The Significance of Degenerate Processes to Enantioselective Olefin Metathesis Reactions Promoted by Stereogenic-at-Mo Complexes

Simon J. Meek,[†] Steven J. Malcolmson,[†] Bo Li,[†] Richard R. Schrock,[‡] and
Amir H. Hoveyda,[†,*]

[†]*Department of Chemistry, Merkert Chemistry Center, Boston College*
Chestnut Hill, Massachusetts 02467
[‡]*Department of Chemistry, Massachusetts Institute of Technology*
Cambridge, Massachusetts 02139

SUPPORTING INFORMATION

General: All reactions were carried out in oven- (135 °C) or flame-dried glassware under an inert atmosphere of dry N_2 unless otherwise stated. Alcohol **4** and substrates **5**, d_3-**5**, **7**, **12**, **15**, d_3-**15**, and **26** were dried by azeotropic distillation with C_6H_6 prior to use in reactions with Mo-based reagents. (The numbering of compounds refers to those in the main body of the text; other compounds, mentioned here, are abbreviated by letters.) Substrates **5**[1], **7**[2], **A**[3], **C**[3], **E**[4], **G**[5], and **I**[1] were synthesized according to previously reported procedures. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR Mode) spectrometer, υ_{max} in cm^{-1}. Bands are characterized as strong (s), medium (m), or weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuteration as the internal reference ($CDCl_3$: δ 7.26, C_6D_6: δ 7.16). ^{1}H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet), and coupling constants (Hz). ^{2}H NMR spectra were recorded on a Varian INOVA 500 (76.7 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the natural abundance of deuterium in the solvent as the internal reference ($CDCl_3$ in $CHCl_3$: δ 7.26). ^{13}C-NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.16, C_6D_6: δ 128.06). In the case of coupling to deuterium, the data are reported as follows: chemical shift, multiplicity (d = doublet, t = triplet), coupling constants (C–D, Hz). Enantiomer ratios were determined by HPLC (Chiral Technologies Chiralpak OD column (4.6 mm x 250 mm)) or by GLC analysis (Alltech Associates Chiraldex GTA (CDGTA, 30 m x 0.25 mm)) in comparison with authentic racemic materials. High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Boston College Mass Spectrometry Facility. Elemental analysis was performed at Midwest Microlab, LLC (Indianapolis, IN). Optical rotation values were recorded on a Rudolph Research Analytical Autopol IV polarimeter. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. X-ray crystallography was performed at the Boston College X-ray Crystallographic Laboratory.

Solvents: Solvents were purged with argon and purified under a positive pressure of dry argon by a modified Innovative Technologies purification system: diethyl ether (Aldrich) was passed through activated alumina columns; benzene (Aldrich) and pentane[6] (J T. Baker) were passed successively through activated Cu and alumina columns. Tetrahydrofuran (Aldrich) was distilled from sodium benzophenone ketyl.

---

(1) Dolman, S. J.; Sattely, E. S.; Hoveyda, A. H; Schrock, R. R. *J. Am. Chem. Soc*. **2002**, *124*, 6991–6997.

(2) Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc*. **2009**, *131*, 943–953.

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

(4) Kiely, A. F.; Jernelius, J. A.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc*. **2002**, *124*, 2868–2869.

(5) Hansen, E. C.; Lee, D. *Org. Lett*. **2004**, *6*, 2035–2038.

(6) *n*-Pentane was allowed to stir over concentrated H_2SO_4 for three days, washed with water, followed by a saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and filtered before use in the solvent purification system.

Metal-based Complexes: Mo-based bis-pyrrolide **3** was prepared according to published procedures.[7] Mo-based monoaryloxide-monopyrrolide *S*-**1** was prepared based on published procedures.[8] Mo complexes were handled in an N_2-filled dry box.

REAGENTS:

***d*₄-Acetic acid** (99.93%) was purchased from Cambridge Isotope Laboratories and used as received.

Allyl bromide was purchased from Aldrich and distilled from CaH_2 prior to use.

Allyl ether was purchased from Aldrich and distilled from CaH_2 into activated 4 Å molecular sieves prior to use.

d_6-Benzene was purchased from Cambridge Isotope Laboratories and distilled from Na into activated 4 Å molecular sieves prior to use.

Benzyl potassium was prepared according to the literature procedure.[9]

***n*-Butyl lithium** (15% in hexanes) was purchased from Strem and titrated with *s*-butanol (1,10-phenanthroline as indicator) prior to use.

Deuterium gas (99.9%) was purchased from Cambridge Isotope Laboratories and used as received.

***N*,*N*-Dimethylformamide** was purchased from Acros (extra dry with molecular sieves) and used as received.

Lindlar's catalyst (5% w/w Pd on $CaCO_3$, poisoned with Pb) was purchased from Aldrich and used as received.

Phosphorus tribromide was purchased from Aldrich and used as received.

Potassium carbonate was purchased from Fisher and used as received.

Potassium fluoride was purchased from Aldrich and used as received.

Propargyl bromide (80% w/w solution in toluene) was purchased from Aldrich and used as received.

Quinoline was purchased from Aldrich and distilled from Na_2SO_4 prior to use.

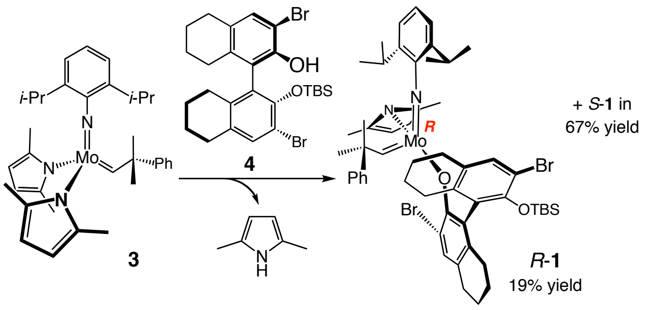
---

(7) Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P. M.; Hoveyda, A. H. *Organometallics* **2007**, *26*, 2528–2539.

(8) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2008**, *456*, 933–937.

(9) Schlosser, H.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508–509.

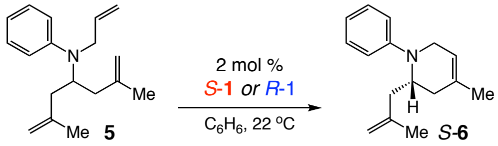
Synthesis of *Diastereomerically Pure* Complex *R*-1:



In an N_2-filled dry box, a 25-mL pear-shaped flask with magnetic stir bar was charged with Mo bis(pyrrolide) complex **3** (224 mg, 379 mmol, 1.00 equiv) and Et_2O (5 mL). The flask was sealed and allowed to cool to –50 °C (glovebox freezer). An 8-mL vial was charged with alcohol **4** (211 mg, 379 mmol, 1.00 equiv) and Et_2O (1 mL). The vial was tightly capped and allowed to cool to –50 °C (glovebox freezer). The bis(pyrrolide) solution was allowed to stir and the chilled alcohol solution was added to it by pipet; the vial containing the alcohol was rinsed with Et_2O (0.3 mL, –50 °C), which was similarly transferred to the mixture. The resulting solution was allowed to warm to 22 °C. As the reaction progressed, the mixture turned from bright yellow to red. After 1 h at 22 °C, volatiles were removed under reduced pressure and the resulting residue (red solid) was dissolved in *n*-pentane (5 mL), which was subsequently removed *in vacuo* to afford a red-orange powder (alternatively, this procedure can be repeated until a powder is obtained). The powder was dissolved in *n*-pentane (2 mL) with vigorous stirring; once all solid had dissolved entirely, the flask was sealed and allowed to cool to –50 °C (glovebox freezer) for 48 h, after which large red crystals appeared. The crystals were collected by vacuum filtration and washed with cold *n*-pentane (~5 mL, –50 °C) to afford diastereomerically pure *S*-**1** (contains one molecule of *n*-pentane per 1 molecule of *S*-**1**) (289 mg, 255 mmol, 67.0% yield). The resulting mother liquor (enriched in the *R* diasteromer; 4:1 *R*-**1**:*S*-**1**) was concentrated *in vacuo* to afford a red-orange powder. The powder was dissolved in *n*-pentane (0.5 mL) with vigorous stirring; once the solid had completely dissolved, the flask was sealed and allowed to cool to –50 °C (glovebox freezer) for 48 h, after which small red crystals appeared. The crystals were collected by vacuum filtration and washed with cold *n*-pentane (~2 mL, –50 °C) to afford diastereomerically pure *R*-**1** (contains 1 molecule of *n*-pentane per one molecule of *R*-**1**) (84.0 mg, 74.0 mmol, 19.5% yield). The physical and spectral data were identical to those previously reported for chiral complex *S*-**1**.

R-**1**·*n*-pentane: ^{1}H NMR (400 MHz, C_6D_6): δ 12.90 (1H, s), 7.37-7.33 (3H, m), 7.18-7.12 (3H, m), 7.05-6.98 (4H, m), 5.99 (2H, br s), 3.67 (2H, apparent br s), 2.60-1.75 (15H, m), 1.86 (3H, s), 1.62 (3H, s), 1.57-0.79 (19H, m), 1.21 (3H, s), 1.19 (3H, s), 0.95 (9H, s), 0.88 (6H, t, J = 6.8 Hz), 0.25 (3H, s), 0.03 (3H, s); ^{13}C NMR (100 MHz, C_6D_6): δ 295.1, 158.0, 153.5, 148.5, 148.2, 136.8, 136.6, 134.1, 132.6, 132.1, 131.7, 130.9, 129.2, 128.8, 128.5, 126.5, 126.2, 123.5 br, 112.7, 112.0, 109.3 br, 55.8, 34.5, 33.0, 30.4, 29.6, 28.9 br, 27.9, 27.6, 26.5, 24.2 br, 23.3, 23.2, 23.0, 22.9, 22.7, 18.9, 17.5 br, 14.3, –2.2, –3.0; Anal. calcd for $C_{59}H_{82}Br_2MoN_2O_2Si$: C, 62.43; H, 7.28; N, 2.47; found: C, 62.47; H, 7.24; N, 2.42.

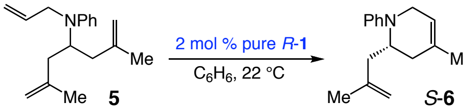
General Procedure for Catalytic Enantioselective Olefin Metathesis with Diastereomerically Pure Mo Complexes *S*-1 or *R*-1: In an N_2-filled dry box, a 4-mL vial equipped with a magnetic stir bar was charged with substrate. A separate 2-mL vial was charged with isolated Mo complex *S*-**1** or *R*-**1** and then C_6H_6. The solution of catalyst was transferred to substrate by syringe and the resulting mixture allowed to stir for the required period of time. The vessel was removed from the dry box and the reaction quenched by the addition of benchtop Et_2O (~1 mL). The mixture was concentrated *in vacuo* (% conversion determined by 400 MHz ^1H NMR analysis). Purification was performed by silica gel chromatography.[8] Enantiomeric purity of the product of the olefin metathesis reaction was determined by GLC or HPLC analysis in comparison with authentic racemic material.



S-**1**: 20 min; >98% conv, 88%, 96.5:3.5 er
R-**1**: 180 min; >98% conv, 81%, 96:4 er

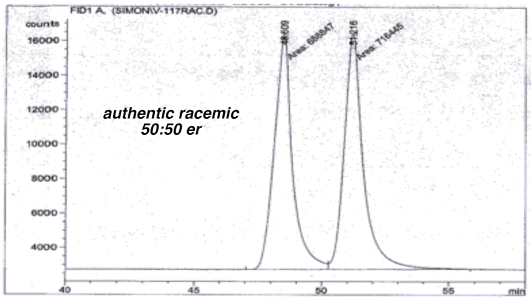
(*S*)-4-Methyl-2-(2-methylallyl)-1-phenyl-1,2,3,6-tetrahydropyridine[1,8] **(6).** The physical and spectral data were identical to those previously reported for this heterocycle. m.p. = 55–57 ºC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91-7.87 (2H, m), 7.28–7.23 (2H, m), 6.79-6.74 (1H, m), 5.54-5.50 (1H, m), 4.79-4.75 (1H, m), 4.69-4.66 (1H, m), 4.23 (1H, dddd, J_{ABX} = 10.0, 5.2, 4.0, 0.8 Hz), 3.80 (1H, app dt, J_{ABX} = 16.8, 1.6 Hz), 3.51 (1H, ddddd, J_{ABX} = 16.8, 3.6, 2.4, 2.0, 2.0 Hz), 2.40 (1H, br d, J_{AB} = 16.8 Hz), 2.21 (1H, dd, J_{AB} = 13.2, 10.6 Hz), 2.07 (1H, dd, J_{ABX} = 13.6, 4.0 Hz), 2.03 (1H, d, J_{AB} = 17.2 Hz), 1.76 (3H, br s), 1.74 (3H, d, J = 0.8 Hz); $[\alpha]_D^{20}$ –169 (*c* 0.500, $CHCl_3$) for a sample of 96.5:3.5 er [Lit.[1,8] $[\alpha]_D^{20}$ +181 (*c* 0.950, $CHCl_3$) for a sample of 99:1 er]. The enantiomeric purity of **6** (96.5:3.5 er) was determined by GLC analysis (CDGTA column, 20 psi, 130 °C) in comparison with authentic racemic material. The enantiomer formed in this reaction was assigned through inference with that detailed previously.[1]

Table 1. Time Dependence of Conversion and Selectivity in Catalytic RCM with Pure *R*-**1**

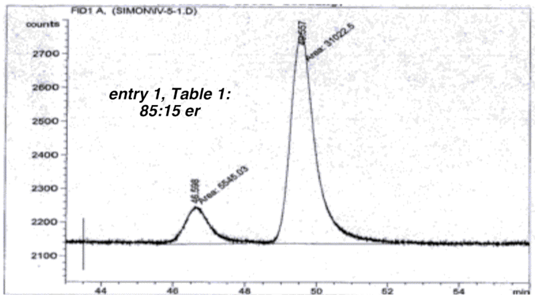


entry	time (min)	conv (%)[a]	er (*S*:*R*)[b]
1[c]	30	5	85.5:14.5
2	45	15	94:6
3	60	23	95:5
4	180	>98	96:4

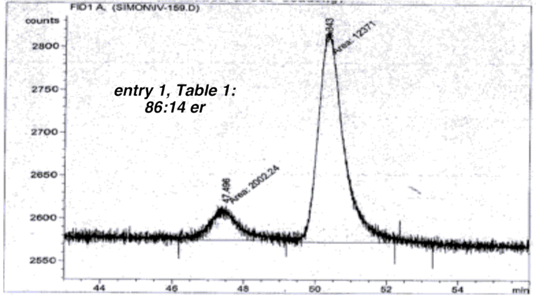
[a] Based on 400 MHz ^1H NMR analysis of unpurified mixtures. [b] Based on GLC analysis (see below). [c] Variation in er with respect to conversion was observed due to limits in ^1H NMR detection, therefore the values reported are an average of two experiments.



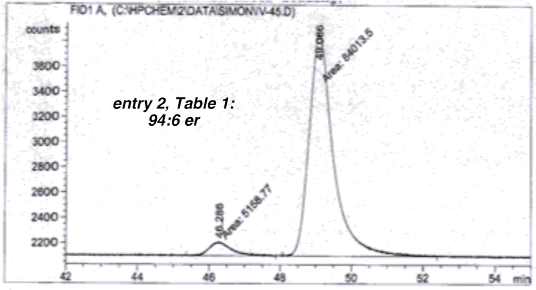
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  48.509 MF    0.8323 6.88847e5  1.37947e4  49.01806
   2  51.216 FM    0.8685 7.16445e5  1.37492e4  50.98194
```



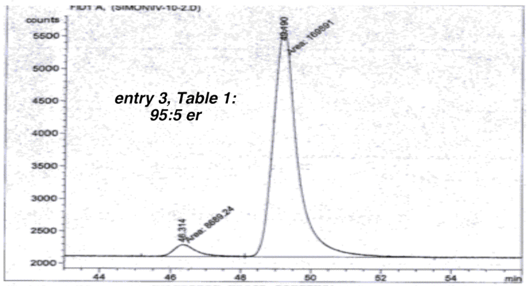
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  46.598 MM    0.8084 5545.03369  114.32389 15.16380
   2  49.557 MM    0.8211 3.10225e4   629.65698 84.83620
```



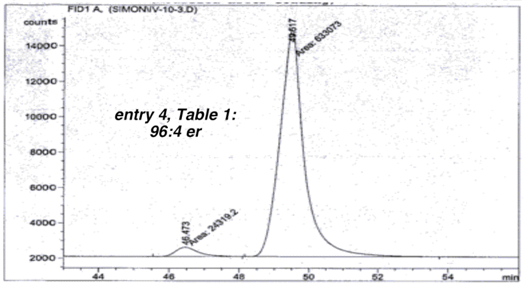
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  47.496 MM    0.8137 2002.23706   41.01082 13.93033
   2  50.343 MM    0.8261 1.23710e4   249.58965 86.06967
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  46.286 MM    0.7486 5158.76660  114.84943  5.78517
   2  49.086 MM    0.7934 8.40135e4  1764.81702 94.21483
```

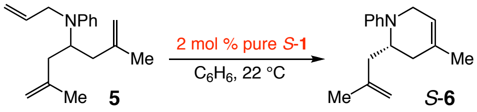


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  46.314 MM    0.7636 8689.24023  189.65724  4.86572
   2  49.190 MM    0.8030 1.69891e5  3526.10547 95.13428
```



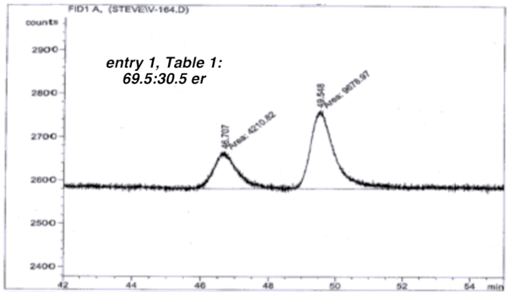
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  46.473 MM    0.7443 2.43192e4   544.58014  3.69934
   2  49.517 MM    0.8220 6.33073e5  1.28364e4  96.30066
```

Table 2. Time Dependence of Conversion and Selectivity in Catalytic RCM with Pure *S*-**1**

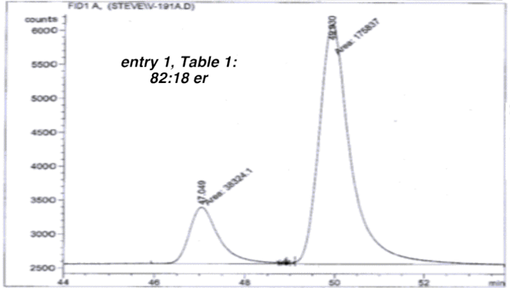


entry	time (min)	conv (%)[a]	er (*S*:*R*)[b]
1[c]	2	4	76:24
2[c]	2.5	7	87.5:12.5
3	3	13	93.5:6.5
4	20	>98	96.5:3.5

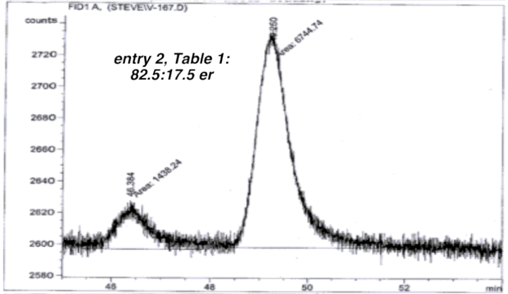
[a] Based on 400 MHz ^{1}H NMR analysis of unpurified mixtures. [b] Based on HPLC analysis (see below). [c] Variation in er with respect to conversion was observed due to limits in ^{1}H NMR detection, therefore the values reported are an average of two experiments.



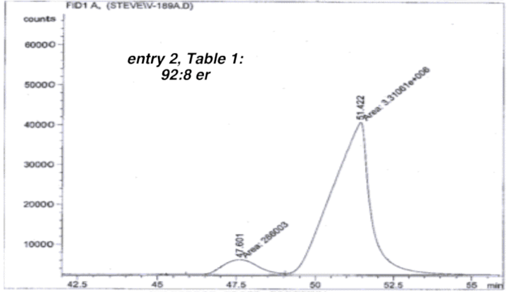
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  46.707 MF    0.7998 4210.81689   87.74249 30.31592
   2  49.548 FM    0.8817 9678.97070  182.95580 69.68408
```



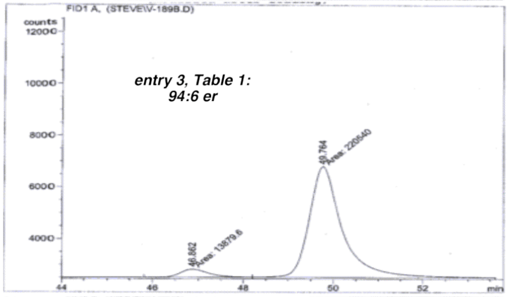
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  47.049 MF    0.7611 3.83241e4  839.17712 17.89496
   2  49.930 FM    0.8265 1.75837e5 3545.62036 82.10504
```



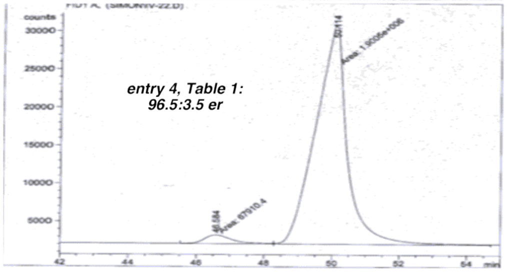
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  46.384 MM    0.7509 1438.23535   31.92254 17.57594
   2  49.250 MM    0.8056 6744.74316  139.54701 82.42406
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  47.601 MF    1.2839 2.86003e5 3712.75293  7.95200
   2  51.422 FM    1.4374 3.31061e6 3.83856e4  92.04800
```

