SUPPORTING INFORMATION

for

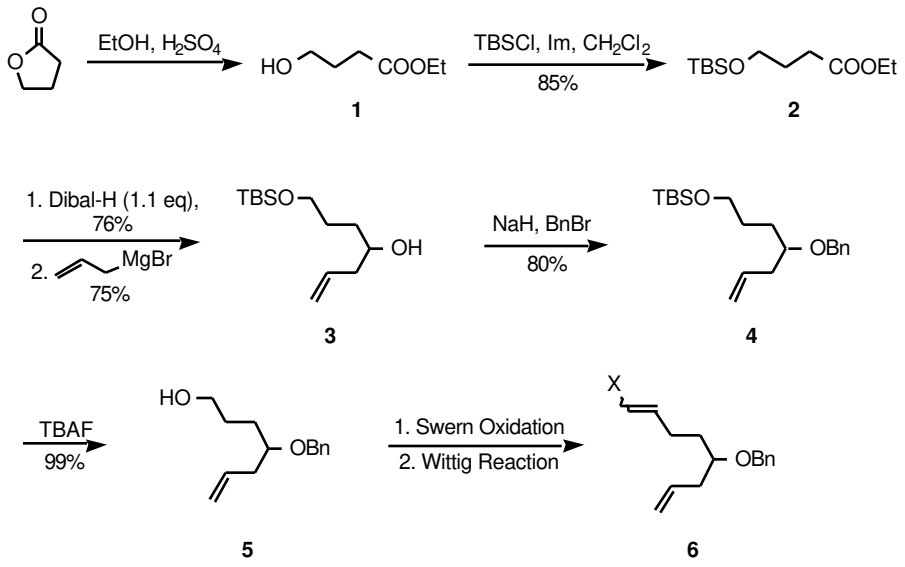
"**Relative Rate Profile for Ring-Closing Metathesis of a Series of 1-Substituted-1,7-Octadienes as Promoted by a 4,5-Dihydroimidazol-2-ylidene Coordinated Ruthenium Catalyst**"

by Xin Guo, Kallol Basu, Jose A. Cabral, and Leo A. Paquette

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

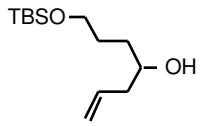
(11 Pages)

Kinetic Study on dienes



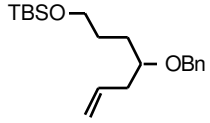
Experimental

To a mixture of alcohol **1** (2 g, 15 mmol) and imidazole (3.12 g, 45.5 mmol) in dry CH_2Cl_2 (30 mL), TBSCl (2.9 g, 19.7 mmol) was added at rt under N_2. The mixture was stirred overnight at rt and quenched by adding 50 mL of water. The CH_2Cl_2 layer was separated and the aqueous layer was further extracted with CH_2Cl_2 (2 x 30 mL). The combined CH_2Cl_2 layers were washed with brine, dried and concentrated to give a yellow residue. This residue was purified by silica gel chromatography (elution with 20:1 petroleum ether:ether) to afford 3.7 g (85%) of pure **2** as a colorless liquid: IR (neat, cm^{-1}) 2930, 1738, 1255; ^1H NMR (300 MHz, $CDCl_3$) δ 4.15-4.08 (q, *J* = 7.1 Hz, 2 H), 3.64-3.61 (t, *J* = 6.1 Hz, 2 H), 2.38-2.33 (t, *J* = 7.4 Hz, 2 H), 1.84-1.79 (m, 2 H), 1.26-1.21 (t, *J* = 7.1 Hz, 3 H), 0.88 (s, 9 H), 0.03 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 62.0, 60.1, 30.7, 28.0, 25.9 (3 C), 18.3, 14.2, -5.4 (2 C); ES MS *m/z* (M^+) calcd 246.1651, obsd 246.1622.



