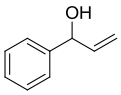
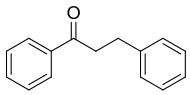
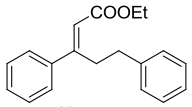
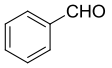
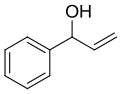
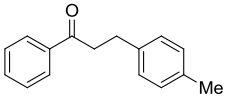
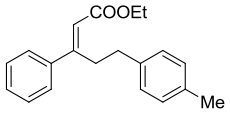
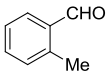
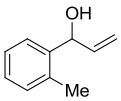
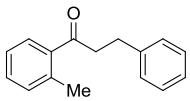
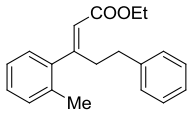
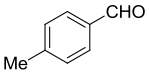
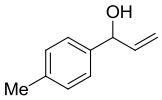
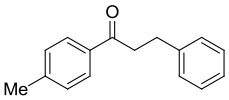
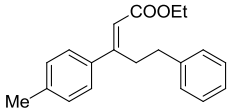
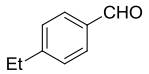
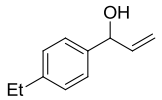
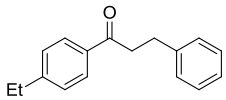
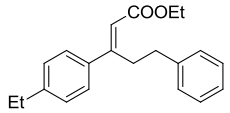
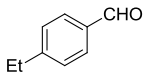
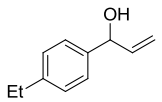
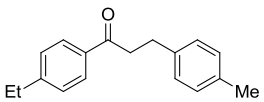
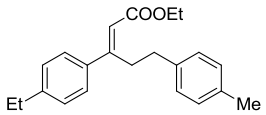
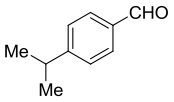
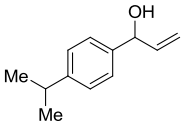
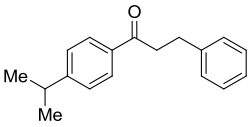
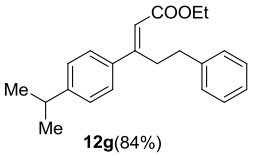
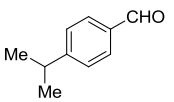
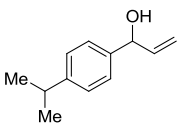
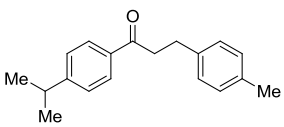
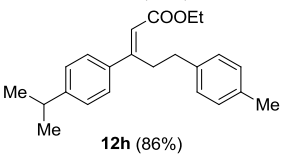
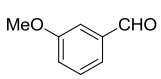
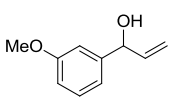
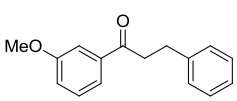
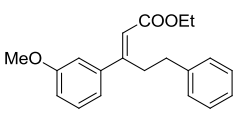
Scheme II.26: Plausible reaction mechanism for the formation of indenones **5** and indanones **7**.

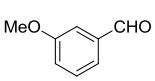
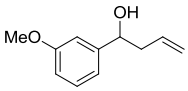
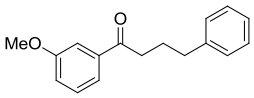
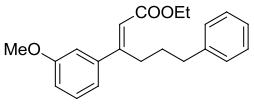
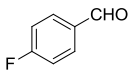
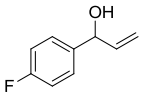
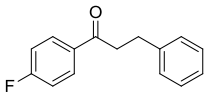
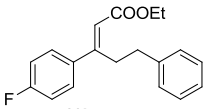
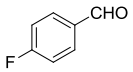
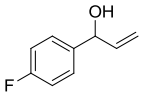
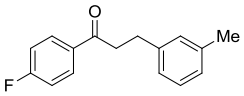
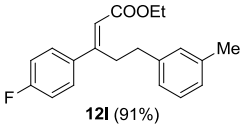
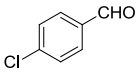
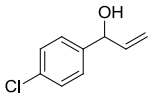
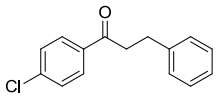
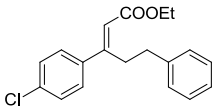
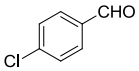
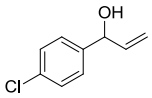
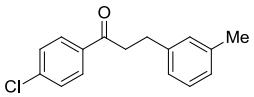
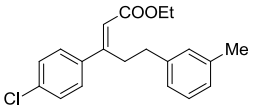
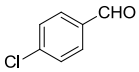
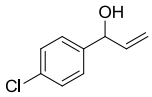
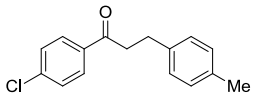
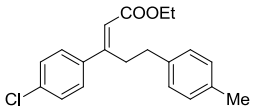
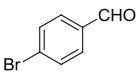
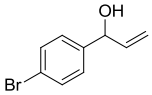
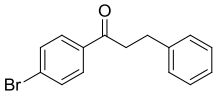
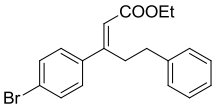
II.3.3 Synthesis of spirotetracyclic indanone and indenes via one-pot acid catalysis:

After successful accomplishment of indenones **5**, and indanones **7**, through acid catalysis, further we became interested in checking the outcome, when the ester moiety has pendant aryl groups **12**. The requisite pendant β-aryl α,β-unsaturated ester **12** derivatives were readily obtained in three reaction steps starting from benzaldehydes **8**. Thus, addition of vinylmagnesium bromide Grignard reagent to the benzaldehydes **8a-8i**, gave the corresponding allyl alcohols **9a-9i** in excellent yields (76-89%, Table II.5). The Jeffrey-Heck coupling of the allyl alcohols **9** with iodo arenes **10**, furnished the 1,3-diphenylpropan-1-ones **11a-11p** in good to very good yields (65-79%). Finally, the pendant β-aryl α,β-unsaturated esters **12** were readily synthesized from the corresponding carbonyl compounds (ketones) using standard Wittig-Horner-Wadsworth-Emmons conditions in excellent yields (84-96%, Table II.5).

Table II.5: Synthesis of pendant β-aryl α,β-unsaturated esters **12a-12p** from corresponding benzaldehydes **8a-8i**.[a]



 **8a**	 **9a** (86%)	 **11a** (78%)	 **12a** (92%)
 **8a**	 **9a** (86%)	 **11b** (72%)	 **12b** (96%)
 **8b**	 **9b** (89%)	 **11c** (76%)	 **12c** (90%)
 **8c**	 **9c** (82%)	 **11d** (78%)	 **12d** (96%)
 **8d**	 **9d** (82%)	 **11e** (70%)	 **12e** (92%)
 **8d**	 **9d** (82%)	 **11f** (70%)	 **12f** (92%)
 **8e**	 **9e** (78%)	 **11g** (72%)	 **12g**(84%)
 **8e**	 **9e** (78%)	 **11h** (76%)	 **12h** (86%)
 **8f**	 **9f** (80%)	 **11i** (79%)	 **12i** (92%)

 **8f**	 **9g** (80%)	 **11j** (65%)	 **12j** (90%)
 **8g**	 **9h** (87%)	 **11k** (78%)	 **12k** (94%)
 **8g**	 **9h** (87%)	 **11l** (70%)	 **12l** (91%)
 **8h**	 **9i** (86%)	 **11m** (68%)	 **12m** (90%)
 **8h**	 **9i** (86%)	 **11n** (72%)	 **12n** (92%)
 **8h**	 **9i** (76%)	 **11o** (71%)	 **12o** (90%)
 **8i**	 **9j** (76%)	 **11p** (74%)	 **12p** (94%)

[a]Yields in the parentheses are isolated yields of chromatographically pure products.

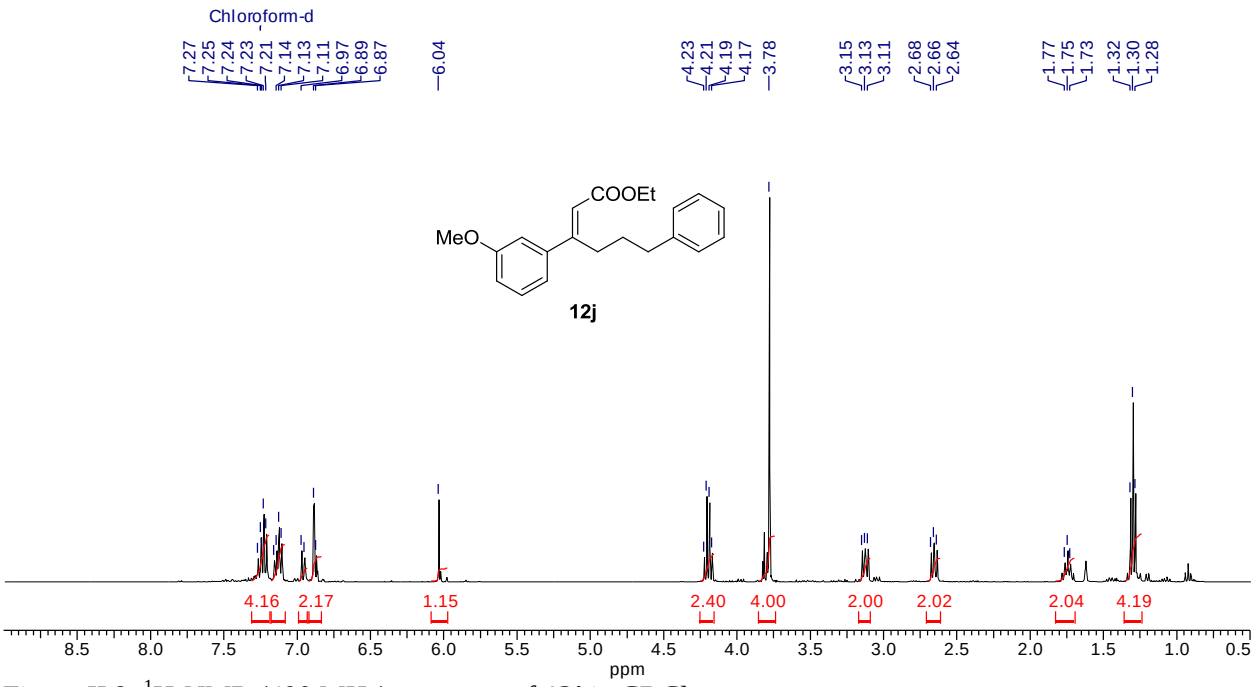


Figure II.9: ^{1}H-NMR (400 MHz) spectrum of **12j** in $CDCl_3$

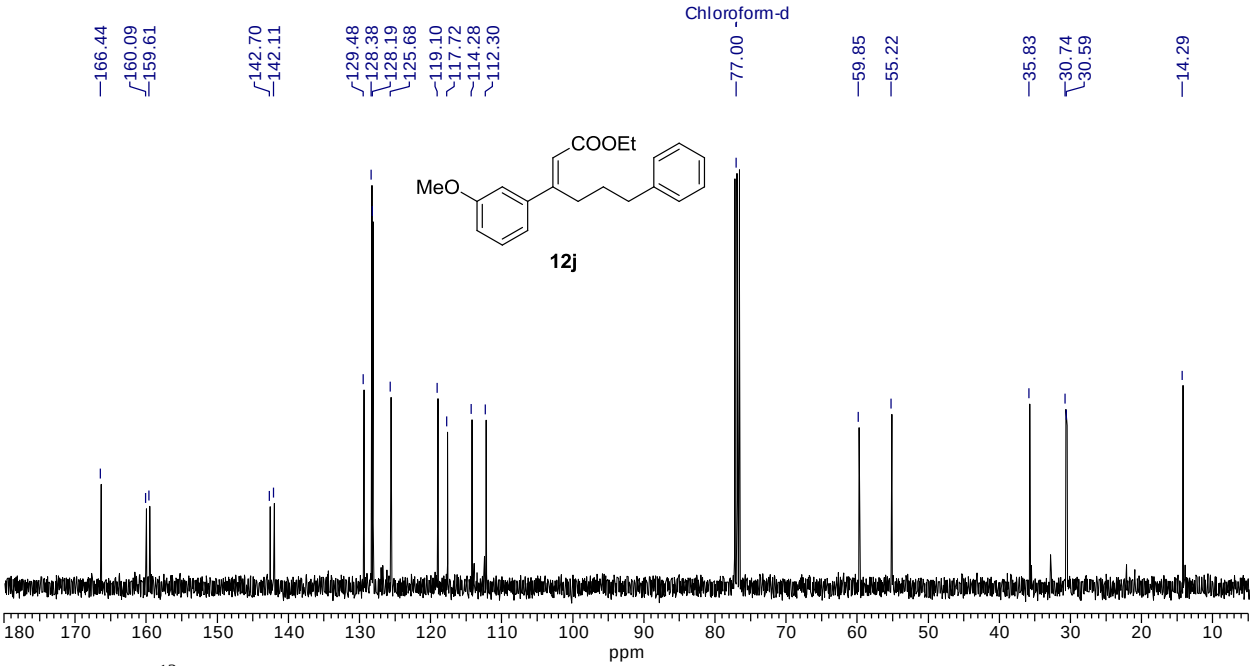


Figure II.10: ^{13}C-NMR (100 MHz) spectrum of **12j** in $CDCl_3$

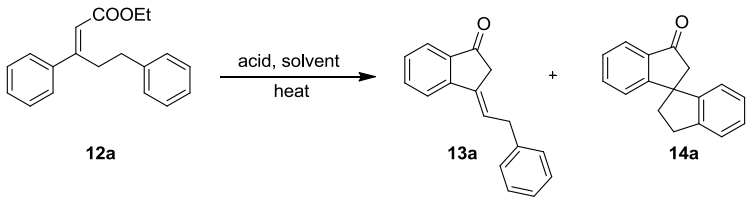
The structure of ethyl (2*E*)-3-(3-methoxyphenyl)-6-phenylhex-2-enoate **12j** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1712 cm^{-1} due to C=O stretching. In the ^{1}H-NMR spectrum (Figure II.9), presence of two

multiplets at δ 7.29–7.19 and 7.17–7.09 due to six aromatic protons, presence of one doublet at δ 6.97 (*J*=8.3 Hz) due to one aromatic proton, presence of one doublet of doublets at δ 6.89 (*J*=7.3 and 1.5 Hz) due to two aromatic protons, presence of one singlet at δ 6.04 due to olefinic proton, presence of one quartet at δ 4.21 (*J*=7.3 Hz) due to two protons of methylene moiety of ethyl group, presence of one singlet at δ 3.78 due to three protons of aromatic methoxy group, presence two triplets at δ 3.13 (*J*=7.8 Hz) and 2.66 (*J*=7.8 Hz) due to four protons of two methylene groups, presence of one multiplet at δ 1.83–1.67 due to two protons of methylene group, presence of one triplet at δ 1.30 (*J*=7.3 Hz) due to three protons of methyl moiety of ethyl group, established the structure of ester **12j**. In 19 lines ^{13}C-NMR spectrum (Figure II.10), presence of one quaternary carbon resonance at δ 166.4 indicates the C=O group, presence of four quaternary carbons resonances at δ 160.1, 159.6, 142.7 and 142.1 due to three aromatic and one olefinic carbons, nine aromatic methine carbons at δ 129.5, 128.4 (2C), 128.2 (2C), 125.7, 119.1, 117.7 and 114.3, one olefinic carbon at δ 112.3, one aromatic methoxy carbon at δ 59.9, four methylene carbons resonances at δ 55.2, 35.8, 30.7 and 30.6, and presence of one methyl carbon at δ 14.3 ppm, confirmed the structure of ester **12j**. Presence of the $[M+H]^+$ peak at m/z $[C_{21}H_{25}O_3]^+$=325.1798 in the mass spectrum further established the structure of ester **12j**.

With the required pendant β-aryl α,β-unsaturated esters **12** in hand, the reaction was explored to sort out the best optimized reaction conditions under various acids and the results are summarized in Table II.6. Thus, the pendant β-aryl α,β-unsaturated ester **12** [i.e., the major (*E*)-isomer] was chosen as the model system for this study. The initial attempts either with *p*-TSA or with $TiCl_4$ were unsuccessful in yielding any product (Table II.6, entries 1, 2, 3 & 4). Whereas, the reaction in the presence of Brønsted superacid (TfOH) at room temperature, furnished the expected product **14** along with indenone **13** in which the double bond was isomerized to the *exo*-cyclic position of the five membered ketone. The spirocyclic 1-indanone product **14**, whose yield increased in parallel to the quantity of the acid used, subsequent increase of temperature as well as the quantity of the Lewis acid and time, started to furnish the spirocyclic 1-indanone product **14** with the increased yield (Table II.6, entries 5 to 7). The reaction in the presence of Brønsted superacid (TfOH, 6 equiv), gave a promising result of **14** as an exclusive product in very good yield (76%, Table II.6 entry 8). On the other hand, the reaction with $AlCl_3$ was

inconclusive (Table II.6, entry 9). Using $CHCl_3$ as medium, gave the product in decreased yield (Table II.6, entry 10).

Table II.6: Optimization conditions for the synthesis of spirocyclic 1-indanone **14**.

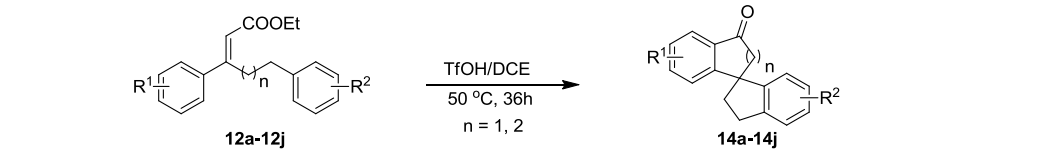


Entry[a]	Acid (equiv)	Solvent (mL)	Temp (^oC)	Time (h)	Yield (%)[b]	
					13a	**14a**
1	*p*-TSA (2)	DCE (2)	Rt	12	0[c]	0[c]
2	$TiCl_4$ (2)	DCM (2)	Rt	24	0[c]	0[c]
3	H_2SO_4 (3)	DCM (2)	Rt	12	-[e]	-[e]
4	TfOH (3)	DCE (2)	0-Rt	12	0[c]	0[c]
5	TfOH (3)	DCE (2)	Rt	12	60	20
6	TfOH (3)	DCE (2)	50	24	20	40
7	TfOH (6)	DCE (2)	50	24	0[d]	60
8	**TfOH (6)**	**DCE (2)**	**50**	**30**	**0** [d]	**76**
9	$AlCl_3$ (3)	DCE (2)	50	30	-[e]	-[e]
10	TfOH (6)	$CHCl_3$ (2)	50	30	0[d]	50

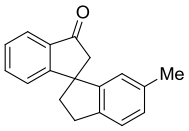
[a]All reactions were carried out on 0.25 mmol scale of **12a** (*E*-isomer). [b]Isolated yields of chromatographically pure products. [c]only starting material **12a** was recovered. [d]No **13a** was formed. [e]Neither the product **13a** and **14a** nor starting material **12a** was recovered.

Among the screened conditions, the conditions mentioned in entry 8 of Table II.6, were best with regard to the yield of spirocyclic 1-indanone product **14**. Therefore, these conditions were applied to the other systems **12a-12j** (*E*-isomers and *E*+*Z*-mixture of isomers) to examine the scope and limitations. Interestingly, this optimized reaction condition proved to be amenable for various systems possessing and furnished the cyclized products **14a-14j** in very good to excellent yields (Table II.7).

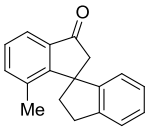
Table II.7: Synthesis of spirocyclic 1-Indanones **14a-14j** through acid catalyzed addition–spirocyclization of **12a-12j**.[a,b]



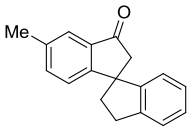
14a (76%)



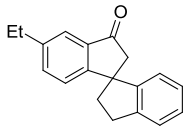
14b (87%)



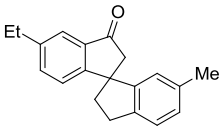
14c (78%)



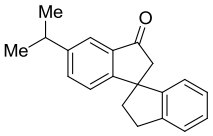
14d (86%)



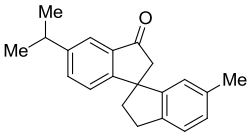
14e (90%)



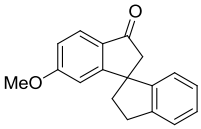
14f (84%)



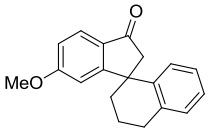
14g (86%)



14h (85%)



14i (77%)



14j (78%)

[a]All reactions were carried out on 0.25 mmol scale of **12**. [b]Yields of chromatographically pure products **14**.

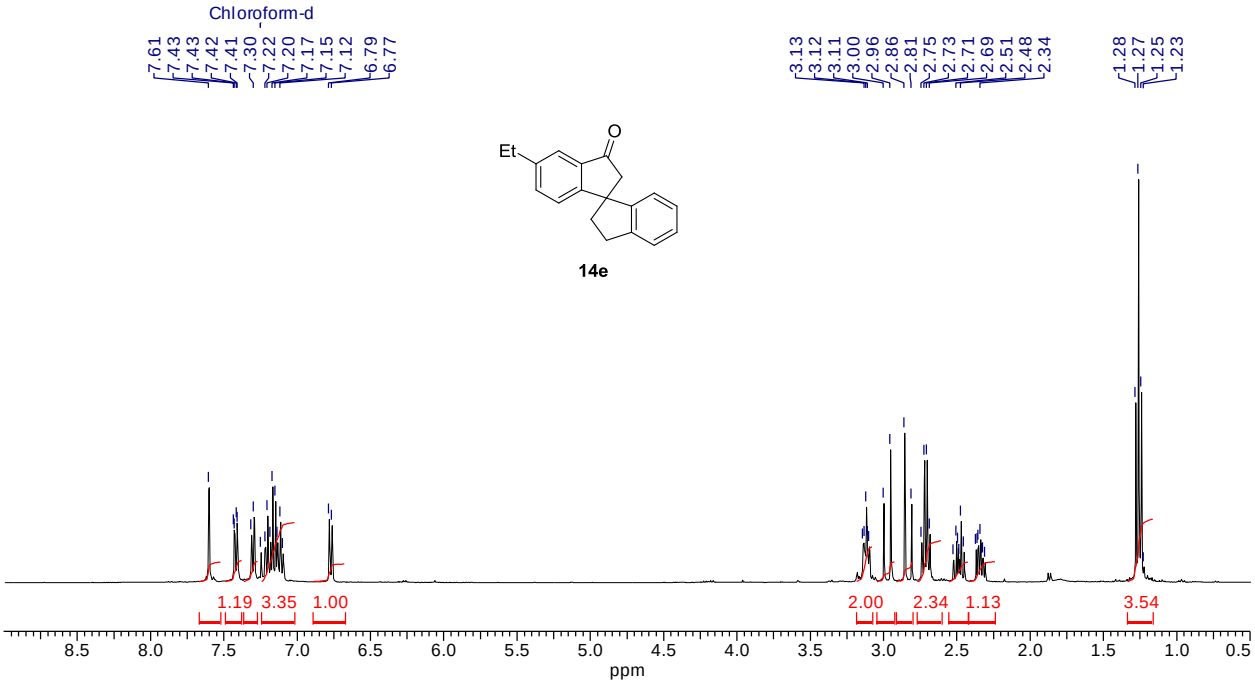


Figure II.11: ^{1}H-NMR (400 MHz) spectrum of **14e** in $CDCl_3$

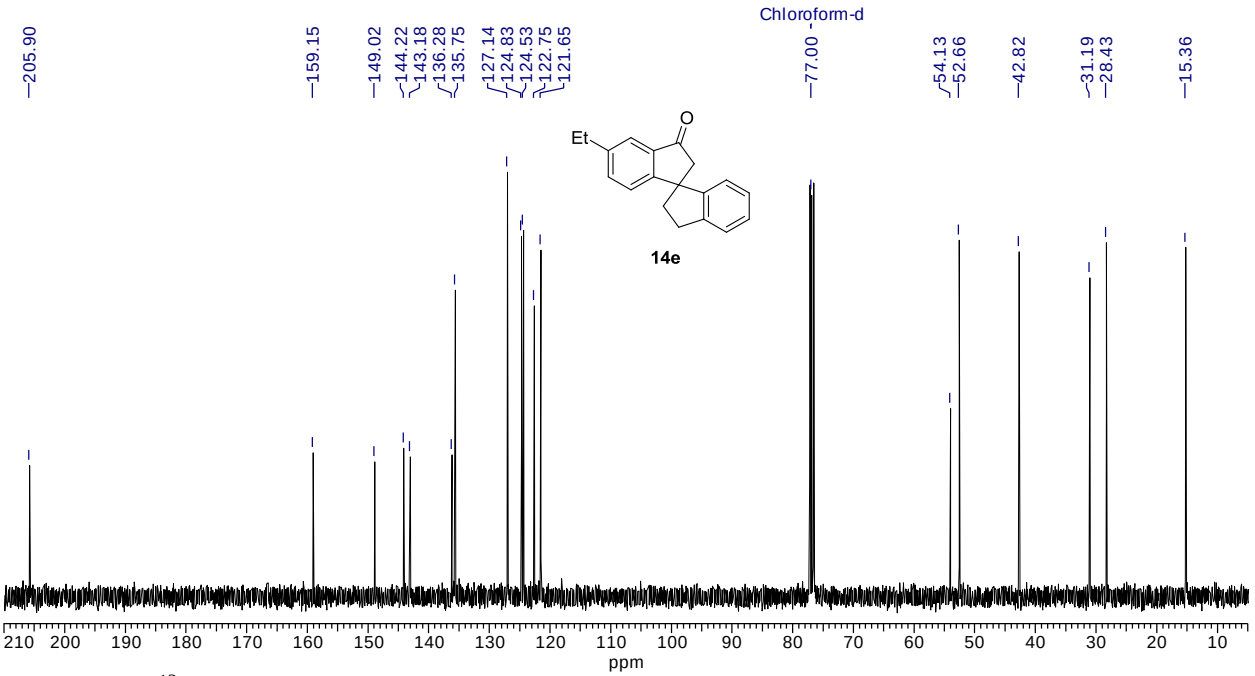


Figure II.12: ^{13}C-NMR (100 MHz) spectrum of **14e** in $CDCl_3$

The structure of 5-ethyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2*H*)-one **14e** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1708 cm^{-1} due

to C=O stretching. In the ^{1}H-NMR spectrum (Figure II.11), presence of one singlet at δ 7.61 due to one aromatic proton, one doublet of doublets at δ 7.43 (*J*=7.8 and 1.5 Hz) due to one aromatic proton, presence of one doublet at δ 7.32 (*J*=7.3 Hz) due to one aromatic proton, presence of one multiplet at δ 7.24–7.07 due to three aromatic protons, presence of one doublet at δ 6.79 (*J*=7.8 Hz) due to one aromatic proton, presence of one multiplet at δ 3.16–3.07 due to one methylene protons, presence of two individual doublets at δ 3.00 (*J*=18.6 Hz) and 2.86 (*J*=18.6 Hz) due to one methylene protons, presence of one quartet at δ 2.73 (*J*=7.8 Hz) due to two protons of methylene moiety of ethyl group, presence of two multiplets at δ 2.55–2.43 and 2.39–2.29 due to four protons of two methylene groups, presence of one triplet at δ 1.27 (*J*=7.3 Hz) due to three protons of methyl moiety ethyl group, established the structure of spirocyclic 1-indanone **14e**. In 19 lines ^{13}C-NMR spectrum (Figure II.12), presence of one quaternary carbon resonances at δ 205.9 indicates the C=O group, five quaternary carbons resonances at δ 159.2, 149.0, 144.2, 143.2 and 136.3 due to aromatic carbons, seven aromatic methine carbons at δ 135.8, 127.1 (2C), 124.8, 124.5, 122.8, and 121.7, one quaternary carbon at δ 54.1, four methylene carbons at δ 52.7, 42.8, 31.2 and 28.4, presence of one methyl carbon at δ 15.4 ppm, confirmed the structure of spirocyclic 1-indanone **14e**. Presence of the $[M+H]^{+}$ peak at m/z $[C_{19}H_{19}O]^{+}$=263.1438 in the mass spectrum further established the structure of spirocyclic 1-indanone **14e**. These structures have been further confirmed by the recent report on the synthesis of spiro tetracyclic systems.[36]

In addition to the ^{1}H and ^{13}C NMR studies, the chemical structures of spiro-tetracyclic ketones 14 were confirmed by 2D-NMR analysis such as COSY, HSQC, HMBC and NOESY spectra:

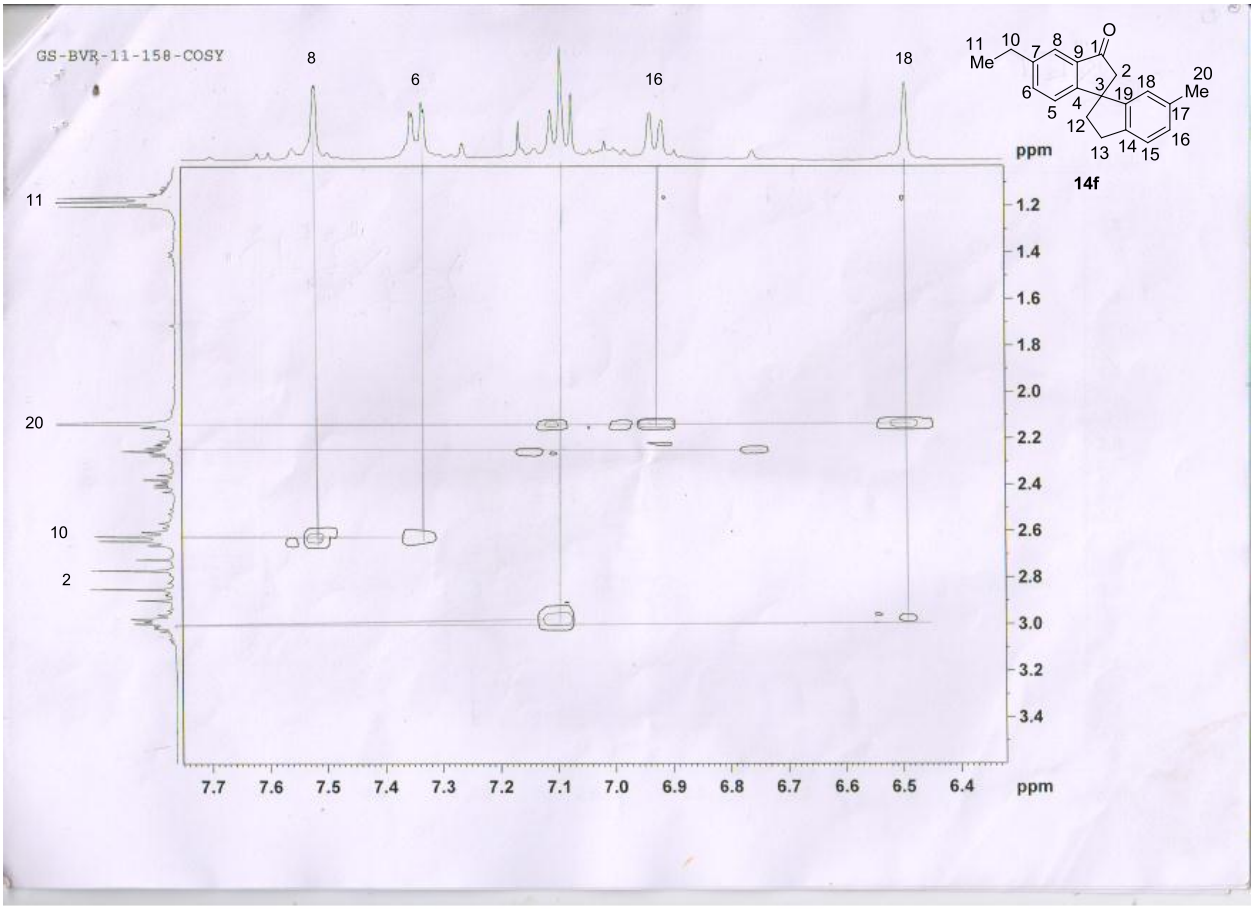


Figure II.13: COSY-NMR (400 MHz) spectrum of **14f** in $CDCl_3$

Analysis Based on COSY: COSY is a useful method for determining which signals arise from neighboring protons (usually up to four bonds). Correlations appear when there is spin-spin coupling between protons, but where there is no coupling, no correlation is expected to appear. The methylene signal at δH_{10}=2.72 ppm (Fig.II.13) is a quartet due to coupling with three protons of an adjacent methyl group with the coupling constant *J*=7.6 Hz. The methyl protons signal at δH_{11}=1.28 ppm is a triplet indicating due to two neighboring vicinal protons with the coupling constant *J*=7.6 Hz. Based on the COSY spectrum, we can see that methylene protons at δH_{10}=2.73 ppm are in correlation with aromatic protons (δH_8=7.62 ppm, s; and δH_6=7.44 ppm, dd). Also, it was observed that the protons at δH_{20}=2.23 ppm were in strong correlation between aromatic protons at (δH_{18}=6.60 ppm, s; and δH_{16}=7.03 ppm d).

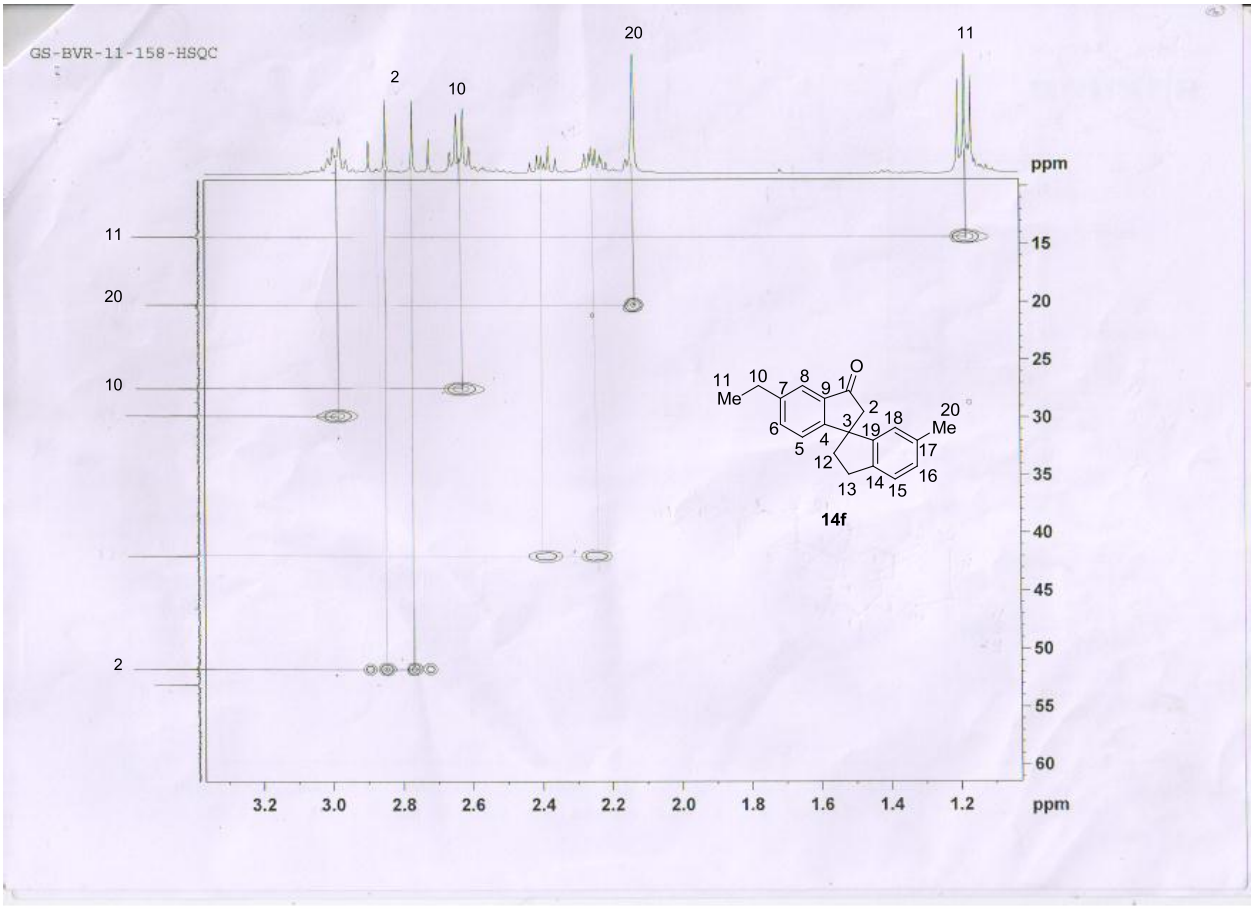


Figure II.14: HSQC-NMR (400 MHz) spectrum of **14f** in $CDCl_3$

Analysis Based on HSQC: The HSQC (Heteronuclear Single-Quantum Correlation) experiment permits to obtain a 2D heteronuclear chemical shift correlation map between directly-bonded ^{1}H and X-heteronuclear (^{13}C, ^{15}N etc.). This method provides crucial information about which proton connected to which carbon. The δC_{20}=21.3 ppm carbon correlates with protons δH_{20}=2.24 ppm. Whereas, δC_{11}=15.4 ppm carbon has strong correlation with protons δH_{11}=1.28 ppm. Also, δC_{10}=28.5 ppm carbon shows strong correlation with protons δH_{11}=2.74 ppm and δC_{2}=52.8 ppm correlates with the protons δH_{2}=2.95 ppm.

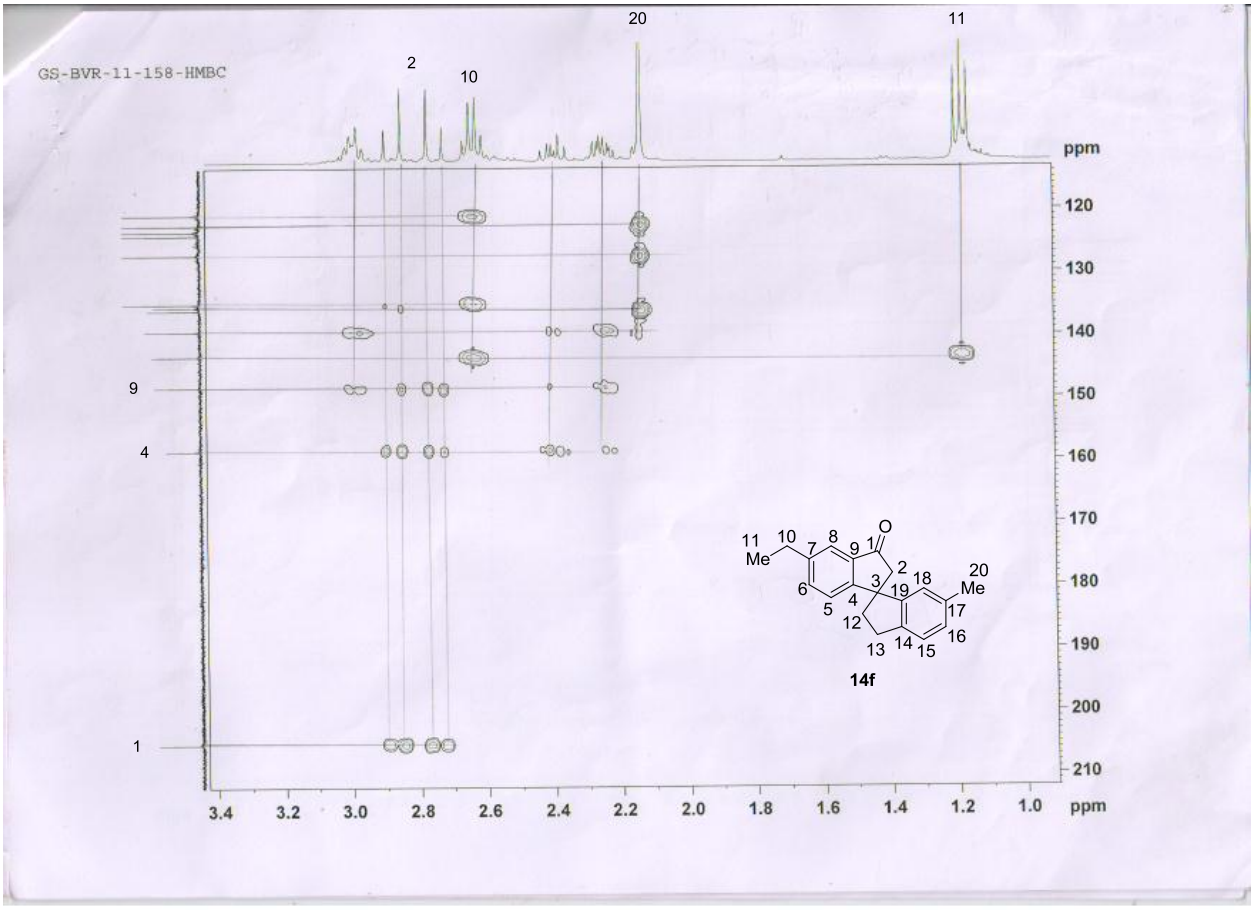


Figure II.15: HMBC-NMR (400 MHz) spectrum of **14f** in $CDCl_3$

Analysis Based on HMBC: The HMBC (Heteronuclear Multiple Bond Correlation) experiment gives correlations between carbons and protons that are separated by two, three and sometimes in conjugated systems distanced by four bonds. While direct one-bond correlations are suppressed. In HMBC spectrum, the H_2 protons (δH_2=2.95, d, *J*=18.9 Hz) exhibited cross peak with δC_1=206.1 ppm, which is suggestive that the H_2 protons connected C_2-carbon. Also, the same H_2 protons exhibited cross peaks with δC_4=159.4 and δC_9=149.2 carbons. The methylene protons (H_{10}) exhibited cross peaks with δC_7=144.2, δC_8=135.8 and δC_6=121.7 ppm carbon atoms. The protons of H_{20} exhibited cross peaks with δC_{17}=136.3, δC_{18}=128.1 and δC_{16}=123.4 ppm carbons.

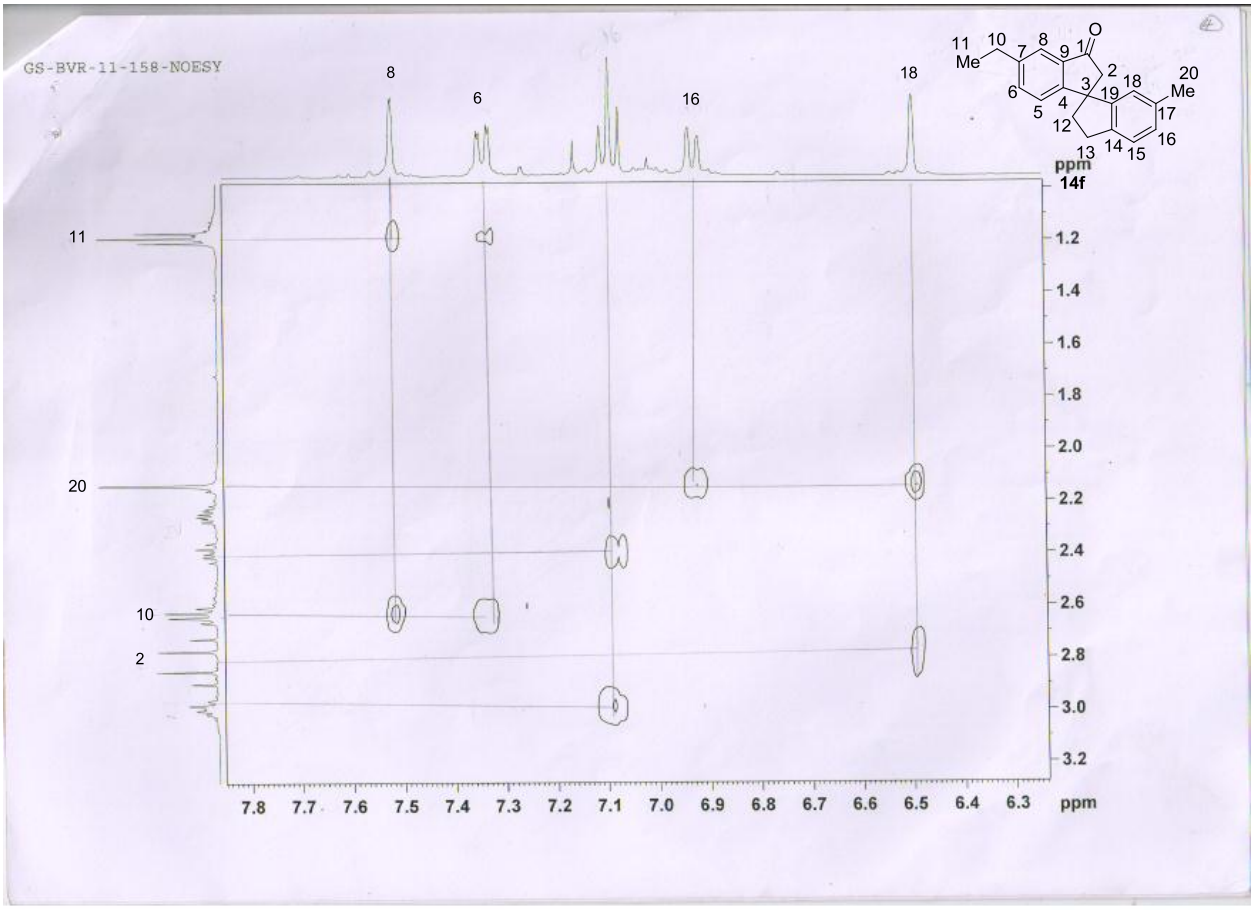


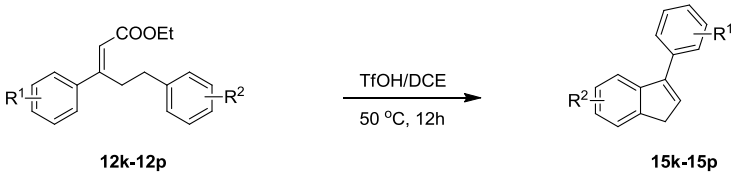
Figure II.16: NOESY-NMR (400 MHz) spectrum of **14f** in $CDCl_3$

Based on NOESY: which is useful for determining which signals arise from protons that are close to each other in space even if they are not bonded. From this NOESY spectrum, we can see that methyl protons (H_{11}) has strong correlation with aromatic protons (H_8 & H_6). The methylene protons (H_{10}) shows correlation with (H_8 & H_6). The methyl protons (H_{20}) have strong correlation with aromatic protons (H_{18} & H_{16}). Also, the H_2 protons are strongly correlated with aromatic proton H_{18}. Therefore, based on all the above 2D-NMR analysis, the chemical structures of **14** were further unambiguously confirmed.

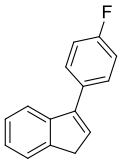
Surprisingly, when β-aryl group has electron deactivating groups such as fluoro, chloro and bromo substitutents, the reaction took different mechanistic path and gave aryl-indenes **15** as the final products (Table II.8). This may be due to the low reactivity of the β-aryl moiety due to

which it would not prefer acylation, but would rather allow the fragmentation of the ester group followed by internal rearrangement.

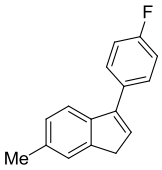
Table II.8: Synthesis of indenes **15a-15p** via intramolecular acylation from pendant β-aryl α,β-unsaturated esters **12k-12p**.[a,b]



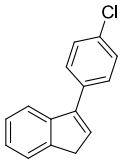
12k-12p **15k-15p**



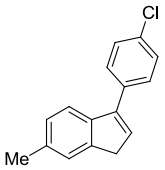
15k (68%)



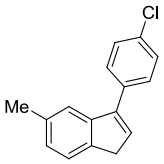
15l (70%)



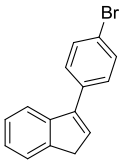
15m (76%)



15n (78%)



15o (75%)



15p (77%)

[a]All reactions were carried out on 0.25 mmol scale of **12**. [b]Yields of chromatographically pure products **15**.

