Supplementary Material (ESI) for Chemical Communications

Convenient route to water-sensitive sol-gel precursors using click chemistry

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Contents

Caution

Azide compounds are potentially explosive. Great care and protection are needed for heating of these compounds.

General

3-azidopropyltriethoxysilane (AzPTES),[1] 11-azidoundecyltriethoxysilane,[2] dipropargyl tartrate[3] and $CuBr(PPh_3)_3$[4] were prepared according to published procedures. The alkynes were purshased from Aldrich. Dry, oxygen-free solvents were employed.

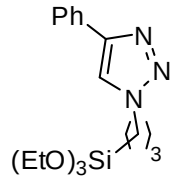
All the manipulations were carried out using Schlenk techniques under a dry atmosphere of nitrogen. NMR spectra were recorded in dry $CDCl_3$ at 298 K on a Bruker Advance 400 apparutus. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si, and ^{19}F chemical shifts are reported in ppm relative to $CFCl_3$.

Microwave reactions were carried out in sealed tubes using a CEM Discover Microwave Reactor equipped with an infrared temperature sensor.

General procedure for the click reaction:

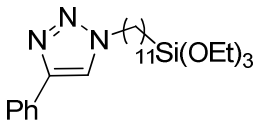
A microwave tube was filled under nitrogen with the alkyne (2 mmol), the azide (2 mmol / alkyne function), $[CuBr(PPh_3)_3]$ (0.01 mmol / alkyne function), dry triethylamine (0.5 mL) and dry thf (0.5 mL) then sealed. After 5 minutes under microwave irradiation at 100 °C (maximum power = 200 W) [Alternatively, some reactions were carried out at room temperature for 48 h], the reaction mixture was allowed to cool, then the solvents were removed under vacuum. After addition of dry pentane, the mixture was filtered then the filtrate was concentrated to afford the title compounds.

2a:



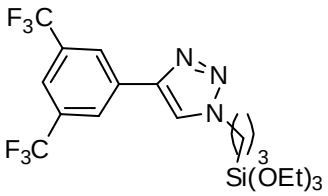
Yield: 95 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.64 (m, 2 H), 1.22 (t, *J* = 7.0 Hz, 9 H), 2.07 (m, 2 H), 3.82 (q, *J* = 7.0 Hz, 6 H), 4.41 (t, *J* = 7.1 Hz, 2 H), 7.32 (m, 1 H), 7.42 (m, 2 H), 7.77 (s, 1 H), 7.82 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 6.9 (CH_2), 17.8 (CH_3), 23.8 (CH_2), 51.9 (CH_2), 58.0 (CH_2), 119.5 (CH), 125.1(CH), 127.5(CH), 128.3(CH), 130.4 (C), 146.9 (C). HRMS (ESI$^+$): calcd for $C_{17}H_{28}N_3O_3Si$, 350.1900; found, 350.1893.

2b:



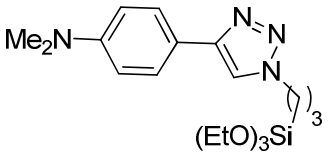
Yield: 97 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.56 (m, 2 H), 1.15 (t, *J* = 7.0 Hz, 9 H), 1.15-1.40 (m, 16 H), 1.82 (m, 2 H), 3.75 (q, *J* = 7.0 Hz, 6 H), 4.26 (t, *J* = 7.2 Hz, 2 H), 7.22 (m, 1 H), 7.32 (m, 2 H), 7.72 (s, 1 H), 7.76 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 10.1 (CH_2), 18.0 (CH_3), 22.5 (CH_2), 26.2 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.17 (CH_2), 29.22 (CH_2), 30.0 (CH_2), 32.9 (CH_2), 50.1 (CH_2), 58.0 (CH_2), 119.3 (CH), 125.3 (CH), 127.7(CH), 128.5 (CH), 130.5 (C), 147.3 (C). HRMS (ESI$^+$): calcd for $C_{25}H_{44}N_3O_3Si$, 462.3152; found, 462.3142.

2c:



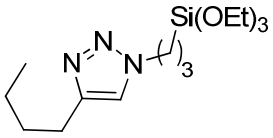
Yield: 95 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.63 (m, 2 H), 1.21 (t, *J* = 7.0 Hz, 9 H), 2.09 (m, 2 H); 3.82 (q, *J* = 7.0 Hz, 6 H), 4.44 (t, *J* = 7.1 Hz, 2 H), 7.81 (br s, 1 H), 7.95 (br s, 1 H), 8.28 (br s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.5 (CH_2), 18.3 (CH_3), 24.3 (CH_2), 52.7 (CH_2), 58.6 (CH_2), 120.7 (CH), 121.4 (sept, *J* = 3.9 Hz, CH), 123.2 (q, *J* = 272 Hz, C), 125.5 (CH), 132.2 (q, *J* = 33 Hz, C), 132.9 (C), 144.9 (C). ^{19}F NMR ($CDCl_3$, 235 MHz): δ = 63.0. Mp 95-97 °C. HRMS (ESI$^+$): calcd for $C_{19}H_{26}N_3O_3SiF_6$, 486.1648; found, 486.1633.

2d:



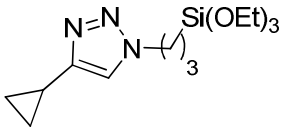
Yield: 90 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.62 (m, 2 H), 1.21 (t, *J* = 7.0 Hz, 9 H), 2.04 (m, 2 H), 2.97 (s, 6 H), 3.80 (q, *J* = 7.0 Hz, 6 H), 4.35 (t, *J* = 7.1 Hz, 2 H), 6.75 (d, *J* = 8.9 Hz, 2 H), 7.62 (s, 1 H), 7.68 (d, *J* = 8.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.4 (CH_2), 18.2 (CH_3), 24.2 (CH_2), 40.4 (CH_3), 52.3 (CH_2), 58.4 (CH_2), 112.4 (CH), 118.1 (CH), 119.0 (C), 126.5(CH), 148.0 (C), 150.3 (C). Mp 65-68 °C. HRMS (ESI$^+$): calcd for $C_{19}H_{33}N_4O_3Si$, 393.2322; found, 393.2305.

2e:



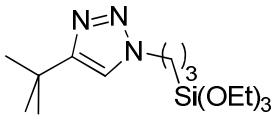
Yield: 92 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.57 (m, 2 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 1.18 (t, *J* = 7.0 Hz, 9 H), 1.35 (m, 2 H), 1.62 (m, 2 H), 1.98 (m, 2 H), 2.68 (t, *J* = 7.6 Hz, 2 H), 3.78 (q, *J* = 6.9 Hz, 6 H), 4.30 (t, *J* = 7.0 Hz, 2 H), 7.34 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 6.9 (CH_2), 13.2 (CH_3), 17.7 (CH_3), 21.7 (CH_2), 23.7 (CH_2), 24.8 (CH_2), 31.1 (CH_2), 51.6 (CH_2), 57.9 (CH_2), 120.2 (CH), 147.5 (C). HRMS (ESI^+): calcd for $C_{15}H_{32}N_3O_3Si$, 330.2213; found, 330.2206.

2f:



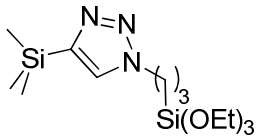
[Reaction carried out at room temperature for 48 h using 3 eqv of alkyne]. Yield: 94 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.58 (m, 2 H), 0.81 (m, 2 H), 0.91 (m, 2 H), 1.19 (t, *J* = 7.0 Hz, 9 H), 1.88-2.02 (m, 3 H), 3.79 (q, *J* = 7.0 Hz, 6 H), 4.26 (t, *J* = 7.2 Hz, 2 H), 7.21 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 6.7 (CH), 7.4 (CH_2), 7.7 (CH_2), 18.3 (CH_3), 24.2 (CH_2), 52.3 (CH_2), 58.5 (CH_2), 119.6 (CH), 150.0 (C). HRMS: calcd for $C_{14}H_{28}N_3O_3Si$, 314.1900; found, 314.1889.

2g:



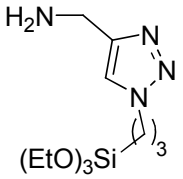
[Reaction carried out at room temperature for 48 h using 3 eqv of alkyne]. Yield: 88 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.58 (m, 2 H), 1.19 (t, *J* = 7.0 Hz, 9 H), 1.31 (s, 9 H), 1.98 (m, 2 H), 3.78 (q, *J* = 7.0 Hz, 6 H), 4.27 (t, *J* = 7.2 Hz, 2 H), 7.23 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.4 (CH_2), 18.2 (CH_3), 24.2 (CH_2), 30.3 (CH_3), 30.6 (C), 52.1 (CH_2), 58.4 (CH_2), 118.9 (CH), 157.4 (C). HRMS: calcd for $C_{15}H_{32}N_3O_3Si$, 330.2213; found, 330.2220.

2h:



[Reaction carried out at room temperature for 48 h using 3 eqv of alkyne]. Yield: 95 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.23 (s, 9 H), 0.53 (m, 2 H), 1.13 (t, *J* = 7.0 Hz, 9 H), 1.94 (m, 2 H), 3.73 (q, *J* = 7.0 Hz, 6 H), 4.30 (t, *J* = 7.1 Hz, 2 H), 7.47 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = -1.3 (CH_3), 7.3 (CH_2), 18.1 (CH_3), 24.1 (CH_2), 51.6 (CH_2), 58.3 (CH_2), 128.8 (CH), 146.0 (C). HRMS: calcd for $C_{14}H_{32}N_3O_3Si_2$, 346.1982; found, 346.1971.

