Supporting Information

Z-Selective Homodimerization of Terminal Olefins with a Ruthenium Metathesis Catalyst

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General Information.

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed with bubbling argon.[1,2] NMR solvents were dried over CaH_2 and vacuum transferred to a dry Schlenk flask and subsequently degassed with bubbling argon. Commercially available reagents were degassed with bubbling argon unless otherwise noted.

NMR experiments were conducted on a Varian 600 MHz spectrometer equipped with a Triax (^{1}H, ^{13}C, ^{15}N) probe, a Varian Inova 400 MHz spectrometer, or a Varian 500 MHz spectrometer equipped with an AutoX probe. Experiments and pulse sequences from Varian's Chempack 4 software were used without modification except for changes in the number of FIDs , scans per FID, and delay time. Reaction conversions and the percentage of *Z*-olefin were obtained by comparing integral values. The identity of *Z*-olefin was confirmed by comparison with literature values for both ^{1}H and ^{13}C NMR spectra, and in some cases, by gas chromatography.[3,4] Chemical shifts are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 6.2.0 – 7163.[5]

General procedure for reactions at elevated temperature.

In a glovebox, a Schlenk flask was charged with **1** (3.5 mg, 0.005 mmol), **5** (30 μL, 0.131 mmol), and d_8-THF (0.5 mL). The flask was sealed, removed from the glovebox, and placed on a vacuum line where it was cooled to -78 °C and evacuated to ca. 300-500 mTorr (usually the onset of bubbling). The flask was sealed under static vacuum, warmed to RT, and heated to 70 °C. Aliquots were collected periodically by cooling the flask to RT, backfilling with Ar, and removing ca. 50 μL of solution which was immediately quenched upon exposure to oxygen. Following removal of the aliquot, the flask was evacuated in the same manner as above and heating was resumed. The aliquot was diluted with $CDCl_3$ (0.7 mL) and conversion and selectivity were determined via ^{1}H NMR spectroscopy (see below).

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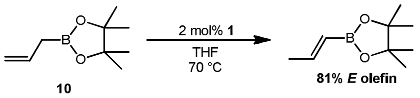
(1) Love, J.A.; Morgan, J.P.; Trnka, T.M.; Grubbs, R.H. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035.
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(3) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630.
(4) Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740-5745.
(5) www.mestrelab.com



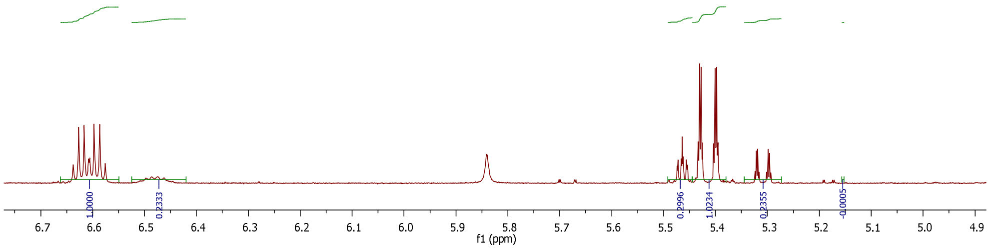
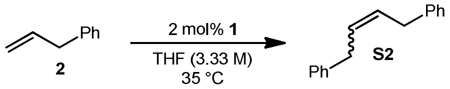


Figure S1. Olefinic region for the cross-metathesis of **10** with **1** at 70 °C under static vacuum (1st time point, 3h). Structural assignments were in accordance with literature reports.[6]

General procedure for reactions at 35 °C.

In a glovebox, a 4 mL vial was charged with **1** (9 mg, 0.0153 mmol) and d_8-THF (50 µL). Olefin (**5**, 150 µL, 0.667 mmol) was added and the vial was placed into an aluminum block (IKA #3904400) preheated to 35 °C using a temperature controlled hotplate. The temperature of the plate was further confirmed using a separate K-type thermocouple probe (VWR # 14224-534) and thermometer. The vial was left open to the glovebox atmosphere and stirred until completion of the reaction (determined by ^{1}H NMR spectroscopy). After completion, the vial was removed from the glovebox and the product was isolated according to the procedures below.

Alternatively, in a glovebox, a Schlenk flask was charged with **1** (12.3 mg, 0.0183 mmol), d_8-THF (70 µL), and **5** (206 µL, 0.915 mmol). The flask was sealed, removed from the glovebox, and placed under an argon atmosphere before heating to 35 °C. Reactions conducted using these conditions tended to result in slightly lower conversions (75% conv. of **5** after 6 h) and thus were not preferred.



S2:[4] The crude reaction mixture was filtered through a plug of silica gel using hexanes and concentrated *in vacuo*. *Z*-**S2**: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.39 – 7.32 (m, 4H), 7.31 – 7.22 (m, 6H), 5.78 (m, 2H), 3.58 (d, *J* = 5.6 Hz, 4H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 140.82, 129.11, 128.52, 128.42, 126.01, 33.56.

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(6) Althaus, M.; Mahmood, A.; Suárez, J. R.; Thomas, S. P.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2010**, *132*, 4025.