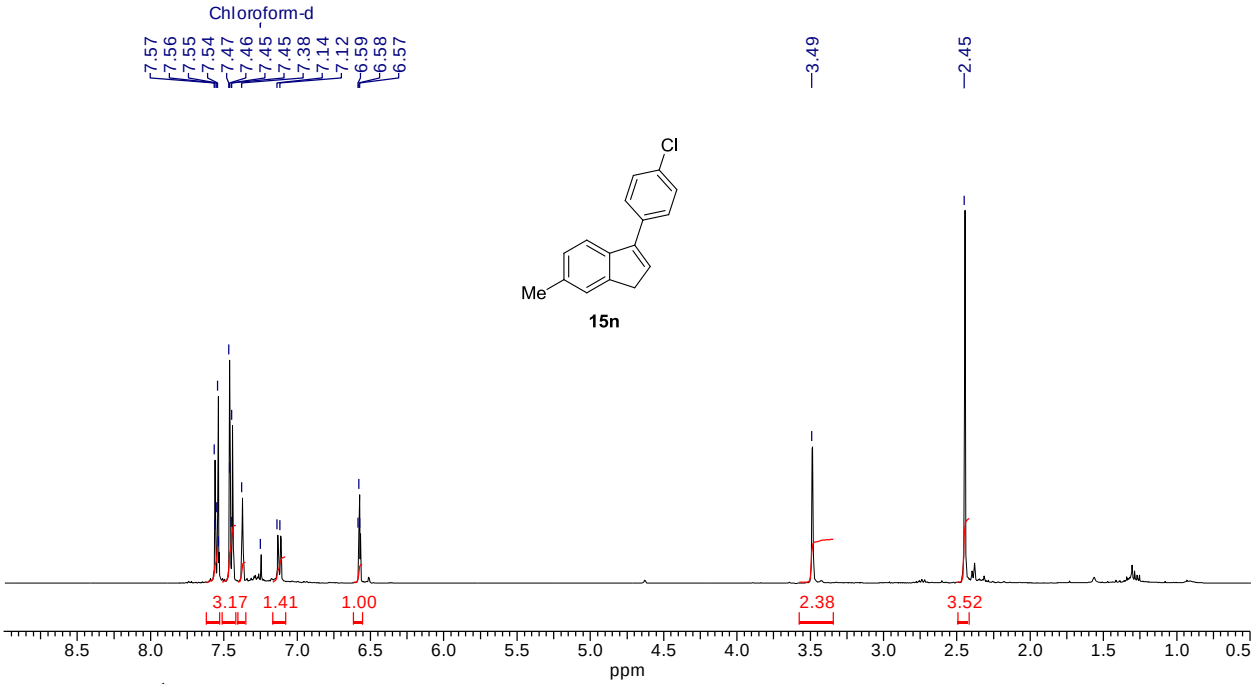


Figure II.17: ^{1}H-NMR (400 MHz) spectrum of **15n** in $CDCl_3$

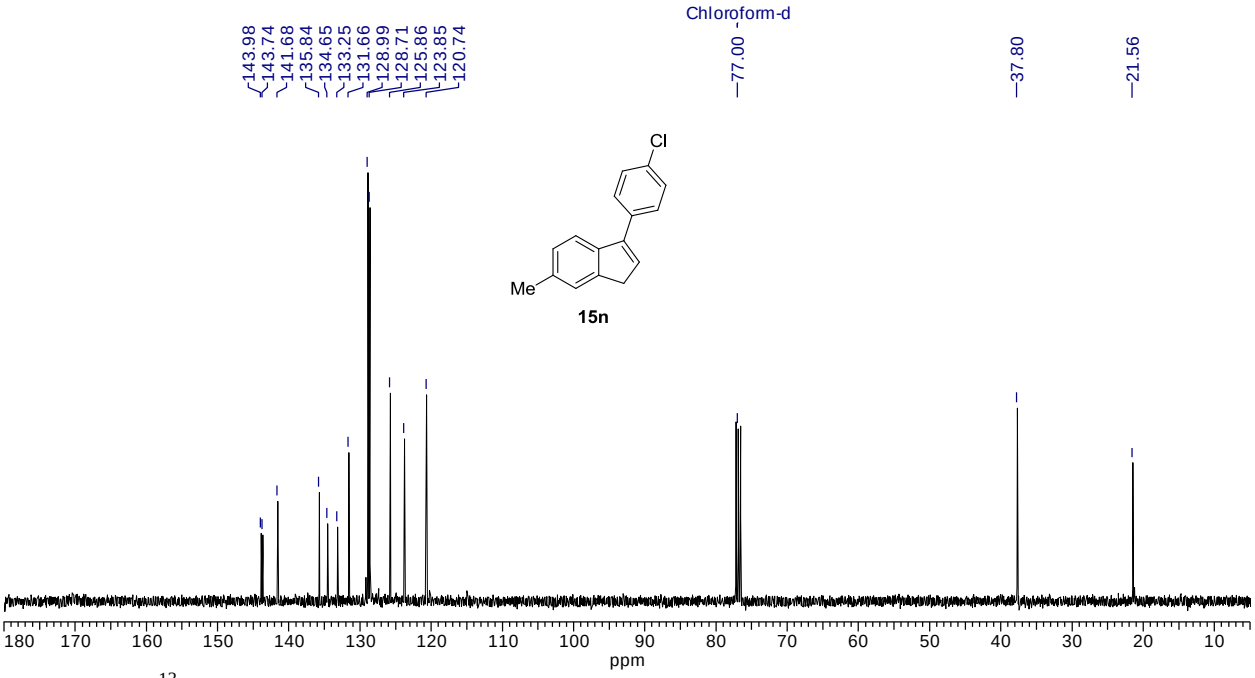


Figure II.18: ^{13}C-NMR (100 MHz) spectrum of **15n** in $CDCl_3$

The structure of 3-(4-chlorophenyl)-6-methyl-1*H*-indene **15n** was confirmed from its spectral data. IR spectra shows the presence of strong absorption band at 1487 cm^{-1} due to C=C stretching. In the ^{1}H-NMR spectrum (Figure II.17), presence of one multiplet at δ 7.59–7.53 due

to two aromatic protons, presence of one multiplet at δ 7.49–7.42 due to three aromatic protons, presence of one singlet at δ 7.38 due to one aromatic proton, presence of one doublet at δ 7.14 (*J*=8.3 Hz) due to one aromatic proton, presence of one triplet at δ 6.58 (*J*=2.0 Hz) due to one olefinic proton, presence of one doublet at δ 3.49 (*J*=2.0 Hz) due to two protons of methylene group, presence of one singlet at δ 2.45 due to three protons of one aromatic methyl group, established the structure of indene **15n**. In 14 lines ^{13}C-NMR spectrum (Figure II.18), six quaternary carbons resonances at δ 144.0, 143.7, 141.7, 135.8, 134.6 and 133.3 due to five aromatic and one olefinic carbons, seven aromatic methine carbons at δ 131.7, 129.0 (2C), 128.7 (2C), 125.9 and 123.9, one olefinic methine carbon at δ 120.7, one methylene carbon at δ 37.8, presence of one aromatic methyl carbon at δ 21.6 ppm, confirmed the structure of indene **15n**. Presence of the $[M+H]^+$ peak at m/z $[C_{16}H_{13}Cl]^+$=241.0787 in the mass spectrum further established the structure of indene **15n**.

In addition to the ^{1}H, ^{13}C NMR studies, the chemical structures of spiro-tetracyclic ketones **15** were confirmed by 2D-NMR analysis such as COSY, HSQC, HMBC and NOESY spectra:

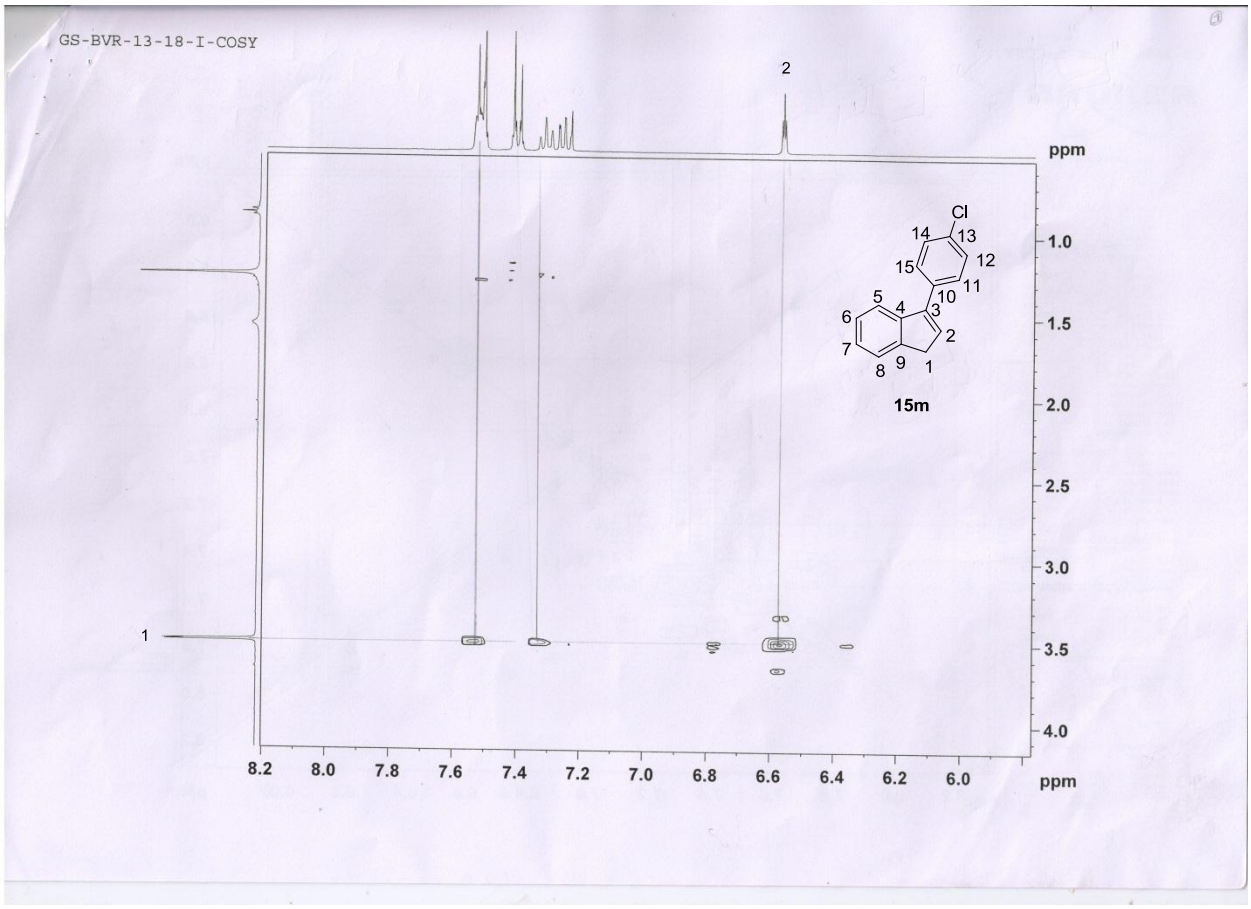


Figure II.19: COSY-NMR (400 MHz) spectrum of **15m** in $CDCl_3$

Analysis Based on COSY: With ^{1}H-NMR the methylene protons signal at δH_1=3.50 ppm (Fig.II.19) appears to be a doublet resulting from one proton on adjacent carbon with smaller coupling constant *J*=2.2 Hz. The olefin proton signal at δH_2=6.57 ppm is a triplet indicating two neighboring proton with small coupling constant *J* = 2.2 Hz connected to the adjacent carbon atom. This is in very good agreement that in cyclopentenes the couplings of an adjacent CH_2 group to the vinyl hydrogens is typically around ^3J = 2.1 Hz. Based on the COSY spectrum, we can see that methylene protons (δH_1=3.50 ppm, d) showed strong correlation with one olefin proton (δH_2=6.56 ppm, t). Also, the methylene protons at δH_1=3.50 ppm have engaged in correlation with aromatic proton (H_8). Although, it is not very clear, there might be a correlation between H_1 protons and the aromatic protons (H_5, H_{11} & H_{15}).

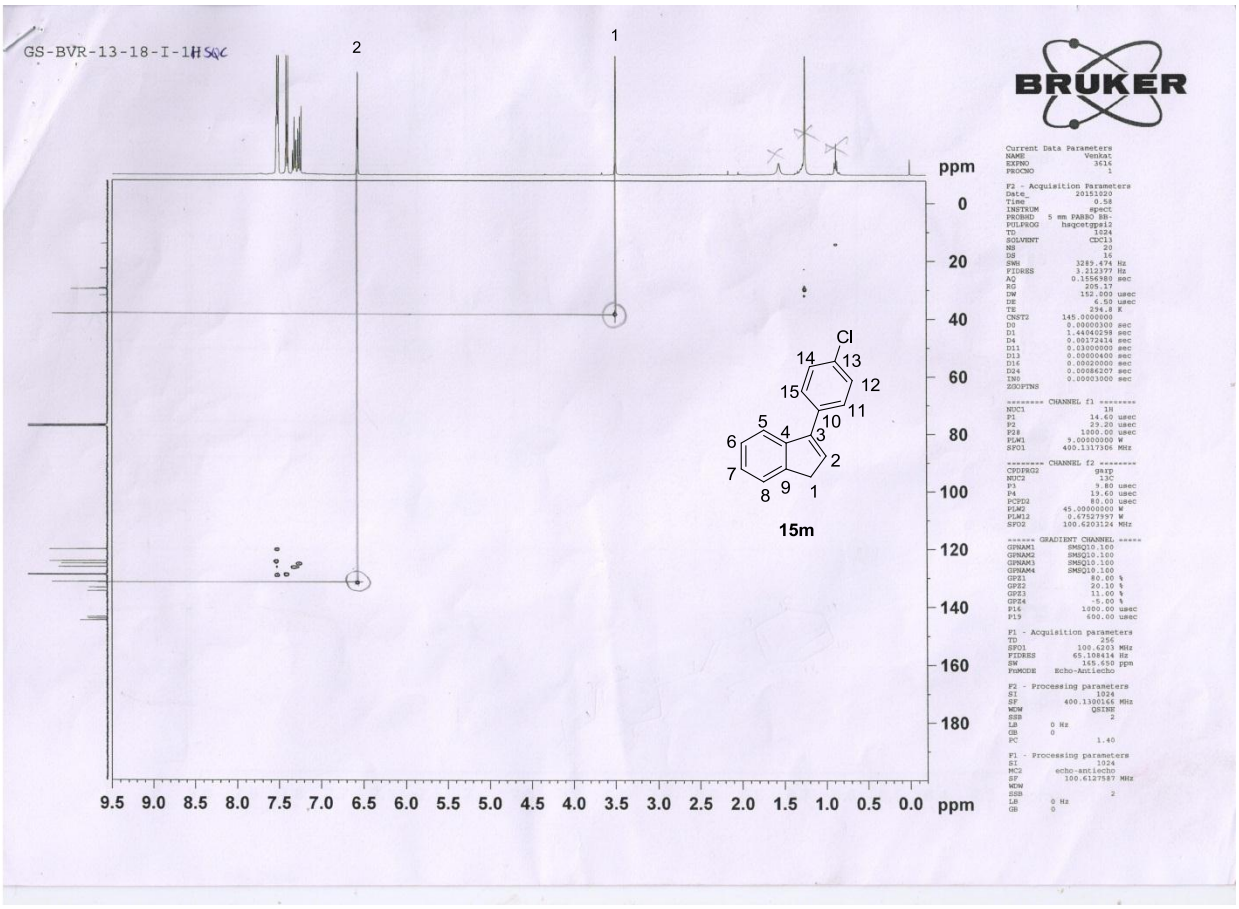


Figure II.20: HSQC-NMR (400 MHz) spectrum of **15m** in $CDCl_3$

Analysis Based on HSQC: This spectral analysis gave crucial information about which proton connected which carbon atom of the compound. Aaccording to the HSQC analysis, the C_2-carbon (δC_2=131.4 ppm) correlated well with H_2 olefinic proton with chemical shift δH_2=6.56 ppm. Similarly, the C_1 carbon with chemical shift δC_1=38.25 ppm has strong correlation with H_1 methylene protons (δH_1=3.50 ppm).

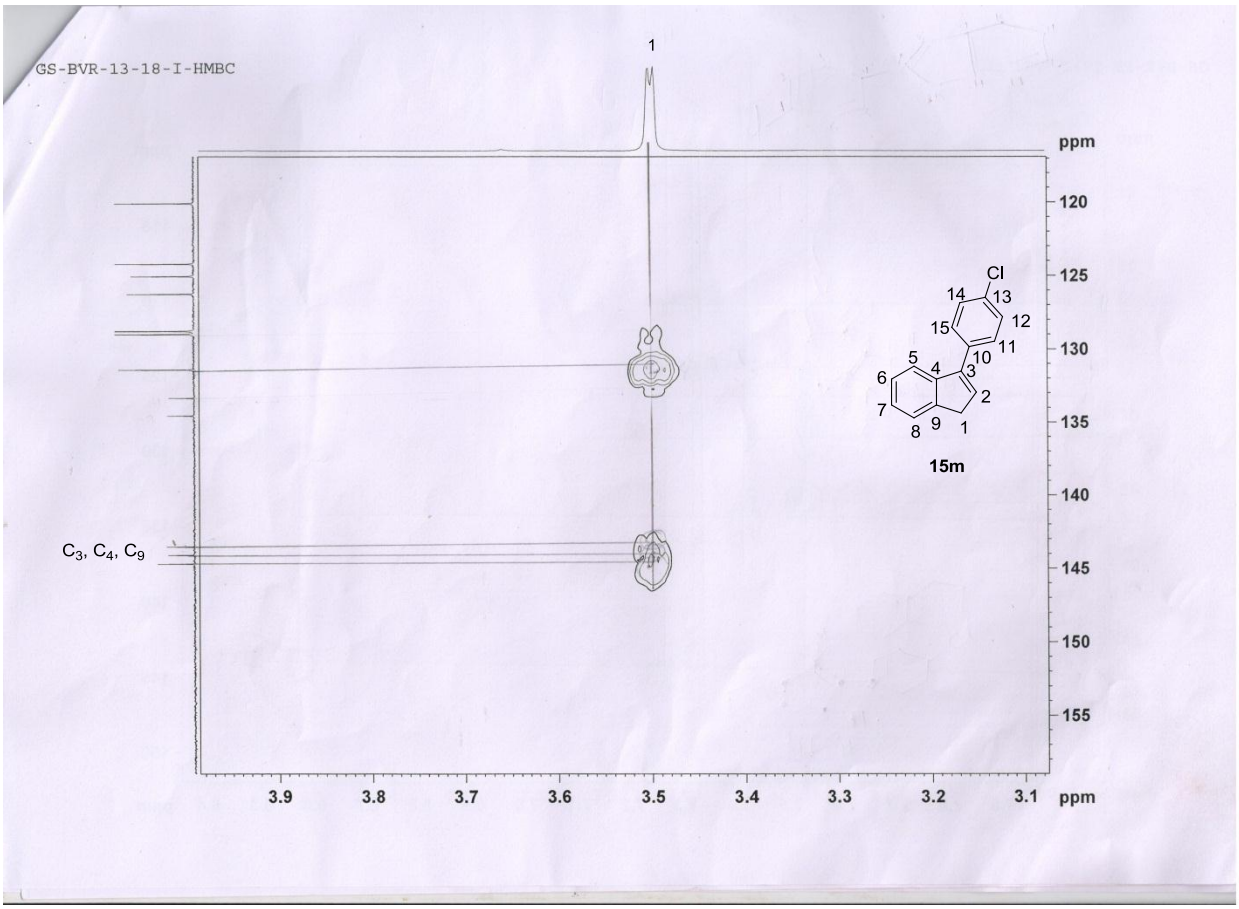


Figure II.21: HMBC-NMR (400 MHz) spectrum of **15m** in $CDCl_3$

Analysis Based on HMBC: In this HMBC spectrum, the H_1 protons (δH_1=3.50, d, J = 2.3 Hz) exhibits a cross peak with δC_2=131.4 ppm. While the H_1 protons connected to C_1-carbon shows cross peaks with δC_3=143.6 ppm, δC_4=144.1 ppm and δC_9=144.7 ppm.

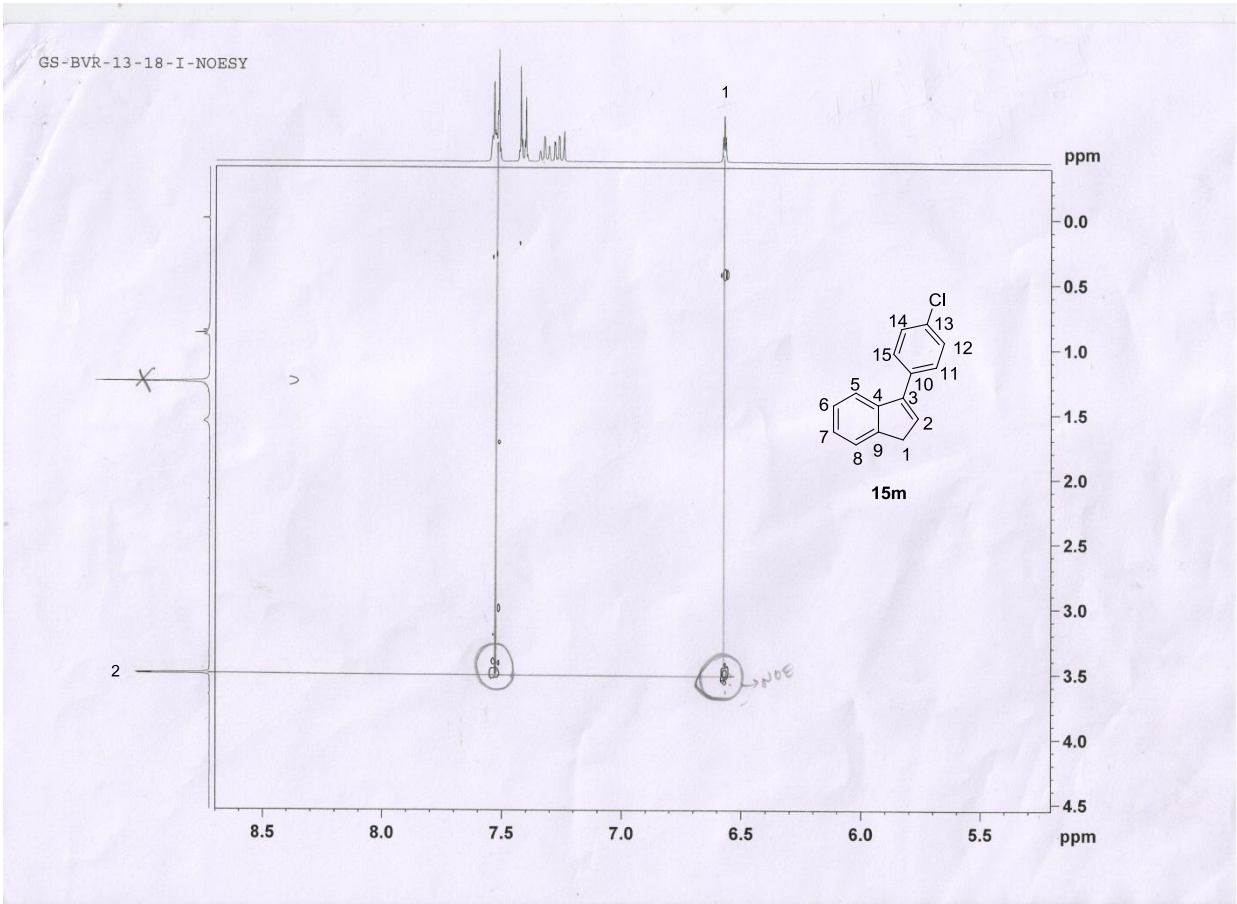


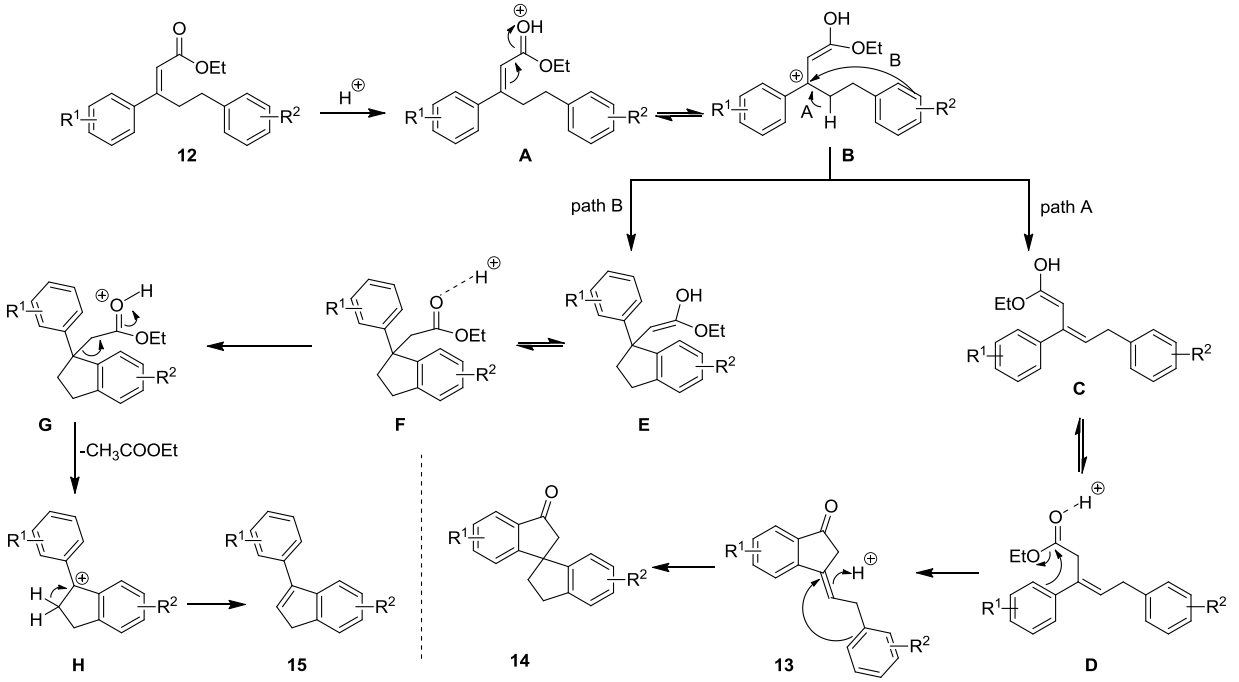
Figure II.22: NOESY-NMR (400 MHz) spectrum of **15m** in $CDCl_3$

Based on NOESY: This spectrum furnished some useful information that which signal arise from protons that are close to each other in space even if they are not bonded. It is noticed that methylene protons (δH_1=3.50 ppm) have strong correlation with olefin proton (H_2) with chemical shift δH_2=6.56 ppm. Also, the methylene protons at δH_1=3.50 ppm might have some correlation with aromatic protons (H_5, H_8, H_{11} & H_{15}). Therefore, based on all the above 2D-NMR analysis, the chemical structures of **15** were further unambiguously confirmed.

A plausible reaction mechanism for the formation of spirocyclic indanones **14** and indenes **15** is shown in Scheme II.27. Initially, the protic acid could activate and isomerize the ketone group of the esters **12** to yield the equilibrating structures **A, B**. Deprotonation of intermediate **B** would be form resonance structures **C** and **D.** Intramolecular Friedel-Crafts acylation of **D** and rearomatization leads to the indenones **13**. Subsequent intramolecular Friedel-Crafts alkylation of indenones **13** with second internal arene affords spirocyclic indanones **14**.

On the other hand, when the β-aryl moiety is relatively electron deficient than that of pedant aryl group, the pedant arene might preferentially reacts through intramolecular Friedel-Crafts alkylation and gives indane esters **E** from **A** or **B**. Since, **E** resonance with **F** the arene is not electron rich enough to participate in intramolecular Friedel-Crafts acylation, it rather undergoes acid mediated fragmentation to give the carbocation intermediates **G** via the liberation of ethyl acetate. Now, 1,2-hydride shift of **G** leads to the formation of indene **15**. via the intermediates **G** and **H**, respectively.

Scheme II.27: Plausible reaction mechanism for the formation of spirocyclic indanones **14** and indenes **15**.

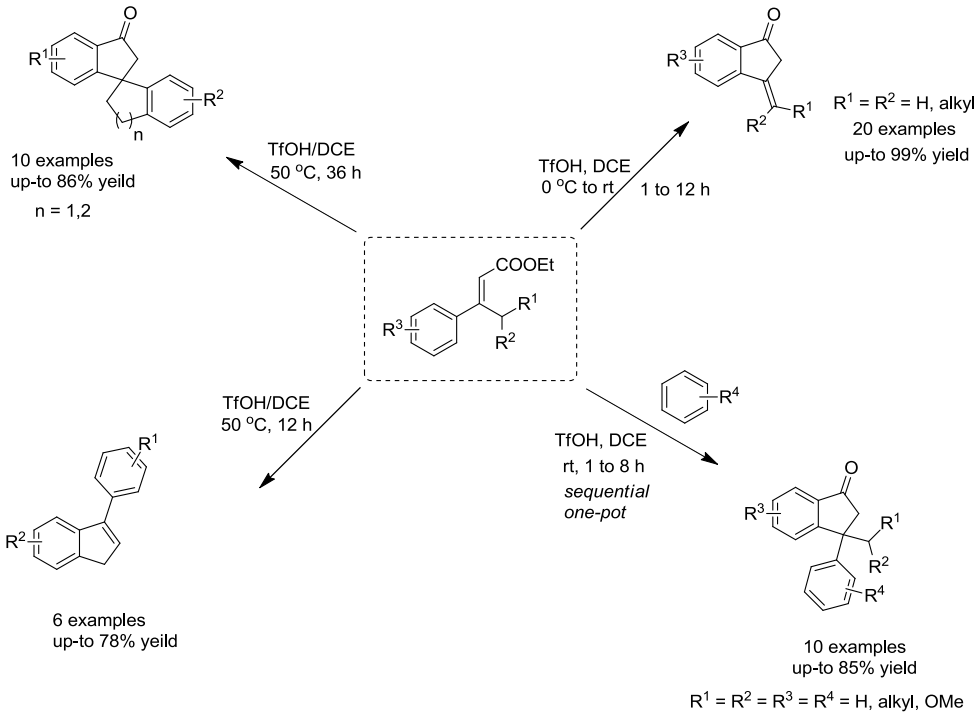


Scheme II.27

II.4. CONCLUSIONS:

We have disclosed an efficient method for the synthesis of indenones via intramolecular Friedel-Crafts acylation and double bond isomerization of cinnamic acid esters. Further, the protocol was extended to the synthesis of indanones by treatment of in-situ generated indenones with external arenes. Significantly, the present method limits the external arene only to the Friedel-Crafts alkylation which was not possible in our previous protocol for the synthesis of

indanones. In addition, the strategy was successfully applied to the synthesis of novel spiro-tetracyclic indanones using pendant β-aryl α,β-unsaturated esters. On the other hand, the reaction with relatively electron poor β-aryl moiety of the α,β-unsaturated esters, furnished indenes as end products.



Scheme II.28

II.5 EXPERIMENTAL SECTION:

Table II.9: Compounds (**4a**, **4d**, **4f**),[20] (**4b, 4c, 4e)**,[37] **4g**[38] and **4l**[39] are known in the literature.

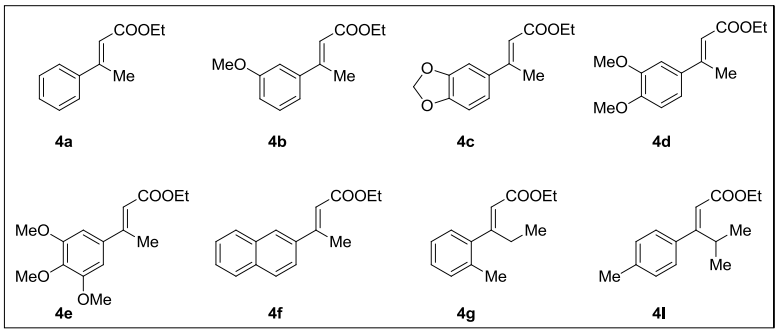


Table II.10: Compounds (**5a**, **5c**, **5d**)[13] are known in the literature.

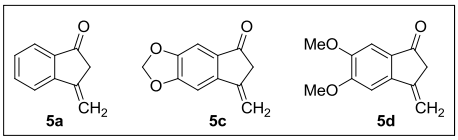


Table II.11: compounds (**7a**, **7e**, **7i**)[20] are known in the literature.

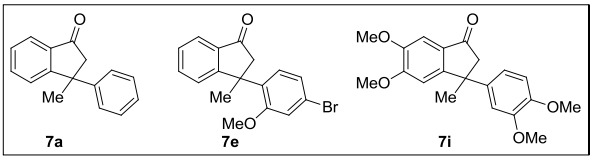


Table II.12: List of arenes **6** that are employed for the preparation of indanones **7**.

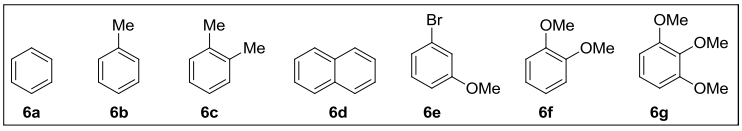


Table II.13: compounds (**14a**, **14d**, **14i**)[36] are known in the literature.

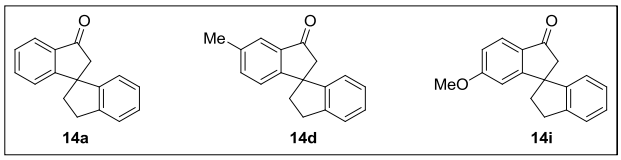
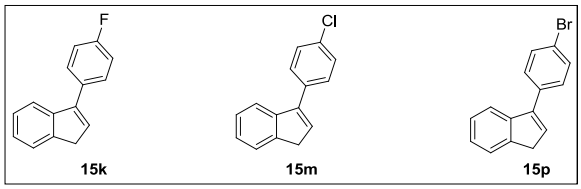
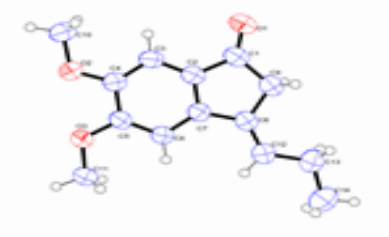


Table II.14: compounds (**15k**, **15m**, **15p**)[40] are known in the literature.



X-Ray crystal structure data for **5m**: (CCDC 1408325)



Operator	**K. Ravikumar**
Instrument	**Oxford SuperNova**
Identification code	exp_3546-9-217
Empirical formula	$C_{13}H_{12}O_3$
Formula weight	232.28
Temperature/K	298
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.4655(6)
b/Å	15.5172(9)
c/Å	8.5918(7)
α/°	90
β/°	103.799(8)
γ/°	90
Volume/Å^3	1225.52(15)
Z	4
ρ_{calc}g/cm^3	1.2588
μ/mm^{-1}	0.712
F(000)	497.6
Crystal size/mm^3	0.18 × 0.14 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.62 to 142.12
Index ranges	$-8 \le h \le 11$, $-16 \le k \le 18$, $-7 \le l \le 10$
Reflections collected	4389
Independent reflections	2330 [R_{int} = 0.0253, R_{sigma} = 0.0333]
Data/restraints/parameters	2330/0/164
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1498

GP-1 (General Procedure for Witting-Horner-Wadsworth-Emmons reaction of ketones):

To an oven dried round bottom flask under nitrogen atmosphere charged with 60% NaH (240 mg, 6.0 mmol), THF (10 mL) and cooled to ice temperature. Then TEPA (1.8 ml, 9.0 mmol) was added drop-wise until the solution becomes a clear solution. To the resulted ylide, ketone **3** (360–714 mg, 3.0 mmol) was added, the reaction mixture was stirred at 0 °C for 30 minutes and then heated at 60 °C for 6 to 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NH_4Cl and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the ester **4** (72–96%).

GP-2 (General Procedure for Friedel-Crafts Intramolecular Acylation of Cinnamic acid esters):

To an oven dried Schlenk tube under nitrogen atmosphere, were added ester **4** (95–154 mg, 0.5 mmol) and DCE (2 mL), followed by the addition of triflic acid (0.1–1 mL, 1.5–12 mmol). The resultant reaction mixture was stirred at 0 °C-rt for 1–12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indenone **5** (52–99%).

GP-3 (General Procedure for indanones):

To an oven dried Schlenk tube, were charged with ester **4** (95–140 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1–1 mL, 1.5–12 mmol). The resulted reaction mixture was stirred at rt for 1–8 h. Progress of the reaction was monitored by TLC until the reaction was completed. Then external arene **6** (0.75–6 mmol), was added and continued to stir the reaction mixture for additional 1–12 h at rt. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated

NaCl solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished indanone **7** (70–85%).

GP-4 (General Procedure for Witting-Horner-Wadsworth-Emmons reaction of 1,3-diphenylpropan-1-ones):

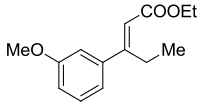
To an oven dried round bottom flask under nitrogen atmosphere charged with 60% NaH (120 mg, 3.0 mmol), THF (10 mL) and cooled to ice temperature. Then TEPA (0.9 ml, 4.5 mmol) was added drop-wise until the solution becomes a clear solution. To the resulted ylide, 1,3-diphenylpropan-1-ones **11** (315–399 mg, 1.5 mmol) was added, the reaction mixture was stirred at 0 °C for 30 minutes and then heated at 60 °C for 6 to 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NH_4Cl and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the pendant β-aryl α,β-unsaturated ester **12** (84–96 %).

GP-5 (General Procedure for Spiro cyclic indanones):

To an oven dried Schlenk tube under nitrogen atmosphere, were added pendant β-aryl α,β-unsaturated ester **12** (70–84 mg, 0.25 mmol) and DCE (2 mL), followed by the addition of triflic acid (0.1 mL, 1.5 mmol). The resultant reaction mixture was stirred at 50 °C for 30 to 36 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the Spiro cyclic indanone **14** (76–90%).

GP-6 (General Procedure for indenes):

To an oven dried Schlenk tube under nitrogen atmosphere, were added pendant β-aryl α,β-unsaturated ester **12** (95–154 mg, 0.25 mmol) and DCE (2 mL), followed by the addition of triflic acid (0.1 mL, 1.5 mmol). The resultant reaction mixture was stirred at 50 °C for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indenes **15** (68–78%).



4h

Ethyl (2*E*)-3-(3-methoxyphenyl) pent-2-enoate (4h):

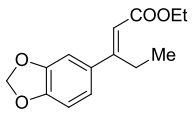
GP-1 was followed to **3h** (492 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the ester **4h** (598 mg, 85 %) as pale yellow viscous liquid. [TLC control R_f(**3h**)=0.40, R_f(**4h**)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2981, 2920, 1706 (C=O), 1636, 1449, 1309, 1268, 1162, 1036, 978, 766, 711 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.25 (dd, 1H, *J*=7.8 and 7.8 Hz, ArH), 6.85 (dd, 1H, *J*=7.8 and 2.4 Hz, ArH), 6.74 (dd, 1H, *J*=7.8 and 2.4 Hz, ArH), 6.68 (dd, 1H, *J*=2.4 and 1.5 Hz, ArH), 5.84 (s, 1H, ArC=C*H*), 3.97 (q, 2H, *J*=6.8 Hz, O*CH*$_2$CH$_3$), 3.79 (s, 3H, ArOCH$_3$), 2.45 (q, 2H, *J*=7.3 Hz, CH$_2$), 1.07 (t, 3H, *J*=7.3 Hz, CH$_3$), 1.05 (t, 3H, *J*=7.3 Hz, CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.1 (s, C=O), 160.6 (s, *C*=CH), 159.1 (s, ArC), 141.8 (s, ArC), 128.8 (d, CH), 119.4 (d, CH), 116.3 (d, CH), 112.8 (d, CH), 112.6 (d, CH), 59.7 (t, CH$_2$), 55.1 (q, ArOCH$_3$), 33.2 (t, CH$_2$), 13.9 (q, CH$_3$), 12.0 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{14}H_{22}NO_3]^+$=$[M+NH_4]^+$: 252.1594; found: 252.1594.



4i

Ethyl (2*E*)-3-(1, 3-benzodioxol-5-yl) pent-2-enoate (4i):

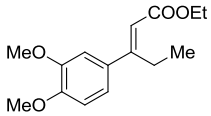
GP-1 was followed to **3i** (534 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 88:12) furnished the ester **4i** (681 mg, 92 %) as pale yellow viscous liquid. [TLC control R_f(**3i**)=0.40, R_f(**4i**)=0.60, (petroleum ether/ethyl acetate 88:12, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2963, 2924, 1708 (C=O), 1604, 1488, 1438, 1244, 1221, 1037, 932, 857, 807 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=6.95 (ddd, 2H, *J*=8.3, 7.8 and 2.0 Hz, ArH), 6.85 (d, 1H, *J*=8.3 Hz, ArH), 5.97 (s, 2H, O-CH_2-O), 5.94 (s, 1H, C=C*H*), 4.19 (q, 2H, *J*=6.8 Hz, OC*H*$_2$$CH_3$), 3.05 (q, 2H, *J*=7.8 Hz, CH_2), 1.29 (t, 3H, *J*=6.8 Hz, CH_3), 1.06 (t, 3H, *J*=7.8 Hz, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 161.4 (s, *C*=CH), 148.3 (s, ArC), 147.9 (s, ArC), 135.1 (s, ArC), 120.7 (d, CH), 115.6 (d, CH), 108.2 (d, CH), 107.0 (d, CH), 101.3 (t, O-CH_2-O), 59.7 (t, CH_2), 24.3 (t, CH_2), 14.3 (q, CH_3), 13.6 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $C_{14}H_{17}O_4]^+$=$[M+H]^+$: 249.1121; found: 249.1122.



4j

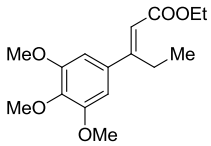
Ethyl (2*E*)-3-(3,4-dimethoxyphenyl) pent-2-enoate (4j):

GP-1 was followed to **3j** (582 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 92:8 to 84:16) furnished the ester **4j** (707 mg, 89%) as pale yellow viscous liquid. [TLC control R_f(**3j**)=0.45, R_f(4**j**)=0.60, (petroleum ether/ethyl acetate 84:16, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2982, 1709 (C=O), 1627, 1444, 1349, 1272, 1161, 1039, 872, 766 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.07 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.97 (d, 1H, *J*=8.3 Hz, ArH), 6.86 (d, 1H, *J*=2.5 Hz, ArH), 5.99 (s, 1H, C=C*H*), 4.21 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 3.90 (s, 3H, ArOCH$_3$), 3.89 (s, 3H, ArOCH$_3$), 3.09 (q, 2H, *J*=7.3 Hz, CH$_2$), 1.30 (t, 3H, *J*=6.8 Hz, CH$_3$), 1.08 (t, 3H, *J*=7.8 Hz, CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.5 (s, C=O), 161.7 (s, *C*=CH), 149.9 (s, ArC), 148.8 (s, ArC), 137.5 (s, ArC), 119.5 (d, CH), 115.2 (d, CH), 110.8 (d, CH), 109.7 (d, CH), 59.7 (t, CH$_2$), 55.9 (q, 2C, 2 × ArOCH$_3$), 14.3 (t, CH$_2$), 13.8 (q, CH$_3$) ppm.



4k

Ethyl (2*E*)-3-(3,4,5-trimethoxyphenyl)pent-2-enoate (4k):

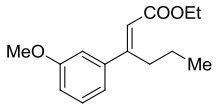
GP-1 was followed to **3k** (672 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 84:16) furnished the ester **4k** (814 mg, 92 %) as pale yellow viscous liquid. [TLC control R_f(**3k**)=0.40, R_f(**4k**)=0.65, (petroleum ether/ethyl acetate 84:16, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2851, 1705 (C=O), 1601, 1450, 1316, 1261, 1175, 750 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=6.64 (s, 2H, ArH), 5.97 (s, 1H, C=C*H*), 4.21 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 3.88 (s, 6H, 2 × ArOCH$_3$), 3.86 (s, 3H, ArOCH$_3$), 3.07 (q, 2H, *J*=7.3 Hz, CH$_2$), 1.31 (t, 3H, *J*=7.3 Hz, CH$_3$), 1.08 (t, 3H, *J*=7.3 Hz, CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 162.0 (s, *C*=CH), 153.1 (s, 2C, ArC), 138.7 (s, ArC), 136.8 (s, ArC), 116.3 (d, 2C, ArCH), 103.9 (d, C=*C*H), 60.9 (t, CH$_2$), 59.9 (q, ArOCH$_3$), 56.2 (q, 2C, 2 × ArOCH$_3$), 24.5 (t, CH$_2$), 14.3 (q, CH$_3$), 13.6 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{26}NO_5]^+$=$[M+NH_4]^+$: 312.1805; found: 312.1807.



4l

Ethyl (2*E*)-3-(3-methoxyphenyl)hex-2-enoate (4l):

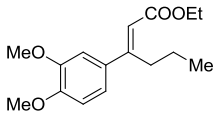
GP-1 was followed to **3l** (534 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the ester **4l** (665 mg, 89%) as pale yellow viscous liquid. [TLC control R_f(**3l**)=0.50, R_f(**4l**)=0.65, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2933, 1710 (C=O), 1623, 1577, 1463, 1206, 1153, 1039, 866, 780, 696 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.26 (dd, 1H, *J*=7.8 and 7.8 Hz, ArH), 7.01 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 6.94 (dd, 1H, *J*=2.5 and 2.0 Hz, ArH), 6.89 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.02 (s, 1H, C=C*H*), 4.19 (q, 2H, *J*=6.8 Hz, OCH_2CH$_3$), 3.81 (s, 3H, ArOCH$_3$), 3.05 (t, 2H, *J*=7.3 Hz, CH$_2$), 1.50–1.36 (m, 2H, CH$_2$), 1.30 (t, 3H, *J*=6.8 Hz, CH$_3$), 0.92 (t, 3H, *J*=7.3 Hz, CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.5 (s, C=O), 160.4 (s, *C*=CH), 159.6 (s, ArC), 143.0 (s, ArC), 129.4 (d, CH), 119.1 (d, CH), 117.6 (d, CH), 114.0 (d, CH), 112.5 (d, CH), 59.8 (t, CH$_2$), 55.2 (q, ArOCH$_3$), 32.9 (t, CH$_2$), 22.2 (t, CH$_2$), 14.3 (q, CH$_3$), 14.0 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{15}H_{21}O_3]^+$=$[M+H]^+$: 249.1485; found: 249.1489.



4m

Ethyl (2*E*)-3-(3,4-dimethoxyphenyl)hex-2-enoate (4m):

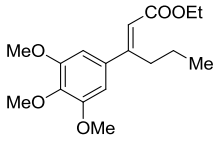
GP-1 was followed to **3m** (624 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 84:16) furnished the ester **4m** (756 mg, 91 %) as pale yellow viscous liquid. [TLC control R_f(**3m**)=0.50, R_f(**4m**)=0.65, (petroleum ether/ethyl acetate 84:16, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2959, 2933, 1707 (C=O), 1618, 1598, 1514, 1462, 1251, 1235, 1143, 1024, 852, 807, 767 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.04 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.95 (d, 1H, *J*= 2.0 Hz, ArH), 6.84 (d, 1H, *J*=8.3 Hz, ArH), 6.00 (s, 1H, C=C*H*), 4.19 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.89 (s, 3H, ArOCH$_3$), 3.88 (s, 3H, ArOCH$_3$), 3.04 (t, 2H, *J*=7.3 Hz, CH$_2$), 1.54–1.40 (m, 2H, CH$_2$), 1.29 (t, 3H, *J*=7.3 Hz, CH$_3$), 0.92 (t, 3H, *J*=7.3 Hz, CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.6 (s, C=O), 160.2 (s, *C*=CH), 149.8 (s, ArC), 148.8 (s, ArC), 133.8 (s, ArC), 119.5 (d, CH), 115.9 (d, CH), 110.8 (d, CH), 109.7 (d, CH), 59.7 (t, CH$_2$), 55.9 (q, 2C, ArOCH$_3$), 32.6 (t, CH$_2$), 22.5 (t, CH$_2$), 14.3 (q, CH$_3$), 14.1 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{23}O_4]^+$=$[M+H]^+$: 279.1591; found: 279.1591.



