Supporting Information for

Dicobalt Octacarbonyl-Catalyzed Tandem [2+2+1] and [2+2+2] Cycloaddition Reaction of Diynes with Two Phenylacetylenes Under CO

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Characterization of new compounds:

1A: IR ν_{CO} (enone) 1698 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 7.90 (d, 7.2 Hz, 2 H), 7.33 (d, 7.7 Hz, 2 H), 7.22-7.08 (m, 7 H), 5.70 (s, 1 H), 5.14 (m, 1 H), 3.97 (q, 6.9 Hz, 2 H), 3.89 (q, 7.1 Hz, 2 H), 3.23 (m, 1 H), 3.18 (d, 18.0 Hz, 1 H), 3.15 (d, 18.0 Hz, 1 H), 3.15 (dd, 17.0, 2.2 Hz, 1H), 2.80 (dd, 16.0, 2.2 Hz, 1 H), 0.93 (t, 7.1 Hz, 3 H), 0.85 (t, 7.1 Hz, 3 H) ppm; ^{13}C NMR (75 MHz, C_6D_6): δ 206.4, 171.1, 170.8, 157.2, 145.5, 141.4, 136.3, 136.1, 132.0, 129.0, 128.8, 127.6, 126.1, 120.2, 114.9, 61.6, 61.5, 59.3, 59.0, 50.9, 39.2, 39.1, 14.0, 13.9 ppm; ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 7.2 Hz, 2 H, Ph), 7.69 (d, 2.5 Hz, 1 H, H10), 7.40 (t, 7.1 Hz, 2H, Ph) 7.34 (t, 7.2 Hz, 1H, Ph) 7.31 (t, 7.6 Hz, 2H, Ph) 7.22 (t, 7.3 Hz, 1H , Ph) 7.17 (d, 7.3Hz , 2H, Ph) 5.60 (d, 4.2Hz, 1H, H12) 5.56 (s, 1 H, H2), 4.29-4.15 (m, 4H, Et), 3.58 (m, 1H, H8), 3.19 (d, 16.5 Hz, 1 H, H6), 3.12 (d, 16.7

Hz, 1 H, H4), 2.99 (d 16.5 Hz, 1H, H4') 2.96 (d, 16.3 Hz, 1H, H6'), 1.27 (t, 7.1 Hz, 3H, Et) 1.21 (t, 7.1 Hz, 3H Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.15(C, C1), 171.04(C), 170.86(C), 157.47(CH,C10), 144.36(C), 141.38(C), 136.01(C), 135.97(C), 131.21(C), 128.69(CH), 128.59(CH), 128.39(CH), 127.15(CH), 126.91(CH), 119.43(CH, C2), 114.40(CH, C12), 61.68(CH_2), 61.62(CH_2), 58.88(C), 58.64(C), 50.56(CH,C8), 38.92(CH_2, C4 or C6), 38.63(CH_2, C4 or C6), 13.98(CH_3), 13.91(CH_3) ppm; HRMS M^+ calcd. 468.1937, obsd. 468.1927.

2A: IR ν_{CO} (enone) 1698 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 7.88 (d, 7.0 Hz, 2 H), 7.32 (d, 7.1 Hz, 2 H), 7.23-7.09 (m, 7 H), 5.68 (s, 1 H), 5.22 (m, 1 H), 3.47 (s, 2 H), 3.42 (s, 1 H), 3.41 (s, 1 H), 3.27 (m, 1 H), 2.41 (d, 16.0 Hz, 1 H), 2.31 (d, 16.0 Hz, 1 H), 2.28 (dd, 16.0, 2.1 Hz, 1 H), 2.12 (dd, 16.0, 2.1 Hz, 1 H), 0.12 (s, 9 H), 0.04 (s, 9 H) ppm; ^{13}C NMR (75 MHz, C_6D_6): δ 206.6, 157.3, 145.8, 141.1, 138.5, 138.4, 132.1, 128.9, 128.7, 128.6, 127.5, 127.0, 120.2, 114.8, 64.9, 64.2, 59.4, 51.0, 48.5, 36.4, 36.2, -0.45, -0.51 ppm; HRMS M^+ calcd. 528.2516, obsd. 528.2516.

