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Regioselective synthesis of naphthalenes from modified Baylis–Hillman adducts via a Pd-catalyzed cyclization: 5-*exo*-carbopalladation, C(sp^3)–H activation to cyclopropane, ring-opening, and aromatization cascade

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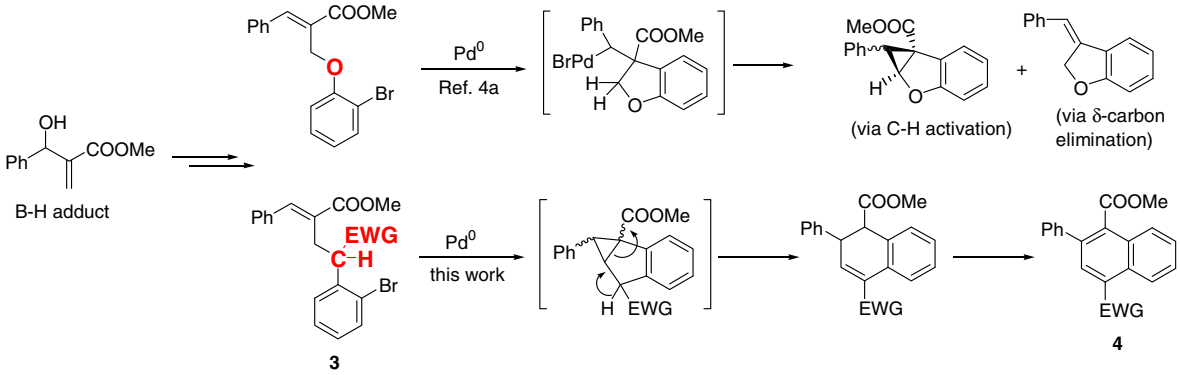
ABSTRACT

Modified Baylis–Hillman adducts having 2-bromophenyl acetonitrile moiety at the primary position underwent a Pd-catalyzed cascade reaction to provide poly-substituted naphthalene derivatives in reasonable yields. The reaction involved a sequential 5-*exo*-carbopalladation, C(sp^3)–H activation to cyclopropane, ring-opening and concomitant aromatization processes.

Chemical transformations of Baylis–Hillman adducts have received much attention during the last two decades.[1–3] Various cyclic and acyclic compounds have been prepared from Baylis–Hillman adducts and their derivatives.[1–3] Although Pd-catalyzed chemical transformations of Baylis–Hillman adducts started very recently, they have provided many interesting heterocyclic compounds.[1h,2,3,4a,b]

Recently we reported the synthesis of cyclopropane-fused dihydrobenzofuran derivatives from the modified Baylis–Hillman adducts having 2-bromophenol moiety as shown in Scheme 1.[4a] The formation of cyclopropane derivative involved a C(sp^3)–H bond activation process of the palladium intermediate.[4a,5] In addition, a trace amount of benzylidene compound was formed together via a δ-carbon elimination process.[4a] During the studies we reasoned out that if we replace the oxygen atom to a carbon linkage accompanying an electron-withdrawing substituent such as a nitrile group, then the corresponding cyclopropane ring could be opened to a dihydronaphthalene derivative, and eventually made to form the naphthalene **4** via an aerobic oxidation process (Scheme 1). Literature survey stated that Liron and Knochel also observed such a ring-expansion of cyclopropane into a dihydronaphthalene derivative.[5a] In these contexts, we decided to examine the synthesis of poly-substituted naphthalenes[6,7] from the starting materials **3**.

The starting materials **3a–g** were prepared by the reactions of cinnamyl bromides **1a–d**, prepared from the corresponding Baylis–Hillman adducts,[8] and 2-bromobenzyl derivatives **2a–d** under the influence of K_2CO_3 in DMF at room temperature (Scheme 2).



Scheme 1.