4n

Ethyl (2*E*)-3-(3,4,5-trimethoxyphenyl)hex-2-enoate (4n):

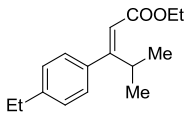
GP-1 was followed to **3n** (714 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished the ester **4n** (812 mg, 88 %) as pale yellow viscous liquid. [TLC control R_f(**3n**)=0.50, R_f(**4n**)=0.65, (petroleum ether/ethyl acetate 80:20, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2934, 1709 (C=O), 1620, 1578, 1505, 1453, 1412, 1239, 1151, 1125, 1005, 834, 736 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=6.61 (s, 2H, ArH), 5.97 (s, 1H, *C*=C*H*), 4.18 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.85 (s, 6H, 2 × ArOCH$_3$), 3.83 (s, 3H, ArOCH$_3$), 3.01 (t, 2H, *J*=7.3 Hz, CH$_2$), 1.51–1.36 (m, 2H, CH$_2$), 1.28 (t, 3H, *J*=7.3 Hz, CH$_3$), 0.91 (t, 3H, *J*=7.3 Hz, CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 160.6 (s, *C*=CH), 153.0 (s, 2C, ArC), 138.7 (s, ArC), 137.1 (s, ArC), 117.0 (d, 2C, ArCH), 103.9 (d, C=*C*H), 60.8 (q, ArOCH$_3$), 59.8 (t, CH$_2$), 56.1 (q, 2C, 2 × ArOCH$_3$), 32.9 (t, CH$_2$), 22.3 (t, CH$_2$), 14.3 (q, CH$_3$), 14.1 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{25}O_5]^+$=$[M+H]^+$: 309.1697; found: 309.1696.



4p

Ethyl (2*E*)-3-(4-ethylphenyl)-4-methylpent-2-enoate (4p):

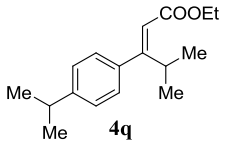
GP-1 was followed to **3p** (528 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished the ester **4p** (708 mg, 96 %) as pale yellow viscous liquid. [TLC control R_f(**3p**)=0.60, R_f(**4p**)=0.70, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 2851, 1697 (C=O), 1510, 1263, 1184, 1025, 829, 757 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.14 (dd, 4H, *J*=8.3 and 2.5 Hz, ArH), 5.70 (s, 1H, ArC=C*H*), 4.19 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 4.16–4.05 (m, 1H, CH), 2.66 (q, 2H, *J*=7.3 Hz, C*H*$_2$CH$_3$), 1.29 (t, 3H, *J*=6.8 Hz, CH$_3$), 1.24 (t, 3H, *J*=7.3 Hz, CH$_3$), 1.10 (d, 6H, *J*=6.8 Hz, CH$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=167.2 (s, C=O), 143.6 (s, *C*=CH), 138.1 (s, ArC), 138.3 (s, ArC), 127.6 (d, 2C, CH), 127.2 (d, 2C, CH), 118.2 (d, CH), 59.8 (t, CH$_2$), 29.6 (d, CH), 28.5 (t, CH$_2$), 21.4 (q, 2C, CH$_3$), 15.4 (q, CH$_3$), 14.3 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{23}O_2]^+$=$[M+H]^+$: 247.1693; found: 247.1685.



4q

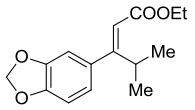
Ethyl (2*E*)-3-(4-isopropylphenyl)-4-methylpent-2-enoate (4q):

GP-1 was followed to **3q** (570 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the ester **4q** (643 mg, 93 %) as pale yellow viscous liquid. [TLC control R_f(**3q**)=0.55, R_f(**4q**)=0.65, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2854, 1714, 1456, 1282, 1252, 1172, 1108, 828 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.16 (dd, 2H, *J*=7.8 and 2.0 Hz, ArH), 7.03 (dd, 2H, *J*=8.3 and 2.0 Hz, ArH), 5.70 (s, 1H, CH), 4.19 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 2.95–2.85 (m, 1H, C*H*$_2$CH$_3$), 2.69–2.58 (m, 1H, C*H*$_2$CH$_3$), 1.29 (t, 3H, *J*=6.8 Hz, CH_3), 1.26 (d, 6H, *J*=6.8 Hz, CH_3), 1.08 (d, 6H, *J*=6.8 Hz, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=167.2 (s, C=O), 166.3 (s, *C*=CH), 148.2 (s, ArC), 138.2 (s, ArC), 127.6 (d, 2C, CH), 127.2 (d, 2C, CH), 118.2 (d, CH), 59.7 (t, CH_2), 37.2 (d, CH), 33.7 (d, CH), 23.9 (q, 2C, CH_3), 21.4 (q, 2C, CH_3), 14.3 (q, CH_3) ppm.



4r

Ethyl (2*E*)-3-(1,3-benzodioxol-5-yl)-4-methylpent-2-enoate (4r):

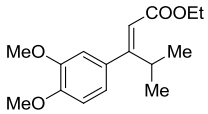
GP-1 was followed to **3r** (576 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished the ester **4r** (726 mg, 92 %) as pale yellow viscous liquid. [TLC control R_f(**3r**)=0.50, R_f(**4r**)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2962, 2925, 1713 (C=O), 1628, 1503, 1487, 1468, 1369, 1223, 1174, 1164, 1038, 936, 862, 811 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=6.74 (d, 1H, *J*=7.8 Hz, ArH), 6.70 (d, 1H, *J*=1.5 Hz ArH), 6.68 (dd, 1H, *J*=7.8 and 2.0 Hz, ArH), 5.95 (s, 2H, O-CH$_2$-O), 5.68 (s, 1H, C=C*H*), 4.18 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 4.13–3.99 (m, 1H, CH), 1.28 (t, 3H, *J*=7.3 Hz, CH_3), 1.08 (d, 6H, *J*=6.8 Hz, 2 × CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.6 (s, C=O), 166.2 (s, *C*=CH), 147.1 (s, ArC), 147.0 (s, ArC), 134.7 (s, ArC), 121.2 (d, CH), 118.4 (d, CH), 108.3 (d, CH), 107.7 (d, CH), 101.1 (t, O-CH$_2$-O), 59.8 (t, CH_2), 29.6 (d, CH), 21.4 (q, 2C, 2 × CH_3), 14.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{15}H_{19}O_4]^+$=$[M+H]^+$: 263.1278; found: 263.1274.



4s

Ethyl (2*E*)-3-(3,4-dimethoxyphenyl)-4-methylpent-2-enoate (4s):

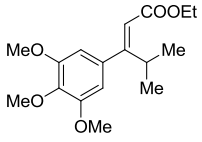
GP-1 was followed to **3s** (624 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 84:16) furnished the ester **4s** (693 mg, 72 %) as pale yellow viscous liquid. [TLC control R_f(**3s**)=0.50, R_f(**4s**)=0.60, (petroleum ether/ethyl acetate 84:16, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2961, 2927, 1713 (C=O), 1621, 1579, 1504, 1463, 1410, 1369, 1344, 1241, 1153, 1127, 1038, 1009, 879, 840, 826 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=6.80 (d, 1H, *J*=8.3 Hz, ArH), 6.78 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.73 (d, 1H, *J*=2.0 Hz, ArH), 5.71 (s, 1H, C=C*H*), 4.19 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 4.14–4.03 (m, 1H, CH), 3.87 (s, 3H, ArOCH$_3$), 3.86 (s, 3H, ArOCH$_3$), 1.29 (t, 3H, *J*=6.8 Hz, CH$_3$), 1.10 (d, 6H, *J*=6.9 Hz, 2 × CH$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=166.8 (s, C=O), 166.3 (s, *C*=CH), 148.6 (s, ArC), 148.1(s, ArC), 133.6 (s, ArC), 120.1 (d, CH), 118.2 (d, CH), 111.2 (d, CH), 110.4 (d, CH), 59.8 (t, CH$_2$), 55.9 (q, ArOCH$_3$), 55.8 (q, ArOCH$_3$), 29.6 (d, CH), 21.4 (q, 2C, 2 × CH$_3$), 14.3 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{23}O_4]^+$=$[M+H]^+$: 279.1591; found: 279.1591.



4t

Ethyl (2*E*)-4-methyl-3-(3,4,5-trimethoxyphenyl)pent-2-enoate (4t):

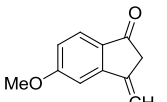
GP-1 was followed to **3t** (714 mg, 3.0 mmol) with 60% NaH (240 mg, 6.0 mmol), THF (10 mL), TEPA (1.8 mL, 9.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished the ester **4t** (885 mg, 96 %) as pale yellow viscous liquid. [TLC control R_f(**3t**)=0.50, R_f(**4t**)=0.60, (petroleum ether/ethyl acetate 80:20, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2961, 2927, 1713 (C=O), 1621, 1579, 1504, 1463, 1410, 1369, 1344, 1241, 1153, 1127, 1038, 1009, 879, 840, 826 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=6.38 (s, 2H, ArH), 5.71 (s, 1H, C=C*H*), 4.19 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 4.13–4.01 (m, 1H, CH), 3.84 (s, 9H, 3 × ArOCH$_3$), 1.29 (t, 3H, *J*=6.8 Hz, CH$_3$), 1.10 (d, 6H, *J*=6.8 Hz, 2 × CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.9 (s, C=O), 166.2 (s, *C*=CH), 152.5 (s, 2C, ArC), 137.5 (s, ArC), 136.4 (s, ArC), 118.4 (d, 2C, ArCH), 105.1 (d, C=*C*H), 60.9 (q, ArOCH$_3$), 59.9 (t, CH$_2$), 56.1 (q, 2C, 2 × ArOCH$_3$), 29.6 (d, CH), 21.5 (q, 2C, 2 × CH$_3$), 14.3 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{17}H_{25}O_5]^+$=$[M+H]^+$: 309.1697; found: 309.1690.



5b

5-methoxy-3-methyleneindan-1-one (5b):

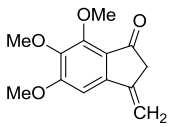
GP-2 was carried out with ester **4b** (110 mg, 0.5 mmol), DCE (2 mL) and triflic acid (1 mL, 12.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 94:6) furnished indenone **5b** (67 mg, 77%) as pale yellow semisolid. [TLC control R_f(**4b**)=0.60, R_f(**5b**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2851, 1704 (C=O), 1594, 1487, 1462, 1297, 1235, 1083, 1034, 1018, 827, 632, 611, 577 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.70 (d, 1H, *J*=8.8 Hz, ArH), 7.14 (d, 1H, *J*=2.0 Hz, ArH), 6.97 (dd, 1H, *J*=8.8 and 2,0 Hz, ArH), 5.79 (t, 1H, *J*=1.9 Hz, CH=C*H*$_a$H$_b$), 5.31 (t, 1H, *J*=1.5 Hz, CH=CH$_a$*H*$_b$), 3.91(s, 3H, ArOCH$_3$), 3.27 (t, 2H,CH$_2$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=201.1 (s, C=O), 165.4 (s, ArC), 152.3 (s, ArC), 139.8 (s, ArC), 131.0 (s, ArC), 125.1 (d, ArCH), 117.7 (d, ArCH), 107.8 (t, ArCH$_2$), 103.6 (d, ArCH), 55.7 (q, ArOCH$_3$), 42.3(t, CH$_2$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{11}H_{11}O_2]^+$=$[M+H]^+$: 175.0754; found: 175.0753.



5e

5,6,7-trimethoxy-3-methyleneindan-1-one (5e):

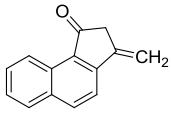
GP-2 was carried out with ester **4e** (140 mg, 0.5 mmol), DCE (2 mL) and triflic acid (1 mL, 12.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished indenone **5e** (84 mg, 72%) as pale yellow viscous liquid. [TLC control R_f(**4e**)=0.70, R_f(**5e**)=0.40, (petroleum ether/ethyl acetate 80:20, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2925, 2851, 1702 (C=O), 1585, 1481, 1465, 1329, 1248, 1144, 1089, 1009, 838,637 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=6.94 (s, 1H, ArH), 5.69 (t, 1H, J=2.0 Hz, CH=CH_aH$_b$), 5.23 (t, 1H, J=2.0 Hz, CH=CH$_a$$H_b$), 4.03 (s, 3H, ArOCH$_3$), 3.97 (s, 3H, ArOCH$_3$), 3.87 (s, 3H, ArOCH$_3$), 3.23 (t, 2H, J=1.5 Hz, CH$_2$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=198.9 (s, C=O), 159.7 (s, C=CH$_2$), 151.1 (s, ArC), 147.4 (s, ArC), 142.6 (s, ArC), 139.5 (s, ArC), 123.6 (s, ArC), 106.7 (t, C=CH$_2$), 98.1 (d, ArCH), 61.3 (q, ArOCH$_3$), 61.4 (q, ArOCH$_3$), 56.3 (q, ArOCH$_3$), 47.8 (t, CH$_2$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{13}$H$_{15}$O$_4$]$^+$=[M+H]$^+$: 235.0965; found: 235.0966.



5f

3-Methylene-2,3-dihydro-(1*H*)-cyclopenta[*b*]naphthalen-1-one (5f):

GP-2 was carried out with ester **4f** (120 mg, 0.5 mmol), DCE (2 mL) and triflic acid (1 mL, 12.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 94:6) furnished indenone **5f** (65 mg, 66%) as pale yellow semisolid. [TLC control R_f(**4f**)=0.60, R_f(**5f**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

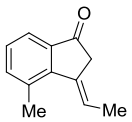
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2851, 1702 (C=O), 1605, 1469, 1307, 1237, 1033, 729, 696 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=9.16 (d, 1H, J=7.8 Hz, ArH), 8.06 (d, 1H, J=8.3 Hz, ArH), 7.88 (d, 1H, J=8.3 Hz, ArH), 7.81 (d, 1H, J=8.3 Hz, ArH), 7.68 (ddd, 1H, J=8.3, 6.8 and

1.0 Hz, ArH), 7.57 (ddd, 1H, *J*=8.3, 6.8 and 1.0 Hz, ArH), 5.91 (t, 1H, *J*=2.0 Hz, CH=C*H*$_a$H$_b$), 5.40 (t, 1H, *J*=2.0 Hz, CH=CH$_a$*H*$_b$), 3.40 (t, 2H, *J*=2.0 Hz, CH_2) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=203.3 (s, C=O), 151.6 (s, *C*=CH_2), 140.0 (s, ArC), 135.9 (d, ArCH), 133.5 (s, ArC), 131.4 (s, ArC), 129.2 (d, ArCH), 129.0 (s, ArC), 128.1 (d, ArCH), 127.2 (d, ArCH), 125.0 (d, ArCH), 118.2 (d, ArCH), 108.3 (t, C=*C*H_2), 42.5 (t, CH_2) ppm.

HR-MS (APCI+): m/z calculated for $[C_{14}H_{11}O]^+$=$[M+H]^+$: 195.0804; found: 195.0800.



5g

(3*E*)-3-ethylidene-4-methylindan-1-one (5g):

GP-2 was carried out with ester **4g** (109 mg, 0.5 mmol), DCE (2 mL) and triflic acid (1 mL, 12.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indenone **5g** (68 mg, 79 %) as brown color solid, recrystallized the solid with dichloromethane/hexane, [TLC control R_f(**4g**)=0.70, R_f(**5g**)=0.50, (petroleum ether/ethyl acetate 94:6, UV detection)].

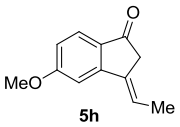
M.p.:100–102 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2852, 1707 (C=O), 1598, 1462, 1312, 1271, 1061, 797, 746 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.64 (d, 1H, *J*=7.3 Hz, ArH), 7.37 (d, 1H, *J*=7.3 Hz, ArH), 7.23 (dd, 1H, *J*=7.3 and 1.5 Hz, ArH), 6.39–6.29 (m, 1H, CH=C*H*CH_3), 3.21 (s, 2H, CH_2), 2.55 (s, 3H, ArCH_3), 1.90 (d, 3H, *J*=6.8 Hz, CH=CH*C*H_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=203.2 (s, C=O), 147.9 (s, ArC), 137.9 (s, *C*=CH), 137.3 (d, ArCH), 134.9 (s, ArC), 134.6 (s, ArC), 127.4 (d, ArCH), 123.4 (d, ArCH), 121.3 (d, ArCH), 40.3 (t, CH_2), 22.0 (q, ArCH_3), 16.10 (q, CH=CH*C*H_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{12}H_{13}O]^+$=$[M+H]^+$: 173.0961; found: 173.0962.



5h

(3*E*)-3-Ethylidene-5-methoxyindan-1-one (5h):

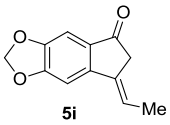
GP-2 was carried out with ester **4h** (117 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 94:6) furnished indenone **5h** (94 mg, 80%) as colorless viscous liquid. [TLC control R_f(**4h**)=0.70, R_f(**5h**)=0.50, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 2850, 1698 (C=O), 1594, 1485, 1440, 1289, 1268, 1225, 1091, 1017, 831, 816, 628 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.65 (d, 1H, *J*=8.3 Hz, ArH), 7.05 (d, 1H, *J*=2.5 Hz, ArH), 6.88 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.33–6.22 (m, 1H, C=CHC*H*$_3$), 3.88 (s, 3H, ArOCH$_3$), 3.15 (s, 2H, CH$_2$), 1.86 (d, 3H, *J*=6.8 Hz, C=CH*CH*$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=201.1 (s, C=O), 165.3 (s, ArC), 153.2 (s, ArC), 132.8 (s, *C*=CH), 130.3 (s, ArC), 125.1 (d, ArCH), 119.3 (d, ArCH), 116.6 (d, ArCH), 102.9 (d, C=*C*H), 55.6 (q, ArOCH$_3$), 40.0 (t, CH$_2$), 15.2 (q, CH=CH*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{12}H_{13}O_2]^+$=$[M+H]^+$: 189.0910; found: 189.0907.



5i

(7*E*)-7-Ethylidene-6,7-dihydro-(5*H*)-indeno[5,6-*d*][1,3]dioxol-5-one (5i):

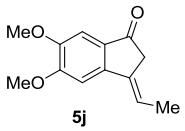
GP-2 was carried out with ester **4i** (124 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indenone **5i** (56 mg, 56%) as brown color solid. recrystallized the solid with dichloromethane/hexane, [TLC control R_f(**4i**)=0.60, R_f(**5i**)=0.40, (petroleum ether/ethyl acetate 90:10, UV detection)].

M.p.: 158–160 °C

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2852, 1700, 1470, 1296, 1232, 1038, 941 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.06 (s, 1H, ArH), 7.00 (s, 1H, ArH), 6.16–6.05 (m, 1H, C=CHC*H*$_3$), 6.05 (s, O-CH$_2$-O), 3.14 (s, 2H, CH$_2$), 1.84 (d, 3H, *J*=6.8 Hz, C=CH*CH*$_3$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=200.8 (s, C=O), 154.4 (s, ArC), 149.0 (s, ArC), 148.7 (d, ArC), 132.6 (s, *C*=CH), 132.0 (s, ArC), 117.8 (d, ArCH), 102.2 (d, ArCH), 101.8 (t, O-CH_2-O), 99.6 (d, 1H, C=*C*H), 39.8 (t, CH_2), 15.2 (q, CH=CH*C*H_3) ppm.

HR-MS (APCI+): calculated for $[C_{12}H_{11}O_3]^+$=$[M+H]^+$: 203.0703; found: 203.0702.



5j

(3*E*)-3-Ethylidene-5,6-dimethoxyindan-1-one (5j):

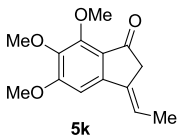
GP-2 was carried out with ester **4j** (132 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished indenone **5j** (107 mg, 98%) as colorless viscous liquid. [TLC control R_f(**4j**)=0.60, R_f(**5j**)=0.40, (petroleum ether/ethyl acetate 85:15, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2847, 1695 (C=O), 1594, 1591, 1400, 1304, 1215, 1142, 1091, 1118, 1056, 1034, 861 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.13 (s, 1H, ArH), 7.04 (s, 1H, ArH), 6.20–6.10 (m, 1H, C=CHCH_3), 3.97 (s, 3H, $ArOCH_3$), 3.90 (s, 3H, $ArOCH_3$), 3.14 (s, 2H, CH_2), 1.86 (d, 3H, *J*=6.8 Hz, C=CH*C*H_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=201.5 (s, C=O), 155.6 (s, ArC), 150.3 (s, ArC), 146.2 (s, ArC), 132.7 (s, *C*=CH), 130.1 (s, ArC), 117.3 (s, ArCH), 103.6 (d, ArCH), 101.2 (d, C=*C*H), 56.2 (q, $ArOCH_3$), 56.1 (q, $ArOCH_3$), 39.4 (t, CH_2), 15.2 (q, CH=CH*C*H_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{13}H_{15}O_3]^+$=$[M+H]^+$: 219.1016; found: 219.1015.



5k

(3*E*)-3-Ethylidene-5,6,7-trimethoxyindan-1-one (5k):

GP-2 was carried out with ester **4k** (147 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished indenone **5k** (118 mg, 95%) as pale yellow solid.

recrystallized the solid with dichloromethane/hexane, [TLC control R_f(**4k**)=0.60, R_f(**5k**)=0.40, (petroleum ether/ethyl acetate 80:20, UV detection)].

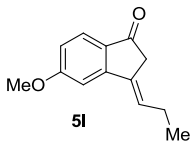
M.p.: 124–126 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2852, 1604 (C=O), 1501, 1454, 1310, 1260, 1216, 1059, 947, 859, 757 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=6.85 (s, 1H, ArH), 6.23–6.14 (m, 1H, C=CHC*H*$_3$), 4.01 (s, 3H, ArOCH$_3$), 3.94 (s, 3H, ArOCH$_3$), 3.84 (s, 3H, ArOCH$_3$), 3.12 (s, 2H, CH$_2$), 1.84 (d, 3H, *J*=7.3 Hz, C=CH*CH*$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=199.1 (s, C=O), 159.7 (s, ArC), 151.2 (s, ArC), 148.5 (s, ArC), 141.7 (s, ArC), 132.4 (s, *C*=CH), 122.9 (s, ArC), 118.3 (d, C=*C*H), 97.3 (d, ArCH), 61.9 (q, ArOCH$_3$), 61.4 (q, ArOCH$_3$), 56.2 (q, ArOCH$_3$), 40.2 (t, CH$_2$), 15.2 (q, CH=CH*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{14}H_{17}O_4]^+$=$[M+H]^+$: 249.1121; found: 249.1117.



5l

(3*E*)-5-Methoxy-3-propylideneindan-1-one (5l):

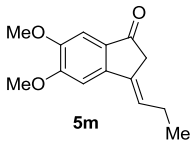
GP-2 was carried out with ester **4l** (124 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indenone **5l** (87 mg, 86%) as brown color viscous liquid. [TLC control R_f(**4l**)=0.60, R_f(**5l**)=0.40, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2920, 2851, 1706 (C=O), 1597, 1461, 1289, 1268, 1223, 1097, 1025, 823, 761 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.66 (d, 1H, *J*=8.8 Hz, ArH), 7.07 (d, 1H, *J*=2.0 Hz, ArH), 6.89 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.24–6.17 (m, 1H, C=CHC*H*$_3$), 3.89 (s, 3H, ArOCH$_3$), 3.15 (s, 2H, CH$_2$), 2.29–2.18 (m, 2H, CHC*H*$_2$CH$_3$), 1.09 (t, 3H, *J*=7.8 Hz, C=CHCH$_2$*CH*$_3$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=201.2 (s, C=O), 165.3 (s, ArC), 153.4 (s, ArC), 131.3 (s, *C*=CH), 130.4 (s, ArC), 126.5 (d, ArCH), 125.1 (d, ArCH), 116.8 (d, ArCH), 102.9 (d, C=*C*H), 55.6 (q, $ArOCH_3$), 39.7 (t, CH_2), 23.2 (t, CH_2), 13.7 (q, CH=CH*C*H_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{13}H_{15}O_2]^+$=$[M+H]^+$: 203.1067; found: 203.1064.



5m

(3*E*)-5,6-Dimethoxy-3-propylideneindan-1-one (5m):

GP-2 was carried out with ester **4m** (139 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished indenone **5m** (114 mg, 98%) as white solid. [TLC control R_f(**4m**)=0.70, R_f(**5m**)=0.50, (petroleum ether/ethyl acetate 80:20, UV detection)].

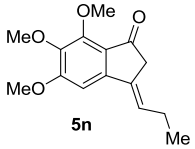
M.p.: 122–124 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2852, 1695 (C=O), 1601, 1497, 1461, 1312, 1292, 1212, 1126, 1017, 855 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.09 (s, 1H, ArH), 7.03 (s, 1H, ArH), 6.07–6.00 (m, 1H, C=CHCH_3), 3.95 (s, 3H, $ArOCH_3$), 3.86 (s, 3H, $ArOCH_3$), 3.09 (s, 2H, CH_2), 2.25–2.13 (m, 2H, CHC$H_2$$CH_3$), 1.06 (t, 3H, J=7.3 Hz, C=CHCH_2*C*H_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=201.4 (s, C=O), 155.5 (s, ArC), 150.3 (s, ArC), 146.1 (s, *C*=CH), 131.2 (s, ArC), 130.1 (s, ArC), 124.3 (d, ArCH), 103.5 (d, ArCH), 101.2 (d, C=*C*H), 56.1 (q, $ArOCH_3$), 56.0 (q, $ArOCH_3$), 39.3 (t, CH_2), 23.1 (t, CH_2), 13.8 (q, CH=CH*C*H_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{14}H_{17}O_3]^+$=$[M+H]^+$: 233.1172; found: 233.1170.



5n

(3*E*)-5,6,7-trimethoxy-3-propylideneindan-1-one (5n):

GP-2 was carried out with ester **4n** (154 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished indenone **5n** (130 mg, 99%) as pale yellow solid.

recrystallized the solid with dichloromethane/hexane, [TLC control R_f(**4n**)=0.60, R_f(**5n**)=0.40, (petroleum ether/ethyl acetate 80:20, UV detection)].

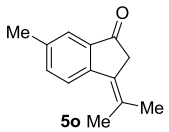
M.p.: 96–98 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 2851, 1700 (C=O), 1588, 1332, 1254, 1200, 1145, 1089, 1008, 832 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.86 (s, 1H, ArH), 6.12–6.05 (m, 1H, C=CHC*H*$_3$), 3.98 (s, 3H, ArOCH_3), 3.93 (s, 3H, ArOCH_3), 3.81 (s, 3H, ArOCH_3), 3.10 (s, 2H, CH_2), 2.23–2.12 (m, *J*=7.3 Hz, CHC*H*$_2$CH_3), 1.05 (t, 3H, *J*=7.3 Hz, C=CHCH_2*C*H_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=198.9 (s, C=O), 159.7 (s, ArC), 151.1 (s, ArC), 148.4 (s, ArC), 141.7 (s, ArC), 130.9 (s, *C*=CH), 125.3 (d, ArCH), 122.9 (s, ArC), 97.4 (d, C=*C*H), 61.8 (q, ArOCH_3), 61.3 (q, ArOCH_3), 56.2 (q, ArOCH_3), 40.1 (t, CH_2), 23.1 (t, CH_2), 13.6 (q, CH=CH*C*H_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{15}H_{19}O_4]^+$=$[M+H]^+$: 263.1278; found: 263.1276.



6-Methyl-3-(1-methylethylidene) indan-1-one (5o):

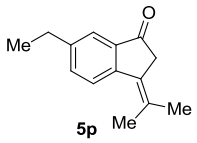
GP-2 was carried out with ester **4o** (116 mg, 0.5 mmol), DCE (2 mL) and triflic acid (1 mL, 12.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone **5o** (73 mg, 78%) as brown color viscous liquid. [TLC control R_f(**4o**)=0.70, R_f(**5o**)=0.50, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2853, 1701 (C=O), 1483, 1280, 821, 748 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.73 (d, 1H, *J*=8.3 Hz, ArH), 7.58 (d, 1H, *J*=1.0 Hz, ArH), 7.43 (dd, 1H, *J*=7.8 and 1.5 Hz, ArCH), 3.20 (s, 2H, CH_2), 2.40 (s, 3H, ArCH_3), 2.17 (s, 3H, CH_3), 1.93 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=203.6 (s, C=O), 148.3 (s, ArC), 138.0 (s, ArC), 137.0 (s, ArC), 135.9 (d, ArCH), 130.8 [s, C=*C*$(CH_3)_2$], 125.8 [s, *C*=C$(CH_3)_2$], 124.9 (d, ArCH), 123.6 (d, ArCH), 42.7 (t, CH_2), 24.7 (q, CH_3), 21.8 (q, CH_3), 21.0 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{13}H_{15}O]^+$=$[M+H]^+$: 187.1117; found: 187.1111.



5p

6-Ethyl-3-(1-methylethylidene) indan-1-one (5p):

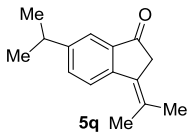
GP-2 was carried out with ester **4p** (123 mg, 0.5 mmol), DCE (2 mL) and triflic acid (1 mL, 12.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indanone **5p** (60 mg, 60%) as brown color viscous liquid. [TLC control R_f(**4p**)=0.70, R_f(**5p**)=0.50, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2932, 2851, 1701 (C=O), 1588, 1481, 1332, 1258, 1200, 1145, 1092, 1007, 836, 702 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.75 (d, 1H, *J*=8.3 Hz, ArH), 7.62 (d, 1H, *J*=1.0 Hz , ArH), 7.45 (dd, 1H, *J*=7.8 and 1.5 Hz, ArCH), 3.21 (s, 2H, CH_2), 2.71 (q, 2H, *J*=7.3 Hz, CH_2), 2.17 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.25 (t, 3H, *J*=7.8 Hz, $CH_2C\mathit{H}_3$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=203.7 (s, C=O), 148.5 (s, ArC), 143.3 (s, ArC), 138.1 (s, ArC), 135.0 (d, ArCH), 130.8 [s, C=*C*$(CH_3)_2$], 125.8 [s, *C*=C$(CH_3)_2$], 125.0 (d, ArCH), 122.3 (d, ArCH), 42.7 (t, CH_2), 28.4 (t, CH_2), 24.7 (q, CH_3), 21.8 (q, CH_3), 15.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{14}H_{17}O]^+$=$[M+H]^+$: 201.1274; found: 201.1267.



5q

6-Isopropyl-3-(1-methylethylidene) indan-1-one (5q):

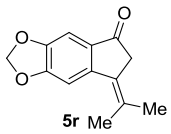
GP-2 was carried out with ester **4q** (130 mg, 0.5 mmol), DCE (2 mL) and triflic acid (1 mL, 12.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indenone **5q** (73 mg, 68%) as brown color viscous liquid. [TLC control R_f(**4q**)=0.60, R_f(**4q**)=0.40, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2923, 2851, 1704 (C=O), 1596, 1487, 1457, 1287, 1253, 1052, 764 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.76 (d, 1H, *J*=8.3 Hz, ArH), 7.66 (d, 1H, *J*=2.0 Hz, ArH), 7.50 (dd, 1H, *J*=8.3 and 2.0 Hz, ArCH), 3.21 (s, 2H, CH_2), 3.01–2.92 (m, 1H, CH), 2.17 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.27 [d, 6H, CH(CH_3)$_2$] ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=203.8 (s, C=O), 148.7 (s, ArC), 148.0 (s, ArC), 138.1 (s, ArC), 133.8 (d, ArCH), 130.9 [s, C=*C*(CH$_3$)$_2$], 125.8 [s, *C*=C(CH$_3$)$_2$], 125.1 (d, ArCH), 120.8 (d, ArCH), 42.8 (t, CH_2), 33.8 (d, CH), 24.7 (q, CH_3), 23.8 (q, 2C, CH_3), 21.8 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{15}H_{19}O]^+$=$[M+H]^+$: 215.1430; found: 215.1429.



5r

7-(1-Methylethylidene)-6,7-dihydro-5*H*-indeno[5,6-*d*][1,3]dioxol-5-one (5r):

GP-2 was carried out with ester **4r** (131 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished indenone **5r** (84 mg, 78%) as brown color solid. recrystallized the solid with dichloromethane/hexane, [TLC control R_f(**4r**)=0.60, R_f(**5r**)=0.40, (petroleum ether/ethyl acetate 85:15, UV detection)].

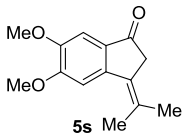
M.p.: 136–138 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2919, 2853, 1691 (C=O), 1603, 1503, 1484, 1312, 1258, 1053, 935, 874, 842 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.24 (s, 1H, ArH), 7.14 (s, 1H, ArH), 6.07 (s, 2H, O-CH_2-O), 3.19 (s, 2H, CH_2), 2.13 (s, 3H, CH_3), 1.92 (s, 3H, CH_3) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=201.2 (s, C=O), 154.2 (s, ArC), 148.1 (s, ArC), 147.7 (s, ArC), 133.3 (s, ArC), 130.1 [s, C=*C*(CH$_3$)$_2$], 125.8 [s, *C*=C(CH$_3$)$_2$], 104.5 (t, CH_2), 102.3 (d, 2C, ArCH), 42.9 (t, CH_2), 24.8 (q, CH_3), 21.6 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{13}H_{13}O_3]^+$=$[M+H]^+$: 217.0859; found: 217.0869.



5,6-Dimethoxy-3-(1-methylethylidene)indan-1-one (5s):

GP-1 was carried out with ester **4s** (139 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished indenone **5s** (106 mg, 91%) as white solid. [TLC control R_f(**4s**)=0.60, R_f(**5s**)=0.40, (petroleum ether/ethyl acetate 80:20, UV detection)].

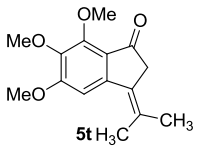
M.p.: 124–126 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2920, 2851, 1684 (C=O), 1600, 1495, 1440, 1306, 1263, 1243, 1073, 1023, 855, 837 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.23 (s, 1H, ArH), 7.19 (s, 1H, ArH), 3.97 (s, 3H, $ArOCH_3$), 3.90 (s, 3H, $ArOCH_3$), 3.16 (s, 2H, CH_2), 2.16 (s, 3H, CH_3), 1.92 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=201.9 (s, C=O), 154.9 (s, ArC), 149.1 (s, ArC), 145.9 (s, ArC), 131.3 (s, ArC), 129.4 [s, C=*C*$(CH_3)_2$], 125.8 [s, *C*=C$(CH_3)_2$], 106.3 (d, ArCH), 104.0 (d, ArCH), 56.0 (q, 2C, 2 × $ArOCH_3$), 42.5 (t, CH_2), 24.7 (q, CH_3), 21.7 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{14}H_{17}O_3]^+$=$[M+H]^+$: 233.1172; found: 233.1177.



5,6,7-Trimethoxy-3-(1-methylethylidene)indan-1-one (5t):

GP-2 was carried out with ester **4t** (154 mg, 0.5 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished indenone **5t** (128 mg, 98 %) as brown color solid. [TLC control R_f(**4t**)=0.60, R_f(**5t**)=0.40, (petroleum ether/ethyl acetate 80:20, UV detection)].

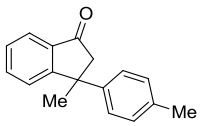
M.p.: 138–140 °C.

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2932, 2851, 1694 (C=O), 1582, 1481, 1322, 1254, 1145, 1090, 1010, 864, 719 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.03 (s, 1H, ArH), 4.01 (s, 3H, $ArOCH_3$), 3.95 (s, 3H, $ArOCH_3$), 3.86 (s, 3H, $ArOCH_3$), 3.17 (s, 2H, CH_2), 2.16 (s, 3H, CH_3), 1.92 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=199.3 (s, C=O), 159.1 (s, ArC), 151.4 (s, ArC), 148.3 (s, ArC), 140.8 (s, ArC), 130.6 (s, ArC), 125.7 [s, C=*C*$(CH_3)_2$], 124.0 [s, *C*=C$(CH_3)_2$], 102.9 (d, ArCH), 61.9 (q, $ArOCH_3$), 61.4 (q, $ArOCH_3$), 56.1 (q, $ArOCH_3$), 43.6 (t, CH_2), 25.0 (q, CH_3), 21.7 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{15}H_{19}O_4]^+$=$[M+H]^+$: 263.1278; found: 263.1275.



7b

3-Methyl-3-(4-methylphenyl)indan-1-one (7b):

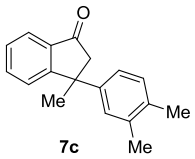
GP-3 was carried out with ester **4a** (95 mg, 0.5 mmol), DCE (2 mL), triflic acid (1 mL, 12 mmol) and external arene **6b** (552 mg, 6.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone **7b** (85 mg, 72 %) as pale yellow viscous liquid. [TLC control R_f(**4a**)=0.60, R_f(**7b**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2964, 2922, 1711 (C=O), 1601, 1512, 1462, 1287, 1235, 768, 757 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.78 (d, 1H, *J*=7.8 Hz, ArH), 7.57 (ddd, 1H, *J*=8.8, 7.3 and 1.0 Hz, ArH), 7.40 (dd, 1H, *J*=7.8 and 1.0 Hz, ArH), 7.28 (d, 1H, *J*=7.8 Hz, ArH), 7.08 (dd, 4H, *J*=9.3 and 6.4 Hz, ArH), 2.95 (d, 1H, *J*=19.1 Hz, C*H*$_a$H$_b$CO), 2.88 (d, 1H, *J*=19.1 Hz, CH*H*$_b$CO), 2.30 (s, 3H, $ArCH_3$), 1.81 [s, 3H, Ar-C(CH_2CO)C*H*$_3$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=205.9 (s, C=O), 163.0 (s, ArC), 144.3 (s, ArC), 135.9 (s, ArC), 135.6 (s, ArC), 135.2 (d, ArCH), 129.1 (d, 2C, ArCH), 127.6 (d, ArCH), 126.0 (d, 2C, ArCH), 125.5 (d, ArCH), 123.2 (d, ArCH), 55.7 (t, *C*H_2CO), 45.6 (s, $ArCH_3$*C*CH_2), 28.3 [q, Ar-C(CH_2CO)*C*H_3], 20.8 (q, $ArCH_3$) ppm.

HR-MS (APCI+): (APCI+) m/z calculated for $[C_{17}H_{17}O]^+$=$[M+H]^+$: 237.1274; found: 237.1270.



7c

3-(3,4-Dimethylphenyl)-3-methylindan-1-one (7c):

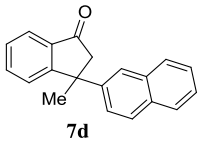
GP-3 was carried out with ester **4a** (95 mg, 0.5 mmol), DCE (2 mL), triflic acid (1 mL, 12 mmol) and external arene **6c** (636 mg, 6.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 92:8) furnished indanone **7c** (88 mg, 71 %) as pale yellow viscous liquid. [TLC control R_f(**4a**)=0.60, R_f(**7c**)=0.40, (petroleum ether/ethyl acetate 92:8, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2919, 2850, 1712 (C=O), 1601, 1462, 1286, 1235, 769, 757 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.79 (d, 1H, *J*=7.8 Hz, ArH), 7.58 (ddd, 1H, *J*=8.8, 7.3 and 1.0 Hz, ArH), 7.41 (dd, 1H, *J*=8.3 and 7.3 Hz, ArH), 7.30 (d, 1H, *J*= 7.8 Hz, ArH), 7.05 (d, 1H, *J*= 7.8 Hz, ArH), 6.94 (dd, 1H, *J*=8.3 and 3.0 Hz, ArH), 6.93 (d, 1H, *J*= 8.3 Hz, ArH), 2.97 (d, 1H, *J*=18.6 Hz, CH_aH$_b$CO), 2.88 (d, 1H, *J*=18.6 Hz, CHH_bCO), 2.22 (s, 3H, ArCH$_3$), 2.21 (s, 3H, ArCH$_3$), 1.81 [s, 3H, Ar-C(CH$_2$CO)CH_3] ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=206.1 (s, C=O), 163.1 (s, ArC), 144.7 (s, ArC), 136.6 (s, ArC), 135.6 (s, ArC), 135.2 (d, ArCH), 134.6 (s, ArC), 129.6 (d, ArCH), 127.6 (d, ArCH), 127.5 (d, ArCH), 125.5 (d, ArCH), 123.5 (d, ArCH), 123.2 (d, ArCH), 55.8 (t, *C*H$_2$CO), 45.6 (s, ArCH$_3$*C*CH$_2$), 28.3 [q, Ar-C(CH$_2$CO)*C*H$_3$], 19.9 (q, ArCH$_3$), 19.2 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{18}$H$_{19}$O]$^+$=[M+H]$^+$: 251.1430; found: 251.1429.



7d

3-Methyl-3-(2-naphthyl)indan-1-one (7d):

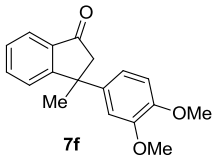
GP-3 was carried out with ester **4a** (95 mg, 0.5 mmol), DCE (2 mL), triflic acid (1 mL, 12 mmol) and external arene **6d** (96 mg, 0.75 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indanone **7d** (108 mg, 79%) as pale yellow viscous liquid. [TLC control R_f(**4a**)=0.60, R_f(**7d**)=0.30, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2964, 2918, 1707 (C=O), 1599, 1512, 1462, 1286, 1234, 818, 748 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.84 (d, 1H, *J*=7.8 Hz, ArH), 7.81–7.75 (m, 2H, ArH), 7.75 (d, 2H, *J*=8.8 Hz, ArH), 7.59 (ddd, 1H, *J*= 8.3, 7.3 and 1.0 Hz, ArH), 7.52–7.40 (m, 3H, ArH), 7.29 (d, 1H, *J*=8.8 Hz, ArH), 7.18 (dd, 1H, *J*=8.8 and 2.5 Hz, ArH), 3.07 (d, 1H, *J*=19.1 Hz, CH_aH$_b$CO), 2.96 (d, 1H, *J*=19.1 Hz, CHH_bCO), 1.94 [s, 3H, Ar-C(CH$_2$CO)CH_3] ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=205.7 (s, C=O), 162.8 (s, ArC), 144.3 (s, ArC), 135.8 (s, ArC), 135.3 (d, ArCH), 133.0 (s, ArC), 131.9 (s, ArC), 128.4 (d, ArCH), 127.9 (d, ArCH), 127.8 (d, ArCH), 127.4 (d, ArCH), 126.3 (d, ArCH), 125.9 (d, ArCH), 125.6 (d, ArCH), 125.1 (d, ArCH), 124.1 (d, ArCH), 123.4(d, ArCH), 55.3 (t, *C*H$_2$CO), 46.1 (s, ArCH$_3$*C*CH$_2$), 28.2 [q, Ar-C(CH$_2$CO)*C*H$_3$] ppm.

HR-MS (APCI+): m/z calculated for [C$_{20}$H$_{17}$O]$^+$=[M+H]$^+$: 273.1274; found: 274.1271.



7f

3-(3,4-Dimethoxyphenyl)-3-methylindan-1-one (7f):

GP-2 was carried out with ester **4a** (95 mg, 0.5 mmol), DCE (2 mL), triflic acid (1 mL, 12 mmol) and external arene **6f** (103 mg, 0.75 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indanone **7f** (99 mg, 77 %) as pale yellow viscous liquid. [TLC control R_f(**4a**)=0.60, R_f(**7f**)=0.30, (petroleum ether/ethyl acetate 80:20, UV detection)].

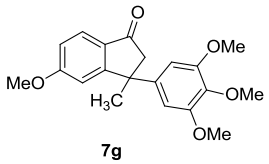
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2919, 2850, 1714 (C=O), 1519, 1463, 1258, 1145, 1027 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.77 (d, 1H, *J*=7.3 Hz, ArH), 7.59 (ddd, 1H, *J*=8.3, 7.3 and 1.0 Hz, ArH), 7.41 (dd, 1H, *J*= 7.3 and 1.0 Hz, ArH), 7.29 (d, 1H, *J*= 7.3 Hz, ArH), 6.76 (d, 1H, *J*=8.3 Hz, ArH), 6.74 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.62 (d, 1H, *J*=2.0 Hz, ArH), 3.83 (s, 3H, ArOCH$_3$), 3.74 (s, 3H, ArOCH$_3$), 2.95 (d, 1H, *J*=18.6 Hz, CH_aH$_b$CO), 2.87 (d, 1H, *J*=18.6 Hz, CHH_bCO), 1.80 [s, 3H, Ar-C(CH$_2$CO)CH_3] ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=205.9 (s, C=O), 162.9 (s, ArC), 148.8 (s, ArC), 147.6 (s, ArC), 139.9 (s, ArC), 135.6 (s, ArC), 135.2 (d, ArCH), 127.8 (d, ArCH), 125.5 (d, ArCH),

123.3 (d, ArCH), 118.3 (d, ArCH), 110.9 (d, ArCH), 110.0 (d, ArCH), 55.9 (q, 2 × $ArOCH_3$), 55.8 (t, CH_2CO), 45.7 [s, Ar-$C(CH_2CO)CH_3$], 28.7 [q, Ar-$C(CH_2CO)CH_3$] ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{19}O_3]^+$=$[M+H]^+$: 283.1329; found: 283.1319.



7g

3-(3,4-Dimethoxyphenyl)-5-methoxy-3-methylindan-1-one (7g):

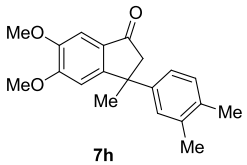
GP-3 was carried out with ester **4b** (110 mg, 0.5 mmol), DCE (2 mL) triflic acid (0.1 mL, 3 mmol) and external arene **6g** (126 mg, 0.75 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished indanone **7g** (171 mg, 70%) as pale yellow viscous liquid. [TLC control R_f(**4b**)=0.60, R_f(**7g**)=0.30, (petroleum ether/ethyl acetate 80:20, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2930, 1692 (C=O), 1591, 1497, 1462, 1289, 1251, 1212, 1145, 1026, 858, 811, 732, 605 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.18 (s, 1H, ArH), 6.76 (dd, 2H, J=10.3 and 8.3 Hz, ArH), 6.61 (s, 2H, ArH), 3.93 (s, 3H, $ArOCH_3$), 3.86 (s, 3H, $ArOCH_3$), 3.84 (s, 3H, $ArOCH_3$), 3.75 (s, 3H, $ArOCH_3$), 2.87 (d, 1H, J=19.1 Hz, CH_aH$_b$CO), 2.83 (d, 1H, J=19.1 Hz, CH$_a$$H_b$CO), 1.78 [s, 3H, Ar-$C(CH_2CO)CH_3$] ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.4 (s, C=O), 158.3 (s, ArC), 155.8 (s, ArC), 149.7 (s, ArC), 148.9 (s, ArC), 147.6 (s, ArC), 140.1 (s, ArC), 128.7 (s, ArC), 118.2 (d, ArCH), 110.8 (d, ArCH), 109.9 (d, ArCH), 106.1 (d, ArCH), 103.5 (d, ArCH), 56.3 (q, $ArOCH_3$), 56.1 (q, $ArOCH_3$), 56.0 (t, CH_2CO), 55.9 (q, $ArOCH_3$), 55.8 (q, $ArOCH_3$), 45.4 [s, Ar-$C(CH_2CO)CH_3$], 28.2 [q, Ar-$C(CH_2CO)CH_3$] ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_5]^+$=$[M+H]^+$: 343.1540; found: 343.1538.



7h

3-(3,4-Dimethylphenyl)-5,6-dimethoxy-3-methylindan-1-one (7h):

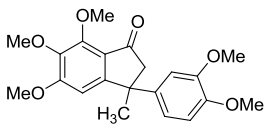
GP-3 was carried out with ester **4d** (125 mg, 0.5 mmol), DCE (2 mL), triflic acid (1 mL, 12 mmol) and external arene **6c** (636 mg, 6.0 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indanone **7h** (125 mg, 81 %) as pale yellow viscous liquid. [TLC control R_f(**4d**)=0.50, R_f(**7h**)=0.35, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2917, 2849, 1696 (C=O), 1592, 1497, 1462, 1296, 1282, 1212, 1032 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.19 (s, 1H, ArH), 7.04 (d, 1H, *J*=8.3 Hz, ArH), 6.92 (d, 1H, *J*=6.4 Hz, ArH), 6.91 (d, 1H, *J*= 6.4 Hz, ArH), 6.62 (s, 1H, ArH), 3.93 (s, 3H, ArOCH$_3$), 3.85 (s, 3H, ArOCH$_3$), 2.87 (d, 1H, *J*=18.6 Hz, C*H*$_a$H$_b$CO), 2.82 (d, 1H, *J*=18.6 Hz, CH*H*$_b$CO), 2.21 (s, 3H, ArCH$_3$), 2.20 (s, 3H, ArCH$_3$), 1.78 [s, 3H, Ar-C(CH$_2$CO)C*H*$_3$] ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=204.5 (s, C=O), 158.4 (s, ArC), 155.8 (s, ArC), 149.6 (s, ArC), 144.9 (s, ArC), 136.6 (s, ArC), 134.6 (s, ArC), 129.6 (d, ArCH), 128.8 (s, ArC), 127.4 (d, ArCH), 123.4 (d, ArCH), 106.2 (d, ArCH), 103.5 (d, ArCH), 56.3 (q, ArOCH$_3$), 56.2 (q, ArOCH$_3$), 56.1 (t, *C*H$_2$CO), 45.3 (s, ArCH$_3$*C*CH$_2$), 28.0 [q, Ar-C(CH$_2$CO)*C*H$_3$], 20.0 (q, ArCH$_3$), 19.2 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_3]^+$=$[M+H]^+$: 311.1643; found: 311.1638.



