Electronic Supplementary Information

The synthesis, characterization, and theoretical analysis of novel *Si*-substituted silylethyl derivatives of 2-mercaptobenzoxazole and 2-mercaptobenzothiazole

Olga Trofimova,* Ekaterina Grebneva, Yuliya Bolgova, Elena Belogolova, Artem Emel'yanov, Alexander Albanov, Tat'yana Borodina, Anastasiya Ivanova, Svetlana Korzhova, and Alexander Pozdnyakov

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy Sciences, 1 Favorsky St., 664033 Irkutsk, Russian Federation. E-mail: *omtrof@irioch.irk.ru*

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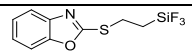
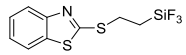
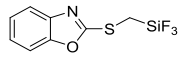
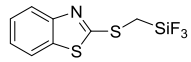
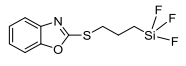
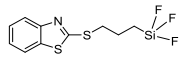
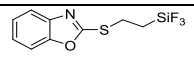
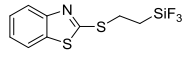
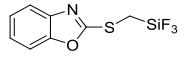
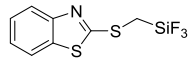
Table S1 Selected B3PW91/6-311G(d,p) and MP2/6-311G(2d,p) structural parameters[a] of the open forms of molecules **3**-**8** in the gas phase and in chloroform solution (C-PCM solvation model)

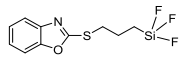
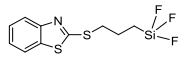
		B3PW91		MP2	
		gas	$CHCl_3$	gas	$CHCl_3$
3: 	d_{SiF}	1.597	1.600	1.580	1.583
	Δ_{Si}	0.539	0.530	0.546	0.539
	$\angle CSiF^1$	111.3	111.6	111.7	112.0
	$\angle CSiF^2$	111.3	112.5	110.7	111.6
	$\angle CSiF^3$	112.5	112.9	111.5	111.7
	$\angle CSCN$	-0.2	-1.9	-2.2	-3.2
	$\angle CCSC$	-73.8	-74.5	-73.4	-73.7
	$\angle SiCCS$	-176.2	-177.0	-178.7	-180.0
4: 	d_{SiF}	1.597	1.601	1.581	1.583
	Δ_{Si}	0.538	0.529	0.545	0.539
	$\angle CSiF^1$	111.3	111.6	111.8	112.1
	$\angle CSiF^2$	111.5	112.5	110.9	111.8
	$\angle CSiF^3$	112.4	112.9	111.4	111.6
	$\angle CSCN$	-1.2	-2.9	-4.5	-6.1
	$\angle CCSC$	-75.2	-75.7	-73.4	-73.2
	$\angle SiCCS$	-177.2	-177.5	178.7	177.6
5: 	d_{SiF}	1.595	1.596	1.578	1.579
	Δ_{Si}	0.528	0.528	0.533	0.531
	$\angle CSiF^1$	109.9	110.4	109.6	109.8
	$\angle CSiF^2$	111.8	112.4	111.5	111.8
	$\angle CSiF^3$	112.0	112.2	111.2	111.6
	$\angle CSCN$	-2.4	-3.3	-0.8	0.0
	$\angle SiCSC$	135.2	145.5	166.7	172.0
6: 	d_{SiF}	1.596	1.598	1.579	1.580
	Δ_{Si}	0.526	0.528	0.531	0.529
	$\angle CSiF^1$	109.9	110.8	109.7	110.0
	$\angle CSiF^2$	112.0	112.5	111.7	112.0
	$\angle CSiF^3$	112.1	112.2	111.2	111.6
	$\angle CSCN$	-2.8	-2.6	-1.2	-1.3
	$\angle SiCSC$	132.1	132.0	165.7	170.4
7: 	d_{SiF}	1.598	1.603	1.583	1.586
	Δ_{Si}	0.534	0.531	0.530	0.527
	$\angle CSiF^1$	111.9	112.9	111.1	111.9
	$\angle CSiF^2$	112.2	112.7	111.1	111.6
	$\angle CSiF^3$	111.6	112.2	112.2	112.6
	$\angle CSCN$	-1.1	-2.1	-2.5	-3.5
	$\angle CCSC$	-77.6	-77.7	-75.0	-74.6
	$\angle CCCS$	-63.0	-63.8	-62.6	-63.4

	∠SiCCC	-179.8	-180.0	-178.9	-179.3
8: 	d_{SiF}	1.599	1.603	1.583	1.586
	Δ_{Si}	0.534	0.531	0.530	0.527
	$\angle CSiF^1$	112.0	112.9	111.1	111.9
	$\angle CSiF^2$	112.2	112.8	111.2	111.7
	$\angle CSiF^3$	111.6	112.1	112.2	112.7
	∠CSCN	-2.2	-4.5	-5.1	-6.7
	∠CCSC	-78.3	-78.8	-74.4	-73.9
	∠CCCS	-62.6	-63.4	-62.8	-63.5
	∠SiCCC	-179.9	-179.6	-179.2	-179.0

[a] The internuclear distances (*d*, Å); bond and dihedral angles (degrees); the displacement of Si from the equatorial CFF plane (Δ_{Si}, Å). The positive sign of Δ_{Si} corresponds to its shift toward the axial atom F.

Table S2 Selected B3PW91/6-311G(d,p) and MP2/6-311G(2d,p) structural parameters[a] of the closed forms of molecules **3-8** in the gas phase and in chloroform solution (C-PCM solvation model)

		B3PW91		MP2	
		gas	$CHCl_3$	gas	$CHCl_3$
3: 	d_{SiN}	2.323	2.148	2.737	2.273
	d_{SiFax}	1.631	1.654	1.595	1.626
	η_e	83	93	52	84
	Δ_{Si}	0.228	0.142	0.381	0.223
	$\angle NSiF_{ax}$	174.8	173.2	174.4	174.2
	$\angle NSiC$	87.8	91.2	82.8	87.3
	$\angle CSiF_{ax}$	97.0	95.3	102.4	98.1
	$\angle SiNCS$	26.1	20.0	49.4	24.0
	$\angle CSiNC$	-26.4	-20.9	-50.6	-20.7
	$\angle CSCN$	16.4	19.1	4.0	15.6
	$\angle CCSC$	-67.1	-63.2	-76.9	-66.2
	$\angle SiCCS$	73.6	70.1	71.9	77.7
4: 	d_{SiN}	2.849	2.776	2.824	2.804
	d_{SiFax}	1.611	1.619	1.593	1.598
	η_e	52	59	47	50
	Δ_{Si}	0.382	0.354	0.401	0.389
	$\angle NSiF_{ax}$	172.9	171.8	173.2	172.2
	$\angle NSiC$	83.6	84.6	82.7	83.2
	$\angle CSiF_{ax}$	102.9	103.0	103.5	104.0
	$\angle SiNCS$	39.9	37.0	48.7	47.7
	$\angle CSiNC$	-44.1	-40.2	-52.1	-50.4
	$\angle CSCN$	9.9	11.4	4.5	4.9
	$\angle CCSC$	-80.9	-78.9	-80.0	-79.5
	$\angle SiCCS$	74.9	75.8	72.8	73.4
5: 	d_{SiN}	2.026	1.985	2.035	1.994
	d_{SiFax}	1.639	1.654	1.624	1.637
	η_e	95	97	93	96
	Δ_{Si}	0.130	0.097	0.149	0.117
	$\angle NSiF_{ax}$	176.3	177.6	176.0	177.1
	$\angle NSiC$	85.5	86.6	84.9	86.0
	$\angle CSiF_{ax}$	90.8	90.9	91.1	91.1
	$\angle SiNCS$	-0.1	0.0	-0.1	0.0
	$\angle CSCN$	0.0	0.0	0.0	0.0
	$\angle SiCSC$	0.1	0.0	0.1	0.0
6: 	d_{SiN}	2.060	2.013	2.066	2.021
	d_{SiFax}	1.639	1.654	1.624	1.638
	η_e	94	97	92	95
	Δ_{Si}	0.137	0.102	0.156	0.123
	$\angle NSiF_{ax}$	177.5	178.9	177.1	178.3

	∠NSiC	85.9	87.1	85.2	86.4
	∠CSiF_{ax}	91.6	91.7	91.9	91.9
	∠SiNCS	0.0	0.0	0.0	0.0
	∠CSCN	0.0	0.0	0.0	0.0
	∠SiCSC	0.1	0.1	0.0	0.0
7: 					
	d_{SiN}	3.055	3.065	2.953	2.943
	d_{SiFax}	1.609	1.613	1.593	1.597
	η_e	35	36	34	36
	Δ_{Si}	0.448	0.445	0.447	0.441
	∠NSiF_{ax}	177.2	175.6	177.2	176.0
	∠NSiC	74.7	75.3	75.0	75.7
	∠CSiF_{ax}	108.1	109.0	107.7	108.3
	∠SiNCS	18.6	21.9	28.0	31.0
	∠CSCN	13.6	12.2	10.7	9.3
	∠CCSC	-92.8	-93.0	-92.8	-92.5
	∠CCCS	68.5	67.9	66.0	65.2
	∠SiCCC	67.4	67.6	70.1	70.1
	∠CSiNC	22.2	19.1	14.1	11.5
8: 					
	d_{SiN}	3.314	3.311	3.100	3.090
	d_{SiFax}	1.606	1.610	1.591	1.594
	η_e	25	26	28	29
	Δ_{Si}	0.479	0.476	0.468	0.463
	∠NSiF_{ax}	176.6	175.5	176.5	175.4
	∠NSiC	72.0	73.1	74.5	75.1
	∠CSiF_{ax}	109.6	110.5	108.7	109.3
	∠SiNCS	21.3	28.6	35.2	38.9
	∠CSCN	14.6	10.5	9.6	7.3
	∠CCSC	-98.6	-98.2	-97.2	-96.4
	∠CCCS	69.2	68.1	64.6	64.0
	∠SiCCC	72.5	72.7	74.0	73.7
	∠CSiNC	17.7	11.6	5.2	2.4

[a] The internuclear distances (d, Å); bond and dihedral angles (degrees); the pentacoordinate character of the Si atom (η_e, %); the displacement of Si from the equatorial CFF plane (Δ_{Si}, Å). Positive sign of Δ_{Si} corresponds to its shift toward the axial atom F.

Table S3 NBO and AIM charges on the Si and N atoms of molecules **3-8** in chloroform

	AIM q_{Si}, e	NBO q_{Si}, e	AIM q_N, e	NBO q_N, e
3	3.17	2.43	-1.19	-0.69
4	3.18	2.47	-1.13	-0.63
5	3.20	2.39	-1.32	-0.73
6	3.19	2.39	-1.31	-0.71
7	3.18	2.47	-1.11	-0.64
8	3.18	2.47	-1.12	-0.61

[a] Results at C-PCM MP2/6-311G(2d,p) geometry.

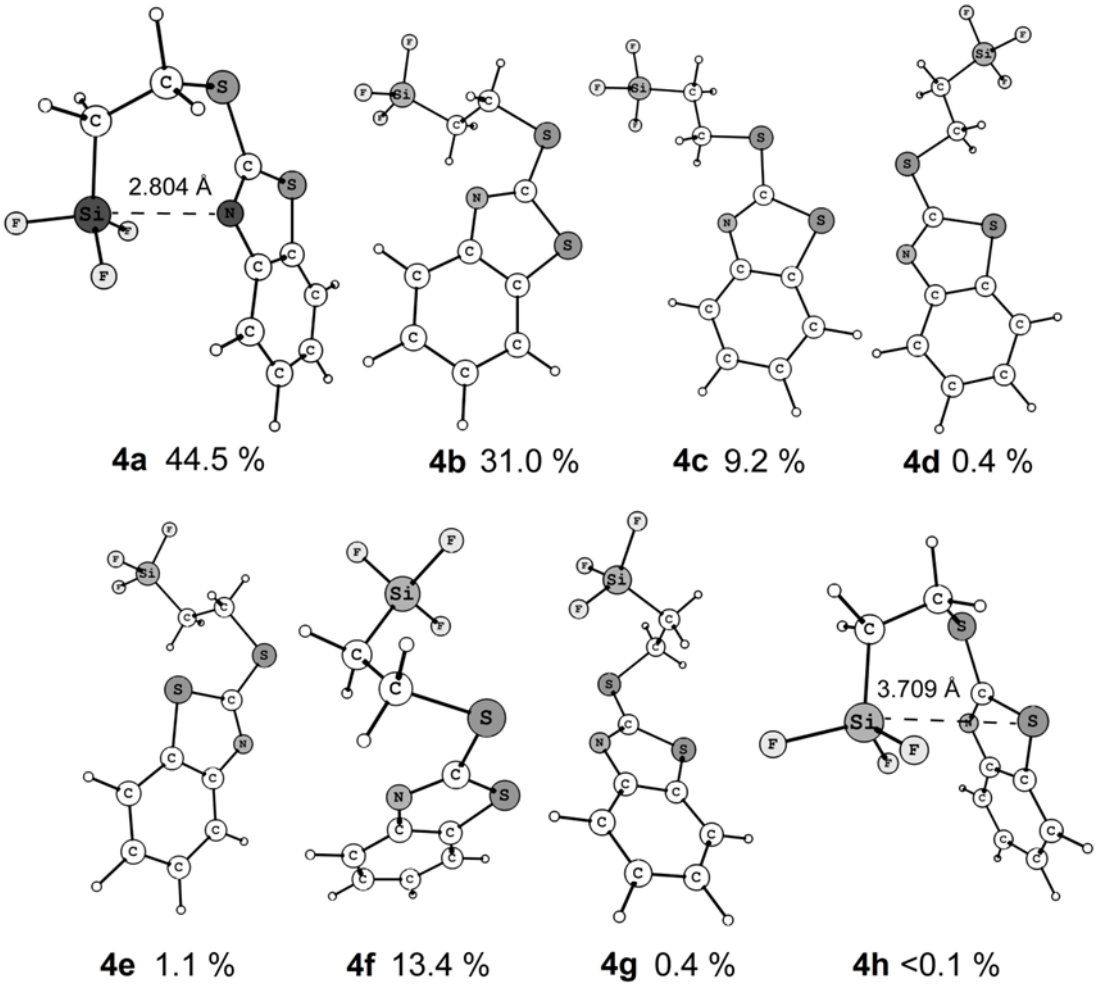


Fig. S1 The open and closed forms of **4** in chloroform with the molar fraction of each as calculated at the C-PCM MP2/6-311G(2d,p) theory level.

