SUPPORTING INFORMATION FOR

Liquid/Solid Phase Transfer Activation of Grubbs-Type Alkene Metathesis Catalysts; Application of Silver Salts of Sulfonated Polystyrene†

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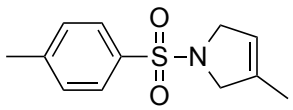
Experimental Section

General. All reactions were conducted under nitrogen. The CH_2Cl_2 was purified using a Glass Contour Solvent System. Tridecane (Aldrich or Alfa Aesar), ethyl vinyl ether (Alfa Aesar), Amberlyst 15 hydrogen form (Aldrich), HCl (Macron), HNO_3 (VWR), NaCl (Mallinckrodt), PCy_3 (Alfa Aesar), $ClPPh_2$ (TCI), Grubbs' second generation catalyst (**1a**; Aldrich), and all deuterated solvents (Cambridge) were used as received. The PS-SO_3Ag (dried as reported under vacuum for 24 h or until a constant weight was achieved),[s1] $(H_2IMes)(Cy_2PCH_2CH_2N(CH_3)_3^+)(Cl)_2Ru(=CHPh)$ Cl^- (**1c**),[s2] $Cy_2PCH_2CH_2NMe_3^+$ Cl^-,[s3] *N*-allyl-*N*-methallyl-*p*-tosylamide (**2**),[s4] diethyl 2-allyl-2-methallylmalonate (**4**),[s5] and *N*-allyl-*N*-(3-methyl-3-butenyl)-*p*-tosylamide (**6**)[s4] were prepared by literature procedures.

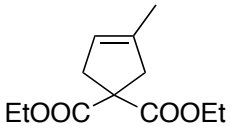
NMR spectra were recorded on modern Varian spectrometers at ambient probe temperatures at the field strengths indicated. Samples were referenced as follows (δ, ppm): ^1H, residual internal $CHDCl_2$ (5.32), $CHCl_3$ (7.26), or CHD_2OD (3.34); ^{13}C, internal CD_2Cl_2 (53.2), $CDCl_3$ (77.0); ^{31}P, external H_3PO_4 (0.00). GC data were acquired using a Shimadzu GC 2010 instrument fitted with a capillary column (SHRXI-5MS-0.25 μm; 15 m × 0.25 mm).

Standardization of PS-SO_3Ag.[s1] A vial was charged with HNO_3 (1.0 M, 15.0 mL) and PS-SO_3Ag (0.7142 g) and mechanically shaken (2.5 h). The sample was filtered, and the filter cake was washed with HNO_3 (1.0 M, 2.0 mL). The filtrate was transferred to a round bottom flask. Then NaCl (1.17 g, 20 mmol) was added with stirring. The white precipitate was isolated by centrifugation and dried under oil pump vacuum to give AgCl (0.154 g, 1.07 mmol). This indicated a silver loading (PS-SO_3Ag) of 1.5 mmol Ag^+/g resin.

Characterization of ring closing metathesis products.

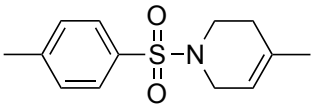
3 

Alkene **3**.[s4] NMR (δ (ppm), $CDCl_3$): ^1H (500 MHz) 7.72 (d, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 8.0 Hz), 5.25 (m, 1H), 4.07 (m, 2H), 3.96 (br s, 2H), 2.42 (s, 3H), 1.65 (s, 3H); $^{13}C\{^1H\}$ (125 MHz) 143.3, 135.0, 134.2, 129.7, 127.4, 119.0, 57.6, 55.1, 21.5, 14.0. MS (ESI, *m/z*): 238 ($M + H^+$).



5

Alkene **5**.[s6] NMR (δ (ppm), $CDCl_3$): ^1H (500 MHz) 5.16 (m, 1H), 4.17 (q, 4H, *J* = 7.0 Hz), 2.94 (m, 2H), 2.87 (br s, 2H), 1.68 (s, 3H), 1.22 (t, 6H, *J* = 7.0 Hz); $^{13}C\{^1H\}$ (125 MHz) 172.3, 137.4, 121.2, 61.4, 59.3, 44.5, 40.7 16.0, 14.0. MS (ESI, *m/z*): 227 ($M + H^+$).

