Supporting information

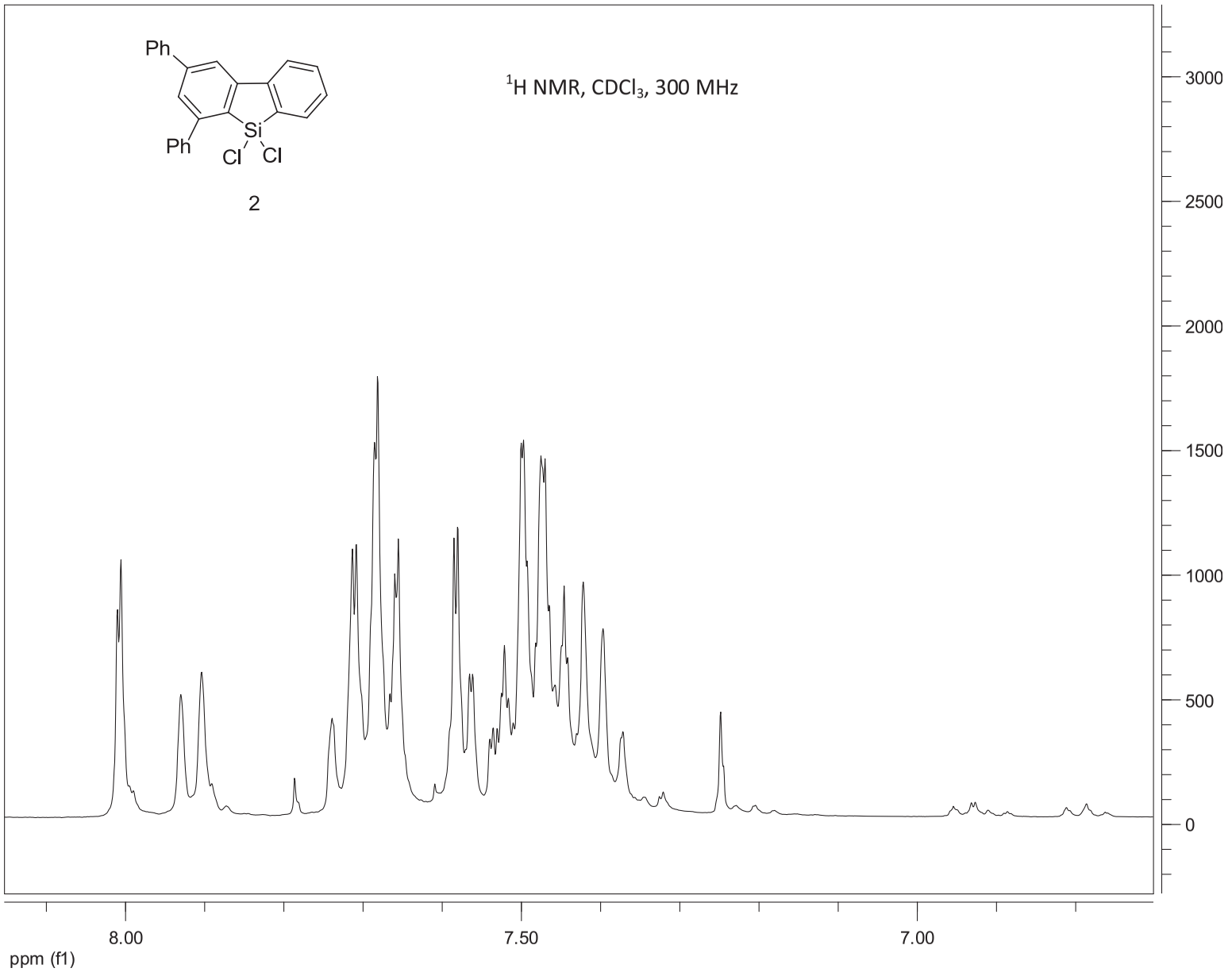
Synthesis and Photophysical Properties of a New Asymmetric 9,9-dichloro-2,4-diphenyl-9-silafluorene and its Derivatives

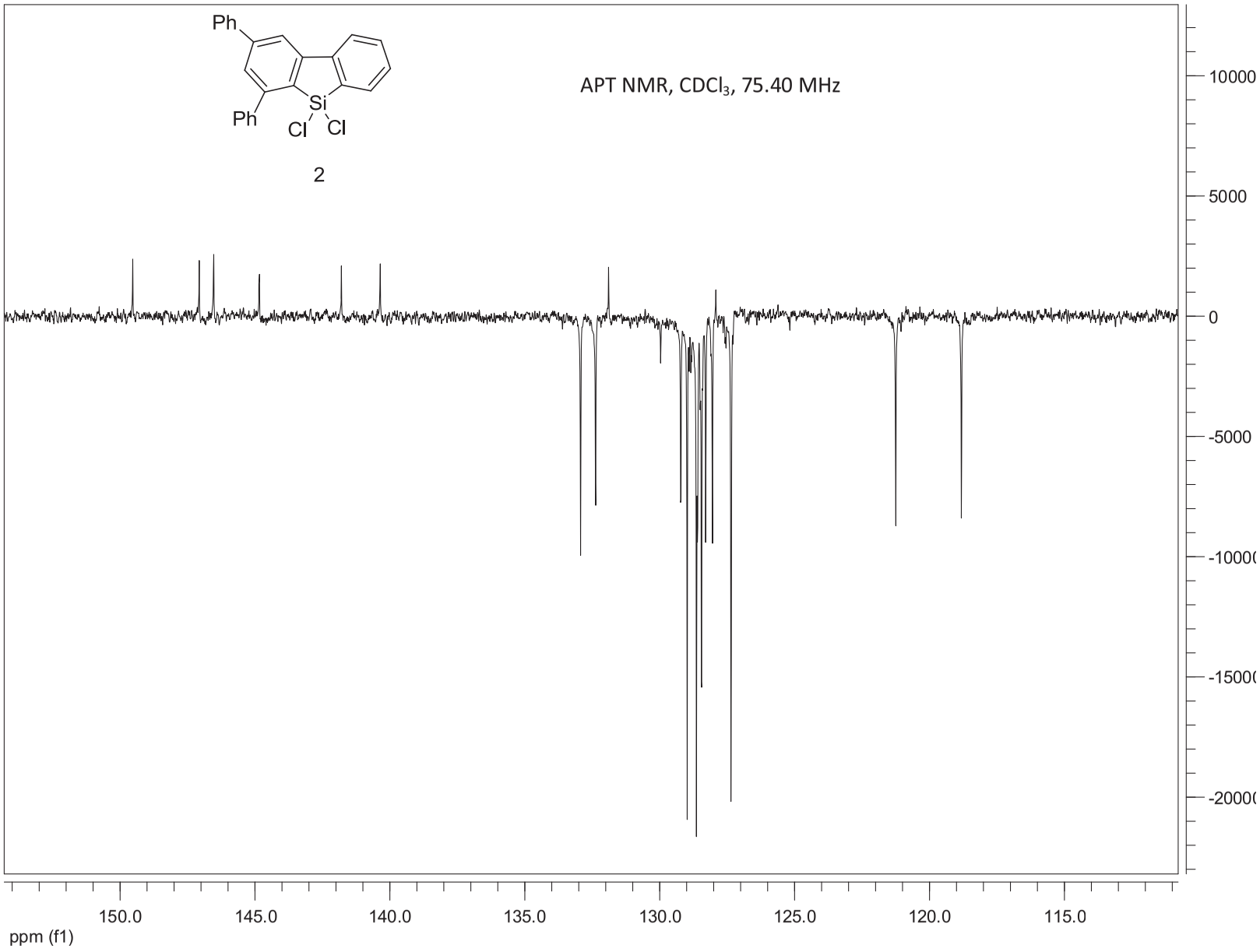
Erika Pusztai,[1] Irina S.Toulokhonova,[1] Nicole Temple,[1] Haley Albright,[1] Uzma I. Zakai,[1] Song Guo,[2] and Robert West[1]*

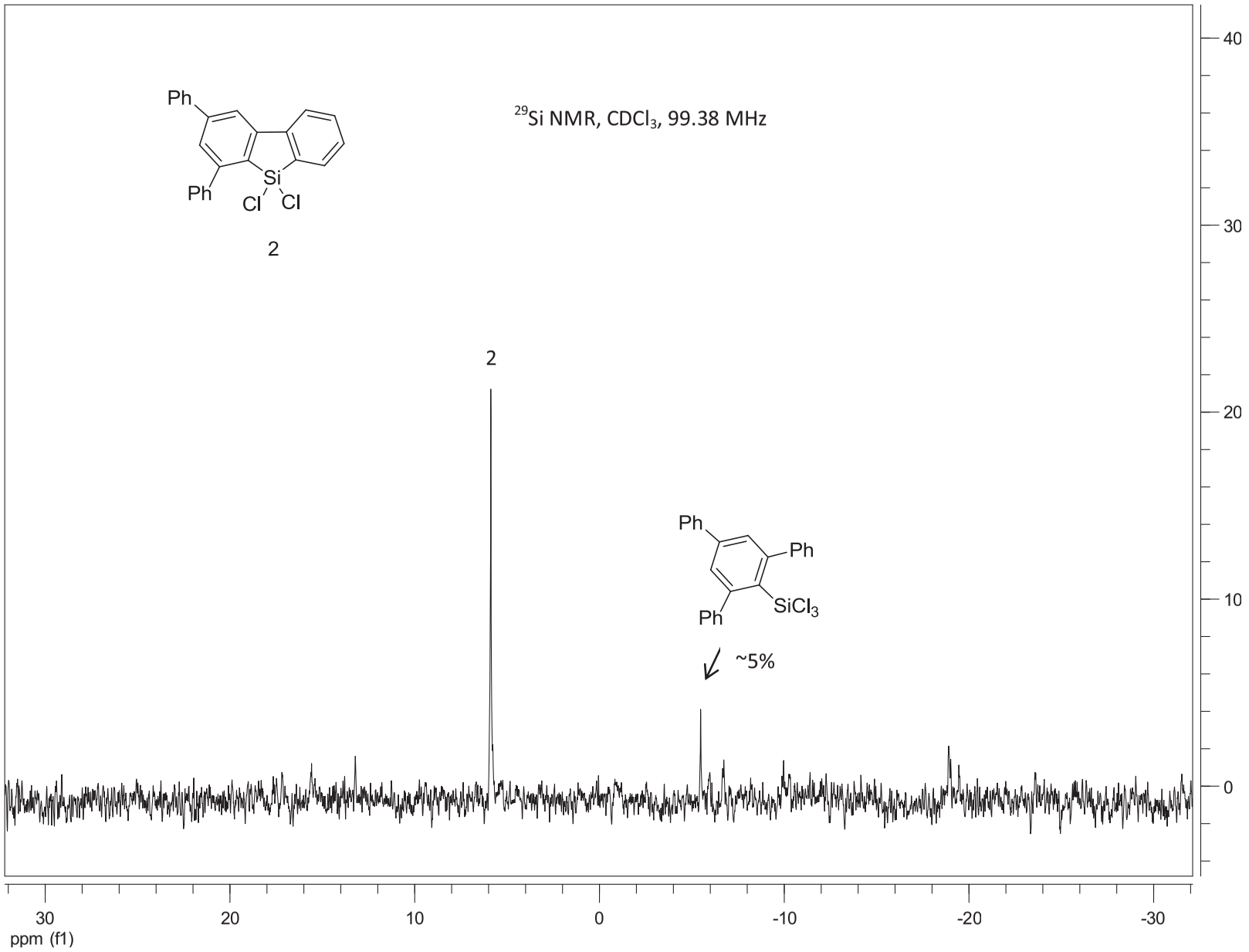
[1]*Organosilicon Research Center, Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave., Madison WI, 53706 USA*

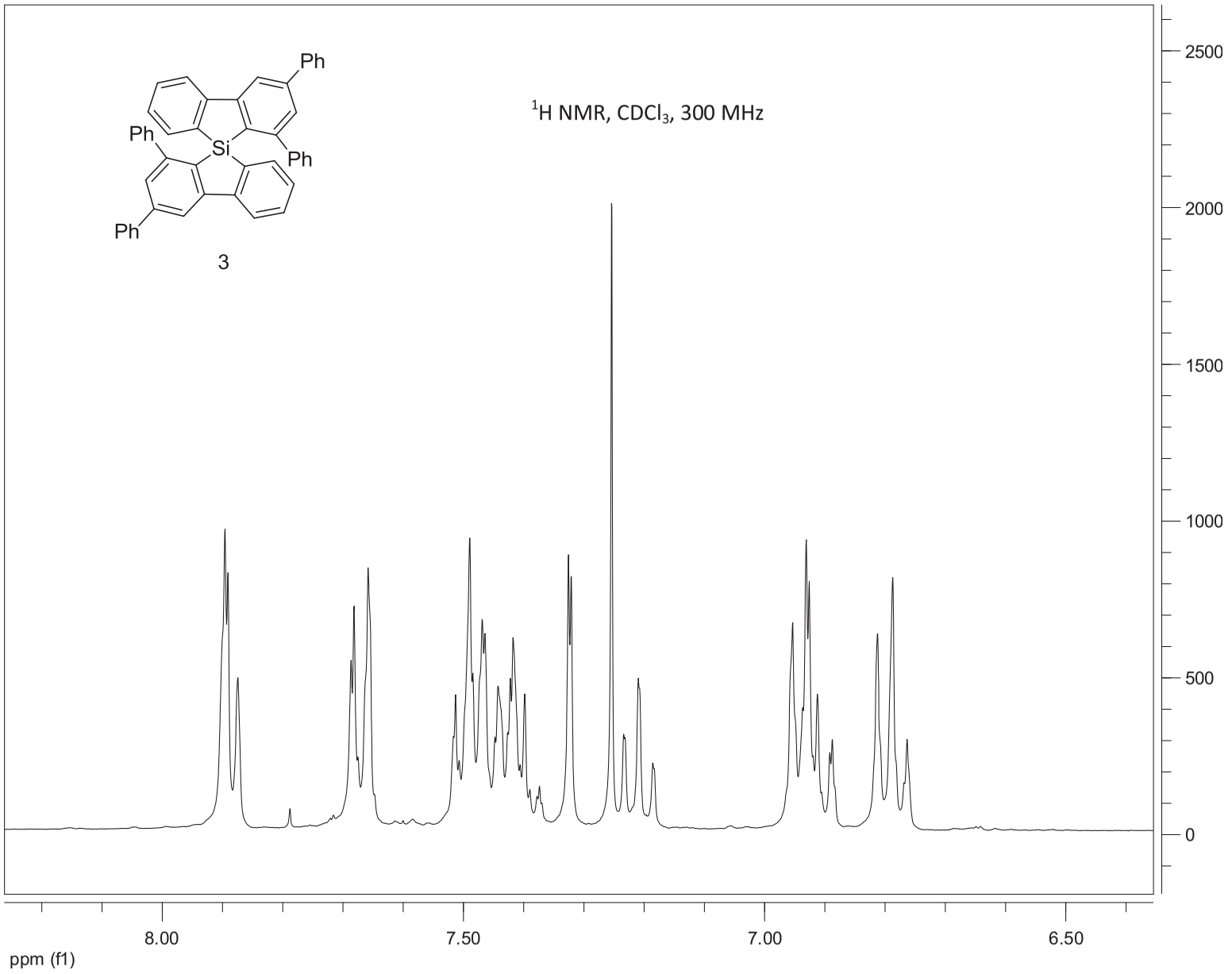
[2]*Carbone Cancer Center, Wisconsin Institutes for Medical Research, 1111 Highland Avenue, Madison, WI 53705*

