A new and more powerfully activating diamine for practical and scalable enantioselective aldehyde crotylsilylation reactions

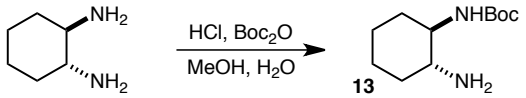
Linda M. Suen, Michael L. Steigerwald and James L. Leighton

Department of Chemistry, Columbia University, New York, NY, 10027

Supporting Information

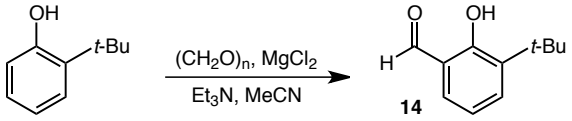
General Information. All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise indicated. Degassed solvents were purified by passage through an activated alumina column. Thin-layer chromatography (TLC) was carried out on glass backed silica gel TLC plates (250 mm) from Silicycle; visualization by UV light and/or phosphomolybdic acid (PMA). HPLC analysis was carried out on an Agilent 1200 Series using either a Chiralpak AD-H (250 x 4.5 mm ID) column or Chiralcel OD-H (250x4.5 mm ID) column. ^{1}H NMR spectra were recorded on a Bruker AVIII 300 (300 MHz), AVIII 400 (400 MHz), AVIII 500 (500 MHz) or AVIII 500 Ascend (500 MHz) spectrometer and are reported in ppm, relative to residual protonated solvent peak ($CDCl_3$, 7.26 ppm; C_6D_6, 7.16 ppm). Data are reported as follows: (bs= broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, td = triplet of doublets; coupling constant(s) in Hz; integration). Proton decoupled ^{13}C NMR spectra were recorded on a Bruker AVIII 400 (100 MHz), AVIII 500 (126 MHz) or AVIII 500 Ascend (126 MHz) spectrometer and are reported in ppm from $CDCl_3$ internal standard (77.23 ppm). ^{29}Si NMR spectra were recorded on a Bruker AVIII 400 (79 MHz) or AVIII 500 (100 MHz) and are reported in ppm relative to TMS (0.00 ppm) internal standard. ^{19}F NMR spectra were recorded on a Bruker AVIII 400 (376 MHz) and are reported in ppm relative to α,α,α-trifluorotoluene (-63.72 ppm) internal standard. Infrared spectra were recorded on a Nicolet Avatar 370DTGS FT-IR. Optical rotations were recorded on a Jasco DIP-1000 digital polarimeter. (APCI)-MS was conducted on a JMS-LCmate LCMS (JEOL). Melting points were determined using a Stanford Research Systems DigiMelt apparatus.

Preparation of diaminophenol 6:



13

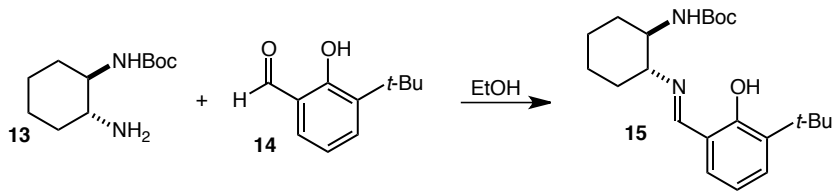
Compound **13** was prepared using a modified literature procedure.[1] To a cooled (0 °C) solution of conc. HCl (32.4 mL, 394 mmol) in MeOH (126 mL) was added (*R,R*)-diaminocyclohexane (45.0 g, 394 mmol). The ice water bath was removed, and after 15 min, water (42.0 mL) was added. After 30 min, a solution of Boc_2O (90.6 mL, 394 mmol) in MeOH (42 mL) was added slowly and the resulting mixture was stirred for 12 h. The mixture was concentrated and the residue was resuspended in Et_2O (100 mL), and collected by filtration, rinsing with Et_2O to remove any unprotected diaminocyclohexane. The resulting residue was treated with 3 N NaOH (285 mL) and extracted with CH_2Cl_2 (3 x 125 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated to give **13** as a beige solid (55.2 g, 257 mmol, 65%) that was used without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.43 (bs, 1H), 3.23-2.95 (m, 1H), 2.31 (td, *J* = 10.4, 4.0 Hz, 1H), 2.06-1.88 (m, 2H), 1.78-1.63 (m, 2H), 1.45 (s, 9H), 1.38-0.99 (m, 6H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[1,2]



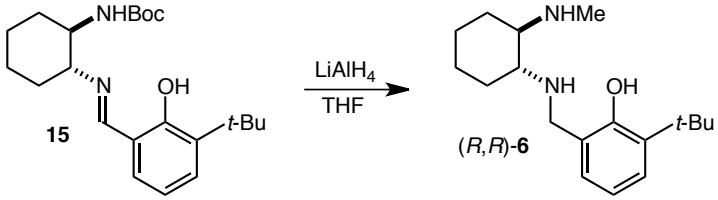
14

Aldehyde **14** was prepared using a modified literature procedure.[3] To a solution of 2-*tert*-butyl phenol (30.6 mL, 200 mmol) in acetonitrile (400 mL) was added paraformaldehyde (40.4 g, 1.35 mol), $MgCl_2$ (28.6 g, 300 mmol) and Et_3N (104.4 mL, 748 mmol). The resulting mixture was heated to reflux and stirred for 5 h. The mixture was cooled to room temperature and 5% HCl (200 mL) was added. The mixture was extracted with CH_2Cl_2 (3 x 125 mL). The combined organic layers were concentrated and the residue was partitioned between Et_2O (250 mL) and H_2O (250 mL). The layers were separated and the Et_2O layer was washed with brine (1 x 100 mL), dried over Na_2SO_4, filtered and concentrated. The resulting oil was vacuum distilled (bp ~73 °C @ ~5 mm Hg) to give aldehyde **14** as a pale yellow oil (20.7 g, 116 mmol, 58% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 11.78 (s, 1H), 9.88 (s, 1H), 7.53 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.40 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 1.43 (s, 9H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[3]

(1) D. W. Lee, H. Ha and W. K. Lee, *Synth. Commun.*, 2007, **37**, 737-742.
(2) X. Zhang, T. J. Emge and K. C. Hultzsch, *Angew. Chem. Int. Ed.*, 2012, **51**, 394-398.
(3) N. Gisch, J. Balzarini and C. Meier, *J. Med. Chem.*, 2007, **50**, 1658-1667.



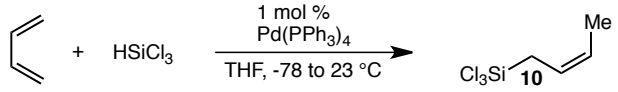
To a solution of compound **13** (24.9 g, 116 mmol) in EtOH (1.1 L), was added aldehyde **14** (20.7 g, 116 mmol). The mixture was heated to reflux and stirred for 3 h. The mixture was cooled to room temperature and concentrated. The residue was recrystallized from minimal boiling EtOH to give imine **15** as long yellow crystals (39.2 g, 105 mmol, 90% yield). **m.p.** 153-155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.73 (bs, 1H), 8.35 (s, 1H), 7.32 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 4.37 (bs, 1H), 3.73-3.40 (m, 1H), 3.04 (bs, 1H), 2.18-2.02 (m, 1H), 1.98-1.87 (m, 1H), 1.87-1.64 (m, 3H), 1.46-1.30 (m, 3H) 1.45 (s, 9H), 1.31 (s, 9H); **^{13}C** NMR (101 MHz, $CDCl_3$) δ 165.02, 160.64, 155.39, 137.55, 129.85, 129.44, 118.87, 117.82, 79.49, 77.43, 72.87, 54.55, 35.02, 33.64, 32.00, 29.57, 28.37, 25.06, 24.31; **IR** (thin film, cm^{-1}) 3437, 3338, 2936, 2859, 2243, 1688, 1630, 1505, 1436, 1390, 1365, 1267, 733; **HRMS (FAB+)**: calcd for $C_{22}H_{35}O_3N_2$ $[M+H]^+$: 375.2648, found 375.2654.



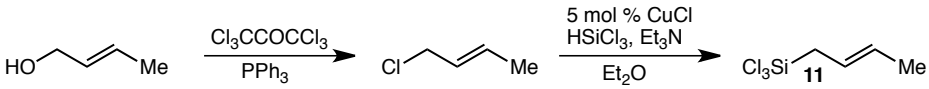
A 2-L roundbottom flask equipped with an addition funnel was charged with $LiAlH_4$ (13.0 g, 343 mmol) and THF (600 mL) and the resulting mixture was cooled to 0 °C. A solution of **15** (42.8 g, 114 mmol) in THF (300 mL) was added slowly *via* the addition funnel, with a THF rinse (100 mL). The mixture was warmed to room temperature and stirred for 2 h. The addition funnel was replaced with a reflux condenser and the mixture was heated to reflux for 12 h. The mixture was cooled to 0 °C, and the reaction was quenched by the ***CAREFUL*** and ***SLOW*** addition of water (100 mL). The mixture was extracted with Et_2O (5 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The resulting beige solid was purified by recrystallization from minimal boiling hexanes to give diaminophenol (*R*,*R*)-**6** as white crystals (30.2 g, 104 mmol, 91% yield). **m.p.** 114-116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.92-6.80 (m, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 4.01 (d, *J* = 13.4 Hz, 1H), 3.83 (d, *J* = 13.5 Hz, 1H), 2.39 (s, 3H), 2.24-2.08 (m, 4H), 1.82-1.64 (m, 2H), 1.42 (s, 9H), 1.31-1.11 (m, 3H), 1.03-0.85 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.49, 136.88, 126.27, 125.77, 124.47, 118.16, 62.46, 62.22, 51.02, 34.85, 33.59, 31.24, 31.16, 29.74, 25.33, 24.83; **IR** (thin

film, cm^{-1}) 3299, 3217, 2927, 2854, 2797, 2641, 1590, 1430, 1352, 1240, 1084, 747; **HRMS (FAB+)**: calcd for $C_{18}H_{31}ON_2$ $[M+H]^+$: 291.2436, found 291.2443.

Preparation of *cis*-crotyltrichlorosilane 10 and *trans*-crotyltrichlorosilane 11:



cis-Crotyltrichlorosilane **10** was prepared using a modified literature procedure.[4,5] To a cooled (-78 °C) solution of $Pd(PPh_3)_4$ (0.88 g, 0.76 mmol) in THF (400 mL) was added 1,3-butadiene (50 mL, 573 mmol, condensed into a graduated cylinder cooled to -78 °C) followed by trichlorosilane (38.6 mL, 382 mmol). After 15 min, the cooling bath was removed and the mixture was allowed to warm to room temperature. After 17 h, an aliquot was removed and ^{1}H NMR analysis showed complete consumption of the trichlorosilane. The reaction flask was fitted with a short-path distillation head and the THF was removed by distillation. The residue was transferred to a distillation-head equipped, 250-mL roundbottom flask with a THF rinse. The THF was removed by distillation and the residue was distilled under reduced pressure (bp ~60 °C @ ~30 mm Hg) to give **10** as a clear and colorless liquid (56.2 g, 297 mmol, 78% yield). ^{1}H NMR spectroscopic analysis revealed that the *cis* to *trans* ratio was ≥99:1. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.84-5.62 (m, 1H), 5.54-5.31 (m, 1H), 2.50-2.24 (m, 2H), 1.76-1.58 (m, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[5]

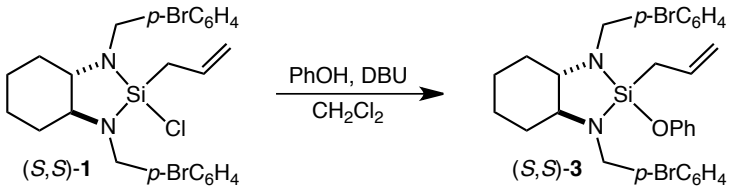


trans-Crotyltrichlorosilane **11** was prepared according to a modified literature procedure.[5,6] *trans*-Crotylalcohol was purchased from Sigma Aldrich as a 19:1 (E:Z) mixture, which was confirmed by ^{1}H NMR spectroscopic analysis. To a cooled (0 °C) solution of *trans*-crotylalcohol (121 mL, 1.41 mol) in hexachloroacetone (470 mL) was added PPh_3 (386 g, 1.47 mol) portion-wise over 3 h. The ice/water bath was allowed to melt and warm to room temperature slowly, and after 12 h the reaction flask was fitted with a short-path distillation head. Distillation (bp ~85°C @ 760 mm Hg) gave *trans*-crotylchloride as a clear and colorless liquid (83.2 g, 919 mmol, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.88-5.73 (m, 1H), 5.69-5.52 (m, 1H), 4.06-3.98 (m, 2H), 1.75-1.68 (m, 3H).

(4) J. Tsuji, M. Hara and K. Ohno, *Tetrahedron*, 1974, **30**, 2143-2146.
(5) K. Iseki, Y. Kuroki, M. Takahashi, S. Kishimoto and Y. Kobayashi, *Tetrahedron*, 1997, **53**, 3513-3526.
(6) M. Kira, T. Hino and H. Sakurai, *Tetrahedron Lett*., 1989, **30**, 1099-1102.

