

The reaction of chloroalkyl(vinyl)silanes with *N,N*-dichloro sulfonamides

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Synthesis and compound characterization

Melting points were determined on a Boetius Block apparatus (VEB Analytik) and are uncorrected. IR spectra were taken on a Varian 3100 FT-IR or Bruker Vertex 70 spectrophotometer in thin layer. ^1H , ^{13}C , ^{19}F , and ^{29}Si NMR spectra were recorded on a Bruker DPX 400 spectrometer at working frequencies 400 (^1H), 100 (^{13}C), 376 (^{19}F), and 79.5 (^{29}Si) MHz in CDCl_3 ; ^1H , ^{13}C , ^{29}Si NMR chemical shifts are reported in ppm downfield to TMS, ^{19}F NMR in ppm downfield to CFCl_3 . The assignment of ^{13}C NMR signals to CHCl , CH_2Cl and CH_2N groups was done using J_{mod} experiments. Elemental analysis was done on a Thermo-Finnigan Flash EA analyzer. All solvents were dried and purified before use by standard procedures. Commercial chloromethyl(dimethyl)vinylsilane **1** (CAS 16709-86-7) and (3-chloropropyl)dimethyl(vinyl)silane **1'** (CAS 88820-71-7) were used. All *N,N*-dichloro sulfonamides RSO_2NCl_2 ($\text{R} = p\text{-Tol}$, $p\text{-ClC}_6\text{H}_4$, CF_3) were synthesized by the known procedures [V. P. Nazaretyan, O. A. Radchenko and L. M. Yagupol'skii, *Zh. Org. Khim.*, 1974, **10**, 2460]. The reactions were monitored by ^1H NMR spectroscopy. The products were separated by column chromatography on silica gel (Alfa Aesar 0.063–0.2 mm) eluted with hexane/ether 3:1 or methylene chloride/hexane from 1.5 to 2:1.

Reaction of vinylsilane 1 with N,N-dichloro-p-toluenesulfonamide. To a solution of vinylsilane **1** (1.6 g, 12 mmol) in CCl_4 (15 ml) cooled to $-10\text{ }^\circ\text{C}$, a solution of *N,N*-dichloro-*p*-toluenesulfonamide (1.4 g, 6 mmol) in CCl_4 (15 ml), was added dropwise within 1 h. The reaction was warmed to room temperature, and it was complete in 1 h. The solvent was removed, the residue was separated on a silica gel column eluted with dichloromethane/hexane 2:1 to give products **2a** (1.06 g, 52%) and **3a** (0.67 g, 30%).

N-{2-Chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-*p*-toluenesulfonamide **2a**. Colorless crystals, m. p. $37\text{ }^\circ\text{C}$. IR, ν , cm^{-1} : 3280, 2958, 2955, 1598, 1411, 1330, 1265, 1162, 1092, 974, 843, 815, 666. ^1H NMR, δ , ppm: 0.25 s (3H, CH_3), 2.44 s (3H, $\underline{\text{C}}\text{H}_3\text{C}_6\text{H}_4$), 2.90 s (2H, CH_2Cl), 3.17–3.24 m (1H, CHCl), 3.32–3.47 m (1H, CH_2), 4.98 t (1H, NH , J 6.0 Hz), 7.33 d (2H, H^m , J 8.5 Hz), 7.71 d (2H, H^o , J 8.5 Hz). ^{13}C NMR, δ , ppm: -6.08 (SiMe), 21.60 ($\underline{\text{C}}\text{H}_3\text{C}_6\text{H}_4$), 27.82 (CH_2Cl), 46.41 (NCH_2), 47.87 (CHCl), 127.11 (C^o), 129.95 (C^m), 136.78 (C^i), 143.89 (C^p). ^{29}Si NMR, δ : -9.02 ppm. Found, %: C, 42.18; H, 5.28; Cl 20.61; N, 3.98; S, 9.55; Si, 7.87. Calcd. for $\text{C}_{12}\text{H}_{19}\text{Cl}_2\text{NO}_2\text{SSi}$ (%): C, 42.35; H, 5.63; Cl, 20.83; N, 4.12; S, 9.42; Si, 8.25.

N-Chloro-*N*-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-*p*-toluenesulfonamide **3a**. Colorless liquid. IR, ν , cm^{-1} : 2961, 2904, 1428, 1373, 1230, 1195, 1146, 1075, 974, 849. ^1H NMR, δ , ppm: 0.34 s (3H, CH_3), 2.50 s (3H, $\text{CH}_3\text{C}_6\text{H}_4$), 2.98 s (2H, CH_2Cl), 3.53–3.59 m (1H, CHCl), 3.63–3.73 m (1H, CH_2), 7.22 d (2H, Ar, J 8.4 Hz), 7.84 d (2H, Ar, J 8.4 Hz). ^{13}C NMR, δ , ppm: –6.22 (SiMe), –6.11 (SiMe), 21.81 ($\text{CH}_3\text{C}_6\text{H}_4$), 28.22 (CH_2Cl), 42.77 (NCH_2), 59.47 (CHCl), 129.65 (C^o), 129.90 (C^i), 129.97 (C^m), 145.92 (C^p). ^{29}Si NMR, δ : –8.44 ppm. Found, %: C, 38.16; H, 4.69; Cl 29.20; N, 3.59; S, 7.98; Si, 7.53. Calcd. for $\text{C}_{12}\text{H}_{18}\text{Cl}_3\text{NO}_2\text{SSi}$ (%): C, 38.46; H, 4.84; Cl, 28.38; N, 3.74; S, 8.55, Si, 7.49.

Reaction of vinylsilane 1 with 4,N,N-trichlorobenzenesulfonamide. The reaction was performed and treated as above. After 3 h the solvent was removed and the residue eluted on silica gel with hexane/ether 3:1 to afford 1.3 g (48%) of compound **2b** and 0.8 g (27%) of compound **3b**.

N-{2-Chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-4-chlorobenzenesulfonamide **2b**. Colorless crystals, m. p. 68 °C. IR, ν , cm^{-1} : 3093, 2962, 2929, 1585, 1476, 1374, 1256, 1172, 1093, 1013, 826, 756, 639. ^1H NMR, δ , ppm: 0.22 s (3H, CH_3), 0.23 s (3H, CH_3), 2.83 s (2H, CH_2Cl), 3.38–3.43 m (H, CHCl), 3.60–3.69 m (1H, CH_2), 4.96 d (1H, NH, J 9.6 Hz), 7.47d (1H, H^o , J 8.4 Hz), 7.47 d (1H, H^o , J 8.4 Hz). ^{13}C NMR, δ , ppm: –5.52 (SiMe), –5.26 (SiMe), 28.42 (CH_2Cl), 44.64 (CHCl), 47.20 (NCH_2), 128.68 (C^o), 129.58 (C^m), 140.26 (C^p), 139.60 (C^i). ^{29}Si NMR, δ : –9.00 ppm. Found, %: C, 36.88; H, 4.42; Cl 28.80; N, 3.36; S, 8.67; Si, 7.65. Calcd. for $\text{C}_{11}\text{H}_{16}\text{Cl}_3\text{NO}_2\text{SSi}$ (%): C, 36.62; H, 4.47; Cl, 29.48; N, 3.88; S, 8.89; Si, 7.79.

