Palladium-Catalyzed Addition of Mono and Dicarbonyl Compounds to Conjugated Dienes

*Andreas Leitner, Jens Larsen, Christian Steffens and John F. Hartwig**

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

john.hartwig@yale.edu

Supporting Information

Reactions with 2,3-Dimethylbutadiene. Representative procedure: 1-(2,3-Dimethylbut-2-enyl)-2-tetralone. In a drybox, a screw-capped vial containing a small stir bar was charged with β -tetralone (292 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) as a solution in 0.1 mL DME and CpPd(allyl) (8.5 mg, 0.040 mmol) as a solution in 0.05 mL DME. The vial was sealed with a cap containing a PTFE septum and removed from the drybox. After being stirred at room temperature for 8 h, the reaction mixture was dissolved in CH₂Cl₂, and the volatile materials were evaporated under reduced pressure. Automated column chromatography (diethyl ether/pentane gradient from 2/98 to 4/96) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 96:4 as slightly yellow oil

(309.5 mg, 68% yield). ^1H NMR: (400.13 MHz, CDCl_3) δ 7.22–7.13 (m, 3H), 6.89 (d, $J = 7.3$ Hz, 1H), 3.46 (dd, $J = 9.6, 6.1$ Hz, 1H), 3.31–3.23 (m, 1H), 2.99 (ddd, $J = 15.7, 6.4, 3.4$ Hz, 1H), 2.76 (ddd, $J = 17.7, 5.4, 3.4$ Hz, 1H), 2.56–2.42 (m, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 1.19 (s, 3H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 213.3 (1C), 137.1 (1C), 135.9 (1C), 128.9 (1C), 128.3 (1C), 127.6 (1C), 126.7 (1C), 126.4 (1C), 123.3 (1C), 53.3 (1C), 38.3 (1C), 37.7 (1C), 27.6 (1C), 20.6 (1C), 19.8 (1C), 18.6 (1C); Anal. calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: C, 84.16; H, 8.83. Found: C, 84.22; H, 9.10. Selected ^1H NMR of minor isomer: 7.01 (d, $J = 8.1$ Hz, 1H), 4.82 (s, 1H), 4.60 (s, 1H), 1.85 (s, 1H), 1.12 (s, 1H), 1.09 (s, 1H).

6,7-Dimethyl-4-phenyl-oct-6-en-3-one: The reaction was performed according to the representative procedure with 1-Phenyl-butan-2-one (296 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (43.7 mg, 0.100 mmol) in 0.05 mL DME and CpPd(allyl) (21.3 mg, 0.100 mmol) in 0.05 mL DME at 90 °C for 10.5 h. Automated column chromatography (diethyl ether/pentane gradient from 0/100 to 2/98) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 96:4 as a slightly yellow oil (447 mg, 97% yield). ^1H NMR: (400.13 MHz, CDCl_3) δ 7.31–7.18 (m, 5H), 3.77 (t, $J = 7.2$ Hz, 1H), 2.75 (dd, $J = 13.6, 7.2$ Hz, 1H), 2.48–2.30 (m, 3H), 1.55 (s, 3H), 1.53 (s, 3H), 1.46 (s, 3H), 0.97 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 211.3 (1C), 139.3 (1C), 128.5 (2C), 128.3 (2C), 127.0 (1C), 126.7 (1C), 124.6 (1C), 57.2 (1C), 37.5 (1C), 35.6 (1C), 20.6 (1C), 20.3 (1C), 18.7 (1C), 7.9 (1C); Anal. calcd for $\text{C}_{16}\text{H}_{22}\text{O}$: C, 83.43; H, 9.63. Found: C, 83.53; H, 9.89. Selected ^1H NMR of minor isomer: 4.80 (s, 1H), 4.73 (s, 1H), 3.79 (s, 1H), 1.81 (s, 3H), 1.22 (s, 3H).

1-(2,3-Dimethyl-but-2-enyl)-3-isochromanone: The reaction was performed according to the representative procedure with 3-Isochromanone (296 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME,

