

## Supplementary information

### Ru(II)-catalyzed [2 + 2 + 2] cycloaddition of 1,2-bis(propioyl)benzenes with monoalkynes leading to substituted anthraquinones

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## Experimental Procedures

**General.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained for samples in CDCl<sub>3</sub> solution. Flash chromatography was performed with a silica gel column (Merck Silica gel 60) eluted with mixed solvents [hexane / AcOEt]. Elemental analyses were performed by the Microanalytical Center of Kyoto University. Melting points were obtained in sealed capillary tubes and are uncorrected. 1,2-Dichloroethane was distilled from CaH<sub>2</sub>, and degassed. RuCl<sub>3</sub>·xH<sub>2</sub>O was purchased from N. E. Chemcat Corporation. Cp\*Ru(cod)Cl was obtained according to the literature procedures. 1,2-Bis(propioyl)benzenes **1a**,<sup>2</sup> **1b**,<sup>3</sup> and an anthraquinone **3bj**<sup>3</sup> were reported in the literature. Anthraquinone **3ag** and 2-tert-butylantraquinone **3af** were identified by comparison with authentic samples.

## Analytical Data for Anthraquinones

**3aa:** mp. 89.2-89.8 °C; IR (CHCl<sub>3</sub>): 1673, 1595 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.65 (t, *J* = 7.5 Hz, 3H), 1.32-1.45 (m, 2 H), 1.93-1.73 (m, 2 H), 2.77 (t, *J* = 7.8 Hz, 2 H), 7.58 (dd, *J* = 7.8, 2.0 Hz, 1 H), 7.77 (dd, *J* = 6.0, 3.0 Hz, 2 H), 8.09 (d, *J* = 2.0 Hz, 1 H), 8.20 (d, *J* = 7.8 Hz, 1 H), 8.28 (dd, *J* = 6.0, 3.0 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 13.97, 22.39, 33.11, 35.94, 126.76, 127.00, 127.03,

127.34, 131.34, 133.34, 133.48, 133.76, 133.87, 134.20, 150.04 (2C), 182.77, 183.24; MS (FAB):  $m/z$  (%): 265 (100)  $[MH^+]$ , 209 (20)  $[MH^+-CH_2=CHCH_2CH_3]$ ; EA calcd (%) for  $C_{18}H_{16}O_2$  (264.32): C, 81.79; H, 6.10. Found: C, 81.71; H, 6.18.

**3ab**: mp. 135.4-136.3 °C; IR ( $CHCl_3$ ): 1674, 1595  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  3.48 (s, 3H), 4.63 (s, 2 H), 7.77-7.79 (m, 1 H), 7.81 (dd,  $J = 5.7, 3.6$  Hz, 2 H), 8.25-8.27 (m, 1 H), 8.30 (s, 1 H), 8.32 (dd,  $J = 5.7, 3.3$  Hz, 2 H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  58.68, 73.68, 125.56, 127.09, 127.11, 127.47, 132.48, 132.63, 133.41 (2C), 133.92, 133.98, 145.18 (2C), 182.67, 182.87; MS (FAB):  $m/z$  (%): 253 (100)  $[MH^+]$ , 237 (15)  $[M^+-CH_3]$ , 221 (25)  $[M^+-OCH_3]$ , 209 (10)  $[M^+-CH_2OCH_3]$ ; EA calcd (%) for  $C_{16}H_{12}O_3$  (252.26): C, 76.18; H, 4.79. Found: C, 76.27; H, 4.70.

**3ac**: mp. 119.4-120.1 °C; IR ( $CHCl_3$ ): 1673, 1595  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  2.12-2.22 (m, 2 H), 2.96 (t,  $J = 7.8$  Hz, 2 H), 3.56 (t,  $J = 6.3$  Hz, 2 H), 7.62 (dd,  $J = 7.8, 1.5$  Hz, 1 H), 7.78 (dd,  $J = 6.0, 3.3$  Hz, 2 H), 8.11 (d,  $J = 1.8$  Hz, 1 H), 8.22 (d,  $J = 8.1$  Hz, 1 H), 8.28 (dd,  $J = 6.0, 3.3$  Hz, 2 H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  33.08, 33.40, 42.90, 126.81, 127.04, 127.07, 127.56, 131.72, 133.40, 133.51, 133.86, 133.98, 134.28, 147.77 (2C), 182.61, 183.02; MS (FAB):  $m/z$  (%): 285 (100)  $[MH^+]$ , 249 (10)  $[M^+-Cl]$ , 221 (18)  $[M^+-CH_2CH_2Cl]$ , 209 (14)  $[MH^+-CH_2=CHCH_2Cl]$ ; EA calcd (%) for  $C_{17}H_{13}ClO_2$  (284.74): C, 71.71; H, 4.60. Found: C, 71.45; H, 4.89.

**3ad**: mp. 109.8-110.1 °C; IR ( $CHCl_3$ ): 1731, 1673, 1596  $cm^{-1}$ ;  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  1.99-2.10 (m, 2 H), 2.38 (t,  $J = 7.5$  Hz, 2 H), 2.84 (t,  $J = 7.5$  Hz, 2 H), 3.68 (s, 3 H), 7.61 (dd,  $J = 7.8, 1.8$  Hz, 1 H), 7.78 (dd,  $J = 5.7, 3.3$  Hz, 2 H), 8.11 (d,  $J = 1.8$  Hz, 1 H), 8.23 (d,  $J = 7.8$  Hz, 1 H), 8.30 (dd,  $J = 5.4, 3.6$  Hz, 2 H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  25.94, 33.26, 35.28, 51.61, 126.75, 126.97, 127.00, 127.44, 131.57, 133.37 (2C), 133.78, 133.89, 134.14, 148.40 (2C), 173.18, 182.58, 182.99; MS (FAB):  $m/z$  (%): 309 (76)  $[MH^+]$ , 277 (100)  $[M^+-OMe]$ , 221 (35)  $[M^+-CH_2CH_2CO_2Me]$ ; EA calcd (%) for  $C_{19}H_{16}O_4$  (308.33): C, 74.01; H, 5.23. Found: C, 73.78; H, 5.33.

**3ae**: mp. 235.2-236.4 °C; IR (CHCl<sub>3</sub>): 1717, 1676, 1596 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 5.02 (1, 2 H), 7.75 (dd, *J* = 5.7, 3.0 Hz, 2 H), 7.79 (dd, *J* = 6.0, 3.3 Hz, 2 H), 7.81 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.89 (dd, *J* = 5.7, 3.0 Hz, 2 H), 8.27 (s, 1 H), 8.29 (s, 1 H), 8.29 (dd, *J* = 5.7, 3.3 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 41.28, 123.55 (2C), 126.53, 127.13, 127.17, 127.87, 131.84, 132.82, 133.32, 133.38, 133.55, 133.72, 134.03, 134.05, 134.17 (2C), 142.72 (2C), 167.65 (2C), 182.52, 182.58; MS (FAB): *m/z* (%): 368 (100) [MH<sup>+</sup>], 221 (50) [M<sup>+</sup>-Phthalimide]; EA calcd (%) for C<sub>17</sub>H<sub>13</sub>ClO<sub>2</sub>•H<sub>2</sub>O (385.37): C, 71.68; H, 3.92; N, 3.63. Found: C, 71.60; H, 3.98; N, 3.64.

**3ah**: mp. 160.6-161.0 °C; IR (CHCl<sub>3</sub>): 1672, 1595 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.42-7.55 (m, 3 H), 7.71-7.76 (m, 2 H), 7.80-7.83 (m, 2 H), 8.02 (dd, *J* = 8.0, 1.8 Hz, 1 H), 8.31-8.36 (m, 2 H), 8.38 (d, *J* = 8.0 Hz, 1 H), 8.54 (d, *J* = 1.8 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 125.36, 127.03, 127.09, 127.16 (2C), 127.85, 128.70, 128.97 (2C), 131.95, 132.14, 133.42, 133.45, 133.68, 133.85, 133.97, 138.72, 146.59, 182.54, 182.87; MS (FAB): *m/z* (%): 285 (100) [MH<sup>+</sup>], 152 (100) [PhC<sub>6</sub>H<sub>3</sub>], 134 (98) [C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>+2H]; EA calcd (%) for C<sub>20</sub>H<sub>12</sub>O<sub>2</sub> (284.31): C, 84.49; H, 4.25. Found: C, 84.41; H, 4.32.

**3ai**: mp. 126.3-126.8 °C; IR (CHCl<sub>3</sub>): 1671, 1593 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.32 (t, *J* = 7.5 Hz, 6H), 2.80 (q, *J* = 7.5 Hz, 4 H), 7.77 (dd, *J* = 5.7, 3.3 Hz, 2 H), 8.09 (s, 2 H), 8.29 (dd, *J* = 5.7, 3.3 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.73, 25.88, 126.86, 126.95, 131.39, 133.58, 133.71, 148.95, 183.12; MS (FAB): *m/z* (%): 265 (100) [MH<sup>+</sup>]; EA calcd (%) for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub> (264.32): C, 81.79; H, 6.10. Found: C, 81.53; H, 6.21.

**3bi**: mp. 131.8-133.2 °C; IR (CHCl<sub>3</sub>): 1665, 1595 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.20 (t, *J* = 7.5 Hz, 6H), 2.73 (s, 6 H), 2.85 (q, *J* = 7.5 Hz, 4 H), 7.69 (dd, *J* = 5.7, 3.3 Hz, 2 H), 8.09 (dd, *J* = 5.7, 3.3 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.29, 18.06, 23.43, 125.97, 132.31, 132.91, 134.74, 137.57, 147.70, 186.95; MS (FAB): *m/z* (%): 293 (100) [MH<sup>+</sup>], 277 (10) [M<sup>+</sup>-CH<sub>3</sub>]; EA calcd (%) for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> (292.37): C, 82.16; H, 6.89. Found: C, 82.11; H, 6.86.

**3ba**: mp. 110.0-110.6 °C; IR (CHCl<sub>3</sub>): 1665, 1595 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.97 (t, *J* = 7.5 Hz, 3 H), 1.36-1.50 (m, 2 H), 1.53-1.63 (m, 2 H), 2.70 (s, 3 H), 2.74 (t, *J* = 7.8 Hz, 2 H), 2.78 (s, 3 H), 7.32 (s, 1 H), 7.71 (m, 2 H), 8.14 (m, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.04, 17.69, 22.86, 23.81, 32.47, 34.32, 126.12, 126.27, 130.84, 133.04, 133.11, 133.94, 134.68, 137.84, 138.45, 139.14, 148.50 (2C), 185.53, 186.89; MS (FAB): *m/z* (%): 293 (100) [MH<sup>+</sup>], 237 (40) [MH<sup>+</sup>-CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>3</sub>]; EA calcd (%) for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub> (292.37): C, 82.16; H, 6.89. Found: C, 82.05; H, 6.97.

**Synthesis of Ruthenacycle 4.** To a solution of Cp\*RuCl(cod) (130.2 mg, 0.34 mmol) in degassed 1,2-dichloroethane (1 mL) was added a solution of a diketodiyne **1c** (140.2 mg, 0.42 mmol) in degassed 1,2-dichloroethane (3 mL) at 0 °C. The solution was further stirred at room temperature for 30 min. The solution was concentrated in vacuo and the residue was recrystallized from CHCl<sub>3</sub> / ether to afford **4**•CHCl<sub>3</sub> (196.3 mg, 79.5%) as dark red crystals: mp. 178.5-178.9 °C; IR (CHCl<sub>3</sub>): 1656, 1592, 1251 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.03 (s, 15 H), 7.01 (d, *J* = 7.2 Hz, 4 H), 7.20 (t, *J* = 7.2 Hz, 4 H), 7.46 (tt, *J* = 7.5, 1.5 Hz, 2 H), 7.64 (dd, *J* = 6.0, 3.3 Hz, 2 H), 8.05 (dd, *J* = 6.0, 3.3 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 10.20, 108.45, 125.63, 127.04, 127.07, 127.62, 133.19, 133.71, 148.59, 155.67, 178.28, 263.89; MS (FAB): *m/z* (%): 606 (39) [M<sup>+</sup>], 571 (100) [M<sup>+</sup>-Cl]; EA calcd (%) for C<sub>34</sub>H<sub>29</sub>ClO<sub>2</sub>Ru (606.09): C, 57.94; H, 4.17. Found: C, 58.07; H, 4.15.

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