

SUPPORTING INFORMATION

***In Situ ortho*-Lithiation/Functionalization of Pentafluorosulfanyl Arenes**

Thanh V. Le and Olafs Daugulis*

Department of Chemistry, University of Houston, Houston, TX 77204-5003

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General considerations:

Reactions were performed mostly in 2-dram vials using screw caps with 13 mm hole and white silicone septum with white teflon face (from SUPELCO). Column chromatography was performed on 60 Å silica gel (Sorbent Technologies). GC-MS analyses were performed on a Shimadzu GCMS-QP5000 chromatograph equipped with a Restek column (Rtx-XLB, 30 m x 0.25 mm I.D.). The ^1H , ^{19}F and ^{13}C NMR spectra were recorded on JEOL EC-400 or JEOL EC-600 spectrometers using TMS or residual solvent peak as a reference. Compounds for HRMS were analyzed by positive and negative mode electrospray ionization (APCI or ESI) using Agilent QTOF mass spectrometer in the Mass Spectrometry Facility (MSF) of the Department of Chemistry of University of Texas at San Antonio and Texas A&M University. Temperature was monitored by Fluke 54 II B Dual Input Digital Thermometer with Data Logging. Analytical thin layer chromatography was performed on silica gel IB-F (Baker-flex) by J. T. Baker. Low temperature reactions were performed using Cryo Immersion Cooler FC100 with Flexi Probe from SP Scientific. All procedures were performed under nitrogen atmosphere unless otherwise noted. Room temperature is 23 °C. Anhydrous solvents were used for all reactions.

Materials: The following starting materials were obtained from commercial sources and were used without further purification: pentafluorosulfanyl benzene, 2,2,6,6-tetramethylpiperidine (TMPH), dicyclohexylamine, diisopropylamine, 1-adamantyl bromide, 1-adamantyl amine, chlorodimethylsilane, sodium methoxide, 3-fluoropentafluorosulfanyl benzene, 3-bromopentafluorosulfanyl benzene, 3-iodopentafluorosulfanyl benzene, 4-pentafluorosulfanyl toluene, 3-aminopentafluorosulfanyl benzene, 4-aminopentafluorosulfanyl benzene, 3-nitropentafluorosulfanyl benzene, potassium methoxide, 3-cyanopentafluorosulfanyl benzene, 3-acetylpentafluorosulfanyl benzene, 3-(pentafluorosulfanyl) benzaldehyde, acetic anhydride, benzoic anhydride, chlorotrimethylsilane, chloro(methyl)phenylsilane, chlorotrimethylgermane, chlorotriethylgermane, and bis(tributyltin).

General Notes:

If dimethylsilyl(-SiHMe₂) group is at ortho position to the SF₅ group. ^{19}F NMR will show a coupling between hydrogen of dimethylsilyl group and the four equatorial fluorine atoms of the

SF₅ group. This allows the assignment of silylation regioselectivity. Please see ¹⁹F NMR spectra for details.

The position of dimethylsilyl (-SiHMe₂) group in mono-silylated product was determined based on the H-F coupling between hydrogen of dimethylsilyl group and the four equatorial fluorine atoms of the SF₅ group. It was also confirmed by the X-ray diffraction analysis of *N*-(3-dimethylsilyl-4-(pentafluorosulfanyl)phenyl)benzamide, by benzylation of silylation product of 4-aminopentafluorosulfanyl benzene which delivered *N*-(3-dimethylsilyl-4-(pentafluorosulfanyl)phenyl)benzamide, and by X-ray crystallographic analyses of 2,4-bis(hydroxydimethylsilyl)-3-fluoropentafluorosulfanyl benzene and 2,4-bis(hydroxydimethylsilyl)-5-bromopentafluorosulfanyl benzene.

TMPLi, Cy₂NLi, and LDA:

A 200 mL oven-dried Schlenk flask equipped with a magnetic stir bar and a septum was evacuated and backfilled with nitrogen 5 times. TMPH (2,2,6,6-tetramethylpiperidine; 12 g, 85 mmol) or Cy₂NH (dicyclohexylamine, 15 g, 85 mmol) or diisopropylamine (8.6 g, 85 mmol) was added via syringe, followed by anhydrous pentane to give approximately 30 mL of solution. The mixture was cooled to -78 °C (dry ice-acetone bath) and stirred for 10 minutes. *n*-BuLi (2.5 M in hexanes, 40 mL, 100 mmol) was then added dropwise and reaction mixture was stirred for 30 minutes at -78 °C, then warmed to room temperature (23 °C) and stirred overnight. The solvent was cannula transferred away from the solid. The solid was washed with pentane 3 times using cannula to remove the supernatant solution and then dried under vacuum to remove all solvent. Residue was dried under vacuum for at least 12 hours. A light-yellow powder of solid TMPLi (12 g, 95 %), or Cy₂NLi (14 g, 88 %), or LDA (8.5 g, 94 %) was obtained.

Di-1-adamantylamine:

Method used previously was employed.¹ A thick-walled glass tube (12-inch diameter and 800 ml volume) was filled with powdered 1-adamantyl bromide (215 g, 1.0 mol) and 1-adamantylamine (272 g, 1.8 mol). Tube was evacuated for 24 h and then vacuum-sealed and placed into a metal container. The metal container was placed in furnace. The temperature was increased from room temperature to 240 °C over 5 hours and maintained at 240 °C for 72 h. The mass inside the tube (487 g) converted to a hard solid by cooling to 25 °C. The solid was carefully crushed with a

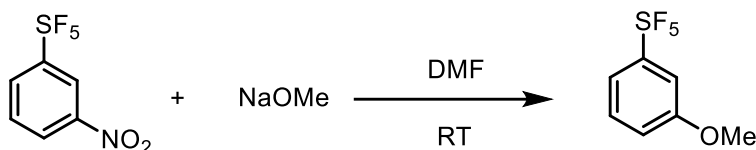
mortar and pestle. About 3.3 % of the powder (16 g) was dissolved in a mixture of hot aqueous NaOH (20 %, 250 mL) and diethyl ether (250 mL). It is important to dissolve powder in NaOH solution first and then add ether. The solution was placed into separatory funnel. It was shaken vigorously only after the reaction mixture cooled down. The ether layer was separated and shaken with aqueous HCl solution (300 mL, 10 %) to precipitate di-1-adamantylamine as the hydrochloride salt which is insoluble. The precipitate was collected by filtration and washed twice with water. The resulting white solid was shaken with warm aqueous NaOH (20 %, 200 mL) and after 3 minutes, ether (250 mL) solution to regenerate di-1-adamantylamine. The ether layer was separated and dried over anhydrous K₂CO₃. After filtering off the drying agent and evaporating the solvent in vacuo, 7.02 g (75 %) of di-1-adamantylamine was obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 1.99 (apparent s, 6H), 1.75 (d, 12H), 1.59 (apparent s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 52.6, 46.6, 36.6, 30.1. This compound is known.²

Lithium di-1-admantylamide (LDAM):

Di-1-adamantylamine (14 g) was placed in oven-dried 500 ml Schlenk flask equipped with a stir bar. Flask was sealed with rubber septum and Teflon tape. Flask was filled with N₂ gas and evacuated at least 5 times (each time 10 minutes). Anhydrous pentane (240 mL) was added to the flask via syringe. *n*-BuLi (1.6 M in hexane, 36.0 mL) was injected dropwise via syringe into the suspension at room temperature. After injecting about 23 ml of *n*-BuLi, suspension became completely transparent as amine dissolved and after 2 to 3 hours it turned into a white suspension. Stirring was continued for 24 hours and then the suspension was allowed to settle. The transparent supernatant solution was removed via syringe and anhydrous pentane (100 mL) was added to the suspension. Suspension was stirred for 5 minutes and after settling, the transparent supernatant was removed via syringe. The same procedure was repeated once more. The residue was dried under vacuum for 8 hours. The product (12.2 g, 86 %) was used without further purification. ¹H NMR (600 MHz, – 60 °C in THF-*d*₈.) δ 1.87 (apparent s, 6H), 1.65 – 1.40 (m, 24H). ¹³C NMR (151 MHz, CDCl₃) δ 54.0, 51.7, 37.9, 31.2. This compound is known.¹

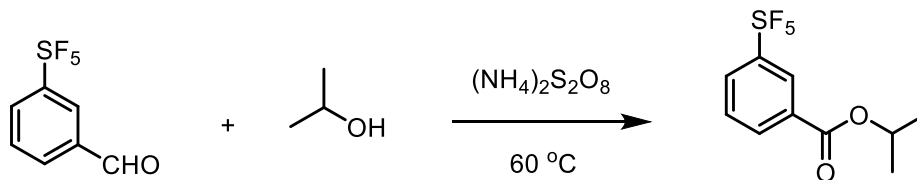
Synthesis of starting materials:

Synthesis of 3-methoxypentafluorosulfanyl benzene:



Following a slightly modified procedure described by Beier,³ NaOMe (0.86 g, 16 mmol, 1.1 equiv) was added in one portion to a solution of 3-nitropentafluorosulfanyl benzene (3.5 g, 14 mmol) in DMF (3 mL) at room temperature and the solution was stirred for 1 hour. Then another portion of NaOMe (0.86 g, 16 mmol, 1.1 equiv) was added in portions every hour until complete conversion was observed by monitoring ¹⁹F NMR spectrum. Saturated aqueous NH₄Cl was added and followed by extraction with CH₂Cl₂ (3x10 mL). The combined organic layers were washed with water (3x10 mL), then once with brine (10 mL), dried over Na₂SO₄, and concentrated under vacuo. The crude product was purified by column chromatography (hexanes/ethyl acetate 95:5, R_f = 0.45) to afford the title compound as a colorless liquid (3.2 g, 98 %). The NMR spectra are consistent with those reported in the literature: ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.33 (m, 2H), 7.29 – 7.28 (m, 1H), 7.05 – 7.03 (dd, *J* = 7.3, 3.0 Hz, 1H), 3.85 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.4, 154.9 (quintet, *J* = 17.2 Hz), 129.5, 118.2 (quintet, *J* = 4.7 Hz), 117.2, 112.2 (quintet, *J* = 4.7 Hz), 55.7. ¹⁹F NMR (376 MHz, CDCl₃) δ 84.62 (quintet, *J* = 149.2 Hz, 1F), 62.75 (d, *J* = 149.2 Hz, 4F). This compound is known.³

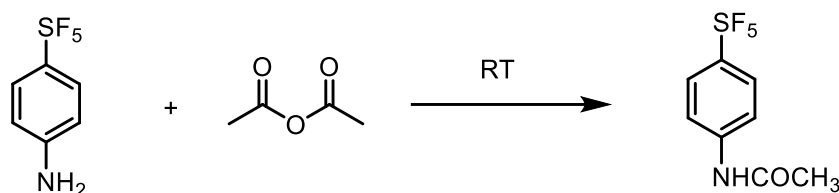
Synthesis of isopropyl 3-(pentafluorosulfanyl) benzoate:



A suspension of 3-(pentafluorosulfanyl) benzaldehyde (1.0 g, 4.3 mmol) and (NH₄)₂S₂O₈ (1.96 g, 8.6 mmol, 2 equiv) in isopropanol (4.2 g, 70 mmol) was stirred at 60 °C for 24 h. After cooling to room temperature, distilled water (20 mL) was used to dissolve the solid and the product was extracted by ethyl acetate (3 × 30 mL). The combined organic extract was concentrated and then purified by column chromatography on silica gel (hexanes/ethyl acetate 30:1) providing 1.2

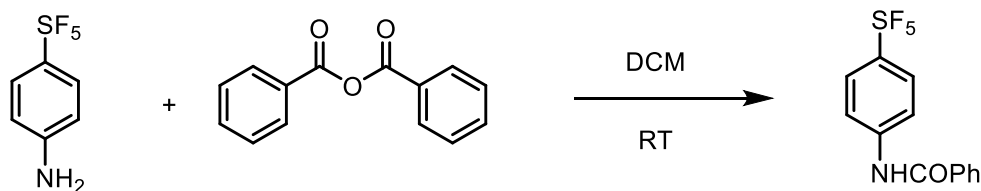
g (95%) of isopropyl 3-(pentafluorosulfanyl) benzoate as a colorless liquid. **¹H NMR** (400 MHz, CDCl₃) δ 8.40 (s, 1H), 8.18 (d, *J* = 7.9 Hz, 1H), 7.91 (d, *J* = 11.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 5.28 (septet, *J* = 6.2 Hz, 1H), 1.38 (d, *J* = 6.2 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 164.4, 153.9 (quintet, *J* = 18.4 Hz), 132.5, 131.9, 129.9 (quintet, *J* = 4.9 Hz), 128.9, 127.2 (quintet, *J* = 4.7 Hz), 69.6, 21.9. **¹⁹F NMR** (376 MHz, CDCl₃) δ 83.35 (quintet, *J* = 150.2 Hz, 1F), 62.69 (d, *J* = 150.2 Hz, 4F). **HRMS (+APCI)** calc. for C₁₀H₁₁F₅O₂S [M+H]⁺ : 291.0473; found: 291.0468.

Synthesis of 4-acetamidopentafluorosulfanyl benzene:



Following a modified procedure described by Bowden,⁴ 4-aminopentafluorosulfanyl benzene (1.0 g, 4.57 mmol) was added to acetic anhydride (3 mL) and the resulting mixture was stirred overnight at RT. Dichloromethane (50 mL) was added and the organic phase was washed with water (3×50 mL) and dried over Na₂SO₄. After column chromatography (hexanes/ethyl acetate 4:1 *R_f* = 0.4), 4-acetamidopentafluorosulfanyl benzene was isolated as colorless crystals (1.1 g, 92 %). **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.39 (s, 1H), 7.82 – 7.76 (m, 4H), 2.08 (s, 3H). **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 169.5, 147.3 (quintet, *J* = 16.4 Hz), 142.9, 127.1 – 127.0 (m), 118.8, 24.4. **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ 89.40 (quintet, *J* = 150.8 Hz, 1F), 65.53 (d, *J* = 150.8 Hz, 4F). **HRMS (ESI)** calc. for C₈H₈F₅NOS [M+H]⁺ : 262.0320; found: 262.0319. This compound is known.⁴

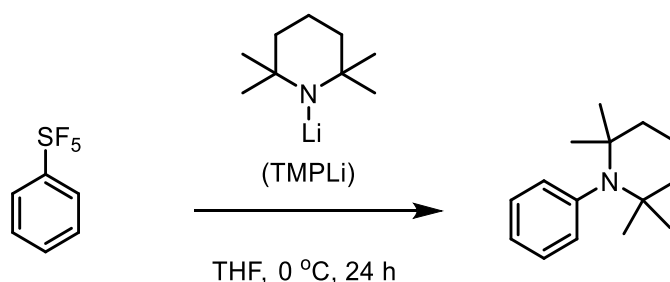
Synthesis of *N*-(4-(pentafluorosulfanyl)phenyl)-benzamide:



4-Aminopentafluorosulfanyl benzene (1.0 g, 4.57 mmol) and benzoic anhydride (3.1 g, 13.71 mmol) were added to CH₂Cl₂ (3.5 mL) and the resulting mixture was stirred overnight. Dichloromethane (50 mL) was added and the organic phase was washed with water (3×50 mL) and

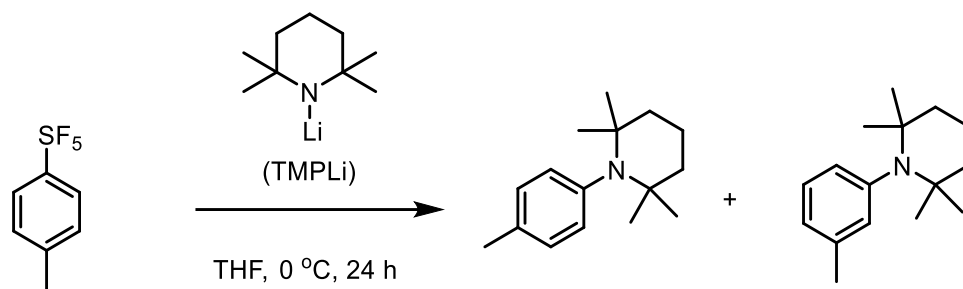
dried over Na₂SO₄. After column chromatography (hexanes/ethyl acetate 5:1 R_f = 0.5), *N*-(4-(pentafluorosulfanyl)phenyl)-benzamide was obtained as colorless crystals (1.3 g, 88 %). **¹H NMR** (400 MHz, DMSO-*d*6) δ 10.68 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H). **¹³C NMR** (101 MHz, DMSO-*d*6) δ 166.3, 147.8 – 147.5 (m), 142.7, 134.5, 132.2, 128.7, 128.1, 126.9 – 126.8 (m), 120.0. **¹⁹F NMR** (376 MHz, DMSO-*d*6) δ 85.13 (quintet, *J* = 149.8 Hz, 1F), 63.57 (d, *J* = 149.8 Hz, 4F). **HRMS (ESI)** calc. for C₁₃H₁₀F₅NOS [M+H]⁺ : 324.0476; found: 324.0475.

Reaction of pentafluorosulfanyl benzene with TMPLi at 0 °C:



Outside the glovebox, one 2-dram vial was equipped with a magnetic stir bar (13x3 mm). The vial was placed inside the glovebox. To the vial was added solid TMPLi (1 mmol, 147 mg), and THF (1.5 mL). The sealed vial was then taken out of the glovebox and stirred for 10 minutes at 0 °C. In another 2-dram vial, pentafluorosulfanyl benzene (0.2 mmol, 41 mg) was dissolved in THF (0.5 mL). Pentafluorosulfanyl benzene solution was then added dropwise to TMPLi solution via syringe at 0 °C. The reaction is very exothermic. The solution color immediately turned from light-yellow to dark-brown after the first drop of pentafluorosulfanyl benzene. Grease was then put on the top of the septa to maintain an inert atmosphere. The resulting mixture was stirred at 0 °C for 24 hrs. After completion, the reaction was quenched with methanol (0.5 mL). Silica gel was then added to the quenched solution and the mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes : ethyl acetate (4:1) to elute the product. PhTMP, 17 mg (40 %) was isolated as a yellowish oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.35 – 7.24 (m, 5H), 1.83 – 1.78 (m, 2H), 1.66 – 1.63 (m, 4H), 1.10 (s, 12H). This compound is known.^{5a}

Reaction of 4-pentafluorosulfanyl toluene with TMPLi at 0 °C:



Outside the glovebox, one 2-dram vial was equipped with a magnetic stir bar (13x3 mm). The vial was placed inside the glovebox. To the vial was added solid TMPLi (1 mmol, 147 mg), and THF (1.5 mL). The sealed vial was then taken out of the glovebox and stirred for 10 minutes at 0 °C. In another 2-dram vial, 4-pentafluorosulfanyl toluene (0.2 mmol, 44 mg) was dissolved in THF (0.5 mL). 4-Pentafluorosulfanyl toluene solution was then added dropwise to TMPLi solution via syringe at 0 °C. The reaction is very exothermic. The solution color immediately turned from light-yellow to dark-brown after the first drop of 4-pentafluorosulfanyl toluene. Grease was then put on the top of the septa to maintain an inert atmosphere. The resulting mixture was stirred at 0 °C for 24 hrs. After completion, the reaction was quenched with methanol (0.5 mL). Silica gel was then added to the quenched solution and the mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes : ethyl acetate (5:1) to elute the product. The 1:0.6 mixture of isomers was isolated as a yellowish oil (21 mg, 45 %). ¹H NMR (400 MHz, CDCl₃) δ 7.14 – 7.00 (4H, isomer signal overlapped), 2.34 and 2.33 (s, 3H), 1.72 (2H, isomer signal overlapped), 1.59 – 1.52 (4H, isomer signal overlapped), 1.01 and 1.02 (s, 12H). This compound is known.^{5b}

Table S1: Optimization for Silylation of Pentafluorosulfanyl Benzene

Entry	TMPLi (x eq)	Me ₂ HSiCl (y eq)	Solvent	Temp. (°C)	Yield (%) ^a
1 ^b	2	10	Pentane	-78	N.R
2	2	10	THF	-78	5
3	5	10	THF	-78	20
4	5	10	Et ₂ O	-78	N.R
5	5	10	Et ₂ O/Pentane (1:1)	-78	N.R
6	5	10	Et ₂ O/THF (49:1)	-78	5
7	5	10	Et ₂ O/THF (3:1)	-78	25
8	5	10	THF	-60	30
9	5	10	Et ₂ O/THF (3:1)	-60	35
10	5	10	THF/Pentane (1:1)	-60	45
11	5	10	THF/Pentane (1:3)	-60	77
12	5	7	THF/Pentane (1:3)	-60	75 (70) ^g
13	3	7	THF/Pentane (1:3)	-60	47
14 ^c	5	7	THF/Pentane (1:3)	-60	N.R
15	5	7	THF/Pentane (1:3)	-50	70
16	5	7	THF/Pentane (1:3)	-40	56
17 ^d	5	7	THF/Pentane (1:3)	-60	N.R
18 ^e	5	7	THF/Pentane (1:3)	-60	N.R
19 ^f	5	7	THF/Pentane (1:3)	-60	N.R

^a Yields are ¹⁹F NMR yields using hexafluorobenzene as internal standard. ^b *n*-BuLi/TMEDA(2 equiv) used instead of LiTMP. ^c Me₂HSiCl was added after deprotonation for 24 hr. ^d LDA used instead of TMPLi. ^e Cy₂NLi used instead of LiTMP. ^f LDAM used instead of LiTMP. ^g Isolated yield.

General procedure for reactions:

Outside the glovebox, one 2-dram vial was equipped with a magnetic stir bar (13x3 mm). The vial was placed inside the glovebox. To the vial was added solid TMPLi (1.0 mmol, 147 mg) and two thirds of solvent or solvent mixture (1.0 mL). The sealed vial was then taken out of the glovebox and placed into cooling machine at reaction temperature. Vial was stirred for 5 – 10 minutes at reaction temperature. In one 2-dram vial, pentafluorosulfanyl benzene (0.2 mmol, 41 mg) was dissolved in solvent (0.25 mL) and in another 2-dram vial, chlorodimethylsilane (1.4 mmol, 132 mg) was dissolved in solvent (0.25 mL). Both 2-dram vials were placed in cooling machine (5 – 10 minutes) to reach reaction temperature. Pentafluorosulfanyl benzene solution was rapidly (3 sec) added to TMPLi solution via syringe following by rapid addition of chlorodimethylsilane solution. Grease was then put on the top of the septa to maintain an inert atmosphere. The reaction

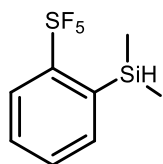
was stirred at 1500 rpm for 24 hours. After completion, the reaction was quenched by adding methanol (0.5 mL) prior to the addition of hexafluorobenzene as internal standard. Yield was calculated based on the ^{19}F NMR.

For the isolation process, after quenching with methanol, silica gel was added and then mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes followed by appropriate solvent to elute the products. After concentrating the fractions containing the product, the residue was dried under reduced pressure to yield pure product. The product was characterized by ^1H , ^{13}C , ^{19}F NMR and HR-MS.

Note: Almost all of the remaining PhSF_5 was evaporated when concentrating the mixture on rotary evaporator system.

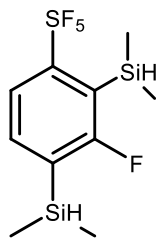
For ArSF_5 derivatives that underwent double-silylation, silica gel was directly added to the crude mixture after completion of the reaction. Methanol should not be added to quench the reaction mixture with double-silylated compounds. We observed the decomposition of product in reaction mixture after the addition of methanol. With mono-silylated products, adding methanol to quench did not lead to any decomposition of the desired product.

2-Dimethylsilylpentafluorosulfanyl benzene (Table 2, Entry 1)



Pentafluorosulfanyl benzene (0.5 mmol, 102 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), $-60\text{ }^\circ\text{C}$, 24 hours. After column chromatography (hexanes), 92 mg (70 %) of colorless liquid was obtained. $R_f = 0.8$ (hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.83 (m, 1H), 7.73 – 7.70 (m, 1H), 7.49 – 7.47 (m, 2H), 4.76 – 4.67 (m, 1H), 0.37 (d, $J = 4$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.7 – 159.4 (m), 136.6, 136.4, 130.7, 129.5, 127.3 (quintet, $J = 5.7$ Hz), -2.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ 86.18 (quintet, $J = 148.5$ Hz, 1F), 64.68 (dd, $J = 148.5, 8.1$ Hz, 4F).

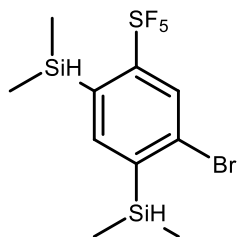
2,4-bis(Dimethylsilyl)-3-fluoropentafluorosulfanyl benzene (Table 2, Entry 2)



3-Fluoropentafluorosulfanyl benzene (0.5 mmol, 111 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), $-78\text{ }^\circ\text{C}$, 10 hours. After column chromatography (hexanes), 145 mg (86 %) of a light yellowish oil was obtained. $R_f = 0.8$ (hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.63 (m, 1H), 7.59 – 7.55 (m, 1H), 4.84 – 4.72 (m, 1H), 4.51 – 4.48 (m, 1H), 0.44

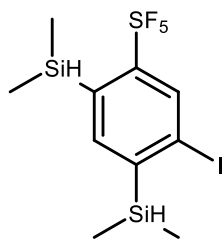
-0.40 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.5 (d, $J = 236.3$ Hz), 161.4 – 161.0 (m), 145.4, 137.1 (d, $J = 13.0$ Hz), 127.8 (d, $J = 38.2$ Hz), 123.2, -2.8 (d, $J = 6.4$ Hz), -4.2. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ 85.28 (quintet, $J = 149.8$ Hz, 1F), 66.23 (dd, $J = 149.8, 11.6$ Hz, 4F), -79.48 (s, 1F).

2,4-bis(Dimethylsilyl)-5-bromopentafluorosulfanyl benzene (Table 2, Entry 3)



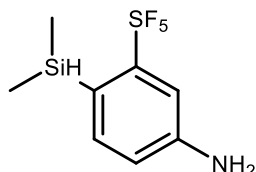
3-Bromopentafluorosulfanyl benzene (0.5 mmol, 142 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -78 °C, 9 hours. After column chromatography (hexanes), 190 mg (95 %) of a light yellowish oil was obtained. $R_f = 0.80$ (hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.84 (s, 1H), 4.77 – 4.68 (m, 1H), 4.62 – 4.58 (m, 1H), 0.51 – 0.40 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.0 (quintet, $J = 16.2$ Hz), 144.3, 143.3, 134.2 – 134.1 (m), 131.6, 130.5 (quintet, $J = 5.9$ Hz), -2.2, -3.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ 83.44 (quintet, $J = 149.3$ Hz, 1F), 63.90 (dd, $J = 149.3, 7.7$ Hz, 4F).

2,4-bis(Dimethylsilyl)-5-iodopentafluorosulfanyl benzene (Table 2, Entry 4)



3-Iodopentafluorosulfanyl benzene (0.5 mmol, 165 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 24 hours. After column chromatography (hexanes), 194 mg (87 %) of a light yellowish oil was obtained. $R_f = 0.85$ (hexanes). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.20 (s, 1H), 7.70 (s, 1H), 4.69 – 4.61 (m, 1H), 4.54 – 4.50 (m, 1H), 0.47 – 0.36 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.3 – 159.9 (m), 147.3, 143.9, 136.9 – 136.8 (m), 134.6, 105.0, -2.2, -3.7. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ 84.68 (quintet, $J = 149.1$ Hz, 1F), 64.53 (dd, $J = 149.1, 7.8$ Hz, 4F).

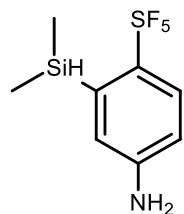
2-Dimethylsilyl-5-aminopentafluorosulfanyl benzene (Table 2, Entry 5)



3-Aminopentafluorosulfanyl benzene (0.5 mmol, 109 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (1.0 mL), pentane (1.0 mL), -60 °C, 24 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 20:1), 99 mg (72 %) of a yellowish oil was obtained. $R_f = 0.5$ (hexanes/ethyl acetate 20:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.0$ Hz, 1H), 7.13 (s, 1H), 6.76 (d, $J = 8$ Hz, 1H), 4.64 – 4.56 (m, 1H), 3.94 (s, 2H), 0.31 (d, $J = 3.7$ Hz, 6H). $^{13}\text{C NMR}$ (101

MHz, CDCl₃) δ 160.8 – 160.6 (m), 147.5, 137.4, 123.3, 116.8, 113.9 – 113.8 (m), -1.8. **¹⁹F NMR** (376 MHz, CDCl₃) δ 86.67 (quintet, J = 148.6 Hz, 1F), 64.44 (dd, J = 148.6, 7.5 Hz, 4F). **HRMS (ESI)** calc. for C₈H₁₂F₅NSSi [M+H]⁺ : 278.0453; found: 278.0450.

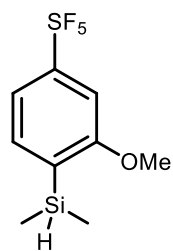
2-Dimethylsilyl-4-aminopentafluorosulfanyl benzene (Table 2, Entry 6)



4-Aminopentafluorosulfanyl benzene (0.5 mmol, 109 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (1.0 mL), pentane (1.0 mL), -60 °C, 24 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 20:1), 107 mg (77 %) of a yellowish oil was obtained. R_f = 0.5

(hexanes/ethyl acetate 20:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.61 (d, J = 8.9 Hz, 1H), 6.86 (s, 1H), 6.63 (d, J = 8.9 Hz, 1H), 4.66 – 4.58 (m, 1H), 3.98 (s, 2H), 0.34 (d, J = 3.7 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 150.2 – 149.9 (m), 147.9, 137.9, 129.0 – 128.9 (m), 121.2, 114.2, -2.0. **¹⁹F NMR** (376 MHz, CDCl₃) δ 89.19 (quintet, J = 148.9 Hz, 1F), 66.94 (dd, J = 148.9, 8.4 Hz, 4F). **HRMS (ESI)** calc. for C₈H₁₂F₅NSSi [M+H]⁺ : 278.0453; found: 278.0450.

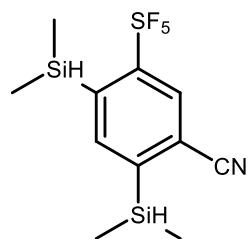
4-Dimethylsilyl-3-methoxypentafluorosulfanyl benzene (Table 2, Entry 7)



3-Methoxypentafluorosulfanyl benzene (0.5 mmol, 117 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (1.0 mL), pentane (1.0 mL), -60 °C, 24 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 20:1), 73 mg (50 %) of a colorless oil was obtained. R_f = 0.4

(hexanes/ethyl acetate 20:1). **¹H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 6.9 Hz, 1H), 7.34 – 7.32 (dd, J = 8.0, 1.9 Hz, 1H), 7.13 (d, J = 1.9 Hz, 1H), 4.39 (septet, J = 3.8 Hz, 1H), 3.87 (s, 3H), 0.34 (d, J = 3.8 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 163.9, 156.5 – 156.2 (m), 135.7, 130.7, 118.0 – 117.9 (m), 107.1 – 107.0 (m), 55.7, -4.1. **¹⁹F NMR** (376 MHz, CDCl₃) δ 84.81 (quintet, J = 148.8 Hz, 1F), 62.58 (d, J = 148.8 Hz, 4F).

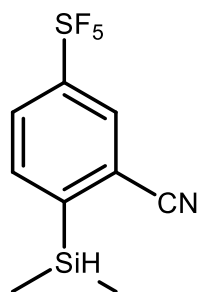
2,4-bis(Dimethylsilyl)-5-cyanopentafluorosulfanyl benzene (Table 2, Entry 8)



3-Cyanopentafluorosulfanyl benzene (0.5 mmol, 114 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (1.0 mL), pentane (1.0 mL), -60 °C, 24 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 25:1), 155 mg (90 %) of a colorless oil was obtained. R_f = 0.6 (hexanes/ethyl acetate 25:1). **¹H NMR** (400 MHz,

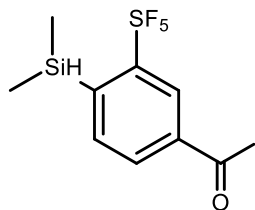
CDCl₃) δ 8.07 (s, 1H), 7.98 (s, 1H), 4.74 – 4.69 (m, 1H), 4.64 – 4.62 (m, 1H), 0.51 (d, J = 3.8 Hz, 6H), 0.40 (d, J = 3.7 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 160.2 – 159.9 (m), 145.2, 143.5, 141.5, 131.0 – 130.9 (m), 119.2, 117.7, -2.3, -4.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ 83.45 (quintet, J = 149.0 Hz, 1F), 64.23 (dd, J = 149.0, 8.2 Hz, 4F). **HRMS (+APCI)** calc. for C₁₁H₁₆F₅NSSi₂ [M+H]⁺ : 346.0535; found: 346.0530.