7 

Alkene **7**.[s4] NMR (δ (ppm), $CDCl_3$): ^1H (500 MHz) 7.67 (d, 2H, *J* = 8.5 Hz), 7.32 (d, 2H, *J* = 8.5 Hz), 5.30 (m, 1H), 3.52 (m, 2H), 3.16 (t, 2H, *J* = 6.0 Hz), 2.42 (s, 3H), 2.10 (br s, 2H), 1.65 (s, 1H); $^{13}C\{^1H\}$ (125 MHz) 143.4, 133.3, 132.7, 129.5, 127.7, 116.5, 44.7, 42.8, 29.9, 22.8, 21.4. MS (ESI, *m/z*): 252 ($M + H^+$).

Experiments in Figure 1. **A**. (◆) A Schlenk tube was charged with **1c** (0.0025 g, 0.0028 mmol) under nitrogen. Then **2** (0.0268 g, 0.101 mmol), tridecane (GC standard, 0.0187 g, 0.102 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0105 g) were added to give a 0.051 M solution of **2**. The mixture was stirred and aliquots were periodically removed, quenched with ethyl vinyl ether in CH_2Cl_2 (0.10 M), and assayed by GC. **B**. (■) A Schlenk tube was charged with **1c** (0.0022 g, 0.0025 mmol) under nitrogen. Then **2** (0.0269 g, 0.102 mmol), tridecane (0.0190 g, 0.103 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0212 g) were added to give a 0.051 M solution of **2** that was treated as in A. **C**. (▼) A Schlenk tube was charged with **1c** (0.0022 g, 0.0025 mmol) under nitrogen. Then **2** (0.0263 g, 0.099 mmol), tridecane (0.0188 g, 0.102 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0335 g) were added to give a 0.049 M solution of **2** that was treated as in A. **D.** (▲) A Schlenk tube was charged with **1c** (0.0022 g, 0.0025 mmol) under nitrogen. Then **2** (0.0266 g, 0.100 mmol), tridecane (0.0185 g, 0.101 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0423 g) were added to give a 0.050 M solution of **2** that was treated as in A. **E.** (◀) A Schlenk tube was charged with **1c** (0.0022 g, 0.0025 mmol) under nitrogen. Then **2** (0.0268 g, 0.101 mmol), tridecane (0.0189 g, 0.103 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0520 g)

were added to give a 0.051 M solution of **2** that was treated as in A. **F.** (▶) A Schlenk tube was charged with **1c** (0.0022 g, 0.0025 mmol) under nitrogen. Then **2** (0.0263 g, 0.099 mmol), tridecane (0.0186 g, 0.101 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.1020 g) were added to give a 0.049 M solution of **2** that was treated as in A.