7j

3-(3,4-Dimethoxyphenyl)-5,6,7-trimethoxy-3-methylindan-1-one (7j):

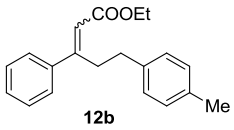
GP-3 was carried out with ester **4e** (140 mg, 0.5 mmol), DCE (2 mL), triflic acid (0.1 mL, 1.5 mmol) and external arene **6f** (103 mg, 0.75 mmol), was added to the reaction mixture and stirred at rt for 1 h. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished indanone **7j** (149 mg, 80 %) as pale yellow viscous liquid. [TLC control R_f(**4e**)=0.70, R_f(**7j**)=0.30, (petroleum ether/ethyl acetate 80:20, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2934, 2836, 1734 (C=O), 1697, 1585, 1513, 1480, 1461, 1309, 1252, 1197, 1142, 1086, 1023, 1011, 960, 901, 810, 768, 733 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=6.77 (dd, 2H, *J*=8.3 and 2.0 Hz, ArH), 6.63 (d, 1H, *J*=2.0 Hz, ArH), 6.36 (s, 1H, ArH), 4.08 (s, 3H, $ArOCH_3$), 3.85 (s, 3H, $ArOCH_3$), 3.84 (s, 3H, $ArOCH_3$), 3.81 (s, 3H, $ArOCH_3$), 3.77 (s, 3H, $ArOCH_3$), 2.87 (d, 1H, *J*=18.6 Hz, CH_aH_bCO), 2.80 (d, 1H, *J*=18.6 Hz, CH_aH_bCO), 1.75 [s, 3H, Ar-$C(CH_2CO)CH_3$] ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=201.6 (s, C=O), 161.1 (s, ArC), 159.9 (s, ArC), 150.7 (s, ArC), 148.8 (s, ArC), 147.6 (s, ArC), 140.7 (s, ArC), 140.0 (s, ArC), 1.122 (s, ArC), 118.3 (d, ArCH), 110.8 (d, ArCH), 109.9 (d, ArCH), 102.4 (d, ArCH), 61.9 (q, $ArOCH_3$), 61.3 (q, $ArOCH_3$), 56.5 (t, CH_2CO), 56.3 (q, $ArOCH_3$), 55.9 (q, $ArOCH_3$), 55.8 (q, $ArOCH_3$), 45.1 [s, Ar-$C(CH_2CO)CH_3$], 28.4 [q, Ar-$C(CH_2CO)CH_3$] ppm.

HR-MS (APCI+): m/z calculated for $[C_{21}H_{25}O_6]^+$=$[M+H]^+$: 373.1646; found: 373.1635.



12b

Ethyl (2*E*)-5-(4-methylphenyl)-3-phenylpent-2-enoate (12b):

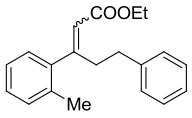
GP-4 was followed to **11b** (336 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester **12b** (423 mg, 96%) as pale yellow viscous liquid. [TLC control R_f(**11b**)=0.40, R_f(**12b**)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2924, 2853, 1724, 1636, 1454, 1278, 1159, 1043, 748 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.53 (d, 2H, *J*=8.3 Hz, ArH), 7.33 (d, 2H, *J*=8.3 Hz, ArH), 7.20–6.98 (m, 5H, ArH), 6.05 (s, 1H, C=CH), 4.23 (q, 2H, *J*=7.3 Hz, OCH_2CH_3), 3.36 (t, 2H, *J*=7.8 Hz, CH_2), 2.69 (t, 2H, *J*=7.8 Hz, CH_2), 2.33 (s, 3H, $ArCH_3$), 1.32 (t, 3H, *J*=7.3 Hz, OCH_2CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.0 (s, C=O), 158.0 (s, *C*=CH), 139.9 (s, ArC), 138.1 (s, ArC), 135.4 (s, ArC), 131.7 (d, 2C, ArCH), 128.9 (d, 3C, ArCH), 128.3 (d, 3C, ArCH), 123.3 (d, ArCH), 118.1 (d, 1H, *C*H=C), 59.9 (t, OCH_2CH_3), 34.6 (t, CH_2), 33.1 (t, CH_2), 21.0 (q, $ArCH_3$), 14.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_2]^+$=$[M+H]^+$: 295.1693; found: 295.1690.



E:*Z* = 1:1

12c

Ethyl (2*E*)-3-(2-methylphenyl)-5-phenylpent-2-enoate (12c):

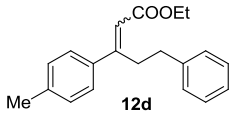
GP-4 was followed to **11c** (336 mg, 1.5 mmol) with 60% NaH (240 mg, 3.0 mmol), THF (10 mL), TEPA (1.8 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester **12c** (397 mg, 90%) as pale yellow viscous liquid. [TLC control R_f(**11c**)=0.40, R_f(**12c**)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2925, 1709, 1626, 1490, 1224, 1157, 1012, 808 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.48 (d, 1H, *J*=7.3 Hz, ArH), 7.44–7.30 (m, 3H, ArH), 7.21 (d, 2H, *J*=7.8 Hz, ArH), 7.10 (ddd, 3H, *J*=7.8, 7.8 and 7.3 Hz, ArH), 6.08 (s, 1H, C=CH), 4.23 (q, 2H, *J*=7.3 Hz, O*CH*$_2$CH$_3$), 3.39 (t, 2H, *J*=7.3 Hz, CH$_2$), 2.81–2.60 (m, 2H, CH$_2$), 2.32 (s, 3H, ArCH$_3$), 1.32 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.3 (s, C=O), 159.4 (s, *C*=CH), 141.1 (s, ArC), 138.5 (s, ArC), 135.5 (s, ArC), 129.1 (d, ArCH), 128.9 (d, ArCH), 128.6 (d, ArCH), 128.3 (d, ArCH), 128.1 (d, ArCH), 127.9 (d, ArCH), 127.7 (d, ArCH), 127.2 (d, ArCH), 126.7 (d, ArCH), 117.7 (d, 1H, *C*H=C), 59.8 (t, O*C*H$_2$CH$_3$), 42.2 (t, CH$_2$), 34.7 (t, CH$_2$), 21.0 (q, ArCH$_3$), 14.3 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_2]^+$=$[M+H]^+$: 295.1693; found: 295.1712.



12d

E:*Z* = 1:1

Ethyl (2*E*)-3-(4-methylphenyl)-5-phenylpent-2-enoate (12d):

GP-4 was followed to **11d** (336 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester **12d** (423 mg,

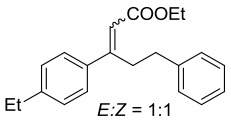
96%) as pale yellow viscous liquid. [TLC control R_f(**11d**)=0.40, R_f(**12d**)=0.60, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2922, 2930, 1707, 1584, 1446, 1244, 1121, 1004, 761 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.53 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 7.34–7.01 (m, 8H, ArH), 6.07 (d, 1H, *J*=5.9 Hz, C=CH), 4.09–3.93 (m, 2H, O*C*$H_2$$CH_3$), 3.46–3.33 (m, 2H, CH_2), 2.83–2.64 (m, 2H, CH_2), 2.39 (s, 3H, ArCH_3), 1.38–1.24 (m, 3H, OCH_2C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 159.2 (s, *C*=CH), 141.7 (s, ArC), 139.1 (s, ArC), 137.5 (s, ArC), 129.3 (d, ArCH), 128.6 (d, ArCH), 128.4 (d, 2C, ArCH), 128.3 (d, 2C, ArCH), 127.2 (d, ArCH), 126.6 (d, ArCH), 126.0 (d, ArCH), 117.3 (d, 1H, *C*H=C), 59.8 (t, O*C*$H_2$$CH_3$), 42.1 (t, CH_2), 35.2 (t, CH_2), 21.3 (q, ArCH_3), 14.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_2]^+$=$[M+H]^+$: 295.1693; found: 295.1691.



12e

Ethyl (2*E*)-3-(4-ethylphenyl)-5-phenylpent-2-enoate (12e):

GP-4 was followed to **11e** (357 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester **12e** (425 mg, 92%) as pale yellow viscous liquid. [TLC control R_f(**11e**)=0.40, R_f(**12e**)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)].

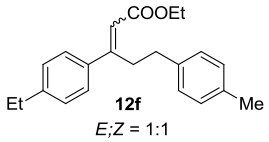
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2965, 2930, 1707, 1622, 1454, 1224, 1155, 1033, 831, 698 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.42 (d, 2H, *J*=8.3 Hz, ArH), 7.34–7.05 (m, 7H, ArH), 6.08 (s, 1H, C=CH), 4.21 (q, 2H, *J*=6.8 Hz, O*C*$H_2$$CH_3$), 3.39 (q, 2H, *J*=7.8 Hz, CH_2), 2.81–2.56 (m, 4H, CH_2), 1.30 (t, 3H, *J*=7.8 Hz, CH_2C*H*$_3$), 1.07 (t, 3H, *J*=6.8 Hz, OCH_2C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 159.2 (s, *C*=CH), 145.4 (s, ArC), 141.7 (s, ArC), 138.2 (d, ArC), 128.4 (d, 2C, ArCH), 128.2 (d, 2C, ArCH), 128.1 (d, ArCH), 127.4 (d, 2C, ArCH), 126.7 (d, ArCH), 126.0 (d, ArCH), 117.3 (d, 1H, *C*H=C), 59.8 (t,

O*C*H_2CH$_3$), 42.1 (t, CH_2), 35.3 (t, CH_2), 33.9 (t, CH_2), 15.3 (q, CH_2*C*H_3), 14.3 (q, OCH$_2$*C*H_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{21}H_{25}O_2]^+$=$[M+H]^+$: 309.1849; found: 309.1861.



12f

E;*Z* = 1:1

Ethyl (2*E*)-3-(4-ethylphenyl)-5-(4-methylphenyl) pent-2-enoate (12f):

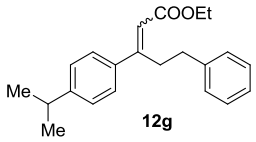
GP-4 was followed to **11f** (378 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester **12f** (444 mg, 92%) as pale yellow viscous liquid. [TLC control R_f(**11f**)=0.45, R_f(**12f**)=0.65, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2965, 2928, 1708, 1623, 1513, 1454, 1223, 1155, 1038, 808 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.44 (dd, 2H, *J*=8.3 and 2.0 Hz, ArH), 7.31–6.99 (m, 6H, ArH), 6.10 (s, 1H, C=CH), 4.23 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.39 (q, 2H, *J*=7.8 Hz, CH_2), 2.87–2.59 (m, 4H, CH_2), 2.33 (s, 3H, ArCH$_3$), 1.33 (t, 3H, *J*=7.8 Hz, CH$_2$C*H*$_3$), 1.10 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=166.4 (s, C=O), 159.3 (s, *C*=CH), 145.4 (s, ArC), 138.6 (s, ArC), 137.8 (d, ArC), 135.4 (d, ArC), 129.0 (d, 2C, ArCH), 128.3 (d, ArCH), 128.1 (d, 2C, ArCH), 127.3 (d, 2C, ArCH), 126.6 (d, ArCH), 117.2 (d, 1H, *C*H=C), 59.7 (t, O*C*H$_2$CH$_3$), 42.2 (t, CH_2), 34.8 (t, CH_2), 28.6 (t, CH_2), 21.0 (q, ArCH$_3$), 15.3 (q, CH$_2$*C*H$_3$), 14.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{22}H_{27}O_2]^+$=$[M+H]^+$: 323.2006; found: 323.2011.



12g

E:*Z* = 1:1

Ethyl (2*E*)-3-(4-isopropylphenyl)-5-phenylpent-2-enoate (12g):

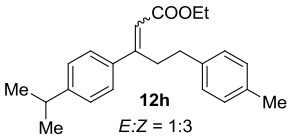
GP-4 was followed to **11g** (378 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester **12g** (406 mg, 84%) as pale yellow viscous liquid. [TLC control R_f(**11g**)=0.40, R_f(**12g**)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2926, 2856, 1712, 1682, 1495, 1452, 1226, 1180, 744 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.42 (d, 2H, *J*=8.3 Hz, ArH), 7.32–7.07 (m, 7H, ArH), 6.08 (s, 1H, C=CH), 4.20 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 3.43–3.34 (m, 2H, CH$_2$), 2.99–2.85 (m, 1H, CH), 2.81–2.65 (m, 2H, CH$_2$), 1.30 (t, 3H, *J*=6.8 Hz, OCH$_2$C*H*$_3$), 1.28 (d, 6H, *J*=2.9 Hz, 2×CH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 159.2 (s, *C*=CH), 150.0 (s, ArC), 141.7 (s, ArC), 138.3 (d, ArC), 128.4 (d, 2C, ArCH), 128.2 (d, 2C, ArCH), 127.3 (d, ArCH), 126.7 (d, ArCH), 126.0 (d, ArCH), 125.9 (d, 2C, ArCH), 117.3 (d, 1H, *C*H=C), 59.8 (t, O*C*H$_2$CH$_3$), 42.0 (t, CH$_2$), 35.3 (t, CH$_2$), 33.8 (d, CH), 23.9 (q, 2 × CH$_3$), 14.3 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{22}H_{27}O_2]^+$=$[M+H]^+$: 323.2006; found: 323.2010.



Ethyl (2*E*)-3-(4-isopropylphenyl)-5-(4-methylphenyl)pent-2-enoate (12h):

GP-4 was followed to **11h** (399 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester **12h** (430 mg, 85%) as pale yellow viscous liquid. [TLC control R_f(**11h**)=0.40, R_f(**12h**)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)].

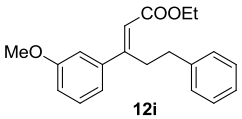
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2960, 2869, 1710, 1621, 1456, 1264, 1158, 1036, 808 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.34–6.94 (m, 8H, ArH), 5.90 (s, 1H, C=CH), 3.99 (q, 2H, *J*=6.8 Hz, OC*H*$_2$CH$_3$), 3.42–3.31 (m, 2H, CH$_2$), 3.01–2.84 (m, 1H, CH), 2.78–2.61 (m, 2H,

CH_2), 2.31 (s, 3H, $ArCH_3$), 1.27 (s, 6H, *J*=2.9 Hz, 2×CH_3), 1.05 (t, 3H, *J*=6.8 Hz, OCH_2CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.1 (s, C=O), 158.6 (s, *C*=CH), 148.3 (s, ArC), 138.6 (s, ArC), 137.9 (d, ArC), 135.4 (d, ArC), 129.0 (d, 2C, ArCH), 128.1 (d, 2C, ArCH), 127.2 (d, 2C, ArCH), 126.6 (d, ArCH), 125.9 (d, ArCH), 117.2 (d, 1H, *C*H=C), 59.7 (t, OCH_2CH_3), 42.2 (t, CH_2), 33.8 (d, CH), 33.5 (t, CH_2), 23.9 (q, 2 × CH_3), 20.9 (q, CH_3), 14.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{23}H_{29}O_2]^+$=$[M+H]^+$: 337.2162; found: 337.2175.



12i

Ethyl (2*E*)-3-(3-methoxyphenyl)-5-phenylpent-2-enoate (12i):

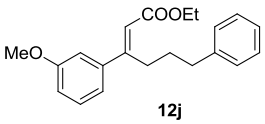
GP-4 was followed to **11i** (360 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 92:8) furnished the ester **12i** (428 mg, 92%) as pale yellow viscous liquid. [TLC control R_f(**11i**)=0.40, R_f(**12i**)=0.60, (petroleum ether/ethyl acetate 92:8, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2924, 2855, 1718, 1681, 1607, 1456, 1233, 1180, 1077, 806 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.53 (dd, 2H, *J*=8.3 and 1.5 Hz, ArH), 7.42–7.34 (m, 3H, ArH), 7.15 (dd, 2H, *J*=8.8 and 2.0 Hz, ArH), 6.81 (dd, 2H, *J*=8.8 and 2.0 Hz, ArH), 6.05 (s, 1H, C=CH), 4.21 (q, 2H, *J*=6.8 Hz, OCH_2CH_3), 3.77 (s, 3H, $ArOCH_3$), 3.39–3.32 (m, 2H, CH_2), 2.70–2.63 (m, 2H, CH_2), 1.30 (t, 3H, *J*=6.8 Hz, OCH_2CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 159.4 (s, *C*=CH), 157.8 (s, ArC), 141.1 (s, ArC), 133.7 (s, ArC), 129.4 (d, 2C, ArCH), 128.9 (d, 2C, ArCH), 128.6 (d, 2C, ArCH), 126.7 (d, 2C, ArCH), 117.8 (d, ArCH), 113.7 (d, 1H, *C*H=C), 59.9 (t, OCH_2CH_3), 55.2 (q, $ArOCH_3$), 34.3 (t, CH_2), 33.4 (t, CH_2), 14.3 (q, OCH_2CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{23}O_3]^+$=$[M+H]^+$: 311.1642; found: 311.1642.



12j

Ethyl (2*E*)-3-(3-methoxyphenyl)-6-phenylhex-2-enoate (12j):

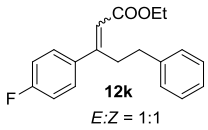
GP-4 was followed to **11j** (381 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 92:8) furnished the ester **12j** (437 mg, 90%) as pale yellow viscous liquid. [TLC control R_f(**11j**)=0.40, R_f(**12j**)=0.60, (petroleum ether/ethyl acetate 92:8, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2929, 2870, 1712, 1682, 1514, 1281, 1162, 835, 698 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.29–7.19 (m, 4H, ArH), 7.17–7.09 (m, 3H, ArH), 6.97 (d, 1H, *J*=8.3 Hz, ArH), 6.89 (dd, 1H, *J*=7.3 and 1.5 Hz, ArH), 6.04 (s, 1H, C=CH), 4.21 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.78 (s, 3H, ArOCH$_3$), 3.13 (t, 2H, *J*=7.8 Hz, CH$_2$), 2.66 (t, 2H, *J*=7.8 Hz, CH$_2$), 1.83–1.67 (m, 2H, CH$_2$), 1.30 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.4 (s, C=O), 160.1 (s, *C*=CH), 159.6 (s, ArC), 142.7 (s, ArC), 142.1 (s, ArC), 129.5 (d, ArCH), 128.4 (d, 2C, ArCH), 128.2 (d, 2C, ArCH), 125.7 (d, ArCH), 119.1 (d, ArCH), 117.7 (d, ArCH), 114.3 (d, ArCH), 112.3 (d, 1H, *C*H=C), 59.9 (t, O*C*H$_2$CH$_3$), 55.2 (q, ArOCH$_3$), 35.8 (t, CH$_2$), 30.7 (t, CH$_2$), 30.6 (t, CH$_2$), 14.3 (q, OCH$_2$*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{21}H_{25}O_3]^+$=$[M+H]^+$: 325.1798; found: 325.1798.



Ethyl (2*E*)-3-(4-fluorophenyl)-5-phenylpent-2-enoate (12k):

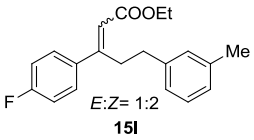
GP-4 was followed to **11k** (342 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester **12k** (420 mg, 94%) as pale yellow viscous liquid. [TLC control R_f(**11k**)=0.40, R_f(**12k**)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2965, 2931, 1713, 1681, 1454, 1284, 1166, 1081, 834, 699 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.50 (dd, 2H, *J*=8.8 and 8.3 Hz, ArH), 7.35–7.22 (m, 3H, ArH), 7.22–7.15 (m, 2H, ArH), 7.12 (d, 1H, *J*=6.8 Hz, ArH), 7.07 (d, 1H, *J*=8.3 Hz, ArH), 6.03 (s, 1H, C=CH), 4.00 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.40–3.31 (m, 1H, CH_2), 2.79–2.63 (m, 3H, CH_2), 1.10 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.1, 158.0, 141.2, 140.5, 138.6, 131.8, 131.1, 130.0, 128.5, 128.3, 126.2, 123.2, 121.9, 118.3, 60.0, 41.9, 35.0, 14.3 ppm.

HR-MS (APCI+): m/z calculated for $[C_{19}H_{20}FO_2]^+$=$[M+H]^+$: 299.1442; found: 299.1452.



15l

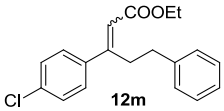
Ethyl (2*E*)-3-(4-fluorophenyl)-5-(3-methylphenyl)pent-2-enoate (15l):

GP-1 was followed to **14l** (363.3 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester **15l** (435 mg, 93%) as pale yellow viscous liquid. [TLC control R_f(**14l**)=0.40, R_f(**15l**)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2962, 2930, 1713, 1621, 1536, 1453, 1161, 1048, 986, 819 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.47 (dd, 2H, *J*=8.3 and 6.8 Hz, ArH), 7.40 (dd, 1H, *J*=8.8 and 2.0 Hz, ArH), 7.32–7.20 (m, 1H, CH_2), 7.19–7.08 (m, 1H, CH_2), 7.07–6.85 (m, 3H, CH_2), 6.00 (d, 1H, C=CH), 4.19 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.36–3.24 (m, 2H, CH_2), 2.72–2.57 (m, 2H, CH_2), 2.28 (s, ArCH$_3$), 1.28 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=171.0 (s, C=O), 166.1 (s, *C*=CH), 158.1 (s, ArC), 141.2 (s, ArC), 138.7 (s, ArC), 138.0 (s, ArC), 131.1 (d, ArCH), 128.9 (d, 2C, ArCH), 128.3 (d, 2C, ArCH), 126.9 (d, 2C, ArCH), 121.8 (d, ArCH), 118.1 (d, 1H, *C*H=C), 59.9 (t, O*C*H$_2$CH$_3$), 41.9 (t, CH_2), 34.9 (t, CH_2), 21.3 (q, ArCH$_3$), 14.3 (q, OCH$_2$*C*H$_3$) ppm.



12m

E:*Z* = 1:1

Ethyl (2*E*)-3-(4-chlorophenyl)-5-phenylpent-2-enoate (12m):

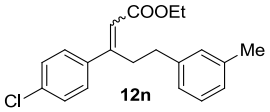
GP-4 was followed to **11m** (366 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the ester **12m** (424 mg, 90%) as pale yellow viscous liquid. [TLC control R_f(**11m**)=0.40, R_f(**12m**)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2981, 2934, 1711, 1626, 1492, 1225, 1162, 1093, 828, 699 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.40–7.30 (m, 3H, ArH), 7.30–7.22 (m, 2H, ArH), 7.22–7.16 (m, 2H, ArH), 7.16–7.07 (m, 2H, ArH), 6.03 (s, 1H, C=CH), 4.21 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.40–3.31 (m, 1H, CH$_2$), 2.78–2.63 (m, 3H, CH$_2$), 1.30 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=166.1 (s, C=O), 157.9 (s, *C*=CH), 141.2 (s, ArC), 139.5 (s, ArC), 133.7 (s, ArC), 128.8 (d, ArCH), 128.7 (d, ArCH), 128.5 (d, 2C, ArCH), 128.3 (d, 2C, ArCH), 128.2 (d, ArCH), 128.0 (d, ArCH), 126.2 (d, ArCH), 118.3 (d, 1H, *C*H=C), 59.9 (t, O*C*H$_2$CH$_3$), 41.9 (t, CH$_2$), 35.0 (t, CH$_2$), 14.3 (q, OCH$_2$*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{19}H_{20}ClO_2]^+$=$[M+H]^+$: 315.1146; found: 315.144.



12n

E:*Z* = 1:2

Ethyl (2*E*)-3-(4-chlorophenyl)-5-(3-methylphenyl)pent-2-enoate (12n):

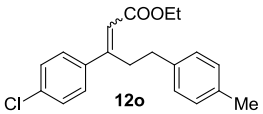
GP-4 was followed to **11n** (387 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester **12n** (453 mg, 92%) as pale yellow viscous liquid. [TLC control R_f(**11n**)=0.40, R_f(**12n**)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2964, 2931, 1707, 1680, 1412, 1228, 1180, 1030, 986, 699 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.43–7.29 (m, 2H, ArH), 7.14 (dd, 2H, *J*=8.3 and 6.8 Hz, ArH), 7.02 (d, 2H, *J*=6.8 Hz, ArH), 6.93 (d, 2H, *J*=6.8 Hz, ArH), 6.04 (d, 1H, C=CH), 4.01 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.35 (t, 1H, *J*=7.8 Hz, CH$_2$), 2.77–2.60 (m, 3H, CH$_2$), 2.31 (s, ArCH$_3$), 1.11 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.1 (s, C=O), 158.0 (s, *C*=CH), 141.2 (s, ArC), 139.5 (s, ArC), 138.2 (s, ArC), 134.9 (s, ArC), 129.2 (d, ArCH), 128.8 (d, 2C, ArCH), 128.4 (d, ArCH), 128.2 (d, 2C, ArCH), 126.9 (d, ArCH), 125.2 (d, ArCH), 118.1 (d, 1H, *C*H=C), 59.4 (t, O*C*H$_2$CH$_3$), 42.0 (t, CH$_2$), 35.0 (t, CH$_2$), 21.3 (q, ArCH$_3$), 14.3 (q, OCH$_2$*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{22}ClO_2]^+$=$[M+H]^+$: 329.1303; found: 329.1299.



12o
E:*Z* = 1:2

Ethyl (2*E*)-3-(4-chlorophenyl)-5-(4-methylphenyl)pent-2-enoate (12o):

GP-4 was followed to **11o** (387 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6) furnished the ester **12o** (453 mg, 92%) as pale yellow viscous liquid. [TLC control R_f(**11o**)=0.40, R_f(**12o**)=0.60, (petroleum ether/ethyl acetate 94:6, UV detection)].

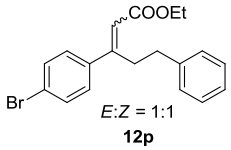
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2924, 2853, 1714, 1624, 1454, 1281, 1165, 1045, 749, 698 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.43–7.27 (m, 2H, ArH), 7.17–7.04 (m, 4H, ArH), 7.04–6.96 (m, 2H, ArH), 6.02 (d, 1H, *J*=4.8 Hz, C=CH), 4.08–3.94 (m, 2H, OC*H*$_2$CH$_3$), 3.39–3.28 (m, 1H, CH$_2$), 2.76–2.58 (m, 3H, CH$_2$), 2.30 (s, ArCH$_3$), 1.36–1.23 (m, 3H, OCH$_2$C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=166.1 (s, C=O), 158.0 (s, *C*=CH), 138.2 (s, ArC), 135.7 (s, 2C, ArC), 133.6 (s, ArC), 129.1 (d, ArCH), 129.0 (d, ArCH), 128.8 (d, ArCH), 128.7

(d, ArCH), 128.3 (d, ArCH), 128.2 (d, ArCH), 128.1 (d, 2C, ArCH), 118.2 (d, 1H, *C*H=C), 60.0 (t, O*C*$H_2$$CH_3$), 42.1 (t, CH_2), 33.3 (t, CH_2), 21.0 (q, ArCH_3), 14.3 (q, OCH_2*C*H_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{22}ClO_2]^+$=$[M+H]^+$: 329.1303; found: 329.1299.



12p

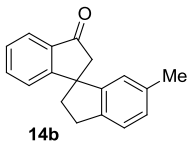
Ethyl (2*E*)-3-(4-bromophenyl)-5-phenylpent-2-enoate (12p):

GP-1 was followed to **11p** (433 mg, 1.5 mmol) with 60% NaH (120 mg, 3.0 mmol), THF (10 mL), TEPA (0.9 mL, 4.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the ester **12p** (503 mg, 94%) as pale yellow viscous liquid. [TLC control R_f(**11p**)=0.40, R_f(**12p**)=0.60, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2964, 2930, 1713, 1681, 1607, 1413, 1227, 1180, 985, 818 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.46–7.31 (m, 2H, ArH), 7.31–6.89 (m, 7H, ArH), 5.98 (s, 1H, C=CH), 4.17 (q, 2H, *J*=7.3 Hz, OC*H*$_2$$CH_3$), 3.38–3.28 (m, 1H, CH_2), 2.75–2.60 (m, 3H, CH_2), 1.27 (t, 3H, *J*=7.3 Hz, OCH_2C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=165.8 (s, C=O), 163.2 (s, *C*=CH), 157.1 (s, ArC), 141.0 (s, ArC), 136.8 (s, ArC), 135.2 (s, ArC), 128.8 (d, ArCH), 128.2 (d, ArCH), 128.1 (d, 2C, ArCH), 127.9 (d, 2C, ArCH), 125.8 (d, ArCH), 117.8 (d, ArCH), 115.3 (d, ArCH), 114.7 (d, 1H, *C*H=C), 59.6 (t, O*C*$H_2$$CH_3$), 41.7 (t, CH_2), 34.7 (t, CH_2), 13.6 (q, OCH_2*C*H_3) ppm.



14b

6'-Methyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2*H*)-one (14b):

GP-5 was carried out with ester **12b** (74 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indanone **14b** (54 mg, 87%) as brown color viscous

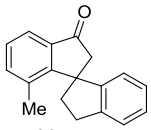
liquid. [TLC control R_f(**12b**)=0.50, R_f(**14b**)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2922, 2851, 1710, 1601, 1461, 1287, 1236, 816, 763 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.79 (d, 1H, *J*=7.8 Hz, ArH), 7.57 (ddd, 1H, *J*=7.3, 7.3 and 1.0 Hz, ArH), 7.41 (ddd, 1H, *J*=7.3, 7.3 and 1.0 Hz, ArH), 7.27 (d, 1H, *J*=7.8 Hz, ArH), 7.21 (d, 1H, *J*=7.8 Hz, ArH), 7.08 (d, 1H, *J*=7.8 Hz, ArH), 6.57 (s, 1H, ArH), 3.19–3.00 (m, 2H, CH_2), 2.94 (d, 1H, *J*=18.6 Hz, CH_aH$_b$), 2.87 (d, 1H, *J*=18.6 Hz, CH$_a$$H_b$), 2.55–2.44 (m, 1H, CH_2), 2.40–2.30 (m, 1H, CH_2), 2.22 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=205.9 (s, C=O), 161.6 (s, ArC), 149.0 (s, ArC), 140.2 (s, ArC), 136.9 (d, ArC), 136.0 (s, ArC), 135.4 (d, ArCH), 128.1 (d, ArCH), 127.8 (d, ArCH), 125.1 (d, ArCH), 124.3 (d, ArCH), 123.3 (d, ArCH), 123.0 (d, ArCH), 54.4 [s, *C*(CH$_2$)$_2$], 52.4 (t, CH_2), 42.9 (t, CH_2), 30.8 (t, CH_2), 21.2 (q, ArCH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{18}$H$_{17}$O]$^+$=[M+H]$^+$: 249.1274; found: 249.1279.



14c

7-Methyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2*H*)-one (14c):

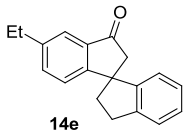
GP-5 was carried out with ester **12c** (74 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indanone **14c** (49 mg, 78%) as brown color viscous liquid. [TLC control R_f(**12c**)=0.50, R_f(**14c**)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2953, 2850, 1708, 1602, 1583, 1477, 1457, 1279, 1267, 1173, 1063, 909, 727 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.67 (dd, 1H, *J*=7.3 and 1.0 Hz, ArH), 7.41–7.26 (m, 3H, ArH), 7.21 (ddd, 1H, *J*=7.3, 7.3 and 1.0 Hz, ArH), 7.13 (dd, 1H, *J*=7.3 and 7.3 Hz, ArH), 6.82 (d, 1H, *J*=7.3 Hz, ArH), 3.24–3.06 (m, 2H, CH_2), 3.01 (d, 1H, *J*=19.1 Hz, CH_aH$_b$), 2.73 (d, 1H, *J*=19.1 Hz, CH$_a$$H_b$), 2.70–2.58 (m, 1H, CH_2), 2.23–2.13 (m, 1H, CH_2), 1.92 (s, 3H, ArCH$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=206.0 (s, C=O), 157.3 (s, ArC), 147.9 (s, ArC), 142.8 (s, ArC), 137.8 (d, ArCH), 137.2 (s, ArC), 136.2 (s, ArC), 128.3 (d, ArCH), 127.2 (d, ArCH), 127.1 (d, ArCH), 124.7 (d, ArCH), 122.6 (d, ArCH), 120.9 (d, ArCH), 55.0 [s, $C(CH_2)_2$], 53.9 (t, CH_2), 40.2 (t, CH_2), 31.1 (t, CH_2), 18.6 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{17}O]^+$=$[M+H]^+$: 248.1196; found: 248.1181.



14e

5-Ethyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2*H*)-one (14e):

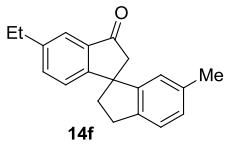
GP-5 was carried out with ester **12e** (77 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 96:4) furnished indanone **14e** (59 mg, 90%) as brown color viscous liquid. [TLC control R_f(**12e**)=0.65, R_f(**14e**)=0.45, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2962, 2929, 1708, 1613, 1577, 1485, 1456, 1241, 1159, 1020, 761 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.61 (s, 1H, ArH), 7.43 (dd, 1H, J=7.8 and 1.5 Hz, ArH), 7.32 (d, 1H, J=7.3 Hz, ArH), 7.24–7.07 (m, 3H, ArH), 6.79 (d, 1H, J=7.8 Hz, ArH), 3.16–3.07 (m, 2H, CH_2), 3.00 (d, 1H, J=18.6 Hz, CH_aH_b), 2.86 (d, 1H, J=18.6 Hz, CH_aH_b), 2.73 (q, 2H, J=7.8 Hz, CH_2CH_3), 2.55–2.43 (m, 1H, CH_2), 2.40–2.28 (m, 1H, CH_2), 1.27 (t, 3H, J=7.8 Hz, CH_2CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=205.9 (s, C=O), 159.2 (s, ArC), 149.0 (s, ArC), 144.2 (s, ArC), 143.2 (s, ArC), 136.3 (s, ArC), 135.8 (d, ArCH), 127.1 (d, 2C, ArCH), 124.8 (d, ArCH), 124.5 (d, ArCH), 122.8 (d, ArCH), 121.7 (d, ArCH), 54.1 [s, -$C(CH_2)_2$], 52.7 (t, CH_2), 42.8 (t, CH_2), 31.2 (t, CH_2), 28.4 (t, CH_2), 15.4 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{19}H_{19}O]^+$=$[M+H]^+$: 263.1430; found: 263.1438.



14f

5-Ethyl-6'-methyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2*H*)-one(14f):

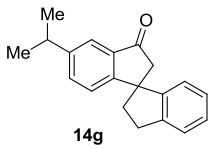
GP-5 was carried out with ester **12f** (81 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone **14f** (58 mg, 84%) as brown color viscous liquid. [TLC control R_f(**12f**)=0.65, R_f(**14f**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2961, 2922, 1713, 1614, 1487, 1456, 1284, 1241, 1159, 1032, 814 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.61 (s, 1H, ArH), 7.44 (dd, 1H, *J*=7.8 and 2.0 Hz, ArH), 7.18 (dd, 2H, *J*=7.3 and 7.8 Hz, ArH), 7.03 (d, 1H, *J*=7.8 Hz, ArH), 6.59 (s, 1H, ArH), 3.15–3.01 (m, 2H, CH_2), 2.94 (d, 1H, *J*=18.6 Hz, CH_aH$_b$), 2.86 (d, 1H, *J*=18.6 Hz, CH$_a$$H_b$), 2.73 (q, 2H, *J*=7.8 Hz, CH_2), 2.54–2.40 (m, 1H, CH_2), 2.39–2.28 (m, 1H, CH_2), 2.23 (s, 3H, ArCH_3), 1.28 (t, 3H, *J*=7.8 Hz, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=206.0 (s, C=O), 159.3 (s, ArC), 149.1 (s, ArC), 144.1 (s, ArC), 140.1 (s, ArC), 136.8 (s, ArC), 136.3 (s, ArC), 135.7 (d, ArCH), 128.0 (d, ArCH), 124.9 (d, ArCH), 124.3 (d, ArCH), 123.4 (d, ArCH), 121.6 (d, ArCH), 54.1 [s, -*C*(CH_2)$_2$], 52.7 (t, CH_2), 43.0 (t, CH_2), 30.8 (t, CH_2), 28.4 (t, CH_2), 21.2 (q, ArCH_3), 15.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{21}O]^+$=$[M+H]^+$: 277.1587; found: 277.1596.



14g

5-Isopropyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2*H*)-one (14g):

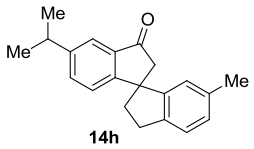
GP-5 was carried out with ester **12g** (81 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone **14g** (60 mg, 86%) as brown color viscous liquid. [TLC control R_f(**12g**)=0.65, R_f(**14g**)=0.50, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2932, 1709, 1676, 1585, 1456, 1413, 1127, 1014 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.65 (s, 1H, ArH), 7.47 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 7.32 (d, 1H, *J*=7.3 Hz, ArH), 7.24–7.08 (m, 3H, ArH), 6.80 (d, 1H, *J*=7.3 Hz, ArH), 3.21–3.05 (m, 2H, CH_2), 3.04–2.91 (m, 2H, CH_2), 2.86 (d, 1H, *J*=18.6 Hz, CH_aH_b), 2.56–2.43 (m, 1H, CH_2), 2.40–2.28 (m, 1H, CH), 1.28 (d, 3H, *J*=1.5 Hz, CH_3), 1.27 (d, 3H, *J*=1.5 Hz, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=206.0 (s, C=O), 159.3 (s, ArC), 149.0 (s, ArC), 148.9 (s, ArC), 143.2 (s, ArC), 136.2 (s, ArC), 134.6 (d, ArCH), 127.1 (d, 2C, ArCH), 124.8 (d, ArCH), 124.5 (d, ArCH), 122.7 (d, ArCH), 120.1 (d, ArCH), 54.1 (s, -C-), 52.7 (t, CH_2), 42.8 (t, CH_2), 33.8 (d, CH), 31.2 (t, CH_2), 23.8 (q, 2 × CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{21}O]^+$=$[M+H]^+$: 277.1587; found: 277.1602.



14h

5-Isopropyl-6'-methyl-2',3'-dihydro-1,1'-spirobi[inden]-3(2*H*)-one (14h):

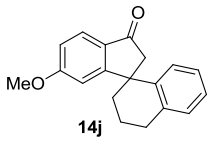
GP-5 was carried out with ester **12h** (84 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone **14h** (62 mg, 85%) as brown color viscous liquid. [TLC control R_f(**12h**)=0.60, R_f(**14h**)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2930, 1710, 1674, 1586, 1456, 1412, 1127, 1014 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.65 (s, 1H, ArH), 7.47 (dd, 1H, *J*=7.8 and 1.5 Hz, ArH), 7.19 (dd, 2H, *J*=7.8 and 7.8 Hz, ArH), 7.03 (d, 1H, *J*=7.8 Hz, ArH), 6.60 (s, 1H, ArH), 3.20–3.04 (m, 2H, CH_2), 3.03–2.92 (m, 2H, CH_2), 2.94 (d, 1H, *J*=18.6 Hz, CH_aH_b), 2.54–2.43 (m, 1H, CH), 2.38–2.27 (m, 2H, CH_2), 2.23 (s, 3H, $ArCH_3$), 1.30 (d, 3H, *J*=2.0 Hz, CH_3), 1.26 (d, 3H, *J*=2.0 Hz, CH_3) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=206.1 (s, C=O), 159.4 (s, ArC), 149.1 (s, ArC), 148.8 (s, ArC), 140.2 (s, ArC), 136.8 (s, ArC), 136.2 (s, ArC), 134.6 (d, ArCH), 128.0 (d, ArCH), 124.8 (d, ArCH), 124.2 (d, ArCH), 123.3 (d, ArCH), 120.1 (d, ArCH), 54.0 [s, -*C*$(CH_2)_2$], 52.7 (t, CH_2), 43.0 (t, CH_2), 33.8 (d, CH), 30.8 (t, CH_2), 23.8 (q, 2 × CH_3), 21.2 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{21}H_{23}O]^+$=$[M+H]^+$: 291.1743; found: 291.1731.



14j

6-Methoxy-3',4'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-3(2*H*)-one (14j):

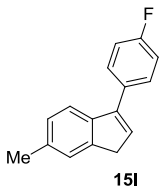
GP-5 was carried out with ester **12j** (81 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indanone **14j** (54 mg, 78%) as brown color viscous liquid. [TLC control R_f(**12j**)=0.65, R_f(**14j**)=0.45, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2925, 2852, 1703, 1597, 1487, 1454, 1274, 1087, 1021, 733 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.73 (d, 1H, *J*=8.3 Hz, ArH), 7.16–7.06 (m, 2H, ArH), 7.05–6.97 (m, 2H, CH_2), 6.95 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 6.61 (dd, 1H, *J*=8.3 and 2.0 Hz, ArH), 3.78 (s, 3H, ArOMe), 3.03–2.91 (m, 2H, CH_2), 2.89 (d, 1H, *J*=18.6 Hz, CH_aH$_b$), 2.81 (d, 1H, *J*=18.6 Hz, CH$_a$$H_b$), 2.15–1.98 (m, 2H, CH_2), 1.97–1.79 (m, 2H, CH_2) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=204.1 (s, C=O), 167.0 (s, ArC), 165.7 (s, ArC), 142.0 (s, ArC), 136.7 (s, ArC), 130.0 (s, ArC), 129.0 (d, ArCH), 128.2 (d, ArCH), 126.6 (d, ArCH), 126.3 (d, ArCH), 124.9 (d, ArCH), 115.9 (d, ArCH), 108.6 (d, ArCH), 56.0 [s, *C*(CH_2)$_2$], 55.7 (t, CH_2), 46.7 (q, ArOMe), 39.4 (t, CH_2), 29.7 (t, CH_2), 21.0 (t, CH_2) ppm.

HR-MS (APCI+): m/z calculated for [$C_{19}H_{19}O_2$]$^+$=[M+H]$^+$: 279.1380; found: 279.1386.



15l

3-(4-fluorophenyl)-6-methyl-1*H*-indene (15l):

GP-6 was carried out with ester **12l** (78 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished indene **15l** (39 mg, 70%) as brown color viscous

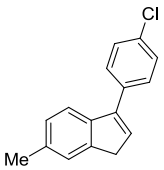
liquid. [TLC control R_f(**12l**)=0.45, R_f(**15l**)=0.65, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2934, 1731, 1597, 1452, 1368, 1221, 1158, 1031, 747, 697 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.65–7.53 (m, 2H, ArH), 7.46 (d, 1H, *J*=7.8 Hz, ArH), 7.37 (s, 1H, ArH), 7.22–7.09 (m, 3H, ArH), 6.55 (t, 1H, *J*=2.0 Hz, CH=C), 3.5 (s, 2H, CH_2), 2.44 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=163.5, 144.1, 141.7, 135.8, 132.3, 131.2, 129.3, 129.2, 125.8, 123.8, 120.8, 115.8, 115.3, 37.7, 21.6 ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{14}F]^+$=$[M+H]^+$: 225.1074; found: 225.1079.



15n

3-(4-chlorophenyl)-6-methyl-1*H*-indene (15n):

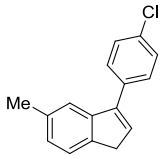
GP-6 was carried out with ester **12n** (82 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished indene **15n** (46 mg, 77%) as brown color viscous liquid. [TLC control R_f(**12n**)=0.45, R_f(**15n**)=0.60, (petroleum ether/ethyl acetate 97:3, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2923, 1705, 1661, 1489, 1379, 1256, 1092, 1014, 818 cm^{-1}.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ=7.56–7.50 (m, 2H, ArH), 7.45–7.38 (m, 3H, ArH), 7.36 (s, 1H, ArH), 7.15 (d, 1H, *J*=7.8 Hz, ArH), 6.50 (t, 1H, *J*=2.0 Hz, CH=C), 2.47 (d, 1H, *J*=2.0 Hz, CH_2), 2.43 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR (CDCl$_3$, 100 MHz): δ=145.0 (s, ArC), 143.9 (s, ArC), 140.9 (s, ArC), 134.8 (d, ArC), 134.7 (s, ArC), 133.2 (s, ArC), 130.4 (d, ArCH), 128.9 (d, 2C, ArCH), 128.7 (d, 2C, ArCH), 126.9 (d, ArCH), 125.1 (d, ArCH), 119.7 (d, CH=C), 38.0 (t, CH_2), 21.4 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{14}Cl]^+$=$[M+H]^+$: 241.0779; found: 241.0783.



15o

3-(4-chlorophenyl)-5-methyl-1*H*-indene (15o):

GP-6 was carried out with ester **12o** (82 mg, 0.25 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.5 mmol). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3) furnished indene **15o** (47 mg, 78%) as brown color viscous liquid. [TLC control R_f(**12o**)=0.45, R_f(**15o**)=0.60, (petroleum ether/ethyl acetate 97:3, UV detection)].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2920, 1726, 1613, 1487, 1393, 1288, 1093, 1014, 885, 803, 731 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ=7.57 (dd, 2H, *J*=8.3 and 2.0 Hz, ArH), 7.47 (dd, 3H, *J*=8.3 and 2.0 Hz, ArH), 7.38 (s, 1H, ArH), 7.14 (d, 1H, *J*=8.3 Hz, ArH), 6.58 (t, 1H, *J*=2.0 Hz, CH=C), 3.49 (d, 1H, *J*=2.0 Hz, CH_2), 2.45 (s, 3H, $ArCH_3$) ppm.

^{13}C-NMR ($CDCl_3$, 100 MHz): δ=144.0 (s, ArC), 143.7 (s, ArC), 141.7 (s, ArC), 135.8 (d, ArC), 134.6 (s, ArC), 133.3 (s, ArC), 131.7 (d, ArCH), 129.0 (d, 2C, ArCH), 128.7 (d, 2C, ArCH), 125.9 (d, ArCH), 123.9 (d, ArCH), 120.7 (d, CH=C), 37.8 (t, CH_2), 21.6 (q, $ArCH_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{16}H_{14}Cl]^+$=$[M+H]^+$: 241.0779; found: 241.0787.