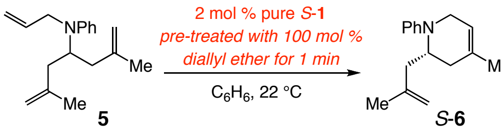


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  46.862 MF    0.7244 1.38796e4  319.34003  5.92084
   2  49.764 FM    0.8550 2.20540e5 4298.84619 94.07916
```



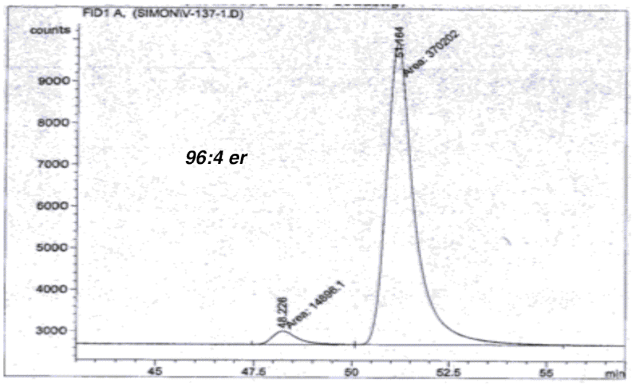
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  46.584 MF    0.9710 6.79104e4 1165.68884  3.45001
   2  50.114 FM    1.1004 1.90050e6 2.87851e4  96.54999
```

Pre-established Curtin-Hammett Conditions in a Catalytic Enantioselective RCM (eq 5):



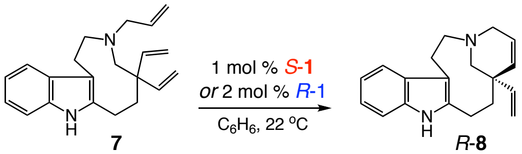
~10 seconds: 6% conv, 96:4 er

In an N_2-filled dry box, a 4-mL vial equipped with a magnetic stir bar was charged with substrate **5** (10.0 mg, 0.0392 mmol, 1.00 equiv). A separate 2-mL vial was charged with isolated Mo complex *S*-**1** (0.90 mg, 0.783 μmol, 0.0200 equiv), C_6H_6 (392 μL) and then diallyl ether (3.8 μL, 0.0392 mmol, 1.00 equiv). The resulting solution was allowed to stand for one minute; the solution changed color form light orange to dark orange. The solution of catalyst was transferred to substrate by syringe and the resulting mixture was allowed to stir for 10 seconds. At that time, the reaction was quenched by the addition of benchtop Et_2O (~1 mL) and concentrated *in vacuo*. The unpurified brown solid was dissolved in minimal MeOH (0.5 mL), and KF (4.80 mg, 0.083 mmol, 106 equiv with respect to *S*-**1**) was added (to desilylate phenol **4**, which has the same R_f as **6**). The mixture was allowed to stir for 30 min. Silica gel was added and the mixture concentrated and purified by silica gel chromatography (50:1 pet ether:Et_2O) to afford *S*-**6** as a white solid.



```
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  48.226 MM    0.7522 1.48961e4  330.04489  3.86812
   2  51.164 MM    0.8454 3.70202e5 7298.33496 96.13188
```

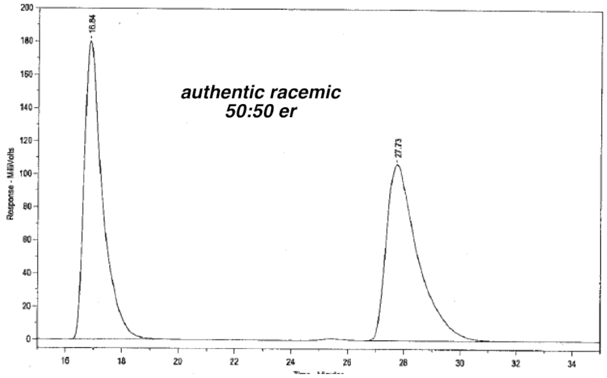
Mo-Catalyzed enantioselective RCM in eq 1:



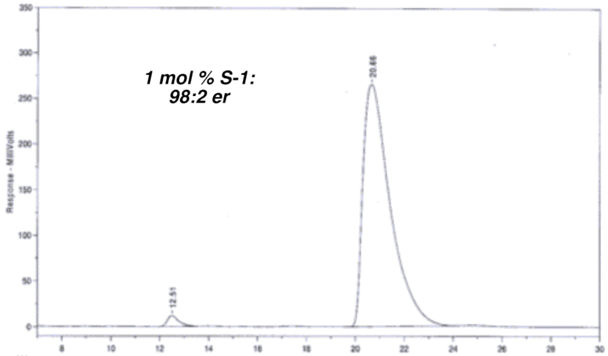
S-**1**: 1 h; >98% conv, 91%, 98:2 er
R-**1**: 12 h; >98% conv, 88%, 98:2 er

Tetradehydro (+)-quebrachamine (8). The physical and spectral data were identical to those previously reported for compound **8**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (1H, br s), 7.51–7.47 (1H, m), 7.31–7.28 (1H, m), 7.13–7.05 (2H, m), 5.90 (1H, ddd, *J* = 9.9, 4.8, 1.5 Hz), 5.61 (1H, dd, J_{ABX} = 17.5, 10.5 Hz), 5.44 (1H, ddd, *J* = 9.9, 4.0, 2.0 Hz), 4.92 (1H, dd, *J* = 6.8, 1.3 Hz), 4.88 (1H, s), 3.73 (1H, ddd, J_{ABX} = 14.2, 10.5, 1.5 Hz), 3.32–3.25 (1H, m), 3.13-3.07 (1H, m), 2.88–2.82 (1H, m), 2.80–2.64 (4H, m), 2.42-2.33 (2H, m), 2.01-1.86 (2H, m). $[\alpha]_D^{20}$ +99.2 (*c* 0.513,

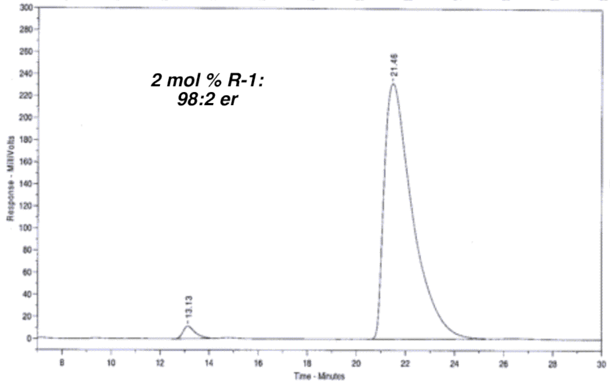
$CHCl_3$) for a sample of 98:2 er. The enantiomeric purity of **8** (98:2 er) was determined by HPLC analysis (Chiralpak OD, 95:5 hexanes:*i*-PrOH, 1.0 mL/min, 254 nm) in comparison with authentic racemic material.



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	16.84		0.00	N/A	8212891	49.750	BB	0.65
2	27.73		0.00	N/A	8295533	50.250	BB	1.13

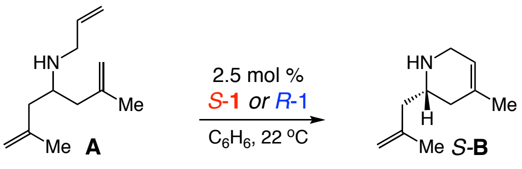


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	12.51		0.00	N/A	403493	1.915	BB	0.50
2	20.66		0.00	N/A	20664280	98.085	BB	1.16



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	13.13		0.00	N/A	386773	2.048	BB	0.51
2	21.46		0.00	N/A	18502320	97.952	BB	1.18

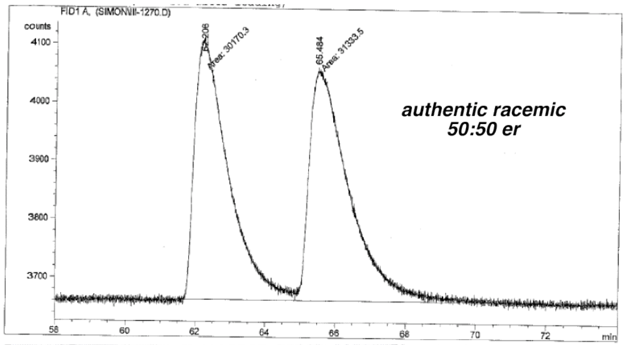
■ Additional Examples of Enantioselective RCM with *S*-1 and *R*-1:



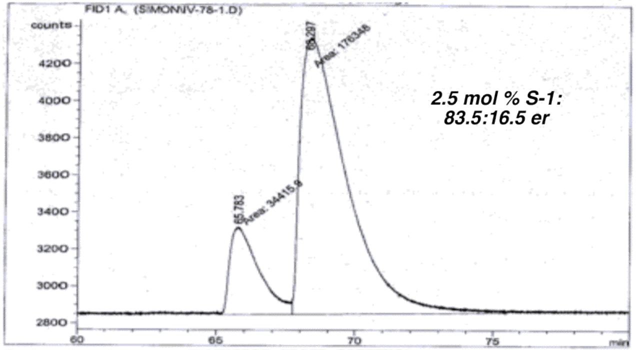
S-**1**: 1 h; >98% conv, 71%, 83.5:16.5 er
R-**1**: 3 h; >98% conv, 60%, 83.5:16.5 er

(*S*)-4-Methyl-2-(2-methylallyl)-1,2,3,6-tetrahydropyridine (B). The physical and spectral data were identical to those previously reported for this heterocycle. ^1H NMR (400 MHz, $CDCl_3$): δ 5.43–5.38 (1H, m), 4.83-4.81 (1H, m), 4.78–4.76 (1H, m), 3.40–3.28 (2H, m), 2.84 (1H, dddd,

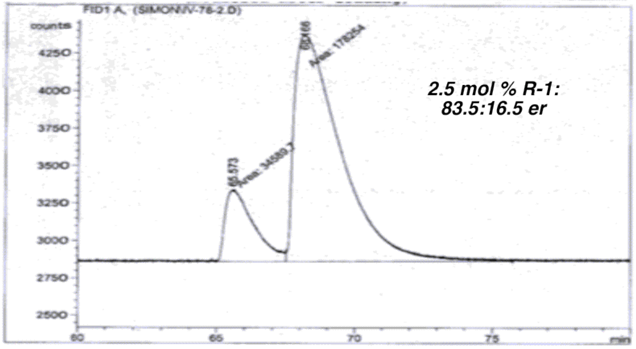
J_{AX} = 9.6, 7.6, 6.0, 4.4 Hz), 2.16-2.11 (2H, m), 1.90–1.62 (3H, m), 1.73 (3H, s), 1.67 (3H, s). $[\alpha]_D^{20}$ +71.6 (*c* 0.993, $CHCl_3$) for a sample of 83.5:16.5 er [Lit.[3,8] $[\alpha]_D^{20}$ +77.0 (*c* 1.00, $CHCl_3$) for a sample of 93.5:6.5 er]. The enantiomeric purity of **B** (83.5:16.5 er) was determined by acylation to the corresponding amide as previously reported[3] and GLC analysis (CDGTA column, 15 psi, 120 °C) in comparison with authentic racemic material.



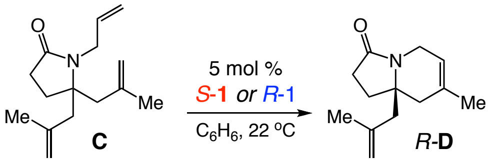
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  62.206 MF     1.1148 3.01703e4  451.06265 49.05433
   2  65.484 FM     1.3021 3.13335e4  401.06723 50.94567
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  65.783 MF     1.2054 3.44159e4  475.85483 16.32913
   2  68.297 FM     1.9601 1.76348e5 1499.50549 83.67087
```

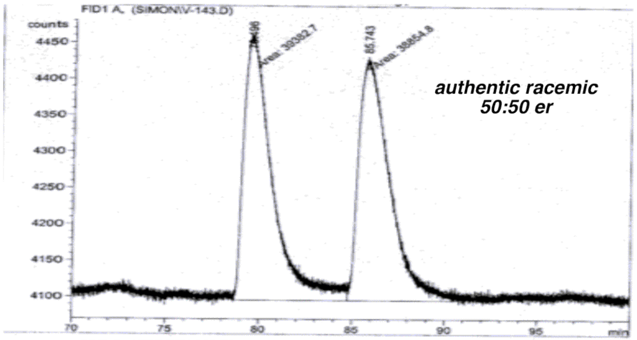


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1  65.573 MF     1.1903 3.45897e4  484.33340 16.25122
   2  68.166 FM     1.9570 1.78254e5 1518.10559 83.74878
```



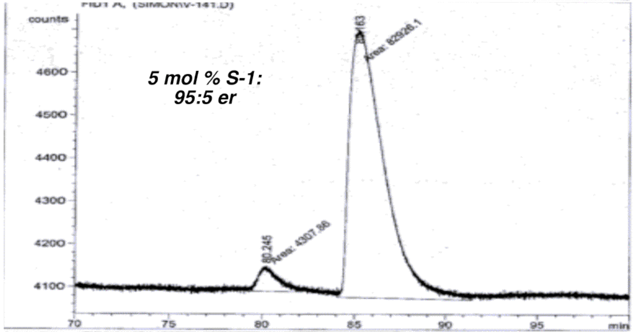
S-**1**: 1 h; >98% conv, 97%, 95:5 er
R-**1**: 3 h; >98% conv, >98%, 95.5:4.5 er

(*R*)-7-methyl-8a-(2-methylallyl)-1,2,8,8a-tetrahydroindolizin-3(5*H*)-one (D). The physical and spectral data were identical to those previously reported for this bicyclic amide. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41–5.37 (1H, m), 4.90 (1H, dddd, J_{ABX} = 2.0, 1.5, 1.5, 1.5 Hz), 4.73–4.71 (1H, m), 4.32 (1H, br d, J_{AB} = 18.4 Hz), 3.43 (1H, d, J_{AB} = 18.4 Hz), 2.49-2.22 (5H, m), 2.14-2.03 (2H, m), 1.83-1.74 (1H, m), 1.75 (3H, s), 1.70 (3H, s). $[\alpha]_D^{20}$ –109 (*c* 0.513, $CHCl_3$) for a sample of 95.5:4.5 er [Lit.[3] $[\alpha]_D^{20}$ +103 (c 1.00, $CHCl_3$) for a sample of >99:1 er]. The enantiomeric purity of **D** (95.5:4.5 er) was determined by GLC analysis (CDGTA column, 20 psi, 140 °C) in comparison with authentic racemic material.



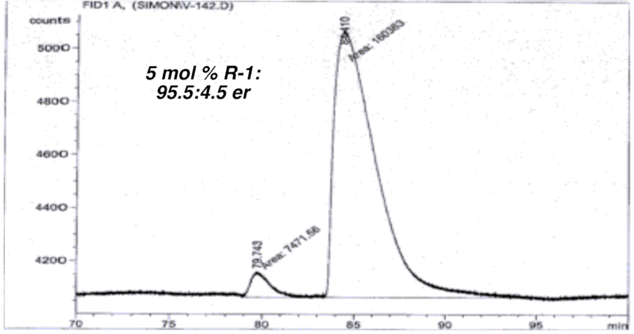
authentic racemic
50:50 er

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  79.496 MF    1.7877 3.93827e4  367.16183 50.33739
   2  85.743 FM    1.9139 3.88548e4  338.35355 49.66261
```



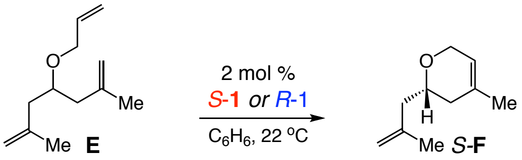
5 mol % S-1:
95:5 er

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  80.245 MM    1.1954 4307.86182   60.06274  4.93828
   2  85.163 MM    2.1987 8.29261e4  628.59418 95.06172
```



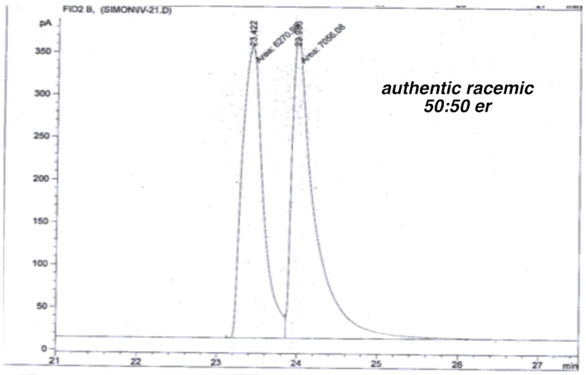
5 mol % R-1:
95.5:4.5 er

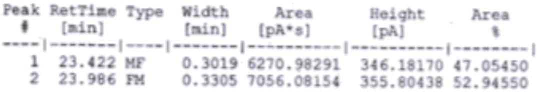
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]   .    [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  79.743 MM    1.2491 7471.55518   99.69023  4.45173
   2  84.410 MM    2.6471 1.60363e5 1009.66101 95.54827
```



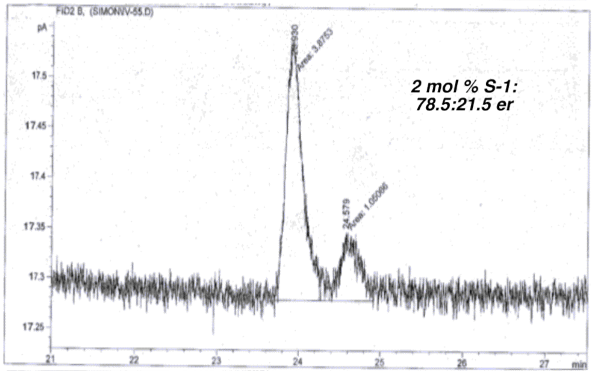
S-**1**: 30 min; >98% conv, 79%, 78.5:21.5 er
R-**1**: 180 min; >98% conv, 74%, 75.5:24.5 er

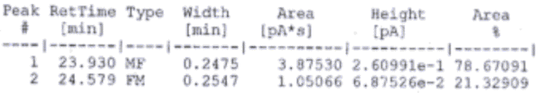
(*S*)-4-methyl-2-(2-methylallyl)-3,6-dihydro-2*H*-pyran (F). The physical and spectral data were identical to those previously reported for this unsaturated pyran. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42–5.39 (1H, br s), 4.83-4.81 (1H, m), 4.79-4.76 (1H, m), 4.22-4.08 (2H, m), 3.67 (1H, dddd, J = 9.6, 7.5, 5.7, 3.6 Hz), 2.35 (1H, dd, J = 14.4, 7.6 Hz), 2.18 (1H, dd, J = 14.4, 6.0 Hz), 2.00-1.90 (1H, m), 1.87-1.79 (1H, m), 1.77 (3H, s), 1.69 (3H, s). $[\alpha]_D^{20}$ = –25.95 (c = 2.05, $CHCl_3$) for a sample of 78.5:21.5 er. The enantiomeric purity of **F** (78.5:21.5 er) was determined by GLC analysis (CDGTA column, 15 psi, 60 °C) in comparison with authentic racemic material.



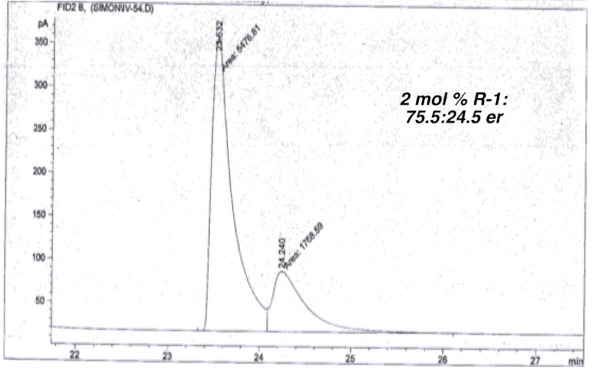


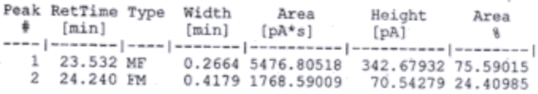
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
  1  23.422 MF     0.3019 6270.98291  346.18170 47.05450
  2  23.986 FM     0.3305 7056.08154  355.80438 52.94550
```





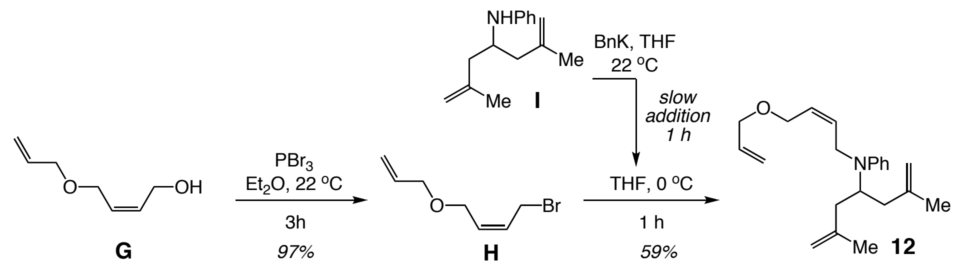
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
  1  23.930 MF     0.2475    3.87530 2.60991e-1 78.67091
  2  24.579 FM     0.2547    1.05066 6.87526e-2 21.32909
```





