Supporting information for:

Enantioselective Si–H insertion Reactions of Diarylcarbenes for the Synthesis of Silicon-Stereogenic Silanes

Jake R. Jagannathan, James C. Fettinger, Jared T. Shaw*, and Annaliese K. Franz*

Department of Chemistry, One Shields Ave, University of California, Davis, CA 95616
* jtshaw@ucdavis.edu * akfranz@ucdavis.edu *

CAUTION Diazo compounds are high energy compounds and require careful treatment. We observed no problems throughout our work, but care should always be taken when handling large quantities of diazo compounds. See Bull *et. al.*[1] for risk analysis for related diazo compounds.

I. General Information

The following abbreviations are used throughout: trimethylsilyl (TMS), Phenyltrimethylsilane (PhenylTMS), dirhodiumtetraacetate (Rh$_2$(OAc)$_4$), Tetrakis[(*R*)-(1-adamantyl)-(N-phthalimido)acetate]dirhodium(II) (Rh$_2$(*R*-PTAD)$_4$), Tetrakis[(*S*)-(N-phthalimido)-*tert*-lucinato]dirhodium(II) (Rh$_2$(*S*-PTTL)$_4$), Tetrakis[(*S*)-(N-biphenylphthalimido)-*tert*-lucinato]dirhodium(II) (Rh$_2$(*S*-BPTTL)$_4$), Tetrakis[(*S*)-N-(p-dodecylphenylsulfonyl)prolinato]dirhodium(II) (Rh$_2$(*S*-DOSP)$_4$), Tetrakis[(*S*)-[(1*S*)-1-(4-bromophenyl)-2,2-diphenylcyclopropanecarboxylato]dirhodium(II) (Rh$_2$(*S*-BTPCP)$_4$), Tetrakis[(*S*)-(N-tetrachlorophthalimido)-*tert*-lucinato]dirhodium(II) (Rh$_2$(*S*-TCPTTL)$_4$), Dirhodium(II)tetrakis[methyl 2-pyrrolidone-5(*S*)-carboxylate], (Rh$_2$(5*R*-MEPY)$_4$), Tetrakis[N-phthalimido-(S)-valinato]dirhodium (Rh$_2$(*S*-PTV)$_4$), ethyl acetate (EtOAc), isopropanol (IPA), tetrahydrofuran (THF), toluene (PhMe), dichloromethane (DCM), 1,2-dibromoethane (DBE), enantiomeric ratio (er), diastereomeric ratio (dr).

Materials.

Cyclohexylphenylsilane,[2] triethylsiloxyphenylsilane,[3] 2-methoxybenzophenone,[4] naphthylphenylketone,[5] 2-triflouoromethyl benzophenone,[6] diphenyldiazomethane,[6] 4,4'-(diazomethylene)bis(chlorobenzene),[7] 4,4'-(diazomethylene) bis(methoxybenzene)[7] were made from previously published procedures. (Rh$_2$(S-TCPTTL)$_4$ was purchased from TCI; Rh$_2$(OAc)$_4$, Rh$_2$(R-PTAD)$_4$ and Rh$_2$(S-BTPCP)$_4$ purchased from Strem Chemicals Inc. Rh$_2$(*S*-PTV)$_4$, Rh$_2$(*S*-PTTL)$_4$, (Rh$_2$(*S*-BPTTL)$_4$ were donated by the Fox group. Dry CH_2Cl_2, THF, Et_2O and PhMe were dispensed from a solvent purification system that passes solvent through two columns of dry neutral alumina prior to use. All other reagents, unless otherwise noted, were purchased from commercial sources. NOTE: it is necessary that the MnO_2 used for the oxidation of hydrazones be ~85% pure with an average particle size of 2 microns, appearing as a fine black powder (e.g. Oakwood Chemical, CAS #: 1313-13-9, cat. #: 094454, lot #: 094454K03K or Sigma Aldrich, cat: 217646-100G, Lot # MKCJ7777).

Synthesis, Purification and Analysis.

All reactions were performed in oven-dried and argon-purged glassware (including 8 mL KIMAX Borosilicate glass vials fitted with rubber septa). Molecular sieves (4Å) were activated by flame-drying, then cooled under vacuum (<1 torr). All microwave experiments were run in a Biotage Initiator EXP EU 400W microwave synthesizer 2.0 (serial number 11031). Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature at 600, 400 MHz. Spectra obtained on Bruker Avance IIIHD Nanobay Spectrometer (400 MHz for ^{1}H; 100 MHz for ^{13}C; 292 MHz for ^{19}F; 79 MHz for ^{29}Si), and/or Varian VNMRS (600 MHz for ^{1}H; 151 MHz for ^{13}C, 119 MHz for ^{29}Si). The ^{1}H spectral data are reported as follows: chemicals shifts were reported in parts per million downfield from tetramethylsilane internal standard on the δ scale, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; s, septet; m, multiplet; dd, doublet of doublets, and b, broadened), coupling constant (Hz), and integration. Carbon NMR chemical shifts are reported in ppm from tetramethylsilane with the solvent reference employed as the internal standard (deuterochloroform ($CDCl_3$) at 77.16 ppm). All silicon NMR's were taken with 0.05 M Cr(Acac)$_3$ as a T$_1$ Relaxation agent.

Compound **9** was analyzed by high resolution mass spectrometry (HRMS) using Thermo Fisher Orbitrap (San Jose, CA) using electrospray in the negative or positive ion mode >60,000 resolution and using typical ESI source values. Mass spectrometry data was obtained at the Mass Spectrometry Facilities of University of California, Davis. Insertion products were also analyzed by mass spectrometry on a Bruker UltraFlextreme MALDI mass spectrometer (Bruker Corp, Billeraca, MA) in reflectron mode. Samples were first mixed in a 1:1 ratio with a saturated solution of alpha-hydroxycinnamic acid (Sigma Chemical Co) in high-purity water:MeCN (35%:65%) and 1mg of NaI to promote cationization was added before being spotted on the plate and allowed to air dry. Samples were analyzed using the minimum laser fluence to obtain adequate signal (s/n > 20), generally requiring 1000 shots per sample. Data was analyzed in FlexAnalysis. Diazo compounds **3a**-**3d** were analyzed using low-resolution mass spectrometry with an Advion© ASAP-APCI-MS was achieved and the corresponding data is reported for those samples. Several samples (including silanes) did not ionize with any technique used and are noted in their characterization data.

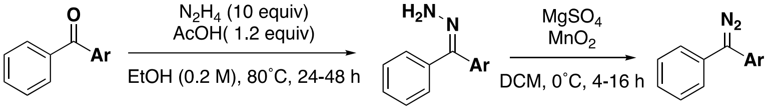
Kinetic Analysis was performed using a Mettler Toldedo ReactIR 700 (serial number B929971514) with a liquid N_2 MCT detector fitted with a DiComp probe (serial number B939349478). The system was filled with liquid N_2 and allowed to cool for 1 h before kinetic experiments begun. Initial trends were found using iC IR 7.1 and further analyzed using Microsoft Excel.

High performance liquid chromatography (HPLC) data were obtained on Shimadzu LC-20AB system with CHIRALPAK® AD-H column (4.6 x 250 mm, 5 μm), CHIRALPAK® OD-H column (4.6 x 250 mm, 5 μm) or CHIRALPAK® AS column (4.6 x 250 mm, 5 μm) and Shimadzu SPD-M20A photodiode array detector. Each HPLC sample was eluted at a constant flow rate with isocratic (90:10 hexanes/isopropanol)/hexanes or (90:10 heptane/isopropanol)/heptane system and 40 °C column oven temperature.

II. General Synthetic Procedures

IIa. Procedures for Starting Material Syntheses

Method A: Synthesis of donor/donor diazo compounds

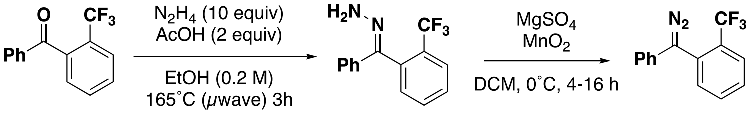


A 50-mL two-neck round-bottom flask with a stir bar and condenser was charged with ketone in anhydrous EtOH (0.2 M). Hydrazine (10 equiv), followed by AcOH (1.2 equiv) were added, the solution was heated to reflux. The reaction was monitored by TLC (7:3 hexanes/EtOAc) until the ketone was fully consumed. The reaction was allowed to cool to room temperature, and the solvent was removed via rotary evaporator. The resulting slurry was dissolved in Et_2O (20 mL), washed with H_2O (10 mL), brine (10 mL), and dried with Na_2SO_4. The solution was filtered, and the solvent was removed via rotary evaporator. The resulting hydrazone was verified to be present by TLC (7:3 hexanes EtOAc) and $_1$H NMR, then carried on without further purification.

The crude hydrazone mixture was transferred into a flame dried round bottom flask purged with argon and charged with a stir bar. DCM (0.5M) was added, followed by $MgSO_4$ (100 mg/mmol). The solution was cooled down to 0˚C, and MnO_2 (8.0 equiv) was added in one portion. The solution was monitored by TLC (7:3 hexanes/ EtOAc) until all hydrazone was consumed. The solution was then filtered through celite, washed with DCM (3 x 10 mL), and the solvent was removed via rotary evaporator. Diazo products were purified by column chromatography using (99:1 hexanes: Et_3N) on basic alumina.

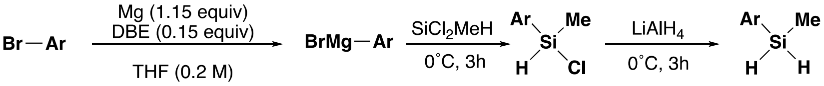
Diazo compounds **3a**-**d** were found to be stable for > 48h at room temperature when stored under argon, and ~6 weeks at -23˚C. Diazo compound **2a** was found to readily decompose within 24 h at room temperature, so it was stored at -23˚C under argon, which increased stability to 2 weeks.

Method B: Synthesis of 3c



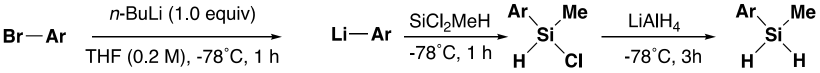
A 20-mL microwave vial with a stir bar was flamed dried, allowed to cool, then sealed. With an Ar balloon to equilibrate pressure, the vial was charged with 2-trifluoromethylbenzophenone in 10 mL EtOH (4 mmol, 0.4 M). Hydrazine (40 mmol, 1.28 mL), followed by AcOH (5 mmol, 286 μL) were added, and the solution was sparged with Ar for 5 min. The microwave vial was heated in a microwave reactor to 165 ˚C for 3 h, with 15 sec of pre-stirring. The reaction was allowed to cool to room temperature, and the solvent was removed via rotary evaporator. The resulting slurry was dissolved in Et_2O (20 mL), washed with H_2O (10 mL), brine (10 mL), and dried with Na_2SO_4. The solution was filtered, and the solvent was removed via rotary evaporator. The crude hydrazone mixture was transferred into a flame dried round bottom flask purged with argon and charged with a stir bar. DCM (0.5M) was added, followed by $MgSO_4$ (100 mg/mmol). The solution was cooled down to 0˚C, and MnO_2 (32 mmol, 2.78 g) was added in one portion. The solution was monitored by TLC (7:3 hexanes/ EtOAc) until all hydrazone was consumed. The solution was then filtered through celite, washed with DCM (3 x 10 mL), and the solvent was removed via rotary evaporator. Diazo products were purified by column chromatography using (99:1 hexanes: Et_3N) on basic alumina to furnish diazo **3c** as a red liquid in 44% yield (461.5 mg) over 2 steps.

Method C: Synthesis of aryl-alkyl silanes using Grignards



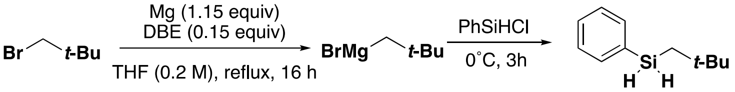
Magnesium turnings (1.15 equiv) were added to THF in an argon-purged 2-neck flask followed by the addition of DBE (0.15 equiv). The solution stirred for 1 h and turned black. The aryl bromide (1.0 equiv) was slowly added dropwise over a 20-minute period, and the solution was brought to reflux for up to 16 h, or until magnesium was no longer observed in the flask. The reaction was allowed to cool to room temperature and stirred an additional 15 minutes. The reaction was cooled to 0 ˚C with vigorous stirring, and an alkyldichlorosilane was added quickly in one portion, and stirred for an additional 2-3 hours with no further cooling. The reaction was cooled to 0˚C again, and $LiAlH_4$ (4.0 M solution in Et_2O, 1.0 equiv) was added dropwise over a 5-minute period and stirred for an additional 2 h. The reaction was slowly quenched with the addition of saturated aq. Rochelle's salt, and filtered over celite. The organic layer was separated and the aqueous layer was washed with Et_2O, then the organic layers were combined and washed with brine, dried with $MgSO_4$, filtered, and then concentrated *in vacuo*. The products were purified either by bulb-to-bulb distillation via kugelrohr, sublimation, or column chromatography in hexanes.

Method D: Synthesis of aryl-alkyl silanes using lithiates



A round-bottom flask with stir bar was charged with an aryl bromide (1.0 equiv), and THF. The reaction was cooled to -78 ˚C with vigorous stirring, and *n*-BuLi (2.5 M solution in hexanes, 1.0 equiv) was added dropwise, and the reaction stirred for 1 h. The alkyldichlorosilane (1.0 equiv) was added quickly in one portion and stirred for an additional 1 h at -78˚C. $LiAlH_4$ (4.0 M solution in Et_2O, 1.0 equiv) was added dropwise over a 5 minute period and stirred for an additional 2 h. The reaction was slowly quenched with the addition of saturated aq. Rochelle's salt, and filtered over celite. The organic layer was separated and the aqueous layer was washed with Et_2O, then the organic layers were combined and washed with brine, dried with $MgSO_4$, filtered, and then concentrated *in vacuo*. The products were purified either by bulb-to-bulb distillation via kugelrohr, sublimation, or column chromatography in hexanes to furnish pure silanes.

Method E: Synthesis of 1m



Magnesium turnings (1.15 equiv, 5.75 mmol, 140 mg) were added to an argon-purged, 25-mL 2-neck flask. THF (10 mL), followed by the addition of DBE (0.15 equiv) were added. The solution stirred for 1 h and turned black. Neopentyl bromide (1.0 equiv, 5.0 mmol, 630 µL) was added dropwise, and the solution was brought to reflux for up to 16 h. The reaction was allowed to cool to room temperature and stirred an additional 15 minutes. The reaction was cooled to 0 ˚C with vigorous stirring, and chlorophenylsilane (1.0 equiv, 5.0 mmol, 666 µL) was added quickly in one portion and stirred for an additional 2-3 hours with no further cooling. The reaction was slowly quenched with the addition of saturated aqueous NH_4Cl (10 mL) and filtered over celite. The organic layer was separated and the aqueous layer was washed with Et_2O, then the organic layers were combined and washed with brine, dried with $MgSO_4$, filtered, and then concentrated *in vacuo*. The crude mixture was purified by column chromatography (100 % hexanes) to furnish silane **1m** as an oil in 25% yield (231 mg, 1.3 mmol).

IIb. Procedures for Enantioselective Si–H insertions (4a-o; 5a-j)

Method E: Synthesis of racemic standard for HPLC analysis

A 4 mL reaction vial equipped with stir bar and 50 mg 4Å molecular sieves was heated under flame and dried under high vacuum (>1 torr). After the vial cooled to room temperature, it was purged with argon and Rh_2OAc_4 (0.002 mmol), silane (0.5 mmol). The vial was re-purged with argon, and 1 mL of DCM was added. A diazo compound (0.1 mmol) was weighed into a separate flame-dried vial, and 1 mL of DCM was added, then drawn into a syringe. Using a long needle, the syringe was placed on a syringe pump with the needle *in* the stirring solution. The syringe pump was program to add the solution over a period of 1 hour at room temperature. After 1 h, the solution was diluted with 5 mL of hexane, and filtered through celite, and concentrated *in vacuo*. The presence of insertion product was verified by $_1$H NMR analysis, and HPLC analysis was then conducted.

Method F: General procedure for enantioselective dirhodium(II)-catalyzed insertion with donor/donor carbenes (prochiral and symmetrical)

A 8 mL reaction vial equipped with stir bar and 100 mg 4Å molecular sieves was heated under flame and dried under high vacuum (>1 torr). After the vial cooled to room temperature, it was purged with argon, followed by addition of Rh_2(*S*-TCPTTL)$_4$ (0.002 mmol, 3.6 mg) and silane **1a** (1 mmol, 137 µL). The vial was re-purged with argon, and 2 mL of PhMe was added. Diazo compound **3a** (0.2 mmol, 39.0 mg)) was weighed into a separate flame-dried vial, and 2 mL of PhMe was added, then drawn into a syringe. Using a long needle, the syringe was placed on a syringe pump with the needle *in* the stirring solution. The syringe pump was programed to add the solution over a period of 1 h at room temperature.

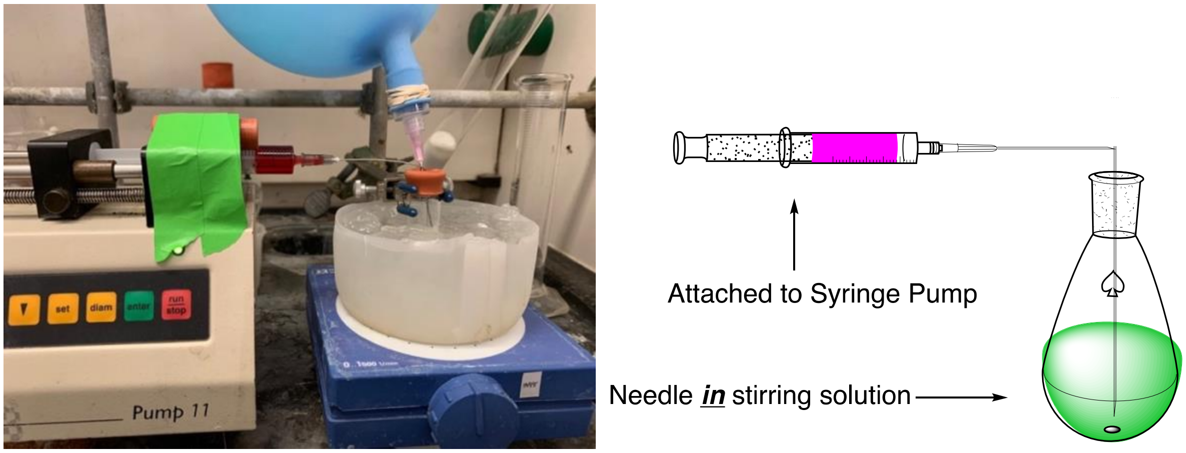


Figure S1. Example insertion with diagram

Thirty minutes after diazo addition, the solution was diluted with 5 mL of hexane, and filtered through celite, and concentrated *in vacuo*. The crude mixture was diluted in hexanes and ran through a short silica plug (4 cm in a Pasteur pipette) to remove catalyst, and concentrated *in vacuo*. The crude mixture was analyzed by NMR to determine dr, via the methyl resonance off the benzene ring. The product was then purified using column chromatography (dry loaded sample in silica, 98:2 hexanes/DCM) to furnish silane **5a** as an oil in 91% yield (55.0 mg, 0.18 mmol, 93:7 dr, 93:7 er).

Method G: Procedure for gram-scale enantioselective dirhodium(II)-catalyzed insertion of diazo 3a and methylphenylsilane 1a

A 100 mL round-bottom flask equipped with stir bar and 2.50 g of 4Å molecular sieves was heated in the oven for 24 h and dried under high vacuum (>1 torr). After the flask cooled to room temperature, Rh_2(*S*-TCPTTL)$_4$ (0.0025 mmol, 5.1 mg) and methylphenylsilane **1a** (25.5 mmol, 3.50 mL) were added. The flask was purged with Ar, followed by addition of PhMe (25 mL). Diazo compound **3a** (5.1 mmol, 1.00 g) was weighed into a separate flame-dried vial, and 25 mL of PhMe was added, then drawn into a 30-mL syringe. Using a long needle, the syringe was placed on a syringe pump with the needle *in* the stirring solution. The syringe pump was programed to add the solution over a period of 2.5 h at room temperature.

Figure S2. Gram-scale insertion

After 2.5 h, the solution was filtered, and concentrated *in vacuo*. The crude mixture was analyzed by NMR to determine dr, via the methyl resonance off the benzene ring. The product was then purified using column chromatography (dry loaded sample in silica, 98:2 hexanes/DCM) to furnish silane **5a** as an oil in 89% yield (93:7 dr, 1.34 g, 4.5 mmol).

Silane **5a** was found to be stable to air and atmospheric moisture for >3 weeks with minimal decomposition and no loss of dr or er.

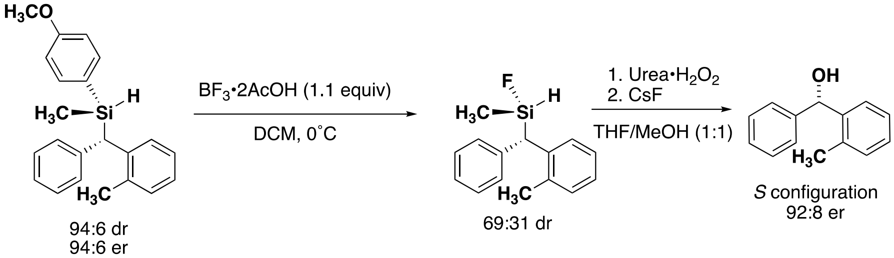
IIc. Procedures for HPLC samples

Method H: General procedure for hydrolysis for HPLC Analysis

Silane was added to a 4 mL reaction vial, (10 mg) followed by THF/H_2O (99:1 v/v, 0.5 mL), then Pd/C (10 mg) (preactivated with $PhSiH_3$). The reaction was monitored by TLC until full consumption of the silane was observed. The reaction was filtered through celite and concentrated *in vacuo*. DCM (0.1 mL) was added, and the sample was spotted onto a TLC plate (5 x 5 cm). The plate was placed in a TLC chamber to develop, and the silanol was etched off the plate with a razor blade. The loose silica was washed with 70:30 hexanes:IPA (1.0 mL) and filtered through celite to furnish HPLC samples.

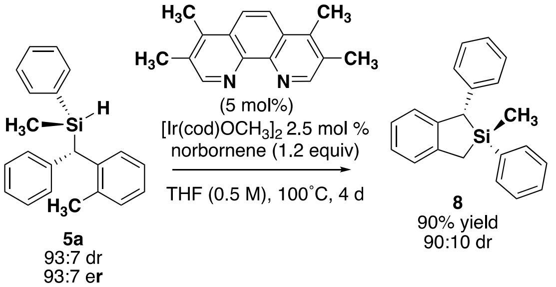
IId. Procedures for Functionalization

Method I: Tamao-Fleming Oxidation[8]



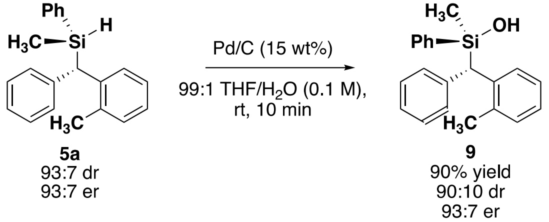
To a flame-dried, Ar-purged 8-mL reaction vial charged with stir bar, silane **5e** (258 mg, 0.77 mmol) was dissolved in DCM (3 mL) and added to the vial. The vial was cooled to 0˚C, and BF_3•2AcOH (120 ul, 0.85 mmol) was added to the vial while stirring. The conversion of the arylsilane to the silyl-fluoride was monitored using TLC (9:1 hexanes/EtOAc). Once the reaction was complete the reaction was diluted with 10 mL of DCM. Saturated aqueous $NaHCO_3$ solution (8 mL) was added and stirred until the evolution of gas ceased completely. The organic layer was separated, collected, and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to afford a silyl-fluoride intermediate that could be isolated as a clear viscous oil and was identified using $_1$H NMR and $_{19}$F NMR spectroscopy. The silyl-fluoride was not purified and was carried forward directly into the next step. The crude mixture was dissolved in 1:1 MeOH:THF (5 mL), and transferred to a flame-dried flask charged with a stir bar. Next, urea hydrogen peroxide was added (80.0 mg, 0.85 mmol), and the reaction was monitored by TLC until full consumption of the silyl fluoride was observed. Lastly, CsF was added (128.4 mg, 0.85 mmol), and the reaction was monitored by TLC until benzhydrol **12** was observed (based on TLC). The reaction mixture was filtered though celtie, washed with H2O (5 mL), and dried over Na2SO4. The solution was filtered and concentrated *in vacuo* to furnish crude benzhydrol **12**. An HPLC sample of the reaction mixture was prepared and analyzed using CSP-HPLC (92:8 er); when compared to literature values, they matched with previously reported data with the *S*-configuration.

Method J: C–H Silylation[9]



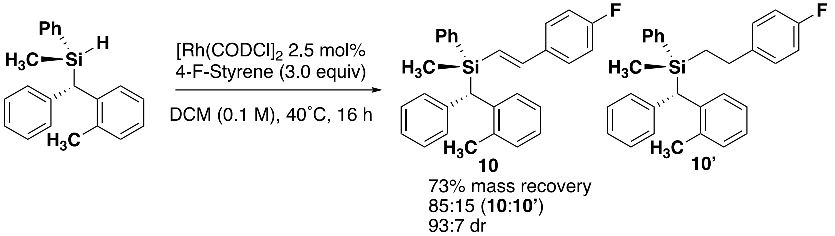
To a flame-dried, 4-mL reaction vial charged with stir bar, silane **5a** (100 mg, 0.33 mmol), norbornene, 3,4,7,8-tetramethyl-1,10-phenthroline (2.0 mg, 0.0084 mmol), $[Ir(cod)OMe]_2$, (5.5 mg, 0.084 mmol) was purged with argon, then dissolved in THF (0.7 mL) and screwed tightly. The vial was heated to 100˚C and stirred for 4 days. The reaction was allowed to cool to room temperature, then diluted with hexanes (10 mL), and filtered through a pad of celite. The organic solution was concentrated *in vacuo*, and the product was purified using column chromatography (98:2 hexanes/DCM) to furnish silane **11** as an oil in 90 % yield (89.2 mg, 90:10 dr).

Method K: General Procedure for Pd/C Hydrolysis



To a 4-mL reaction vial charged with stir bar, silane **5a** (100 mg, 0.33 mmol, 93:7 dr; 93:7 er), Pd/C (15.0 mg, 15 wt%) was purged with argon, then dissolved in THF (containing ~1% v/v H_2O). The consumption of starting material was monitored by TLC, about 10 min. Once fully consumed, DCM (5 mL) was added, and the reaction was filtered through a thin pad of celite. The solution was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The product was purified using column chromatography (95:5 hexanes/EtOAc) to furnish silanol **9** as an oil in 90% yield (94.6 mg, 90:10 dr, 93:7 er).

Method L: Dehydro-coupling reaction

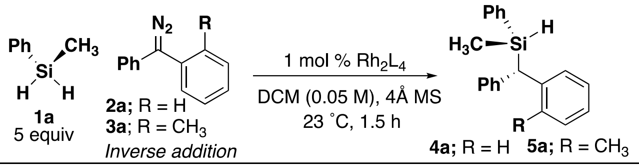


To a flame-dried, 8-mL reaction vial charged with stir bar, silane **5a** (104 mg, 0.34 mmol, 93:7 dr; 93:7 er), 4-fluorostyrene (19 µL, 1.0 mmol) was purged with argon, then dissolved in DCM (3.5 mL). After 5 min, $[Rh(COD)Cl]_2$ (0.03 equiv, 5.2 mg, 0.01 mmol) was added, and the solution turned yellow, and was heated to 40˚C and stirred for 16 h. The reaction was diluted with hexanes and filtered through a thin silica pad to remove catalyst. The solvent was removed via rotary evaporator, and the product was purified using column chromatography (98:2→90:10 hexanes/DCM) to furnish silane **10** as an oil in 62% yield (73% mass recovery (104.1 mg); 85:15 mixture with hydrosilylation product **10'**, 93:7 dr by ^{19}F NMR). The determination of 85:15 was confirmed using ^{1}H NMR Spectroscopy by comparing the relative integrals of the peaks at 4.10 and 3.97 ppm.

III. Analysis and Optimization

IIIa. Optimization of enantioselective donor/donor carbene insertion of prochiral silanes

Table S1. Optimization of Enantioselective donor/donor insertion into prochiral silanes



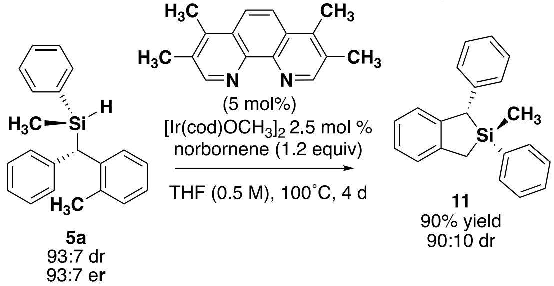
Entry	R	Catalyst	% loading	Solvent	Temp	additive	% yield[a]	dr[b]	er[c]
1	H	Cu(OTf)$_2$	10	DCM	rt	-	<5	-	-
2	H	Cu[MeCN]$_4$PF$_6$	10	DCM	rt	-	<5	-	-
3	H	(Ir[COD]Cl)$_2$	5	DCM	rt	-	<5	-	-
4	H	[IrCpCl]$_2$	5	DCM	rt	-	<5	-	-
5	H	[Ru(p-cymeme)Cl]$_2$	5	DCM	rt	-	<5	-	-
6	H	Fe(OTf)$_2$	20	DCM	rt	-	<5	-	-
7	H	Rh$_2$OAc$_4$	1	DCM	rt	-	35	-	50:50
8	H	Rh$_2$(*R*-PTAD)$_4$	1	DCM	rt	-	72	-	61:39
9	H	Rh$_2$(S-PTTL)$_4$	1	DCM	rt	-	62	-	64:36
10	H	Rh$_2$(S-BPTTL)$_4$	1	DCM	rt	-	62	-	64:36
11	H	Rh$_2$(S-PTV)$_4$	1	DCM	rt	-	67	-	59:41
12	H	Rh$_2$(S-DOSP)$_4$	1	DCM	rt	-	64	-	55:45
13	H	Rh$_2$(*S*-BTPCP)$_4$	1	DCM	rt	-	<5	-	ND
14	H	Rh$_2$(5*R*-MEPY)$_4$	1	DCM	rt	-	<5	-	ND
15	H	Rh$_2$(S-TCPTTL)$_4$	1	DCM	rt	4 Å MS[d]	76	-	76:24
16	H	Rh$_2$(S-TCPTTL)$_4$	3	Heptane	rt	4 Å MS[d]	78	-	82:18
17	H	Rh$_2$(S-TCPTTL)$_4$	3	Benzene	rt	4 Å MS[d]	74	-	82:18
18	H	Rh$_2$(S-TCPTTL)$_4$	3	Cyclohexane	rt	4 Å MS[d]	74	-	82:18
19	H	Rh$_2$(S-TCPTTL)$_4$	3	PhMe	rt	4 Å MS[e]	78	-	82:18
20	CH$_3$	Rh$_2$OAc$_4$	1	PhMe	rt	4 Å MS[e]	45	55:45	50:50
21	CH$_3$	Rh$_2$OAc$_4$	1	PhMe	rt	4 Å MS[e]	45	55:45	50:50
22	CH$_3$	Rh$_2$(*R*-PTAD)$_4$	1	PhMe	rt	4 Å MS[e]	75	63:37	ND
24	CH$_3$	Rh$_2$(S-DOSP)$_4$	1	PhMe	rt	4 Å MS[e]	70	61:39	ND
25	CH$_3$	Rh$_2$(*S*-BTPCP)$_4$	1	PhMe	rt	4 Å MS[e]	<5	-	ND
26	CH$_3$	Rh$_2$(S-TCPTTL)$_4$	1	PhMe	rt	4 Å MS[e]	91	92:8	93:7
27	CH$_3$	Rh$_2$(S-TCPTTL)$_4$	0.1	PhMe	rt	4 Å MS[e]	85	93:7	93:7
28	CH$_3$	Rh$_2$(S-TCPTTL)$_4$	0.01	PhMe	rt	4 Å MS[e]	88	93:7	93.5:6.5
29	CH$_3$	Rh$_2$(S-TCPTTL)$_4$	0.001	PhMe	rt	4 Å MS[e]	32	93:7	93.5:6.5
30[f]	CH$_3$	Rh$_2$(S-TCPTTL)$_4$	0.05	PhMe	rt	4 Å MS[e]	89	93:7	93.5:6.5

Entry	R	Catalyst	% loading	Solvent	Temp	additive	% yield[a]	dr[b]	er[c]
31[g]	CH_3	Rh_2(S-TCPTTL)$_4$	1	PhMe	rt	4 Å MS[e]	40	92:8	93:7
32[h]	CH_3	Rh_2(S-TCPTTL)$_4$	1	PhMe	rt	4 Å MS[e]	81	92:8	93:7
33	CH_3	Rh_2(S-TCPTTL)$_4$	1	PhMe	0˚C	4 Å MS[e]	78	93:7	93:7
34	CH_3	Rh_2(S-TCPTTL)$_4$	1	PhMe,	-30˚C	4 Å MS[e]	<5	-	ND
35	CH_3	Rh_2(S-TCPTTL)$_4$	1	PhMe,	-78˚C	4 Å MS[e]	<5	-	ND

[a] Determined using ^{1}H NMR a1nalysis using PhTMS as an internal standard. [b] Determined using ^{1}H NMR analysis of isolated product prior to purification. [c] Determined using CSP-HPLC after Pd/C hydrolysis. [d] MS were heated under high vacuum (>1 torr) and cooled to rt prior to use. [e] MS were flame dired and dried under high vacuum (>1 torr). [f] Reaction run on gram scale for **3a** (5.1 mmol) at 0.1 M PhMe. [g] Diazo was added in a single portion. [h] Diazo added dropwise by hand over 5 minutes.

IIIb. Optimization of C–H silylation of Silane 5a

Table S2. Optimization of C–H silylation

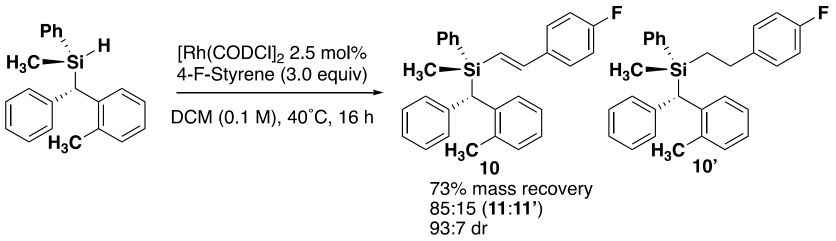


Entry	R	R’	Time (h)	% yield[a]	dr[b]
1	H	H	24	<5	ND
2	H	CH_3	24	<5	ND
3	CH_3	CH_3	96	85	90:10
4	CH_3	CH_3	96	90[b]	90:10

[a] Determined using ^{1}H NMR analysis using PhTMS as an internal standard, 0.1 mmol silane **5a**. [b] 0.33 mmol 5a; isolated yield.

IIIc. Optimization of dehydrocoupling of Silane 5a

Table S3. Optimization of dehydrocoupling



entry	**5a** (mg)	Catalyst, % loading	solvent	time (h)	temp	equiv styrene	**5a** consumption (%)[a]	**10:10'**[a]	% Mass Recovery
1	30	Pt(dvs), 2.5	Pentane	16 h	rt	1.2	> 95	-	ND
2	102	Pt(dvs), 5	DCM	16 h	rt	1.2	> 95	-	ND
3	104	Pt(dvs), 5	DCE	16 h	80	1.2	> 95	-	ND
4	32	Pt(dvs), 5	DCE	12 h	80	1.2	> 95	-	ND
5	31	Pt•NHC[c], 10	DCE	12 h	rt	1.2	10	-	ND
6	32	PtO_2, 10	DCE	12 h	rt	1.2	> 95	-	ND
7	16	$[Rh(COD)Cl]_2$, 2.5	DCM	16	40	1.2	> 95	85:15	ND
8	102	$[Rh(COD)Cl]_2$, 2.5	DCM	16	40	1.2	> 95	50:50	75
9	31	$[Rh(COD)Cl]_2$, 2.5	DCE	16	80	3	> 95	75:25	80
10	103	$[Rh(COD)Cl]_2$, 2.5	DCM	16	40	3	> 95	85:15	82
11	33	$[Rh(PPh_3)Cl]$	DCM	16	40	3	> 95	75:25	ND

[a, b] Determined using ^{1}H NMR Spectroscopy. [c] Weight percent used

IIId. Determination of absolute configuration

Based on the results of the Tamao-Fleming oxidation (*vide infra*), the *S* configuration is assigned to the chiral carbon formed in the reaction after HPLC analysis compared to previously reported traces.[10]

For the assigning stereochemistry at silicon, a ^{1}H NOESY experiment was conducted on **11**, which was synthesized in 90:10 dr. Assuming retention of stereochemistry during the Si–H insertion step,[11,12] NOE transfer between the methyl group and benzhydryl proton indicates a *cis* relationship, thereby assigning an *S* configuration to the silicon for the insertion product.

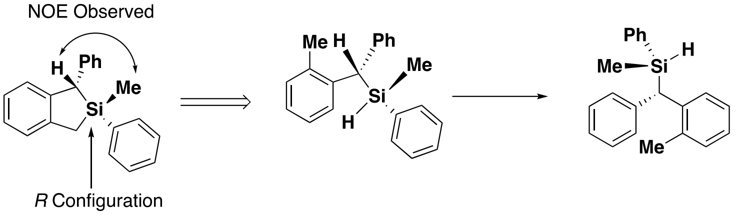


Figure S3. Reasoning for absolute configuration

The stereochemical outcome is applied to all other substrates based on analogy.

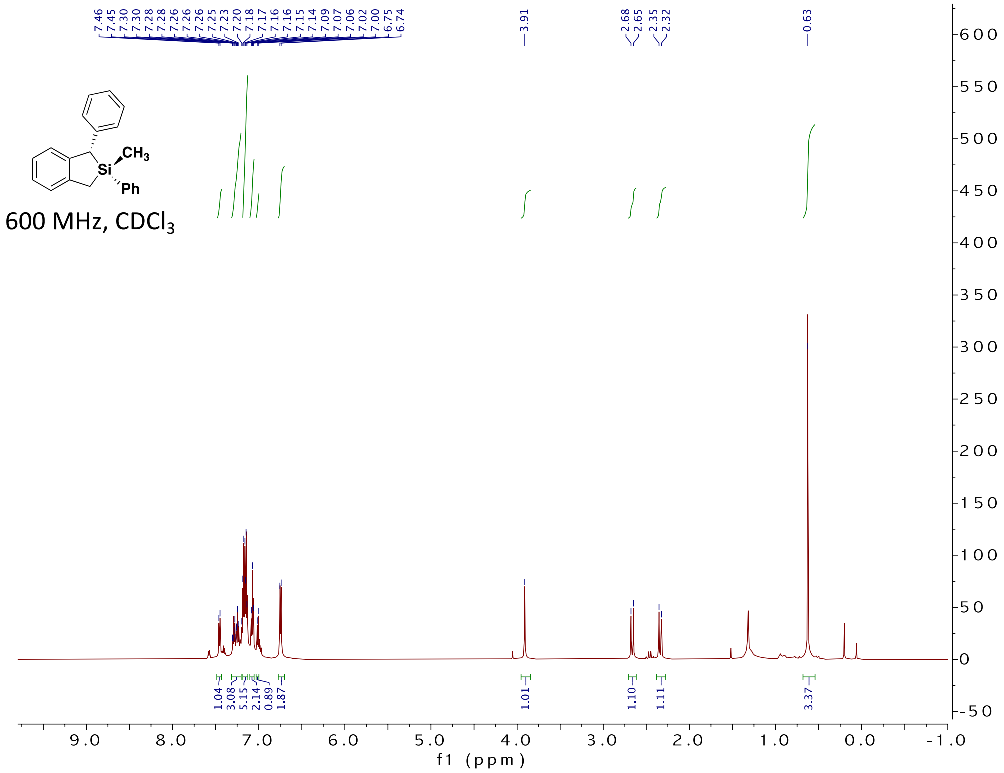


Figure S4. ^{1}H spectrum of **11**.

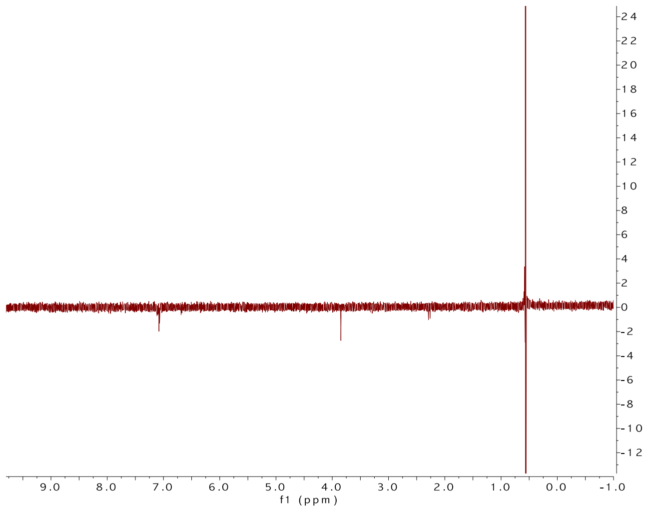


Figure S5. ^{1}H NOESY experiment after Si–CH$_3$ irradiation. Transfer was observed to the benzhydryl peak at ~3.8 ppm

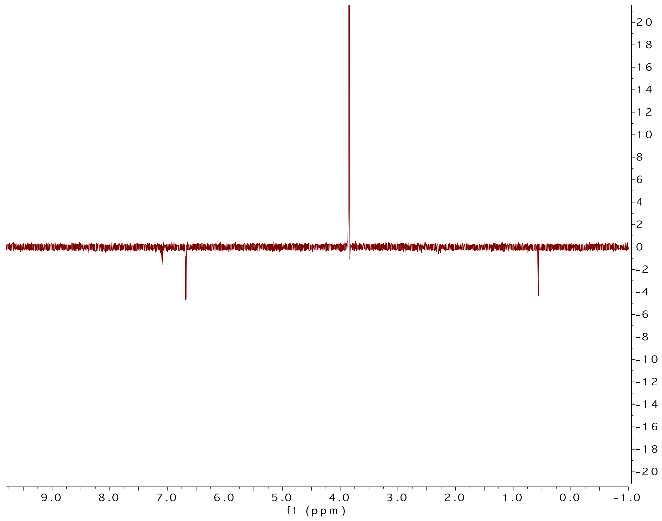


Figure S6. ^{1}H NOESY experiment after benzyhydryl C–H irradiation. Transfer was observed to the Si–CH$_3$ irradiation at ~0.5 ppm.

IV. Procedure for *in situ* ReactIR Analysis (Figure 2)

A 5-mL microwave reaction vial charged with stir bar, 4 Å MS (100 mg), then flame-dried and cooled under vacuum (>1 torr). After cooling, the vial was sealed, and PhMe (3mL) was added. A hole was punctured using a spatula, then quickly fitted to the ReactIR probe for background scans. The diazo was added as a solution (44.0 mg in 1.5 mL PhMe), and more background scans were taken to identify the diazo on the IR spectrum (2000-2100 cm^{-1}). Rh_2(*S*-TCPTTL)$_4$ was added as a solution in PhMe (0.5 mL of 0.3 mg/mL solution), and the disappearance of diazo **2a** or **3a** was monitored to determine a 1st order rate constant (*k*).

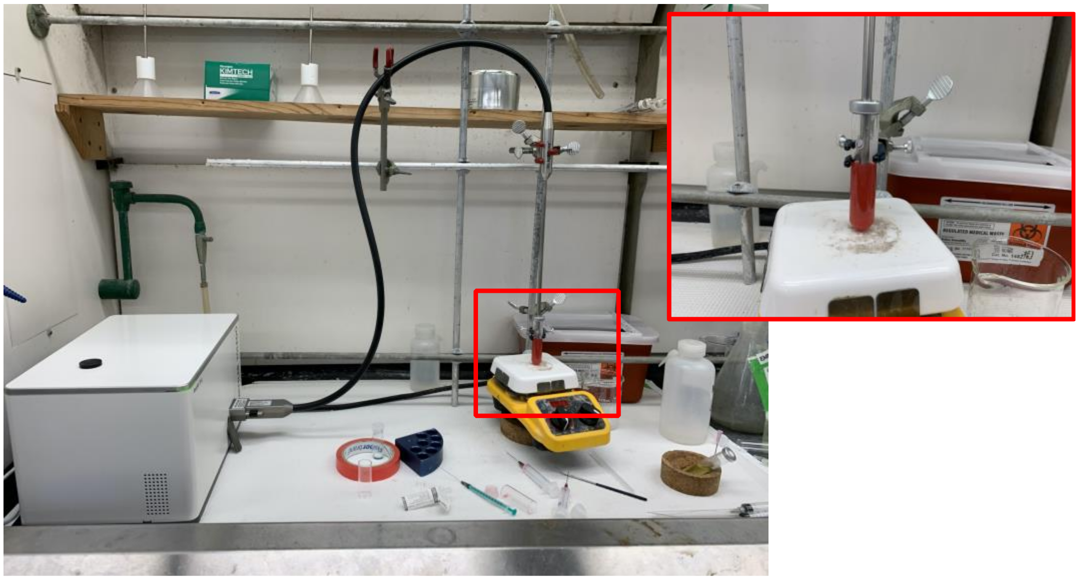


Figure S7. Example of ReactIR setup used for kinetic analysis.

The disappearance of diazo compounds **2a** and **3a** was monitored at 2041 cm^{-1}and the trend data was transferred to Microsoft Excel for analysis. The values on the x-axis were manipulated to reflect the total number of minutes after addition of diazo for determination of rate constants. The values on the Y-axis were calculated to conversion by dividing by the maximum absorbance seen. The initial point used for 1st order rate constant determination was set to when Rh_2(*S*-TCPTTL)$_4$ was added to the reaction vial. For the determination of reaction order, and R_2 value, the final point was identified when the concentration plateaued. The reactions were then filtered through a celite plug, and azines **7** and **8** were characterized by NMR. NMR yields using Ph-TMS were >90% for all trials. We then assumed the relative rates of diazo consumption were equivalent to the relative rates of azine formation.

Trial 1

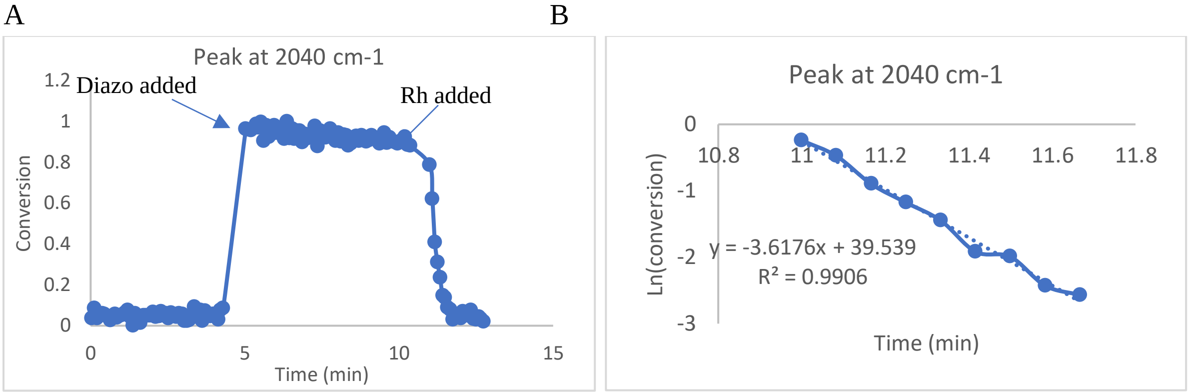


Figure S8. A: Data graphed for reaction with **2a** catalyzed by Rh_2(*S*-TCPTTL)$_4$: A) Graph of conversion vs. time. B) Graph of ln[conv] vs. time once catalyst was added.

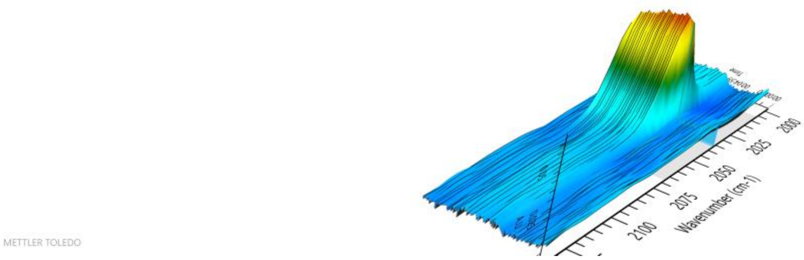


Figure S9. ReactIR surface plot for trial 1

Trial 2

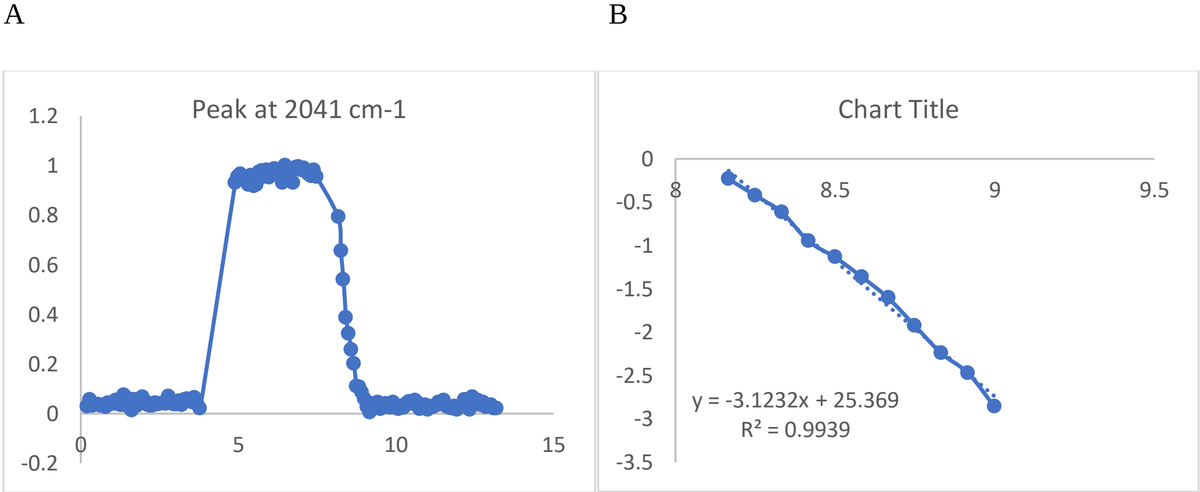


Figure S10. A: Data graphed for reaction with diazo compound **3a** catalyzed by Rh_2(*S*-TCPTTL)$_4$: A) Graph of conversion vs. time. B) Graph of ln[conv] vs. time once catalyst was added.

Trial 1

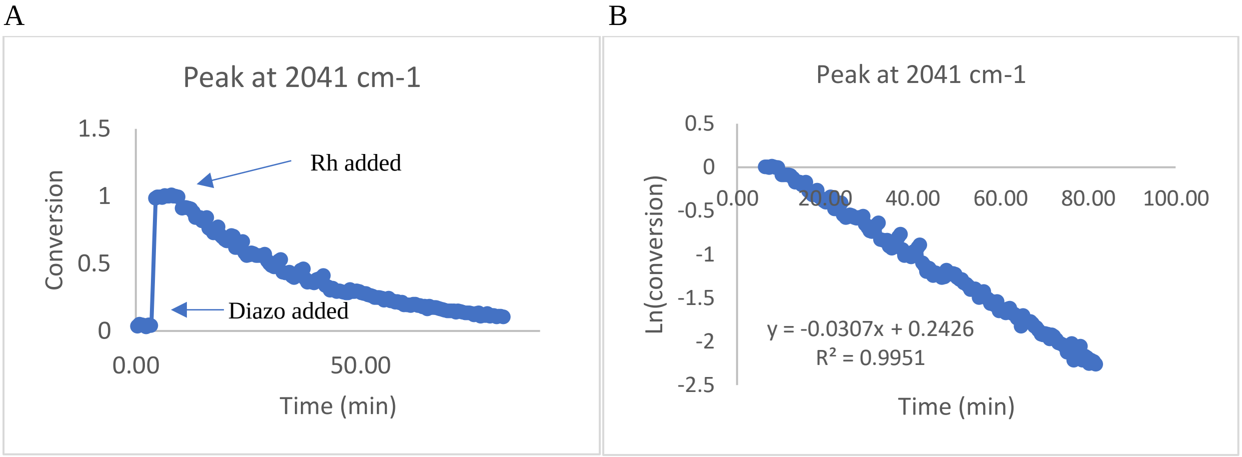


Figure S11. A: Data graphed for reaction with diazo compound **3a** catalyzed by Rh_2(*S*-TCPTTL)$_4$: A) Graph of conversion vs. time. B) Graph of ln[conv] vs. time once catalyst was added.

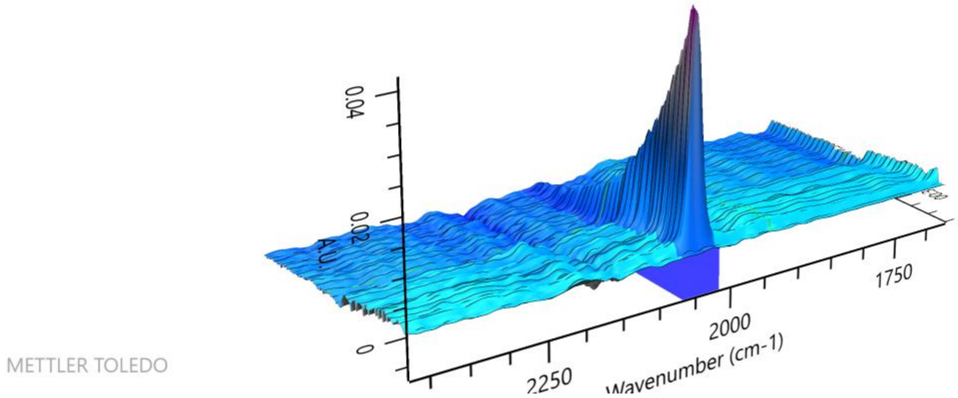


Figure S12. ReactIR surface plot for trial 1

Trial 2

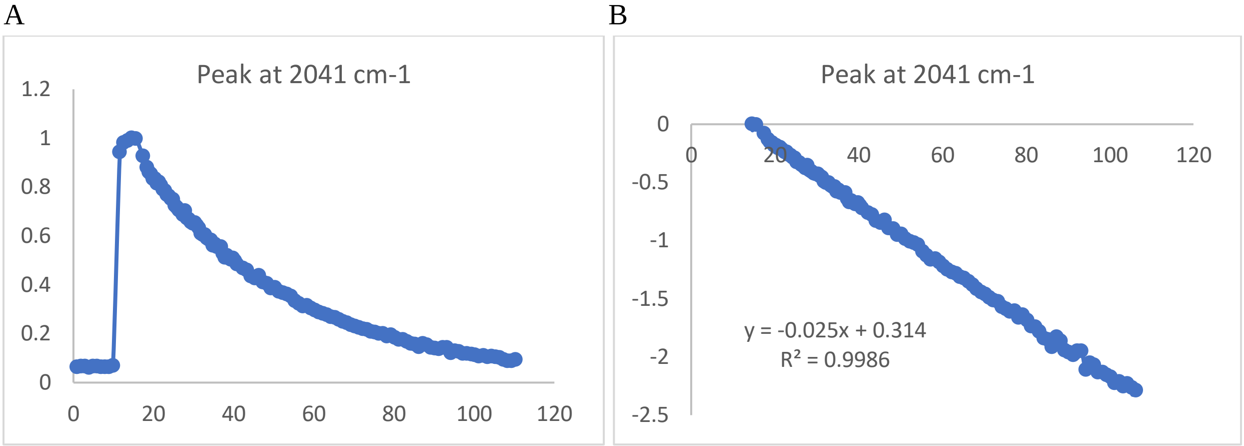
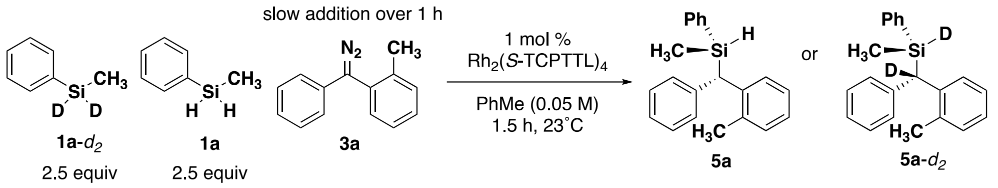


Figure S13. A: Data graphed for reaction with diazo compound **3a** catalyzed by Rh_2(*S*-TCPTTL)$_4$: A) Graph of conversion vs. time. B) Graph of ln[conv] vs. time once catalyst was added.

Based on the data observed, $k_{rel} = k_{\mathbf{2a}}/k_{\mathbf{3a}}$ = 117.8 for trial 1 and 127.2 for trial 2.

V. Procedure for kinetic isotope effect (Figure 2)



A 8 mL reaction vial equipped with stir bar and 100 mg 4Å molecular sieves was heated under flame and dried under high vacuum (>1 torr). After the vial cooled to room temperature, it was purged with argon, followed by addition of Rh_2(*S*-TCPTTL)$_4$ (0.002 mmol, 3.6 mg) and silane **1a** (1 mmol, 61 mg) and silane **1a**-d_2 (0.5 mmol, 61 mg). The vial was re-purged with argon, and 2 mL of PhMe was added. Diazo compound **3a** (0.2 mmol, 39.0 mg)) was weighed into a separate flame-dried vial, and 2 mL of PhMe was added, then drawn into a syringe. Using a long needle, the syringe was placed on a syringe pump with the needle *in* the stirring solution. The syringe pump was programed to add the solution over a period of 1 h at room temperature.

Thirty minutes after diazo addition, the solution was diluted with 5 mL of hexane, and filtered through celite, and concentrated *in vacuo*. The crude mixture was diluted in hexanes and ran through a short silica plug (4 cm in a Pasteur pipette) to remove catalyst, and concentrated *in vacuo*. The product was then purified using column chromatography (dry loaded sample in silica, 98:2 hexanes/DCM) to furnish a mixture of silane **5a** and **5a**-d_2 as an oil.

The kinetic isotope effect was determined using an integration ratio of the benzhydryl resonance for the major diastereomer present at 3.78. ppm and both benzyl resonances observed at 2.25 ppm (major diastereomer) using Equation 1:

$$KIE = \frac{I_A}{\frac{I_B}{3} - I_A} \qquad \text{(Eq. 1)}$$

Where I_A is the integral of the benzhydryl resonance, and I_B is the integral of both benzyl resonances. This equation takes into account both stoichiometry and the combined integration of both **5a** and **5a**-d_2 at 2.25 ppm.

Trial 1
I_A = 1.00
I_B =4.91
KIE = 1.57

Trial 2
I_A = 1.0
I_B = 4.90
KIE = 1.58

Based on the trials 1 and 2 , the calculated KIE is 1.575, which is rounded to 1.6.

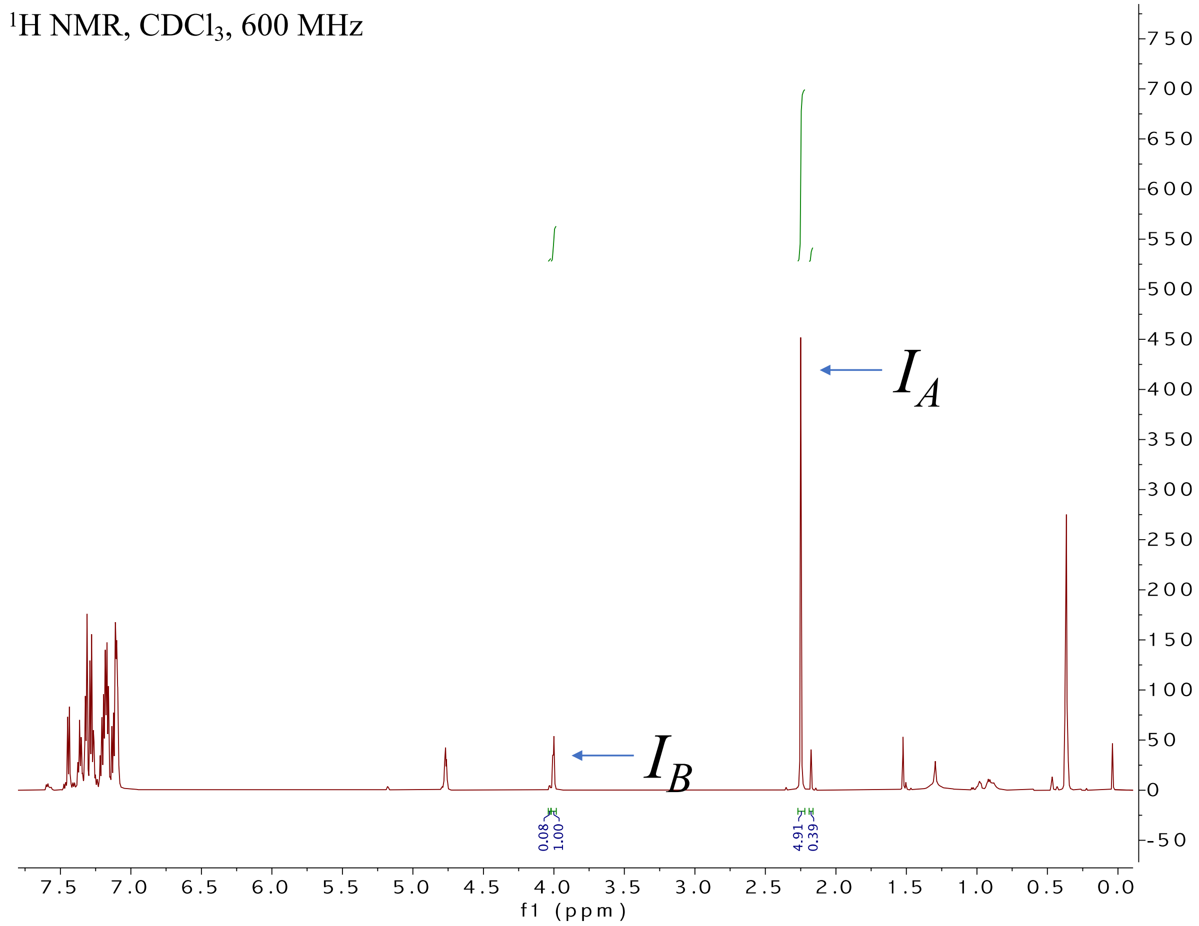
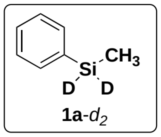


Figure S14. ^{1}H NMR of **5a** and **5a**-*d*$_2$ mixture, with I_A and I_B shown.

VI. Characterization Data

Silanes:

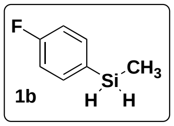
methyl(phenyl)silane-*d*$_2$ (1a-*d*$_2$)


1a-*d*$_2$

Made using previously reported procedures.[13] Spectrrum matches with previous report.[13]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (m, 2H), 7.45 – 7.35 (m, 3H), 0.43 (s, 3H).

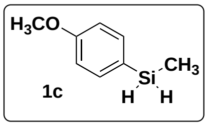
(4-fluorophenyl)(methyl)silane (1b)


1b

Synthesized according to the general procedure B for silane formation using 1-bromo-4-fluorobenzene (1.88 mL, 15.0 mmol), *n*-BuLi (15.0 mmol, 6 mL solution in hexanes) and dichloromethylsilane (1.09 mL, 15.0 mmol) and purified using bulb-to-bulb distillation to give a clear liquid that can be isolated in 45% yield (1.15 g, 6.75 mmol) over 2 steps from addition of the chlorosilane.

^{1}H NMR (600 MHz, C_6D_6) δ 7.19 – 7.16 (m, 1H), 6.79 (t, *J* = 8.7 Hz, 1H), 4.37 (q, *J* = 4.3 Hz, 1H), 0.10 (t, *J* = 4.3 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (d, *J* = 248.7 Hz), 137.0 (d, *J* = 7.6 Hz), 128.9 (d, *J* = 3.8 Hz), 115.4 (d, *J* = 19.9 Hz), -7.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.16. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -35.8

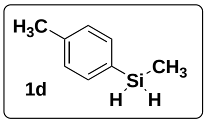
(4-methoxyphenyl)(methyl)silane (1c)


1c

Synthesized according to the general procedure for silane formation using 4-bromoanisole (1.88 mL, 15.0 mmol) and dichloromethylsilane (1.09 mL, 15.0 mmol) and purified using column chromatography (hexanes) to give a clear liquid that can be isolated in 81% yield (1.85 g, 12.2 mmol) over 2 steps from addition of the chlorosilane.

^{1}H NMR (600 MHz, C_6D_6) δ 7.41 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 4.55 (q, *J* = 4.0 Hz, 2H), 3.27 (s, 3H), 0.23 (t, *J* = 4.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 136.5, 124.2, 114.0, 55.2, -7.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -36.4.

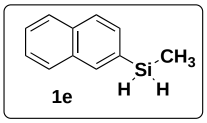
Methyl(*p*-tolyl)silane (1d)


1d

Synthesized according to the general procedure A for silane formation using 1-bromo-4-methylbenzene (1.85 mL, 15.0 mmol) and dichloromethylsilane (1.09 mL, 15.0 mmol) and purified using bulb-to-bulb distillation to give a clear liquid that can be isolated in 63% yield (1.29 g) over 2 steps from the addition of the chlorosilane.

^{1}H NMR (600 MHz, C_6D_6) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 4.53 (q, *J* = 4.1 Hz, 2H), 2.09 (s, 3H), 0.22 (t, *J* = 4.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 135.0, 129.8, 129.0, 21.6, -7.4. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -36.1.

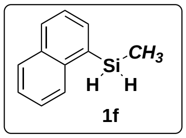
Methyl(naphthalen-2-yl)silane (1e)


1e

Synthesized according to the general procedure A for silane formation using 2-bromonaphthalene (3.26 g) in 5 mL THF and dichloromethylsilane (1.09 mL, 15.0 mmol) and purified using bulb-to-bulb distillation via kugelrohr (150˚C, 20 torr) followed by sublimation (70˚C, 760 torr) to give a clear liquid that can be isolated in 50% yield (1.29 g, 7.5 mmol, based on Si) over 2 steps from the addition of chlorosilane.

^{1}H NMR (600 MHz, C_6D_6) δ 7.99 (s, 1H), 7.61 (t, *J* = 7.2 Hz, 3H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.22 (m, 2H), 4.60 (q, *J* = 4.3 Hz, 0H), 0.25 (t, *J* = 4.2 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 134.0, 133.1, 131.0, 130.9, 128.1, 127.9, 127.4, 126.7, 126.2, -7.4. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -35.4.

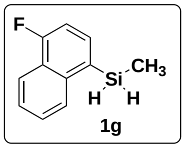
Methyl(naphthalen-1-yl)silane (1f)


1f

Synthesized according to the general procedure B for silane formation using 1-bromonaphthalene (2.10 mL, 15.0 mmol), *n*-BuLi (15.0 mmol, 6 mL solution in hexanes) and dichloromethylsilane (1.09 mL, 15.0 mmol) and purified using bulb-to-bulb distillation via kugelrohr (150˚C, 20 torr) followed by sublimation (70˚C, 760 torr) to give a clear liquid that can be isolated in 50% yield (1.29 g, 7.5 mmol) over 2 steps from addition of the chlorosilane.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.54 (m, 3H), 7.29 – 7.23 (m, 1H), 7.24 – 7.19 (m, 1H), 7.19 – 7.14 (m, 1H), 4.75 (q, *J* = 4.2 Hz, 2H), 0.24 (t, *J* = 4.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.2, 135.3, 133.2, 132.2, 130.6, 129.0, 127.7, 126.3, 125.9, 125.4, -7.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -38.6.

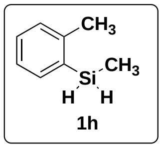
(4-fluoronaphthalen-1-yl)(methyl)silane (1g)


1g

Synthesized according to the general procedure for silane formation using 4-fluoro-1-bromonaphthalene (3.38 g, 15.0 mmol in 5 mL THF) and dichloromethylsilane (1.09 mL, 15.0 mmol)) and purified using bulb-to-bulb distillation via kugelrohr (150 ˚C, 50 torr for 30 min then 105 ˚C, 10 torr to give a clear liquid that can be isolated in 21% yield (597.0 mg, 3.1 mmol, based off Si) over 2 steps from addition of the chlorosilane.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 6.7 Hz, 1H), 7.60 (dt, *J* = 16.1, 7.0 Hz, 2H), 7.18 – 7.12 (m, 1H), 4.65 (q, *J* = 4.2, 3.7 Hz, 2H), 0.54 (t, *J* = 3.9 Hz, 3H). ^{13}C NMR (150MHz, $CDCl_3$ δ 160.78 (d, J_{CF} = 255.0 Hz), 138.82 (d, J_{CCCF}= 4.4 Hz), 135.28 (d, J_{CCF}= 8.3 Hz), 127.80 (d, J_{CCCF}= 4.8 Hz), 127.57 (d, *J* = 3.1 Hz), 127.32, 126.21 (d, J_{CCCCF} = 1.7 Hz), 121.40 (d, J_{CCCF} = 6.1 Hz), 109.17 (d, J_{CCF} = 18.6 Hz), -7.19. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.24. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -35.8

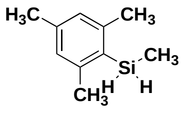
Methyl(*o*-tolyl)silane (1h)


1h

Synthesized according to the general procedure for silane formation using 2-bromotoluene (1.80 mL, 15.0 mmol) and dichloromethylsilane (1.09 mL, 15.0 mmol) and purified using column chromatography (hexanes) to give a clear liquid that can be isolated in 72% yield (1.47g, 10.8 mmol) over 2 steps from the addition of the chlorosilane. Matches with previously reported spectra.[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.21 – 7.16 (m, 2H), 4.37 (q, *J* = 4.2 Hz, 2H), 2.46 (s, 3H), 0.43 (t, *J* = 4.2 Hz, 3H).

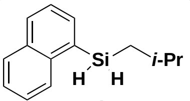
Mesityl(methyl)silane (1i)


1i

Synthesized according to the general procedure for silane formation using 2-bromomesitylene (2.30 mL, 15 mmol) and dichloromethylsilane (1.09 mL, 15.0 mmol) and purified using column chromatography (hexanes) to give a clear liquid that can be isolated in 87% yield (2.14 g, 13.0 mmol) over 2 steps from addition of the chlorosilane. Spectral data matches previously reported values.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 2H), 4.45 (q, *J* = 4.2 Hz, 2H), 2.47 (s, 6H), 2.30 (s, 3H), 0.36 (t, *J* = 4.2 Hz, 3H).

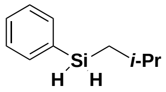
Isobutyl(naphthalen-1-yl)silane (1j)


1j

Synthesized according to Method C for silane formation using 1-bromonaphthalene (2.10 mL, 15.0 mmol), *n*-BuLi (15.0 mmol, 6 mL solution in hexanes), and dichlorosiobutylsilane (2.28 mL, 15.0 mmol) and purified using bulb-to-bulb distillation via kugelrohr (150 ˚C, 20 torr) followed by sublimation (70˚C, 760 torr) that can be isolated as a clear liquid in 21% yield (675.0 mg, 3.2 mmol, based of Si) over 2 steps from addition of the chlorosilane.

^{1}H NMR (600 MHz, C_6D_6) δ 8.14 (m, 1H), 7.74 (m, 1H), 7.65 (m, 2H), 7.33 (m, 1H), 7.27 (m, 1H), 7.23 (m, 1H), 4.83 (t, *J* = 3.8 Hz, 2H), 1.76 (hept, *J* = 6.7 Hz, 1H), 0.94 (dd, *J* = 7.1, 3.7 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 137.37, 135.85, 133.23, 131.87, 130.53, 129.04, 127.92, 126.31, 125.86, 125.39, 26.09, 25.62, 20.80. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -36.0.

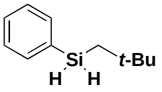
Isobutyl(phenyl)silane (1k)


1k

Synthesized according to method C for silane formation using bromobenzene (1.58 mL, 15.0 mmol) and dichlorosiobutylsilane (2.28 mL, 15.0 mmol) and purified using bulb-to-bulb distillation (150 ˚C, 100 torr) to give a liquid that can be isolated as a clear liquid in 41% yield (1.01 g, 6.15 mmol) over 2 steps from addition of the chlorosilane.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (m, 2H), 7.36 (m, 3H), 4.31 (t, *J* = 3.9 Hz, 2H), 1.85 (dh, *J* = 13.4, 6.7 Hz, 1H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.95 (dt, *J* = 7.5, 3.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.35, 133.10, 129.58, 128.09, 25.75, 25.62, 20.61. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -33.8.

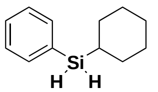
Neopentyl(phenyl)silane (1l)


1l

Synethsized using method H. Isolated as a clear liquid in 25 % yield (231 mg, 1.3 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.4 Hz, 1H), 7.36 (hept, *J* = 6.7, 6.2 Hz, 2H), 4.34 (t, *J* = 4.2 Hz, 2H), 1.08 (t, *J* = 4.2 Hz, 2H), 1.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.35, 133.53, 129.51, 128.08, 33.07, 32.31, 27.09. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -37.8.

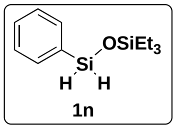
Cyclohexylphenylsilane (1m)


1m

Made using previously reported procedures.[15] Spectra matches with previous report.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 6.5, 1.5 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.37 – 7.33 (m, 2H), 4.16 (d, *J* = 3.0 Hz, 2H), 1.83 – 1.58 (m, 7H), 1.22 – 0.91 (m, 4H).

1,1,1-Triethyl-3-phenyldisiloxane (1n)

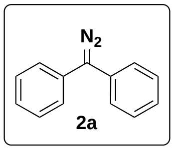

1n

Made using previously reported procedure.[3] Spectra matches with previous report.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.52 – 7.35 (m, 3H), 5.14 (s, 1H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.60 (q, *J* = 8.0 Hz, 6H).

Diazo compounds:

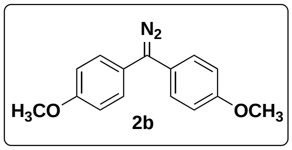
Diphenyldiazomethane (2a)


2a

Synthesized using previously reported procedures. Spectrum matches previous report.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.7 Hz, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H).

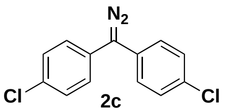
4,4'-(diazomethylene)bis(methoxybenzene) (2b)


2b

Made using previously published procedures. Spectrum matches previous report.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.8 Hz, 4H), 6.94 (d, *J* = 8.8 Hz, 4H), 3.82 (s, 3H).

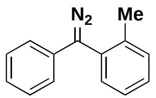
4,4'-(diazomethylene)bis(chlorobenzene) (2c)


2c

Made using previously published procedures. Spectrum matches previous report.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 4H), 7.18 (d, *J* = 8.7 Hz, 4H).

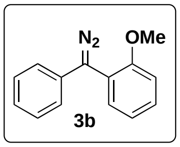
Phenyl(*o*-tolyl)diazomethane (3a)


3a

Synthesized using procedure A for diazo formation using 2-methylbenzophenone (0.36 mL, 2.0 mmol) to give a purple liquid that can be isolated in 60% yield (243.0 mg) over 2 steps.

^{1}H NMR (400 MHz, $CDCl_3$δ 7.43 (d, *J* = 7.1 Hz, 1H), 7.31 (m, 5H), 7.07 (t, *J* = 7.3 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 131.5, 131.25, 131.0, 129.1, 128.7, 127.2, 126.7, 124.1, 122.6, 20.6. APCI *m/z* calc for $C_{14}H_{12}N_2$ [M + H – N_2]

Phenyl(*o*-methoxyphenyl)diazomethane (3b)

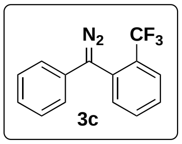


3b

Synthesized using procedure A using 2-methoxybenzphenone (457.0 mg, 2.2 mmol) to give a purple oil that can be isolated in 68% yield (761.9 mg) over 2 steps.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.31 (q, *J* = 6.9 Hz, 3H), 7.08 (m, 3H), 7.04 – 6.96 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 131.6, 130.1, 129.0, 124.2, 123.2, 121.2, 117.2, 111.7, 55.7. APCI *m/z* calc for $C_{14}H_{12}N_2O$ $[M + H – N_2]^+$. 197.1. Found 196.5.

Phenyl(*o*-trifluoromethylphenyl)diazomethane (3c)

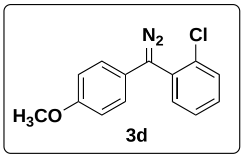


3c

Synthesized using method B to give a red liquid that can be isolated in 44% yield (461.5 mg) over 2 steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.59 (ddt, *J* = 23.5, 15.2, 7.6 Hz, 3H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 132.6, 131.1 (q, J_{CCF} = 30 Hz), 131.6, 129.2, 129.1 127.4 (q, J_{CCCF} = 5.4 Hz), 127.0, 124.3, 124.0 (q, J_{CF} = 275 Hz) 122.5.^{19}F NMR (376 MHz, $CDCl_3$) δ -61.93. APCI *m/z* calc for $C_{14}H_9F_3N_2$ $[M + H – N_2]^+$. 235.1. Found 234.4.

1-chloro-2-(diazo(4-methoxyphenyl)methyl)benzene (3d)

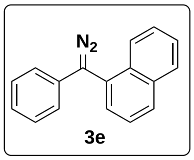


3d

Synthesized according to previous procedures and isolated as a red oil.[16] Spectrum matches previous report. [16]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 5.9 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.27 (m, *J* 2H), 6.96 (d, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 3H), 3.80 (s, 1H).

Phenyl(1-naphthyl)diazomethane (3e)



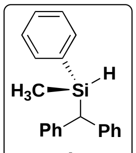
3e

Synthesized according to the general procedure for diazo formation using 1-napthylphenylketone (1.340 g, 5.7 mmol) to give a purple solid that can be isolated in 68% yield (828.9 mg) over 2 steps.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 6.7 Hz, 1H), 7.56 (dt, *J* = 21.5, 7.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.08 (t, *J* = 7.1 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5, 132.2, 131.9, 129.5, 129.3, 129.1, 128.9, 126.8, 126.5, 126.0, 125.6, 125.44, 124.2, 122.7. APCI *m/z* calc for $C_{17}H_{12}N_2$ $[M + H – N_2]^+$. 217.1. Found 216.5.

Insertion Products:

(*S*)-benzhydryl(methyl)(phenyl)silane (4a)

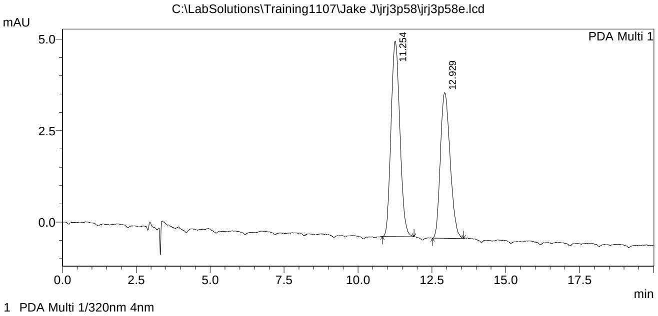


4a

Synthesized using method F with diazo compound **2a** (1.0 mmol, 181.0 mg) in PhMe (20 mL total) to give a white solid in 78% yield (0.78 mmol, 225.0 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® OD-H column (2% IPA/ hexanes), 1.0 mL/min. t$_R$ (**4aa**) = 11.3 min, t$_R$ (**4ab**) = 12.9 min, 82:18 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a.**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 (m, 2H), 7.28 – 7.21 (m, 7H), 7.18 (m, 4H), 7.12 (m, 2H), 4.84 – 4.59 (m, 1H), 3.81 (d, *J* = 3.7 Hz, 1H), 0.30 (d, *J* = 3.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.3, 142.1, 135.0, 134.8, 129.6, 129.1, 129.0, 128.6, 128.5, 127.8, 125.6, 125.6, 43.3, -5.9. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -11.1. MALDI *m/z* calc for C$_{20}$H$_{20}$Si [M + H]$^+$. 289.141. Found 289.153.

Racemic Standard for **4a**:



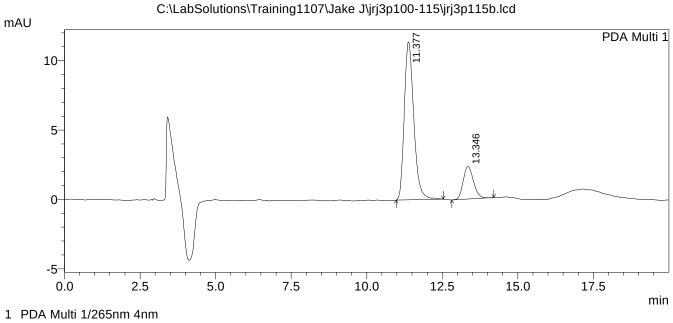
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p58\jrj3p58e.lcd

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.254	111525	5344	54.926	57.328
2	12.929	91520	3978	45.074	42.672
Total		203045	9322	100.000	100.000

Enantiomerically enriched (*S*) **4a** using *S*-TCPTTL:



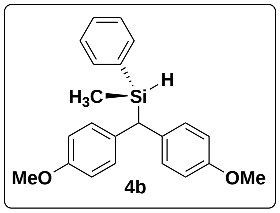
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p100-115\jrj3p115b.lcd

PDA Ch1 265nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.377	249390	11382	81.855	82.869
2	13.346	55284	2353	18.145	17.131
Total		304673	13735	100.000	100.000

(*S*)-(bis(4-methoxyphenyl)methyl)(methyl)(phenyl)silane (4b)



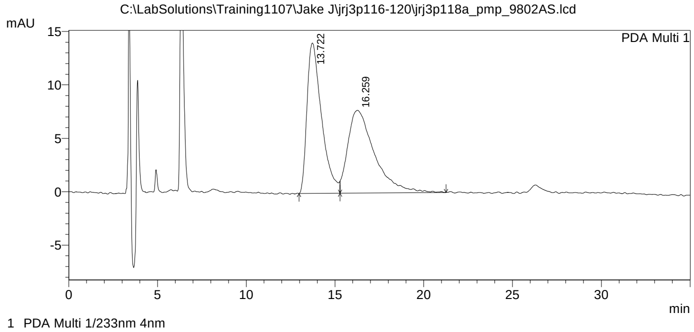
4b

Synthesized using method F with diazo compound **2b** (0.2 mmol, 42.0 mg) to give a white solid in 45% yield (0.09 mmol, 31.3 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AS column (2% IPA/ hexanes), 1.0 mL/min. t_R (**4ba**) = 13.7 min, t_R (**4bb**) = 16.2 min, 81:19 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a**.

^{1}H NMR (600 MHz, C_6D_6) δ 7.41 – 7.36 (m, 2H), 7.17 (m, 2H), 7.15 – 7.09 (m, 5H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 4.96 (p, *J* = 3.6 Hz, 1H), 3.72 (d, *J* = 3.9 Hz, 1H), 3.31 (s, 3H), 3.27 (s, 3H), 0.29 (d, *J* = 3.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 157.5, 135.1, 135.0, 134.8, 134.7, 129.9, 129.8, 129.56, 127.8, 114.0, 113.9, 55.4, 55.3, 40.9, -5.8. Did not ionize using ESI, MALDI or APCI.

Racemic Standard for **4b**:

<Chromatogram>



< Peak Table >

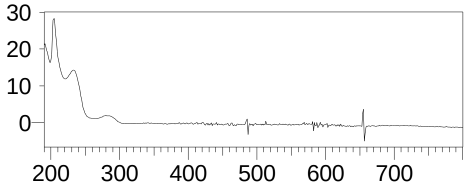
PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p116-120\jrj3p118a_pmp_9802AS.lcd

PDA Ch1 233nm 4nm

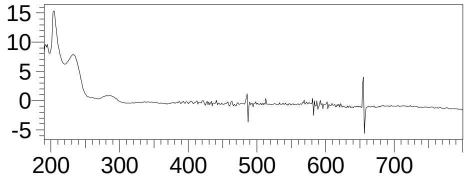
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.722	805317	14077	49.974	64.499
2	16.259	806151	7748	50.026	35.501
Total		1611469	21826	100.000	100.000

Spectrum index for racemic standard of **4b**:

Peak# : 1
Retension Time : 13.722

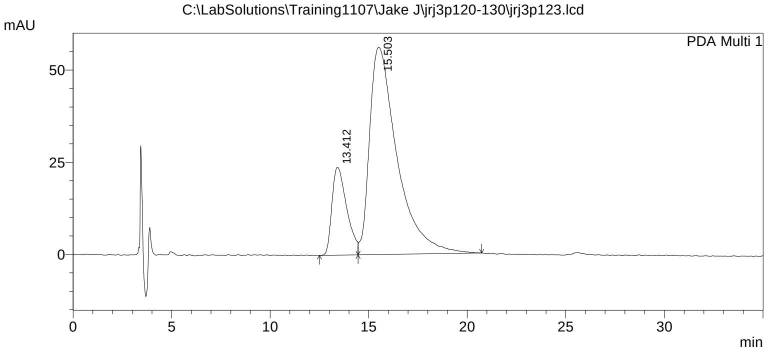


Peak# : 2
Retension Time : 16.259



Enantiomerically enriched (*S*) **4b** using *S*-TCPTTL:

<Chromatogram>



1 PDA Multi 1/233nm 4nm

< Peak Table >

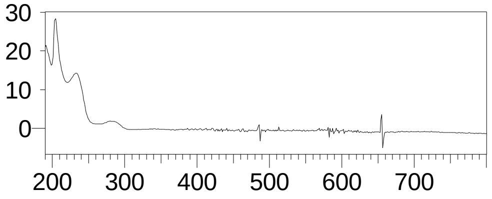
PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p120-130\jrj3p123.lcd

PDA Ch1 233nm 4nm

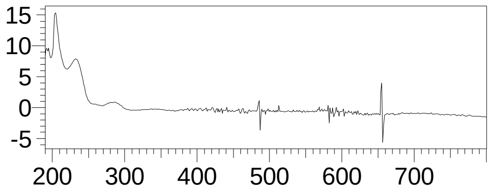
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.412	1249142	23869	18.595	29.783
2	15.503	5468390	56276	81.405	70.217
Total		6717532	80145	100.000	100.000

Spectrum index for enantioenriched sample of **4b**:

Peak# : 1
Retension Time : 13.722

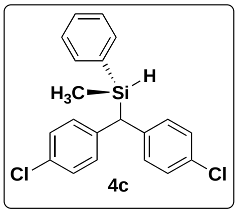


Peak# : 2
Retension Time : 16.259



Spectrum indices between racemic standard and enantioenriched are identical, indicating the peaks are identical despite slightly different retention times.

(*S*)-(bis(4-chlorophenyl)methyl)(methyl)(phenyl)silane (4c)

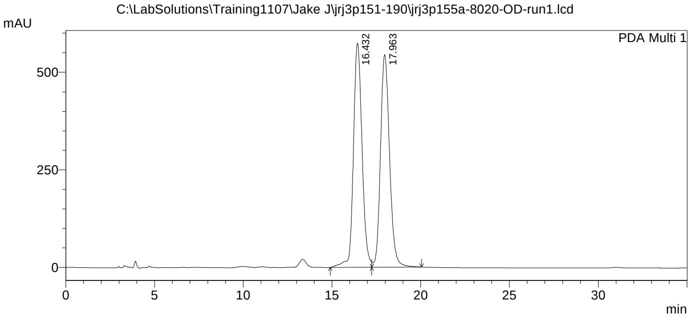


4c

Synthesized using method F with diazo compound **2c** (0.2 mmol, 52.6 mg) to give a white solid in 91% yield (0.158 mmol, 65.7 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® OD-H column (2% IPA/ hexanes), 1.0 mL/min. t_R (**4ca**) = 16.4 min, t_R (**4cb**) = 18.0 min, 74:26 er (Si-OH product). Absolute configuration was assigned to be (*S*, *S)* based on analogy to **5a**.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 1H), 7.30 – 7.25 (m, 4H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 4.67 (p, *J* = 4.5, 4.1 Hz, 1H), 3.75 (d, *J* = 3.7 Hz, 1H), 0.30 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 140.0, 134.8, 133.7, 131.5, 131.4, 130.1, 130.0, 129.9, 128.7, 128.6, 127.9, 41.9, -6.2. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -10.8. MALDI *m/z* calc for $C_{20}H_{18}Cl_2Si$ [M + Na]$^{+}$ 379.045. Found 379.220.

Racemic Standard for **4c**:



1 PDA Multi 1/232nm 4nm

< Peak Table >

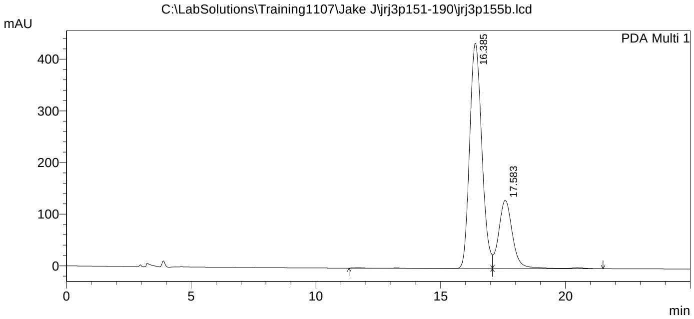
PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p155a-8020-OD-run1.lcd

PDA Ch1 232nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.432	19469494	574519	50.125	51.331
2	17.963	19372708	544721	49.875	48.669
Total		38842201	1119240	100.000	100.000

Enantiomerically enriched (*S*) **4c** using *S*-TCPTTL:

<Chromatogram>



1 PDA Multi 1/232nm 4nm

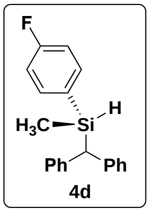
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p155b.lcd

PDA Ch1 232nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.385	14732848	435744	74.301	76.728
2	17.583	5095809	132161	25.699	23.272
Total		19828657	567905	100.000	100.000

(*S*)-benzhydryl(4-fluorophenyl)(methyl)silane (4d)

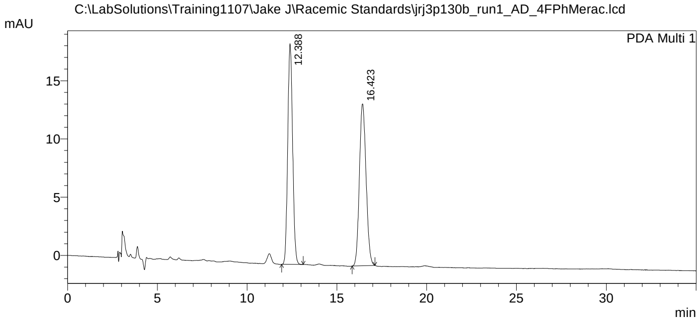


4d

Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 66% yield (0.132 mmol, 40.4 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t_R (**4da**) = 10.2 min, t_R (**4db**) = 12.9 min 80:20 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (dd, *J* = 9.4, 5.8 Hz, 3H), 7.28 – 7.23 (m, 5H), 7.23 – 7.13 (m, 4H), 6.99 (t, *J* = 8.7 Hz, 2H), 4.76 (p, *J* = 3.9 Hz, 1H), 3.82 (d, *J* = 3.9 Hz, 1H), 0.35 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.0 (d, J_{CF} = 249.0 Hz), 141.9, 141.75, 136.8 (d, J_{CCCF} = 7.4 Hz), 130.1 (d, J_{CCCCF} = 3.9 Hz), 128.9, 128.8, 128.6, 128.4, 125.6, 125.6, 115.0 (d, J_{CCF} = 19.8 Hz), 43.2, -5.9. ^{19}F NMR (376 MHz, CDCl$_3$) δ -110.96. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -11.1. MALDI *m/z* calc for $C_{20}H_{19}FSi$ [M + Na]$^+$ 329.113. Found 329.158.

Racemic Standard for **4d**:



1 PDA Multi 1/265nm 4nm

< Peak Table >

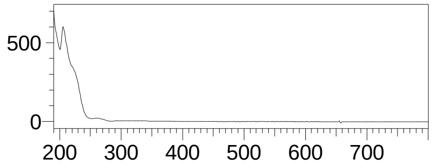
PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p130b_run1_AD_4FPhMerac.lcd

PDA Ch1 265nm 4nm

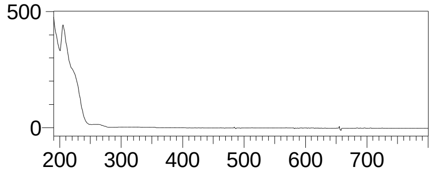
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.388	358819	18961	49.906	57.700
2	16.423	360171	13901	50.094	42.300
Total		718991	32862	100.000	100.000

Spectrum index for racemic standard of **4d**:

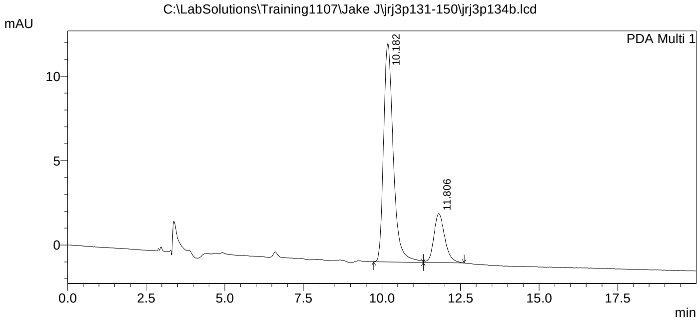
Peak# : 1
Retension Time : 12.388



Peak# : 2
Retension Time : 16.423



Enantiomerically enriched (*S*) **4d** using *S*-TCPTTL:



1 PDA Multi 1/254nm 4nm

< Peak Table >

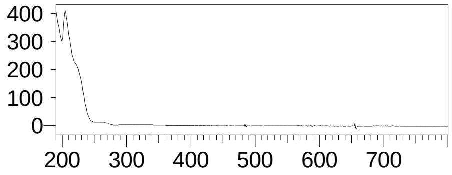
PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p131-150\jrj3p134b.lcd

PDA Ch1 254nm 4nm

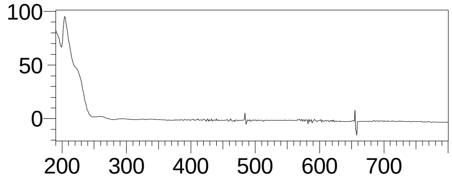
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.182	278783	12928	79.816	81.628
2	11.806	70500	2910	20.184	18.372
Total		349283	15838	100.000	100.000

Spectrum index for enantioenriched sample of **4d**:

Peak# : 1
Retension Time : 10.182

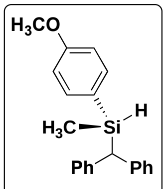


Peak# : 2
Retension Time : 11.806



Spectrum indices between racemic standard and enantioenriched are identical, indicating the peaks are identical despite slightly different retention times.

(*S*)-benzhydryl(4-methoxyphenyl)(methyl)silane (4e)

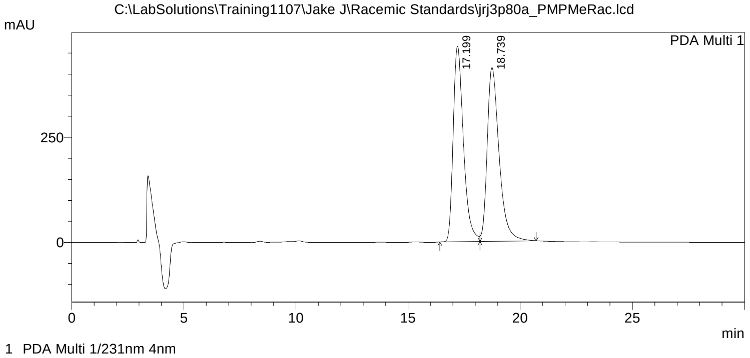


4e

Synthesized using method F with diazo compound **2a** (0.2 mmol, 42.0 mg) to give a white solid in 72% yield (0.144 mmol, 45.9 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® OD-H column (1% IPA/ hexanes), 1.0 mL/min. t$_R$ (**4ea**) = 17.2, t$_R$ (**4eb**) = 18.7, 50:50 er (Si-OH product). Absolute configuration was assigned to be (*S*, *S)* based on analogy to **5a**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.31 – 7.08 (m, 13H), 6.81 (d, *J* = 8.5 Hz, 2H), 4.70 (p, *J* = 3.7 Hz, 1H), 3.79 (d, *J* = 1.6 Hz, 4H), 0.28 (d, *J* = 3.6 Hz, 3H).^{13}C NMR (151 MHz, CDCl$_3$) δ 160.7, 142.3, 142.0, 141.4, 136.8, 136.3, 129.0, 128.8, 125.4, 125.3, 113.5, 113.1, 55.7, 43.4, -7.3. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -11.6. MALDI *m/z* calc for C$_{21}$H$_{22}$OSi [M + H]$^+$ 319.151. Found 319.245.

Racemic Standard for **4e**:

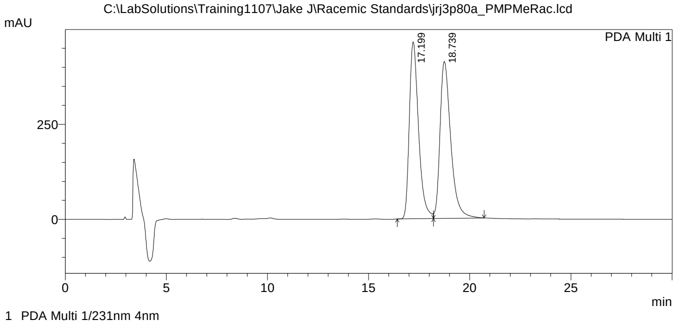


< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p80a_PMPMeRac.lcd
PDA Ch1 231nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.199	14775321	465125	49.202	52.976
2	18.739	15254421	412863	50.798	47.024
Total		30029742	877988	100.000	100.000

HPLC trace of **4e** using *S*-TCPTTL:

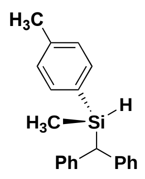


< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p80a_PMPMeRac.lcd
PDA Ch1 231nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.199	14775321	465125	49.202	52.976
2	18.739	15254421	412863	50.798	47.024
Total		30029742	877988	100.000	100.000

(*S*)-benzhydryl(4-methylphenyl)(methyl)silane (4f)

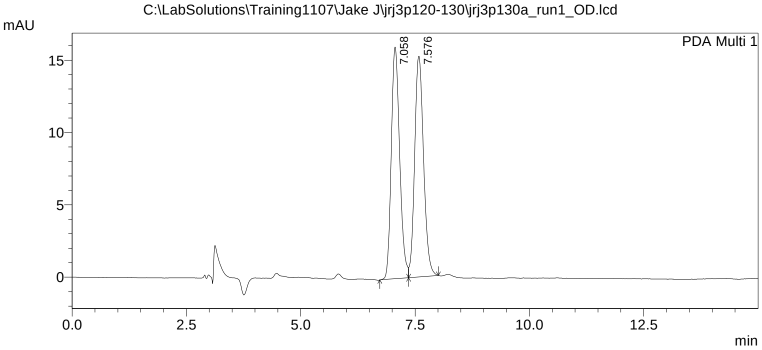


4f

Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 76% yield (0.152 mmol, 46.0 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t$_R$ (**4fa**) = 9.9 min, t$_R$ (**4fb**) = 10.7 min, 74:26 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.31 – 7.24 (m, 5H), 7.22 (dd, *J* = 8.8, 2.4 Hz, 5H), 7.20 – 7.12 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 4.73 (p, *J* = 3.8 Hz, 1H), 3.83 (d, *J* = 3.9 Hz, 1H), 2.34 (s, 3H), 0.31 (d, *J* = 3.7 Hz, 3H).^{13}C NMR (151 MHz, CDCl$_3$) δ 142.4, 142.2, 139.5, 135.1, 131.0, 129.1, 129.0, 128.7, 128.6, 128.5, 125.5, 44.2, 22.1, -5.8. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -11.3. MALDI *m/z* calc for $C_{21}H_{22}Si$ [M + H]$^+$ 328.138. Found 325.207.

Racemic Standard for **4f**:



1 PDA Multi 1/254nm 4nm

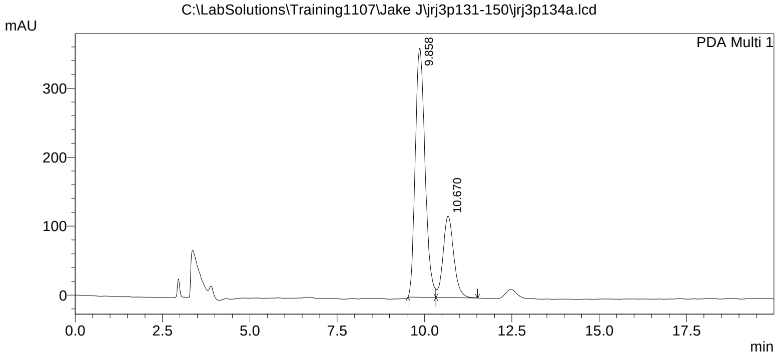
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p120-130\jrj3p130a_run1_OD.lcd

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.058	205950	16014	49.944	51.207
2	7.576	206416	15259	50.056	48.793
Total		412367	31273	100.000	100.000

Enantiomerically enriched (*S*) **4f** using *S*-TCPTTL:



1 PDA Multi 1/205nm 4nm

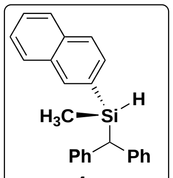
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p131-150\jrj3p134a.lcd

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.858	7044481	361590	73.577	75.312
2	10.670	2529844	118530	26.423	24.688
Total		9574324	480120	100.000	100.000

(*S*)-benzhydryl(methyl)(naphthalen-2-yl)silane (4g)

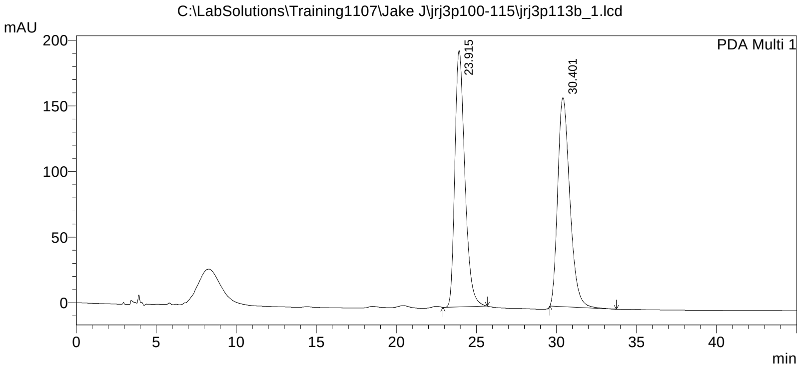


4g

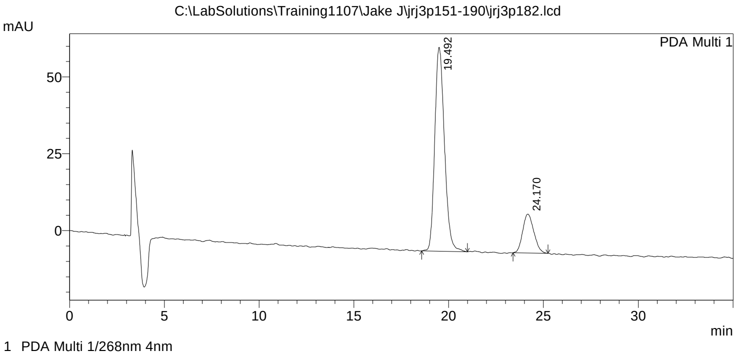
Synthesized according to the general procedure for enantioselective donor/donor insertion using **2a** (0.2 mmol, 38.8 mg) to give a white solid in 69% yield (0.158 mmol, 46.7 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (1% IPA/ hexanes), 1.0 mL/min. t_R (**4ga**) = 19.5 min, t_R (**4gb**) = 24.2 min, 82:18 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a**.

^{1}H NMR (600 MHz, C_6D_6)δ 7.86 (s, 1H), 7.61 – 7.49 (m, 3H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.18 (m, 6H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.04 (dt, *J* = 13.7, 7.4 Hz, 3H), 6.97 (t, *J* = 7.3 Hz, 1H), 5.04 (p, *J* = 3.6 Hz, 1H), 3.83 (d, *J* = 3.8 Hz, 1H), 0.32 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 142.0, 136.1, 134.0, 132.9, 132.3, 130.9, 129.1, 129.0, 128.66, 128.5, 128.2, 127.8, 127.0, 126.7, 126.0, 125.7, 125.6, 43.3, -5.7. ^{29}Si NMR (119 MHz, C_6D_6) δ -10.9 MALDI *m/z* calc for $C_{24}H_{22}Si$ $[M + Na]^+$ 361.1383. Found 363.1318.

Racemic Standard for **4g**:



Enantiomerically enriched (*S*) **4g** using *S*-TCPTTL:



1 PDA Multi 1/268nm 4nm

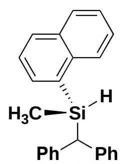
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p182.lcd

PDA Ch1 268nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.492	2360689	66341	82.092	83.988
2	24.170	514989	12648	17.908	16.012
Total		2875678	78989	100.000	100.000

(*S*)-benzhydryl(methyl)(naphthalen-1-yl)silane (4h)

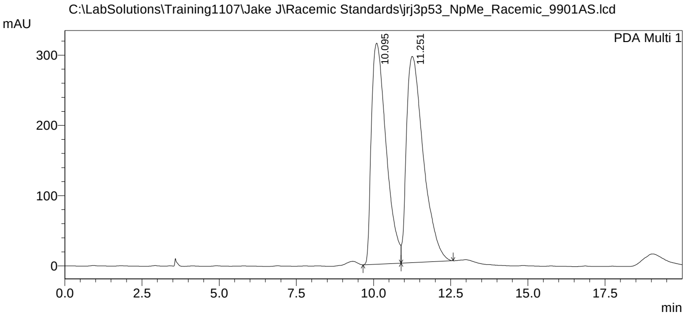


4h

Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 60% yield (0.12 mmol, 40.6 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (1% IPA/ hexanes), 1.0 mL/min. t_R (**4ha**) = 10.1 min, t_R (**4hb**) = 11.2 min, 77:23 er (Si-OH product). Absolute configuration was assigned to be (*S*, *S)* based on analogy to **5a.**

^{1}H NMR (600 MHz, C_6D_6) δ 8.08 – 8.01 (m, 1H), 7.63 – 7.58 (m, 2H), 7.54 – 7.49 (m, 1H), 7.25 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 4H), 7.14 (s, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 7.03 – 6.96 (m, 3H), 6.91 (t, *J* = 7.3 Hz, 1H), 5.33 (p, *J* = 3.6 Hz, 1H), 4.05 (d, *J* = 4.0 Hz, 1H), 0.36 (d, *J* = 3.7 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 142.2, 137.1, 135.2, 133.3, 133.3, 130.4, 129.0, 129.0, 128.6, 128.4, 127.8, 126.0, 125.6, 125.5, 125.1, 43.1, -5.0. ^{29}Si NMR (79 MHz, $CDCl_3$) δ -15.6. MALDI *m/z* calc for $C_{24}H_{22}Si$ $[M + Na]^+$ 361.1383. Found 361.1446.

Racemic Standard for **4h**:



1 PDA Multi 1/284nm 4nm

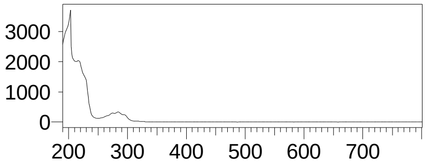
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p53_NpMe_Racemic_9901AS.lcd
PDA Ch1 284nm 4nm

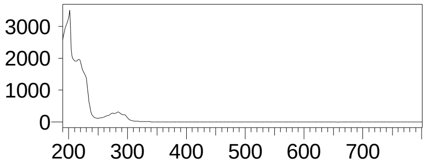
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.095	10468276	314759	48.236	51.733
2	11.251	11233883	293668	51.764	48.267
Total		21702159	608427	100.000	100.000

Spectrum index for racemic standard of **4h**:

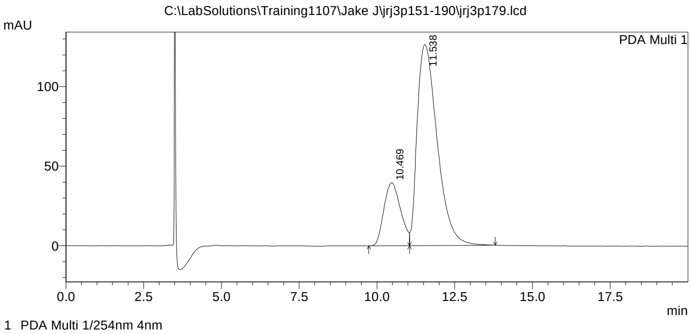
Peak# : 1
Retension Time : 10.095



Peak# : 2
Retension Time : 11.251



Enantiomerically enriched (*S*) **4h** using *S*-TCPTTL:



< Peak Table >

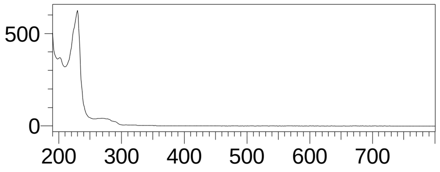
PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p179.lcd

PDA Ch1 254nm 4nm

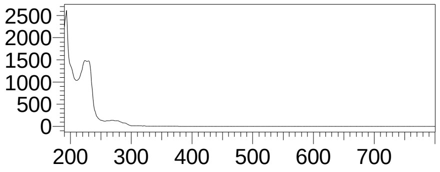
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.469	1482658	39621	20.760	23.884
2	11.538	5659377	126271	79.240	76.116
Total		7142035	165892	100.000	100.000

Spectrum index for enantioenriched sample of **4h**:

Peak# : 1
Retension Time : 10.469

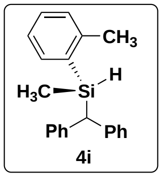


Peak# : 2
Retension Time : 11.538



Spectrum indices between racemic standard and enantioenriched are identical, indicating the peaks are identical despite slightly different retention times.

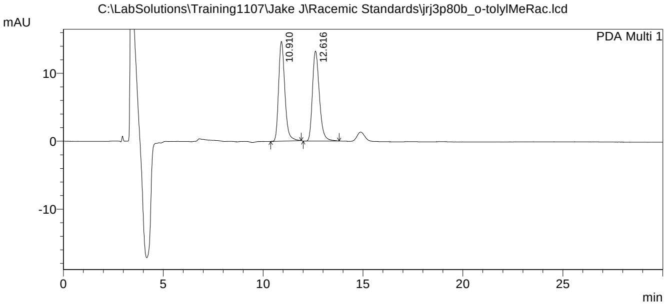
(*S*)-benzhydryl(2-methylphenyl)(methyl)silane (4i)



Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 55% yield (0.110 mmol, 33.2 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® OD-H column (1% IPA/ hexanes), 1.0 mL/min. t$_R$ (**4ia**) = 10.9 min, t$_R$ (**4ib**) = 12.6 min, 69:31 er (Si-OH product). Absolute configuration was assigned to be (*S*, *S)* based on analogy to **5a.**

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.34 (m, 1H), 7.27 (m, 1H), 7.25 – 7.21 (m, 4H), 7.15 (m, 5H), 7.11 – 7.04 (m, 3H), 4.82 (p, *J* = 3.7 Hz, 1H), 3.86 (d, *J* = 4.3 Hz, 1H), 2.17 (s, 3H), 0.28 (d, *J* = 3.7 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 144.3, 142.4, 142.3, 135.6, 133.8, 129.8, 129.7, 129.1, 128.8, 128.6, 128.4, 125.6, 125.5, 125.0, 43.2, 22.6, -5.4. ^{29}Si NMR (119 MHz, CDCl$_3$) δ -13.7 MALDI *m/z* calc for $C_{21}H_{22}Si$ [M + H]$^+$ 328.138. Found 325.227.

Racemic Standard for **4i**:



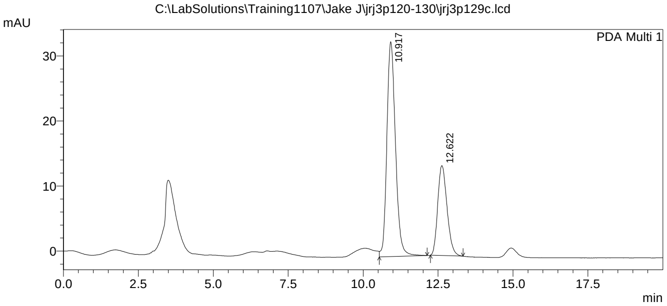
1 PDA Multi 1/254nm 4nm

< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p80b_o-tolylMeRac.lcd
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.910	318494	14704	50.034	52.599
2	12.616	318058	13251	49.966	47.401
Total		636552	27956	100.000	100.000

Enantiomerically enriched (*S*,*S*) **4i** using *S*-TCPTTL:



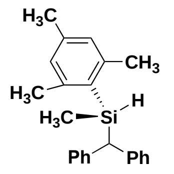
1 PDA Multi 1/254nm 4nm

< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p120-130\jrj3p129c.lcd
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.917	660519	33039	68.790	70.490
2	12.622	299672	13831	31.210	29.510
Total		960191	46870	100.000	100.000

(*S*)-benzhydryl(mesityl)(methyl)silane (4j)

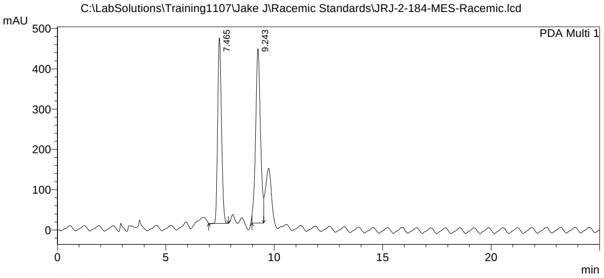


4j

Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 64% yield (0.128 mmol, 42.3 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® OD-H column (2% IPA/ hexaness), 1.0 mL/min. t$_R$ (**4ja**) = 6.8 min, t$_R$ (**4jb**) = 8.6 min, 60:40 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a.**

^{1}H NMR (400 MHz, CDCl$_3$)δ 7.31 (m, 3H), 7.28 – 7.13 (m, 2H), 7.10 (d, *J* = 4.7 Hz, 4H), 7.04 (m, 1H), 6.75 (s, 2H), 4.94 (p, *J* = 4.3 Hz, 1H), 3.92 (d, *J* = 5.4 Hz, 1H), 2.24 (s, 9H), 0.29 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.7, 142.7, 142.4, 139.4, 129.3, 129.1, 128.7, 128.6, 128.4, 128.3, 125.7, 125.3, 43.4, 24.1, 21.2, -3.7. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -18.0. MALDI *m/z* calc for $C_{23}H_{26}Si$ [M + Na]$^+$ 353.170. Found 353.248.

Racemic Standard for **4j**:



1 PDA Multi 1/207nm 4nm

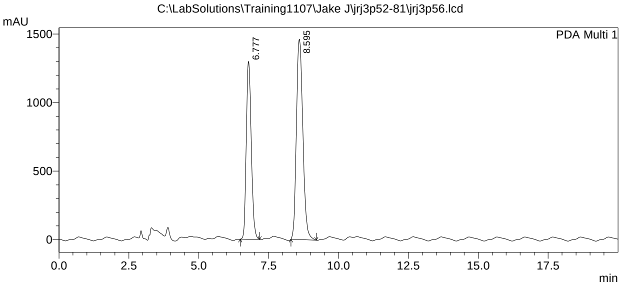
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\JRJ-2-184-MES-Racemic.lcd

PDA Ch1 207nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.465	5633456	460567	45.645	51.548
2	9.243	6708400	432898	54.355	48.452
Total		12341856	893465	100.000	100.000

Enantiomerically enriched (*S*,*S*) **4j** using *S*-TCPTTL:



1 PDA Multi 1/207nm 4nm

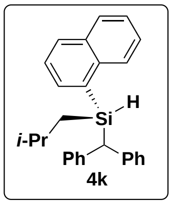
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p52-81\jrj3p56.lcd

PDA Ch1 207nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.777	16197961	1298528	40.801	47.019
2	8.595	23502137	1463158	59.199	52.981
Total		39700098	2761686	100.000	100.000

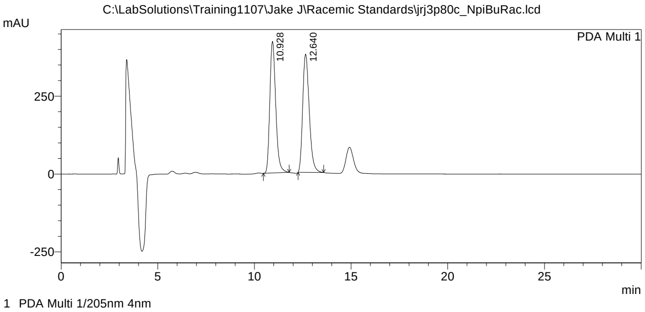
(*S*)-benzhydryl(isobutyl)(naphthalen-1-yl)silane (4k)



Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 60% yield (0.120 mmol, 41.3 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (1% IPA/ hexanes), 1.0 mL/min. t_R (**4ka**) = 10.9 min, t_R (**4kb**) = 12.6 min, 82:18 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.83 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.59 (dd, *J* = 6.7, 1.2 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.40 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.36 (td, *J* = 7.3, 6.7, 1.2 Hz, 1H), 7.30 – 7.26 (m, 5H), 7.26 – 7.23 (m, 1H), 7.17 (ddd, *J* = 8.5, 5.1, 1.8 Hz, 1H), 7.09 (d, *J* = 6.8 Hz, 2H), 7.07-7.03 (m 2H), 7.00 (td, *J* = 6.9, 1.4 Hz, 1H), 5.11 (td, *J* = 5.0, 2.2 Hz, 1H), 4.04 (d, *J* = 4.5 Hz, 1H), 1.59 (ddt, *J* = 12.9, 7.7, 6.5 Hz, 1H), 1.03 (dt, *J* = 14.8, 5.8 Hz, 1H), 0.89 (dtd, *J* = 14.3, 7.1, 6.4, 2.3 Hz, 1H), 0.82 (t, *J* = 6.3 Hz, 7H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 142.4, 142.4, 137.3, 135.9, 133.3, 132.8, 130.3, 129.2, 129.0, 128.8, 128.6, 128.3, 127.9, 125.9, 125.7, 125.5, 125.3, 125.1, 41.4, 26.2, 25.5, 25.4, 22.5. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -9.5. MALDI *m/z* calc for $C_{27}H_{28}Si$ $[M - H]^+$ 379.1877. Found 379.220.

Racemic Standard for **4k**:



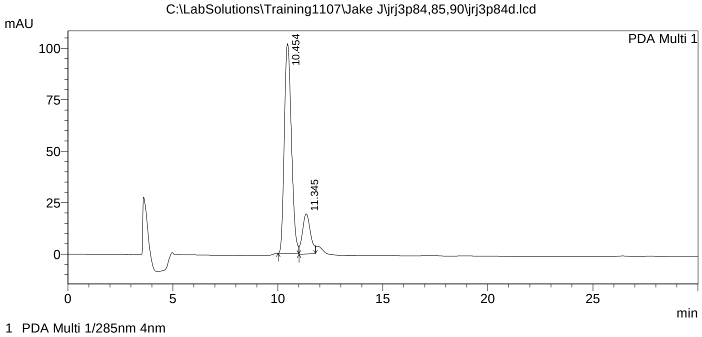
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p80c_NpiBuRac.lcd

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.928	8992685	422849	50.155	52.701
2	12.640	8937207	379512	49.845	47.299
Total		17929892	802361	100.000	100.000

Enantiomerically enriched (*S*,*S*) **4k** using *S*-TCPTTL:



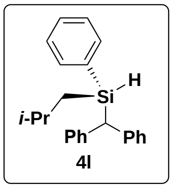
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p84,85,90\jrj3p84d.lcd

PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.454	2402971	101957	82.469	83.984
2	11.345	510822	19444	17.531	16.016
Total		2913793	121400	100.000	100.000

(*S*)-benzhydryl(isobutyl)(phenyl)silane (4l)



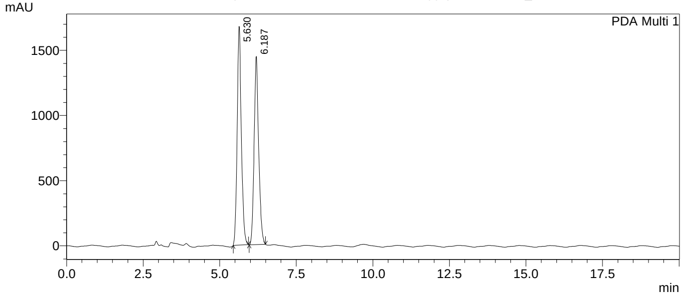
4l

Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) and isobutylphenylsilane (164.3 mg) to give a white solid in 45% yield (0.090 mmol, 29.7 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® OD-H column (1% IPA/ hexanes), 1.0 mL/min. t_R (**4la**) = 5.6 min, t_R (**4lb**) = 6.2 min, 86:14 er (Si-OH product). Absolute configuration was assigned to be (*S*, *S)* based on analogy to **5a.**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.31 (m, 3H), 7.29 (d, *J* = 5.5 Hz, 6H), 7.25 – 7.15 (m, 5H), 7.12 (t, *J* = 6.8 Hz, 1H), 4.74 (h, *J* = 2.2 Hz, 1H), 3.86 (d, *J* = 3.9 Hz, 1H), 1.68 (dh, *J* = 12.5, 6.3 Hz, 1H), 0.93 (d, *J* = 5.9 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.80 (dd, *J* = 14.7, 7.7 Hz, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 142.4, 142.2, 135.4, 134.3, 129.5, 129.1, 129.0, 128.6, 128.4, 127.8, 125.6, 125.4, 42.8, 26.1, 25.5, 25.2, 21.7. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -8.7. Did not ionize using ESI-MS or MALDI-TOF.

Racemic Standard for **4l**:

C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p49a-racemic_iBuPh.lcd



1 PDA Multi 1/195nm 4nm

< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\Racemic Standards\jrj3p49a-racemic_iBuPh.lcd

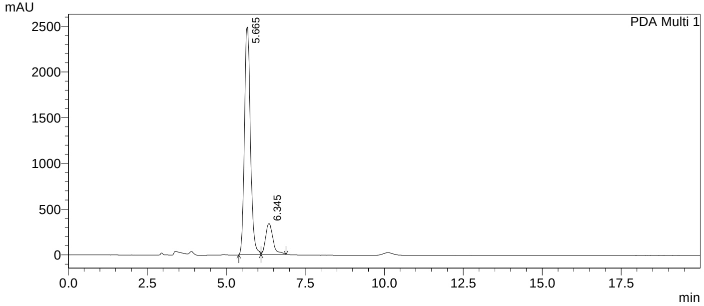
PDA Ch1 195nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.630	15800629	1676986	51.577	53.732
2	6.187	14834414	1444032	48.423	46.268
Total		30635043	3121017	100.000	100.000

Enantiomerically enriched (*S*) **4l** using *S*-TCPTTL:

<Chromatogram>

C:\LabSolutions\Training1107\Jake J\jrj3p120-130\jrj3p128.lcd



1 PDA Multi 1/194nm 4nm

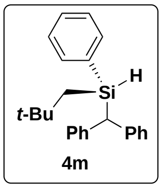
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p120-130\jrj3p128.lcd

PDA Ch1 194nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.665	32779438	2487817	85.694	88.076
2	6.345	5472326	336794	14.306	11.924
Total		38251764	2824612	100.000	100.000

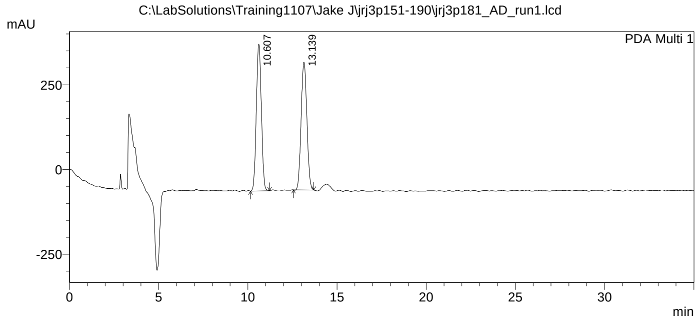
(*S*)-benzhydryl(neopentyl)(phenyl)silane (4m)



Synthesized using method F with diazo compound **2a** (0.2 mmol, 42.0 mg) to give a white solid in 60% yield (0.120 mmol, 41.3 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (1% IPA/ heptane), 1.0 mL/min. t$_R$ (**4ma**) = 10.6 min, t$_R$ (**4mb**) = 13.1 min, 50:50 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a**.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.30 (m, 3H), 7.30 – 7.21 (m, 6H), 7.18 (t, *J* = 6.8 Hz, 3H), 7.15 – 7.04 (m, 3H), 4.81 (t, *J* = 4.7 Hz, 1H), 3.80 (d, *J* = 4.0 Hz, 1H), 1.08 (dd, *J* = 14.7, 5.4 Hz, 1H), 0.93 (s, 1H), 0.89 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.4, 142.2, 135.4, 135.3, 129.4, 129.3, 128.9, 128.6, 128.3, 127.7, 125.6, 125.3, 43.3, 32.5, 30.6, 27.45. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -11.1. Did not ionize using ESI, MALDI or APCI.

Racemic Standard for **4m**:



1 PDA Multi 1/205nm 4nm

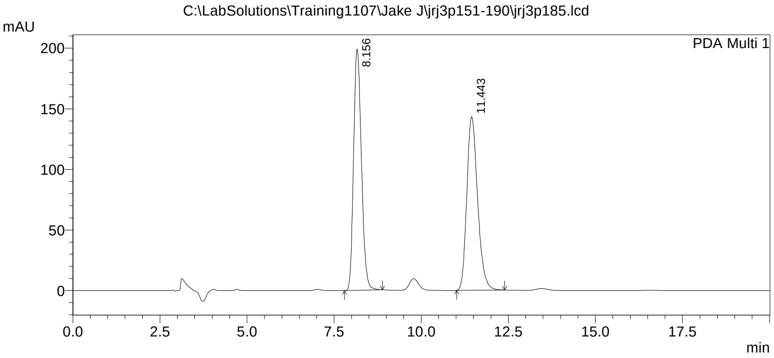
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p181_AD_run1.lcd

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.607	8549235	433259	50.265	53.471
2	13.139	8459167	377007	49.735	46.529
Total		17008402	810266	100.000	100.000

Enantiomerically enriched (*S*) **4m** using *S*-TCPTTL:



1 PDA Multi 1/285nm 4nm

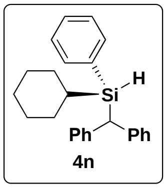
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p185.lcd

PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.156	3118650	199177	50.230	58.155
2	11.443	3090035	143318	49.770	41.845
Total		6208685	342495	100.000	100.000

(*S*)-benzhydryl(cyclohexyl)(phenyl)silane (4n)

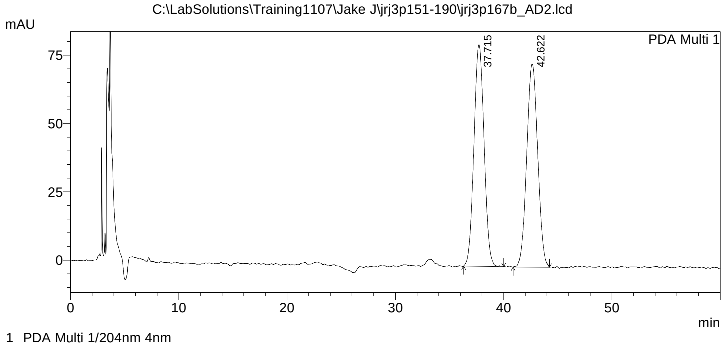


4n

Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 77% yield (0.158 mmol, 54.9 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t_R (**4na**) = 37.7 min, t_R (**4nb**) = 42.6 min, 70:30 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a.**

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.34 – 7.27 (m, 6H), 7.27 – 7.20 (m, 4H), 7.19 – 7.10 (m, 5H), 7.07 – 7.01 (m, 1H), 4.48 (dd, *J* = 4.5, 2.9 Hz, 1H), 3.96 (d, *J* = 4.4 Hz, 1H), 1.72 – 1.62 (m, 1H), 1.65 – 1.55 (m, 4H), 1.17 – 1.01 (m, 5H), 1.00 – 0.90 (m, 1H).NMR (151 MHz, CDCl$_3$) δ 142.6, 142.3, 135.8, 133.2, 129.4, 129.2, 129.0, 128.6, 128.4, 127.7, 125.7, 125.4, 40.5, 28.5, 28.1, 27.8, 26.8, 22.9. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -2.8. MALDI *m/z* calc for $C_{25}H_{28}Si$ [M + Na]$^+$ 379.185. Found 379.140.

Racemic Standard for **4n**:



< Peak Table >

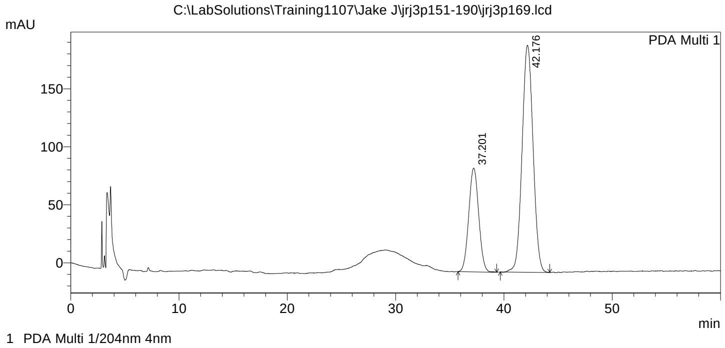
PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p167b_AD2.lcd

PDA Ch1 204nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.715	5281022	81077	50.124	52.165
2	42.622	5254858	74346	49.876	47.835
Total		10535880	155423	100.000	100.000

Enantiomerically enriched (*S*,*S*) **4n** using *S*-TCPTTL:

<Chromatogram>



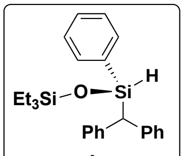
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p151-190\jrj3p169.lcd

PDA Ch1 204nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.201	5726477	89443	29.288	31.364
2	42.176	13826155	195731	70.712	68.636
Total		19552632	285174	100.000	100.000

(*S*)-3-benzhydryl-1,1,1-triethyl-3-phenyldisiloxane (4o)



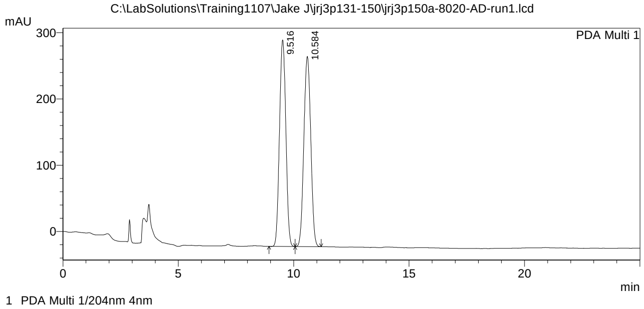
4o

Synthesized using method F with diazo compound **2a** (0.2 mmol, 38.8 mg) to give a white solid in 60% yield (0.120 mmol, 41.3 mg). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t_R (**4oa**) = 9.5 min, t_R (**4ob**) = 10.6 min, 61:39 er (Si-OH product). Absolute configuration was assigned to be (*S)* based on analogy to **5a**.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.37 – 7.31 (m, 1H), 7.31 – 7.25 (m, 8H), 7.25 – 7.20 (m, 3H), 7.20 – 7.09 (m, 3H), 5.30 (d, *J* = 2.6 Hz, 1H), 3.80 (d, *J* = 2.6 Hz, 1H), 0.80 (t, *J* = 8.0 Hz, 6H), 0.41 (q, *J* = 7.7 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 141.1, 141.0, 135.5, 134.1, 130.0, 129.5, 129.1, 128.5, 128.5, 127.7, 125.7, 125.6, 44.4, 6.7, 6.0. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -14.5, -18.4/ Did not ionize using ESI, MALDI or APCI.

Racemic Standard for **4o**:

<Chromatogram>



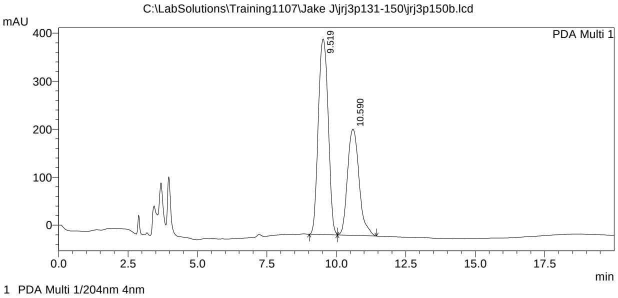
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p131-150\jrj3p150a-8020-AD-run1.lcd

PDA Ch1 204nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.516	5973920	311973	49.931	52.058
2	10.584	5990388	287304	50.069	47.942
Total		11964308	599277	100.000	100.000

Enantiomerically enriched (*S*,*S*) **4o** using *S*-TCPTTL:



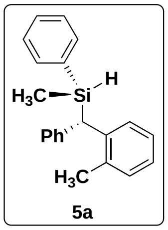
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj3p131-150\jrj3p150b.lcd

PDA Ch1 204nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.519	10084552	407338	61.079	64.804
2	10.590	6426044	221227	38.921	35.196
Total		16510595	628565	100.000	100.000

(*S*)-methyl(phenyl)((*S*)-phenyl(*o*-tolyl)methyl)silane (5a):

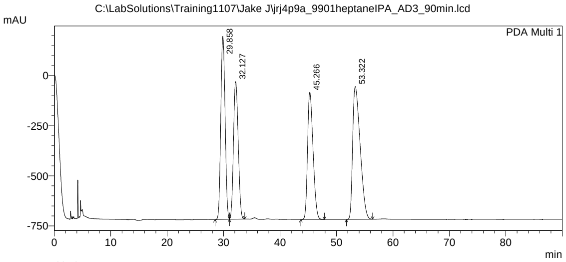


5a

Synthesized using method G with Diazo compound **3a** (5.1 mmol, 1.00 g) to give a clear oil in 89% yield (93:7 dr, 1.34 g, 4.5 mmol). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (1% IPA/ heptane), 1.0 mL/min. t$_R$ (**5aa**) = 29.9 min, t$_R$ (**5ab**) = 32.1 min, t$_R$ (**5aa'**) = 45.3 min, t$_R$ (**5ab'**) = 53.3 min, 93:7 er (Si-OH product, **5ab**:**5ab'**). Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5e** and **11**.

^{1}H NMR (600 MHz, CDCl$_3$)) δ 7.45 – 7.04 (m, 14H), 4.72 (q, *J* = 3.6 Hz, 3H), 3.96 (d, *J* = 4.0 Hz, 1H), 2.21 (s, 3H), 0.33 (d, *J* = 3.6 Hz, 3H).^{13}C NMR (151 MHz, CDCl$_3$) δ 142.0, 140.5, 137.0, 135.1, 135.0, 139.0, 129.7, 129.6, 128.9, 128.3, 127.8, 126.1, 125.9, 125.2, 38.7, 20.3, -5.6. ^{29}Si NMR (119 MHz, CDCl$_3$) δ -10.2. MALDI *m/z* calc for $C_{21}H_{22}Si$ $[M + H]^+$ 303.156. Found 303.154.

Racemic Standard for **5a**:



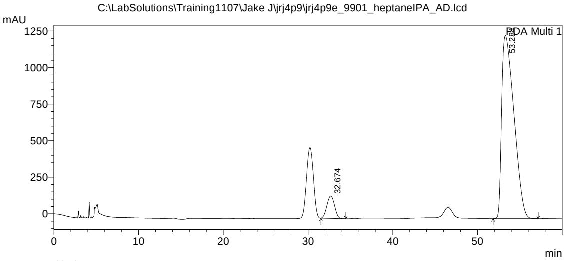
1 PDA Multi 1/208nm 4nm

< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p9a_9901heptaneIPA_AD3_90min.lcd
PDA Ch1 208nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.858	48239523	914305	25.085	31.533
2	32.127	40004513	687079	20.802	23.696
3	45.266	42953904	635333	22.336	21.912
4	53.322	61108498	662816	31.777	22.859
Total		192306438	2899533	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5a** using *S*-TCPTTL:



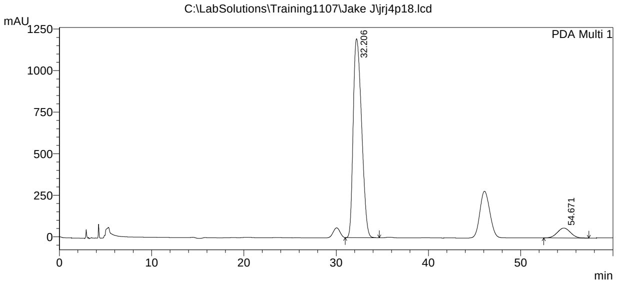
1 PDA Multi 1/205nm 4nm

< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p9\jrj4p9e_9901_heptaneIPA_AD.lcd
PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.674	9589040	153329	7.062	10.913
2	53.284	126202061	1251634	92.938	89.087
Total		135791101	1404963	100.000	100.000

Enantiomerically enriched (*R*,*R*) **5a** using *R*-TCPTTL:



1 PDA Multi 1/205nm 4nm

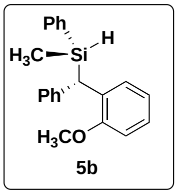
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p18.lcd

PDA Ch1 205nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.206	75751446	1197113	92.871	95.280
2	54.671	5815274	59299	7.129	4.720
Total		81566720	1256412	100.000	100.000

(*S*)-((*S*)-(2-methoxyphenyl)(phenyl)methyl)(methyl)(phenyl)silane (5b):

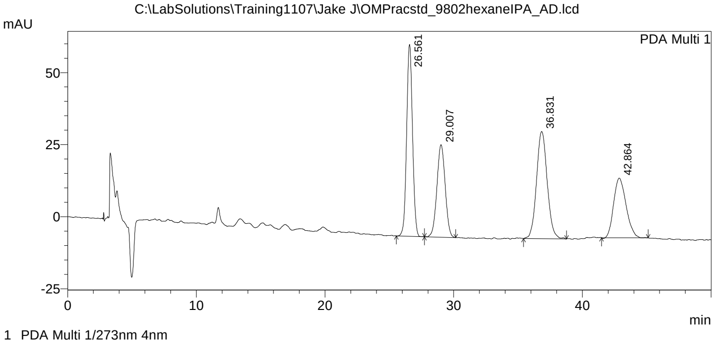


5b

Synthesized using method F with diazo compound **3b** (0.2 mmol, 48.9 mg) to give a clear solid in 91% yield (0.182 mmol, 58.0 mg, 90:10 dr). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t$_R$ (**5ba**) = 26.6 min, t$_R$ (**5bb**) = 29.0 min, t$_R$ (**5ba'**) = 36.8 min, t$_R$ (**5bb'**) = 42.9 min, 95:5 er (Si-OH product, **5ba'**:**5ba**) Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5a.**

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.24 (dt, *J* = 11.6, 5.4 Hz, 3H), 7.19 – 7.11 (m, 5H), 7.09 – 7.05 (m, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.70 – 4.66 (m, 1H), 4.26 (d, *J* = 3.5 Hz, 1H), 3.72 (s, 3H), 0.25 (d, *J* = 3.4 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 156.9, 142.5, 136.0, 134.9, 131.0, 130.2, 129.3, 129.2, 128.3, 127.7, 126.8, 125.2, 120.7, 110.6, 55.3, 35.3, -5.7.^{29}Si NMR (76 MHz, CDCl$_3$) δ -12.5. ESI-MS *m/z* calc for $C_{21}H_{22}O_2Si$ (Si–OH) [M - H]$^-$ 333.1316. Found: 333.1304.

Racemic Standard for **5b**:



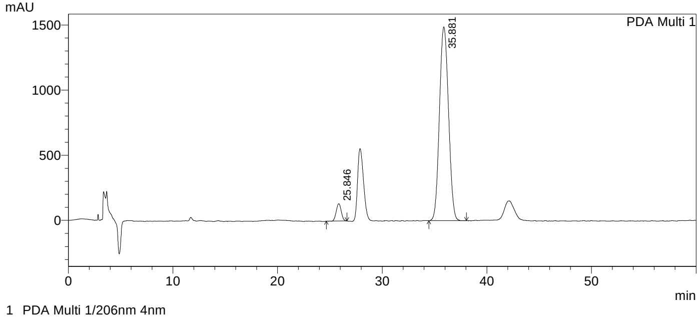
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\OMPracstd_9802hexaneIPA_AD.lcd

PDA Ch1 273nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.561	2108170	66513	29.761	42.517
2	29.007	1436247	32070	20.275	20.500
3	36.831	2148115	37141	30.325	23.741
4	42.864	1391142	20716	19.639	13.242
Total		7083674	156439	100.000	100.000

Enantiomerically enriched (*S,S*) **5b** using *S*-TCPTTL:



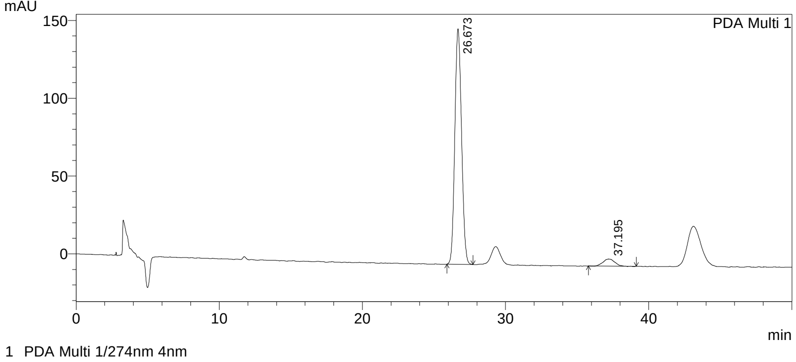
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p84_9802hexaneIPA_AD.lcd

PDA Ch1 206nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.846	4372963	132933	4.655	8.202
2	35.881	89566615	1487798	95.345	91.798
Total		93939577	1620731	100.000	100.000

Enantiomerically enriched (*R*,*R*) **5b** using *R*-TCPTTL:



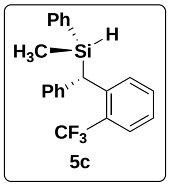
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p87_9802HexIPA_AD.lcd

PDA Ch1 274nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.673	4936920	151331	95.059	97.064
2	37.195	256588	4577	4.941	2.936
Total		5193508	155909	100.000	100.000

(*S*)-methyl(phenyl)((*S*)-phenyl(2-(trifluoromethyl)phenyl)methyl)silane (5c):

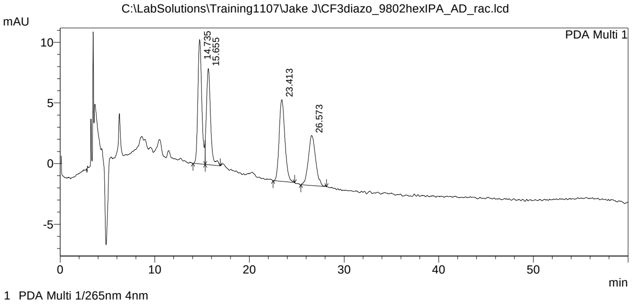


5c

Synthesized using method F with diazo compound **3c** (0.2 mmol, 42.0 mg) to give a white solid in 93% yield (0.186 mmol, 66.3 mg, 98:2 dr (determined using ^{19}F NMR). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t_R (**5ca**) = 14.7 min, t_R (**5cb**) = 15.7 min, t_R (**5cb’**) = 23.4 min, t_R (**5ca’**) = 26.6 min, 93:7 er (Si-OH product, **5cb’**:**5cb**) Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5a.**

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.63 (dd, *J* = 12.3, 7.9 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 3H), 7.29 – 7.22 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 4.76 (p, *J* = 4.0 Hz, 1H), 4.22 (d, *J* = 4.7 Hz, 1H), 0.20 (d, *J* = 3.7 Hz, 4H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 141.7,141.7, 141.4, 134.9, 134.3, 131.9, 131.4, 129.8, 128.8, 128.5, 128.5 (q, J_{CCCF} = 7.0 Hz),128.3, 128.1 (q, J_{CCF} = 36.0 Hz), 127.9, 126.4 (q, J_{CCF} = 5.9 Hz, 125.8, 125.7, 124.8 (q, J_{CF} = 274 Hz), 37.80, -5.80. ^{19}F NMR (376 MHz, CDCl$_3$) δ -58.2**.** ^{29}Si NMR (76 MHz, CDCl$_3$) δ -9.2. MALDI *m/z* calc for $C_{21}H_{19}F_3Si$ [M + Na]$^+$ 379.110. Found 379.100

Racemic Standard for **5c**:



< Peak Table >

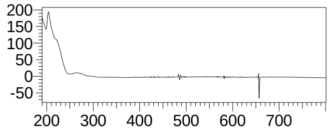
PeakTable C:\LabSolutions\Training1107\Jake J\CF3diazo_9802hexIPA_AD_rac.lcd

PDA Ch1 265nm 4nm

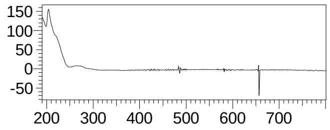
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.735	296985	10257	28.532	35.312
2	15.655	238179	7932	22.883	27.310
3	23.413	284555	6737	27.338	23.194
4	26.573	221156	4120	21.247	14.184
Total		1040875	29046	100.000	100.000

Spectrum index for racemic standard of **5c**:

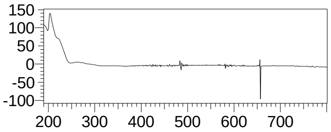
Peak# : 1
Retension Time : 14.735



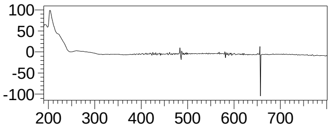
Peak# : 2
Retension Time : 15.655



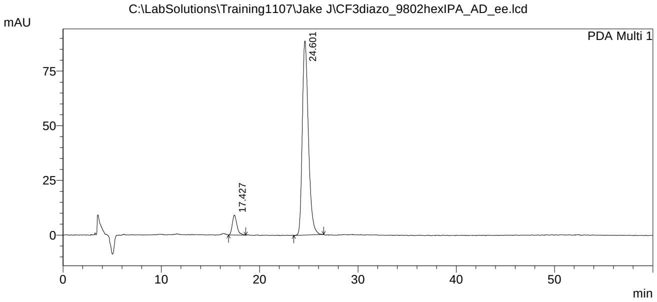
Peak# : 3
Retension Time : 23.413



Peak# : 4
Retension Time : 26.573



Enantiomerically enriched (*S*,*S*) **5c** using *S*-TCPTTL:



1 PDA Multi 1/266nm 4nm

< Peak Table >

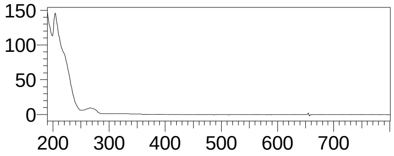
PeakTable C:\LabSolutions\Training1107\Jake J\CF3diazo_9802hexIPA_AD_ee.lcd

PDA Ch1 266nm 4nm

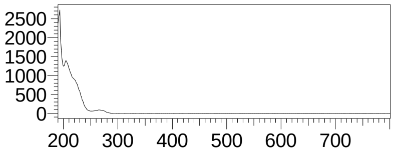
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.427	301249	9119	7.286	9.308
2	24.601	3833358	88855	92.714	90.692
Total		4134607	97974	100.000	100.000

Spectrum index for enantioenriched sample of **5c**:

Peak# : 1
Retension Time : 17.427

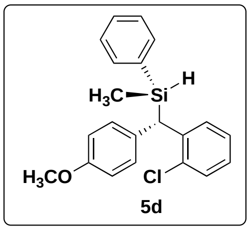


Peak# : 2
Retension Time : 24.601



Spectrum indices between racemic standard and enantioenriched are identical, indicating the peaks are identical despite slightly different retention times.

(*S*)-((*S*)-(2-chlorophenyl)(4-methoxyphenyl)methyl)(methyl)(phenyl)silane (5d)

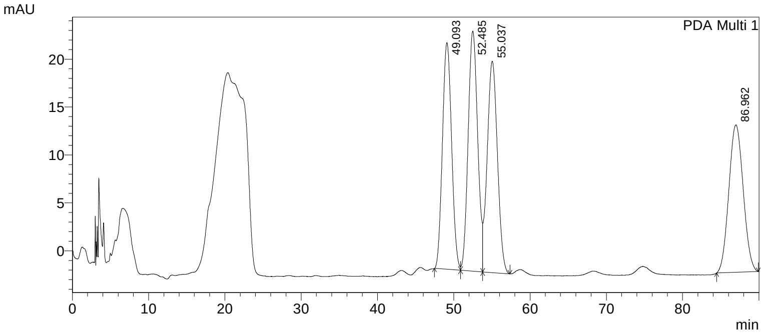


5d

Synthesized using method F with diazo compound **3e** (0.2 mmol, 52.0 mg) to give a white solid in 98% yield (0.196 mmol, 69.0 mg, 90:10 dr. Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ heptane), 1.0 mL/min. t_R (**5da**) = 49.1 min, t_R (**5db**) = 52.5 min, t_R (**5da'**) = 55.0 min, t_R (**5db'**) = 87.0 min, 89:11 er (Si-OH product, **5da'**:**5da**) Absolute configuration was assigned to be (*S, S*) based on analogy to **5a.**

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.39 (m, 5H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.82 – 4.76 (m, 1H), 4.45 (d, *J* = 4.5 Hz, 1H), 3.76 (s, 3H), 0.38 (d, *J* = 3.4 Hz, 3H).^{13}C NMR (151 MHz, CDCl$_3$) δ 157.7, 140.7, 135.0, 134.6, 134.1, 133.3, 130.4, 130.3, 129.9, 129.7, 127.9, 127.0, 126.8, 113.9, 75.9, 53.2, 36.2, -5.2. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -11.34. MALDI *m/z* calc for $C_{21}H_{21}ClOSi$ $[M - H]^+$ 351.097. Found 351.083.

Racemic Standard for **5d**:



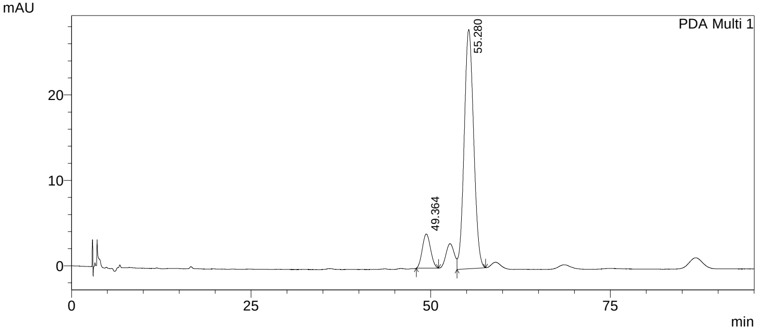
1 PDA Multi 1/233nm 4nm

< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p185a_9802hepIPA_ADonODvalve.lcd
PDA Ch1 233nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.093	1980775	23674	24.047	27.467
2	52.485	2179913	25065	26.465	29.081
3	55.037	2060887	22061	25.020	25.596
4	86.962	2015386	15391	24.468	17.857
Total		8236960	86192	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5d** using *S*-TCPTTL:



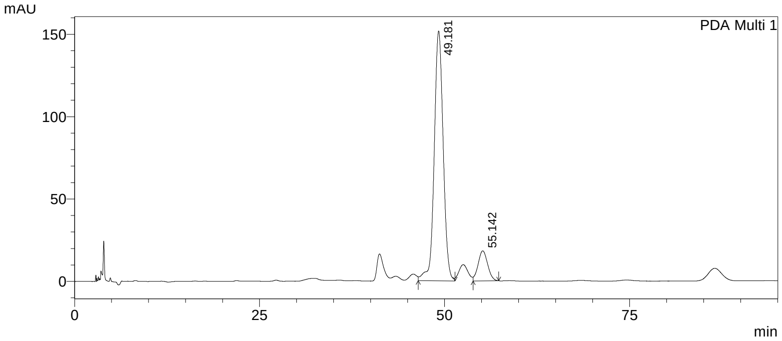
1 PDA Multi 1/254nm 4nm

< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p185b_9802hepIPA_ADonODvalve.lcd
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.364	317147	3994	10.972	12.473
2	55.280	2573303	28030	89.028	87.527
Total		2890450	32024	100.000	100.000

Enantiomerically enriched (*R*,*R*) **5d** using *R*-TCPTTL:



1 PDA Multi 1/233nm 4nm

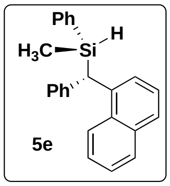
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p185c_9802hepIPA_ADonODvalve.lcd

PDA Ch1 233nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.181	12792352	151676	88.662	89.256
2	55.142	1635909	18258	11.338	10.744
Total		14428261	169934	100.000	100.000

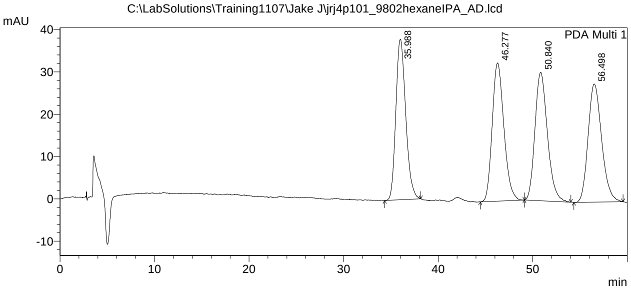
(*S*)-methyl((*S*)-naphthalen-1-yl(phenyl)methyl)(phenyl)silane (5e):



Synthesized using method F with diazo compound **3d** (0.2 mmol, 48.9 mg) to give a white solid in 78% yield (0.158 mmol, 52.8 mg, 85:15 dr). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t_R (**5ea**) = 36.0 min, t_R (**5ea'**) = 46.3 min, t_R (**5eb**) = 50.8 min, t_R (**5eb'**) = 56.5 min, 61:39 er (Si-OH product, **5ea**:**5ea'**) Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5a.**

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 1H), 7.82 – 7.78 (m, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 3H), 7.46 – 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 7.27 – 7.16 (m, 1H), 7.11 (m, 3H), 7.08 – 7.00 (m, 1H), 4.83 (p, *J* = 3.2 Hz, 1H), 4.56 (d, *J* = 4.2 Hz, 1H), 0.33 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 138.2, 135.1, 134.5, 132.8, 129.7, 129.0, 128.7, 128.5, 128.4, 127.8, 127.4, 126.9, 126.0, 125.6, 125.4, 125.3, 124.2, 38.1, -5.4.^{29}Si NMR (119 MHz, $CDCl_3$) δ -10.0. Did not ionize using ESI, MALDI or APCI.

Racemic Standard for **5e**:



1 PDA Multi 1/284nm 4nm

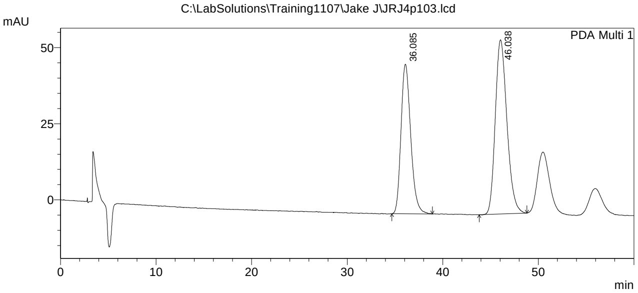
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p101_9802hexaneIPA_AD.lcd

PDA Ch1 284nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.988	2750234	37927	24.688	29.426
2	46.277	2813267	32673	25.254	25.349
3	50.840	2789483	30380	25.041	23.570
4	56.498	2786868	27912	25.017	21.655
Total		11139853	128892	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5e** using *S*-TCPTTL:



1 PDA Multi 1/283nm 4nm

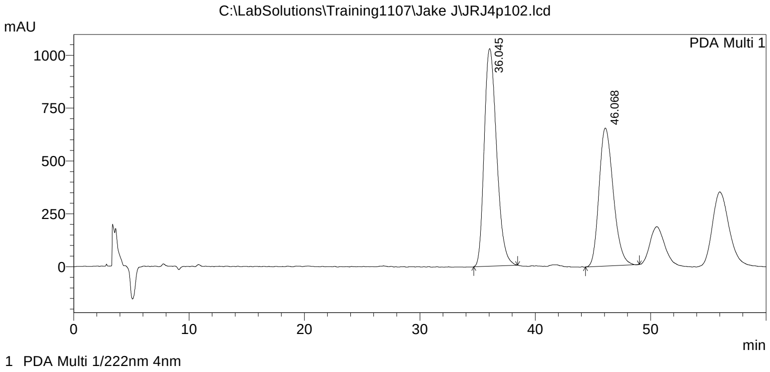
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\JRJ4p103.lcd

PDA Ch1 283nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.085	3479088	49147	41.817	46.219
2	46.038	4840630	57187	58.183	53.781
Total		8319718	106334	100.000	100.000

Enantiomerically enriched (*R*,*R*) **5e** using *R*-TCPTTL:



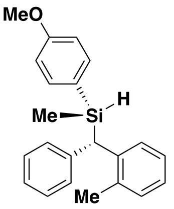
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\JRJ4p102.lcd

PDA Ch1 222nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.045	76982519	1029081	57.866	61.189
2	46.068	56053744	652716	42.134	38.811
Total		133036262	1681797	100.000	100.000

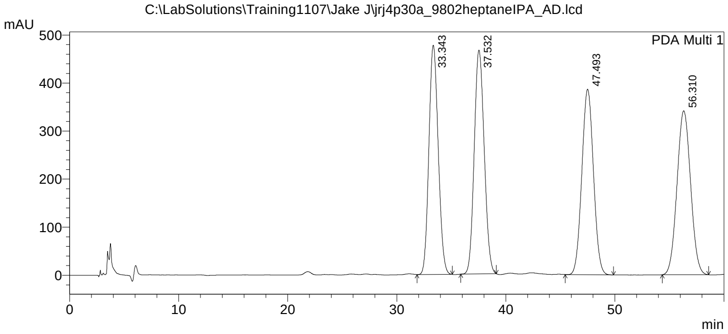
(*S*)-(4-methoxyphenyl)(methyl)((*S*)-phenyl(*o*-tolyl)methyl)silane (5f):



Synthesized using method F with diazo compound **3a** (0.2 mmol, 42.0 mg) to give a clear oil in 85% yield (0.170 mmol, 56.5 mg, 94:6 dr). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (1% IPA/ heptane), 1.0 mL/min. t_R (**5fa**) = 33.3 min, t_R (**5fb**) = 37.5 min, t_R (**5fa'**) = 47.5 min, t_R (**5fb'**) = 56.3 min, 93.5:6.5 er (Si-OH product, **5fb'**:**5fb**). Absolute configuration was assigned to be (*S*,*S*) based Tamao-Fleming oxidation results and analogy to **11.**

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.04-7.23 (m, 4H), 6.80 (d, *J* = 7.9 Hz, 1H), 4.73 – 4.67 (m, 1H), 3.93 (d, *J* = 3.7 Hz, 1H), 3.79 (s, 1H), 2.22 (s, 1H), 0.31 (d, *J* = 3.5 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 160.9, 142.13, 140.7, 137.0, 136.6, 130.9, 129.7, 128.9, 128.3, 126.0, 125.9, 125.7, 125.2, 113.6, 55.2, 39.0, 20.4, -5.4. ^{9}Si NMR (119 MHz, CDCl$_3$) δ -11.4. Did not ionize using ESI, MALDI or APCI.

Racemic Standard for **5f**:



1 PDA Multi 1/230nm 4nm

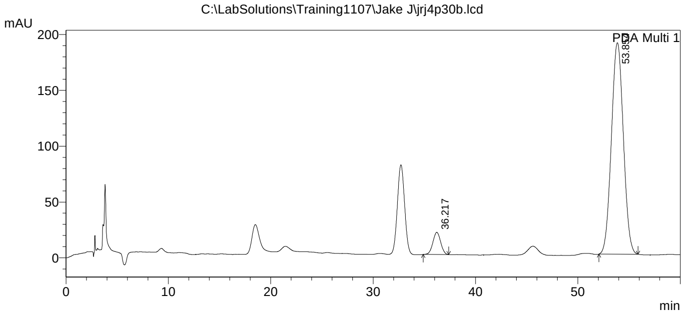
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p30a_9802heptaneIPA_AD.lcd

PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.343	28394457	477248	24.430	28.566
2	37.532	29672263	466046	25.530	27.895
3	47.493	28590025	386124	24.598	23.111
4	56.310	29570529	341290	25.442	20.428
Total		116227274	1670708	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5f** using *S*-TCPTTL:



1 PDA Multi 1/229nm 4nm

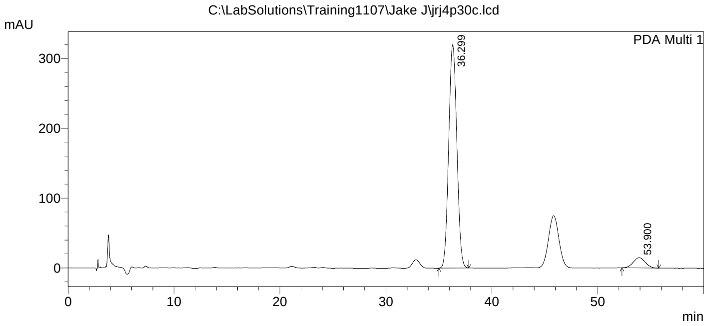
< Peak Table >

PDA Ch1 229nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.217	1055937	19918	6.437	9.516
2	53.854	15348653	189387	93.563	90.484
Total		16404589	209306	100.000	100.000

Enantiomerically enriched (*R*,*R*) **5f** using *R*-TCPTTL:

<Chromatogram>



1 PDA Multi 1/232nm 4nm

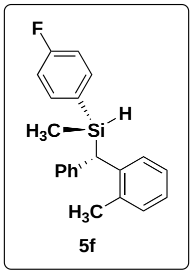
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p30c.lcd

PDA Ch1 232nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.299	17064389	319925	93.596	95.572
2	53.900	1167520	14823	6.404	4.428
Total		18231909	334749	100.000	100.000

(*S*)-(4-fluorophenyl)(methyl)((*S*)-phenyl(*o*-tolyl)methyl)silane (5g):

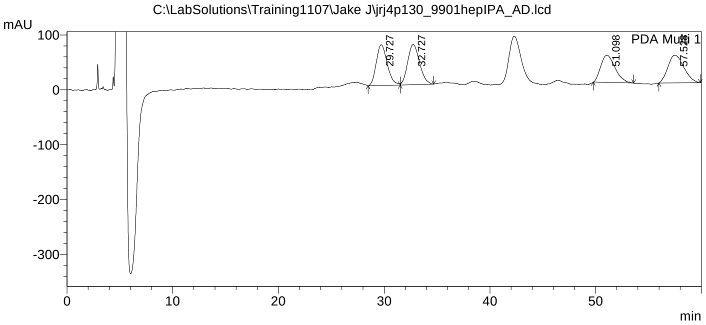


5f

Synthesized using method F with diazo compound **3a** (0.2 mmol, 42.0 mg) to give an oil in 90% yield (0.180 mmol, 57.7 mg, 90:10 dr). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ hexanes), 1.0 mL/min. t_R (**5ga**) = 36.0 min, t_R (**5gb**) = 46.3 min, t_R (**5ga'**) = 50.8 min, t_R (**5gb'**) = 56.5 min, 61:39 er (Si-OH product, **5gb'**:**5gb**) Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5a**.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.23 – 7.15 (m, 4H), 7.15 – 7.05 (m, 4H), 7.01 – 6.94 (m, 2H), 4.76 (p, *J* = 3.7 Hz, 1H), 3.96 (d, *J* = 4.1 Hz, 1H), 2.24 (s, 3H), 0.37 (d, *J* = 3.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1 (d, J_{CF} = 248.9 Hz), 141.8, 140.26, 137.0 (d, J_{CCCF} = 7.5 Hz), 137.0, 130.9, 129.6, 128.9, 128.5, 128.4, 126.1, 126.0, 125.3, 115.0 (d, J_{CCF} = 19.7 Hz), 38.8, 20.3, -5.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.97. ^{29}Si NMR (76 MHz, $CDCl_3$) δ -10.9. MALDI *m/z* calc for $C_{21}H_{21}FSi$ $[M + Na]^+$ 343.129. Found 343.134.

Racemic Standard for **5g**:



1 PDA Multi 1/203nm 4nm

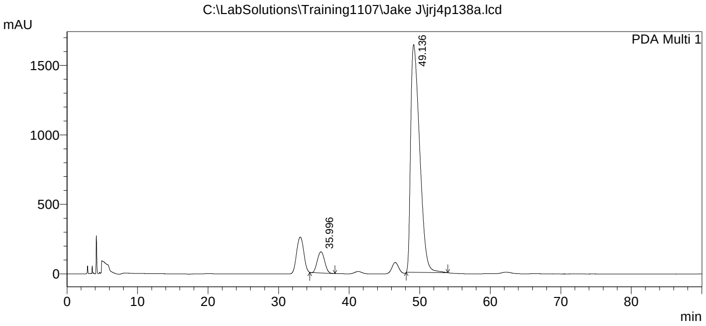
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p130_9901hepIPA_AD.lcd

PDA Ch1 203nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.727	5340505	74092	25.353	29.986
2	32.727	5722663	73381	27.167	29.698
3	51.098	4693375	49413	22.281	19.998
4	57.528	5308366	50207	25.200	20.319
Total		21064908	247094	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5g** using *S*-TCPTTL:



1 PDA Multi 1/203nm 4nm

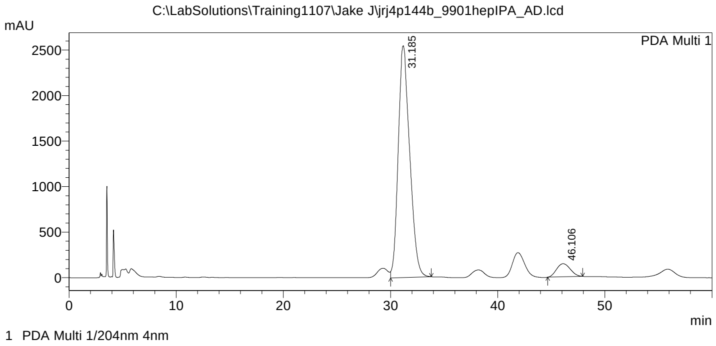
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p138a.lcd

PDA Ch1 203nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.996	10899260	152350	6.957	8.501
2	49.136	145765515	1639890	93.043	91.499
Total		156664775	1792240	100.000	100.000

Enantiomerically enriched (*R*,*R*) **5g** using *R*-TCPTTL:



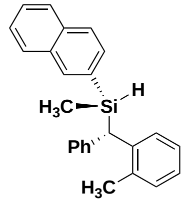
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p144b_9901hepIPA_AD.lcd

PDA Ch1 204nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.185	189219089	2547395	93.621	94.628
2	46.106	12893569	144617	6.379	5.372
Total		202112657	2692012	100.000	100.000

(*S*)-methyl(naphthalen-2-yl)((*S*)-phenyl(*o*-tolyl)methyl)silane (5h):

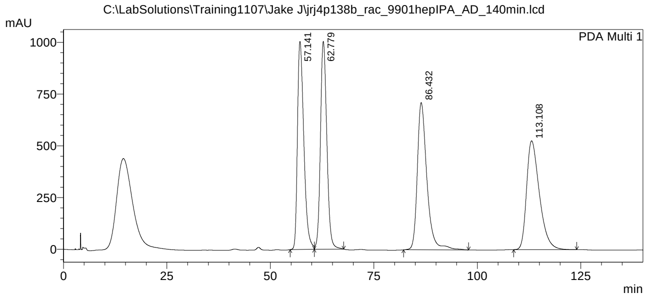


5g

Synthesized using method F with diazo compound **3a** (0.2 mmol, 42.0 mg) to give a white solid in 95% yield (0.190 mmol, 66.9 mg, 91:9 dr). Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (1% IPA/ heptane), 1.0 mL/min. t_R (**5ha**) = 57.1 min, t_R (**5hb**) = 62.8 min, t_R (**5ha'**) = 86.4 min, t_R (**5hb'**) = 113.1 min, 92:8 er (Si-OH product, **5hb'**:**5hb**) Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5a.**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.77 (dd, *J* = 12.3, 8.0 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.21 (td, *J* = 15.6, 14.8, 7.9 Hz, 4H), 7.17 – 7.09 (m, 4H), 4.93 (p, *J* = 3.8 Hz, 1H), 4.11 (d, *J* = 3.7 Hz, 1H), 2.29 (s, 3H), 0.48 (d, *J* = 3.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.9, 140.5, 137.0, 136.2, 134.0, 132.9, 132.5, 131.0, 130.9, 129.7, 128.9, 128.4, 128.2, 127.8, 126.9, 126.7, 126.1, 126.0, 126.0, 125.3, 38.8, 20.4, -5.4. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -10.1. MALDI *m/z* calc for $C_{25}H_{24}Si$ $[M + Na]^+$ 375.154. Found 375.166.

Racemic Standard for **5h**:



1 PDA Multi 1/229nm 4nm

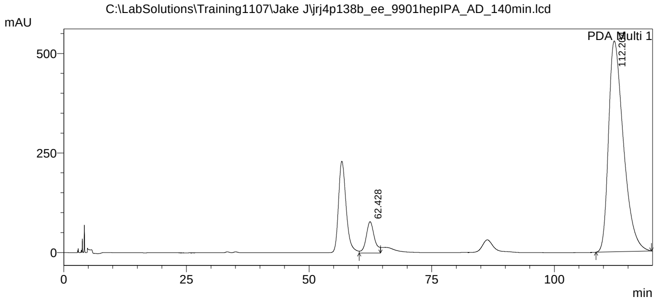
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p138b_rac_9901hepIPA_AD_140min.lcd

PDA Ch1 229nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	57.141	107678104	1005424	24.285	30.955
2	62.779	107704834	1004970	24.291	30.941
3	86.432	115186832	711986	25.978	21.921
4	113.108	112830097	525615	25.447	16.183
Total		443399867	3247994	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5h** using *S*-TCPTTL:



1 PDA Multi 1/222nm 4nm

< Peak Table >

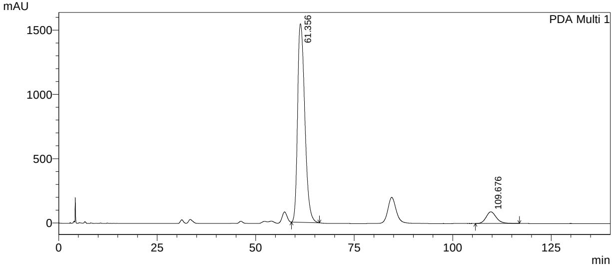
PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p138b_ee_9901hepIPA_AD_140min.lcd

PDA Ch1 222nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.428	9205162	78804	7.609	12.948
2	112.204	111770364	529829	92.391	87.052
Total		120975526	608633	100.000	100.000

Enantiomerically enriched (*R*,*R*) **5h** using *R*-TCPTTL:

C:\LabSolutions\Training1107\Jake J\jrj4p144a_9901hepIPA_AD.lcd



1 PDA Multi 1/229nm 4nm

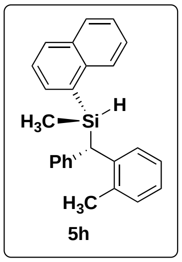
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p144a_9901hepIPA_AD.lcd

PDA Ch1 229nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	61.356	196868375	1545840	92.289	94.460
2	109.676	16447848	90670	7.711	5.540
Total		213316223	1636509	100.000	100.000

(*S*)-methyl(naphthalen-1-yl)((*S*)-phenyl(*o*-tolyl)methyl)silane (5i):

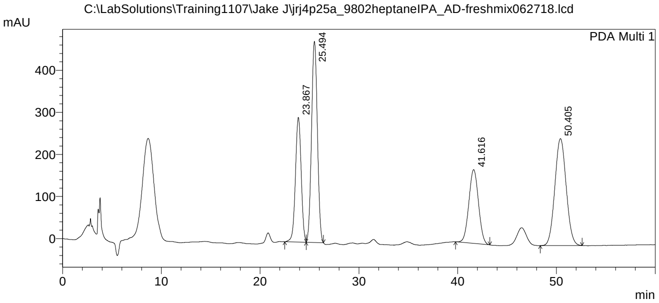


5h

Synthesized using method F with diazo compound **3a** (0.2 mmol, 42.0 mg) to give a white solid in 55% yield (0.11 mmol, 38.8 mg, 82:18 dr. Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ heptane), 1.0 mL/min. t_R (**5ia**) = 23.9 min, t_R (**5ib**) = 25.5 min, t_R (**5ia’**) = 41.6 min, t_R (**5ib’**) = 50.4 min, 92:8 er (Si-OH product, **5ia**’:**5ia**) Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5a.**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.75 (m, 4H), 7.57 (d, *J* = 6.7 Hz, 1H), 7.53 – 7.38 (m, 3H), 7.34 (dt, *J* = 8.5, 4.5 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.08 (m, 2H), 7.02 (m, 1H), 6.95 (m,1H), 5.16 (p, *J* = 4.1 Hz, 1H), 4.23 (d, *J* = 4.5 Hz, 1H), 2.17 (s, 3H), 0.45 (d, *J* = 3.8 Hz, 3H). NMR (101 MHz, $CDCl_3$) δ 142.3, 14.0, 137.2, 136.9, 135.2, 133.5, 133.3, 130.9, 130.4, 129.8, 127.0, 128.7, 128.3, 127.7, 126.1, 126.0, 125.9, 125.6, 125.2, 125.1, 38.5, 20.3, -4.64.^{29}Si NMR (119 MHz, $CDCl_3$) δ -10.6. MALDI *m/z* calc for $C_{25}H_{24}Si$ $[M + Na]^+$ 375.154. Found 375.163.

Racemic Standard for **5i**:



1 PDA Multi 1/225nm 4nm

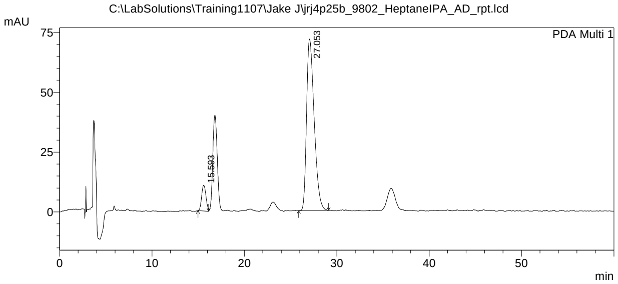
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p25a_9802heptaneIPA_AD-freshmix062718.lcd

PDA Ch1 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.867	11999034	296453	18.768	24.617
2	25.494	19735208	478133	30.868	39.703
3	41.616	11911651	175483	18.631	14.572
4	50.405	20288125	254205	31.733	21.109
Total		63934018	1204274	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5i** using *S*-TCPTTL:



1 PDA Multi 1/254nm 4nm

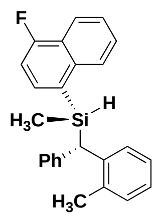
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p25b_9802_HeptaneIPA_AD_rpt.lcd

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.593	350639	10711	7.891	13.008
2	27.053	4093054	71632	92.109	86.992
Total		4443693	82343	100.000	100.000

(*S*)-(4-fluoronaphthalen-1-yl)(methyl)((*S*)-phenyl(*o*-tolyl)methyl)silane (5j):

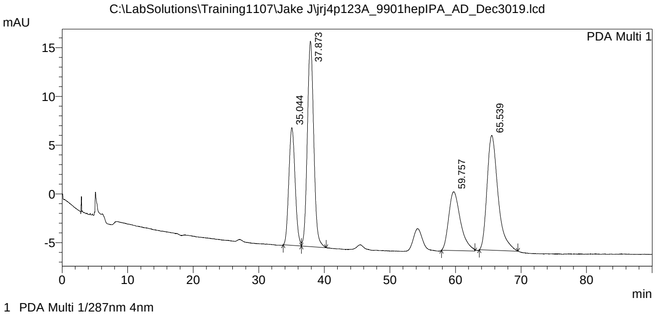


5i

Synthesized using method F with diazo compound **3a** (0.2 mmol, 42.0 mg) to give a white solid in 66% yield (0.132 mmol, 48.9 mg, 84:16 dr. Enantiomeric ratio was determined by HLPC after hydrolysis with a Daicel CHIRALPAK ® AD-H column (2% IPA/ heptane), 1.0 mL/min. t_R (**5ja**) = 35.0 min, t_R (**5jb**) = 37.9 min, t_R (**5ja'**) = 59.8 min, t_R (**5jb'**) = 65.6 min, 92:8 er (Si-OH product, **5ja'**:**5ja**) Absolute configuration was assigned to be (*S*, *S*) based on analogy to **5a.**

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.42 (m, 4H), 7.25 – 7.00 (m, 9H), 5.20 (q, *J* = 5.9, 4.0 Hz, 1H), 4.24 (d, *J* = 4.4 Hz, 1H), 2.23 (s, 3H), 0.52 (d, *J* = 3.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 160.5 (d, J_{CF} = 255.0 Hz), 140.2, 136.8, 135.2 (d, J_{CCCF} = 8.3 Hz), 130.9, 129.66, 129.1 (d, J_{CCCF} = 4.9 Hz), 128.7, 128.6, 128.4, 128.2, 127.4 (d, J_{CCCF} = 3.2 Hz), 126.8, 126.0, 125.9, 125.8 (d, J_{CCCCF} = 1.6 Hz), 125.1, 123.7 (d, J_{CCF} = 15.0 Hz), 121.1 (d, J_{CCCF} = 6.3 Hz), 108.9 (d, J_{CCF}= 18.5 Hz), 38.5, 20.2, -4.8. ^{19}F NMR (376 MHz, CDCl$_3$) δ -120.35. ^{29}Si NMR (76 MHz, CDCl$_3$) δ -12.7 MALDI *m/z* calc for $C_{25}H_{23}FSi$ [M + H]$^+$ 371.163. Found 371.151.

Racemic Standard for **5j**:

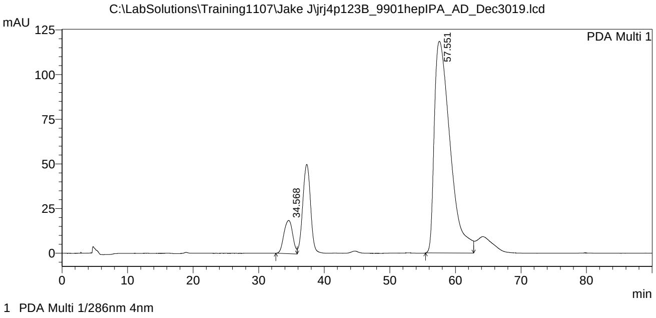


< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p123A_9901hepIPA_AD_Dec3019.lcd
PDA Ch1 287nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.044	807448	12083	18.458	23.694
2	37.873	1433974	21093	32.780	41.363
3	59.757	756270	6031	17.288	11.826
4	65.539	1376912	11788	31.475	23.117
Total		4374605	50995	100.000	100.000

Enantiomerically enriched (*S*,*S*) **5j** using *S*-TCPTTL:



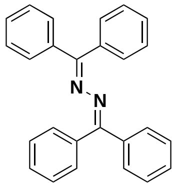
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p123B_9901hepIPA_AD_Dec3019.lcd
PDA Ch1 286nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.568	1735561	18627	8.022	13.578
2	57.551	19900422	118563	91.978	86.422
Total		21635983	137190	100.000	100.000

Functionalization Products and Miscellaneous:

1,2-bis(diphenylmethylene)hydrazine (6):

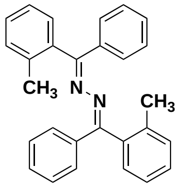


6

Spectrum matches previous report.[17]

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47 (d, *J* = 7.7 Hz, 4H), 7.39 (dt, *J* = 11.4, 6.5 Hz, 6H), 7.36 – 7.31 (m, 6H), 7.27 (t, *J* = 7.5 Hz, 4H).

(1*E*,2*E*)-1,2-bis(phenyl(*o*-tolyl)methylene)hydrazine (7):

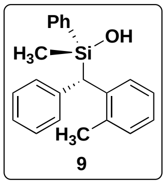


7

Observed and isolated during kinetics experiments as a yellow solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.37 (m, 4H), 7.29 (m, 6H), 7.22 (m, 6H), 2.23 (s, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 137.8, 136.6, 130.3, 123.0, 129.9, 128.3, 128.3, 128.2, 128.0, 125.4, 20.2

(*R*)-methyl(phenyl)((*S*)-phenyl(*o*-tolyl)methyl)silanol (9):

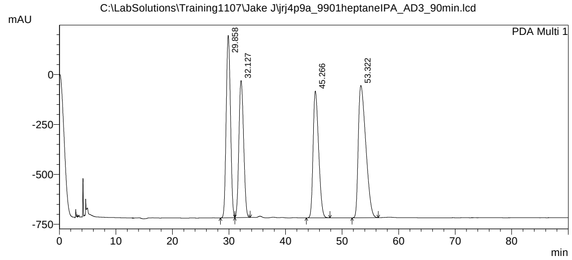


9

Synthesized using method K **5a** (0.33 mmol, 100.0 mg) to give a clear oil in 90% yield (0.3 mmol, 94.5 mg, 93:7 dr). Enantiomeric ratio was determined by HLPC with a Daicel CHIRALPAK ® AD-H column (1% IPA/ heptane), 1.0 mL/min. t_R (**9a**) = 29.9 min, t_R (**9b**) = 32.1 min, t_R (**9a'**) = 45.3 min, t_R (**9b'**) = 53.3 min, 93:7 er (**9b**:**9b'**). Absolute configuration was assigned to be (*R, S)* based on analogy to **5a**, and formed through a retentive process.[11]

^{1}H NMR (400 MHz, C_6D_6) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.12 – 7.06 (m, 5H), 7.05 – 6.88 (m, 4H), 3.96 (s, 1H), 2.03 (s, 3H), 1.57 (s, 1H), 0.29 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 139.7, 137.1, 136.9, 134.0, 130.9, 130.0, 129.9, 129.0, 128.4, 127.8, 126.0, 125.9, 125.4, 41.6, 20.4, -1.6. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 1.66. MALDI *m/z* calc for $C_{22}H_{22}Si$ [M + Na]$^+$ 341.1332. Found 341.212.

Racemic Standard for **9**:



1 PDA Multi 1/208nm 4nm

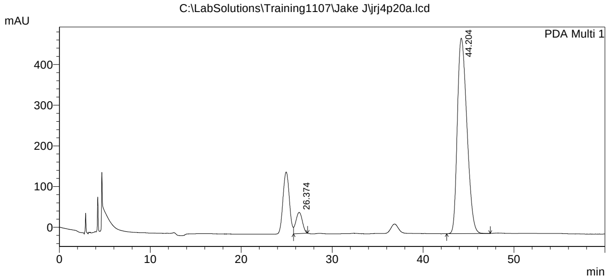
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p9a_9901heptaneIPA_AD3_90min.lcd

PDA Ch1 208nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.858	48239523	914305	25.085	31.533
2	32.127	40004513	687079	20.802	23.696
3	45.266	42953904	635333	22.336	21.912
4	53.322	61108498	662816	31.777	22.859
Total		192306438	2899533	100.000	100.000

Enantiomerically enriched (*S*,*S*) **9** using *S*-TCPTTL:



1 PDA Multi 1/204nm 4nm

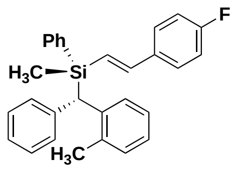
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p20a.lcd

PDA Ch1 204nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.374	2588118	52218	6.858	9.805
2	44.204	35149381	480353	93.142	90.195
Total		37737499	532571	100.000	100.000

(*R*)-((*E*)-4-fluorostyryl)(methyl)(phenyl)((*S*)-phenyl(*o*-tolyl)methyl)silane (10):

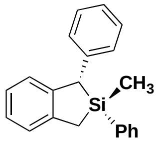


10

Synthesized using method L with **5a** (0.33 mmol, 100.0 mg) to give a clear oil in 62% yield (104.1 mg, 85:15 **10**:**10'**, 93:7 dr). Absolute configuration was assigned to be (*R, S)* based on analogy to **5a** and assuming retention of configuration.[11] The E aisomer was assigned based off *J* values of the alkene protons.Could not separate using CSP-HPLC.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.41 – 7.32 (m, 6H), 7.29 (m 2H), 7.20 – 7.13 (m, 3H), 7.13 – 7.06 (m, 4H), 7.02 (m, 3H), 6.81 (d, *J* = 19.2 Hz, 1H), 6.50 (d, *J* = 19.2 Hz, 1H), 4.11 (s, 1H), 2.22 (s, 3H), 0.46 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 162.9 (d, J_{CF} = 250.4 Hz), 145.8, 141.7, 140.5, 137.0, 136.8, 135.0, 130.9, 130.3, 129.4, 129.1, 128.9, 128.4, 128.3, 128.2, 127.8, 125.8 (d, J_{CCCF} = 6.3 Hz), 125.1, 124.1 (d, J_{CCCCF} = 2.3 Hz), 115.6 (d, J_{CCF}= 21.6 Hz), 40.1, 20.4, -3.9.MALDI *m/z* calc for $C_{29}H_{27}FSi$ [M + H$_3$O]$^+$. 441.204. Found 441.158. ^{19}F NMR (376 MHz, CDCl$_3$) δ -113.3. ^{29}Si NMR (79 MHz, CDCl$_3$) δ -12.0.

(1*S*,2*R*)-2-methyl-1,2-diphenyl-2,3-dihydro-1*H*-benzo[*c*]silole (11):

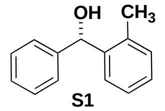


11

Synthesized using method J with **5a** (0.33 mmol, 100.0 mg) to give a clear oil in 90% yield (0.3 mmol, 89.2 mg, 90:10 dr). Absolute configuration was assigned to be (*S*, *S)* based on analogy to **5f**, and ^{1}H NOESY experiments. Could not separate using CSP-HPLC.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.20 (m, 1H), 7.19 – 7.12 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 1H), 2.66 (d, *J* = 17.3 Hz, 1H), 2.34 (d, *J* = 17.3 Hz, 1H), 0.63 (s, 3H).^{13}C NMR (151 MHz, CDCl$_3$) δ 144.8, 142.9, 142.1, 134.5, 129.6, 129.0, 128.9, 128.1, 127.9, 127.6, 126.6, 124.3, 43.4, 18.9, -4.6. ^{29}Si NMR (79 MHz, CDCl$_3$) δ 15.7. MALDI *m/z* calc for $C_{21}H_{20}Si$ [M + Na]$^+$ 323.123. Found 323.166.

(*S*)-phenyl(*o*-tolyl)methanol (S1)

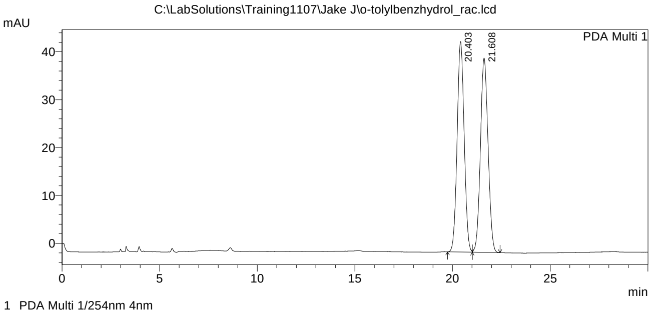


S1

Synthesized using procedure for Tamao-Fleming oxidation.HPLC retention times match previously reported syntheses. Enantiomeric ratio was determined by HLPC with a Daicel CHIRALPAK ® OD-H column (2% IPA/ hexanes), 0.5 mL/min. t_R (**S1a**) = 20.4 min, t_R (**S1b**) = 21.6 min, 91.5:8.5 er. Absolute configuration was assigned to be (*S)* based on previous reports.[10]

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.31 (m, 4H), 7.27 – 7.21 (m, 2H), 7.19 (td, *J* = 7.4, 1.6 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 5.97 (s, 1H), 2.23 (s, 3H).

Racemic Standard:



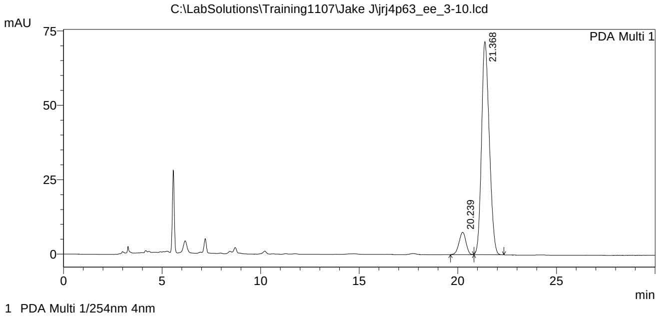
< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\o-tolylbenzhydrol_rac.lcd

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.403	1104154	43993	50.043	51.995
2	21.608	1102272	40617	49.957	48.005
Total		2206427	84609	100.000	100.000

HPLC trace after Tamao-Fleming Oxidation of **5f**:



< Peak Table >

PeakTable C:\LabSolutions\Training1107\Jake J\jrj4p63_ee_3-10.lcd

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.239	183861	7514	8.569	9.489
2	21.368	1961798	71672	91.431	90.511
Total		2145659	79186	100.000	100.000

VII. X-ray Crystallography Data

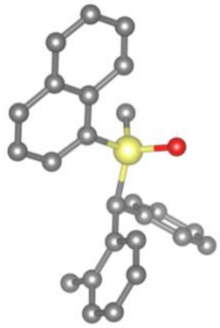


Figure S15. X-ray[18] of (+/-) **5i** hydrolysis product; H's are removed for clarity as well as the distorted enantiomer.

Crystals were grown from slow diffusion in DCM/Benzene. A colorless plate with approximate orthogonal dimensions 0.282 x 0.425 x 0.755mm^3 was placed and optically centered on the Bruker Duo[19] APEXII CCD system at –183°C(90K). Indexing of the unit cell used a random set of reflections collected from three series of 0.5° wide ω-scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Data were collected [MoKα] with 0.3° wide scans, variable time per frame dependent upon detector 2θ angle and varying φ and omega angles such that nearly all unique reflections were collected at least once. The crystal to detector distance was 5.00cm, thus providing a complete sphere of data to $2\theta_{max}$=54.97°.

Structural determination and Refinement:

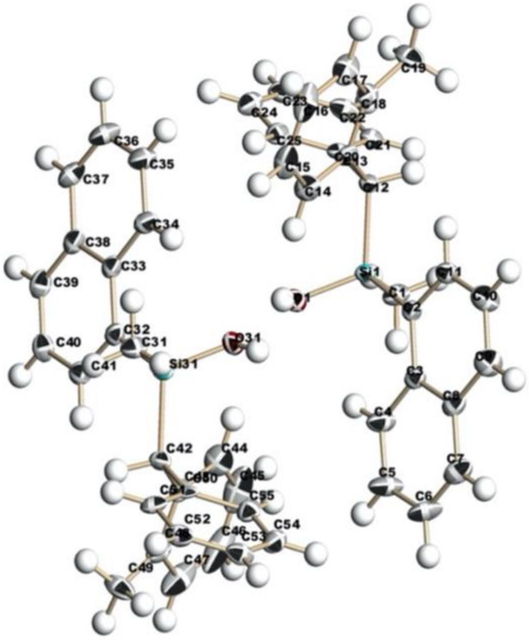


Figure S16. ORTEP of (+/-) **5i** hydrolysis product. Thermal Ellipsoids are at 50%.

All crystallographic calculations were performed on an Intel Xeon E5-1620v2 at 3.70GHz with eight core processor and 16GB of extended memory. Determination of the unit cell required Cellnow[20] and the reciprocal lattice viewing

(Rlatt) capabilities of the APEX2 program to determine the true lattice. Cellnow[20] determined the twin relationship between the two components, a rotation of 179.8° about the real axis 1 0 -1 produced the transformation matrix -0.344 0 -0.650 0 -1 0 -1.356 0 0.344, generated the orientation matrices for the components and output a useable multiple matrices input file for the integration program SAINT[19]. Saint was run six times using the output optimized merged matrix file from the previous run. Data collected were now corrected for absorption using TWINABS [21,22] and Blessing's method and merged generating both single component HKLF4 and multi-component HKLF5 files. The SHELXTL[23] program package was now implemented to determine, based upon systematic absences and intensity statistics, the non-centrosymmetric monoclinic space group $P2_1$ (no. 4). The structure was determined by direct methods with a majority of the non-hydrogen atoms from the two nearly identical molecules being located directly using the program XT.[24] Refinement of the structure was achieved using the program XL.[25] One of the ortho-methyl-benzyl groups was found to be disordered over two positions in one of the molecules, while the other molecule was fully ordered. The OH groups were also found to be 50% disordered and optimized with one hydrogen directed towards the other molecules hydroxyl oxygen and the other away for each molecule. The data collected were merged for least squares refinement to 8983 unique data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were idealized but their thermal parameters were allowed to refine freely but for those attached to the oxygen atoms; those were fixed to be equal to each other. The final structure was refined to convergence with R(F)=3.49%, wR(F^2)=9.64%, GOF=1.043 for all 8893 unique reflections [R(F)=3.33, wR(F^2)=9.49% for those 8671 data with Fo > 4σ(Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. The absolute configuration structure parameter, Flack(x),[26] was determined to be 0.06(7) indicating that the structure is correct.

Table S4. Crystal data and structure refinement for [$C_{25}H_{24}OSi$].

Identification code	JF2862TW51 (JRJNpMeSi)	
Empirical formula	C25 H24 O Si	
Formula weight	368.53	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.9375(6) Å	〈= 90°.
	b = 20.4070(15) Å	®= 104.2477(10)°.
	c = 12.5011(9) Å	© = 90°.
Volume	1962.6(3) Å^3	
Z, Z’	4, 2	
Density (calculated)	1.247 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	784	
Crystal size	0.755 x 0.425 x 0.282 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Bruker APEX-II CCD	
Theta range for data collection	1.681 to 27.477°.	
Index ranges	-10<=h<=10, -26<=k<=26, -16<=l<=16	
Reflections collected	8983	
Independent reflections	8983	
Observed reflections (I > 2sigma(I))	8671	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9542 and 0.8639	
Solution method	SHELXT (Sheldrick, 2014)	
Refinement method	SHELXL-2018/3 (Sheldrick, 2018) Full-matrix least-squares on F^2	
Data / restraints / parameters	8983 / 8 / 588	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0949	
R indices (all data)	R1 = 0.0349, wR2 = 0.0964	
Absolute structure parameter	0.06(7)	
Largest diff. peak and hole	0.231 and -0.204 e.Å^{-3}	

VIII. References

(1) Green, S. P.; Wheelhouse, K. M.; Payne, A. D.; Hallett, J. P.; Miller, P. W.; Bull, J. A. Thermal Stability and Explosive Hazard Assessment of Diazo Compounds and Diazo Transfer Reagents. *Org. Process Res. Dev.* **2020**, *24* (1), 67–84. https://doi.org/10.1021/acs.oprd.9b00422.

(2) Yasutomi, Y.; Suematsu, H.; Katsuki, T. Iridium(III)-Catalyzed Enantioselective Si−H Bond Insertion and Formation of an Enantioenriched Silicon Center. *J. Am. Chem. Soc.* **2010**, *132* (13), 4510–4511. https://doi.org/10.1021/ja100833h.

(3) Satoh, Y.; Igarashi, M.; Sato, K.; Shimada, S. Highly Selective Synthesis of Hydrosiloxanes by Au-Catalyzed Dehydrogenative Cross-Coupling Reaction of Silanols with Hydrosilanes. *ACS Catal.* **2017**, *7* (3), 1836–1840. https://doi.org/10.1021/acscatal.6b03560.

(4) Lamb, K. N.; Squitieri, R. A.; Chintala, S. R.; Kwong, A. J.; Balmond, E. I.; Soldi, C.; Dmitrenko, O.; Castiñeira Reis, M.; Chung, R.; Addison, J. B.; Fettinger, J. C.; Hein, J. E.; Tantillo, D. J.; Fox, J. M.; Shaw, J. T. Synthesis of Benzodihydrofurans by Asymmetric C−H Insertion Reactions of Donor/Donor Rhodium Carbenes. *Chem. – A Eur. J.* **2017**, *23* (49), 11843–11855. https://doi.org/10.1002/chem.201701630.

(5) Chen, J.; Chen, C.; Ji, C.; Lu, Z. Cobalt-Catalyzed Asymmetric Hydrogenation of 1,1-Diarylethenes. *Org. Lett.* **2016**, *18* (7), 1594–1597. https://doi.org/10.1021/acs.orglett.6b00453.

(6) Brown, E.; Chevalier, C.; Huet, F.; Le Grumelec, C.; Lézé, A.; Touet, J. Determination of the Enantiomeric Excesses of Chiral Acids by 19F NMR Studies of Their Esters Deriving from (R)-(+)-2-(Trifluoromethyl)Benzhydrol. *Tetrahedron: Asymmetry* **1994**, *5* (7), 1191–1194. https://doi.org/https://doi.org/10.1016/0957-4166(94)80154-1.

(7) Wu, C.; Hu, F.; Liu, Z.; Deng, G.; Ye, F.; Zhang, Y.; Wang, J. Cu(I)-Catalyzed Coupling of Diaryldiazomethanes with Terminal Alkynes: An Efficient Synthesis of Tri-Aryl-Substituted Allenes. *Tetrahedron*. 2015, pp 9196–9201. https://doi.org/10.1016/j.tet.2015.10.043.

(8) Cobo, A. A.; Armstrong, B. M.; Fettinger, J. C.; Franz, A. K. Catalytic Asymmetric Synthesis of Cyclopentene-Spirooxindoles Bearing Vinylsilanes Capable of Further Transformations. *Org. Lett.* **2019**, *21* (20), 8196–8200. https://doi.org/10.1021/acs.orglett.9b02852.

(9) Karmel, C.; Chen, Z.; Hartwig, J. F. Iridium-Catalyzed Silylation of C–H Bonds in Unactivated Arenes: A Sterically Encumbered Phenanthroline Ligand Accelerates Catalysis. *J. Am. Chem. Soc.* **2019**, *141* (17), 7063–7072. https://doi.org/10.1021/jacs.9b01972.

(10) Touge, T.; Nara, H.; Fujiwhara, M.; Kayaki, Y.; Ikariya, T. Efficient Access to Chiral Benzhydrols via Asymmetric Transfer Hydrogenation of Unsymmetrical Benzophenones with Bifunctional Oxo-Tethered Ruthenium Catalysts. *J. Am. Chem. Soc.* **2016**, *138* (32), 10084–10087. https://doi.org/10.1021/jacs.6b05738.

(11) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. Stereochemistry at Silicon. *Topics in Stereochemistry*. January 1, 1984, pp 43–198. https://doi.org/doi:10.1002/9780470147245.ch2.

(12) Oestreich, M. Chirality Transfer from Silicon to Carbon. *Chem. – A Eur. J.* **2006**, *12* (1), 30–37. https://doi.org/10.1002/chem.200500782.

(13) Zhang, J.; Park, S.; Chang, S. Catalytic Access to Bridged Sila-N-Heterocycles from Piperidines via Cascade Sp3 and Sp2 C–Si Bond Formation. *J. Am. Chem. Soc.* **2018**, *140* (41), 13209–13213. https://doi.org/10.1021/jacs.8b08733.

(14) Koga, S.; Ueki, S.; Shimada, M.; Ishii, R.; Kurihara, Y.; Yamanoi, Y.; Yuasa, J.; Kawai, T.; Uchida, T. A.; Iwamura, M.; Nozaki, K.; Nishihara, H. Access to Chiral Silicon Centers for Application to Circularly Polarized Luminescence Materials. *J. Org. Chem.* **2017**, *82* (12), 6108–6117. https://doi.org/10.1021/acs.joc.7b00583.

(15) Yasutomi, Y.; Suematsu, H.; Katsuki, T. Iridium(III)-Catalyzed Enantioselective Si−H Bond Insertion and Formation of an Enantioenriched Silicon Center. *J. Am. Chem. Soc.* **2010**, *132* (13), 4510–4511. https://doi.org/10.1021/ja100833h.

(16) Lee, M.; Ren, Z.; Musaev, D. G.; Davies, H. M. L. Rhodium-Stabilized Diarylcarbenes Behaving as Donor/Acceptor Carbenes. *ACS Catal.* **2020**, 6240–6247. https://doi.org/10.1021/acscatal.0c01131.

(17) Lasri, J.; Aly, M. M.; Eltayeb, N. E.; Babgi, B. A. Synthesis of Symmetrical and Asymmetrical Azines from Hydrazones and/or Ferrocenecarboxaldehyde as Potential Antimicrobial–Antitumor Agents. *J. Mol. Struct.* **2018**, *1164*, 1–8. https://doi.org/https://doi.org/10.1016/j.molstruc.2018.03.030.

(18) Momma, K.; Izumi, F. {\it VESTA3} for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *J. Appl. Crystallogr.* **2011**, *44* (6), 1272–1276. https://doi.org/10.1107/S0021889811038970.

(19) Bruker (2013) APEXII (Version 2014.9-1) and (2016) SAINT (Version 8.37a). Bruker AXS Inc., Madison, Wisconsin, USA.

(20) Sheldrick, G.M., CELLNOW, Twin matrix determination program, Universität Göttingen: Göttingen, Germany, Version 2008/3.

(21) An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). Acta Cryst., A51, 33-38.

(22) Sheldrick, G.M., TWINABS Version 2012/1‘An Empirical Correction for Absorption Anisotropy applied to Twinned crystals’. Universität Göttingen: Göttingen, Germany.

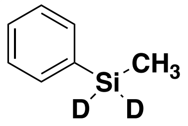
(23) Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

(24) Sheldrick, G. M., (2014). SHELXT. Universität Göttingen: Göttingen, Germany.

(25) Sheldrick, G. M., SHELXL2017/3 structure refined program - unpublished.

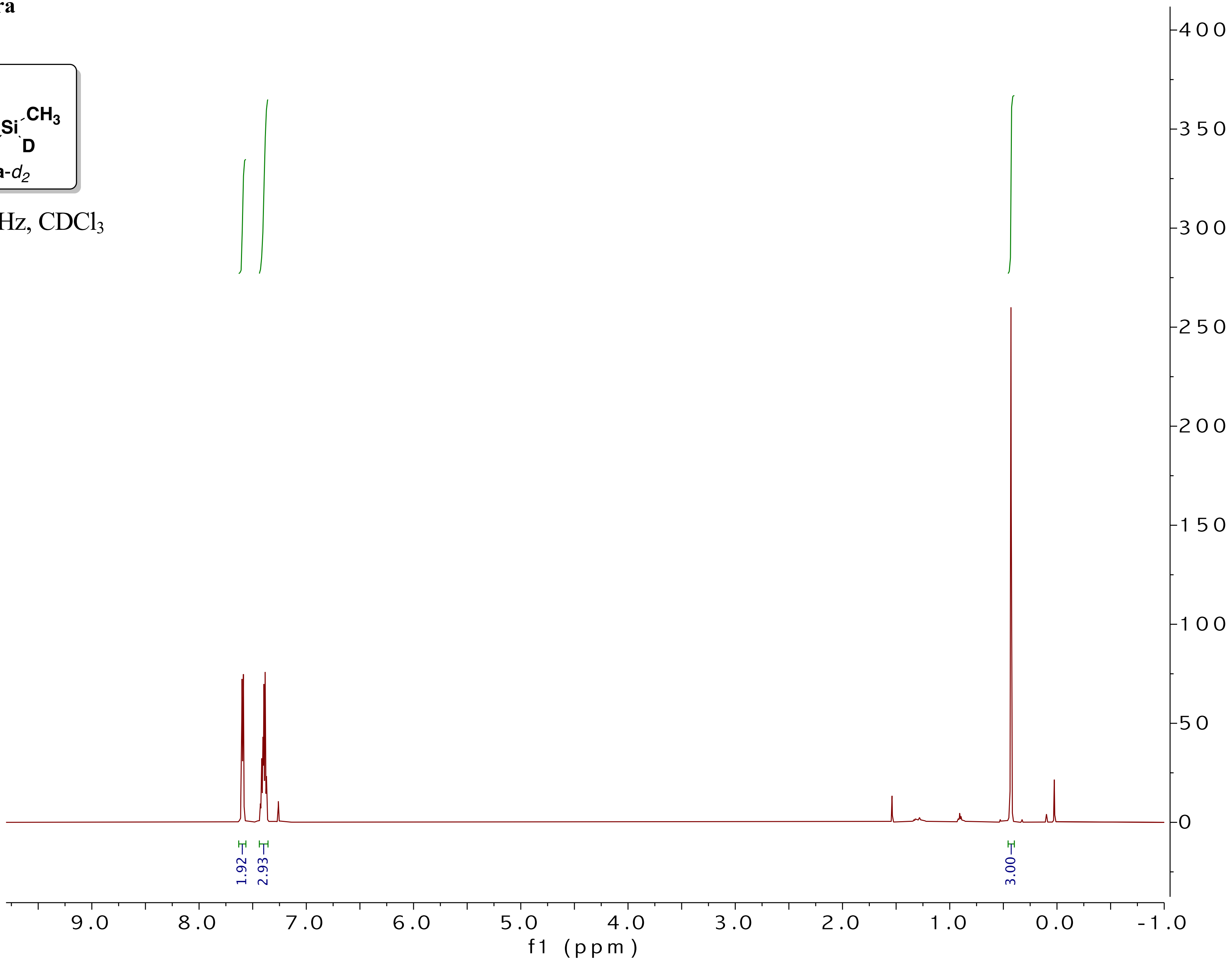
(26) On Enantiomorph-Polarity Estimation, Flack, H.D. (1983). Acta Cryst., A39, 876-881.