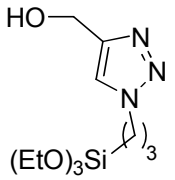
2i:



Yield: 93 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.58 (m, 2 H), 1.19 (t, *J* = 6.9 Hz, 9 H), 1.99 (m, 2 H), 3.78 (q, *J* = 6.9 Hz, 6 H), 4.31 (t, *J* = 7.0 Hz, 2 H), 7.49 (s, 1 H) (C*H*$_2$-N and N*H*$_2$ not observed). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.2 (CH_2), 17.9 (CH_3), 23.9 (CH_2), 52.1

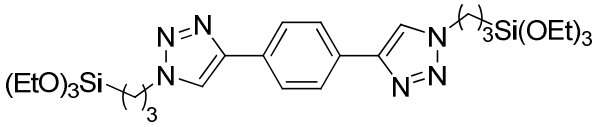
(CH_2), 58.1 (CH_2), 121.0 (CH), 154.7 (C). HRMS (ESI^+): calcd for $C_{12}H_{27}N_4O_3Si$, 303.1852; found, 303.1834.

2j:



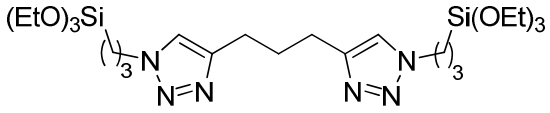
Yield: 98 %. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.46 (m, 2 H), 1.06 (t, *J* = 7.0 Hz, 9 H), 1.86 (m, 2 H), 3.66 (q, *J* = 7.0 Hz, 6 H), 4.19 (t, *J* = 7.1 Hz, 2 H), 4.61 (br s, 2 H), 4.71 (br s, 1 H), 7.49 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.1 (CH_2), 17.9 (CH_3), 23.8 (CH_2), 52.1 (CH_2), 55.6 (CH_2), 58.1 (CH_2), 121.8 (CH), 147.7 (C). HRMS (ESI^+): calcd for $C_{24}H_{49}N_6O_7Si_2$, 304.1693; found, 304.1662.

3a:



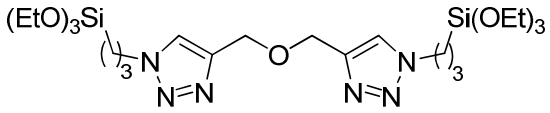
Yield: 87 %. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.51 (m, 2 H), 1.08 (t, *J* = 7.0 Hz, 9 H), 1.94 (m, 2 H), 3.68 (q, *J* = 7.0 Hz, 6 H), 4.27 (t, *J* = 7.1 Hz, 2 H), 7.75 (s, 2 H), 7.78 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.1 (CH_2), 17.9 (CH_3), 23.9 (CH_2), 52.1 (CH_2), 58.1 (CH_2), 119.7 (CH), 125.6 (CH), 130.4 (C), 146.7 (C). HRMS (ESI^+): calcd for $C_{28}H_{49}N_6O_6Si_2$, 621.3252; found, 621.3237.

3b:



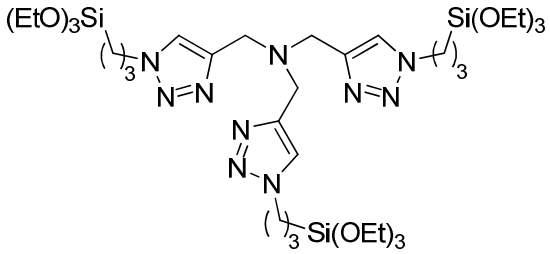
Yield: 95 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.60 (m, 4 H), 1.21 (t, *J* = 7.0 Hz, 18 H), 1.95-2.11 (m, 6 H), 2.77 (t, *J* = 7.5 Hz, 4 H), 3.77 (q, *J* = 7.0 Hz, 12 H), 4.31 (t, *J* = 7.1 Hz, 4 H), 7.33 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.0 (CH_2), 17.8 (CH_3), 23.8 (CH_2), 24.5 (CH_2), 28.8 (CH_2), 51.8 (CH_2), 58.0 (CH_2), 120.6 (CH), 146.9 (C). HRMS (ESI^+): calcd for $C_{25}H_{50}N_6O_6Si_2$, 587.3409; found, 587.3425.

3c:



Yield: 94 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.60 (m, 4 H), 1.21 (t, *J* = 7.0 Hz, 18 H), 2.01 (m, 4 H), 3.80 (q, *J* = 7.0 Hz, 12 H), 4.34 (t, *J* = 7.1 Hz, 4 H), 4.70 (s, 2 H), 7.58 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.1 (CH_2), 17.9 (CH_3), 23.9 (CH_2), 52.1 (CH_2), 58.2 (CH_2), 63.2 (CH_2), 122.6 (CH), 144.1 (C). HRMS (ESI^+): calcd for $C_{24}H_{49}N_6O_7Si_2$, 589.3201; found, 589.3213.

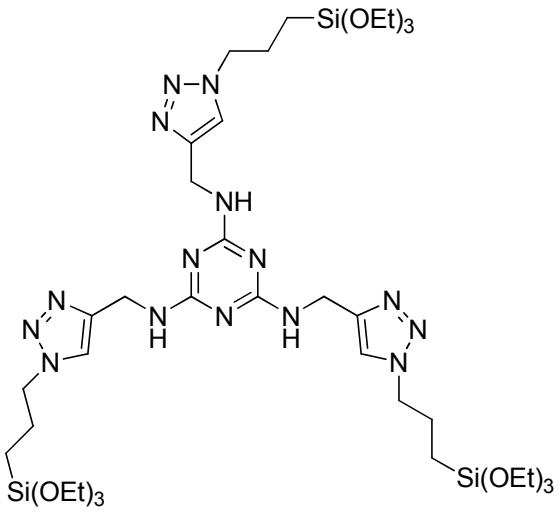
3d:



Yield: 91 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.60 (m, 2 H), 1.20 (t, *J* = 7.0 Hz, 9 H), 2.02 (m, 2 H), 3.74 (s, 2 H), 3.79 (q, *J* = 7.0 Hz, 6 H), 4.34 (t, *J* = 7.3 Hz, 2 H), 7.76 (s, 1 H). ^{13}C

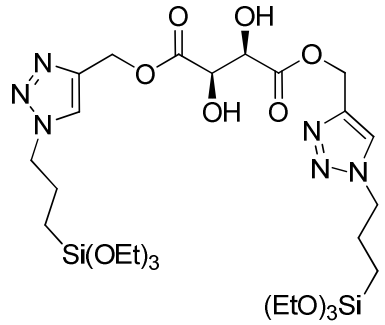
NMR ($CDCl_3$, 100 MHz): δ = 6.8 (CH_2), 17.6 (CH_3), 23.6 (CH_2), 46.4 (CH_2), 51.7 (CH_2), 57.8 (CH_2), 123.2 (CH), 143.1 (C). HRMS (ESI^+): calcd for $C_{36}H_{73}N_{10}O_9Si_3$, 873.4870; found, 873.4854.

3e:



Yield: 92 %. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.53 (m, 2 H), 1.13 (t, J = 7.0 Hz, 9 H), 1.92 (br, 2 H), 3.73 (q, J = 7.0 Hz, 6 H), 4.22 (br, 2 H), 4.62 (br, 2 H), 7.60 (br, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.3 (CH_2), 18.1 (CH_3), 24.0 (CH_2), 35.9 (CH_2), 52.2 (CH_2), 58.3 (CH_2), 122.1 (CH), 146.1 (C), 165.7 (C). HRMS (ESI^+): calcd for $C_{39}H_{76}N_{15}O_9Si_3$, 982.5258; found, 982.5273.

3f:



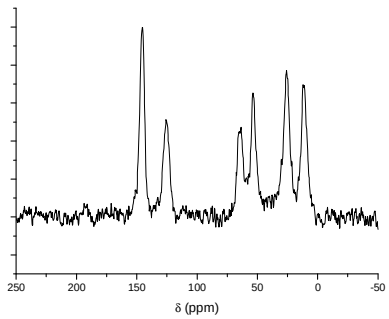
Yield: 81 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.51 (m, 4 H), 1.14 (t, *J* = 7.0 Hz, 18 H), 1.93 (m, 4 H), 3.73 (q, *J* = 7.0 Hz, 12 H), 4.02 (br s, 2 H), 4.27 (t, *J* = 7.3 Hz, 4 H), 4.54 (s, 2 H), 5.26 (d, *J* = 13.0 Hz, 2 H), 5.30 (d, *J* = 13.0 Hz, 2 H), 7.61 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 7.4 (CH_2), 18.3 (CH_3), 24.1 (CH_2), 52.5 (CH_2), 58.5 (CH_2), 59.2 (CH_2), 72.2 (CH), 123.8 (CH), 141.9 (C), 171.2 (C=O). HRMS: calcd for $C_{28}H_{53}N_6O_{12}Si_2$, 721.3260; found, 721.3261.

General procedures for the syntheses of the materials:

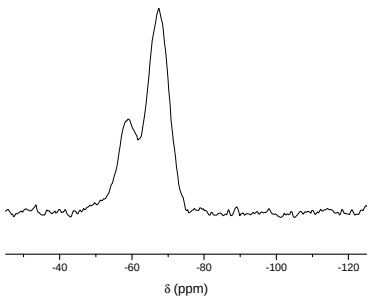
Method A: To a suspension of precursor (2.5 mmol) in water (54 mL, 3.0 mol) under vigorous stiring was added hydrochloric acid (37 $\%_w$, 1 mL, 10 mmol). The mixture was stirred at 80°C for 3 days. After cooling, the solid was filtered off, washed with water, ethanol then acetone, and the resulting powder was dried under vacuum for 6 hours.

Method B: To a solution of precursor (2.5 mmol) in thf (5 mL) under vigorous stirring was added water (0.25 mL / silyl group, 6 mmol / silyl group) and a tetrabutylammonium fluoride solution (1 M in thf, 50 µL / silyl group, 0.02 mmol / silyl group). After one minute under stirring, the solution was left standing for 3 days at room temperature. Gelification took place within few minutes. The gel was crushed, filtered off, washed with water, ethanol then acetone and the resulting powder dried under vacuum for 6 hours.

M1: *method A* from **3c**; 0.49 g, white solid.

