Supporting Information for

**Stereoselective Intramolecular 1,3 C-H Insertion in
Rh(II) Carbene Reactions**

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General information. All reactions with air- and moisture-sensitive components were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. CH₂Cl₂ was freshly distilled from CaH₂ and THF was freshly distilled from Na before use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H and ¹³C NMR spectra were recorded at 200 and 50 MHz with a Varian Mercury 200 spectrometer or 300 and 75 MHz with a Varian Mercury 300 spectrometer. Chemical shifts are reported by ppm using tetramethylsilane as internal standard. Mass spectra were obtained on a VG ZAB-HS mass spectrometer.

General procedure for nucleophilic substitution of 1a~e with sodium *p*-toluenesulfinate.

In a dry two-necked flask were added sodium *p*-toluenesulfinate (2 mmol) and DMF (30 mL). The mixture was stirred until it turned to be a homogenous solution. β-Acetoxy α-diazo carbonyl compound **1a~e** (1 mmol) was added to the solution and stirring was continued for 7 days until all the starting material disappeared as judged by TLC check. DMF was removed under reduced pressure and distilled water was then added to the crude residue. The mixture was extracted with ethyl ether (3 x 15 mL). The combined ethereal solution was washed with saturated aqueous NaCl and then dried with anhydrous MgSO₄. Removal of the solvent gave a crude product, which was purified by silica gel column.

Ethyl 2-Diazo-3-(*p*-tolylsulfonyl)-pentanoate (2a). TLC *R_f* = 0.21 (petroleum ether : acetone = 10 : 1); IR 2981, 2099, 1699, 1286, 1145 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.05-1.10 (m, 6H), 1.65-1.79 (m, 1H), 2.39-2.46 (m, 1H), 2.43 (s, 3H), 3.80-3.99 (br, 3H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 11.07, 14.18, 17.48, 21.59, 61.09, 61.28, 128.63, 129.56, 134.25, 144.64; MS *m/z* (EI) 310 (*M*⁺, 0.55), 282 [(*M*-28)⁺, 0.36], 218 (3), 172 (4), 155 (24), 127 (72), 91 (95), 81 (26), 65 (33), 55 (43), 29 (100). HMRS calcd for 310.0987. Found: 310.0997.

Ethyl 2-Diazo-3-(*p*-tolylsulfonyl)-hexanoate (2b). TLC *R_f* = 0.21 (petroleum ether : acetone = 10 : 1); IR 2964, 2099, 1698, 1321, 1142 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 0.93-1.09 (m, 6H), 1.41-1.52 (m, 2H), 1.64-1.79 (m, 1H), 2.23-2.70 (m, 1H), 2.43 (s, 3H), 3.86-3.98 (m, 3H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 13.43, 14.15, 19.74, 21.55, 25.47, 59.32, 61.22, 128.72, 129.61, 134.43, 144.96, 154.96; MS *m/z* (EI) 324 (*M*⁺, 0.09), 296 [(*M*-28)⁺, 0.02], 251 (9), 169 (55), 139 (98), 113 (100), 91 (95), 65 (64), 55 (48). Anal. calcd for C₁₅H₂₀N₂O₄S: C, 55.54; H, 6.21; N, 8.64. Found: C, 55.56; H, 6.26; N, 8.65.

3-Diazo-4-(*p*-tolylsulfonyl)-hexan-2-one (2c). TLC *R_f* = 0.29 (petroleum ether : acetone = 5 : 1); IR 2917, 2086, 1649, 1315, 1145 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.67-1.77 (m, 1H), 2.06 (s, 3H), 2.29-2.47 (m, 1H), 2.43 (s, 3H), 4.07 (br, d, *J* = 11 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 9.6 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 10.91, 17.25, 21.59, 24.66, 59.02, 128.36, 129.62, 134.21, 145.11, 188.19. MS *m/z* (EI) 280 (*M*⁺, 0.36), 252 (0.26), 150 (15), 139 (39), 119 (22), 97 (87), 65 (33), 43(100), 41 (32). Anal. calcd for C₁₃H₁₆N₂O₃S: C, 55.70; H, 5.75; N, 9.99. Found: C, 55.74; H, 5.79; N, 9.86.

1-Diazo-2-(*p*-tolylsulfonyl)butyl phenyl ketone (2d). TLC R_f = 0.39 (petroleum ether : acetone = 5 : 1); IR 2928, 2083, 1621, 1292, 1148 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.13 (t, J = 7.5 Hz, 3H), 1.74-1.90 (m, 1H), 2.43-2.52 (m, 1H), 2.40 (s, 3H), 4.30 (br, 1H), 7.27-7.51 (m, 7H), 7.80-7.86 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 11.02, 17.19, 21.60, 59.80, 126.74, 129.04, 129.73, 129.91, 131.82, 134.35, 136.20, 145.17. MS m/z (EI) 314 $[(\text{M}-28)^+, 1.00]$, 176 (55), 159 (37), 139 (41), 131 (97), 115 (44), 105 (100), 91 (87), 77 (83). Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$: C, 63.14; H, 5.30; N, 8.18. Found: C, 62.96; H, 5.36; N, 7.84.

Ethyl 2-Diazo-3-(*p*-tolylsulfonyl)-heptanoate (2e). TLC R_f = 0.38 (petroleum ether : acetone = 5 : 1); IR 2959, 2097, 1698, 1322, 1146 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 0.91 (t, J = 7.2 Hz, 3H), 1.06 (t, J = 6.3 Hz, 3H), 1.26-1.80 (br, 5H), 2.23-2.33 (br, 1H), 2.43 (s, 3H), 3.84-3.99 (br, 4H), 7.33 (d, J = 7.8 Hz, 2H), 7.73-7.84 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.56, 14.05, 21.47, 21.92, 23.10, 28.40, 59.49, 61.18, 128.77, 129.65, 134.45, 145.04, 164.92; MS m/z (EI) 338 (M^+ , 0.20), 310 (0.15), 127 (77), 109 (50), 91 (66), 81 (92), 55 (49), 29 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$: C, 56.78; H, 6.55; N, 8.28. Found: C, 56.76; H, 6.58; N, 8.28.

Ethyl 2-Diazo-3-(*p*-tolylsulfonyl)-nonanoate (2f). TLC R_f = 0.59 (petroleum ether : acetone = 5 : 1); IR 2929, 2098, 1698, 1324, 1141 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.87 (t, 3H, J = 6.7 Hz), 1.07 (br, 3H), 1.26-1.43 (m, 8H), 1.61-1.73 (m, 1H), 2.27 (br, 1H), 2.43 (s, 3H), 3.86-3.98 (m, br, 3H), 7.33 (d, 2H, J = 8.1 Hz), 7.76 (d, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 14.2, 21.6, 22.4, 23.5, 26.4, 28.5, 31.3, 59.6, 61.2, 128.8, 129.6, 134.5, 145.0; MS m/z (EI) 366 (M^+ , 0.38), 338 (0.69), 293 (3), 211 (10), 183 (62), 155 (51), 139 (52), 109 (100), 91 (81), 67 (39), 55 (47), 29 (99). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{SO}_4\text{N}_2$: C, 58.99; H, 7.15; N, 7.64. Found: C, 58.96; H, 7.10; N, 7.51.

β -Tosyl α -diazo carbonyl compounds **7a** and **7b** were prepared similarly from the corresponding β -hydroxy α -diazo carbonyl compounds.

Ethyl 3-Cyclopentyl-2-diazo-3-(*p*-tolylsulfonyl)propanoate (7a). TLC R_f = 0.34 (petroleum ether : acetone = 10 : 1); IR 2960, 2096, 1697, 1303, 1143 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.03 (t, J = 7.2 Hz, 3H), 1.26-1.44 (m, 1H), 1.65-1.74 (m, 5H), 1.81-1.95 (m, 1H), 2.17-2.26 (m, 1H), 2.42 (s, 3H), 2.52-2.56 (m, 1H), 3.80 (d, J = 10 Hz, 1H), 3.82-3.90 (m, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.04, 21.41, 23.94, 25.32, 31.03, 31.53, 36.85, 61.04, 63.74, 128.27, 129.36, 135.26, 144.67. MS m/z (EI) 350 (M^+ , 0.24), 195 (13), 167 (15), 139 (100), 121 (67), 91 (60), 65 (26), 29 (45). Anal. calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$: C, 58.27; H, 6.33; N, 7.99. Found: C, 58.25; H, 6.38; N, 7.99.

Ethyl 3-Cyclohexyl-2-diazo-3-(*p*-tolylsulfonyl)propanoate (7b). TLC R_f = 0.39 (petroleum ether : acetone = 10 : 1); IR 2930, 2097, 1697, 1318, 1142 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.03-1.42 (m, 9H), 1.63-2.04 (m, 5H), 2.42 (s, 3H), 3.75-3.93 (m, 3H), 7.32 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.22, 21.57, 25.82, 25.92, 25.96, 29.89, 31.88, 36.90, 61.27, 63.97, 128.11, 129.57, 135.85, 144.75. MS m/z (EI) 181 (29), 153 (61), 135 (100), 107 (76), 91 (62), 79 (48), 67 (41). Anal. calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$: C, 59.32; H, 6.64; N, 7.69. Found: C, 59.37; H, 6.60; N, 7.64.

General procedure for Rh₂(OAc)₄-catalyzed reaction of 2a~e and 7a,b.

Freshly distilled CH₂Cl₂ or benzene (30 mL) was treated by bubbling with N₂ gas for 10 min and then sealed with rubber stopper. Under a stream of N₂ gas, Rh₂(OAc)₄ (5 % mmol) was added to a three-necked round-bottom flask, which was equipped with a drop funnel. To the flask was added the N₂-treated CH₂Cl₂ or benzene. The diazo compound (1 mmol) was dissolved in the above N₂-treated CH₂Cl₂ or benzene and added to the flask through drop funnel. The system was kept under N₂ atmosphere with a balloon. The stirring was continued for 12 h, during which the N₂ balloon is changed several times in order to strictly excluding oxygen. After completion of the reaction, solvent was removed under reduced pressure and the crude residue was separated with silica gel column (petroleum ether : acetone = 10 : 1).

Similar procedure was followed when the reaction was carried out under reflux.

***r*-1, *trans*-2, *trans*-3, Ethyl 1-Methyl-3-(*p*-tolylsulfonyl)cyclopropylformate (3a).** TLC *R_f* = 0.09 (petroleum ether : acetone = 10 : 1); IR 2980, 1735, 1317, 1151 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.20 (d, *J* = 6.1 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.99 (dd, *J* = 9.0, 7.1 Hz, 1H), 2.39-2.43 (m, 1H), 2.44 (s, 3H), 2.56 (dd, *J* = 9.0, 6.1 Hz, 1H), 4.13-4.21 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 13.75, 16.10, 19.22, 21.40, 30.64, 46.73, 61.39, 127.55, 129.65, 137.71, 144.44, 167.08; MS *m/z* (EI) 282 (M⁺, 2), 237 (11), 209 (5), 155 (5), 139 (15), 127 (65), 99 (100), 91 (31), 81 (12), 71 (13), 65 (15), 53 (15), 43 (37), 39 (16), 29 (23), 27 (18). Anal. calcd for C₁₄H₁₈O₄S: C, 59.55; H, 6.43. Found: C, 59.37; H, 6.55.

***r*-1, *trans*-2, *trans*-3, Ethyl 1-Ethyl-3-(*p*-tolylsulfonyl)cyclopropylformate (3b).** TLC *R_f* = 0.11 (petroleum ether : acetone = 10 : 1); IR 2966, 1737, 1324, 1144 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.39-1.64 (m, 2H), 2.03 (dd, *J* = 9.2, 7.0 Hz, 1H), 2.28-2.41 (m, 1H), 2.45 (s, 3H), 2.55 (dd, *J* = 9.2, 6.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 12.44, 13.94, 21.59, 24.39, 26.31, 29.75, 45.89, 61.56, 127.72, 129.64, 137.61, 144.45, 167.15; MS *m/z* (EI) 296 (M⁺, 0.70), 251 (14), 223 (7), 141 (99), 139 (18), 113 (100), 95 (62), 91 (33), 67 (25), 41 (23), 29 (27). Anal. calcd for C₁₅H₂₀O₄S: C, 60.79; H, 6.80. Found: C, 60.34; H, 6.89.

***r*-1, *trans*-2, *trans*-3, 1-Methyl-3-(*p*-tolylsulfonyl)cyclopropyl Methyl Ketone (3c).** TLC *R_f* = 0.16 (petroleum ether : acetone = 5 : 1); IR 2965, 1713, 1303, 1148 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.14 (d, *J* = 6.0 Hz, 3H), 2.15 (dd, *J* = 9.3, 7.1 Hz, 1H), 2.29 (s, 3H), 2.35-2.38 (m, 1H), 2.67 (dd, *J* = 9.3, 6.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 16.01, 19.48, 21.42, 30.89, 37.95, 48.43, 127.37, 129.65, 137.59, 144.43, 200.63; MS *m/z* (EI) 252 (M⁺, 2), 210 (3), 155 (4), 97 (100), 91 (30), 43 (99), 41 (28), 27 (12). Anal. calcd for C₁₃H₁₆O₃S: C, 61.88; H, 6.39. Found: C, 61.72; H, 6.46.

***r*-1, *trans*-2, *trans*-3, 1-Methyl-3-(*p*-tolylsulfonyl)cyclopropyl Phenyl Ketone (3d).** TLC *R_f* = 0.24 (petroleum ether : acetone = 5 : 1); IR 3031, 1678, 1312, 1151 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.27 (d, *J* = 5.7 Hz, 3H), 2.33 (s, 3H), 2.65-2.69 (m, 2H), 2.87-2.92 (m, 1H),

7.11 (d, $J = 8.4$ Hz, 2H), 7.32-7.37 (m, 2H), 7.49-7.55 (m, 3H), 7.86 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.43, 18.52, 21.45, 34.78, 49.01, 127.48, 128.27, 128.40, 129.45, 133.02, 136.95, 137.39, 144.17, 191.28. MS m/z (EI) 314 (M^+ , 0.3), 250 (14), 207 (4), 159 (100), 144 (11), 131 (24), 115 (10), 105 (81), 91 (37), 77 (55), 65 (10), 43 (70). Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3\text{S}$: C, 68.76; H, 5.77. Found: C, 68.58; H, 5.83.

***cis*-1-(*p*-tolylsulfonyl)-2-carboethoxyspiro[2.4]heptane (8a).** TLC $R_f = 0.15$ (petroleum ether : acetone = 10 : 1); IR 2955, 1737, 1321, 1146 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.32 (t, $J = 7.2$ Hz, 3H), 1.63-1.88 (m, 7H), 2.16 (d, $J = 9.2$ Hz, 1H), 2.25-2.39 (m, 1H), 2.44 (s, 3H), 2.65 (d, $J = 9.2$ Hz, 1H), 4.16-4.32 (m, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.86 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 13.96, 21.55, 24.19, 25.87, 26.06, 32.09, 36.10, 38.21, 47.93, 61.11, 127.45, 129.59, 138.83, 144.22, 166.76. MS m/z (EI) 277 [$(\text{M}-45)^+$, 3], 249 (6), 209 (2), 167 (93), 139 (68), 121 (100), 91 (39), 77 (21), 55 (16), 41 (14), 39 (11), 27 (7). Anal. calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4\text{S}$: C, 63.33; H, 6.88. Found: C, 63.30; H, 6.78.

***cis*-1-(*p*-tolylsulfonyl)-2-carboethoxyspiro[2.4]octane (8b).** TLC $R_f = 0.19$ (petroleum ether : acetone = 10 : 1); IR 2931, 1737, 1319, 1147 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.23-1.39 (m, 4H), 1.54-1.76 (m, 7H), 1.97-2.37 (m, 4H), 2.39-2.45 (m, 3H), 4.21-4.30 (m, 2H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.87 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.99, 21.57, 25.22, 25.69, 33.26, 33.67, 38.87, 48.89, 61.15, 127.55, 129.60, 139.15, 144.21, 166.77; MS m/z (EI) 291 [$(\text{M}-45)^+$, 3], 263 (5), 181 (94), 153 (15), 135 (100), 117 (14), 107 (34), 91 (42), 79 (39), 67 (26), 41 (18), 29 (29). Anal. calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4\text{S}$: C, 64.26; H, 7.19. Found: C, 64.25; H, 7.21.

X-ray structure of 2b