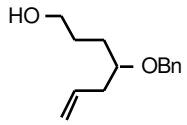
To a solution of above ester **2** (2.2 g, 8.9 mmol) in dry CH_2Cl_2 (20 mL) was slowly added Dibal-H (9 mL of 1.0 M solution in hexane, 8.9 mmol) at –78 ^oC. The resulting mixture was stirred at –78 ^oC for 1.5 h, quenched with a saturated solution of potassium sodium tartrate (15 mL), allowed to come to rt, and stirred overnight. The separated aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic phases were concentrated and purified by chromatography (silica gel, elution with 15:1 petroleum ether: ether) to furnish 1.4 g (76 %) of the aldehyde as a colorless liquid.

To a stirred solution of this aldehyde (1.4 g, 6.4 mmol) under N_2 in 25 mL of dry THF was added at –78 ^oC a solution of allylmagnesium bromide (9.7 mL of 1.0 M solution in THF, 9.7 mmol). The reaction mixture was stirred at –78 ^oC for 1 h, warmed to room temperature, stirred at rt for 30 min, and quenched with a saturated solution of NH_4Cl (30 mL). The aqueous layer was extracted with ether (3 x 30 mL) and the combined organic phases were washed with saturated $NaHCO_3$ solution and brine, dried, and concentrated. The residue was chromatographed on silica gel (5:1 petroleum ether: ether) to give 1.2 g (75%) of the pure alcohol as a colorless liquid: IR (neat, cm^{-1}) 3363, 2928, 2857, 1642; ^1H NMR (300 MHz, $CDCl_3$) δ 5.90-5.75 (m, 1 H), 5.14-5.08 (m, 2 H), 3.68-3.64 (m, 3 H), 2.27-2.19 (m, 2 H), 1.67-1.60 (m, 3 H), 1.58-1.48 (m, 1 H), 0.89 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 117.5, 70.6, 63.4, 41.9, 33.9, 29.1, 25.9 (3C), 18.3, -5.3 (2C).

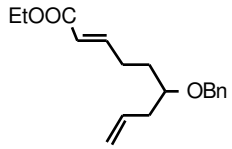


The above alcohol (0.7 g, 2.87 mmol) was dissolved in dry DMF (5 mL), treated portionwise with NaH (0.24 g of 60% mixture in oil, 5.74 mmol) at 0 ^oC, and stirred at this temperature for 20 min prior to the addition of benzyl bromide (0.42 mL, 3.6 mmol). The

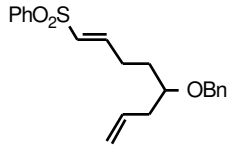
resulting mixture was stirred at 0 ^{o}C for 1 h and overnight at rt, carefully quenched with H_2O (20 mL), and diluted with ether (50 mL). The separated aqueous layer was extracted with ether (3 x 40 mL). The combined ethereal layers were washed with H_2O (2 x 20 mL), dried and concentrated. The residue was purified by chromatographically (silica gel, elution with 60:1 petroleum ether: ether) to furnish 0.77 g (80%) of the pure ether as a colorless liquid: IR (neat, cm^{-1}) 3066, 3030, 2929, 2857, 1641; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5 H), 5.91-5.75 (m, 1 H), 5.15-5.06 (m, 2 H), 4.61-4.49 (q, *J* = 11.6 Hz, 2 H), 3.64-3.61 (m, 2 H), 3.51-3.49 (m, 1 H), 2.39-2.33 (m, 2 H), 1.66-1.56 (m, 4 H), 0.91 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 134.9, 128.3 (2C), 127.7 (2C), 127.4, 116.9, 78.3, 70.8, 63.1, 38.3, 29.9, 28.6, 25.9 (3C), 18.3, -5.3 (2C); ES HRMS *m/*z $(M + Na)^+$ calcd 357.2220, obsd 357.2239.



