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Regioselective synthesis of poly-substituted naphthalenes via a Pd-catalyzed cyclization of modified Baylis–Hillman adducts: selective 6-*endo* Heck reaction and an aerobic oxidation cascade

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ABSTRACT

Poly-substituted naphthalenes were synthesized via a Pd-catalyzed cyclization of modified Baylis–Hillman adducts having an *o*-bromophenyl acetonitrile moiety at the secondary position, in reasonable yields. The reaction involved a sequential 6-*endo* Heck reaction and an aerobic oxidation process.

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 by various chemical transformations from Baylis–Hillman adducts.[1–3] Although Pd-catalyzed chemical transformations of modified Baylis–Hillman adducts started very recently, they have provided many interesting carbo- and heterocyclic compounds.[2,3]

Recently, we reported a Pd-catalyzed synthesis of tetracyclic indeno[1,2-*a*]indanes from modified Baylis–Hillman adducts, as shown in Scheme 1.[3a] In the reaction, indeno[1,2-*a*]indane was formed as the major product via a Pd-catalyzed 5-*exo*-trig cyclization and aryl C–H activation when the EWG is an ester group (Eq. 1). When the EWG is a nitrile, carbopalladation occurred in a 6-*endo* mode to provide a naphthalene derivative exclusively (Eq. 2). The selectivity between 5-*exo* and 6-*endo* modes was explained based on the change of conformations according to the bulkiness of OTBS moiety and EWG.[3a,4] Based on our previous results we expected that if we replace the bulky OTBS to a small nitrile group the proportion of 6-*endo* carbopalladation would increase irrespective of the size of EWG,[3a,4] and we could obtain poly-substituted naphthalenes[5] as shown in Scheme 1 (Eq. 3).

Thus we decided to examine the Pd-catalyzed cyclizations of modified Baylis–Hillman adducts **3**. The starting materials **3a–f** were prepared by the reactions of cinnamyl bromides **1a–e**[3a,6] and 2-bromoaryl acetonitriles **2** in the presence of K_2CO_3 via the corresponding DABCO salts of **1a–e**, in good to moderate yields (Table 2), as reported.[7] (Scheme 2).

The reactions of **3a** under various conditions were examined, and we observed the formation of four compounds **4a**, **5a**, **6a,** and **7a**, in variable yields as shown in Table 1.[8] When we applied the conditions of Eq. 1 (Scheme 1),[3a] the starting material **3a** was decomposed completely at 110 °C. Thus we examined the reaction at slightly lower temperature (90 °C, entry 1); however, **4a** was isolated in low yield (22%) along with a indeno[1,2-*a*]indane **6a** (11%). The use of K_2CO_3 (entry 2) and tetrabutylammonium bromide (entry 3) increased the yield of **4a**. Although the yield of **4a** was moderate (44–66%) we found that 6-*endo* carbopalladation is a preferred pathway as expected. When the reaction was performed in toluene (entry 4) the yield of **4a** was reasonable (64%) although a somewhat longer reaction time (5 h) was required. Finally, the optimum condition was found to be the one using TBAB in toluene (entry 5) in respects of both the yield of **4a** and the selectivity of products (**4a**/**5a** + **6a** + **7a**). It is interesting to note that the use of Et_3N as a base produced **7a** as the major product (entry 6). Under the influence of such a weak base (Et_3N), further oxidation of **7a** (or **5a**) at the benzylic position to ketone[9] was not observed as in our previous report.[3b]

The mechanism for the formation of **4a–7a** could be postulated, as shown in Scheme 3. The 6-*endo* carbopalladation of the arylpalladium intermediate (**I**) to (**II**) and a following β-H elimination produced the dihydronaphthalene derivative **5a**. Aerobic oxidation of **5a** afforded naphthalene **4a**.[3b] The 5-*exo* carbopalladation of (**I**)