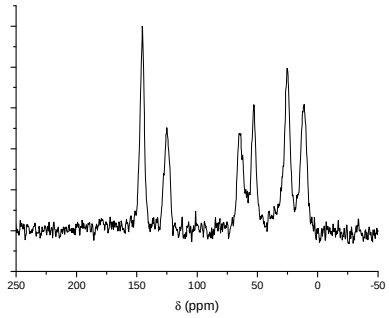


^{13}C CPTOSS solid state NMR

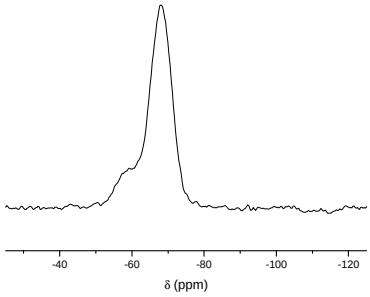


^{29}Si CPMAS solid state NMR

M2: *method B* from **3c**; 0.51 g; light brown solid.

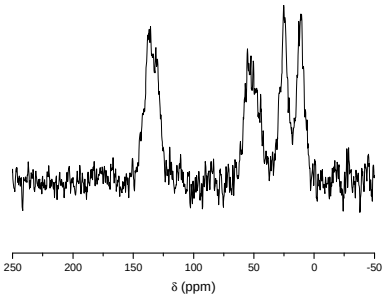


^{13}C CPTOSS solid state NMR

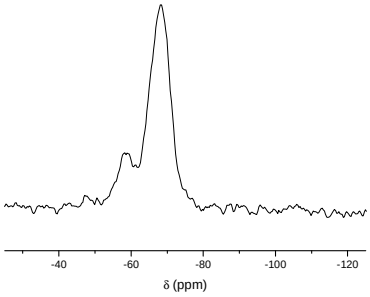


^{29}Si CPMAS solid state NMR

M3: *method A* from **3d**; 0.70 g, yellow solid.

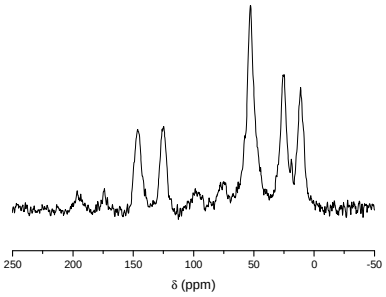


^{13}C CPTOSS solid state NMR

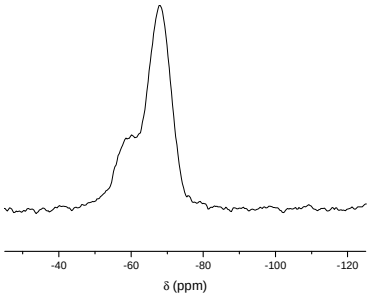


^{29}Si CPMAS solid state NMR

M4: *method B* from **3d**; 0.75 g, light yellow solid.

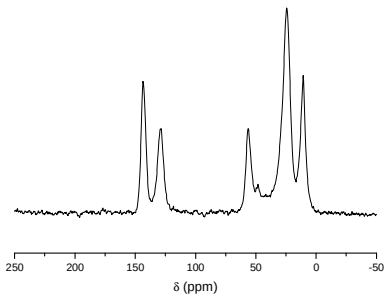


^{13}C CPTOSS solid state NMR

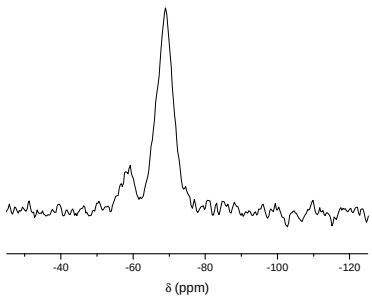


^{29}Si CPMAS solid state NMR

M5: *method A* from **3b**; 0.78 g, yellow solid.

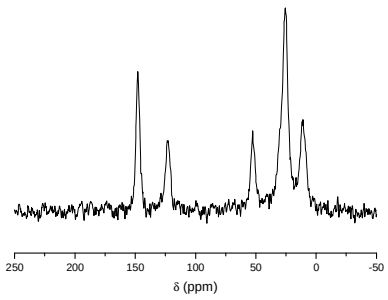


^{13}C CPTOSS solid state NMR

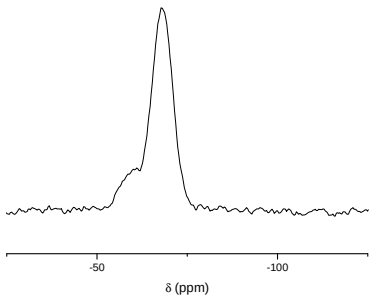


^{29}Si CPMAS solid state NMR

M6: *method B* from **3b**; 0.85 g, yellow solid.



^{13}C CPTOSS solid state NMR



^{29}Si CPMAS solid state NMR

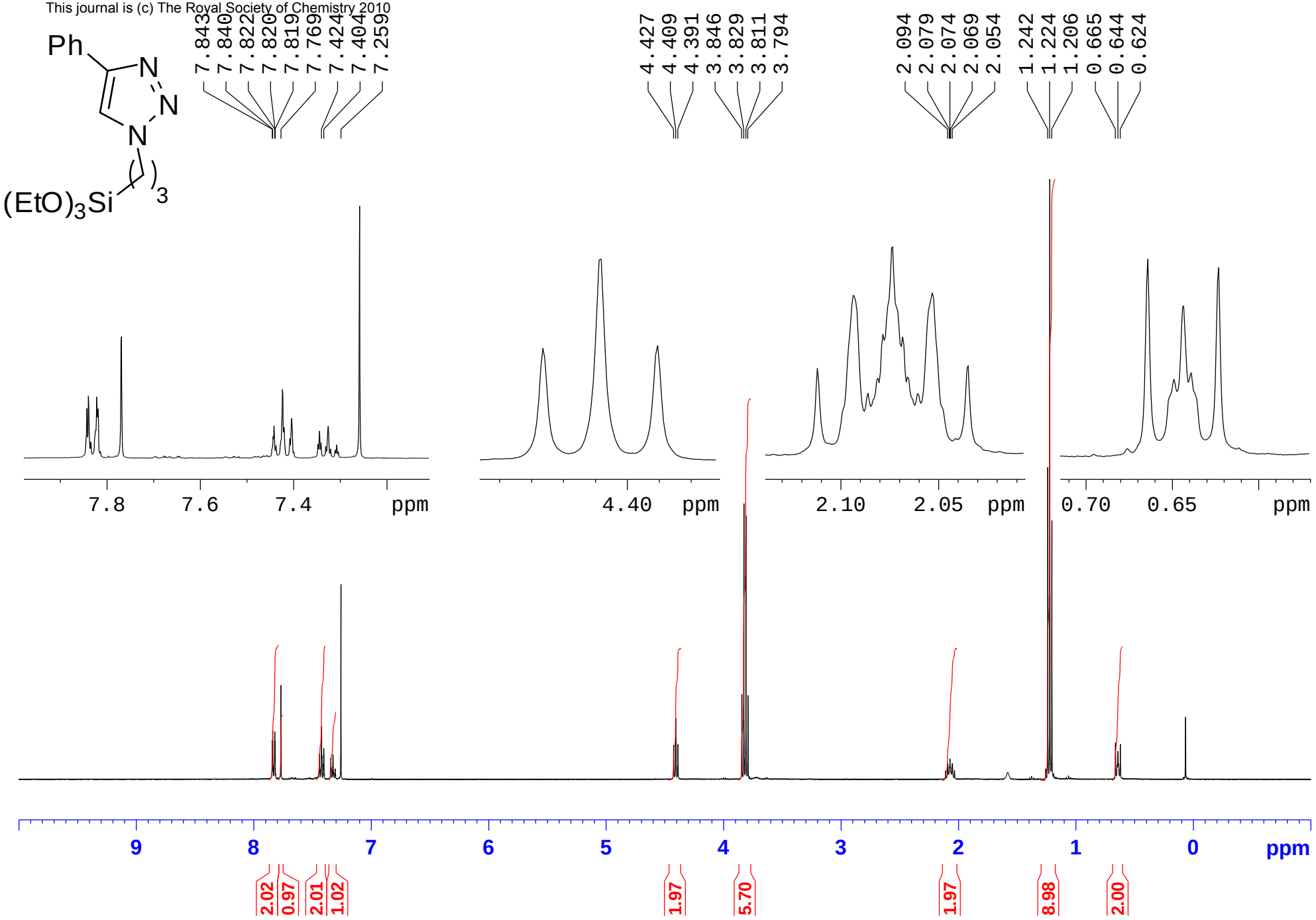
References

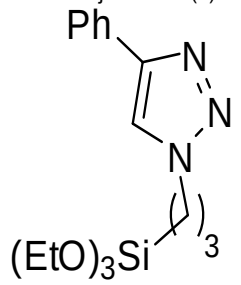
(1) Malvi, B.; Sarkar, B. R.; Pati, D.; Mathew, R.; Ajithkumar, T. G.; Sen Gupta, S. *Journal of Materials Chemistry* **2009**, *19*, 1409.

(2) Pichon, B. P.; Wong Chi Man, M.; Bied, C.; Moreau, J. J. E. *Journal of Organometallic Chemistry* **2006**, *691*, 1126.

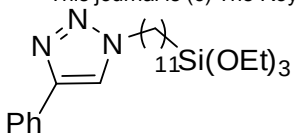
(3) Desrat, S.; van de Weghe, P. *Journal of Organic Chemistry* **2009**, *74*, 6728.

(4) Van Allen, D.; Venkataraman, D. *Journal of Organic Chemistry* **2003**, *68*, 4590.

