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

Jonnada Krishna, Alavala Gopi Krishna Reddy, Gedu Satyanarayana*

Indian Institute of Technology (IIT) Hyderabad, Ordnance Factory Estate Campus, Yeddumailaram – 502 205, Medak District, Andhra Pradesh, India
Fax +91(40)23016032; E-mail: gvsatya@iith.ac.in

Received: 18.01.2013; Accepted after revision: 03.04.2013

This paper is affectionately dedicated to Professor Kavirayani R. Prasad, Department of Organic Chemistry, Indian Institute of Science, Bangalore, India

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 is proposed to proceed via intermolecular homobiaryl coupling and intramolecular aldol condensation.

Key words: Pd catalysis, homobiaryl 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 a significant area in synthetic organic chemistry.[1] In this regard, transition-metal catalysis is considered to be a powerful technique for constructing C–C bonds efficiently and palladium, in particular, has been used to develop such novel interconversions.[2,3] Generally, it has been observed that, in the presence of inherent intramolecular ring constraints, the initially formed Pd intermediates prefer to undergo intermolecular homo- or heterocoupling rather than intramolecular reaction.[4,5] For example, when we recently subjected α,α-disubstituted (2-haloaryl)methanols to 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, but rather furnished 6,6-dialkyl-6*H*-benzo[*c*]chromenes via an efficient homobiaryl coupling.[5h]

In continuation of our interest in transition-metal catalysis,[6] we present herein 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 pathway to yield structures present as the carbon core of biologically active natural products such as the 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.

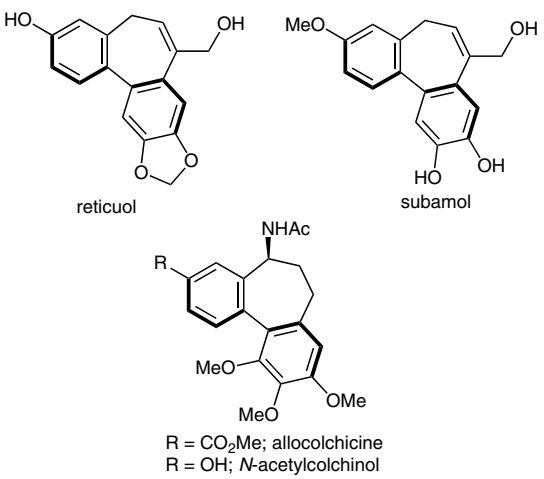


Figure 1

The required 1-(2-bromophenyl)ethanones **1** for this study were prepared from the corresponding *ortho*-halobenzaldehydes using an 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 **1c** was subjected to numerous conditions (for complete details see Supporting Information). Treatment of **1c** in the presence of $Pd(OAc)_2$ (5 mol%), dppf (10 mol%), and base K_3PO_4 (4 equiv) in hot DMF at 100 °C for 10 hours gave the product **3c**, 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** returned it to 25% (Table 1, entry 3). Other ligands **L3**, **L4**, PCy_3, and $Pd(PPh_3)_4$ also proved ineffective (Table 1, entries 4–7). Interestingly, the use of different catalysts improved the yield (Table 1, entries 8 and 9). Gratifyingly, the reaction in the presence of ligand **L5** improved the yield to 50% (Table 1, entry 10). Disappointingly, addition of various additives was unsuccessful in improving the yield further (Table 1, entries 11–14).

Although the yield of **3c** is moderate, it is still in an acceptable range because each individual step (i.e., biphenyl

SYNLETT 2013, 24, 0967–0972
Advanced online publication: 11.04.2013
DOI: 10.1055/s-0033-1338438; Art ID: ST-2013-D0061-L

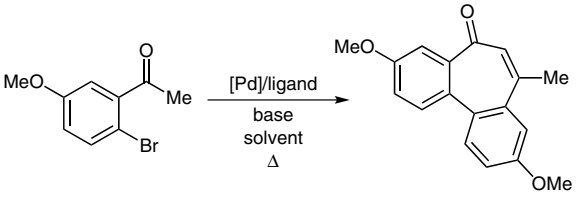
coupling and aldol condensation) accounts for nearly 70% yield. Moreover, the present method compares well with previous reports, which involve not less than four steps with poor overall yield,[12] for the synthesis of such structurally relevant compounds.

Thus, to study the scope and limitations of the present method, these optimized conditions were applied to other 1-(2-bromophenyl)ethanones **1**. Pleasingly, the reaction progressed well with the other substrates and gave the biaryl-cyclized products **3a**–**g** in comparable yields (Scheme 1).