TON and TOF values for every data point in Figure 1.[s7] **A**. (◆) TON: 16.6 (15 min); 17.6 (30 min); 18.0 (45 min); 22.0 (60 min); 25.3 (75 min); 27.7 (90 min); 29.6 (105 min); 31.7 (120 min); 34.6 (180 min); 35.6 (240 min); 35.7 (300 min); 35.7 (360 min). TOF (min^{-1}): 1.106 (15 min); 0.587 (30 min); 0.400 (45 min); 0.367 (60 min); 0.337 (75 min); 0.309 (90 min); 0.282 (105 min); 0.264 (120 min); 0.192 (180 min); 0.148 (240 min); 0.119 (300 min); 0.099 (360 min). **B**. (■) TON: 27.3 (15 min); 32.6 (30 min); 33.9 (45 min); 38.3 (60 min); 39.6 (75 min); 40.0 (90 min); 40.0 (105 min); 40.4 (120 min); 40.4 (180 min); 40.4 (240 min); 40.4 (300 min); 40.4 (360 min). TOF (min^{-1}): 1.820 (15 min); 1.087 (30 min); 0.753 (45 min); 0.638 (60 min); 0.528 (75 min); 0.444 (90 min); 0.381 (105 min); 0.337 (120 min); 0.224 (180 min); 0.168 (240 min); 0.135 (300 min); 0.112 (360 min). **C**. (▼) TON: 26.5 (15 min); 31.7 (30 min); 38.0 (45 min); 38.0 (60 min); 38.4 (75 min); 39.2 (90 min); 39.2 (105 min); 39.2 (120 min); 39.2 (180 min); 39.2 (240 min); 39.2 (300 min); 39.2 (360 min). TOF (min^{-1}): 1.767 (15 min); 1.057 (30 min); 0.844 (45 min); 0.633 (60 min); 0.512 (75 min); 0.436 (90 min); 0.373 (105 min); 0.327 (120 min); 0.218 (180 min); 0.163 (240 min); 0.131 (300 min); 0.109 (360 min). **D.** (▲) TON: 30.4 (15 min); 34.4 (30 min); 36.8 (45 min); 37.6 (60 min); 38.4 (75 min); 38.4 (90 min); 38.8 (105 min); 38.8 (120 min); 39.2 (180 min); 39.2 (240 min); 39.2 (300 min); 39.6 (360 min). TOF (min^{-1}): 2.027 (15 min); 1.147 (30 min); 0.818 (45 min); 0.627 (60 min); 0.512 (75 min); 0.427 (90 min); 0.370 (105 min); 0.323 (120 min); 0.218 (180 min); 0.163 (240 min); 0.130 (300 min); 0.110 (360 min). **E.** (◀) TON: 26.3 (15 min); 28.7 (30 min); 30.7 (45 min); 31.5 (60 min); 33.5 (75 min); 34.3 (90 min); 35.1 (105 min); 35.6 (120 min); 36.4 (180 min); 36.8 (240 min); 37.2 (300 min); 37.2 (360 min). TOF (min^{-1}): 1.753 (15 min); 0.957 (30 min); 0.682 (45 min); 0.525 (60 min); 0.447 (75 min); 0.381 (90 min); 0.334 (105 min); 0.297 (120 min); 0.202 (180 min); 0.153 (240 min); 0.124 (300 min); 0.103 (360 min). **F.** (▶) TON: 23.0 (15 min); 28.1 (30 min);

30.1 (45 min); 31.7 (60 min); 32.9 (75 min); 34.1 (90 min); 34.4 (105 min); 35.2 (120 min); 36.4 (180 min); 36.8 (240 min); 37.2 (300 min); 37.2 (360 min). TOF (min^{-1}): 1.533 (15 min); 0.936 (30 min); 0.667 (45 min); 0.528 (60 min); 0.439 (75 min); 0.379 (90 min); 0.328 (105 min); 0.293 (120 min); 0.202 (180 min); 0.153 (240 min); 0.124 (300 min); 0.103 (360 min).

Experiments in Figure 2. **A**. (◆) A Schlenk tube was charged with **1c** (0.0023 g, 0.0026 mmol) under nitrogen. Then **2** (0.0263 g, 0.099 mmol), tridecane (GC standard, 0.0189 g, 0.102 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.049 M solution of **2**. The mixture was stirred and aliquots were periodically removed, quenched with ethyl vinyl ether in CH_2Cl_2 (1.0 M), and assayed by GC. **B**.[s2] (■) A Schlenk tube was charged with **1c** (0.0024 g, 0.0027 mmol) and freshly degassed distilled water (1.0 mL) under nitrogen. Then **2** (0.0269 g, 0.101 mmol), tridecane (0.0191 g, 0.104 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.051 M solution of **2**. The biphasic mixture was stirred and aliquots were periodically removed from the organic phase, quenched with ethyl vinyl ether in CH_2Cl_2 (0.10 M) and assayed by GC. **C**.[s2] (▲) A Schlenk tube was charged with **1c** (0.0022 g, 0.0025 mmol) under nitrogen and freshly degassed aqueous HCl (0.010 M, 1.0 mL) was added. Then **2** (0.0261 g, 0.098 mmol), tridecane (0.0189 g, 0.102 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.049 M solution of **2** that was treated as in B. **D.** (▼) This experiment is identical with C in Figure 1.