To a solution of above ether (1 g, 3 mmol) in dry THF (8 mL) was slowly added TBAF (3 mL of 1.0 M solution of THF, 3 mmol) at rt. The resulting mixture was stirred at rt for 45 min and quenched by the addition of water (10 mL). The separated aqueous layer was extracted with ether (2 x 15 mL) and the combined organic layers were dried and concentrated prior to chromatographic purification (elution with 3:1 petroleum ether: ether). There was obtained 0.5 g (99%) of the pure alcohol as a colorless liquid: IR (neat, cm^{-1}) 3382, 3068, 2921, 1641; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.27 (m, 5 H), 5.92-5.78 (m, 1 H), 5.16-5.06 (m, 2 H), 4.62 (d, *J* = 11.5 Hz, 1 H), 4.50 (d, *J* = 11.5 Hz, 1 H), 3.63-3.59 (m, 2 H), 3.54-3.49 (m, 1 H), 2.44-2.31 (m, 2 H), 2.21 (s, 1 H), 1.71-1.59 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 134.6, 128.3 (2C), 127.8 (2C), 127.6, 117.2, 78.3, 70.9, 62.8, 38.0, 30.2; ES HRMS *m/*z $(M + Na)^+$ calcd 243.1356, obsd 243.1349.

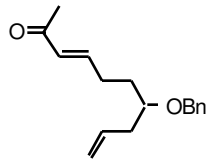


To a solution of the aldehyde (0.5 g, 2.3 mmol) in dry THF (5 mL), was added $Ph_3PCHCOOEt$ (1.5 g, 4.6 mmol) at rt. The resulting mixture was heated under reflux for 3 h, cooled, and quenched with water (5 mL). The separated aqueous layer was extracted with ether (2 x 5 mL) and the combined organic layers were dried and concentrated prior to chromatography on silica gel (elution with 20:1 petroleum ether: ether) to deliver 0.55 g (84%) of pure ester as a colorless liquid: IR (neat, cm^{-1}) 3066, 2979, 1722, 1651, 1166; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5 H), 7.00-6.90 (m, 1 H), 5.90-5.77 (m, 2 H), 5.14-5.07 (m, 2 H), 4.60 (d, *J* = 11.5 Hz, 1 H), 4.46 (d, *J* = 11.5 Hz, 1 H), 4.22-4.15 (q, *J* = 7.1 Hz, 2 H), 3.51-3.43 (m, 1H), 2.42-2.21 (m, 4 H), 1.72-1.65 (m, 2 H), 1.31-1.26 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 148.8, 138.6, 134.4, 128.3 (2C), 127.7 (2C), 127.6, 121.5, 117.3, 77.5, 71.0, 60.1, 38.1, 32.2, 28.1, 14.2; ES HRMS *m/z* $(M + Na)^+$ calcd 311.1617, obsd 311.1624. *Anal.* Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.08; H, 8.40.



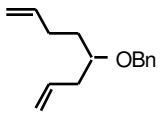
To a stirred suspension of NaH (68 mg of 60% in oil, 1.7 mmol) in dry THF (5mL) was added dropwise at 0 ^oC under N_2 a solution of $(EtO)_2POCH_2SO_2Ph$ (0.5 g, 1.8 mmol) in dry THF (5 mL). After 10 min, a solution of the aldehyde (0.3 g, 1.4 mmol) in dry THF (5 mL) was slowly introduced at 0 ^oC. After the addition was complete, the reaction mixture was heated at reflux for 45 min, cooled, and quenched with 10 mL of saturated NH_4Cl solution. The separated aqueous layer was extracted with ether (2 x 15 mL) and the combined organic layers were dried and concentrated. The residue was chromatographed on

silica gel (elution with 5:1 petroleum ether: ether) to afford 0.48 g (98%)of pure sulfone as a colorless liquid: IR (neat, cm^{-1}) 3065, 2926, 1641, 1626, 1446, 1317, 1147; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2 H), 7.63-7.49 (m, 3 H), 7.35-7.25 (m, 5 H), 7.01-6.91 (m, 1 H), 6.28-6.21 (d, *J* = 17.9 Hz, 1 H), 5.86-5.72 (m, 1 H), 5.12-5.02 (m, 2 H), 4.58 (d, *J* = 11.6 Hz, 1 H), 4.39 (d, *J* = 11.6 Hz, 1 H), 3.47-3.39 (m, 1 H), 2.43-2.20 (m, 4 H), 1.70-1.63 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 140.6, 138.2, 133.9, 133.0, 130.5, 129.0 (2C), 128.2 (2C), 127.6, 127.5 (2C), 127.4 (2C), 117.4 (1C), 77.3, 70.8, 37.8, 31.6, 27.3; ES HRMS *m/z* $(M + Na)^+$ calcd 379.1338, obsd 379.1354. *Anal.* Calcd for $C_{21}H_{24}O_3S$: C, 70.75; H, 6.79. Found: C, 71.04; H, 6.62.

