Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Efficient Ruthenium-catalysed S-S, S-Si and S-B bond forming reactions

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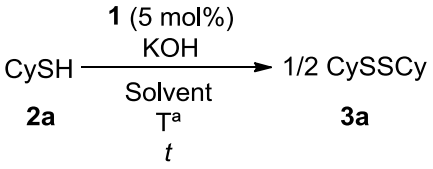
Contents

GENERAL CONSIDERATIONS:

Complex **1** was synthesized according to the reported procedure.[1] Thiols (**2**), silanes (**4**) and boranes (**6**) were purchased from Sigma Aldrich and used as received. Toluene, dichloromethane, acetone, *i*-propanol and methanol were dispensed from a solvent purification system from Innovative Technology ^{1}H, ^{11}B, ^{29}Si and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 300 or Bruker Avance II 400 Ultrashield NMR spectrometers. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre at Swansea University, Grove building, Singleton Park, Swansea, SA2 8PP, Wales, UK.

OPTIMIZATION TABLES:

Solvent optimization table of thiol coupling.

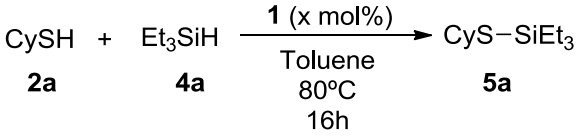


Entry	Solvent	Temperature (ºC)	*t* (h)	Conversion (%)[b]
1	DCM	r.t.	3	60
2	DCM	r.t.	16	>99 (50)[c]
3	Acetone	60	24	60
4	Toluene	60	24	40
5	*i*PrOH	60	24	0
6	H_2O	60	24	0
7	MeOH	60	1.5	>99 (79)[c]

[a] Reactions conditions: CySH (0.25 mmol), 1 (5 mol %), KOH (0.25 mmol), dissolved in toluene (0.5 mL). [b] Conversion determined by ^{1}H NMR. [c] Determined by GC using *n*-tetradecane as internal standard.

[1] S. Manzini, C. A. Urbina-Blanco, A. Poater, A. M. Z. Slawin, L. Cavallo, S. P. Nolan, *Angew. Chem., Int. Ed.* **2012**, *51*, 1042-1045.

Catalyst loading optimization table of dehydrogenative coupling reaction of thiols with silanes.



Entry	Cat. loading (mol %)	Conversion[a] (%)
1	0	0
2	2.5	>99
3	1	>99
4	0.5	>99
5	0.25	69

[b] Determined by ^{1}H NMR spectroscopy.

EXPERIMENTAL PROCEDURES AND CHARACTERIZATIONS:

General procedure for the disulfide synthesis.

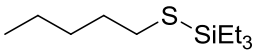
In a vial fitted with a screw cap, in the glove box, **1** (0.00625 mmol) and KOH (0.25 mmol) were dissolved in MeOH (0.5 mL). Then, outside of the glovebox, the corresponding thiol (**2**) (0.25 mmol) and *n*-tetradecane (10 µL) were added and the resulting mixture was stirred at 60ºC. The reaction progress was monitored by GC. After the indicated time (Table 2) the solvent was removed under vacuum and the crude reaction was analyzed by GC.

Dehydrogenative coupling reaction of thiols with silanes catalyzed by 1.

In a vial fitted with a screw cap, in the glovebox, **1** (0.00125 mmol) and the silane **4** (0.55 mmol) were dissolved in toluene (0.5 mL). Then, outside of the glovebox, the thiol **2** (0.25 mmol) was added and the resulting mixture was stirred at 110ºC for 16h. After this time, the solvent was removed under vacuum. The residue was dissolved in pentane and filtered through a pad of celite to remove the catalyst (**1**). The volatile materials were removed under vacuum to afford the desired silylthioethers.

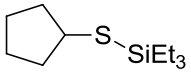
The silylthioethers $CySSiEt_3$[2] (**5a**), $BnSSiEt_32$ (**5d**), $PhSSiEt_32$ (**5e**), $CySSiPh_3$[3] (**5h**) and $PhSSiPh_33$ (**5p**) produced were identified by the comparison of the NMR spectra of the authentic compounds prepared according to the literature method.

Triethyl(pentylthio)silane (5b).



Compound **5b** was obtained from pentane-1-thiol (**2a**) and triethylsilane (**4a**). Yield: 96% (colorless oil). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.46 (t, *J* = 7.4 Hz, 2H), 1.64-1.54 (m, 2H), 1.42-1.25 (m, 3H), 1.02-0.97 (m, 9H), 0.89 (t, *J* = 7.1 Hz, 3H), 0.74 (dt, *J* = 16.3, 6.2 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 32.9, 31.0, 25.7, 22.3, 14.0, 7.3, 5.4. ^{29}Si (79.3 MHz, CD_2Cl_2): δ 22.6. HRMS (EI+): *m/z* calcd for $C_{11}H_{26}SSi$: 218.1519, found 218.1518.

(Cyclopentylthio)triethylsilane (5c).

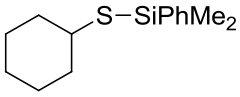


Compound **5c** was obtained from cyclopentanethiol (**2i**) and triethylsilane (**4a**). Yield: 94% (colorless oil). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.00-2.92 (m, 1H), 1.99 – 1.89 (m, 2H), 1.74 – 1.63 (m,

[2] K. Fukumoto, M. Kasa, T. Oya, M. Itazaki, H. Nakazawa, *Organometallics*, **2011**, *30* , 3461–3463.
[3] C. Behloul, D. Guijarro, M. Yus, *Tetrahedron*, **2005**, *61*, 6908-6915.

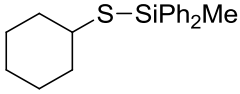
2H), 1.53 – 1.43 (m, 4H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.69 (dt, *J* = 12.1, 7.8 Hz, 6H).[13]C NMR (100 MHz, CD_2Cl_3): δ 39.6, 37.9, 24.6, 7.3, 5.7. [29]Si (79.3 MHz, CD_2Cl_2): δ 21.5. HRMS (EI+): *m/z* calcd for $C_{11}H_{24}SSi$: 216.1368, found 216.1369

(Cyclohexylthio)dimethyl(phenyl)silane (5f).



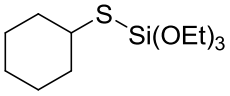
Compound **5f** was obtained from cyclohexanethiol (**2a**) and dimethylphenyl silane (**4b**). Yield: 97% (colorless oil). [1]H NMR (400 MHz, $CDCl_3$): δ 7.60-7.57 (m, 2H), 7.34-7.31 (m, 3H), 2.65-2.58 (m, 1H), 1.81-1.74 (m, 2H), 1.66-1.58 (m, 2H), 1.48-1.42 (m, 1H), 1.36-1.27 (m, 2H), 1.18-1.11 (m, 3H), 0.50 (s, 6H). [13]C NMR (100 MHz, $CDCl_3$): δ 138.8, 134.8, 134.0, 130.6, 128.9, 128.7, 42.0, 38.7, 27.3, 26.5, 0.90. [29]Si (79.3 MHz, CD_2Cl_2): δ 7.6. HRMS (EI+): *m/z* calcd for $C_{14}H_{22}SSi$: 250.1206, found 250.1207.

(Cyclohexylthio)(methyl)diphenylsilane (5g).



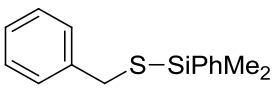
Compound **5g** was obtained from cyclohexanethiol (**2a**) and diphenylmethylsilane (**4c**). Yield: 96% (colorless oil). [1]H NMR (400 MHz, $CDCl_3$): δ 7.61-7.57 (m, 4H), 7.35-7.31 (m, 6H), 2.69-2.60 (m, 1H), 1.78-1.73 (m, 2H), 1.62-1.58 (m, 2H), 1.43-1.25 (m, 3H), 1.14-1.06 (m, 3H), 0.80 (s, 3H). [13]C NMR (100 MHz, $CDCl_3$): δ 137.2, 136.1, 136.0, 131.2, 129.3, 129.3, 42.8, 38.9, 27.6, 26.8, -0.0. [29]Si (79.3 MHz, CD_2Cl_2): δ 4.1. HRMS (EI+): *m/z* calcd for $C_{19}H_{24}SSi$: 312.1362, found 312.1365.

***S*-Cyclohexyl *O,O,O*-triethyl orthosilicothioate (5i).**



Compound **5i** was obtained from cyclohexanethiol (**2a**) and triethoxysilane (**4e**). Yield: 99% (colorless oil). [1]H NMR (400 MHz, $CDCl_3$): δ 3.79 (q, *J* = 7.0 Hz, 6H), 2.92-285 (m, 1H), 1.96-1.89 (m, 2H), 1.71-1.62 (m, 2H), 1.54-1.45 (m, 1H), 1.42-1.31 (m, 2H), 1.31-1.19 (m, 3H), 1.15 (t, *J* = 7.0 Hz, 9H). [13]C NMR (100 MHz, $CDCl_3$): δ 59.3, 40.8, 37.4, 26.5, 25.6, 17.9. [29]Si (79.3 MHz, CD_2Cl_2): δ -56.2. HRMS (EI+): *m/z* calcd for $C_{12}H_{26}O_3SSi$: 278.1288, found 278.1284.

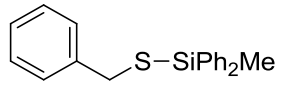
(Benzylthio)dimethyl(phenyl)silane (5j).



Compound **5j** was obtained from benzylmercaptan (**2d**) and dimethylphenylsilane (**4b**). Yield: 92% (colorless oil). [1]H NMR (400 MHz, $CDCl_3$): δ 7.58-7.53 (m, 2H), 7.36-7.29 (m, 3H), 7.16-7.07 (m, 5H), 3.51 (s, 2H), 0.44 (s, 6H). [13]C NMR (100 MHz, $CDCl_3$): δ 142.3, 138.3, 135.6, 134.7, 131.5,

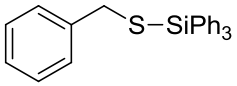
130.2, 130.1, 129.7, 129.4, 128.5, 32.6, 0.9. ^{29}Si (79.3 MHz, CD_2Cl_2): δ 9.6. HRMS (EI+): *m/z* calcd for $C_{15}H_{18}SSi$: 258.0893, found 258.0892.

(Benzylthio)(methyl)diphenylsilane (5k).



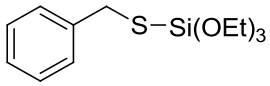
Compound **5k** was obtained from benzylmercaptan (**2d**) and diphenylmethylsilane (**4c**). Yield: 97% (colorless oil). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.53 (m, 2H), 7.34-7.27 (m, 7H), 7.15-7.09 (m, 2H), 7.09-7.03 (m, 2H), 3.51 (s, 2H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 140.3, 134.8, 134.8, 134.7, 133.9, 133.9, 130.1, 129.8, 129.6, 129.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 126.8, 31.3, -2.01. ^{29}Si (79.3 MHz, CD_2Cl_2): δ 3.6. HRMS (EI+): *m/z* calcd for $C_{20}H_{20}SSi$: 320.1049, found 320.1052.

(Benzylthio)triphenylsilane (5l).



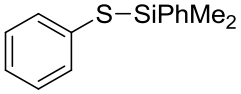
Compound **5l** was obtained from benzylmercaptan (**2d**) and triphenylsilane (**4d**). **5d** could not be separated from the triphenylsilane (**4d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.62 (m, 6H), 7.44-7.39 (m, 3H), 7.39-7.33 (m, 6H), 7.19-7.15 (m, 3H), 7.08-7.03 (m, 2H), 3.57 (s, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 140.0, 135.7, 133.0, 130.2, 128.5, 128.4, 128.1, 126.7, 31.6. ^{29}Si (79.3 MHz, CD_2Cl_2): δ -1.98 . HRMS (EI+): *m/z* calcd for $C_{25}H_{22}SSi$: 382.1206, found 382.1207.

***S*-benzyl *O,O,O*-triethyl orthosilicothioate (5m).**



Compound **5m** was obtained from benzylmercaptan (**2d**) and triethoxysilane (**4c**). Yield: 99% (colorless oil). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.29-7.11 (m, 5H), 3.81-3.74 (m, 8H), 1.15 (t, *J* = 7.0 Hz, 9H), 0.69 (dt, *J*= 12.1, 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 129.0, 128.9, 127.5, 77.9, 77.4, 77.0, 59.8, 30.6, 18.4. ^{29}Si (79.3 MHz, CD_2Cl_2): δ -53.9. HRMS (EI+): *m/z* calcd for $C_{13}H_{22}O_3SSi$: 286.1053, found 286.1053.

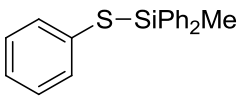
Dimethyl(phenyl)(phenylthio)silane (5n).



Compound **5n** was obtained from thiophenol (**2e**) and dimethylphenylsilane (**4b**). Yield: 95% (colorless oil). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.51-7.46 (m, 2H), 7.34-7.29 (m, 3H), 7.23-7.19 (m, 3H), 7.14-7.09 (m, 2H), 0.47 (s, 3H), 0.28 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 138.4, 136.9,

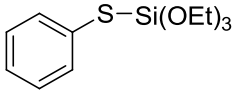
135.6, 134.9, 132.9, 131.7, 130.5, 129.7, 129.5, 128.7, 0.9. ^{29}Si (79.3 MHz, CD_2Cl_2): δ 9.9. HRMS (EI+): *m/z* calcd for $C_{14}H_{16}SSi$: 244.0736, found 244.0739.

Methyldiphenyl(phenylthio)silane (5o).



Compound **5o** was obtained from thiophenol (**2e**) and diphenylmethyl silane (**4c**). Yield: 96% (colorless oil). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.55-7.49 (m, 4H), 7.35-7.25 (m, 6H), 7.18-7.13 (m, 2H), 7.10-6.98 (m, 3H), 0.65 (s, 1H).^{13}C NMR (100 MHz, CD_2Cl_2) δ 137.7, 134.9, 134.8, 134.7, 133.9, 130.7, 130.1, 129.8, 129.6, 129.5, 129.2, 129.1, 128.7, 128.0, 127.9, 127.8, 126.9, 125.5, -2.3. ^{29}Si (79.3 MHz, CD_2Cl_2): δ 3.2. HRMS (EI+): *m/z* calcd for $C_{19}H_{18}$ SSi: 306.0893, found 306.0899.

***O,O,O*-Triethyl S-phenyl orthosilicothioate (5q).**

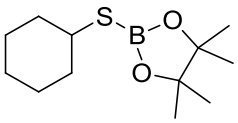


Compound **5q** was obtained from thiophenol (**2e**) and triethoxysilane silane (**4e**). Yield: 99% (colorless oil). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47-7.39 (m, 2H), 7.21-7.12 (m, 3H), 3.79 (q, *J* = 7.0 Hz, 6H), 1.11 (t, *J* = 7.0 Hz, 9H).^{13}C NMR (100 MHz, CD_2Cl_2) δ 134.2, 129.5, 129.3, 127.1, 60.1, 18.3. ^{29}Si (79.3 MHz, CD_2Cl_2): δ -58.2. HRMS (EI+): *m/z* calcd for $C_{12}H_{20}O_3SSi$: 272.0902, found 272.0903.

Dehydrogenative coupling reactions of thiols with pinacolborane catalyzed by 1.

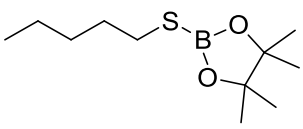
In a vial fitted with a screw cap, in the glove box, 1 (0.00125 mmol) and pinacolborane 6a (0.55 mmol) were dissolved in toluene (0.5 mL). Then, outside of the glovebox, the thiol (2) (0.25 mmol) was added and the resulting mixture was stirred at 60ºC for 16h. After this time, the solvent and the pinacolborane were removed under vacuum. The compounds were so hygroscopic that the correct elemental analysis or HRMS data could not be obtained, though satisfactory spectroscopic data were obtained.

2-(Cyclohexylthio)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a).



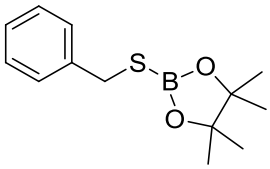
Compound **7a** was obtained from cyclohexanethiol (**2a**). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.05-2.92 (m, 1H), 1.93-1.83 (m, 2H), 1.68-1.58 (m, 2H), 1.49-1.45 (m, 1H), 1.29 (m, 5H), 1.2 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 85.2, 41.3, 37.2, 27.0, 26.3, 25.1, 25.0. ^{11}B NMR (128 MHz, CD_2Cl_2) 33.5.

4,4,5,5-Tetramethyl-2-(pentylthio)-1,3,2-dioxaborolane (7b).



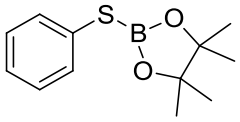
Compound **7b** was obtained from pentane-1-thiol (**2b**).[1]H NMR (400 MHz, CD_2Cl_2): δ 2.58 (t, *J* = 7.3 Hz, 2H), 1.57-1.46 (m, 2H), 1.31-1.23 (m, 4H), 1.21 (s, 12H), 0.85-0.78 (m, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 85.0, 32.5, 31.0, 27.0, 24.9, 22.6, 14.3. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.7.

2-(Benzylthio)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7c).



Compound **7c** was obtained from benzyl mercaptan (**2d**).[1]H NMR (400 MHz, CD_2Cl_2): δ 7.27-7.07 (m, 4H), 3.78 (s, 2H), 1.19 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 141.6, 129.3, 129.2, 127.6, 85.9, 31.3, 25.1. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 33.5.

4,4,5,5-Tetramethyl-2-(phenylthio)-1,3,2-dioxaborolane (7d).

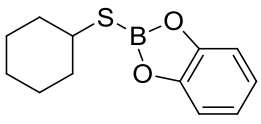


Compound **7c** was obtained from thiophenol (**2e**). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.51-7.48 (m, 2H), 7.32-7.26 (m, 3H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 133.3, 129.6, 128.7, 126.9, 85.4, 24.3. ^{11}B NMR (128 MHz, CD_2Cl_2) δ 32.8.

Dehydrogenative coupling reactions of thiols with catecholborane catalyzed by 1.

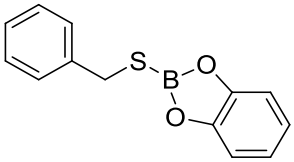
In a vial fitted with a screw cap, in the glove box, **1** (0.00125 mmol) and catecholborane **6b** (0.55 mmol) were dissolved in toluene (0.5 mL). Then, outside of the glovebox, the thiol (**2**) (0.25 mmol) was added and the resulting mixture was stirred at 60ºC for 16h. After this time, the solvent was removed under vacuum. Due to the obtained partial conversion and the instability of these compounds, they could not be isolated as pure compounds. Thus, the correct characterization could not be completely carried out.

2-(Cyclohexylthio)benzo[*d*][1,3,2]dioxaborole (7e).



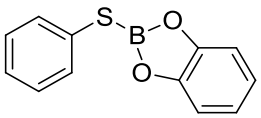
Compound **7e** was obtained from cyclohexanethiol (**2a**). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.15-7.13 (m, 1H), 7.11-7.09 (m, 1H), 7.03-7.01 (m, 1H), 6.99-6.96 (m, 1H), 3.4-3.32 (m, 1), 2.04-1.98 (m, 2H), 1.73-1.67 (m, 2H), 1.52-1.42 (m, 3H), 1.37-1.29 (m, 3H).

