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Regioselective Synthesis of Fluorenones *via* the Consecutive In-Mediated Barbier Reaction, Pd-Catalyzed Cyclization, and Friedel-Crafts Reaction Starting from Baylis-Hillman Adducts

Ko Hoon Kim, Sung Hwan Kim, Ka Young Lee,† and Jae Nyoung Kim*

Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea
**E-mail: kimjn@chonnam.ac.kr*
†Document and Image Division, National Forensic Service, Seoul 158-707, Korea
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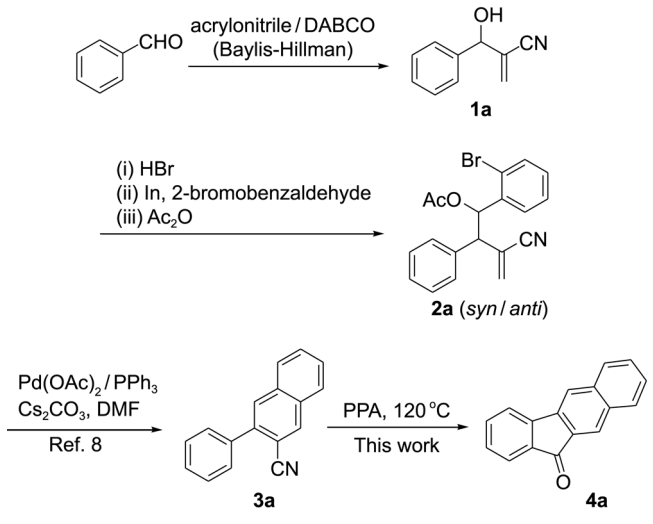
Recently, various kinds of aromatic compounds have been synthesized from Baylis-Hillman adducts including benzenes, naphthalenes, pyridines, quinolines, pyrroles, and furans.[1,2] During our continuous efforts on the synthesis of regioselectively-substituted aromatic compounds from Baylis-Hillman adducts,[2] we decided to develop an efficient synthetic approach of fluorenone derivatives. Our synthetic approach of benzo[*b*]fluoren-11-one (**4a**) is schematically depicted in Scheme 1, as a representative example.

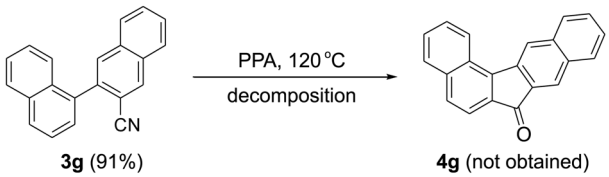
Fluorenone subunits have received much attention because of their occurrence in many bioactive substances.[3] Typically, fluorenone and its derivatives have been synthesized using a palladium-catalyzed cyclization,[4] Friedel-Crafts reaction,[5] and a [4+2] cycloaddition approach.[6] Among the numerous approaches,[4-7] the use of Friedel-Crafts reaction is the most promising approach when the precursor is readily available. Very recently, we found a facile synthetic method of 3-phenylnaphthalene-2-carbonitrile (**3a**) from Baylis-Hillman adduct *via* a Pd-catalyzed 6-*endo* cyclization.[8] The naphthalene could be used as a suitable precursor for the construction of fluorenone derivative. Herein we described the synthesis of various fluorenone derivatives from the corresponding naphthalene precursors *via* a Friedel-Crafts reaction.



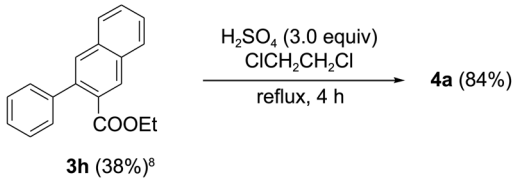
Scheme 1

As shown in Scheme 1, the required naphthalene **3a** was prepared according to the reported palladium-catalyzed cyclization of **2a**,[8] which was prepared from the Baylis-Hillman adduct **1a** in three steps in good yield. Acid-catalyzed Friedel-Crafts reaction of **3a** was examined, and the use of PPA (polyphosphoric acid) was found to be the best choice.[9] Encouraged by the successful results, we prepared various naphthalenes (**3b**, **3e**) and phenanthrenes (**3c**, **3d**, **3f**) in good yields according to the reported method.[8] With these starting materials, syntheses of the corresponding fluorenone derivatives **4b-f** were performed under the influence of PPA (120 °C, 12 h). Various fluorenones were obtained in good yields. In addition all of the fluorenones were obtained in analytically pure state by simple extractive workup with $CHCl_3$. This point is very important in a practical sense. The solubility of carbon-rich fluorenone derivative is rather limited in most organic solvents, thus a synthetic method free from column chromatographic purification process is highly required. It is interesting to note that only single regioisomer was formed for the naphthalene derivatives **3e** and **3f** (entries 5 and 6). The 1-position of the naphthalene moiety reacted selectively to provide **4e** and **4f**.[9a]

As a next entry, we examined the Friedel-Crafts reaction of **3g** (Scheme 2); however, we could not obtain any trace amount of **4g**. Intractable polar spots were observed on TLC.

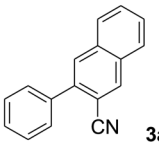
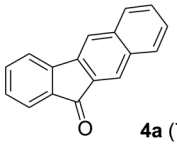
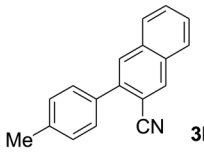
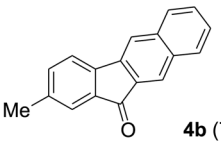
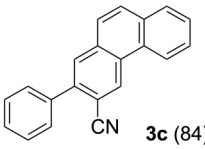
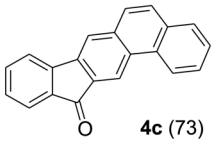
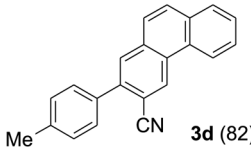
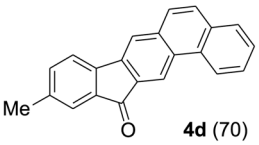
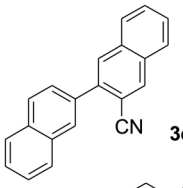
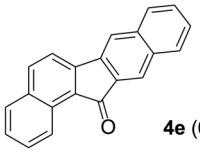
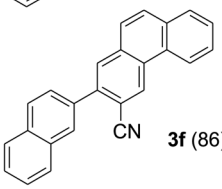
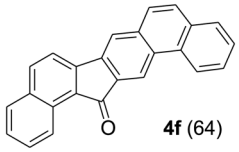


Scheme 2



Scheme 3

Table 1. Synthesis of fluorenone derivatives

Entry	Substrate (%)[a]	Product (%)[b]
1	 **3a** (88)	 **4a** (76)
2	 **3b** (83)	 **4b** (75)
3	 **3c** (84)	 **4c** (73)
4	 **3d** (82)	 **4d** (70)
5	 **3e** (91)	 **4e** (69)
6	 **3f** (86)	 **4f** (64)

[a]Prepared from the corresponding homoallylic acetate **2** under the influence of $Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %), Cs_2CO_3 (2.0 equiv), DMF, 110 °C, 1 h. [b]Conditions: PPA, 120 °C, 12 h.

From the results, the 2-position of naphthalene moiety was found to be much less reactive than the 1-position in Friedel-Crafts reaction.[9a]

Synthesis of benzo[*b*]fluoren-11-one (**4a**) from the ester derivative **3h** was also carried out under the influence of H_2SO_4 in 84%, as shown in Scheme 3. However, the yield of **3h** was much lower than the nitrile derivative **3a**,[8] thus we used nitrile derivatives throughout the whole entries in Table 1.

In summary, we disclosed an efficient synthesis of various fluorenone derivatives in high yields *via* the Friedel-Crafts reaction in PPA. The required starting materials were prepared easily from Baylis-Hillman adduct *via* the following four steps: bromination, indium-mediated Barbier reaction with aldehyde, acetylation, and Pd-catalyzed cyclization.

Experimental Section

Typical Procedure for the Synthesis of 3a.[8] The Baylis-Hillman adduct **1a** was converted to a cinnamyl bromide derivative, 2-(bromomethyl)-3-phenylacrylonitrile, by treatment with aqueous HBr as reported.[1,2,8] To a stirred solution of 2-(bromomethyl)-3-phenylacrylonitrile (222 mg, 1.0 mmol, *E*/*Z* = 9:1) and 2-bromobenzaldehyde (203 mg, 1.1 mmol) in aqueous THF (1:1, 3 mL) was added indium powder (125 mg, 1.1 mmol) and stirred at room temperature for 1 h. The reaction mixture was poured into water (10 mL), extracted with diethyl ether (30 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to obtain crude homoallylic alcohol. To a stirred solution of this crude homoallylic alcohol in CH_2Cl_2 (3 mL) acetic anhydride (102 mg, 1.0 mmol), pyridine (158 mg, 2.0 mmol), and DMAP (12 mg, 0.1 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by column chromatographic purification process (hexanes/EtOAc, 10:1) to afford **2a** as colorless oil, 236 mg (overall 64%). A solution of **2a** (148 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 10 mol %), PPh_3 (21 mg, 20 mol %), and Cs_2CO_3 (260 mg, 0.8 mmol) in DMF (2 mL) was heated to 110 °C for 1 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature, quenched with water (10 mL), and extracted with diethyl ether (30 mL × 3). The combined organic layers were washed with dilute HCl solution, brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatographic purification process (hexanes/EtOAc, 15:1) to afford compound **3a** (81 mg, 88%) as a yellow solid.[8] Other compounds were prepared similarly, and the spectroscopic data of unknown compounds **3b-g** are as follows.

Compound 3b: 83%; pale yellow solid, mp 122-124 °C; IR (KBr) 3018, 2222 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, 3H), 7.29-7.32 (m, 2H), 7.51-7.65 (m, 4H), 7.85-7.89 (m, 3H), 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.20, 109.52, 118.99, 127.31, 127.96, 128.01, 128.84 (2C), 129.26, 129.36, 131.03, 134.74, 135.34, 135.80, 138.35, 139.61; ESIMS *m/z* 244 (M^++H). Anal. Calcd for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.65; H, 5.53; N, 5.61.

Compound 3c: 84%; white solid, mp 188-190 °C; IR (KBr) 3055, 2223 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.43-7.55 (m, 3H), 7.61-7.72 (m, 5H), 7.81-7.89 (m, 3H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 109.26, 119.27, 122.50, 126.02, 127.70, 127.75, 128.56, 128.65, 128.72, 128.84, 128.95, 129.06, 129.52, 129.87, 130.62, 132.06, 134.30, 138.00, 141.14; ESIMS *m/z* 280 (M^++H). Anal. Calcd for $C_{21}H_{13}N$: C, 90.29; H, 4.69; N, 5.01. Found: C, 90.03; H, 4.77; N, 4.93.

Compound 3d: 82%; pale yellow solid, mp 180-182 °C; IR (KBr) 3020, 2225 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 7.32-7.35 (m, 2H), 7.57-7.59 (m, 2H), 7.64-7.75 (m, 3H), 7.85-7.93 (m, 3H), 8.60 (d, *J* = 7.8 Hz, 1H), 9.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.26, 109.36, 119.42, 122.53, 126.09, 127.65, 127.76, 128.57, 128.84, 128.86, 129.17, 129.40, 129.47, 129.88, 130.59, 132.07, 134.39, 135.16, 138.56, 141.28; ESIMS *m/z* 294 (M^++H).

Anal. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77. Found: C, 89.88; H, 5.42; N, 4.56.

Compound 3e: 91%; pale yellow solid, mp 199-200 °C; IR (KBr) 3054, 2222 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.50-7.57 (m, 2H), 7.58-7.68 (m, 2H), 7.74 (dd, *J* = 8.4 and 1.8 Hz, 1H), 7.89-8.00 (m, 6H), 8.09 (s, 1H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 109.62, 118.93, 126.53, 126.62, 126.64, 127.52, 127.70, 128.04, 128.10, 128.34 (2C), 128.40, 129.40 (2C), 131.18, 132.97, 133.21, 134.74, 135.63, 135.97, 139.54; ESIMS *m/z* 280 (M^++H). Anal. Calcd for $C_{21}H_{13}N$: C, 90.29; H, 4.69; N, 5.01. Found: C, 90.34; H, 4.86; N, 5.24.

Compound 3f: 86%; pale yellow solid, mp 218-220 °C; IR (KBr) 3052, 2223 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53-7.56 (m, 2H), 7.65-7.81 (m, 4H), 7.87-8.04 (m, 6H), 8.14 (s, 1H), 8.62 (d, *J* = 8.1 Hz, 1H), 9.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 109.51, 119.35, 122.59, 126.10, 126.56, 126.58, 126.70, 127.73, 127.76, 127.83, 128.40 (2C), 128.51, 128.76, 128.90, 129.15, 129.88, 130.03, 130.74, 132.15, 133.05, 133.25, 134.40, 135.41, 141.16; ESIMS *m/z* 330 (M^++H). Anal. Calcd for $C_{25}H_{15}N$: C, 91.16; H, 4.59; N, 4.25. Found: C, 90.98; H, 4.87; N, 4.21.

Compound 3g: 91%; sticky solid; IR (KBr) 3056, 2224 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42 (ddd, *J* = 8.4, 6.9 and 1.5 Hz, 1H), 7.49-7.71 (m, 6H), 7.87-7.99 (m, 5H), 8.40 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 111.56, 118.29, 125.17, 125.34, 126.08, 126.56, 127.66, 127.85, 128.10, 128.18, 128.48, 129.08, 129,42, 130.58, 131.45, 131.86, 133.67, 134.42, 135.14, 135.95, 138.34; ESIMS *m/z* 280 (M^++H). Anal. Calcd for $C_{21}H_{13}N$: C, 90.29; H, 4.69; N, 5.01. Found: C, 90.45; H, 4.90; N, 4.94.

Typical Procedure for the Synthesis of 4a. A mixture of **3a** (69 mg, 0.3 mmol) and PPA (1.0 mL) was heated to 120 °C for 12 h. The reaction mixture was allowed to cool to room temperature, quenched with water (15 mL), and extracted with $CHCl_3$ (30 mL × 5). The combined organic layers were washed with dilute $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated under vacuum to afford compound **4a** (52 mg, 76%) as a yellow solid.[4c,7a,d] Other compounds were synthesized similarly, and the spectroscopic data of unknown compounds **4b-f** are as follows.

Compound 4b: 75%; pale yellow solid, mp 158-160 °C; IR (KBr) 2963, 1697, 1633 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.38-7.53 (m, 4H), 7.71-7.83 (m, 3H), 8.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.35, 118.44, 120.73, 124.81, 125.43, 126.61, 128.59, 128.81, 130.68, 133.02, 133.35, 135.64, 136.32, 136.90, 138.47, 139.34, 142.24, 193.23; ESIMS *m/z* 245 (M^++H). Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.32; H, 5.16.

Compound 4c: 73%; pale yellow solid, mp 212-214 °C; IR (KBr) 3051, 1712, 1627 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.29 (ddd, *J* = 7.5, 7.5 and 0.9 Hz, 1H), 7.46-7.70 (m, 6H), 7.74-7.83 (m, 3H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 119.79, 119.82, 120.77, 122.80, 124.35, 126.95, 127.05, 127.36, 128.73, 129.12, 129.97, 130.63, 131.33, 132.16, 132.71, 134.86, 135.82, 136.37, 140.09, 144.56, 193.39; ESIMS *m/z* 281 (M^++H). Anal. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.31. Found: C, 89.87; H, 4.65.

Compound 4d: 70%; pale yellow solid, mp 222-224 °C; IR (KBr) 2917, 1701, 1611 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.46-7.48 (m, 2H), 7.54-7.58 (m, 1H), 7.61-7.65 (m, 2H), 7.74-7.77 (m, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 8.59 (d, *J* = 8.1 Hz, 1H), 8.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.36, 119.38, 119.68, 120.59, 122.76, 124.90, 126.91, 126.96, 127.32, 128.71, 129.85, 130.33, 131.40, 132.10, 133.01, 135.46, 136.07, 136.42, 139.37, 140.31, 142.00, 193.62; ESIMS *m/z* 295 (M^++H). Anal. Calcd for $C_{22}H_{14}O$: C, 89.77; H, 4.79. Found: C, 89.49; H, 5.02.

Compound 4e: 69%; pale yellow solid, mp 198-200 °C; IR (KBr) 2962, 1697, 1633 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40-7.53 (m, 3H), 7.58-7.63 (m, 1H), 7.74-7.85 (m, 5H), 7.98-8.05 (m, 2H), 9.05 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 109.71, 118.43, 118.85, 124.56, 124.98, 126.70, 126.94, 128.49, 128.81 (2C), 129.41, 130.12, 130.76, 133.38, 133.90, 134.20, 136.19, 136.70, 138.04, 146.44, 194.11; ESIMS *m/z* 281 (M^++H). Anal. Calcd for $C_{21}H_{12}O$: C, 89.98; H, 4.31. Found: C, 90.17; H, 4.09.

Compound 4f: 64%; pale yellow solid, mp 278-280 °C; IR (KBr) 3044, 1697, 1631 cm^{-1}; ^1H NMR ($CDCl_3/CS_2$ = 5:1, 300 MHz) δ 7.40-7.45 (m, 1H), 7.55-7.58 (m, 2H), 7.63-7.85 (m, 7H), 8.00 (d, *J* = 8.1 Hz, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.83 (s, 1H), 9.01 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR was not obtained because of poor solubility; ESIMS *m/z* 331 (M^++H). Anal. Calcd for $C_{25}H_{14}O$: C, 90.89; H, 4.27. Found: C, 90.57; H, 4.54.

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