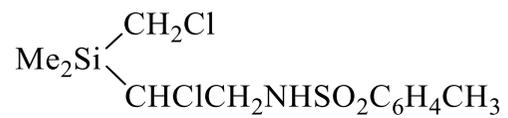
N,4-Dichloro-*N*-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}benzenesulfonamide **3b**. Colorless liquid. IR, ν , cm^{-1} : 3093, 2962, 2929, 1585, 1476, 1374, 1256, 1172, 1093, 1013, 826, 756, 639. ^1H NMR, δ , ppm: 0.32 s (3H, CH_3), 2.96 s (2H, CH_2Cl), 3.51–3.58 m (H, CHCl), 3.69–3.76 m (1H, CH_2), 7.60, (1H, H^o , J 8.4 Hz), 7.89, (1H, H^o , J 8.3 Hz). ^{13}C NMR, δ , ppm: –6.21 (SiMe), –6.12 (SiMe), 28.06 (CH_2Cl), 42.31 (NCH_2), 59.33 (CHCl), 129.30 (C^o), 130.84 (C^m), 131.52 (C^p), 141.52 (C^i). ^{29}Si NMR, δ : –8.44 ppm. Found, %: C, 33.43; H, 3.83; Cl 35.88; N, 3.54; S, 8.11; Si, 7.11. Calcd. for $\text{C}_{11}\text{H}_{15}\text{Cl}_4\text{NO}_2\text{SSi}$ (%): C, 32.91; H, 3.71; Cl, 35.00; N, 3.06; S, 8.25; Si, 7.65.

4-Chloro-3,3-dimethyl-1-[(trifluoromethyl)sulfonyl]-1,3-azasilolidine 4. To a solution of vinylsilane **1** (1.22 g, 9 mmol) in CCl_4 (10 ml) cooled to –10 °C, a solution of *N,N*-dichlorotriflamide (1 g, 4.6 mmol) in CCl_4 (15 ml) was added within 30 min allowing the mixture to warm to 0 °C. After 1 h the reaction was completed, the solvent was removed, the residue was purified by chromatography on alumina (0.063–0.2 mm) eluting with chloroform/hexane 1:3 (could not be purified on silica gel). Yield 0.96 g (75%), colorless liquid. IR, ν , cm^{-1} : 2966, 2917, 1454, 1386, 1254, 1225, 1187, 1133, 1072, 1056, 987, 839, 647, 598. ^1H NMR, δ , ppm: 0.35 s (3H, SiMe), 0.48 s (3H, SiMe) 2.87 d (2H, SiCH^A , J 13.5 Hz), 3.05 d (1H, SiCH^B , J 13.5 Hz), 3.58 t (1H, CHCl , J 3.8 Hz), 3.82 d (1H, NCH^A , J 12.5 Hz), 3.96 d (1H, NCH^B , J 12.5 Hz). ^{13}C NMR, δ , ppm: –5.31 (SiMe), –3.74 (SiMe), 34.84 (SiCH_2), 42.95 (CHCl), 57.33 (NCH_2), 120.42 q (CF_3 , J 324.3 Hz). ^{19}F NMR, δ : –77.09 ppm. ^{29}Si NMR, δ : 4.99 ppm. Found, %: C, 25.15; H, 3.89; Cl, 11.92; F, 20.55; N, 4.97; S, 11.55; Si, 9.74. Calcd. for $\text{C}_6\text{H}_{11}\text{ClF}_3\text{NO}_2\text{SSi}$ (%): C, 25.58; H, 3.94; Cl, 12.58; F, 20.23; N, 4.97; S, 11.38; Si, 9.97.

Reaction of vinylsilane 1' with N,N-dichlorotriflamide. To a solution of vinylsilane **1'** (1.89 g, 11 mmol) in CCl₄ (15 ml) cooled to -10 °C, a solution of *N,N*-dichlorotriflamide (1.2 g) in CCl₄ (15 ml) was added dropwise for 30 min. The mixture was stirred at room temperature for 5 h, the solvent was removed, the residue was purified on a silica gel column with dichloromethane/hexane 1:5 to give compounds **5a** (2.2 g, 58%) and **5b** (0.6 g, 30%).

N-{2-Chloro-2-[3-chloropropyl(dimethyl)silyl]ethyl}triflamide **5a**. Colorless liquid. IR, ν , cm⁻¹ : 3312, 2957, 1428, 1376, 1257, 1232, 1196, 1073, 840, 616. ¹H NMR, δ , ppm: 0.188 s (3H, SiMe), 0.191 s (3H, SiMe), 0.74–0.90 m (2H, SiCH₂), 1.76–1.86 m (1H, CCH₂C), 3.37–3.47 m (2H, NCH₂), 3.53 t (2H, CH₂Cl, *J* 6.7 Hz), 3.67–3.79 m (1H, CHCl), 5.54 br.s (1H, NH). ¹³C NMR, δ , ppm: -5.41 (SiMe), -5.21 (SiMe), 10.82 (SiCH₂), 27.00 (CCH₂C), 47.48 (CH₂Cl), 47.76 (NCH₂), 49.87 (CHCl), 119.69 q (CF₃, *J* 324.6 Hz). ¹⁹F NMR, δ : -77.17 ppm. ²⁹Si NMR, δ : -5.83 ppm. Found, %: C, 28.43; H, 4.67; Cl 19.72; F, 16.78; N, 3.74; S, 8.75, Si, 8.35. Calcd. for C₈H₁₆Cl₂F₃NO₂SSi (%):C, 27.75; H, 4.66; Cl, 20.48; F, 16.46; N, 4.05; S, 9.26; Si, 8.11.

N-Chloro-*N*-{2-chloro-2-[(3-chloropropyl)(dimethyl)silyl]ethyl}triflamide **5b**. Colorless liquid. IR, ν , cm⁻¹: 2954, 29.25, 1564, 1410, 1312, 1257, 1205, 11346, 1072, 833, 644. ¹H NMR, δ , ppm: 0.21 (3H, SiMe), 0.22 (3H, SiMe), 0.81–0.92 m (2H, SiCH₂), 1.74–1.91 m (2H, CCH₂C), 3.54 t (2H, CH₂Cl, *J* 6.7 Hz), 3.77 d.d (1H, CHCl, *J* 14.4, 3.0 Hz), 3.64 d.d (1H, NCH^A, *J* 11.3, 6.6 Hz), 4.03 d.d (1H, NCH^B, *J* 14.4, 11.3 Hz). ¹³C NMR, δ , ppm: -5.31 (SiMe), -5.03 (SiMe), 10.98 (SiCH₂), 27.03 (CCH₂C), 43.76 (CH₂Cl), 47.47 (NCH₂), 60.38 (CHCl), 119.86 q (CF₃, *J* 325.5 Hz). ¹⁹F NMR, δ : -70.76 ppm. ²⁹Si NMR, δ : -5.44 ppm. Found, %: C, 26.16; H, 3.88; Cl 19.72; F, 16.78; N, 3.74; S, 7.97, Si, 8.12. Calcd. for C₈H₁₅Cl₃F₃NO₂SSi (%): C, 25.24; H, 3.97; Cl, 24.71; F, 19.51; N, 3.54; S, 8.42; Si, 7.38.