2-(Benzylthio)benzo[*d*][1,3,2]dioxaborole (7f).



Compound **7c** was obtained from benzyl mercaptan (**2d**). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.34-7.31 (m, 1H), 7.27-7.19 (m, 3H), 7.16-7.08 (m, 3H), 7.02-6.95 (m, 2H), 3.98 (s, 2H).

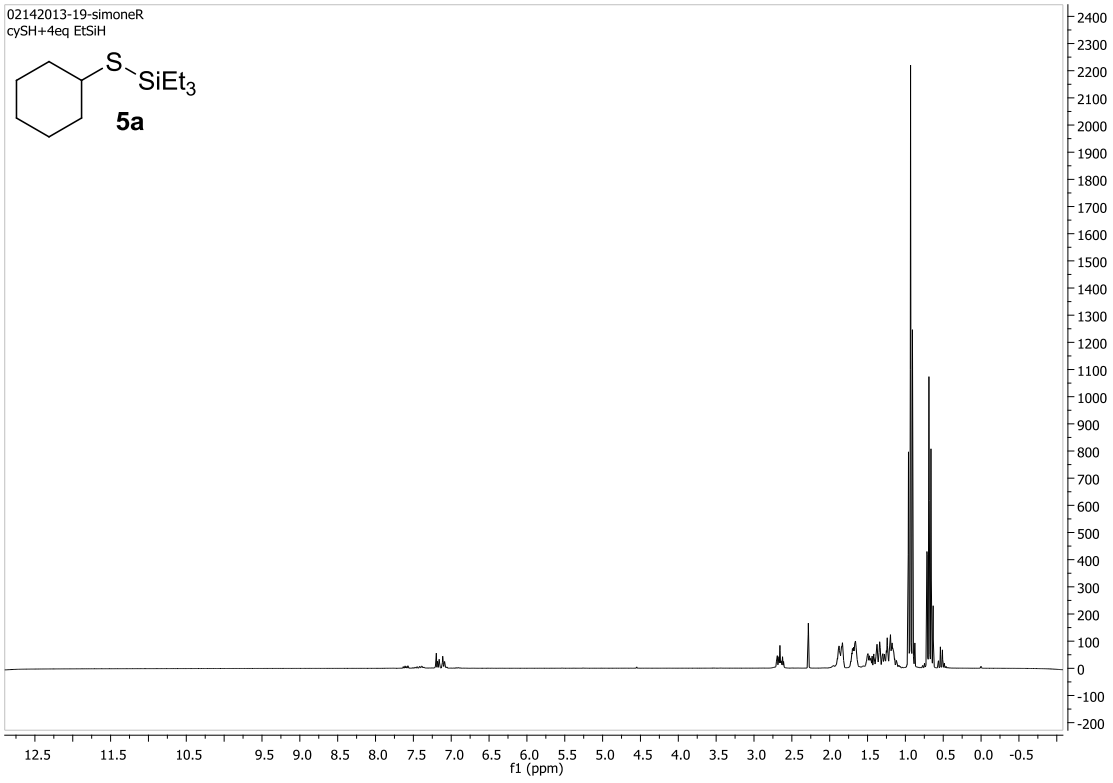
2-(Phenylthio)benzo[*d*][1,3,2]dioxaborole (7g).



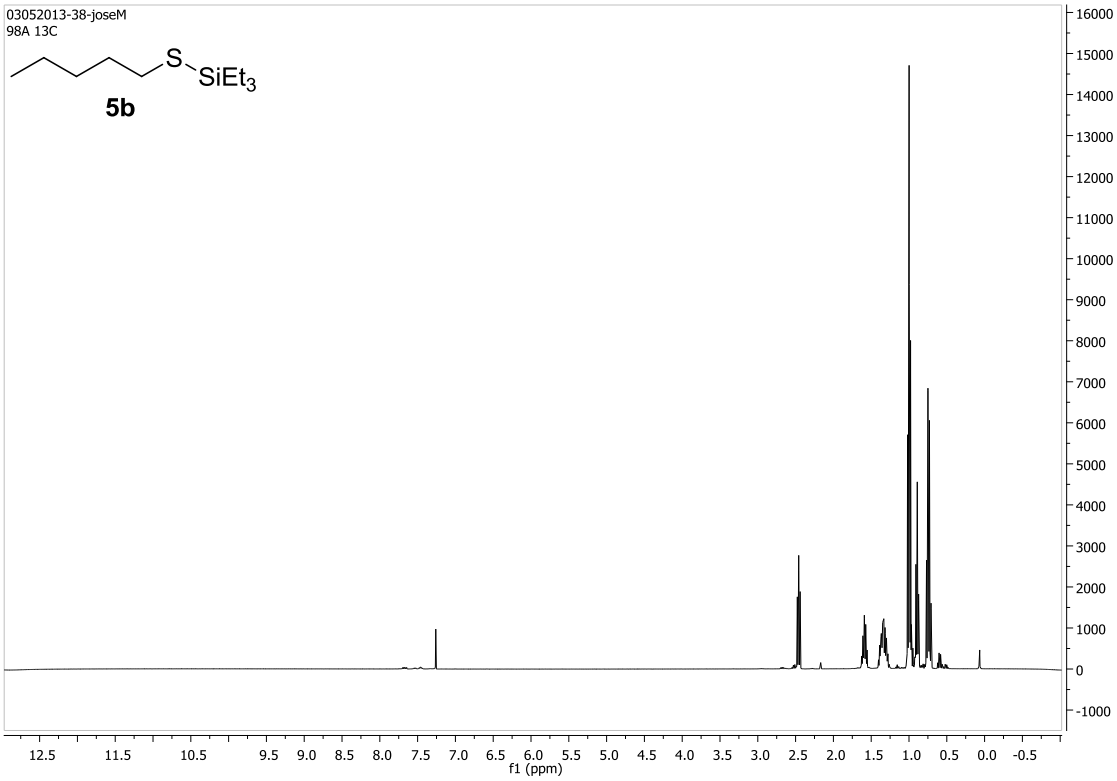
Compound **7c** was obtained from thiophenol (**2e**). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.51-7.47 (m, 1H), 7.40-7.34 (m, 2H), 7.28-7.22 (m, 6H).

NMR-Spectra of all compounds

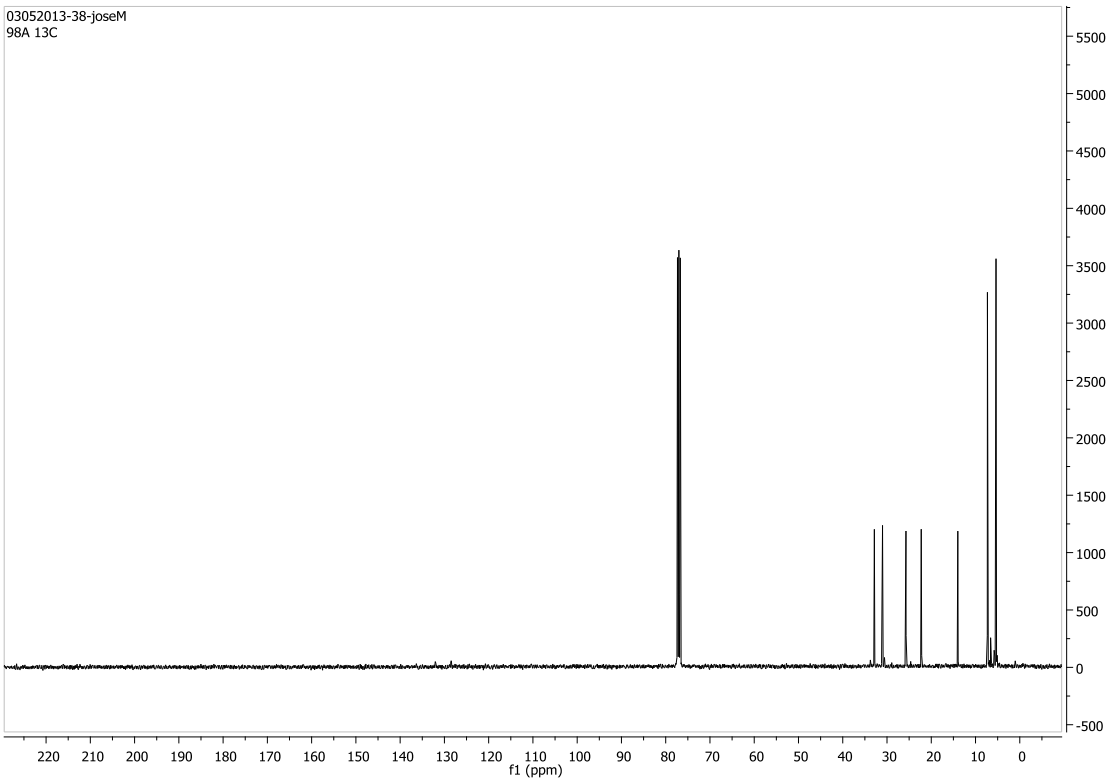
^{1}H-NMR of **5a**.



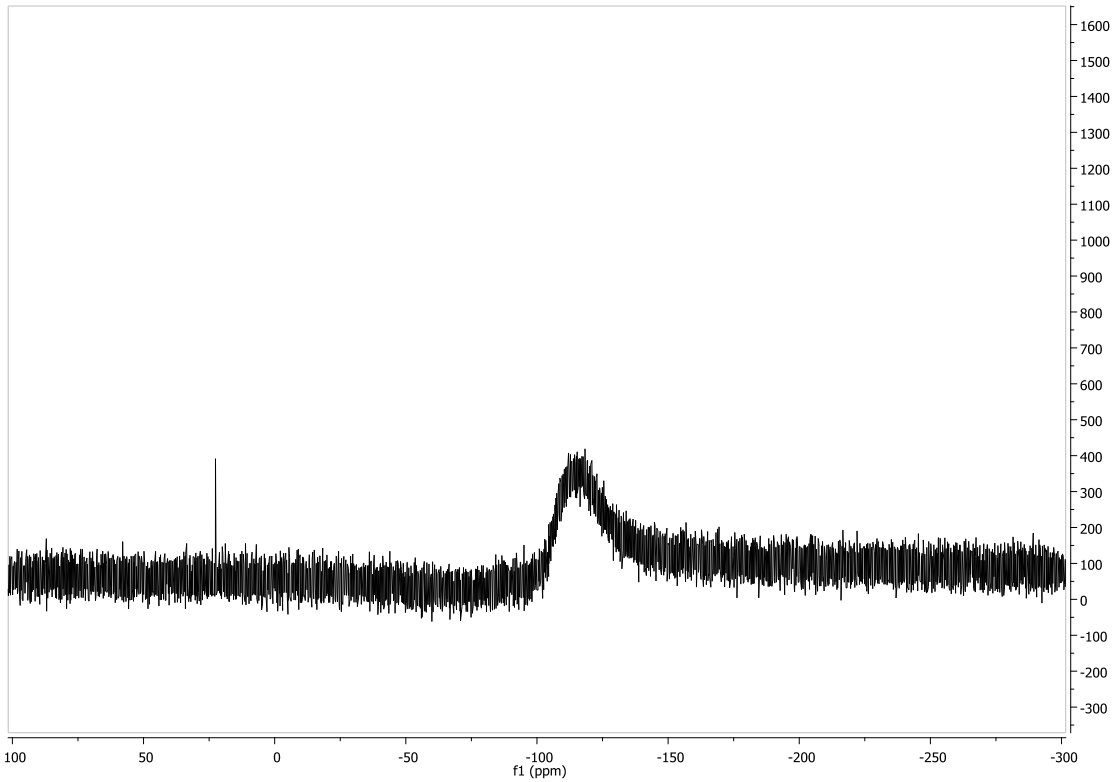
^{1}H-NMR of **5b**.



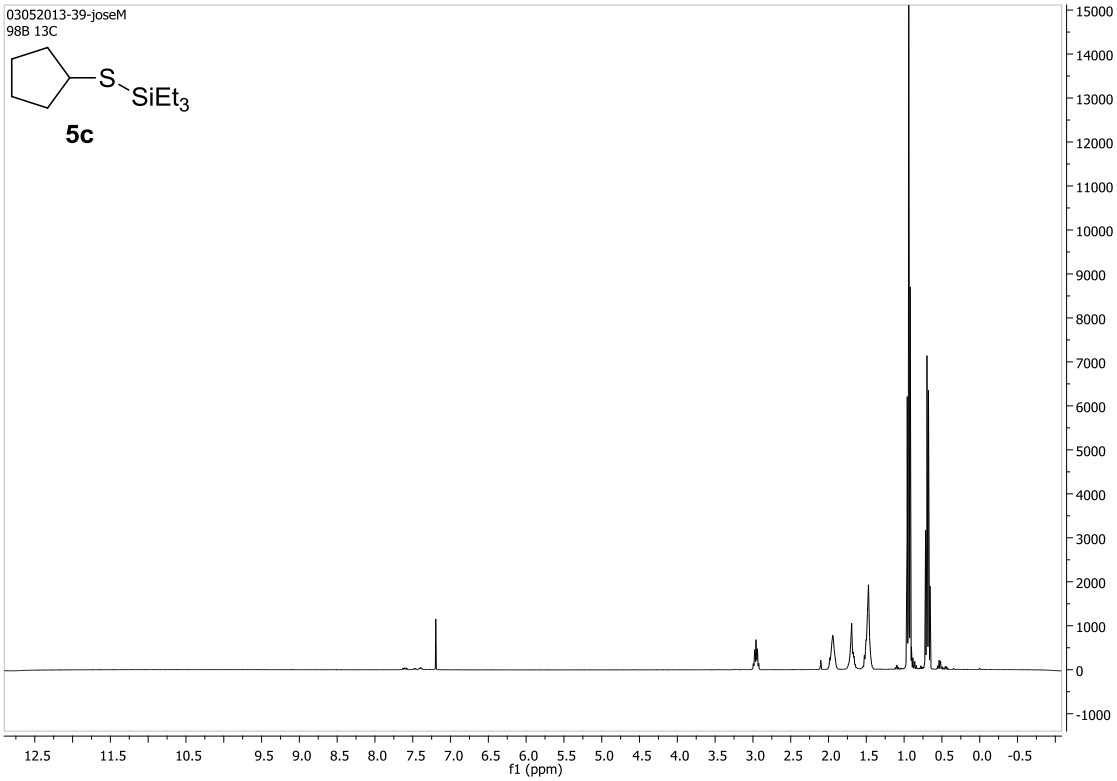
^{13}C-NMR of **5b**.



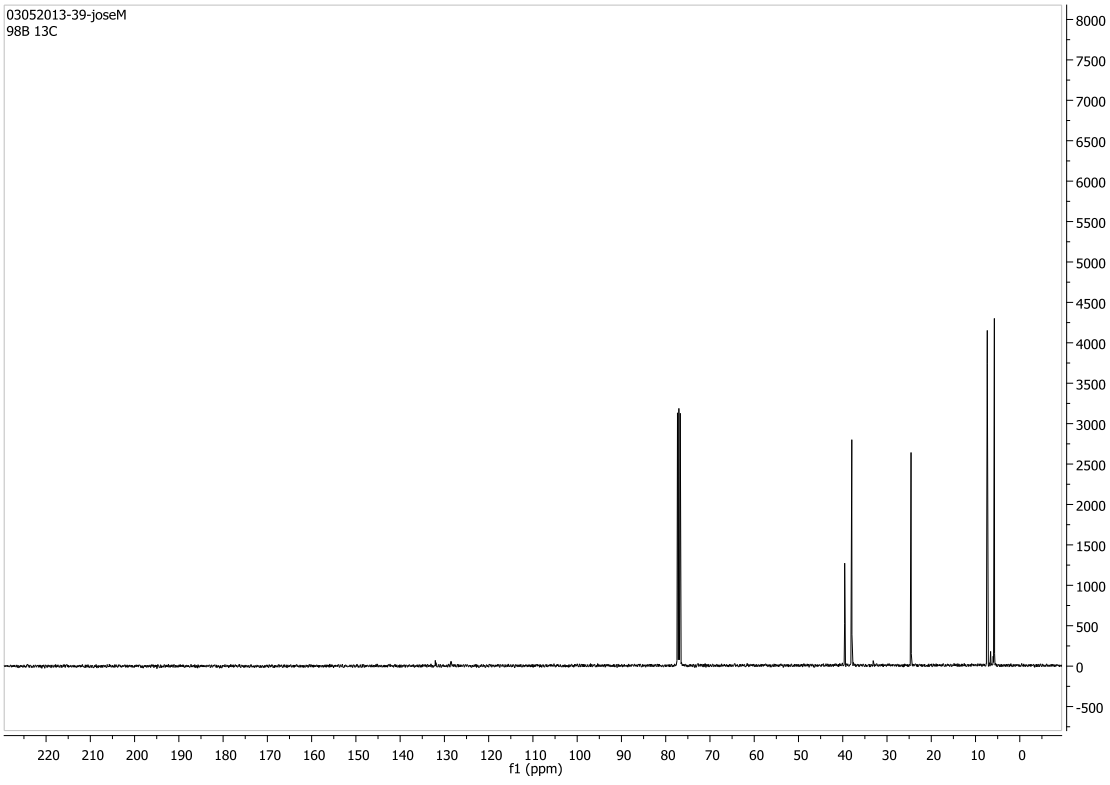
^{29}Si-NMR of **5b**.



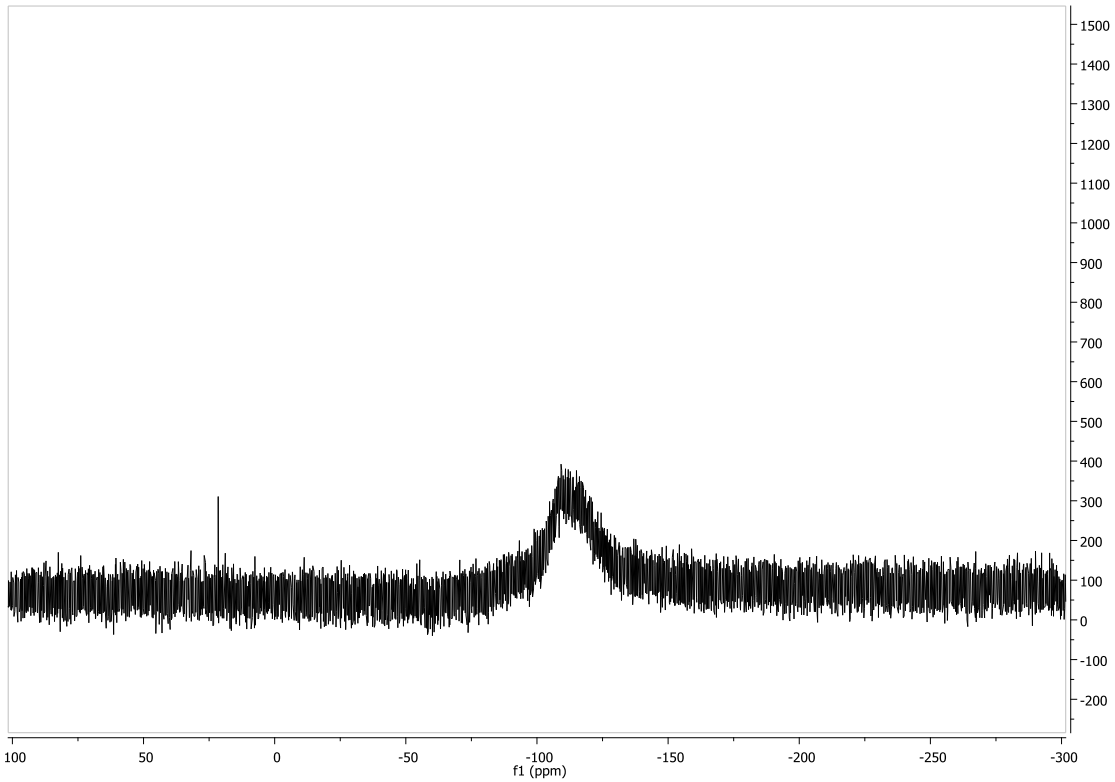
^{1}H-NMR of **5c**.



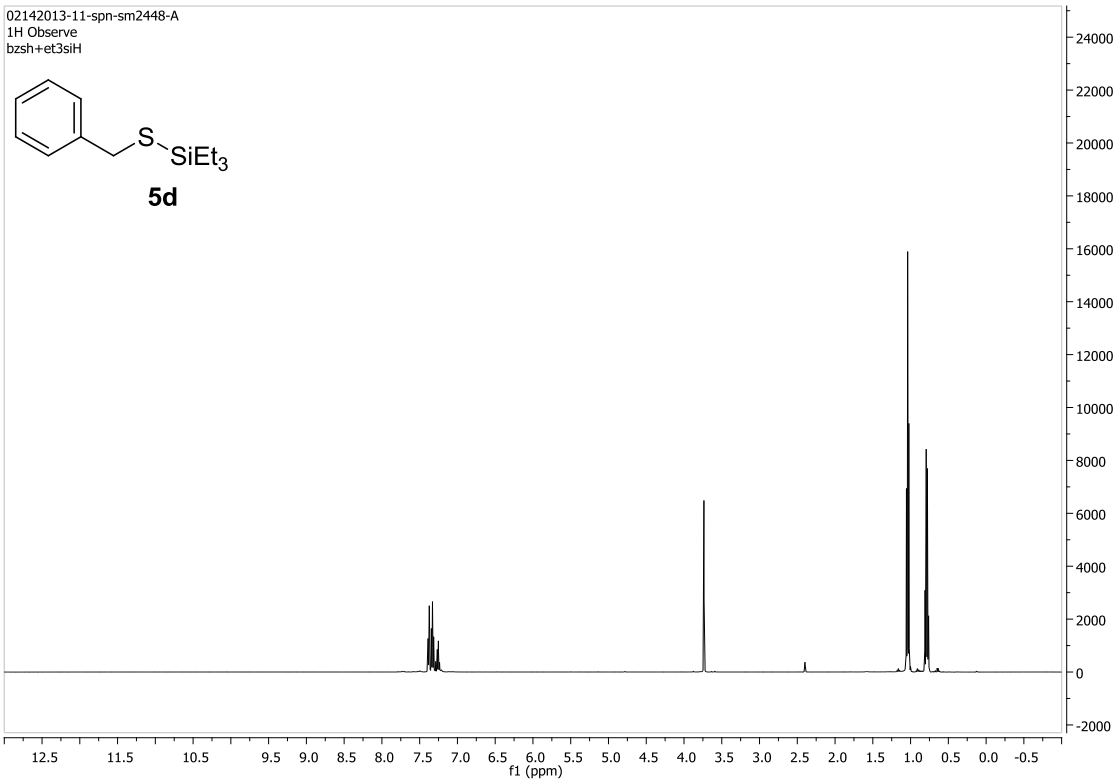
^{13}C-NMR of **5c**.



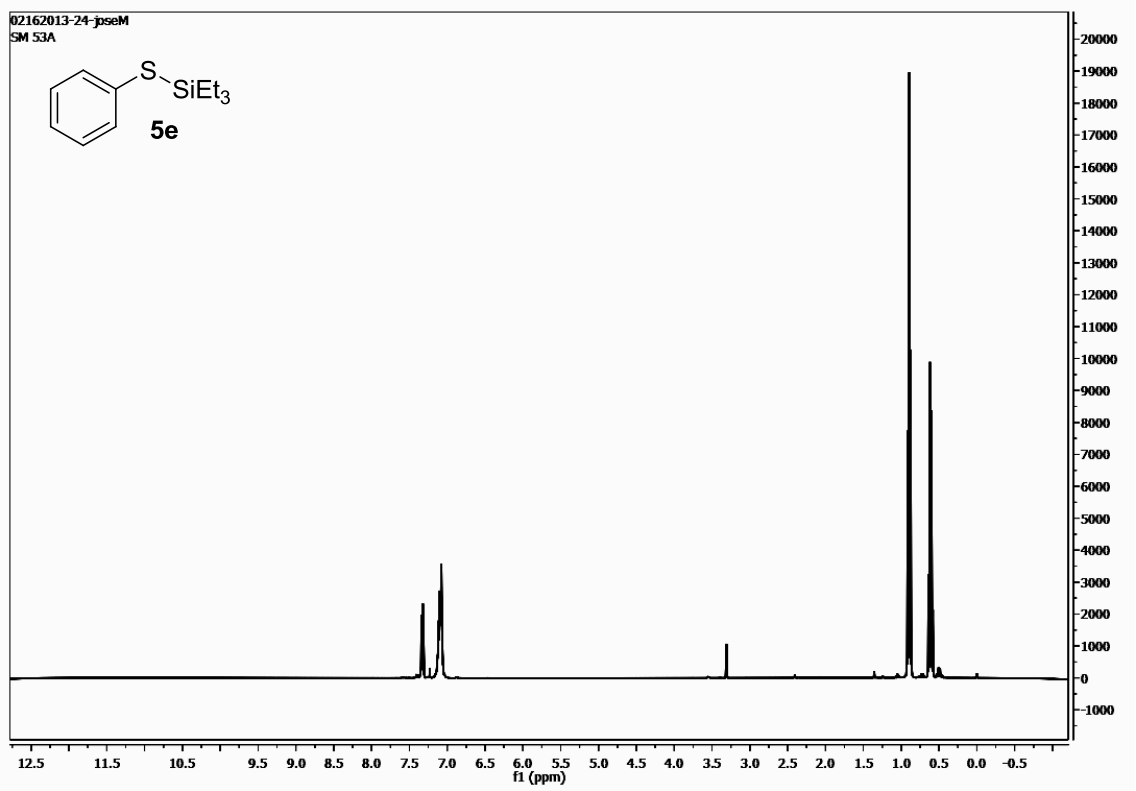
^{29}Si-NMR of **5c**.



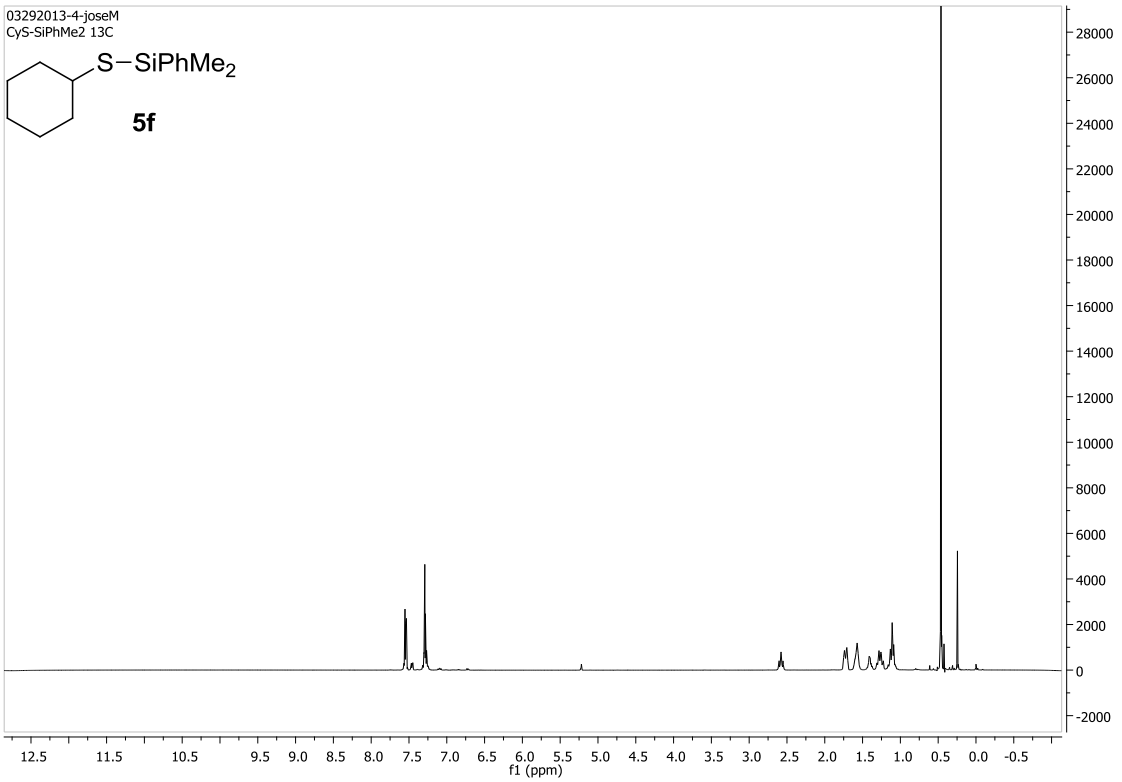
^{1}H-NMR of **5d**.


02142013-11-spn-sm2448-A
1H Observe
bzsh+et3siH
S
SiEt3
5d
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

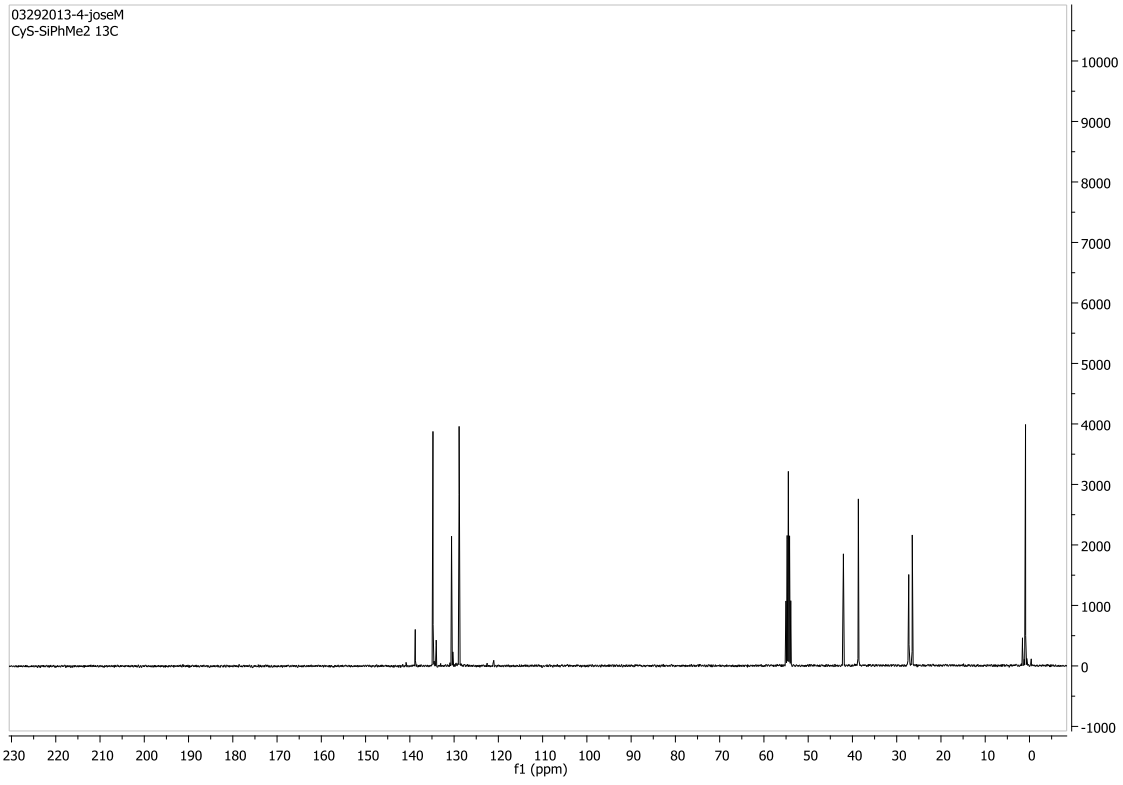
^{1}H-NMR of **5e**.



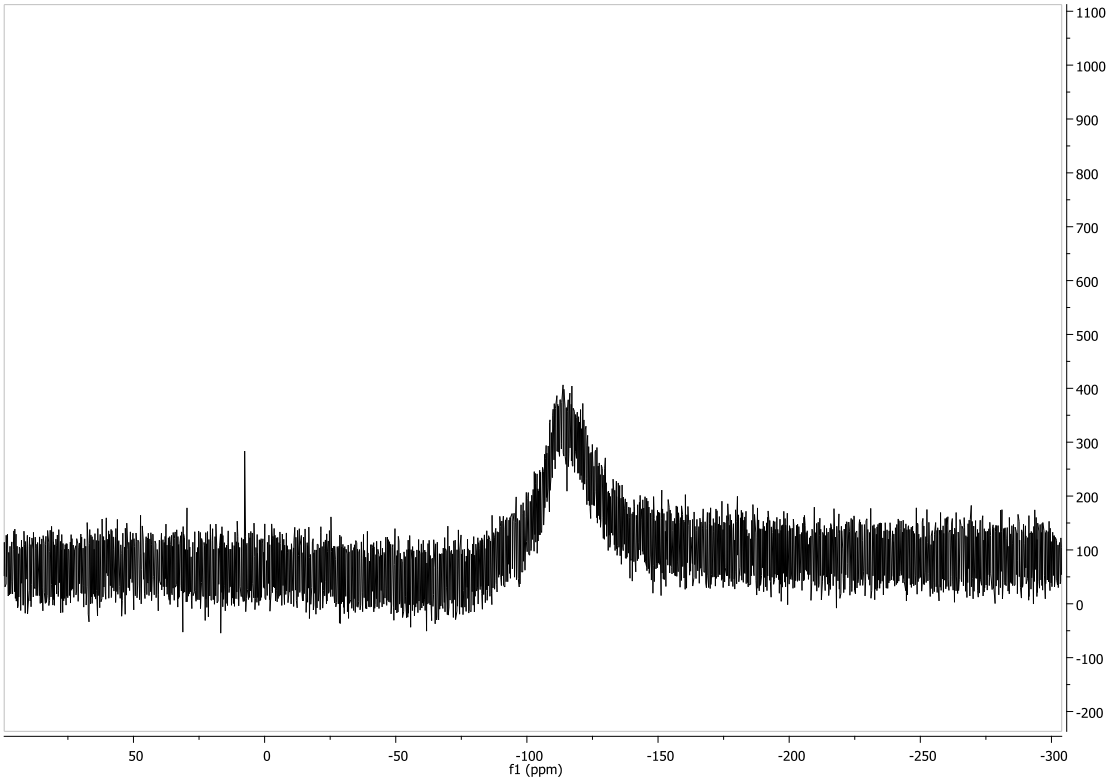
^{1}H-NMR of **5f**.



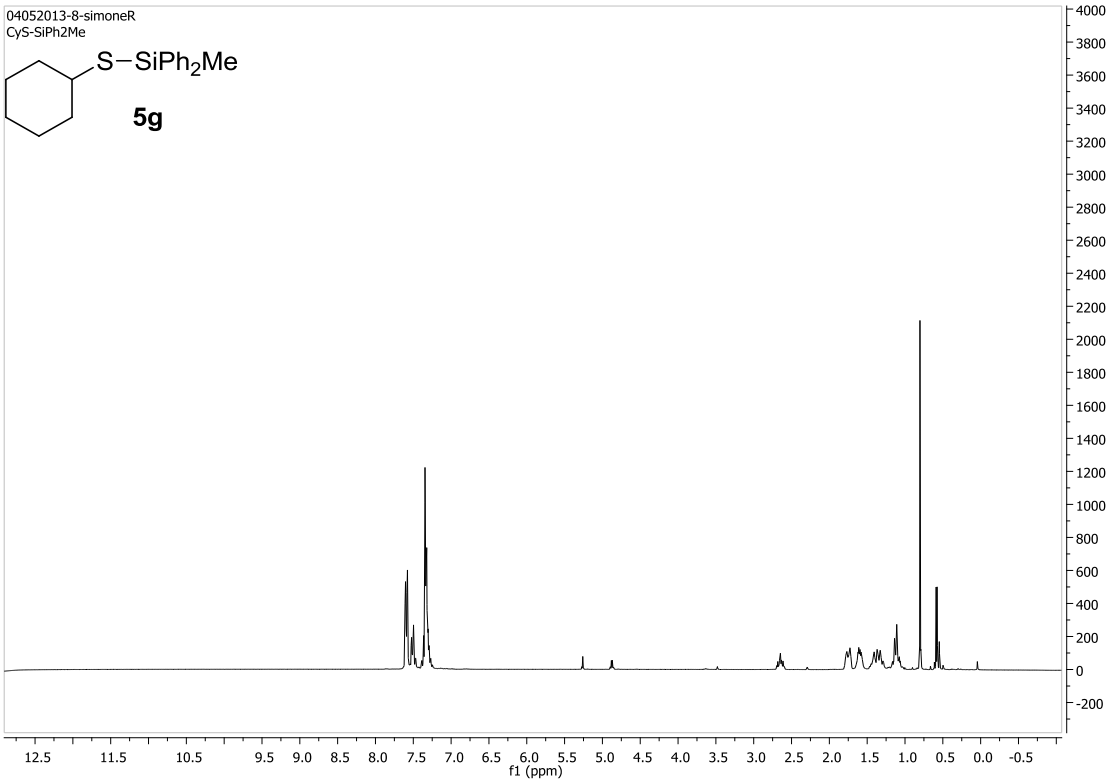
^{13}C-NMR of **5f**.



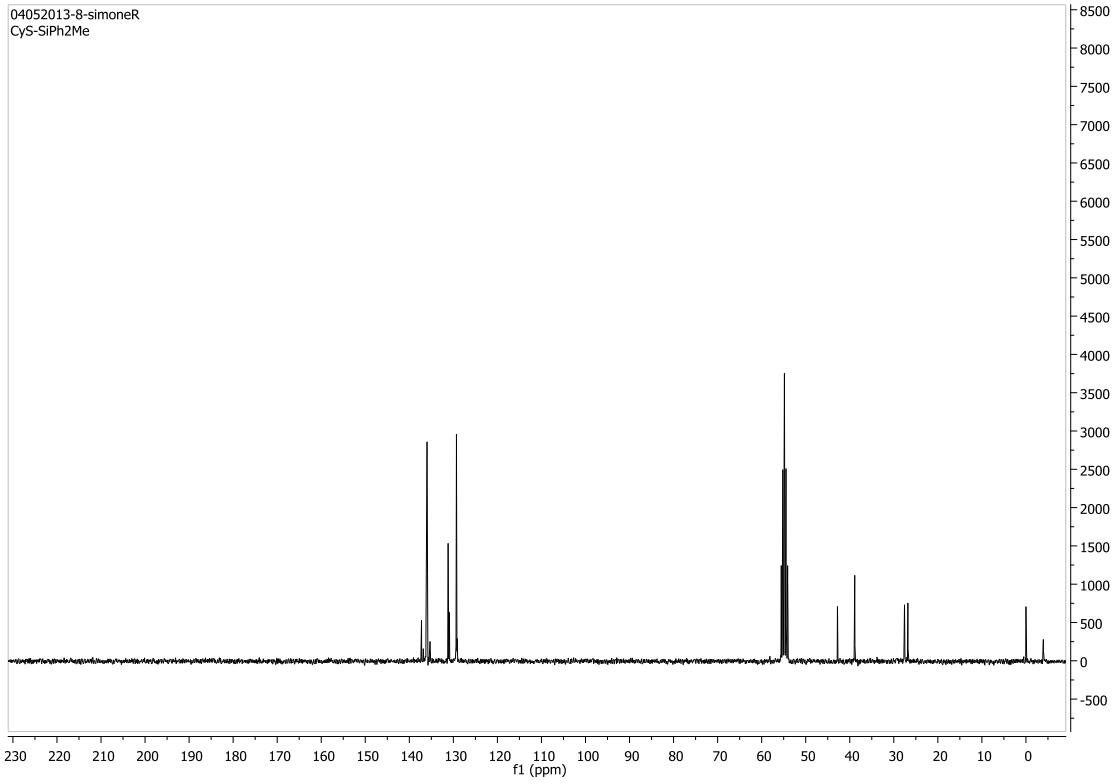
^{29}Si-NMR of **5f**..



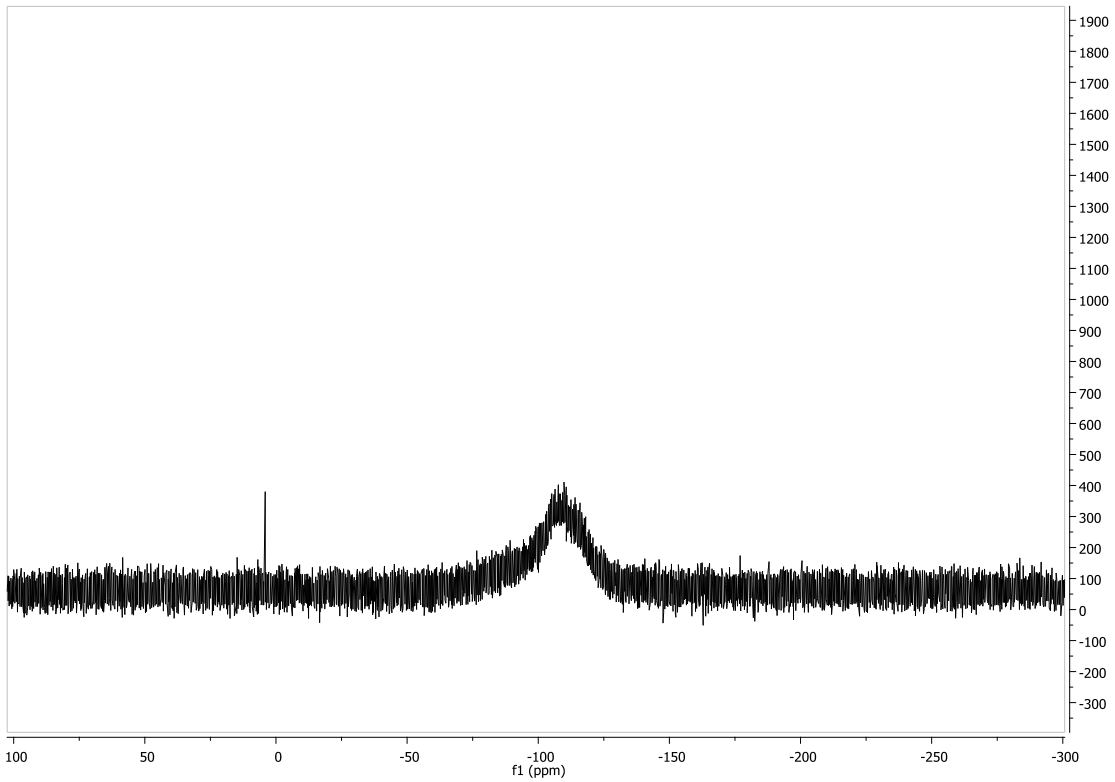
^{1}H-NMR of **5g**.



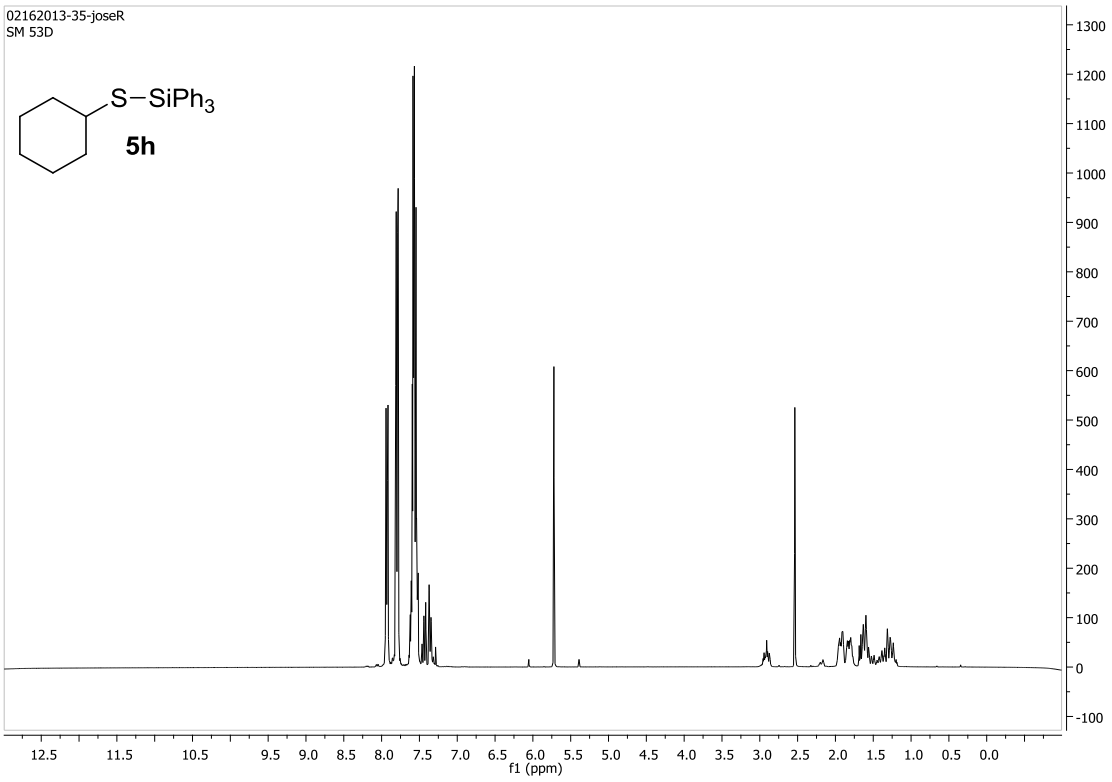
^{13}C-NMR of **5g**.



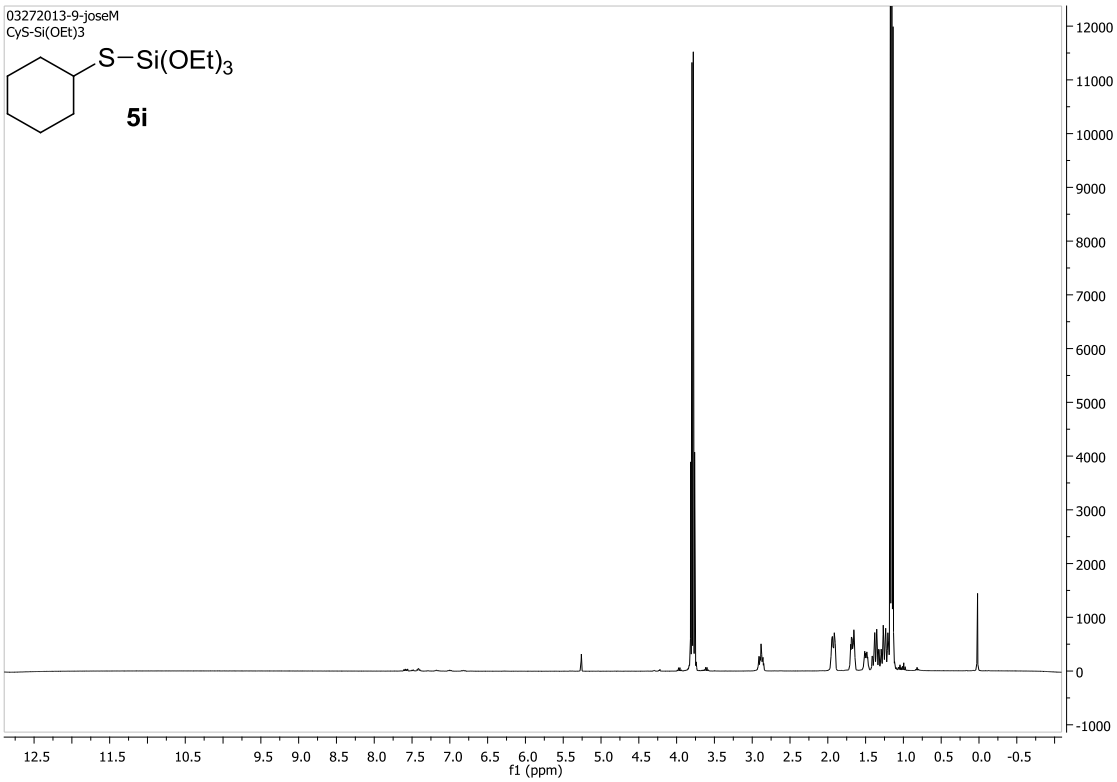
^{29}Si-NMR of **5f**.



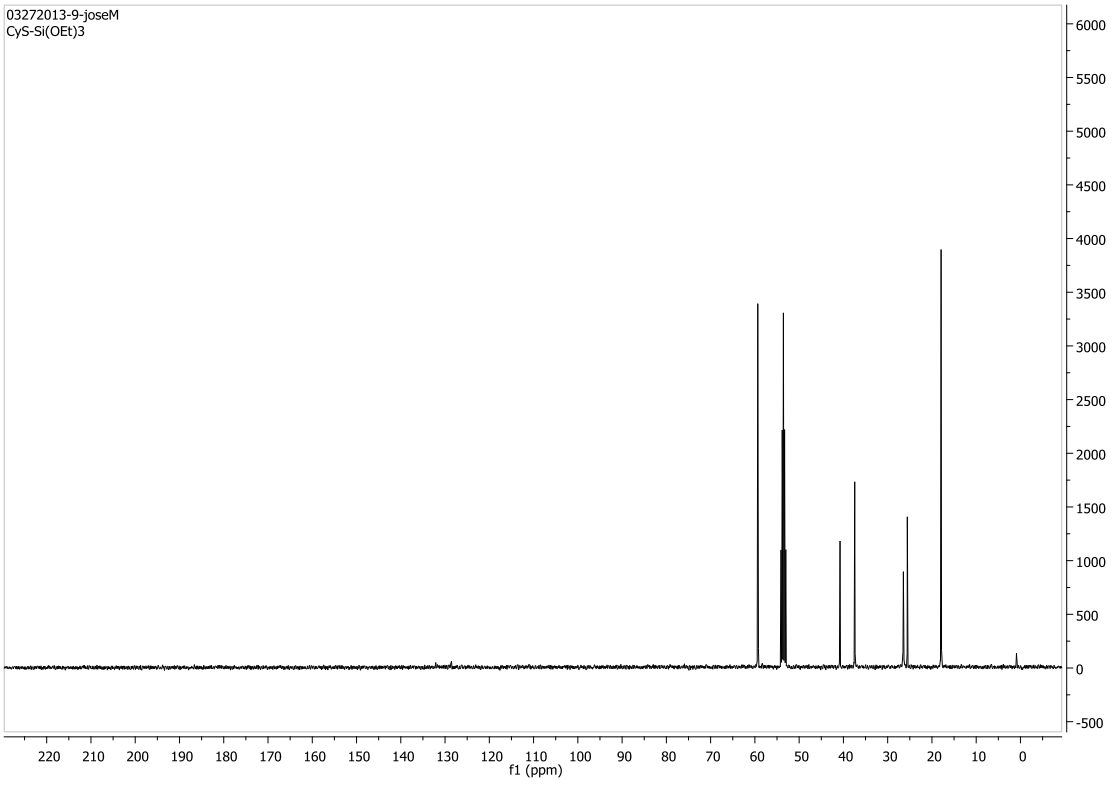
^{1}H-NMR of **5h**.



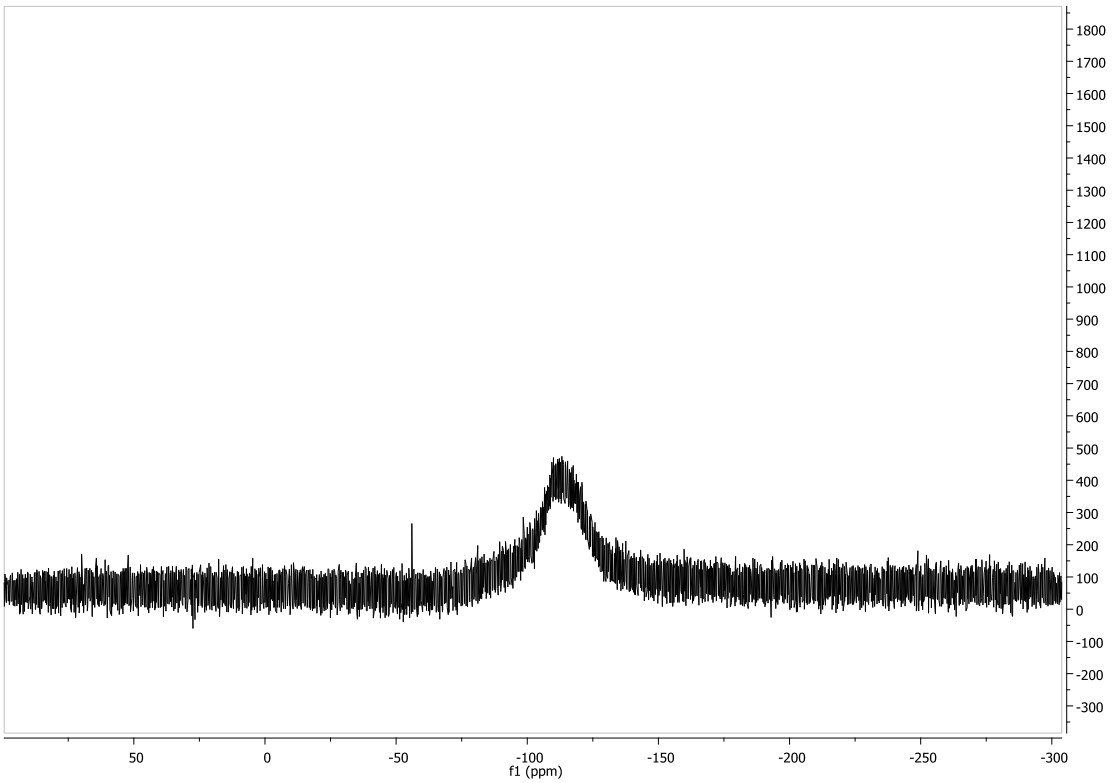
^{1}H-NMR of **5i**.



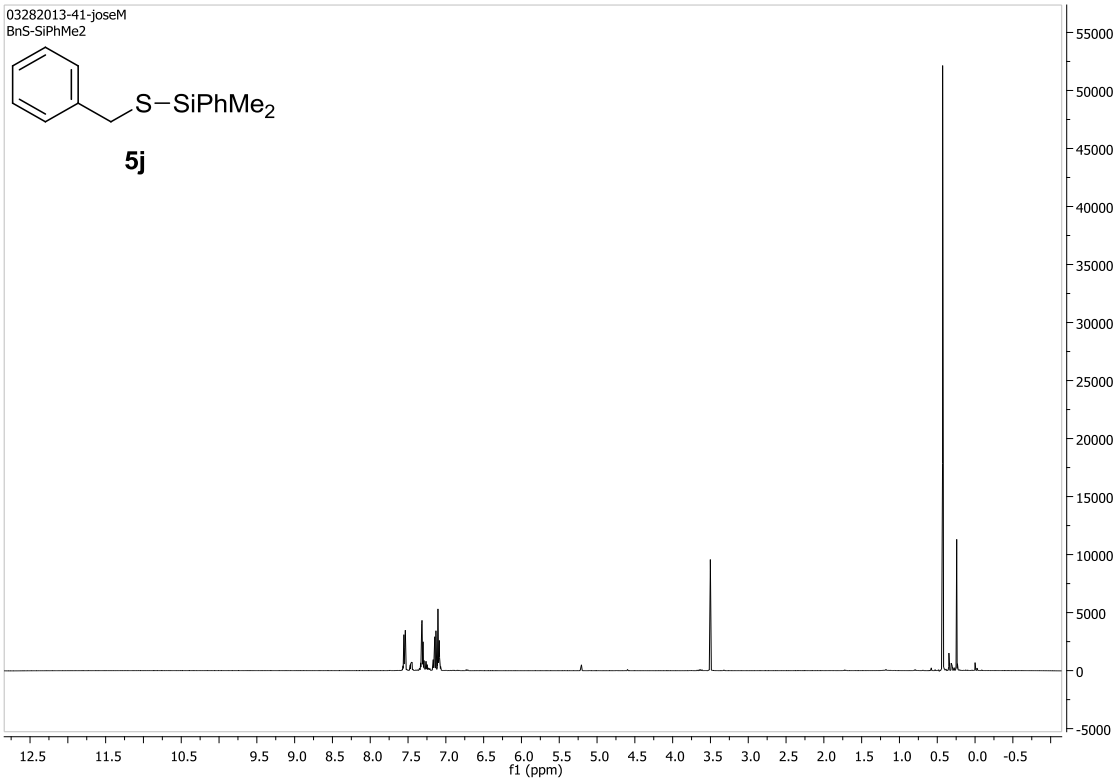
^{13}C-NMR of **5i**.



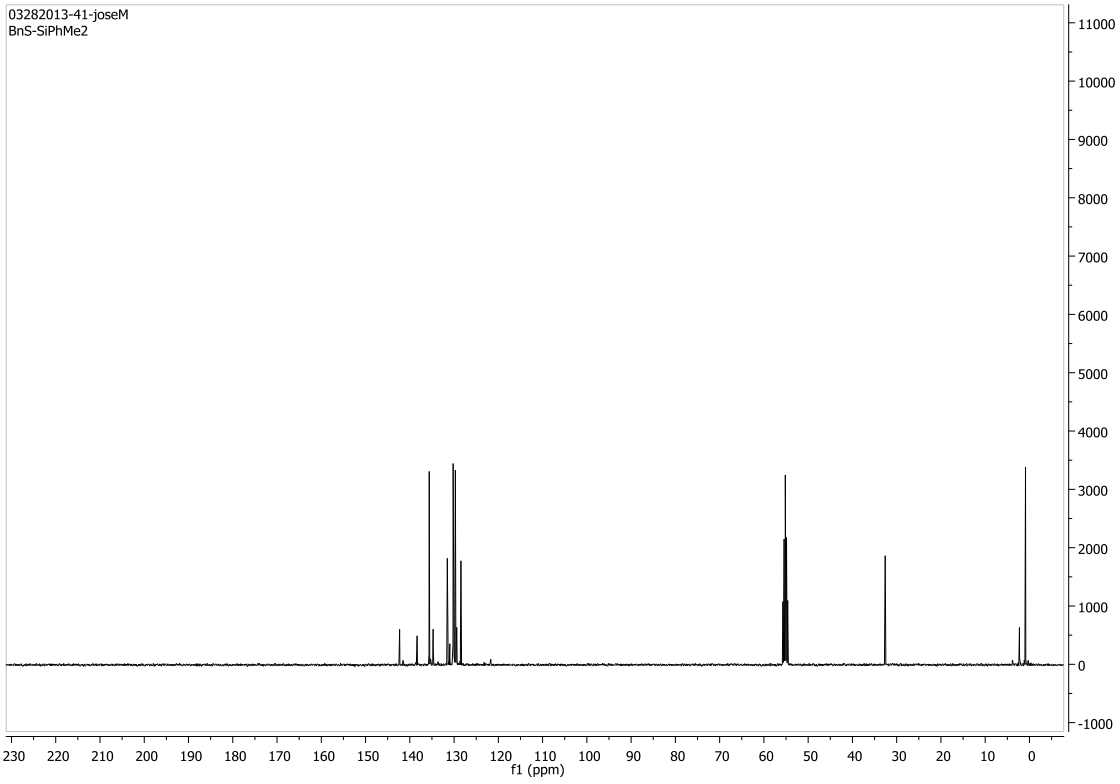
^{29}Si-NMR of **5i**.



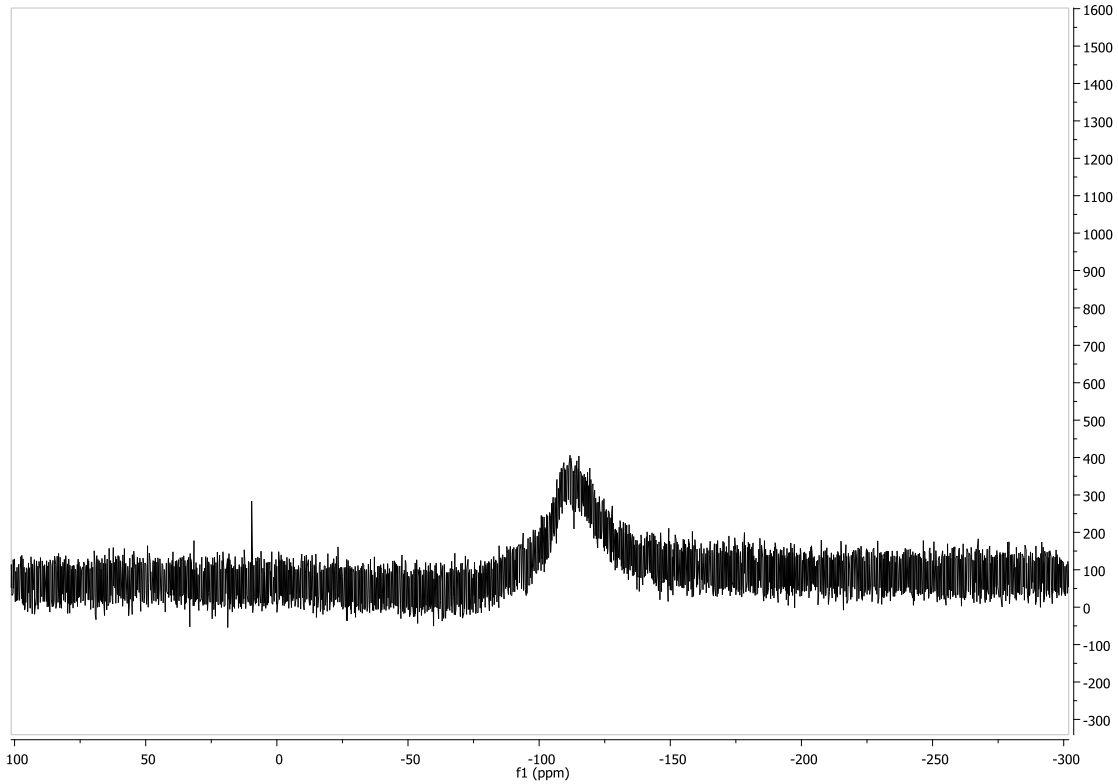
^{1}H-NMR of **5j**.



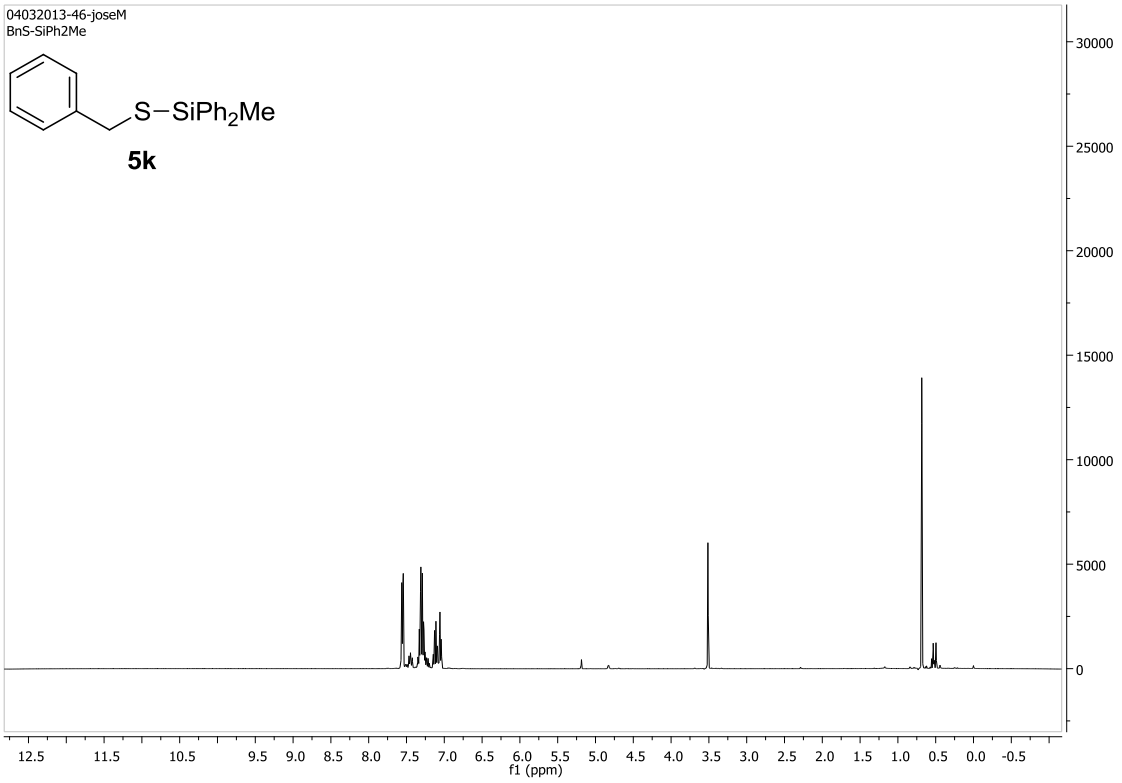
^{13}C-NMR of **5j**.



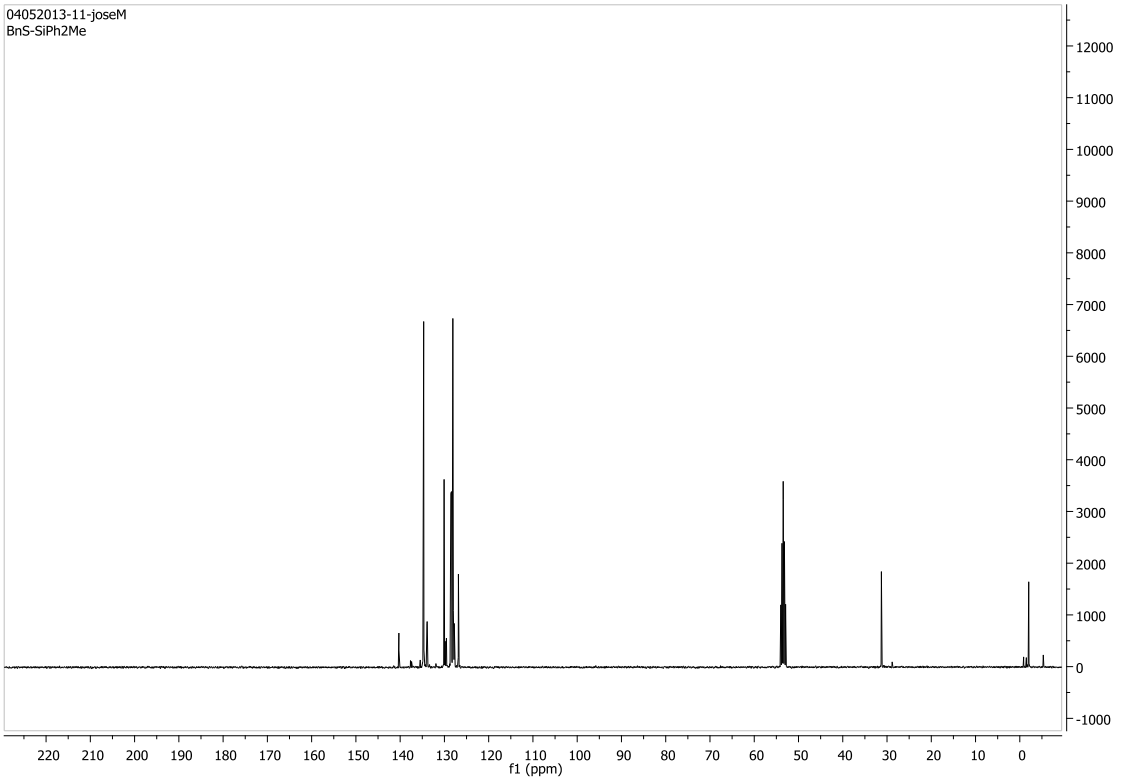
^{13}C-NMR of **5j**.


1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

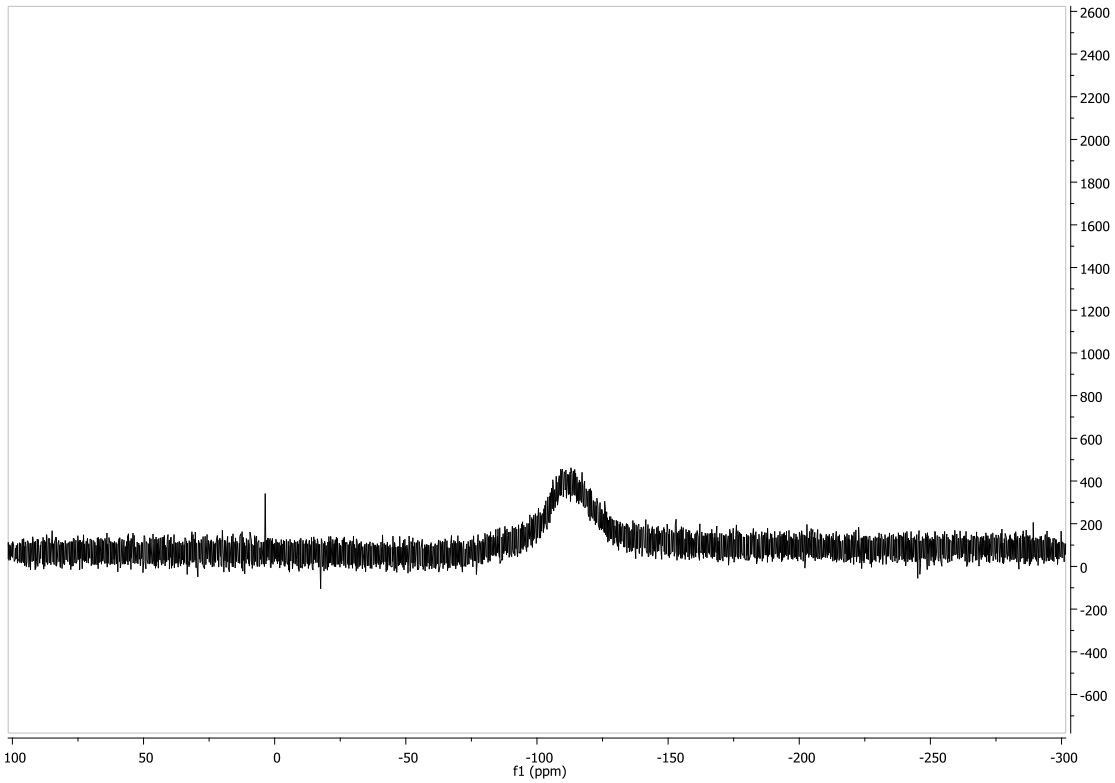
^{1}H-NMR of **5k**.



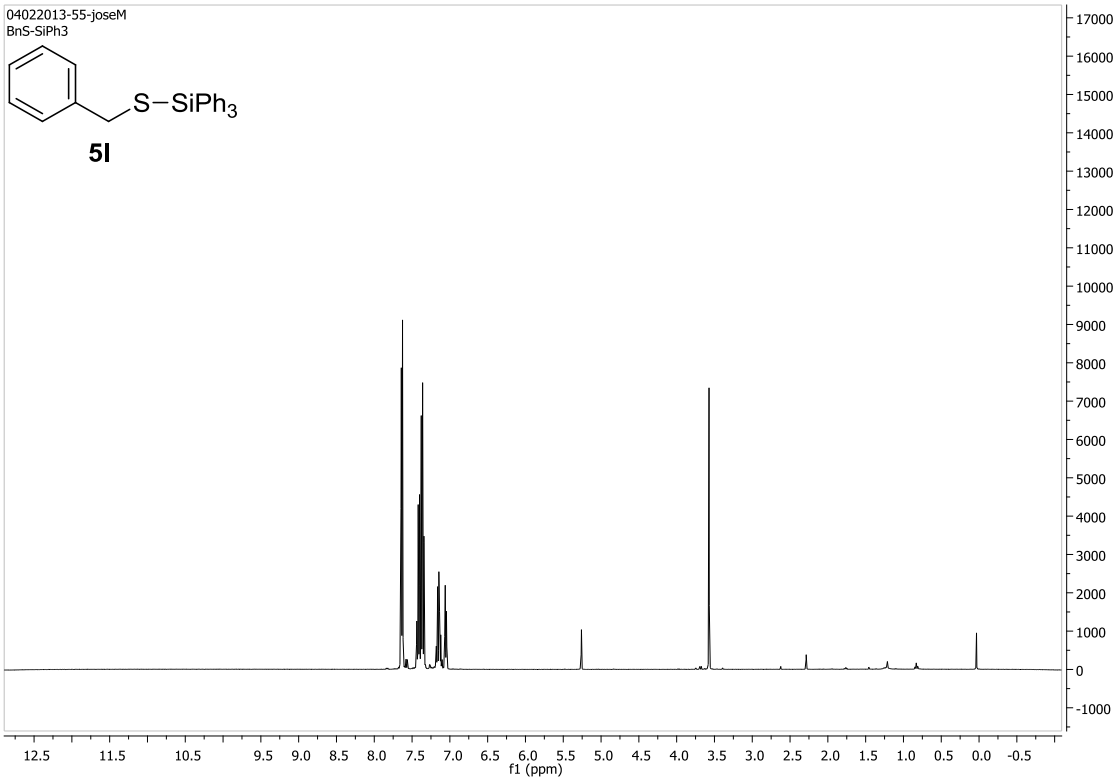
^{13}C-NMR of **5k**.



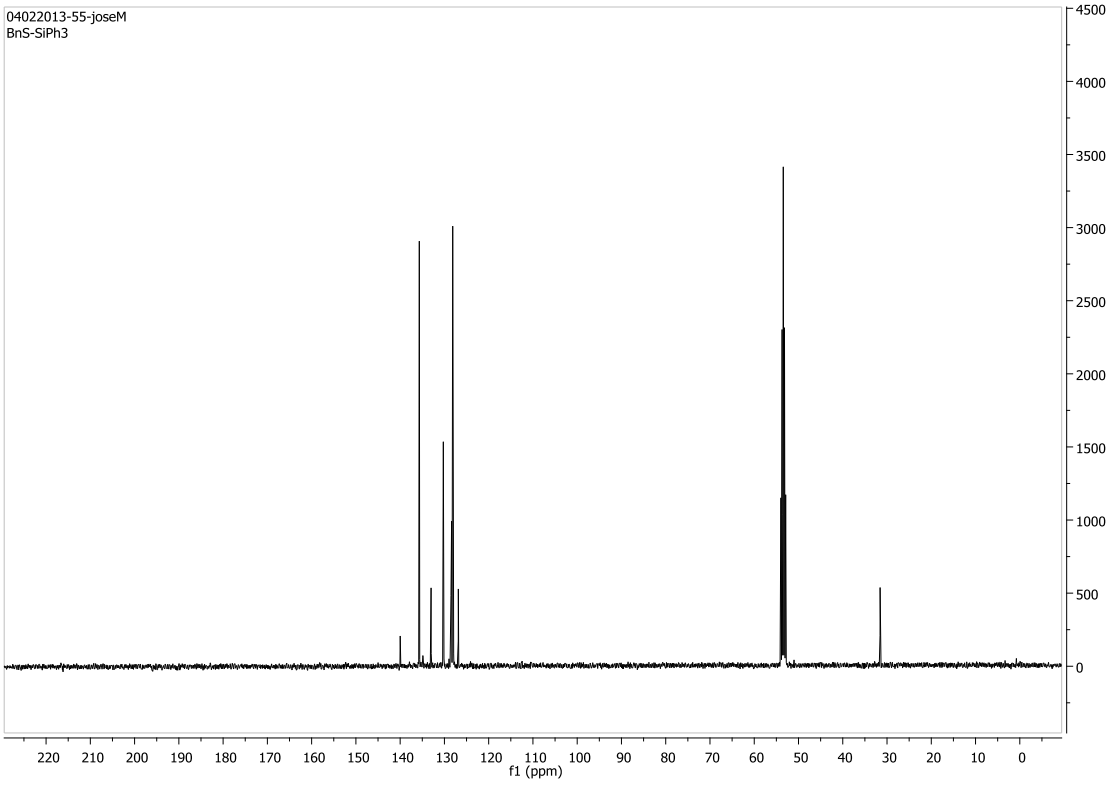
^{29}Si-NMR of **5k**.



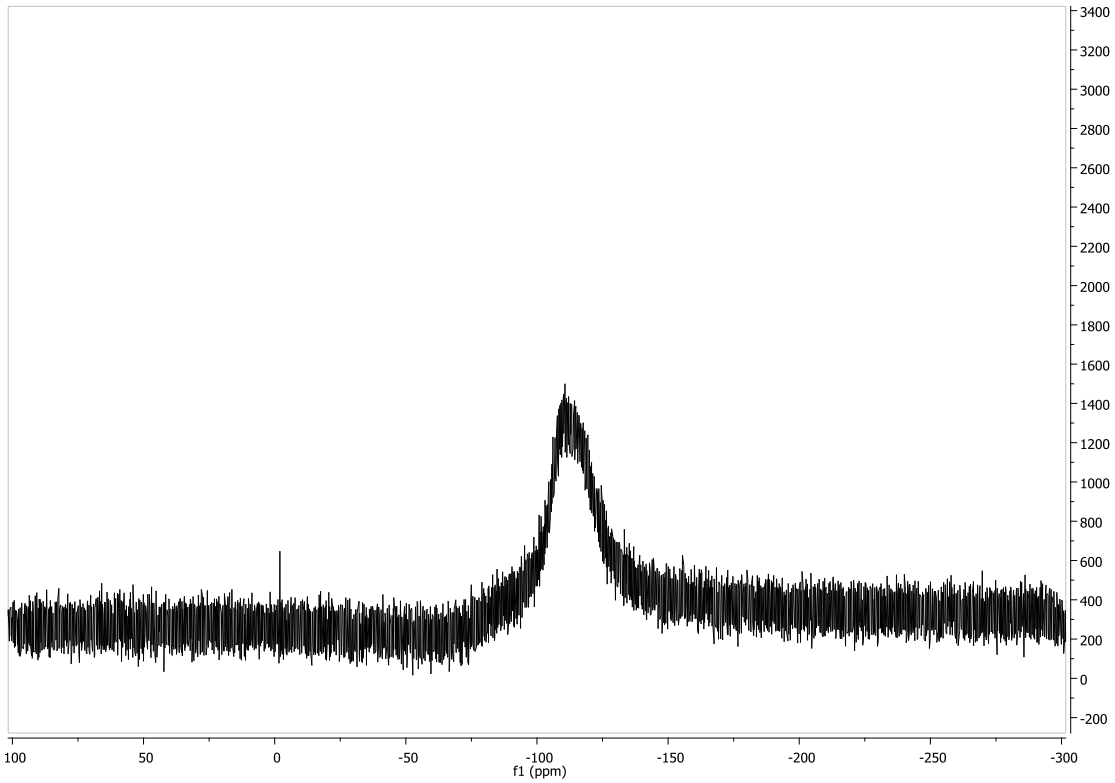
^{1}H-NMR of **5l**.



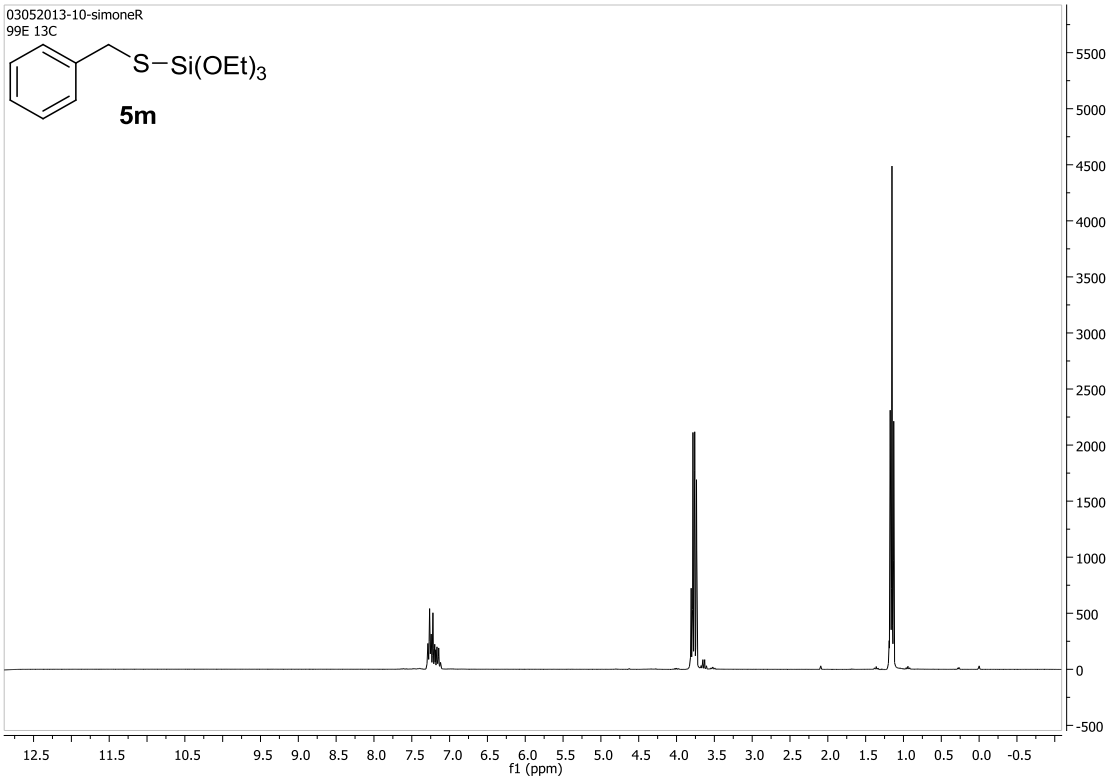
^{13}C-NMR of **5l**.



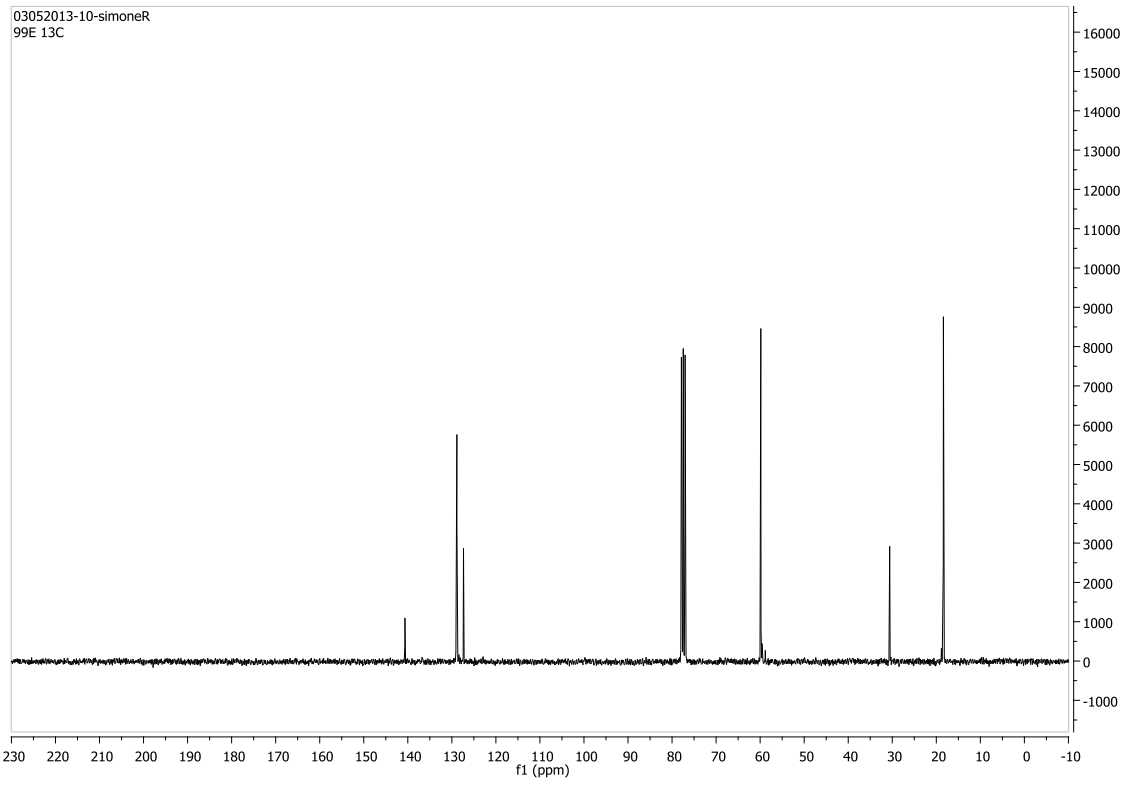
^{29}Si-NMR of **5l**.



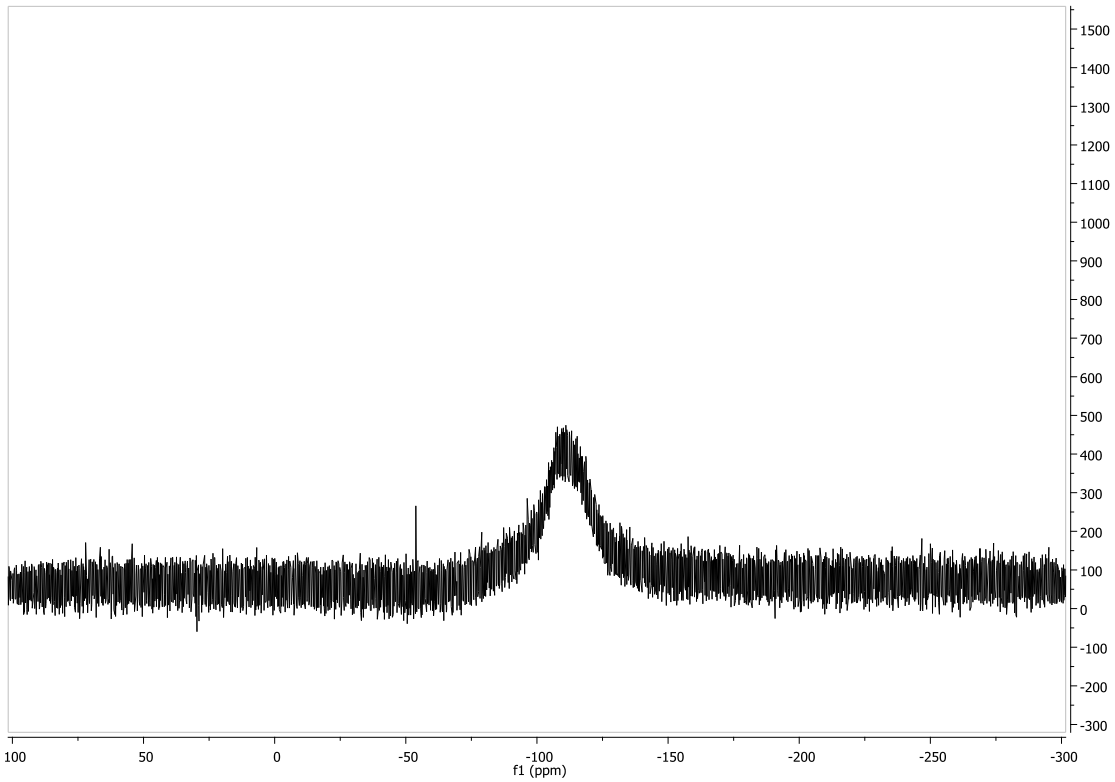
^{1}H-NMR of **5m**.



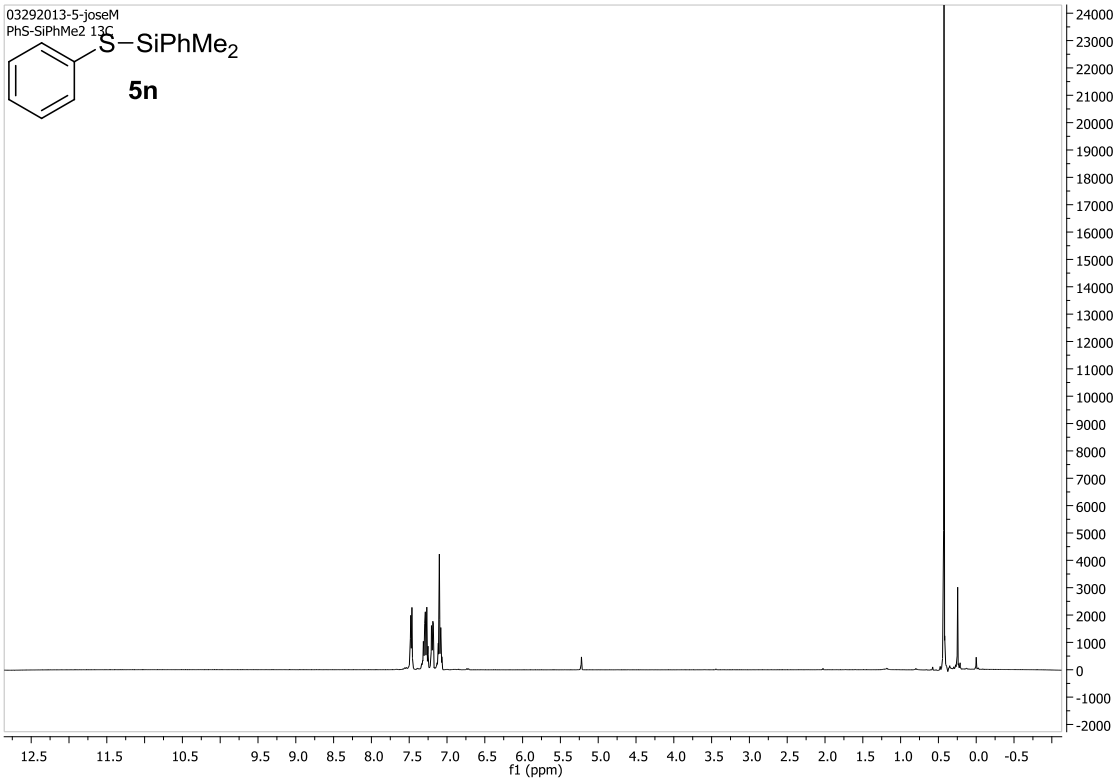
^{13}C-NMR of **5m**.



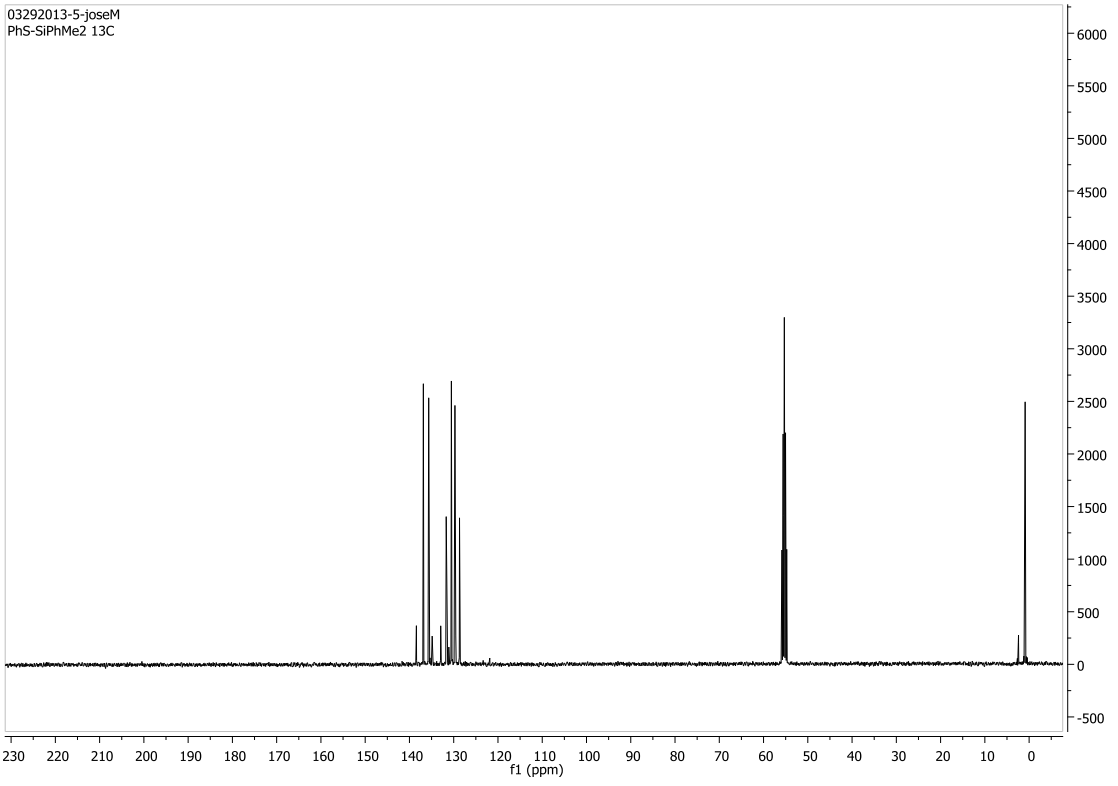
^{29}Si-NMR of **5m**.



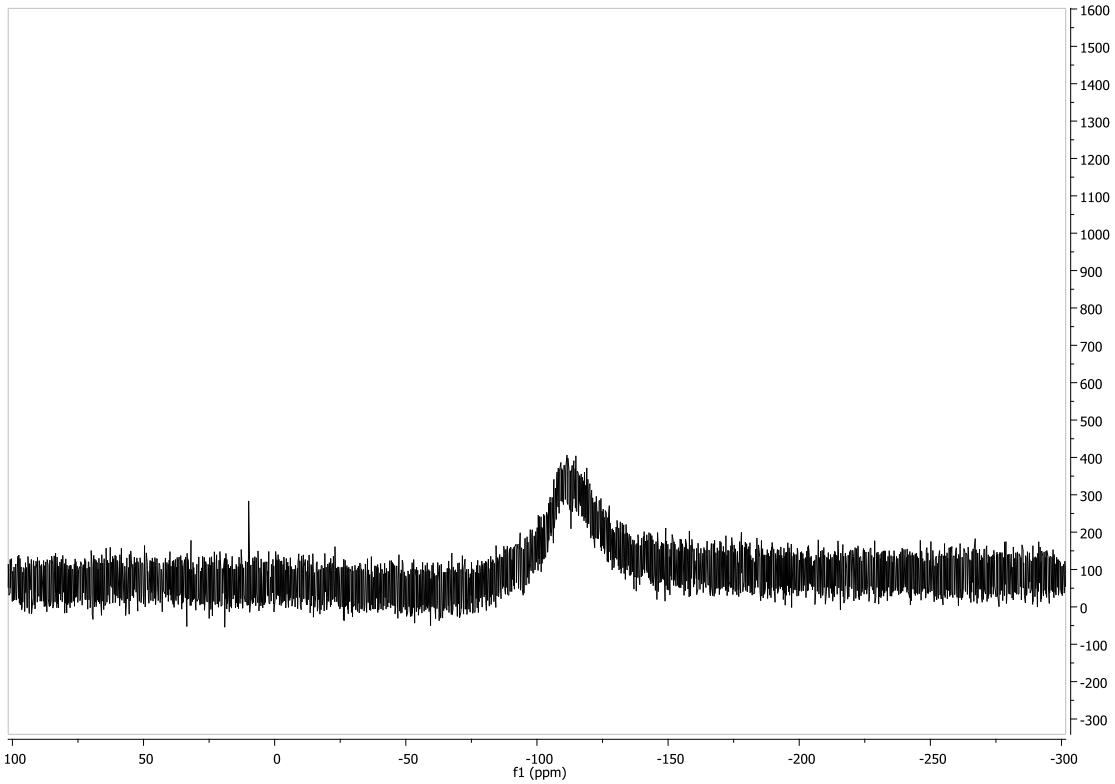
^{1}H-NMR of **5n**.



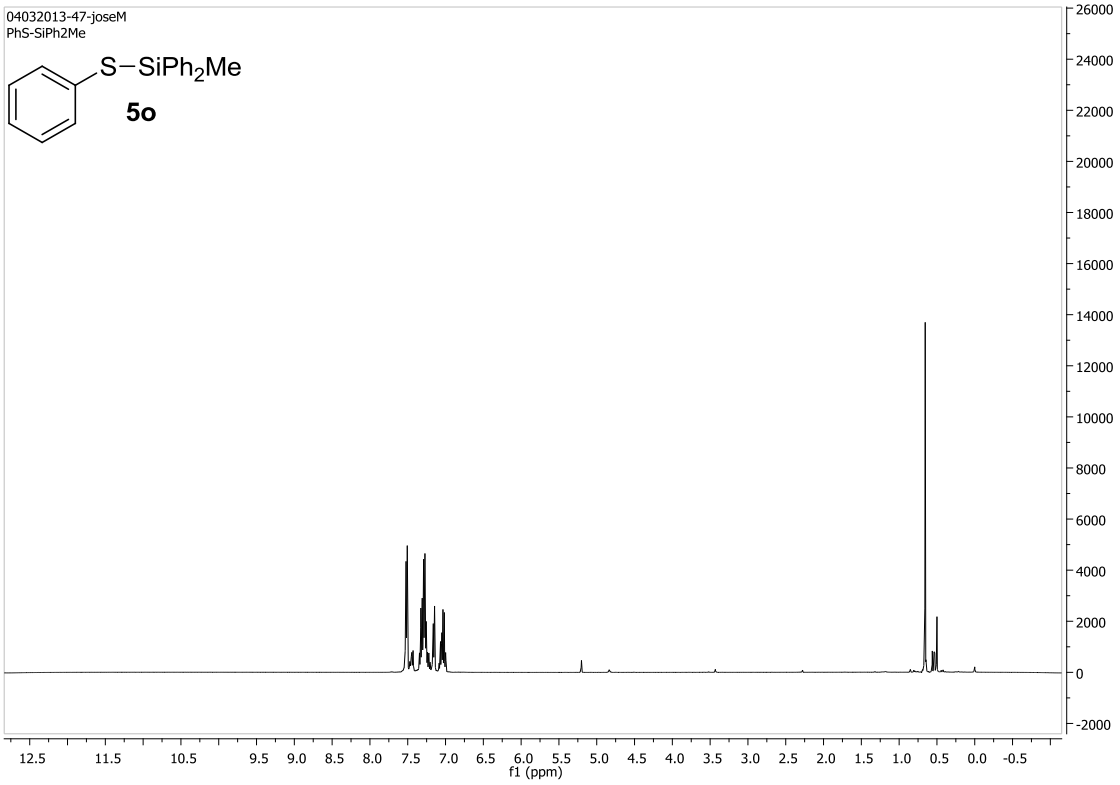
^{13}C-NMR of **5n**.



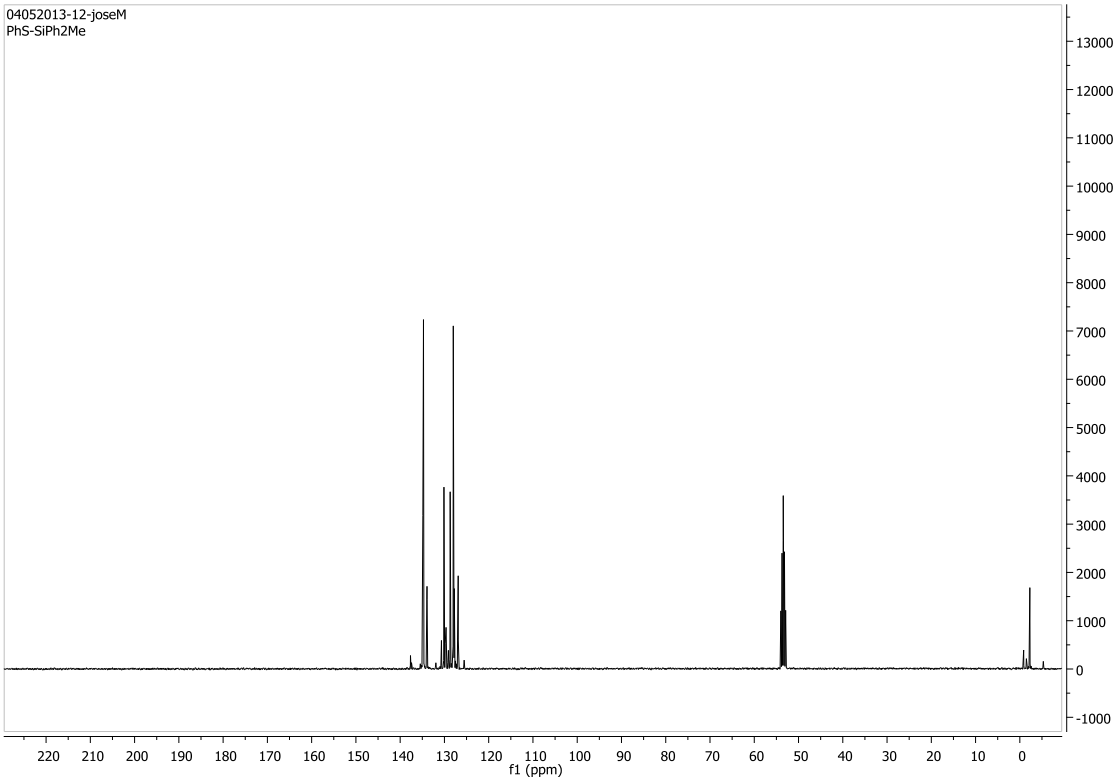
^{29}Si-NMR of **5n**.



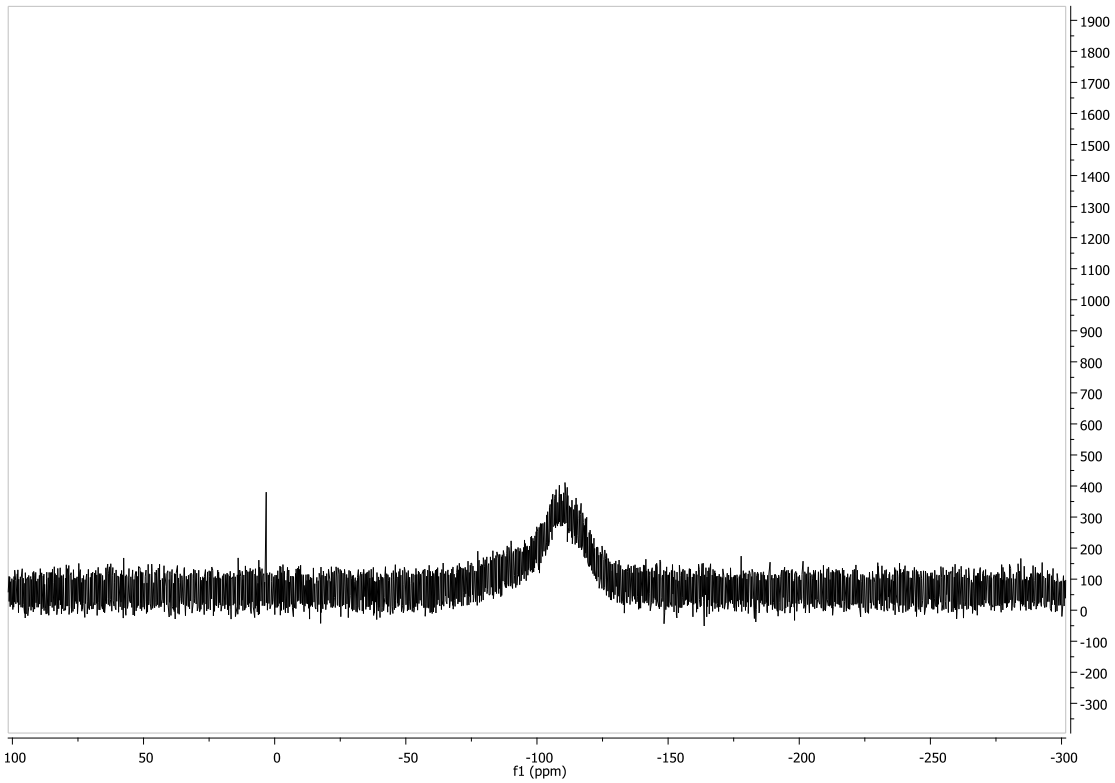
^{1}H-NMR of **5o**.



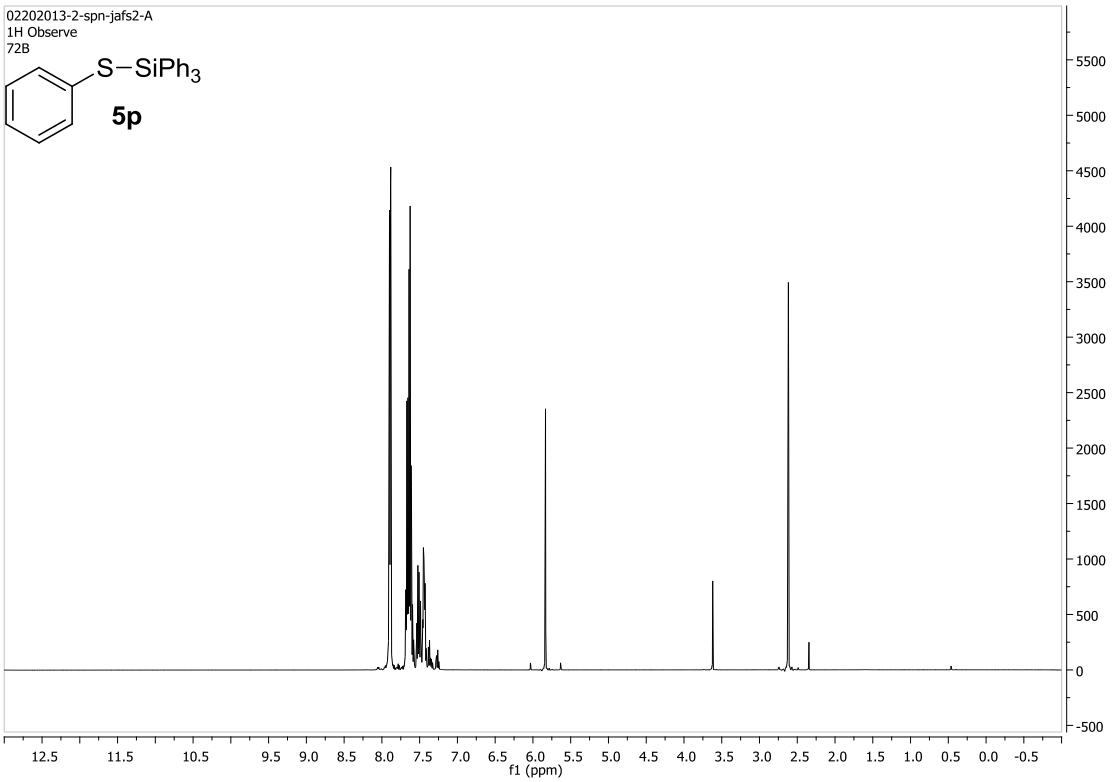
^{13}C-NMR of **5o**.



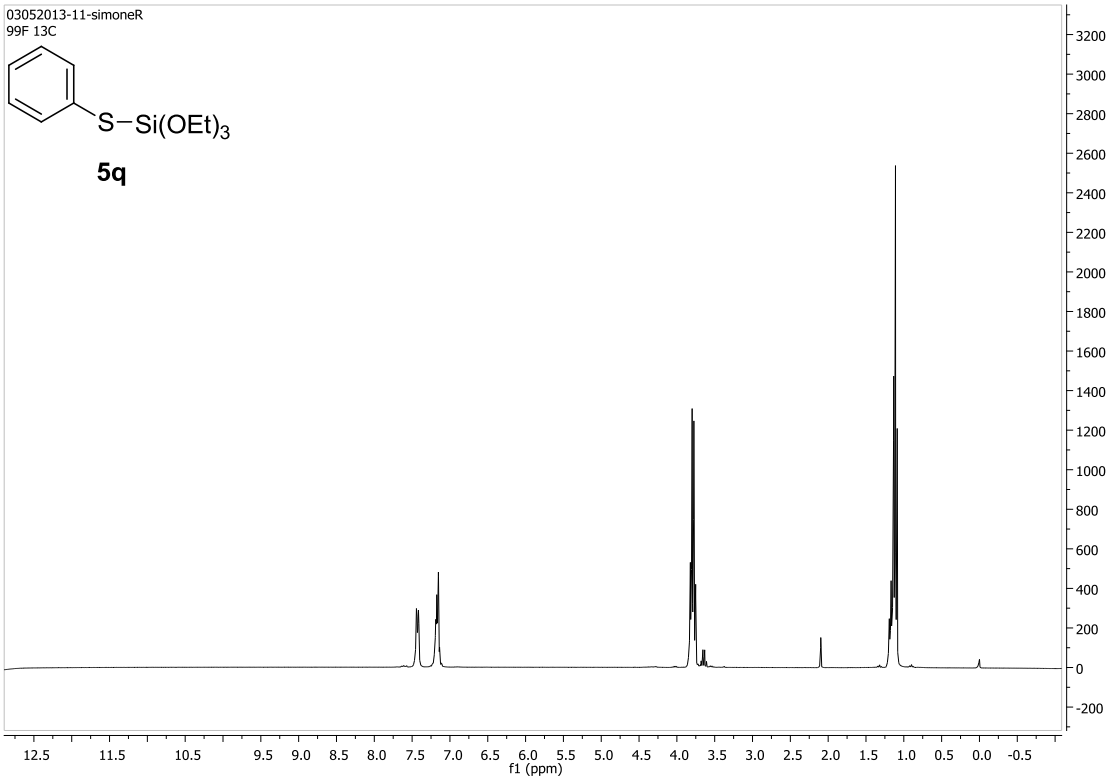
^{29}Si-NMR of **5o**.



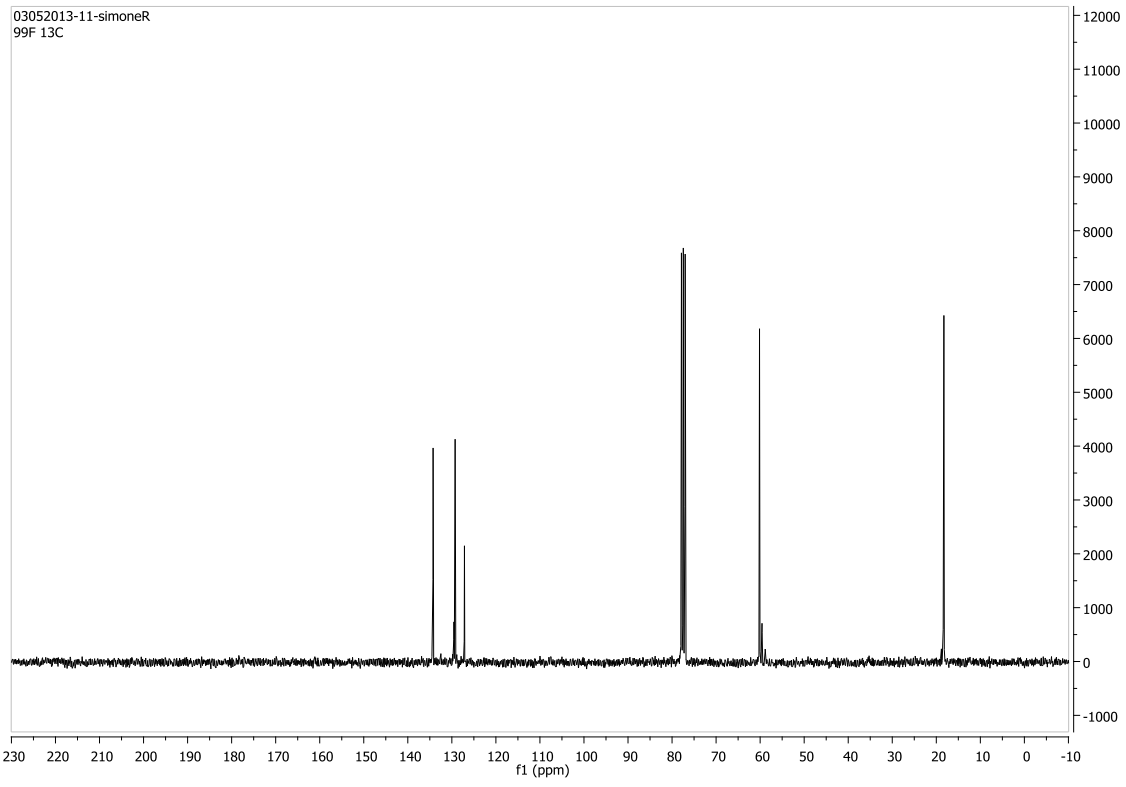
^{1}H-NMR of **5p**.


02202013-2-spn-jafs2-A
1H Observe
72B
S−SiPh3
5p
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

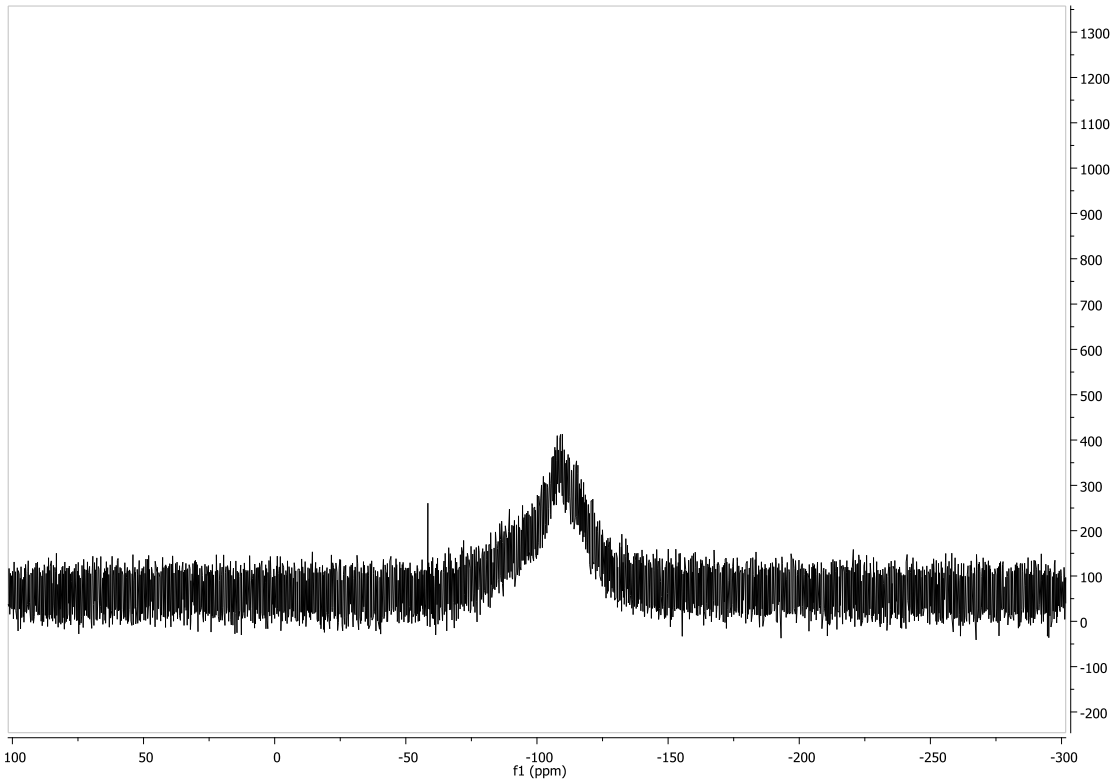
^{1}H-NMR of **5q**.



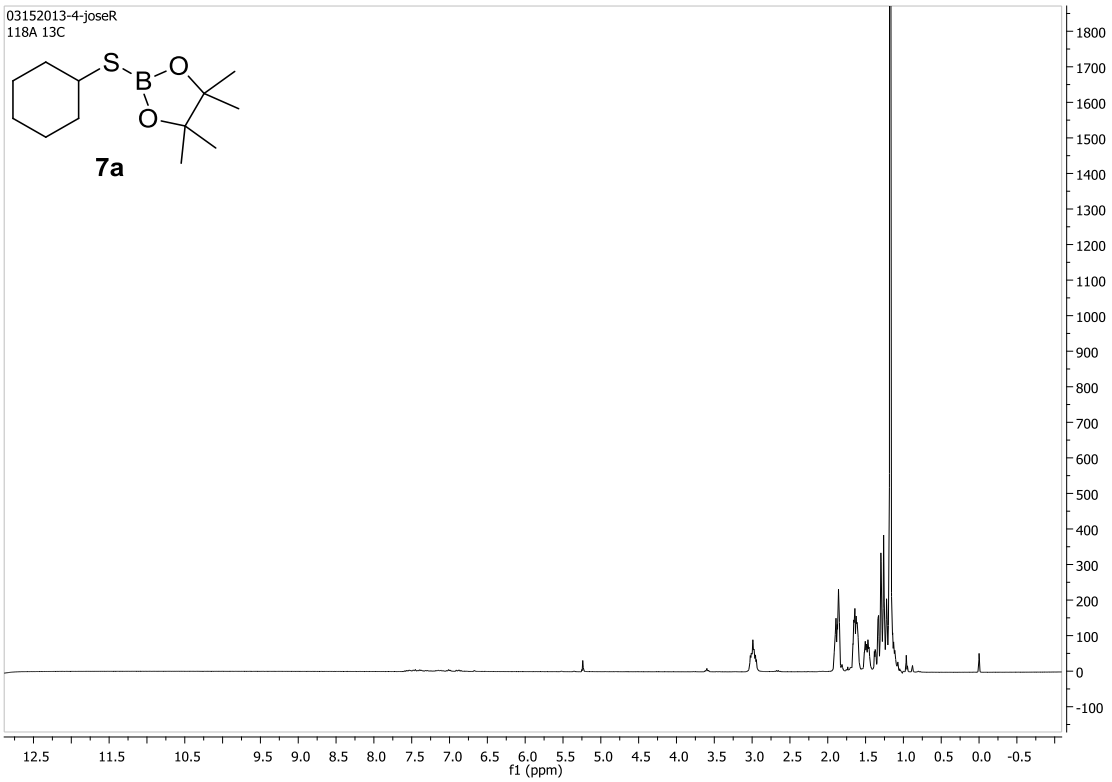
^{13}C-NMR of **5q**.



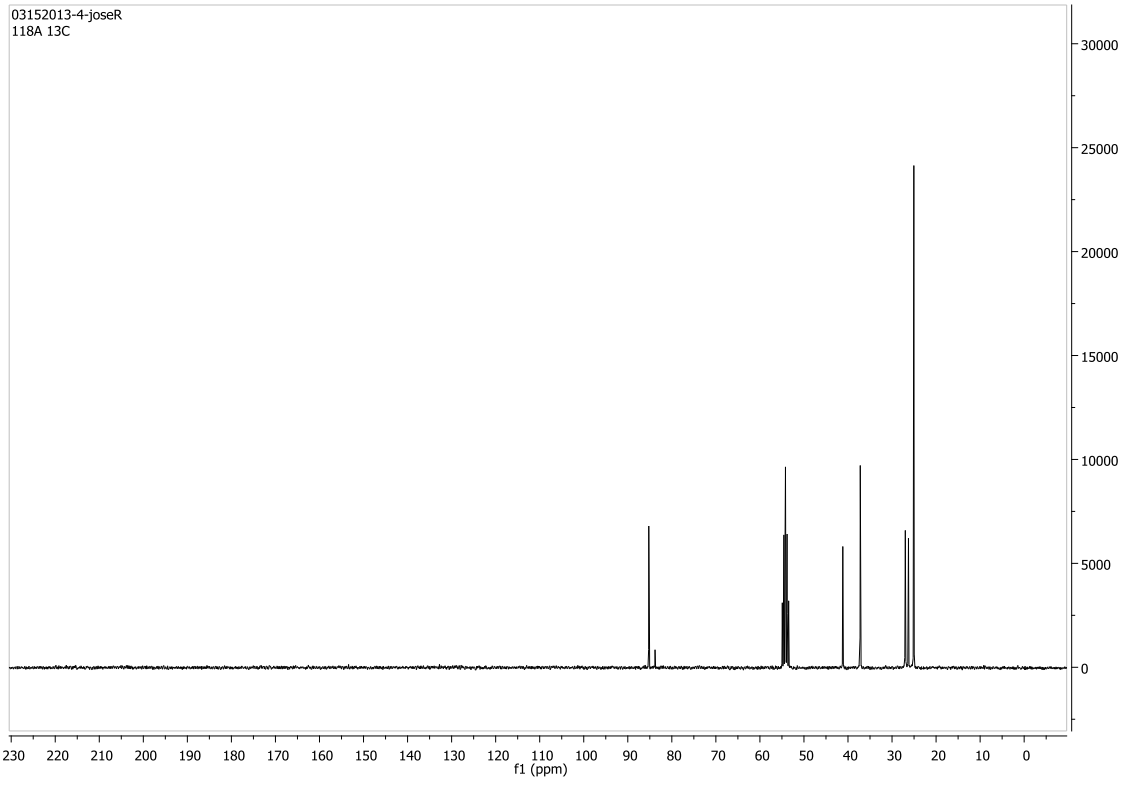
^{29}Si-NMR of **5q**.



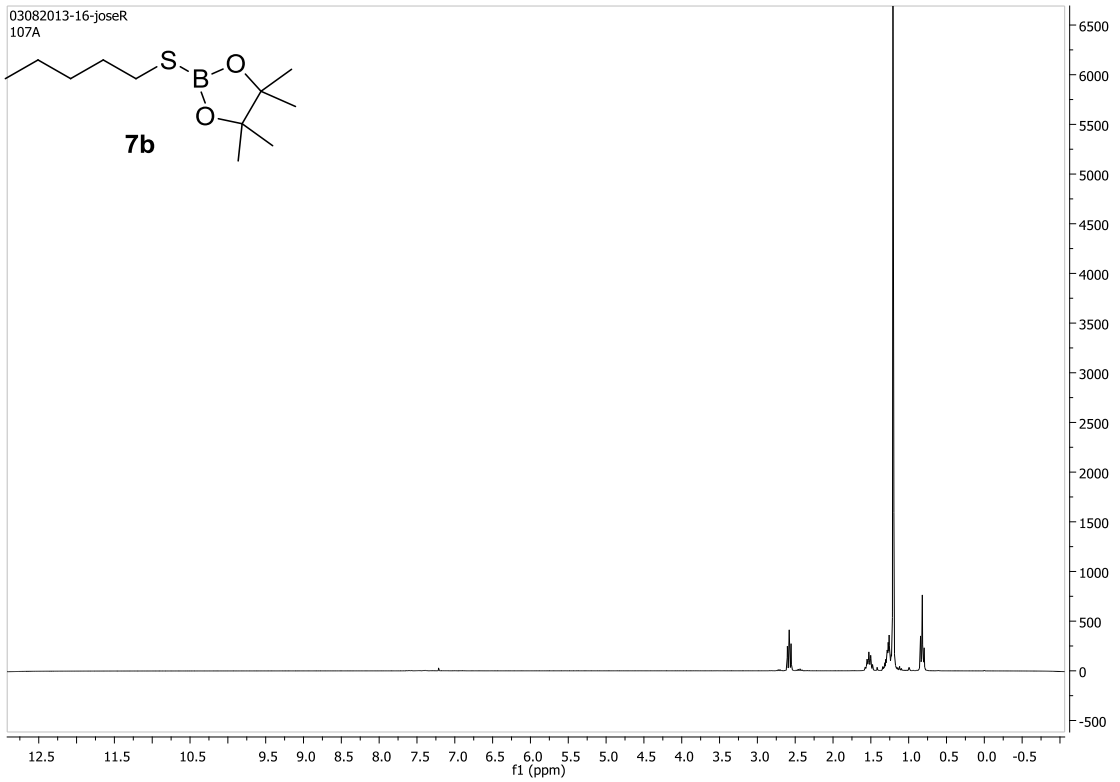
^{1}H-NMR of **7a**.



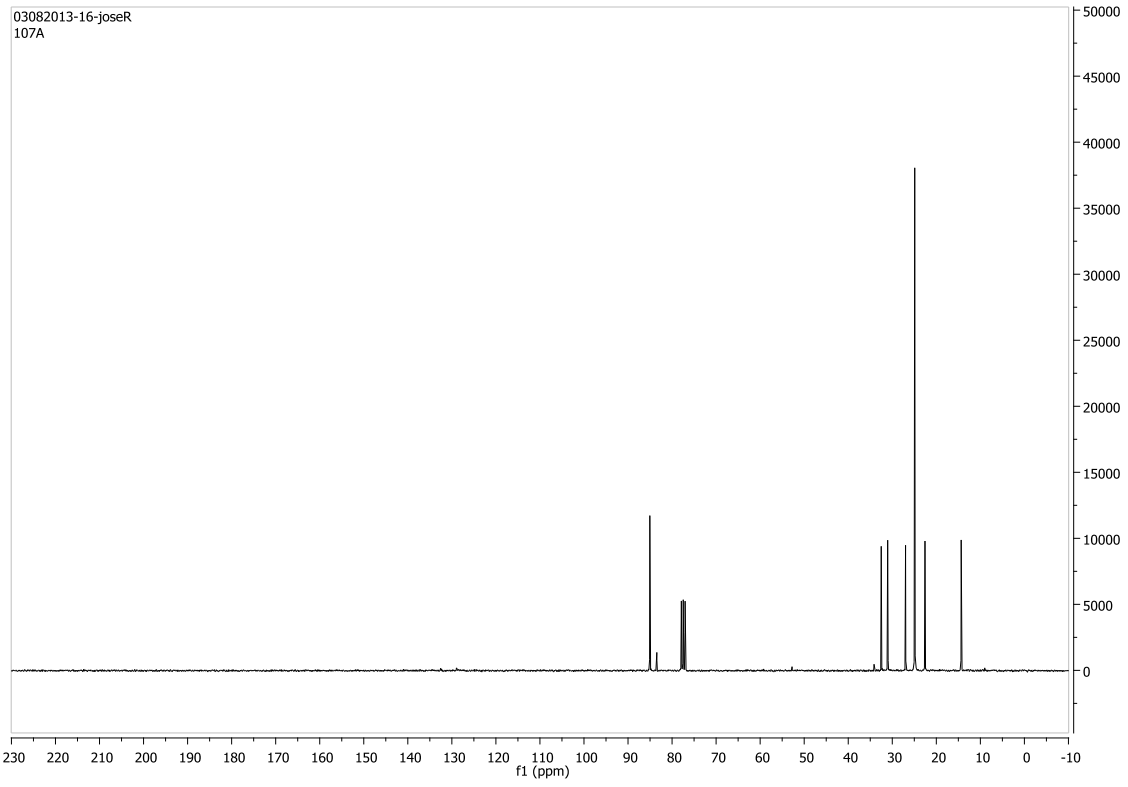
^{13}C-NMR of **7a**.



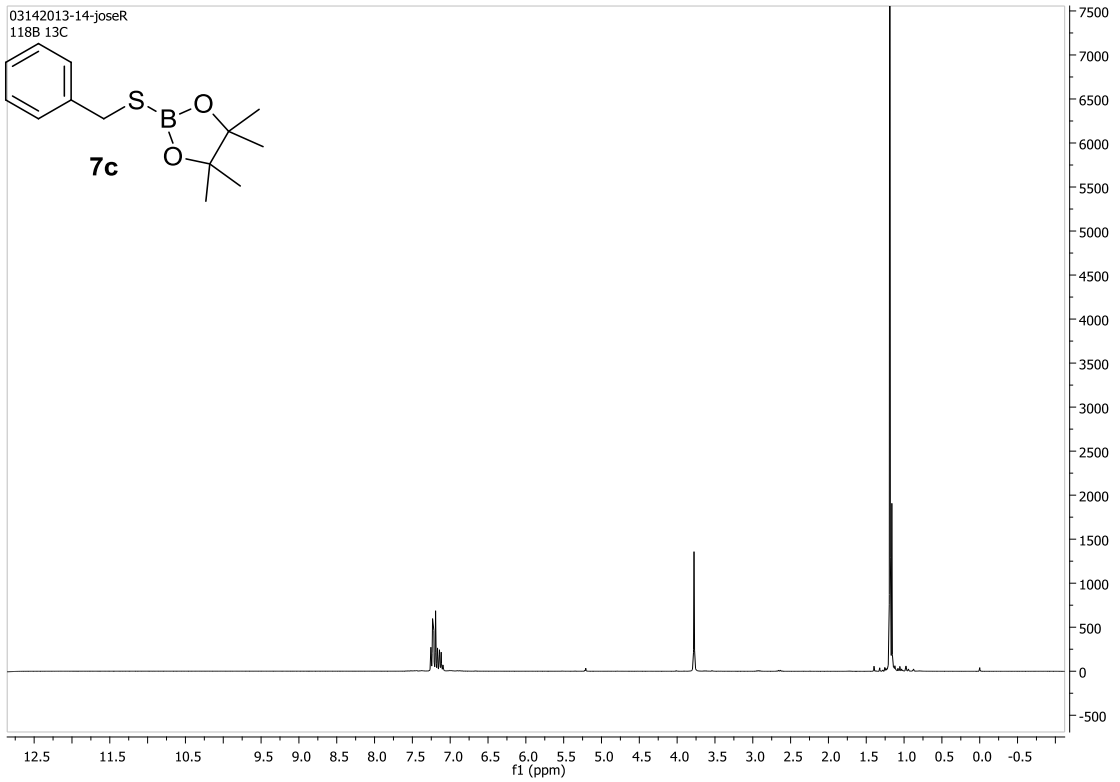
^{1}H-NMR of **7b**.



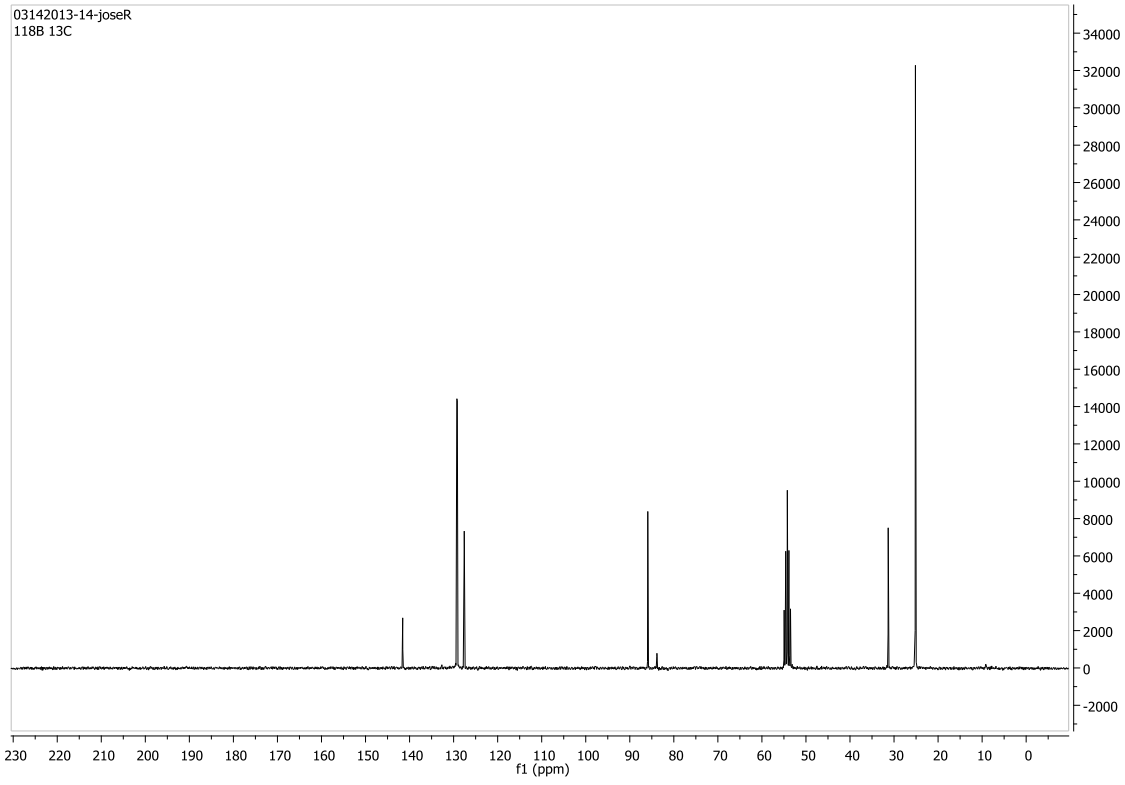
^{13}C-NMR of **7b**.



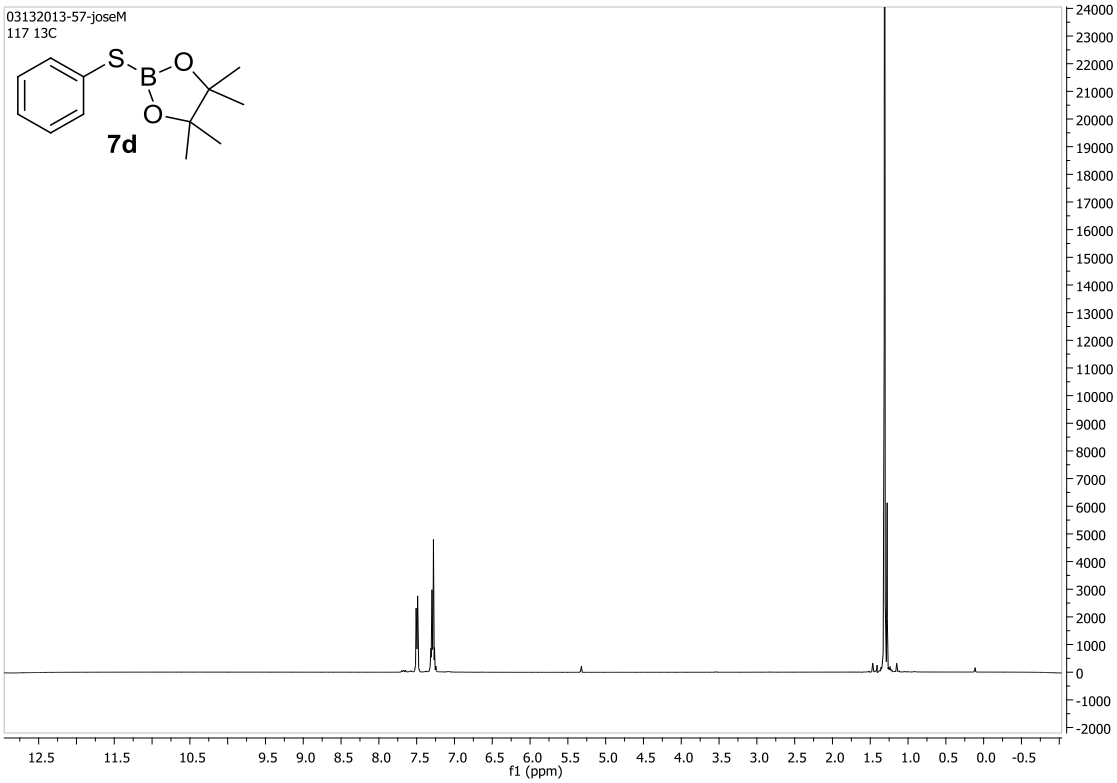
^{1}H-NMR of **7c**.



^{13}C-NMR of **7c**.



^{1}H-NMR of **7d**.



^{13}C-NMR of **7d**.