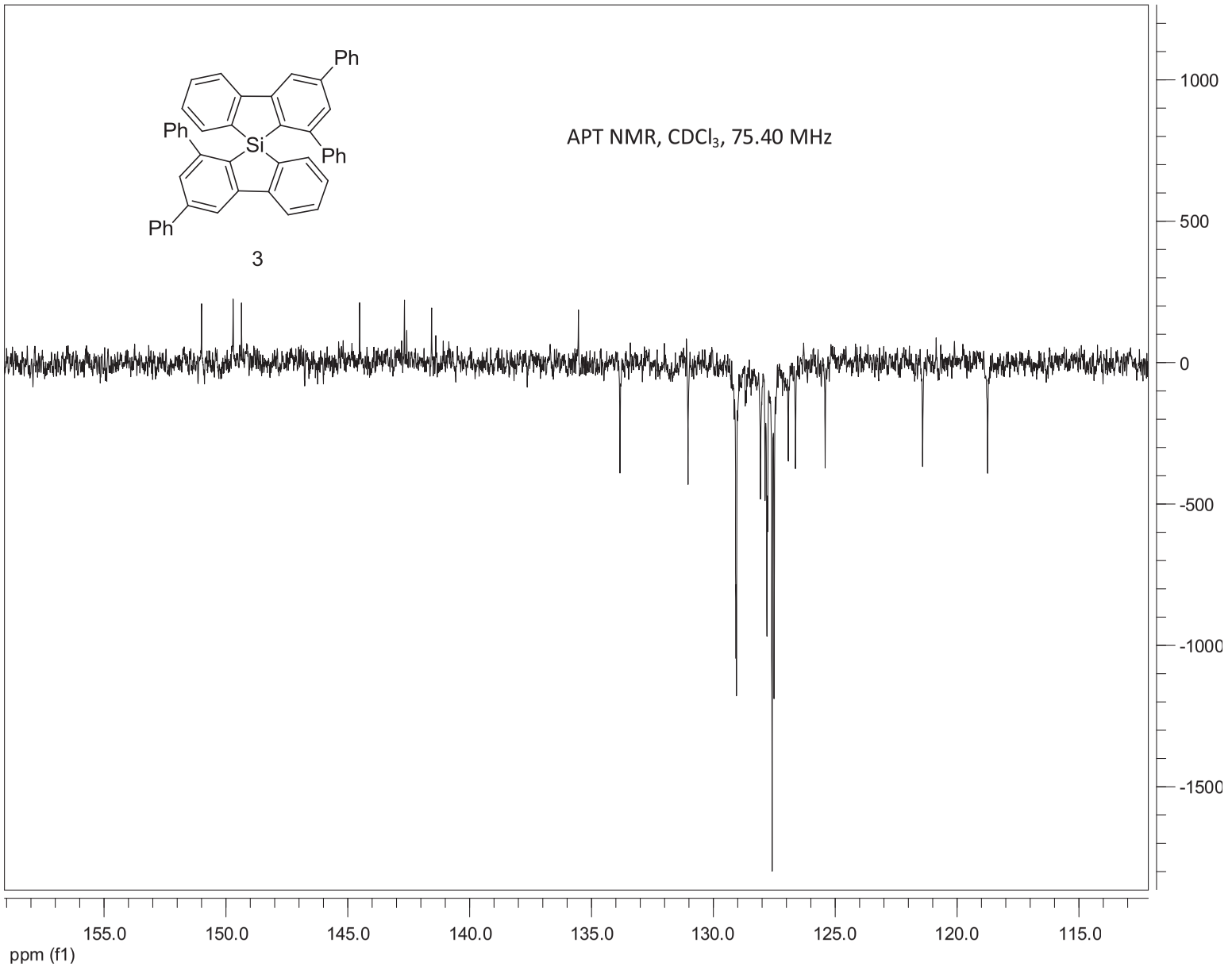
Table of Content

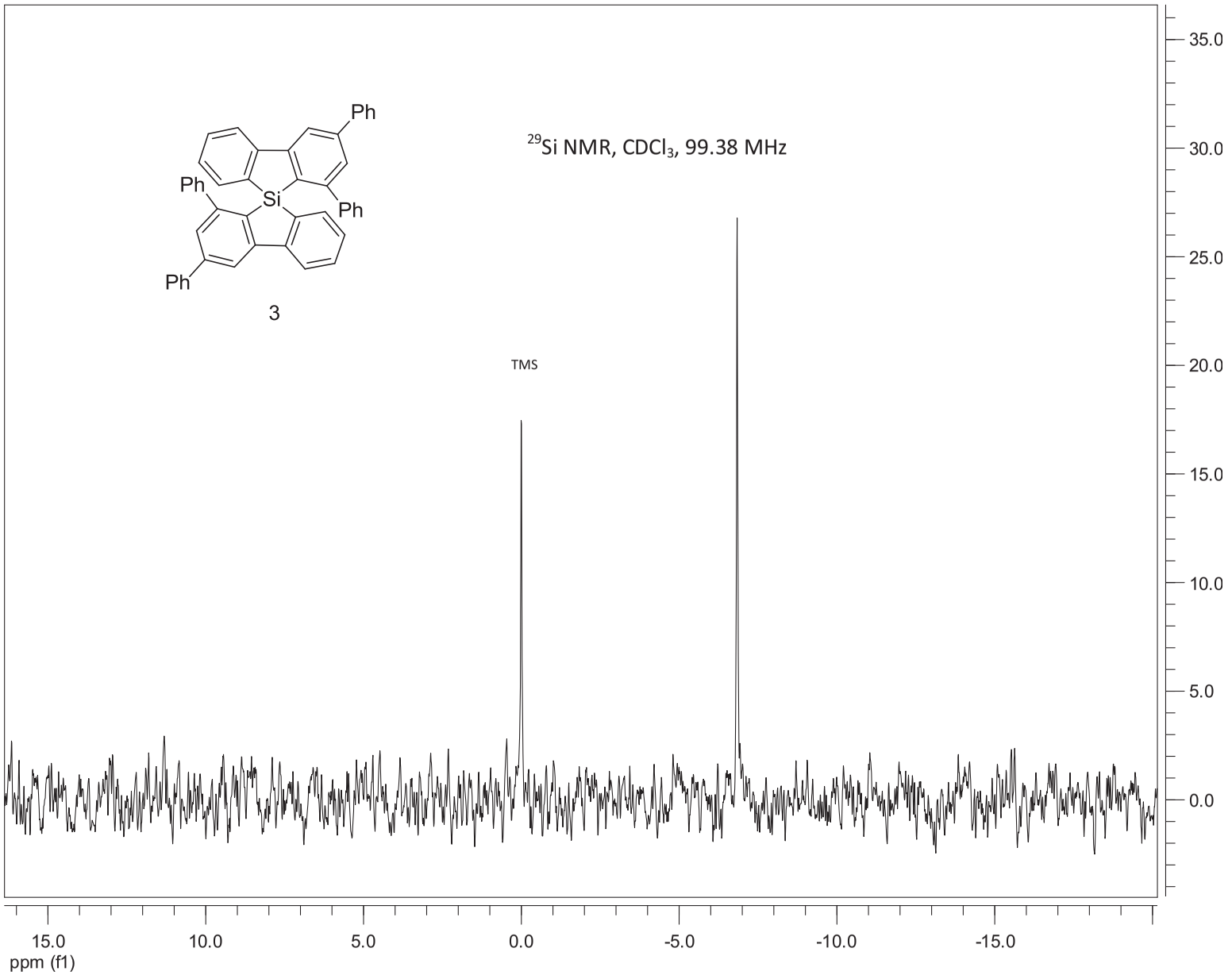

Ph
Ph
Si
Cl
Cl
2
^{1}H NMR, $CDCl_3$, 300 MHz
3000
2500
2000
1500
1000
500
0
8.00
7.50
7.00
ppm (f1)

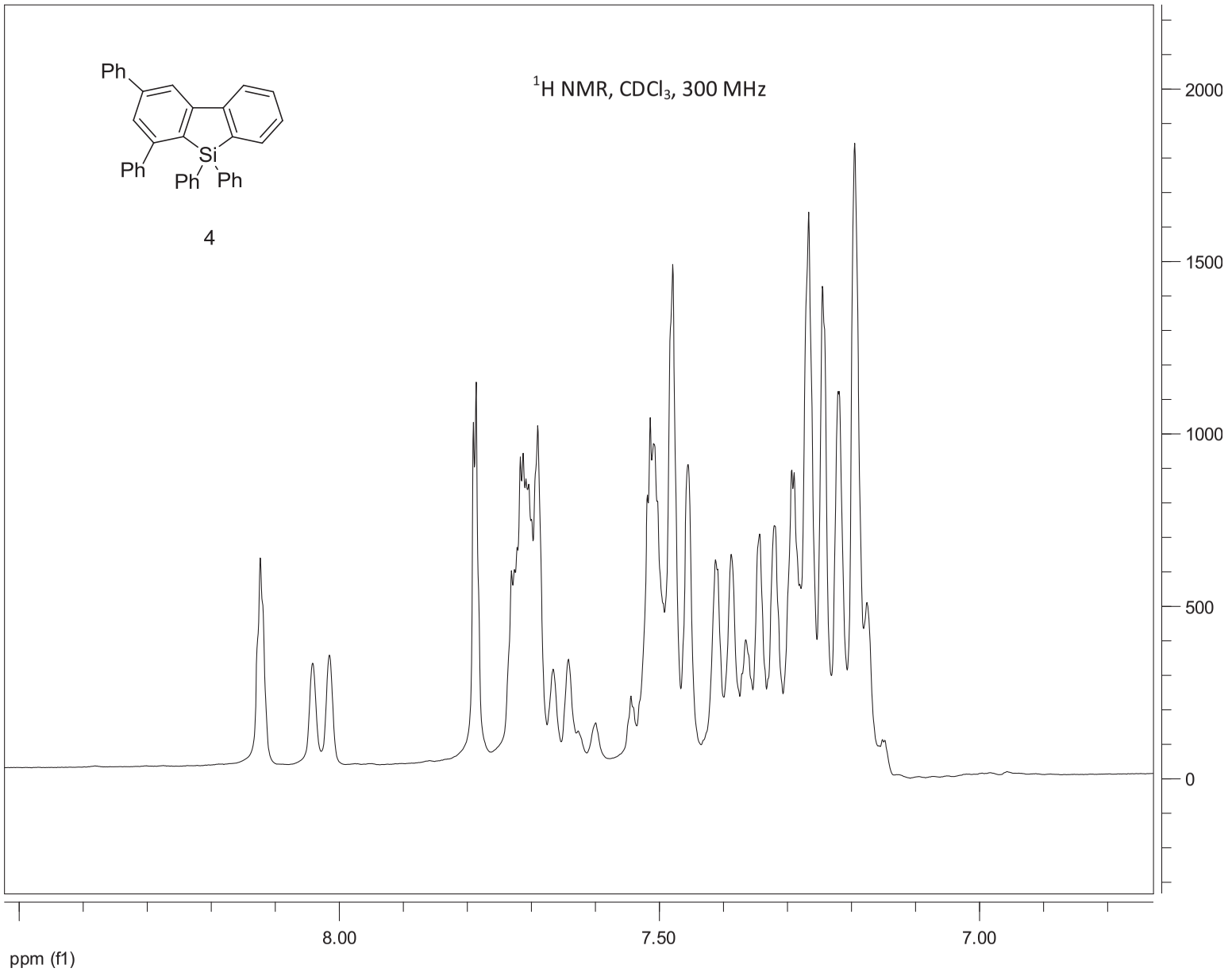

Ph
Ph
Si
Cl
Cl
2
APT NMR, CDCl3, 75.40 MHz
10000
5000
0
-5000
-10000
-15000
-20000
150.0
145.0
140.0
135.0
130.0
125.0
120.0
115.0
ppm (f1)

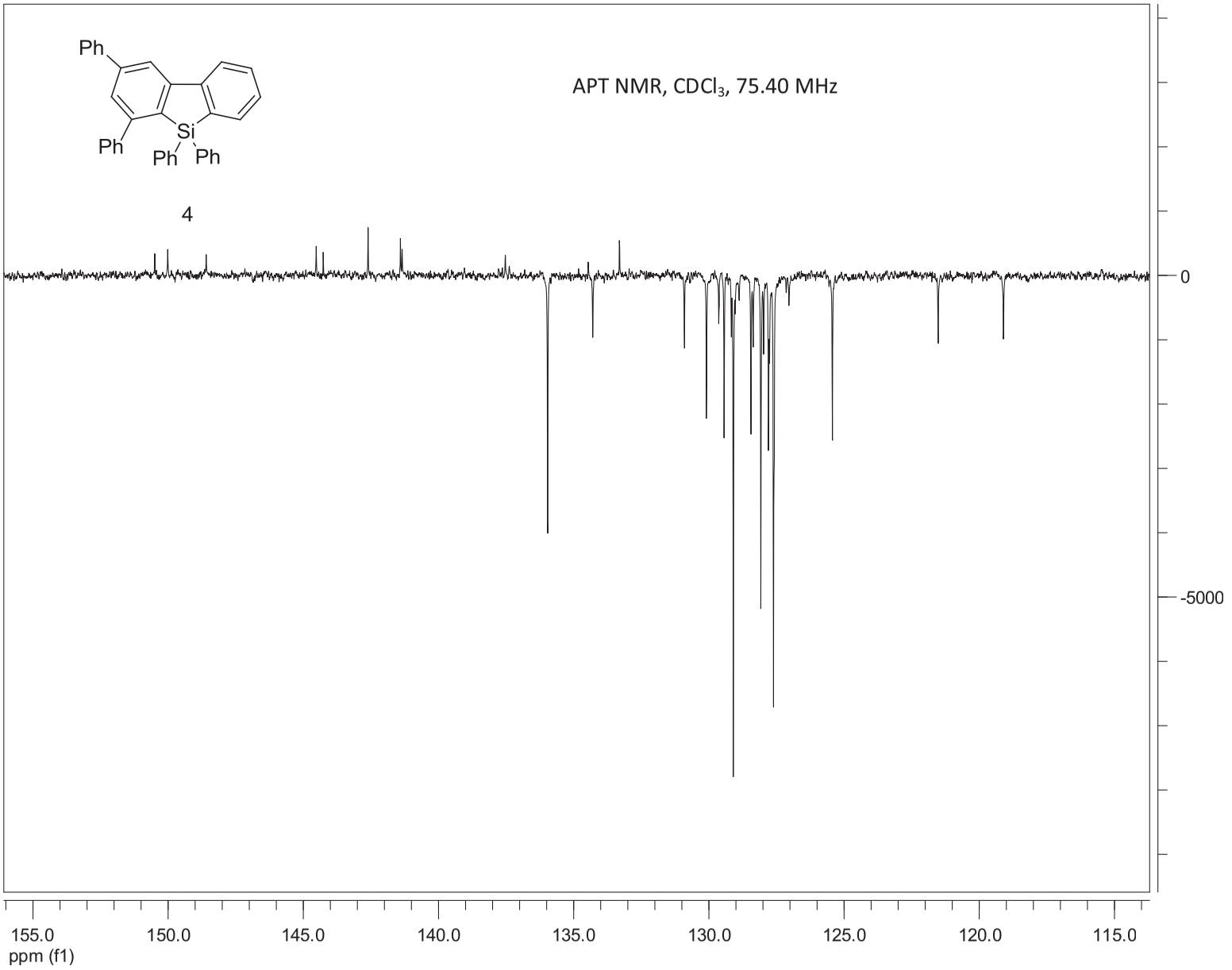

Ph
Ph
Si
Cl
Cl
2
^{29}Si NMR, $CDCl_3$, 99.38 MHz
2
Ph
Ph
Ph
$SiCl_3$
~5%
40
30
20
10
0
30
20
10
0
-10
-20
-30
ppm (f1)

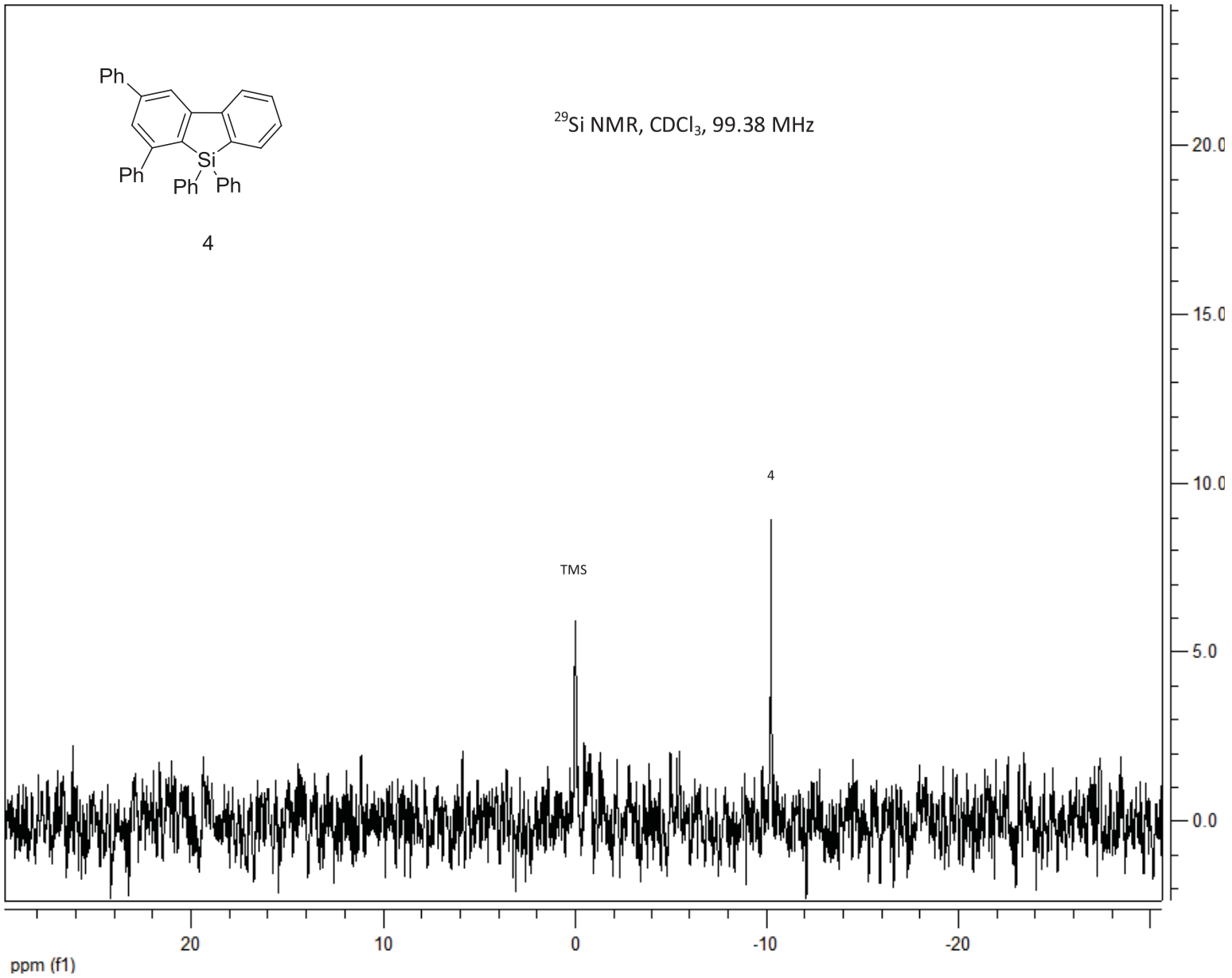

Ph
Ph
Si
Ph
Ph
3
^{1}H NMR, $CDCl_3$, 300 MHz
2500
2000
1500
1000
500
0
8.00
7.50
7.00
6.50
ppm (f1)