4-Dimethylsilyl-3-cyanopentafluorosulfanyl benzene (Table 2, Entry 9)



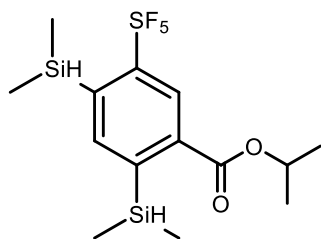
3-Cyanopentafluorosulfanyl benzene (0.5 mmol, 114 mg), chlorodimethylsilane (0.6 mmol, 57 mg), TMPLi (0.55 mmol, 81 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 24 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 12:1), 86 mg (60 %) of a colorless oil was obtained. R_f = 0.8 (hexanes/ethyl acetate 12:1). **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 2.2 Hz, 1H), 7.92 (dd, J = 8.3, 2.2 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 4.65 (septet, J = 3.8 Hz, 1H), 0.51 (d, J = 3.8 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 154.9 – 154.5 (m), 147.8, 136.4, 130.6 (quintet, J = 4.8 Hz), 129.2 – 129.1 (m), 119.1, 117.4, -4.2. **¹⁹F NMR** (376 MHz, CDCl₃) δ 81.94 (quintet, J = 150.6 Hz, 1F), 62.42 (d, J = 150.6 Hz, 4F).

2-Dimethylsilyl-5-acetylpentafluorosulfanyl benzene (Table 2, Entry 10)



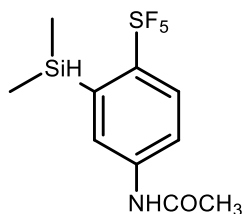
3-Acetylpentafluorosulfanyl benzene (0.5 mmol, 123 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 36 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 15:1), 100 mg (66 %) of a yellowish oil was obtained. R_f = 0.6 (hexanes/ethyl acetate 15:1). **¹H NMR** (400 MHz, CDCl₃) δ 8.38 (s, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 4.77 – 4.69 (m, 1H), 2.64 (s, 3H), 0.39 (d, J = 3.8 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.3, 160.0 – 159.7 (m), 142.7 – 142.6 (m), 138.0, 137.0, 129.8, 126.8 – 126.7 (m), 26.8, -2.2. **¹⁹F NMR** (376 MHz, CDCl₃) δ 84.87 (quintet, J = 149.0 Hz, 1F), 64.58 (dd, J = 149.0, 8.0 Hz, 4F). **HRMS (ESI)** calc. for C₁₀H₁₃F₅OSSi [M+H]⁺ : 305.0449; found: 305.0448.

Isopropyl 2,4-bis(dimethylsilyl)-5-(pentafluorosulfanyl) benzoate (Table 2, Entry 11)



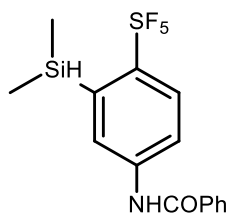
Isopropyl 3-(pentafluorosulfanyl) benzoate (0.5 mmol, 145 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 24 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 10:1), 193 mg (95 %) of a colorless oil was obtained. $R_f = 0.5$ (hexanes/ethyl acetate 10:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.42 (s, 1H), 8.08 (s, 1H), 5.28 (septet, $J = 6.4$ Hz, 1H), 4.76 – 4.69 (m, 1H), 4.58 – 4.55 (m, 1H), 1.41 (d, $J = 6.4$ Hz, 6H), 0.42 – 0.39 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.1, 160.9 – 160.3 (m), 144.6, 144.0, 140.5 – 140.1 (m), 137.4, 127.6 – 126.3 (m), 69.9, 22.0, -2.2, -2.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ 84.95 (quintet, $J = 149.3$ Hz, 1F), 64.18 (dd, $J = 149.3, 8.1$ Hz, 4F). **HRMS (+APCI)** calc. for $\text{C}_{14}\text{H}_{23}\text{F}_5\text{O}_2\text{SSi}_2$ $[\text{M}-\text{H}]^+$: 405.0794; found: 405.0787.

2-Dimethylsilyl-4-acetamidopentafluorosulfanyl benzene (Table 2, Entry 12)



4-Acetamidopentafluorosulfanyl benzene (0.5 mmol, 130 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (1.0 mL), pentane (1.0 mL), -78 °C, 10 hours. After column chromatography (hexanes/ethyl acetate 1:1), 111 mg (70 %) of a white solid was obtained. $R_f = 0.4$ (hexanes/ethyl acetate 1:1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (s, 1H), 7.76 (s, 2H), 7.72 (s, 1H), 4.66 – 4.62 (m, 1H), 2.21 (s, 3H), 0.33 (d, $J = 3.9$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.1, 154.7 – 154.5 (m), 139.7, 137.9, 128.5 – 128.4 (m), 126.3, 119.9, 24.7, -2.2. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ 86.84 (quintet, $J = 149.3$ Hz, 1F), 65.68 (dd, $J = 149.3, 7.9$ Hz, 4F). **HRMS (ESI)** calc. for $\text{C}_{10}\text{H}_{14}\text{F}_5\text{NOSSi}$ $[\text{M}+\text{H}]^+$: 320.0558; found: 320.0555.

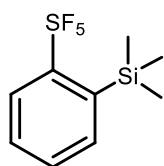
N-(3-Dimethylsilyl-4-(pentafluorosulfanyl)phenyl)benzamide (Table 2, Entry 13)



N-(4-(Pentafluorosulfanyl)phenyl)benzamide (0.5 mmol, 161 mg), chlorodimethylsilane (3.5 mmol, 329 mg), TMPLi (2.5 mmol, 367 mg), THF (1.0 mL), pentane (1.0 mL), -60 °C, 24 hours. After column chromatography (hexanes/ethyl acetate 4:1), 142 mg (75 %) of a white solid was obtained. $R_f = 0.55$ (hexanes/ethyl acetate 4:1). X-ray quality crystals were obtained by slow evaporation in CH_2Cl_2 . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.39 (s, 1H), 7.90 – 7.78 (m, 5H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.43 (t,

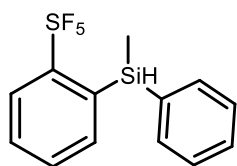
$J = 7.7$ Hz, 2H), 4.70 – 4.63 (m, 1H), 0.35 (d, $J = 4.0$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.5, 155.0 – 154.5 (m), 139.8, 138.1, 134.3, 132.5, 128.9, 128.6 – 128.5 (m), 127.3, 126.9, 120.4, -2.2. ^{19}F NMR (376 MHz, CDCl_3) δ 86.81 (quintet, $J = 149.3$ Hz, 1F), 65.71 (dd, $J = 149.3$, 8.0 Hz, 4F). HRMS (ESI) calc. for $\text{C}_{15}\text{H}_{16}\text{F}_5\text{NOSSi}$ $[\text{M}+\text{H}]^+$: 382.0715; found: 382.0711.

2-Trimethylsilylpentafluorosulfanyl benzene (Scheme 3, compound 7)



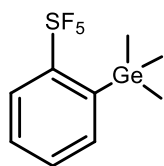
Pentafluorosulfanyl benzene (0.5 mmol, 102 mg), chlorotrimethylsilane (3.5 mmol, 381 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 48 hours. After column chromatography (hexanes), 83 mg (60 %) of a colorless oil was obtained. $R_f = 0.8$ (hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.83 (m, 1H), 7.79 – 7.75 (m, 1H), 7.47 – 7.44 (m, 2H), 0.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.3 – 159.1 (m), 138.5, 136.7, 130.6, 129.2, 127.5 – 127.3 (m), 1.4. ^{19}F NMR (376 MHz, CDCl_3) δ 86.28 (quintet, $J = 148.1$ Hz, 1F), 64.46 (d, $J = 148.1$ Hz, 4F).

2-(Methylphenylsilyl)pentafluorosulfanyl benzene (Scheme 3, compound 8)



Pentafluorosulfanyl benzene (0.5 mmol, 102 mg), chloro(methyl)phenylsilane (3.5 mmol, 549 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 48 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 10:1), 81 mg (50 %) of a colorless oil was obtained. $R_f = 0.6$ (hexanes/ethyl acetate 10:1). ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.2$ Hz, 1H), 7.62 (d, $J = 7.2$ Hz, 1H), 7.53 (d, $J = 6.7$ Hz, 2H), 7.50 – 7.44 (m, 1H), 7.44 – 7.35 (m, 4H), 5.30 – 5.22 (m, 1H), 0.67 (d, $J = 3.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.3 – 159.8 (m), 137.4, 135.2, 134.9, 134.8, 130.7, 129.9, 129.8, 128.2, 127.5 – 127.4 (m), -3.7. ^{19}F NMR (376 MHz, CDCl_3) δ 86.22 (quintet, $J = 148.9$ Hz, 1F), 65.26 (dd, $J = 148.9$, 8.9 Hz, 4F). HRMS (+APCI) calc. for $\text{C}_{13}\text{H}_{13}\text{F}_5\text{SSi}$ $[\text{M}-\text{H}]^+$: 323.0344; found: 323.0338.

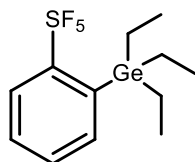
2-Trimethylgermylpentafluorosulfanyl benzene (Scheme 3, compound 9)



Pentafluorosulfanyl benzene (0.5 mmol, 102 mg), chlorotrimethylgermane (3.5 mmol, 536 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 36 hours. After column chromatography (hexanes), 104 mg (65 %) of a colorless oil was obtained. $R_f = 0.8$ (hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.67 (d, $J = 6.8$ Hz, 1H), 7.47 – 7.40 (m, 2H), 0.48 (s, 9H). ^{13}C NMR (101 MHz,

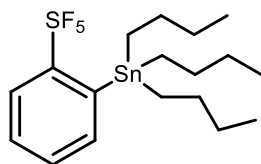
CDCl_3) δ 159.3 – 159.0 (m), 140.8, 135.9, 130.7, 128.7, 127.5 (quintet, $J = 5.7$ Hz), 1.3. ^{19}F NMR (376 MHz, CDCl_3) δ 86.25 (quintet, $J = 148.4$ Hz, 1F), 63.56 (d, $J = 148.4$ Hz, 4F).

2-Triethylgermylpentafluorosulfanyl benzene (Scheme 3, compound 10)



Pentafluorosulfanyl benzene (0.5 mmol, 102 mg), chlorotriethylgermane (3.5 mmol, 682 mg), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 36 hours. After column chromatography (hexanes), 104 mg (57 %) of a colorless oil was obtained. $R_f = 0.8$ (hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 7.0$ Hz, 1H), 7.61 (d, $J = 5.1$ Hz, 1H), 7.45 – 7.39 (m, 2H), 1.11 (q, $J = 7.8$ Hz, 6H), 1.00 (t, $J = 7.8$ Hz, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.3 – 160.0 (m), 138.5, 136.6, 130.4, 128.5, 127.8 – 127.6 (m), 8.9, 6.2. ^{19}F NMR (376 MHz, CDCl_3) δ 86.42 (quintet, $J = 148.2$ Hz, 1F), 63.21 (d, $J = 148.2$ Hz, 4F).

2-Tributylstannylpentafluorosulfanyl benzene (Scheme 3, compound 11)



Pentafluorosulfanyl benzene (0.5 mmol, 102 mg), bis(tributyltin) (3 mmol, 1.7 g), TMPLi (2.5 mmol, 367 mg), THF (0.5 mL), pentane (1.5 mL), -60 °C, 48 hours. After performing preparative TLC (hexanes), 98 mg (40 %) of a colorless oil was obtained. Less than 5 % of another isomer was observed in ^{19}F NMR spectrum or crude reaction mixture. $R_f = 0.8$ (hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.81 (m, 1H), 7.58 – 7.56 (m, 1H), 7.41 – 7.37 (m, 2H), 1.50 – 1.44 (m, 6H), 1.36 – 1.29 (m, 6H), 1.11 (t, $J = 8.3$ Hz, 6H), 0.88 (t, $J = 7.3$ Hz, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.2, 141.9, 137.8, 130.5 – 130.4 (m), 128.3, 127.4 – 127.3 (m), 28.8, 27.4, 13.8, 11.8. ^{19}F NMR (376 MHz, CDCl_3) δ 86.94 (quintet, $J = 148.9$ Hz, 1F), 61.07 (d, $J = 148.9$ Hz, 4F). HRMS (-APCI) calc. for $\text{C}_{18}\text{H}_{31}\text{F}_5\text{SSn}$ $[\text{M}-\text{Bu}]^-$: 437.0379; found: 437.0382. Note: 22 mg (20 %) of 1-phenyl-2,2,6,6-tetramethylpiperidine (PhTMP) byproduct was isolated as well.

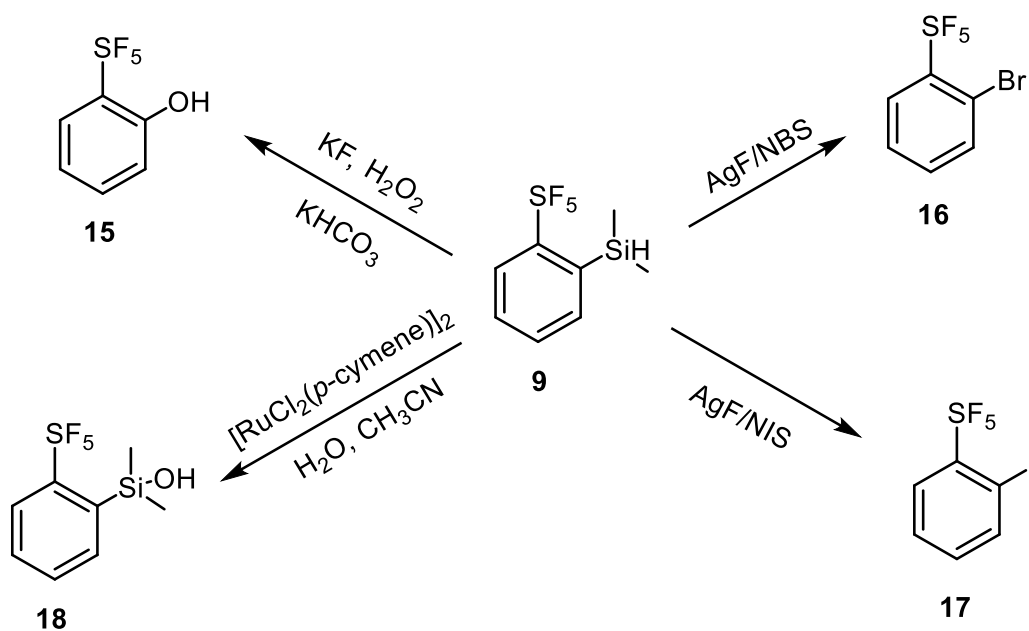
Procedure for gram-scale synthesis of 2-dimethylsilylpentafluorosulfanyl benzene (Table 2, Entry 1)

Outside the glovebox, a 100 mL round bottom flask was equipped with a magnetic stir bar (0.5 x 3 cm). The flask was placed inside the glovebox. To the flask was added solid TMPLi (50 mmol, 7.35 g) and solvent mixture (THF/pentane 1/3, 30 mL total). The flask was then taken out

of the glovebox and placed into cooling machine at $-60\text{ }^{\circ}\text{C}$. Precise temperature regime is extremely important for reproducibility of the silylation reactions. Flask was stirred for 10 – 15 minutes at $-60\text{ }^{\circ}\text{C}$. In one 2-dram vial, pentafluorosulfanyl benzene (10 mmol, 2.04 g) was dissolved in solvent mixture (THF/pentane 1/3, 2 mL) and in another 2-dram vial, chlorodimethylsilane (70 mmol, 6.58 g) was dissolved in solvent (THF/pentane 1/3, 2 mL). Both 2-dram vials were placed in cooling machine (10 - 15 minutes) to reach reaction temperature. Pentafluorosulfanyl benzene solution was rapidly (3 sec) added to TMPLi solution via syringe following by rapid addition of chlorodimethylsilane solution. Grease was then put on the top of the septum stopper to maintain an inert atmosphere. The reaction was stirred at 1500 rpm for 72 hours at $-60\text{ }^{\circ}\text{C}$. After completion, the reaction was quenched by adding methanol (10 mL) prior to the addition of silica gel and then mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes to elute the product. After concentrating the fractions containing the product, the residue was dried under reduced pressure overnight to yield a colorless liquid silylation product (1.70 g, 65 %).

Unsuccessful substrates for silylation reaction: Under the standard silylation reaction conditions, the silylated product was not observed for 1-pentafluorosulfanyl naphthalene and the $\text{C}(\text{sp}^2)\text{-H}/\text{C}(\text{sp}^3)\text{-H}$ silylation was obtained for 4-pentafluorosulfanyl toluene substrate.

Functionalization of 2-dimethylsilylpentafluorosulfanyl benzene

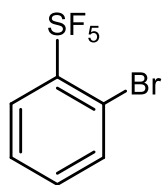


2-Hydroxypentafluorosulfanyl benzene



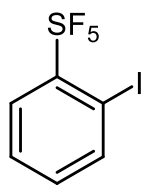
A known procedure for a different substrate was followed.⁶ To 2-dimethylsilylpentafluorosulfanyl benzene (0.5 mmol, 131 mg) in THF/MeOH (1/1, 1.5 mL total volume) was added KF (3.0 equiv, 87 mg), KHCO₃ (3.0 equiv, 150 mg) and H₂O₂ (2.6 equiv, 148 μL of 30% w/w in H₂O). The mixture was stirred at room temperature for 24 h and then partitioned between H₂O and ethyl acetate (4 mL each). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (4 mL). The combined organic layer was washed with H₂O (3 mL) and brine (2 mL), dried over Na₂SO₄, and concentrated. The ¹⁹F NMR yield with hexafluorobenzene as internal standard is 85 %. The residue was purified by flash column chromatography (pentane followed by pentane/ethyl acetate 3:1) to afford the product as a colorless oil. This compound is known.⁷ ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.22 (s, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ 86.33 (quintet, *J* = 149.2 Hz, 1F), 67.65 (d, *J* = 149.2 Hz, 4F). **Note:** The product is very volatile and quickly evaporates together with solvent when placed under vacuum for 30 minutes. Thus, the isolated yield is variable.

2-Bromopentafluorosulfanyl benzene



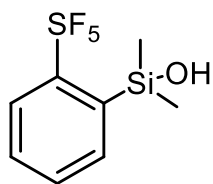
A known procedure for a different substrate was followed.⁸ To 2-dimethylsilylpentafluorosulfanyl benzene (0.5 mmol, 131 mg) in acetonitrile (2.0 mL) was added AgF (3.0 equiv, 190 mg) and *N*-bromosuccinimide (4.0 equiv, 356 mg), and the mixture was stirred at room temperature for 24 h. The mixture was then partitioned between ethyl acetate (4 mL) and an aqueous K₂CO₃ (4 mL, 20 %). The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (4 mL). The combined organic layer was washed with water (4 mL), brine (4 mL), and dried over Na₂SO₄, and filtered. The volatile materials were evaporated, and the residue was purified by flash column chromatography (pentane) to afford the product as a colorless liquid (127 mg, 90 %). This compound is known.⁹ ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 153.9 – 153.6 (m), 136.6, 132.5, 130.3 (quintet, *J* = 5.5 Hz), 127.4, 117.5. ¹⁹F NMR (376 MHz, CDCl₃) δ 83.33 (quintet, *J* = 151.9 Hz, 1F), 65.45 (d, *J* = 151.9 Hz, 4F). The product is somewhat volatile.

2-Iodopentafluorosulfanyl benzene



A known procedure for a different substrate was followed.⁸ To 2-dimethylsilylpentafluorosulfanyl benzene (0.5 mmol, 131 mg) in acetonitrile (2.0 mL) was added AgF (3.0 equiv, 190 mg) and *N*-iodosuccinimide (4.0 equiv, 450 mg), and the mixture was stirred at room temperature for 24 h. The mixture was then partitioned between ethyl acetate (4 mL) and an aqueous K₂CO₃ solution (4 mL, 20 %). The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (4 mL). The combined organic layer was washed with water (4 mL), brine (4 mL), and dried over Na₂SO₄, and filtered. The volatile materials were evaporated, and the residue was purified by flash column chromatography (pentane) to afford the product as a yellowish liquid (157 mg, 95 %). This compound is known.¹⁰ **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.5 (quintet, *J* = 16.2 Hz), 144.0, 132.3, 130.3 (quintet, *J* = 5.5 Hz), 128.0, 88.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ 84.12 (quintet, *J* = 150.3 Hz, 1F), 64.07 (d, *J* = 150.3 Hz, 4F). The product is somewhat volatile.

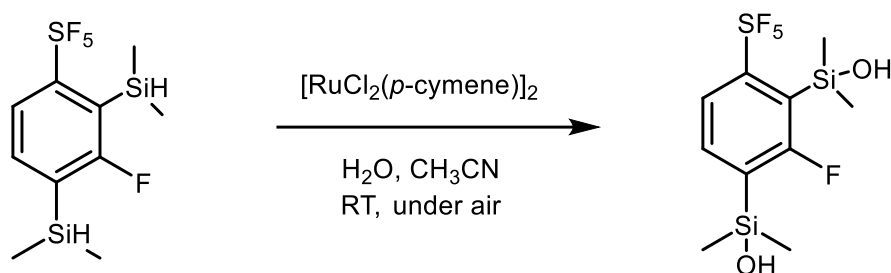
2-(Hydroxydimethylsilyl)pentafluorosulfanyl benzene



Following a modified procedure by Denmark,¹¹ a 8 mL vial equipped with a magnetic stir bar was charged with 2-dimethylsilylpentafluorosulfanyl benzene (0.5 mmol, 131 mg). Dry acetonitrile (1.5 mL) was added followed by H₂O (0.18 mL, 10.0 mmol, 20 equiv). [RuCl₂(*p*-cymene)]₂ (16 mg, 0.025 mmol, 5 mol %) was then added to the reaction mixture. The reaction vial was sealed with a hole cap and a septa. A small needle was used to puncture the septum to ensure that the reaction mixture was exposed to air. The reaction was stirred at RT overnight. After the completion of reaction, the reaction solution was diluted with CH₂Cl₂ (10 mL) and poured into H₂O (10 mL). The resulting mixture was extracted with CH₂Cl₂ (3 x 25 mL). The combined organic layers were dried over Na₂SO₄. Silica gel was then added to the solution and the mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes : ethyl acetate (4:1) to elute the product. Silanol (132 mg, 95 %) was isolated as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.03 – 8.01 (m, 1H), 7.85 – 7.84 (m, 1H), 7.51 – 7.46 (m, 2H), 2.65 (s, 1H), 0.45 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.9 (quintet, *J* = 15.6 Hz), 137.4 (quintet, *J* = 3.4 Hz), 136.5, 131.0, 129.8, 127.2 (quintet, *J* =

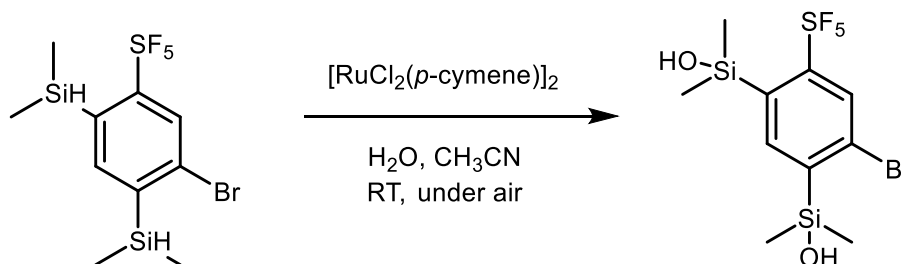
6.0 Hz), 1.7 (quintet, $J = 2.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 86.57 (quintet, $J = 149.0$ Hz, 1F), 64.54 (d, $J = 149.0$ Hz, 4F). HRMS (-APCI) calc. for $\text{C}_8\text{H}_{11}\text{F}_5\text{OSSi}$ $[\text{M}-\text{H}]^-$: 277.0136; found: 277.0143.

Synthesis of 2,4-bis(hydroxydimethylsilyl)-3-fluoropentafluorosulfanyl benzene (S1):



Following a modified procedure by Denmark,¹¹ a 8-mL vial equipped with a magnetic stir bar was charged with 2,4-bis(dimethylsilyl)-3-fluoropentafluorosulfanyl benzene (338 mg, 1.0 mmol). Dry acetonitrile (2 mL) was added followed by H_2O (0.36 mL, 20.0 mmol, 20 equiv). $[\text{RuCl}_2(\text{p-cymene})]_2$ (31 mg, 0.05 mmol, 5 mol %) was then added to the reaction mixture. The reaction vial was sealed with a hole cap and a septa. A needle was used to puncture the septum to ensure that the reaction mixture was exposed to air. The reaction was stirred at RT overnight. After the completion of reaction, the reaction solution was diluted with CH_2Cl_2 (10 mL) and poured into H_2O (10 mL). The resulting mixture was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 . Silica gel was then added to the solution and the mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes : ethyl acetate (4:1) to elute the product. Silanol, 359 mg (97 %), was isolated as a white solid. X-ray quality crystals were obtained by slow evaporation of solution in CH_2Cl_2 . ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.62 (m, 2H), 2.65 (s, 1H), 2.45 (s, 1H), 0.50 (s, 6H), 0.45 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.6 (d, $J = 233.7$ Hz), 160.2 – 159.7 (m), 136.4 (d, $J = 14.2$ Hz), 129.9 (d, $J = 39.5$ Hz), 124.9 (d, $J = 34.2$ Hz), 123.5 – 123.4 (m), 2.2 (d, $J = 4.9$ Hz), 0.4. ^{19}F NMR (376 MHz, CDCl_3) δ 85.34 (quintet, $J = 149.2$ Hz, 1F), 65.71 (d, $J = 149.2$ Hz, 4F), -80.31 (s, 1F).

Synthesis of 2,4-bis(hydroxydimethylsilyl)-5-bromopentafluorosulfanyl benzene (S2):



Following a modified procedure by Denmark,¹¹ a 8-mL vial equipped with a magnetic stir bar was charged with 2,4-bis(dimethylsilyl)-5-bromopentafluorosulfanyl benzene (400 mg, 1.0 mmol). Dry acetonitrile (2 mL) was added followed by H₂O (0.36 mL, 20.0 mmol, 20 equiv). [RuCl₂(*p*-cymene)]₂ (31 mg, 0.05 mmol, 5 mol %) was then added to the reaction mixture. The reaction vial was sealed with a hole cap and a septa. A needle was used to puncture the septum to ensure that the reaction mixture was exposed to air. The reaction was stirred at RT overnight. After the completion of reaction, the reaction solution was diluted with CH₂Cl₂ (10 mL) and poured into H₂O (10 mL). The resulting mixture was extracted with CH₂Cl₂ (3 x 25 mL). The combined organic layers were dried over Na₂SO₄. Silica gel was then added to the solution and the mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes : ethyl acetate (4:1) to elute the product. Silanol, 425 mg (98 %), was obtained as a white solid. X-ray quality crystals were obtained by slow evaporation of solution in CH₂Cl₂. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.95 (s, 1H), 5.05 (s, 1H), 4.87 (s, 1H), 0.44 (s, 6H), 0.36 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 160.3 (quintet, *J* = 16.4 Hz), 144.2, 144.0, 134.5, 130.5 – 130.3 (m), 130.1, 1.3, 0.2. ¹⁹F NMR (376 MHz, CDCl₃) δ 84.82 (quintet, *J* = 148.6 Hz, 1F), 64.44 (d, *J* = 148.6 Hz, 4F).

X-ray Crystallographic Data

The measurements were made with a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector using CuK α radiation at 123 K. The reflections were collected using a narrow-frame algorithm with scan widths of 0.50% in omega and an exposure time of 20 s/frame. The data were integrated using the Bruker Apex-II program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The data were scaled, and an absorption correction was applied

using SADABS. Redundant reflections were averaged. The structure was solved by direct method and refined with the program SHELXL 2014. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically with riding displacement parameters.

Crystallographic Information for **2,4-bis(hydroxydimethylsilyl)-3-fluoropentafluorosulfanyl benzene (S1)**:

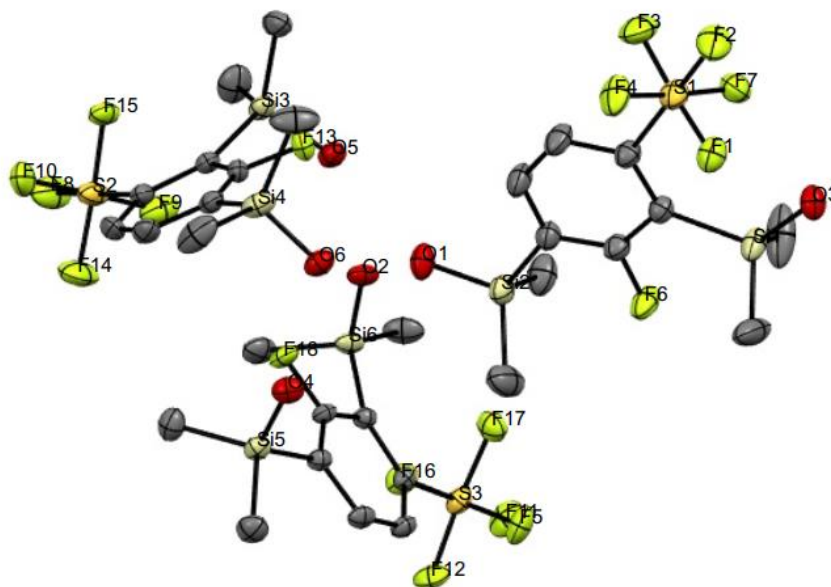


Table S2: Crystal data and structure refinement for 2,4-bis(hydroxydimethylsilyl)-3-fluoropentafluorosulfanyl benzene (S1).

Identification code	XW318_10
Empirical formula	C ₁₀ H ₁₆ O ₂ F ₆ Si ₂ S
Formula weight	370.47
Temperature/K	123(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.6888(5)
b/Å	12.0275(5)
c/Å	18.7864(7)
α/°	89.4300(10)
β/°	85.9810(10)
γ/°	68.9520(10)
Volume/Å ³	2458.52(17)
Z	6
ρ _{calc} /cm ³	1.501

μ/mm^{-1}	3.762
F(000)	1140.0
Crystal size/ mm^3	$0.19 \times 0.07 \times 0.02$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54178$)
2θ range for data collection/ $^\circ$	4.716 to 133.104
Index ranges	$-13 \leq h \leq 13, -14 \leq k \leq 14, -22 \leq l \leq 22$
Reflections collected	35068
Independent reflections	8368 [$R_{\text{int}} = 0.0381, R_{\text{sigma}} = 0.0350$]
Data/restraints/parameters	8368/1/586
Goodness-of-fit on F^2	1.041
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0355, wR_2 = 0.0909$
Final R indexes [all data]	$R_1 = 0.0378, wR_2 = 0.0926$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.53/-0.50

Crystallographic Information for **2,4-bis(hydroxydimethylsilyl)-5-bromopentafluorosulfanyl benzene (S2)**.

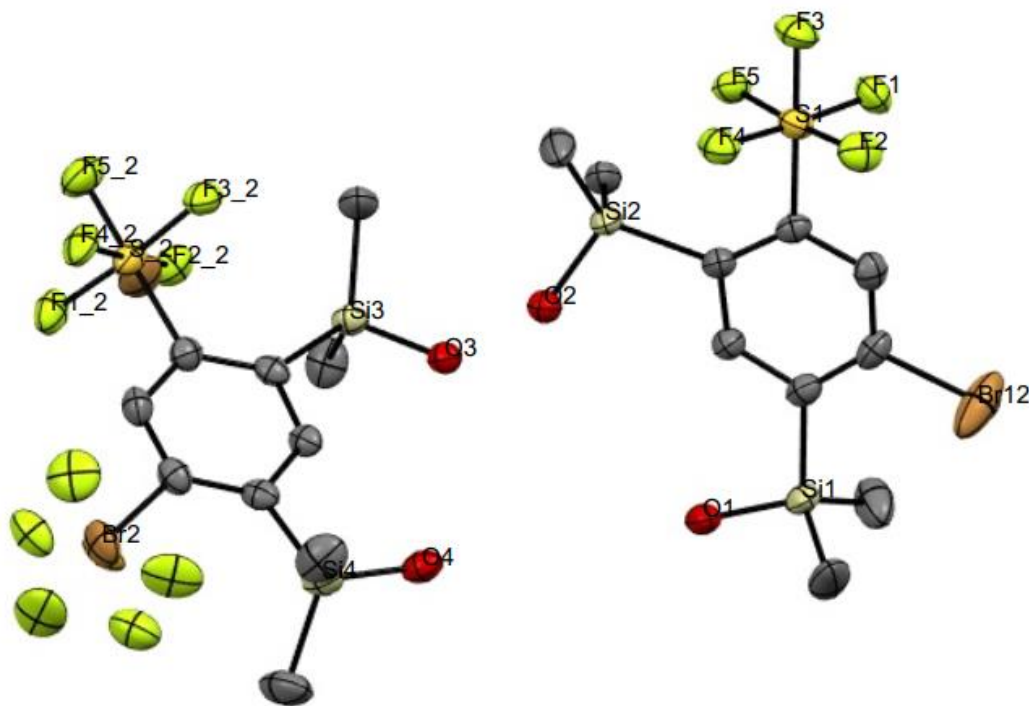


Table S3: Crystal data and structure refinement for 2,4-bis(hydroxydimethylsilyl)-5-bromopentafluorosulfanyl benzene (S2).