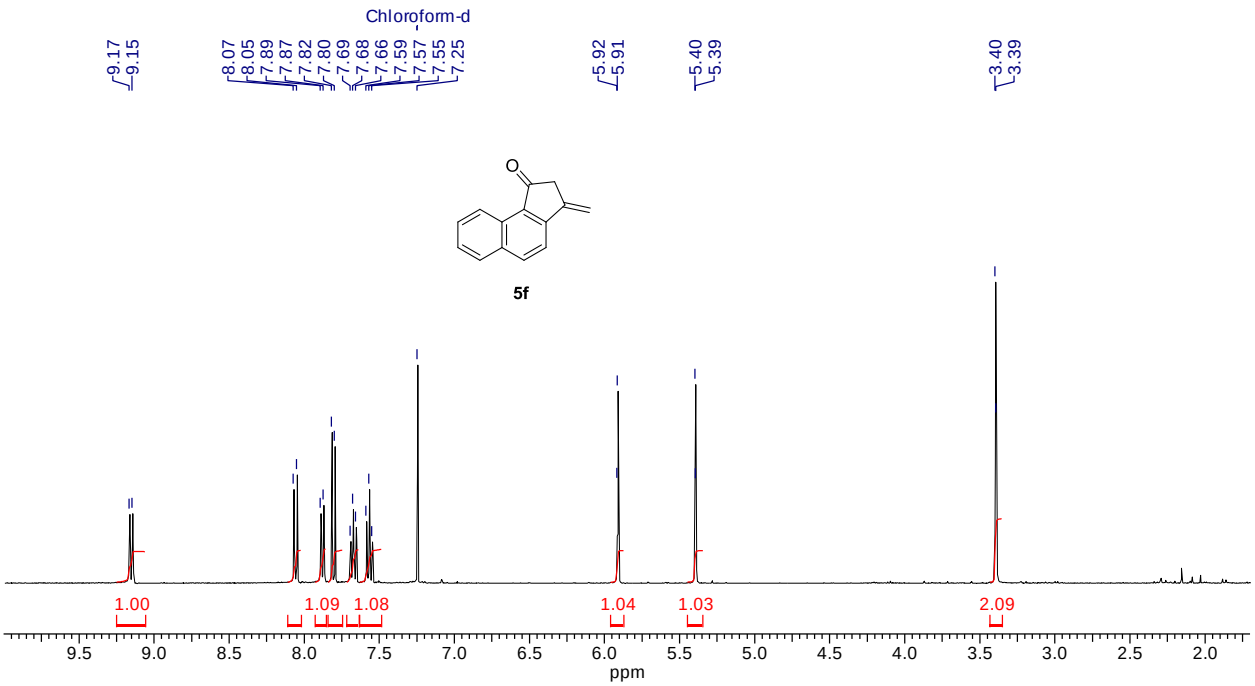


Figure II.23: ^{1}H-NMR (400 MHz) spectrum of **5f** in $CDCl_3$

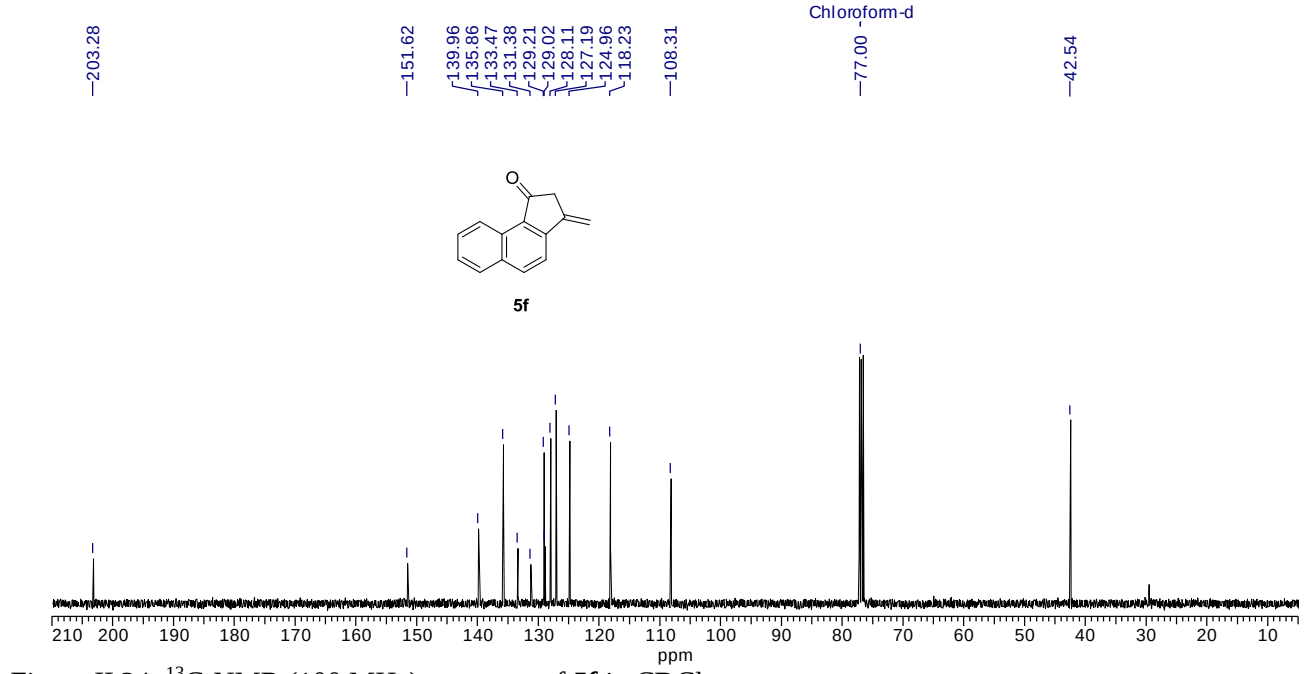


Figure II.24: ^{13}C-NMR (100 MHz) spectrum of **5f** in $CDCl_3$

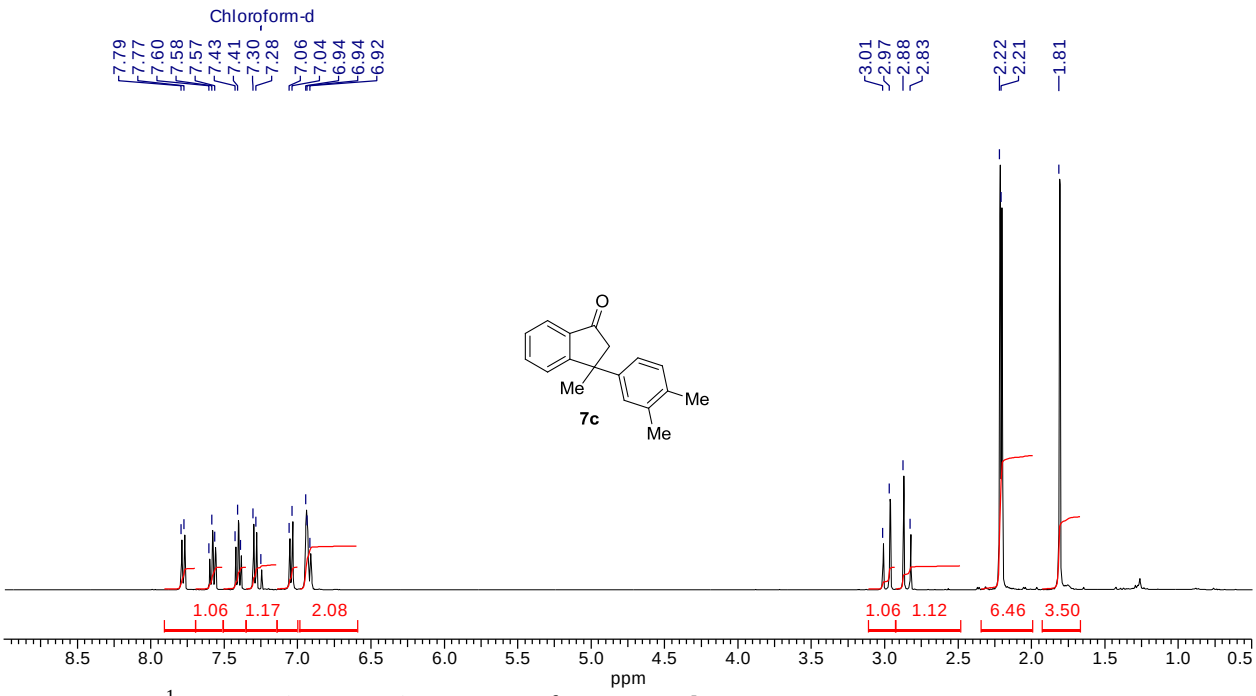


Figure II.25: ^{1}H-NMR (400 MHz) spectrum of **7c** in $CDCl_3$

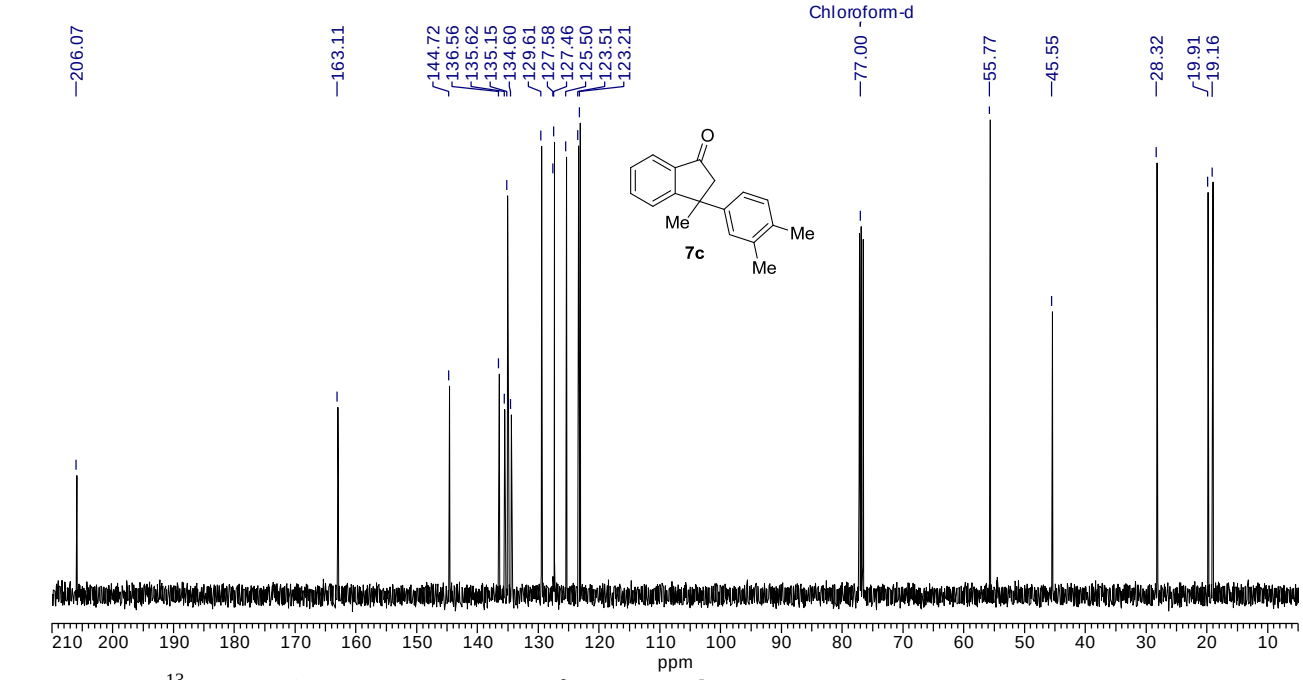


Figure II.26: ^{13}C-NMR (100 MHz) spectrum of **7c** in $CDCl_3$

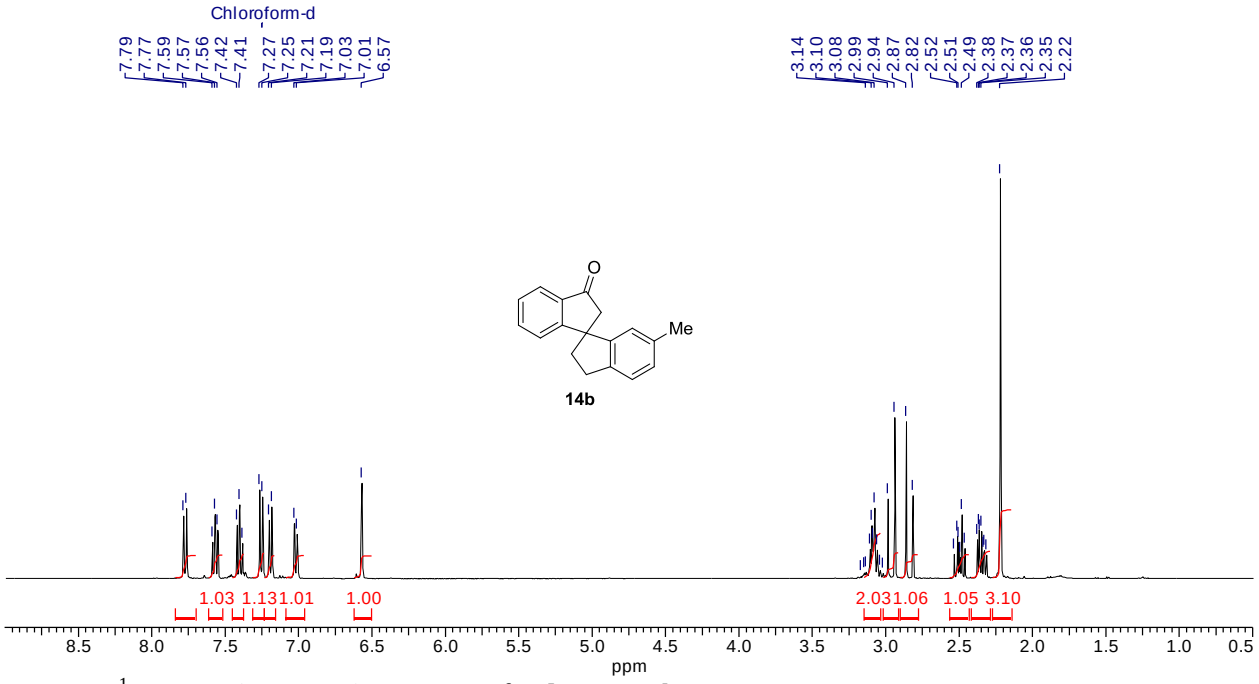


Figure II.27: ^{1}H-NMR (400 MHz) spectrum of **14b** in $CDCl_3$

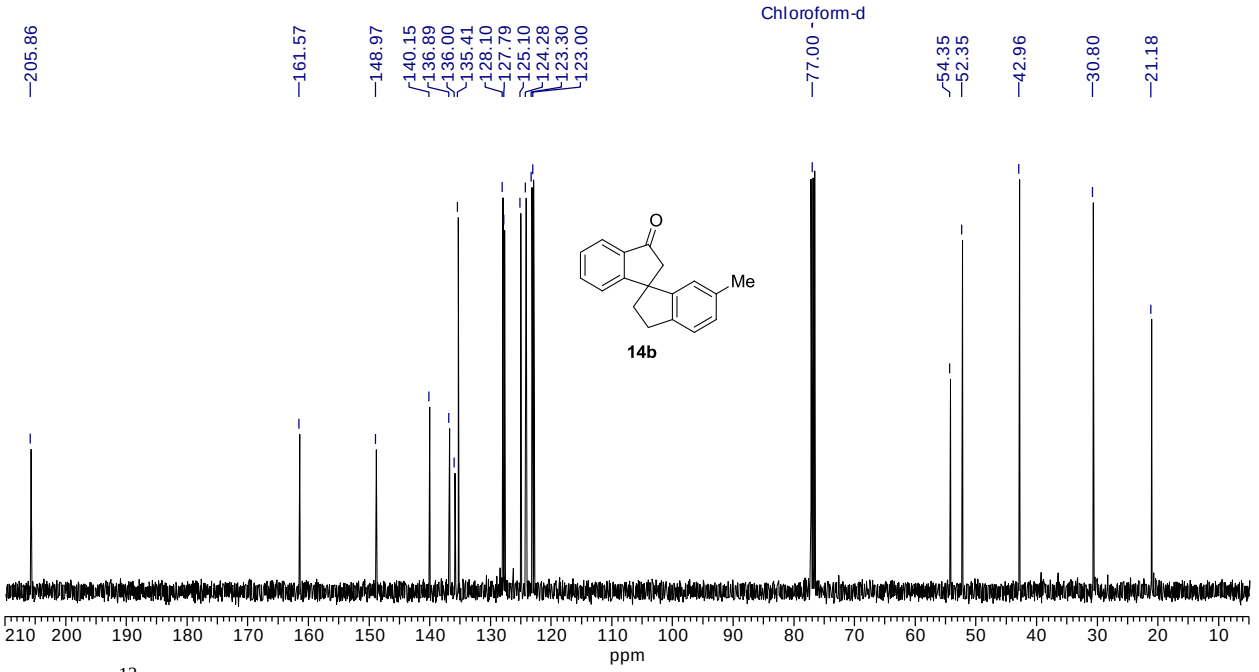


Figure II.28: ^{13}C-NMR (100 MHz) spectrum of **14b** in $CDCl_3$

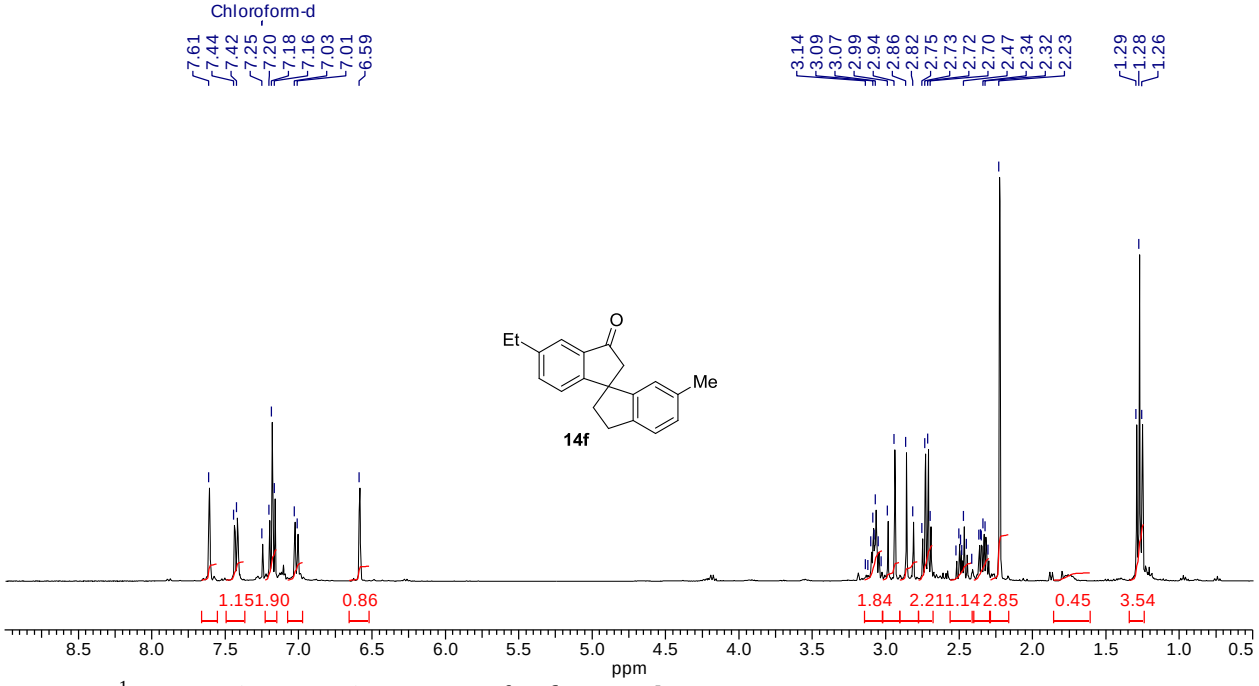


Figure II.29: ^{1}H-NMR (400 MHz) spectrum of **14f** in $CDCl_3$

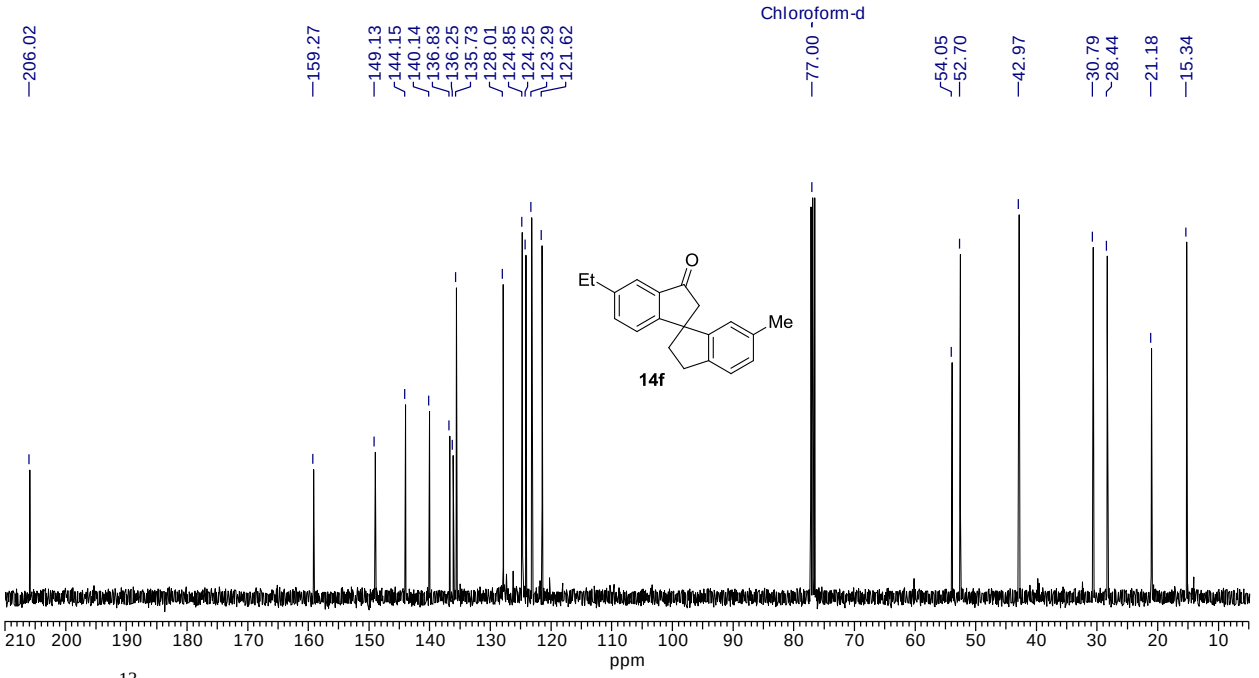


Figure II.30: ^{13}C-NMR (100 MHz) spectrum of **14f** in $CDCl_3$

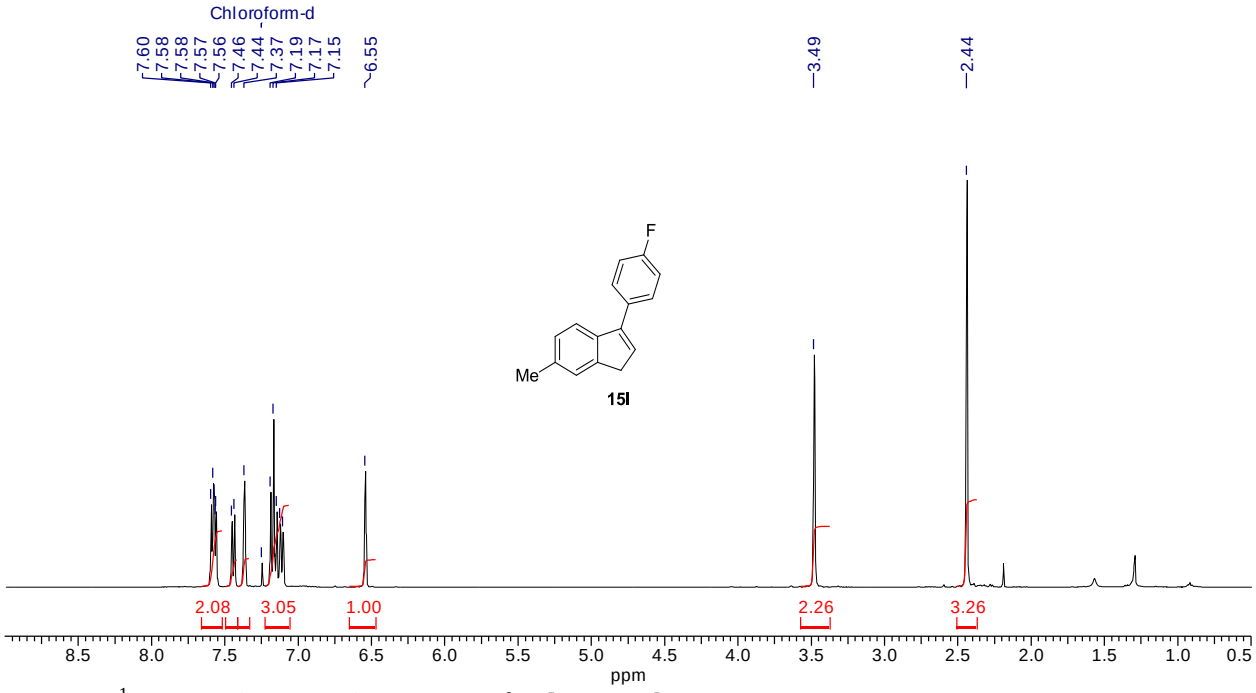


Figure II.31: ^{1}H-NMR (400 MHz) spectrum of **15l** in $CDCl_3$

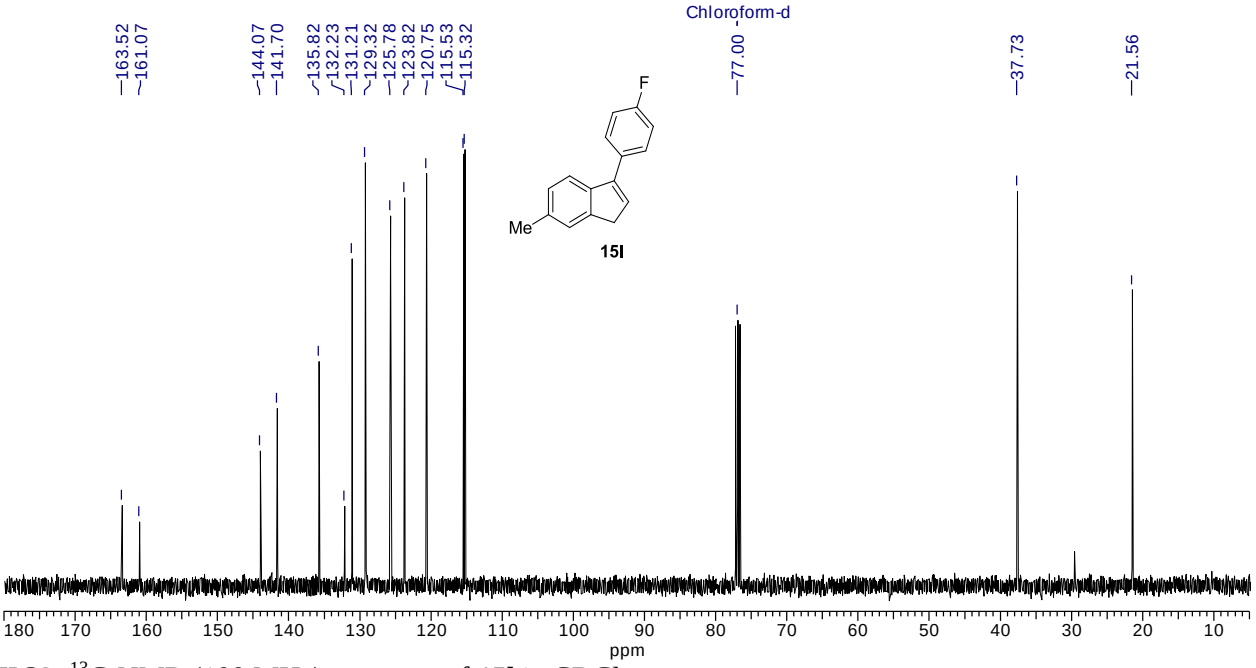


Figure II.32: ^{13}C-NMR (100 MHz) spectrum of **15l** in $CDCl_3$

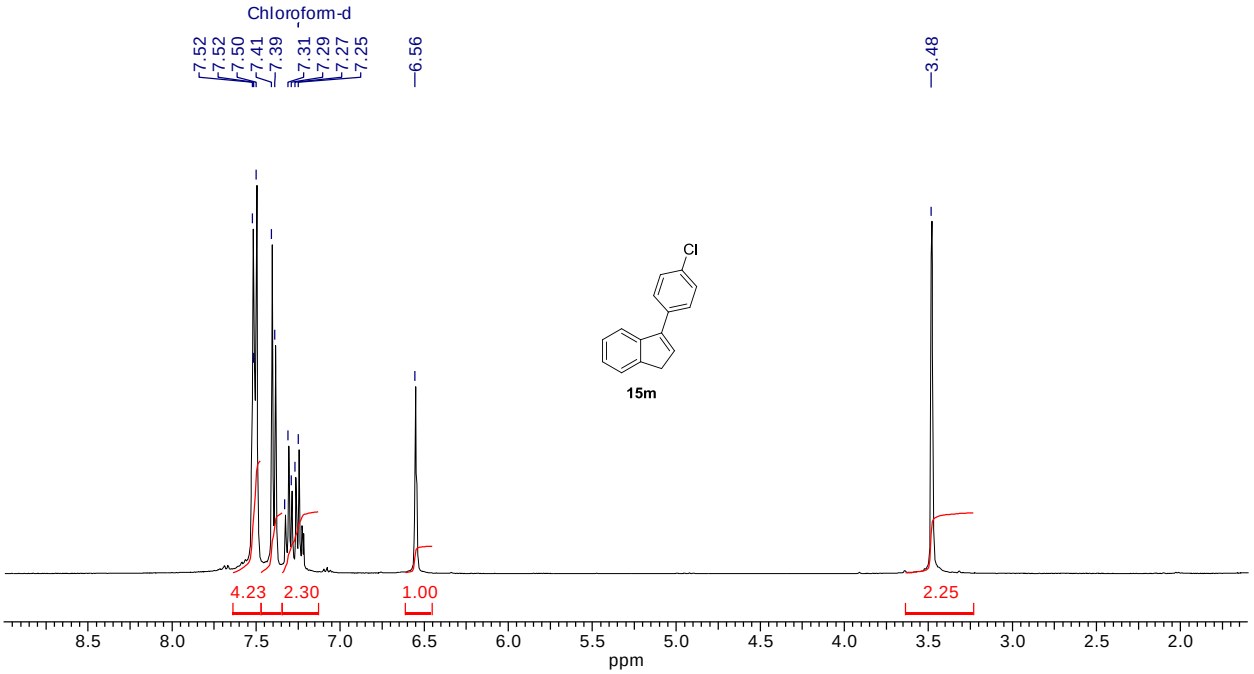


Figure II.33: ^{1}H-NMR (400 MHz) spectrum of **15m** in $CDCl_3$

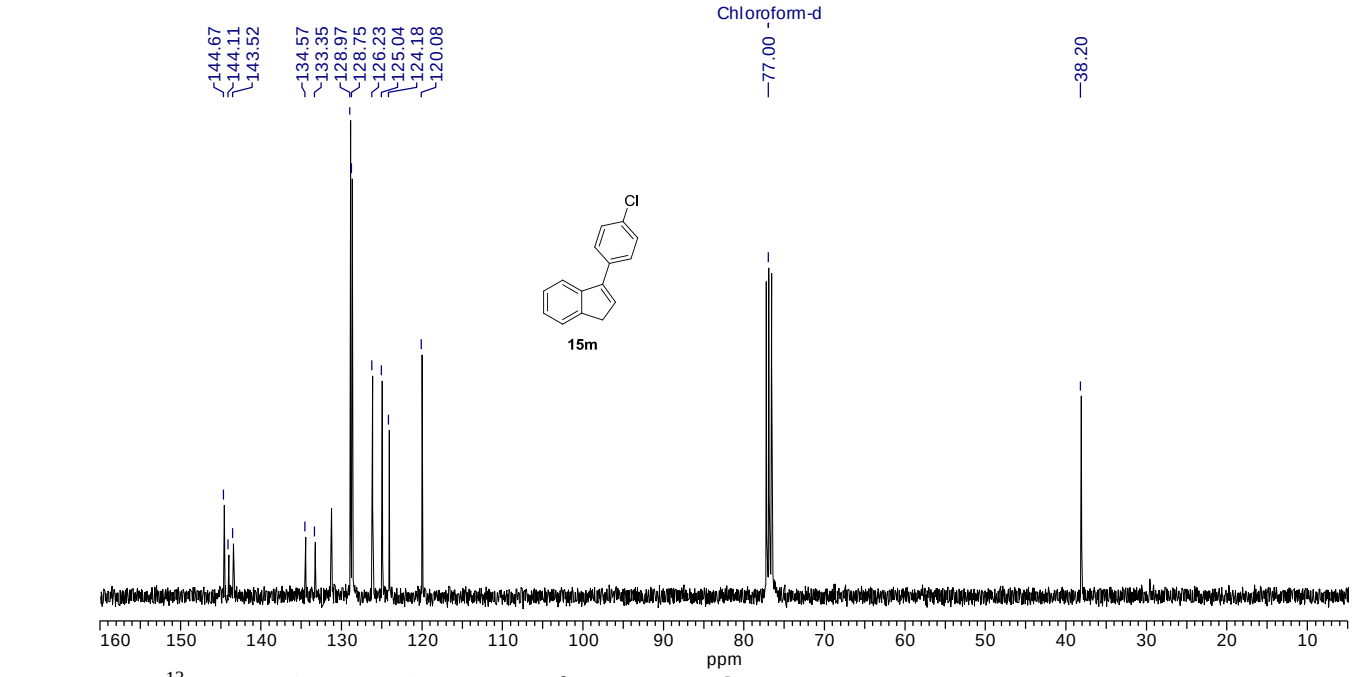


Figure II.34: ^{13}C-NMR (100 MHz) spectrum of **15m** in $CDCl_3$

Notes and references:

1) Friedel, C.; Crafts, J. M. *C. R. Hebd. Seances Acad. Sci.* **1877**, *84*, 1450.
2) For monographs on the Friedel-Crafts acylation reaction, see; a) Heaney, H.; *In Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Pergamon Press: Oxford, UK, **1991**, *2*, 733. (b) *In Friedel−Crafts and Related Reactions*; Olah, G. A.; Ed. John Wiley & Sons Inc.; London, **1964**, *3*, Part I, p 1. (c) Olah, G. A.; Klumpp, D. A.; *Superelectrophiles and Their Chemistry*; Wiley: New York, **2008**.
3) (a) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227. (b) Poulsen, T. B.; Jorgensen, K. A. *Chem. Rev.* **2008**, *108*, 2903. (c) Sartori, G.; Maggi, R. *Chem. Rev.* **2011**, *111*, 181. (d) Rueping, M.; Nachtsheim, B. J. *Beils. J. Org. Chem.* **2010**, *6*, 6. (e) Shi, M.; Lu, J.-M.; Wei, Y.; Shao, L.-X. *Acc. Chem. Res.* **2012**, *45*, 641. (f) Corma, A.; Garcia, H.; *Chem. Rev.* **2003**, *103*, 4307. (g) Gore, P. H. *Chem. Rev.* **1955**, *55*, 229. (h) Johnson, W. S. *Org. React.* **1944**, *2*, 114.
4) a) Sai, K. K. S.; Tokarz, M. J.; Malunchuk, A. P.; Zheng, C.; Gilbert, T. M.; Klumpp, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 14388. (b) Zhang, Y.; Sheets, M. R.; Raja, E. K.; Boblak, K. N.; Klumpp, D. A. *J. Am. Chem. Soc.* **2011**, *133*, 8467. (c) Evans, D. A.; Fandrick, K. R. *Org. Lett.* **2006**, *8*, 2249. (d) Rose, M. D.; Cassidy, M. P.; Rashatasakhon, P.; Padwa, A. *J. Org. Chem.* **2007**, *72*, 538. (e) Wu, Y.-C.; Liu, L.; Liu, Y.-L.; Wang, D.; Chen, Y.-J. *J. Org. Chem.* **2007**, *72*, 9383.
5) a) Ito, T.; Tanaka, T.; Iinuma, M.; Nakaya, K.-i.; Takahashi, Y.; Sawa, R.; Murata, J.; Darnaedi, D. *J. Nat. Prod.* **2004**, *67*, 932. (b) Palermo, J. A.; Brasco, M. F. R.; Spagnuolo, C.; Seldes, A. M. *J. Org. Chem.* **2000**, *65*, 4482. (c) Sugimoto, H.; Iimura, Y.; Yamanishi, Y.; Yamatsu, K. *J. Med. Chem.* **1995**, *38*, 4821. (d) Oshima, Y.; Ueno, Y.; *Phytochemistry*, **1993**, *33*, 179. (e) Lopes, L. M. X.; Yoshida, M.; Gottlieb, O. R. *Phytochemistry*, **1984**, *23*, 2021. (f) Harrowven, D. C.; Newman, N. A.; Knight, C. A. *Tetrahedron Lett.* **1998**, *39*, 6757. (g) Park, C. H.; Siomboing, X.; Yous, S.; Gressier, B.; Luyckx, M. Chavatte, P. *Eur. J. Med. Chem.* **2002**, *37*, 461. (h) Watanabe, N.; Ikeno, A.; Minato, H.; Nakagawa, H.; Kohayakawa, C.; Tsuji, J. *J. Med. Chem.* **2003**, *46*, 3961. (i) Barbera, J.; Rakitin, O. A.; Ros, M. B.; Torroba, T. *Angew. Chem. Int. Ed.* **1998**, *37*, 296.

6) a) Shintani, R. Hayashi, T. *Org*. *Lett.* **2005**, ***7***, 2071. (b) Yamabe, H.; Mizuno, A.; Kusama, H.; Iwasawa, N. *J. Am. Chem*. *Soc*. **2005**, *127*, 3248. (c) Shintani, R.; Okamoto, K.; Hayashi, T. *J. Am*. *Chem*. *Soc*. **2005**, *127*, 2872.

7) a) Lawrence, N. J.; Armitage, E. M. S.; Greedy, B.; Cook, D.; Ducki, S.; McGown, A. T.; *Tetrahedron Lett*. **2006**, *47*, 1637. (b) Yin, W.; Ma, Y.; Xu, J.; Zhao, Y.; *J*. *Org*. *Chem*. **2006**, *71*, 4312.

8) a) Fukuyama, T.; Chatani, N.; Kakiushi, F.; Murai, S.; *J*. *Org*. *Chem*. **1997**, *62*, 5647. (b) Guo, Z. Xi, R.; Mito, S.; Yan, H.; Kanno, K.-I.; Nakajima, K.; Takahashi, Y. *J*. *Org*. *Chem*. **2003**, *68*, 1252. (c) Rayabarapu, D. K.; Yang, C-H.; Cheng, C-H. *J*. *Org*. *Chem*. **2003**, *68*, 6726. d) Chang, K-J.; Rayabarapu, D. K.; Cheng, C.-H. *J*.*Org*. *Chem*. **2004**, *69*, 4781.

9) a) Larock, R. C.; Doty, M. J.; Cacchi, S. *J*. *Org*. *Chem*. **1993**, *58*, 4579. (b) Gevorgyan, V.; Quan, L. G.; Yamamoto, Y. *Tetrahedron Lett*, **1999**, *40*, 4089. (c) Quan, L. G.; Gevorgyan, V. Yamamoto, Y. *J*. *Am*. *Chem*. *Soc.* **1999**, *121*, 3545.

10) Brocato, E.; Castagnoli, C.; Catellani, M.; Chiusoli, G. P. *Tetrahedron Lett*. **1992**, *33*, 7433.

11) Minatti, A.; Zheng, X.-L.; Buchwald, S. L. *J*. *Org*. *Chem*. **2007**, *72*, 9253.

12) Pi, S.-F.; Yang, X.-H.; Huang, X.-C.; Liang, Y.; Yang, G.-N.; Zhang, X.-H.; Li, J.-H. *J*. *Org*. *Chem*. **2010**, *75*, 3484.

13) Nagao, Y.; Lee, W.-S.; Kim, K. *Chem*. *Lett*. **1994**, 389.

14) a) Wang, L.-J.; Zhu, H.-T.; Wang, A.-Q.; Qiu, Y.-F.; Liu, X.-Y.; Liang, Y.-M. *J*. *Org*. *Chem*. **2014**, *79*, 204. (b) Yang, F.; Qiu, Y.-F.; Ji, K.-G.; Niu, Y.-N.; Ali, S.; Liang, Y.-M. *J*. *Org*. *Chem*. **2012**, *77*, 9029. (c) Qiu, Y.-F.; Yang, F.; Qiu, Z.-H.; Zhong, M.-J.; Wang, L.-J.; Ye, Y.-Y. ; Song, B.; Liang, Y.-M. *J*. *Org*. *Chem*. **2013**, *78*, 12018.

15) Kurouchi, H.; Sugimoto, H.; Otani, Y.; Ohwada, T. *J*. *Am*. *Chem*. *Soc*. **2010**, *132*, 807.

16) a) Womack, G. B.; Angeles, J. G.; Fanelli, V. E.; Heyer, C. A. *J*. *Org*. *Chem*. **2007**, *72*, 7046.

17) a) Rendy, R.; Zhang, Y.; McElrea, A.; Gomez, A.; Klumpp, D. A. *J*. *Org*. *Chem*. **2004**, *69*, 2340. (b) Boblak, K. N.; Klumpp, D. A. *J*. *Org*. *Chem*. **2014**, *79*, 5852. (c) Klumpp, D. A.; Baek, D. N.; Prakash, G. K. S.; Olah, G. A. *J*. *Org*. *Chem*. **1997**, *62*, 6666. (d)

Raja, E. K.; DeSchepper, D. J.; Lill, S. O. N.; Klumpp, D. A. *J. Org. Chem.* **2012**, *77*, 5788.

18) a) Fillion, E.; Fishlock, D.; Wilsily, A.; Goll, J. M. *J. Org. Chem.* **2005**, *70*, 1316. (b) Fillion, E.; Dumas, A. M.; Kuropatwa, B. A.; Malhotra, N. R.; Sitler, T. C. *J. Org. Chem.* **2006**, *71*, 409.

19) a) Nishimoto, Y.; Babu, S. A.; Yasuda, M.; Baba, A. *J. Org. Chem.* **2008**, *73*, 9465. (b) Babu, S. A.; Yasuda, M.; Baba, A. *Org. Lett.* **2007**, *9*, 405.

20) (a) Ramulu, B. V.; Reddy, A. G. K.; Satyanarayana, G. *Synlett*, **2013**, *24*, 868. (b) Ramulu, B. V.; Niharika, P.; Satyanarayana, G. *Synthesis*, **2015**, *47*, 1255.

21) Das, A.; Reddy, A. G. K.; Krishna, J.; Satyanarayana, G. *RSC Adv*. **2014**, *4*, 26662.

22) Trahanovsky, W. S.; Amah, A. N.; Cassady, T. J. *J. Am. Chem. Soc*. **1984**, *106*, 2691.

23) a) Fukuyama, T.; Chatani, N.; Kakiushi, F.; Murai, S. *J. Org. Chem*.**1997**, *62*, 5647. b) Xi, Z.; Guo, R.; Mito, S.; Yan, H.; Kanno, K-I.; Nakajima, K.; Takahashi, Y. *J. Org. Chem*. **2003**, *68*, 1252. c) Rayabarapu, D. K.; Yang, C.-H.; Cheng, C.-H. *J. Org. Chem*., **2003**, *68*, 6726. d) Chang, K.-J.; Rayabarapu, D. K.; Cheng, C.-H. *J.Org. Chem*. **2004**, *69*, 4781.

24) Xi, Z.; Guo, R.; Mito, S.; Yan, H.; Kanno, K.; Nakajima, K.; Takahashi, T. *J. Org. Chem*. **2003**, *68*, 1252.

25) (a) Fan, Y. C.; Kwon, O. *Org. Lett.* **2015**, *17*, 2058. (b) Fan, Y. C.; Kwon, O. *Org. Lett*. **2012**, *14*, 3264.

26) Campaigne, E. Frierson, M. R. J.; *Heterocyclic Chem*. **1979**, *16*, 235.

27) Nosel, P.; Comprido, L. N. S.; Lauterbach, T.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *J. Am. Chem. Soc*. **2013**, *135*, 15662.

28) (a) Dethe, D. H.; Murhade, G. *Org. Lett*. **2013**, *15*, 429. (b) Dethe, D. H.; Murhade, G. M. *Chem. Commun*. **2015**, *51*, 10891.

29) Galatsis, P.; Manwell, J. J.; Blackell, J. M. *Can. j. Chem*. **1994**, *72*. 1656.

30) Mondal, S.; Mohamed, R. K.; Manoharan, M.; Phan, H.; Alabugin, I. V. *Org. Lett*. **2013**, *15*, 5650.

31) (a) Sun, L.; Zhu, Y.; Wang, J.; Lu, P.; Wang, Y. *Org. Lett*. **2015**, *17*, 242. (b) Mothe, S.R.; Novianti, M. L.; Ayers, B. J.; Chan, P.W. H. *Org. Lett*. **2014**, *16*, 4110.

32) Han, Y.-Y. W.-Y. Han, X. Hou, X.-M. Zhang and W.-C. Yuan, *Org. Lett*. **2012**, *14*, 4045.

33) (a) England, D. B.; Merey, G.; Padwa, A. *Org. Lett*. **2007**, *9*, 3805. (b) Beckett, A. H.; Daisley, R. W.; Walker, J. *Tetrahedron* **1968**, *24*, 6093.

34) Takahashi, T.; Tsutsui, H.; Tamura, M.; Kitagaki, S.; Nakajima, M.; Hashimoto, S. *Chem. Commun*. **2001**, 1604.

35) (a) Matsuda, T.; Suda, Y.; Takahashi, A. *Chem. Commun*. **2012**, *48*, 2988. (b) Hayashi, T.; Inoue, K.; Taniguchi, N.; Ogasawara, M. *J. Am. Chem. Soc*. **2001**, *123*, 9918. (c) Miura, T.; Sasaki, T.; Nakazawa, H. Murakami, M. *J. Am. Chem. Soc*. **2005**, *127*, 1390. (d) Shintani, R.; Isobe, M.; Takeda, M.; Hayashi, T. *Angew. Chem., Int. Ed*. **2010**, *49*, 3795.

36) Matsuda, T.; Yasuoka, S.; Watanuki, S.; Fukuhar, K. *Synlett*, **2015**, *26*, 1233.

37) Reddy, A. G. K.; Mahendar, L.; Satyanarayana, G. *Synth. Commun.* **2014**, *44*, 2076.

38) Budhram, R. S.; Palaniswamy, V. A.; Eisenbraun, E. J. *J. Org. Chem.* **1986**, *51*, 1402.

39) Mantilli, L.; Gerard, D.; Torche, S.; Besnard, C.; Mazet, C. *Chem. Eur. J.* **2010**, *16*, 12736.

40) Paulis, T.; Betts, C. R.; Smith, H. E. *J. Med. Chem*, **1981**, *24*, 1023.

CHAPTER III

Lewis Acid Catalyzed Mild Method for Head to Tail Dimerization or Cyclization of tert-Alcohols

III.1 INTRODUCTION:

The indane ring system is an attractive scaffold for biologically active compounds due to the combination of aromatic and aliphatic properties fused together in one rigid system. This bicyclic structure provides a wide range of possibilities to incorporate specific substituents in different directionalities, thus being an attractive scaffold for medicinal chemists. Interestingly, many indane-based compounds have been used to treat various diseases, such as indinavir,[1] an HIV-1 protease inhibitor; indantadol,[2] a potent MAO-inhibitor; the amine uptake inhibitor indatraline,[3] and the ultra–long–acting β-adrenoreceptor agonist indacaterol. These drugs act on the diversity of targets, one could argue that the indane ring system is a privileged substructure, just like indole, the nitrogen atom containing unsaturated version of it.[4] The substructure of indane found in many natural products such as pterosins, indanomycin and stawamycin, also present in widely marketed drug molecules like indinavir, an HIV-1 protease inhibitor, indantadol, a potent MAO-inhibitor, the amine uptake inhibitor indatraline, the anti-

inflammatory clidinac, antiarrhythmic agent indecainide,[5] diuretic indacrinone[6] and the anticoagulant hedulin.[7]

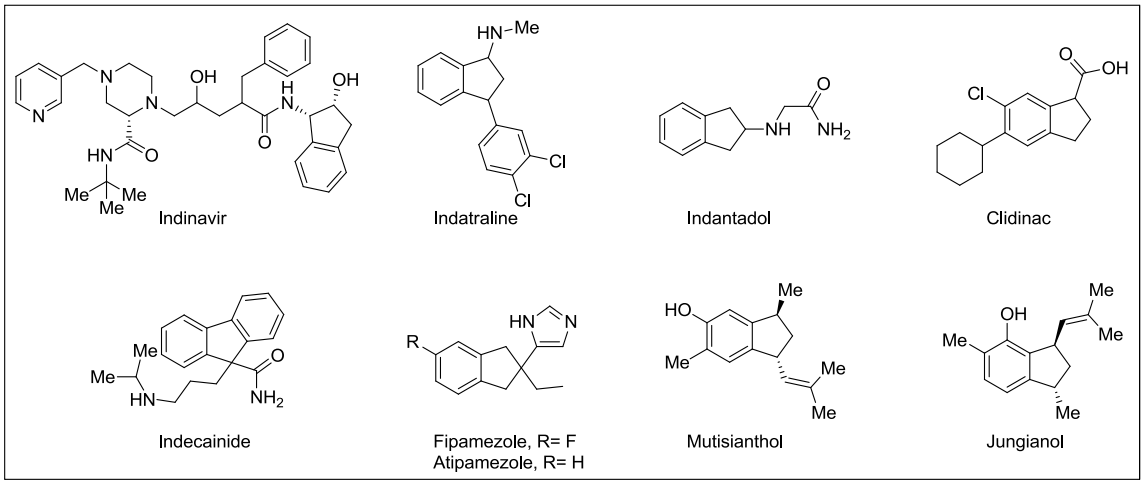


Figure III.1: Naturally occurring indanes and pharmaceutically important indane scaffolds.