```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
  1  23.532 MF     0.2664 5476.80518  342.67932 75.59015
  2  24.240 FM     0.4179 1768.59009   70.54279 24.40985
```

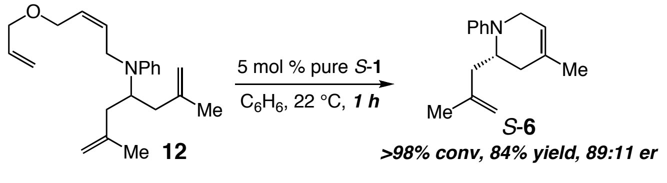
Synthesis of Tetraene 12:



Synthesis of (*Z*)-*N*-(4-(allyloxy)but-2-enyl)-*N*-(2,6-dimethylhepta-1,6-dien-4-yl) aniline (12). A 250-mL round-bottom flask with stir bar was charged with alcohol **G** (4.00 g, 31.2 mmol, 1.00 equiv) and Et_2O (95 mL). Phosphorus tribromide (3.43 mL, 36.5 mmol, 1.17 equiv) was then added slowly over 2 min and the resulting mixture allowed to stir for 2 h at 22 ºC. At this time, the reaction was allowed to cool to 0 °C and H_2O (5 mL) was added *slowly*; the Et_2O boils rapidly if the reaction is quenched too quickly. The biphasic solution was diluted with H_2O (50 mL) and transferred to a separating funnel. The organic layer was collected and the aqueous layer washed with Et_2O (2 x 25 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (50 mL) and a saturated aqueous solution of NaCl (50 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford **H** (5.77 g, 30.2 mmol, 96.8% yield) as colorless oil. Allylic bromide **H** is unstable and was used without further purification.

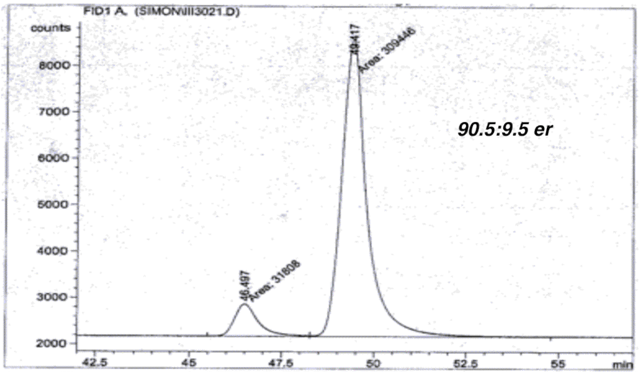
A 50-mL round-bottom flask with stir bar was charged with aniline **I** (1.00 g, 4.64 mmol, 1.00 equiv) and THF (6 mL). In an N_2 filled glove box, benzyl potassium (605 mg, 4.64 mmol, 1.00 equiv) was added to the solution of the aniline in one portion and the mixture allowed to stir at 22 ºC for 10 min. A separate 25-mL round-bottom flask with stir bar was charged with allylic bromide **H** (1.77 g, 9.28 mmol, 2.00 equiv) and THF (9 mL) and the mixture allowed to cool to 0 ºC. The THF solution of the potassium amide was added dropwise over 1 h to bromide **H** by syringe pump; THF (0.5 mL) was used to rinse any remaining potassium amide from the syringe and added similarly to the reaction mixture. The resulting mixture was allowed to stir at 0 °C for 1 h, then quenched by addition of H_2O (10 mL) and transferred to a separatory funnel. The organic layer was separated and the aqueous layer washed with Et_2O (3 x 20 mL). The combined organic layers were washed with saturated aqueous NaCl (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude residue was purified by silica gel column chromatography (30:1 pet ether:Et_2O) to afford **12** (847 mg, 2.72 mmol, 58.6% yield) as a colorless oil. IR (neat): 3073 (m), 3024 (w), 2968 (m), 2915 (m), 2850 (m), 1647 (m), 1596 (s), 1501 (s), 1446 (m), 1394 (m), 1373 (m), 1347 (m), 1347 (m), 1213 (m), 1142 (m), 1080 (s), 924 (s), 886 (s), 690 (s); ^1H NMR (400 MHz, C_6D_6): δ 7.24-7.17 (2H, m), 6.77-6.73 (2H, m), 6.69 (1H, tt, J = 7.2, 1.2 Hz), 5.98 (1H, ddt, J = 17.2, 10.4, 5.6 Hz), 5.66-5.59 (1H, m), 5.56-5.50 (1H, m), 5.34 (1H, ddd, J = 17.2, 3.6, 1.6 Hz), 5.24 (1H, ddd, J = 10.4, 3.2, 1.2 Hz), 4.77 (2H, br s), 4.73 (2H, br s), 4.23 (1H, quintet, J = 7.2 Hz), 4.15 (2H, dd, J = 6.4, 1.6 Hz), 4.06 (2H, ddd, 5.6, 1.2, 1.2 Hz), 3.90-3.86 (2H, m), 2.29 (2H, dd, J = 14.4, 7.6 Hz), 2.23 (2H, dd, J = 14.4, 6.8 Hz), 1.73 (6H, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 143.0, 134.8, 133.5, 129.2, 126.6, 117.2, 116.6, 113.5, 112.7, 71.5, 66.0, 54.7, 41.3, 40.8, 22.5; HRMS (ESI^+) $[M+H]^+$ calcd for $C_{22}H_{31}NO$: 326.2484, found: 326.2492.

Enantioselective RCM of Tetraene 12 (eq 2):

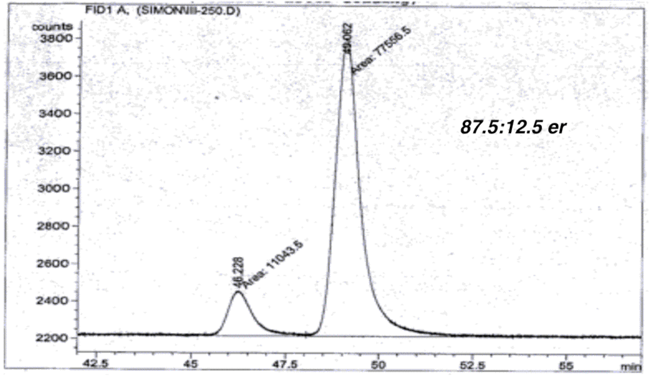


(*S*)-4-Methyl-2-(2-methylallyl)-1-phenyl-1,2,3,6-tetrahydropyridine (6). Following the general procedure, substrate **12** (7.00 mg, 22.5 μmol, 1.00 equiv) was treated with chiral complex *S*-**1** (1.3 mg, 1.12 μmol, 0.0500 equiv) in C_6H_6 (225 μL). The vial was tightly capped and the solution was allowed to stir for 1 h at 22 ºC. At this time, the reaction vessel was removed from the dry box and the reaction quenched by the addition of benchtop Et_2O (1 mL). The mixture concentrated *in vacuo*. The unpurified brown solid was dissolved in minimal

MeOH (0.5 mL), and KF (4.80 mg, 0.0830 mmol, 74.1 equiv with respect to *S*-**1**) was added (to desilylate the phenol ligand **4**, which has the same R_f as **6**). The mixture was allowed to stir for 30 min at 22 °C. Silica gel was added and the mixture concentrated *in vacuo* and purified by silica gel chromatography (50:1 pet ether:Et_2O) to afford *S*-**6** (4.3 mg, 18.9 μmol, 84.0% yield) as a white solid. The physical and spectral data were identical to those previously reported for compound **6**.[1] The enantiomeric purity of **6** (90:10 er) was determined by GLC analysis (CDGTA column, 20 psi, 130 °C) in comparison with authentic racemic material.

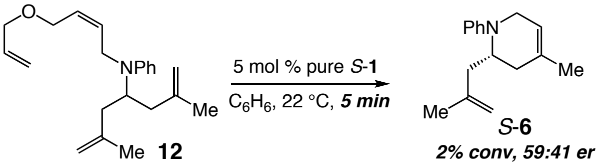


```
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
  1   46.497 MF    0.7533 3.18080e4  703.75873  9.32091
  2   49.417 FM    0.8019 3.09446e5 6431.90234 90.67909
```

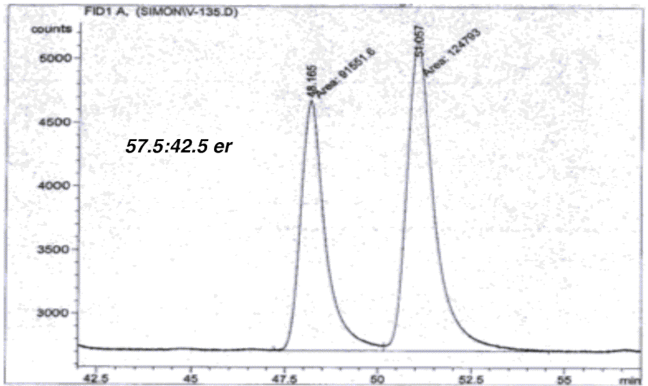


```
Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
  1   46.228 MF    0.7586 1.10435e4  242.62390 12.46439
  2   49.062 FM    0.8101 7.75565e4 1595.58130 87.53561
```

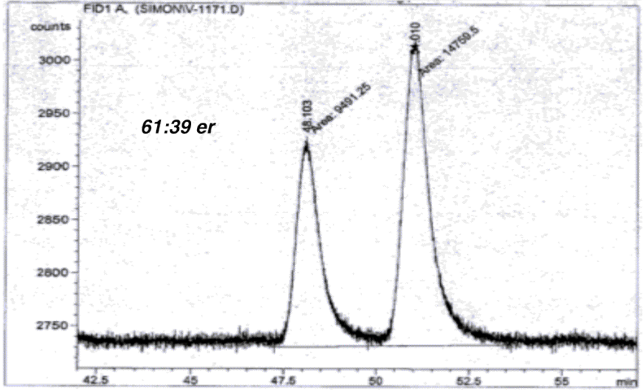
Enantioselective RCM of Tetraene 12 at 2% Conversion (eq 6):



(*S*)-4-Methyl-2-(2-methylallyl)-1-phenyl-1,2,3,6-tetrahydropyridine (6). Following the general procedure, substrate **12** (12.9 mg, 41.4 μmol, 1.00 equiv) was treated with chiral complex *S*-**1** (2.4 mg, 2.07 μmol, 0.0500) in C_6H_6 (414 μL). The vial was tightly capped and the solution allowed to stir for 5 min at 22 ºC. At this time, the reaction vessel was removed from the dry box and the reaction quenched by the addition of benchtop Et_2O (1 mL). The solution concentrated *in vacuo*. The product was barely visible by 400 MHz ^1H NMR analysis but was easily visualized by TLC (hexanes:Et_2O 50:1, R_f ~0.4, UV: –254 nm and CAM stain). The unpurified brown solid was dissolved in minimal MeOH (0.5 mL), and KF (4.80 mg, 0.0830 mmol, 40.0 equiv with respect to *S*-**1**) was added (to desilylate the phenol **4**, which has the same R_f as **6**). The mixture was allowed to stir for 30 min at 22 ºC. Silica gel was added and the mixture concentrated *in vacuo* and purified by silica gel chromatography (50:1 pet ether:Et_2O) to afford *S*-**6** as a white solid.

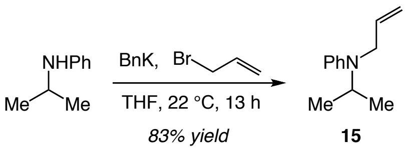


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]  counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
  1  48.165 MF    0.7729 9.15516e4 1974.14453 42.31748
  2  51.057 FM    0.8512 1.24793e5 2443.54590 57.68252
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]  counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
  1  48.103 MF    0.7937 9491.24609  199.30679 39.13794
  2  51.010 FM    0.8456 1.47595e4   290.90262 60.86206
```

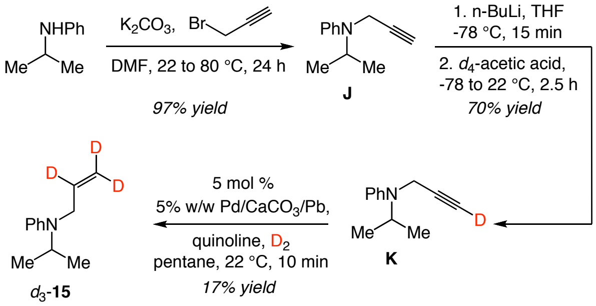
Synthesis of Allylamine 15:



***N*-allyl-*N*-isopropylaniline (15):** A 50-mL round-bottom flask with magnetic stir bar was brought into an N_2-filled dry box, charged with benzyl potassium (900 mg, 6.91 mmol, 1.00 equiv), sealed, and brought to the fume hood. THF (13 mL) was added and the mixture allowed to stir. *N*-Isopropylaniline (1.00 mL, 6.91 mmol, 1.00 equiv) was added dropwise by syringe; a light orange color remained. Allyl bromide (1.80 mL, 20.8 mmol, 3.00 equiv) was added dropwise by syringe (caution: the reaction is exothermic and should be cooled); LiBr precipitated immediately. The mixture was allowed to stir for 13 h at 22 ºC at which time it was quenched by the addition of H_2O (20 mL). The solution was washed with Et_2O (3 x 25 mL). The combined organic layers were washed with H_2O (2 x 50 mL) and saturated aqueous NaCl (50 mL), then dried over $MgSO_4$, filtered, and concentrated *in vacuo* to light yellow oil. The material was purified by silica gel chromatography (50:1 hexanes:Et_2O) to afford **15** (1.01 g, 5.76 mmol, 83.4% yield) as a light yellow oil. IR (neat): 2970 (s), 2929 (w), 2872 (w), 1595 (s), 1572 (w), 1502 (s), 1464 (m), 1390 (s), 1365 (m), 1348 (m), 1330 (m), 1314 (m), 1300 (m), 1249 (s), 1187 (s), 1160 (m), 1122 (m), 1087 (w), 1035 (m), 1002 (m), 985 (m), 919 (s), 744 (s), 691 (s); ^1H

NMR (400 MHz, $CDCl_3$): δ 7.22-7.18 (2H, m), 6.76-6.72 (2H, m), 6.67 (1H, dd, *J* = 7.2, 7.2 Hz), 5.89 (1H, dddd, *J* = 17.2, 10.4, 4.4, 4.4 Hz), 5.23 (1H, ddd, *J* = 17.2, 1.6, 1.6 Hz), 5.13 (1H, ddd, *J* = 10.4, 2.0, 2.0 Hz), 4.13 (1H, septet, *J* = 6.4 Hz), 3.82-3.78 (2H, m), 1.18 (6H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 136.9, 129.2, 116.2, 115.3, 113.1, 48.0, 46.9, 20.0; HRMS (ESI$^+$) $[M+H]^+$ calcd for $C_{12}H_{18}N$: 176.1439, found 176.1432.

Synthesis of Substrate *d*$_3$-15:[10]



***d*$_3$-*N*-allyl-*N*-isopropylaniline (*d*$_3$-15):** A 100-mL round-bottom flask with magnetic stir bar was charged with *N*-isopropylaniline (1.00 mL, 6.91 mmol, 1.00 equiv) and DMF (35 mL); the mixture was allowed to stir. K_2CO_3 (1.43 g, 10.3 mmol, 1.50 equiv) was added quickly in one portion; much of the K_2CO_3 remained undissolved. Propargyl bromide (1.85 mL, 80% w/w in toluene, 20.8 mmol, 3.00 equiv) was added dropwise by syringe. The vessel was fitted with a flame-dried reflux condenser and the mixture heated to 80 °C. After 20 h, the mixture was allowed to cool to 22 °C and was diluted with H_2O (50 mL). The mixture was washed with EtOAc (3 x 75 mL). The combined organic layers were washed with H_2O (2 x 175 mL) and saturated aqueous NaCl (175 mL), then dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yellow oil. The material was purified by silica gel chromatography (30:1 hexanes:Et_2O) to afford **J** (1.16 g, 6.69 mmol, 96.9% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.23 (2H, m), 6.94-6.89 (2H, m), 6.77 (1H, ddd, *J* = 7.2, 7.2, 0.8 Hz), 4.11 (1H, septet, *J* = 6.8 Hz), 3.95 (2H, d, *J* = 2.4 Hz), 2.17 (1H, dd, *J* = 2.4, 2.4 Hz), 1.26 (6H, d, *J* = 6.4 Hz).

A 100-mL round-bottom flask with magnetic stir bar was charged with alkyne **J** (1.16 g, 6.69 mmol, 1.00 equiv) and THF (25 mL). The mixture was allowed to stir and cool to -78 °C; the mixture was yellow. *n*-BuLi (4.70 mL, 1.56 M in hexanes, 7.33 mmol, 1.10 equiv) was added dropwise by syringe. After 15 min, *d*$_4$-acetic acid (540 mL, 10.0 mmol, 1.49 equiv) was added dropwise (syringe) and the mixture was allowed to warm to 22 °C. After 2.5 h, the reaction was quenched by the addition of H_2O (20 mL). The mixture was washed with Et_2O (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yellow oil, which was purified by silica gel chromatography (30:1 hexanes:Et_2O) to deliver **K** (817 mg, 4.69 mmol, 70.1% yield) as a yellow oil. ^1H NMR (400 MHz) indicated >98% deuterium incorporation. ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.23 (2H, m), 6.94-6.89

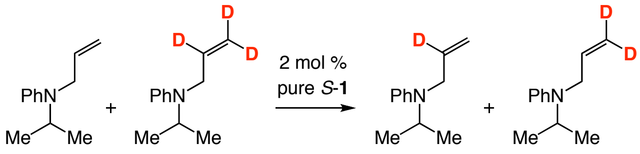
---

(10) For an example of deuterium incorporation into an olefin through Lindlar reduction of an alkyne, see: Ridgway, B. H.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 458–460.

(2H, m), 6.77 (1H, dd, *J* = 7.2 Hz), 4.11 (1H, septet, *J* = 6.8 Hz), 3.95 (2H, s), 1.26 (6H, d, *J* = 6.8 Hz).

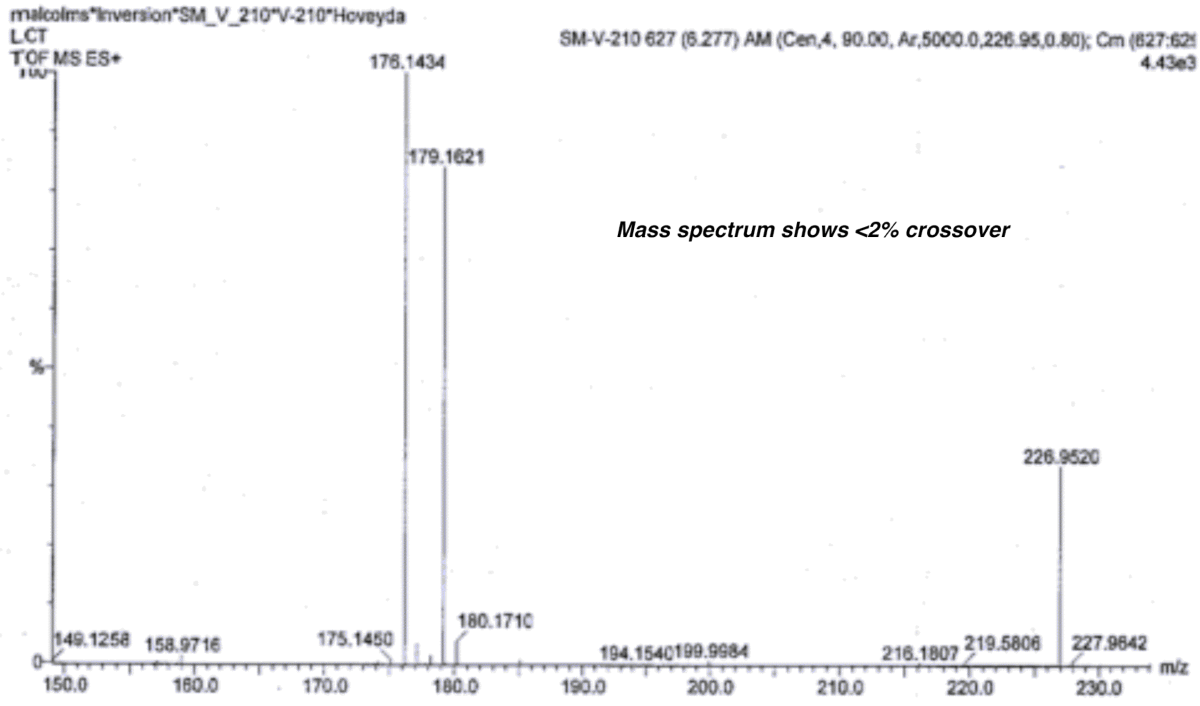
A 50-mL round-bottom flask with magnetic stir bar was charged with Lindlar's catalyst (5% w/w Pd on $CaCO_3$ poisoned with Pb, 123 mg, 0.0580 mmol, 0.0500 equiv), pentane (20 mL), d_1-alkyne **K** (202 mg, 1.16 mmol, 1.00 equiv), and quinoline (137 mL, 1.16 mmol, 1.00 equiv). The mixture was allowed to stir and the atmosphere was purged with a balloon of D_2. The reaction vessel was fitted with a balloon of D_2. After 10 min at 22 °C, the balloon was removed and the vessel was flushed with N_2. The mixture was passed through a plug of Celite® (eluted with Et_2O) and concentrated *in vacuo* to a lightly yellow oil. The mixture was purified by silica gel chromatography (70:1 hexanes:Et_2O) to afford d_3-**15** (35.0 mg, 0.196 mmol, 16.9% yield). ^{1}H NMR (400 MHz) indicated >98% deuterium incorporation. IR (neat): 3023 (s), 2971 (w), 2928 (w), 1598 (s), 1504 (s), 1464 (w), 1391 (m), 1365 (w), 1349 (m), 1330 (m), 1314 (m), 1250 (m), 1189 (s), 1160 (w), 1041 (w), 747 (s), 715 (m), 691 (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.18 (2H, m), 6.76-6.72 (2H, m), 6.67 (1H, ddd, *J* = 7.2, 7.2, 1.2 Hz), 4.13 (1H, septet, *J* = 6.8 Hz), 3.79 (2H, s), 1.18 (6H, d, *J* = 6.4 Hz); ^{2}H NMR (76.7 MHz, $CDCl_3$): δ 5.391 (1D, br s), 5.25 (1D, br s), 5.15 (1D, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 136.4 (t, $J_{C\text{–}D}$ = 23.6 Hz), 129.2, 116.2, 114.7 (dt, $J_{C\text{–}D}$ = 47.8, 23.9 Hz), 113.1, 48.0, 46.8, 20.0; HRMS (ESI$^+$) $[M+H]^+$ calcd for $C_{12}{}^1H_{15}{}^2H_3N$: 179.1628, found: 179.1631.