Table S4 Crystallographic data for compounds **9** and **10**

Compound	**9**	**10**
Empirical formula	$C_{15}H_{20}N_2O_4SSi$	$C_{15}H_{20}N_2O_3S_2Si$
Formula mass [g/mol]	352.48	368.54
Temperature [K]	100(2)	100(2)
Crystal sistem	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c
a [Å]	13.936(8)	13.187(5)
b [Å]	7.336(4)	10.587(4)
c [Å]	15.771(8)	13.213(5)
α [°]	90	90
β [°]	95.94(3)	117.361(16)
γ [°]	90	90
V [Å^3]	1603.7(15)	1638.4(10)
Z	4	4
$D_{calcd.}$ [g·cm^{-3}]	1.460	1.494
μ [mm^{-1}]	0.298	0.414
θ range [°]	2.60–28.00	2.59–27.99
Reflections collected	44273	47504
Independent reflections	3854 [R_{int} = 0.0435]	3929 [R_{int} = 0.0295]
R_1, wR_2 [$I > 2\sigma(I)$]	0.0286, 0.0750	0.0239, 0.0644
R_1, wR_2 (all data)	0.0332, 0.0783	0.0254, 0.0656
Completeness [%]	99.7	99.5
Crystal size [mm]	0.42×0.17×0.14	0.43×0.34×0.24
Goodness of fit	1.067	1.102

Table S5 Selected bond lengths (*d*, Å) and angles (ω, °) in the crystal structures of **9** and **10**

9		**10**	
	d		*d*
Si(1)–N(1)	2.146(1)	Si(1)–N(1)	2.122(1)
Si(1)–C(15)	1.893(2)	Si(1)–C(15)	1.891(1)
Si(1)–O(1)	1.670(1)	Si(1)–O(1)	1.672(1)
Si(1)–O(2)	1.671(1)	Si(1)–O(2)	1.678(1)
Si(1)–O(3)	1.670(1)	Si(1)–O(3)	1.671(1)
N(1)–C(4)	1.475(2)	N(1)–C(4)	1.479(1)
N(1)–C(5)	1.478(2)	N(1)–C(5)	1.475(2)
N(1)–C(6)	1.473(2)	N(1)–C(6)	1.481(2)
C(15)–C(14)	1.522(2)	C(14)–C(15)	1.525(2)
S(1)–C(14)	1.827(2)	S(1)–C(14)	1.822(1)
S(1)–C(7)	1.727(1)	S(1)–C(7)	1.737(2)
N(2)–C(7)	1.299(2)	C(7)–N(2)	1.301(2)
O(4)–C(7)	1.379(2)	C(7)–S(2)	1.760(1)
O(4)–C(9)	1.385(2)	S(2)–C(9)	1.742(1)
N(2)–C(8)	1.407(2)	N(2)–C(8)	1.398(2)
C(8)–C(9)	1.390(2)	C(8)–C(9)	1.409(2)
O(1)–C(1)	1.424(2)	O(1)–C(1)	1.420(1)
O(2)–C(2)	1.426(2)	O(2)–C(2)	1.419(1)
O(3)–C(3)	1.428(2)	O(3)–C(3)	1.421(2)
C(1)–C(4)	1.519(2)	C(1)–C(4)	1.526(2)
C(2)–C(5)	1.517(2)	C(2)–C(5)	1.524(2)
C(3)–C(6)	1.520(2)	C(3)–C(6)	1.522(2)
ΔSi	0.186	ΔSi	0.181
ΔN	0.382	ΔN	0.382
11		**12**	
	ω		ω
N(1)–Si(1)–C(15)	179.61(5)	N(1)–Si(1)–C(15)	177.94(5)
O(1)–Si(1)–O(2)	118.18(5)	O(2)–Si(1)–O(1)	117.60(4)
O(1)–Si(1)–O(3)	118.57(5)	O(3)–Si(1)–O(1)	118.60(5)
O(2)–Si(1)–O(3)	119.57(5)	O(3)–Si(1)–O(2)	120.32(4)
O(1)–Si(1)–N(1)	83.43(4)	O(1)–Si(1)–N(1)	83.83(4)
O(2)–Si(1)–N(1)	83.50(4)	O(2)–Si(1)–N(1)	83.89(4)
O(3)–Si(1)–N(1)	83.87(4)	O(3)–Si(1)–N(1)	83.64(4)
O(1)–Si(1)–C(15)	96.21(5)	O(1)–Si(1)–C(15)	95.71(5)
O(2)–Si(1)–C(15)	96.54(5)	O(2)–Si(1)–C(15)	98.10(5)
O(3)–Si(1)–C(15)	96.44(5)	O(3)–Si(1)–C(15)	94.84(5)
Si(1)–O(1)–C(1)	122.12(8)	Si(1)–O(1)–C(1)	122.94(8)
Si(1)–O(2)–C(2)	121.79(8)	Si(1)–O(2)–C(2)	122.29(8)
Si(1)–O(3)–C(3)	121.61(8)	Si(1)–O(3)–C(3)	122.86(7)
Si(1)–C(15)–C(14)	111.33(8)	Si(1)–C(15)–C(14)	115.04(8)
S(1)–C(14)–C(15)	111.34(9)	S(1)–C(14)–C(15)	108.10(8)
C(7)–S(1)–C(14)	98.50(6)	C(7)–S(1)–C(14)	100.86(5)

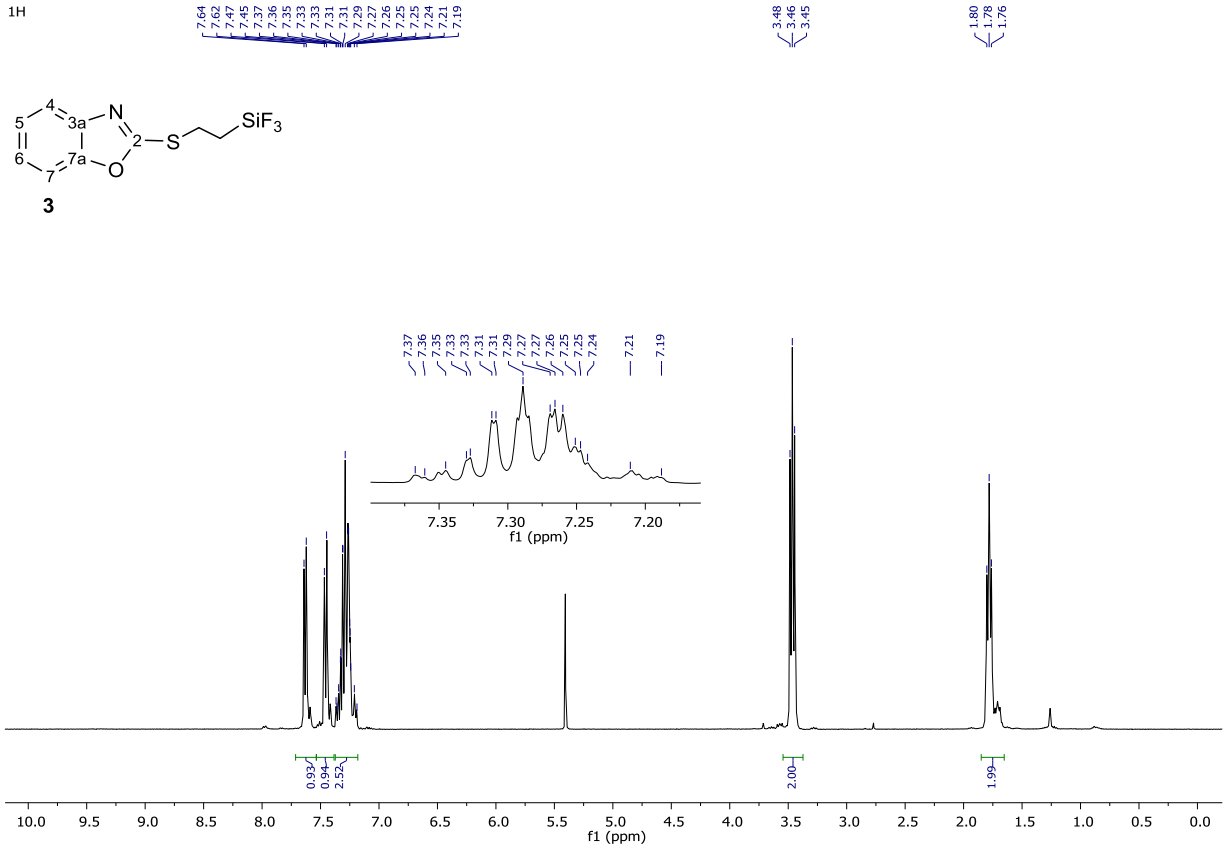


Fig. S2 ^{1}H NMR (400.13 MHz, $CDCl_3$) of compound **3**.

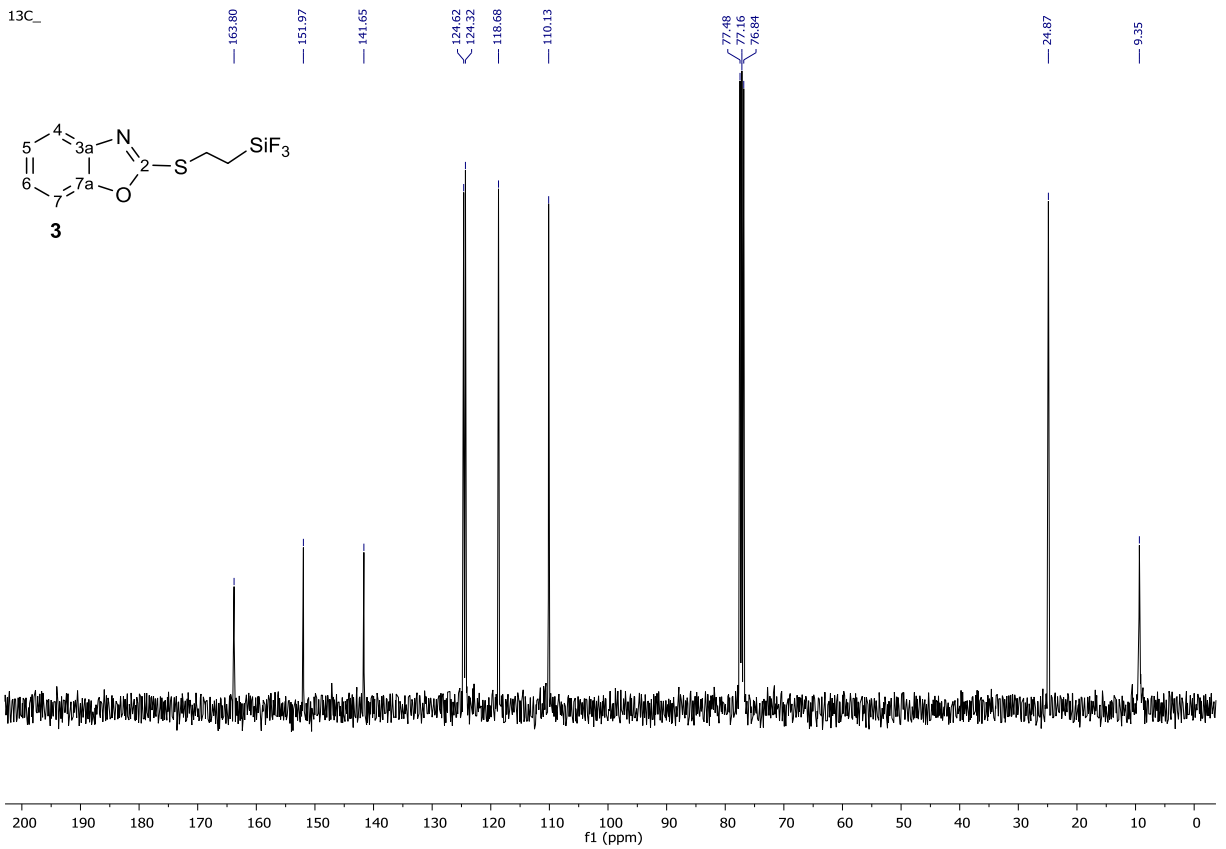


Fig. S3 ^{13}C NMR (100.62 MHz, $CDCl_3$) of compound **3**.

