Supporting Information for

Highly Efficient Intra- and Intermolecular [4+2] Cycloaddition Reaction Catalyzed by Rhodium Complex

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Experimental Procedure

Materials: Complex 1 was synthesized by the published procedure.[4] ^{1}H NMR spectra were recorded on Bruker 300 MHz spectrometer. GC-MS spectra were recorded on HP 6890 Series GC system with HP 5973 mass selective detector.

Rhodium-catalyzed [4+2] cycloaddition: Compounds 2,3-dimethyl-1,3-butadiene (0.57 mL, 4.7 mmol) and 3-phenyl-1-propyne (0.29 mL, 2.3 mmol) was added via syringe to a solution of 1 (10 mg, 0.023 mmol) in 10 mL of CH_2Cl_2. The solution was stirred for 15 min at 15 °C, evaporated to dryness, extracted with hexane, and chromatographed on a silica gel column eluting with hexane. Evaporation of the solvent gave the product in 98% yield (0.45 g). ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 2 H), 7.42 (m, 3 H), 5.72 (m, 1 H), 3.57 (s, 2 H), 2.88 (m, 2 H), 2.69 (m, 2 H), 1.87 (s, 3 H), 1.83 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 139.8, 134.7, 128.8, 128.2, 125.9, 123.0, 122.7, 120.5, 43.7, 35.7, 33.9, 18.4, 18.1 ppm; HRMS (M^+) calcd. 198.1409, obsd. 198.1411. Products in entries 1, 5, and 10-11 were previously reported (Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* 1990, *112*, 4965; Levy, L. A. *J. Org. Chem.* 1978, *43*, 3068; Davis, A. P.;. Whitham, G. H. *J. Chem. Soc., Chem. Commun.* 1980, 639.)

Characterization of New Compounds:

Entry 3 in Table 1. ^{1}H NMR ($CDCl_3$): δ 5.37 (m, 1 H), 2.58 (m, 2 H), 1.94 (m, 2 H), 1.63 (s, 6 H), 1.40 (m, 2 H), 1.27 (m, 6 H), 0.88 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 130.6, 118.1, 113.3, 72.9, 32.0, 31.0, 28.8, 26.8, 24.1, 22.5, 17.6, 13.5, 13.2, 9.1 ppm; HRMS (M^+) calcd. 192.1878, obsd. 192.1874.

Entry 4 in Table 1. ^{1}H NMR ($CDCl_3$): δ 5.41 (m, 2 H), 2.59 (m, 4 H), 2.51 (m, 4 H), 1.95 (m, 4 H), 1.64 (s, 12 H), 1.55 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$): δ 135.4, 123.1, 123.0, 118.4, 36.9, 36.0, 33.8, 27.1, 18.5, 18.2 ppm; HRMS (M^+) calcd. 270.2348, obsd. 270.2359.

Entry 6 in Table 1. ^{1}H NMR ($CDCl_3$): δ 5.69 (m, 1 H), 4.62 (m, 1 H), 4.11 (d, 12.0 Hz, 1 H), 3.87 (d, 12.0 Hz, 1 H), 3.85 (m, 1 H), 3.51 (m, 1 H), 2.62 (s, 4 H), 1.66 (s, 3 H), 1.63 (s, 3 H), 1.86-1.52 (br, 6 H) ppm; ^{13}C NMR ($CDCl_3$): δ 132.1, 122.6, 122.4, 122.1, 97.1, 70.5, 61.7, 33.6, 33.3, 30.4, 25.3, 19.2, 18.2, 18.0 ppm; HRMS (M^+) calcd. 222.1620, obsd. 222.1627.

Entry 7 in Table 1. Mp 69 °C; ^{1}H NMR ($CDCl_3$): δ 5.32 (m, 1 H), 4.10 (s, 5 H), 4.07 (s, 2 H), 4.05 (s, 2 H), 3.01 (s, 2 H), 2.55 (m, 2 H), 2.48 (m, 2 H), 1.60 (s, 6 H) ppm; Anal. Calcd. for $C_{19}H_{22}Fe$: C, 74.52; H, 7.24. Found: C, 74.22; H, 7.54.

Entry 8 in Table 1. ^{1}H NMR ($CDCl_3$): δ 7.39 (m, 2 H), 7.27 (m, 3 H), 2.84 (m, 2 H), 2.70 (m, 2 H), 2.04 (s, 6 H), 1.68 (s, 3 H), 1.66 (s, 3 H), 1.58 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 143.0, 130.0, 128.3, 128.0, 126.7, 126.1, 123.6, 123.1, 40.0, 39.9, 19.5, 18.0, 17.9 ppm; HRMS (M^+) calcd. 198.1409, obsd. 198.1411.

Entry 9 in Table 1. A: ^{1}H NMR ($CDCl_3$): δ 7.42 (d, 7.0 Hz, 2 H), 7.33 (t, 7.1 Hz, 2 H), 7.24 (t, 7.2 Hz, 1 H), 6.13 (m, 1 H), 5.49 (m, 1 H), 2.96 (m, 2 H), 2.89 (m, 2 H), 1.77 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 141.4, 133.7, 131.2, 128.2, 126.8, 124.9, 121.6, 117.9, 32.8, 28.2, 23.3 ppm. B: ^{1}H NMR ($CDCl_3$): δ 7.42 (d, 7.0 Hz, 2 H), 7.33 (t, 7.1 Hz, 2 H), 7.24 (t, 7.2 Hz, 1 H), 6.13 (m, 1 H), 5.55 (m, 1 H), 3.07 (m, 2 H), 2.77 (m, 2 H), 1.74 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 141.4, 133.7, 130.6, 128.6, 127.1, 124.9, 121.6, 118.7, 32.1, 28.9, 22.9 ppm. HRMS (M^+) calcd. 170.1096, obsd. 170.1089.

