

Enantioselective Olefin Metathesis with Cyclometalated Ruthenium Complexes

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Supporting Information

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General Information.

All reactions were carried out in dry glassware under an Argon atmosphere using standard Schlenk line techniques or in a Vacuum Atmospheres glovebox under nitrogen atmosphere. All solvents were purified by passage through solvent purification columns and further degassed with Argon.¹ NMR solvents for air-sensitive compounds were degassed by sparging with nitrogen and passed through a solvent purification column prior to use. Commercially available reagents were used as received unless otherwise noted. Substrates in the liquid state were degassed with Argon and passed through a plug of neutral alumina prior to use. Solid substrates were used after purification by silica gel column chromatography. Silica gel used for the purification of transition metal complexes was dried at 220 °C and 100 mTorr for 24 h prior to use.

Standard NMR spectroscopy experiments were conducted on a Varian INOVA 500 (¹H: 500 MHz, ¹³C: 125 MHz) spectrometer. Chemical shifts are referenced to the residual solvent peak (CDCl₃ or C₆D₆) multiplicity is reported as follows: (s: singlet, d: doublet, t: triplet: q: quartet, br: broad, m: multiplet). Spectra were analyzed and processed using MestReNova.

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with an Agilent HP-5 5% phenyl methyl siloxane capillary column (J&W Scientific). GC instrument conditions: Inlet temperature-

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996**, *15*, 1518-1520.

250 °C; Detector temperature- 300 °C; Hydrogen flow- 30 mL/min; Air flow- 400 mL/min; Makeup flow- 25 mL/min. GC method: 50 °C for 1 min, then temperature ramp (35 °C/min) for 7 min to 300 °C followed by an isothermal period at 300 °C for 3 min.

High-resolution mass spectra (HRMS) data was obtained on a JEOL MSRoute mass spectrometer using FAB+, EI+, or MALDI-TOF methods.

Analytical SFC data was obtained on a Mettler SFC supercritical CO₂ analytical chromatography system equipped with Chiracel OD-H, OJ-H or Chirapak AD-H columns (4.6 mm x 25 cm). Column temperature was maintained at 40°C. Preparative HPLC was conducted on an Agilent HPLC system equipped with Chiral Technologies Chiralpak AD-H column (21 x 250 mm). Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm.

Resolution of Complex *rac-5*

Complex *rac-5* was resolved according to the procedure previously reported.² A modification of the original procedure is described herein. The mixture of diastereomers **6a** and **6b** (0.260 g, 0.349 mmol) was triturated with 1:1 Et₂O/pentane (5 x 3 mL) at 23°C under a N₂ atmosphere. The remaining solid was dried under vacuum and assayed by ¹H NMR (>95% de **6a**, 100 mg, 0.136 mmol, 77% of theoretical yield).

² Hartung, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 10183-10185.

Synthesis of Substrates for AROCM

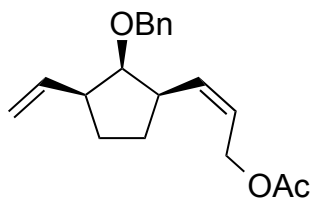
Substrates for AROCM were synthesized as previously reported in the literature:

9d,³ **9e**⁴ were synthesized according to the provided references.

General Procedure for AROCM

In a glovebox, alkene **9d** (40 mg, 0.2 mmol, 1 equiv) and allyl acetate (140 mg, 1.4 mmol, 7 equiv) were dissolved in 0.4 mL THF. To this solution was added catalyst **5** (1.27 mg, 0.002 mmol). The reaction vial was capped and stirred for 1 h and then quenched with an excess of ethyl vinyl ether. The reaction mixture was concentrated and conversion was determined by 500 MHz ¹H NMR. The crude was subjected to flash chromatography or preparative TLC to afford the desired ARCM product (**11d**, 33 mg, 56% yield, 15:85 *Z/E* ratio, 94% ee (*Z*), 93% ee (*E*)). Pure products were submitted to analytical SFC to determine ee.

Characterization Data for AROCM Products



Z-11d.

56% combined (*E* and *Z* products) yield, 15:85 *Z/E* ratio (GC).

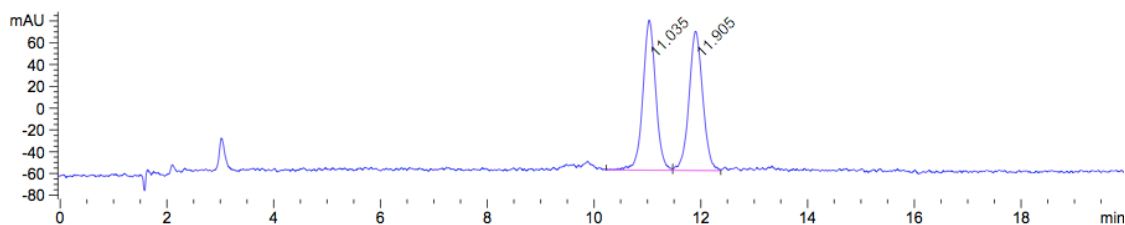
³ La, D. S.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7767-7778.

⁴ Coe, J. W.; Wirtz, M. C.; Bashore, C. G.; Candler, J. *Org. Lett.* **2004**, *6*, 1589-1592.

$[\alpha]_D^{25} = -23.9^\circ$ ($c = 0.21$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.35 – 7.24 (m, 5H), 5.99 (ddd, $J = 17.1, 10.2, 8.2$ Hz, 1H), 5.90 – 5.83 (m, 1H), 5.55 (dtd, $J = 11.1, 7.0, 1.0$ Hz, 1H), 5.08 (ddd, $J = 17.2, 2.1, 1.0$ Hz, 1H), 5.02 (ddd, $J = 10.2, 2.0, 0.8$ Hz, 1H), 4.62 (dt, $J = 7.1, 1.1$ Hz, 2H), 4.55 (d, $J = 11.7$ Hz, 1H), 4.50 (d, $J = 11.7$ Hz, 1H), 3.76 (t, $J = 4.1$ Hz, 1H), 2.91 (qd, $J = 9.1, 4.3$ Hz, 1H), 2.62 (qd, $J = 8.6, 3.9$ Hz, 1H), 2.06 (s, 2H), 1.82 (dq, $J = 9.4, 6.9$ Hz, 3H), 1.75 – 1.67 (m, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 139.25, 139.09, 136.26, 128.34, 127.74, 127.52, 123.45, 115.04, 86.93, 73.76, 60.77, 50.32, 43.45, 30.53, 30.11, 28.99, 21.14. HRMS (FAB+) calculated for $\text{C}_{19}\text{H}_{24}\text{NaO}_3$ $[\text{M}+\text{Na}]$: 323.1623; found 323.1627.

Separation conditions: OJ-H, 1% IPA, 2.5 mL/min. 94% ee

Racemate:

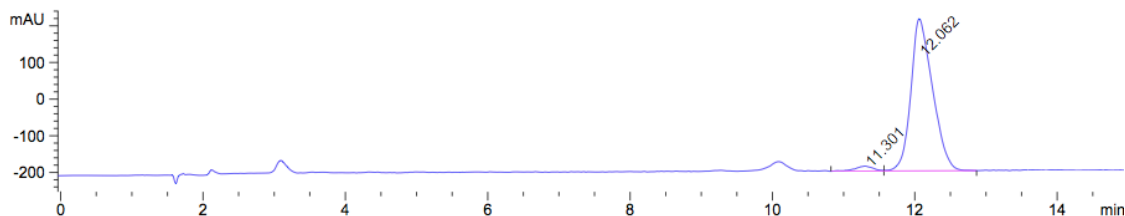


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.035	BV	0.2512	2302.19849	137.56712	50.2543
2	11.905	VV	0.2763	2278.89893	127.66735	49.7457

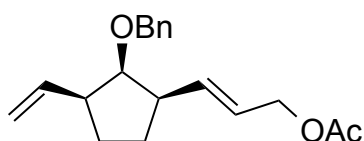
Totals : 4581.09741 265.23447

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.301	BV	0.2214	239.09720	13.58221	2.6496
2	12.062	VB	0.3154	8784.66992	414.32910	97.3504
Totals :				9023.76712	427.91131	

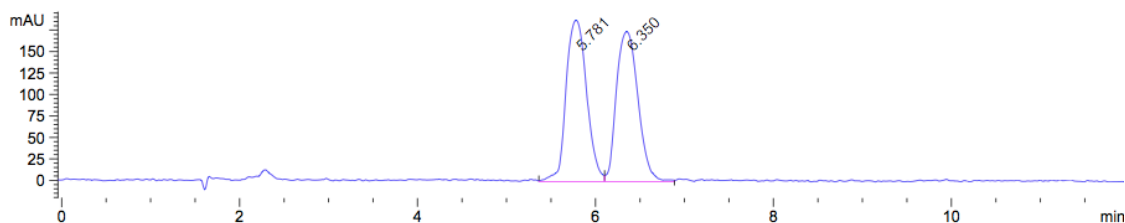


***E*-11d.**

$[\alpha]_D^{25} = -1.1^\circ$ ($c = 0.67$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.40 – 7.23 (m, 5H), 6.07 – 5.97 (m, 1H), 5.95 – 5.88 (m, 1H), 5.61 (dt, $J = 15.8, 6.4$ Hz, 1H), 5.09 (d, $J = 17.3$ Hz, 1H), 5.03 (dd, $J = 10.4, 1.9$ Hz, 1H), 4.57 (d, $J = 11.9$ Hz, 1H), 4.54 – 4.51 (m, 2H), 4.49 (dd, $J = 11.8, 1.5$ Hz, 1H), 3.79 (t, $J = 4.3$ Hz, 1H), 2.62 (dt, $J = 9.7, 4.6$ Hz, 2H), 2.05 (d, $J = 1.5$ Hz, 3H), 1.87 – 1.75 (m, 4H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 139.37, 139.10, 136.73, 128.31, 127.82, 127.53, 124.18, 114.96, 86.98, 73.70, 65.35, 50.14, 48.54, 28.91, 21.11. HRMS (FAB+) calculated for $\text{C}_{19}\text{H}_{24}\text{NaO}_3$ $[\text{M}+\text{Na}]$: 323.1623; found 323.1628.

Separation conditions: AD-H, 2% IPA, 2.5 mL/min. 93% ee

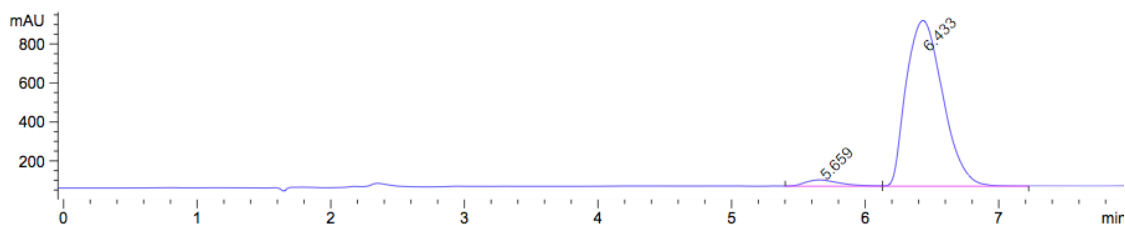
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

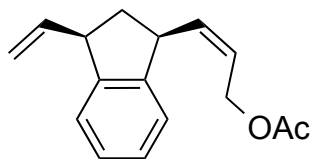
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.781	VV	0.2561	3036.30420	188.30795	50.6709
2	6.350	VV	0.2732	2955.90186	174.83788	49.3291
Totals :				5992.20605	363.14583	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.659	VV	0.2846	596.53467	32.73715	3.5544
2	6.433	VV	0.3100	1.61865e4	850.61707	96.4456
Totals :				1.67830e4	883.35422	



11e.

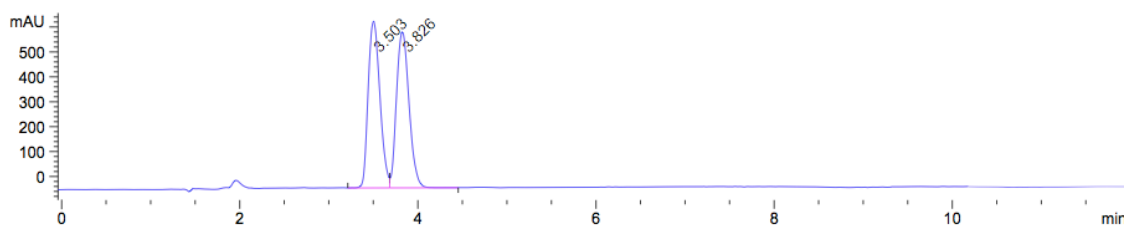
55% yield, 76:14 *Z/E* ratio.

Z-11e: $[\alpha]_D^{25} + 41.4^\circ$ ($c = 0.65$, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.20 (m, 2H), 7.19 – 7.14 (m, 1H), 7.11 – 7.07 (m, 1H), 5.89 – 5.81 (m, 1H), 5.80 – 5.75 (m, 1H), 5.67 (ddd, $J = 10.7, 9.6, 1.1$ Hz, 1H), 5.25 (ddd, $J = 17.0, 1.9, 1.0$ Hz, 1H), 5.18 (dd, $J = 10.0, 1.8$ Hz, 1H), 4.78 (dt, $J = 6.9, 1.0$ Hz, 2H), 4.15 – 4.03 (m, 1H), 3.76 (dt, $J = 10.3, 7.7$ Hz, 1H), 2.54 (dt, $J = 12.3, 7.0$ Hz, 1H), 2.11

(d, $J = 0.8$ Hz, 2H), 1.64 (dt, $J = 12.2, 10.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 145.72, 145.25, 140.55, 137.57, 127.04, 124.77, 124.30, 124.12, 116.02, 60.59, 49.13, 42.79, 41.59, 21.16. HRMS (FAB+) calculated for $\text{C}_{16}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}-\text{H}_2]$: 241.1229; found 241.1221.

Separation conditions: AD-H, 3% IPA, 2.5 mL/min. >98% ee

Racemate:

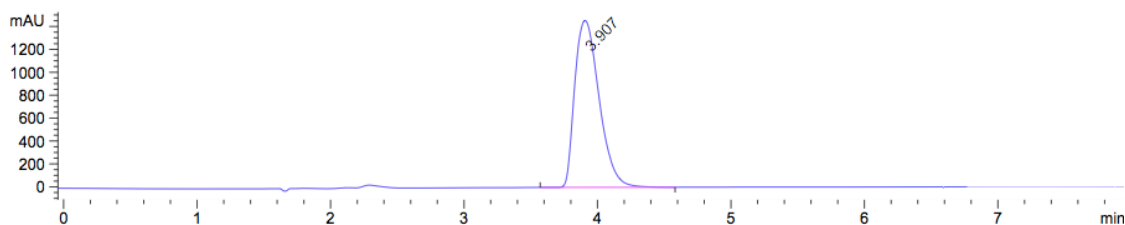


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.503	BV	0.1472	6139.82520	668.11780	49.9774
2	3.826	VB	0.1547	6145.36768	625.22028	50.0226

Totals : 1.22852e4 1293.33807

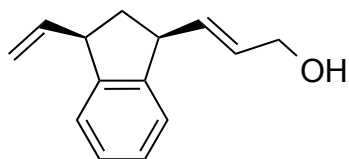
Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.907	BB	0.2003	1.85037e4	1456.06311	100.0000

Totals : 1.85037e4 1456.06311



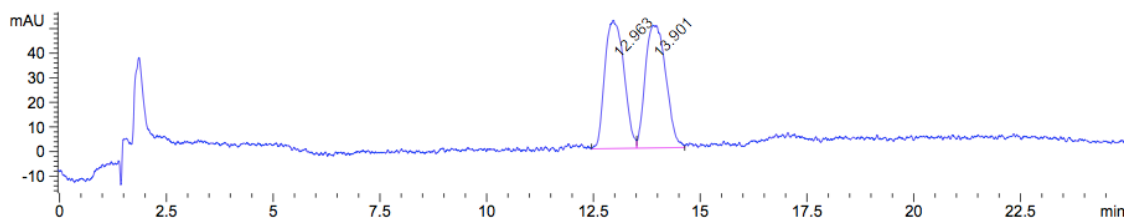
S1.

E-11e was deacetylated to the compound shown above in order to aid purification.

¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.10 (m, 3H), 5.91 – 5.79 (m, 2H), 5.77 – 5.69 (m, 1H), 5.22 (ddd, *J* = 17.1, 1.8, 0.9 Hz, 1H), 5.15 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.20 (t, *J* = 5.7 Hz, 2H), 3.73 (dq, *J* = 16.8, 8.3 Hz, 2H), 2.52 (dt, *J* = 12.4, 7.1 Hz, 1H), 1.66 (dt, *J* = 12.4, 10.3 Hz, 1H), 1.32 (t, *J* = 5.7 Hz, 1H).

Separation conditions: AD-H, 3% IPA, 2.5 mL/min. >98% ee

Racemate:

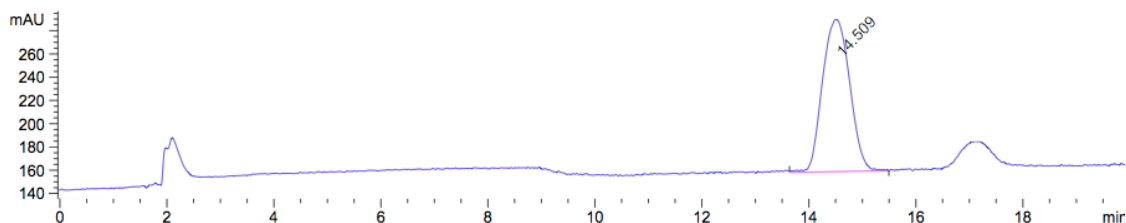


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.963	BV	0.3805	1630.66382	52.19287	49.3447
2	13.901	VV	0.4567	1673.97461	49.73441	50.6553

Totals : 3304.63843 101.92728

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

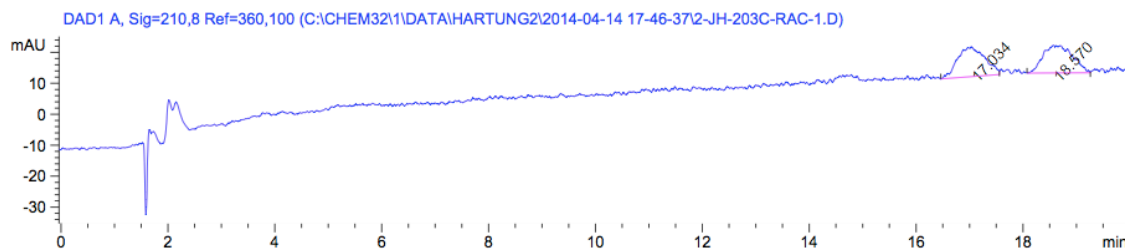
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.509	VB	0.5751	4652.46533	130.76849	100.0000

Totals : 4652.46533 130.76849

Z and *E* isomers of **S1** were hydrogenated (H_2 , 1 atm, 10% Pd/H, EtOAc) to afford the tetrahydro derivative. 1H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 4H), 3.78 – 3.66 (m, 2H), 3.13 – 2.90 (m, 3H), 2.53 (ddt, $J = 20.8, 12.3, 6.8$ Hz, 2H), 2.22 – 2.00 (m, 2H), 1.83 – 1.63 (m, 1H), 1.48 – 1.35 (m, 2H), 1.05 – 0.97 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.67, 147.50, 126.46, 126.41, 123.40, 123.30, 63.42, 45.30, 43.39, 39.23, 31.15, 31.04, 29.86, 27.67, 26.94, 12.05. HRMS (EI+) calculated for $C_{14}H_{20}O$ [M+]: 204.1514; found 204.1517.