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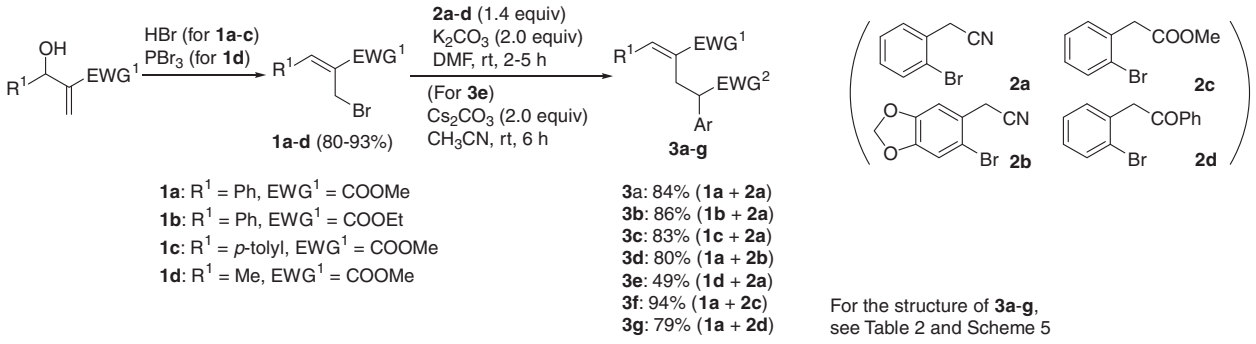


Scheme 2.

Table 1
Optimization reaction conditions of **3a**[a]

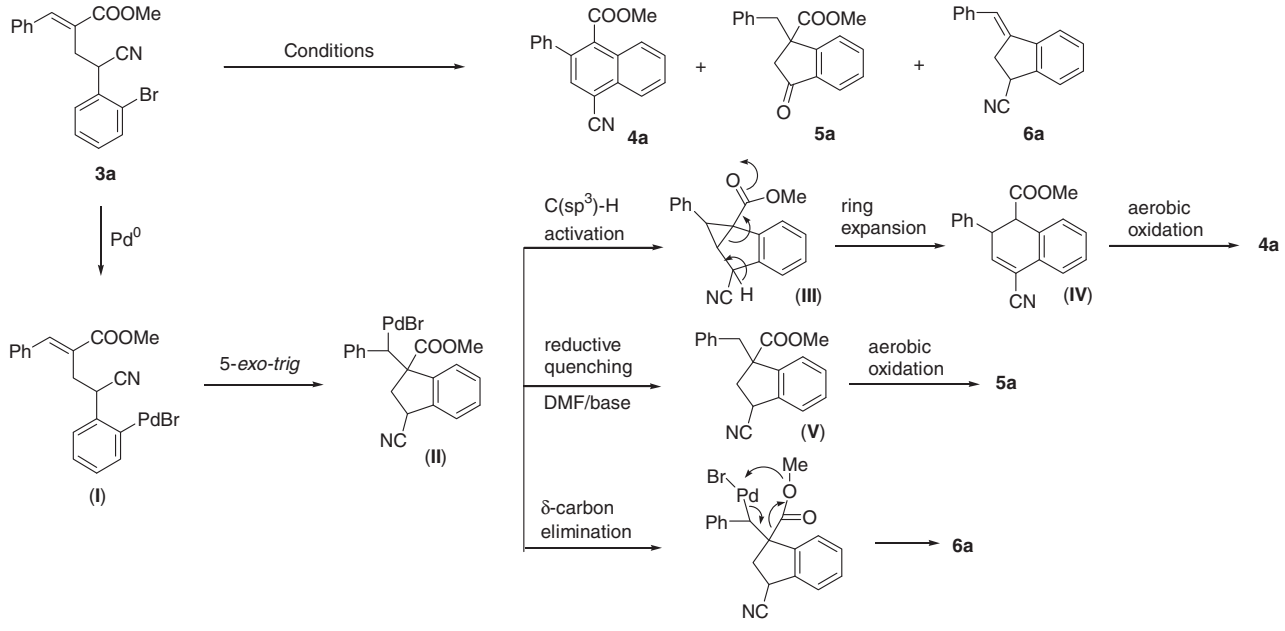
Entry	Conditions	**4a** (%)/ **5a** (%)/ **6a** (%)[b]
1	TBAB (1.0 equiv), K_2CO_3 (2.0. equiv), CH_3CN, reflux, 24 h	39/8/0
2	TBAB (1.0 equiv), K_2CO_3 (2.0. equiv), DMF, 60 °C, 2 h	[c]
3	TBAB (1.0 equiv), K_2CO_3 (2.0 equiv), DMF, 80–90 °C, 30 min	54/7/0
4	TBAB (1.0 equiv), K_2CO_3 (2.0 equiv), DMF, 110 °C, 30 min	24/9/0
5	TBAB (1.0 equiv), Cs_2CO_3 (2.0 equiv), DMF, 80–90 °C, 30 min	[d]
6	PPh_3 (20 mol %), K_2CO_3 (2.0 equiv), DMF, 110 °C, 1 h	[d]
7	PPh_3 (20 mol %), Et_3N (5.0 equiv), DMF, 110 °C, 1 h	0/0/34

[a] Conditions: $Pd(OAc)_2$ (10 mol %) is common.
[b] Isolated yields.
[c] Sluggish reaction.
[d] Severe decomposition was observed.

