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An Access to Benzo[*a*]fluorenes, Benzo[*b*]fluorenes, and Indenes Triggered by Simple Lewis Acid

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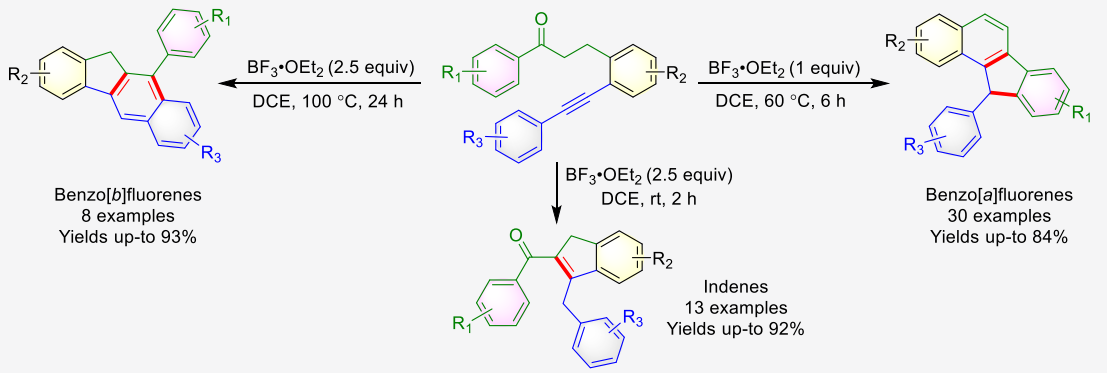

ABSTRACT: This report illustrates $BF_3{\cdot}OEt_2$ promoted intramolecular cascade cycloaromatization of 1,7-ynones toward synthesizing structurally diverse benzofluorene scaffolds. Remarkably, the present protocol promotes the formation of two consecutive C−C bonds intramolecularly and undergoes aromatization under mild reaction conditions to afford the tetracyclic benzo[*a*]fluorene frameworks. Besides, the formation of indenes was observed when 1-bromo-2-iodoarenes are relatively more electron-rich when compared with the one originating from the terminal arylacetylenes, under controlled conditions, wherein triple bond polarity has been just reversed due to the change of electronic effects exerted by the strong +M group of 1-bromo-2-iodoarenes, which is in conjugation to the connected triple bond. The same concept to generate indenes has also been extended by using aliphatic alkyne tethered ynones. Further, it was noticed that 1,7-ynones bearing the more electron-rich 1-bromo-2-iodoarenes than the arene ring arriving from the terminal arylacetylenes lead to benzo[*b*]fluorenes, under thermodynamic conditions, instead of delivering the benzo[*a*]fluorenes. In addition, this method features metal-free conditions, easily accessible starting materials, operational simplicity, gram-scale synthesis, and a wide range of substrate scopes.

INTRODUCTION

Chemists are fascinated with polyaromatic hydrocarbons because of their far-reaching applications in electronic and optical devices, luminous materials, and organic semiconductors, as well as the widespread curiosity with electronically delocalized systems.[1] On account of their stability, fluorescence properties, enormous ability to carry the charge, and presence of fused ring structures, these derivatives of polyarylated cores are of particular interest.[2] Considering their distinctive features, polycyclic aromatic hydrocarbons (PAHs) such as naphthalenes, phenanthrenes, anthracenes, fluorenes, and their analogues like benzo[*a*]fluorenones and benzo[*b*]fluorenes show potential applications in pharmaceutical and materials chemistry.[3] Furthermore, benzo[*a*]fluorene motifs can be found in natural products and are at the epicenter of several pharmaceutically active molecules. For instance, the naturally occurring benzo[*a*]fluorene core structured products such as veratramine, isoprekinamycin, dasyscyphins B, D−E, fluostatins A−H are class antibiotics, herbicides, and malarial drugs as shown in Figure 1.[4]

On the other hand, tandem or cascade reactions have an outstanding ability to introduce molecular complexity from reasonably simple starting materials; these transformations are especially intriguing when multiple rings are formed.[5] Recently, in the field of synthetic organic chemistry, electrophilic cascade reactions have received a lot of attention.[6]

The literature reports toward the synthesis of benzo[*a*]-fluorene frameworks are seldom, in comparison to the synthesis of benzo[*b*] and benzo[*c*]fluorenes. In this regard, the research group of Alabugin has demonstrated a couple of protocols toward the construction of benzo[*a*]fluorenes, in a radical cascade manner via traceless directing groups.[7a,b]

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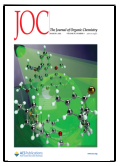

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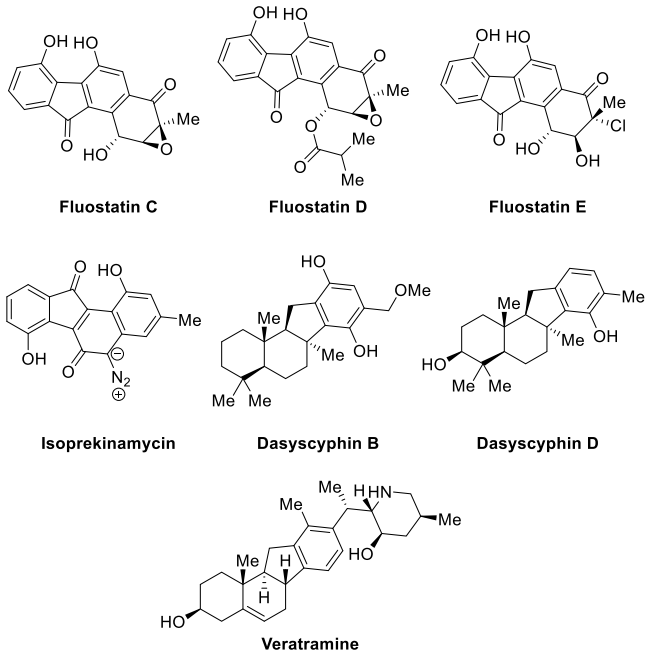


Figure 1. Representative natural products on a benzo[*a*]fluorene core.

Similarly, Shintani et al. have also unveiled a couple of synthetic methods for accessing benzo[*a*]fluorenes by employing rhodium catalysis.[8a,b] Also, the research group of Balamuragan has been active in synthesizing PAH by using acid-mediated cyclizations. For example, in 2012, the group has reported the construction of benzo[*a*]fluorene frameworks via [2 + 2] cycloaddition/alkyne acetal coupling of in situ generated acetals, starting with *ortho*-alkynyl benzaldehydes and aryl alkynes.[9a] Later, in the year 2018, the same research group revealed a cationic cycloisomerization of enynones promoted by triflic acid for accomplishing benzo[*a*]fluorene and benzo[*a*]fluorenone derivatives.[9b] Similarly, very recently, triflic acid-induced synthesis of benzo[*a*] and benzo[*b*]-fluorenes have been demonstrated via the formation of in situ generated acetals.[9c] While an efficient gold-catalyzed synthesis of benzo[*a*]fluorenes via 1,7-carbene transfer reaction starting from 1,6-diynyl dithioacetals was reported by Liu et al,[10] another gold-catalyzed tandem cyclization of alkylidene-cyclopropane-tethered alkynes for the construction of benzo-[*a*]fluorenes was reported by Shi and co-workers.[11] In addition, Wang and co-workers have demonstrated the synthesis of a broad range of benzo[*a*]fluorene derivatives via aromatic C−H functionalization of electron-rich-arenes with 1,5 enynes anchored by conjugates.[12]

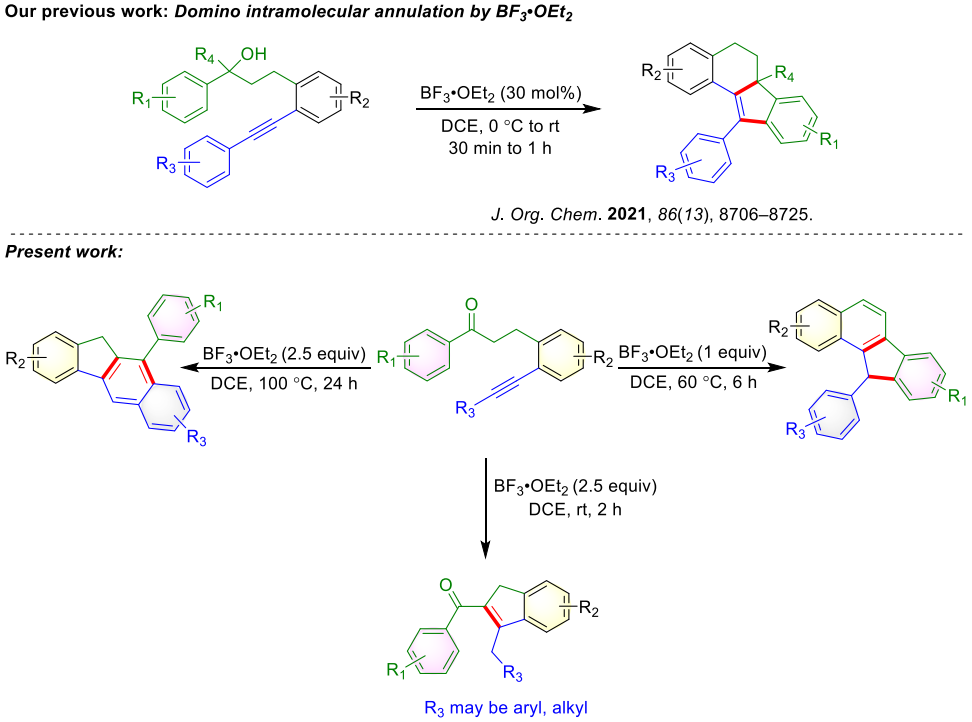
In this line, very recently, our group has demonstrated the synthesis of dihydrobenzo[*a*]fluorene derivatives via the intramolecular domino cyclization of alkynols by using a catalytic amount of $BF_3{\cdot}OEt_2$ as shown in Scheme 1.[13] Inspired by these results, herein, we present an intramolecular cascade cycloaromatization of ynones catalyzed by $BF_3{\cdot}OEt_2$, which affords the benzo[*a*]fluorene and benzo[*b*]fluorene derivatives with different substitution patterns. The synthesis of indene derivatives were also shown in this report.

RESULTS AND DISCUSSION

It was anticipated that the fabrication of benzo[*a*]fluorenes could be accessed starting from the ynones in the presence of a suitable acid. Accordingly, the precursor's ynones **5a**−**5ar** can be synthesized in a two-step Heck and Sonogashira sequence starting from allylic alcohols **1** and 1-bromo-2-iodoarenes **2** (for details see the Supporting Information).

With the required synthetic precursors **5a**−**5ar** in hand, we began our optimization studies for constructing the final tetracyclic benzo[*a*]fluorenes. Consequently, we have chosen 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-one **5a** (62

Scheme 1. Previous Work vs Current Work



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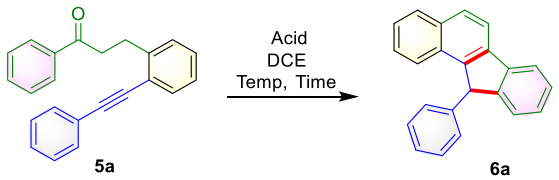
mg, 0.20 mmol) as a prototypical substrate. In this context, we chose 1,2-dichloroethane (DCE) as solvent, based on our previous observations with acid catalysis. Initially, only an 18% yield of **6a** was observed when the reaction was performed with 0.5 equiv of CH_3CO_2H with alkynone **5a** at 80 °C (Table 1, entry 1). Next, the reactions were carried out using varying amounts of $FeCl_3$ such as 30 mol % and 1 equiv, and observed only starting material **5a** in the case of the reaction with a catalytic amount of $FeCl_3$ (Table 1, entry 2). In contrast, a 32% yield of benzo[*a*]fluorene **6a** was isolated when the stoichiometric amounts of $FeCl_3$ were used (Table 1, entry 3). Surprisingly, when **5a** was treated with 1 equiv of $BF_3{\cdot}OEt_2$, benzo[*a*]fluorene **6a** was isolated in 62% yield (Table 1, entry 4). Later, the reaction was attempted with various quantities of $BF_3{\cdot}OEt_2$ at different temperatures (Table 1, entries 5 to 9), and we finally achieved the highest yield for the synthesis of benzo[*a*]fluorene **6a** with 1 equiv of $BF_3{\cdot}OEt_2$ at 60 °C for 6 h (Table 1, entry 8). Similarly, when the reaction is performed with 1 equiv of *p*-TSA at different temperatures 60 and 80 °C, the requisite product **6a** was provided in 62% and 74% yields, respectively (Table 1, entries 11 and 12). Notably, the metal triflates such as $Sc(OTf)_3$, $In(OTf)_3$, and $Cu(OTf)_2$ were employed in catalytic amounts (30 mol %) and delivered the desired product in decent yields up to 71% (Table 1, entries 13 to 15). Similarly, a catalytic amount of $AgSbF_6$ was utilized for triggering the transformation and yielded 76% of the required product **6a** (Table 1, entry 16). Furthermore, the attempts toward increasing the yields with superacid such as TfOH did not give positive outcomes and led to 61% yield of **6a** at room temperature (Table 1, entries 17 and 18).

Table 1. Optimizing Reaction Conditions for the Synthesis of Benzo[*a*]fluorene 6a[a,b,c]



entry	acid catalyst	temp (°C)	time (h)	yield[b] **6a** (%)
1	CH_3CO_2H (0.5 equiv)	80	3	18
2	$FeCl_3$ (30 mol %)	80	12	–
3	$FeCl_3$ (1 equiv)	80	4	32
4	$BF_3{\cdot}OEt_2$ (1 equiv)	80	6	62
5	$BF_3{\cdot}OEt_2$ (1 equiv)	rt	12	trace
6	$BF_3{\cdot}OEt_2$ (50 mol %)	60	8	47
7	$BF_3{\cdot}OEt_2$ (50 mol %)	80	8	53
8	**$BF_3{\cdot}OEt_2$ (1 equiv)**	**60**	**6**	**78**
9	$BF_3{\cdot}OEt_2$ (1 equiv)	80	6	73
10[c]	$BF_3{\cdot}OEt_2$ (1 equiv)	60	6	71
11	*p*-TSA (1 equiv)	60	6	62
12	*p*-TSA (1 equiv)	80	6	74
13	$Sc(OTf)_3$ (30 mol %)	80	8	62
14	$In(OTf)_2$ (30 mol %)	80	8	71
15	$Cu(OTf)_2$ (30 mol %)	80	6	68
16	$AgSbF_6$ (30 mol %)	80	6	76
17	TfOH (1 equiv)	80	1.5	52
18	TfOH (1 equiv)	rt	3	61

[a]Reaction conditions: Reactions were carried out with 62.4 mg (0.20 mmol) of 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-one **5a** in solvent DCE (1 mL). [b]Isolated yields. [c]HFIP is used as the solvent instead of DCE.

Among all the conditions screened, the parameters of entry 8 from Table 1 were found to be good concerning the yield of benzo[*a*]fluorene **6a**, wherein 1 equiv of $BF_3{\cdot}OEt_2$ was utilized as the acid catalyst. Various substitutions flanked on the three-arene rings were explored to prove the current method's scope and applicability. So, initially, the substrate scope was examined with ynones having diverse substituents on the arene ring of the allylic alcohol (i.e., with R_1 functional moieties). The reaction is exceptionally compatible with mild electron-donating groups such as Me, Et, and *i*-Pr groups situated at the *para*-position to the aromatic ring, and yielded the benzo[*a*]fluorenes **6b**, **6c**, and **6d** in 76%, 80%, and 71% yields, respectively (Table 2). Additionally, the structure of **6d** was unambiguously confirmed by single-crystal X-ray diffraction (SC-XRD) analysis (CCDC: 2120375). Notably, when a strong electron-donating group such as −OMe is anchored at the *meta*-position on the arene ring of the allylic alcohol, as anticipated, it furnishes an inseparable mixture of two feasible regioisomers **6e** and **6e′** in a ratio of 3:1. Also, the corresponding tetracyclic derivative **6f** was isolated in a yield of 73%, derived from the pipernal-ynone system. Besides, the reaction was also well compatible with a mild electron-withdrawing group, like an F substituent that is flanked at the *para*-position on the arene ring of allylic alcohol, but yielded **6g** in a somewhat lower yield of 57%, which makes it evident that electron-deactivating systems would impede the electrophilic aromatic substitution during the formation of benzo[*a*]fluorenes. Significantly, the pentacyclic product **6h** was isolated in a good yield of 75% (Table 2). Remarkably, the protocol was also flexible with the heterocyclic system, like thiophene derivative, and delivered the corresponding tetracyclic product **6i** in a 61% yield. Altogether, R_1 substituents ranging from strongly electron-donating, mild electron-donating, to mild electron-deactivating groups allowed the ease of synthesis of the desired products. Following these encouraging results, it was planned to investigate the possibilities on the alkyne-bearing ring (i.e., R_3 substituents on the ynone). Thus, initially, the ynones containing simple functional groups such as Me group at altered positions (*meta* and *para*), Et, *n*-butyl, and *t*-butyl groups are flanked at *para*-position on the arene ring of alkyne terminus, which has offered the requisite products **6j**−**6p** in decent yields ranging from 65% to 82%. Besides, to show the synthetic utility of the present protocol, a gram scale experiment was conducted for affording **6n** by taking **5n** on the 2.6 millimolar scale. Gratifyingly, the method is successful for large-scale synthesis and delivered the corresponding benzo[*a*]fluorene **6n** with a good yield of 76%. On the flip side, the ynones bearing reasonably electron-donating OMe group was also found to be good in accomplishing the benzo[*a*]fluorene derivatives **6q**, **6r**, **6s**, and **6t** in good to very good yields. Moreover, the present method is effective with electron-deactivating chloro- and fluoro-tethered ynone (R_3) groups on the alkyne terminus and has bestowed the final products' yield up to 73% (**6u**, **6v**, **6w**, **6x**, and **6y**). Next, we shifted our attention to examine the ynones bearing various substituents on the arene ring derived from the 1-bromo-2-iodoarene ring (i.e., R_2 group-containing aromatic ring). As predicted, the benzo[*a*]fluorene scaffolds **6z**, **6aa**, **6ab**, and **6ac** were isolated with good yields of around 79% when electron-donating groups such as Me and OMe are placed at *para*-position to the iodo substituent (Table 2).

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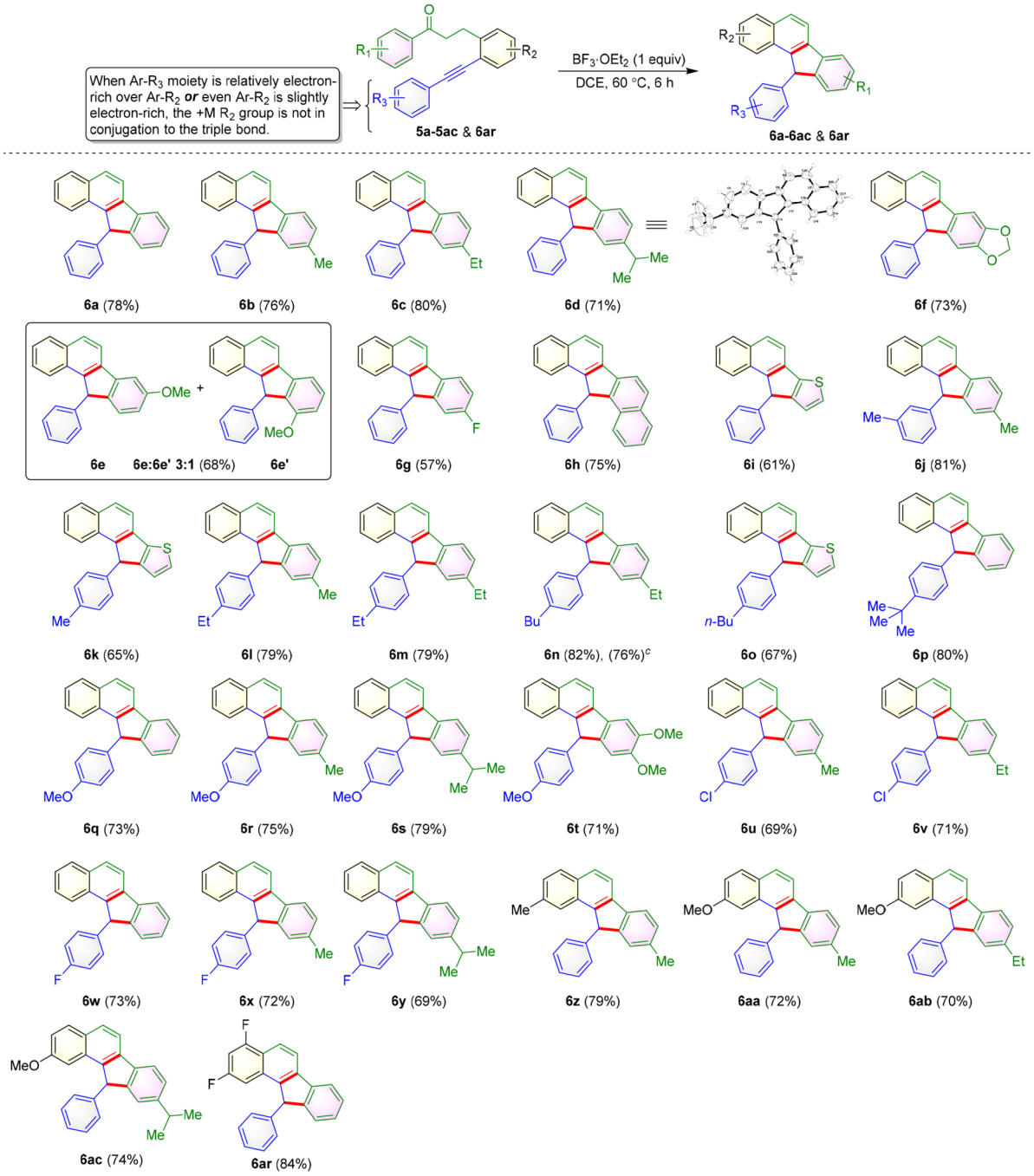
Table 2. Substrate Scope of Benzo[*a*]fluorenes 6a−6ac and 6ar[a,b]



[a]Reaction conditions: compound **5a−5ac** and **5ar** (0.2 mmol), $BF_3{\cdot}OEt_2$ (1 equiv), DCE (1.0 mL), 60 °C, 6 h. [b]Isolated yields of the products **6a−6ac** and **6ar**. [c]Yields isolated for 1 g scale reaction.

It is worth noting that the electronic effect exerted by the strong +M OMe group of 1-bromo-2-iodoarene connected to the triple bond is not sufficient enough to alter the polarity of the triple bond, as the OMe group is not in conjugation to the triple bond, and hence selectively gave **6z**, **6aa**, **6ab**, and **6ac**. Besides, the electron-deactivating fluoro groups bearing 1-bromo-2-iodoarene ring of ynone precursor **5ar** are also found to be smooth in delivering the anticipated benzo[*a*]fluorene **6ar** in a yield of 84%.

After evaluating the mild donating groups like Me and strong electron-donating group OMe group as R_2 substituent on the arene ring, we next focused on ynones flaking dimethoxy groups on the ring derived from 1-bromo-2-iodo arenes under the standard conditions (Table 1, entry 8). Surprisingly, instead of affording the usual benzo[*a*]fluorene scaffolds under the standard conditions of Table 1, a mixture of indene **7ad** and benzo[*b*]fluorene **8ad** were isolated in 52% and 21% yields, respectively.[14] Indeed, this sort of reverse polarization of triple bonds is quite possible due to electron-releasing effects of a conjugate methoxy group(s) flanked to the arene ring (i.e., from 1-bromo-2-iodoarene). On the basis of this exciting outcome, it was presumed that under controlled conditions, it is possible to isolate **7ad** and **8ad** as exclusive products. So, we began to identify the optimal conditions by

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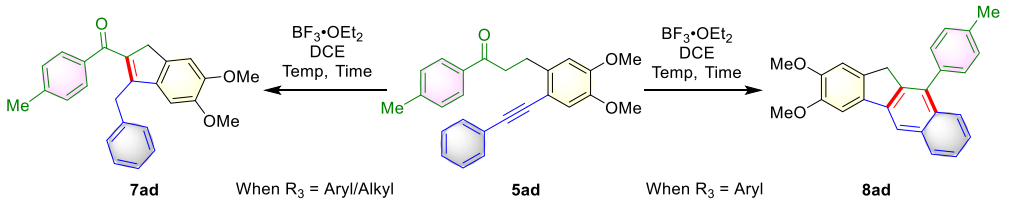
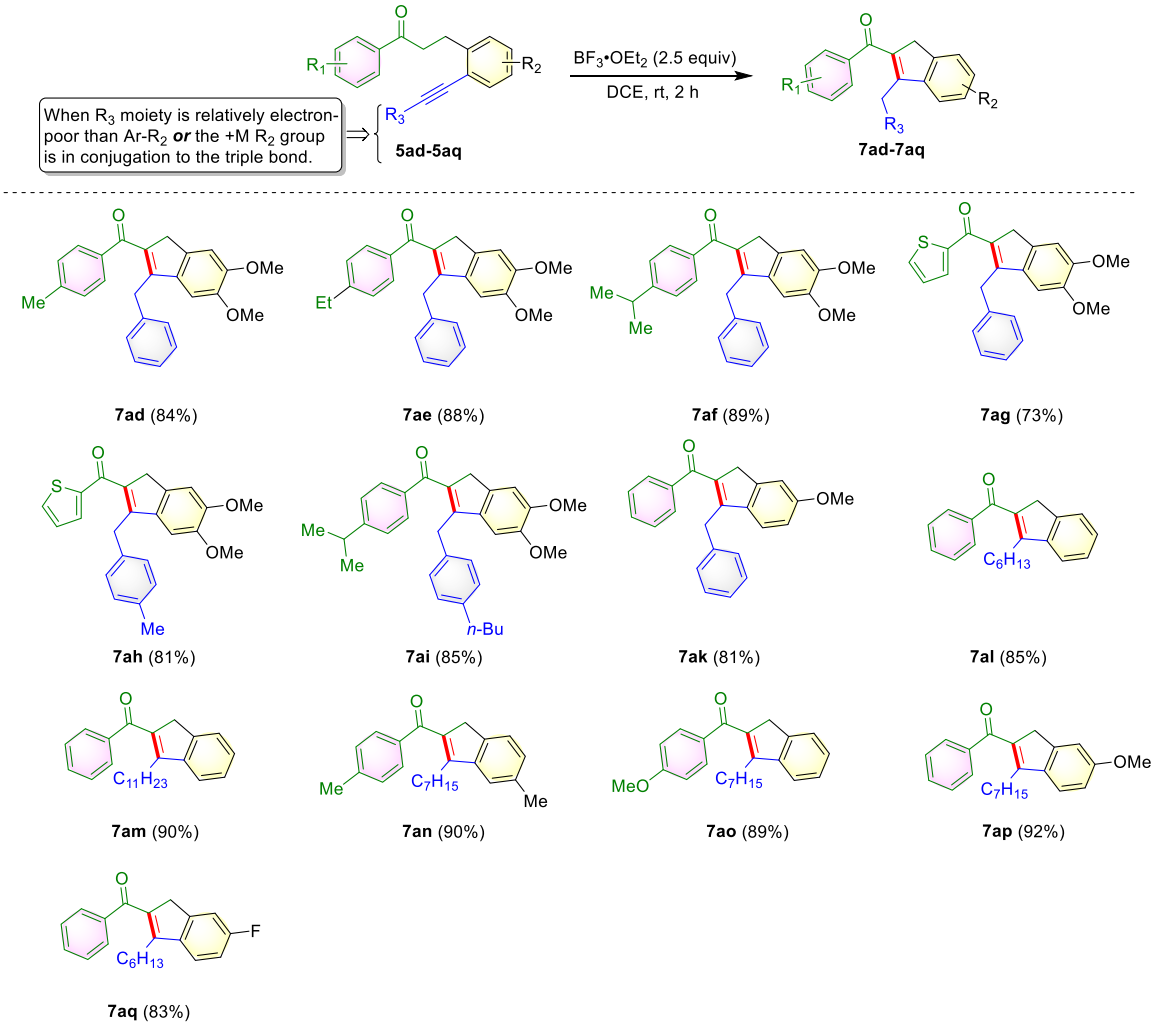
Table 3. Screening Conditions for the Formation of 7ad and 8ad[a,b]



entry	$BF_3{\cdot}OEt_2$ (equiv)	temp (°C)	time (h)	yield[b] **7ad** (%)	yield[b] **8ad** (%)
1	1	60	6	52	21
2	1	rt	12	62	trace
3	1	rt	24	75	<10
4	**2.5**	**rt**	**2**	**84**	–
5	2.5	80	12	28	64
6	2.5	100	12	18	78
7	**2.5**	**100**	**24**	–	**90**

[a]Reaction conditions: Reactions were carried out with 76.8 mg (0.20 mmol) of 3-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-one, in solvent DCE (1.0 mL). [b]Isolated yields.

Table 4. Substrate Scope of Functionalized Indenes 7ad–7aq[a,b]



[a]Reaction conditions: compound **5ad–5aq** (0.2 mmol), $BF_3{\cdot}OEt_2$ (2.5 equiv), DCE (1.0 mL), room temperature, 2 h. [b]Isolated yields of tetracyclic products **7ad–7aq**.

considering **5ad** as a model substrate. Thus, initially, the reaction is performed with 1 equiv of $BF_3{\cdot}OEt_2$ at room temperature for 12 h and isolated the indene **7ad** in 62% yield along with a trace amount of **8ad** (Table 3, entry 1). Further extending the time to 24 h improved the yield of indene **7ad** to 75%, along with the formation of **8ad** (<10%). Gratifyingly,

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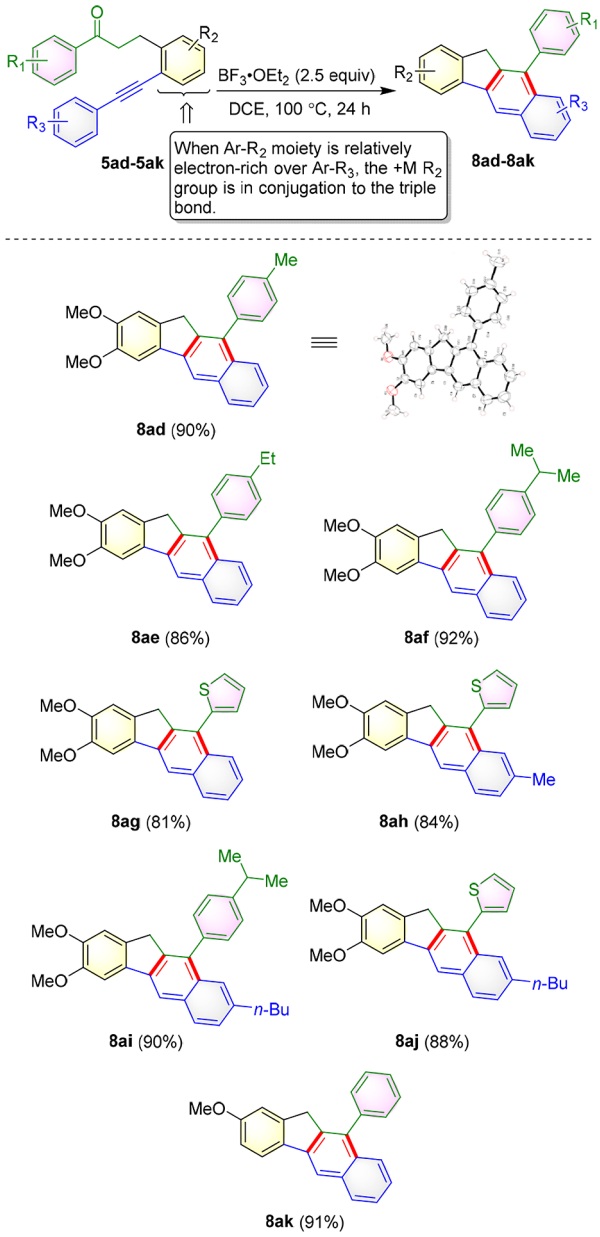
when BF_3·OEt_2 loading is increased to 2.5 equiv and the reaction was performed at room temperature and for less time (2 h), the indene **7ad** was furnished exclusively in a very good yield, 84% (Table 3, entry 4). Thus, it is evident that at an elevated temperature, it would lead to the formation of the benzo[*b*]fluorene **8ad** as a significant product. Moreover, the formation of **8ad** could proceed through the indene **7ad** as an intermediate product. So, the conditions were tuned at an elevated temperature like 80 and 100 °C by taking 2.5 equiv of BF_3·OEt_2 as an acid catalyst for triggering the transformation. Among the trials, it was found that 100 °C for 24 h afforded exclusively **8ad** in an excellent yield of 90% without even a trace amount of indene **7ad** (Table 3, entry 7).

With the optimized mild reaction conditions in hand for the formation of indene **7ad** (Table 3, entry 4), we aimed to check the feasibility of the reaction with other substituents. Notably, the reaction is amenable with the ynones **5ae**, **5af**, **5ai**, and **5ak** having different substituents originating from the allylic alcohols (i.e., R_1 = Et, *i*-Pr and H groups), from alkyne arene moiety (R_3 = H and Me), and with dimethoxy or methoxy functionalies from 1-bromo-2-iodoarene ring, and afforded the indene products **7ae**, **7af**, **7ai**, and **7ak** in satisfactory yields of 88%, 89%, 85% and 81%, respectively (Table 4). Significantly, the thiophene tethered ynones **5ag** and **5ah** were also compatible and yielded the corresponding indene derivatives **7ag** and **7ah** in 73% and 81% yields. Furthermore, to exemplify the applicability of the method, aliphatic alkyne tethered ynones **5al**–**5aq** were also screened under the optimized conditions of Table 3. As anticipated, the desired indene products **7al**–**7aq** were afforded in up to 92% yield, as detailed in Table 4. It is important to note that the electronic effect exerted by the strong +M OMe group(s) of 1-bromo-2-iodoarene connected to the triple bond must be in conjugation to alter the polarity of the triple bond and to deliver the indene products **7ad**–**7ak**, wherein both aromatic rings are flanked to the triple bond as shown in Table 4.

We next moved on with the optimized conditions in hand (Table 3, entry 7) for the formation of benzo[*b*]fluorene **8ad**. Besides, single-crystal X-ray diffraction (SC-XRD) analysis unambiguously confirmed the structure of **8ad** (CCDC: 2120374). Therefore, the feasibility of the reaction was tested with other simple electron-donating groups like Et and *i*-Pr groups (i.e., R_3 of alkyne arene) being evaluated. Gratifyingly, as predicted, the protocol was quite successful and delivered the benzo[*b*]fluoroene products **8ae**, **8af**, and **8ai** in 86%, 92%, and 90% excellent yields, respectively (Table 5). Also, the reaction was found to be successful with single methoxy substrate **5ak** in delivering the corresponding benzo[*b*]fluorene **8ak** in excellent (91%) yield. Besides, the construction of benzo[*b*]fluorenes from the thiophene heterocyclic ring containing ynones **5ag**, **5ah**, and **5aj** having different substituents (e.g., R_3 = H, Me, and *n*-Bu) was also quite amenable and afforded **8ag**, **8ah**, and **8aj** in 81%, 84%, and 88% yields, respectively (Table 5). It is worth mentioning that the electronic effect exerted by the strong +M OMe group(s) of 1-bromo-2-iodoarene connected to the triple bond must be in conjugation to alter the polarity of the triple bond and to deliver the final cyclized products benzo[*b*]fluorenes **8ad**–**8ak**, wherein the aromatic ring derived from the terminal arylacetylenes could be involved in the final cyclization via the indenes **7ad**–**7ak**.

On the basis of the above observations (Tables 4 and 5), particularly, for the yonone precursors having arene linkages to

Table 5. Synthesis of Benzo[*b*]fluorenes 8ad–8ak with Electron Rich Methoxy Substituents[a,b]



[a]Reaction conditions: compound **5ad**–**5ak** (0.2 mmol), BF_3·OEt_2 (2.5 equiv), DCE (1.0 mL), 100 °C, 24 h. [b]Isolated yields of tetracyclic products **8ad**–**8ak**.

the triple bond, it can be understood that the indenes **7ad**–**7ak** are potential reaction intermediates to generate the final cyclized products benzo[*b*]fluorenes **8ad**–**8ak**. Thus, to prove this prediction, it was planned to perform the final cyclization reaction using the intermediate indene **7ad** to afford the benzo[*b*]fluorenes **8ad**. As anticipated, the benzo[*b*]fluorene **8ad** is isolated in an outstanding yield of 93%, under thermodynamic conditions of Table 5, as illustrated in Scheme 2.

The plausible mechanism is as depicted in Scheme 3. So, when the nature of the R_2 group is mild electron-donating group to electron-withdrawing group, the reaction is expected to proceed via the ***path-a***, wherein initially the Lewis acid BF_3·OEt_2 would coordinate with the oxygen atom of the ketone

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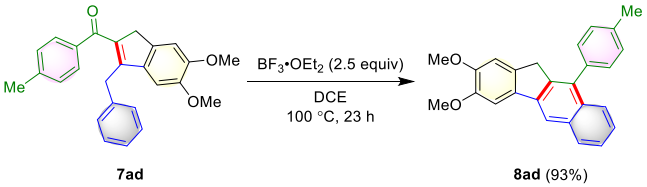
Scheme 2. Synthesis of Benzo[*b*]fluorene from the Intermediate 7ad



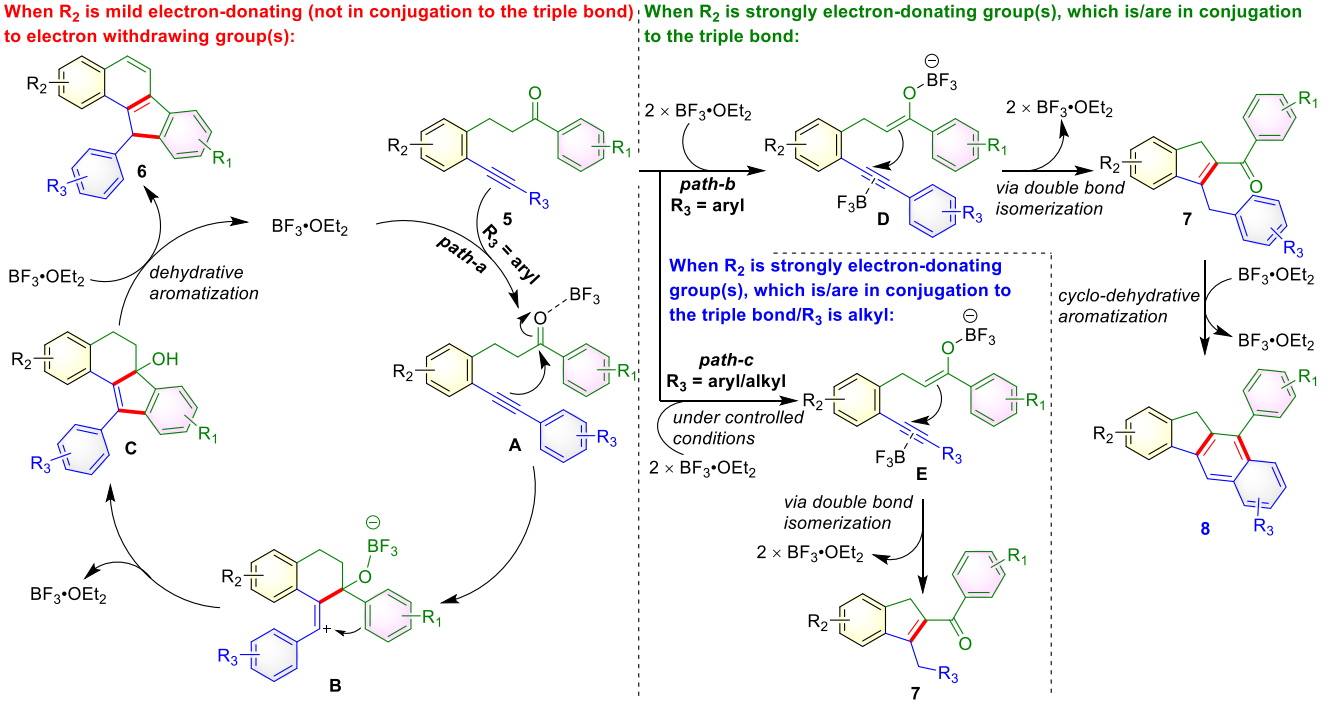
moiety of alkynone **5** to furnish the activated species **A**. Subsequently, intramolecular nucleophilic attack by the internal alkyne yields the intermediate **B**. Afterward, the intermediate **C** is attributed with the intramolecular aromatic electrophilic substitution and expulsion of $BF_3{\cdot}OEt_2$, from the unstable intermediate **B**. Finally, the corresponding tetracyclic intermediate **C** would undergo dehydrative aromatization triggered by the Lewis acid $BF_3{\cdot}OEt_2$ generating benzo[*a*]-fluorenes **6**. In contrast, when the presence of electron-rich R_2 group(s) flanked to the arene ring derived from 1-bromo-2-iodobenzene is in conjugation with alkyne triple bond of alkynones **5**, the ***path-b*** is anticipated, in which two molecules of $BF_3{\cdot}OEt_2$ would probably coordinate with the alkyne triple bond and the carbonyl group of alkynone **5** to furnish the corresponding 1,6-enyne intermediate **D**. Further, the indenes **7** are formed via the intramolecular nucleophilic addition of α-carbon of ketone across the alkyne bond followed by double bond isomerization and removal of $BF_3{\cdot}OEt_2$. Finally, the cyclo-dehydrative aromatization of indenes **7** in the presence of $BF_3{\cdot}OEt_2$ affords benzo[*b*]fluorenes **8**. Similarly, the ***path-c*** is presumed under the controlled reaction conditions (when R_3 = alkyl or aryl) for the formation of indenes **7** via the intermediate **E** via nucleophilic addition of α-carbon of carbonyl group onto the triple bond of alkyne and then double bond isomerization.

In conclusion, we have successfully developed an efficient intramolecular cascade cycloaromatization method for the efficient synthesis of benzo[*a*]fluorenes. Significantly, a wide range of benzo[*a*]fluorenes having different electronic effects was achieved using this protocol. Besides, the method was successfully applied for the synthesis of functionalized indenes. Notably, when strong +M OMe group(s) are flanked on 1-bromo-2-iodoarene ring of ynones, which are in conjugation to the triple bond, this has altered the mode of cyclization and delivered benzo[*b*]fluorene derivatives.

EXPERIMENTAL SECTION

General Methods. IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on a 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 concerning either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CDCl_3$ (δ_H = 7.25 ppm). ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ_C = 77.00 ppm (central line of the triplet)]. In the ^{13}C{^{1}H} 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{^{1}H} CPD, and 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 reactions were carried out by using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; for petroleum ether, the boiling range of 60−80 °C was used. $Pd(OAc)_2$, K_3PO_4, xantphos, and $BF_3{\cdot}OEt_2$ (48−50% essay) were purchased from Sigma-Aldrich and used as received. Substituted benzaldehydes,

Scheme 3. Plausible Mechanism to Benzo[*a*]fluorenes 6, Benzo[*b*]fluorenes 8, and Indenes 7



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vinyl magnesium bromide (1 M in THF), 1-alkynes, 1-heptyne, 1-octyne, 1-dodecyne, and triethylamine were purchased from Sigma/TCI/local. Solvents THF and toluene were dried over sodium metal, whereas DCE was dried over calcium hydride. Acme's silica gel (60−120 mesh) was used for column chromatography (approximately 20 g per 1 g of crude material).

General Procedure 1 (GP-1) Preparation of 3-(2-Bromophenyl)-1-phenylpropan-1-ones (3a−3v). To an oven-dried Schlenk tube under nitrogen atmosphere were added allylic alcohol **1a−1k** (134−194.1 mg, 1 mmol), 1-iodo-2-bromoarene **2a−2g** (338−410 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), and triethylamine (303 mg, 3 equiv) followed by dry acetonitrile (2 mL). The resulted reaction mixture was stirred at 80 °C for 24 h in an oil bath. Progress of the reaction was monitored by TLC until the reaction was completed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvents under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the alcohols **3a−3v** (69−82%) as a viscous liquid.

3-(2-Bromophenyl)-1-phenylpropan-1-one (3a). This compound is synthesized by using the previous literature reports (this compound is reported in ref 7a in the Supporting Information).

3-(2-Bromophenyl)-1-(p-tolyl)propan-1-one (3b). GP-1 was carried out with allylic alcohol **1b** (148.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3b** (247.6 mg, 82%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**1b**) = 0.2, R_f (**3b**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2920, 1682, 1607, 1472, 1294, 1080, 972, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.84 (m, 2H, Ar−H), 7.55 (dd, J = 8.0 and 1.2 Hz, 1H, Ar−H), 7.31 (dd, J = 7.6 and 1.8 Hz, 1H, Ar−H), 7.28−7.21 (m, 3H, Ar−H), 7.13−7.03 (m, 1H, Ar−H), 3.32−3.23 (m, 2H, CH_2), 3.22−3.14 (m, 2H, CH_2), 2.41 (s, 3H, Ar−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 143.9, 140.7, 134.3, 132.8, 130.8, 129.3 (2 × Ar−CH), 128.2 (2 × Ar−CH), 128.0, 127.6, 124.3, 38.5, 30.9, 21.6 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{16}H_{15}Br^{79}NaO$ 325.0198, found 325.0185; $[(M + Na)]^+$ calcd for $C_{16}H_{15}Br^{81}NaO$ 327.0178, found 327.0165.

3-(2-Bromophenyl)-1-(4-ethylphenyl)propan-1-one (3c). GP-1 was carried out with allylic alcohol **1c** (163.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3c** (252.8 mg, 80%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**1c**) = 0.2, R_f (**3c**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2966, 1681, 1606, 1471, 1361, 1180, 1025, 978, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.88 (m, 2H, Ar−H), 7.55 (dd, J = 8.0 and 1.2 Hz, 1H, Ar−H), 7.27−7.20 (m, 4H, Ar−H), 7.11−7.03 (m, 1H, Ar−H), 3.32−3.23 (m, 2H, CH_2), 3.22−3.14 (m, 2H, CH_2), 2.70 (q, J = 7.6 Hz, 2H, CH_2), 1.25 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 150.1, 140.7, 134.5, 132.8, 130.8, 129.3 (2 × Ar−CH), 128.1 (2 × Ar−CH), 127.9, 127.6, 124.3, 38.5, 30.8, 28.9, 15.2 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{17}H_{17}Br^{79}NaO$ 339.0355, found 339.0348; $[(M + Na)]^+$ calcd for $C_{17}H_{17}Br^{81}NaO$ 341.0335, found 341.0329.

3-(2-Bromophenyl)-1-(4-isopropylphenyl)propan-1-one (3d). GP-1 was carried out with allylic alcohol **1d** (176.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 99:01 to 98:02) furnished the ketone **3d** (234.4 mg, 71%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate: 98:02, R_f (**1c**) = 0.2, R_f (**3d**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2959, 2586, 1922, 1672, 1568, 1470, 1308, 1051, 738, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.90 (m, 2H, Ar−H), 7.55 (dd, J = 8.0 and 1.2 Hz, 1H, Ar−H), 7.36−7.28 (m, 3H, Ar−H), 7.23 (dd, J = 7.5 and 1.2 Hz, 1H, Ar−H), 7.08 (td, J = 7.7 and 1.8 Hz, 1H, Ar−H), 3.36−3.24 (m, 2H, CH_2), 3.24−3.13 (m, 2H, CH_2), 3.02−2.92 (m, 1H, CH), 1.27 (d, J = 6.9 Hz, 6H, 2 × CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 154.6, 140.6, 134.6, 132.8, 130.8, 128.3 (2 × Ar−CH), 127.9, 127.6, 126.7 (2 × Ar−CH), 124.4, 38.5, 34.3, 30.9, 23.7 (2 × CH_3) ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{18}H_{19}Br^{79}NaO$ 353.0511, found 353.0499; $[(M + Na)]^+$ calcd for $C_{18}H_{19}Br^{81}NaO$ 355.0491, found 355.0482.

3-(2-Bromophenyl)-1-(3-methoxyphenyl)propan-1-one (3e). GP-1 was carried out with allylic alcohol **1e** (164.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the ketone **3e** (225.8 mg, 76%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**1e**) = 0.4, R_f (**3e**) = 0.55, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2938, 1687, 1631, 1597, 1429, 1359, 1253, 1193, 1167, 995, 876, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.52 (m, 2H, Ar−H), 7.50 (dd, J = 2.5 and 1.6 Hz, 1H, Ar−H), 7.38−7.29 (m, 2H, Ar−H), 7.27−7.21 (m, 1H, Ar−H), 7.14−7.03 (m, 2H, Ar−H), 3.85 (s, 3H, $ArOCH_3$), 3.35−3.30 (m, 2H, CH_2), 3.22−3.12 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.7, 159.8, 140.5, 138.0, 132.8, 130.7, 129.5, 127.9, 127.6, 124.3, 120.7, 119.6, 112.2, 55.4, 38.7, 30.8 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{16}H_{15}Br^{79}NaO_2$ 341.0148, found 341.0170; $[(M + Na)]^+$ calcd for $C_{16}H_{15}Br^{81}NaO_2$ 343.0127, found 343.0121.

1-(Benzo[d][1,3]dioxol-5-yl)-3-(2-bromophenyl)propan-1-one (3f). GP-1 was carried out with allylic alcohol **1f** (178.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3f** (239.1 mg, 72%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 97:03, R_f (**1f**) = 0.2, R_f (**3f**) = 0.5, UV detection]. This compound is reported in ref 7b in the Supporting Information.

3-(2-Bromophenyl)-1-(4-fluorophenyl)propan-1-one (3g). GP-1 was carried out with allylic alcohol **1g** (152.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 99:01 to 98:02) furnished the ketone **3g** (232.5 mg, 75%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate: 98:02, R_f (**1g**) = 0.2, R_f (**3g**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3063, 1734, 1684, 1596, 1507, 1362, 1297, 1231, 1025, 978 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−7.97 (m, 2H, Ar−H), 7.55 (dd, J = 8.0 and 1.2 Hz, 1H, Ar−H), 7.31 (dd, J = 7.6 and 1.7 Hz, 1H, Ar−H), 7.23 (dd, J = 7.5 and 1.2 Hz, 1H, Ar−H), 7.15−7.05 (m, 3H, Ar−H), 3.32−3.23 (m, 2H, CH_2), 3.23−3.14 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.3, 165.8 (J_{C-F} = 255 Hz), 140.4, 133.3 (J_{C-F} = 3 Hz), 132.9, 130.8, 130.7, 130.6, 128.3, 127.6, 124.3, 115.8, 115.6, 38.5, 30.8 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{15}H_{12}Br^{79}FNaO$ 328.9948, found 328.9936; $[(M + Na)]^+$ calcd for $C_{15}H_{12}Br^{81}FNaO$ 330.9927, found 330.9925.

3-(2-Bromophenyl)-1-(naphthalen-2-yl)propan-1-one (3h). GP-1 was carried out with allylic alcohol **1h** (184.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 99:01 to 98:02) furnished the ketone **3h** (236.6 mg, 70%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate: 98:02, R_f (**1h**) = 0.2, R_f (**3h**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3053, 1677, 1596, 1469, 1438, 1415, 1367, 1208, 1186, 1122, 934 cm^{-1}. ^1H NMR

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(400 MHz, $CDCl_3$) δ 8.45 (s, 1H, Ar−H), 8.02 (dd, J = 8.7 and 1.7 Hz, 1H, Ar−H), 7.90 (d, J = 8.0 Hz, 1H, Ar−H), 7.84 (t, J = 7.9 Hz, 2H, Ar−H), 7.58−7.47 (m, 3H, Ar−H), 7.33 (dd, J = 7.6 and 1.7 Hz, 1H, Ar−H), 7.27−7.19 (m, 1H, Ar−H), 7.06 (td, J = 7.7 and 1.7 Hz, 1H, Ar−H), 3.44−3.40 (m, 2H, CH_2), 3.27−3.17 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 140.5, 135.5, 133.9, 132.8, 132.4, 130.8, 129.7, 129.5, 128.4, 128.4, 127.9, 127.7, 127.6, 126.7, 124.3, 123.7, 38.8, 30.9 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{19}H_{16}Br^{79}O$ 339.0379, found 339.0387; $[(M + H)]^+$ calcd for $C_{19}H_{16}Br^{81}O$ 341.0359, found 341.0374.

3-(2-Bromophenyl)-1-(thiophen-2-yl)propan-1-one (3i). GP-1 was carried out with allylic alcohol **1i** (140.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the ketone **3i** (202.5 mg, 69%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**1i**) = 0.2, R_f (**3i**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3101, 1657, 1518, 1471, 1439, 1415, 1355, 1063, 1025, 931, 722 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 3.7 Hz, 1H, Ar−H), 7.62 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.54 (d, J = 8.0 Hz, 1H, Ar−H), 7.31 (dd, J = 7.6 and 1.6 Hz, 1H, Ar−H), 7.27−7.19 (m, 1H, Ar−H), 7.13−7.09 (m, 1H, Ar−H), 7.07 (dd, J = 7.5 and 1.5 Hz, 1H, Ar−H), 3.28−3.21 (m, 2H, CH_2), 3.21−3.14 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.8, 144.0, 140.1, 133.6, 132.8, 131.9, 130.8, 128.1, 128.0, 127.6, 124.3, 39.1, 31.1 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{13}H_{11}Br^{79}NaSO$ 316.9606, found 316.9554; $[(M + Na)]^+$ calcd for $C_{13}H_{11}Br^{81}NaSO$ 318.9586, found 318.9562.

3-(2-Bromophenyl)-1-(3,4-dimethoxyphenyl)propan-1-one (3j). GP-1 was carried out with allylic alcohol **1j** (194.1 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3j** (303.1 mg, 79%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 97:03, R_f (**1j**) = 0.2, R_f (**3j**) = 0.5, UV detection]. This compound is reported in ref 7b in the Supporting Information.

3-(2-Bromophenyl)-1-(4-methoxyphenyl)propan-1-one (3k). GP-1 was carried out with allylic alcohol **1k** (164.2 mg, 1 mmol), 1-bromo-2-iodobenzene **2a** (346.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3k** (241.7 mg, 76%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 97:03, R_f (**1k**) = 0.2, R_f (**3k**) = 0.5, UV detection]. This compound is reported in ref 7c in the Supporting Information.

3-(2-Bromo-4-methylphenyl)-1-(p-tolyl)propan-1-one (3l). GP-1 was carried out with allylic alcohol **1b** (148.1 mg, 1 mmol), 2-bromo-1-iodo-4-methylbenzene **2b** (354.0 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3l** (247.2 mg, 78%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**1b**) = 0.2, R_f (**3l**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 1682, 1606, 1489, 1203, 1180, 1038, 808 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90−7.80 (m, 2H, Ar−H), 7.37 (d, J = 0.9 Hz, 1H, Ar−H), 7.25−7.20 (m, 2H, Ar−H), 7.19 (d, J = 7.7 Hz, 1H, Ar−H), 7.04 (dd, J = 7.7 and 1.0 Hz, 1H, Ar−H), 3.28−3.21 (m, 2H, CH_2), 3.13−3.10 (m, 2H, CH_2), 2.41 (s, 3H, Ar−CH_3), 2.30 (s, 3H, Ar−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 143.8, 137.8, 137.4, 134.2, 133.2, 130.5, 129.2 (2 × Ar−CH), 128.3, 128.2 (2 × Ar−CH), 124.0, 38.6, 30.4, 21.6, 20.5 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{17}H_{17}Br^{79}NaO$ 339.0355, found 339.0366; $[(M + Na)]^+$ calcd for $C_{17}H_{17}Br^{81}NaO$ 341.0335, found 341.0350.

3-(2-Bromo-4-methoxyphenyl)-1-(p-tolyl)propan-1-one (3m). GP-1 was carried out with allylic alcohol **1b** (148.1 mg, 1 mmol), 2-bromo-1-iodo-4-methoxybenzene **2c** (373.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the ketone **3m** (242.4 mg, 73%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 93:07, R_f (**1b**) = 0.2, R_f (**3m**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2938, 2836, 1681, 1568, 1493, 1440, 1202, 974, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.86 (m, 2H, Ar−H), 7.28−7.24 (m, 2H, Ar−H), 7.21 (d, J = 8.5, 1H, Ar−H), 7.11 (d, J = 2.6 Hz, 1H, Ar−H), 6.80 (dd, J = 8.5 and 2.6 Hz, 1H, Ar−H), 3.78 (s, 3H, $ArOCH_3$), 3.33−3.21 (m, 2H, CH_2), 3.11 (dd, J = 8.4 and 6.6 Hz, 2H, CH_2), 2.41 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 158.5, 143.8, 134.3, 132.5, 131.1, 129.2 (2 × Ar−CH), 128.2 (2 × Ar−CH), 124.3, 118.0, 113.7, 55.5, 38.8, 30.0, 21.6 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{17}H_{17}Br^{79}NaO_2$ 355.0304, found 355.0286; $[(M + Na)]^+$ calcd for $C_{17}H_{17}Br^{81}NaO_2$ 357.0284, found 357.0268.

3-(2-Bromo-4-methoxyphenyl)-1-(4-ethylphenyl)propan-1-one (3n). GP-1 was carried out with allylic alcohol **1c** (162.1 mg, 1 mmol), 2-bromo-1-iodo-4-methoxybenzene **2c** (373.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the ketone **3n** (245.7 mg, 71%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 93:07, R_f (**1c**) = 0.2, R_f (**3n**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3968, 1681, 1631, 1605, 1492, 1283, 1239, 1180 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.86 (m, 2H, Ar−H), 7.27 (dd, J = 5.4 and 4.3 Hz, 2H, Ar−H), 7.21 (d, J = 8.5 Hz, 1H, Ar−H), 7.10 (d, J = 2.6 Hz, 1H, Ar−H), 6.80 (dd, J = 8.5 and 2.6 Hz, 1H, Ar−H), 3.77 (s, 3H, $ArOCH_3$), 3.31−3.20 (m, 2H, CH_2), 3.16−3.06 (m, 2H, CH_2), 2.70 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.25 (t, J = 7.6 Hz, 2H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 158.7, 150.2, 134.6, 132.7, 131.3, 128.5 (2 × Ar−CH), 128.3 (2 × Ar−CH), 124.5, 118.2, 113.8, 55.6, 38.9, 30.1, 29.0, 15.3 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{18}H_{19}Br^{79}NaO_2$ 369.0461, found 369.0458; $[(M + Na)]^+$ calcd for $C_{18}H_{19}Br^{81}NaO_2$ 371.0440, found 371.0440.

3-(2-Bromo-4-methoxyphenyl)-1-(4-isopropylphenyl)propan-1-one (3o). GP-1 was carried out with allylic alcohol **1d** (176.1 mg, 1 mmol), 2-bromo-1-iodo-4-methoxybenzene **2c** (373.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the ketone **3o** (252.0 mg, 70%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 93:07, R_f (**1d**) = 0.2, R_f (**3o**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2961, 2836, 1682, 1605, 1568, 1493, 1462, 1284, 1239, 1183, 978 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.85 (m, 2H, Ar−H), 7.35−7.28 (m, 2H, Ar−H), 7.22 (d, J = 8.5, 1H, Ar−H), 7.11 (d, J = 2.6 Hz, 1H, Ar−H), 6.83−6.77 (m, 1H, Ar−H), 3.78 (s, 3H, $ArOCH_3$), 3.27−3.24 (m, 2H, CH_2), 3.13−3.09 (m, 2H, CH_2), 2.99−2.93 (m, 1H, $CH(CH_3)$), 1.26 (d, J = 6.9 Hz, 6H, 2 × CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 158.5, 154.6, 134.7, 132.5, 131.1, 128.3 (2 × Ar−CH), 126.7 (2 × Ar−CH), 124.3, 118.0, 113.7, 55.7, 38.8, 34.2, 29.9, 23.6 (2 × CH_3) ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{19}H_{21}Br^{79}NaO_2$ 383.0617, found 383.0601; $[(M + Na]^+$ calcd for $C_{19}H_{21}Br^{81}NaO_2$ 385.0597, found 385.0584.

3-(2-Bromo-4,5-dimethoxyphenyl)-1-(p-tolyl)propan-1-one (3p). GP-1 was carried out with allylic alcohol **1b** (148.5 mg, 1 mmol), 1-bromo-2-iodo-4,5-dimethoxybenzene **2d** (409.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 93:07 to 90:10) furnished the ketone **3p** (264.3 mg, 73%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate

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93:07, R_f (**1b**) = 0.2, R_f (**3p**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2987, 1681, 1604, 1505, 1464, 1455, 1425, 1371, 1266, 1199, 1161, 1030, 829 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H, Ar−H), 7.23 (d, J = 8.1 Hz, 2H, Ar−H), 6.99 (s, 1H, Ar−H), 6.81 (s, 1H, Ar−H), 3.83 (s, 6H, 2 × OCH_3), 3.24 (t, J = 7.6 Hz, 2H, CH_2), 3.08 (t, J = 7.6 Hz, 2H, CH_2), 2.39 (s, 3H, Ar−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 148.3, 147.9, 143.8, 134.2, 132.5, 129.2 (2 × Ar−CH), 128.1 (2 × Ar−CH), 115.4, 113.8, 113.3, 56.1, 56.0, 38.7, 30.6, 21.5 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{18}H_{19}Br^{79}NaO_3$ 385.0410, found 385.0423; $[(M + Na)]^+$ calcd for $C_{18}H_{19}Br^{81}NaO_3$ 387.0389, found 387.0405.

3-(2-Bromo-4,5-dimethoxyphenyl)-1-(4-ethylphenyl)propan-1-one (3q). GP-1 was carried out with allylic alcohol **1c** (162.1 mg, 1 mmol), 1-bromo-2-iodo-4,5-dimethoxybenzene **2d** (409.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 93:07 to 90:10) furnished the ketone **3q** (270.7 mg, 72%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 93:07, R_f (**1c**) = 0.4, R_f (**3q**) = 0.55, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2962, 1676, 1604, 1509, 1440, 1257, 1219, 1033, 981 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.84 (m, 2H, Ar−H), 7.30−7.26 (m, 2H, Ar−H), 7.00 (s, 1H, Ar−H), 6.82 (s, 1H, Ar−H), 3.84 (s, 3H, $ArOCH_3$), 3.83 (s, 3H, $ArOCH_3$), 3.30−3.19 (m, 2H, CH_2), 3.15−3.02 (m, 2H, CH_2), 2.68 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.24 (d, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 150.1, 148.3, 148.0, 134.5, 132.6, 128.1 (2 × Ar−CH), 128.0 (2 × Ar−CH), 115.4, 113.8, 113.7, 56.1, 56.0, 38.8, 30.6, 28.8, 15.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{19}H_{21}Br^{79}O_3$ 399.0566, found 399.0549; $[(M + H)]^+$ calcd for $C_{19}H_{21}Br^{81}O_3$ 401.0546, found 401.0534.

3-(2-Bromo-4,5-dimethoxyphenyl)-1-(4-isopropylphenyl)-propan-1-one (3r). GP-1 was carried out with allylic alcohol **1d** (176.1 mg, 1 mmol), 1-bromo-2-iodo-4,5-dimethoxybenzene **2d** (409.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 93:07 to 90:10) furnished the ketone **3r** (308.1 mg, 79%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 93:07, R_f (**1d**) = 0.4, R_f (**3r**) = 0.55, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2960, 1678, 1604, 1511, 1440, 1385, 1293, 1257, 1220, 1167, 981 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06−7.81 (m, 2H, Ar−H), 7.31−7.26 (m, 2H, Ar−H), 7.00 (s, 1H, Ar−H), 6.82 (s, 1H, Ar−H), 3.85 (s, 3H, $ArOCH_3$), 3.84 (s, 3H, $ArOCH_3$), 3.32−3.19 (m, 2H, CH_2), 3.13−3.05 (m, 2H, CH_2), 3.01−2.88 (m, 1H, CH), 1.26 (d, J = 6.9 Hz, 6H, 2 × CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.8, 154.6, 148.3, 148.0, 134.6, 132.6, 128.3 (2 × Ar−CH), 126.6 (2 × Ar−CH), 115.4, 113.8, 113.7, 56.1, 56.0, 38.8, 34.2, 30.6, 23.6 (2 × CH_3) ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{20}H_{24}Br^{79}O_3$ 391.0903, found 391.0868; $[(M + H)]^+$ calcd for $C_{20}H_{24}Br^{81}O_3$ 393.0883, found 393.0849.

3-(2-Bromo-4,5-dimethoxyphenyl)-1-(thiophen-2-yl)propan-1-one (3s). GP-1 was carried out with allylic alcohol **1i** (140.1 mg, 1 mmol), 1-bromo-2-iodo-4,5-dimethoxybenzene **2d** (409.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 93:07 to 90:10) furnished the ketone **3s** (247.1 mg, 70%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 93:07, R_f (**1i**) = 0.4, R_f (**3s**) = 0.55, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3090, 2839, 1665, 1601, 1503, 1467, 1415, 1376, 1266 1188, 809 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.61 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.09 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 6.99 (s, 1H, Ar−H), 6.80 (s, 1H, Ar−H), 3.83 (s, 3H, $ArOCH_3$), 3.82 (s, 3H, $ArOCH_3$), 3.20 (ddd, J = 7.5, 5.5, and 0.9 Hz, 2H, CH_2), 3.13−3.04 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 192.1, 148.3, 148.1, 144.1, 133.7, 132.0, 132.0, 128.1, 115.4, 113.8, 113.4, 56.1, 55.9, 39.5, 30.9 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{15}H_{15}Br^{79}NaO_3S$ 376.9817, found 376.9797; $[(M + Na)]^+$ calcd for $C_{15}H_{15}Br^{79}NaO_3S$ 378.9797, found 378.9764.

3-(2-Bromo-5-methoxyphenyl)-1-phenylpropan-1-one (3t). GP-1 was carried out with allylic alcohol **1a** (134.1 mg, 1 mmol), 1-bromo-2-iodo-4-methoxybenzene **2e** (373.2 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3t** (232.1 mg, 73%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**1a**) = 0.2, R_f (**3t**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2937, 1686, 1598, 1473, 1384, 1287, 1241, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.4 and 1.3 Hz, 2H, Ar−H), 7.56 (d, J = 7.4 Hz, 1H, Ar−H), 7.51−7.36 (m, 3H, Ar−H), 6.87 (d, J = 3.1 Hz, 1H, Ar−H), 6.65 (dd, J = 8.8 and 1.3 Hz, 1H, Ar−H), 3.77 (s, 3H, OCH_3), 3.34−3.25 (m, 2H, CH_2), 3.14 (dd, J = 8.6 and 6.8 Hz, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.9, 159.0, 141.5, 136.7, 133.3, 133.2, 128.6 (2 × Ar−CH), 128.1 (2 × Ar−CH), 116.3, 114.7, 113.6, 55.4, 38.6, 31.0 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{16}H_{15}Br^{79}O_2$ 319.0328, found 319.0358; $[(M + H)]^+$ calcd for $C_{16}H_{15}Br^{81}NaO_2$ 321.0308, found 319.0332.

3-(2-Bromo-5-fluorophenyl)-1-phenylpropan-1-one (3u). GP-1 was carried out with allylic alcohol **1a** (134.1 mg, 1 mmol), 1-bromo-4-fluoro-2-iodobenzene **2f** (358.8 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3u** (232.1 mg, 76%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**1a**) = 0.2, R_f (**3u**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3078, 1681, 1601, 1487, 1122, 873 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00−7.93 (m, 2H, Ar−H), 7.60−7.52 (m, 1H, Ar−H), 7.50−7.43 (m, 2H, Ar−H), 7.33−7.27 (m, 2H, Ar−H), 6.96 (td, J = 8.3 and 2.6 Hz, 1H, Ar−H), 3.36−3.25 (m, 2H, CH_2), 3.17−3.14 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.7, 160.9 (d, J_{C-F} = 248 Hz, Ar−C), 136.6, 136.3 (d, J_{C-F} = 4 Hz, Ar−C), 133.2, 131.5 (d, J_{C-F} = 8 Hz, Ar−CH), 128.6 (2 × Ar−CH), 128.0 (2 × Ar−CH), 124.0 (d, J_{C-F} = 9 Hz, Ar−C), 119.9 (d, J_{C-F} = 24 Hz, Ar−CH), 114.6 (d, J_{C-F} = 21 Hz, Ar−CH), 38.5, 29.8 ppm.

3-(2-Bromo-4,6-difluorophenyl)-1-phenylpropan-1-one (3v). GP-1 was carried out with allylic alcohol **1a** (134.1 mg, 1 mmol), 1-bromo-3,5-difluoro-2-iodobenzene **2g** (381.4 mg, 1.2 mmol), $Pd(OAc)_2$ (4.5 mg, 2 mol %), triethylamine (303 mg, 3 equiv) and dry acetonitrile (2 mL) at 80 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the ketone **3v** (232.1 mg, 73%) as a viscous liquid. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**1a**) = 0.2, R_f (**3v**) = 0.5, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2978, 1685, 1562, 1460, 1266, 943 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00−7.94 (m, 2H, Ar−H), 7.61−7.54 (m, 1H, Ar−H), 7.48−7.44 (m, 2H, Ar−H), 7.19 (m, 1H, Ar−H), 6.86−6.77 (m, 1H, Ar−H), 3.26−3.15 (m, 4H, 2 × CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.5, 161.0 (dd, J_{C-F} = 248 and 1 Hz, ArC), 160.9 (dd, J_{C-F} = 249 and 3 Hz, ArC), 136.5, 133.2, 128.6 (d, 2 × ArCH), 128.0 (d, 2 × ArCH), 124.9 (dd, J_{C-F} = 13 and 8 Hz, ArC), 124.7 (dd, J_{C-F} = 18 and 4 Hz, ArC), 116.1 (dd, J_{C-F} = 24 and 6 Hz, ArCH), 103.5 (dd, J_{C-F} = 25 and 2 Hz, ArCH), 37.4, 23.4 ppm.

General Procedure 2 (GP-2) Preparation of 1-Phenyl-3-(2-(phenylethynyl)phenyl)propan-1-ones (5a−5ar). In an oven-dried Schlenk tube were added ketone **3a−3v** (86.4−117 mg, 0.30 mmol), phenylacetylene/alkyl acetylene (61.2−102 mg, 0.6 mmol), $Pd(OAc)_2$ (2.7 mg, 4 mol %), xantphos (12.8 mg, 8 mol %), and K_3PO_4 (266.4 mg, 1.2 mmol) followed by dry toluene (1.5 mL) at room temperature under nitrogen atmosphere, and we allowed the reaction mixture to stir at 120 °C for 2 to 4 h in an oil bath. Progress of the reaction was monitored by TLC until the reaction was

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completed. Then, the cooled reaction mixture was filtered through Celite in DCM. Evaporation of the solvents under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the alkynones **5a**−**5ar** (62−82%) as a viscous liquid/semisolid.

1-Phenyl-3-(2-(phenylethynyl)phenyl)propan-1-one (5a). GP-2 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-one **3a** (86.4 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5a** (68.8 mg, 74%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3a**) = 0.70, R_f (**5a**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3059, 1955, 1683, 1579, 1290, 1205, 984, 756, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−8.01 (m, 2H, Ar−H), 7.55−7.42 (m, 1H, Ar−H), 7.46−7.40 (m, 3H, Ar−H), 7.36−7.32 (m, 2H, Ar−H), 7.28−7.20 (m, 5H, Ar−H), 7.19−7.14 (m, 1H, Ar−H), 3.34 (ddd, J = 8.8, 5.0, and 1.8 Hz, 2H, CH_2), 3.37−3.33 (m, 2H, CH_2) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.4, 143.2, 136.7, 132.9, 132.3, 131.5 (2 × Ar−CH), 129.1, 128.6, 128.5 (2 × Ar−CH), 128.3 (2 × Ar−CH), 128.2, 128.1 (2 × Ar−CH), 126.2, 123.1, 122.5, 93.4, 87.8, 39.5, 29.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{23}H_{19}O$ 311.1430, found 311.1420.

3-(2-(Phenylethynyl)phenyl)-1-(p-tolyl)propan-1-one (5b). GP-2 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-one **3b** (90.6 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5b** (75.8 mg, 78%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3b**) = 0.70, R_f (**5b**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3923, 1680, 1606, 1493, 1180, 756, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.78 (m, 2H, Ar−H), 7.49 (dd, J = 7.6 and 1.2 Hz, 1H, Ar−H), 7.46−7.40 (m, 2H, Ar−H), 7.29−7.25 (m, 4H, Ar−H), 7.25−7.20 (m, 1H, Ar−H), 7.20−7.14 (m, 1H, Ar−H), 7.12 (d, J = 8.0 Hz, 2H, Ar−H), 3.36−3.28 (m, 2H, CH_2), 3.27−3.20 (m, 2H, CH_2), 2.31 (s, 3H, Ar−CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.1, 143.7, 143.3, 134.2, 132.3, 131.5 (2 × Ar−CH), 129.2 (2 × Ar−CH), 129.1, 128.6, 128.3 (2 × Ar−CH), 128.2, 128.2 (2 × Ar−CH), 126.2, 123.2, 122.5, 93.4, 87.8, 39.4, 29.7, 21.5 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{21}O$ 325.1587, found 325.1583.

1-(4-Ethylphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-one (5c). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-one **3c** (94.8 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5c** (81.7 mg, 81%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3c**) = 0.70, R_f (**5c**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2965, 2930, 1681, 1606, 1493, 1290, 1180, 977, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2H, Ar−H), 7.53 (dd, J = 7.5 and 1.2 Hz, 1H, Ar−H), 7.50−7.43 (m, 2H, Ar−H), 7.34−7.26 (m, 4H, Ar−H), 7.25 (ddd, J = 8.8, 7.5, and 1.5 Hz, 1H, Ar−H), 7.22−7.19 (m, 3H, Ar−H), 3.37−3.33 (m, 2H, CH_2), 3.31−3.26 (m, 2H, CH_2), 2.64 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.21 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.0, 149.8, 143.3, 134.4, 132.3, 131.5 (2 × Ar−CH), 129.1, 128.6, 128.3 (4 × Ar−CH), 128.2, 128.0 (2 × Ar−CH), 126.2, 123.2, 122.5, 93.4, 87.8, 39.4, 29.7, 28.9, 21.5 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{23}O$ 339.1743, found 339.1730.

1-(4-Isopropylphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-one (5d). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-isopropylphenyl)propan-1-one **3d** (99.0 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5d** (76.0 mg, 72%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3d**) = 0.70, R_f (**5d**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3058, 2961, 1681, 1604, 1493, 977, 756, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.91 (m, 2H, ArH), 7.55 (dd, J = 7.5 and 1.2 Hz, 1H, ArH), 7.50 (ddd, J = 5.5, 3.0, and 1.6 Hz, 2H, ArH), 7.36−7.31 (m, 4H, ArH), 7.29 (td, J = 7.4 and 1.5 Hz, 1H, ArH), 7.25−7.20 (m, 3H, ArH), 3.41−3.34 (m, 2H, CH_2), 3.34−3.27 (m, 2H, CH_2), 2.99−2.87 (m, 1H, Ar$CH(CH_3)_2$), 1.24 (d, J = 6.9 Hz, 6H, $ArCH(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 154.5, 143.4, 134.7, 132.4, 131.6 (2 × Ar−CH), 129.2, 128.7, 128.5 (2 × Ar−CH), 128.4 (2 × Ar−CH), 128.3, 126.7 (2 × Ar−CH), 126.3, 123.3, 122.6, 93.4, 87.9, 39.6, 34.2, 29.9, 23.7 (2 × CH_3) ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{26}H_{25}O$ 353.1900, found 353.1883.

1-(3-Methoxyphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-one (5e). GP-2 was carried out with 3-(2-bromophenyl)-1-(3-methoxyphenyl)propan-1-one **3e** (95.4 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 95:05) furnished the product **5e** (72.4 mg, 71%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3e**) = 0.70, R_f (**5e**) = 0.67, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3059, 2936, 2833, 1686, 1596, 1492, 1262, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.51 (m, 2H, Ar−H), 7.48 (m, 3H, Ar−H), 7.34−7.29 (m, 4H, Ar−H), 7.26 (ddd, J = 7.7, 4.1, and 1.6 Hz, 2H, Ar−H), 7.21 (td, J = 7.4 and 1.7 Hz, 1H, Ar−H), 7.06 (ddd, J = 8.3, 2.7, and 0.9 Hz, 1H, Ar−H), 3.82 (s, 3H, $ArOCH_3$), 3.38 (ddd, J = 8.6, 5.0, and 1.8 Hz, 2H, CH_2), 3.32−3.27 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 159.7, 143.2, 138.2, 132.3, 131.5 (2 × Ar−CH), 129.5, 129.1, 128.6, 128.3 (2 × Ar−CH), 128.3, 126.3, 123.2, 122.6, 120.8, 119.6, 112.0, 93.5, 87.7, 55.4, 39.5, 29.8 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{21}O_2$ 341.1536, found 341.1542.

1-(Benzo[d][1,3]dioxol-5-yl)-3-(2-(phenylethynyl)phenyl)propan-1-one (5f). GP-2 was carried out with 1-(benzo[*d*][1,3]dioxol-5-yl)-3-(2-bromophenyl)propan-1-one **3f** (99.6 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5f** (65.7 mg, 62%) as brown oil. [TLC (petroleum ether/ethyl acetate 97:03, R_f (**3f**) = 0.70, R_f (**5f**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3058, 2899, 1675, 1602, 1489, 1246, 1038, 756, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (ddd, J = 7.3, 5.4, and 2.5 Hz, 2H, Ar−H), 7.49−7.44 (m, 2H, Ar−H), 7.41 (d, J = 7.6 Hz, 1H, Ar−H), 7.32−7.21 (m, 5H, Ar−H), 7.17 (td, J = 7.3 and 1.7 Hz, 1H, Ar−H), 6.66 (d, J = 8.2 Hz, 1H, Ar−H), 5.91 (s, 2H, OCH_2), 3.31−3.20 (m, 4H, 2 × CH_2) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 197.2, 151.5, 147.9, 143.2, 132.2, 131.5, 131.4 (2 × Ar−CH), 128.9, 128.5, 128.2 (2 × Ar−CH), 128.2, 126.1, 124.2, 123.0, 122.4, 107.7, 107.6, 101.6 (t, -OCH_2O−), 93.3, 87.7, 39.1, 29.7 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{19}O_3$ 355.1329, found 355.1325.

1-(4-Fluorophenyl)-3-(2-(phenylethynyl)phenyl)propan-1-one (5g). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-fluorophenyl)propan-1-one **3g** (91.8 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5g** (66.9 mg, 68%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3g**) = 0.70, R_f (**5g**) = 0.67, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3061, 2929, 1684, 1597, 1493, 1231, 1156, 839, 756 cm^{-1}. ^1H

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NMR (400 MHz, $CDCl_3$) δ 8.03−7.96 (m, 2H, Ar−H), 7.55 (dd, J = 7.5 and 1.0 Hz, 1H, Ar−H), 7.52−7.45 (m, 2H, Ar−H), 7.35−7.28 (m, 4H, Ar−H), 7.28−7.24 (m, 1H, Ar−H), 7.22 (dd, J = 7.1 and 1.8 Hz, 1H, Ar−H), 7.07−7.00 (m, 2H, Ar−H), 3.39−3.33 (m, 2H, CH_2), 3.33−3.26 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 165.6 (J_{C-F} = 243 Hz), 143.1, 132.2 (J_{C-F} = 4 Hz), 132.4, 131.5 (2 × Ar−CH), 130.8, 130.7, 129.2, 128.7, 128.4 (2 × Ar−CH), 128.4, 126.4, 123.1, 122.5, 115.7, 115.6, 93.5, 87.7, 39.5, 29.8 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{23}H_{18}FO$ 329.1336, found 329.1321.

1-(Naphthalen-2-yl)-3-(2-(phenylethynyl)phenyl)propan-1-one (5h). GP-2 was carried out with 3-(2-bromophenyl)-1-(naphthalen-2-yl)propan-1-one **3h** (101.4 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5h** (70.2 mg, 65%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3h**) = 0.70, R_f (**5h**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 1682, 1384, 756, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H, Ar−H), 8.07 (dd, J = 8.6 and 1.7 Hz, 1H, Ar−H), 7.84 (m, 3H, Ar−H), 7.62−7.54 (m, 2H, Ar−H), 7.54−7.44 (m, 3H, Ar−H), 7.40−7.20 (m, 6H, Ar−H), 3.60−3.49 (m, 2H, CH_2), 3.44−3.33 (m, 2H, CH_2) ppm. ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ 199.4, 143.3, 135.5, 134.1, 132.5, 132.4, 131.5 (2 × Ar−CH), 129.8, 129.5, 129.2, 128.6, 128.4, 128.4 (3 × Ar−CH), 128.3, 127.6, 126.6, 126.3, 123.9, 123.1, 122.6, 93.7, 87.8, 39.6, 29.7 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{21}O$ 361.1587, found 361.1605.

3-(2-(Phenylethynyl)phenyl)-1-(thiophen-2-yl)propan-1-one (5i). GP-2 was carried out with 3-(2-bromophenyl)-1-(thiophen-2-yl)-propan-1-one **3i** (88.2 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5i** (66.4 mg, 70%) as brown oil. [TLC (petroleum ether/ethyl acetate 97:03, R_f (**3i**) = 0.70, R_f (**5i**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3058, 2930, 1654, 1598, 1493, 1374, 1237 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.55 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.50 (dd, J = 7.5 and 1.1 Hz, 1H, Ar−H), 7.48−7.44 (m, 2H, Ar−H), 7.32−7.25 (m, 4H, Ar−H), 7.24−7.19 (m, 1H, Ar−H), 7.19−7.13 (m, 1H, Ar−H), 6.96 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 3.34−3.10 (m, 4H, 2 × CH_2) ppm. ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ 192.4, 144.1, 142.9, 133.6, 132.3, 132.1, 131.5 (2 × Ar−CH), 129.2, 128.6, 128.4 (2 × Ar−CH), 128.3, 128.1, 126.4, 123.2, 122.5, 93.5, 87.7, 40.2, 30.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{21}H_{17}OS$ 317.0995, found 317.1009.

1-(p-Tolyl)-3-(2-(m-tolylethynyl)phenyl)propan-1-one (5j). GP-2 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-one **3b** (90.6 mg, 0.3 mmol), 1-ethynyl-3-methylbenzene **4b** (69.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5j** (77.1 mg, 76%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3b**) = 0.70, R_f (**5j**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3587, 3024, 2920, 1680, 1607, 1484, 1180, 783, 757, 690 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.85 (m, 2H, Ar−H), 7.59−7.51 (m, 1H, Ar−H), 7.38−7.25 (m, 4H, Ar−H), 7.25−7.21 (m, 2H, Ar−H), 7.19 (d, J = 8.4 Hz, 2H, Ar−H), 7.16−7.11 (m, 1H, Ar−H), 3.37 (ddd, J = 5.8 Hz, 4.3 and 1.9 Hz, 2H, CH_2), 3.34−3.27 (m, 2H, CH_2), 2.38 (s, 3H, Ar−CH_3), 2.31 (s, 3H, Ar−CH_3) ppm. ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ 199.1, 143.7, 143.3, 137.9, 134.2, 132.3, 132.1, 129.2 (2 × Ar−CH), 129.2, 129.1, 128.6, 128.5, 128.2 (3 × Ar−CH), 126.2, 123.0, 122.6, 93.6, 87.5, 39.4, 29.8, 21.5, 21.1 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{23}O$ 339.1743, found 339.1733.

1-(Thiophen-2-yl)-3-(2-(p-tolylethynyl)phenyl)propan-1-one (5k). GP-2 was carried out with 3-(2-bromophenyl)-1-(thiophen-2-yl)propan-1-one **3i** (88.1 mg, 0.3 mmol), 1-ethynyl-4-methylbenzene **4b** (69.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5k** (72.3 mg, 73%) as brown oil. [TLC (petroleum ether/ethyl acetate 97:03, R_f (**3i**) = 0.70, R_f (**5k**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3058, 2930, 1654, 1598, 1493, 1374, 1237 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.60 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.57−7.55 (m, 1H, Ar−H), 7.42 (d, J = 8.0 Hz, 2H, Ar−H), 7.31 (d, J = 1.4 Hz, 1H, Ar−H), 7.28−7.20 (m, 2H, Ar−H), 7.16 (d, J = 8.0 Hz, 2H, Ar−H), 7.02 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 3.34−3.20 (m, 4H, 2 × CH_2), 2.38 (s, 3H, ArCH_3) ppm. ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ 192.4, 144.1, 142.7, 138.5, 133.5, 132.2, 132.1, 131.4 (2 × Ar−CH), 129.1 (2 × Ar−CH), 129.1, 128.4, 128.0, 126.3, 122.7, 120.0, 93.7, 87.1, 40.1, 29.9, 21.4 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{22}H_{19}OS$ 331.1151, found 331.1168.

3-(2-((4-Ethylphenyl)ethynyl)phenyl)-1-(p-tolyl)propan-1-one (5l). GP-2 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-one **3b** (94.8 mg, 0.3 mmol), 1-ethyl-4-ethynylbenzene **4c** (69.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5l** (98.7 mg, 81%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3b**) = 0.70, R_f (**5l**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3031, 2961, 2929, 1681, 1606, 1509, 1360, 1180, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.85 (m, 2H, Ar−H), 7.53 (dd, J = 7.5 and 1.3 Hz, 1H, Ar−H), 7.43−7.41 (m, 1H, Ar−H), 7.41−7.38 (m, 1H, Ar−H), 7.30 (td, J = 7.4 and 1.5 Hz, 1H, Ar−H), 7.26 (td, J = 4.4 and 1.5 Hz, 1H, Ar−H), 7.22 (dd, J = 7.4 and 1.7 Hz, 1H, Ar−H), 7.20−7.12 (m, 4H, Ar−H), 3.38−3.30 (m, 2H, CH_2), 3.32−3.22 (m, 2H, CH_2), 2.64 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.38 (s, 3H, Ar−CH_3), 1.23 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ 199.2, 144.7, 143.7, 143.3, 134.3, 132.2, 131.5 (2 × Ar−CH), 129.2 (2 × Ar−CH), 129.1, 128.4, 128.3 (2 × Ar−CH), 127.9 (2 × Ar−CH), 126.2, 122.7, 120.4, 93.6, 87.2, 39.5, 29.8, 28.8, 21.6, 15.4 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{26}H_{24}ONa$ 375.1719, found 375.1723.

1-(4-Ethylphenyl)-3-(2-((4-ethylphenyl)ethynyl)phenyl)propan-1-one (5m). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-one **3c** (94.8 mg, 0.3 mmol), 1-ethyl-4-ethynylbenzene **4c** (78 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5m** (77.9 mg, 71%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3c**) = 0.70, R_f (**5m**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2965, 2930, 1916, 1681, 1606, 1412, 1180, 832, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.84 (m, 2H, Ar−H), 7.54 (dd, J = 7.5 and 1.2 Hz, 1H, Ar−H), 7.46−7.40 (m, 2H, Ar−H), 7.33−7.29 (m, 1H, Ar−H), 7.26−7.23 (m, 2H, Ar−H), 7.21−7.15 (m, 4H, Ar−H), 3.31−3.34 (m, 2H, CH_2), 3.34−3.26 (m, 2H, CH_2), 2.68 (dd, J = 7.5 and 5.4 Hz, 2H, CH_2), 2.65 (dd, J = 7.6 and 5.4 Hz, 2H, CH_2), 1.27−1.24 (m, 3H, CH_3), 1.24−1.19 (m, 3H, CH_3) ppm. ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ 199.2, 149.9, 144.7, 143.3, 134.5, 132.2, 131.5 (2 × Ar−CH), 129.1, 128.4, 128.4 (2 × Ar−CH), 128.0 (2 × Ar−CH), 127.9 (2 × Ar−CH), 126.2, 122.7, 120.4, 93.6, 87.1, 39.5, 29.8, 28.8, 28.8, 15.4, 15.1 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{27}O$ 367.2056, found 367.2060.

3-(2-((4-Butylphenyl)ethynyl)phenyl)-1-(4-ethylphenyl)propan-1-one (5n). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-one **3c** (94.8 mg, 0.3 mmol), 1-butyl-4-ethynylbenzene **4d** (96.8 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4

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mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5n** (89.8 mg, 76%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3c**) = 0.70, R_f (**5n**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2962, 2929, 1681, 1606, 1510, 1180, 977, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.1 Hz, 2H, Ar−H), 7.42 (d, J = 7.5 Hz, 1H, Ar−H), 7.29 (d, J = 7.9 Hz, 2H, Ar−H), 7.19 (t, J = 8.3 Hz, 1H, Ar−H), 7.16−7.10 (m, 1H, Ar−H), 7.09−7.07 (m, 3H, Ar−H), 7.02 (d, J = 8.0 Hz, 2H, Ar−H), 3.28−3.22 (m, 2H, CH_2), 3.18−3.16 (m, 2H, CH_2), 2.61−2.53 (m, 2H, CH_2), 2.53−2.48 (m, 2H, CH_2), 1.52−1.44 (m, 2H, CH_2), 1.27−1.21 (m, 2H, CH_2), 1.12 (t, J = 7.6 Hz, 3H, CH_3), 0.82 (t, J = 7.3 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.1, 149.8, 143.4, 143.3, 134.5, 132.2, 131.5 (2 × Ar−CH), 129.1, 128.4 (2 × Ar−CH), 128.4, 128.3 (2 × Ar−CH), 128.0 (2 × Ar−CH), 126.2, 122.7, 120.3, 93.6, 87.2, 39.5, 35.5, 33.3, 29.8, 28.8, 22.4, 15.1, 13.9 ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{29}H_{31}O$ 395.2369, found 395.2384.

3-(2-((4-Butylphenyl)ethynyl)phenyl)-1-(thiophen-2-yl)propan-1-one (5o). GP-2 was carried out with 3-(2-bromophenyl)-1-(thiophen-2-yl)propan-1-one **3i** (88.1 mg, 0.3 mmol), 1-butyl-4-ethynylbenzene **4d** (94.8 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5o** (88.4 mg, 78%) as brown oil. [TLC (petroleum ether/ethyl acetate 97:03, R_f (**3i**) = 0.70, R_f (**5o**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2933, 2862, 1663, 1510, 1414, 1253, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.59 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.54 (dd, J = 7.5 and 1.5 Hz, 1H, Ar−H), 7.46−7.39 (m, 2H, Ar−H), 7.33−7.27 (m, 1H, Ar−H), 7.24−7.18 (m, 2H, Ar−H), 7.16 (d, J = 8.1 Hz, 2H, Ar−H), 7.01 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 3.33−3.29 (m, 4H, 2 × CH_2), 2.63 (t, J = 7.6 Hz, 2H, CH_2), 1.67−1.53 (m, 2H, CH_2), 1.41−1.32 (m, 2H, CH_2), 0.93 (t, J = 7.3 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 192.4, 144.1, 143.5, 142.7, 133.5, 132.2, 132.1, 131.4 (2 × Ar−CH), 129.1, 128.5 (2 × Ar−CH), 128.4, 128.0, 126.3, 122.7, 120.3, 93.7, 87.1, 40.2, 35.5, 33.4, 30.2, 22.2, 13.9 ppm. HRMS (ESI) m/z [(M + Na)]$^+$ calcd for $C_{25}H_{24}NaOS$ 395.1440, found 395.1426.

3-(2-((4-(tert-Butyl)phenyl)ethynyl)phenyl)-1-phenylpropan-1-one (5p). GP-2 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-one **3a** (84.4 mg, 0.3 mmol), 1-(*tert*-butyl)-4-ethynylbenzene **4e** (94.8 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5p** (88.0 mg, 82%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3a**) = 0.70, R_f (**5p**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3061, 2963, 1686, 1596, 1579, 1363, 1179, 973, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−7.92 (m, 2H, Ar−H), 7.57−7.47 (m, 2H, Ar−H), 7.47−7.42 (m, 2H, Ar−H), 7.39 (dd, J = 5.5 and 4.0 Hz, 1H, Ar−H), 7.36−7.27 (m, 4H, Ar−H), 7.25 (dd, J = 7.7 and 1.3 Hz, 1H, Ar−H), 7.20 (td, J = 7.4 and 1.6 Hz, 1H, Ar−H), 3.38 (ddd, J = 9.9, 6.3, and 2.1 Hz, 2H, CH_2), 3.35−3.24 (m, 2H, CH_2), 1.31 (s, 9H, $ArC(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 151.6, 143.2, 136.8, 133.0, 132.3, 131.3 (2 × Ar−CH), 129.2, 128.6 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.2, 126.3, 125.4 (2 × Ar−CH), 122.8, 120.2, 93.6, 87.2, 39.6, 34.8, 31.2 (3 × CH_3), 29.8 ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{27}H_{27}O$ 367.2056, found 367.2041.

3-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-phenylpropan-1-one (5q). GP-2 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-one **3a** (86.4 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **4f** (79.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 95:05) furnished the product **5q** (77.6 mg, 76%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3a**) = 0.70, R_f (**5q**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3060, 2930, 2211, 1684, 1510, 1287, 1249, 1030, 832 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01−7.98 (m, 2H, Ar−H), 7.55−7.51 (m, 2H, Ar−H), 7.45−7.36 (m, 4H, Ar−H), 7.33−7.26 (m, 1H, Ar−H), 7.26−7.18 (m, 2H, Ar−H), 6.88−6.81 (m, 2H, Ar−H), 3.80 (s, 3H, $ArOCH_3$), 3.42−3.38 (m, 2H, CH_2), 3.33−3.29 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 159.6, 143.0, 136.7, 133.0, 132.9 (2 × Ar−CH), 132.1, 129.1, 128.1 (2 × Ar−CH), 128.3, 128.1 (2 × Ar−CH), 126.2, 122.8, 115.3, 113.9 (2 × Ar−CH), 93.4, 86.5, 55.2, 39.5, 29.7 ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{24}H_{21}O_2$ 341.1536, found 341.1526.

3-(2-((4-Methoxyphenyl)ethynyl)phenyl)-1-(p-tolyl)propan-1-one (5r). GP-2 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)propan-1-one **3b** (90.6 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **4f** (79.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5r** (79.7 mg, 75%) as brown oil. [TLC (petroleum ether/ethyl acetate 93:07, R_f (**3b**) = 0.70, R_f (**5r**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2933, 2211, 1681, 1606, 1511, 1448, 1246, 1030, 832 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.86 (m, 2H, Ar−H), 7.52 (dd, J = 7.5 and 1.3 Hz, 1H, Ar−H), 7.45−7.39 (m, 2H, Ar−H), 7.30−7.26 (m, 1H, Ar−H), 7.26−7.17 (m, 4H, Ar−H), 6.86−6.81 (m, 2H, Ar−H), 3.81 (s, 3H, $ArOCH_3$), 3.36 (ddd, J = 6.2, 4.8, and 1.9 Hz, 2H, CH_2), 3.33−3.24 (m, 2H, CH_2), 2.36 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 159.6, 143.7, 143.1, 134.3, 133.0 (2 × Ar−CH), 132.1, 129.2 (2 × Ar−CH), 129.1, 128.3, 128.2 (2 × Ar−CH), 126.2, 122.9, 115.3, 113.9 (2 × Ar−CH), 93.4, 86.5, 55.2, 39.4, 29.7, 21.6 ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{25}H_{23}O_2$ 355.1693, found 355.1688.

1-(4-Isopropylphenyl)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)-propan-1-one (5s). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-isopropylphenyl)propan-1-one **3d** (99.0 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **4f** (79.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5s** (82.5 mg, 72%) as brown oil. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**3d**) = 0.70, R_f (**5s**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2960, 2836, 1680, 1605, 1509, 1287, 1284 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.90 (m, 2H, Ar−H), 7.52 (dd, J = 7.5 and 1.3 Hz, 1H, Ar−H), 7.47−7.39 (m, 2H, Ar−H), 7.34−7.25 (m, 2H, Ar−H), 7.25−7.20 (m, 3H, Ar−H), 6.89−6.83 (m, 2H, Ar−H), 3.82 (s, 3H, $ArOCH_3$), 3.43−3.32 (m, 2H, CH_2), 3.32−3.24 (m, 2H, CH_2), 2.93 (sept, J = 6.9 Hz, 1H, $Ar-CH(CH_3)_2$), 1.24 (d, J = 6.9 Hz, 6H, $Ar-CH(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 159.6, 154.4, 143.2, 134.7, 133.0 (2 × Ar−CH), 132.1, 129.1, 128.4 (2 × Ar−CH), 128.3, 126.6 (2 × Ar−CH), 126.2, 122.9, 115.4, 114.0 (2 × Ar−CH), 93.4, 86.5, 55.3, 39.6, 34.2, 29.9, 23.7 (2 × CH_3) ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{27}H_{27}O_2$ 383.2006, found 383.1988.

1-(3,4-Dimethoxyphenyl)-3-(2-((4-methoxyphenyl)ethynyl)-phenyl)propan-1-one (5t). GP-2 was carried out with 3-(2-bromophenyl)-1-(3,4-dimethoxyphenyl)propan-1-one **3j** (104.4 mg, 0.3 mmol), 1-ethynyl-4-methoxybenzene **4f** (79.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 88:12 to 85:15) furnished the product **5t** (85.2 mg, 71%) as brown oil. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**3j**) = 0.70, R_f (**5t**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3318, 2955, 2834, 2210, 1670, 1596, 1436, 1159, 1022, 825 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.4 and 2.0 Hz, 1H, Ar−H), 7.55−7.49 (m, 2H, Ar−H), 7.45−7.40 (m, 2H, Ar−H), 7.30 (dd, J = 7.6 and 1.4

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Hz, 1H, Ar−H), 7.28−7.25 (m, 1H, Ar−H), 7.25−7.21 (m, 1H, Ar−H), 6.88−6.81 (m, 2H, Ar−H), 6.70 (d, J = 8.4 Hz, 1H, Ar−H), 3.91 (s, 3H, $ArOCH_3$), 3.88 (s, 3H, $ArOCH_3$), 3.81 (s, 3H, $ArOCH_3$), 3.37−3.30 (m, 2H, CH_2), 3.30−3.24 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 159.6, 153.1, 148.9, 143.1, 133.0 (2 × Ar−CH), 132.1, 130.0, 129.1, 128.3, 126.2, 122.9, 122.8, 115.3, 114.0 (2 × Ar−CH), 110.0, 109.9, 93.3, 86.5, 55.9, 55.8, 55.2, 39.1, 30.2 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{26}H_{25}O_4$ 401.1747, found 401.1728.

3-(2-((4-Chlorophenyl)ethynyl)phenyl)-1-(p-tolyl)propan-1-one (5u). GP-2 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)-propan-1-one **3b** (90.6 mg, 0.3 mmol), 1-chloro-4-ethynylbenzene **4g** (81.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5u** (87.8 mg, 82%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3b**) = 0.70, R_f (**5u**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3059, 2928, 1686, 1571, 1589, 1492, 1203, 1091, 976 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.85 (m, 2H, Ar−H), 7.55−7.49 (m, 1H, Ar−H), 7.43−7.37 (m, 2H, Ar−H), 7.34−7.27 (m, 4H, Ar−H), 7.23 (dd, J = 7.2 and 2.0 Hz, 1H, Ar−H), 7.21−7.16 (m, 2H, Ar−H), 3.41−3.32 (m, 2H, CH_2), 3.32−3.23 (m, 2H, CH_2), 2.38 (s, 3H, Ar−CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 198.7, 143.5, 143.1, 133.9, 132.9 (2 × Ar−CH), 132.0, 128.9 (2 × Ar−CH), 128.8, 128.6, 128.4 (2 × Ar−CH), 128.2, 128.2 (2 × Ar−CH), 125.9, 121.9, 121.4, 91.9, 88.4, 39.1, 29.3, 21.3 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{20}ClO$ 359.1197, found 359.1203.

3-(2-((4-Chlorophenyl)ethynyl)phenyl)-1-(4-ethylphenyl)propan-1-one (5v). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-ethylphenyl)propan-1-one **3c** (94.8 mg, 0.3 mmol), 1-chloro-4-ethynylbenzene **4g** (81.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5v** (84.7 mg, 76%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3c**) = 0.70, R_f (**5v**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3059, 2928, 1686, 1571, 1589, 1492, 1203, 1091, 976 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H, Ar−H), 7.35−7.29 (m, 1H, Ar−H), 7.22−7.16 (m, 2H, Ar−H), 7.16−7.07 (m, 4H, Ar−H), 7.06 (s, 1H, Ar−H), 7.02−7.00 (m, 2H, Ar−H), 3.22−3.11 (m, 2H, CH_2), 3.10−3.04 (m, 2H, CH_2), 2.48 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.05 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.0, 150.0, 143.4, 134.5, 134.2, 132.7 (2 × Ar−CH), 132.3, 129.1, 128.9, 128.7 (2 × Ar−CH), 128.3 (2 × Ar−CH), 128.1 (2 × Ar−CH), 126.3, 122.2, 121.7, 92.3, 88.8, 39.5, 29.7, 28.9, 21.3 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{22}ClO$ 373.1354, found 373.1384.

3-(2-((4-Fluorophenyl)ethynyl)phenyl)-1-phenylpropan-1-one (5w). GP-2 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-one **3a** (86.4 mg, 0.3 mmol), 1-ethynyl-4-fluorobenzene **3h** (72.0 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5w** (75.1 mg, 76%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3a**) = 0.70, R_f (**5w**) = 0.67, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3063, 2928, 1684, 1597, 1230, 835, 743 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.91 (m, 2H, Ar−H), 7.50 (tt, J = 5.8 and 1.2 Hz, 2H, Ar−H), 7.46−7.41 (m, 2H, Ar−H), 7.39−7.37 (m, 2H, Ar−H), 7.32−7.24 (m, 2H, Ar−H), 7.20 (ddd, J = 9.0, 6.4, and 2.8 Hz, 1H, Ar−H), 7.02−6.93 (m, 2H, Ar−H), 3.38−3.32 (m, 2H, CH_2), 3.29−3.25 (m, 2H, CH_2) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.3, 162.4 (J_{C-F} = 249 Hz), 143.2, 136.7, 134.4, 133.3, 133.0, 132.2, 129.1, 128.7, 128.5 (2 × Ar−CH), 128.0 (2 × Ar−CH), 126.3, 122.4, 119.2 (J_{C-F} = 4 Hz), 115.7, 115.5, 92.3, 87.4, 39.5, 29.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{23}H_{18}FO$ 329.1336, found 329.1329.

3-(2-((4-Fluorophenyl)ethynyl)phenyl)-1-(p-tolyl)propan-1-one (5x). GP-2 was carried out with 3-(2-bromophenyl)-1-(*p*-tolyl)-propan-1-one **3b** (90.6 mg, 0.3 mmol), 1-ethynyl-4-fluorobenzene **4h** (72.0 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5x** (72.8 mg, 71%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3b**) = 0.70, R_f (**5x**) = 0.67, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2923, 1680, 1605, 1508, 1230, 835, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.83 (m, 2H, Ar−H), 7.53 (dd, J = 7.6 and 1.0 Hz, 1H, Ar−H), 7.49−7.44 (m, 2H, Ar−H), 7.30 (dtd, J = 9.1, 7.6, and 1.5 Hz, 2H, Ar−H), 7.23 (dd, J = 7.4 and 1.8 Hz, 1H, Ar−H), 7.20 (d, J = 7.9 Hz, 2H, Ar−H), 7.05−6.97 (m, 2H, Ar−H), 3.40−3.32 (m, 2H, CH_2), 3.32−3.23 (m, 2H, CH_2), 2.39 (s, 3H, Ar−CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.0, 162.4 (J_{C-F} = 248 Hz), 143.8, 143.3, 134.3, 133.4, 133.3, 132.3, 129.2 (2 × Ar−CH), 129.1, 128.7, 128.2 (2 × Ar−CH), 126.2, 122.4, 119.3 (J_{C-F} = 4 Hz), 115.7, 115.5, 92.3, 87.5, 39.4, 29.6, 21.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{20}FO$ 343.1493, found 343.1489.

3-(2-((4-Fluorophenyl)ethynyl)phenyl)-1-(4-isopropylphenyl)-propan-1-one (5y). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-isopropylphenyl)propan-1-one **3d** (99.0 mg, 0.3 mmol), 1-ethynyl-4-fluorobenzene **4h** (72.0 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5y** (76.6 mg, 69%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3d**) = 0.70, R_f (**5y**) = 0.67, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2962, 1681, 1604, 1508, 1231, 977, 835, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 2H, ArH), 7.52 (dd, J = 7.5 and 0.8 Hz, 1H, ArH), 7.49−7.42 (m, 2H, ArH), 7.34−7.25 (m, 2H, ArH), 7.25−7.17 (m, 3H, ArH), 7.09−6.97 (m, 2H, ArH), 3.40−3.31 (m, 2H, CH_2), 3.31−3.23 (m, 2H, CH_2), 2.93 (sept, J = 6.8 Hz, 1H, $ArCH(CH_3)_2$), 1.24 (d, J = 6.9 Hz, 6H, $ArCH(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 162.4 (J_{C-F} = 243 Hz), 154.5, 143.4, 134.6, 133.4, 133.3, 132.3, 129.1, 128.7, 128.3 (2 × Ar−CH), 126.7 (2 × Ar−CH), 126.3, 122.3, 119.4 (J_{C-F} = 3.5 Hz), 115.7, 115.5, 92.4, 87.5, 39.5, 34.2, 29.8, 23.6 (2 × CH_3) ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{26}H_{23}FNaO$ 393.1625, found 393.1609.

3-(4-Methyl-2-(phenylethynyl)phenyl)-1-(p-tolyl)propan-1-one (5z). GP-2 was carried out with 3-(2-bromo-4-methylphenyl)-1-(*p*-tolyl)propan-1-one **3l** (94.8 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5z** (83.1 mg, 82%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3l**) = 0.70, R_f (**5z**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2924, 1682, 1606, 1498, 1443, 1180, 810, 755, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.87 (m, 2H, Ar−H), 7.54−7.47 (m, 2H, Ar−H), 7.39 (s, 1H, Ar−H), 7.37−7.29 (m, 3H, Ar−H), 7.23−7.18 (m, 3H, Ar−H), 7.10 (dd, J = 4.8 and 3.5 Hz, 1H, Ar−H), 3.40−3.32 (m, 2H, CH_2), 3.31−3.22 (m, 2H, CH_2), 2.39 (s, 3H, $ArCH_3$), 2.35 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 143.7, 140.3, 135.8, 134.3, 132.7, 129.5 (2 × Ar−CH), 129.5, 129.2 (2 × Ar−CH), 129.0, 128.3 (2 × Ar−CH), 128.2 (2 × Ar−CH), 128.2, 123.3, 122.3, 93.0, 88.0, 39.6, 29.3, 21.6, 20.8 ppm. HRMS (ESI) m/z $[(M + NH_4) + (-H_2O)]^+$ calcd for $C_{25}H_{24}N$ 338.1903, found 338.1910.

3-(4-Methoxy-2-(phenylethynyl)phenyl)-1-(p-tolyl)propan-1-one (5aa). GP-2 was carried out with 3-(2-bromo-4-methoxyphenyl)-1-(*p*-tolyl)propan-1-one **3m** (99.6 mg, 0.3 mmol), 1- ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5aa** (75.4 mg, 71%) as brown

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oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3m**) = 0.70, R_f (**5aa**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2932, 2833, 1681, 1605, 1499, 1096, 1180, 1035 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H, Ar−H), 7.52−7.47 (m, 2H, Ar−H), 7.36−7.30 (m, 3H, Ar−H), 7.22 (d, J = 8.5 Hz, 1H, Ar−H), 7.18 (d, J = 8.0 Hz, 2H, Ar−H), 7.07 (d, J = 2.8 Hz, 1H, Ar−H), 6.85 (dd, J = 8.5 and 2.8 Hz, 1H, Ar−H), 3.82 (s, 3H, $ArOCH_3$), 3.36−3.28 (m, 2H, CH_2), 3.23 (dt, J = 8.1 and 2.4 Hz, 2H, CH_2), 2.37 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 157.7, 143.7, 135.7, 134.4, 131.6 (2 × Ar−CH), 130.2, 129.2 (2 × Ar−CH), 128.4 (2 × Ar−CH), 128.3, 128.2 (2 × Ar−CH), 123.3, 123.2, 116.7, 115.3, 93.2, 87.9, 55.4, 39.8, 29.0, 21.6 ppm. HRMS (ESI) m/z [(M + Na)]$^+$ calcd for $C_{25}H_{22}NaO_2$ 377.1512, found 377.1493.

1-(4-Ethylphenyl)-3-(4-methoxy-2-(phenylethynyl)phenyl)-propan-1-one (5ab). GP-2 was carried out with 3-(2-bromo-4-methoxyphenyl)-1-(4-ethylphenyl)propan-1-one **3n** (103.8 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5ab** (79.5 mg, 72%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3n**) = 0.70, R_f (**5ab**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2966, 1680, 1631, 1605, 1499, 1230 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.88 (m, 2H, Ar−H), 7.50 (ddd, J = 4.1, 3.0, and 1.7 Hz, 2H, Ar−H), 7.37−7.30 (m, 3H, Ar−H), 7.23−7.18 (m, 3H, Ar−H), 7.07 (d, J = 2.8 Hz, 1H, Ar−H), 6.85 (dd, J = 8.5 and 2.8 Hz, 1H, Ar−H), 3.82 (s, 3H, $ArOCH_3$), 3.33 (ddd, J = 8.5, 5.5, and 2.5 Hz, 2H, CH_2), 3.23 (dt, J = 8.1 and 2.5 Hz, 2H, CH_2), 2.67 (q, J = 7.6 Hz, 2H, Ar−CH_2CH_3), 1.23 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 157.7, 149.9, 135.7, 134.6, 131.6 (2 × Ar−CH), 130.2, 128.4 (3 × Ar−CH), 128.4, 128.3, 128.1 (2 × Ar−CH), 123.2, 123.1, 116.7, 115.4, 93.1, 87.8, 55.4, 39.8, 29.0, 28.9, 15.1 ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{26}H_{25}O_2$ 369.1849, found 369.1844.

1-(4-Isopropylphenyl)-3-(4-methoxy-2-(phenylethynyl)phenyl)-propan-1-one (5ac). GP-2 was carried out with 3-(2-bromo-4-methoxyphenyl)-1-(4-isopropylphenyl)propan-1-one **3o** (108.0 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5ac** (83.6 mg, 73%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3o**) = 0.70, R_f (**5ac**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2833, 1683, 1443, 1441, 1290, 1183, 1036, 814 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.88 (m, 2H, Ar−H), 7.51 (ddd, J = 5.4, 3.0, and 1.5 Hz, 2H, Ar−H), 7.36−7.30 (m, 3H, Ar−H), 7.22−7.20 (m, 3H, Ar−H), 7.08 (d, J = 2.8 Hz, 1H, Ar−H), 6.86 (dd, J = 8.5 and 2.8 Hz, 1H, Ar−H), 3.82 (s, 3H, $ArOCH_3$), 3.36−3.28 (m, 2H, CH_2), 3.26−3.19 (m, 2H, CH_2), 2.93 (sept, J = 6.9 Hz, 1H, Ar−$CH(CH_3)_2$), 1.24 (d, J = 6.9 Hz, 6H, Ar−$CH(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 157.7, 154.4, 135.7, 134.7, 131.6 (2 × Ar−CH), 130.2, 128.4 (2 × Ar−CH), 128.4 (2 × Ar−CH), 128.3, 126.6 (2 × Ar−CH), 123.3, 123.1, 116.7, 115.3, 93.1, 87.9, 55.4, 39.8, 34.2, 29.0, 23.7 (2 × CH_3) ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{27}H_{27}O_2$ 383.2006, found 383.1988.

3-(4,5-Dimethoxy-2-(phenylethynyl)phenyl)-1-(p-tolyl)propan-1-one (5ad). GP-2 was carried out with 3-(2-bromo-4,5-dimethoxyphenyl)-1-(*p*-tolyl)propan-1-one **3p** (108.6 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5ad** (83.0 mg, 72%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3p**) = 0.70, R_f (**5ad**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 1684, 1515, 1252, 1091, 755, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.86 (m, 2H, Ar−H), 7.52−7.43 (m, 2H, Ar−H), 7.36−7.29 (m, 3H, Ar−H), 7.20−7.14 (m, 2H, Ar−H), 7.03 (s, 1H, Ar−H), 6.82 (s, 1H, Ar−H), 3.89 (s, 6H, 2 × OCH_3), 3.36−3.30 (m, 2H, CH_2), 3.26−3.18 (m, 2H, CH_2), 2.37 (s, 3H, Ar−CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.3, 149.4, 147.1, 143.8, 136.9, 134.3, 131.4 (2 × Ar−CH), 129.2 (2 × Ar−CH), 128.3 (2 × Ar−CH), 128.2 (2 × Ar−CH), 128.0, 123.4, 114.5, 114.1, 112.2, 91.9, 88.1, 56.9, 56.9, 39.8, 29.7, 21.6 ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{26}H_{25}O_3$ 385.1798, found 385.1817.

3-(4,5-Dimethoxy-2-(phenylethynyl)phenyl)-1-(4-ethylphenyl)-propan-1-one (5ae). GP-2 was carried out 3-(2-bromo-4,5-dimethoxyphenyl)-1-(4-ethylphenyl)propan-1-one **3q** (112.8 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05 to 93:07) furnished the product **5ae** (95.6 mg, 80%) as brown oil. [TLC (petroleum ether/ethyl acetate: 95:05, R_f (**3q**) = 0.70, R_f (**5ae**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2964, 2206, 1679, 1605, 1512, 1350, 1248, 1091, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.88 (m, 2H, Ar−H), 7.51−7.45 (m, 2H, Ar−H), 7.35−7.29 (m, 3H, Ar−H), 7.19 (d, J = 8.4 Hz, 2H, Ar−H), 7.03 (s, 1H, Ar−H), 6.82 (s, 1H, Ar−H), 3.89 (s, 6H, 2 × OCH_3), 3.38−3.31 (m, 2H, CH_2), 3.28−3.20 (m, 2H, CH_2), 2.66 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.22 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.3, 149.9, 149.4, 147.1, 136.9, 134.9, 131.4 (2 × Ar−CH), 128.3 (2 × Ar−CH), 128.3 (2 × Ar−CH), 128.1 (2 × Ar−CH), 128.0, 123.4, 114.5, 114.0, 112.2, 91.9, 88.0, 56.0, 55.9, 39.9, 29.7, 28.8, 15.1 ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{27}H_{27}O_3$ 399.1955, found 399.1956.

3-(4,5-Dimethoxy-2-(phenylethynyl)phenyl)-1-(4-isopropylphenyl)propan-1-one (5af). GP-2 was carried out with 3-(2-bromo-4,5-dimethoxyphenyl)-1-(4-isopropylphenyl)propan-1-one **3r** (117 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5af** (88.9 mg, 72%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3r**) = 0.70, R_f (**5af**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2961, 2207, 1680, 1604, 1513, 1462, 1350, 1092 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.88 (m, 2H, Ar−H), 7.51−7.45 (m, 2H, Ar−H), 7.34−7.30 (m, 3H, Ar−H), 7.22−7.19 (m, 2H, Ar−H), 7.03 (s, 1H, Ar−H), 6.82 (s, 1H, Ar−H), 3.89 (s, 6H, 2 × OCH_3), 3.37−3.29 (m, 2H, CH_2), 3.24−3.21 (m, 2H, CH_2), 2.92 (sept, J = 6.9 Hz, 1H, CH), 1.23 (d, J = 6.9 Hz, 6H, 2 × CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.3, 154.5, 149.4, 147.1, 137.0, 134.6, 131.4 (2 × Ar−CH), 128.4 (2 × Ar−CH), 128.3 (2 × Ar−CH), 128.0, 126.6 (2 × Ar−CH), 123.4, 114.5, 114.0, 112.2, 91.9, 88.0, 56.0, 55.9, 39.9, 34.2, 29.8, 23.6 (q, 2 × CH_3) ppm. HRMS (ESI) m/z [(M + H)]$^+$ calcd for $C_{28}H_{29}O_3$ 413.2111, found 413.2110.

3-(4,5-Dimethoxy-2-(phenylethynyl)phenyl)-1-(thiophen-2-yl)-propan-1-one (5ag). GP-2 was carried out with 3-(2-bromo-4,5-dimethoxyphenyl)-1-(thiophen-2-yl)propan-1-one **3s** (106.2 mg, 0.3 mmol), ethynylbenzene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5ag** (82.3 mg, 73%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3s**) = 0.70, R_f (**5ag**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2925, 1655, 1513, 1415, 1353, 1248, 1216, 1091, 858 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.59 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.51−7.49 (m, 2H, Ar−H), 7.34−7.26 (m, 3H, Ar−H), 7.02 (s, 1H, Ar−H), 6.99 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 6.80 (s, 1H, Ar−H), 3.89 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.32−3.27 (m, 2H, CH_2), 3.27−3.22 (m, 2H, CH_2) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100

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MHz) δ 192.7, 149.4, 147.1, 144.2, 136.5, 133.7, 132.2, 131.4 (2 × Ar−CH), 128.4 (2 × Ar−CH), 128.1 (2 × Ar−CH), 123.4, 114.6, 114.1, 112.2, 92.0, 88.0, 56.0, 55.9, 40.5, 30.0 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{23}H_{21}NaSO_3$ 399.1025, found 399.1029.

3-(4,5-Dimethoxy-2-(p-tolylethynyl)phenyl)-1-(thiophen-2-yl)-propan-1-one (5ah). GP-2 was carried out with 3-(2-bromo-4,5-dimethoxyphenyl)-1-(thiophen-2-yl)propan-1-one **3s** (106.2 mg, 0.3 mmol), 1-ethynyl-4-methylbenzene **4b** (69.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5ah** (81.9 mg, 71%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3s**) = 0.60, R_f (**5ah**) = 0.55, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3097, 1654, 1601, 1517, 1409, 1352, 1247, 1212, 1088 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.58 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.38 (d, J = 8.1 Hz, 2H, Ar−H), 7.14 (d, J = 7.9 Hz, 2H, Ar−H), 7.01 (s, 1H, Ar−H), 6.99 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 6.79 (s, 1H, Ar−H), 3.88 (s, 6H, 2 × OCH_3), 3.32−3.26 (m, 2H, CH_2), 3.26−3.20 (m, 2H, CH_2), 2.36 (s, 3H, $ArCH_3$) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 192.6, 149.2, 147.1, 144.1, 138.2, 136.3, 133.6, 132.2, 131.2 (2 × Ar−CH), 129.1 (2 × Ar−CH), 128.1, 120.3, 114.5, 114.2, 112.2, 92.1, 87.2, 55.9, 55.8, 40.5, 29.9, 21.4 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{23}SO_3$ 391.1362, found 391.1476.

3-(2-((4-Butylphenyl)ethynyl)-4,5-dimethoxyphenyl)-1-(4-isopropylphenyl)propan-1-one (5ai). GP-2 was carried out with 3-(2-bromo-4,5-dimethoxyphenyl)-1-(4-isopropylphenyl)propan-1-one **3r** (117 mg, 0.3 mmol), 1-butyl-4-ethynylbenzene **4d** (94.8 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5ai** (99.6 mg, 71%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3r**) = 0.60, R_f (**5ai**) = 0.55, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2961, 1681, 1605, 1516, 1463, 1384, 1248, 1216, 1090 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.88 (m, 2H, Ar−H), 7.44−7.37 (m, 2H, Ar−H), 7.20 (d, J = 8.2 Hz, 2H, Ar−H), 7.14 (d, J = 8.3 Hz, 2H, Ar−H), 7.02 (s, 1H, Ar−H), 6.81 (s, 1H, Ar−H), 3.89 (s, 6H, 2 × OCH_3), 3.39−3.28 (m, 2H, CH_2), 3.28−3.18 (m, 2H, CH_2), 2.98−2.88 (m, 1H, C*H*), 2.68−2.56 (m, 2H, CH_2), 1.59−1.55 (m, 2H, CH_2), 1.35−1.33 (m, 2H, CH_2), 1.23 (d, J = 6.9 Hz, 6H, 2 × CH_3), 0.93 (t, J = 7.3 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.4, 154.4, 149.2, 147.0, 143.2, 136.8, 134.6, 131.3 (2 × Ar−CH), 128.4 (2 × Ar−CH), 128.4 (2 × Ar−CH), 126.6 (2 × Ar−CH), 120.5, 114.5, 114.3, 112.2, 92.1, 87.3, 55.9, 55.9, 39.9, 35.4, 34.2, 33.5, 29.9, 23.7 (2 × CH_3), 22.4, 14.0 ppm. HRMS (ESI) m/z $[(M + NH_4)]^+$ calcd for $C_{32}H_{40}NO_3$ 486.3003, found 486.3004.

3-(2-((4-Butylphenyl)ethynyl)-4,5-dimethoxyphenyl)-1-(thiophen-2-yl)propan-1-one (5aj). GP-2 was carried out with 3-(2-bromo-4,5-dimethoxyphenyl)-1-(thiophen-2-yl)propan-1-one **3s** (106.2 mg, 0.3 mmol), 1-butyl-4-ethynylbenzene **4d** (94.8 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **5aj** (76.3 mg, 78%) as brown oil. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**3s**) = 0.70, R_f (**5aj**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3093, 2954, 2208, 1654, 1601, 1464, 1309, 1271, 778, 600 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.58 (dd, J = 4.9 and 1.1 Hz, 1H, Ar−H), 7.43−7.36 (m, 2H, Ar−H), 7.14 (d, J = 8.3 Hz, 2H, Ar−H), 7.01 (s, 1H, Ar−H), 6.98 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 6.79 (s, 1H, Ar−H), 3.88 (s, 6H, 2 × OCH_3), 3.34−3.26 (m, 2H, CH_2), 3.26−3.18 (m, 2H, CH_2), 2.65−2.56 (m, 2H, CH_2), 1.66−1.53 (m, 2H, CH_2), 1.38−1.32 (m, 2H, CH_2), 0.93 (t, J = 7.3 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 192.7, 149.2, 147.1, 144.2, 143.2, 136.3, 133.6, 132.2, 131.3 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.1, 120.5, 114.5, 114.3, 112.2, 92.1, 87.2, 55.9, 55.8, 40.5, 35.5, 33.4, 30.0, 22.2, 13.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{29}SO_3$ 433.1832, found 433.1826.

3-(5-Methoxy-2-(phenylethynyl)phenyl)-1-phenylpropan-1-one (5ak). GP-2 was carried out with 3-(2-bromo-5-methoxyphenyl)-1-phenylpropan-1-one **3t** (95.4 mg, 0.3 mmol), phenyl acetylene **4a** (66.1 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5ak** (81.5 mg, 80%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3t**) = 0.70, R_f (**5ak**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3052, 2928, 1684, 1596, 1497, 1236, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−7.97 (m, 2H, Ar−H), 7.55−7.50 (m, 1H, Ar−H), 7.50−7.45 (m, 3H, Ar−H), 7.42−7.36 (m, 2H, Ar−H), 7.34−7.29 (m, 3H, Ar−H), 6.87 (d, J = 2.6 Hz, 1H, Ar−H), 6.77 (dd, J = 8.5 and 2.7 Hz, 1H, Ar−H), 3.82 (s, 3H, OCH_3), 3.44−3.27 (m, 2H, CH_2), 3.33−3.24 (m, 2H, CH_2) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.4, 159.1, 144.1, 136.8, 133.6, 133.0, 131.3 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.3 (2 × Ar−CH), 128.1 (2 × Ar−CH), 127.9, 123.5, 114.7, 114.7, 111.1, 92.1, 87.8, 55.2, 39.5, 29.9 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{21}O_2$ 341.1536, found 341.1551.

3-(2-(Hept-1-yn-1-yl)phenyl)-1-phenylpropan-1-one (5al). GP-2 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-one **3a** (86.4 mg, 0.3 mmol), hept-1-yne **4i** (57.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5al** (69.3 mg, 76%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3a**) = 0.70, R_f (**5al**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2917, 1625, 1482, 1451, 1325, 847, 821 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dt, J = 8.5 and 1.7 Hz, 2H, Ar−H), 7.57−7.52 (m, 1H, Ar−H), 7.46−7.44 (m, 2H, Ar−H), 7.44−7.39 (m, 1H, Ar−H), 7.27−7.21 (m, 1H, Ar−H), 7.21−7.12 (m, 2H, Ar−H), 3.38−3.30 (m, 2H, CH_2), 3.25−3.17 (m, 2H, CH_2), 2.41 (t, J = 7.1 Hz, 2H, CH_2), 1.61−1.51 (m, 2H, CH_2), 1.43−1.33 (m, 2H, CH_2), 1.33−1.28 (m, 2H, CH_2), 0.85 (t, J = 7.1 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.3, 142.9, 136.7, 132.9, 132.2, 128.9, 128.4 (2 × Ar−CH), 127.9 (2 × Ar−CH), 127.7, 126.0, 123.3, 94.5, 78.9, 39.4, 31.0, 29.3, 28.4, 22.1, 19.4, 13.8 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{22}H_{25}O$ 305.1900, found 305.1904.

3-(2-(Dodec-1-yn-1-yl)phenyl)-1-phenylpropan-1-one (5am). GP-2 was carried out with 3-(2-bromophenyl)-1-phenylpropan-1-one **3a** (86.4 mg, 0.3 mmol), dodec-1-yne **4k** (99.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5am** (85.2 mg, 76%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3a**) = 0.70, R_f (**5am**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3060, 2925, 2850, 1688, 1597, 1484, 1448, 1203, 743, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.74 (m, 2H, Ar−H), 7.59−7.51 (m, 3H, Ar−H), 7.46 (ddd, J = 6.6, 4.5, and 1.2 Hz, 2H, Ar−H), 7.43−7.33 (m, 2H, Ar−H), 3.83 (s, 2H, CH_2), 2.67−2.57 (m, 2H, CH_2), 1.60−1.49 (m, 2H, CH_2), 1.29−1.15 (m, 16H, 8 × CH_2), 0.92−0.83 (m, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.3, 142.9, 136.8, 132.9, 132.3, 128.9, 128.5 (2 × Ar−CH), 128.0 (2 × Ar−CH), 127.7, 126.0, 123.4, 94.5, 78.9, 39.4, 31.9, 29.5, 29.4, 29.4, 29.3, 29.1, 28.9, 28.8, 22.6, 19.5, 14.1 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{35}O$ 375.2682, found 375.2686.

3-(4-Methyl-2-(oct-1-yn-1-yl)phenyl)-1-(p-tolyl)propan-1-one (5an). GP-2 was carried out with 3-(2-bromo-4-methylphenyl)-1-(*p*-tolyl)propan-1-one **3l** (94.8 mg, 0.3 mmol), oct-1-yne **4j** (66 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for

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4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5an** (82.0 mg, 79%) as brown oil. [TLC (petroleum ether/ethyl acetate: 98:02, R_f (**3l**) = 0.70, R_f (**5an**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2930, 2857, 1683, 1607, 1497, 1293, 810, 772 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.84 (m, 2H, Ar−H), 7.26−7.23 (m, 3H, Ar−H), 7.12 (d, J = 7.8 Hz, 1H, Ar−H), 7.01 (dd, J = 7.8 and 1.3 Hz, 1H, Ar−H), 3.31−3.23 (m, 2H, Ar−H), 3.16−3.10 (m, 2H, Ar−H), 2.42−2.35 (m, 5H, CH_2 and CH_3), 2.38 (s, 3H, CH_3), 1.57−1.50 (m, 2H, CH_2), 1.42−1.35 (m, 2H, CH_2), 1.31−1.19 (m, 4H, 2 × CH_2), 0.85 (t, J = 7.6 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.2, 143.6, 140.1, 135.6, 134.4, 132.8, 129.2 (2 × Ar−CH), 128.8, 128.6, 128.2 (2 × Ar−CH), 123.2, 94.1, 79.1, 39.5, 31.3, 29.1, 28.8, 28.6, 22.5, 21.6, 20.7, 19.5, 14.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{31}O$ 347.2369, found 347.2375.

1-(4-Methoxyphenyl)-3-(2-(oct-1-yn-1-yl)phenyl)propan-1-one (5ao). GP-2 was carried out with 3-(2-bromophenyl)-1-(4-methoxyphenyl)propan-1-one **3k** (95.4 mg, 0.3 mmol), oct-1-yne **4j** (66 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5ao** (78.3 mg, 75%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3k**) = 0.70, R_f (**5ao**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2959, 2853, 1678, 1600, 1509, 1259, 1169, 1111, 976, 836 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04−7.94 (m, 2H, Ar−H), 7.40 (dd, J = 7.5 and 1.3 Hz, 1H, Ar−H), 7.26−7.19 (m, 2H, Ar−H), 7.19−7.11 (m, 1H, Ar−H), 6.94−6.88 (m, 2H, Ar−H), 3.86 (s, 3H, OCH_3), 3.31−3.25 (m, 2H, Ar−H), 3.21−3.16 (m, 2H, Ar−H), 2.41 (t, J = 7.1 Hz, 2H, CH_2), 1.57−1.51 (m, 2H, CH_2), 1.40−1.27 (m, 2H, CH_2), 1.35−1.17 (m, 4H, 2 × CH_2), 0.85 (t, J = 8.4 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 198.0, 163.3, 143.2, 132.2, 130.3 (2 × CH), 129.9, 128.9, 127.7, 126.0, 123.4, 113.6 (2 × CH), 94.5, 78.9, 55.4, 39.1, 31.3, 29.6, 28.7, 28.6, 22.5, 19.5, 14.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{29}O_2$ 349.2162, found 349.2163.

3-(5-Methoxy-2-(oct-1-yn-1-yl)phenyl)-1-phenylpropan-1-one (5ap). GP-2 was carried out with 3-(2-bromo-5-methoxyphenyl)-1-phenylpropan-1-one **3t** (95.4 mg, 0.3 mmol), oct-1-yne **4j** (66.1 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5ap** (82.5 mg, 79%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3t**) = 0.70, R_f (**5ap**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2929, 1686, 1605, 1497, 1231, 1204, 1040 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01−7.96 (m, 2H, Ar−H), 7.59−7.51 (m, 1H, Ar−H), 7.47−7.41 (m, 2H, Ar−H), 7.33 (d, J = 8.3 Hz, 1H, Ar−H), 6.79 (s, 1H, Ar−H), 6.69 (dd, J = 8.5 and 2.7 Hz, 1H, Ar−H), 3.78 (s, 3H, Ar−H), 3.37−3.29 (m, 2H, CH_2), 3.16 (dd, J = 8.9 and 6.7 Hz, 2H, CH_2), 2.38 (t, J = 7.1 Hz, 2H, CH_2), 1.55−1.45 (m, 2H, CH_2), 1.41−1.30 (m, 2H, CH_2), 1.30−1.20 (m, 4H, 2 × CH_2), 0.84 (t, J = 6.9 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.4, 159.1, 144.7, 136.8, 133.5, 133.0, 128.5 (2 × Ar−CH), 128.1 (2 × Ar−CH), 115.7, 114.6, 111.7, 92.9, 78.7, 55.2, 39.4, 31.3, 29.7, 28.9, 28.6, 22.5, 19.5, 14.0 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{24}H_{28}NaO_2$ 371.1982, found 371.1986.

3-(5-Fluoro-2-(hept-1-yn-1-yl)phenyl)-1-phenylpropan-1-one (5aq). GP-2 was carried out with 3-(2-bromo-5-fluorophenyl)-1-phenylpropan-1-one **3u** (91.8 mg, 0.3 mmol), hept-1-yne **4i** (57.6 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:02 to 97:03) furnished the product **5aq** (69.6 mg, 72%) as brown oil. [TLC (petroleum ether/ethyl acetate: 98:02, R_f (**3u**) = 0.70, R_f (**5aq**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2937, 1682, 1572, 1373, 1290, 1096 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02−7.93 (m, 2H, Ar−H), 7.59−7.53 (m, 1H, Ar−H), 7.49−7.37 (m, 2H, Ar−H), 7.20 (dd, J = 8.5 and 5.8 Hz, 1H, Ar−H), 7.09 (dd, J = 9.4 and 2.8 Hz, 1H, Ar−H), 6.90 (td, J = 8.5 and 2.8 Hz, 1H, Ar−H), 3.36−3.28 (m, 2H, CH_2), 3.18−3.15 (m, 2H, CH_2), 2.40 (t, J = 7.1 Hz, 2H, CH_2), 1.58−1.52 (m, 2H, CH_2), 1.42−1.34 (m, 2H, CH_2), 1.32−1.24 (m, 2H, CH_2), 0.85 (t, J = 7.2 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 199.2, 160.8 (d, J_{C-F} = 242 Hz, Ar−C), 138.8 (d, J_{C-F} = 3 Hz, Ar−C), 136.7, 133.0, 133.4 (d, J_{C-F} = 8 Hz, Ar−CH), 128.5 (2 × Ar−CH), 128.0 (2 × Ar−CH), 124.9 (d, J_{C-F} = 9 Hz, Ar−C), 118.6 (d, J_{C-F} = 23 Hz, ArCH), 114.8 (d, J_{C-F} = 23 Hz, ArCH), 95.6, 78.1 (d, J_{C-F} = 3 Hz, C ≡ C), 39.3, 31.1, 28.6, 28.3, 22.1, 19.4, 13.9 ppm.

3-(2,4-Difluoro-6-(phenylethynyl)phenyl)-1-phenylpropan-1-one (5ar). GP-2 was carried out with 3-(2-bromo-4,6-difluorophenyl)-1-phenylpropan-1-one **3v** (97.2 mg, 0.3 mmol), phenylacetylene **4a** (61.2 mg, 0.60 mmol), $Pd(OAc)_2$ (2.6 mg, 4 mol %), xantphos (13.8 mg, 8 mol %), K_3PO_4 (266.4 mg, 1.2 mmol) and dry Toluene (2 mL) at 120 °C for 4 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **5ar** (82.5 mg, 79%) as brown oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**3v**) = 0.70, R_f (**5ar**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2938, 1682, 1590, 1426, 1151, 752 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.5 and 1.6 Hz, 2H, Ar−H), 7.54 (ddd, J = 6.9, 4.7, and 1.2 Hz 1H, Ar−H), 7.49−7.46 (m, 2H, Ar−H), 7.43−7.40 (m, 2H, Ar−H), 7.37−7.30 (m, 3H, Ar−H) 7.08 (ddd, J = 8.8, 2.6, and 1.4 Hz, 1H, Ar−H), 6.82 (ddd, J = 9.7, 8.7, and 2.6 Hz, 1H, ArH), 3.35−3.27 (m, 4H, 2 × CH_2) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 198.9, 161.0 (dd, J_{C-F} = 235 and 13 Hz, Ar−C), 159.8 (dd, J_{C-F} = 232 and 13 Hz, Ar−C), 136.6, 133.1, 131.8 (2 × ArCH), 128.9, 128.6 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.1 (2 × Ar−CH), 126.1 (dd, J_{C-F} = 17 and 4 Hz, Ar−C), 125.6 (dd, J_{C-F} = 13 and 8 Hz, Ar−C), 122.2, 114.8 (dd, J_{C-F} = 23 and 4 Hz, Ar−CH), 104.3 (dd, J_{C-F} = 27 and 3 Hz, Ar−CH), 95.0, 85.6 (dd, J_{C-F} = 4 and 1 Hz, C≡C), 39.2, 22.0 (d, J_{C-F} = 3 Hz, CH_2) ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{23}H_{17}F_2O$ 347.1242, found 347.1242.

General Procedure 3 (GP-3) for the Synthesis of 11-Phenyl-11*H*-benzo[*a*]fluorenes (6a−6ac and 6ar). To the solution of alkynones **5a**−**5ac** and **5ar** (62.2−80.1 mg, 0.2 mmol) in a Schlenk tube in dry DCE (1 mL) was added $BF_3{\cdot}OEt_2$ (1 equiv), and the reaction mixture was stirred at 60 °C for 6 h in an oil bath. Progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate: 100:0 to 95:05). The reaction mixture was then quenched with aqueous ammonium chloride and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine, dried over (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude residue by column chromatography on silica gel (100−200 mesh) by using hexane/ethyl acetate solvent system as eluent afforded the cyclized product **6a**−**6ac** and **6ar** (57−84%) as a viscous liquid/semisolid/solid.

11-Phenyl-11H-benzo[a]fluorene (6a).[7b] GP-3 was carried out with 1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-one **5a** (62.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100 to 99:01) furnished the product **6a** (45.5 mg, 78%) as colorless solid. mp = 198−201 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5a**) = 0.50, R_f (**6a**) = 0.90, UV detection].

9-Methyl-11-phenyl-11H-benzo[a]fluorene (6b). GP-3 was carried out with 3-(2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5b** (64.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product the product **6b** (46.5 mg, 76%) as a yellow solid. mp = 204−208 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5b**) = 0.50, R_f (**6b**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3019, 1479, 1451, 1159, 1029, 815, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.84 (m, 3H, Ar−H), 7.72 (d, J = 7.7 Hz, 1H, Ar−H), 7.68−

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7.62 (m, 1H, Ar−H), 7.37 (ddd, J = 8.2, 5.5, and 1.3 Hz, 1H, Ar−H), 7.33−7.27 (m, 1H, Ar−H), 7.24 (ddd, J = 5.6, 3.1, and 1.2 Hz, 2H, ArH), 7.22−7.17 (m, 2H, Ar−H), 7.17−7.10 (m, 3H, ArH), 5.29 (s, CH), 2.35 (s, 3H, ArCH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.4, 142.3, 141.9, 139.4, 138.3, 136.8, 133.2, 130.4, 128.9, 128.9 (2 × Ar−CH), 128.7, 128.0 (2 × Ar−CH), 128.0, 126.7, 126.3, 125.6, 124.9, 124.4, 119.3, 118.4, 53.9, 21.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{19}$ 307.1481, found 307.1476.

9-Ethyl-11-phenyl-11H-benzo[a]fluorene (6c). GP-3 was carried out with 1-(4-ethylphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-one **5c** (67.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6c** (51.2 mg, 80%) as a pale yellow solid. mp = 168−172 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5c**) = 0.50, R_f (**6c**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2964, 2930, 1596, 1449, 1154, 824, 750, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 2.7 Hz, 2H, Ar−H), 7.85 (d, J = 8.4 Hz, 1H, Ar−H), 7.71 (d, J = 7.7 Hz, 1H, Ar−H), 7.61 (d, J = 8.2 Hz, 1H, Ar−H), 7.34−7.31 (m, 1H, Ar−H), 7.29−7.23 (m, 1H, Ar−H), 7.24−7.15 (m, 4H, ArH), 7.14 (s, 1H, Ar−H), 7.10 (d, J = 7.2 Hz, 2H, ArH), 5.25 (s, CH), 2.62 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.20 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.4, 143.4, 142.3, 141.9, 139.4, 138.6, 133.2, 130.4, 128.9, 128.8 (2 × Ar−CH), 128.7, 128.1 (2 × Ar−CH), 126.8, 126.7, 126.2, 124.9, 124.5 (2 × Ar−CH), 119.4, 118.4, 53.9, 29.0, 15.8 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{21}$ 321.1638, found 321.1634.

9-Isopropyl-11-phenyl-11H-benzo[a]fluorene (6d). GP-3 was carried out with 1-(4-isopropylphenyl)-3-(2-(phenylethynyl)phenyl)-propan-1-one **5d** (70.5 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6d** (47.5 mg, 71%) as a white solid. mp = 197−200 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5d**) = 0.50, R_f (**6d**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3446, 2955, 2922, 1599, 1492, 1051, 822, 758 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.91 (m, 2H, ArH), 7.90−7.85 (m, 1H, ArH), 7.74 (d, J = 7.8 Hz, 1H, ArH), 7.63 (d, J = 8.3 Hz, 1H, ArH), 7.35 (ddd, J = 8.2, 6.9, and 1.3 Hz, 1H, ArH), 7.32−7.27 (m, 1H, ArH), 7.27−7.16 (m, 5H, ArH), 7.12 (dd, J = 7.9 and 1.4 Hz, 2H, ArH), 5.29 (s, 1H, ArCH), 2.93−2.86 (m, 1H, Ar$CH(CH_3)_2$), 1.22 (dd, J = 7.9 Hz, 6H, $ArCH(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 148.4, 142.7, 142.2, 139.7, 139.1, 133.6, 130.7, 129.2, 129.1 (2 × Ar−CH), 129.1, 128.4 (2 × Ar−CH), 127.0, 126.6, 125.5, 125.2, 124.8, 123.5, 119.7, 118.8, 54.4, 34.6, 24.7, 24.2 ppm. HRMS (ESI) m/z $[(M + NH_4)]^+$ calcd for $C_{26}H_{26}N$ 352.2060, found 352.2048.

8-Methoxy-11-phenyl-11H-benzo[a]fluorene + 10-Methoxy-11-phenyl-11H-benzo[a]fluorene (6e+6e′). GP-3 was carried out with 1-(3-methoxyphenyl)-3-(2-(phenylethynyl)phenyl)propan-1-one **5e** (68 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 95:05) furnished the product **6e+6e′** (43.8 mg, 68%) as a yellow solid. mp = 169−172 °C. [TLC (petroleum ether/ethyl acetate 97:5, R_f (**5e**) = 0.50, R_f (**6e+6e′**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3059, 3018, 1616, 1580, 1261, 1251, 1177, 825 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) ***according to the major isomer*** δ 7.94−7.95 (m, 2H, ArH), 7.91 (ddd, J = 2.8, 2.3, and 1.8 Hz, 1H, ArH), 7.67 (d, J = 8.3 Hz, 1H, ArH), 7.40−7.30 (m, 2H, ArH), 7.34−7.29 (m, 1H, ArH), 7.23−7.20 (m, 3H, ArH), 7.16 (d, J = 5.4 Hz, 1H, ArH), 7.12 (d, J = 1.7 Hz, 2H, ArH), 6.80 (dd, J = 8.3 and 2.5 Hz, 1H, ArH), 5.30 (s, 1H, ArCH), 3.90 (s, 3H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) ***according to the major isomer*** δ 159.5, 143.8, 142.2, 142.0, 141.5, 139.1, 133.5, 130.4, 128.9, 128.8 (2 × Ar−CH), 128.8, 127.9 (2 × Ar−CH), 126.7, 126.4, 125.5, 125.2, 124.5, 118.4, 112.9, 104.9, 55.5, 53.3 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{19}O$ 323.1430, found 323.1422.

12-Phenyl-12H-benzo[7,8]fluoreno[2,3-d][1,3]dioxole (6f). GP-3 was carried out with 1-(benzo[d][1,3]dioxol-5-yl)-3-(2-(phenylethynyl)phenyl)propan-1-one **5f** (70.8 mg, 0.2 mmol), (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:1) furnished the product **6f** (63.5 mg, 73%) as a yellow solid. mp = 206−208 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5f**) = 0.50, R_f (**6f**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2884, 1611, 1497, 1478, 1469, 1317, 1239, 1041, 820, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H, Ar−H), 8.00−7.97 (m, 2H, Ar−H), 7.61 (s, 1H, Ar−H), 7.59−7.49 (m, 1H, Ar−H), 7.39−7.31 (m, 2H, Ar−H), 7.28−7.14 (m, 3H, Ar−H), 7.13−7.09 (m, 2H, Ar−H), 6.81 (s, 1H, Ar−H), 6.02 (d, 2H, J = 16 Hz, -OCH_2O−), 5.40 (s, CH) ppm. $^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$) δ 147.2, 143.3, 142.3, 141.8, 139.1, 134.2, 132.4, 129.6, 128.9 (2 × CH), 128.7, 127.8 (2 × CH), 126.7, 126.8, 126.4, 124.9, 123.9, 118.6, 105.8, 101.2 (t, -OCH_2−), 101.0, 52.7 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{17}O_2$ 337.1223, found 337.1221.

9-Fluoro-11-phenyl-11H-benzo[a]fluorene (6g).[7b] GP-3 was carried out with 1-(4-fluorophenyl)-3-(2-(phenylethynyl)phenyl)-propan-1-one **5g** (65.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6g** (35.3 mg, 57%) as a yellow solid. mp = 170−173 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5g**) = 0.50, R_f (**6g**) = 0.90, UV detection].

13-Phenyl-13H-dibenzo[a,i]fluorene (6h).[7b] GP-3 was carried out with 1-(naphthalen-2-yl)-3-(2-(phenylethynyl)phenyl)propan-1-one **5h** (62.3 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6h** (45.0 mg, 75%) as pale brown solid. mp = 191−193 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5h**) = 0.50, R_f (**6h**) = 0.90, UV detection].

10-Phenyl-10H-benzo[4,5]indeno[2,1-b]thiophene (6i). GP-3 was carried out with 3-(2-(phenylethynyl)phenyl)-1-(thiophen-2-yl)-propan-1-one **5i** (63.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 98:02) furnished the product **6i** (36.5 mg, 61%) as pale yellow crystalline solid. mp = 160−162 °C. [TLC (petroleum ether/ethyl acetate 92:2, R_f (**5i**) = 0.50, R_f (**6i**) = 0.85, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3057, 3018, 1631, 1600, 1491, 1450, 830, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−7.84 (m, 2H, Ar−H), 7.76 (d, J = 8.3 Hz, 1H, Ar−H), 7.62 (dd, J = 8.4 and 1.0 Hz, 1H, Ar−H), 7.37−7.28 (m, 3H, Ar−H), 7.28−7.17 (m, 4H, Ar−H), 7.15−7.09 (m, 2H, Ar−H), 5.36 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 145.9, 145.8, 141.1, 137.1, 131.9, 130.4, 129.1, 129.0 (2 × Ar−CH), 128.9, 128.7, 127.8 (2 × Ar−CH), 127.0, 126.3, 124.5, 123.5, 118.7, 118.3, 51.9 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{21}H_{15}S$ 299.0889, found 299.0897.

9-Methyl-11-(m-tolyl)-11H-benzo[a]fluorene (6j). GP-3 was carried out with 1-(p-tolyl)-3-(2-(m-tolylethynyl)phenyl)propan-1-one **5j** (67.7 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6j** (53.5 mg, 81%) as a yellow solid. mp = 157−160 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5j**) = 0.50, R_f (**6j**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3432, 2915, 1604, 1481, 1364, 898, 711, 817 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 2.3 Hz, 2H, Ar−H), 7.94−7.89 (m, 1H, Ar−H), 7.74 (d, J = 7.7 Hz, 1H, Ar−H), 7.69 (d, J = 8.3 Hz, 1H, Ar−H), 7.41−7.31 (m, 2H, Ar−H), 7.25−7.15 (m, 3H, Ar−H), 7.05 (d, J = 7.5 Hz, 1H, ArH), 6.98 (d, J = 7.5 Hz, 1H, Ar−H), 6.93 (s, 1H, Ar−H), 5.28 (s, CH), 2.38 (s, 3H, Ar−CH_3), 2.27 (s, 3H, Ar−CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz,

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$CDCl_3$) δ 149.5, 142.4, 141.8, 139.5, 138.4, 138.3, 136.9, 133.3, 130.5, 128.9, 128.7 (2 × Ar−CH), 128.6, 127.9, 127.5, 126.3, 125.6, 125.2, 124.9, 124.5, 119.3, 118.4, 53.2, 21.6, 21.5 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{21}$ 321.1638, found 321.1633.

10-(p-Tolyl)-10H-benzo[4,5]indeno[2,1-b]thiophene (6k). GP-3 was carried out with 1-(thiophen-2-yl)-3-(2-(*p*-tolylethynyl)phenyl)-propan-1-one **5k** (66.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6k** (40.6 mg, 65%) as colorless solid. mp = 188−190 °C. [TLC (petroleum ether/ethyl acetate 99:2, R_f (**5k**) = 0.50, R_f (**6k**) = 0.85, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3423, 1582, 1509, 1347, 1106, 828, 747 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92−7.88 (m, 2H, Ar−H), 7.77 (d, J = 8.3 Hz, 1H, Ar−H), 7.66 (dd, J = 8.1 and 1.2 Hz, 1H, Ar−H), 7.36−7.35 (m, 1H, Ar−H), 7.35−7.27 (m, 3H, Ar−H), 7.08−7.00 (m, 4H, Ar−H), 5.36 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 145.9, 145.8, 138.0, 137.0, 136.6, 131.9, 130.5, 129.7 (2 × Ar−CH), 129.1, 129.0, 128.7, 127.6 (2 × Ar−CH), 126.3, 124.6, 123.5, 118.8, 118.3, 51.6, 21.1 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{22}H_{17}S$ 313.1045, found 313.1047.

11-(4-Ethylphenyl)-9-methyl-11H-benzo[a]fluorene (6l). GP-3 was carried out with 3-(2-((4-ethylphenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5l** (70.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6l** (52.7 mg, 79%) as light yellow solid. mp = 202−206 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5l**) = 0.50, R_f (**6l**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2926, 2868, 1509, 1480, 1455, 831, 804, 744 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 2.5 Hz, 2H, Ar−H), 7.90 (dd, J = 6.1 and 5.2 Hz, 1H, Ar−H), 7.72 (d, J = 7.6 Hz, 1H, Ar−H), 7.70−7.65 (m, 1H, Ar−H), 7.37 (ddd, J = 8.1, 6.8, and 1.4 Hz, 1H, Ar−H), 7.32 (ddd, J = 8.2, 6.8, and 1.4 Hz, 1H, Ar−H), 7.22−7.14 (m, 2H, ArH), 7.09 (d, J = 8.2 Hz, 2H, Ar−H), 7.07−7.00 (m, 2H, ArH), 5.29 (s, CH), 2.61 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.36 (s, 3H, $ArCH_3$), 1.21 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 142.4 (2 × Cq), 139.3, 138.9, 138.3, 136.8, 133.2, 130.4, 128.9, 128.6, 128.3 (2 × Ar−CH), 127.9, 127.8 (2 × Ar−CH), 126.2, 125.6, 124.8, 124.6, 119.3, 118.4, 53.5, 28.4, 21.6, 15.3 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{26}H_{23}$ 335.1794, found 335.1777.

9-Ethyl-11-(4-ethylphenyl)-11H-benzo[a]fluorene (6m). GP-3 was carried out with 1-(4-ethylphenyl)-3-(2-((4-ethylphenyl)-ethynyl)phenyl)propan-1-one **5m** (73.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6m** (54.9 mg, 79%) as a white solid. mp = 156−160 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5m**) = 0.50, R_f (**6m**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2963, 2924, 2852, 1509, 1384, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92−7.88 (m, 3H, Ar−H), 7.74 (d, J = 7.7 Hz, 1H, Ar−H), 7.68 (d, J = 8.2 Hz, 1H, Ar−H), 7.37 (ddd, J = 8.1, 6.9, and 1.3 Hz, 2H, Ar−H), 7.33−7.29 (m, 1H, Ar−H), 7.23−7.17 (m, 1H, ArH), 7.10−7.03 (m, 4H, Ar−H), 5.30 (s, 1H, CH), 2.66 (q, J = 7.6 Hz, 2H, CH_2), 2.61 (q, J = 7.4 Hz, 2H, CH_2), 1.24 (t, J = 5.8 Hz, 3H, CH_3), 1.20 (t, J = 5.8 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.6, 143.3, 142.5, 142.4, 139.4, 138.9, 138.6, 133.2, 130.5, 128.9, 128.6, 128.3 (2 × Ar−CH), 127.9 (2 × Ar−CH), 126.7, 126.2, 124.9, 124.6, 124.5, 119.4, 118.4, 53.6, 29.0, 28.4, 15.8, 15.3 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{25}$ 349.1951, found 349.1955.

11-(4-Butylphenyl)-9-ethyl-11H-benzo[a]fluorene (6n). GP-3 was carried out with 3-(2-((4-butylphenyl)ethynyl)phenyl)-1-(4-ethylphenyl)propan-1-one **5n** (78.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6n** (57.2 mg, 82%) as a pale yellow solid. mp = 150−154 °C. For gram scale synthesis of 11-(4-butylphenyl)-9-ethyl-11*H*-benzo[*a*]fluorene (**6n**): GP-3 was carried out with 3-(2-((4-butylphenyl)ethynyl)phenyl)-1-(4-ethylphenyl)propan-1-one **5n** (1000 mg, 2.54 mol), $BF_3{\cdot}OEt_2$ (750 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: Hexane to 99:1) furnished the product **6n** (725 mg, 76%) as a pale yellow solid. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3446, 2960, 1509, 816, 744, 611 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, J = 6.2 Hz, 2H, Ar−H), 7.92−7.61 (m, 1H, Ar−H), 7.76 (d, J = 7.7 Hz, 1H, Ar−H), 7.69 (d, J = 8.2 Hz, 1H, Ar−H), 7.42−7.39 (m, 1H, Ar−H), 7.33 (ddd, J = 8.1, 6.9, and 1.3 Hz, 1H, Ar−H), 7.24 (d, J = 7.8 Hz, 1H, ArH), 7.20 (s, 1H, Ar−H), 7.08 (d, J = 8.2 Hz, 2H, ArH), 7.05 (d, J = 8.2 Hz, 2H, ArH), 5.30 (s, 1H, CH), 2.68 (q, J = 7.6 Hz, 2H, CH_2CH_3), 2.64−2.58 (m, 2H, CH_2), 1.61−1.54 (m, 2H, CH_2), 1.42−1.29 (m, 2H, CH_2), 1.26 (t, J = 7.6 Hz, 3H, CH_3), 0.93 (t, J = 7.6 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 143.2, 142.6, 141.0, 139.2, 138.7, 138.5, 133.2, 130.4, 128.8, 128.7 (2 × Ar−CH), 128.6, 127.7 (2 × Ar−CH), 126.6, 126.1, 124.7, 124.5, 124.4, 119.3, 118.4, 53.5, 35.2, 33.4, 28.9, 22.3, 15.7, 13.9 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{29}H_{29}$ 377.2264, found 377.2269.

10-(4-Butylphenyl)-10H-benzo[4,5]indeno[2,1-b]thiophene (6o). GP-3 was carried out with 3-(2-((4-butylphenyl)ethynyl)phenyl)-1-(thiophen-2-yl)propan-1-one **5o** (74.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6o** (47.4 mg, 67%) as a yellow solid. mp = 120−122 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5o**) = 0.50, R_f (**6o**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2924, 1586, 1509, 828, 765, 747, 677, 614 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, J = 8.5 Hz, 2H, Ar−H), 7.76 (d, J = 8.3 Hz, 1H, Ar−H), 7.68−7.59 (m, 1H, Ar−H), 7.39−7.25 (m, 4H, Ar−H), 7.08−6.94 (m, 4H, Ar−H), 5.34 (s, 1H, CH), 2.61−2.53 (m, 2H, CH_2), 1.61−1.40 (m, 2H, CH_2), 1.38−1.25 (m, 2H, CH_2), 0.88 (t, J = 7.6 Hz, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 145.9, 145.8, 141.6, 138.1, 137.0, 131.9, 130.5, 129.0 (3 × Ar−CH), 128.9, 128.6, 127.5 (2 × Ar−CH), 126.3, 124.2, 123.2, 118.7, 118.3, 51.6, 35.3, 33.4, 22.4, 13.9 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{23}S$ 355.1515, found 355.1512.

11-(4-(tert-Butyl)phenyl)-11H-benzo[a]fluorene (6p). GP-3 was carried out with 3-(2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)-1-phenylpropan-1-one **5p** (73.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6p** (52.7 mg, 80%) as yellow crystalline solid. mp = 218−222 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5p**) = 0.50, R_f (**6p**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2958, 1511, 1464, 1267, 827, 755, 610 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, J = 8.1 Hz, 2H, Ar−H), 7.94−7.89 (m, 1H, Ar−H), 7.84 (dd, J = 7.4 and 1.0 Hz, 1H, Ar−H), 7.74−7.69 (m, 1H, Ar−H), 7.44−7.37 (m, 2H, Ar−H), 7.37−7.31 (m, 2H, Ar−H), 7.25 (ddt, J = 5.4, 3.2, and 1.6 Hz, 3H, Ar−H), 7.08−7.01 (m, 2H, Ar−H), 5.34 (s, 1H, Ar−C*H*), 1.28 (s, 9H, Ar−C$(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 149.3, 142.8, 140.9, 139.2, 138.3, 133.5, 130.4, 128.9, 128.7, 127.5 (2 × Ar−CH), 127.1, 126.8, 126.3, 125.7 (2 × Ar−CH), 125.1, 124.9, 124.8, 119.6, 118.5, 53.6, 34.3, 31.3 (3 × CH_3) ppm. HRMS (ESI) m/z $[(M + K)]^+$ calcd for $C_{27}H_{24}K$ 387.1510, found 387.1510.

11-(4-Methoxyphenyl)-11H-benzo[a]fluorene (6q).[7b] GP-3 was carried out with 3-(2-((4-methoxyphenyl)ethynyl)phenyl)-1-phenylpropan-1-one **5q** (68.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **6q** (47.0 mg, 73%) as a pale yellow solid. mp = 184−187 °C.

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11-(4-Methoxyphenyl)-9-methyl-11H-benzo[a]fluorene (6r). GP-3 was carried out with 3-(2-((4-methoxyphenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5r** (70.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **6r** (50.4 mg, 75%) as a brown solid. mp = 194−198 °C. [TLC (petroleum ether/ethyl acetate 97:3, R_f (**5r**) = 0.30, R_f (**6r**) = 0.70, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2826, 1605, 1507, 1457, 1245, 1176, 1027, 816 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.85 (m, 3H, Ar−H), 7.71 (d, J = 7.7 Hz, 1H, Ar−H), 7.67 (d, J = 8.2 Hz, 1H, Ar−H), 7.37 (ddd, J = 8.1, 6.9, and 1.3 Hz, 1H, Ar−H), 7.31 (ddd, J = 8.2, 6.9, and 1.4 Hz, 1H, Ar−H), 7.19 (d, J = 7.6 Hz, 1H, Ar−H), 7.14 (s, 1H, Ar−H), 7.08−7.01 (m, 2H, Ar−H), 6.83−6.75 (m, 2H, Ar−H), 5.27 (s, 1H, CH), 3.76 (s, 3H, OCH_3), 2.36 (s, 3H, Ar−CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 149.7, 142.4, 139.2, 138.2, 136.8, 133.8, 133.3, 130.5, 129.0 (2 × Ar−CH), 128.9, 128.7, 127.9, 126.2, 125.6, 124.9, 124.5, 119.3, 118.4, 114.3 (2 × Ar−CH), 55.2, 53.1, 21.7 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{25}H_{20}NaO$ 359.1406, found 359.1395.

9-Isopropyl-11-(4-methoxyphenyl)-11H-benzo[a]fluorene (6s). GP-3 was carried out with 1-(4-isopropylphenyl)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)propan-1-one **6s** (76.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **6s** (57.5 mg, 79%) as a white solid. mp = 146−150 °C. [TLC (petroleum ether/ethyl acetate 97:3, R_f (**5s**) = 0.50, R_f (**6s**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3055, 2956, 2830, 1612, 1509, 1402, 1252, 1174, 1037, 820. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.87 (m, 3H, Ar−H), 7.74 (d, J = 7.8 Hz, 1H, Ar−H), 7.67 (dd, J = 8.2 and 0.5 Hz, 1H, Ar−H), 7.36 (ddd, J = 8.1, 6.9, and 1.3 Hz, 1H, Ar−H), 7.30 (ddd, J = 8.1, 6.9, and 1.3 Hz, 1H, Ar−H), 7.25 (dd, J = 4.8 and 3.5 Hz, 1H, Ar−H), 7.18 (s, 1H, Ar−H), 7.07−7.01 (m, 2H, Ar−H), 6.83−6.75 (m, 2H, Ar−H), 5.26 (s, 1H, CH), 3.75 (s, 3H, $ArOCH_3$), 2.91 (dt, J = 13.8 and 6.9 Hz, 1H, Ar−$CH(CH_3)_2$), 1.24 (t, J = 7.1 Hz, 6H, Ar−$CH(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 149.6, 148.0, 142.6, 139.2, 138.7, 133.8, 133.2, 130.4, 129.1 (2 × Ar−CH), 128.9, 128.7, 126.2, 125.1, 124.9, 124.5, 123.1, 119.4, 118.4, 114.2 (2 × Ar−CH), 55.1, 53.2, 34.3, 24.4, 23.9 ppm. HRMS (ESI) m/z $[(M + K)]^+$ calcd for $C_{27}H_{24}KO$ 403.1459, found 403.1452.

8,9-Dimethoxy-11-(4-methoxyphenyl)-11H-benzo[a]fluorene (6t). GP-3 was carried out with 1-(3,4-dimethoxyphenyl)-3-(2-((4-methoxyphenyl)ethynyl)phenyl)propan-1-one **5t** (80.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 93:07 to 90:10) furnished the product **6t** (53.9 mg, 71%) as a brown solid. mp = 165−170 °C. [TLC (petroleum ether/ethyl acetate 93:7, R_f (**5t**) = 0.50, R_f (**6t**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2928, 2831, 1606, 1509, 1492, 1321, 1240 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.82 (m, 3H, Ar−H), 7.70−7.62 (m, 1H, Ar−H), 7.37−7.27 (m, 3H, Ar−H), 7.08−6.99 (m, 2H, Ar−H), 6.85 (s, 1H, Ar−H), 6.83−6.76 (m, 2H, Ar−H), 5.20 (s, 1H, CH), 4.02 (s, 3H, $ArOCH_3$), 3.85 (s, 3H, $ArOCH_3$), 3.76 (s, 3H, $ArOCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 148.9, 142.7, 142.2, 139.4, 133.8, 133.3, 132.8, 132.7, 130.3, 128.9 (2 × Ar−CH), 128.9, 128.7, 126.3, 124.7, 124.2, 118.0, 114.3 (2 × Ar−CH), 108.2, 102.8, 56.2, 56.1, 55.2, 53.2 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{26}H_{23}O_3$ 383.1642, found 383.1629.

11-(4-Chlorophenyl)-9-methyl-11H-benzo[a]fluorene (6u). GP-3 was carried out with 3-(2-((4-chlorophenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5u** (71.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6u** (46.9 mg, 69%) as a pale yellow solid. mp = 205−209 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5u**) = 0.50, R_f (**6u**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2922, 2852, 1487, 1087, 816, 800, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H, Ar−H), 7.90 (d, J = 7.5 Hz, 1H, Ar−H), 7.72 (d, J = 7.7 Hz, 1H, Ar−H), 7.51 (d, J = 8.1 Hz, 1H, Ar−H), 7.39 (ddd, J = 8.1, 6.9, and 1.3 Hz, 1H, Ar−H), 7.33 (ddd, J = 8.2, 6.8, and 1.4 Hz, 1H, Ar−H), 7.25−7.17 (m, 3H, ArH), 7.11 (d, 1H, J = 0.6 Hz, Ar−H), 7.08−7.03 (m, 2H, ArH), 5.27 (s, CH), 2.37 (s, 3H, $ArCH_3$) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 148.9, 141.7, 140.4, 139.5, 138.3, 137.0, 133.3, 132.4, 130.3, 129.4 (2 × Ar−CH), 129.1 (2 × Ar−CH), 129.0, 129.0, 128.2, 126.4, 125.6, 125.1, 124.2, 119.5, 118.5, 53.1, 21.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{18}Cl$ 341.1092, found 341.1024.

11-(4-Chlorophenyl)-9-ethyl-11H-benzo[a]fluorene (6v). GP-3 was carried out with 3-(2-((4-chlorophenyl)ethynyl)phenyl)-1-(4-ethylphenyl)propan-1-one **5v** (74.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6v** (50.2 mg, 71%) as a pale yellow semisolid. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5v**) = 0.50, R_f (**6v**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2922, 2852, 1487, 1406, 1087, 816, 800, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H, Ar−H), 7.92−7.88 (m, 1H, Ar−H), 7.75 (d, J = 7.7 Hz, 1H, Ar−H), 7.60 (d, J = 8.2 Hz, 1H, Ar−H), 7.38 (dd, J = 8.1 and 1.3 Hz, 1H, Ar−H), 7.34 (dd, J = 8.2 and 1.3 Hz, 1H, Ar−H), 7.27−7.20 (m, 3H, ArH), 7.14 (s, 1H, Ar−H), 7.09−7.02 (m, 2H, ArH), 5.28 (s, CH), 2.65 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.24 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 148.9, 143.6, 141.8, 140.5, 139.5, 138.6, 133.3, 132.3, 130.3, 129.4 (2 × Ar−CH), 129.1 (2 × Ar−CH), 129.0, 129.0, 127.0, 126.5, 125.1, 124.4, 124.2, 119.6, 118.5, 53.2, 29.0, 15.8 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{25}H_{19}ClNa$ 377.1073, found 377.1011.

11-(4-Fluorophenyl)-11H-benzo[a]fluorene (6w). GP-3 was carried out with 3-(2-((4-fluorophenyl)ethynyl)phenyl)-1-phenylpropan-1-one **5w** (65.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6w** (44.0 mg, 73%) as pale yellow crystalline. mp = 158−161 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5w**) = 0.50, R_f (**6w**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3059, 3019, 1605, 1506, 1465, 1158, 816, 604 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 2.7 Hz, 2H, Ar−H), 7.95−7.93 (m, 1H, Ar−H), 7.85 (d, J = 7.5 Hz, 1H, Ar−H), 7.65 (d, J = 8.3 Hz, 1H, Ar−H), 7.46−7.31 (m, 4H, Ar−H), 7.30−7.23 (m, 1H, Ar−H), 7.09 (dd, J = 8.5 and 5.5 Hz, 2H, ArH), 6.96 (d, J = 8.7 Hz, 2H, Ar−H), 5.32 (s, CH) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (J_{C-F} = 248 Hz), 149.0, 142.4, 140.9, 139.3, 137.4 (J_{C-F} = 3 Hz), 133.6, 130.3, 129.5, 129.4, 129.1, 129.0, 127.4, 127.1, 126.5, 125.3, 124.9, 124.5, 119.8, 118.6, 115.9, 115.7, 53.2 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{23}H_{16}F$ 311.1231, found 311.1238.

11-(4-Fluorophenyl)-9-methyl-11H-benzo[a]fluorene (6x). GP-3 was carried out with 3-(2-((4-fluorophenyl)ethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5x** (68.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography(petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6x** (46.6 mg, 72%) as a pale yellow solid. mp = 180−183 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5x**) = 0.50, R_f (**6x**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2921, 1605, 1606, 1227, 1158, 817, 803 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H, Ar−H), 7.90 (dd, J = 7.7 and 1.1 Hz, 1H, Ar−H), 7.72 (d, J = 7.7 Hz, 1H, Ar−H), 7.61 (d, J = 8.2 Hz, 1H, Ar−H), 7.39−7.28 (m, 2H, Ar−H), 7.24−7.17 (m, 1H, Ar−H), 7.17−7.02 (m, 3H, ArH), 7.01−6.90 (m, 2H, Ar−H), 5.28 (s, CH), 2.37 (s, 3H, $ArCH_3$) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7 (J_{C-F} = 243 Hz), 149.2, 141.9, 139.4, 138.2, 137.7, 137.0, 133.3, 130.3, 129.5, 129.4, 129.0, 128.9, 128.1, 126.4, 125.5, 125.0, 124.3, 119.5, 118.5, 115.9, 115.7, 53.0, 21.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{18}F$ 325.1387, found 325.1394.

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11-(4-Fluorophenyl)-9-isopropyl-11H-benzo[a]fluorene (6y). GP-3 was carried out with 3-(2-((4-fluorophenyl)ethynyl)phenyl)-1-(4-isopropylphenyl)propan-1-one **5y** (74.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6y** (48.5 mg, 69%) as a white solid. mp = 196−200 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5y**) = 0.50, R_f (**6y**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2959, 1603, 1507, 1223, 1156, 825, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.85 (m, 3H, Ar−H), 7.73 (d, J = 7.8 Hz, 1H, Ar−H), 7.59 (d, J = 8.2 Hz, 1H, Ar−H), 7.39−7.34 (m, 1H, Ar−H), 7.30 (ddd, J = 8.1, 6.9, and 1.2 Hz, 1H, Ar−H), 7.27−7.23 (m, 1H, Ar−H), 7.15 (s, 1H, Ar−H), 7.12−7.02 (m, 2H, Ar−H), 6.93 (t, J = 8.7 Hz, 2H, Ar−H), 5.25 (s, 1H, CH), 2.91 (dt, J = 13.8 and 6.9 Hz, 1H, Ar−C*H*$(CH_3)_2$), 1.23 (t, J = 7.3 Hz, 6H, Ar−CH$(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (J = 243 Hz), 149.2, 148.2, 142.1, 139.4, 138.7, 137.5 (J_{C-F} = 3 Hz), 133.3, 130.3, 129.6, 129.5, 129.0, 128.9, 126.3, 125.4, 125.0, 124.3, 123.0, 119.5, 118.5, 115.8, 115.6, 53.2, 34.3, 24.3, 23.9 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{26}H_{21}FNa$ 375.1519, found 375.1547.

2,9-Dimethyl-11-phenyl-11H-benzo[a]fluorene (6z). GP-3 was carried out with 3-(4-methyl-2-(phenylethynyl)phenyl)-1-(*p*-tolyl)-propan-1-one **5z** (67.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6z** (56.4 mg, 79%) as a pale yellow solid. mp = 212−216 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5z**) = 0.50, R_f (**6z**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3018, 2917, 2853, 1625, 1482, 1451, 847, 821 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H, Ar−H), 7.77 (d, J = 8.3 Hz, 1H, Ar−H), 7.69 (d, J = 7.7 Hz, 1H, Ar−H), 7.39 (s, 1H, Ar−H), 7.24−7.15 (m, 5H, Ar−H), 7.13−7.07 (m, 3H, Ar−H), 5.30 (d, 1H, CH), 2.38 (s, 3H, $ArCH_3$), 2.37 (s, 3H, Ar−CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 141.9, 141.6, 139.4, 138.4, 136.7, 135.9, 131.5, 130.6, 128.8 (2 × Ar−CH), 128.7, 128.5, 128.0 (2 × Ar−CH), 127.9, 127.3, 126.6, 125.6, 123.5, 119.3, 117.5, 53.8, 21.9, 21.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{21}$ 321.1638, found 321.1623.

2-Methoxy-9-methyl-11-phenyl-11H-benzo[a]fluorene (6aa). GP-3 was carried out with 3-(4-methoxy-2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5aa** (70.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6aa** (48.4 mg, 72%) as a pale yellow semisolid. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5aa**) = 0.50, R_f (**6aa**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2939, 1622, 1482, 1463, 1224, 1036, 843, 824 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 1H, Ar−H), 7.77−7.74 (m, 2H, Ar−H), 7.70 (d, J = 7.7 Hz, 1H, Ar−H), 7.28−7.16 (m, 4H, Ar−H), 7.12 (t, J = 4.1 Hz, 3H, Ar−H), 7.00 (dd, J = 8.9 and 2.5 Hz, 1H, Ar−H), 6.87 (d, J = 2.5 Hz, 1H, Ar−H), 5.20 (d, 1H, CH), 3.58 (s, 3H, $ArOCH_3$), 2.34 (s, 3H, Ar−CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 149.4, 141.8, 141.3, 139.7, 138.6, 136.9, 131.4, 130.3, 128.8 (2 × Ar−CH), 128.6, 128.4, 128.2 (2 × Ar−CH), 128.0, 126.7, 125.6, 119.4, 117.6, 116.1, 102.7, 54.9, 54.0, 21.6 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{21}O$ 337.1587, found 337.1570.

9-Ethyl-2-methoxy-11-phenyl-11H-benzo[a]fluorene (6ab). GP-3 was carried out with 1-(4-ethylphenyl)-3-(4-methoxy-2-(phenylethynyl)phenyl)propan-1-one **5ab** (73.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **6ab** (49.0 mg, 70%) as a pale yellow solid. mp = 142−148 °C. [TLC (petroleum ether/ethyl acetate 97:3, R_f (**5ab**) = 0.50, R_f (**6ab**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2963, 1892, 1626, 1462, 1365, 1268, 1136, 1034, 836 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84−7.77 (m, 2H, Ar−H), 7.74 (t, J = 8.7 Hz, 2H, Ar−H), 7.28−7.16 (m, 4H, Ar−H), 7.15−7.13 (m, 3H, Ar−H), 7.00 (dd, J = 8.9 and 2.5 Hz, 1H, Ar−H), 6.87 (d, J = 2.5 Hz, 1H, Ar−H), 5.20 (s, 1H, CH), 3.58 (s, 3H, $ArOCH_3$), 2.64 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.22 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 149.6, 143.6, 142.0, 141.6, 139.9, 139.1, 131.6, 130.5, 129.0 (2 × Ar−CH), 128.8, 128.6, 128.5 (2 × Ar−CH), 127.0, 126.8, 124.7, 119.7, 117.8, 116.3, 102.9, 55.1, 54.3, 29.2, 16.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{26}H_{23}O$ 351.1743, found 351.1740.

9-Isopropyl-2-methoxy-11-phenyl-11H-benzo[a]fluorene (6ac). GP-3 was carried out with 1-(4-isopropylphenyl)-3-(4-methoxy-2-(phenylethynyl)phenyl)propan-1-one **5ac** (76.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6ac** (53.9 mg, 74%) as a pale yellow semisolid. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5ac**) = 0.50, R_f (**6ac**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2958, 2867, 1642, 1519, 1463, 1224, 1034, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88−7.81 (m, 2H, Ar−H), 7.81−7.75 (m, 2H, Ar−H), 7.30−7.25 (m, 3H, Ar−H), 7.25−7.19 (m, 2H, Ar−H), 7.19−7.15 (m, 2H, Ar−H), 7.03 (dd, J = 8.9 and 2.5 Hz, 1H, Ar−H), 6.91 (d, J = 2.5 Hz, 1H, Ar−H), 5.24 (s, 1H, CH), 3.61 (s, 3H, OCH_3), 2.97−2.90 (m, 1H, Ar−C*H*$(CH_3)_2$), 1.26 (t, J = 7.3 Hz, 6H, Ar−CH$(CH_3)_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 149.4, 148.1, 141.9, 141.5, 139.7, 139.1, 131.5, 130.4, 128.8 (2 × Ar−CH), 128.7, 128.4 (2 × Ar−CH), 128.4, 126.7, 125.3, 123.2, 119.5, 117.6, 116.2, 102.8, 54.9, 54.2, 34.3, 24.4, 23.9 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{25}O$ 365.1900, found 365.1888.

2,4-Difluoro-11-phenyl-11H-benzo[a]fluorene (6ar). GP-3 was carried out with 3-(2,4-difluoro-6-(phenylethynyl)phenyl)-1-phenylpropan-1-one **5ar** (69.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (56.8 mg [50% assay], 1 equiv) in dry DCE (2 mL) at 60 °C for 6 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 100:0 to 99:01) furnished the product **6ar** (59.8 mg, 84%) as a pale yellow semisolid. mp = 167−170 °C. [TLC (petroleum ether/ethyl acetate 99:1, R_f (**5ar**) = 0.50, R_f (**6ar**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2917, 1625, 1482, 1383, 841 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 1H, Ar−H), 7.98 (d, J = 8.6 Hz, 1H, Ar−H), 7.86 (d, J = 7.6 Hz, 1H, Ar−H), 7.44−7.35 (m, 1H, Ar−H), 7.34 (dd, J = 7.0 and 0.6 Hz, 1H, Ar−H), 7.31−7.21 (m, 4H, Ar−H), 7.11−7.03 (m, 3H, Ar−H), 6.93−6.81 (m, 1H, Ar−H), 5.26 (s, 1H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (dd, J_{C-F} = 248 and 7 Hz, Ar−C), 160.0 (dd, J_{C-F} = 235 and 7 Hz, Ar−C), 149.1, 141.9 (dd, J_{C-F} = 6 and 3 Hz, Ar−C), 141.5, 140.6, 140.2, 131.5 (dd, J_{C-F} = 11 and 6 Hz, Ar−C), 129.1 (2 × Ar−CH), 127.9 (2 × Ar−CH), 127.8, 127.4, 127.1, 125.0, 121.5 (dd, J_{C-F} = 5 and 2 Hz, Ar−CH), 120.6 (dd, J_{C-F} = 15 and 1 Hz, Ar−C), 120.1 (2 × Ar−CH), 118.7 (t, J_{C-F} = 2 Hz, ArCH), 104.1 (dd, J_{C-F} = 23 and 4 Hz, ArCH), 101.7 (dd, J_{C-F} = 29 and 24 Hz, ArCH), 54.2 ppm.

General Procedure 4 (GP-4) for the Synthesis of Indenes (7ad−7aq). To the solution of alkynones **5ad−5aq** (60.8−85.2 mg, 0.2 mmol) in a Schlenk tube in dry DCE (1 mL) was added $BF_3{\cdot}OEt_2$ (148 mg, 2.5 equiv), and the reaction mixture was stirred at room temperature for 2 h. Progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate: 98:02 to 90:10). The reaction mixture was then quenched with aqueous ammonium chloride and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine, dried over (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude residue by column chromatography on silica gel (100−200 mesh) by using hexane/ethyl acetate solvent system as eluent afforded the cyclized product **7ad−7aq** (78−92%) as a viscous liquid/semisolid/solid.

(3-Benzyl-5,6-dimethoxy-1H-inden-2-yl)(p-tolyl)methanone (7ad). GP-4 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5ad** (76.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 90:10) furnished the product **7ad** (64.5 mg, 84%) as a yellow

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oil. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**5ad**) = 0.70, R_f (**7ad**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2938, 2838, 1613, 1355, 1237, 849, 833 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.64 (m, 2H, Ar−H), 7.24−7.19 (m, 4H, Ar−H), 7.19−7.11 (m, 3H, Ar−H), 7.05 (s, 1H, Ar−H), 6.78 (s, 1H, Ar−H), 4.06 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.85 (s, 2H, CH_2), 3.74 (s, 3H, OCH_3), 2.41 (s, 3H, Ar−CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 194.6, 149.9, 149.5, 148.5, 142.7, 139.0, 138.7, 137.5, 137.2, 137.1, 128.9 (2 × Ar−CH), 128.9 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.4 (2 × Ar−CH), 126.2, 107.1, 105.2, 56.1, 55.9, 40.6, 33.4, 21.6 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{26}H_{24}O_3Na$ 407.1618, found 407.1624.

(3-Benzyl-5,6-dimethoxy-1H-inden-2-yl)(4-ethylphenyl)-methanone (7ae). GP-4 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1-(4-ethylphenyl)propan-1-one **5ae** (79.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 90:10) furnished the product **7ae** (70.1 mg, 88%) as brown oil. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**5ae**) = 0.50, R_f (**7ae**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2933, 1708, 1607, 1495, 1247, 1008, 844 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.67 (m, 2H, Ar−H), 7.25−7.19 (m, 4H, Ar−H), 7.19−7.11 (m, 3H, Ar−H), 7.05 (s, 1H, Ar−H), 6.79 (s, 1H, Ar−H), 4.06 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.85 (s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 2.70 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.26 (t, J = 7.6 Hz, 3H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 194.6, 149.9, 149.5, 148.9, 148.4, 139.0, 138.8, 137.7, 137.2, 137.1, 129.0 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.4 (2 × Ar−CH), 127.8 (2 × Ar−CH), 126.2, 107.1, 105.1, 56.1, 55.9, 40.6, 33.4, 28.9, 15.3 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{27}H_{26}NaO_3$ 421.1774, found 421.1752.

(3-Benzyl-5,6-dimethoxy-1H-inden-2-yl)(4-isopropylphenyl)-methanone (7af). GP-4 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1-(4-isopropylphenyl)propan-1-one **5af** (82.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 90:10) furnished the product **7af** (73.2 mg, 89%) as a white solid: mp = 176−180 °C. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**5af**) = 0.70, R_f (**7af**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2959, 2832, 1604, 1562, 1493, 1358, 1211, 1064, 847 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.66 (m, 2H, Ar−H), 7.27−7.23 (m, 2H, Ar−H), 7.23−7.18 (m, 2H, Ar−H), 7.18−7.13 (m, 3H, Ar−H), 7.05 (s, 1H, Ar−H), 6.80 (s, 1H, Ar−H), 4.07 (s, 2H, CH_2), 3.92 (s, 3H, OCH_3), 3.86 (s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 2.96 (sept, J = 6.9 Hz, 2H, $CH(CH_3)_2$), 1.27 (d, J = 6.9 Hz, 6H, 2 × CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 194.6, 153.4, 149.9, 149.6, 148.5, 139.0, 138.8, 137.9, 137.2, 137.1, 129.0 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.4 (2 × Ar−CH), 126.4 (2 × Ar−CH), 126.2, 107.1, 105.1, 56.1, 55.9, 40.6, 34.2, 33.4, 23.7 (2 × CH_3) ppm. HRMS (ESI) m/z $[(M + K)]^+$ calcd for $C_{28}H_{28}O_3K$ 451.1670, found 451.1681.

(3-Benzyl-5,6-dimethoxy-1H-inden-2-yl)(thiophen-2-yl)-methanone (7ag). GP-4 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1-(thiophen-2-yl)propan-1-one **5ag** (75.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 90:10) furnished the product **7ag** (54.9 mg, 73%) as a yellow solid: mp = 108−110 °C. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**5ag**) = 0.70, R_f (**7ag**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 1592, 1537, 1441, 1592, 1247, 1064, 1006, 856, 711 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.63 (dd, J = 4.9 and 0.9 Hz, 1H, Ar−H), 7.30−7.20 (m, 4H, Ar−H), 7.17 (d, J = 7.1 Hz, 1H, Ar−H), 7.12−7.10 (m, 1H, Ar−H), 7.06 (s, 1H, Ar−H), 6.86 (s, 1H, Ar−H), 4.35 (s, 2H, CH_2), 3.99 (s, 2H, CH_2), 3.92 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 184.4, 152.4, 149.9, 148.6, 146.0, 138.8, 137.1, 136.9, 133.0, 132.2, 128.6 (2 × Ar−CH), 128.4 (2 × Ar−CH), 127.8, 126.2, 107.0, 105.1, 56.1, 55.9, 40.5, 33.4 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{23}H_{21}O_3S$ 377.1206, found 377.1212.

(5,6-Dimethoxy-3-(4-methylbenzyl)-1H-inden-2-yl)(thiophen-2-yl)methanone (7ah). GP-4 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1-(thiophen-2-yl)propan-1-one **5ah** (78.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 90:10) furnished the product **7ah** (63.2 mg, 81%) as a yellow oil. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**5ah**) = 0.70, R_f (**7ah**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2930, 1602, 1526, 1359, 1242, 1006, 855 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 3.8 and 1.1 Hz, 1H, Ar−H), 7.63 (dd, J = 5.0 and 1.1 Hz, 1H, Ar−H), 7.20−7.15 (m, 2H, Ar−H), 7.11 (dd, J = 4.9 and 3.8 Hz, 1H, Ar−H), 7.08−7.00 (m, 3H, Ar−H), 6.88 (s, 1H, Ar−H), 4.30 (s, 2H, CH_2), 3.98 (s, 2H, CH_2), 3.92 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 2.27 (s, 3H, Ar−CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 184.4, 152.6, 149.9, 148.6, 146.1, 137.1, 137.0, 136.8, 135.7, 135.6, 132.9, 132.2, 129.1 (2 × Ar−CH), 128.5 (2 × Ar−CH), 127.8, 107.0, 105.1, 56.1, 56.0, 40.5, 33.0, 21.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{23}O_3S$ 391.1362, found 391.1363.

(3-(4-Butylbenzyl)-5,6-dimethoxy-1H-inden-2-yl)(4-isopropylphenyl)methanone (7ai). GP-4 was carried out with 3-(2-((4-butylphenyl)ethynyl)-4,5-dimethoxyphenyl)-1-(4-isopropylphenyl)propan-1-one **5ai** (93.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 90:10) furnished the product **7ai** (80.1 mg, 85%) as a yellow solid. mp = 85−89 °C. [TLC (petroleum ether/ethyl acetate 90:10, R_f (**5ai**) = 0.70, R_f (**7ai**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2961, 1716, 1604, 1541, 1464, 1354, 1248 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.66 (m, 2H, Ar−H), 7.25 (dd, J = 5.8 and 4.1 Hz, 2H, Ar−H), 7.10−7.05 (m, 5H, Ar−H), 6.81 (s, 1H, Ar−H), 4.02 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.85 (s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 2.95 (sept, J = 6.9 Hz, 2H, $CH(CH_3)_2$), 2.58−2.48 (m, 2H, CH_2), 1.59−1.47 (m, 2H, CH_2), 1.34−1.27 (m, 2H, CH_2), 1.27 (d, J = 6.9 Hz, 6H, 2 × CH_3), 0.89 (t, J = 7.3 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 194.7, 153.4, 150.2, 149.5, 148.4, 140.7, 138.9, 137.9, 137.2, 137.2, 135.9, 129.0 (2 × Ar−CH), 128.4 (2 × Ar−CH), 128.4 (2 × Ar−CH), 126.4 (2 × Ar−CH), 107.1, 105.2, 56.1, 55.9, 40.6, 35.1, 34.2, 33.6, 33.1, 23.7 (2 × CH_3), 22.2, 13.9 ppm. HRMS (ESI) m/z $[(M + K)]^+$ calcd for $C_{32}H_{36}O_3K$ 507.2296, found 507.2316.

(3-Benzyl-6-methoxy-1H-inden-2-yl)(phenyl)methanone (7ak). GP-4 was carried out with 3-(5-methoxy-2-(phenylethynyl)phenyl)-1-phenylpropan-1-one **5ak** (68.0 mg, 0.3 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 93:07 to 90:05) furnished the product **7ak** (55.1 mg, 81%) as a yellow solid. mp = 108−110 °C. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**5ak**) = 0.70, R_f (**7ak**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3451, 2934, 1611, 1448, 1291, 1243, 1184, 1025 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76−7.70 (m, 2H, Ar−H), 7.53−7.47 (m, 1H, Ar−H), 7.43−7.35 (m, 2H, Ar−H), 7.28−7.22 (m, 1H, Ar−H), 7.22−7.16 (m, 2H, Ar−H), 7.16−7.11 (m, 3H, Ar−H), 7.05 (d, J = 2,2 Hz, 1H, Ar−H), 6.82 (dd, J = 8.5 and 2.4 Hz, 1H, Ar−H), 4.04 (s, 2H, CH_2), 3.87 (s, 2H, CH_2), 3.81 (s, 3H, OCH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 195.1, 160.1, 150.5, 148.2, 140.4, 138.7, 138.1, 137.6, 131.9, 128.6 (2 × CH), 128.5 (2 × Ar−CH), 128.5 (2 × Ar−CH), 128.4 (2 × CH), 126.2, 123.3, 113.2, 109.7, 55.6, 40.7, 33.2 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{21}O_2$ 341.1536, found 341.1538.

(3-Hexyl-1H-inden-2-yl)(phenyl)methanone (7al). GP-3 was carried out with 3-(2-(hept-1-yn-1-yl)phenyl)-1-phenylpropan-1-one **5al** (60.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the

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crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the product **7al** (51.7 mg, 85%) as a yellow oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**5al**) = 0.70, R_f (**7al**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2928, 2857, 2200, 1686, 1448, 1204 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.73 (m, 2H, Ar−H), 7.59−7.50 (m, 3H, Ar−H), 7.46 (ddd, J = 6.6, 4.4, and 1.1 Hz, 2H, Ar−H), 7.42−7.33 (m, 2H, Ar−H), 3.83 (s, 2H, CH_2), 2.67−2.53 (m, 2H, CH_2), 1.59−1.47 (m, 2H, CH_2), 1.30−1.07 (m, 6H, 3 × CH_2), 0.83 (t, J = 7.0 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 195.9, 152.6, 144.6, 143.9, 140.1, 138.5, 132.0, 128.6 (2 × Ar−CH), 128.3 (2 × Ar−CH), 127.3, 126.7, 124.1, 121.5, 40.5, 31.4, 29.4, 29.1, 27.1, 22.5, 14.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{22}H_{25}O$ 305.1900, found 305.1886.

Phenyl(3-undecyl-1H-inden-2-yl)methanone (7am). GP-3 was carried out with 3-(2-(dodec-1-yn-1-yl)phenyl)-1-phenylpropan-1-one **5am** (74.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the product **7am** (70.5 mg, 90%) as a yellow oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**5am**) = 0.70, R_f (**7am**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3062, 2924, 2856, 1640, 1590, 1462, 1253, 723, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.74 (m, 2H, Ar−H), 7.59−7.51 (m, 3H, Ar−H), 7.48−7.44 (m, 2H, Ar−H), 7.43−7.33 (m, 2H, Ar−H), 3.83 (s, 2H, CH_2), 2.67−2.57 (m, 2H, CH_2), 1.60−1.49 (m, 2H, CH_2), 1.29−1.15 (m, 16H, 8 × CH_2), 0.87 (t, J = 7.0 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 195.9, 152.6, 144.6, 143.9, 140.1, 138.5, 132.0, 128.6 (2 × Ar−CH), 128.3 (2 × Ar−CH), 127.3, 126.7, 124.1, 121.5, 40.5, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 29.2, 29.2, 27.1, 22.7, 14.1 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{35}O$ 375.2682, found 375.2686.

(3-Heptyl-5-methyl-1H-inden-2-yl)(p-tolyl)methanone (7an). GP-3 was carried out with 3-(4-methyl-2-(oct-1-yn-1-yl)phenyl)-1-(*p*-tolyl)propan-1-one **5an** (69.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the product **7an** (62.2 mg, 90%) as a yellow oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**5an**) = 0.70, R_f (**7an**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2925, 2855, 2094, 1635, 1410, 1262, 1177 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71−7.65 (m, 2H, Ar−H), 7.39 (d, J = 7.6 Hz, 1H, Ar−H), 7.32 (d, J = 0.6 Hz, 1H, Ar−H), 7.28−7.23 (m, 2H, Ar−H), 7.19−7.13 (m, 1H, Ar−H), 3.76 (s, 2H, CH_2), 2.64−2.54 (m, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 1.56−1.51 (m, 2H, CH_2), 1.31−1.14 (m, 8H, 4 × CH_2), 0.85 (t, J = 7.0 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 195.8, 151.7, 144.9, 142.8, 140.9, 139.1, 137.3, 136.3, 129.0, 128.9 (2 × Ar−CH), 128.1 (2 × Ar−CH), 123.8, 121.9, 40.2, 31.7, 29.7, 29.1, 28.9, 27.1, 22.6, 21.6, 21.6, 14.1 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{25}H_{31}O$ 347.2369, found 347.2383.

(3-Heptyl-1H-inden-2-yl)(4-methoxyphenyl)methanone (7ao). GP-4 was carried out with 1-(4-methoxyphenyl)-3-(2-(oct-1-yn-1-yl)phenyl)propan-1-one **5ao** (69.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 99:01 to 98:02) furnished the product **7ao** (62.0 mg, 89%) as a yellow oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**5ao**) = 0.70, R_f (**7ao**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2921, 2850, 1599, 1508, 1457, 1419, 1308, 1168, 1029 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83−7.76 (m, 2H, Ar−H), 7.54−7.40 (m, 2H, Ar−H), 7.40−7.32 (m, 2H, Ar−H), 6.98−6.93 (m, 2H, Ar−H), 3.88 (s, 3H, OCH_3), 3.82 (s, 2H, CH_2), 2.63−2.54 (m, 2H, CH_2), 1.57−1.52 (m, 2H, CH_2), 1.29−1.11 (m, 8H, 2 × CH_2), 0.84 (t, J = 7.0 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 194.9, 163.1, 150.2, 144.7, 143.7, 139.1, 132.3, 131.3 (2 × CH), 126.9, 126.6, 124.1, 121.3, 113.6 (2 × CH), 55.5, 40.7, 31.7, 29.7, 29.1, 28.9, 27.1, 22.6, 14.1 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{29}O_2$ 349.2162, found 349.2164.

(3-Heptyl-6-methoxy-1H-inden-2-yl)(phenyl)methanone (7ap). GP-4 was carried out with 1-(4-methoxyphenyl)-3-(2-(oct-1-yn-1-yl)phenyl)propan-1-one **5ap** (69.7 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **7ap** (64.0 mg, 92%) as a yellow oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**5ap**) = 0.70, R_f (**7ap**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2929, 2853, 1626, 1561, 1362, 1290, 1240, 1106 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74−7.68 (m, 2H, Ar−H), 7.57−7.50 (m, 1H, Ar−H), 7.48−7.41 (m, 3H, Ar−H), 7.07 (d, J = 2.2 Hz, 1H, Ar−H), 6.94 (dd, J = 8.4 and 2.4 Hz, 1H, Ar−H), 3.87 (s, 3H, OCH_3), 3.80 (s, 2H, CH_2), 2.63−2.54 (m, 2H, CH_2), 1.26−1.17 (m, 8H, 4 × CH_2), 0.85 (t, J = 7.0 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 195.3, 160.1, 153.9, 146.3, 140.7, 137.7, 136.4, 131.6, 128.4, 128.2, 122.5, 113.2, 109.6, 55.5, 40.3, 31.7, 29.7, 29.3, 28.9, 27.3, 22.6, 14.1 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{24}H_{28}NaO_2$ 371.1982, found 371.1987.

(6-Fluoro-3-hexyl-1H-inden-2-yl)(phenyl)methanone (7aq). GP-4 was carried out with 3-(5-fluoro-2-(hept-1-yn-1-yl)phenyl)-1-phenylpropan-1-one **5aq** (64.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 98:02 to 97:03) furnished the product **7aq** (53.4 mg, 83%) as a yellow oil. [TLC (petroleum ether/ethyl acetate 98:02, R_f (**5aq**) = 0.70, R_f (**7aq**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2965, 2931, 1626, 1606, 1510, 1450, 1416 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79−7.73 (m, 2H, Ar−H), 7.60−7.54 (m, 1H, Ar−H), 7.51−7.44 (m, 2H, Ar−H), 7.44−7.39 (m, 1H, ArH), 7.18 (dd, J = 9.0 and 2.4 Hz, 1H, Ar−H), 7.05 (ddd, J = 9.3, 8.3, and 2.4 Hz, 1H, ArH), 3.78 (s, 2H, CH_2), 2.59−2.52 (m, 2H, CH_2), 1.55−1.49 (m, 2H, CH_2), 1.29−1.14 (m, 6H, 3 × CH_2), 0.82 (t, J = 7.0 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ 195.8, 162.6 (d, J_{C-F} = 240 Hz, ArC), 151.9, 146.7 (d, J_{C-F} = 12 Hz, ArC), 140.7, 139.8, 139.2 (d, J_{C-F} = 2 Hz, ArC), 132.4, 128.8 (2 × ArCH), 128.6 (2 × ArCH), 125.2 (d, J_{C-F} = 9 Hz, ArCH), 114.3 (d, J_{C-F} = 23 Hz, ArCH), 108.4 (d, J_{C-F} = 23 Hz, ArCH), 40.1, 31.5, 29.5, 29.1, 27.2, 22.6, 14.8 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{22}H_{24}FO$ 323.1806, found 323.1794.

General Procedure 5 (GP-5) for the Synthesis of 11-Phenylbenzo[*b*]fluorene/2-(11*H*-benzo[*b*]fluoren-10-yl)thiophene (8ad−8ak). To the solution of alkynones **5ad**−**5ak** (76.8−86.0 mg, 0.2 mmol) in a Schlenk tube in dry DCE (1 mL) was added $BF_3{\cdot}OEt_2$ (148 mg, 2.5 equiv), and the reaction mixture was stirred at 100 °C for 24 h in an oil bath. Progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate: 97:03 to 93:07). The reaction mixture was then quenched with aqueous ammonium chloride and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine, dried over (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude residue by column chromatography on silica gel (100−200 mesh) by using hexane/ethyl acetate solvent system as eluent afforded the cyclized product **8ad**−**8ak** (81−93%) as a viscous liquid/semisolid/solid.

2,3-Dimethoxy-10-(p-tolyl)-11H-benzo[b]fluorene (8ad). GP-5 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)phenyl)-1-(*p*-tolyl)propan-1-one **5ad** (76.8 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **8ad** (65.9 mg, 90%) as a brown solid. mp = 215−218 °C. [TLC (petroleum ether/ethyl acetate 95:05, R_f (**5ad**) = 0.30, R_f (**8ad**) = 0.60, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2933, 1608, 1506, 1384, 1273, 1217, 1100, 815 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H, Ar−H), 7.99−7.88 (m, 1H, Ar−H), 7.66 (d, J = 8.6 Hz, 1H, Ar−H), 7.49−7.46 (m, 1H, Ar−H), 7.45 (s, 1H, Ar−H), 7.39−7.31 (m, 5H, Ar−H), 6.99 (s, 1H, ArH),

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4.04 (s, 3H, $ArOCH_3$), 3.92 (s, 3H, $ArOCH_3$), 3.76 (s, 2H, CH_2), 2.50 (s, 3H, $ArCH_3$) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 148.8, 140.2, 140.1, 136.9, 136.6, 136.0, 135.5, 133.6, 131.3, 129.7 (2 × Ar−CH), 129.2 (2 × Ar−CH), 128.0, 125.9, 125.2, 124.8, 115.8, 107.9, 103.3, 56.1, 56.0, 36.4, 21.3 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{26}H_{23}O_2$ 367.1693, found 367.1672.

10-(4-Ethylphenyl)-2,3-dimethoxy-11H-benzo[b]fluorene (8ae). GP-5 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)-phenyl)-1-(4-ethylphenyl)propan-1-one **5ae** (79.6 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **8ae** (65.4 mg, 86%) as a yellow solid. mp = 170−172 °C. [TLC (petroleum ether/ethyl acetate 95:5, R_f (**5ae**) = 0.30, R_f (**8ae**) = 0.60, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2933, 1608, 1506, 1272, 1217, 1101, 669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H, Ar−H), 7.95 (d, J = 8.1 Hz, 1H, Ar−H), 7.67 (d, J = 8.5 Hz, 1H, Ar−H), 7.51−7.40 (m, 2H, Ar−H), 7.43−7.30 (m, 5H, Ar−H), 7.00 (s, 1H, ArH), 4.04 (s, 3H, $ArOCH_3$), 3.92 (s, 3H, $ArOCH_3$), 3.77 (s, 2H, CH_2), 2.80 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.37 (t, J = 7.6 Hz, 2H, CH_2CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 148.9, 143.2, 140.2, 140.2, 136.6, 136.2, 135.6, 133.6, 133.6, 131.3, 129.8 (2 × Ar−CH), 128.0, 128.0 (2 × Ar−CH), 126.0, 125.2, 124.8, 115.8, 107.9, 103.3, 56.2, 56.1, 36.4, 28.7, 15.5 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{27}H_{25}O_2$ 381.1849, found 381.1852.

10-(4-Isopropylphenyl)-2,3-dimethoxy-11H-benzo[b]fluorene (8af). GP-5 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)-phenyl)-1-(4-isopropylphenyl)propan-1-one **5af** (82.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **8af** (72.5 mg, 92%) as a brown solid. mp = 188−190 °C. [TLC (petroleum ether/ethyl acetate 95:5, R_f (**5af**) = 0.30, R_f (**8af**) = 0.60, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2947, 1607, 1505, 1462, 1307, 1273, 1217 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H, Ar−H), 7.95 (d, J = 8.1 Hz, 1H, Ar−H), 7.69 (d, J = 8.5 Hz, 1H, Ar−H), 7.49−7.43 (m, 2H, Ar−H), 7.43−7.31 (m, 5H, Ar−H), 7.00 (s, 1H, ArH), 4.04 (s, 3H, $ArOCH_3$), 3.92 (s, 3H, $ArOCH_3$), 3.77 (s, 2H, CH_2), 3.05 (sept, J = 6.9 Hz, 1H, $CH(CH_3)_2$), 1.38 (t, J = 6.9 Hz, 6H, 2 × CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 148.8, 147.7, 140.2, 140.2, 136.7, 136.3, 135.6, 133.6, 133.6, 131.3, 129.7 (2 × Ar−CH), 128.0, 126.5 (2 × Ar−CH), 126.0, 125.2, 124.8, 115.8, 107.9, 103.3, 56.1, 56.0, 36.4, 33.9, 24.1 (2 × CH_3) ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{28}H_{27}O_2$ 395.2006, found 395.2002.

2-(2,3-Dimethoxy-11H-benzo[b]fluoren-10-yl)thiophene (8ag). GP-5 was carried out with 3-(4,5-dimethoxy-2-(phenylethynyl)-phenyl)-1-(thiophen-2-yl)propan-1-one **5ag** (75.2 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **8ag** (57.9 mg, 81%) as a white solid. mp = 200−204 °C. [TLC (petroleum ether/ethyl acetate 95:5, R_f (**5ag**) = 0.70, R_f (**8ag**) = 0.65, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 1607, 1506, 1384, 1270, 1219, 1102, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H, Ar−H), 7.96−7.91 (m, 1H, Ar−H), 7.87 (d, J = 8.4 Hz, 1H, Ar−H), 7.52 (dd, J = 5.2 and 1.1 Hz, 1H, Ar−H), 7.48−7.45 (m, 1H, ArH), 7.43−7.40 (m, 1H, Ar−H), 7.39 (t, J = 1.5 Hz, 1H, Ar−H), 7.26−7.23 (m, 1H, Ar−H), 7.16 (dd, J = 3.4 and 1.1 Hz, 1H, Ar−H), 7.01 (s, 1H, Ar−H), 4.03 (s, 3H, $ArOCH_3$), 3.92 (s, 3H, $ArOCH_3$), 3.88 (s, 2H, CH_2) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.6, 148.7, 142.4, 140.2, 139.1, 136.3, 133.5, 133.3, 132.0, 128.0, 127.9, 127.8, 127.2, 125.9, 125.7, 125.5, 125.3, 116.9, 107.9, 103.3, 56.1, 56.0, 36.8 ppm. HRMS (ESI) m/z $[(M + H)]$ calcd for $C_{23}H_{10}O_2S$ 359.1100, found 359.1100.

2-(2,3-Dimethoxy-8-methyl-11H-benzo[b]fluoren-10-yl)-thiophene (8ah). GP-5 was carried out with 3-(4,5-dimethoxy-2-(*p*-tolylethynyl)phenyl)-1-(thiophen-2-yl)propan-1-one **5ah** (78.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **8ah** (62.4 mg, 84%) as a brown solid. mp = 162−164 °C. [TLC (petroleum ether/ethyl acetate 95:5, R_f (**5ah**) = 0.50, R_f (**8ah**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 1612, 1510, 1465, 1270, 1105, 836, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H, Ar−H), 7.83 (d, J = 8.3 Hz, 1H, Ar−H), 7.61 (s, 1H, Ar−H), 7.52 (dd, J = 5.2 and 1.2 Hz, 1H, Ar−H), 7.40 (s, 1H, ArH), 7.30 (dd, J = 8.3 and 1.6 Hz, 1H, Ar−H), 7.24 (dd, J = 3.4 and 1.7 Hz, 1H, Ar−H), 7.13 (dd, J = 3.4 and 1.1 Hz, 1H, Ar−H), 6.99 (s, 1H, Ar−H), 4.01 (s, 3H, $ArOCH_3$), 3.91 (s, 3H, $ArOCH_3$), 3.85 (s, 2H, CH_2), 2.44 (s, 3H, $Ar-CH_3$) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.4, 148.9, 142.5, 139.3 (2 × C), 136.2, 135.0, 133.5, 132.2, 131.7, 127.8, 127.7 (2 × Ar−CH), 127.3, 127.2, 125.8, 124.7, 116.8, 108.0, 103.2, 56.1, 56.0, 36.8, 22.0 ppm. HRMS (ESI) m/z $[(M + H)]^+$ calcd for $C_{24}H_{21}O_2S$ 373.1257, found 373.1270.

8-Butyl-10-(4-isopropylphenyl)-2,3-dimethoxy-11H-benzo[b]-fluorene (8ai). GP-5 was carried out with 3-(2-((4-butylphenyl)-ethynyl)-4,5-dimethoxyphenyl)-1-(4-isopropylphenyl)propan-1-one **5ai** (93.4 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **8ai** (81.0 mg, 90%) as a brown semisolid. [TLC (petroleum ether/ethyl acetate 95:5, R_f (**5ai**) = 0.50, R_f (**8ai**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2945, 1637, 1508, 1270, 1216, 1106 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H, Ar−H), 7.88 (d, J = 8.4 Hz, 1H, Ar−H), 7.47−7.40 (m, 4H, Ar−H), 7.39−7.30 (m, 3H, Ar−H), 6.99 (s, 1H, ArH), 4.04 (s, 3H, $ArOCH_3$), 3.91 (s, 3H, $ArOCH_3$), 3.75 (s, 2H, CH_2), 3.05 (sept, J = 6.9 Hz, 1H, $CH(CH_3)_2$), 2.72−2.61 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 1.40 (t, J = 6.9 Hz, 6H, 2 × CH_3), 1.39−1.33 (m, 2H, CH_2), 0.91 (t, J = 7.3 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.3, 148.8, 147.6, 140.3, 139.5, 139.4, 136.5, 136.5, 135.1, 133.8, 132.0, 131.4, 129.7 (2 × Ar−CH), 127.9, 127.6, 126.5 (2 × Ar−CH), 124.5, 115.7, 107.9, 103.2, 56.1, 56.0, 36.5, 36.0, 33.9, 33.7, 24.1 (2 × CH_3), 22.4, 14.0 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{32}H_{34}NaO_2$ 473.2451, found 473.2462.

2-(8-Butyl-2,3-dimethoxy-11H-benzo[b]fluoren-10-yl)thiophene (8aj). GP-5 was carried out with 3-(2-((4-butylphenyl)ethynyl)-4,5-dimethoxyphenyl)-1-(thiophen-2-yl)propan-1-one **5aj** (86.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05 to 93:07) furnished the product **8aj** (72.8 mg, 88%) as a brown oil. [TLC (petroleum ether/ethyl acetate 95:5, R_f (**5aj**) = 0.50, R_f (**8aj**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 2962, 1610, 1509, 1268, 1100 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H, Ar−H), 7.87 (d, J = 8.3 Hz, 1H, Ar−H), 7.63 (s, 1H, Ar−H), 7.54 (dd, J = 5.1 and 1.2 Hz, 1H, Ar−H), 7.41 (s, 1H, ArH), 7.34 (dd, J = 8.3 and 1.7 Hz, 1H, Ar−H), 7.27 (dd, J = 5.1 and 3.3 Hz, 1H, Ar−H), 7.16 (dd, J = 3.4 and 1.2 Hz, 1H, Ar−H), 7.01 (s, 1H, Ar−H), 4.04 (s, 3H, $ArOCH_3$), 3.93 (s, 3H, $ArOCH_3$), 3.87 (s, 2H, CH_2), 2.73−2.67 (m, 2H, CH_2), 1.65−1.59 (m, 2H, CH_2), 1.36−1.26 (m, 2H, CH_2), 0.92 (t, J = 7.3 Hz, 3H, CH_3) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 149.4, 148.8, 142.4, 140.0, 139.4, 136.1, 133.5, 132.1, 131.9, 127.9, 127.7, 127.4, 127.2, 126.9, 125.8, 124.2, 116.7, 107.9, 103.2, 56.1, 56.0, 36.8, 36.1, 22.7, 22.4, 13.9 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{27}H_{26}NaO_2S$ 437.1532, found 437.1546.

2-Methoxy-10-phenyl-11H-benzo[b]fluorene (8ak). GP-5 was carried out with 3-(5-methoxy-2-(phenylethynyl)phenyl)-1-phenyl-propan-1-one **5ak** (68.0 mg, 0.2 mmol), $BF_3{\cdot}OEt_2$ (148 mg [50% assay], 2.5 equiv) in dry DCE (2 mL) at 100 °C for 24 h in an oil bath. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 97:03 to 95:05) furnished the product **8ak** (58.6 mg, 91%) as a brown solid. mp = 176−178 °C. [TLC (petroleum ether/ethyl acetate 95:5, R_f (**5ak**) = 0.50, R_f (**8ak**) = 0.90, UV detection]. IR (MIR-ATR, 4000−600 cm^{-1}) ν_{max} 3054, 2927, 1483, 1258, 1025, 819, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H, Ar−H), 7.96 (d, J = 8.2 Hz, 1H,

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Ar−H), 7.86 (d, J = 8.3 Hz, 1H, Ar−H), 7.64 (d, J = 8.4 Hz, 1H, Ar−H), 7.59−752 (s, 2H, ArH), 7.50−7.47 (m, 2H, Ar−H), 7.45−7.41 (m, 2H, Ar−H), 7.37−7.32 (m, 1H, Ar−H), 7.02−6.97 (m, 2H, Ar−H), 3.86 (s, 3H, $ArOCH_3$), 3.81 (s, 2H, CH_2) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 159.8, 145.7, 139.7, 139.6, 139.1, 135.6, 134.1, 133.6, 131.2, 129.8 (2 × Ar−CH), 128.1 (2 × Ar−CH), 127.3, 125.8, 125.2, 124.9, 121.4, 116.3, 113.2, 110.4, 55.5, 36.6 ppm. HRMS (ESI) m/z $[(M + Na)]^+$ calcd for $C_{24}H_{18}NaO$ 345.1250, found 345.1254.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c02724.

Copies of ^1H and $^{13}C\{^1H\}$ NMR spectra for all starting materials and final compounds (PDF)

Accession Codes

CCDC 2120374−2120375 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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