The chemical structures of **3a**–**g** have been further unambiguously confirmed by the single-crystal X-ray diffraction analysis of **3g**[13] (Figure 2 and Supporting Information).

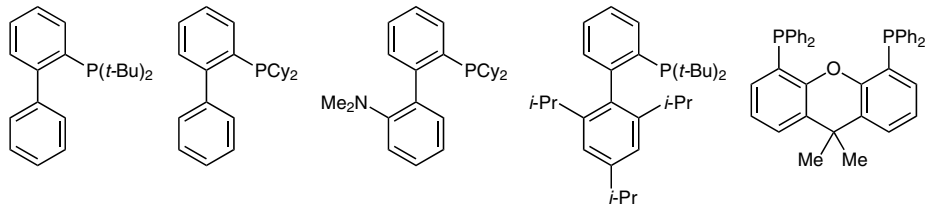
After the accomplishment of one-pot synthesis of **3a**–**g**, we became interested in looking at the scope and limitations of the methodology by changing the alkyl group of

Table 1 Optimization Reaction Conditions for the Synthesis of 3,9-Dimethoxy-7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (**3c**)



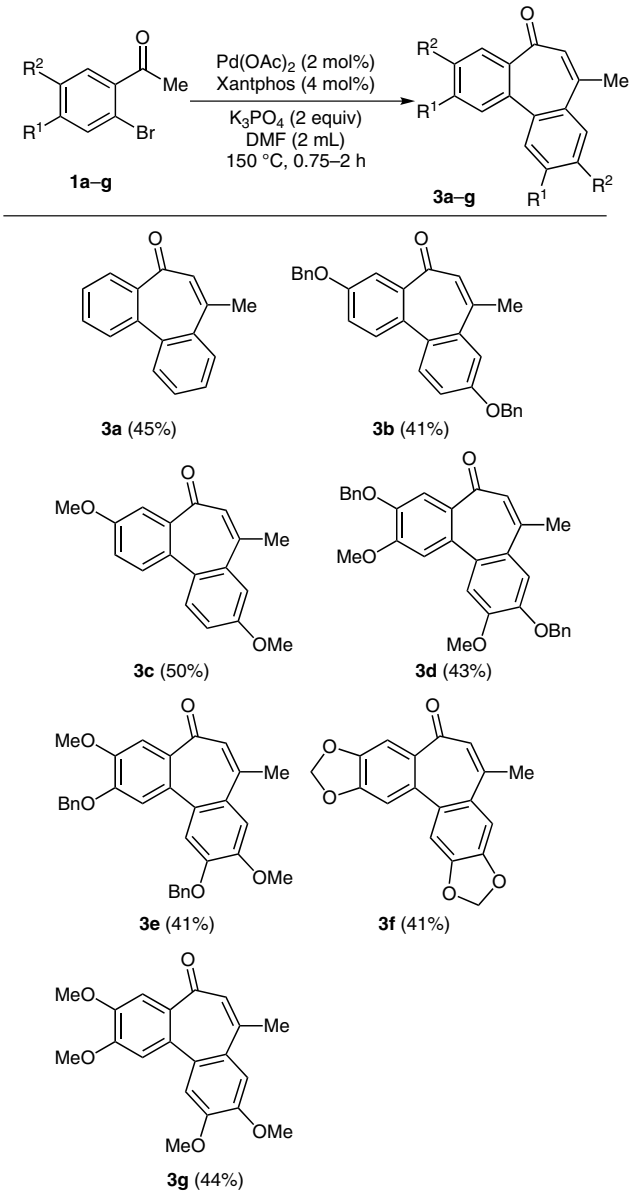
1c **3c**

Entry[a,b]	[Pd] (mol%)	Ligand (mol%)	Base (equiv)	Time (h)	Yield of **3c** (%)[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]



L1: JohnPhos **L2:** Cyclohexyl JohnPhos **L3:** DavePhos **L4:** *tert*-Butyl XPhos **L5:** Xantphos

[a] All reactions were performed on 100 mg (0.44 mmol) scale of **1c** at 0.22 M concentration, in DMF (2 mL).
[b] All reactions were heated to 150 °C except in entries 1 (100 °C) and 7 (120 °C).
[c] Isolated yields of chromatographically pure products.
[d] 4 Å MS (100 mg) were used as additive.
[e] H_2O (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.



Scheme 1 Scope of one-pot Pd-catalyzed homobiaryl coupling. *Reagents and conditions*: **1a**–**g** (100–150 mg, 0.30–0.58 mmol), 0.15–0.25 M in DMF. Yields in the parentheses are isolated yields of chromatographically pure products.

the ketone. Unpromisingly, Pd catalysis of 1-(2-bromophenyl)propan-1-one **5ac** was sluggish (Scheme 2). This can be reasoned to be based on the availability of the 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.