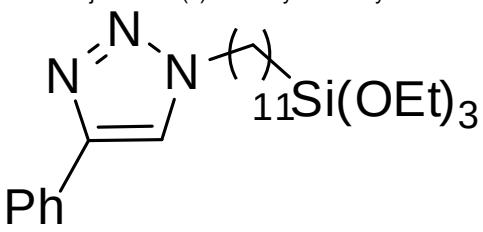



Ph
N
N
N
(EtO)3Si
3

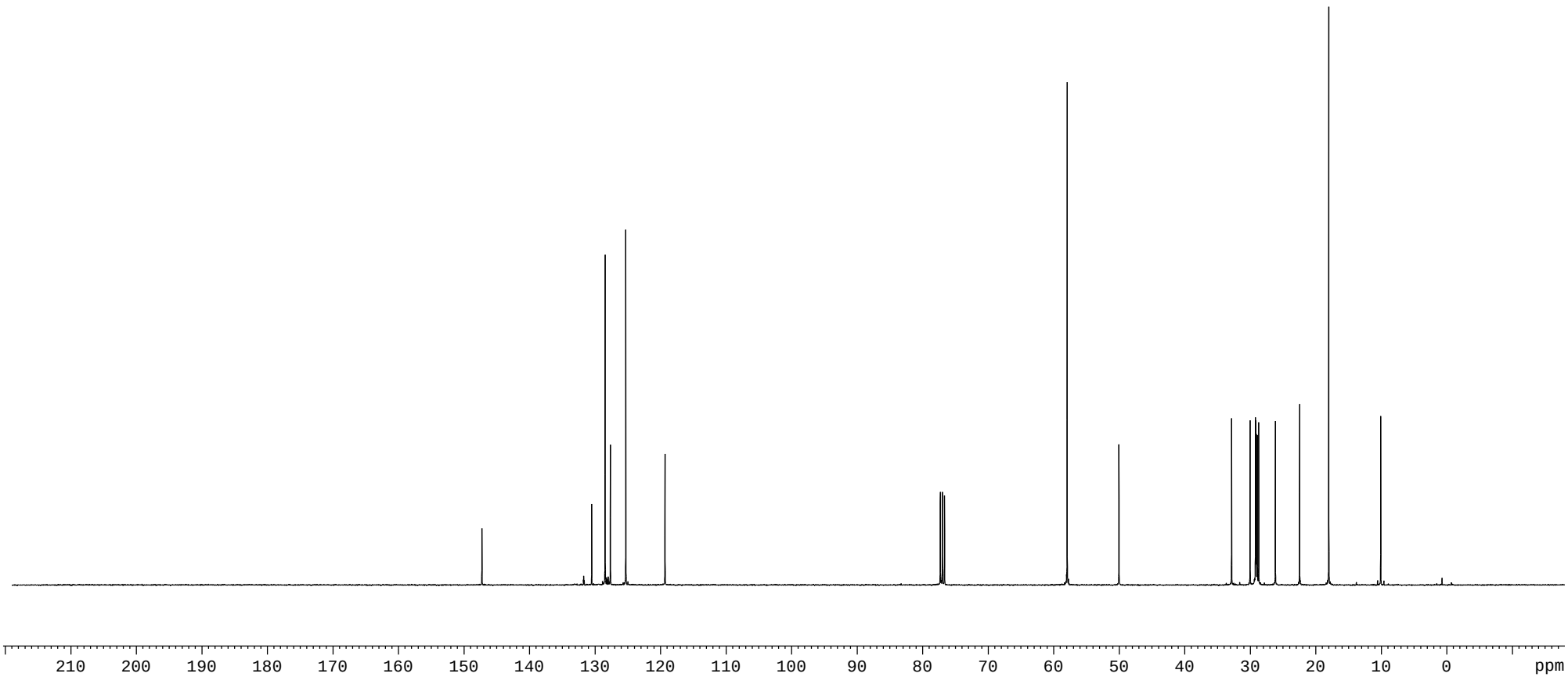
146.94
130.42
128.30
127.45
125.11
119.51
77.32
77.00
76.68
57.98
51.93
23.79
17.81
6.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

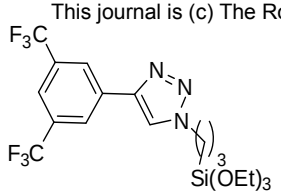


Supplementary Material (ESI) for Chemical Communications

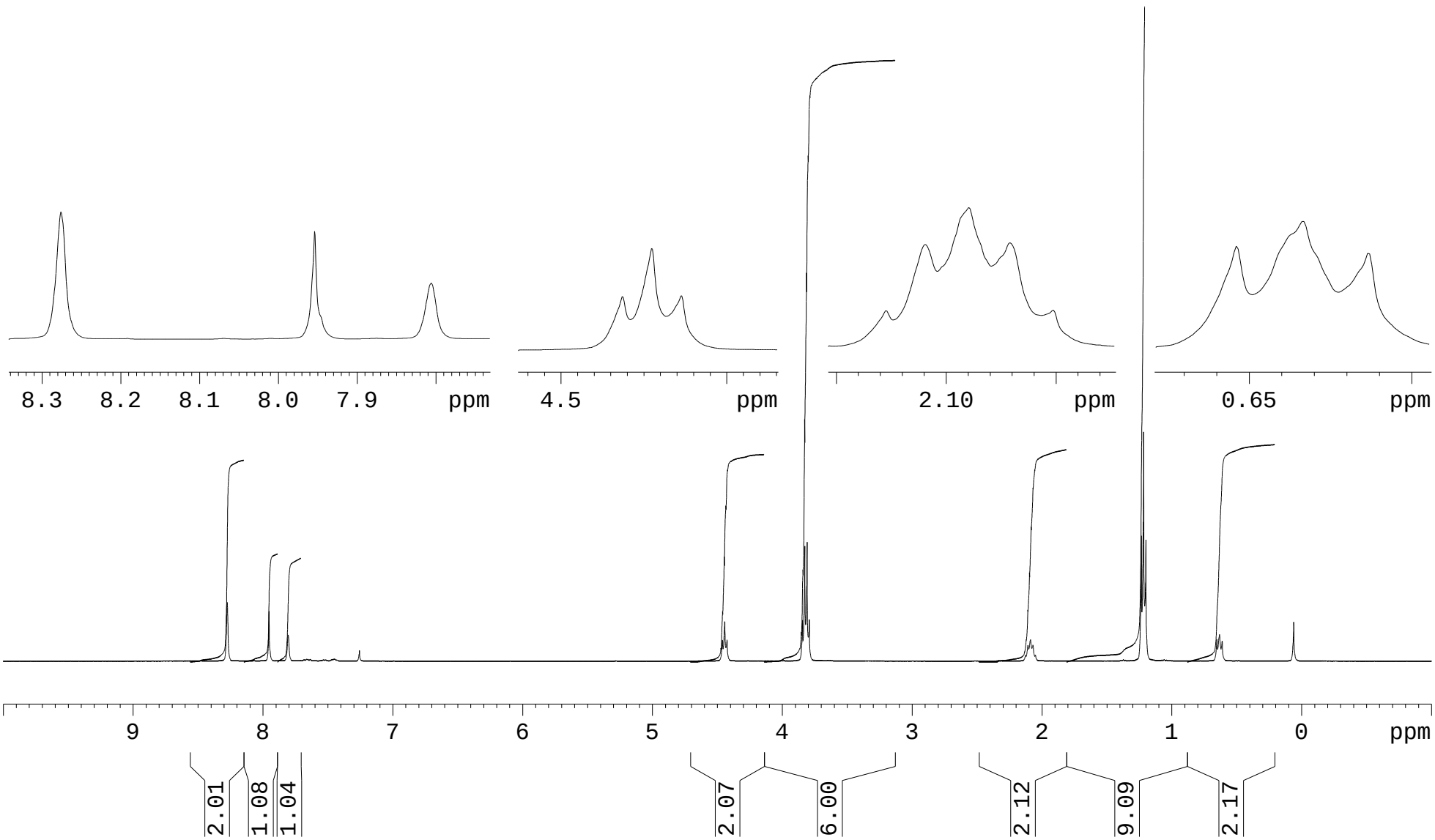


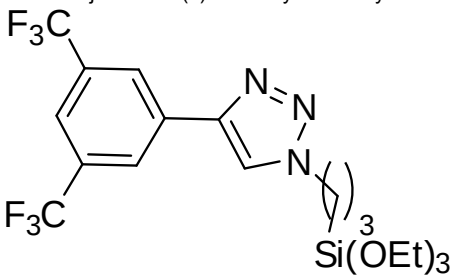
147.28
130.53
128.48
127.68
125.32
119.34
77.32
77.20
77.00
76.68
57.96
50.05
32.86
30.04
29.22
29.17
29.09
28.93
28.72
26.18
22.48
18.03
10.10





8.276 7.954 7.806 4.463 4.445 4.428 3.846 3.829 3.814 3.811 3.794 2.128 2.110 2.090 2.071 2.052 1.236 1.218 1.204 1.201 0.654 0.634 0.614





144.92
132.95
132.74
132.41
132.07
131.74
127.31
125.53
124.60
121.89
121.45
121.41
121.37
120.75
119.18