TON and TOF values for every data point in Figure 2.[s7] **A**. (◆) TON: 5.3 (15 min); 7.6 (30 min); 10.7 (45 min); 11.4 (60 min); 12.2 (75 min); 14.1 (90 min); 14.8 (105 min); 15.2 (120 min); 15.6 (180 min); 16.4 (240 min); 16.8 (300 min); 19.0 (360 min). TOF (min^{-1}): 0.353 (15 min); 0.253 (30 min); 0.238 (45 min); 0.190 (60 min); 0.163 (75 min); 0.157 (90 min); 0.141 (105 min); 0.127 (120 min); 0.087 (180 min); 0.068 (240 min); 0.056 (300 min); 0.053 (360 min). **B**. (■) TON: 13.5 (15 min); 15.7 (30 min); 16.4 (45 min); 17.2 (60 min); 17.6 (75 min); 19.8 (90 min); 23.2 (105 min); 24.3 (120 min); 25.4 (180 min); 26.9 (240 min); 27.7 (300 min); 29.2 (360 min). TOF (min^{-1}): 0.900 (15 min); 0.523 (30 min); 0.364 (45 min); 0.287 (60 min); 0.235 (75 min); 0.220 (90 min); 0.221 (105 min); 0.202 (120 min); 0.141 (180 min); 0.112 (240 min); 0.092 (300 min); 0.081 (360 min). **C**. (▲) TON: 25.5 (15 min); 27.4 (30 min); 28.2 (45

min); 28.2 (60 min); 29.4 (75 min); 29.8 (90 min); 30.1 (105 min); 30.6 (120 min); 31.0 (180 min); 32.9 (240 min); 33.7 (300 min); 34.5 (360 min). TOF (min^{-1}): 1.700 (15 min); 0.913 (30 min); 0.627 (45 min); 0.470 (60 min); 0.392 (75 min); 0.331 (90 min); 0.287 (105 min); 0.255 (120 min); 0.172 (180 min); 0.137 (240 min); 0.112 (300 min); 0.096 (360 min). **D.** (▼) This data is identical with C in Figure 1.

Experiments in Figure 3A. **A**. (◆) A Schlenk tube was charged with **1c** (0.0026 g, 0.0029 mmol) under nitrogen. Then **4** (0.0255 g, 0.100 mmol), tridecane (GC standard, 0.0186 g, 0.101 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.050 M solution of **4**. The mixture was stirred and aliquots were periodically removed, quenched with ethyl vinyl ether in CH_2Cl_2 (0.10 M), and assayed by GC. **B**.[s2] (■) A Schlenk tube was charged with **1c** (0.0024 g, 0.0026 mmol) and freshly degassed distilled water (1.0 mL) under nitrogen. Then **4** (0.0259 g, 0.102 mmol), tridecane (0.0181 g, 0.098 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.051 M solution of **4**. The biphasic mixture was stirred and aliquots were periodically removed from the organic phase, quenched with ethyl vinyl ether in CH_2Cl_2 (0.10 M), and assayed by GC. **C**.[s2] (▲) A Schlenk tube was charged with **1c** (0.0022 g, 0.0025 mmol) and freshly degassed aqueous HCl (0.010 M, 1.0 mL) under nitrogen. Then **4** (0.0258 g, 0.102 mmol), tridecane (0.0195 g, 0.106 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.051 M solution **4** that was treated as in B. **D**. (▼) A Schlenk tube was charged with **1c** (0.0023 g, 0.0026 mmol) under nitrogen. Then **4** (0.0254 g, 0.100 mmol), tridecane (0.0184 g, 0.100 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0305 g) were added to give a 0.050 M solution of **4** that was treated as in A.

TON and TOF values for every data point in Figure 3A.[s7] **A.** (◆) TON: 1.4 (15 min); 1.7 (30 min); 1.7 (45 min); 1.7 (60 min); 1.7 (75 min); 1.7 (90 min); 2.1 (105 min); 2.1 (120 min); 2.1 (180 min); 2.4 (240 min); 5.2 (300 min); 7.9 (360 min). TOF (min^{-1}): 0.093 (15 min); 0.057 (30 min); 0.038 (45 min); 0.028 (60 min); 0.023 (75 min); 0.019 (90 min); 0.020 (105 min); 0.018 (120 min); 0.012 (180 min); 0.010 (240 min); 0.017 (300 min); 0.022 (360 min). **B**. (■) TON: 3.9 (15 min); 5.1 (30 min); 5.5 (45 min); 6.7 (60 min); 7.1 (75 min); 7.8 (90 min); 8.2 (105 min); 10.6 (120 min); 12.2 (180 min); 13.7 (240 min); 14.5 (300 min); 14.9 (360 min). TOF