1H.1.1.1r

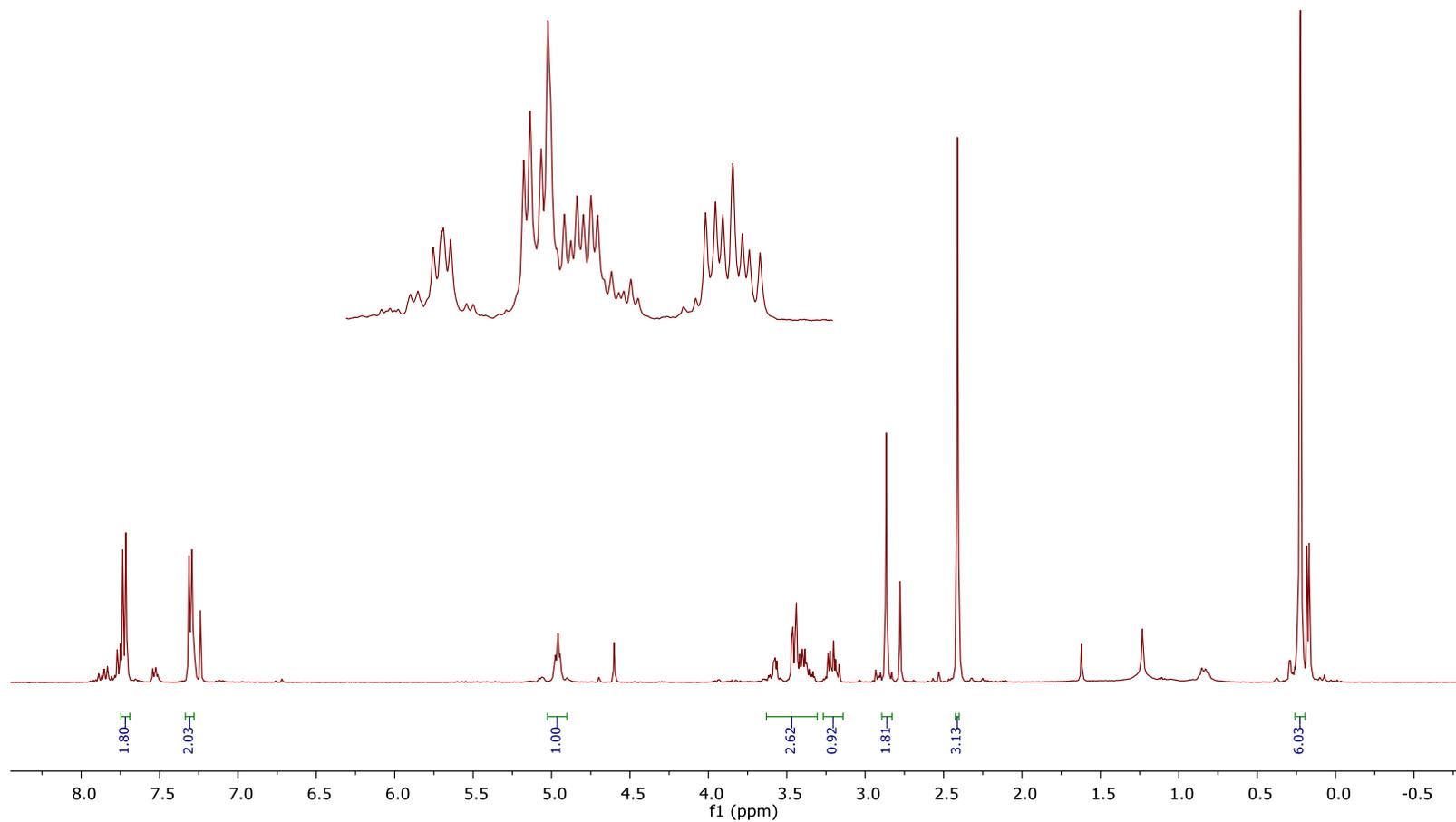


Figure S1. ^1H NMR spectrum of *N*-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-*p*-toluenesulfonamide 2a

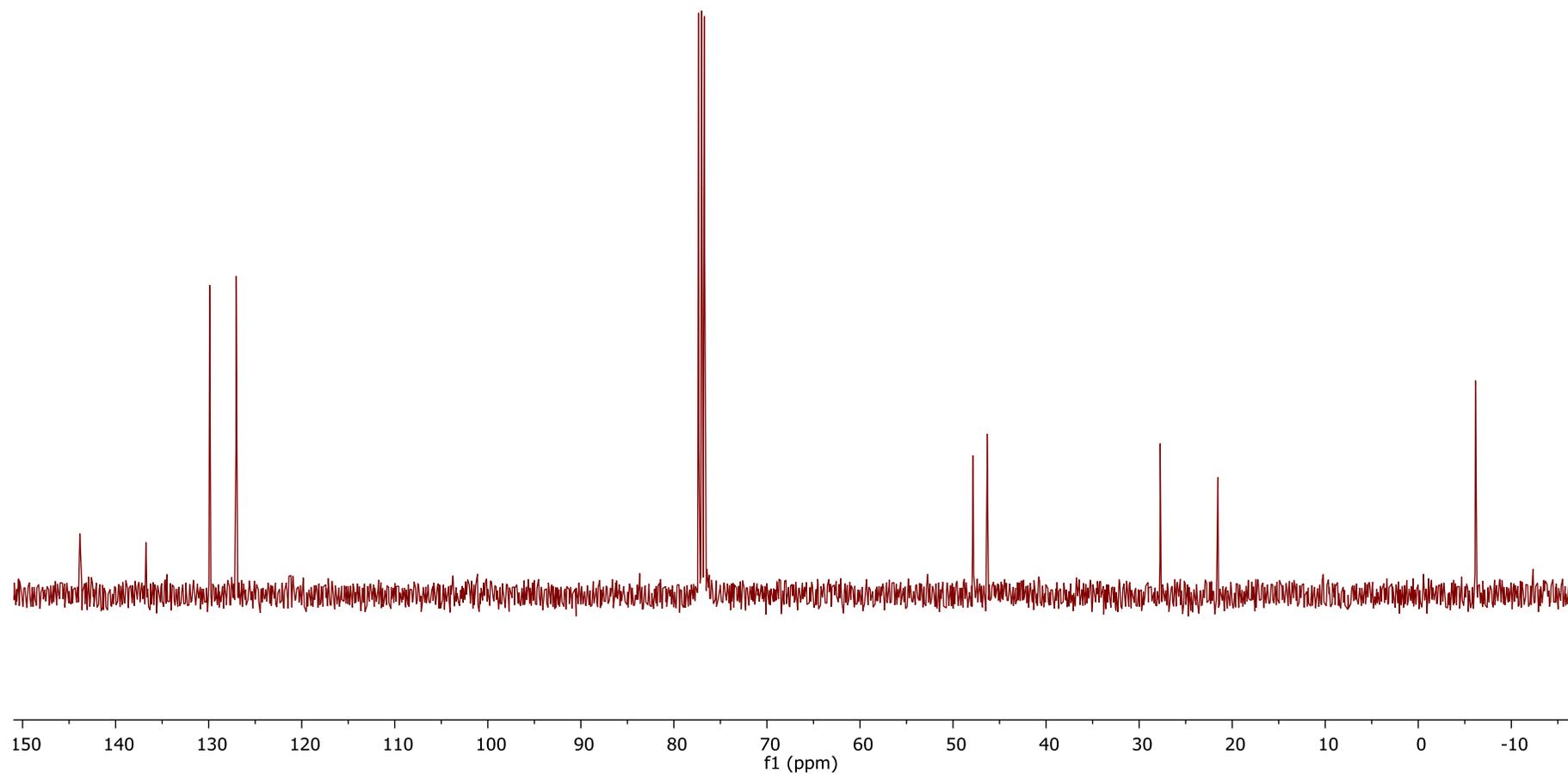
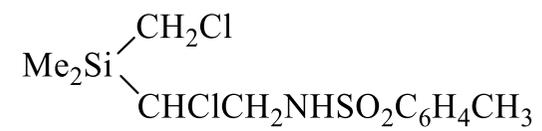