Separation Conditions: AD–H, 3% IPA, 2.5 mL/min

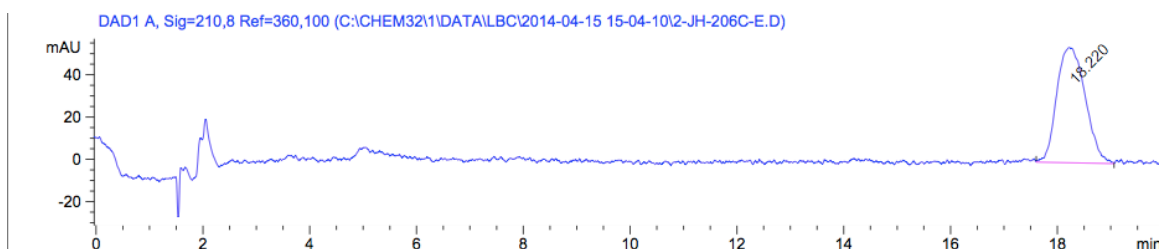
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.034	BV	0.4357	342.30624	9.51427	50.0045
2	18.570	BV	0.4539	342.24460	9.03542	49.9955
Totals :				684.55084	18.54969	

Enantioenriched:



Preparation of Silver Carboxylates

Following a known procedure,⁵ L-N-acetyl alanine (200 mg, 1.53 mmol, 2 equiv.) was added to a stirring suspension of silver oxide (177 mg, 0.762 mmol, 1 equiv.) in 4 mL acetonitrile, shielded from light. The reaction was vigorously stirred for 24 h, at which time a light gray precipitate had formed. The mixture was filtered and washed with acetonitrile and ether. The resultant solid was dried under vacuum overnight while shielded from light to provide 268 mg (1.13 mmol, 74% yield) of the silver carboxylate. ¹H NMR (500 MHz, DMSO-d₆) δ 7.76 (d, *J* = 7.7 Hz, 1H), 4.15 (p, *J* = 7.2 Hz, 1H), 1.80 (s, 3H), 1.21 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (125 MHz, DMSO-d₆) δ 176.19, 168.11, 49.43, 22.68, 19.15.

The above procedure was followed substituting L-N-acetyl valine (200 mg, 1.26 mmol) for L-N-acetyl alanine to afford the corresponding silver carboxylate (121

⁵ Dorta, R.; Shimon, L.; Milstein, D. *J. Organomet. Chem.* **2004**, 689, 751-758.

mg, 0.457 mmol, 36% yield). ^1H NMR (500 MHz, DMSO-d_6) δ 7.53 (d, $J = 9.0$ Hz, 1H), 4.10 (dd, $J = 9.0, 5.3$ Hz, 1H), 2.02 (m, 1H), 1.84 (s, 3H), 0.81 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 175.40, 169.28, 59.43, 31.03, 22.88, 19.77, 18.51.

The above procedure was followed substituting (*S*)-2-phenyl butyric acid (200 mg, 1.22 mmol) for *L-N* acetyl alanine to afford the corresponding silver carboxylate (212 mg, 0.785 mmol, 64% yield). ^1H NMR (500 MHz, DMSO-d_6) δ 7.30 – 7.25 (m, 2H), 7.25 – 7.20 (m, 2H), 7.16 – 7.11 (m, 1H), 3.37 – 3.27 (m, 1H), 1.99 – 1.88 (m, 1H), 1.60 (m, 1H), 0.79 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 177.56, 142.76, 128.07, 128.05, 126.09, 56.10, 27.56, 12.88.

Synthesis of Catalysts 6c-i

To a solution of enantiopure ruthenium iodide ent-7 (1.92 mg, 0.0028 mmol) in 0.5 mL THF was added silver carboxylate from above (0.055 mmol, 2 equiv.). The mixture was stirred for 30 min and then concentrated. The resultant solid was redissolved in C_6D_6 and filtered through a short pad of Celite. The resultant purple solution was assayed by ^1H NMR, concentrated, redissolved in THF, and then used directly in the ARCM reaction. ^1NMR spectra of complexes **6c-e**

matched previously reported spectra of the corresponding racemic complexes.⁶

Diagnostic benzylidene signals (C_6D_6) of novel compounds are listed below:

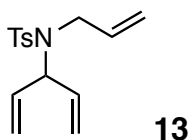
6b: 15.00 ppm

6f: 14.99 ppm

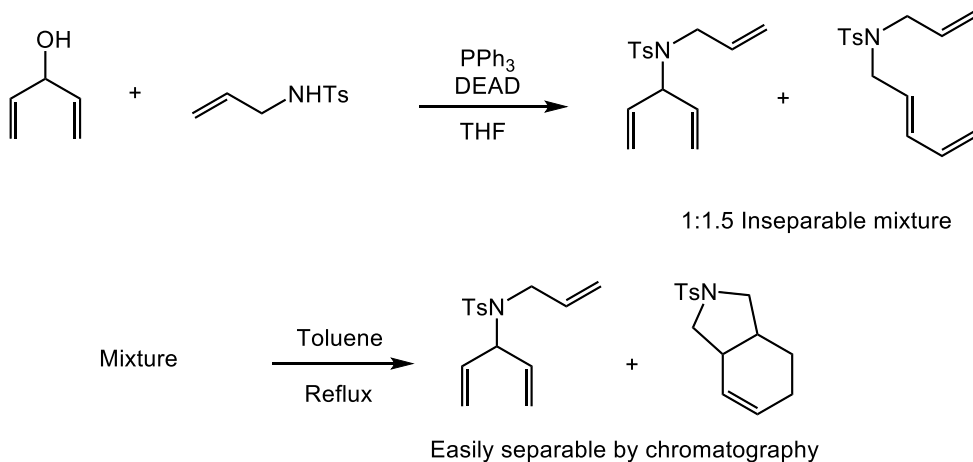
6g: 15.10 ppm

6i: 15.11 ppm

Synthesis of Substrates for ARCM



A procedure adapted from Jeong et al.⁷ was used:

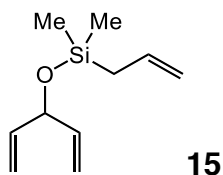


To a flame dried round bottom flask was added N-tosyl allyl amine (4.23 g, 20 mmol, 1.0 eq), triphenylphosphine (6.56 g, 25 mmol, 1.25 eq), THF (100 mL) and 1,4-pentadien-3-ol (2.43 mL, 25 mmol, 1.25 eq). The mixture was cooled to 0 °C,

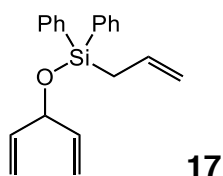
⁶ Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.*, **2012**, *134*, 693–699.

⁷ Jeong, N.; Kim, D. H.; Choi, J. H. *Chem. Commun.* **2004**, 1134.

and then diethylazodicarboxylate (40 wt % in Toluene, 11.38 mL, 25 mmol, 1.25 eq). The mixture was stirred at 0 °C for 30 min and then warmed to ambient temperature for 12 hr. The reaction was quenched with sat'd NaHCO₃ and extracted with ether (3 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried with MgSO₄ and concentrated *in vacuo*. Ether (30 mL) was then added, and the mixture was filtered on a glass frit to remove triphenylphosphine oxide. The solid was washed with ether, and the filtrate was concentrated *in vacuo*. The material was purified by column chromatography (10% ethyl acetate / hexanes) to yield 3.386 g of an inseparable mixture of the title compound and the corresponding S_N2' conjugated diene product in a 1:1.5 ratio. This mixture was dissolved in toluene (24 mL) and heated to reflux for 22 hr in order to convert the undesired conjugated diene to the Diels-Alder adduct. Compound **13** was then purified by column chromatography (7.5% ethyl acetate / hexanes) to give a clear oil (960 mg, 17%). ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.25 (m, 2H), 5.81 – 5.73 (m, 3H), 5.19 (dt, *J* = 10.4, 1.3 Hz, 2H), 5.16 (m, 3H), 5.07 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.96 (tt, *J* = 6.0, 1.6 Hz, 1H), 3.78 (dt, *J* = 6.1, 1.5 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.2, 138.2, 135.7, 135.3, 129.6, 127.6, 118.7, 117.5, 62.4, 47.7, 21.6. HRMS (FAB+) *m/z* calculated for [C₁₅H₁₉NSO₂+H]⁺: 278.1215; found: 278.1221.

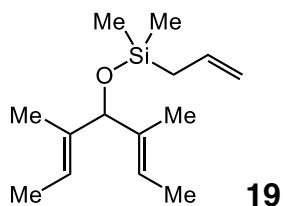


To a flame dried flask under argon was added CH_2Cl_2 (60 mL), 4-dimethylaminopyridine (88 mg, 0.72 mmol, 0.05 eq), triethylamine (2.4 mL, 17.2 mmol, 1.2 eq), 1,4-pentadien-3-ol (1.38 mL, 14.1 mmol, 1.0 eq) and then allyldimethylsilyl chloride (2.2 mL, 15.0 mmol, 1.06 mmol). The mixture was stirred at room temperature for 20 hr, and then quenched with H_2O (20 mL). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine (20 mL), dried with Na_2SO_4 and concentrated in vacuo. The crude material was passed through a pad of neutral alumina with 5% ether in pentane and then concentrated in vacuo to give **15** (2.46 g, 96%). ^1H NMR (500 MHz, CDCl_3) δ 5.82 (ddd, $J = 17.1, 10.3, 5.7$ Hz, 2H), 5.83 – 5.74 (m, 1H), 5.22 (dt, $J = 17.1, 1.6$ Hz, 2H), 5.09 (dt, $J = 10.3, 1.5$ Hz, 2H), 4.92 – 4.84 (m, 2H), 4.62 (tp, $J = 5.7, 1.5$ Hz, 1H), 1.65 (dt, $J = 8.1, 1.2$ Hz, 2H), 0.14 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 140.1, 134.2, 114.4, 113.8, 74.9, 25.1, -1.7. HRMS (EI+) m/z calculated for $[\text{C}_{10}\text{H}_{18}\text{OSi}]^+$: 182.1127; found: 182.1137.

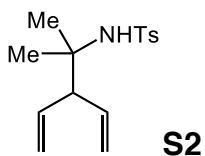


To a flame dried round bottom flask under argon was added diphenyldichlorosilane (0.421 mL, 2.0 mmol, 1.33 eq) and THF (10 mL).

Imidazole (102 mg, 1.5 mmol, 1.0 eq) was then added, and the cloudy mixture was stirred for 5 minutes and then cooled to -78 °C. 1,4-pentadien-3-ol (0.146 mL, 1.5 mmol, 1.0 eq) was then added, and the mixture was stirred for 15 min, warmed to 0 °C for 1 hr, and then stirred at ambient temperature for 1 hr. Allyl magnesium bromide (2 M in THF, 5 mL, 10 mmol) was then added dropwise. The clear yellow solution was stirred for 2.5 hr, and then quenched with sat'd NH₄Cl (15 mL). The mixture was extracted with ethyl acetate (2 x 30 mL). The combined organic extracts were washed with brine (20 mL), dried with MgSO₄, and concentrated *in vacuo*. The product was isolated by column chromatography (0 → 3% ethyl acetate / hexanes) to give a 5:1 mixture of the desired product and the disilanol byproduct (347 mg, 61% corrected yield). Analytically pure material can be obtained by preparatory TLC (0.8% ethyl acetate / hexanes, run twice). ¹H NMR (500 MHz, CDCl₃) δ 7.65-7.62 (m, 4H), 7.46-7.42 (m, 2H), 7.41-7.36 (m, 4H), 5.90-5.81 (m, 3H), 5.21 (dt, J = 17.2, 1.5 Hz, 2H), 5.09 (dt, J = 10.3, 1.4 Hz, 2H), 4.96 (ddt, J = 17.0, 2.1, 1.5 Hz, 1H), 4.91 (ddt, J = 10.1, 2.1, 1.1 Hz, 1H), 4.73 (tp, J = 5.7, 1.4 Hz, 1H), 2.23 (dt, J = 7.9, 1.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.7, 135.1, 134.9, 133.2, 130.0, 127.8, 115.3, 114.7, 75.7, 22.6. HRMS (EI+) *m/z* calculated for [C₂₀H₂₂OSi]⁺: 306.1440; found: 306.1452.



Compound **19** was synthesized according to a literature procedure.⁸



A procedure adapted from Gomez, et al.⁹ was followed. 5-Bromopenta-1,3-diene was synthesized by dropwise addition of 1,4-pentadien-3-ol (0.97 mL, 10 mmol) to a solution of PBr₃ (0.38 mL, 4 mmol) in 5 mL ether at 0°C. Upon complete conversion of the alcohol, as determined by TLC, the reaction was quenched with brine. The organic layer was separated, washed with saturated NaHCO₃ solution, dried over MgSO₄, filtered and carefully concentrated at 23°C under a stream of Ar.

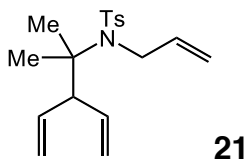
Toluenesulfonamide (0.58 g, 3.4 mmol), Indium powder (0.49 g, 4.2 mmol, 1.25 equiv), titanium (IV) ethoxide (1.78 mL, 8.48 mmol, 2.5 equiv), and acetone (0.27 mL, 3.7 mmol, 1.1 equiv) were dissolved in 20 mL THF and the mixture was stirred at 65°C for 14 h. The bromide prepared above (1.04 g crude weight) was added directly to the reaction and heated at 65°C for an additional 8 h. After cooling to 23°C, the reaction mixture was added to a 4:1 EtOAc/brine mixture and

⁸ Funk, T. W.; Berlin, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 1840.

⁹ Bosque, I.; Bagdatli, E.; Foubelo, F.; Gonzalez-Gomez, J. C. *J. Org. Chem.* **2014**, *79*, 1796.

filtered through Celite. The crude residue was concentrated and subjected to flash chromatography to afford 0.42 g **S2** (1.50 mmol, 44% yield with respect to toluenesulfonamide).

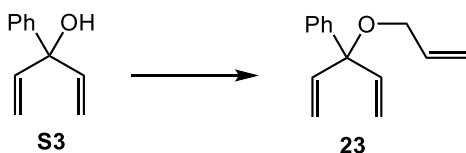
^1H NMR (500 MHz, CDCl_3) δ 7.78 – 7.73 (m, 2H), 7.30 – 7.26 (m, 2H), 5.77 (ddd, $J = 17.1, 10.3, 8.5$ Hz, 2H), 5.20 (ddd, $J = 10.3, 1.7, 0.7$ Hz, 2H), 5.17 (dd, $J = 1.7, 1.0$ Hz, 1H), 5.13 (dd, $J = 1.7, 1.0$ Hz, 1H), 4.58 (s, 1H), 2.85 (tt, $J = 8.5, 0.9$ Hz, 1H), 2.42 (s, 3H), 1.16 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 143.00, 140.84, 135.85, 129.58, 127.17, 118.94, 59.48, 58.25, 25.06, 21.64. HRMS (FAB+) calculated for $\text{C}_{15}\text{H}_{22}\text{SNO}_2$ [M+H]: 280.1371; found 280.1370.



At 0°C , **S2** (200 mg, 0.717 mmol) was added to a suspension of KH (31.6 mg, 0.788 mmol, 1.1 equiv) in 4 mL THF. After stirring for 1 h, allyl bromide (250 μL , 2.87 mmol, 4 equiv) and HMPA (4 mL) were added and the reaction was warmed to 23°C . After stirring for 24 h, the reaction was carefully quenched with water at 0°C . Excess water was added and the solution extracted with ether. The combined organic layers were washed with brine and dried over MgSO_4 . Filtration and concentration afforded a crude residue, which was subjected to flash chromatography to afford **21** (107 mg, 0.335 mmol, 47% yield).

^1H NMR (500 MHz, CDCl_3) δ 7.76 – 7.71 (m, 2H), 7.25 (dt, $J = 8.0, 0.8$ Hz, 2H), 5.91 – 5.77 (m, 3H), 5.15 (qd, $J = 1.9, 1.0$ Hz, 2H), 5.12 (tt, $J = 1.9, 0.9$ Hz, 3H),

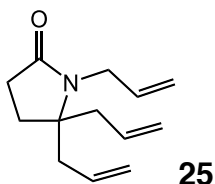
5.09 (m, 1H), 5.07 (dq, $J = 10.2, 1.4$ Hz, 1H), 4.02 (dt, $J = 6.1, 1.5$ Hz, 2H), 3.66 (tt, $J = 7.7, 1.1$ Hz, 1H), 2.40 (s, 3H), 1.32 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 142.74, 140.85, 137.62, 137.09, 129.41, 127.51, 117.86, 116.64, 65.35, 56.64, 49.58, 25.58, 21.56. HRMS (FAB+) calculated for $\text{C}_{18}\text{H}_{26}\text{NSO}_2$ [M+H]: 320.1684; found 320.1679.