(min^{-1}): 0.260 (15 min); 0.170 (30 min); 0.122 (45 min); 0.112 (60 min); 0.095 (75 min); 0.087 (90 min); 0.078 (105 min); 0.088 (120 min); 0.068 (180 min); 0.057 (240 min); 0.048 (300 min); 0.041 (360 min). **C**. (▲) TON: 7.3 (15 min); 10.6 (30 min); 14.7 (45 min); 16.4 (60 min); 20.8 (75 min); 21.2 (90 min); 22.4 (105 min); 23.7 (120 min); 27.3 (180 min); 29.4 (240 min); 31.0 (300 min); 31.8 (360 min). TOF (min^{-1}): 0.487 (15 min); 0.353 (30 min); 0.327 (45 min); 0.273 (60 min); 0.277 (75 min); 0.236 (90 min); 0.213 (105 min); 0.198 (120 min); 0.152 (180 min); 0.122 (240 min); 0.103 (300 min); 0.088 (360 min). **D.** (▼) TON: 2.7 (15 min); 8.1 (30 min); 15.8 (45 min); 21.9 (60 min); 24.6 (75 min); 28.1 (90 min); 30.4 (105 min); 32.7 (120 min); 36.5 (180 min); 37.3 (240 min); 37.7 (300 min); 38.1 (360 min). TOF (min^{-1}): 0.180 (15 min); 0.270 (30 min); 0.351 (45 min); 0.365 (60 min); 0.328 (75 min); 0.312 (90 min); 0.290 (105 min); 0.272 (120 min); 0.203 (180 min); 0.155 (240 min); 0.126 (300 min); 0.106 (360 min).

Experiments in Figure 3B. **A**. (◆) A Schlenk tube was charged with **1c** (0.0019 g, 0.0021 mmol) under nitrogen and cooled to 0 °C. Then **6** (0.0562 g, 0.201 mmol), tridecane (GC standard, 0.0369 g, 0.200 mmol), and cold CH_2Cl_2 (4.0 mL) were added to give a 0.050 M solution of **6**. The mixture was stirred at 0 °C and aliquots were periodically removed, quenched with ethyl vinyl ether in CH_2Cl_2 (0.10 M), and assayed by GC. **B**.[s2] (■) A Schlenk tube was charged with **1c** (0.0017 g, 0.0019 mmol) and freshly degassed distilled water (2.0 mL) under nitrogen and cooled to 0 °C. Then **6** (0.0563 g, 0.201 mmol), tridecane (0.0371 g, 0.202 mmol), and cold CH_2Cl_2 (4.0 mL) were added to give a 0.050 M solution of **6**. The biphasic mixture was stirred at 0 °C and aliquots were periodically removed from the organic phase, quenched with 0.10 M ethyl vinyl ether in CH_2Cl_2, and assayed by GC. **C**.[s2] (▲) A Schlenk tube was charged with **1c** (0.0018 g, 0.0020 mmol) and freshly degassed aqueous HCl (0.010 M, 2.0 mL) under nitrogen and cooled to 0 °C. Then **6** (0.0558 g, 0.200 mmol), tridecane (0.0362 g, 0.196 mmol), and cold CH_2Cl_2 (4.0 mL) were added to give a 0.050 M solution of **6** that was treated as in B. **D**. (▼) A Schlenk tube was charged with **1c** (0.0019 g, 0.0021 mmol) under nitrogen and cooled to 0 °C. Then **6** (0.0558 g, 0.200 mmol), tridecane (0.0364 g, 0.198 mmol), cold CH_2Cl_2 (4.0 mL), and PS-SO_3Ag (0.0243 g) were added to give a 0.050 M solution of **6** that was treated as in A.