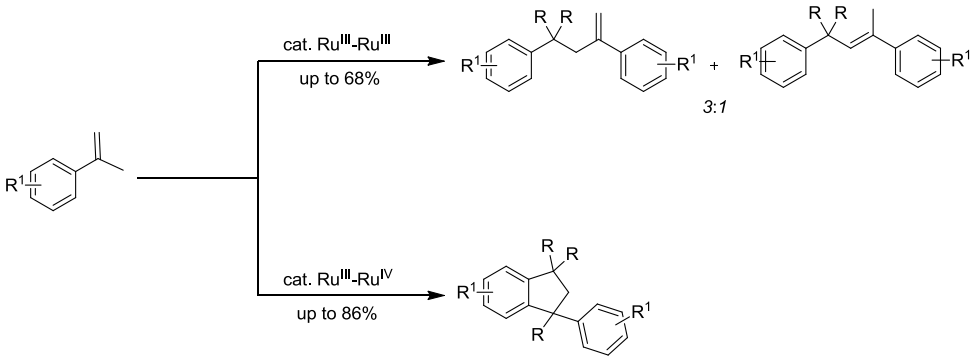
Due to the relative abundance of the indane core in natural products having interesting biological activities, numerous methods were reported in literature by different research groups. A number of synthetic approaches have been reported for the synthesis of the indane ring system. The reaction proceeds with Markovnikov selectivity in both C–C bond forming steps. Several Lewis acids,[8] including $FeCl_3$, $AlCl_3$,[9] $BiCl_3$[10] and $RuCl_3$,[11] and also Brønsted acids have been reported to catalyze this reaction.[12] Unsaturated dimer is an important chain transfer reagent in the production of polymers.[13]

III.2 BACKGROUND:

Due to the relative abundance of the indane core in natural products having interesting biological activities, numerous methods were reported in literature by different research groups. A number of synthetic approaches have been reported for the synthesis of the indane ring system.

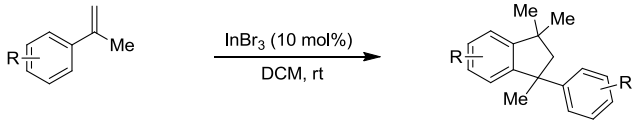
Yoshiaki Nishibayashi in 2011 presented the dicationic diruthenium complex Ru(III)−Ru(III) wich catalytically promotes the dimerization of α-methylstyrenes into the corresponding acyclic dimers, while the use of the mixed-valence diruthenium complex

Ru(III)−Ru(IV) generated from Ru(III)−Ru(III) and cinnamyl chloride as an active catalyst affords the corresponding indanes via cyclization of the acyclic dimers. The selectivity of the catalytic dimerization of α-methylstyrenes depends on the nature of electrophilicity due to valence electrons in the diruthenium cores between Ru(III)−Ru(III) and Ru(III)−Ru(IV) (Scheme III.1).[14]



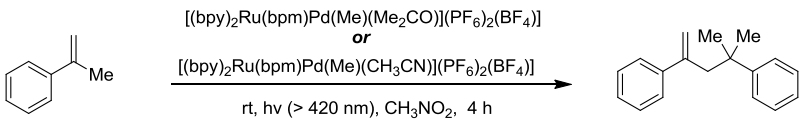
Scheme III.1

Clovis Peppe in 2004 reported the indium (III) bromide catalyzed dimerization of α-substituted vinylarenes. Chemoselectivity towards open chain or cyclic dimers depends on the nature of the substituent at the aryl group of the vinylarene (Scheme III.2).[15]



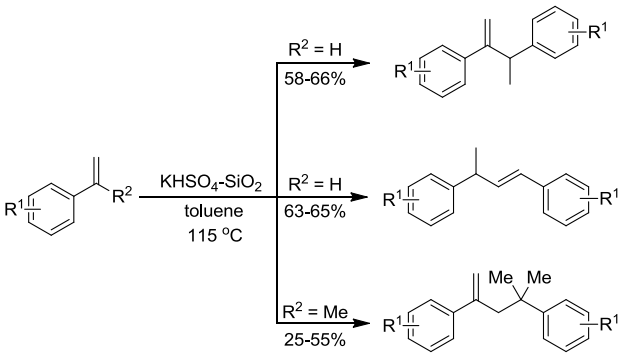
Scheme III.2

Munetaka Akita in 2005 disclosed a novel dinuclear complex containing the photo-sensitizing Ru unit and a Pd center is effective towards selective catalytic dimerization of α-methylstyrene leading to 2,4-diphenyl-4-methyl-1-pentene under visible-light irradiated conditions (Scheme III.3).[16]



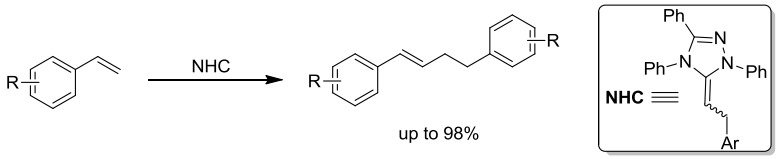
Scheme III.3

In the year of 2010 Amrit Goswami et al. described a $KHSO_4$-catalyzed activation of styrenes which involves dimerization through head-to-tail or tail-to-tail coupling (Scheme III.4).[17]



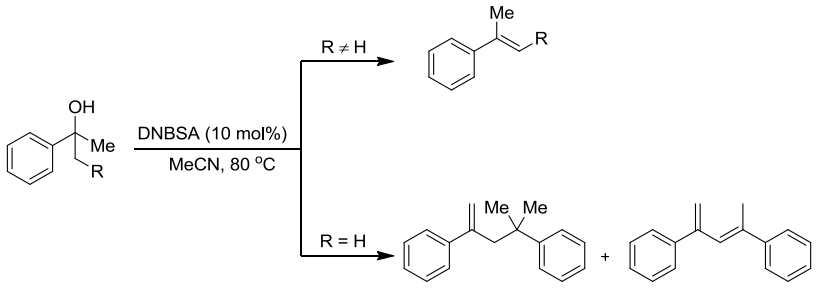
Scheme III.4

Frank Glorius et al.[18] have developed an efficient method for dimerizations in presence of NHC (N-heterocyclic carbene) (Scheme III.5).



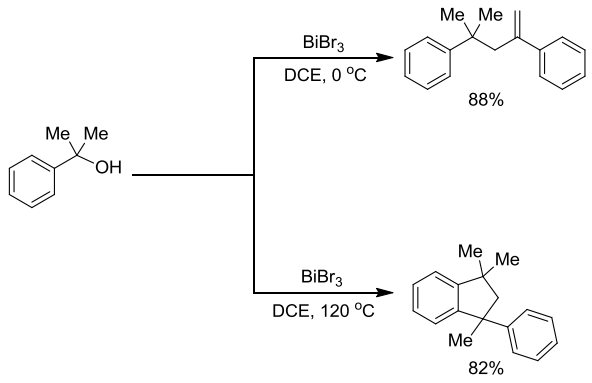
Scheme III.5

Roberto Sanz in 2007 reported formation of 2,4-diarylpentene derivatives from 2-aryl-2-propanol derivatives (R = H) under Brønsted acid catalyzed conditions (Scheme III.6).[19]



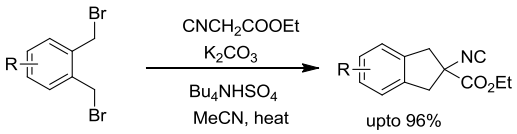
Scheme III.6

Joseph S. M. Samec in 2010 disclosed that the reaction of 2-phenylpropan-2-ol mediated by $BiBr_3$, yield selectively either 4-methyl-2,4-diphenyl-2-pentene or 1,1,3-trimethyl-3-phenylindane (Scheme III.7).[20]



Scheme III.7

Kotha et al. reported in 2000, dibromo-o-xylenes with ethyl isocyanoacetate in the presence of potassium carbonate and TBAHS in acetonitrile gave the Indane products. (Scheme III.8).[21]



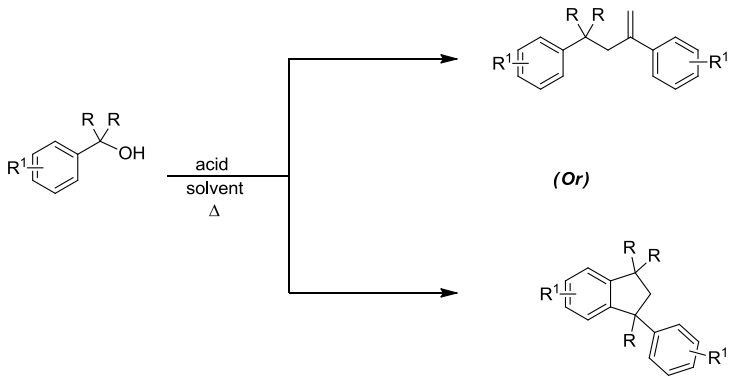
Scheme III.8

III.3. RESULTS AND DISCUSSION:

III.3.1 Synthesis of indanes via acid mediated catalysis:

With this background and based on our research interest on acid mediated as well as transition-metal catalyzed one-pot domino/sequential one-pot domino processes[22] to develop new synthetic methods, we became interested in explore the acid catalysis on *tert*-alcohol.

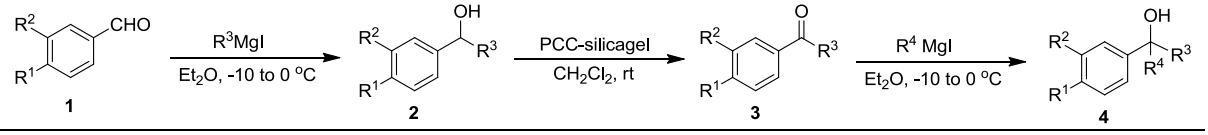
Herein we presented the synthesis of simple dimeric and indane products from *tert*-alcohols using Lewis acid as mild catalyst (Scheme III.9).

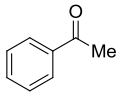
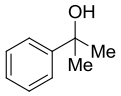
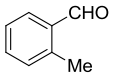
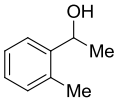
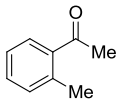
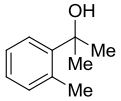
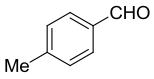
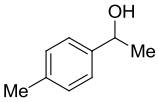
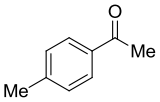
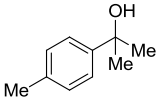
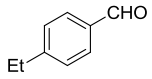
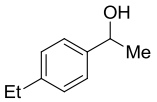
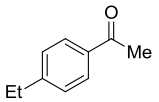
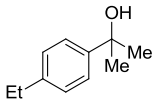
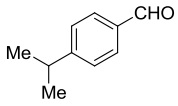
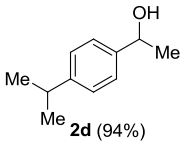
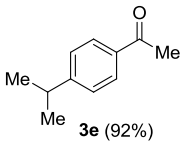
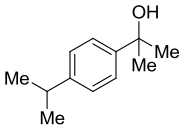
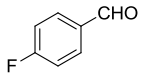
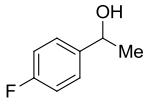
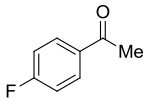
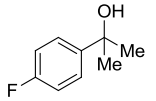
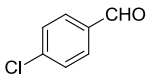
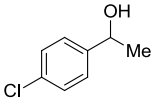
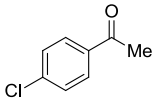
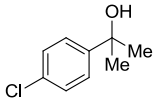
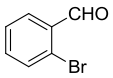
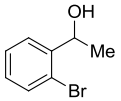
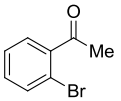
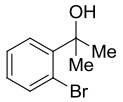
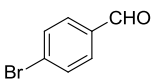
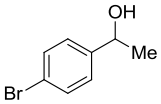
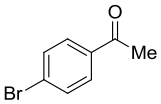
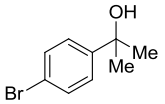
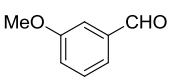
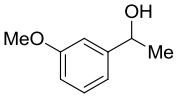
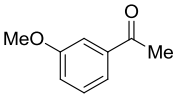
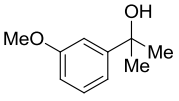


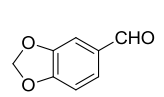
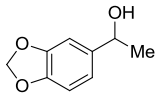
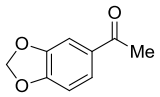
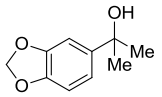
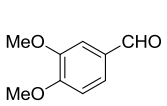
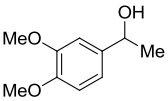
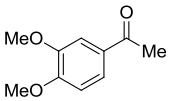
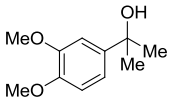
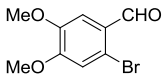
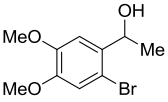
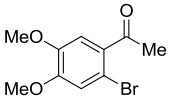
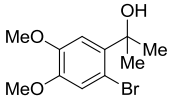
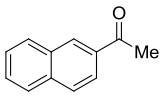
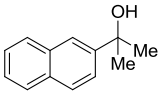
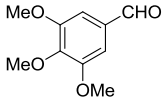
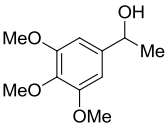
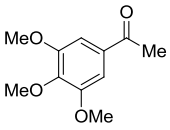
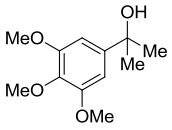
Scheme III.9

Thus, the synthetic study was initiated with the preparation of *tert*-alcohols **4** from benzaldehydes **1**. The required *tert*-alcohols **4** were accomplished using standard alkyl Grignard reagent addition, oxidation, and Grignard addition protocol. Therefore, addition of methyl Grignard reagent to benzaldehydes **1** furnished secondary alcohols **2** in very good to excellent yields (82-96%, Table III.1). Oxidation of the resulting secondary alcohols with PCC-silica gel, gave acetophenones **3** in good to excellent yields (86-96%, Table III.1). Treatment of acetophenones **3** with methyl Grignard reagent, gave the corresponding *tert*-alcohols **4** (84-96%, Table III.1).

Table III.1: Synthesis of *tert*-alcohols **4a-4o** from corresponding benzaldehydes **1a-1m**.[a]



1	2	3	4
—	—	 **3a**	 **4a** (86%)
 **1a**	 **2a** (82%)	 **3b** (94%)	 **4b** (88%)
 **1b**	 **2b** (92%)	 **3c** (96%)	 **4c** (90%)
 **1c**	 **2c** (84%)	 **3d** (90%)	 **4d** (92%)
 **1d**	 **2d** (94%)	 **3e** (92%)	 **4e** (87%)
 **1e**	 **2e** (86%)	 **3f** (93%)	 **4f** (89%)
 **1f**	 **2f** (94%)	 **3g** (91%)	 **4g** (87%)
 **1g**	 **2g** (91%)	 **3h** (90%)	 **4h** (88%)
 **1h**	 **2h** (90%)	 **3i** (94%)	 **4i** (93%)
 **1i**	 **2i** (96%)	 **3j** (96%)	 **4j** (86%)

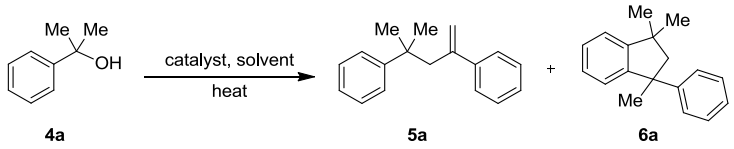
 **1j**	 **2j** (86%)	 **3k** (90%)	 **4k** (92%)
 **1k**	 **2k** (92%)	 **3l** (98%)	 **4l** (87%)
 **1l**	 **2l** (90%)	 **3m** (96%)	 **4m** (88%)
—	—	 **3n** (92%)	 **4n** (84%)
 **1m**	 **2m** (90%)	 **3o** (86%)	 **4o** (96%)

[a]Yields in the parentheses are isolated yields of chromatographically pure products.

In fact the results are quite accidental, because initially, we tried to explore the [Ru]-catalyzed *ortho* C-H activation of these benzyl tertiary alcohols. Thus we explored the reaction in the presence of $RuCl_2$(*p*-cymene)$_2$ (3 mol %) catalyst in combination with $AgSbF_6$ (3 mol%), using phenylacetylene as coupling partner, in DCE (2 mL) at 100 ^oC. To our surprise, no *ortho* C-H activation product was observed, rather gave the self dimerized indane product **6a** in 80% yield. To better understand the reaction path, the reaction was performed in the absence of coupling agent diphenyl acetylene and in the presence of [Ru]-catalyst/$AgSbF_6$, formation of the same indane product **6a** concluded that there is no role of the external coupling partner in this reaction. Further to check the feasibility of this reaction, the reaction was explored under different solvent systems; consistency of the reaction in giving the same product **6a**, confimred that the reaction clearly prefer self-dimerization exclusively. Obviously, the reaction must proceed via the standard dehydration path (i.e. through the formation of styrene). Now the task is to know whether or not the role of [Ru]-catalyst to trigger the self-dimerization. Therefore, the reaction was performed with the [Ru]-catalyst without the Lewis acid $AgSbF_6$. No progress of the reaction revealed the essence of $AgSbF_6$ catalyst to promote self-dimerization.

Since, it was very clear that $AgSbF_6$ act as the sole catalyst to promote the reaction, to find out the best conditions, the reaction was explored with $AgSbF_6$ under various conditions and the results are summarized in Table III.2. Interestingly, the yield of **6a** increased in parallel with the decrease in acid quantity and time (Table III.2, entries 1 to 2). Gratifyingly, the reaction in the presence of [$AgSbF_6$ (1 mol%)], at 100 °C furnished the target indane **6a** as an exclusive product, in excellent yield (96%, Table III.2, entry 3). No progress was seen at RT in DCE and at 100 °C in H_2O or DMF, which led to the recovery of the starting material **4a** (Table III.2, entries 4 to 6). Interestingly, when the reaction was conducted at 50 °C, it was found to be highly selective and lead to the formation of 4-methyl-2,4-diphenyl-2-pentene **5a**, in excellent yield (94%, Table III.2, entry 7). Whereas, at 60 °C the yield was slightly decreased (Table III.2, entry 8).

Table III.2: Optimization conditions for the synthesis of dimerized olefin **5a** and indane **6a**.



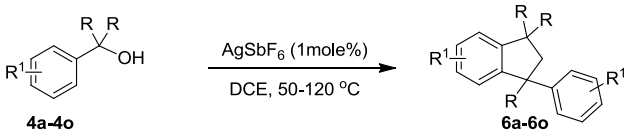
4a **5a** **6a**

Entry[a]	Catalyst (mol %)	Solvent (mL)	Temp (^oC)	Time (h)	Yield (%)[b]	
					5a	**6a**
1	$AgSbF_6$ (20)	DCE	100	12	0[d]	70
2	$AgSbF_6$ (10)	DCE	100	2	0[d]	80
3	**$AgSbF_6$ (1)**	**DCE**	**100**	**30 min**	**0[d]**	**96**
4	$AgSbF_6$ (1)	DCE	rt	1	0[c]	0[c]
5	$AgSbF_6$ (1)	H_2O	100	1	0[c]	0[c]
6	$AgSbF_6$ (1)	DMF	100	1	0[c]	0[c]
7	**$AgSbF_6$ (1)**	**DCE**	**50**	**1**	**94**	**0[e]**
8	$AgSbF_6$ (1)	DCE	60	1	90	0[e]

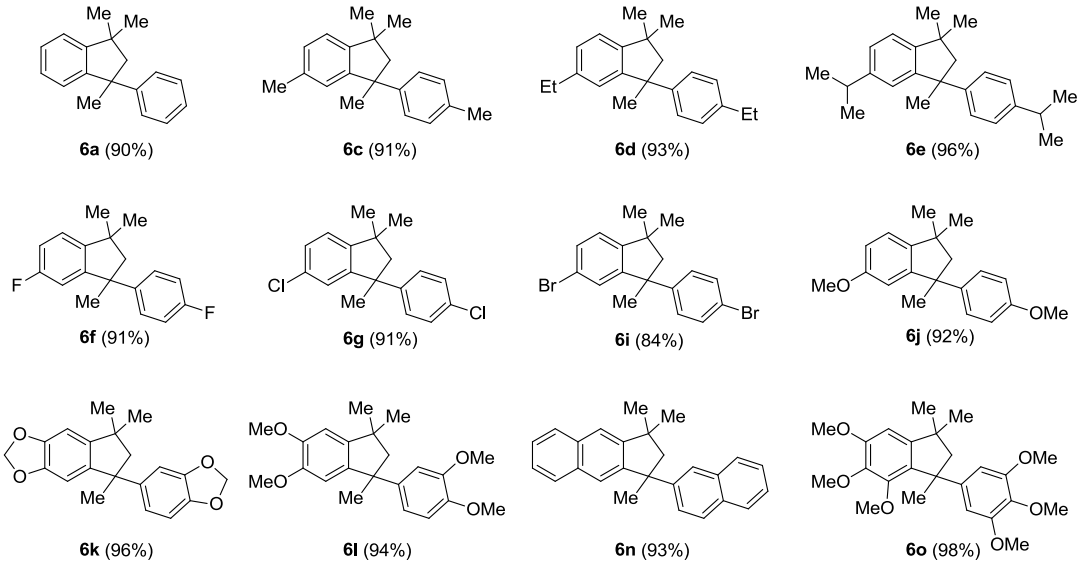
[a]All reactions were carried out on 0.25 mmol scale of **4a**. [b]Isolated yields of chromatographically pure products. [c]Only starting material **4a** was recovered. [d]No **5a** was formed. [e]No **6a** was identified.

After optimization of the reaction conditions we have concluded that the $AgSbF_6$ (1 mol%) furnish the indane **6a** at 100 °C and dimerized products **5a** at 50 °C. With these clearly distinguished standard reaction conditions, we intended to explore the reaction to check the scope and generality of the method. Hence, we have employed the above optimized conditions (Table III.2, entry 3) to other *tert*-alcohols **4**, for the synthesis of the indane products **6** (Table 2). Gratifyingly, the method was quite successful for the systems **4c**-**4o** containing electron withdrawing to donating substituents on the aromatic ring and gave the corresponding indanes **6c**-**6o**, in very good to excellent yields (Table III.3). Significantly, unlike the previous reports, the present method is sustainable and mild enough to enable the synthesis of indanes **6j**, **6k**, **6l** and **6o** with highly electron rich aromatic rings. Usually, electron rich aromatic systems do not furnish indanes as end products, as they are sensitive enough and hence would further promote unwanted side reactions. Notably, unlike any other earlier reports, the present method was applied to synthesis of many indane systems.

Table III.3: Scope of Lewis acid mediated one-pot formation of indanes **6** from various *tert*-alcohols **4**.[a,b]



4a-4o → **6a-6o**



6a (90%) **6c** (91%) **6d** (93%) **6e** (96%)

6f (91%) **6g** (91%) **6i** (84%) **6j** (92%)

6k (96%) **6l** (94%) **6n** (93%) **6o** (98%)

[a]All reactions were carried out on 0.25 mmol scale of **4**. [b]Yields of chromatographically pure products.

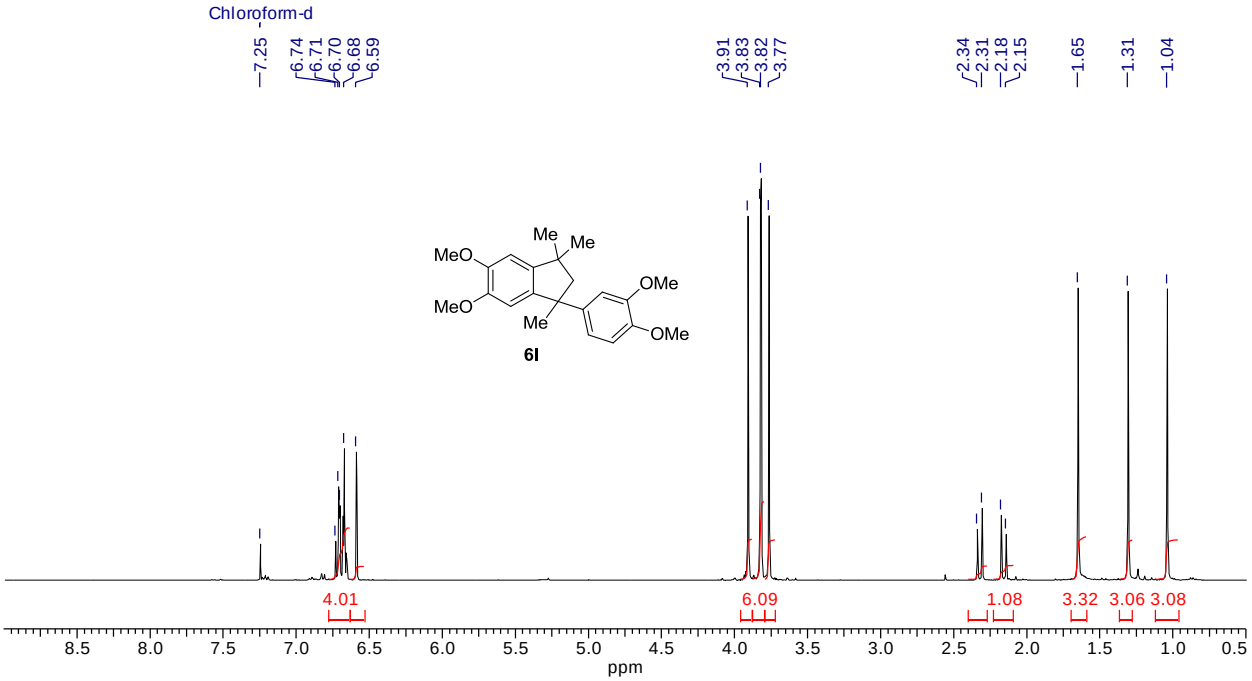


Figure III.2: ^{1}H-NMR (400 MHz) spectrum of **6l** in $CDCl_3$.

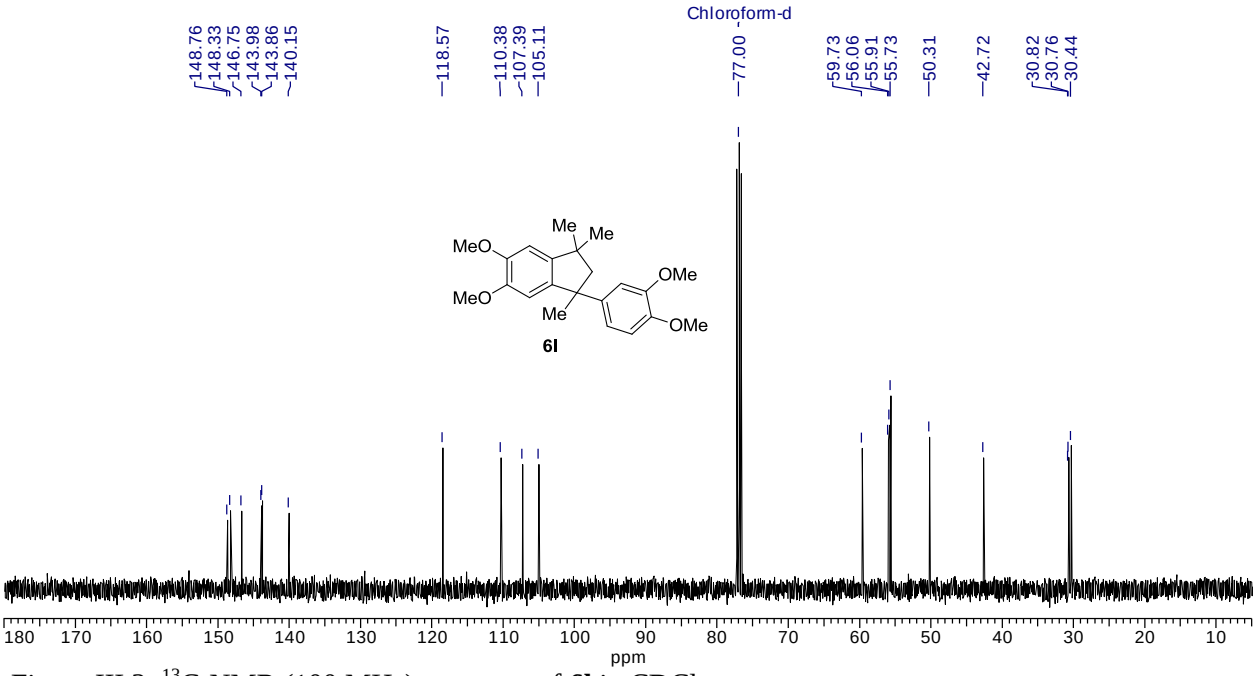
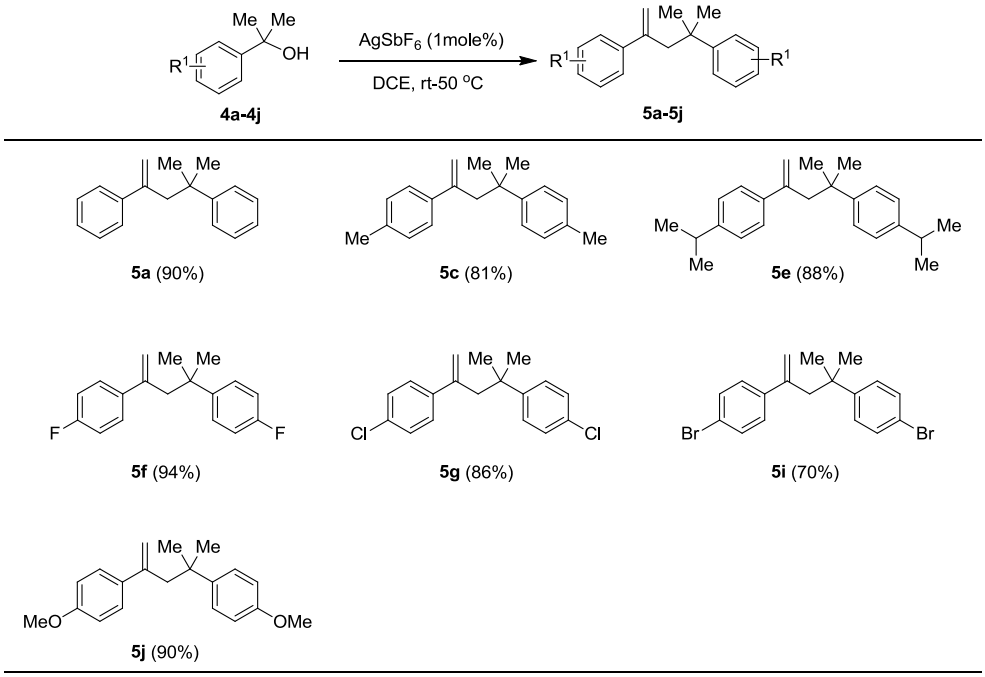


Figure III.3: ^{13}C-NMR (100 MHz) spectrum of **6l** in $CDCl_3$.

The structure of 1-(3,4-dimethoxyphenyl)-5,6-dimethoxy-1,3,3-trimethylindane **6l** was confirmed from its spectral data. IR spectra show the presence of strong absorption band at 2953 cm^{-1} due to C-H stretching of alkane. In the ^{1}H-NMR spectrum (Figure III.2), presence of multiplet at δ 7.76–6.64 due to four aromatic protons, one singlet at δ 6.59 due to one aromatic proton, four singlets at δ 3.91, 3.83, 3.82 and δ 3.77 due to twelve protons of four aromatic methoxy groups, presence of two doublets at δ 2.34 (*J*=12.7 Hz) and δ 2.18 (*J*=12.7 Hz) due to two protons of a methylene group, presence of three singlets at δ 1.65, 1.31 and 1.04 due to nine protons of three methyl groups, established the structure of indane **6l**. In 22 lines ^{13}C-NMR spectrum (Figure III.3), presence of seven quaternary carbons resonances at δ 148.8, 148.3 (2C), 146.8, 143.9 (2C) and 140.2 due to aromatic carbons, five aromatic methine carbons at δ 118.6, 110.4, 110.3, 107.4 and 105.1, one methylene carbon at δ 59.7, four aromatic methoxy carbons at δ 56.1, 55.9, 55.8 and δ 55.7, two quaternary carbons at δ 50.3 and 42.7, presence of three methyl carbons at δ 30.8, 30.7 and 30.4 ppm, confirmed the structure of indane **6l**. Presence of the $[M+H]^+$ peak at m/z $[C_{22}H_{29}O_4]^+$=357.2054 in the mass spectrum further established the structure of indane **6l**.

In the above described method for the selective formation of 2,4-diaryl-4-methylpent-2-enes and indanes **6a-6o** (Table III.3), the reaction proceeds with Markovnikov selectivity in both C–C bond-forming steps. The fact that the reaction impeded after the dimerization at lower temperatures implies that it is the kinetic product **5a**, while the indane **6a** is the thermodynamic product. On the other hand, unsaturated dimer is an important chain transfer reagent in the production of polymers. Due to the importance of being able to generate the dimerization product selectively, in a controlled manner to generate dimerization olefin product **5a** (Table III.2, entry 7), we thought that this strategy can be extend for the synthesis of dimeric products as well. Since, the reaction was quite successful in delivering the dimeric product **5a** at 50 ^{o}C, we felt that RT to 50 ^{o}C temperature range would be ideal to produce the dirmeric products depending on the nature of substituents on the aromatic ring. Therefore, we have applied the above optimized conditions (Table III.2, entry 7) to other *tert*-alcohols **4a-4j** and the results are as shown in the Table III.4. Gratifyingly, the method was quite successful and amenable for the systems having electron withdrawing to donating substituents on the aromatic ring and gave the corresponding dimers **5a-5j**, in good to excellent yields (Table III.4).

Table III.4: Scope of Lewis acid mediated one-pot formation of (1,1-dimethyl-3-phenylbut-3-enyl)benzenes **5** from various *tert*-alcohols **4**.[a,b]



[a]All reactions were carried out on 0.25 mmol scale of **4**. [b]Yields of chromatographically pure products.

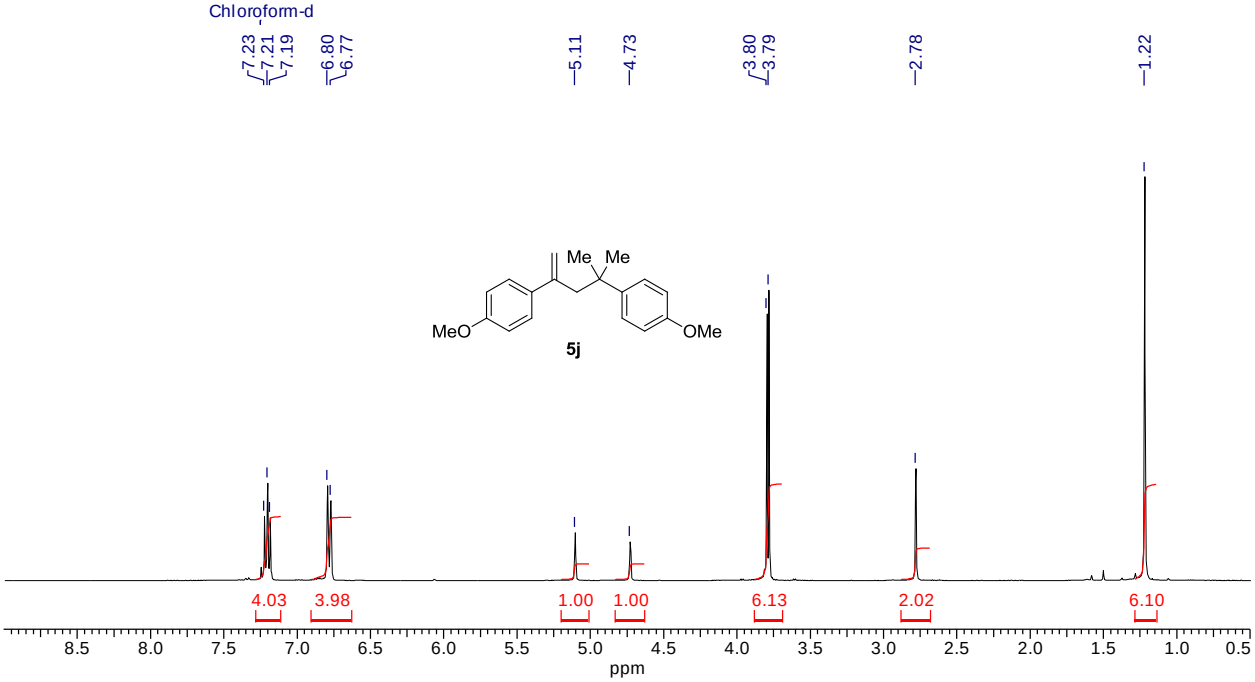


Figure III.4: ^{1}H-NMR (400 MHz) spectrum of **5j** in $CDCl_3$.

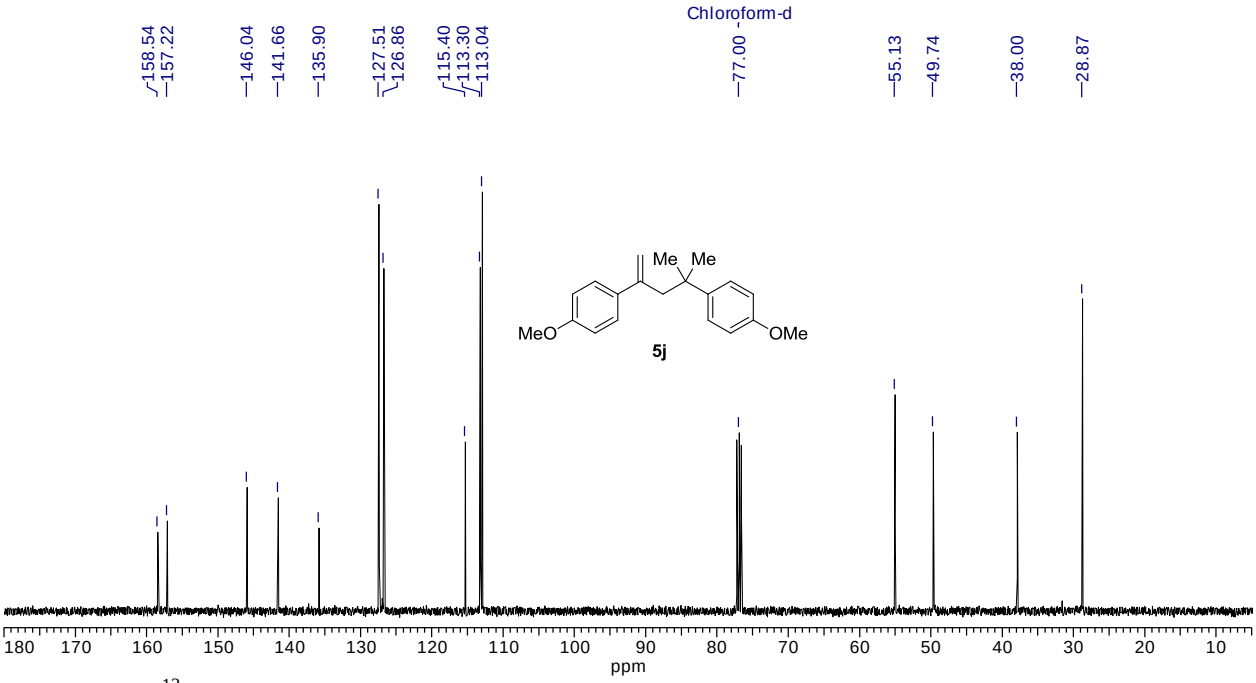


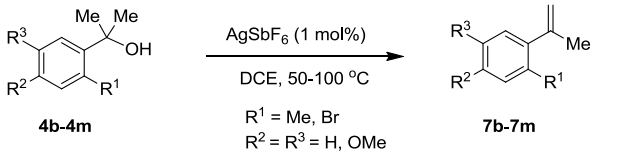
Figure III.5: ^{13}C-NMR (100 MHz) spectrum of **5j** in $CDCl_3$.

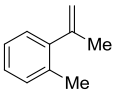
The structure of 1-methoxy-4-[3-(4-methoxyphenyl)-1,1-dimethylbut-3-enyl]benzene **5j** was confirmed from its spectral data. IR spectra show the presence of strong absorption band at 2959 cm^{-1} due to C-H stretching of alkane. In the ^{1}H-NMR spectrum (Figure III.4), presence of two doublet of doublets at δ 7.21 (*J*=8.8 and 7.3 Hz) and 6.80 (*J*=8.8 and 1.5 Hz) due to eight aromatic protons, two doublets at δ 5.11 (*J*=2.0 Hz) and 4.73 (*J*=2.0 Hz) due to two olefinic protons, two singlets at δ 3.80 and δ 3.79 due to six protons of two aromatic methoxy groups, presence of one singlet at δ 2.78 due to two protons of a methylene group, presence of one singlet at δ 1.22 due to six protons of two methyl groups, established the structure of 1-methoxy-4-[3-(4-methoxyphenyl)-1,1-dimethylbut-3-enyl]benzene **5j**. In 15 lines ^{13}C-NMR spectrum (Figure III.5), five quaternary carbons resonances at δ 158.5, 157.2, 146.0, 141.7 and 135.9 due to four aromatic and one olefinic carbons, eight aromatic methine carbons at δ 127.5 (2C), 126.9 (2C), 113.3 (2C) and 113.0 (2C), one terminal olefinic carbon at δ 115.4, two methoxy carbons at δ 55.3 and 55.2, one methylene carbon at δ 49.7, one quaternary carbon at δ 38.0 ppm, presence of tow methyl carbons at δ 28.9 ppm, confirmed the structure of 1-methoxy-4-[3-(4-methoxyphenyl)-1,1-dimethylbut-3-enyl]benzene **5j**. Presence of the $[M+H]^+$ peak at m/z

$[C_{20}H_{25}O_2]^+$=297.1830 in the mass spectrum further established the structure of 1-methoxy-4-[3-(4-methoxyphenyl)-1,1-dimethylbut-3-enyl]benzene **5j**.

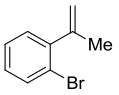
On the other hand, quite surprisingly, when there is *ortho*-substituent, the reaction stopped just after dehydration and gave the corresponding styrenes **7b**, **7h** and **7m** (Table III.5). The exact reason for no further progress of the reaction after the formation of styrenes is not clear. However, it may be presumed due to the steric crowding of the *ortho*-substituent. All compounds are fully characterized based on their spectroscopic evidence. In addition, the compounds **2f** and **3f** were further characterized by ^{19}F-NMR.

Table III.5: Lewis acid mediated formation of styrenes **7** from various *tert*-alcohols **4**.[a,b]

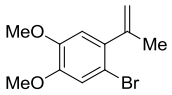




7b (86%)



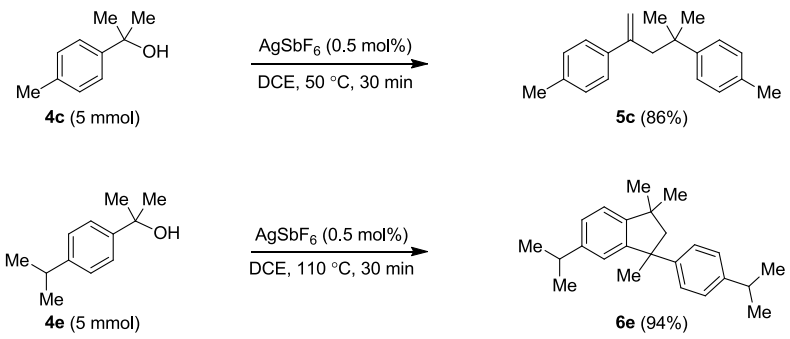
7h (78%)



7m (82%)

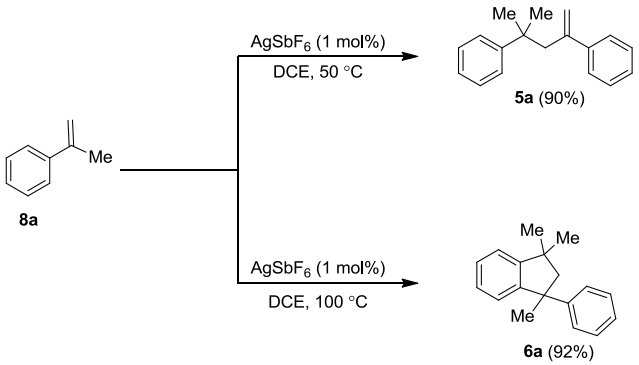
[a]All reactions were carried out on 0.25 mmol scale of **4**. [b]Yields of chromatographically pure products.

Further to show so the emenability of the reaction conditions on larger scale, we have conducted the reaction on 5 mmol scale of *tert*-alcohols **4c** and **4e**, for their conversion to dimer and indane, respectively (Scheme III.10). Since, it is on larger scale, the reaction was performed with only 0.5 mol% of the catalyst. To our delight, the reaction was found to be very smooth and gave the corresponding dimer **5c** (86%) and indane **6e** (94%) in comparable yields to that of small scale experiments (Tables III. 3 & Tables III.4).



Scheme III.10: Scope of the method to give dimer **5c** and indane **6e** on 5 mmol scale.

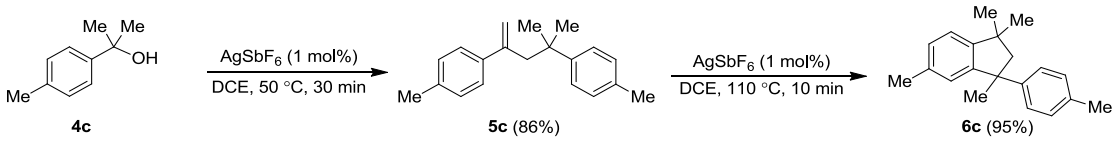
It was further concluded that the reaction must proceed via the formation of styrene intermediate, we rationalized that the treatment of styrene under standard reaction conditions, would furnish the same dimeric and indane products. Therefore, the methyl styrene **8a** was also treated with $AgSbF_6$ (1 mol%) at 50 and 100 °C, respectively. As anticipated, the products (1,1-dimethyl-3-phenylbut-3-enyl)benzene **5a** and indane **6a** were obtained in excellent yields (Scheme III. 11). However, it is noteworthy that under standard conditions, the reaction of simple styrene, did not promote to give any product except complete recovery of starting material. This further confirms the mild nature of the present protocol.



Scheme III.11: Synthesis of dimer **5a** and indane **6a** from methylstyrene **8a**.

In order to understand the reaction path, separately, the *tert*-alcohol **4c** was dimerized to **5c**, under standard conditions. After column purification of **5c**, it was treated with the catalyst $AgSbF_6$ (1 mol%), at elevated temperature 110 °C for 10 min. As anticipated, the indane **6c** was

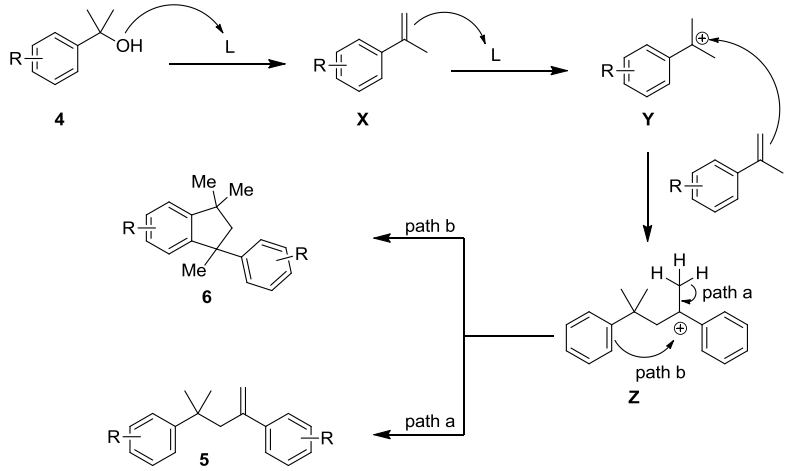
obtained excellent yield (95 %). Thus, claims the intermediacy of the linear dimer **5c** in reaction path to give indane **6c** as the end product (Scheme III.12).