CpPd(allyl) (8.5 mg, 0.040 mmol) in 0.1 mL DME, and an additional 0.5 mL of DME at 60 °C for 16 h. Automated column chromatography (diethyl ether/pentane gradient from 4/96 to 15/85) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 82:18 as a colorless oil (337 mg, 73% yield). ¹H NMR: (400.13 MHz, CDCl₃) δ 7.30–7.26 (m, 2H), 7.19–7.16 (m, 1H), 7.01–6.98 (m, 1H), 5.57 (d, *J* = 14.3 Hz, 1H), 5.27 (d, *J* = 14.3 Hz, 1H), 3.75 (dd, *J* = 8.8, 6.6 Hz, 1H), 2.64–2.54 (m, 2H), 1.66 (s, 3H), 1.61 (s, 3H), 1.25 (s, 3H); ¹³C NMR: (100.5 MHz, CDCl₃) δ 172.9 (1C), 134.5 (1C), 130.5 (1C), 129.0 (1C), 128.3 (1C), 127.6 (1C), 127.2 (1C), 124.2 (1C), 122.6 (1C), 69.7 (1C), 45.2 (1C), 36.3 (1C), 20.7 (1C), 19.8 (1C), 18.6 (1C); Anal. calcd for C₁₅H₁₈O₂: C, 78.23; H, 7.88. Found: C, 77.98; H, 8.07. ¹H NMR of minor isomer: 7.30–7.26 (m, 2H), 7.14–7.12 (m, 1H), 7.07–7.05 (m, 1H), 5.61 (d, *J* = 14.8 Hz, 1H), 5.17 (d, *J* = 14.8 Hz, 1H), 4.88 (s, 1H), 4.62 (s, 1H), 3.73 (s, 1H), 1.87 (s, 3H), 1.23 (s, 3H), 1.15 (s, 3H); ¹³C NMR of minor isomer: 172.9 (1C), 148.8 (1C), 131.9 (1C), 131.5 (1C), 129.9 (1C), 127.4 (2C), 124.0 (1C), 113.2 (1C), 71.1 (1C), 53.3 (1C), 45.4 (1C), 25.8 (1C), 25.3 (1C), 20.3 (1C).

4,5-Dimethyl-2-phenyl-hex-4-enoic acid ethyl ester: The reaction was performed according to the general procedure with phenyl-acetic acid ethyl ester (164.2 mg, 1.00 mmol), 2,3-dimethylbutadiene (131 mg, 1.59 mmol), DCyPP (43.7 mg, 0.100 mmol) in 0.1 mL DME, CpPd(allyl) (21.3 mg, 0.100 mmol) in 0.05 mL DME, and an additional 0.25 mL of DME at 90 °C for 10 d. Automated column chromatography (diethyl ether/pentane gradient from 0/100 to 1/99) afforded the title compound as a colorless oil (180 mg, 73% yield). ¹H NMR: (400.13 MHz, CDCl₃) δ 7.34–7.21 (m, 5H), 4.16 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.06 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.68 (t, *J* = 7.7 Hz, 1H), 2.85 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.46 (dd, *J* = 13.6, 7.7 Hz, 1H), 1.59 (br s, 3H), 1.58 (s, 3H), 1.54 (br s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR: (100.5, MHz, CDCl₃) δ 174.0 (1C), 139.4 (1C), 128.4 (2C), 128.0 (2C), 127.2 (1C), 127.0 (1C), 124.3 (1C),

60.6 (1C), 50.6 (1C), 38.9 (1C), 20.7 (1C), 20.3 (1C), 18.4 (1C), 14.1 (1C); Anal. calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.84; H, 9.07.

Ethyl phenylcyano-(2,3-dimethyl-but-2-enyl)-acetate: The reaction was performed according to the representative procedure with ethyl phenylcyanoacetate (378 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME and CpPd(allyl) (8.5 mg, 0.040 mmol) in 0.1 mL DME at 60 °C for 16.5 h. Automated column chromatography (diethyl ether/pentane going from 1/99 to 3/97) afforded the title compound as colorless oil (525 mg, 97% yield). 1H NMR: (400.13 MHz, $CDCl_3$) δ 7.58 (d, J = 6.8 Hz, 2H), 7.41–7.36 (m, 3H), 4.32–4.17 (m, 2H), 3.23 (d, J = 13.9 Hz, 1H), 2.98 (d, J = 13.9 Hz, 1H), 1.66 (s, 3H), 1.62 (s, 3H), 1.54 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR: (100.5 MHz, $CDCl_3$) δ 168.1 (1C), 135.4 (1C), 132.2 (1C), 128.9 (2C), 128.6 (1C), 126.2 (2C), 121.3 (1C), 118.4 (1C), 63.2 (1C), 53.8 (1C), 43.0 (1C), 21.1 (1C), 21.0 (1C), 19.0 (1C), 13.8 (1C); Anal. calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.28; H, 7.81; N, 5.25.

3,3,4-Trimethyl-2-phenyl-pent-4-enenitrile: The reaction was performed according to the representative procedure with benzyliyanide (234 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (43.7 mg, 0.100 mmol) in 0.05 mL DME and CpPd(allyl) (21.3 mg, 0.100 mmol) in 0.05 mL DME at 60 °C for 10.5 h. Automated column chromatography (diethyl ether/pentane gradient from 0/100 to 1/99) gave the title compound as a mixture of isomers **1:2:3** in a ratio of a 55:59:2 as a slightly yellow oil (369 mg, 90% yield (**1+2**) + 1.6% yield (**3**)). 1H NMR (**2**): (400.13 MHz, $CDCl_3$) δ 7.39–7.26 (m, 5H), 4.94 (s, 1H), 4.79 (s, 1H), 3.90 (s, 1H), 1.82 (s, 3H), 1.27 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (**2**): (100.5 MHz, $CDCl_3$) δ 147.6 (1C), 132.9 (1C), 129.4 (2C), 128.12 (2C), 128.06 (1C), 120.1 (1C), 113.8 (1C), 46.7 (1C), 42.8 (1C), 24.6 (1C), 24.1 (1C), 19.9 (1C); 1H NMR (**1**): (400.13 MHz, $CDCl_3$) δ 7.39–7.26 (m, 5H),