77.34
77.02
76.70

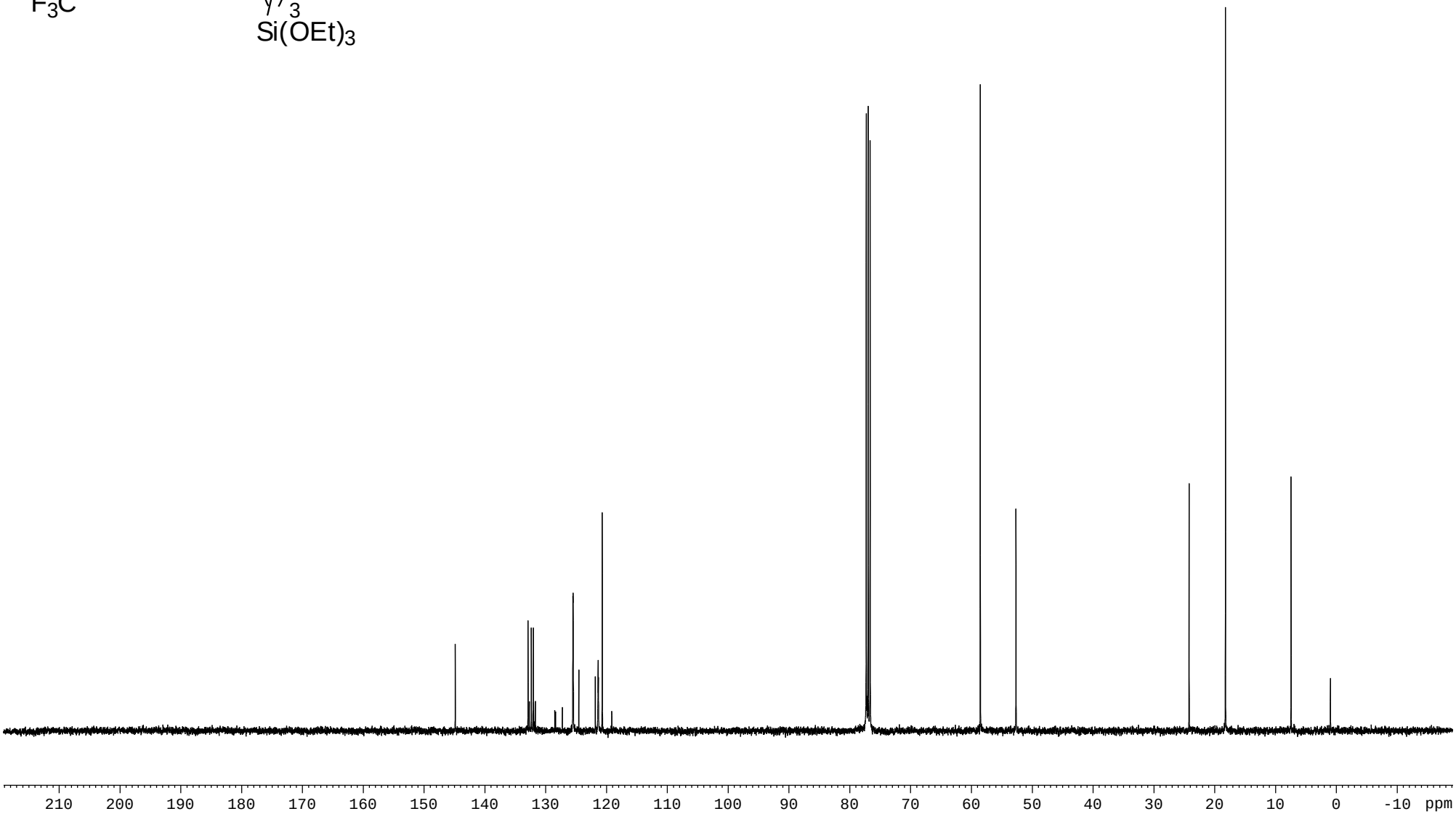
58.58

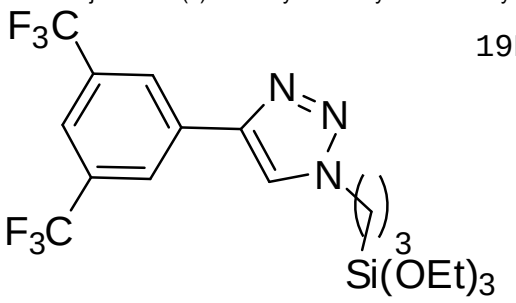
52.72

24.25

18.27

7.48

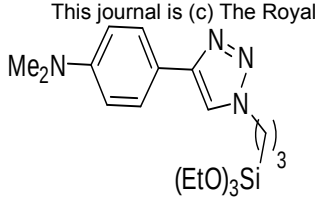




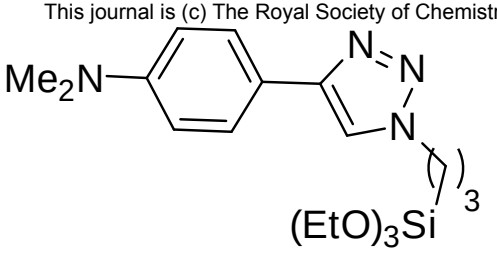
19F

-63.02

-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 ppm


Me2N
N
N
N
3
(EtO)3Si

7.695
7.673
7.623
7.259
6.765
6.743
4.370
4.352
4.335
3.827
3.810
3.804
3.792
3.775
2.967
2.076
2.058
2.038
2.019
1.999
1.225
1.207
1.190
0.645
0.624
0.604
7.7 ppm
6.8 6.7 ppm
4.4 ppm
2.05 ppm
0.65 ppm
9 8 7 6 5 4 3 2 1 0 ppm
3.09
2.03
2.00
5.80
6.18
2.09
9.00
2.13


Me2N
N
N
N
3
(EtO)3Si

150.26
148.01
126.53
119.00
118.09
112.41
77.32
77.00
76.68
58.43
52.32
40.39
24.19
18.21
7.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

Supplementary Material (ESI) for Chemical Communications
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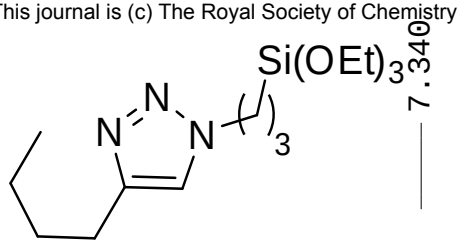
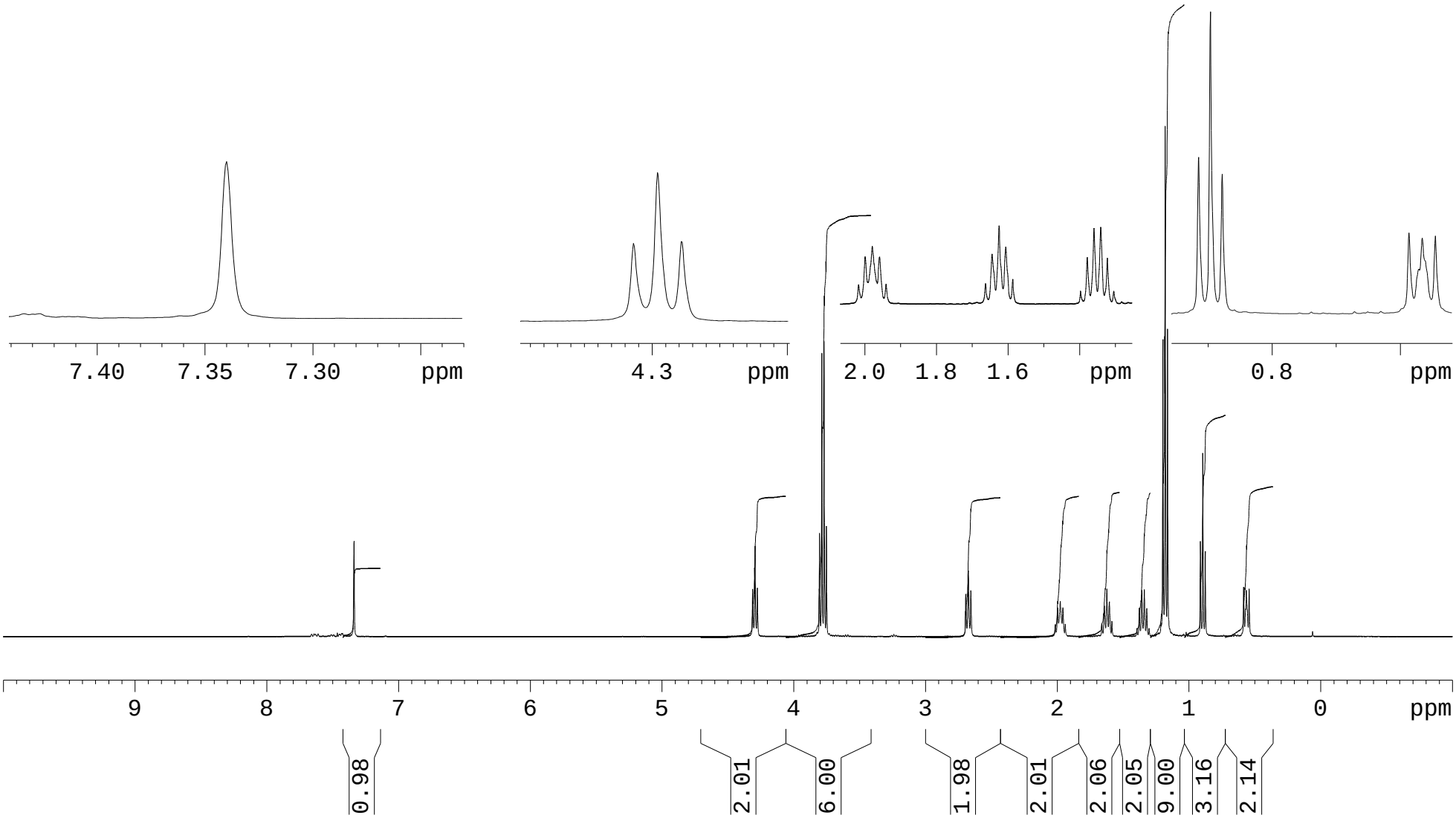
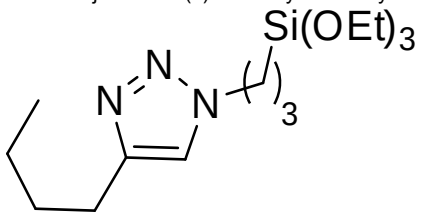


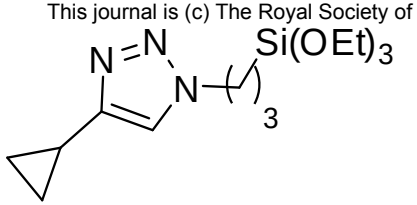
7.340

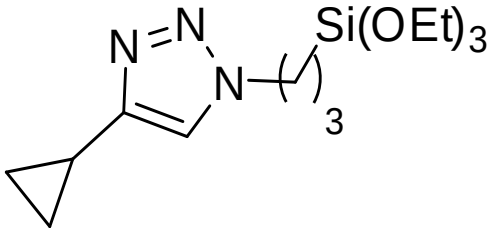
4.314 4.296 4.278 3.807 3.789 3.772 3.754 2.696 2.677 2.658 2.017 1.999 1.991 1.979 1.959 1.941 1.663 1.644 1.625 1.606 1.587 1.397 1.378 1.360 1.341 1.322 1.304 1.200 1.182 1.165 0.915 0.897 0.878

