Supporting Information

Synthesis of 4*H*-Benz[*de*]anthracen-4-ones via 1,2-Addition of Metal Acetylides to Benzanthrone

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1. General

FT-IR spectra were recorded on a JASCO FT/IR-4100 instrument. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz on a JEOL AL400 or ECS400. Chemical shifts were reported in ppm relative to tetramethylsilane or residual solvent as the internal standard. Mass spectral analyses were performed on a JEOL JMS-700 spectrometer for EI and FAB ionization. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm x 20 mm JAIGEL-1H and 2H GPC columns with CHCl_3 as an eluent. All reagents were obtained from commercial suppliers and used without purification.

2. Investigation of Effect of Additive Procedure for Formation 3a from 2a (Table 1)

Entry	Additive	Solvent	Result
1	acidic SiO_2	CHCl_3	proceed
2 ^a	acidic SiO_2	CHCl_3	proceed
3	neutral SiO_2	CHCl_3	proceed
4	acidic SiO_2	CHCl_3 ; Et_3N (9 : 1)	recover
5	neutral Al_2O_3	CHCl_3	proceed
6	basic Al_2O_3	CHCl_3	recover
7	-	CHCl_3	recover
8	aq. HCl ^b	CHCl_3	decompose

^a Under N_2 .

^b A small portion of dilute aq. HCl was added.

A solution of benzanthrone (**1**) (230 mg, 1.0 mmol) in THF (8.0 mL) was added to a solution of lithium acetylide (1.2 mmol), which was prepared from *n*-BuLi (1.2 mmol, 0.75 mL; 1.6 M in hexane solution) and phenylacetylene (1.2 mmol, 123 mg) in THF (2.0 mL) at $-78\text{ }^\circ\text{C}$ for 30 min. After being stirred at $0\text{ }^\circ\text{C}$ for 6 h, to the reaction mixture was added water, then the resulting mixture was extracted several times with ethyl acetate. The organic fraction was washed with brine and dried over MgSO_4 . After removal of the drying agent and solvent, the reaction mixture including **2a** was diluted with *Solvent* (30 mL) and added *Additive* (10 g) or a small portion of dilute aq. HCl (for entry 8). The solution was stirred under air or N_2 (for entry 2) at room temperature for 5 h. After removal of *Additive*, the organic solution was concentrated under reduced pressure and the residue was measured by ^1H NMR.

When the silica gel loading was decreased to 1 g, the reaction partially proceeded to form **3a**.

3. General Procedure for Synthesis of 4*H*-benz[*de*]anthracen-4-ones **3** (Table 2)

A solution of benzanthrone (**1**) (230 mg, 1.0 mmol) in THF (8.0 mL) was added to a solution of lithium acetylide (1.2 mmol), which was prepared from *n*-BuLi (1.2 mmol, 0.75 mL; 1.6 M in hexane solution) and the corresponding terminal alkynes (1.2 mmol) in THF (2.0 mL) at -78 °C for 30 min. After stirring at 0 °C for 6 h, to the reaction mixture was added water, then the resulting mixture was extracted several times with ethyl acetate. The organic fraction was washed with brine and dried over MgSO₄. After removal of the drying agent and solvent, the reaction mixture including **2** was diluted with CHCl₃ (30 mL) and added acidic silica gel (10 g). The solution was stirred under air at room temperature for 5 h. After removal of the silica gel, the organic solution was concentrated under reduced pressure and the residue was purified by chromatography on silica gel followed by a recyclable preparative HPLC to give **3**.

2a: ¹H NMR (400 MHz, CDCl₃) δ 8.39 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H), 8.30-8.28 (m, 1H), 8.24 (d, *J* = 6.8 Hz, 1H), 8.19-8.17 (m, 1H), 7.93 (dd, *J* = 0.8 Hz, 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 7.2 Hz, 8.0 Hz, 1H), 7.61 (dd, *J* = 7.6 Hz, 8.0 Hz, 1H), 7.52-7.46 (m, 4H), 7.34-7.30 (m, 3H), 2.76 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.2, 135.8, 133.2, 131.7, 130.2, 129.2, 129.1, 129.0, 128.61, 128.55, 128.2, 127.7, 127.1, 126.6, 126.3, 124.8, 123.2, 122.5, 120.7, 92.2, 87.5, 68.9. (one signal of aromatic carbon missing due to overlap)

3a: Yellow solid; mp 211-213 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.78 (d, *J* = 8.0, Hz, 1 H), 8.57-8.51 (m, 3 H), 8.40 (d, *J* = 10.0 Hz, 1 H), 7.80 (dd, *J* = 8.0, 7.6 Hz, 1 H), 7.74-7.65 (m, 4 H), 7.48-7.46(m, 3 H), 6.76 (d, *J* = 10.0 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 185.4, 140.0, 131.9, 130.8, 130.7, 129.5, 129.4, 129.2, 128.73, 128.66, 128.6, 128.0, 127.94, 127.92, 127.8, 126.4, 125.6, 122.9, 122.3, 104.0, 85.0 (two signals of aromatic carbon missing due to overlap); IR (KBr) 3063, 2198, 1638, 1581, 1516, 1490, 1442, 1332, 1292, 1217, 1167, 1025, 914, 818, 751 cm⁻¹; MS (EI): *m/z* 330 (M⁺); HRMS (EI): calcd for C₂₅H₁₄O : 330.1045. found 330.1031.

3b: Yellow solid; mp 217-219 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, *J* = 7.6 Hz, 1 H), 8.46 (dd, *J* = 7.4, 1.0 Hz, 1 H), 8.42 (d, *J* = 8.0 Hz, 1 H), 8.39 (dd, *J* = 7.8, 1.0 Hz, 1 H), 8.25 (d, *J* = 10.0 Hz, 1 H), 7.69 (dd, *J* = 8.0, 7.6 Hz, 1 H), 7.65-7.58 (m, 2 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 6.66 (d, *J* = 10.0 Hz, 1 H), 2.43 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 185.3, 139.8, 131.7, 130.7, 130.6, 129.4, 129.2, 129.0, 128.9, 128.54, 128.52, 128.50, 127.73, 127.71, 127.6, 127.5, 126.3, 125.8, 122.7, 119.3, 104.4, 100.5, 84.5, 21.7; IR (KBr) 3063, 2196, 1628, 1578, 1557, 1518, 1482, 1460, 1425, 1332, 1291, 1218, 1165, 1122, 1030, 992, 815, 749 cm⁻¹; MS (FAB): *m/z* 345 (M+H⁺); HRMS (FAB): calcd for C₂₆H₁₇O : 345.1279. found 345.1303.

3c: Yellow solid; mp 185-187 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.65 (d, $J = 7.6$ Hz, 1 H), 8.47 (dd, $J = 7.6$, 1.2 Hz, 1 H), 8.44 (d, $J = 7.6$ Hz, 1 H), 8.40 (dd, $J = 7.8$, 1.2 Hz, 1 H), 8.27 (d, $J = 10.0$ Hz, 1 H), 7.70 (dd, $J = 8.0$, 7.6 Hz, 1 H), 7.66-7.57 (m, 4 H), 6.96-6.92 (m, 2 H), 6.68 (d, $J = 10.0$ Hz, 1 H), 3.88 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.3, 160.6, 139.9, 133.5, 130.7, 130.6, 129.2, 129.1, 128.8, 128.6, 128.5, 127.7, 127.42, 127.39, 126.4, 126.1, 122.7, 114.4, 114.3, 104.6, 84.2, 55.4 (two signals of aromatic carbon missing due to overlap); IR (KBr) 3072, 3008, 2959, 2927, 2833, 2194, 1636, 1611, 1583, 1516, 1462, 1442, 1351, 1332, 1292, 1251, 1219, 1172, 1124, 1107, 1032, 994, 822, 752 cm^{-1} ; MS (FAB): m/z 360 ($\text{M}+\text{H}^+$); HRMS (FAB): calcd for $\text{C}_{26}\text{H}_{17}\text{O}_2$: 361.1229. found 361.1231.

3e: Yellow solid; mp 264-266 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.95 (dd, $J = 8.0$, 0.8 Hz, 1 H), 8.72 (dd, $J = 8.0$, 0.8 Hz, 1 H), 8.64 (dd, $J = 7.2$, 1.2 Hz, 1 H), 8.58 (dd, $J = 8.0$, 1.2 Hz, 1 H), 8.48 (d, $J = 10.0$ Hz, 1 H), 7.93 (dd, $J = 8.0$, 7.6 Hz, 1 H), 7.86-7.76 (m, 6 H), 6.87 (d, $J = 10.0$ Hz, 1 H); ^{13}C NMR data could not be obtained due to quite low solubility; IR (KBr) 3034, 2225, 1644, 1602, 1583, 1557, 1517, 1500, 1459, 1406, 1355, 1333, 1292, 1263, 1218, 1174, 1121, 840, 822, 764, 752 cm^{-1} ; MS (FAB): m/z 356 ($\text{M}+\text{H}^+$); HRMS (FAB): calcd for $\text{C}_{26}\text{H}_{14}\text{ON}$: 356.1030. found 356.1050.

3f: Orange oil; ^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, $J = 8.4$ Hz, 1 H), 8.55 (d, $J = 7.6$ Hz, 2 H), 8.46 (d, $J = 8.0$ Hz, 1 H), 8.36 (d, $J = 10.0$ Hz, 1 H), 7.78 (dd, $J = 7.6$, 8.0 Hz, 1 H), 7.73-7.64 (m, 2 H), 6.75 (d, $J = 10.0$ Hz, 1 H), 2.70 (t, $J = 7.0$ Hz, 2 H), 1.88-1.79 (m, 2 H), 1.20 (t, $J = 7.6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.6, 140.4, 131.1, 130.8, 129.2, 129.1, 128.9, 128.8, 128.6, 128.4, 127.9, 127.7, 127.4, 126.9, 126.5, 122.8, 106.2, 22.20, 22.15, 13.9 (two signals of aromatic carbon missing due to overlap); IR (KBr) 3066, 2961, 2932, 2871, 2216, 1668, 1636, 1607, 1586, 1557, 1517, 1483, 1460, 1445, 1427, 1350, 1332, 1293, 1246, 1203, 1175, 1154, 1134, 1106, 847, 823, 781, 762, 751 cm^{-1} ; MS (FAB): m/z 297 ($\text{M}+\text{H}^+$); HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{17}\text{O}$: 297.1235. found 297.1264.

4. ^1H and ^{13}C NMR Spectra of 2a, 3a-c, 3e, and 3f

Fig. S1 ^1H (400 MHz) and ^{13}C -NMR (100 MHz) spectra of crude 2a in CDCl_3

Fig. S2 ^1H (400 MHz) and ^{13}C -NMR (100 MHz) spectra of **3a** in CDCl_3

Fig. S3 ^1H (400 MHz) and ^{13}C -NMR (100 MHz) spectra of **3b** in CDCl_3

6-ethynyl-(4-CH3OC6H4)-BA.als
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 1H
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 OBSET 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7992.01 Hz
 SCANS 32
 ACQTM 4.1001 sec
 PD 2.9000 sec
 PW1 6.50 usec
 IRNUC 1H
 CTMP 22.9 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 13

auto

6-ethynyl-(4-CH3OC6H4)-BA 13C.als
 auto
 Sat Oct 23 10:43:56 2010
 13C
 BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27118.64 Hz
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 ACQTM 1.2083 sec
 PD 1.7920 sec
 PW1 5.70 usec
 IRNUC 1H
 CTMP 23.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 24

Fig. S4 ¹H (400 MHz) and ¹³C-NMR (100 MHz) spectra of 3c in CDCl₃

S9

auto

F:\ヘテロ原子化学研究室\測定DATA\NMR\400NMR\1H\単離\6-ethynyl-3f-ethynyl\H7-BA.als

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RGAIN 15

auto

F:\ヘテロ原子化学研究室\測定DATA\NMR\400NMR\1H\単離\6-ethynyl-3f-ethynyl\3H7-BA 13C.als

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IRNUC 1H
CTEMP 14.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25

Fig. S6 ^1H (400 MHz) and ^{13}C -NMR (100 MHz) spectra of **3f** in CDCl_3