Crossover Experiment in eq 3:



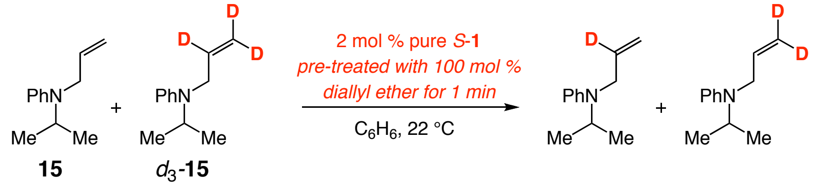
15 d_3-**15**

In an N_2-filled dry box, a 4-mL vial with stir bar was charged with **15** (5.2 mg, 30 μmol, 1.2 equiv), d_3-**15** (4.5 mg, 25 μmol, 1.0 equiv), and C_6H_6 (450 μL). A 4-mL vial was charged with (*S*)-**1**·*n*-pentane (1.2 mg, 1.1 μmol, 0.020 equiv with respect to **15** + d_3-**15**) and C_6H_6 (55 μL). The catalyst solution was transferred to the reaction mixture by a pipet; the vial containing the catalyst was rinsed with C_6H_6 (45 μL) and similarly transferred. The vial was tightly capped and the mixture was allowed to stir for 30 min at 22 °C. The vessel was removed from the dry box and the reaction quenched by the addition of benchtop Et_2O (~0.5 mL). The mixture was concentrated *in vacuo* to afford brown oil, which was dissolved in MeOH (~0.5 mL). KF (19.1 mg, 0.330 mmol, 300 equiv with respect to *S*-**1**) was added in order to remove the silyl group of the phenol ligand **4**. After the sample was allowed to stand for 30 min at 22 °C, silica gel was added and the mixture concentrated *in vacuo* and purified by silica gel chromatography (50:1 hexanes:Et_2O). A mixture of **15** and d_3-**15** was recovered as colorless oil (6.3 mg, 36.0 μmol, 65% recovery). High-resolution mass spectroscopic analysis indicated that crossover to generate d_1-**15** and d_2-**15** had not occurred. HRMS (ESI$^+$) $[M+H]^+$ calcd for $C_{12}H_{18}N$: 176.1439, found: 176.1437; calcd for $C_{12}{}^1H_{17}{}^2H_1N$: 177.1502, not found; calcd for $C_{12}{}^1H_{16}{}^2H_2N$: 178.1565, not found; calcd for $C_{12}{}^1H_{15}{}^2H_3N$: 179.1628, found: 179.1624.



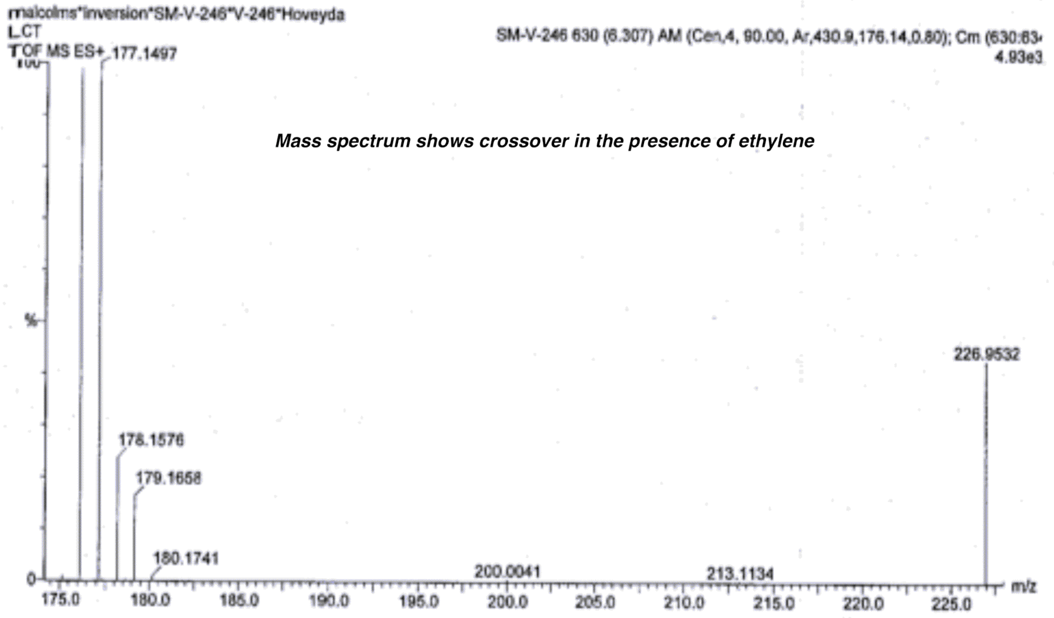
Mass spectrum shows <2% crossover

Crossover Experiment in the Presence of Ethylene:



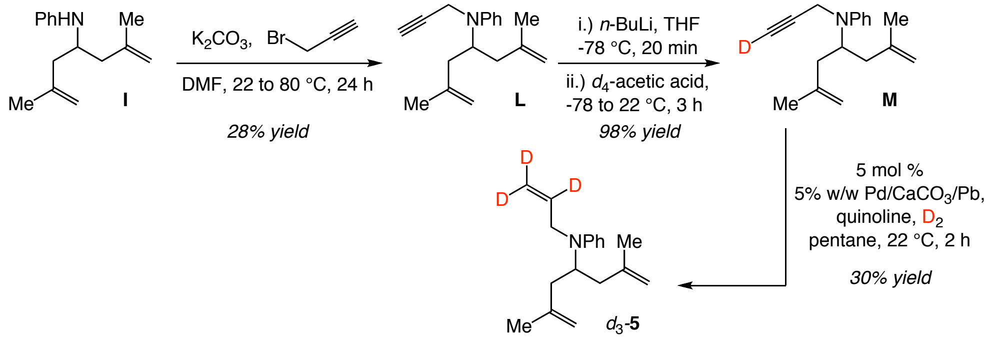
In an N_2-filled dry box, a 2-mL vial with stir bar was charged with **15** (6.0 mg, 34 μmol, 1.1 equiv), ***d*₃-15** (5.4 mg, 30 μmol, 1.0 equiv), and C_6H_6 (100 μL). A 4-mL vial was charged with (*S*)-**1**·*n*-pentane (1.5 mg, 1.3 μmol, 0.020 equiv with respect to **15** + ***d*₃-15**) and C_6H_6 (340 μL). Diallyl ether (8 μL, 65 μmol, 1.0 equiv with respect to **15** + ***d*₃-15**) was added to the catalyst solution by syringe. The vial was tightly capped and the mixture was allowed to stir for one minute at 22 °C. At that time, the solution of **15** + ***d*₃-15** was transferred to the reaction mixture by a pipet; the vial containing the catalyst was rinsed with C_6H_6 (2 x 100 μL) and similarly transferred. The vial was tightly capped and the mixture was allowed to stir for 30 minutes at 22 °C. The vessel was removed from the dry box and the reaction quenched by the addition of benchtop Et_2O (~1 mL). The mixture was concentrated *in vacuo* to furnish brown oil, which was dissolved in MeOH (~0.5 mL). KF (22.7 mg, 0.390 mmol, 300 equiv with respect to *S*-**1**) was added in order to remove the silyl unit of the phenol ligand **4**. After standing for 30 min at 22 °C, silica gel was added and the mixture concentrated *in vacuo*; the resulting tan-colored solid was purified by silica gel chromatography (50:1 hexanes:Et_2O). A mixture of **15**, ***d*₁-15**, ***d*₂-15**, and ***d*₃-15** (unquantifiable ratio) was recovered as colorless oil (8.2 mg, ~46.0 μmol, ~72% recovery). High-resolution mass spectroscopic analysis indicated that cross-over to generate *d*₁-**15** and *d*₂-**15** had occurred. HRMS (ESI$^+$) $[M+H]^+$ calcd for $C_{12}H_{18}N$: 176.1439, found:

176.1434; calcd for $C_{12}{}^1H_{17}{}^2H_1N$: 177.1502, found: 177.1497; calcd for $C_{12}{}^1H_{16}{}^2H_2N$: 178.1565, found: 178.1564; calcd for $C_{12}{}^1H_{15}{}^2H_3N$: 179.1628, found: 179.1634.



Mass spectrum shows crossover in the presence of ethylene

Synthesis of Triene d_3-5:[10]

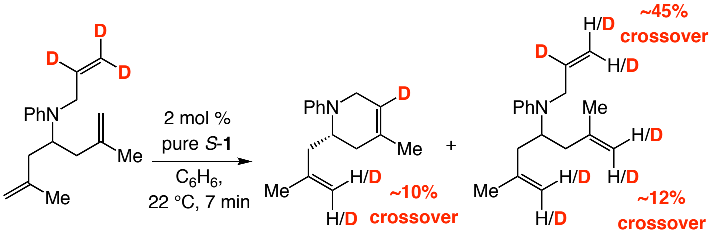


***d_3-N*-allyl-*N*-(2,6-dimethylhepta-1,6-dien-4-yl)aniline (d_3-5):** A 25-mL round-bottom flask with magnetic stir bar was charged with K_2CO_3 (733 mg, 5.30 mmol, 1.50 equiv) and DMF (5 mL); the mixture was allowed to stir. A solution of aniline **I** (761 mg, 3.53 mmol, 1.00 equiv) in DMF (1 mL) was added by cannula (flask containing aniline **I** was rinsed with 1 mL DMF and similarly transferred). Propargyl bromide (1.75 mL, 80% w/w in toluene, 14.1 mmol, 3.99 equiv) was added dropwise by syringe; the mixture became orange. The reaction vessel was fitted with a flame-dried reflux condenser and the mixture heated to 80 °C. After 24 h, the mixture was allowed to cool to 22 °C and was diluted with H_2O (10 mL). The mixture was washed with EtOAc (4 x 40 mL). The combined organic layers were washed with H_2O (125 mL) and saturated aqueous NaCl (125 mL), then dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yellow oil. The material was purified by silica gel chromatography (100:1 hexanes:Et_2O) to afford **L** (254 mg, 1.00 mmol, 28.3% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (2H, m), 6.98-6.90 (2H, m), 6.77 (1H, dd, J = 7.2, 7.2 Hz), 4.79 (4H, apparent s), 4.28 (1H, quintet, *J* = 7.2 Hz), 3.97 (2H, d, *J* = 2.4 Hz), 2.44-2.32 (4H, m), 2.15 (1H, dd, *J* = 2.4, 2.4 Hz), 1.77 (6H, s).

A 25-mL round-bottom flask with magnetic stir bar was charged with alkyne **L** (254 mg, 1.00 mmol, 1.00 equiv) and THF (4 mL). The mixture was allowed to stir and cool to -78 °C; the mixture was yellow. *n*-BuLi (710 mL, 1.56 M in hexanes, 1.11 mmol, 1.11 equiv) was added dropwise by syringe; the mixture became orange After 20 min, d_4-acetic acid (80 mL, 1.49 mmol, 1.49 equiv) was added dropwise by syringe and the mixture once again became yellow. The mixture was allowed to warm to 22 °C. After 3 h, the reaction was quenched by the addition of H_2O (10 mL). The mixture was washed with Et_2O (3 x 25 mL). The combined organic layers were washed with H_2O (75 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to a yellow oil, which was purified by silica gel chromatography (70:1 hexanes:Et_2O) to deliver **M** (250 mg, 0.983 mmol, 98.3% yield) as a yellow oil. ^1H NMR (400 MHz) indicated >98% incorporation of deuterium. ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (2H, m), 6.98-6.90 (2H, m), 6.77 (1H, dd, *J* = 7.2, 7.2 Hz), 4.79 (4H, apparent s), 4.28 (1H, quintet, *J* = 7.2 Hz), 3.97 (2H, s), 2.44-2.32 (4H, m), 1.77 (6H, s).

A round-bottom flask with magnetic stir bar was charged with Lindlar's catalyst (5% w/w Pd on $CaCO_3$ poisoned with Pb, 102 mg, 0.0480 mmol, 0.0500 equiv), pentane (14 mL), d_1-alkyne **M** (244 mg, 0.959 mmol, 1.00 equiv), and quinoline (115 mL, 0.973 mmol, 1.01 equiv). The mixture was allowed to stir and the atmosphere was purged with a balloon of D_2. The reaction vessel was then fitted with a balloon of D_2. After 2 h at 22 °C, the balloon was removed and the reaction vessel was flushed with N_2. The mixture was passed through a plug of Celite® (eluted with Et_2O) and concentrated *in vacuo* to a light yellow oil. The mixture was purified by silica gel chromatography (top half of solid phase was 15% w/w $AgNO_3$-impregnated silica gel, bottom half was silica gel, 1:1 hexanes:Et_2O) to afford d_3-**5** (74.0 mg, 0.286 mmol, 29.8% yield). ^1H NMR (400 MHz) indicated >98% incorporation of deuterium. IR (neat): 3211 (w), 3072 (w), 2968 (w), 2917 (w), 2852 (w), 1648 (w), 1597 (s), 1501 (s), 1445 (m), 1393 (m), 1373 (m), 1346 (m), 1321 (m), 1291 (m), 1250 (m), 1214 (m), 1175 (w), 1147 (m), 1038 (w), 987 (w), 957 (w), 886 (s), 745 (s), 713 (s), 689 (s); ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.16 (2H, m), 6.82-6.76 (2H, m), 6.68 (1H, dd, *J* = 7.2, 7.2 Hz), 4.76 (2H, s), 4.73 (2H, s), 4.24 (1H, quintet, *J* = 7.2 Hz), 3.84 (2H, s), 2.30 (2H, dd, J_{AB} = 14.4 Hz, J_{AX} = 7.2 Hz), 2.23 (2H, dd, J_{AB} = 14.4 Hz, J_{BX} = 7.2 Hz), 1.73 (6H, s); ^2H NMR (76.7 MHz, $CDCl_3$): δ 5.83 (1D, br s), 5.22 (1D, br s), 5.13 (1D, br s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 143.2, 136.4 (t, J_{C-D} = 23.5 Hz), 129.1, 116.6, 115.3 (dt, J_{C-D} = 47.5, 23.9 Hz), 113.8, 112.7, 54.8, 46.5, 40.9, 22.6; HRMS (ESI$^+$) $[M+H]^+$ calcd for $C_{18}{}^1H_{23}{}^2H_3N$: 259.2254, found: 259.2257.

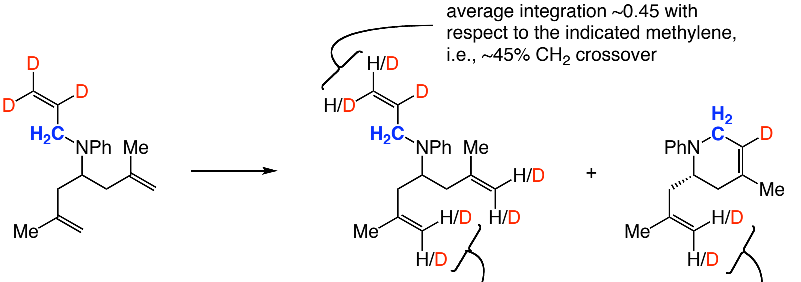
Enantioselective RCM Crossover Experiment in eq 4:



d_3-**5** d_1/d_3-**6** *56% conv, 95.5:4.5 er* **34%**

In an N_2-filled dry box, a 4-mL vial with stir bar was charged with **5** (9.8 mg, 38 μmol, 1.0 equiv), and C_6H_6 (280 μL). A 2-mL vial was charged with (*S*)-**1**·*n*-pentane (0.9 mg, 0.76 μmol, 0.020 equiv) and C_6H_6 (50 μL). The catalyst solution was transferred to the reaction mixture by pipet; the vial containing the catalyst was rinsed with C_6H_6 (50 μL) and similarly transferred. The vial was tightly capped and the mixture was allowed to stir for 7 min. The reaction vessel was removed from the dry box and the reaction quenched by the addition of benchtop Et_2O (~0.5 mL). The mixture was concentrated *in vacuo* to brown oil. ^{1}H NMR analysis (400 MHz) indicated 56% conversion to **6** plus remaining **5**. The mixture was dissolved in MeOH (~0.5 mL) and KF (13.2 mg, 0.228 mmol, 300 equiv with respect to *S*-**1**) was added in order to desilylate the phenol ligand **4**, which has the same R_f as **6**. After standing for 30 min at 22 ºC, silica gel was added and the mixture concentrated *in vacuo* and purified by silica gel chromatography (hexanes to elute **5** and then 50:1 hexanes:Et_2O to elute **6**). $d_1/d_3/d_5/d_7$-**5** (3.3 mg, ~13.0 μmol, ~34% recovery) was obtained as a colorless oil and $d_1/d_3/d_5$-**6** (4.4 mg, ~19 μmol, ~50% yield) obtained as a white solid. The spectral data for **5** and **6** were identical to those detailed previously except for deuterium incorporation at the relevant sites (see below). The enantiomeric purity of **6** (95.5:4.5 er) was determined by GLC analysis (CDGTA column, 20 psi, 130 °C) in comparison with authentic racemic material.

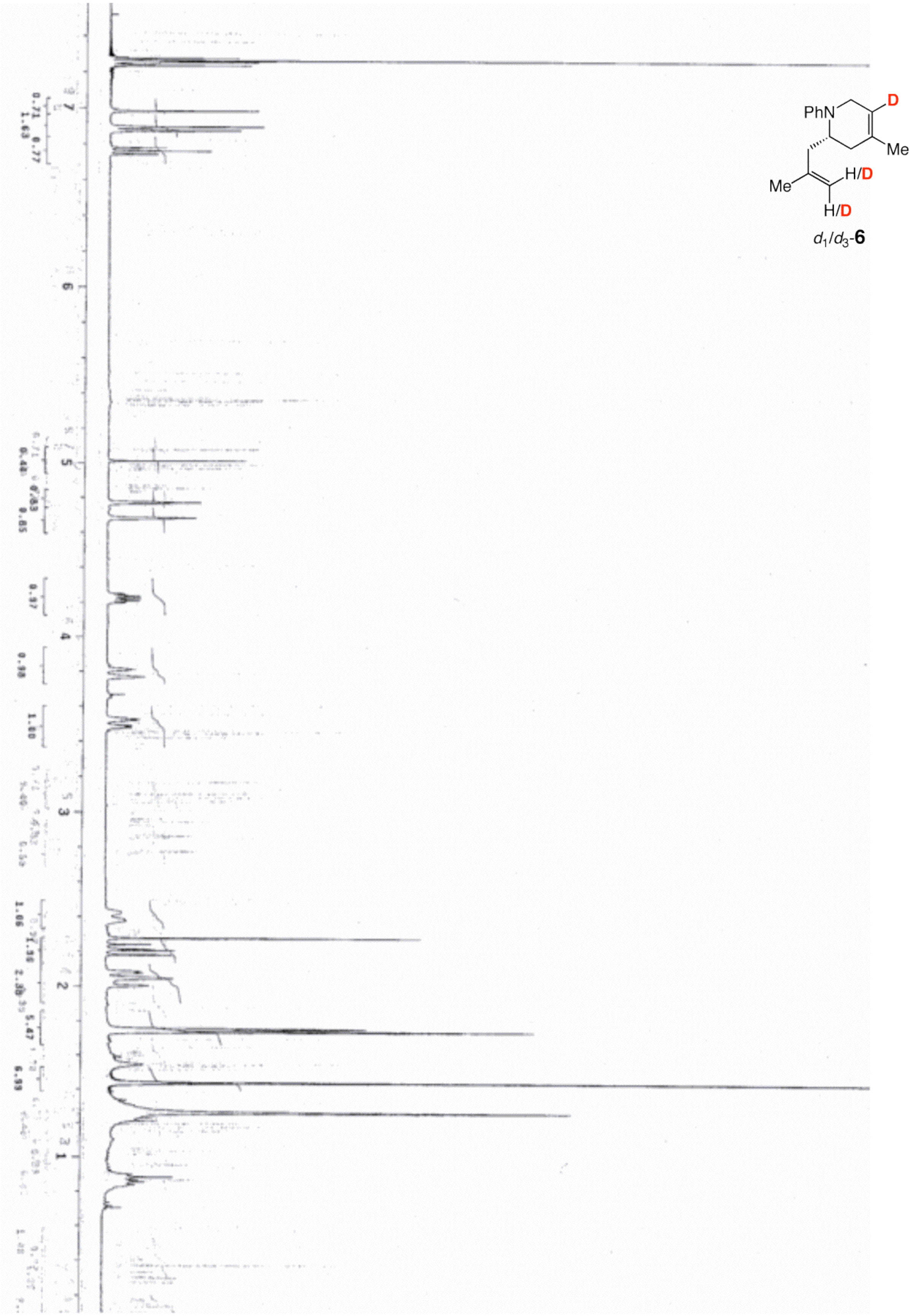
average integration ~0.45 with respect to the indicated methylene, i.e., ~45% CH_2 crossover



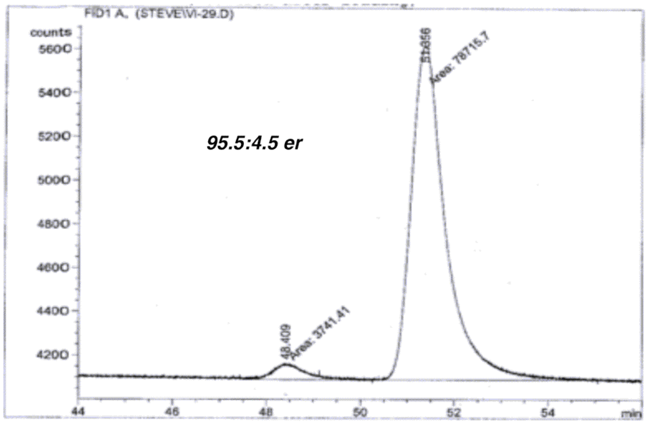
d_3-**5** d_1,d_3,d_5,d_7-**5** d_1,d_3-**5**

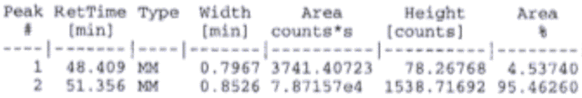
average integration ~1.76 with respect to the indicated methylene, i.e., ~12% CD_2 crossover

average integration ~0.90 with respect to the indicated methylene, i.e., ~10% CD_2 crossover


7
6
5
4
3
2
1
0.71
0.77
1.63
0.48
0.83
0.85
0.97
0.98
1.00
1.06
1.56
2.80
5.47
6.99
PhN
D
Me
H/D
Me
H/D

d$_1$/*d*$_3$-**6**





```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1  48.409 MM    0.7967 3741.40723   78.26768  4.53740
   2  51.356 MM    0.8526 7.87157e4  1538.71692 95.46260
```

■ Addendum to Reference 10:

Additional examples of Curtin-Hammett kinetics reported in the connection with catalytic enantioselective reactions:

(1) MacNeil, P. A.; Roberts, N. K.; Bosnich, B. *J. Am. Chem. Soc.* **1981**, *103*, 2273–2280.