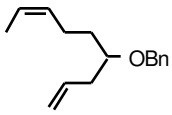


To a stirred suspension of NaH (90 mg of 60% in oil, 2.2 mmol) in dry THF (5mL) was added dropwise at 0 °C under N_2 a solution of $(EtO)_2POCH_2COCH_3$ (0.45 g, 2.30 mmol) in dry THF (5 mL). After 10 min, a solution of the aldehyde (0.4 g, 1.8 mmol) in dry THF (5 mL) was slowly introduced at 0 °C. After the addition was complete, the reaction mixture was stirred at rt overnight and quenched with 10 mL of saturated NH_4Cl solution. The separated aqueous layer was extracted with ether (2 x 15 mL) and the combined organic layers were dried and concentrated. The residue was chromatographed on silica gel (elution with 5:1 petroleum ether: ether) to afford 0.39 g (82%) of ketone as a colorless liquid: IR (neat, cm^{-1}) 3066, 3006, 2928, 1697, 1626; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5 H), 6.82-6.72 (m, 1 H), 6.03 (d, *J* = 16.0 Hz, 1 H), 5.90-5.76 (m, 1 H), 5.15-5.08 (m, 2 H), 4.61 (d, *J* = 11.6 Hz, 1 H), 4.45 (d, *J* = 11.5 Hz, 1 H), 3.51-3.43 (m, 1 H), 2.39-2.23 (m, 4 H), 2.19 (s, 3 H), 1.75-1.66 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 148.0, 138.5, 134.3, 131.3, 128.3 (2C), 127.7 (2C), 127.6, 117.4, 77.5, 71.0, 38.1, 32.3, 28.4, 26.8; ES

HRMS *m/z* $(M + Na)^+$ calcd 281.1512, obsd 281.1513. *Anal.* Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.21; H, 8.50.

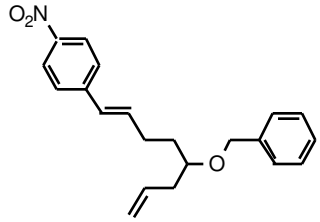


Ph_3PCH_3Br (1.0 g, 2.76 mmol) was added to 4 mL of dry THF under N_2. The resulting mixture was cooled to –78 °C, KHMDS (5.6 mL of 0.37 M solution in toluene, 2.1 mmol) was introduced, and stirring was maintained at –78 °C for 30 min prior to addition of the aldehyde (0.3 g, 1.4 mmol) dissolved in dry THF (5 mL). The resulting mixture was stirred at –78 °C for 45 min, warmed to 0 °C, and quenched with saturated aqueous NH_4Cl solution (10 mL). The separated aqueous layer was extracted with ether (2 x 10 mL) and the combined organic layers were dried and concentrated to leave a residue that was chromatographed on silica gel (elution with 40:1 petroleum ether: ether) to afford 0.25 g (84%) of pure diene: IR (neat, cm^{-1}) 3075, 2935, 2860, 1641; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5 H), 5.94-5.79 (m, 2 H), 5.17-5.06 (m, 3 H), 5.02-4.97 (m, 1 H), 4.62 (d, *J* = 11.6 Hz, 1 H), 4.51 (d, *J* = 11.5 Hz, 1 H), 3.55-3.47 (m, 1 H), 2.41-2.35 (m, 2 H), 2.24-2.13 (m, 2 H), 1.72-1.62 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.6, 134.8, 128.3 (2C), 127.7 (2C), 127.5, 117.0, 114.5, 77.8, 70.9, 38.2, 33.0, 29.6; ES HRMS *m/z* (M^+) calcd 216.1514, obsd 216.1502. *Anal.* Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.14; H, 9.38.