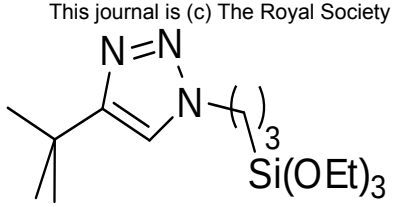



Si(OEt)3
N
N
N
3

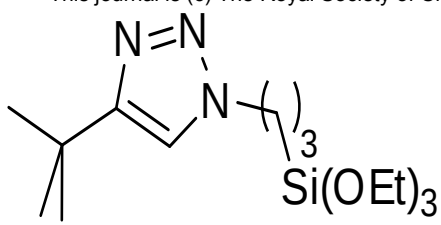
147.51
120.19
77.31
76.99
76.67
57.87
51.63
31.07
24.80
23.73
21.72
17.69
13.22
7.05
6.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm



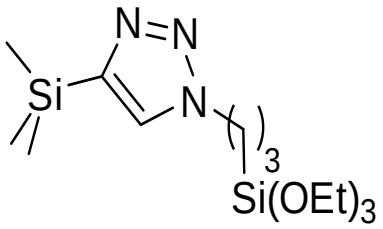



N
N
N
3
Si(OEt)3

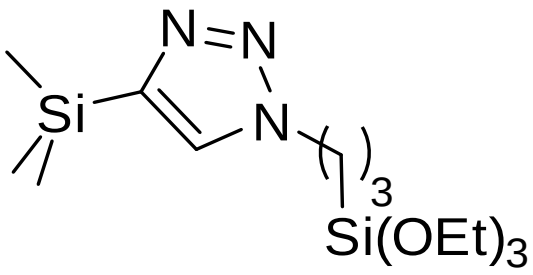
7.227
4.293
4.275
4.257
3.809
3.808
3.792
3.790
3.773
3.755
2.011
1.992
1.983
1.972
1.958
1.953
1.933
1.317
1.315
1.205
1.188
1.187
1.169
0.602
0.581
0.561
ppm
4.30
4.25 ppm
2.00
1.95 ppm
0.60
ppm
9
8
7
6
5
4
3
2
1
0
ppm
0.99
2.03
5.96
2.11
9.00
9.06
2.13


N
N
N
3
Si(OEt)3

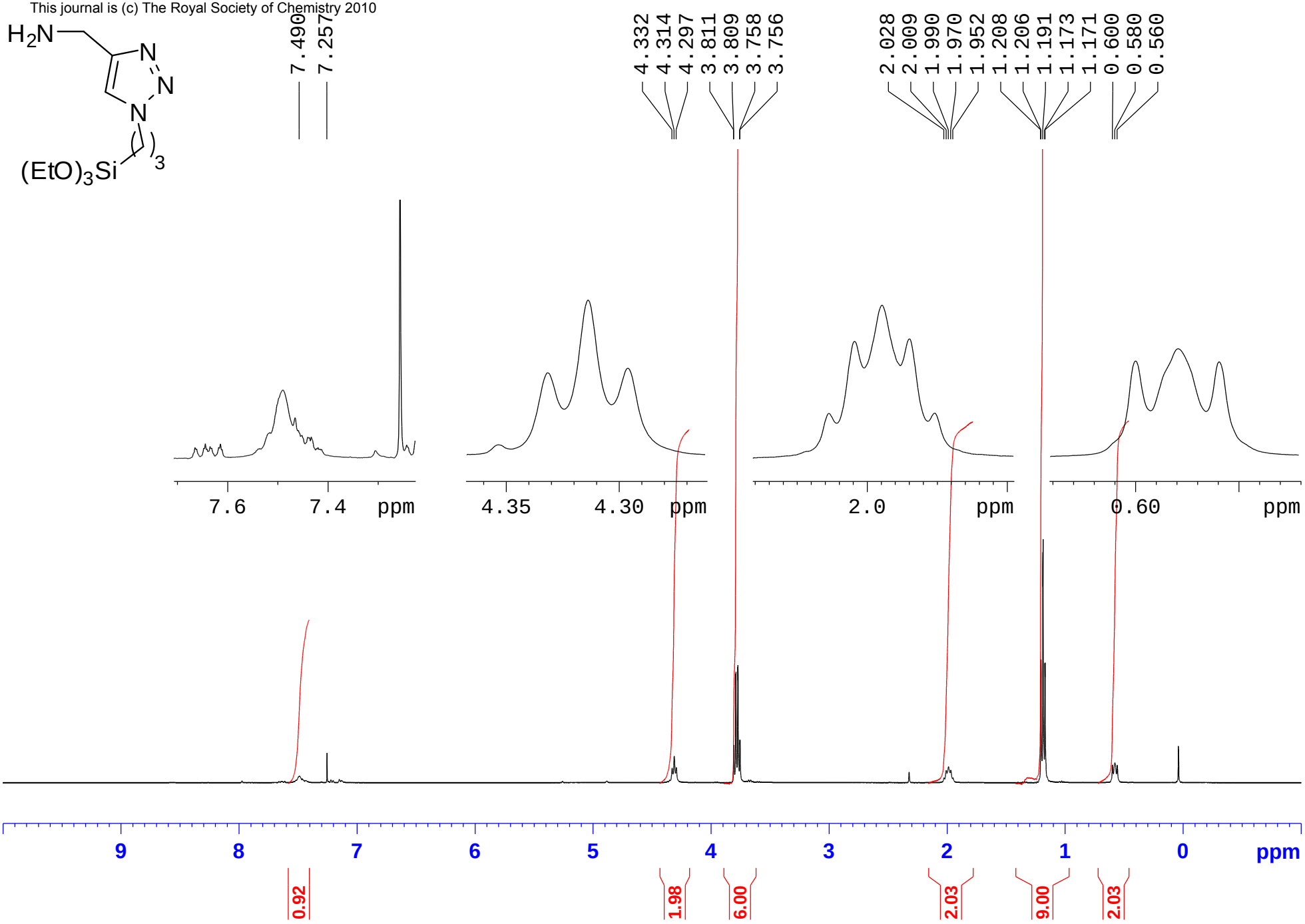
157.42
118.37
77.31
77.00
76.68
58.42
52.15
30.62
30.32
24.19
18.20
7.41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

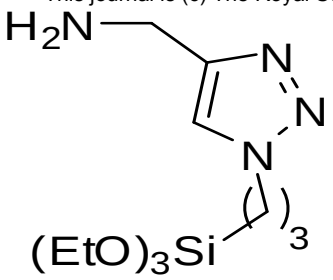

N
N
Si
N
3
Si(OEt)3

7.466
4.317
4.299
4.281
3.754
3.737
3.719
3.702
1.980
1.961
1.942
1.922
1.903
1.149
1.131
1.114
0.548
0.527
0.506
0.233
7.5 ppm
4.3 ppm
1.95 ppm
0.55 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.06
2.08
6.02
2.10
9.00
2.10
9.13

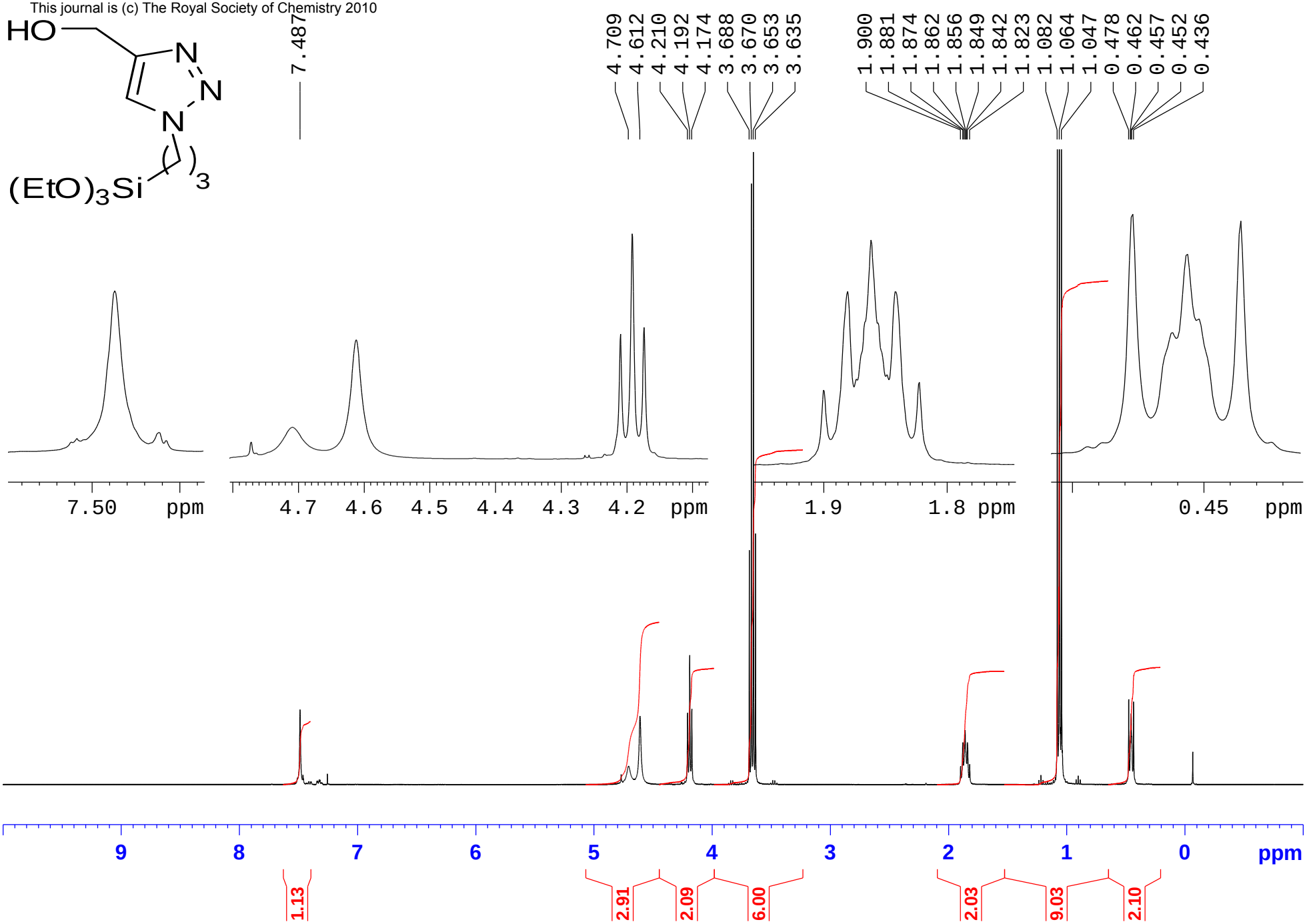

N
N
Si
N
3
Si(OEt)3

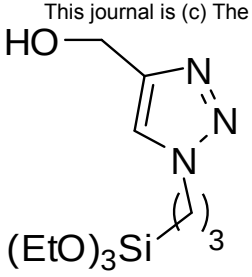
146.01
128.78
77.32
77.00
76.68
58.28
51.60
24.14
18.07
7.29
-1.29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