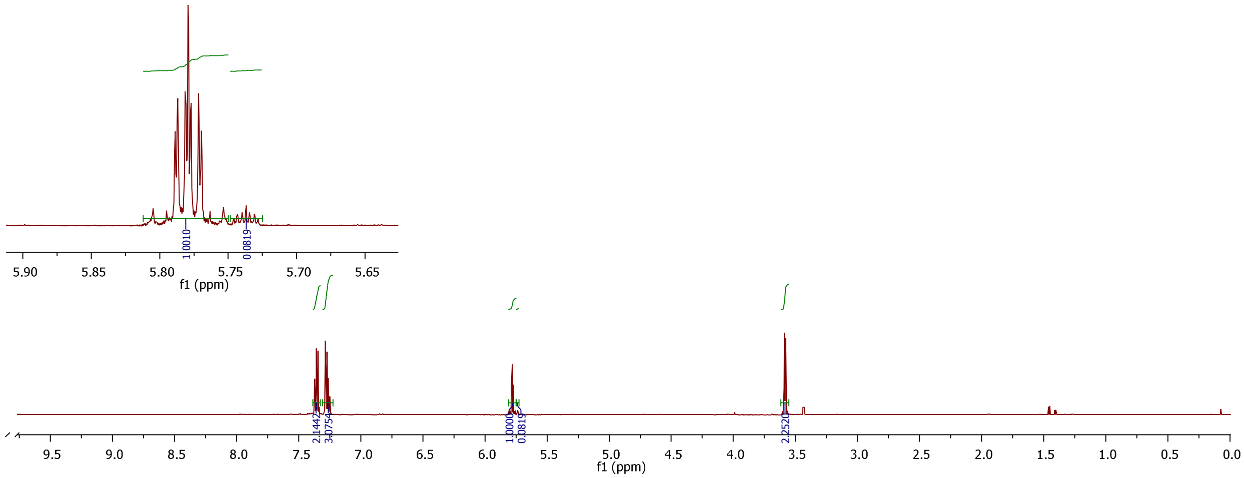


Figure S2. ^{1}H NMR ($CDCl_3$, 600 MHz) of **S2**.

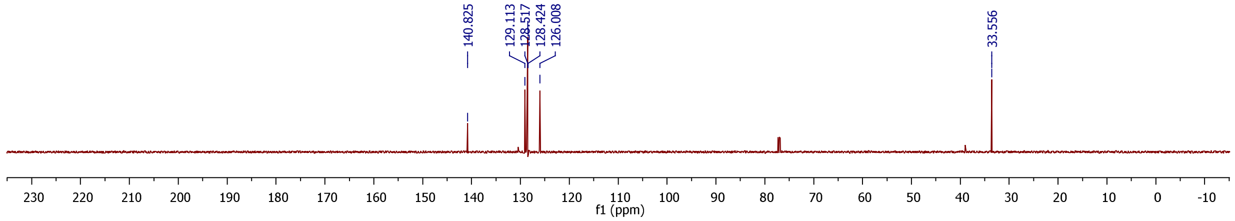
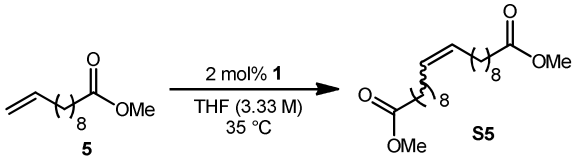


Figure S3. ^{13}C NMR ($CDCl_3$, 151 MHz) of **S2**.



S5:[3] The crude product was purified by column chromatography on silica gel using 10% Et_2O in hexanes as eluant. *Z*-**S5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 – 5.19 (m, 2H), 3.61 (s, 6H), 2.25 (t, *J* = 7.6 Hz, 4H), 1.94 (m, 4H), 1.67 – 1.47 (m, 4H), 1.41 – 1.13 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.18, 129.78, 51.33, 34.02, 29.66, 29.53, 29.28, 29.16, 29.08, 27.12, 24.89.

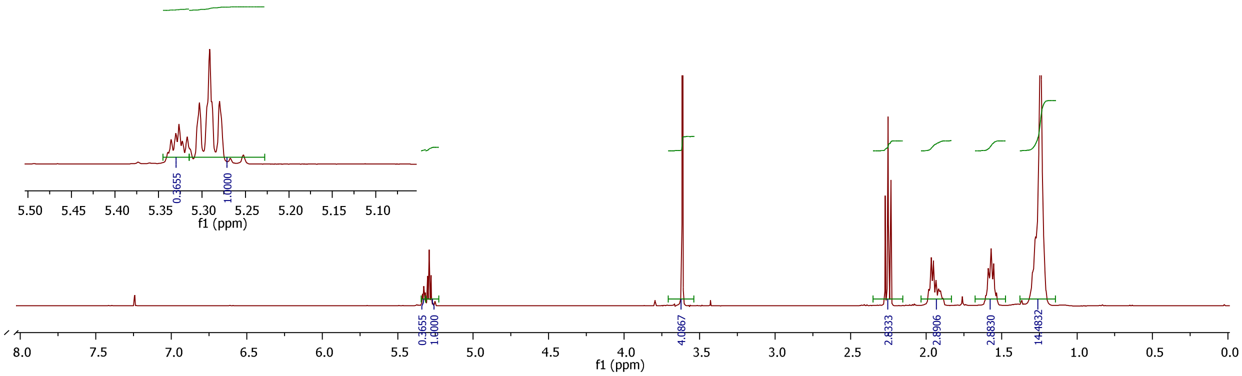


Figure S4. ^{1}H NMR (CDCl$_3$, 400 MHz) of **S5**.