3A: IR ν_{CO} (enone) 1700 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 7.88 (d, 7.1 Hz, 2 H), 7.73 (d, 7.1 Hz, 2 H), 7.67 (d, 7.6 Hz, 2 H), 7.25-7.10 (m, 9 H), 6.83-6.77 (m, 4 H), 5.41 (s, 1 H), 5.00 (m, 1 H), 3.84-3.68 (m, 4 H), 3.17 (m, 1 H), 2.05 (d, 16.0 Hz, 1 H), 194-1.89 (m, 2 H), 1.93 (s, 3 H), 1.89 (s, 3 H), 1.65 (d, 16.0 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, C_6D_6): δ 206.5, 157.5, 145.4, 144.9, 144.8, 141.3, 135.7, 135.3, 133.2, 133.1, 131.9, 130.2, 130.1, 129.1, 128.9, 128.1, 127.6, 127.5, 1`27.2, 120.9, 115.9, 71.3, 70.4, 59.1, 50.9, 45.4, 36.3, 36.1, 21.2 ppm; HRMS M^+ calcd. 692.1902, obsd. 692.1900.

4A: : IR ν_{CO} (enone) 1698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, 6.9 Hz, 2 H), 7.64 (d, 2.6 Hz, 1 H), 7.39-7.15 (m, 8 H), 5.54 (m, 1 H), 5.51 (s, 1 H), 3.66 (s, 1 H), 3.63

(s, 1 H), 3.60 (s, 2 H), 3.54 (m, 1 H), 2.52 (d, 16.0 Hz, 1 H), 2.47 (d, 16.0 Hz, 1 H), 2.31 (d, 16.0 Hz, 1 H), 2.24 (dd, 16.0, 1.5 Hz, 1 H), 1.43 (s, 6 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.2, 157.5, 144.5, 141.0, 137.0, 136.8, 131.2, 128.6, 128.5, 128.3, 127.0, 126.8, 119.8, 114.9, 97.9, 67.9, 67.5, 58.9, 50.5, 40.4, 37.9, 37.8, 23.9, 23.3 ppm; HRMS M^+ calcd. 424.2038, obsd. 424.2032.

5A: IR ν_{CO} (enone) 1698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 7.2 Hz, 2 H, Ph), 7.72 (d, 2.6 Hz, 1 H, H10), 7.39 (t, 7.1 Hz, 2H, Ph) 7.34 (t, 7.2 Hz, 1 H, Ph), 7.31 (t, 7.2 Hz, 2 H, Ph), 7.22 (t, 7.3 Hz, 1 H, Ph), 7.15 (d, 7.3 Hz, 2 H, Ph), 5.39 (s, 1 H, H12), 4.28-4.15 (m, 4 H, Et), 3.37 (m, 1 H, H8), 3.19 (d, 16.5 Hz, 1 H, H6), 3.15 (d, 16.5 Hz, 1 H, H4), 2.95 (d, 16.3 Hz, 1 H, H4'), 2.95 (d, 16.3 Hz, 1 H, H6')1.93 (s, 3 H, Me), 1.27 (t, 7.2 H, 3H, Et), 1.22 (t, 7.1 H, 3H, Et) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.69, 171.20, 171.07, 156.28, 144.16, 141.83, 136.73, 130.74, 128.61, 128.58, 128.41, 127.24, 127.03, 126.9, 125.82, 123.12, 116.49, 61.65, 61.60, 60.12, 58.49, 55.76, 39.33, 37.06, 18.02, 13.97, 13.92 ppm; HRMS M^+ calcd. 482.2093, obsd. 482.2086.

6A: IR ν_{CO} (enone) 1699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, 8.0 Hz, 2 H), 7.54 (d, 2.7 Hz, 1 H), 7.24-7.05 (m, 8 H), 5.38 (m, 1 H), 5.36 (s, 1 H), 3.43 (m, 1 H), 2.33 (m, 2 H), 2.23 (m, 2 H), 1.61 (m, 2 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.7, 157.9, 144.9, 141.1, 139.8, 139.6, 131.5, 128.6, 128.5, 128.4, 127.2, 126.9, 126.8, 117.8, 112.9, 59.1, 50.8, 31.5, 31.3, 24.7 ppm; HRMS M^+ calcd. 324.1514, obsd. 324.1513.

6B: IR ν_{CO} (enone) 1702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.94 (s, 1 H), 5.80 (m, 1 H), 5.45 (s, 1 H), 2.97 (d, 5.2 Hz, 1 H), 2.73 (m, 2 H), 2.29 (m, 5 H), 2.08 (m, 2 H), 1.70 (m, 2 H), 1.30 (dd, 11.0, 1.4 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.6, 192.8,

139.6, 137.6, 124.6, 118.1, 114.4, 56.3, 56.1, 39.7, 31.3, 31.0, 25.1, 24.8, 22.4 ppm; HRMS M^+ calcd. 212.1201, obsd. 212.1199.