Figure S2. ^{13}C NMR spectrum of *N*-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-*p*-toluenesulfonamide 2a

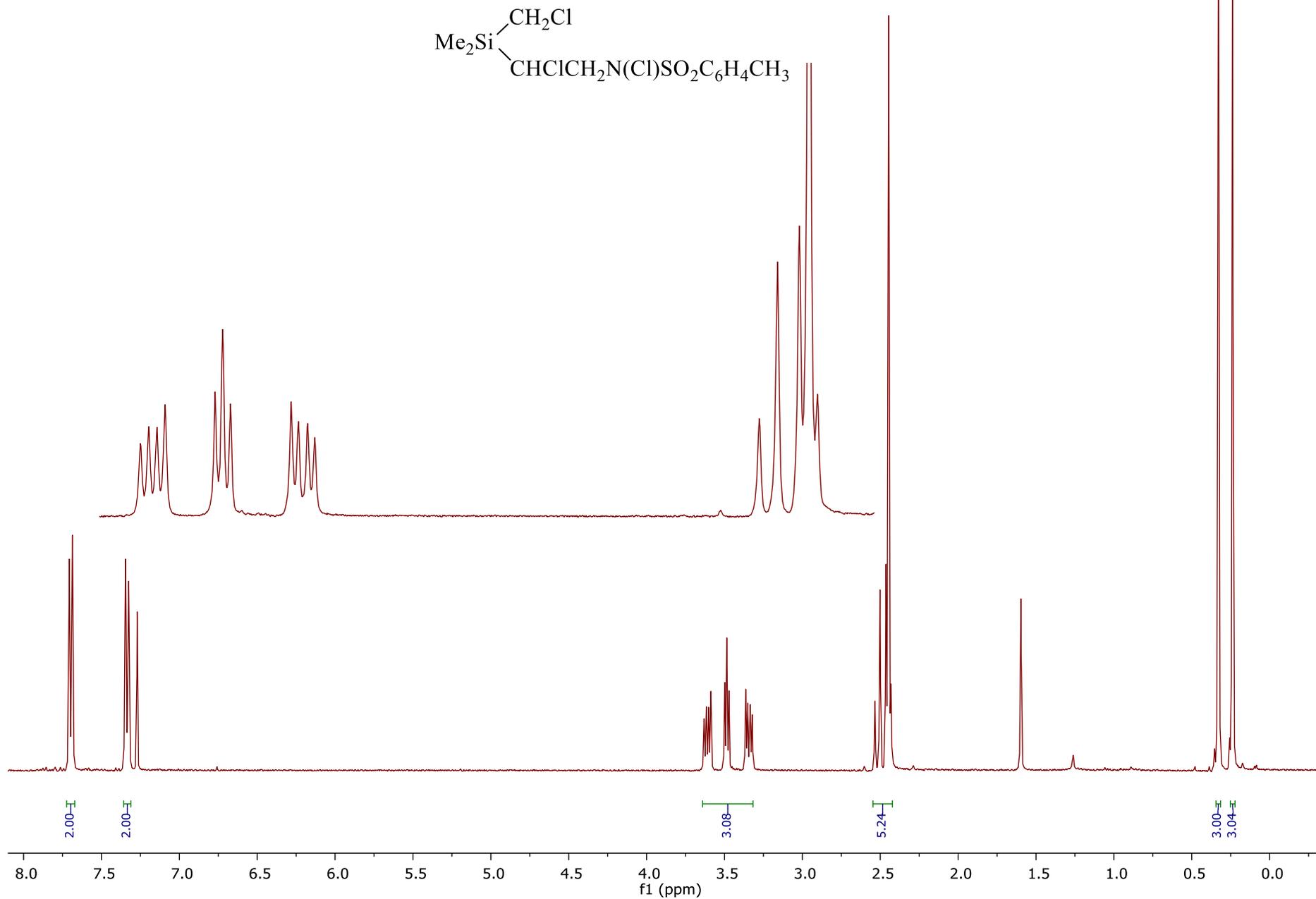


Figure S3. ^1H NMR spectrum of *N*-chloro-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-*p*-toluenesulfonamide **3a**