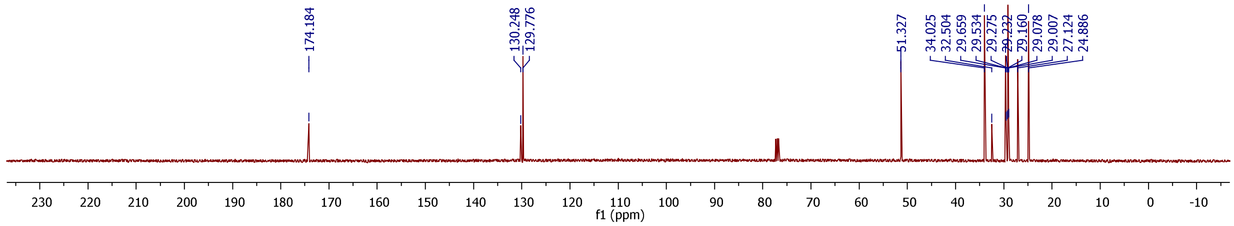
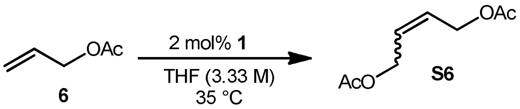


Figure S5. ^{13}C NMR (CDCl$_3$, 101 MHz) of **S5**.



S6:[4] The crude reaction mixture was filtered through a plug of silica gel using hexanes and concentrated *in vacuo*. *Z*-**S6**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.75 (m, 2H), 4.68 (dd, J = 4.0, 1.2 Hz, 4H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 170.75, 128.12, 60.05, 20.94.

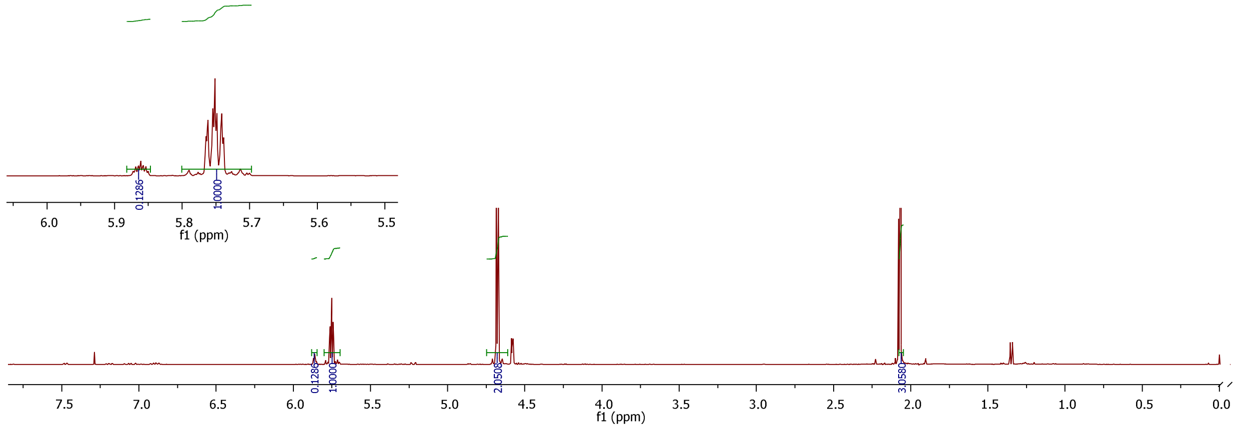


Figure S6. ^{1}H NMR (CDCl$_3$, 400 MHz) of **S6**.

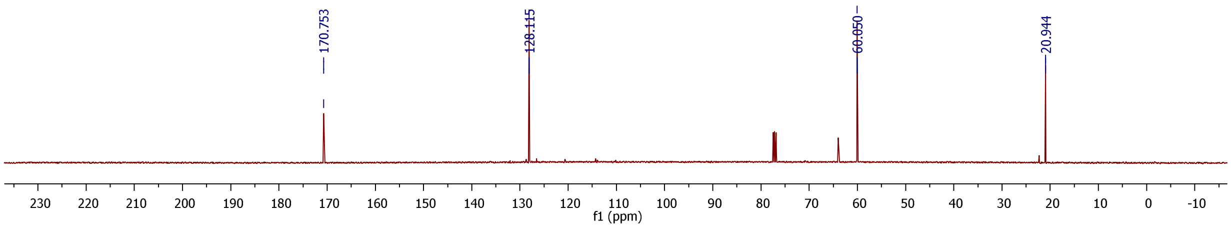
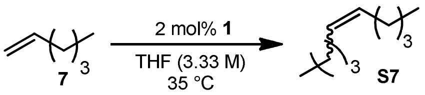


Figure S7. ^{13}C NMR (CDCl$_3$, 101 MHz) of **S6**.