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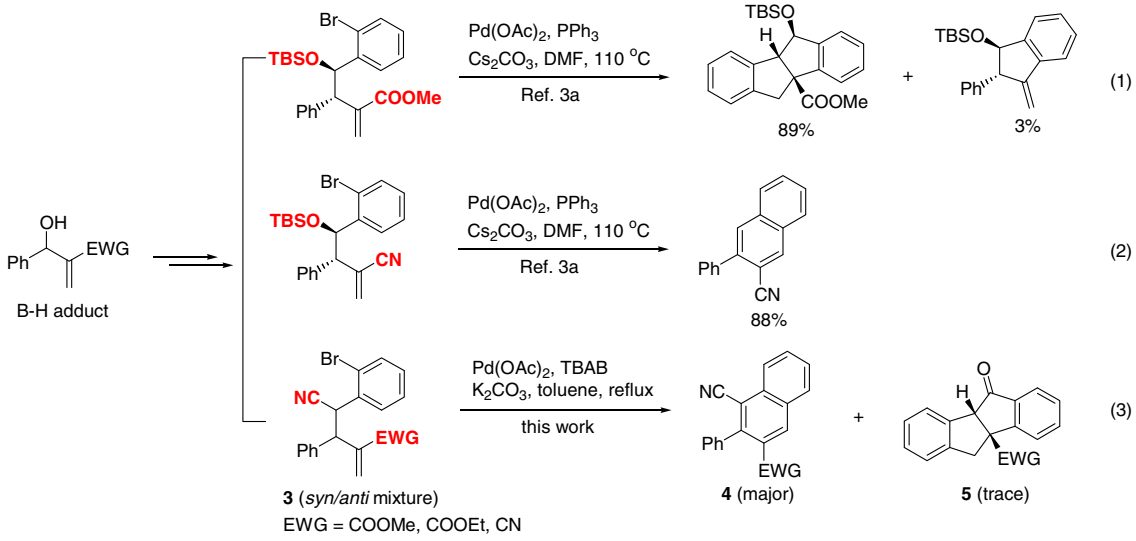


Scheme 1.

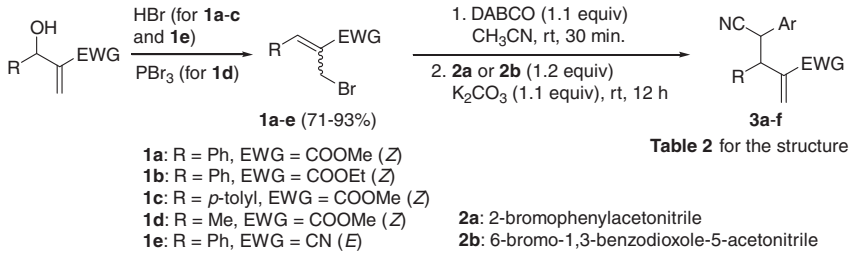
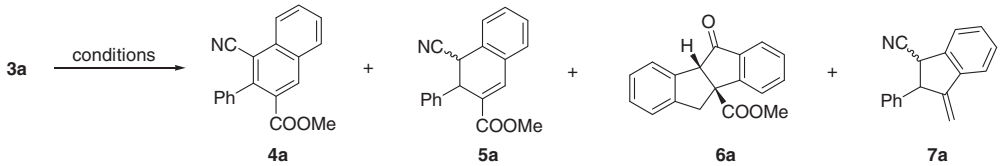


Table 2 for the structure of **3a-f**

Scheme 2.

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



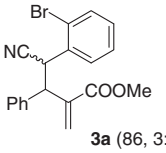
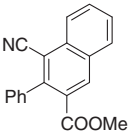
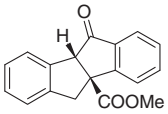
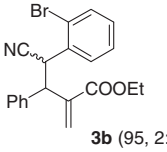
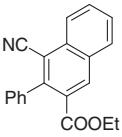
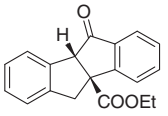
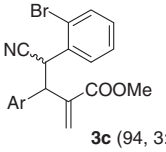
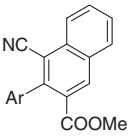
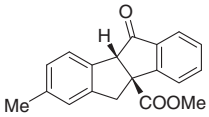
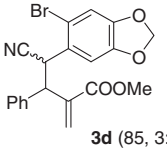
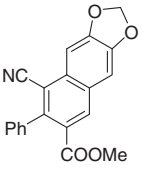
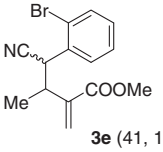
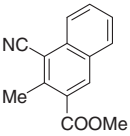
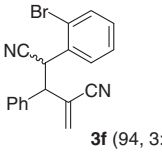
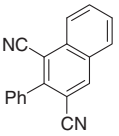
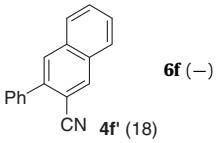
Entry	Conditions	**4a** (%)[b]	**5a** (%)[bc]	**6a** (%)[b]	**7a** (%)[b,c]
1	PPh_3 (10 mol %), Cs_2CO_3 (2.0 equiv), DMF, 90 °C, 30 min	22	0	11	0
2	PPh_3 (10 mol %), K_2CO_3 (2.0 equiv), DMF, 90 °C, 30 min	66	0	6	0
3	TBAB (1.0 mol %), K_2CO_3 (2.0 equiv), DMF, 90 °C, 30 min	44	0	5	0
4	PPh_3 (10 mol %), K_2CO_3 (2.0 equiv), toluene, reflux, 5 h	64	2	5	0
5	TBAB (1.0 mol %), K_2CO_3 (2.0 equiv), toluene, reflux, 3 h	74	0	3	0
6	PPh_3 (10 mol %), Et_3N (1.2 equiv), DMF, 110 °C, 1 h	20	19	0	46

[a] Conditions: $Pd(OAc)_2$ (10 mol %) is common.
[b] Isolated yields.
[c] Mixture of *cis*/*trans*.

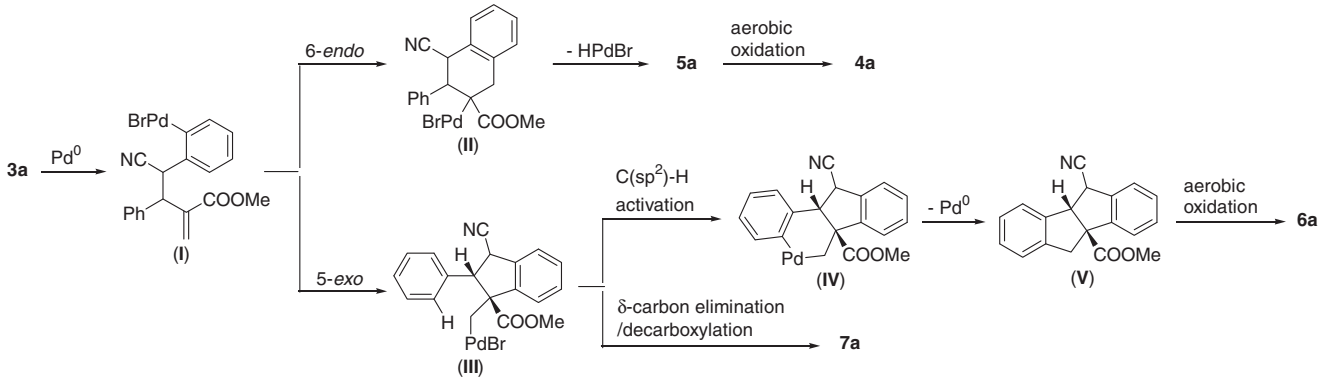
provided an alkylpalladium intermediate (**III**). Aromatic C–H activation[3a] of (**III**) to form (**V**) via the palladacycle (**IV**) and the following base-mediated aerobic oxidation of (**V**) produced an indeno[1,2-*a*]indane **6a**. Similar air oxidation of benzylic cyanides was reported under basic conditions.[9] Competitive δ-carbon elimination and concomitant decarboxylation of (**III**) generated methyleneindane **7a**, as observed many times in similar cases.[3a,3b,10]

Thus we chose the conditions in entry 5 (Table 1) as the best ones and carried out the synthesis of poly-substituted naphthalenes **4a**–**f**, and the results are summarized in Table 2. The reactions of **3b**–**d** showed very similar results with that of **3a**. Naphthalenes **4b**–**d** were obtained in moderate yields (65–79%) along with small amounts of indeno[1,2-*a*]indane derivatives **6b**–**c** (3–5%). The reaction of **3e** produced a somewhat lower yield of **4e** (47%) than other entries. However, the yield of **4e** increased to 61% when the reaction was performed under the conditions of TBAB/K_2CO_3/DMF (entry 3 in Table 1). The reaction of **3f** afforded **4f** (57%) along with a small amount of **4f′** (18%). This compound must be formed via a base-mediated elimination of HCN from the corresponding dihydronaphthalene.

Table 2
Synthesis of naphtahlenes **4a–f**

Entry	Substrate (%)[a]	Products (%)[b]	
1	 **3a** (86, 3:2)	 **4a** (74)	 **6a** (3)
2	 **3b** (95, 2:1)	 **4b** (77)	 **6b** (3)
3[c]	 **3c** (94, 3:2)	 **4c** (79)	 **6c** (5)
4	 **3d** (85, 3:1)	 **4d** (65)	**6d** (–)
5	 **3e** (41, 1:1)[d]	 **4e** (47)[e]	**6e** (–)
6	 **3f** (94, 3:2)	 **4f** (57)	 **6f** (–) **4f'** (18)

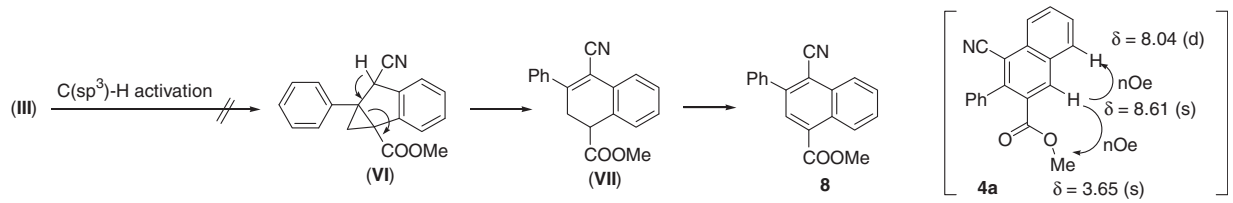
[a] Formed as a *syn*/*anti* mixture and used without separation.
[b] Isolated yield.
[c] Ar is *p*-tolyl.
[d] The yield of **3e** was low (41%) due to the competitive formation of a primary adduct (24%).
[e] Compound **4e** was obtained in 61% under the conditions of entry 3 in Table 1.



Scheme 3.

The structure of **4a** was unequivocally confirmed by NOE experiments, as shown in Scheme 4. From the NOE data of **4a** we could rule out the possibility for the formation of another plausible naphthalene **8**, which could be formed from the intermediate (**III**) via a C(sp^3)–H activation to form the cyclopropane intermediate (**VI**), base-mediated ring-opening to dihydronaphthalene (**VII**), and the following aerobic oxidation process.[3b]

In summary, we disclosed the synthesis of poly-substituted naphthalenes from the modified Baylis–Hillman adducts having an *o*-bromophenyl acetonitrile moiety at the secondary position



Scheme 4.

via a Pd-catalyzed cascade reaction in reasonable yields. Further studies on the reaction progress and mechanistic details are underway.[11]

Acknowledgment

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7. For the introduction of nucleophiles at the secondary position of Baylis–Hillman adducts using DABCO salt concept, see: (a) Chung, Y. M.; Gong, J. H.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2001**, *42*, 9023–9026; (b) Lee, K. Y.; Gowrisankar, S.; Lee, Y. J.; Kim, J. N. *Tetrahedron* **2006**, *62*, 8798–8804. and further references cited therein.
8. *Typical procedure for the synthesis 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 toluene (1.0 mL) was heated to reflux for 3 h. After the usual aqueous workup and column chromatographic purification process (hexanes/EtOAc, 20:1), compounds **4a** (106 mg, 74%) and **6a**[3a] (4 mg, 3%) were obtained. Other compounds were prepared similarly, and the selected spectroscopic data of **4a**, **4b**, **4d**, **4f**, **6c**, and **7a** are as follows.
Compound **4a**: 74% yield; white solid, mp 167–169 °C; IR (KBr) 2223, 1731, 1299, 1212 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.65 (s, 3*H*), 7.39–7.56 (m, 5*H*), 7.70 (t, *J* = 8.1 Hz, 1*H*), 7.82 (t, *J* = 8.4 Hz, 1*H*), 8.04 (d, *J* = 8.1 Hz, 1*H*), 8.34 (d, *J* = 8.4 Hz, 1*H*), 8.61 (s, 1*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.41, 111.77, 116.38, 125.60, 128.24 (2C), 128.66, 128.73, 129.39, 129.45, 130.87, 131.16, 133.64, 135.14, 137.76, 145.25, 167.07; ESIMS *m*/*z* 288 (M^++1). Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.66; H, 4.78; N, 4.65.
Compound **4b**: 77% yield; white solid, mp 79–81 °C; IR (KBr) 2222, 1720, 1239, 1209 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, *J* = 7.2 Hz, 3*H*), 4.10 (q, *J* = 7.2 Hz, 2*H*), 7.40–7.51 (m, 5*H*), 7.71 (t, *J* = 8.1 Hz, 1*H*), 7.82 (t, *J* = 8.4 Hz, 1*H*), 8.04 (d, *J* = 8.1 Hz, 1*H*), 8.33 (d, *J* = 8.4 Hz, 1*H*), 8.60 (s, 1*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.57, 61.53, 111.66, 116.45, 125.60, 128.20, 128.23, 128.60, 128.84, 129.39, 130.03, 130.78, 131.21, 133.59, 135.04, 138.00, 145.15, 166.93; ESIMS *m*/*z* 302 (M^++1). Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.81; H, 5.31; N, 4.56.
Compound **4d**: 65% yield; white solid, mp 191–193 °C; IR (KBr) 2220, 1709, 1465, 1246 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.63 (s, 3*H*), 6.18 (s, 2*H*), 7.26 (s, 1*H*), 7.35–7.51 (m, 5*H*), 7.61 (s, 1*H*), 8.41 (s, 1*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.28, 102.19, 102.29, 104.91, 110.76, 116.80, 127.52, 128.15, 128.47, 128.69, 128.77, 132.46, 133.74, 138.02, 143.68, 149.41, 152.05, 167.12; ESIMS *m*/*z* 332 (M^++1). Anal. Calcd for $C_{20}H_{13}NO_4$: C, 72.50; H, 3.95; N, 4.23. Found: C, 72.86; H, 4.09; N, 4.18.
Compound **4f**: 57% yield; white solid, mp 208–210 °C; IR (KBr) 2228, 1492 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.56–7.65 (m, 5*H*), 7.77 (t, *J* = 8.1 Hz, 1*H*), 7.91 (t, *J* = 8.4 Hz, 1*H*), 8.04 (d, *J* = 8.4 Hz, 1*H*), 8.38 (d, *J* = 8.4 Hz, 1*H*), 8.54 (s, 1*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 111.08, 111.63, 115.67, 116.96, 125.94, 128.92, 128.99, 129.04, 129.52, 130.14, 130.96, 132.10, 133.91, 134.87, 139.30, 146.10; ESIMS *m*/*z* 255 (M^++1). Anal. Calcd for $C_{18}H_{10}N_2$: C, 85.02; H, 3.96; N, 11.02. Found: C, 84.87; H, 4.13; N, 10.89.
Compound **6c**: 5% yield; colorless oil; IR (film) 1732, 1719, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.27 (s, 3*H*), 3.45 (d, *J* = 17.4 Hz, 1*H*), 3.71 (s, 3*H*), 3.99 (d, *J* = 17.4 Hz, 1*H*), 4.59 (s, 1*H*), 6.95 (s, 1*H*), 7.03 (d, *J* = 7.8 Hz, 1*H*), 7.40–7.46 (m, 2*H*), 7.61–7.72 (m, 3*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.23, 42.56, 52.93, 59.63, 62.71, 124.40, 124.42, 125.40, 125.48, 128.30, 129.15, 134.84, 135.09, 135.45, 138.26, 140.63, 155.24, 173.84, 203.38; ESIMS *m*/*z* 293 (M^++1). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.19; H, 5.76.
Compound **7a**: Major isomer (36% yield): pale yellow oil; IR (film) 2239, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.19 (d, *J* = 7.5 Hz, 1*H*), 4.40 (dt, *J* = 7.5 and 2.4 Hz, 1*H*), 4.85 (d, *J* = 2.4 Hz, 1*H*), 5.66 (d, *J* = 2.4 Hz, 1*H*), 7.28–7.60 (m, 9*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.65, 55.98, 107.36, 120.10, 121.32, 124.77, 127.81, 128.37, 128.97, 129.27, 129.86, 137.38, 139.71, 140.09, 149.65; ESIMS *m*/*z* 232 (M^++1). Minor isomer (10% yield): pale yellow oil; IR (film) 2242, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.47 (dt, *J* = 9.0 and 1.8 Hz, 1*H*), 4.62 (d, *J* = 9.0 Hz, 1*H*), 5.04 (d, *J* = 1.8 Hz, 1*H*), 5.71 (d, *J* = 1.8 Hz, 1*H*), 7.21–7.63 (m, 9*H*); ESIMS *m*/*z* 232 (M^++1).
During the evaluation process one of the reviewers suggested that we carry out the reaction of **3a** under the PEG-catalyzed conditions. The reaction of **3a** in DMF (90 °C, 30 min) under the influence of $Pd(OAc)_2$/PEG-3400/K_2CO_3 showed a similar result in entry 2 in Table 1 (65% of **4a** and 5% of **6a**).
9. 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.
10. For the similar examples on δ-carbon elimination, see: (a) Kim, H. S.; Lee, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 3154–3157; (b) Kim, H. S.; Gowrisankar, S.; Kim, E. S.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 6569–6572; (c) Kim, H. S.; Gowrisankar, S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 3858–3861.

11. In order to get some insights, we ran the reactions with major-**3a** and minor-**3a** separately. The products distributions were somewhat different with each other, although syn and anti derivatives showed the same reactivity in our previous synthesis of naphthalenes from OTBS derivatives (Eq. 2 in Scheme 1).[3a] Thus confirmation of the stereochemistry of starting materials **3** and the studies on the difference of reactivity are currently underway.