3.84 (dd, $J = 8.9, 6.9$ Hz, 1H), 2.76 (dd, $J = 13.5, 8.9$ Hz, 1H), 2.49 (dd, $J = 13.5, 6.9$ Hz, 1H), 1.71 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (**1**): (100.5 MHz, CDCl_3) δ 136.0 (1C), 129.8 (1C), 128.9 (2C), 127.9 (1C), 127.3 (2C), 122.4 (1C), 121.0 (1C), 41.2 (1C), 36.4 (1C), 20.8 (1C), 20.4 (1C), 18.6 (1C); Selected ^1H NMR of (**3**): 3.04 (d, $J = 13.6$ Hz, 2H), 2.57 (d, $J = 13.6$ Hz, 2H), 1.63 (s, 6H), 1.45 (s, 6H).

2-Benzoyl-4,5-dimethyl-hex-4-enenitrile: The reaction was performed according to the representative procedure with benzoylacetone nitrile (290 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (43.7 mg, 0.100 mmol) in 0.1 mL DME, CpPd(allyl) (21.3 mg, 0.100 mmol) in 0.1 mL DME, and an additional 0.5 mL DME at 90 °C for 14 h. Automated column chromatography (diethyl ether/pentane gradient from 5/95 to 10/90) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 93:7 as a slightly yellow oil (246 mg, 54% yield). ^1H NMR: (400.13 MHz, CDCl_3) δ 7.97 (dd, $J = 7.6, 1.3$ Hz, 2H), 7.66 (dt, $J = 7.6, 1.3$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 4.44 (dd, $J = 9.6, 5.8$ Hz, 1H), 2.88 (dd, $J = 13.8, 9.6$ Hz, 1H), 2.64 (dd, $J = 13.8, 5.8$ Hz, 1H), 1.74 (s, 3H), 1.72 (s, 3H), 1.66 (s, 3H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 191.3 (1C), 134.4 (1C), 134.2 (1C), 130.6 (1C), 129.1 (2C), 128.7 (2C), 121.5 (1C), 117.5 (1C), 38.7 (1C), 35.0 (1C), 20.9 (1C), 20.7 (1C), 18.4 (1C); Anal. calcd for $\text{C}_{15}\text{H}_{17}\text{NO}$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.18; H, 7.78; N, 6.24. Selected ^1H NMR of minor isomer: 7.90 (dd, $J = 8.3, 1.0$ Hz, 2H), 4.91 (s, 1H), 4.86 (s, 1H), 4.66 (s, 1H), 1.39 (s, 3H), 1.29 (s, 3H).

2-Benzenesulfonyl-4,5-dimethyl-hex-4-enenitrile: The reaction was performed according to the representative procedure with (phenylsulfonyl)acetone nitrile (362 mg, 2.00 mmol), 2,3-dimethylbutadiene (225 mg, 2.74 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME, CpPd(allyl) (8.5 mg, 0.040 mmol) in 0.05 mL DME, and an additional 0.5 mL DME at

room temperature for 21 h. Automated column chromatography (diethyl ether/pentane gradient from 5/95 to 10/90) gave the title compound as a white powder (473 mg, 90% yield). ^1H NMR: (400.13 MHz, CDCl_3) δ 8.04 (br d, $J = 8.1$ Hz, 2H), 7.78 (br t, $J = 7.5$ Hz, 1H), 7.67 (t, $J = 7.8$ Hz, 2H), 3.95 (dd, $J = 10.5, 5.4$ Hz, 1H), 2.86–2.76 (m, 2H), 1.68 (br s, 9H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 135.6 (1C), 135.3 (1C), 132.0 (1C), 129.6 (4C), 119.5 (1C), 114.1 (1C), 56.2 (1C), 31.3 (1C), 20.9 (1C), 20.5 (1C), 18.3 (1C); Anal. calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$: C, 63.85; H, 6.51; N, 5.32. Found: C, 63.91; H 6.43.