S7:[3] The crude reaction mixture was filtered through a plug of silica using hexanes and concentrated *in vacuo* to remove unreacted starting material. *Z*-**S7**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.37 – 5.22 (m, 2H), 2.12 – 1.87 (m, 4H), 1.45 – 1.20 (m, 8H), 0.90 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 129.85, 31.98, 26.91, 22.35, 14.00.

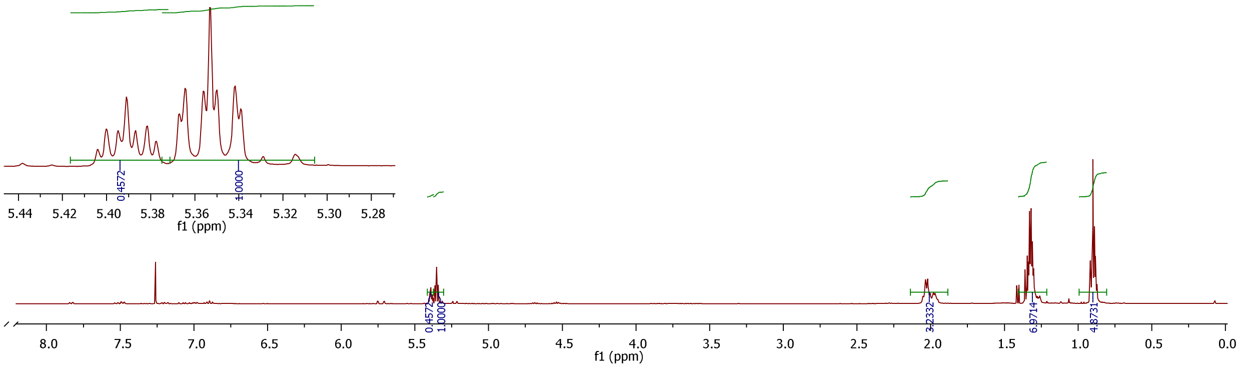


Figure S8. ^{1}H NMR (CDCl$_3$, 400 MHz) of **S7**.

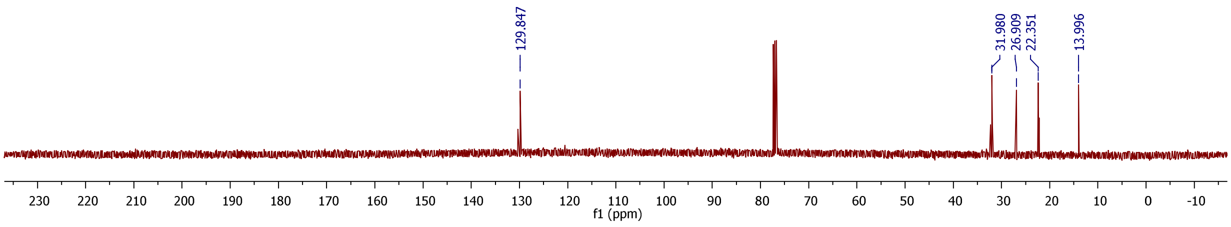
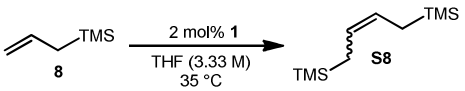


Figure S9. ^{13}C NMR (CDCl$_3$, 101 MHz) of **S7**.



S8:[3] The crude reaction mixture was filtered through a plug of silica using hexanes and concentrated *in vacuo* to remove unreacted starting material. *Z*-**S8**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.30 (ddd, *J* = 6.8, 5.4, 1.4 Hz, 2H), 1.40 (d, *J* = 6.8 Hz, 4H), 0.00 (d, *J* = 0.8 Hz, 18H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 123.13, 17.80, -1.71.