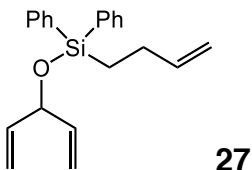
Compound **3** was synthesized as previously reported.¹⁰ To a suspension of sodium hydride (60% dispersion, 0.125 g, 3.13 mmol, 2 equiv) in THF was added **3** (0.250 g, 1.56 mmol) as a solution in THF at 0°C (total volume THF = 10 mL). The reaction was stirred for 2 h, at which time allyl bromide (0.54 mL, 6.25 mmol, 4 equiv) was added dropwise. The reaction was warmed to room temperature and stirred for 16 h, at which time a conversion of about 30% was observed. The reaction was heated to 65°C for 4 h, at which time complete conversion was observed. The reaction was cooled to room temperature, quenched with water, and diluted with ether. The organic layer was separated and washed with water and subsequently brine. The resultant organic layer was dried over MgSO_4 , filtered, and concentrated to afford the crude product. Column chromatography afforded pure **23** (0.307 g, 1.53 mmol, 98% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.46-7.42 (m, 2H), 7.37-7.32 (m, 2H), 7.27 (tt, $J = 7.2, 1.3$ Hz, 1H), 6.14 (dd, $J =$

¹⁰ Ndungu, J. M.; Larson, K. K.; Sarpong, R. *Org. Lett.* **2005**, *7*, 5845-5848.

17.4, 10.8 Hz, 2H), 5.96 (ddt, $J = 17.2, 10.3, 5.0$ Hz, 1H), 5.36 (dq, $J = 17.0, 2.0$ Hz, 1H), 5.34 (dd, $J = 10.8, 1.4$ Hz, 2H), 5.30 (dd, $J = 17.4, 1.4$ Hz, 2H), 5.15 (dq, $J = 10.5, 1.7$ Hz, 1H), 3.90 (dt, $J = 5.1, 1.7$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.82, 140.18, 135.71, 128.23, 127.38, 127.33, 116.34, 115.60, 82.78, 64.95. HRMS (FAB+) calculated for $\text{C}_{14}\text{H}_{15}\text{O}$ [$\text{M}+\text{H}-\text{H}_2$]: 199.1123; found 199.1171.



Compound **25** was synthesized according to a literature procedure.¹¹



To a flame dried round bottom flask under argon was added diphenyldichlorosilane (0.421 mL, 2.0 mmol, 2.0 eq) and THF (10 mL). The solution was cooled to -78°C and imidazole (68 mg, 1.0 mmol, 1.0 eq) was then added. The mixture was warmed to ambient temperature, stirred for 15 min, and then the cloudy mixture was cooled back to -78°C . 1,4-pentadien-3-ol (0.097 mL, 1.0 mmol, 1.0 eq) was added, and the mixture was stirred for 1 hr. Subsequently the mixture was warmed to ambient temperature and stirred for 2 hr. Meanwhile, to a flame dried 2-neck round bottom flask under argon was added magnesium

¹¹ Sattely, E. S.; Cortez, G. A.; Moebius, D. C.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 8526-8533.

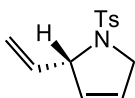
turnings (204 mg, 8.4 mmol) and a small crystal of I₂ (5 mg). The flask was heated with a heat gun until a pink glow was observed, and then allowed to cool to ambient temperature. THF (10 mL) was then added, and a reflux condenser was attached. 4-bromobut-1-ene (0.812 mL, 8.0 mmol) was added, and the mixture began to heat spontaneously. The reaction achieved reflux without external heat for 15 minutes, at which point the magnesium was mostly consumed. The reaction was allowed to cool to room temperature. The Grignard solution was then added dropwise to the flask containing the silane in a 0 °C ice bath. The clear yellow solution was stirred for 2 hr, and then quenched with sat'd NH₄Cl (15 mL). The mixture was extracted with diethyl ether (2 x 30 mL). The combined organic extracts were washed with brine (20 mL), dried with MgSO₄, and concentrated *in vacuo*. The product was isolated by column chromatography (1-4% ethyl acetate / hexanes) to give a clear oil (207 mg, 65%) containing a trace impurity of the bis(homoallyl)silane byproduct. Analytically pure material can be obtained by preparatory TLC (1.5 % ethyl acetate / hexanes, run twice).

¹H NMR (500 MHz, CDCl₃) δ 7.62-7.59 (m, 4H), 7.44-7.40 (m, 2H), 7.39-7.35 (m, 4H), 5.89 (ddt, *J* = 17.1, 10.2, 6.2 Hz, 1H), 5.83 (ddd, *J* = 17.1, 10.3, 5.8 Hz, 2H), 5.18 (dt, *J* = 17.2, 1.5 Hz, 2H), 5.06 (dt, *J* = 10.3, 1.4 Hz, 2H), 4.99 (dq, *J* = 17.1, 1.7 Hz, 2H), 4.89 (ddt, *J* = 10.1, 1.9, 1.4 Hz, 2H), 4.67 (tp, *J* = 5.7, 1.4 Hz, 2H), 2.16 (dddd, *J* = 12.3, 6.1, 3.1, 1.5 Hz, 2H), 1.30 – 1.25 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 141.3, 139.8, 135.3, 135.0, 130.0, 127.9, 114.7, 113.0, 75.6, 27.2, 13.8. HRMS (EI+) *m/z* calculated for [C₂₁H₂₄OSi]⁺: 320.1596; found: 320.1608.

General Procedure for ARCM

In a glovebox, triene **13** (27.7 mg, 0.1 mmol) was dissolved in 35 μL THF. To this solution was added 165 μL of a stock solution (0.03 M in THF) of catalyst **5**. The reaction vial was capped and stirred for 24 h and then quenched with an excess of ethyl vinyl ether outside of the glovebox. The reaction mixture was concentrated and conversion was determined by 500 MHz ^1H NMR. The crude was subjected to flash chromatography or preparative TLC to afford the desired ARCM product (**14**, 22.6 mg, 95% yield, 54% ee). Pure products were submitted to analytical SFC to determine ee.

Characterization data for ARCM products



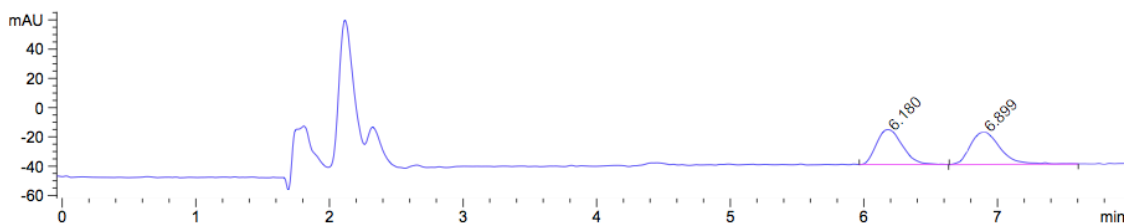
14.

95% yield

$[\alpha]_{\text{D}}^{25} = +113^{\circ}$ ($c = 1.09$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, $J = 8.2$ Hz, 2H), 7.31 – 7.28 (m, 2H), 5.79 (ddd, $J = 17.1, 10.1, 7.0$ Hz, 1H), 5.67 (dq, $J = 6.1, 2.0$ Hz, 1H), 5.53 (dq, $J = 6.3, 2.2$ Hz, 1H), 5.28 (dt, $J = 17.1, 1.1$ Hz, 1H), 5.13 (dt, $J = 10.1, 1.1$ Hz, 1H), 4.92 – 4.87 (m, 1H), 4.17 – 4.14 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.5, 137.7, 135.6, 129.8, 129.2, 127.6, 125.3, 116.3, 69.1, 55.4, 21.6. HRMS (FAB+) m/z calculated for $[\text{C}_{13}\text{H}_{15}\text{NSO}_2+\text{H}]^+$: 250.0902; found: 250.0901.

Separation conditions: AD-H, 10% IPA, 2.5 mL/min, 54% ee

Racemate:

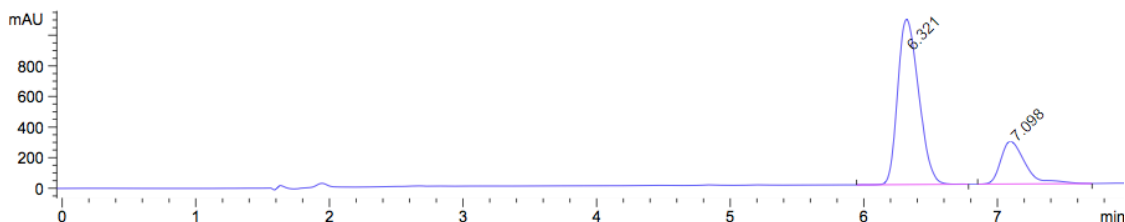


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.180	BB	0.2099	323.44040	23.90183	48.4021
2	6.899	BB	0.2410	344.79550	22.22880	51.5979

Totals : 668.23590 46.13063

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

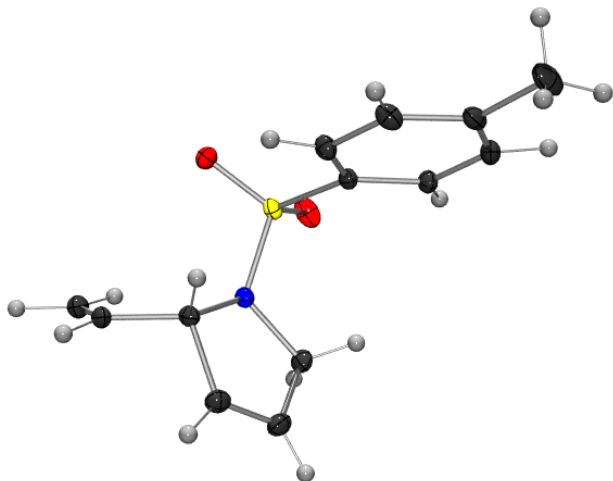
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.321	BB	0.1756	1.18006e4	1078.98083	76.8463
2	7.098	BB	0.1966	3555.49561	279.14224	23.1537

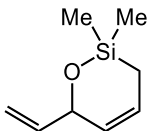
Totals : 1.53561e4 1358.12308

Determination of absolute configuration:

A racemic sample was synthesized according to the general procedure using triene **5** (83.1 mg, 0.3 mmol, 1.0 eq), rac-**4** (0.375 μ L, 0.04M in THF, 0.015 mmol, 0.05 eq) and THF (225 μ L). Racemic **6** was isolated by column chromatography (10-20% Ethyl acetate / hexanes) to give a crystalline white solid (64 mg, 86%).

This material was resolved by chiral prep-HPLC (Chiral Technologies AD-H SFC column, 21x250 mm, 5 μ m particle, 20% IPA / Hexanes, 10 ml/min, 30 injections of 1 μ g in 50 μ L IPA, retention time = 18 min, 20 min). The combined fractions of the faster eluting enantiomer (F1) were concentrated to afford a >99% ee sample (15 mg), which was then re-purified by preparative TLC (20% Ethyl acetate / hexanes) to remove a faint yellow color. A single crystal suitable for X-ray diffraction was grown by slow diffusion of pentane into a solution of F1 in diethyl ether. X-ray crystallographic analysis indicated that the absolute configuration of F1 is (*S*). The Flack and van Hooft parameters were 0.026(7) and 0.021(7) respectively.

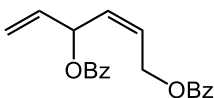




16.

Due to volatility of the product, the yield was determined by NMR.

In a glovebox, 167 μL of a stock solution of catalyst **5** (0.03M in THF) was concentrated. A solution of triene **15** in 200 μL d_8 -THF was then added, and the capped vial was stirred at room temperature for 24 hr. Mesitylene (0.1 mmol, 13.9 μL , 1 equiv) was then added as an internal standard, and the mixture was diluted to 700 μL with d_8 -THF. The yield of product **16** was then determined by integration of the ^1H NMR spectrum to be 65%. ^1H NMR (500 MHz, THF- d_8) δ 5.88-5.82 (m, 2H), 5.57 (ddt, $J = 10.8, 2.9, 2.0$ Hz, 1H), 5.20 (dt, $J = 17.0, 1.8$ Hz, 1H), 4.98 (dt, $J = 10.3, 1.8$ Hz, 1H), 4.87-4.81 (m, 1H), 1.26 (dt, $J = 4.9, 2.4$ Hz, 1H), 1.23 (ddd, $J = 5.6, 2.9, 1.8$ Hz, 1H), 0.16 (d, $J = 5.2$ Hz, 6H). ^{13}C NMR (125 MHz, THF- d_8) δ 141.3, 132.2, 124.6, 113.1, 74.4, 12.8, 0.5, -0.5.

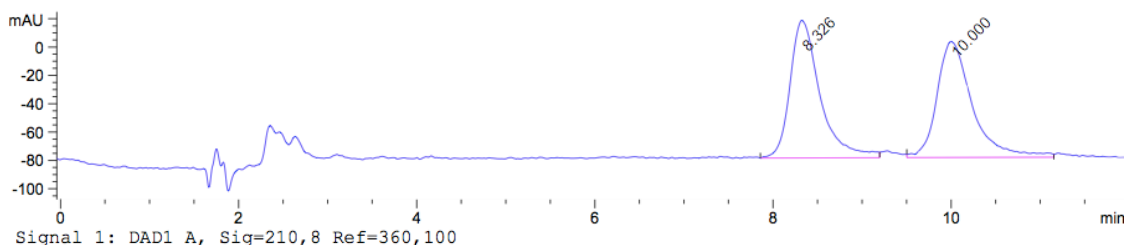


Product **16** was converted to the derivative shown above by treatment with Tamao-Fleming conditions (10 equiv 30% H_2O_2 , 5 equiv KF, 2.5 equiv KHCO_3 , 1:1 THF/MeOH, 23 $^\circ\text{C}$, 13 hr) and subsequent standard benzylation conditions (10 equiv BzCl, 10 equiv NEt_3 , 1 equiv DMAP, CH_2Cl_2 , 0 $^\circ\text{C}$, 3 hr) to afford a product amenable to ee determination.

$[\alpha]_D^{25} = -6.6^\circ$ ($c = 0.07$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.09 – 8.01 (m, 4H), 7.59 – 7.51 (m, 2H), 7.50 – 7.39 (m, 4H), 6.31 (ddq, $J = 8.2, 5.6, 1.4$ Hz, 1H), 6.00 (ddd, $J = 17.3, 10.5, 5.5$ Hz, 1H), 5.94 (dtd, $J = 11.1, 6.6, 1.1$ Hz, 1H), 5.77 (ddt, $J = 11.0, 8.7, 1.5$ Hz, 1H), 5.44 (dt, $J = 17.2, 1.3$ Hz, 1H), 5.29 (dt, $J = 10.5, 1.2$ Hz, 1H), 5.11 (ddd, $J = 13.4, 6.5, 1.6$ Hz, 1H), 5.04 (ddd, $J = 13.3, 6.7, 1.4$ Hz, 1H). HRMS (MM) m/z calculated for $[\text{C}_{13}\text{H}_{13}\text{O}_2]^+$ (M-OBz): 201.0916; found: 201.0905.

Separation conditions: OJ-H, 5% IPA, 2.5 mL/min. 69% ee

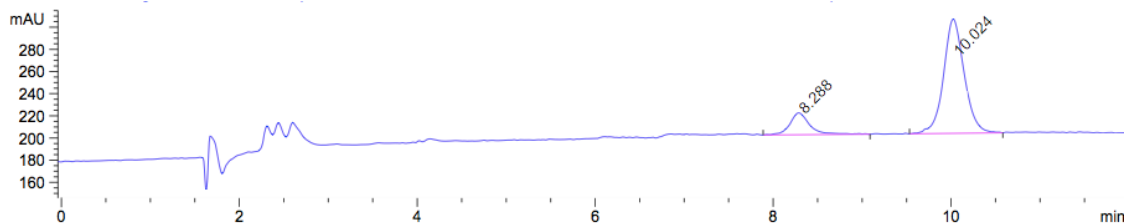
Racemate:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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2	10.000	VV	0.4070	2262.84082	81.72294	49.8664

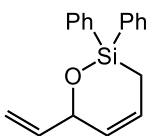
Totals : 4537.80249 178.86124

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.288	BV	0.2330	312.42465	19.70367	15.7730
2	10.024	BB	0.2447	1668.33032	103.14931	84.2270
Totals :				1980.75497	122.85299	



18.

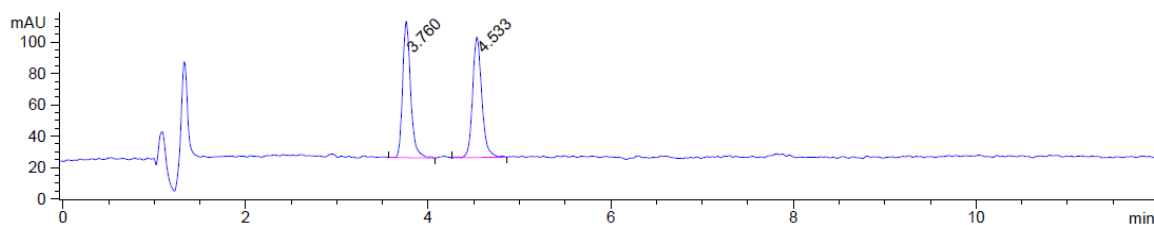
29% yield

$[\alpha]_D^{25} = -66.3^\circ$ ($c = 0.37$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.65-7.60 (m, 4H), 7.45-7.35 (m, 6H), 6.03 (dddd, $J = 10.6, 5.9, 4.6, 2.0$ Hz, 1H), 5.94 (ddd, $J = 17.0, 10.2, 5.9$ Hz, 1H), 5.68 (dddd, $J = 10.8, 3.0, 2.2, 1.6$ Hz, 1H), 5.32 (dt, $J = 17.0, 1.5$ Hz, 1H), 5.10 (dt, $J = 10.2, 1.5$ Hz, 1H), 5.10-5.06 (m, 1H), 1.82-1.78 (m, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 139.6, 135.8, 135.7, 134.6, 134.5, 131.8, 130.2, 130.2, 128.1, 128.0, 124.1, 114.2, 74.4, 10.3.

HRMS (FAB+) m/z calculated for $[\text{C}_{18}\text{H}_{17}\text{OSi}]^+$ ($\text{M}+\text{H}^+-\text{H}_2$): 277.1049; found: 277.1054.