TON and TOF values for every data point in Figure 3B.[s7] **A**. (◆) TON: 15.3 (15 min); 17.2 (30 min); 21.1 (45 min); 25.8 (60 min); 29.7 (75 min); 32.5 (90 min); 33.5 (105 min); 34.4 (120 min); 38.3 (180 min); 39.2 (240 min); 47.9 (300 min); 50.7 (360 min). TOF (min^{-1}): 1.020 (15 min); 0.573 (30 min); 0.469 (45 min); 0.430 (60 min); 0.396 (75 min); 0.361 (90 min); 0.319 (105 min); 0.286 (120 min); 0.213 (180 min); 0.163 (240 min); 0.160 (300 min); 0.141 (360 min). **B**. (■) TON: 28.6 (15 min); 28.6 (30 min); 31.7 (45 min); 32.8 (60 min); 34.9 (75 min); 40.2 (90 min); 43.4 (105 min); 43.4 (120 min); 45.5 (180 min); 48.7 (240 min); 49.7 (300 min); 56.1 (360 min). TOF (min^{-1}): 1.907 (15 min); 0.953 (30 min); 0.704 (45 min); 0.547 (60 min); 0.465 (75 min); 0.447 (90 min); 0.413 (105 min); 0.362 (120 min); 0.253 (180 min); 0.203 (240 min); 0.166 (300 min); 0.156 (360 min). **C**. (▲) TON: 29.0 (15 min); 40.0 (30 min); 41.0 (45 min); 42.0 (60 min); 46.0 (75 min); 47.0 (90 min); 52.0 (105 min); 55.0 (120 min); 65.0 (180 min); 68.0 (240 min); 77.0 (300 min); 79.0 (360 min). TOF (min^{-1}): 1.933 (15 min); 1.333 (30 min); 0.911 (45 min); 0.700 (60 min); 0.613 (75 min); 0.522 (90 min); 0.495 (105 min); 0.458 (120 min); 0.361 (180 min); 0.283 (240 min); 0.257 (300 min); 0.219 (360 min). **D.** (▼) TON: 11.4 (15 min); 38.1 (30 min); 44.8 (45 min); 57.1 (60 min); 82.9 (75 min); 83.8 (90 min); 87.6 (105 min); 89.5 (120 min); 92.4 (180 min); 93.3 (240 min); 94.3 (300 min); 94.3 (360 min). TOF (min^{-1}): 0.760 (15 min); 1.270 (30 min); 0.995 (45 min); 0.952 (60 min); 1.105 (75 min); 0.931 (90 min); 0.834 (105 min); 0.746 (120 min); 0.513 (180 min); 0.389 (240 min); 0.314 (300 min); 0.262 (360 min).

Experiments in Figure s1. **A**. (◆) A Schlenk tube was charged with **1a** (0.020 M CH_2Cl_2 solution; 0.050 mL, 0.0010 mmol) under nitrogen. Then **4** (0.0257 g, 0.101 mmol), tridecane (GC standard, 0.0189 g, 0.103 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0052 g) were added to give a 0.051 M solution of **4**. The mixture was stirred and aliquots were periodically removed, quenched with ethyl vinyl ether in CH_2Cl_2 (0.10 M), and assayed by GC. **B**. (■) A Schlenk tube was charged with **1a** (0.020 M CH_2Cl_2 solution; 0.050 mL, 0.0010 mmol) under nitrogen. Then **4** (0.0254 g, 0.100 mmol), tridecane (0.0186 g, 0.101 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0105 g) were added to give a 0.050 M solution of **4** that was treated as in A.

C. (▲) A Schlenk tube was charged with **1a** (0.020 M CH_2Cl_2 solution; 0.050 mL, 0.0010 mmol) under nitrogen. Then **4** (0.0257 g, 0.101 mmol), tridecane (0.0185 g, 0.101 mmol), CH_2-Cl_2 (2.0 mL), and PS-SO_3Ag (0.0150 g) were added to give a 0.051 M solution of **4** that was treated as in A.