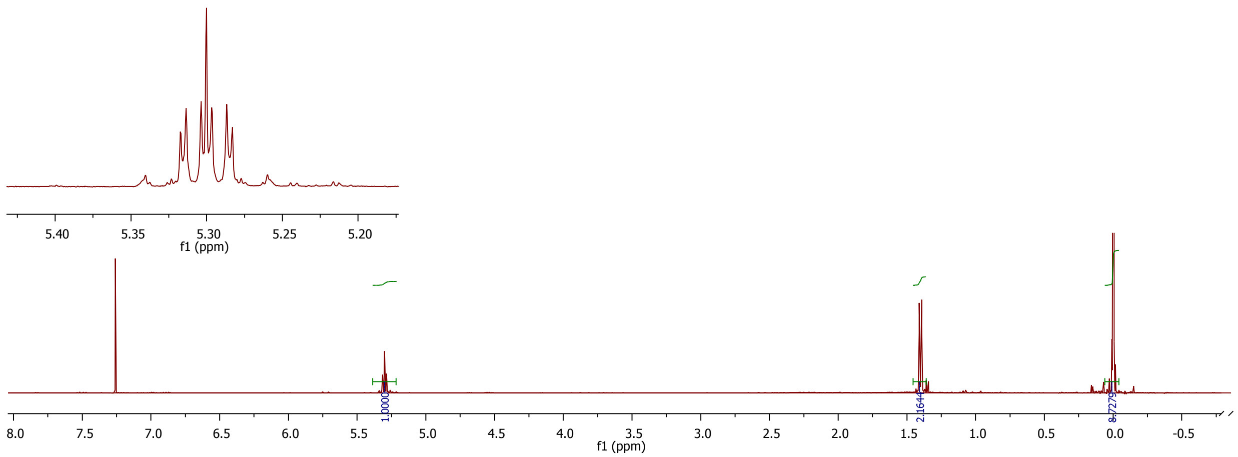


Figure S10. ^{1}H NMR ($CDCl_3$, 400 MHz) of **S8**.

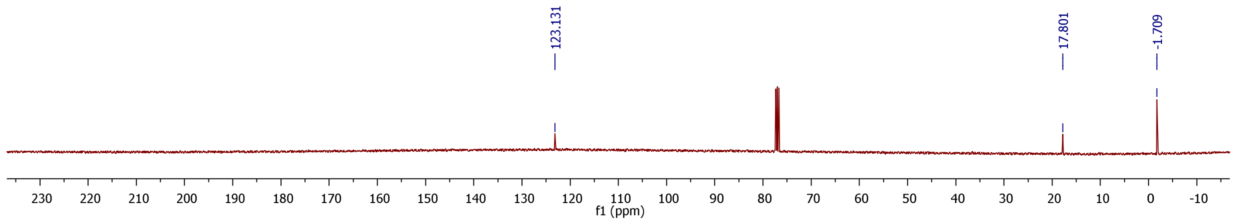
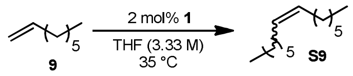


Figure S11. ^{13}C NMR ($CDCl_3$, 101 MHz) of **S8**.



S9:[3] The crude reaction mixture was filtered through a plug of silica gel using hexanes and concentrated *in vacuo*. *Z*-**S9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 – 5.15 (m, 2H), 2.05 – 1.81 (m, 4H), 1.36 – 1.09 (m, 16H), 0.91 – 0.67 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.05, 31.97, 29.93, 29.17, 27.40, 22.84, 14.26.

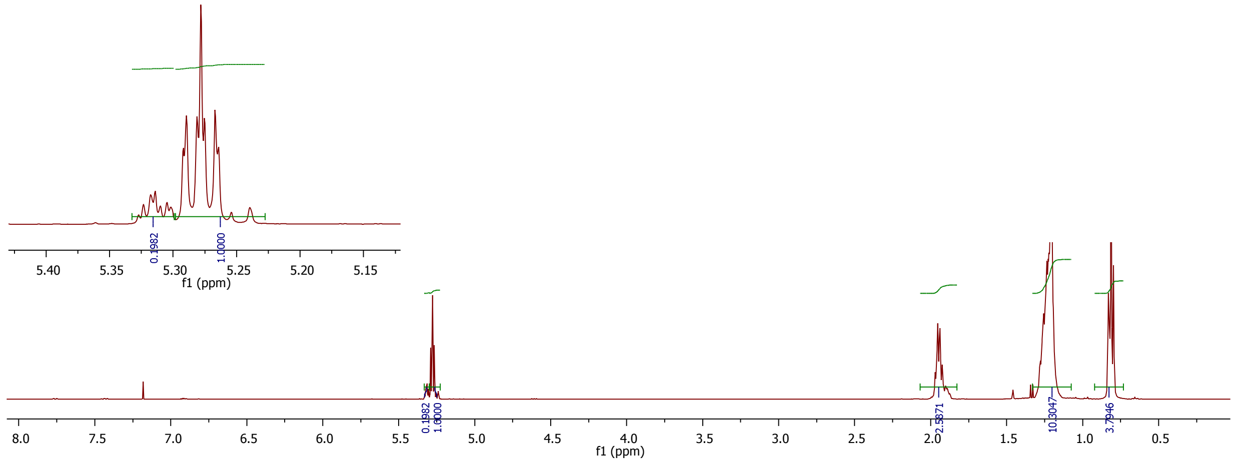


Figure S12. ^{1}H NMR ($CDCl_3$, 400 MHz) of **S9**.

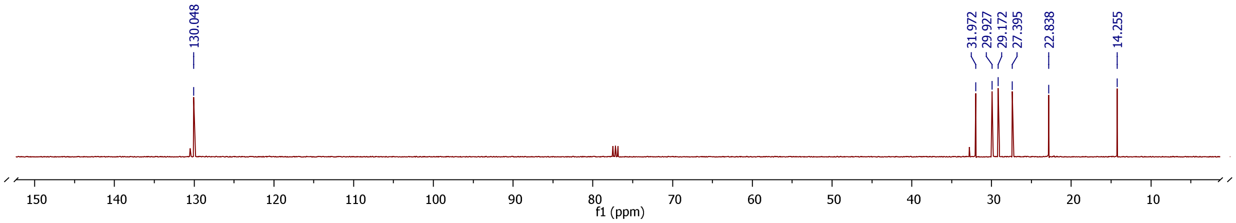
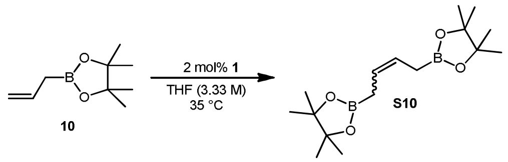


Figure S13. ^{13}C NMR (CDCl$_3$, 101 MHz) of **S9**.