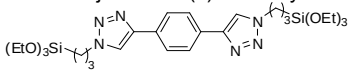

H2N
N
N
N
3
(EtO)3Si

154.68
120.98
77.82
77.50
77.17
58.10
52.06
23.93
17.95
7.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

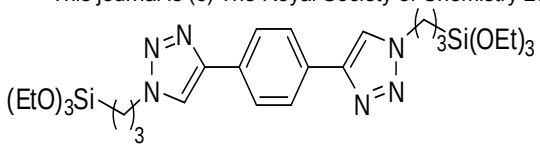

HO
N
N
N
(EtO)3Si
3
7.487
4.709
4.612
4.210
4.192
4.174
3.688
3.670
3.653
3.635
1.900
1.881
1.874
1.862
1.856
1.849
1.842
1.823
1.082
1.064
1.047
0.478
0.462
0.457
0.452
0.436
7.50 ppm
4.7 4.6 4.5 4.4 4.3 4.2 ppm
1.9 1.8 ppm
0.45 ppm
9 8 7 6 5 4 3 2 1 0 ppm
1.13
2.91
2.09
6.00
2.03
9.03
2.10


HO
N
N
N
(EtO)3Si
3

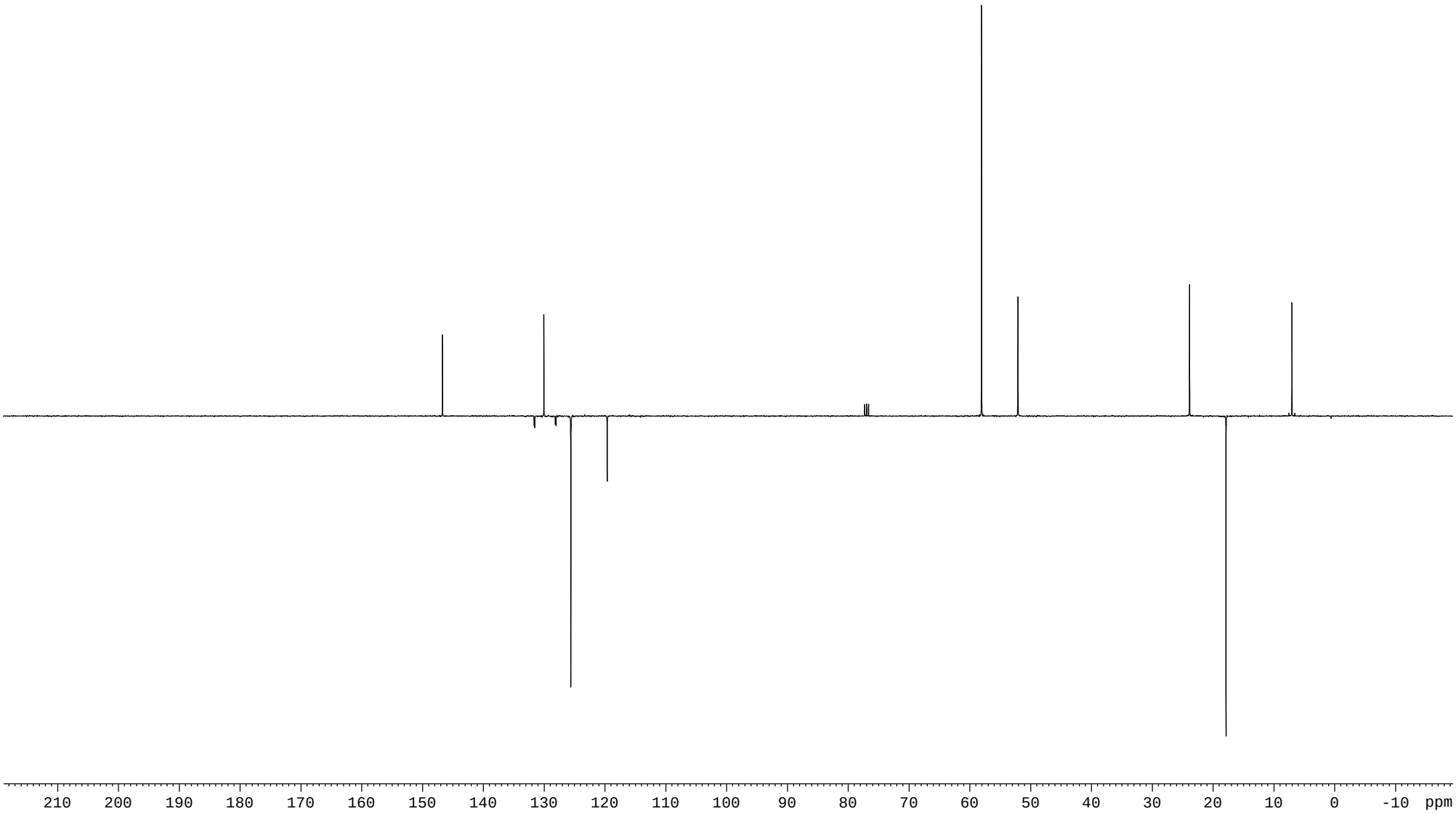
147.70
121.90
121.75
77.32
77.00
76.68
58.15
55.59
52.11
23.83
17.90
7.09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

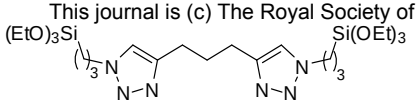

(EtO)3Si
3Si(OEt)3

7.779
7.755
4.292
4.274
4.256
3.706
3.688
3.671
3.654
1.978
1.959
1.940
1.920
1.901
1.098
1.080
1.063
0.528
0.513
0.508
0.504
0.487
7.80
7.75
ppm
4.30
4.25
ppm
2.00
1.95
ppm
0.55
0.50
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.98
2.01
6.00
2.04
9.05
2.09

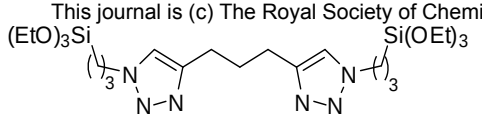


146.75
130.37
130.08
125.64
119.67
77.32
77.00
76.68
58.11
52.13
23.91
17.91
7.07

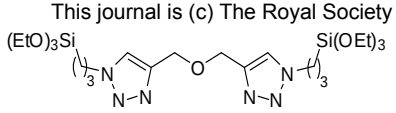



(EtO)3Si
Si(OEt)3
N
N
N
N

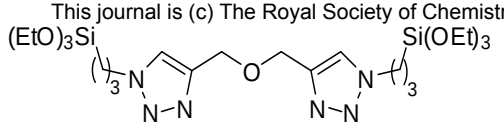
7.326
7.260
4.328
4.310
4.292
3.832
3.815
3.797
3.780
2.793
2.774
2.755
2.076
2.057
2.038
2.019
2.012
2.008
2.000
1.994
1.987
1.980
1.961
1.230
1.212
1.195
0.620
0.605
0.600
0.579
7.4
7.3
ppm
4.2
4.0
ppm
2.1
2.0
ppm
0.6
ppm
9
8
7
6
5
4
3
2
1
0
ppm
1.89
4.02
11.82
3.99
6.15
18.00
4.10

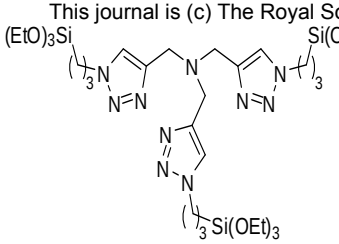

(EtO)3Si
Si(OEt)3
3
3
N
N
N
N

146.90
120.60
77.32
77.00
76.68
58.03
51.84
28.79
24.52
23.83
17.84
7.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


(EtO)3Si
Si(OEt)3
N
N
O
N
N

7.580
7.258
4.702
4.357
4.338
4.320
3.827
3.809
3.792
3.774
2.051
2.032
2.025
2.013
1.994
1.974
1.223
1.206
1.188
0.623
0.603
0.582
7.6 ppm
4.7 4.6 4.5 4.4 ppm
2.05 2.00 ppm
0.60 ppm
9 8 7 6 5 4 3 2 1 0 ppm
2.00
3.95
4.12
12.00
4.11
18.10
4.15