Separation conditions: AD-H, 7% IPA, 2.5 mL/min. 67% ee

Racemate:

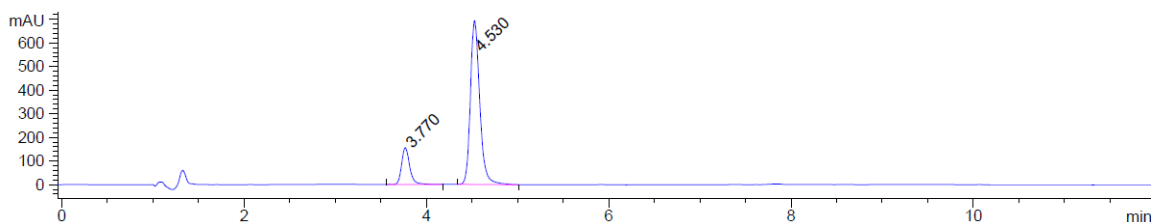


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.760	BB	0.0917	534.37006	86.91824	49.6471
2	4.533	BB	0.1104	541.96741	76.74262	50.3529

Totals : 1076.33746 163.66087

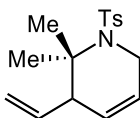
Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.770	BB	0.0965	965.57025	155.38515	16.3200
2	4.530	BB	0.1075	4950.90234	691.71661	83.6800

Totals : 5916.47260 847.10176



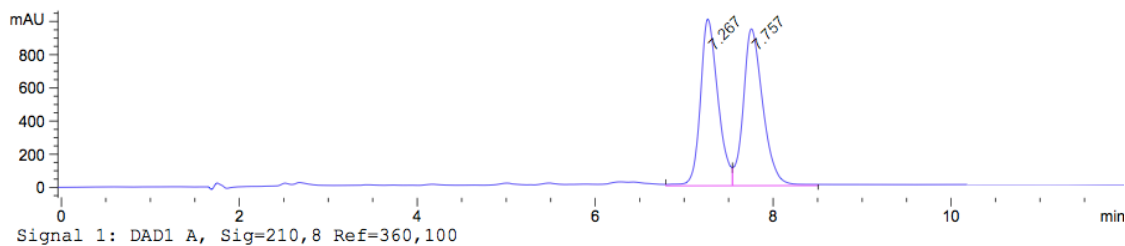
22.

90% yield

$[\alpha]_D^{25} = -107^\circ$ ($c = 0.92$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 5.77 – 5.71 (m, 1H), 5.62 (dt, $J = 17.2, 9.6$ Hz, 1H), 5.58 – 5.52 (m, 1H), 5.06 – 5.03 (m, 1H), 5.03 – 4.99 (m, 1H), 4.17 (dd, $J = 18.0, 2.7$ Hz, 1H), 4.12 – 4.03 (m, 1H), 2.53 (ddd, $J = 8.9, 4.2, 2.1$ Hz, 1H), 2.43 (s, 3H), 1.24 (s, 3H), 1.21 (s, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 143.03, 140.18, 137.30, 129.58, 127.59, 127.24, 122.95, 117.23, 58.46, 52.73, 44.73, 24.86, 24.53, 21.63. HRMS (FAB+) calculated for $\text{C}_{16}\text{H}_{22}\text{NO}_2\text{S}$ $[\text{M}+\text{H}]$: 292.1371; found 292.1366.

Separation conditions: OJ-H, 5% IPA, 2.5 mL/min. 57% ee

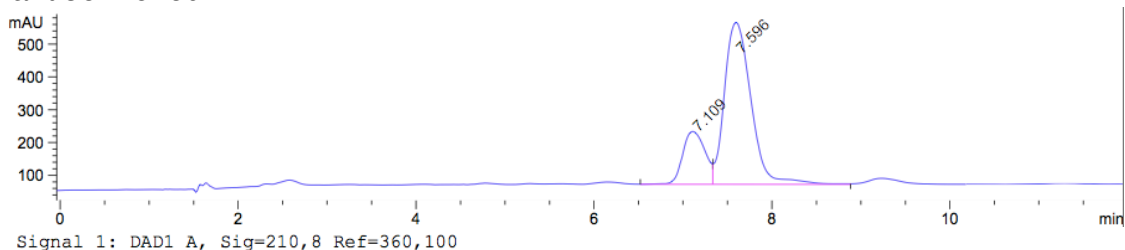
Racemate:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.267	VV	0.2086	1.38281e4	1004.54449	48.8340
2	7.757	VV	0.2309	1.44885e4	944.94611	51.1660

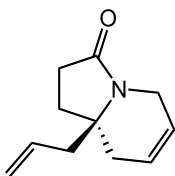
Totals : 2.83166e4 1949.49060

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.109	BV	0.2805	2822.48462	161.03967	21.5419
2	7.596	VV	0.3311	1.02798e4	493.33197	78.4581

Totals : 1.31023e4 654.37164



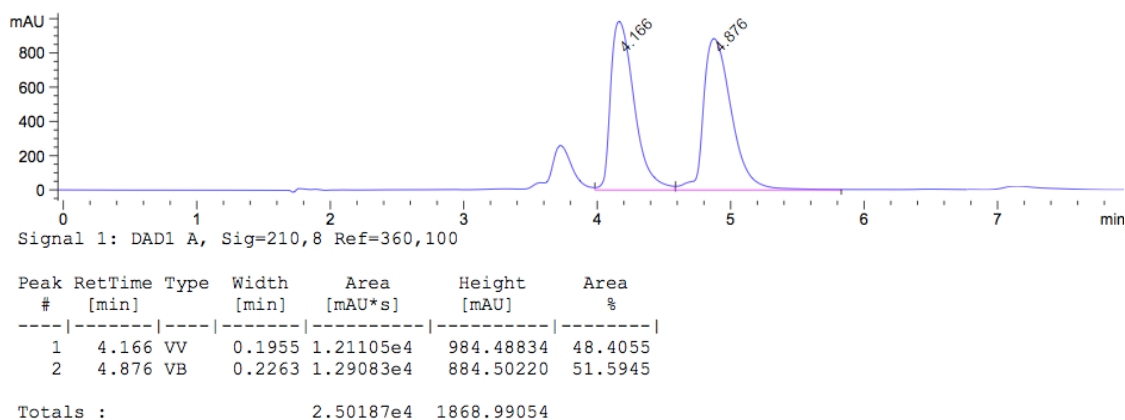
26.

72% yield. Spectral characterization of **26** matches a previous report of its synthesis; material produced by **5** has the opposite sign of the optical rotation, which indicates that the enantiomer (absolute configuration shown above) is

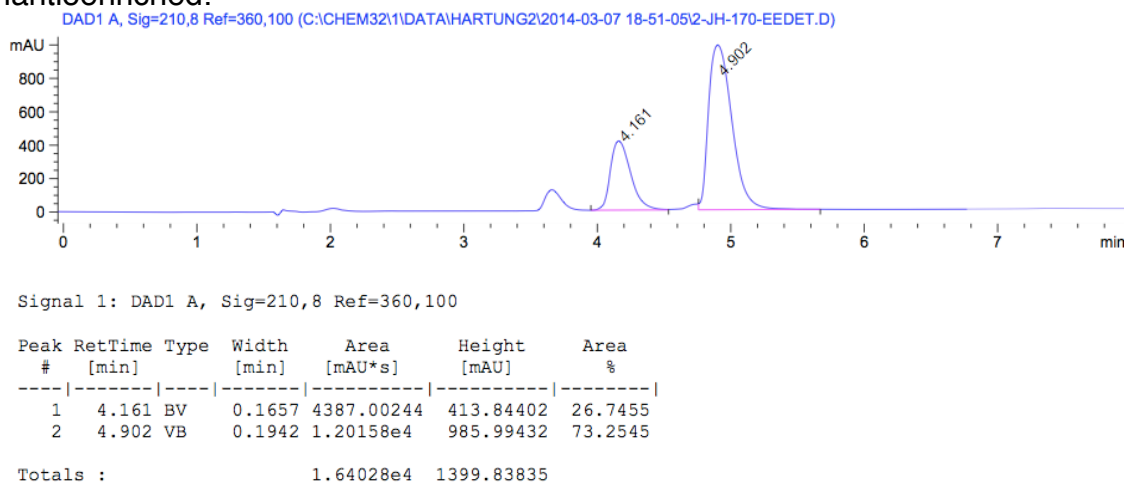
formed in preference.¹² Lit. $[\alpha]_D^{25} = +57.7^\circ$ (88% ee, $c = 1$, CHCl_3); $[\alpha]_D^{25} = -28.4^\circ$ (47% ee, $c = 1.27$, CHCl_3).

Separation conditions: AD-H, 10% IPA, 2.5 mL/min. 47% ee

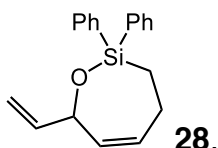
Racemate:



Enantioenriched:



¹² Sattely, E. S.; Cortez, G. A.; Moebius, D. C.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 8526-8533.



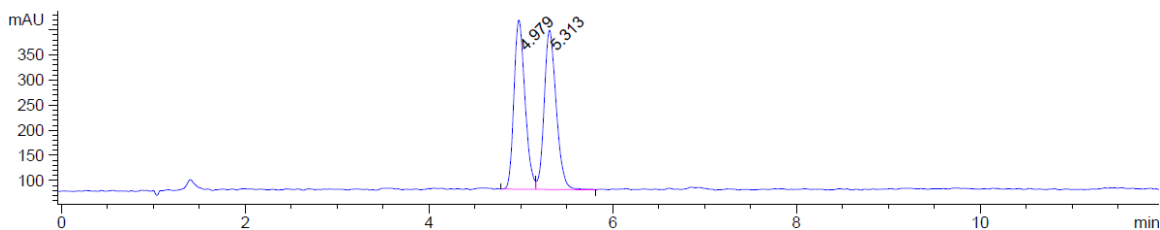
Following the general procedure for ARCM (capped vial), diene **28** was isolated in 61% yield, 0% ee. In order to prevent reversibility caused by the presence of ethylene, the procedure was modified:

In a glovebox, triene **27** (15 mg, 0.047 mmol, 1 equiv) was dissolved in 67 μ L THF. To this solution was added 33 μ L of a stock solution (0.03 M in THF) of catalyst **5**. The reaction vial was left uncapped and stirred for 24 h. The reaction was then diluted with 500 μ L ether and quenched with an excess of ethyl vinyl ether outside of the glovebox. The mixture was purified as above to yield the desired product (**28**, 7.0 mg, 51% yield, 37% ee).

$[\alpha]_D^{25} = +23^\circ$ (c = 0.51, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.67-7.57 (m, 4H), 7.45-7.32 (m, 6H), 6.02 (ddd, J = 17.1, 10.3, 5.2 Hz, 1H), 5.96 (dtd, J = 11.3, 6.9, 2.1 Hz, 1H), 5.66 (ddt, J = 11.3, 4.9, 1.2 Hz, 1H), 5.41 (dt, J = 16.9, 1.6 Hz, 1H), 5.15 (dt, J = 10.2, 1.7 Hz, 1H), 5.16-5.12 (m, 1H), 2.52 (qt, J = 6.6, 1.1 Hz, 2H), 1.55-1.48 (m, 1H), 1.31 (ddd, J = 15.0, 7.3, 5.7 Hz, 1H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 140.1, 136.4, 135.8, 134.6, 134.4, 134.1, 133.1, 130.0, 129.9, 128.2, 127.9, 114.0, 71.2, 22.2, 12.5. HRMS (EI+) m/z calculated for $[\text{C}_{19}\text{H}_{20}\text{OSi}]^+$: 292.1284; found: 292.1286.

Separation conditions: AD-H, 2% IPA, 2.5 mL/min, 37% ee.

Racemic:

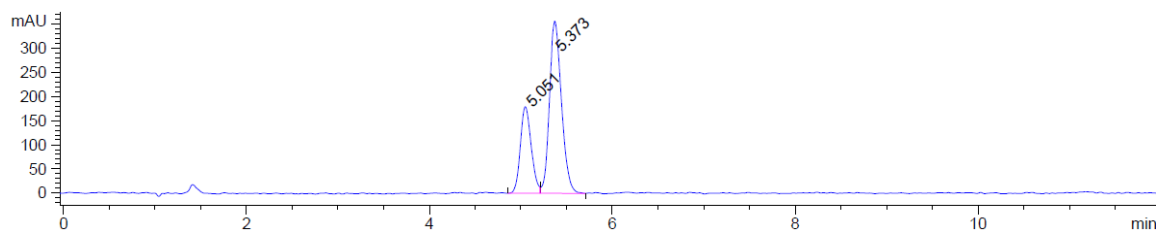


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.979	BV	0.1294	2814.38550	337.09122	49.3308
2	5.313	VB	0.1383	2890.73926	317.17126	50.6692

Totals : 5705.12476 654.26248

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.051	BV	0.1295	1486.54932	177.90808	31.3495
2	5.373	VB	0.1391	3255.30908	354.55859	68.6505

Totals : 4741.85840 532.46667

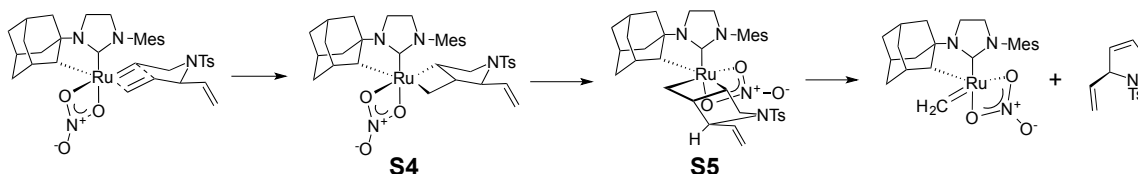
Tentative model for ARCM enantioinduction

Based on previous computational studies of terminal olefin homodimerization with catalyst *rac*-5,¹³ we propose a side-bound ruthenacyclobutane mechanism.

The non-reacting vinyl group is located on a pseudo-equatorial position of an

¹³ Liu, P.; Xu, X.; Dong, X.; Keitz, B. K.; Herbert, M. B.; Grubbs, R. H.; Houk, K. N. *J. Am. Chem. Soc.* **2012**, *134*, 1464–1467.

envelope-type conformation in **S4**. Isomerization of the ruthenacyclobutane leads to **S5**, followed by retro-[2+2] to release the product.



Asymmetric Cross Metathesis Procedure

In a glovebox, TBS-protected alcohol **29** (20 mg, 0.1 mmol) and *cis*-1,4-diacetoxy-2-butene (86 mg, 0.5 mmol) were added to a glass vial and the mixture dissolved in 0.3 mL THF. Catalyst **5** was added to the mixture as a stock solution (5 mol%, 0.005 mmol, 165 μ L of a 0.03 M solution) and the reaction heated to 35°C for 18 h while uncapped. The reaction was removed from the glovebox, quenched with ethyl vinyl ether, and concentrated. Flash chromatography afforded 9.5 mg *Z*-**31** (0.035 mmol, 35% yield, 93% *Z*). TBS deprotection (TBAF, THF, 23 °C, 12 hr), and acylation (5 equiv (*S*)-MTPA-Cl, excess NEt₃, 1 equiv DMAP, CH₂Cl₂, 23 °C) enabled determination of ee (50%) and absolute configuration (*R*).

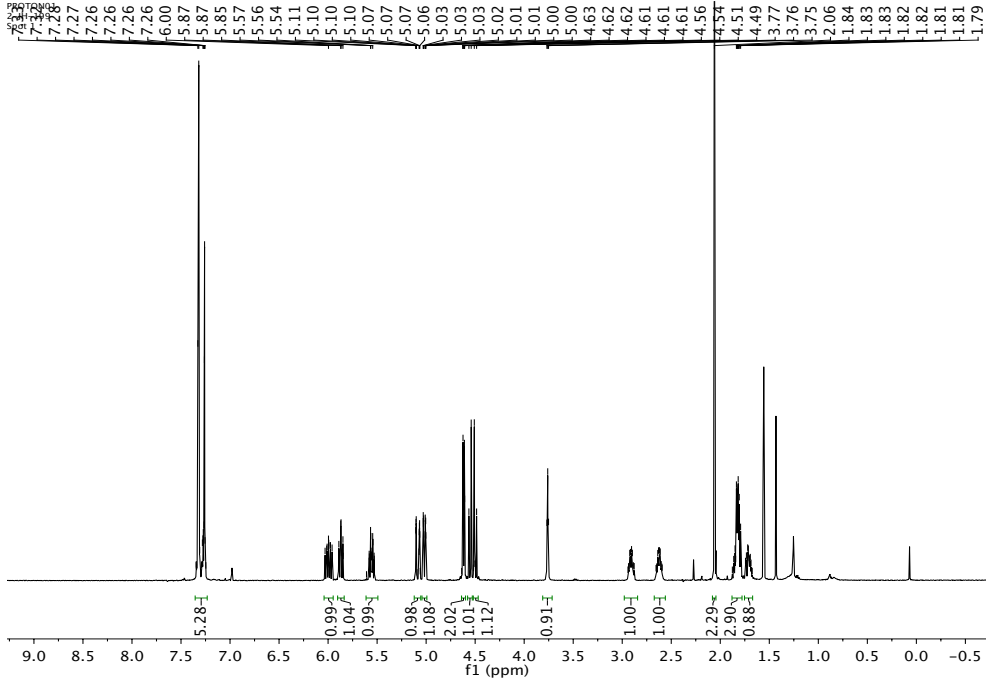
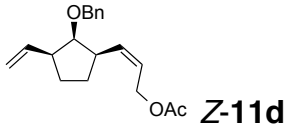
¹H NMR (500 MHz, CDCl₃) δ 5.78 (ddd, *J* = 17.2, 10.3, 5.1 Hz, 1H), 5.61 – 5.48 (m, 2H), 5.23 (dt, *J* = 17.1, 1.6 Hz, 1H), 5.06 (dt, *J* = 10.3, 1.6 Hz, 1H), 4.93 (ddt, *J* = 6.7, 5.1, 1.5 Hz, 1H), 4.73 – 4.66 (m, 1H), 4.64 – 4.58 (m, 1H), 2.06 (s, 3H), 0.89 (s, 8H), 0.07 (s, 3H), 0.06 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.72, 136.75, 123.25, 114.00, 70.23, 60.54, 25.98, 20.99, 18.41, -4.55.

Table S1. Optimization of ACM Reaction of 29 with rac-5^a

Equiv. 29	Cross Partner	Equiv. of Cross Partner	Cat. Loading (%)	mL THF	Yield Z-31(%) ^b
1	allyl acetate	5	5	0.3	15
5	allyl acetate	1	5	0.3	35
1	<i>cis</i> -1,4-diacetoxy-2-butene	5	5	0.3	35
1	<i>cis</i> -1,4-diacetoxy-2-butene	5	2.5	0.3	35
1	<i>cis</i> -1,4-diacetoxy-2-butene	5	1	0.3	6
1	<i>cis</i> -1,4-diacetoxy-2-butene	5	5	0.2	30
1	<i>cis</i> -1,4-diacetoxy-2-butene	5	5	0.1	30

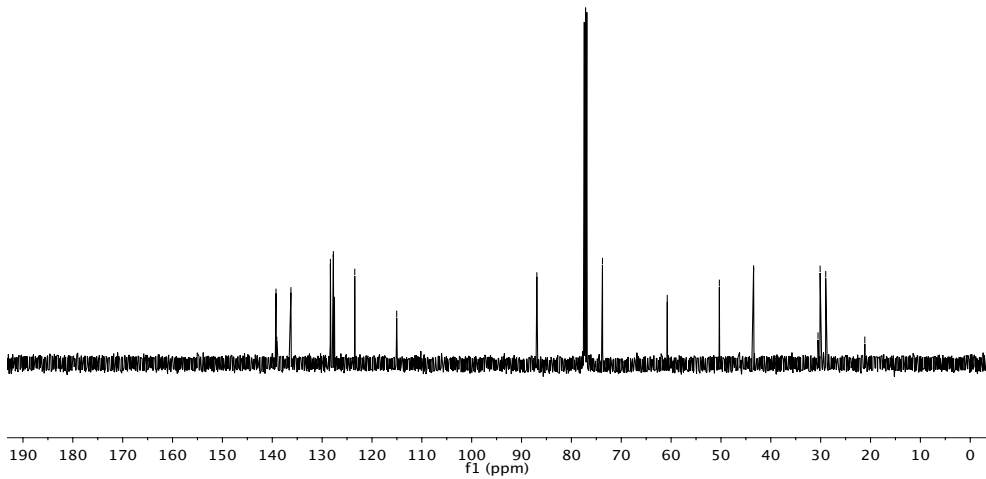
^a All reactions conducted with 0.1 mmol of limiting reagent at 35°C for 18 h in an open vial under inert atmosphere (glove box); ^b Yield with respect to limiting reactant; determined by integration relative to an internal standard (mesitylene) in the ¹H NMR of the crude reaction mixture.

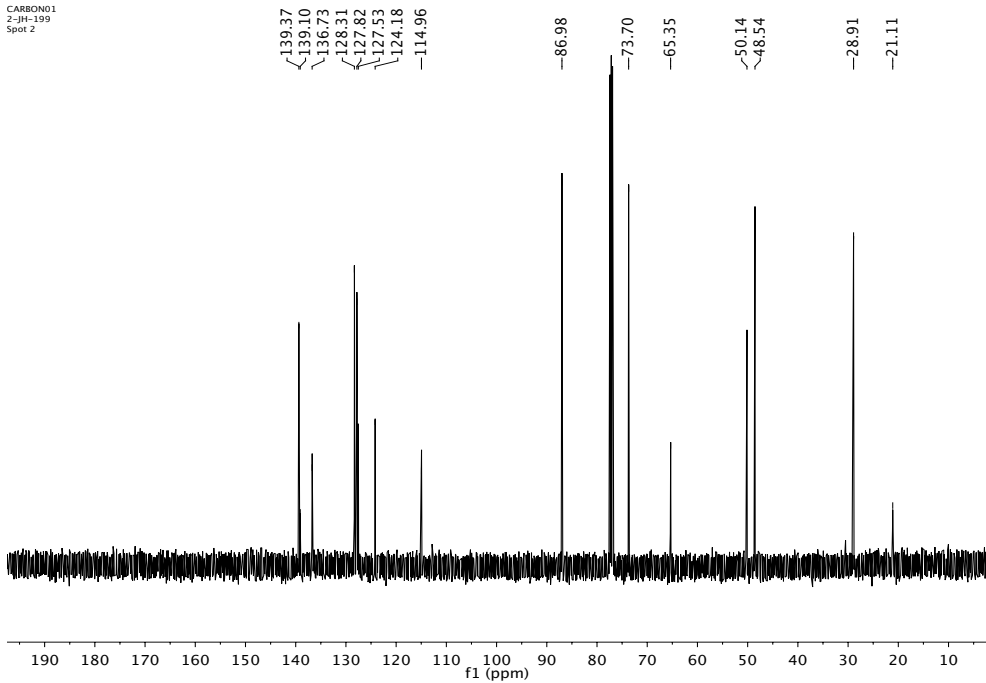
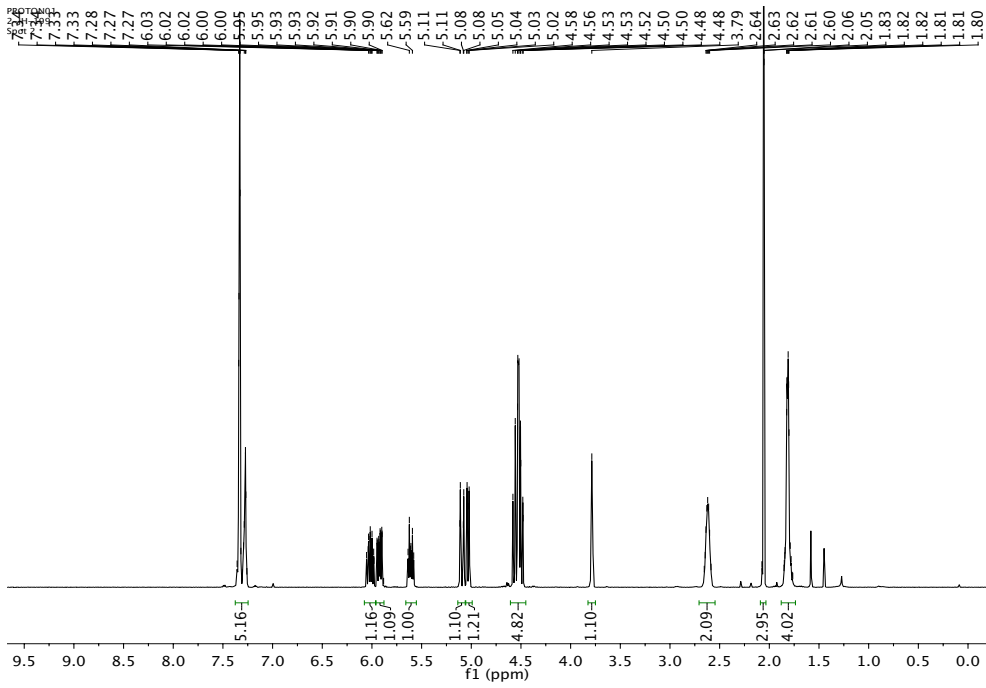
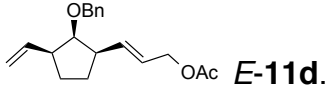
NMR Spectra

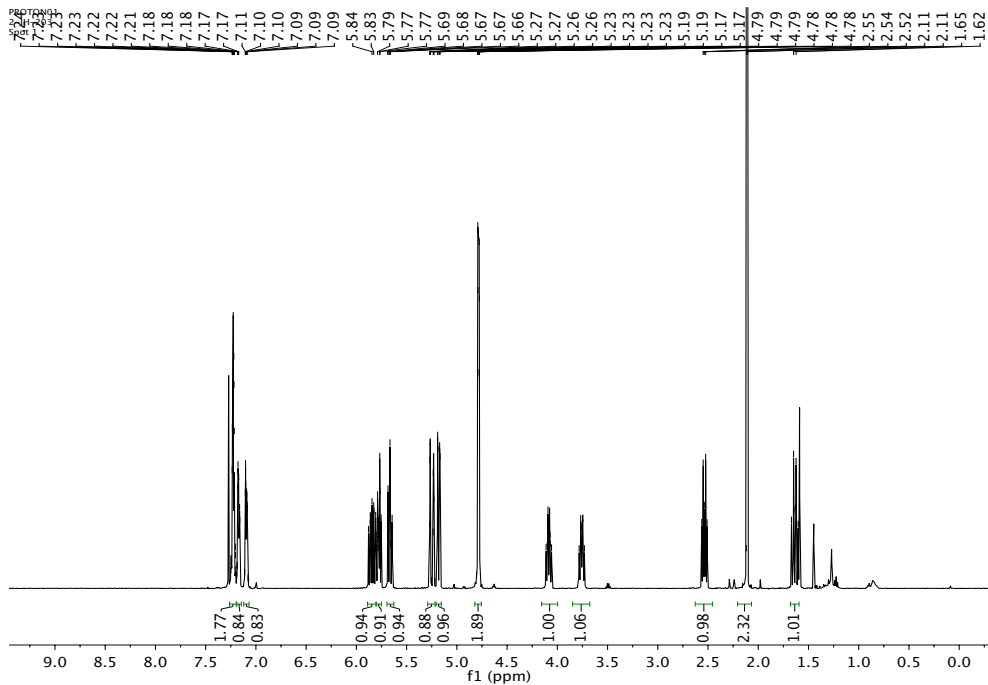
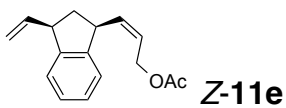


CARBON01
2-JH-199
Spot 1

139.25
139.09
136.26
128.34
127.74
127.52
123.45
115.04
-86.93
-73.76
-60.77
-50.32
-43.45
30.53
30.11
28.99
-21.14

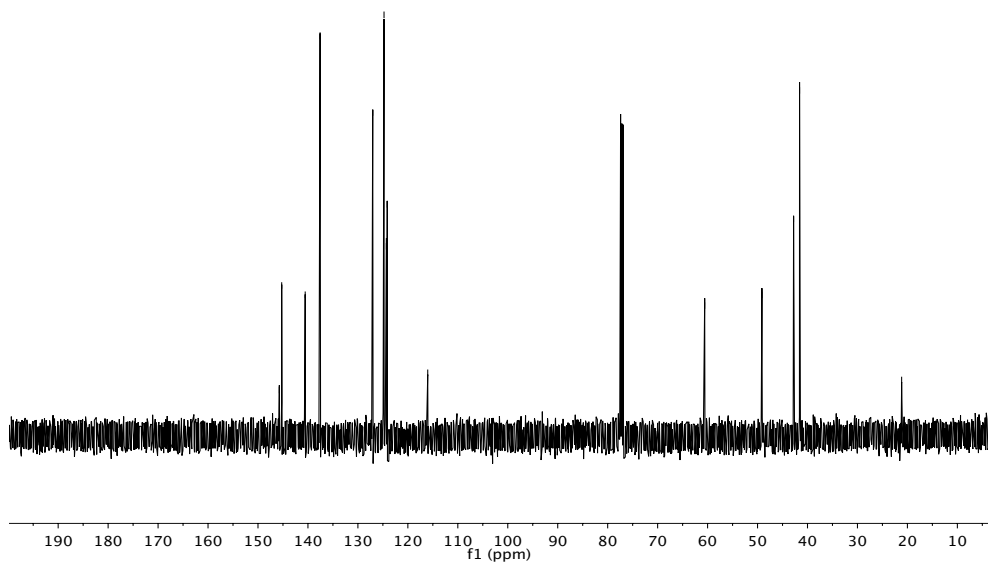


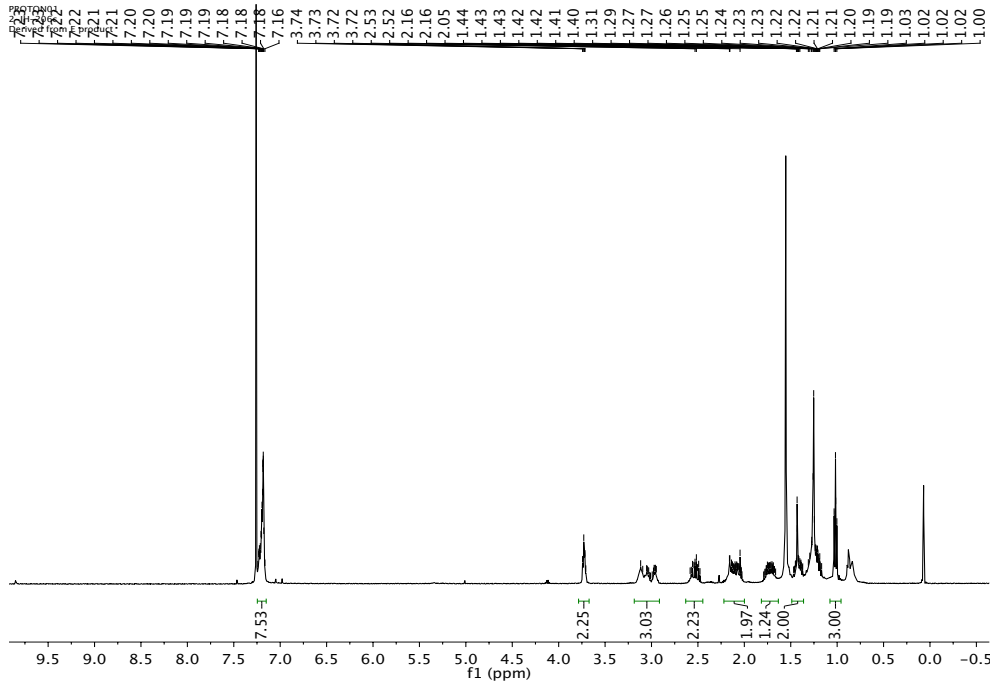
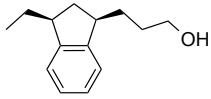




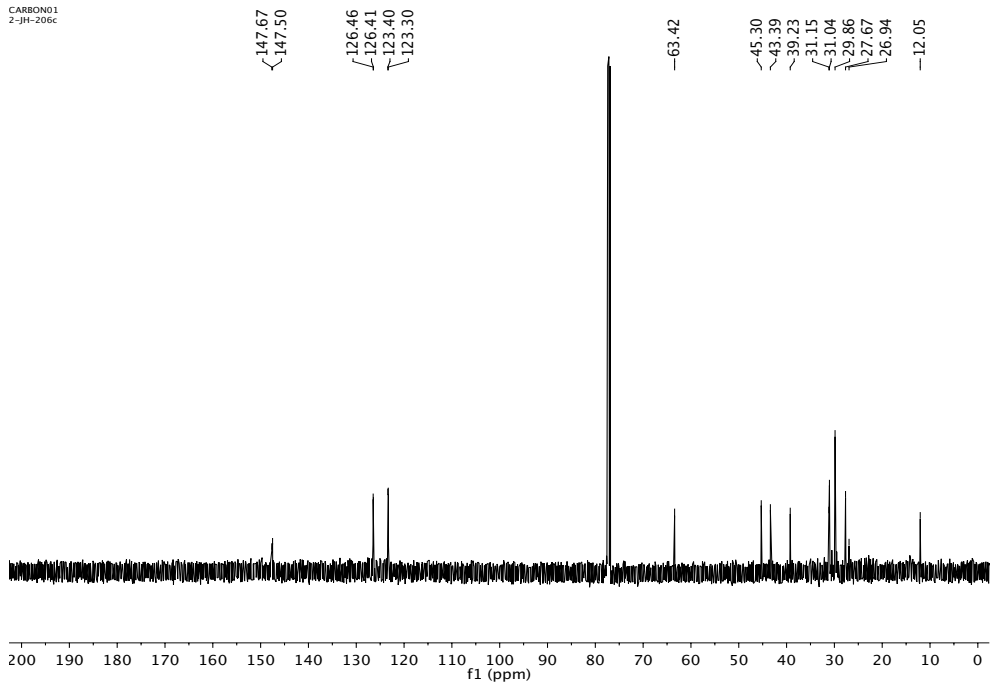
CARBON01
 2-JH-203
 Spot 1

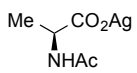
145.72
 145.25
 140.55
 137.57
 127.04
 124.77
 124.30
 124.32
 116.02
 60.59
 49.13
 42.79
 41.59
 21.16



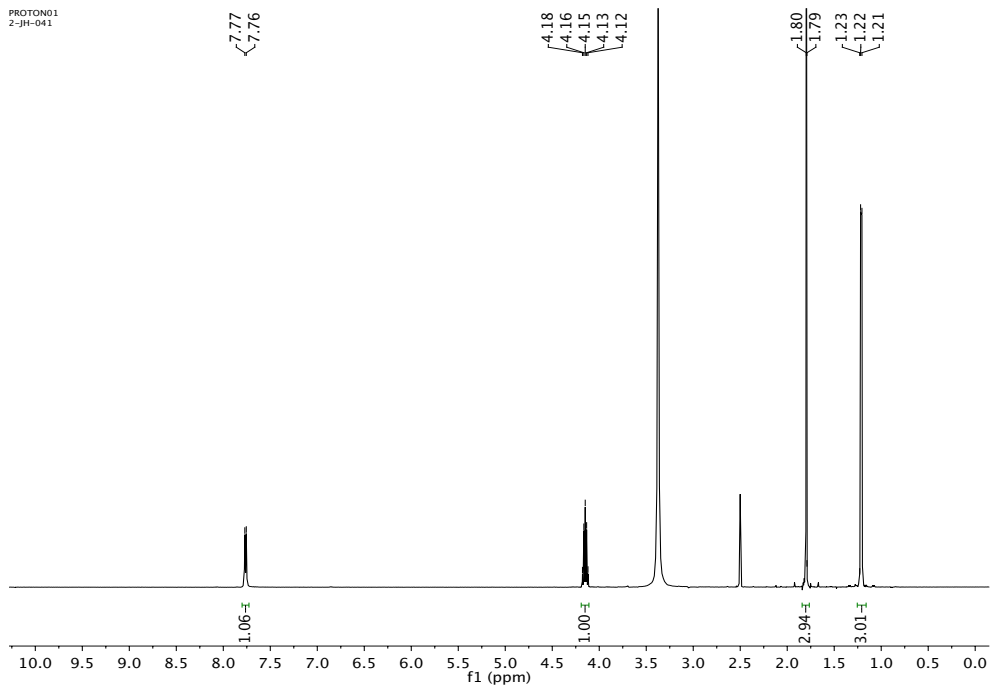


CARBON1
2-JH-206c

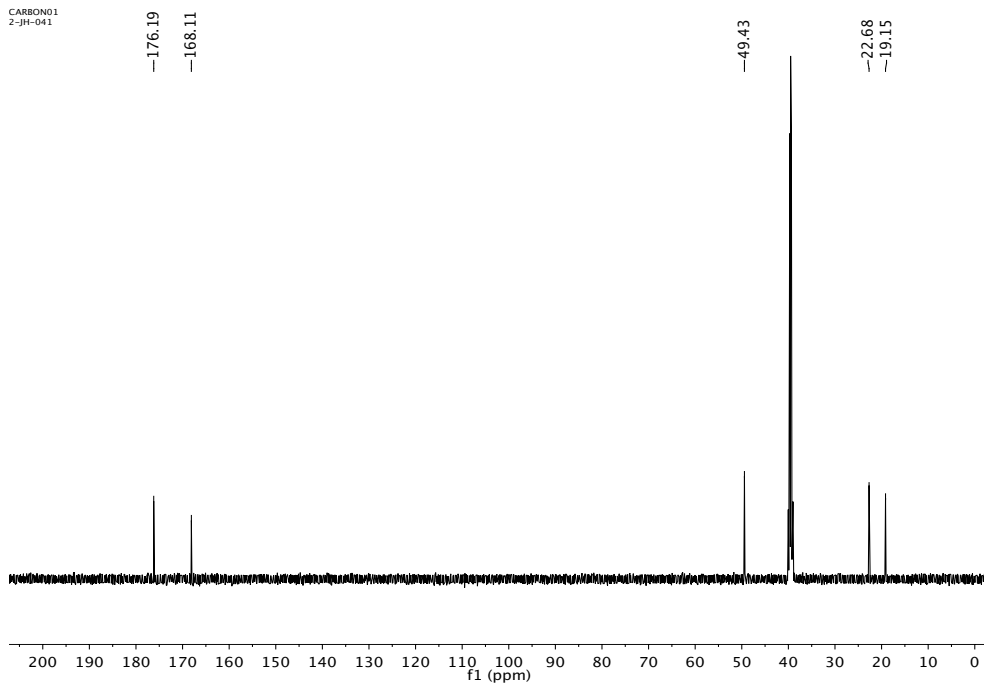


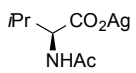


PROTON01
2-JH-041

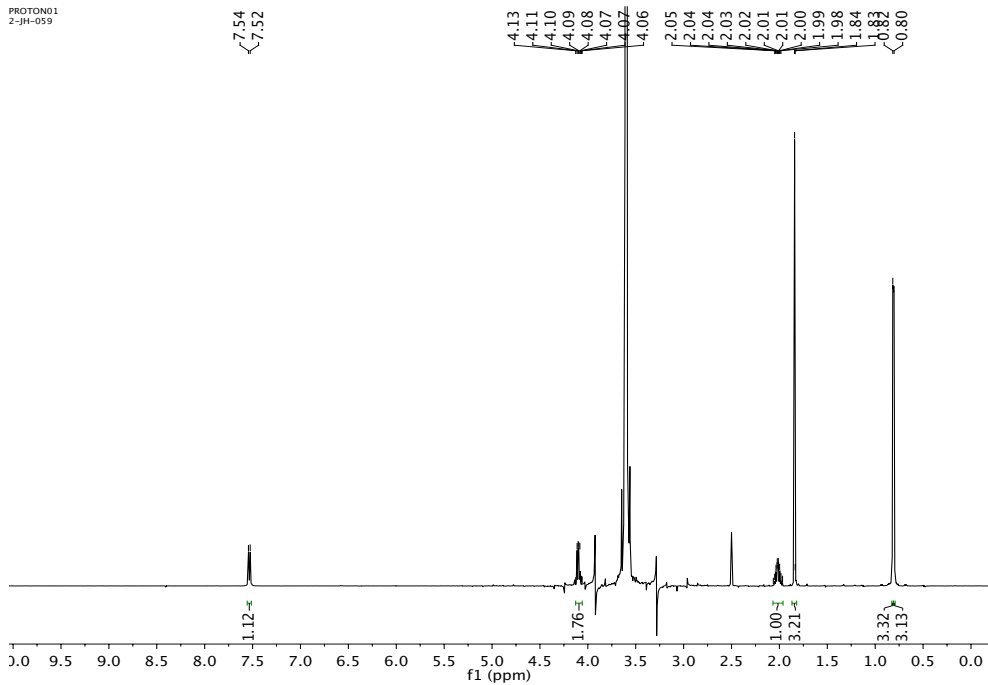


CARBON01
2-JH-041

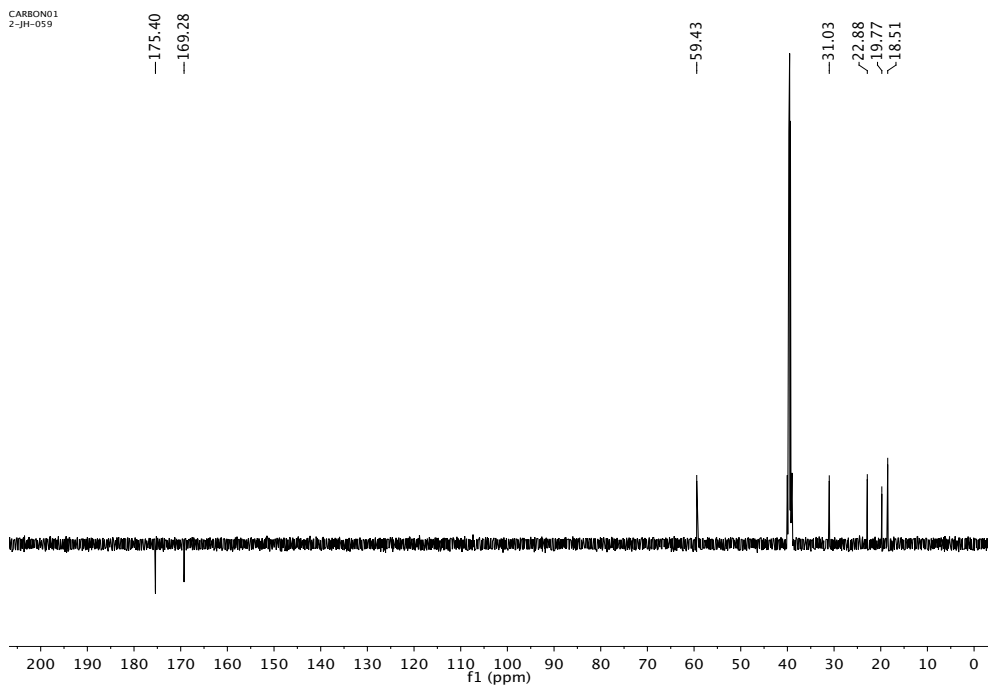


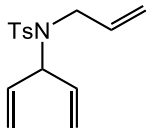


PROTON01
2-JH-059

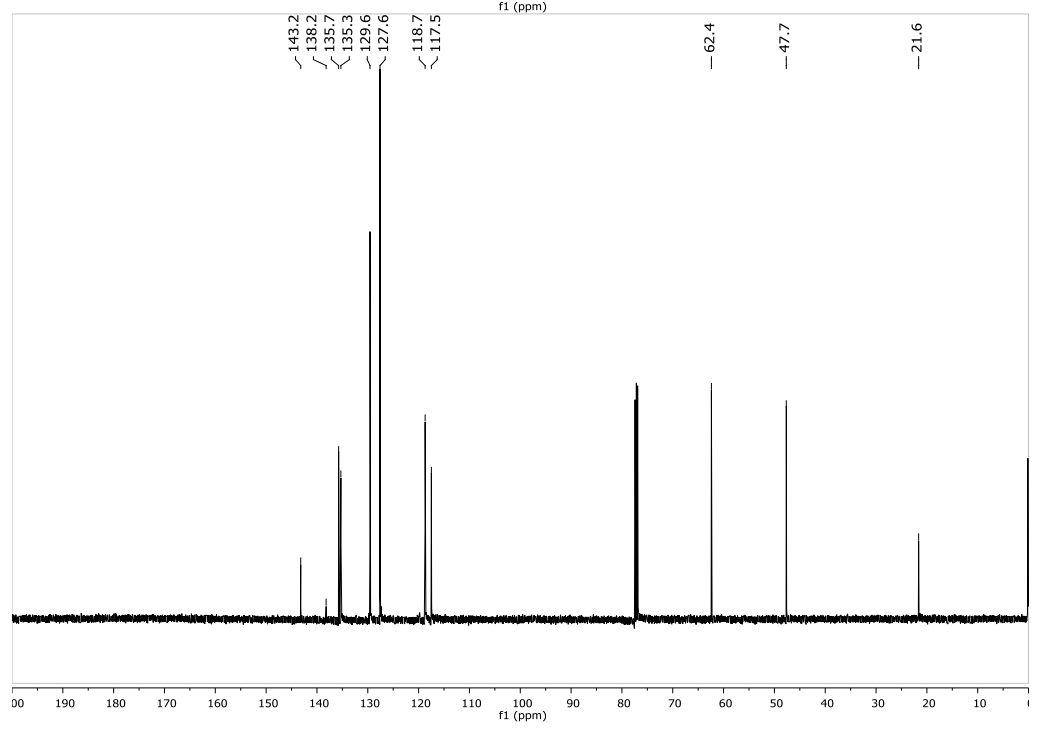
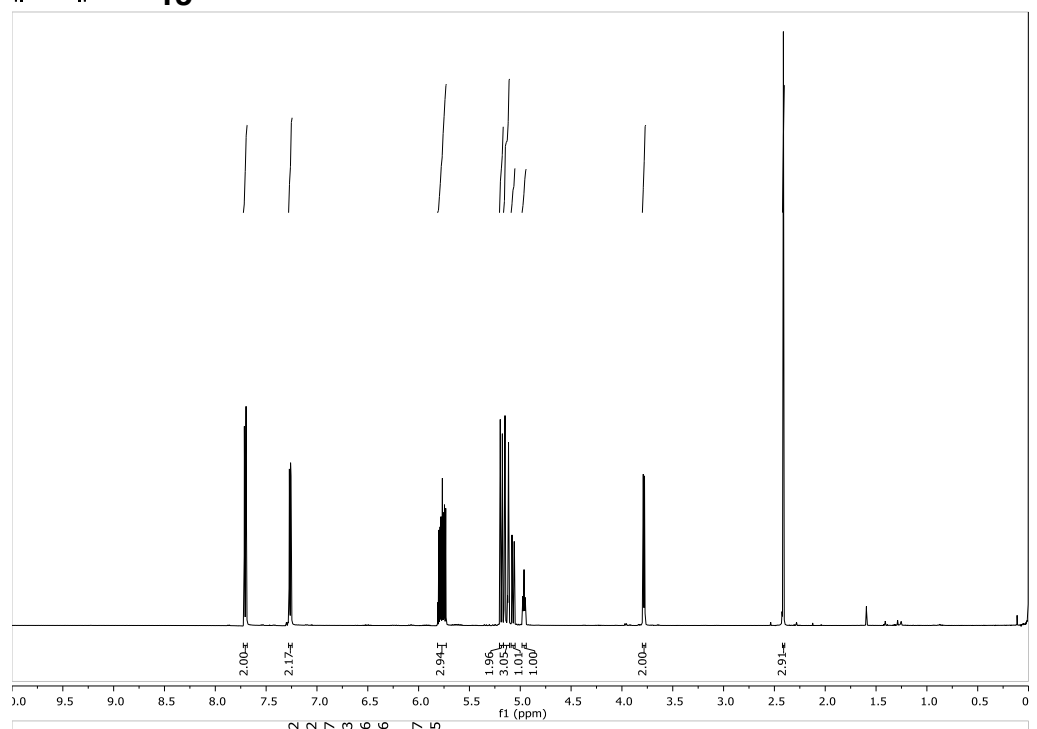


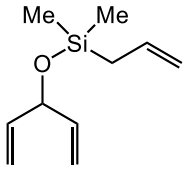
CARBON01
2-JH-059



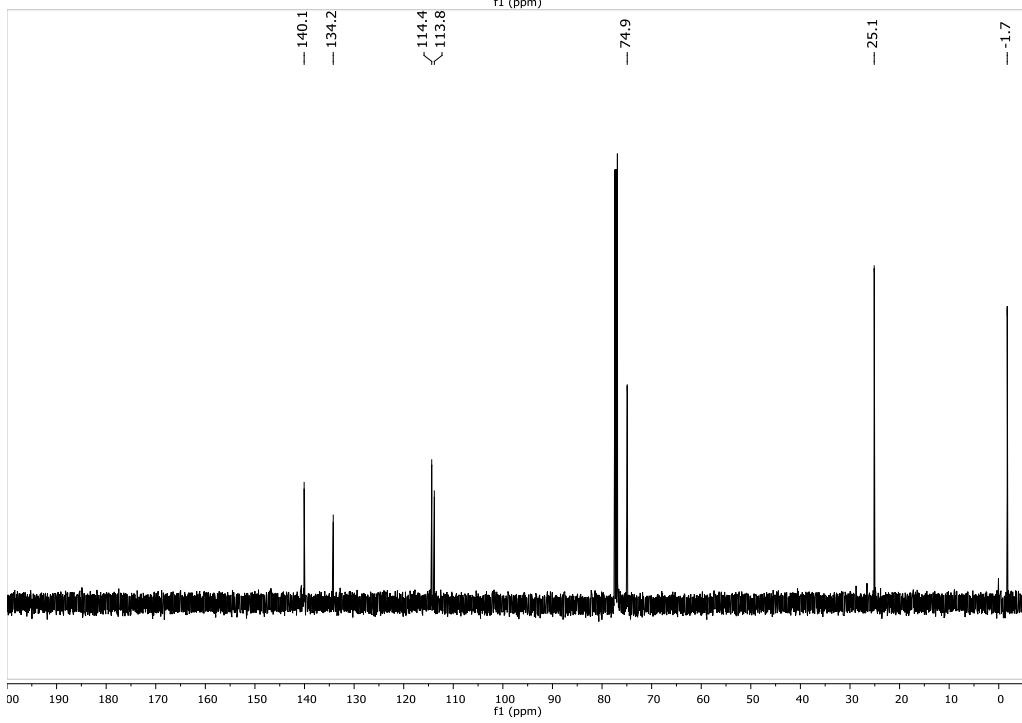
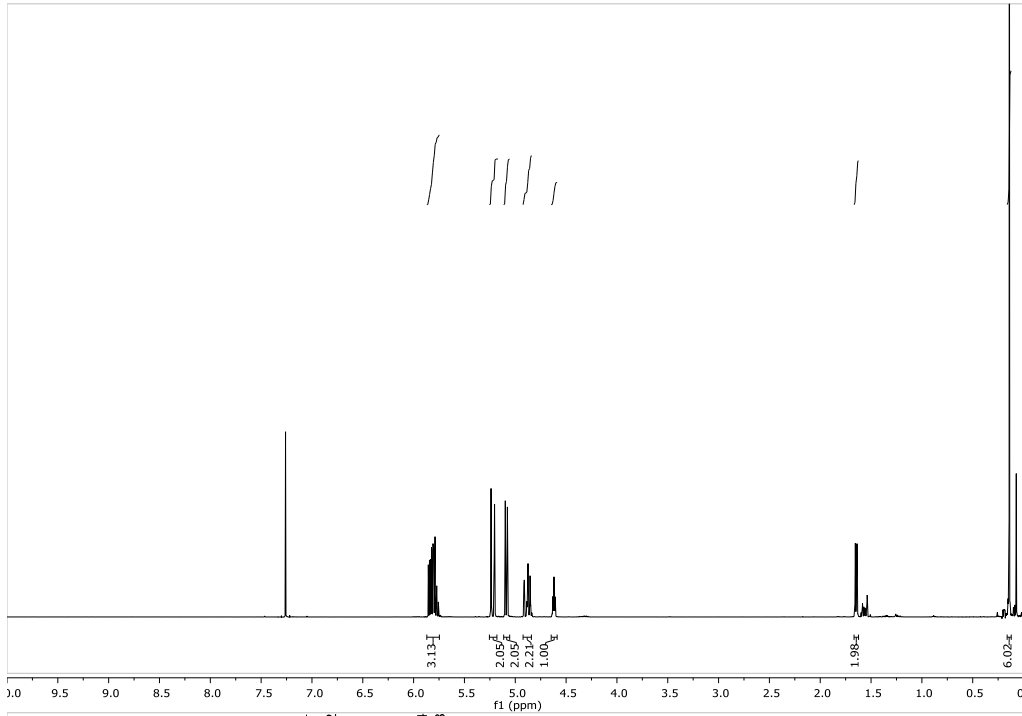


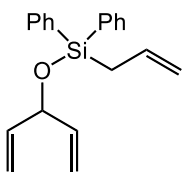
13



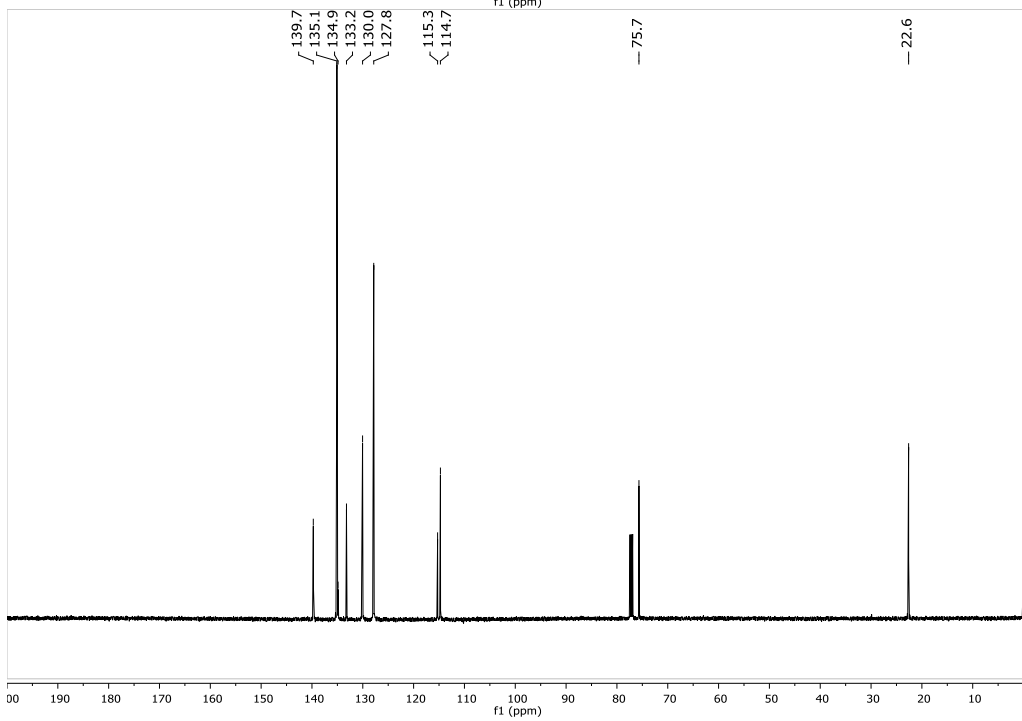
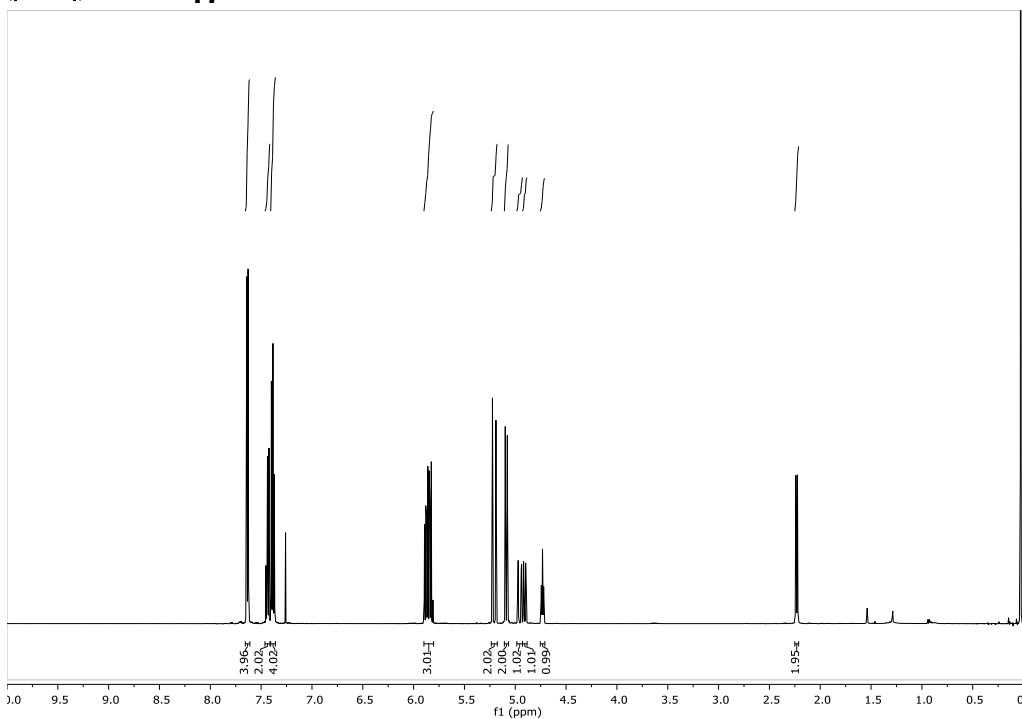