TON and TOF values for every data point in Figure s1.[s7] **A.** (◆) TON: 20.2 (5 min); 25.3 (10 min); 33.3 (15 min); 41.4 (20 min); 48.5 (25 min); 52.5 (30 min); 60.6 (35 min); 65.7 (40 min); 68.7 (45 min); 73.7 (50 min); 75.8 (55 min); 78.8 (60 min). TOF (min^{-1}): 4.040 (5 min); 2.530 (10 min); 2.220 (15 min); 2.070 (20 min); 1.940 (25 min); 1.750 (30 min); 1.731 (35 min); 1.643 (40 min); 1.527 (45 min); 1.474 (50 min); 1.378 (55 min); 1.313 (60 min). **B**. (■) TON: 23.0 (5 min); 31.0 (10 min); 43.0 (15 min); 49.0 (20 min); 58.0 (25 min); 69.0 (30 min); 73.0 (35 min); 77.0 (40 min); 81.0 (45 min); 87.0 (50 min); 89.0 (55 min); 91.0 (60 min). TOF (min^{-1}): 4.600 (5 min); 3.100 (10 min); 2.867 (15 min); 2.450 (20 min); 2.320 (25 min); 2.300 (30 min); 2.086 (35 min); 1.925 (40 min); 1.800 (45 min); 1.740 (50 min); 1.618 (55 min); 1.517 (60 min). **C**. (▲) TON: 7.1 (5 min); 20.2 (10 min); 23.2 (15 min); 27.3 (20 min); 31.3 (25 min); 36.4 (30 min); 41.4 (35 min); 45.5 (40 min); 49.5 (45 min); 53.5 (50 min); 57.6 (55 min); 61.6 (60 min). TOF (min^{-1}): 1.420 (5 min); 2.020 (10 min); 1.547 (15 min); 1.365 (20 min); 1.252 (25 min); 1.213 (30 min); 1.183 (35 min); 1.138 (40 min); 1.100 (45 min); 1.070 (50 min); 1.047 (55 min); 1.027 (60 min).

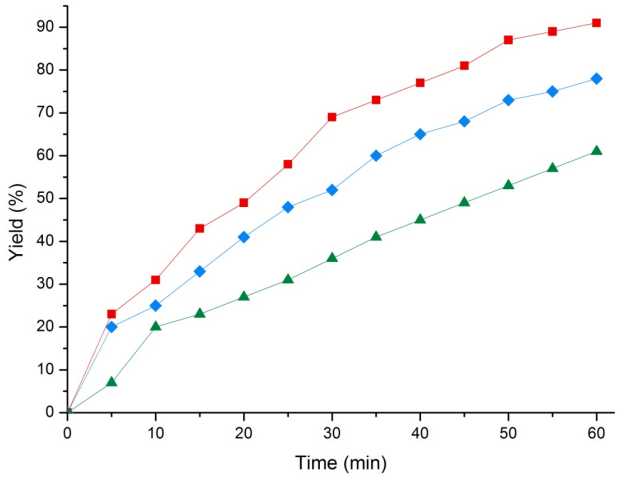


Figure s1. Rates of formation of **5** (room temperature, $[4]_0$ = 0.050−0.051 M, 1.0 mol % **1a**) in 2.0 mL CH_2Cl_2 in the presence of PS-SO_3Ag resin. Resin loading: ◆ 0.005 g (0.0075 mmol Ag^+); ■ 0.010 g (0.015 mmol Ag^+); ▲ 0.015 g (0.0225 mmol Ag^+).

Experiments in Figure 4. **A**. (◆) A Schlenk tube was charged with **1a** (0.020 M CH_2Cl_2 solution; 0.050 mL, 0.0010 mmol) under nitrogen. Then **4** (0.0269 g, 0.102 mmol), tridecane (GC standard, 0.0186 g, 0.101 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.051 M solution of **4**. The mixture was stirred and aliquots were periodically removed, quenched with ethyl vinyl ether in CH_2Cl_2 (0.10 M) and assayed by GC. **B**. (■) This experiment is identical with B in Figure s1. **C**. (◇) A Schlenk tube was charged with **1a** (0.020 M CH_2Cl_2 solution; 0.050 mL, 0.0010 mmol) under nitrogen. Then **2** (0.0269 g, 0.102 mmol), tridecane (GC standard, 0.0187 g, 0.102 mmol), and CH_2Cl_2 (2.0 mL) were added to give a 0.051 M solution of **2** that was treated as in **A**. **D**. (□) A Schlenk tube was charged with **1a** (0.020 M CH_2Cl_2 solution; 0.050 mL, 0.0010 mmol) under nitrogen. Then **2** (0.0266 g, 0.100 mmol), tridecane (0.0185 g, 0.101 mmol), CH_2Cl_2 (2.0 mL), and PS-SO_3Ag (0.0105 g) were added to give a 0.050 M solution of **2** that was treated as in **A**.