The yields of **3a**–**g** were good (79–94%) except **3e**. The yield of **3e** was low due to the formation of many intractable side products under the same conditions. However, a reasonable yield of **3e** (49%) was obtained under the influence of Cs_2CO_3 in CH_3CN (rt, 6 h). With these compounds **3a**–**g** we examined the Pd(0)-catalyzed synthesis of naphthalene derivatives.

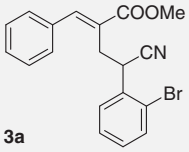
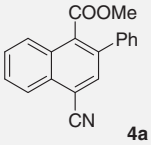
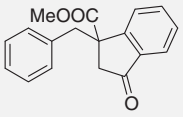
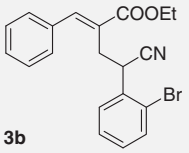
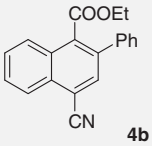
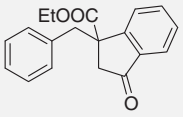
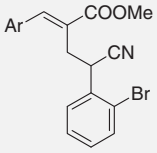
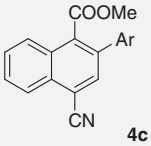
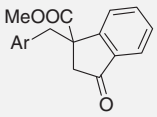
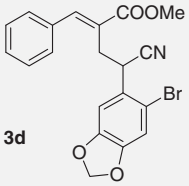
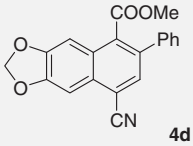
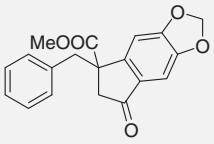
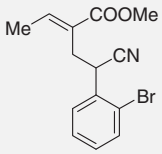
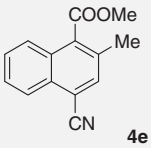
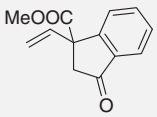
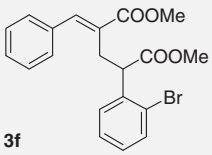
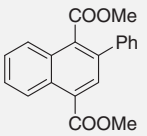
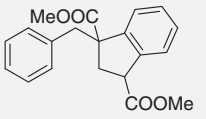
The reaction of **3a** was examined under various Pd-catalyzed conditions, and we observed the formation of three compounds **4a**, **5a** and **6a**, in variable yields, as shown in Table 1 and in Scheme 3.[8,9] The reaction of **3a** was effective at around 80–90 °C, and the use of DMF as a solvent was better than CH_3CN (entries 1–3). The reactions at higher temperature (entries 4 and 6) or the use of Cs_2CO_3 (entry 5) were not fruitful. It is interesting to note that compound **6a** was isolated as the sole product when we used Et_3N (entry 7), albeit in low yield, via the δ-carbon elimination and concomitant decarboxylation process,[4] as shown in Scheme 3. Further oxidation of **6a** at the benzylic position to the corresponding indanone derivative was not observed under the influence of a weak base Et_3N (vide infra).

The formation of naphthalene **4a** could be explained as in our previous Letter[4a] involving the sequential oxidative addition of Pd(0) to form (**I**), 5-*exo*-carbopalladation to form (**II**), C(sp^3)–H activation to give cyclopropane (**III**),[4a,5a] base-mediated ring-opening to dihydronaphthalene (**IV**), and an aerobic oxidation. The aerobic oxidation of dihydronaphthalene occurred during the reaction concomitantly as in our previous synthesis of quinolines.[3e] The formation of trace amounts of indanone **5a** must be the result of a reductive Heck type reaction caused by the solvent DMF[10] to pro-