(2) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.

(3) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046–2054.

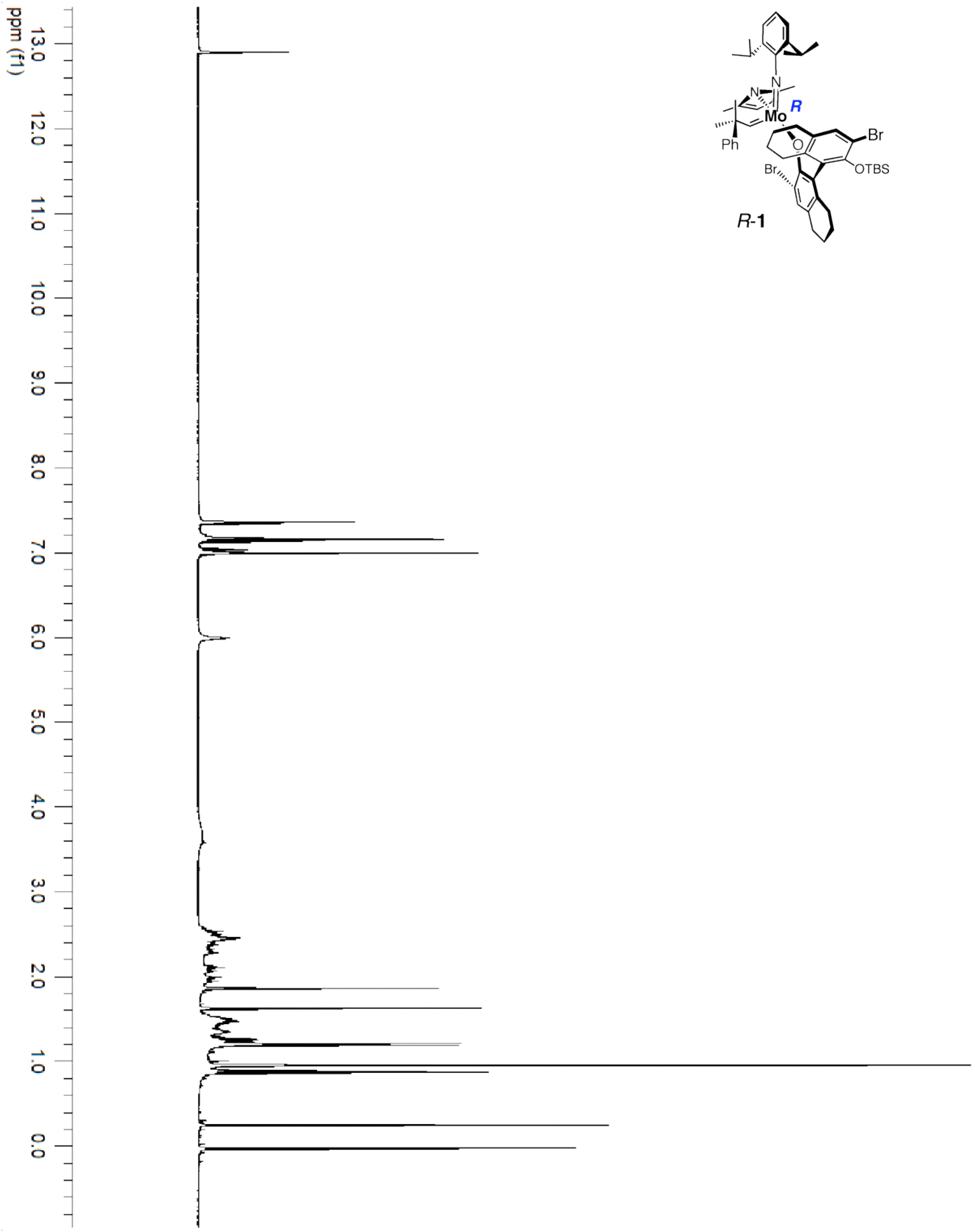
(4) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 4545–4554.

(5) Hughes, D. L.; Palucki, M.; Yasuda, N.; Reamer, R. A.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 2762–2768.

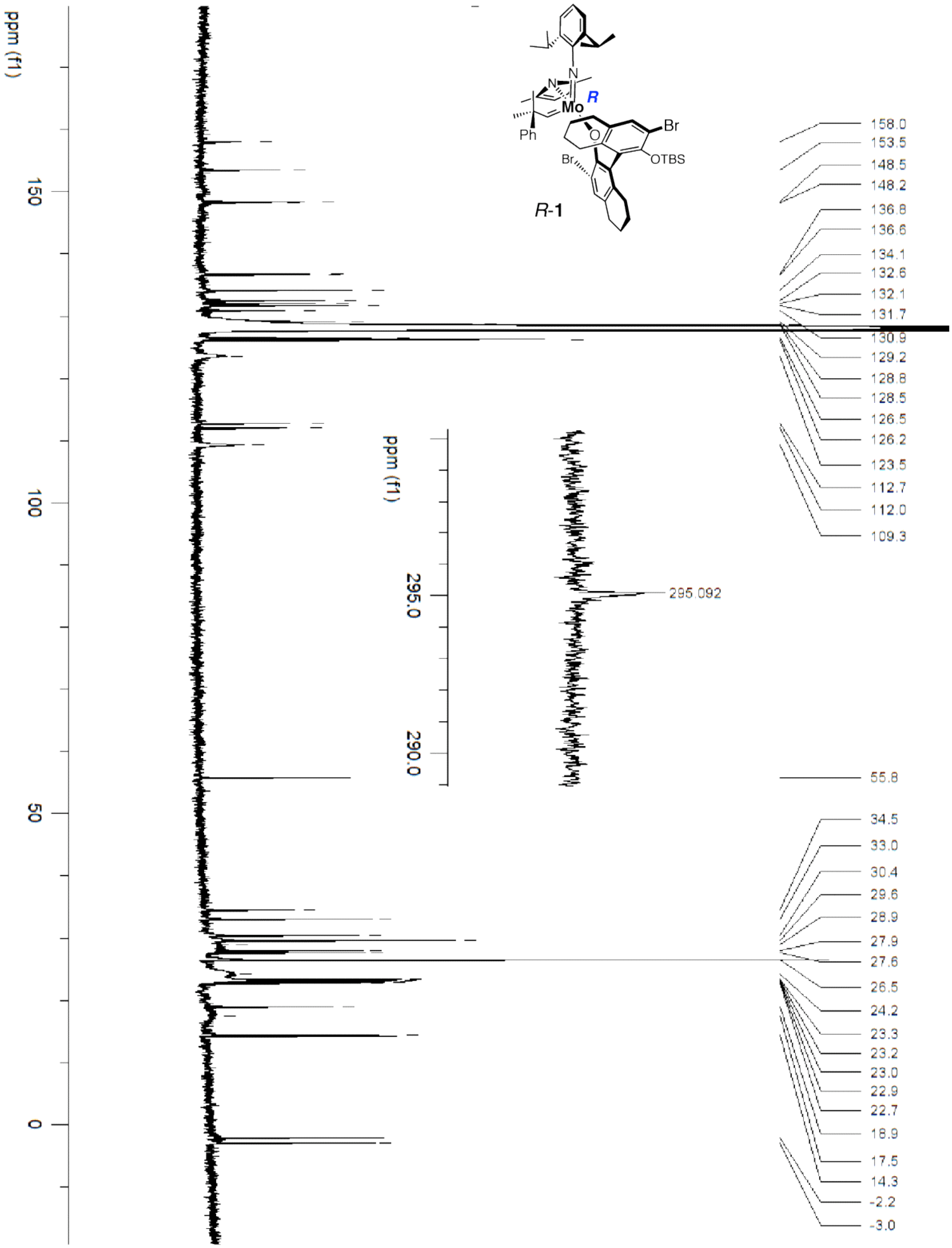
(6) Solladié-Cavallo, A.; Jierry, L.; Klein, A.; Schmitt, M.; Welter, R. *Tetrahedron: Asymmetry* **2004**, *15*, 3891–3898.

(7) Denmark, S. E.; Bui, T. *J. Org. Chem.* **2005**, *70*, 10393–10399.

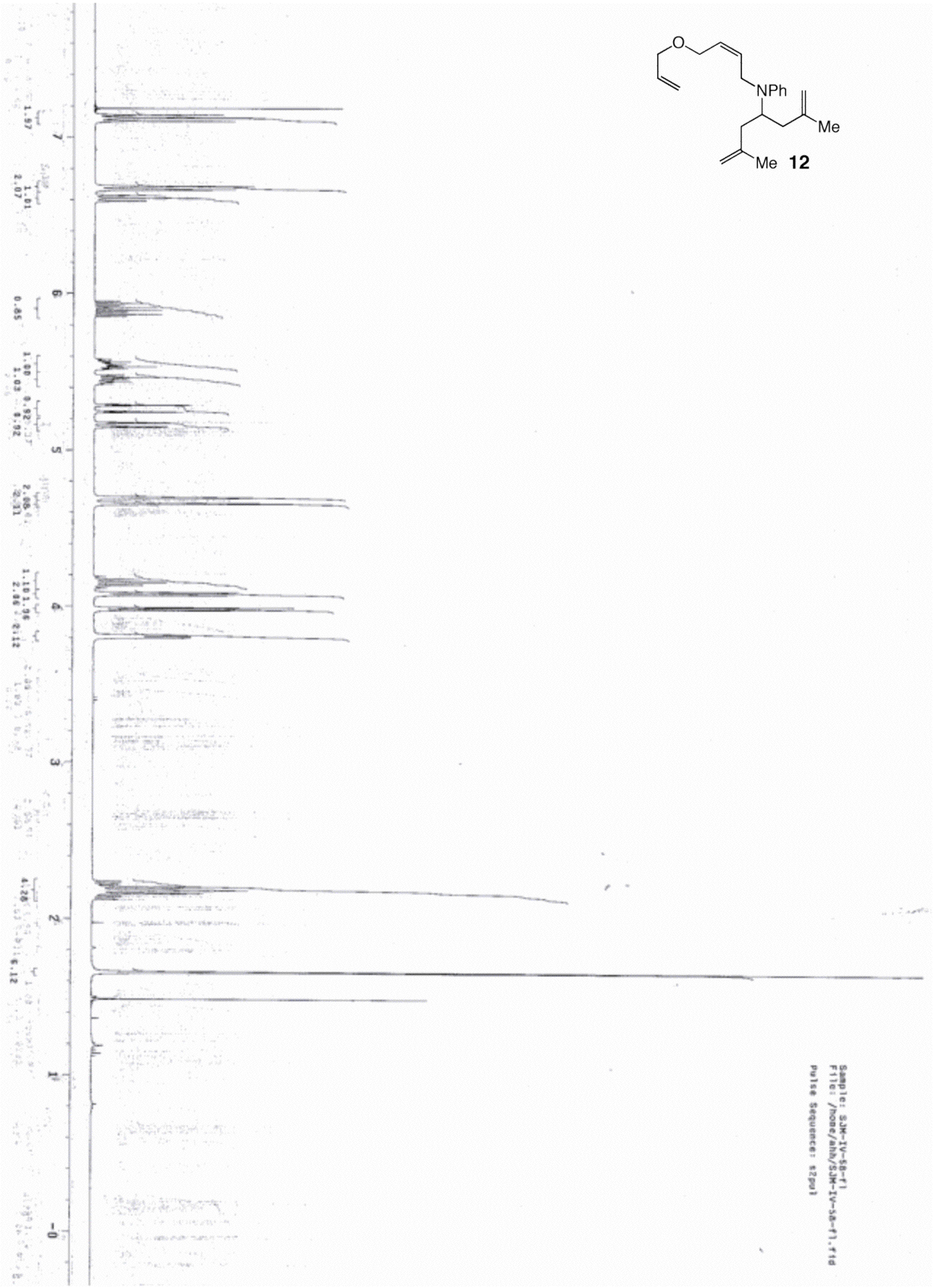
(8) Blank, N. F.; Moncarz, J. R.; Brunker, T. J.; Scriban, C.; Anderson, B. J.; Amir, O.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2007**, *129*, 6847–6858.


ppm (f1)
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
N
N
Mo
R
Br
O
OTBS
Br
Ph