Identification code	XW320_11
Empirical formula	$\text{C}_{10}\text{H}_{16}\text{BrF}_5\text{O}_2\text{SSi}_2$

Formula weight	431.38
Temperature/K	123(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	24.1980(9)
b/Å	13.1680(5)
c/Å	22.6970(8)
α /°	90
β /°	109.697(2)
γ /°	90
Volume/Å ³	6809.0(4)
Z	16
ρ_{calc} /cm ³	1.683
μ /mm ⁻¹	6.278
F(000)	3456.0
Crystal size/mm ³	0.24 × 0.19 × 0.03
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection/°	7.754 to 132.316
Index ranges	-27 ≤ h ≤ 28, -15 ≤ k ≤ 15, -26 ≤ l ≤ 26
Reflections collected	31467
Independent reflections	5860 [R_{int} = 0.0529, R_{sigma} = 0.0440]
Data/restraints/parameters	5860/664/465
Goodness-of-fit on F ²	1.202
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0506, wR_2 = 0.1250
Final R indexes [all data]	R_1 = 0.0517, wR_2 = 0.1256
Largest diff. peak/hole / e Å ⁻³	0.48/-0.56

Please note that there are two symmetry-independent molecules. One has its Br atom site slightly split. The other molecule has an exchanged position of its Br and SF₅ group.

Crystallographic Information for *N*-(3-dimethylsilyl-4-(pentafluorosulfanyl)phenyl)benzamide
(Table 2, Entry 12)

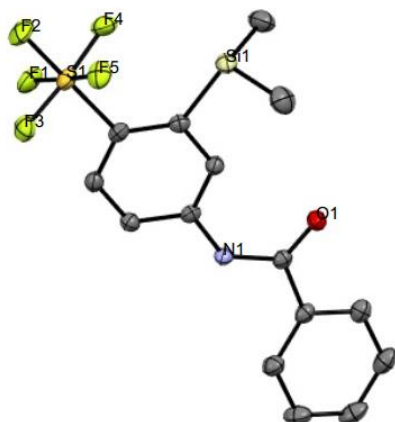


Table S4: Crystal data and structure refinement for *N*-(3-dimethylsilyl-4 (pentafluorosulfanyl)phenyl)benzamide (Table 2, Entry 12).

Identification code	TL33_XW317
Empirical formula	C ₁₅ H ₁₆ NOF ₅ SiS
Formula weight	381.44
Temperature/K	123(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.9576(3)
b/Å	15.6343(3)
c/Å	9.2554(2)
α/°	90
β/°	99.1670(10)
γ/°	90
Volume/Å ³	1708.19(7)
Z	4
ρ _{calc} /cm ³	1.483
μ/mm ⁻¹	2.872
F(000)	784.0
Crystal size/mm ³	0.52 × 0.21 × 0.19
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.488 to 131.868
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 18, -10 ≤ l ≤ 10
Reflections collected	12808
Independent reflections	2952 [R _{int} = 0.0257, R _{sigma} = 0.0208]

Data/restraints/parameters	2952/0/222
Goodness-of-fit on F ²	1.042
Final R indexes [I>2σ (I)]	R ₁ = 0.0304, wR ₂ = 0.0788
Final R indexes [all data]	R ₁ = 0.0306, wR ₂ = 0.0789
Largest diff. peak/hole / e Å ⁻³	0.25/-0.37

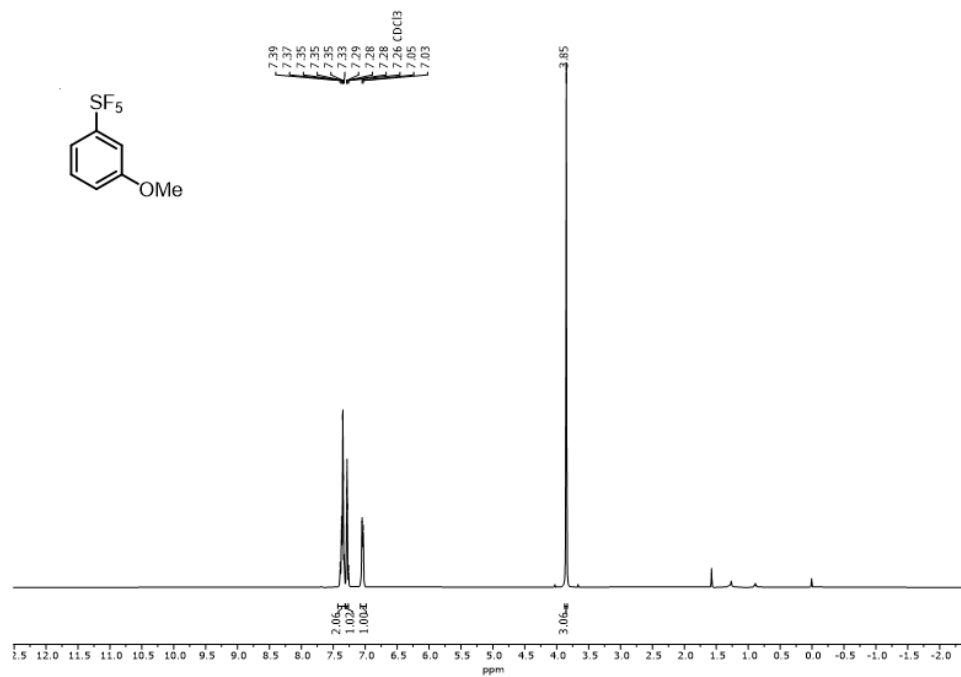
References:

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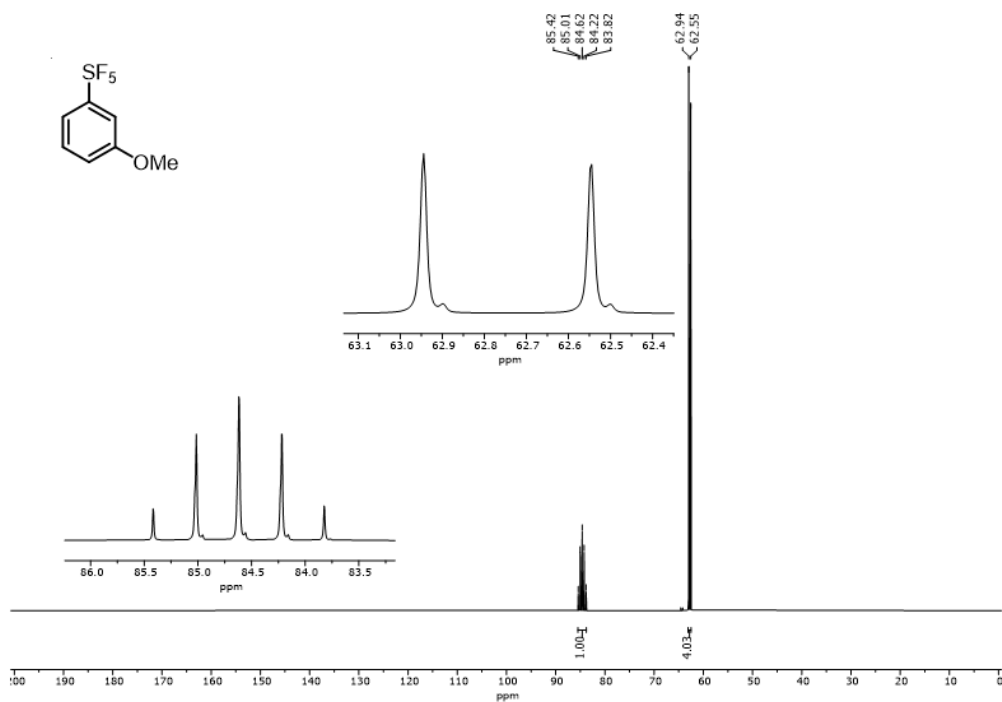
NMR data

3-Methoxy-pentafluorosulfanyl benzene (Starting material)

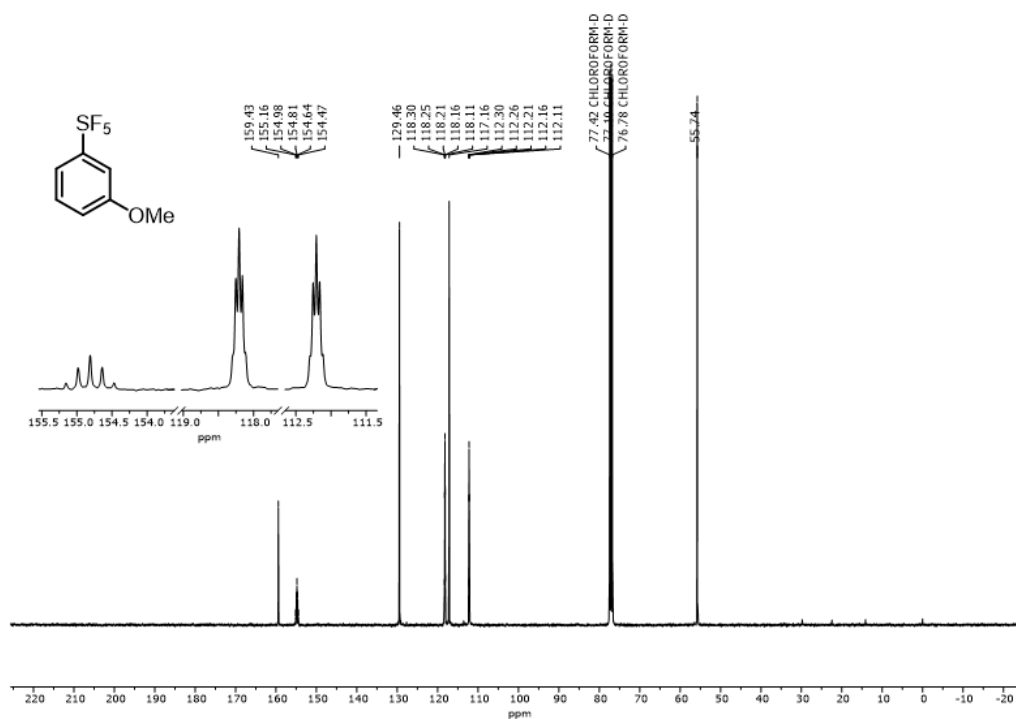
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

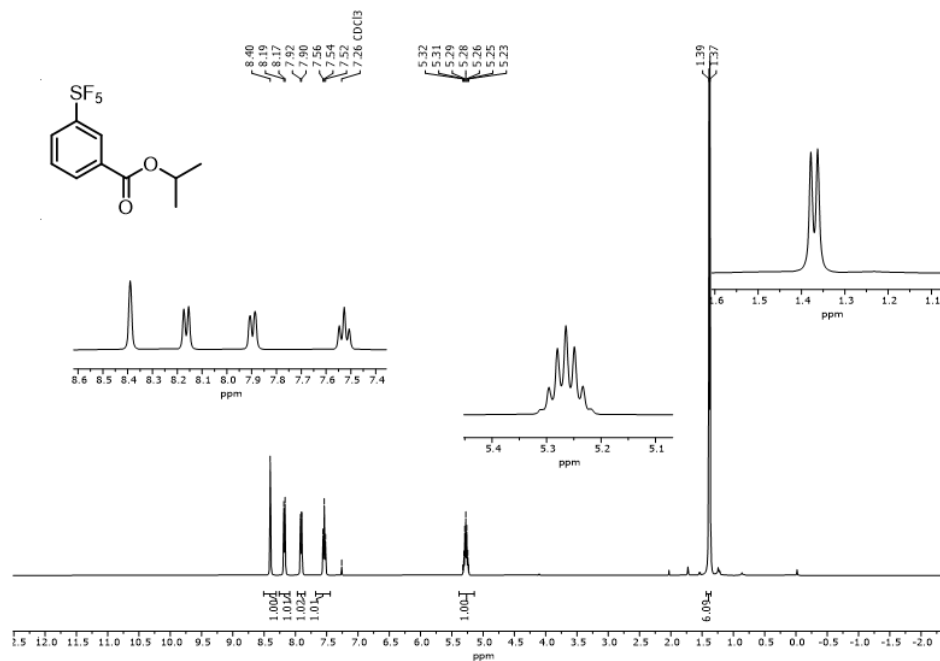


^{13}C NMR (101 MHz, CDCl_3)

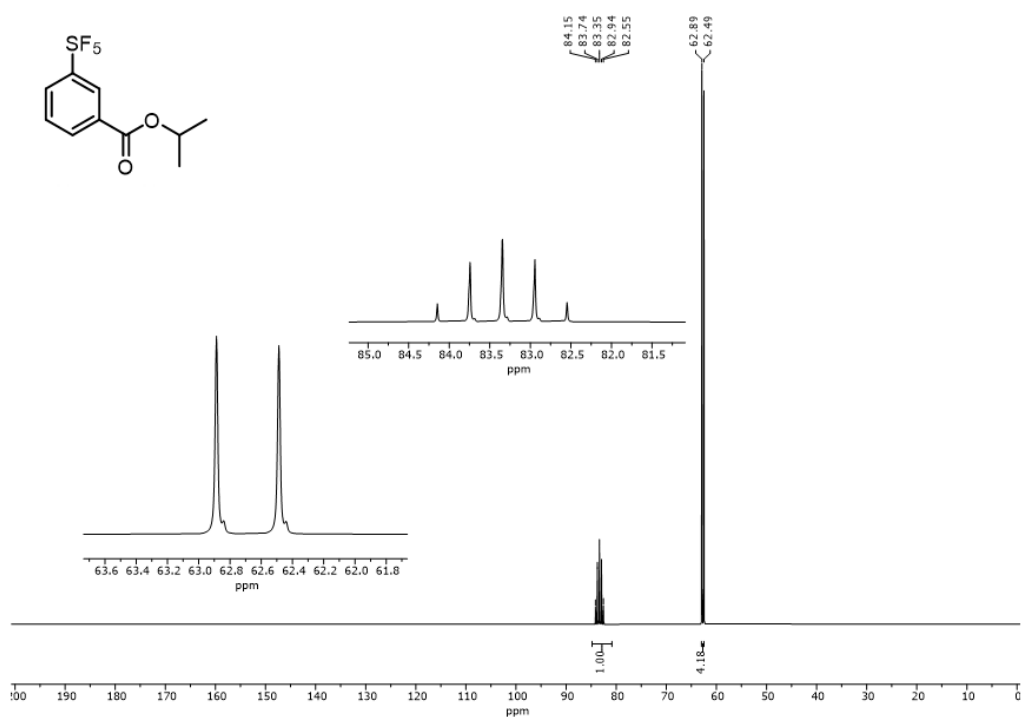


Isopropyl 3-(pentafluorosulfonyl) benzoate (Starting material)

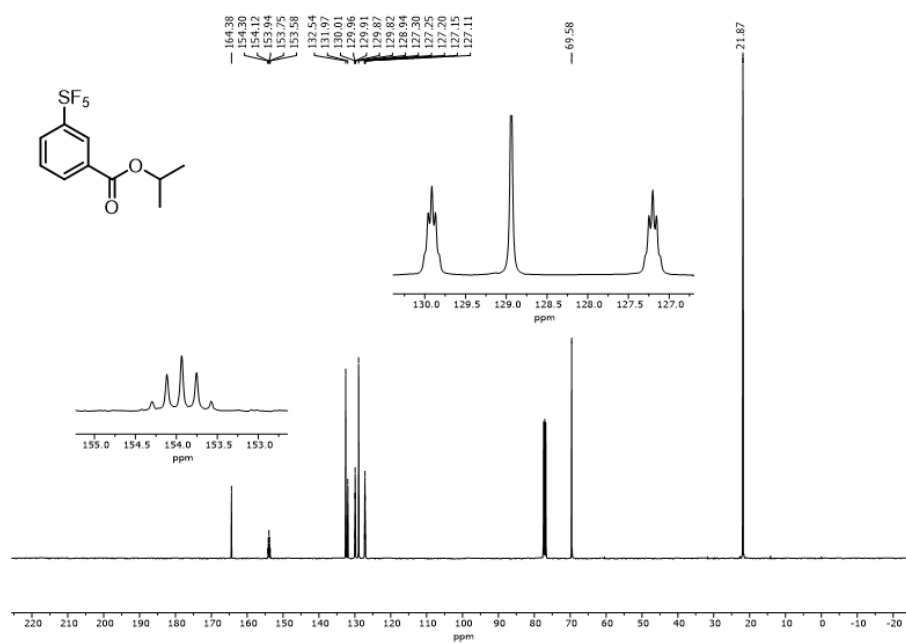
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

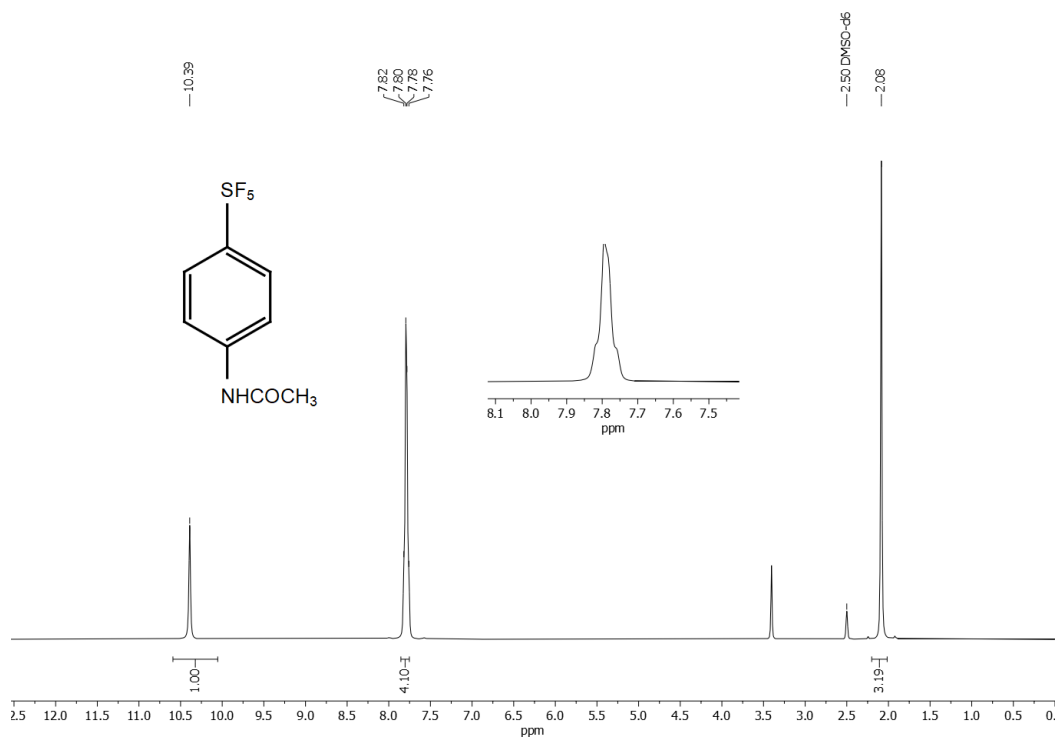


^{13}C NMR (101 MHz, CDCl_3)

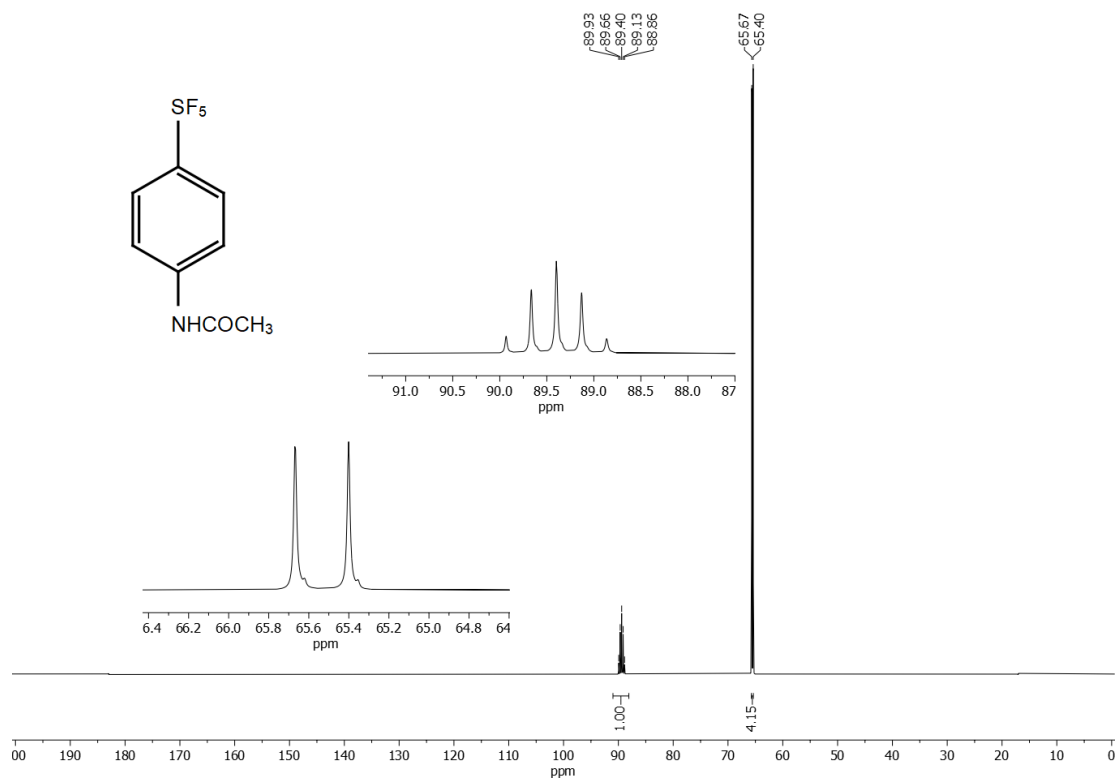


4-Acetamidopentafluorosulfanyl benzene (Starting material)

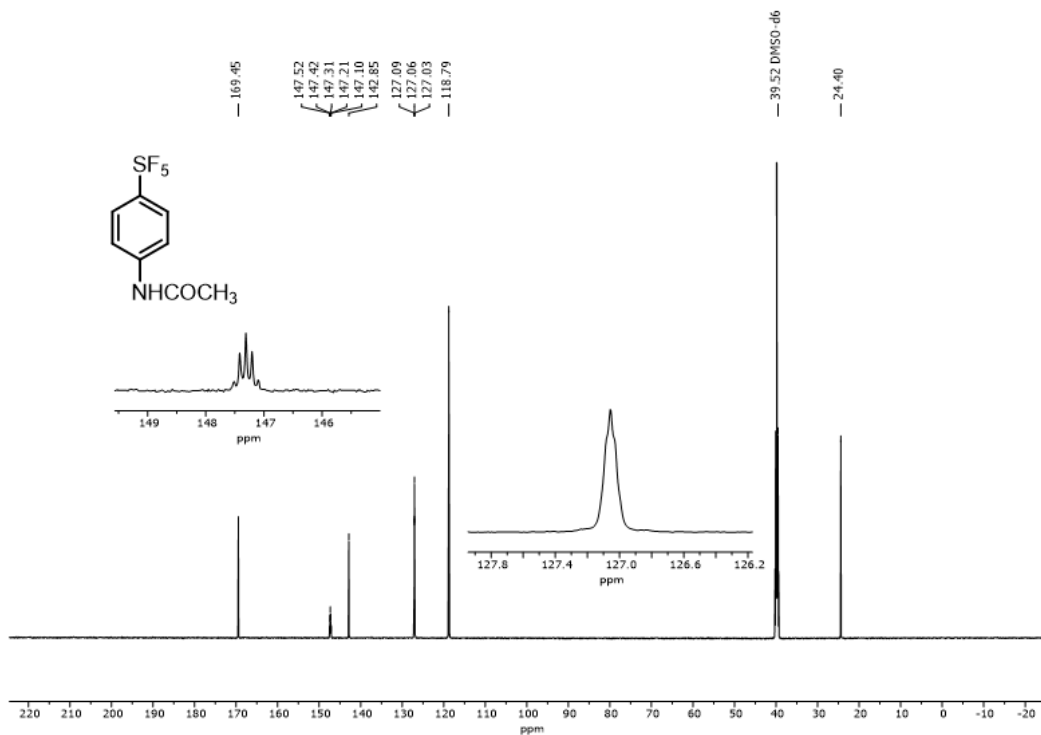
^1H NMR (400 MHz, DMSO- d_6)



^{19}F NMR (376 MHz, DMSO- d_6)

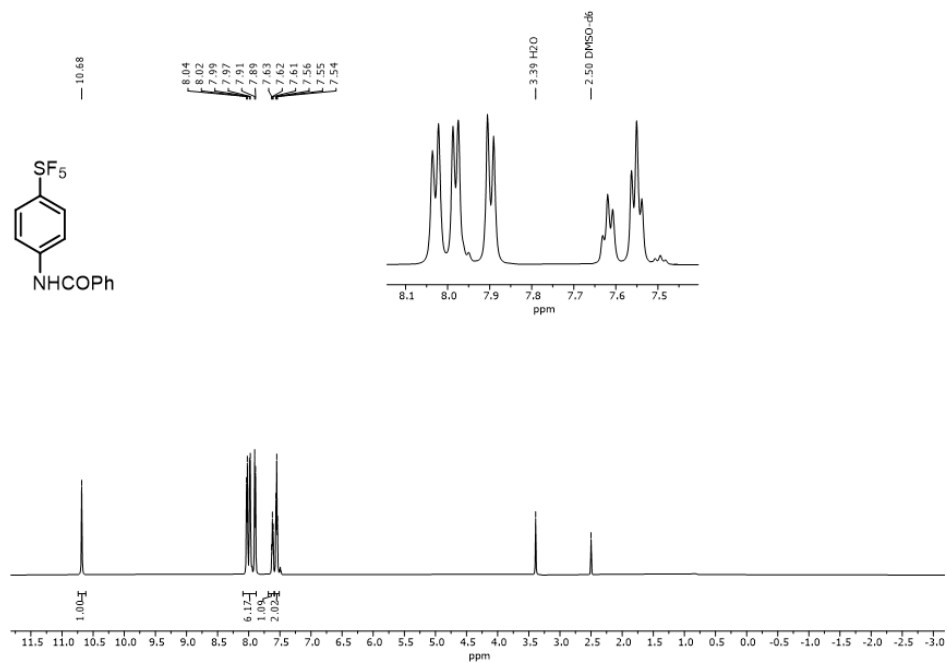


^{13}C NMR (101 MHz, DMSO- d_6)

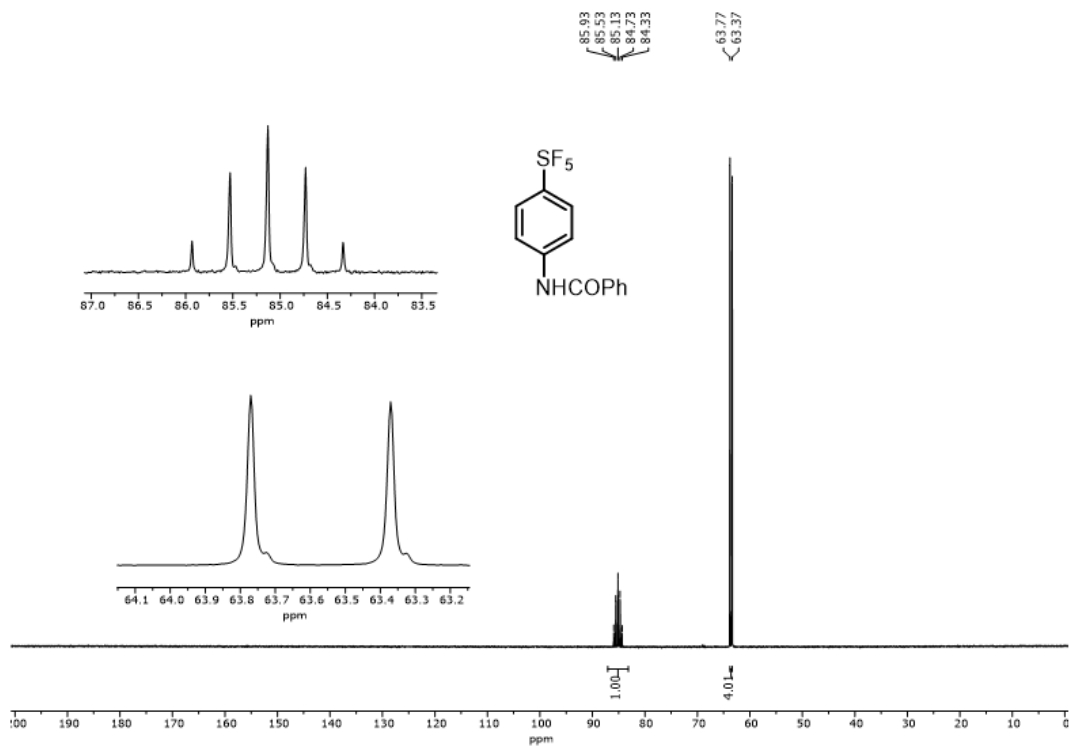


***N*-(4-(pentafluorosulfanyl)phenyl)benzamide (Starting material)**

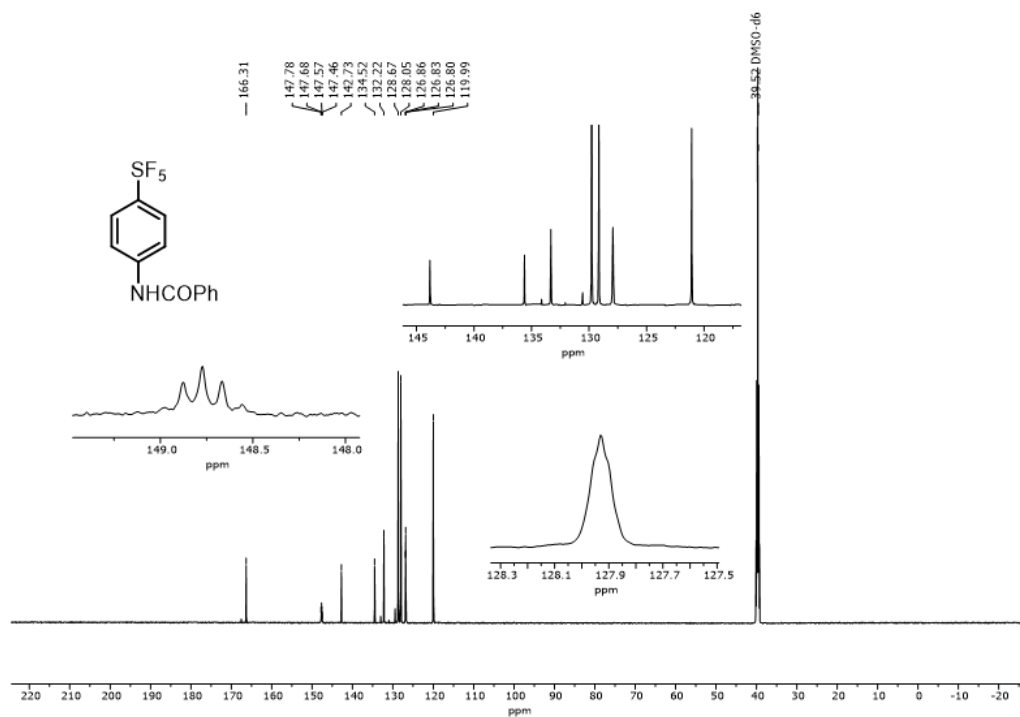
^1H NMR (400 MHz, DMSO- d_6)



^{19}F NMR (376 MHz, DMSO-*d*₆)



^{13}C NMR (101 MHz, DMSO-*d*₆)

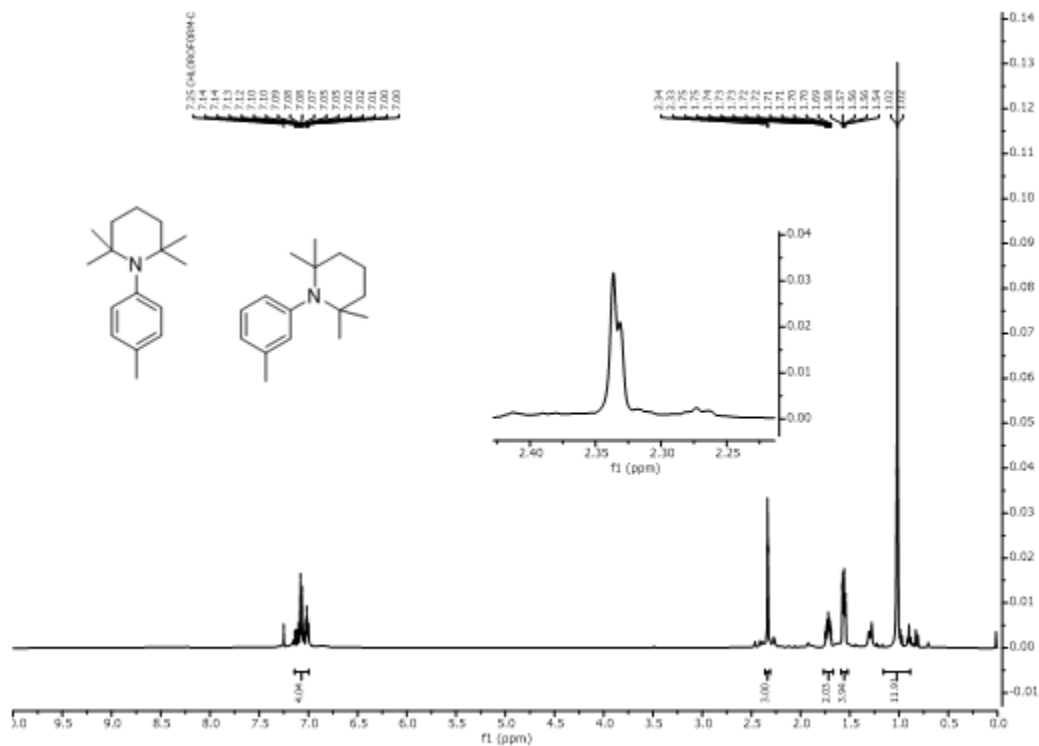


1-Phenyl-2,2,6,6-tetramethylpiperidine

^1H NMR (400 MHz, CDCl_3)

