Supporting Information

Lewis Acid-Catalyzed Benzannulation via Unprecedented [4+2] Cycloaddition of *o*-Alkynyl(oxo)benzenes and Enynals with Alkynes

Naoki Asao,* Tsutomu Nogami, Sunyoung Lee, and Yoshinori Yamamoto*

*Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578, Japan*

2-Methyl-3-phenylnaphthalene (5a).¹ Colorless liquid; ¹H-NMR (CDCl₃, 300MHz) 7.79 (brd, *J* = 6.5 Hz, 2H), 7.71 (s, 1H), 7.69(s, 1H), 7.47-7.22 (m, 7H), 2.40 (s, 3H). ¹³C-NMR (CDCl₃, 75 MHz) 141.8, 140.9, 133.9, 132.9, 132.0, 129.3, 128.4, 128.2, 128.1, 127.6, 127.0, 126.9, 125.9, 125.4, 21.1. IR (neat) 3053, 3022, 2922, 1597, 1491, 1443, 881, 762, 746, 702 cm⁻¹. MS (EI) *m/z* 218 (M⁺). HRMS Calcd for C₁₇H₁₄ (M⁺) 218.1095, Found 218.1107. Anal. Calcd for C₁₇H₁₄: C, 93.54; H, 6.46. Found C, 93.24; H, 6.55.

2-Phenylnaphthalene (5b).² White solid; ¹H-NMR (CDCl₃, 300MHz) 8.05 (brs, 1H), 7.94-7.86 (m, 3H), 7.77-7.72 (m, 3H), 7.54-7.47 (m, 4H), 7.39 (brt, *J* = 6.9 Hz, 1H). ¹³C-NMR (CDCl₃, 75 MHz) 141.1, 138.5, 133.6, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.5. IR (KBr) 3053, 1495, 1452, 860, 772, 758, 689 cm⁻¹. MS (EI) *m/z* 204 (M⁺). HRMS Calcd for C₁₆H₁₂ (M⁺) 204.0938, Found 204.0932. mp 98-100 °C.

2-Butylnaphthalene (5c). Colorless liquid; ¹H-NMR (CDCl₃, 300MHz) 7.78 (d, *J* = 9.1 Hz, 1H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.60 (s, 1H), 7.46-7.37 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 2.77 (t, *J* = 7.5 Hz, 2H), 1.69 (tt, *J* = 7.3, 7.5 Hz, 2H), 1.39 (sext, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ¹³C-NMR (CDCl₃, 75 MHz) 140.4, 133.6, 131.9, 127.7, 127.6, 127.4, 127.4, 126.3, 125.8, 125.0, 35.8, 33.5, 22.4, 14.0. IR (neat) 3051, 2957, 2930, 2856, 1601, 1508, 1466, 851, 816, 745 cm⁻¹. MS (EI) *m/z* 184 (M⁺). HRMS Calcd for C₁₄H₁₆ (M⁺) 184.1251, Found 184.1245.

2, 3-Diphenylnaphthalene (5d).³ White solid; ¹H-NMR (CDCl₃, 300MHz) 7.87 (s, 1H), 7.84 (dd, *J* = 3.0, 6.3 Hz, 2H), 7.46 (dd, *J* = 3.4, 6.3 Hz, 2H), 7.21 (brs, 10H). ¹³C-NMR (CDCl₃, 75

MHz) 141.4, 139.1, 132.7, 130.0, 129.4, 127.8, 127.7, 126.5, 126.3. IR (neat) 3055, 3022, 1601, 1491, 891, 766, 700 cm^{-1} . MS (EI) m/z 280 (M^+). HRMS Calcd for $\text{C}_{22}\text{H}_{16}$ (M^+) 280.1252, Found 280.1247. mp 87-87.5 $^{\circ}\text{C}$.

2, 3-Dipropylnaphthalene (5e).⁴ Colorless liquid; ^1H -NMR (CDCl_3 , 300MHz) 7.72 (dd, J = 3.2, 5.9 Hz, 1H), 7.59 (s, 2H), 7.34 (dd, J = 3.2, 5.9 Hz, 1H), 2.74 (t, J = 7.7 Hz, 4H), 1.70 (tq, J = 7.5, 7.7 Hz, 4H), 1.03 (t, J = 7.5 Hz, 4H). ^{13}C -NMR (CDCl_3 , 75 MHz) 139.3, 132.2, 127.0, 127.0, 124.9, 34.9, 24.1, 14.2. IR (neat) 2959, 2932, 1464, 743 cm^{-1} . MS (EI) m/z 212 (M^+). HRMS Calcd for $\text{C}_{16}\text{H}_{20}$ (M^+) 212.1565, Found 212.1560.

2-Bromo-3-phenylnaphthalene (5f). Pale yellow oil; ^1H -NMR (CDCl_3 , 300MHz) 8.19 (s, 1H), 7.83–7.77 (m, 3H), 7.54–7.41 (m, 7H). ^{13}C -NMR (CDCl_3 , 75 MHz) 141.0, 140.1, 133.5, 132.2, 131.6, 129.9, 129.7, 127.9, 127.8, 127.6, 126.8, 126.6, 126.6, 120.8. IR (neat) 3055, 1589, 1489, 1421, 953, 881, 761, 746, 700 cm^{-1} . MS (EI) m/z 282 (M^+). HRMS Calcd for $\text{C}_{16}\text{H}_{11}\text{Br}$ (M^+) 282.0044, Found 282.0039.

2-Phenyl-3-phenylsulfanylnaphthalene (5g). Pale brown solid; ^1H -NMR (CDCl_3 , 300MHz) 7.81 (brt, J = 4.2 Hz, 1H), 7.76 (s, 1H), 7.68 (s, 1H), 7.67 (brt, J = 4.5 Hz, 1 H), 7.49–7.47 (m, 7H), 7.30–7.25 (m, 5H). ^{13}C -NMR (CDCl_3 , 75 MHz) 140.7, 140.7, 140.3, 135.2, 133.9, 133.0, 132.2, 130.0, 129.6, 129.3, 129.2, 127.9, 127.6, 127.4, 127.3, 127.0, 126.4, 126.2. IR (neat) 3053, 3018, 1580, 1475, 897, 745, 696 cm^{-1} . MS (EI) m/z 312 (M^+). HRMS Calcd for $\text{C}_{22}\text{H}_{16}\text{S}$ (M^+) 312.0973, Found 312.0967. Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{S}$: C, 84.57; H, 5.16; S, 10.26. Found C, 84.48; H, 5.31; S, 10.51. mp 70–70.5 $^{\circ}\text{C}$.

Naphthalene-2-carboxylic acid ethyl ester (5h).⁵ Yellow oil; ^1H -NMR (CDCl_3 , 300MHz) 8.61 (s, 1H), 8.07 (dd, J = 1.8, 8.7 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.87 (m, 2H), 7.56 (m, 2H), 4.44 (q, J = 7.2 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H). ^{13}C -NMR (CDCl_3 , 75 MHz) 166.8, 135.5, 132.5, 130.9, 129.3, 128.1, 128.1, 127.7, 127.7, 126.6, 125.2, 61.1, 14.4. IR (neat) 3060, 2982, 1717, 1286, 1097, 779, 762 cm^{-1} . MS (EI) m/z 200 (M^+). HRMS Calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$ (M^+) 200.0837, Found 200.0849.

6-Phenyl-1,2,3,4-tetrahydronaphthalene (8a). Colorless liquid; ^1H -NMR (CDCl_3 , 300MHz) 7.57 (d, J = 7.8 Hz, 1H), 7.56 (s, 1H), 7.44–7.38 (m, 2H), 7.34–7.28 (m, 3H), 7.14 (d, J = 7.8 Hz,

1H), 2.82 (brs, 4H), 1.83 (brs, 4H). ¹³C-NMR (CDCl₃, 75 MHz) 141.3, 138.5, 137.5, 136.3, 129.5, 128.6, 127.8, 127.0, 126.9, 124.3, 29.5, 29.1, 23.2, 23.2. IR (neat) 2928, 1483, 760, 696 cm⁻¹. MS (EI) m/z 208 (M⁺). HRMS Calcd for C₁₆H₁₆ (M⁺) 208.1252, Found 208.1247. Anal. Calcd for C₁₆H₁₆: C, 92.26; H, 7.74. Found C, 92.46; H, 7.73.

***m*-Terphenyl (8b).**⁶ White solid; ¹H-NMR (CDCl₃, 300MHz) 7.81 (brt, *J* = 1.8 Hz, 1H), 7.67-7.66 (m, 4H), 7.60-7.44 (m, 7H), 7.40-7.34 (m, 2H). ¹³C-NMR (CDCl₃, 75 MHz) 141.8, 141.2, 129.2, 128.8, 127.4, 127.3, 126.2, 126.1. IR (KBr) 3061, 1595, 1568, 1472, 1078, 893, 750, 700, 611 cm⁻¹. MS (EI) m/z 230 (M⁺). HRMS Calcd for C₁₈H₁₄ (M⁺) 230.1096, Found 230.1090. mp 85.5-86.5 °C.

- 1) op den Brouw, P. M.; Laarhoven, W. H. *J. Chem. Soc. Perkin Trans II*. **1982**, 795-799.
- 2) Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001**, 3, 3049-3051.
- 3) Nakayama, J.; Kuroda, M.; Hoshino, M. *Heterocycles* **1986**, 24, 1233-1236.
- 4) Azzena, U.; Demartis, S.; Melloni, G. *J. Org. Chem.* **1996**, 61, 4913-4919.
- 5) Morley, J. A.; Woolsey, N. F. *J. Org. Chem.* **1992**, 57, 6487-6495.
- 6) Tiecco, M.; Testaferri, L.; Tingoli, M.; Wenkert, E. *Tetrahedron* **1983**, 39, 2289-2294.

5a

5b

5c

5d

5e

5f

5g

5h

8a

8b