13C_1.1.1r

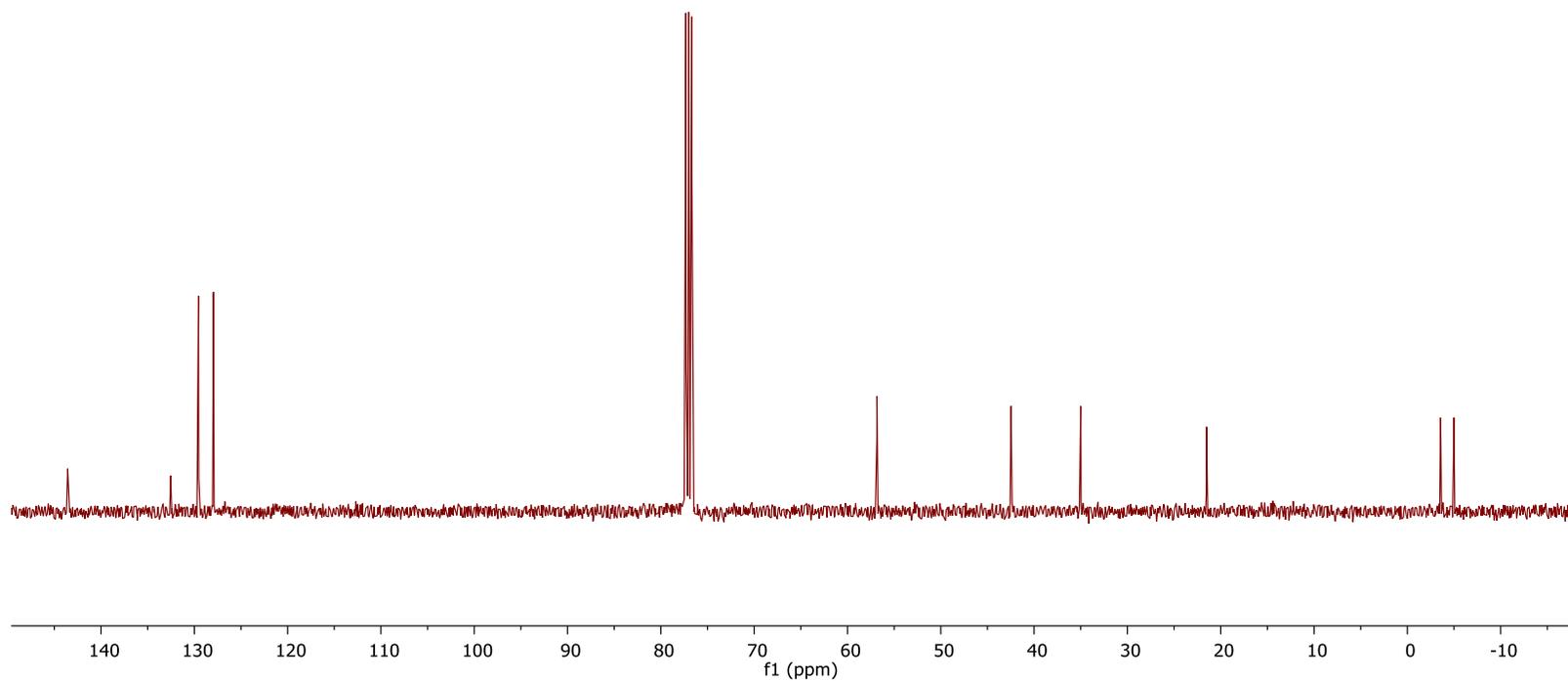


Figure S4. ^{13}C NMR spectrum of *N*-chloro-2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl-*p*-toluenesulfonamide 3a



1H.1.1.1r

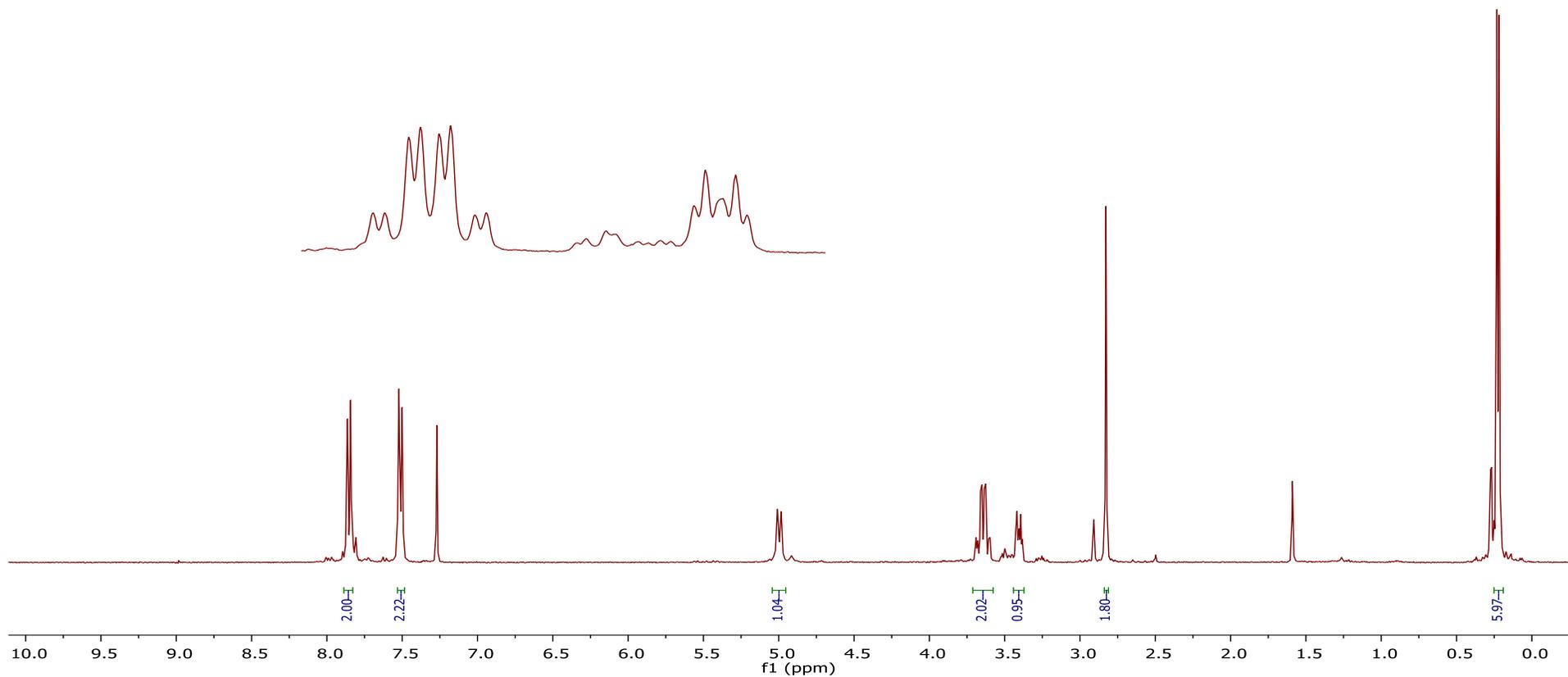
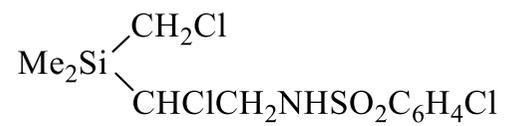


Figure S5. ^1H NMR spectrum of *N*-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-4-chlorobenzenesulfonamide **2b**