Entry 10 in Table 1. A: ^{1}H NMR ($CDCl_3$): δ 7.24 (m, 2 H), 7.18 (m, 3 H), 5.47 (br., 1 H), 5.35 (br., 1 H), 3.27 (s, 2 H), 2.59 (d, 8.1 Hz, 2 H), 2.51 (d, 6.9 Hz, 2 H), 1.64 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 139.8, 134.3, 130.9, 128.9, 128.2, 125.9, 120.2, 118.6, 43.8, 31.7, 29.8, 22.9 ppm. B: ^{1}H NMR ($CDCl_3$): δ 7.24 (m, 2 H), 7.18 (m, 3 H), 5.47 (br., 1 H), 5.35 (br., 1 H), 3.27 (s, 2 H), 2.69 (br., 2 H), 2.39 (t, 7.9 Hz, 2 H), 1.61 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 139.7, 134.3, 131.2, 128.9, 128.2, 125.8, 120.1, 118.2, 44.0, 33.6, 27.8, 23.1 ppm. HRMS (M^+) calcd. 184.1252, obsd. 184.1262.

Entry 11 in Table 1. A: ^{1}H NMR ($CDCl_3$): δ 7.28 (d, 6.8 Hz, 2 H), 7.19 (t, 6.8 Hz, 3 H), 5.60 (br., 2 H), 5.42 (br., 1 H), 3.28 (s, 2 H), 2.79 (q, 5.8 Hz, 1 H), 2.47 (d, 7.7 Hz, 2 H), 1.06 (d, 7.2 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 140.2, 130.7, 129.5, 129.3, 128.6, 127.3, 126.4, 123.4, 44.4, 31.6, 29.3, 22.9 ppm. B: ^{1}H NMR ($CDCl_3$): δ 7.28 (d, 6.8 Hz, 2 H), 7.19 (t, 6.8 Hz, 3 H), 5.60 (br., 2 H), 5.42 (br., 1 H), 3.36 (s, 2 H), 2.67 (br., 2 H), 1.10 (d, 6.8 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 140.3, 133.7, 131.6, 129.3, 128.6, 128.3, 123.2, 121.1, 42.0, 32.4, 27.5, 21.ppm. HRMS (M^+) calcd. 184.1252, obsd. 184.1259.

Entry 12 in Table 1. A: ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 2 H), 7.11 (m, 3 H), 5.35 (br., 1 H), 5.27 (br., 1 H), 3.20 (s, 2 H), 2.56 (br., 1 H), 2.40 (br., 2 H), 1.60 (s, 3 H), 1.01 (d, 7.0 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 139.9, 135.6, 133.2, 128.8, 128.2, 127.3, 125.9, 118.7, 43.6, 35.3, 29.8, 21.2, 20.ppm. B: ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 2 H), 7.11 (m, 3 H), 5.35 (br., 1 H), 5.27 (br., 1 H), 3.29 (d, 7.0 Hz, 2 H), 2.56 (br., 2 H), 2.33 (q, 5.9 Hz, 1 H), 1.59 (s, 3 H), 1.05 (d, 6.8 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 139.9, 136.7, 129.0, 128.2, 127.3, 125.9, 120.6, 118.7, 41.8, 36.8, 27.4, 21.5, 18.5 ppm. HRMS (M^+) calcd. 198.1408, obsd. 198.1405.

Entry 13 in Table 1. A: ^{1}H NMR ($CDCl_3$): δ 7.28 (m, 2 H), 7.20 (m, 3 H), 5.42 (br., 1 H), 5.30 (br., 1 H), 3.30 (s, 2 H), 2.78 (m, 1 H), 2.36 (d, 7.3 Hz, 2 H), 1.62 (s, 3 H), 1.04 (d, 7.2 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 139.9, 133.2, 130.2, 128.9, 128.2, 126.8, 125.9, 124.9, 43.9, 33.7, 32.2, 22.9, 22.5.ppm. B: ^{1}H NMR ($CDCl_3$): δ 7.28 (m, 2 H), 7.20 (m, 3 H), 5.42 (br., 1 H), 5.30 (br., 1 H), 3.35 (d, 3.4 Hz, 2 H), 2.78 (m, 1 H), 2.57 (br., 2 H), 1.66 (s, 3 H), 1.07 (d, 7.2 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 139.2, 129.9, 129.0, 128.8, 128.2, 125.9, 125.8, 120.7, 41.2, 32.9, 31.8, 22.8, 20.7 ppm. HRMS $(M+1)^+$ calcd. 199.1480, obsd. 199.1487.

Entry 3 in Table 2. ^{1}H NMR ($CDCl_3$): δ 7.71 (d, 8.2 Hz, 2 H), 7.29 (d, 8.8 Hz, 2 H), 5.61 (s, 2 H), 5.37 (s, 1 H), 4.00 (d, 13.0 Hz, 1 H), 3.83 (t, 8.4 Hz, 1 H), 3.72 (d, 13.0 Hz, 1 H), 2.92 (q, 9.8 Hz, 1 H), 2.73 (m, 1 H), 2.65 (dd, 8.9, 11.0 Hz, 1 H), 2.42 (s, 3 H), 1.04 (d, 7.4 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$): δ 143.6, 137.6, 136.2, 133.0, 129.8, 128.5, 127.6, 123.1, 122.3, 53.6, 53.5, 21.5, 21.2 ppm; HRMS (M^+) calcd. 289.1137, obsd. 289.1139.