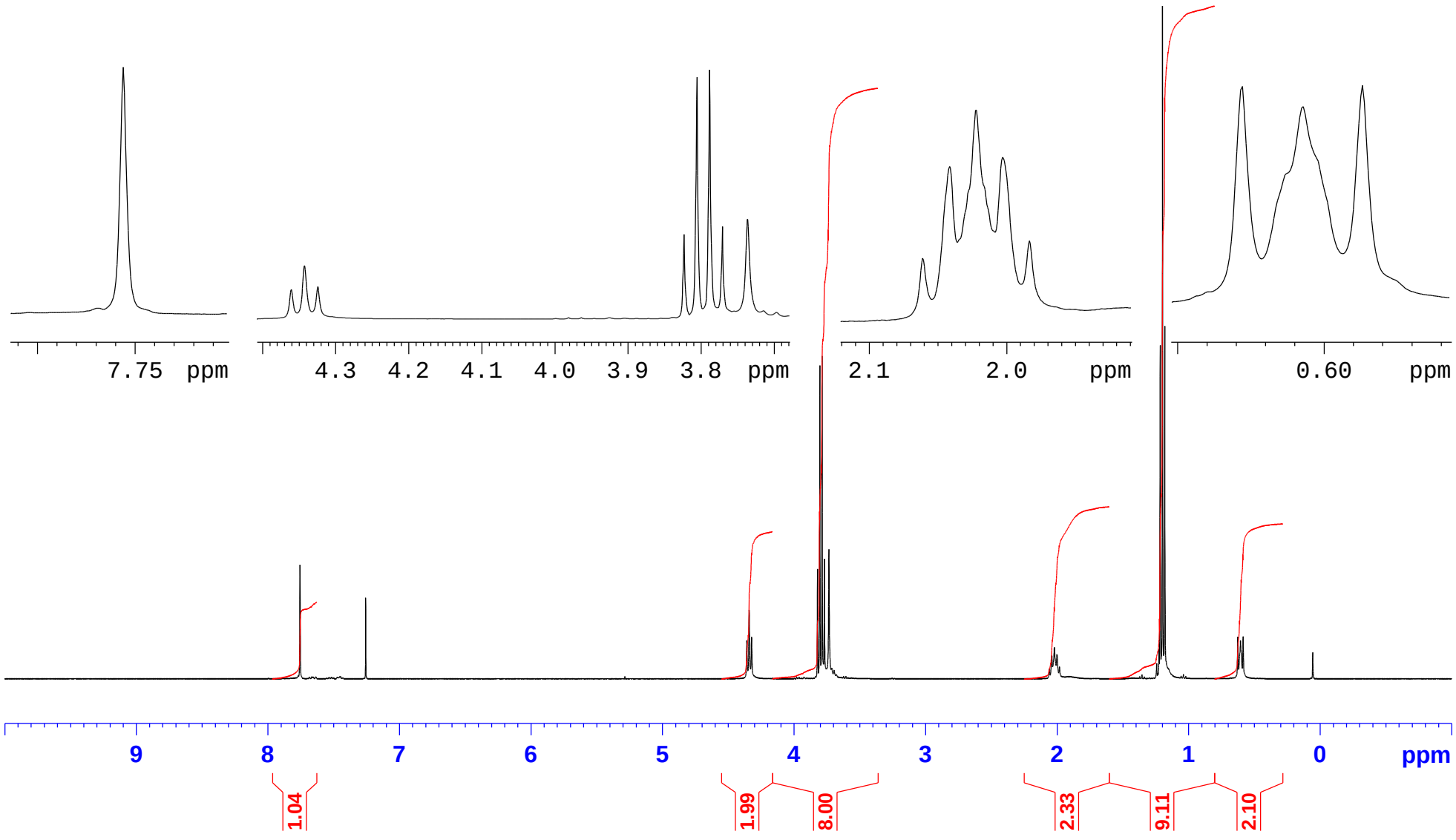


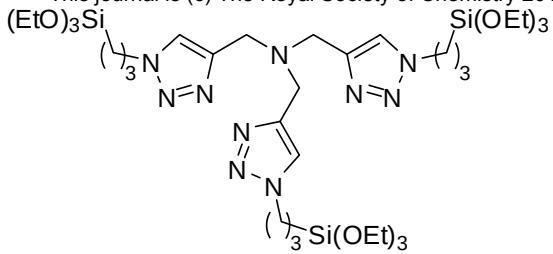


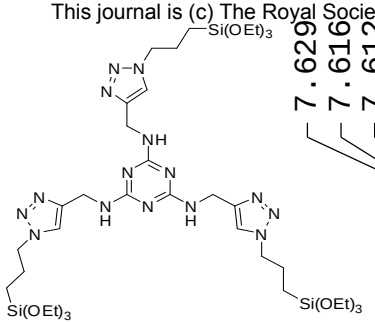
7.756
7.259

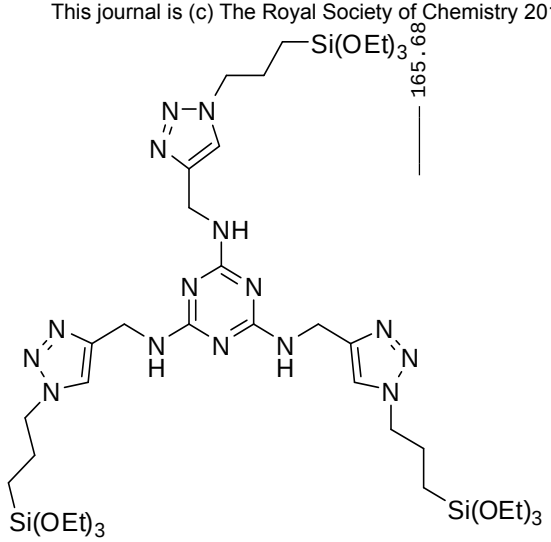
4.361
4.343
4.325
3.824
3.806
3.789
3.771
3.737

2.061
2.042
2.023
2.003
1.984
1.218
1.201
1.183
0.628
0.608
0.587

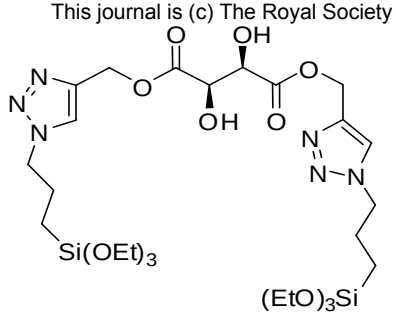


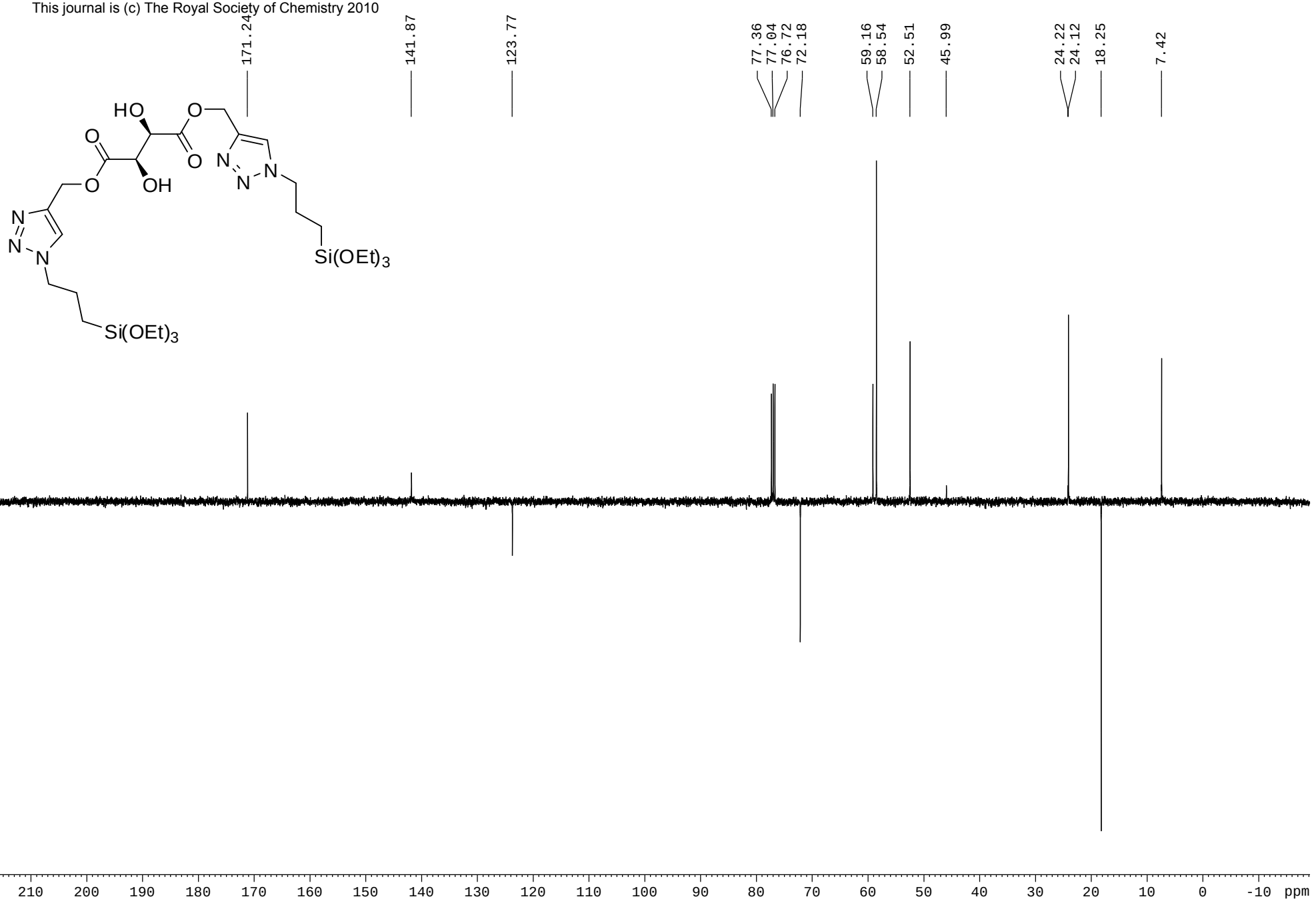





Si(OEt)3
NH
N
N
N
N
N
N
N
N
N
N
N
N
N
N
Si(OEt)3
Si(OEt)3

165.68
146.15
122.10
77.31
76.99
76.67
58.28
52.22
35.85
24.05
18.08
7.31
146.146
150
145
140
ppm
44
42
40
38
36
34
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm




171.24
141.87
123.77
77.36
77.04
76.72
72.18
59.16
58.54
52.51
45.99
24.22
24.12
18.25
7.42
HO
O
O
O
O
OH
N
N
N
N
N
Si(OEt)3
Si(OEt)3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm