A Domino Palladium-Catalysis: Synthesis of 7-Methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-ones

Jonnada Krishna, Alavala Gopi Krishna Reddy and Gedu Satyanarayana*

Indian Institute of Technology (IIT) Hyderabad, Ordnance Factory Estate Campus, Yeddumailaram – 502 205, Medak District, Andhra Pradesh, India.

Fax: +91(40) 2301 6032

E-mail: gvsatya@iith.ac.in

Received: The date will be inserted once the manuscript is accepted.

Abstract: A domino Pd-catalyzed reaction of 1-(2-bromophenyl) ethanones for the synthesis of novel 7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-ones, a carbon core structure present in colchicinoid natural products, is presented. The reaction might proceed via an unprecedented path that benefits the entire process by constructing a C-C σ-bond (intermolecular homo biaryl coupling) and a C=C π-bond (intramolecular Aldol type condensation).

Key words: Pd-catalysis; homo biaryl coupling; domino reaction; Aldol condensation; 2-bromoacetophenones.

The invention of efficient and viable synthetic methods to accomplish complex molecules by employing one-pot processes is significant and an inspiring task in synthetic organic chemistry.[1] In this regard, transition-metal catalysis is considered to be the most powerful technique for constructing inter- and/or intramolecular C-C bonds efficiently. Quite frequently, palladium in particular, has been used as one of the metals to develop such novel inter-conversions.[2,3] Generally, it has been observed that, particularly, in the presence of inherent intramolecular ring constraints, the initially formed Pd-intermediates preferred homo/hetero intermolecular coupling rather than intramolecular one.[4,5] For example, recently, when we subjected α,α-disubstituted-(2-haloaryl)-methanols for Pd(0)-catalysis, the reaction did not proceed via intramolecular coupling to yield the expected 8,8-dialkyl-7-oxabicyclo[4.2.0]octa-1,3,5-trienes rather preferred to furnish 6,6-dialkyl-6*H*-benzo[*c*]chromenes via an efficient homo biaryl coupling.[5h]

In continuation of our research interest on transition metal-catalysis,[6] herein, we present a novel one-pot process based on a hitherto unexplored domino palladium-catalysis of 1-(2-bromophenyl)ethanones **1** for the effective construction of 7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-ones **3**. This process involves an unprecedented mechanistic path, especially to yield **3**, which in turn is identified as a carbon core structure present in biologically active natural products such as colchicinoids (Figure 1).[7] It is worth mentioning that this method delivers these systems via a novel domino C-C σ-bond and C=C π-bond forming process, using simple 1-(2-bromophenyl)ethanones **1**, unlike the usual methods, such as intermolecular Suzuki-Miyaura coupling followed by Aldol condensation,[8] intramolecular Heck reaction,[9] biaryl oxidative coupling[10] and Lewis acid mediated Nicholas cyclization[11] that facilitate the biaryl tricyclic systems in a step-wise manner.

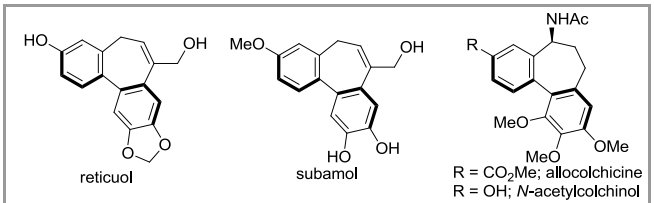
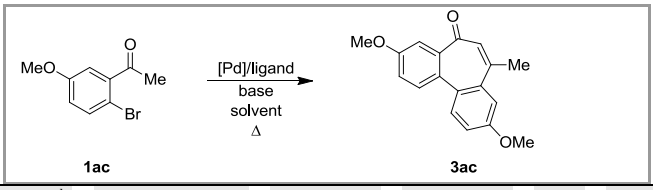


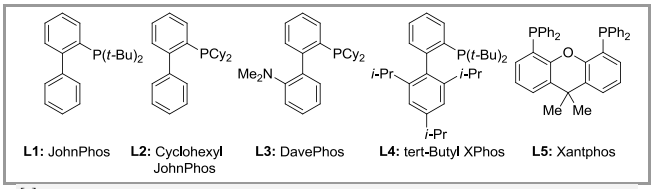
Figure 1 Naturally occuring compounds.

The required 1-(2-bromophenyl)ethanones **1** for this study were prepared from corresponding *ortho*-halobenzaldehydes using alkyl Grignard addition and oxidation protocol (see supporting information). Having obtained the requisite 1-(2-bromophenyl)ethanones **1**, the Pd-mediated transformation of the 1-(2-bromophenyl)ethanone **1ac** was subjected to numerous conditions (for complete details see supporting information). As a result, treatment of **1ac** in the presence of the catalyst $Pd(OAc)_2$ (5 mol%), dppf (10 mol%) and base K_3PO_4 (4 equiv) in hot DMF at 100 °C for 10 h, gave the product **3ac**, in poor yield (26%, Table 1, entry 1). The reaction with the ligand **L1** further decreased the yield (8%, Table 1, entry 2), whereas, ligand **L2** increased it to 25% (Table 1, entry 3). While, with other ligands **L3**, **L4** & PCy_3 and also with the catalyst $Pd(PPh_3)_4$ were not that effective (Table 1, entries 4, 5, 6 and 7). Fascinatingly, use of different catalysts improved the yield (Table 1, entries 8 and 9). Gratifyingly, the reaction in the presence of ligand **L5** improved the **3ac** yield (50% Table 1, entry 10). Unpromisingly, addition of various additives was unsuccessful to improve the yield further (Table 1, entries 11 to 14).

Table 1 Optimization reaction conditions for the synthesis of 3,9-dimethoxy-7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-one **3ac**.



entry[a,b]	[Pd] (mol %)	ligand (mol %)	base (equiv)	time (h)	**3ac** (%)[c]
1	$Pd(OAc)_2$ (5)	dppf (10)	K_3PO_4 (4)	10	26
2	$Pd(OAc)_2$ (2)	**L1** (4)	K_3PO_4 (4)	3	8
3	$Pd(OAc)_2$ (2)	**L2** (4)	K_3PO_4 (4)	3	25
4	$Pd(OAc)_2$ (2)	**L3** (4)	K_3PO_4 (4)	3	15
5	$Pd(OAc)_2$ (2)	**L4** (4)	K_3PO_4 (4)	3	16
6	$Pd(OAc)_2$ (5)	$P(Cy)_3$ (10)	K_3PO_4 (4)	3	16
7	$Pd(PPh_3)_4$ (2)	-	Cs_2CO_3 (4)	34	11
8	$Pd(dppf)Cl_2$ (2)	-	Cs_2CO_3 (2)	18	32
9	$Pd(PPh_3)_2Cl_2$ (2)	-	K_3PO_4 (4)	3	30
10	**$Pd(OAc)_2$ (2)**	**L5 (4)**	**K_3PO_4 (2)**	**2**	**50**
11	$Pd(OAc)_2$ (2)	**L5** (4)	K_3PO_4 (2)	2	45[d]
12	$Pd(OAc)_2$ (2)	**L5** (4)	K_3PO_4 (2)	12	23[e]
13	$Pd(OAc)_2$ (2)	**L5** (4)	K_3PO_4 (2)	2	36[f]
14	$Pd(OAc)_2$ (2)	**L5** (4)	K_3PO_4 (2)	3	25[g]

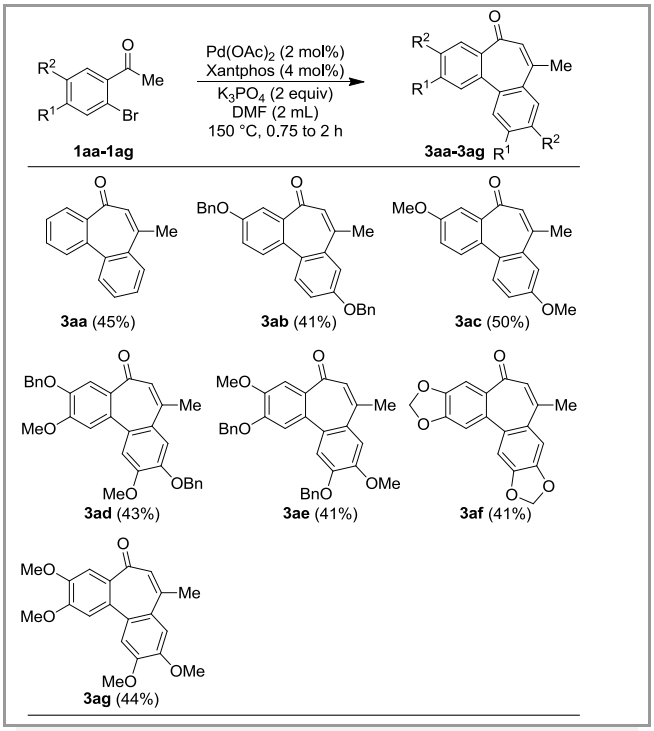


[a] All reactions were performed on 100 mg (0.44 mmol) scale of **1ac**, in 0.22 M concentration, in DMF (2 mL). [b] All reactions were heated at 150 °C except in entries 1 (100 °C) and 7 (120 °C). [c] Isolated yields of chromatographically pure products. [d] 4 Å molecular sieves (100 mg) were used as additive. [e] Water (40 equiv) was used as additive. [f] $ZnCl_2$ (0.2 equiv) was used as additive. [g] *n*-Bu_4NBr (0.2) was used as additive.

Although, the yield of **3ac** is moderate, it is still in an acceptable range because each individual step (i.e. biphenyl coupling and Aldol condensation) accounts for nearly 70% yield. Moreover, it is noteworthy that the present method has its own importance and credentials when compared with previous reports which involved not less than four steps with poor overall yield[12]- for the synthesis of such structurally relevant compounds.

Among all conditions of Table 1, entry 10 was found to be the best to furnish **3**. Thus, to study the scope and limitations of the present method, these optimized conditions were applied to the other systems of 1-(2-bromophenyl)ethanones **1**. Agreeably, the reaction progressed well on the other systems and gave the biaryl cyclic products **3aa-3ag** in comparable yields (Table 2).

Table 2 Scope of one-pot Pd-catalyzed homo biaryl coupling.



Reaction conditions: **1aa-1ag** (100-150mg, 0.30 to 0.58 mmol), 0.15-0.25 M in DMF. Yields in the parentheses are isolated yields of chromatographically pure products.

The chemical structures of **3aa-3ag** have been further unambiguously confirmed by the single crystal X-ray diffraction analysis of **3ag**[13] as shown in Figure 2 (see supporting information).

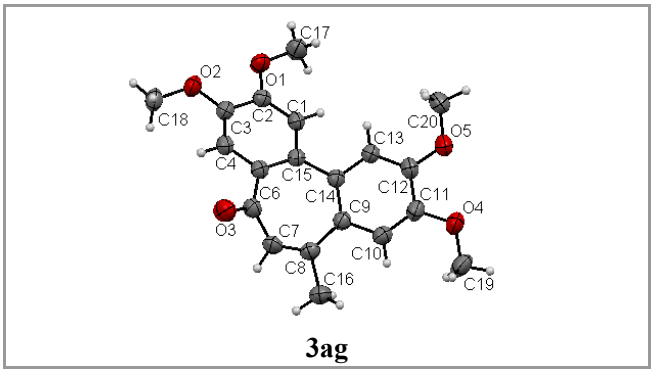
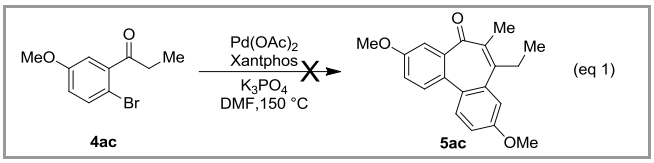
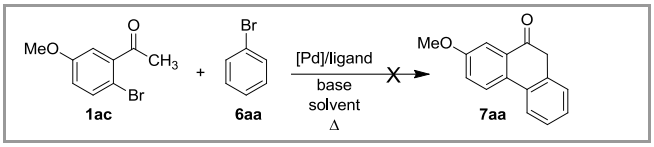


Figure 2 X-ray structures of **3ag.** Thermal ellipsoids are drawn at 50% probability level.

After the accomplishment of **3aa-3ag**, we became interested to look at the scope and constraint of the method by changing the alkyl group of the ketone domain. Unpromisingly, Pd-catalysis of 1-(2-bromophenyl)propan-1-one **5ac** was sluggish (eq 1). This can be reasoned based on the availability of β-hydrogen to initially formed aryl Pd-five membered species, which in turn may collapse quickly by preferring intramolecular *syn*-elimination rather than the intermolecular biaryl coupling.

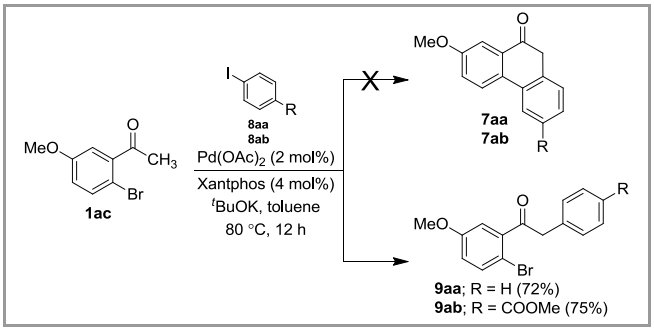


Furthermore, Pd-catalysis of **1ac** with the other halobenzene **6aa** were also explored, in-order to achieve heterobiaryl variant. However, after performing the Pd-catalysis under many different conditions, neither allowed us to recover back the starting material nor gave the expected product **7aa** as depicted in Scheme 1.



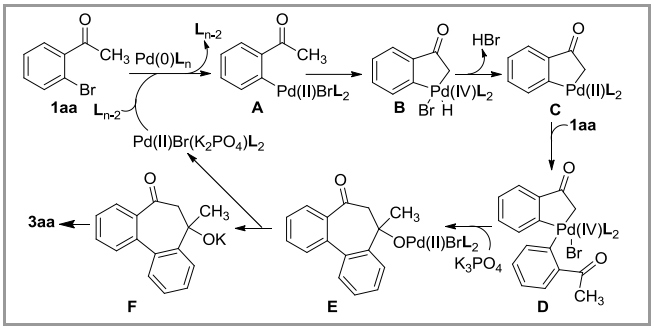
Scheme 1 Attempts for the synthesis of **7aa** via heterobiaryl coupling.

Since, the formation of heterobiaryl system **7aa** was not successful, we turned to our interest to alter the method to generate such biaryls via a preferential α-arylation of 2-bromoacetophenone **1ac** with more reactive iodoarene followed by intramolecular Heck reaction. Nevertheless, the treatment of **1ac** with iodoarenes **8aa** and **8ab** did not furnish the expected product rather gave only α-arylation products **9aa** and **9ab** respectively in a controlled fashion (Scheme 2). This is in parallel way to the already reported α-arylations,[14] of course in the present case the bromine atom comes from 2-bromoacteophenone **1ac**.



Scheme 2 α-Arylation of **1ac** with **8aa** and **8ab**.

The plausible mechanism for the formation of **3aa** is reminiscent to that reported in our earlier work.[5h] The five membered palladacycle **B** could be formed via the insertion of primarily formed aryl-palladium(II) species **A**, into the sp^3 C-H bond of the ketone (Scheme 3). The Pd(IV) intermediate **B** converts to the reactive Pd(II) species **C** through HBr elimination. The key Pd-cyclic species **C** combines with a second molecule **1aa** via C-Br bond insertion and generates Pd(IV) complex **D**.[2b,15] Biaryl coupling leads to the Pd(II) intermediate, which on nucleophilic addition to keto group of second aromatic ring furnishes Pd(II) species **E**. Expulsion of Pd-complex **E**[16] by base yields tertiaryalkoxide **F** and Pd(II)-species. Finally, tertiaryalkoxide **F** transforms into the product **3aa** by elimination and Pd(II) to Pd(0) completes the catalytic cycle (Scheme 3).



Scheme 3 Plausible catalytic cycle for the formation of **3aa**.[a]

In summary, we have developed an unprecedented domino Pd-catalysis for the synthesis of novel 7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-ones,[17] a carbon core structure present in biologically active natural products. The application of this process for the synthesis of various important heterocyclic systems is in progress.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

Financial support by the Council of Scientific and Industrial Research [(CSIR), 02(0018)/11/EMR-II], New Delhi is gratefully acknowledged. J.K., A.G.K., thank CSIR, New Delhi, for the award of research fellowship.

References

(1) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115–136.
(2) For reviews on C–H activations see: (a) Shibasaki, M.; Vogl, E. M.; Ohshima, T. *Adv. Synth. Catal.* **2004**, *346*, 1533–1552. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174–238. (c) Souza, D. M. D'.; Müller, T. J. J. *Chem. Soc. Rev.* **2007**, *36*, 1095–1108. (d) Minatti, A.; Muñiz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142–1152. (e) Catellani, M.; Motti, E.; Della Ca′, N. *Acc. Chem. Res.* **2008**, *41*, 1512–1522. (f) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074–1086. (g) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem.* **2009**, *121*, 5196–5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115. (h) Muñiz, K. *Angew. Chem.* **2009**, *121*, 9576–9588; *Angew. Chem. Int. Ed.* **2009**, *48*, 9412–9423. (i) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712–733. (j) Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824–889. (k) Lyons, T.W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147–1169. (l) Bras, J. L.;

Muzart, J. *Chem. Rev.* **2011**, *111*, 1170–1214. (m) Ackermann, L. *Chem. Rev.* **2011**, *111,* 1315–1345.

(3) For recent Pd-catalyzed domino transformations, see: (a) Thirunavukkarasu, V. S.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem.* **2008**, *120*, 9604–9607; *Angew. Chem. Int. Ed.* **2008**, *47,* 9462–9465. (b) Cvengroš, J.; Schütte, J.; Schlörer, N.; Neudörfl, J.; Schmalz, H.-G. *Angew. Chem.* **2009**, *121*, 6264–6267; *Angew. Chem. Int. Ed.* **2009**, *48*, 6148–6151. (c) Hu, Y.; Yu, C.; Ren, D.; Hu, Q.; Zhang, L.; Cheng, D. *Angew. Chem.* **2009**, *121*, 5556–5559; *Angew. Chem. Int. Ed.* **2009**, *48*, 5448–5451. (d) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796–2797. (e) Tietze, L. F.; Düfert, A.; Lotz, F.; Sölter, L.; Oum, K.; Lenzer, T.; Beck, T.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2009**, *131*, 17879–17884. (f) Tietze, L. F.; Redert, T.; Bell, H. P.; Hellkamp, S.; Levy, L. M. *Chem. Eur. J.* **2008**, *14*, 2527–2535. (g) Tietze, L. F.; Düfert, M. A.; Hungerland, T.; Oum, K.; Lenzer, T. *Chem. Eur. J.* **2011**, *17*, 8452–8461. (h) Satyanarayana, G.; Maichle-Mössmer, C.; Maier, M. E. *Chem. Commun.* **2009**, 1571–1573. (i) Wang, S.; Xie, K.; Tan, Z.; An, X.; Zhou, X.; Guo, C.-C.; Peng, Z. *Chem. Commun.* **2009**, 6469–6471. (j) Li, R.-J.; Pi, S.-F.; Liang, Y.; Wang, Z.-Q.; Song, R.-J.; Chen, G.-X.; Li, J.-H. *Chem. Commun.* **2010**, *46*, 8183–8185. (k) Chen, X.; Wang, H.; Jin, X.; Feng, J.; Wang, Y.; Lu, P. *Chem. Commun.* **2011**, *47,* 2628–2630. (l) Bryan, C. S.; Lautens, M. *Org. Lett.* **2008**, *10*, 4633–4636. (m) Jana, R.; Chatterjee, I.; Samanta, S.; Ray, J. K. *Org. Lett.* **2008**, *10*, 4795–4797. (n) Luo, Y.; Pan, X.; Wu, J. *Org. Lett.* **2011**, *13*, 1150–1153. (o) Motti, E.; Ca', N. D.; Xu, D.; Piersimoni, A.; Bedogni, E.; Zhou, Z.-M.; Catellani, M. *Org. Lett.* **2012**, *14*, 5792–5795. (p) Piou, T.; Neuville, L.; Zhu, J. *Angew. Chem.* **2012**, *124,* 11729–11733; *Angew. Chem. Int. Ed.* **2012**, *51,* 11561–11565. (q) Hashmi, A. S. K.; Ghanbari, M.; Rudolph, M.; Rominger, F. *Chemistry - A European Journal*, **2012**, *18*, 8113–8119. (r) Hashmi, A. S. K.; Lothschütz, C.; Döpp, R.; Ackermann, M.; Becker, J. D. B.; Rudolph, M.; Scholz, C.; Rominger, F. *Adv. Synth. Catal.* **2012**, *354*, 133–137. (s) Hashmi, A. S. K.; Lothschütz, C.; Döpp, R.; Rudolph, M.; Ramamurthi, T. D.; Rominger, F. *Angew. Chem.* **2009**, *121*, 8392–8395; *Angew. Chem. Int. Ed.* **2009**, *48*, 8243–8246.

(4) For a review of palladacyclces, see: Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527–2571.

(5) (a) Gandeepan, P.; Parthasarathy, K.; Cheng, C.-H. *J. Am. Chem. Soc.* **2010**, *132*, 8569–8571. (b) Mousseau, J. J.; Vallée, F.; Lorion, M. M.; Charette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 14412–14414. (c) Zhang, H.-j.; Wei, J.; Zhao, F.; Liang, Y.; Wang, Z.; Xi, Z. *Chem. Commun.* **2011**, *46,* 7439–7441. (d) Furuta, T.; Kitamura, Y.; Hashimoto, A.; Fujii, S.; Tanaka, K.; Kan, T. *Org. Lett.* **2007**, *9*, 183–186. (e) Wang, G.-W.; Yuan, T.-T.; Li, D.-D. *Angew. Chem.* **2011**, *123,* 1416–1419; *Angew. Chem. Int. Ed.* **2011**, *50,* 1380–1383. (f) Satyanarayana, G.; Maier, M. E. *Org. Lett.* **2008**, *10*, 2361–2364. (g) Satyanarayana, G.; Maier, M. E. *Eur. J. Org. Chem.* **2008**, 5543–5552 (h) Mahendar, L.; Krishna, J.; Reddy, A. G. K.; Ramulu, B. V.; Satyanarayana, G. *Org. Lett.* **2012**, *14*, 628–631.

(6) (a) Reddy, A. G. K.; Krishna, J.; Satyanarayana, G. *Synlett* **2011**, 1756–1760. (b) Krishna, J.; Reddy, A. G. K.; Mahendar, L.; Ramulu, B. V. *Synlett* **2012,** *23*, 375–380. (c) Suchand, B.; Krishna, J.; Ramulu, B. V.; Dibyendu, D.; Reddy, A. G. K.; Mahendar, L. *Tetrahedron Lett.* **2012**, *53*, 3861–3864. (d) Reddy, A. G. K.; Satyanarayana, G. *Tetrahedron* **2012**, *68*, 8003–8010. (e) Reddy, A. G. K.; Krishna, J.; Satyanarayana, G. *Tetrahedron Lett.* **2012**, *53*, 5635–5640.

(7) (a) Chia, Y.-C.; Yeh, H.-C.; Yeh, Y.-T.; Chen, C.-Y. *Chem. Nat. Compd.* **2011**, *47*, 220–222. (b) Chen, C.-Y.; Yang, W.-L.; Hsui, Y.-R. *Nat. Prod. Res.* **2010**, *24*, 423–427. (c) Nakagawa-Goto, K.; Jung, M. K.; Hamel, E.; Wu, C.-C.; Bastow, K. F.; Brossi, A.; Ohta, S.; Lee, K.-H.; *Heterocycles* **2005**, *65*, 541–550.

(8) Choi, Y. L.; Yu, C.-M.; Kim, B. T.; Heo, J.-N. *J. Org. Chem.* **2009**, *74*, 3948–3951.

(9) Lablanc, M.; Fagnou, K.; *Org. Lett.* **2005**, *7*, 2849–2852.

(10) Takada, T.; Arisawa, M.; Gyoten, M.; Hamada, R.; Tohma, H.; Kita, Y. *J. Org. Chem.* **1999**, *63*, 7698–7706.

(11) Djurdjevic, S.; Green, R. R. *Org. Lett.* **2007**, *9*, 5505–5508.

(12) (a) Weitzberg, M.; Abu-Shakra, E.; Azeb, A.; Aizenshtat, Z.; Blum, J. *J. Org. Chem.* **1987**, *52*, 529–536. (b) Ghera, E.; Gaoni, Y.; Shoua, S. *J. Am. Chem. Soc.* **1976**, *98*, 3627–3632. (c) Boyé, O.; Brossi, A. *Can. J. Chem.* **1992**, *70*, 1237–1249. (d) Rapoport, H.; Williams, A. R.; Cisney, M. E. *J. Am. Chem. Soc.* **1951**, *73*, 1414–1421. (e) Seganish, W. M.; DeShong, P. *Org. Lett.* **2006**, *8*, 3951–3954. (f) Besong, G.; Billen, D.; Dager, I.; Kocienski, P.; Sliwinski, E.; Tai, L. R.; Boyle, F. T. *Tetrahedron* **2008**, *64*, 4700–4710. (g) Hackelöer, K.; Waldvogel, S. R.; *Tetrahedron Lett.* **2012**, *53*, 1579–1581.

(13) Crystal data for **3ag**: CCDC 910650.

(14) (a) Willis, M. C.; Taylor, D.; Gillmore, A. T. *Org. Lett.* **2004**, *6*, 4755–4757. (b) Carril, M.; SanMartin, R.; Domínguez, E.; Tellitu, I. *Tetrahedron,* **2007**, *63*, 690–702 (c) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108–11109. (d) Ahman, J.; Wolfe, P. J.; Troutman, M. V.; Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*,1918–1919. (e) Kawatsura, M.; John F. J. *J. Am. Chem. Soc.* **1999**, *121*, 1473–1478. (f) Fox, J. M.; Huang, X.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360–1370.(g) Willis, M. C.; Taylor, D.; Gillmore A. T. *Tetrahedron* **2006,** *62*, 11513–11520.

(15) For reviews of intermediate palladium species with higher oxidation states, see: (a) Muñiz. K. *Angew. Chem.* **2009**, *121*, 9576–9588; *Angew. Chem. Int. Ed.* **2009**, *48*, 9412–9423. (b) Desai, L. V.; Malik, H. A.; Sanford, M. S. *Org. Lett.* **2006**, *8*, 1141–1144. (c) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z-J. *Chem. Soc. Rev.* **2010**, *39*, 712–733. (c) Canty, A. J. *Platinum Metals Rev.,* **1993**, *37*, 2–7.

(16) (a) Quan, L. G.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3545–3546. (b) Solé, D.; Vallverdú, L.; Solans, X.; Font-Bardía, M.; Bonjoch, J. *J. Am. Chem. Soc.* **2003**, *125*, 1587–1594. (c) Zhao, Y.-B.; Mariampillai, B.; Candito, D. A.; Laleu, B.; Li. M.; Lautens, M. *Angew. Chem.* **2009**, *121,* 1881–1884; *Angew. Chem. Int. Ed.* **2009**, *48,* 1849–1852. (d) Solé, D.; Serrano, O. *Angew. Chem.* **2007**, *119,* 7408–7410; *Angew. Chem. Int. Ed.* **2007**, *46,* 7270–7272.

(17) **General Procedure-1 (GP-1) for Pd-mediated Cyclization:** In an oven dried Schlenk tube under nitrogen atmosphere, were added *ortho*-bromoacetophenone **1aa-ag** (100–150 mg, 0.30 to 0.58 mmol), $Pd(OAc)_2$ (2 mol%), Xantphos (4 mol%) and K_3PO_4 (0.60 to 1.16 mmol) followed by addition of dry DMF (2 mL). The resulted reaction mixture was stirred at 150 °C for 45 min to 2 h. Progress of the reaction was monitored by TLC till the reaction is completed. The reaction mixture was then quenched with saturated aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under in vacuo.

The crude product **3aa-ag** was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent.

Representative Analytical Data:

For 7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (3aa): (25 mg, 45%), as viscous liquid. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3062, 2957, 2853, 1652, 1593, 1439, 1377, 1356, 1307, 1250, 1121, 1003, 850, 771, 735, 621cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.79 (dd, 2H, *J*=7.6 and 5.3 Hz, Ar-H), 7.74 (m, 2H, Ar-H), 7.63 (ddd, 1H, *J*=8.7, 7.4 and 1.3 Hz, Ar-H), 7.53 (dd, 1H, *J*=7.7 and 7.6 Hz, Ar-H), 7.48 (2H, *J*=Hz, Ar-H), 6.62 (s, 1H, Ar-H), 2.44 (s, 3H, CH=CCH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 194.0 (s, Ar-C=O), 144.8 (s, CH=*C*CH_3), 142.0 (s, Ar-C), 137.5 (s, Ar-C), 137.3 (s, Ar-C), 135.7 (s, Ar-C), 133.2 (d, Ar-CH), 131.9 (d, *C*H=CCH_3), 131.2 (d, Ar-CH), 130.8 (d, Ar-CH), 128.6 (d, Ar-CH), 128.1 (d, Ar-CH), 127.8 (d, Ar-CH), 127.3 (d, Ar-CH), 127.1 (d, Ar-CH), 24.4 (q, CH=CCH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{32}H_{25}O_2]^+$=$[2(M+H)]^+$: 441.1849; found 441.1836.

For 3,9-dimethoxy-7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (3ac): m. p.: 125–127 °C. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3001, 2934, 2837, 1643, 1603, 1571, 1484, 1408, 1337,1281, 1240, 1174, 1039, 814, 753, 722, 614 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.69 (d, *J*=8.9 Hz, Ar-H), 7.66 (d, *J*=8.9 Hz, Ar-H), 7.28 (d, 1H, *J*=2.9 Hz, Ar-H), 7.20 (d, 1H, *J*=2.8 Hz, Ar-H), 7.18 (dd, 1H, *J*=8.9 and 2.9 Hz, Ar-H), 7.04 (dd, 1H, *J*=8.9 and 2.8 Hz, Ar-H), 6.61 (d, 1H, *J*=0.9 Hz, Ar-H), 3.89 (s, 3H, Ar-OCH_3), 3.89 (s, 3H, Ar-OCH_3), 2.43 (d, 3H, *J*=0.9 Hz, CH=CCH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 193.6 (s, Ar-C=O), 159.0 (s, Ar-C), 158.4 (s, Ar-C), 144.8 (s, CH=*C*CH_3), 142.3 (s, Ar-C), 136.3 (s, Ar-C), 132.9 (d, *C*H=CCH_3),132.8 (d, Ar-CH), 131.3 (d, Ar-CH), 130.5 (s, Ar-C), 130.4 (s, Ar-C), 119.4 (d, Ar-CH), 114.5 (d, Ar-CH), 112.2 (d, Ar-CH), 109.7 (d, Ar-CH), 55.6 (q, Ar-OCH_3), 55.4 (q, Ar-OCH_3), 24.6 (q, CH=C*C*H_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{17}O_3]^+$=$[M+H]^+$: 281.1172; found 281.1161.