13C_1.1.1r

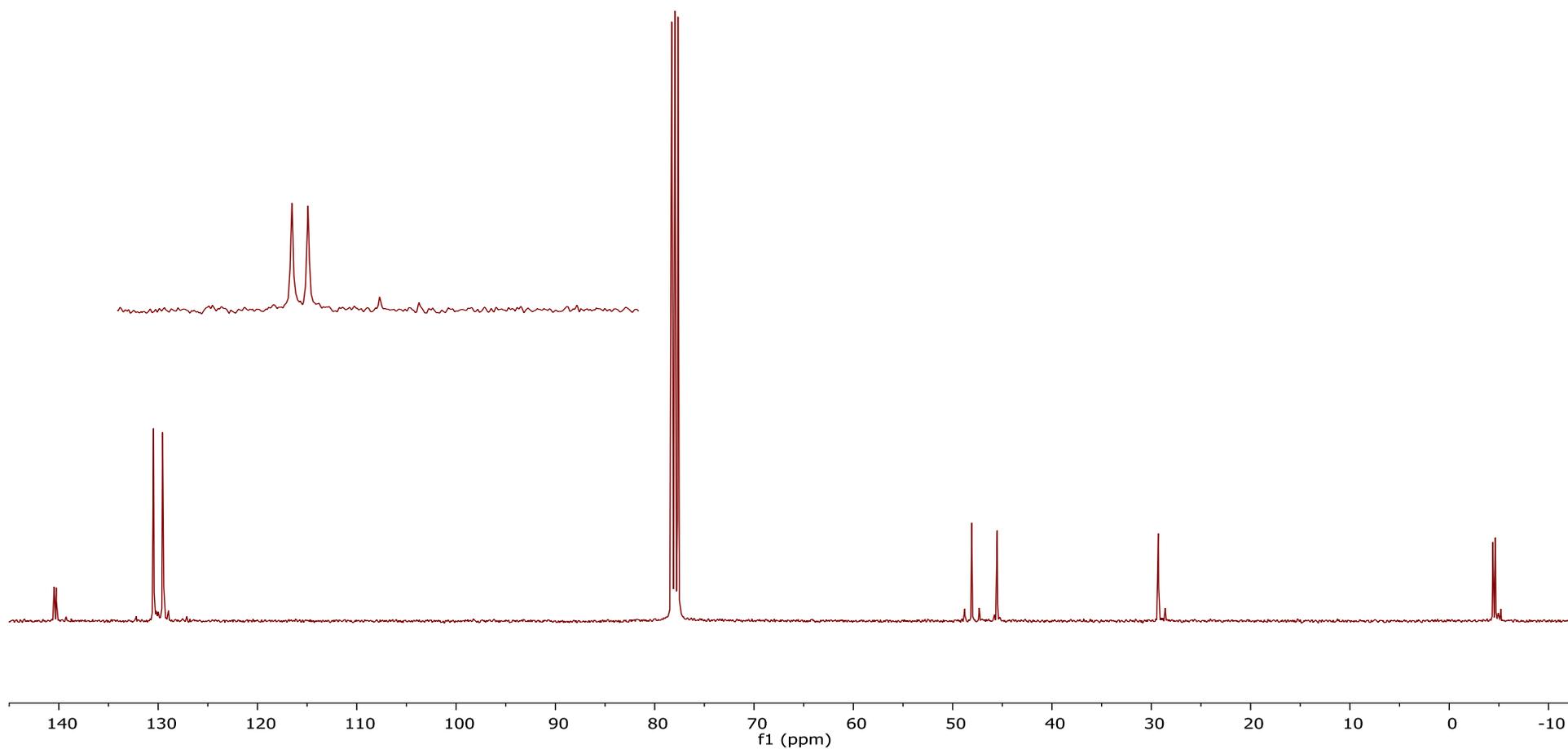


Figure S6. ¹³C NMR spectrum of *N*-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}-4-chlorobenzenesulfonamide **2b**

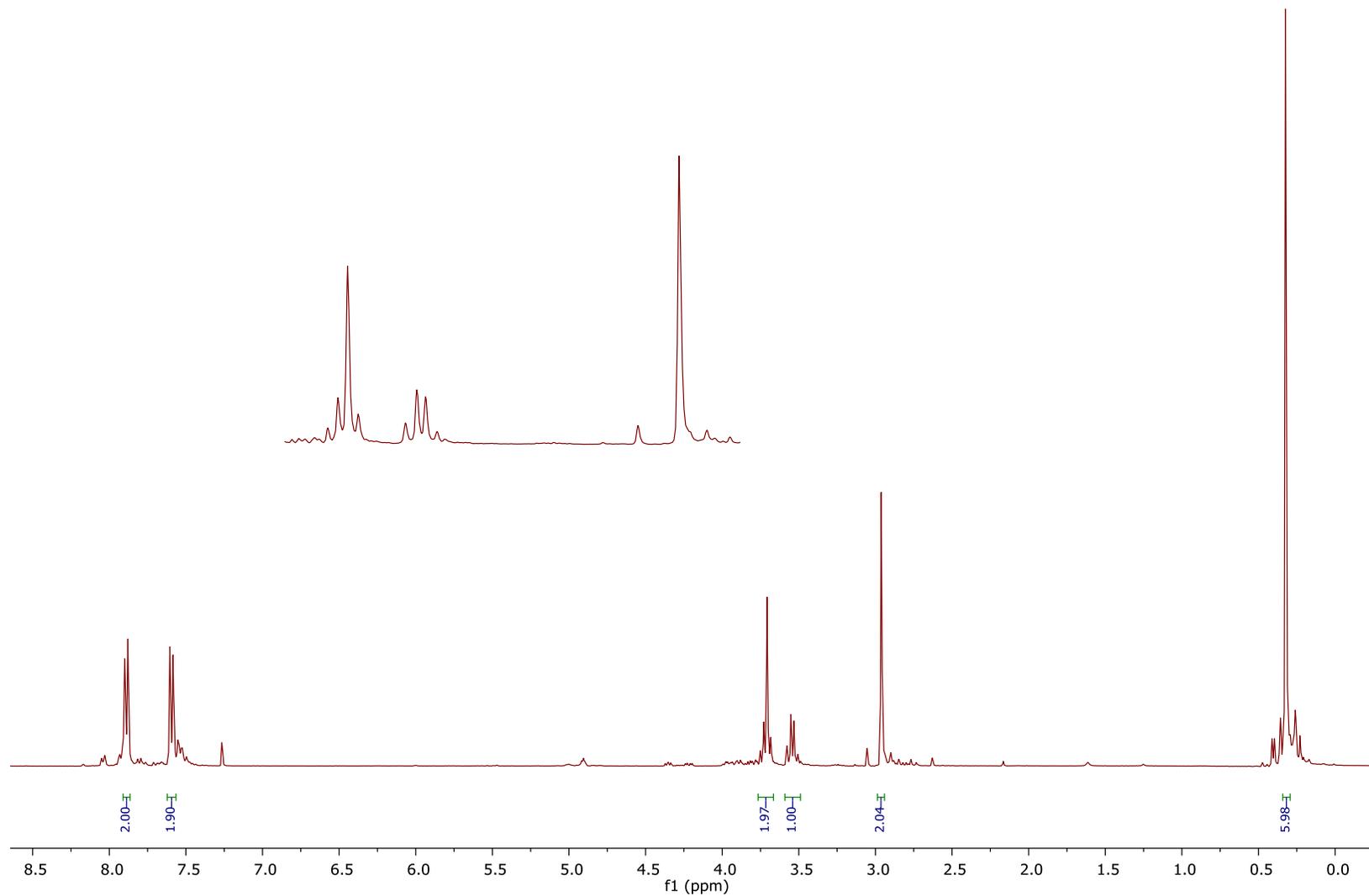
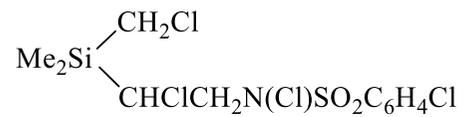
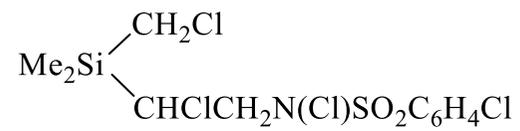