Scheme III.12: Formation of indane **6c** from the dimer **5c**.

A plausible reaction mechanism for the formation of indanes **6** and (1,1-dimethyl-3-phenylbut-3-enyl)benzenes **5** is shown in Scheme III.13. Initially, the Lewis acid could promote dehydration of the *tert*-alcohol **4** to give the styrene **X**. Then the Lewis acid coordinates to the double bond of the styrene **X**, which will be attacked by another molecule of **X** in Markovnikov (head to tail mode) selectivity to generate intermediate **Z**, via an intermolecular Friedel–Crafts-type reaction. Then the intermediate **Z** depending on the temperature applied either leads to the indanes **6** or **(**1,1-dimethyl-3-phenylbut-3-enyl)benzenes **5**.

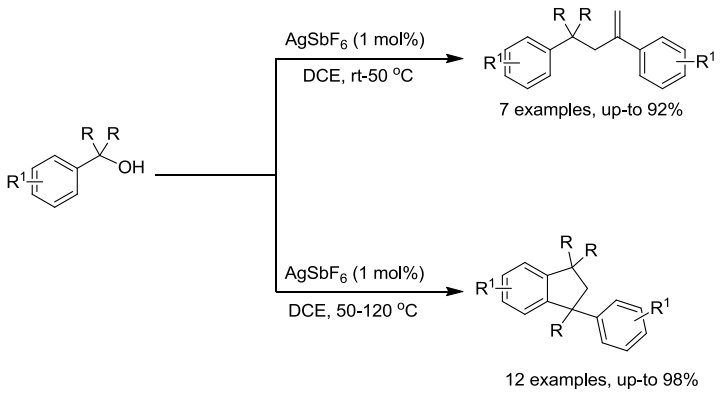
Scheme III.13: Plausible reaction mechanism for the formation of indanes **6** and dimers **5**.



Scheme III.13

III.4. CONCLUSIONS:

We have developed a mild and practical method for the synthesis of (1,1-dimethyl-3-phenylbut-3-enyl)benzenes and indanes. The reaction was temperature dependent and furnished the products with excellent selectivity. In the case of simple dimerization Markovnikov head to tail coupling took place. Whereas, for the formation of indanes, the same trend was noticed, in addition, intramolecular Friedel-Crafts attack took place. Notably, even electron rich aromatic systems were compatible for the formation of indanes, which is not usual, thus revealing the advantages of mild reaction conditions of present protocol. Reasonably good number of examples has been prepared using this strategy unlike any other earlier reports.



Scheme III.14

III.5 EXPERIMENTAL SECTION:

Table III.6: Compounds (**6a**, **6c**, **6d, 6e, 6f, 6g, 6j, 6n**) [12] are known in the literature.

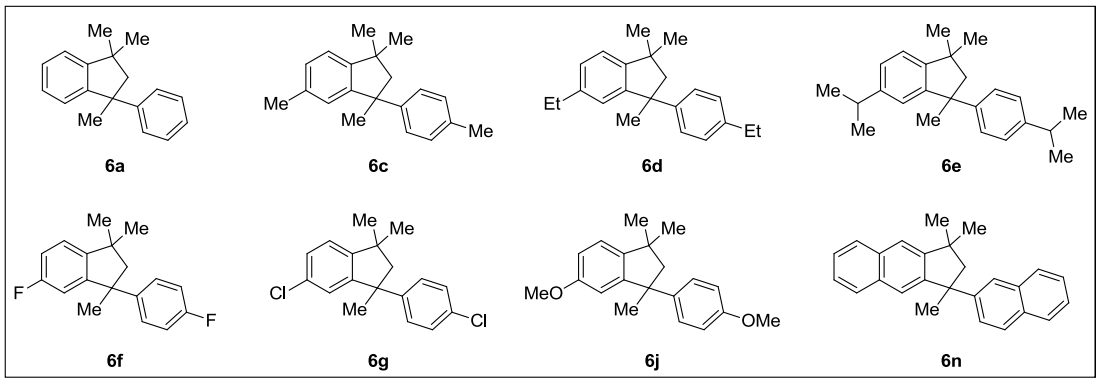
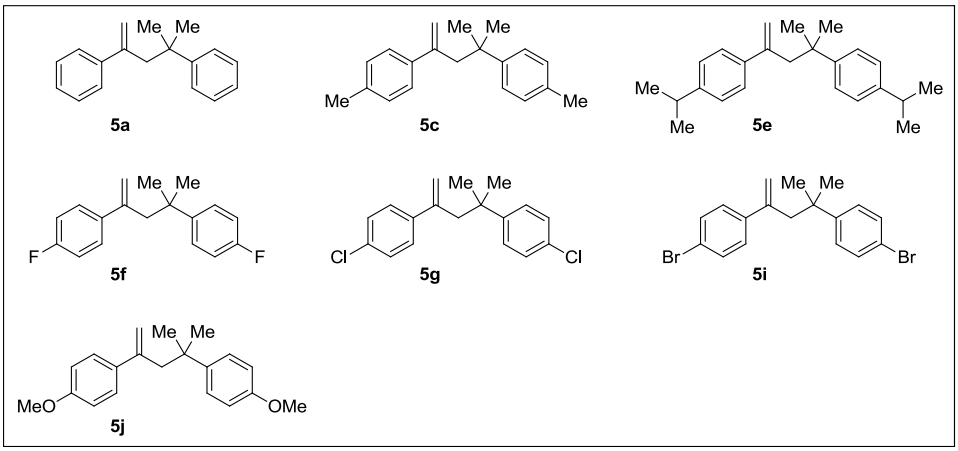


Table III.7: Compounds (**5a**, **5c**, 5**e, 5f, 5g, 5i, 5j**) [11] are known in the literature.

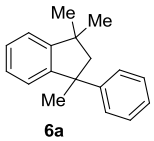


GP-1 General Procedure for indanes:

To an oven dried Schlenk tube under nitrogen atmosphere, were added alcohol **4** (34–57 mg, 0.25 mmol) and $AgSbF_6$ (1 mol%) followed by the addition of DCE (2 mL). The resultant reaction mixture was stirred at 50 to 120 °C for 10 to 30 mins. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indanes **6** (84–98%).

GP-2 General Procedure for (1,1-dimethyl-3-phenylbut-3-enyl)benzenes:

To an oven dried Schlenk tube under nitrogen atmosphere, were added alcohol **4** (34–57 mg, 0.25 mmol) and $AgSbF_6$ (1 mol%) followed by the addition of DCE (2 mL). The resultant reaction mixture was stirred at RT to 50 °C for 10 mins to 2 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the dimer **5** (70–95%).



6a

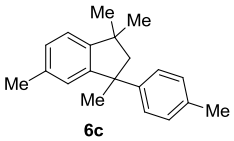
1,1,3-Trimethyl-3-phenylindane (6a):

GP-1 was carried out with alcohol **4a** (34 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished indane **6a** (27 mg, 90%) as brown color viscus liquid. [TLC control R_f(**4a**)=0.50, R_f(**6a**)=0.80, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2958, 1487, 1400, 1093, 1011, 821, 724 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.30-7.08 (m, 9H, ArH), 2.39 (d, 1H, *J*=13.2 Hz, C*H*$_a$H$_b$), 2.20 (d, 1H, *J*=13.2 Hz, CH$_a$*H*$_b$), 1.67 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=152.2 (s, ArC), 151.0 (s, ArC), 148.7 (s, ArC), 128.0 (d, 2C, ArCH), 127.2 (d, ArCH), 126.7 (d, 2C, ArCH), 126.6 (d, ArCH), 125.4 (d, ArCH), 125.0 (d, ArCH), 122.5 (d, ArCH), 59.2 (t, CH_2), 50.8 [s, $C(Me)_2$], 42.8 [s, $C(Me)_2$], 30.9 (q, CH_3), 30.6 (q, CH_3), 30.4 (q, CH_3) ppm.



6c

1,1,3,5-Tetramethyl-3-(4-methylphenyl)indane (6c):

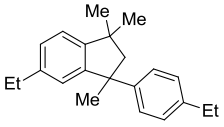
GP-1 was carried out with alcohol **4c** (38 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished indane **6c** (30 mg, 91%) as brown color viscus liquid. [TLC control R_f(**4c**)=0.50, R_f(**6c**)=0.80, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): *vmax*=2956, 1510, 1453, 1361, 1312, 1189, 1019, 815, 723 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.20-7.05 (m, 6H, ArH), 6.95 (s, 1H, ArH), 2.41 (d, 1H, *J*=13.2 Hz, C*H*$_a$H$_b$), 2.40 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.23 (d, 1H, *J*=13.2 Hz, CH$_a$*H*$_b$), 1.71 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.09 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.3 (s, ArC), 149.1 (s, ArC), 148.1 (s, ArC), 136.1 (s, ArC), 134.8 (s, ArC), 128.6 (d, 2C, ArCH), 128.0 (d, ArCH), 126.6 (d, 2C, ArCH), 125.4 (d, ArCH), 122.2 (d, ArCH), 59.5 (t, CH_2), 50.3 [s, $C(Me)_2$], 42.5 [s, C(Me)Ar], 30.8 (q, 2C, CH_3), 30.5 (q, CH_3), 21.4 (q, CH_3), 20.9 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{28}N]^+$=$[M+NH_4]^+$: 282.2216; found: 282.2219.



6d

5-Ethyl-3-(4-ethylphenyl)-1,1,3-trimethylindane (**6d)**:

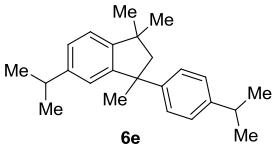
GP-1 was carried out with alcohol **4d** (41 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished indane **6d** (34 mg, 93%) as brown color viscus liquid. [TLC control R_f(**4d**)=0.60, R_f(**6d**)=0.75, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2962, 1511, 1456, 1368, 1312, 1016, 829, 565 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.20-7.05 (m, 6H, ArH), 6.94 (s, 1H, ArH), 2.75-2.55 [m, 4H, Ar-(CH_2CH$_3$)$_2$], 2.36 (d, 1H, *J*=12.7 Hz, CH_aH$_b$), 2.18 (d, 1H, *J*=12.7 Hz, CH$_a$ H_b), 1.67 (s, 3H, CH$_3$), 1.33 (s, 3H, CH$_3$), 1.30-1.15 [m, 6H, Ar(CH$_2$CH_3)$_2$], 1.03 (s, 3H, CH$_3$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.5 (s, Ar-C), 149.0 (s, ArC), 148.3 (s, ArC), 142.6 (s, ArC), 141.1 (s, ArC), 127.3 (d, 2C, ArCH), 126.8 (d, ArCH), 126.6 (d, 2C, ArCH), 124.3 (d, ArCH), 122.2 (d, ArCH), 59.5 (t, CH$_2$), 50.4 [s, C(Me)$_2$], 42.5 [s, C(Me)Ar], 30.9 (q, CH$_3$), 30.7 (q, CH$_3$), 30.5 (q, CH$_3$), 28.8 (t, Ar-*C*H$_2$CH$_3$), 28.2 (t, Ar-*C*H$_2$CH$_3$), 15.8 (q, Ar-CH$_2$*C*H$_3$), 15.4 (q, Ar-CH$_2$*C*H$_3$) ppm.

HR-MS (APCI+): m/z calculated for [$C_{22}H_{32}N$]$^+$=[M+NH_4]$^+$: 310.2529; found: 310.2528.



6e

5-Isopropyl-3-(4-isopropylphenyl)-1,1,3-trimethylindane (6e):

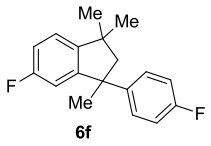
GP-1 was carried out with alcohol **4e** (46 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished indane **6e** (40 mg, 96%) as brown color viscus liquid. [TLC control R_f(**4e**)=0.50, R_f(**6e**)=0.70, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2957, 1510, 1458, 1364, 1057, 828 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.23-7.10 (m, 6H, ArH), 7.05 (s, 1H, ArH), 3.03-2.85 (m, 2H, CH$_2$), 2.45 (d, 1H, *J*=12.7 Hz, CH_aH$_b$), 2.24 (d, 1H, *J*=12.7 Hz, CH$_a$$H_b$), 1.73 (s, 3H, CH$_3$), 1.38 (s, 3H, CH$_3$), 1.32 (d, 6H, 2 × CH$_3$), 1.28 (d, 6H, 2 × CH$_3$), 1.06 (s, 3H, CH$_3$) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.7 (s, ArC), 148.8 (s, ArC), 148.3 (s, ArC), 147.3 (s, ArC), 145.7 (s, ArC), 126.5 (d, 2C, ArCH), 125.9 (d, 2C, ArCH), 125.3 (d, ArCH), 122.9 (d, ArCH), 122.1 (d, ArCH), 59.5 (t, CH$_2$), 50.5 [s, *C*(CH$_3$)$_2$], 42.4 [s, *C*(CH$_3$)], 34.1 (d, CH), 33.5 (d, CH), 31.0 (q, CH$_3$), 30.7 (q, CH$_3$), 30.5 (q, CH$_3$), 24.3 (q, 2C, CH$_3$), 24.0 (q, CH$_3$), 23.9 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{24}H_{33}]^+$=$[M+H]^+$: 321.2577; found: 321.3577.



6f

5-Fluoro-3-(4-fluorophenyl)-1,1,3-trimethylindane (6f):

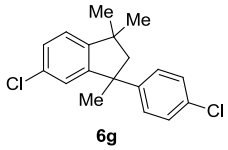
GP-1 was carried out with alcohol **4f** (39 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished indane **6f** (31 mg, 91%) as brown color viscus liquid. [TLC control R_f(**4f**)=0.50, R_f(**6f**)=0.70, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): v*max*=2959, 1605, 1507, 1422, 1227, 1163, 1015, 821, 532 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.16-7.08 (m, 3H, ArH), 7.01-6.89 (m, 3H, ArH), 6.77 (dd, 1H, *J*=9.3 and 2.5 Hz, ArCH), 2.37 (d, 1H, *J*=12.7 Hz, CH_aH_b), 2.23 (s, 1H, *J*=12.7 Hz, CH_aH_b), 1.66 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.5 (d, *J*=243.6 Hz, ArC), 162.2 (d, *J*=244.3 Hz, ArC), 150.8 (d, *J*=7.3 Hz, ArC), 147.5 (s, ArC), 146.0 (d, *J*=2.9 Hz, ArC), 128.1 (d, 2C, *J*=7.3 Hz, ArCH), 123.8 (d, *J*=8.8 Hz, ArCH), 114.8 (d, 2C, *J*=21.3 Hz, ArCH), 114.4 (d, *J*=22.0 Hz, ArCH), 111.4 (d, *J*=22.0 Hz, ArCH), 59.5 (t, CH_2), 50.2 [d, *J*=1.5 Hz, *C*$(CH_3)_2$], 42.4 [s, *C*(CH_3)], 30.8 (q, CH_3), 30.7 (q, CH_3), 30.4 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{19}F_2]^+$=$[M+H]^+$: 273.1449; found: 273.1425.



6g

5-Chloro-3-(4-chlorophenyl)-1,1,3-trimethylindane (6g):

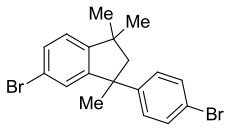
GP-1 was carried out with alcohol **5g** (43 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished indane **6g** (35 mg, 91%) as brown color viscus liquid. [TLC control R_f(**4g**)=0.50, R_f(**6g**)=0.60, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2958, 1487, 1400, 1093, 1011, 821, 724 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.28-7.16 (m, 3H, ArH), 7.15-7.06 (m, 3H, ArH), 7.03 (d, 1H, *J*=1.9 Hz, ArH), 2.34 (d, 1H, *J*=12.7 Hz, CH_aH$_b$), 2.20 (d, 1H, *J*=13.2 Hz, CH$_a$ H_b), 1.64 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=150.6 (s, ArC), 150.3 (s, ArC), 148.7 (s, ArC), 132.4 (s, ArC), 131.5 (s, ArC), 128.2 (d, 2C, ArCH), 128.0 (d, 2C, ArCH), 127.7 (d, ArCH), 124.9 (d, ArCH), 123.9 (d, ArCH), 59.1 (t, CH_2), 50.4 [s, $C(Me)_2$], 42.6 [s, C(Me)Ar], 30.6 (q, 2C, CH_3), 30.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{22}Cl_2N]^+=[M+NH_4]^+$: 322.1118; found: 322.1163.



6i

5-Bromo-3-(4-bromophenyl)-1,1,3-trimethylindane (6i):

GP-1 was carried out with alcohol **4i** (54 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished indane **6i** (42 mg, 84%) as brown color viscus liquid. [TLC control R_f(**4i**)=0.50, R_f(**6i**)=0.70, (petroleum ether/ethyl acetate 98:2, UV detection)].

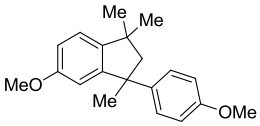
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2961, 2927, 1485, 1463, 1395, 1369, 1073, 1008, 1018, 827, 632 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.41 (dd, 1H, *J*=7.8 and 2.0 Hz, ArH), 7.37 (dd, 2H, *J*=8.3 and 2.0 Hz, ArH), 7.19 (d, 1H, *J*=2.0 Hz, ArH), 7.08 (d, 1H, *J*=7.8 Hz, ArH), 7.04 (dd, 2H, *J*=8.3 and 2.0 Hz, ArH), 2.36 (d, 1H, *J*=13.2 Hz, CH_aH$_b$), 2.36 (d, 1H, *J*=13.2 Hz, CH$_a$$H_b$), 1.64 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=151.2 (s, ArC), 150.7 (s, ArC), 149.3 (s, ArC), 131.2 (d, 2C, ArCH), 130.6 (d, ArCH), 128.5 (d, 2C, ArCH), 127.9 (d, ArCH), 124.5 (d, ArCH), 120.5

(s, ArC), 119.7 (s, ArC), 59.1 (t, CH_2), 50.6 [s, *C*$(CH_3)_2$], 42.7 [s, *C*(CH_3)], 30.6 (q, 2C, 2×CH_3), 30.3 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{18}Br_2K]^+$=$[M+K]^+$: 430.9407; found: 430.9410.



6j

5-Methoxy-3-(4-methoxyphenyl)-1,1,3-trimethylindane (6j):

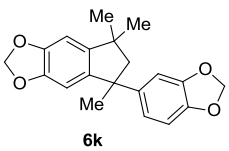
GP-1 was carried out with alcohol **4j** (42 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 96:4 to 92:8) furnished indane **6j** (35 mg, 92%) as brown color viscus liquid. [TLC control R_f(**4j**)=0.50, R_f(**6j**)=0.60, (petroleum ether/ethyl acetate 92:8, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): *v*max=2955, 1608, 1508, 1310, 1248, 1181, 1034, 827, 664 cm^{-1}.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.15-7.05 (m, 3H, ArH), 6.90-6.75 (m, 3H, ArH), 6.63 (s, 1H, Ar-H), 3.78 (s, 3H, $ArOCH_3$), 3.77 (s, 3H, $ArOCH_3$), 2.34 (d, 1H, *J*=13.2 Hz, C*H*$_a$H$_b$), 2.19 (d, 1H, *J*=13.2 Hz, CH_{2a} *H*$_{2b}$), 1.66 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=158.9 (s, Ar-C), 157.3 (s, Ar-C), 150.5 (s, Ar-C), 144.5 (s, Ar-C), 143.0 (s, Ar-C), 127.6 (d, 2C, Ar-CH), 123.1 (d, Ar-CH), 113.2 (d, 2C, Ar-CH), 113.1 (d, Ar-CH), 109.9 (d, Ar-CH), 59.7 (t, CH_2), 55.4 [t, Ar(OMe)], 55.2 [t, Ar(OMe)], 50.1 [s, C$(Me)_2$], 42.1 [s, C(Me)Ar], 30.9 (q, 2C, CH_3), 30.8 (q, CH_3), 30.5 (q, CH_3) ppm.

HR-MS (ESI+): m/z calculated for $[C_{20}H_{24}O_2]^+$=$[M]^+$: 296.1771; found: 296.1785.



6k

5-(1,3-Benzodioxol-5-yl)-5,7,7-trimethyl-6,7-dihydro-5*H*-indeno[5,6-*d*][1,3]dioxole (6k):

GP-1 was carried out with alcohol **4k** (45 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography

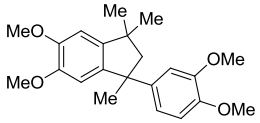
(petroleum ether/ethyl acetate 92:8 to 90:10) furnished indane **6k** (39 mg, 96%) as brown color viscus liquid. [TLC control R_f(**4k**)=0.40, R_f(**6k**)=0.65, (petroleum ether/ethyl acetate 90:10, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2957, 2891, 1477, 1431, 1280, 1235, 1213, 1036, 936, 812, 735 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=6.70–6.59 (m, 4H, ArH), 6.51 (s, 1H, ArH), 5.95 (dd, 2H, J=5.9 and 1.5 Hz, O-CH$_2$-O), 5.90 (dd, 2H, J=5.9 and 1.5 Hz, O-CH$_2$-O), 2.34 (d, 1H, J=13.2 Hz, CH_aH$_b$), 2.17 (d, 1H, J=13.2 Hz, CH$_a$$H_b$), 1.60 (s, 3H, CH$_3$), 1.28 (s, 3H, CH$_3$), 1.03 (s, 3H, CH$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=147.4 (s, ArC), 147.2 (s, ArC), 146.7 (s, ArC), 145.3 (s, ArC), 145.2 (s, 2C, ArC), 141.5 (s, ArC), 119.4 (d, ArCH), 107.6 (d, ArCH), 107.4 (d, ArCH), 104.9 (d, ArCH), 102.8 (d, ArCH), 101.0 (t, O-CH$_2$-O), 100.8 (t, O-CH$_2$-O), 59.7 (t, 2C, CH$_2$), 50.3 [s, C(CH$_3$)$_2$], 42.6 [s, C(CH$_3$)], 30.9 (q, CH$_3$), 30.8 (q, CH$_3$), 30.4 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{20}$H$_{24}$NO$_4$]$^+$=[M+NH$_4$]$^+$: 342.1700; found: 342.1705.



6l

1-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1,3,3-trimethylindane (6l):

GP-1 was carried out with alcohol **4l** (49 mg, 0.25 mmol), AgSbF$_6$ (0.9mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 88:12 to 84:16) furnished indane **6l** (42 mg, 94%) as brown color viscus liquid. [TLC control R_f(**4l**)=0.40, R_f(**6l**)=0.60, (petroleum ether/ethyl acetate 84:16, UV detection)].

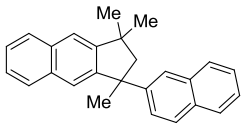
IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2953, 2859, 1503, 1462, 1286, 1253, 1239, 1144, 1027, 854, 762 cm^{-1}.

^{1}H NMR (CDCl$_3$, 400 MHz): δ=6.75–6.65 (m, 4H, ArH), 6.59 (s, 1H, ArH), 3.91 (s, 3H, ArOMe), 3.83 (s, 3H, ArOMe), 3.82 (s, 3H, ArOMe), 3.77 (s, 3H, ArOMe), 2.34 (d, 1H,

J=12.7 Hz, C*H*$_a$H$_b$), 2.18 (d, 1H, *J*=12.7 Hz, CH$_a$*H*$_b$), 1.65 (s, 3H, CH$_3$), 1.31 (s, 3H, CH$_3$), 1.04 (s, 3H, CH$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=148.8 (s, ArC), 148.3 (s, ArC), 148.2 (s, ArC), 146.7 (s, ArC), 144.0 (s, ArC), 143.9 (s, ArC), 140.2 (s, ArC), 118.6 (d, ArCH), 110.4 (d, ArCH), 110.3 (d, ArCH), 107.4 (d, ArCH), 105.1 (d, ArCH), 59.7 (t, CH$_2$), 56.1 (q, ArOMe), 55.9 (q, ArOMe), 55.7 (q, ArOMe), 50.3 [s, *C*(CH$_3$)$_2$], 42.7 [s, *C*(CH$_3$)], 30.8 (q, CH$_3$), 30.7 (q, CH$_3$), 30.4 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for [C$_{22}$H$_{29}$O$_4$]$^+$=[M+H]$^+$: 357.2060; found: 357.2054.



6n

1,1,3-Trimethyl-3-(2-naphthyl)-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene (6n):

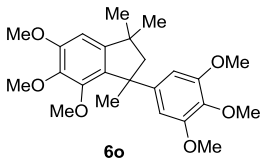
GP-1 was carried out with alcohol **4n** (47 mg, 0.25 mmol), AgSbF$_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 94:6) furnished indane **6n** (40 mg, 93%) as brown color viscus liquid. [TLC control R_f(**4n**)=0.50, R_f(**6n**)=0.65, (petroleum ether/ethyl acetate 94:6, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2958, 1597, 1454, 1376, 1277, 1137, 817, 747 cm-1.

^{1}H NMR (CDCl$_3$ 400 MHz): δ=7.90-7.70 (m, 5H, Ar-H), 7.63 (d, 1H, *J*=8.3 Hz, ArH), 7.50-7.20 (m, 4H, ArH), 7.27 (dd, 1H, *J*=8.3 and 6.8 Hz, ArH), 7.20 (d, 1H, *J*=6.8 Hz, ArH), 7.08 (dd, 1H, *J*=8.3 and 6.8 Hz, ArH), 2.44 (d, 1H, *J*=13.7 Hz, C*H*$_a$H$_b$), 2.36 (d, 1H, *J*=13.7 Hz, CH$_a$*H*$_b$), 2.06 (s, 3H, CH$_3$), 1.43 (s, 3H, CH$_3$), 1.39 (s, 3H, CH$_3$) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): δ=149.4 (s, ArC), 148.6 (s, ArC), 142.7 (s, ArC), 133.9 (s, ArC), 133.3 (s, ArC), 131.7 (s, ArC), 129.7 (s, ArC), 128.8 (d, ArCH), 128.7 (d, ArCH), 128.1 (d, ArCH), 128.0 (d, ArCH), 127.4 (d, ArCH), 126.3 (d, ArCH), 125.8 (d, ArCH), 125.6 (d, ArCH), 125.3 (d, ArCH), 125.0 (d, ArCH), 124.5 (d, ArCH), 123.5 (d, ArCH), 121.3 (d, ArCH), 61.3 (t, CH$_2$), 52.1 [s, C(Me)$_2$], 43.3 [s, C(Me)Ar], 31.4 (q, CH$_3$), 31.3 (q, CH$_3$), 28.1 (q, CH$_3$) ppm.

HR-MS (APCI+): m/z calculated for $[C_{26}H_{28}N]^+=[M+NH_4]^+$: 354.2216; found: 354.2210.



6o

4,5,6-trimethoxy-1,3,3-trimethyl-1-(2,3,4-trimethoxyphenyl)indane (6o):

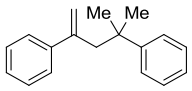
GP-1 was carried out with alcohol **4o** (56 mg, 0.25 mmol), $AgSbF_6$ (0.9mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished indane **6o** (51 mg, 98%) as brown color viscus liquid. [TLC control R_f(**4o**)=0.40, R_f(**6o**)=0.60, (petroleum ether/ethyl acetate 80:20, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2955, 2866, 1589, 1508, 1460, 1409, 1332, 1238, 1125, 1020, 832 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.45 (s, 1H, ArH), 6.39 (s, 2H, ArH), 3.88 (s, 3H, ArOMe), 3.81 (s, 3H, ArOMe), 3.79 (s, 3H, ArOMe), 3.74 (s, 6H, 2×ArOMe), 3.59 (s, 3H, ArOMe), 2.32 (d, 1H, J=13.2 Hz, CH_aH$_b$), 2.13 (d, 1H, J=13.2 Hz, CH$_a$$H_b$), 1.74 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.06 (s, 3H, CH_3) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=153.8 (s, ArC), 152.4 (s, 2C, ArC), 150.2 (s, ArC), 147.7 (s, ArC), 146.9 (s, ArC), 140.9 (s, ArC), 135.6 (s, ArC), 132.7 (s, ArC), 103.8 (d, 2C, ArCH), 100.8 (d, ArCH), 60.8 (q, ArOMe), 60.5 (q, ArOMe), 60.1 (t, CH_2), 60.0 (q, ArOMe), 56.0 (q, ArOMe), 55.9 (q, ArOMe), 51.0 [s, $C(CH_3)_2$], 43.4 [s, $C(CH_3)$], 31.0 (q, CH_3), 30.5 (q, CH_3), 29.1 (q, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{24}H_{33}O_6]^+=[M+H]^+$: 417.2272; found: 417.2270.



5a

(1,1-Dimethyl-3-phenylbut-3-enyl)benzene (5a):

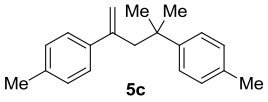
GP-1 was carried out with alcohol **4a** (34 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography

(petroleum ether/ethyl acetate 100:0 to 98:2) furnished the dimer **5a** (27 mg, 90%) as brown color viscus liquid. [TLC control R_f(**4a**)=0.60, R_f(**5a**)=0.80, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2958, 1487, 1400, 1093, 1011, 821, 724 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.35-7.05 (m, 10H, ArH), 5.12 (d, 1H, *J*=2.0 Hz, C*H*$_a$H$_2$), 4.77 (d, 1H, *J*=1.0 Hz, CH$_a$ *H*$_b$), 2.82 (s, 2H, CH_2), 1.21 [s, 6H, $(CH_3)_2$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.4 [s, ArC$(CH_2)_2$], 146.7 (s, ArC), 143.4 (s, ArC), 128.0 (d, 2C, ArCH), 127.8 (d, 2C, ArCH), 126.8 (d, ArCH), 126.5 (d, 2C, ArCH), 125.9 (d, 2C, ArCH), 125.4 (d, ArCH), 116.9 (t, CH_2), 49.5 (t, CH_2), 38.6 [s, C$(Me)_2$], 28.7 (q, 2C, CH_3) ppm.



5c

1-[1,1-Dimethyl-3-(4-methylphenyl)but-3-enyl]-4-methylbenzene (5c):

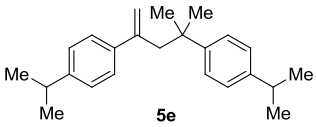
GP-1 was carried out with alcohol **4c** (38 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the dimer **5c** (27 mg, 81%) as brown color viscus liquid. [TLC control R_f(**4c**)=0.55, R_f(**5c**)=0.75, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2961, 1511, 1452, 1348, 1285, 1184, 1019, 814, 732 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.16 (dd, 4H, *J*=8.8 and 8.3 Hz, ArH), 7.10-6.98 (m, 4H, ArH), 5.10 (d, 1H, *J*=2.0 Hz, C*H*$_a$H$_b$), 4.72 (d, 1H, *J*=1.0 Hz, CH$_a$*H*$_b$), 2.76 (s, 2H, CH_2), 2.29 (s, 3H, ArCH_3), 2.27 (s, 3H, ArCH_3), 1.16 [s, 6H, $(CH_3)_2$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=146.7 [s, ArC$(CH_2)_2$], 146.5 (s, ArC), 140.6 (s, ArC), 136.4 (s, ArC), 134.8 (s, ArC), 128.7 (d, 2C, ArCH), 128.5 (d, 2C, ArCH), 126.3 (d, 2C, ArCH), 125.7 (d, 2C, ArCH), 116.1 (t, CH_2), 49.4 (t, CH_2), 38.3 [s, C$(Me)_2$], 28.7 (q, 2C, CH_3), 21.0 (q, ArCH_3), 20.8 (q, ArCH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{28}N]^+$=$[M+NH_4]^+$: 282.2216; found: 282.2209.



5e

1-Isopropyl-4-[3-(4-isopropylphenyl)-1,1-dimethylbut-3-enyl]benzene (5e):

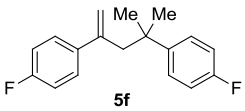
GP-1 was carried out with alcohol **4e** (46 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the dimer **5e** (40 mg, 96%) as brown color viscus liquid. [TLC control R_f(**4e**)=0.50, R_f(**5e**)=0.70, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2959, 1511, 1462, 1385, 1053, 831, 573 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.15 (d, 2H, *J*=8.3 Hz, ArH), 7.10 (d, 2H, *J*=8.3 Hz, ArH), 7.05-6.95 (m, 4H, ArH), 5.09 (d, 1H, *J*=1.0 Hz, C$H_{2a}H_{2b}$), 4.73 (s, 1H, CH_a H_b), 2.86-2.70 [m, 4H, Ar-C*H* $(Me)_2$ and CH_2], 1.20-1.10 [m, 18H, $(CH(CH_3)_2)_2$ and $C(CH_3)_2$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=147.3 [s, $ArC(CH_2)_2$], 146.9 (s, ArC), 146.6 (s, ArC), 145.7 (s, ArC), 140.8 (s, ArC), 126.3 (d, 2C, ArCH), 125.9 (d, 2C, ArCH), 125.7 (d, 2C, ArCH), 125.7 (d, 2C, ArCH), 116.1 (t, CH_2), 49.5 (t, CH_2), 38.2 [s, $C(Me)_2$], 33.6 [q, Ar*C*$H(CH_3)_2$], 33.5 [q, Ar-*C*$H(CH_3)_2$], 28.7 (q, 2C, CH_3), 24.0 [q, 2C, Ar-CH(*C*$H_3)_2$], 23.9 [q, 2C, Ar-CH(*C*$H_3)_2$] ppm.

HR-MS (ESI+): m/z calculated for $[C_{24}H_{36}N]^+$=$[M+NH_4]^+$: 338.2842; found: 338.2836.



5f

1-Fluoro-4-[3-(4-fluorophenyl)-1,1-dimethylbut-3-enyl]benzene (5f):

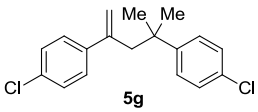
GP-1 was carried out with alcohol **4f** (36 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the dimer **5f** (30 mg, 94%) as brown color viscus liquid. [TLC control R_f(**4f**)=0.50, R_f(**5f**)=0.70, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2959, 1602, 1506, 1485, 1229, 1162, 1014, 827, 580 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.22-7.08 (m, 4H, Ar-H), 6.94-6.80 (m, 4H, Ar-H), 5.08 (d, 1H, *J*=1.5 Hz, C$H_{2a}H_{2b}$), 4.78 (s, 1H, CH_{2a} H_{2b}), 2.77 (s, 2H, CH_2), 1.23 [s, 6H, $(CH_3)_2$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.1 (d, *J*=245.0 Hz, ArC), 162.0 (d, *J*=243.6 Hz, ArC), 145.6 (s, ArC), 144.4 (d, *J*=2.9 Hz, ArC), 139.1 (d, *J*=2.9 Hz, ArC), 127.9 (d, 2C, *J*=7.3 Hz, ArCH),, 127.4 (d, 2C, *J*=8.1 Hz, ArCH), 116.9 (t, CH_2), 114.6 (d, 2C, *J*=21.3 Hz, ArCH), 114.2 (d, 2C, *J*=21.3 Hz, ArCH), 50.1 (t, CH_2), 38.2 [s, $C(Me)_2$], 29.0 (q, 2C, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{19}F]^+$=$[M+H]^+$: 273.1481; found: 273.1459.



5g

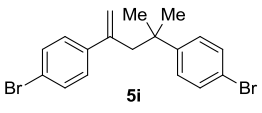
1-Chloro-4-[3-(4-chlorophenyl)-1,1-dimethylbut-3-enyl]benzene (5g):

GP-1 was carried out with alcohol **4g** (43 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 96:4) furnished the dimer **5g** (33 mg, 86%) as brown color viscus liquid. [TLC control R_f(**4g**)=0.60, R_f(**5g**)=0.75, (petroleum ether/ethyl acetate 96:4, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2958, 1489, 1397, 1249, 1094, 1012, 820, 758 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.20-7.13 (m, 6H, Ar-H), 7.09 (d, 2H, *J*=8.3 Hz, Ar-H), 5.11 (d, 1H, *J*=2.0 Hz, C$H_{2a}H_{2b}$), 4.79 (d, 1H, *J*=1.0 Hz, CH_{2a} H_{2b}), 2.76 (s, 2H, CH_2), 1.21 [s, 6H, $(CH_3)_2$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=147.3 [s, $ArC(CH_2)_2$], 145.4 (s, ArC), 141.5 (s, ArC), 132.6 (s, ArC), 131.3 (s, ArC), 128.1 (d, 2C, ArCH), 127.8 (d, 2C, ArCH), 127.7 (d, 2C, ArCH), 127.4 (d, 2C, ArCH), 117.5 (t, CH_2), 49.7 (t, CH_2), 38.4 [s, $C(Me)_2$], 28.7 (q, 2C, CH_3) ppm.



5i

1-Bromo-4-[3-(4-bromophenyl)-1,1-dimethylbut-3-enyl]benzene (5i):

GP-1 was carried out with alcohol **4i** (54 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography

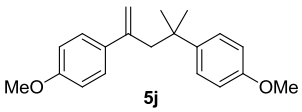
(petroleum ether/ethyl acetate 100:0 to 98:2) furnished the dimer **5i** (35 mg, 70%) as brown color viscus liquid. [TLC control R_f(**4i**)=0.60, R_f(**5i**)=0.75, (petroleum ether/ethyl acetate 98:2, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2960, 1488, 1393, 1262, 1101, 1007, 825, 733 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.30 (dd, 4H, *J*=9.3 and 8.8 Hz, Ar-H), 7.08 (d, 2H, *J*=8.8 Hz, Ar-H), 7.02 (d, 2H, *J*=8.8 Hz, Ar-H), 5.11 (d, 1H, *J*=2.0 Hz, C$H_{2a}H_{2b}$), 4.80 (d, 1H, *J*=1.0 Hz, CH_{2a} H_{2b}), 2.75 (s, 2H, CH_2), 1.20 [s, 6H, $(CH_3)_2$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.1 [s, $ArC(CH_2)_2$], 145.7 (s, ArC), 142.3 (s, ArC), 131.4 (d, 2C, ArCH), 131.1 (d, 2C, ArCH), 128.4 (d, 2C, ArCH), 128.2 (d, 2C, ArCH), 121.1 (s, ArC), 119.7 (s, ArC), 117.9 (t, CH_2), 50.0 (t, CH_2), 38.8 [s, $C(Me)_2$], 29.0 (q, 2C, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{18}H_{18}NaBr_2]^+$=$[M+Na]^+$: 414.9667; found: 414.9631.



5j

1-Methoxy-4-[3-(4-methoxyphenyl)-1,1-dimethylbut-3-enyl]benzene (5j):

GP-1 was carried out with alcohol **4j** (42 mg, 0.25 mmol), $AgSbF_6$ (0.9 mg, 0.0025 mmol) and DCE (2 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 98:2 to 92:8) furnished the dimer **5j** (34 mg, 91%) as brown color viscus liquid. [TLC control R_f(**4j**)=0.45, R_f(**5j**)=0.65, (petroleum ether/ethyl acetate 92:8, UV detection)].

IR (neat; MIR-ATR, 4000–600 cm-1): ν*max*=2958, 1607, 1510, 1463, 1246, 1180, 1035, 828, 553 cm-1.

^{1}H NMR ($CDCl_3$ 400 MHz): δ=7.21 (dd, 4H, *J*=8.8 and 7.3 Hz, Ar-H), 6.79 (d, 4H, *J*=8.8 Hz, ArH), 5.11 (d, 1H, *J*=2.0 Hz, CH_aH_b), 4.73 (s, 1H, CH_a H_b), 3.80 (s, 3H, $ArOCH_3$), 3.79 (s, 3H, $ArOCH_3$), 2.78 (s, 2H, CH_2), 1.22 [s, 6H, $(CH_3)_2$] ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): δ=158.5 [s, $ArC(CH_2)_2$], 157.2 (s, ArC), 146.0 (s, ArC), 141.7 (s, ArC), 135.9 (s, ArC), 127.5 (d, 2C, ArCH), 127.9 (d, 2C, ArCH), 116.1 (t, CH_2), 113.3 (d, 2C, ArCH), 113.0 (d, 2C, ArCH), 55.1 (q, 2C, $ArOCH_3$), 49.7 (t, CH_2), 38.0 [s, $C(Me)_2$], 28.9 (q, 2C, CH_3) ppm.

HR-MS (APCI+): m/z calculated for $[C_{20}H_{28}NO_2]^+=[M+NH_4]^+$: 314.2115; found: 314.2130.

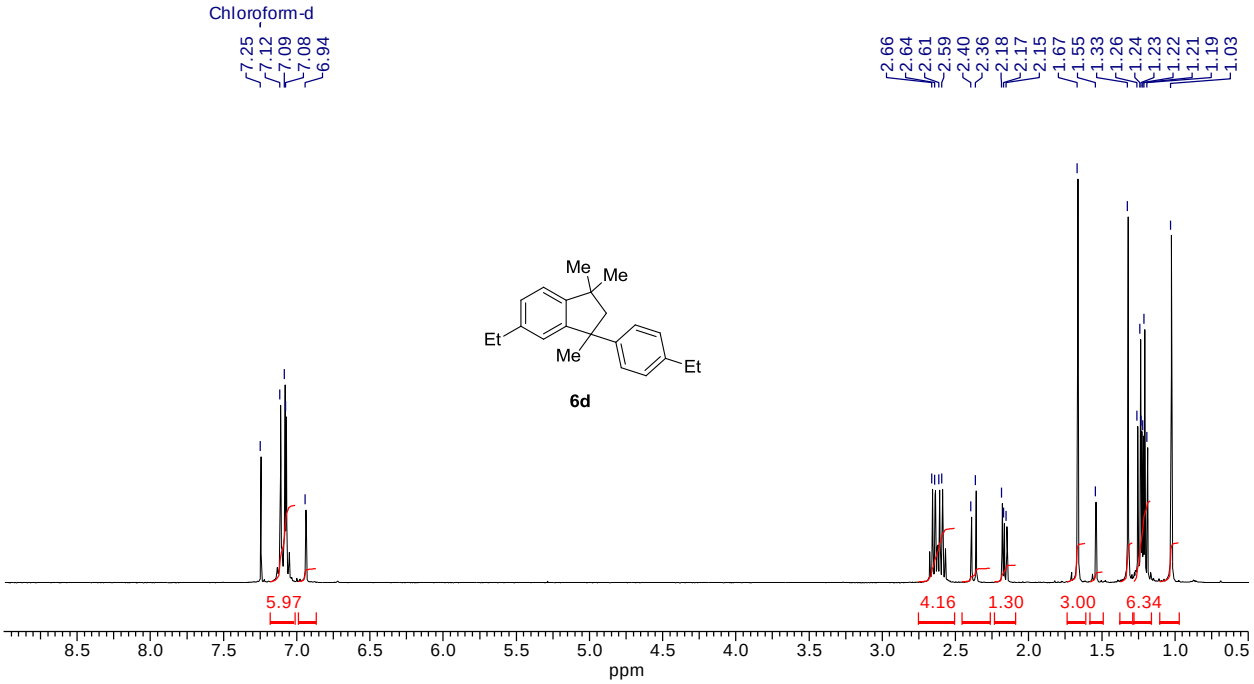


Figure III.6: ^{1}H-NMR (400 MHz) spectrum of **6d** in $CDCl_3$.

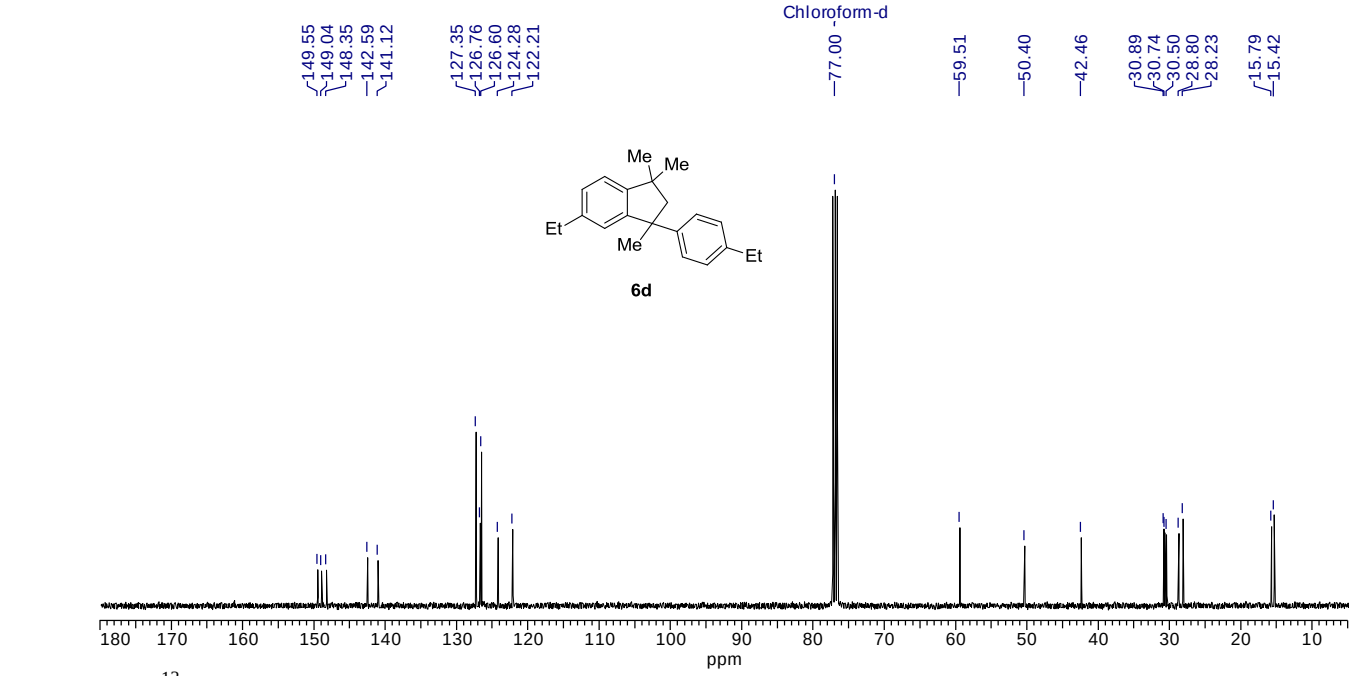


Figure III.7: ^{13}C-NMR (100 MHz) spectrum of **6d** in $CDCl_3$.

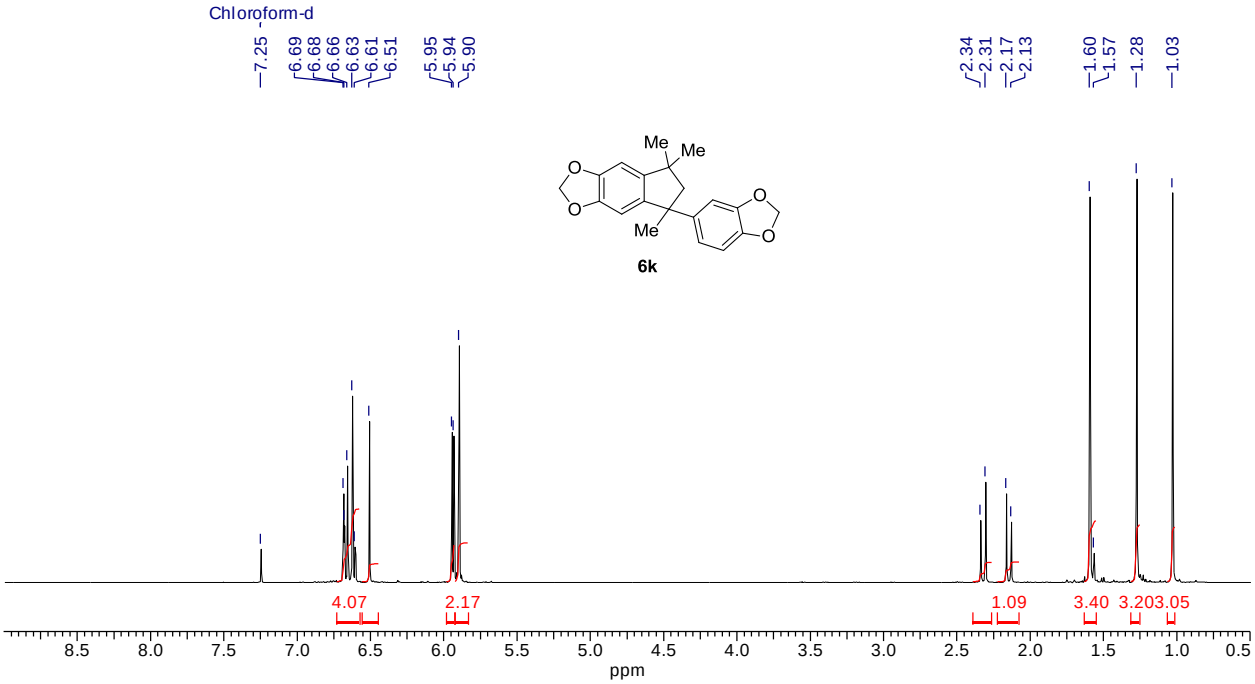


Figure III.8: ^{1}H-NMR (400 MHz) spectrum of **6k** in $CDCl_3$.