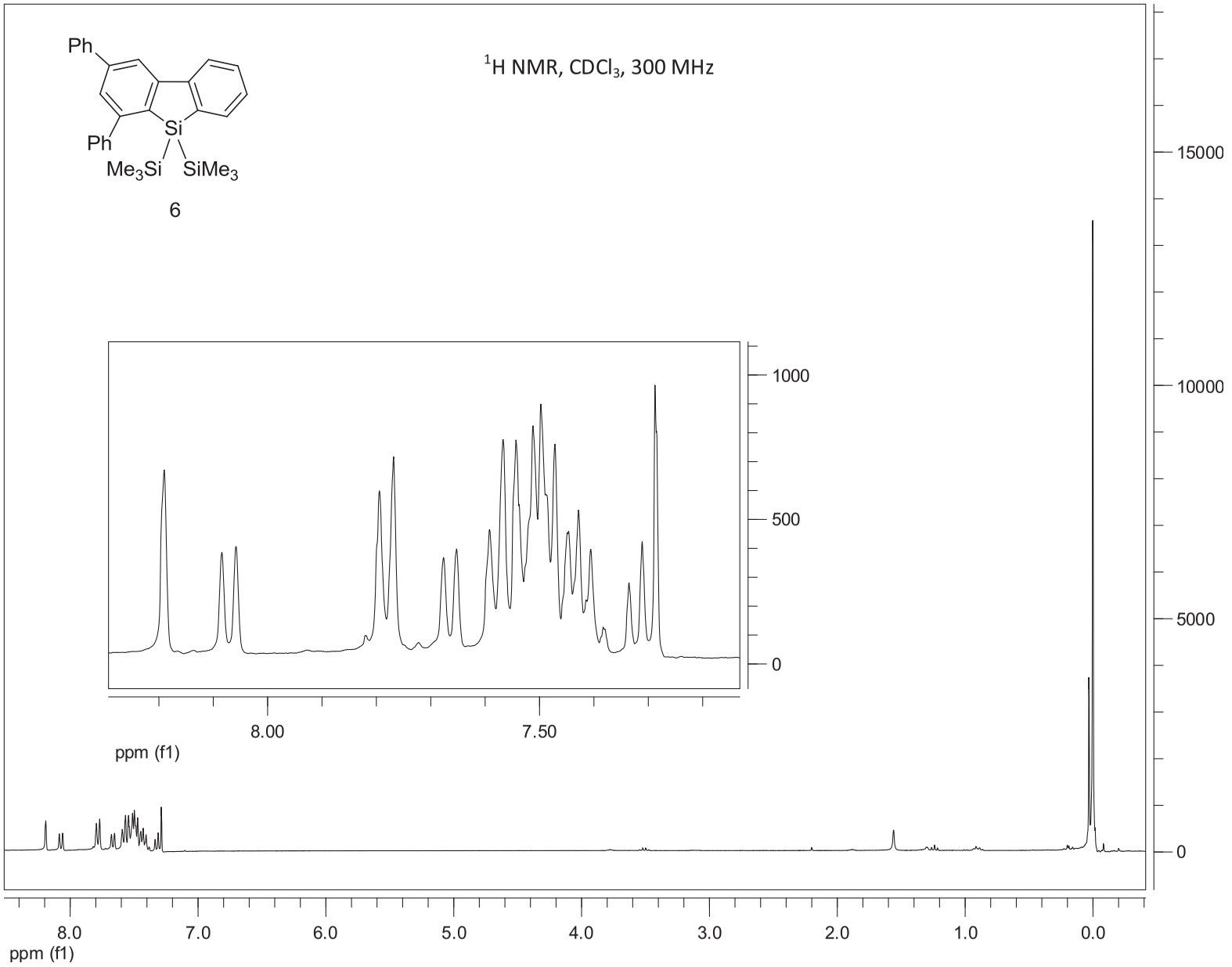

Ph
Ph
Si
Ph
Ph
3
APT NMR, CDCl3, 75.40 MHz
1000
500
0
-500
-1000
-1500
155.0
150.0
145.0
140.0
135.0
130.0
125.0
120.0
115.0
ppm (f1)

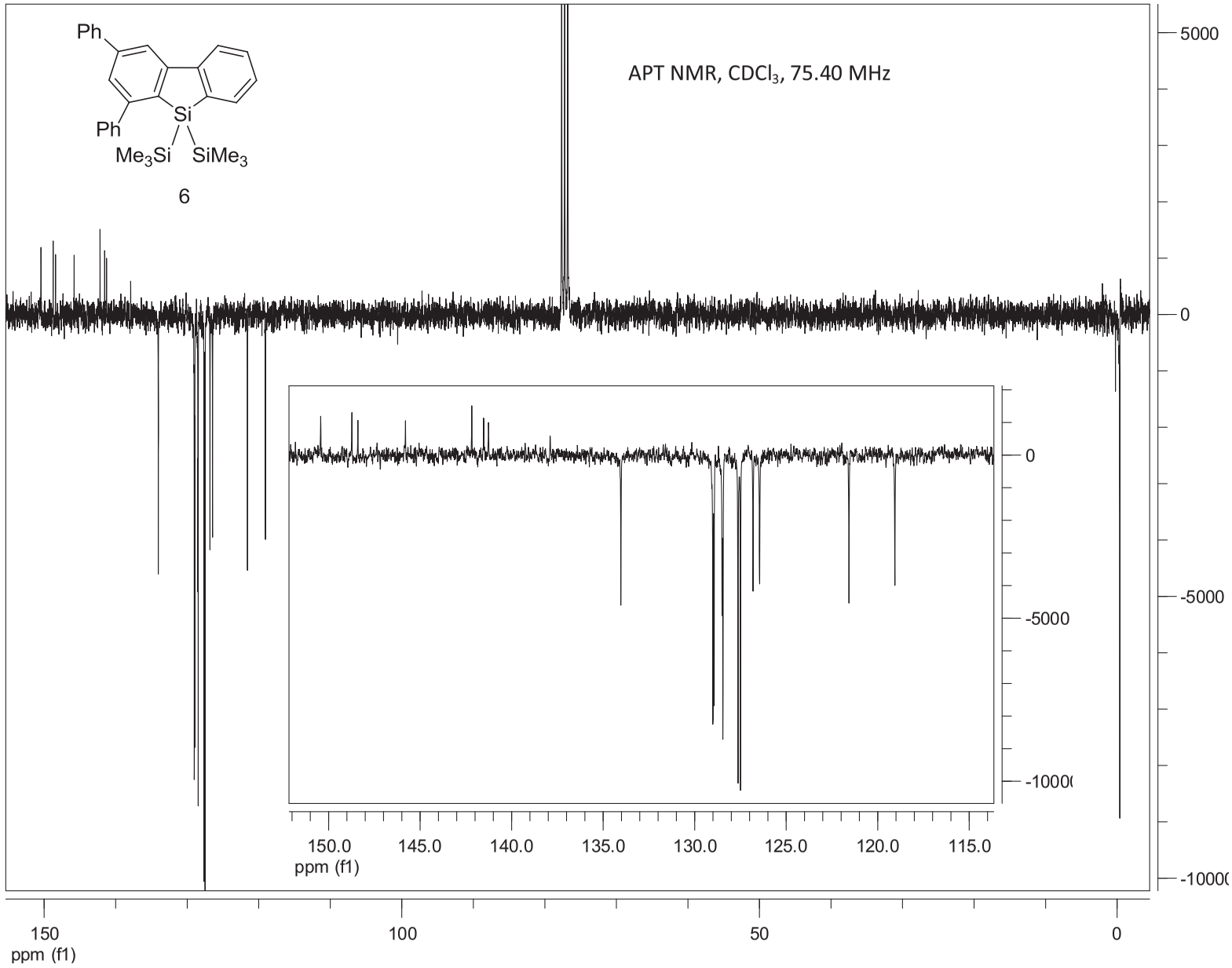

Ph
Ph
Si
Ph
Ph
3
^{29}Si NMR, $CDCl_3$, 99.38 MHz
TMS
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
15.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
ppm (f1)

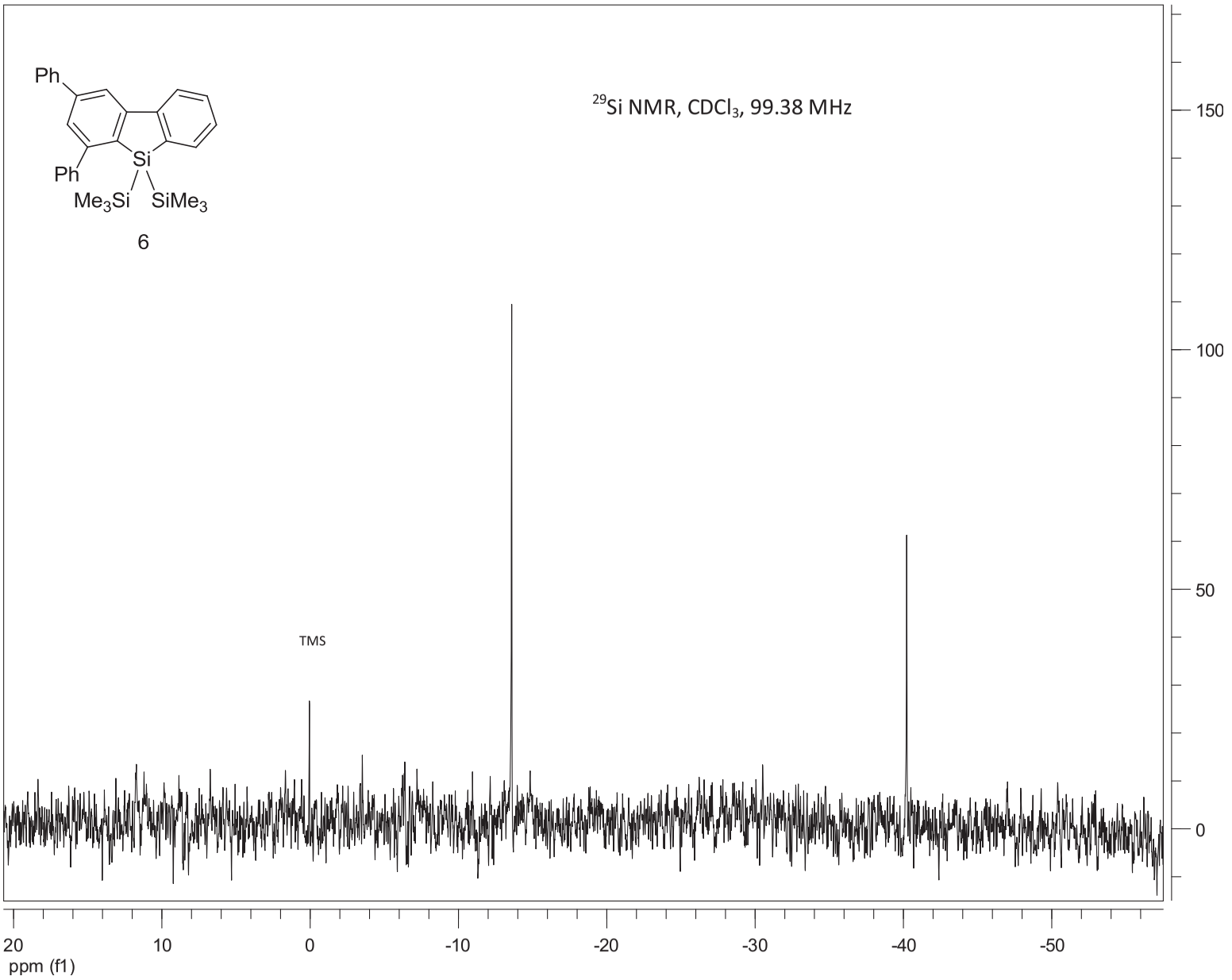

Ph
Ph
Si
Ph
Ph
4
^{1}H NMR, $CDCl_3$, 300 MHz
2000
1500
1000
500
0
8.00
7.50
7.00
ppm (f1)

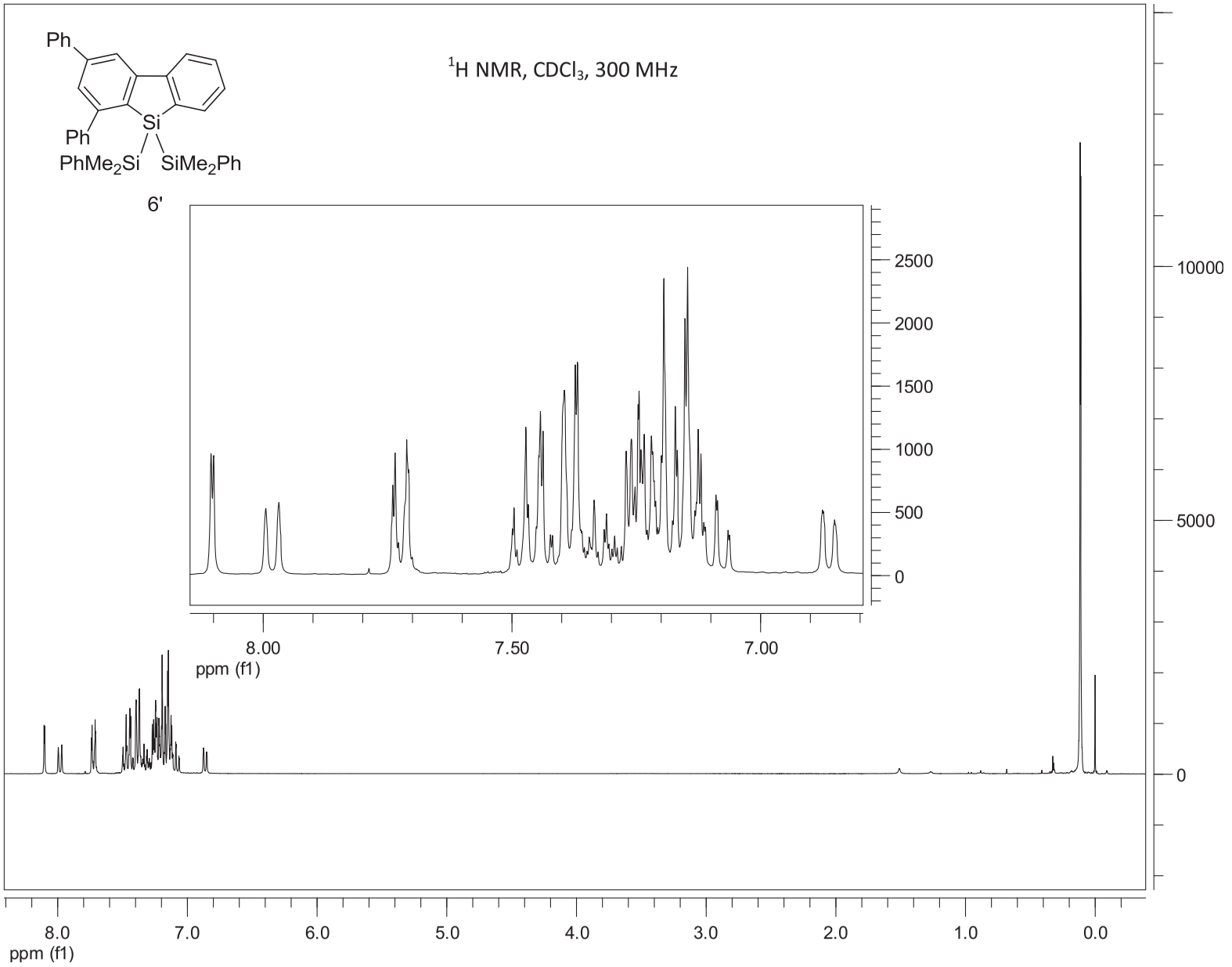

Ph
Ph
Si
Ph
Ph
4
APT NMR, CDCl3, 75.40 MHz
0
-5000
155.0
150.0
145.0
140.0
135.0
130.0
125.0
120.0
115.0
ppm (f1)

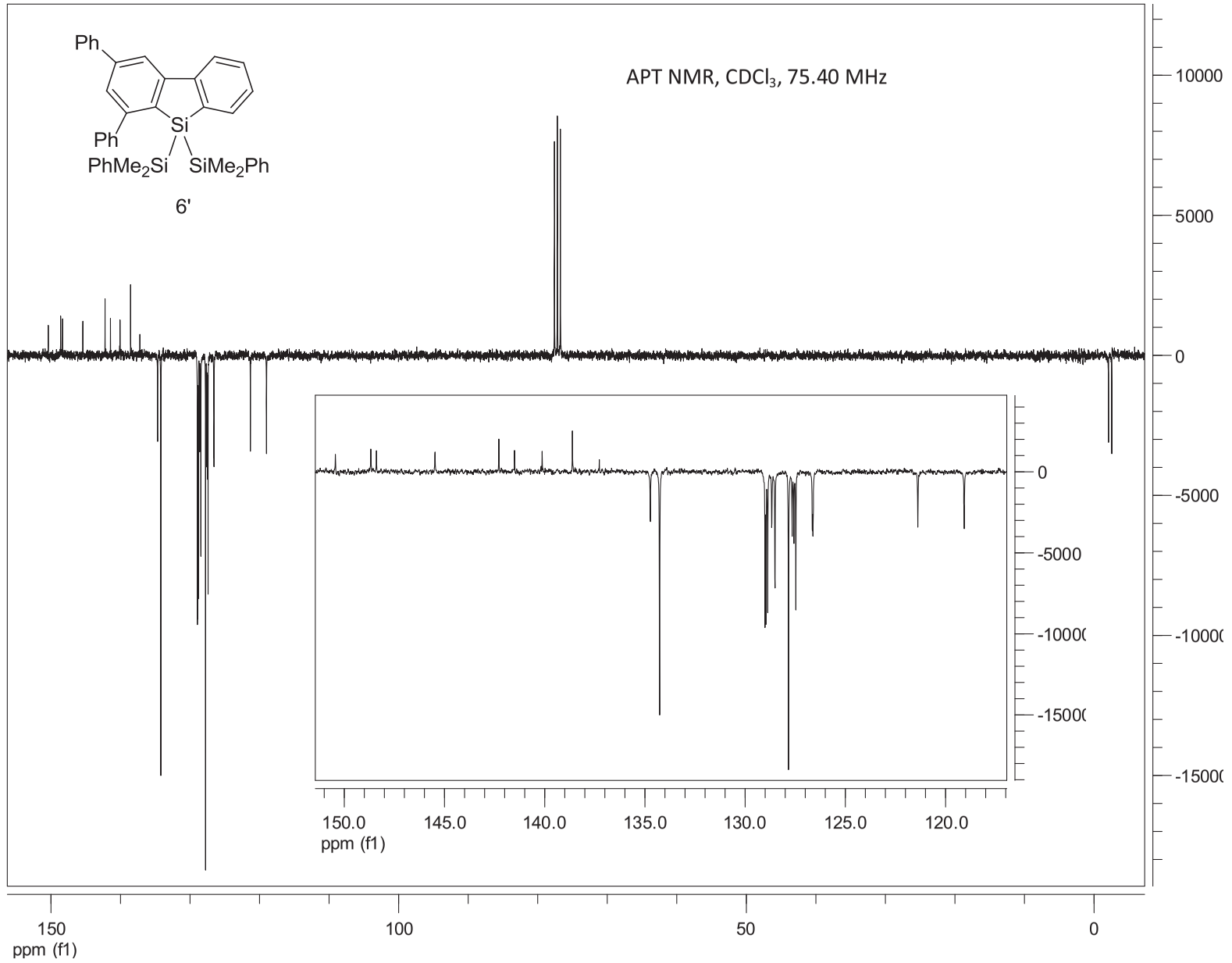

Ph
Ph
Si
Ph
Ph
4
^{29}Si NMR, $CDCl_3$, 99.38 MHz
4
TMS
20.0
15.0
10.0
5.0
0.0
20
10
0
-10
-20
ppm (f1)

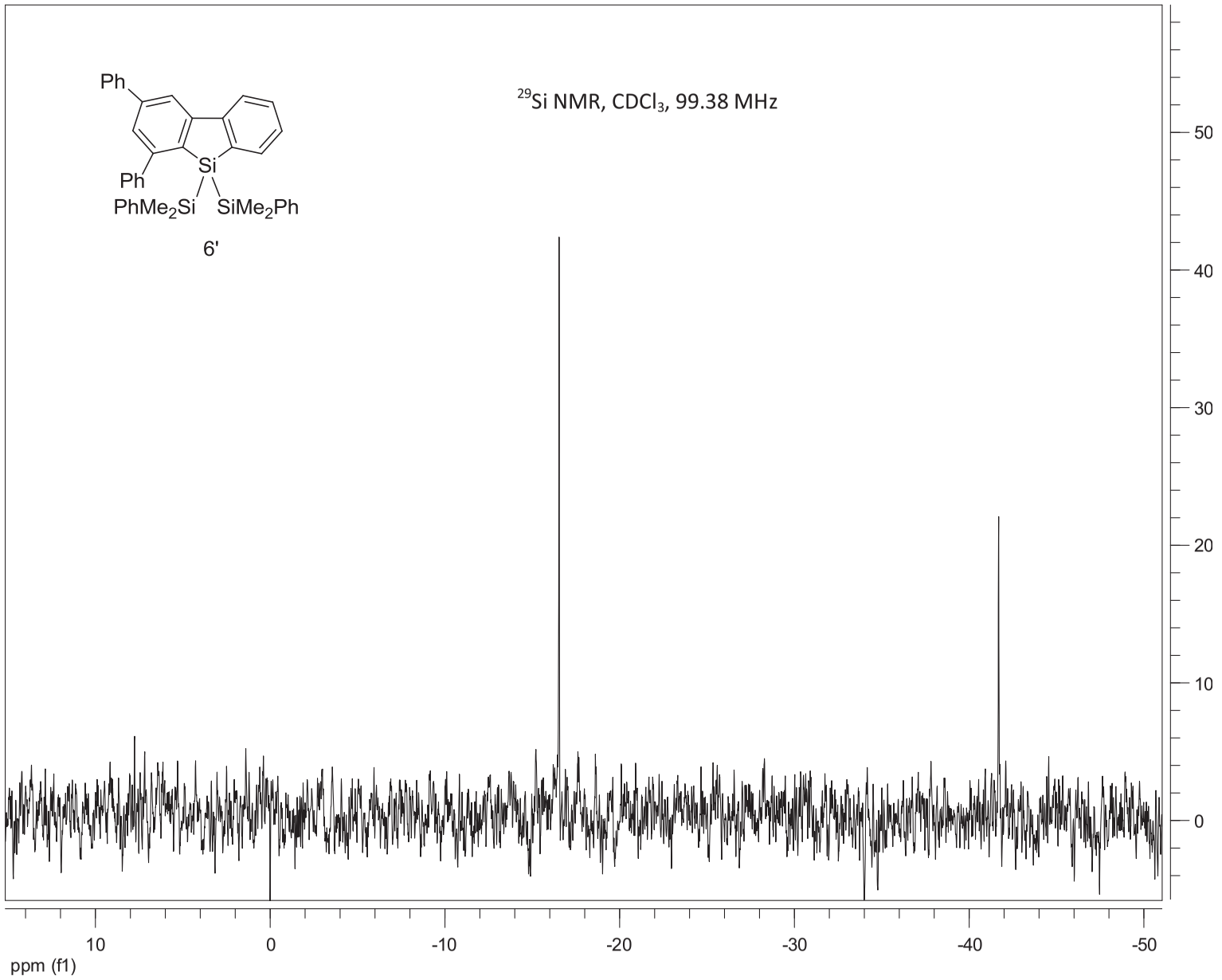

Ph
Si
Ph
Me3Si
SiMe3
6
1H NMR, CDCl3, 300 MHz
15000
10000
5000
0
1000
500
0
8.00
7.50
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


Ph
Ph
Si
Me3Si
SiMe3
6
APT NMR, CDCl3, 75.40 MHz
5000
0
-5000
-10000
150
ppm (f1)
100
50
0
0
-5000
-10000
150.0
145.0
140.0
135.0
130.0
125.0
120.0
115.0
ppm (f1)

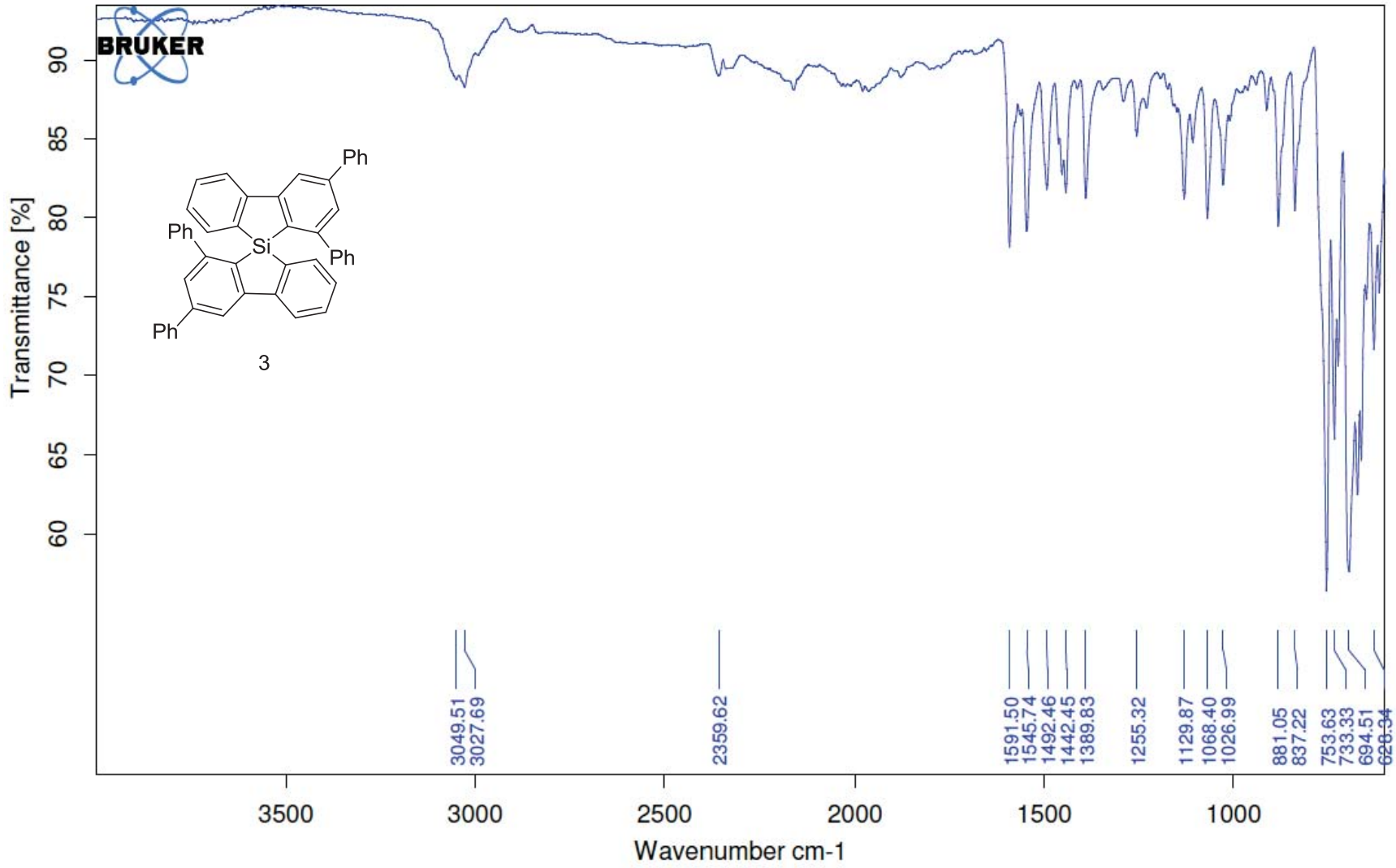

Ph
Ph
Si
Me3Si
SiMe3
6
29Si NMR, CDCl3, 99.38 MHz
TMS
150
100
50
0
20
10
0
-10
-20
-30
-40
-50
ppm (f1)

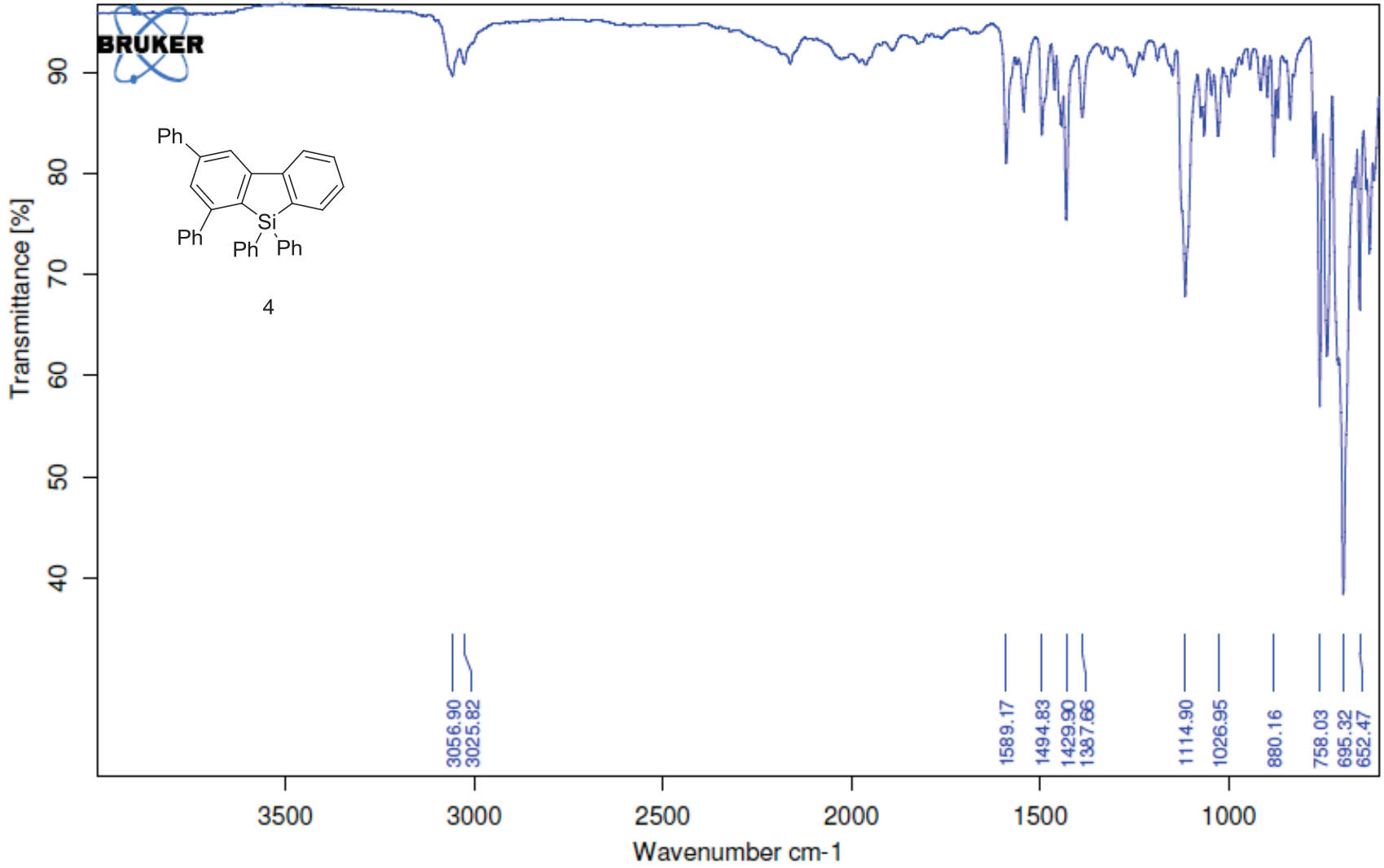

Ph
Si
Ph
PhMe2Si
SiMe2Ph
6'
1H NMR, CDCl3, 300 MHz
2500
2000
1500
1000
500
0
8.00
7.50
7.00
ppm (f1)
10000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

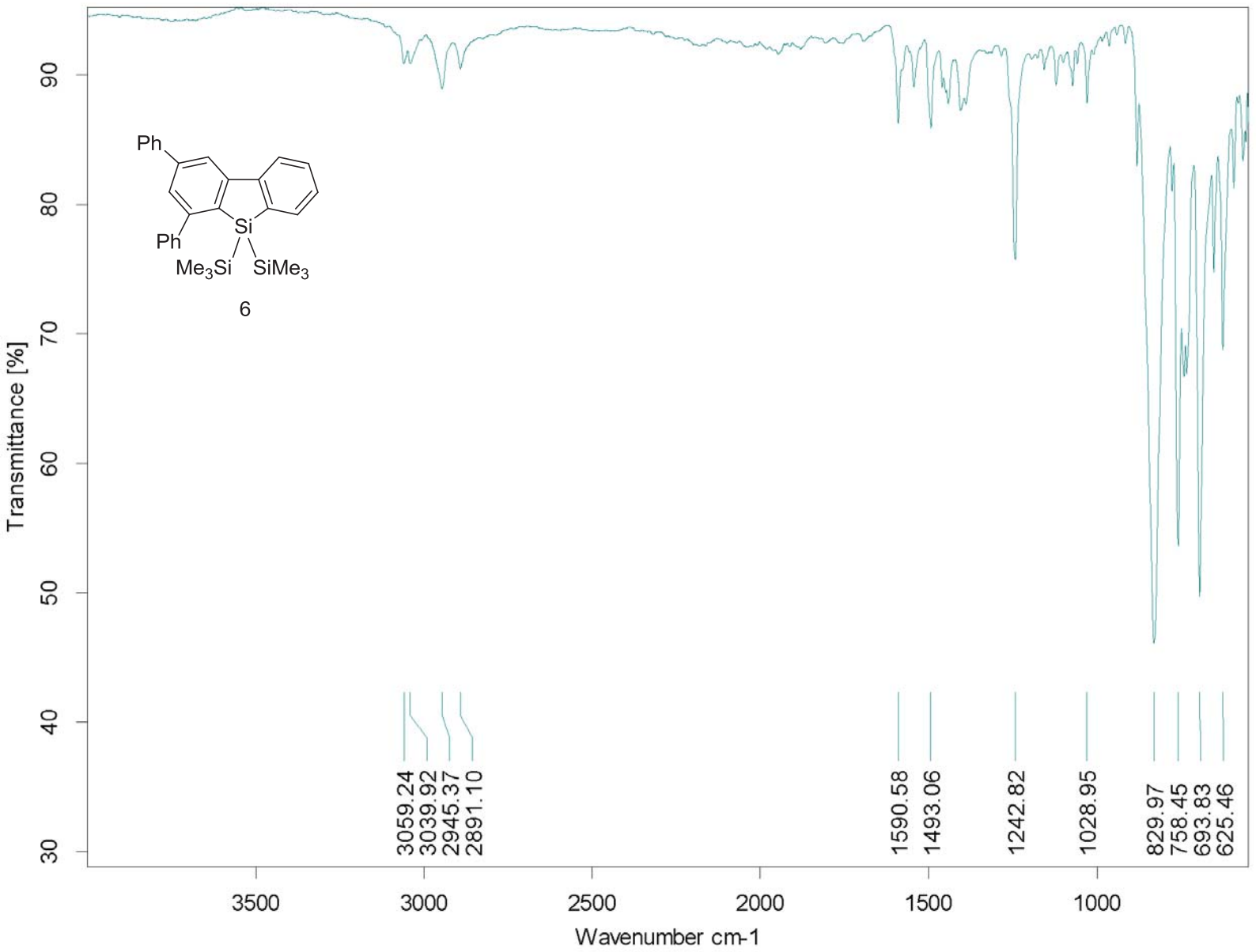

Ph
Si
Ph
PhMe2Si
SiMe2Ph
6'
APT NMR, CDCl3, 75.40 MHz
10000
5000
0
-5000
-10000
-15000
0
-5000
-10000
-15000
150.0
145.0
140.0
135.0
130.0
125.0
120.0
ppm (f1)
150
100
50
0
ppm (f1)

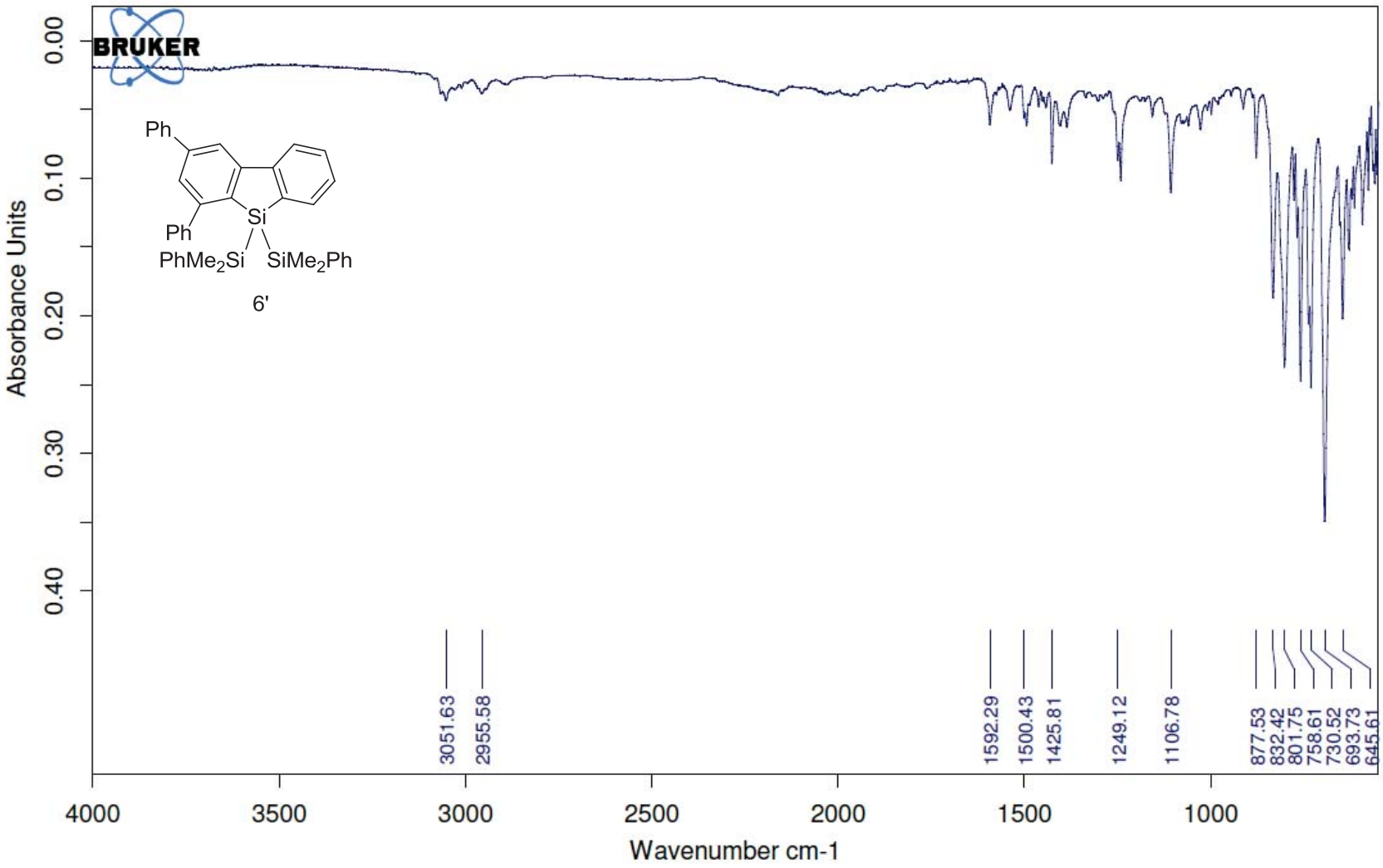

Ph
Si
Ph
PhMe2Si
SiMe2Ph
6'
29Si NMR, CDCl3, 99.38 MHz
50
40
30
20
10
0
10
0
-10
-20
-30
-40
-50
ppm (f1)

IR Spectra:

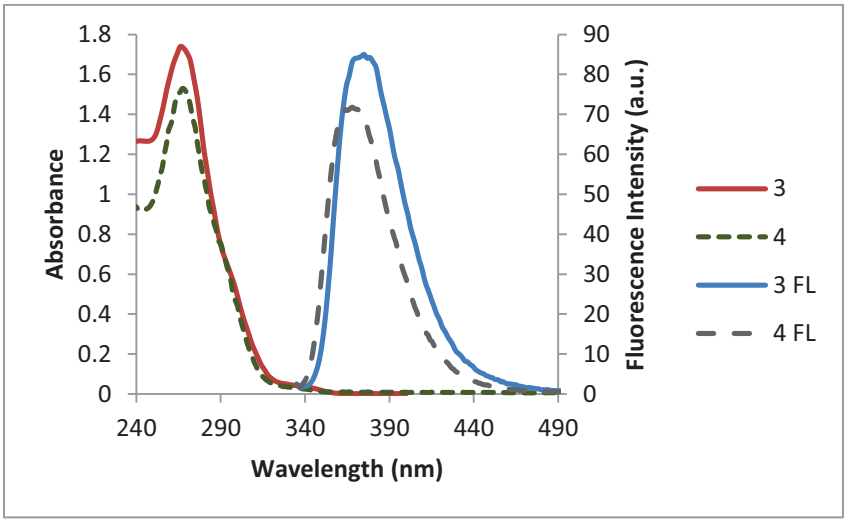

BRUKER
Ph
Ph
Si
Ph
Ph
3
Transmittance [%]
90
85
80
75
70
65
60
3049.51
3027.69
2359.62
1591.50
1545.74
1492.46
1442.45
1389.83
1255.32
1129.87
1068.40
1026.99
881.05
837.22
753.63
733.33
694.51
628.34
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

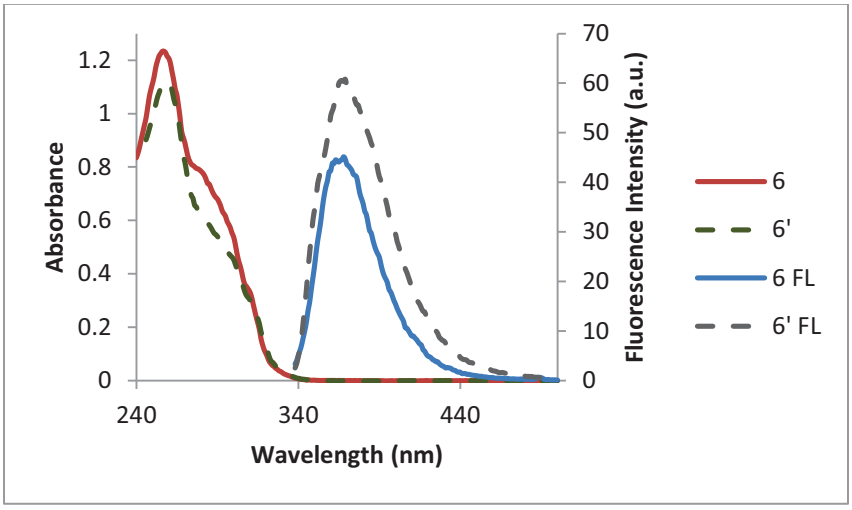

BRUKER
Ph
Ph
Si
Ph
Ph
4
Transmittance [%]
90
80
70
60
50
40
3056.90
3025.82
1589.17
1494.83
1429.90
1387.66
1114.90
1026.95
880.16
758.03
695.32
652.47
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

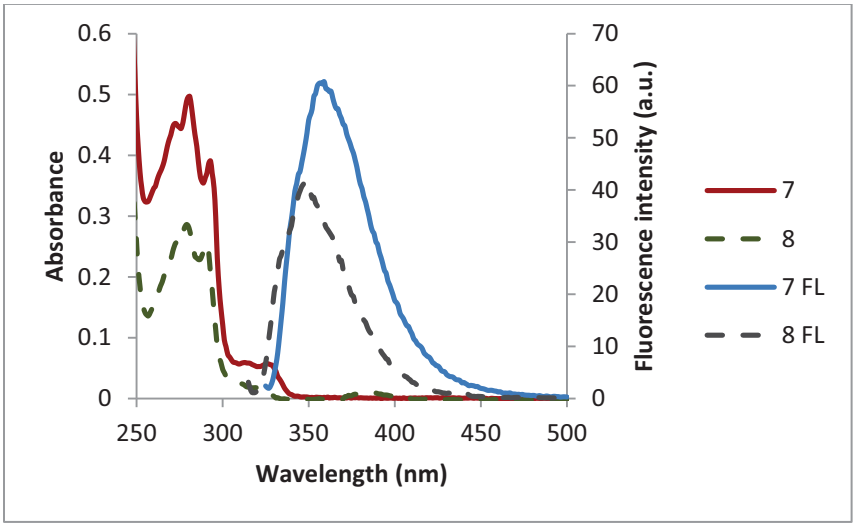

Ph
Si
Ph
Me3Si
SiMe3
6
Transmittance [%]
90
80
70
60
50
40
30
3059.24
3039.92
2945.37
2891.10
1590.58
1493.06
1242.82
1028.95
829.97
758.45
693.83
625.46
3500
3000
2500
2000
1500
1000
Wavenumber cm-1


BRUKER
Ph
Si
Ph
PhMe2Si
SiMe2Ph
6'
Absorbance Units
0.00
0.10
0.20
0.30
0.40
3051.63
2955.58
1592.29
1500.43
1425.81
1249.12
1106.78
877.53
832.42
801.75
758.61
730.52
693.73
645.61
4000
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

UV and Fluorescence Spectra







Gradients:

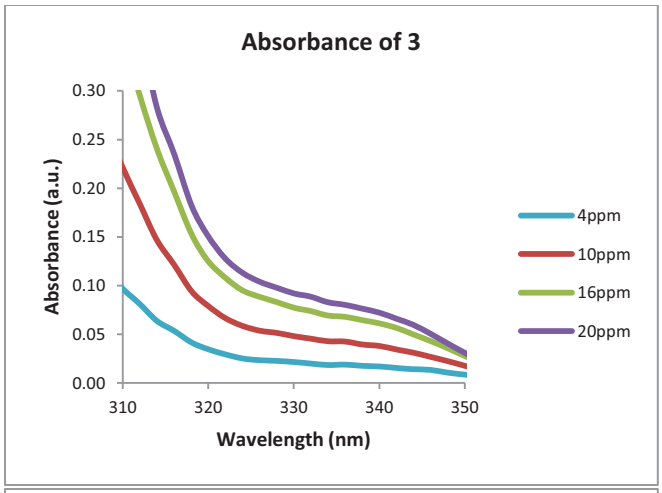
In order to calculate quantum yield efficiency values, the gradient of all compounds were determined after the following equation:

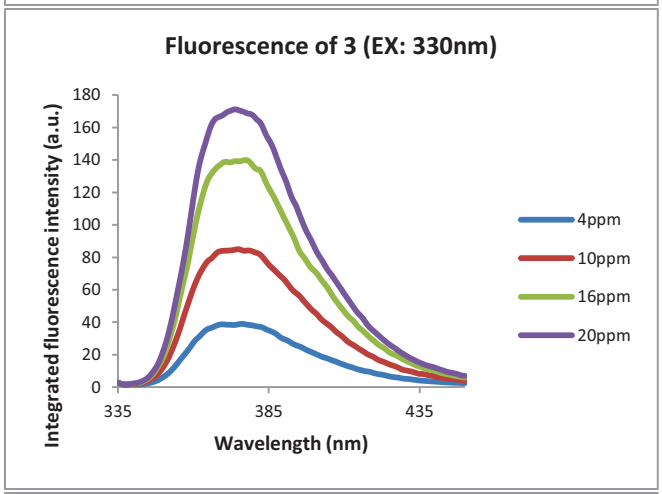
$$(\Phi_{fl})_x = (\Phi_{fl})_{st}(Grad_x/Grad_{st})(\eta_x^2/\eta_{st}^2)$$

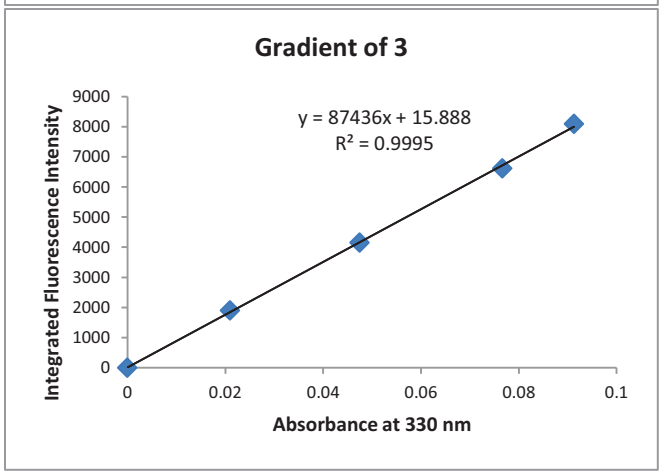
$(\Phi_{fl})_x$ is unknown quantum efficiency, $(\Phi_{fl})_{st}$ is the quantum efficiency of the standard, *Grad* is the slope of the plot of integrated fluorescence intensity *vs* absorbance, and η the refractive index of the solvent (*x* and *st* refer to the unknown compound and the standard respectively).[1] In case of all compounds 2-aminopyridine was used as reference in 1 M H_2SO_4 aqueous solution.

All measurements were carried out in dichloromethane solution.

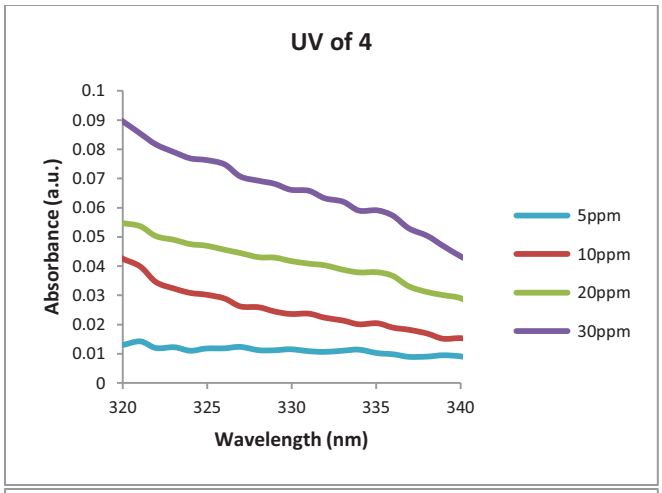
[1] Eaton, D. F. *Pure and Applied Chemistry* **1988**, *60*, 1107

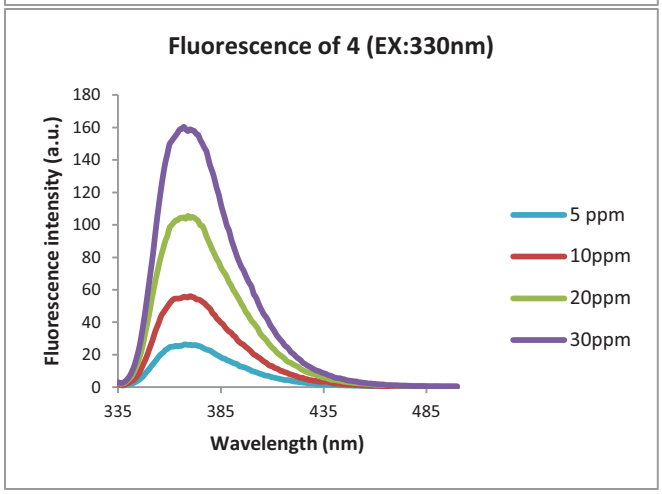


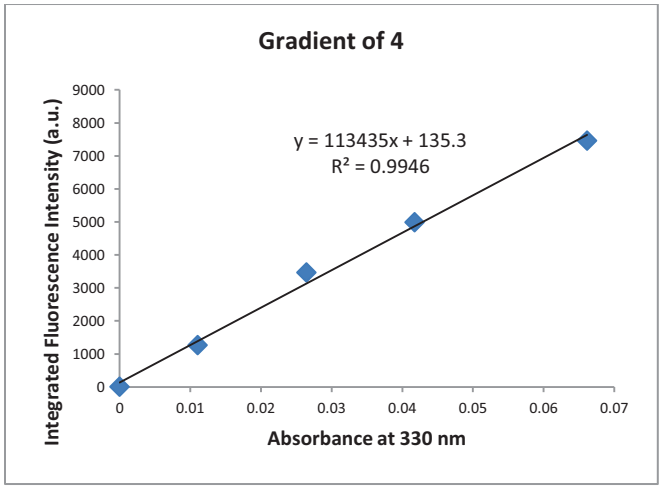




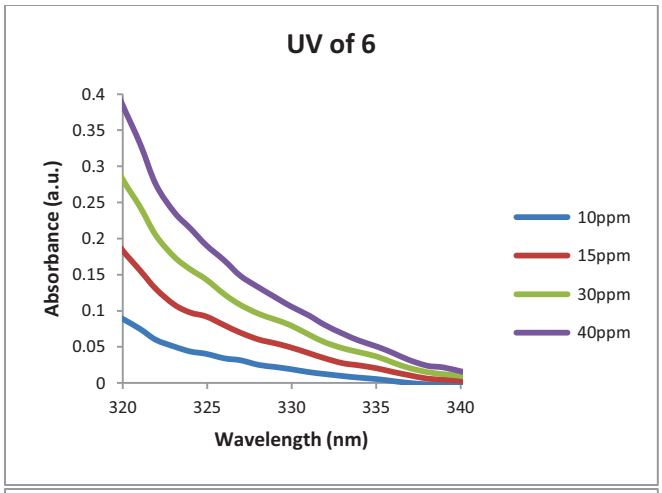
$$\phi_{FL}(3) = 0.6 \cdot \frac{87436}{452662} \cdot \left(\frac{1.424}{1.33}\right)^2 = 0.1329$$

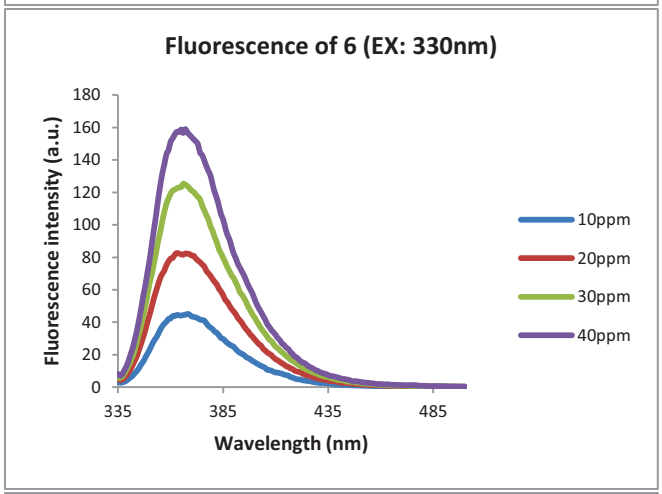


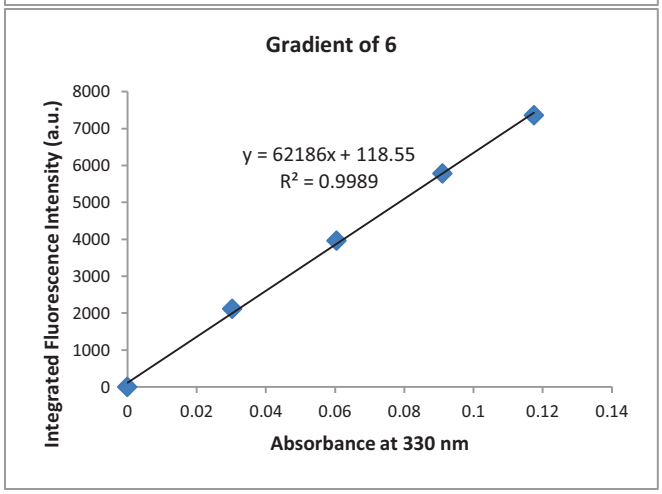




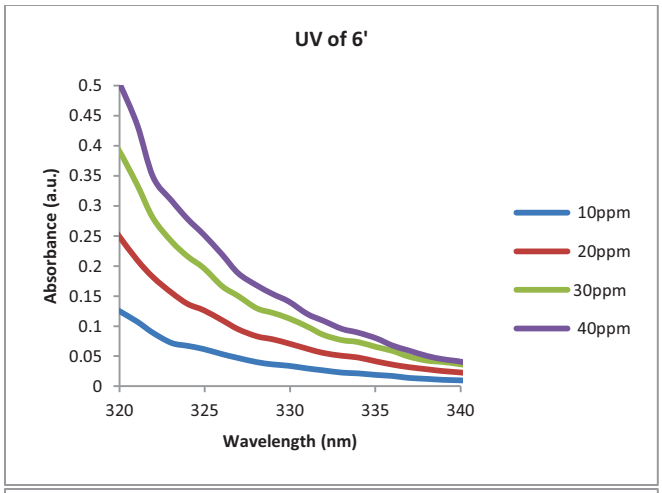
$$\phi_{FL}(4) = 0.6 \cdot \frac{113435}{452662} \cdot \left(\frac{1.424}{1.33}\right)^2 = 0.1724$$

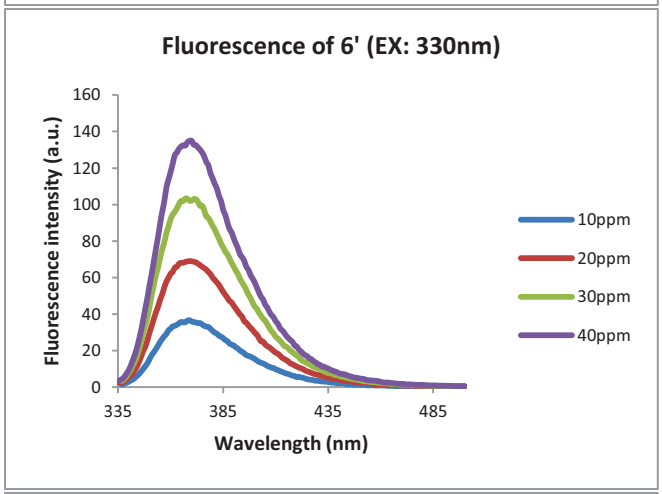


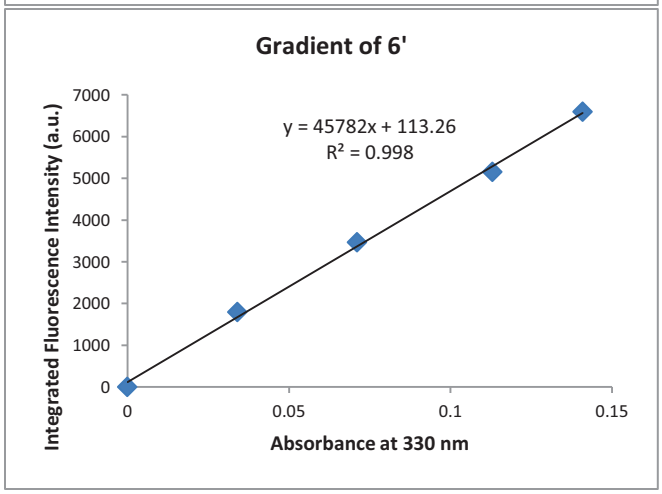




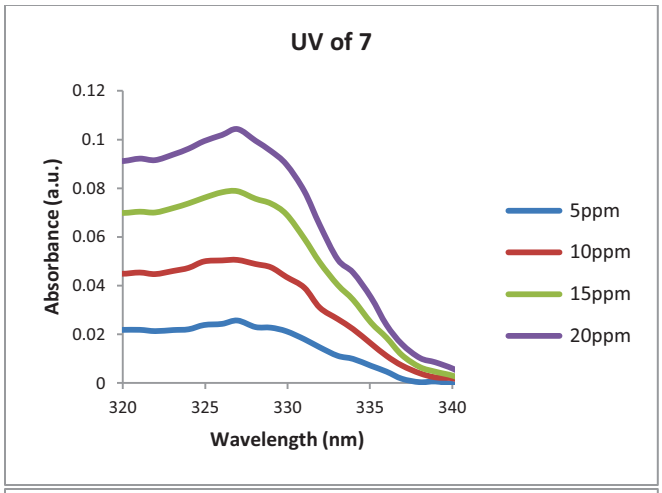
$$\phi_{FL}(6) = 0.6 \cdot \frac{62186}{452662} \cdot \left(\frac{1.424}{1.33}\right)^2 = 0.0945$$

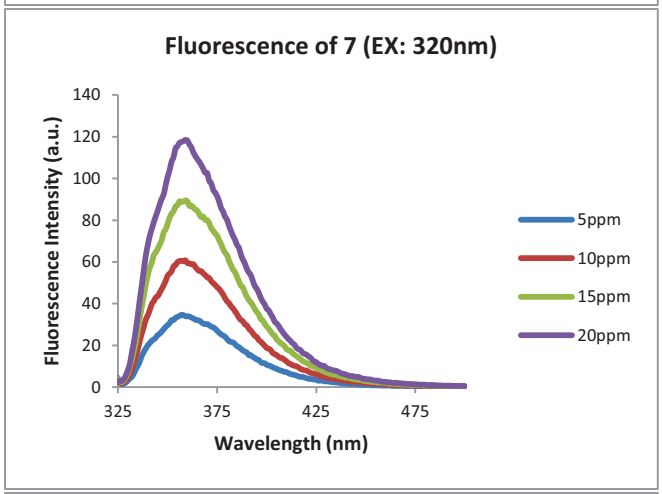


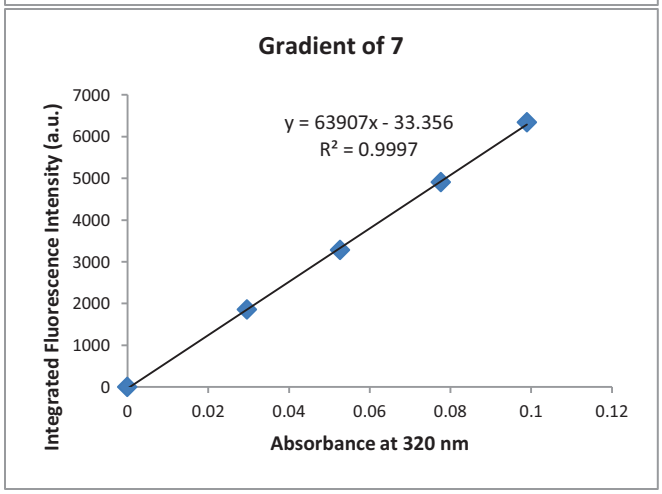




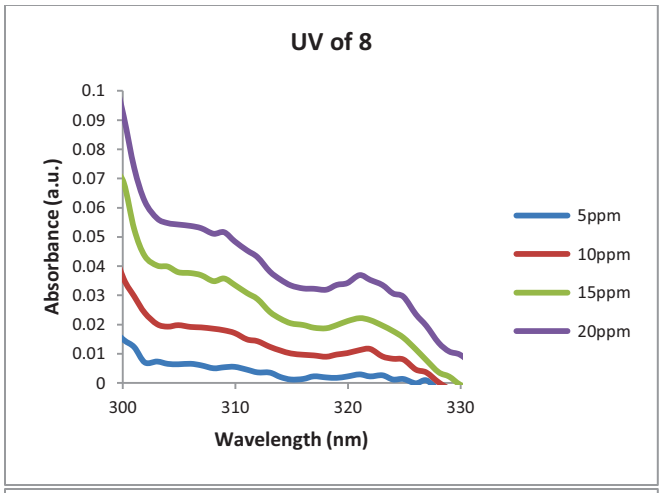
$$\phi_{FL}(6') = 0.6 \cdot \frac{45782}{452662} \cdot \left(\frac{1.424}{1.33}\right)^2 = 0.06957$$

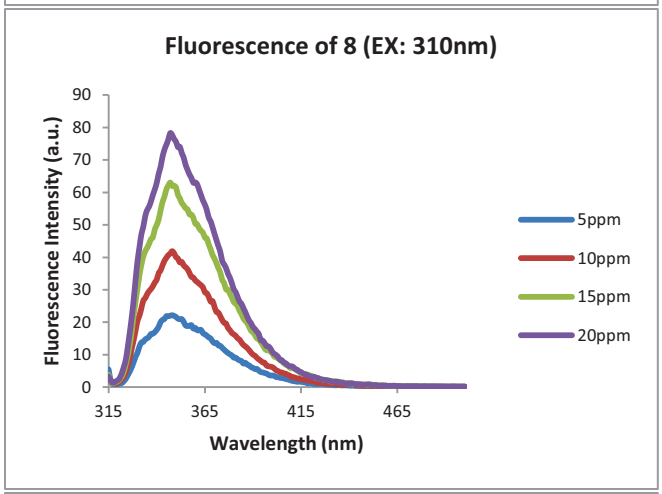


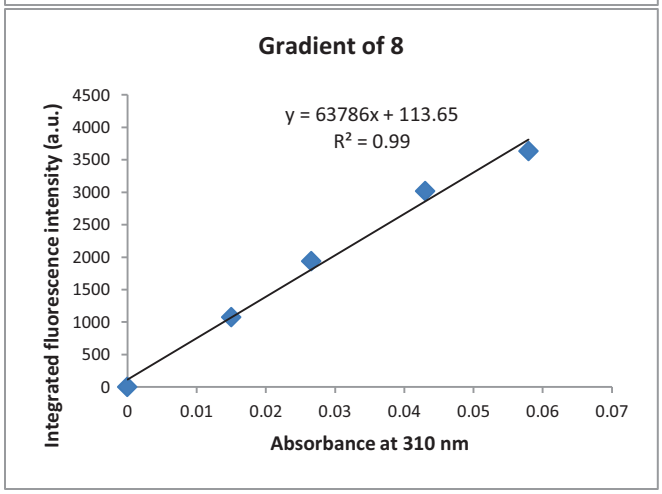




$$\phi_{FL}(7) = 0.6 \cdot \frac{63907}{452662} \cdot \left(\frac{1.424}{1.33}\right)^2 = 0.0971$$





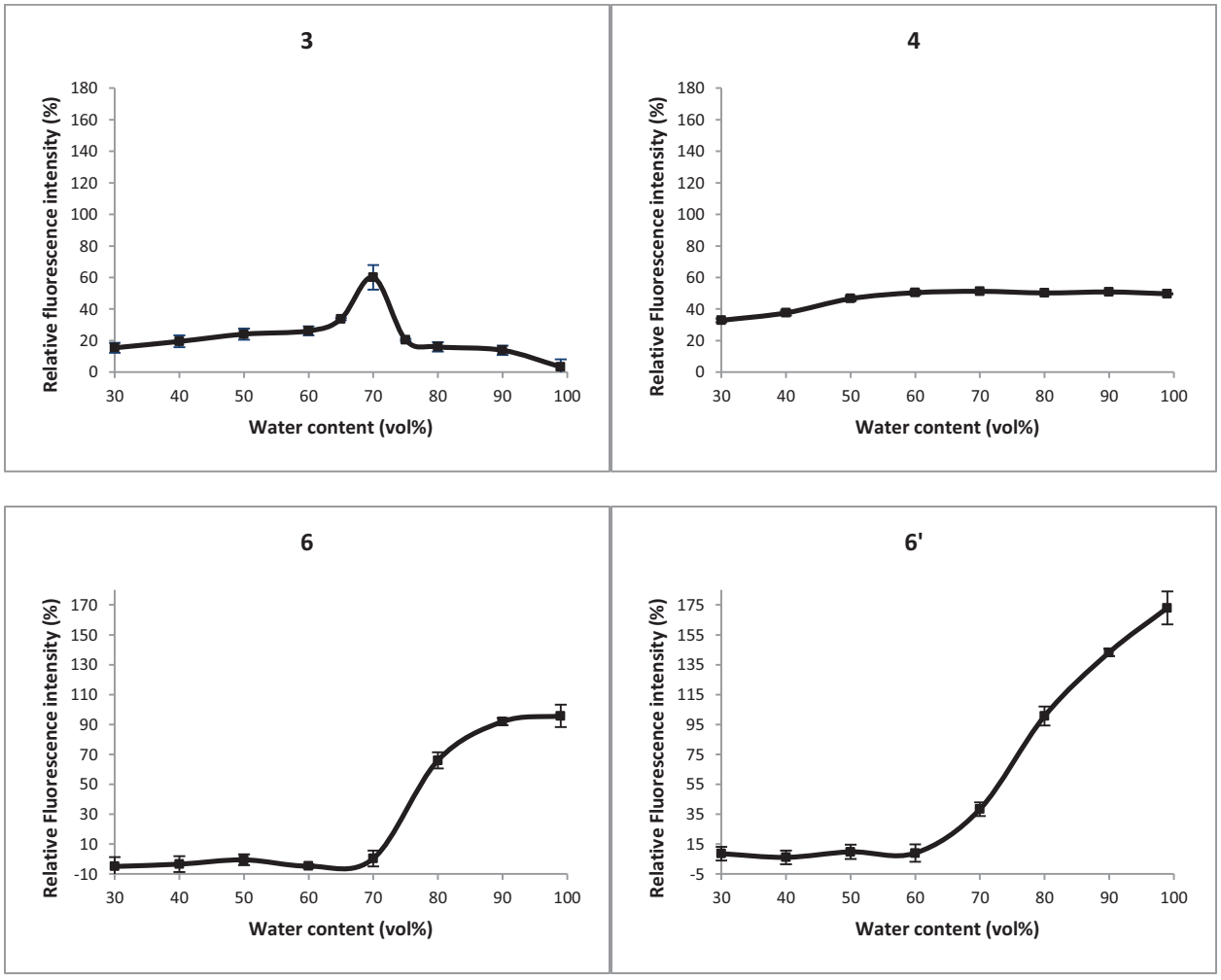


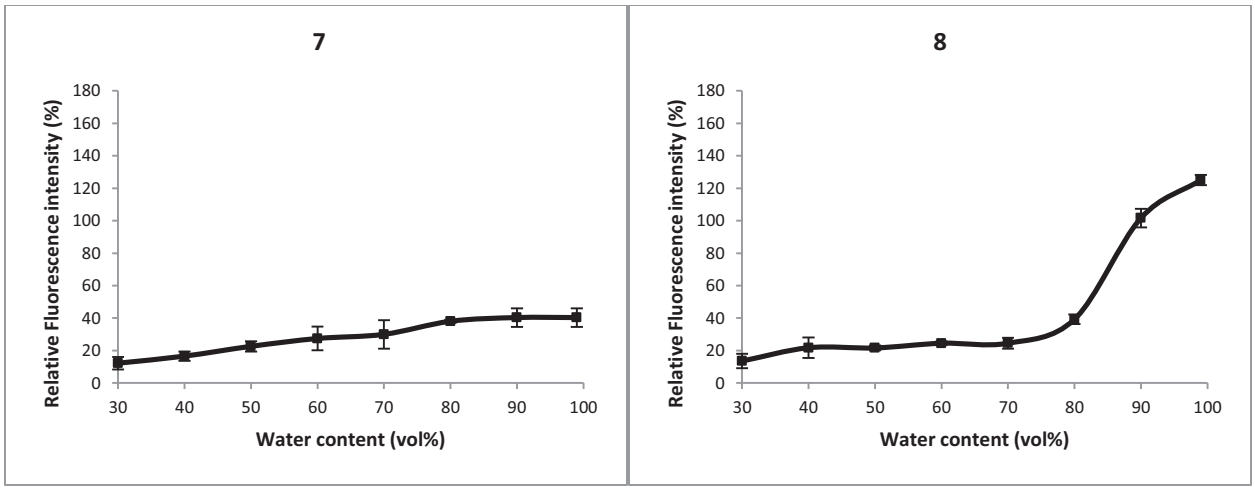
$$\phi_{FL}(8) = 0.6 \cdot \frac{63786}{452662} \cdot \left(\frac{1.424}{1.33}\right)^2 = 0.0969$$

Aggregation Enhanced Emission (AEE)

Fluorescence properties of all compounds were investigated when aggregated.

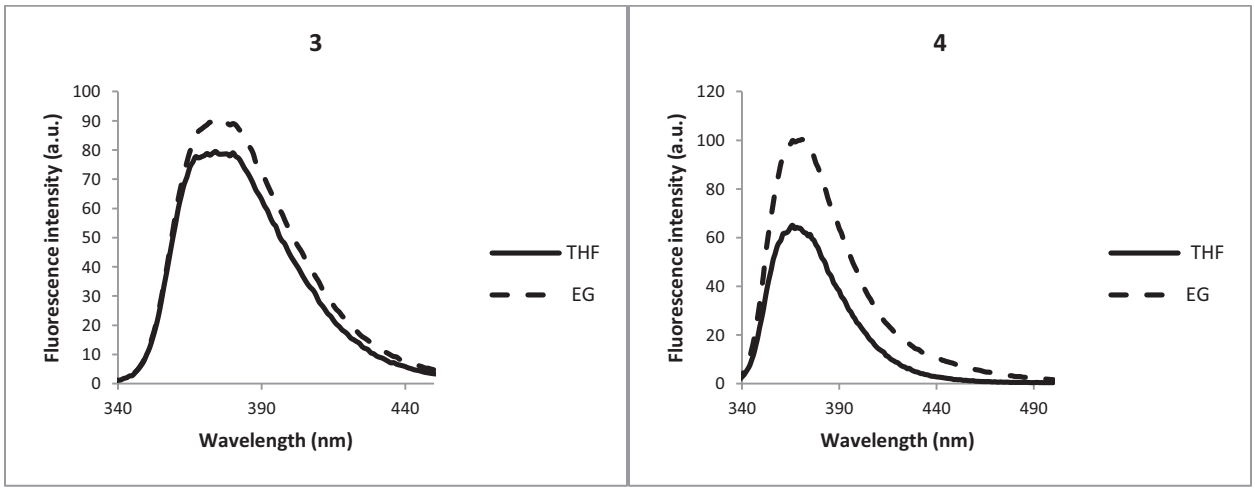
Aggregation was induced by preparing solutions with the same concentration but with different water content in THF. Solutions containing 10 ppm (10mg/l) fluorescent compound were prepared with the following technique: 0.1 ml of 1000 ppm stock solution in THF was injected in 9.9 ml of the appropriate water-THF mixture at vigorous stirring. The solution was stirred 1 minute long, and measured. Solutions with 30 – 99% water content were prepared. From each composition three samples were prepared for repeated measurements. Error bars are represented on each graph.

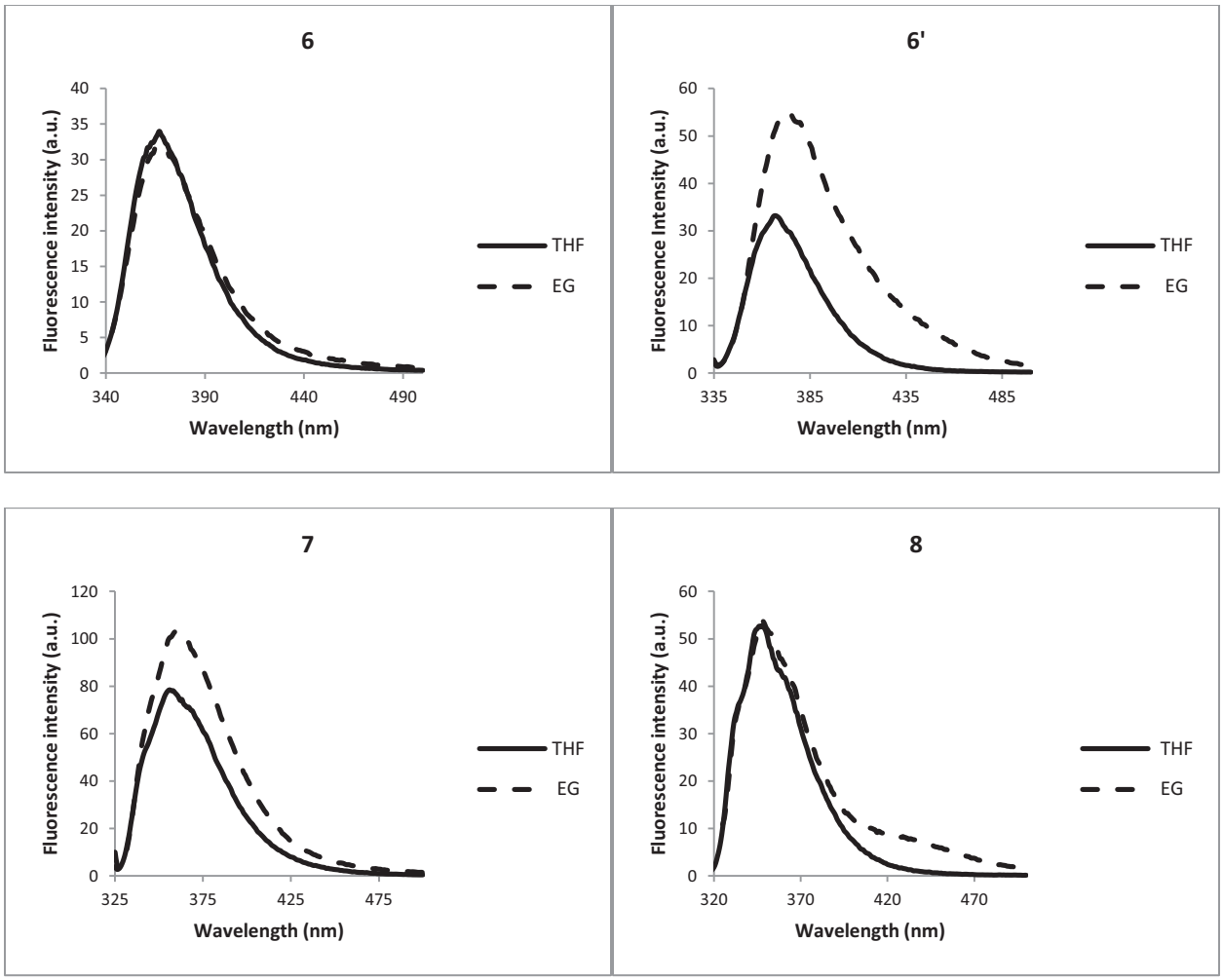




Restriction of intramolecular rotation (RIR)

RIR was studied with measuring all compounds in THF and in ethylene glycol solvents. Each solution contained 10 ppm of the fluorescent compound and each measurement was repeated three times. The curves show the average values.

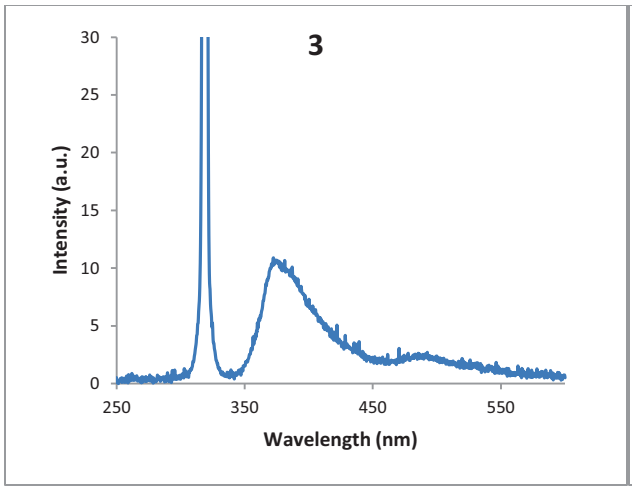


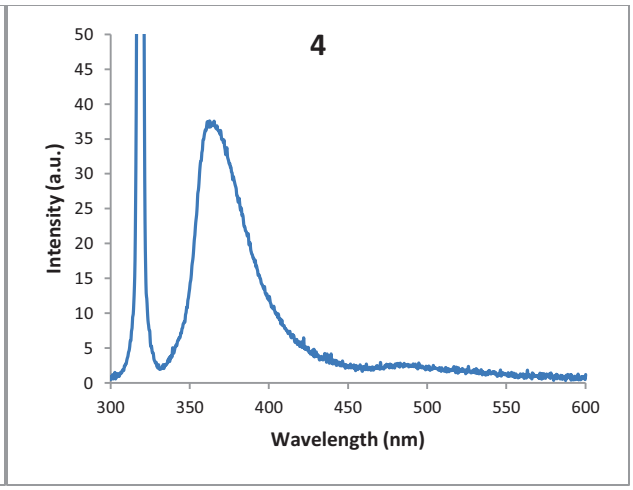


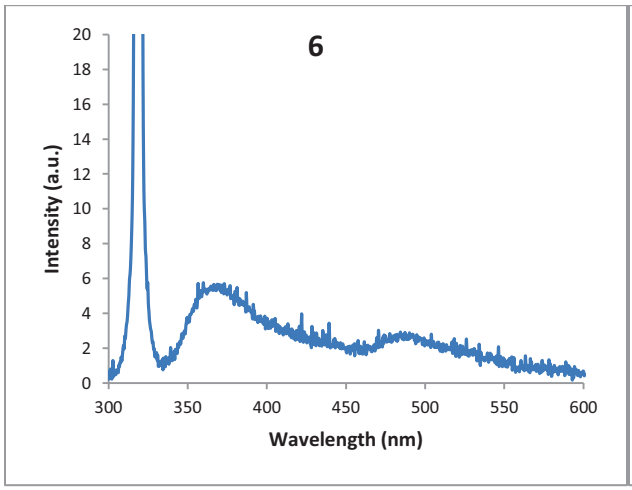
Solid state fluorescence

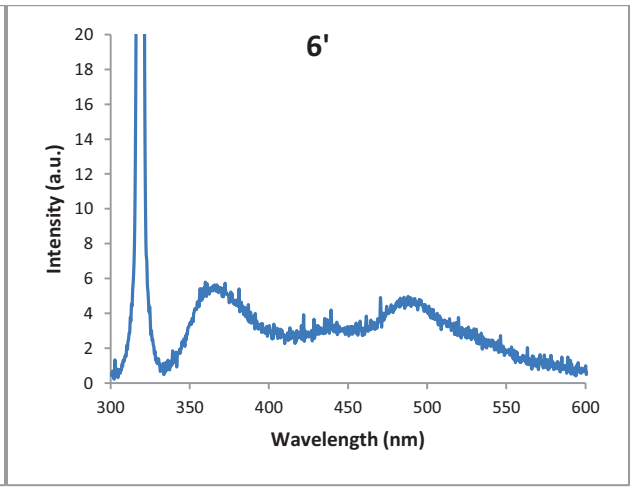
Solid state fluorescence measurements were carried out according to the method described by de Mello et al.[2], using 325 nm CW light from a He-Cd laser for excitation and an Ocean Optics USB2000 miniature fiber optics spectrometer.

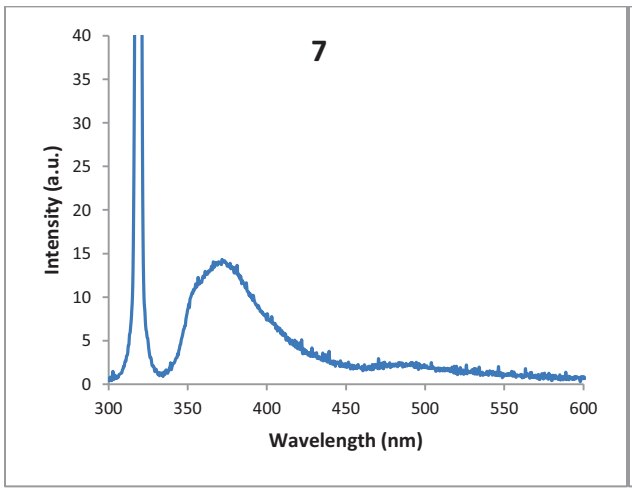
[2] J. C. de Mello, H. F. Wittmann, and R. H. Friend, *Advanced Materials* **1997**, *9*, 230-232.

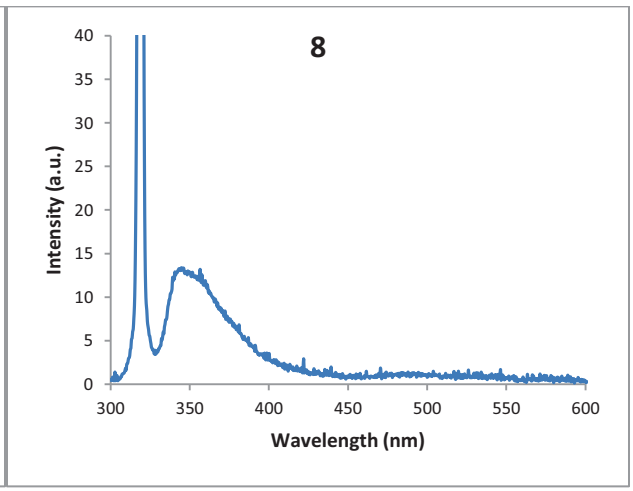

3
Intensity (a.u.)
Wavelength (nm)
0
5
10
15
20
25
30
250
350
450
550


4
Intensity (a.u.)
Wavelength (nm)
0
5
10
15
20
25
30
35
40
45
50
300
350
400
450
500
550
600


6
Intensity (a.u.)
Wavelength (nm)
0
2
4
6
8
10
12
14
16
18
20
300
350
400
450
500
550
600


6'
Intensity (a.u.)
Wavelength (nm)
0
2
4
6
8
10
12
14
16
18
20
300
350
400
450
500
550
600


7
Intensity (a.u.)
Wavelength (nm)
0
5
10
15
20
25
30
35
40
300
350
400
450
500
550
600


8
Intensity (a.u.)
Wavelength (nm)
0
5
10
15
20
25
30
35
40
300
350
400
450
500
550
600

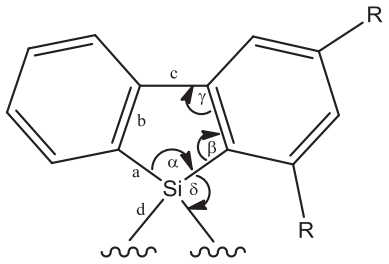
X-Ray crystallography

	2	**3**	**4**	**6***	**6'**	**7**	**8#**
formula	$C_{24}H_{16}Cl_2Si$	$C_{48}H_{32}Si$	$C_{36}H_{26}Si$	$C_{30}H_{34}Si_3$	$C_{40}H_{38}Si_3$	$C_{24}H_{16}Si$	$C_{24}H_{18}Si$
MW	403.36	636.83	486.66	478.84	602.97	332.46	334.47
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Tetragonal	Monoclinic
Space group	P1	P1	$P2_1/c$	P1	$P2_1/c$	$P4_12_12$	$P2_1/c$
Z	2	2	4	2	4	4	4
T, K	100	100	297	110	100	100	100
a, Å	9.622(4)	9.6128(13)	10.718(4)	10.0191(8)	9.575(6)	8.5597(3)	6.649
b, Å	10.580(4)	10.4695(10)	19.313(7)	11.4409(7)	9.741(6)	8.5597(3)	11.482
c, Å	11.616(4)	17.0230(15)	13.299(5)	13.2205(10)	35.41(2)	23.7678(8)	23.034
α, deg	67.30(2)	99.632(7)	90	103.812(4)	90	90	90
β, deg	65.942(7)	91.463(10)	101.050(16)	104.060(4)	94.5 (4)	90	91.47
γ, deg	75.289(7)	93.566(5)	90	102.427(10)	90	90	90
V, $Å^3$	989.6(7)	1684.7(3)	2701.8(17)	1366.17(17)	3292(4)	1741.43(10)	1758.10
d_{calc}, g cm^{-3}	1.354	1.255	1.196	1.164	1.216	1.268	1.264
μ mm^{-1}	0.395	0.867	0.110	1.702	0.172	1.180	1.169
Θ range, deg	2.03-27.49	2.63-69.59	2.20-25.49	3.62-72.32	1.15-26.05	5.49-69.59	3.84-72.03
reflns collected	22864	39235	30088	25289	50362	28830	28558
independent reflns	4508	10954	4969	5058	6393	1643	3269
GOF (F^2)	1.010	1.022	0.937	1.018	1.149	1.093	1.056
R_1, (wR_2), %	3.21(8.39)	3.99(10.51)	4.48(10.57)	3.5(9.51)	4.64 (11.89)	2.75(7.16)	3.88(10.19)

* Also published by Millevolte et al.[3]; # Also published by Bel'skii et al.[4]

[3] Millevolte, A. J.; Winkel, Y.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5375.

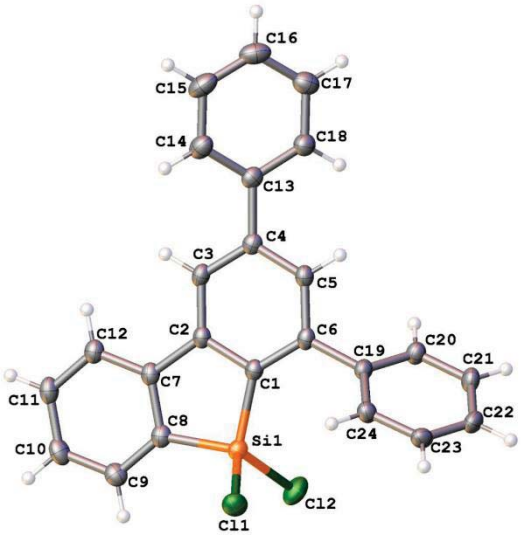
[4] Bel'skii, V. K.; Dzyabchenko, A. V. *Journal of Structural Chemistry* **1985**, *26*, 78-83.



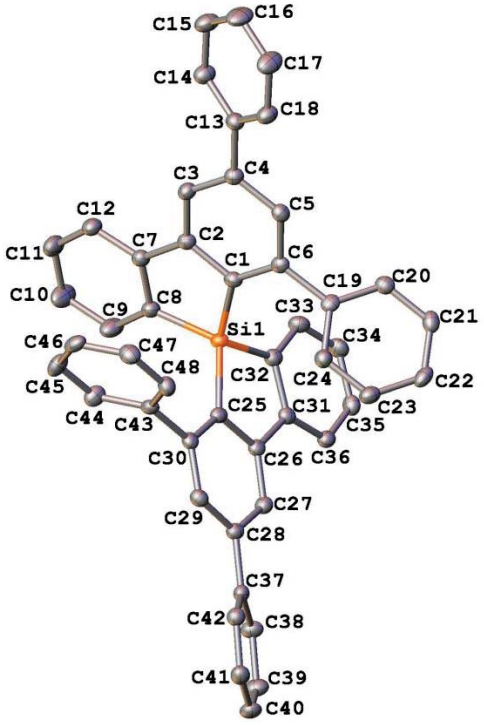
	2	3	4	6(*)	6’	7	8
formula	$C_{24}H_{16}Cl_2Si$	$C_{48}H_{32}Si$	$C_{36}H_{26}Si$	$C_{30}H_{34}Si_3$	$C_{40}H_{38}Si_3$	$C_{24}H_{16}Si$	$C_{24}H_{18}Si$
MW	403.36	636.83	486.66	478.84	602.97	332.46	334.47
a	1.843	1.861	1.870	1.893	1.895	1.880	1.874
b	1.408	1.410	1.404	1.415	1.416	1.418	1.419
c	1.490	1.491	1.488	1.486	1.483	1.489	1.487
d	2.060	1.870	1.861	2.361	2.372	1.869	1.875
α	94.26	92.02	91.31	90.24	90.94	92.10	91.5
β	107.27	108.45	109.15	109.77	108.33	108.79	109.1
γ	115.29	115.5	114.85	115.19	115.71	115.12	114.9
δ	114.25	118.97	112.36	111.76	119.64	116.46	109.2

Thermal ellipsoid diagrams

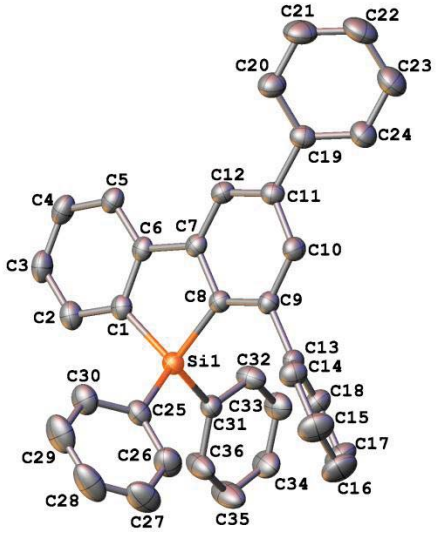
Structure of **2**



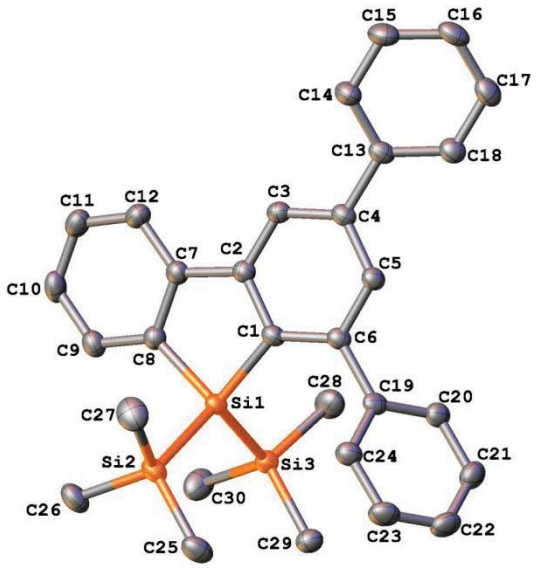
Structure of **3**



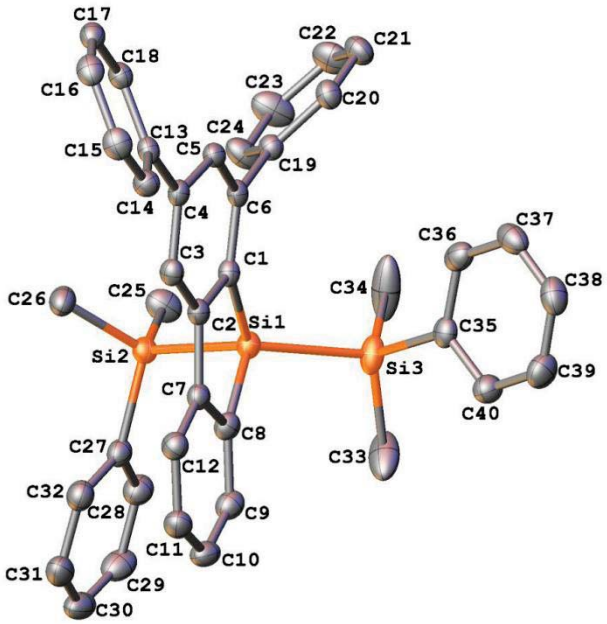
Structure of **4**



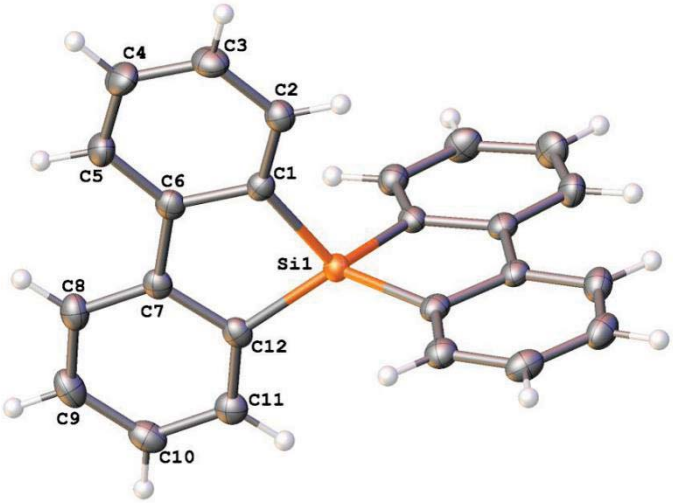
Structure of **6**



Structure of **6'**



Structure of **7**

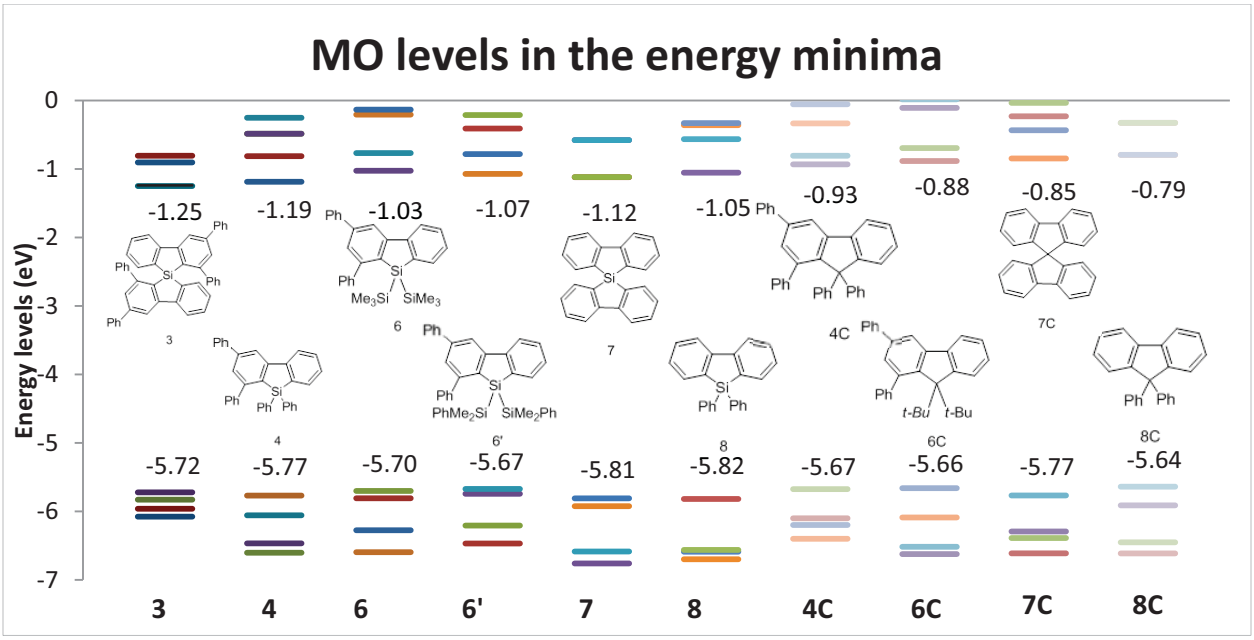


Theoretical calculations

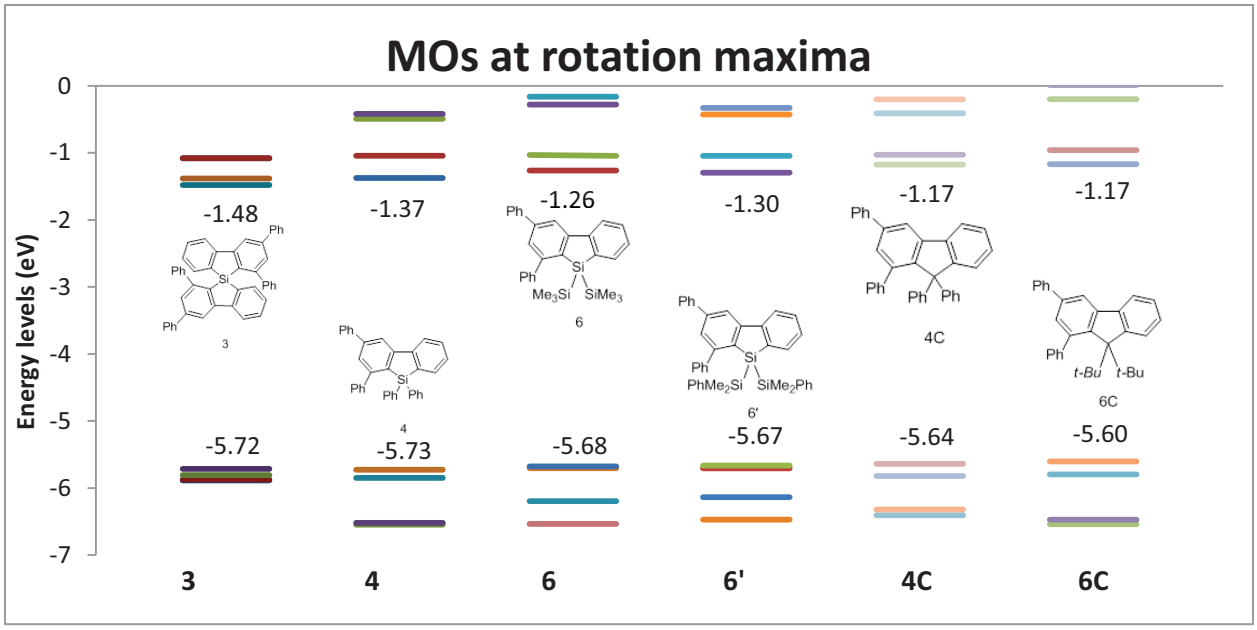
Molecular orbital calculations were performed with TD-DFT method at the B3LYP/6-31G* level using Gaussian 09 package. The calculated energies from HOMO-3 to LUMO+3 are shown in Figure x. The new phenyl substituted silafluorene compounds were compared to their unsubstituted and to their carbon analogs.

Comparing the silafluorenes with their carbon analogs all energy levels decrease, but the HOMO levels lower with less than the LUMO levels, thus the HOMO-LUMO gap is decreased. Compound **7** shows the biggest decline with 0.23 eV.

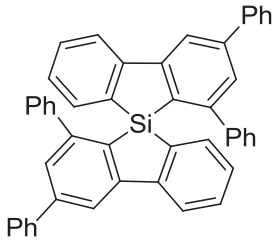
Comparing the phenyl substituted silafluorenes with their unsubstituted analogs (**3** and **4** with **7** and **8**) the HOMO levels raise slightly and the LUMO levels lower narrowing the HOMO-LUMO gap with 0.22 and 0.19 eV respectively. This is in good agreement with the UV spectra, where **7** and **8** has absorption at around 280 nm while the silafluorene ring of **3** and **4** has absorption at 298 nm, which shows up as a shoulder because of the very intensive peak of the substituent phenyl groups.



Molecular orbital calculations were carried out also for electronically advantageous conformations, where the phenyl groups are in the same plane with the silafluorene ring and the aromatic rings can conjugate. These conformations are at the rotation barrier maxima, thus the probability of these conformations is low, but according to the calculated excited states they are responsible for the broad absorption bands in the UV spectra at around 330 nm. The conjugating phenyl groups do not cause big change in the HOMO levels but lower the LUMO levels and decrease the HOMO-LUMO gap with 0.23-0.35 eV (Figure xx.).



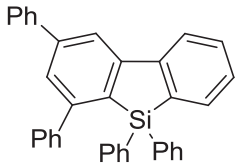
Structures:



3

Molecular formula: $C_{48}H_{32}Si$

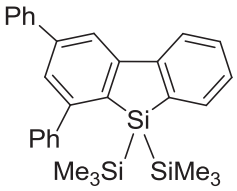
Molecular weight: 636.2 g/mol



4

Molecular formula: $C_{36}H_{26}Si$

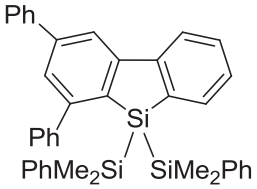
Molecular weight: 486.1 g/mol



6

Molecular formula: $C_{30}H_{34}Si_3$

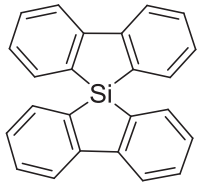
Molecular weight: 478.1 g/mol



6'

Molecular formula: $C_{40}H_{38}Si_3$

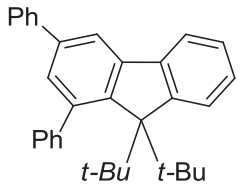
Molecular weight: 602.2 g/mol



7

Molecular formula: $C_{24}H_{16}Si$

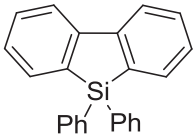
Molecular weight: 332.5 g/mol



6C

Molecular formula: $C_{33}H_{34}$

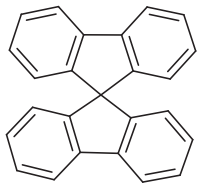
Molecular weight: 430.1 g/mol



8

Molecular formula: $C_{24}H_{18}Si$

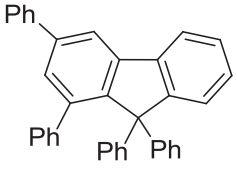
Molecular weight: 334.5 g/mol



7C

Molecular formula: $C_{25}H_{16}$

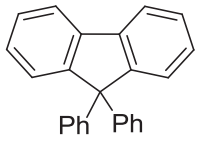
Molecular weight: 316.5 g/mol



4C

Molecular formula: $C_{37}H_{26}$

Molecular weight: 470.1 g/mol



8C

Molecular formula: $C_{25}H_{18}$

Molecular weight: 318.5 g/mol

Calculated Absorption maxima and oscillation strengths in the energy minima:

Compound	ABS MAX (nm)	ABS MAX (eV)	oscillation strength (f)	excited state (singlet)
3	320	3.87	0.0357	1
	320	3.88	0.0135	2
	299	4.14	0.1488	5
4	312	3.97	0.0319	1
	294	4.22	0.0576	2
	271	4.58	0.6309	3
6	306	4.05	0.0075	1
	292	4.24	0.2325	2
	280	4.43	0.3040	3
6'	312	3.98	0.0110	1
	300	4.14	0.3635	2
	285	4.36	0.2136	3
7	304	4.08	0.0371	1
	304	4.08	0.0374	2
	273	4.55	0.0656	5
8	298	4.17	0.0621	1
	273	4.54	0.0592	2
	258	4.81	0.0153	3

Calculated Absorption maxima and oscillation strengths at rotation maxima:

Compound	ABS MAX (nm)	ABS MAX (eV)	oscillation strength (f)	excited state (singlet)
3	342	3.62	0.0476	1
	338	3.66	0.0217	2
	321	3.86	0.0898	4
	306	4.05	0.2943	7
4	337	3.68	0.0305	1
	306	4.05	0.1441	2
	289	4.29	0.3646	3
6	333	3.72	0.0079	1
	308	4.02	0.2801	2
	296	4.19	0.1652	3
	287	4.32	0.2751	4
6'	334	3.71	0.0076	1
	315	3.9372	0.4215	2
	299	4.1458	0.1299	3

Protocol for Toxicity Assays [5, 6]

Compound Handling: Working stocks were prepared at a final concentration of 100X in anhydrous DMSO. Serial dilutions were made in DMSO in 96 well polypropylene plates using the Precision XS liquid handler (BioTek, Inc.). Compounds were divided equally into the corresponding wells of a 384 well plate in all 4 quadrants using a Biomek FX liquid handler with 96 channel pipetting head (Beckman-Coulter, Inc.). Compounds were stored at -20 degrees in 100% DMSO until the day of the assay(s). Freeze-thaw cycles are minimized to a maximum of 10 per plate.

Cytotoxicity Assays: The cell line was maintained as previously reported. Cells were harvested by trypsinization using 0.05% trypsin and 0.1% EDTA and then counted in a Cellometer Auto T4 cell counter (Nexcelom, inc), before dilution for assay plating. Cell plating, compound handling and assay set up were performed as previously reported[35] except that the cells were plated in 50 μL volumes in 384 well clear bottoms; tissue culture plates (Corning-Costar, Inc). Compounds were added from the 384-well compound stock plates at a 1:100 dilution using a Biomek FX liquid handler equipped with a 384 channel head (Beckman Coulter, Inc.). 15μL of cell titer-glo reagent (Promega Corporation, Inc.) was added and incubated for 10 min at room temperature with gentle agitation to lyse the cells.

Data Analysis: IC_{50}s for cytotoxicity assays were determined by cell-titer glo using XLfit 5.0 as previously reported. The IC_{50} determined using the best fit curve for dosage response is reported as the final IC_{50}. The best fit curve is defined as the curve that has the lowest standard error. If the standard error exceeded 10% of the IC_{50}, the assay was deemed a failure and repeated.

Compound	**3**	**4**	**6**	**6'**
IC50 (μM)	>100	>100	>100	>100

Cytotoxicity data of **3, 4, 6**, and **6'** measured in normal adult human primary dermal fibroblast cells.

[5] Langenhan, J. M.; Peters, N. R.; Guzei, I. A.; Hoffmann, F. M.; Thorson, J. S. *PNAS,* **2005,** *30*, 12305-10.
[6] Ahmed, A.; Peters, N. R.; Fitzgerald, M. K.; ;Watson Jr., J. A.; Hoffman, F. M.; Thorson, J. S., *JACS*, **2006,** *128*, 14224-14225.

Summarized toxicity results of the new silafluorenes:

Compound	3	4	6	6'
Conc. (μM)	%Inhibition	%Inhibition	%Inhibition	%Inhibition
100.00	9.04	4.06	13.80	56.31
100.00	18.83	16.74	11.56	11.40
100.00	-2.54	4.56	23.14	36.48
100.00	12.17	22.44	14.41	23.62
50.00	22.14	1.64	20.14	13.09
50.00	-3.95	5.61	26.64	15.99
50.00	-8.73	24.97	13.39	17.15
50.00	11.55	9.16	9.60	1.26
25.00	9.90	19.40	21.69	1.27
25.00	0.95	33.12	1.93	5.97
25.00	-3.75	19.77	8.85	11.67
25.00	-2.35	20.82	24.56	21.83
12.50	29.48	41.20	10.30	8.64
12.50	27.79	12.92	20.14	-0.90
12.50	-2.86	-15.62	19.29	29.95
12.50	1.32	-9.73	11.60	9.79
6.25	-5.76	10.49	-4.57	-7.20
6.25	-2.09	9.15	25.88	10.89
6.25	0.27	17.15	0.48	19.04
6.25	19.71	44.09	9.02	-16.41
3.13	-5.99	-15.12	23.21	-0.60
3.13	-10.59	-19.04	23.96	14.63
3.13	-1.68	11.22	9.23	-6.07
3.13	1.48	14.11	26.12	-6.10
1.56	-3.29	7.79	15.10	2.04
1.56	13.55	-7.70	5.48	-5.24
1.56	9.75	5.24	6.81	24.76
1.56	-3.22	-1.59	2.21	14.16
0.78	-5.60	-3.50	10.42	37.43
0.78	16.08	-0.40	-3.97	11.68
0.78	10.17	-2.92	1.25	11.83
0.78	0.30	1.18	-5.31	3.72