Figure S7. ^1H NMR spectrum of *N*,4-dichloro-*N*-{2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl}benzenesulfonamide **3b**



13C_1.1.1r

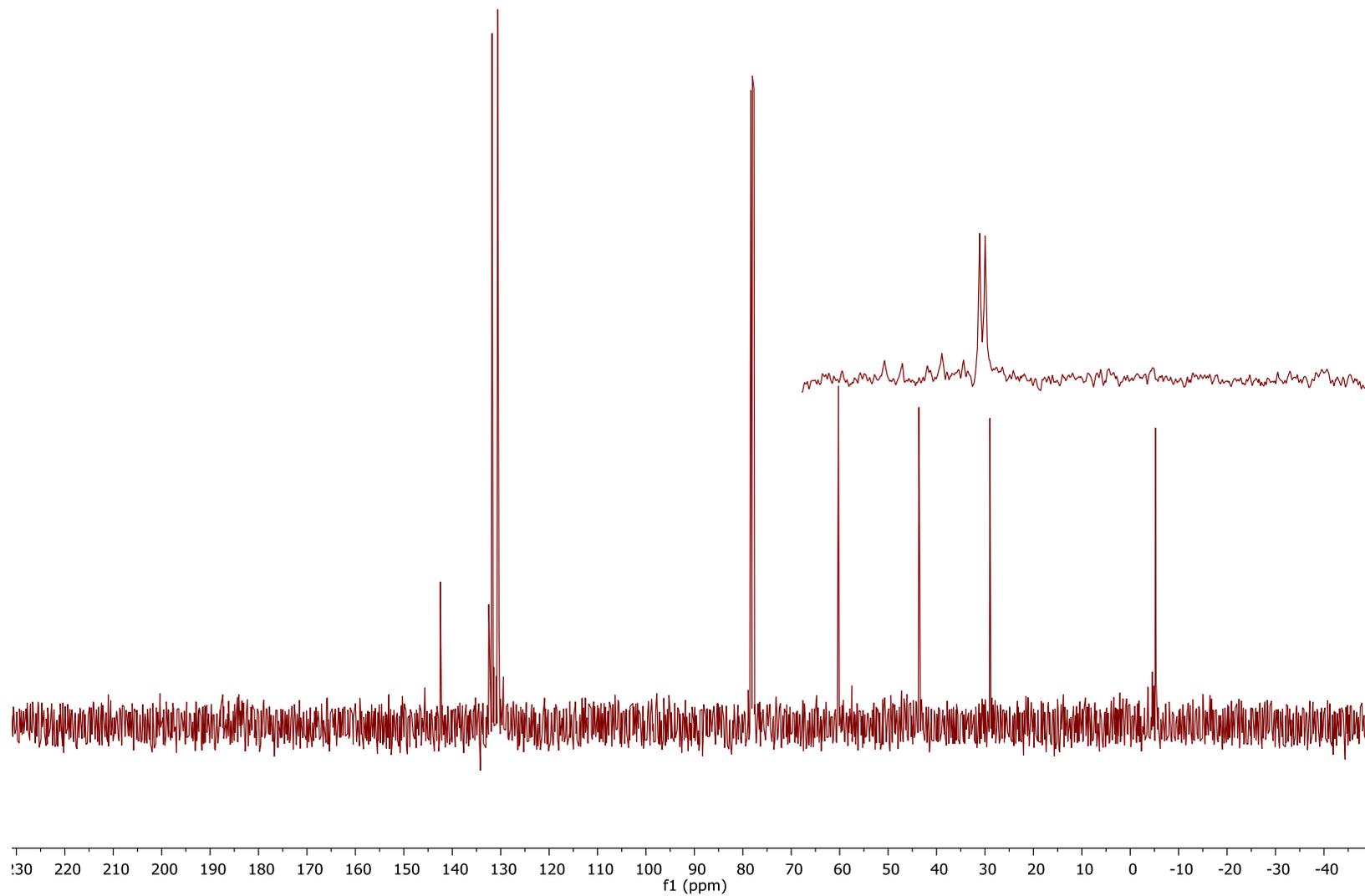


Figure S8. ^{13}C NMR spectrum of *N*,4-dichloro-*N*-[2-chloro-2-[(chloromethyl)(dimethyl)silyl]ethyl]benzenesulfonamide **3b**