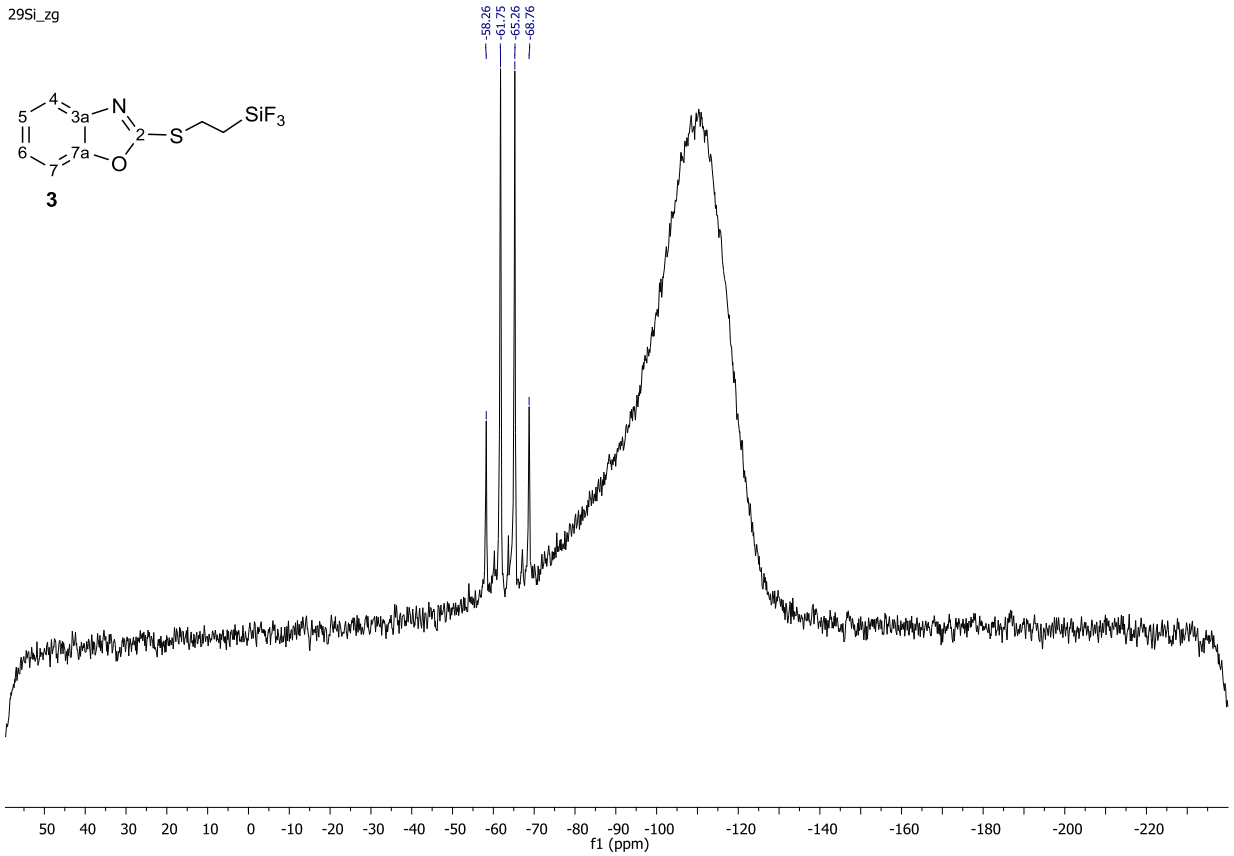


Fig. S4 ^{29}Si NMR (79.50 MHz, $CDCl_3$) of compound **3**.

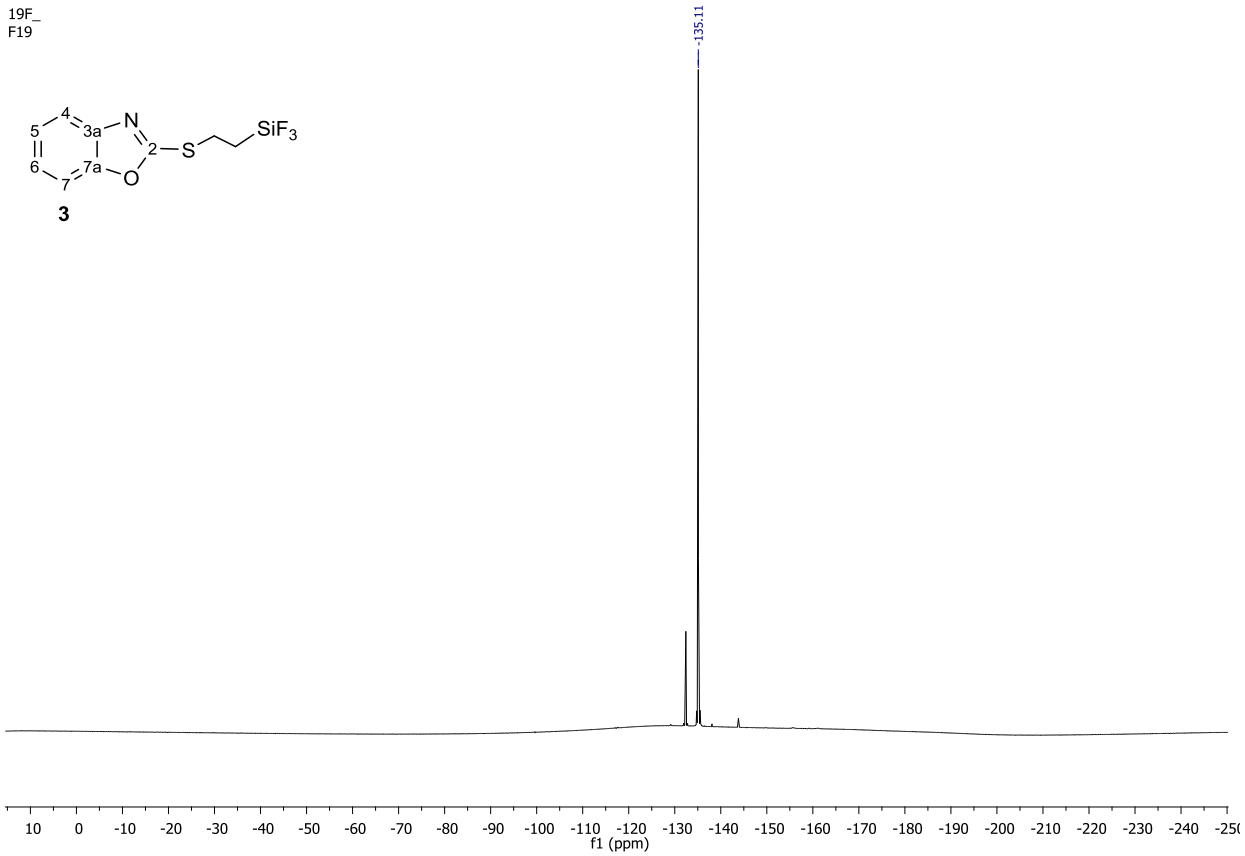


Fig. S5 ^{19}F NMR (376.50 MHz, $CDCl_3$) of compound **3**.

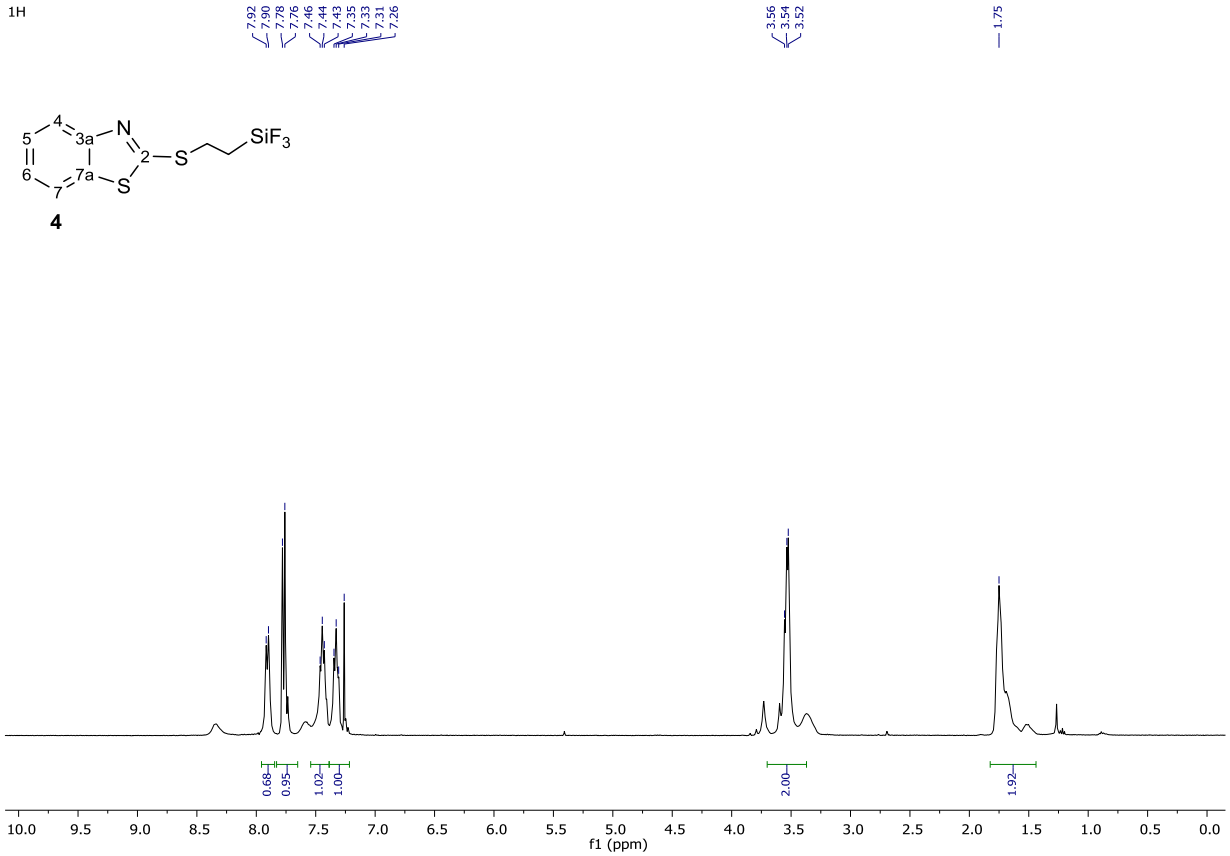


Fig. S6 ^{1}H NMR (400.13 MHz, $CDCl_3$) of compound **4**.

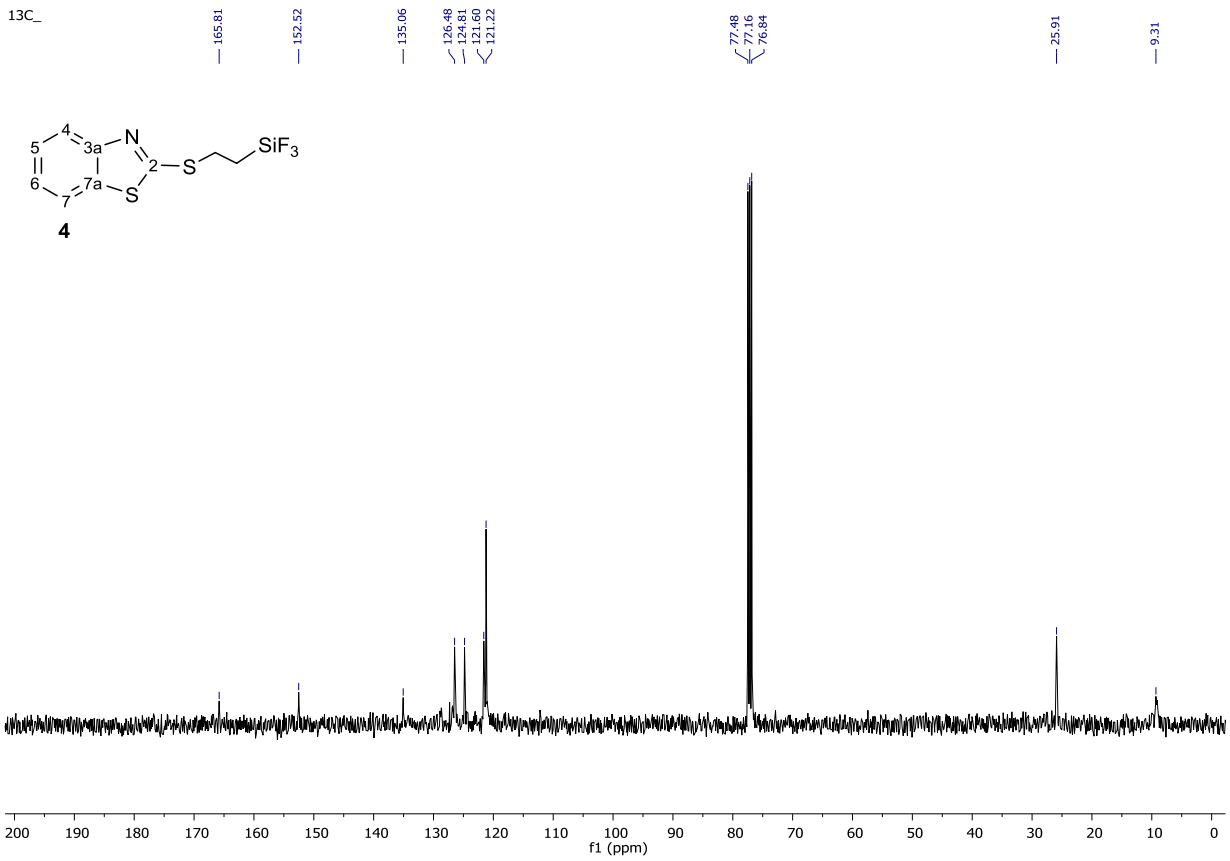


Fig. S7 ^{13}C NMR (100.62 MHz, $CDCl_3$) of compound **4**.

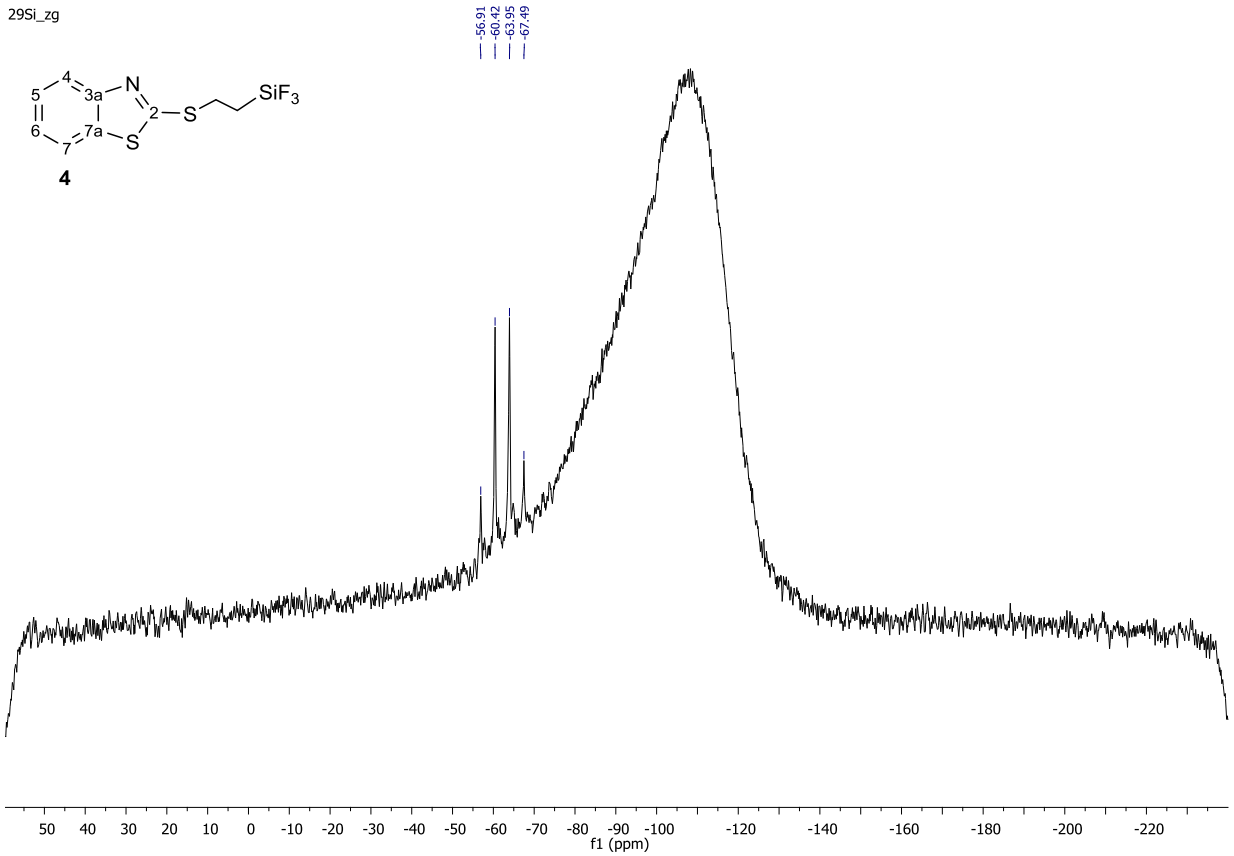


Fig. S8 ^{29}Si NMR (79.50 MHz, $CDCl_3$) of compound **4**.

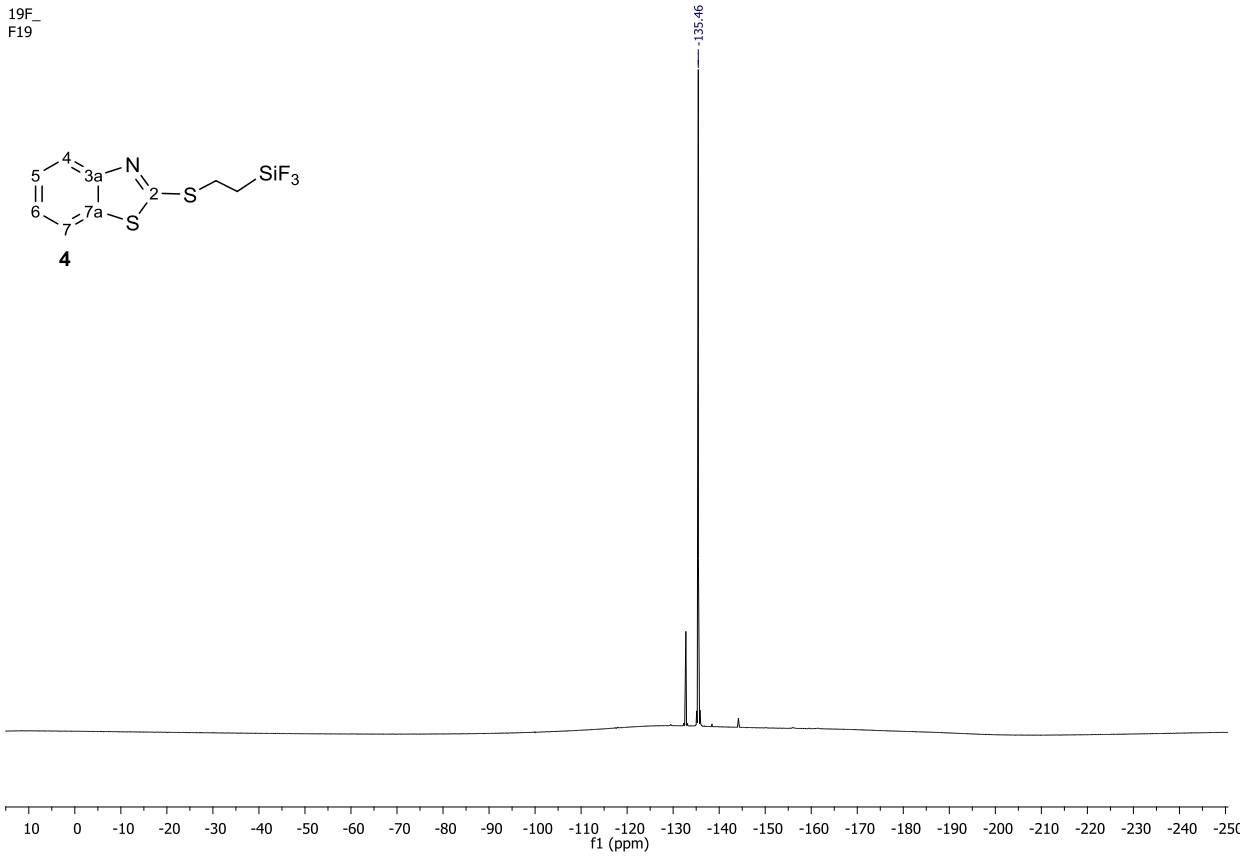


Fig. S9 ^{19}F NMR (376.50 MHz, $CDCl_3$) of compound **4**.

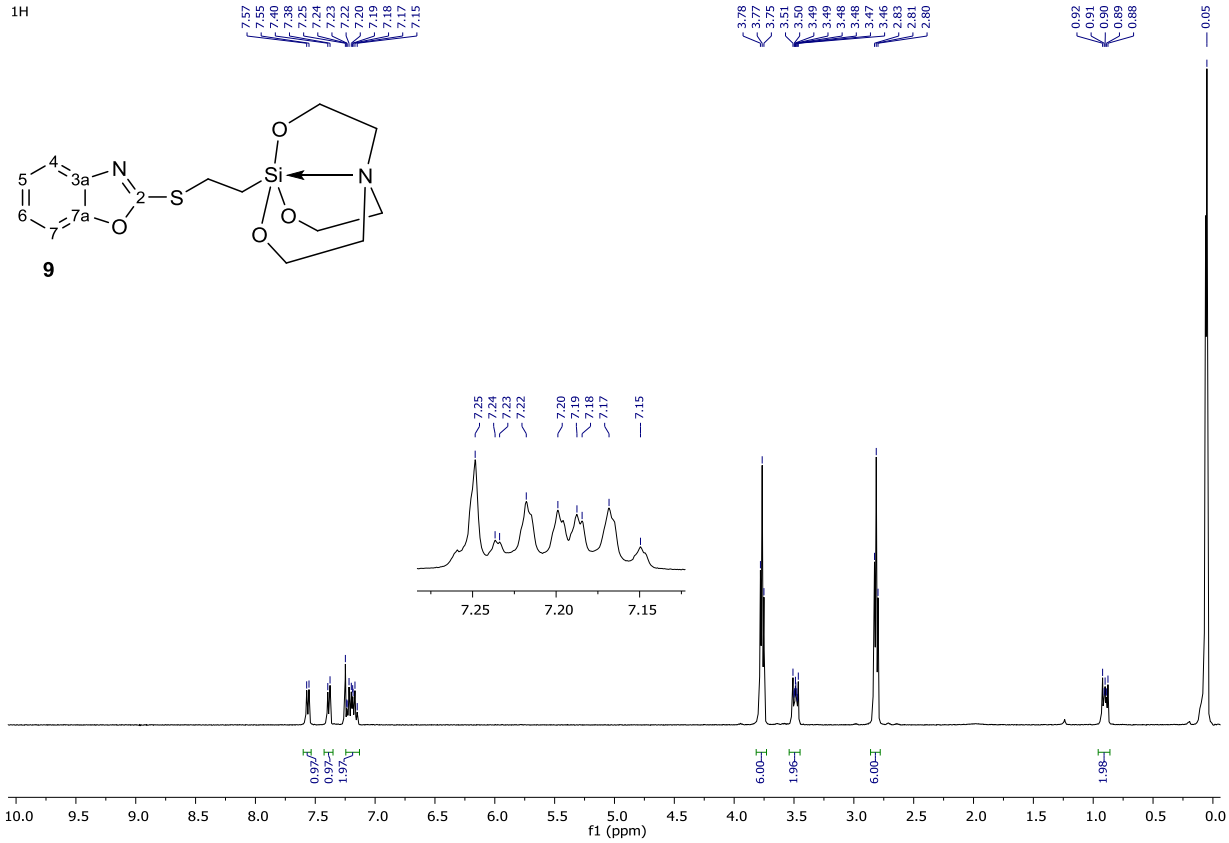


Fig. S10 ^{1}H NMR (400.13 MHz, $CDCl_3$) of compound **9**.

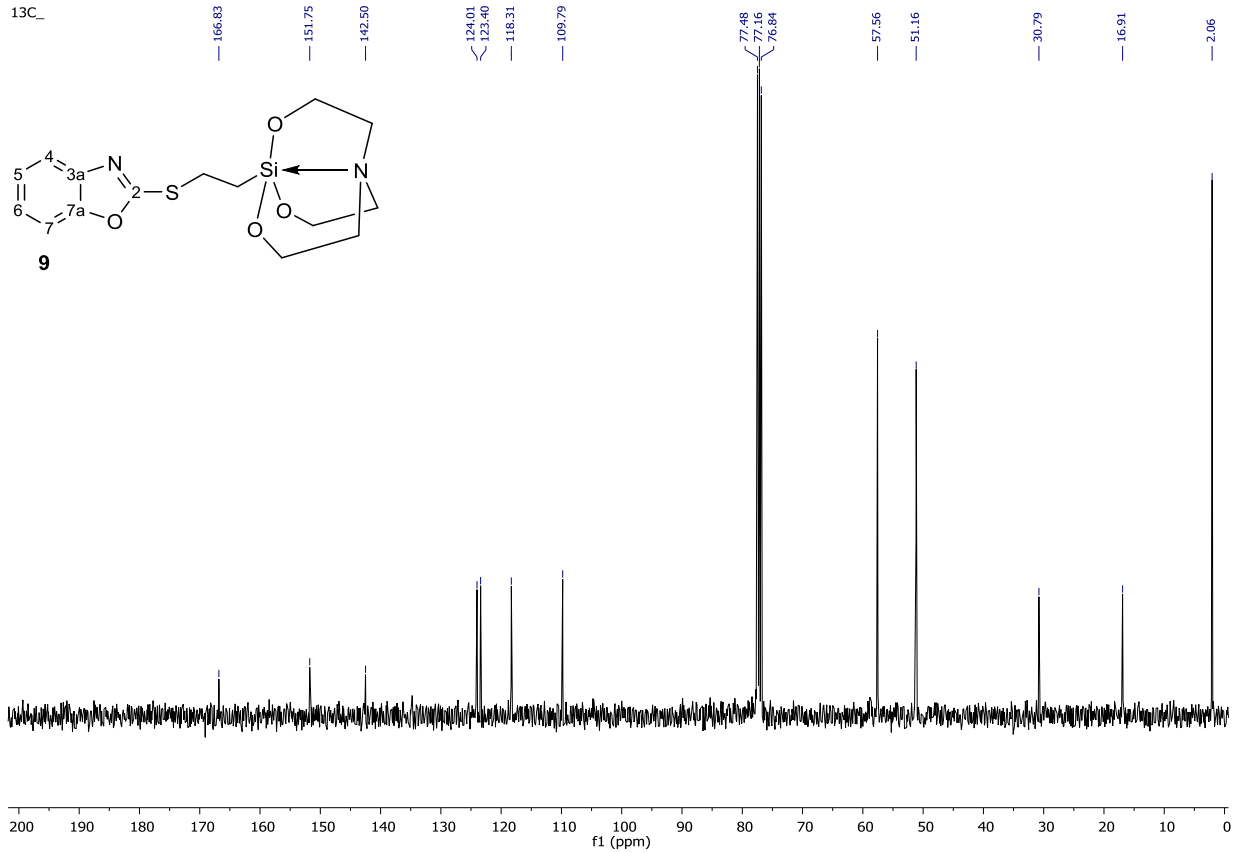


Fig. S11 ^{13}C NMR (100.62 MHz, $CDCl_3$) of compound **9**.

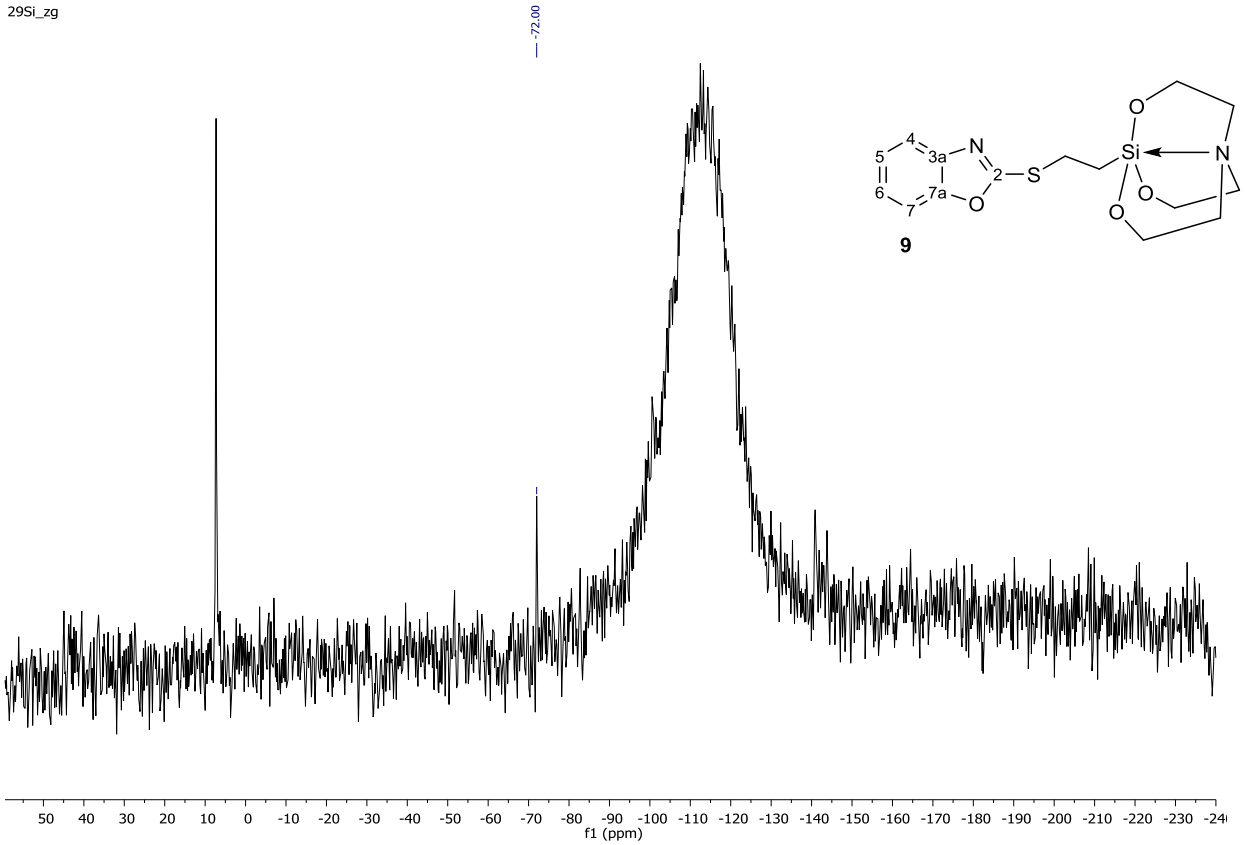


Fig. S12 ^{29}Si NMR (79.50 MHz, $CDCl_3$) of compound **9**.

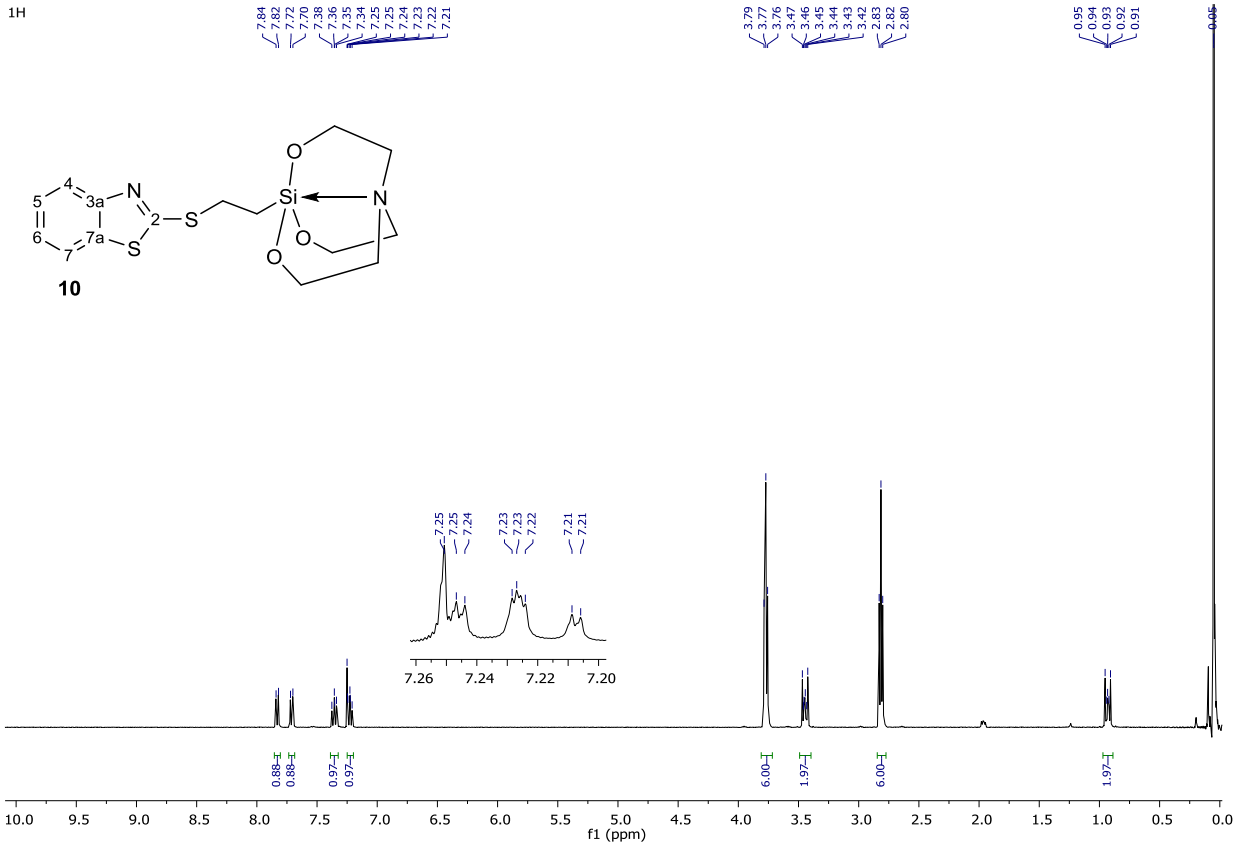


Fig. S13 ^{1}H NMR (400.13 MHz, $CDCl_3$) of compound **10**.

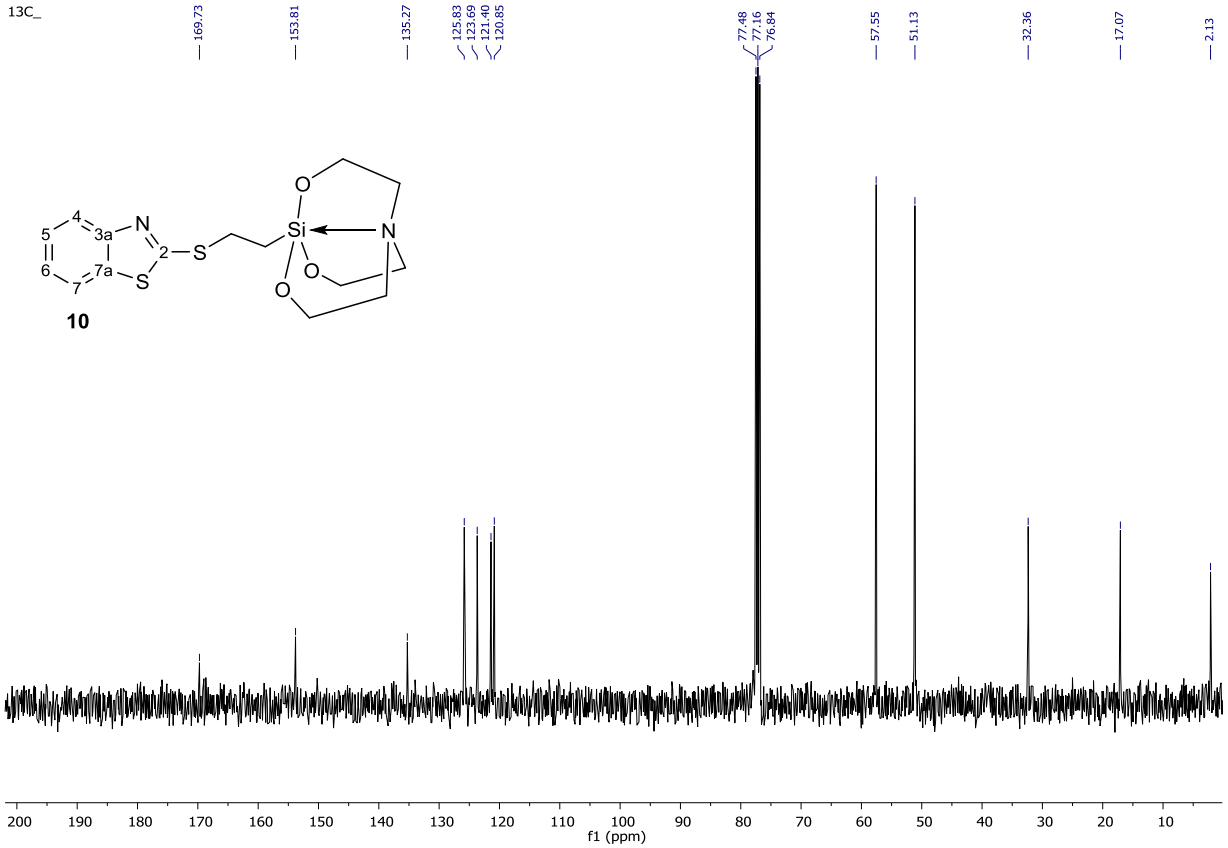


Fig. S14 ^{13}C NMR (100.62 MHz, $CDCl_3$) of compound **10**.

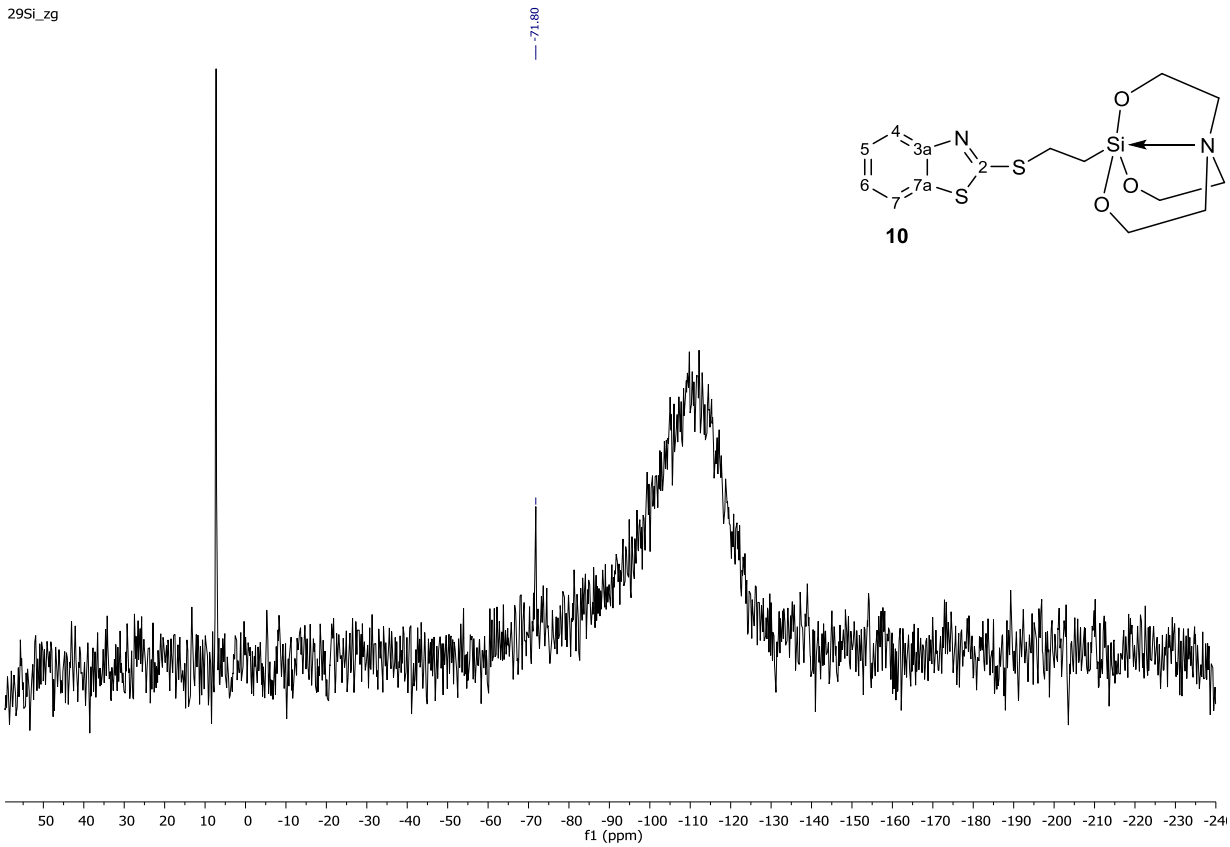


Fig. S15 ^{29}Si NMR (79.50 MHz, $CDCl_3$) of compound **10**.

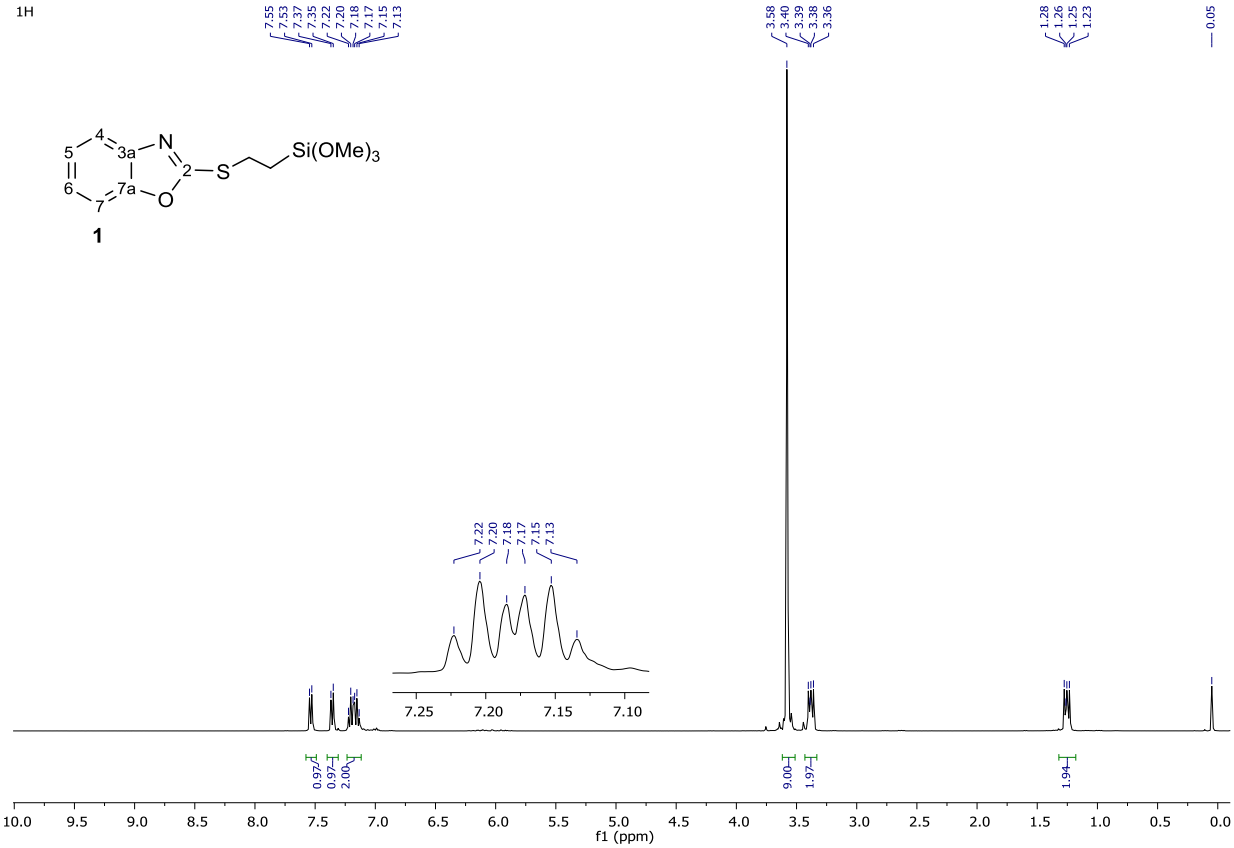


Fig. S16 ^{1}H NMR (400.13 MHz, $CDCl_3$) of compound **1**.

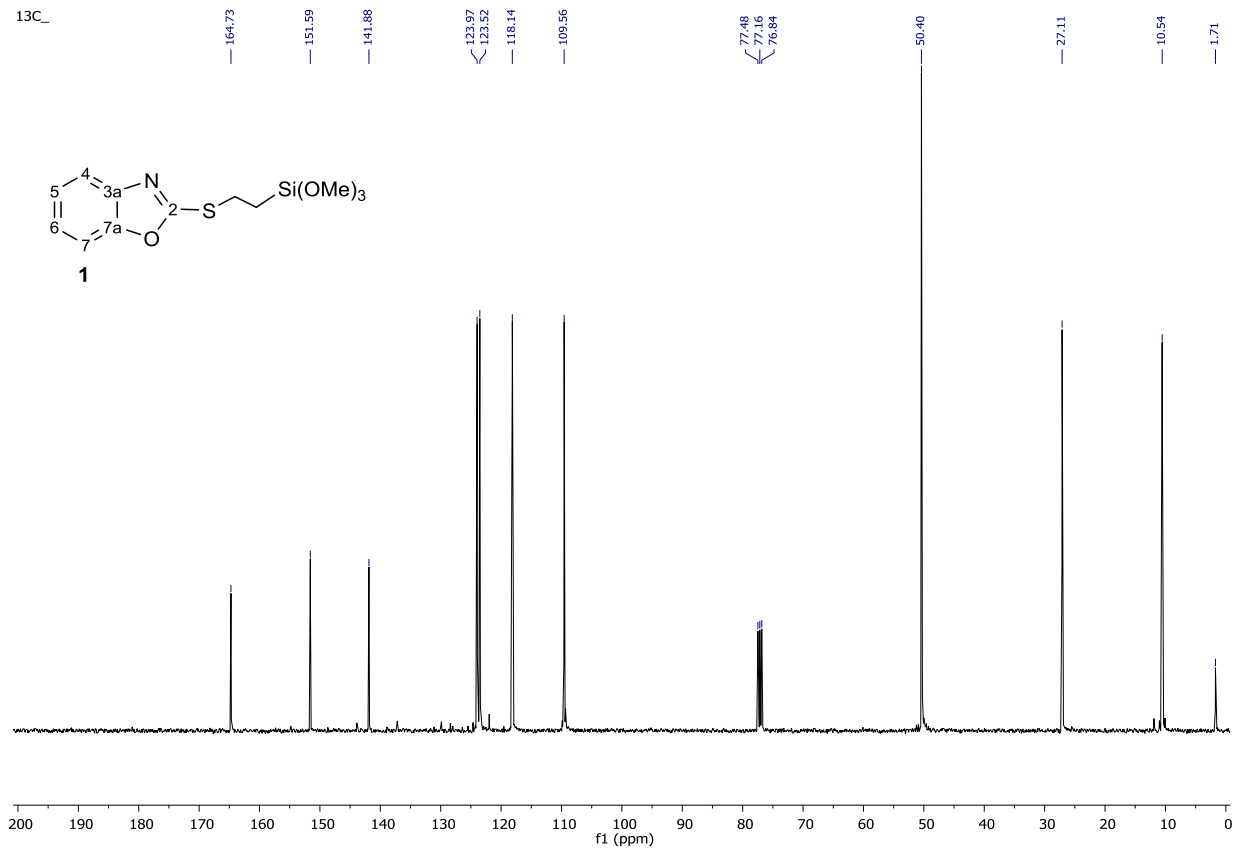


Fig. S17 ^{13}C NMR (100.62 MHz, $CDCl_3$) of compound **1**.

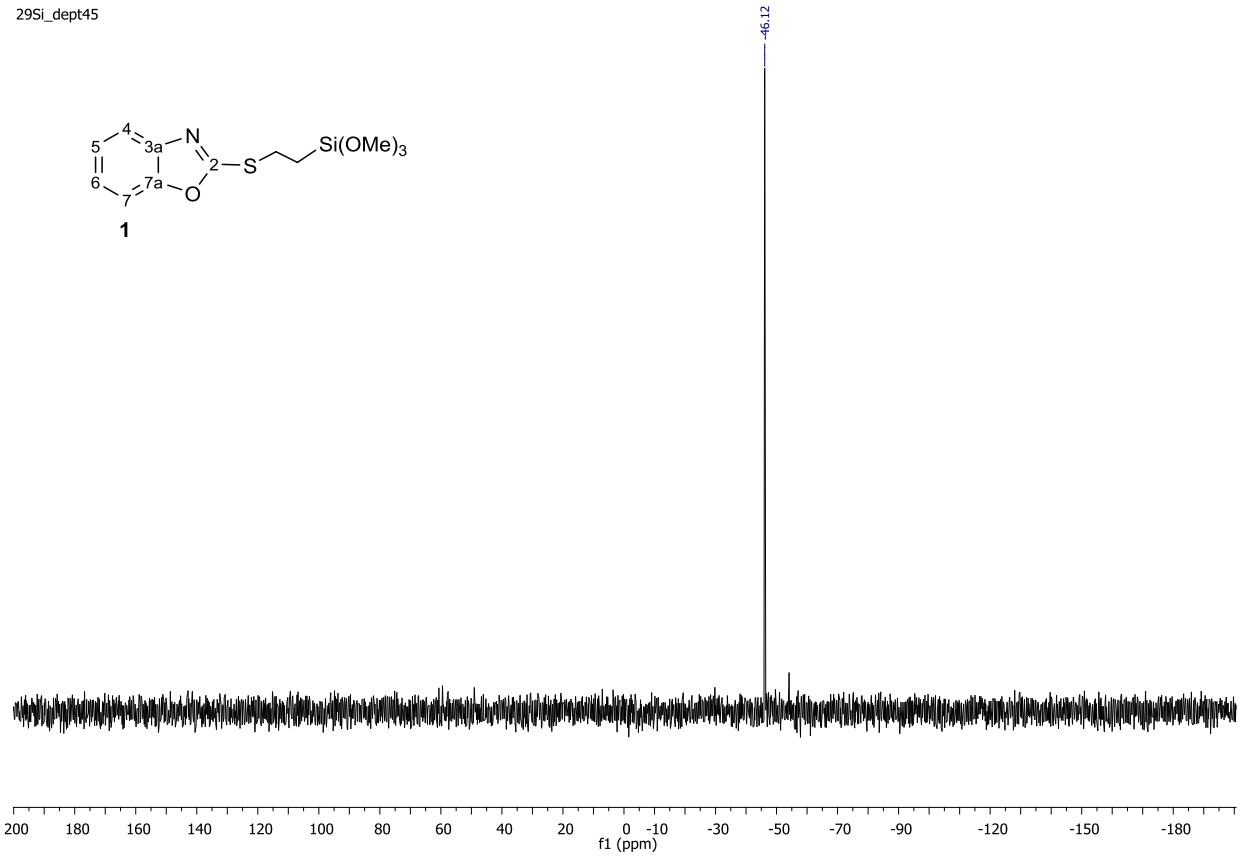


Fig. S18 ^{29}Si NMR (79.50 MHz, $CDCl_3$) of compound **1**.

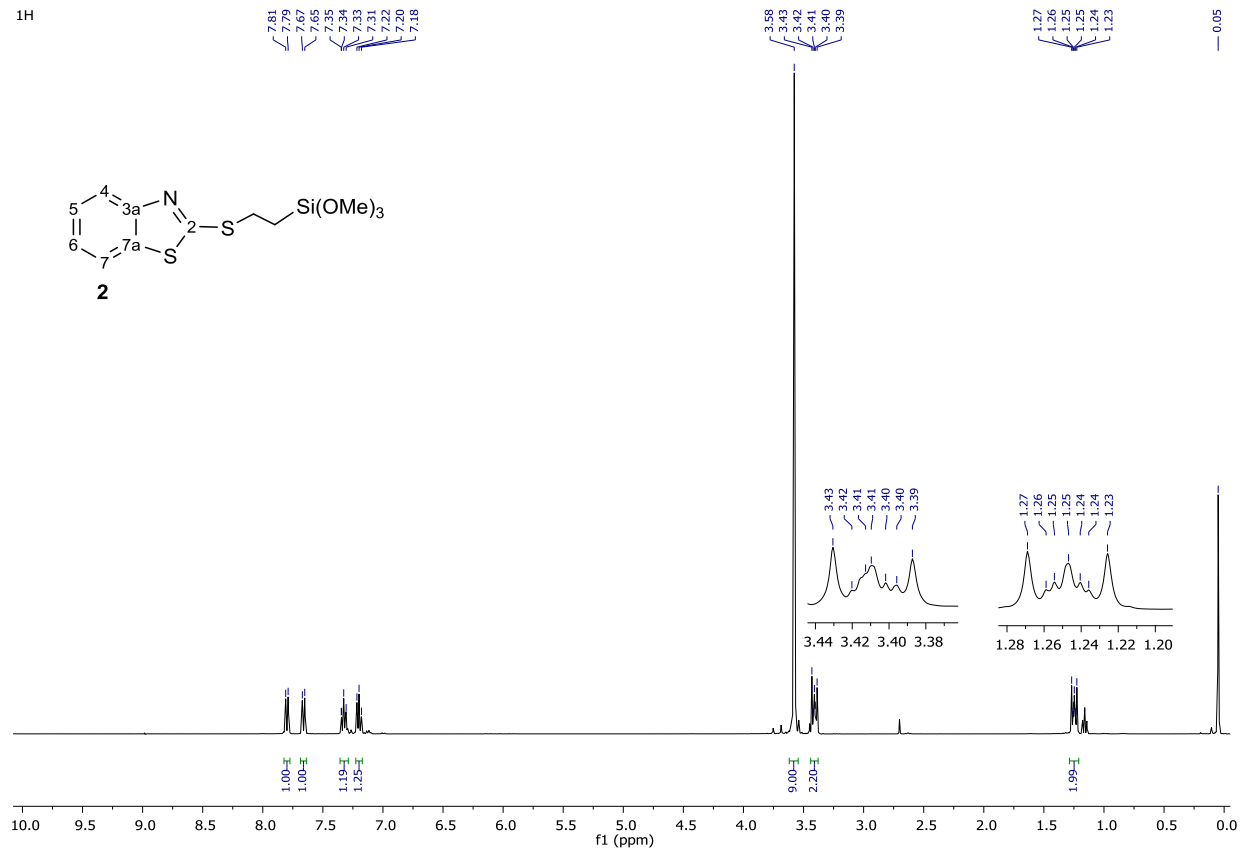


Fig. S19 ^{1}H NMR (400.13 MHz, $CDCl_3$) of compound **2**.

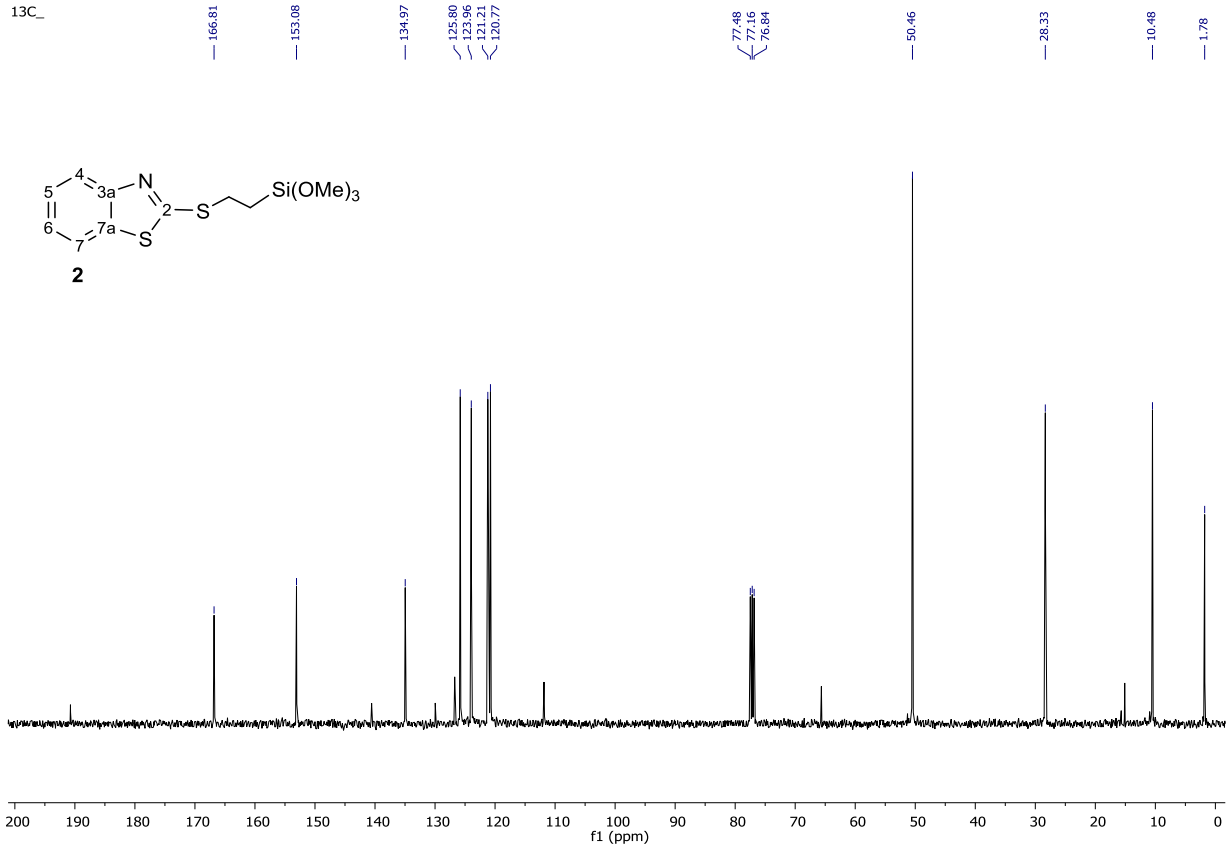


Fig. S20 ^{13}C NMR (100.62 MHz, $CDCl_3$) of compound **2**.

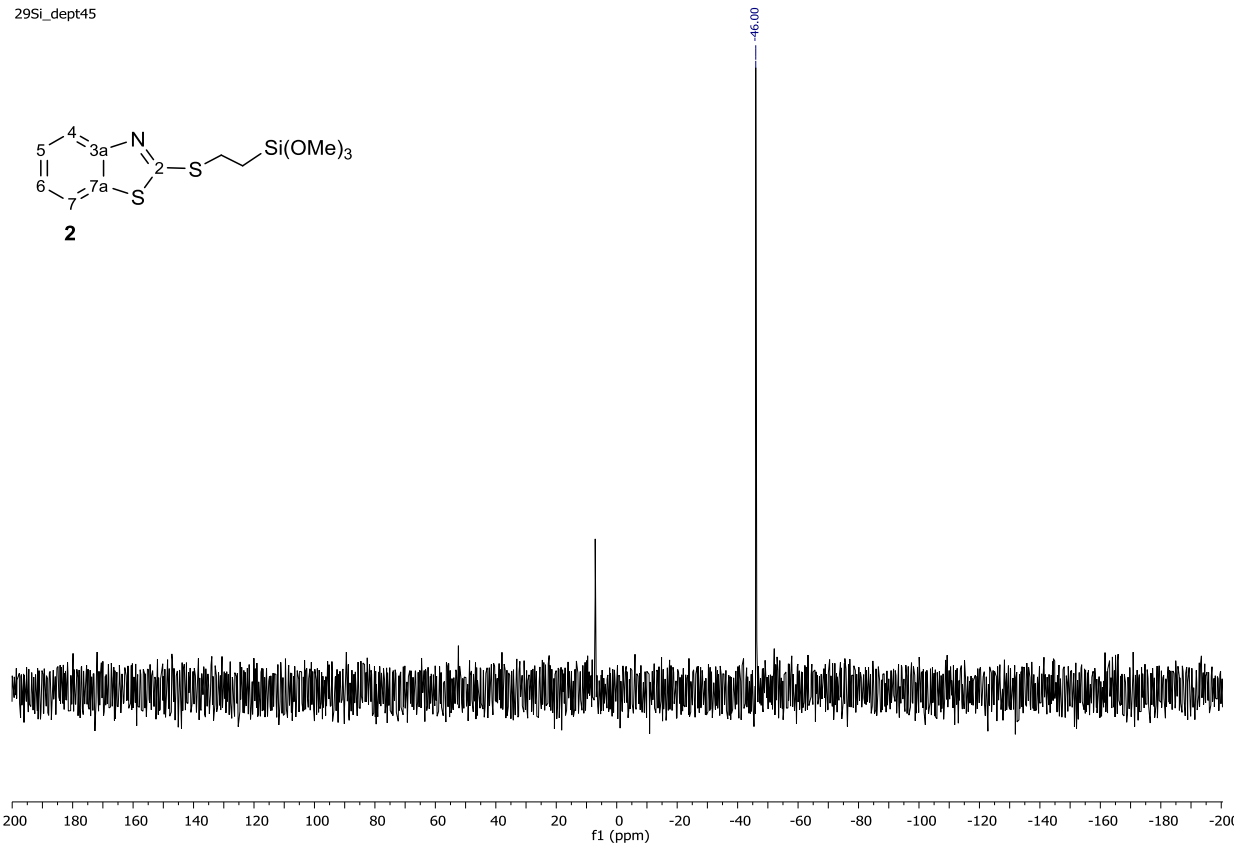


Fig. S21 ^{29}Si NMR (79.50 MHz, $CDCl_3$) of compound **2**.

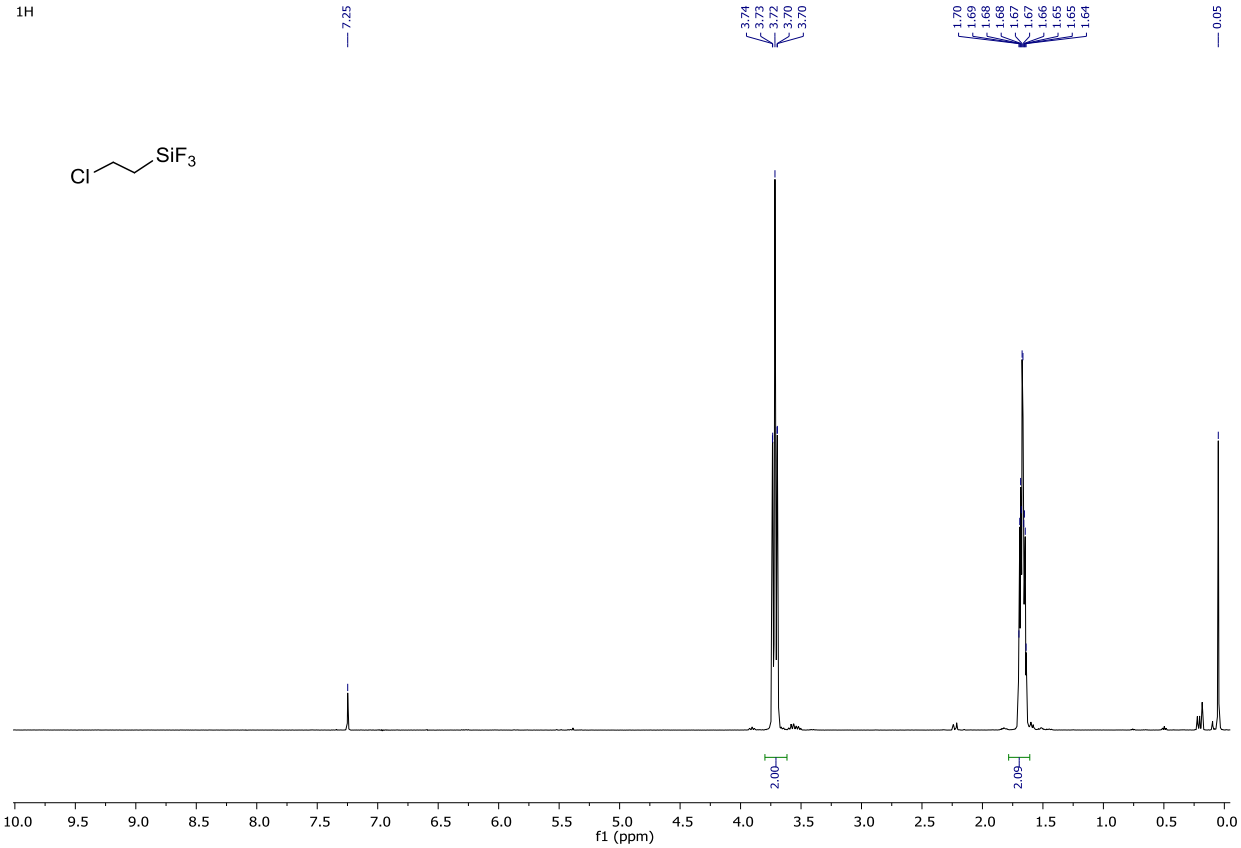


Fig. S22 ^{1}H NMR (400.13 MHz, $CDCl_3$) of **$ClCH_2CH_2SiF_3$**.

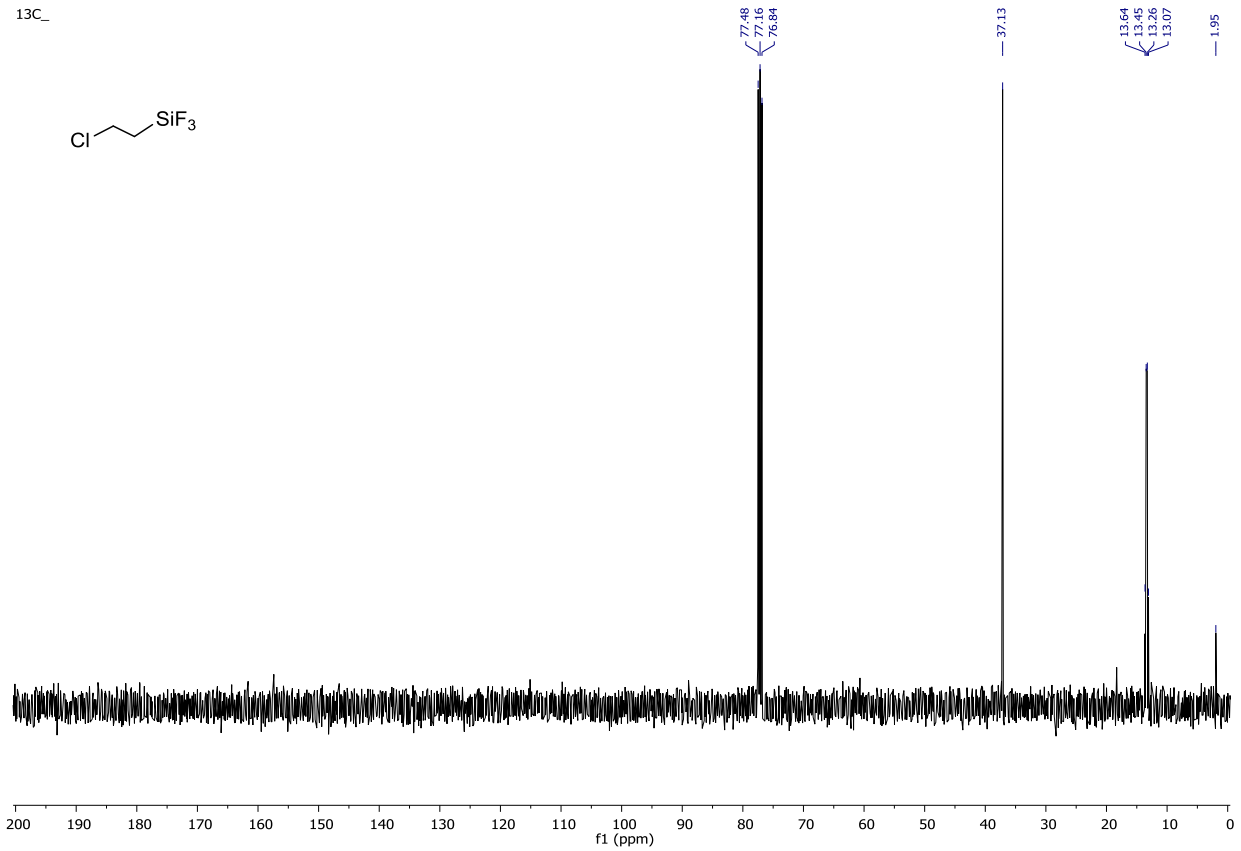


Fig. S23 ^{13}C NMR (100.62 MHz, $CDCl_3$) of **$ClCH_2CH_2SiF_3$**.

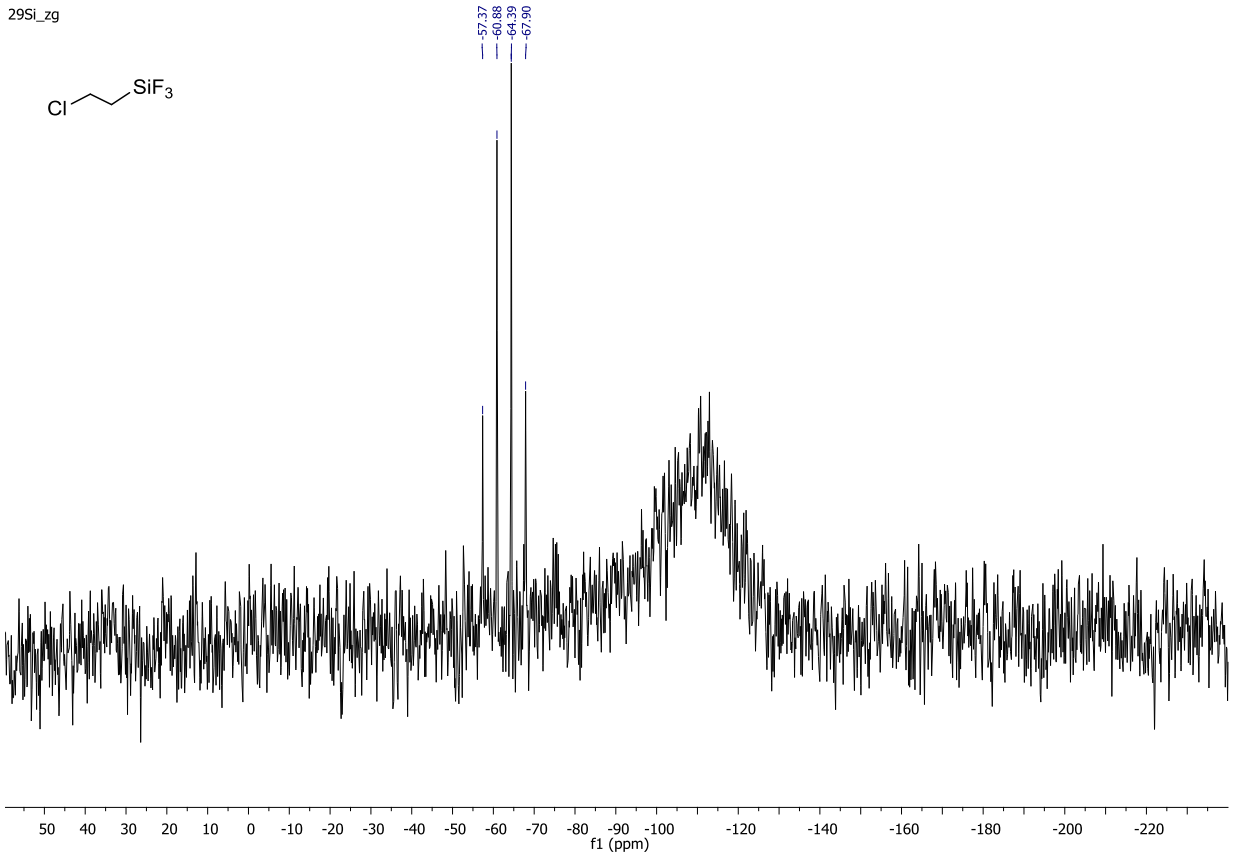


Fig. S24 ^{29}Si NMR (79.50 MHz, $CDCl_3$) of **$ClCH_2CH_2SiF_3$**.

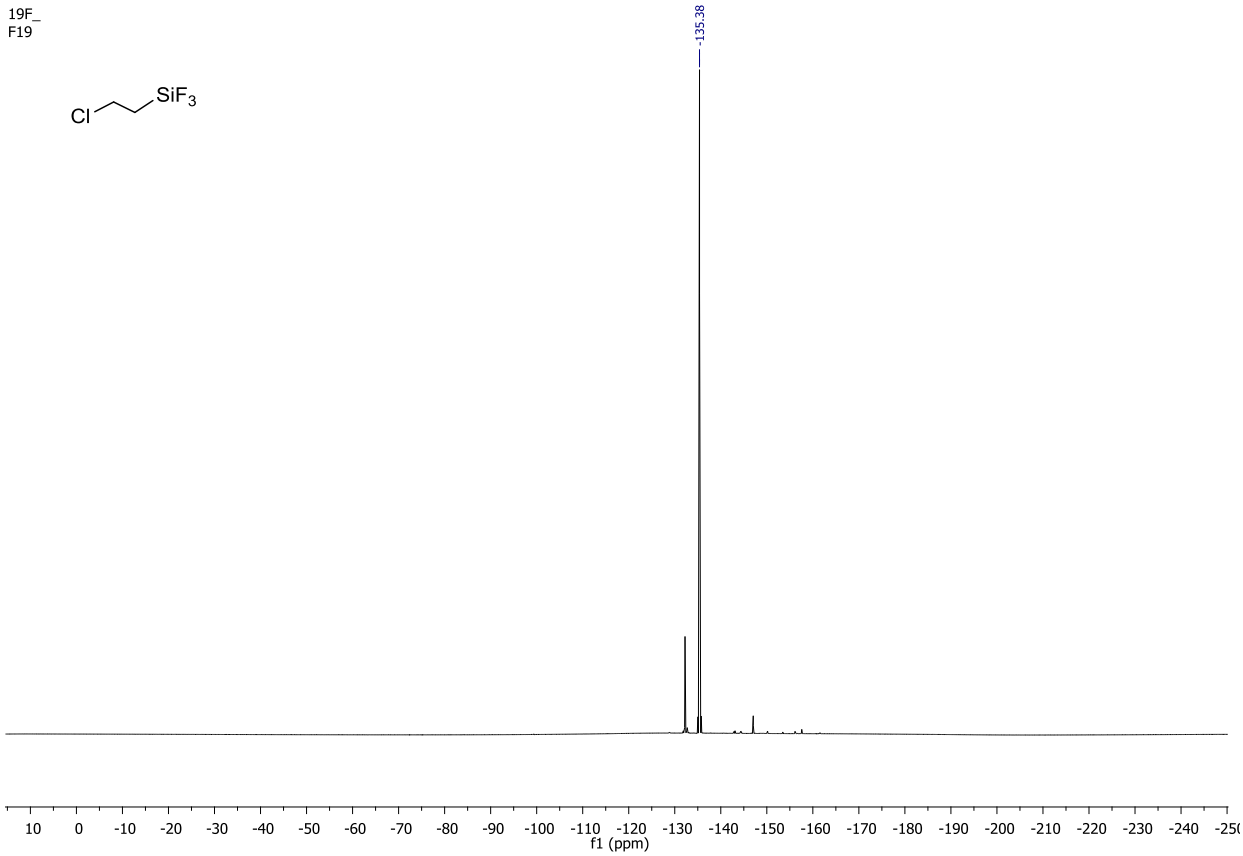


Fig. S25 ^{19}F NMR (376.50 MHz, $CDCl_3$) of **$ClCH_2CH_2SiF_3$**.