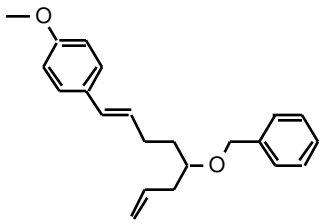
$Ph_3PCH_2CH_3I$ (1.14 g, 2.76 mmol) was added to 5 mL of dry THF under N_2. The resulting mixture was cooled to 0 °C, KHMDS (5.6 mL of 0.37 M solution in toluene, 2.1 mmol)

was introduced, and stirring was maintained at 0 ^{o}C for 30 min prior to addition of the aldehyde (0.3 g, 1.4 mmol) dissolved in dry THF (5 mL). The resulting mixture was stirred at rt overnight, and quenched with saturated aqueous NH_4Cl solution (10 mL). The separated aqueous layer was extracted with ether (2 x 10 mL) and the combined organic layers were dried and concentrated to leave a residue that was chromatographed on silica gel (elution with 40:1 petroleum ether: ether) to afford 0.17 g (55%) of pure diene:IR (neat, cm^{-1}) 3012, 2928, 2858; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5 H), 5.92-5.80 (m, 1 H), 5.49-5.36 (m, 2 H), 5.14-5.06 (m, 2 H), 4.59 (d, *J* = 11.5 Hz, 1 H), 4.49 (d, *J* = 11.5 Hz, 1 H), 3.52-3.44 (m, 1 H), 2.38-2.29 (m, 2 H), 2.16-2.09 (m, 2 H), 1.70-1.51 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 134.9, 130.2, 128.3 (2C), 127.7 (2C), 127.4, 124.1, 116.9, 78.0, 70.9, 38.2, 33.6, 22.7, 12.8; ES HRMS *m/z* (M^+) calcd 230.1671, obsd 230.1728.



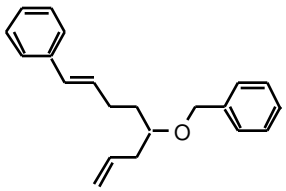
To a stirred solution of *p*-$NO_2PhCH_2P(OEt)_2$ (0.53 g, 1.93 mmol) in dry THF (8 mL), *n*-BuLi (1.12 mL of 1.6 M solution in hexane, 1.8 mmol) was added at 0 ^{o}C under N_2. At this point the solution turned dark purple. The resulting solution was stirred at 0 ^{o}C for 30 min prior to addition of the aldehyde (0.3 g, 1.4 mmol) dissolved in dry THF (5 mL). After the addition was complete, the reaction mixture was stirred at rt overnight and quenched with 10 mL of saturated NH_4Cl solution. The separated aqueous layer was extracted with ether (2 x 15 mL) and the combined organic layers were dried and concentrated. The residue was chromatographed on silica gel (elution with 25:1 petroleum ether: ether) to afford 0.31 g (67%) of desired compound as a colorless liquid: IR (neat, cm^{-1}) 3075, 3030, 2932, 1651,

1596, 1514, 1337; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17-8.13 (d, *J* = 8.8 Hz, 2 H), 7.44-7.27 (m, 7 H), 6.42-6.39 (m, 2 H), 5.94-5.80 (m, 1 H), 5.17-5.09 (m, 2 H), 4.64 (d, *J* = 11.6 Hz, 1 H), 4.49 (d, *J* = 11.6 Hz, 1 H), 3.56-3.49 (m, 1 H), 2.48-2.29 (m, 4 H), 1.78-1.44 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 144.3, 138.6, 136.1, 134.5, 128.4 (2C), 128.3 (2C), 127.8, 127.6, 126.3 (2C), 123.9 (2C), 117.3, 77.6, 70.9, 38.1, 33.1, 29.2; ES HRMS *m/z* $(M + Na)^+$ calcd 360.1570, obsd 360.1586. *Anal.* Calcd for $C_{21}H_{23}NO_2$: C, 74.75; H, 6.87. Found: C, 75.13; H, 6.81.

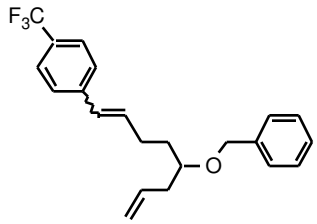


$Ph_3PCH_2C_6H_4OMeBr$ (1.3 g, 2.8 mmol) was added to 8 mL of dry THF under N_2. The resulting mixture was cooled to 0 ^{o}C, *n*-BuLi (1.58 mL of 1.33 M solution in hexane, 2.1 mmol) was introduced, and stirring was maintained at 0 ^{o}C for 30 min prior to addition of the aldehyde (0.3 g, 1.4 mmol) dissolved in dry THF (5 mL). The resulting mixture was stirred at rt overnight, and quenched with saturated aqueous NH_4Cl solution (10 mL). The separated aqueous layer was extracted with ether (2 x 25 mL) and the combined organic layers were dried and concentrated. The residue was chromatographed on silica gel (elution with 35:1 petroleum ether: ether) to afford 0.23 g (52%) of desired product as a colorless liquid: IR (neat, cm^{-1}) 3067, 3030, 2934, 2836, 1607, 1511, 1248; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.27 (m, 7 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 6.34 (d, *J* = 15.8 Hz, 1 H), 6.13-6.03 (m, 1 H), 5.95-5.86 (m, 1 H), 5.18-5.11 (m, 2 H), 4.64 (d, *J* = 11.5 Hz, 1 H), 4.53 (d, *J* = 11.6 Hz, 1 H), 3.83 (s, 3 H), 3.57-3.53 (m, 1 H), 2.43-2.27 (m, 4 H), 1.78-1.64 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 138.7, 134.8, 130.5, 129.3, 128.3 (3C), 127.8 (2C),

127.5, 126.9 (2C), 117.0, 114.0, 113.8, 77.7, 70.9, 55.2, 38.2, 33.6, 28.9; ES HRMS *m/z* (M + Na)$^+$ calcd 345.1825, obsd 345.1818.



$Ph_3PCH_2C_6H_5Br$ (1.2 g, 2.8 mmol) was added to 8 mL of dry THF under N_2. The resulting mixture was cooled to 0 ^oC, *n*-BuLi (1.58 mL of 1.33 M solution in hexane, 2.1 mmol) was introduced, and stirring was maintained at 0 ^oC for 30 min prior to addition of the aldehyde (0.3 g, 1.4 mmol) dissolved in dry THF (5 mL). After the addition was complete, the reaction mixture was stirred at rt overnight and quenched with 10 mL of saturated NH_4Cl solution. The separated aqueous layer was extracted with ether (2 x 25 mL) and the combined organic layers were dried and concentrated. The residue was chromatographed on silica gel (elution with 40:1 petroleum ether: ether) to afford 0.25 g (61%) of desired compound as a colorless liquid: IR (neat, cm^{-1}) 3066, 3031, 2936, 2832, 1605; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.21 (m, 10 H), 6.42 (d, *J* = 15.9 Hz, 2 H), 6.29-6.19 (m, 1 H), 5.99-5.85 (m, 1 H), 5.20-5.12 (m, 2 H), 4.66 (d, *J* = 11.6 Hz, 1 H), 4.54 (d, *J* = 11.6 Hz, 1 H), 3.60-3.53 (m, 1 H), 2.48-2.29 (m, 4 H), 1.81-1.71 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 137.7, 134.7, 130.5, 130.0, 128.4 (2C), 128.3 (2C), 127.8 (2C), 127.5, 126.8, 125.9 (2C), 117.1, 77.7, 70.9, 38.2, 33.5, 28.9; ES MS *m/z* (M + Na)$^+$ calcd 315.1719, obsd 315.1707.



$Ph_3PCH_2C_6H_4CF_3Br$ (0.46 g, 0.92 mmol) was added to 4 mL of dry THF under N_2. The resulting mixture was cooled to 0 ^oC, *n*-BuLi (0.52 mL of 1.33 M solution in hexane, 0.83 mmol) was introduced, and stirring was maintained at 0 ^oC for 30 min prior to addition of the aldehyde (0.1 g, 0.46 mmol) dissolved in dry THF (3 mL). After the addition was complete, the reaction mixture was stirred at rt overnight and quenched with 8 mL of saturated NH_4Cl solution. The separated aqueous layer was extracted with ether (2 x 15 mL) and the combined organic layers were dried and concentrated. The residue was chromatographed on silica gel (elution with 25:1 petroleum ether: ether) to afford 95 mg (57%) of desired compound as a colorless liquid: IR (neat, cm^{-1}) 2932, 2858, 1642, 1615, 1496, 1454, 1415, 1326, 1164, 1123, 1068, 1016, 968, 916, 857; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.28 (m, 9 H), 6.49-6.29 (m, 1.5 H), 5.96-5.77 (m, 1.5 H), 5.19-5.10 (m, 2 H), 4.67 (d, *J* = 11.6 Hz, 0.54 H), 4.61 (d, *J* = 11.4 Hz, 0.46 H), 4.53 (d, *J* = 11.6 Hz, 0.54 H), 4.41 (d, *J* = 11.4 Hz, 0.46 H), 3.58-3.48 (m, 1 H), 2.55-2.29 (m, 4 H), 1.83-1.69 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 141.5, 139.2, 139.0, 135.1, 135.06, 135.04, 133.9, 129.4, 129.3, 128.8, 128.7, 128.4, 128.3, 128.2, 128.01, 127.99, 126.5, 125.8 (q, *J* = 3.8 Hz), 125.5 (q, *J* = 3.8 Hz), 124.74 (1, *J* = 270.6 Hz), 124.71 (q, *J* = 270.5 Hz), 117.7, 117.6, 78.3, 78.1, 71.5, 71.4, 38.7, 38.6, 34.3, 33.8, 29.4, 25.0 (one C not observed); ES HRMS *m/z* $(M+Na)^+$ calcd 383.1599, obsd 383.1602.

NMR Measurements Involving 1 Mol Percent of Catalyst. A flame-dried 5 mL pear-shaped flask was tared and placed into a glove box. Approximately 1.2 mg of **2** was transferred into the flask inside the glove box and the flask was capped. The exact weight of the catalyst was recorded on a more accurate balance after the flask was taken from the

glove box. The approximate amount of CD_2Cl_2 was added to make a 0.0015 M solution of the catalyst and it was kept under N_2 protection. At the same time, about 0.6 mL of 0.0375 M **6** in CD_2Cl_2 was prepared in another flame-dried pear-shaped flask which was likewise under N_2. At this point, 0.1 mL of the freshly prepared catalyst solution was placed in a dry 5 mm NMR tube capped by a rubber septum by way of a 1 mL disposable syringe. With the Bruker 400 MHz NMR spectrometer set up for measurement, 0.4 mL of the substrate solution was introduced by way of another 1 mL syringe and the counting of time began. The progress of reaction was monitored by recording spectra continually until all of the substrate was consumed. The product/substrate ratio at any point in time was defined by integration of appropriate proton signals, and this ratio was used to calculate the concentration of substrate at that time.

NMR Measurements Involving 5 Mol Percent of Catalyst. These measurements were made in an entirely analogous manner.

General Preparative Procedure. The preparative experiments were performed with 5 mol percent catalyst in the manner defined above. When the consumption of substrate was judged to be complete by TLC analysis, 1.5 equiv (relative to the ruthenium catalyst) of lead tetraacetate was added and the reaction mixture was stirred overnight prior to solvent removal in vacuo. The residue was purified by flash chromatography on silica gel (elution with 10% ethyl acetate in hexane) to give the known **7**.