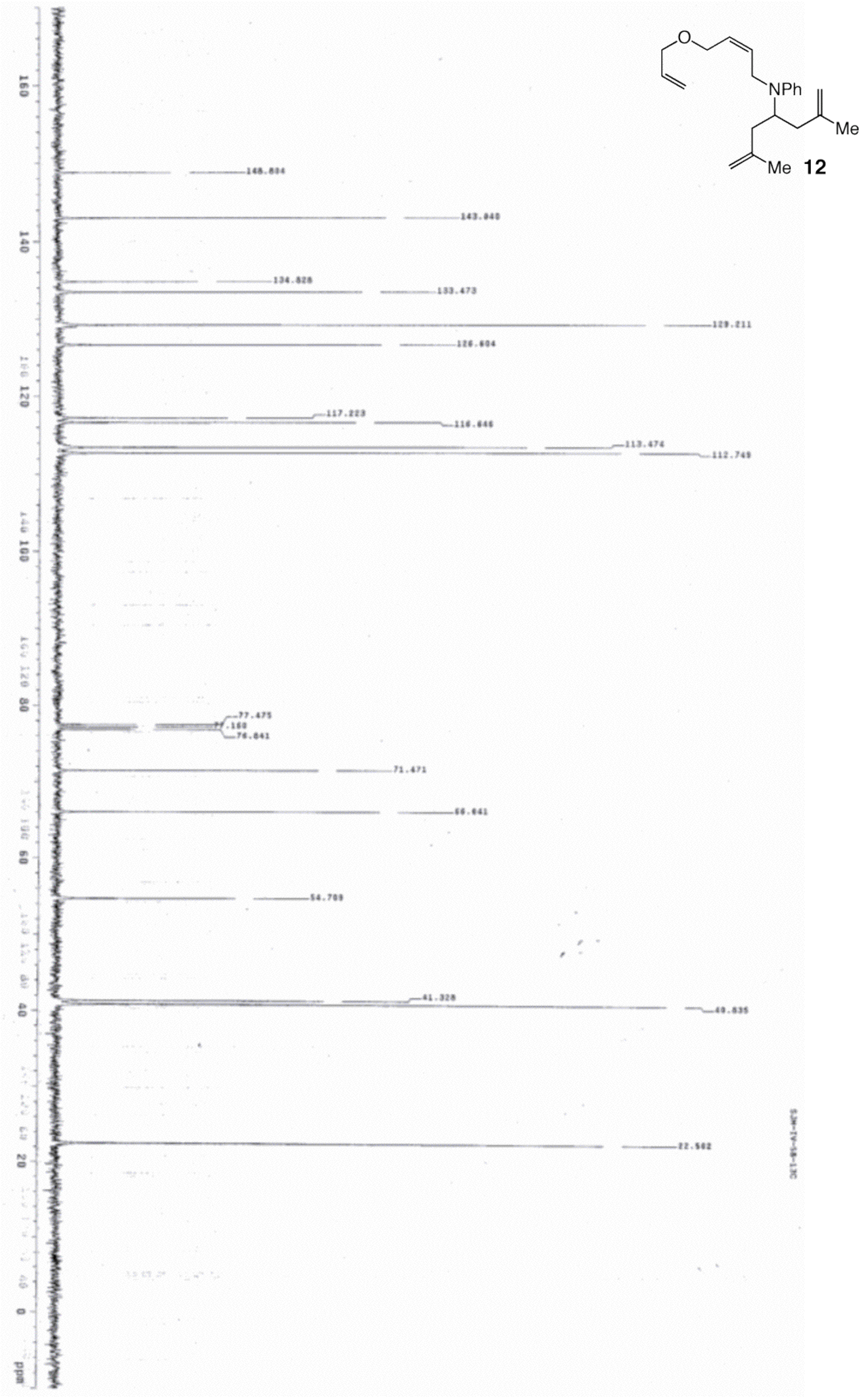
R-**1**

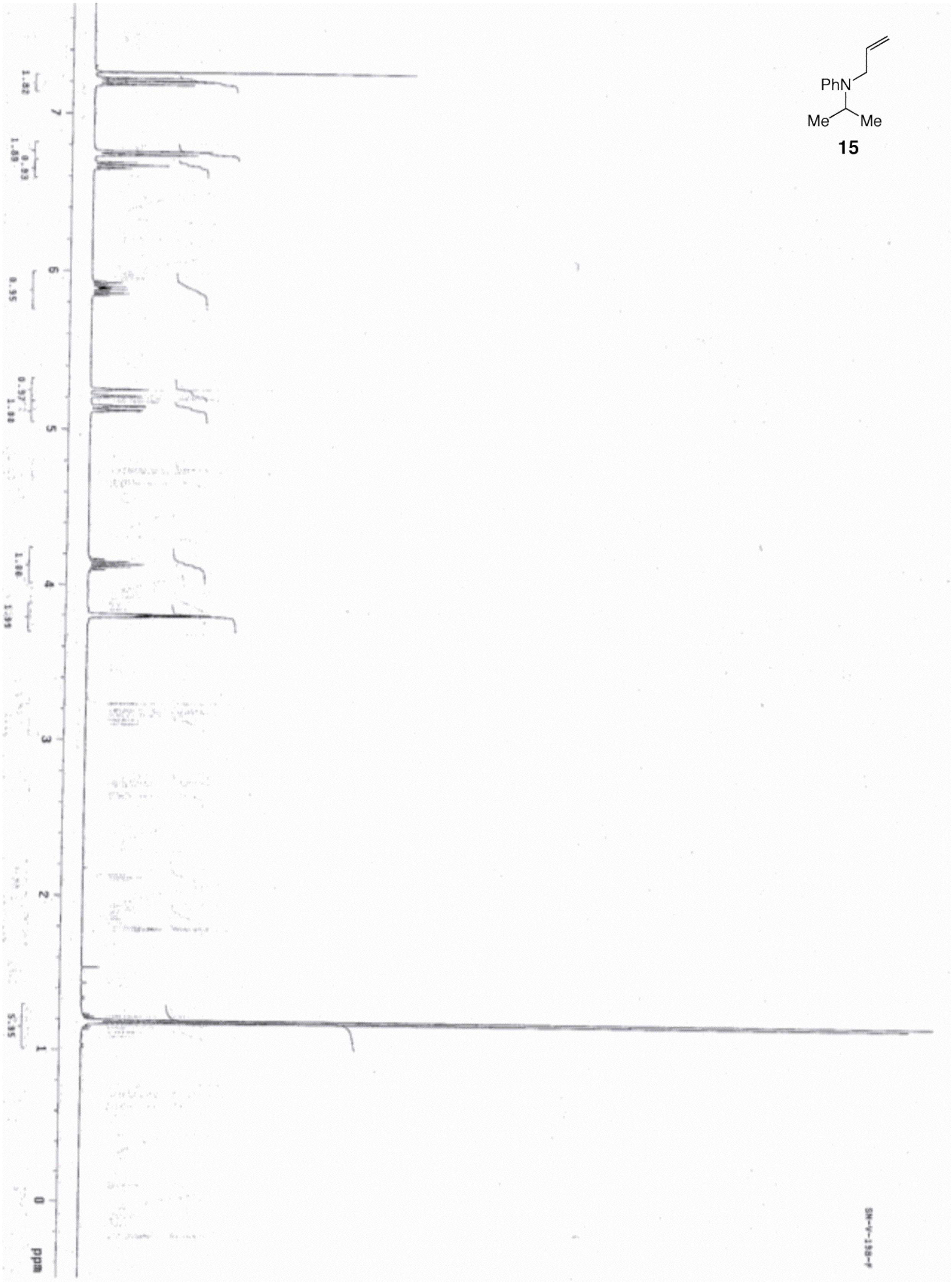

R-1

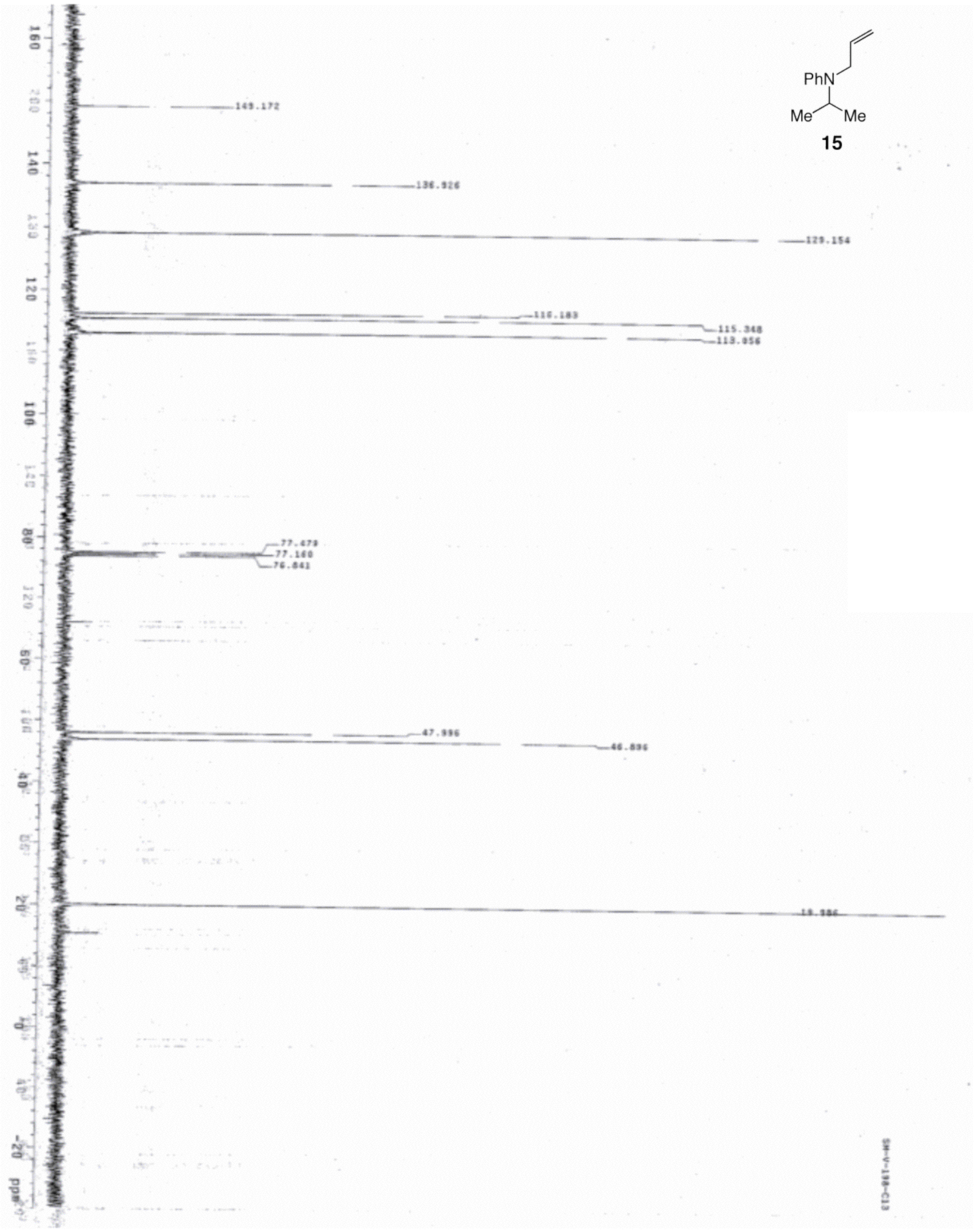
Mo
R
N
Br
OTBS
O
Ph
ppm (f1)
150
100
50
0
295.0
290.0
295.092
158.0
153.5
148.5
148.2
136.8
136.6
134.1
132.6
132.1
131.7
130.9
129.2
128.8
128.5
126.5
126.2
123.5
112.7
112.0
109.3
55.8
34.5
33.0
30.4
29.6
28.9
27.9
27.6
26.5
24.2
23.3
23.2
23.0
22.9
22.7
18.9
17.5
14.3
-2.2
-3.0

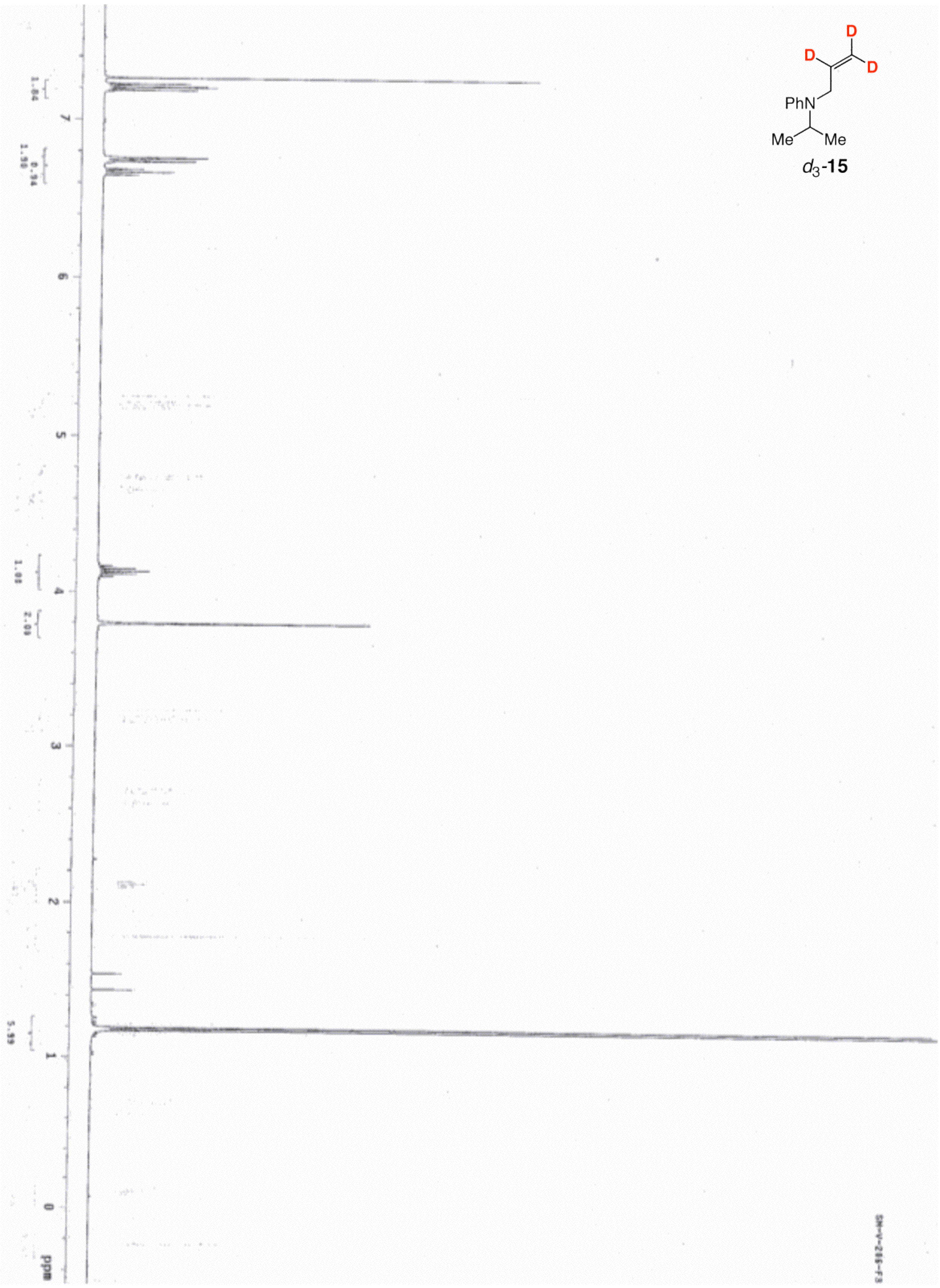

12

O
NPh
Me
Me
7
6
5
4
3
2
1
0
1.97
2.07
1.01
0.85
1.00
1.03
0.92
0.92
2.08
2.01
1.10
1.96
2.06
2.12
4.26
6.12
Sample: SJM-IV-58-f1
File: /home/ahh/SJM-IV-58-f1.fid
Pulse Sequence: s2pul

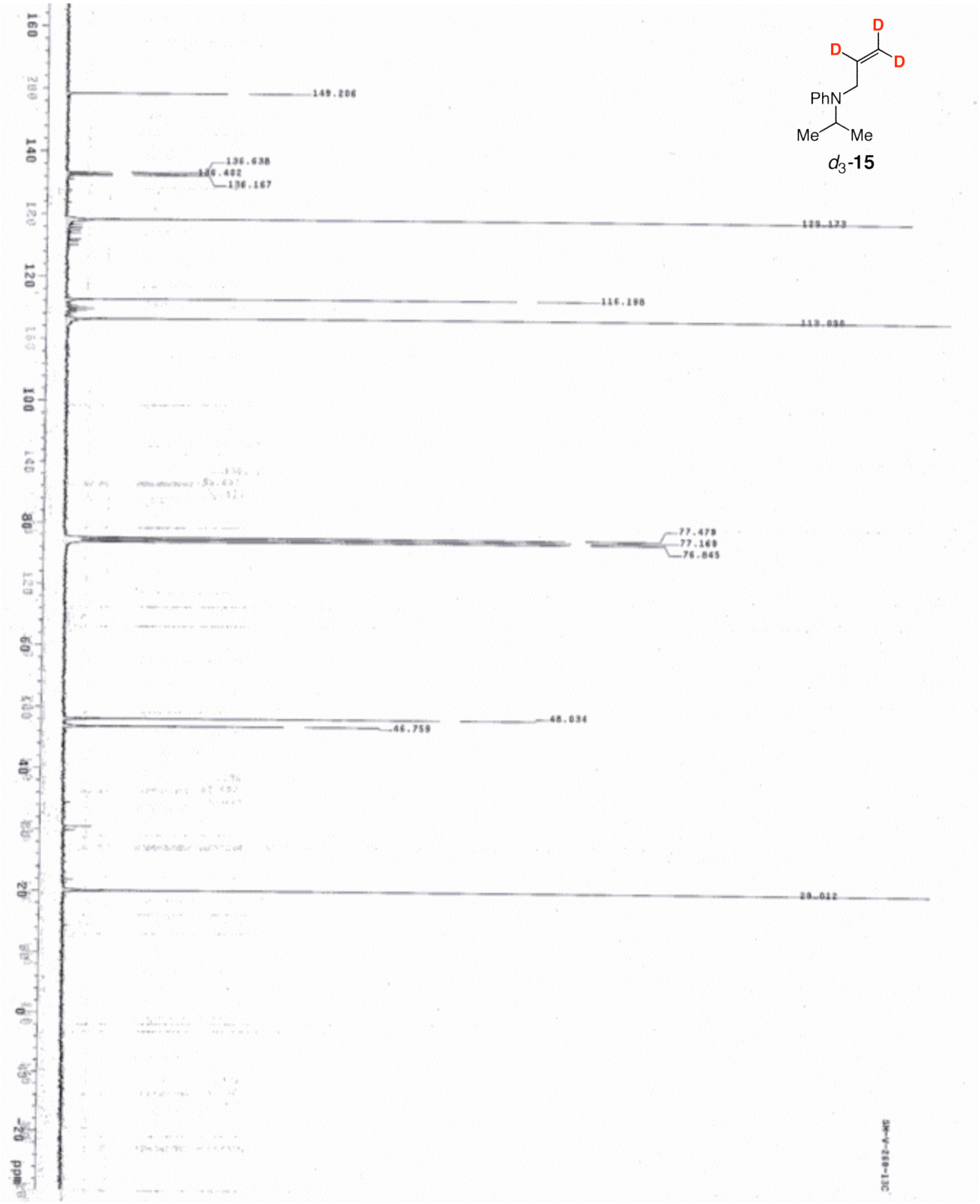

O
NPh
Me
Me
12
148.804
143.040
134.828
133.473
129.211
126.604
117.223
116.646
113.474
112.749
77.475
77.160
76.841
71.471
66.641
54.709
41.328
40.835
22.562
160
140
120
100
80
60
40
20
0
ppm
SJM-IV-58-13C


PhN
Me
Me
15
ppm
7
6
5
4
3
2
1
0
1.82
1.89
0.93
0.95
0.97
1.00
1.00
1.99
5.95
SN-V-138-F

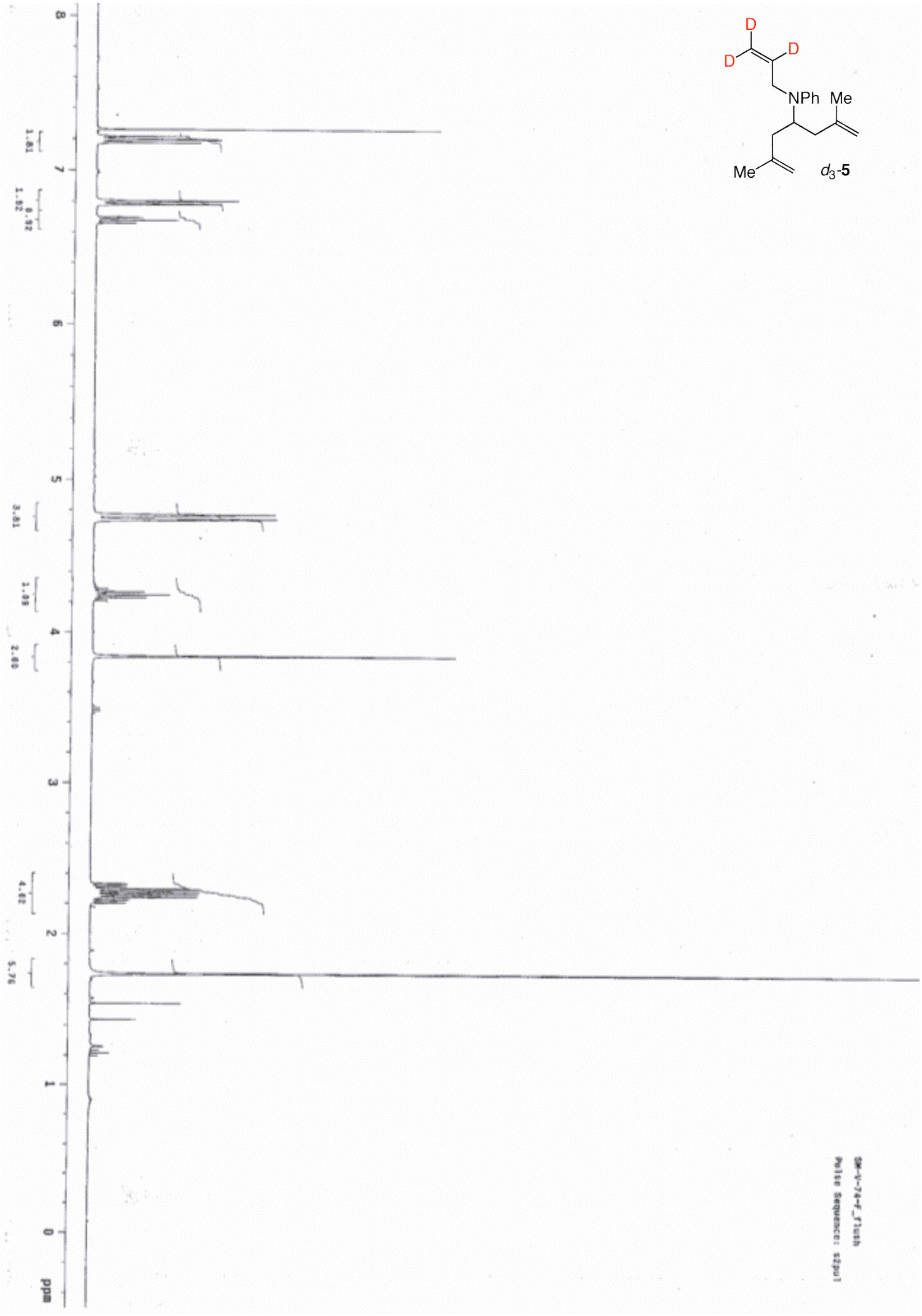

PhN
Me
Me
15
149.172
136.926
129.154
116.183
115.348
113.056
77.479
77.160
76.841
47.996
46.896
19.986
160
140
120
100
80
60
40
20
0
-20
ppm
SM-V-138-C13

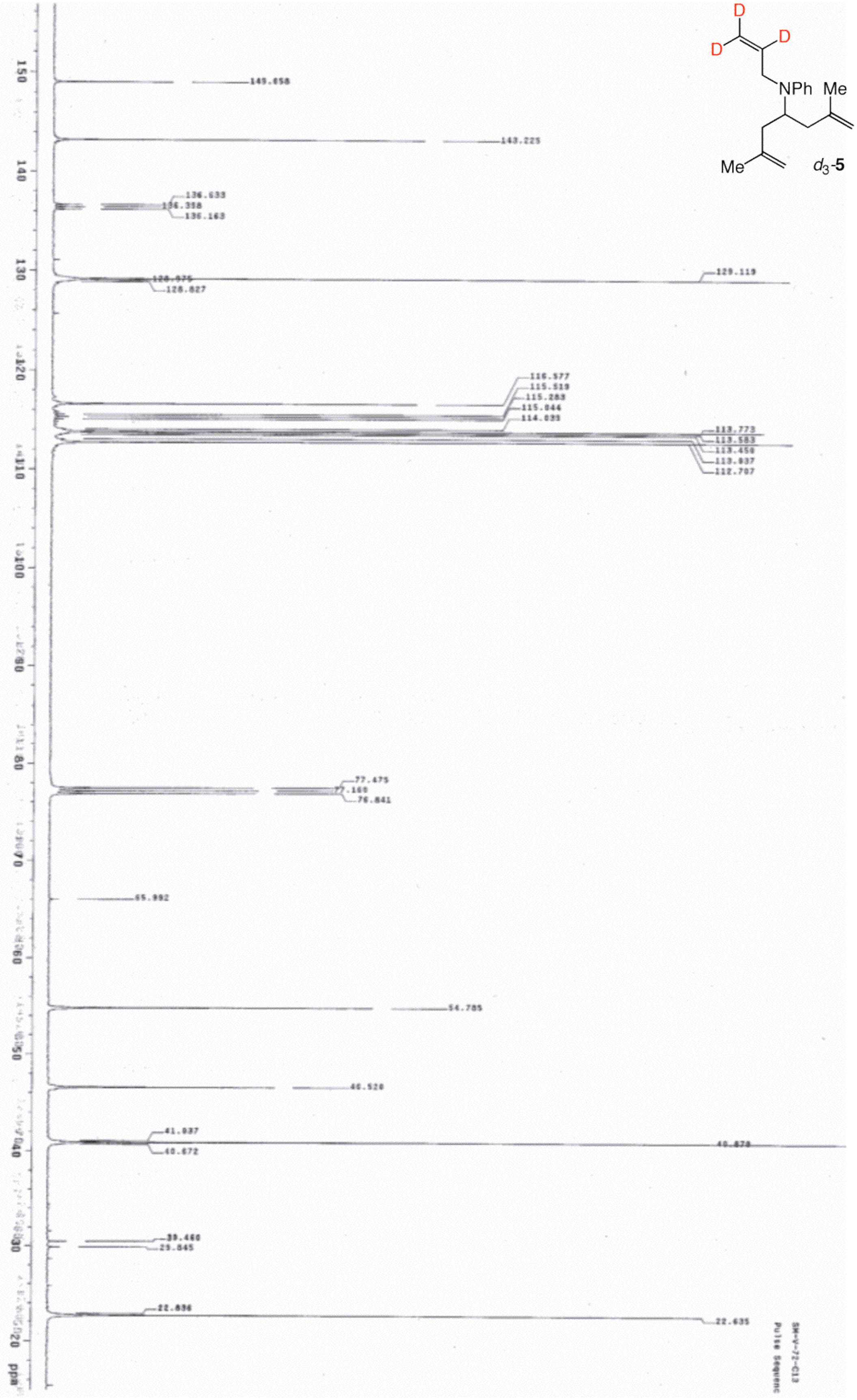


d$_3$-**15**


D
D
D
PhN
Me
Me
149.206
136.638
136.402
136.167
129.173
116.198
113.036
77.479
77.160
76.845
48.034
46.759
20.012
160
140
120
100
80
60
40
20
0
-20
ppm
SM-V-260-13C

d_3-**15**


D
D
D
NPh
Me
Me
d_3-**5**
8
7
6
5
4
3
2
1
0
ppm
1.81
1.92
0.92
3.81
1.09
2.00
4.02
5.76
SM-V-74-F_flash
Pulse Sequence: s2pul


D
D
D
NPh
Me
Me
d_3-**5**
149.058
143.225
136.633
136.358
136.163
129.119
128.975
128.827
116.577
115.519
115.283
115.044
114.035
113.773
113.583
113.450
113.037
112.707
77.475
77.160
76.841
65.992
54.785
46.520
41.037
40.872
40.878
30.460
29.845
22.896
22.635
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
SM-V-72-C13
Pulse Sequenc

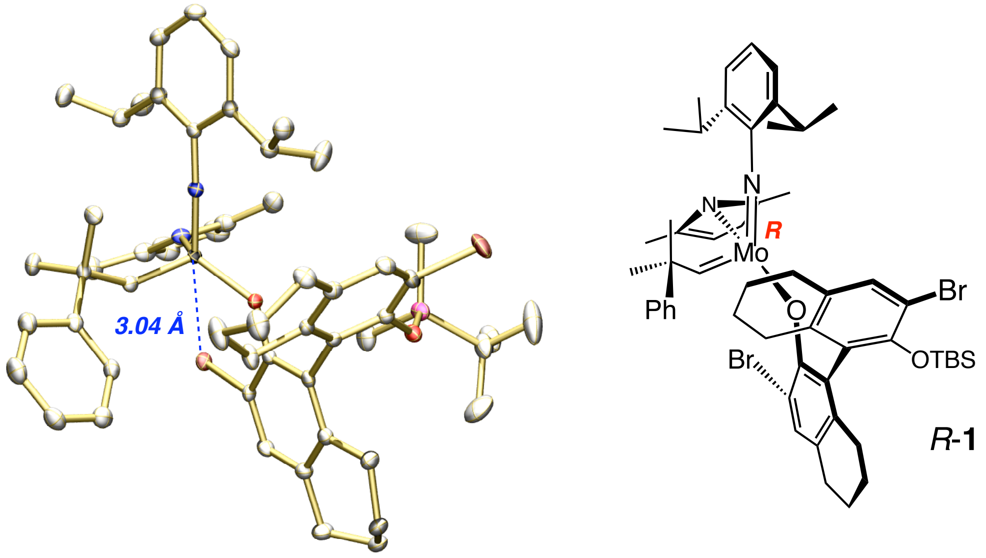


Figure 1. X-ray Crystal Structure of *R*-**1**

Table 3. Crystal data and structure refinement for *R*-**1**

Identification code	C59H82Br2MoN2O2Si	
Empirical formula	C59 H82 Br2 Mo N2 O2 Si	
Formula weight	1135.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.1036(9) Å	α= 90∞.
	b = 12.5845(11) Å	β= 100.5680(10)∞.
	c = 20.5049(17) Å	γ = 90∞.
Volume	2816.6(4) Å^3	
Z	2	
Density (calculated)	1.338 Mg/m^3	
Absorption coefficient	1.714 mm^{-1}	
F(000)	1184	
Crystal size	0.25 x 0.15 x 0.03 mm^3	
Theta range for data collection	1.95 to 28.00°.	
Index ranges	-14<=h<=14, -16<=k<=16, -26<=l<=26	
Reflections collected	33266	
Independent reflections	13252 [R(int) = 0.0232]	
Completeness to theta = 28.00∞	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9504 and 0.6738	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13252 / 597 / 611
Goodness-of-fit on F^2	0.941
Final R indices [I>2sigma(I)]	R1 = 0.0237, wR2 = 0.0531
R indices (all data)	R1 = 0.0257, wR2 = 0.0535
Absolute structure parameter	0.007(3)
Extinction coefficient	na
Largest diff. peak and hole	0.773 and -0.251 e.Å^{-3}

Table 4. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters ($\approx^2$x 10^3) for *R*-**1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Mo(1)	5819(1)	1994(1)	2571(1)	14(1)
Br(1)	6598(1)	2989(1)	1363(1)	20(1)
Br(2)	-613(1)	4193(1)	2195(1)	33(1)
Si(1)	1326(1)	3586(1)	886(1)	25(1)
O(1)	4731(1)	3196(1)	2257(1)	17(1)
O(2)	1508(1)	4535(1)	1459(1)	21(1)
C(1)	4809(2)	4097(2)	1907(1)	16(1)
C(2)	5622(2)	4194(2)	1466(1)	17(1)
C(3)	5647(2)	5070(2)	1070(1)	21(1)
C(4)	4849(2)	5910(2)	1100(1)	21(1)
C(5)	4879(2)	6856(2)	642(1)	28(1)
C(6)	3694(2)	7496(2)	558(1)	27(1)
C(7)	3405(2)	7757(2)	1236(1)	26(1)
C(8)	3144(2)	6747(2)	1601(1)	24(1)
C(9)	4036(2)	5850(2)	1548(1)	19(1)
C(10)	4007(2)	4945(2)	1942(1)	16(1)
C(11)	3092(2)	4862(2)	2397(1)	16(1)
C(12)	1879(2)	4612(2)	2130(1)	19(1)
C(13)	1033(2)	4549(2)	2551(1)	21(1)
C(14)	1369(2)	4760(2)	3220(1)	22(1)
C(15)	2567(2)	5039(2)	3490(1)	20(1)
C(16)	2894(2)	5322(2)	4222(1)	26(1)
C(17)	4059(2)	5962(2)	4388(1)	34(1)
C(18)	5056(2)	5455(2)	4092(1)	36(1)
C(19)	4743(2)	5401(2)	3345(1)	26(1)
C(20)	3436(2)	5076(2)	3078(1)	17(1)
C(21)	777(3)	2341(2)	1220(1)	48(1)
C(22)	2792(2)	3300(2)	604(1)	36(1)
C(23)	213(2)	4213(2)	189(1)	34(1)
C(24)	-1063(2)	4355(4)	358(1)	66(1)
C(25)	106(2)	3536(2)	-433(1)	42(1)
C(26)	728(3)	5313(2)	59(1)	54(1)
N(1)	5240(1)	1302(1)	3169(1)	16(1)
C(27)	4828(2)	577(2)	3597(1)	17(1)
C(28)	3794(2)	848(2)	3877(1)	18(1)

C(29)	3361(2)	97(2)	4269(1)	24(1)
C(30)	3932(2)	-883(2)	4397(1)	26(1)
C(31)	4968(2)	-1114(2)	4134(1)	26(1)
C(32)	5439(2)	-398(2)	3732(1)	21(1)
C(33)	3158(2)	1901(2)	3719(1)	22(1)
C(34)	2587(2)	2323(2)	4290(1)	28(1)
C(35)	2208(2)	1819(2)	3081(1)	37(1)
C(36)	6562(2)	-702(2)	3443(1)	23(1)
C(37)	6218(2)	-1491(2)	2877(1)	34(1)
C(38)	7597(2)	-1141(2)	3972(1)	31(1)
N(2)	6276(2)	781(1)	2004(1)	21(1)
C(39)	7352(2)	480(2)	1789(1)	28(1)
C(40)	7041(3)	-45(2)	1205(1)	40(1)
C(41)	5732(3)	-80(2)	1034(1)	37(1)
C(42)	5294(2)	410(2)	1529(1)	26(1)
C(43)	8592(2)	701(2)	2180(1)	34(1)
C(44)	3988(2)	568(2)	1609(1)	31(1)
C(45)	7280(2)	2505(2)	3086(1)	17(1)
C(46)	7994(2)	2597(2)	3796(1)	18(1)
C(47)	7276(2)	2135(2)	4294(1)	23(1)
C(48)	9179(2)	1943(2)	3818(1)	25(1)
C(49)	8327(2)	3756(2)	3978(1)	19(1)
C(50)	9121(2)	3986(2)	4573(1)	26(1)
C(51)	9444(2)	5017(2)	4755(1)	31(1)
C(52)	8976(2)	5855(2)	4351(1)	28(1)
C(53)	8181(2)	5649(2)	3767(1)	26(1)
C(54)	7861(2)	4605(2)	3583(1)	21(1)
C(55)	-1643(3)	7031(3)	1695(2)	62(1)
C(56)	-294(3)	7225(2)	1986(2)	53(1)
C(57)	-100(3)	7583(3)	2691(2)	61(1)
C(58)	1238(4)	7814(3)	2999(2)	57(1)
C(59)	1852(3)	8744(3)	2696(2)	42(1)
C(58X)	1241(3)	7813(3)	2996(2)	57(1)
C(59X)	1128(3)	7920(3)	3675(2)	58(4)

Table 5. Bond lengths [≈] and angles [∞] for *R*-**1**

Mo(1)-N(1)	1.7220(16)
Mo(1)-C(45)	1.8791(19)
Mo(1)-O(1)	1.9692(13)
Mo(1)-N(2)	2.0386(17)
Br(1)-C(2)	1.8985(19)
Br(2)-C(13)	1.8930(19)
Si(1)-O(2)	1.6611(15)
Si(1)-C(21)	1.856(3)
Si(1)-C(22)	1.860(2)
Si(1)-C(23)	1.883(2)
O(1)-C(1)	1.352(2)
O(2)-C(12)	1.365(2)
C(1)-C(2)	1.397(2)
C(1)-C(10)	1.400(3)
C(2)-C(3)	1.372(3)
C(3)-C(4)	1.387(3)
C(3)-H(3A)	0.9500
C(4)-C(9)	1.403(3)
C(4)-C(5)	1.521(3)
C(5)-C(6)	1.525(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.517(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.529(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.518(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.401(3)
C(10)-C(11)	1.503(3)
C(11)-C(12)	1.394(3)
C(11)-C(20)	1.405(3)
C(12)-C(13)	1.391(3)
C(13)-C(14)	1.379(3)
C(14)-C(15)	1.389(3)

C(14)-H(14A)	0.9500
C(15)-C(20)	1.395(3)
C(15)-C(16)	1.521(3)
C(16)-C(17)	1.508(3)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.498(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.509(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.510(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(25)	1.520(4)
C(23)-C(24)	1.530(3)
C(23)-C(26)	1.540(4)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
N(1)-C(27)	1.399(2)
C(27)-C(32)	1.406(3)
C(27)-C(28)	1.416(3)
C(28)-C(29)	1.383(3)
C(28)-C(33)	1.509(3)
C(29)-C(30)	1.389(3)
C(29)-H(29A)	0.9500

C(30)-C(31)	1.389(3)
C(30)-H(30A)	0.9500
C(31)-C(32)	1.385(3)
C(31)-H(31A)	0.9500
C(32)-C(36)	1.525(3)
C(33)-C(34)	1.525(3)
C(33)-C(35)	1.526(3)
C(33)-H(33A)	1.0000
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-C(37)	1.521(3)
C(36)-C(38)	1.531(3)
C(36)-H(36A)	1.0000
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
N(2)-C(39)	1.400(3)
N(2)-C(42)	1.402(3)
C(39)-C(40)	1.355(3)
C(39)-C(43)	1.488(3)
C(40)-C(41)	1.432(4)
C(40)-H(40A)	0.9500
C(41)-C(42)	1.353(3)
C(41)-H(41A)	0.9500
C(42)-C(44)	1.502(3)
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800
C(45)-C(46)	1.528(3)
C(45)-H(45A)	0.9500

C(46)-C(47)	1.522(3)
C(46)-C(49)	1.534(3)
C(46)-C(48)	1.545(3)
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-C(54)	1.383(3)
C(49)-C(50)	1.397(3)
C(50)-C(51)	1.380(3)
C(50)-H(50A)	0.9500
C(51)-C(52)	1.382(3)
C(51)-H(51A)	0.9500
C(52)-C(53)	1.376(3)
C(52)-H(52A)	0.9500
C(53)-C(54)	1.395(3)
C(53)-H(53A)	0.9500
C(54)-H(54A)	0.9500
C(55)-C(56)	1.526(4)
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-C(57)	1.491(4)
C(56)-H(56A)	0.9900
C(56)-H(56B)	0.9900
C(57)-C(58)	1.531(5)
C(57)-C(58X)	1.533(5)
C(57)-H(57A)	0.9900
C(57)-H(57B)	0.9900
C(58)-C(59)	1.540(6)
C(58)-H(58A)	0.9900
C(58)-H(58B)	0.9900
C(59)-H(59A)	0.9800
C(59)-H(59B)	0.9800
C(59)-H(59C)	0.9800
C(58X)-C(59X)	1.4261
C(58X)-H(58C)	0.9900
C(58X)-H(58D)	0.9900

C(59X)-H(59D)	0.9800
C(59X)-H(59E)	0.9800
C(59X)-H(59F)	0.9800

N(1)-Mo(1)-C(45)	99.76(8)
N(1)-Mo(1)-O(1)	109.54(7)
C(45)-Mo(1)-O(1)	109.63(7)
N(1)-Mo(1)-N(2)	101.03(7)
C(45)-Mo(1)-N(2)	107.31(8)
O(1)-Mo(1)-N(2)	126.20(6)
O(2)-Si(1)-C(21)	110.62(10)
O(2)-Si(1)-C(22)	111.02(9)
C(21)-Si(1)-C(22)	108.46(14)
O(2)-Si(1)-C(23)	102.32(10)
C(21)-Si(1)-C(23)	114.81(12)
C(22)-Si(1)-C(23)	109.53(11)
C(1)-O(1)-Mo(1)	136.23(11)
C(12)-O(2)-Si(1)	137.58(13)
O(1)-C(1)-C(2)	121.94(17)
O(1)-C(1)-C(10)	120.60(16)
C(2)-C(1)-C(10)	117.31(18)
C(3)-C(2)-C(1)	122.66(18)
C(3)-C(2)-Br(1)	120.13(14)
C(1)-C(2)-Br(1)	116.91(15)
C(2)-C(3)-C(4)	120.21(18)
C(2)-C(3)-H(3A)	119.9
C(4)-C(3)-H(3A)	119.9
C(3)-C(4)-C(9)	118.77(19)
C(3)-C(4)-C(5)	118.86(18)
C(9)-C(4)-C(5)	122.37(19)
C(4)-C(5)-C(6)	111.52(17)
C(4)-C(5)-H(5A)	109.3
C(6)-C(5)-H(5A)	109.3
C(4)-C(5)-H(5B)	109.3
C(6)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	108.0
C(7)-C(6)-C(5)	109.52(17)
C(7)-C(6)-H(6A)	109.8
C(5)-C(6)-H(6A)	109.8
C(7)-C(6)-H(6B)	109.8

C(5)-C(6)-H(6B)	109.8
H(6A)-C(6)-H(6B)	108.2
C(6)-C(7)-C(8)	111.04(18)
C(6)-C(7)-H(7A)	109.4
C(8)-C(7)-H(7A)	109.4
C(6)-C(7)-H(7B)	109.4
C(8)-C(7)-H(7B)	109.4
H(7A)-C(7)-H(7B)	108.0
C(9)-C(8)-C(7)	113.46(17)
C(9)-C(8)-H(8A)	108.9
C(7)-C(8)-H(8A)	108.9
C(9)-C(8)-H(8B)	108.9
C(7)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.7
C(10)-C(9)-C(4)	120.43(19)
C(10)-C(9)-C(8)	118.65(17)
C(4)-C(9)-C(8)	120.89(18)
C(1)-C(10)-C(9)	120.59(18)
C(1)-C(10)-C(11)	119.13(17)
C(9)-C(10)-C(11)	120.27(17)
C(12)-C(11)-C(20)	120.07(17)
C(12)-C(11)-C(10)	119.09(17)
C(20)-C(11)-C(10)	120.78(17)
O(2)-C(12)-C(13)	120.54(17)
O(2)-C(12)-C(11)	120.26(17)
C(13)-C(12)-C(11)	118.88(18)
C(14)-C(13)-C(12)	121.07(18)
C(14)-C(13)-Br(2)	119.69(15)
C(12)-C(13)-Br(2)	119.23(15)
C(13)-C(14)-C(15)	120.65(18)
C(13)-C(14)-H(14A)	119.7
C(15)-C(14)-H(14A)	119.7
C(14)-C(15)-C(20)	119.06(18)
C(14)-C(15)-C(16)	119.38(18)
C(20)-C(15)-C(16)	121.54(18)
C(17)-C(16)-C(15)	112.80(17)
C(17)-C(16)-H(16A)	109.0
C(15)-C(16)-H(16A)	109.0
C(17)-C(16)-H(16B)	109.0
C(15)-C(16)-H(16B)	109.0

H(16A)-C(16)-H(16B)	107.8
C(18)-C(17)-C(16)	110.4(2)
C(18)-C(17)-H(17A)	109.6
C(16)-C(17)-H(17A)	109.6
C(18)-C(17)-H(17B)	109.6
C(16)-C(17)-H(17B)	109.6
H(17A)-C(17)-H(17B)	108.1
C(17)-C(18)-C(19)	112.4(2)
C(17)-C(18)-H(18A)	109.1
C(19)-C(18)-H(18A)	109.1
C(17)-C(18)-H(18B)	109.1
C(19)-C(18)-H(18B)	109.1
H(18A)-C(18)-H(18B)	107.9
C(18)-C(19)-C(20)	114.00(18)
C(18)-C(19)-H(19A)	108.8
C(20)-C(19)-H(19A)	108.8
C(18)-C(19)-H(19B)	108.8
C(20)-C(19)-H(19B)	108.8
H(19A)-C(19)-H(19B)	107.6
C(15)-C(20)-C(11)	120.21(18)
C(15)-C(20)-C(19)	121.04(18)
C(11)-C(20)-C(19)	118.66(17)
Si(1)-C(21)-H(21A)	109.5
Si(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
Si(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Si(1)-C(22)-H(22A)	109.5
Si(1)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
Si(1)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(25)-C(23)-C(24)	108.8(2)
C(25)-C(23)-C(26)	109.4(2)
C(24)-C(23)-C(26)	108.8(3)
C(25)-C(23)-Si(1)	109.99(18)
C(24)-C(23)-Si(1)	112.48(17)
C(26)-C(23)-Si(1)	107.21(16)

C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(27)-N(1)-Mo(1)	169.74(14)
N(1)-C(27)-C(32)	119.48(17)
N(1)-C(27)-C(28)	118.69(17)
C(32)-C(27)-C(28)	121.83(18)
C(29)-C(28)-C(27)	117.76(19)
C(29)-C(28)-C(33)	121.73(18)
C(27)-C(28)-C(33)	120.44(17)
C(28)-C(29)-C(30)	121.38(19)
C(28)-C(29)-H(29A)	119.3
C(30)-C(29)-H(29A)	119.3
C(29)-C(30)-C(31)	119.6(2)
C(29)-C(30)-H(30A)	120.2
C(31)-C(30)-H(30A)	120.2
C(32)-C(31)-C(30)	121.7(2)
C(32)-C(31)-H(31A)	119.2
C(30)-C(31)-H(31A)	119.2
C(31)-C(32)-C(27)	117.68(19)
C(31)-C(32)-C(36)	119.52(19)
C(27)-C(32)-C(36)	122.78(18)
C(28)-C(33)-C(34)	112.67(17)
C(28)-C(33)-C(35)	110.27(18)
C(34)-C(33)-C(35)	111.27(17)

C(28)-C(33)-H(33A)	107.5
C(34)-C(33)-H(33A)	107.5
C(35)-C(33)-H(33A)	107.5
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(33)-C(35)-H(35A)	109.5
C(33)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(33)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(37)-C(36)-C(32)	110.60(18)
C(37)-C(36)-C(38)	110.81(19)
C(32)-C(36)-C(38)	112.10(17)
C(37)-C(36)-H(36A)	107.7
C(32)-C(36)-H(36A)	107.7
C(38)-C(36)-H(36A)	107.7
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(36)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(39)-N(2)-C(42)	106.89(17)
C(39)-N(2)-Mo(1)	134.33(15)
C(42)-N(2)-Mo(1)	113.73(13)
C(40)-C(39)-N(2)	108.5(2)
C(40)-C(39)-C(43)	128.9(2)
N(2)-C(39)-C(43)	122.62(19)
C(39)-C(40)-C(41)	108.3(2)

C(39)-C(40)-H(40A)	125.8
C(41)-C(40)-H(40A)	125.8
C(42)-C(41)-C(40)	106.9(2)
C(42)-C(41)-H(41A)	126.6
C(40)-C(41)-H(41A)	126.6
C(41)-C(42)-N(2)	109.4(2)
C(41)-C(42)-C(44)	129.0(2)
N(2)-C(42)-C(44)	121.59(18)
C(39)-C(43)-H(43A)	109.5
C(39)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(39)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(42)-C(44)-H(44A)	109.5
C(42)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(42)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(46)-C(45)-Mo(1)	143.60(15)
C(46)-C(45)-H(45A)	108.2
Mo(1)-C(45)-H(45A)	108.2
C(47)-C(46)-C(45)	111.45(16)
C(47)-C(46)-C(49)	109.37(17)
C(45)-C(46)-C(49)	111.32(16)
C(47)-C(46)-C(48)	108.97(17)
C(45)-C(46)-C(48)	106.18(16)
C(49)-C(46)-C(48)	109.47(17)
C(46)-C(47)-H(47A)	109.5
C(46)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(46)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(46)-C(48)-H(48A)	109.5
C(46)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(46)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5

H(48B)-C(48)-H(48C)	109.5
C(54)-C(49)-C(50)	117.4(2)
C(54)-C(49)-C(46)	122.98(17)
C(50)-C(49)-C(46)	119.63(18)
C(51)-C(50)-C(49)	121.5(2)
C(51)-C(50)-H(50A)	119.3
C(49)-C(50)-H(50A)	119.3
C(50)-C(51)-C(52)	120.3(2)
C(50)-C(51)-H(51A)	119.8
C(52)-C(51)-H(51A)	119.8
C(53)-C(52)-C(51)	119.2(2)
C(53)-C(52)-H(52A)	120.4
C(51)-C(52)-H(52A)	120.4
C(52)-C(53)-C(54)	120.3(2)
C(52)-C(53)-H(53A)	119.9
C(54)-C(53)-H(53A)	119.9
C(49)-C(54)-C(53)	121.33(19)
C(49)-C(54)-H(54A)	119.3
C(53)-C(54)-H(54A)	119.3
C(56)-C(55)-H(55A)	109.5
C(56)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(56)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(57)-C(56)-C(55)	112.6(3)
C(57)-C(56)-H(56A)	109.1
C(55)-C(56)-H(56A)	109.1
C(57)-C(56)-H(56B)	109.1
C(55)-C(56)-H(56B)	109.1
H(56A)-C(56)-H(56B)	107.8
C(56)-C(57)-C(58)	114.4(3)
C(56)-C(57)-C(58X)	114.2(3)
C(58)-C(57)-C(58X)	0.2(2)
C(56)-C(57)-H(57A)	108.7
C(58)-C(57)-H(57A)	108.7
C(58X)-C(57)-H(57A)	108.8
C(56)-C(57)-H(57B)	108.7
C(58)-C(57)-H(57B)	108.7
C(58X)-C(57)-H(57B)	108.7