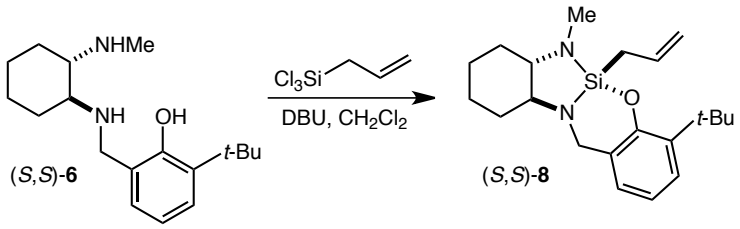
A 2 L round bottom flask equipped with an addition funnel was charged with Et_3N (104 mL, 1.03 mol) and Et_2O (450 mL). The solution was cooled to 0 °C and copper(I) chloride (4.2 g, 43 mmol) was added. A solution of trichlorosilane (104 mL, 1.03 mol) and *trans*-crotylchloride (77.4 g, 855 mmol) in Et_2O (150 mL) was prepared and transferred to the addition funnel. This solution was then added *very slowly* (over the course of 1 h) to the reaction mixture, so as to maintain a reaction mixture temperature near 0 °C. After the addition was complete, the mixture was allowed to warm to room temperature and after 2 h, analysis of an aliquot by ^{1}H NMR spectroscopy showed complete consumption of the *trans*-crotylchloride. The solution was transferred to a 2 L round bottom flask by cannulation through a glass microfiber filter (Grade GF/D) equipped teflon tube (3/16 i.d.) to filter the Et_3N•HCl salts. The flask was fitted with a distillation head and the Et_2O and Et_3N were removed by distillation. The residue was transferred to a 250 mL pear-shaped flask by cannula with an Et_2O rinse. The flask was fitted with a short-path distillation head and the excess Et_2O was removed by distillation and the residue was distilled (bp ~140-145 °C @ 760 mm Hg) to give *trans*-crotyltrichlorosilane **11** as a clear and colorless liquid (74.4 g, 392 mmol, 46% yield). ^{1}H NMR spectroscopic analysis revealed that the *trans* to *cis* ratio was 95:5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.67-5.53 (m, 1H), 5.48-5.32 (m, 1H), 2.31-2.20 (m, 2H), 1.76-1.69 (m, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[5]

Preparation and characterization of silanes (*S*,*S*)-3 and (*S*,*S*)-8:



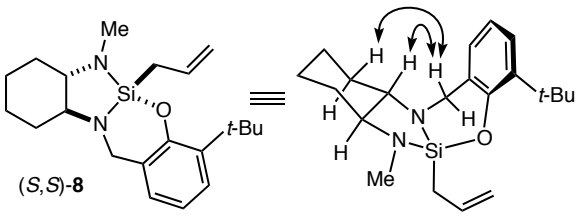
To a cooled (0 °C) solution of (*S*,*S*)-**1** (1.00 g, 1.8 mmol) in CH_2Cl_2 (7.0 mL) was added DBU (270 μL, 1.8 mmol) followed by freshly distilled phenol (170 mg, 1.8 mmol). The ice/water bath was removed and after 1.5 h, the flask was fitted with a distillation head and the volatiles were removed by distillation. The residue was treated with pentane (10 mL) and the mixture was stirred vigorously for 10 min to ensure complete precipitation of the DBU•HCl salts. The mixture was then filtered through an air-free filter frit, and the filtrate was concentrated to give (*S*,*S*)-**3** as a thick oil, which was analyzed without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.19 (m, 4H), 7.08-6.97 (m, 3H), 6.90-6.84 (m, 2H), 5.04-4.84 (m, 2H), 4.09 (dd, *J* = 15.6, 3.6 Hz, 2H), 3.80 (dd, *J* = 18.8, 15.6 Hz, 2H), 2.87-2.64 (m, 2H), 1.76-1.48 (m, 6H), 1.22-1.03 (m, 2H), 1.02-0.82 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.62, 141.40, 141.29, 132.80, 131.27, 131.23, 129.62, 129.35, 122.00,

120.46, 120.28, 120.15, 115.37, 66.68, 65.99, 48.12, 48.05, 31.19, 30.94, 24.91, 20.27; **^{29}Si NMR** (79 MHz, $CDCl_3$) δ -25.21.



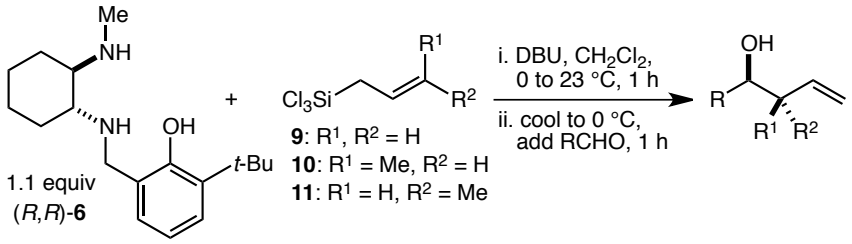
To a cooled (0 °C) solution of (*S*,*S*)-**6** (1.00 g, 3.4 mmol) in CH_2Cl_2 (11 mL) was added DBU (1.54 mL, 10.3 mmol). Allyltrichlorosilane (0.55 mL, 3.8 mmol) was then added slowly. The reaction mixture was allowed to warm to room temperature and after 1 h the flask was fitted with a distillation head and the volatiles were removed by distillation. The residue was treated with Et_2O (15 mL), and the resulting mixture was stirred vigorously for 10 min to ensure complete precipitation of the DBU•HCl salts. The mixture was then filtered through an air-free filter frit, and the filtrate was concentrated to give (*S*,*S*)-**8** as a thick oil, which was analyzed without further purification. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23-7.18 (m, 1H), 6.90-6.84 (m, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 5.95 (ddt, *J* = 16.9, 10.1, 7.8 Hz, 1H), 5.16-5.07 (m, 1H), 5.04-4.95 (m, 1H), 4.23 (d, *J* = 15.6 Hz, 1H), 3.69 (d, *J* = 15.7 Hz, 1H), 2.54-2.42 (m, 1H), 2.47 (s, 3H), 2.13 (ddd, *J* = 10.5, 9.0, 3.3 Hz, 1H), 2.06-1.90 (m, 4H), 1.74-1.63 (m, 2H), 1.39 (s, 9H), 1.26-1.15 (m, 1H), 1.14-1.03 (m, 2H), 0.86-0.73 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.93, 139.64, 135.86, 132.00, 130.16, 129.31, 127.17, 125.92, 121.56, 120.54, 115.69, 64.94, 62.57, 54.65, 48.97, 47.52, 38.13, 34.85, 32.33, 30.26, 30.13, 29.98, 29.94, 29.86, 29.60, 29.31, 24.96, 24.75, 24.29, 19.81, 18.88; **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -15.38; **HRMS (FAB+)**: calcd for $C_{21}H_{33}ON_2Si$ $[M+H]^+$: 357.2362, found 357.2351.

The stereostructure of **8** was proved by NMR spectroscopic analysis. COSY, HSQC, and HMBC experiments allowed the unambiguous assignment of all of the relevant protons in the ^{1}H NMR spectrum, and a NOESY experiment revealed the illustrated interactions which are consistent only with the silicon stereochemistry shown in structure (*S*,*S*)-**8** (Supp. Fig. 1). Copies of the COSY, HSQC, HMBC, and NOESY spectra are provided below.



Supplementary Figure 1. NOESY data confims the stereochemical assignment at silicon in (*S*,*S*)-**8**.

General Procedure for the one-pot allylation or crotylation of aldehydes with (*R*,*R*)-6:



To a cooled (0 °C) solution of (*R*,*R*)-**6** (1.45 g, 5.0 mmol, 1.1 equiv.) in CH_2Cl_2 (16.5 mL) is added DBU (2.24 mL, 15.0 mmol, 3.3 equiv). The allyltrichlorosilane **9** or *cis*-crotyltrichlorosilane **10** or *trans*-crotyltrichlorosilane **11** (**9**: 0.80 mL, **10** or **11**: 0.84 mL, 5.5 mmol, 1.2 equiv) is then added slowly. The ice/water bath is removed and after 1 h the mixture is recooled to 0 °C. The aldehyde (4.5 mmol, 1.0 equiv) is added and the solution is maintained at 0 °C for 1 h. The progress of the reaction may be monitored by TLC, 1 h is generally sufficient for full conversion.

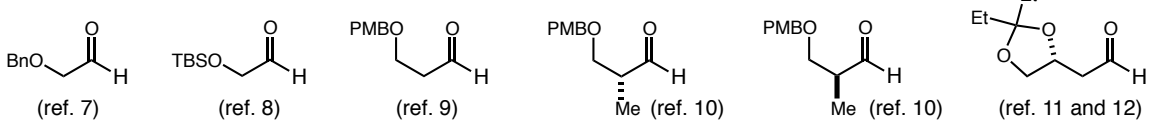
(A) General procedure for the acidic workup with recovery of 6: The mixture is concentrated and the residue is suspended in Et_2O (27.0 mL). The mixture is stirred vigorously for 20 min to ensure complete precipitation of the DBU•HCl salts. The mixture is then filtered through a frit, and the filtrate is treated with *n*-Bu_4NF (5.0 mL, 1 M in THF, 5.0 mmol, 1.1 equiv). After 2 h, 1 M aqueous HCl (25.0 mL, 25.0 mmol, 5.5 equiv) is added and the mixture is transferred to a separatory funnel. The layers are separated and the aqueous layer is extracted with Et_2O (3 x 50.0 mL). The combined organic layers are washed with H_2O (2 x 25.0 mL) and saturated aqueous $NaHCO_3$ (1 x 25.0 mL), dried over $MgSO_4$, filtered and concentrated. The residue is purified by chromatography on silica gel to provide the allylation or crotylation product, and we have found that a simple filtration through a pad of silica is generally sufficient.

Recovery of 6: The combined aqueous layers from above are treated with 1 M aqueous NaOH (50 mL, 50 mmol) and extracted with CH_2Cl_2 (5 x 50.0 mL). The combined organic layers are washed with water (2 x 25.0 mL), dried over $MgSO_4$, filtered and concentrated. The residue is dissolved in minimal hot 9:1 MeOH:H_2O (during the dissolution process the temperature should not be allowed to exceed 80 °C, as the ligand may start to undergo decomposition at higher temperatures). The hot saturated solution is allowed to cool to room temperature, and distilled water (10.0 mL) was added to ensure complete crystallization of **6**. The white solid is collected by filtration through a frit with a cold 1:1 MeOH:H_2O rinse and then dried *in vacuo* (overnight, with gentle warming with an oil bath set to 40 °C) to give recovered diaminophenol **6**.

(B) General procedure for the simplified workup for acid-sensitive substrates without recovery of 6: The reaction mixture is treated with *n*-Bu_4NF (4.5 mL, 1 M in THF, 4.5 mmol, 1.0 equiv) and the ice/water bath is removed. After 30 min the mixture is concentrated and the residue is purified by chromatography on silica gel to provide the allylation or crotylation product.

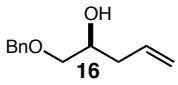
Aldehydes employed in this study:

The six aldehydes employed in Table 1 are all known compounds and were prepared according to the literature procedures.[7,8,9,10,11,12]



(ref. 7) (ref. 8) (ref. 9) (ref. 10) (ref. 10) (ref. 11 and 12)

Data for the products in Table 1:



16

Workup procedure **A** was used. Product **16** was isolated as a colorless oil (83% yield, >99% ee). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.27 (m, 5H), 5.83 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.20-5.04 (m, 2H), 4.56 (s, 2H), 3.92-3.85 (m, *J* = 10.0, 6.7, 3.4 Hz, 1H), 3.52 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.38 (dd, *J* = 9.5, 7.4 Hz, 1H), 2.31 (d, *J* = 3.5 Hz, 1H), 2.29-2.25 (m, 2H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[13] The enantiomeric excess was determined by chiral HPLC analysis: OD-H column, 98.5:1.5 hexanes:*i*PrOH, 1 mL/min, 254 nm. The absolute configuration was determined by optical rotation and comparison to the literature value: $[\alpha]_D^{22}$ +2.3° ($CHCl_3$, *c* 2.0); lit: $[\alpha]_D^{23}$ +2.0° ($CHCl_3$, *c* 2.3) for the (*S*) enantiomer with 94% ee.[13]

(7) S. Sano, Y. Kobayashi, T. Kondo, M. Takebayashi, S. Maruyama, T. Fujita and Y. Nagao, *Tetrahedron Lett.*, 1995, **36**, 2097-2100.
(8) S. F. Vanier, G. Larouche, R. P. Wurz and A. B. Charette, *Org. Lett.*, 2010, **12**, 672-675.
(9) C. L. Flowers and P. Vogel, *Chemistry (Weinheim an der Bergstrasse, Germany)*, 2010, **16**, 14074-14082.
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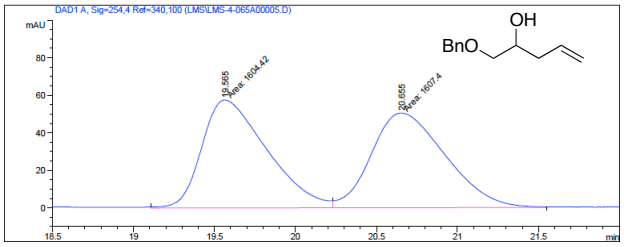
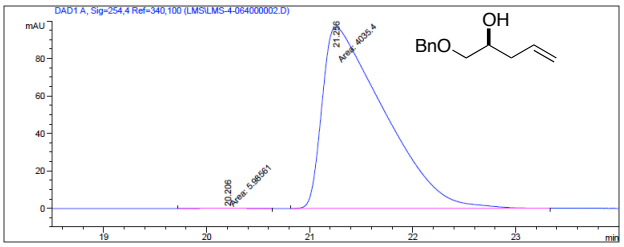
(13) G. E. Keck and D. Krishnamurthy, *Organic Syntheses*, 1998, **75**, 12-18.





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2	20.655	1	FM	1607.39941	50.43341	50.0464

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
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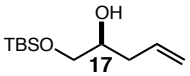
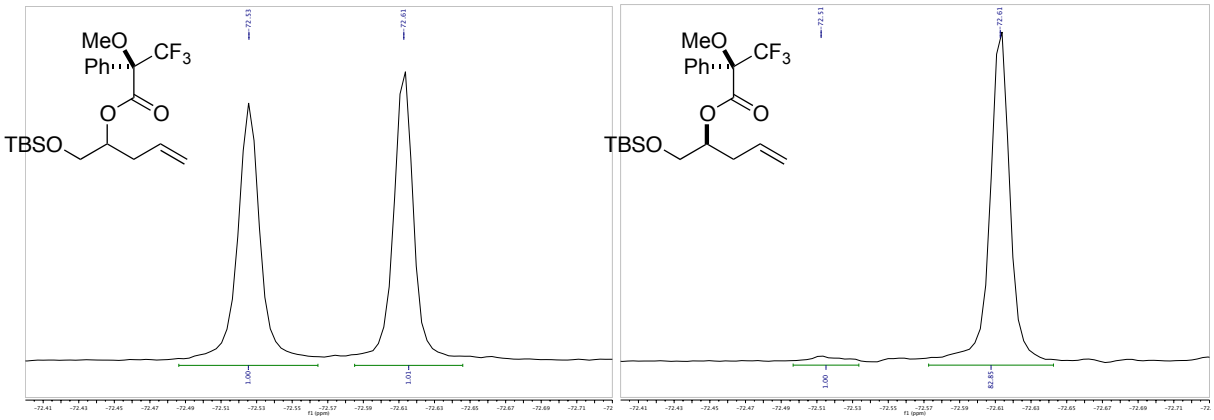
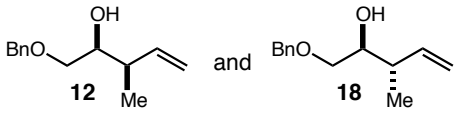
2	21.256	1	MM	4035.39697	96.79804	99.8519



Workup procedure **B** was used and product **17** was isolated as a colorless oil (81% yield, 98% ee). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.17-5.03 (m, 2H), 3.74-3.67 (m, 1H), 3.63 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.46 (dd, *J* = 9.9, 6.9 Hz, 1H), 2.39 (d, *J* = 3.9 Hz, 1H), 2.30-2.19 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[14] The enantiomeric excess was determined by ^{19}F NMR (376 MHz, $CDCl_3$) analysis of the Mosher ester.[15] The absolute configuration was determined by optical rotation and comparison to the literature value: $[\alpha]_D^{22}$ +2.4° ($CHCl_3$, *c* 2.0); lit: $[\alpha]_D^{20}$ +1.7° ($CHCl_3$, *c* 0.24) for the (*S*) enantiomer with 59% ee.[14]



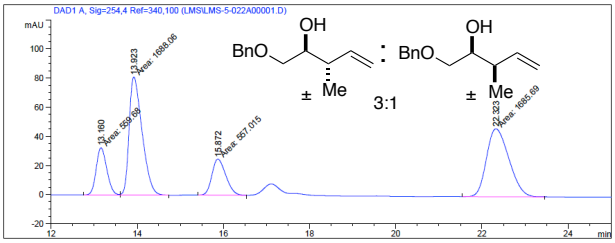
(14) W. R. Roush, L. K. Hoong, M. A. J. Palmer, J. A. Straub and A. D. Palkowitz, *J. Org. Chem.* 1990, **55**, 4117-4126.
(15) (a) J. A. Dale, D. L. Dull and H. S. Mosher, *J. Org. Chem.*, 1969, **34**, 2543-2549; (b) T. R. Hoye, C. S. Jeffrey and F. Shao, *Nature protocols*, 2007, **2**, 2451-2458.



Workup procedure **B** was used to prepare product **12** (for convenience on small scale, not because it is acid sensitive), which was isolated as a colorless oil (94% yield, 96% ee, 98:2 dr). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43-7.27 (m, 5H), 5.74 (ddd, *J* = 17.2, 10.3, 7.9 Hz, 1H), 5.14-4.98 (m, 2H), 4.55 (s, 2H), 3.65-3.62 (m, 1H), 3.56 (dd, *J* = 9.5, 3.1 Hz, 1H), 3.40 (dd, *J* = 9.5, 7.7 Hz, 1H), 2.40-2.27 (m, 2H), 1.08 (d, *J* = 6.8 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[16] The enantiomeric excess and diastereomer ratio were determined by chiral HPLC analysis: OD-H column, 98:2 hexanes:*i*PrOH, 1 mL/min, 254 nm. The assay was developed using a 3:1 *anti*:*syn* mixture of racemic diastereomers. The absolute configuration was determined by optical rotation and comparison to the literature value: $[\alpha]_D^{22}$ +23.8° (CH_2Cl_2, *c* 2.0); lit: $[\alpha]_D^{20}$ +24.6° (CH_2Cl_2, *c* 1.8) for the (*S,R*) enantiomer with 96% ee.[16]

Workup procedure **A** was used to prepare product **18**, which was isolated as a colorless oil (88% yield, 97% ee, 94:6 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 5H), 5.90-5.74 (m, 1H), 5.13-5.03 (m, 2H), 4.59-4.50 (s, 2H), 3.71-3.63 (m, 1H), 3.55 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.43 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.43-2.29 (m, 1H), 2.25 (d, *J* = 3.3 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[17] The enantiomeric excess and diastereomer ratio were determined by chiral HPLC analysis: OD-H column, 98:2 hexanes:*i*PrOH, 1 mL/min, 254 nm. The assay was developed using a ~3:1 *anti*:*syn* mixture of racemic diastereomers. The absolute configuration was determined by optical rotation and comparison to the literature value: $[\alpha]_D^{22}$ -7.1° ($CHCl_3$, *c* 2.0); lit: $[\alpha]_D^{20}$ -5.6° ($CHCl_3$, *c* 1.2) for the (*S,S*) enantiomer with 99% ee.[16]

(16) B. M. Hackman, P. J. Lombardi and J. L. Leighton, *Org. Lett.*, 2004, **6**, 4375-4377.
(17) D. K. Mohapatra, P. P. Das, M. R. Pattanayak and J. S. Yadav, *Chemistry (Weinheim an der Bergstrasse, Germany)*, 2010, **16**, 2072-2078.



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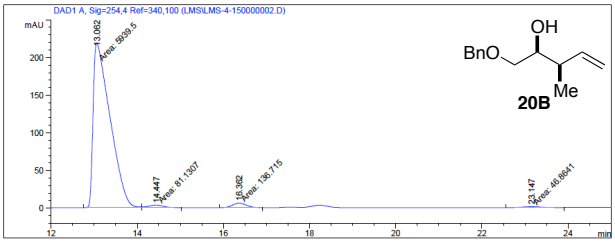
2	13.923	1	FM	1688.06042	81.23139	37.5922
3	15.872	1	MM	557.01508	24.84939	12.4044
4	22.323	1	MM	1685.69287	46.69843	37.5395



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
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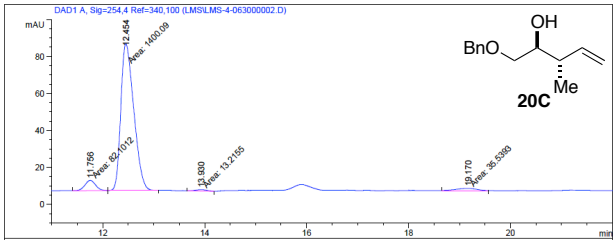
2	14.447	1	FM	81.13065	3.32667	1.3077
3	16.362	1	MM	136.71519	6.04427	2.2036
4	23.147	1	MM	46.86412	1.32124	0.7554



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1	11.756	1	MF	82.10124	5.56342	5.3698
2	12.454	1	FM	1400.09216	79.37217	91.5722
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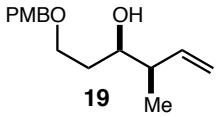
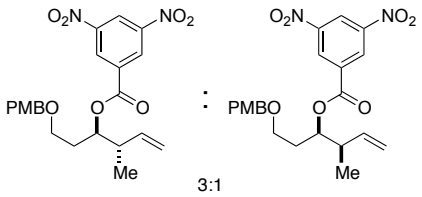
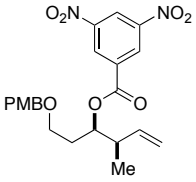
4	19.170	1	MM	35.53928	1.22603	2.3244

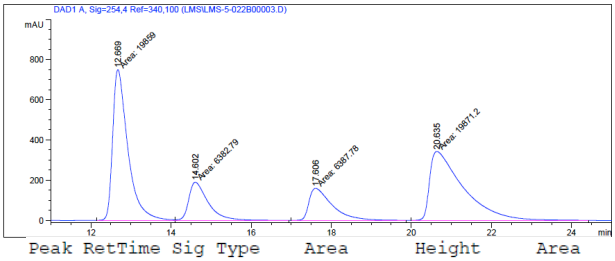


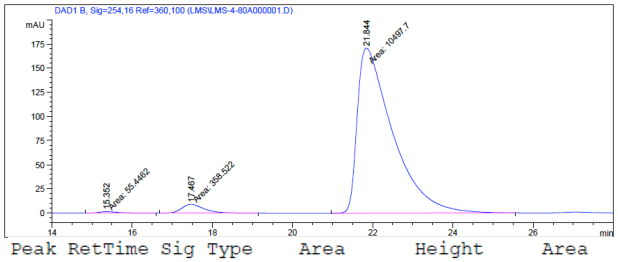
19

Workup procedure **A** was used and product **19** was isolated as a pale yellow oil (92% yield, 93% ee, >99:1 dr). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26-7.14 (m, 2H), 6.94-6.78 (m, 2H), 5.78 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.13-4.98 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.70 (ddd, *J* = 9.2, 5.7, 4.6 Hz, 1H), 3.66 (m, 1H), 3.61 (ddd, *J* = 9.3, 8.2, 4.4 Hz, 1H), 2.87 (d, *J* = 3.0 Hz, 1H), 2.30-2.21 (m, 1H), 1.81-1.64 (m, 2H), 1.05 (d, *J* = 6.8 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[16] The enantiomeric excess and diastereomeric ratio were determined by chiral HPLC analysis of the 3,5-dinitrobenzoate ester derivative: AD-H column, 98:1:1 hexanes:EtOH:MeOH, 1 mL/min, 254 nm. The assay was developed using a ~3:1 *anti*:*syn* mixture of racemic diastereomers. We previously determined that the (*R,R*)-diastereomer elutes third.[16]









Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.669	1	MF	1.98590e4	749.66516	37.8261
2	14.602	1	FM	6382.78760	190.29736	12.1575
3	17.606	1	MM	6387.78125	159.49940	12.1670
4	20.635	1	MM	1.98712e4	342.75272	37.8494

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	15.352	1	MM	55.44622	1.64576	0.5081
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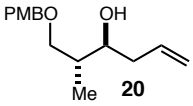
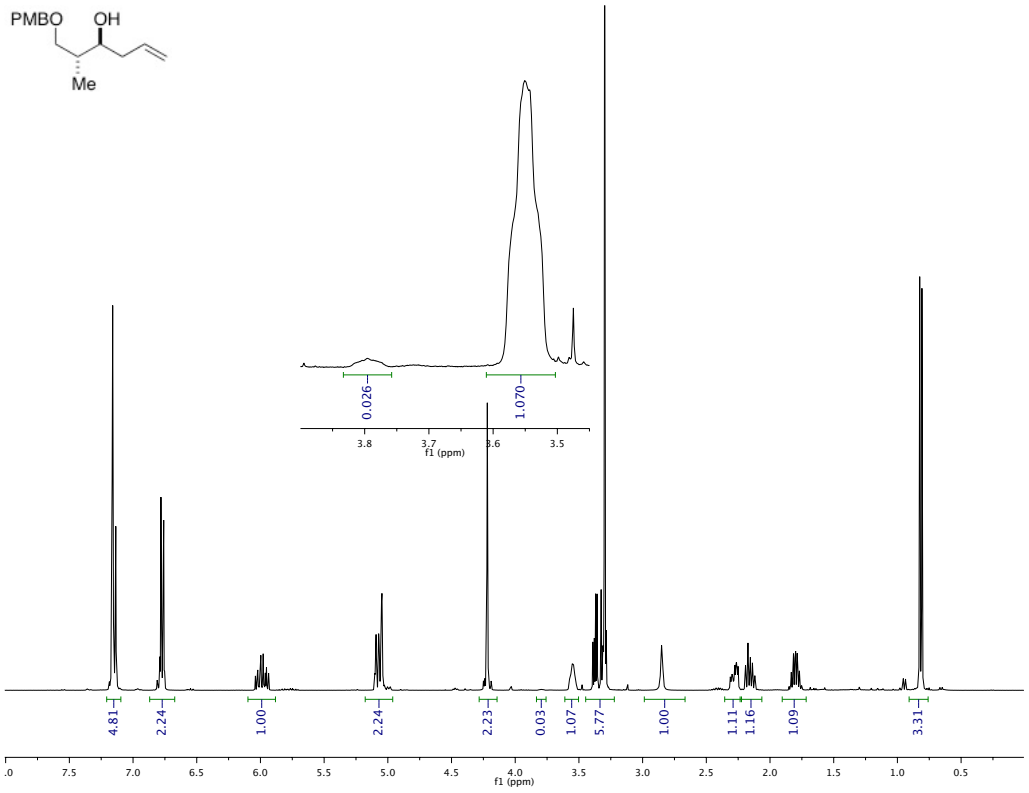
3	21.844	1	MM	1.04977e4	171.06367	96.2062

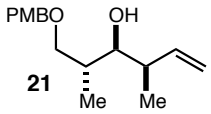


20

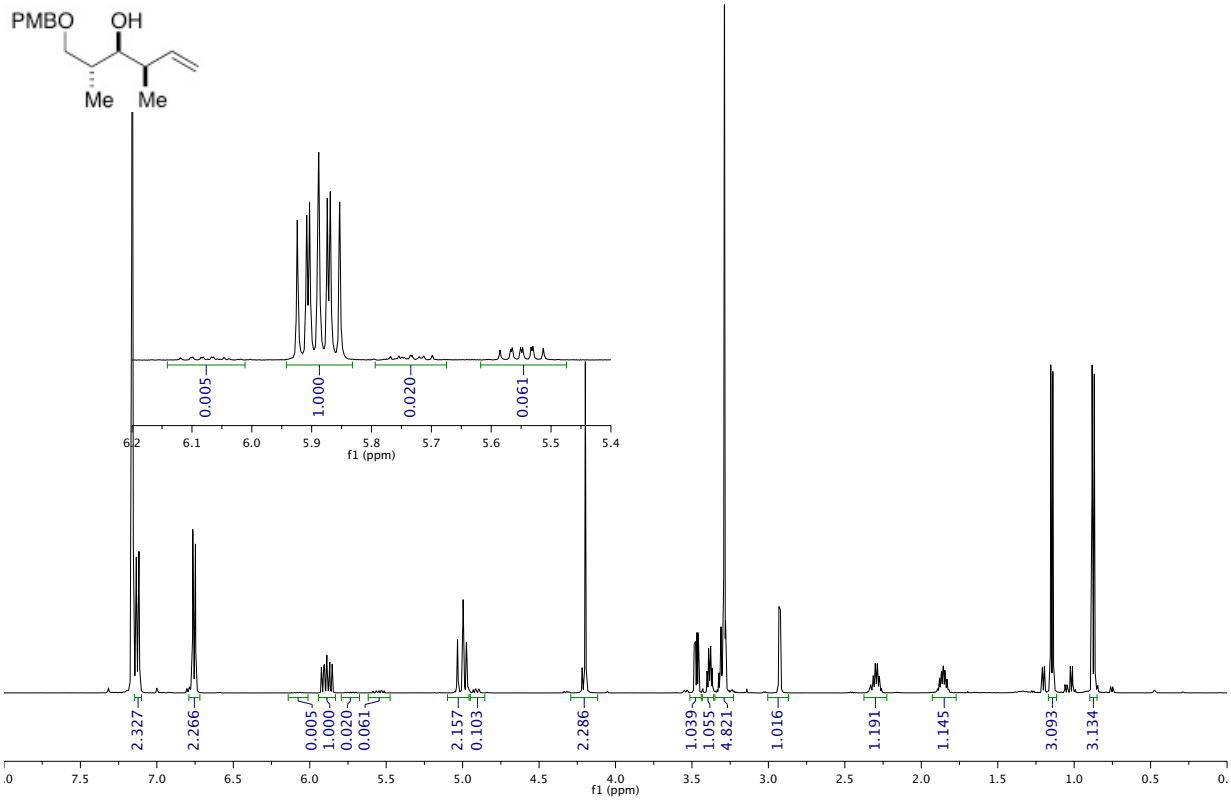
Workup procedure **A** was used and product **20** was isolated as a pale yellow oil (82% yield, 98:2 dr). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26-7.18 (m, 2H), 7.00-6.79 (m, 2H), 6.03-5.79 (m, 1H), 5.23-5.01 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.65-3.52 (m, 2H), 3.46 (dd, *J* = 9.2, 7.1 Hz, 1H), 3.24 (bs, 1H), 2.43-2.27 (m, 1H), 2.26-2.10 (m, 1H), 1.96-1.79 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[18] The diastereomer ratio was determined by ^{1}H NMR spectroscopy (C_6D_6, 400 MHz).



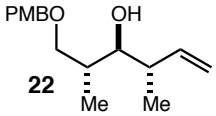
(18) T. M. Trygstad, Y. Pang and C. J. Forsyth, *J. Org. Chem.*, 2009, **74**, 910-913.



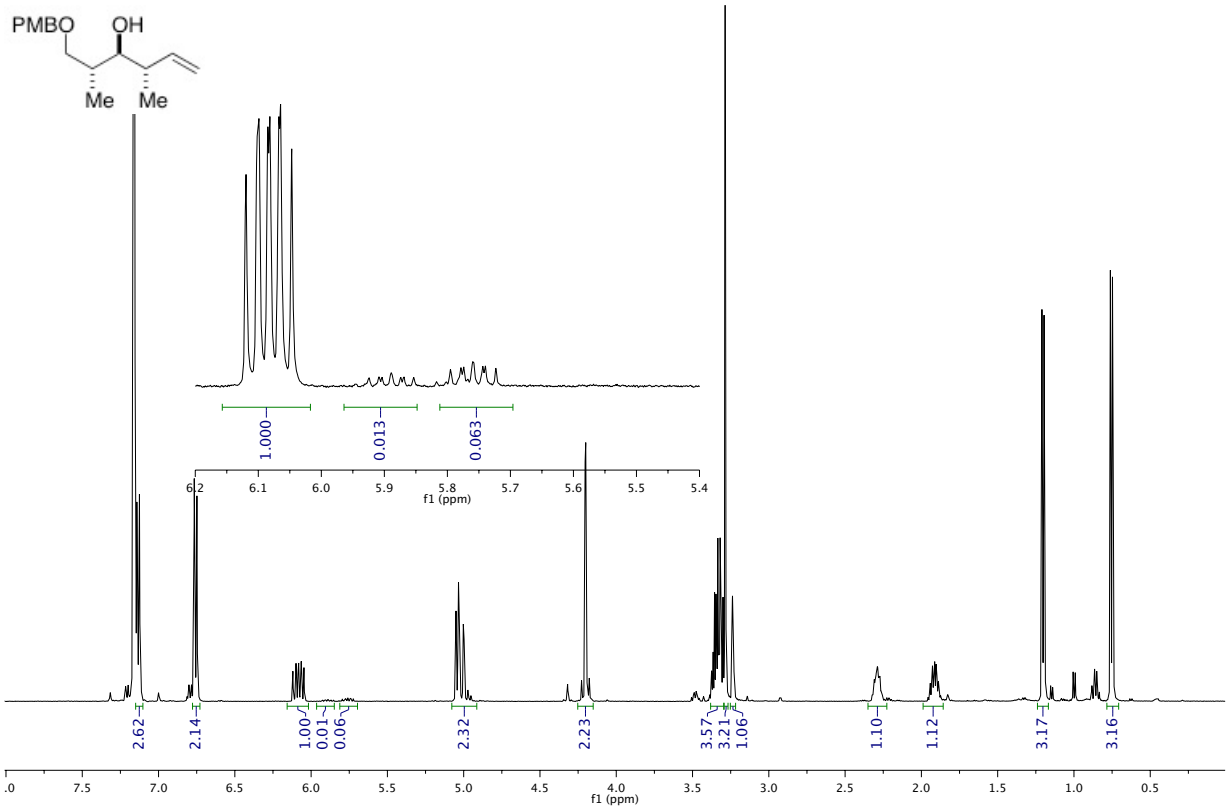
Workup procedure **A** was used and product **21** was isolated as a pale yellow oil (82% yield, 92:8 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26-7.20 (m, 2H), 6.95-6.79 (m, 2H), 5.85 (ddd, *J* = 17.5, 10.5, 7.3 Hz, 1H), 5.10-4.97 (m, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.63 (dd, *J* = 9.1, 4.1 Hz, 1H), 3.46 (dd, *J* = 9.1, 6.4 Hz, 1H), 3.39 (t, *J* = 5.7 Hz, 1H), 3.22 (bs, 1H), 2.39-2.24 (m, 1H), 1.99-1.85 (m, 1H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[19] The diastereomer ratio was determined by ^{1}H NMR spectroscopy (C_6D_6, 400 MHz).



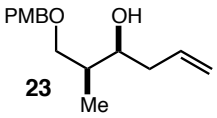
(19) K. Tanaka, Y. Fujimori, Y. Saikawa and M. Nakata, *J. Org. Chem.*, 2008, **73**, 6292-6298.



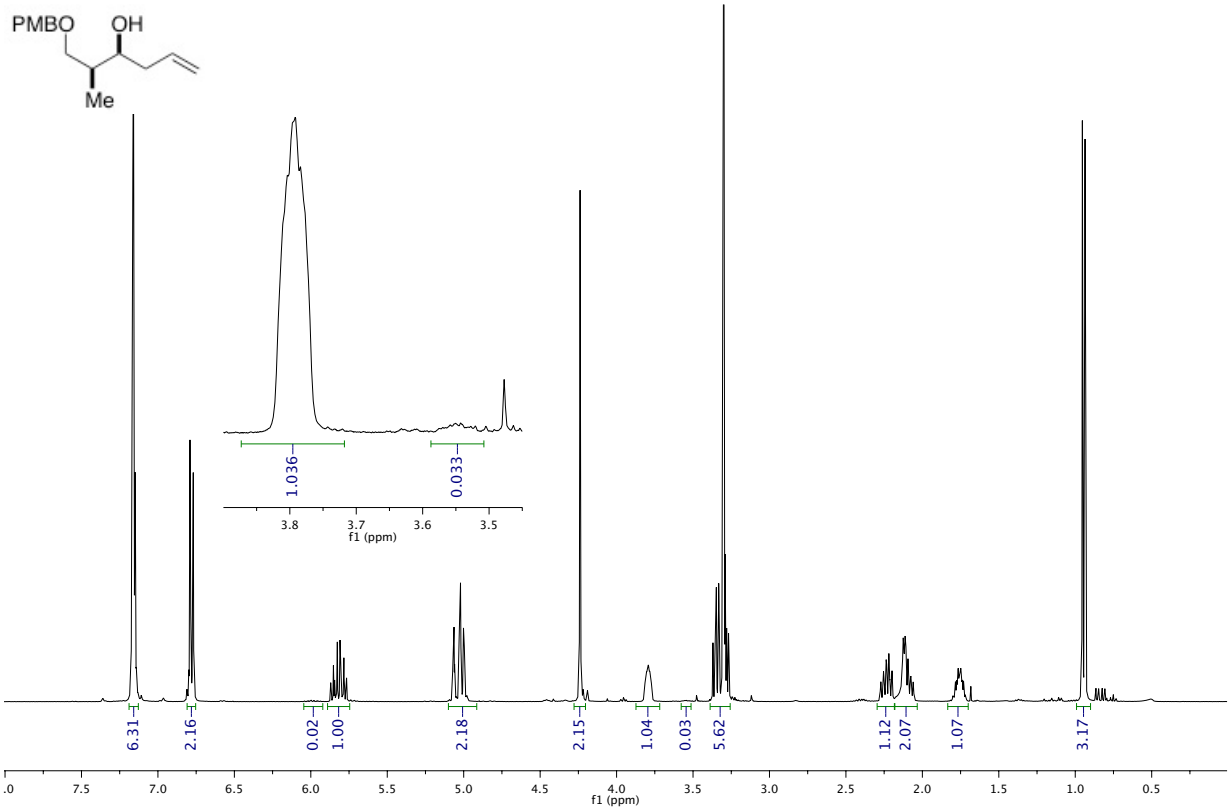
Workup procedure **A** was used and product **22** was isolated as a pale yellow oil (80% yield, 93:7 dr). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.90-6.85 (m, 2H), 5.90 (ddd, *J* = 16.6, 11.0, 8.4 Hz, 1H), 5.10-5.00 (m, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.55 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.48 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.39 (bs, 1H), 3.35 (dd, *J* = 8.0, 3.7 Hz, 1H), 2.41-2.29 (m, 1H), 1.97-1.84 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[20] The diastereomer ratio was determined by ^{1}H NMR spectroscopy (C_6D_6, 400 MHz).



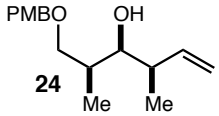
(20) S. R. Chemler and W. R. Roush, *J. Org. Chem.*, 2003, **68**, 1319-1333.



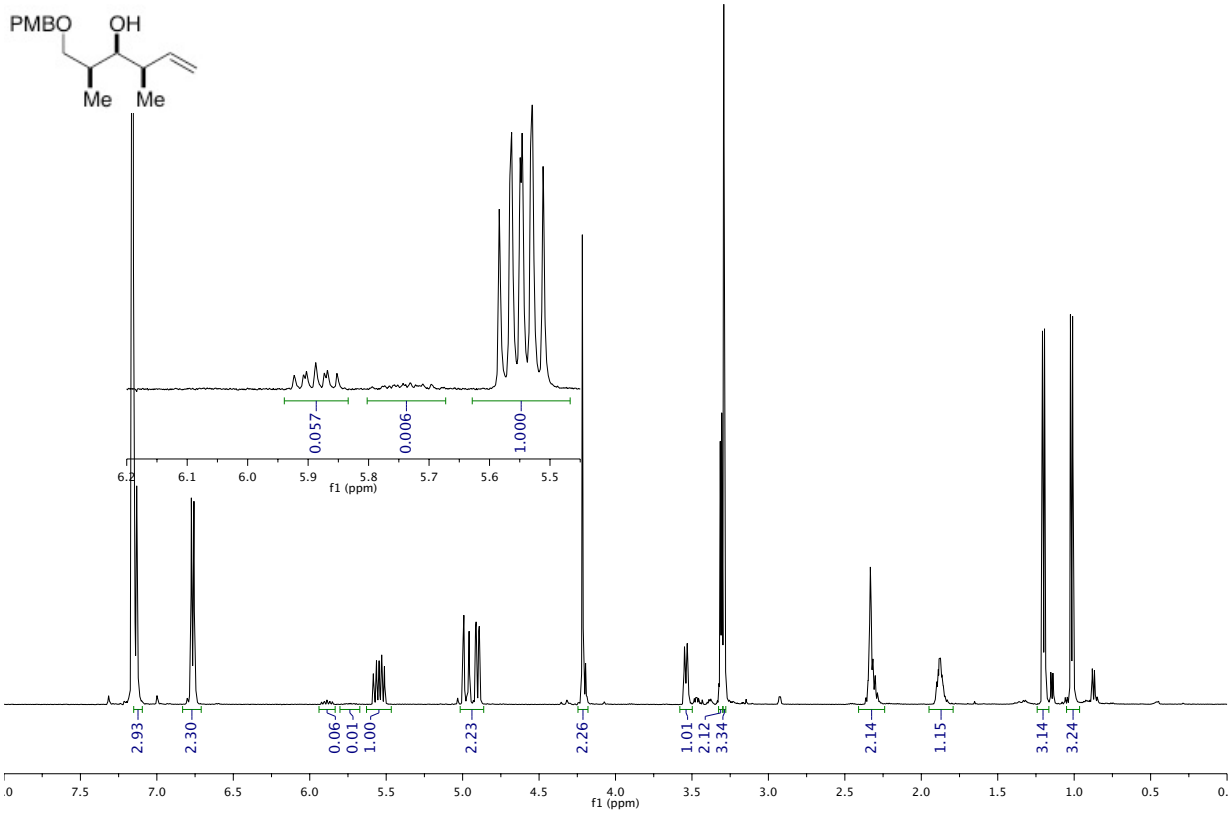
Workup procedure **A** was used and product **23** was isolated as a pale yellow oil (80% yield, 98:2 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.90-6.85 (m, 2H), 5.84 (ddt, *J* = 17.2, 10.1, 7.0 Hz, 1H), 5.16-5.02 (m, 2H), 4.44 (s, 2H), 3.84-3.79 (m, 1H), 3.81 (s, 3H), 3.49 (d, *J* = 5.4 Hz, 2H), 2.52 (d, *J* = 3.8 Hz, 1H), 2.29-2.15 (m, 2H), 1.94-1.81 (m, 1H), 0.95 (d, *J* = 7.1 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[21] The diastereomer ratio was determined by ^{1}H NMR spectroscopy (C_6D_6, 400 MHz).



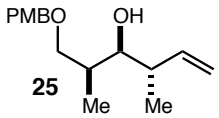
(21) K. C. Nicolaou, A. P. Patron, K. Ajito, P. K. Richter, H. Khatuya, P. Bertinato, R. A. Miller and M. J. Tomaszewski, *Chem. Eur. J.*, 1996, **2**, 847-868.



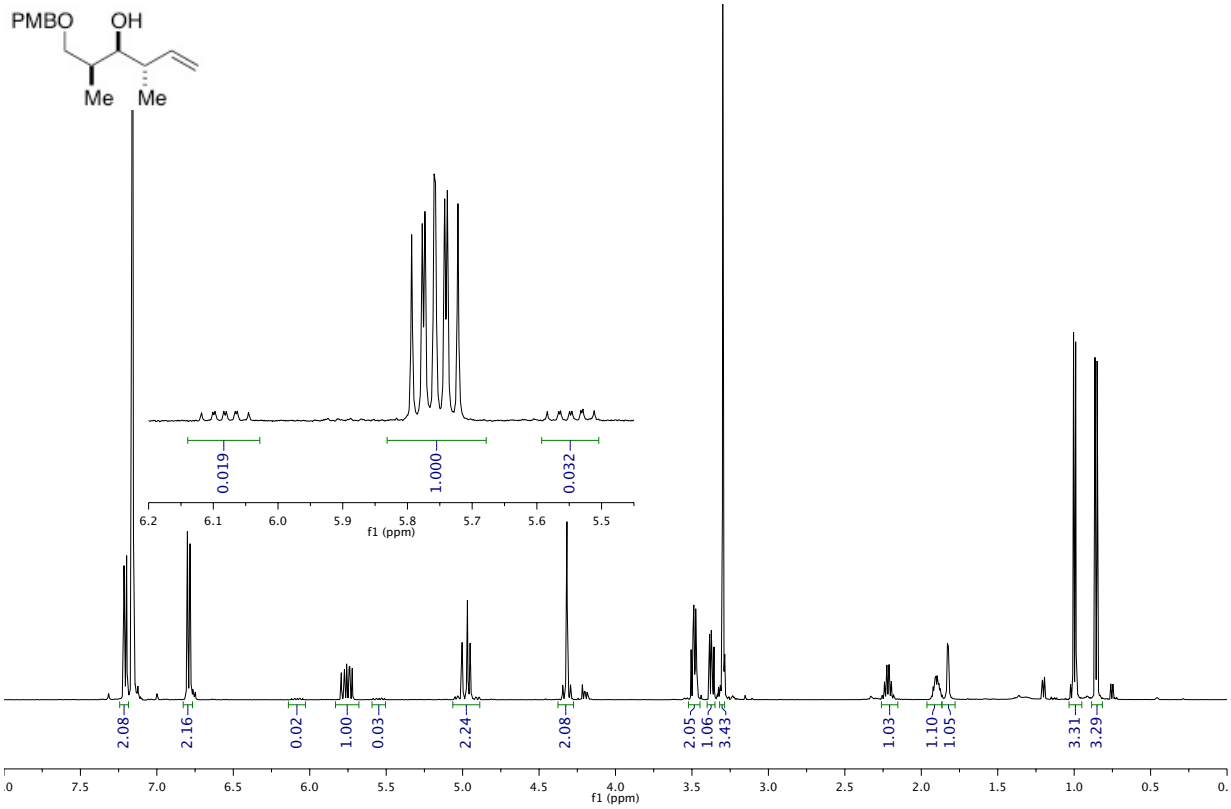
Workup procedure **A** was used and product **24** was isolated as a pale yellow oil (80% yield, 94:6 dr). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26-7.20 (m, 2H), 6.90-6.85 (m, 2H), 5.63 (ddd, *J* = 17.2, 10.3, 8.7 Hz, 1H), 5.10-4.92 (m, 2H), 4.49-4.39 (m, 2H), 3.81 (s, 3H), 3.57-3.46 (m, 3H), 2.62 (bs, 1H), 2.29 (ddt, *J* = 15.5, 8.8, 6.6 Hz, 1H), 1.92 (ddt, *J* = 7.0, 4.8, 2.4 Hz, 1H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[22] The diastereomer ratio was determined by ^{1}H NMR spectroscopy (C_6D_6, 400 MHz).



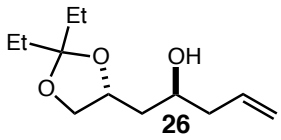
(22) E. de Lemos, F.-H. Porée, A. Bourin, J. Barbion, E. Agouridas, M.-I. Lannou, A. Commerçon, J.-F. Betzer, A. Pancrazi and J. Ardisson, *Chemistry (Weinheim an der Bergstrasse, Germany)*, 2008, **14**, 11092-11112.



Workup procedure **A** was used and product **25** was isolated as a pale yellow oil (80% yield, 95:5 dr). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26-7.23 (m, 2H), 6.91-6.84 (m, 2H), 5.79 (ddd, *J* = 17.3, 10.3, 8.4 Hz, 1H), 5.14-5.05 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.59-3.42 (m, 3H), 2.33-2.19 (m, 2H), 2.01-1.88 (m, 1H), 1.00-0.93 (m, 6H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature.[23] The diastereomer ratio was determined by ^{1}H NMR spectroscopy (C_6D_6, 400 MHz).

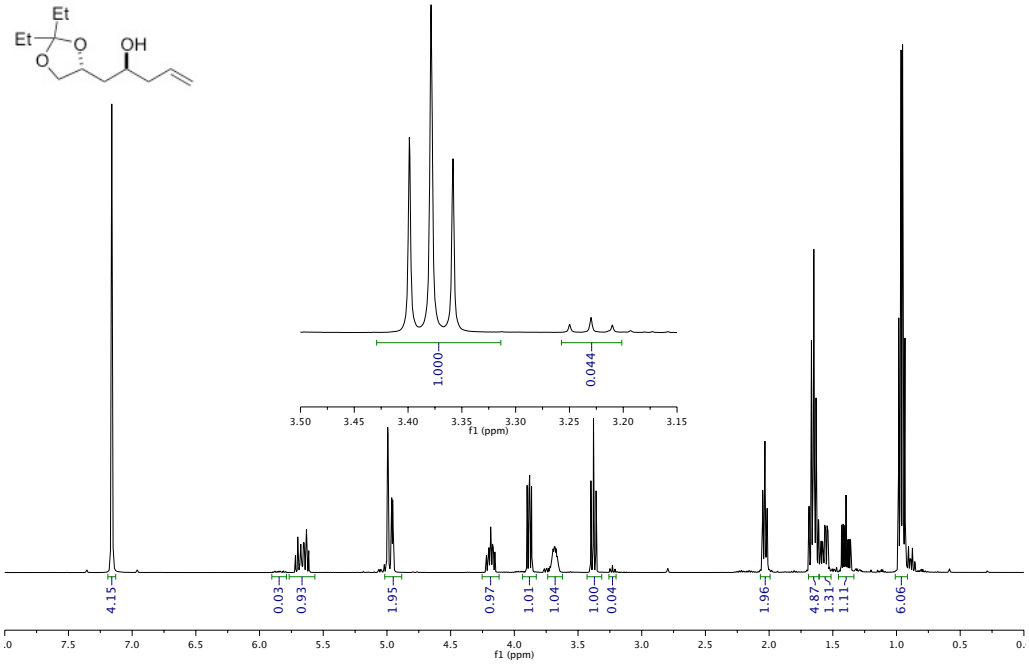


(23) W.-H. Jung, C. Harrison, Y. Shin, J.-H. Fournier, R. Balachandran, B. S. Raccor, R. P. Sikorski, A. Vogt, D. P. Curran and B. W. Day, *J. Med. Chem.*, 2007, **50**, 2951-2966.



26

Workup procedure **B** was used and product **26** was isolated as a colorless oil (87% yield, 96:4 dr). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.91-5.75 (m, 1H), 5.20-5.10 (m, 2H), 4.37-4.28 (m, 1H), 4.09 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.94-3.86 (m, 1H), 3.53 (t, *J* = 8.1 Hz, 1H), 2.36-2.20 (m, 3H), 1.78 (ddd, *J* = 14.2, 7.4, 3.0 Hz, 1H), 1.72-1.67 (m, 1H), 1.67-1.59 (m, 4H), 0.90 (td, *J* = 7.5, 3.0 Hz, 6H). The ^{1}H NMR spectroscopic data is in agreement with data reported in literature and comparison of the optical rotation to the literature value of the enantiomer verifies the absolute configuration of **26**: $[\alpha]_D^{21}$ +8.0° ($CHCl_3$, *c* 2.0); lit: $[\alpha]_D^{20}$ -6.8° ($CHCl_3$, *c* 1.5).[12] The diastereomer ratio was determined by ^{1}H NMR spectroscopy (C_6D_6, 400 MHz).



Summary of Computational Method

All computations were performed using Jaguar, version 7.8, Schrodinger, LLC, New York, NY, 2010.

The geometries of the two silanes were optimized using the B3LYP functional and the 6-31G** basis set. Effective potentials (LACVP) were used for the Br atoms. At the optimized geometries the wavefunctions were recalculated using the cc-pVTZ basis. We include the Cartesian coordinates and final total energies for both optimized geometries below.

Summary of Results for (*S*,*S*)-3:

```
B3LYP/6-31G**/LACVP   final total energy:  -1625.001295 hartrees
B3LYP/cc-pVTZ         final total energy:  -6747.602235 hartrees
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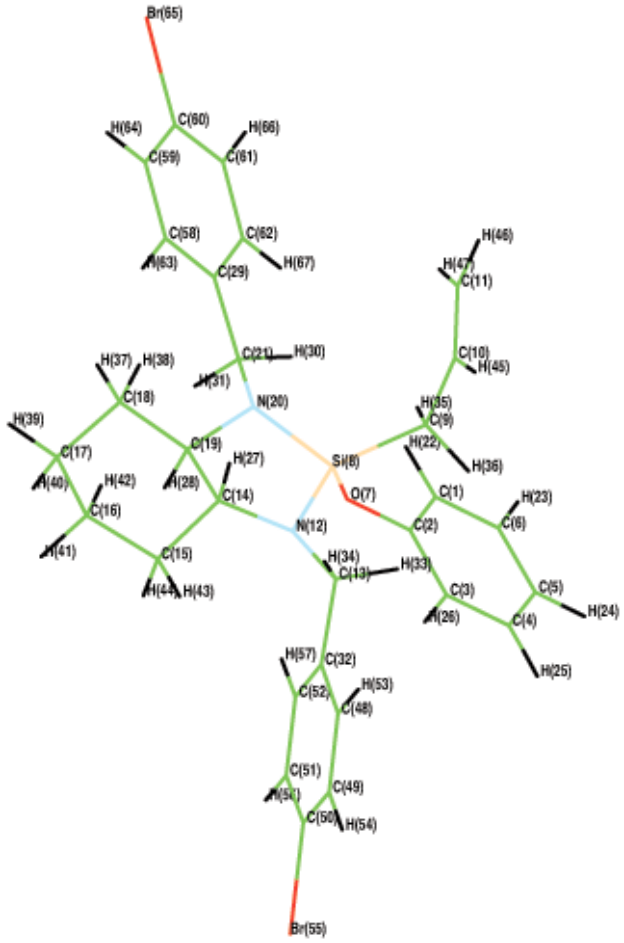


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final geometry:
                                  angstroms
  atom              x                   y                   z
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  C2          -0.1576222468       -0.1958625197        2.1534727283
  C3           1.0727613256        0.4195061570        2.4103339770
  C4           1.9480308209        0.6792080770        1.3545975611
  C5           1.6100992271        0.3226800174        0.0485496634
  C6           0.3863010488       -0.3031291056       -0.1978759771
  O7          -1.0334436822       -0.4956775657        3.1641396989
  Si8         -1.7700455138        0.4549984989        4.3390466916
  C9          -2.0418846886        2.1770231235        3.6001871698
  C10         -2.9453582217        2.2023827073        2.3981006494
  C11         -4.1739416179        2.7254940397        2.3657413176
  N12         -0.9690280043        0.5010854285        5.8820652026
  C13         -0.0182402632        1.5211069219        6.2959736263
```

C14	-1.8832521928	-0.0303815375	6.9120198075
C15	-1.2458034339	-0.6978712367	8.1379147312
C16	-2.3613932726	-1.1446182504	9.1043421478
C17	-3.4133951723	-2.0357962735	8.4171237440
C18	-3.9781515781	-1.4018151944	7.1292920414
C19	-2.8147551025	-1.0311506027	6.2005926724
N20	-3.1562436694	-0.4342479901	4.8919526346
C21	-3.9444448181	-1.2624966286	3.9820337703
H22	-1.4504213607	-1.0553405725	0.6723215627
H23	0.1161663285	-0.5909943474	-1.2102681409
H24	2.2960357665	0.5248909082	-0.7686712377
H25	2.9026480627	1.1563089897	1.5595912761
H26	1.3492056702	0.6661535884	3.4314868324
H27	-2.5132331221	0.7994705880	7.2880968237
H28	-2.2340289456	-1.9584575091	6.0269068021
C29	-5.4539340515	-1.1295751911	4.1239484780
H30	-3.6779750782	-0.9929979915	2.9521214853
H31	-3.6650948037	-2.3234562540	4.0869491238
C32	1.3531507227	1.0026834989	6.7192227862
H33	0.1362551364	2.2254684592	5.4658514117
H34	-0.4373671572	2.1283356211	7.1145561899
H35	-2.4427923510	2.8145502182	4.3979522928
H36	-1.0552203807	2.5812033345	3.3295028244
H37	-4.6593087801	-2.1025063641	6.6351534134
H38	-4.5639154299	-0.5031553137	7.3621598592
H39	-4.2305463587	-2.2563653252	9.1137291298
H40	-2.9544201580	-3.0019942718	8.1640183474
H41	-1.9244707066	-1.6715447829	9.9606146801
H42	-2.8566432472	-0.2515898447	9.5111943039
H43	-0.5640965570	-0.0063261404	8.6456683819
H44	-0.6432242736	-1.5575338546	7.8176766809
H45	-2.5441732871	1.7428642439	1.4944631117
H46	-4.7804541868	2.6966756196	1.4655286638
H47	-4.6152696545	3.2073877397	3.2355323212
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C49	3.4568765913	1.3668567354	7.8907550777
C50	3.9176293209	0.1458346876	7.4075155358
C51	3.1271196752	-0.6574073858	6.5934063563
C52	1.8445041272	-0.2208140995	6.2541827064
H53	1.8076188861	2.7385413777	7.9182807815
H54	4.0833437751	1.9788909381	8.5303746046
Br55	5.7236649228	-0.4575323063	7.8929799115
H56	3.4999892846	-1.6081282321	6.2279784707
H57	1.2090494514	-0.8403520809	5.6287183110
C58	-6.2844097134	-2.2189132765	3.8395641986
C59	-7.6746544207	-2.1053454618	3.8977312124
C60	-8.2296587197	-0.8796223542	4.2485675590
C61	-7.4324588634	0.2231670223	4.5390098918
C62	-6.0453303708	0.0890537655	4.4721939767
H63	-5.8440929298	-3.1764730047	3.5689194189
H64	-8.3093067094	-2.9572251584	3.6794077329
Br65	-10.1857988199	-0.7034761173	4.3440632248
H66	-7.8834537248	1.1710570300	4.8123383374
H67	-5.4074055684	0.9367597894	4.6996228566

Summary of Results for (*S*,*S*)-8:

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B3LYP/6-31G** final total energy: -1293.855729 hartrees
B3LYP/cc-pVTZ final total energy: -1294.193939 hartrees
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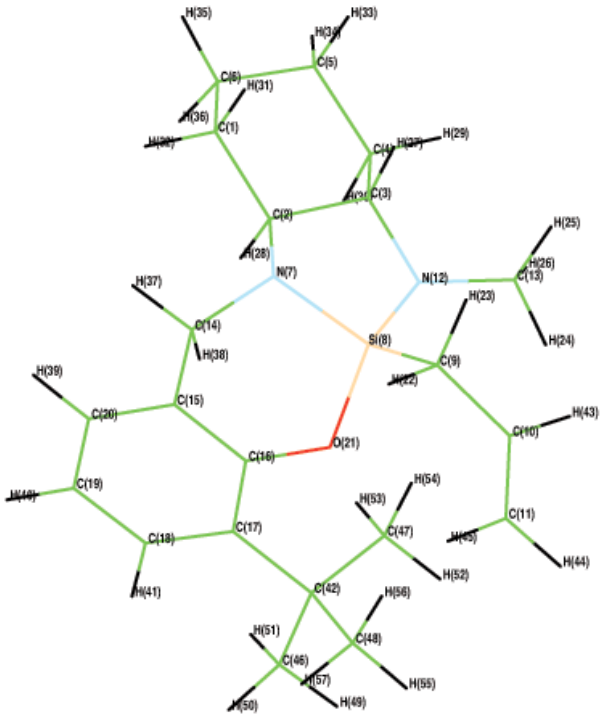


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                                  angstroms
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C3          1.4664736155     -0.0149028333      2.0378823512
C4          2.1427474578     -1.3289760735      1.6257535011
C5          2.1300149303     -1.4461415240      0.0879261775
C6          0.7193075933     -1.2895544495     -0.5104417204
N7         -0.6535704584      1.1496187770      2.1631059257
Si8         0.0148064139      1.2823197407      3.7681395841
C9          0.3494102496      3.0215884364      4.4215168904
C10         0.7041654423      3.1204446970      5.8792273811
C11        -0.1026466933      3.5624936228      6.8463533031
N12         1.3908804297      0.2666592124      3.4834484720
C13         2.6442184381      0.2908123302      4.2189722303
C14        -2.1269295348      1.1061770323      2.1790008072
C15        -2.7025329133      0.0197466015      3.0784920780
C16        -2.1781927671     -0.1643640914      4.3752459941
C17        -2.6797326889     -1.1543016174      5.2506787558
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C18	-3.7359368018	-1.9387187543	4.7633448001
C19	-4.2671304311	-1.7736681485	3.4859143046
C20	-3.7441677001	-0.7990217049	2.6442002246
O21	-1.1723470184	0.6815643042	4.8068671488
H22	-0.5597997914	3.6015111839	4.2175758882
H23	1.1452926756	3.4498737189	3.7972997043
H24	2.4653468474	0.5904070252	5.2558088189
H25	3.3798589514	0.9908582780	3.7872866141
H26	3.1113423419	-0.7008760411	4.2500822614
H27	2.0179625364	0.8042535971	1.5350100017
H28	-0.4553702844	-0.9400544726	1.8583843837
H29	3.1764615814	-1.3676654657	1.9880786055
H30	1.6098807236	-2.1721938379	2.0843766903
H31	0.5107076061	0.8850668941	-0.3909743618
H32	-1.0195164161	0.0111993006	-0.3969239148
H33	2.7849928761	-0.6689301452	-0.3299192143
H34	2.5609537545	-2.4068966077	-0.2166670475
H35	0.7769920619	-1.2886706512	-1.6050991610
H36	0.1131075912	-2.1633214233	-0.2340656024
H37	-2.5131551600	0.9811633042	1.1611089035
H38	-2.4810649071	2.0913835608	2.5142894264
H39	-4.1436649129	-0.6633007225	1.6417144348
H40	-5.0813952376	-2.4101347327	3.1521976933
H41	-4.1587253179	-2.7098327117	5.3953217189
C42	-2.1042793903	-1.3731072697	6.6678066022
H43	1.7080958302	2.7919087048	6.1499752962
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C47	-0.6127836486	-1.7773563136	6.5749118321
C48	-2.2537589989	-0.0852128572	7.5138818867
H49	-2.3940299514	-2.6243878589	8.4115503416
H50	-3.9015873540	-2.2854964171	7.5580759102
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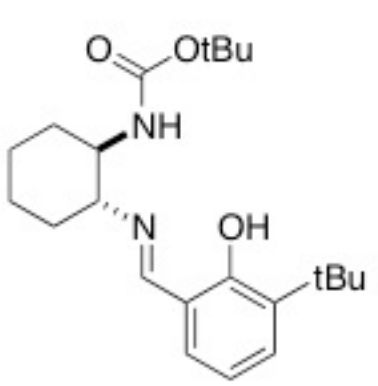
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N
OH
tBu

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0.98
1.00
3.04
12.04
9.24
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
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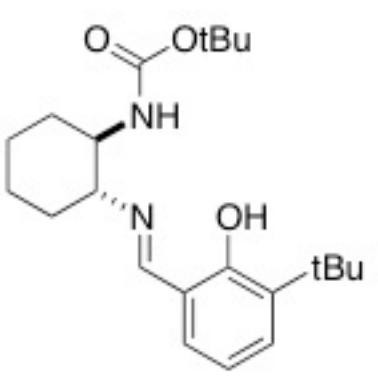

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117.82
79.49
77.43
72.87
54.55
35.02
33.64
32.00
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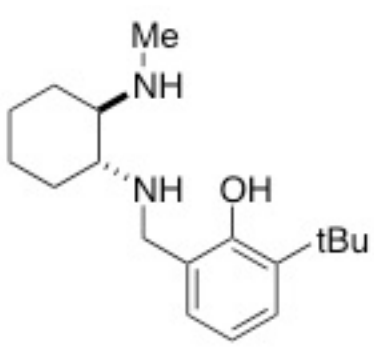
28.37
25.06
24.31

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)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NH
NH
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tBu

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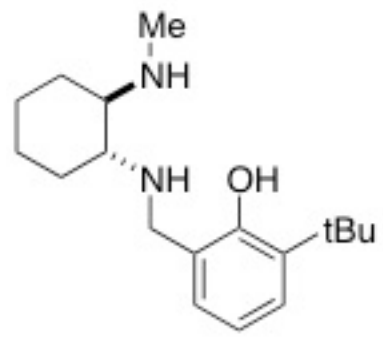

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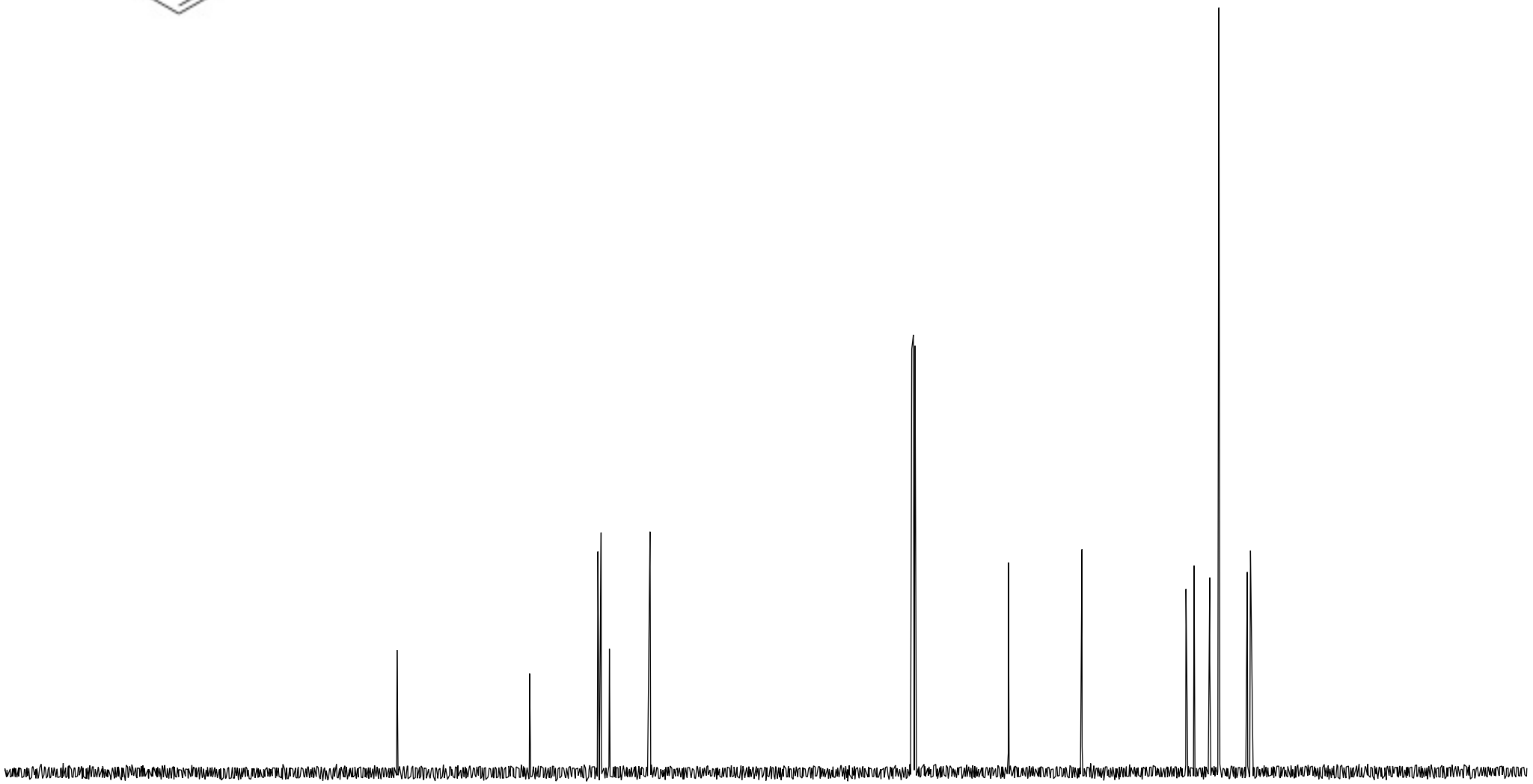

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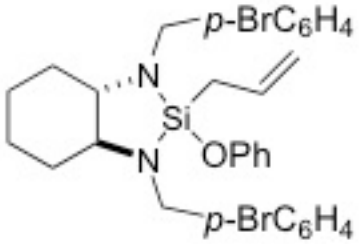
f1 (ppm)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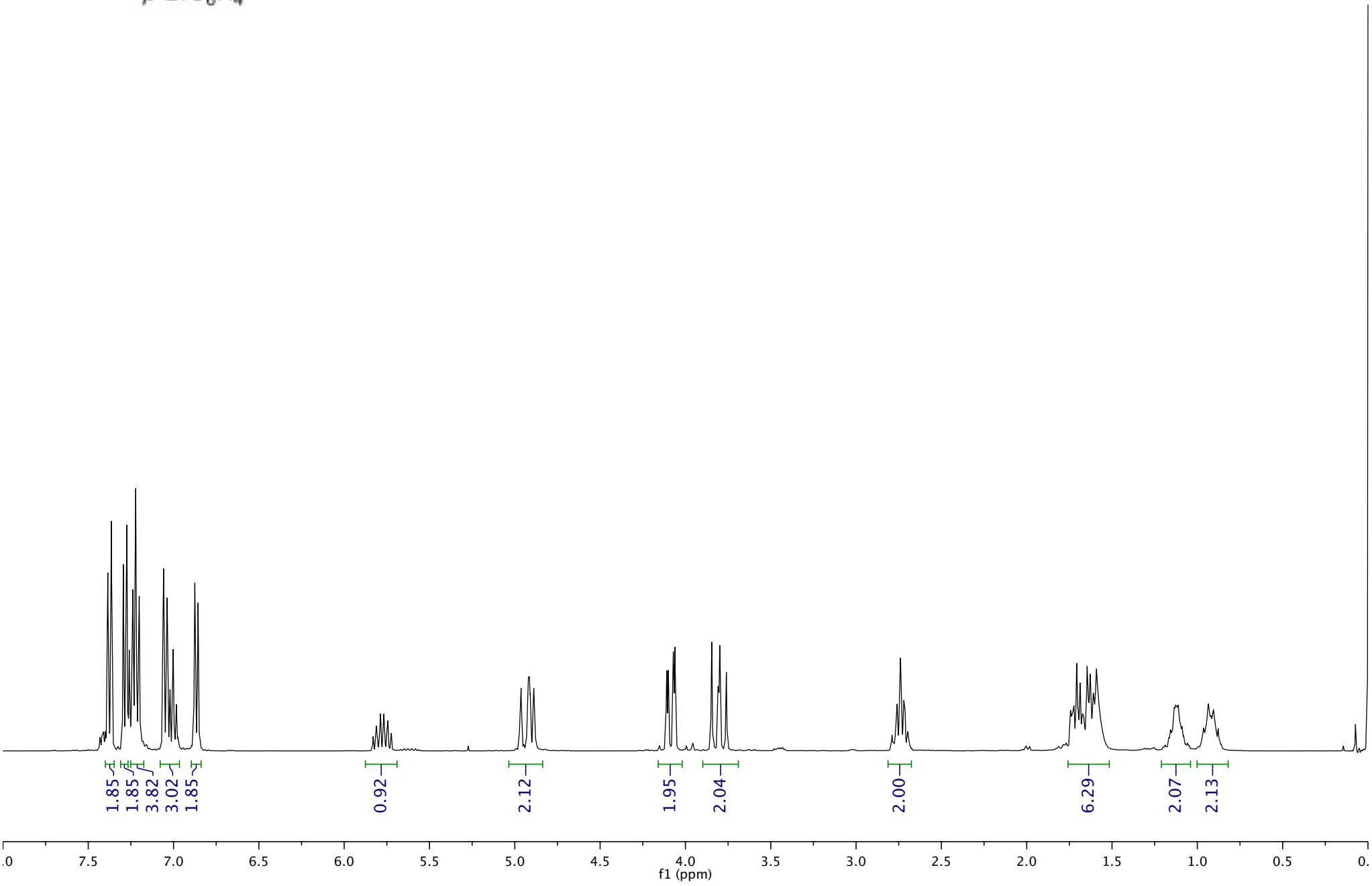
N
Si
OPh
N
p-BrC6H4

^{1}H NMR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1.85
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2.04
2.00
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6.5
6.0
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4.0
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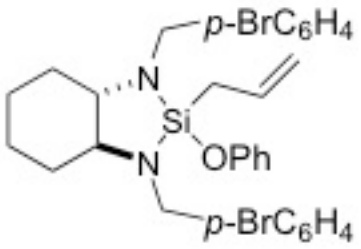
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



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122.00
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120.28
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65.99
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24.91
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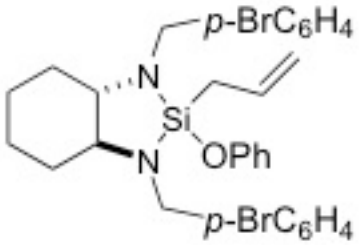
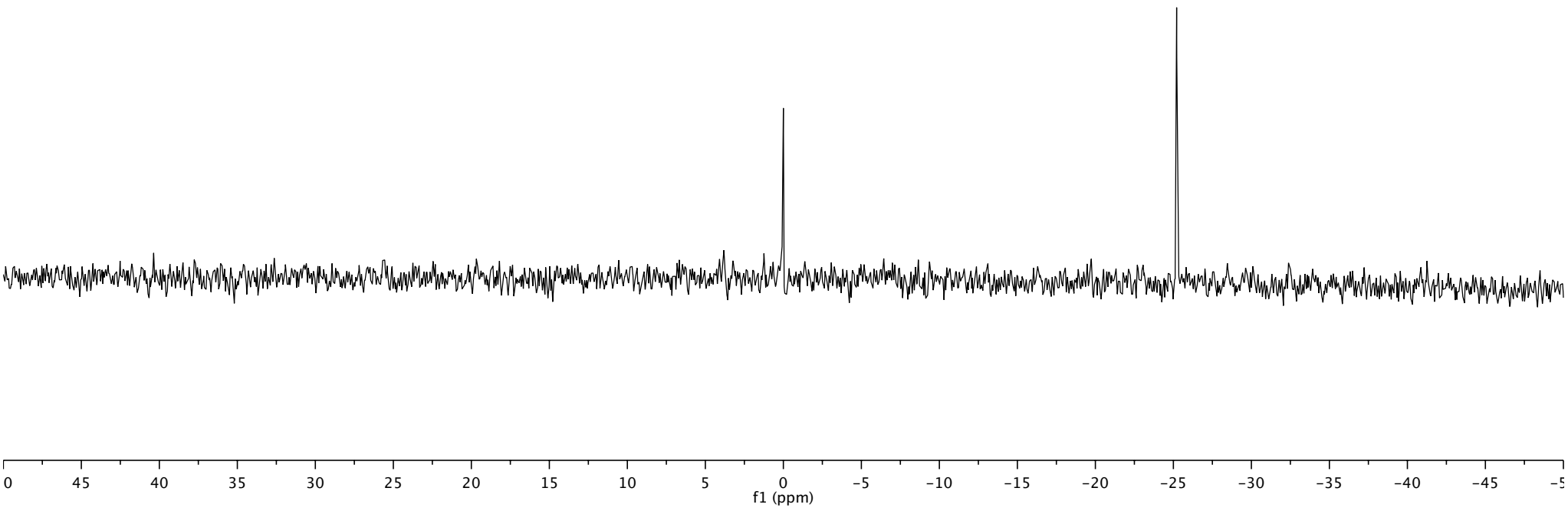
^{13}C NMR

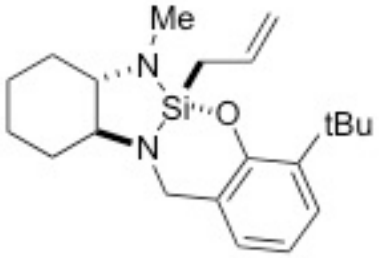
f1 (ppm)



^{29}Si NMR

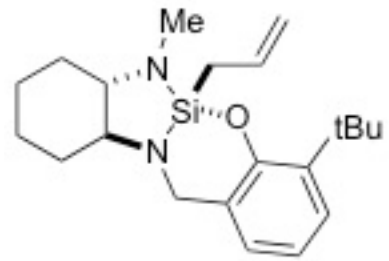
-25.21




Me
N
Si
O
N
tBu

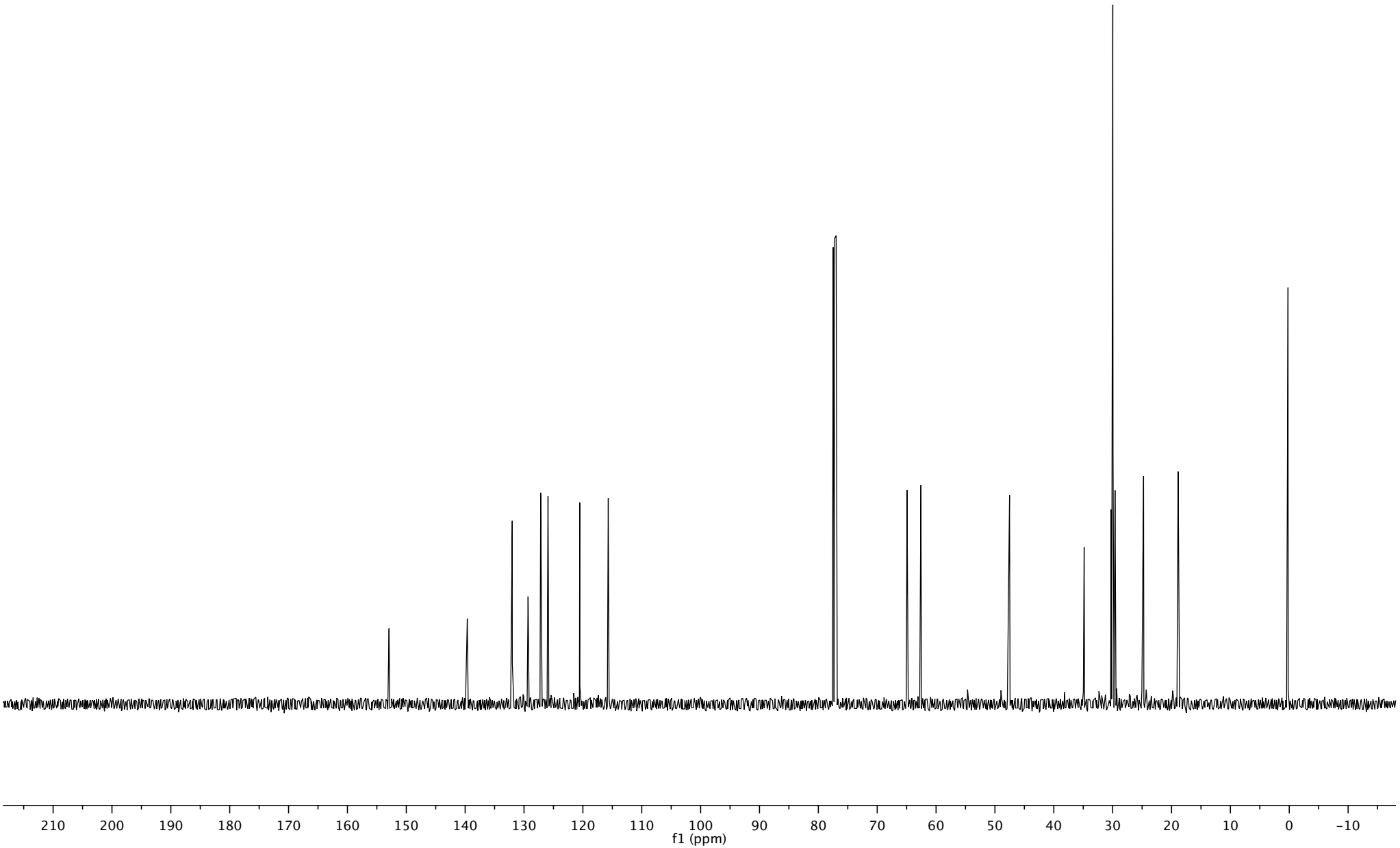
^{1}H NMR

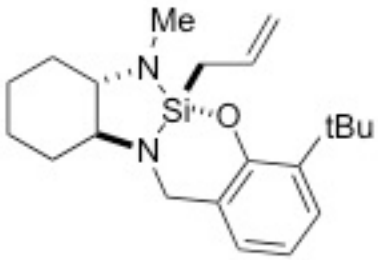
1.10
1.10
1.13
0.89
1.10
1.13
1.00
1.03
4.43
1.26
4.60
2.62
11.59
1.52
2.39
1.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



^{13}C NMR

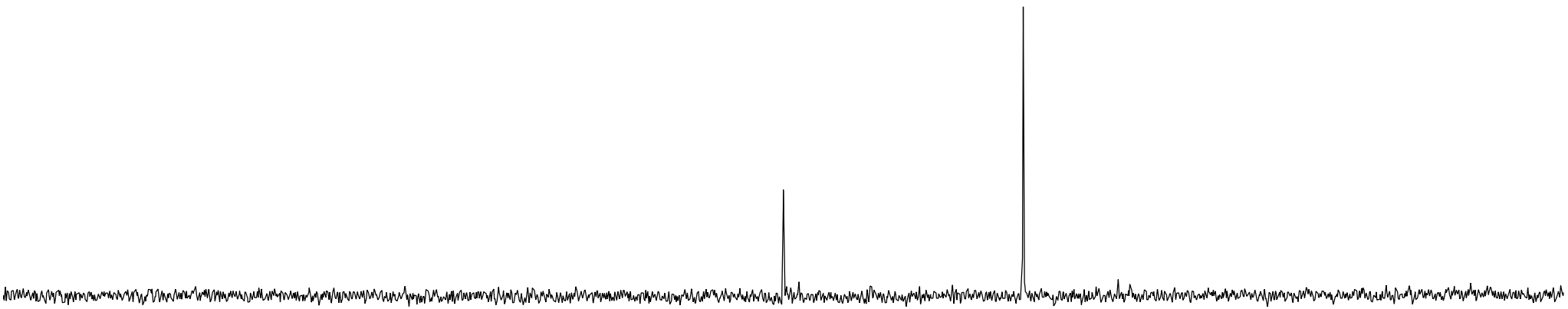
152.93
139.64
132.00
129.31
127.17
125.92
120.54
115.69
64.94
62.57
47.52
34.85
30.26
29.98
29.94
29.60
24.96
24.75
18.88