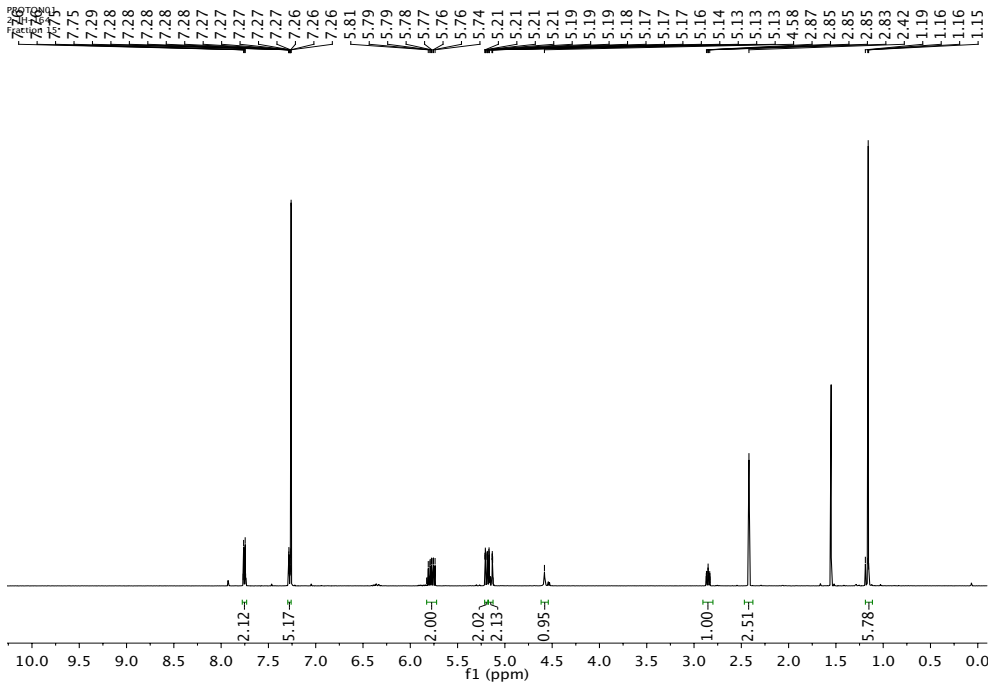
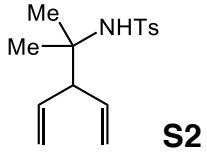
15



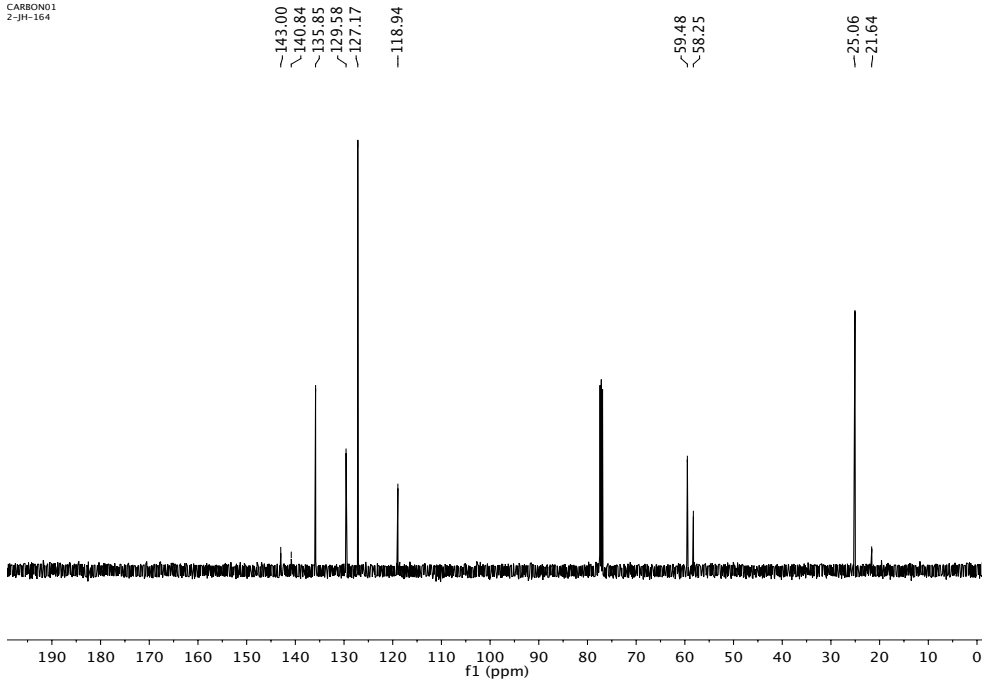


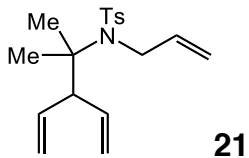
17



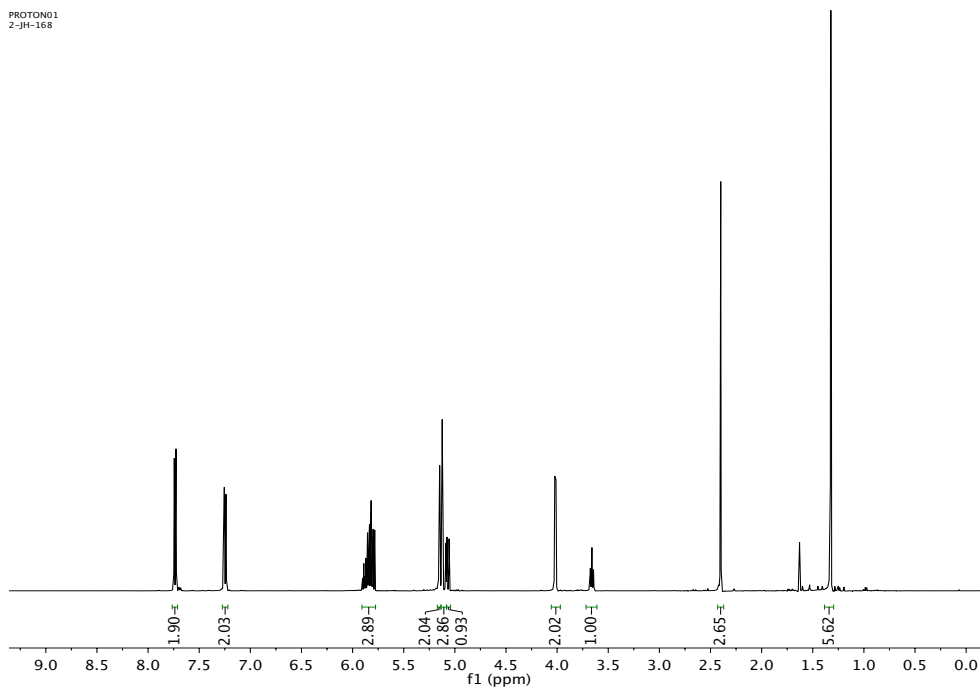


CARBON01
2-JH-164

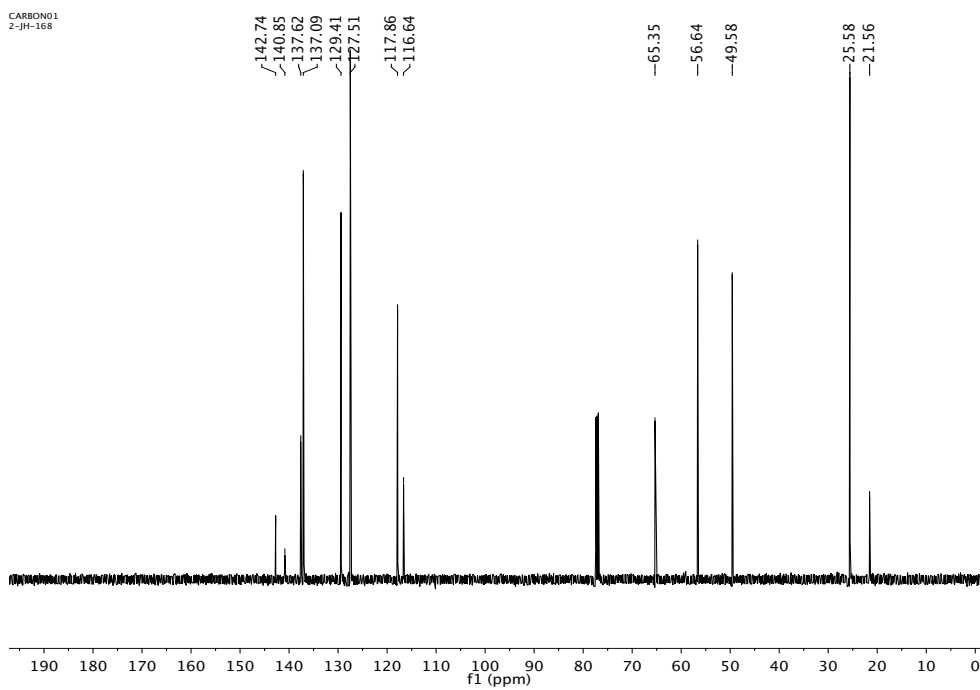


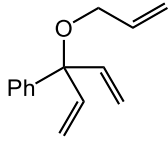


PROTON01
2-JH-168

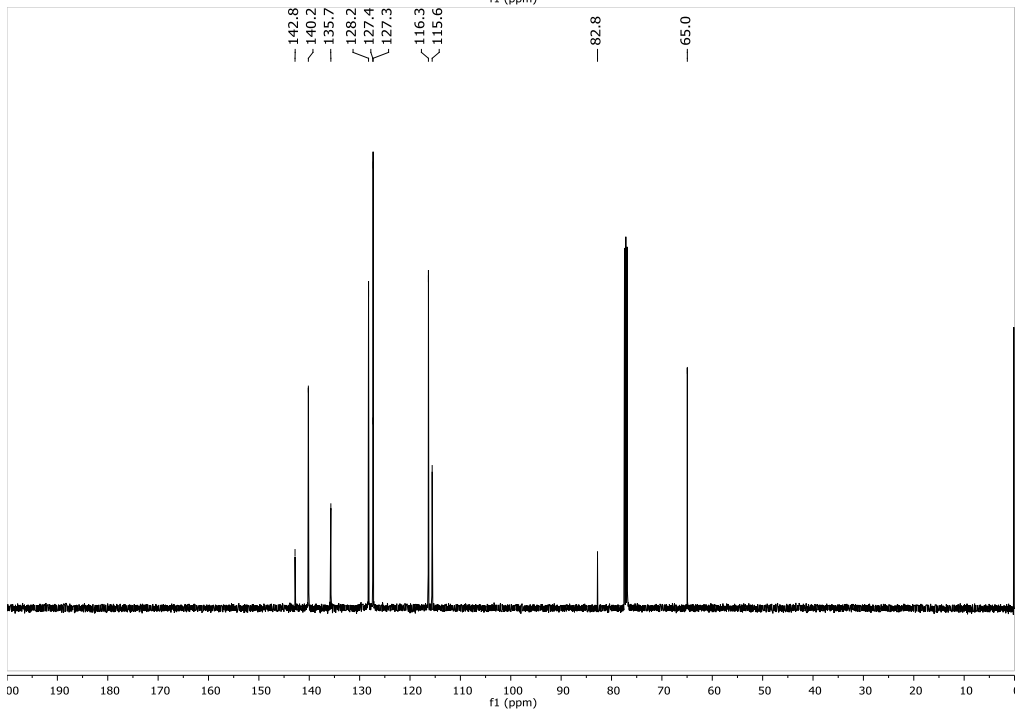
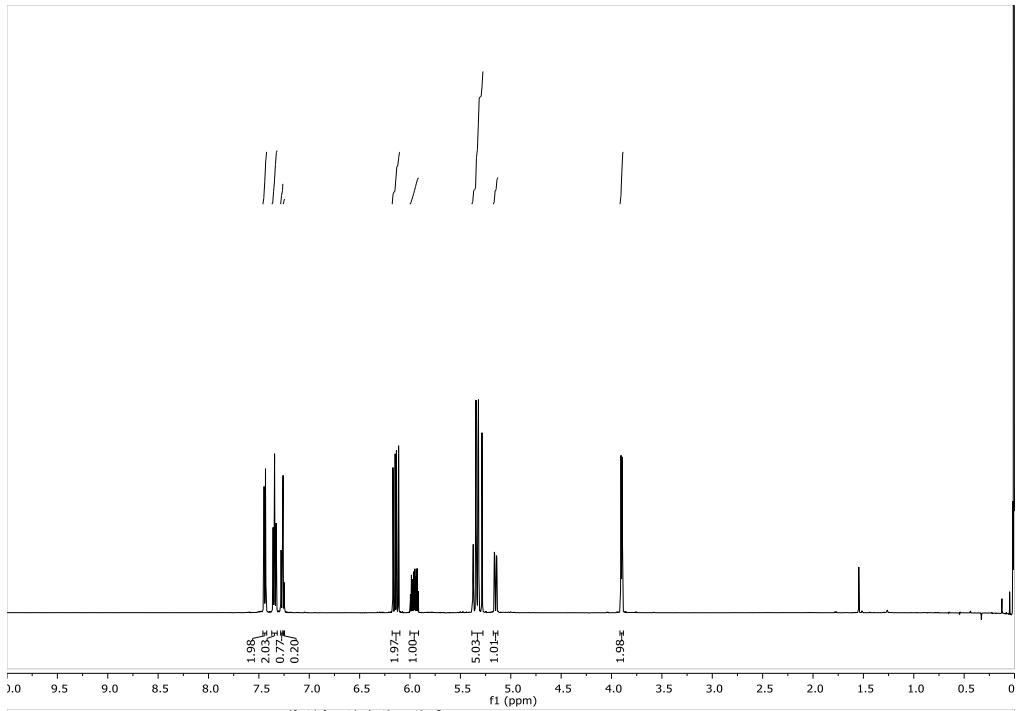


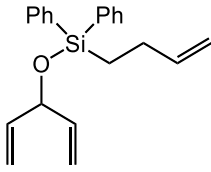
CARBON01
2-JH-168



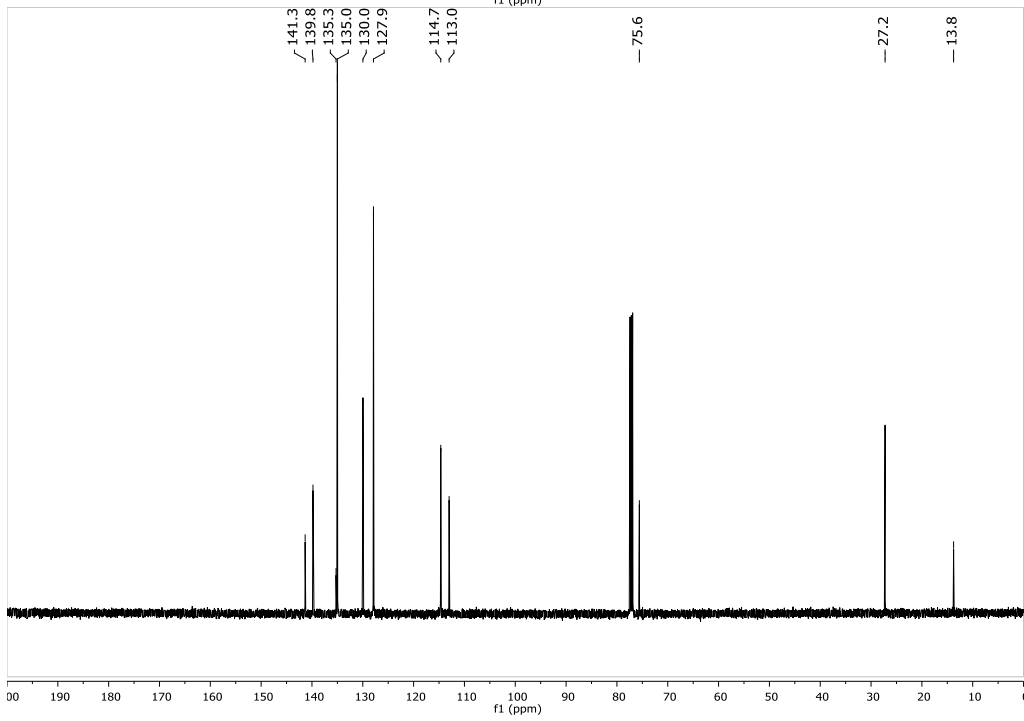
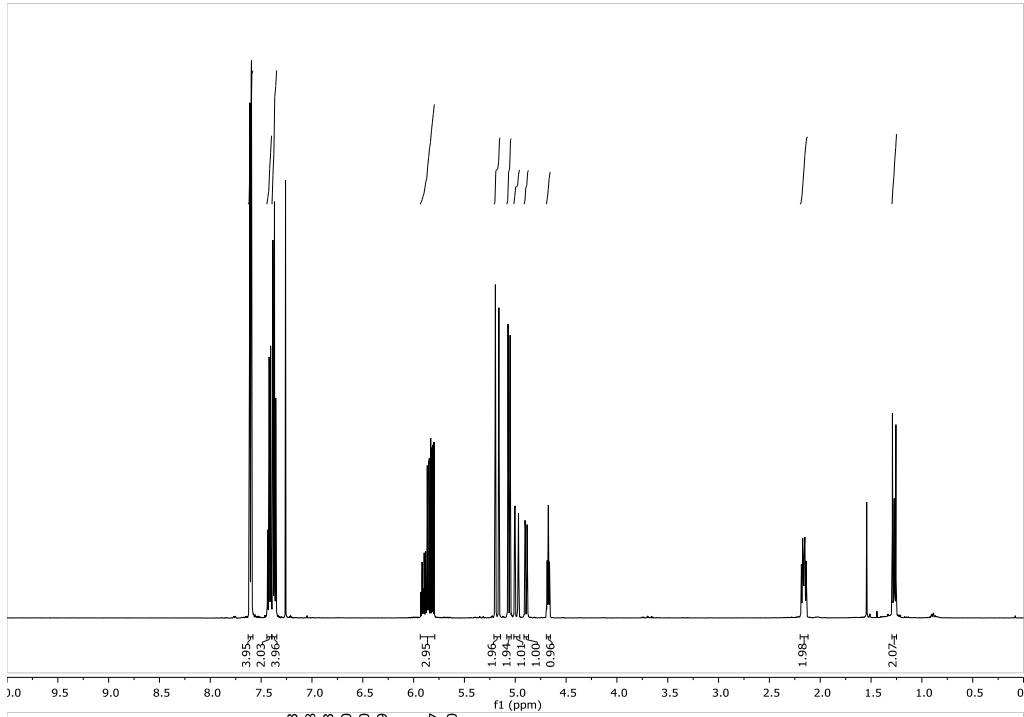


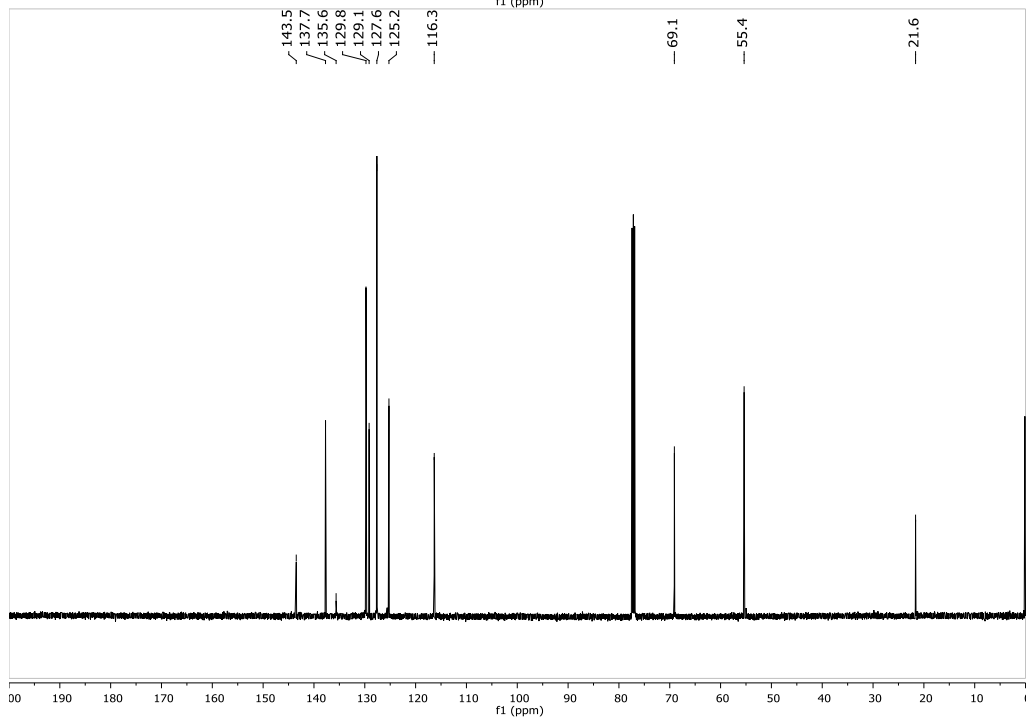
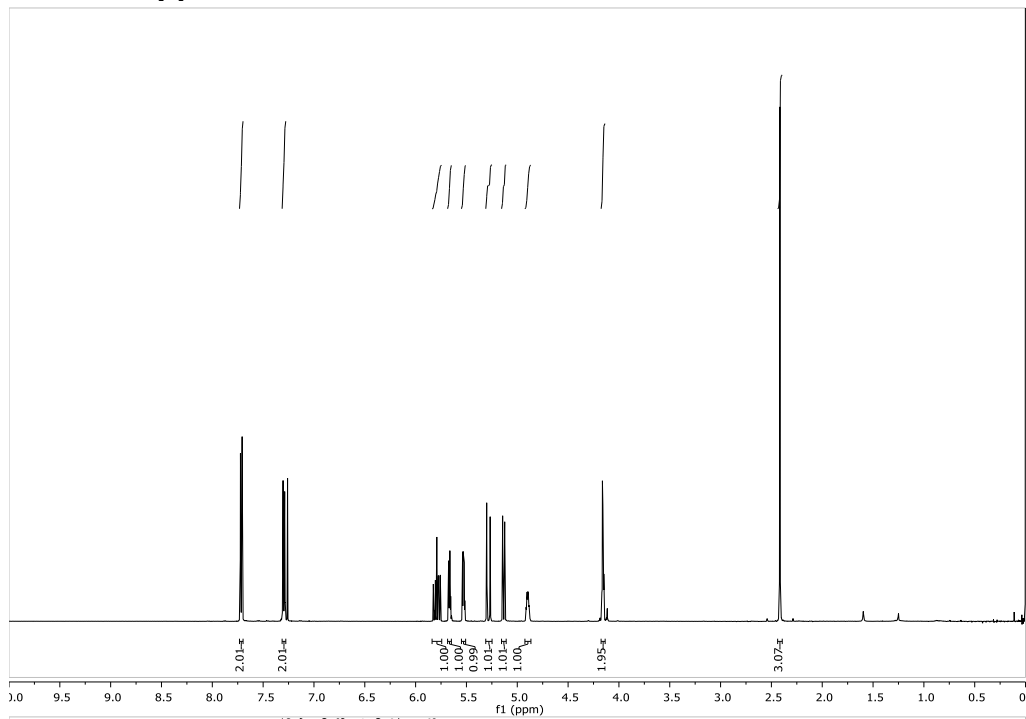
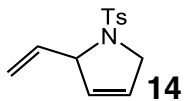
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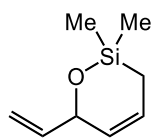




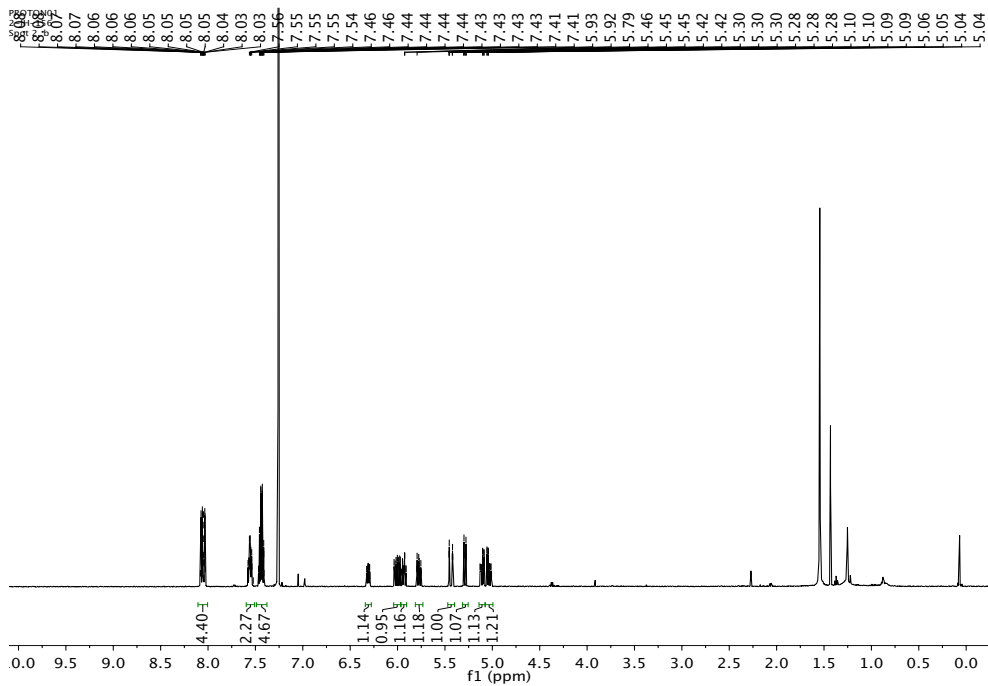
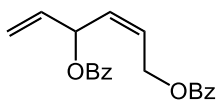
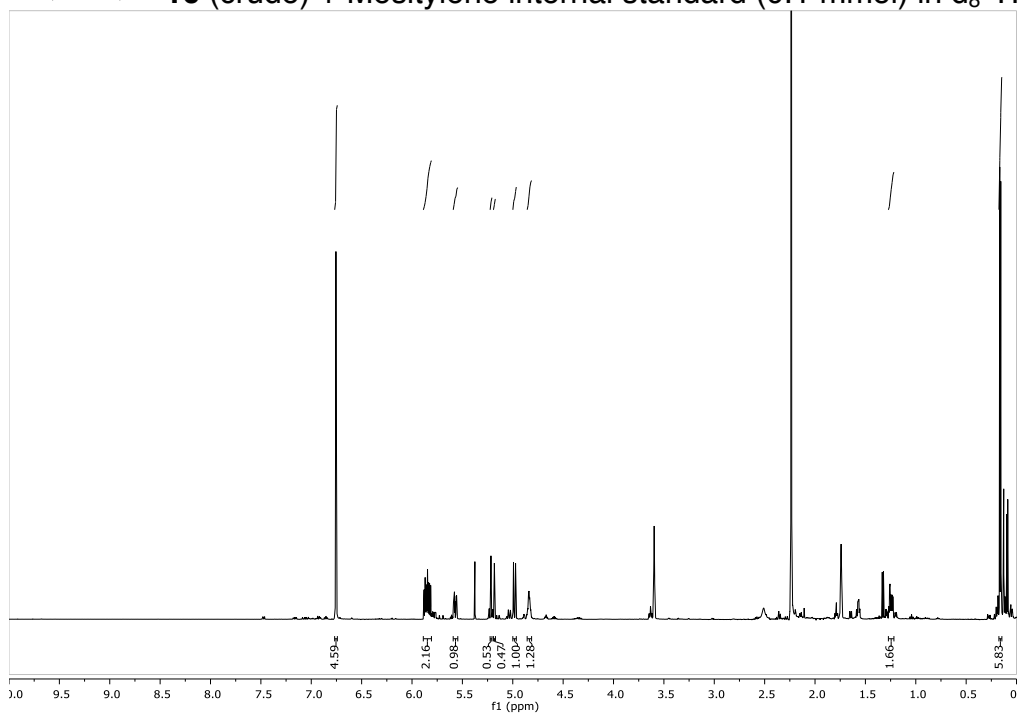
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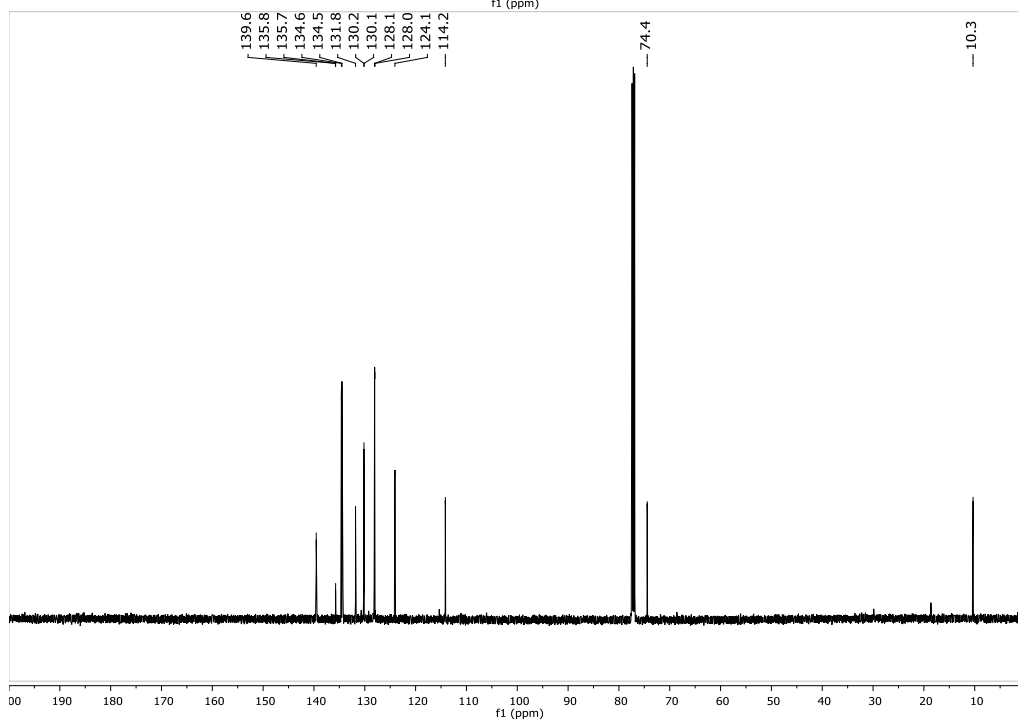
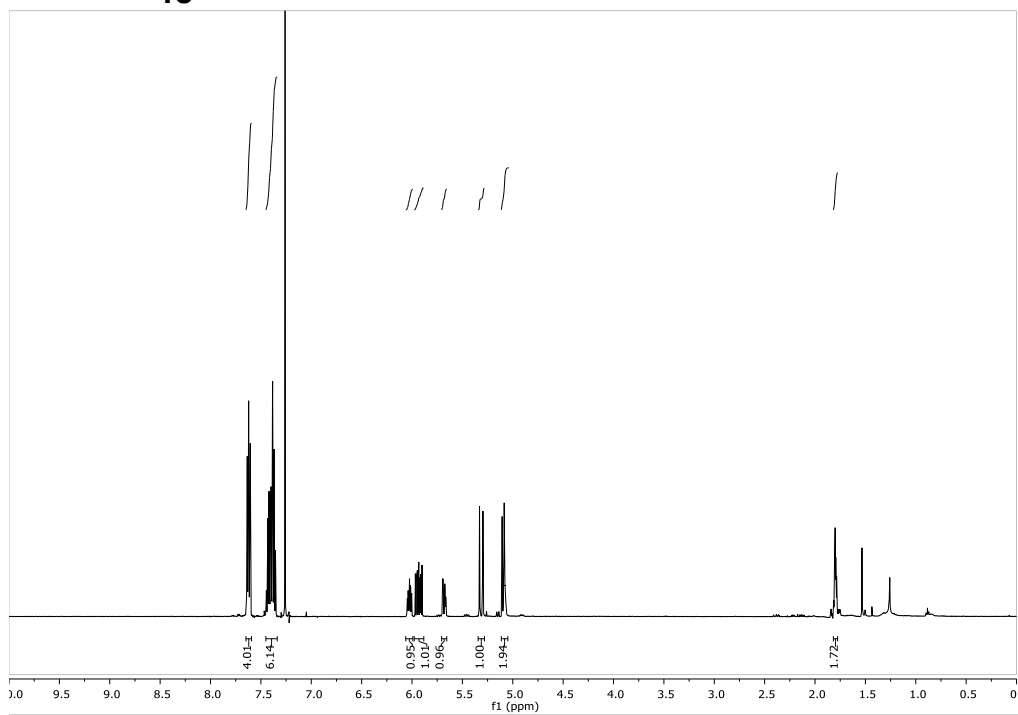
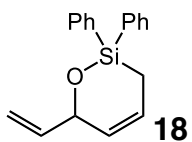


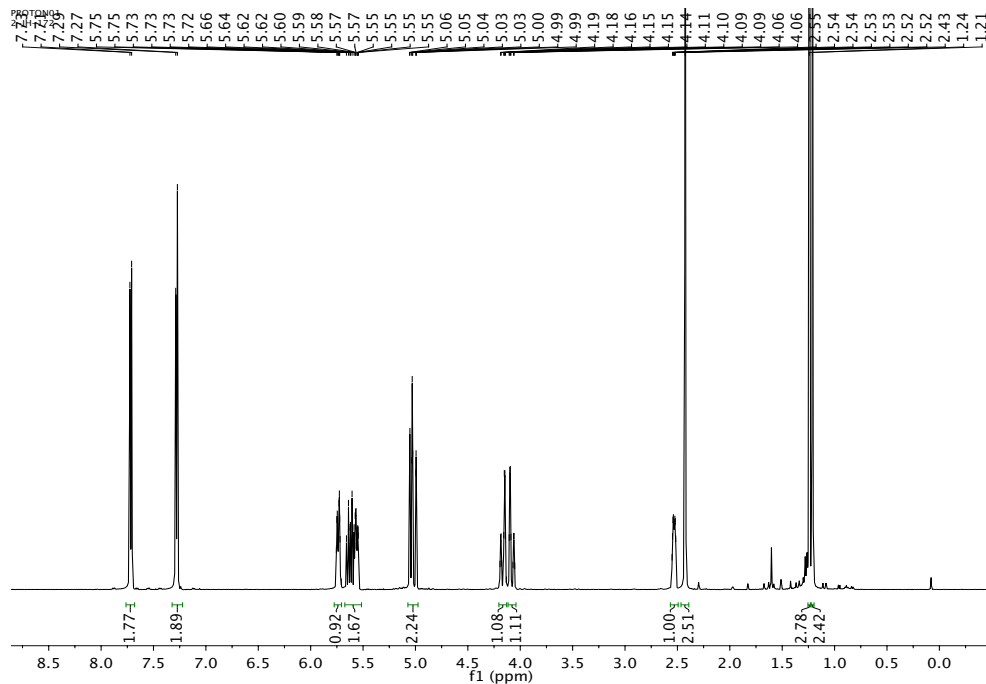
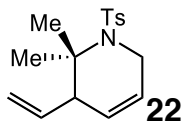




16 (crude) + Mesitylene internal standard (0.1 mmol) in d_8 -THF







CARBON01
2-JH-172

143.03
 140.18
 137.30
 129.58
 127.59
 127.24
 122.95
 117.23
 -58.46
 -52.73
 -44.73
 24.86
 24.53
 21.63