TON and TOF values for every data point in Figure 4.[s7] **A.** (◆) TON: 20.4 (5 min); 21.4 (10 min); 22.4 (15 min); 28.6 (20 min); 32.6 (25 min); 38.8 (30 min); 44.9 (35 min); 47.9 (40 min); 52.0 (45 min); 56.1 (50 min); 59.2 (55 min); 63.2 (60 min). TOF (min^{-1}): 4.080 (5 min); 2.140 (10 min); 1.493 (15 min); 1.430 (20 min); 1.304 (25 min); 1.293 (30 min); 1.282 (35 min); 1.198 (40 min); 1.156 (45 min); 1.122 (50 min); 1.076 (55 min); 1.053 (60 min). **B**. (■) This data is identical with B in Figure 1s. **C**. (◇) TON: 25.5 (5 min); 67.3 (10 min); 88.7 (15 min); 95.9 (20 min); 97.9 (25 min); 100.0 (30 min); 101.0 (35 min); 101.0 (40 min); 101.0 (45 min); 101.0 (50 min); 101.0 (55 min); 101.0 (60 min). TOF (min^{-1}): 5.100 (5 min); 6.730 (10 min); 5.910 (15 min); 4.795 (20 min); 3.916 (25 min); 3.333 (30 min); 2.886 (35 min); 2.525 (40 min); 2.244 (45 min); 2.020 (50 min); 1.836 (55 min); 1.683 (60 min). **D**. (□) TON: 92.0 (5 min); 96.0 (10 min); 97.0 (15 min); 98.0 (20 min); 99.0 (25 min); 99.0 (30 min); 99.0 (35 min); 99.0 (40 min); 99.0 (45 min); 99.0 (50 min); 99.0 (55 min); 99.0 (60 min). TOF (min^{-1}): 18.400 (5 min); 9.600 (10 min); 6.467 (15 min); 4.900 (20 min); 3.960 (25 min); 3.300 (30 min); 2.829 (35 min); 2.475 (40 min); 2.200 (45 min); 1.980 (50 min); 1.800 (55 min); 1.650 (60 min).

Experiments in Figure 5. **A**. (◆) A 1.00 mL volumetric flask was charged with Cy_2P-

$CH_2CH_2NMe_3^+$ Cl^- (0.1284 g, 0.402 mmol)[s3] and CD_3OD in a glove box to give a 0.40 M solution. A J. Young NMR tube was charged with 0.400 mL of this solution and a sealed capillary containing $ClPPh_2$ standard. A $^{31}P\{^1H\}$ NMR spectrum was recorded. Then PS-SO_3Ag (1.5 mmol Ag^+/g resin; 0.0228 g, 0.0342 mmol Ag^+) was added with shaking. $^1P\{^1H\}$ NMR spectra were periodically recorded, which gave the data in Figure 5. **B**. (■) A 1.00 mL volumetric flask was charged with PCy_3 (0.1121 g, 0.400 mmol) and CD_2Cl_2 to give a 0.40 M solution, which was treated as in A but with 0.0215 g (0.0322 mmol Ag^+) of resin.

References

(s1) (a) Bergbreiter, D. E.; Bursten, M. S.; Parsons, G. L. Cook, K. *Appl. Organomet. Chem.* 1987, **1**, 65−72. (b) Bergbreiter, D. E.; Bursten, M. S. *J. Macromol. Sci., Chem.* 1981, **A16**, 369−381.

(s2) Xi, Z.; Bazzi, H. S.; Gladysz, J. A. *Org. Lett.* 2011, **13**, 6188−6191.

(s3) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* 1996, **15**, 4317−4325.

(s4) Yao, Q.; Zhang, Y. *J. Am. Chem. Soc.* 2004, **126**, 74−75.

(s5) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* 1997, **62**, 7310−7318.

(s6) Schweizer, E. E.; O'Nell, J. G. *J. Org. Chem.* 1965, **30**, 2082−2083.

(s7) These data were added at the request of a reviewer.