H(57A)-C(57)-H(57B)	107.6
C(57)-C(58)-C(59)	116.5(3)
C(57)-C(58)-H(58A)	108.2
C(59)-C(58)-H(58A)	108.2
C(57)-C(58)-H(58B)	108.2
C(59)-C(58)-H(58B)	108.2
H(58A)-C(58)-H(58B)	107.3
C(58)-C(59)-H(59A)	109.5
C(58)-C(59)-H(59B)	109.5
H(59A)-C(59)-H(59B)	109.5
C(58)-C(59)-H(59C)	109.5
H(59A)-C(59)-H(59C)	109.5
H(59B)-C(59)-H(59C)	109.5
C(59X)-C(58X)-C(57)	99.42(17)
C(59X)-C(58X)-H(58C)	111.9
C(57)-C(58X)-H(58C)	111.9
C(59X)-C(58X)-H(58D)	111.9
C(57)-C(58X)-H(58D)	111.9
H(58C)-C(58X)-H(58D)	109.6
C(58X)-C(59X)-H(59D)	109.5
C(58X)-C(59X)-H(59E)	109.5
H(59D)-C(59X)-H(59E)	109.5
C(58X)-C(59X)-H(59F)	109.5
H(59D)-C(59X)-H(59F)	109.5
H(59E)-C(59X)-H(59F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 6. Anisotropic displacement parameters ($\approx^2$x 10^3) for *R*-**1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mo(1)	14(1)	14(1)	16(1)	1(1)	4(1)	0(1)
Br(1)	18(1)	23(1)	20(1)	0(1)	6(1)	2(1)
Br(2)	17(1)	52(1)	30(1)	1(1)	5(1)	-12(1)
Si(1)	25(1)	28(1)	18(1)	1(1)	-1(1)	-7(1)
O(1)	15(1)	16(1)	19(1)	3(1)	4(1)	1(1)
O(2)	20(1)	25(1)	18(1)	3(1)	2(1)	-5(1)
C(1)	14(1)	18(1)	16(1)	1(1)	2(1)	-2(1)
C(2)	14(1)	18(1)	18(1)	0(1)	3(1)	2(1)
C(3)	19(1)	27(1)	18(1)	2(1)	6(1)	-4(1)
C(4)	23(1)	21(1)	19(1)	3(1)	2(1)	-4(1)
C(5)	32(1)	24(1)	27(1)	7(1)	9(1)	-2(1)
C(6)	29(1)	22(1)	28(1)	10(1)	0(1)	-2(1)
C(7)	26(1)	19(1)	31(1)	8(1)	2(1)	2(1)
C(8)	24(1)	21(1)	27(1)	5(1)	5(1)	2(1)
C(9)	17(1)	19(1)	19(1)	1(1)	1(1)	-3(1)
C(10)	13(1)	18(1)	17(1)	-2(1)	0(1)	-2(1)
C(11)	17(1)	13(1)	19(1)	3(1)	5(1)	1(1)
C(12)	22(1)	16(1)	18(1)	2(1)	2(1)	-2(1)
C(13)	14(1)	23(1)	27(1)	3(1)	2(1)	-2(1)
C(14)	22(1)	22(1)	23(1)	1(1)	10(1)	-1(1)
C(15)	23(1)	16(1)	21(1)	1(1)	6(1)	1(1)
C(16)	28(1)	29(1)	22(1)	-3(1)	10(1)	-4(1)
C(17)	28(1)	46(2)	26(1)	-9(1)	5(1)	-1(1)
C(18)	23(1)	60(2)	26(1)	-11(1)	3(1)	-4(1)
C(19)	17(1)	39(1)	22(1)	-5(1)	4(1)	-1(1)
C(20)	16(1)	14(1)	21(1)	2(1)	2(1)	1(1)
C(21)	74(2)	37(2)	28(1)	-2(1)	-1(1)	-25(1)
C(22)	31(1)	45(2)	28(1)	-13(1)	-4(1)	1(1)
C(23)	24(1)	54(2)	20(1)	5(1)	-2(1)	-1(1)
C(24)	29(1)	136(3)	32(2)	-1(2)	-1(1)	18(2)
C(25)	33(1)	66(2)	24(1)	2(1)	-3(1)	-10(1)
C(26)	73(2)	48(2)	36(2)	17(1)	-7(2)	8(2)
N(1)	17(1)	15(1)	17(1)	0(1)	4(1)	-1(1)
C(27)	17(1)	18(1)	17(1)	2(1)	1(1)	-3(1)
C(28)	17(1)	19(1)	18(1)	0(1)	1(1)	-2(1)

C(29)	20(1)	30(1)	25(1)	1(1)	7(1)	-5(1)
C(30)	30(1)	25(1)	24(1)	5(1)	8(1)	-6(1)
C(31)	29(1)	20(1)	28(1)	5(1)	4(1)	1(1)
C(32)	21(1)	22(1)	20(1)	1(1)	2(1)	-2(1)
C(33)	21(1)	21(1)	25(1)	3(1)	6(1)	0(1)
C(34)	28(1)	26(1)	30(1)	0(1)	7(1)	4(1)
C(35)	41(1)	45(2)	25(1)	0(1)	2(1)	21(1)
C(36)	24(1)	21(1)	26(1)	2(1)	6(1)	5(1)
C(37)	40(1)	29(1)	35(1)	0(1)	11(1)	6(1)
C(38)	27(1)	34(1)	33(1)	7(1)	5(1)	11(1)
N(2)	26(1)	19(1)	20(1)	0(1)	9(1)	1(1)
C(39)	34(1)	22(1)	32(1)	1(1)	18(1)	4(1)
C(40)	51(2)	35(1)	41(2)	-12(1)	26(1)	-1(1)
C(41)	52(2)	31(1)	31(1)	-10(1)	13(1)	-10(1)
C(42)	35(1)	18(1)	24(1)	-3(1)	6(1)	-5(1)
C(43)	30(1)	35(1)	44(2)	-1(1)	21(1)	6(1)
C(44)	34(1)	23(1)	32(1)	-5(1)	-2(1)	-4(1)
C(45)	16(1)	17(1)	20(1)	2(1)	6(1)	2(1)
C(46)	15(1)	22(1)	18(1)	2(1)	2(1)	1(1)
C(47)	24(1)	29(1)	17(1)	2(1)	2(1)	-5(1)
C(48)	20(1)	27(1)	26(1)	1(1)	0(1)	5(1)
C(49)	16(1)	24(1)	18(1)	0(1)	6(1)	0(1)
C(50)	24(1)	29(1)	24(1)	-1(1)	1(1)	-2(1)
C(51)	26(1)	36(1)	28(1)	-8(1)	0(1)	-5(1)
C(52)	26(1)	25(1)	34(1)	-7(1)	6(1)	-6(1)
C(53)	23(1)	25(1)	31(1)	1(1)	8(1)	2(1)
C(54)	16(1)	26(1)	21(1)	0(1)	3(1)	1(1)
C(55)	48(2)	52(2)	87(2)	1(2)	16(2)	3(2)
C(56)	51(2)	43(2)	71(2)	9(2)	24(2)	3(1)
C(57)	65(2)	67(2)	58(2)	20(2)	33(2)	14(2)
C(58)	62(2)	67(2)	44(2)	12(2)	19(1)	11(2)
C(59)	49(2)	35(2)	41(2)	-3(2)	3(2)	5(2)
C(58X)	62(2)	67(2)	44(2)	12(2)	19(1)	11(2)
C(59X)	50(8)	73(10)	51(6)	-14(8)	10(6)	-19(8)

Table 7. Hydrogen coordinates (x10^4) and isotropic displacement parameters (≈^{2}x 10^3) for *R*-**1**

	x	y	z	U(eq)
H(3A)	6213	5102	775	25
H(5A)	5004	6601	203	33
H(5B)	5578	7321	827	33
H(6A)	3784	8161	314	32
H(6B)	3014	7079	299	32
H(7A)	2683	8231	1182	31
H(7B)	4108	8137	1502	31
H(8A)	3178	6918	2075	29
H(8B)	2303	6501	1417	29
H(14A)	775	4715	3499	26
H(16A)	2214	5735	4349	31
H(16B)	2988	4660	4487	31
H(17A)	3911	6693	4213	40
H(17B)	4317	6006	4875	40
H(18A)	5204	4727	4271	44
H(18B)	5821	5867	4224	44
H(19A)	5300	4887	3186	31
H(19B)	4891	6106	3161	31
H(21A)	1408	2070	1579	71
H(21B)	607	1811	866	71
H(21C)	26	2487	1392	71
H(22A)	3370	2974	968	54
H(22B)	3138	3964	470	54
H(22C)	2639	2811	226	54
H(24A)	-1607	4683	-18	100
H(24B)	-1008	4813	749	100
H(24C)	-1391	3660	452	100
H(25A)	-474	3867	-793	63
H(25B)	-186	2825	-344	63
H(25C)	911	3479	-563	63
H(26A)	170	5664	-303	81
H(26B)	1534	5229	-65	81
H(26C)	806	5747	461	81
H(29A)	2658	254	4455	29
H(30A)	3616	-1392	4664	31

H(31A)	5364	-1780	4231	31
H(33A)	3791	2426	3639	26
H(34A)	3218	2371	4692	41
H(34B)	1937	1840	4369	41
H(34C)	2240	3030	4176	41
H(35A)	2600	1547	2723	56
H(35B)	1862	2523	2960	56
H(35C)	1552	1334	3150	56
H(36A)	6871	-44	3256	28
H(37A)	5562	-1191	2543	51
H(37B)	5935	-2154	3049	51
H(37C)	6936	-1635	2676	51
H(38A)	7812	-617	4327	47
H(38B)	8315	-1287	3770	47
H(38C)	7326	-1800	4155	47
H(40A)	7597	-340	953	48
H(41A)	5261	-388	646	45
H(43A)	9215	419	1943	52
H(43B)	8677	358	2615	52
H(43C)	8703	1470	2238	52
H(44A)	3438	255	1229	46
H(44B)	3817	1330	1631	46
H(44C)	3856	222	2018	46
H(45A)	7751	2827	2797	21
H(47A)	7762	2197	4742	35
H(47B)	7099	1384	4191	35
H(47C)	6506	2525	4269	35
H(48A)	9671	1972	4266	37
H(48B)	9651	2241	3502	37
H(48C)	8967	1203	3700	37
H(50A)	9446	3419	4857	31
H(51A)	9990	5152	5161	37
H(52A)	9202	6566	4475	33
H(53A)	7849	6220	3488	31
H(54A)	7312	4474	3178	26
H(55A)	-1720	6781	1237	93
H(55B)	-2101	7696	1702	93
H(55C)	-1973	6494	1960	93
H(56A)	171	6560	1958	64
H(56B)	33	7770	1718	64

H(57A)	-414	7027	2958	73
H(57B)	-588	8234	2717	73
H(58A)	1723	7163	2963	68
H(58B)	1283	7960	3477	68
H(59A)	2708	8804	2920	64
H(59B)	1418	9405	2754	64
H(59C)	1820	8613	2222	64
H(58C)	1787	7217	2929	68
H(58D)	1537	8477	2819	68
H(59D)	1933	8075	3944	87
H(59E)	811	7256	3828	87
H(59F)	562	8502	3719	87

Table 6. Torsion angles [∞] for *R*-**1**

N(1)-Mo(1)-O(1)-C(1)	164.59(17)
C(45)-Mo(1)-O(1)-C(1)	56.09(18)
N(2)-Mo(1)-O(1)-C(1)	-74.65(19)
C(21)-Si(1)-O(2)-C(12)	35.7(2)
C(22)-Si(1)-O(2)-C(12)	-84.7(2)
C(23)-Si(1)-O(2)-C(12)	158.49(19)
Mo(1)-O(1)-C(1)-C(2)	24.7(3)
Mo(1)-O(1)-C(1)-C(10)	-159.88(14)
O(1)-C(1)-C(2)-C(3)	174.91(18)
C(10)-C(1)-C(2)-C(3)	-0.7(3)
O(1)-C(1)-C(2)-Br(1)	1.2(2)
C(10)-C(1)-C(2)-Br(1)	-174.39(14)
C(1)-C(2)-C(3)-C(4)	0.3(3)
Br(1)-C(2)-C(3)-C(4)	173.79(15)
C(2)-C(3)-C(4)-C(9)	1.0(3)
C(2)-C(3)-C(4)-C(5)	-178.41(18)
C(3)-C(4)-C(5)-C(6)	159.81(19)
C(9)-C(4)-C(5)-C(6)	-19.6(3)
C(4)-C(5)-C(6)-C(7)	51.1(2)
C(5)-C(6)-C(7)-C(8)	-64.7(2)
C(6)-C(7)-C(8)-C(9)	43.7(2)
C(3)-C(4)-C(9)-C(10)	-1.9(3)
C(5)-C(4)-C(9)-C(10)	177.48(19)
C(3)-C(4)-C(9)-C(8)	180.00(19)
C(5)-C(4)-C(9)-C(8)	-0.6(3)
C(7)-C(8)-C(9)-C(10)	170.47(18)
C(7)-C(8)-C(9)-C(4)	-11.4(3)
O(1)-C(1)-C(10)-C(9)	-175.90(17)
C(2)-C(1)-C(10)-C(9)	-0.2(3)
O(1)-C(1)-C(10)-C(11)	2.6(3)
C(2)-C(1)-C(10)-C(11)	178.29(17)
C(4)-C(9)-C(10)-C(1)	1.6(3)
C(8)-C(9)-C(10)-C(1)	179.65(18)
C(4)-C(9)-C(10)-C(11)	-176.96(18)
C(8)-C(9)-C(10)-C(11)	1.1(3)
C(1)-C(10)-C(11)-C(12)	-101.2(2)
C(9)-C(10)-C(11)-C(12)	77.3(2)
C(1)-C(10)-C(11)-C(20)	81.4(2)

C(9)-C(10)-C(11)-C(20)	-100.0(2)
Si(1)-O(2)-C(12)-C(13)	-91.4(2)
Si(1)-O(2)-C(12)-C(11)	95.1(2)
C(20)-C(11)-C(12)-O(2)	171.76(17)
C(10)-C(11)-C(12)-O(2)	-5.6(3)
C(20)-C(11)-C(12)-C(13)	-1.8(3)
C(10)-C(11)-C(12)-C(13)	-179.19(18)
O(2)-C(12)-C(13)-C(14)	-171.65(19)
C(11)-C(12)-C(13)-C(14)	1.9(3)
O(2)-C(12)-C(13)-Br(2)	7.2(3)
C(11)-C(12)-C(13)-Br(2)	-179.17(14)
C(12)-C(13)-C(14)-C(15)	-0.2(3)
Br(2)-C(13)-C(14)-C(15)	-179.06(15)
C(13)-C(14)-C(15)-C(20)	-1.7(3)
C(13)-C(14)-C(15)-C(16)	176.83(19)
C(14)-C(15)-C(16)-C(17)	-159.7(2)
C(20)-C(15)-C(16)-C(17)	18.7(3)
C(15)-C(16)-C(17)-C(18)	-48.4(3)
C(16)-C(17)-C(18)-C(19)	61.5(3)
C(17)-C(18)-C(19)-C(20)	-42.3(3)
C(14)-C(15)-C(20)-C(11)	1.7(3)
C(16)-C(15)-C(20)-C(11)	-176.72(18)
C(14)-C(15)-C(20)-C(19)	178.44(19)
C(16)-C(15)-C(20)-C(19)	0.0(3)
C(12)-C(11)-C(20)-C(15)	0.0(3)
C(10)-C(11)-C(20)-C(15)	177.32(18)
C(12)-C(11)-C(20)-C(19)	-176.77(18)
C(10)-C(11)-C(20)-C(19)	0.5(3)
C(18)-C(19)-C(20)-C(15)	11.6(3)
C(18)-C(19)-C(20)-C(11)	-171.6(2)
O(2)-Si(1)-C(23)-C(25)	169.83(16)
C(21)-Si(1)-C(23)-C(25)	-70.3(2)
C(22)-Si(1)-C(23)-C(25)	52.0(2)
O(2)-Si(1)-C(23)-C(24)	-68.7(2)
C(21)-Si(1)-C(23)-C(24)	51.2(3)
C(22)-Si(1)-C(23)-C(24)	173.5(2)
O(2)-Si(1)-C(23)-C(26)	50.91(19)
C(21)-Si(1)-C(23)-C(26)	170.77(18)
C(22)-Si(1)-C(23)-C(26)	-66.9(2)
C(45)-Mo(1)-N(1)-C(27)	-106.8(8)

O(1)-Mo(1)-N(1)-C(27)	138.2(8)
N(2)-Mo(1)-N(1)-C(27)	3.2(8)
Mo(1)-N(1)-C(27)-C(32)	32.3(9)
Mo(1)-N(1)-C(27)-C(28)	-147.0(7)
N(1)-C(27)-C(28)-C(29)	176.47(18)
C(32)-C(27)-C(28)-C(29)	-2.8(3)
N(1)-C(27)-C(28)-C(33)	-0.5(3)
C(32)-C(27)-C(28)-C(33)	-179.83(18)
C(27)-C(28)-C(29)-C(30)	1.3(3)
C(33)-C(28)-C(29)-C(30)	178.26(19)
C(28)-C(29)-C(30)-C(31)	0.7(3)
C(29)-C(30)-C(31)-C(32)	-1.2(3)
C(30)-C(31)-C(32)-C(27)	-0.2(3)
C(30)-C(31)-C(32)-C(36)	-178.6(2)
N(1)-C(27)-C(32)-C(31)	-177.00(18)
C(28)-C(27)-C(32)-C(31)	2.3(3)
N(1)-C(27)-C(32)-C(36)	1.3(3)
C(28)-C(27)-C(32)-C(36)	-179.37(18)
C(29)-C(28)-C(33)-C(34)	34.2(3)
C(27)-C(28)-C(33)-C(34)	-148.89(19)
C(29)-C(28)-C(33)-C(35)	-90.8(2)
C(27)-C(28)-C(33)-C(35)	86.1(2)
C(31)-C(32)-C(36)-C(37)	74.8(2)
C(27)-C(32)-C(36)-C(37)	-103.5(2)
C(31)-C(32)-C(36)-C(38)	-49.5(3)
C(27)-C(32)-C(36)-C(38)	132.2(2)
N(1)-Mo(1)-N(2)-C(39)	-125.3(2)
C(45)-Mo(1)-N(2)-C(39)	-21.3(2)
O(1)-Mo(1)-N(2)-C(39)	110.32(19)
N(1)-Mo(1)-N(2)-C(42)	83.91(14)
C(45)-Mo(1)-N(2)-C(42)	-172.11(14)
O(1)-Mo(1)-N(2)-C(42)	-40.49(16)
C(42)-N(2)-C(39)-C(40)	0.4(2)
Mo(1)-N(2)-C(39)-C(40)	-151.75(18)
C(42)-N(2)-C(39)-C(43)	-177.7(2)
Mo(1)-N(2)-C(39)-C(43)	30.1(3)
N(2)-C(39)-C(40)-C(41)	0.4(3)
C(43)-C(39)-C(40)-C(41)	178.4(2)
C(39)-C(40)-C(41)-C(42)	-1.2(3)
C(40)-C(41)-C(42)-N(2)	1.5(3)

C(40)-C(41)-C(42)-C(44)	-178.1(2)
C(39)-N(2)-C(42)-C(41)	-1.2(2)
Mo(1)-N(2)-C(42)-C(41)	157.41(16)
C(39)-N(2)-C(42)-C(44)	178.4(2)
Mo(1)-N(2)-C(42)-C(44)	-23.0(2)
N(1)-Mo(1)-C(45)-C(46)	-7.9(2)
O(1)-Mo(1)-C(45)-C(46)	107.0(2)
N(2)-Mo(1)-C(45)-C(46)	-112.8(2)
Mo(1)-C(45)-C(46)-C(47)	-2.2(3)
Mo(1)-C(45)-C(46)-C(49)	-124.6(2)
Mo(1)-C(45)-C(46)-C(48)	116.3(2)
C(47)-C(46)-C(49)-C(54)	-114.0(2)
C(45)-C(46)-C(49)-C(54)	9.6(3)
C(48)-C(46)-C(49)-C(54)	126.6(2)
C(47)-C(46)-C(49)-C(50)	65.1(2)
C(45)-C(46)-C(49)-C(50)	-171.33(17)
C(48)-C(46)-C(49)-C(50)	-54.3(2)
C(54)-C(49)-C(50)-C(51)	-0.9(3)
C(46)-C(49)-C(50)-C(51)	180.0(2)
C(49)-C(50)-C(51)-C(52)	0.4(3)
C(50)-C(51)-C(52)-C(53)	0.4(3)
C(51)-C(52)-C(53)-C(54)	-0.6(3)
C(50)-C(49)-C(54)-C(53)	0.6(3)
C(46)-C(49)-C(54)-C(53)	179.76(19)
C(52)-C(53)-C(54)-C(49)	0.1(3)
C(55)-C(56)-C(57)-C(58)	-178.5(3)
C(55)-C(56)-C(57)-C(58X)	-178.5(3)
C(56)-C(57)-C(58)-C(59)	64.7(5)
C(58X)-C(57)-C(58)-C(59)	58(66)
C(56)-C(57)-C(58X)-C(59X)	-169.2(2)
C(58)-C(57)-C(58X)-C(59X)	4(65)

Symmetry transformations used to generate equivalent atoms: