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Supporting Information

Regiodivergent Hydrosilylation, Hydrogenation, [2π+2π]-Cycloaddition and C–H Borylation using Counterion Activated Earth-abundant Metal Catalysis

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General Experimental Information

Reaction Setup: All reactions were performed in oven (180 °C) dried glassware under an atmosphere of argon, unless otherwise indicated. All air- and moisture sensitive reactions were carried out using standard vacuum line and Schlenk techniques, or in a glovebox with a purified argon atmosphere. All glassware was cleaned using base (KOH, ^{i}PrOH) and acid (HCl_{aq}) baths. All reported reaction temperatures correspond to external bath temperatures. Room temperature (r.t) was approximately 20°C. "Brine" refers to a saturated solution of sodium chloride in H_2O. For the hydrosilylation of olefins, the reactions were typically carried out in a glass vial (10 ml, Fisher Scientific, product code 11563680), under an inert atmosphere of argon, unless otherwise stated.

NMR Spectroscopy: ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on BrukerAvance III 400 and 500 MHz; Bruker AVI 400 MHz; BrukerAvance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C NMR spectra were referenced to the residual deuterated solvent peak ($CHCl_3$: 7.27 ppm, 77.00 ppm; CH_2Cl_2: 5.32 ppm, 54.00 ppm; d_8-THF: 1.73 ppm, 25.37 ppm; CD_3CN: 1.94 ppm, 1.39 ppm). Multiplicities are indicated by app. (apparent), br. (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet).Coupling constants, *J*, are reported in Hertz and rounded to the nearest 0.1 Hz. Integration is provided. ^{1}H and ^{13}C assignments are corroborated through 2-D NMR experiments (COSY, HSQC, HMBC).

Infrared Spectroscopy: Infra-red (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR, or Shimadzu IRAffinity-1 spectrometer (serial no. A213749). Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 0–33% T); m (medium, 34–66% T), w (weak, 67–100% T), and br. (broad).

Mass Spectrometry: Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry Mass Spectrometry Laboratory. High resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

Melting Points: Melting points (mp) were determined on a Stuart Scientific SMP10, or Griffin Gallankamp melting point apparatus in capillary tubes and are uncorrected.

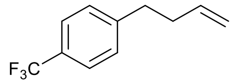
Chromatography: Analytical thin-layer chromatography was performed on aluminium-backed silica plates (Merck 60 F_{254}). Pet. ether refers to petroleum ether 40-60. Product spots were visualised by UV light at 254 nm, and subsequently developed using potassium permanganate solution if appropriate. Flash column chromatography was performed on silica gel (Merck Kielselgel 60, 40-63 μm).

Solvents: All solvents for air- and moisture sensitive techniques were obtained from an anhydrous solvent system (Innovative Technology). Anhydrous *d*$_8$-tetrahydrofuran was distilled from sodium/benzophenone. Reaction solvents tetrahydrofuran (THF) (Fisher, HPLC grade), ether (Et_2O) (Fisher, BHT stabilized ACS grade), and dichloromethane (CH_2Cl_2) (Fisher, unstabilised HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Toluene (ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Solvents for filtration, transfers, chromatography, and recrystallization were dichloromethane (CH_2Cl_2) (ACS grade), ether (Et_2O) (Fisher, BHT stabilized ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), hexane (Optima), methanol (MeOH) (ACS grade), pentane (ACS grade), and petroleum ether (40–60°C, ACS grade).

Chemicals: All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros Organics, Tokyo Chemical Industries UK,Fluorochem, Fisher Scientific UK and Apollo Scientific or synthesised within the laboratory. Iron (II) tetrafluoroborate hexahydrate 97% (product number 401668) was purchased from Sigma Aldrich; anhydrous iron (II) chloride 98% was purchased from Strem Chemicals Inc. (UK) (product number 39957, Lot 19226800); cobalt (II) tetrafluoroborate hexahydrate 99% was purchased from Sigma Aldrich (product number 93-2631, Lot MKBX9974V, 44.00000% Fe, expect 44.059%).

Alkene Synthesis

4-(4-Trifluoromethylphenyl)-1-butene (1g)



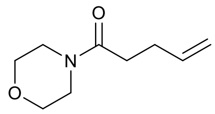
According to a modification of the procedure reported by White and coworkers,[1] 4-Trifluoromethylbenzylbromide (1.00 g, 4.20 mmol, 1.00 equiv.), was dissolved in THF (40 mL) and cooled in an ice bath. Allylmagnesium bromide (0.8 M in Et_2O, 10 mL, 8.00 mmol, 1.90 equiv.) was added dropwise, and the mixture was stirred for 2 hours at 0 °C. Aqueous saturated ammonium chloride (10 mmol) was added to quench the reaction. The aqueous phase was separated and extracted with CH_2Cl_2 (2 x 20 ml). The organic fractions were combined, dried ($MgSO_4$), filtered through celite, and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (24 g SiO_2, 25 mm Ø, pentane:Et_2O 95:5) to give the alkene **1g** (0.624 g, 3.12 mmol, 74%) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.56 (2H, d, J = 8.0 Hz), 7.32 (2H, d, J = 7.9 Hz), 5.86 (1H, ddt, J = 17.0, 10.3, 6.6 Hz), 5.06 (1H, dq, J = 17.2, 1.7), 5.04 – 5.01 (1H, m), 2.8 (2H, t, J = 7.5), 2.44 – 2.39 (2H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
146.0, 137.4, 128.8, 128.3 (q, J = 32.4 Hz), 125.2 (q, J = 4.0 Hz), 124.5 (q, J = 271.8 Hz), 115.4, 35.12, 35.09

Data were in accordance with those previously reported.[1]

1-Morpholinopent-4-en-1-one (1l)



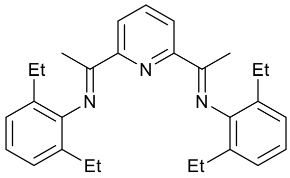
According to a modification of the procedure reported by White and coworkers,[1] dicarbonylimidazole (0.680g, 3.50 mmol, 1.00 equiv.) and 4-pentenoic acid (0.350 g, 3.50 mmol, 1.00 equiv.) were dissolved in anhydrous CH_2Cl_2 (15 mL) under a nitrogen atmosphere. The mixture was stirred for 3 hours at room temperature, at which time morpholine (0.610 g, 7.00 mmol, 2.00 equiv.) was added. The reaction was stirred for 72 hours at ambient temperature. The mixture was concentrated *in vacuo.* The crude product was purified by flash column chromatography (40 g SiO_2, 25 mm Ø, wet loaded, EtOAc:pentane7:3) to give the amide **1l** (380 mg, 64%) as a colourless oil.

^{1}H NMR:	(500 MHz, $CDCl_3$) 5.92–5.82 (1H, m), 5.11-4.97 (2H, m), 3.69-3.66 (4H, m), 3.65-3.60 (2H, m), 3.50-3.43 (2H, m), 2.43-2.37 (4H, m)
^{13}C NMR:	(126 MHz, $CDCl_3$) 170.9, 137.3, 115.3, 67.0, 66.7, 46.0, 41.9, 32.3, 29.1
IR:	ν_{max} (neat) 2859 (s), 1627 (s), 1437 (s), 1224 (s), 1113 (s), 1029 (s)
MS:	(EI) 169.11 ([M^+],
HRMS:	(EI) found: 169.10915 $[M]^+$ $C_9H_{15}NO$ requires 169.10973

Data were in accordance with those previously reported.[1]

Ligand and Pre-Catalyst Preparation

2,6-Bis-[1-(2,6- diethylphenylimino)ethyl]pyridine (^{Et}BIP)

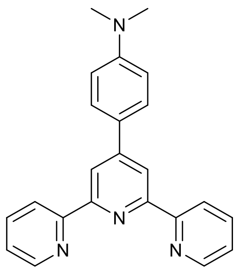


According to our previously reported procedure,[2] 2,6-Diethylaniline (4.5 mL, 27.0 mmol, 2.20 equiv.) was added to a stirred suspension of 2,6-diacetylpyridine (2.00 g, 12.3mmol, 1.00 equiv.) and *p*-toluenesulfonic acid (0.11 g, 0.62 mmol, 0.05 equiv.) in anhydrous toluene (25 mL) and heated under Dean-Stark conditions for 18 hours. The mixture was allowed to cool to ambient temperature. The resulting yellow solid was isolated by filtration, washed with cold CH_2Cl_2 and recrystallised (CH_2Cl_2) to give 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine (3.66 g, 8.61mmol, 70%) as yellow cuboids.

^{1}H NMR: (500 MHz, $CDCl_3$)
8.51 (2H, d, *J* = 7.8 Hz), 7.95 (1H, t, *J* = 7.8 Hz), 7.16 - 7.14 (4H, m), 7.09 – 7.05 (2H, m), 2.51 – 2.34 (8H, m), 2.28 (6H, s), 1.18 (12H,t, *J* = 7.5 Hz)
^{13}C NMR: (126 MHz, $CDCl_3$)
166.9, 155.1, 147.8, 136.9, 131.2, 126.0, 123.4, 122.2, 24.6, 16.8, 13.7
M.P: (CH_2Cl_2) 196–198 °C; lit 185–186°C

Data were in accordance with those previously reported.[2]

2,6-Bispyridyl-4-(4-dimethylaminophenyl)pyridine (4-NMe$_2$-Ph-Terpy)



According to the procedure reported by Chrobok and cowerkers,[3] 2-Acetylpyridine (1.121 mL, 10.0 mmol, 2 equiv.) was added to a stirred solution of 4-Dimethylaminobenzaldehyde (0.746 g, 5.0 mmol, 1 equiv.) in EtOH (37 ml). KOH (0.771 mg, 13.8 mmol, 2.75 equiv.) was added, followed by aqueous ammonia (15 ml) and the solution was stirred for 24 hours at ambient temperature. The resulting bright yellow solid was collected by filtration, washing with water and EtOH. The crude solid was recrystallized ($CHCl_3$:MeOH) to give the terpyridine (0.450g, 1.2 mmol, 27%) as a yellow needles.

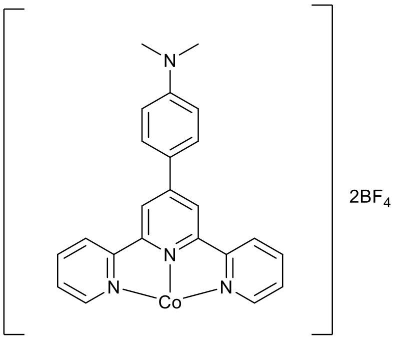
^{1}H NMR: (600 MHz, $CDCl_3$)
8.76 (2H, ddd, *J* = 0.8, 1.8, 4.7), 8.73 (2H, s), 8.69 (2H, dt, *J* = 0.96, 7.9 Hz), 7.90 (2H, m), 7.36 (2H, ddd, *J* = 1.4, 4.7, 7.4), 6.85 (2H, m), 3.02 (6H, s)

^{13}C NMR: (126 MHz, $CDCl_3$)
156.7, 155.7, 151.1, 150.0, 149.1, 136.8, 131.2, 128.1, 125.6, 123.6, 121.4, 117.5, 112.3, 40.4

M.P: ($CHCl_3$, MeOH) 200–205 ºC; lit 205-209 ºC[4]

Data were in accordance with those previously reported.[3]

2,6-Bispyridyl-4-(4-dimethylaminophenyl)pyridine cobalt(II) tetrafluoroborate (1a)

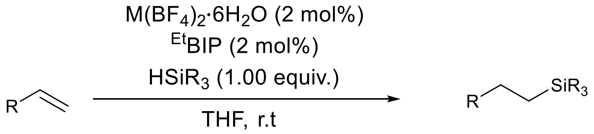


According to the procedure reported by Raithby and coworkers,[5] $CoCl_2$ (0.0676 g, 0.4 mmol, 1.00 equiv.) and 2,6-Bispyridyl-4-(4-dimethylaminophenyl)pyridine (0.141 g, 0.4 mmol, 1.00 equiv.) were added to an oven-dried Schlenk flask under an inert atmosphere, and dissolved in MeOH (20 mL), and stirred under reflux for 15 minutes. A solution of $NaBF_4$ (0.0877 mg, 0.8 mmol, 2 equiv.) in MeOH (10 mL) was then added. The reaction mixture was allowed to cool to room temperature overnight, cooled to 0 °C and filtered, washing with cold MeOH (2 x 10 mL) and cold Et_2O (2x 10 mL) to give the precatalyst **1a** (0.109 g, 0.186 mmol, 47% yield) as an amorphous brown powder.

^{1}H NMR: (500 MHz, CD_2Cl_2)
95.2, 58.3, 52.3, 32.3, 15.2, 9.2, 5.5, 5.0, 1.5
^{11}B NMR: (160 MHz, CD_2Cl_2)
0.05
^{19}F NMR: (470 MHz, CD_2Cl_2)
-150.5

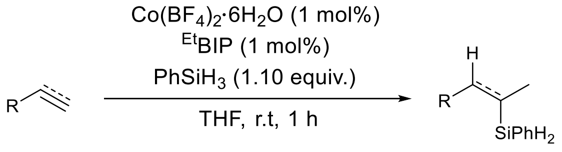
General Experimental Procedures

A. General Procedure for the Hydrosilylation of Octene Using Various Silanes



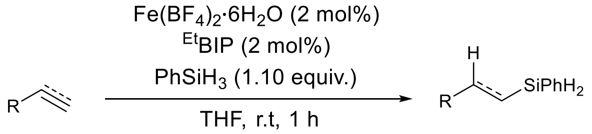
In an 8 ml vial equipped with a magnetic stir bar and under an atmosphere of argon, THF (1.0 mL) was added to a bis(imino)pyridine ligand (0.02 equiv.) and metal tetrafluoroborate hexahydrate salt (0.02 equiv.). This mixture was stirred for 1 minute at ambient temperature to form the catalyst. Octene (0.90 mmol, 1.00 equiv) and silane (0.90 – 0.99 mmol, 1.00 – 1.10 equiv.) were added and the mixture was stirred at ambient temperature for 1 – 3 hour(s). Et_2O (4 mL) was subsequently added. The mixture was passed through a short silica plug (made up in a glass pipette, Et_2O eluent) to remove any iron, and the solvent removed *in vacuo*. 1,3,5-Trimethoxybenzene (30.3 mg, 0.18 mmol, 0.20 equiv.) *or* menthol (28.1 mg, 0.18 mmol, 0.20 equiv.) was added for use as a ^1H NMR ($CDCl_3$) internal standard to determine the reaction yield.

B. General Procedure for the Hydrosilylation of Olefins using $Co(BF_4)_2{\cdot}6H_2O$



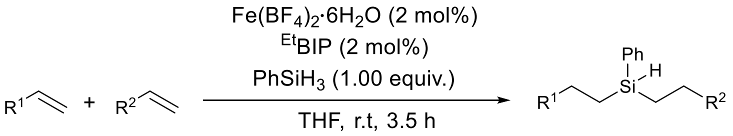
In an 8 ml vial equipped with a magnetic stir bar and under an atmosphere of argon, a bis(imino)pyridine ligand (0.01 equiv.) and cobalt tetrafluoroborate hexahydrate (0.01 equiv.) were dissolved in anhydrous THF (0.5 mL).. This mixture was stirred for 1 minute at ambient temperature to form the catalyst. The olefin (0.90 mmol, 1.00 equiv) and phenylsilane (0.99 mmol, 1.10 equiv.), were added and the mixture was stirred at ambient temperature forl hour. Et_2O (4 mL) was subsequently added. The mixture was passed through a short silica plug (made up in a glass pipette, Et_2O eluent) to remove any iron, and the solvent removed *in vacuo*. 1,3,5-Trimethoxybenzene (30.3 mg, 0.18 mmol, 0.20 equiv.) was added for use as a ^1H NMR ($CDCl_3$) internal standard to determine the reaction yield.

C. General Procedure for the Hydrosilylation of Olefins using $Fe(BF_4)_2{\cdot}6H_2O$



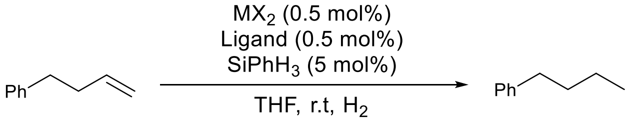
In an 8 ml vial equipped with a magnetic stir bar and under an atmosphere of argon, bis(imino)pyridine ligand (0.02 equiv.) and iron tetrafluoroborate hexahydrate salt (0.02 equiv.) were dissolved in anhydrous THF (0.5 mL). This mixture was stirred for 1 minute at ambient temperature to form the catalyst. The olefin (0.90 mmol, 1.00 equiv) and phenylsilane (0.99 mmol, 1.10 equiv.) were added and the mixture was stirred at ambient temperature for 1 hour. Et_2O (4 mL) was subsequently added. The mixture was passed through a short silica plug (made up in a glass pipette, diethyl ether eluent) to remove any iron residues, and the solvent removed *in vacuo*. 1,3,5-Trimethoxybenzene (30.3 mg, 0.18 mmol, 0.20 equiv.) was added for use as a ^1H NMR ($CDCl_3$) internal standard to determine the reaction yield.

D. General Procedure for the Iterative Hydrosilylation of Olefins to Obtain the Tertiary Silane using $Fe(BF_4)_2{\cdot}6H_2O$



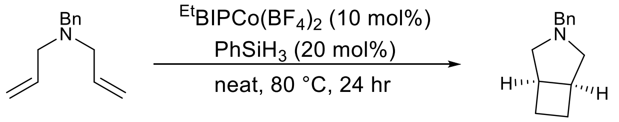
In an 8 ml vial equipped with a magnetic stir bar and under an atmosphere of argon, bis(imino)pyridine ligand (0.02 equiv.) and iron tetrafluoroborate hexahydrate salt (0.02 equiv.) were dissolved in anhydrous THF (1.0 mL). This mixture was stirred for 1 minute at ambient temperature to form the catalyst. The first equivalent of olefin (0.80 mmol, 1.00 equiv) and phenylsilane (0.80 mmol, 1.00 equiv.) were added and the mixture was stirred at ambient temperature for 30 minutes. A second equivalent of olefin (0.8 mmol, 1.00 equiv.) was subsequently added, and this mixture was stirred for a further 3 hours. Et_2O (4 mL) was subsequently added. The mixture was passed through a short silica plug (made up in a glass pipette, Et_2O eluent) to remove any iron residues, and the solvent removed *in vacuo*. 1,3,5-Trimethoxybenzene (26.9 mg, 0.16 mmol, 0.20 equiv.) was added for use as a ^1H NMR ($CDCl_3$) internal standard to determine the reaction yield.

E. General Procedure for the Hydrogenation of Olefins



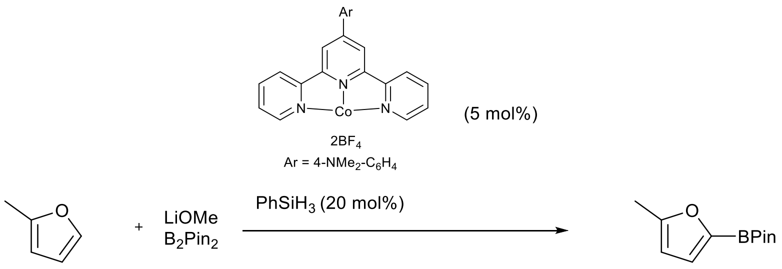
Hydrogenations were performed in an 8 mL glass vial insert equipped with a magnetic stir bar in an autoclave, pressurised with hydrogen gas. Under an atmosphere of argon, a mixture of ligand (0.005 equiv.) and metal salt (0.005 equiv.) was dissolved in anhydrous THF (1.0 mL) in a glass vial inert in an autoclave. The autoclave was sealed and this mixture was stirred for 1 minute at ambient temperature to form the catalyst. 4-Phenylbutene (225 µL, 1.5 mmol, 1.00 equiv.) and phenylsilane (10 µL, 0.08 mmol, 0.05 equiv.) were added to the mixture, which was subsequently purged three times with hydrogen gas. The autoclave was pressurised with hydrogen gas (20 bar), and the reaction mixture was stirred at ambient temperature for 7 hours. Et_2O (4 mL) was subsequently added. The mixture was passed through a short silica plug (Et_2O eluent) to remove any iron, and the solvent was removed *in vacuo*. 1,3,5-Trimethoxybenzene (25.2 mg, 0.15 mmol, 0.10 equiv.) was added for use as a ^{1}H NMR ($CDCl_3$) internal standard to determine the reaction yield.

F. General Procedure for [2+2]-Cycloaddition



In an 8 ml vial equipped with a magnetic stir bar and under an atmosphere of argon, preformed 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine cobalt(II) tetrafluoroborate (38.17 mg, 0.05 mmol, 0.1 equiv.) was added to a glass vial. Diallylamine (0.5 mmol, 1.00 equiv.) and phenylsilane (12.3 µL, 0.1 mmol, 0.20 equiv.) were added and the reaction heated at 80 °C for 24 hours. Et_2O (2 mL) was subsequently added, and the crude reaction mixture washed with distilled water to separate the catalyst from the crude reaction mixture. 1,3,5-Trimethoxybenzene (16.8 mg, 0.1 mmol, 0.20 equiv.) was added for use as a ^{1}H NMR ($CDCl_3$) internal standard to determine the reaction yield.

G. General Procedure for C–H Borylation

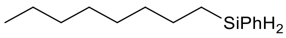


In an 8 mL vial equipped with a magnetic stir bar and under an atmosphere of argon, cobalt catalyst (11.1 mg, 0.019 mmol, 0.02 equiv) was added to a glass vial. 2-methylfuran (514.3 µL, 5.7 mmol, 15 equiv.) was then added, followed by bis(pinacolato)diboron (86.15 mg, 0.38 mmol, 1 equiv.), lithium methoxide (14.4 mg, 0.38 mmol, 1 equiv.) and phenylsilane (10 µL, 0.08 mmol, 0.21 equiv.). The reaction was heated at 80 °C for 24 hours. Et_2O (2 mL) was subsequently added, and the reaction mixture was washed with distilled water to separate the catalyst from the crude reaction mixture. 1,3,5-Trimethoxybenzene (12.8 mg, 0.076 mmol, 0.10 equiv.) was added for use as a ^1H NMR ($CDCl_3$) internal standard to determine the reaction yield.

Iron and Cobalt-Catalysed Hydrosilylation Products: Experimental and Analytical Data

Iron-Catalysed Hydrosilylation Products

Octylsilylbenzene (2a)



According to General Procedure C, $Fe(BF_4)_2{\cdot}6H_2O$ (3.2 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.9 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octene (144 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (10 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 8 mL fractions) to give the silane **2a** (173 mg, 0.783 mmol, 87%, 7:93 B:L) as a colourless oil.
Alternatively, the product silane **2a** could be obtained using Xantphos (5.8 mg, 0.01 mmol, 0.01 equiv.) and $Co(BF_4)_2{\cdot}6H_2O$ (3.4 mg, 0.01 mmol, 0.01 equiv.) using the same purification procedure (180 mg, 0.82 mmol, 82%, 1:>99 B:L)

^{1}H NMR: (500MHz, $CDCl_3$)
7.66 – 7.64 (2H, m), 7.48 – 7.41 (3H, m), 4.39 (2H, t, J = 3.6 Hz), 1.58 – 1.52 (2H, m), 1.46 – 1.35 (10H, m), 1.05 – 1.01 (2H, m), 0.98 (3H, t, J = 6.8 Hz)

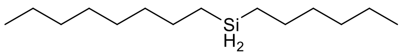
^{13}C NMR: (126 MHz, $CDCl_3$)
135.3, 132.9, 129.5, 128.0, 32.9, 32.0, 29.3, 29.2, 25.2, 22.7, 14.2, 10.1

^{29}Si NMR: (99 MHz, $CDCl_3$)
-30.8

TLC: R_f = 0.7 (pentane) [UV]

Characterisation data for the linear (major) product reported.
Data were in accordance with those previously reported.[4]

Hexyloctylsilane (2b)



According to General Procedure A, $Fe(BF_4)_2·6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octene (141 µL, 0.90 mmol, 1.00 equiv.) and hexylsilane (165 µL, 0.99 mmol, 1.10 equiv.) were added. The mixture was stirred for 1 hour at ambient temperature, and then diluted with Et_2O and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **2b** (197 mg, 0.86 mmol, 96%, 78:22 L:B) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
3.67 (2H, pent., J = 3.6 Hz), 1.44 – 1.30 (20 H, m), 0.92 (6H, t, J = 7.1 Hz), 0.72 – 0.68 (4H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
32.9, 32.6, 31.9, 31.6, 29.3, 29.2, 25.5, 25.4, 22.7, 22.6, 16.5, 14.1, 9.2, 7.9

^{29}Si NMR: (99 MHz, $CDCl_3$)
-28.5

TLC: R_f = 0.9 (pentane) [$KMnO_4$]

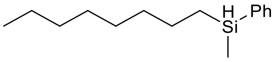
IR: ν_{max} (neat)
2920 (m), 2120 (w), 1458 (w), 941 (w)

MS: (EI^+)
143 ($[CH_3(CH_2)_7SiH_2]^+$, 100), 239 ($[CH_3(CH_2)_5SiH_2]^+$, 83)

HRMS: m/z (EI^+)
found: 229.23460 ($C_{14}H_{33}Si_1$), $[M+H]^+$ requires 229.23461

Characterisation data for the linear (major) product reported.

Methyloctylphenylsilane (2c)



According to General Procedure A, $Fe(BF_4)_2\cdot6H_2O$ (4.7 mg, 0.014 mmol, 0.02 equiv.) and ^{Et}BIP (6.0 mg, 0.014 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octene (110 μL, 0.70 mmol, 1.00 equiv.), methylphenylsilane (106 μL, 0.77 mmol, 1.10 equiv.) and phenylsilane (1 drop) were added. The mixture was stirred for 2 hours at ambient temperature, and then diluted with Et_2O and concentrated *in vacuo* to give **2c** (74%).The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the silane **2c** (119 mg, 0.51 mmol, 72%, 99:1 L:B) as a colourless oil.

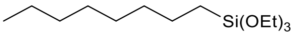
^{1}H NMR: (500 MHz, $CDCl_3$)
7.57 – 7.55 (2H, m), 7.39 – 7.36 (3H, m), 4.37 (1H, sext. J = 3.6 Hz), 1.43 – 1.23 (12H, m), 0.91 – 0.89 (3H, t, J = 7.1 Hz), 0.89 – 0.83 (2H, m), 0.35 (3H, d, J = 3.8 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)
136.9, 134.4, 129.2, 127.9, 33.3, 32.1, 29.4, 29.3, 24.4, 22.8, 14.2, 13.5, -5.6

^{29}Si NMR: (99 MHz, $CDCl_3$)
-13.5

Data were in accordance with those previously reported.

Triethoxy(octyl)silane (2d)



According to General Procedure C, $Fe(BF_4)_2{\cdot}6H_2O$ (4.8 mg, 0.014 mmol, 0.02 equiv.) and ^{Et}BIP (6.0 mg, 0.014 mmol, 0.02 equiv.) were complexed in THF (1 mL) by stirring for 1 minute. 1-Octene (110 μL, 0.70 mmol, 1.00 equiv.) and triethoxysilane (129 μL, 0.70 mmol, 1.00 equiv.) were added. The mixture was stirred for 3 hours at ambient temperature, and then diluted with Et_2O and concentrated *in vacuo* to give the crude silane **2d** (74%). The crude reaction product was purified by flash column chromatography (20 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 90:10, ca. 6 mL fractions) to give the silane **2d** (132 mg, 0.476 mmol, 68%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
3.84 (6H, q, J = 7.0 Hz), 1.46 – 1.40 (2H, m), 1.35 – 1.23 (20 H, m), 0.9 (3H, J = 7.0 Hz,), 0.67 – 0.64 (2H, m)

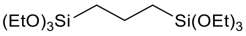
^{13}C NMR: (126 MHz, $CDCl_3$)
58.2, 33.2, 31.9, 29.2, 29.2, 22.7, 22.6, 18.3, 14.0, 10.4

^{29}Si NMR: (99 MHz, $CDCl_3$)
-44.6

This reaction was also run on a large-scale (0.032 mol, 0.02 mol% catalyst loading, 5 min), to provide the same product as a yellow oil (7.551 g, 0.027 mol, 85%)

Data were in accordance with those previously reported.[5]

1,3-Bis(triethoxysilyl)propane (2e)



According to General Procedure E, $Fe(BF_4)_2 \cdot 6H_2O$ (4.8 mg, 0.014 mmol, 0.02 equiv.) and ^{Et}BIP (6.0 mg, 0.014 mmol, 0.02 equiv.) were complexed in THF (1 mL) by stirring for 1 minute. Allyltriethoxysilane (158 µL, 0.70 mmol, 1.00 equiv.) and triethoxysilane (129 µL, 0.70 mmol, 1.00 equiv.) were added. The mixture was stirred for 3 hours at ambient temperature, and then diluted with Et_2O and concentrated *in vacuo* to give crude **2e** (65%). The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 90:10, ca. 6 mL fractions) to give the silane **2e** (155 mg, 0.42 mmol, 60%) as a yellow oil.

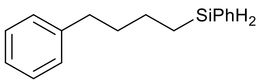
^{1}H NMR: (500 MHz, $CDCl_3$)
3.83 (12H, q, *J* = 7.0 Hz), 1.62 – 1.56 (2H, m), 1.23 (18H, t, *J* = 7.0 Hz), 0.74 (4H, t, *J* = 8.1 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)
58.3, 18.3, 16.5, 14.3

^{29}Si NMR: (99 MHz, $CDCl_3$)
-45.5

Data were in accordance with those previously reported.[6]

1-Phenyl-4-(phenylsilyl)butane (2f)



According to General Procedure C, $Fe(BF_4)_2 \cdot 6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-Phenyl-1-butene (137 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give crude **2f** (>95%).The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 6 mL fractions) to give the silane **2f** (147 mg, 0.65 mmol, 72%, 14:86 B:L). as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.73 – 7.71 (2H, m), 7.56 – 7.48 (3H, m), 7.43 – 7.40 (2H, m), 7.34 – 7.30 (3H, m), 4.48 (2H, t, J = 3.8 Hz), 2.76 (2H, t, J = 7.9 Hz), 1.89 – 1.83 (2H, m), 1.71 – 1.65 (2H, m), 1.16 – 1.11 (2H, m)

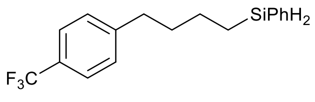
^{13}C NMR: (126 MHz, $CDCl_3$)
142.7, 135.8, 135.4, 129.7, 128.5, 128.4, 128.1, 125.9, 35.7, 34.7, 24.9,10.1

^{29}Si NMR: (99 MHz, $CDCl_3$)
-30.8

TLC: R_f = 0.4 (pentane) [UV]

Characterisation data for the linear (major) product.
Data were in accordance with those previously reported.[7]

1-Trifluoromethyl-4-(4-silylbenzenebutane)benzene (2g)



According to General Procedure C, $Fe(BF_4)_2\cdot 6H_2O$ (4.0 mg, 0.012 mmol, 0.02 equiv.) and ^{Et}BIP (5.1 mg, 0.012 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-(4-Triflouromethylphenyl)-1-butene (110 µL, 0.60 mmol, 1.00 equiv.) and phenylsilane (81 µL, 0.66 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 95:5, ca. 5 mL fractions) to give the *silane* **2g** as a clear oil (143 mg, 0.463 mmol, 77%, 9:91 B:L).

^{1}H NMR: (500 MHz, $CDCl_3$)
7.59 – 7.52 (4H, m), 7.44 – 7.36 (3H, m), 7.27 (2H, d, J = 7.9 Hz), 4.31 (2H, t, J = 3.7 Hz), 2.68 (2H, t, J = 7.6 Hz), 1.76 – 1.69 (2H, m), 1.51 – 1.49 (2H, m), 1.03 – 0.96 (2H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
146.7, 135.7, 135.3, 132.5, 129.7, 128.7, 128.1, 125.2 (q, J = 4.0 Hz), 35.4, 34.2, 27.7, 16.0, 9.9

^{29}Si NMR: (99 MHz, $CDCl_3$)
-30.9

TLC: R_f = 0.8 (pentane:Et_2O 95:5) [UV]

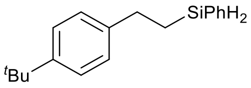
IR: ν_{max} (neat)
2928(w), 2129 (w), 1323 (s), 1117 (m), 835 (m)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 43), 230 ($[C_{11}H_{13}F_3Si]^+$, 100)

HRMS: m/z (EI^+)
found: 308.11960, ($C_{17}H_{19}F_3Si_1$) $[M+H]^+$ requires 308.12027

Characterisation data for the linear (major) product reported.

1-(4-*tert*-butylphenyl)-2-(phenylsilyl)ethane (2h)

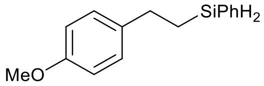


According to General Procedure C, $Fe(BF_4)_2 \cdot 6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-*tert*-Butylstyrene (137 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour at ambient temperature. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give **2h** (86%).The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the silane **2h** (205 mg, 0.762 mmol, 85%, linear product only) as a pale yellow oil.

^{1}H NMR: (500 MHz, CD_2Cl_2)
7.71 – 7.69 (2H, m), 7.51 – 7.44 (5H, m), 7.29 – 7.27 (2H, m), 4.52 (2H, t, J = 3.6 Hz), 2.93 – 2.89 (2H, m), 1.48 (11H, br. app. s)
^{13}C NMR: (126 MHz, $CDCl_3$)
148.8, 141.1, 135.3, 132.4, 129.8, 128.2, 127.8, 125.4, 34.6, 31.7, 30.8, 12.2
^{29}Si NMR: (99 MHz, $CDCl_3$)
-30.7
TLC: R_f = 0.7 (pentane) [UV]

Data were in accordance with those previously reported.[4]

(4-Methoxyphenethyl)(phenyl)silane (2i)



According to General Procedure C, $Fe(BF_4)_2\cdot 6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-Methoxystyrene (123 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 90:10, ca. 5 mL fractions) to give the silane **2i** (172 mg, 0.710 mmol, 79%, linear product only) as a light yellow oil.

^{1}H NMR: (600 MHz, $CDCl_3$)
7.59 – 7.56 (2H, m), 7.44 – 7.37 (3H, m), 7.11 (2H, d, J = 8.7 Hz), 6.84 (2H, d, J = 8.7 Hz), 4.33 (2H, t, J = 3.6 Hz), 3.81 (3H, s), 2.76 – 2.73 (2H, m), 1.32 – 1.28 (2H, m)

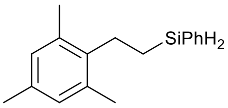
^{13}C NMR: (126 MHz, $CDCl_3$)
157.9, 136.1, 135.3, 132.3, 129.7, 128.9, 128.1, 113.9, 55.3, 30.3, 12.4

^{29}Si NMR: (99 MHz, $CDCl_3$)
-30.9

TLC: R_f = 0.7 (pentane:Et_2O 90:10) [UV]

Data were in accordance with those previously reported.[8]

(1,3,5-Trimethylphenethyl)(phenyl)silane (2j)



According to General Procedure C, $Fe(BF_4)_2\cdot 6H_2O$ (5.4 mg, 0.016 mmol, 0.02 equiv.) and ^{Et}BIP (6.8 mg, 0.016 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 2,4,6-Trimethylstyrene (136 μL, 0.80 mmol, 1.00 equiv.) and phenylsilane (109 μL, 0.88 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* and crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **2j** (160 mg, 0.630 mmol, 78%, linear product only) as a colourless oil.

^{1}H NMR: (600 MHz, $CDCl_3$)
7.64 – 7.62 (2H, m), 7.45 – 7.39 (3H, m), 6.84 (2H, br. s), 4.40 (2H, t, *J* = 3.7 Hz), 2.72 – 2.69 (2H, m), 2.26 (9H, br. s), 1.17 – 1.12 (2H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
138.3, 135.4, 135.3, 135.0, 132.3, 129.8, 129.1, 128.2, 24.5, 20.9, 19.7, 10.1

^{29}Si NMR: (99 MHz, $CDCl_3$)
-30.8

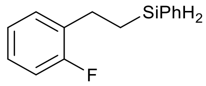
TLC: $R_f = 0.2$ (pentane) [UV]

IR: ν_{max} (neat)
2127 (m), 1427 (w), 1115 (m), 889 (s), 839 (s)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 17), 133 ($[C_{10}H_{13}]^+$, 100)

HRMS: *m/z* (EI^+)
found: 254.14979, ($C_{17}H_{22}Si_1$) $[M+H]^+$ requires 254.14853

1-(2-Fluorophenyl)-2-(phenylsilyl)ethane (2k)



According to General Procedure C, Fe(BF$_4$)$_2$·6H$_2$O (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 2-Flourostyrene (108 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et$_2$O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give the crude silane **2k** (38%).The crude reaction product was purified by flash column chromatography (10 g SiO$_2$, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the silane **2k** (62.3 mg, 0.288 mmol, 32%, linear product only) as a clear oil.

^{1}H NMR: (500 MHz, CDCl$_3$)
7.65 – 7.63 (2H, m), 7.48 – 7.38 (3H, m), 7.26 – 7.19 (2H, m), 7.12 – 7.09 (2H, m), 4.41(2H, t, *J* = 3.6 Hz), 2.89 – 2.85 (2H, m), 1.40 – 1.35 (2H, m)

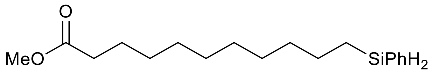
^{13}C NMR: (126 MHz, CDCl$_3$)
161 (d, *J* = 244.8 Hz), 135.3, 132.0, 130.8 (d, *J* = 16.0 Hz), 30.01 (d, *J* = 5.0 Hz), 129.7, 128.1, 127.6 (d, *J* = 8.0 Hz), 124.0 (d, *J* = 4.0 Hz), 115.2 (d, *J* = 21.9 Hz), 24.5 (d, *J* = 2.5 Hz), 10.9

^{29}Si NMR: (99 MHz, CDCl$_3$)
-31.1

TLC: R_f = 0.57 (pentane) [UV]

Data were in accordance with those previously reported.[7]

Methyl ester 11-(phenylsilyl)-undecanoic acid (2l)



According to General Procedure C, $Fe(BF_4)_2\cdot6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. Methyl 10-undecenoate (211 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo* to give crude **2l** (82%).The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 90:10, ca. 8 mL fractions) to give the silane **2l** (207 mg, 0.675 mmol, 75%, 6:94 B:L) as a clear oil.

^{1}H NMR: (600 MHz, $CDCl_3$)
7.60 – 7.58 (2H, m), 7.43 – 7.37 (3H, m), 4.31 (2H, t, *J* = 3.7 Hz), 3.69 (3H, s), 2.32 (2H, t, *J* = 7.6 Hz) 1.67 –1.62 (2H, m), 1.50 – 1.45 (2H, m), 1.36 – 1.35 (2H, m), 1.34 – 1.28 (10H, m), 0.98 – 0.94 (2H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
174.2, 135.2, 132.8, 129.5, 128.0, 51.4, 34.1, 32.8, 29.5, 29.4, 29.3, 29.2, 29.1, 25.1, 25.0, 10.0

^{29}Si NMR: (99 MHz, $CDCl_3$)
-30.8

TLC: R_f = 0.6 (pentane:Et_2O 90:10) [UV]

Characterisation data for the linear (major) product.
Data were in accordance with those previously reported.[4]

Phenyl-(10-pinanyl)-silane (2m)

According to General Procedure C, $Fe(BF_4)_2 \cdot 6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Mes}BIP (7.2 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. β-Pinene (142μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give crude **2m** (82%).The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 4 mL fractions) to give the *silane* **2m** (180 mg, 0.736 mmol, 82%) as a clear oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.59 – 7.57 (2H, m), 7.41 – 7.36 (3H, m), 4.32 – 4.30 (2H, m), 2.33 – 2.31(1H, m), 2.26 – 2.24 (1H, m), 2.09 – 2.05 (1H, m), 2.00 – 1.94 (1H, m), 1.19 – 1.90 (2H, m), 1.87 – 1.83 (1H, m), 1.58 – 1.52 (1H, m), 1.21 – 1.17 (5H, m), 1.08 (3H, s), 0.87 (1H, d, J = 9.6 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)
135.3, 133.1, 129.5, 128.0, 48.8, 41.4, 38.9, 38.2, 34.0, 28.3, 26.7, 25.1, 23.2, 19.9

^{29}Si NMR: (99 MHz, $CDCl_3$)
-33.1

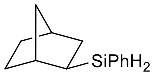
TLC: $R_f = 0.6$ (pentane) [UV]

IR: ν_{max} (neat)
2903 (m), 2128 (w), 1429 (w), 1115 (w), 843 (s)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 100), 166 ($[C_{10}H_{18}Si]^+$, 47)

HRMS: m/z (EI^+)
found: 244.16481 ($C_{16}H_{24}Si_1$), $[M+H]^+$ requires 244.16418

exo-2-(Phenylsilyl)bicyclo[2.2.l]heptane (2n)

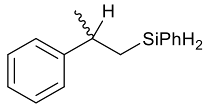


According to General Procedure C, pre-catalyst complex [^{Et}BIPFe(BF$_4$)$_2$] (6.6 mg, 0.010 mmol, 0.02 equiv.) was stirred in THF (0.5 mL) for 1 minute. Norbornene (47 mg, 0.50 mmol, 1.00 equiv.) and phenylsilane (78 µL, 0.55 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et$_2$O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give the crude silane **2n** (82%).The crude reaction product was purified by flash column chromatography (12 g SiO$_2$, 25 mm Ø, wet loaded, pentane, ca. 6 mL fractions) to give the silane **2n** (58.7 mg, 0.29 mmol, 58%) as a colourless oil.

^{1}H NMR: (500 MHz, CDCl$_3$)
7.60 (2H, d, J = 7.8 Hz), 7.43 – 7.36 (3H, m), 4.26 – 4.16 (2H, m), 2.31 – 2.29 (2H, m), 1.60 – 1.53 (4H, m), 1.38 – 1.19 (4H, m), 1.09 – 1.07 (1H, m)
^{13}C NMR: (126 MHz, CDCl$_3$)
135.5, 132.8, 129.5, 128.0, 38.9, 37.4, 37.3, 33.8, 33.6, 29.2, 24.3
^{29}Si NMR: (99 MHz, CDCl$_3$)
-26.8
TLC: R_f = 0.7 (pentane) [UV]

Data were in accordance with those previously reported.[9]

1-(Phenylsilyl)-2-phenylpropane (2o)



According to General Procedure C, $Fe(BF_4)_2{\cdot}6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Mes}BIP (7.2 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. α-methylstyrene (117μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give the crude silane **2o** (82%).The crude reaction product was purified by flash column chromatography (20 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 4 mL fractions) to give the silane **2o** (173 mg, 0.657 mmol, 73%, linear product only) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.63 – 7.61 (2H, m), 7.48 – 7.42 (3H, m), 7.41 – 7.37 (2H, m), 7.32 – 7.27 (3H, m), 4.37 – 4.33(2H, m), 3.08 (1H, sext. J = 7.3 Hz), 1.49 – 1.44 (5H, m)

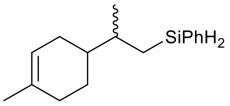
^{13}C NMR: (126 MHz, $CDCl_3$)
148.7, 135.3, 132.5, 129.6, 128.5, 128.1, 126.7, 126.1, 36.9, 25.1, 20.4

^{29}Si NMR: (99 MHz, $CDCl_3$)
-33.2

TLC: R_f = 0.4 (pentane) [UV]

Data were in accordance with those previously reported.[7]

(4*R*)-1-Methyl-4-[(1*R*,*S*)-1-methyl-2-(phenylsilyl)ethyl]-cyclohex-1-ene (2p)



According to General Procedure C, $Fe(BF_4)_2 \cdot 6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Mes}BIP (7.4 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. (*R*)-Limonene (150 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give the crude silane **2p** (86%).The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 4 mL fractions) to give the silane **2p** (156 mg, 0.638 mmol, 71%, 1:1 mixture of diastereoisomers) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.61 – 7.59 (2H, m), 7.42 – 7.36 (3H, m), 5.41 – 5.40 (1H, m),4.38 – 4.33 (2H, m),2.02 – 1.97(3H, m), 1.81 – 1.68 (3H, m), 1.67 (3H, br. s), 1.47 – 1.41 (1H, m), 1.32 – 1.24 (1H, m), 1.18 – 1.13 (1H, m), 1.00 – 0.98 (3H, m), 0.90 – 0.84 (1H, m)

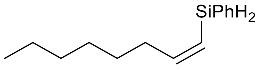
^{13}C NMR: (126 MHz, $CDCl_3$)
135.3, 134.0, 133.1, 129.5, 128.0, 121.0 (d, J = 4.5 Hz), 40.8 (d, J = 5.5 Hz), 34.7, 34.5, 31.0, 30.9, 29.1, 28.1, 26.9, 25.7, 23.5, 19.0, 18.7, 15.6, 15.2

^{29}Si NMR: (99 MHz, $CDCl_3$)
-33.4, -32.5

TLC: R_f = 0.6 (pentane) [UV]

Data were in accordance with those previously reported.[7]

cis-1-Octen-1-ylsilylbenzene (2q)

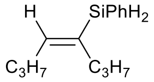


According to General Procedure C, Fe(BF$_4$)$_2$·6H$_2$O (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octyne (137 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et$_2$O and concentrated *in vacuo*.The crude reaction product was purified by flash column chromatography (10 g SiO$_2$, 25 mm Ø, wet loaded, pentane, ca. 8 mL fractions) to give the silane **2q** (156 mg, 0.712 mmol, 79%, (*E:Z*) 27:73) as a colourless oil.

^{1}H NMR: (500 MHz, CDCl$_3$)
7.69 – 7.66 (2H, m), 7.48 – 7.42 (3H, m), 6.73 – 6.67 (1H, dt, *J* = 14.2,7.4 Hz), 5.80 – 5.75 (1H, m), 4.71 (2H, d, *J* = 4.1 Hz), 2.35 – 2.31 (2H, ddd, *J* = 1.1, 7.4, 14.8 Hz), 1.55 – 1.44 (2H, m), 1.42 – 1.31 (6H, m), 1.00 – 0.94 (3H, m)
^{13}C NMR: (126 MHz, CDCl$_3$)
153.7,135.3, 132.4,129.5, 128.0, 118.9, 33.4, 31.7, 29.3, 28.8, 22.6, 14.1
^{29}Si NMR: (99 MHz, CDCl$_3$)
-50.4
TLC: R_f = 0.5 (pentane) [UV]

Characterisation data for the (*Z*)-isomer.
Data were in accordance with those previously reported.[4]

Phenyl [(*E*)-1-propyl-1-pentenyl]silane (2r)



According to General Procedure C, $Fe(BF_4)_2{\cdot}6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-Octyne (132 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 3 hours. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give crude the crude **2r** silane (42%).The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **2r** (65.6 mg, 0.301 mmol, 33%, *E* isomer) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.65 – 7.63 (2H, m), 7.47 – 7.40 (3H, m), 6.11 (1H, t, *J* = 6.9 Hz), 4.62 (2H, s), 2.26 – 2.19 (4H, m), 1.53 – 1.42 (4H, m), 1.00 (3H, t, *J* = 7.4 Hz), 0.94 (3H, t, *J* = 7.4 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)
146.3, 135.6, 134.2, 132.8, 129.5, 128.0, 32.5, 30.9, 22.8, 22.6, 14.2, 13.9

^{29}Si NMR: (99 MHz, $CDCl_3$)
-31.4

TLC: R_f = 0.7(pentane) [UV]

IR: ν_{max} (neat)
2957 (w), 2127 (w), 1429 (s), 843 (m), 696 (m)

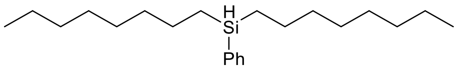
MS: (EI^+)
107 ($[SiPhH_2]^+$, 100), 218 ($[M]^+$, 15)

HRMS: *m/z* (EI^+)
found: 218.14875 ($C_{14}H_{22}Si_1$), $[M+H]^+$ requires 218.14853

(*E*)-isomer formation was confirmed using NOSEY NMR techniques. NOE Contacts: $SiPhH_2$ → =CH

Tertiary Silane Products

Dioctylphenylsilane (2s)



According to General Procedure D, $Fe(BF_4)_2\cdot 6H_2O$ (5.4 mg, 0.016 mmol, 0.02 equiv.) and ^{Et}BIP (6.8 mg, 0.016 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octene (126 μL, 0.80 mmol, 1.00 equiv.) and phenylsilane (99 μL, 0.80 mmol, 1.00 equiv.) were added and the reaction was stirred for 30 minutes. 1-Octene (126 μL, 0.80 mmol, 1.00 equiv.) was subsequently added and stirred for a further 3 hours. The mixture was diluted with Et_2O and concentrated *in vacuo* to give crude **2s** (79%).The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 6 mL fractions) to give the silane **2s** (197 mg, 0.59 mmol, 74%) as a clear oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.56 – 7.54 (2H, m), 7.39 – 7.36 (3H, m), 4.27 (1H, quin. *J* = 3.4 Hz), 1.42 – 1.27 (24H, m), 0.9 (6H, t, *J* = 7.0 Hz), 0.88 – 0.85 (4H, m)

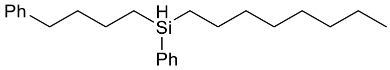
^{13}C NMR: (126 MHz, $CDCl_3$)
136.2, 134.7, 129.1, 127.8, 33.3, 32.0, 29.3, 24.6, 22.7, 14.1, 12.0

^{29}Si NMR: (99 MHz, $CDCl_3$)
-9.4

TLC: $R_f = 0.8$ (pentane) [UV]

Data were in accordance with those previously reported.[10]

1-Phenyl-4-(octylphenylsilyl)butane (2t)



According to General Procedure D, $Fe(BF_4)_2 \cdot 6H_2O$ (5.4 mg, 0.016 mmol, 0.02 equiv.) and ^{Et}BIP (6.8 mg, 0.016 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-Phenylbutene (120 µl, 0.80 mmol, 1.00 equiv.) and phenylsilane (99 µL, 0.80 mmol, 1.00 equiv.) were added and the reaction was stirred for 30 minutes. 1-Octene (126 µL, 0.80 mmol, 1.00 equiv.) was subsequently added and stirred for a further 3 hours. The mixture was diluted with Et_2O and concentrated *in vacuo* to give the crude silane **2t** (95%).The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 6 mL fractions) to give the *silane* **2t** (243 mg, 0.69 mmol, 86%) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.52 – 7.50 (2H, m), 7.39 – 7.33 (3H, m), 7.27 – 7.24 (2H, m), 7.18 – 7.13 (3H, m), 4.28 – 4.21 (1H, m), 2.58 (2H, t, *J* = 7.6 Hz), 1.66 (2H, pent., *J* = 7.7 Hz), 1.48 – 1.24 (16H, m), 0.90 – 0.81 (5H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
142.8, 136.1, 135.8, 134.5, 129.3, 128.6, 128.5, 128.0, 125.8, 35.8, 35.2, 33.5, 32.1, 29.5, 24.8, 24.5, 22.9, 16.3, 14.4, 12.0,

^{29}Si NMR: (99 MHz, $CDCl_3$)
-9.3

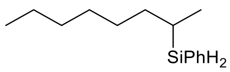
IR: ν_{max} (neat)
2920 (w), 2106 (w), 1113 (w), 696 (m)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 38), 239 ($[Ph(CH_2)_4SiHPh]^+$, 100)

HRMS: *m/z* (EI^+)
found: 352.25733 ($C_{24}H_{36}Si_1$), $[M+H]^+$ requires 352.25808

Cobalt-Catalysed Hydrosilylation Products

Octan-2-yl(phenyl)silane (3a)



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (2.7 mg, 0.008 mmol, 0.01 equiv.) and ^{Et}BIP (3.4 mg, 0.008 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octene (126 µL, 0.80 mmol, 1.00 equiv.) and phenylsilane (109 µL, 0.88 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give crude **3a** (>95%).The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the silane **3a** (152 mg, 0.688 mmol, 86%, 8:92 B:L) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.68 – 7.66 (2H, m), 7.49 – 7.42 (3H, m), 4.36 (1H, dd, *J* = 2.5, 6.0 Hz), 4.32 (1H, dd, *J* = 3.2, 6.0 Hz), 1.64 – 1.59 (1H, m), 1.57 – 1.49 (1H, m), 1.47 – 1.32 (8H, br. m), 1.29 – 1.21 (1H, m), 1.18 –1.16 (3H, m), 0.99 (3H, app. t, *J* = 7.0 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)
135.7, 132.4, 129.5, 127.9, 33.6, 31.9, 29.5, 28.6, 22.8, 16.4, 16.2, 14.2

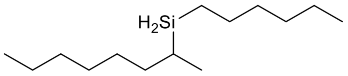
^{29}Si NMR: (99 MHz, $CDCl_3$)
-23.0

TLC: $R_f = 0.6$ (pentane) [UV]

IR: ν_{max} (neat)
2127 (w), 117 (w), 930 (m), 698 (s)

Characterisation data for the branched (major) product reported.
Data were in accordance with those previously reported.[11]

2-(Hexylsilyl)octane (3b)

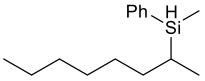


According to General Procedure A, $Co(BF_4)_2\cdot 6H_2O$ (3.1 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.9 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octene (141 μL, 0.90 mmol, 1.00 equiv.) and hexylsilane (165 μL, 0.99 mmol, 1.10 equiv.) were added. The mixture was stirred for 1 hour at ambient temperature, and then diluted with Et_2O and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **3b** (182 mg, 0.79 mmol, 88%, 2:98 L:B) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
3.62 – 3.57 (2H, m), 1.47 – 1.27 (18H, m), 1.05 (3H, d, J = 7.4 Hz), 0.96 – 0.94 (1H, m), 0.92 (6H, t, J = 7.2 Hz), 0.73 – 0.69 (2H, m)
^{13}C NMR: (126 MHz, $CDCl_3$)
34.0, 32.7, 31.9, 31.6, 29.5, 28.6, 25.6, 22.7, 22.6, 16.5, 15.4, 14.1, 7.9
^{29}Si NMR: (99 MHz, $CDCl_3$)
-20.8
TLC: R_f = 0.8 (pentane) [$KMnO_4$]
IR: ν_{max} (neat)
2920 (w), 2117 (w), 1458 (w), 939 (w), 829 (w)
MS: (EI^+)
115 ($[(CH_2)_6SiH_2]^+$, 100), 228 ($[M]^+$, 7)
HRMS: m/z (EI^+)
found: 229.23361, ($C_{14}H_{33}Si_1$) $[M+H]^+$ requires 229.23461

Characterisation data for the branched (major) product reported.

Octan-2-yl(methylphenyl)silane (3c)



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (4.7 mg, 0.014 mmol, 0.02 equiv.) and ^{Et}BIP (6.0 mg, 0.014 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octene (110 µL, 0.70 mmol, 1.00 equiv.), methylphenylsilane (106 µL, 0.77 mmol, 1.10 equiv.) and phenylsilane (1 drop) were added. The mixture was stirred for 2 hours at ambient temperature, and then diluted with Et_2O and concentrated *in vacuo* to give crude **3c** (66%).The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **3c** (81.4 mg, 0.35 mmol, 50%, 11:89 L:B) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)

7.57 – 7.54 (2H, m), 7.41 – 7.36 (3H, m), 4.28 – 4.26 (1H, m), 1.51 – 1.41 (2H, m), 1.32 – 1.22 (8H, m), 1.01 (4H, s), 0.89 (3H, t, J = 7.2 Hz), 0.34 (3H, dd, J = 3.8, 7.7 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)

136.1, 134.7, 129.1, 127.8, 32.7, 31.9, 29.4, 28.4, 22.5, 17.8, 14.8, 14.1, -7.9

^{29}Si NMR: (99 MHz, $CDCl_3$)

-8.0

TLC: R_f = 0.7 (pentane) [UV]

IR: ν_{max} (neat)

2922 (w), 2110 (w), 1427 (w), 829 (m), 698 (m)

MS: (EI^+)

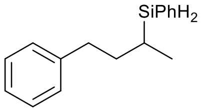
121 ($[HSi(Ph)Me]^+$, 100), 234 ($[M]^+$, 2)

HRMS: *m/z* (EI^+)

found: 234.17882, ($C_{15}H_{26}Si_1$) $[M+H]^+$ requires 234.17983

Characterisation data for the branched (major) product reported.

(4-Phenylbut-2-yl)silylbenzene (3d)



According to General Procedure B, $Co(BF_4)_2{\cdot}6H_2O$ (1.6 mg, 0.0045 mmol, 0.005 equiv.) and ^{Et}BIP (1.9 mg, 0.0045 mmol, 0.005 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-Phenylbutene (135 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give crude **3d** (90%).The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 6 mL fractions) to give the *silane* **3d** (184.4 mg, 0.767 mmol, 85%, 99:1 B:L) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.46 – 7.44 (2H, m), 7.30 – 7.22 (3H, m), 7.17 – 7.14 (2H, m), 7.08 – 7.03 (3H, m), 4.19 (1H, dd, *J* = 2.4, 6.0 Hz), 4.16 (1H, dd, *J* = 3.1, 6.0 Hz), 2.67 – 2.48 (2H, m), 1.79 – 1.72 (1H, m), 1.58 – 1.50 (1H, m), 1.13 – 1.06 (1H, m), 1.04 – 1.02 (3H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
142.6, 135.8, 132.0, 129.7, 128.5 (d, *J* = 12.5 Hz), 128.1, 125.8, 35.5, 34.9, 16.2, 16.1

^{29}Si NMR: (99 MHz, $CDCl_3$)
-22.9

TLC: $R_f = 0.3$ (pentane) [UV]

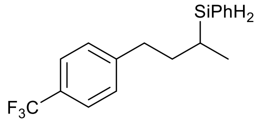
IR: ν_{max} (neat)
2137 (w), 1514 (w), 1115 (w), 928 (m), 698 (s)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 92)

HRMS: *m/z* (EI^+)
found: 240.13176 ($C_{16}H_{20}Si_1$), $[M+H]^+$ requires 240.13288

Characterisation data for the branched (major) product reported.
See **3f** for linear product data.

1-Trifluoromethyl-4-(3-silylbenzenebutane)benzene (3e)



According to General Procedure B, $Co(BF_4)_2\cdot 6H_2O$ (2.0 mg, 0.006 mmol, 0.01 equiv.) and ^{Et}BIP (2.6 mg, 0.006 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-(4-Trifluoromethanephenyl)-1-butene (110 µL, 0.60 mmol, 1.00 equiv.) and phenylsilane (81 µL, 0.66 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo.* The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 97:3, ca. 5 mL fractions) to give the *silane* **3e** (134 mg, 0.434 mmol, 72%, branched product only) as a colourless oil.

^{1}H NMR: (400 MHz, $CDCl_3$)
7.59 – 7.53 (4H, m), 7.46 – 7.36 (3H, m), 7.27 – 7.25 (2H, m), 4.30 (1H, dd, J = 2.5, 6.0 Hz), 4.27 (1H, dd, J = 2.9, 6.0 Hz), 2.86 – 2.66 (2H, m), 1.92 – 1.62 (2H, m), 1.24 (1H, t, J = 7.0 Hz), 1.17 – 1.16 (3H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
146.7, 135.3, 132.5, 129.7, 128.7, 128.1, 125.3 (q, J = 4.0 Hz), 124.5 (q, J = 271.8 Hz), 128.1 (q, J = 31.4 Hz), 35.4, 34.6, 24.7, 16.0, 15.9, 9.9

^{29}Si NMR: (99 MHz, $CDCl_3$)
-23.1

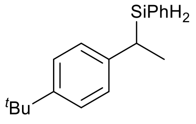
TLC: R_f = 0.8 (pentane:diethyl ether 97:3) [UV]

IR: ν_{max} (neat)
2129 (w), 1323 (s), 1117 (m), 931 (s), 837 (s)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 100), 230 ($[C_{11}H_{13}F_3Si]^+$, 41)

HRMS: *m/z* (EI^+)
found: 308.12008 ($C_{17}H_{19}F_3Si_1$), $[M+H]^+$ requires 308.1027

1-(4-*tert*Butylphenyl)-1-(phenylsilyl)ethane (3f)



According to General Procedure B, Co(BF$_4$)$_2$·6H$_2$O (1.6 mg, 0.0045 mmol, 0.005 equiv.) and ^{Et}BIP (1.9 mg, 0.0045 mmol, 0.005 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. *tert*-Butylstyrene (165 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with diethyl ether and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give crude **3f** (88%).The crude reaction product was purified by flash column chromatography (12 g SiO$_2$, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **3f** (202 mg, 0.751 mmol, 83%, 55:45 B:L) as a colourless oil.

^{1}H NMR: (500 MHz, CDCl$_3$)
7.73 – 7.71 (2H, m, *L*), 7.59 – 7.57 (2H, m, *B*) 7.54 – 7.50 (4H, m, *B/L*), 7.47 – 7.43 (6H, m, *B/L*), 7.30 – 7.28 (2H, m, *L*), 7.22 – 7.20 (2H, m, *B*), 4.52 (2H, t, J = 3.6 Hz, *L*), 4.50*(2H, AB dd, $\Delta\nu_{AB}$14.0 Hz, J_{AB} = 3.8, 6.8Hz, *B*), 2.94 – 2.90 (2H, m, *L*), 2.79 – 2.73 (1H, m, *B*), 1.62 (3H, d, J 7.4 Hz, *B*), 1.48 (20H, br. app. s, *B/L*)

^{13}C NMR: (126 MHz, CDCl$_3$)
148.7 (*L*), 147.9 (*B*), 141.5 (*B*), 141.0 (*L*), 135.8 (*B*), 135.4 (*L*), 132.4 (*L*), 131.8 (*B*), 129.8 (*L*), 129.7 (*B*), 128.2 (*L*), 128.0 (*B*), 127.7 (*L*), 126.9 (*B*), 125.4 (*L*), 125.4 (*B*), 34.5 (*L*), 34.4 (*B*), 31.6 (*L*), 30.7 (*L*), 24.8 (*B*), 16.6 (*B*), 12.1 (*L/B*)

^{29}Si NMR: (99 MHz, CDCl$_3$)
-21.0 (*B*), -30.8 (*L*)

TLC: R_f = 0.7 (pentane) [UV]

IR: ν_{max} (neat)
2137 (w), 1514 (w), 1115 (w), 928 (m), 698 (s)

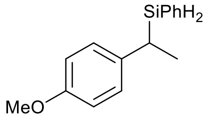
MS: (EI$^+$)
107 ([SiPhH$_2$]$^+$, 100), 268 ([M]$^+$, 27)

HRMS: *m/z* (EI$^+$)
found: 268.16440 (C$_{18}$H$_{24}$Si$_1$), [M+H]$^+$ requires 268.16418

*Signal overlaps with linear Si-H peak

Characterisation data for both branched and linear products reported; (*L*) and (*B*) indicate which product is represented. See **2h** for linear product data.

4-Methoxy-4-[1-(phenylsilyl)ethyl]-benzene (3g)



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (1.6 mg, 0.0045 mmol, 0.005 equiv.) and ^{Et}BIP (1.9 mg, 0.0045 mmol, 0.005 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-Methoxystyrene (121 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O, 90:10, ca. 5 mL fractions) to give the *silane* **3g** (182 mg, 0.750 mmol, 83%, 45:55 B:L) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.59 – 7.58 (2H, m, *L*), 7.44 – 7.37 (6H, m, *L/B*), 7.35 – 7.32 (2H, m, *B*), 7.13 – 7.12 (2H, m, *L*), 7.05 – 7.03 (2H, m, *B*), 6.85 – 6.83 (4H, m, *L/B*), 4.33 – 4.32 (4H, m, *L/B*), 3.81 (6H, br. s, *L/B*), 2.76 – 2. 73 (2H, m, *L*), 2.63 – 2.56 (1H, m, *B*), 1.45 (3H, d, $J =$ 7.6 Hz, *B*), 1.32 – 1.28 (2H, m, *L*)

^{13}C NMR: (126 MHz, $CDCl_3$)
158.0 (*L*), 157.4 (*B*), 136.6 (*B*), 136.2 (*L*), 135.8 (*B*), 135.4 (*L*), 132.4 (*L*), 131.7 (*B*), 129.9 (*B*), 129.8 (*L*), 129.0 (*L/B*), 128.2 (*B*), 128.2 (*L*), 128.0 (*B*), 114.1 (*B*), 113.9 (*L*), 55.3 (*L*), 30.4 (*L*), 24.4 (*B*), 17.0 (*B*), 12.5 (*L*)

^{29}Si NMR: (99 MHz, $CDCl_3$)
-31.0 (*L*), -21.3 (*B*)

TLC: $R_f = 0.7$ (pentane:diethyl ether 90:10) [UV]

IR: ν_{max} (neat)
2129 (m), 1508 (s), 1242 (s), 698 (s)

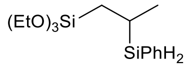
MS: (EI^+)
107 ($[SiPhH_2]^+$, 11), 135 ($[C_9H_{11}O]^+$, 100)

HRMS: *m/z* (EI^+)
found: 242.11094 ($C_{15}H_{18}O_1Si_1$), $[M+H]^+$ requires 242.11215

Characterisation data for both branched and linear products reported; (*L*) and (*B*) indicate which product is represented. See **2i** for linear product data.

Data for the linear product were in accordance with those previously reported.[5]

(3-Triethoxysilyl-2-phenylsilyl)propane (3h)



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (3.2 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.9 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. Allyltriethoxysilane (204 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 95:5), ca. 5 mL fractions) to give the *silane* **3h** (221 mg, 0.707 mmol, 79%) as a colourless oil. The branched product was formed exclusively.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.62 – 7.59 (2H, m), 7.43 – 7.35 (3H, m), 4.26 (1H, dd, *J* = 2.5, 6.4 Hz), 4.23 (1H, dd, *J* = 3.3, 6.4 Hz), 3.83 (6H, q, *J* = 7.0 Hz), 1.40 – 1.35 (1H, m), 1.24 (9H, t, *J* = 7.0 Hz), 1.19 – 1.17 (3H, m), 0.75 (2H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
135.7, 132.3, 129.5, 127.9, 58.3, 18.7, 18.3, 13.9, 10.4

^{29}Si NMR: (99 MHz, $CDCl_3$)
-19.7, -46.3

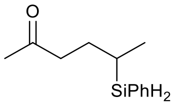
TLC: $R_f = 0.4$ (pentane:diethyl ether) [UV]

IR: ν_{max} (neat)
2972 (w), 2125 (w), 1074 (m), 839 (m)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 16), 163 ($[(EtO)_3Si]^+$, 100)

HRMS: *m/z* (EI^+)
found: 312.15557 ($C_{15}H_{28}O_3Si_2$),$[M+H]^+$ requires 312.15825

5-(Phenylsilyl)-2-hexanone (3i)



According to General Procedure B, Co(BF$_4$)$_2$·6H$_2$O (3.1 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.8 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 5-Hexen-2-one (104 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et$_2$O and concentrated *in vacuo.* The crude reaction product was purified by flash column chromatography (15 g SiO$_2$, 25 mm Ø, wet loaded, pentane:Et$_2$O 95:5, ca. 5 mL fractions) to give the *silane* **3i** (134 mg, 0.650 mmol, 72%, 10:90 B:L) as a colourless oil.

^{1}H NMR: (500 MHz, CDCl$_3$)
7.60 – 7.57 (2H, m), 7.44 – 7.37 (3H, m), 4.28 (1H, dd, *J* = 2.7, 6.0 Hz), 4.24 (1H, dd, *J* = 3.2, 6.0 Hz), 2.60 – 2.42 (2H, m), 2.12 (3H, s), 1.88 – 1.81 (1H, m), 1.69 – 1.60 (1H, m), 1.21 – 1.1 (1H, m), 1.11 – 1.06 (3H, m)

^{13}C NMR: (126 MHz, CDCl$_3$)
208.8, 135.6, 131.5, 129.7, 128.0, 42.6, 29.9, 27.4, 16.0, 15.9

^{29}Si NMR: (99 MHz, CDCl$_3$)
-23.4

TLC: R_f = 0.4 (pentane:diethyl ether 95:5) [UV]

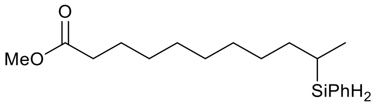
IR: ν_{max} (neat)
2126 (w), 1715 (m), 930 (m), 698 (m)

MS: (EI$^+$)
107 ([SiPhH$_2$]$^+$, 20), 129([C$_6$H$_{13}$OSi]$^+$, 100)

HRMS: *m/z* (EI$^+$)
found: 206.11151 (C$_{12}$H$_{18}$O$_1$Si$_1$), [M+H]$^+$ requires 206.11215

Characterisation data for the branched (major) product reported.

Methyl ester 10-(phenylsilyl)undecanoic acid (3j)



According to General Procedure B, Co(BF$_4$)$_2$·6H$_2$O (3.1 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.8 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. Methyl 10-undecenoate (202 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et$_2$O and concentrated *in vacuo.* The crude reaction product was purified by flash column chromatography (15 g SiO$_2$, 25 mm Ø, wet loaded, pentane:Et$_2$O 99:1, ca. 5 mL fractions) to give the *silane* **3j** (215 mg, 0.702 mmol, 78%, 94:6 B:L) as a colourless oil.

^{1}H NMR: (500 MHz, CDCl$_3$)
7.59 – 7.58 (2H, m), 7.41 – 7.36 (3H, m), 4.25 (1H, dd, *J* = 2.5, 6.0 Hz), 4.21 (1H, dd, *J* = 3.2, 6.0 Hz), 3.69 (3H, s), 2.34 – 2.31 (2H, m), 1.66 – 1.61 (2H, m), 1.36 – 1.29 (12H, m), 1.16 – 1.15 (1H, m), 1.09 (1H, s), 1.07 (1H, s), 0.91 (1H, t, *J* = 7.0 Hz)

^{13}C NMR: (126 MHz, CDCl$_3$)
174.2, 135.6, 132.2, 129.5, 127.9, 51.3, 34.1, 33.5, 29.6, 29.4, 29.3, 29.2, 28.5, 25.0, 16.3, 16.2

^{29}Si NMR: (99 MHz, CDCl$_3$)
-23.1

TLC: R_f = 0.2 (pentane:diethyl ether 99:1) [UV]

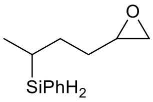
IR: ν_{max} (neat)
2924 (w), 2127 (w), 1740 (m), 731 (m), 698 (m)

MS: (EI$^+$)
107 ([SiPhH$_2$]$^+$, 76), 193 ([C$_6$H$_9$O$_2$]$^+$, 100)

HRMS: *m/z* (EI$^+$)
found: 306.20082 (C$_{18}$H$_{30}$O$_2$Si$_1$), [M+H]$^+$ requires 306.20096

Characterisation data for the branched (major) product.

1,2-Epoxy-(5-phenylsilyl)hexane (3k)



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (3.1 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.8 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1,2-Epoxy-5-hexene (102 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo.* The crude reaction product was purified by flash column chromatography (20 g SiO_2, 25 mm Ø, wet loaded, pentane:Et_2O 95:5, ca. 6 mL fractions) to give the *silane* **3k** (125 mg, 0.605 mmol, 67%, 5:95 B:L, 1:1 mixture of diastereoisomers) as a colourless oil.

^{1}H NMR: (400 MHz, $CDCl_3$)
7.60 – 7.58 (2H, m), 7.45 – 7.36 (3H, m), 4.29 – 4.22 (2H, m), 2.92 – 2.88 (1H, m), 2.77 – 2.74 (1H, m), 2.48 (1H, td, J = 2.7, 7.7 Hz), 1.78 – 1.44 (4H, m), 1.25 – 1.19 (1H, m), 1.12 – 1.10 (3H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
135.6, 131.7, 129.7, 128.0, 52.3, 52.1, 47.1, 47.0, 31.5, 29.6, 29.5, 16.2, 16.1, 16.0

^{29}Si NMR: (99 MHz, $CDCl_3$)
-23.1

TLC: R_f = 0.6 (pentane:diethyl ether 95:5) [UV/$KMNO_4$]

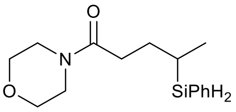
IR: ν_{max} (neat)
2126 (w), 930 (m), 833 (s), 698 (m)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 100), 206 ($[M]^+$, 12)

HRMS: *m/z* (EI^+)
found: 206.11132 ($C_{12}H_{18}O_1Si_1$), $[M+H]^+$ requires 206.11215

Characterisation data for the branched (major) product.

1-(4-Morpholinyl)-4-(phenylsilyl)pentan-1-one (3l)



According to General Procedure B, $Co(BF_4)_2\cdot 6H_2O$ (2.0 mg, 0.006 mmol, 0.01 equiv.) and ^{Et}BIP (2.6 mg, 0.006 mmol, 0.01 equiv.) were complexed in THF by stirring for 1 minute. 1-Morpholinopent-4-en-1-one (99 µL, 0.60 mmol, 1.00 equiv.) and phenylsilane (81 µL, 0.66 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo.* The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane:EtOAc 30:70, ca. 5 mL fractions) to give the *silane* **3l** (67.1 mg, 0.230 mmol, 38%, 7:93 B:L) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.59 – 7.57 (2H, m), 7.42 – 7.35 (3H, m), 4.28 (1H, dd, *J* = 2.9, 5.9 Hz), 4.25 (1H, dd, *J* = 3.0, 5.9 Hz), 3.64 – 3.58 (6H, m), 3.33 – 3.31 (2H, m), 2.43 – 2.27 (2H, m), 1.91– 1.66 (2H, m), 1.25 – 1.19 (1H, m), 1.13 – 1.12 (3H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
171.5, 135.6, 131.6, 129.7, 128.1, 66.9, 66.6, 45.9, 41.9, 32.1, 29.0, 16.2, 16.1

^{29}Si NMR: (99 MHz, $CDCl_3$)
-23.2

TLC: R_f = 0.4 (pentane:EtOAc 30:70) [UV]

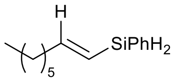
IR: ν_{max} (neat)
2129 (w), 1633 (w), 1115 (w), 906 (m), 839 (m), 725 (s)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 60), 276 ($[M-1]^+$, 100), 277 ($[M]^+$, 33)

HRMS: *m/z* (EI^+)
found: 277.14839 ($C_{15}H_{23}O_2N_1Si_1$), $[M+H]^+$ requires 277.14926

Characterisation data for the branched (major) product.

***trans*-1-Octen-1-ylsilylbenzene (3m)**



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (3.1 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.80 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 1-Octyne (133 µl, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µl, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O and concentrated *in vacuo.* The crude reaction product was purified by flash column chromatography (15 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **3m** (124 mg, 0.565 mmol, 63%, (*E*:*Z*) 83:17) as a colourless oil. Hydrosilylation by-products were also detected in trace amounts.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.66 – 7.64 (2H, m, Ar), 7.47 – 7.41 (3H, m, Ar), 6.47 – 6.41 (1H, dt, *J* = 6.3, 18.4 Hz, =CH), 5.83 – 5.77 (1H, m, =CH), 4.63 (2H, br. d, *J* = 3.2 Hz, SiPhH_2), 2.21 (2H, app. q, *J* = 7.6 Hz, CH_2), 1.46 – 1.42 (2H, m, CH_2), 1.33 – 1.30 (6H, m, CH_2), 0.91 (3H, t, *J* = 7.1 Hz, CH_3)

^{13}C NMR: (126 MHz, $CDCl_3$)
154.2, 135.4, 132.5, 129.6, 128.0, 119.9, 37.0, 31.8, 28.9, 28.5, 22.7, 14.1

^{29}Si NMR: (99 MHz, $CDCl_3$)
-38.0

TLC: R_f = 0.5 (pentane) [UV]

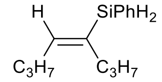
IR: ν_{max} (neat)
2924 (w), 2131 (w), 1429 (w), 842 (s)

MS: (EI^+)
107 ($[SiPhH_2]^+$, 100), 175 ($[C_{11}H_{15}Si]^+$, 29)

HRMS: *m/z* (EI^+)
found: 218.14815 ($C_{14}H_{22}Si_1$), $[M+H]^+$ requires 218.14853

Characterisation data for the (*E)*-isomer.

Phenyl[(*E*)-1-propyl-1-pentenyl]silane (3n)



According to General Procedure B, $Co(BF_4)_2{\cdot}6H_2O$ (6.1 mg, 0.018 mmol, 0.02 equiv.) and ^{Et}BIP (7.7 mg, 0.018 mmol, 0.02 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. 4-Octyne (132 μL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 3 hours. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give crude **3n** (68%).The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **3n** (118 mg, 0.539 mmol, 60%, (*E*)-isomer) as a colourless oil.

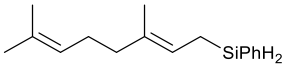
^{1}H NMR: (600 MHz, $CDCl_3$)
7.65 – 7.63 (2H, m), 7.44 – 7.36 (3H, m), 6.11 (1H, t, *J* = 6.9 Hz), 4.62 (2H, s), 2.26 – 2.19 (4H, m), 1.53 – 1.42 (4H, m), 1.00 (3H, t, *J* = 7.4 Hz), 0.94 (3H, t, *J* = 7.4 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)
146.3, 135.6, 134.2, 132.8, 129.5, 128.0, 32.5, 30.9, 22.8, 22.6, 14.2, 13.9

^{29}Si NMR: (99 MHz, $CDCl_3$)
-31.4

TLC: R_f = 0.6 (pentane) [UV]

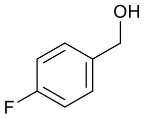
3,7-(Dimethyl)-1-[phenylsilane]octa-2,6-diene (3o)



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (3.2 mg, 0.009 mmol, 0.01 equiv.) and ^{Et}BIP (3.9 mg, 0.009 mmol, 0.01 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. Myrcene (172 µL, 0.90 mmol, 1.00 equiv.) and phenylsilane (122 µL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 2 hours. The mixture was diluted with Et_2O and passed through a short plug of silica. The filtrate was concentrated *in vacuo* to give the crude silane **3o** (73%). The crude reaction product was purified by flash column chromatography (30 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the *silane* **3o** (150 mg, 0.612 mmol, 68%) as a colourless oil.

^{1}H NMR:	(500 MHz, $CDCl_3$) 7.52 – 7.49 (2H, m), 7.16 – 7.11 (3H, m), 5.27 (1H, t, *J* = 7.5 Hz), 5.21 – 5.18 (1H, m), 4.49 (2H, t, *J* = 3.8 Hz), 2.09 – 2.02 (4H, m), 1.79 – 1.76 (2H, m), 1.66 (6H, s), 1.54 (3H, s)
^{13}C NMR:	(126 MHz, $CDCl_3$) 135.2, 134.9, 132.5, 131.5, 129.7, 127.9, 124.4, 119.2, 31.8, 26.5, 25.6, 23.4, 17.4, 11.7
^{29}Si NMR:	(99 MHz, $CDCl_3$) -33.4
TLC:	$R_f = 0.4$ (pentane) [UV]
IR:	ν_{max} (neat) 2926 (w), 2133 (m), 1429 (w), 1115 (m), 931 (s), 835 (s)
MS:	(EI^+) 244 ($[M]^+$, 21), 107 ($[SiPhH_2]^+$, 100)
HRMS:	*m/z* (EI^+) found: 244.16430 ($C_{16}H_{24}Si_1$),$[M+H]^+$ requires 244.16418

4-Fluorobenzyl alcohol (11)



In an 8 mL vial equipped with a magnetic stir bar and under an atmosphere of argon, 4-fluorobenzaldehyde (53 µL, 0.5 mmol, 1.0 equiv.), phenylsilane (61.7 µL, 0.5 mmol, 1.0 equiv.), and tetra-*n*-butylammonium tetrafluoroborate (165 mg, 0.5 mmol, 1 equiv.) were dissolved in anhydrous THF (0.5 mL). The reaction was stirred at ambient temperature for 24 hours. The crude reaction mixture was diluted with Et_2O (10 mL) and water (10 mL). The organic phase extracted and concentrated *in vacuo*. The yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard (54.4 mg, 0.43 mmol, 86%).

^{1}H NMR: (500 MHz, $CDCl_3$)

7.38-7.24 (2H, m), 7.09-7.05 (2H, m) 4.70 (2H, s)

^{13}C NMR: (125 MHz, $CDCl_3$)

162.3 (d, *J* = 243 Hz), 136.6, 128.7, 115.3, 64.68

^{19}F NMR: (470 MHz, $CDCl_3$)

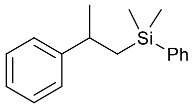
-114.9

MS: (EI^+)

126.6 ($[M]^+$)

HRMS: Found: 126.04758, (C_6H_7OF) $[M]^+$ requires: 126.04754

2-Phenylpropylphenyldimethylsilane (2u)



According to General Procedure B, $Co(BF_4)_2 \cdot 6H_2O$ (10 mg, 0.03 mmol, 0.03 equiv.) and 1-cyanoadamantane (15.0 mg, 0.09 mmol, 0.09 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. α-Methylstyrene (130 µL, 1.00 mmol, 1.00 equiv.) and phenyldimethylsilane (199 µL, 1.30 mmol, 1.30 equiv.) were added. The mixture was stirred for 3 hours at 80 °C, and then diluted with Et_2O and concentrated *in vacuo*. The crude reaction product was purified by flash column chromatography (petroleum ether, Et_2O, 99:1) to give the silane **2u** (61.0 mg, 0.24 mmol, 24%, >99:1 L:B) as a colourless oil.

^{1}H NMR: (400 MHz, $CDCl_3$)

7.51 – 7.48 (2H, m), 7.39 – 7.35 (3H, m), 7.30 – 7.26 (2H, m), 7.21 – 7.18 (3H, m), 2.94 – 2.85 (1H, m), 1.28 – 1.27 (3H, d, J = 14.6 Hz), 1.29 – 1.16 (2H, m), 0.19 (3H, s), 0.13 (3H, s)

^{13}C NMR: (126 MHz, $CDCl_3$)

149.6, 139.7, 133.5, 128.8, 128.3, 127.6, 126.6, 125.8, 36.4, 26.4, 26.1, -2.2, -2.8

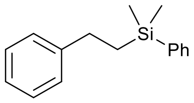
^{29}Si NMR: (79 MHz, $CDCl_3$)

-3.89

TLC: R_f = 0.8 (pentane, diethyl ether 90:10) [UV]

Data were in accordance with those previously reported.[12]

Dimethylphenyl(2-phenylethyl)silane (2v)



According to General Procedure A, $Fe(BF_4)_2·6H_2O$ (10 mg, 0.03 mmol, 0.03 equiv.) and 1-cyanoadamantane (10.0 mg, 0.06 mmol, 0.06 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. Styrene (115 μL, 1.00 mmol, 1.00 equiv.) and phenyldimethylsilane (199 μL, 1.30 mmol, 1.30 equiv.) were added. The mixture was stirred for 3 hours at 80 °C, and then diluted with Et_2O and concentrated *in vacuo*. The crude reaction product was purified through a silica plug using pentane as the eluent to give the silane **2v** (228 mg, 0.95 mmol, 95%, >99:1 L:B) as a colourless oil.

^{1}H NMR: (400 MHz, $CDCl_3$)
7.57 – 7.54 (2H, m), 7.40 – 7.37 (3H, m), 7.30 – 7.26 (2H, m), 7.21 – 7.17 (3H, m), 2.69 – 2.64 (2H, m), 1.17 – 1.13 (2H, m), 0.31 (6H, s)

^{13}C NMR: (126 MHz, $CDCl_3$)
145.0, 139.7, 133.5, 128.9, 128.2, 127.1, 125.6, 29.4, 17.3, -3.23

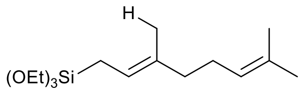
^{29}Si NMR: (79 MHz, $CDCl_3$)
-2.80

TLC: R_f = 0.8 (pentane, diethyl ether 90:10) [UV]

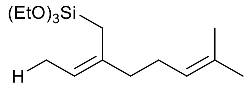
Data were in accordance with those previously reported.[13]

Iron Catalyzed 1,4-Hydrosilylation of Myrcene

(*E*)-(3,7-dimethylocta-2,6-dien-1-yl)triethoxysilane and (*E*)-(2-ethylidene-6-methylhept-5-enyl)triethoxysilane (2w)



Linear



Branched

Under an argon atmosphere, $Fe(BF_4)_2{\cdot}6H_2O$ (16.9 mg, 0.05 mmol, 0.05 equiv.) and 2,6-diisopropyl-N-(pyridin-2-ylmethylene)aniline (13.25 mg, 0.05 mmol, 0.05 equiv.) were complexed in THF (0.5 mL) by stirring for 1 minute. Myrcene (172 μL, 0.90 mmol, 1.00 equiv.) and triethoxysilane (246 μL, 0.99 mmol, 1.10 equiv.) were added and the reaction was stirred for 16 hours at room temperature. The mixture was diluted with Et_2O and water was added. The layers were separated and Et_2O was concentrated *in vacuo*. The isolated products were purified by vacuum distillation (50 °C, 0.15 mbar) to give a mixture of two regioisomers (*E*)-(3,7-dimethylocta-2,6-dien-1-yl)triethoxysilane and (*E*)-(2-ethylidene-6-methylhept-5-enyl)triethoxysilane **2w**, (156 mg, 0.52 mmol, 52%, 39:61 L:B)

Linear Regioisomer:

^{1}H NMR: (600 MHz, C_6D_6)

5.49-5.44 (1H, m), 5.25 – 5.21 (1H, m), 3.85 – 3.79 (6H, m), 2.21 – 2.10 (4H, m), 1.73 – 1.69 (2H, m), 1.68 – 1.65 (6H, m), 1.55 (3H, s), 1.27 – 1.13 (9H, m)

Branched Regioisomer:

^{1}H NMR: (600 MHz, C_6D_6)

5.36-5.29 (2H, m), 3.97 – 3.89 (2H, m), 3.85 – 3.79 (4H, m), 2.35 – 2.28 (4H, m), 1.73 – 1.69 (2H, m), 1.68 – 1.65 (6H, m), 1.59 (3H, s), 1.27 – 1.13 (9H, m)

Mixture of Regioisomers:

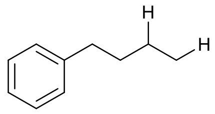
^{13}C NMR: (126 MHz, $CDCl_3$)

135.5, 133.7, 130.7, 124.9, 124.7, 117.9, 116.8, 59.0, 58.3, 40.1, 39.1, 27.0, 26.9, 25.5, 18.3, 18.2, 18.0, 17.4, 15.7, 15.3, 13.6, 12.9

Data were in accordance with those previously reported.[14]

Hydrogenation and Other Products: Experimental and Analytical Data

4-Phenylbutane (6a)



According to General Procedure F, $Co(BF_4)_2 \cdot 6H_2O$ (2.6 mg, 0.0075 mmol, 0.005 equiv.) and ^{Mes}BIP (3.0 mg, 0.0075 mmol, 0.005 equiv.) were complexed in THF (1.0 mL) by stirring for 1 minute. 4-Phenylbutene (225µL, 1.50 mmol, 1.00 equiv.) and phenylsilane (10 µL, 0.075 mmol, 0.05 equiv.) were added. The autoclave reaction vessel was then pressurised with an atmosphere of hydrogen (20 bar), and the reaction was stirred at ambient temperature for 7 hours. The mixture was diluted with Et_2O and concentrated *in vacuo* to give the crude alkane **6a** (91%). The crude reaction product was purified by flash column chromatography (12 g SiO_2, 25 mm Ø, wet loaded, pentane, ca. 5 mL fractions) to give the alkane **6a** (145 mg, 1.08 mmol, 72%) as a colourless oil.

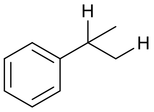
^{1}H NMR: (500 MHz, $CDCl_3$)
7.30 (2H, t, *J* = 7.0 Hz), 7.22 – 7.20 (3H, m), 2.64 (2H, t, *J* = 7.8 Hz), 1.67 – 1.61 (2H, m), 1.4 (2H, sext., *J* = 7.5 Hz), 0.96 (3H, t, *J* = 7.3 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)
142.9, 128.4, 128.2, 125.6, 35.7, 33.7, 22.4, 14.0

TLC: $R_f = 0.7$ (pentane) [UV]

Data were in accordance with those previously reported.[15]

Cumene (6b)



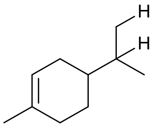
According to General Procedure F, $Co(BF_4)_2 \cdot 6H_2O$ (2.6 mg, 0.0075 mmol, 0.005 equiv.) and ^{Mes}BIP (3.0 mg, 0.0075 mmol, 0.005 equiv.) were complexed in THF (1.0 mL) by stirring for 1 minute. α-Methylstyrene (195μL, 1.50 mmol, 1.00 equiv.) and phenylsilane (10 μL, 0.075 mmol, 0.05 equiv.) were added. The autoclave reaction vessel was then pressurised with an atmosphere of hydrogen (20 bar), and the reaction was stirred at ambient temperature for 16 hours. The mixture was diluted with Et_2O and passed through a silica plug (10 g SiO_2, Et_2O) to give the alkane **6b** (157 mg, 1.3 mmol, 87%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.35 – 7.32 (2H, m), 7.28 – 7.27 (2H, m), 7.23 – 7.21 (1H, m),2.98 – 2.92 (1H, m), 1.31 – 1.28 (6H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
148.9, 128.3, 126.4, 125.8, 34.1, 24.0

Data were in accordance with those previously reported.[16]

4-*iso*Propyl-1-methylcyclohexene (6c)



According to General Procedure F, $Co(BF_4)_2{\cdot}6H_2O$ (10.2mg, 0.03 mmol, 0.01 equiv.) and ^{Mes}BIP (6.0 mg, 0.03 mmol, 0.01 equiv.) were complexed in THF (1.0 mL) by stirring for 1 minute. (*R*)-(+)-Limonene (243 μL, 1.50 mmol, 1.00 equiv.) and phenylsilane (10 μL, 0.075 mmol, 0.05 equiv.) were added. The autoclave reaction vessel was then pressurised with an atmosphere of hydrogen (20 bar), and the reaction was stirred at ambient temperature for 16 hours. The mixture was diluted with Et_2O and passed through a silica plug (10 g SiO_2, Et_2O) to give the alkane **6c** (124 mg, 0.9 mmol, 60%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$)

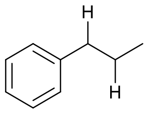
5.41 – 5.40 (1H, m), 2.04 – 1.92 (3H, m), 1.79 – 1.73 (2H, m), 1.66 (3H, s), 1.52 – 1.45 (1H, m), 1.29 – 1.19 (2H, m), 0.91 (6H, t, *J* = 6.9 Hz)

^{13}C NMR: (126 MHz, $CDCl_3$)

133.9, 121.0, 40.0, 32.3, 30.8, 29.0, 26.5, 23.5, 20.0, 19.7

Data were in accordance with those previously reported.[17]

Propylbenzene (6d)



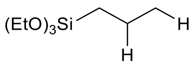
According to General Procedure F, $Co(BF_4)_2 \cdot 6H_2O$ (2.6 mg, 0.0075 mmol, 0.005 equiv.) and ^{Mes}BIP (3.0 mg, 0.0075 mmol, 0.005 equiv.) were complexed in THF (1.0 mL) by stirring for 1 minute. β-Methylstyrene (195 μL, 1.50 mmol, 1.00 equiv.) and phenylsilane (10 μL, 0.075 mmol, 0.05 equiv.) were added. The autoclave reaction vessel was then pressurised with an atmosphere of hydrogen (20 bar), and the reaction was stirred at ambient temperature for 16 hours. The mixture was diluted with Et_2O and passed through a silica plug (10 g SiO_2, Et_2O) to give the alkane **6d** (130 mg, 1.1 mmol, 72%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$)
7.36 – 7.35 (2H, m), 7.26 – 7.25 (3H, m), 2.68 – 2.65 (2H, m), 1.75 – 1.70 (2H, m), 1.04 – 1.00 (3H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)
142.7, 128.5, 128.3, 125.6, 38.1, 24.6, 13.9

Data were in accordance with those previously reported.[18]

Propyltriethoxysilane (6e)



According to General Procedure F, $Co(BF_4)_2 \cdot 6H_2O$ (5.2mg, 0.03 mmol, 0.01 equiv.) and ^{Mes}BIP (6.0 mg, 0.03 mmol, 0.01 equiv.) were complexed in THF (1.0 mL) by stirring for 1 minute. Allyltriethoxysilane (340 μL, 1.50 mmol, 1.00 equiv.) and phenylsilane (10 μL, 0.075 mmol, 0.05 equiv.) were added. The autoclave reaction vessel was then pressurised with an atmosphere of hydrogen (20 bar), and the reaction was stirred at ambient temperature for 16 hours. The mixture was diluted with Et_2O and passed through a silica plug (10 g SiO_2, Et_2O) to give the alkane **6e** (265 mg, 1.3 mmol, 85%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$)

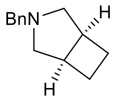
3.84 (6H, q, *J* = 6.9 Hz), 1.50 – 1.46 (2H, m), 1.25 (9H, t, *J* = 6.9 Hz), 1.00 (3H, t, *J* = 14.5 Hz), 0.67 – 0.64 (2H, m)

^{13}C NMR: (126 MHz, $CDCl_3$)

58.3, 18.3, 17.8, 16.4, 12.9

Data were in accordance with those previously reported.[19]

***N*-Benzyl-3-azabicyclo[0.2.3]heptane (8a)**



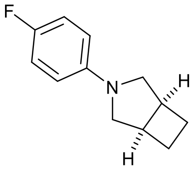
Under an atmosphere of argon, preformed 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine cobalt(II) tetrafluoroborate (38.2 mg, 0.05 mmol, 0.1 equiv.) was added to an 8 mL glass vial, equipped with a stirrer bar. Diallylbenzylamine (102.14 µL, 0.5 mmol, 1.00 equiv.) and phenylsilane (12.3 µL, 0.1 mmol, 0.2 equiv.) were added and the reaction heated at 80 °C for 24 hours. Et_2O (2 mL) was subsequently added, and the reaction mixture was washed with distilled water to separate the catalyst from the crude reaction mixture. 1,3,5-Trimethoxybenzene (16.8 mg, 0.1 mmol, 0.20 equiv.) was added for use as a ^{1}H NMR ($CDCl_3$) internal standard to determine the reaction yield.

^{1}H NMR: (500 MHz, C_6D_6)
7.46-7.41 (2H, m) 7.25-7.18 (2H, m), 7.14-7.09 (1H, m), 3.56 (2H, s), 2.73 (2H, d, *J* = 9.5 Hz), 2.60-2.50 (2H, m), 2.07-1.98 (2H, m), 1.95-1.89 (2H, m), 1.88-1.81 (2H, m).

TLC: R_f = 0.35 (pentane/diethylether 1:1) [KMnO4]

Data were in accordance with those previously reported.[20]

N-4-fluorophenyl-3-azabicyclo[0.2.3]heptane (8b)



Under an atmosphere of argon, preformed 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine cobalt(II) tetrafluoroborate (38.2 mg, 0.05 mmol, 0.1 equiv.) was added to an 8 mL glass vial, equipped with a stirrer bar. *N,N*-Diallyl-4-fluoroaniline (95 µL, 0.5 mmol, 1.00 equiv.) and phenylsilane (12.3 µL, 0.1 mmol, 0.2 equiv.) were added and the reaction was heated at 80 °C for 24 hours. Et_2O (2 mL) was subsequently added, and the reaction mixture was washed with distilled water to separate the catalyst from the crude reaction mixture. 1,3,5-Trimethoxybenzene (16.8 mg, 0.1 mmol, 0.20 equiv.) was added for use as a ^{1}H NMR ($CDCl_3$) internal standard to determine the reaction yield. The crude reaction mixture was purified by flash column chromatography using pentane and Et_2O (99:1) to give the *N*-4-fluorophenyl-3-azabicyclo[0.2.3]heptane **8b** (78 mg, 82% isolated yield) as a yellow liquid.

^{1}H NMR: (600 MHz, $CDCl_3$)
6.99-6.96 (2H, m) 6.70-6.67 (2H, m), 3.47 (2H, d, J = 9.5 Hz), 3.07-3.03 (2H, m), 3.01-2.97 (2H, m), 2.31-2.26(2H, m), 1.84-1.80 (2H, m).

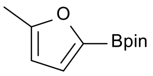
^{13}C NMR: (126 MHz, $CDCl_3$)
115.53, 115.28, 114.53, 114.43, 56.65, 37.52, 24.96

^{19}F NMR: (377 MHz, $CDCl_3$)
-128.87

TLC: R_f = 0.8 (pentane/Et_2O 90:10) [UV]

Data were in accordance with those previously reported.[20]

4,4,5,5-Tetramethyl-2-(5-methylfuran-2-yl)-1,3,2-dioxaborolane (10)



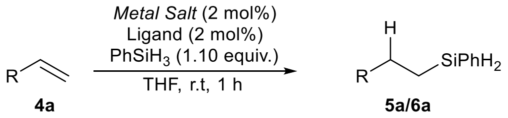
Under an atmosphere of argon, cobalt catalyst (11.1 mg, 0.019 mmol, 0.02 equiv) was added to an 8 mL glass vial, equipped with a magnetic stirrer bar. 2-Methylfuran (514.3 μL, 5.7 mmol, 15 equiv.) was then added, followed by bispinacolatodiboron (86.15 mg, 0.38 mmol, 1 equiv.) and lithium methoxide (14.4 mg, 0.38 mmol, 1 equiv.) and phenylsilane (10 μL, 0.08 mmol, 0.21 equiv.) were added and the reaction heated at 80 °C for 24 hours. Et_2O (2 mL) was subsequently added, and the crude reaction mixture washed with distilled water to separate the catalyst from the crude reaction mixture. 1,3,5-Trimethoxybenzene (12.8 mg, 0.076 mmol, 0.10 equiv.) was added for use as a ^1H NMR ($CDCl_3$) internal standard to determine the reaction yield.

^{1}H NMR: (500 MHz, $CHCl_3$)
7.01 (1H, d, J = 3.7 Hz), 6.11 (1H), 2.38 (3H, s), 1.34 (12H, s)

Data were in accordance with those previously reported.[21]

Supporting Schemes and Tables

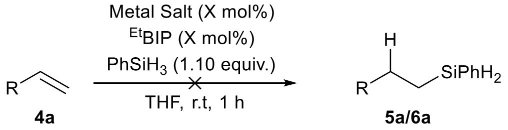
Table SI 1.1: Control Reactions for Hydrosilylation



Entry	**Conditions**	**Result (% Yield)**
1	$AgBF_4 + {}^{Et}BIP$	n.r
2	$TBABF_4 + {}^{Et}BIP$	n.r
3	$Co(BF_4)_2{\cdot}6H_2O + {}^{Et}BIP$	>95% (8:92 B:L)
4	$Cu(BF_4){\cdot}xH_2O + {}^{Et}BIP$	n.r
5	$Fe(BF_4)_2{\cdot}6H_2O$	n.r
6	$Co(BF_4)_2{\cdot}6H_2O$	n.r
7	^{Et}BIP	n.r

Conditions: 1-Octene (1.00 equiv.) with phenylsilane (1.10 equiv.), stirred in THF at ambient temperature, 1 h.

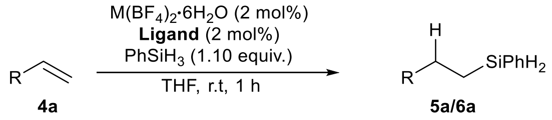
Table SI 1.2: Optimisation for Hydrosilylation



Entry	**Metal Salt**	**Catalytic Loading**	**Result (% Yield)**
1	$Fe(BF_4)_2{\cdot}6H_2O$	0.5	67
2	$Fe(BF_4)_2{\cdot}6H_2O$	1	82
3	$\mathbf{Fe(BF_4)_2{\cdot}6H_2O}$	**2**	**87 (93:7 L:B)**
4	$Fe(BF_4)_2{\cdot}6H_2O$	3	68
5	$Fe(BF_4)_2{\cdot}6H_2O$	4	75
6	$[{}^{Et}BIPFe(BF_4)_2]$[a]	2	77
7	$\mathbf{Co(BF_4)_2{\cdot}6H_2O}$	**1**	**90 (8:92 L:B)**
8	$Co(BF_4)_2{\cdot}6H_2O$	2	82 (95:5 L:B)

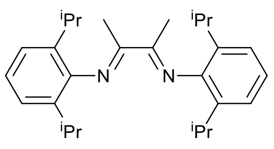
Conditions: 1-Octene (1.00 equiv.) with phenylsilane (1.10 equiv.), stirred at ambient temperature; a) Pre-complexed catalyst had been exposed to air for 2 hours prior to use.

Table SI 1.3: Ligand Screen for Hydrosilylation

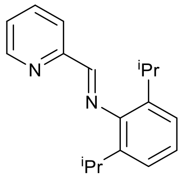


Entry	Metal Salt	Ligand	Result (% Yield)
1	$Fe(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{H}}$BIP	n.r
2	$Co(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{H}}$BIP	84 (86:14 L:B)[a]
3	$Fe(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{Mes}}$BIP	78[b]
4	$Co(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{Mes}}$BIP	68 (3:97 L:B)
5	$Fe(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{Me}}$BIP	trace
6	$Co(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{Me}}$BIP	72 (4:96 L:B)
7	$Fe(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{iPr}}$BIP	trace
8	$Co(BF_4)_2 \cdot 6H_2O$	$^{\mathrm{iPr}}$BIP	31 (16:84 L:B)
9	$Fe(BF_4)_2 \cdot 6H_2O$	**A**	n.r
10	$Co(BF_4)_2 \cdot 6H_2O$	**A**	n.r
11	$Fe(BF_4)_2 \cdot 6H_2O$	**B**	n.r
12	$Co(BF_4)_2 \cdot 6H_2O$	**B**	n.r
13	$Fe(BF_4)_2 \cdot 6H_2O$	**C**	n.r
14	$Co(BF_4)_2 \cdot 6H_2O$	**C**	n.r
15	$Fe(BF_4)_2 \cdot 6H_2O$	TMEDA	n.r
16	$Co(BF_4)_2 \cdot 6H_2O$	TMEDA	n.r
17	$Co(BF_4)_2 \cdot 6H_2O$	Xantphos	82 (>99:1 L:B)
18	$Co(BF_4)_2 \cdot 6H_2O$	dppf	73 (>99:1 L:B)
19	$Co(BF_4)_2 \cdot 6H_2O$	1-adamantyl isocyanide	24%[b,c]
20	$Fe(BF_4)_2 \cdot 6H_2O$	1-adamantyl isocyanide	98%[b,d]

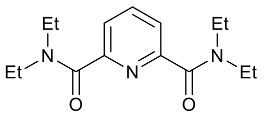
Conditions: 1-Octene (1.00 equiv.) with phenylsilane (1.10 equiv.), stirred at ambient temperature for 1 h; a) Opposite regioselectivity obtained with $^{\mathrm{H}}$BIP *vs.* $^{\mathrm{Et}}$BIP; b) Selective for the linear product; c) α-methylstyrene (1.00 equiv.) with phenyldimethylsilane (1.10 equiv.), 3 mol% $M(BF_4)_2 \cdot 6H_2O$, 6 mol% ligand; d) styrene (1.00 equiv.) with phenyldimethylsilane (1.10 equiv.), 3 mol% $M(BF_4)_2 \cdot 6H_2O$, 6 mol% ligand. TMEDA = *N,N,N',N'*-Tetramethylethylenediamine, Xantphos = 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene, dppf = 1,1'-Ferrocenediyl-bis(diphenylphosphine)



A

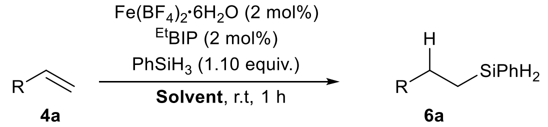


B



C

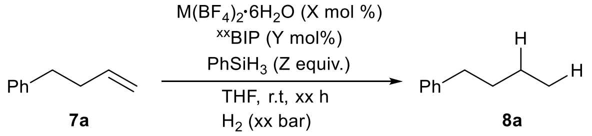
Table SI 1.4: Solvent Screening (Hydrosilylation)



Entry	Solvent	Result (% Yield)
1	CH_2Cl_2	n.r
2	CH_2Cl_2[a]	2.5
3	CH_2Cl_2 + THF[b]	n.r
4	Hexanes	n.r
5	Hexanes[a]	n.r
6	Acetone	n.r
7	Toluene[a]	n.r
8	THF	87 (93:7 L:B)
9	THF[c]	75% (83:17 L:B)
10	DME	76 (84:16 L:B)
11	Anisole	n.r
12	MTBE	n.r
13	EtOAc	n.r
14	NEt_3	n.r
15	Acetic Acid	n.r
16	2-Methyltetrahydrofuran	75 (83:17 L:B)
17	MeOH	n.r
18	Dioxane	24[d]
19	Et_2O	n.r
20	MeCN	n.r

Conditions: 1-Octene (1.00 equiv.) with phenylsilane (1.10 equiv.), stirred for 1 hour at ambient temperature; a) Pre-complexed catalyst was used; b) 1.00 equiv. of THF added to the reaction; c) Solvent used straight from Winchester bottle; d) Selective for linear product.

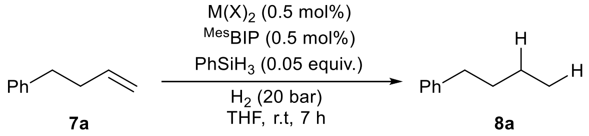
Table SI 1.5: Optimisation for Hydrogenation



Entry	Metal Salt (X equiv.)	Ligand (Y equiv.)	$PhSiH_3$ (Z equiv.)	Time (h)	H_2 (bar)	Result (% Yield)
1	$Fe(BF_4)_2\cdot 6H_2O$ (0.02)	^{Et}BIP (0.02)	-	18 h	5	n.r
2	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Et}BIP (0.02)	-	18 h	5	n.r
3	$Fe(BF_4)_2\cdot 6H_2O$ (0.02)	^{Et}BIP (0.02)	(0.05)	18 h	5	22
4	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Et}BIP (0.02)	(0.05)	18 h	5	53
5	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Et}BIP (0.02)	(0.05)	48 h	5	>95
6	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Mes}BIP (0.02)	(0.05)	18 h	20	91
7	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Mes}BIP (0.02)	(0.05)	18 h	15	22
8	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Mes}BIP (0.02)	(0.05)	18 h	10	38
9	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Et}BIP (0.02)	(0.05)	18 h	10	36
10	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Mes}BIP (0.02)	(0.05)	7 h	20	90
11	**$Co(BF_4)_2\cdot 6H_2O$ (0.005)**	**^{Mes}BIP (0.005)**	**(0.05)**	**7h**	**20**	**>95 (72)**
12	$Fe(BF_4)_2\cdot 6H_2O$ (0.02)	^{Mes}BIP (0.02)	(0.05)	5 h	20	23
13	$Co(BF_4)_2\cdot 6H_2O$ (0.02)	^{Mes}BIP (0.02)	(0.05)	5 h	20	78

Conditions:4-Phenylbutene (1.00 equiv.) stirred under an atmosphere of H_2, ambient temperature.

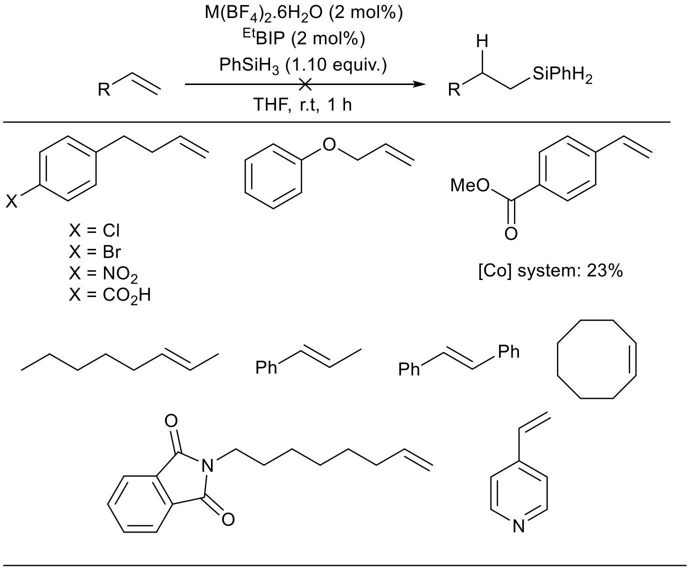
Table SI 1.6: Control Reactions for Hydrogenation



Entry	Metal Salt	Ligand	PhSiH3 (Y/N)	Result (% Yield)
1	$Co(BF_4)_2{\cdot}6H_2O$	-	Y	n.r
2	$CoCl_2$	^{Mes}BIP	Y	n.r
3	$Co(OAc)_2$	^{Mes}BIP	Y	38%
4	$Co(acac)_2$	^{Mes}BIP	Y	33%
6	$Co(BF_4)_2{\cdot}6H_2O$	-	N	n.r
7	-	^{Mes}BIP	Y	n.r
8	$Co(BF_4)_2{\cdot}6H_2O$	^{Mes}BIP	-	n.r
	$Co(BF_4)_2{\cdot}6H_2O$	-	-	n.r
9	-	^{Mes}BIP	-	n.r
10	-	-	Y	n.r

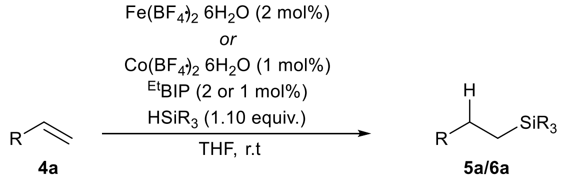
Conditions: 4-Phenylbutene (1.00 equiv.) stirred under an atmosphere of H_2, ambient temperature;

Table SI 1.7: Unreactive Substrates Towards Hydrosilylation



Conditions: Olefin (1.00 equiv.), phenylsilane (1.10 equiv.) stirred under an atmosphere of argon, ambient temperature.

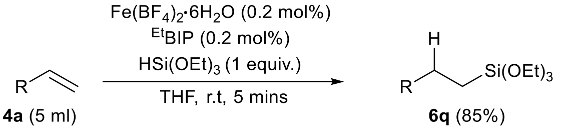
Table SI 1.8: Other Silanes Investigated



Entry	Metal Salt	Silane	'Activator' (1 drop)	Time (h)	Result (% Yield)
1	$Fe(BF_4)_2{\cdot}6H_2O$	Ph_2SiH_2	none	2	n.r
2	$Fe(BF_4)_2{\cdot}6H_2O$	Ph_2SiH_2	$PhSiH_3$	2	n.r
3	$Co(BF_4)_2{\cdot}6H_2O$	Ph_2SiH_2	none	2	53 (53:47 L:B)[a]
4	$Fe(BF_4)_2{\cdot}6H_2O$	Me_2PhSiH	none	1	n.r
5	$Co(BF_4)_2{\cdot}6H_2O$	Me_2PhSiH	none	1	n.r
6	$Fe(BF_4)_2{\cdot}6H_2O$	Me_2PhSiH	$PhSiH_3$	1	n.r
7	$Fe(BF_4)_2{\cdot}6H_2O$	Me_2PhSiH	HBPin	1	n.r
8	$Fe(BF_4)_2{\cdot}6H_2O$	$(EtO)_2MeSiH$	none	3	55 (80:20 L:B)[a]
9	$Fe(BF_4)_2{\cdot}6H_2O$	Hexylsilane	none	1	(96) (78:22 L:B)
10	$Co(BF_4)_2{\cdot}6H_2O$	Hexylsilane	none	1	(88) (2:98 L:B)
11	$Fe(BF_4)_2{\cdot}6H_2O$	$MePhSiH_2$	none	2	n.r
12	$Co(BF_4)_2{\cdot}6H_2O$	$MePhSiH_2$	none	2	(50) (11:89 L:B)
13	$Fe(BF_4)_2{\cdot}6H_2O$	$MePhSiH_2$	$PhSiH_3$	2	(72) (99:1 L:B)
14	$Co(BF_4)_2{\cdot}6H_2O$	$(EtO)_3SiH$[b]	none	3	<15
15	$Fe(BF_4)_2{\cdot}6H_2O$	$(Me_3SiO)_2SiMeH$[b]	none	3	n.r
16	$Co(BF_4)_2{\cdot}6H_2O$	$(Me_3SiO)_2SiMeH$[b]	none	3	n.r
17	$Fe(BF_4)_2{\cdot}6H_2O$	$(Me_3SiO)_2SiMeH$[b]	$PhSiH_3$	3	n.r
18	$Co(BF_4)_2{\cdot}6H_2O$	$(Me_3SiO)_2SiMeH$[b]	$PhSiH_3$	3	n.r
19	$Fe(BF_4)_2{\cdot}6H_2O$	$(Me_3SiO)_2SiMeH$[b]	HBPin	3	n.r
20	$Co(BF_4)_2{\cdot}6H_2O$	$(Me_3SiO)_2SiMeH$[b]	HBPin	3	n.r

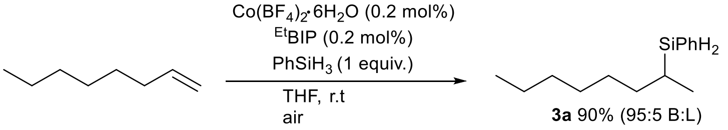
Conditions: 1-Octene (1.00 equiv.), silane, stirred in THF, ambient temperature, [Fe] system 0.02 equiv., [Co] system 0.01 equiv.; a) Product(s) not isolated, unknown isomerisation product also detected; b) 1.00 equivalents of silane added.

Scheme SI 1.9: Large Scale Hydrosilylation using Triethoxysilane



Conditions: 1-Octene (1.00 equiv.) with triethoxysilane (1.00 equiv.), stirred for 5 mins at ambient temperature.

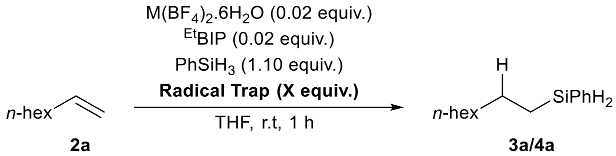
Scheme SI 1.10: Hydrosilylation in air



Conditions: 1-Octene (1.00 equiv.) with $PhSiH_3$ (1.00 equiv.), stirred for 4h at ambient temperature in air

Mechanistic Investigations

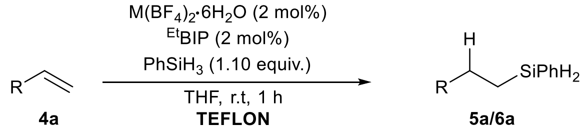
Table SI 1.10 Radical Trap Addition



Entry	Metal Salt	Radical Trap (X equiv.)	Result (% Yield)
1	$Fe(BF_4)_2 \cdot 6H_2O$	TEMPO (0.01)	65 (89:11 L:B)
2	$Co(BF_4)_2 \cdot 6H_2O$[a]	TEMPO (0.01)	66 (8:92 L:B)
3	$Fe(BF_4)_2 \cdot 6H_2O$	TEMPO (0.02)	72 (92:8 L:B)
4	$Co(BF_4)_2 \cdot 6H_2O$	TEMPO (0.02)	68 (6:94 L:B)
5	$Fe(BF_4)_2 \cdot 6H_2O$	TEMPO (0.25)	n.r
6	$Co(BF_4)_2 \cdot 6H_2O$	TEMPO (0.25)	12[b]
7	$Fe(BF_4)_2 \cdot 6H_2O$	TEMPO (1.00)	n.r
8	$Co(BF_4)_2 \cdot 6H_2O$	TEMPO (1.00)	n.r
9	$Fe(BF_4)_2 \cdot 6H_2O$	Galvinoxyl (0.01)	79 (91:9 L:B)
10	$Co(BF_4)_2 \cdot 6H_2O$	Galvinoxyl (0.01)	70 (9:91 L:B)
11	$Fe(BF_4)_2 \cdot 6H_2O$	Galvinoxyl (0.02)	72 (90:10 L:B)
12	$Co(BF_4)_2 \cdot 6H_2O$	Galvinoxyl (0.02)	35 (14:86 L:B)
13	$Fe(BF_4)_2 \cdot 6H_2O$	Galvinoxyl (0.25)	n.r
14	$Fe(BF_4)_2 \cdot 6H_2O$	9,10-Dihydroanthracene (0.01)	78 (95:5 L:B)
15	$Co(BF_4)_2 \cdot 6H_2O$	9,10-Dihydroanthracene (0.01)	85 (5:95 L:B)
16	$Fe(BF_4)_2 \cdot 6H_2O$	9,10-Dihydroanthracene (0.02)	86 (94:6 L:B)
17	$Co(BF_4)_2 \cdot 6H_2O$	9,10-Dihydroanthracene (0.02)	69 (3:97 L:B)
18	$Fe(BF_4)_2 \cdot 6H_2O$	9,10-Dihydroanthracene (0.25)	88 (93:7 L:B)
19	$Co(BF_4)_2 \cdot 6H_2O$	9,10-Dihydroanthracene (0.25)	89 (6:94 L:B)

Conditions: 1-Octene (1.00 equiv.) and phenylsilane (1.20 equiv.) stirred in THF, 1 h, with addition of radical trap; a) [Co] system (0.01 equiv.);b) Selective for branched product.

Table SI 1.12 Teflon™ Reaction Vessel



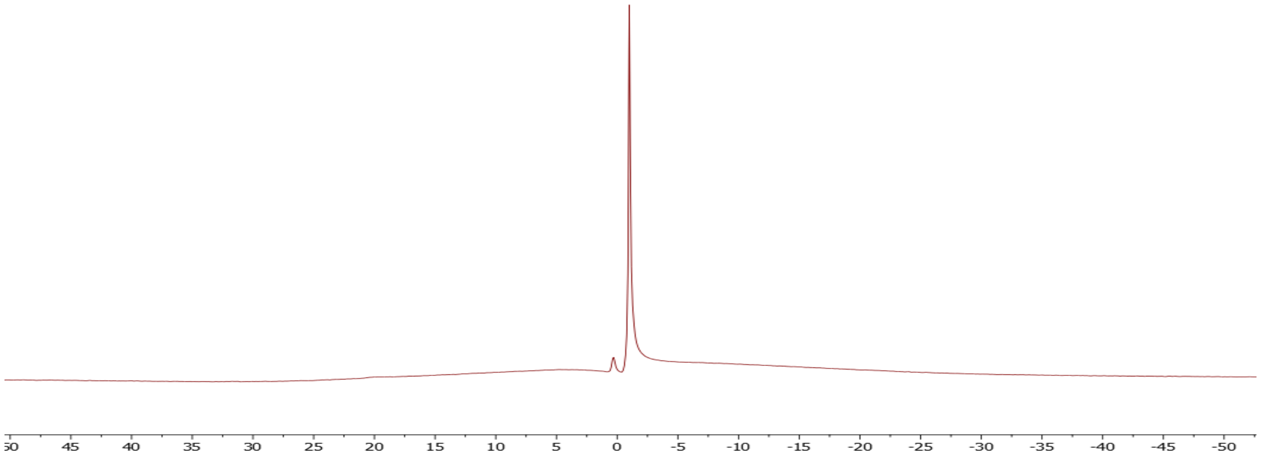
Entry	Metal Salt	Result (% Yield X)
1	$Fe(BF_4)_2 \cdot 6H_2O$	85[a]
2	$Co(BF_4)_2 \cdot 6H_2O$[b]	89 (93:7 B:L)

Conditions: 1-Octene (1.00 equiv.) and phenylsilane (1.20 equiv.) stirred in THF, 1 h, in a Teflon™ reaction vessel; a) Selective for linear product; b) [Co] system (0.01 equiv.).

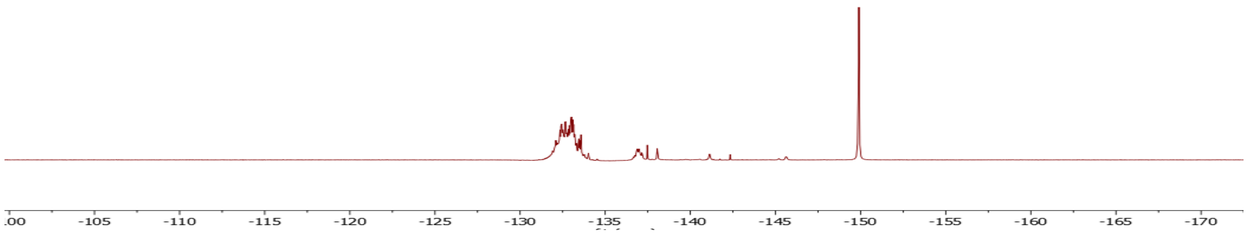
$$\begin{array}{c} \mathrm{Fe(BF_4)_2{\bullet}6H_2O\ (1\ equiv.)} \\ + \\ \mathrm{{}^{Et}BIP\ (1\ equiv.)} \end{array} + \mathrm{PhSiH_3\ (4\ equiv.)} \xrightarrow[\text{THF, r.t., 4 h}]{} \begin{array}{c} \text{Active catalyst} + \mathrm{BF_3} + \mathrm{H_2} \\ + \text{"Si-F" (several species)} \end{array}$$

Phenylsilane was added to a mixture of $Fe(BF_4)_2$•$6H_2O$ (20 mg, 0.06 mmol) and ^{Et}BIP (25.5 mg, 0.06) in d^8-THF (0.6 mL) in a J-Young's NMR tube. The tube was shaken and left for 4 h before addition of water to destroy reactive species (0.05 mL) and the below NMR spectra recorded. *n.b pressure build up within tube*

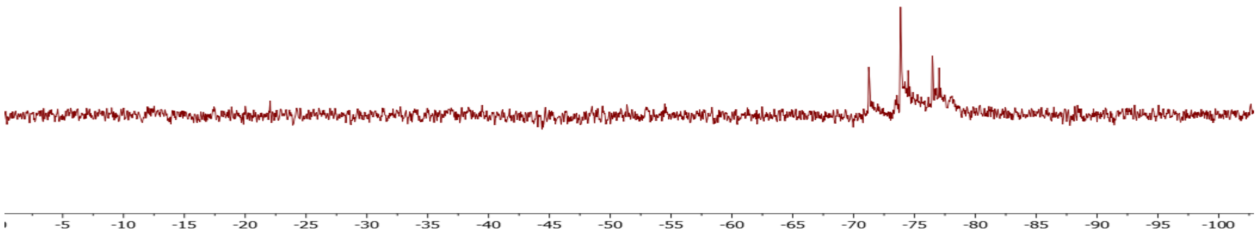
^{11}B NMR (160 MHz, d^8-THF)



^{19}F NMR (470 MHz, d^8-THF)



^{29}Si NMR (99 MHz, d^8-THF)



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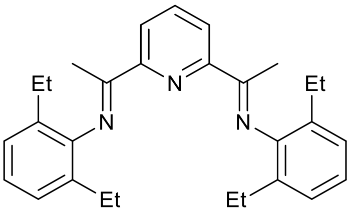
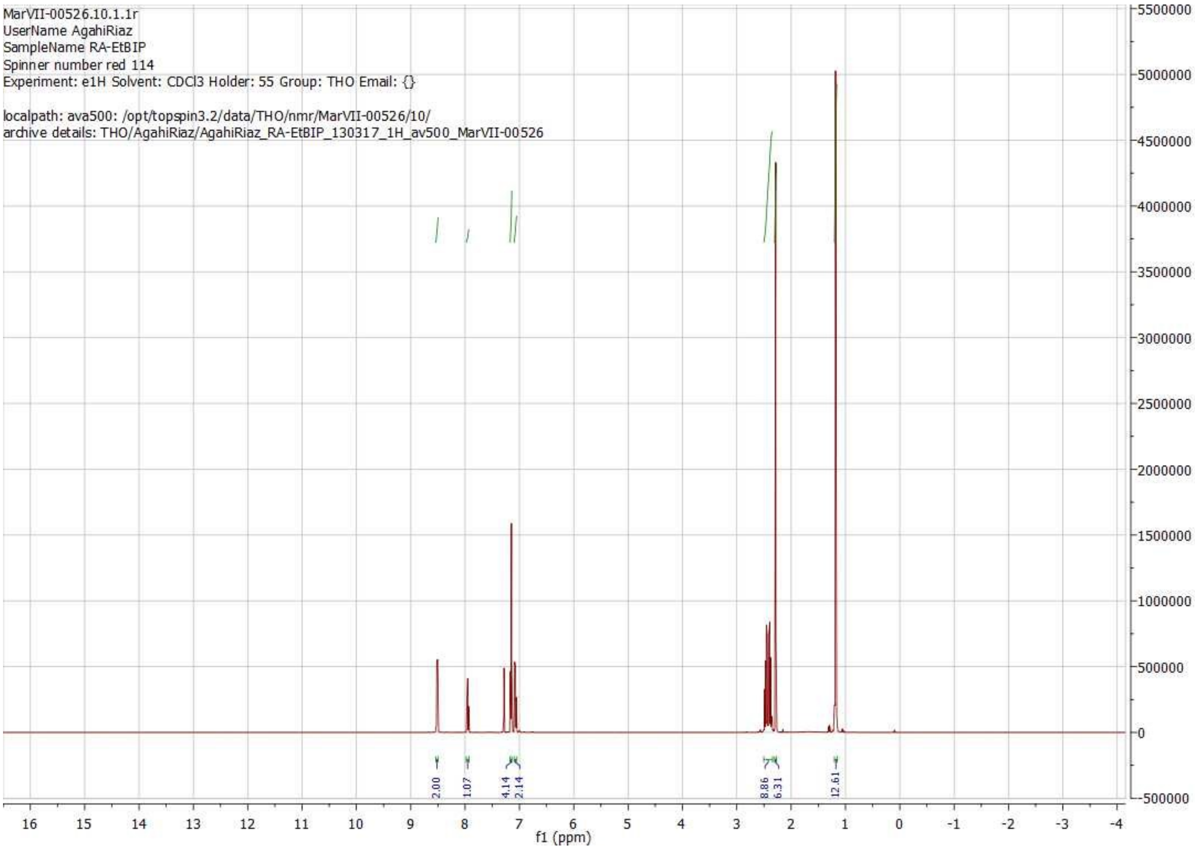
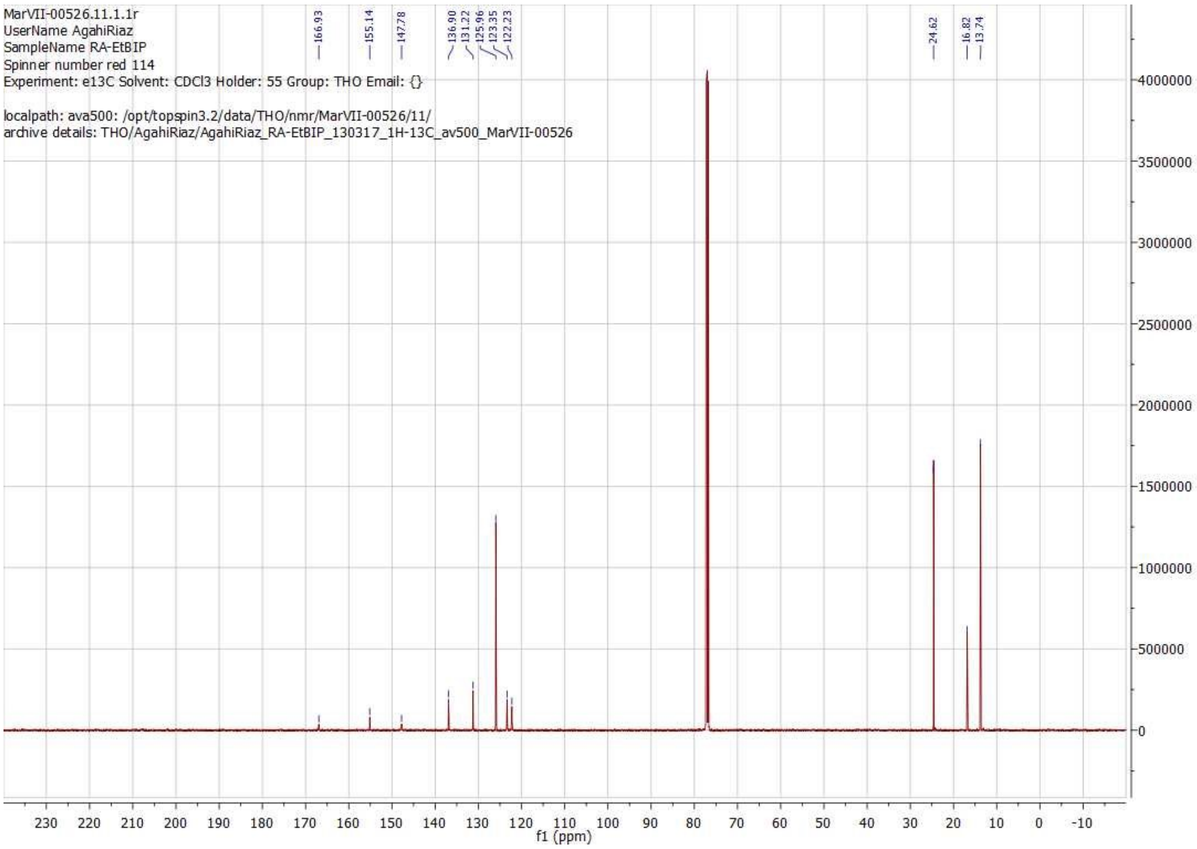
^{1}H and ^{13}C NMR Spectra for novel compounds are provided on the following pages

Ligand and Pre-Catalyst Preparation

2,6-Bis-[1-(2,6- diethylphenylimino)ethyl]pyridine (^{Et}BIP)







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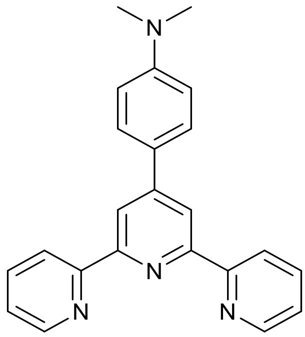
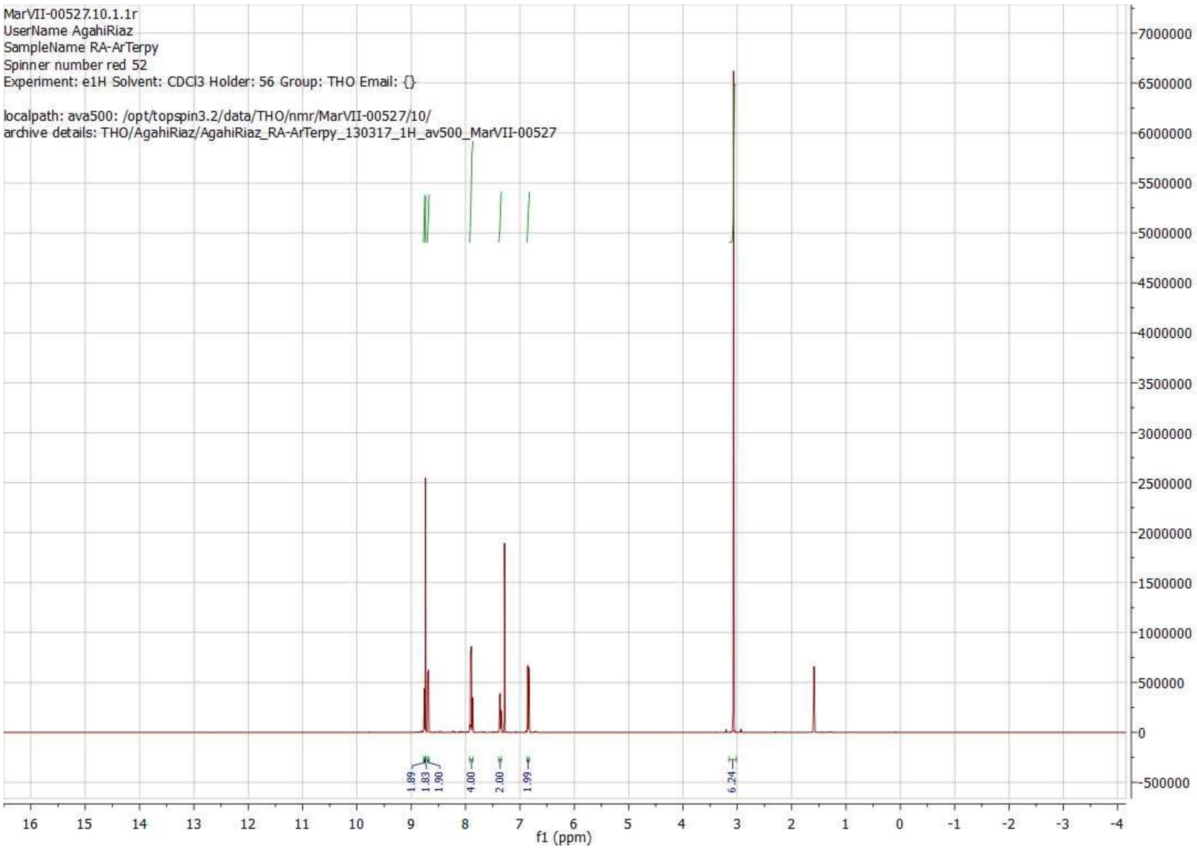
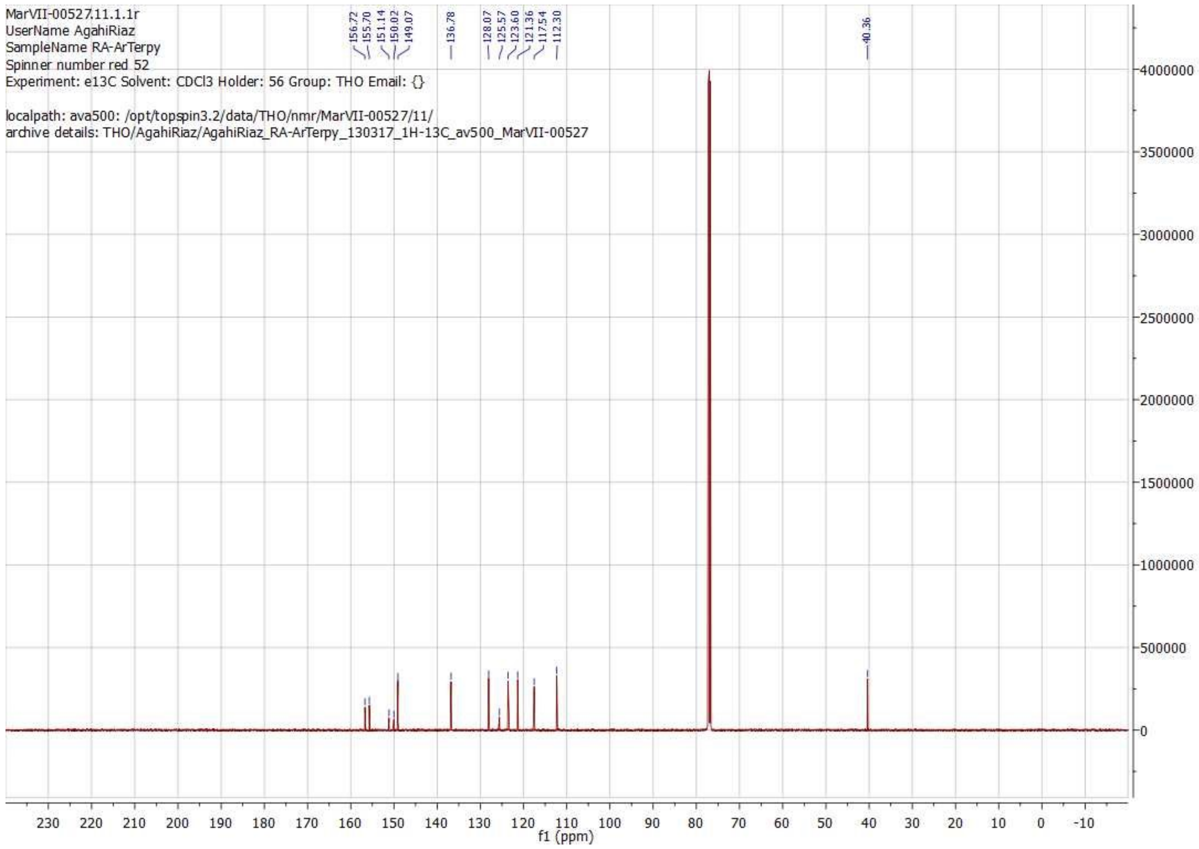
2,6-Bispyridyl-4-(4-dimethylaminophenyl)pyridine (4-NMe$_2$-Ph-Terpy)



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149.07
136.78
128.07
125.57
123.60
121.36
117.54
112.30
40.36
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3000000
2500000
2000000
1500000
1000000
500000
0
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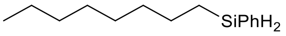
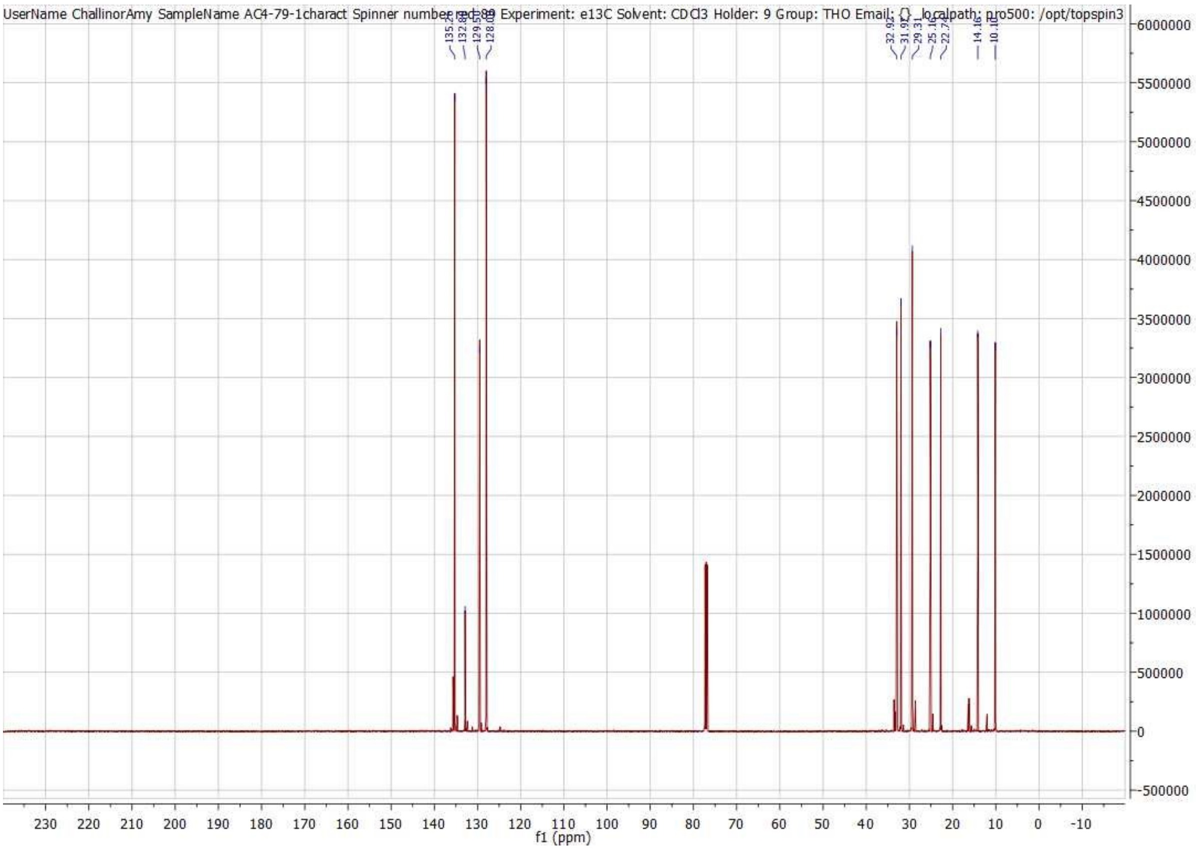
f1 (ppm)

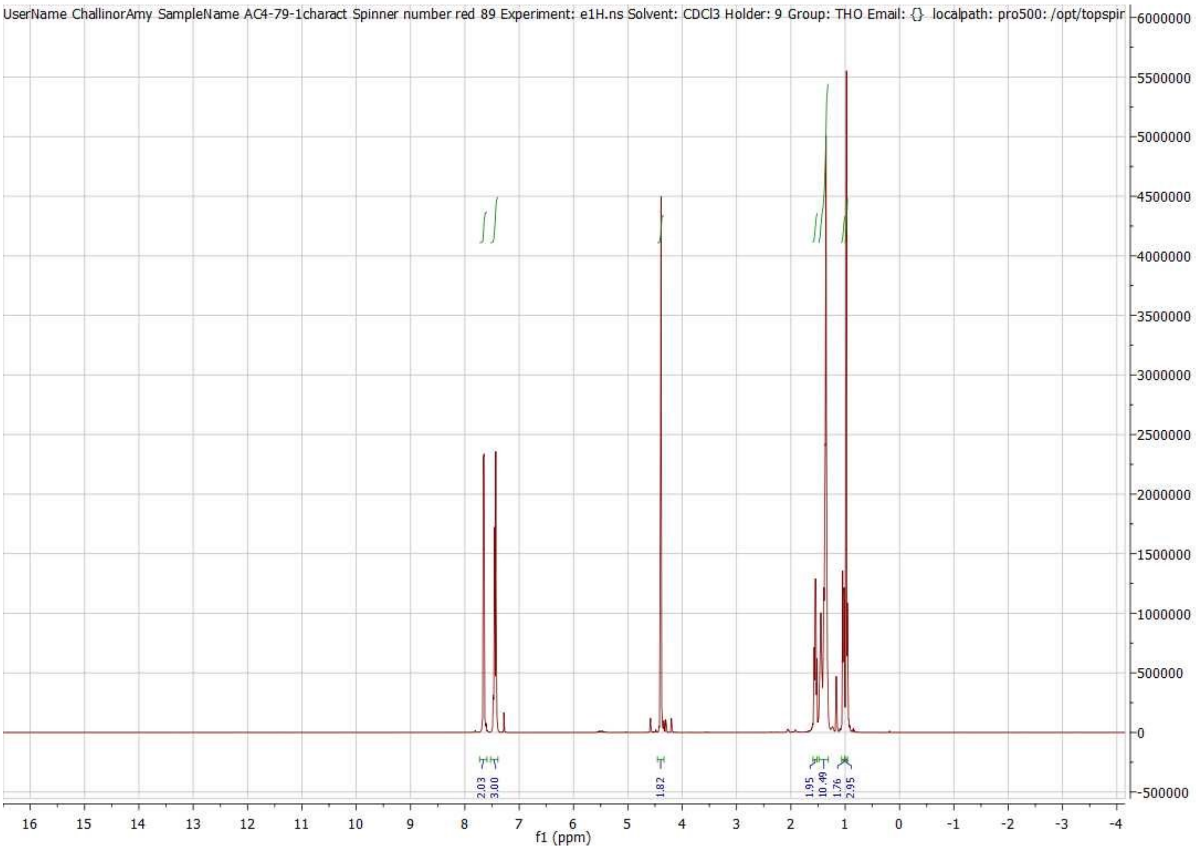
Hydrosilylation

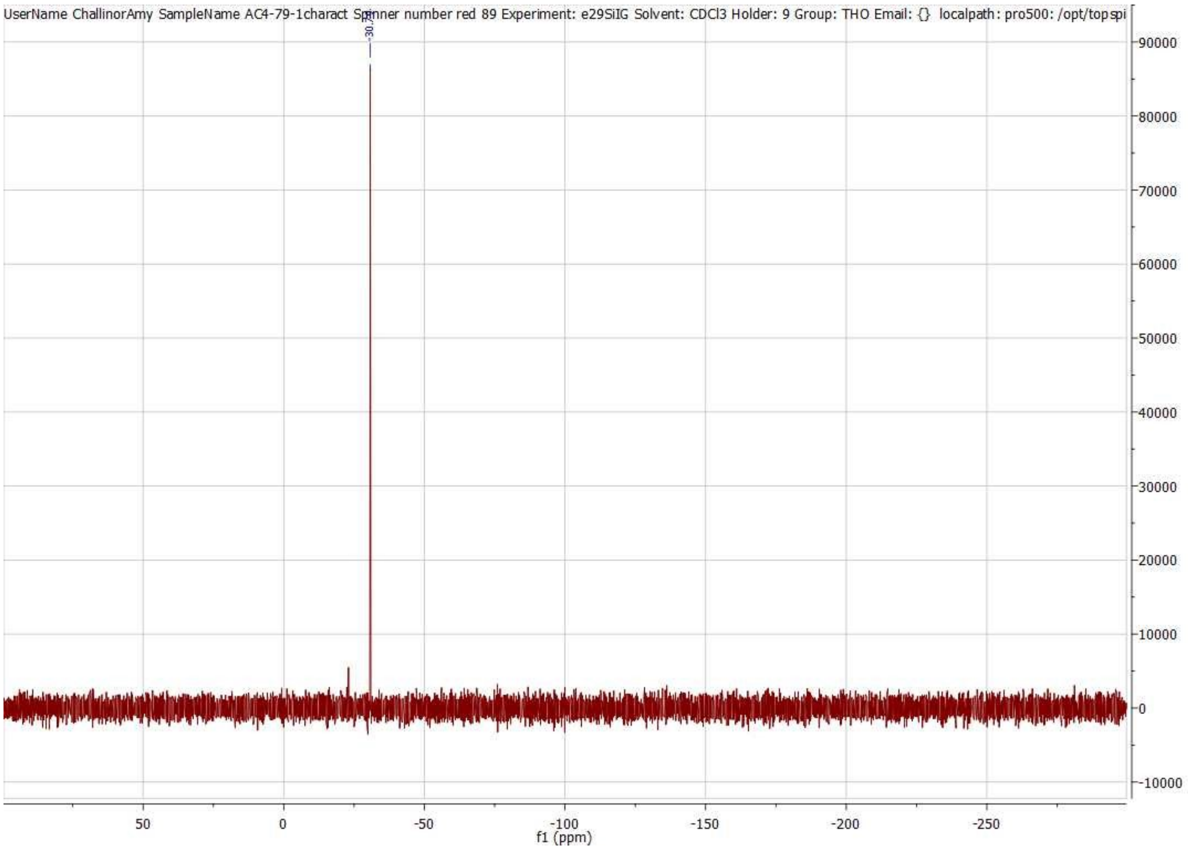
Iron-Catalysed Hydrosilylation Products

Octylsilylbenzene (2a)





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70000
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50000
40000
30000
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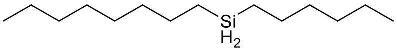
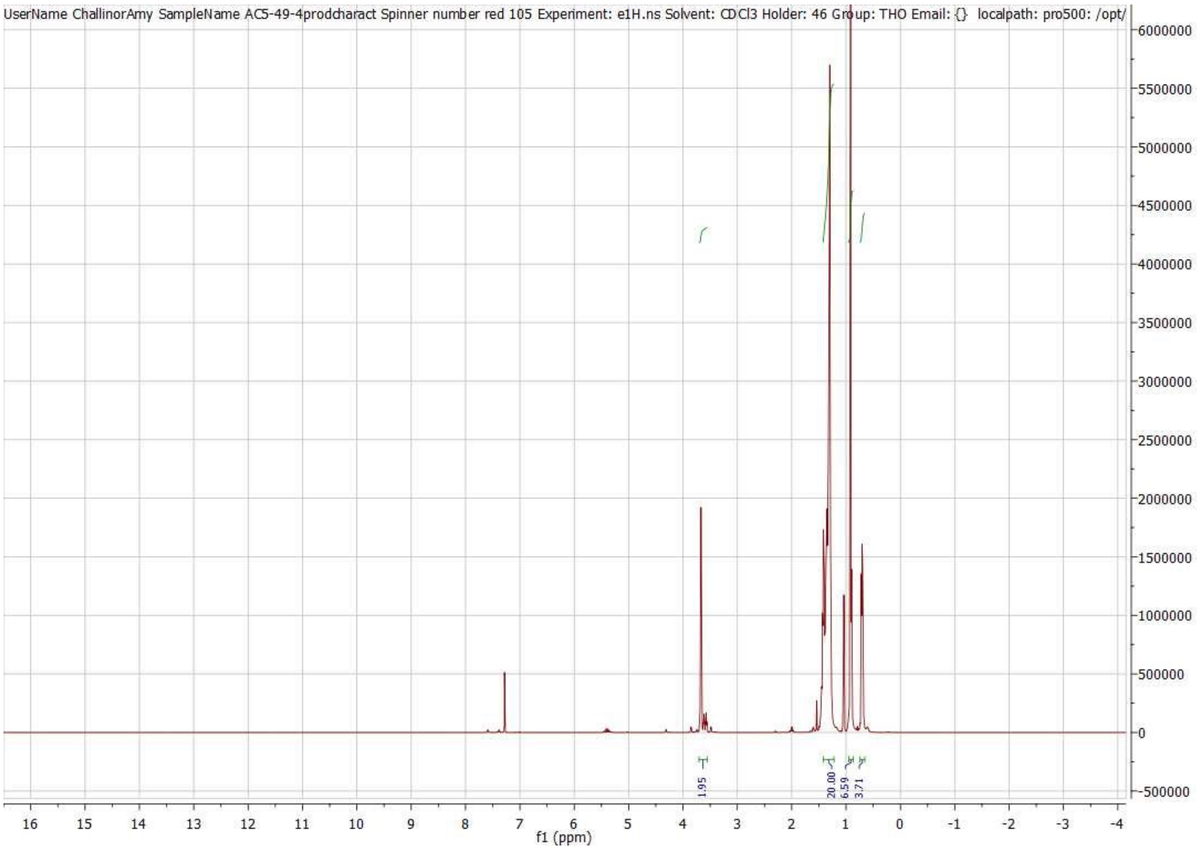
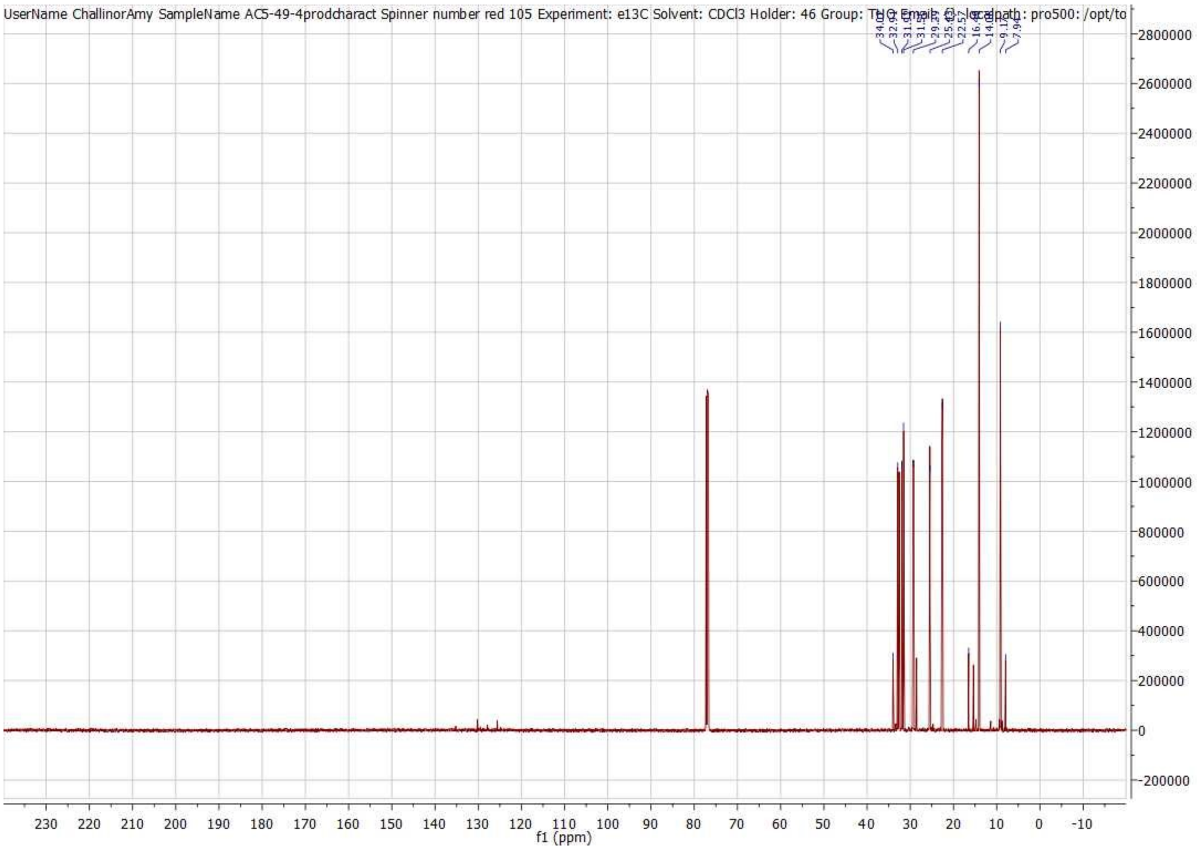
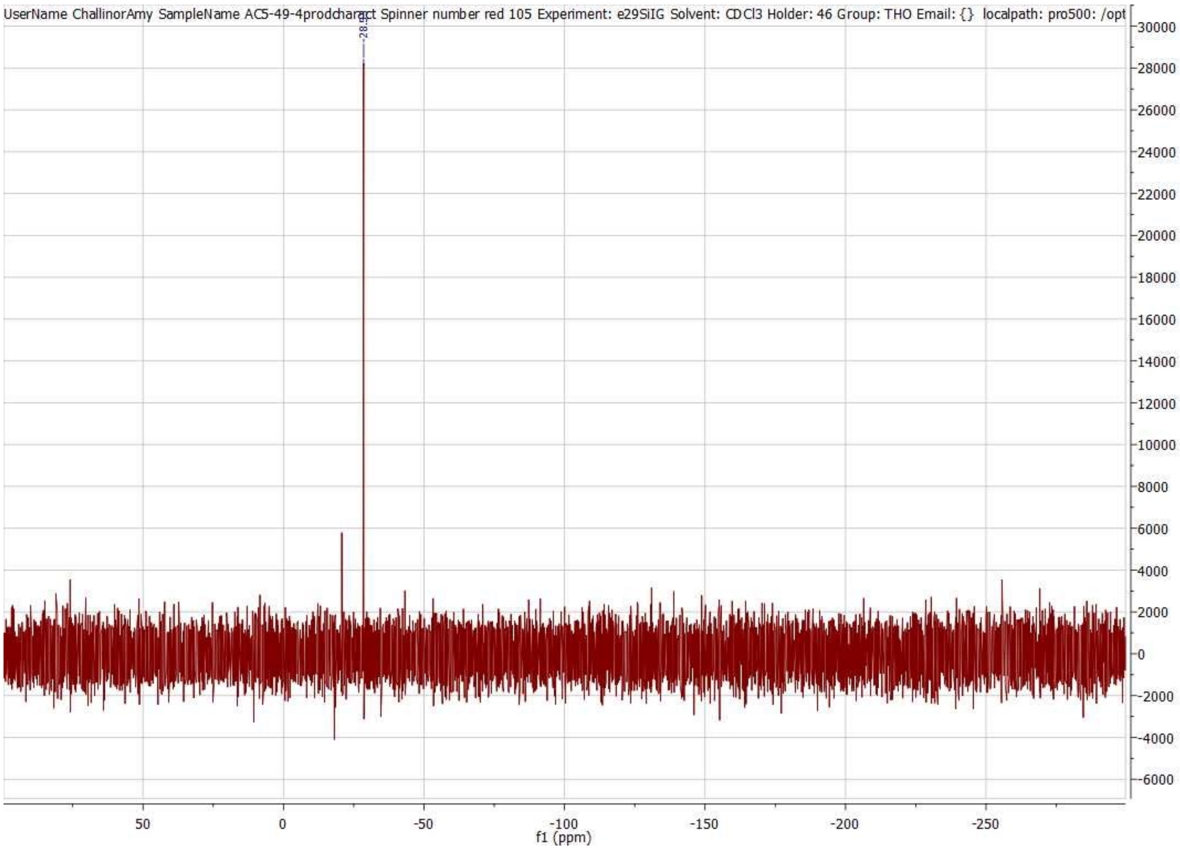
f1 (ppm)

Hexyloctylphenylsilane (2b)

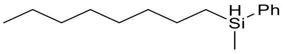


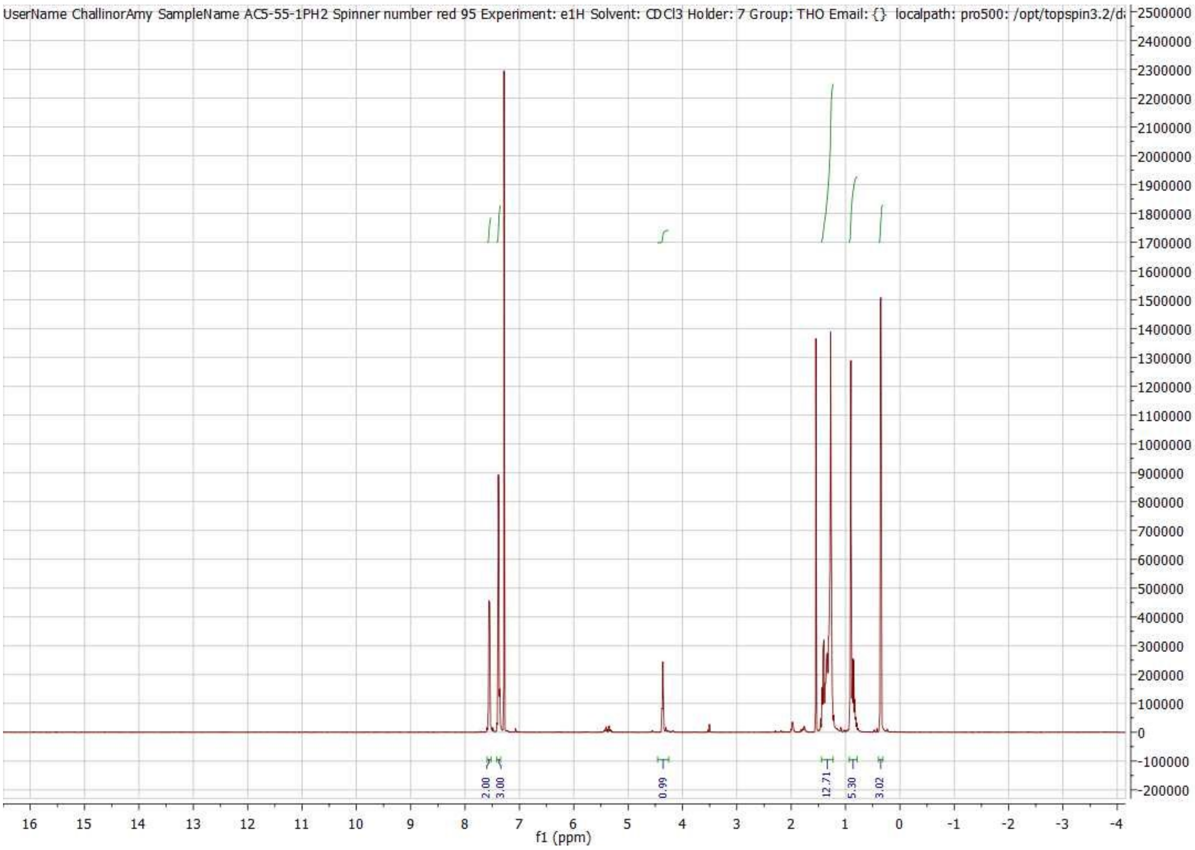


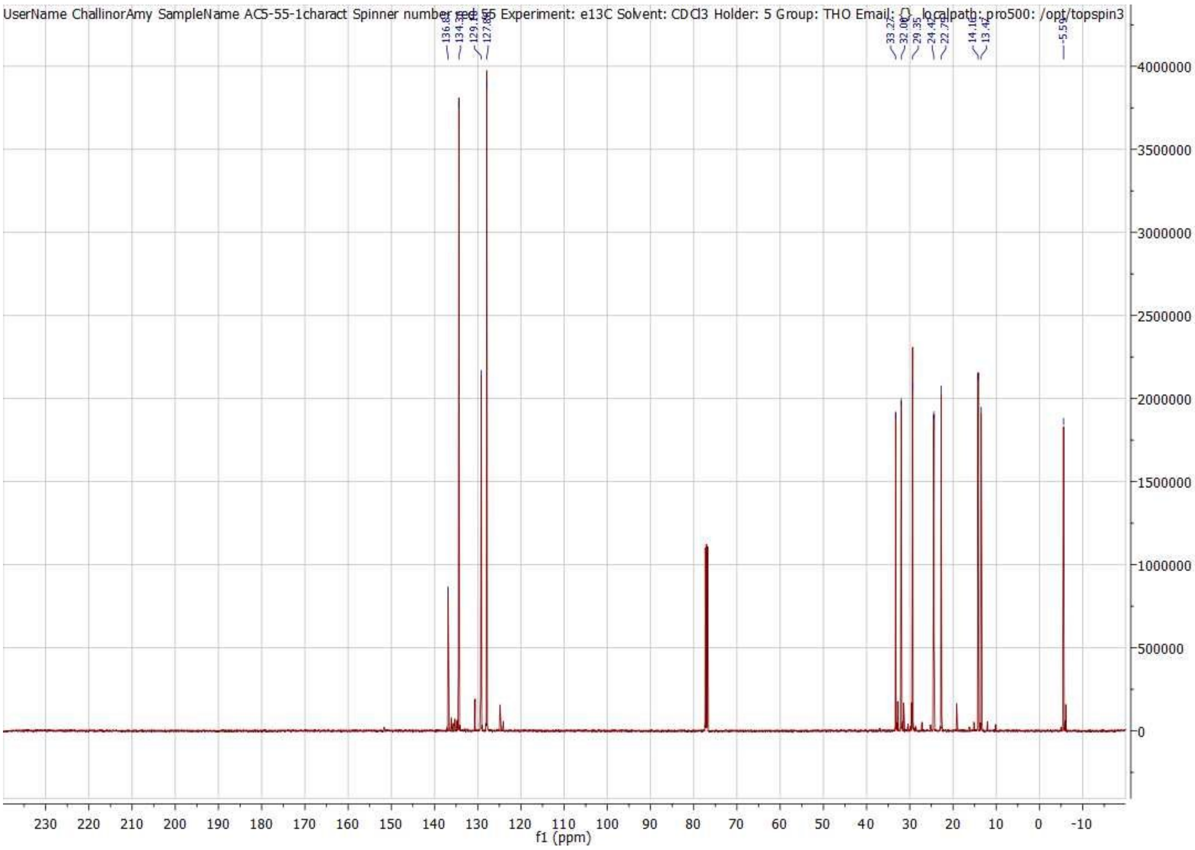


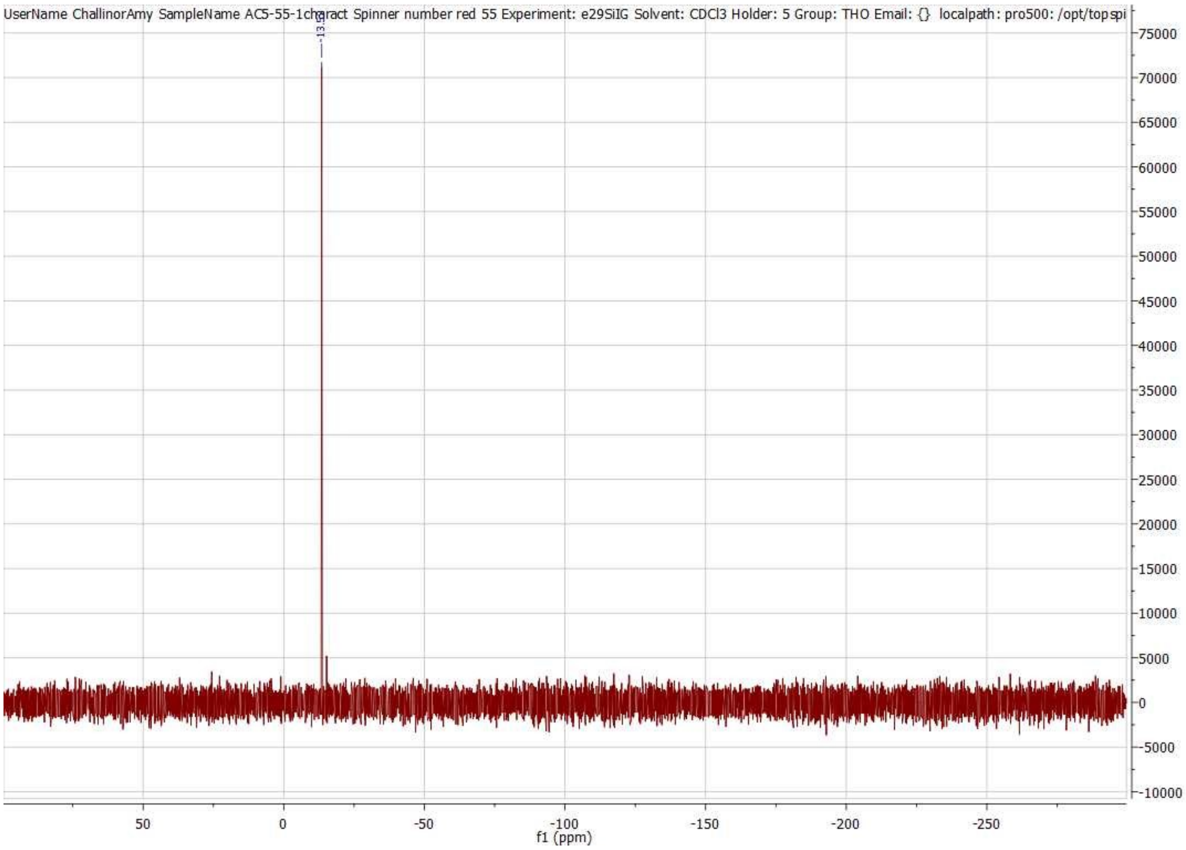

UserName ChallinorAmy SampleName AC5-49-4prodcharact Spinner number red 105 Experiment: e29SiIG Solvent: CDCl3 Holder: 46 Group: THO Email: {} localpath: pro500: /opt
-28.
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

Methyloctylphenylsilane (2c)

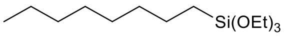


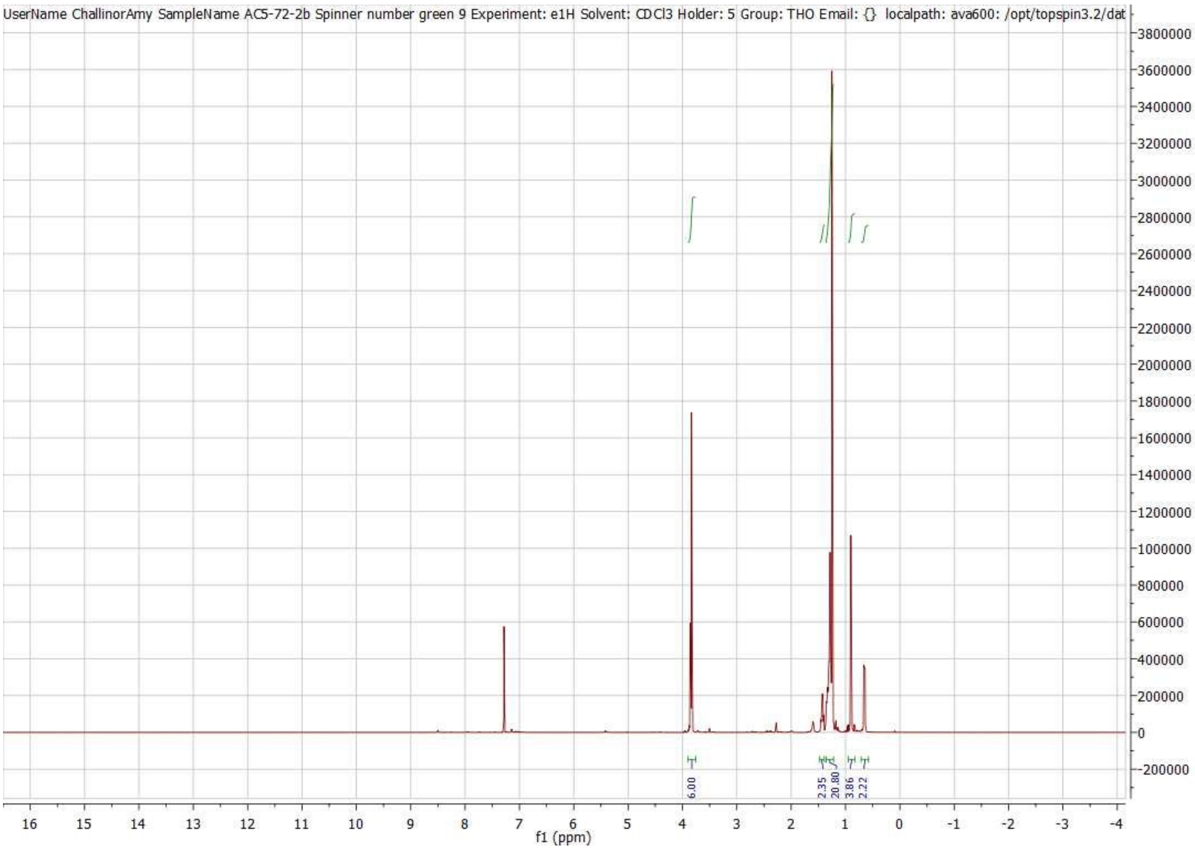


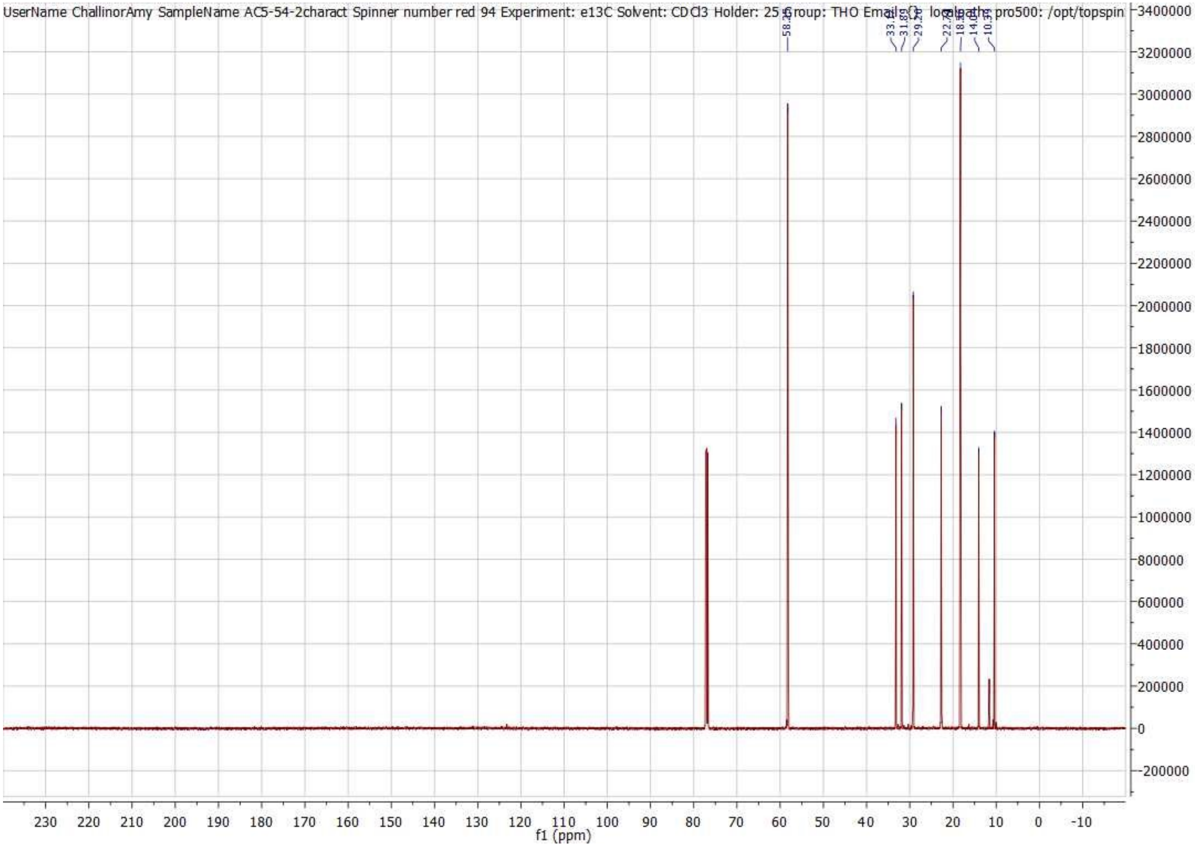


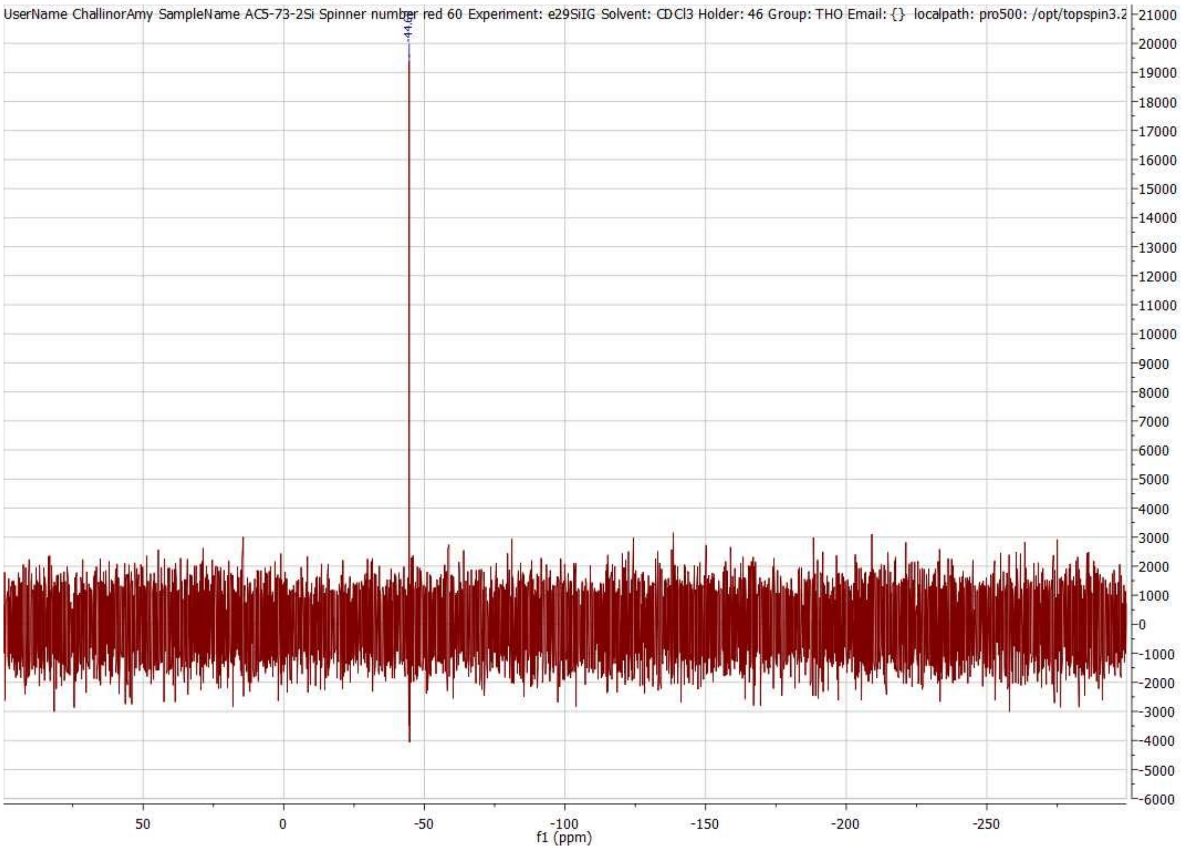

UserName ChallinorAmy SampleName AC5-55-1charact Spinner number red 55 Experiment: e29SiIG Solvent: CDCl3 Holder: 5 Group: THO Email: {} localpath: pro500: /opt/topspi
-13.5
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

Triethoxy(octyl)silane (2d)

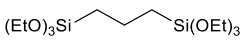


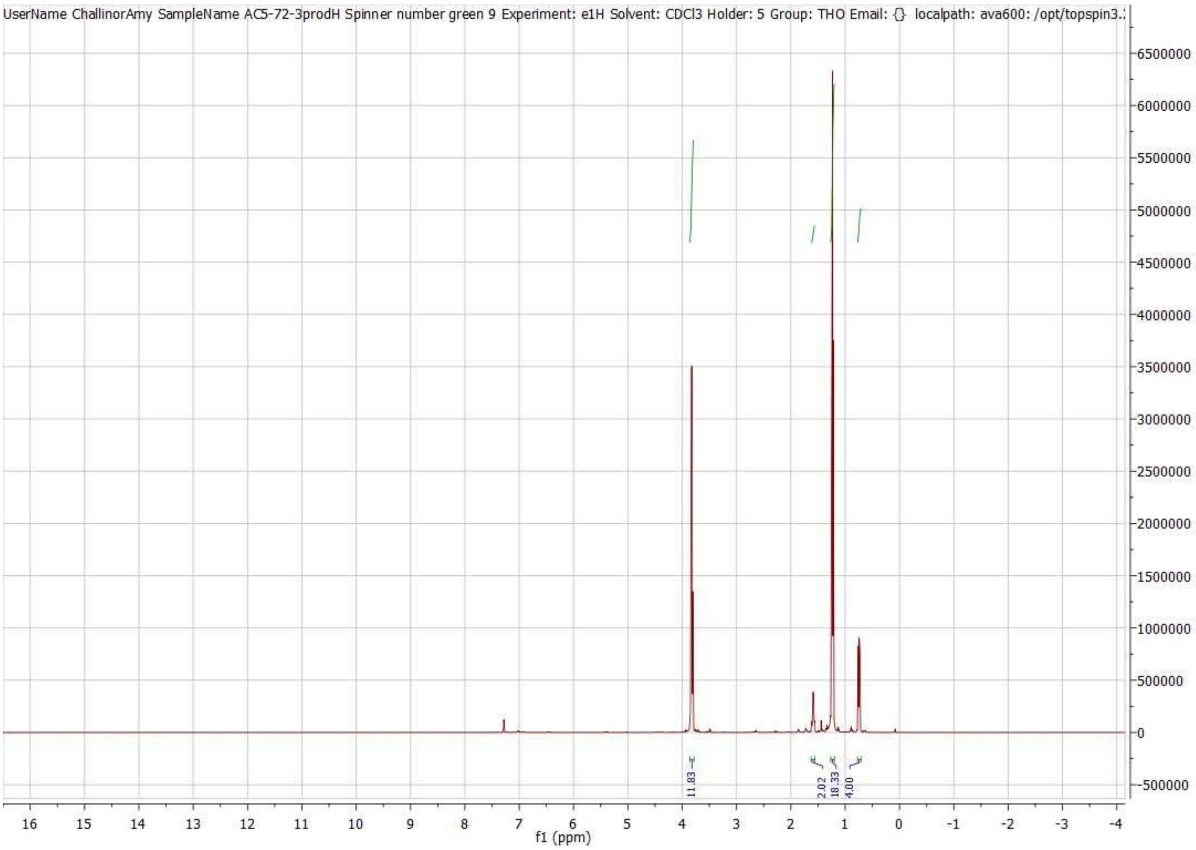


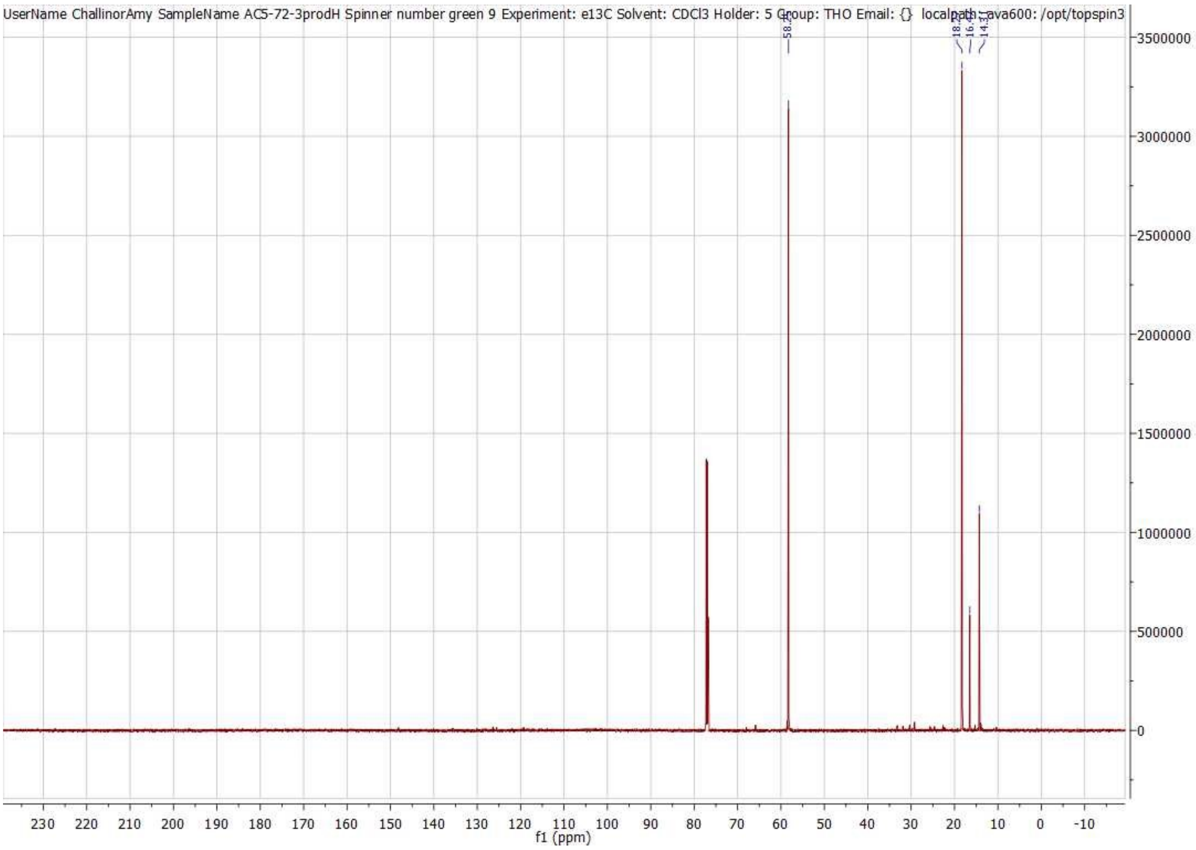


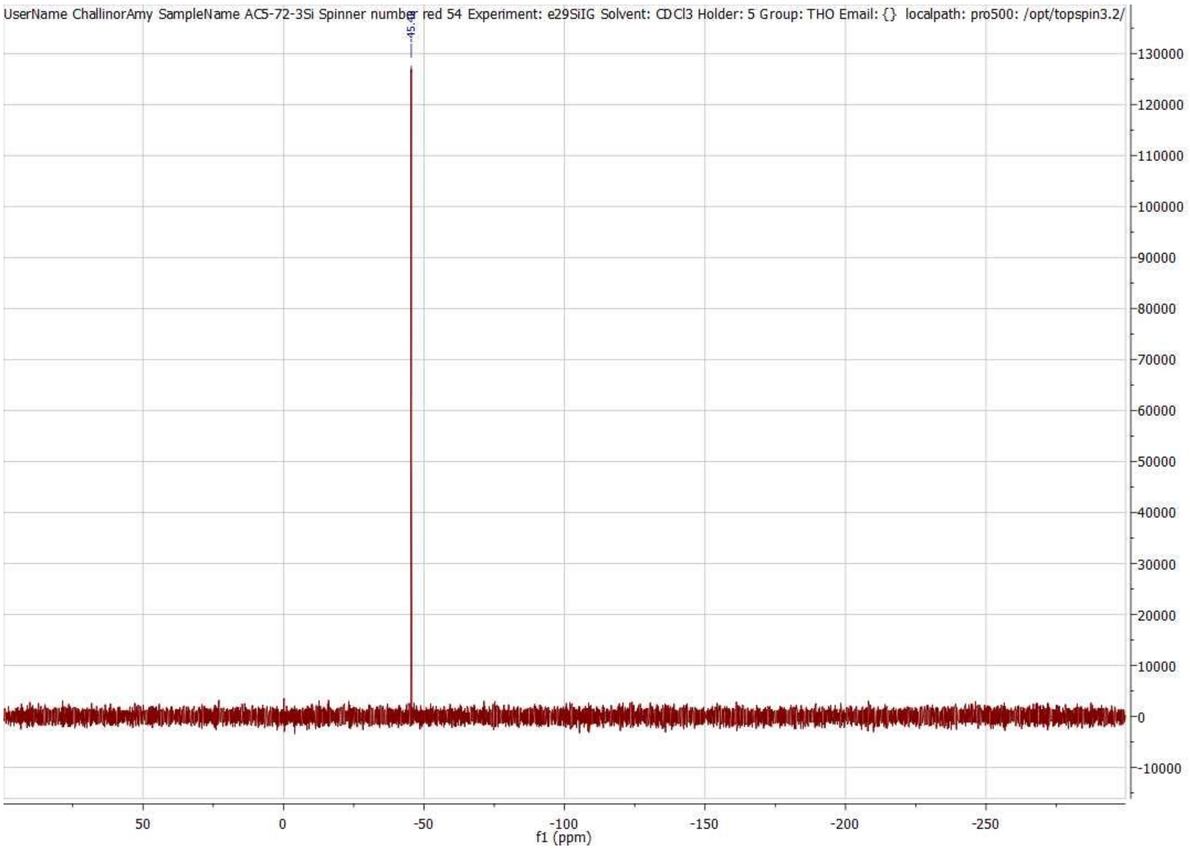

UserName ChallinorAmy SampleName AC5-73-2Si Spinner number red 60 Experiment: e29SIIG Solvent: CDCl3 Holder: 46 Group: THO Email: {} localpath: pro500: /opt/topspin3.2
-44.6
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1,3-Bis(triethoxysilyl)propane (2e)

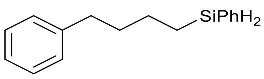


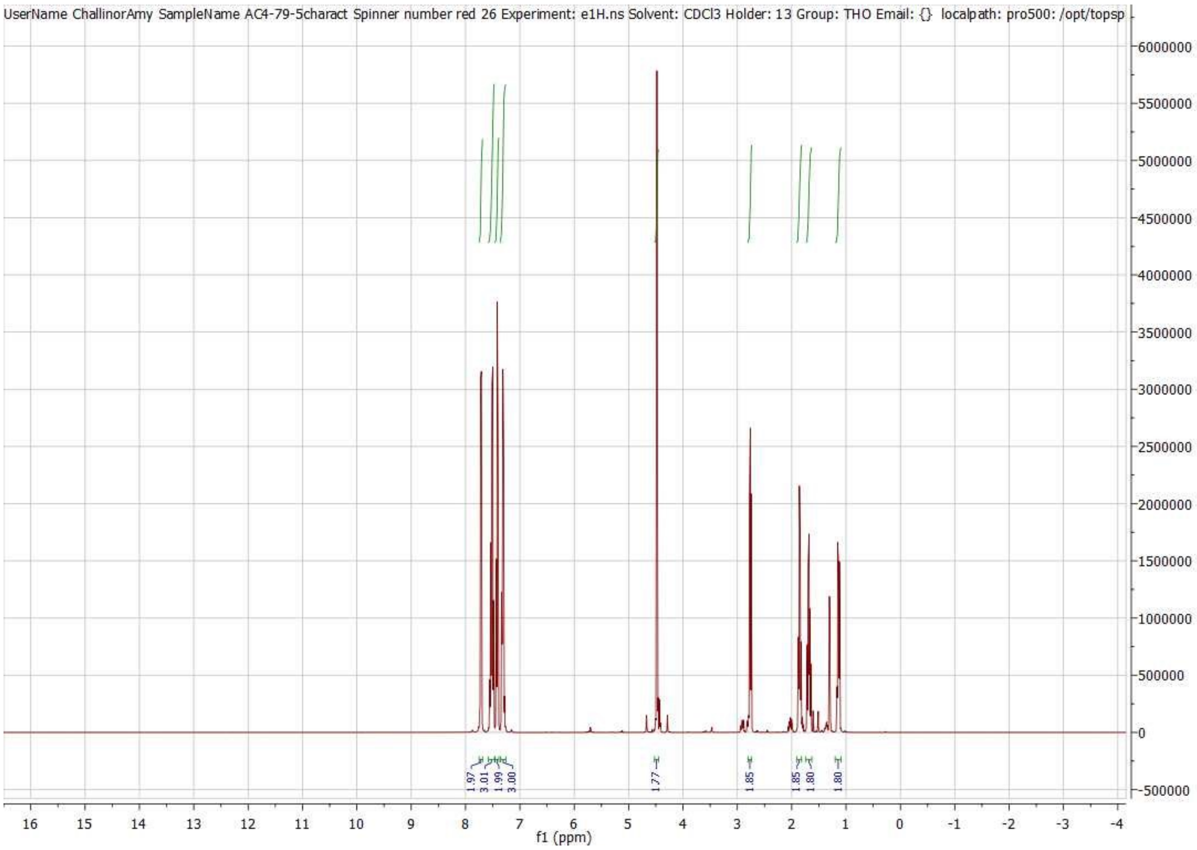


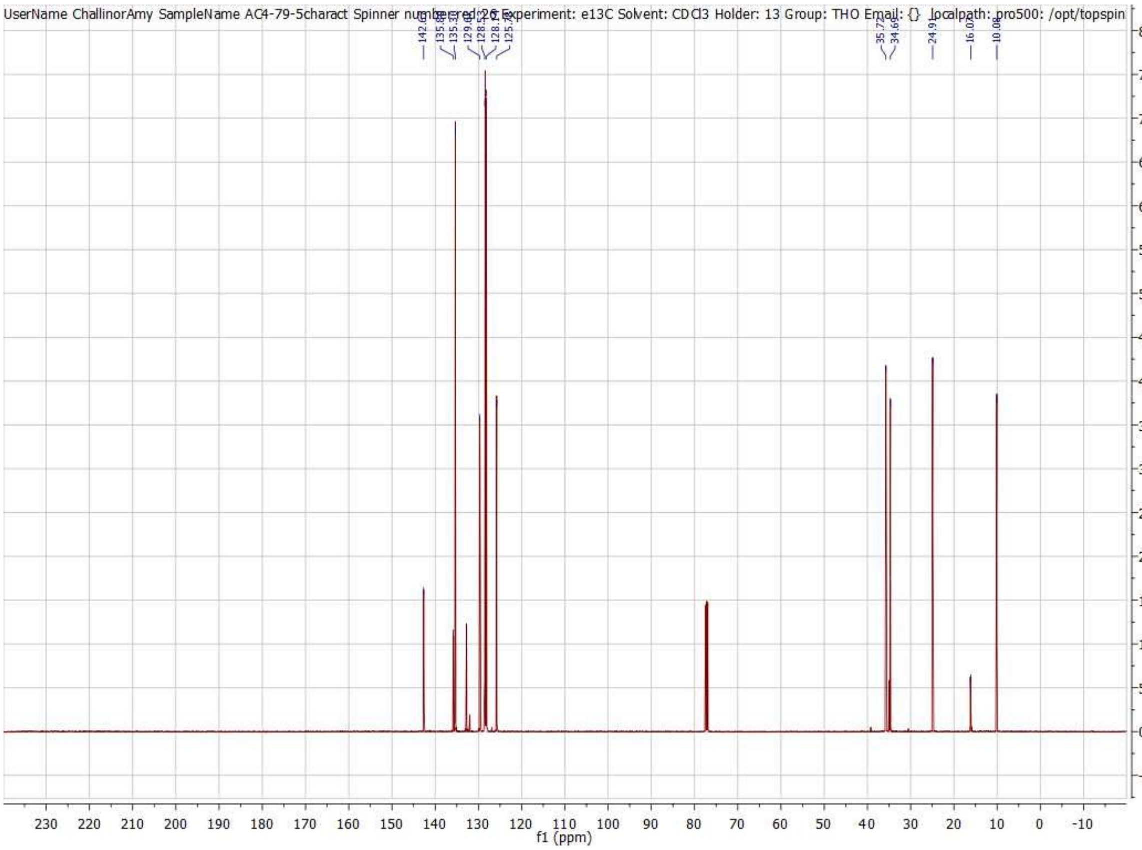


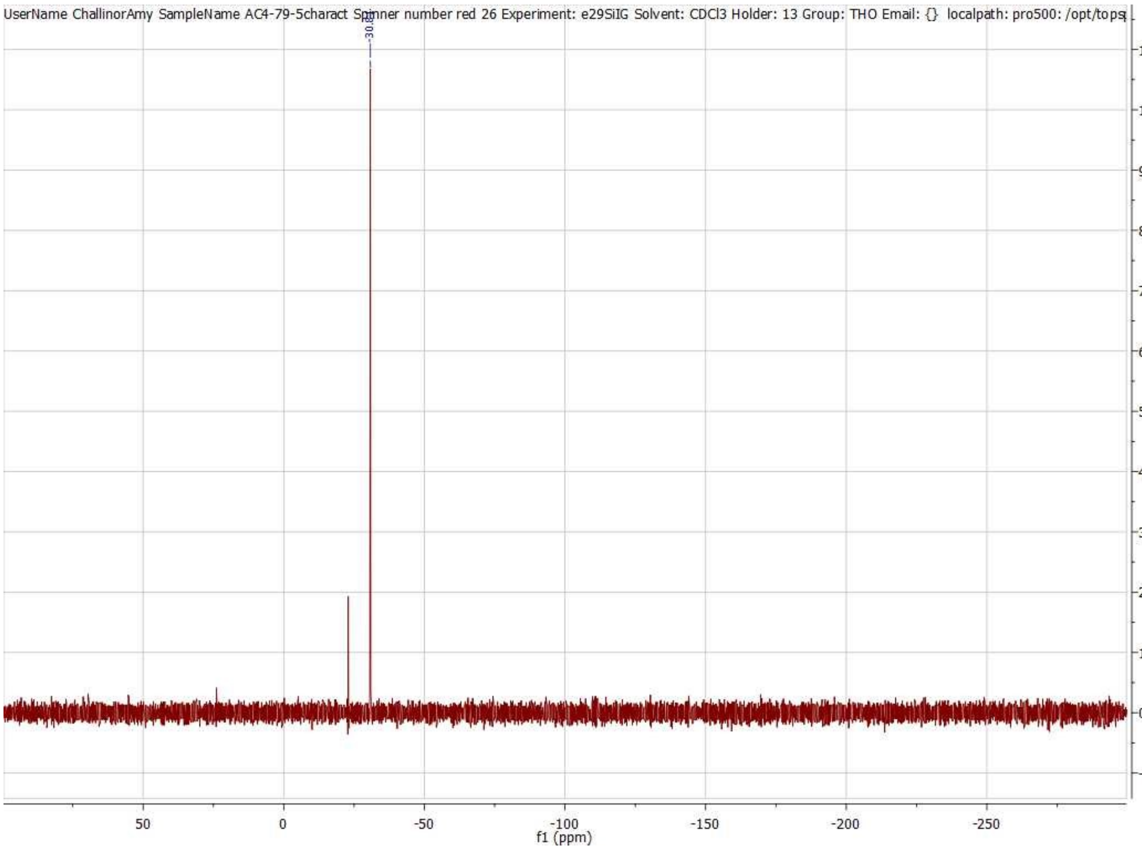

UserName ChallinorAmy SampleName AC5-72-3Si Spinner number red 54 Experiment: e29SIIG Solvent: CDCl3 Holder: 5 Group: THO Email: {} localpath: pro500: /opt/topspin3.2/
-45.4
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-Phenyl-4-(phenylsilyl)butane (2f)

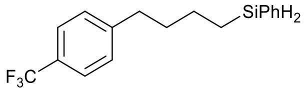


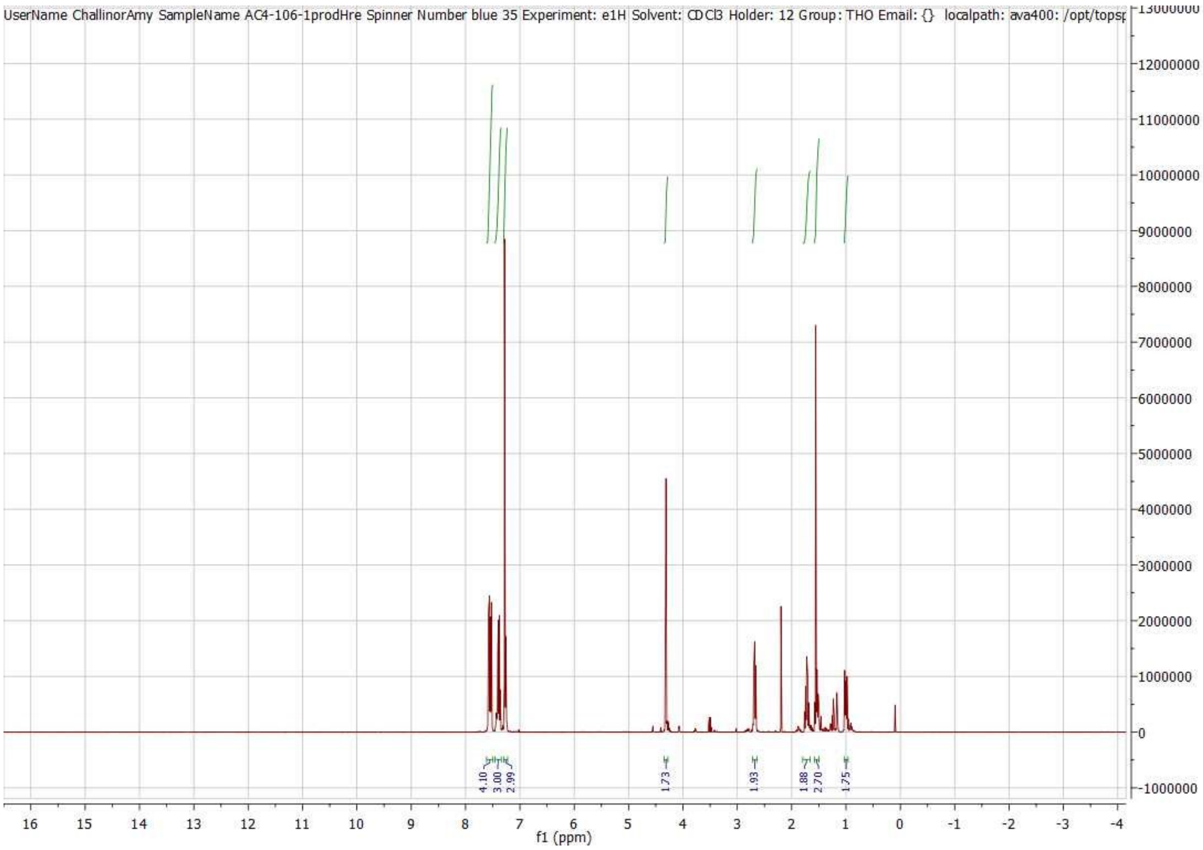


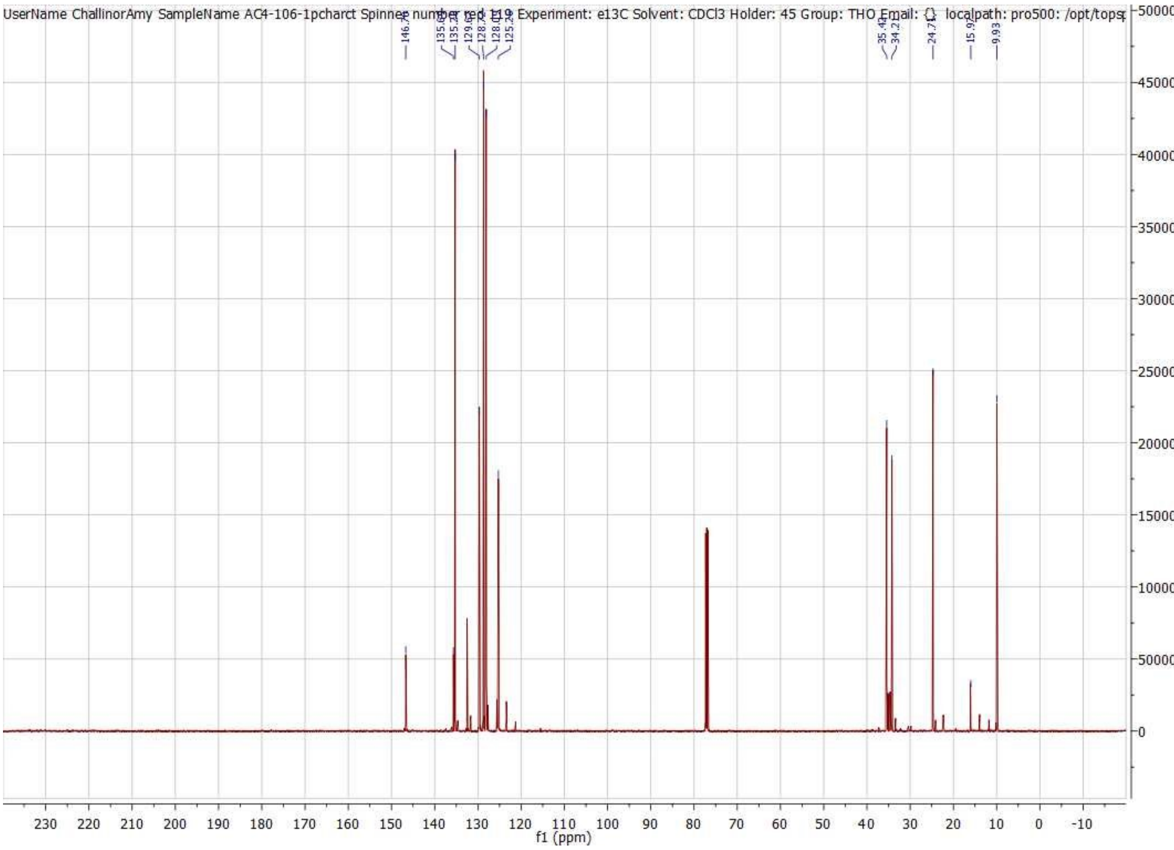

UserName ChallinorAmy SampleName AC4-79-5charact Spinner number red 26 Experiment: e13C Solvent: CDCl3 Holder: 13 Group: THO Email: {} localpath: pro500: /opt/topspin
142.6
135.8
135.3
129.0
128.5
128.1
125.7
35.72
34.69
24.91
16.02
10.08
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

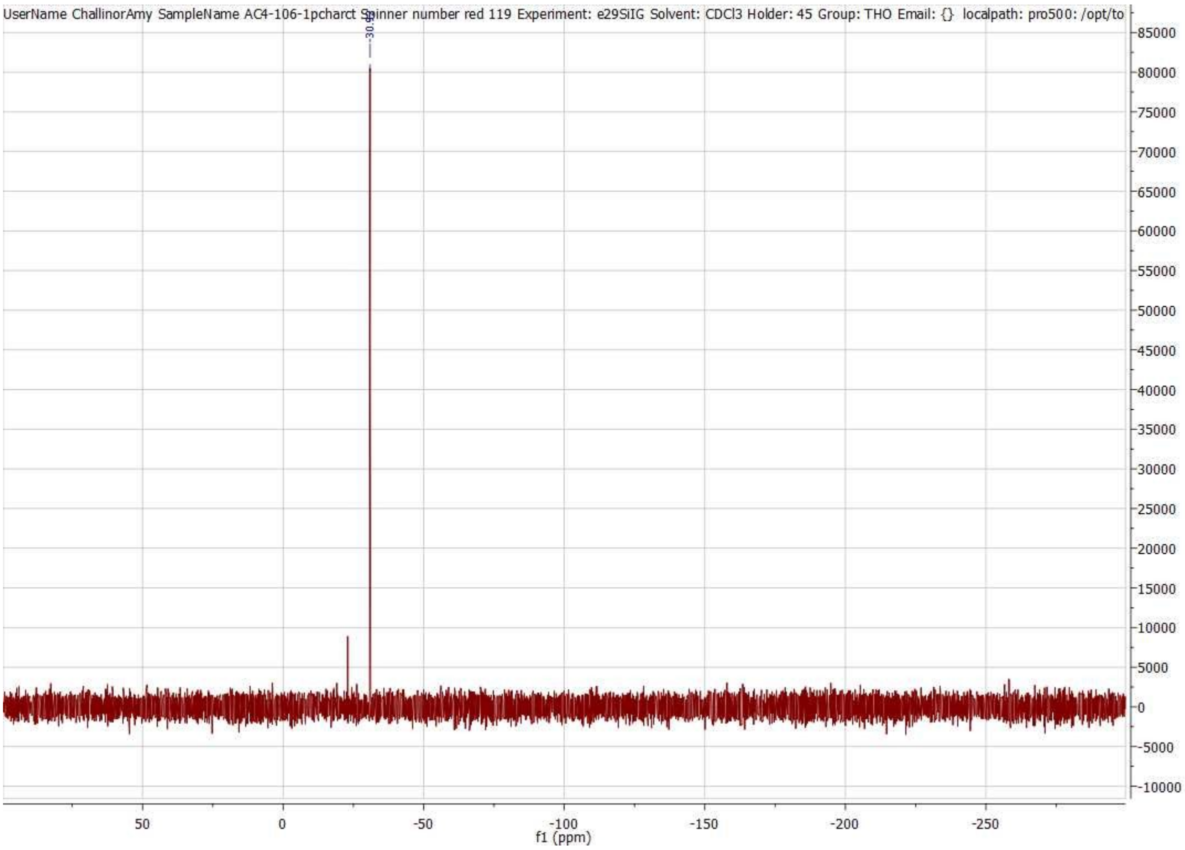

UserName ChallinorAmy SampleName AC4-79-5charact Spinner number red 26 Experiment: e29SiIG Solvent: CDCl3 Holder: 13 Group: THO Email: {} localpath: pro500: /opt/tops
-30.8
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50 0 -50 -100 -150 -200 -250
f1 (ppm)

1-Trifluoromethyl-4-(4-silylbenzenebutane)benzene (2g)

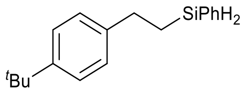


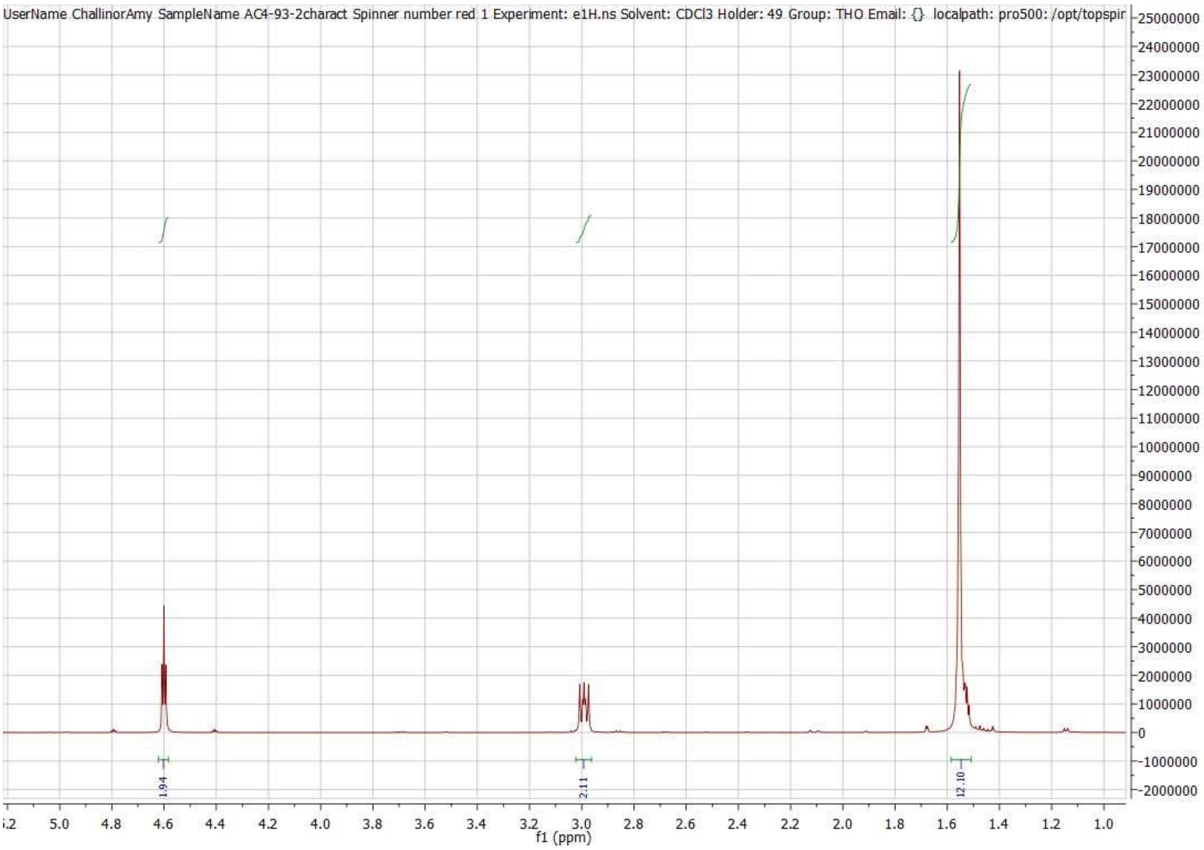


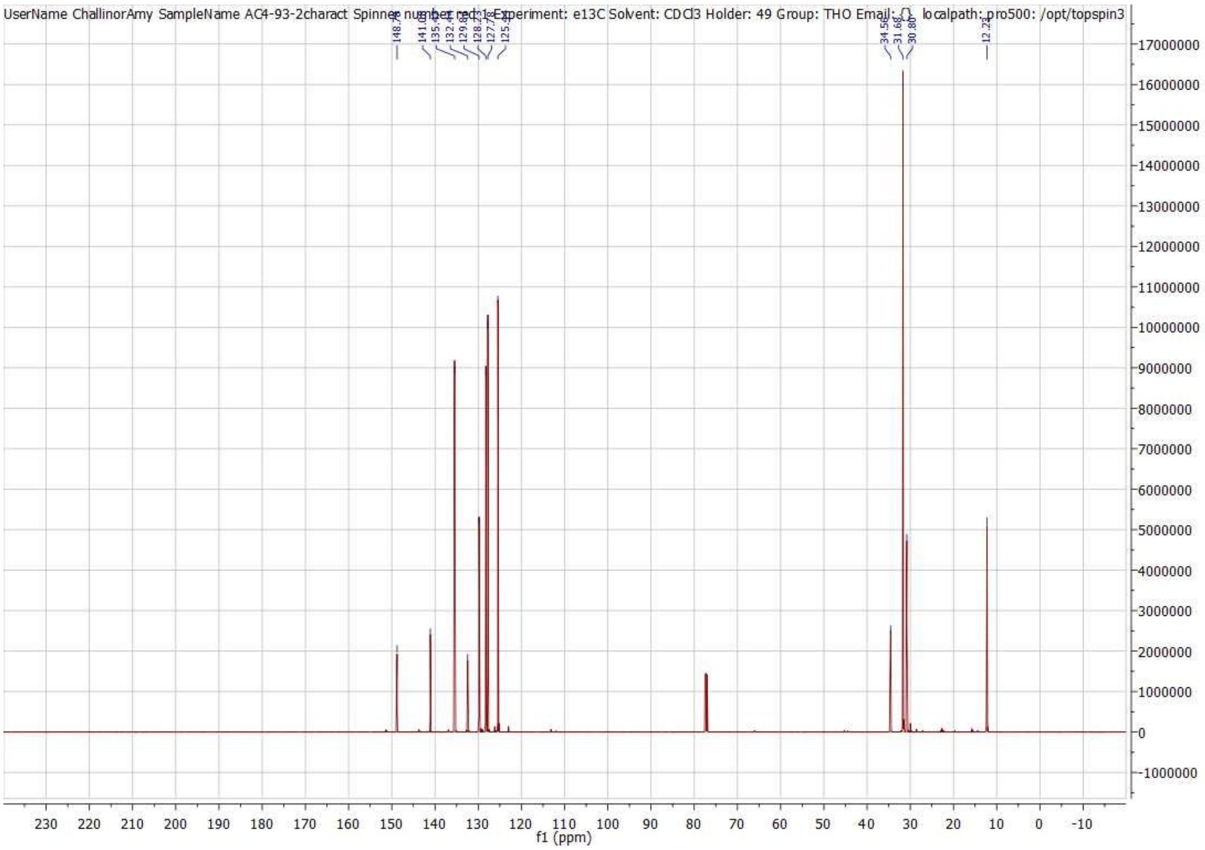

UserName ChallinorAmy SampleName AC4-106-1pcharct Spinner number red 119 Experiment: e13C Solvent: CDCl3 Holder: 45 Group: THO Email: {} localpath: pro500: /opt/tops
146.7
135.6
135.2
129.6
128.7
128.0
125.2
35.4
34.2
24.7
15.9
9.93
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

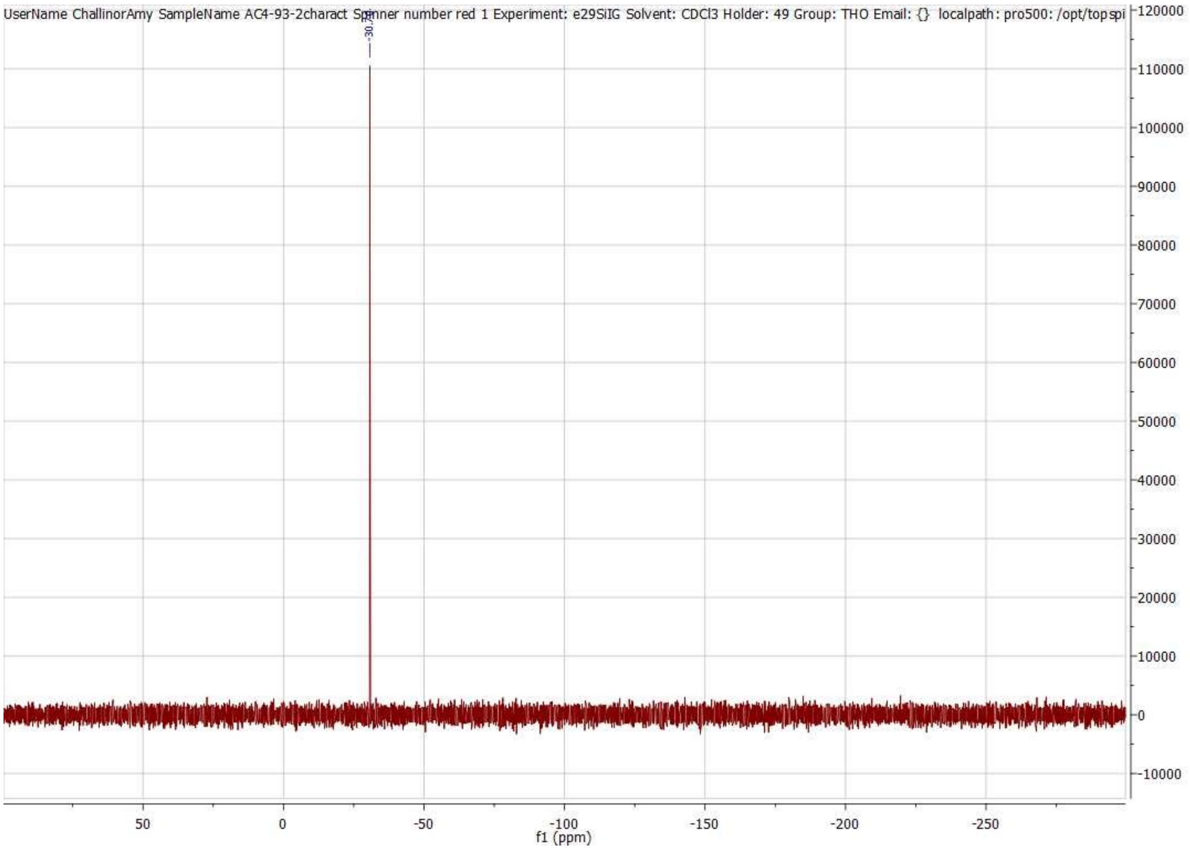

UserName ChallinorAmy SampleName AC4-106-1pcharct Spinner number red 119 Experiment: e29SiIG Solvent: CDCl3 Holder: 45 Group: THO Email: {} localpath: pro500: /opt/to
-30.9
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-(4-*tert*butylphenyl)-2-(phenylsilyl)ethane (2h)

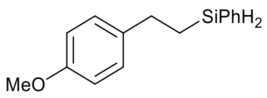


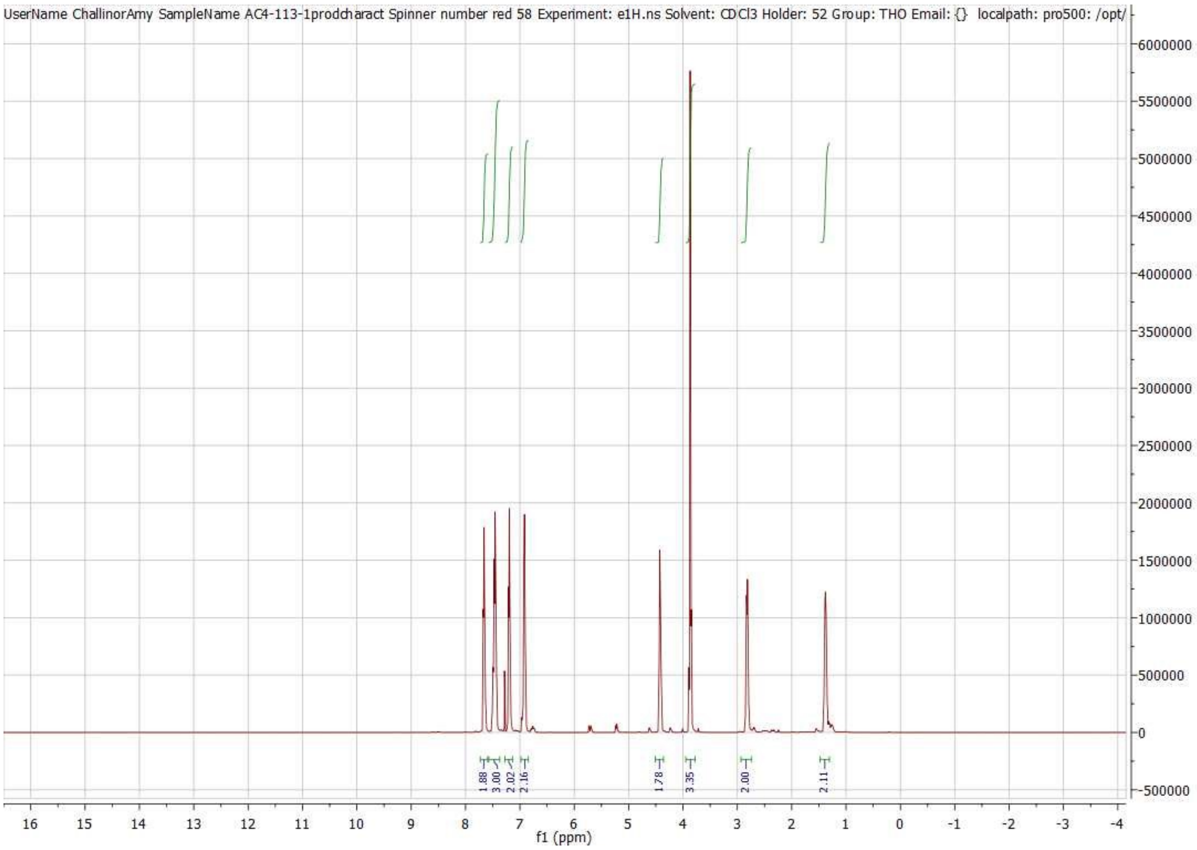


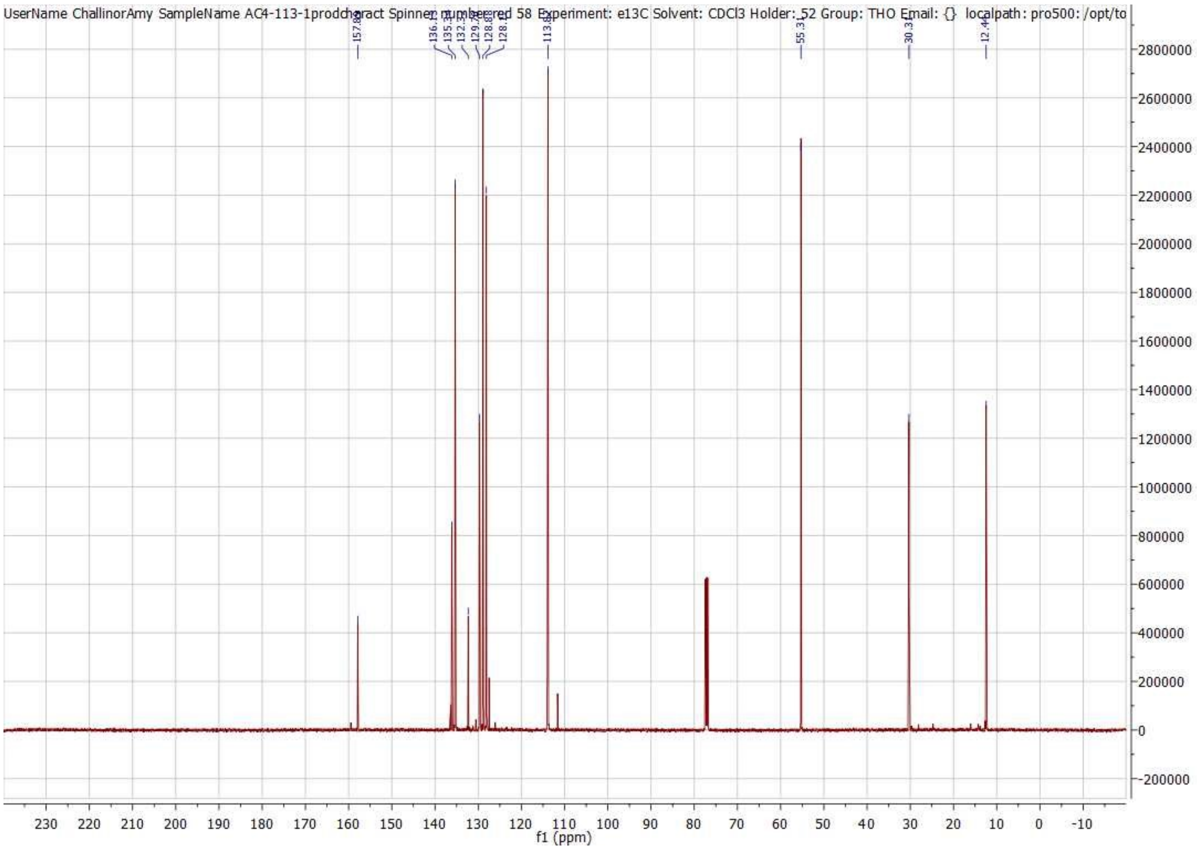

UserName ChallinorAmy SampleName AC4-93-2charact Spinner number red 1 Experiment: e13C Solvent: CDCl3 Holder: 49 Group: THO Email: {} localpath: pro500: /opt/topspin3
148.7
141.0
135.4
132.4
129.8
128.2
127.7
125.4
34.56
31.68
30.80
12.23
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

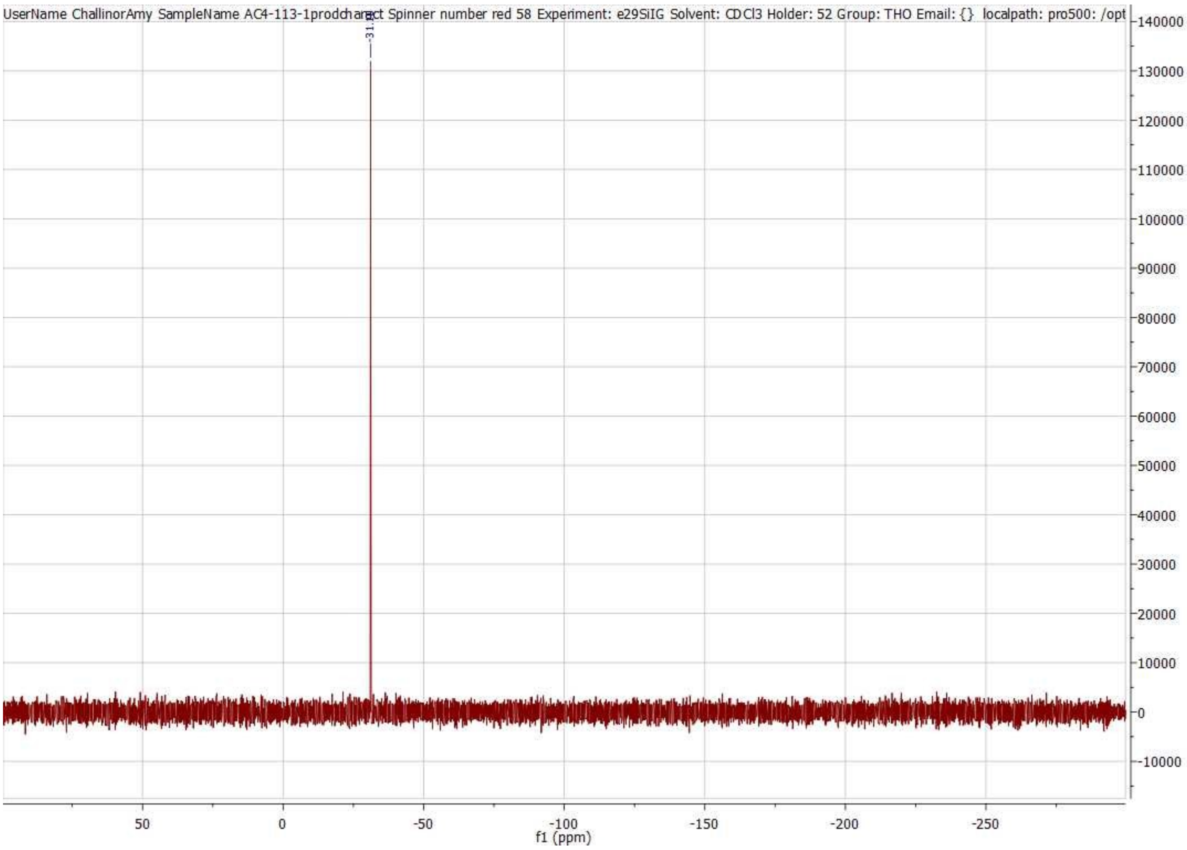

UserName ChallinorAmy SampleName AC4-93-2charact Spinner number red 1 Experiment: e29SiIG Solvent: CDCl3 Holder: 49 Group: THO Email: {} localpath: pro500: /opt/topspi
-30.
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50 0 -50 -100 -150 -200 -250
f1 (ppm)

(4-Methoxyphenethyl)(phenyl)silane (2i)

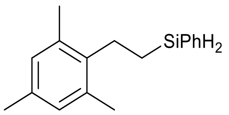


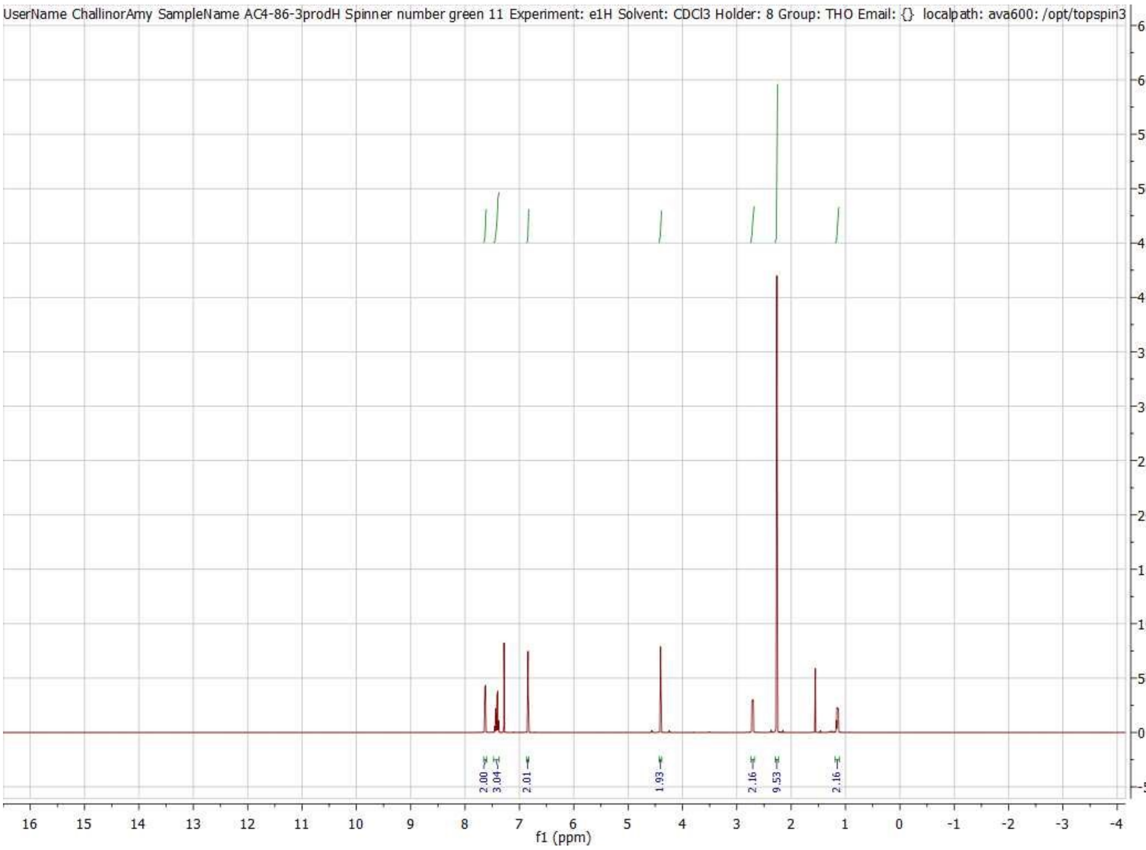


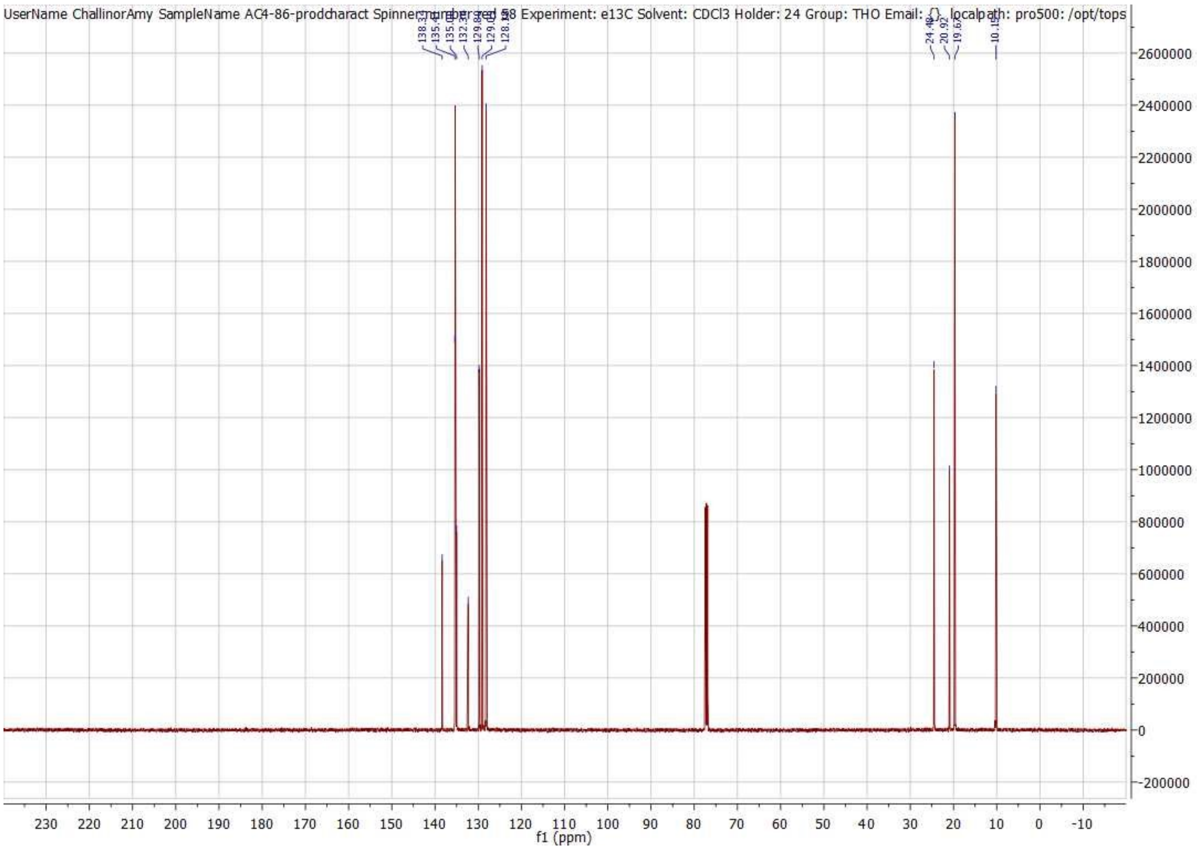


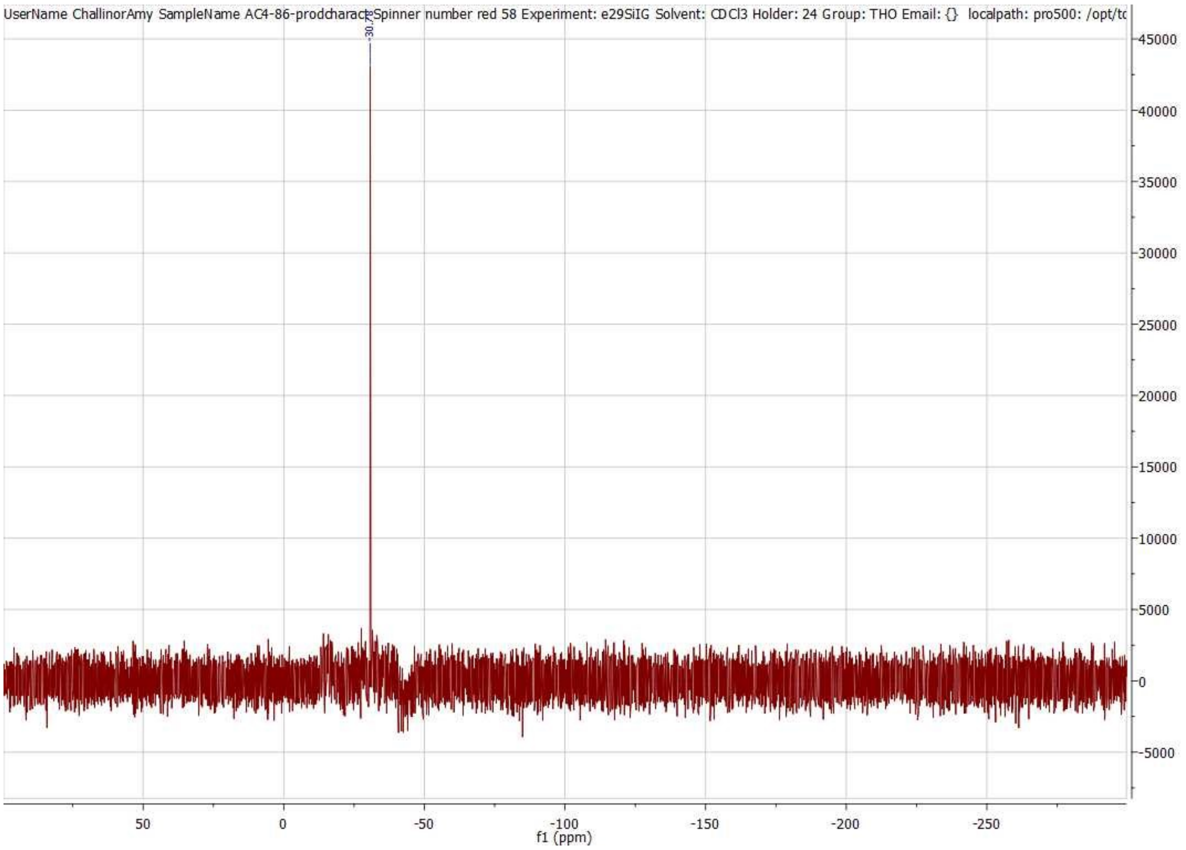

UserName ChallinorAmy SampleName AC4-113-1prodcharact Spinner number red 58 Experiment: e29SIIG Solvent: CDCl3 Holder: 52 Group: THO Email: {} localpath: pro500: /opt
-31.
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

(1,3,5-Trimethylphenethyl)(phenyl)silane (2j)

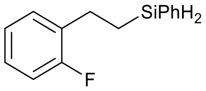


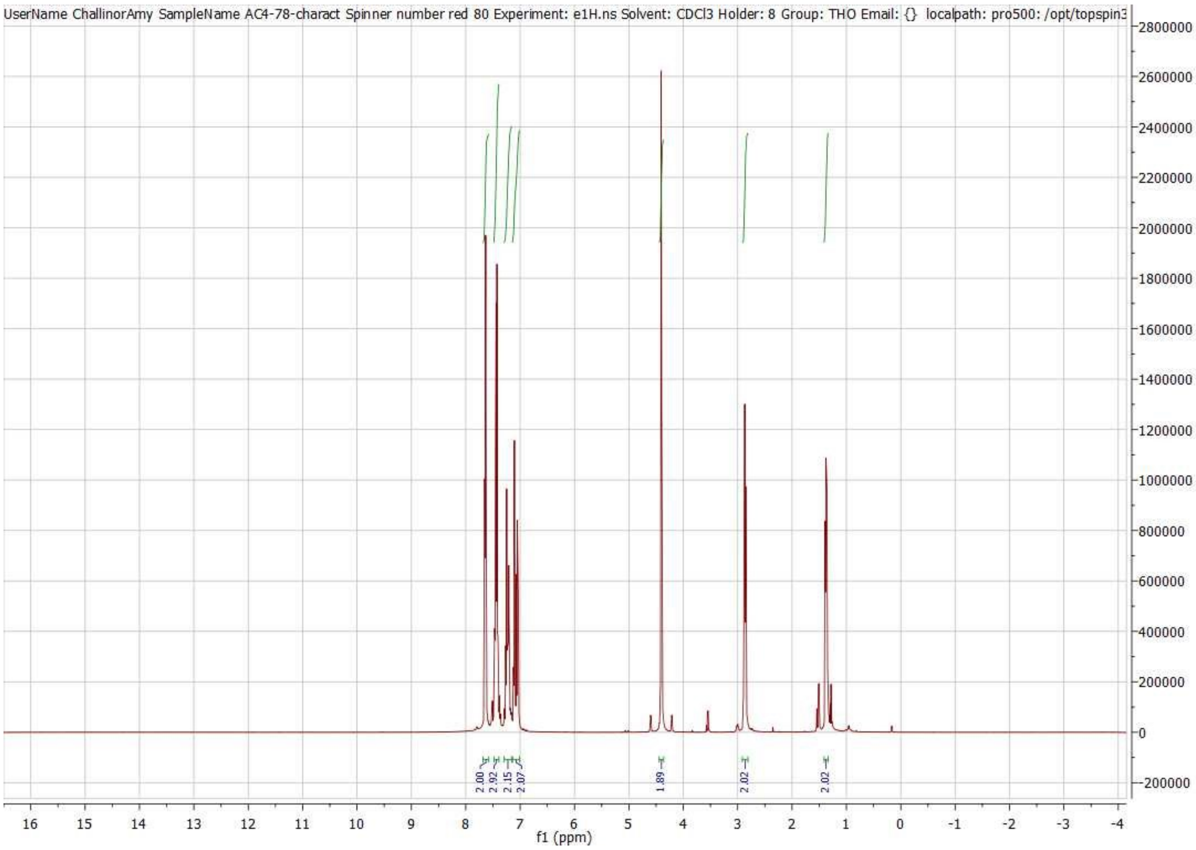


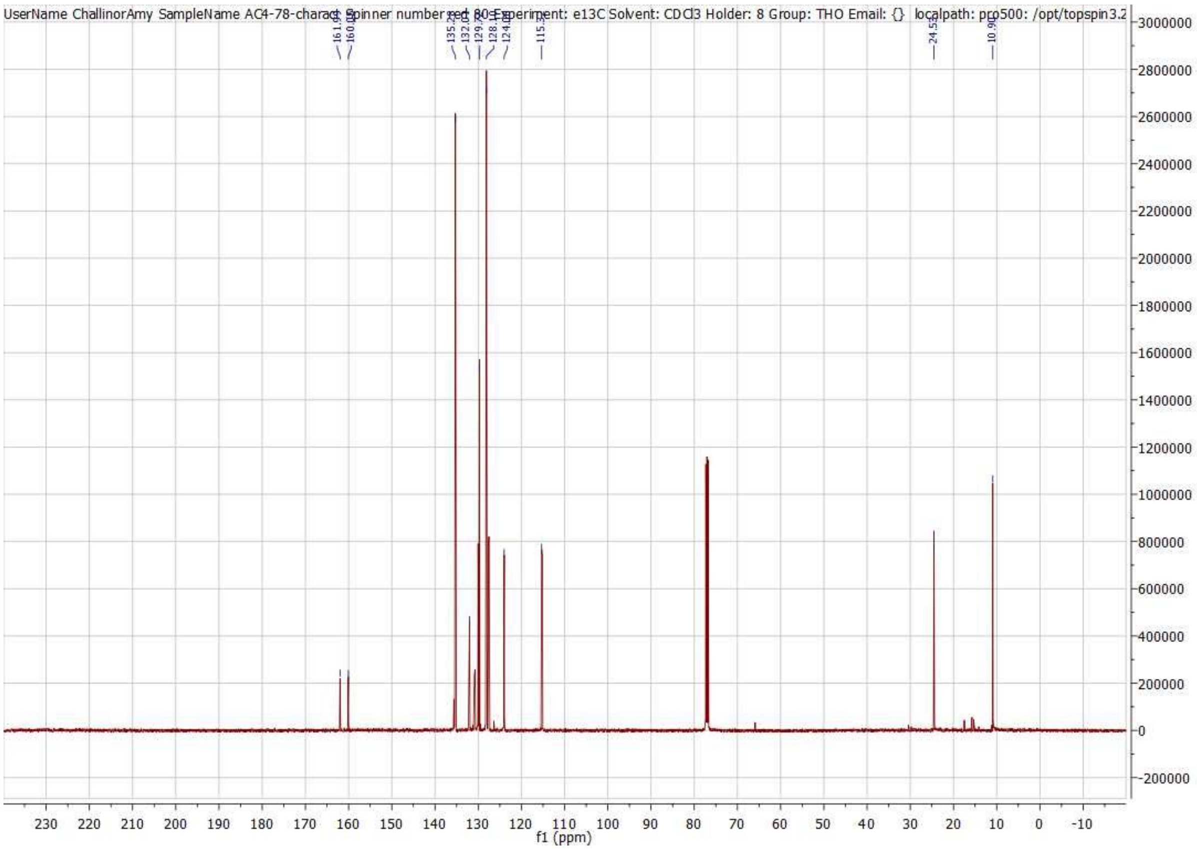

UserName ChallinorAmy SampleName AC4-86-prodcharact Spinner number red 58 Experiment: e13C Solvent: CDCl3 Holder: 24 Group: THO Email: {} localpath: pro500: /opt/tops
138.3
135.4
135.0
132.3
129.8
129.0
128.1
24.48
20.92
19.67
10.15
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

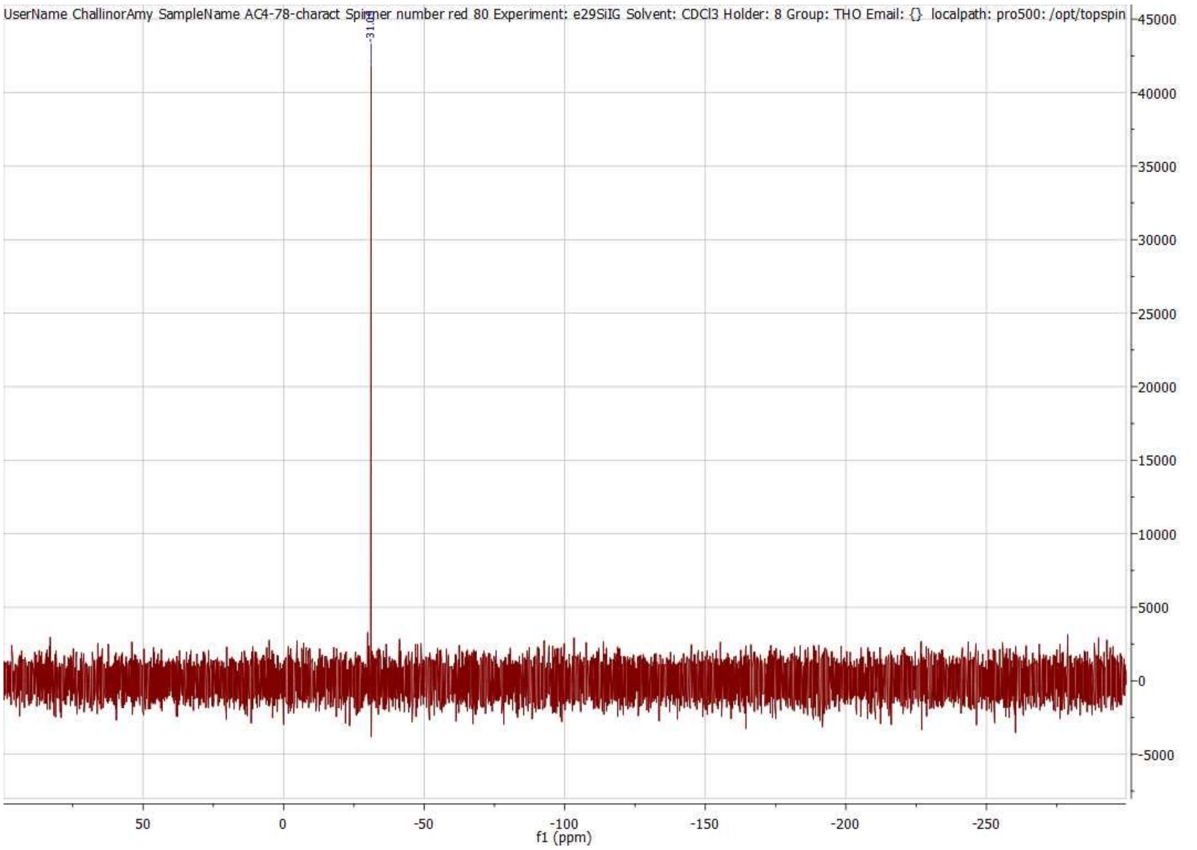

UserName ChallinorAmy SampleName AC4-86-prodcharact Spinner number red 58 Experiment: e29SiIG Solvent: CDCl3 Holder: 24 Group: THO Email: {} localpath: pro500: /opt/tc
-30.7
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50 0 -50 -100 -150 -200 -250
f1 (ppm)

1-(2-Fluorophenyl)-2-(phenylsilyl)ethane (2k)

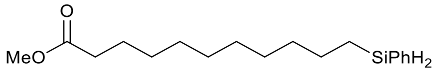


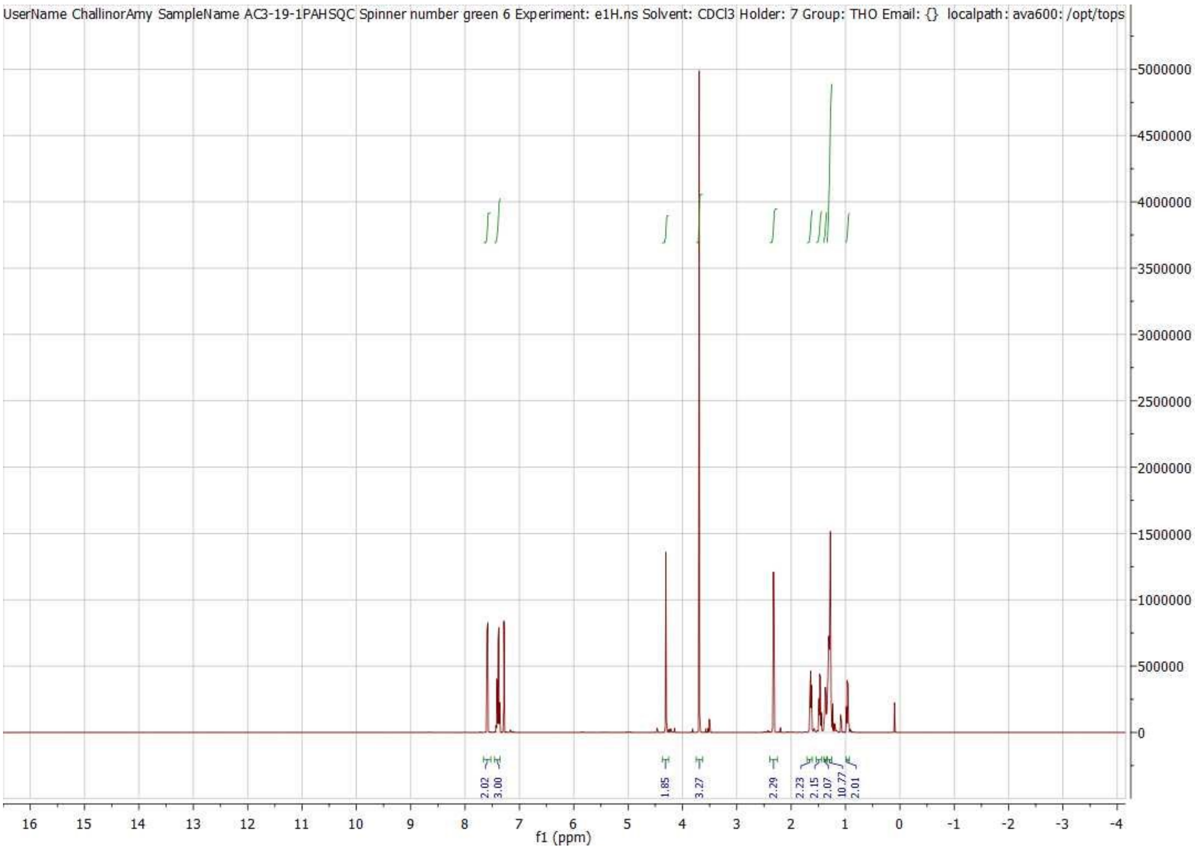


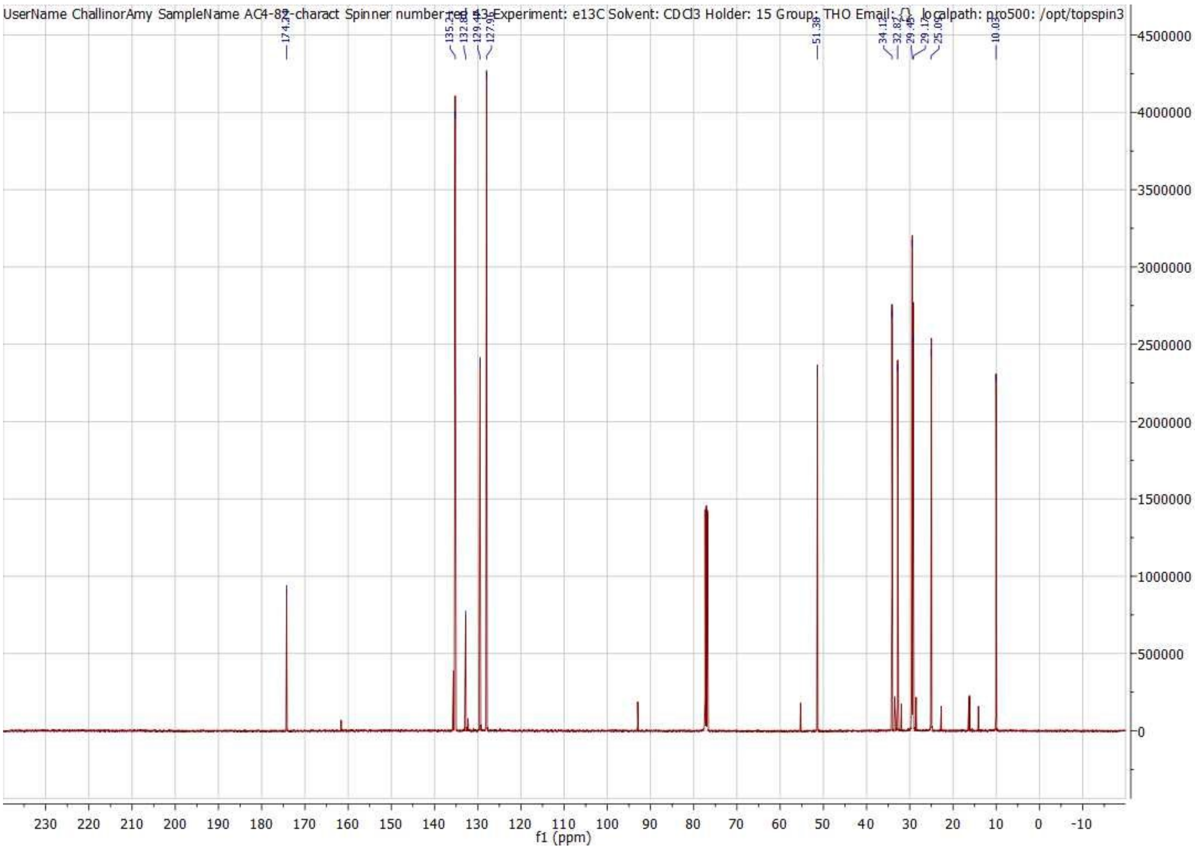

UserName ChallinorAmy SampleName AC4-78-charact Spinner number red 80 Experiment: e13C Solvent: CDCl3 Holder: 8 Group: THO Email: {} localpath: pro500: /opt/topspin3.2
161.9
160.0
135.2
132.0
129.7
128.1
124.0
115.3
24.5
10.9
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

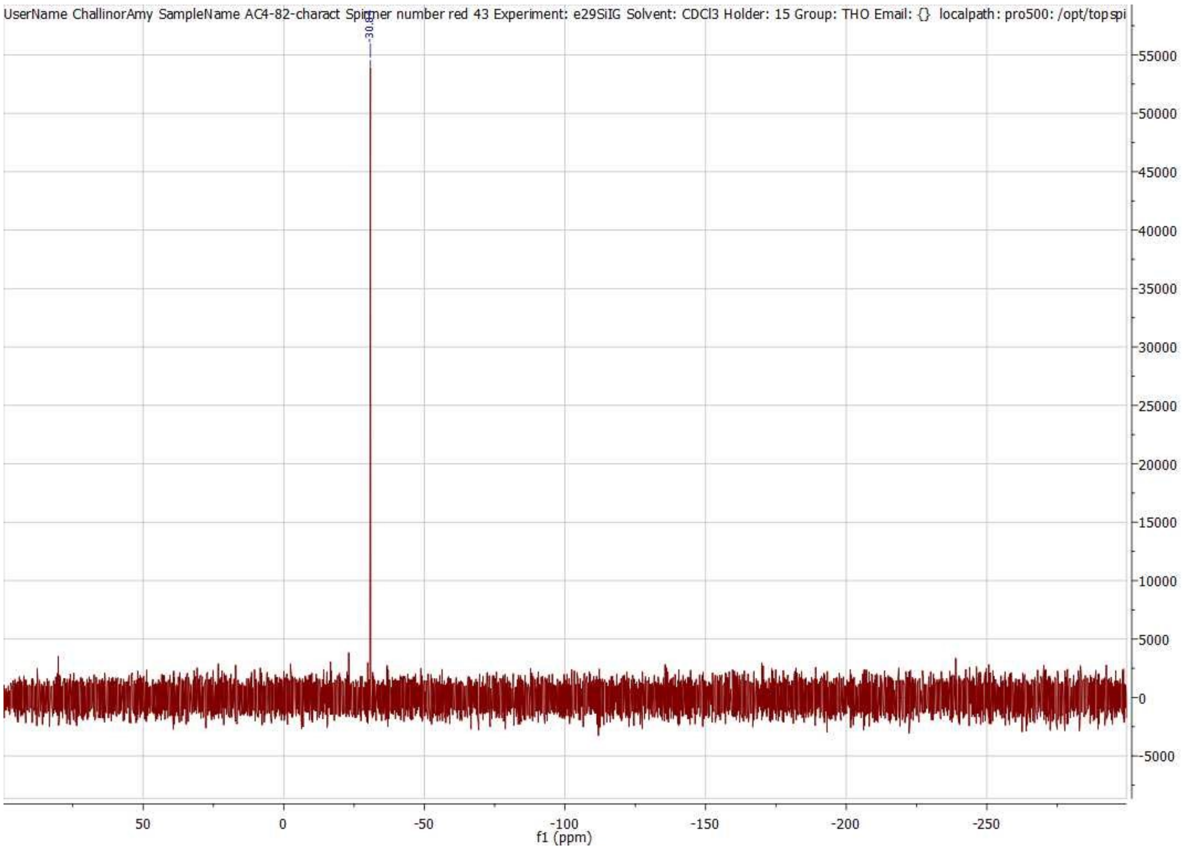

UserName ChallinorAmy SampleName AC4-78-charact Spinner number red 80 Experiment: e29SiIG Solvent: CDCl3 Holder: 8 Group: THO Email: {} localpath: pro500: /opt/topspin
-31.0
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

Methyl ester 11-(phenylsilyl)-undecanoic acid (2l)

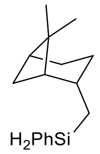


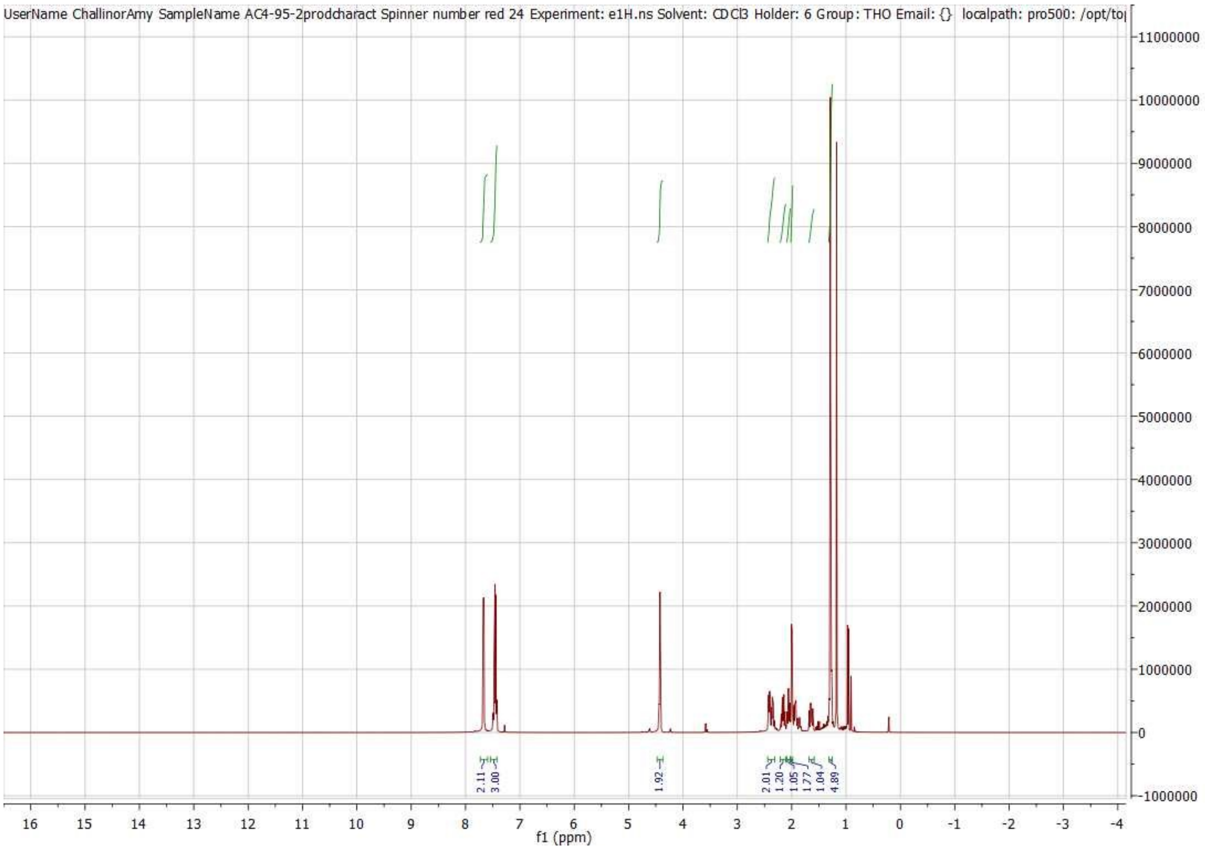


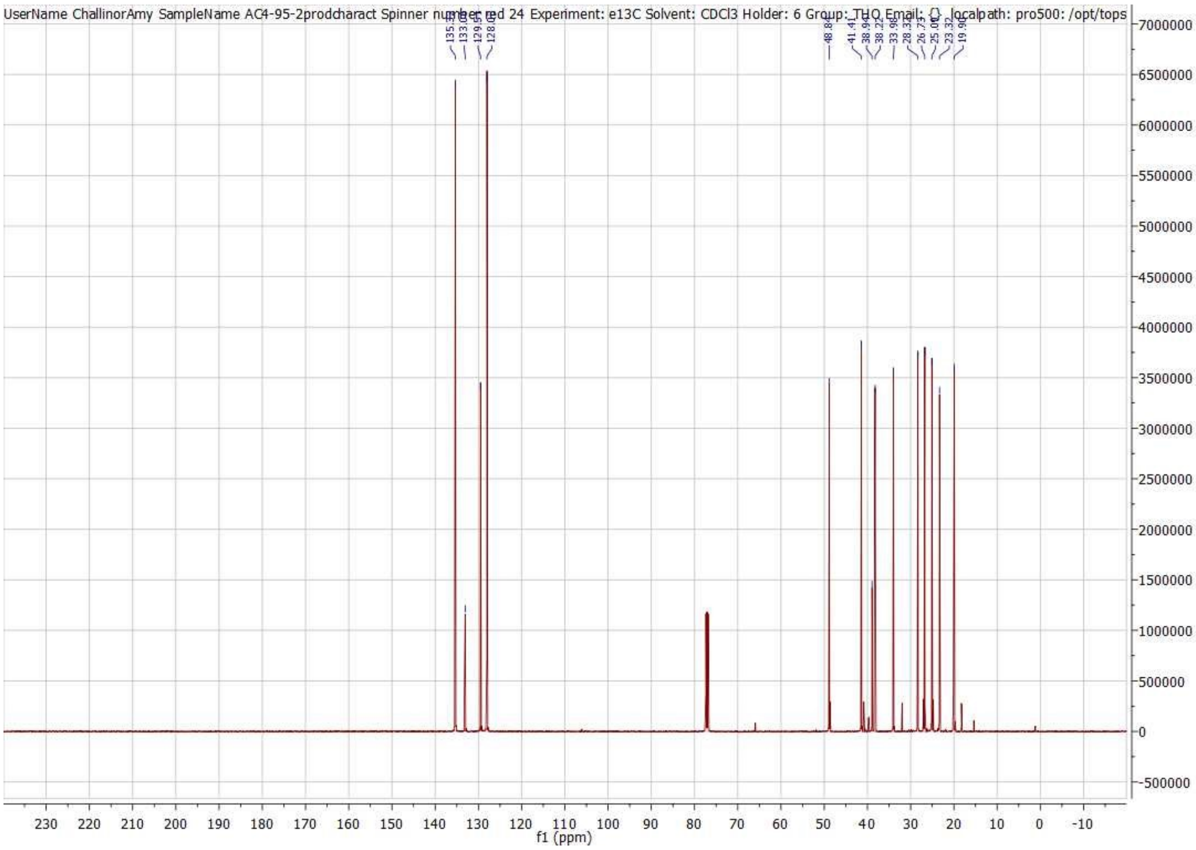


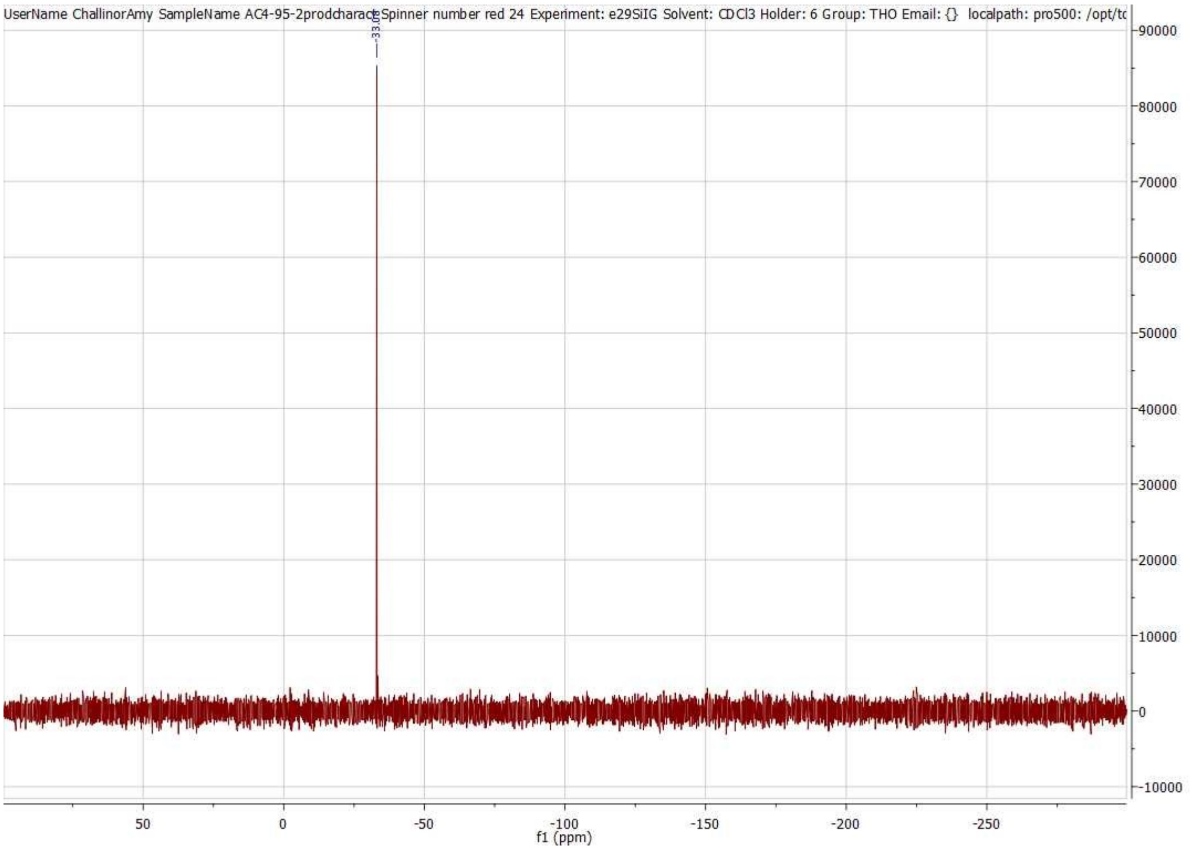

UserName ChallinorAmy SampleName AC4-82-charact Spinner number red 43 Experiment: e29SiIG Solvent: CDCl3 Holder: 15 Group: THO Email: {} localpath: pro500: /opt/topspi
-30.8
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

Phenyl-(10-pinanyl)-silane (2m)

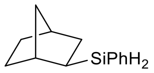


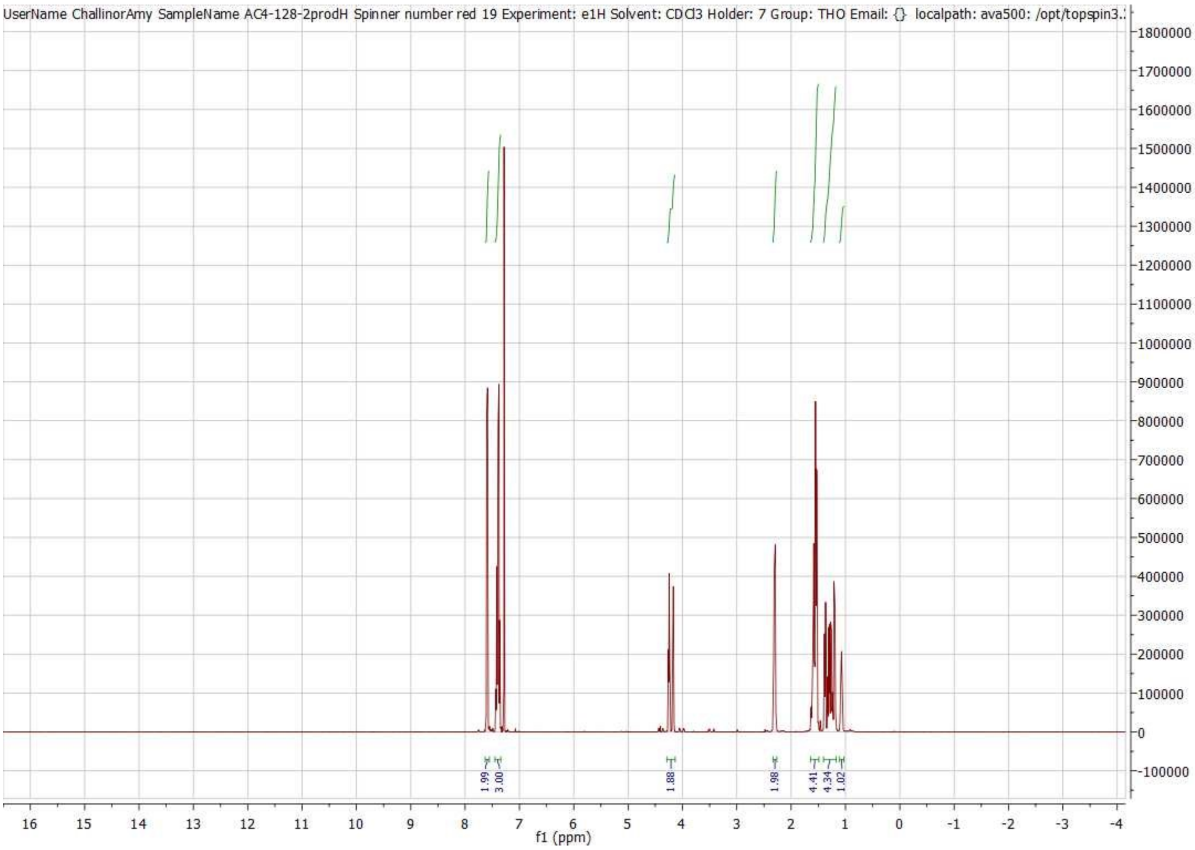


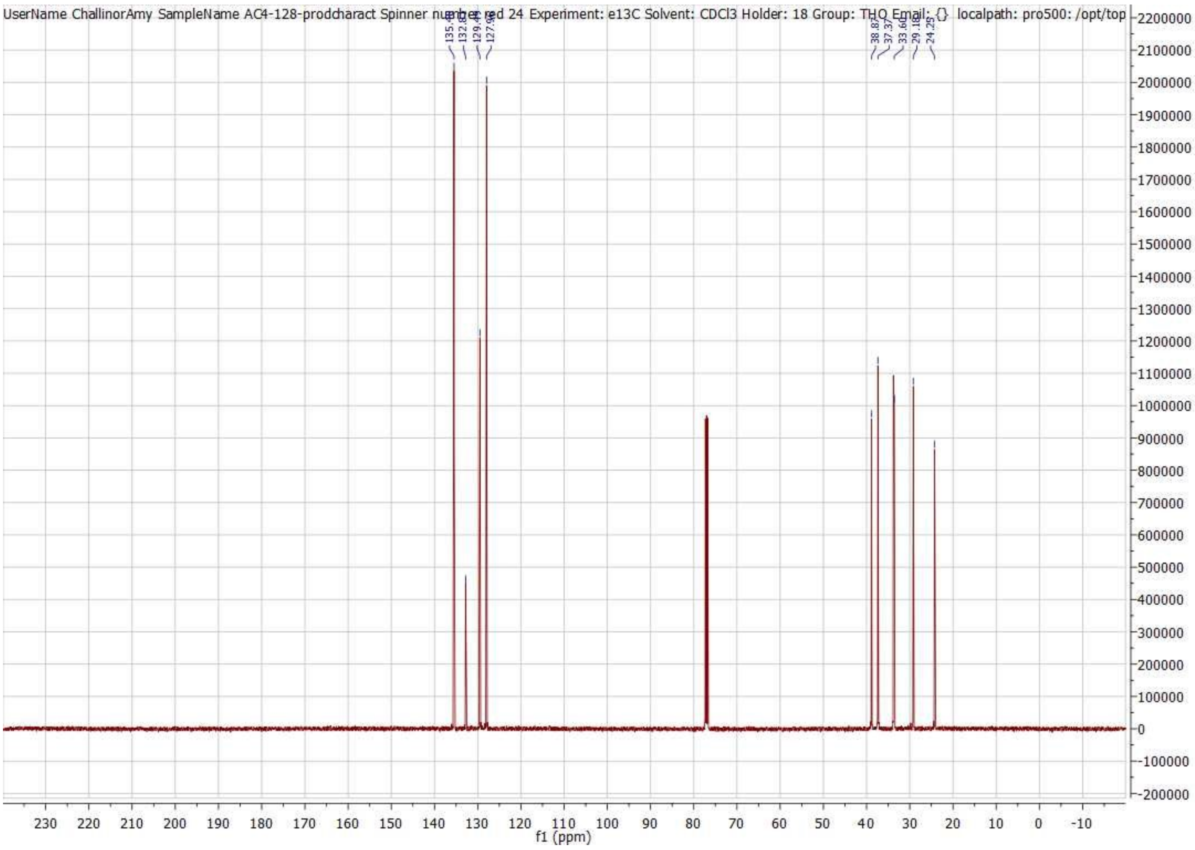

UserName ChallinorAmy SampleName AC4-95-2prodcharact Spinner number red 24 Experiment: e13C Solvent: CDCl3 Holder: 6 Group: THO Email: {} localpath: pro500: /opt/tops
135.3
133.0
129.5
128.0
48.8
41.41
38.94
38.22
33.98
28.34
26.73
25.06
23.32
19.90
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

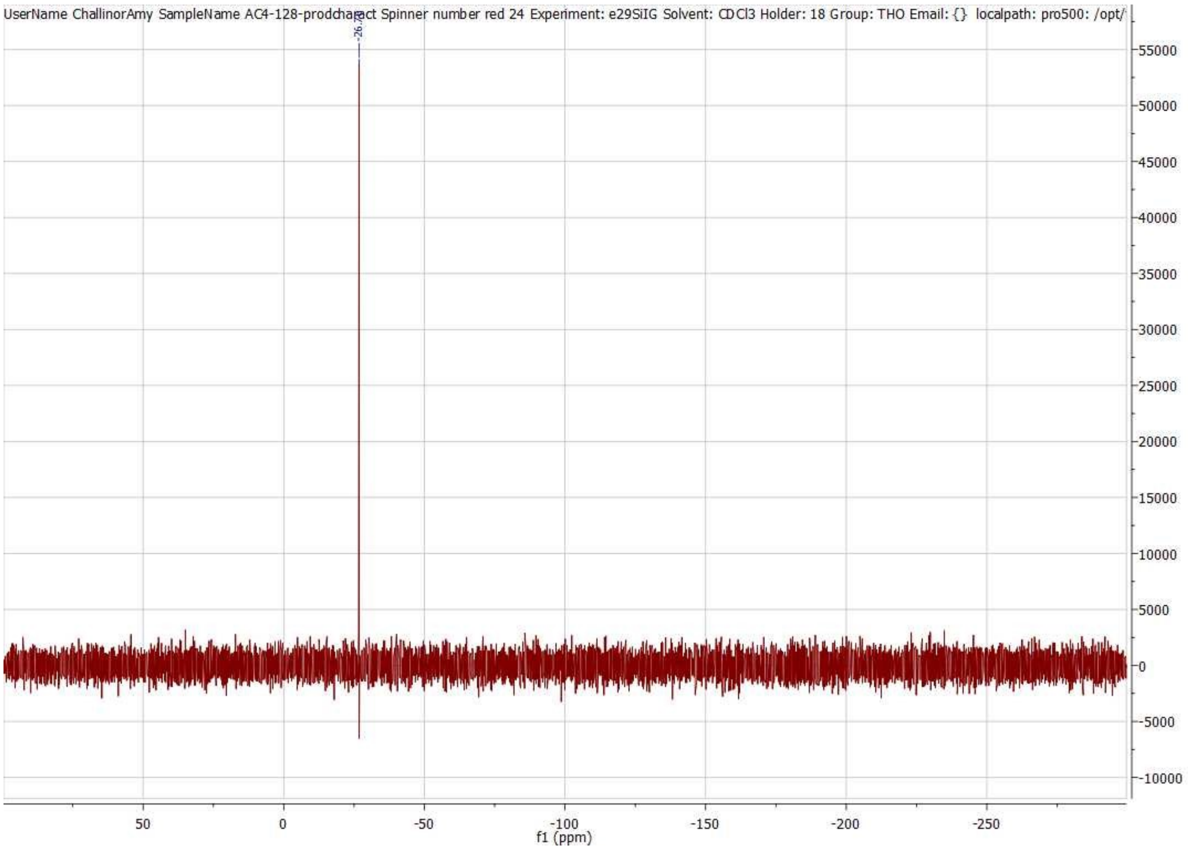

UserName ChallinorAmy SampleName AC4-95-2prodcharact Spinner number red 24 Experiment: e29SiIG Solvent: CDCl3 Holder: 6 Group: THO Email: {} localpath: pro500: /opt/tc
-33.0
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50 0 -50 -100 -150 -200 -250
f1 (ppm)

exo-2-(Phenylsilyl)bicyclo[2.2.l]heptane (2n)

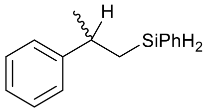


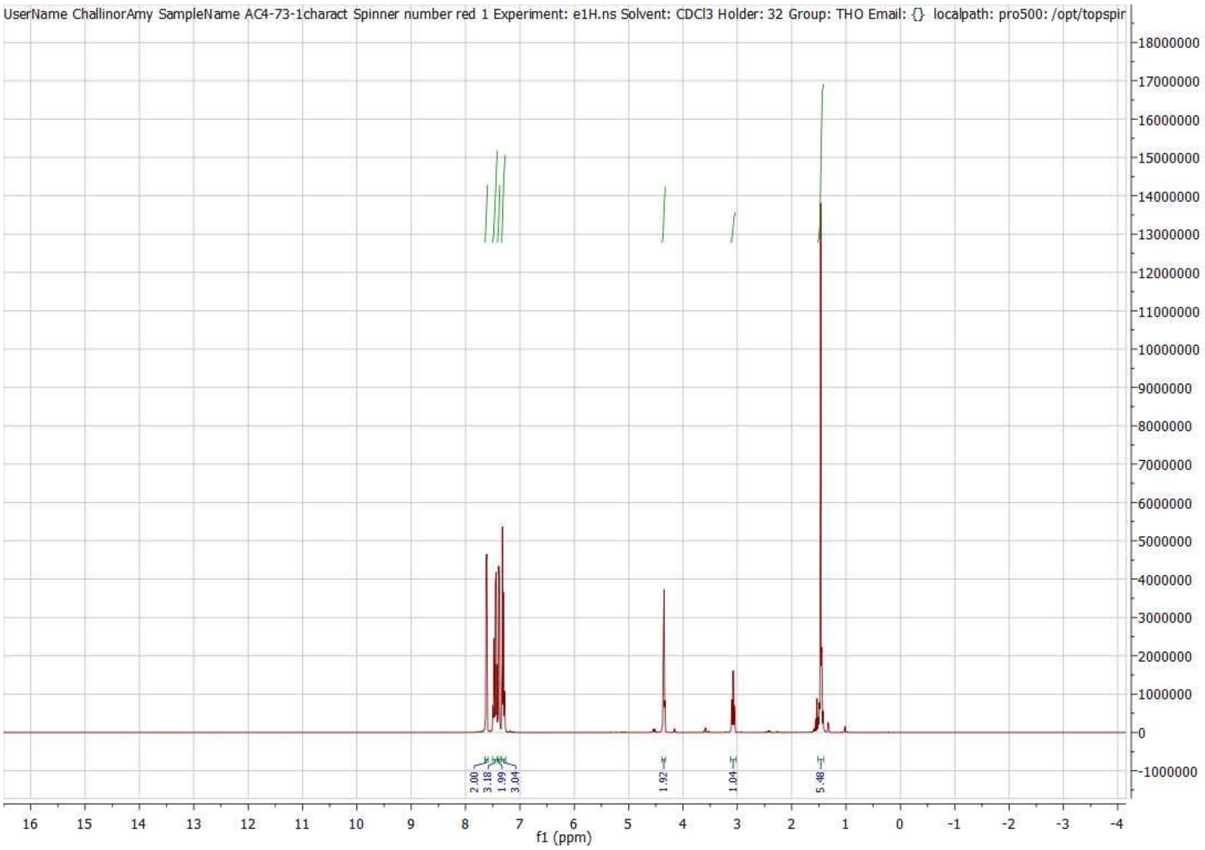


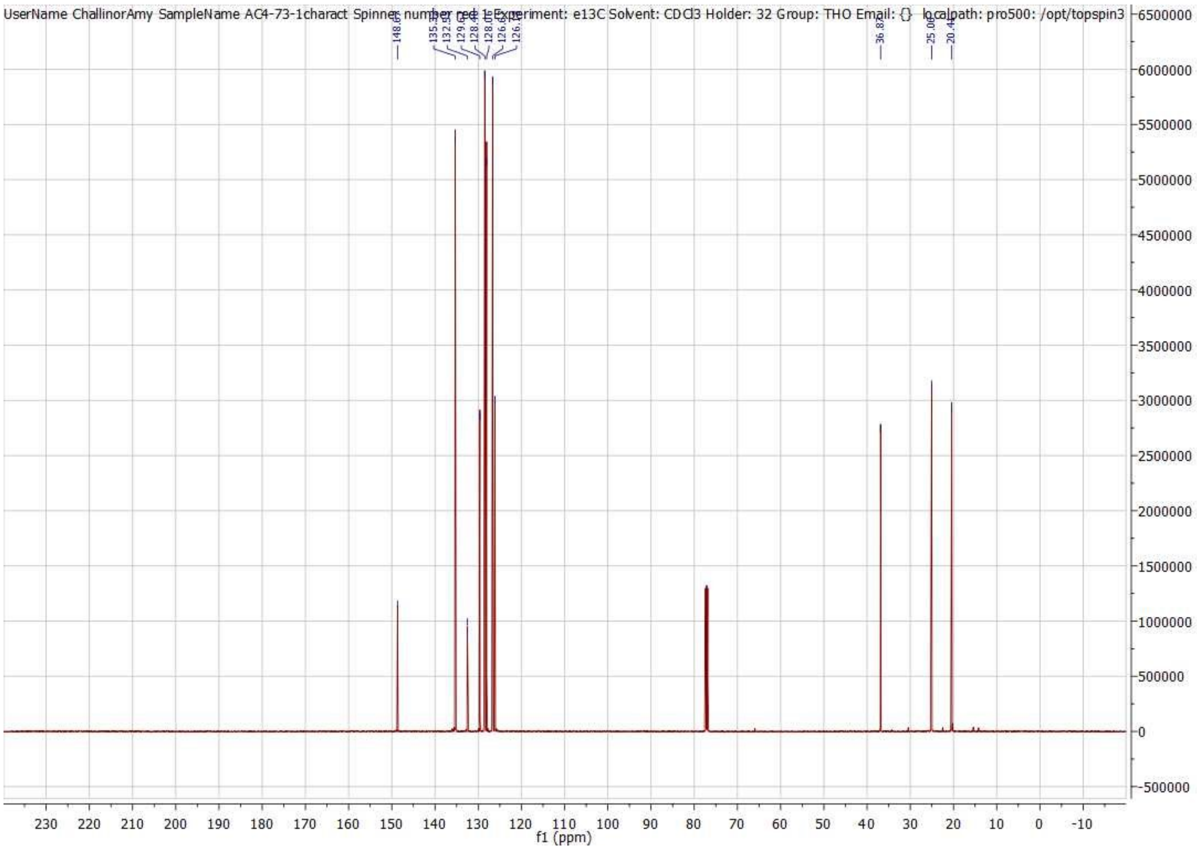


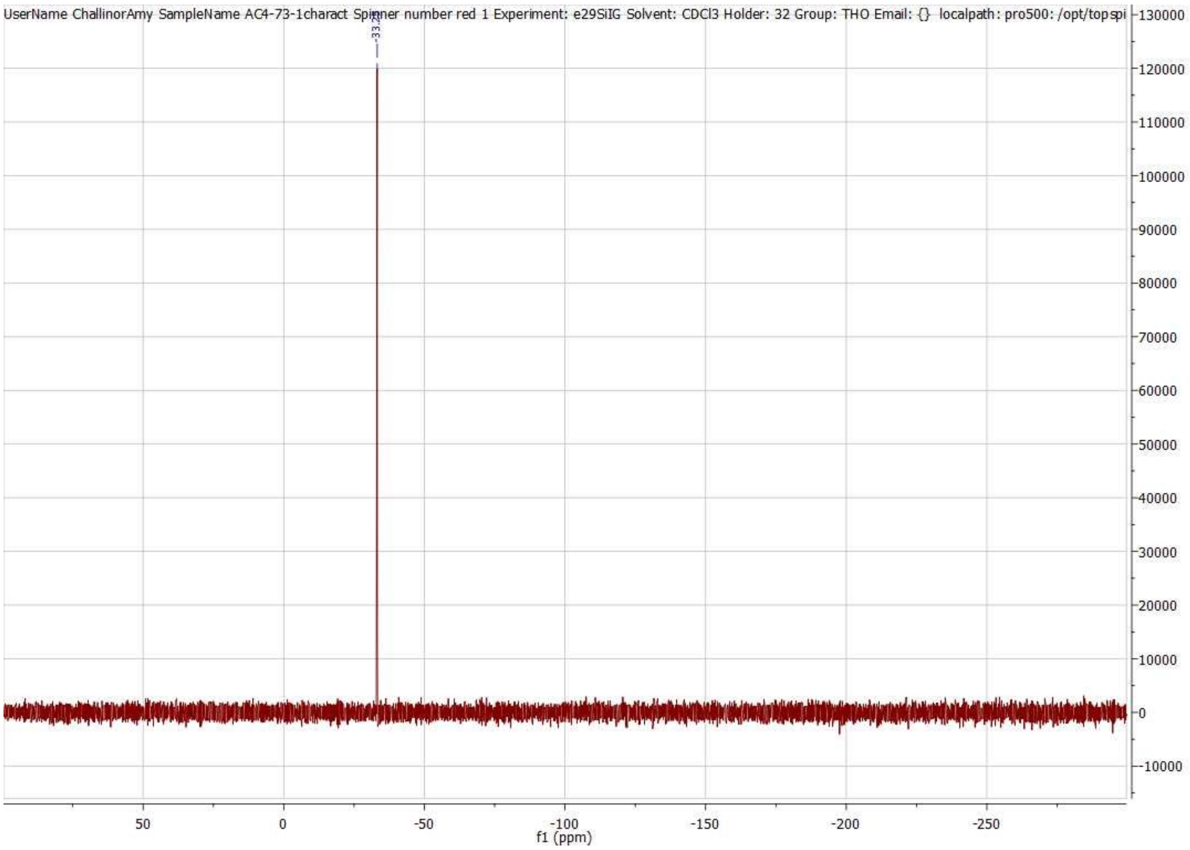

UserName ChallinorAmy SampleName AC4-128-prodcharact Spinner number red 24 Experiment: e29SiIG Solvent: CDCl3 Holder: 18 Group: THO Email: {} localpath: pro500: /opt/
-26.7
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-(Phenylsilyl)-2-phenylpropane (2o)

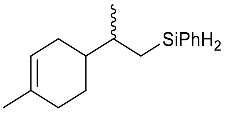


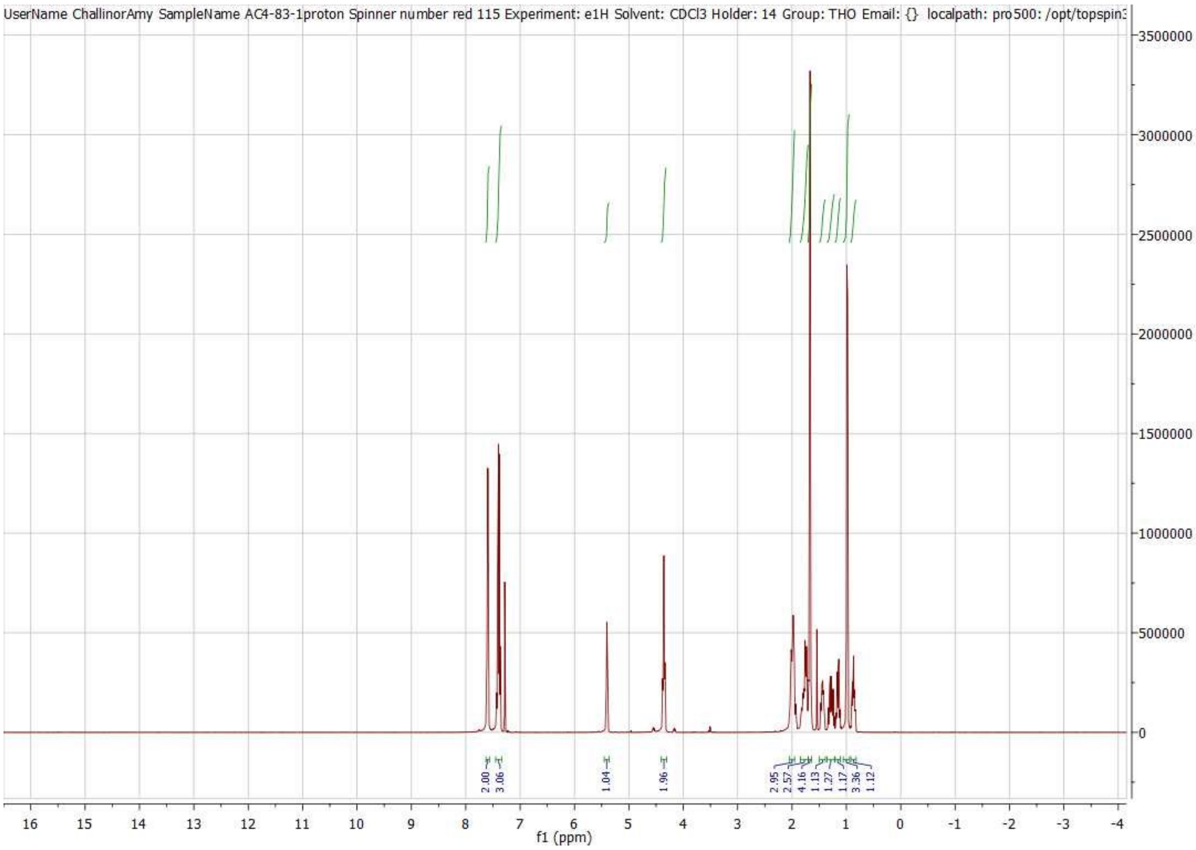


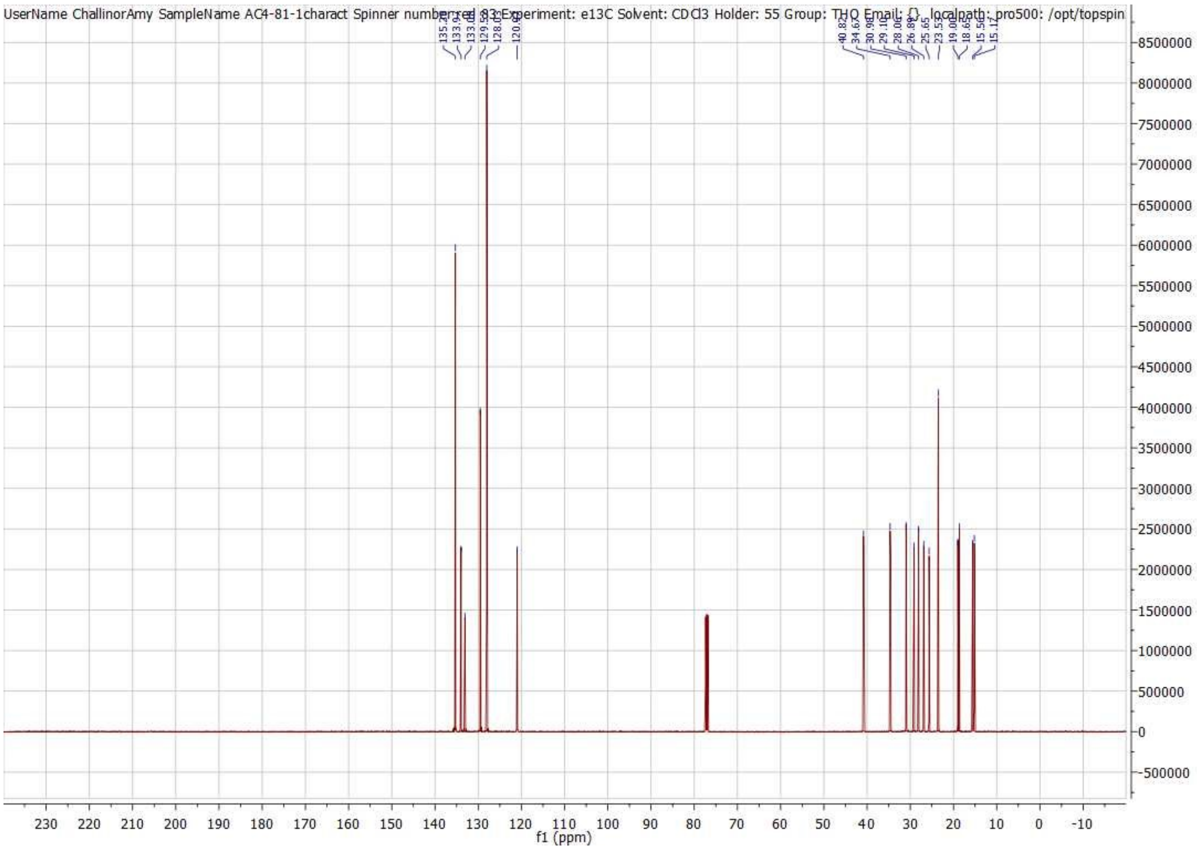

UserName ChallinorAmy SampleName AC4-73-1charact Spinner number red 1 Experiment: e13C Solvent: CDCl3 Holder: 32 Group: THO Email: {} localpath: pro500: /opt/topspin3
148.6
135.3
132.9
129.6
128.4
128.0
126.6
126.1
36.8
25.0
20.4
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

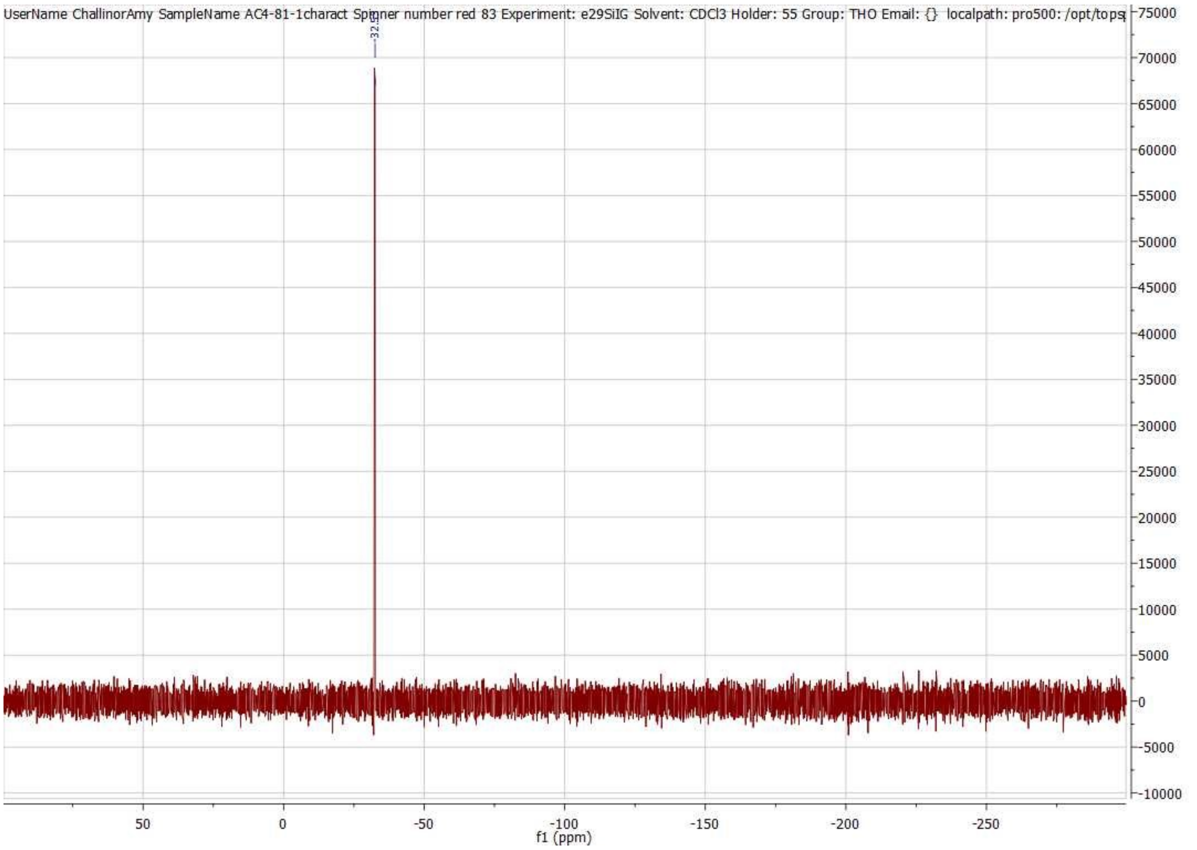

UserName ChallinorAmy SampleName AC4-73-1charact Spinner number red 1 Experiment: e29SiIG Solvent: CDCl3 Holder: 32 Group: THO Email: {} localpath: pro500: /opt/topspi
-33.2
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50 0 -50 -100 -150 -200 -250
f1 (ppm)

(4*R*)-1-Methyl-4-[(1*R*,*S*)-1-methyl-2-(phenylsilyl)ethyl]-cyclohex-1-ene (2p)

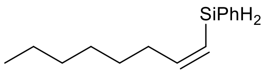


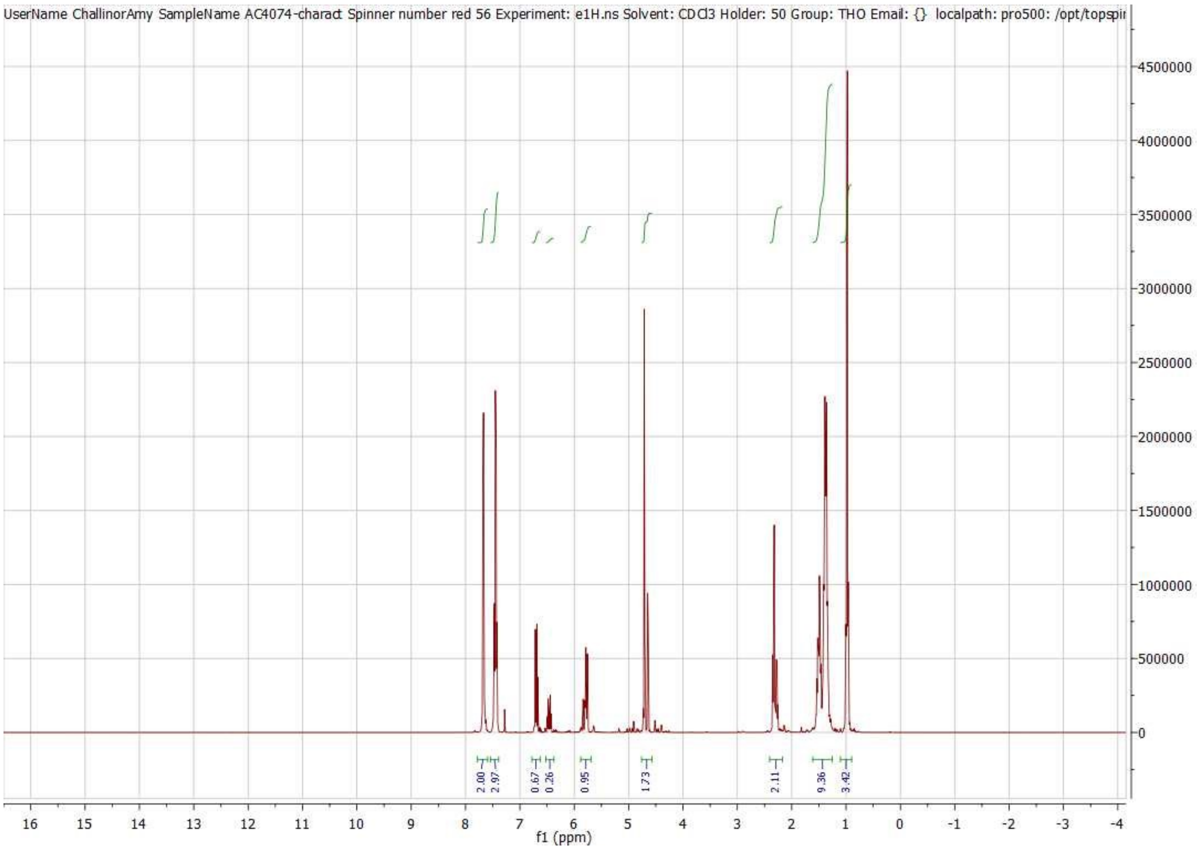


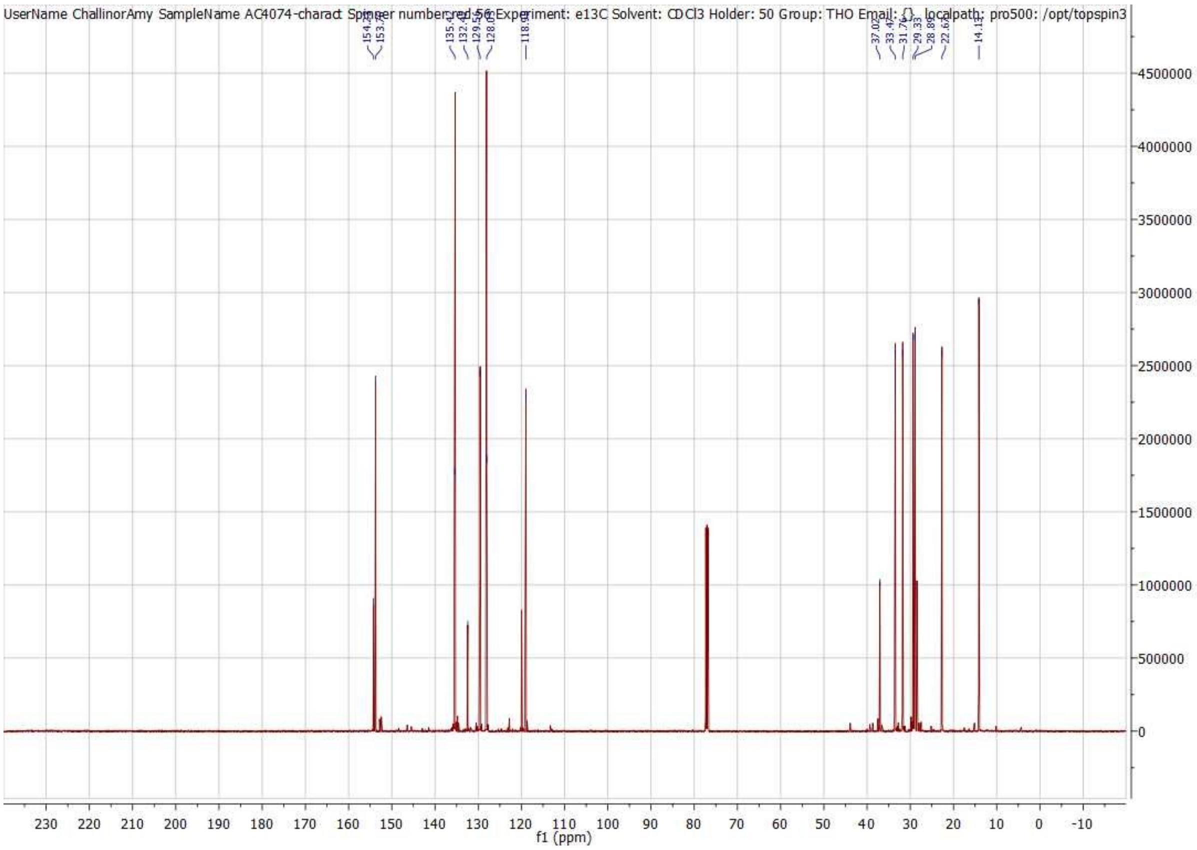

UserName ChallinorAmy SampleName AC4-81-1charact Spinner number red 83 Experiment: e13C Solvent: CDCl3 Holder: 55 Group: THO Email: {} localpath: pro500: /opt/topspin
135.2
133.9
133.0
129.5
128.0
120.9
40.82
34.67
30.98
29.10
28.06
26.89
25.65
23.53
19.00
18.65
15.56
15.17
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

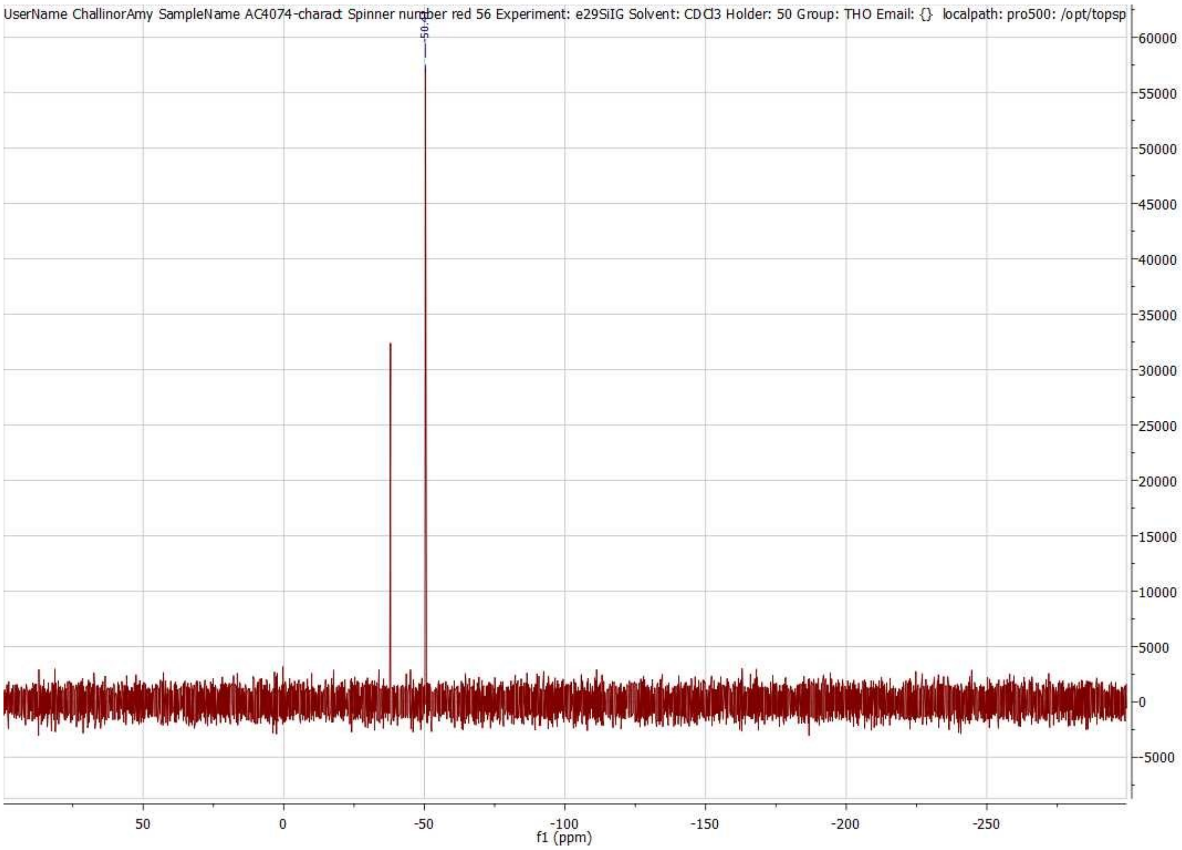

UserName ChallinorAmy SampleName AC4-81-1charact Spinner number red 83 Experiment: e29SiIG Solvent: CDCl3 Holder: 55 Group: THO Email: {} localpath: pro500: /opt/tops
-32.5
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50 0 -50 -100 -150 -200 -250
f1 (ppm)

cis-1-Octen-1-ylsilylbenzene (2q)

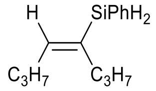


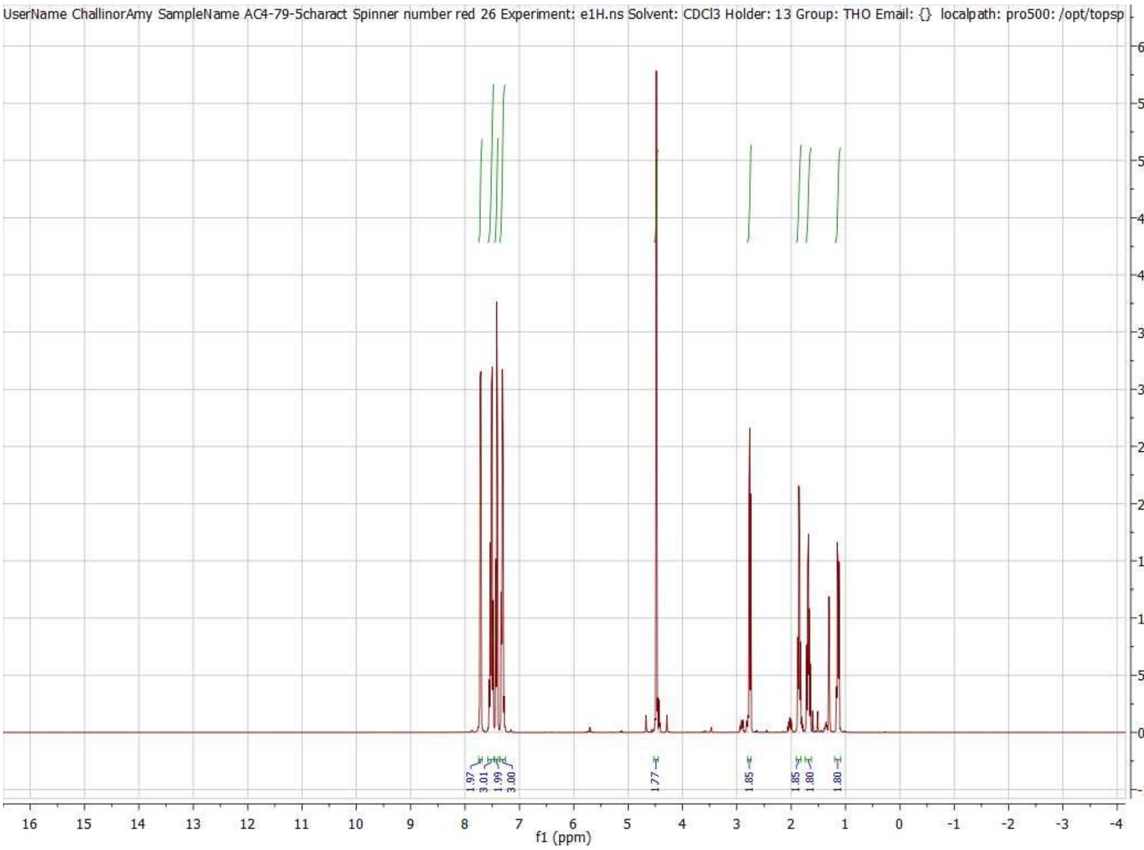


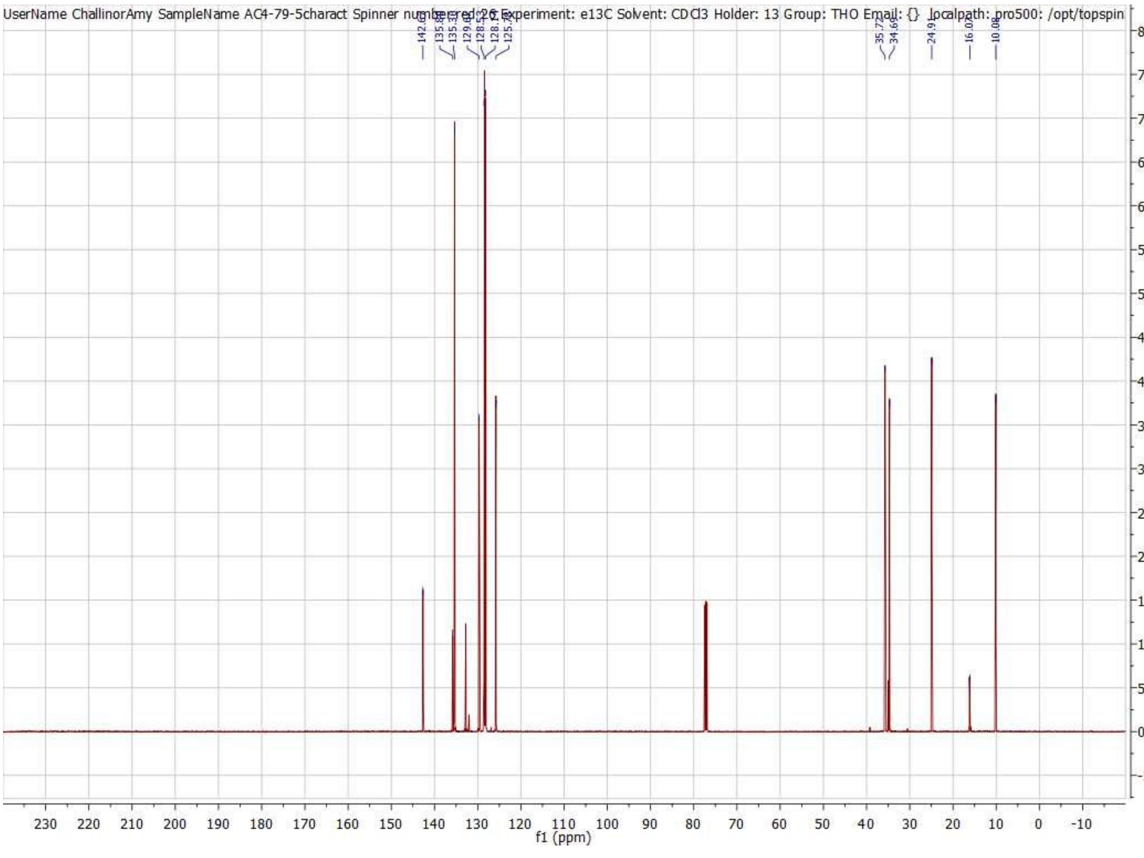


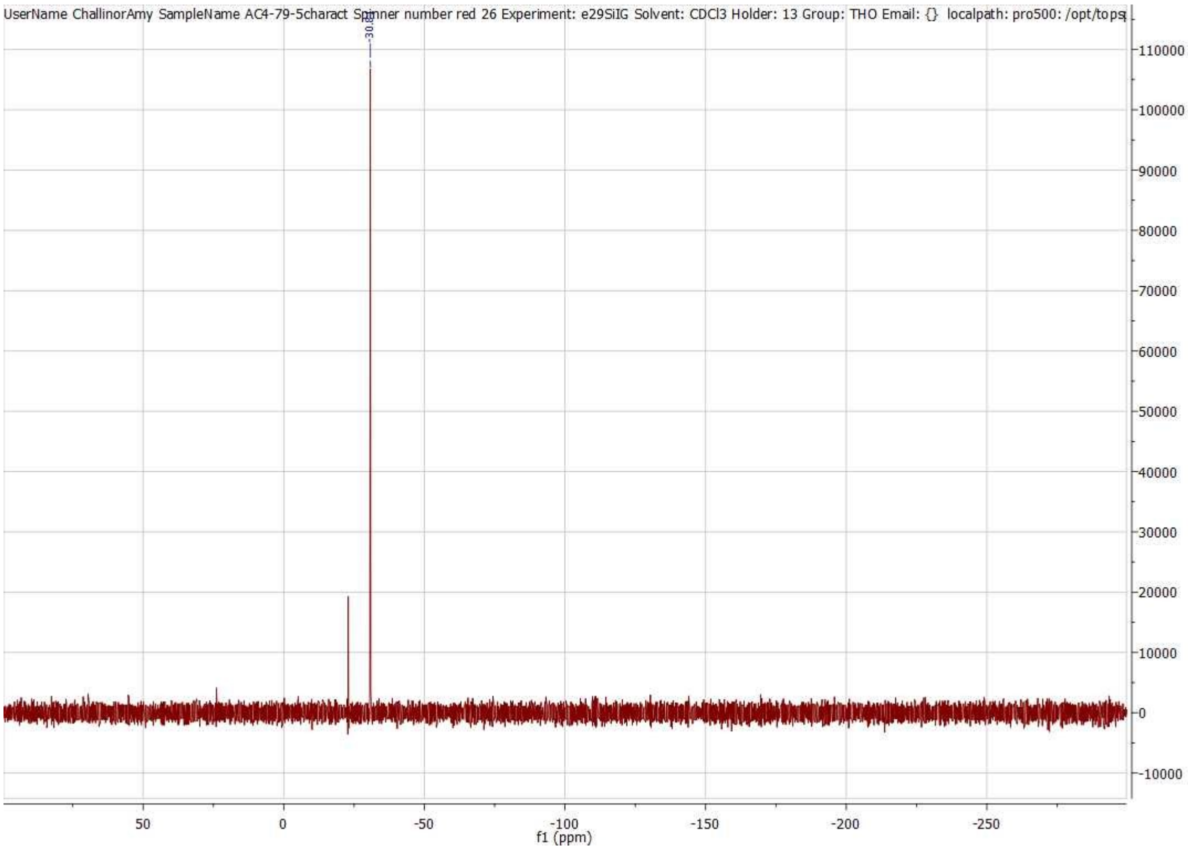

UserName ChallinorAmy SampleName AC4074-charact Spinner number red 56 Experiment: e29SiIG Solvent: CDCl3 Holder: 50 Group: THO Email: {} localpath: pro500: /opt/topsp
-50.4
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

Phenyl[(*E*)-1-propyl-1-pentenyl]silane (2r)



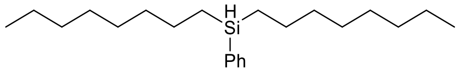


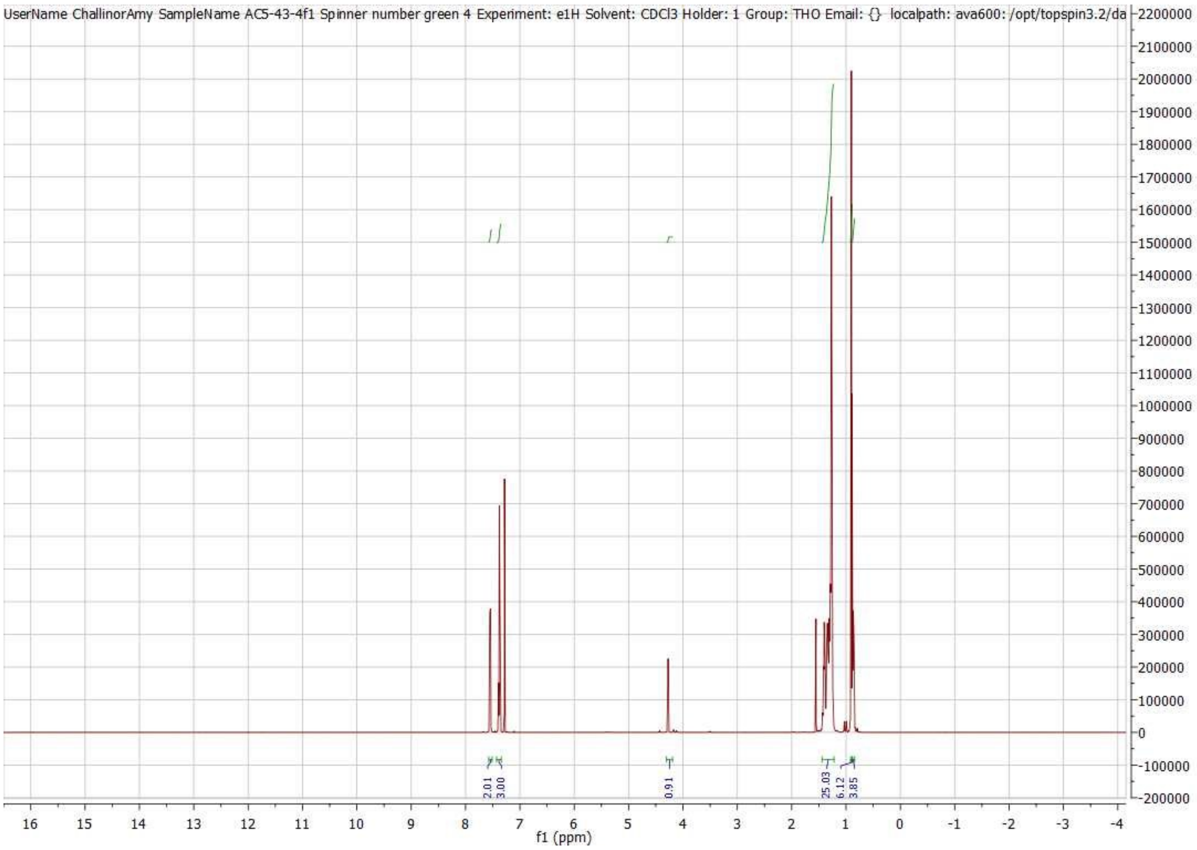


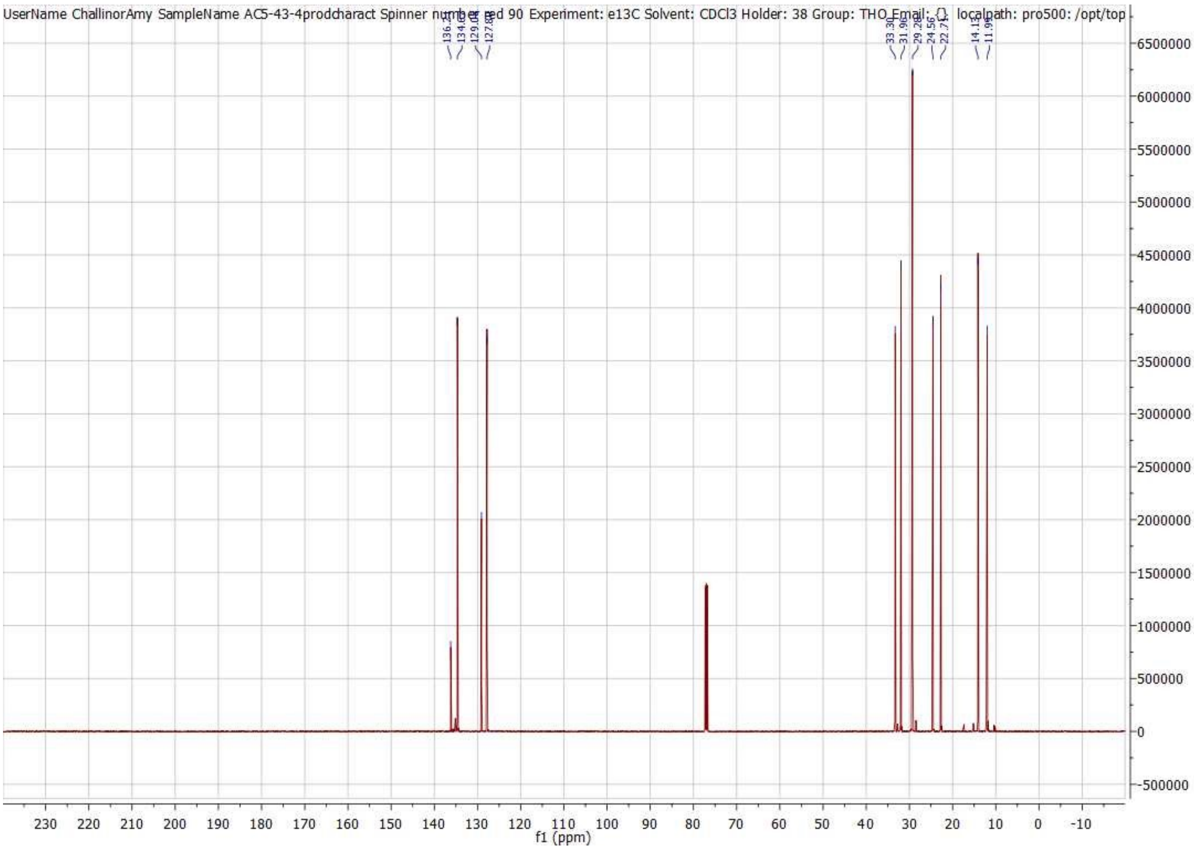

UserName ChallinorAmy SampleName AC4-79-5charact Spinner number red 26 Experiment: e29SiIG Solvent: CDCl3 Holder: 13 Group: THO Email: {} localpath: pro500: /opt/tops
-30.8
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

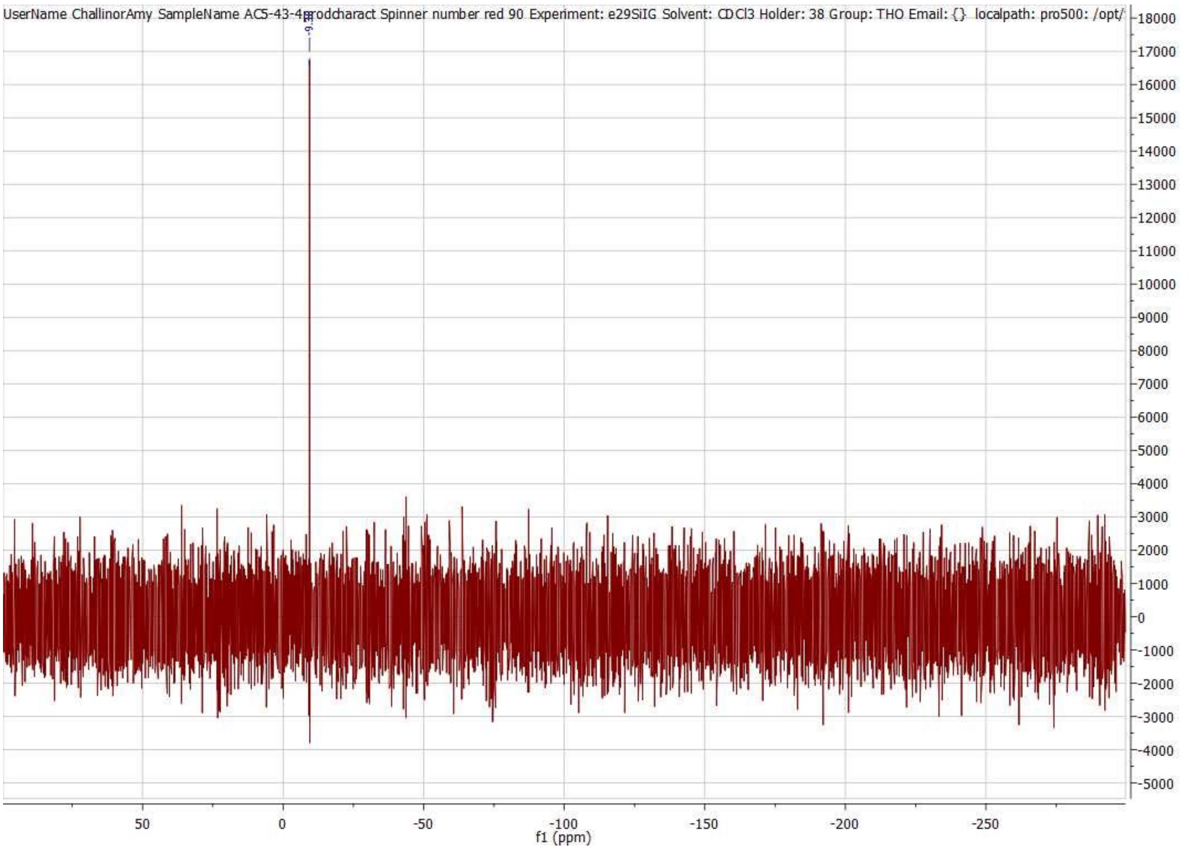
Tertiary Silane Products

Dioctylphenylsilane (2s)

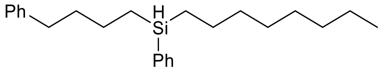


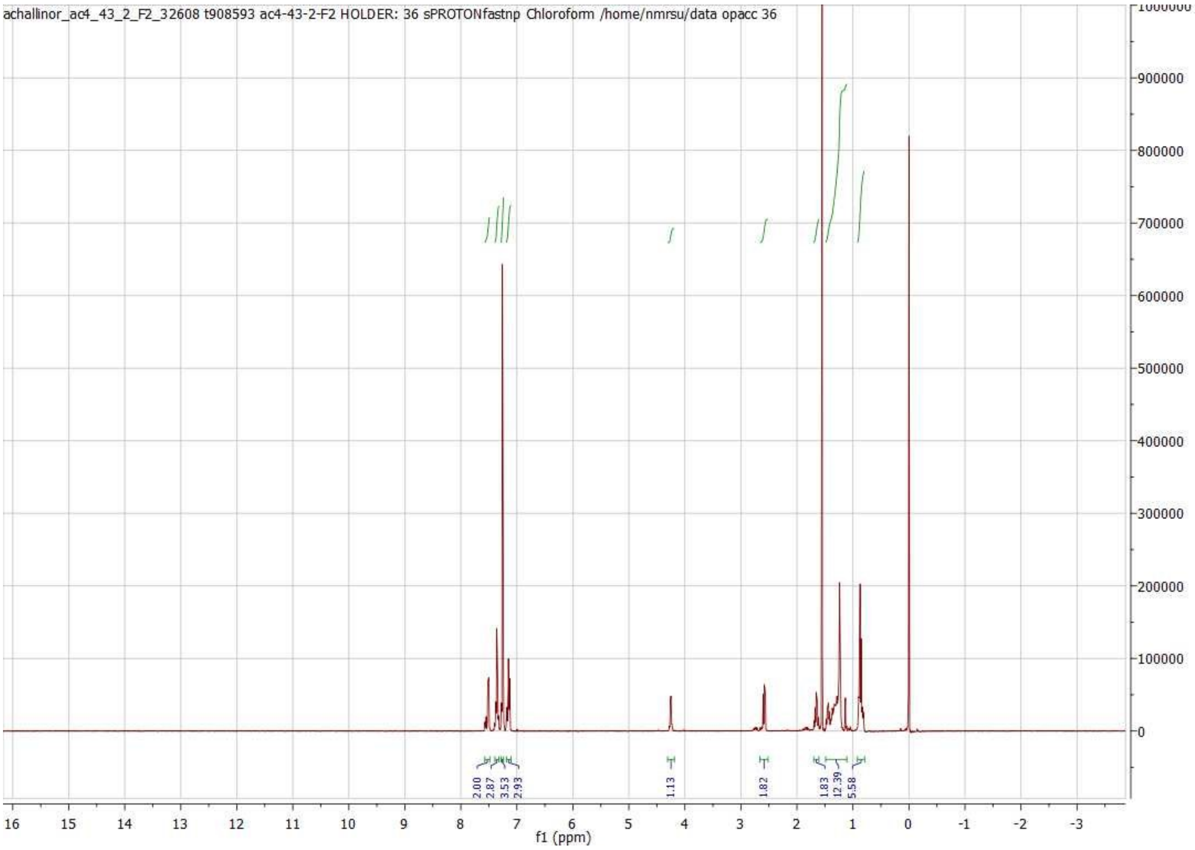


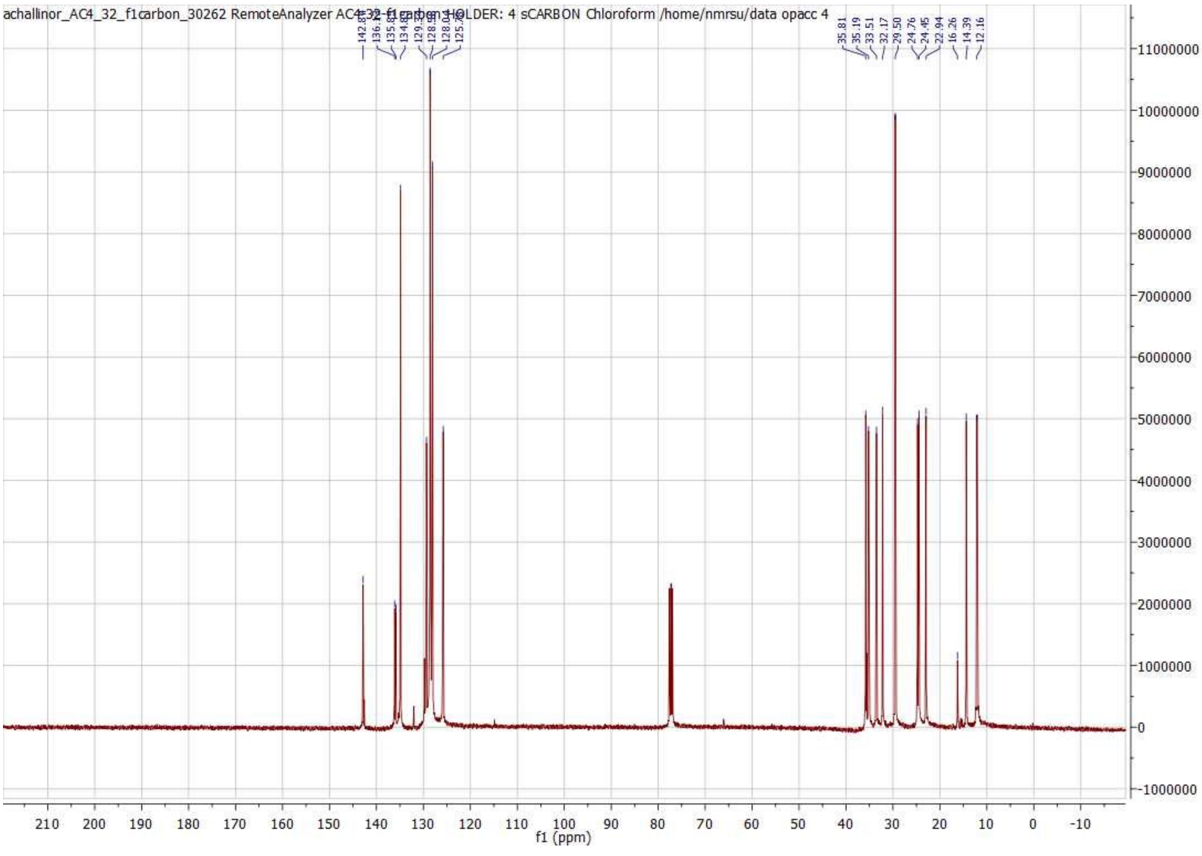

UserName ChallinorAmy SampleName AC5-43-4prodcharact Spinner number red 90 Experiment: e13C Solvent: CDCl3 Holder: 38 Group: THO Email: {} localpath: pro500: /opt/top
136.2
134.6
129.0
127.8
33.30
31.96
29.28
24.56
22.71
14.13
11.95
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

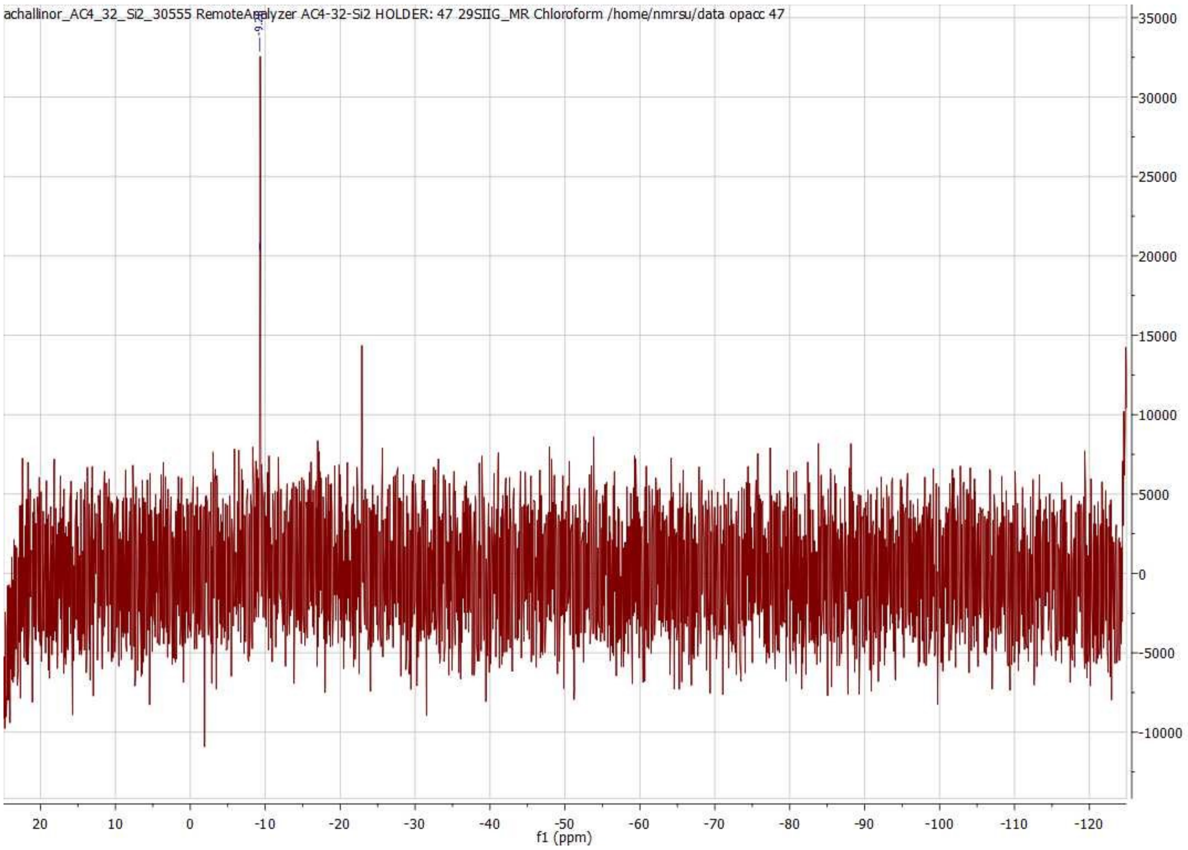

UserName ChallinorAmy SampleName AC5-43-4prodcharact Spinner number red 90 Experiment: e29SiIG Solvent: CDCl3 Holder: 38 Group: THO Email: {} localpath: pro500: /opt/
-9.3
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-Phenyl-4-(octylphenylsilyl)butane (2t)



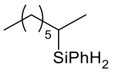


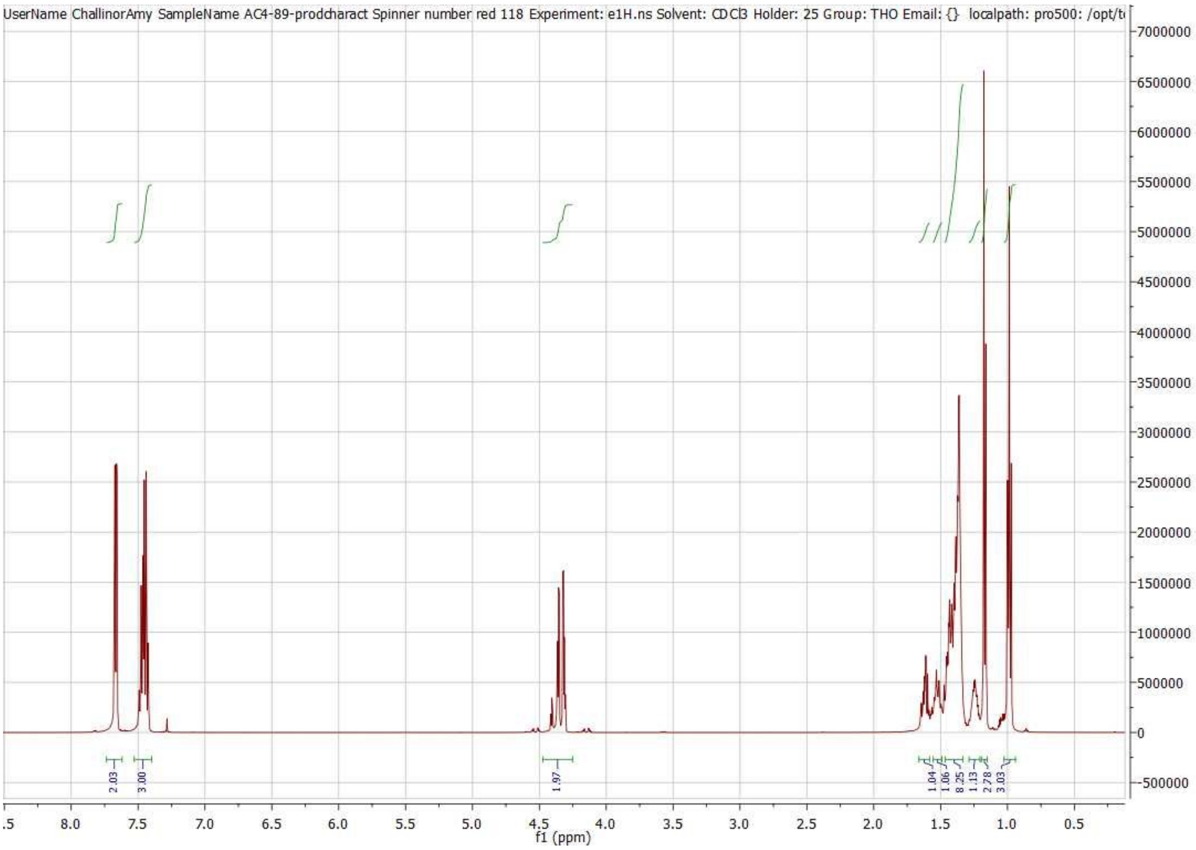


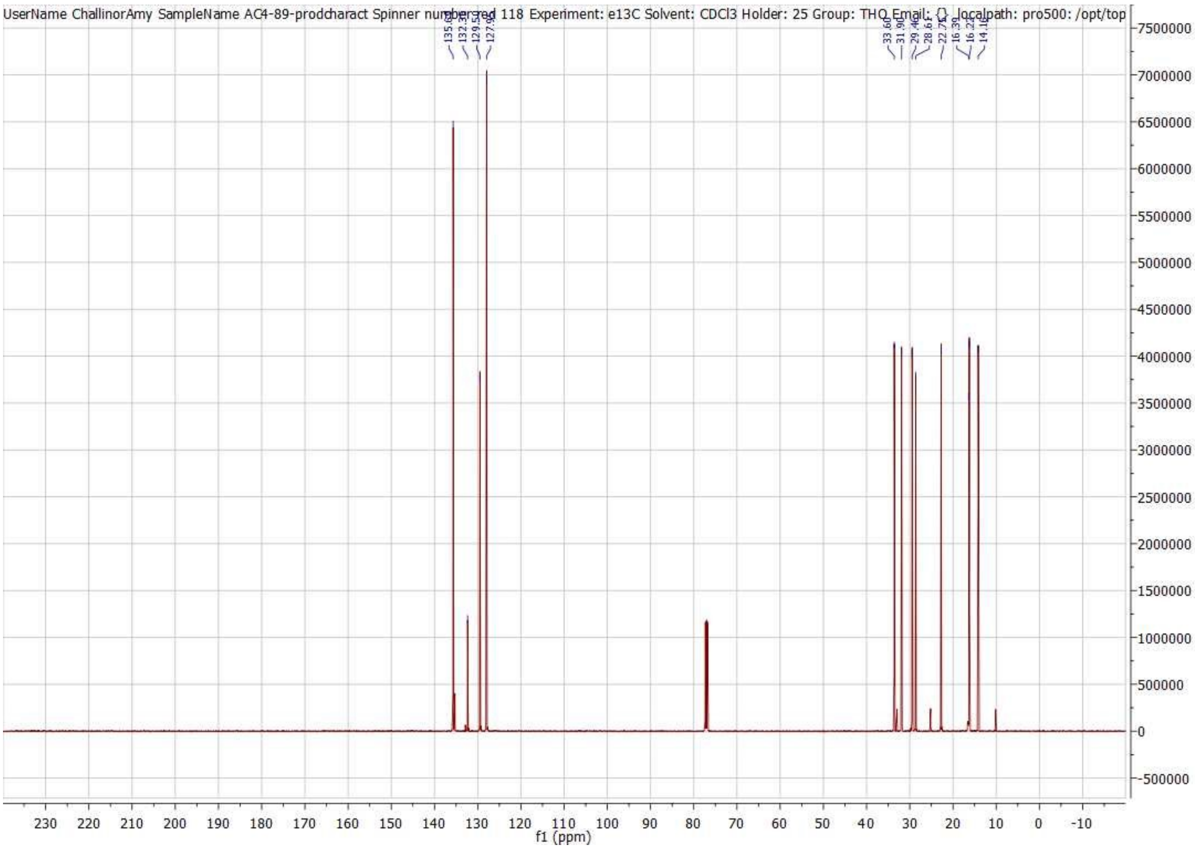

achallinor_AC4_32_Si2_30555 RemoteAnalyzer AC4-32-Si2 HOLDER: 47 29SIIG_MR Chloroform /home/nmrsu/data opacc 47
-9.23
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
f1 (ppm)

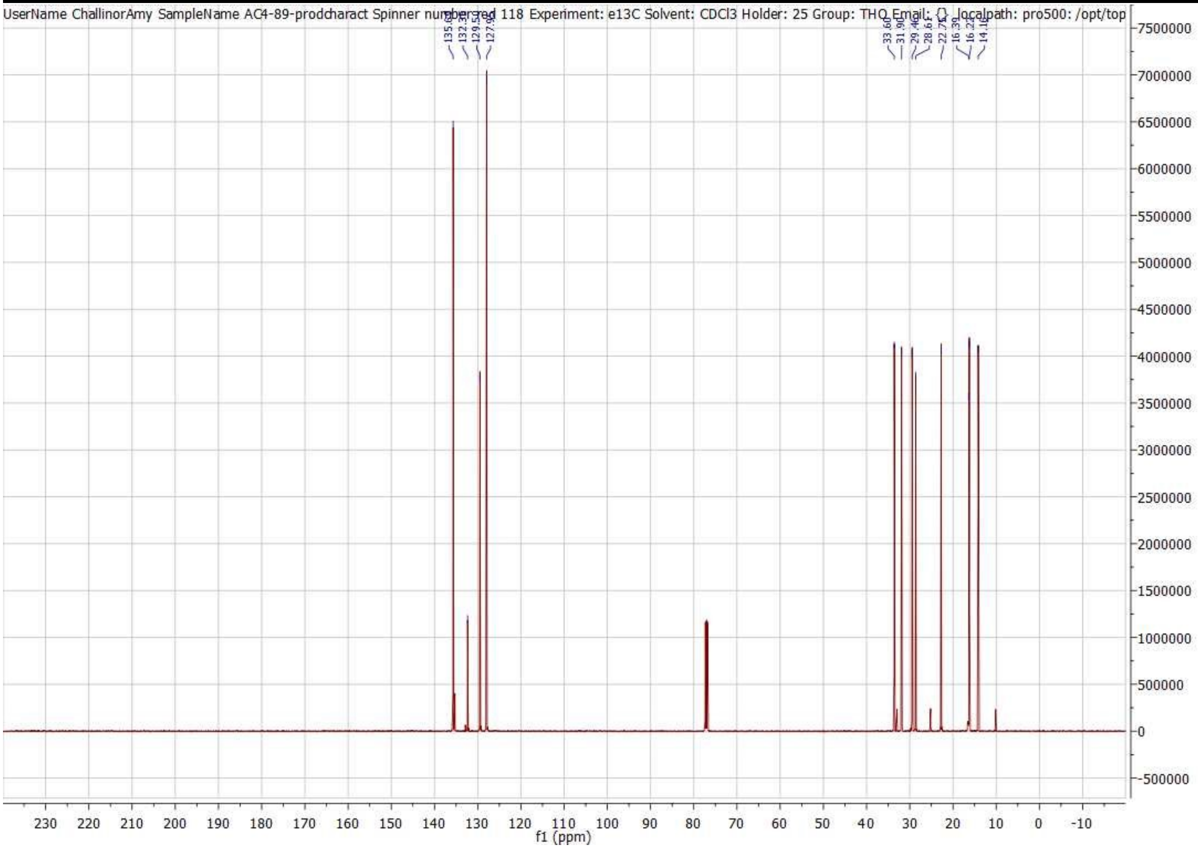
Cobalt-Catalysed

Octan-2-yl(phenyl)silane (3a)

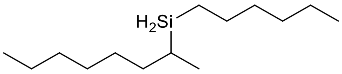


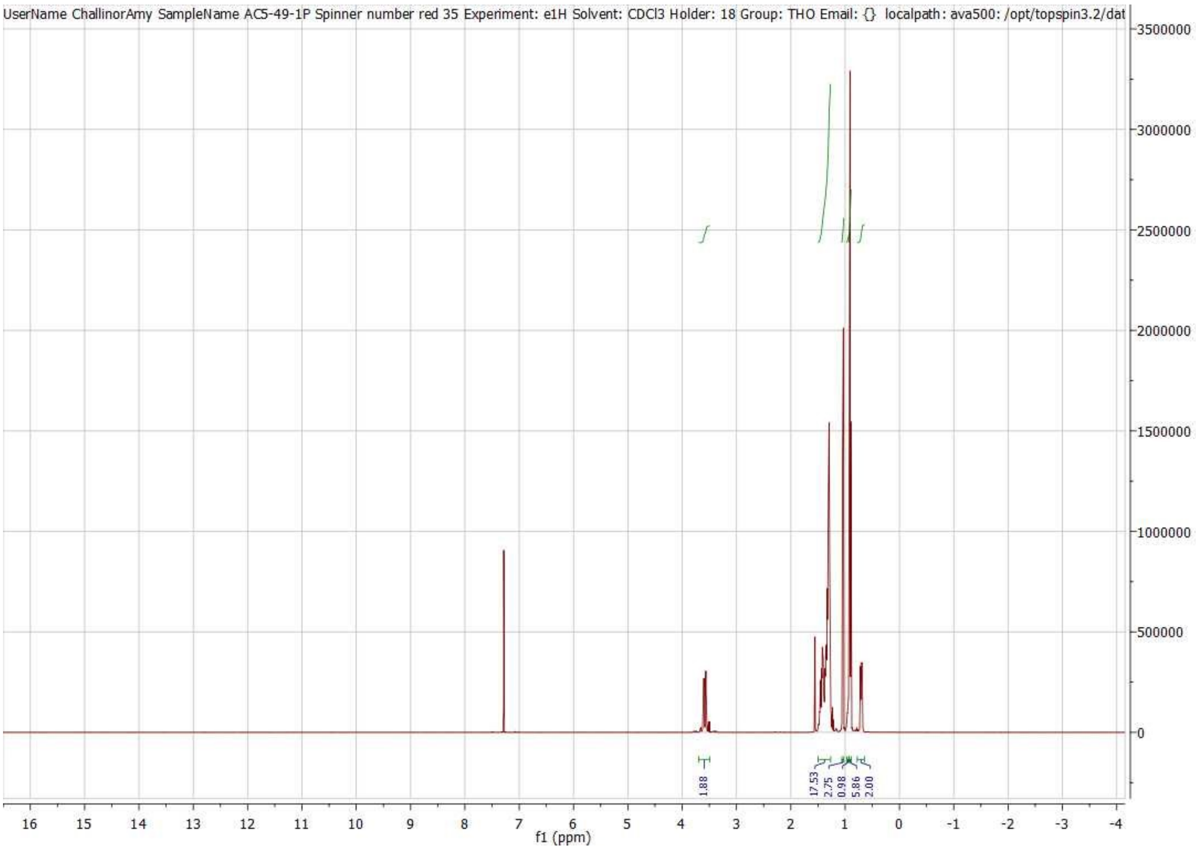


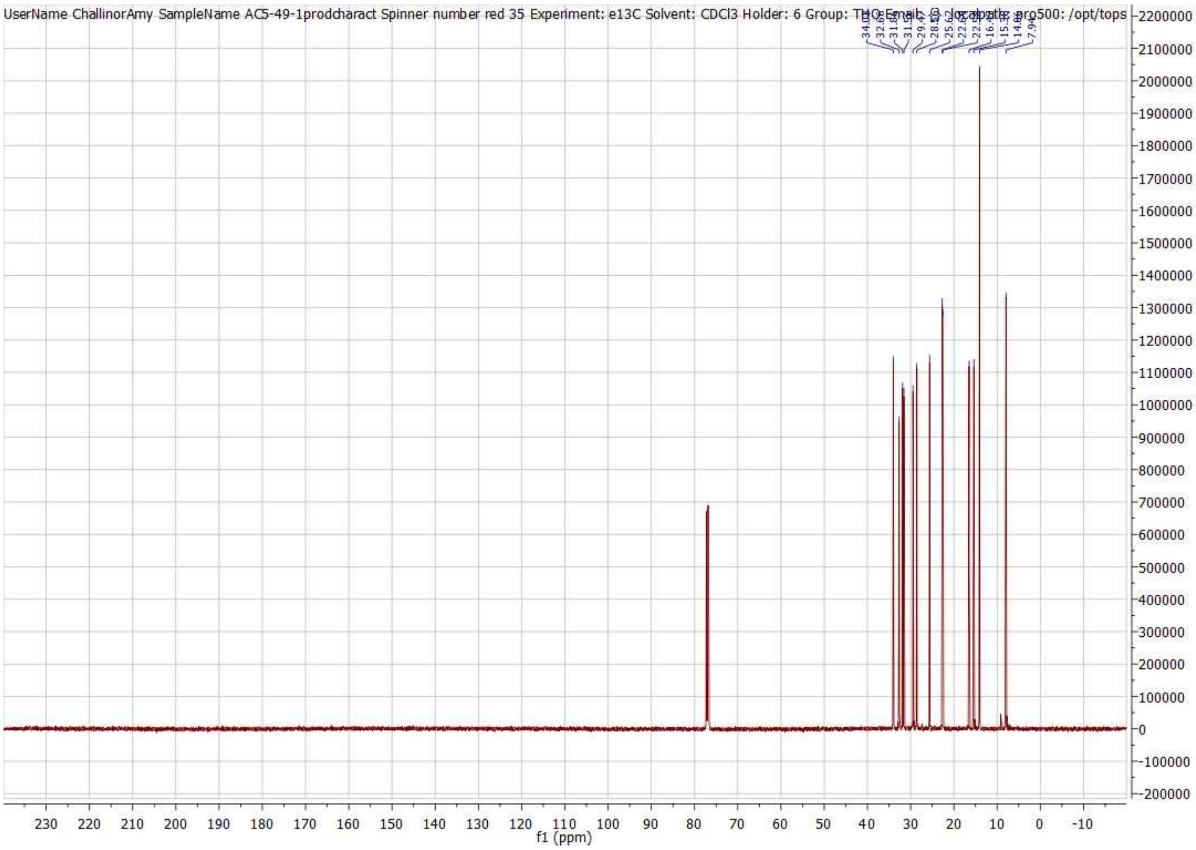

UserName ChallinorAmy SampleName AC4-89-prodcharact Spinner number red 118 Experiment: e13C Solvent: CDCl3 Holder: 25 Group: THQ Email: {} localpath: pro500: /opt/top
135.6
132.3
129.5
127.9
33.60
31.90
29.46
28.6
22.7
16.39
16.22
14.16
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

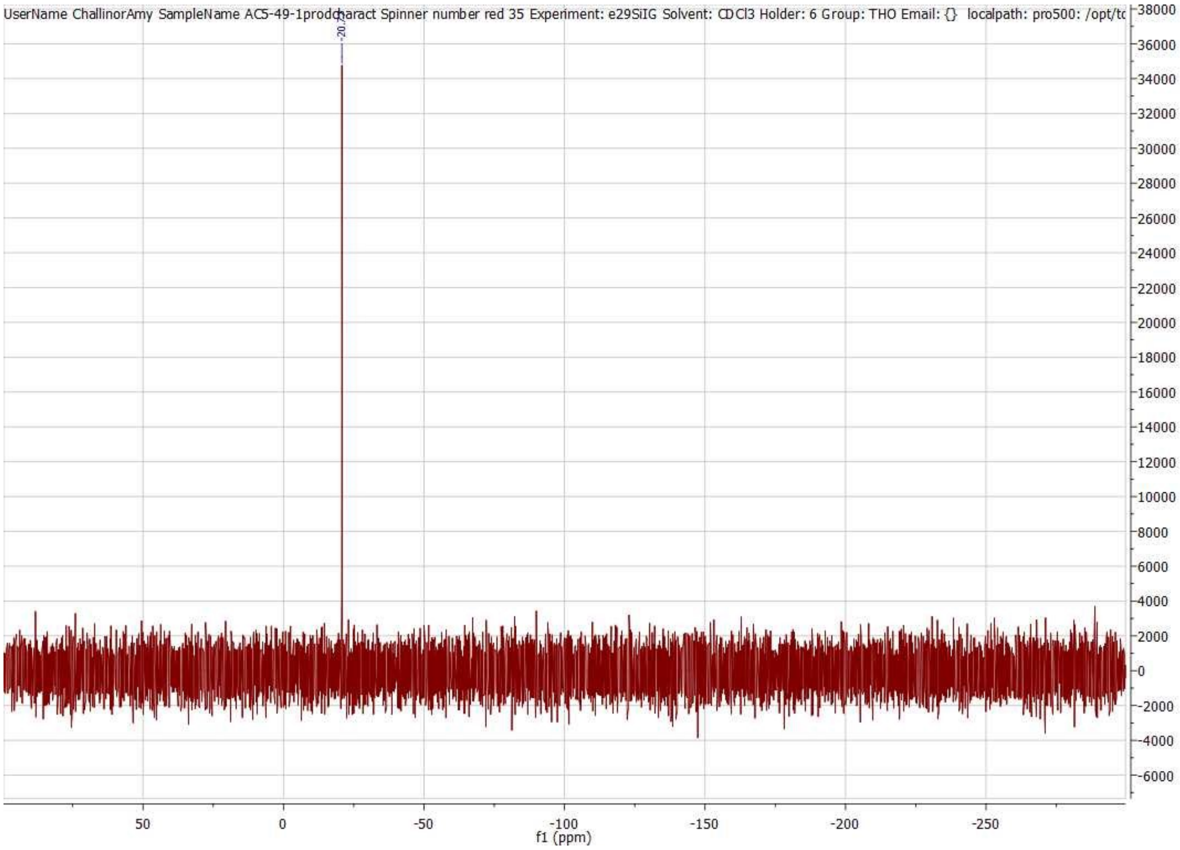

UserName ChallinorAmy SampleName AC4-89-prodcharact Spinner number red 118 Experiment: e13C Solvent: CDCl3 Holder: 25 Group: THQ Email: {} localpath: pro500: /opt/top
135.6
132.3
129.5
127.9
33.60
31.90
29.46
28.6
22.7
16.39
16.22
14.16
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2-(Hexylsilyl)octane (3b)

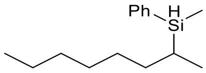


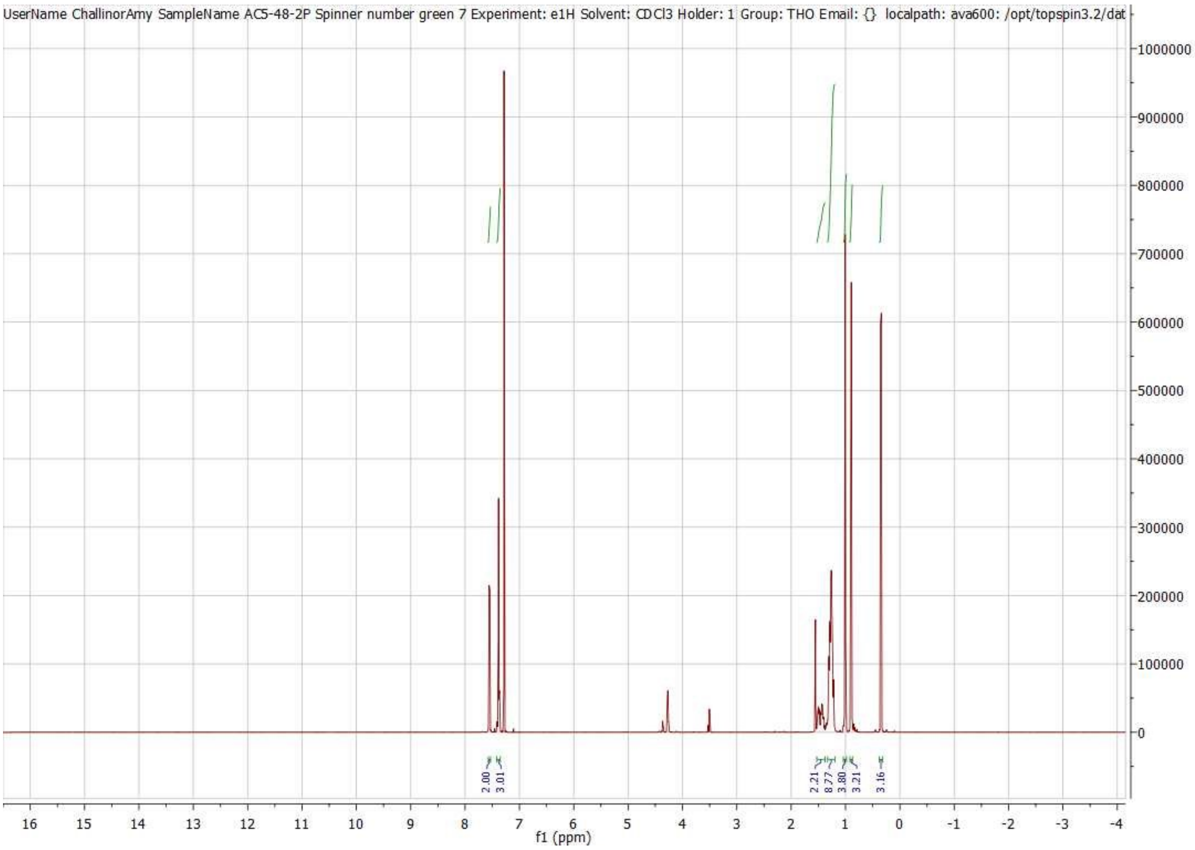


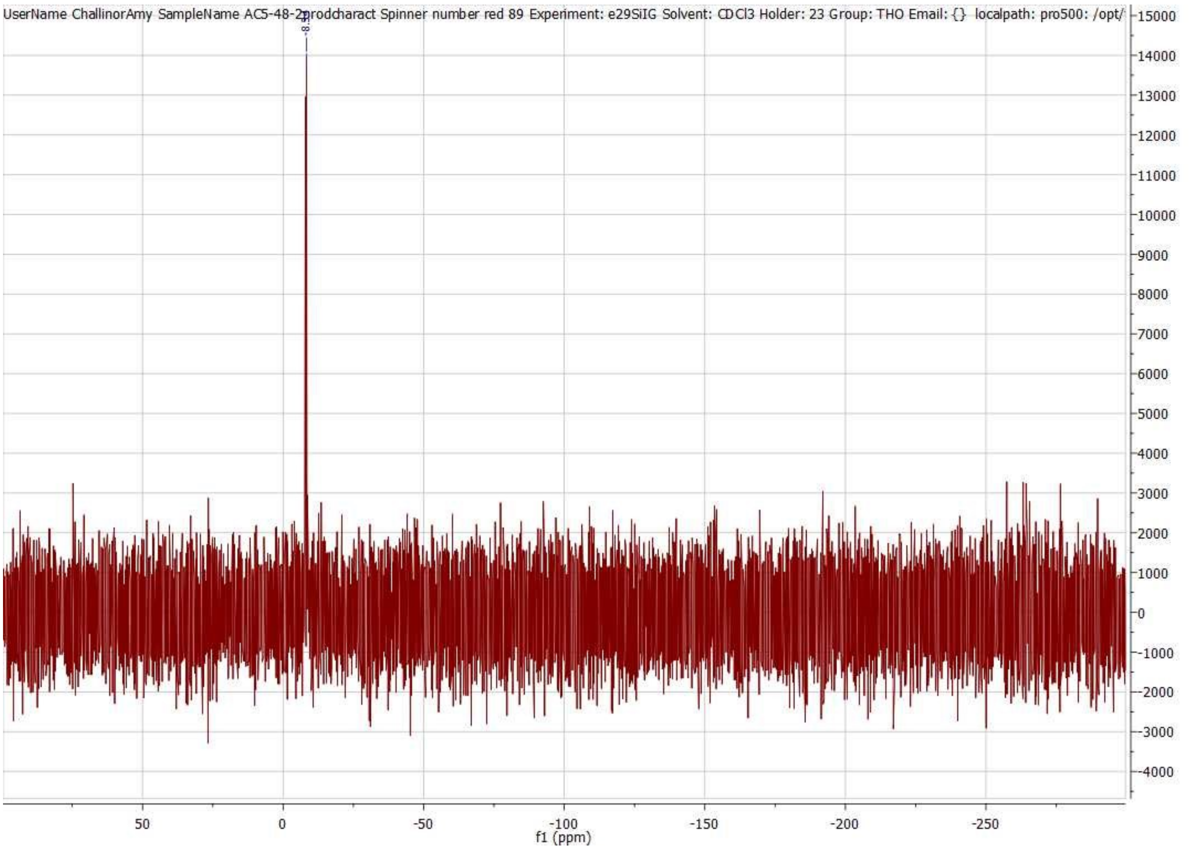

UserName ChallinorAmy SampleName AC5-49-1prodcharact Spinner number red 35 Experiment: e13C Solvent: CDCl3 Holder: 6 Group: THO Email: {} localpath: pro500: /opt/tops
34.0
32.6
31.8
31.5
29.4
28.5
25.6
22.6
22.5
16.4
15.3
14.8
7.94
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


UserName ChallinorAmy SampleName AC5-49-1prodcharact Spinner number red 35 Experiment: e29SiIG Solvent: CDCl3 Holder: 6 Group: THO Email: {} localpath: pro500: /opt/tc
-20.
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

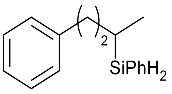
Octan-2-yl(methylphenyl)silane (3c)

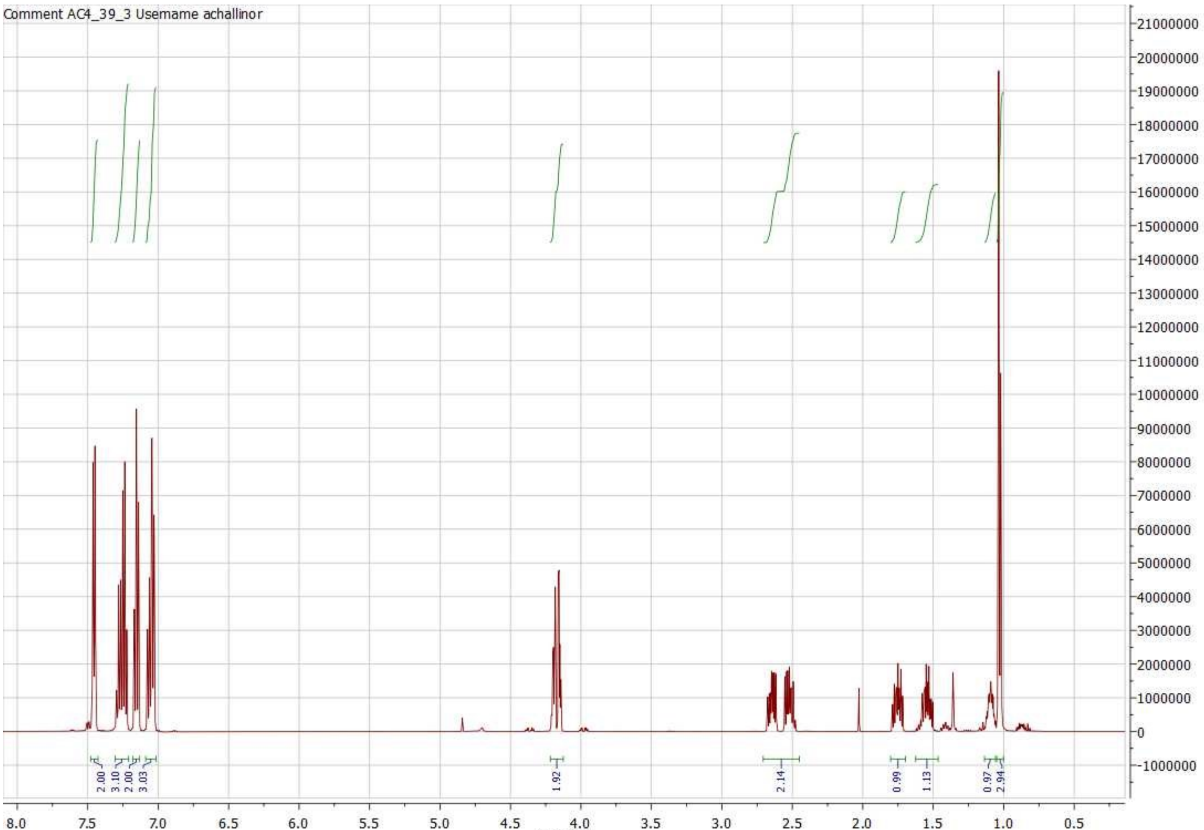


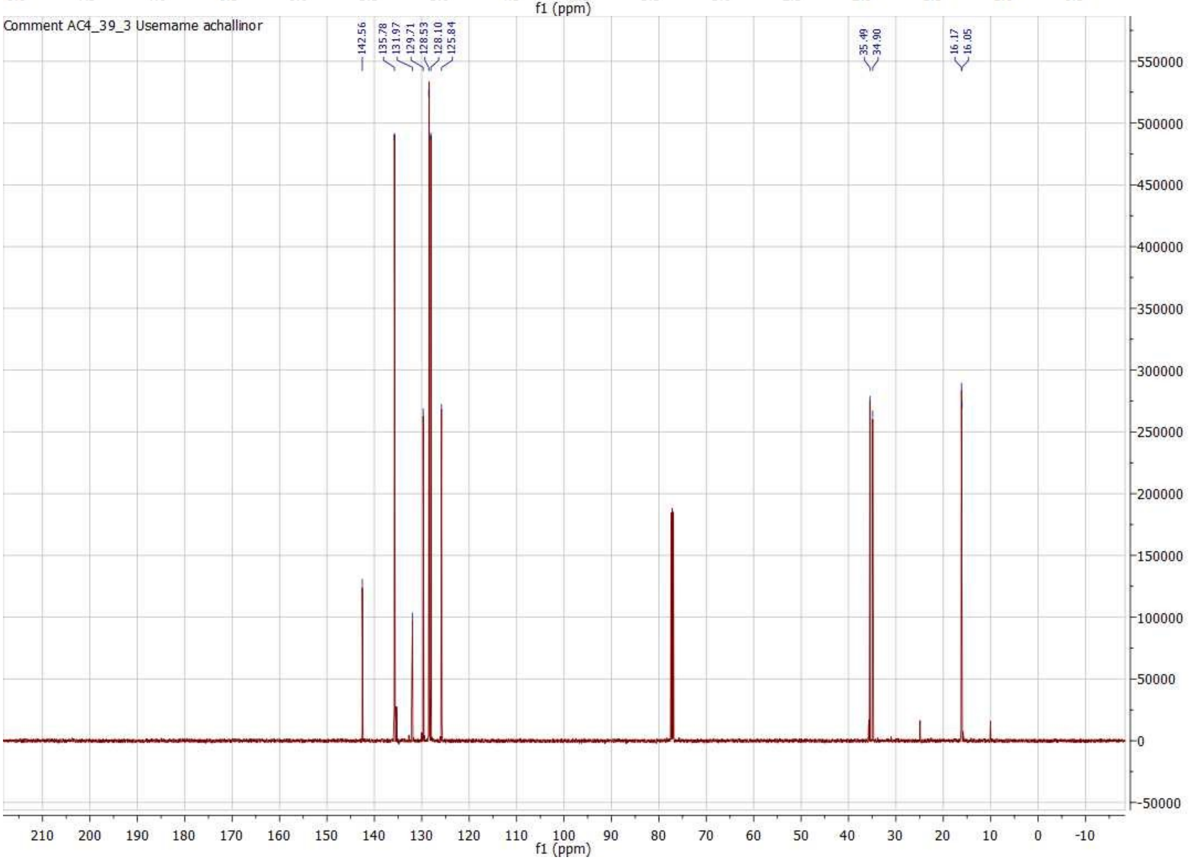


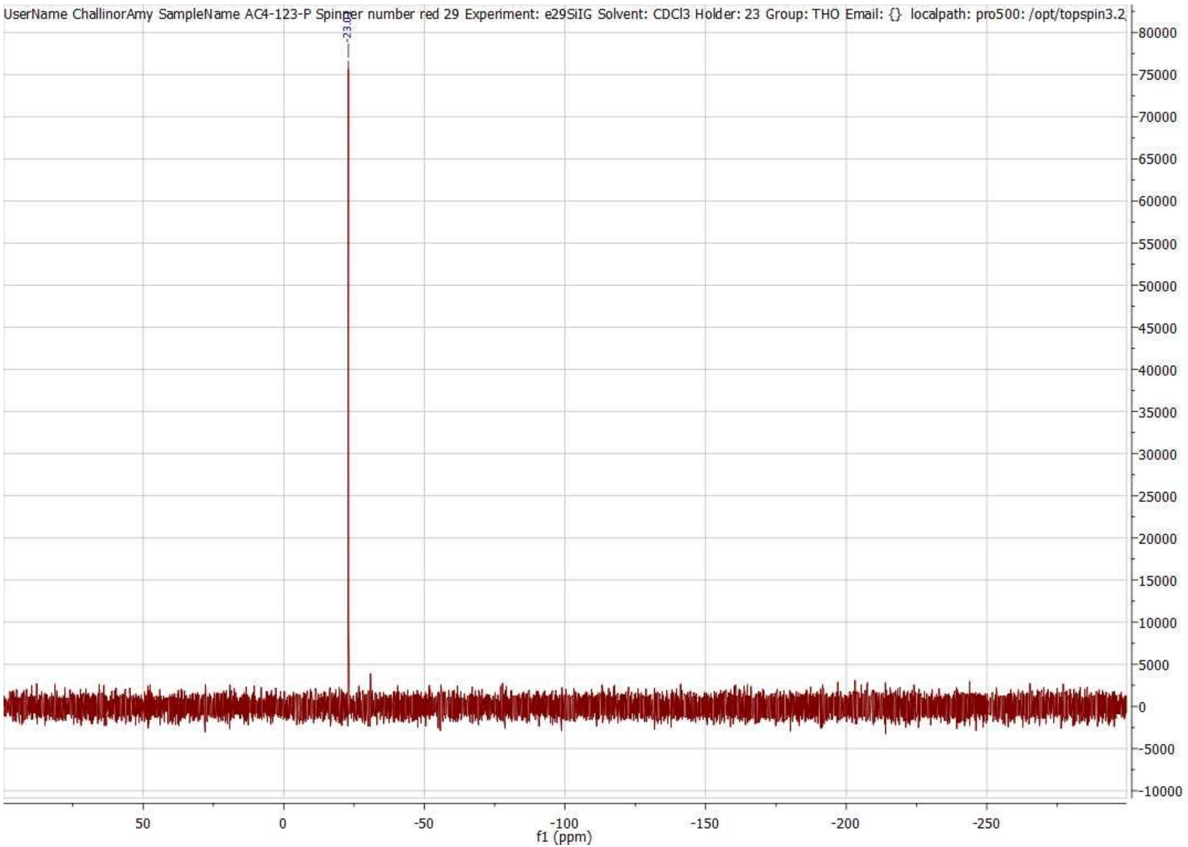


(4-Phenylbut-2-yl)silylbenzene (3d)

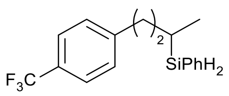


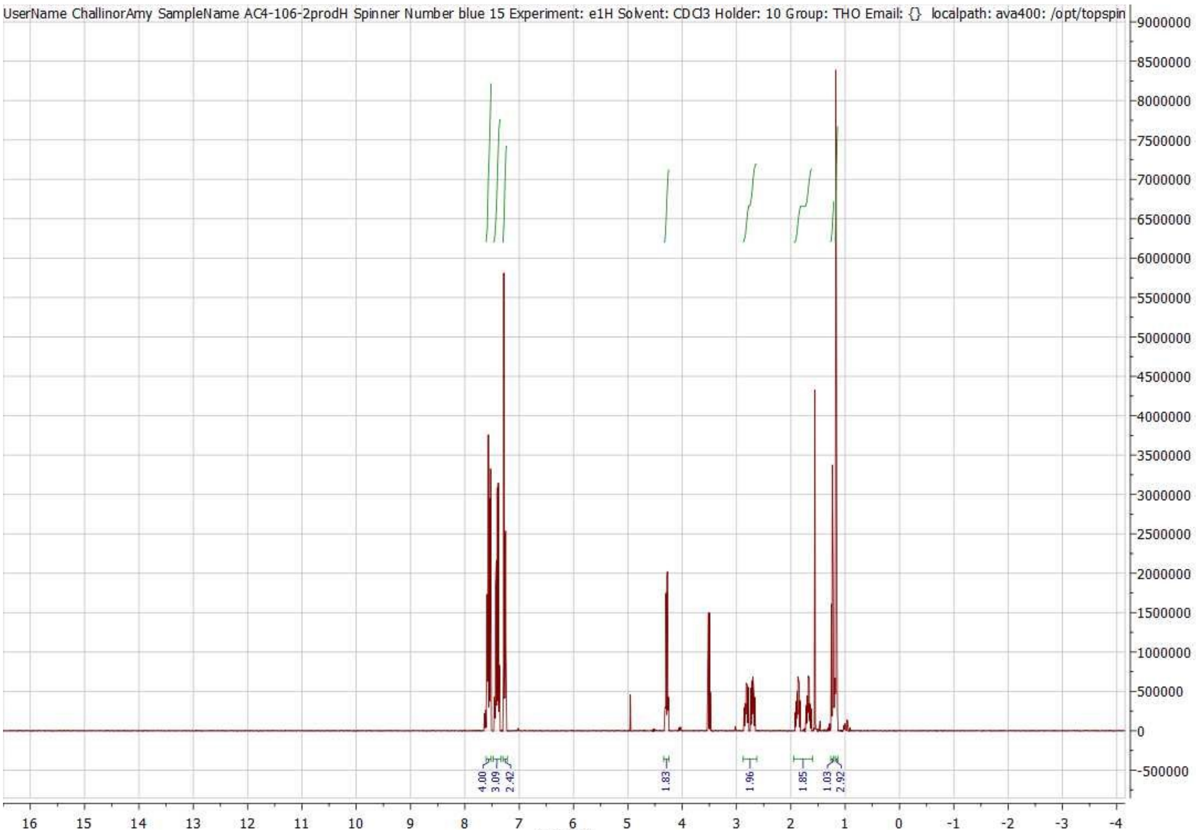


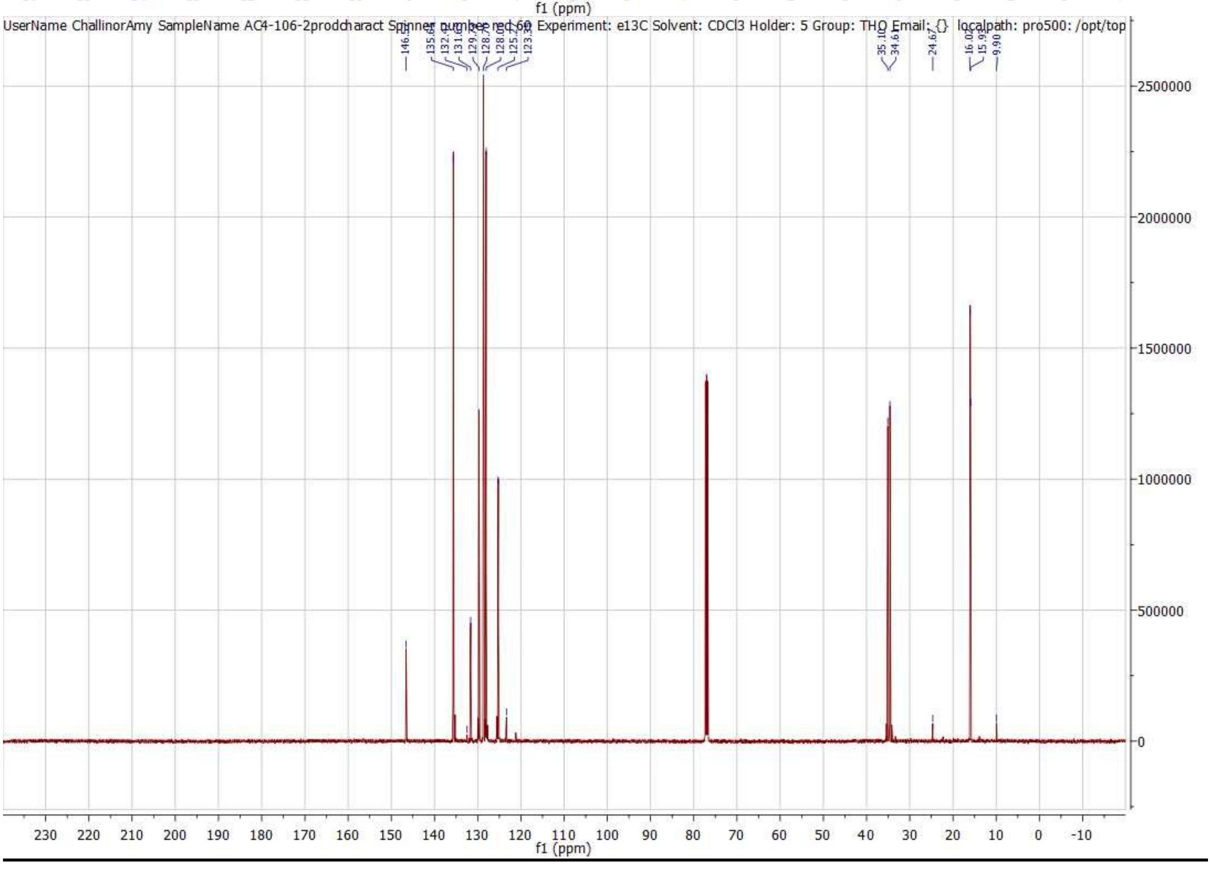


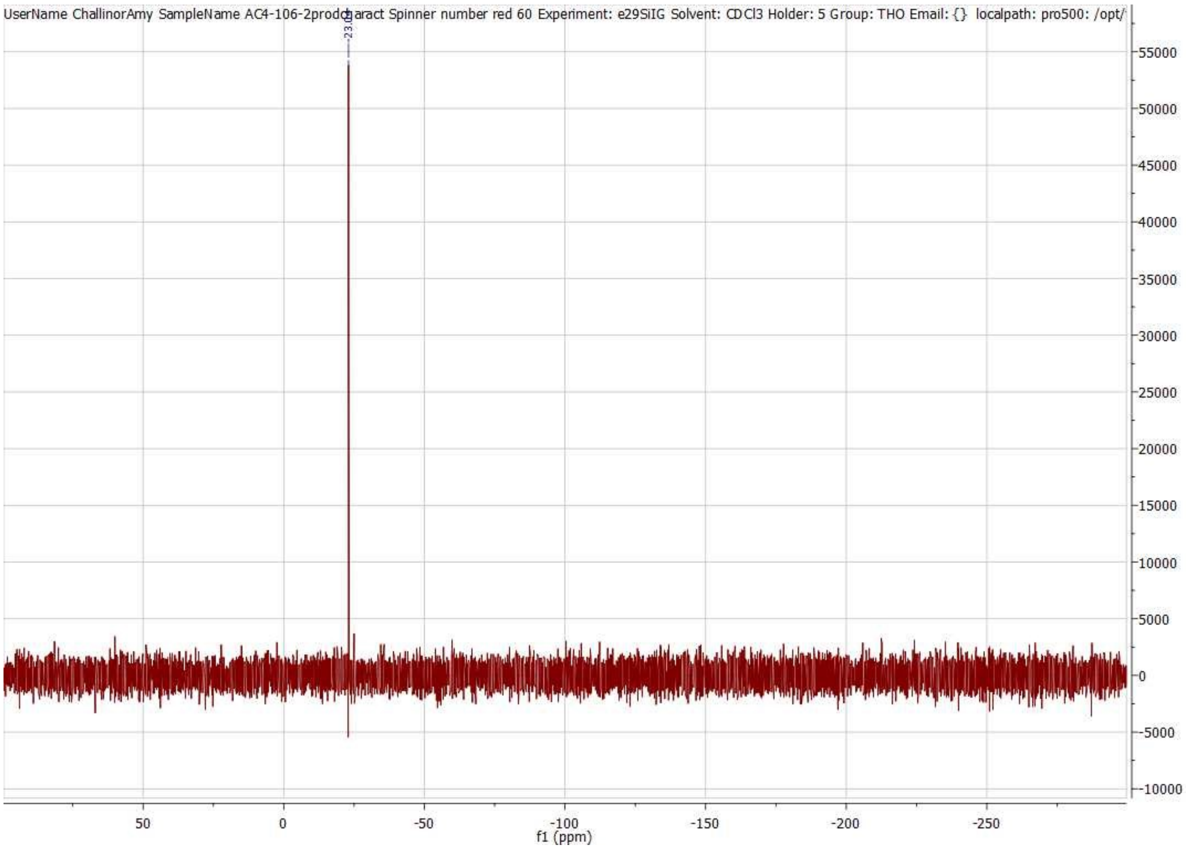

UserName ChallinorAmy SampleName AC4-123-P Spinner number red 29 Experiment: e29SiIG Solvent: CDCl3 Holder: 23 Group: THO Email: {} localpath: pro500: /opt/topspin3.2
-23.0
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-Trifluoromethyl-4-(3-silylbenzenebutane)benzene (3e)

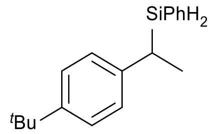


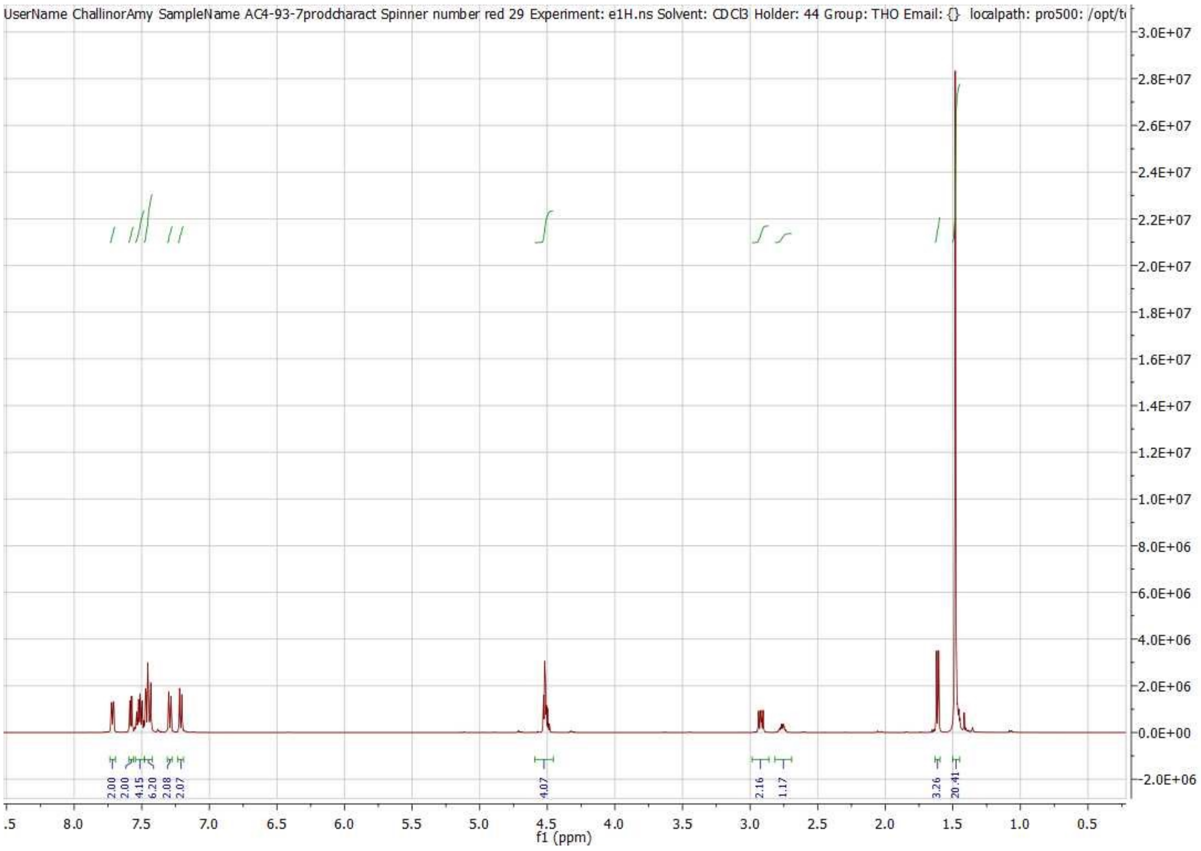


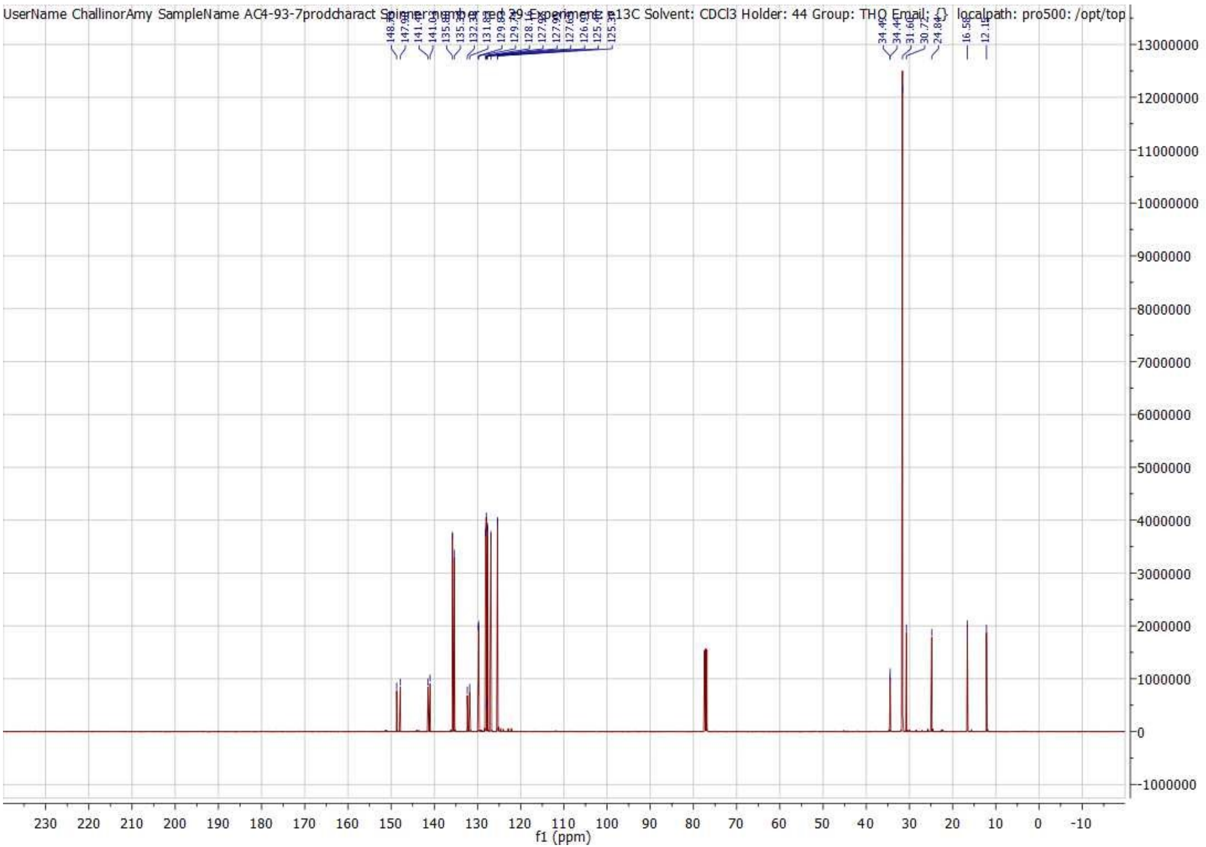


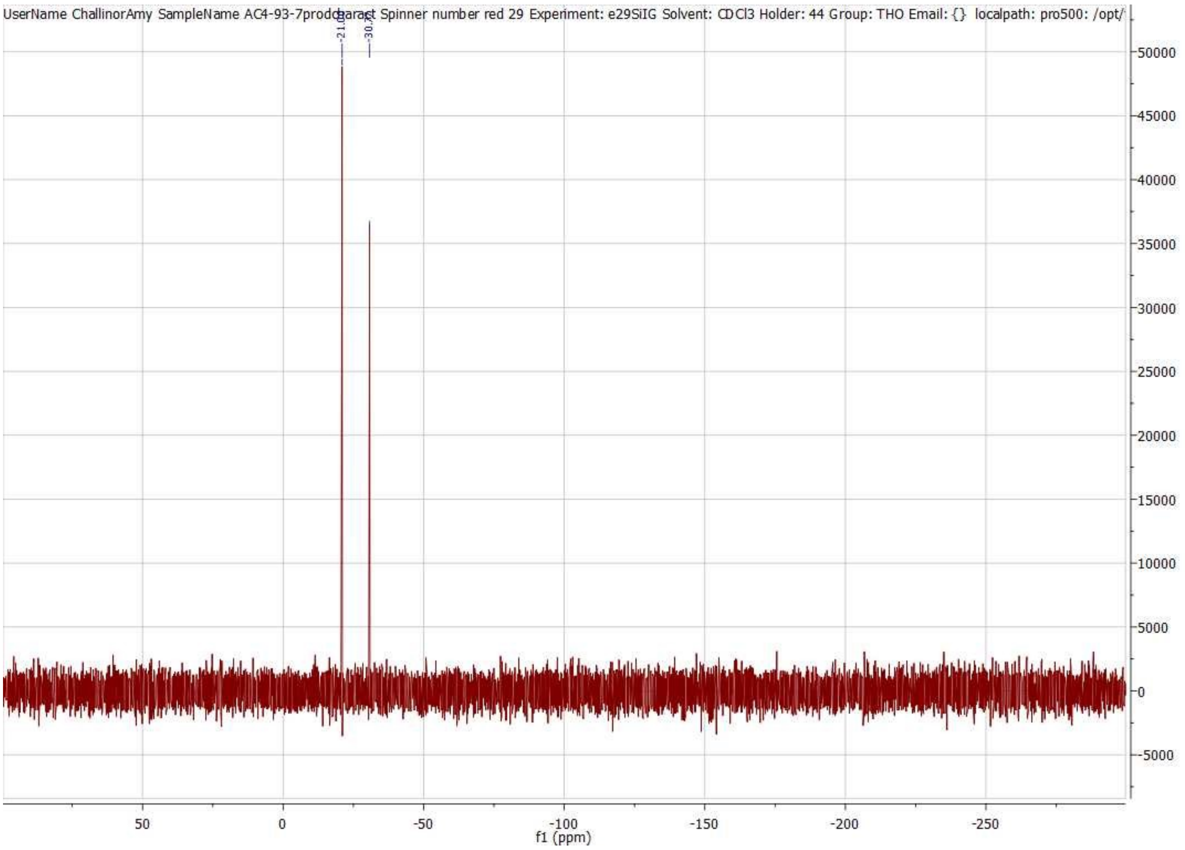

UserName ChallinorAmy SampleName AC4-106-2prodcharact Spinner number red 60 Experiment: e29SiIG Solvent: CDCl3 Holder: 5 Group: THO Email: {} localpath: pro500: /opt/
-23.0
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-(4-*tert*butylphenyl)-1-(phenylsilyl)ethane (3f)

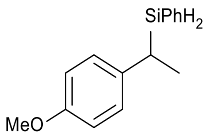


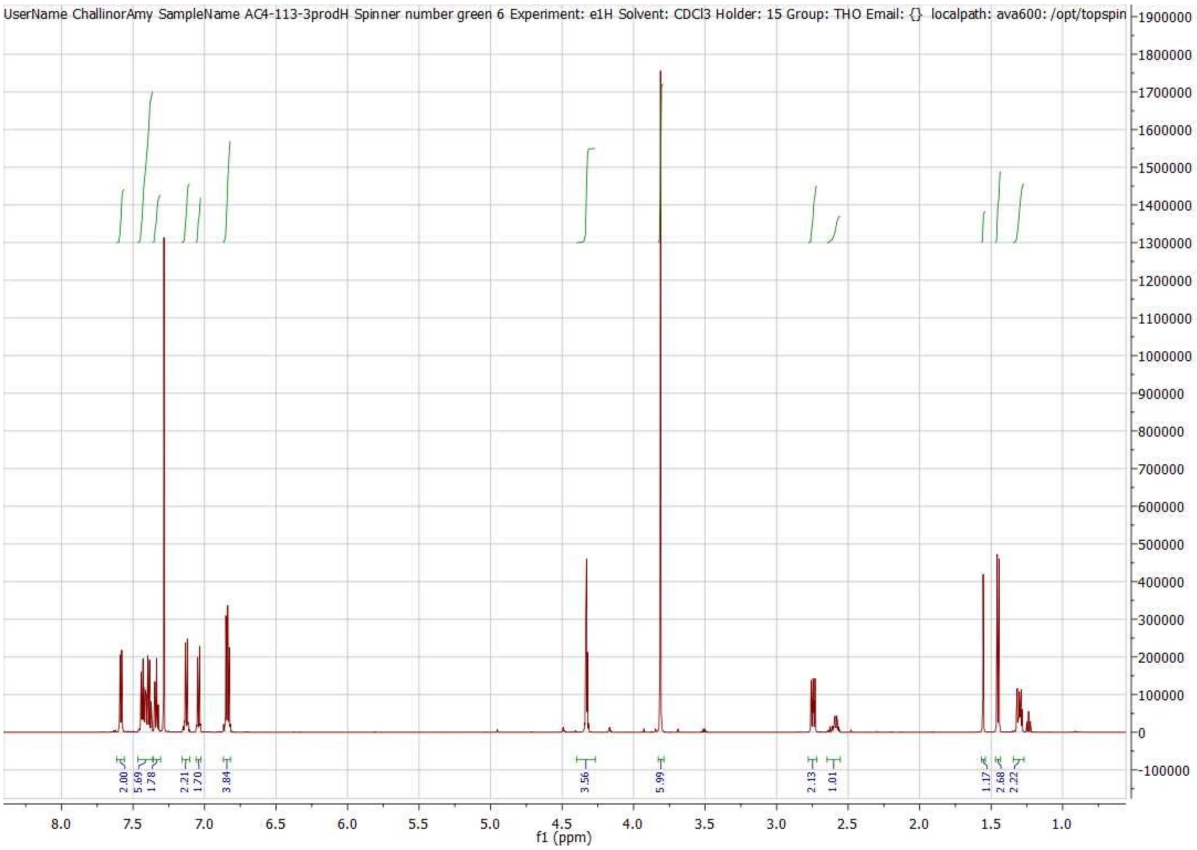


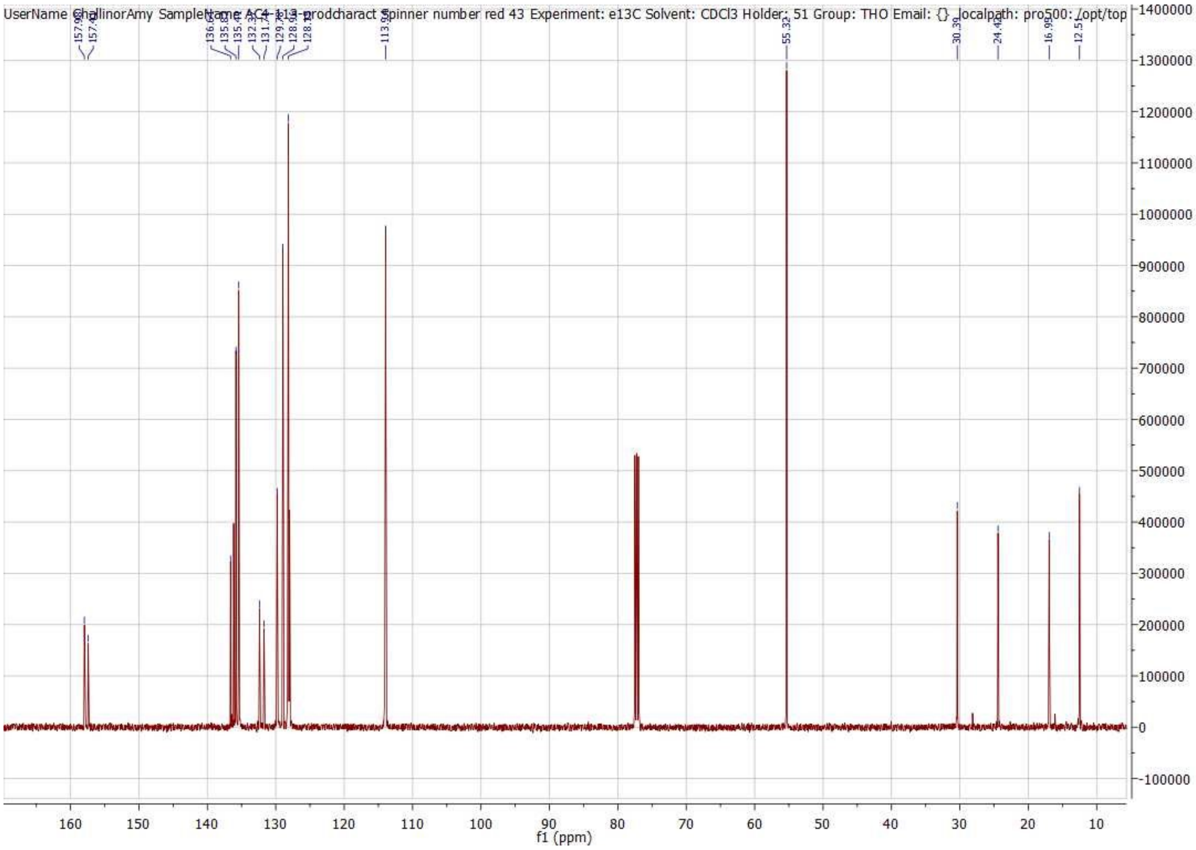

UserName ChallinorAmy SampleName AC4-93-7prodcharact Spinner number red 29 Experiment: e13C Solvent: CDCl3 Holder: 44 Group: THO Email: {} localpath: pro500: /opt/top
148.5
147.9
141.4
141.0
135.8
135.3
132.3
131.8
129.8
129.7
128.1
127.9
127.9
127.6
126.9
125.4
125.3
34.45
34.44
31.60
30.72
24.84
16.58
12.15
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

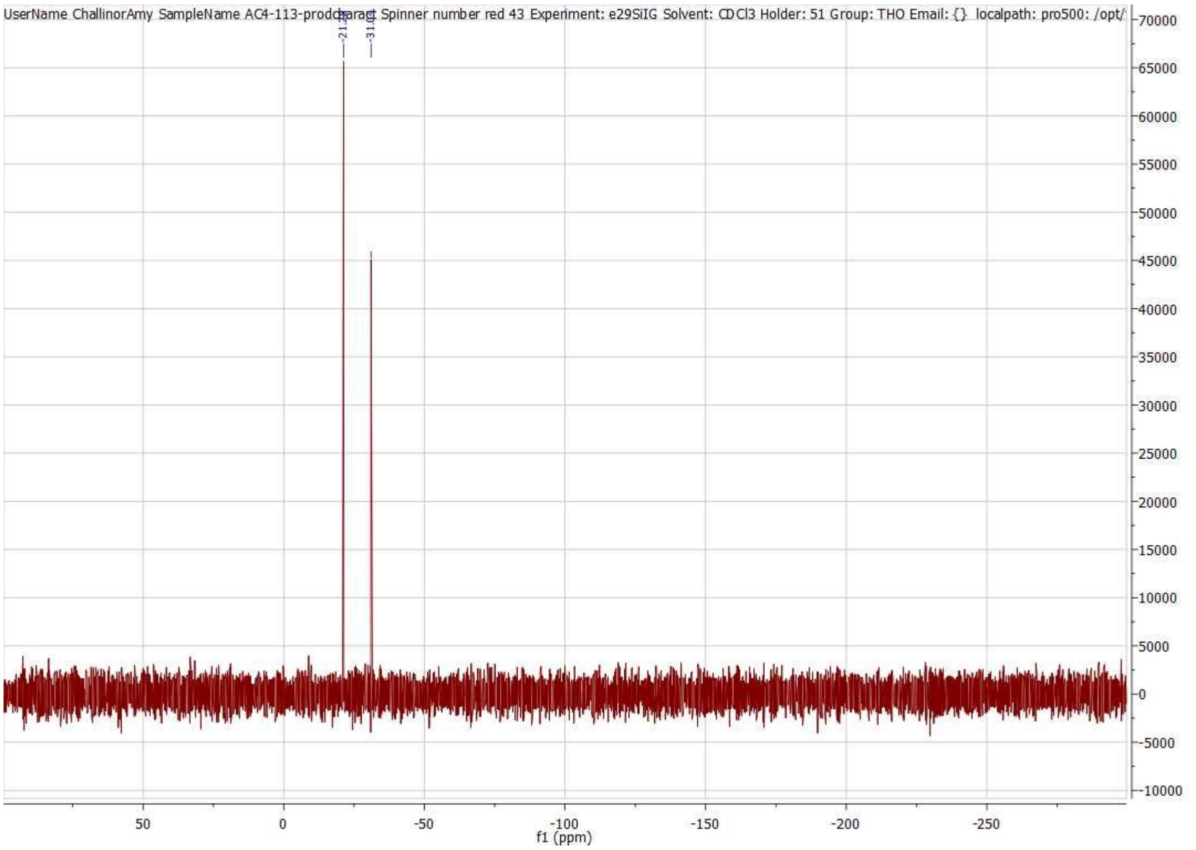

UserName ChallinorAmy SampleName AC4-93-7prodcharact Spinner number red 29 Experiment: e29SiIG Solvent: CDCl3 Holder: 44 Group: THO Email: {} localpath: pro500: /opt/
-21.0
-30.7
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-Methoxy-4-[1-(phenylsilyl)ethyl]-benzene (3g)

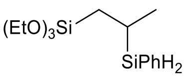


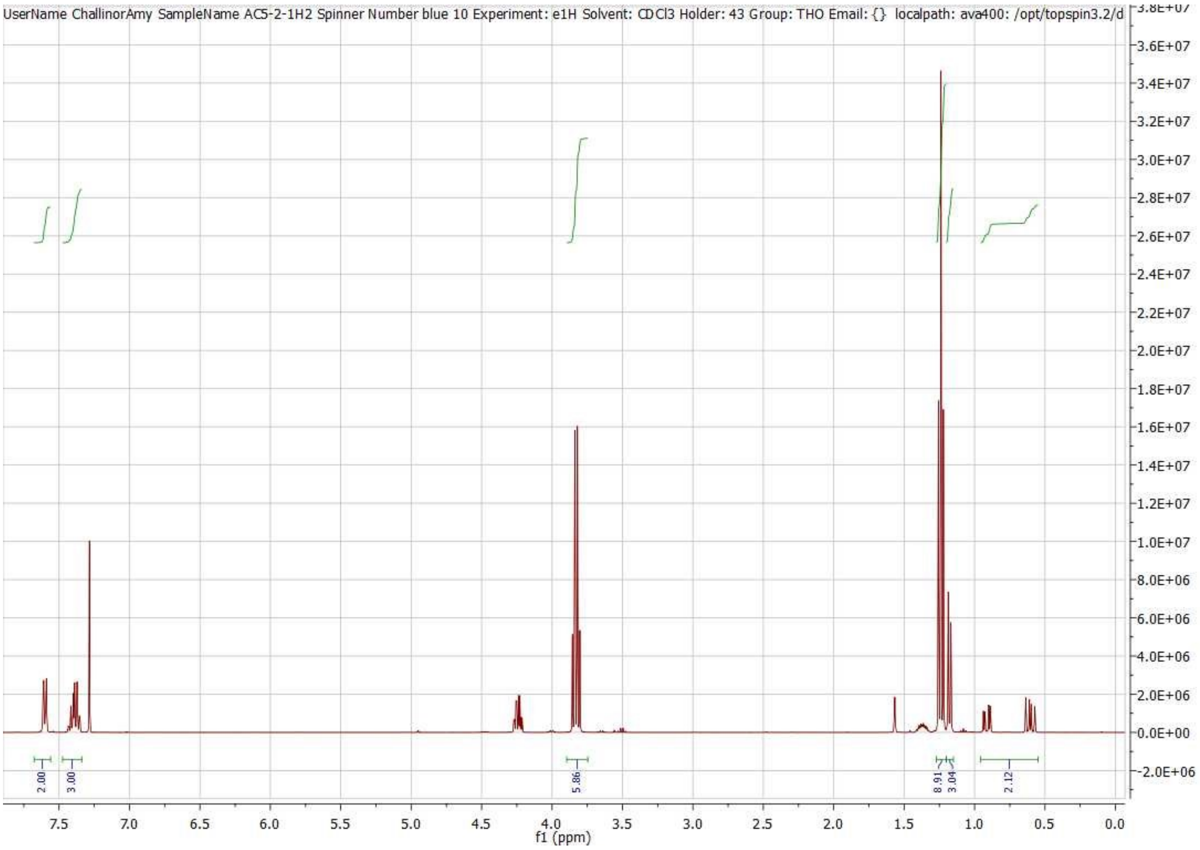


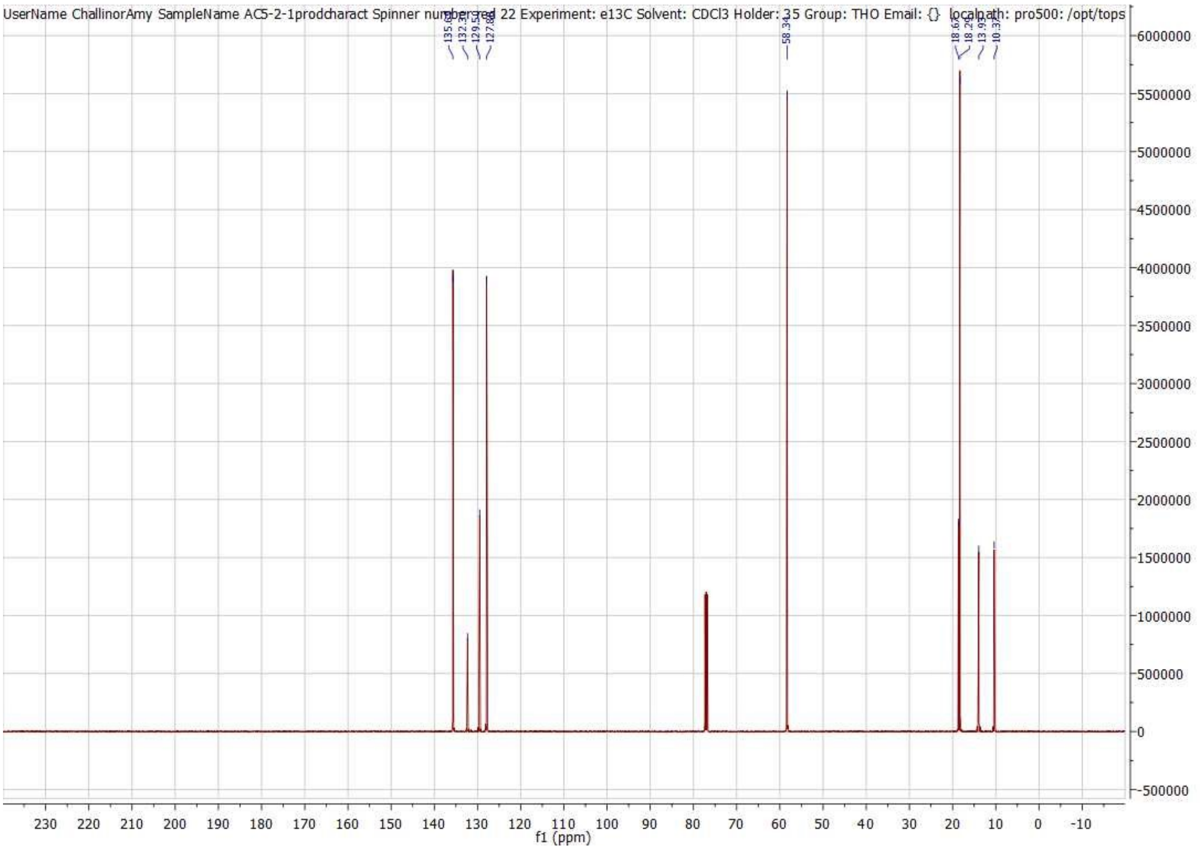

UserName ChallinorAmy SampleName AC4-113-prodcharact Spinner number red 43 Experiment: e13C Solvent: CDCl3 Holder: 51 Group: THO Email: {} localpath: pro500: /opt/top
157.9
157.4
136.6
135.8
135.4
132.3
131.7
129.7
128.9
128.1
113.9
55.32
30.39
24.42
16.99
12.51
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

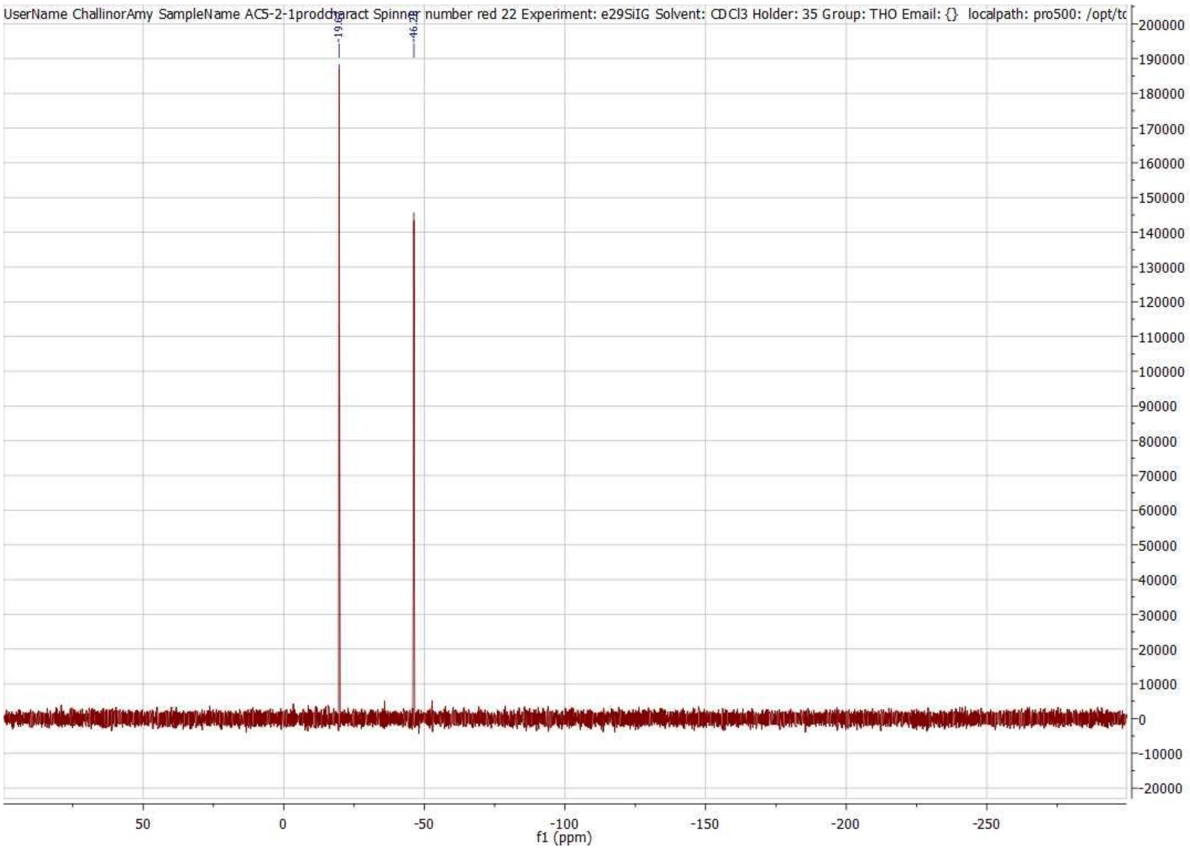

UserName ChallinorAmy SampleName AC4-113-prodcharact Spinner number red 43 Experiment: e29SiIG Solvent: CDCl3 Holder: 51 Group: THO Email: {} localpath: pro500: /opt/
-21.2
-31.0
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

(3-Triethoxysilyl-2-benzylsilyl)propane (3h)

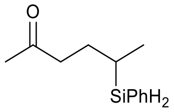


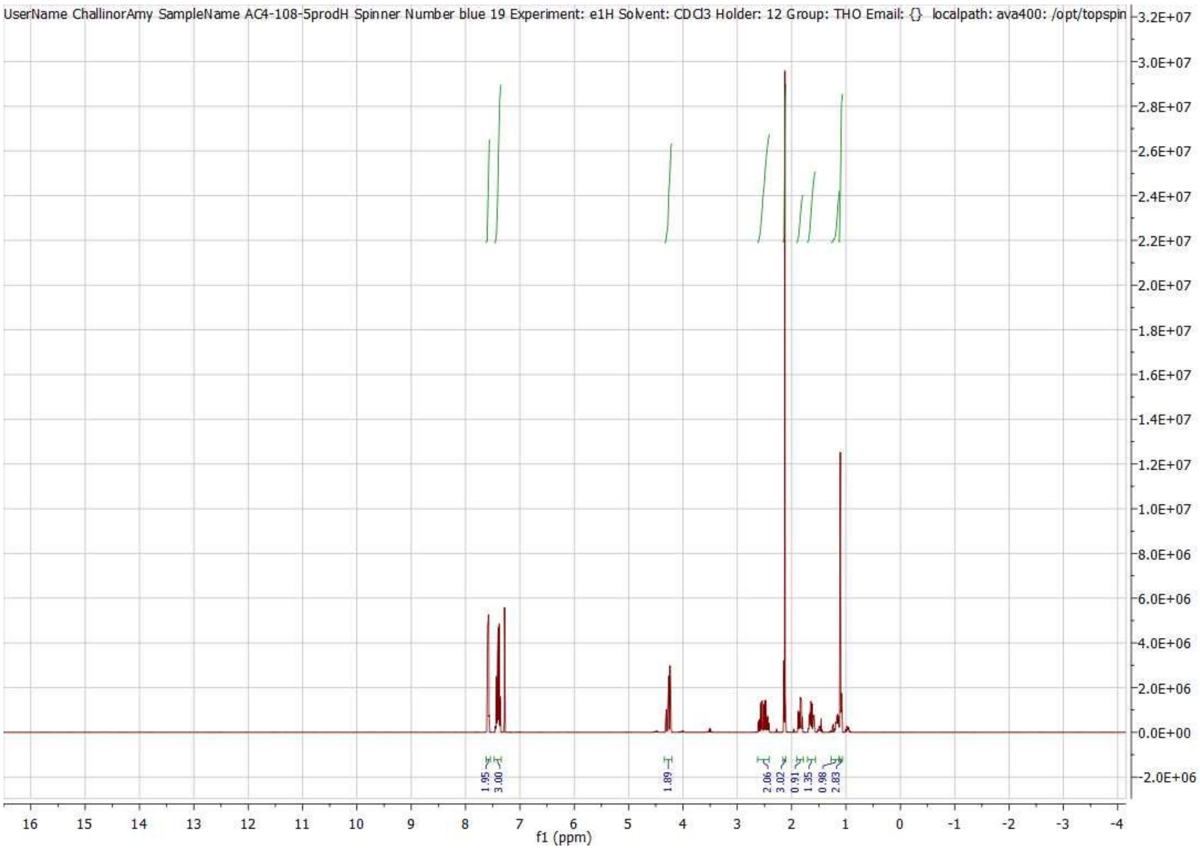


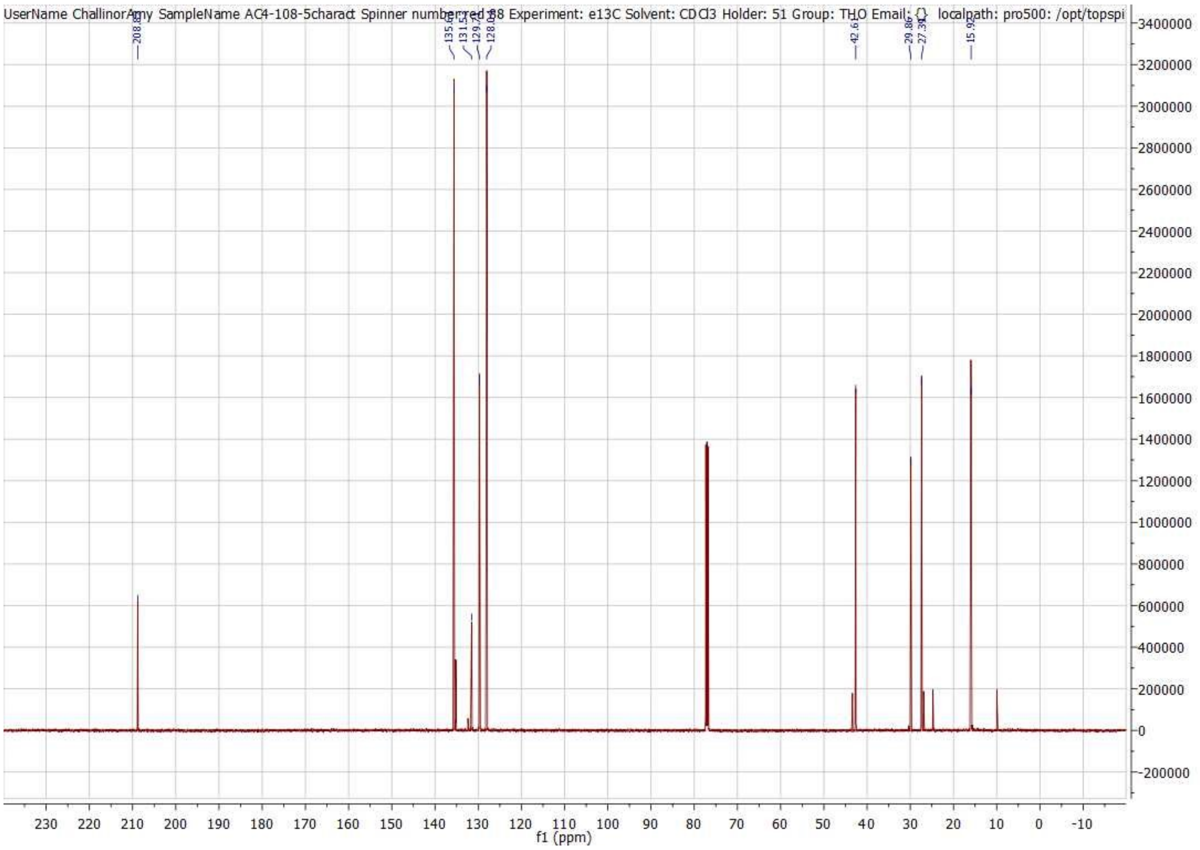


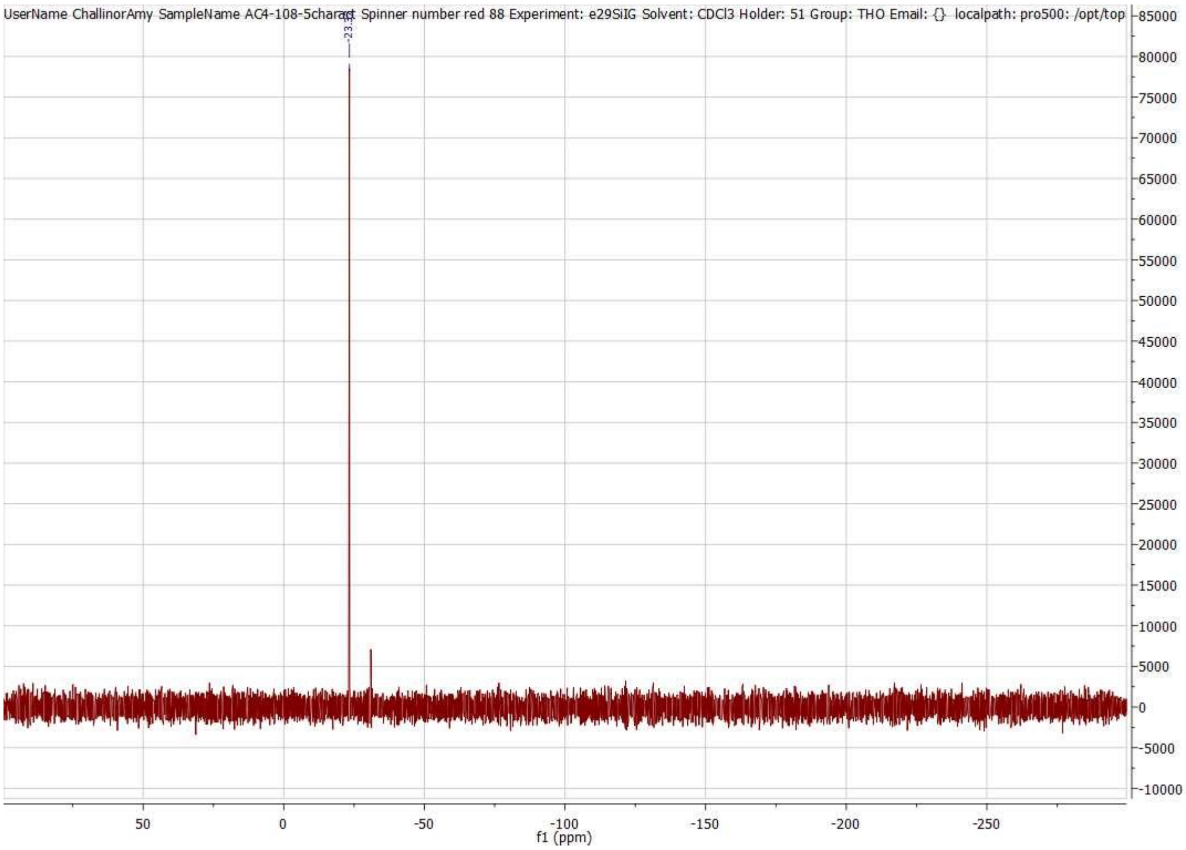

UserName ChallinorAmy SampleName AC5-2-1prodcharact Spinner number red 22 Experiment: e29SiIG Solvent: CDCl3 Holder: 35 Group: THO Email: {} localpath: pro500: /opt/tc
-19.6
-46.2
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

5-(Phenylsilyl)-2-hexanone (3i)

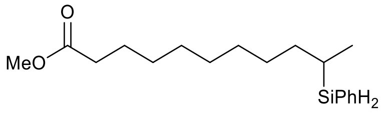


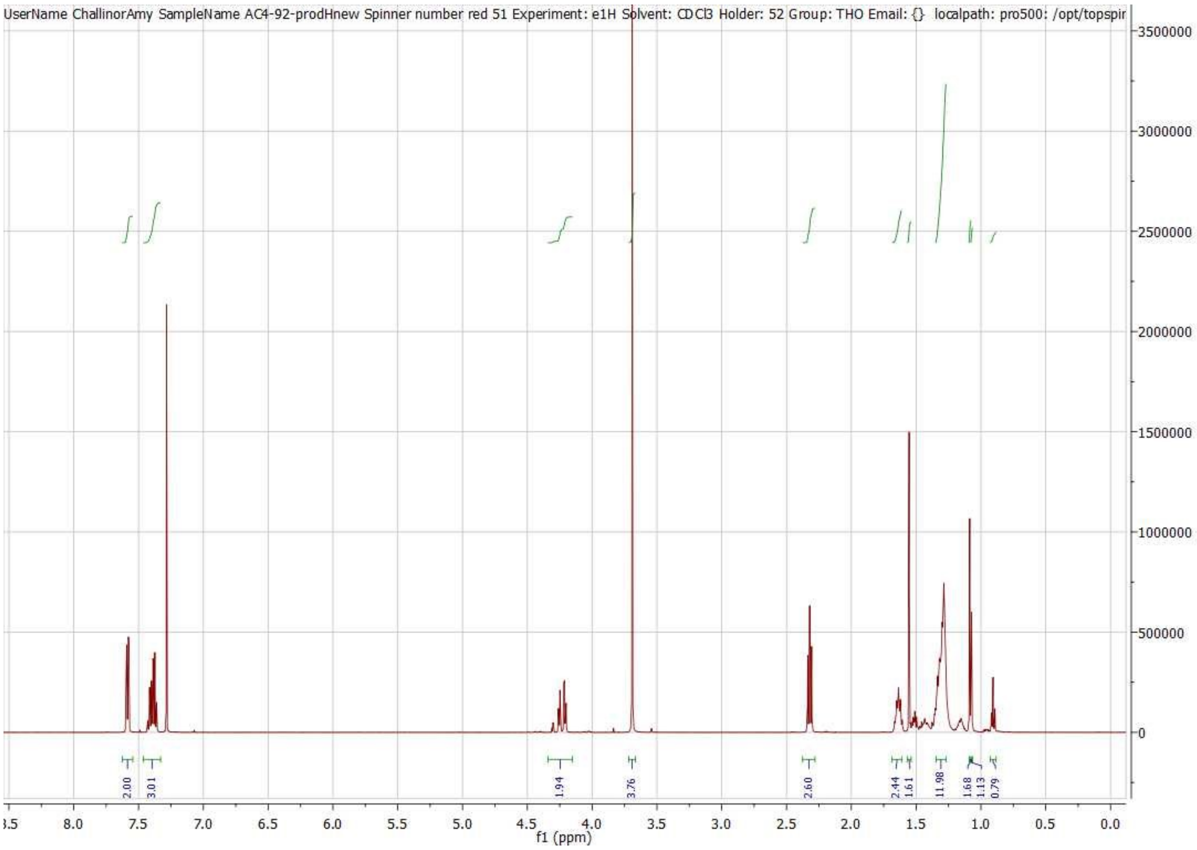


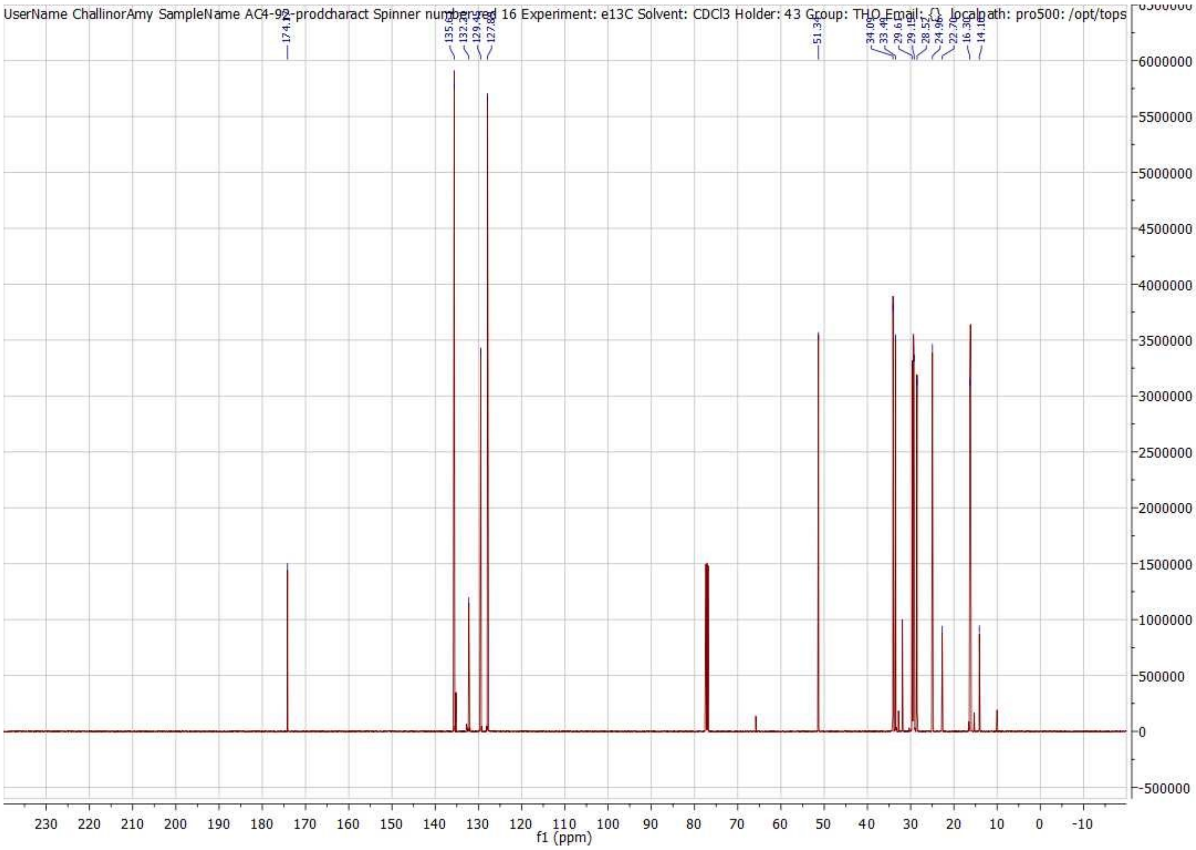


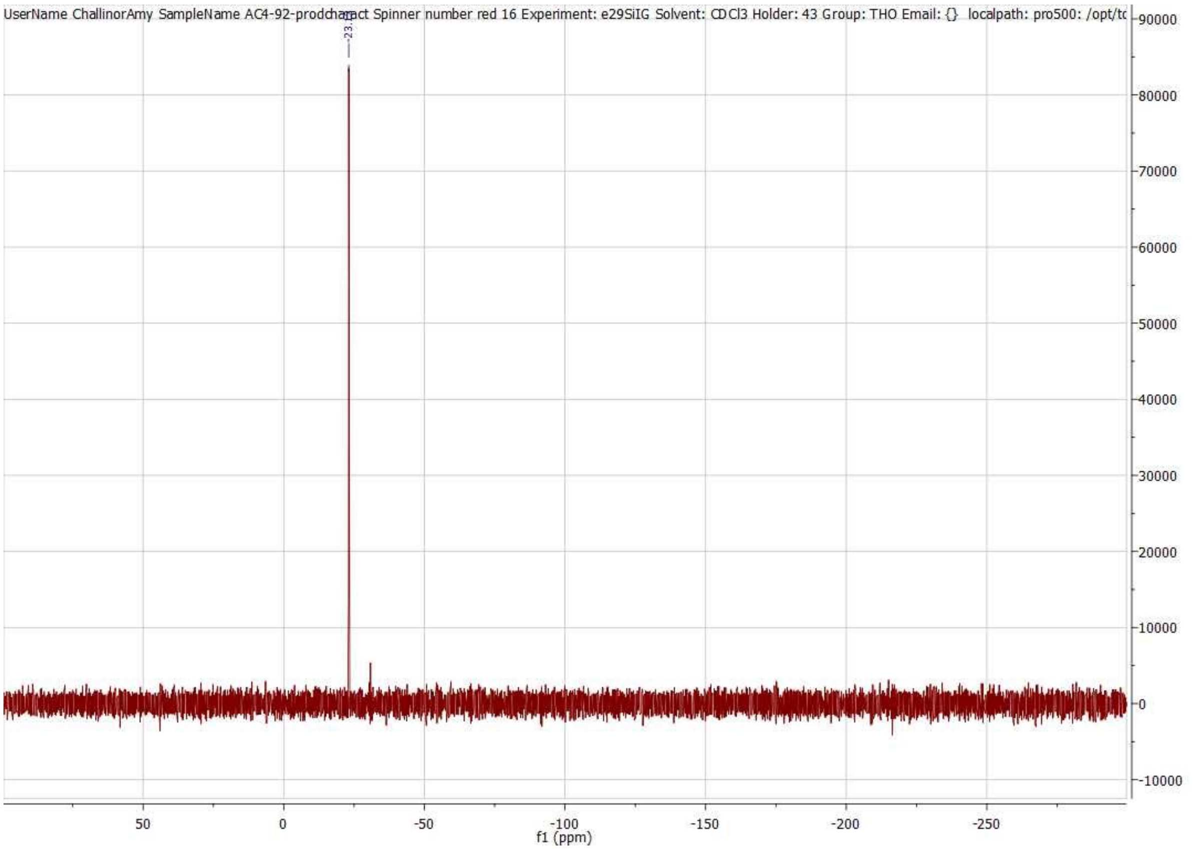

UserName ChallinorAmy SampleName AC4-108-5charact Spinner number red 88 Experiment: e29SiIG Solvent: CDCl3 Holder: 51 Group: THO Email: {} localpath: pro500: /opt/top
-23.3
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

Methyl ester 10-(phenylsilyl)undecanoic acid (3j)

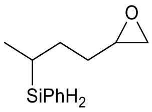


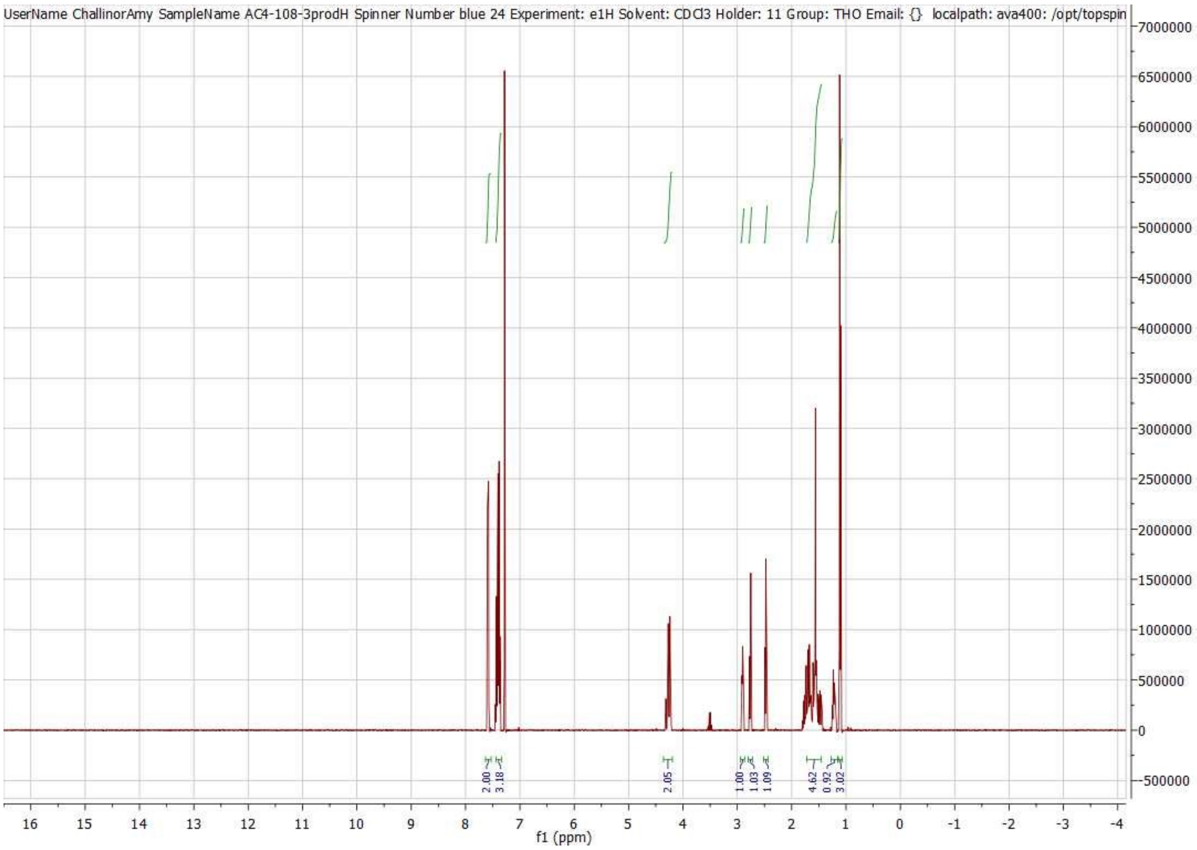


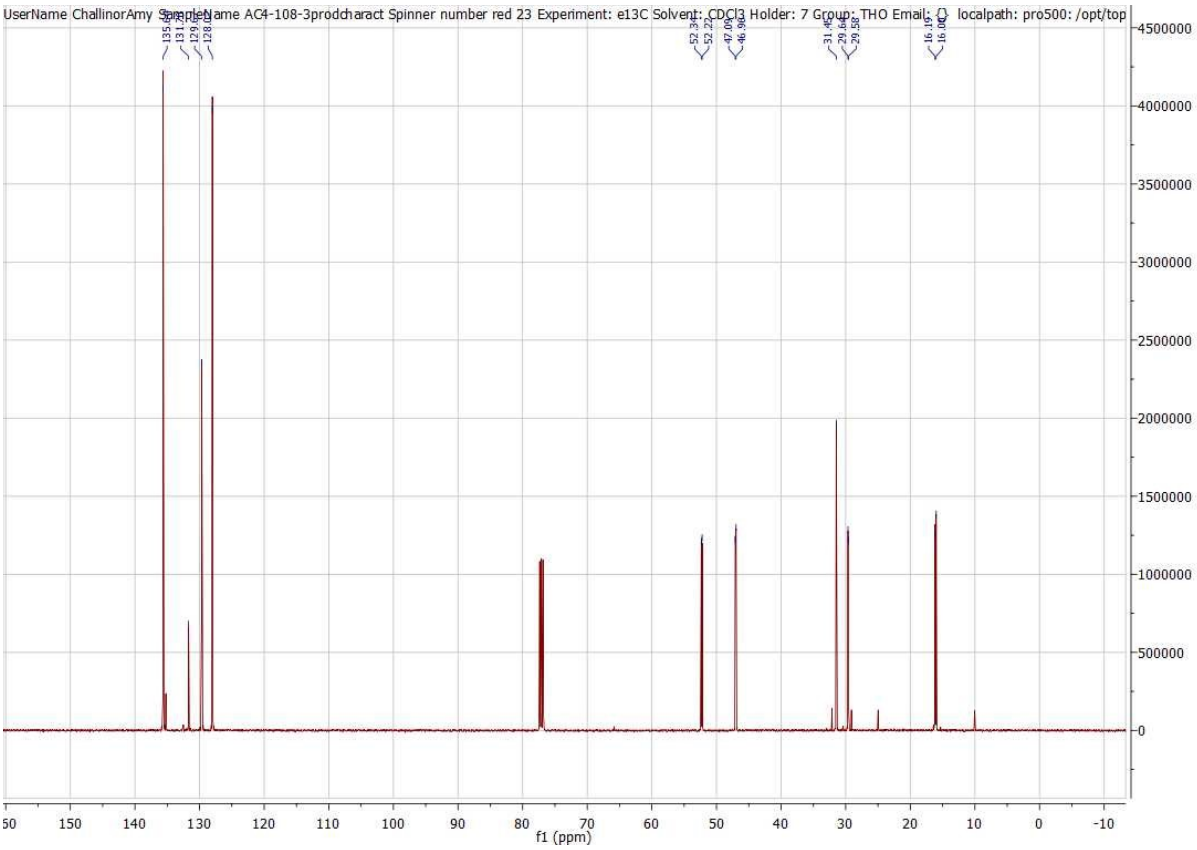

UserName ChallinorAmy SampleName AC4-92-prodcharact Spinner number red 16 Experiment: e13C Solvent: CDCl3 Holder: 43 Group: THO Email: {} localpath: pro500: /opt/tops
174.1
135.6
132.2
129.4
127.8
51.34
34.09
33.49
29.61
29.15
28.57
24.96
22.70
16.30
14.16
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

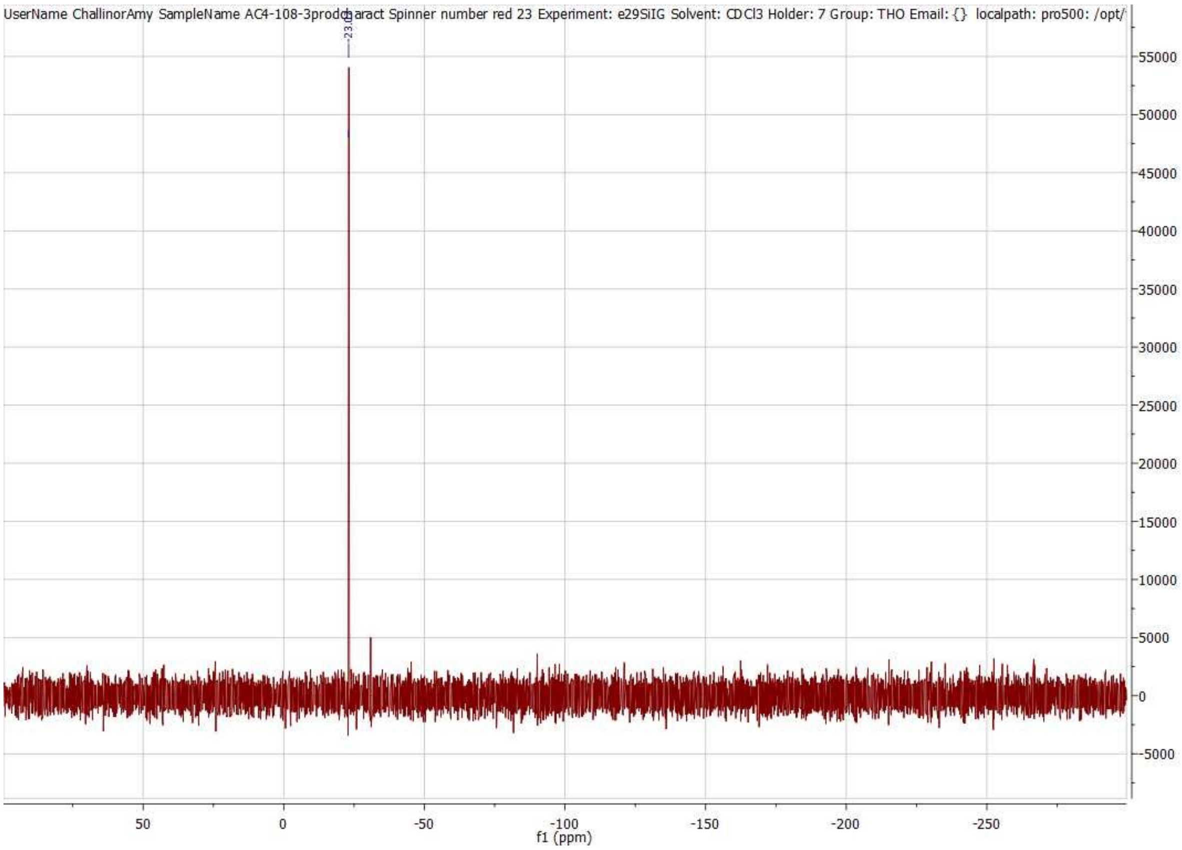

UserName ChallinorAmy SampleName AC4-92-prodcharact Spinner number red 16 Experiment: e29SiIG Solvent: CDCl3 Holder: 43 Group: THO Email: {} localpath: pro500: /opt/tc
-23.1
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50 0 -50 -100 -150 -200 -250
f1 (ppm)

1,2-Epoxy-(5-phenylsilyl)hexane (3k)

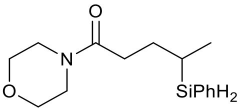


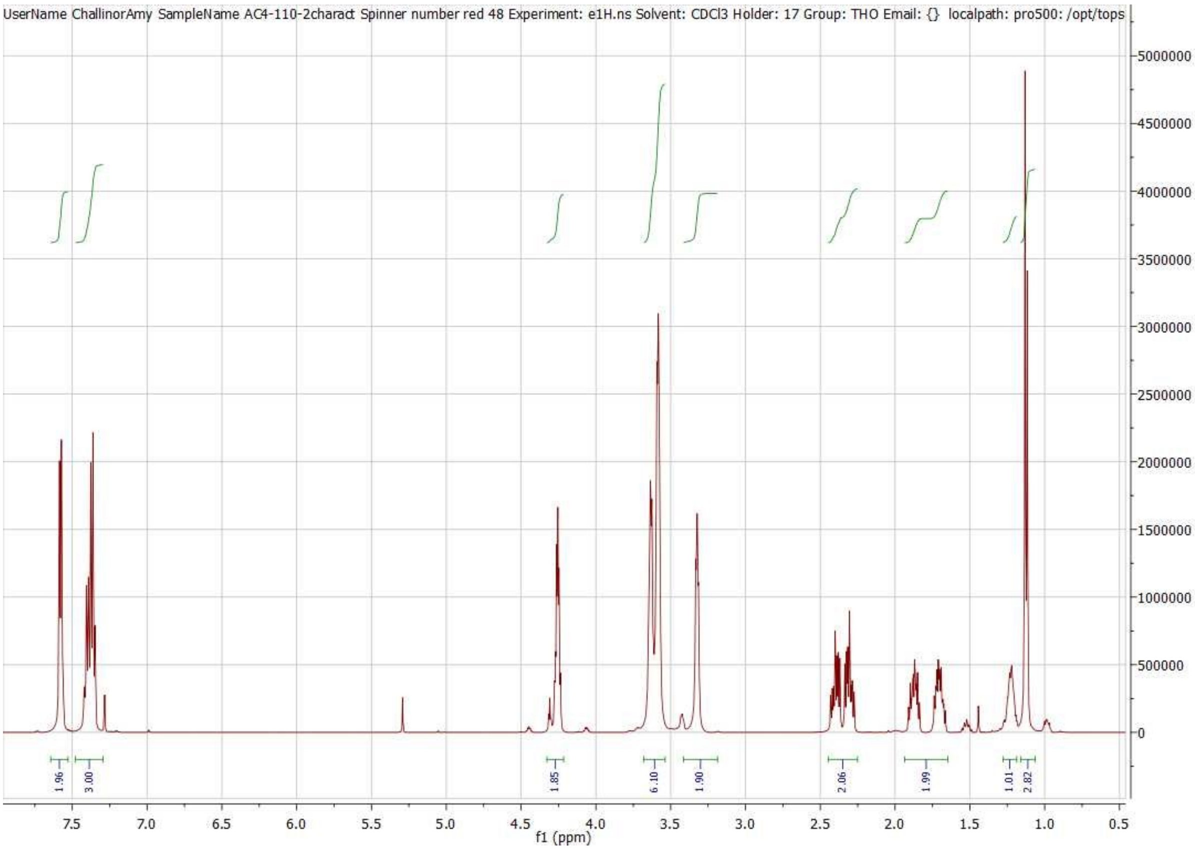


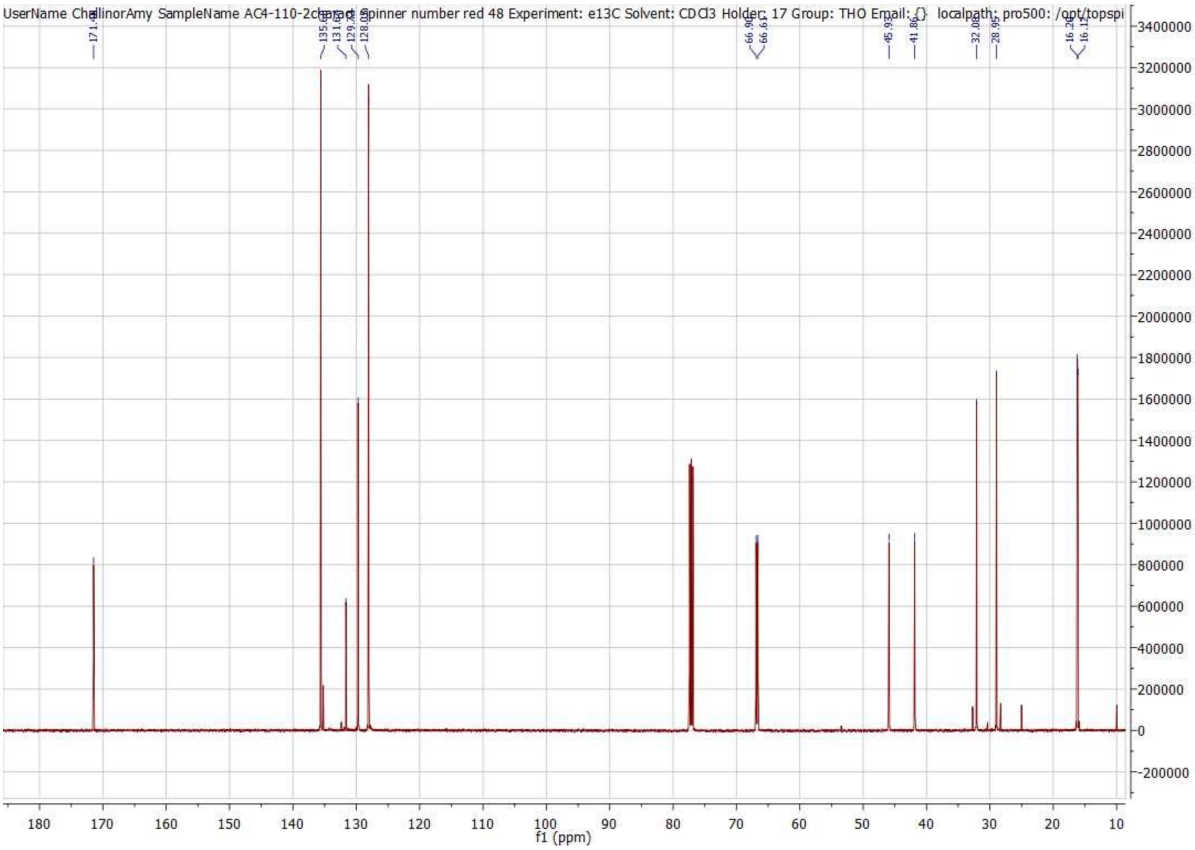


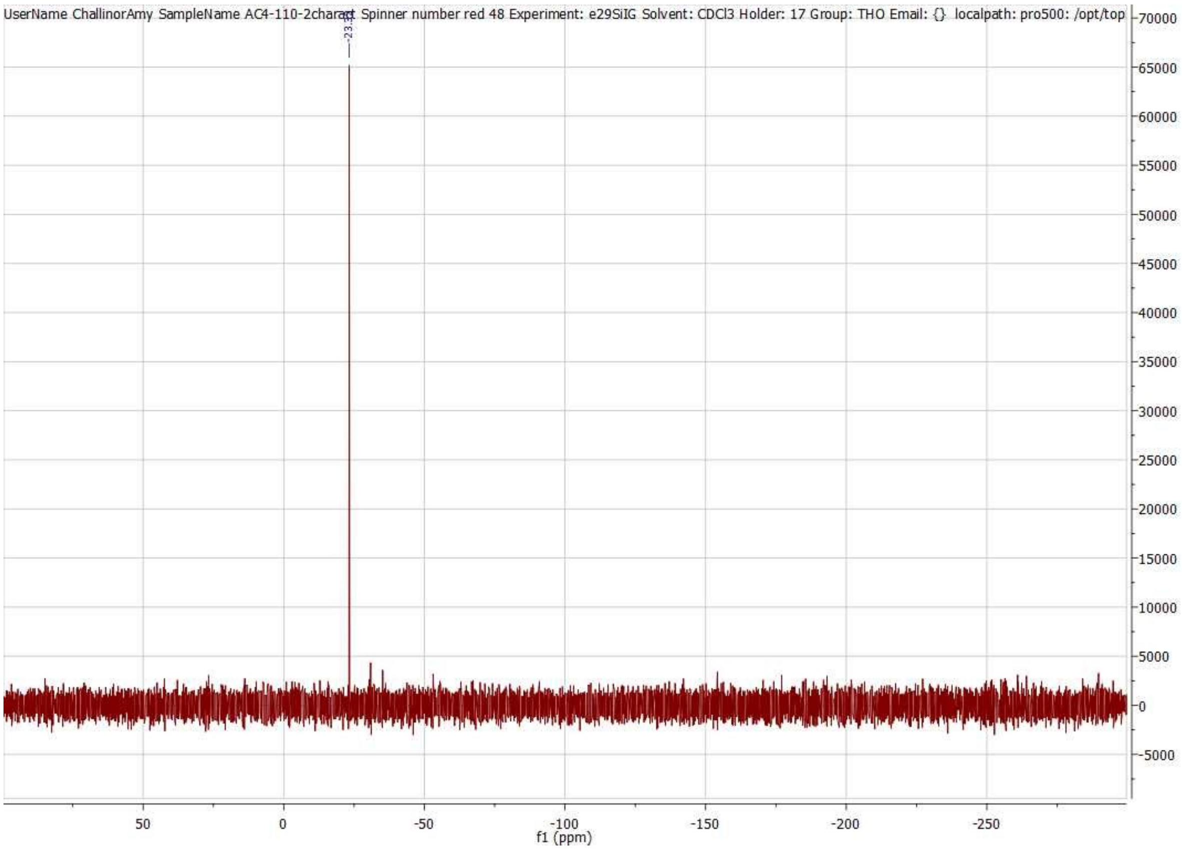

UserName ChallinorAmy SampleName AC4-108-3prodcharact Spinner number red 23 Experiment: e29SiIG Solvent: CDCl3 Holder: 7 Group: THO Email: {} localpath: pro500: /opt/
-23.0
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

1-(4-Morpholinyl)-4-(phenylsilyl)pentan-1-one (3l)

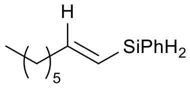


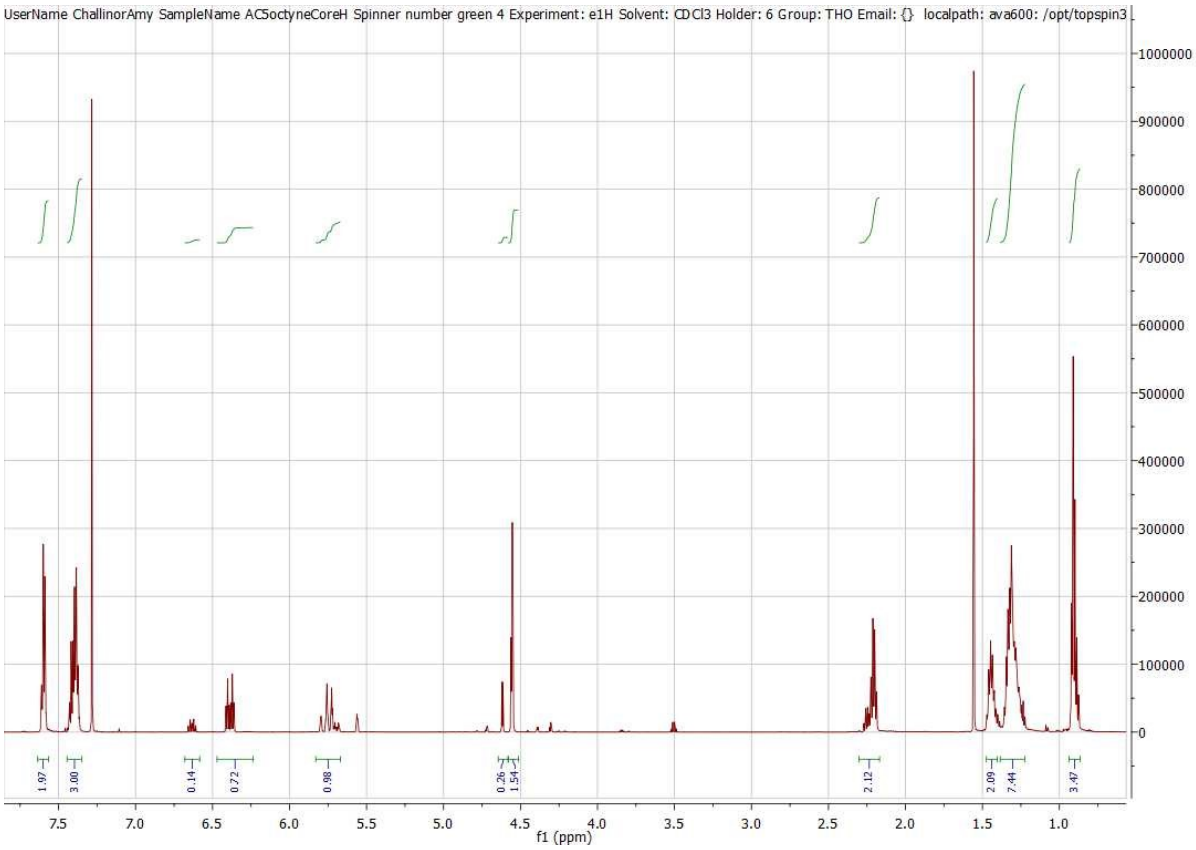


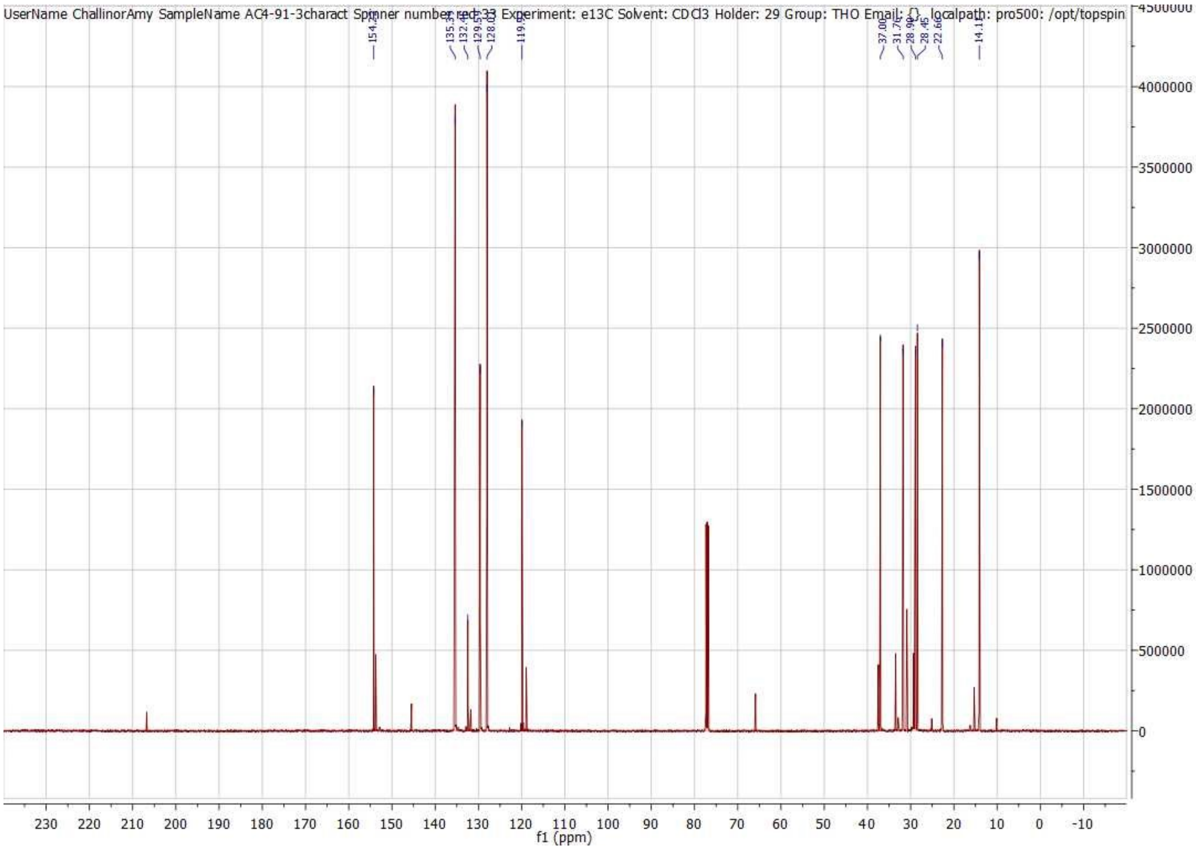


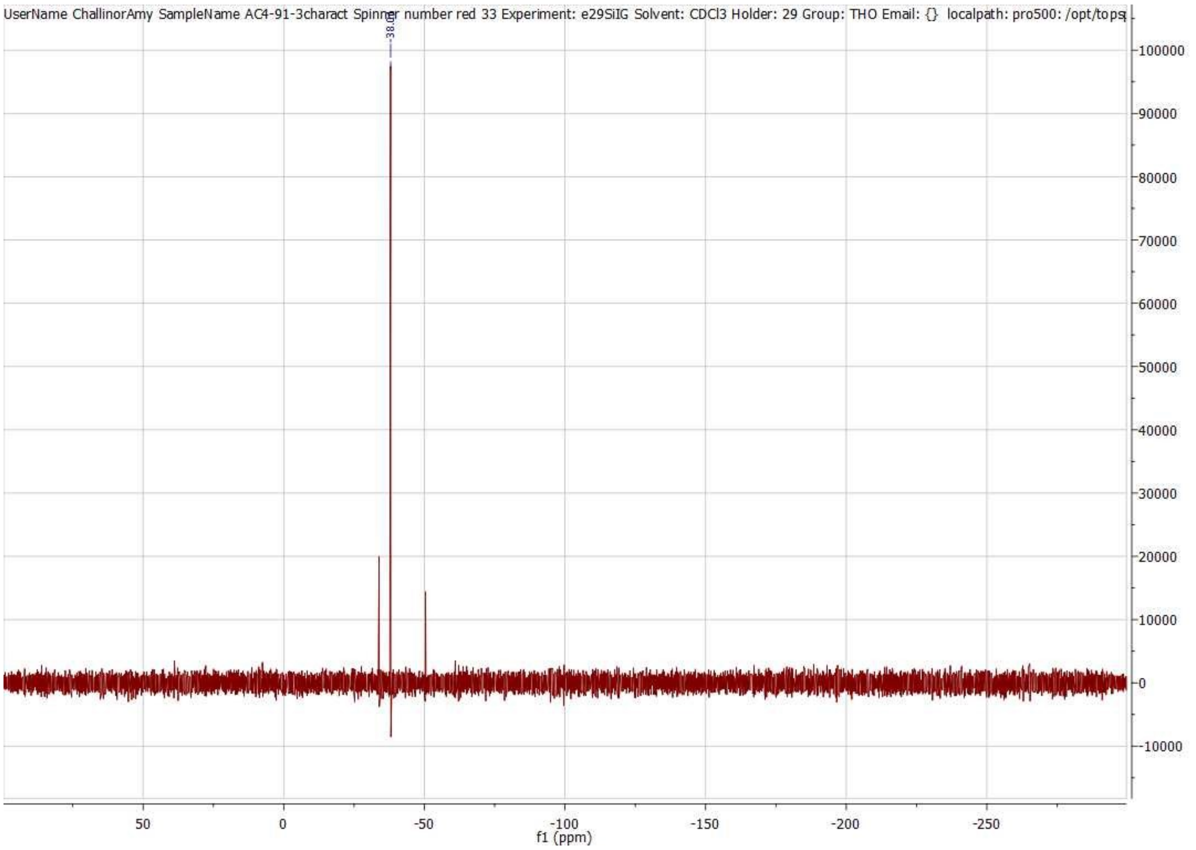

UserName ChallinorAmy SampleName AC4-110-2charact Spinner number red 48 Experiment: e29SIIG Solvent: CDCl3 Holder: 17 Group: THO Email: {} localpath: pro500: /opt/top
-23.3
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

trans-1-Octen-1-ylsilylbenzene (3m)

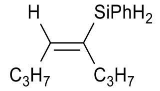


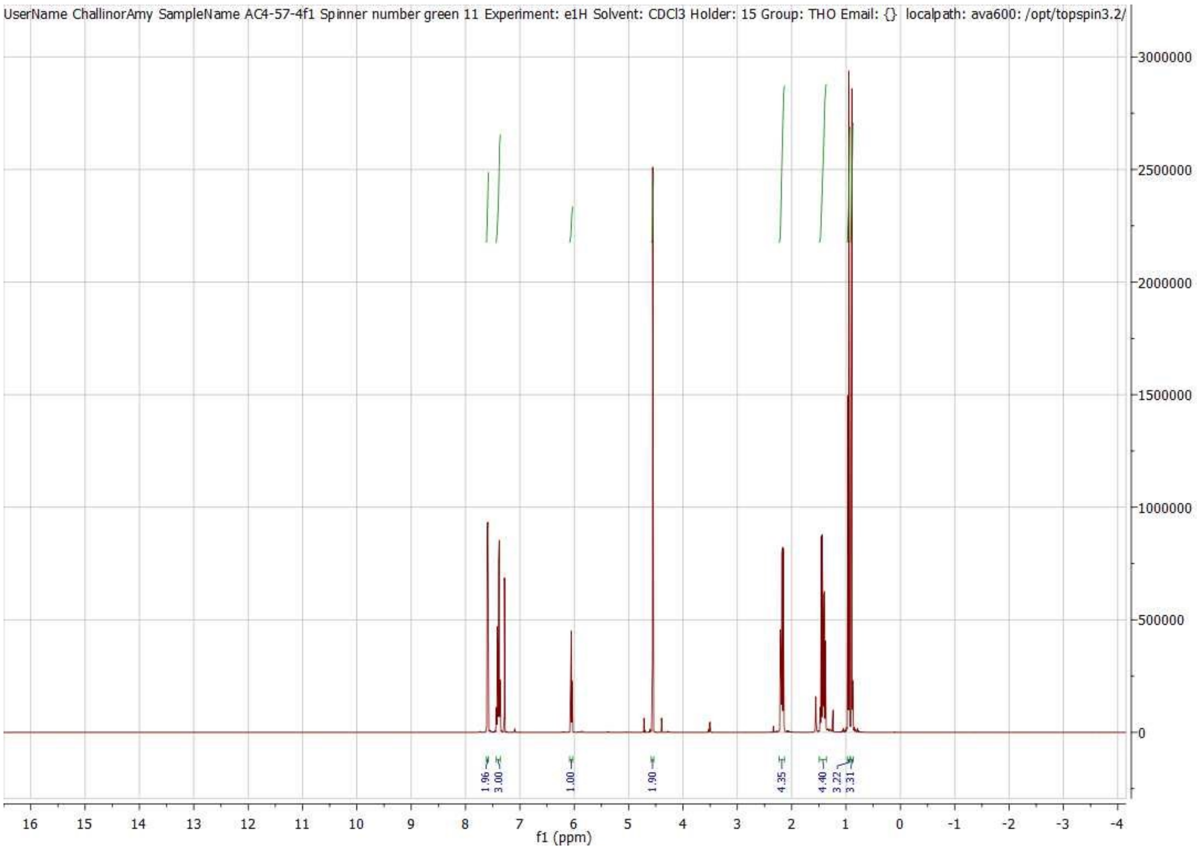


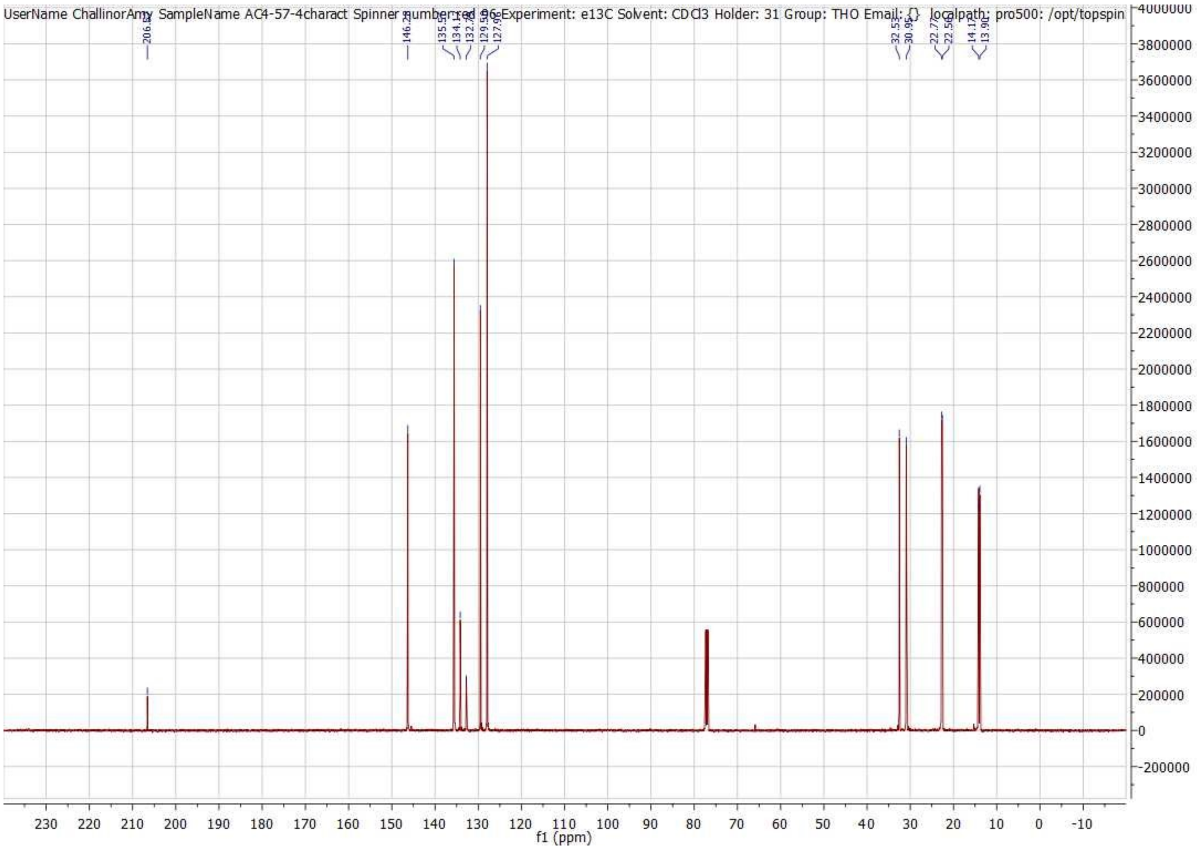

UserName ChallinorAmy SampleName AC4-91-3charact Spinner number red 33 Experiment: e13C Solvent: CDCl3 Holder: 29 Group: THO Email: {} localpath: pro500: /opt/topspin
154.2
135.3
132.4
129.5
128.0
119.9
37.00
31.76
28.90
28.45
22.66
14.11
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

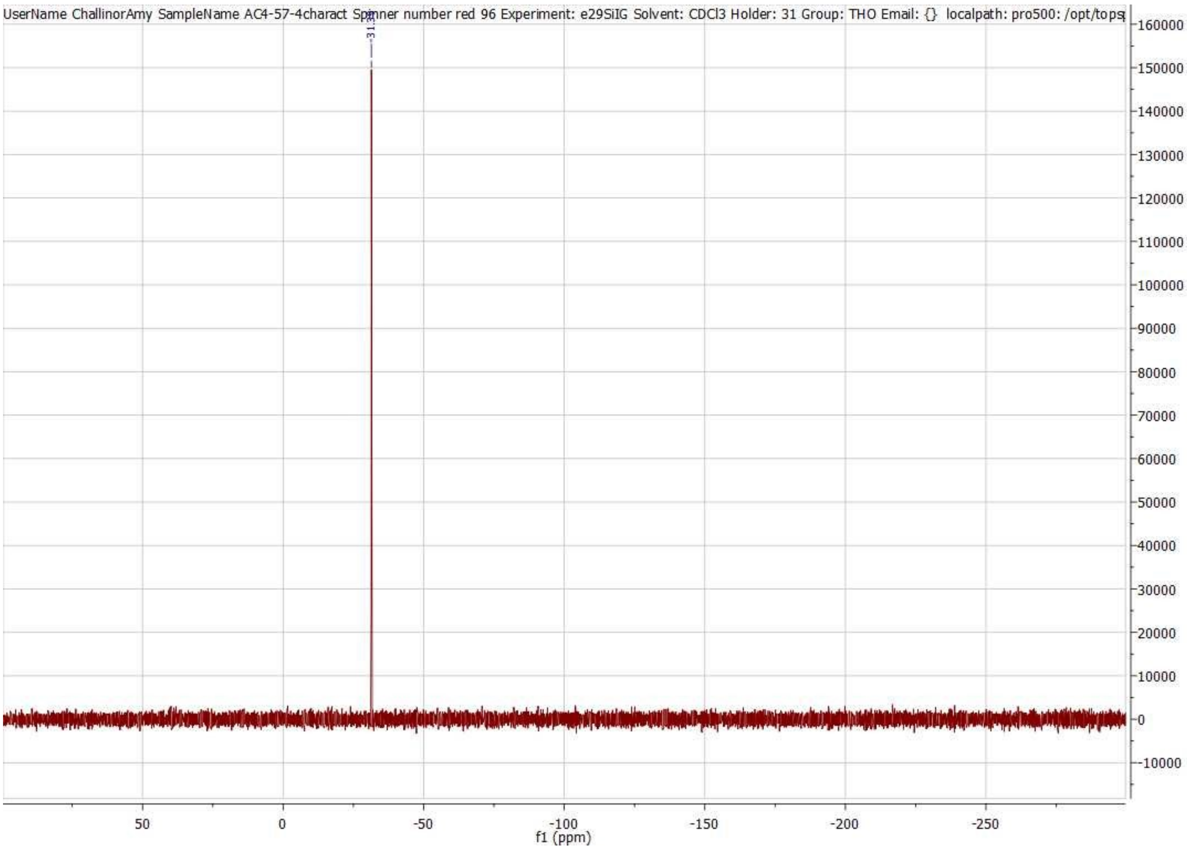

UserName ChallinorAmy SampleName AC4-91-3charact Spinner number red 33 Experiment: e29SiIG Solvent: CDCl3 Holder: 29 Group: THO Email: {} localpath: pro500: /opt/tops
-38.00
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

Phenyl[(*E*)-1-propyl-1-pentenyl]silane (3n)

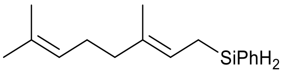


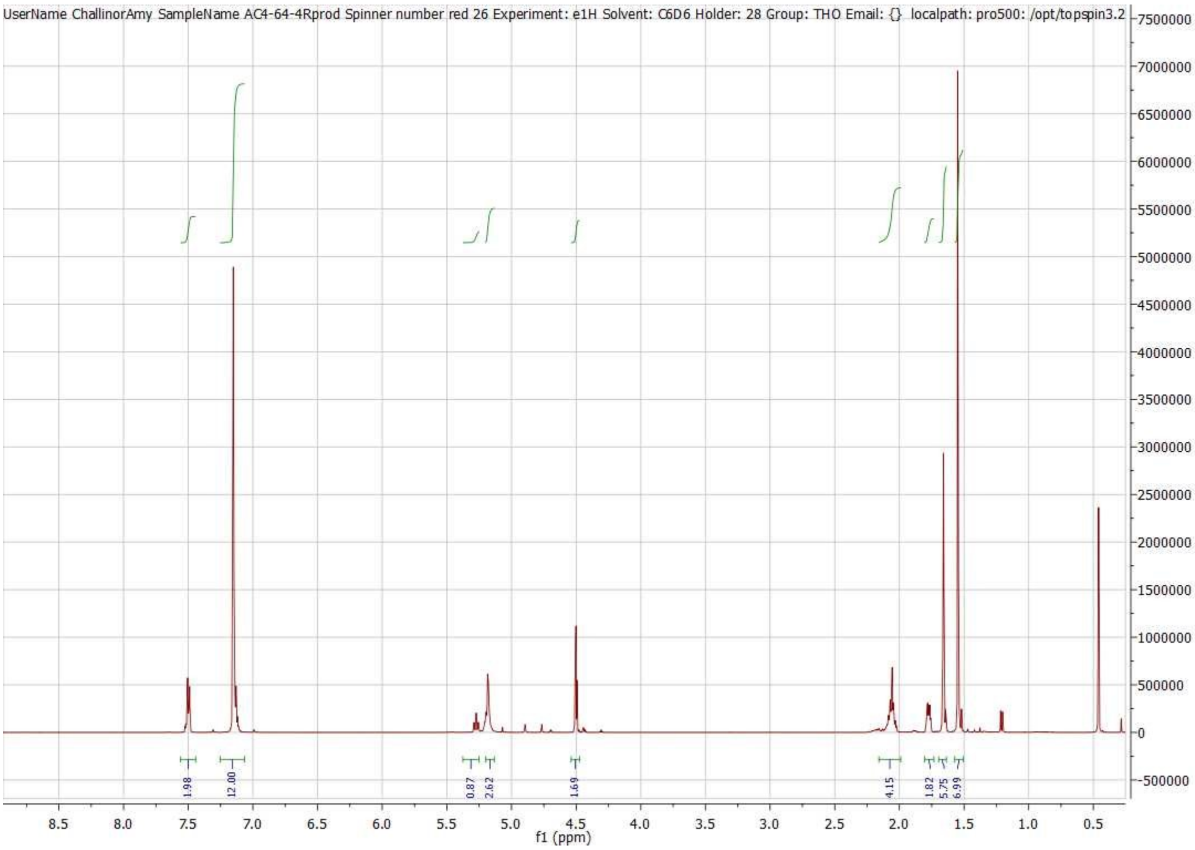


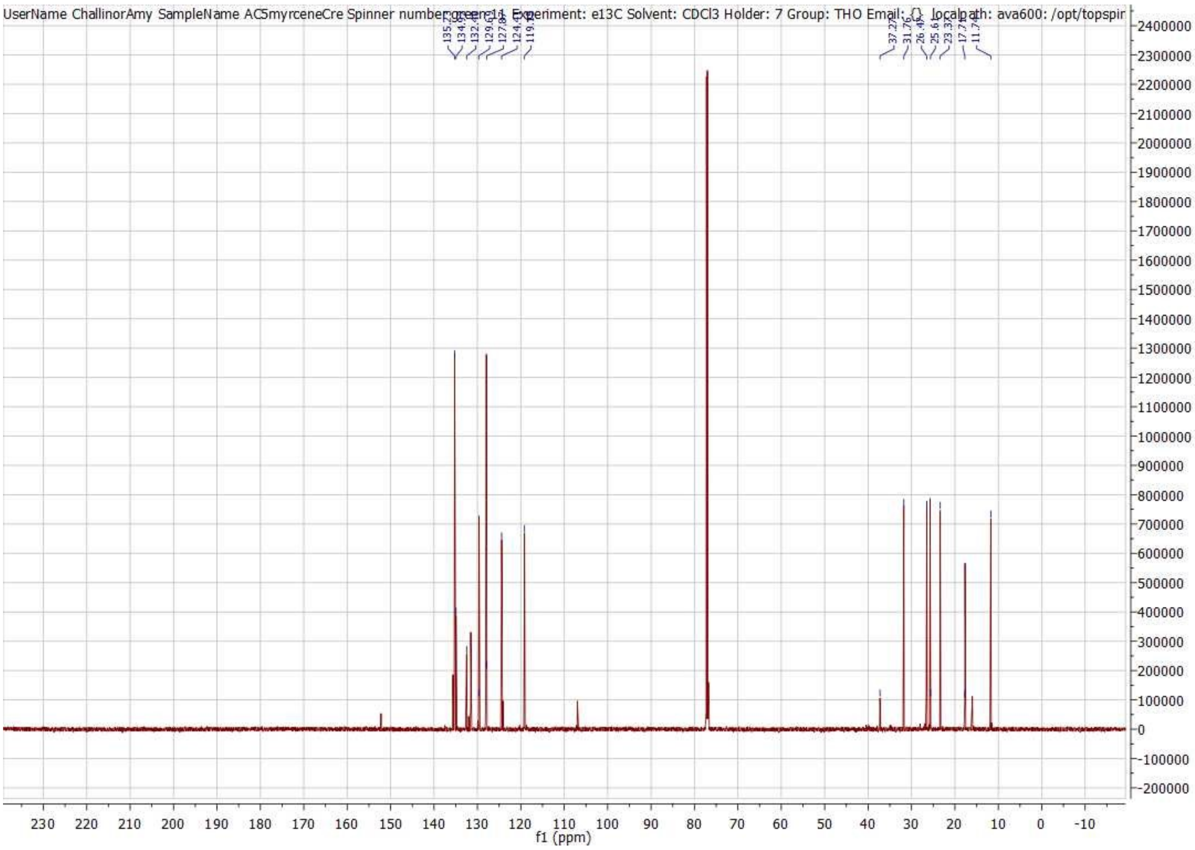


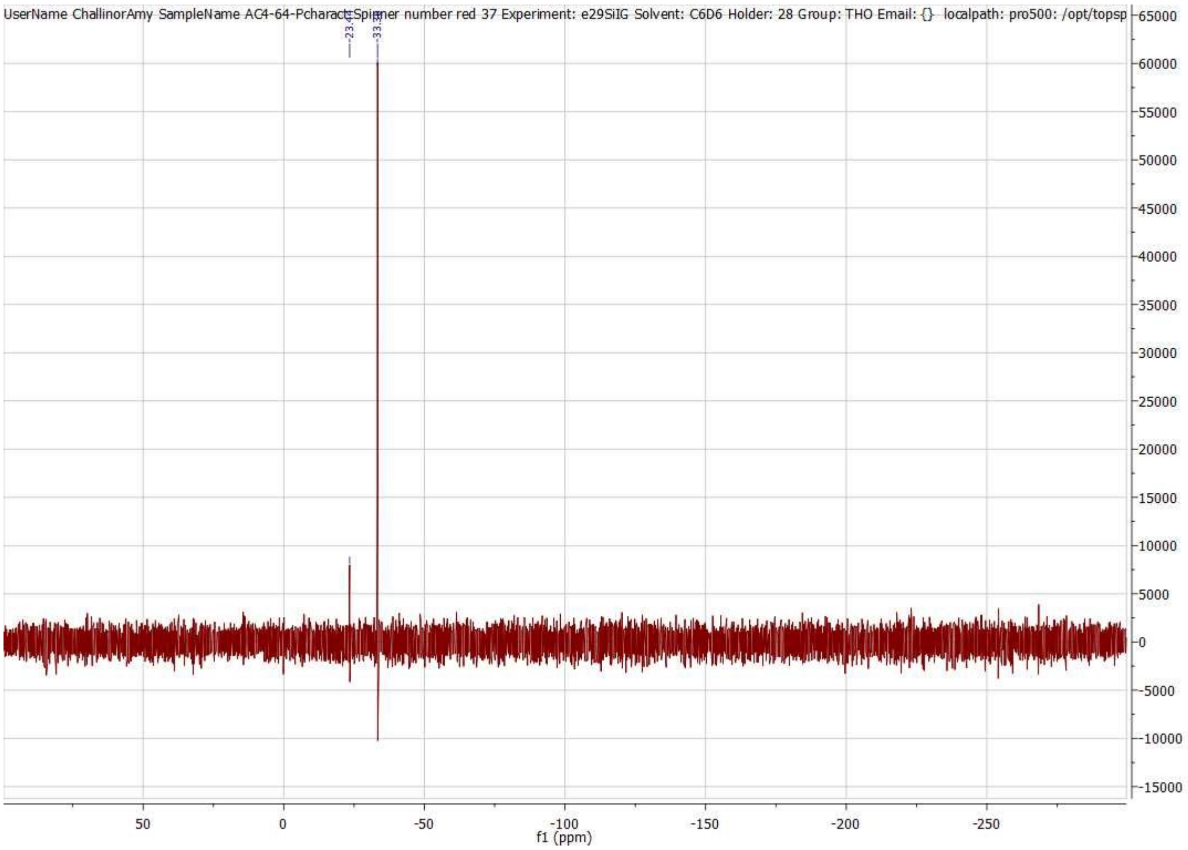

UserName ChallinorAmy SampleName AC4-57-4charact Spinner number red 96 Experiment: e29SiIG Solvent: CDCl3 Holder: 31 Group: THO Email: {} localpath: pro500: /opt/tops
-31.3
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

3,7-(Dimethyl)-1-[phenylsilane]octa-2,6-diene (3o)

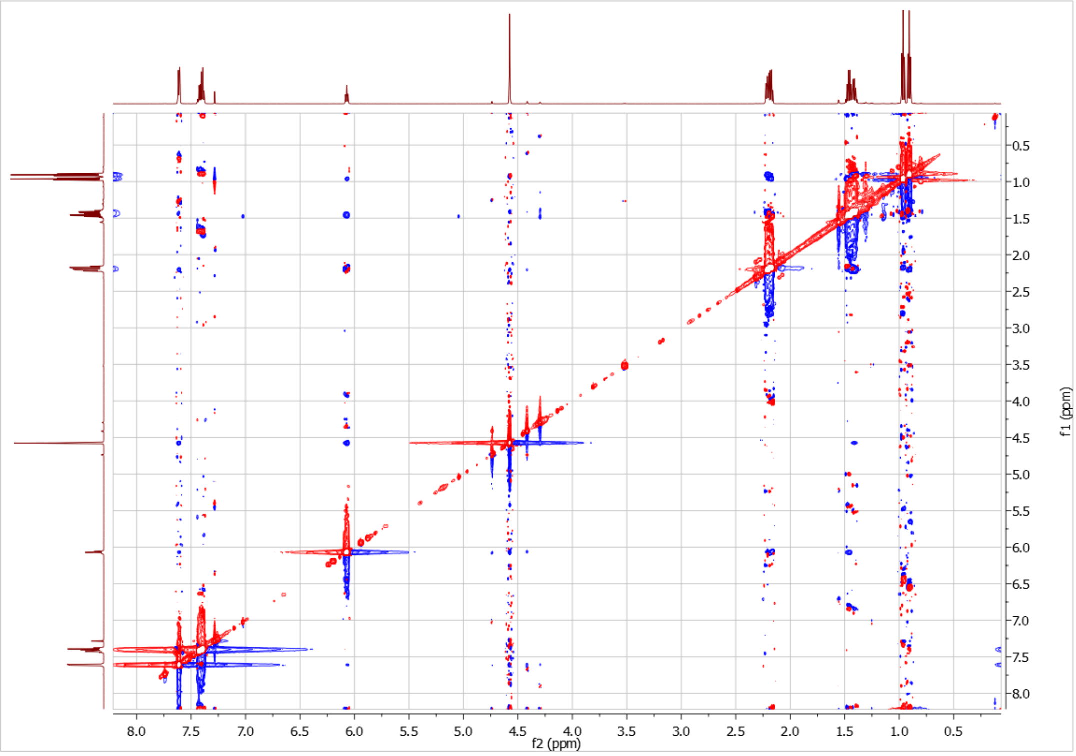




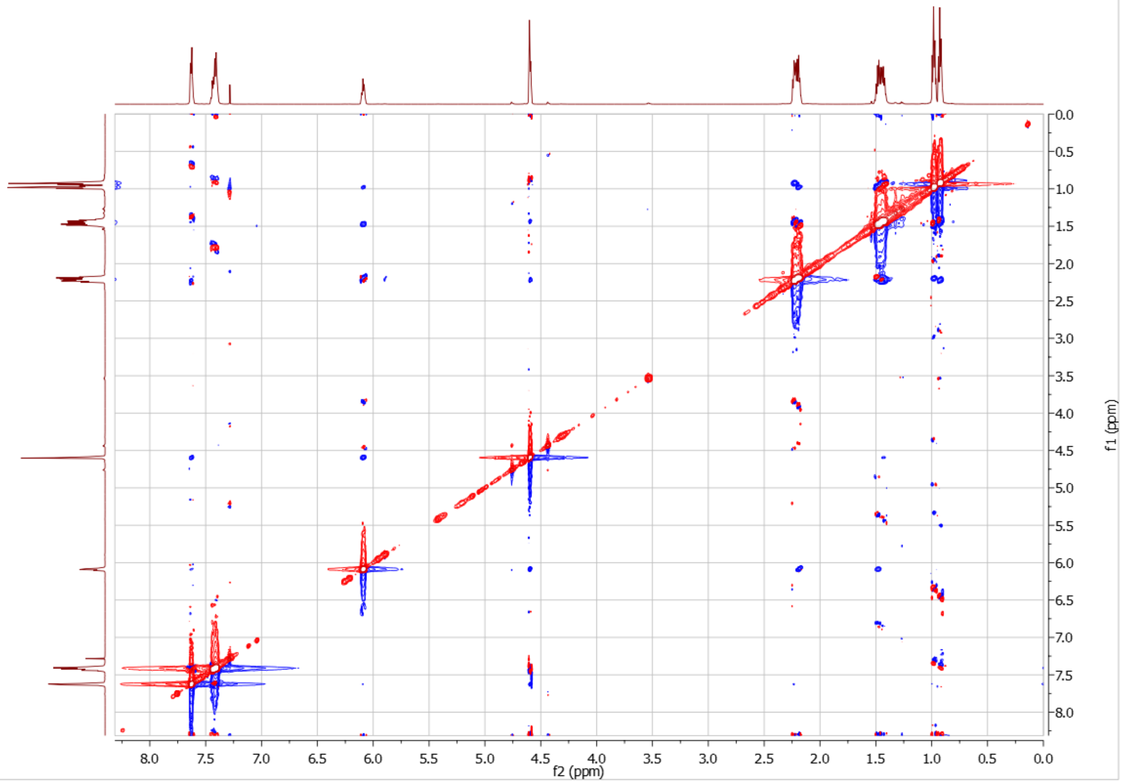



UserName ChallinorAmy SampleName AC4-64-Pcharact Spinner number red 37 Experiment: e29SiIG Solvent: C6D6 Holder: 28 Group: THO Email: {} localpath: pro500: /opt/topsp
-23.4
-33.3
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

NMR Spectra for all novel synthesised compounds are below

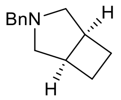


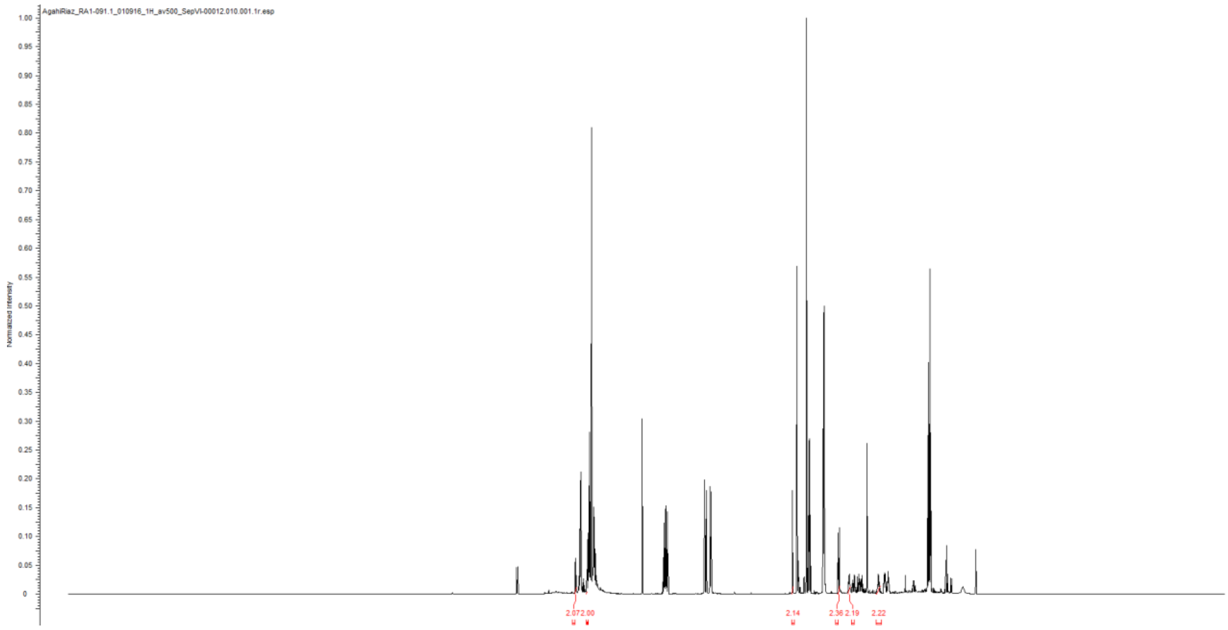
NOESY for 4-octyne product. With Fe



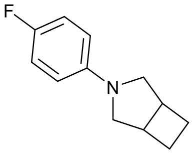
NOSEY for 4-octyne with Co

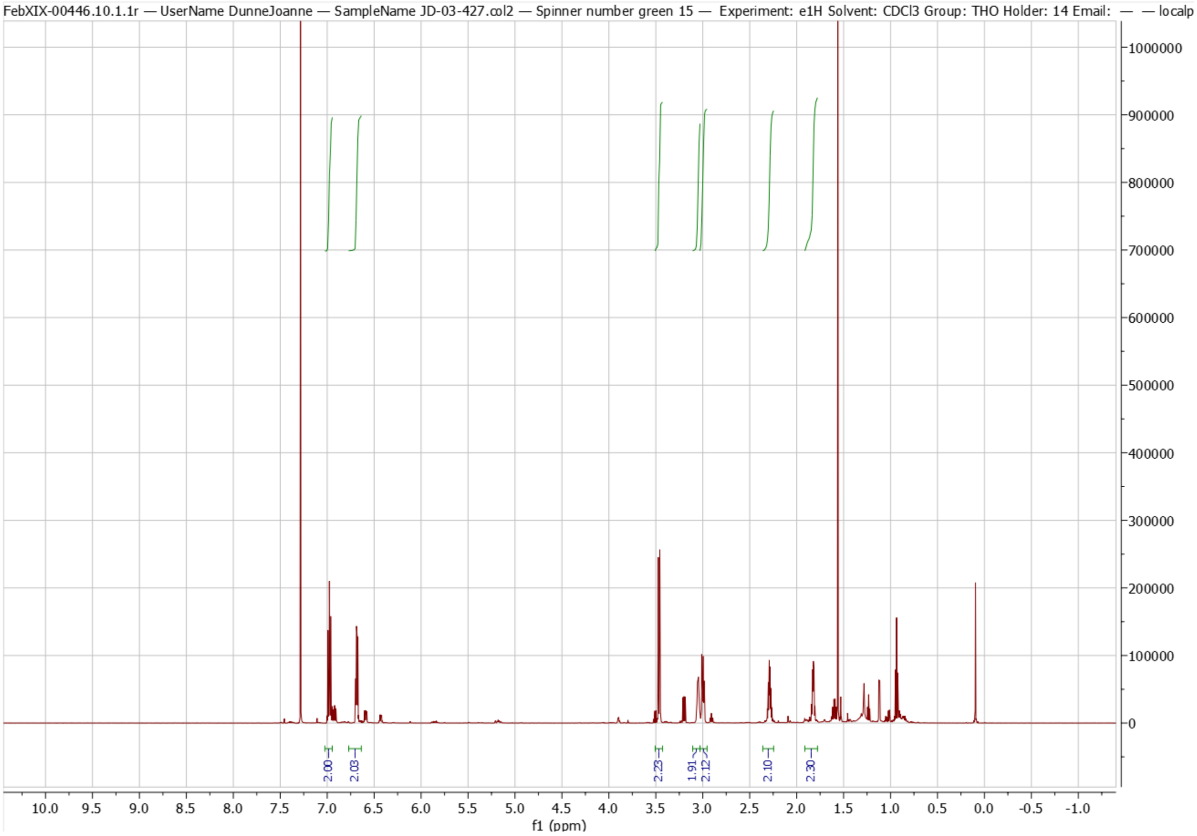
***N*-Benzyl-3-azabicyclo[0.2.3]heptane (8a)**

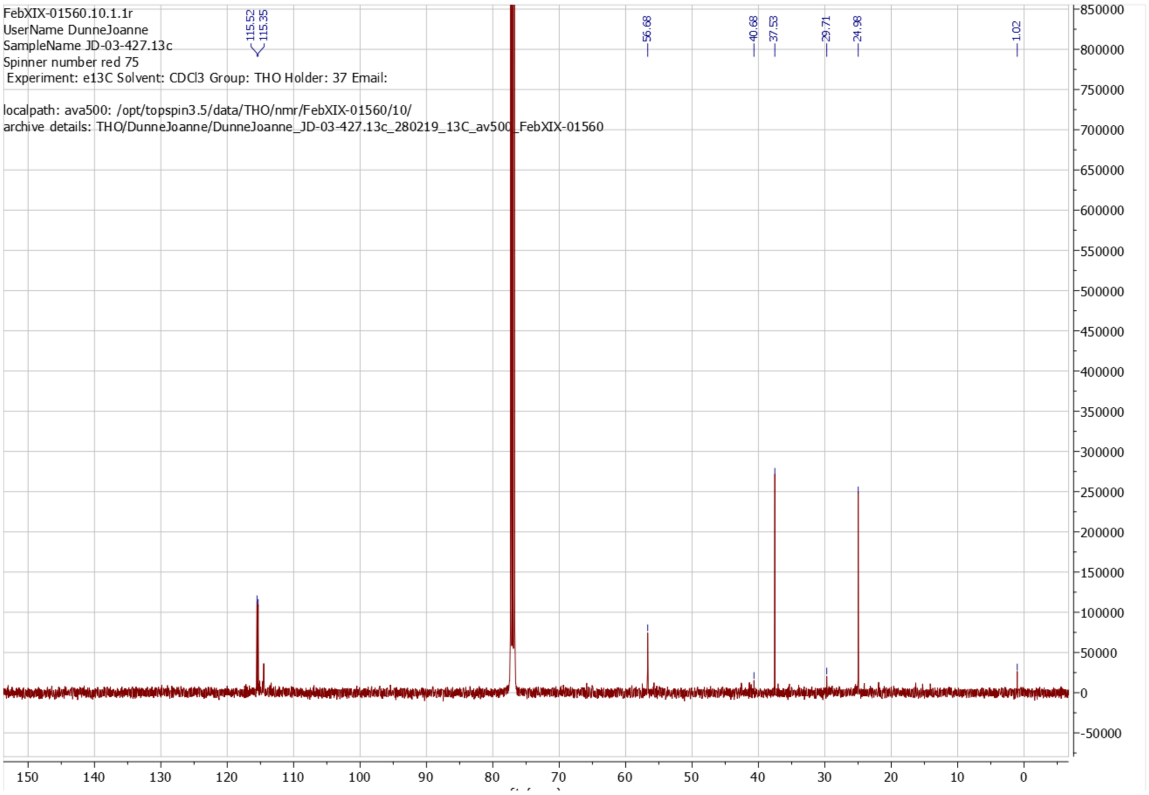


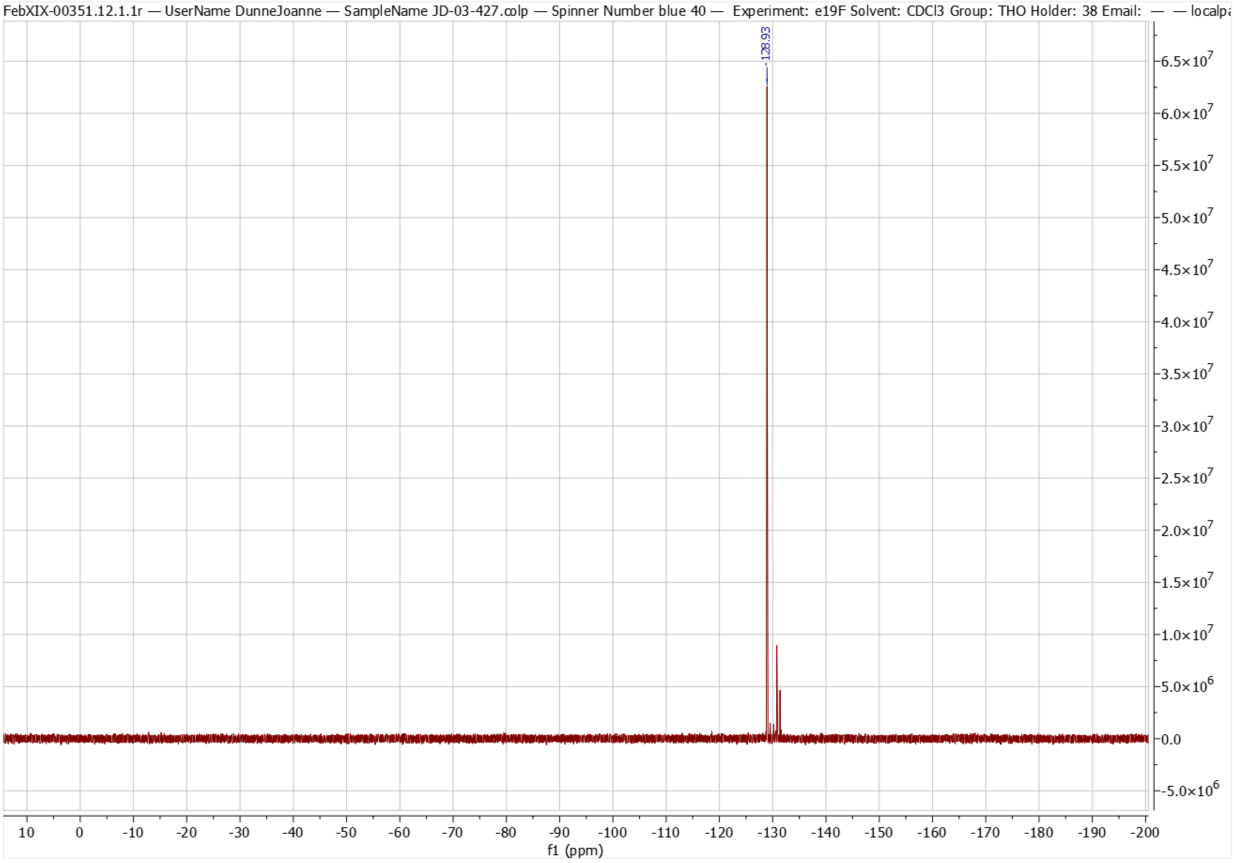


N-4-fluorophenyl-3-azabicyclo[0.2.3]heptane (8b)

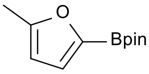


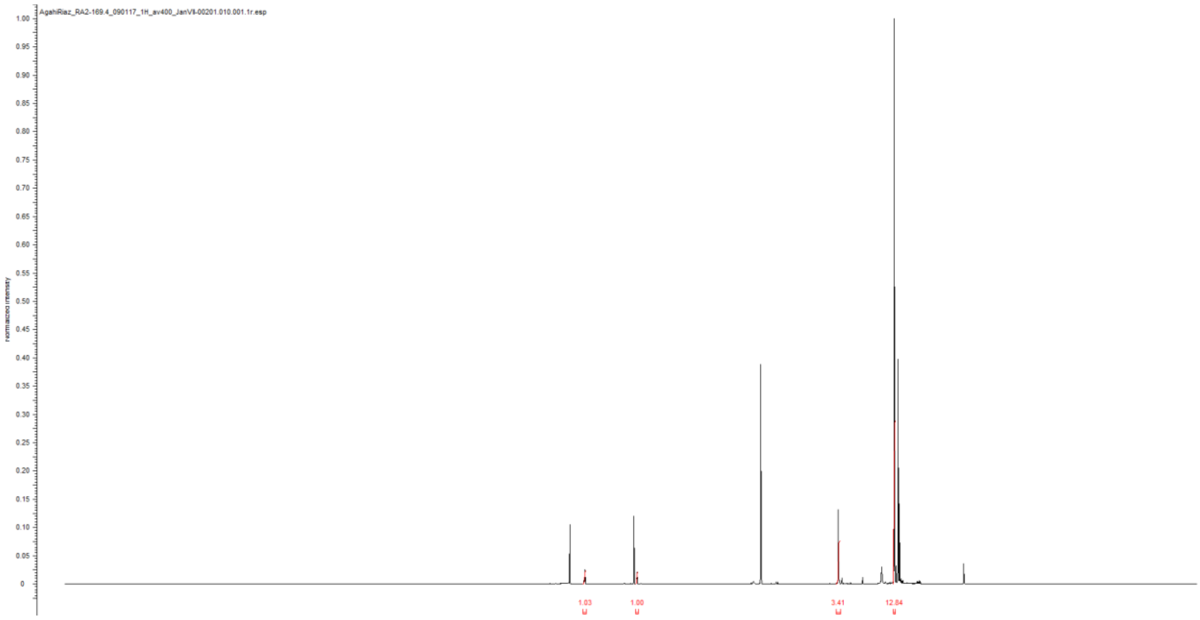




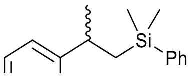

FebXIX-00351.12.1.1r — UserName DunneJoanne — SampleName JD-03-427.colp — Spinner Number blue 40 — Experiment: e19F Solvent: CDCl3 Group: THO Holder: 38 Email: — — localpa
-128.93
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

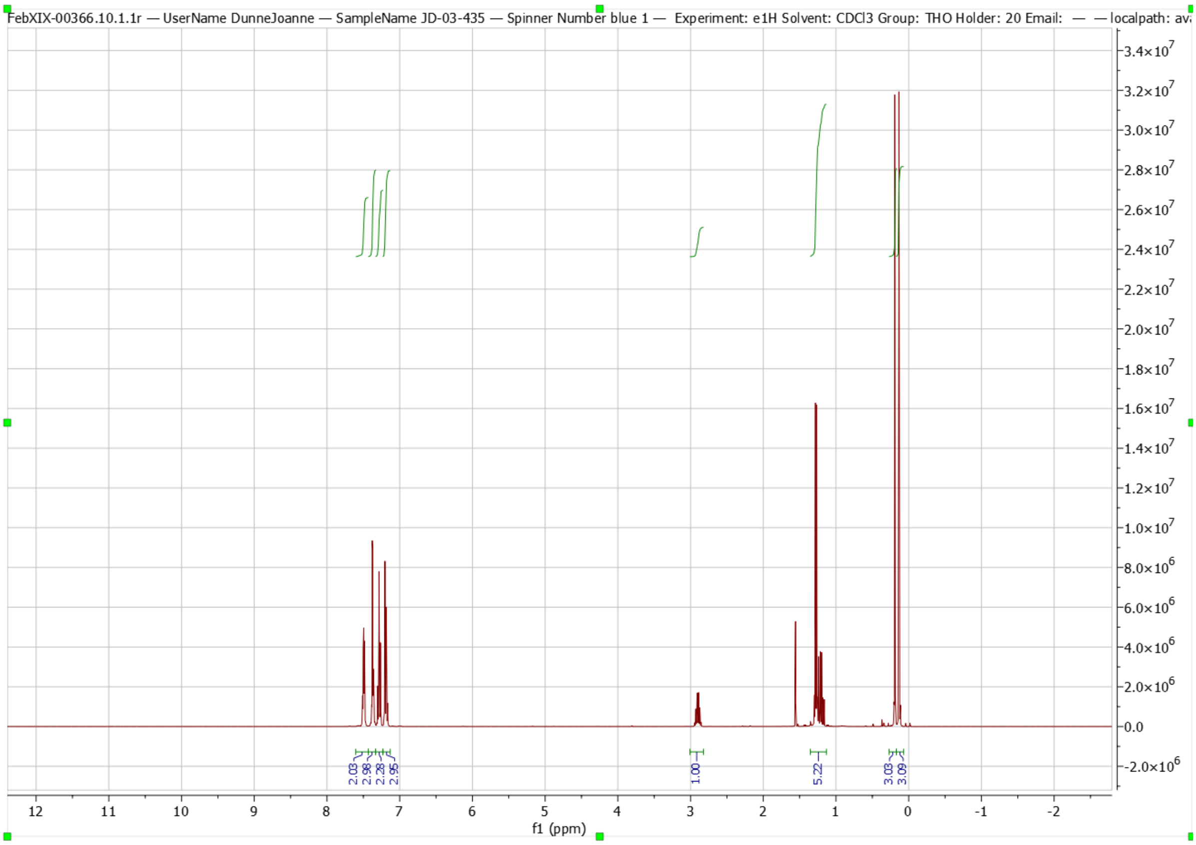
4,4,5,5-tetramethyl-2-(5-methylfuran-2-yl)-1,3,2-dioxaborolane (10)

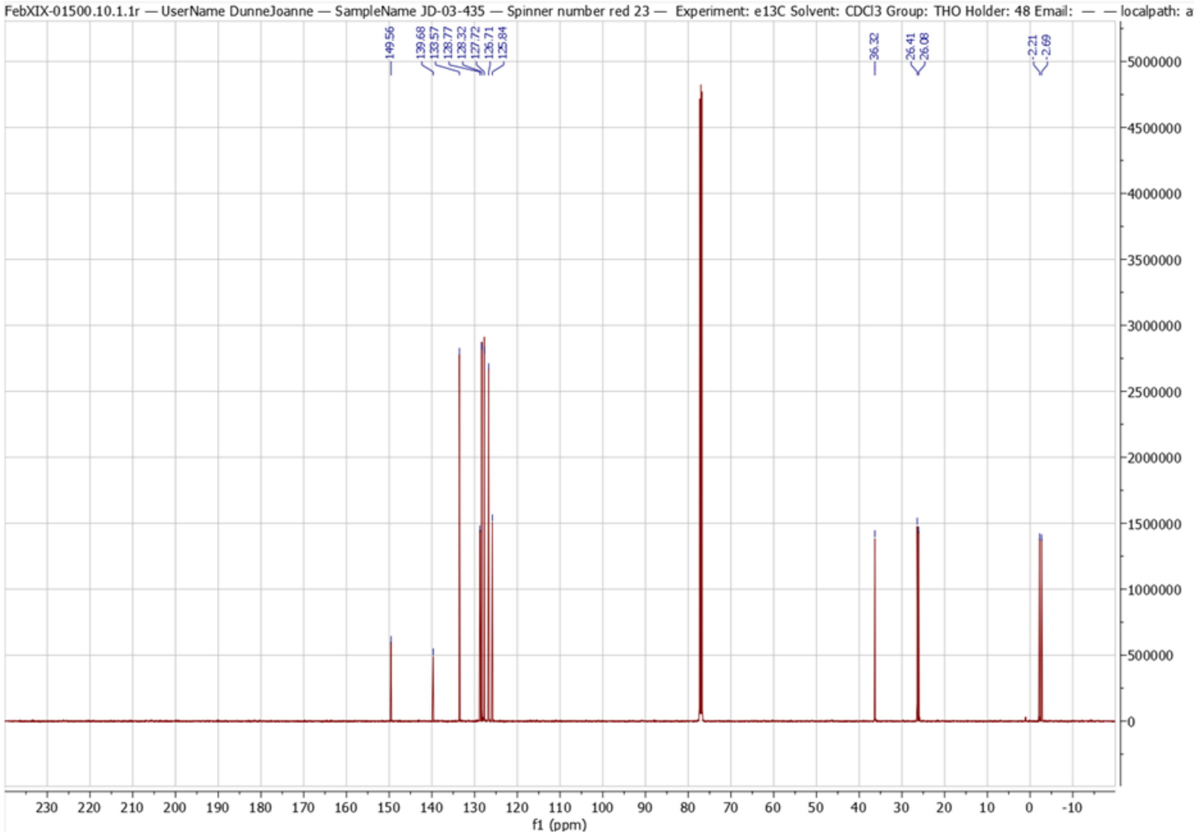


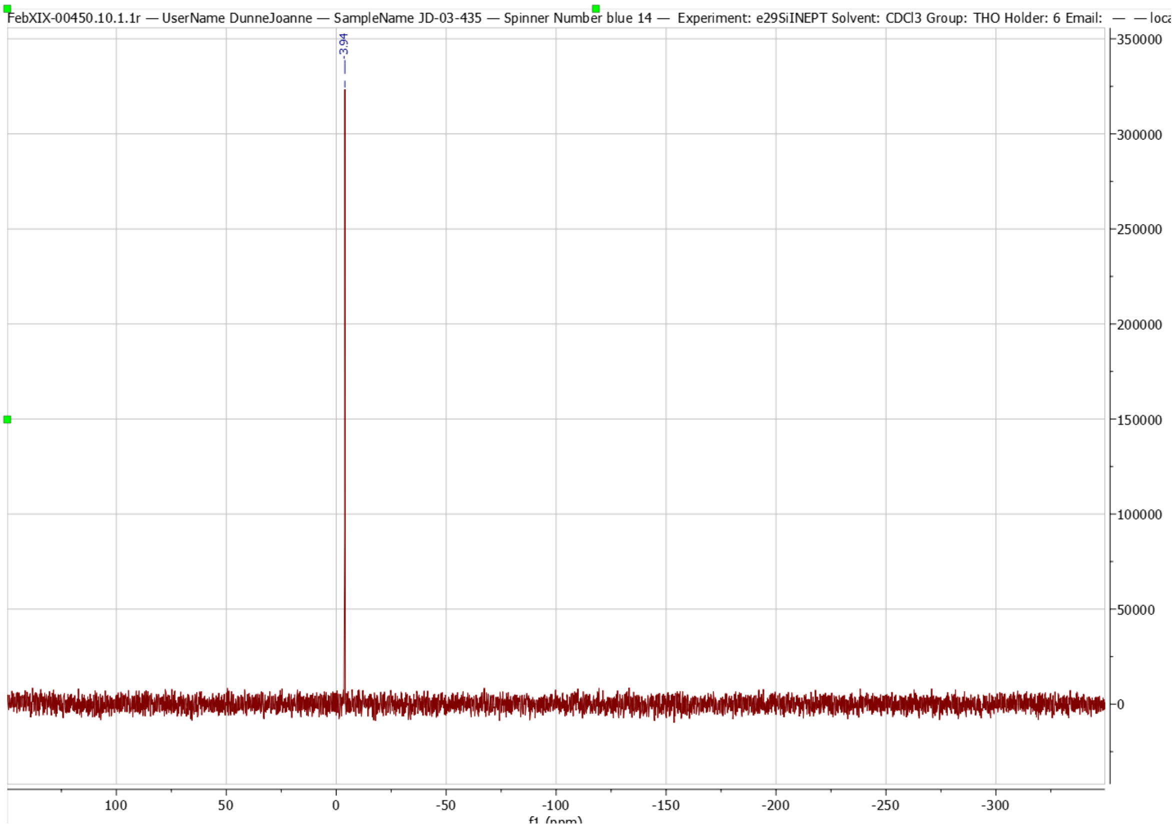


2-Phenylpropylphenyldimethylsilane (2u)

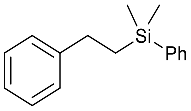


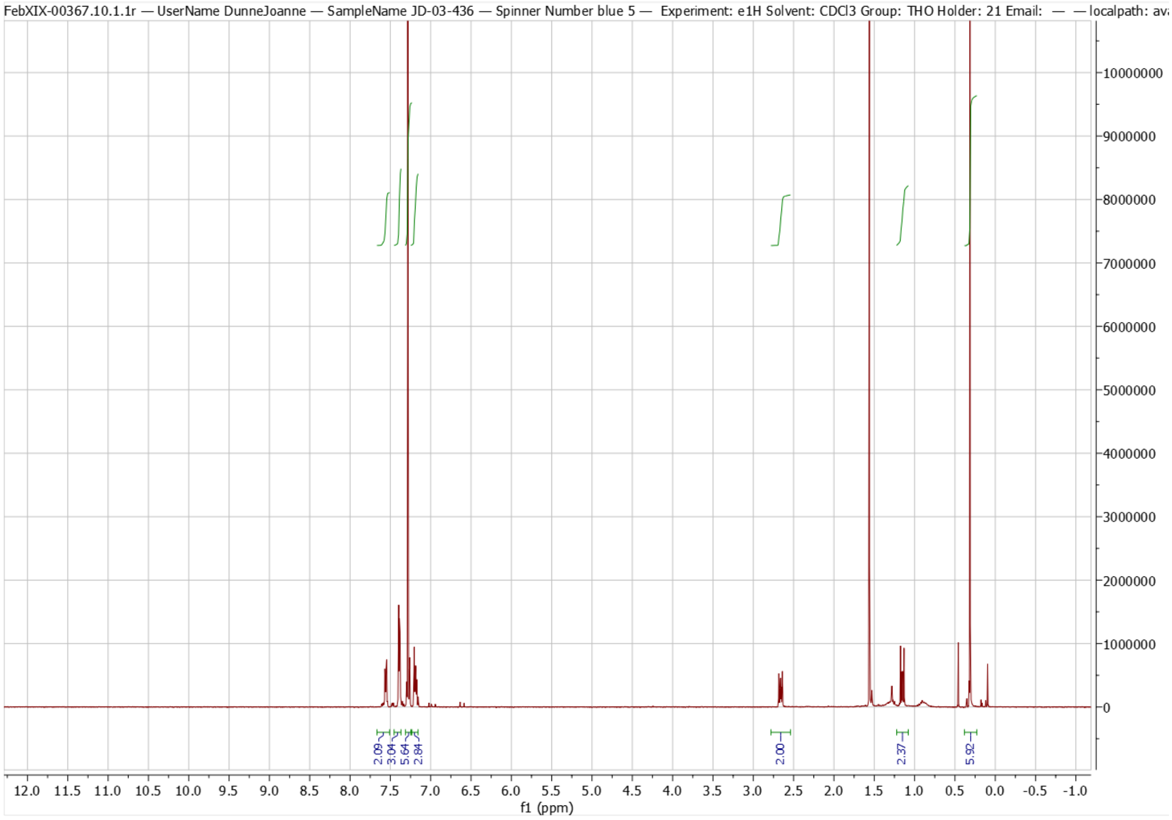


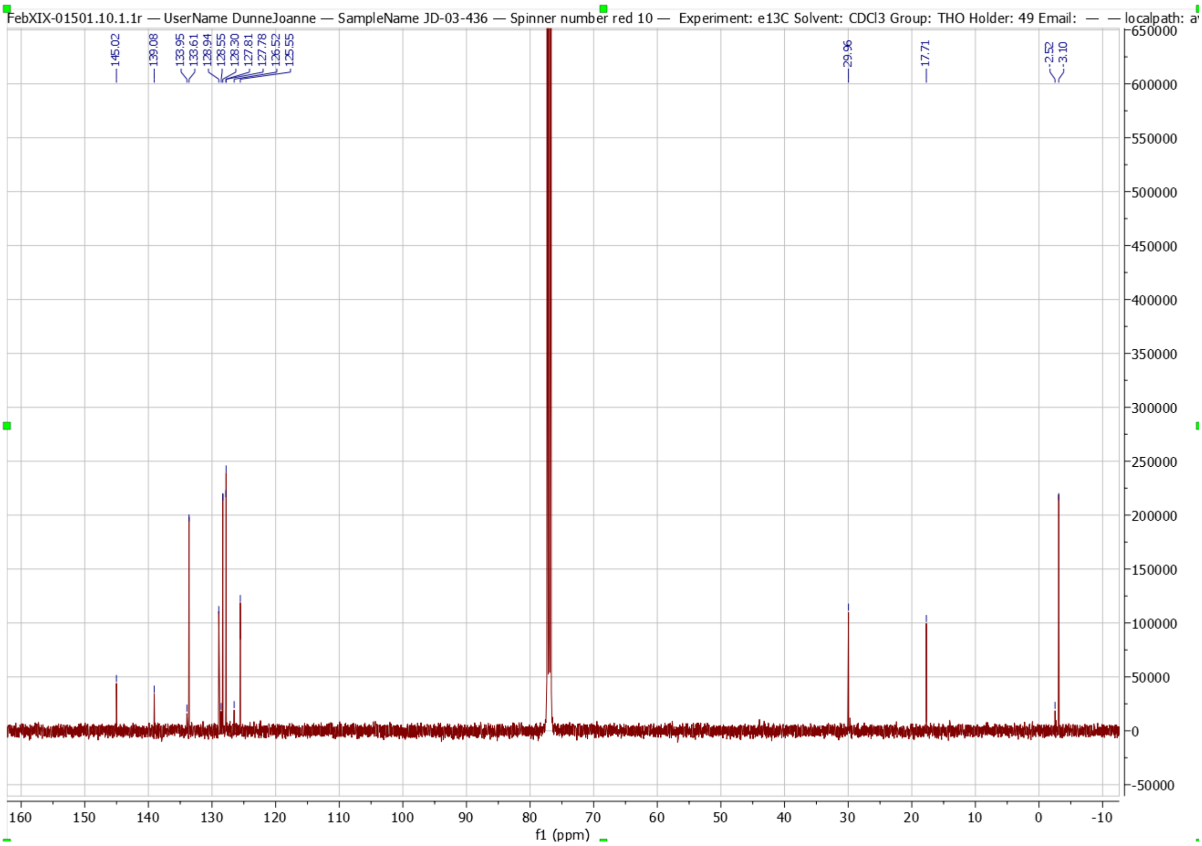


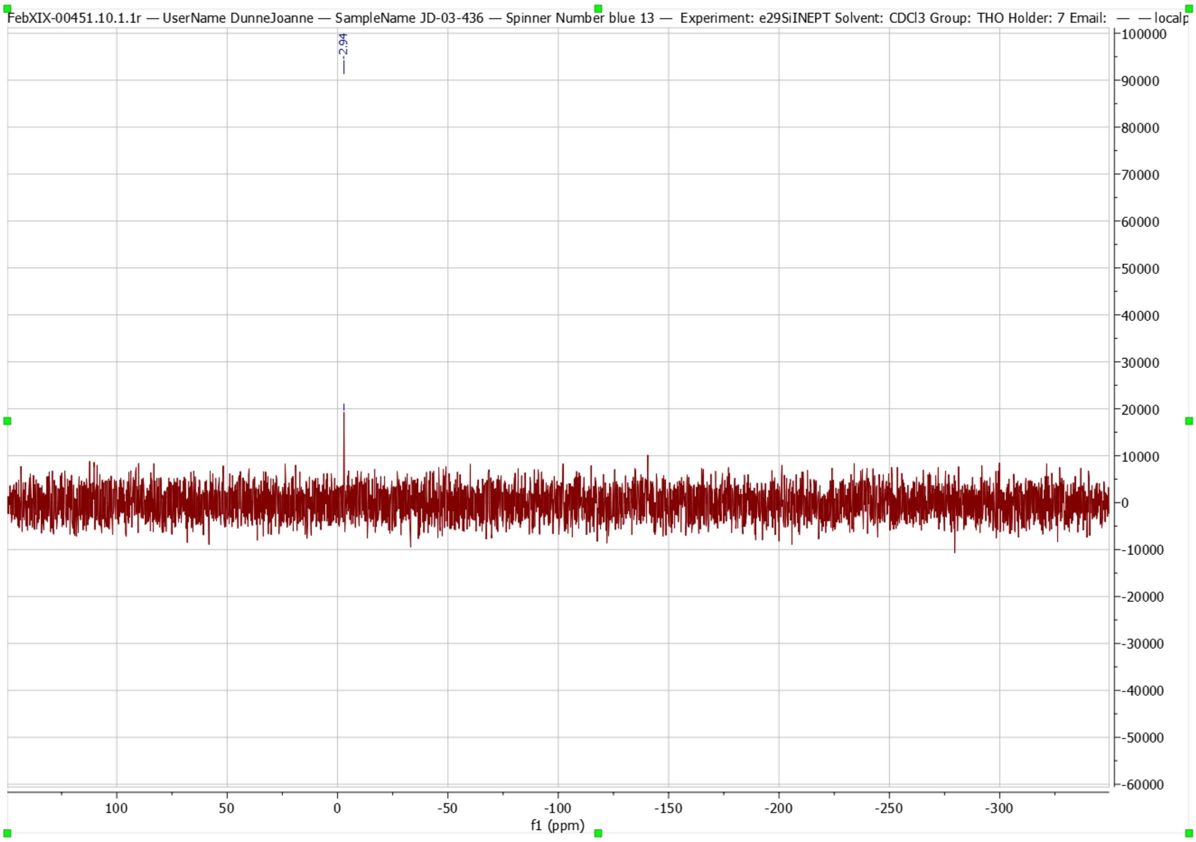

FebXIX-00450.10.1.1r — UserName DunneJoanne — SampleName JD-03-435 — Spinner Number blue 14 — Experiment: e29SiINEPT Solvent: CDCl3 Group: THO Holder: 6 Email: — — loca
-3.94
350000
300000
250000
200000
150000
100000
50000
0
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

Dimethylphenyl(2-phenylethyl)silane (2v)

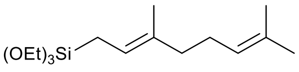




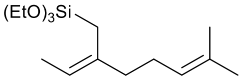



FebXIX-00451.10.1.1r — UserName DunneJoanne — SampleName JD-03-436 — Spinner Number blue 13 — Experiment: e29SiINEPT Solvent: CDCl3 Group: THO Holder: 7 Email: — — localp
-2.94
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
-60000
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

(*E*)-(3,7-dimethylocta-2,6-dien-1-yl)triethoxysilane and (*E*)-(2-ethylidene-6-methylhept-5-enyl)triethoxysilane (2w)



Linear



Branched