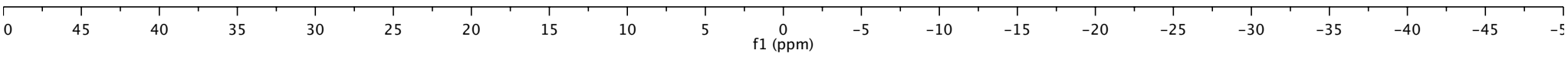


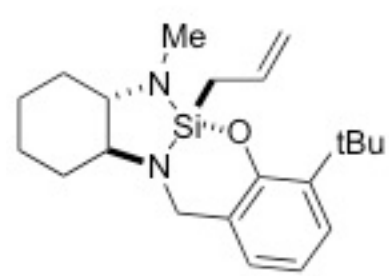


^{29}Si NMR

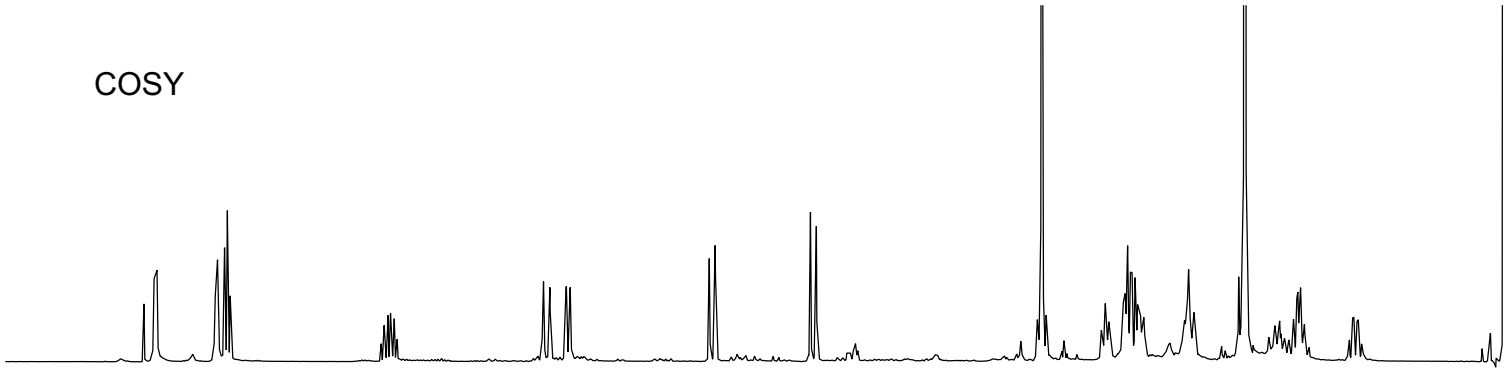
−15.38

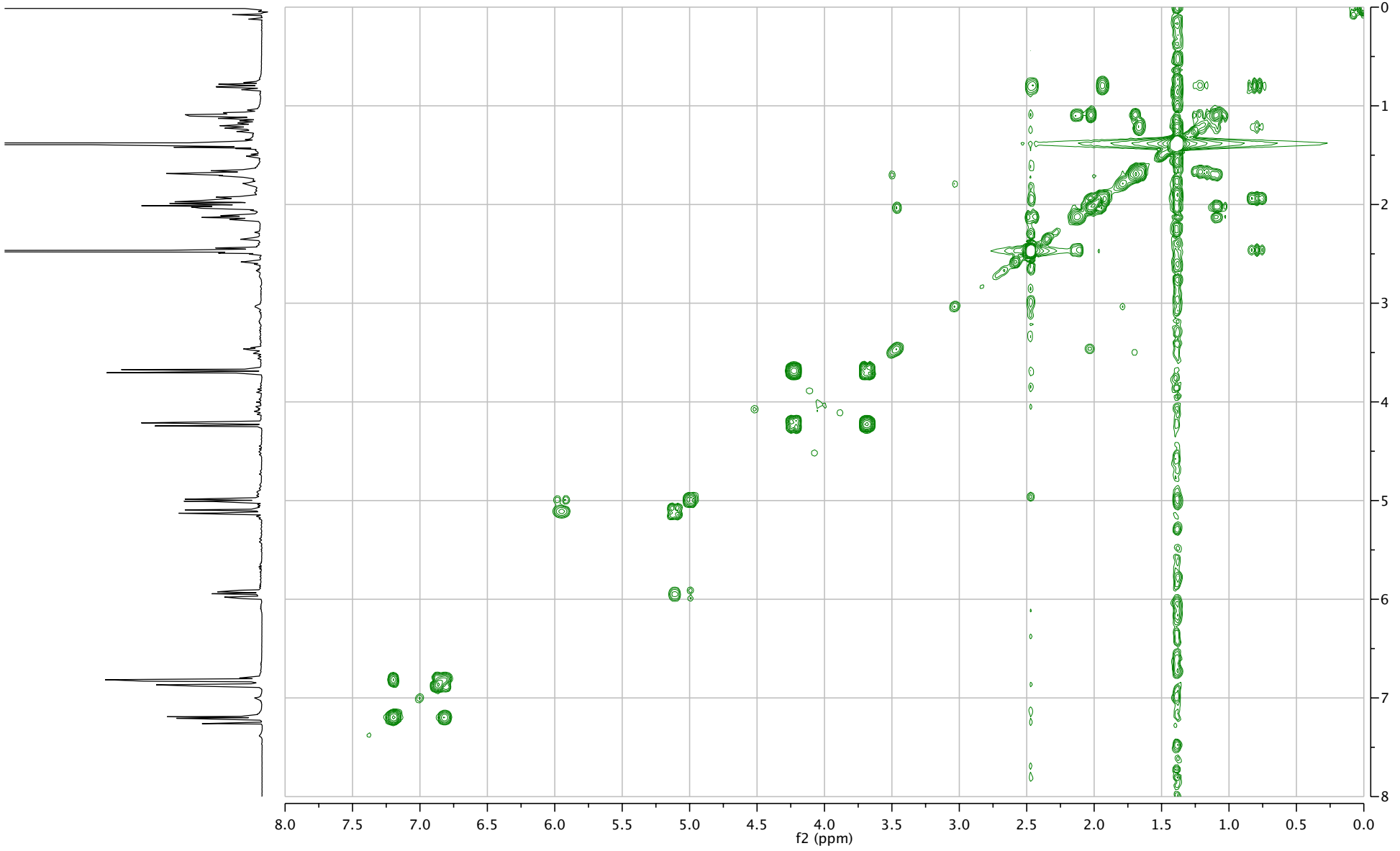


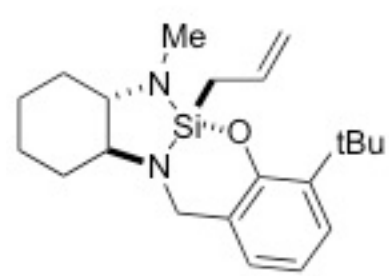



Me
N
Si
O
tBu
N

COSY

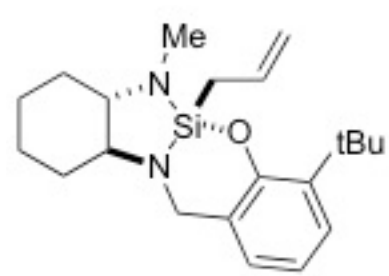



8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

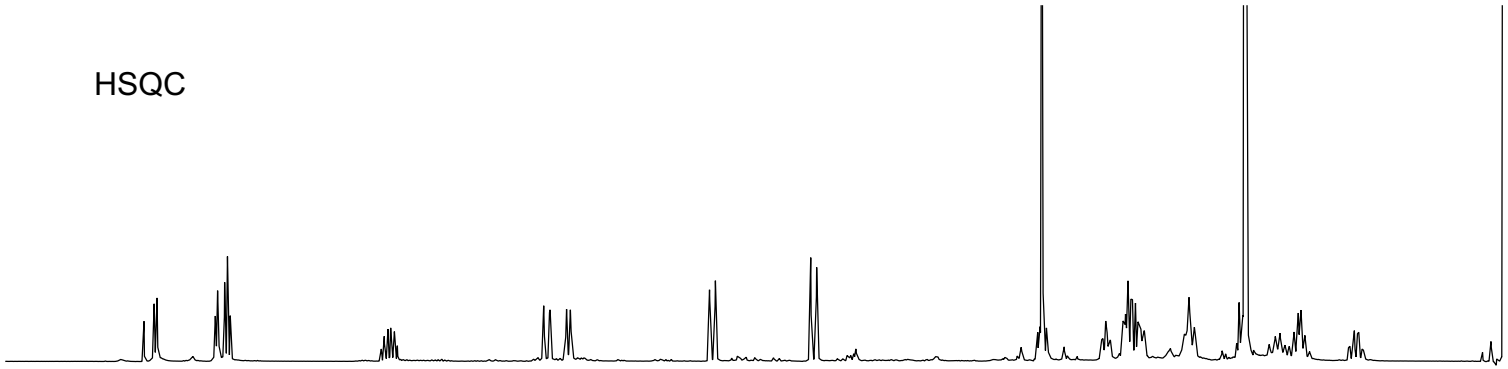

Me
N
Si
O
tBu
N

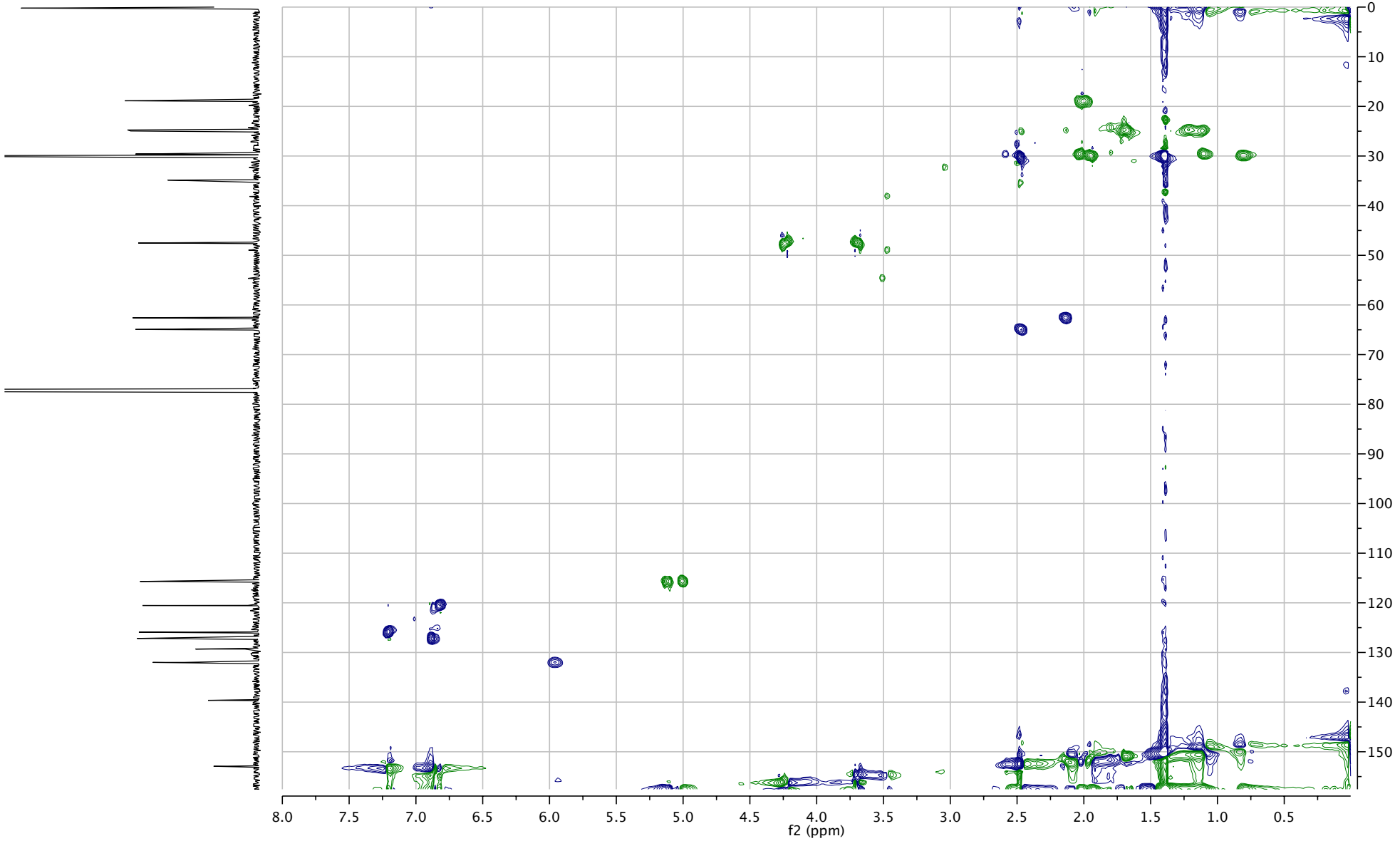
HMBC

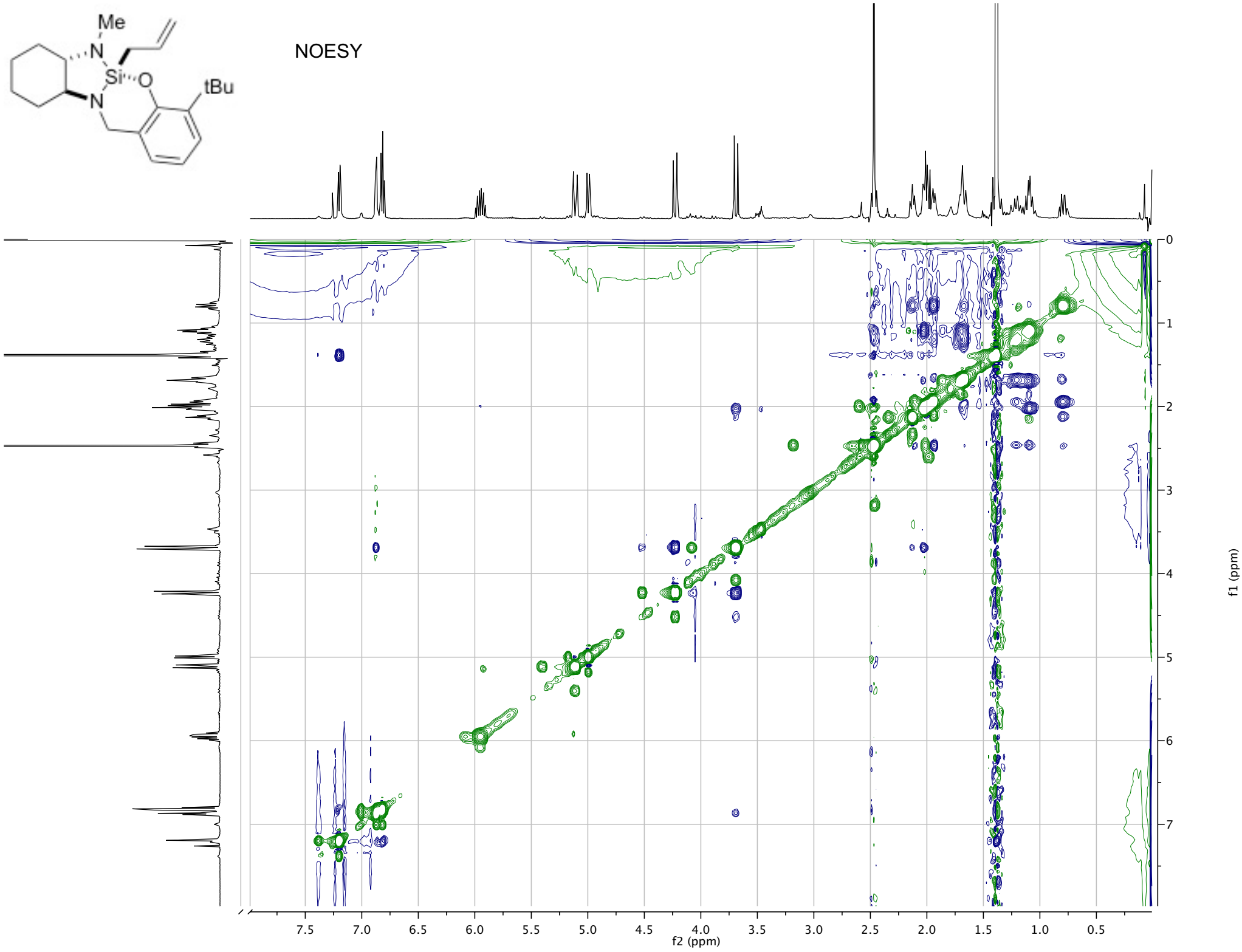
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


Me
N
Si
O
tBu
N

HSQC




8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)


Me
N
Si
O
tBu
N
NOESY
f2 (ppm)
f1 (ppm)