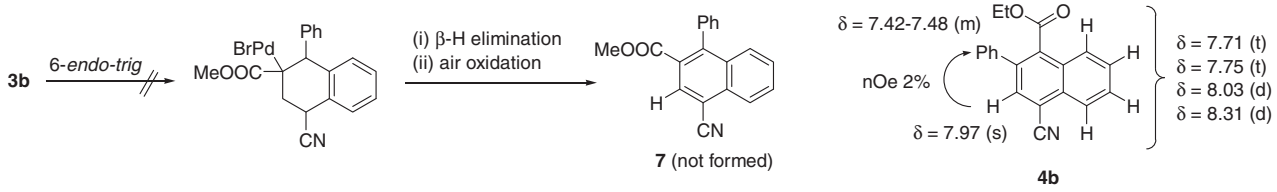


Scheme 3.

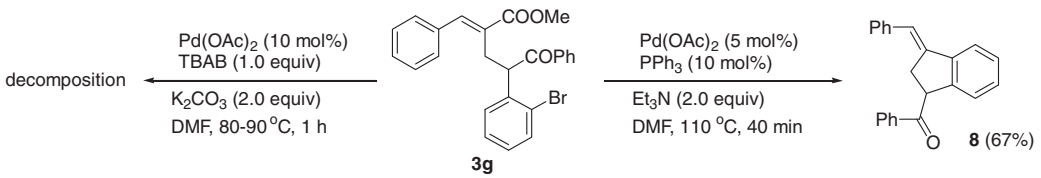
Table 2
Synthesis of poly-substituted naphthalenes **4a**–**f**[a]

Entry	Substrate	Products (%)	
1	 **3a**	 **4a** (54)	 **5a** (7)
2	 **3b**	 **4b** (53)	 **5b** (9)
3[b]	 **3c**	 **4c** (44)	 **5c** (7)
4	 **3d**	 **4d** (36)	 **5d** (6)
5	 **3e**	 **4e** (21)	 **5e** (23)
6	 **3f**	 **4f** (41)	 **5f** (-)

[a] Conditions: substrate **3** (1.0 equiv), $Pd(OAc)_2$ (10 mol %), TBAB (1.0 equiv), K_2CO_3 (2.0 equiv), DMF, 80–90 °C, 30 min.
[b] Ar is 4-tolyl.



Scheme 4.



Scheme 5.

duce (**V**), and the following base-mediated aerobic oxidation to **5a**. Similar aerobic oxidation of benzylic cyanides under basic conditions has been reported.[11]

We chose the conditions in entry 3 (Table 1) and carried out the synthesis of naphthalenes **4a**–**f**, as shown in Table 2. Naphthalene derivatives **4a**–**f** were obtained in reasonable yields (21–54%)

along with trace amounts of indanone derivatives **5a**–**d** (6–9%).[9] It is interesting to note that vinyl compound **5e** was isolated in 23% yield for the ethylidene compound **3e** via the usual β-H elimination process of the palladium intermediate (entry 5). Ester derivative **3f** (entry 6) also produced naphthalene **4f** in a reasonable yield (41%); however, we failed to isolate the corresponding indane derivative **5f**.

The structure of naphthalene was confirmed unequivocally by NOE experiments, as shown in Scheme 4, using compound **4b** as an example. Irradiation of the singlet of naphthalene **4b** at 7.97 ppm showed a NOE increment of the aromatic protons of the phenyl group (7.42–7.48 ppm). As shown in Scheme 4, naphthalene **7** has to be formed if the carbopalladation occurred in a 6-*endo* mode. From the NOE results, the possibility of 6-*endo*-carbopalladation could be ruled out.

The benzoyl derivative **3g** showed the formation of many intractable compounds under the optimized conditions (entry 3 in Table 1), and we failed to obtain the corresponding naphthalene derivative **4g**. However, the reaction under the conditions using Et_3N (entry 7 in Table 1) afforded compound **8** in 67% yield via the δ-carbon elimination process,[4,9] as shown in Scheme 5.

In summary, we disclosed a new synthesis of poly-substituted naphthalenes starting from the Baylis–Hillman adducts having 2-bromophenyl acetonitrile moiety at the primary position via a Pd-catalyzed cascade reaction involving a sequential 5-*exo*-carbopalladation, C(sp^3)–H activation to cyclopropane, ring-opening and aromatization processes.

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References and notes

1. For the general review on Baylis–Hillman reaction, see: (a) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811–891; (b) Singh, V.; Batra, S. *Tetrahedron* **2008**, *64*, 4511–4574; (c) Kim, J. N.; Lee, K. Y. *Curr. Org. Chem.* **2002**, *6*, 627–645; (d) Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Bull. Korean Chem. Soc.* **2005**, *26*, 1481–1490; (e) Langer, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3049–3052; (f) Radha Krishna, P.; Sachwani, R.; Reddy, P. S. *Synlett* **2008**, 2897–2912; (g) Declerck, V.; Martinez, J.; Lamaty, F. *Chem. Rev.* **2009**, *109*, 1–48; (h) Gowrisankar, S.; Lee, H. S.; Kim, S. H.; Lee, K. Y.; Kim, J. N. *Tetrahedron* **2009**, *65*, 8769–8780.
2. For the recent Pd-catalyzed reactions of modified Baylis–Hillman adducts, see: (a) Vasudevan, A.; Tseng, P.-S.; Djuric, S. W. *Tetrahedron Lett.* **2006**, *47*, 8591–8593; (b) Coelho, F.; Veronese, D.; Pavam, C. H.; de Paula, V. I.; Buffon, R. *Tetrahedron* **2006**, *62*, 4563–4572; (c) Kohn, L. K.; Pavam, C. H.; Veronese, D.; Coelho, F.; De Carvalho, J. E.; Almeida, W. P. *Eur. J. Med. Chem.* **2006**, *41*, 738–744; (d) Liu, H.; Yu, J.; Wang, L.; Tong, X. *Tetrahedron Lett.* **2008**, *49*, 6924–6928; (e) Szlosek-Pinaud, M.; Diaz, P.; Martinez, J.; Lamaty, F. *Tetrahedron* **2007**, *63*, 3340–3349; (f) Jellerichs, B. G.; Kong, J.-R.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7758–7759. further references were compiled in Ref. 1h.
3. For our contributions on Pd-catalyzed reactions of modified Baylis–Hillman adducts, see: (a) Kim, K. H.; Lee, H. S.; Kim, S. H.; Kim, S. H.; Kim, J. N. *Chem. Eur. J.* **2010**, *16*, 2375–2380; (b) Kim, J. M.; Kim, S. H.; Lee, H. S.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 1734–1737; (c) Kim, K. H.; Kim, E. S.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 5322–5325; (d) Lee, H. S.; Kim, S. H.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 1773–1776; (e) Gowrisankar, S.; Lee, H. S.; Kim, J. M.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 1670–1673; (f) Gowrisankar, S.; Lee, H. S.; Lee, K. Y.; Lee, J.-E.; Kim, J. N. *Tetrahedron Lett.* **2007**, *48*, 8619–8622; (g) Kim, J. M.; Kim, K. H.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 3248–3251; (h) Lee, H. S.; Kim, S. H.; Gowrisankar, S.; Kim, J. N. *Tetrahedron* **2008**, *64*, 7183–7190; (i) Gowrisankar, S.; Kim, K. H.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 6241–6244.
4. For the similar examples on δ-carbon elimination, see: (a) Kim, H. S.; Gowrisankar, S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 3858–3861; (b) Kim, H. S.; Lee, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 3154–3157; (c) Kim, H. S.; Gowrisankar, S.; Kim, E. S.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 6569–6572. and further references were cited therein.
5. For the similar examples on C(sp^3)–H bond activation, see: (a) Liron, F.; Knochel, P. *Tetrahedron Lett.* **2007**, *48*, 4943–4946; (b) Ren, H.; Li, Z.; Knochel, P. *Chem. Asian J.* **2007**, *2*, 416–433; (c) Ren, H.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3462–3465; (d) Dyker, G. *Angew. Chem., Int. Ed.* **1994**, *33*, 103–105; (e) Dyker, G. *J. Org. Chem.* **1993**, *58*, 6426–6428; (f) Dyker, G. *Angew. Chem., Int. Ed.* **1992**, *31*, 1023–1025; (g) Hitce, J.; Retailleau, P.; Baudoin, O. *Chem. Eur. J.* **2007**, *13*, 792–799; (h) Baudoin, O.; Herrbach, A.; Gueritte, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 5736–5740.
6. For some leading references to naphthalene synthesis, see: (a) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650–12651; (b) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921–10925; (c) Barluenga, J.; Vazquez-Villa, H.; Ballesteros, A.; Gonzalez, J. M. *Org. Lett.* **2003**, *5*, 4121–4123; (d) Barluenga, J.; Vazquez-Villa, H.; Merino, I.; Ballesteros, A.; Gonzalez, J. M. *Chem. Eur. J.* **2006**, *12*, 5790–5805; (e) Patil, N. T.; Konala, A.; Singh, V.; Reddy, V. V. N. *Eur. J. Org. Chem.* **2009**, 5178–5184; (f) Shi, M.; Lu, J.-M. *J. Org. Chem.* **2006**, *71*, 1920–1923; (g) Jiang, X.; Kong, W.; Chen, J.; Ma, S. *Org. Biomol. Chem.* **2008**, *6*, 3606–3610; (h) Dudnik, A. S.; Schwier, T.; Gevorgyan, V. *Tetrahedron* **2009**, *65*, 1859–1870; (i) Balamurugan, R.; Gudla, V. *Org. Lett.* **2009**, *11*, 3116–3119.
7. For our recent synthesis of naphthalene derivatives, see: (a) Kim, S. H.; Kim, Y. M.; Lee, H. S.; Kim, J. N. *Tetrahedron Lett.* **2010**, *51*, 1592–1595; (b) Lee, K. Y.; Kim, S. C.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 977–980; (c) Gowrisankar, S.; Kim, K. H.; Kim, J. N. *Bull. Korean Chem. Soc.* **2008**, *29*, 2537–2539; (d) Im, Y. J.; Lee, K. Y.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2002**, *43*, 4675–4678; (e) Gowrisankar, S.; Lee, H. S.; Kim, J. N. *Tetrahedron Lett.* **2007**, *48*, 3105–3108.
8. For the synthesis of cinnamyl bromide derivatives in a stereoselective manner from Baylis–Hillman adducts, see: (a) Gowrisankar, S.; Kim, S. H.; Kim, J. N. *Bull. Korean Chem. Soc.* **2009**, *30*, 726–728. and further references cited therein; (b) Basavaiah, D.; Reddy, K. R.; Kumaragurubaran, N. *Nat. Protoc.* **2007**, *2*, 2665–2676; (c) Das, B.; Banerjee, J.; Ravindranath, N. *Tetrahedron* **2004**, *60*, 8357–8361; (d) Fernandes, L.; Bortoluzzi, A. J.; Sa, M. M. *Tetrahedron* **2004**, *60*, 9983–9989; (e) Sa, M. M.; Ramos, M. D.; Fernandes, L. *Tetrahedron* **2006**, *62*, 11652–11656; (f) Deng, J.; Hu, X.-P.; Huang, J.-D.; Yu, S.-B.; Wang, D.-Y.; Duan, Z.-C.; Zheng, Z. *J. Org. Chem.* **2008**, *73*, 2015–2017; (g) Lee, K. Y.; Lee, Y. J.; Kim, J. N. *Bull. Korean Chem. Soc.* **2007**, *28*, 143–146; (h) Lee, K. Y.; Park, D. Y.; Kim, J. N. *Bull. Korean Chem. Soc.* **2006**, *27*, 1489–1492.
9. *Typical procedure for the preparation of starting material* **3a***:* A mixture of **1a** (255 mg, 1.0 mmol), **2a** (275 mg, 1.4 mmol), and K_2CO_3 (277 mg, 2.0 mmol) in DMF (3 mL) was stirred at room temperature for 2 h. The usual aqueous workup and column chromatographic purification process (hexanes/diethyl ether, 15:1) afforded compound **3a** as a colorless oil, 312 mg (84%). Other compounds were prepared similarly and the selected spectroscopic data of **3a**, **3b**, and **3g** are as follows.
Compound **3a**: 84%; colorless oil; IR (film) 2242, 1713, 1436, 1263 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.07–3.20 (m, 2H), 3.87 (s, 3H), 4.77 (t, *J* = 8.1 Hz, 1H), 7.10–7.53 (m, 9H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.72, 35.91, 52.30, 119.77, 123.13, 127.54, 128.20, 128.55, 128.63 (2C), 129.30, 129.78, 133.24, 134.71, 134.85, 144.15, 167.59; ESIMS *m*/*z* 392 (M^++Na), 394 (M^++2+Na). Anal. Calcd for $C_{19}H_{16}BrNO_2$: C, 61.64; H, 4.36; N, 3.78. Found: C, 61.95; H, 4.45; N, 3.56.
Compound **3b**: 86%; colorless oil; IR (film) 2242, 1705, 1472, 1260 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.39 (t, *J* = 7.2 Hz, 3H), 3.07–3.20 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.78 (t, *J* = 8.1 Hz, 1H), 7.10–7.52 (m, 9H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.31, 31.69, 35.93, 61.33, 119.81, 123.15, 127.84, 128.21, 128.54, 128.56, 128.63, 129.30, 129.77, 133.23, 134.81, 134.91, 143.89, 167.12; ESIMS *m*/*z* 406 (M^++Na), 408 (M^++2+Na). Anal. Calcd for $C_{20}H_{18}BrNO_2$: C, 62.51; H, 4.72; N, 3.65. Found: C, 62.76; H, 4.69; N, 3.51.
Compound **3g**: 79%; white solid, mp 62–64 °C, IR (KBr) 1710, 1683, 1445, 1436, 1252, 1208 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.19–3.34 (m, 2H), 3.80 (s, 3H), 5.43 (dd, *J* = 9.9 and 4.5 Hz, 1H), 6.83–6.96 (m, 5H), 7.19–7.22 (m, 3H), 7.33–7.38 (m, 2H), 7.44–7.49 (m, 2H), 7.69 (s, 1H), 7.92–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 30.54, 50.21, 52.09, 125.05, 127.67, 127.83, 128.17, 128.48, 128.50, 128.55, 128.68, 129.57, 129.65, 132.87, 133.03, 135.40, 136.03, 137.67, 141.99, 168.49, 199.10; ESIMS *m*/*z* 471 (M^++Na), 473 (M^++2+Na). Anal. Calcd for $C_{25}H_{21}BrO_3$: C, 66.82; H, 4.71. Found: C, 66.97; H, 4.93.
Typical procedure for the preparation of **4a***:* A stirred mixture of **3a** (185 mg, 0.5 mmol), $Pd(OAc)_2$ (12 mg, 10 mol %), TBAB (162 mg, 0.5 mmol), and K_2CO_3 (139 mg, 1.0 mmol) in DMF (1 mL) was heated to 80–90 °C under nitrogen atmosphere for 30 min. After the usual aqueous workup and column chromatographic purification process (hexanes/EtOAc, 20:1), compounds **4a** (78 mg, 54%) and **5a** (10 mg, 7%) were obtained. Other compounds were prepared similarly and the selected spectroscopic data of **4a**, **5a**, **4b**, **5b**, **5e**, **6a**, and **8** are as follows.
Compound **4a**: 54%; white solid, mp 136–138 °C; IR (KBr) 2226, 1732, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.73 (s, 3H), 7.40–7.78 (m, 5H), 7.68–7.78 (m, 2H), 7.98 (s, 1H), 7.98–8.01 (m, 1H), 8.30–8.33 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.60, 112.08, 117.07, 125.43, 125.91, 128.37, 128.47, 128.79, 128.89, 128.97, 129.77, 131.21, 133.93, 134.70, 137.19, 138.65, 168.56; ESIMS *m*/*z* 310 (M^++Na). Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.71; H, 4.66; N, 4.54.
Compound **5a**: 7%; colorless oil; IR (film) 1720, 1241, 1207 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.76 (d, *J* = 18.9 Hz, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 3.26 (d, *J* = 18.9 Hz, 1H), 3.57 (d, *J* = 13.8 Hz, 1H), 3.74 (s, 3H), 6.91–6.94 (m, 2H), 7.17–7.21 (m, 2H), 7.42–7.48 (m, 2H), 7.65–7.70 (m, 2H), 7.80–7.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 44.61, 44.81, 52.79, 54.18, 123.60, 125.96, 127.12, 128.34, 128.93, 129.85, 134.81, 136.10, 136.23, 154.86, 173.76, 203.47; ESIMS *m*/*z* 303 (M^++Na). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.43; H, 5.98.
Compound **4b**: 53%; white solid, mp 83–85 °C; IR (KBr) 2226, 1728, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.01 (t, *J* = 7.2 Hz, 3H), 4.19 (q, *J* = 7.2 Hz, 2H), 7.42–7.48 (m, 5H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.97 (s, 1H), 8.03 (d,

J = 8.1 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.63, 61.88, 111.88, 117.10, 125.39, 125.89, 128.39, 128.53, 128.67, 128.83, 128.92, 129.72, 131.22, 133.92, 134.97, 137.21, 138.73, 167.95; ESIMS m/z 324 (M^++Na).

Compound **5b**: 9%; colorless oil; IR (film) 1720, 1234, 1195 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25 (t, J = 7.2 Hz, 3H), 2.75 (d, J = 18.9 Hz, 1H), 3.19 (d, J = 13.5 Hz, 1H), 3.28 (d, J = 18.9 Hz, 1H), 3.56 (d, J = 13.5 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 6.92–6.97 (m, 2H), 7.15–7.20 (m, 3H), 7.43–7.48 (m, 1H), 7.65–7.70 (m, 2H), 7.80–7.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.04, 44.59, 44.81, 54.17, 61.81, 123.57, 125.93, 127.08, 128.31, 128.87, 129.89, 134.75, 136.21, 136.25, 155.06, 173.23, 203.62; ESIMS m/z 317 (M^++Na).

Compound **5e**: 23%; colorless oil; IR (film) 1732, 1721, 1248, 1236 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.82 (d, J = 18.9 Hz, 1H), 3.49 (d, J = 18.9 Hz, 1H), 3.75 (s, 3H), 4.98 (d, J = 17.1 Hz, 1H), 5.21 (d, J = 10.5 Hz, 1H), 6.39 (dd, J = 17.1 and 10.5 Hz, 1H), 7.46–7.51 (m, 1H), 7.64–7.72 (m, 2H), 7.75–7.79 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 47.21, 53.03, 55.73, 115.45, 123.74, 126.96, 129.00, 134.87, 135.98, 139.08, 153.49, 172.85, 203.18; ESIMS m/z 239 (M^++Na). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.38; H, 5.77.

Compound **6a**: 34%; yellow oil; IR (film) 2240, 1491, 1459, 1261 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.35–3.61 (m, 2H), 4.26 (dd, J = 8.7 and 6.0 Hz, 1H), 7.01 (t, J = 2.4 Hz, 1H), 7.23–7.41 (m, 7H), 7.48–7.52 (m, 1H), 7.62–7.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.72, 36.00, 120.72, 120.77, 121.57, 125.04, 127.23, 128.53, 128.63, 129.10, 129.17, 136.89, 138.30, 138.47, 141.72; ESIMS m/z 254 (M^++Na). Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.13; H, 5.78; N, 5.95.

Compound **8**: 67%; yellow solid; mp 106–108 °C; IR (KBr) 1682, 1596, 1447, 1225 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.36–3.60 (m, 2H), 5.17 (dd, J = 8.4 and 5.1 Hz, 1H), 7.02 (t, J = 2.1 Hz, 1H), 7.09–7.67 (m, 13H), 8.03–8.06 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.98, 50.86, 120.11, 120.59, 125.58, 126.59, 127.88, 128.34, 128.44, 128.59, 128.84, 129.04, 133.34, 136.77, 137.73, 141.35, 142.84, 142.91, 199.27; ESIMS m/z 333 (M^++Na). Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.85; H, 5.92.

10. For the reductive Heck type quenching caused by DMF, see: (a) Zawisza, A. M.; Muzart, J. *Tetrahedron Lett.* **2007**, *48*, 6738–6742; (b) Li, J.; Hua, R.; Liu, T. *J. Org. Chem.* **2010**, *75*, 2966–2970; (c) Legros, J.-Y.; Primault, G.; Toffano, M.; Riviere, M.-A.; Fiaud, J.-C. *Org. Lett.* **2000**, *2*, 433–436; (d) Brenda, M.; Knebelkamp, A.; Greiner, A.; Heitz, W. *Synlett* **1991**, 809–810.
11. For the similar oxidative decyanation of secondary nitriles to ketones, see: (a) Kulp, S. S.; McGee, M. J. *J. Org. Chem.* **1983**, *48*, 4097–4098; (b) Freerksen, R. W.; Selikson, S. J.; Wroble, R. R. *J. Org. Chem.* **1983**, *48*, 4087–4096.