S10: The crude reaction mixture was filtered through a plug of silica gel using hexanes and concentrated *in vacuo*. *Z*-**S10**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.43 (m, 2H), 1.58 (d, *J* = 5.8 Hz, 4H), 1.33 – 0.97 (m, 24H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 124.10, 83.02, 24.69, 24.48. HRMS (EI+): Calculated – 308.2330, Found – 308.2324.

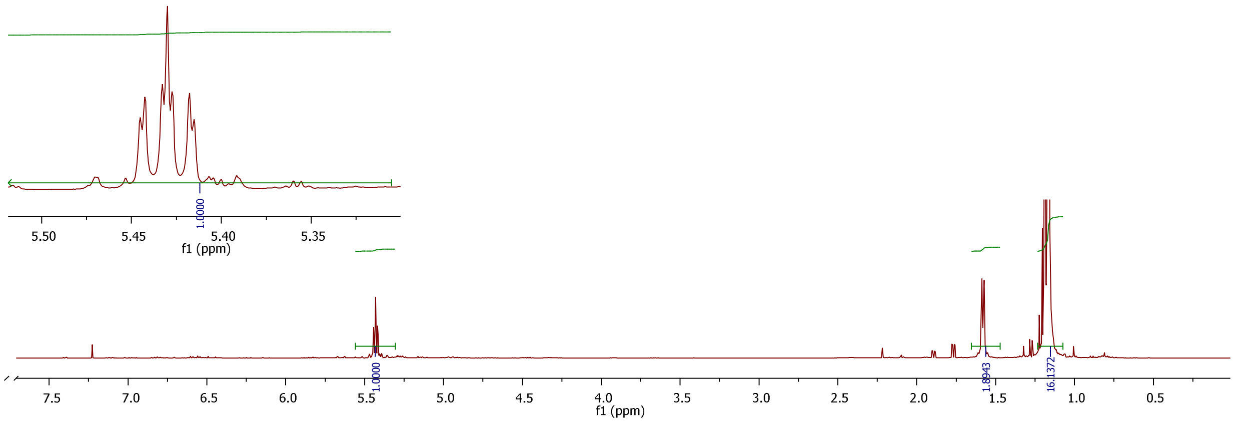


Figure S14. ^{1}H NMR (CDCl$_3$, 400 MHz) of **S10**.

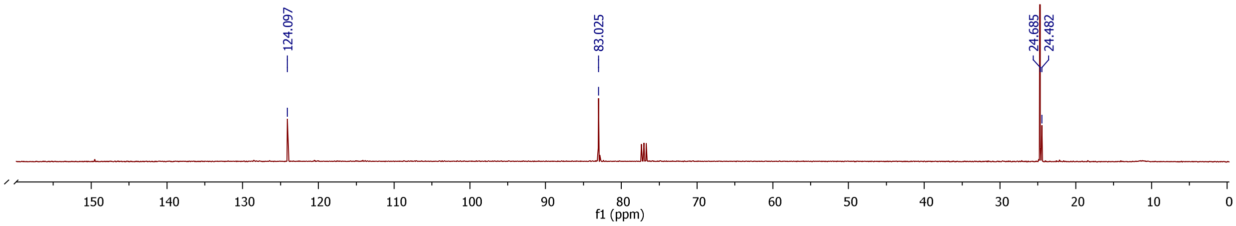
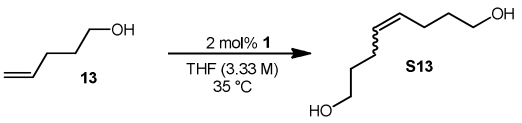


Figure S15. ^{13}C NMR (CDCl$_3$, 101 MHz) of **S10**.



S13:[7] The crude product was purified by column chromatography on silica gel using 40% acetone in CH_2Cl_2 as eluant. *Z*-**S13**: ^1H NMR (600 MHz, $CDCl_3$) δ 5.38 – 5.19 (m, 2H), 3.60 (m, 4H), 2.52 (br s, 2H), 2.15 (m, 4H), 1.66 – 1.53 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.81, 61.77, 32.24, 23.24.

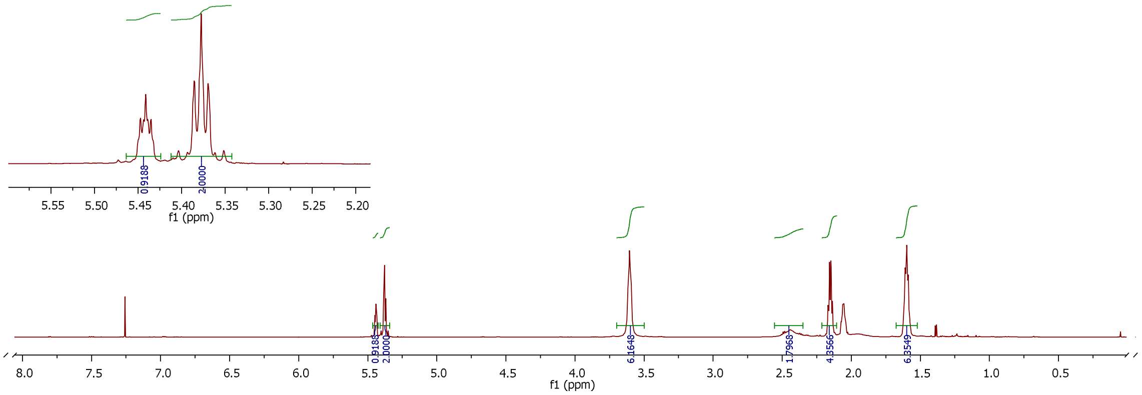


Figure S16. ^1H NMR ($CDCl_3$, 600 MHz) of **S13**.

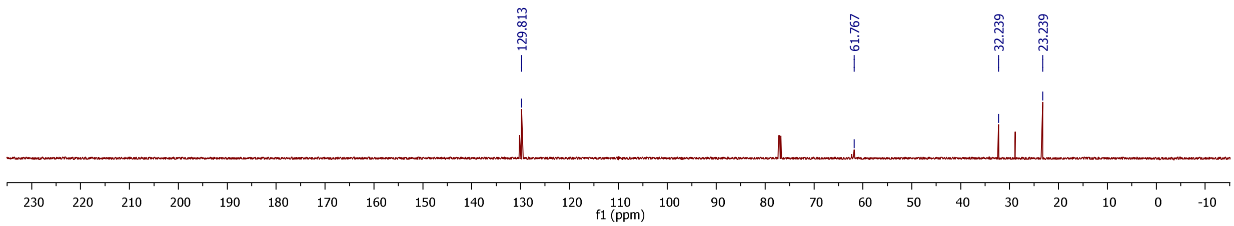
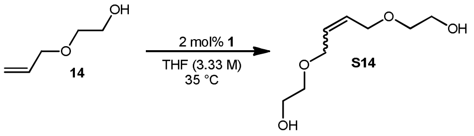


Figure S17. ^{13}C NMR ($CDCl_3$, 151 MHz) of **S13**.



S14: The crude product was purified by column chromatography on silica gel using 40% acetone in CH_2Cl_2 as eluant. *Z*-**S14**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.74 (m, 2H), 4.08 (dd, *J* = 3.8, 1.1 Hz, 4H), 3.70 (m, 4H), 3.58 – 3.49 (m, 4H), 2.71 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.45, 71.57, 66.63, 61.69. HRMS (FAB+) : Calculated – 177.1127, Found – 177.1124.

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(7) Matson, J. B.; Grubbs, R. H. *Macromolecules*. **2010**, *43*, 213-221.

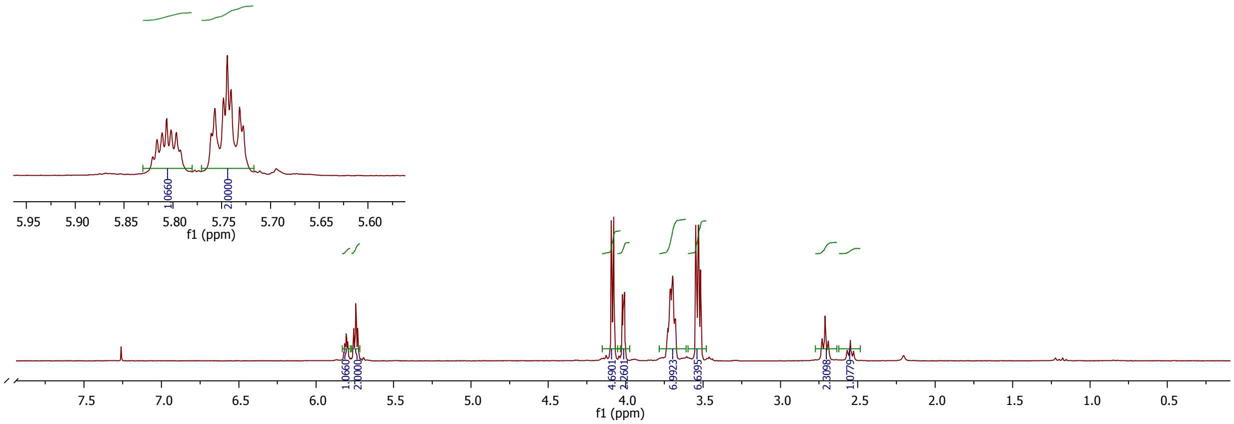


Figure S18. ^{1}H NMR (CDCl$_3$, 300 MHz) of **S14**.

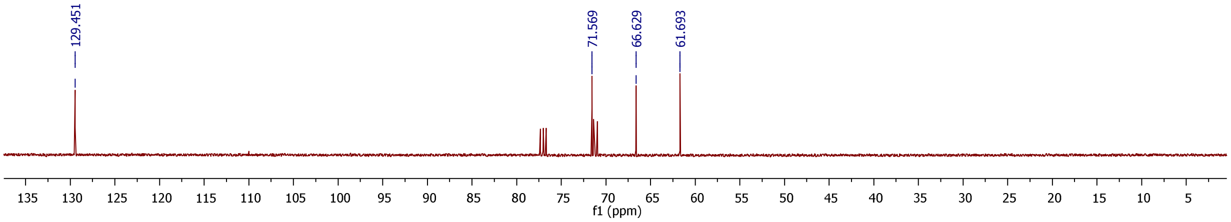
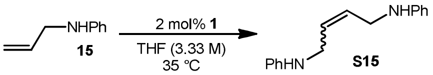


Figure S19. ^{13}C NMR (CDCl$_3$, 101 MHz) of **S14**.



S15:[3] The crude product was purified by column chromatography on silica gel using 30% Et$_2$O in hexanes as eluant. *Z*-**S15**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.09 (m, 4H), 6.83 – 6.69 (m, 2H), 6.69 – 6.55 (m, 4H), 5.78 – 5.66 (m, 2H), 3.86 (d, J = 4.7 Hz, 4H), 3.71 (br s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.97, 129.83, 129.30, 117.82, 113.10, 41.46.

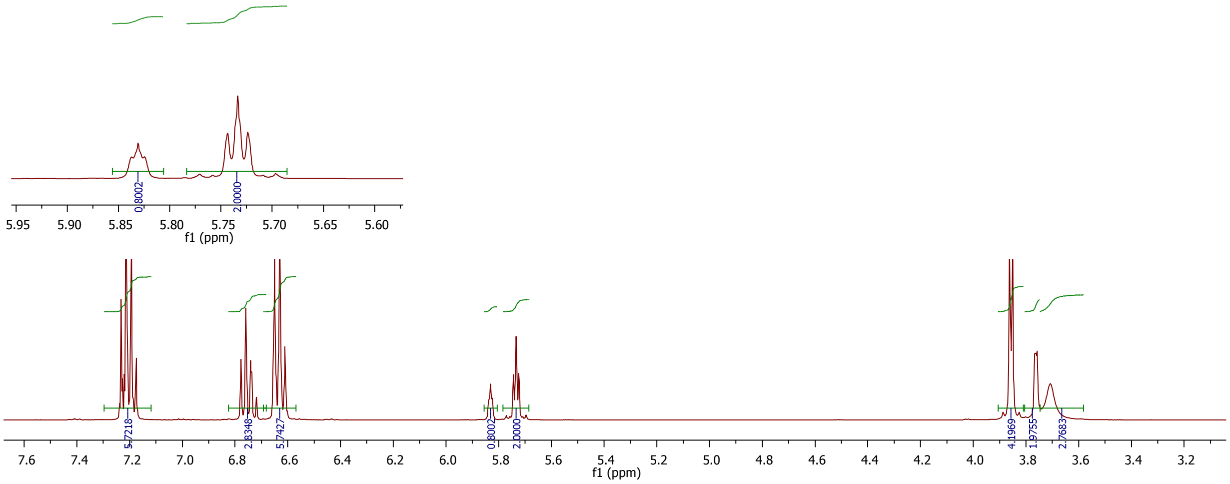


Figure S20. ^{1}H NMR (CDCl$_3$, 400 MHz) of **S15**.

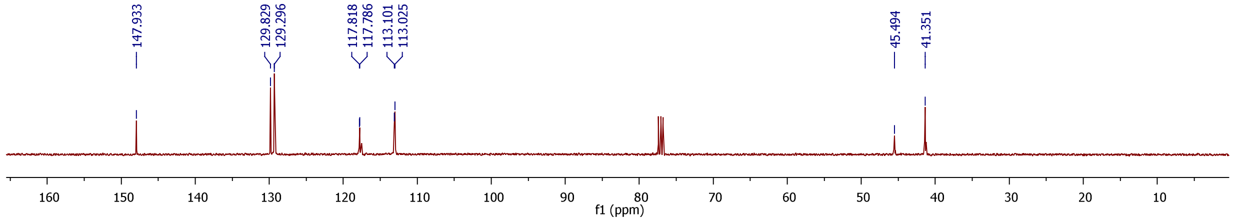


Figure S21. ^{13}C NMR (CDCl$_3$, 101 MHz) of **S15**.

General Procedure for Reactions in Varying Solvent.

In a glovebox, a 4 mL vial was charged with **1** (1.8 mg, 0.0027 mmol), solvent (30 µL, ca. 2.25 M in **5**), and **5** (30 µL, 0.133 mmol). The reaction was stirred at RT while open to the box atmosphere. Aliquots were taken from the reaction mixture and removed from the glovebox, quenched with air, diluted with CDCl$_3$, and analyzed by ^{1}H and ^{13}C NMR spectroscopy.