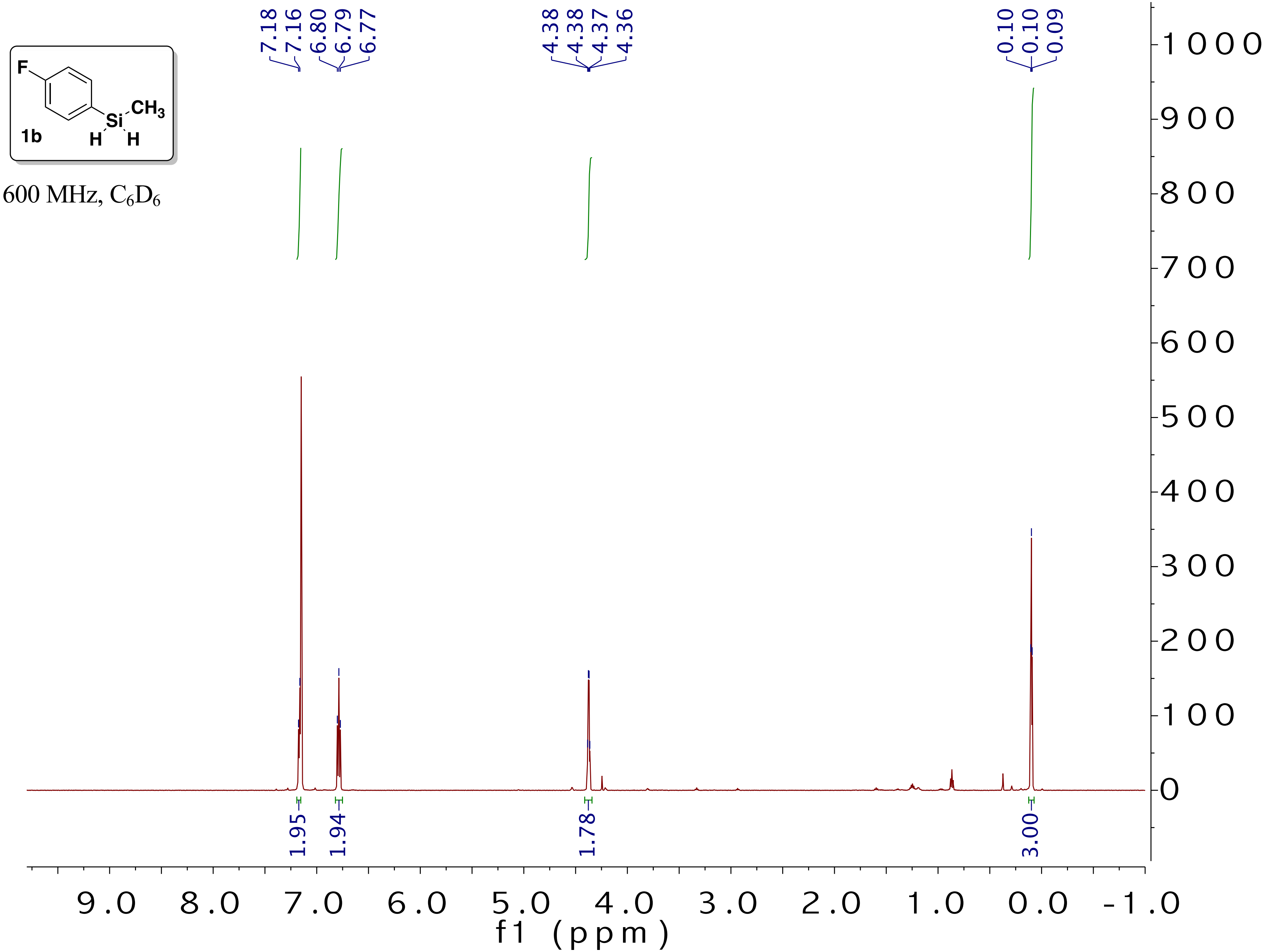
IX. Copies of NMR Spectra



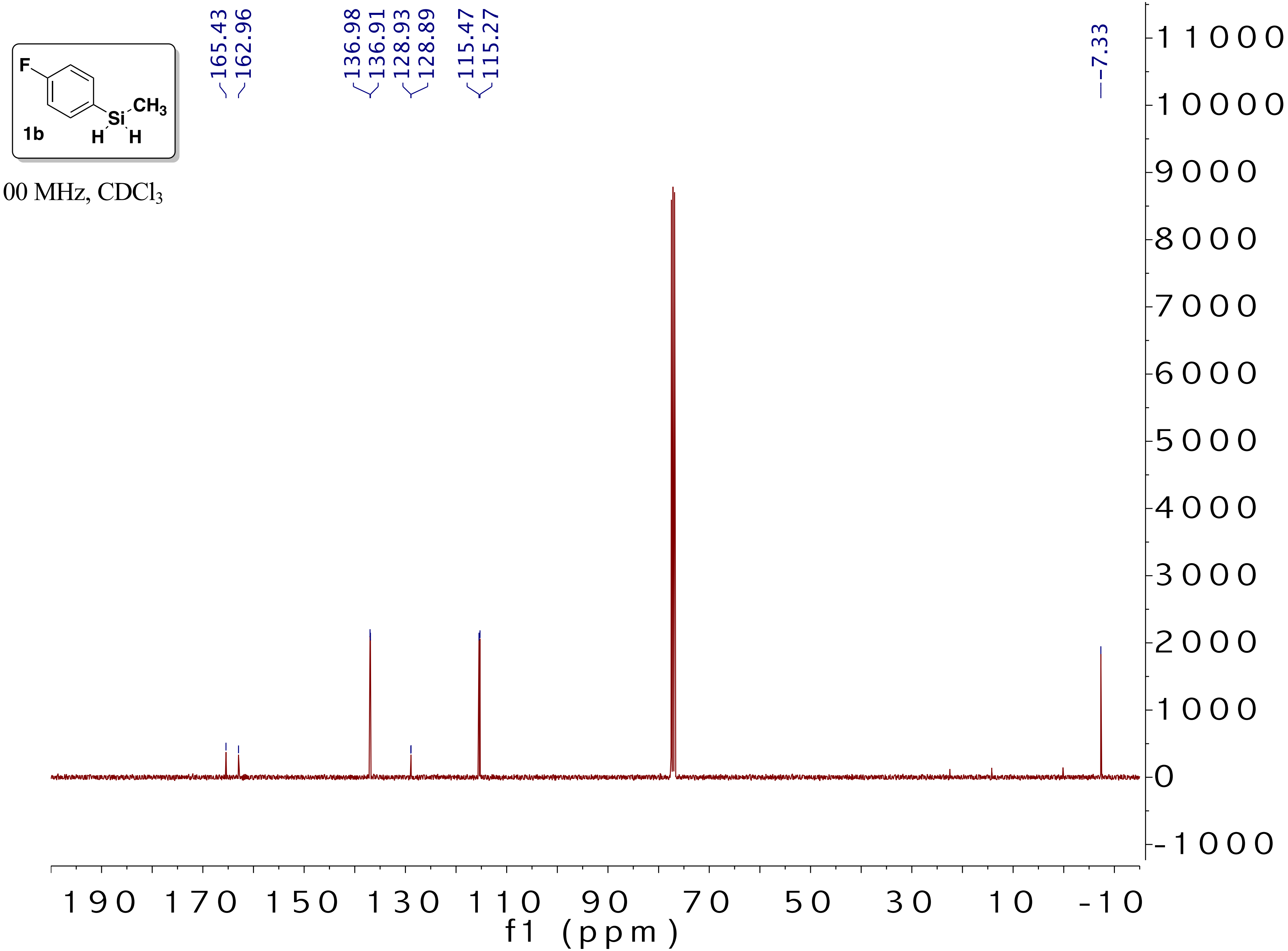
1a-d_2

^{1}H, 600 MHz, CDCl$_3$

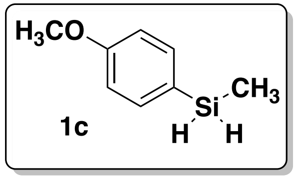




^{1}H, 600 MHz, C_6D_6

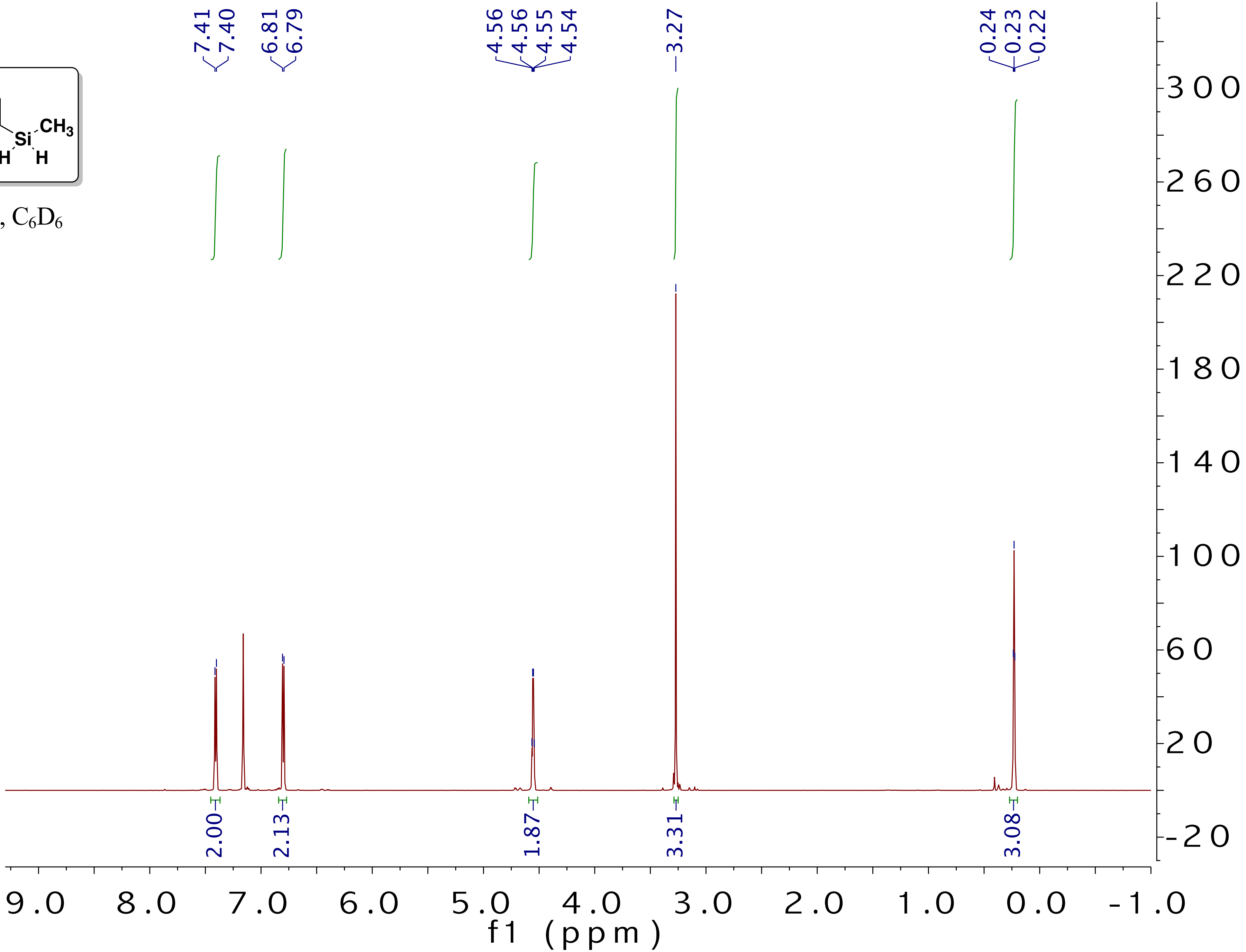

1b

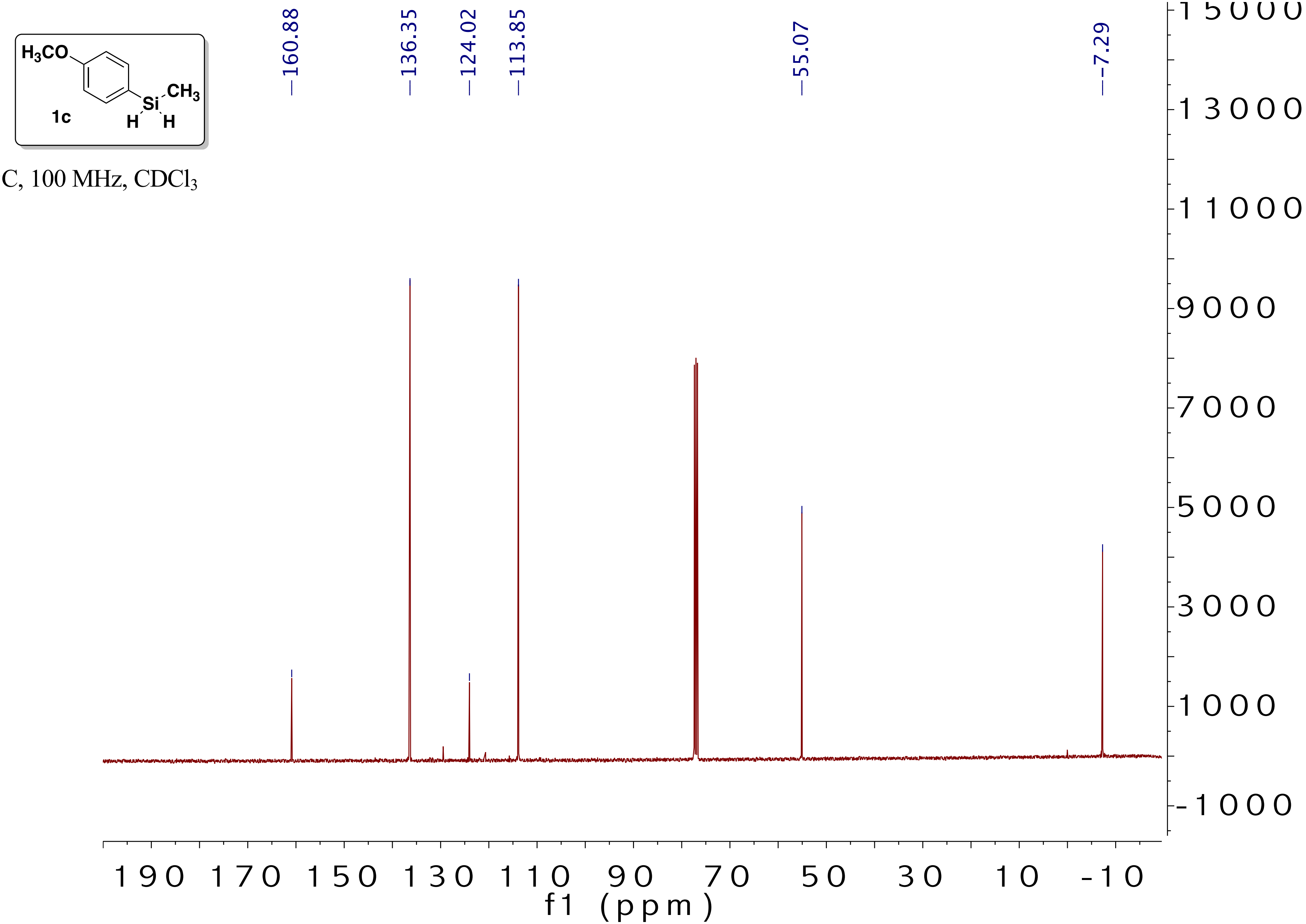
^{13}C, 100 MHz, CDCl$_3$



1c

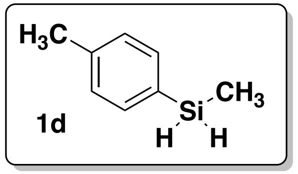
^{1}H, 600 MHz, C_6D_6





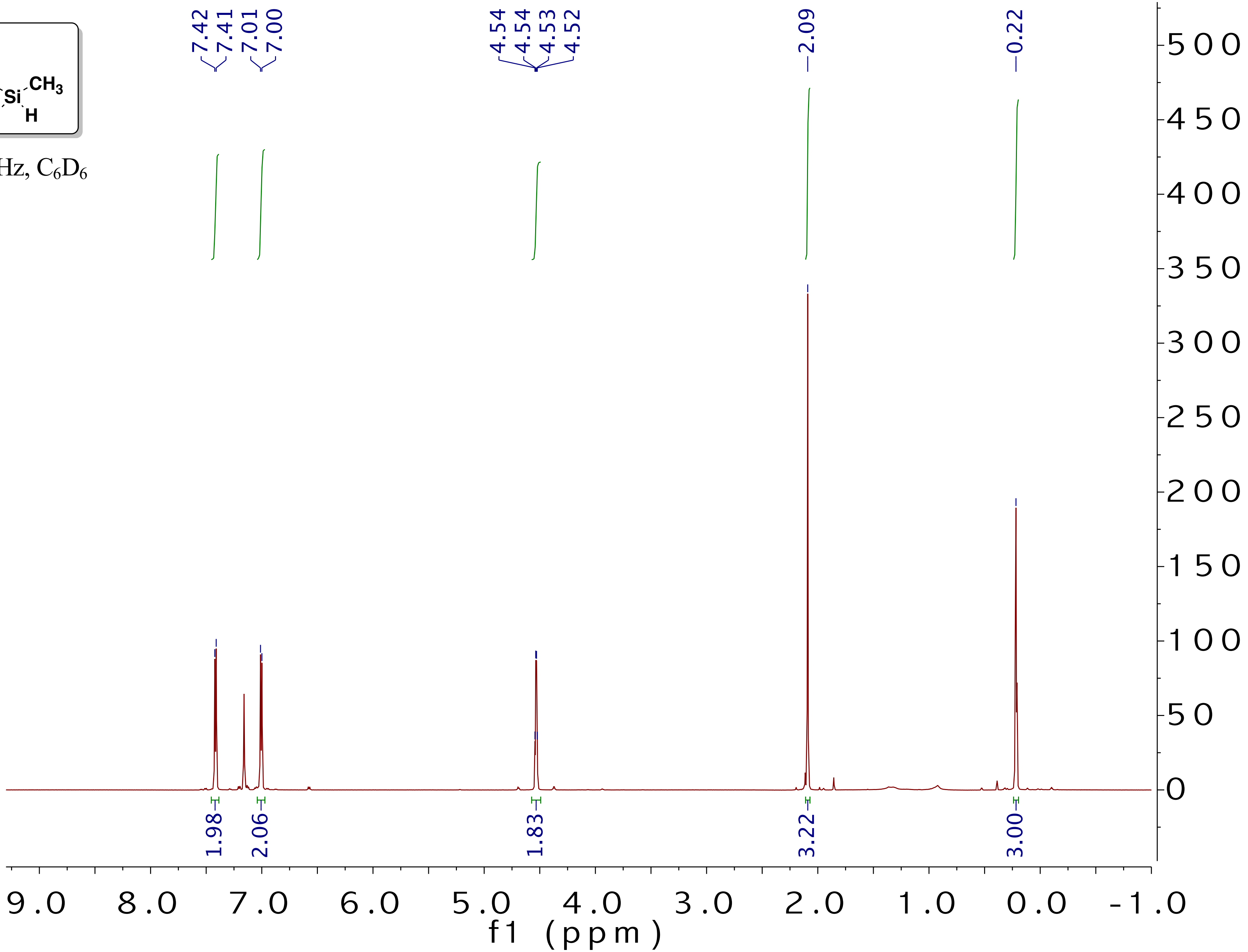
1c

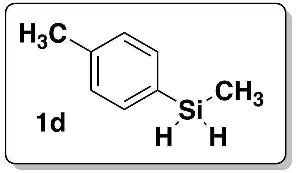
^{13}C, 100 MHz, CDCl$_3$



1d

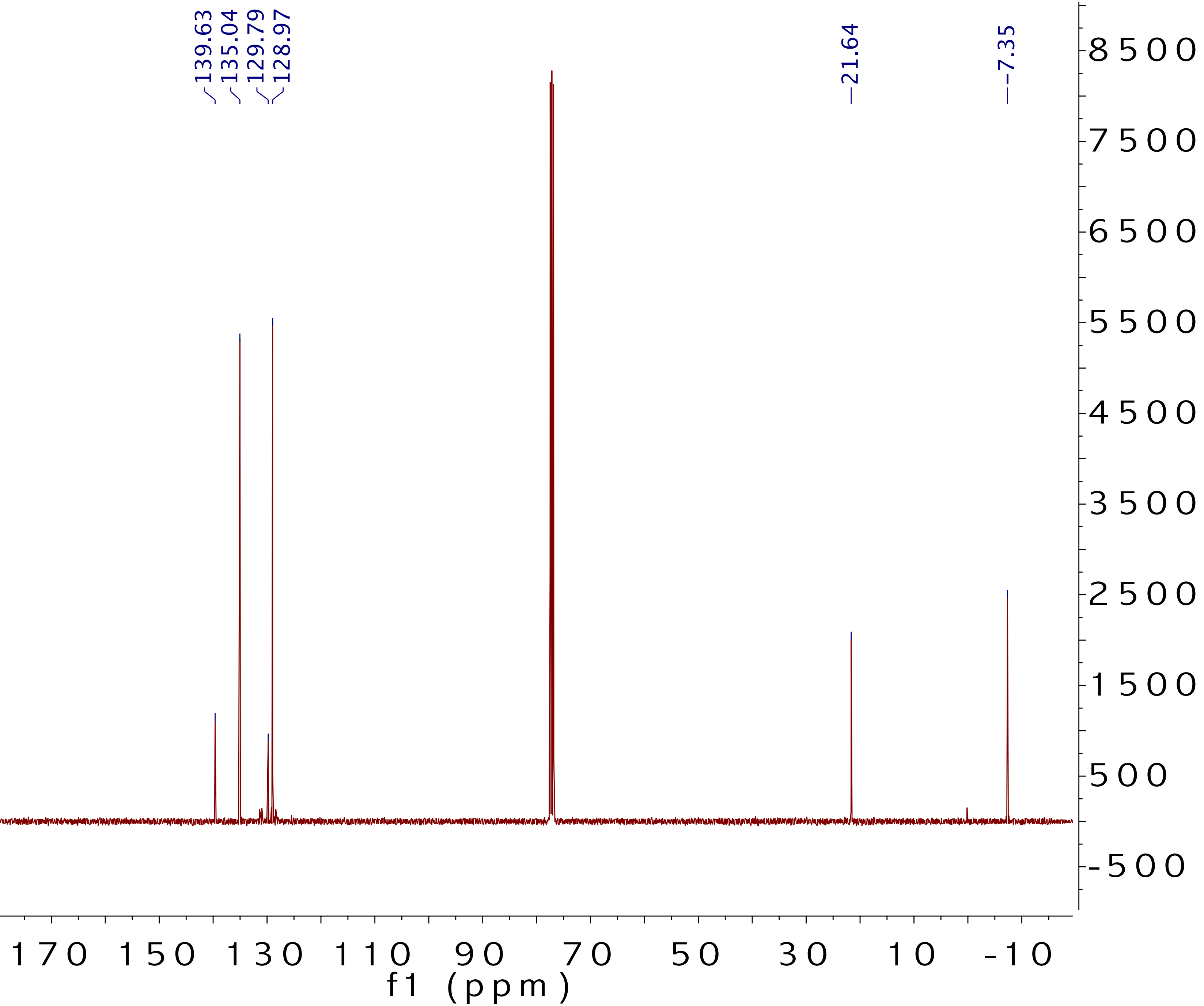
^{1}H, 600 MHz, C_6D_6

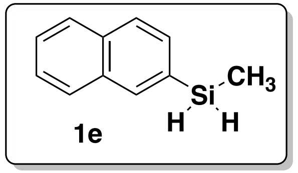




1d

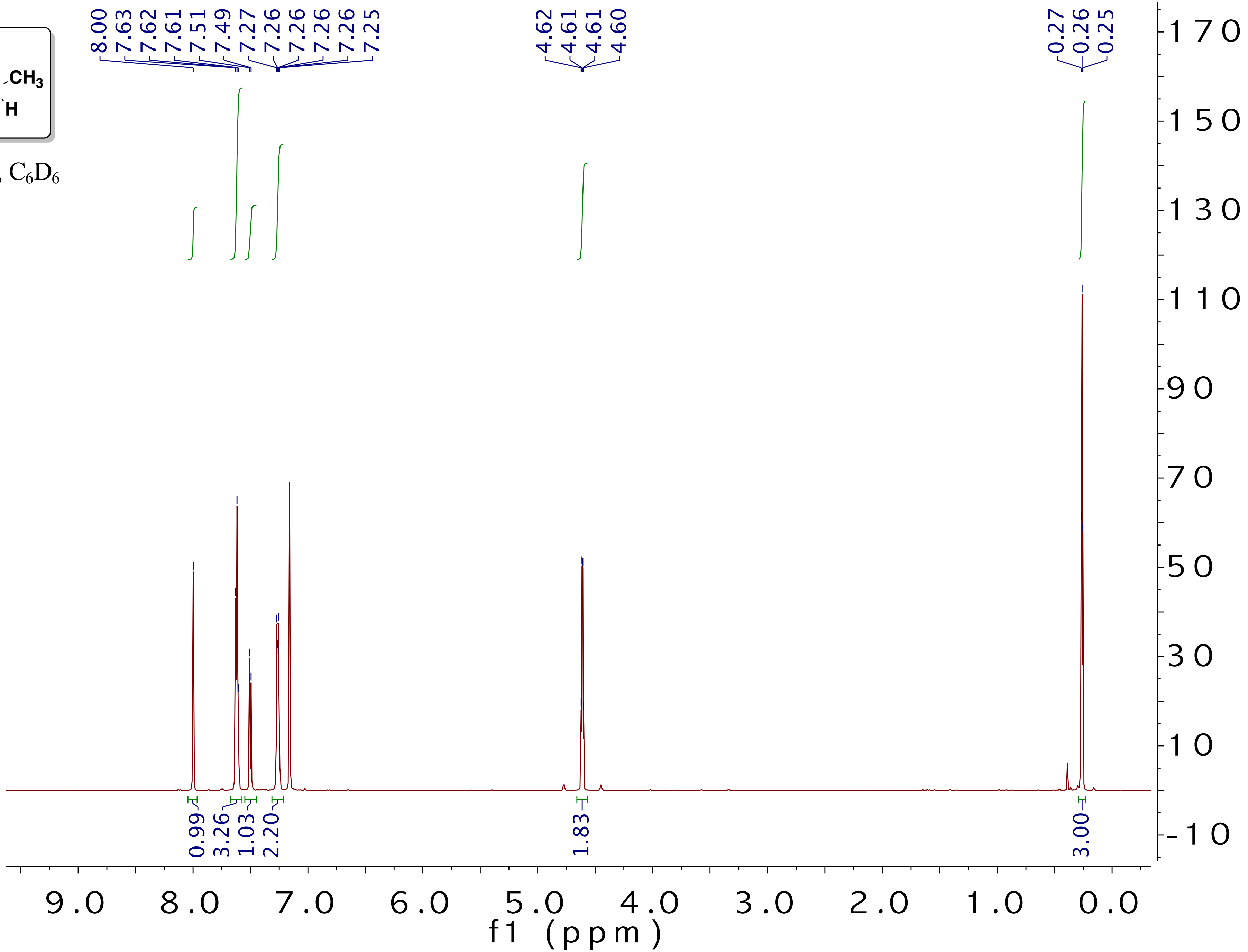
^{13}C, 100 MHz, CDCl$_3$

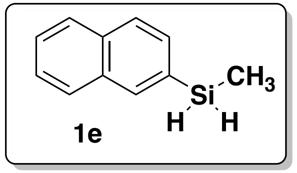




1e

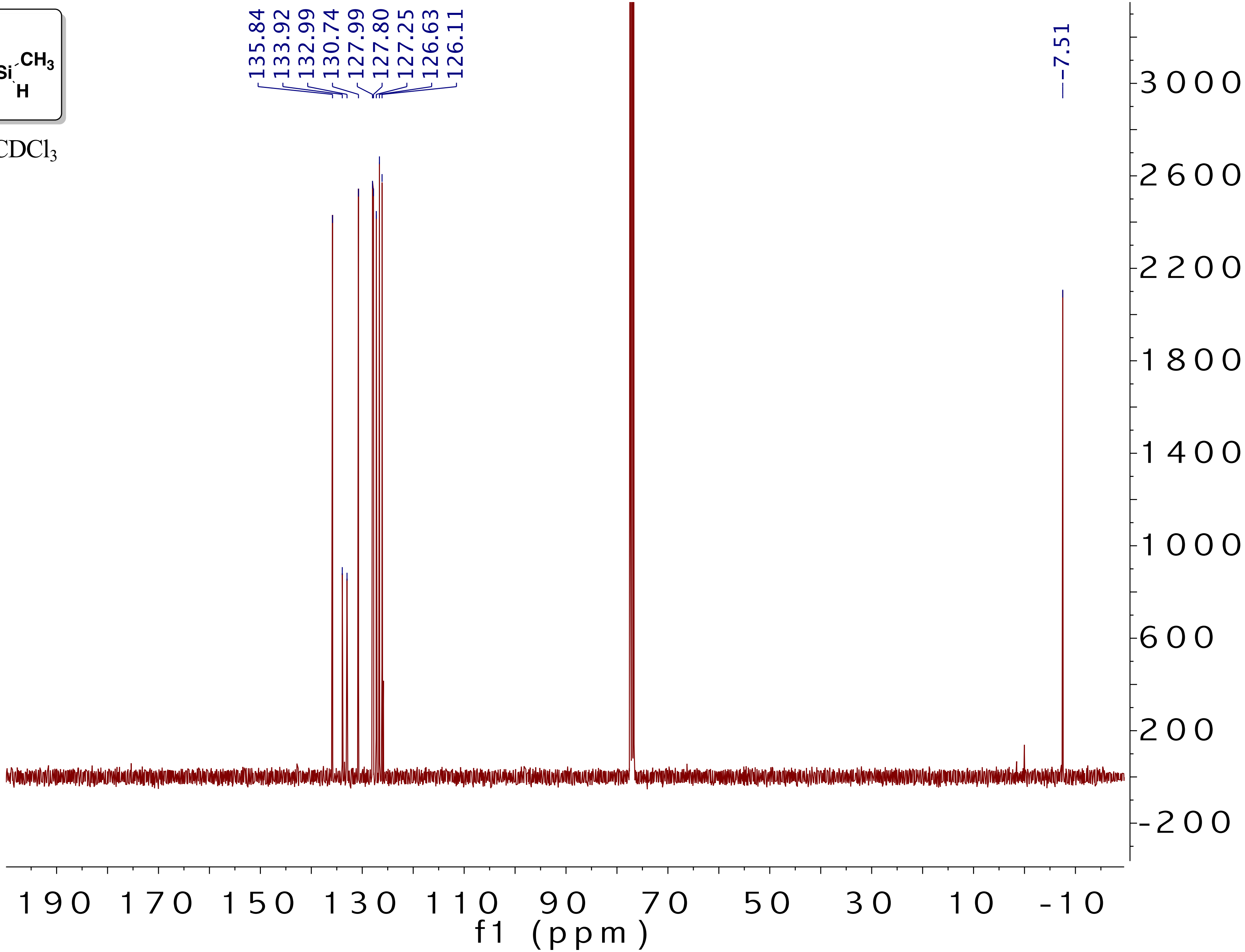
^{1}H, 600 MHz, C_6D_6

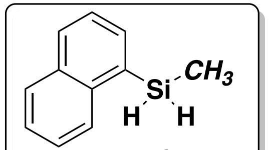




1e

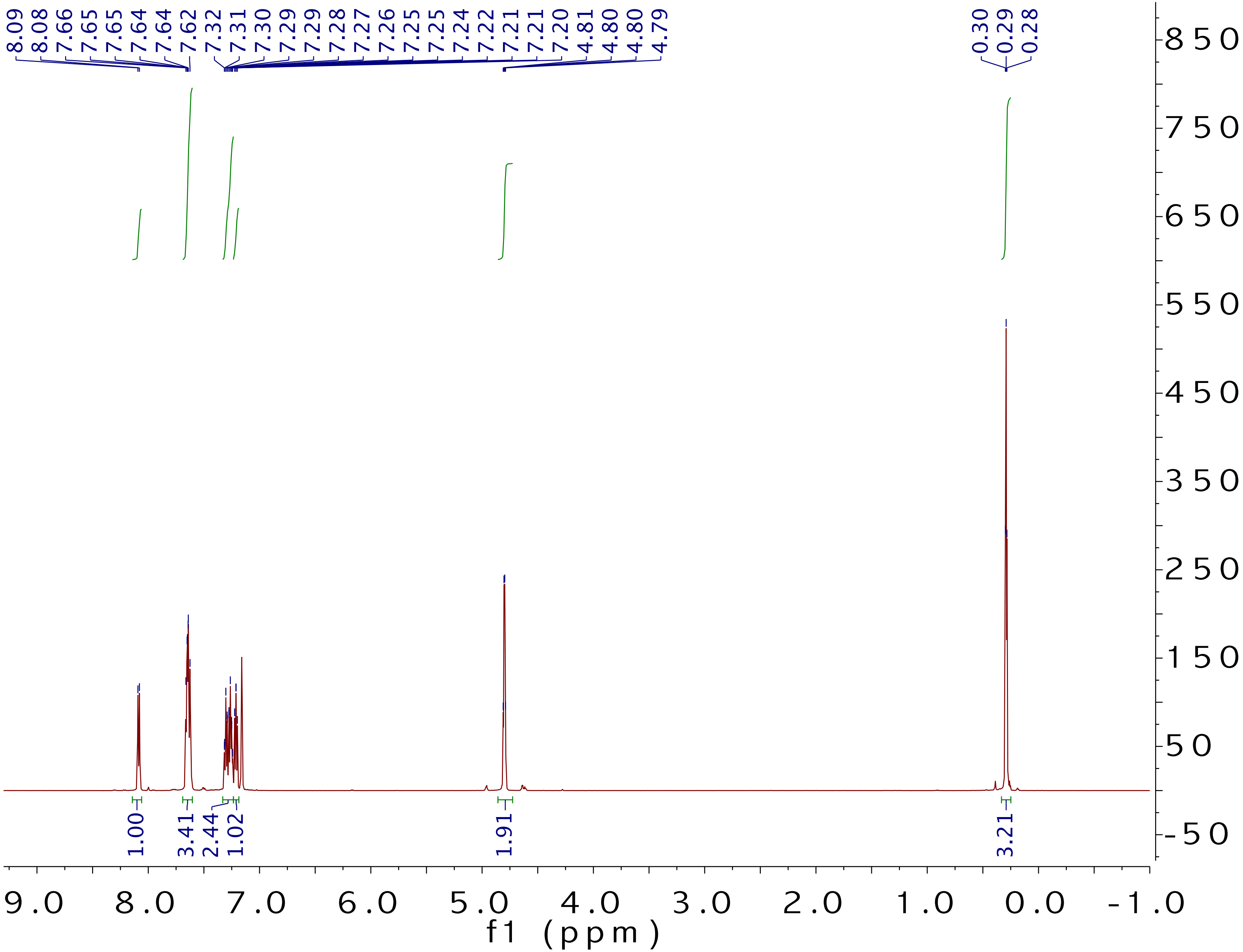
^{13}C, 100 MHz, CDCl$_3$

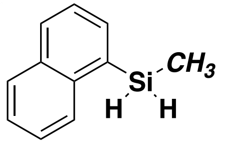




1f

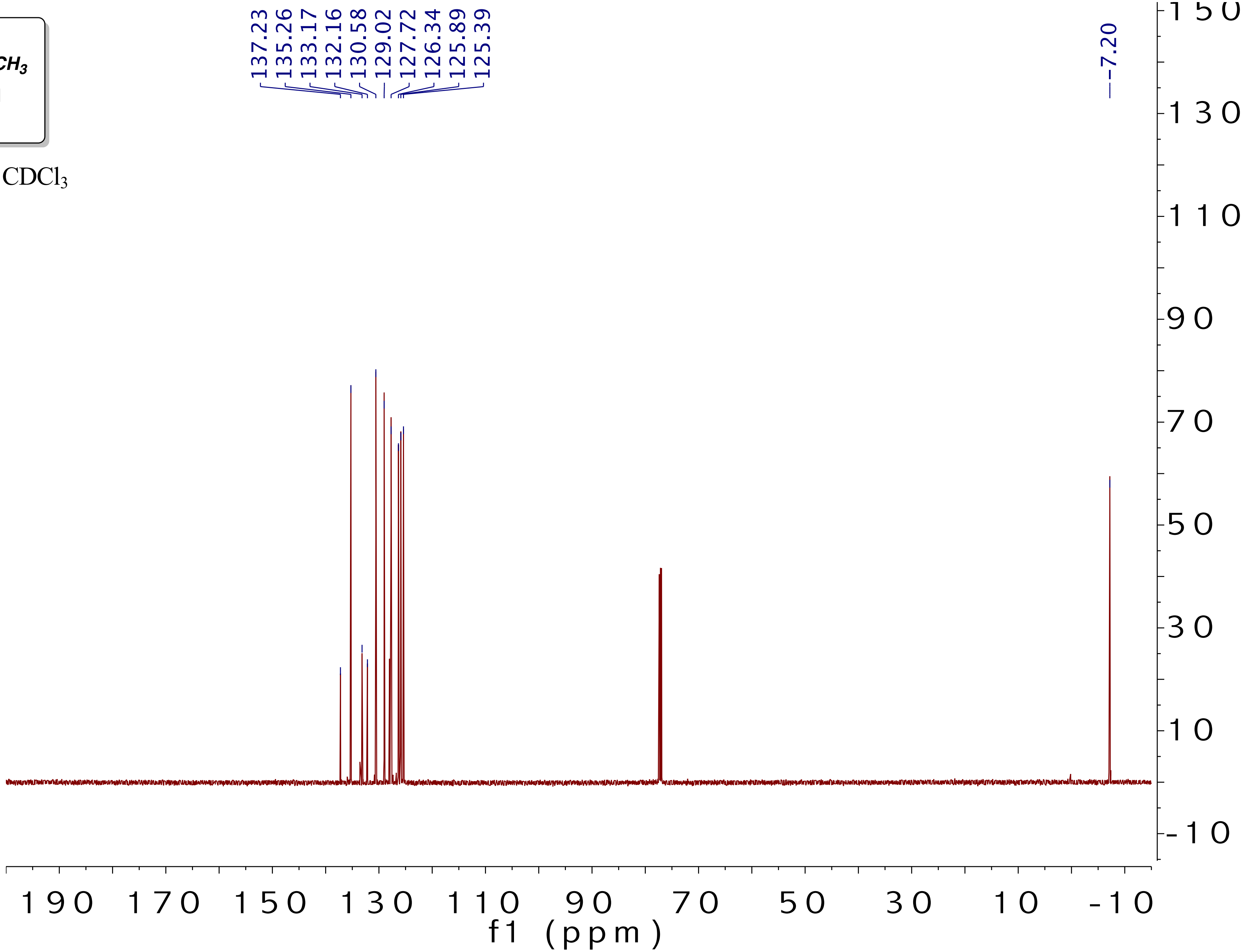
^{1}H, 600 MHz, CDCl$_3$

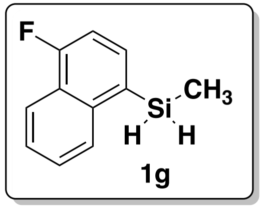




1f

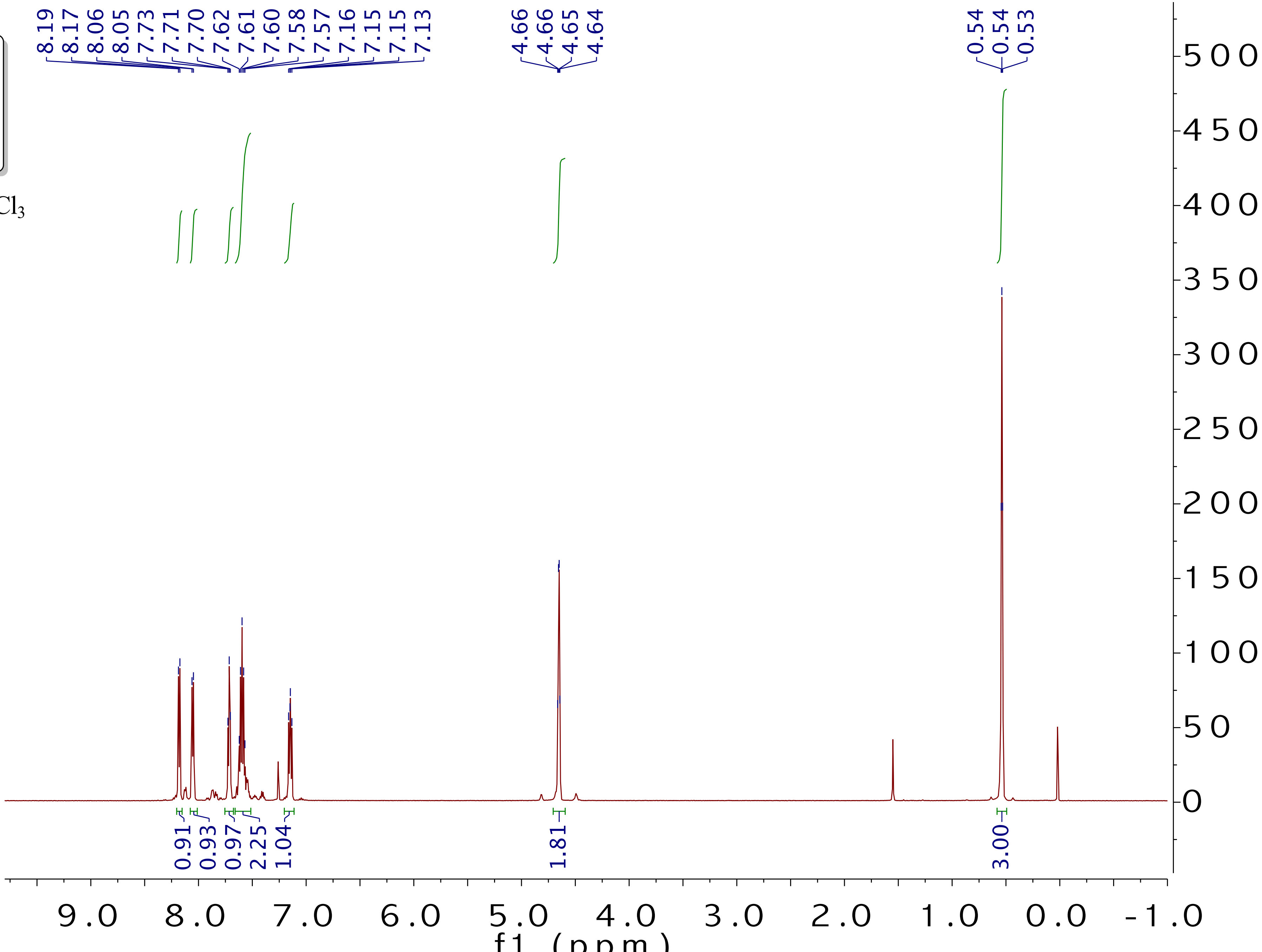
^{13}C, 151 MHz, CDCl$_3$

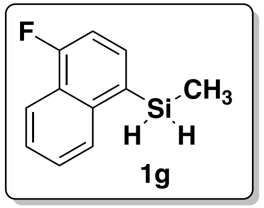




1g

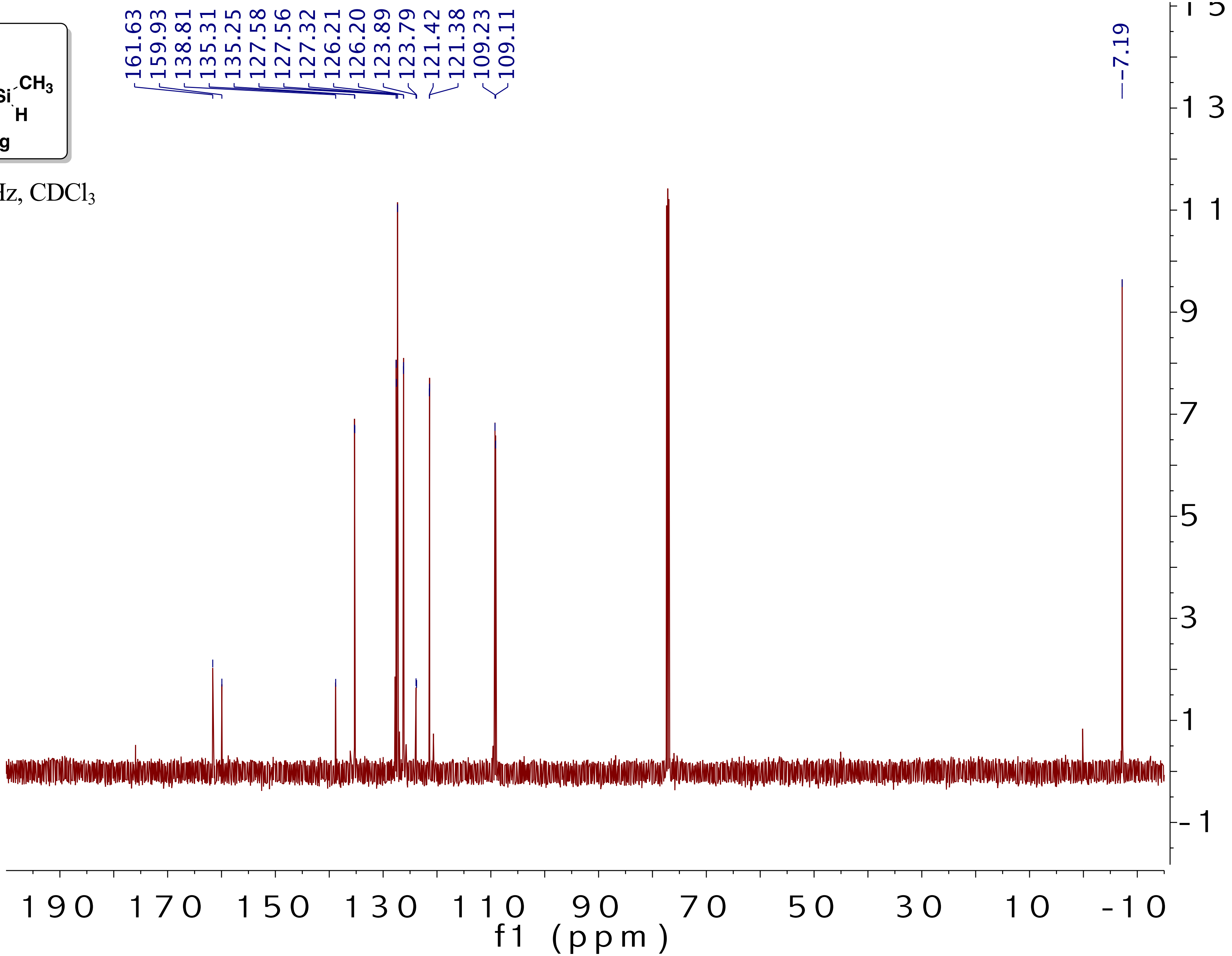
^{1}H, 400 MHz, CDCl$_3$

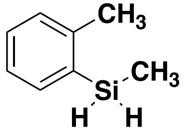




1g

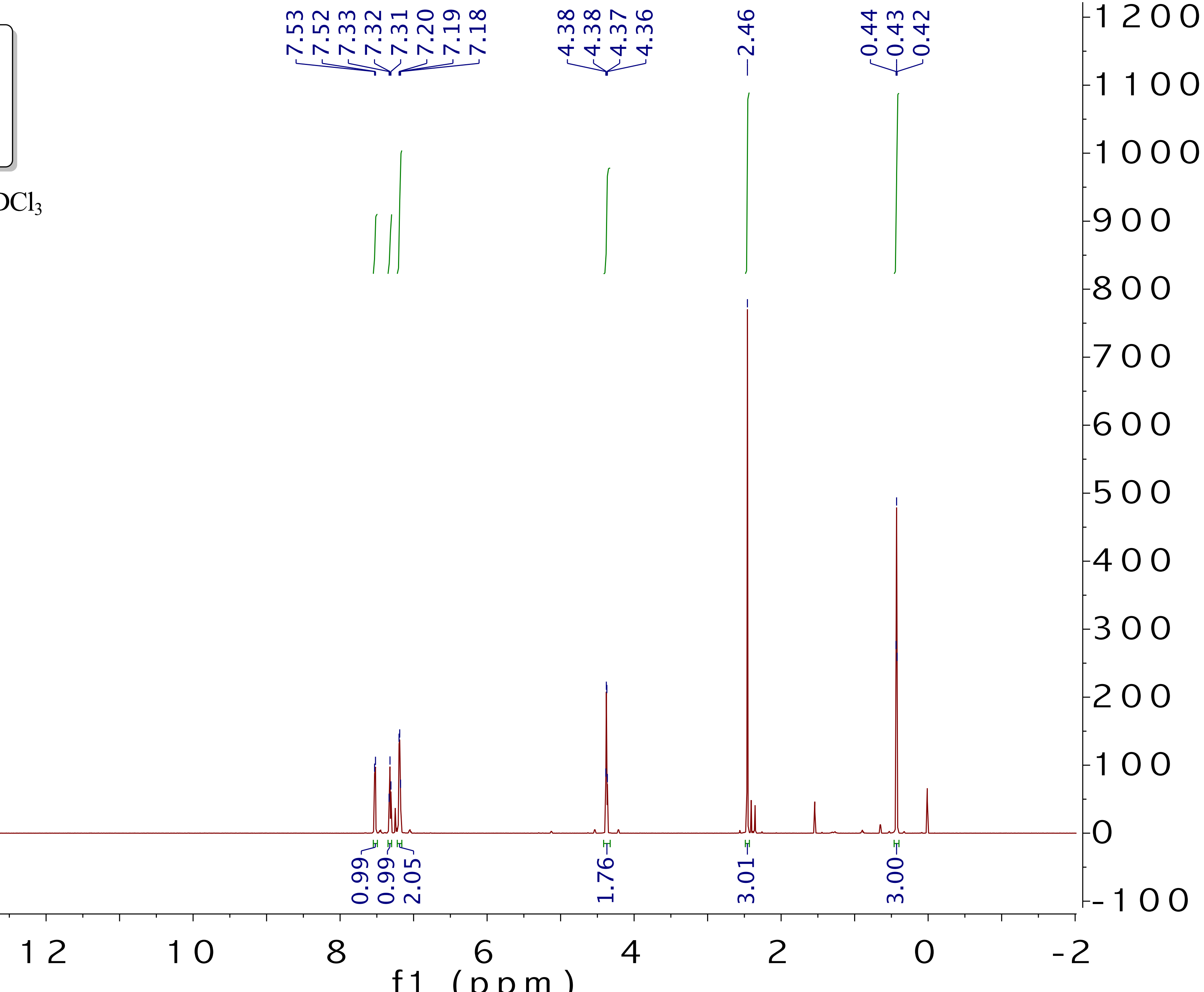
^{13}C, 151 MHz, CDCl$_3$

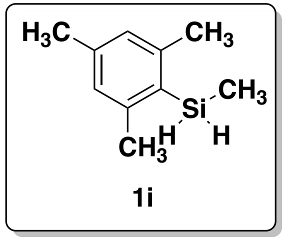




1h

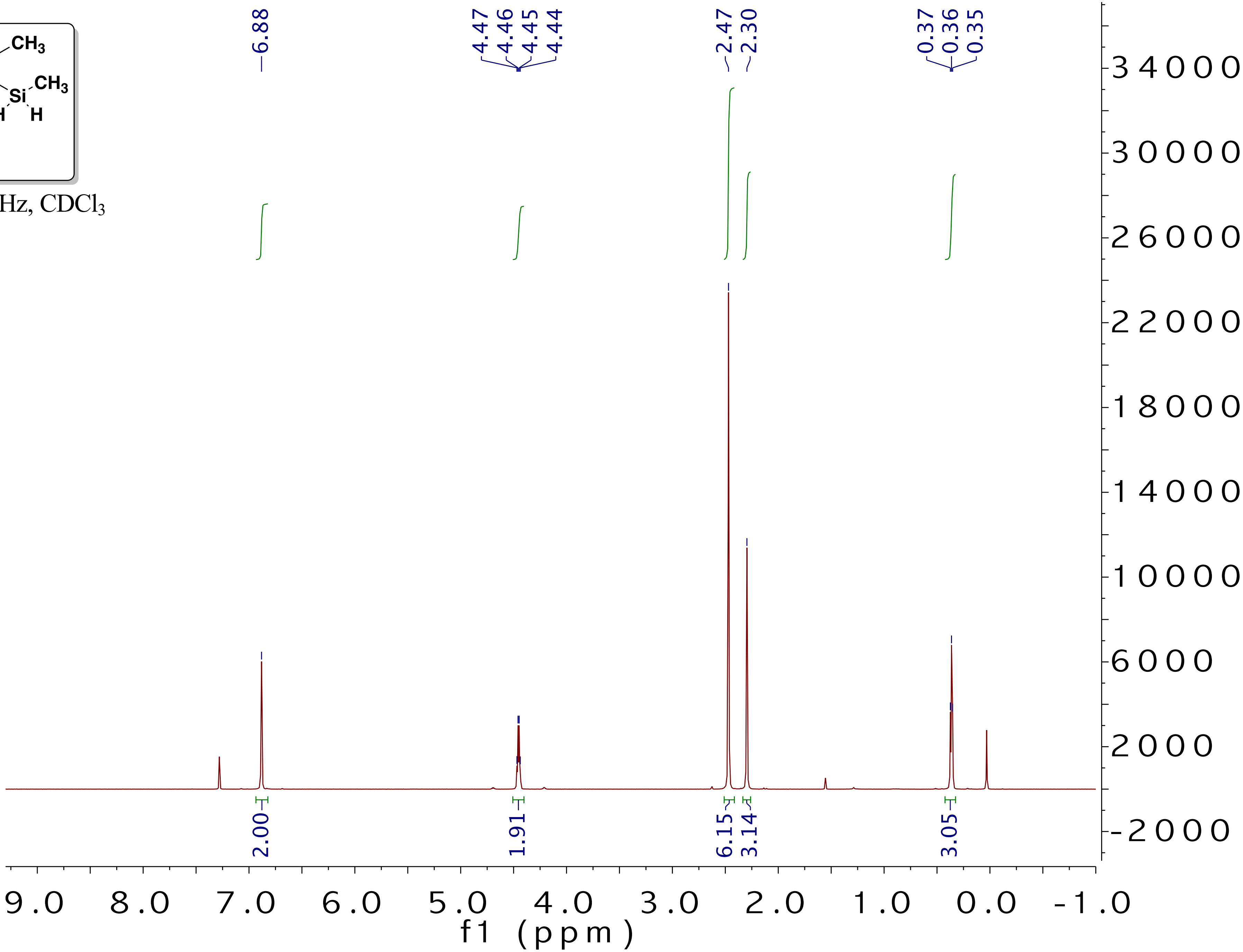
^{1}H, 600 MHz, CDCl$_3$

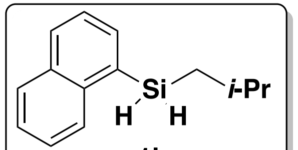




1i

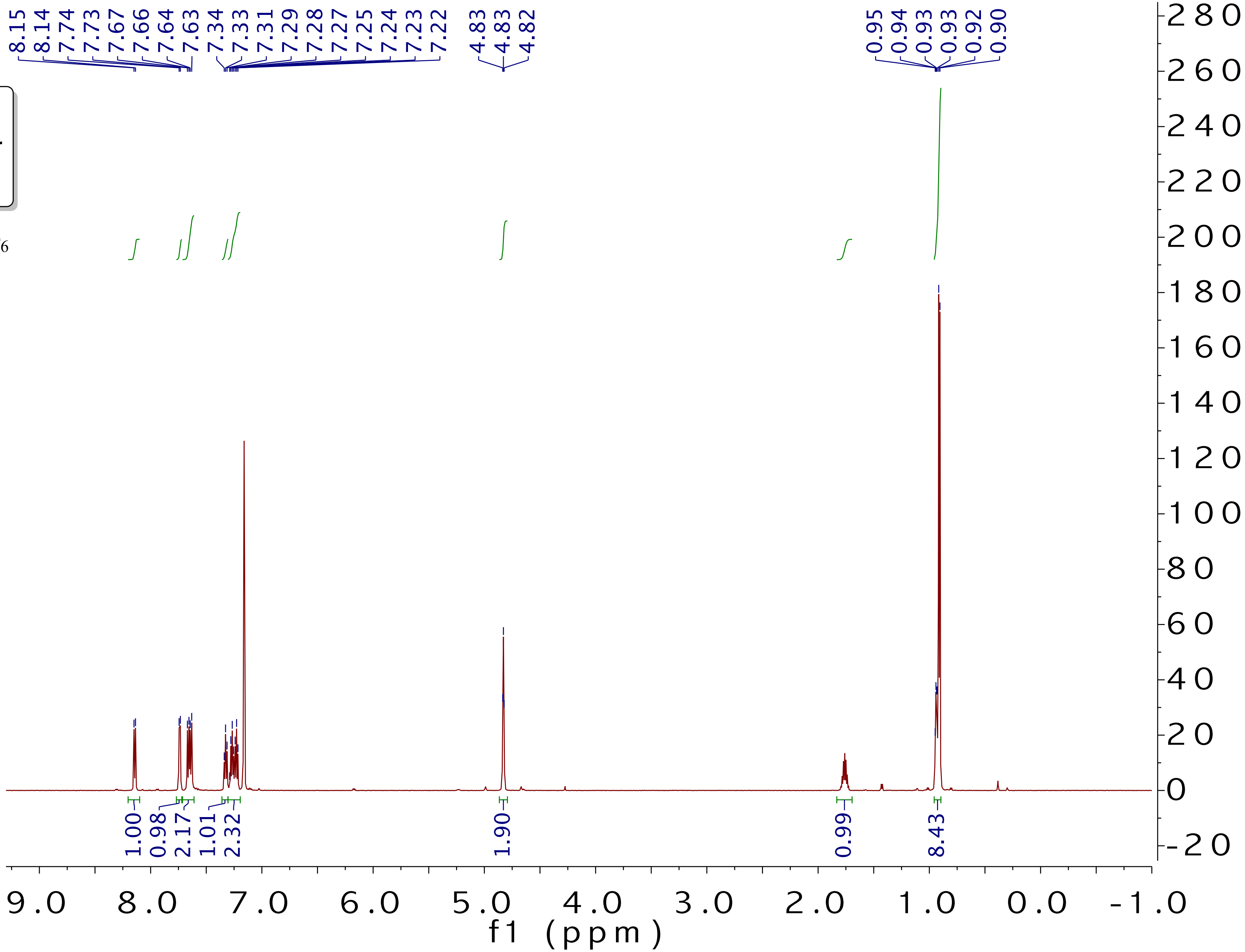
^{1}H, 400 MHz, CDCl$_3$

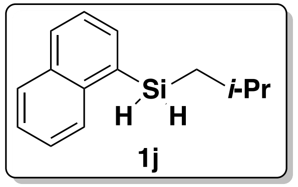




1j

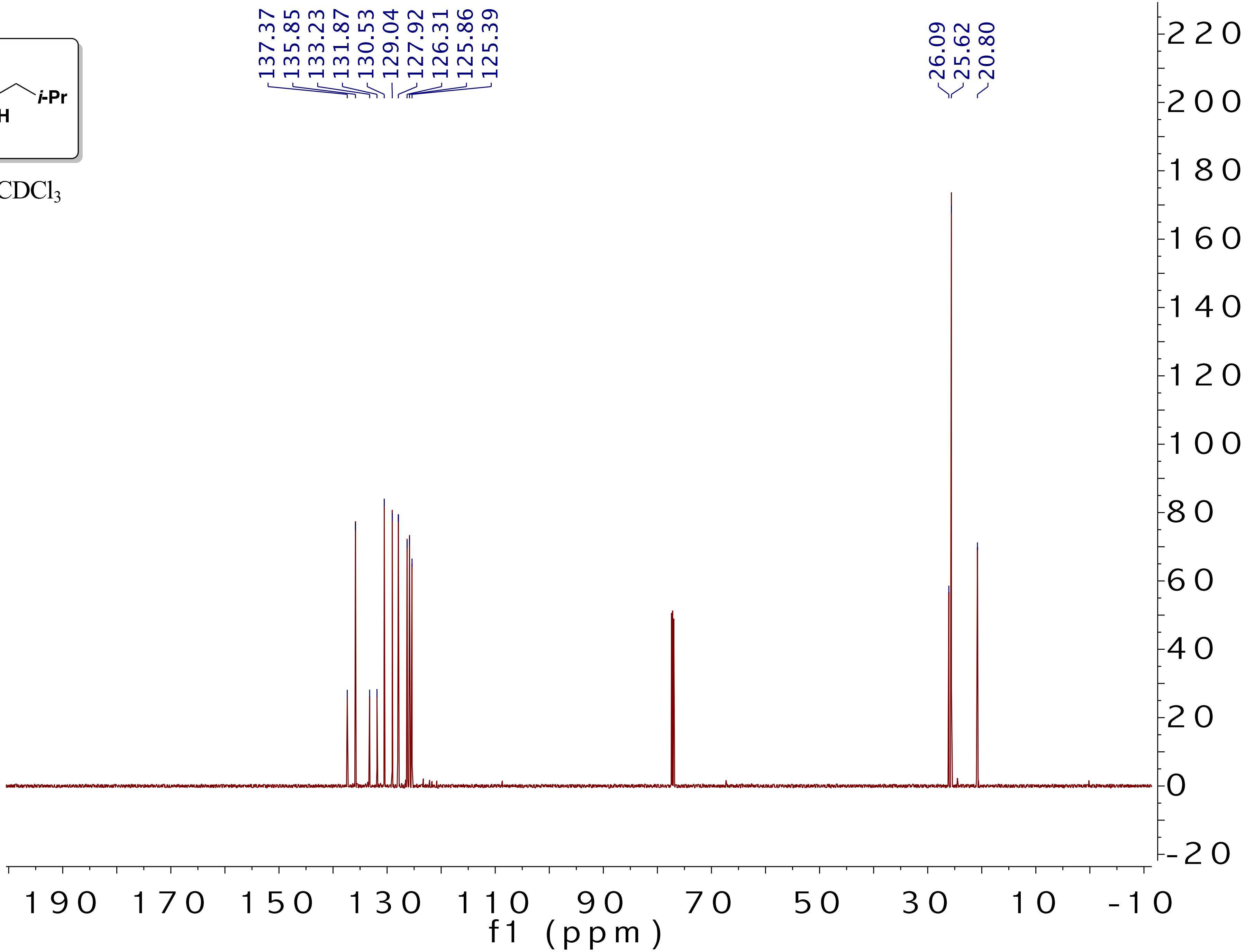
^{1}H, 600 MHz, C_6D_6

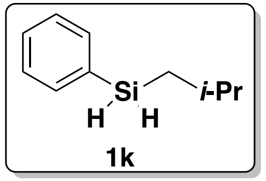




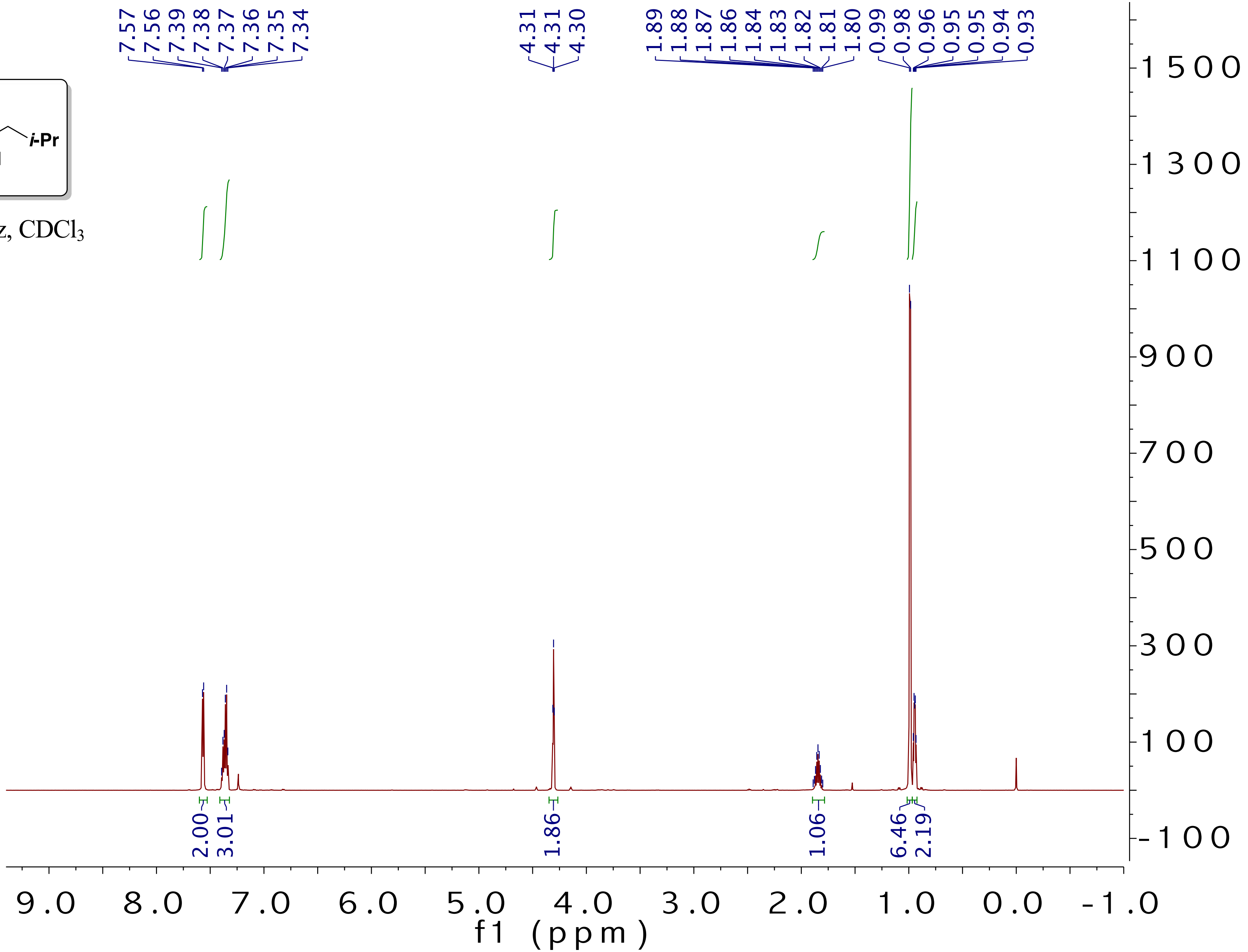
1j

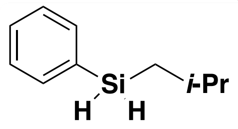
^{13}C, 151 MHz, CDCl$_3$




1k

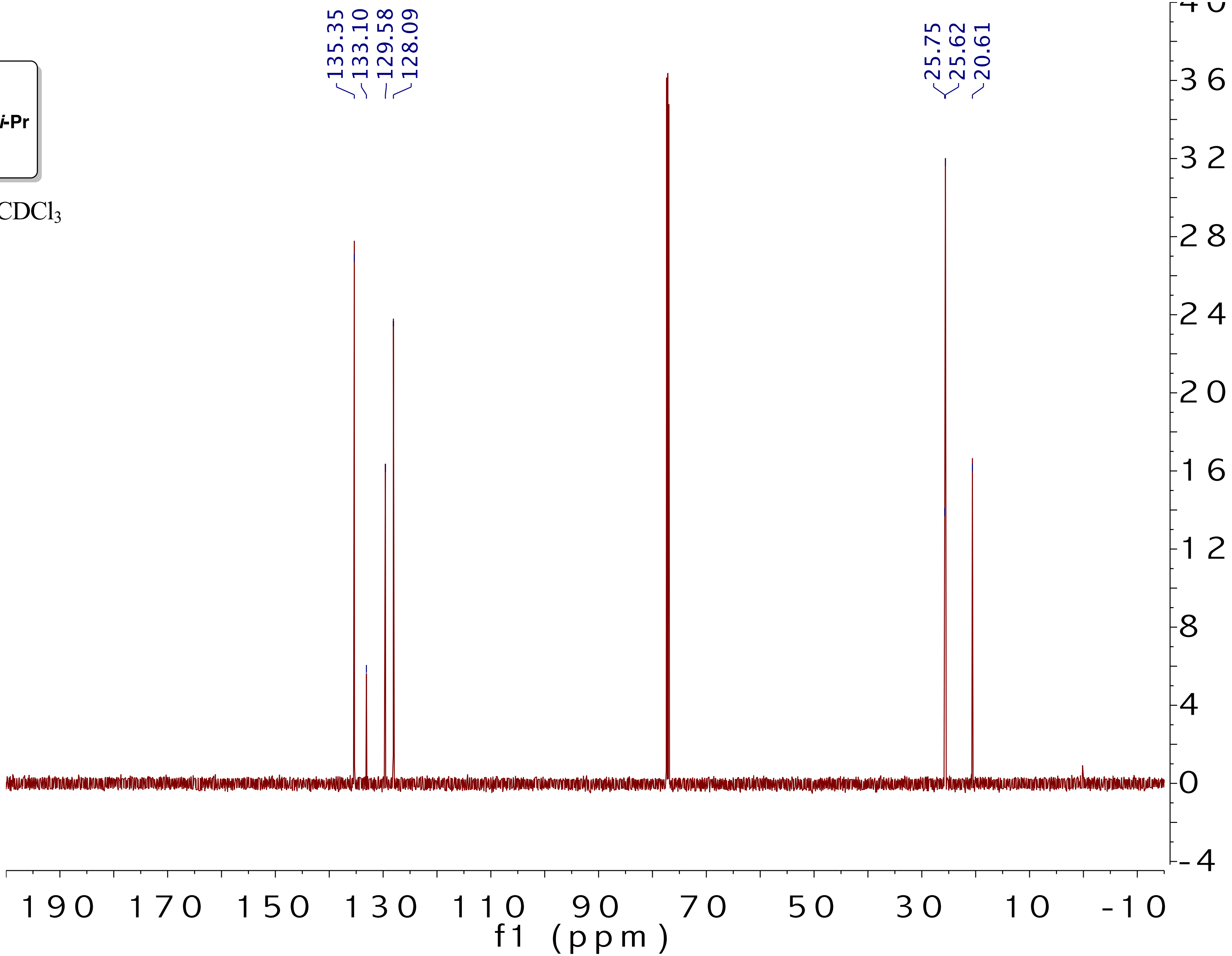
^1H, 600 MHz, $CDCl_3$

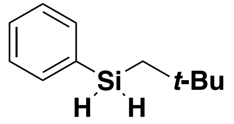




1k

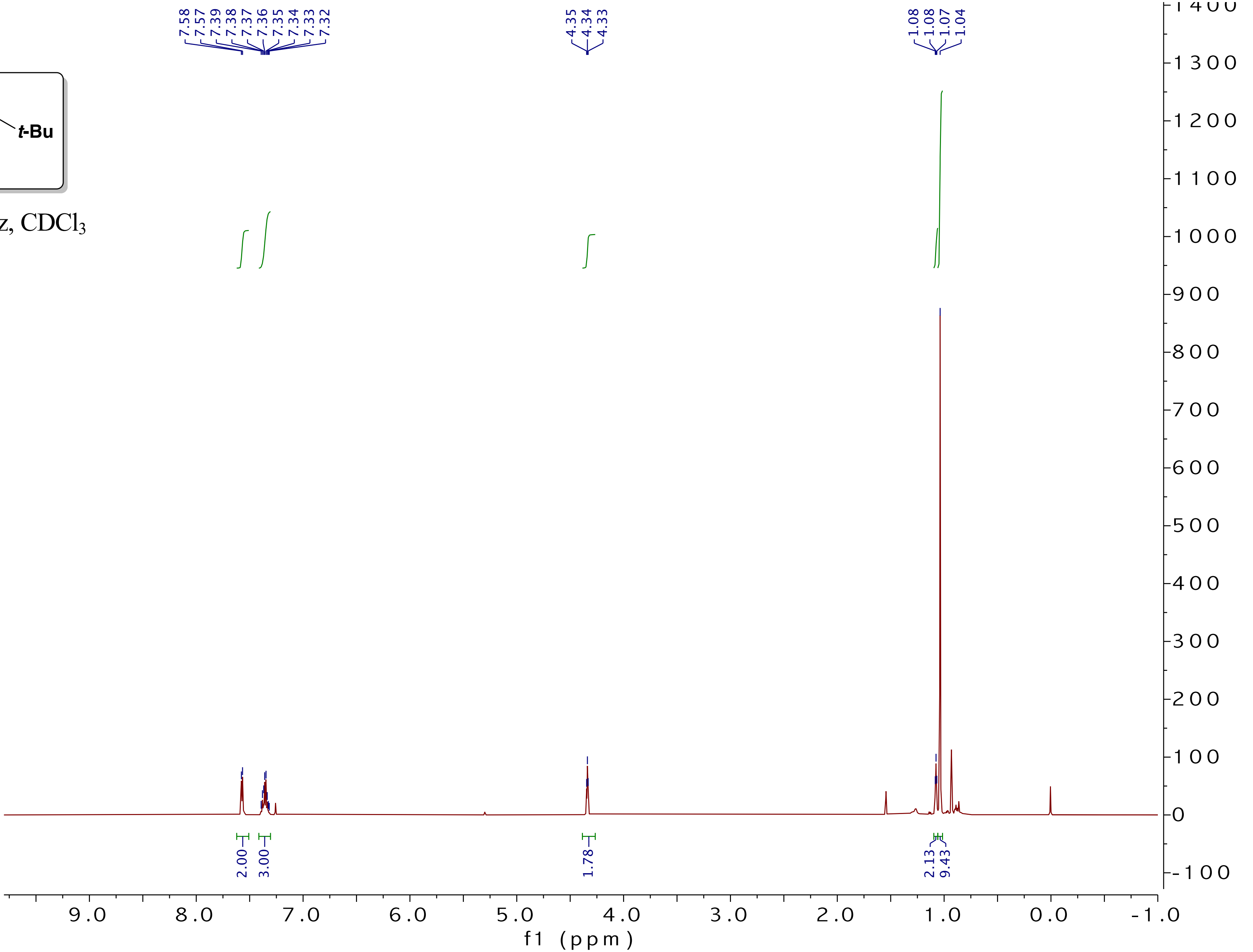
^{13}C, 151 MHz, $CDCl_3$

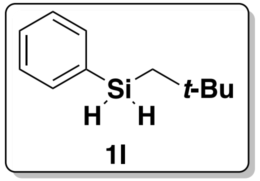




1l

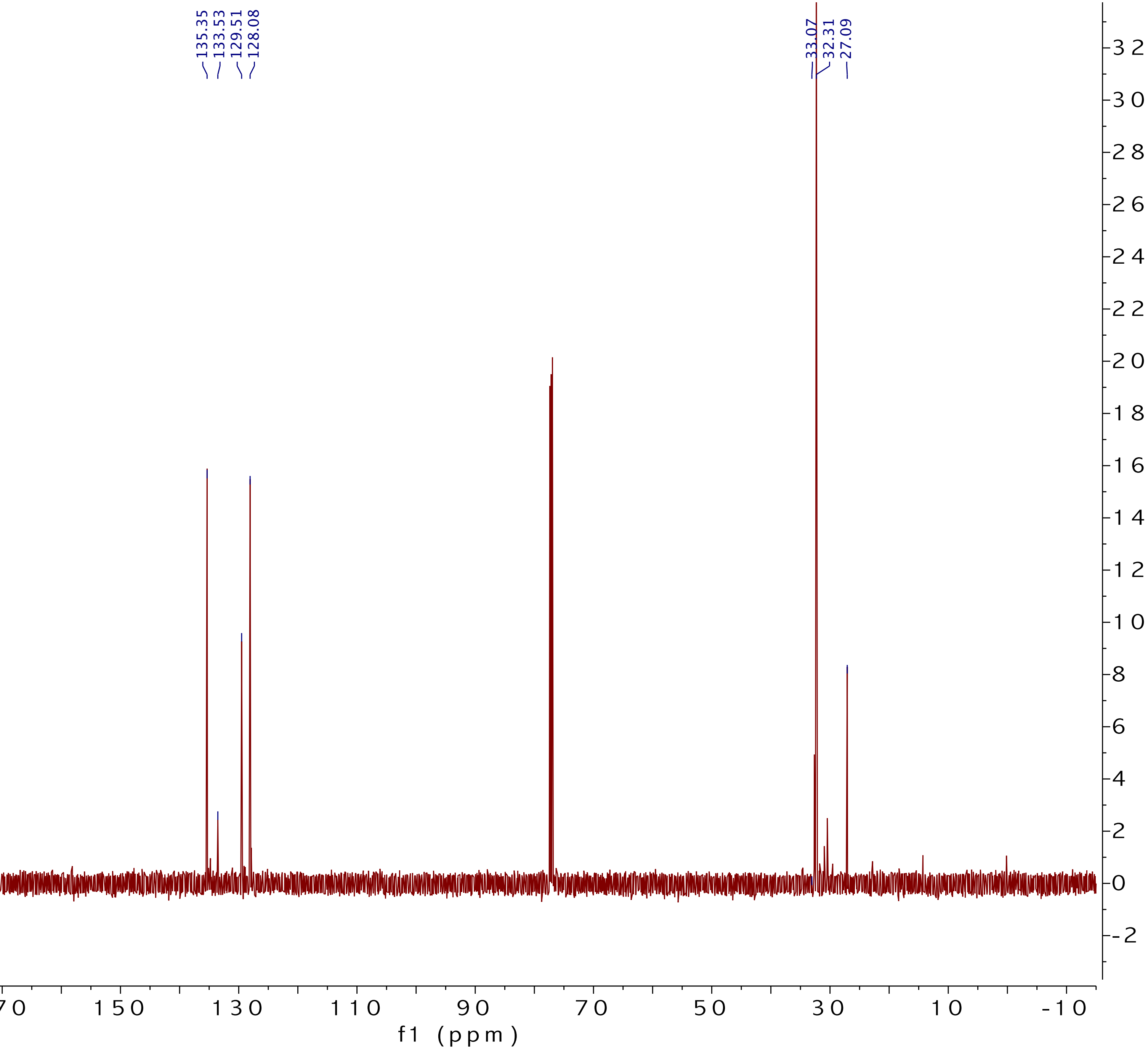
^{1}H, 600 MHz, CDCl$_3$

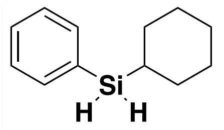




1l

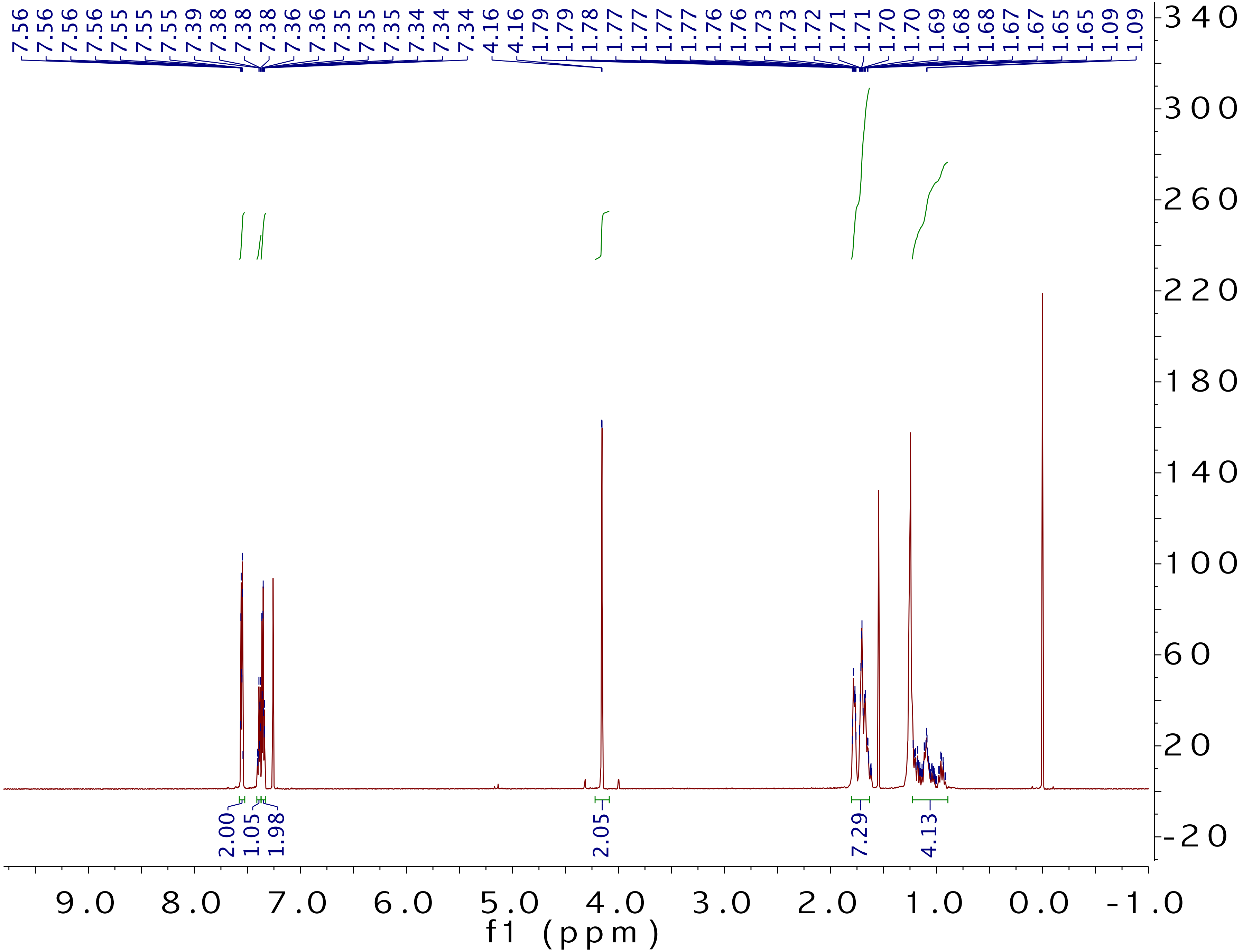
^{13}C, 151 MHz, CDCl$_3$

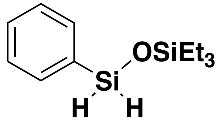




1m

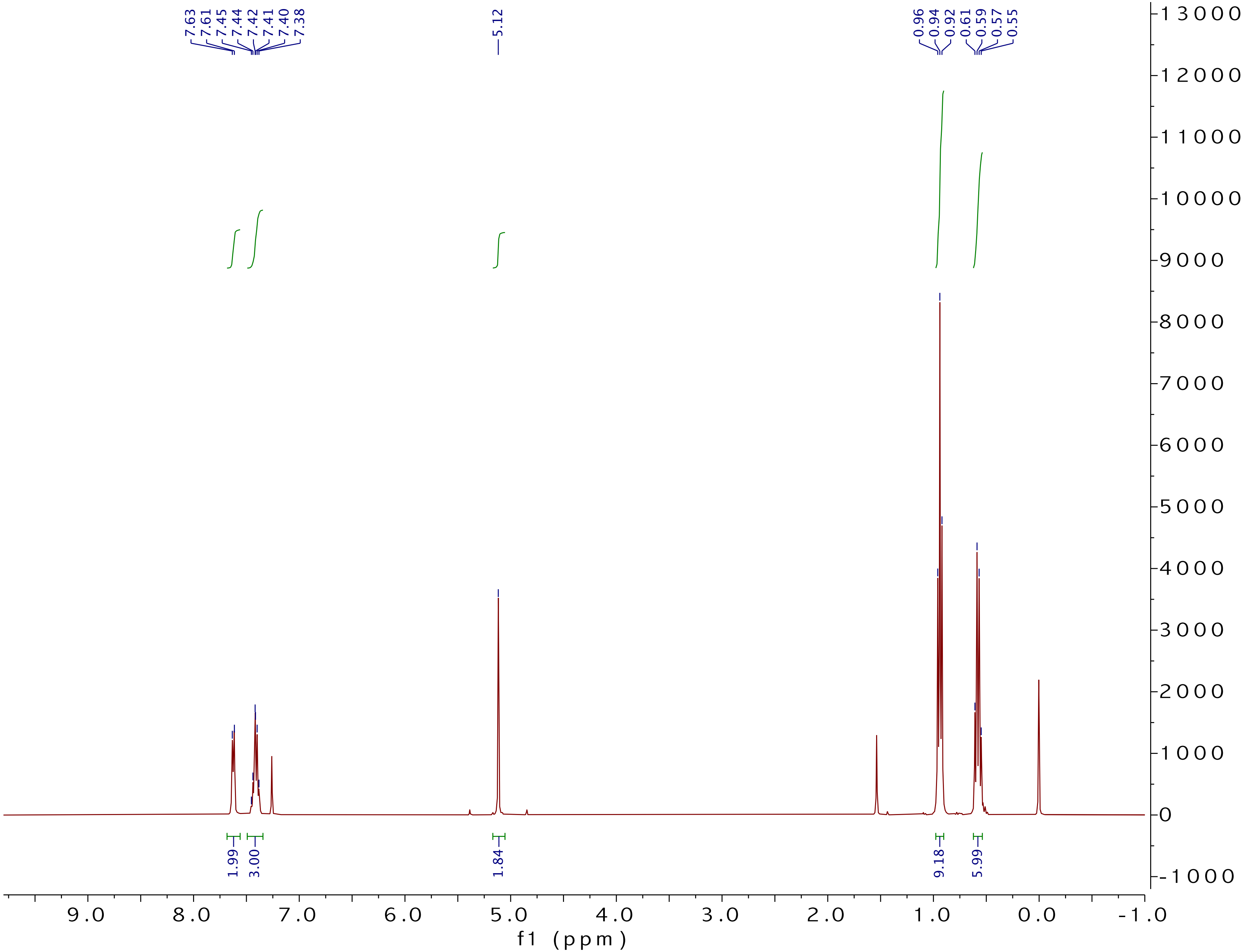
^{1}H, 600 MHz, CDCl$_3$

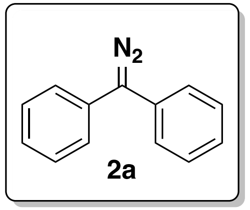




1n

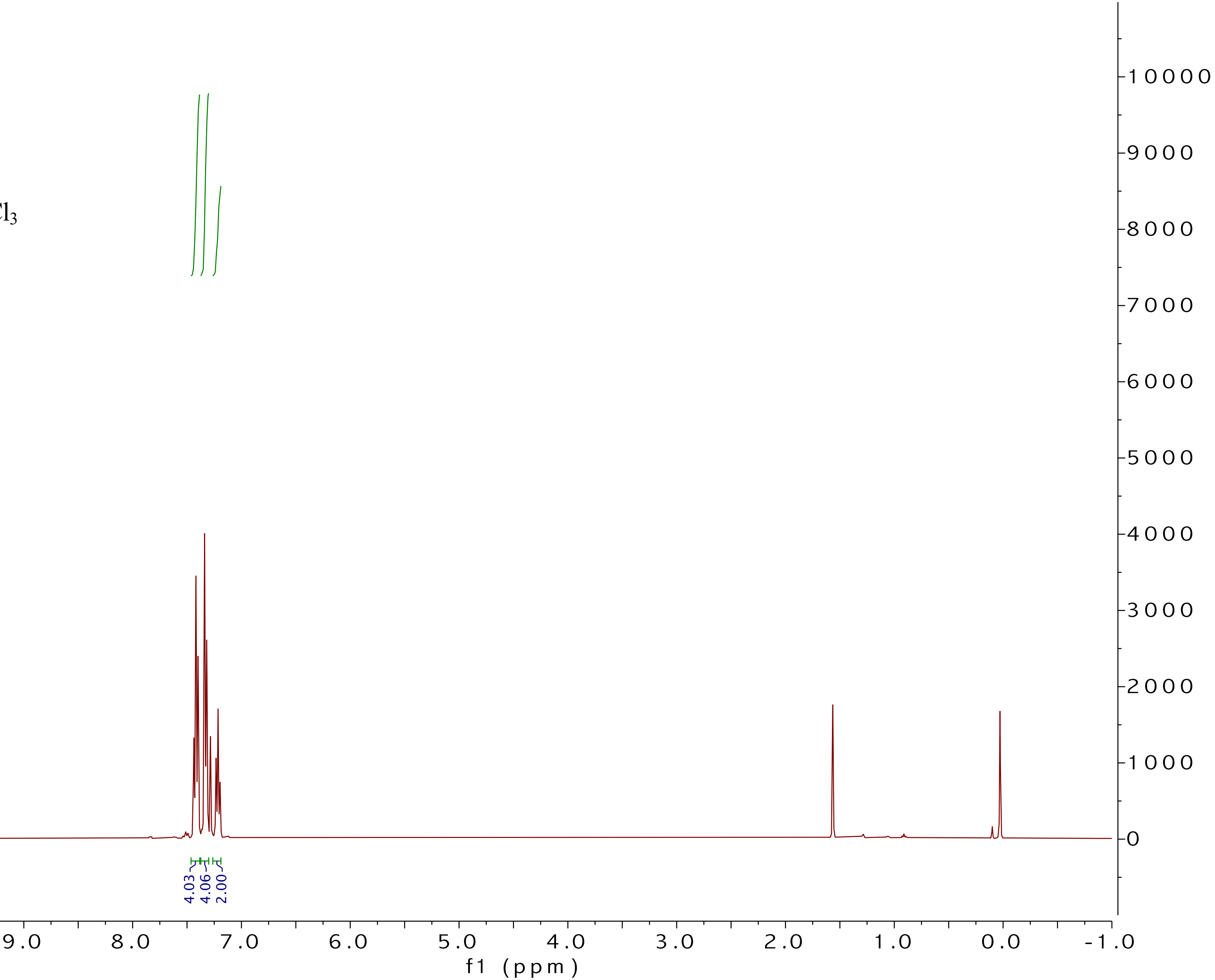
^{1}H, 400 MHz, CDCl$_3$

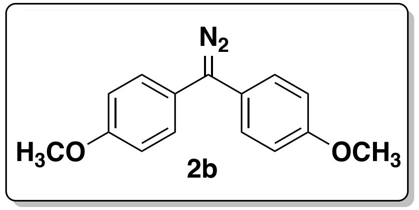




2a

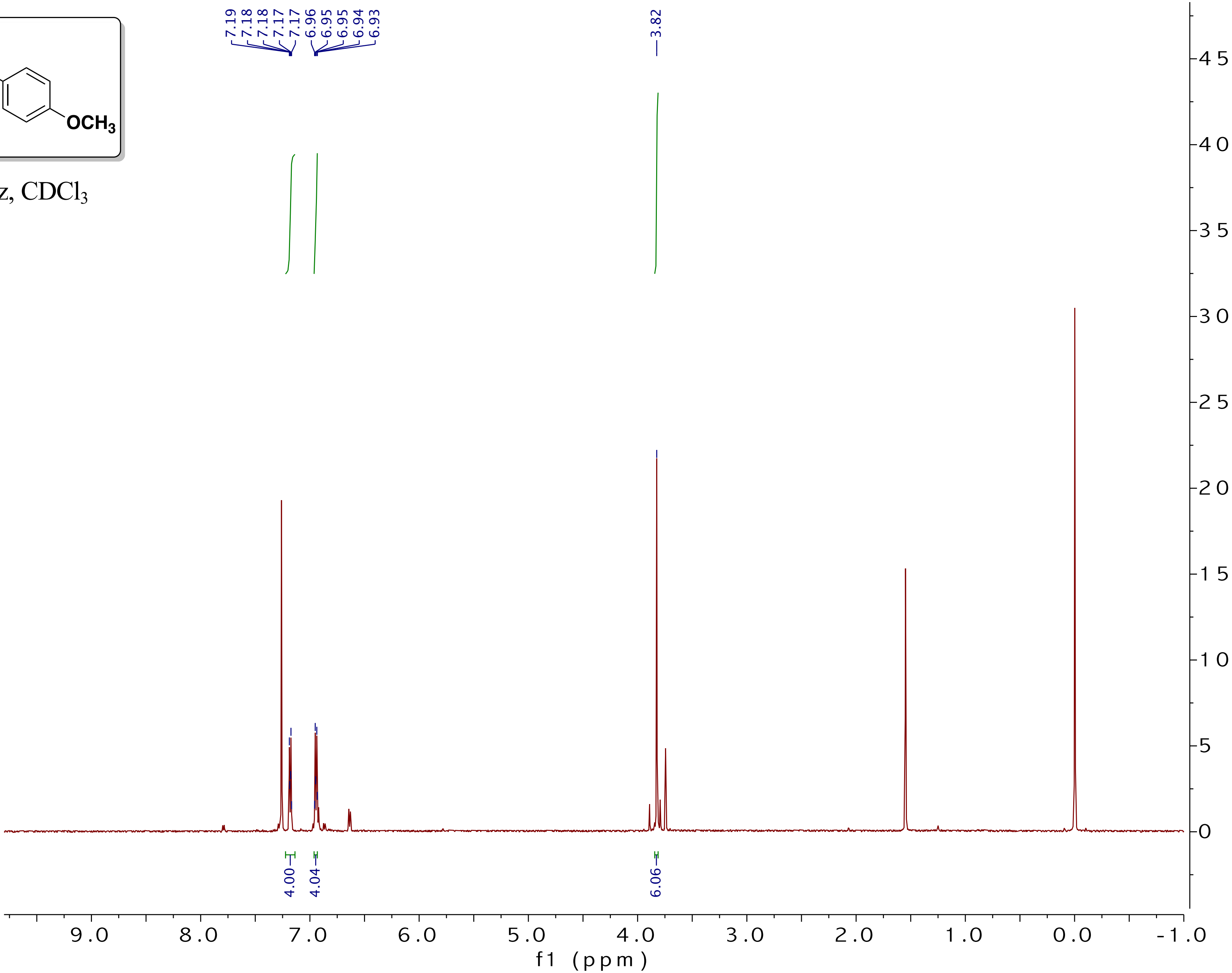
^{1}H, 400 MHz, $CDCl_3$

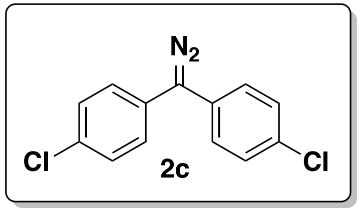




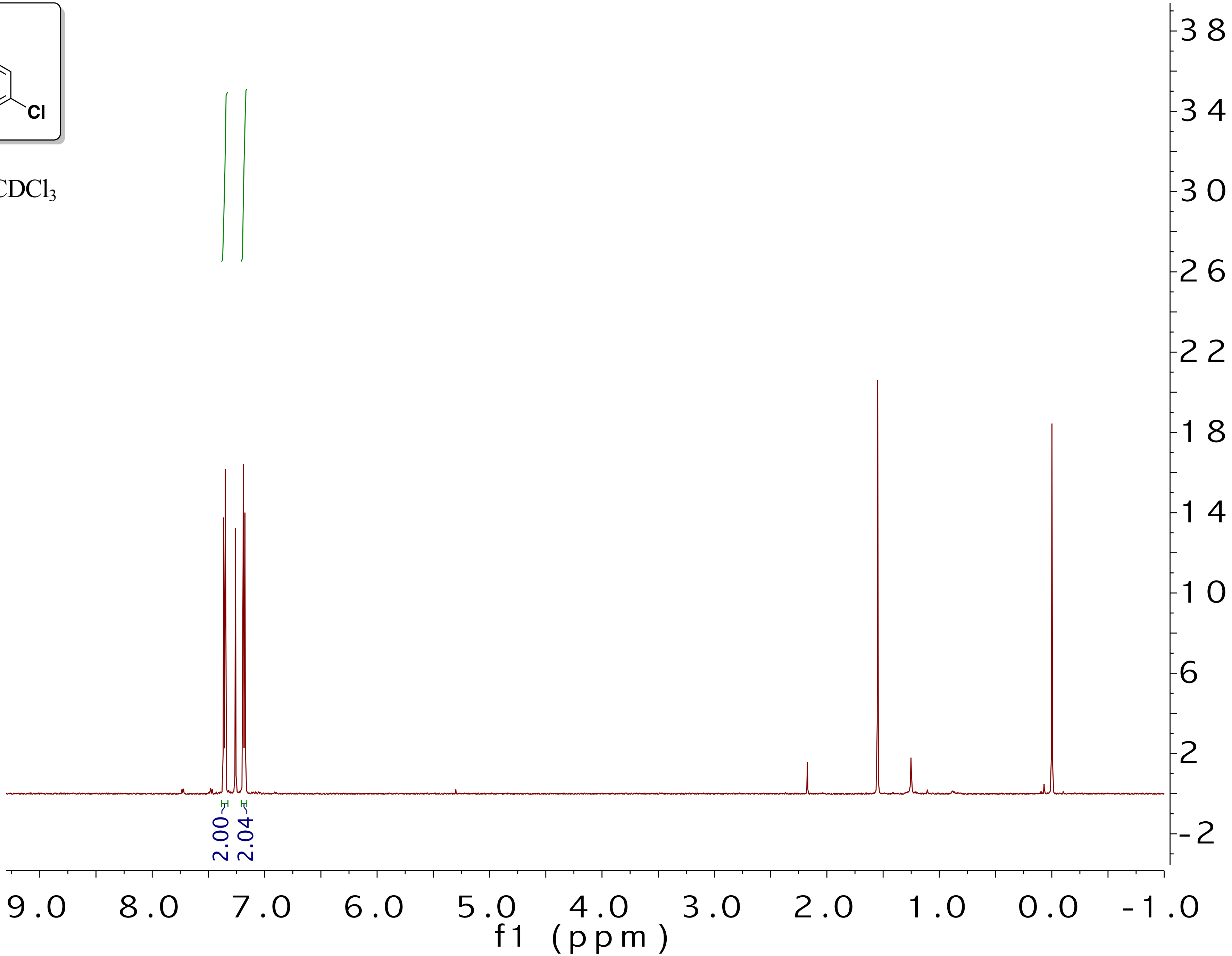
2b

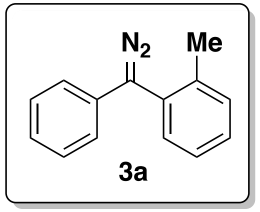
^{1}H, 600 MHz, CDCl$_3$





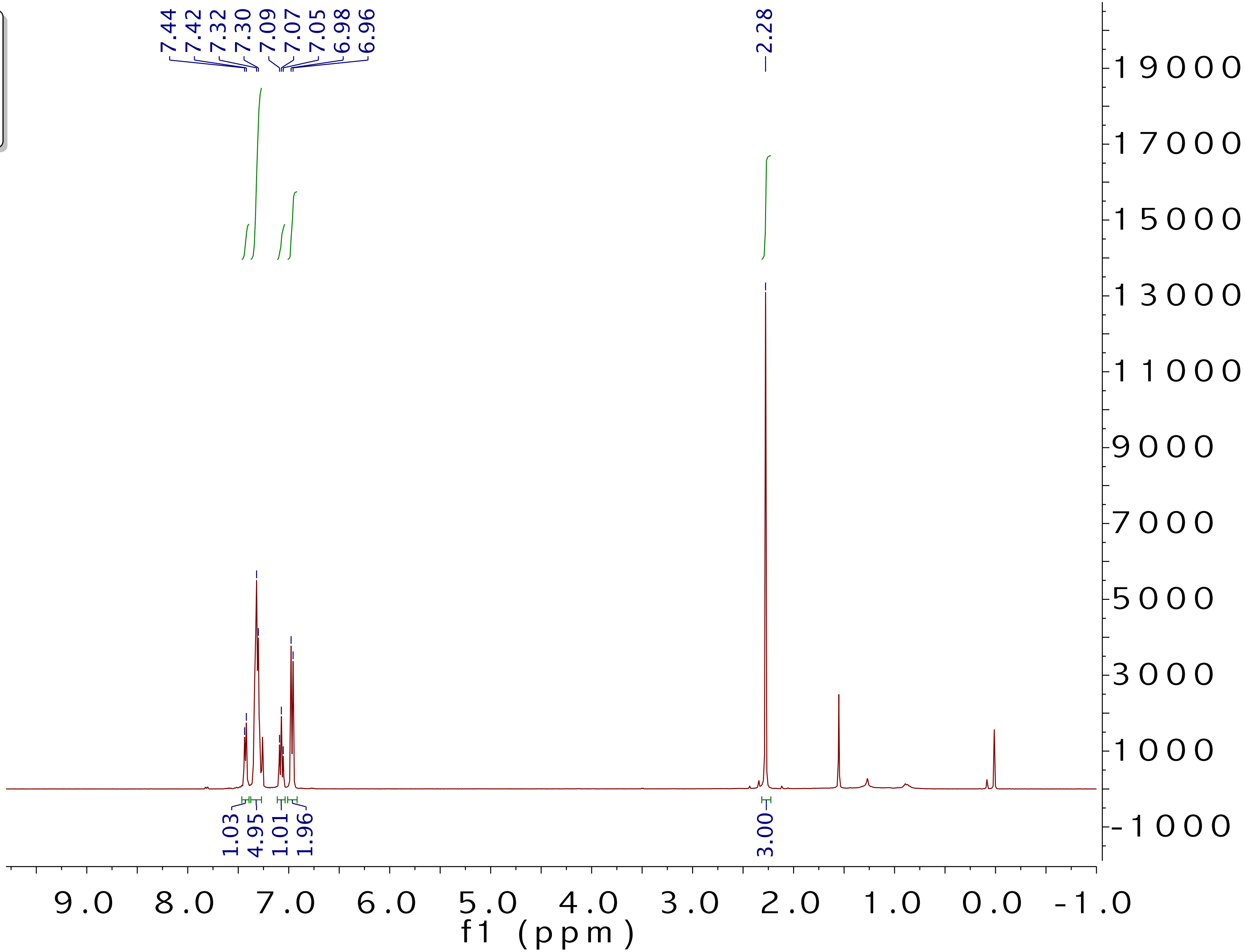
^{1}H, 600 MHz, CDCl$_3$

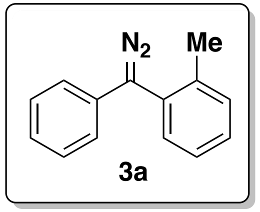




3a

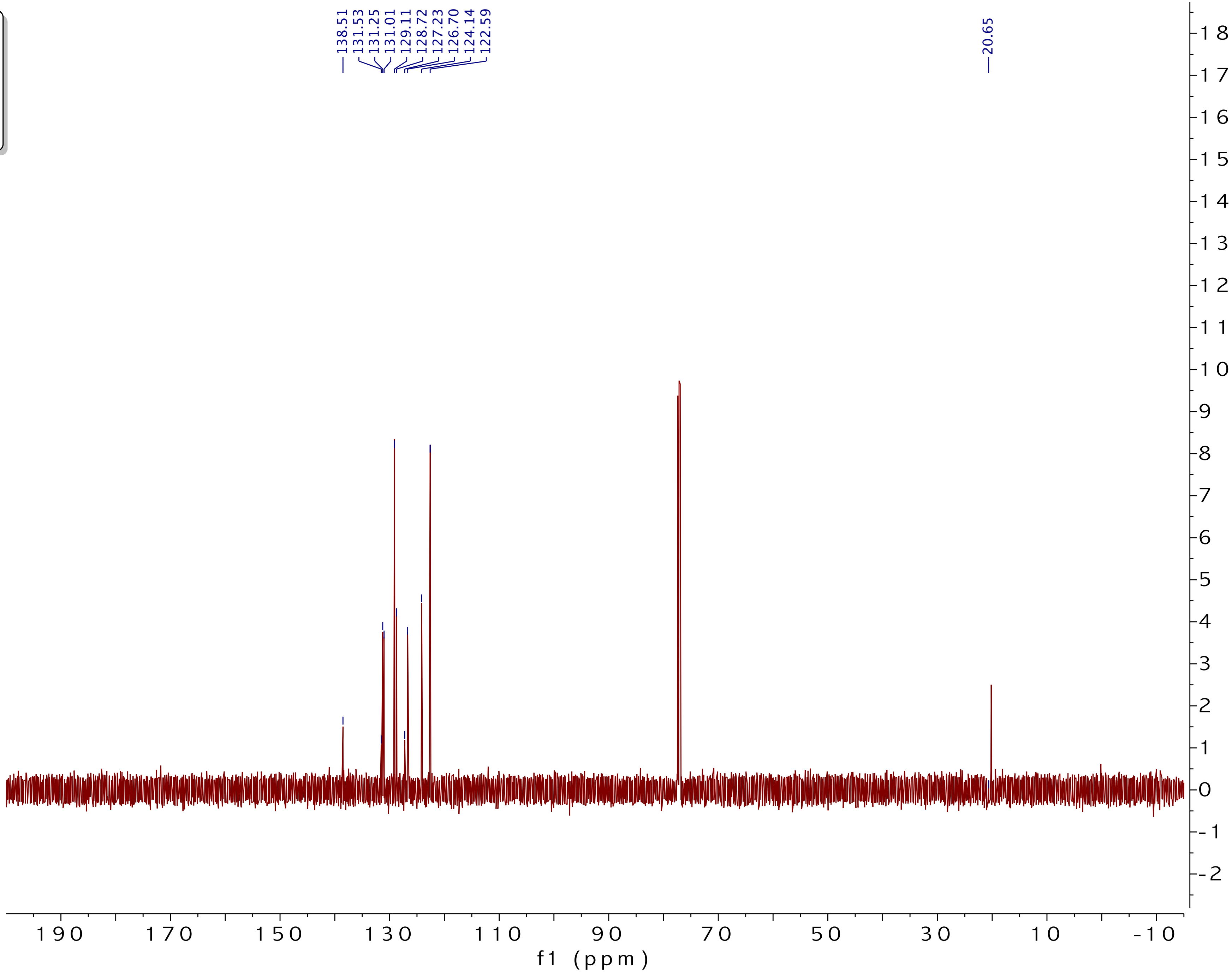
^{1}H, 600 MHz, CDCl$_3$

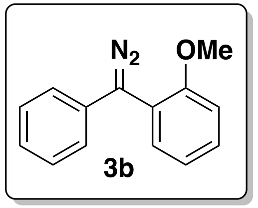




3a

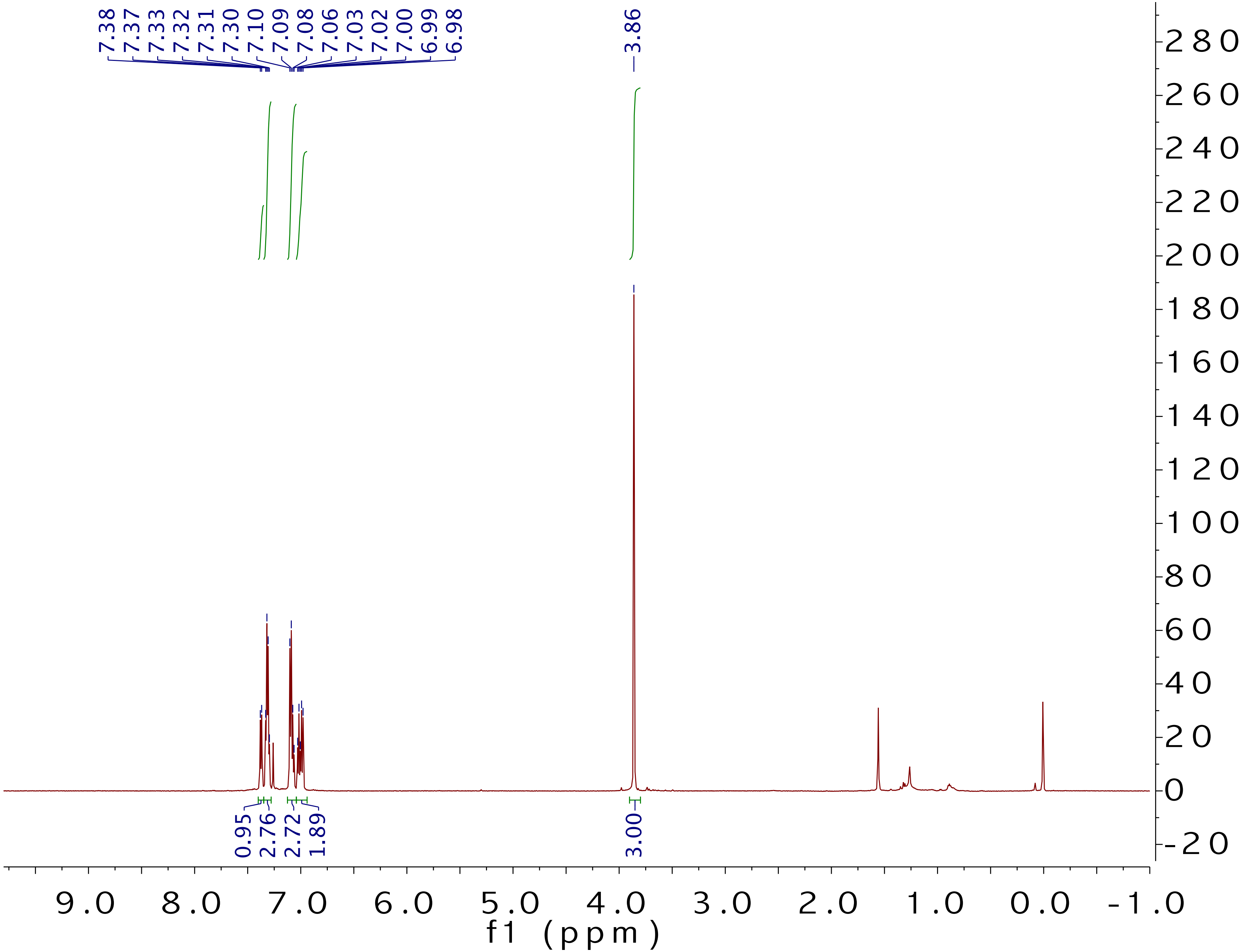
^{13}C, 151 MHz, $CDCl_3$

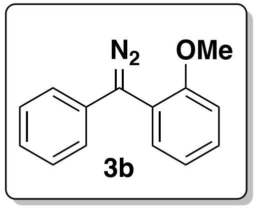




3b

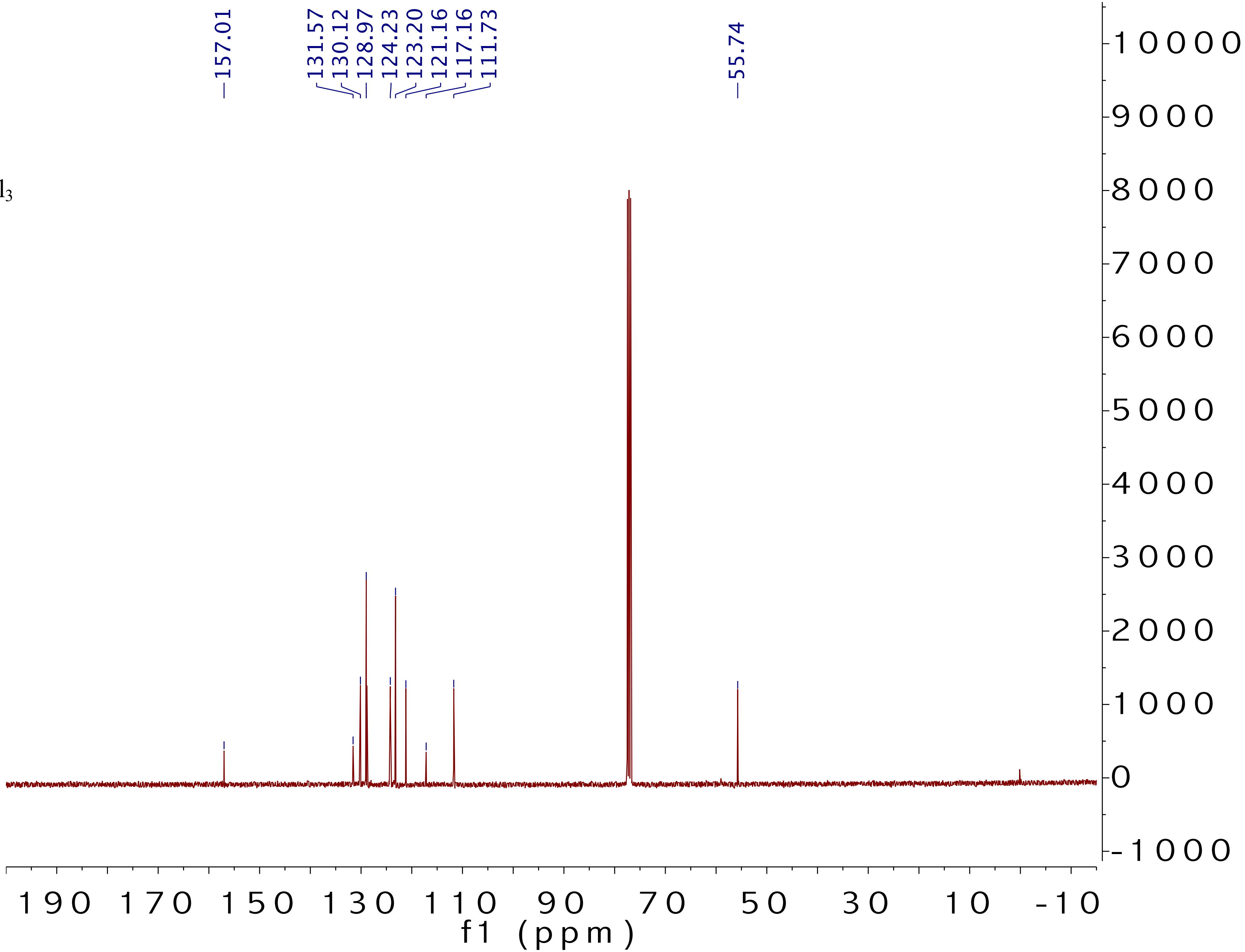
^{1}H, 600 MHz, CDCl$_3$

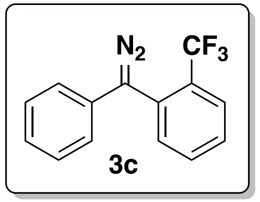




3b

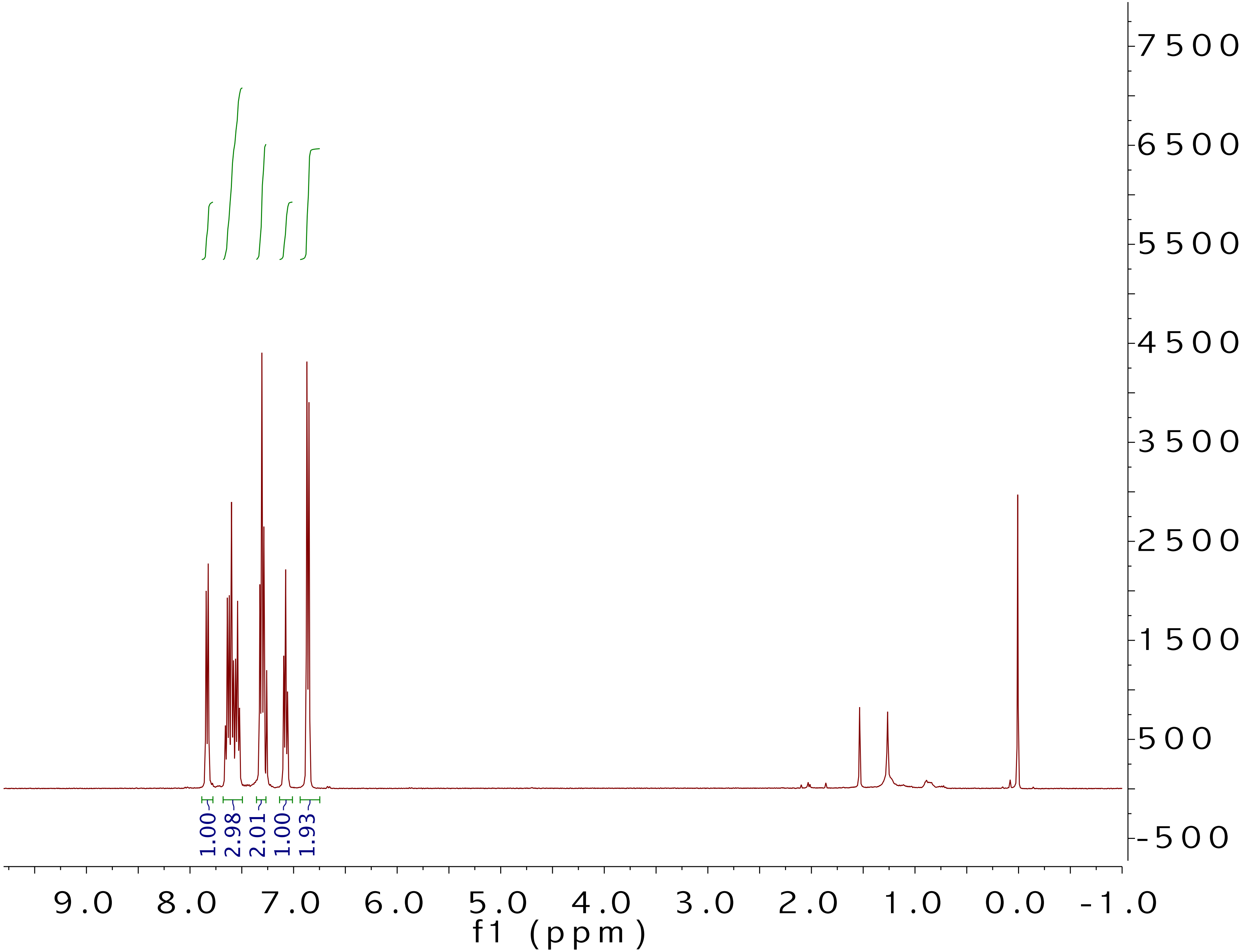
^{13}C, 100 MHz, $CDCl_3$

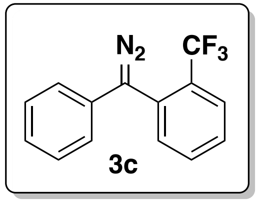




3c

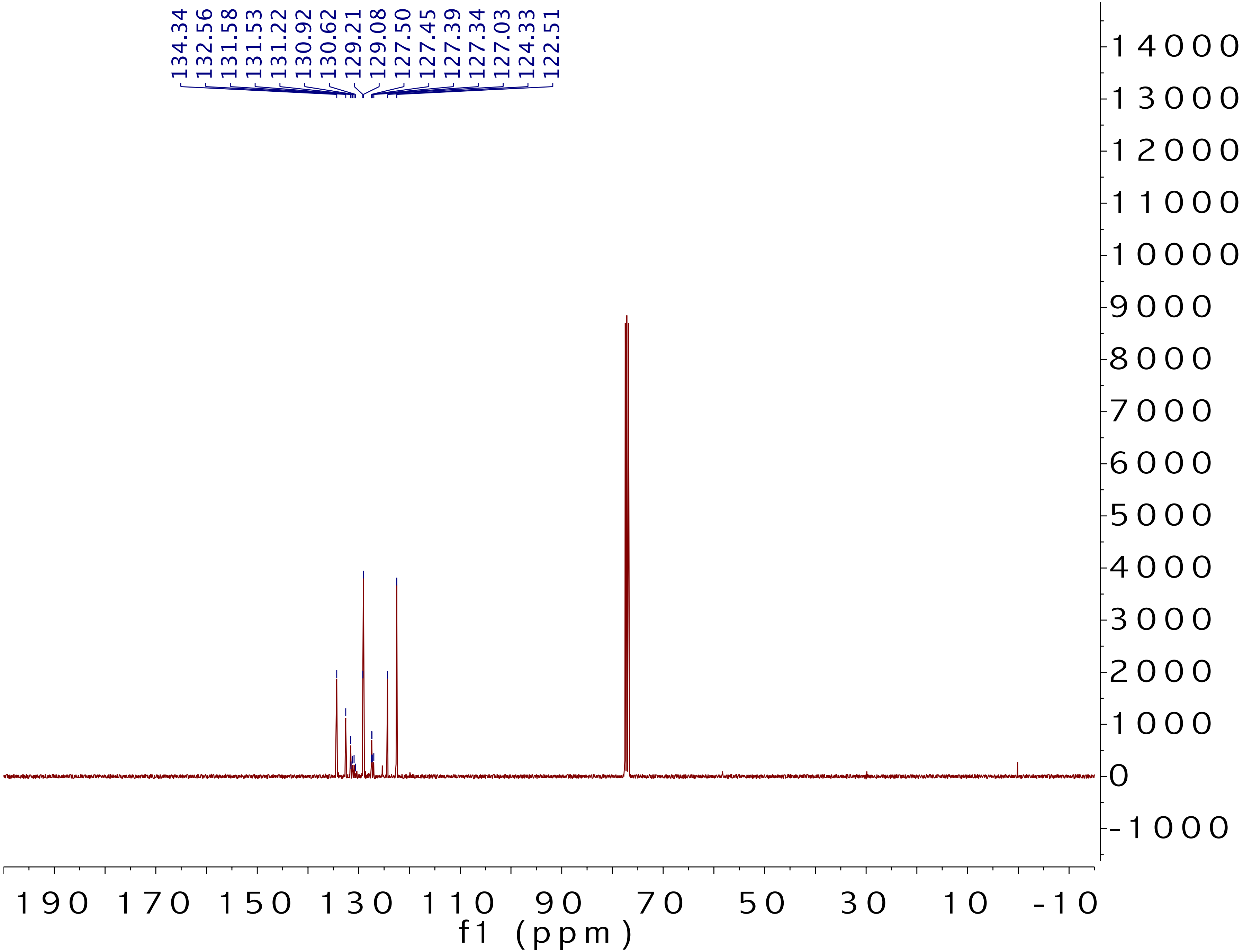
^{1}H, 400 MHz, CDCl$_3$

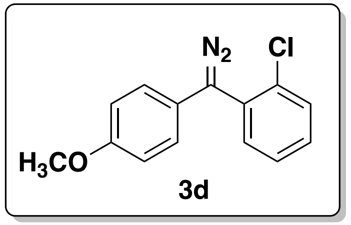




3c

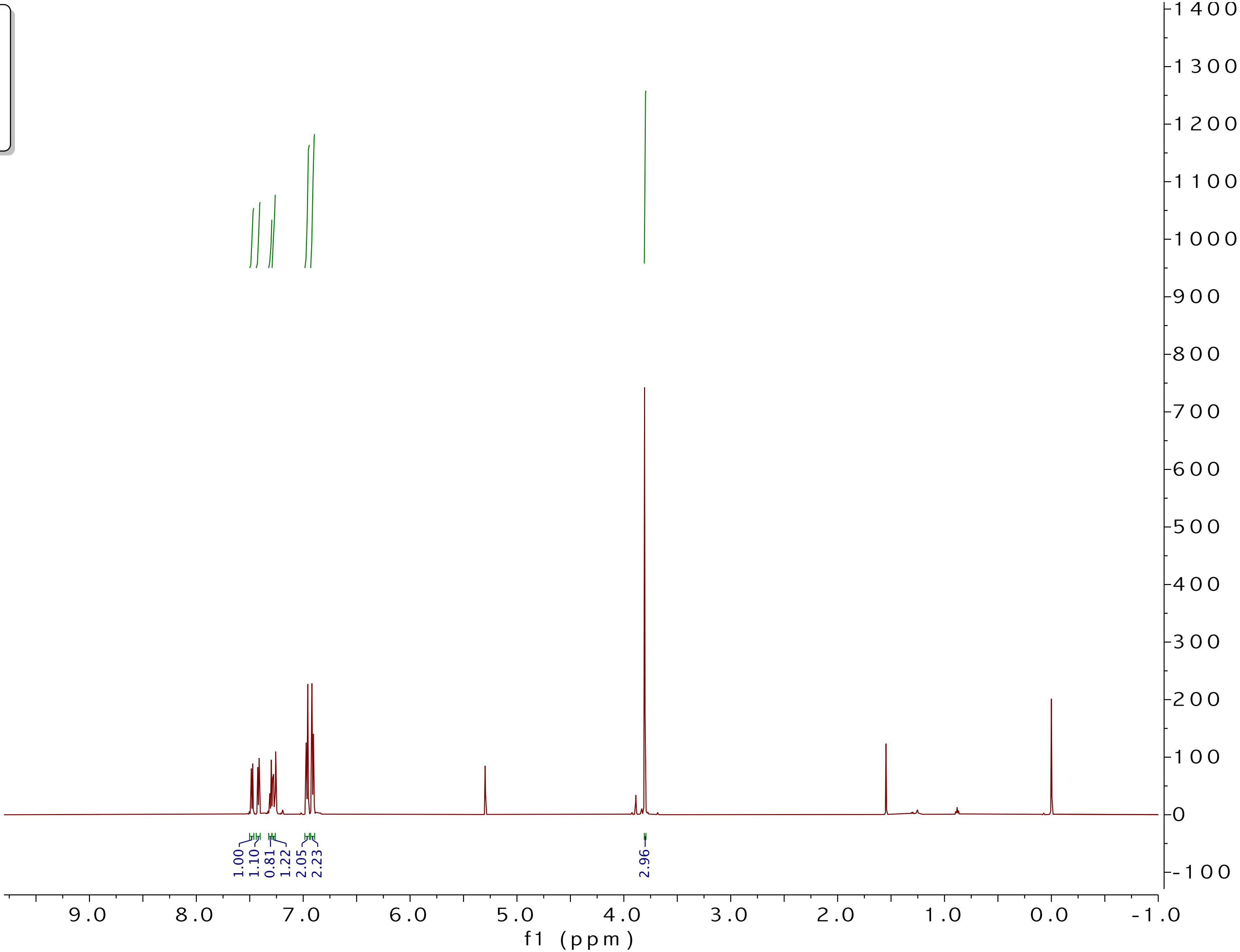
^{13}C, 100 MHz, CDCl$_3$

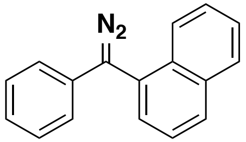




3d

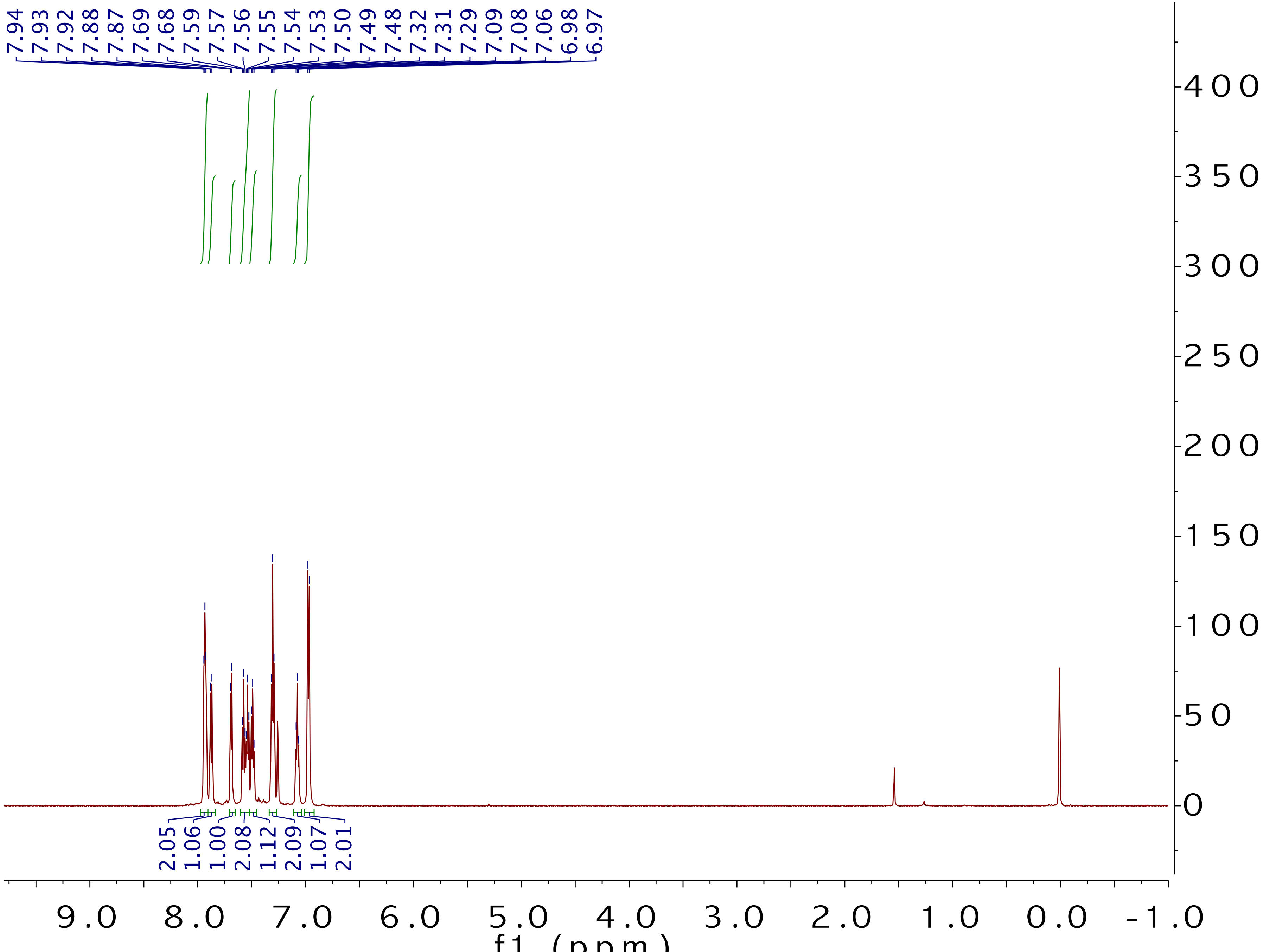
^{1}H, 600 MHz, CDCl$_3$

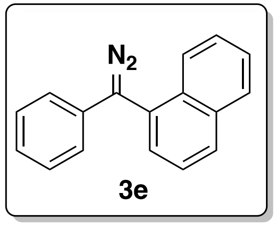




3e

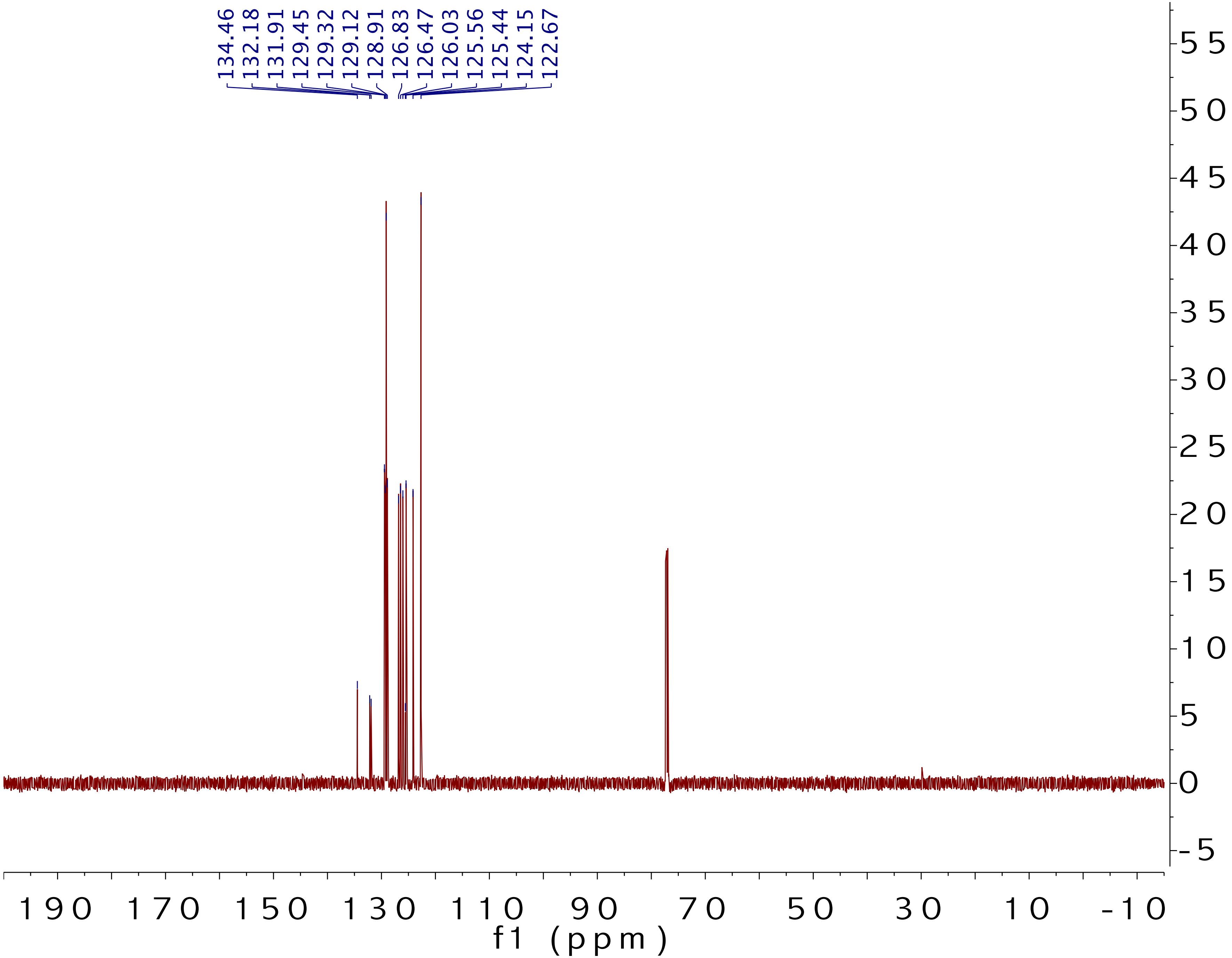
^{1}H, 600 MHz, CDCl$_3$

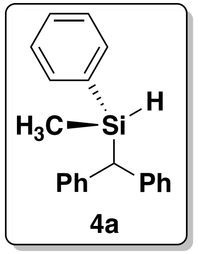




3e

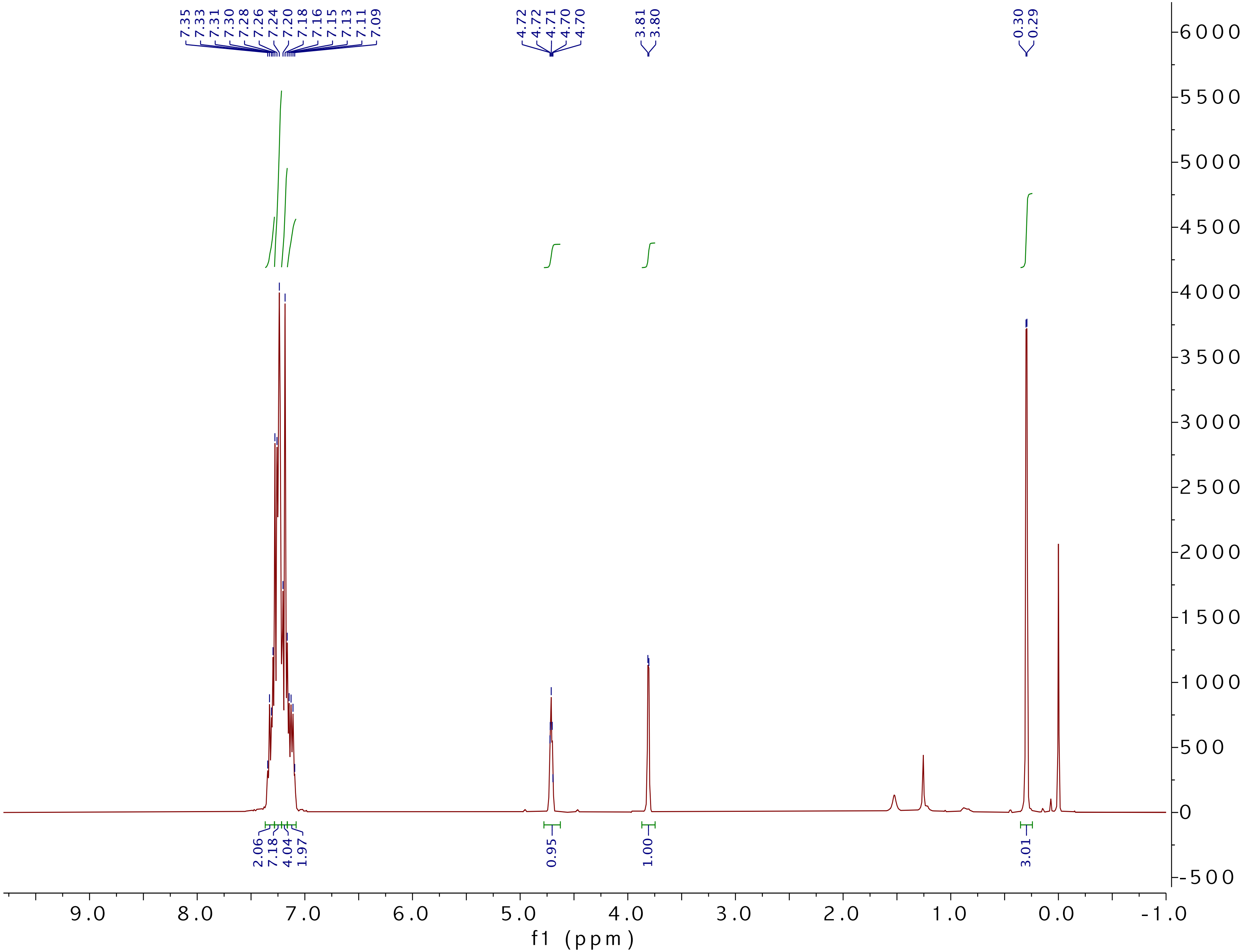
^{13}C, 151 MHz, CDCl$_3$

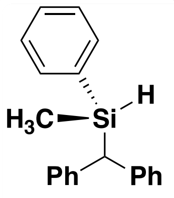




4a

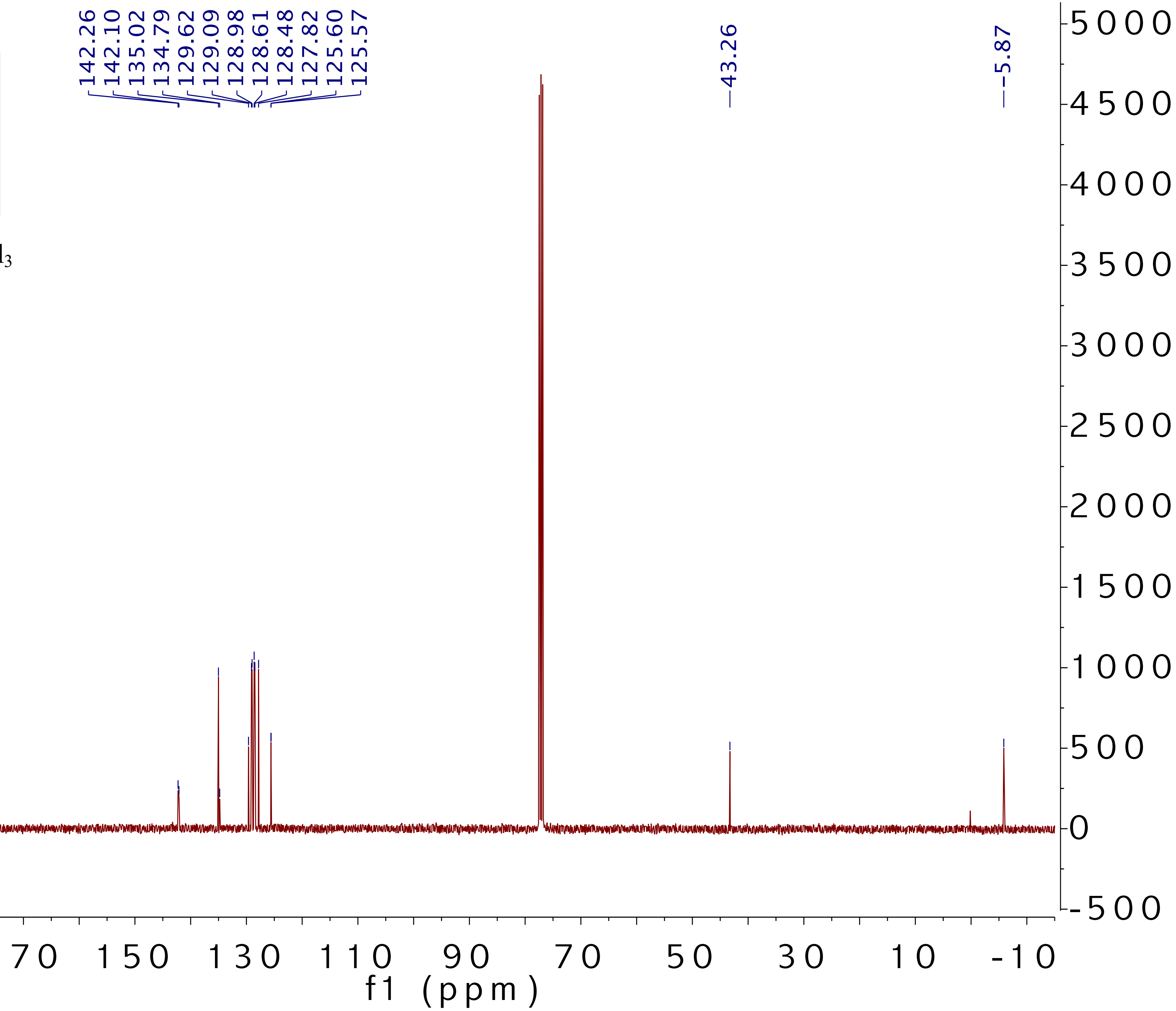
^{1}H, 400 MHz, CDCl$_3$

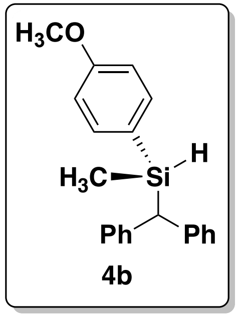




4a

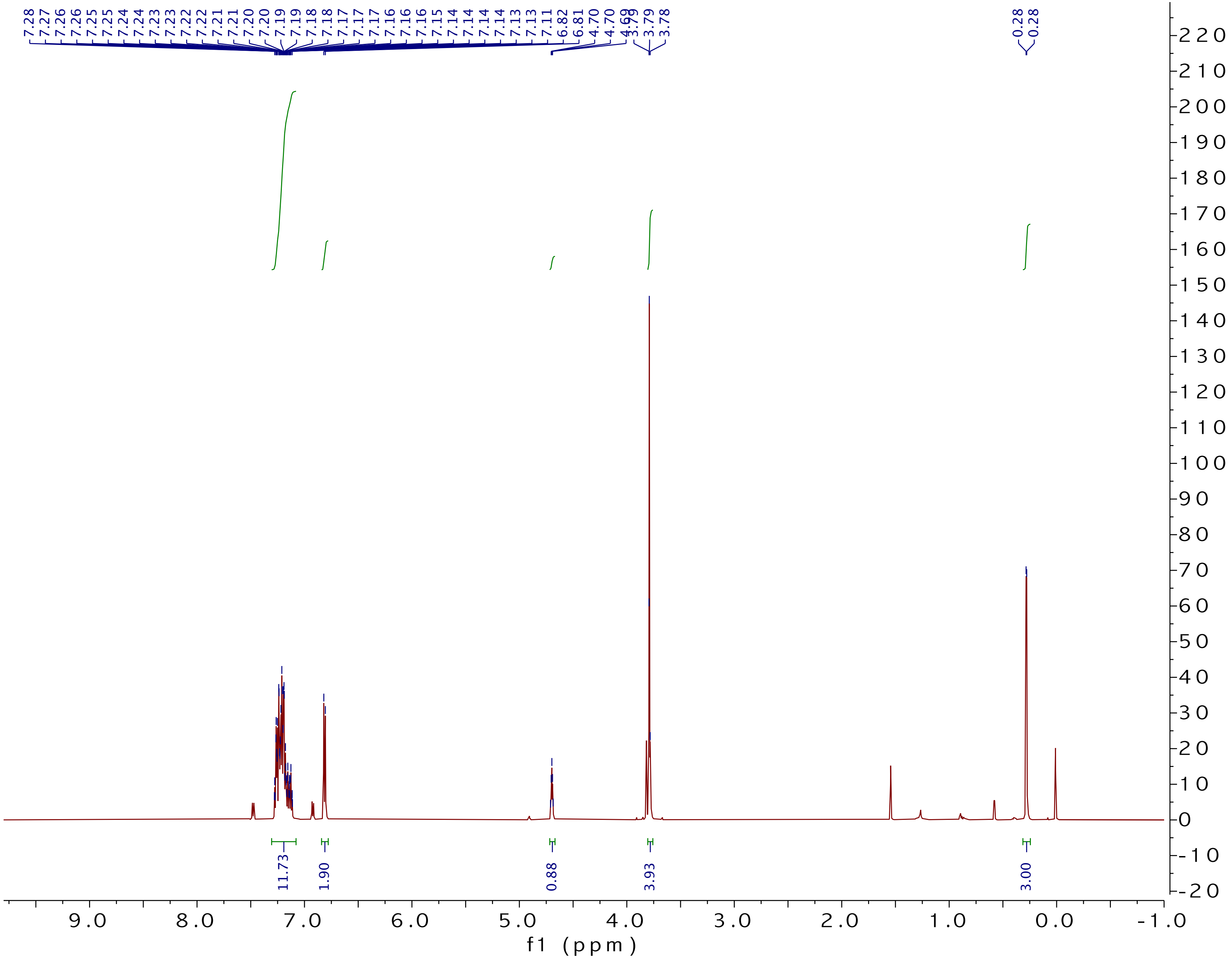
^{13}C, 100 MHz, $CDCl_3$

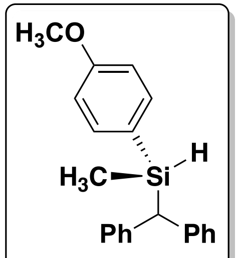




4b

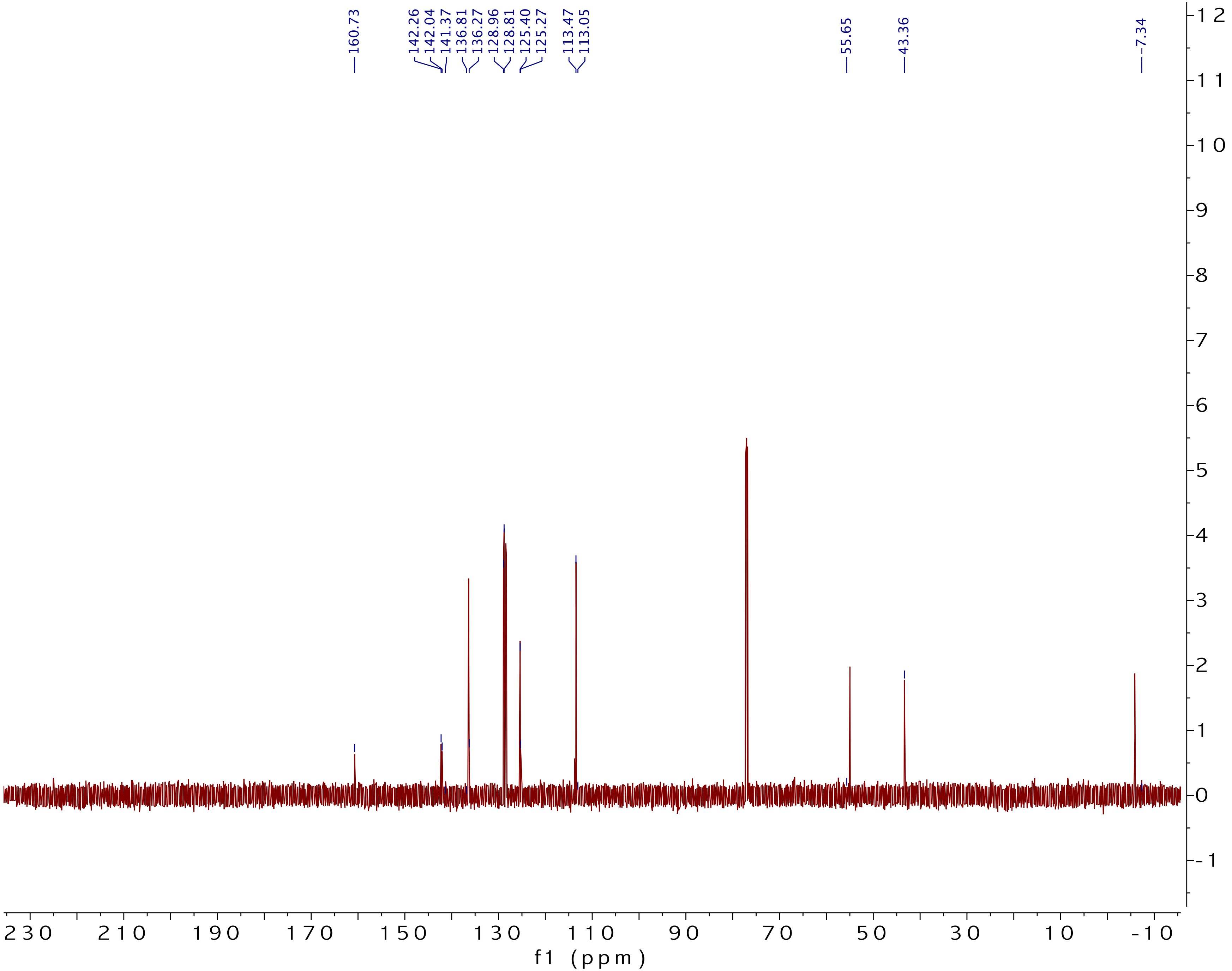
^{1}H, 600 MHz, CDCl$_3$

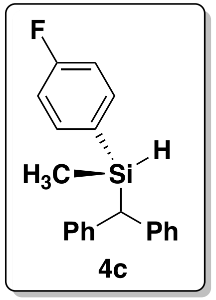




4b