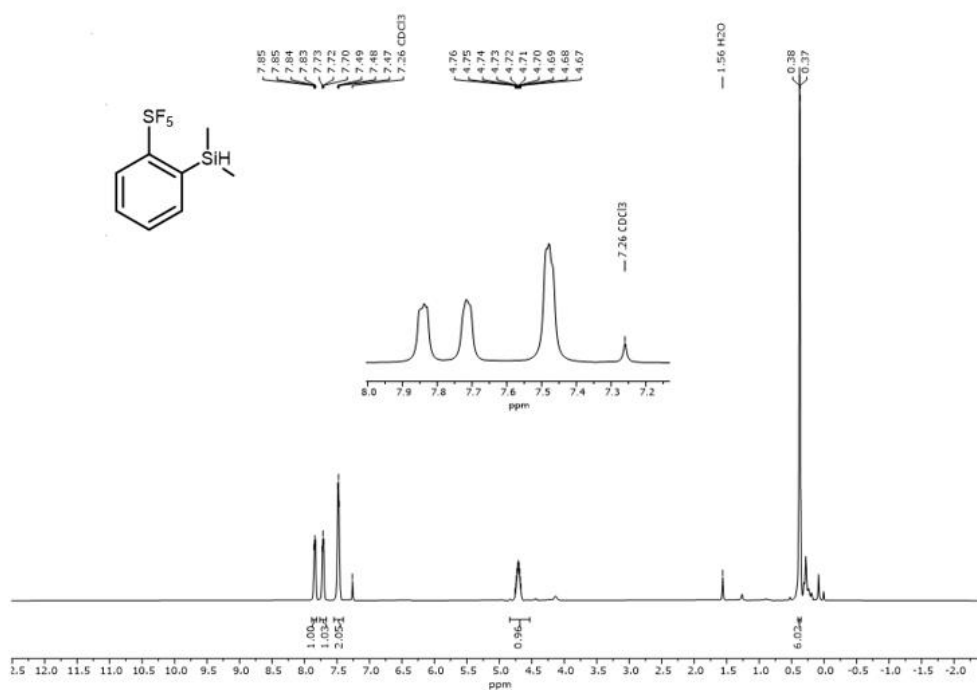


1-(3-tolyl)-2,2,6,6-tetramethylpiperidine and 1-(4-tolyl)-2,2,6,6-tetramethylpiperidine

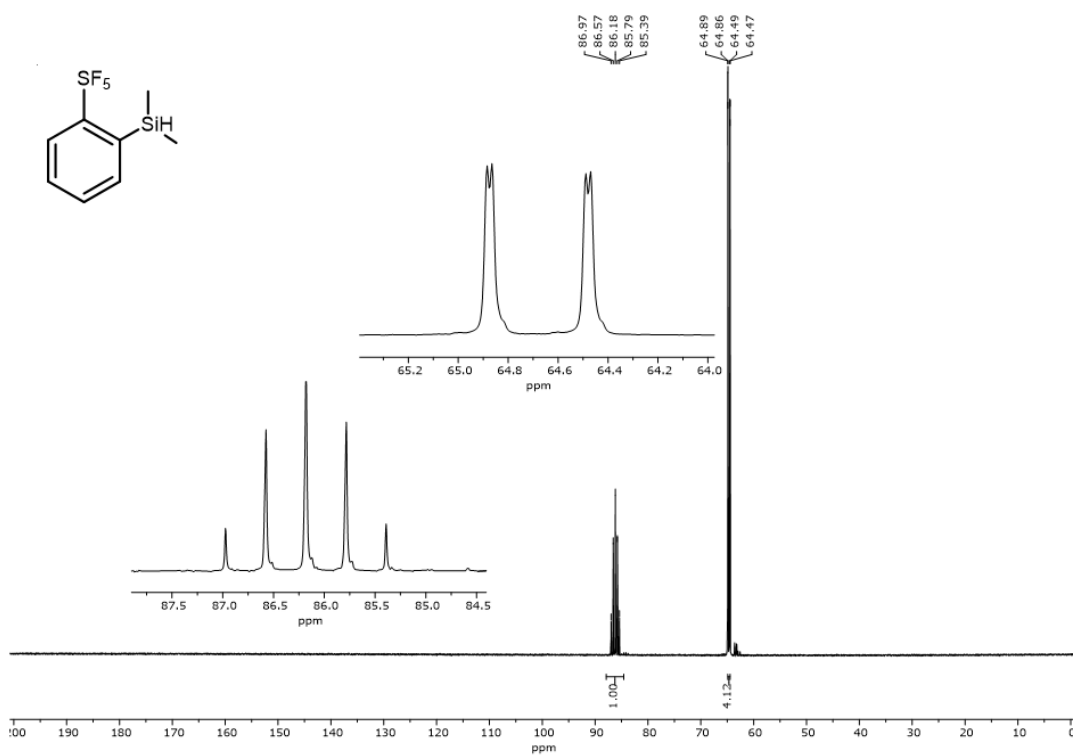


2-Dimethylsilylpentafluorosulfanyl benzene (Table 2, Entry 1)

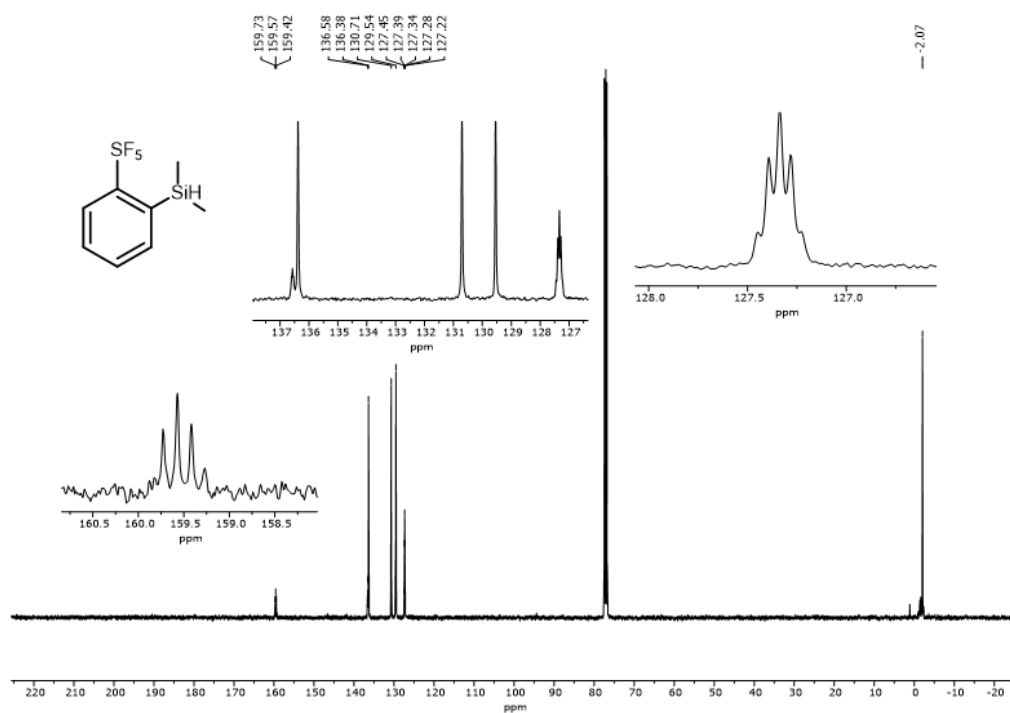
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

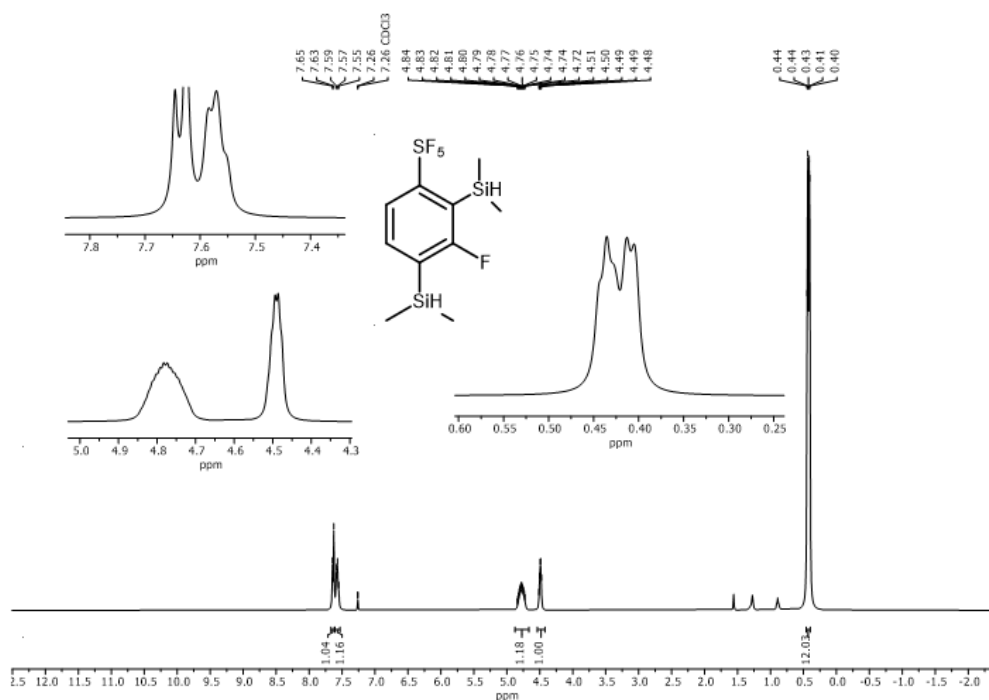


^{13}C NMR (101 MHz, CDCl_3)

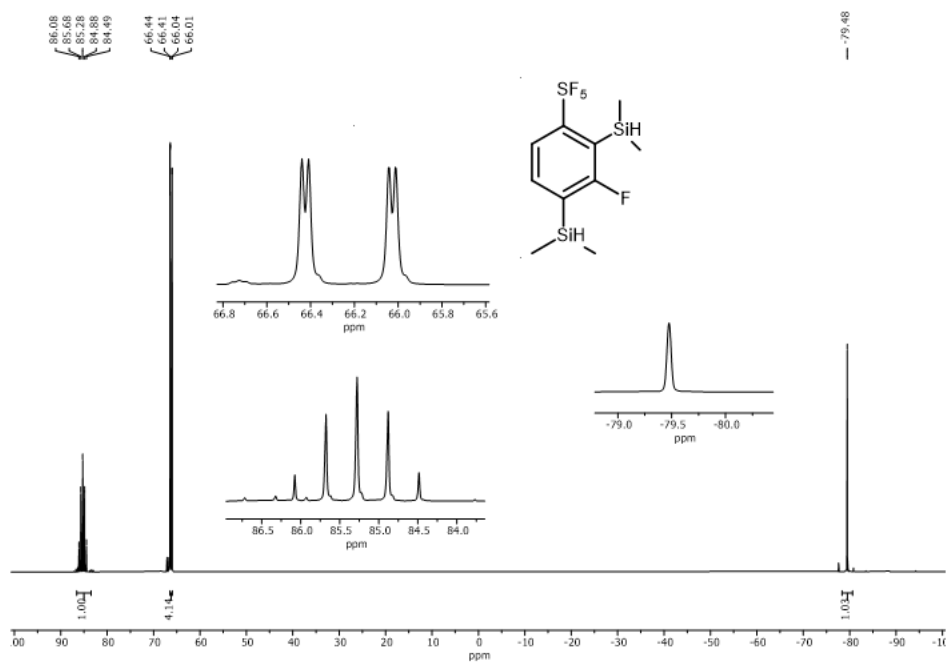


2,4-bis(Dimethylsilyl)-3-fluoropentafluorosulfonyl benzene (Table 2, Entry 2)

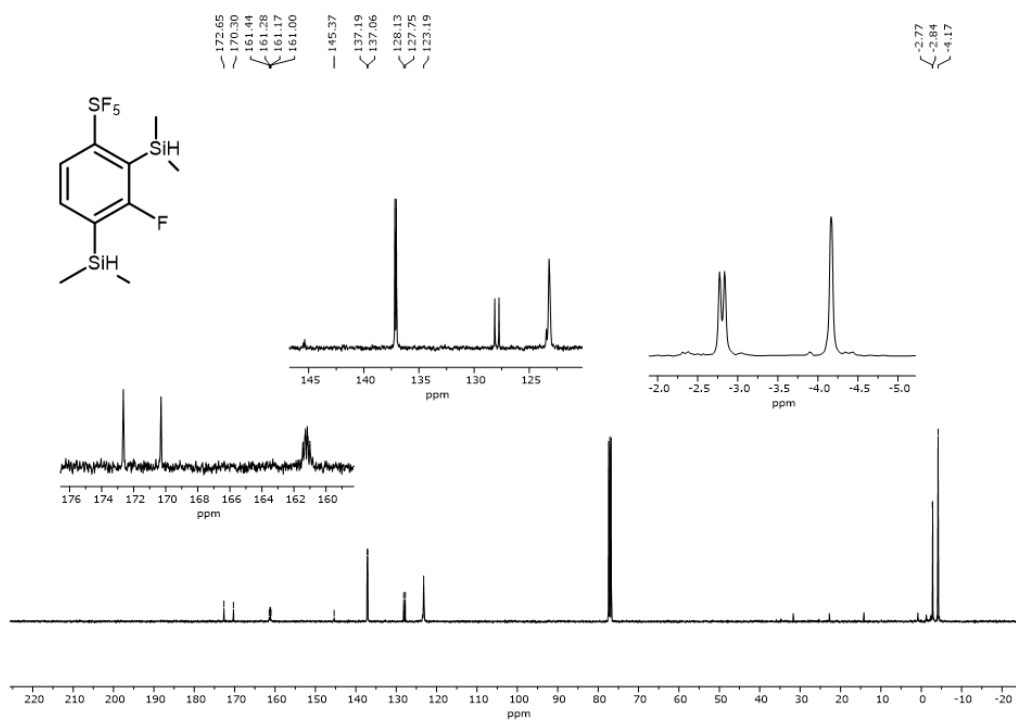
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

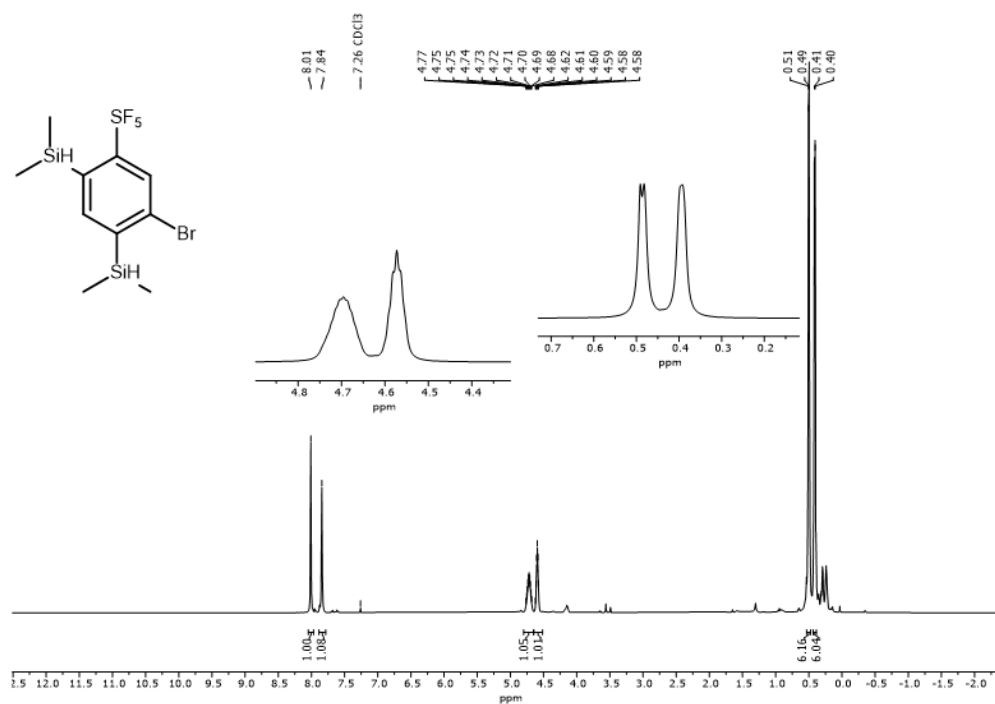


^{13}C NMR (101 MHz, CDCl_3)

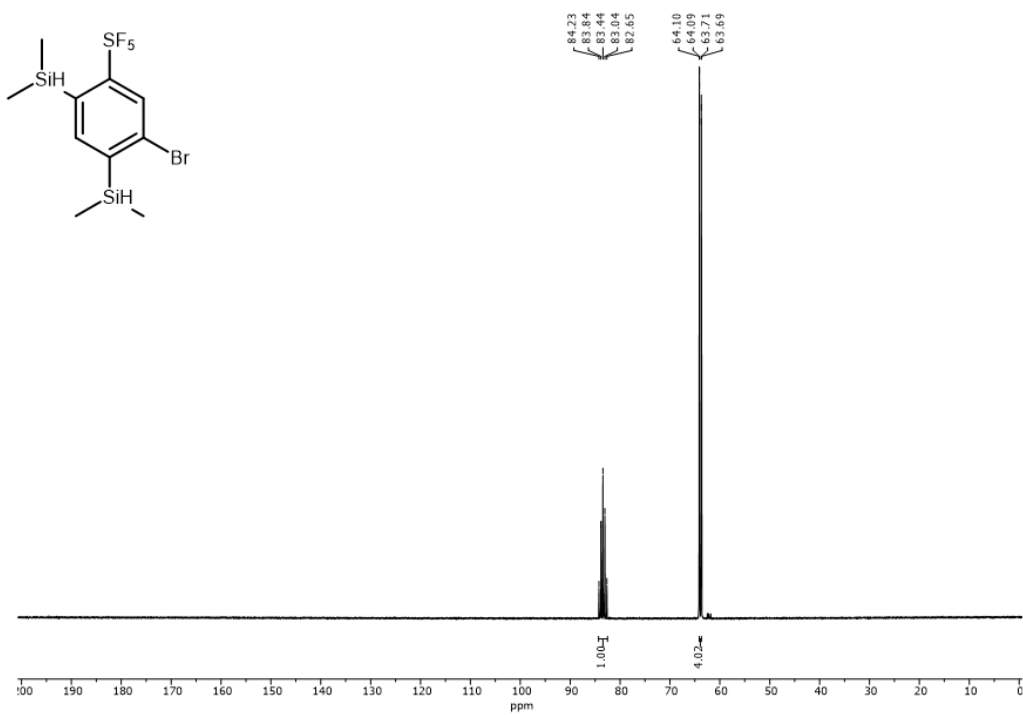


2,4-bis(Dimethylsilyl)-5-bromopentafluorosulfonyl benzene (Table 2, Entry 3)

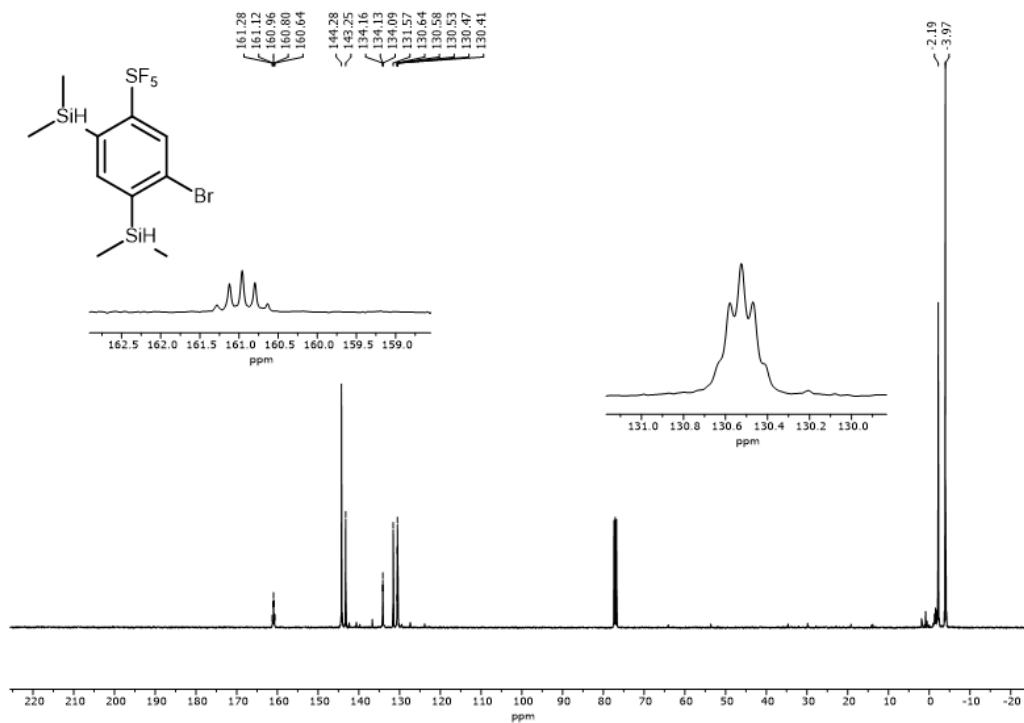
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

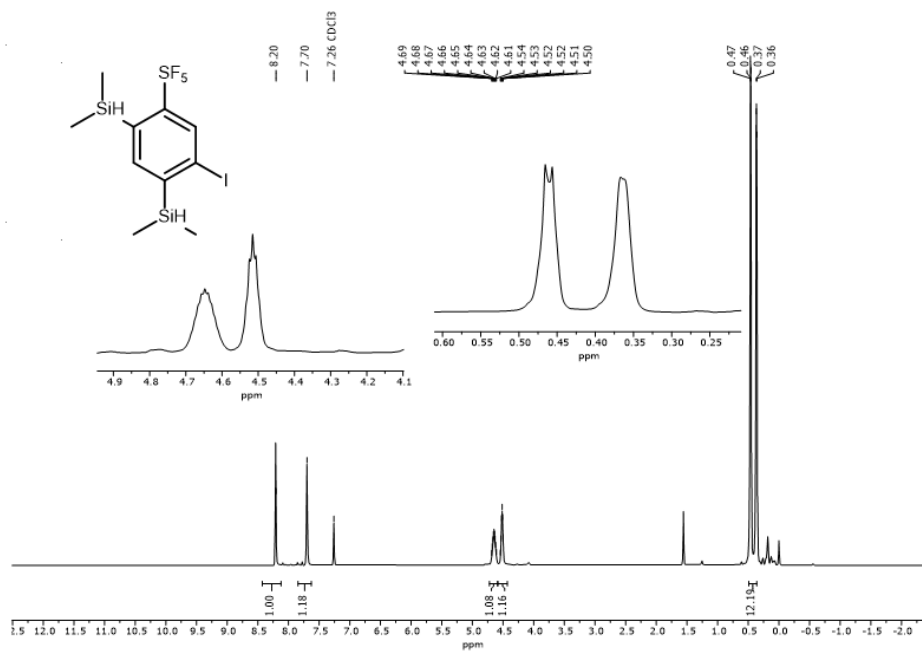


^{13}C NMR (101 MHz, CDCl_3)

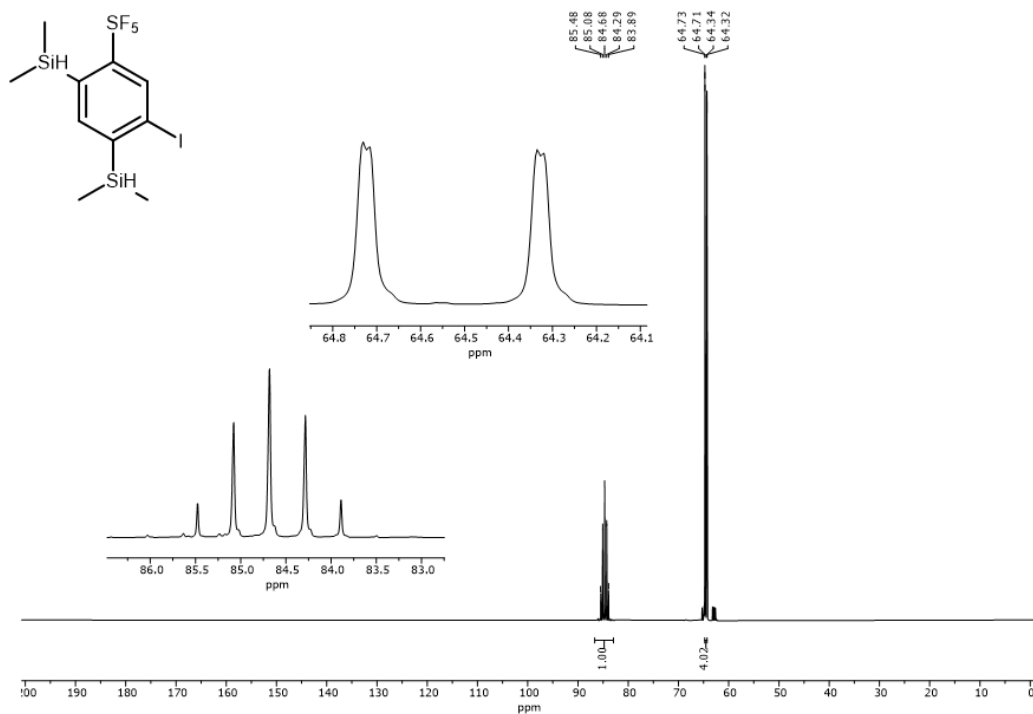


2,4-bis(Dimethylsilyl)-5-iodopentafluorosulfonyl benzene (Table 2, Entry 4)

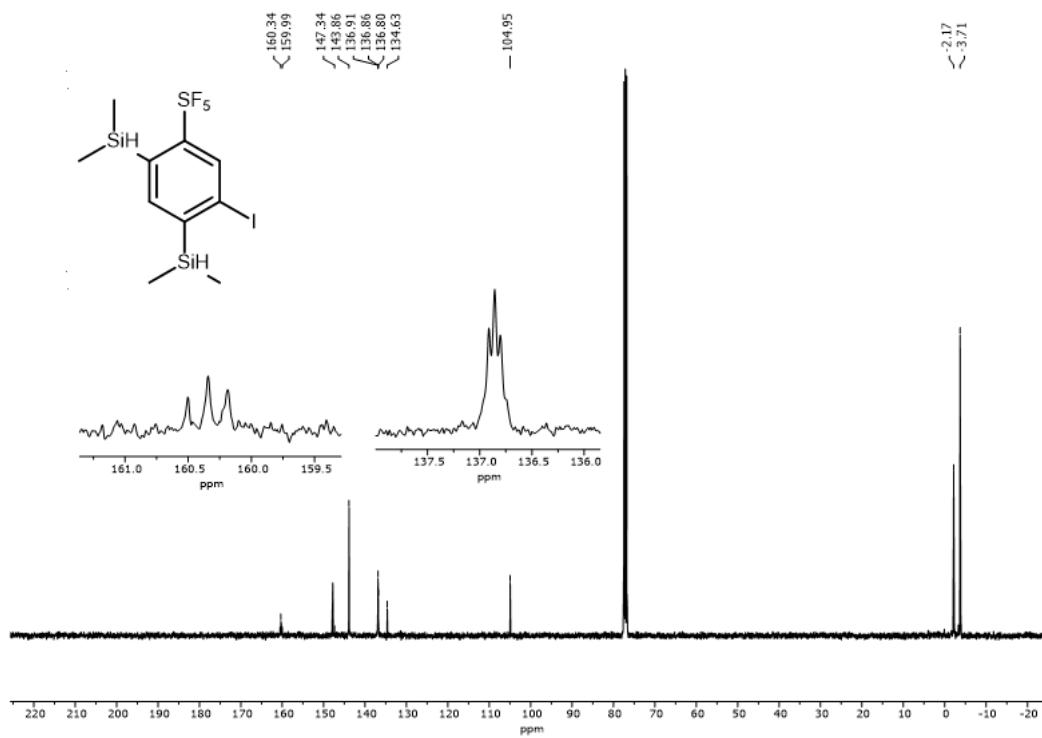
^1H NMR (400 MHz, CDCl_3)



¹⁹F NMR (376 MHz, CDCl₃)

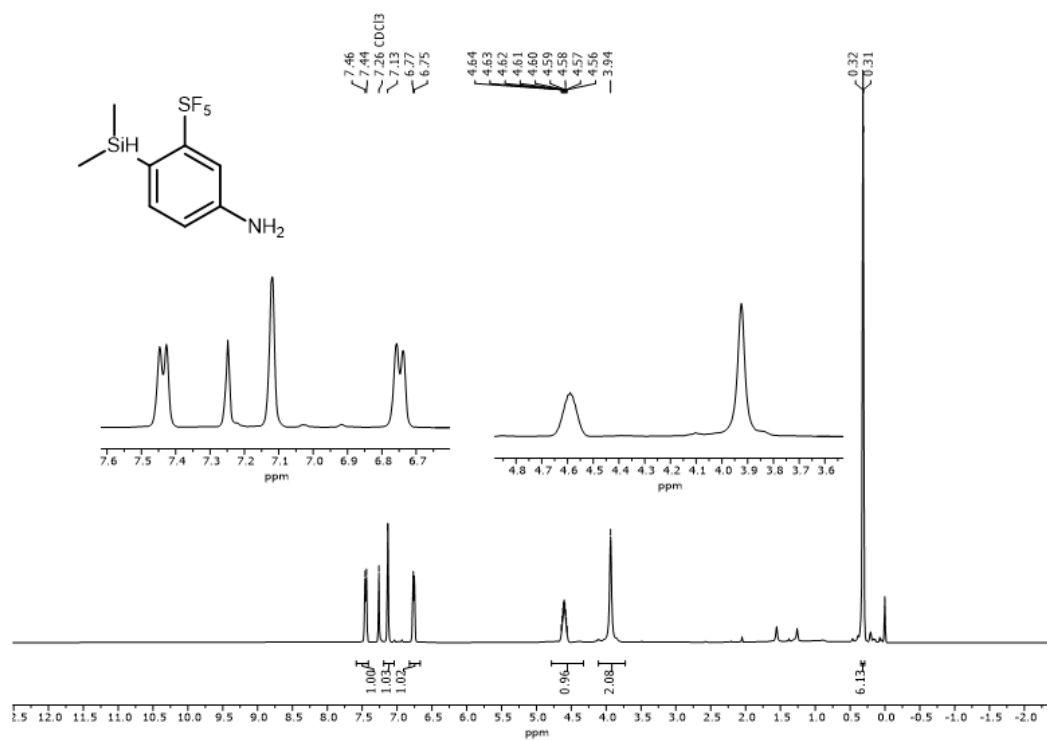


¹³C NMR (101 MHz, CDCl₃)

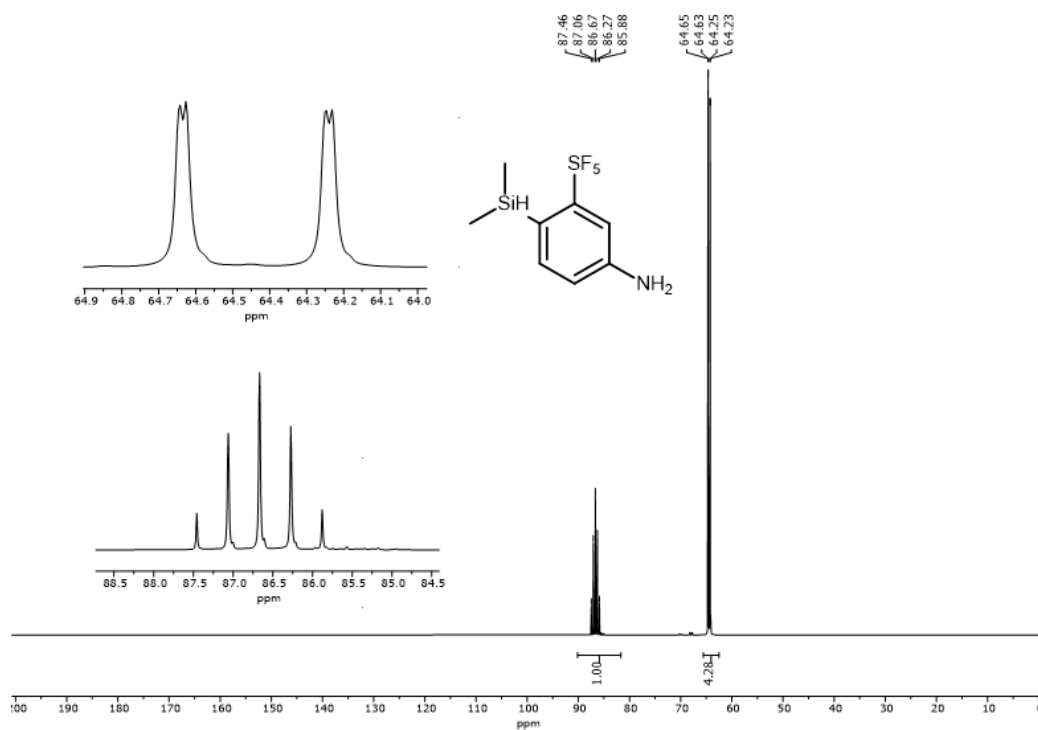


2-Dimethylsilyl-5-aminopentafluorosulfanyl benzene (Table 2, Entry 5)

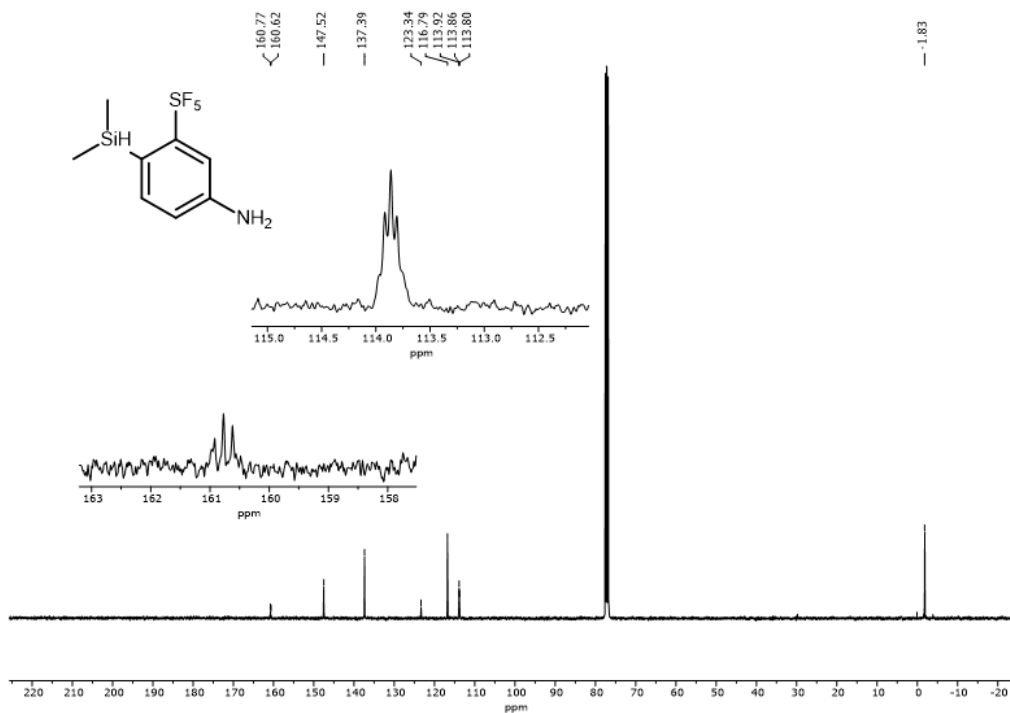
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

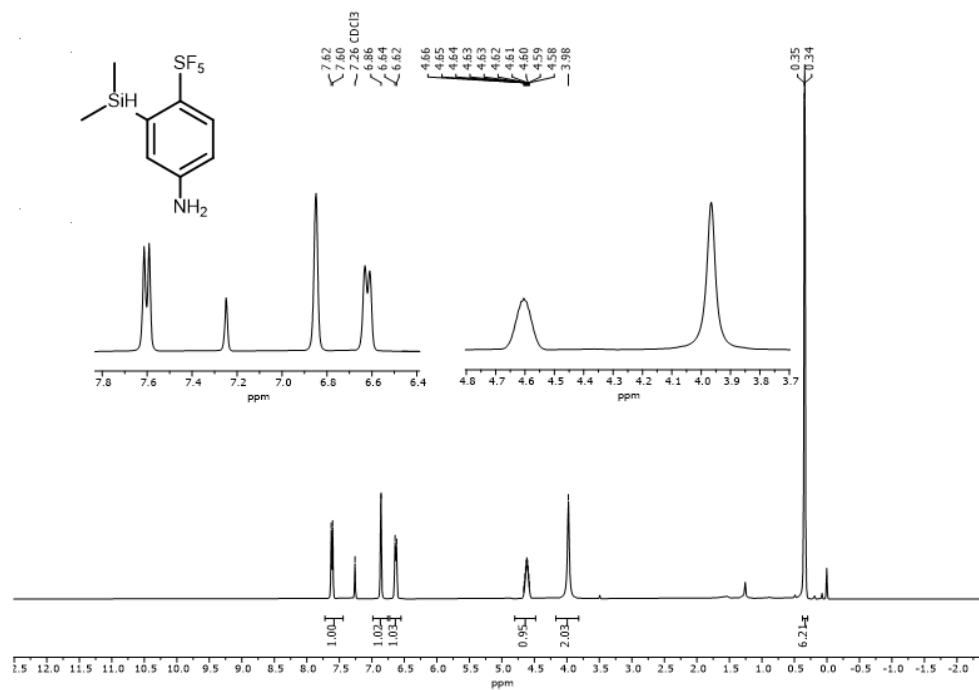


^{13}C NMR (101 MHz, CDCl_3)

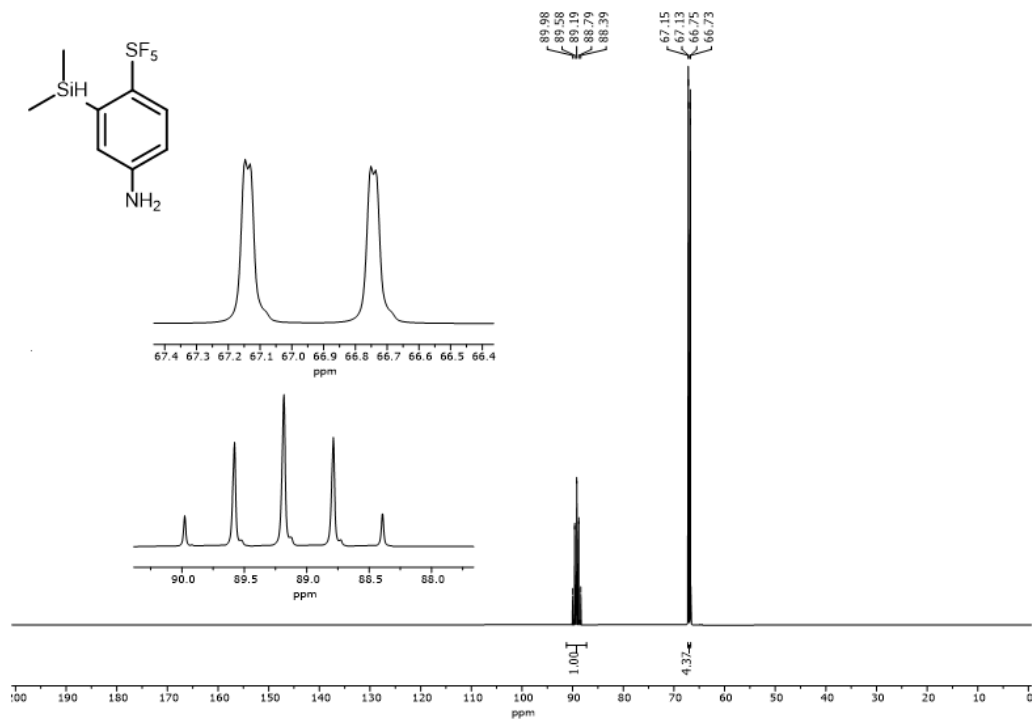


2-Dimethylsilyl-4-aminopentafluorosulfanyl benzene (Table 2, Entry 6)

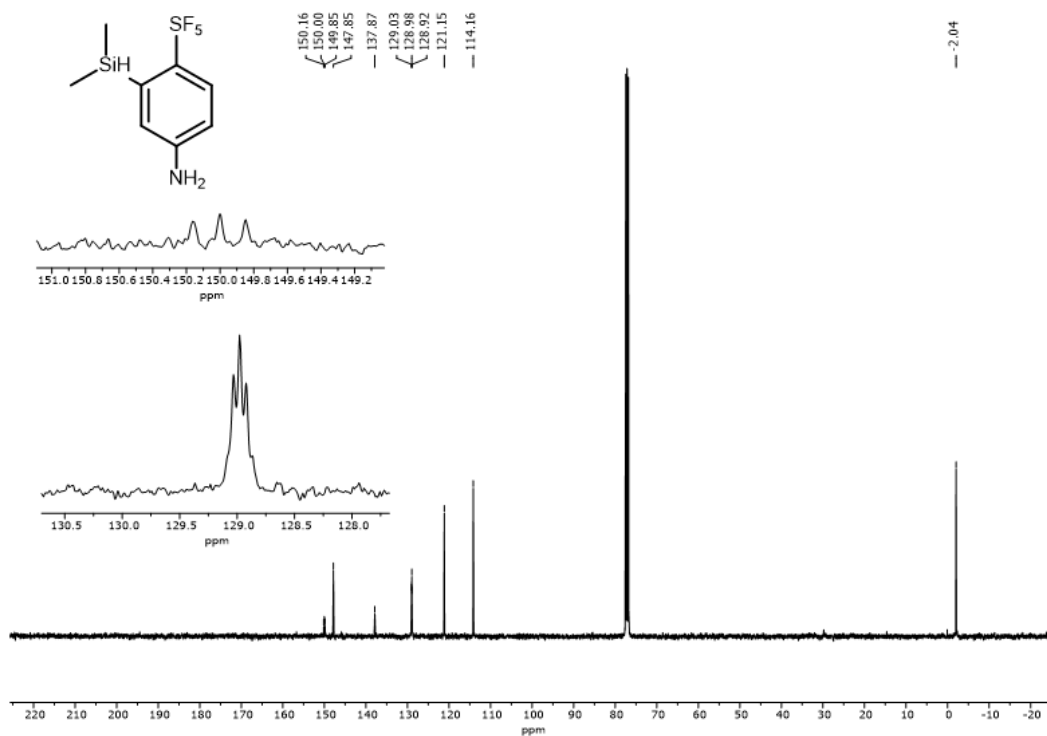
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

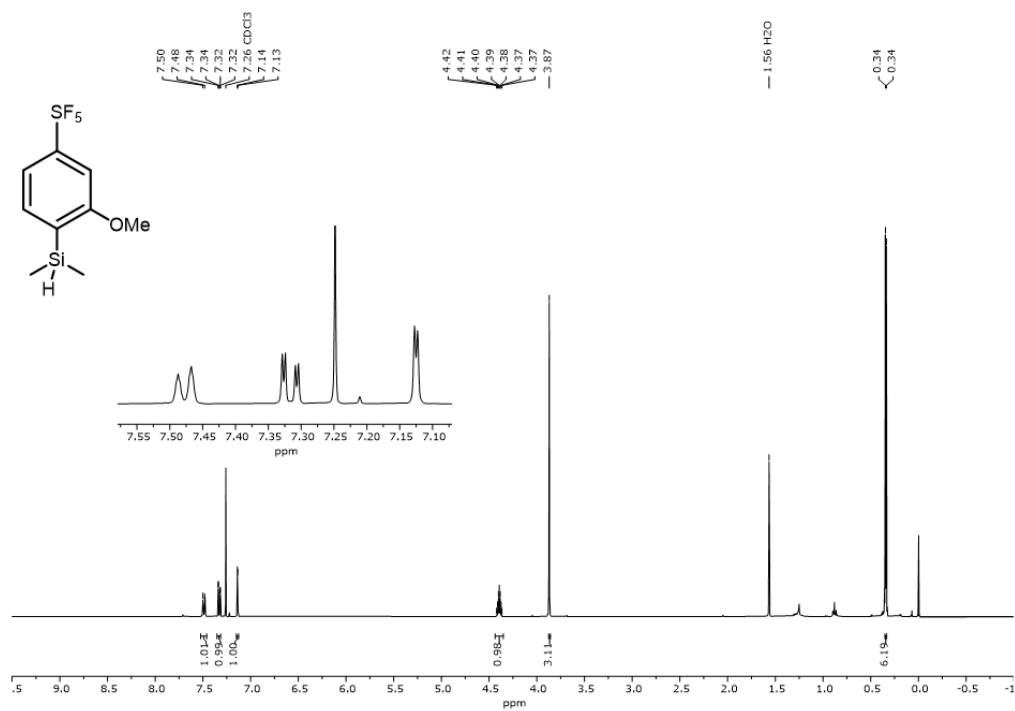


^{13}C NMR (101 MHz, CDCl_3)

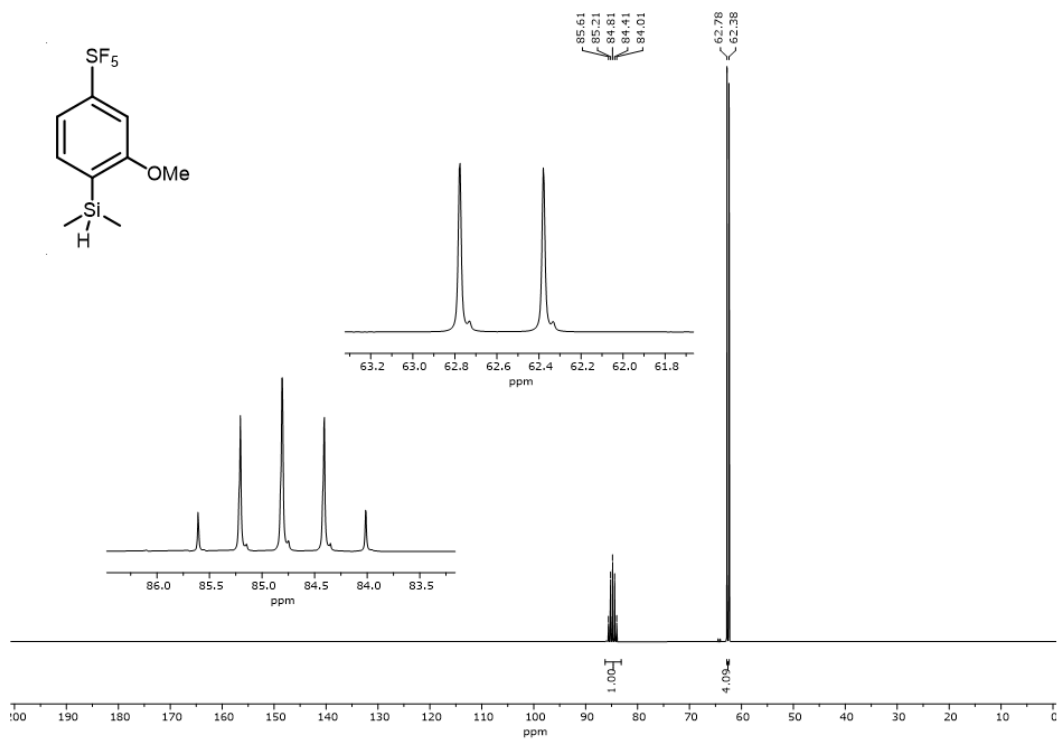


4-Dimethylsilyl-3-methoxy-pentafluorosulfanyl benzene (Table 2, Entry 7)

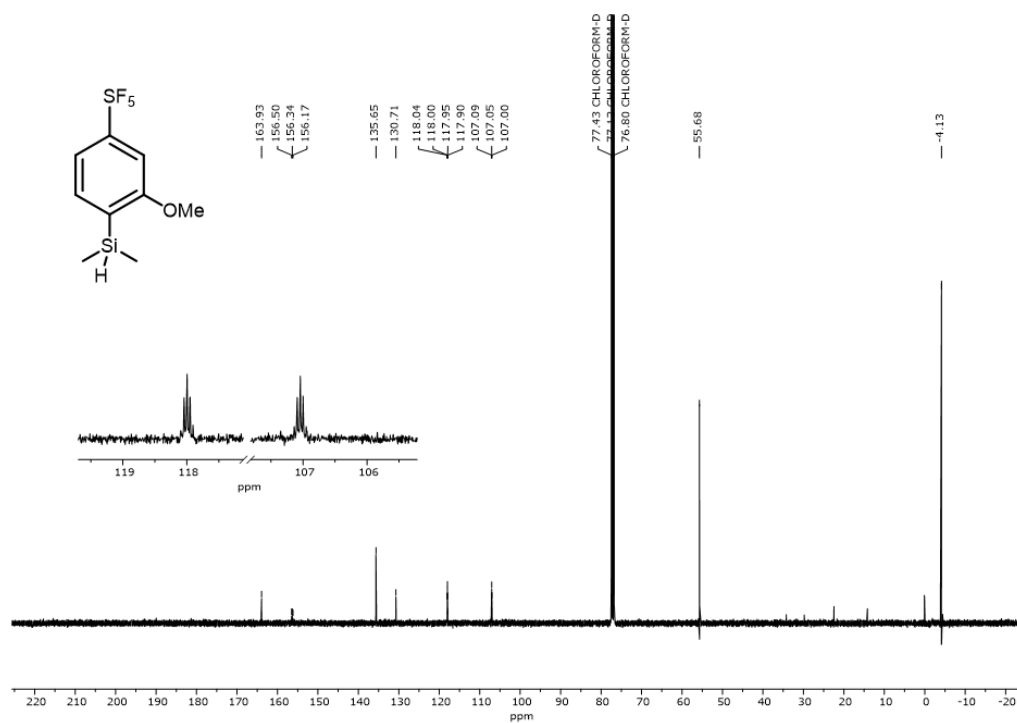
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

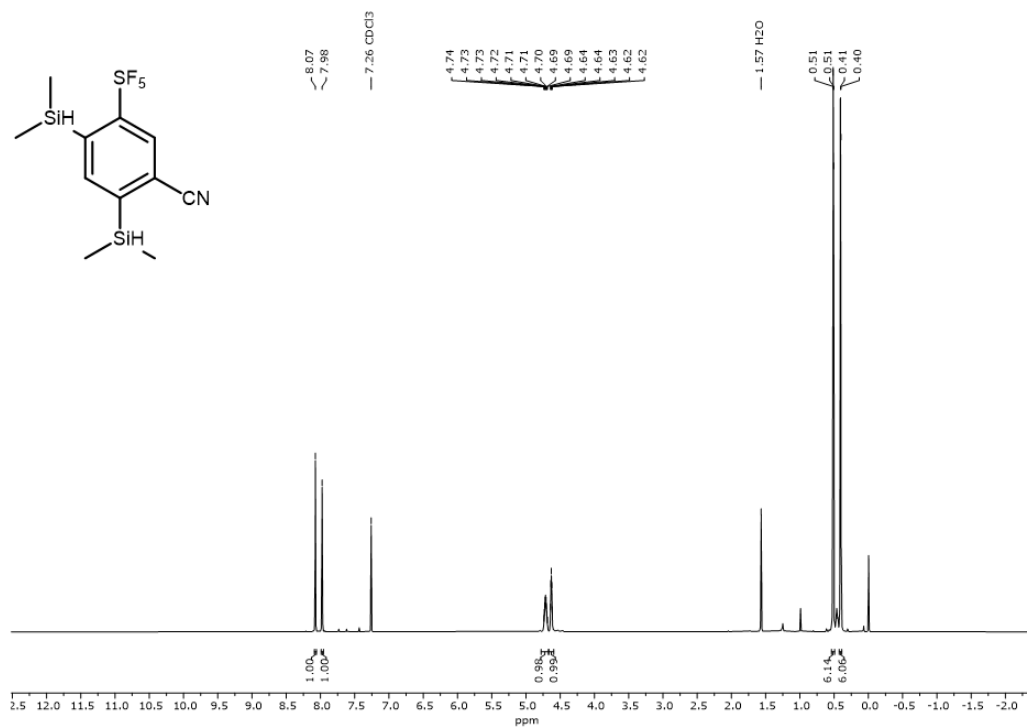


^{13}C NMR (101 MHz, CDCl_3)

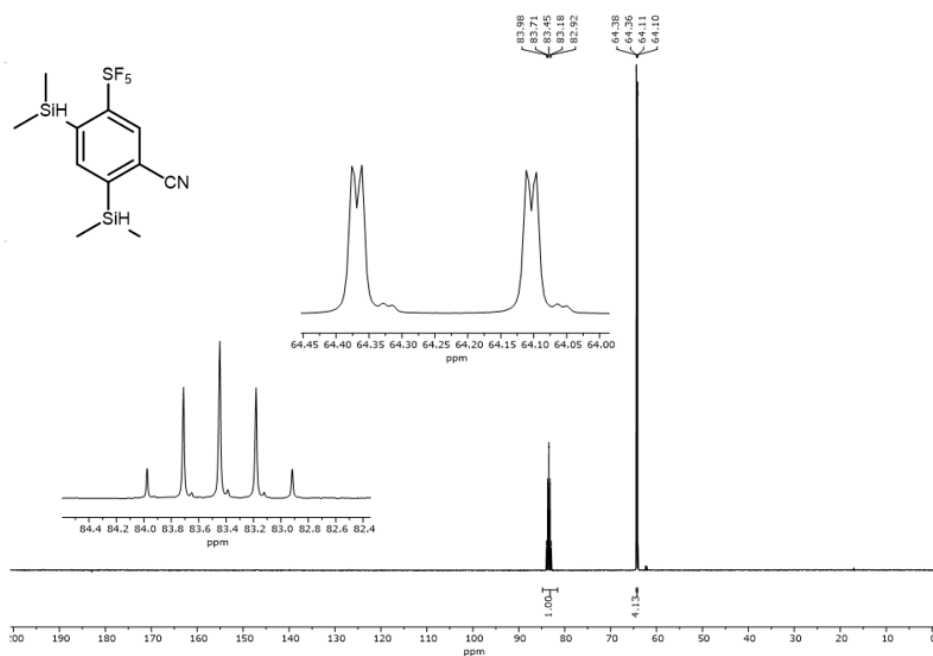


2,4-bis(Dimethylsilyl)-5-cyanopentafluorosulfanyl benzene (Table 2, Entry 8)

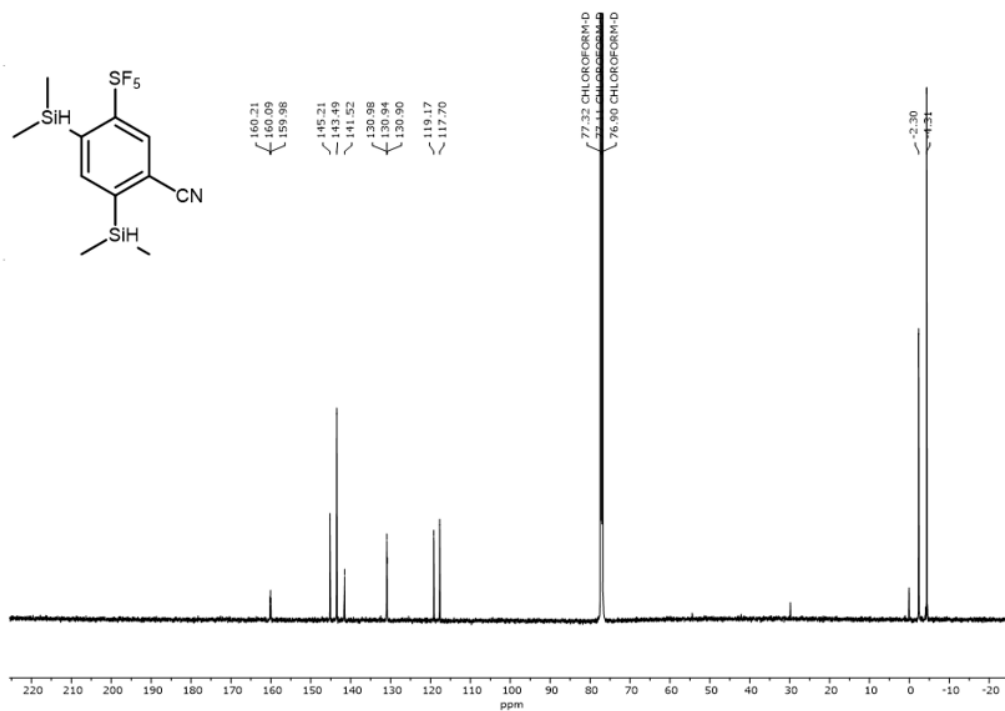
^1H NMR (400 MHz, CDCl_3)



¹⁹F NMR (376 MHz, CDCl₃)

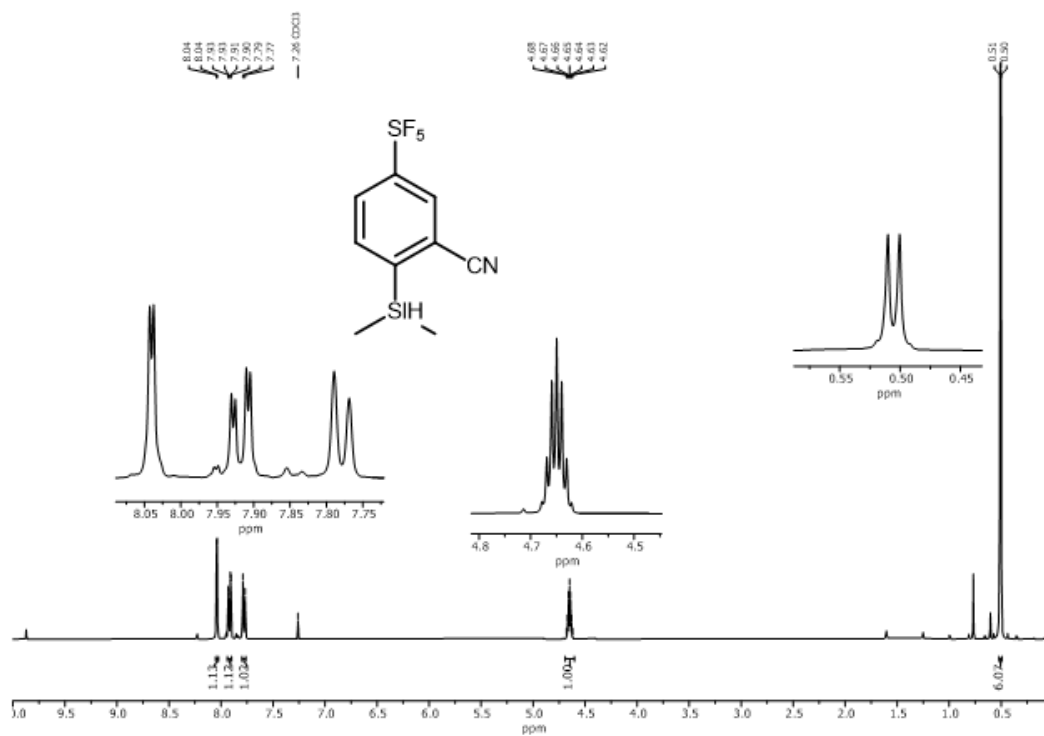


¹³C NMR (101 MHz, CDCl₃)

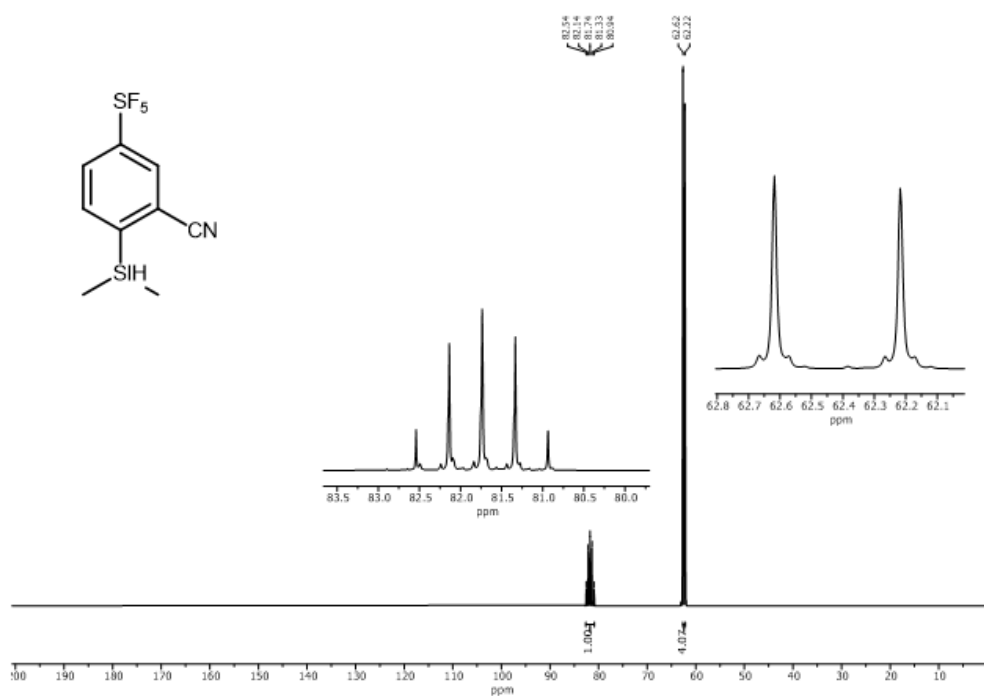


4-Dimethylsilyl-3-cyanopentafluorosulfonyl benzene (Table 2, Entry 9)

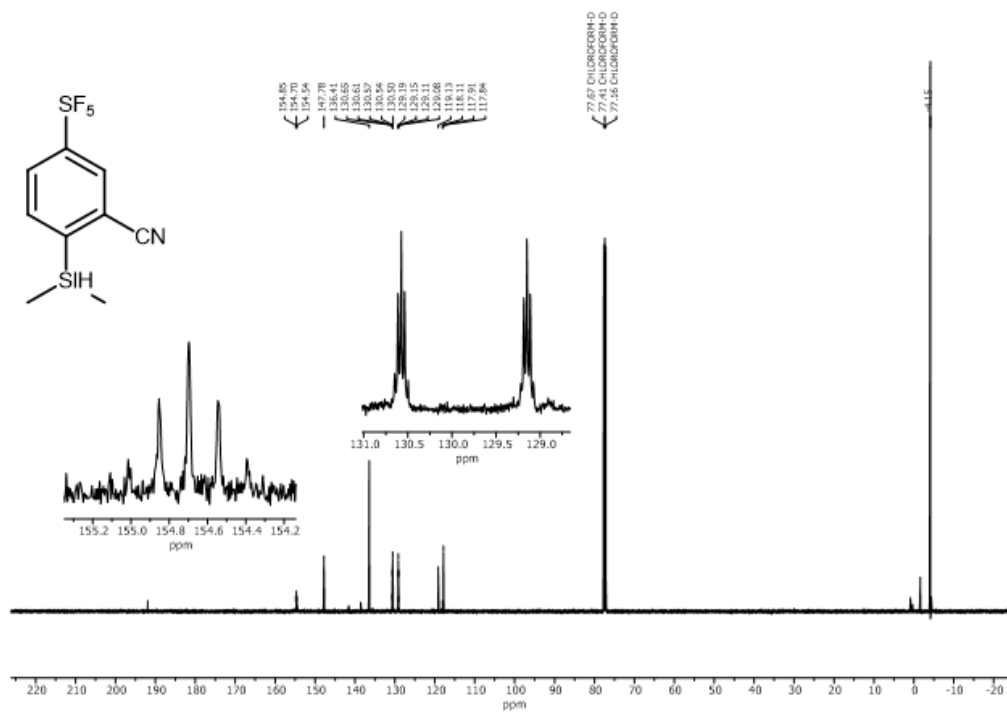
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

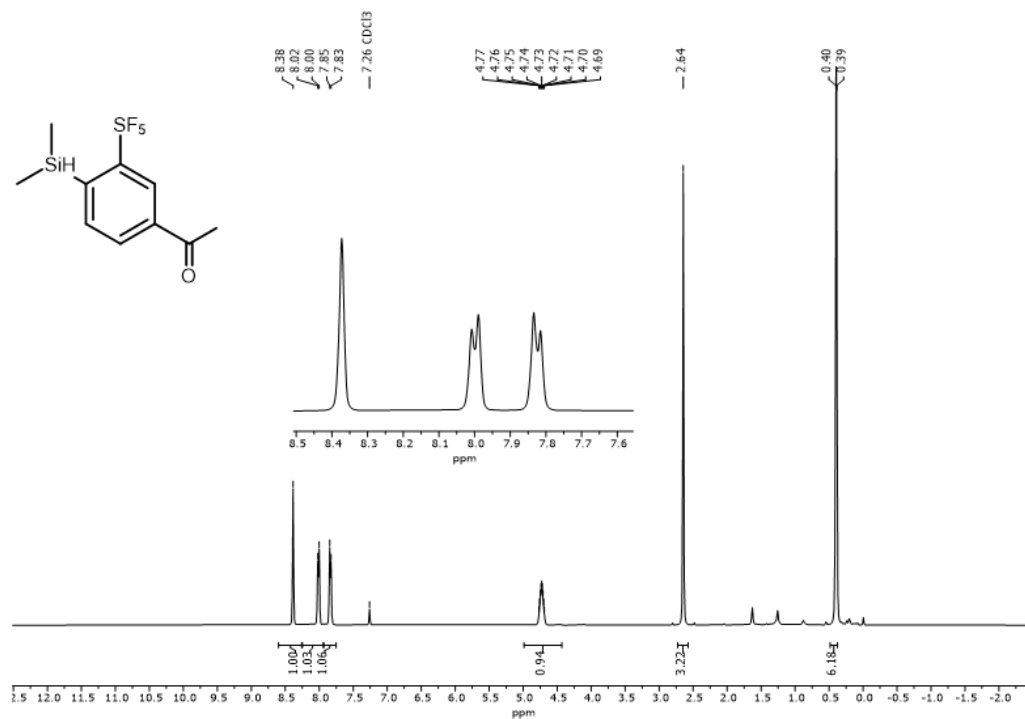


^{13}C NMR (101 MHz, CDCl_3)

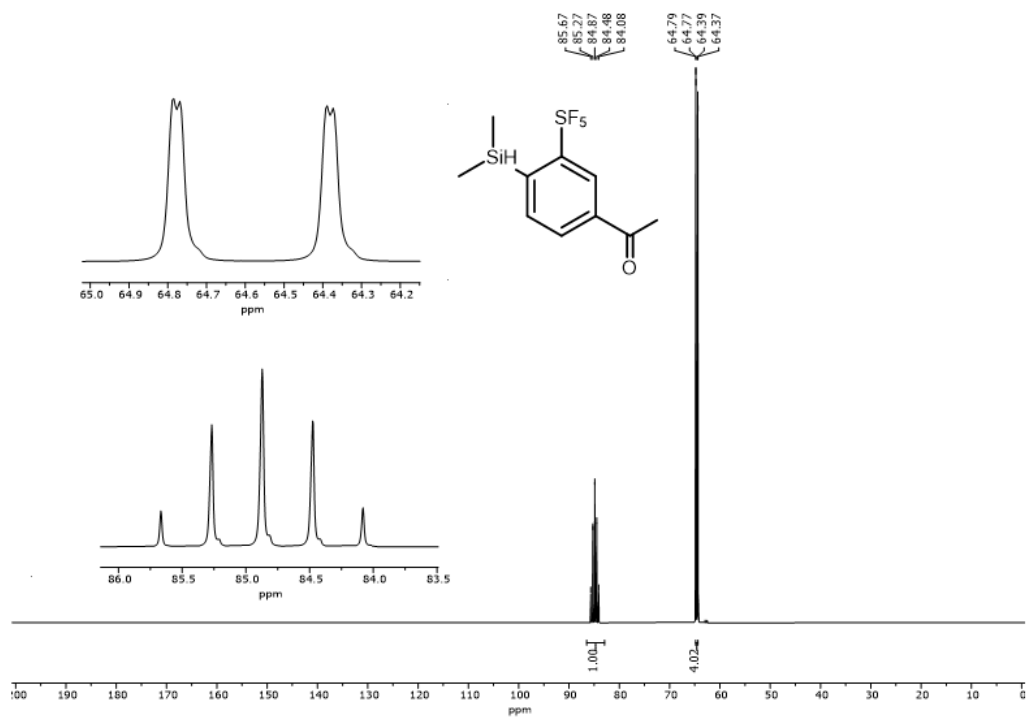


2-Dimethylsilyl-5-acetylpentafluorosulfonyl benzene (Table 2, Entry 10)

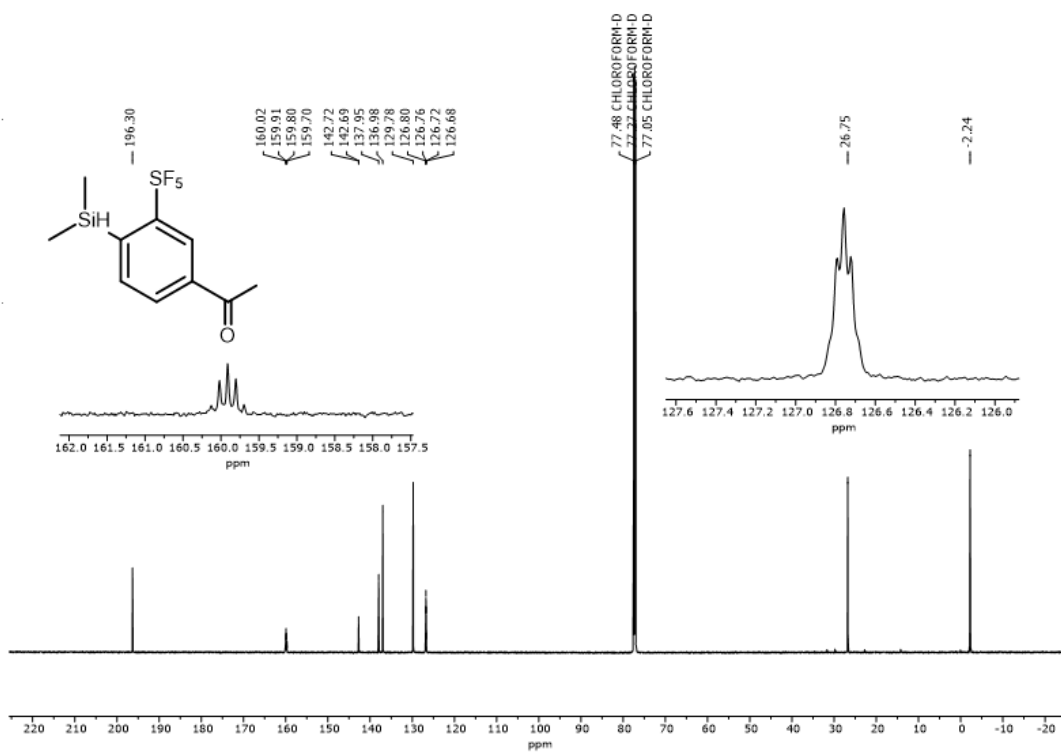
^1H NMR (400 MHz, CDCl_3)



¹⁹F NMR (376 MHz, CDCl₃)

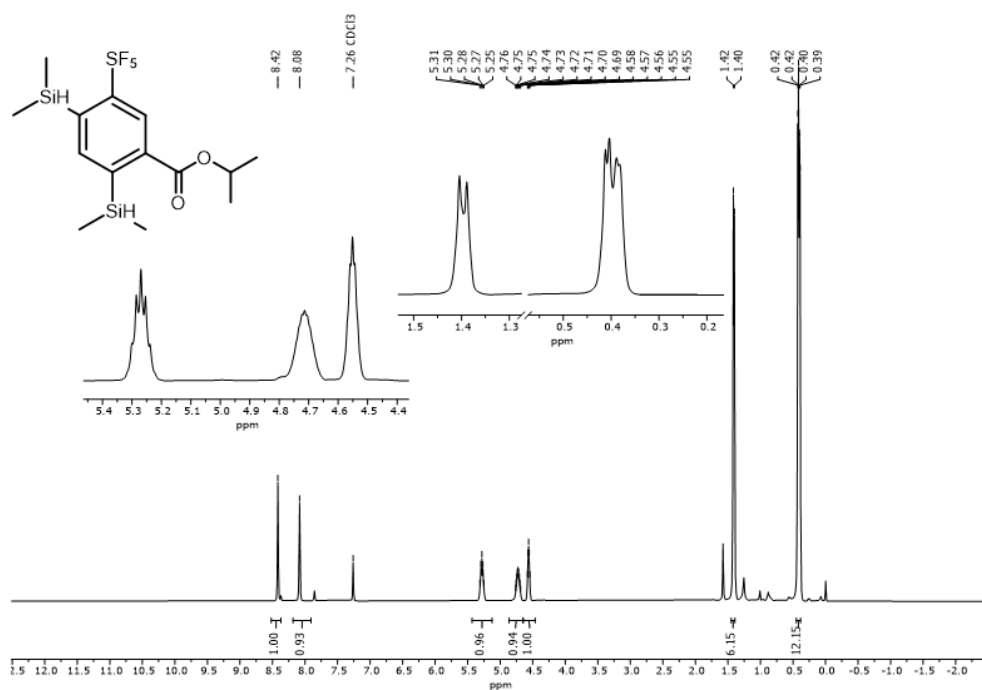


¹³C NMR (101 MHz, CDCl₃)

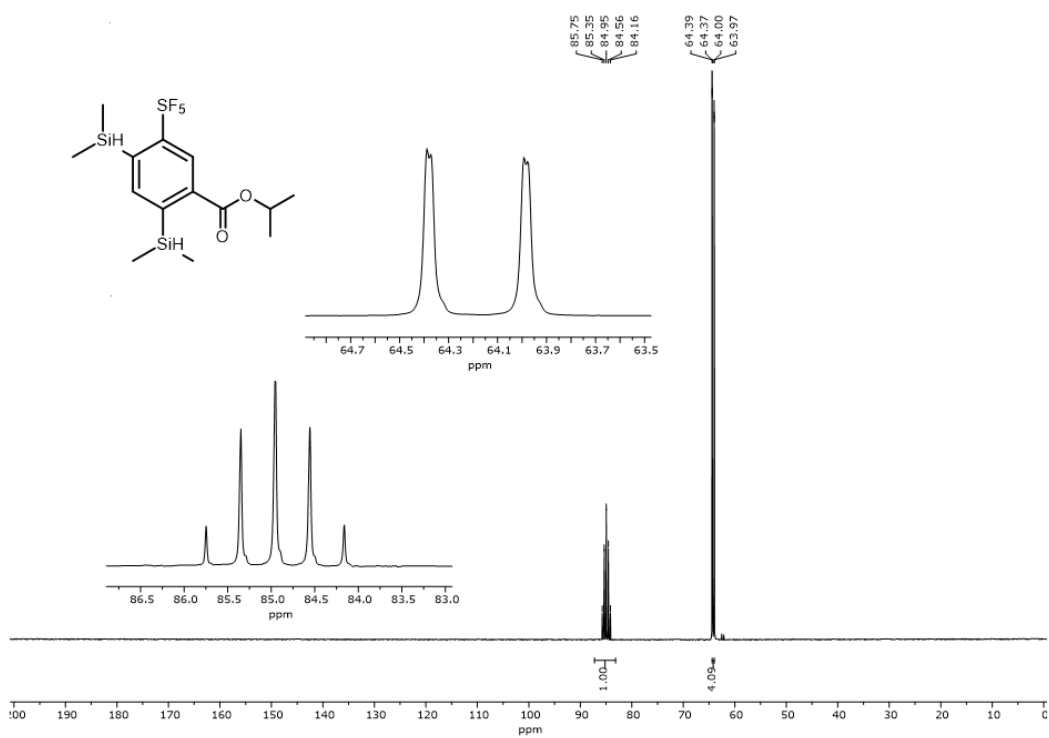


Isopropyl 2,4-bis(dimethylsilyl)-5-(pentafluorosulfanyl) benzoate (Table 2, Entry 11)

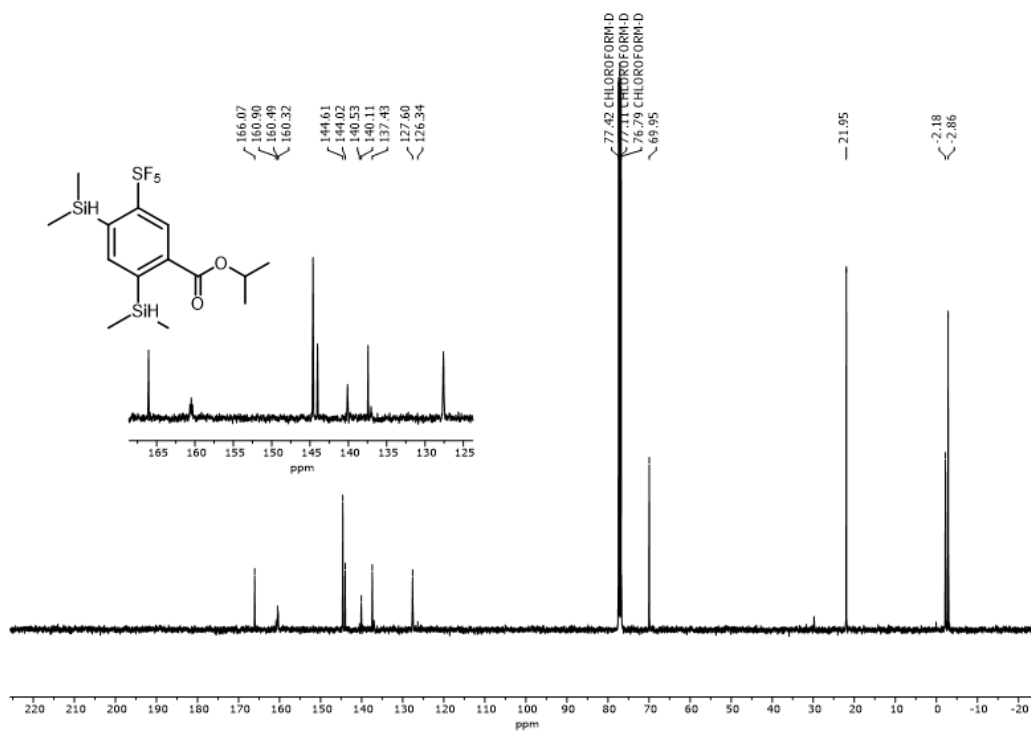
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

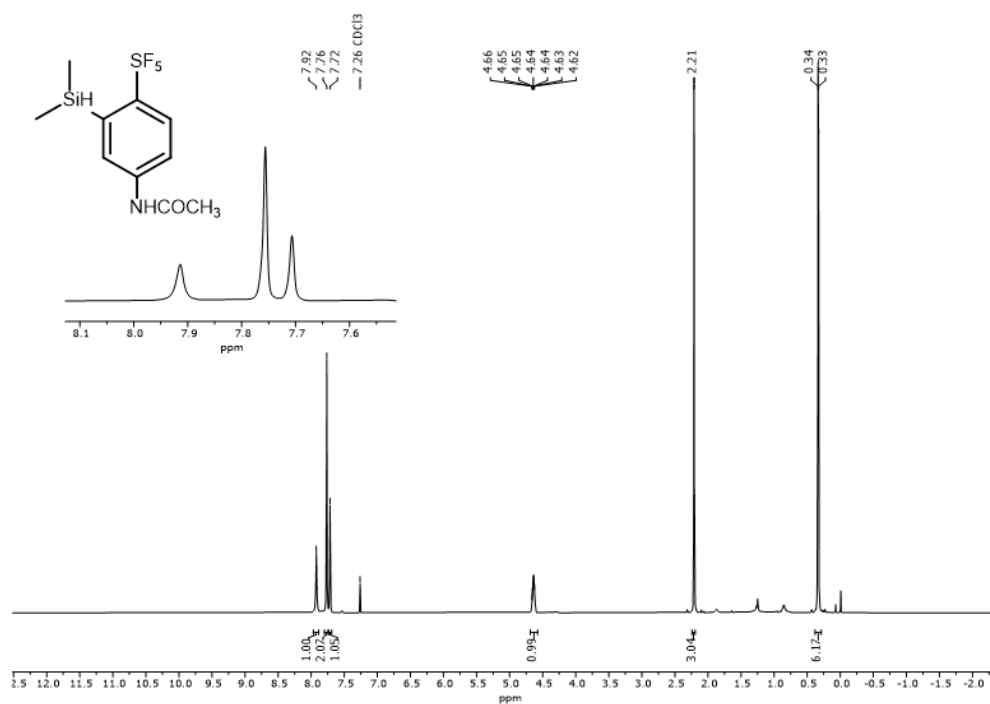


^{13}C NMR (101 MHz, CDCl_3)

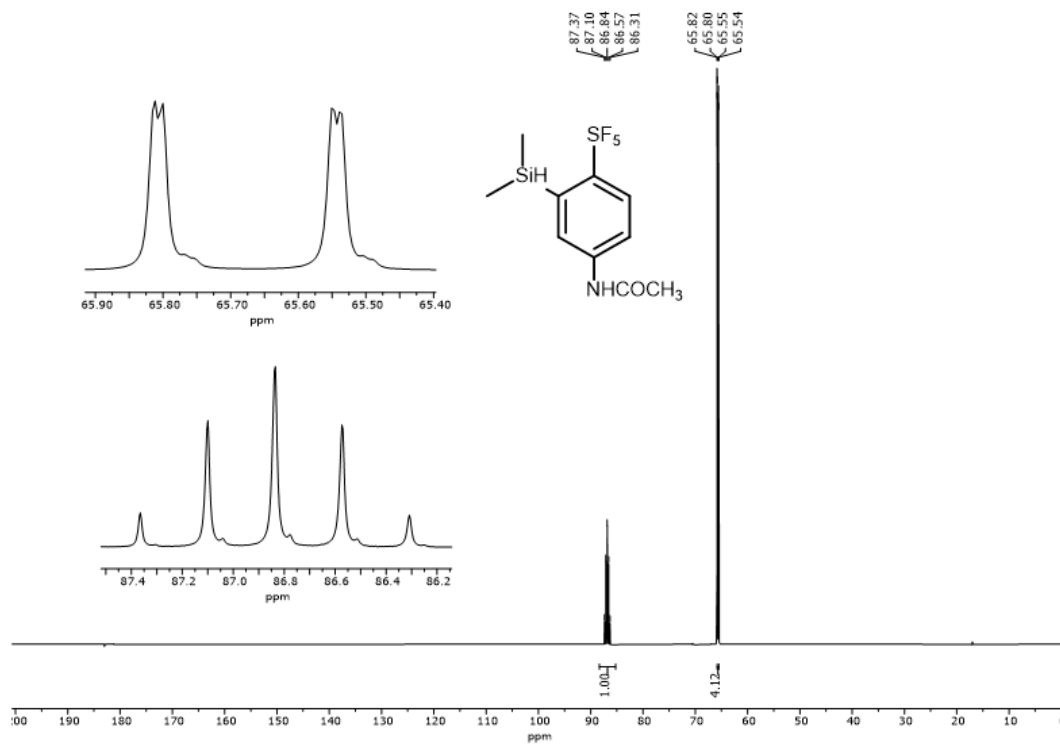


2-Dimethylsilyl-4-acetamidopentafluorosulfanyl benzene (Table 2, Entry 12)

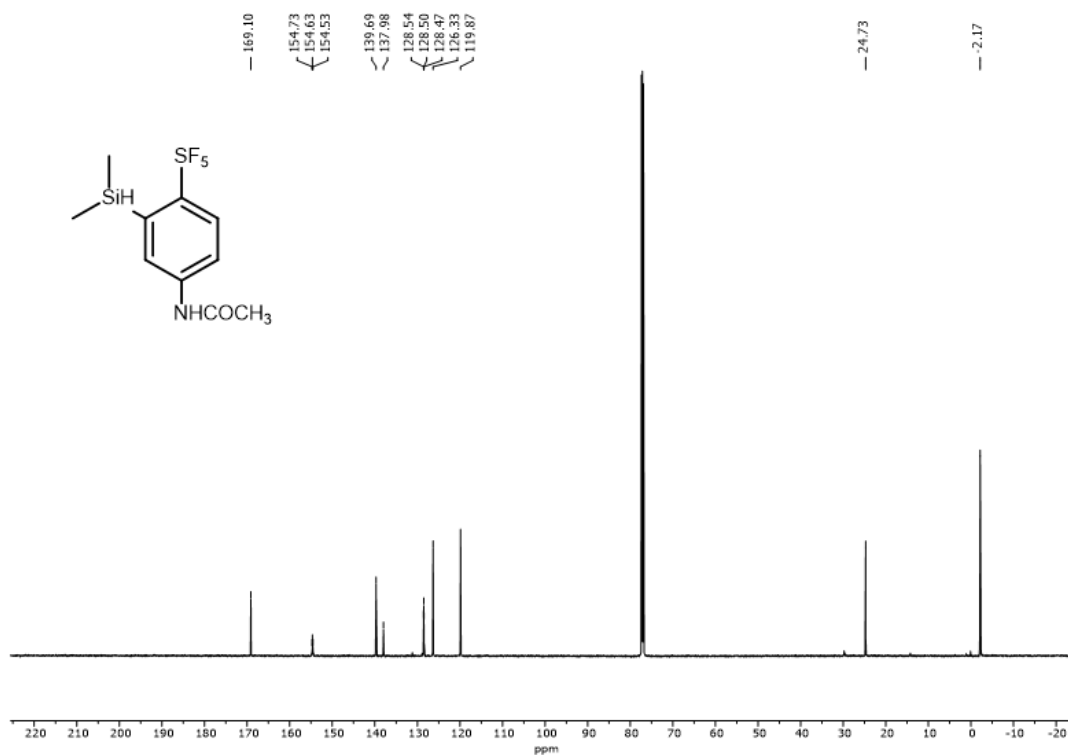
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

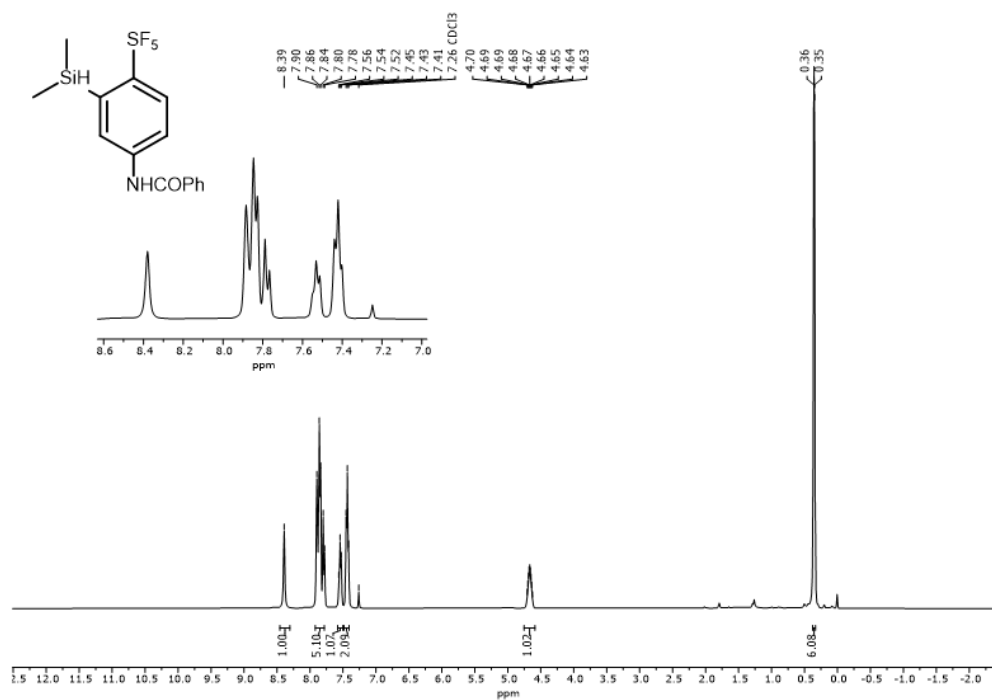


^{13}C NMR (101 MHz, CDCl_3)

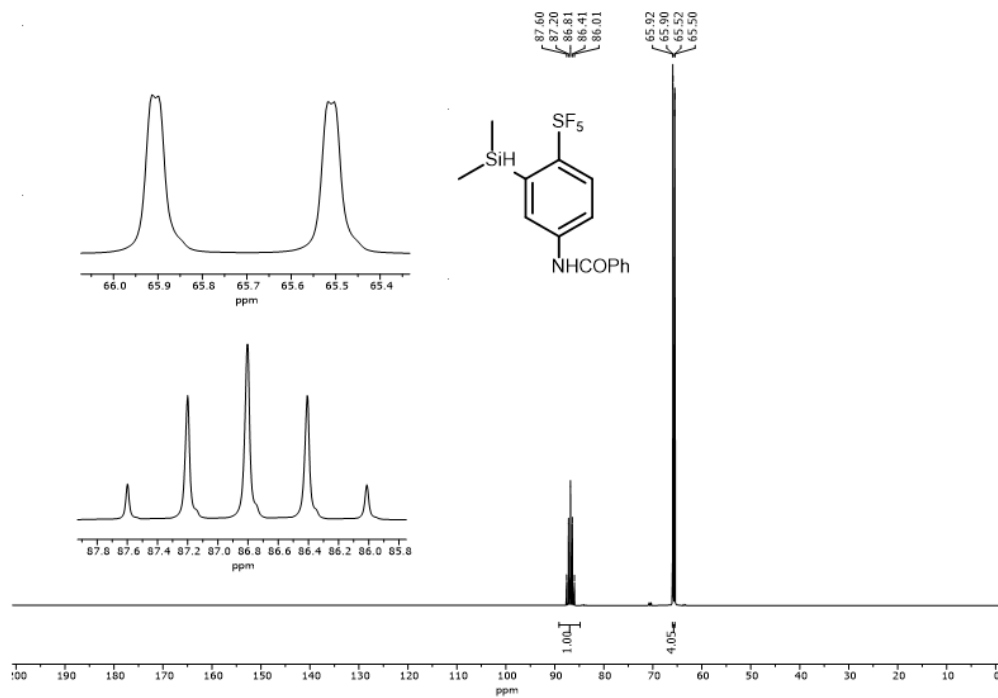


***N*-(3-dimethylsilyl-4-(pentafluorosulfanyl)phenyl)benzamide (Table 2, Entry 13)**

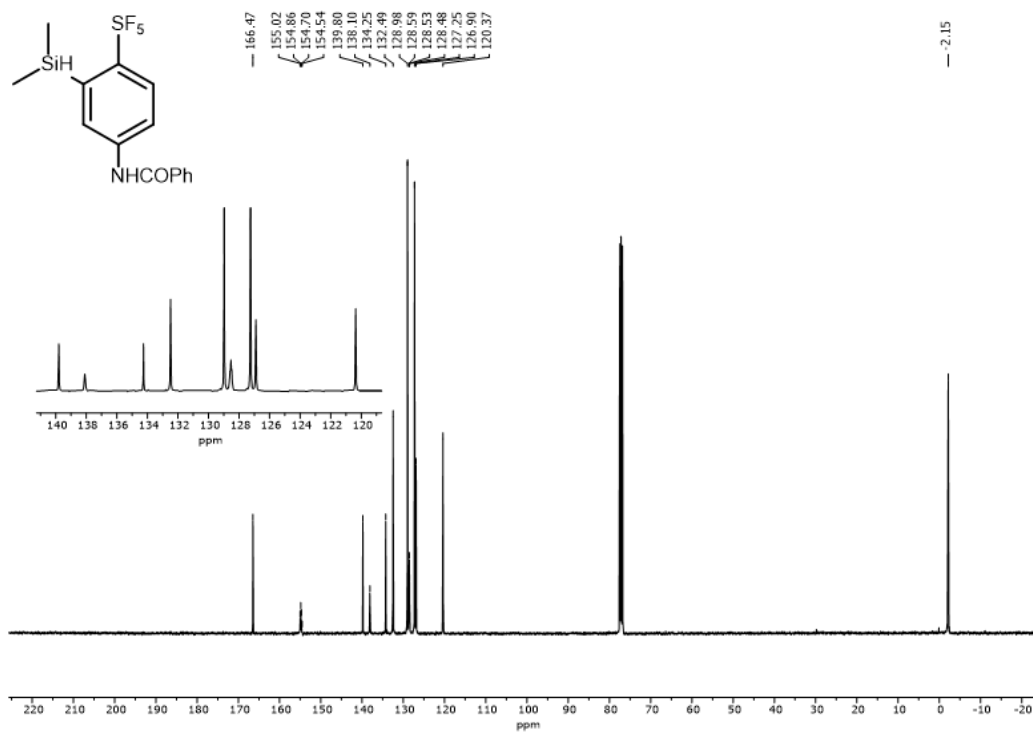
¹H NMR (400 MHz, CDCl₃)



¹⁹F NMR (376 MHz, CDCl₃)

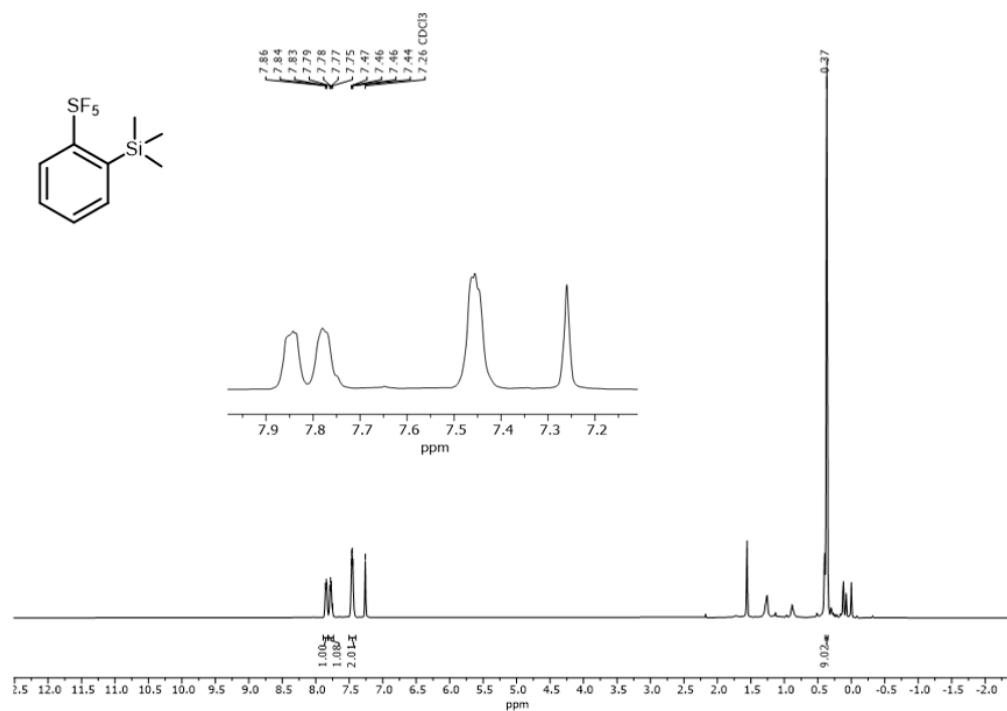


^{13}C NMR (101 MHz, CDCl_3)

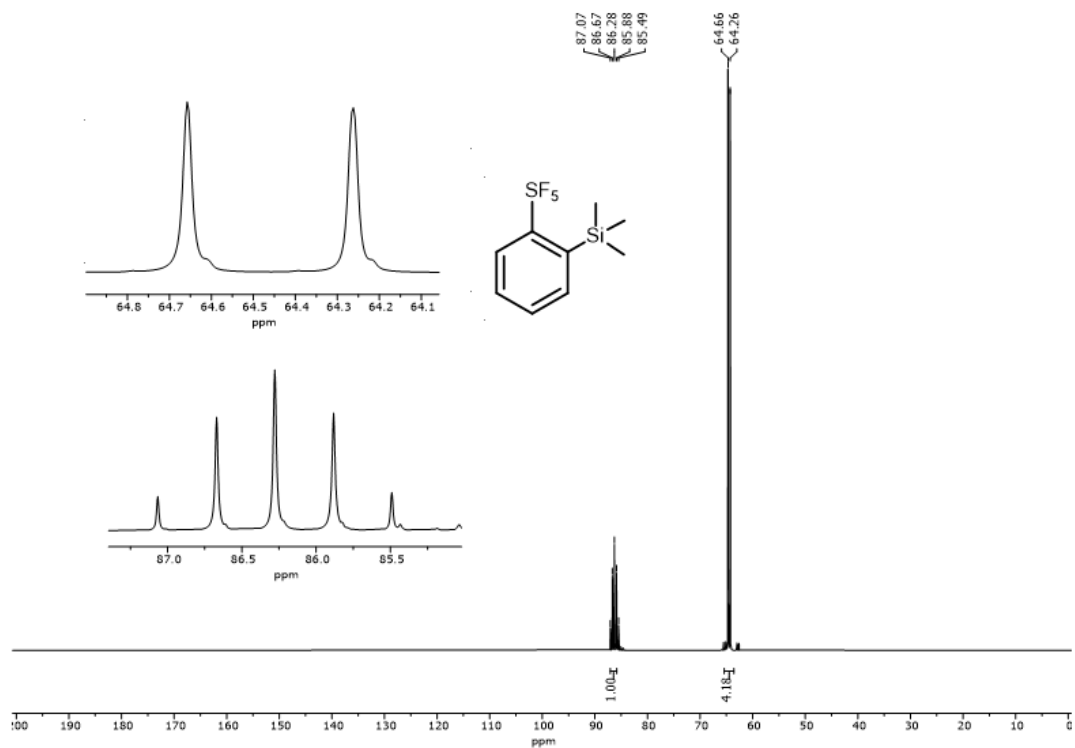


2-Trimethylsilylpentafluorosulfanyl benzene (Scheme 3, Compound 7)

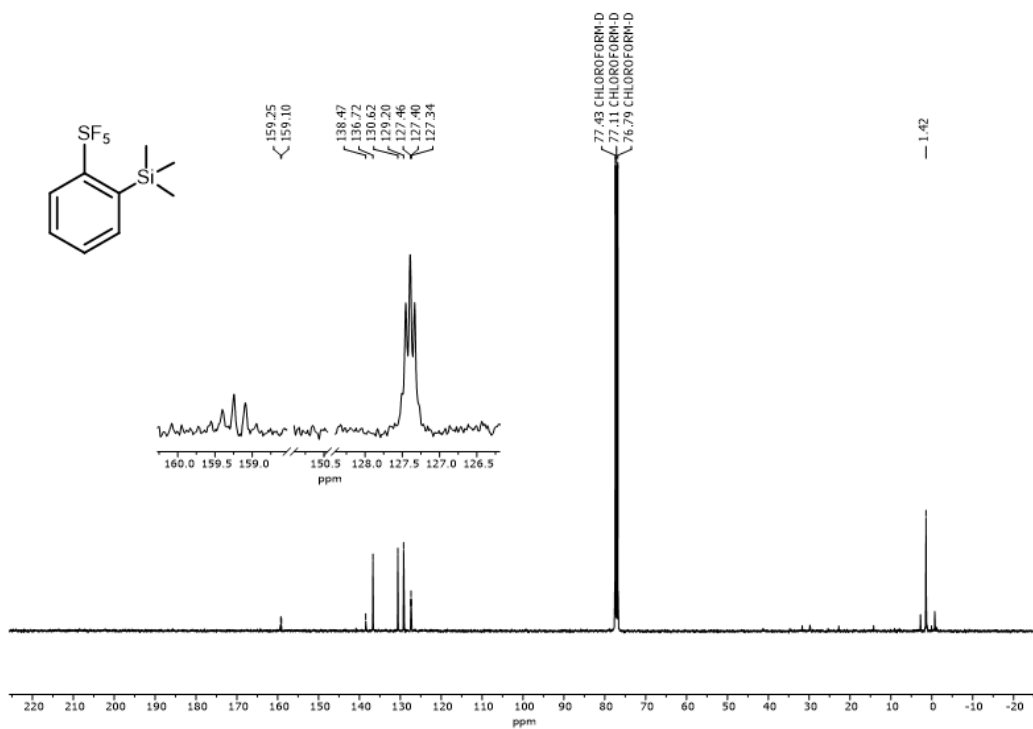
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

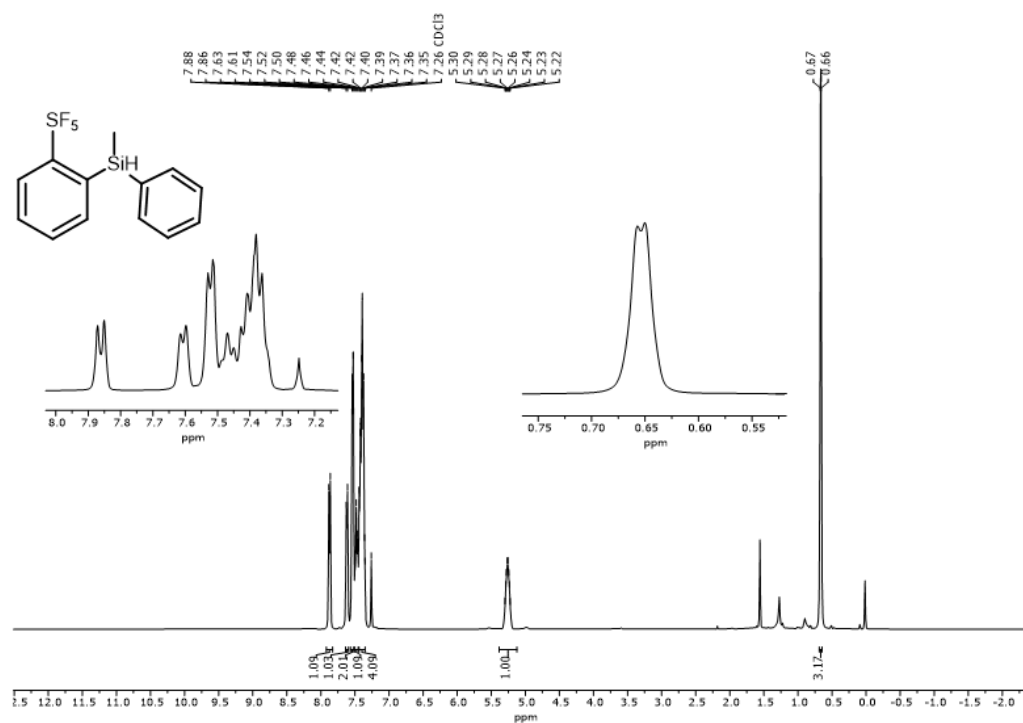


^{13}C NMR (101 MHz, CDCl_3)

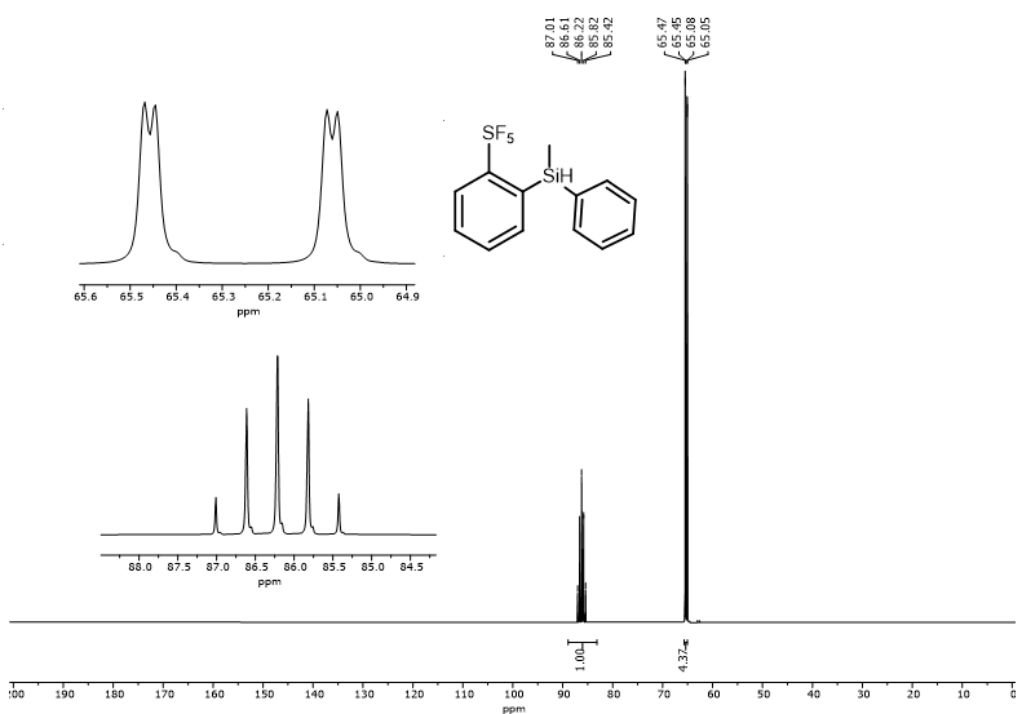


2-(Methylphenylsilyl)pentafluorosulfonyl benzene (Scheme 3, Compound 8)

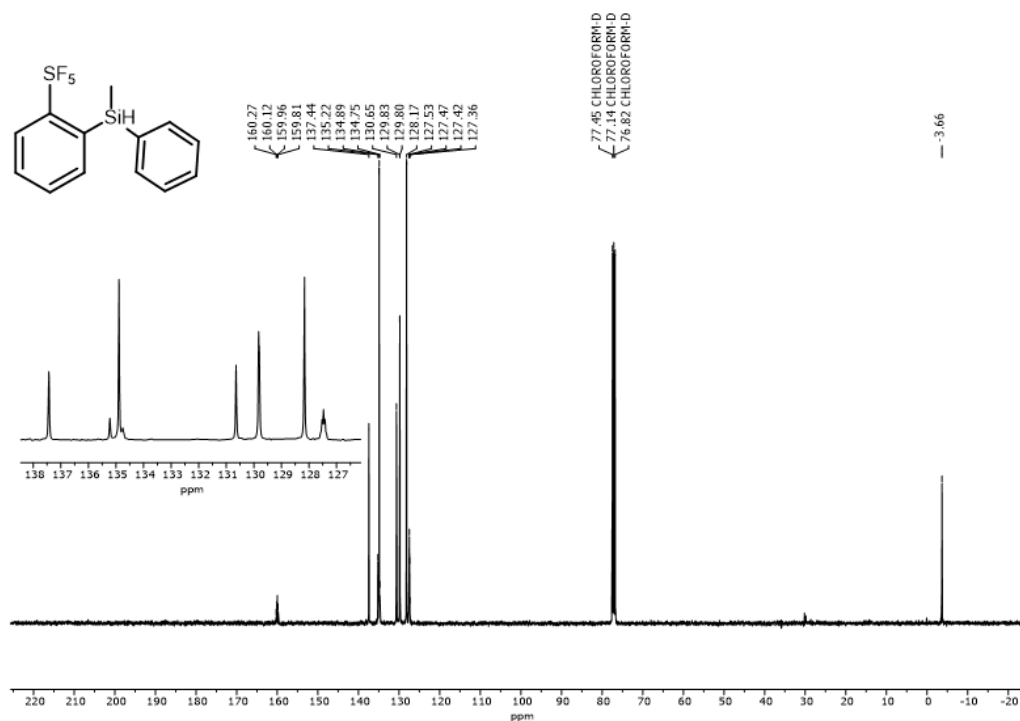
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

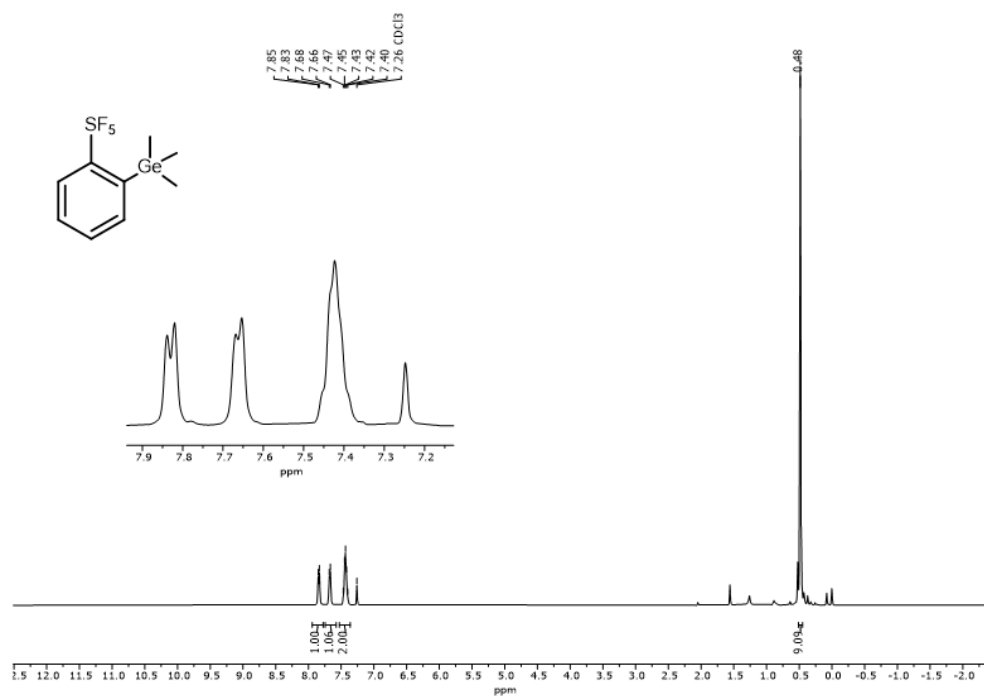


^{13}C NMR (101 MHz, CDCl_3)

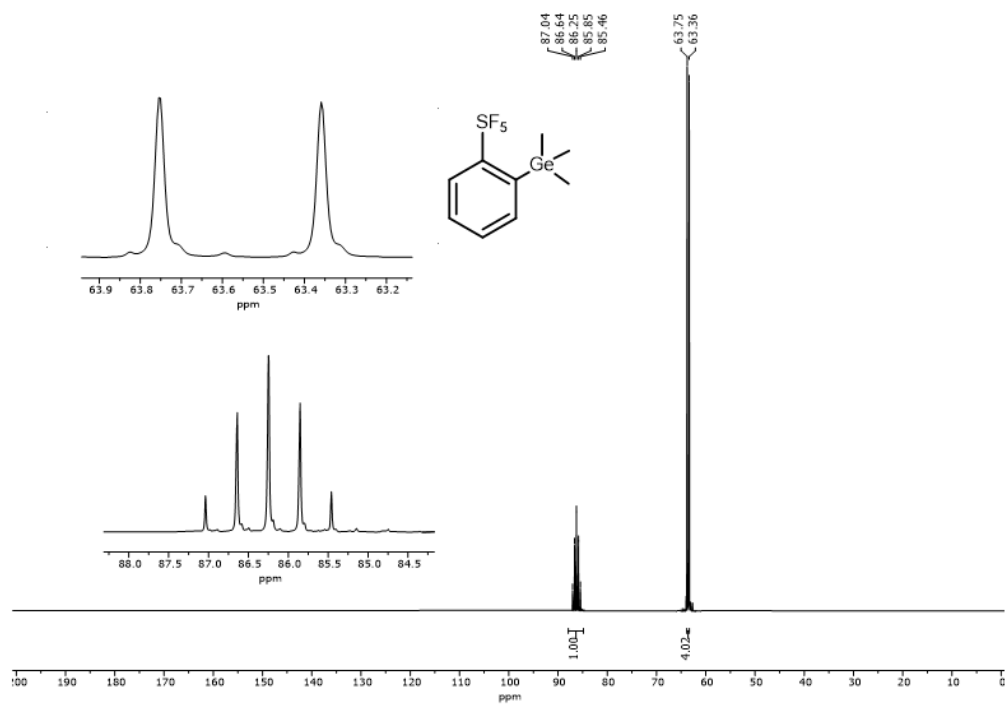


2-Trimethylgermylpentafluorobenzene (Scheme 3, Compound 9)

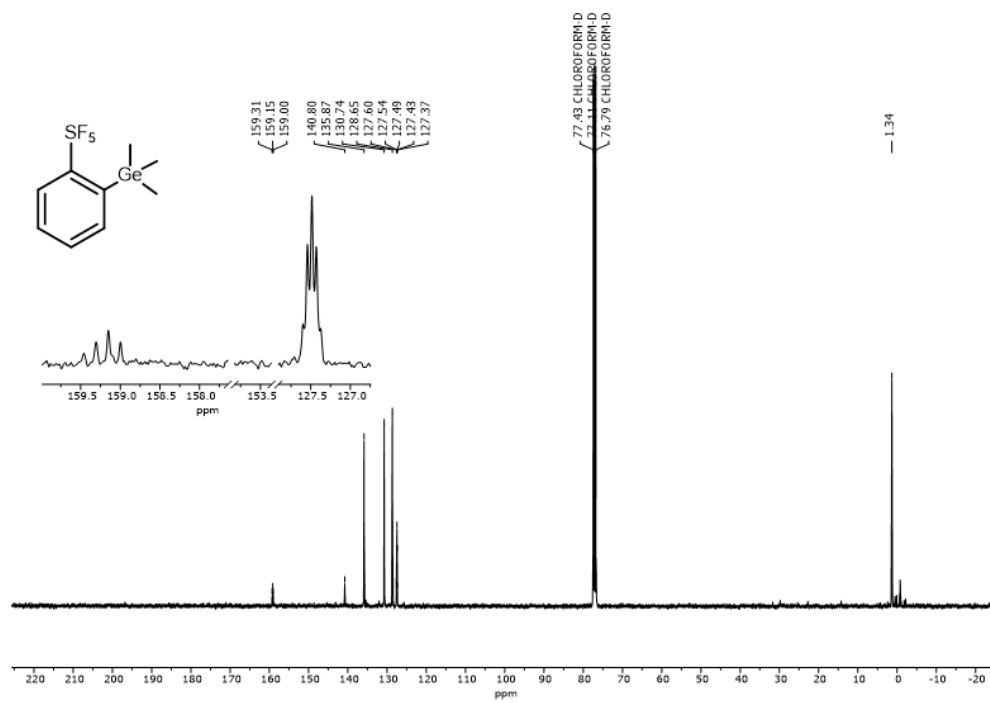
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

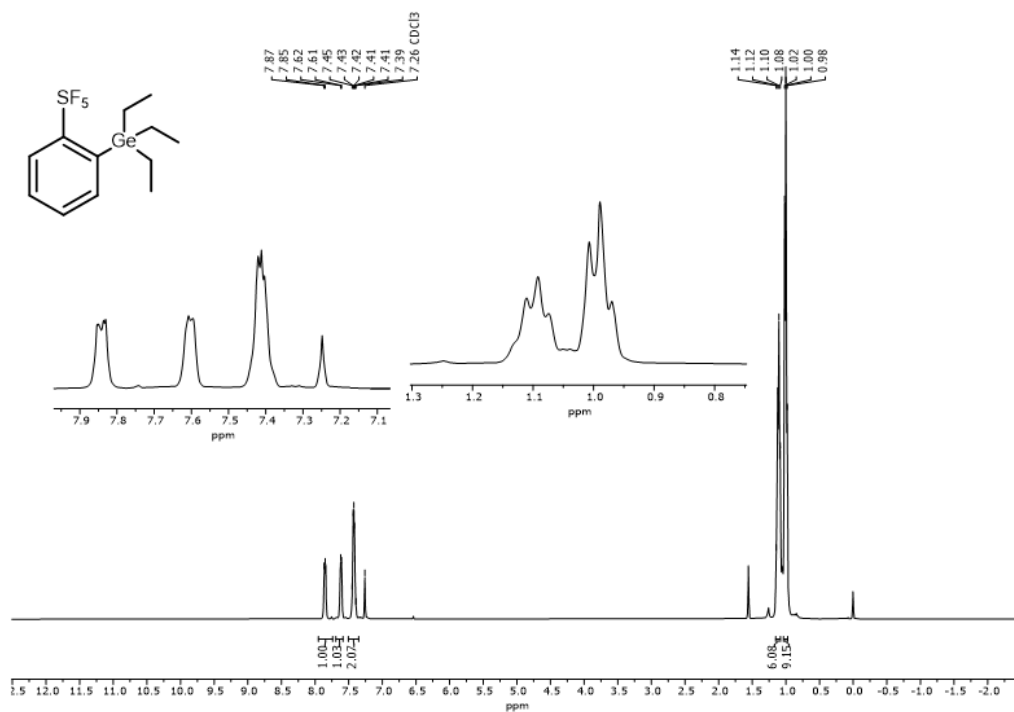


^{13}C NMR (101 MHz, CDCl_3)

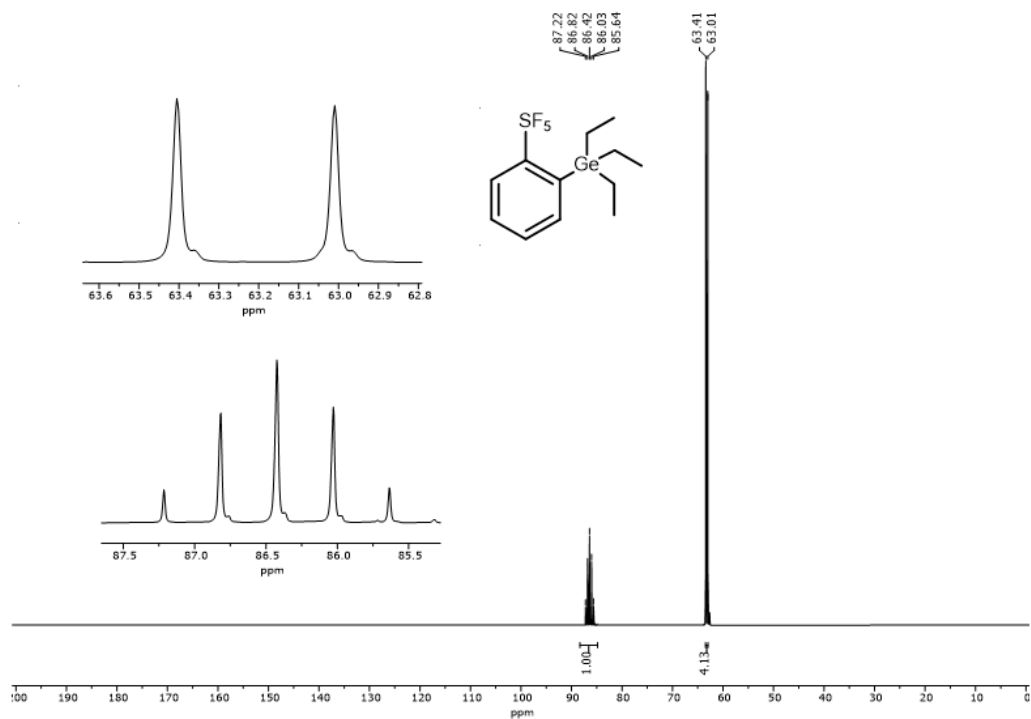


2-Triethylgermylpentafluorosulfanyl benzene (Scheme 3, Compound 10)

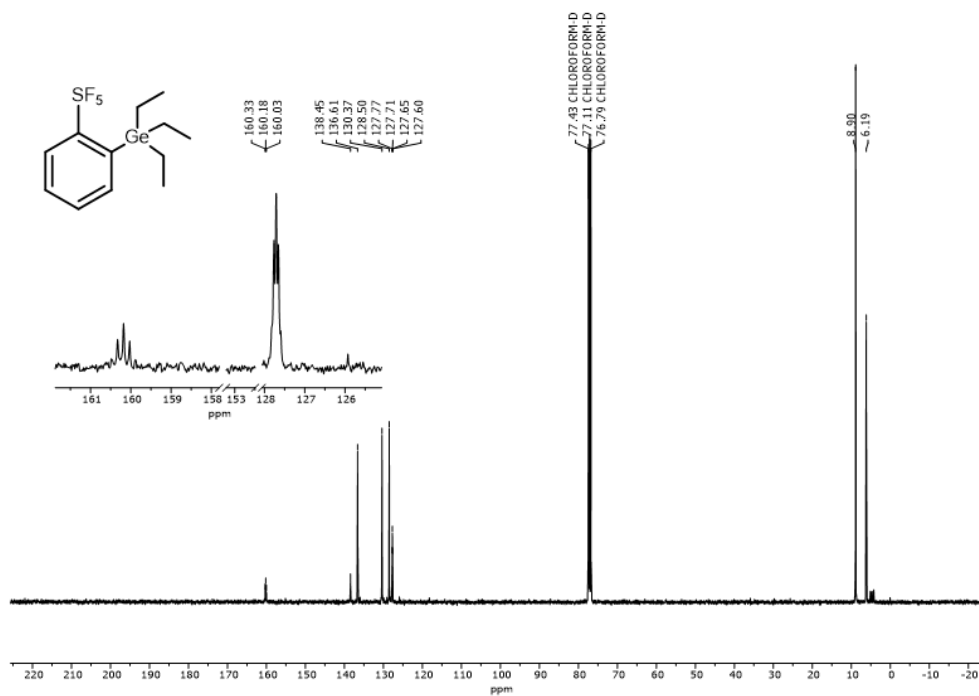
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

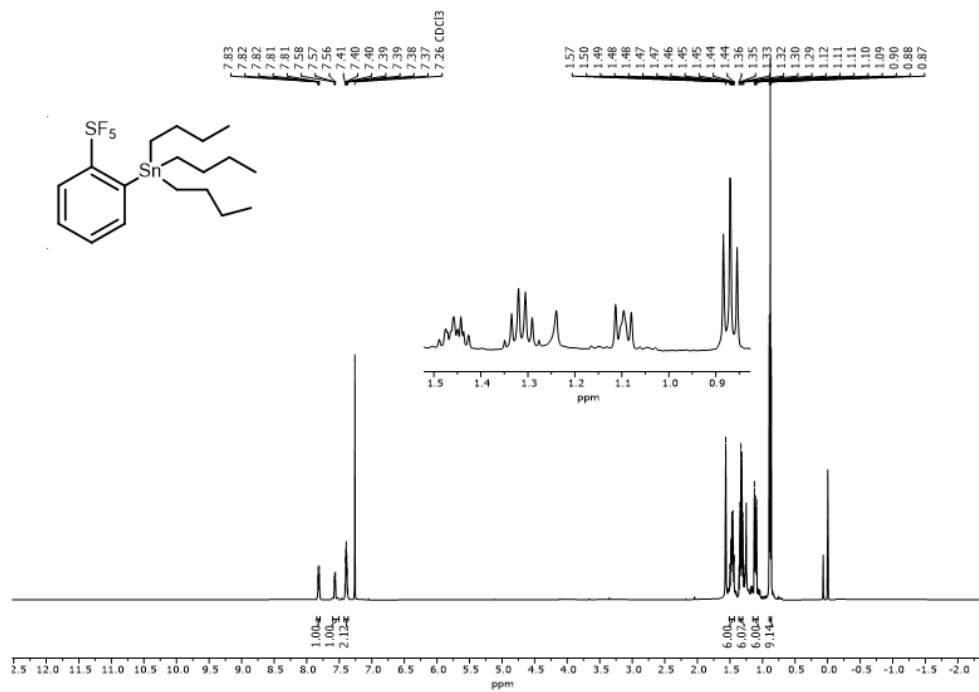


^{13}C NMR (101 MHz, CDCl_3)

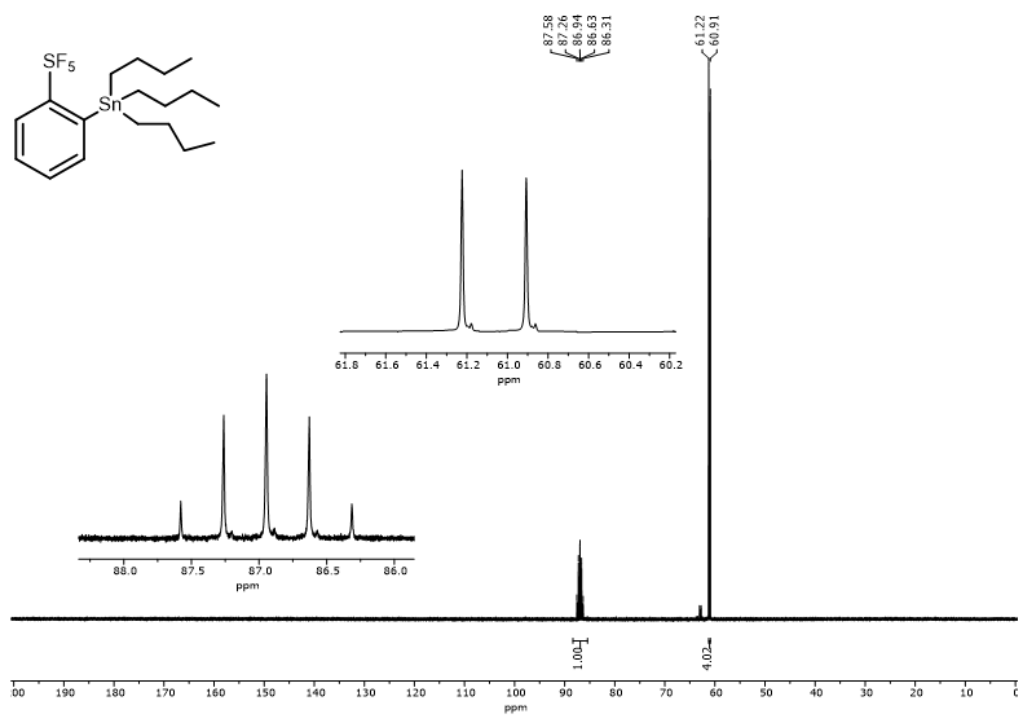


2-Tributylstannylpentafluorosulfanyl benzene (Scheme 3, Compound 11)

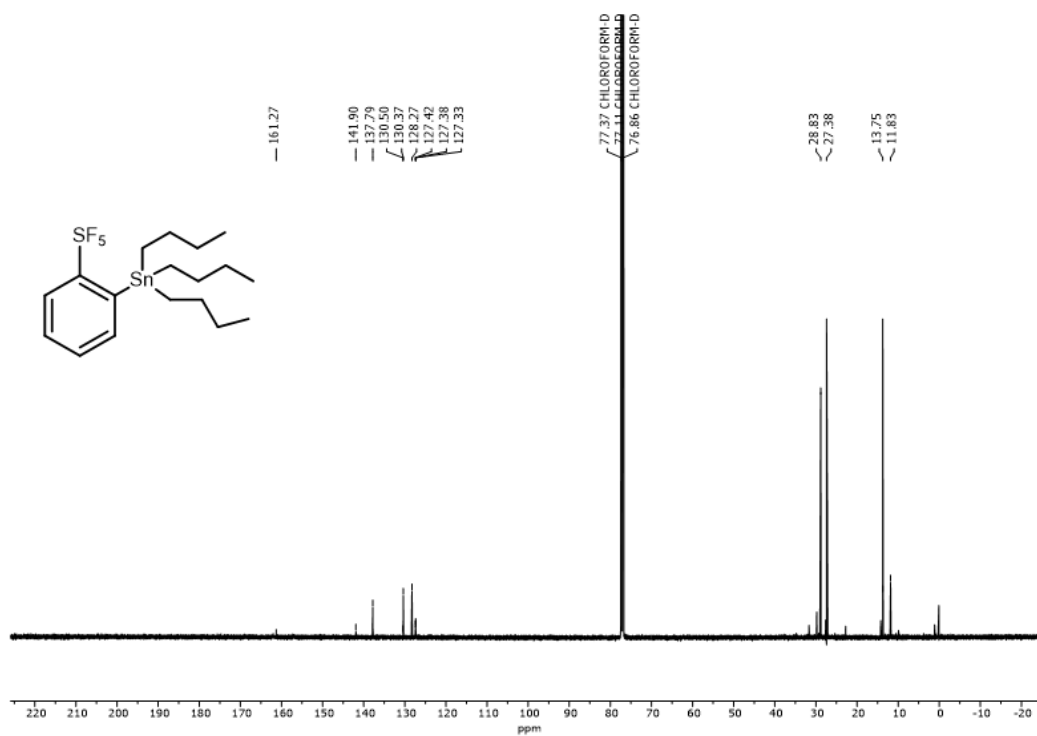
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

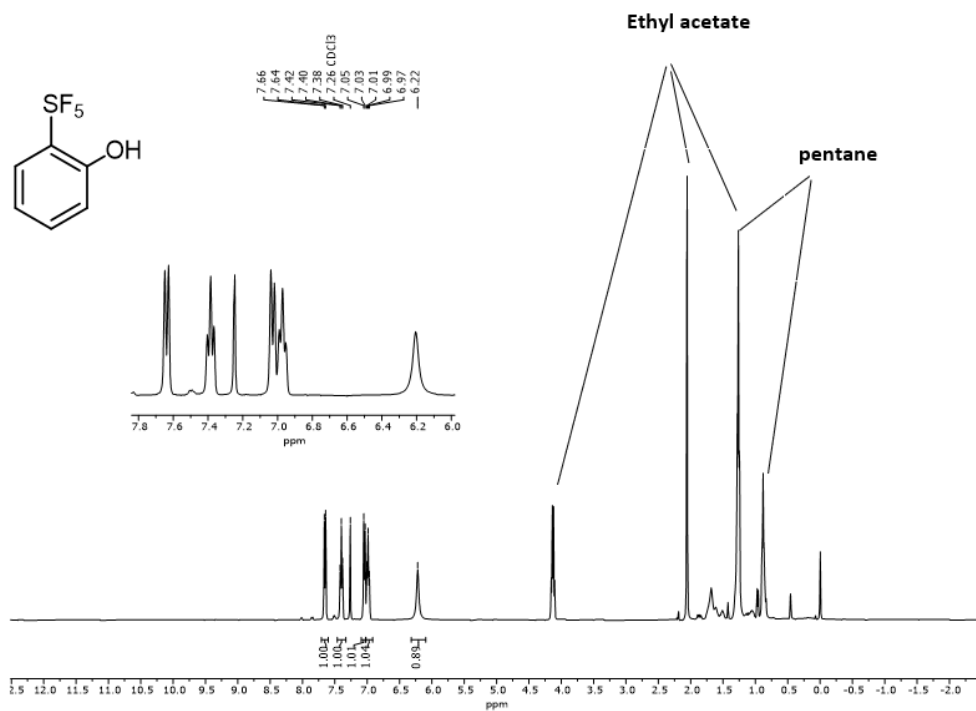


^{13}C NMR (101 MHz, CDCl_3)

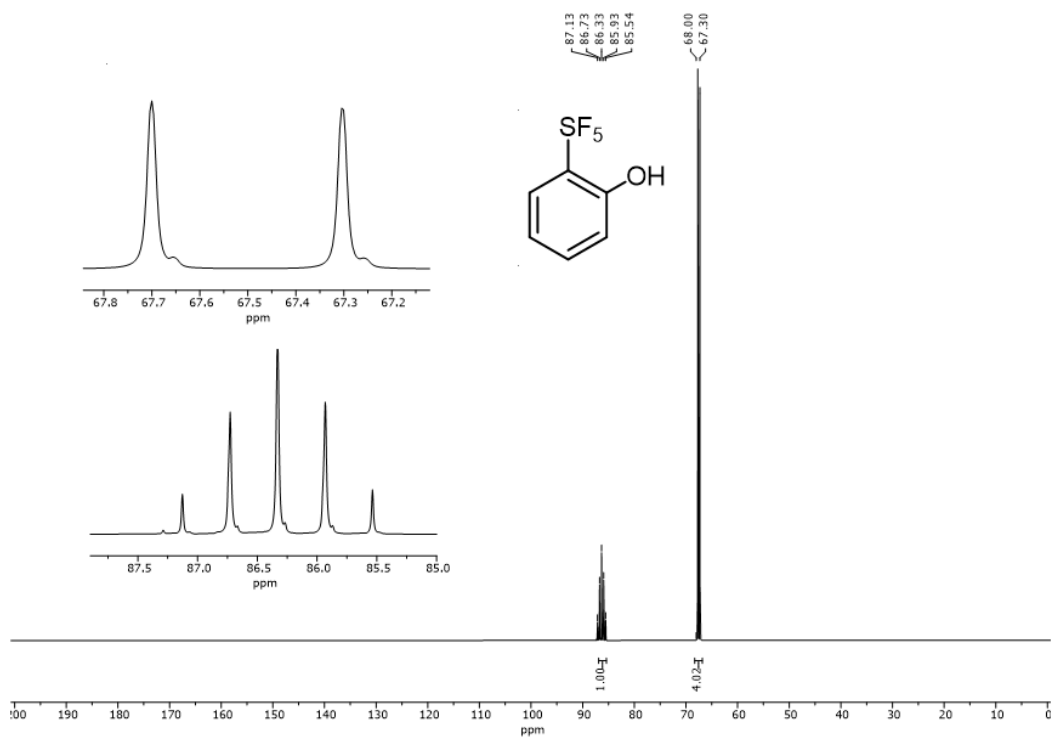


2-Hydroxypentafluorosulfanyl benzene

^1H NMR (400 MHz, CDCl_3)

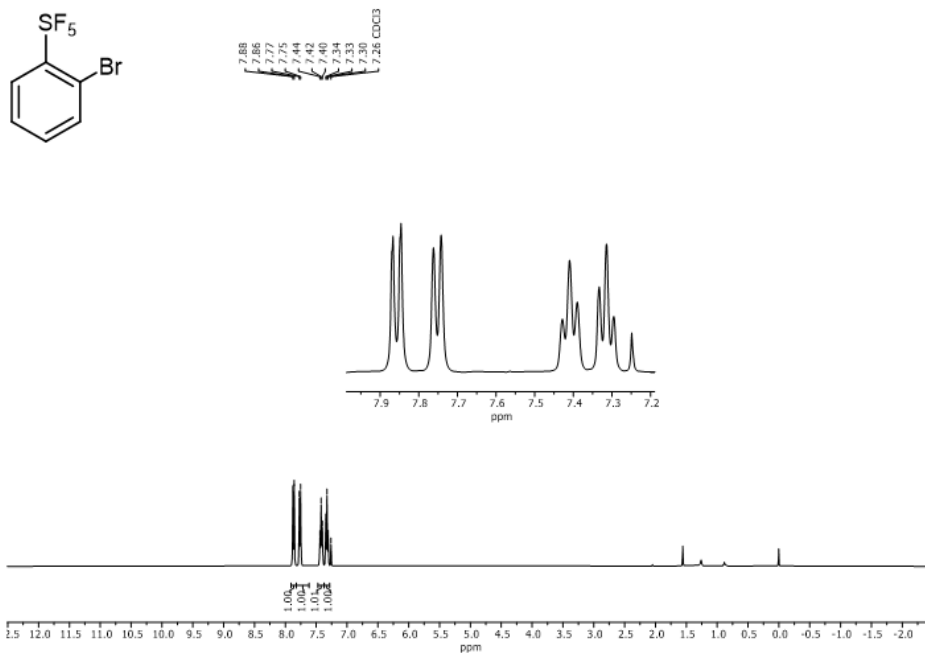


^{19}F NMR (376 MHz, CDCl_3)

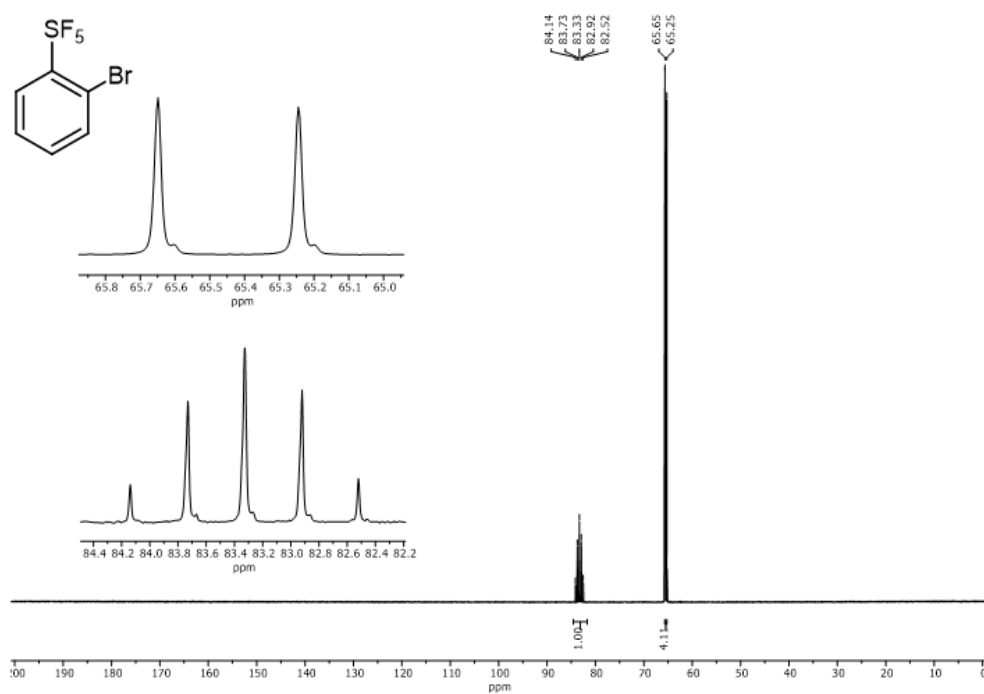


2-Bromopentafluorosulfanyl benzene

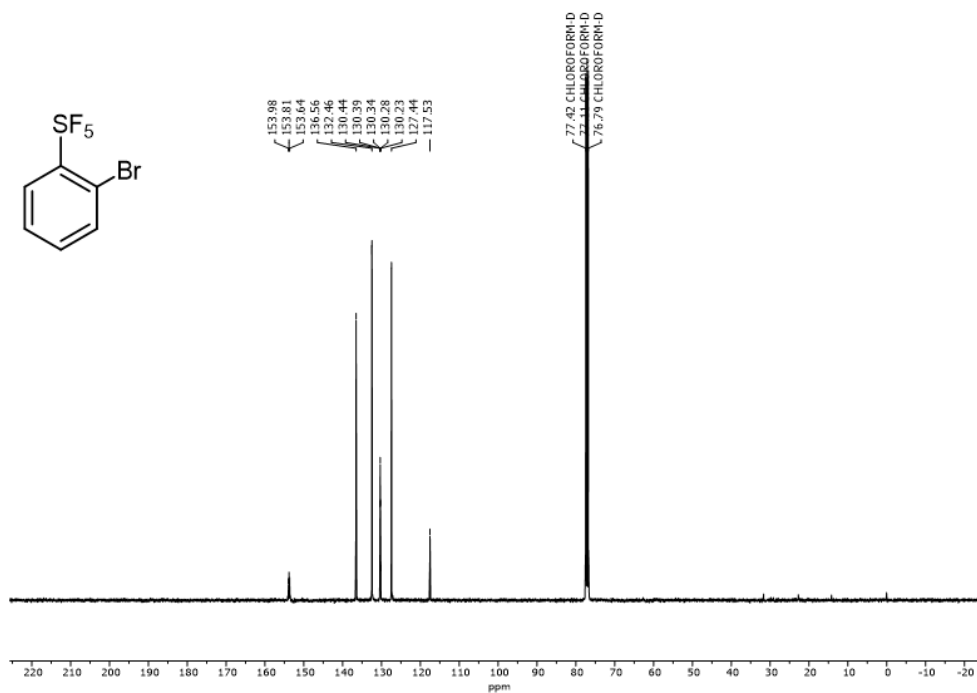
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

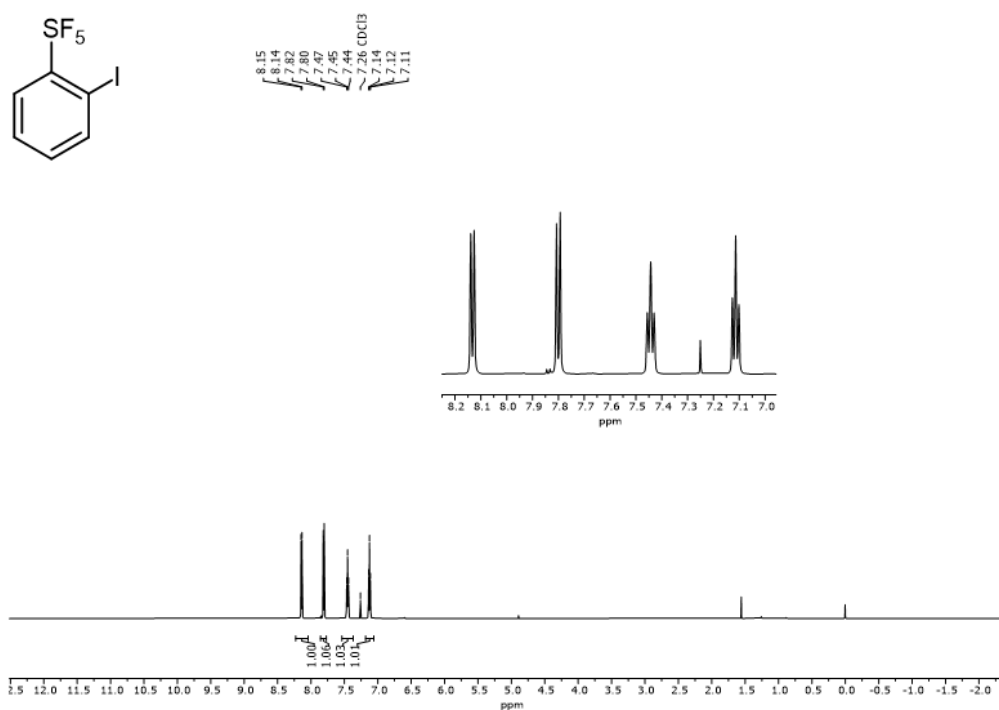


^{13}C NMR (101 MHz, CDCl_3)

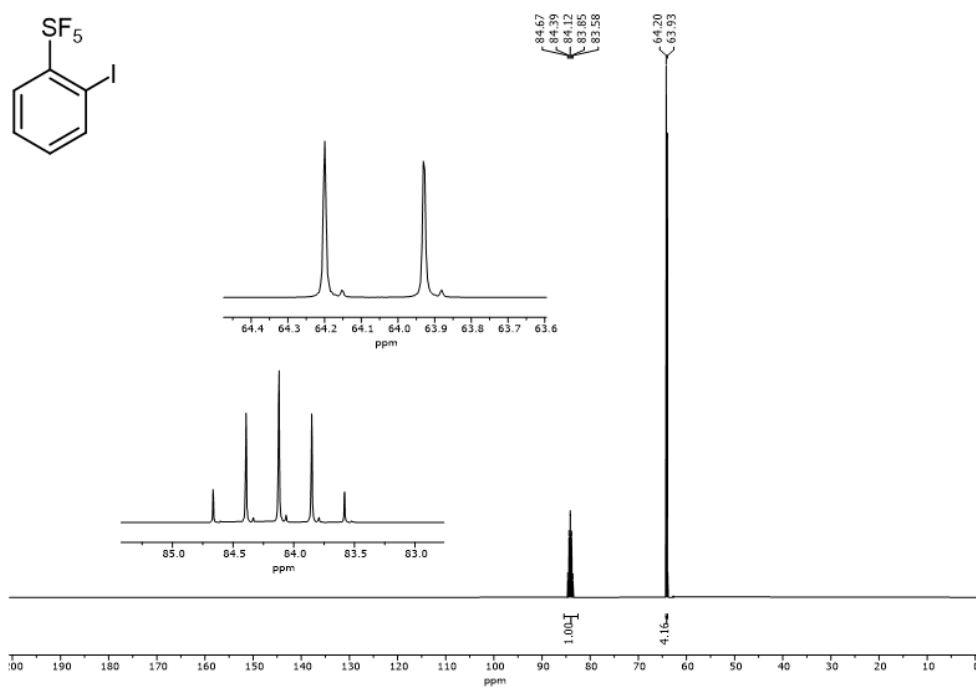


2-Iodopentafluorosulfonyl benzene

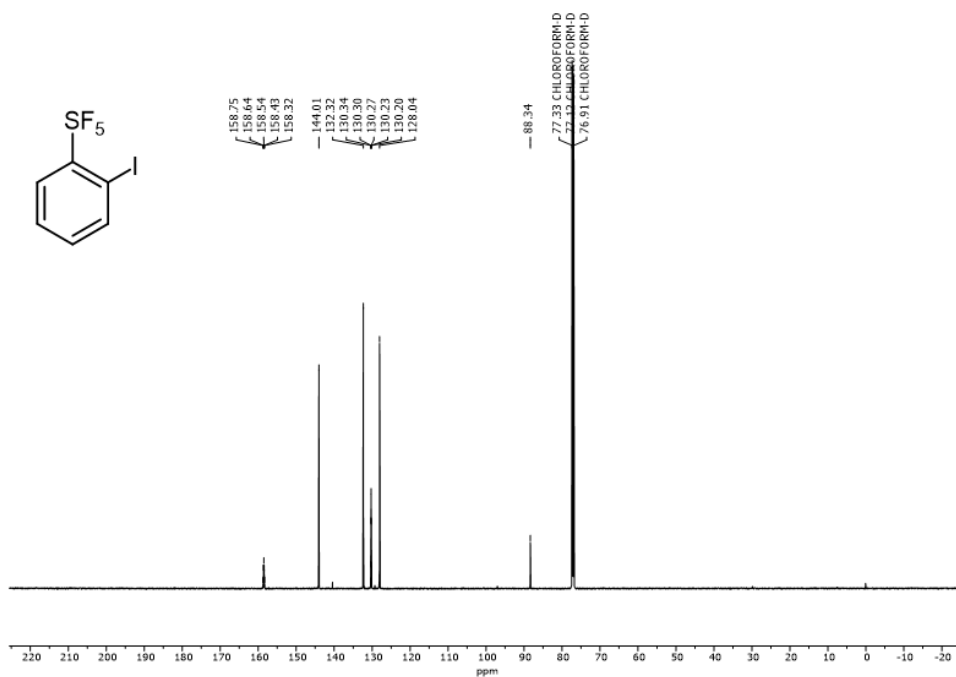
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

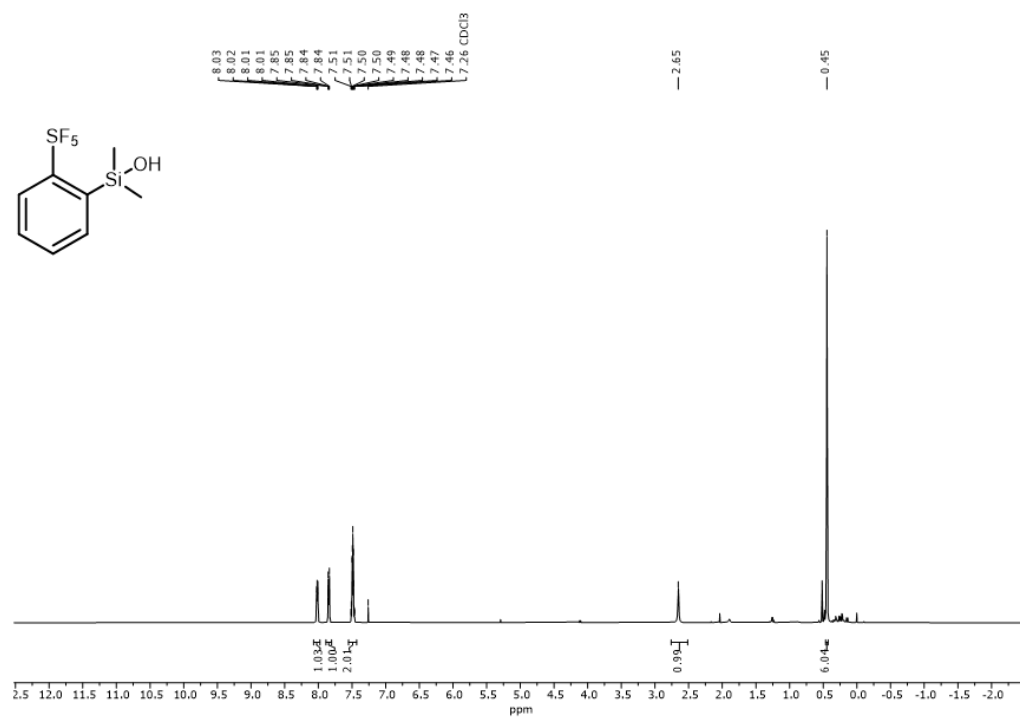


^{13}C NMR (101 MHz, CDCl_3)

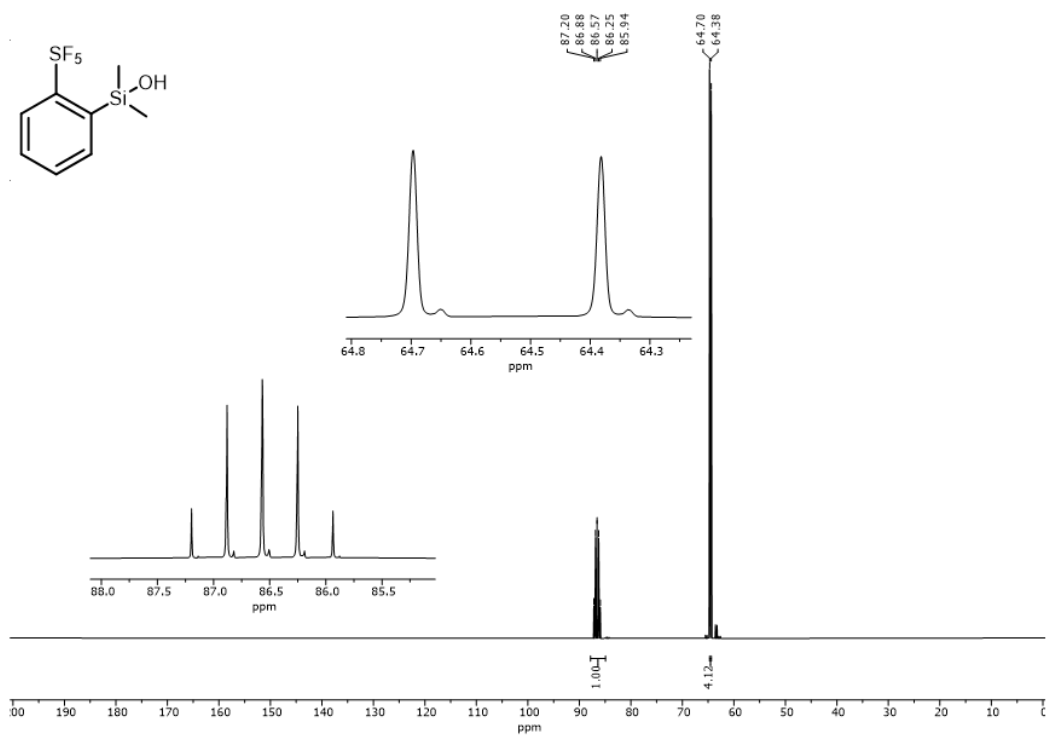


2-(Hydroxydimethylsilyl)pentafluorosulfanyl benzene

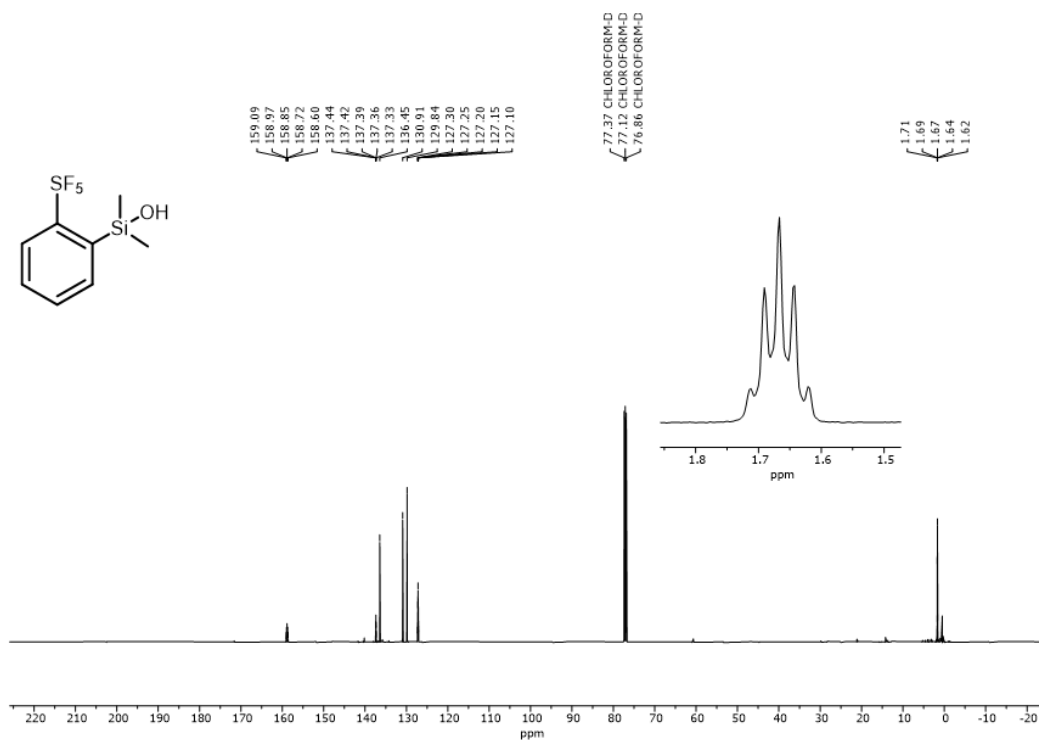
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

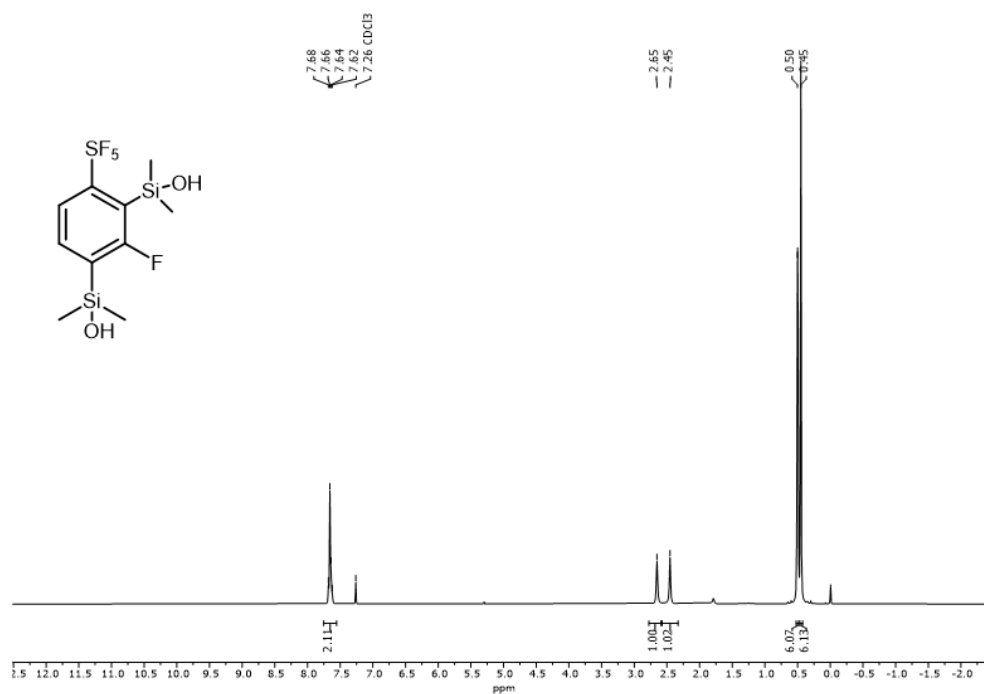


^{13}C NMR (101 MHz, CDCl_3)

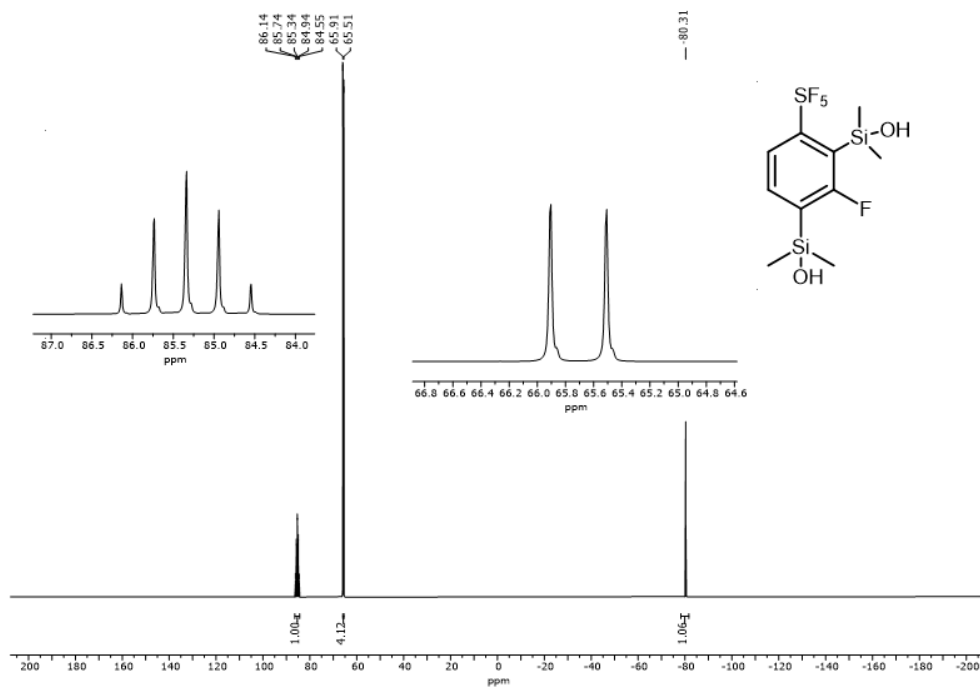


2,4-bis(Hydroxydimethylsilyl)-3-fluoropentafluorosulfanyl benzene (S1).

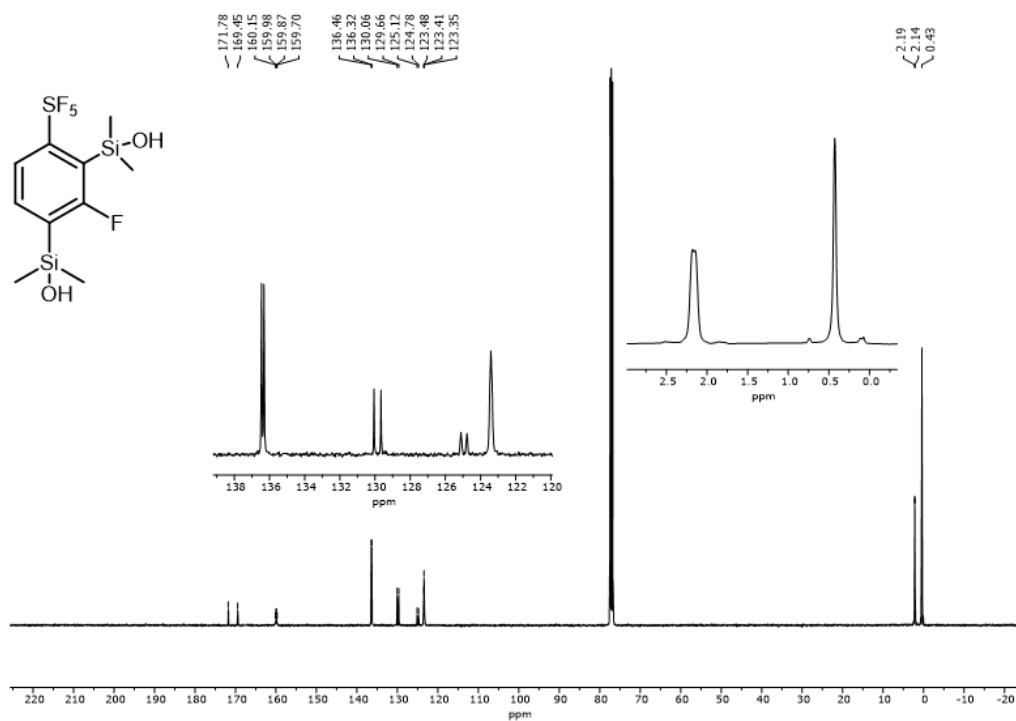
^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)

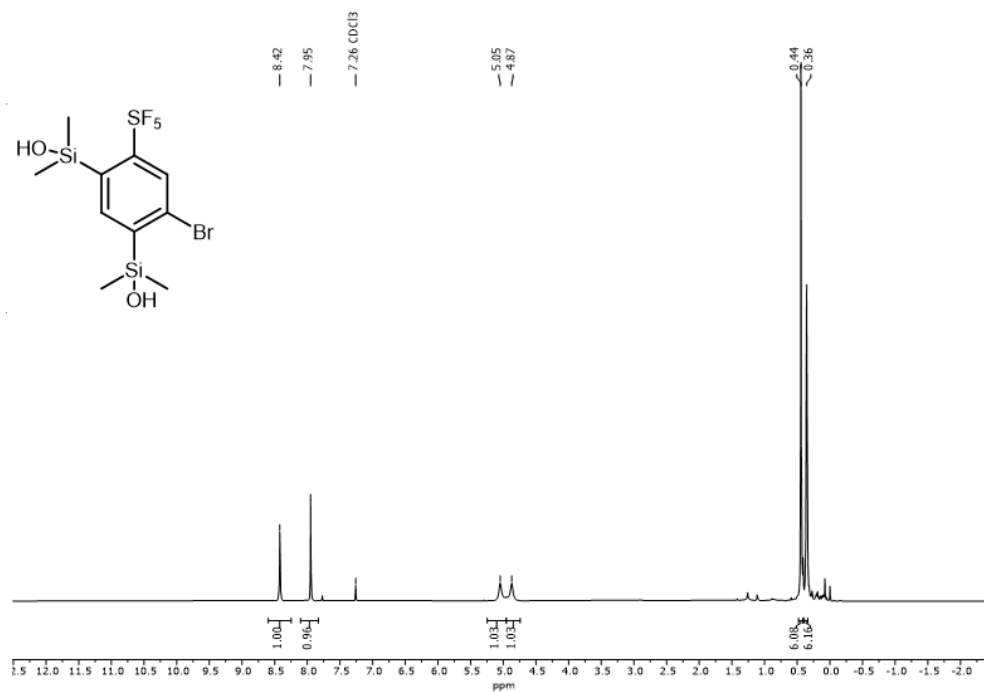


^{13}C NMR (101 MHz, CDCl_3)

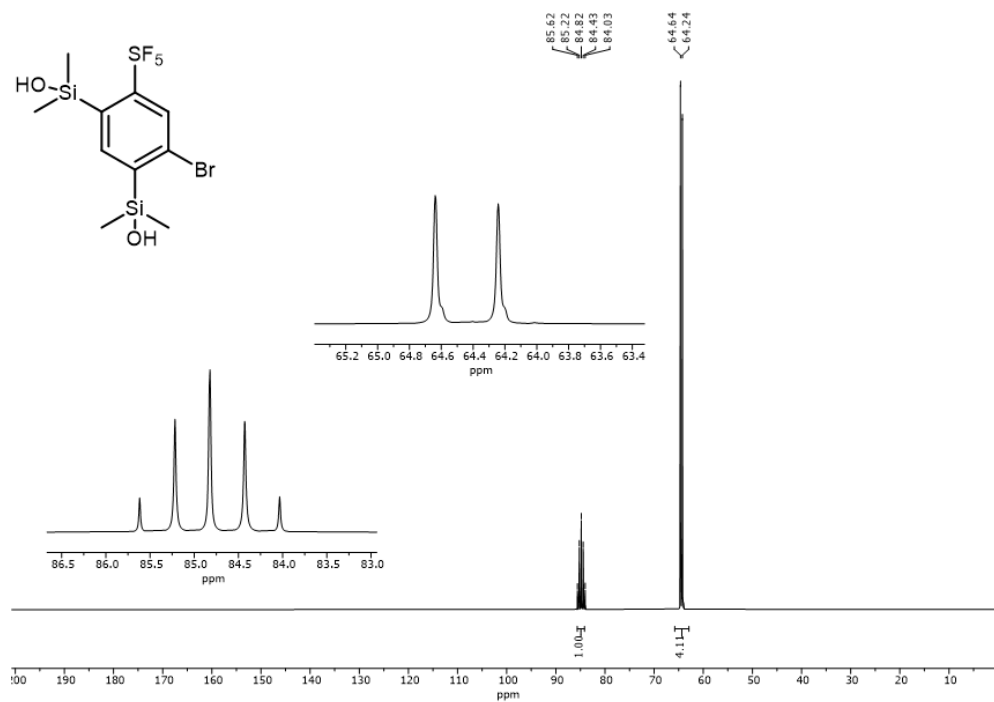


2,4-bis(Hydroxydimethylsilyl)-5-bromopentafluorosulfanyl benzene (S2)

^1H NMR (400 MHz, CDCl_3)



^{19}F NMR (376 MHz, CDCl_3)



^{13}C NMR (101 MHz, CDCl_3)