3-(2,3-Dimethyl-but-2-enyl)-oxindole: The reaction was performed according to the representative procedure with oxindole (266 mg, 2.00 mmol), 2,3-dimethylbutadiene (247 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME, $\text{CpPd}(\text{allyl})$ (8.5 mg, 0.040 mmol) in 0.05 mL DME, and an additional 0.5 mL DME at room temperature for 5.5 h. Automated column chromatography (diethyl ether/pentane gradient from 5/95 to 50/50) gave the title compound as a mixture of isomers **1** (129 mg, 30% yield), **2** (96.5 mg, 22% yield) as white powders. ^1H NMR (**1**): (400.13 MHz, CDCl_3) δ 8.70 (br s, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.94 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 3.54 (dd, $J = 10.7, 4.9$ Hz, 1H), 2.65 (dd, $J = 13.4, 4.9$ Hz, 1H), 2.56 (dd, $J = 13.4, 10.7$ Hz, 1H), 1.80 (s, 3H), 1.73 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (**1**): (100.5 MHz, CDCl_3) δ 180.7 (1C), 141.2 (1C), 129.7 (1C), 128.0 (1C), 127.7 (1C), 124.7 (1C), 123.8 (1C), 122.0 (1C), 109.5 (1C), 44.2 (1C), 35.7 (1C), 20.9 (1C), 20.7 (1C), 18.0 (1C); ^1H NMR (**2**): (CDCl_3) δ 7.72 (br s, 1H), 7.19 (td, $J = 7.6, 1.0$ Hz, 1H), 7.13 (br d, $J = 7.6$ Hz, 1H), 6.94 (td, $J = 7.6, 0.8$ Hz, 1H), 6.82 (br d, $J = 7.6$ Hz, 1H), 4.940–4.935 (m, 1H), 4.72 (s, 1H), 3.50 (s, 1H), 1.97 (br s, 3H), 1.42 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (**2**): (CDCl_3) δ 178.8 (1C), 149.8 (1C), 141.7 (1C), 127.8 (1C), 127.6 (1C), 125.8 (1C), 121.6 (1C), 111.8

(1C), 108.9 (1C), 51.7 (1C), 42.7 (1C), 25.1 (1C), 22.0 (1C), 20.0 (1C); Anal. calcd for $C_{14}H_{17}NO$ (**2**): C, 78.10; H, 7.96; N, 6.51. Found: C, 77.02; H, 7.90; N, 6.28.

3-(2,3-Dimethyl-but-2-enyl)-1,3-dimethyl-oxindole: The reaction was performed according to the representative procedure with 1,3-dimethyl-oxindole (161 mg, 1.00 mmol), 2,3-dimethylbutadiene (123 mg, 1.50 mmol), DCyPP (8.7 mg, 0.020 mmol) in 0.1 mL DME, CpPd(allyl) (4.3 mg, 0.020 mmol) in 0.05 mL DME, and an additional 0.25 mL DME at 60 °C for 4 h. Automated column chromatography (diethyl ether/pentane gradient from 5/95 to 10/90) afforded the title compound as a colorless oil (230 mg, 95% yield). 1H NMR: (400.13 MHz, $CDCl_3$) δ 7.23 (td, $J = 7.6, 1.0$ Hz, 1H), 7.15 (d, $J = 7.3$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 7.8$ Hz, 1H), 3.19 (s, 3H), 2.67–2.60 (m, 2H), 1.50 (s, 3H), 1.48 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H); ^{13}C NMR: (100.5 MHz, $CDCl_3$) δ 181.0 (1C), 143.0 (1C), 134.0 (1C), 128.5 (1C), 127.5 (1C), 123.5 (1C), 123.4 (1C), 121.9 (1C), 107.6 (1C), 48.9 (1C), 42.6 (1C), 26.1 (1C), 23.8 (1C), 21.2 (1C), 20.7 (1C), 19.6 (1C); Anal. calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 78.75; H, 8.84; N, 5.74.

2-Acetyl-4,5-dimethyl-hex-4-enoic acid methylamide: The reaction was performed according to the representative procedure with methyl acetoacetamide (65% aqueous solution) (354 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (43.7 mg, 0.100 mmol) in 0.1 mL DME, CpPd(allyl) (21.3 mg, 0.100 mmol) in 0.05 mL DME, and an additional 0.5 mL DME at 90 °C for 1.5 h. Column chromatography (diethyl ether/pentane gradient from 67/33 to 90/10) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 97:3 as white powder (300 mg, 76% yield). 1H NMR: (400.13 MHz, $CDCl_3$) δ 6.43 (br s, 1H), 3.55 (dd, $J = 8.4, 7.0$ Hz, 1H), 2.80 (d, $J = 4.8$ Hz, 3H), 2.65 (dd, $J = 13.5, 8.4$ Hz, 1H), 2.54 (dd, $J = 13.5, 7.0$ Hz, 1H), 2.21 (s, 3H), 1.65 (s, 9H); ^{13}C NMR: (100.5 MHz, $CDCl_3$) δ 208.8 (1C), 169.4 (1C),

128.2 (1C), 123.3 (1C), 59.1 (1C), 36.6 (1C), 30.8 (1C), 26.4 (1C), 20.8 (1C), 20.4 (1C), 18.2 (1C); Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.95; H, 9.81; N, 7.10. Selected 1H NMR of minor isomer: 6.96 (br s, 1H), 4.88 (s, 1H), 4.78 (s, 1H), 3.83 (s, 1H), 1.88 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H).

2-Acetyl-4,5-dimethyl-hex-4-enoic acid ethyl ester: The reaction was performed according to the representative procedure with ethyl acetoacetate (260 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME and $[CpPd(allyl)]$ (8.5 mg, 0.040 mmol) in 0.05 mL DME at room temperature for 8.5 h. Column chromatography (diethyl ether/pentane 2:98) gave the title compound as a mixture of regioisomers **1:2** in a ratio of afforded a 94:6 as a colorless oil (354 mg, 83% yield). 1H NMR: (400.13 MHz, $CDCl_3$) δ 4.23–4.10 (m, 2H), 3.58 (t, $J = 7.6$ Hz, 1H), 2.67 (dd, $J = 14.0, 8.2$ Hz, 1H), 2.57 (dd, $J = 14.0, 6.8$ Hz, 1H), 2.22 (s, 3H), 1.66 (s, 3H), 1.63 (s, 6H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR: (100.5 MHz, $CDCl_3$) δ 203.4 (1C), 169.9 (1C), 127.7 (1C), 123.2 (1C), 61.3 (1C), 58.3 (1C), 33.0 (1C), 29.1 (1C), 20.8 (1C), 20.4 (1C), 18.0 (1C), 14.1 (1C); Anal. calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.73; H, 9.58. 1H NMR of minor isomer: 4.83–4.82 (m, 2H), 3.72 (s, 1H), 1.80 (s, 3H).

2-Cyano-3,3,4-trimethyl-pent-4-enoic acid ethyl ester: The reaction was performed according to the representative procedure with ethyl cyanoacetate (226 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME, $CpPd(allyl)$ (8.5 mg, 0.040 mmol) in 0.1 mL DME, and an additional 0.5 mL of DME at room temperature for 7.5 h. Column chromatography (diethyl ether/pentane gradient from 2/98 to 6/94) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 38:62 as a colorless oil (286 mg, 73% yield). 1H NMR (**2**): (400.13 MHz, $CDCl_3$) δ 4.93 (s, 1H), 4.92 (s, 1H),

4.28–4.19 (m, 2H), 3.63 (s, 1H), 1.82 (s, 3H), 1.34–1.27 (m, 9H); ^{13}C NMR (**2**): (100.5 MHz, CDCl_3) δ 165.0 (1C), 147.1 (1C), 116.0 (1C), 113.2 (1C), 62.4 (1C), 46.9 (1C), 42.4 (1C), 25.7 (1C), 24.0 (1C), 19.3 (1C), 14.03 (1C); ^1H NMR (**1**): (400.13 MHz, CDCl_3) δ 4.28–4.19 (m, 2H), 3.56 (dd, $J = 9.4, 6.3$ Hz, 1H), 2.77 (dd, $J = 13.6, 9.4$ Hz, 1H), 2.67 (dd, $J = 13.6, 6.3$ Hz, 1H), 1.74 (s, 3H), 1.71 (s, 3H), 1.70 (s, 3H), 1.34–1.37 (m, 3H); ^{13}C NMR (**1**): (100.5 MHz, CDCl_3) δ 166.3 (1C), 130.6 (1C), 121.4 (1C), 116.7 (1C), 62.7 (1C), 36.6 (1C), 34.9 (1C), 20.9 (1C), 20.6 (1C), 18.0 (1C), 14.00 (1C); Anal. calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.80; H, 8.86; N, 7.06.

Dimethyl 2-(2,3-Dimethyl-but-2-enyl)-malonate:ⁱ The reaction was performed according to the representative procedure with dimethyl malonate (264 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME and CpPd(allyl) (8.5 mg, 0.040 mmol) in 0.05 mL DME at room temperature for 22.5 h. Column chromatography (diethyl ether/pentane 3/97) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 88:12 as a colorless oil (377 mg, 88% yield). ^1H NMR (**1**): (400.13 MHz, CDCl_3) δ 3.72 (s, 6H), 3.52 (t, $J = 7.8$ Hz, 1H), 2.68 (d, $J = 7.8$ Hz, 2H), 1.66 (s, 3H), 1.63 (s, 6H); ^{13}C NMR (**1**): (100.5 MHz, CDCl_3) δ 169.8 (2C), 128.1 (1C), 123.0 (1C), 52.4 (2C), 50.5 (1C), 33.6 (1C), 20.8 (1C), 20.3 (1C), 17.9 (1C); Selected ^1H NMR of (**2**): 4.819–4.418 (m, 2H), 3.69 (s, 6H), 1.86 (s, 3H) 1.29 (s, 6H); ^{13}C NMR (**2**): (CDCl_3) δ 168.5 (2C), 150.0 (1C), 111.3 (1C), 58.4 (1C), 52.0 (2C), 41.4 (1C), 24.6 (2C), 19.6 (1C).

2-(1,1,2-Trimethyl-allyl)-malononitrile: The reaction was performed according to the representative procedure with malononitrile (132 mg, 2.00 mmol), 2,3-dimethylbutadiene (246 mg, 3.00 mmol), DCyPP (17.5 mg, 0.0400 mmol) in 0.1 mL DME, CpPd(allyl) (8.5 mg, 0.040 mmol) in 0.05 mL DME, and an additional 0.25 mL DME at 90 °C for 2.5 h. Column

chromatography (diethyl ether/pentane gradient from 4/96 to 10/90) gave the title compound as a mixture of regioisomers **1:2** in a ratio of 29:71 as a colorless oil (188 mg, 63% yield). ^1H NMR (**2**): (400.13 MHz, CDCl_3) δ 5.11 (q, $J = 1.2$ Hz, 1H), 5.06 (s, 1H), 3.79 (s, 1H), 1.82 (d, $J = 1.2$ Hz, 3H), 1.41 (s, 6H); ^{13}C NMR (**2**): (100.5 MHz, CDCl_3) δ 144.6 (1C), 115.0 (1C), 112.0 (2C), 43.0 (1C), 33.8 (1C), 24.4 (2C), 19.2 (1C); ^1H NMR (**1**): (400.13 MHz, CDCl_3) δ 3.75 (t, $J = 7.8$ Hz, 1H), 2.82 (d, $J = 7.8$ Hz, 2H), 1.79 (s, 3H), 1.75 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (**1**): (100.5 MHz, CDCl_3) δ 133.3 (1C), 119.7 (1C), 112.9 (2C), 35.6 (1C), 21.5 (1C), 21.0 (1C), 20.8 (1C), 18.1 (1C); Anal. calcd for $\text{C}_9\text{H}_{12}\text{N}_2$: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.99; H, 8.28; N, 18.85.

Reactions with 1,3-Cyclohexadiene.

Representative Procedure: 3-Cyclohex-2-enyl-3-oxo-3-phenylpropionitrile: The reaction was performed according to the representative procedure with 3-oxo-3-phenylpropionitrile (144.2 mg, 0.99 mmol), 1,3-cyclohexadiene (0.3 ml, 3.10 mmol), DCyPP (23.0 mg, 0.052 mmol) and CpPd(allyl) (11.3 mg, 0.052 mmol) in 1.0 mL DME at 80 °C for 7 h. Column chromatography (hexane/diethylether 7/1) gave the title compound as a colorless oil (204 mg, 91% yield). ^1H NMR (500.13 MHz, CDCl_3) δ 7.98–7.94 (m, 4H), 7.63–7.68 (m, 2H), 7.55–7.54 (m, 4H), 5.75–5.69 (m, 1H), 5.50–5.45 (m, 1H), 4.40 (d, $J = 6.6$ Hz, 1H), 4.30 (d, $J = 6.5$ Hz, 1H), 2.97 (m, 2H), 2.03 (m, 4H), 1.92–1.75 (m, 5H), 1.68–1.43 (m, 5H); ^{13}C NMR: (125.7 MHz, CDCl_3) δ 190.7, 190.6, 134.6, 134.5, 134.40, 134.38, 131.7, 131.5, 129.1, 129.0, 128.69, 128.67, 126.0, 125.1, 116.4, 116.3, 45.7, 45.2, 36.4, 36.3, 27.8, 26.0, 24.62, 24.60, 20.96, 20.7; Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{NO}$: C, 79.97; H, 6.71; N, 6.22; O, 7.10. Found: C, 79.72; H, 6.74.

2-Cyclohex-2-enyl-2-methylmalonicacidmethylester: The reaction was performed according to the representative procedure with 2-methylmalonicaciddimethylester (137.0 mg,

0.94 mmol), 1,3-cyclohexadiene (0.3 mL, 3.10 mmol), DCyPP (22.0 mg, 0.050 mmol) and CpPd(allyl) (10.0 mg, 0.047 mmol) in 1.0 mL DME at 80 °C for 24 h. Column chromatography (hexane/diethylether 10/1) gave the title compound as a colorless oil (196 mg, 92% yield). ^1H NMR (500.13 MHz, CDCl_3) δ 5.78 (m, 1H), 5.48 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.05 (m, 1H), 1.97 (m, 2H), 1.85–1.75 (m, 1H), 1.64–1.49 (m, 4H), 1.33 (s, 3H); ^{13}C NMR: (125.7 MHz, CDCl_3) δ 172.0, 171.9, 129.5, 127.3, 57.0, 52.3, 40.2, 24.8, 24.3, 22.2, 16.0; Anal. calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4$: C, 63.70; H, 8.02; O, 28.28. Found: C, 63.96; H, 8.10.

4-Cyclohex-2-enylisochroman-3-one: The reaction was performed according to the representative procedure with isochroman-3-one (160.0 mg, 1.08 mmol), 1,3-cyclohexadiene (0.30 mL, 3.1 mmol), DCyPP (9.0 mg, 0.021 mmol) and CpPd(allyl) (5.0 mg, 0.023 mmol) in 1.0 mL DME at 80 °C for 18 h. Column chromatography (hexane/diethylether 10/1 gradient to 5/1) gave the title compound as a yellow oil (214 mg, 87% yield). ^1H NMR (400.13 MHz, CDCl_3): 7.40–7.00 (m, 8H), 5.80–5.12 (m, 8H), 3.58–3.33 (m, 2H), 2.66–2.45 (m, 2H), 2.03–1.25 (m, 12H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 171.9, 171.5, 133.7, 133.5, 131.1, 130.9, 130.0, 129.8, 128.8, 128.6, 128.19, 128.17, 127.4, 127.33, 127.32, 126.9, 124.8, 124.6, 69.89, 69.87, 52.1, 51.7, 36.9, 36.2, 27.2, 26.6, 24.9, 24.8, 20.9, 20.7; Anal. calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.92; H, 7.06; O, 14.02. Found: C, 78.58; H, 6.94.

1-Cyclohex-2-enyl-3,4-dihydro-1-H-naphthalen-2-one: The reaction was performed according to the representative procedure with 2-tetralone (46.0 mg, 1.00 mmol), 1,3-cyclohexadiene (0.30 mL, 3.10 mmol), DCyPP (8.5 mg, 0.020 mmol) and CpPd(allyl) (4.2 mg, 0.019 mmol) in 0.5 mL DME at 80 °C for 20 h. Column chromatography (hexane/diethylether 10/1) gave the title compound as a colorless oil (204 mg, 91% yield). ^1H NMR (400.13 MHz, CDCl_3) δ 7.22–7.14 (m, 6H), 7.07 (m, 2H), 5.72–5.66 (m, 1H), 5.64–5.59 (m, 1H), 5.55–5.50 (m,

1H), 5.29-5.25 (m, 1H), 3.28-3.08 (m, 4H), 2.99-2.80 (m, 2H), 2.79 (m, 1H), 2.64–2.54 (m, 3H), 2.42–2.28 (m, 2H), 1.92–1.81 (m, 4H), 1.70–1.52 (m, 3H), 1.47–1.30 (m, 4H), 1.19–1.09 (m, 1H); ¹³C NMR: (100.5 MHz, CDCl₃) δ 212.8, 212.6, 137.9, 137.8, 137.4, 137.3, 130.9, 130.7, 130.0, 129.8, 129.4, 129.1, 129.0, 128.9, 127.9, 127.8, 127.4, 127.3, 61.6, 60.7, 39.1, 38.6, 38.1, 37.9, 28.7, 28.5, 28.4, 27.5, 25.95, 25.89, 22.3, 22.1; Anal. calcd for C₁₆H₁₈O: C, 84.91; H, 8.02; O, 7.07. Found: C, 84.65; H, 8.40.

Cyclohex-2-enyl-(4-trifluoromethylphenyl)acetonitrile: The reaction was performed according to the representative procedure with 4-trifluoromethylacetonitrile (185.0 mg, 1.00 mmol), 1,3-cyclohexadiene (0.3 mL, 3.10 mmol), DCyPP (9.00 mg, 0.021 mmol) and CpPd(allyl) (4.5 mg, 0.021 mmol) in 0.5 mL DME at 80 °C for 20 h. Column chromatography (hexane/diethylether 20/1) gave the title compound as a colorless oil (174.0 mg, 94% yield). ¹H NMR (400.13 MHz, CDCl₃) δ 7.65 (d, *J* = 8.6 Hz, 4H), 7.46 (m, *J* = 8.1 Hz, 4H), 5.95–5.86 (m, 2H), 5.7–5.65 (m, 1H), 5.43–5.38 (m, 1H), 3.83 (d, *J* = 7.3 Hz, 1H), 3.76 (d, *J* = 7.3 Hz, 1H), 2.65 (m, 2H), 2.03 (m, 4H), 1.83–1.68 (m, 4H), 1.59–1.46 (m, 3H), 1.42–1.31 (m, 1H); ¹³C NMR: (100.5 MHz, CDCl₃) δ 138.33, 138.26, 131.57, 130.63, 130.61, 130.3, 130.28, 128.43, 128.40, 126.1, 125.94, 125.92, 125.90, 125.89, 125.86, 125.85, 125.81, 125.3, 125.1, 122.4, 119.4, 119.2, 43.2, 43.0, 40.5, 40.3, 27.3, 26.1, 24.9, 24.8, 20.9, 20.8; Anal. calcd for C₁₅H₁₄F₃N: C, 67.92; H, 5.32; F, 21.48; N, 5.28. Found: C, 67.76; H, 5.23.

1-((Cyclohex-2-enyl)(phenylsulfonyl)methylsulfonyl)benzene: The reaction was performed according to the representative procedure with bis(phenylsulfonyl)methane (148.0 mg, 0.50 mmol), 1,3-cyclohexadiene (0.19 mL, 2.00 mmol), DCyPP (11.00 mg, 0.025 mmol) and CpPd(allyl) (6.0 mg, 0.03 mmol) in 0.5 mL DME at 80 °C for 7 h. Evaporation of all volatiles followed by recrystallization (ether/DCM) gave the title compound as white powder (167.0 mg,

89% yield). ^1H NMR (400.13 MHz, CDCl_3) δ 7.99-7.94 (m, 4H), 7.71-7.64 (m, 2H), 7.58-7.52 (m, 4H), 5.64 (m, 1H), 5.41 (m, 1H), 4.52 (d, $J = 1.7$ Hz, 1H), 3.45 (m, 1H), 2.10-1.76 (m, 6H), 1.50 (m, 2H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 139.8, 138.6, 134.5, 134.3, 129.8, 129.7, 129.4, 129.0, 128.9, 124.8, 87.2, 36.5, 27.2, 24.2, 22.8.

Diethyl-2-(cyclohex-2-enyl)malonate:ⁱⁱ The reaction was performed according to the representative procedure with diethylmalonate (161.0 mg, 1.00 mmol), 1,3-cyclohexadiene (0.40 ml, 4.00 mmol), DCyPP (21.00 mg, 0.05 mmol) and CpPd(allyl) (11.0 mg, 0.05 mmol) in 1.0 mL DME at 80 °C for 18 h. Column chromatography (hexane/diethylether 10/1) gave the title compound as a colorless oil (217.0 mg, 85% yield). ^1H NMR (400.13 MHz, CDCl_3) δ 5.72 (m, 1H), 5.52 (m, 1H), 4.15 (q, $J = 7.2$ Hz, 4H), 3.19 (d, $J = 9.0$ Hz, 1H), 2.86 (m, 1H), 1.95 (m, 2H), 1.78-1.65 (m, 2H), 1.53 (m, 1H), 1.39-1.30 (m, 1H), 1.23 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 168.4, 168.3, 129.3, 127.5, 61.1, 57.0, 35.2, 26.5, 24.8, 20.9, 14.0.

2-(Cyclohex-2-enyl)malononitrile:ⁱⁱⁱ The reaction was performed according to the representative procedure with malononitrile (136.0 mg, 2.10 mmol), 1,3-cyclohexadiene (0.76 ml, 8.00 mmol), DCyPP (18.00 mg, 0.05 mmol) and CpPd(allyl) (11.0 mg, 0.05 mmol) in 2.0 mL DME at RT for 19 h. Column chromatography (hexane/diethylether 10/1) gave the title compound as a colorless oil (206.0 mg, 68% yield). ^1H NMR (400.13 MHz, CDCl_3) δ 6.10 (m, 1H), 5.62 (m, 1H), 3.64 (d, $J = 6.7$ Hz, 1H), 2.81 (m, 1H), 2.11-2.03 (m, 3H), 1.85 (m, 1H), 1.67-1.53 (m, 2H); ^{13}C NMR: (100.5 MHz, CDCl_3) δ 133.8, 123.2, 111.9, 37.2, 28.5, 26.4, 24.4, 20.3.

3-Cyclohex-2-enyl-pentane-2,4-dione: The reaction was performed according to the representative procedure with acetylacetone (190 mg, 1.70 mmol), 1,3-cyclohexadiene (0.40 ml, 4.00 mmol), DCyPP (22.00 mg, 0.05 mmol) and CpPd(allyl) (11.0 mg, 0.05 mmol) in 1.0 mL

DME at 80 °C for 20 h. Column chromatography (hexane/diethylether 10/1) gave the title compound as a colorless oil (263.0 mg, 77% yield).

2-Acetyl-2-(2,3-dimethyl-but-2-enyl)tetralone: In a drybox, a screw-capped vial containing a small stir bar was charged with (*R*)-(-)-1-[(*S*)-2-diphenylphosphino)ferrocenyl]ethyl-di-*t*-butylphosphine (27.1 mg, 0.0500 mmol), 1,3-dimethylbutadiene (167 mg, 2.00 mmol), CpPd(allyl) (10.6 mg, 0.0499 mmol) and 2-acetyltetralone (188 mg, 2.00 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. After being stirred at room temperature for 24 h, the reaction mixture adsorbed on silica gel and eluted with diethylether/hexanes 25/75 to yield 2-acetyl-2-(2,3-dimethyl-but-2-enyl)tetralone as a colorless solid (264 mg, 57% ee, 97% yield.). ¹H NMR (400.13 MHz, CDCl₃) δ 8.40 (dd, *J* = 8, 1 Hz, 1H), 7.13 (dt, *J* = 8, 1 Hz, 1H), 7.06 (t, *J* = 8 Hz, 1H), 6.70 (d, *J* = 8 Hz, 1H), 3.20 (d, *J* = 14 Hz, 1H), 3.17 (ddd, *J* = 13, 8 Hz, 1H), 2.94 (d, *J* = 14 Hz, 1H), 2.63 (ddd, *J* = 13, 5, 4 Hz, 1H), 2.54 (dt, *J* = 17, 4 Hz, 1H), 2.03 (s, 3H), 1.83 (ddd, *J* = 17, 8, 5 Hz, 1H), 1.62 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H); ¹³C NMR: (100.5 MHz, CDCl₃) δ 205.7 (1C), 197.6 (1C), 144.1 (1C), 133.8 (1C), 132.3 (1C), 129.6 (1C), 128.9 (1C), 128.0 (1C), 126.6 (1C), 123.5 (1C), 64.7 (1C), 39.2 (1C), 28.3 (1C), 27.0 (1C), 26.0 (1C), 21.2 (1C), 20.9 (1C), 19.7 (1C).

ⁱ Morimoto, Y.; Shirahama, H. *Tetrahedron* **1996**, 52, 10631-10652.

ⁱⁱ You, S.-L.; Luo, Y.-M.; Deng, W.-P.; Hou, X.-L.; Dai, L.-X. *J. Organomet. Chem.* **2001**, 637, 845-849.

ⁱⁱⁱ Curran, D. P.; Seong, C. M. *Tetrahedron* **1992**, 48, 2175-2190.