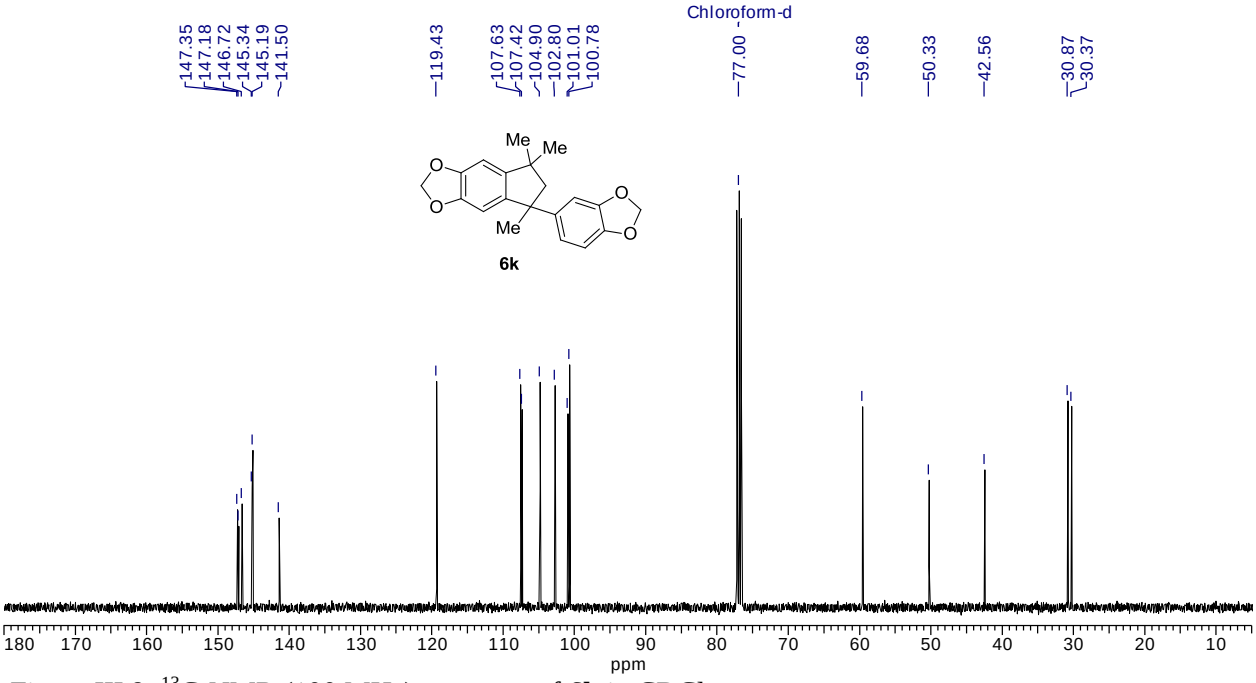


Figure III.9: ^{13}C-NMR (100 MHz) spectrum of **6k** in $CDCl_3$.

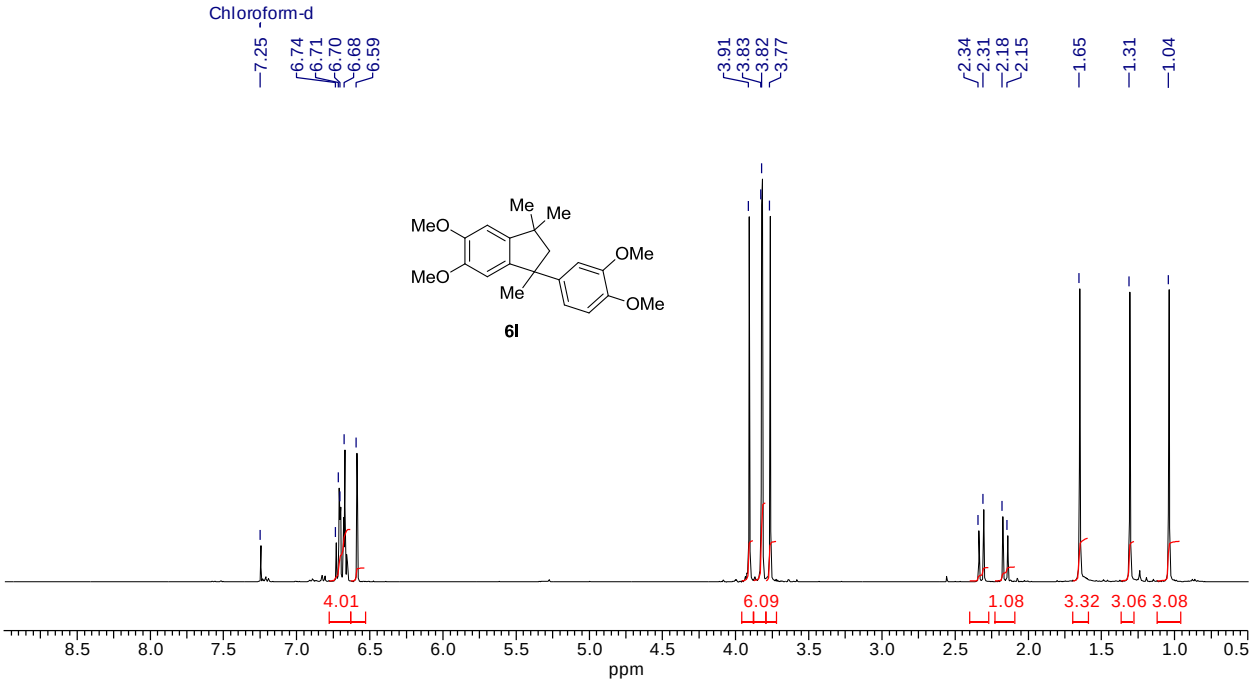


Figure III.10: ^{1}H-NMR (400 MHz) spectrum of **6l** in $CDCl_3$.

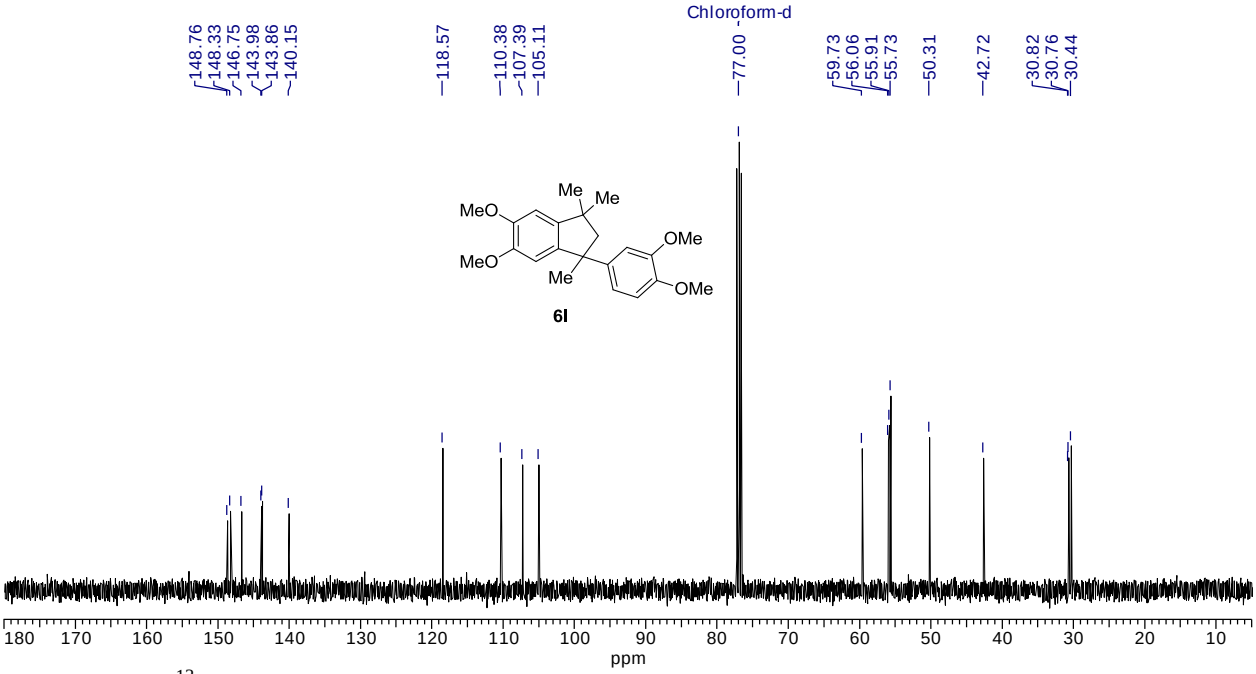


Figure III.11: ^{13}C-NMR (100 MHz) spectrum of **6l** in $CDCl_3$

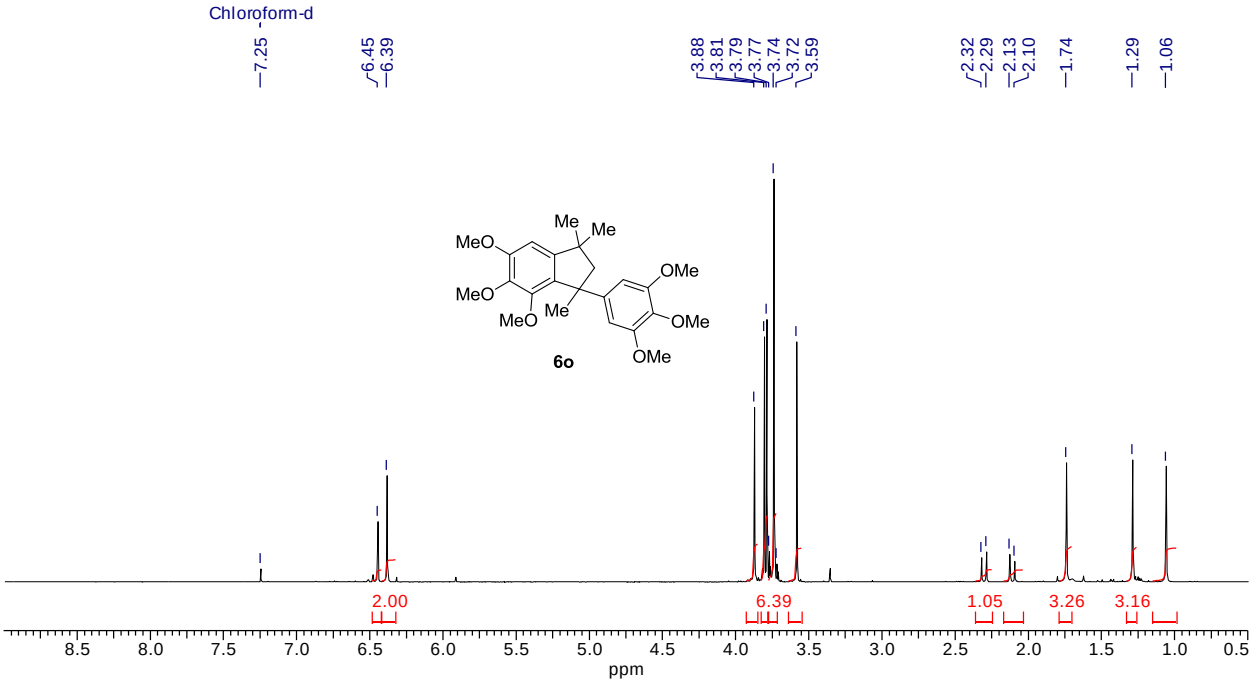


Figure III.12: ^{1}H-NMR (400 MHz) spectrum of **6o** in $CDCl_3$

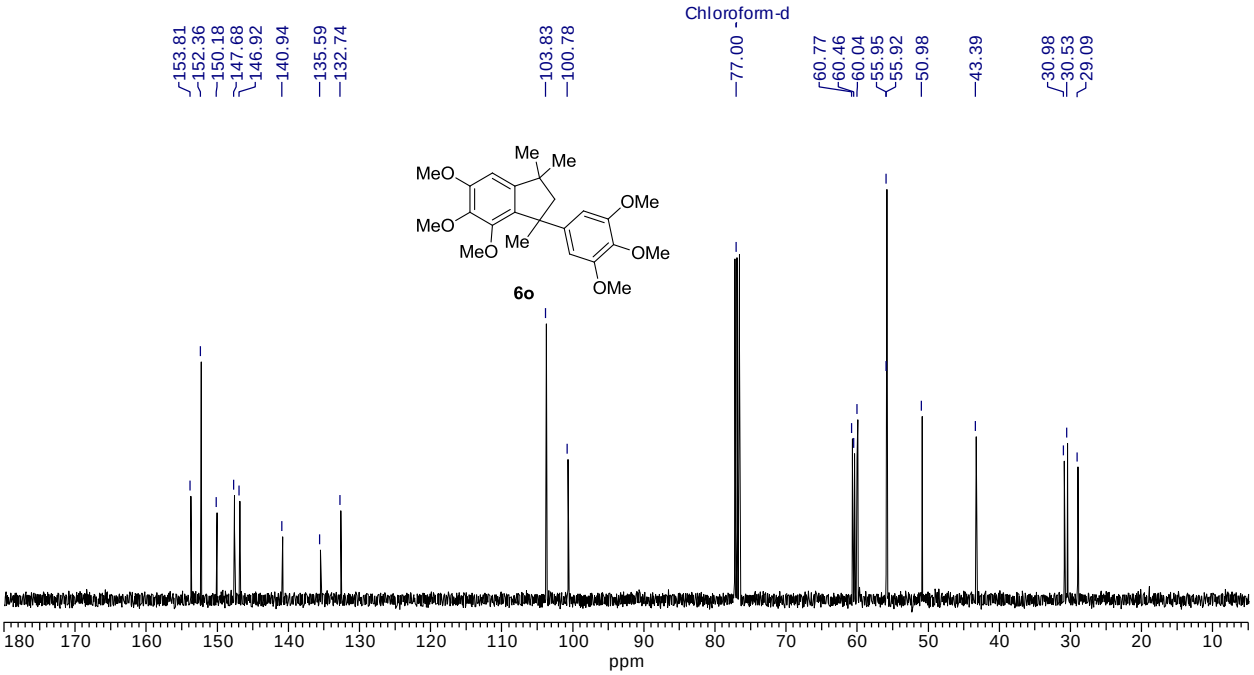


Figure III.13: ^{13}C-NMR (100 MHz) spectrum of **6o** in $CDCl_3$

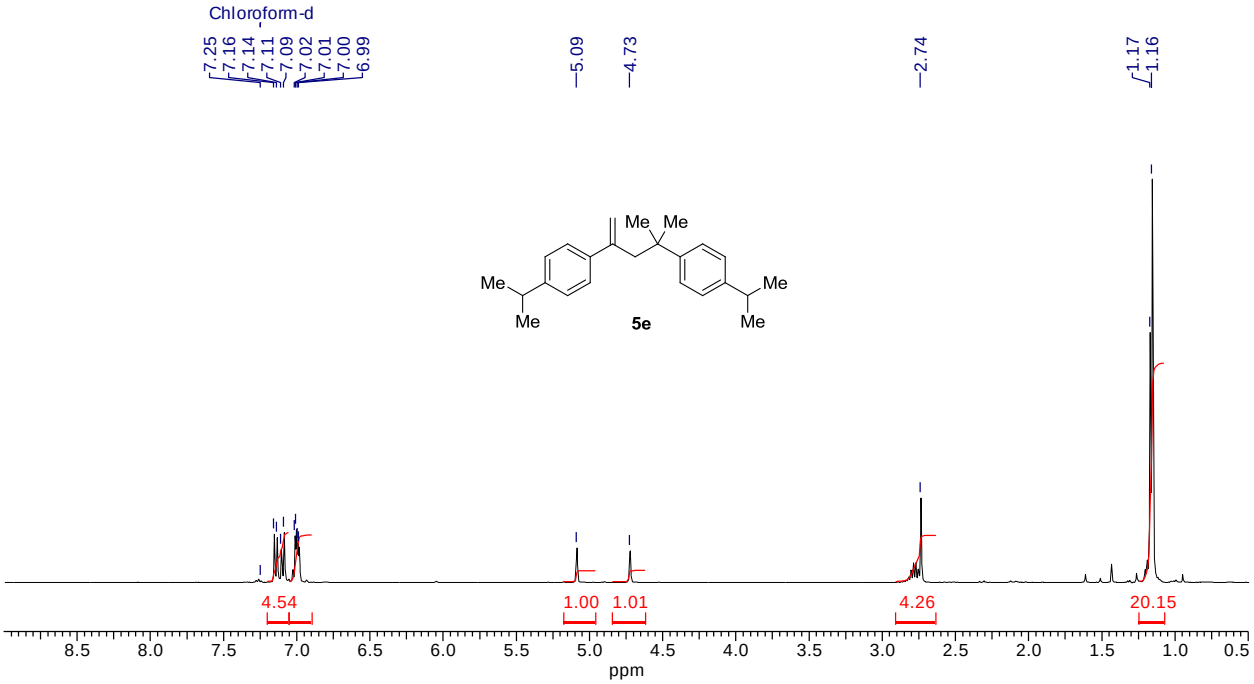


Figure III.14: ^{1}H-NMR (400 MHz) spectrum of **5e** in $CDCl_3$.

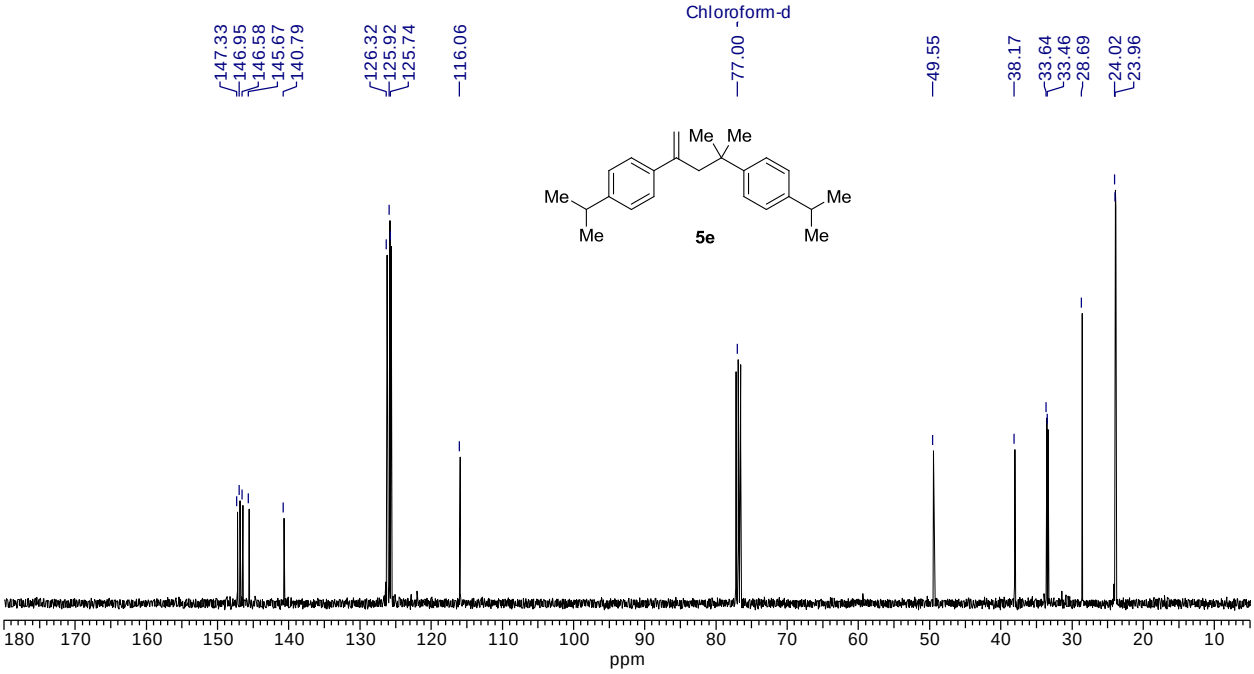


Figure III.15: ^{13}C-NMR (100 MHz) spectrum of **5e** in $CDCl_3$.

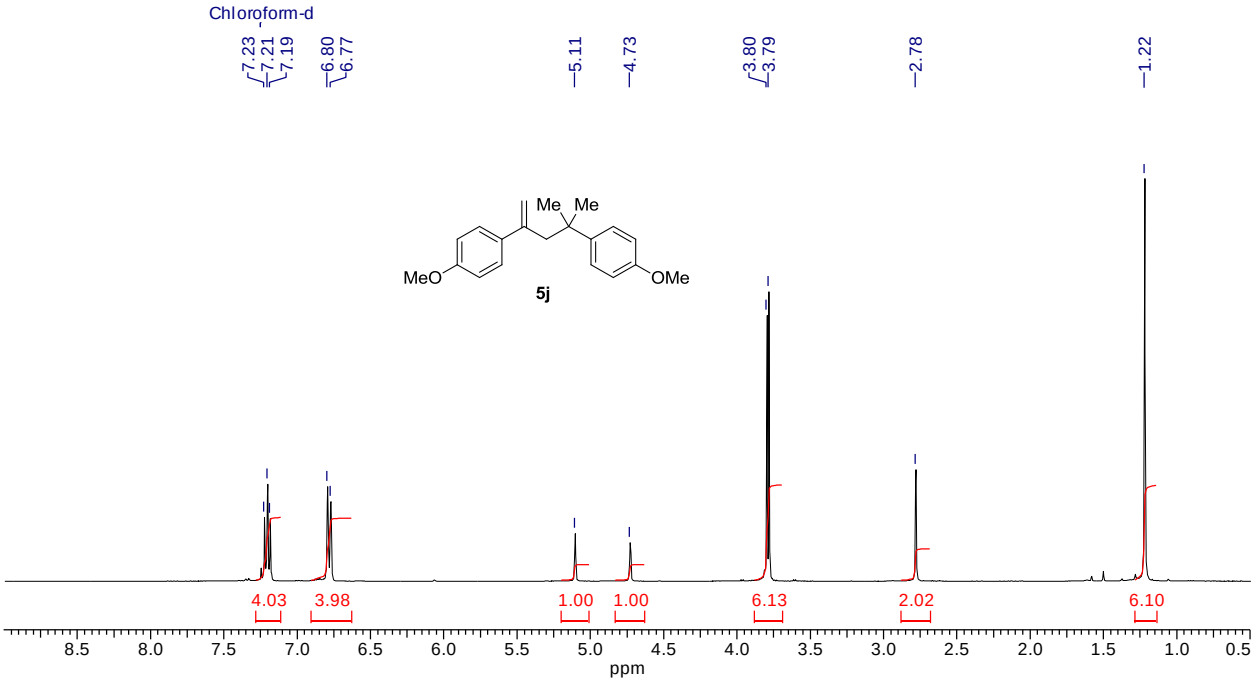


Figure III.16: ^{1}H-NMR (400 MHz) spectrum of **5j** in $CDCl_3$

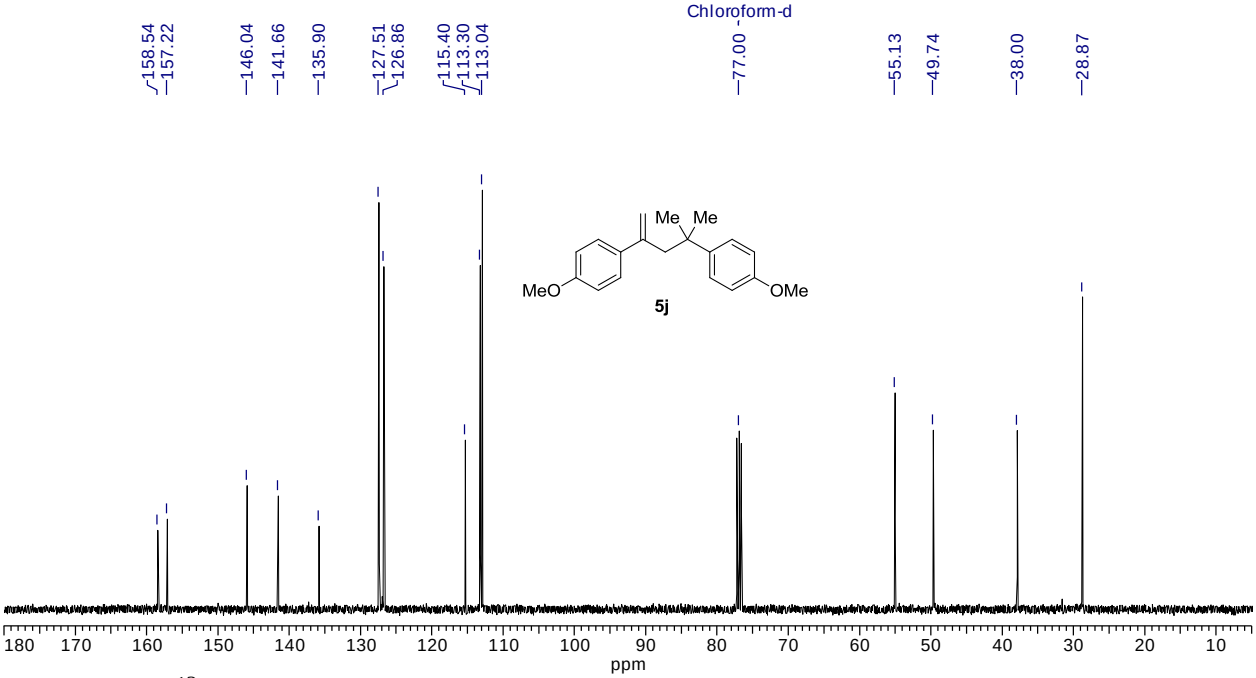


Figure III.17: ^{13}C-NMR (100 MHz) spectrum of **5j** in $CDCl_3$

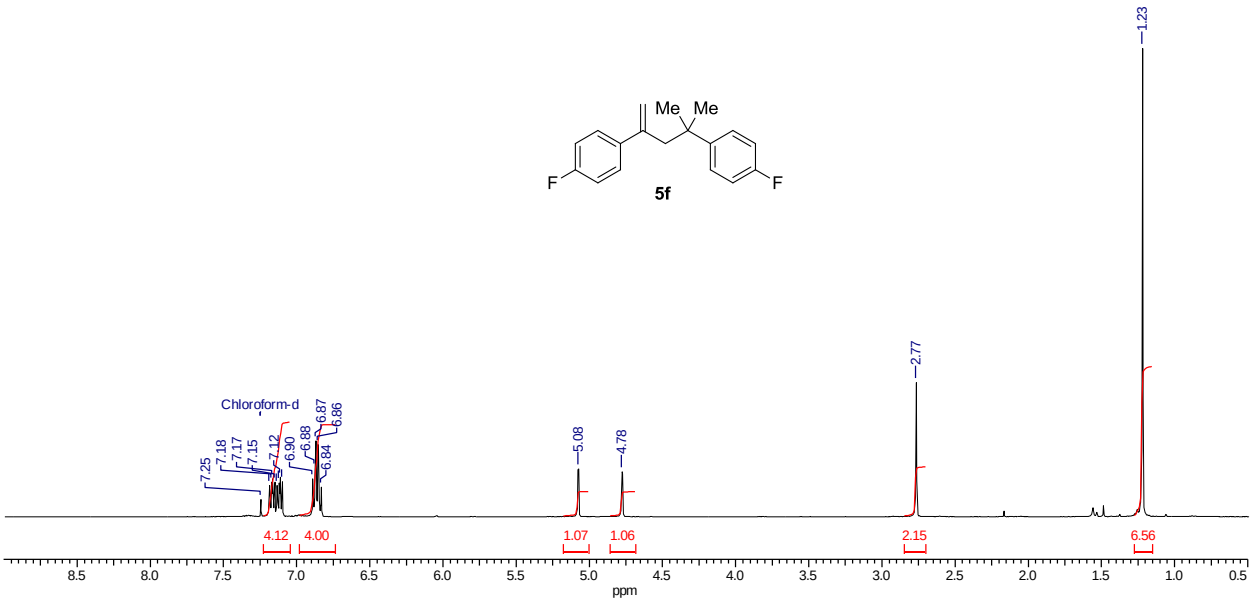


Figure III.18: ^{1}H-NMR (400 MHz) spectrum of **5f** in $CDCl_3$

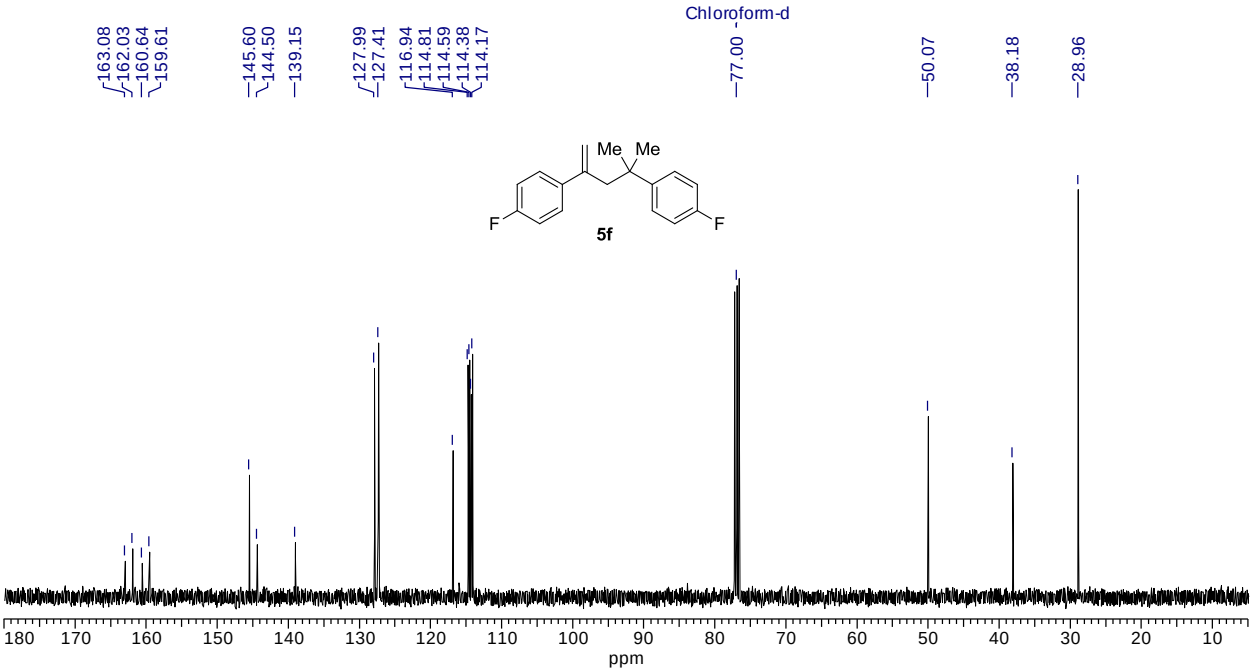


Figure III.19: ^{13}C-NMR (100 MHz) spectrum of **5f** in $CDCl_3$

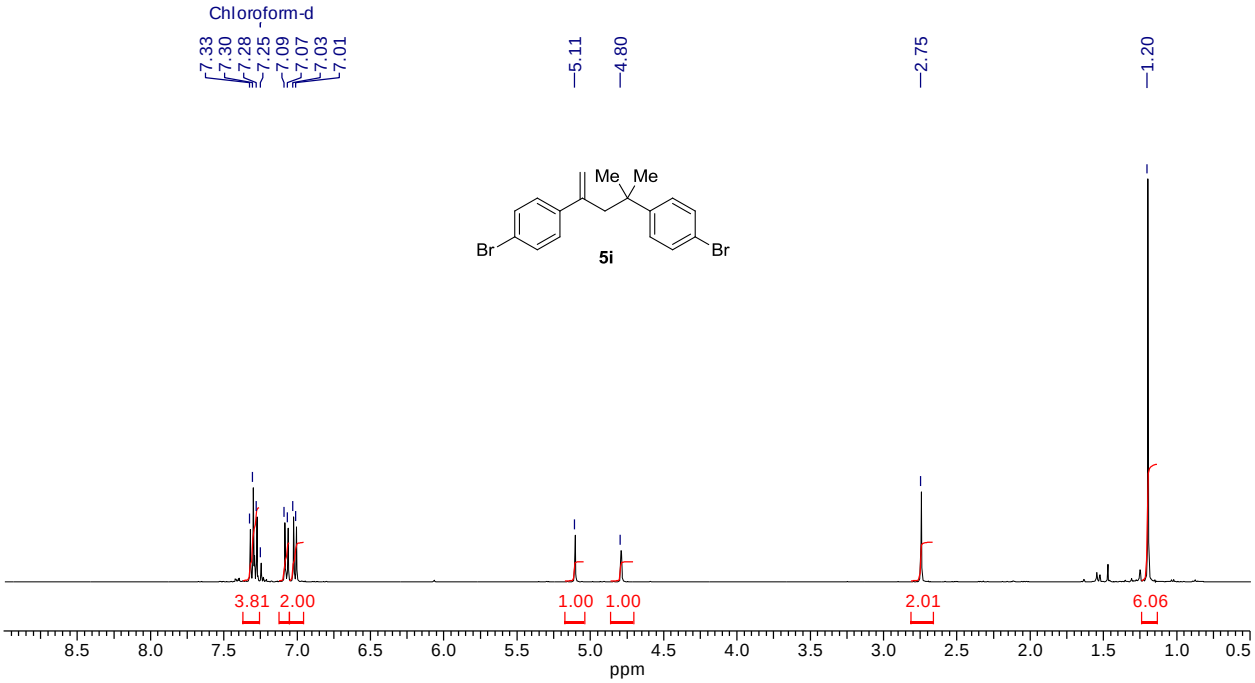


Figure III.20: ^{1}H-NMR (400 MHz) spectrum of **5i** in $CDCl_3$.

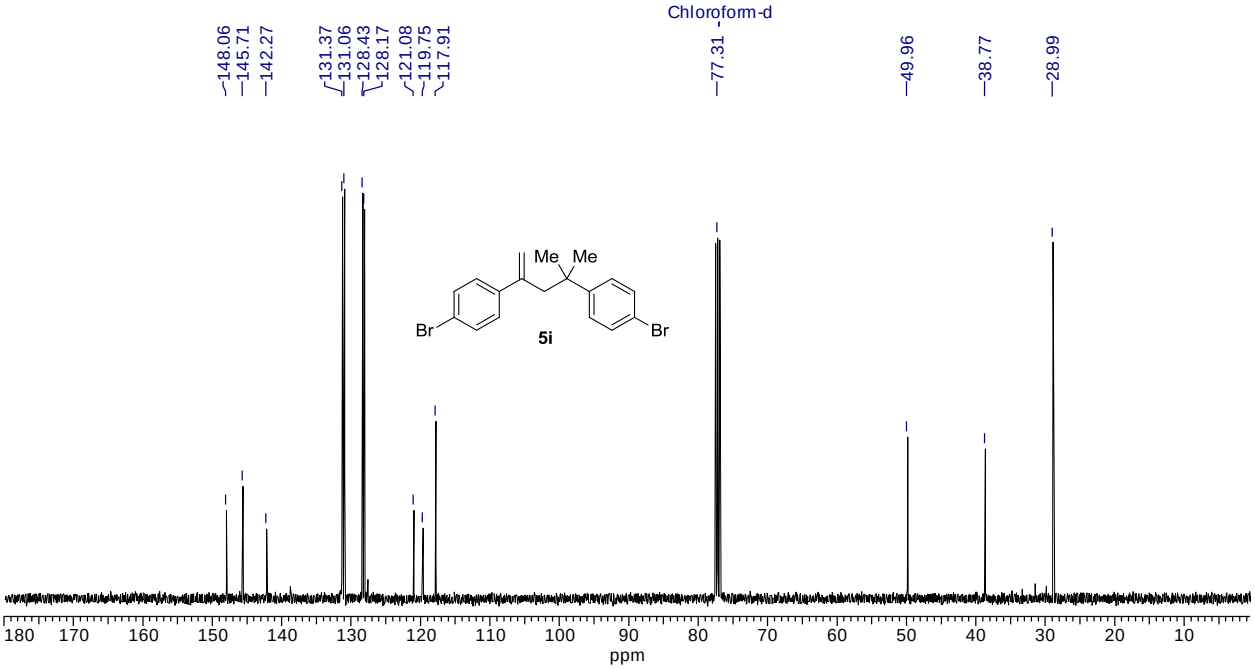


Figure III.21: ^{13}C-NMR (100 MHz) spectrum of **5i** in $CDCl_3$.

Notes and references:

1) Dorsey, B. D.; Levin, R. B., Mcdaniel, S. L.; Vacca, J. P.; Guare, J. P.; Darke, P. L.; Zugay, J. A.; Emini, E. A.; Schleif, W. A.; Quintero, J. C.; Lin, J. H.; Chen, I. W.; Holloway, M. K.; Fitzgerald, P. M. D.,; Axel, M. G.; Ostovic, D.; Anderson, P. S.; Huff, J. R. L. *J. Med. Chem*. **1994**, *37*, 3443.
2) Villetti, G.; Bregola, G.; Bassani, F.; Bergamaschi, M.; Rondelli, I.; Pietra, C.; Simonato, M. *Neuropharmacology*, **2001**, *40*, 866.
3) Yu, H.; Kim, I. J.; Folk, J. E.; Tian, X.; Rothman, R. B.; Baumann, M. H.; Dersch, C. M.; Flippen-Anderson, J. L.; Parrish, D.; Jacobson, A. E.; Rice, K. C. *J. Med. Chem*. **2004**, *47*, 2624.
4) Welsch, M. E.; Snyder, S. A.; Stockwell, B. R. *Curr*. *Opin*. *Chem*. *Biol*. **2010**, *14*, 347.
5) Nestico, P. F.; Morganroth, J.; Horowitz, L. N.; Mulhern, C. *Am. J. Cardiol*. **1987**, *59*, 1332.
6) Woltersdorf, O. W. Jr.; deSolms, S. J.; Stokker, G. E.; Cragoe, E. J. Jr. *J. Med. Chem*. **1984**, *27*, 840.
7) Fisher, M. M.; Wilensky, N. D.; Griffith, R. W.; Drumm, A.; Diefenbach, A. E.; Frankel, G. J. *N. Y. State. J. Med*. **1954**, *54*, 778.
8) (a) Friedel, C.; Crafts, J. M. *C. R. Hebd. Seances Acad. Sci*. **1877**, *84*, 1450.
   For monographs on the Friedel-Crafts acylation reaction, see; b) Heaney, H.; *In Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I.; Pergamon Press: Oxford, UK, **1991**, *2*, 733; (c) *In Friedel−Crafts and Related Reactions*; Olah, G. A.; Ed. John Wiley & Sons Inc.; London, **1964**, *3*, Part I, p 1. (d) Olah, G. A.; Klumpp, D. A.; *Superelectrophiles and Their Chemistry*; Wiley: New York, **2008**.
9) Cai, Q.; Li, J.; Bao, F.; Shan, Y. *Appl*. *Catal. A: Gen.* **2005**, *279*, 139.
10) Sun, H.-B.; Li, B. Hua, R.; Yin, Y. *Eur*. *J*. *Org*. *Chem*. 2006, 4231.
11) Higashimura, M.; Imamura, K.; Yokogawa, Y.; Sakakibara, T. *Chem*. *Lett*. **2004**, *33*, 728.
12) (a) Werstiuk, N. H.; Timmins, G. *Can. J. Chem.* **1988**, *66*, 2309. (b) Chaudhuri, B. *Org*. *Process Res*. *Dev*. **1999**, *3*, 220. (c) Chaudhuri, B. Sharma, M. M.; *Ind. Eng. Chem. Res*. **1989**, *28*, 1757.
13) Kirk-Othmer. *In Encyclopedia of Chemical Technology; Wiley Interscience: New York*, **1978**, *21*, 819.

14) Miyake, Y.; Moriyama, T.; Tanabe, Y.; Onodera, G.; Nishibayashi, Y. *Organometallics*, **2011**, *30*, 5972.

15) (a) Peppe, C.; Lang, E. S.; Molinos de Andrade, F.; Borges de Castro, L. *Synlett*. **2004**, *10*, 1723. (b) Tsuchimoto, T.; Kamiyama, S.; Negoro, R. Shirakawa, E.; Kawakami, Y. *Chem*. *Commun*. **2003**, 852.

16) Inagaki, A.; Edure, S.; Yatsuda, S.; Akita, M. *Chem*. *Commun*. **2005**, 5468.

17) (a) Das, R. N.; Sarma, K.; Pathak, M. G.; Goswami, A. *Synlett*. **2010**, *19*, 2908. (b) Dawans, F. *Tetrahedron Lett*. **1971**, 1943. (c) Wu, G.; Geib, S. J.; Rheingold, A. L.; Heck, R. F. *J*. *Org*. *Chem*. **1988**, *53*, 3238.

18) Schedler, M.; Wurz, N. E.; Daniliuc, C. G.; Glorius, F. *Org*. *Lett*. **2014**, *16*, 3134.

19) Sanz, R.; Martinez, A.; Guilarte, V.; Álvarez-Gutiérrez, J. M.; Rodríguez, F. *Eur*. *J*. *Org*. *Chem*., **2007**, 4642.

20) (a) Howard, F. Sawadjoon, S.; Samec, J. S. M. *Tetrahedron Letters*, **2010**, *51*, 4208. (b) Rueping, M.; Nachtsheim, B. J. *Beilstein J*. *Org*. *Chem*. **2010**, *6*, 6.

21) (a) Kotha, S.; Brahmachary, E., *J*. *Org*. *Chem*., **2000**, *65*, 1359. (b) Kotha, S.; Ghosh, A. *Tetrahedron* **2004**, *60*, 10833. (c) Kotha, S.; Ghosh, A. *Tetrahedron Lett*. **2004**, *45*, 2931. (d) Thallapally, P. K.; Jetti, R. K.; Katz, A. K.; Carrel, H. L.; Singh, K.; Lahiri, K.; Kotha, S.; Bose, R.; Desiraju, G. *Angew. Chem. Int. Ed*. **2004**, *43*, 1149. (e) Kotha, S.; Halder, S.; Lahiri, K. *Synthesis* **2002**, 339. (f) Kotha, S.; Brahmachary, E. *Indian J. Chem*. **2001**, *40*, 1. (g) Kotha, S.; Manivannan, E. *J. Chem. Soc. Perkin Trans***. 2001**, *1*, 2543. (g) Kotha, S.; Brahmachary, E. *J. Org. Chem.* **2000**. *65*, 1359,

22) (a) Reddy, A. G. K.; Krishna, J.; Satyanarayana, G. *Synlett* **2011**, 1756. (b) Krishna, J.; Reddy, A. G. K.; Mahendar, L.; Ramulu, B. V. Satyanarayana, G. *Synlett* **2012**, *23*, 375. (c) Reddy, A. G. K.; Satyanarayana, G. *Tetrahedron* **2012**, *68*, 8003. (d) Reddy, A. G. K.; Krishna, J.; Satyanarayana, G. *Tetrahedron Lett*. **2012**, *53*, 5635. (e) Krishna, J.; Reddy, A. G. K.; Satyanarayana, G. Synlett **2013**, *24*, 967. (f) Reddy, A. G. K.; Krishna, J.; Satyanarayana, G. *Tetrahedron* **2013**, *69*, 10098. (g) Suchand, B.; Krishna, J.; Ramulu, B. V.; Dibyendu, D.; Reddy, A. G. K.; Mahendar, L.; Satyanarayana, G. *Tetrahedron Lett*. **2012**, *53*, 3861. (h) Ramulu, B. V.; Mahendar, L.; Krishna, J.; Reddy, A. G. K.; Suchand, B.; Satyanarayana, G. *Tetrahedron* **2013**, *69*, 8305. (i) Krishna, J.; Reddy, A. G. K.; Satyanarayana, G. *Tetrahedron Lett*. **2014**, *55*, 861. (j) Reddy, A. G. K.;

Satyanarayana, G. Synthesis, **2015**, *47*, 1269. (k) Krishna, J.; Niharika, P.; Satyanarayana, G. *RSC Adv.*, **2015**, *5*, 26749. (l) Pedireddi, N.; Ramulu, B. V.; Satyanarayana, G. *Org*. *Biomol*. *Chem*., **2014**, *12*, 4347.

ABOUT THE AUTHOR

The author, Mr. Bokka Venkat Ramulu, was born on 12th June, 1984 at Salveed, Telangana, India. He had his early education (SSC) in 2001 at Govt. Boys High School, Pargi, Telangana. He completed his intermediate education from Vignan Junior College, Pargi, Telangana in 2003 and obtained B.Sc. (M. P. C) degree in 2006 from Sree Ananthapadmanabha Arts and Science College, Vikarabad, Osmania University, Telangana. He obtained his M.Sc. degree (Organic Chemistry) in 2007 from M. N. R. Degree and P. G. College. Osmania University, Hyderabad, Telangana. Then he joined the Department of Chemistry for the Ph.D. program at Indian Institute of Technology Hyderabad, under the supervision of Dr. G. Satyanarayana. He passed the comprehensive examination in May 2011. Presently he is continuing as a Senior Research Fellow of Council of Scientific Industrial Research, New Delhi, in the department.

LIST OF PUBLICATIONS

1. Superacid-Promoted Dual C–C Bond Formation by Friedel–Crafts Alkylation and Acylation of Ethyl Cinnamates: Synthesis of Indanones, **Ramulu**, **B. V.;** Reddy, A. G. K.; Satyanarayana, G. *Synlett*, **2013**, *24*, 863.
2. Superacid Promoted Dual C-C Bond Formation by Friedel-Crafts Alkylation/Acylation of Cinnamate Esters: Synthesis of Indanones, **Ramulu**, **B. V.;** Niharika, P.; Satyanarayana, G. *Synthesis*, **2015**, *47*, 1255.
3. Transition metals catalyzed C–C and C–O bonds formation: Facile synthesis of flavans and benzoxepines, **Ramulu**, **B**. **V.;** Mahendar, L.; Reddy, A. G. K.; Krishna, J.; Suchand, B.; Satyanarayana, G. *Tetrahedron* **2013**, *69*, 8305.
4. Superacid Mediated Intramolecular Condensation: Facile Synthesis of Indenones and Indanones, **Ramulu, B**. **V.;** Satyanarayana, G. *RSC Adv*., **2015**, *5*, 70972.
5. Synthesis of spirotetracyclic indanone and indenes via one-pot acid catalysis, **Ramulu, B**. **V**.; Satyanarayana, G. *(Manuscript under preparation)*

6. Lewis Acid Catalyzed Mild Method for Head to Tail Dimerization or Cyclization of *tert*-Alcohols, **Ramulu, B**. **V**.; Satyanarayana, G. *(Just Accepted in AJOC)*
7. Lewis acid promoted dual bond formation facile synthesis of dihydro coumarins and spirotetracyclic dihydrocoumarins, Niharika, P.; **Ramulu, B. V.;** Satyanarayana, G. *Org. Biomol. Chem.*, **2014**, *12*, 4347.
8. An efficient intermolecular [Pd]-catalyzed C-C and intramolecular [Cu]-catalyzed C-O bonds formation: Synthesis of functionalized flavans and benzoxepines, Suchand, B.; Krishna, J.; **Ramulu**, **B. V.;** Dibyendu, D.; Reddy, A. G. K.; Mahendar, L.; Satyanarayana, G. *Tetrahedron Lett*., **2012,** *53*, 3861.
9. Palladium mediated highly regio- and stereoselective intermolecular β-arylation on allylic alcohols: Synthesis of functionalized allylic alcohols, Krishna, J.; Reddy, A. G. K.; **Ramulu**, **B. V.;** Mahendar, L.; Satyanarayana, G. *Synlett*, **2012**, *23*, 375.
10. A domino palladium-catalyzed C-C and C-O bonds formation via dual O-H bond activation: Synthesis of 6,6-dialkyl-6*H*-benzo[c]chromenes, Mahendar, L.; Krishna, J.; Reddy, A. G. K.; **Ramulu**, **B. V.;** Satyanarayana, G. *Org. Lett*. **2012**, *14*, 628.