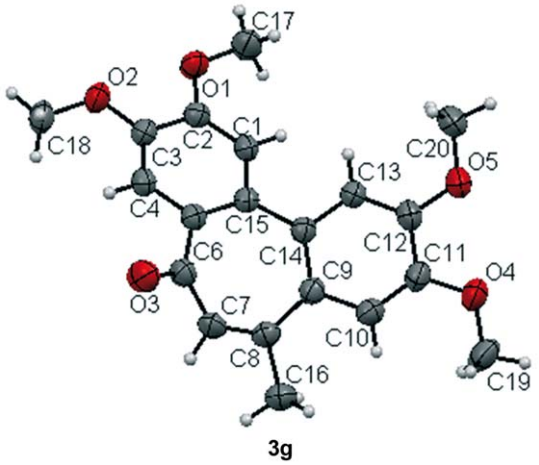
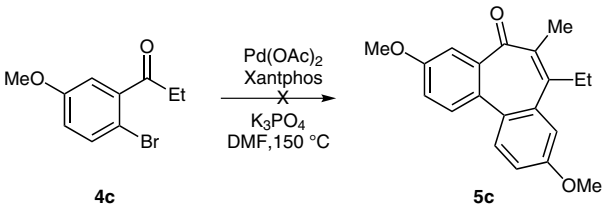
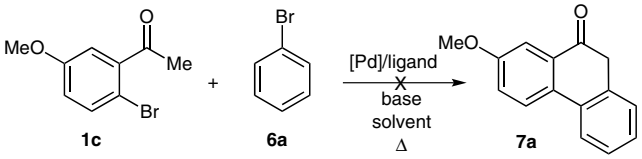


Figure 2 X-ray crystal structure of **3g**. Thermal ellipsoids are drawn at 50% probability level.



Scheme 2

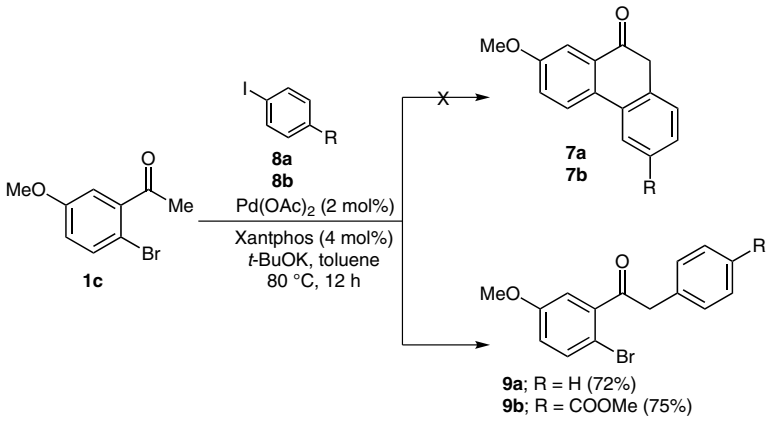
Furthermore, Pd catalysis of **1c** with the simple halobenzenes **6a** was also explored, in order to achieve a heterobiaryl variant of the reaction. However, performing the Pd catalysis under a range of different conditions, neither allowed us to recover back the starting material nor gave the expected product **7a** as depicted in Scheme 3.



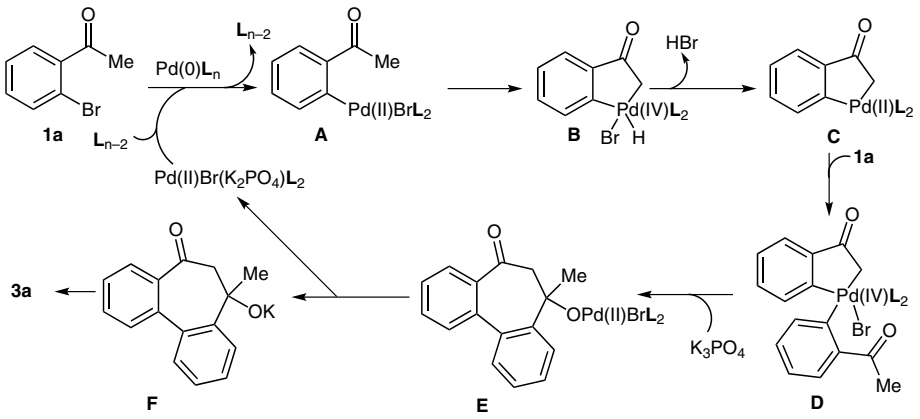
Scheme 3

Since, the formation of heterobiaryl system **7a** was not successful, we turned to our attention to modify the method to generate such biaryls via a preferential α-arylation of 2-bromoacetophenone **1c** with a more reactive iodoarene followed by intramolecular Heck reaction. However, treatment of **1c** with iodoarenes **8a** and **8b** did not furnish the desired products, but gave only α-arylation products **9a** and **9b**, respectively (Scheme 4). This parallels previously reported α-arylations.[14]

A plausible mechanism for the formation of **3a** is similar to that reported in our earlier work.[5h] The five-membered palladacycle **B** could be formed via the insertion of the initially formed aryl-palladium(II) species **A**, into the sp^3 C–H bond of the ketone (Scheme 5). The Pd(IV) interme-



Scheme 4 α-Arylation of **1c** with **8a** and **8b**



Scheme 5 Plausible catalytic cycle for the formation of **3a**

diate **B** converts into the reactive Pd(II) species **C** through HBr elimination. The key Pd cyclic species **C** combines with a second molecule **1a** 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 tertiary alkoxide **F** and a Pd(II) species. Finally, **F** transforms into the product **3a** by elimination, and Pd(II) returning to Pd(0) completes the catalytic cycle (Scheme 5).

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.

Acknowledgment

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

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

Primary Data for this article are available online at http://www.thieme-connect.com/ejournals/toc/synlett and can be cited using the following DOI: 10.4125/pd0045th.

References and Notes

(1) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115.
(2) For reviews on C–H activations, see: (a) Shibasaki, M.; Vogl, E. M.; Ohshima, T. *Adv. Synth. Catal.* **2004**, *346*, 1533. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (c) D'Souza, D. M.; Müller, T. J. J. *Chem. Soc. Rev.* **2007**, *36*, 1095. (d) Minatti, A.; Muñiz, K. *Chem. Soc. Rev.* **2007**, *36*, 1142. (e) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, 1512. (f) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (g) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; *Angew. Chem.* **2009**, *121*, 5196. (h) Muñiz, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 9412; *Angew. Chem.* **2009**, *121*, 9576 . (i) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712. (j) Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824. (k) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (l) Bras, J. L.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170. (m) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315.
(3) For recent Pd-catalyzed domino transformations, see: (a) Thirunavukkarasu, V. S.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem. Int. Ed.* **2008**, *47*, 9462; *Angew. Chem.* **2008**, *120*, 9604. (b) Cvengroš, J.; Schütte, J.; Schlörer, N.;

Neudörfl, J.; Schmalz, H.-G. *Angew. Chem. Int. Ed.* **2009**, *48*, 6148; *Angew. Chem.* **2009**, *121*, 6264 . (c) Hu, Y.; Yu, C.; Ren, D.; Hu, Q.; Zhang, L.; Cheng, D. *Angew. Chem. Int. Ed.* **2009**, *48*, 5448; *Angew. Chem.* **2009**, *121*, 5556 . (d) Levi, Z. U.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 2796. (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. (f) Tietze, L. F.; Redert, T.; Bell, H. P.; Hellkamp, S.; Levy, L. M. *Chem. Eur. J.* **2008**, *14*, 2527. (g) Tietze, L. F.; Düfert, M. A.; Hungerland, T.; Oum, K.; Lenzer, T. *Chem. Eur. J.* **2011**, *17*, 8452. (h) Satyanarayana, G.; Maichle-Mössmer, C.; Maier, M. E. *Chem. Commun.* **2009**, 1571. (i) Wang, S.; Xie, K.; Tan, Z.; An, X.; Zhou, X.; Guo, C.-C.; Peng, Z. *Chem. Commun.* **2009**, 6469. (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. (k) Chen, X.; Wang, H.; Jin, X.; Feng, J.; Wang, Y.; Lu, P. *Chem. Commun.* **2011**, *47*, 2628. (l) Bryan, C. S.; Lautens, M. *Org. Lett.* **2008**, *10*, 4633. (m) Jana, R.; Chatterjee, I.; Samanta, S.; Ray, J. K. *Org. Lett.* **2008**, *10*, 4795. (n) Luo, Y.; Pan, X.; Wu, J. *Org. Lett.* **2011**, *13*, 1150. (o) Motti, E.; Della Ca', N.; Xu, D.; Piersimoni, A.; Bedogni, E.; Zhou, Z.-M.; Catellani, M. *Org. Lett.* **2012**, *14*, 5792. (p) Piou, T.; Neuville, L.; Zhu, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 11561; *Angew. Chem.* **2012**, *124*, 11729. (q) Hashmi, A. S. K.; Ghanbari, M.; Rudolph, M.; Rominger, F. *Chem. Eur. J.* **2012**, *18*, 8113. (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. (s) Hashmi, A. S. K.; Lothschütz, C.; Döpp, R.; Rudolph, M.; Ramamurthi, T. D.; Rominger, F. *Angew. Chem. Int. Ed.* **2009**, *48*, 8243; *Angew. Chem.* **2009**, *121*, 8392.

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

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

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

(7) (a) Chia, Y.-C.; Yeh, H.-C.; Yeh, Y.-T.; Chen, C.-Y. *Chem. Nat. Compd.* **2011**, *47*, 220. (b) Chen, C.-Y.; Yang, W.-L.; Hsui, Y.-R. *Nat. Prod. Res.* **2010**, *24*, 423. (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.

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

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

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

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

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

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

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

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

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

(17) **General Procedure-1 for the Pd-Mediated Cyclization (GP-1)**

In an oven-dried Schlenk tube under nitrogen atmosphere were added *ortho*-bromoacetophenone **1a**–**g** (100–150 mg, 0.30–0.58 mmol), $Pd(OAc)_2$ (2 mol%), Xantphos (4 mol%), and K_3PO_4 (0.60–1.16 mmol) followed by addition of dry DMF (2 mL). The resulted reaction mixture was stirred at 150 °C for 0.75–2 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was then quenched with sat. aq NH_4Cl, and the aqueous layer was extracted with EtOAC (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The crude product **3a**–**g** was purified by column chromatography on silica gel using PE–EtOAc as eluent.

Representative Analytical Data

7-Methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (3a)

Yield: 25 mg, 45%; 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, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, 2 H, *J* = 7.6, 5.3 Hz, ArH), 7.74 (m, 2 H, ArH), 7.63 (ddd, 1 H, *J* = 8.7, 7.4, 1.3 Hz, ArH), 7.53 (dd, 1 H, *J* = 7.7, 7.6 Hz, ArH), 7.48 (2 H, *J* = Hz, ArH), 6.62 (s, 1 H, ArH), 2.44 (s, 3 H, CH=CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0 (s, ArC=O), 144.8 (s, CH=*C*CH$_3$), 142.0 (s, ArC), 137.5 (s, ArC), 137.3 (s, ArC), 135.7 (s, ArC), 133.2 (d, ArCH), 131.9 (d, *C*H=CCH$_3$), 131.2 (d, ArCH), 130.8 (d, ArCH), 128.6 (d, ArCH), 128.1 (d, ArCH), 127.8 (d, ArCH), 127.3 (d, ArCH), 127.1 (d, ArCH), 24.4 (q, CH=CCH_3). HRMS (ESI^+): *m/z* calcd for $[C_{32}H_{25}O_2]^+ = [2\ (M + H)]^+$: 441.1849; found: 441.1836.

3,9-Dimethoxy-7-methyl-5*H*-dibenzo[*a*,*c*][7]annulen-5-one (3c)

Yield: 31 mg, 50%; white solid; mp 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}. ^1H NMR (400 MHz $CDCl_3$): δ = 7.69 (d, *J* = 8.9 Hz, ArH), 7.66 (d, *J* = 8.9 Hz, ArH), 7.28 (d, 1 H, *J* = 2.9 Hz, ArH), 7.20 (d, 1 H, *J* = 2.8 Hz, ArH), 7.18 (dd, 1 H, *J* = 8.9, 2.9 Hz, ArH), 7.04 (dd, 1 H, *J* = 8.9, 2.8 Hz, ArH), 6.61 (d, 1 H, *J* = 0.9 Hz, ArH), 3.89 (s, 3 H, $ArOCH_3$), 3.89 (s, 3 H, $ArOCH_3$), 2.43 (d, 3 H, *J* = 0.9 Hz, CH=CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6 (s, ArC=O), 159.0 (s, ArC), 158.4 (s, ArC), 144.8 (s, CH=*C*CH_3), 142.3 (s, ArC), 136.3 (s, ArC), 132.9 (d, *C*H=CCH_3),132.8 (d, ArCH), 131.3 (d, ArCH), 130.5 (s, ArC), 130.4 (s, ArC), 119.4 (d, ArCH), 114.5 (d, ArCH), 112.2 (d, ArCH), 109.7 (d, ArCH), 55.6 (q, $ArOCH_3$), 55.4 (q, $ArOCH_3$), 24.6 (q, CH=C*C*H_3). HRMS (ESI+): *m/z* calcd for $[C_{18}H_{17}O_3]^+ = [M + H]^+$: 281.1172; found: 281.1161.