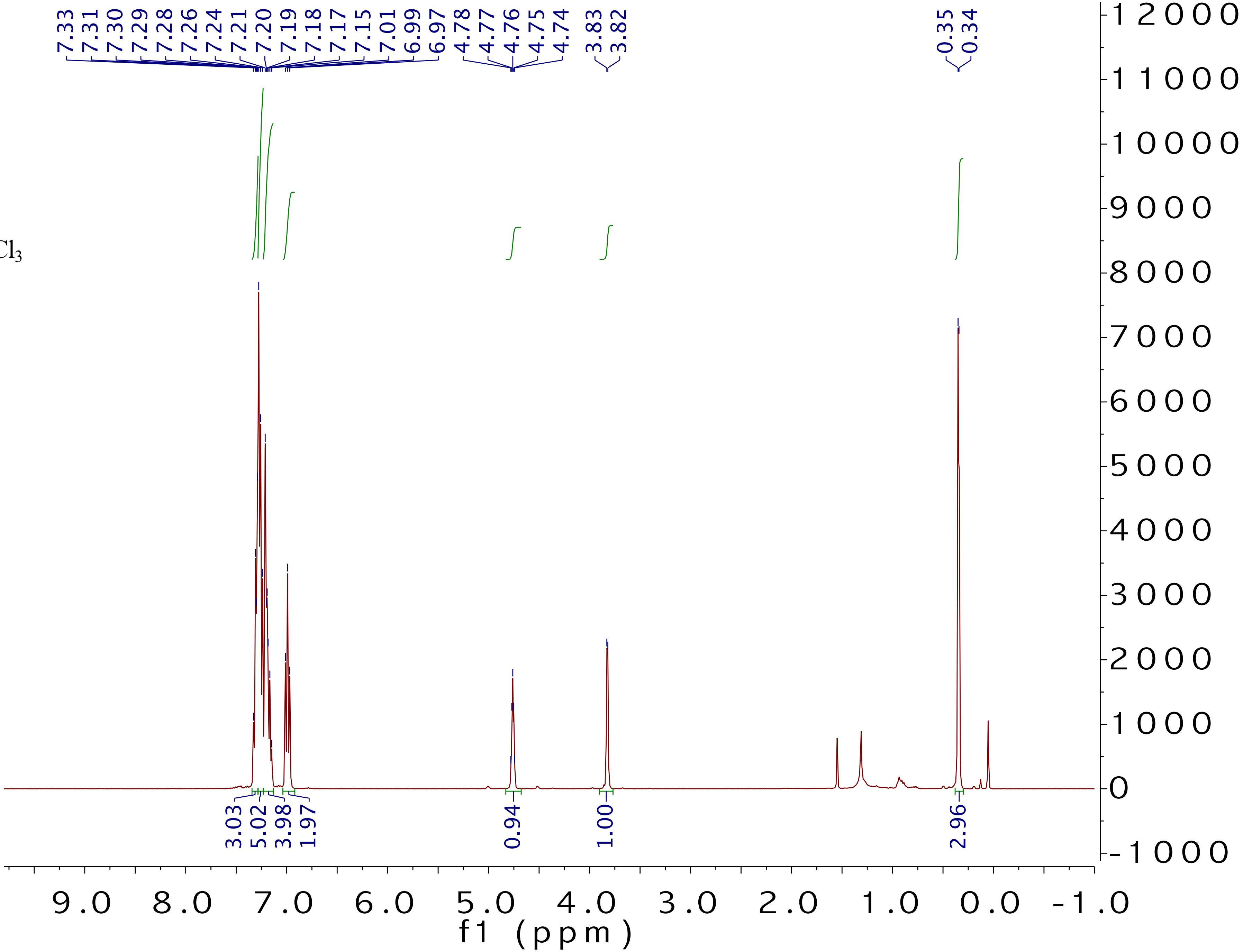
^{13}C, 151 MHz, $CDCl_3$

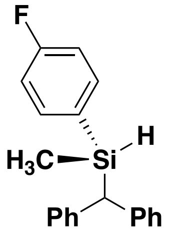




4c

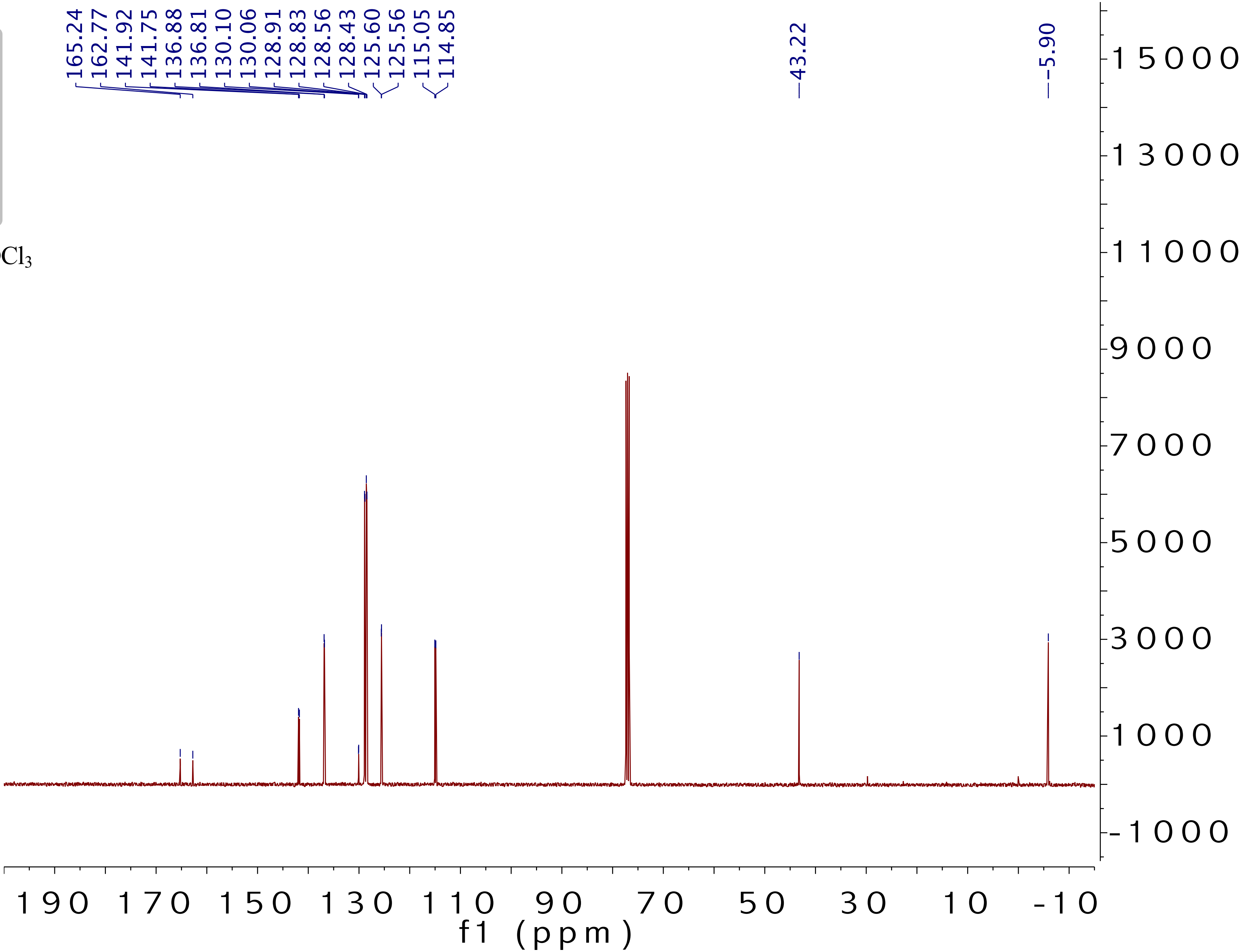
^{1}H, 400 MHz, $CDCl_3$

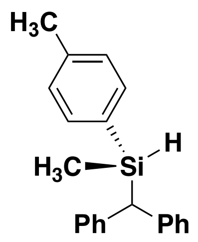




4c

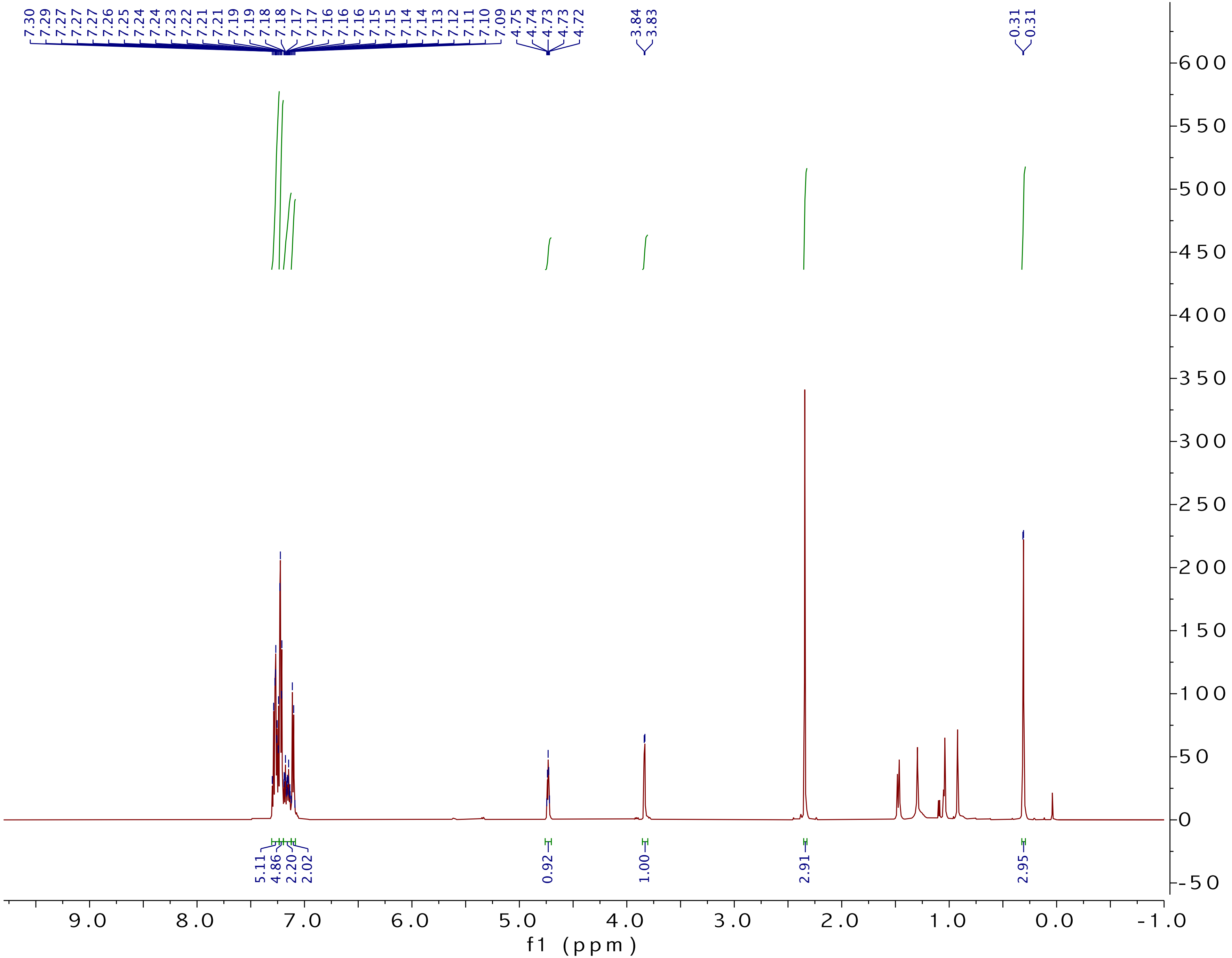
^{13}C, 100 MHz, $CDCl_3$

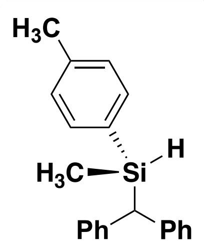




4d

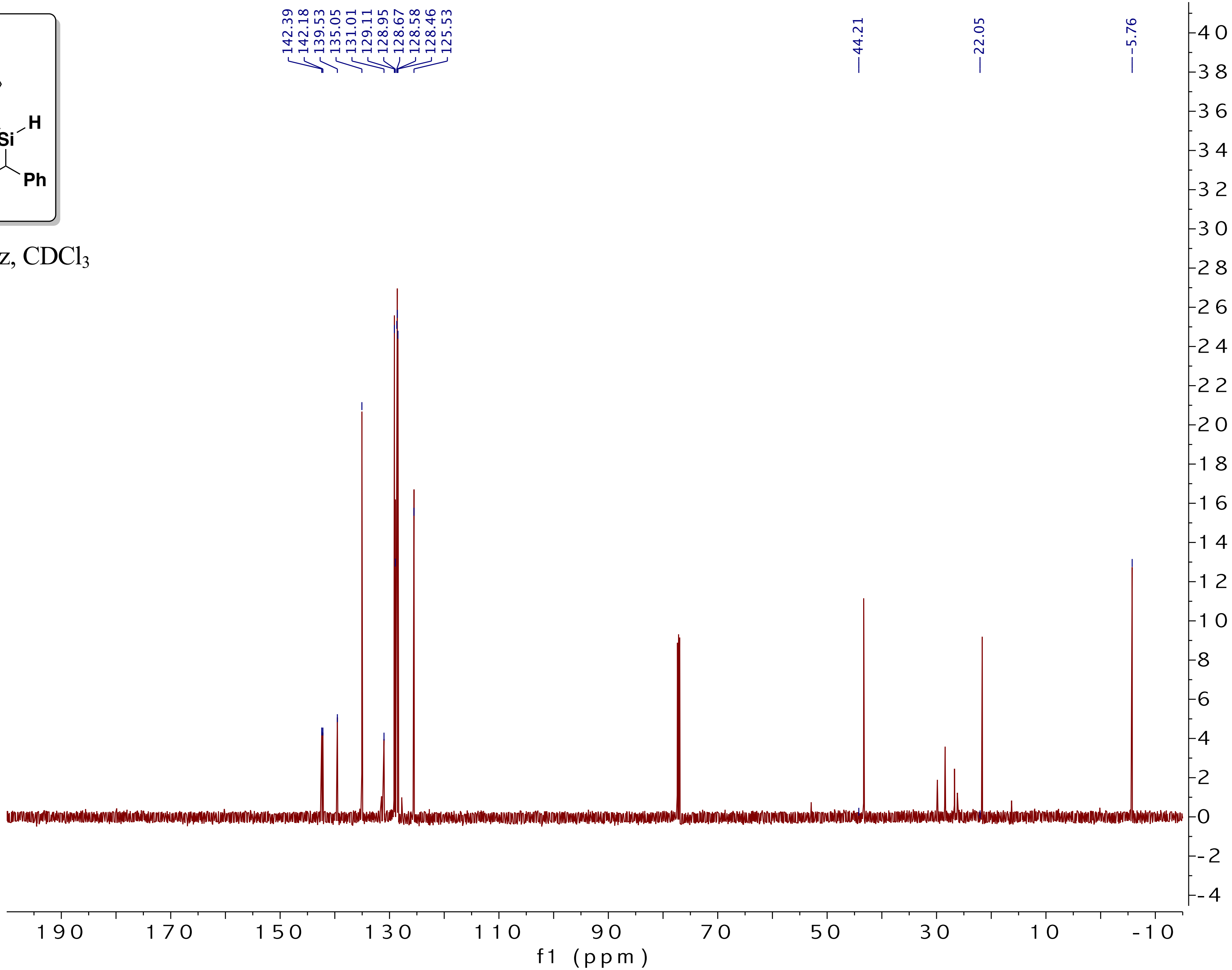
^{1}H, 600 MHz, $CDCl_3$

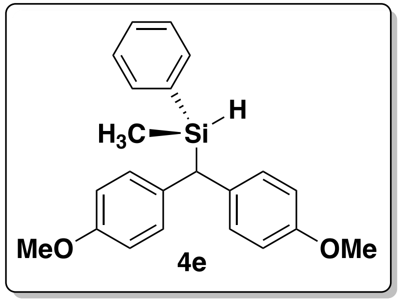




4d

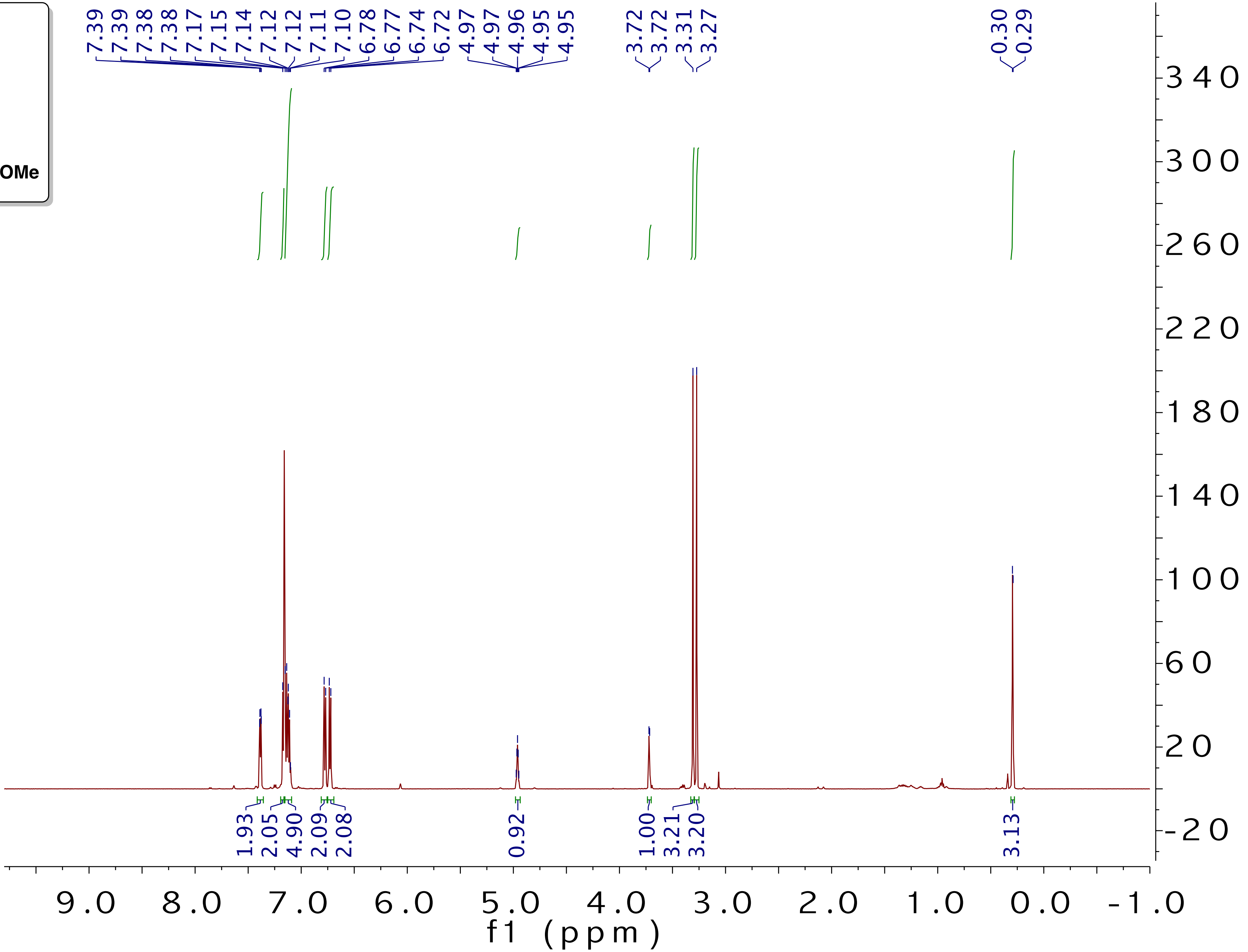
^{13}C, 151 MHz, $CDCl_3$

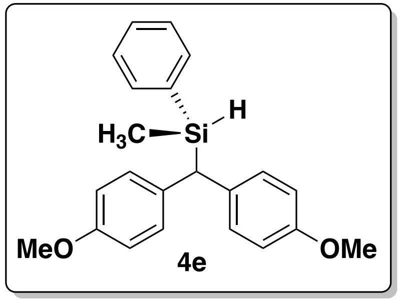




4e

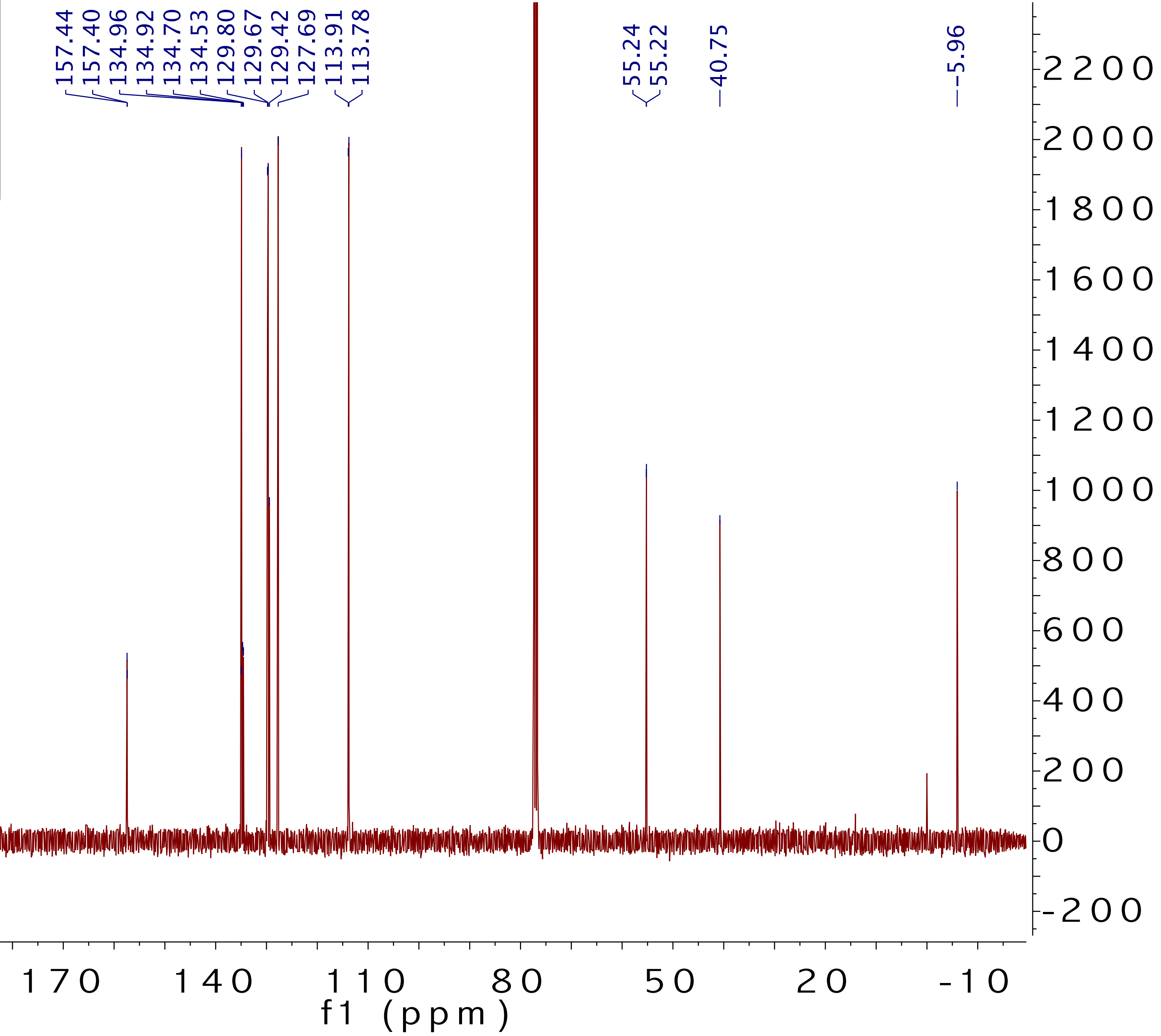
^{1}H, 600 MHz, C_6D_6

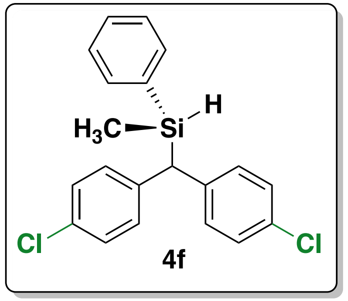




4e

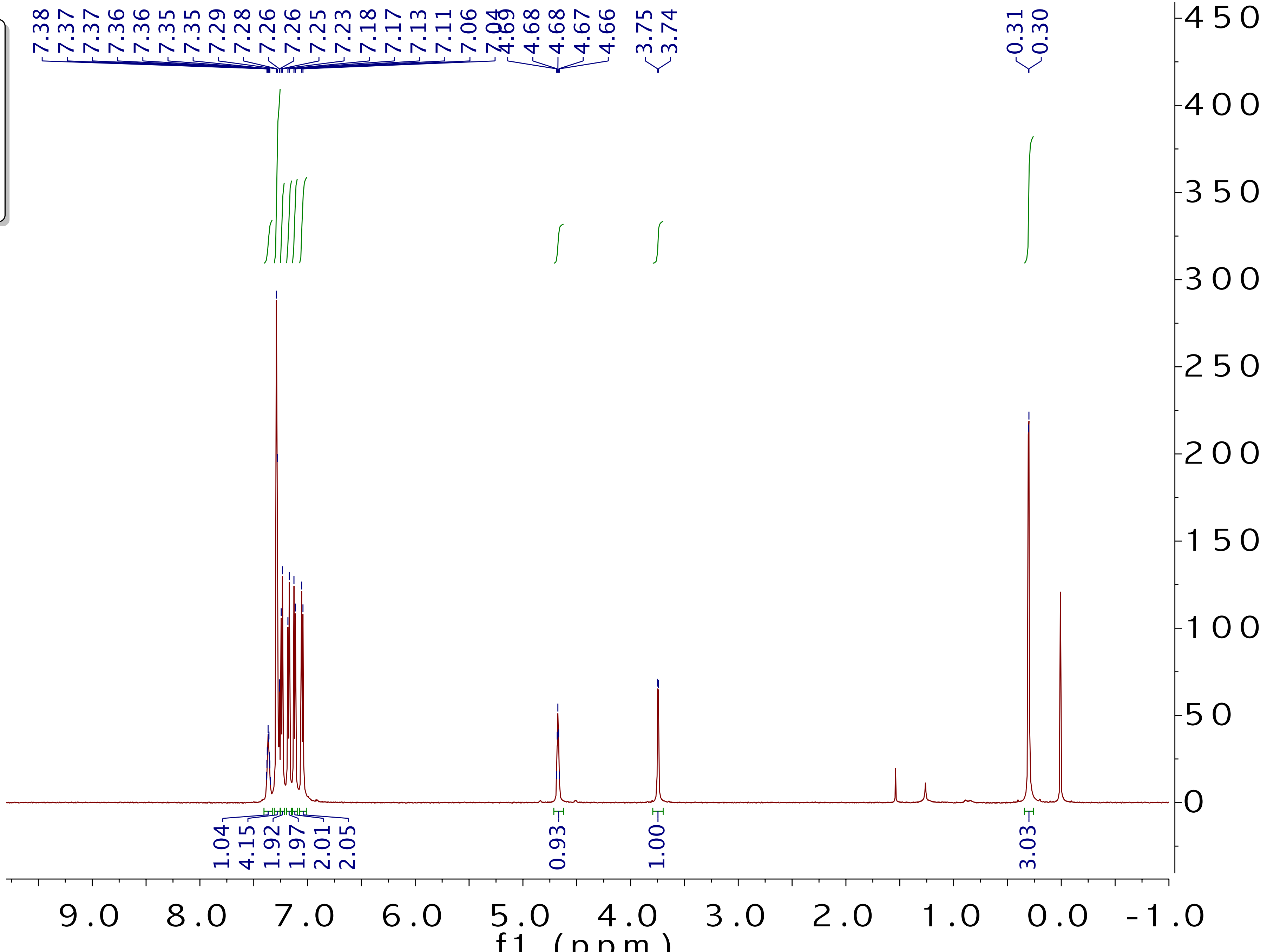
^{13}C, 100 MHz, CDCl$_3$

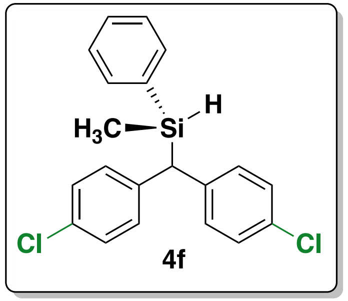




4f

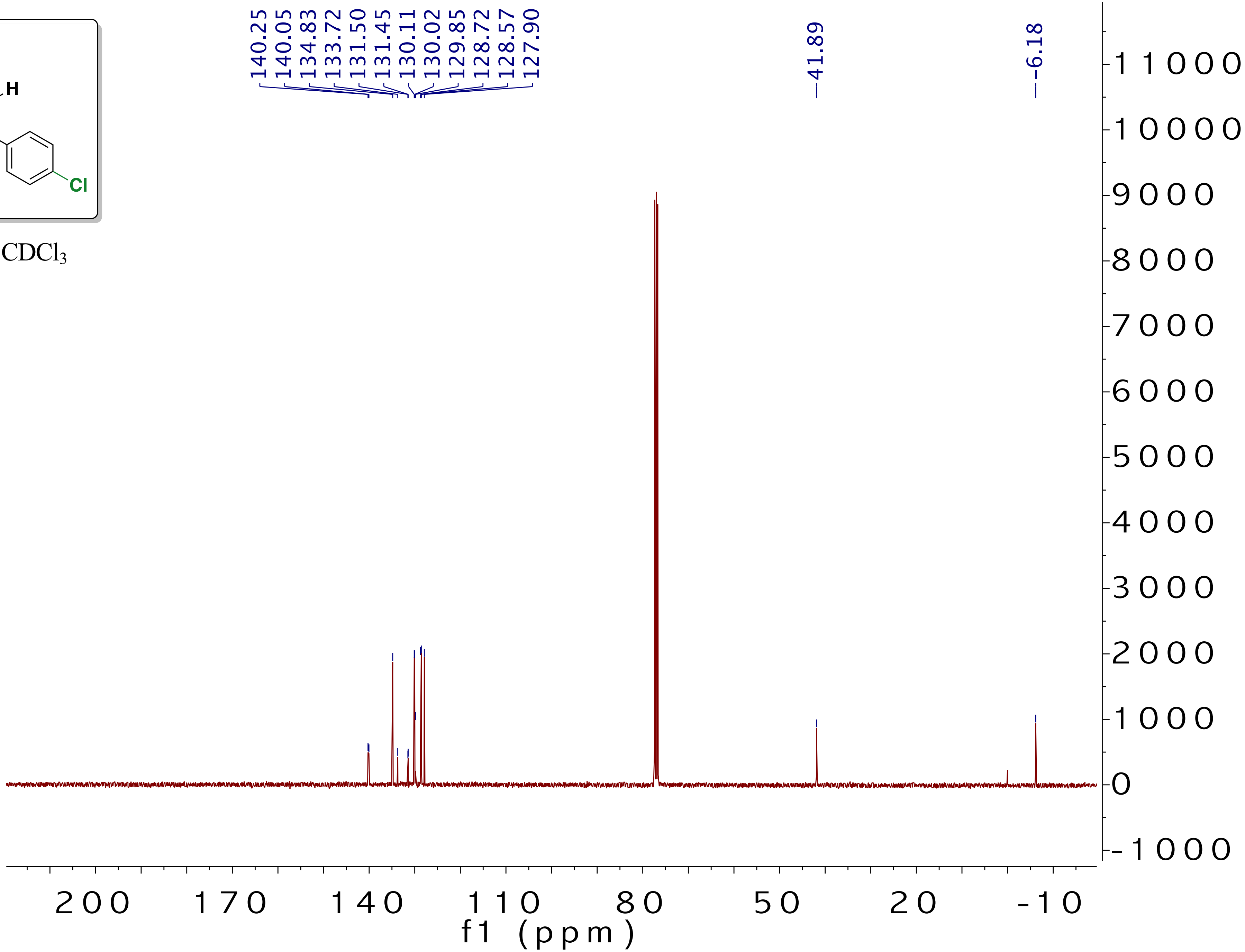
^1H, 600 MHz, $CDCl_3$

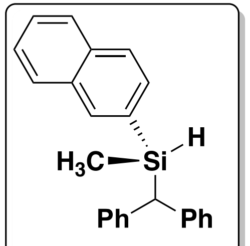




4f

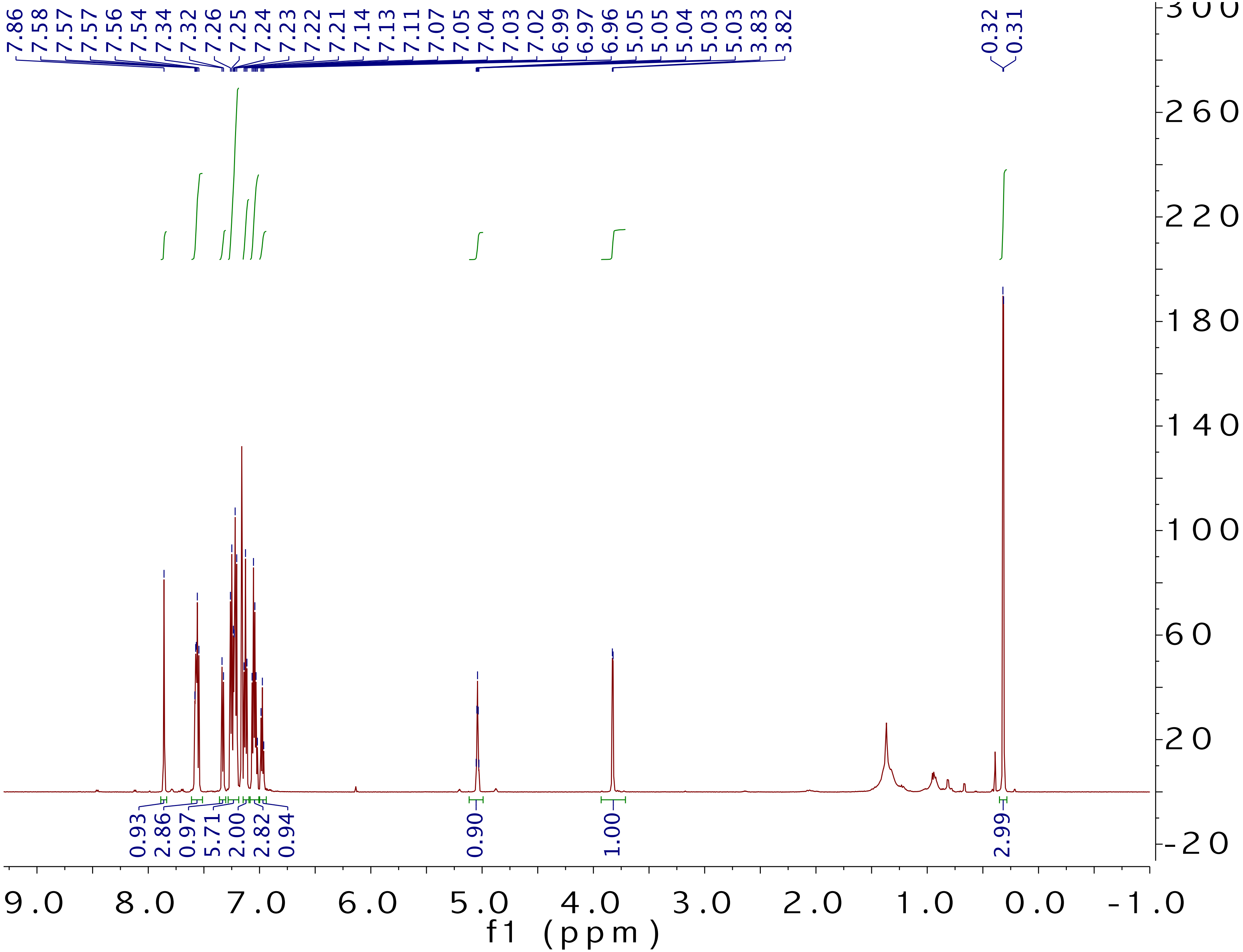
^{13}C, 100 MHz, CDCl$_3$

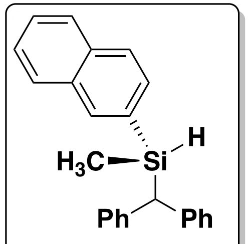




4g

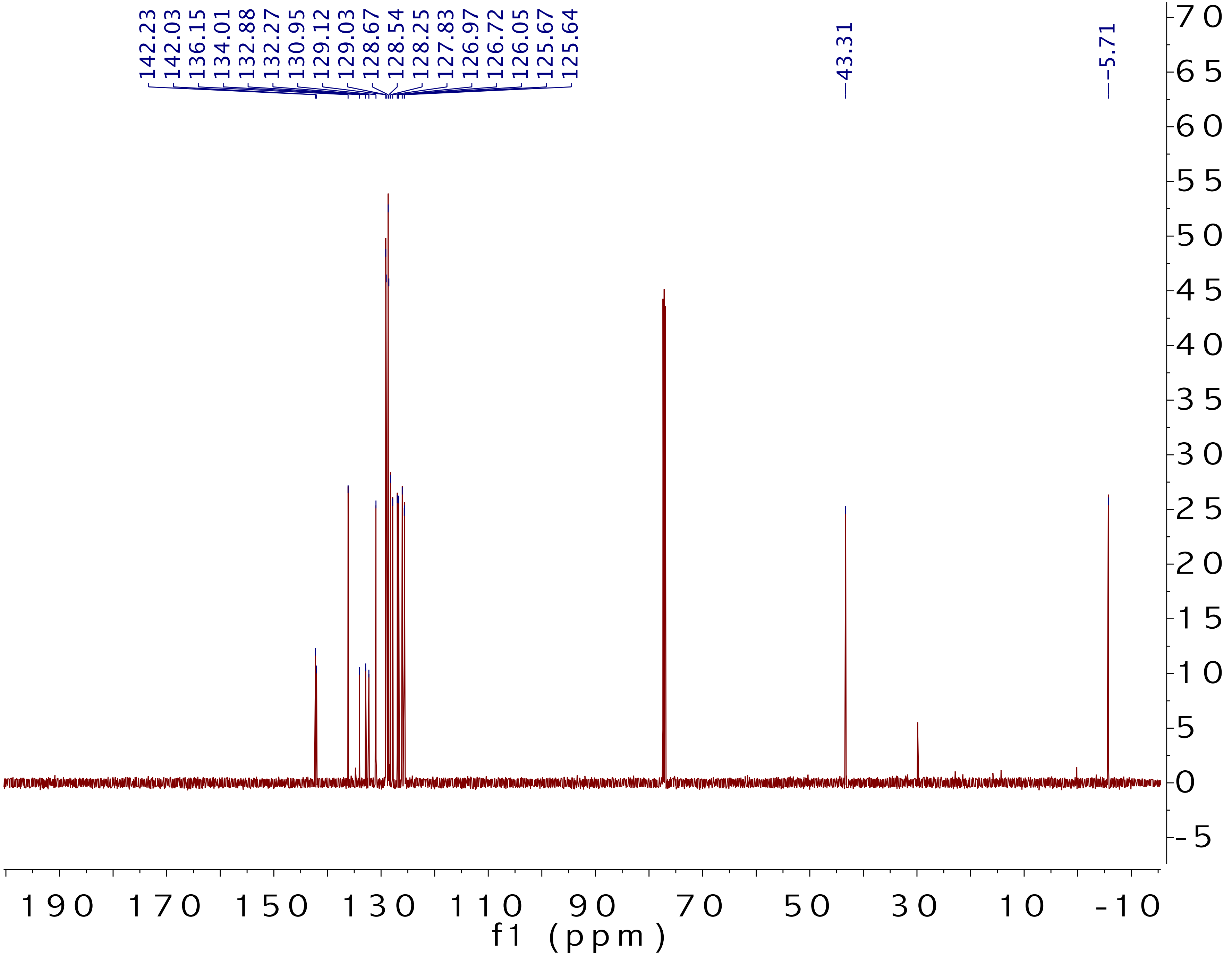
¹H, 600 MHz, C_6D_6

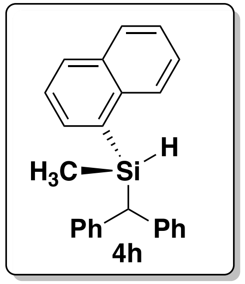




4g

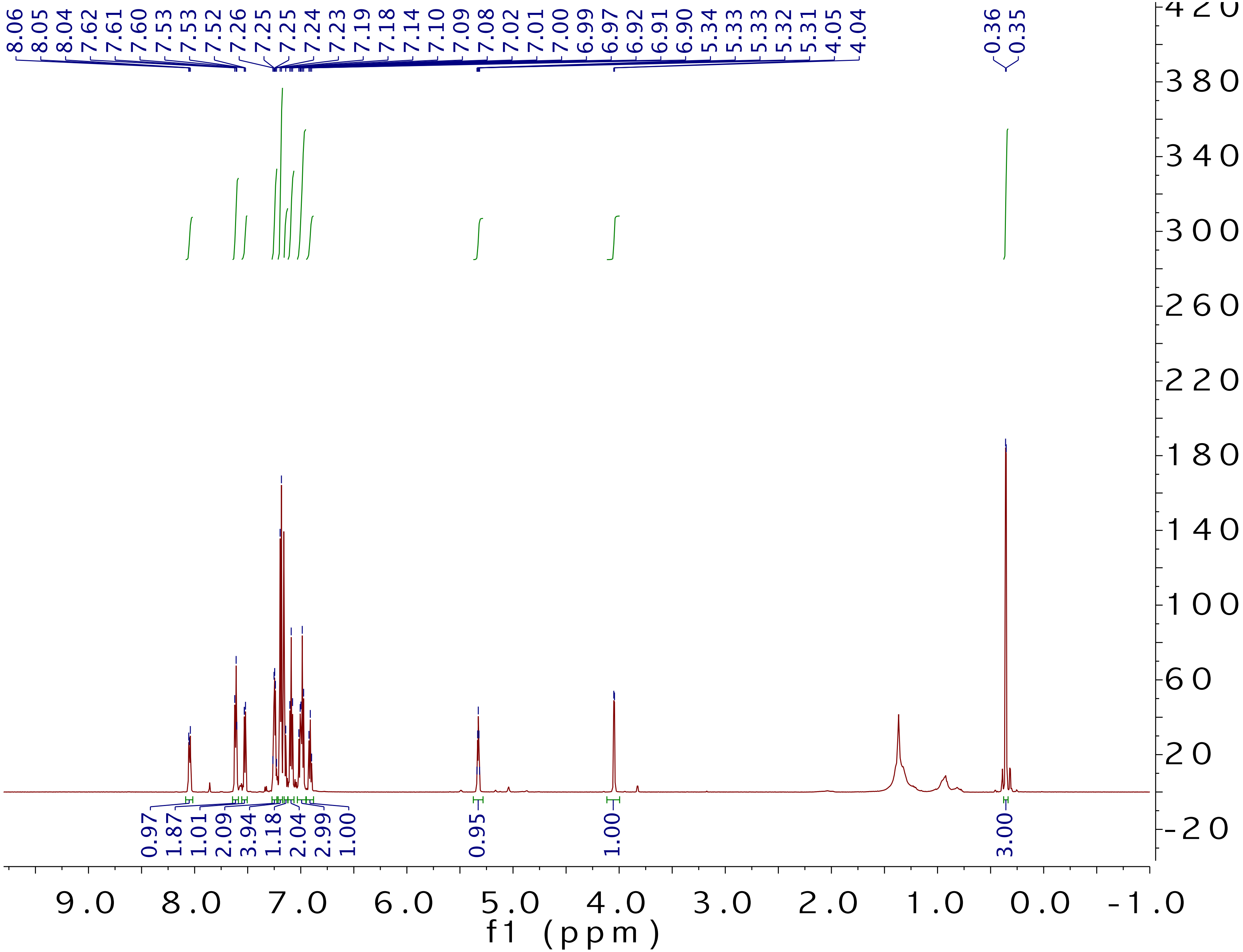
^{13}C, 151 MHz, CDCl$_3$

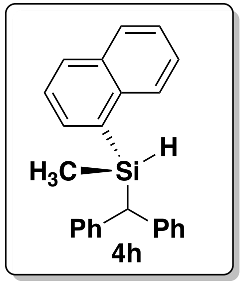




4h

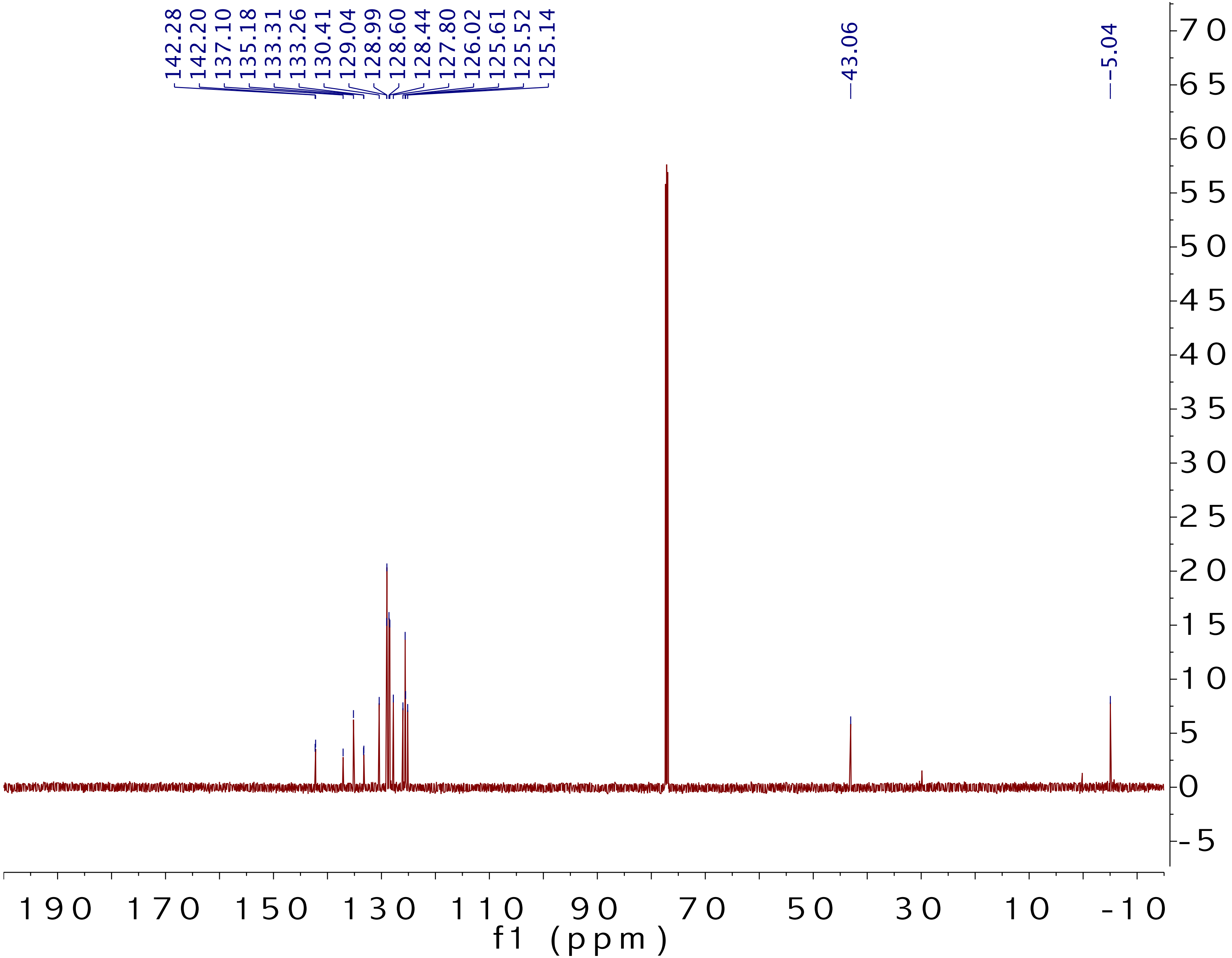
^{1}H, 600 MHz, C_6D_6

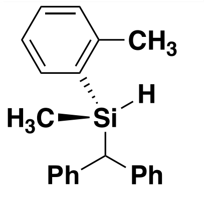




4h

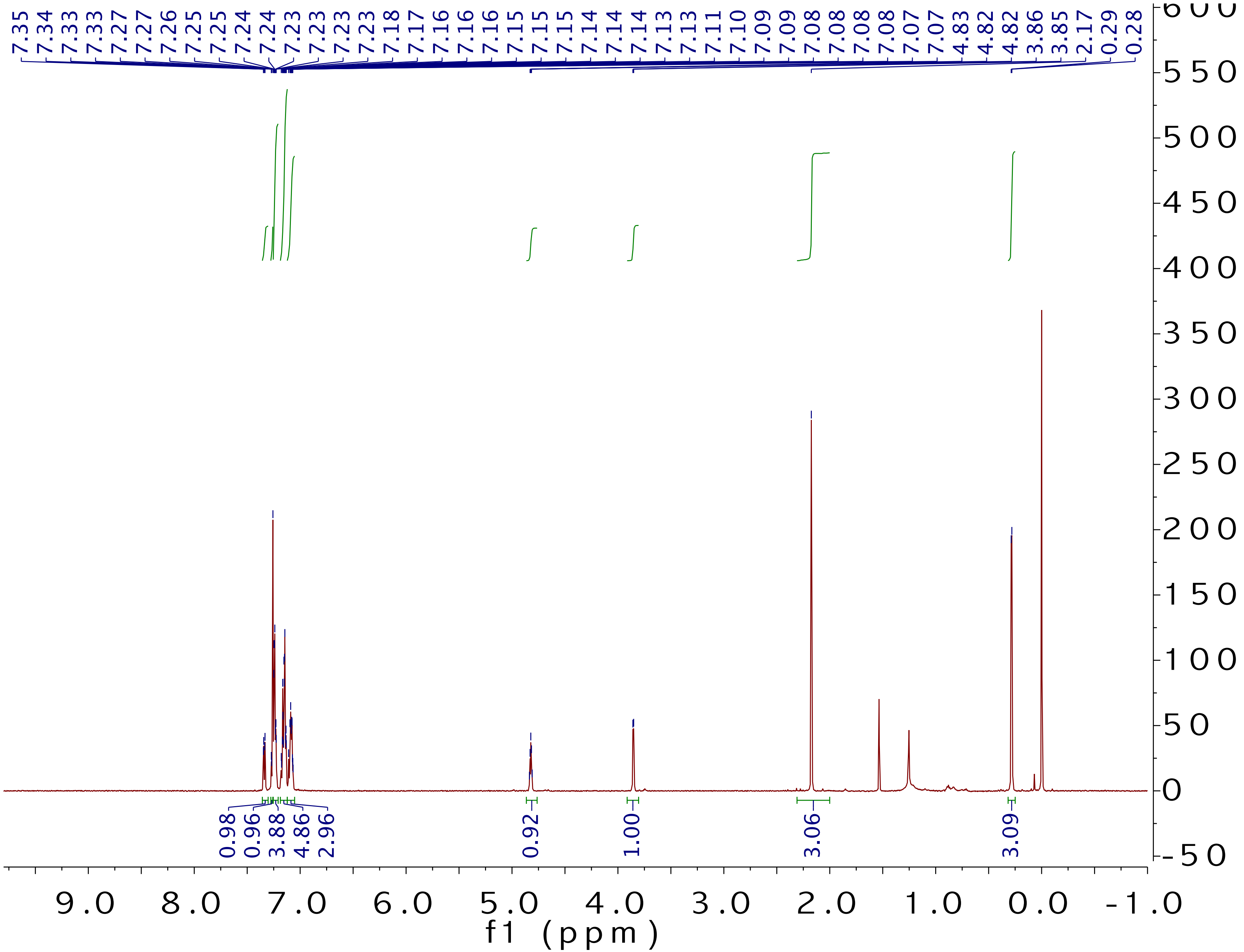
^{13}C, 100 MHz, $CDCl_3$

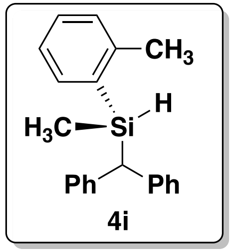




4i

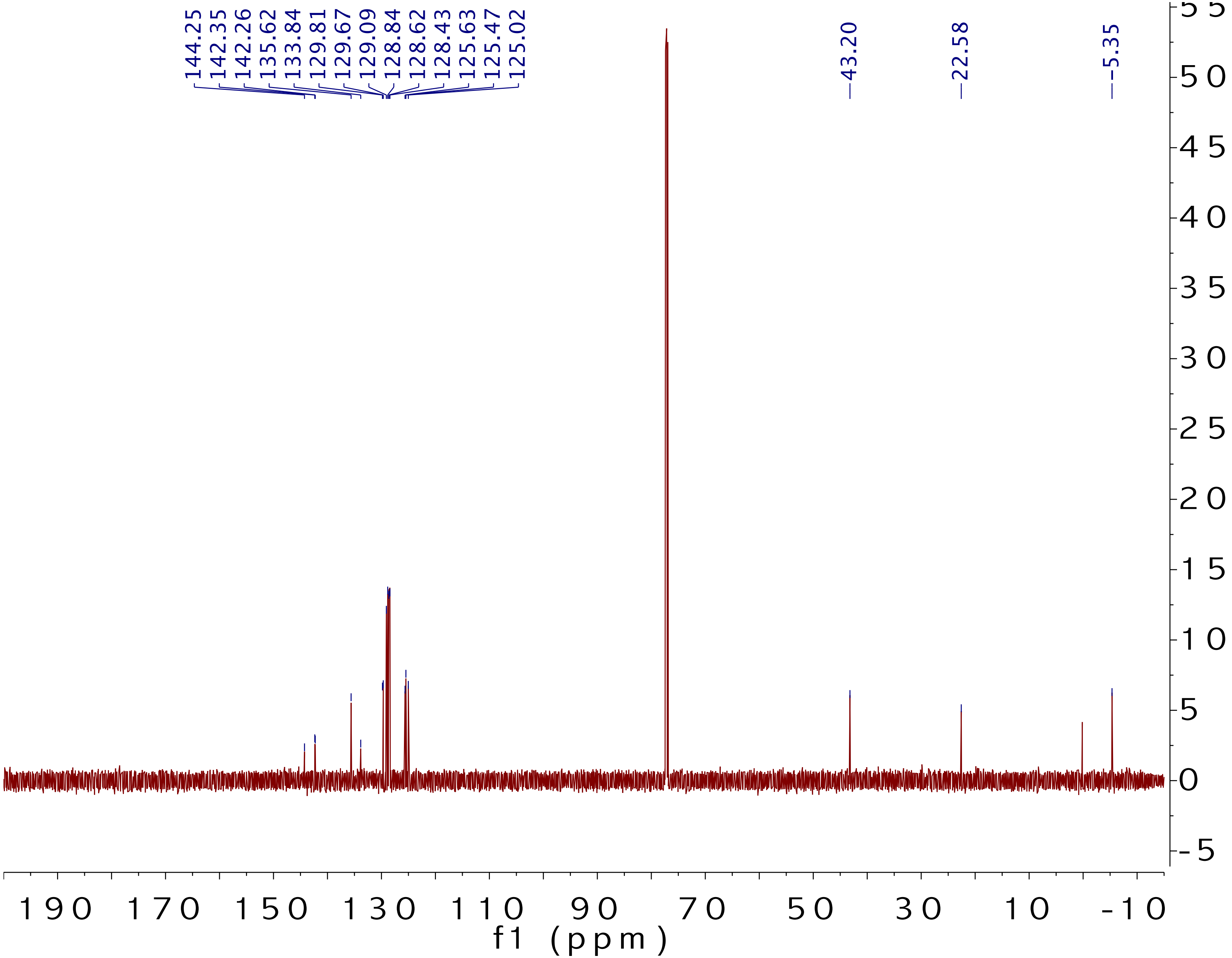
^{1}H, 600 MHz, CDCl$_3$

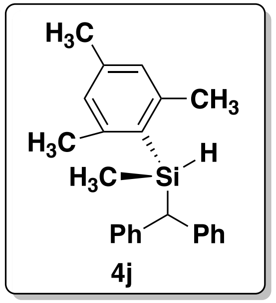




4i

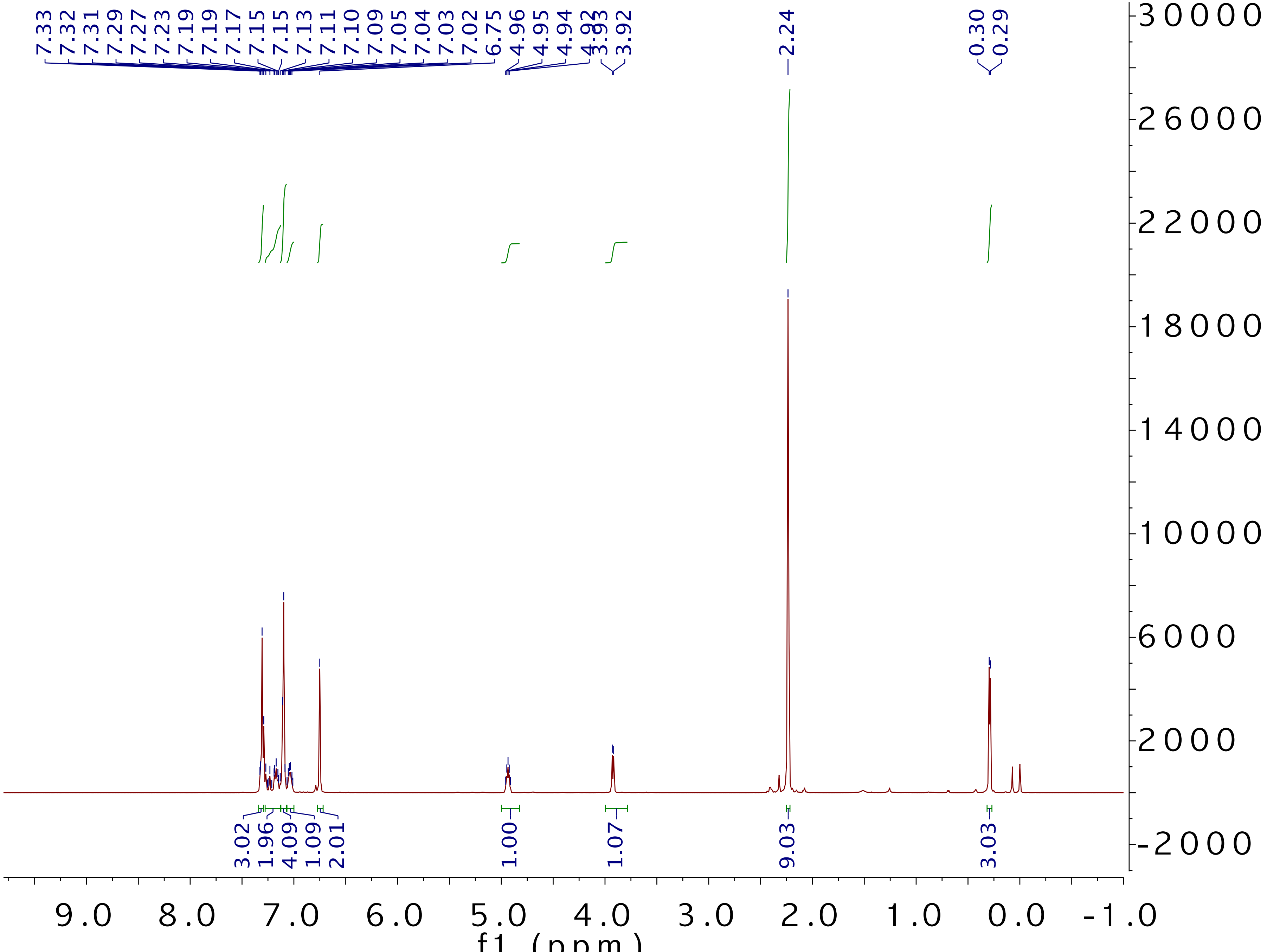
^{13}C, 151 MHz, CDCl$_3$

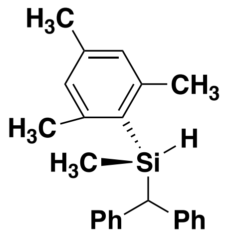




4j

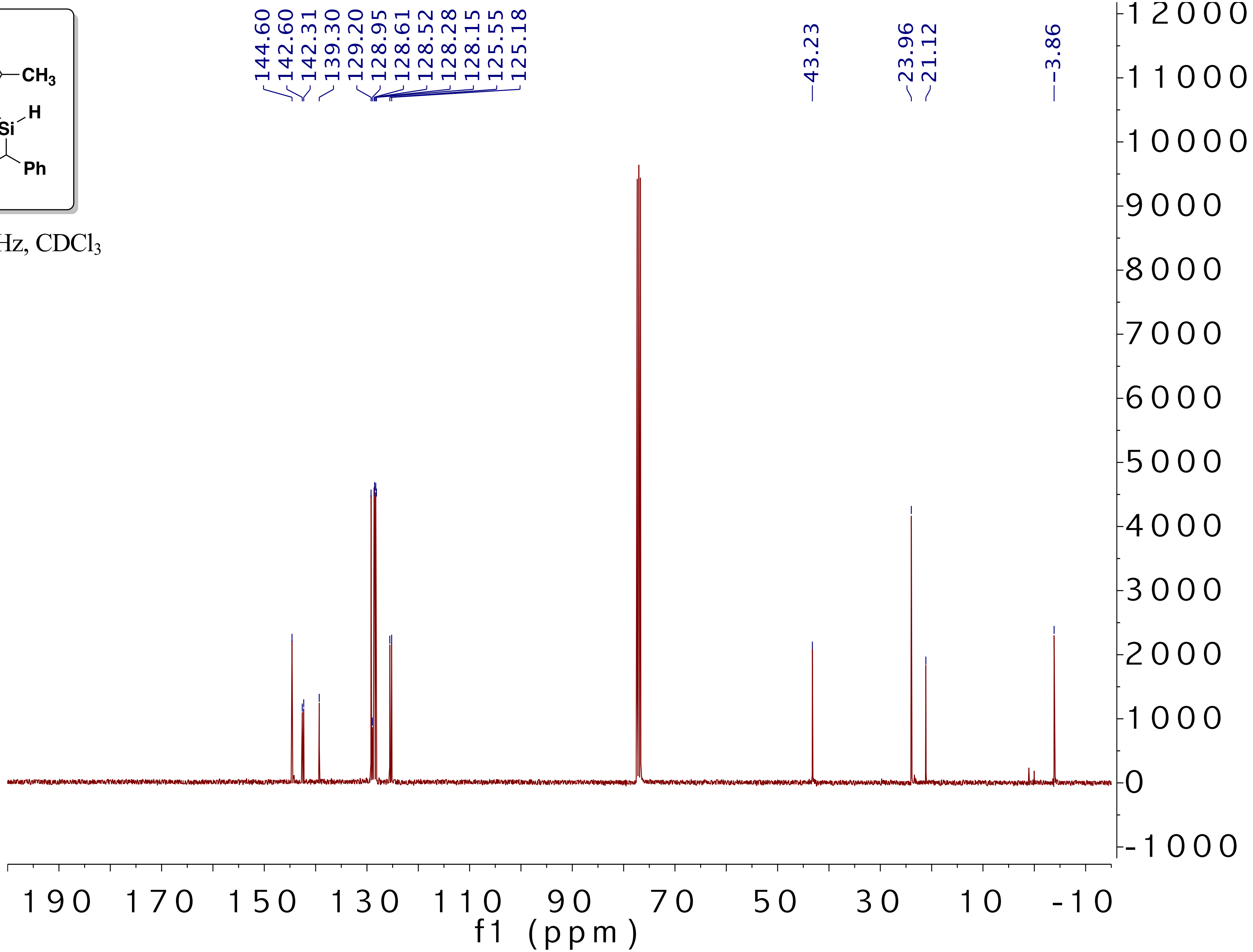
^{1}H, 400 MHz CDCl$_3$

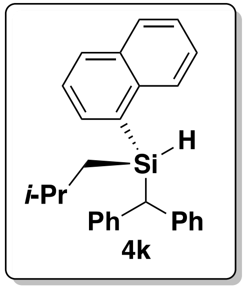




4j

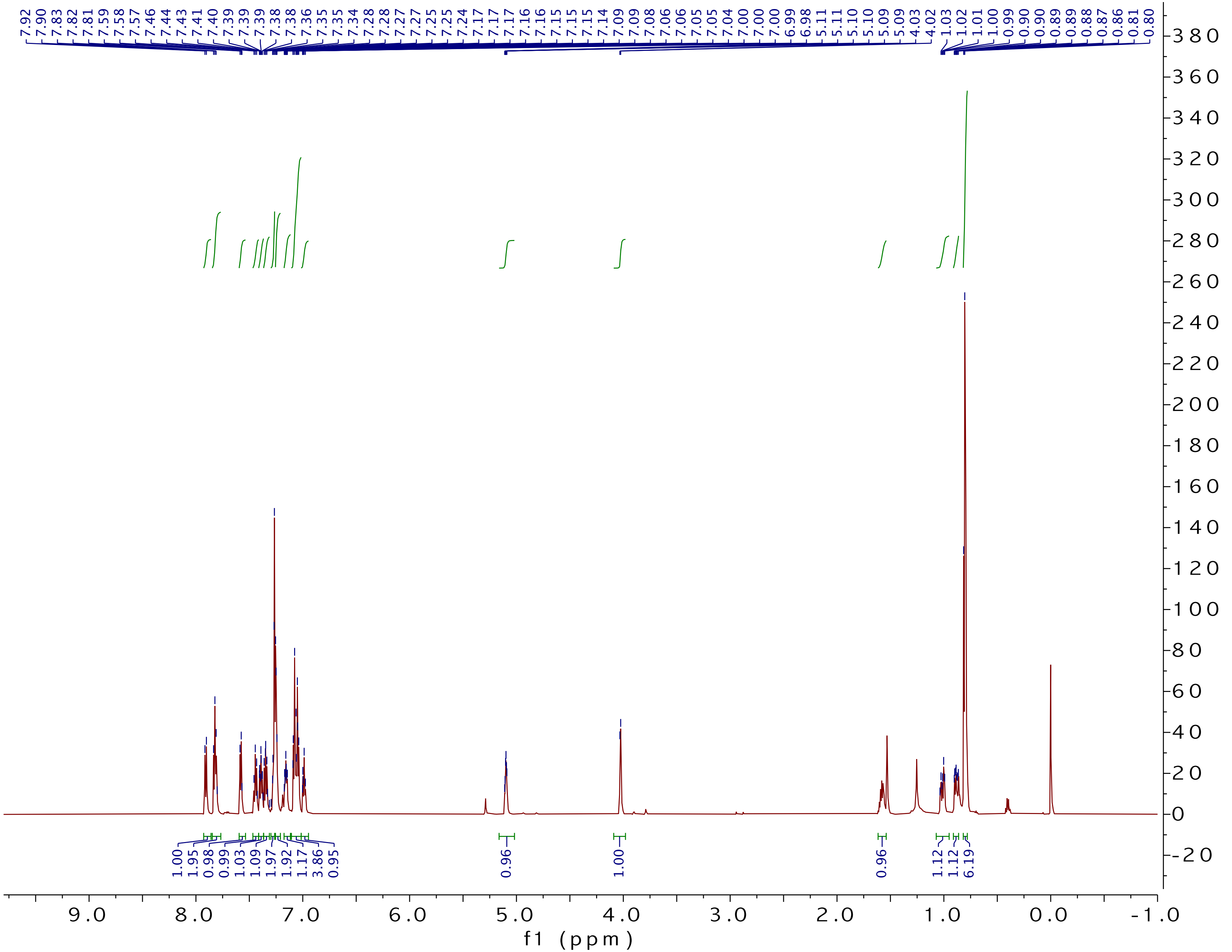
^{13}C, 100 MHz, CDCl$_3$

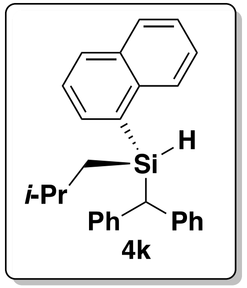




4k

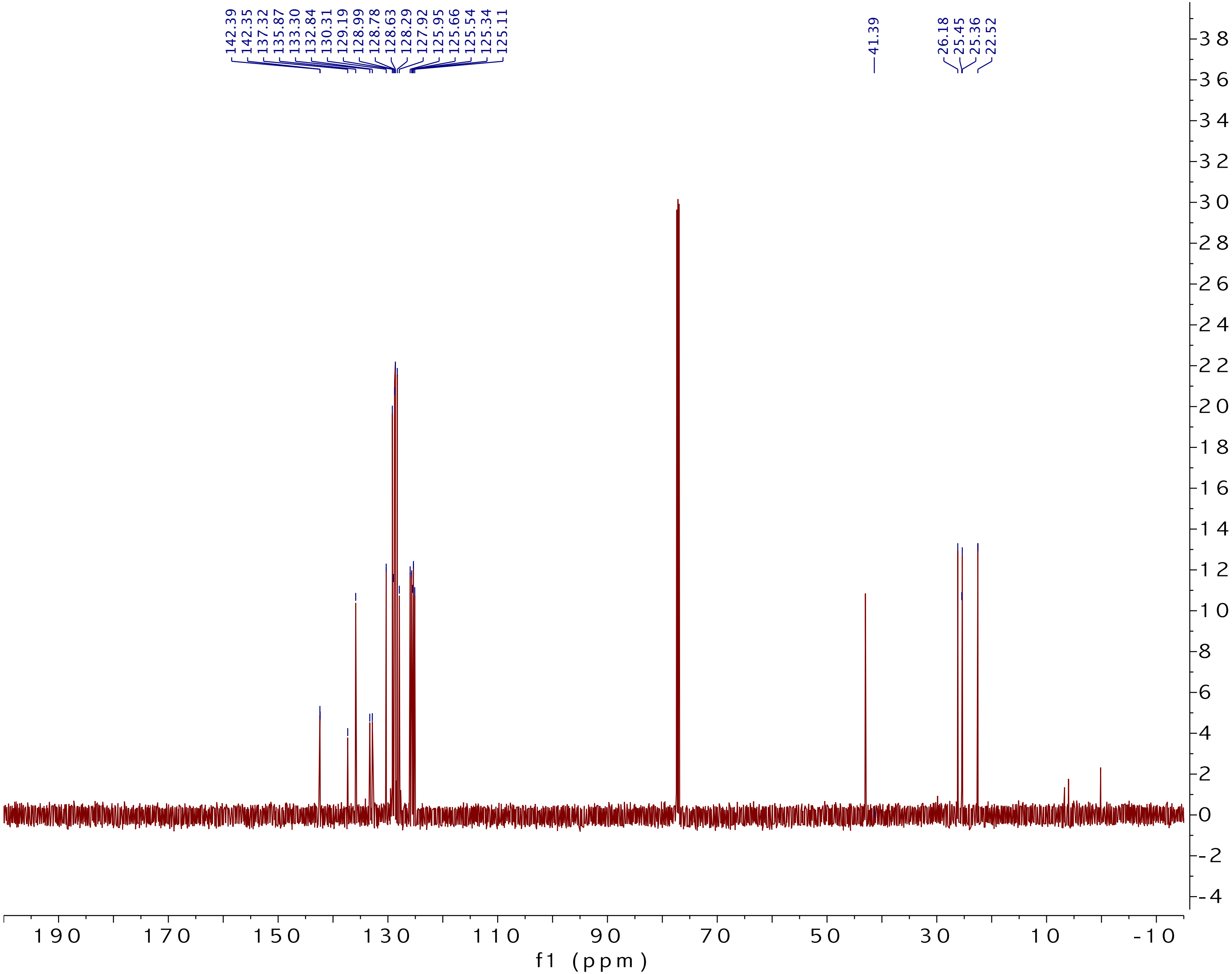
^{1}H, 600 MHz, CDCl$_3$

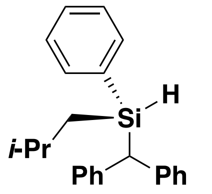




4k

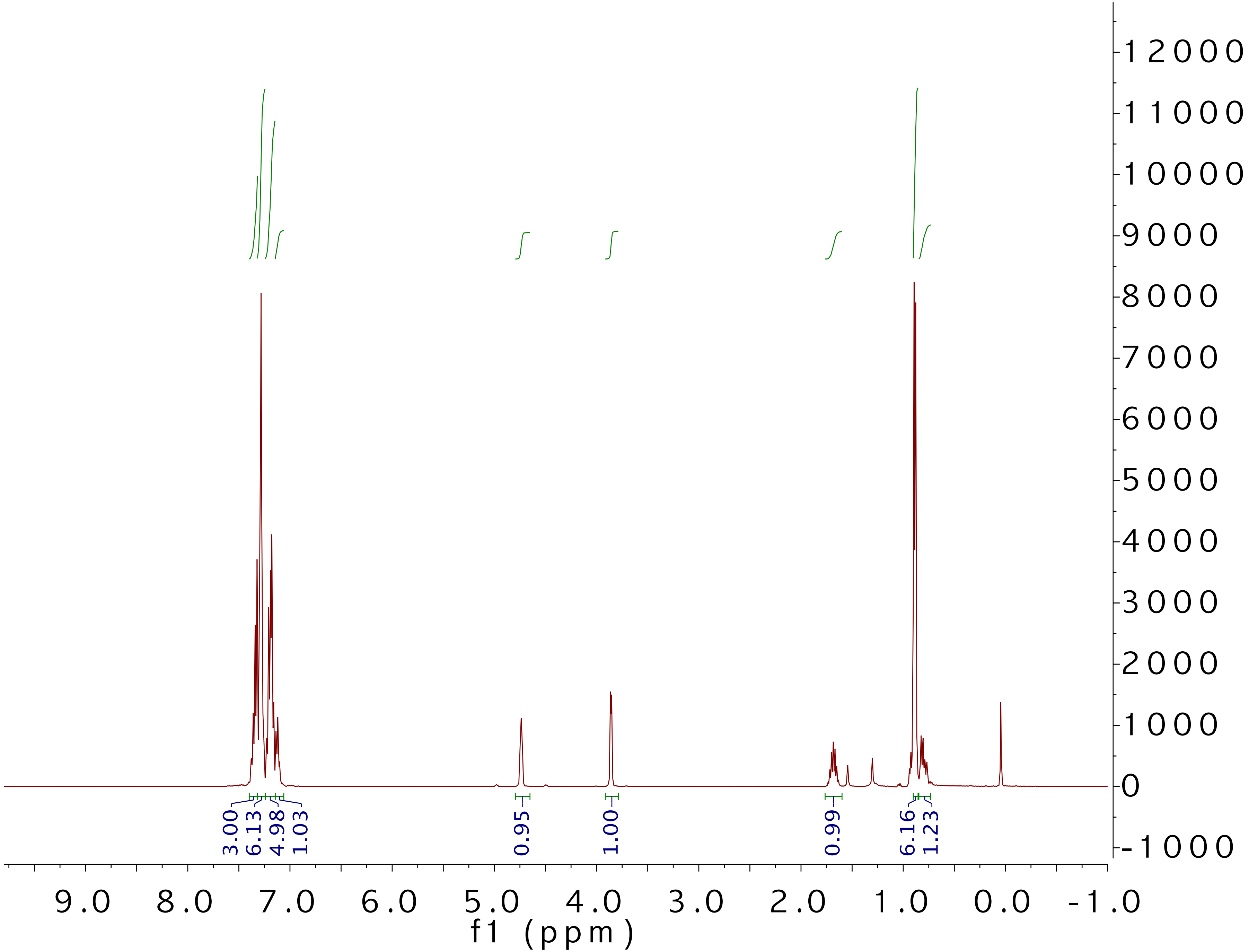
^{13}C, 151 MHz, CDCl$_3$

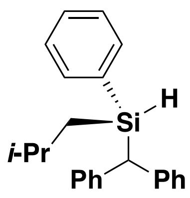




4l

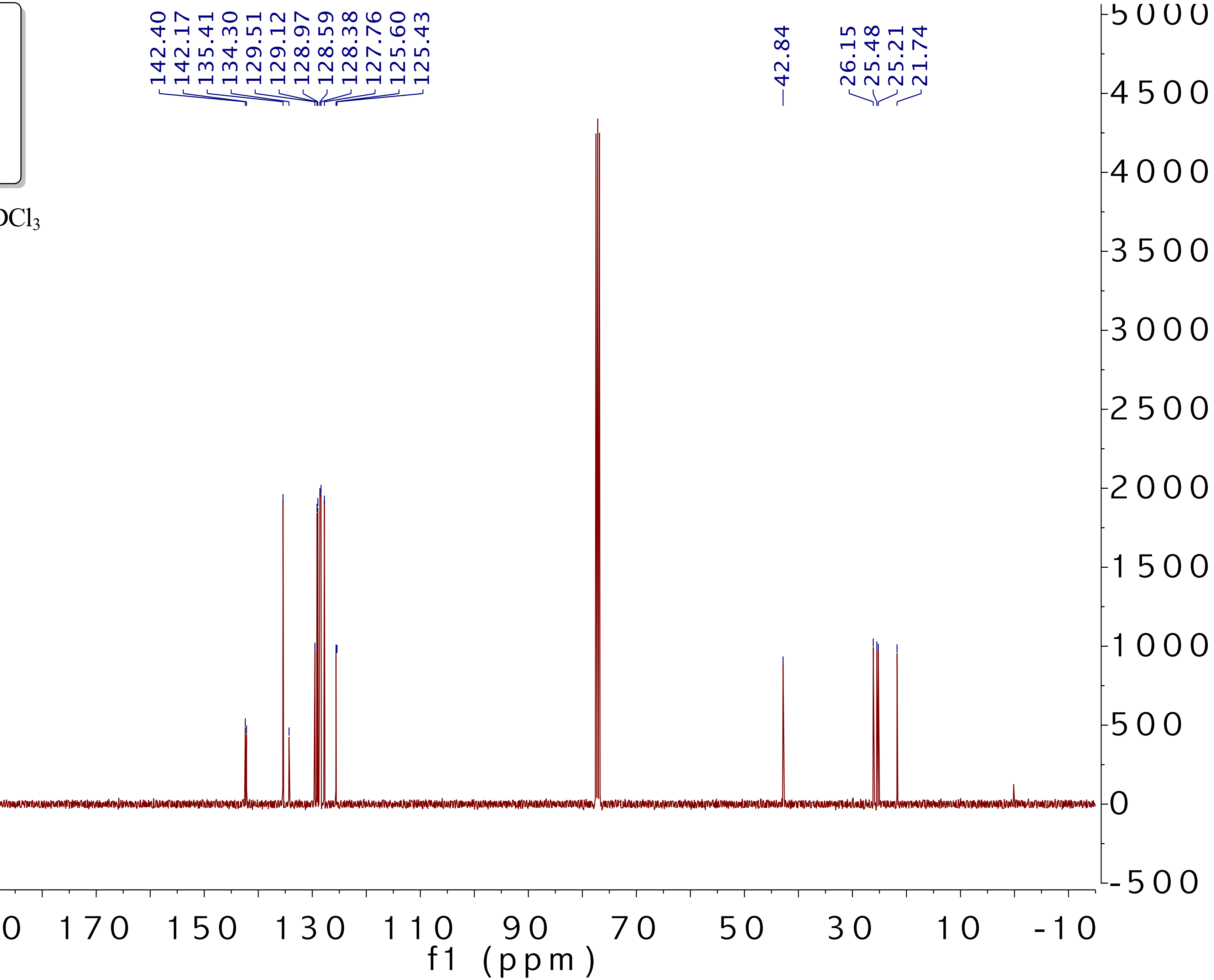
^{1}H, 400 MHz, CDCl$_3$

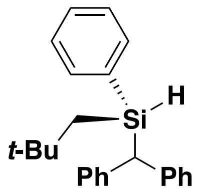




4l

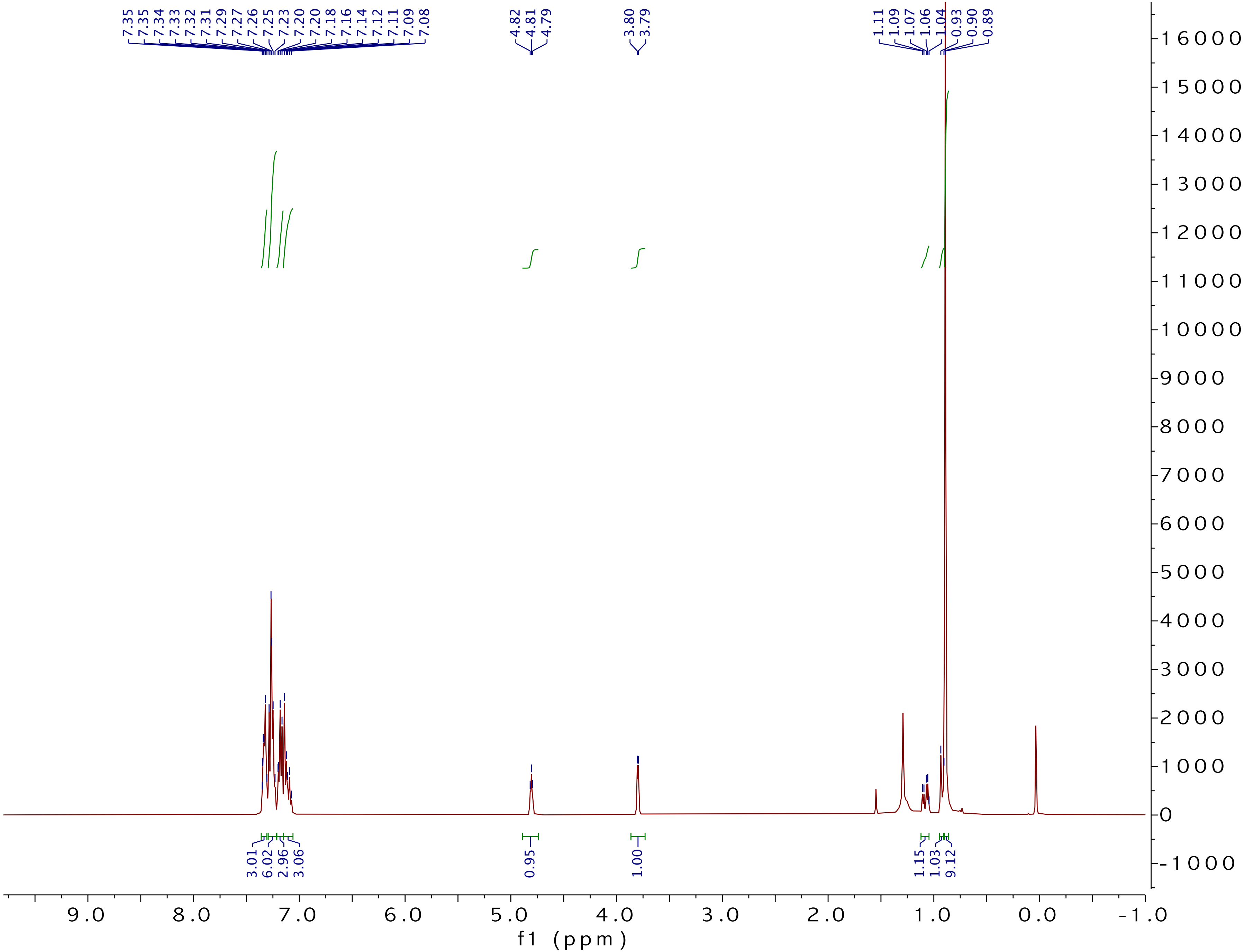
^{13}C, 100 MHz, CDCl$_3$

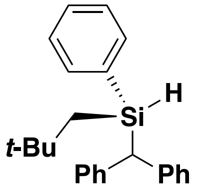




4m

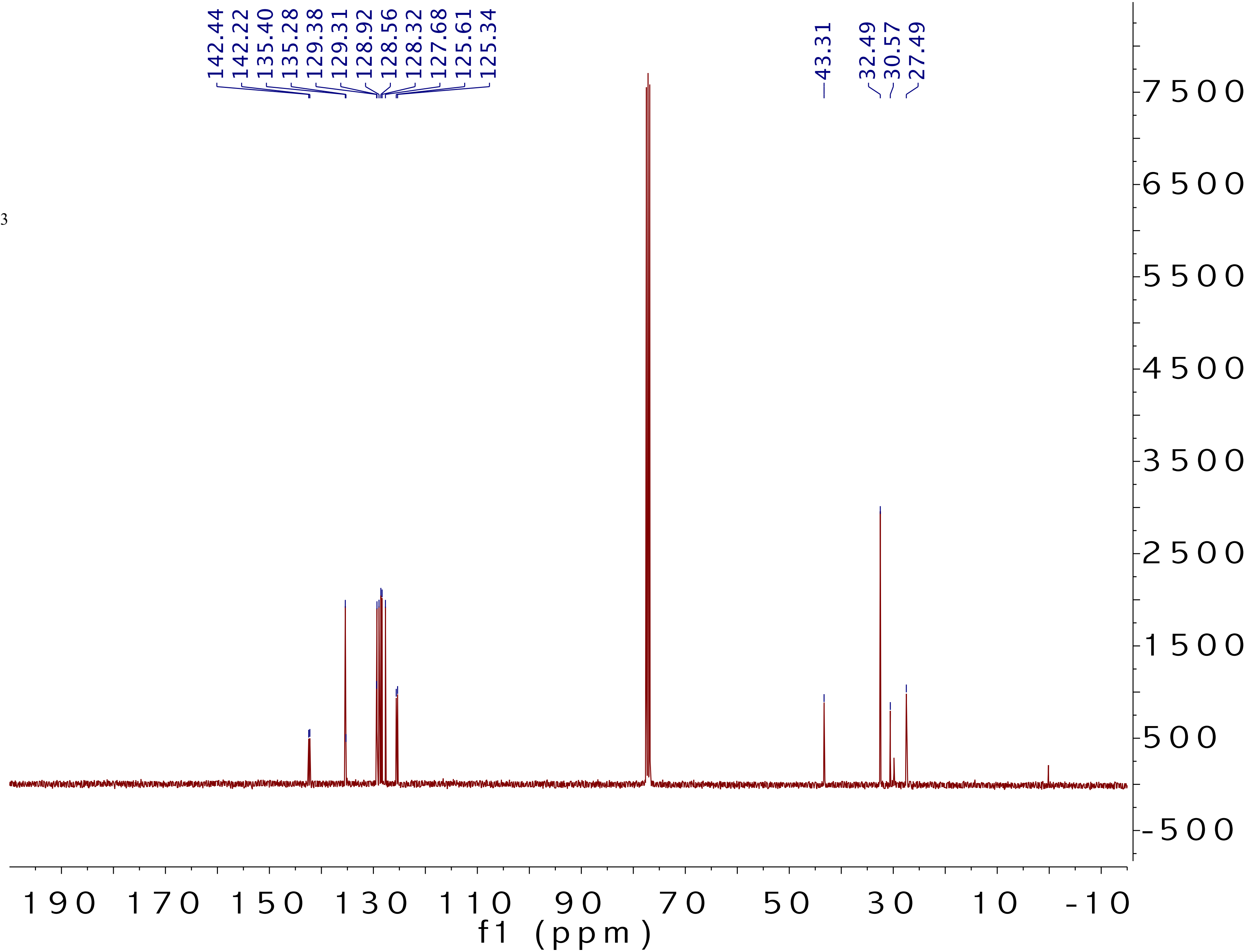
^{1}H, 400 MHz, CDCl$_3$

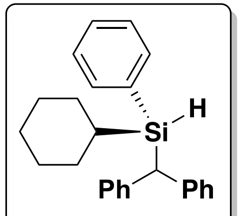




4m

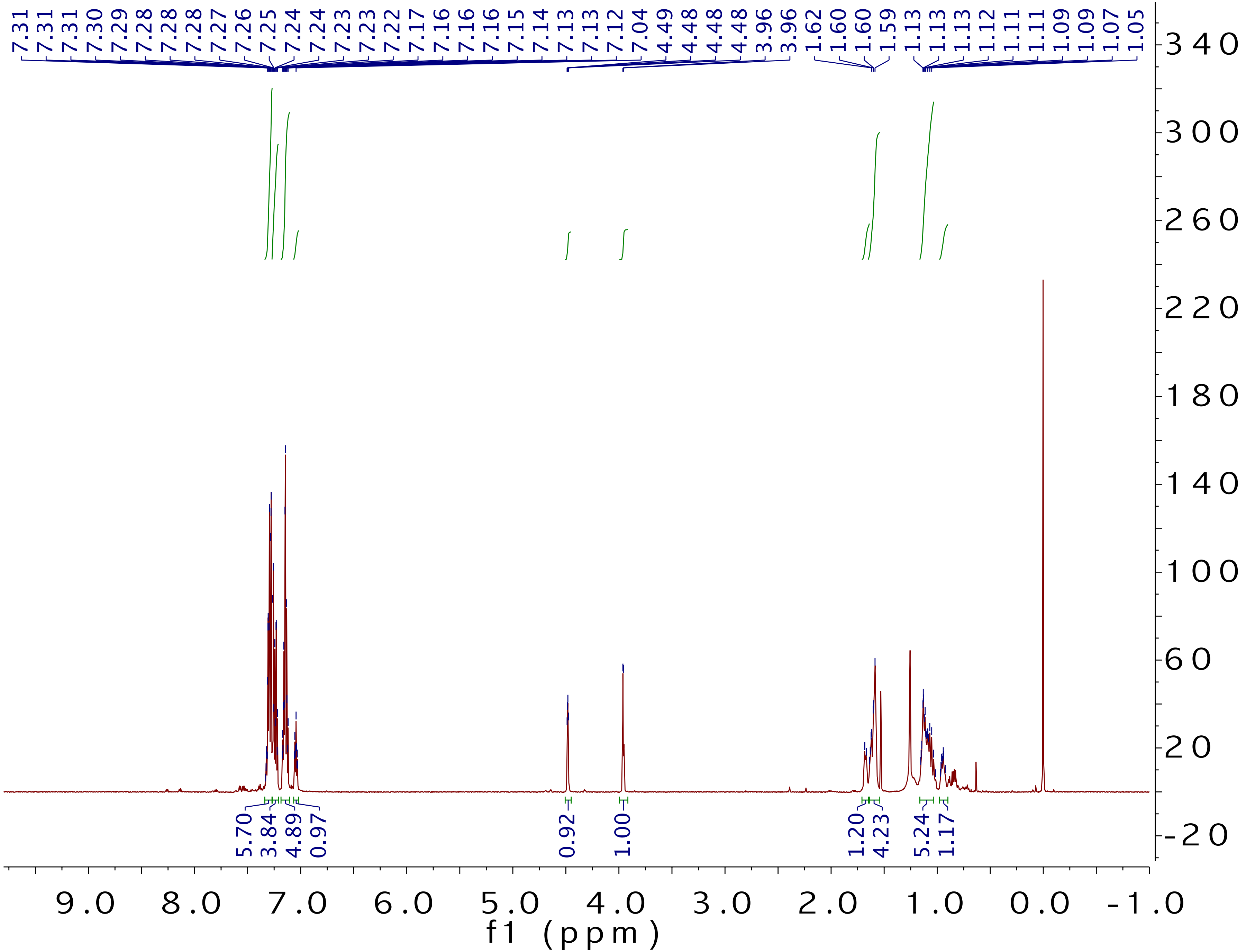
^{13}C, 100 MHz, CDCl$_3$

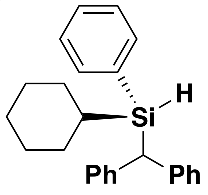




4n

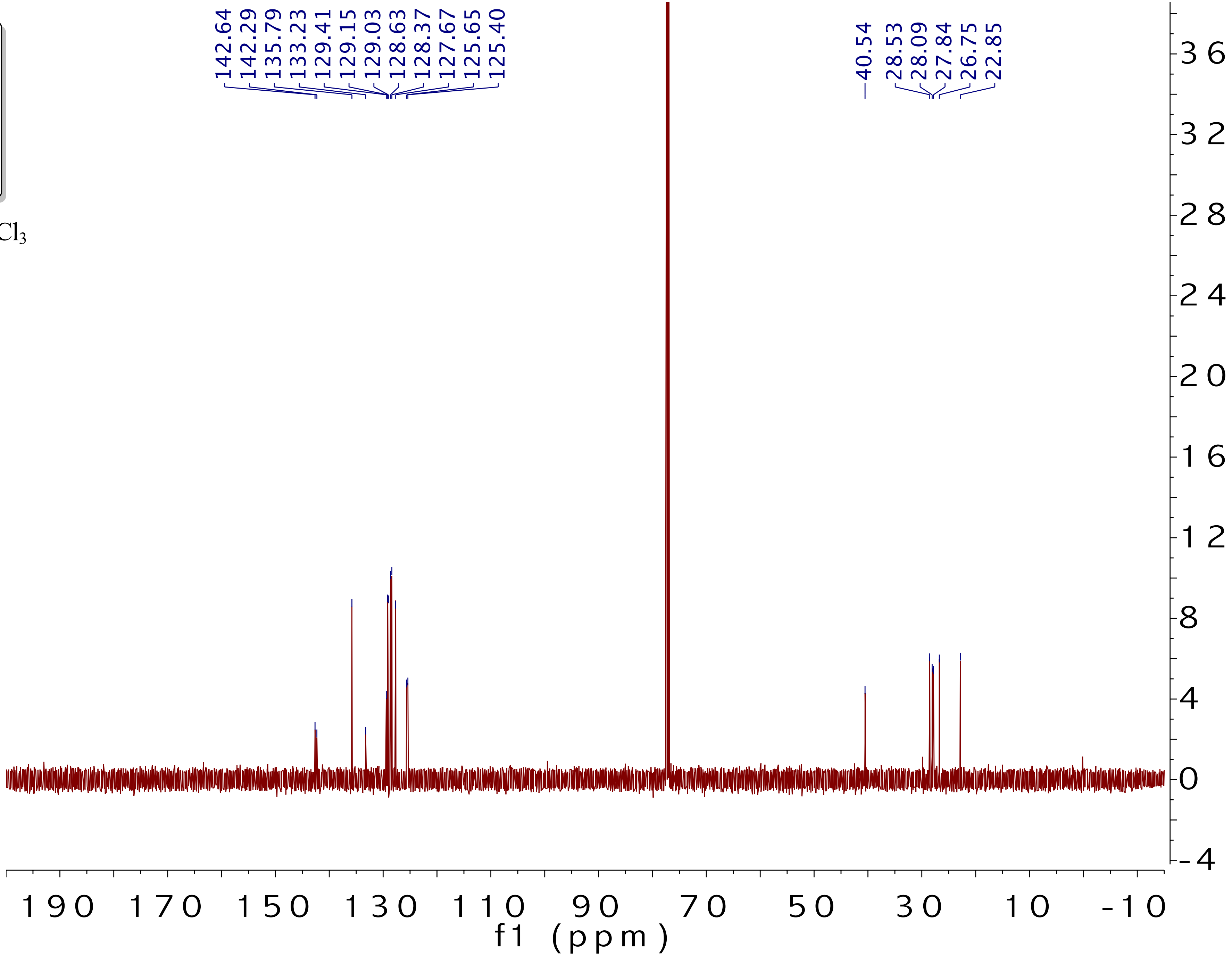
^{1}H, 600 MHz, $CDCl_3$

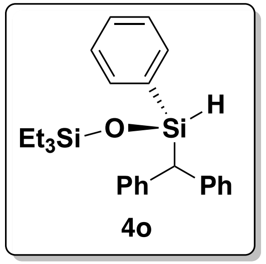




4n

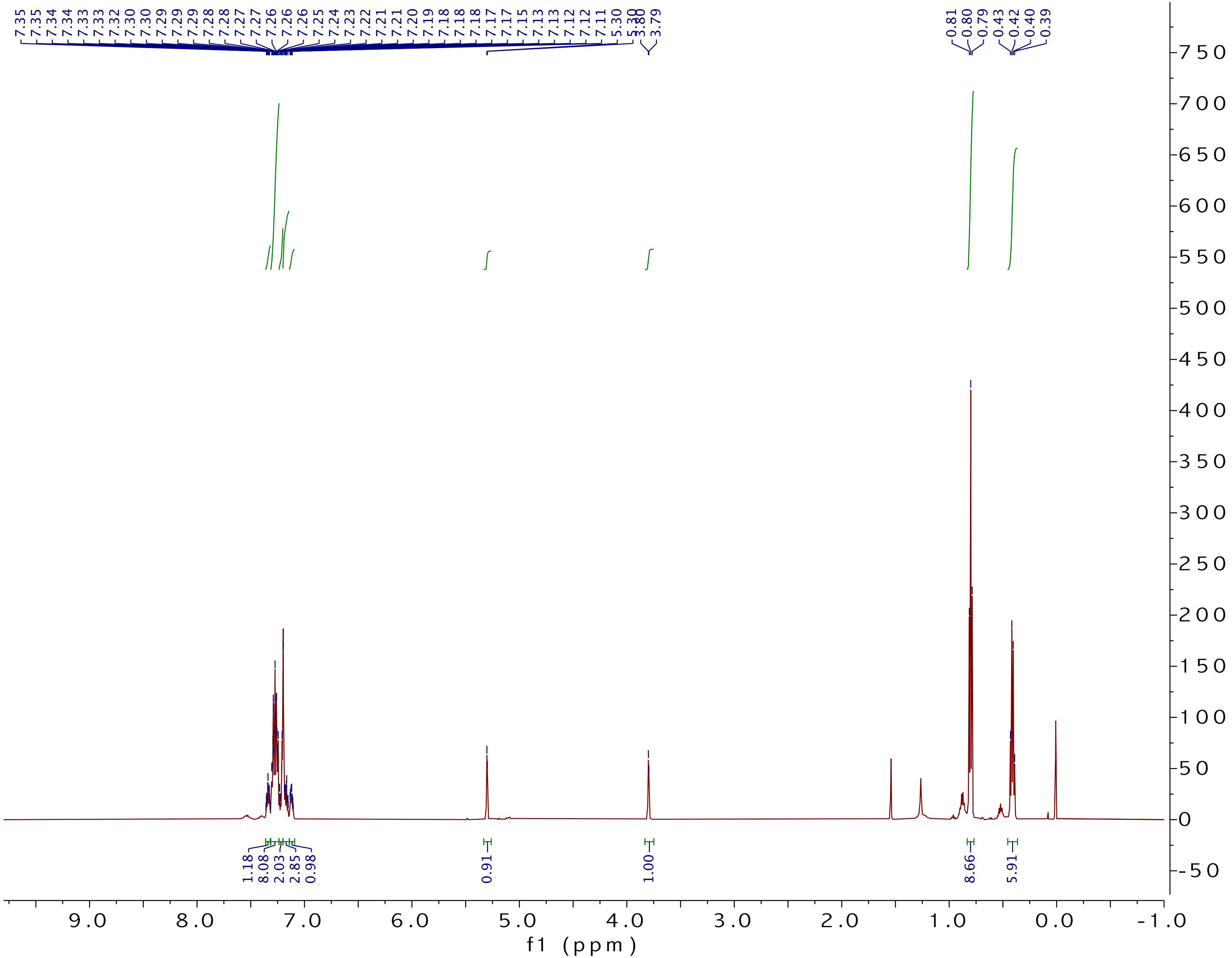
^{13}C, 151 MHz, CDCl$_3$

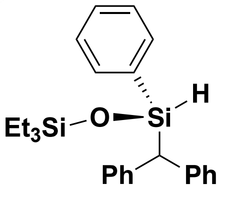




4o

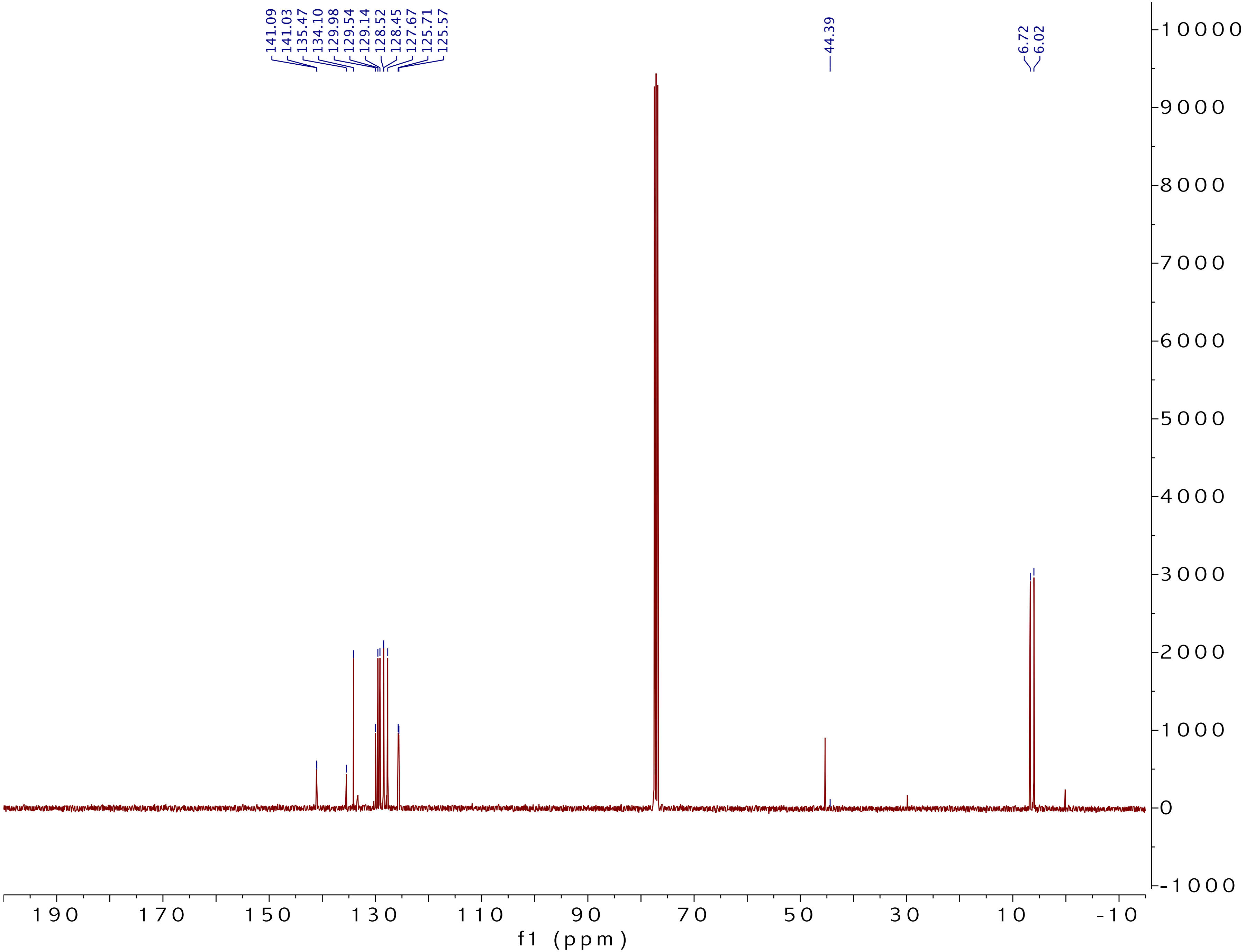
^{1}H, 600 MHz, CDCl$_3$

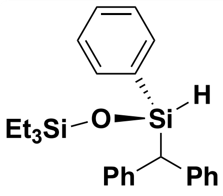




4o

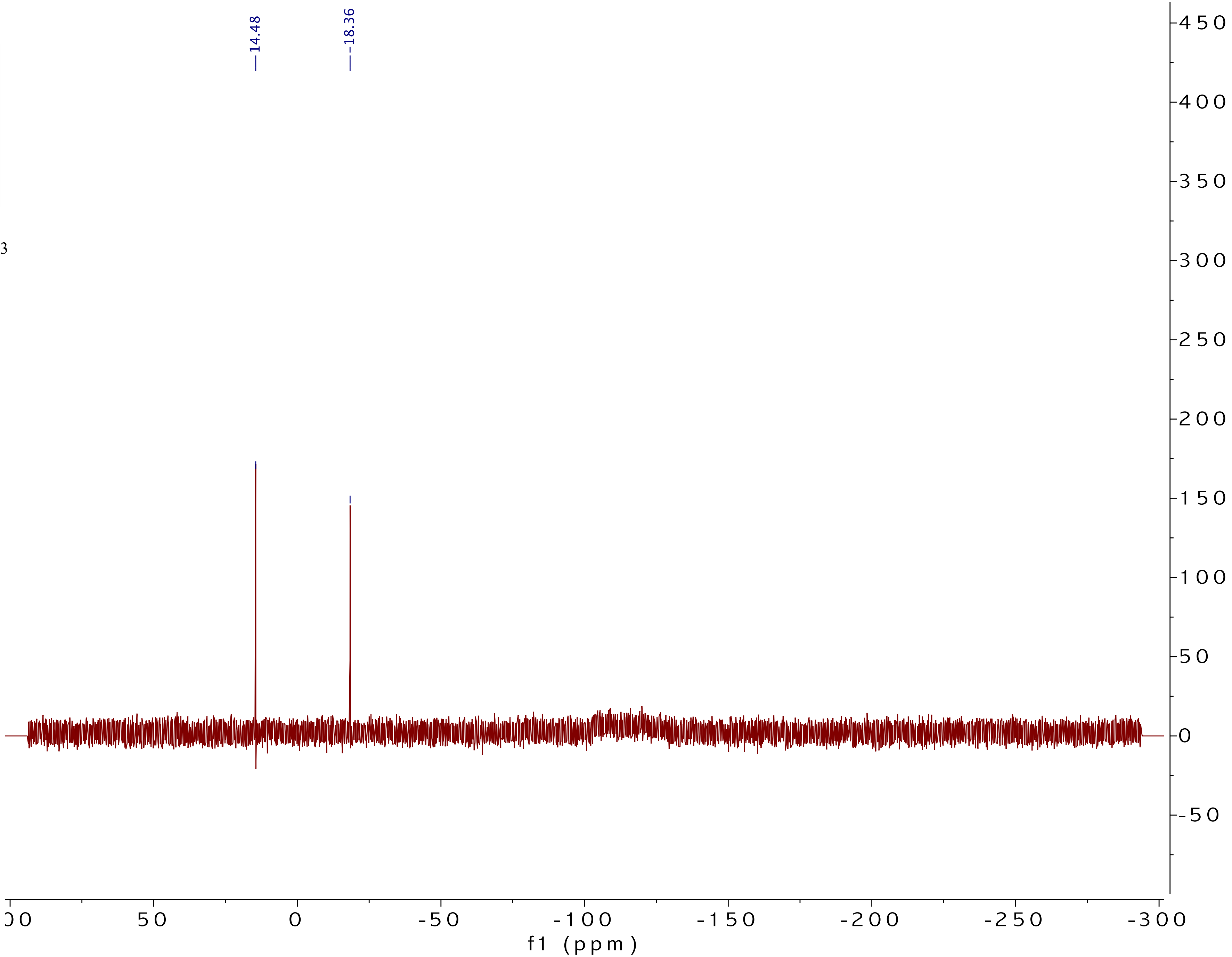
^{13}C, 151 MHz, CDCl$_3$

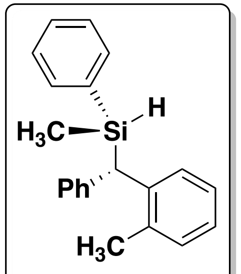




4o

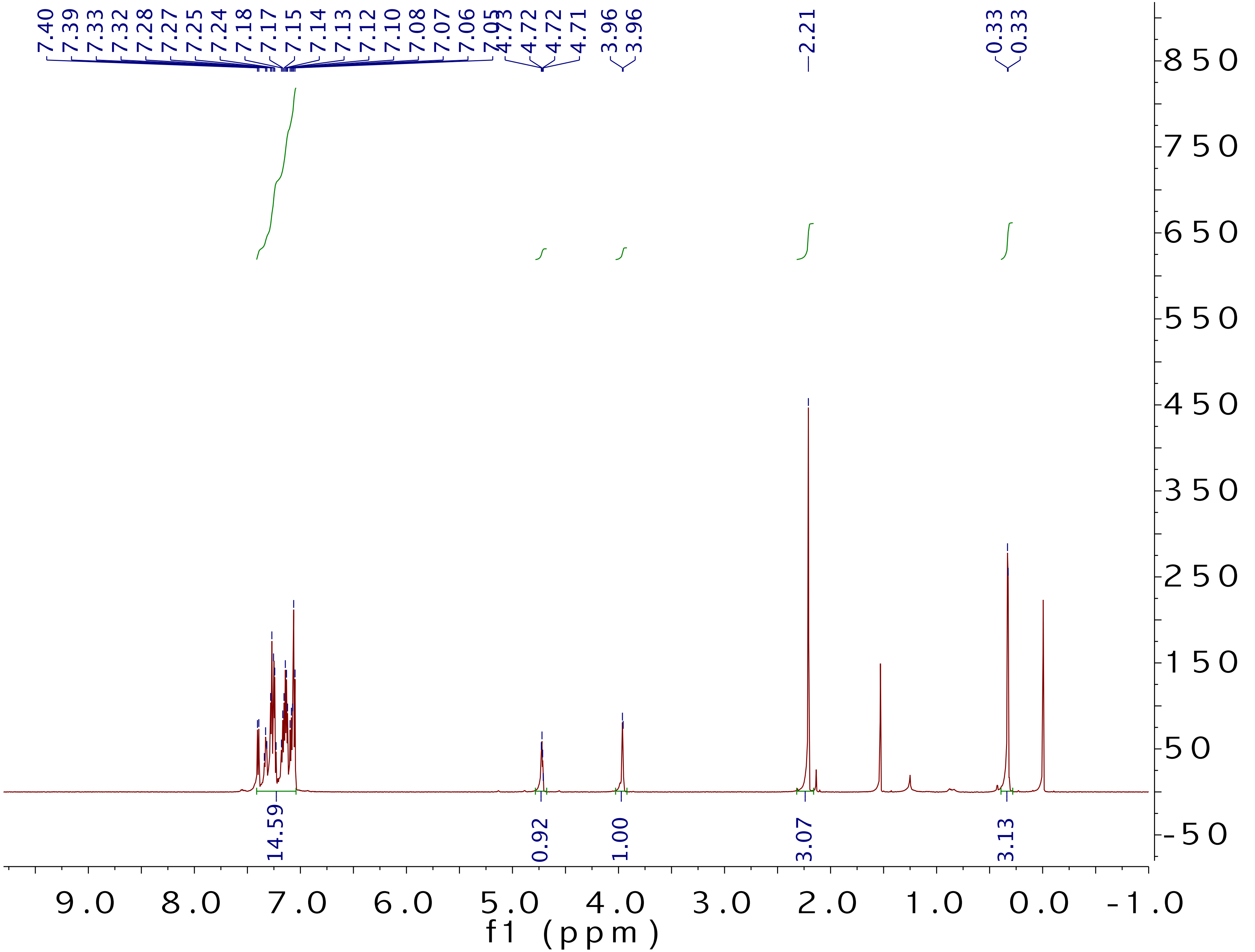
^{29}Si, 76 MHz, CDCl$_3$

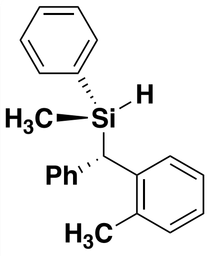




5a

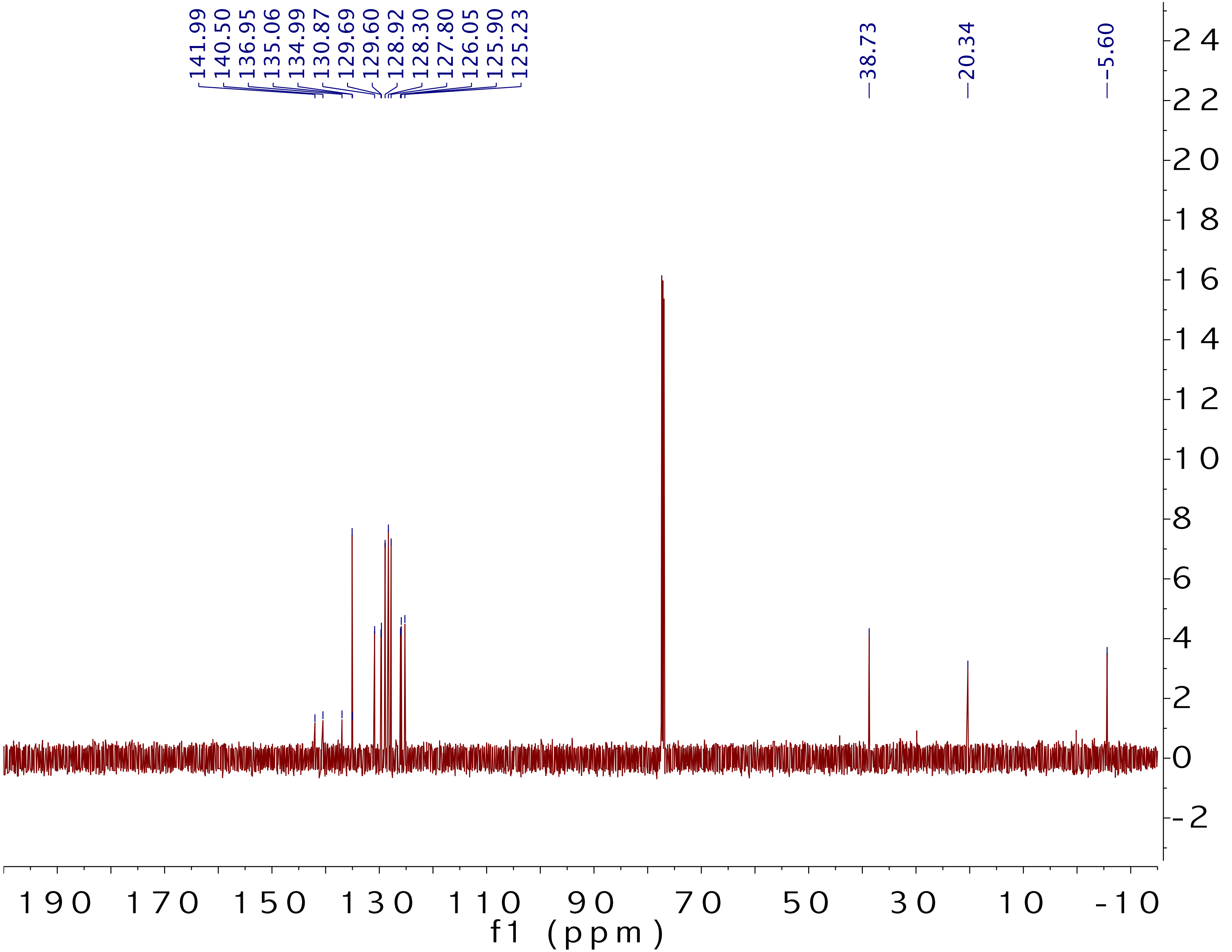
^{1}H, 600 MHz, CDCl$_3$

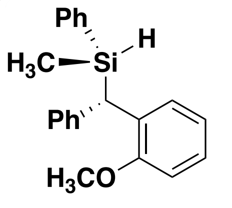




5a

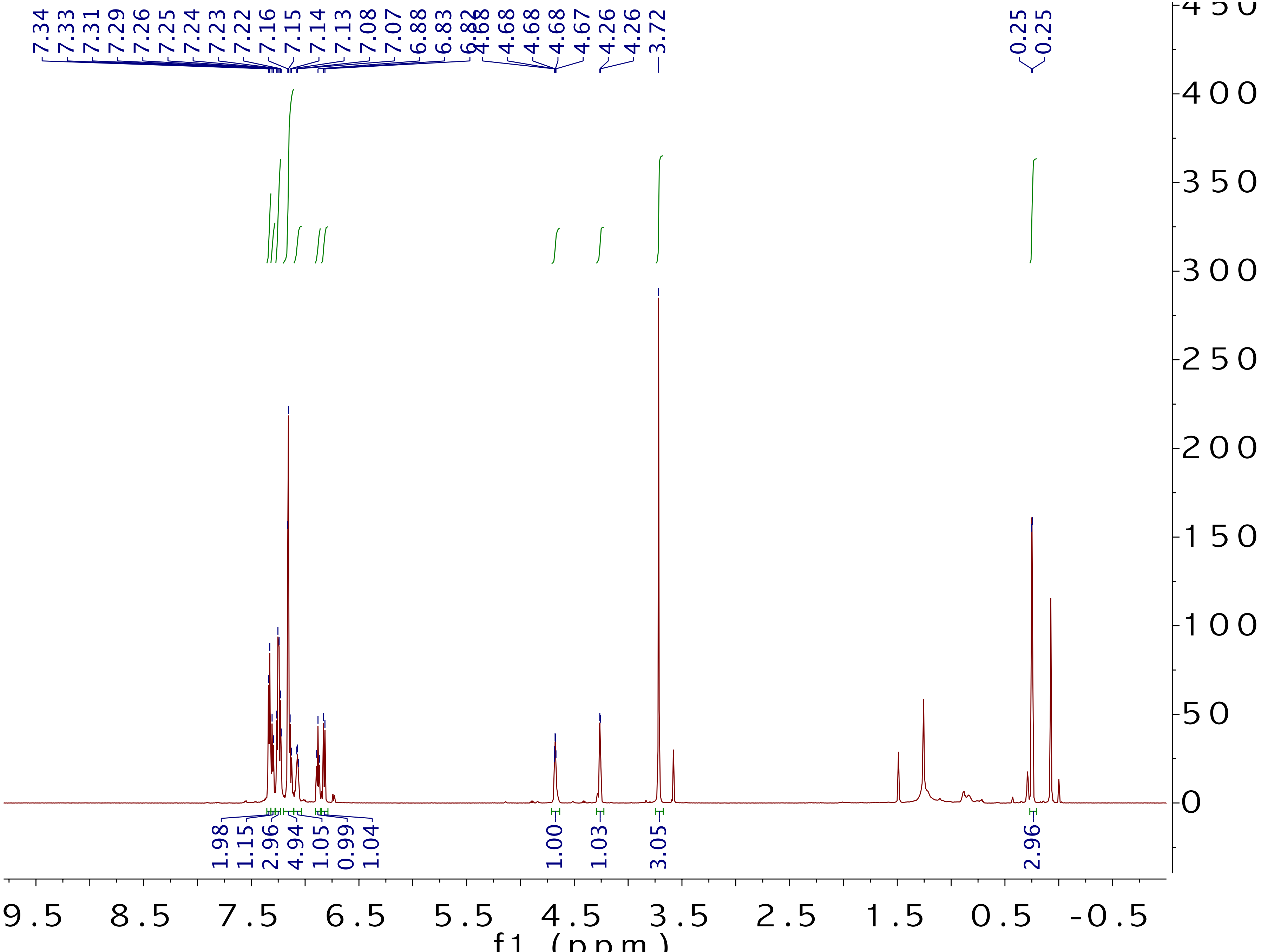
^{13}C, 150 MHz, CDCl$_3$

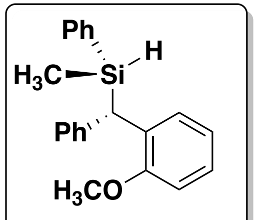




5b

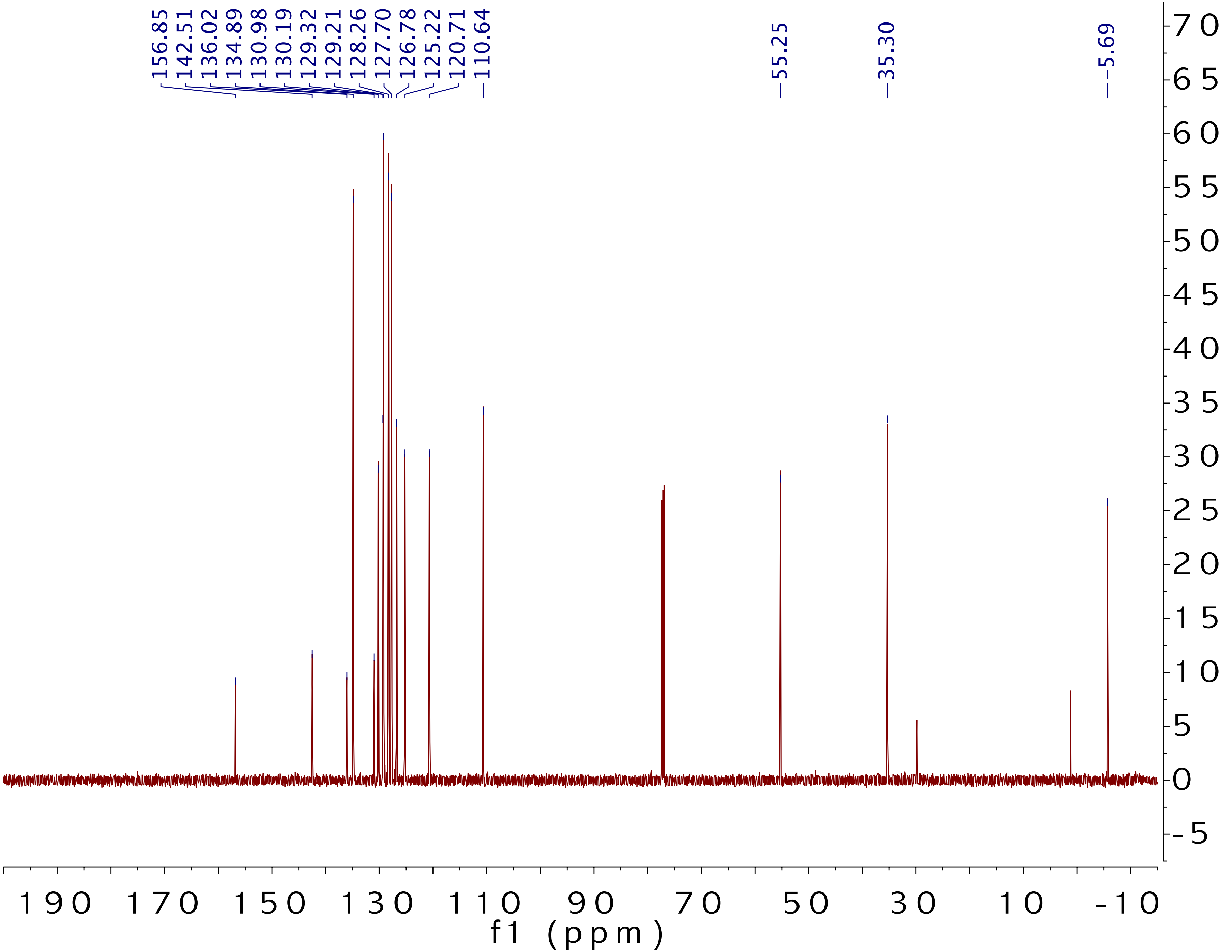
^{1}H, 600 MHz, CDCl$_3$

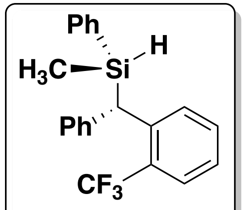




5b

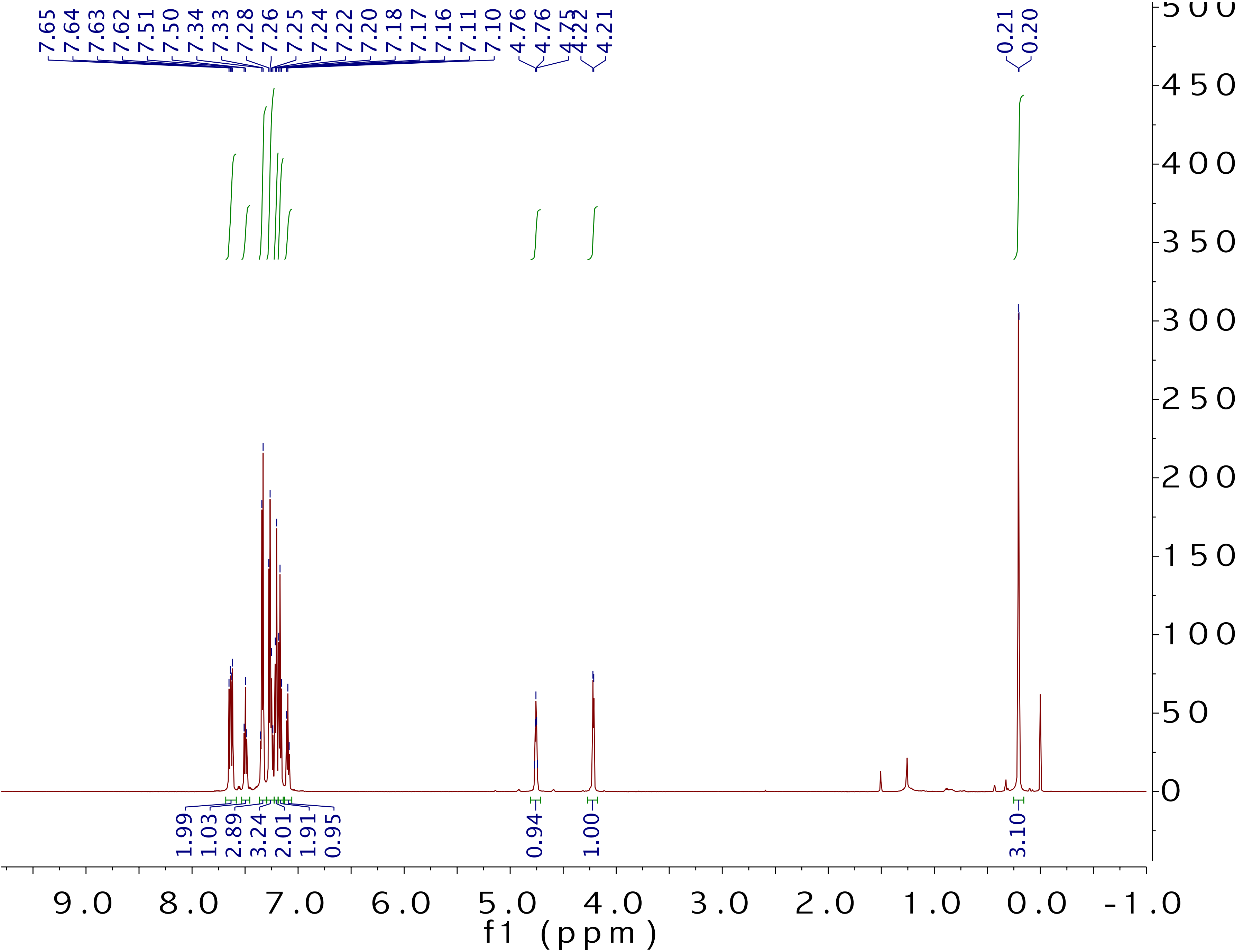
^{13}C, 151 MHz, $CDCl_3$

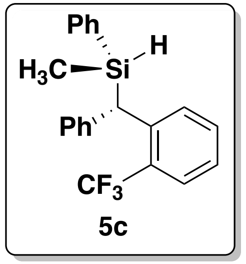




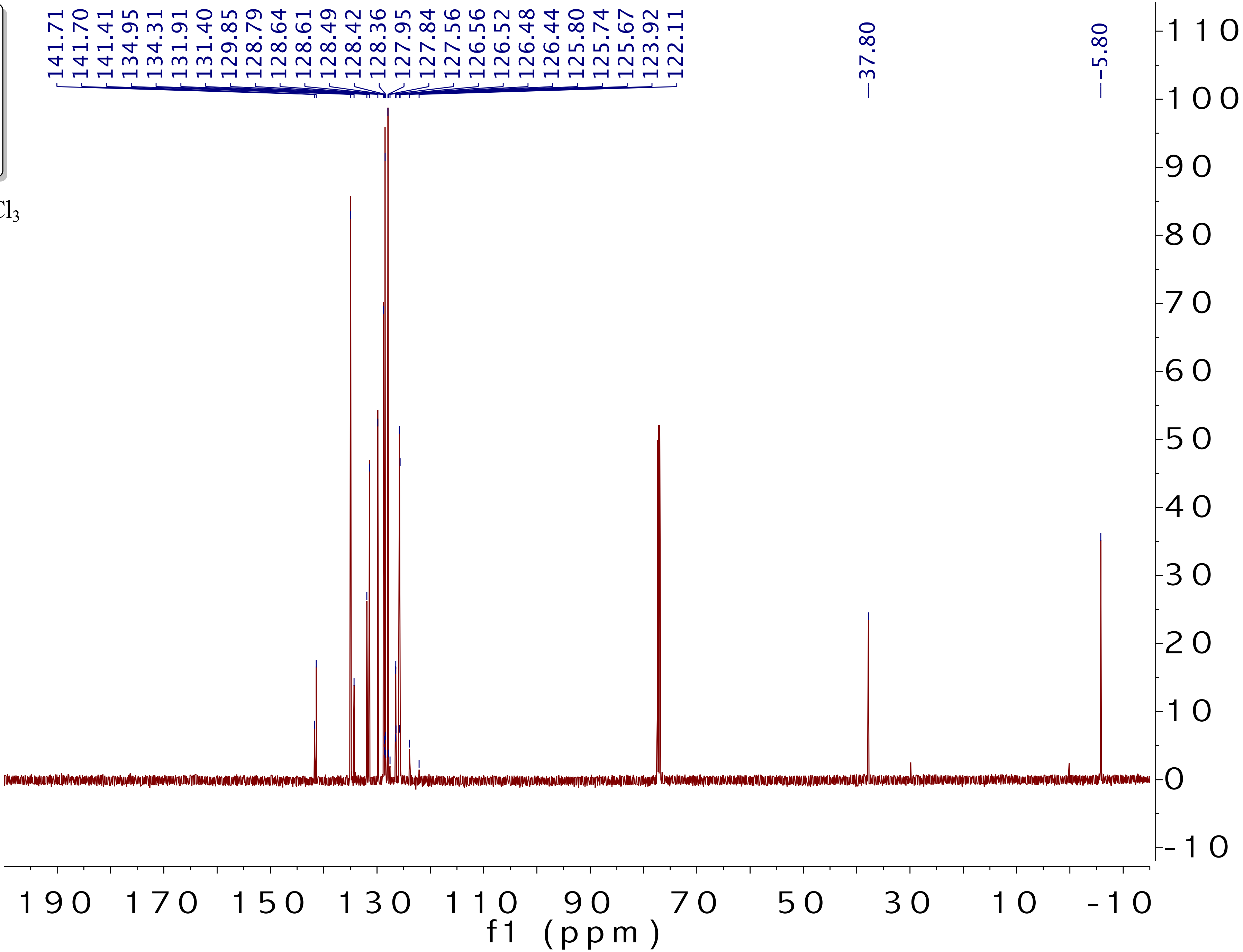
5c

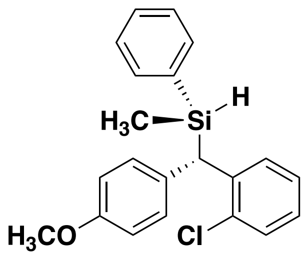
^{1}H, 600 MHz, $CDCl_3$




5c

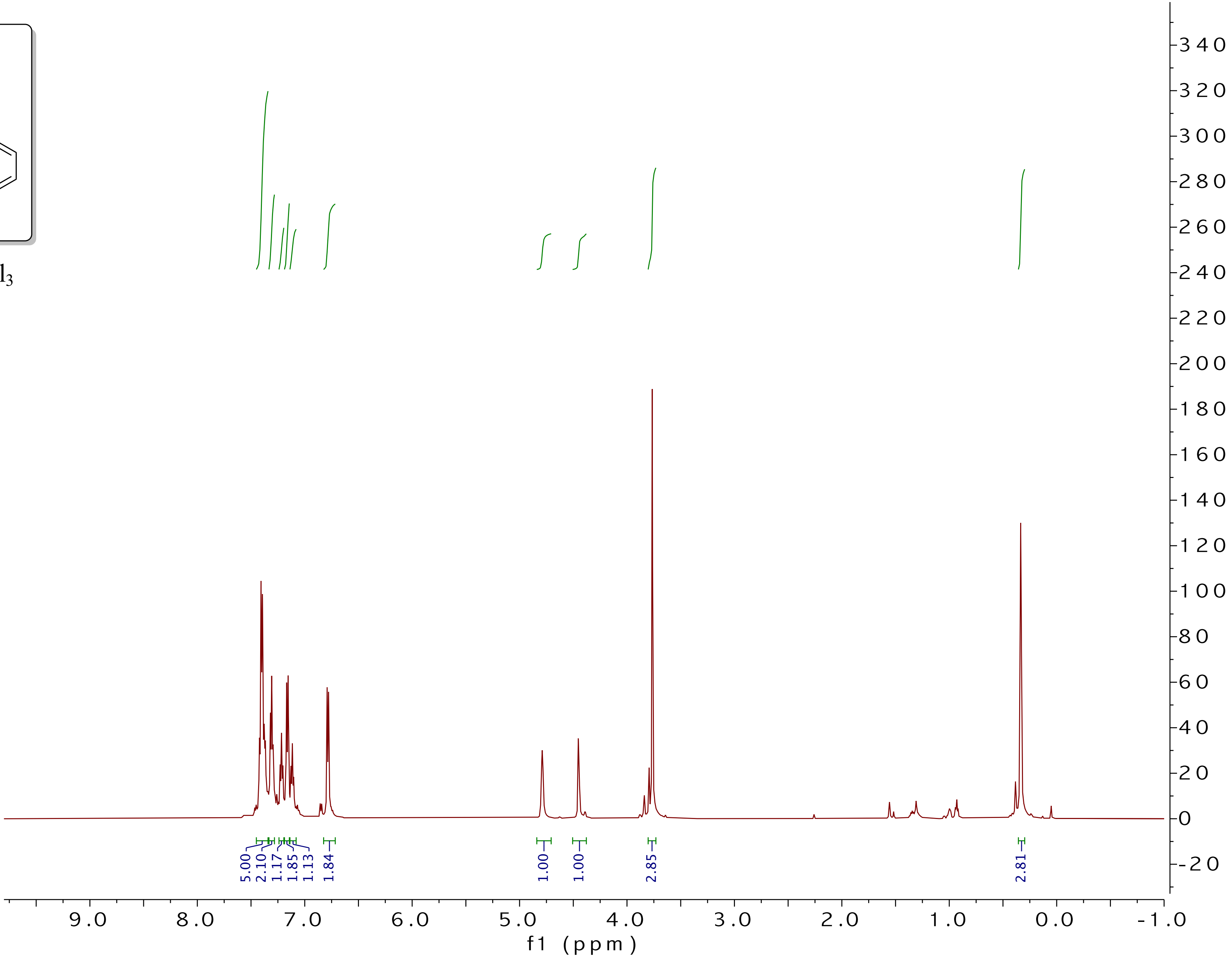
^{13}C, 151 MHz, CDCl$_3$

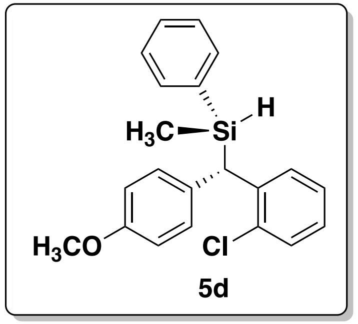




5d

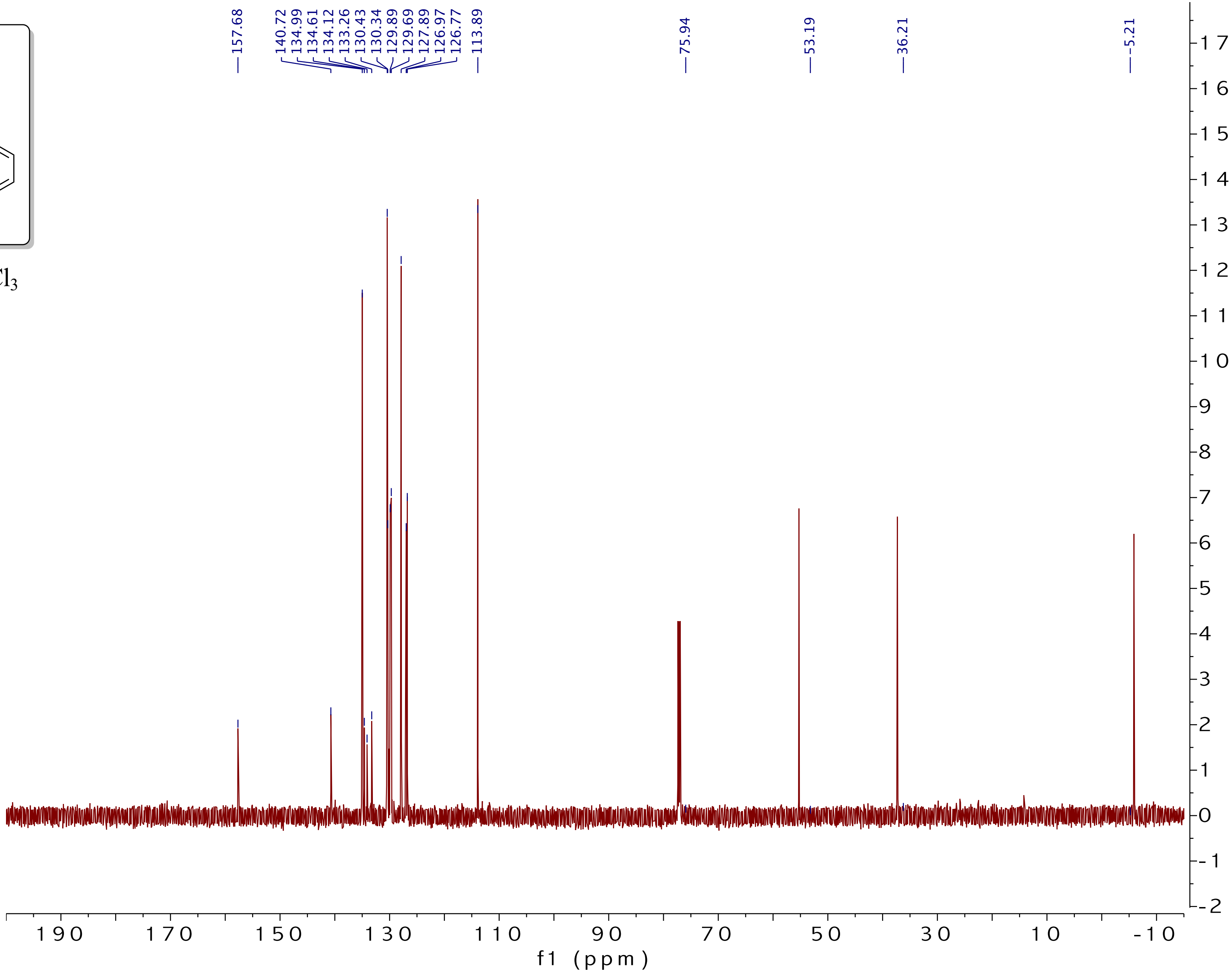
^{1}H, 600 MHz, $CDCl_3$

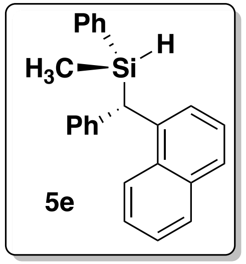




5d

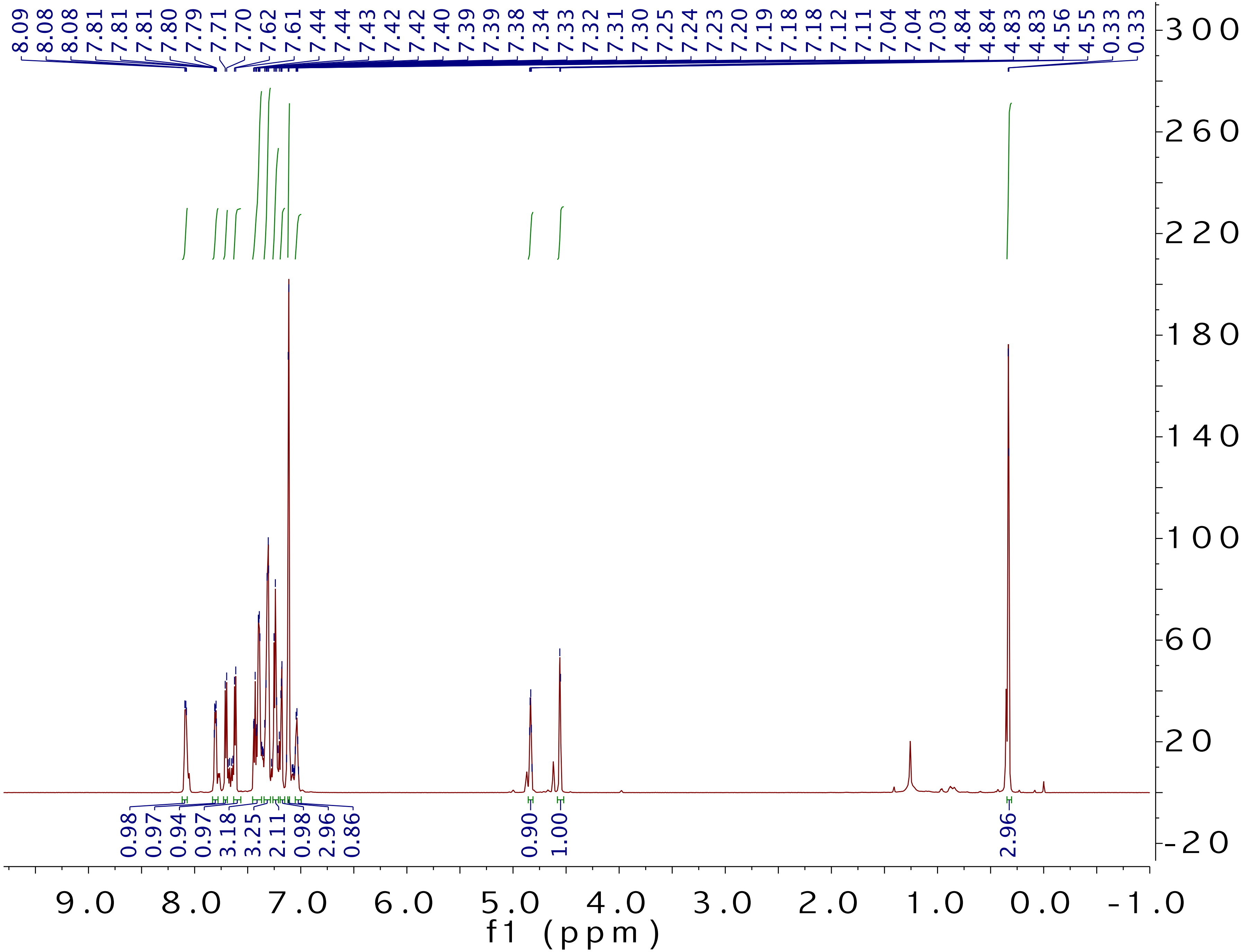
^{13}C, 151 MHz, CDCl$_3$

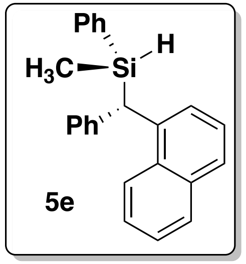




5e

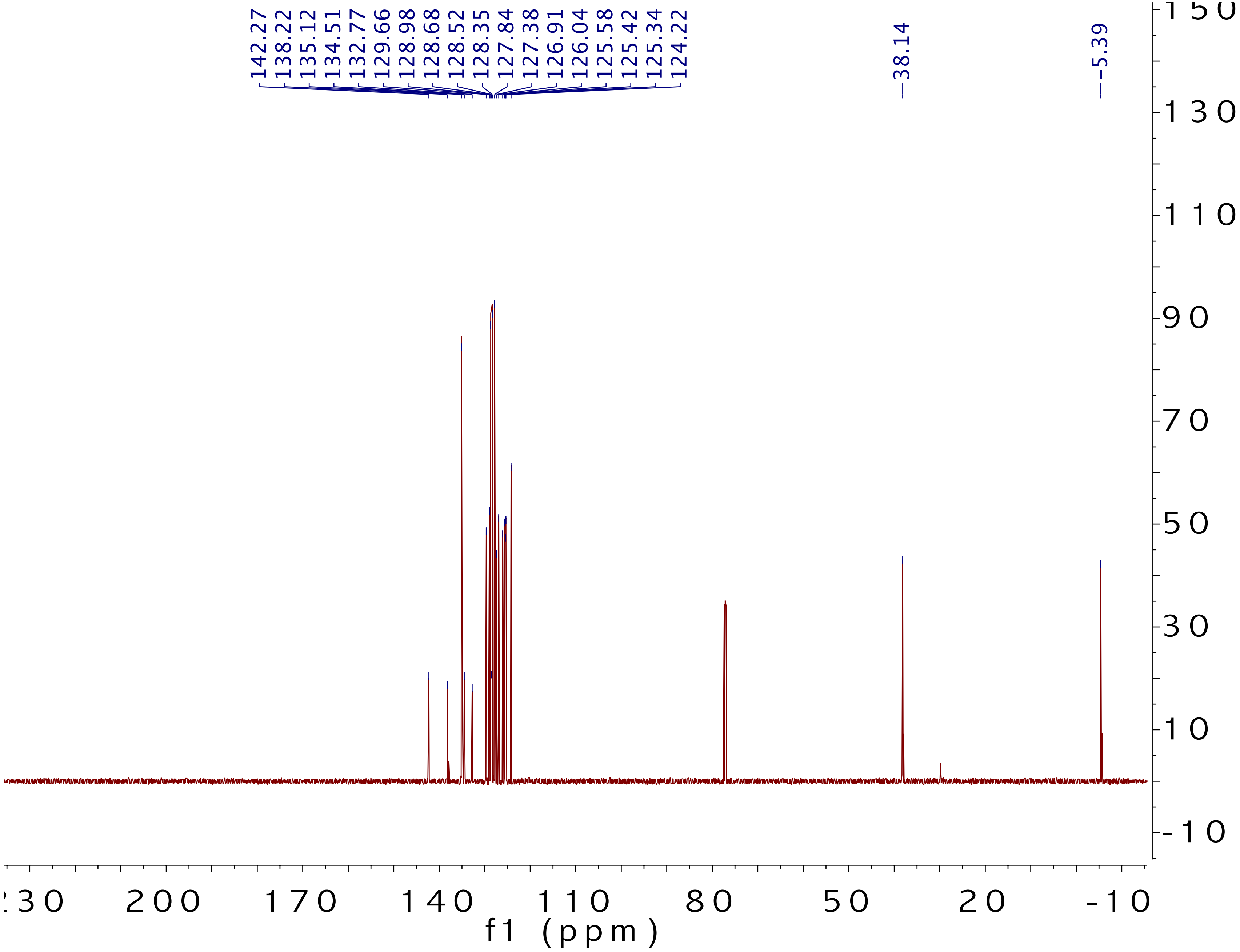
^{1}H, 600 MHz, CDCl$_3$

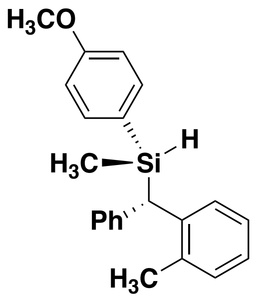




5e

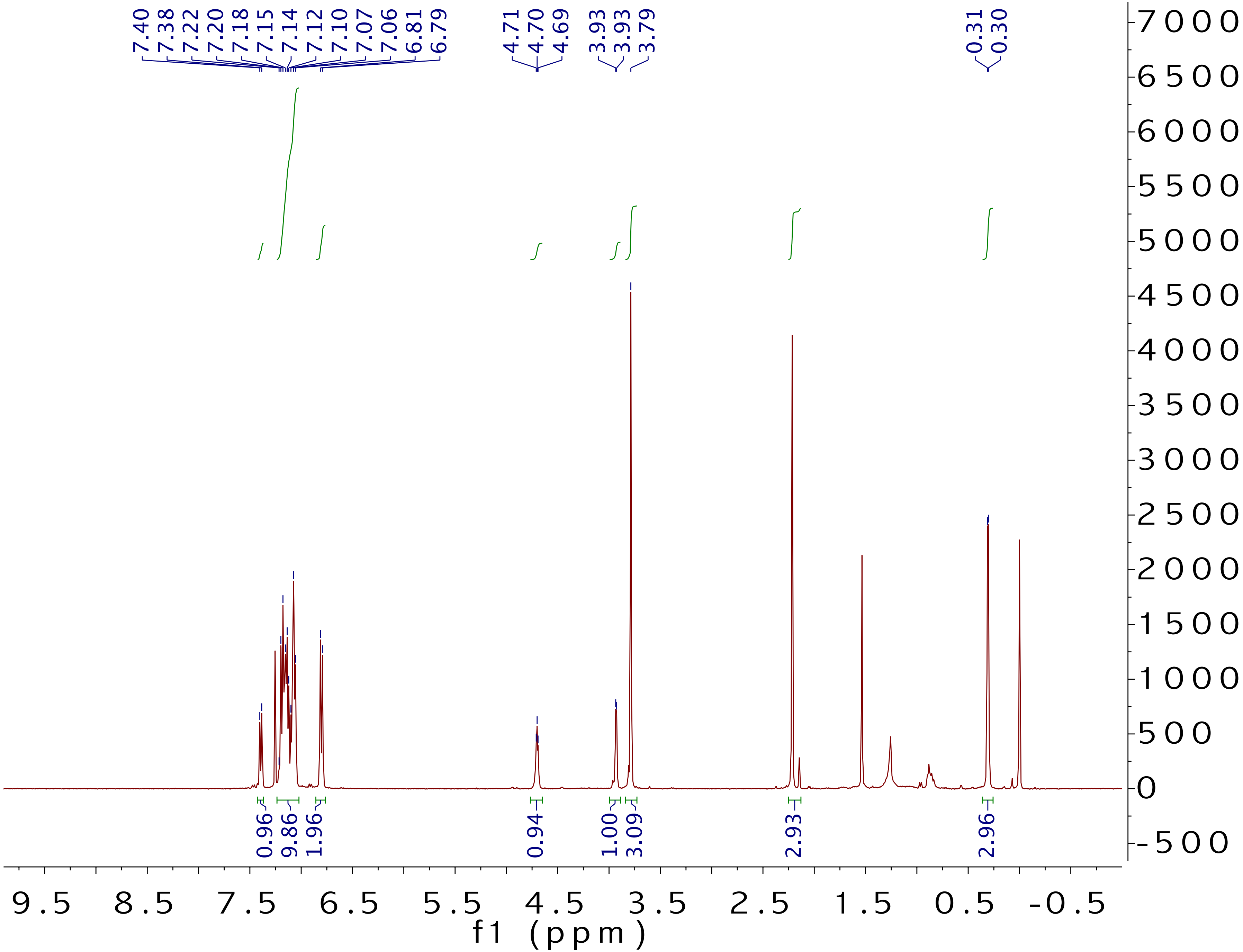
^{13}C, 151 MHz, CDCl$_3$

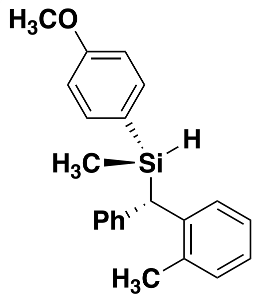




5f

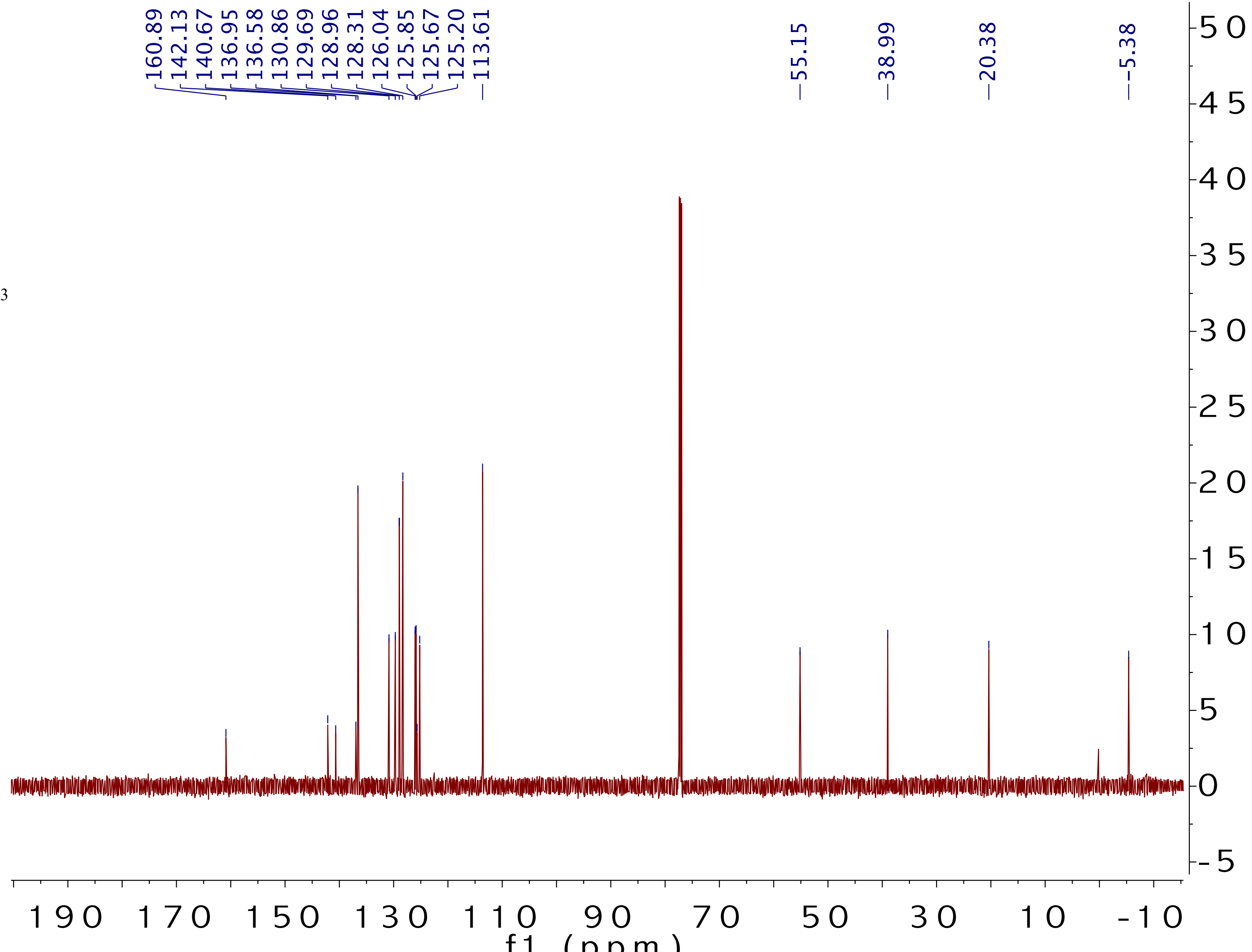
^{1}H, 400 MHz, CDCl$_3$

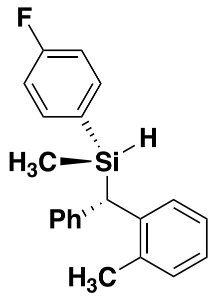




5f

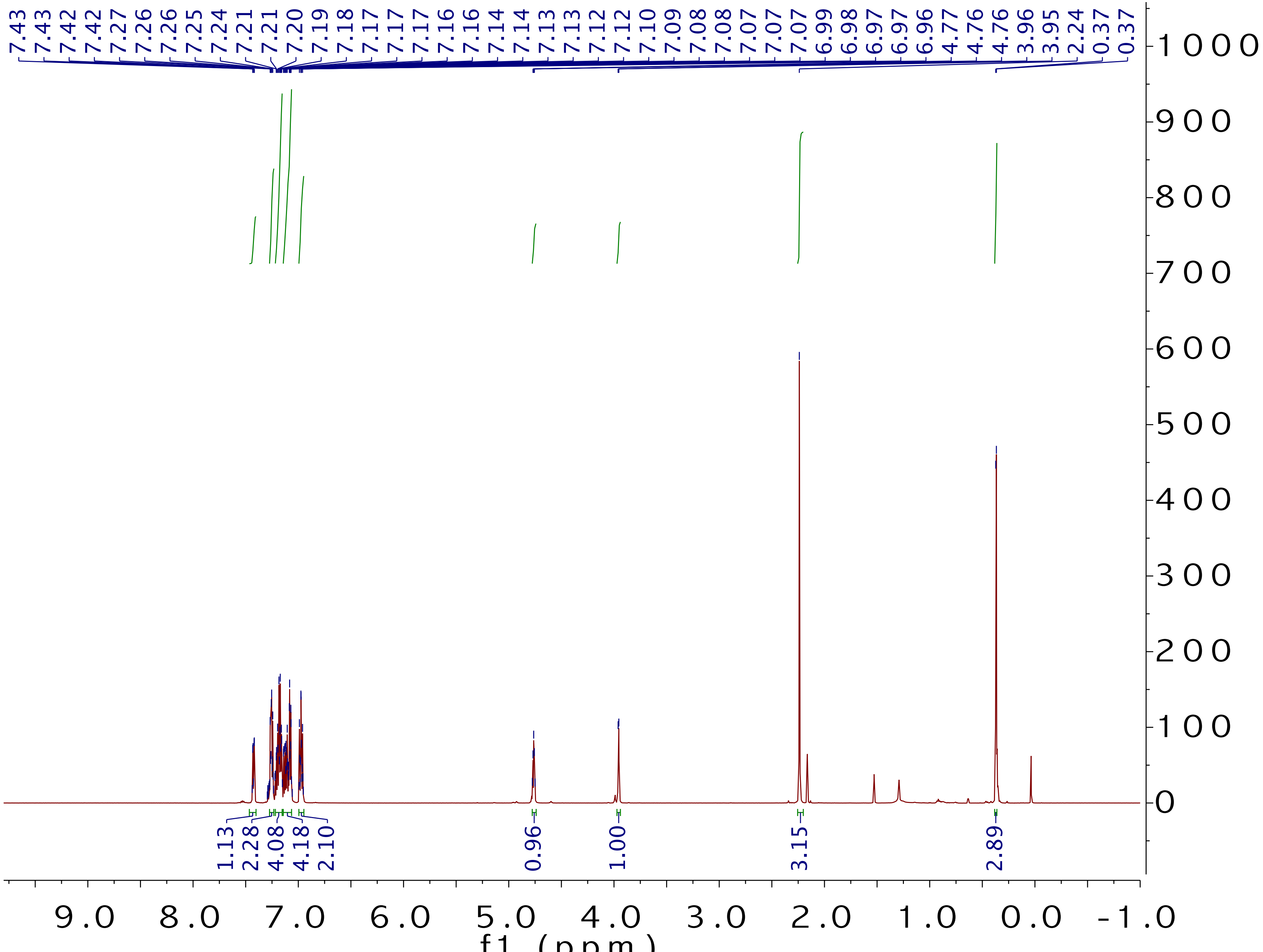
^{13}C, 151 MHz, CDCl$_3$

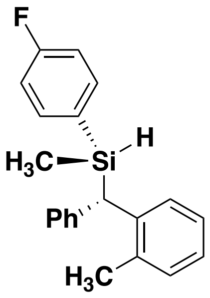




5g

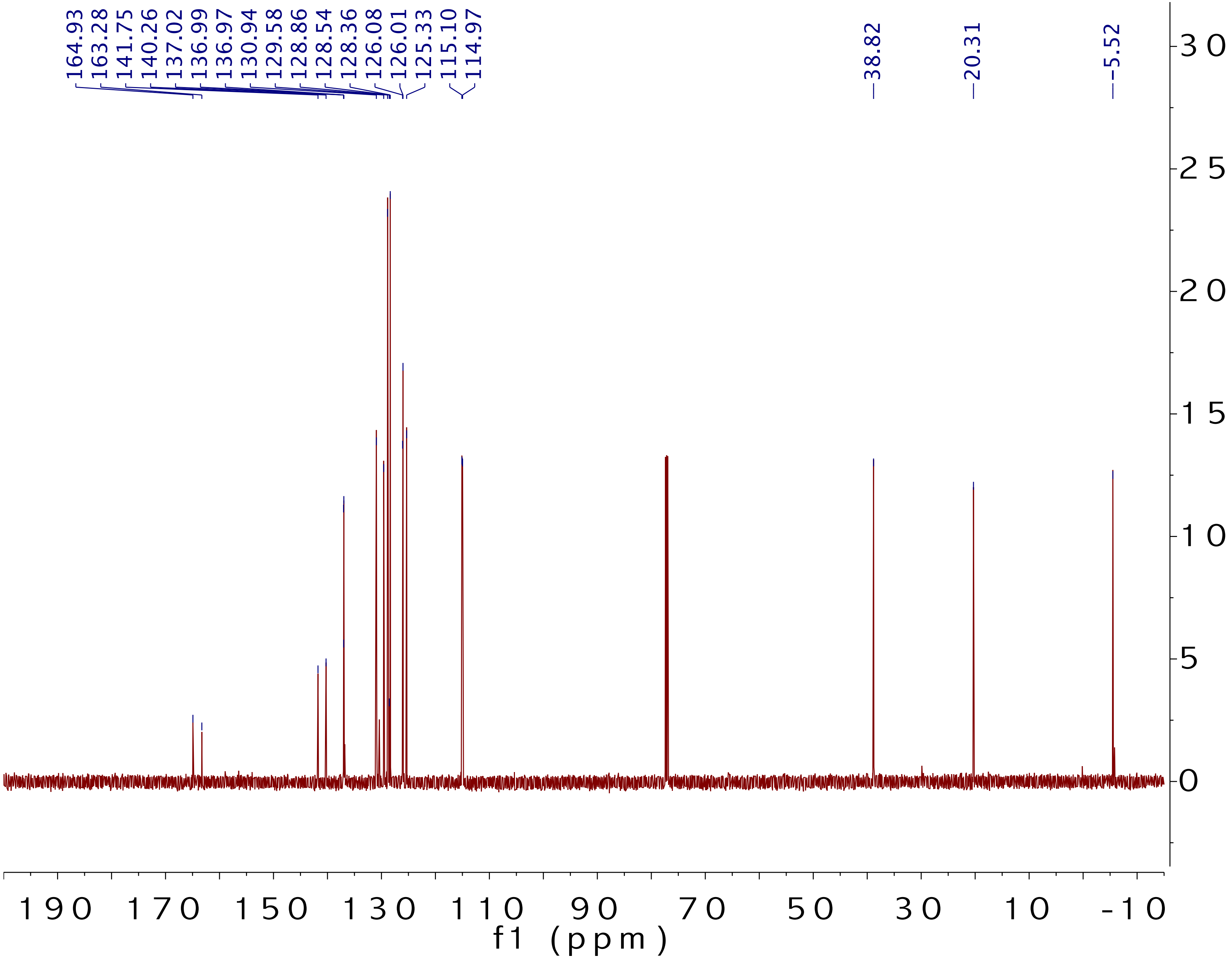
^{1}H, 600 MHz, CDCl$_3$

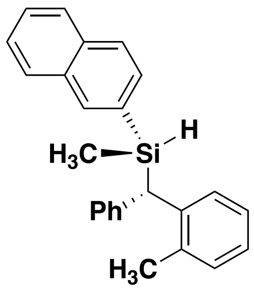




5g

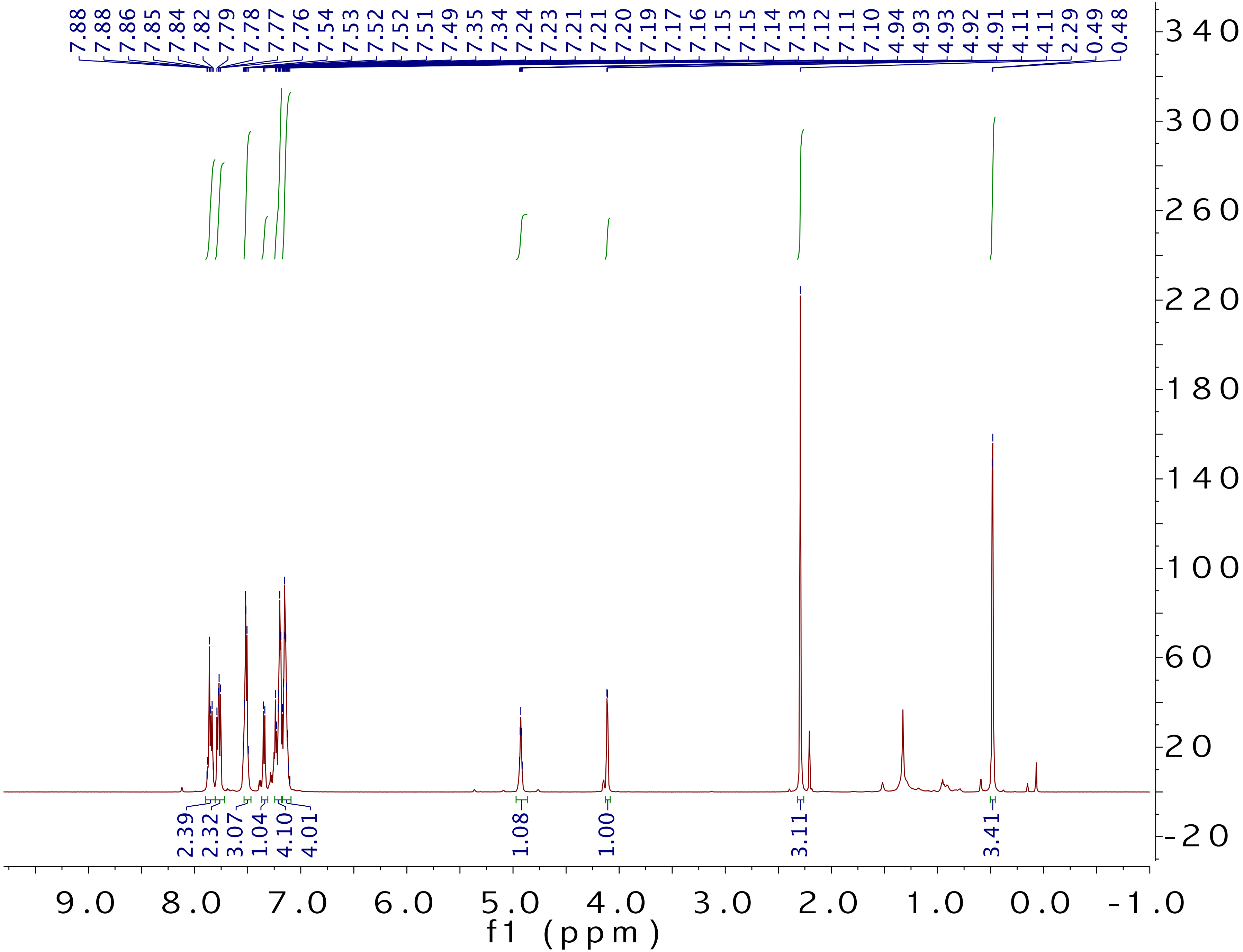
^{13}C, 151 MHz, CDCl$_3$

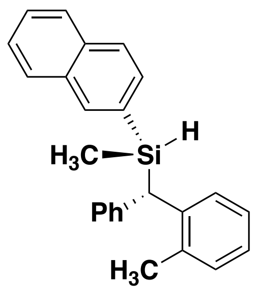




5h

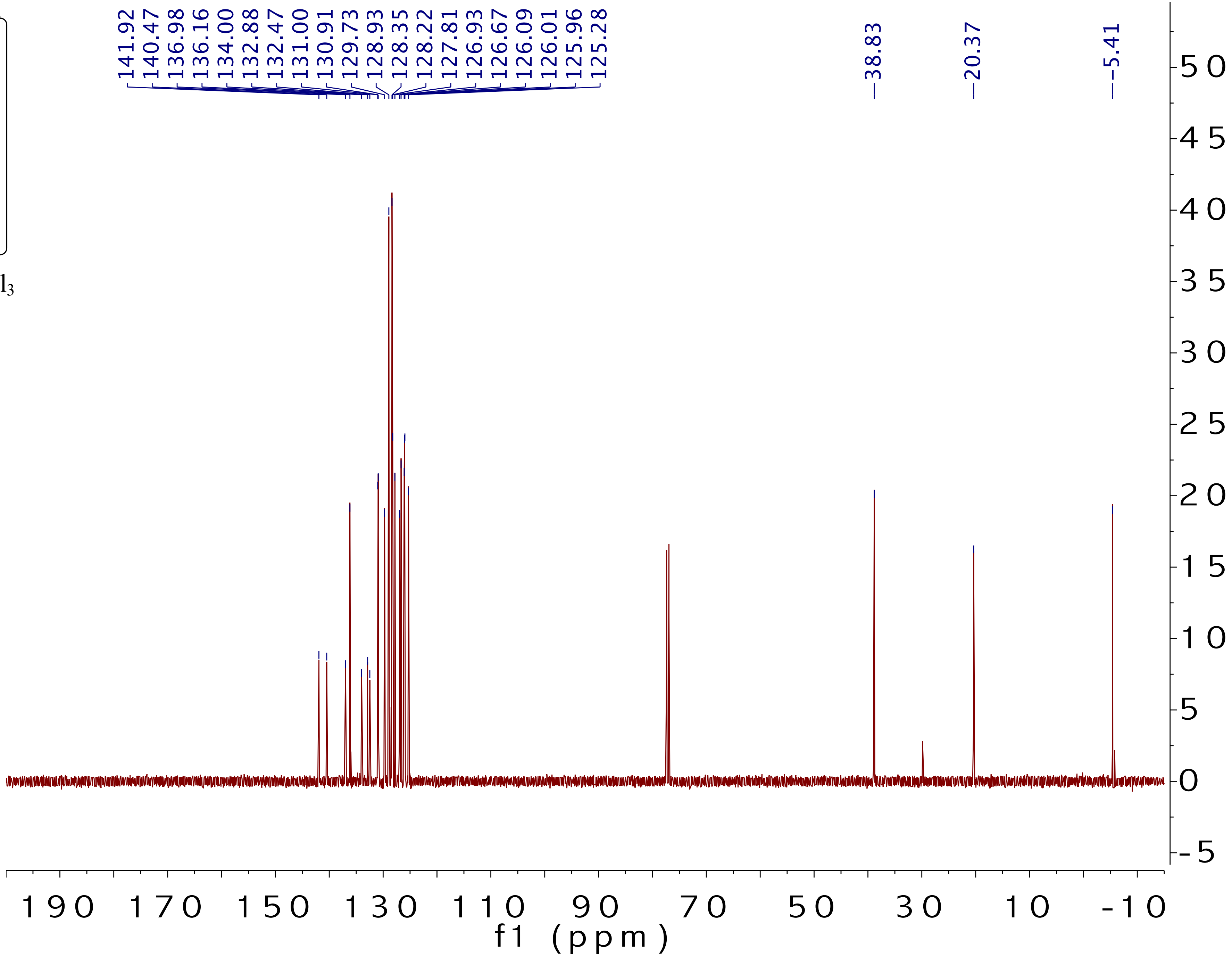
^{1}H, 600 MHz, CDCl$_3$

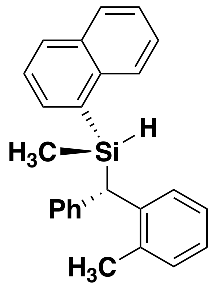




5h

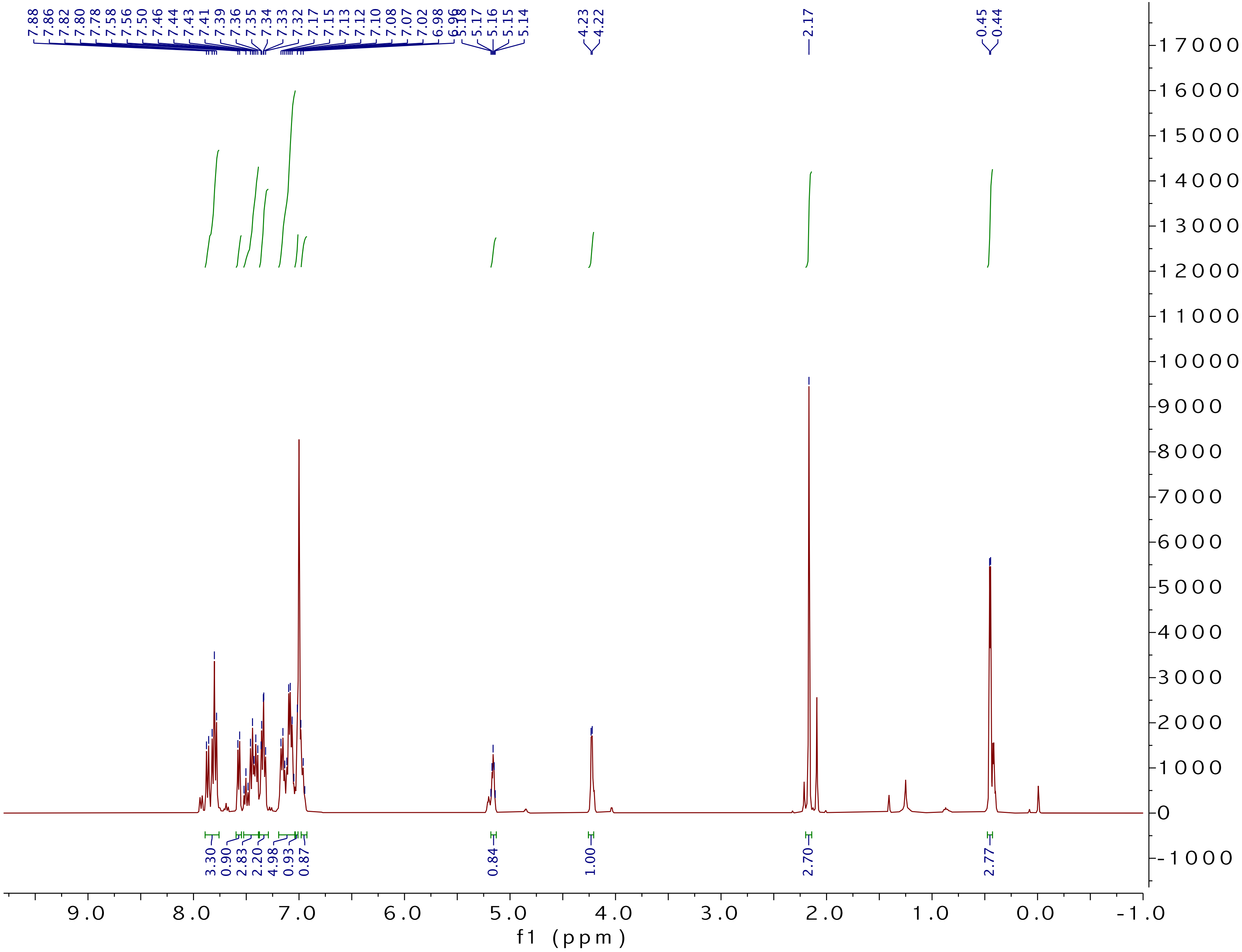
^{13}C, 151 MHz, $CDCl_3$

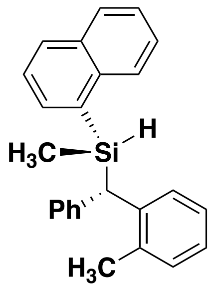




5i

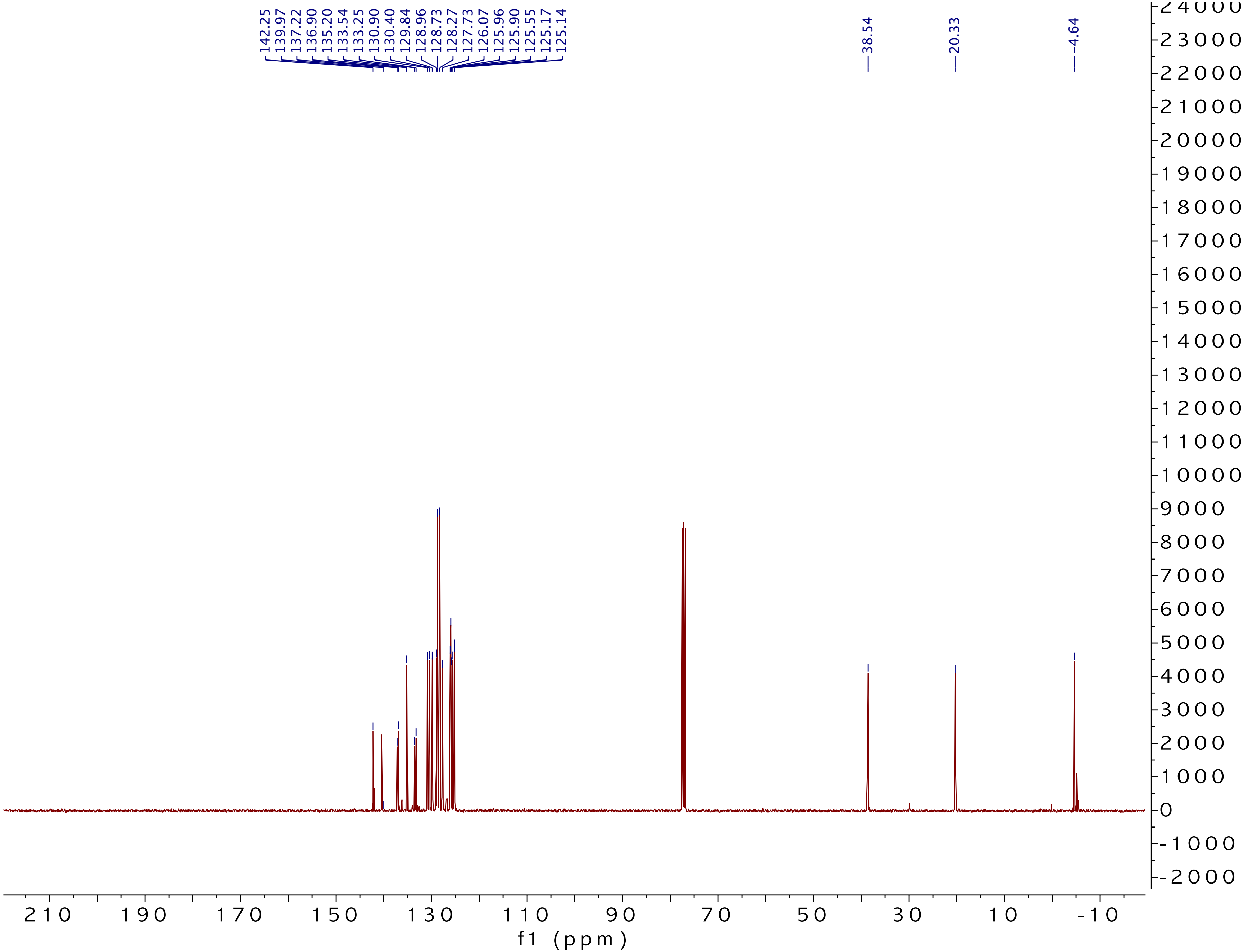
^1H, 400 MHz, $CDCl_3$

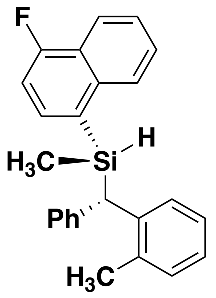




5i

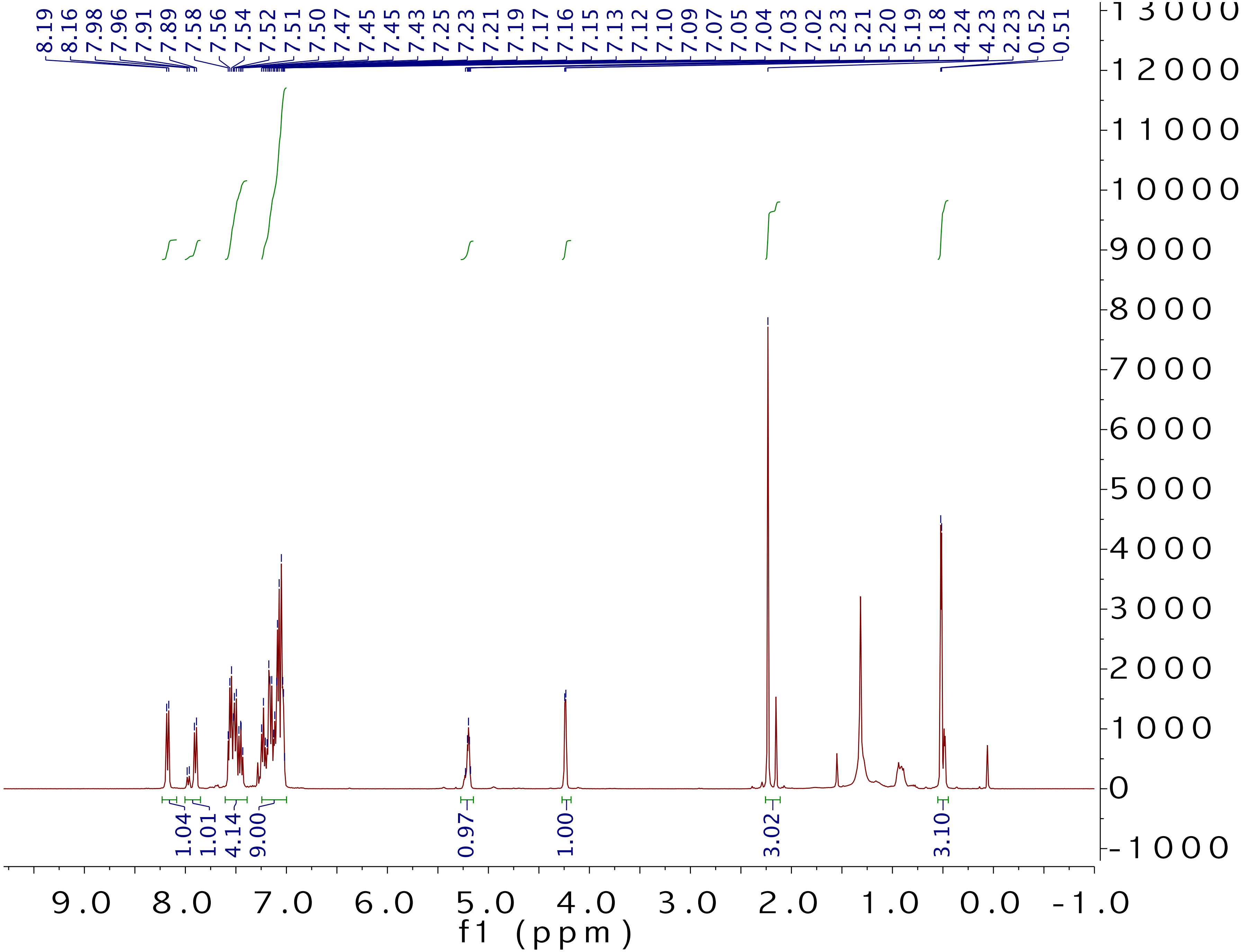
^{13}C, 100 MHz, CDCl$_3$

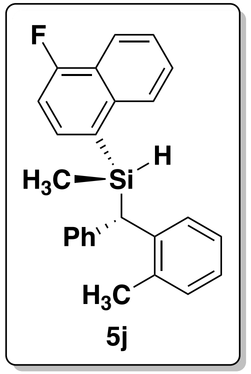




5j

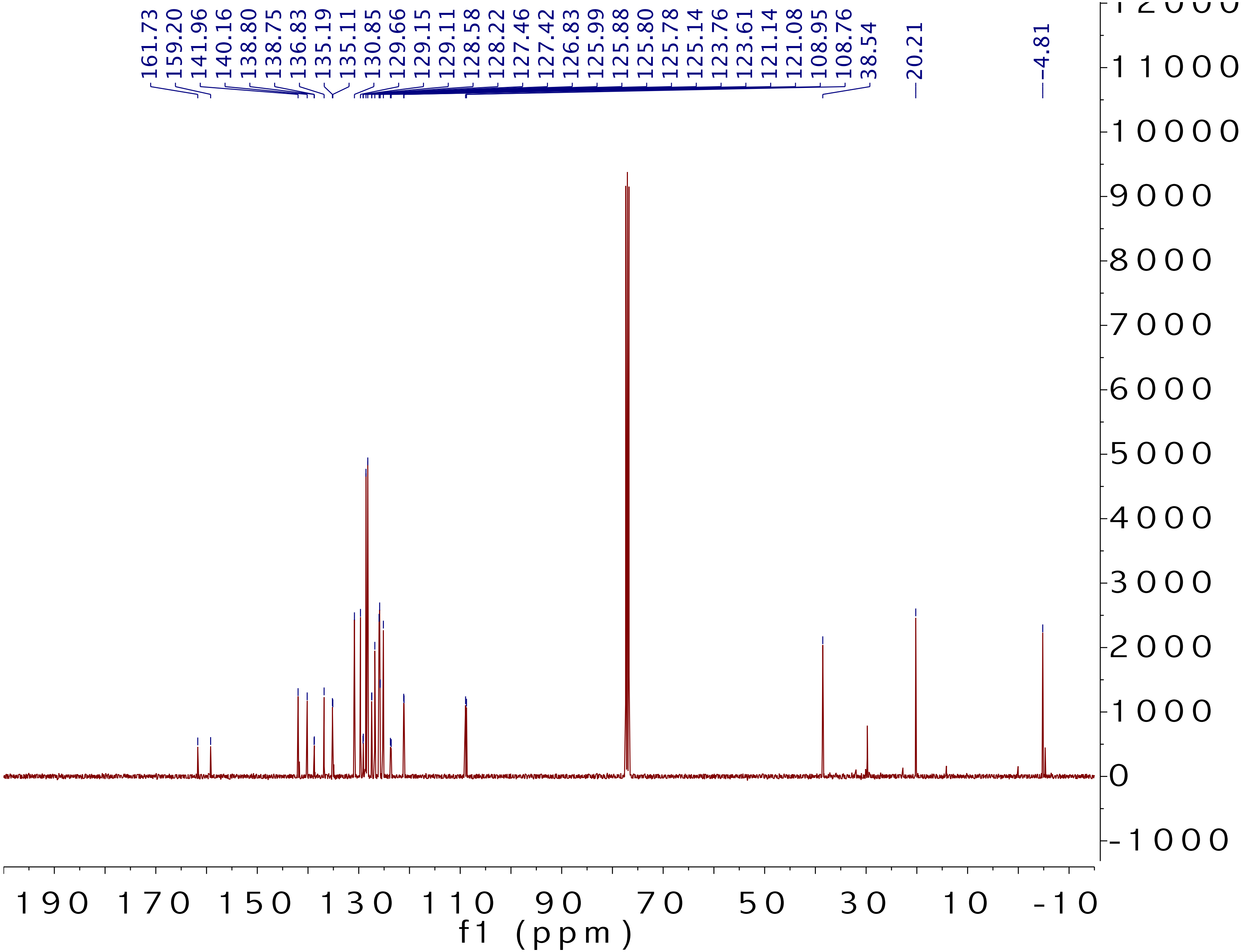
^1H, 600 MHz, $CDCl_3$

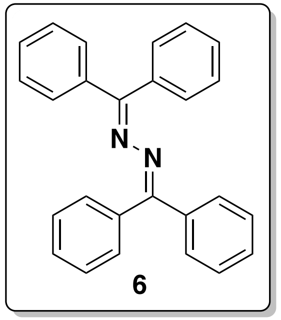




5j

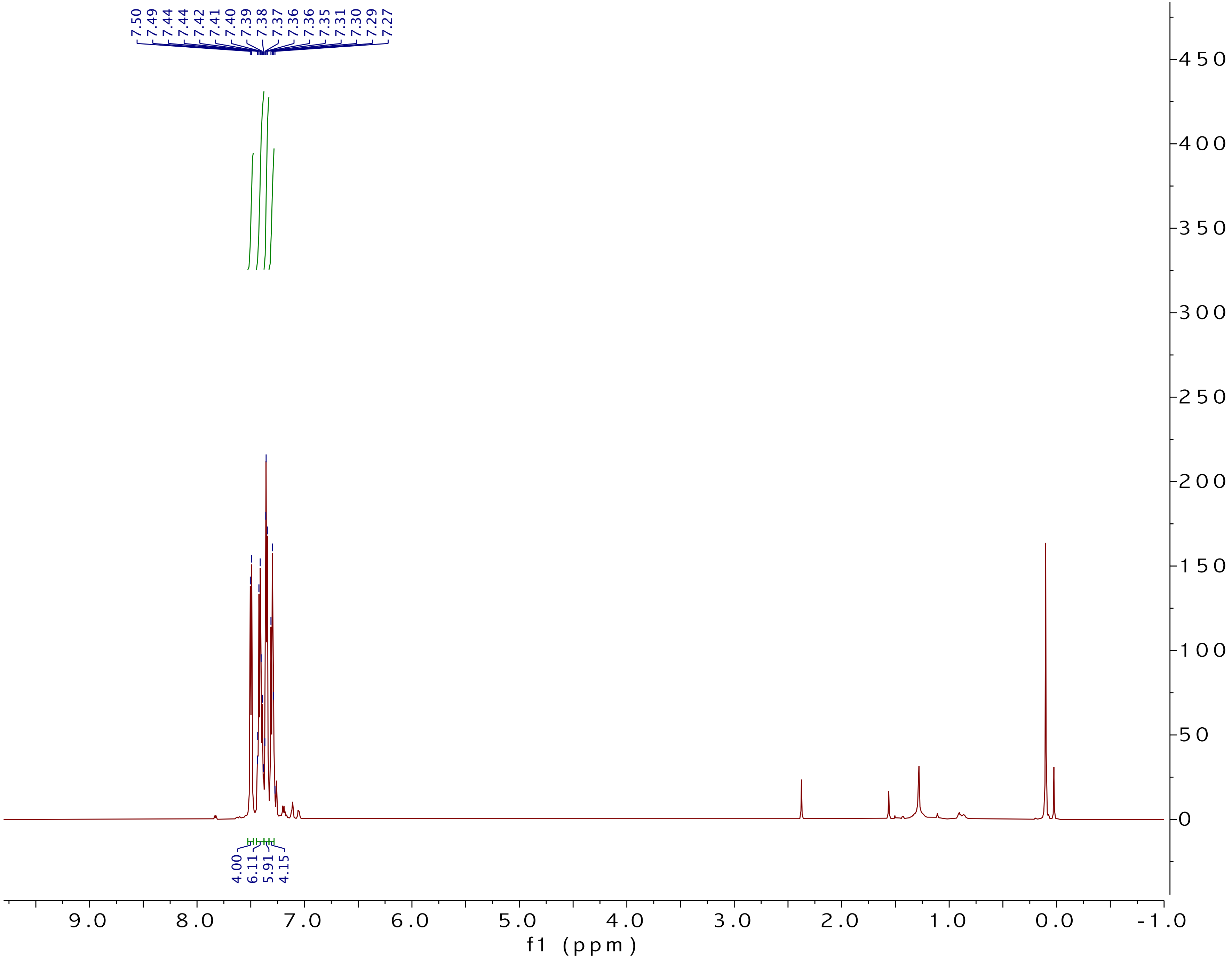
^{13}C, 100 MHz, CDCl$_3$

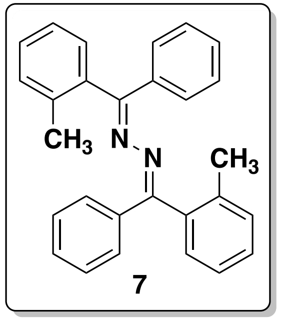




6

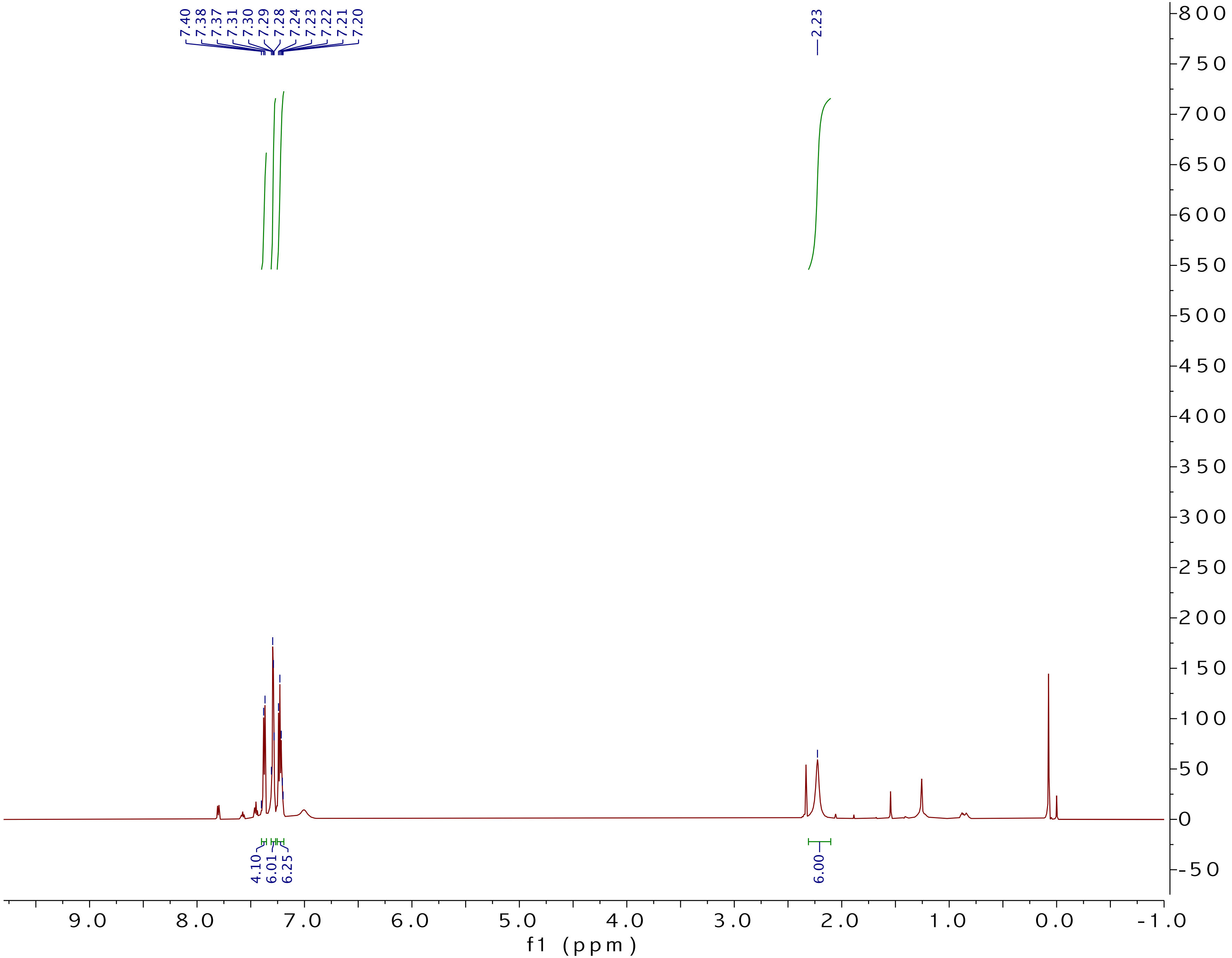
^{1}H, 600 MHz, CDCl$_3$

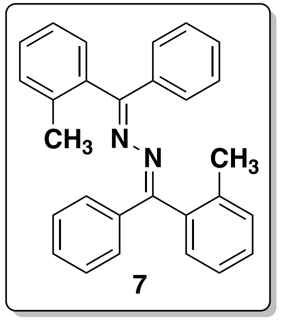




7

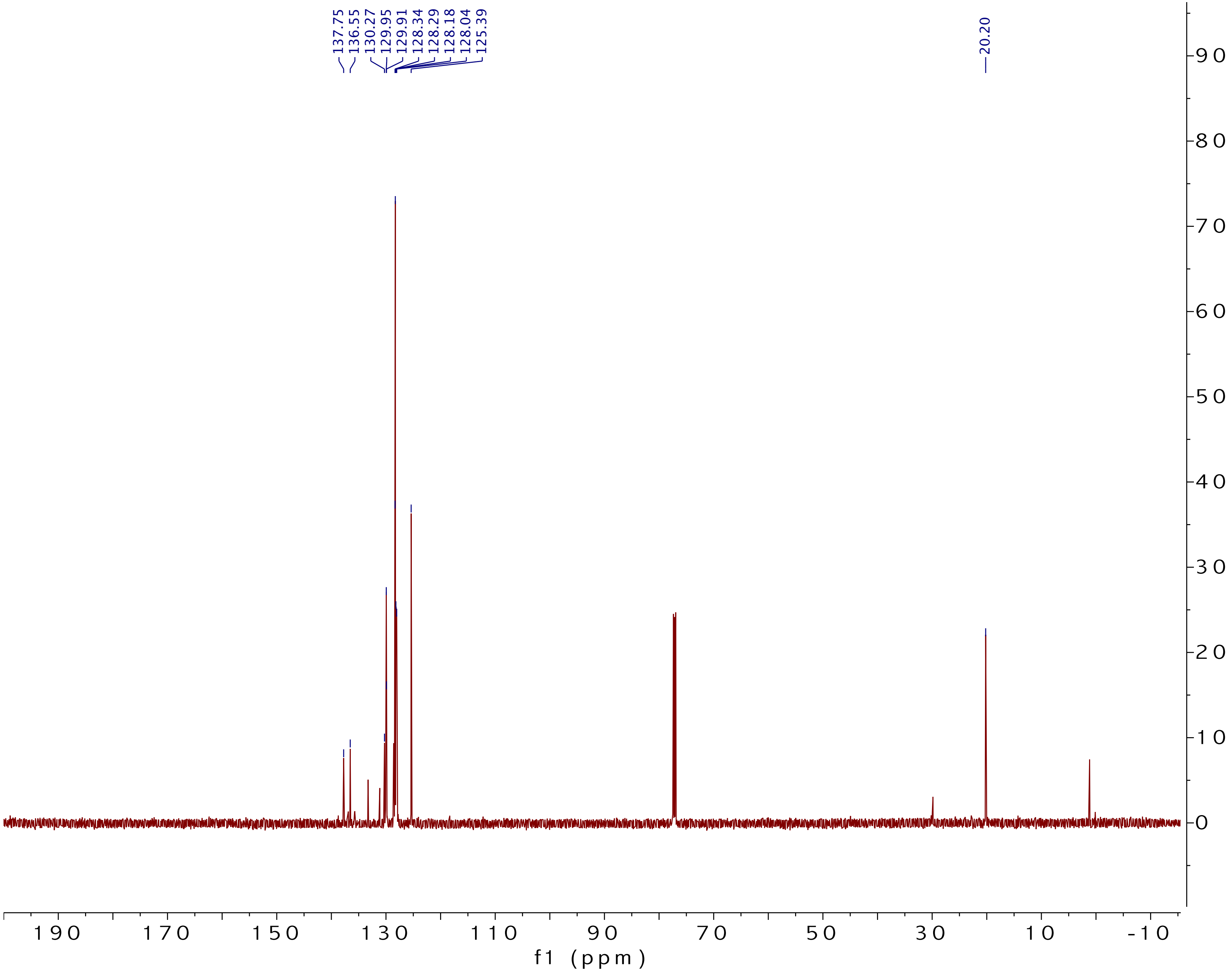
^{1}H, 600 MHz, $CDCl_3$

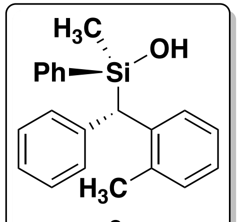




7

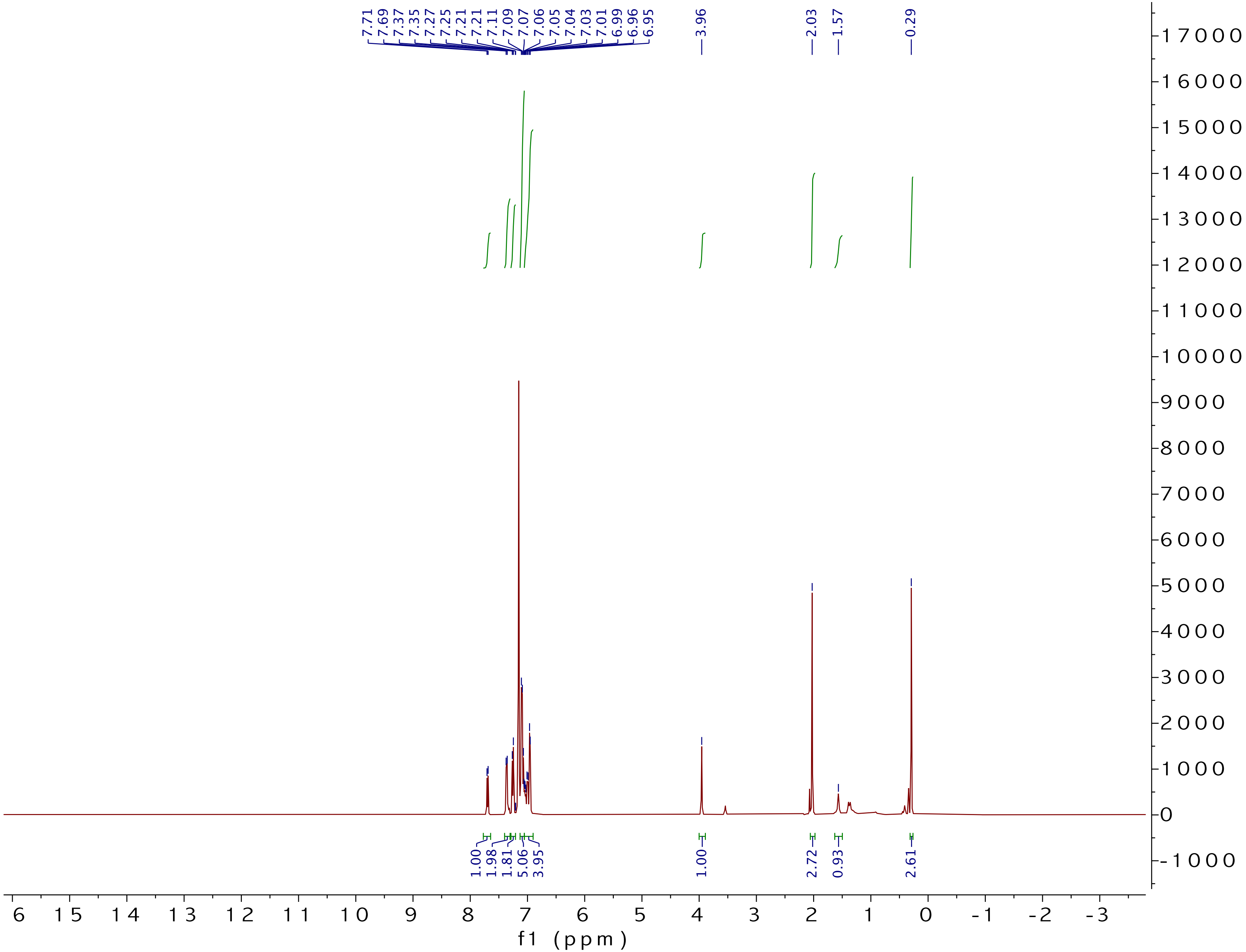
^{13}C, 151 MHz, $CDCl_3$

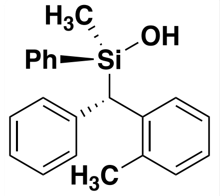




9

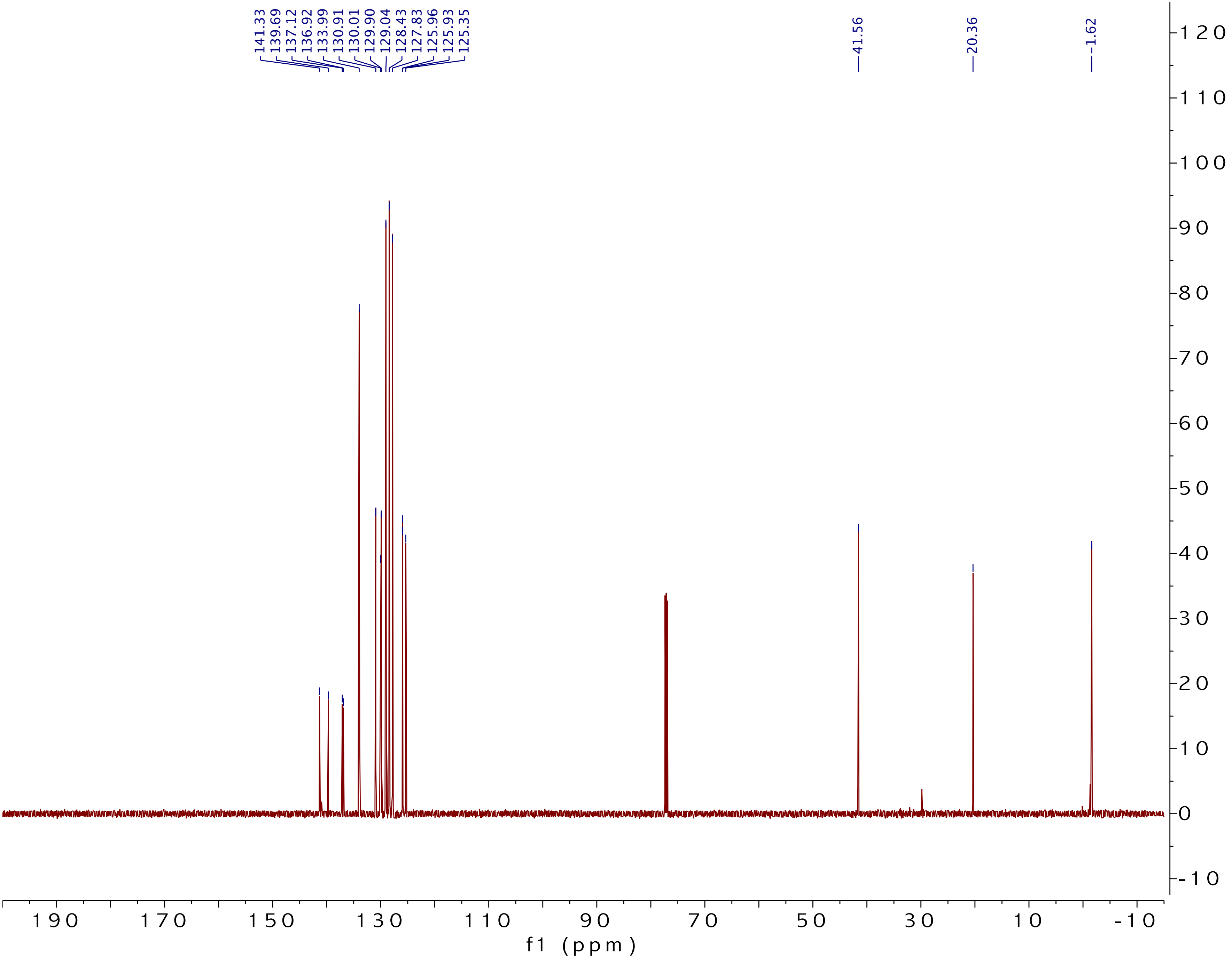
^{1}H, 600 MHz, C_6D_6

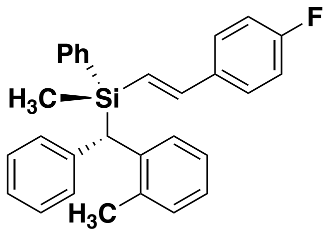




9

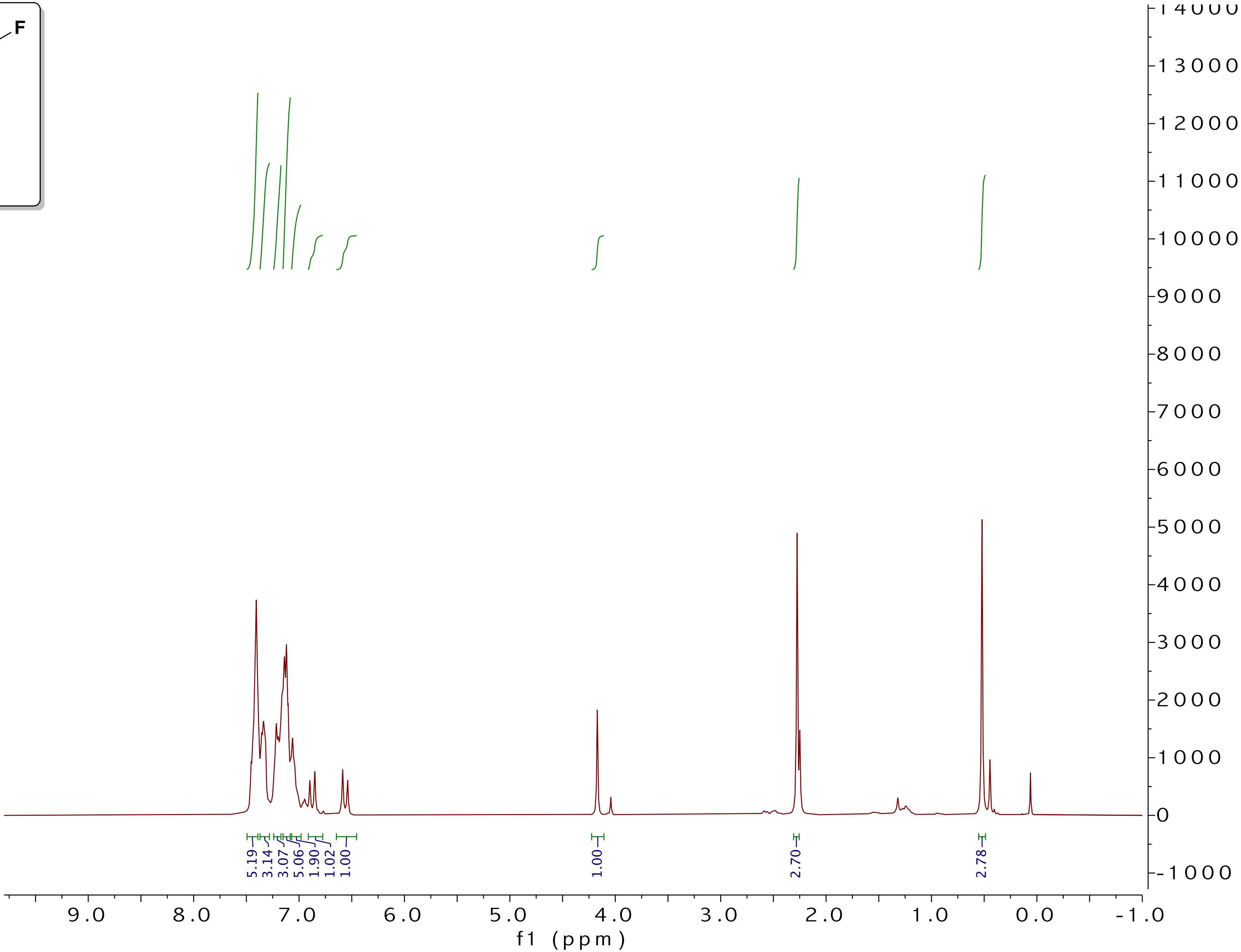
^{13}C, 151 MHz, CDCl$_3$

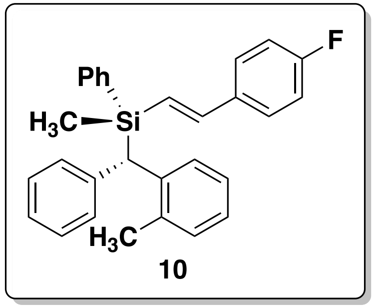




10

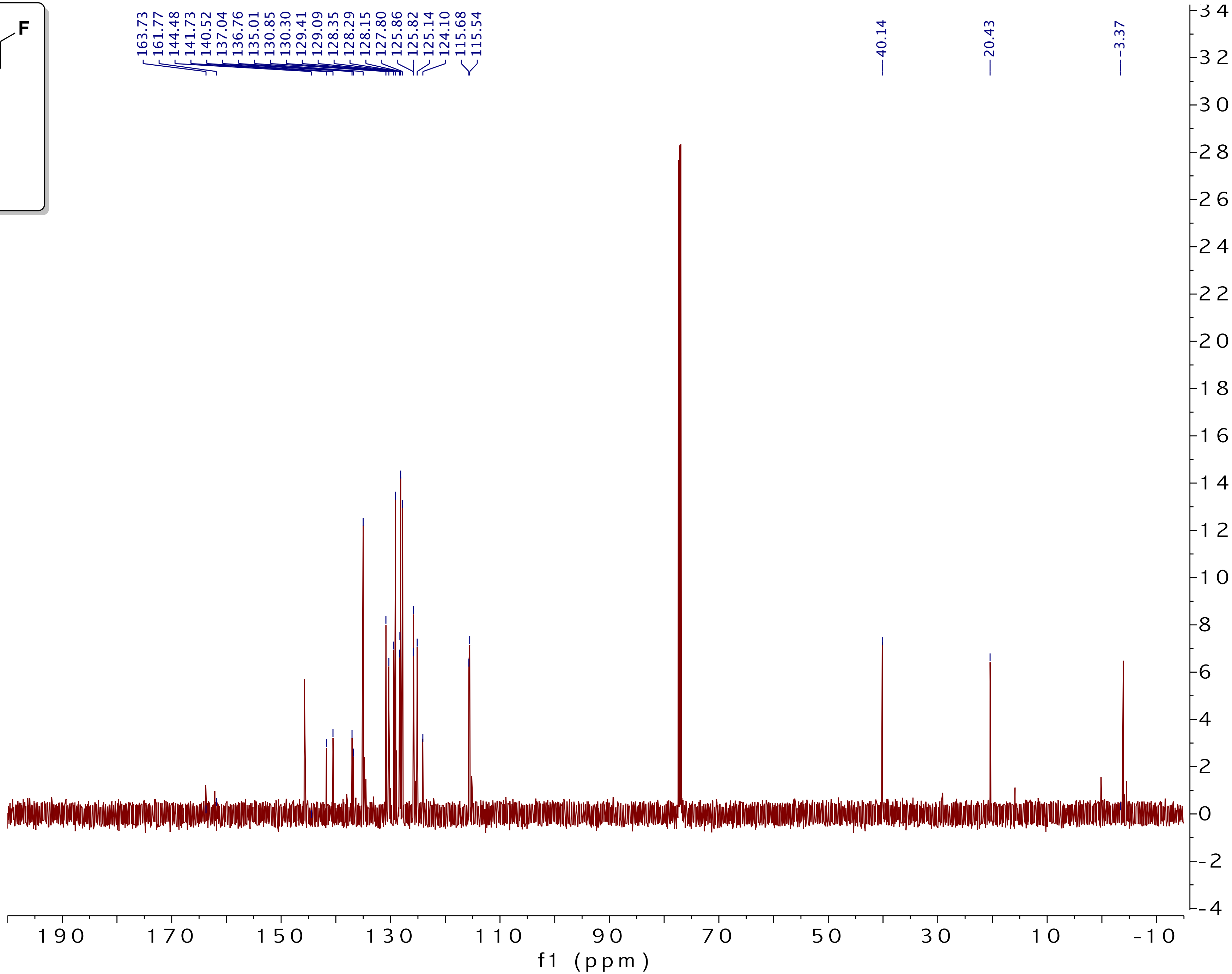
^{1}H, 600 MHz, $CDCl_3$

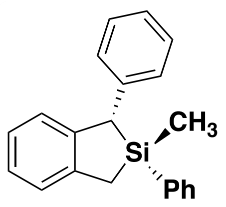




10

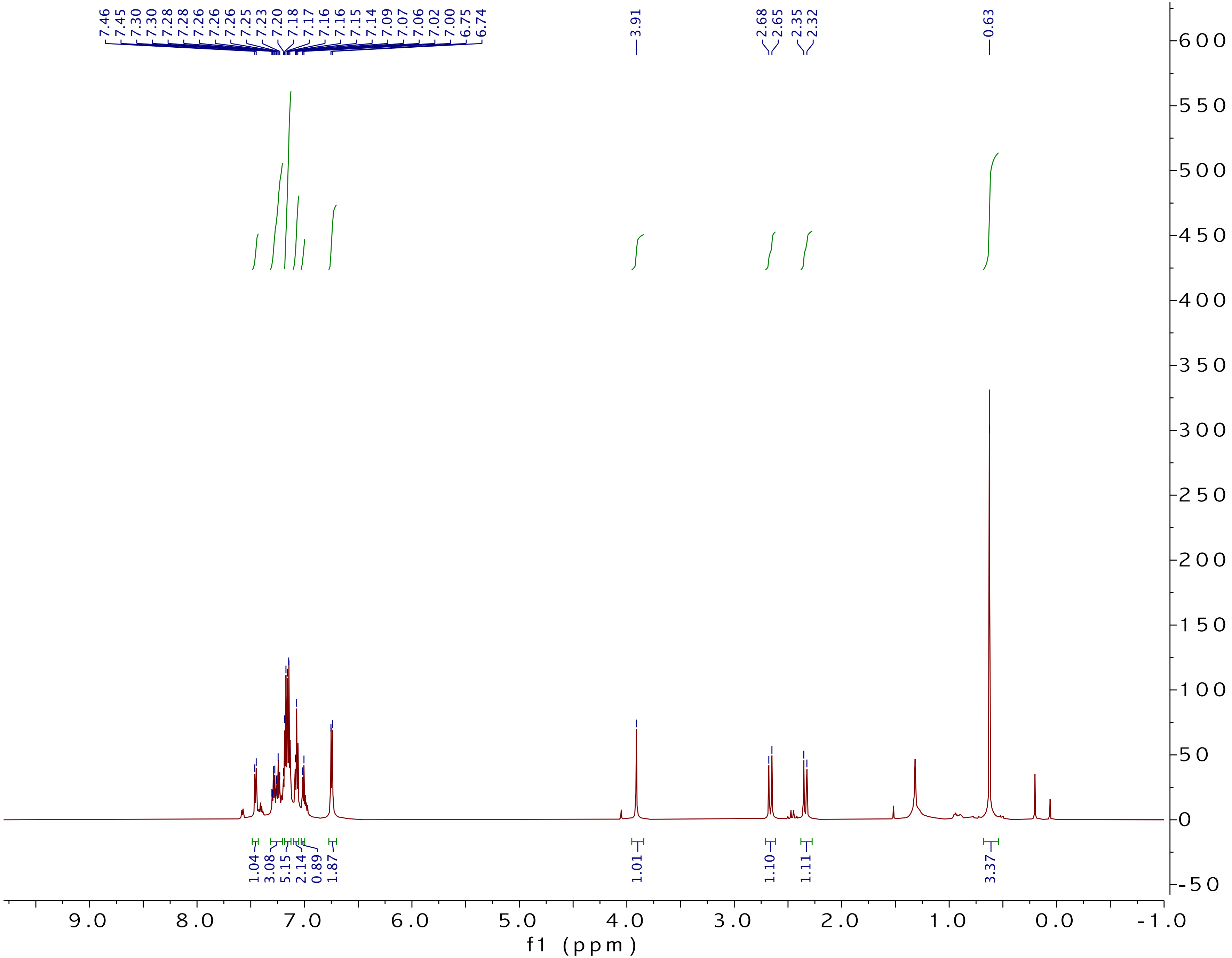
^{13}C, 151 MHz, CDCl$_3$

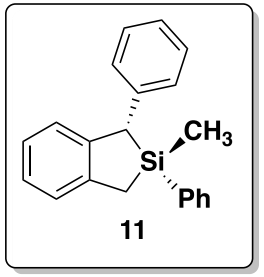




11

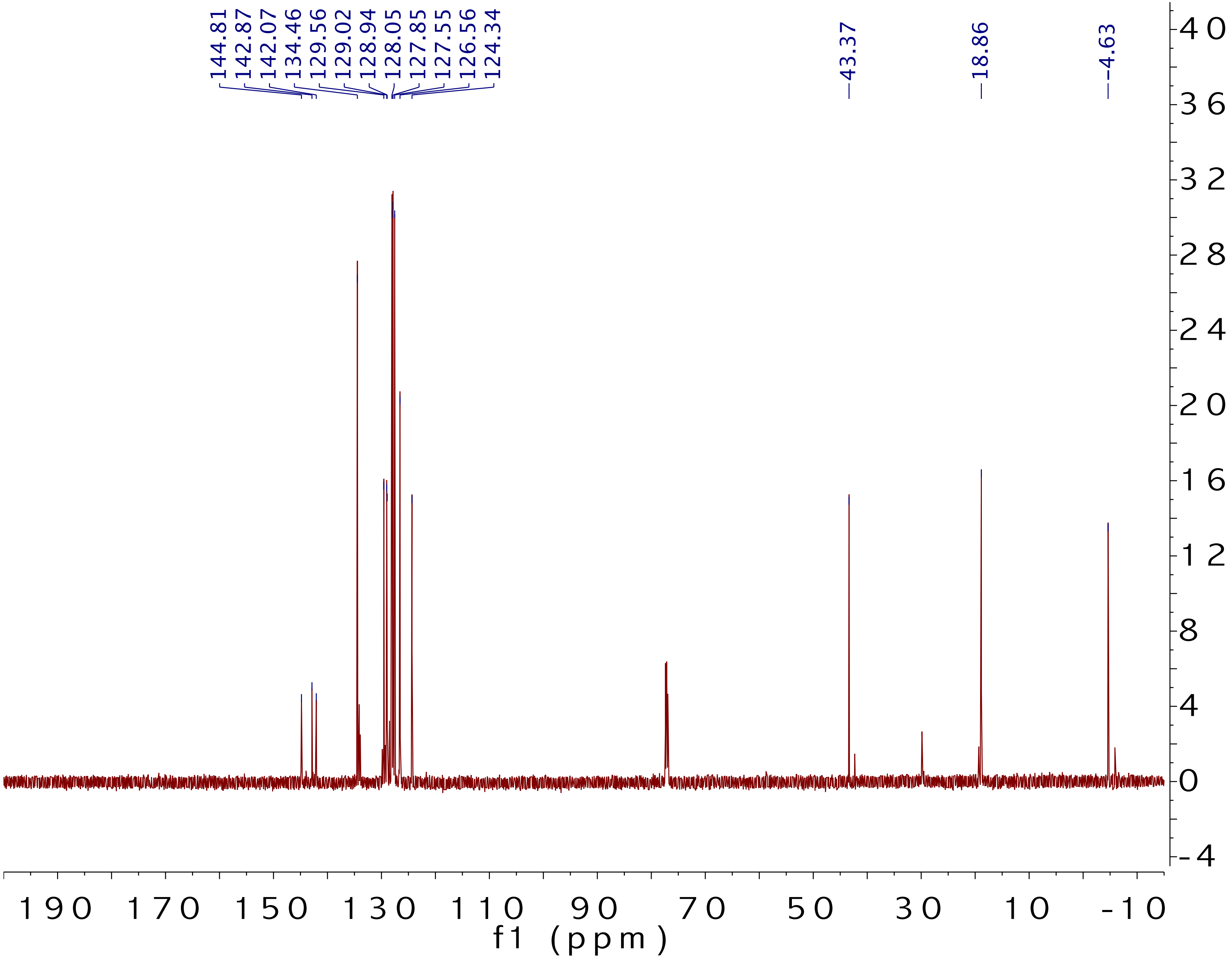
^{1}H, 600 MHz, CDCl$_3$

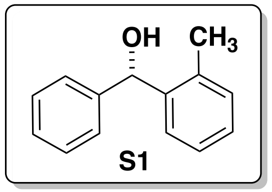




11

^{13}C, 151 MHz, $CDCl_3$





^{1}H, 600 MHz, CDCl$_3$