7C: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68-7.34 (m, 6 H), 7.20 (m, 4 H), 7.11(m, 6 H), 3.09 (t, 7.2 Hz, 2 H), 2.85 (t, 7.3 Hz, 2 H), 2.03 (qn, 7.3 Hz, 2 H)ppm; ^{13}C NMR (75 MHz, $CDCl_3$):144.4, 141.5, 141.2, 141.0, 139.9, 139.6, 137.2, 135.9, 130.1, 129.9, 129.8, 129.2, 128.8, 128.6, 128.2, 127.9, 127.7, 127.1, 126.9, 126.3, 126.1, 33.3, 33.2, 26.0 ppm; HRMS $(M)^+$ calcd. 346.1722, obsd. 346.1736.

8A: IR ν_{CO} (enone) 1699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, 5.0 Hz, 2 H), 7.56 (d, 2.6 Hz, 1 H), 7.41-7.24 (m, 13 H), 5.65 (s, 1 H), 4.77 (dd, 13.6, 1.2 Hz, 1 H), 4.69 (dd, 12.8, 1.5 Hz, 1 H), 4.62 (dd, 13.6, 0.6 Hz, 1 H), 4.50 (dd, 12.8, 2.1 Hz, 1 H), 4.18 (brs 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.8, 156.3, 143.0, 141.0, 136.8, 135.8, 131.7, 129.9, 127.9, 127.8, 127.6, 127.4, 127.2, 127.0, 126.2, 126.1, 126.0, 125.2, 123.5, 115.1, 69.9, 59.4, 52.6 ppm; HRMS $(M+1)^+$ calcd. 403.1698, obsd. 403.1710.

9A: IR ν_{CO} (enone) 1702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-7.24 (m, 12 H), 7.60 (d, 2.8 Hz, 1 H), 7.10 (d, 8.5 Hz, 2 H), 5.61 (m, 1 H), 5.58 (s, 1 H), 4.18 (dd, 14.0, 1.5 Hz, 1 H), 4.16 (dt, 14.0, 1.8 Hz, 1 H), 3.90 (dd, 14.0, 1.9 Hz, 2 H), 3.64 (m, 1 H), 2.38 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.5, 157.2, 143.9, 141.8, 132.6, 132.5, 130.8, 129.8, 129.0, 128.9, 128.5, 127.8, 127.3, 127.2, 126.7, 125.9, 119.2, 114.4, 58.4, 51.2, 51.0, 50.2, 21.5 ppm; HRMS $(M+1)^+$ calcd. 480.1633, obsd. 480.1653.

9C: ^{1}H NMR (300 MHz, C_6D_6): δ 7.79 (d, 8.3 Hz, 2 H), 7.49-7.16 (m, 10 H) , 4.66 (s, 4 H), 2.40 (s, 3 H) ppm; ^{13}C NMR (75 MHz, C_6D_6): δ 144.7, 142.3, 141.5, 137.7, 136.1, 134.6, 130.9, 129.8, 129.7, 129.3, 128.6, 128.5, 128.1, 127.9, 127.3, 123.9, 122.3, 54.7, 54.6, 22.5 ppm; HRMS M^+ calcd. 349.1136, obsd. 349.1134.

10A: IR ν_{CO} (enone) 1698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, 3.5 Hz, 1 H), 7.54 (d, 2.9 Hz, 1H), 7.33 (dd, 5.0, 0.7 Hz, 1 H), 7.22 (dd, 5.0, 1.2 Hz,1 H), 7.07 (dd, 5.1, 5.0 Hz, 1 H), 6.97-6.91 (m, 2 H), 5.59 (m, 1 H), 5.48 (s, 1 H), 3.84 (m, 1 H), 3.38 (d, 1.9 Hz, 2 H), 3.36 (s, 2H), 2.35-2.16 (m, 4H), 0.08 (s, 9H), 0.04 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.3, 152.9, 147.6, 138.6, 138.2, 134.6, 127.4, 126.9, 126.2, 125.9, 124.5, 123.4, 119.2, 114.0, 64.5, 63.9, 55.8, 50.6, 48.3, 35.9, 35.6, -0.6 ppm; HRMS M^+ calcd. 540.1644, obsd. 540.1641.