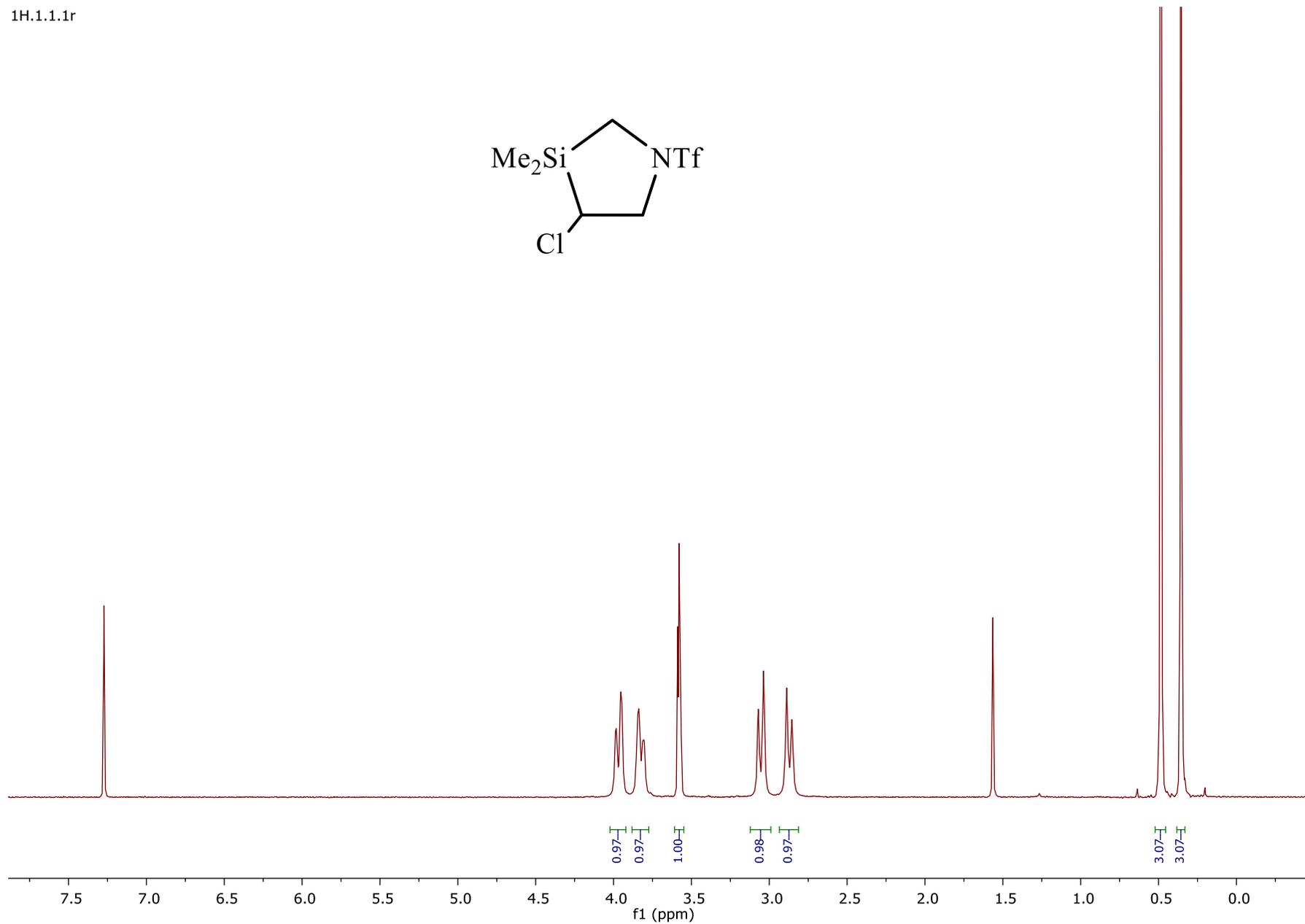
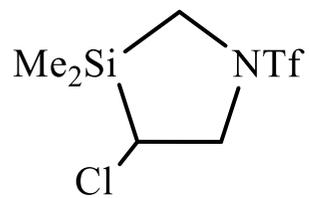


Figure S9. ^1H NMR spectrum of 4-chloro-3,3-dimethyl-1-[(trifluoromethyl)sulfonyl]-1,3-azasilolidine **4**

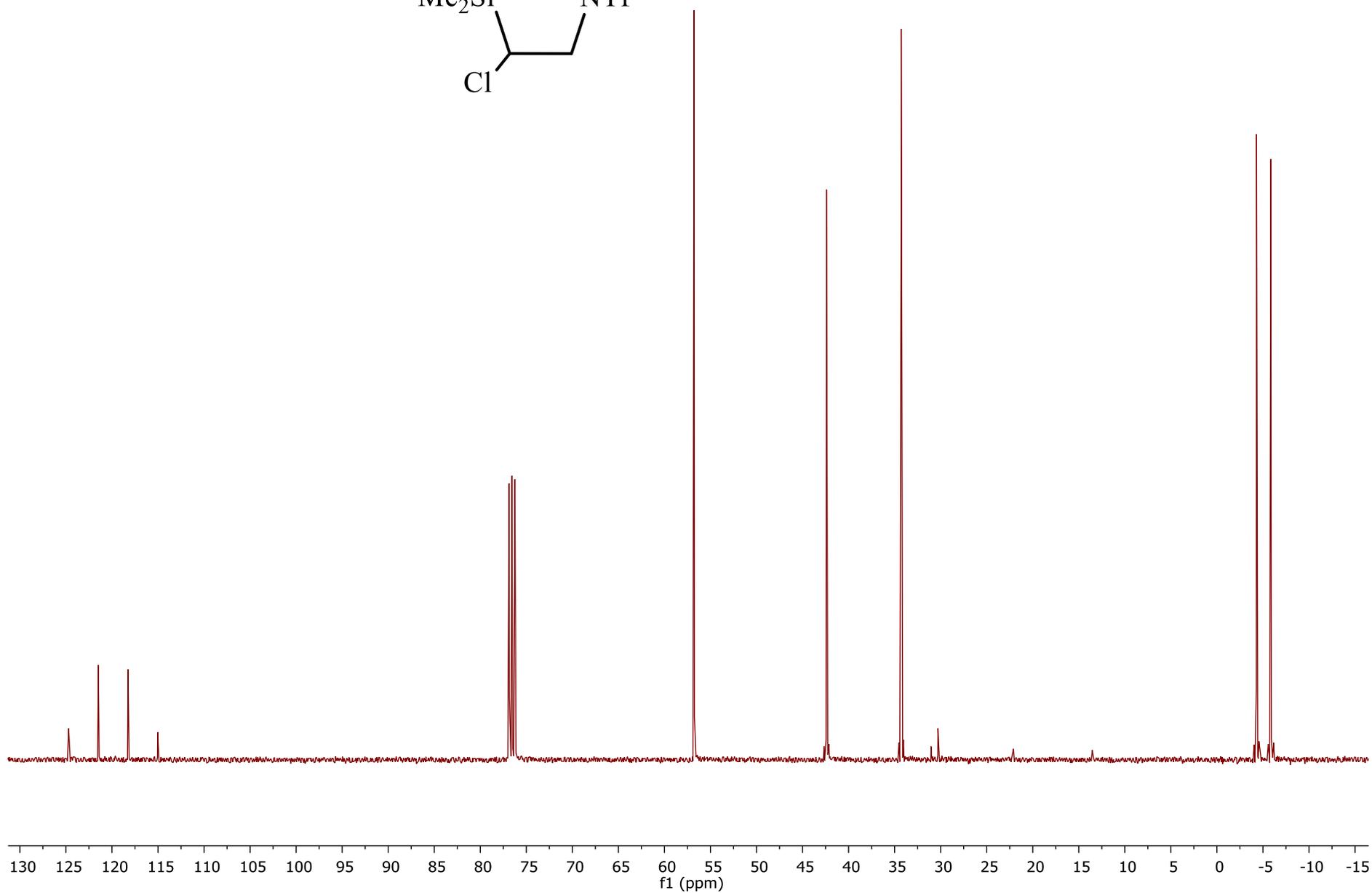
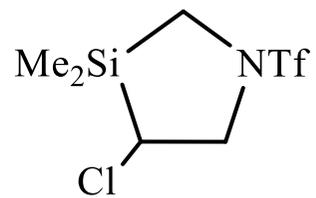


Figure S10. ¹³C NMR spectrum of 4-chloro-3,3-dimethyl-1-[(trifluoromethyl)sulfonyl]-1,3-azasilolidine 4

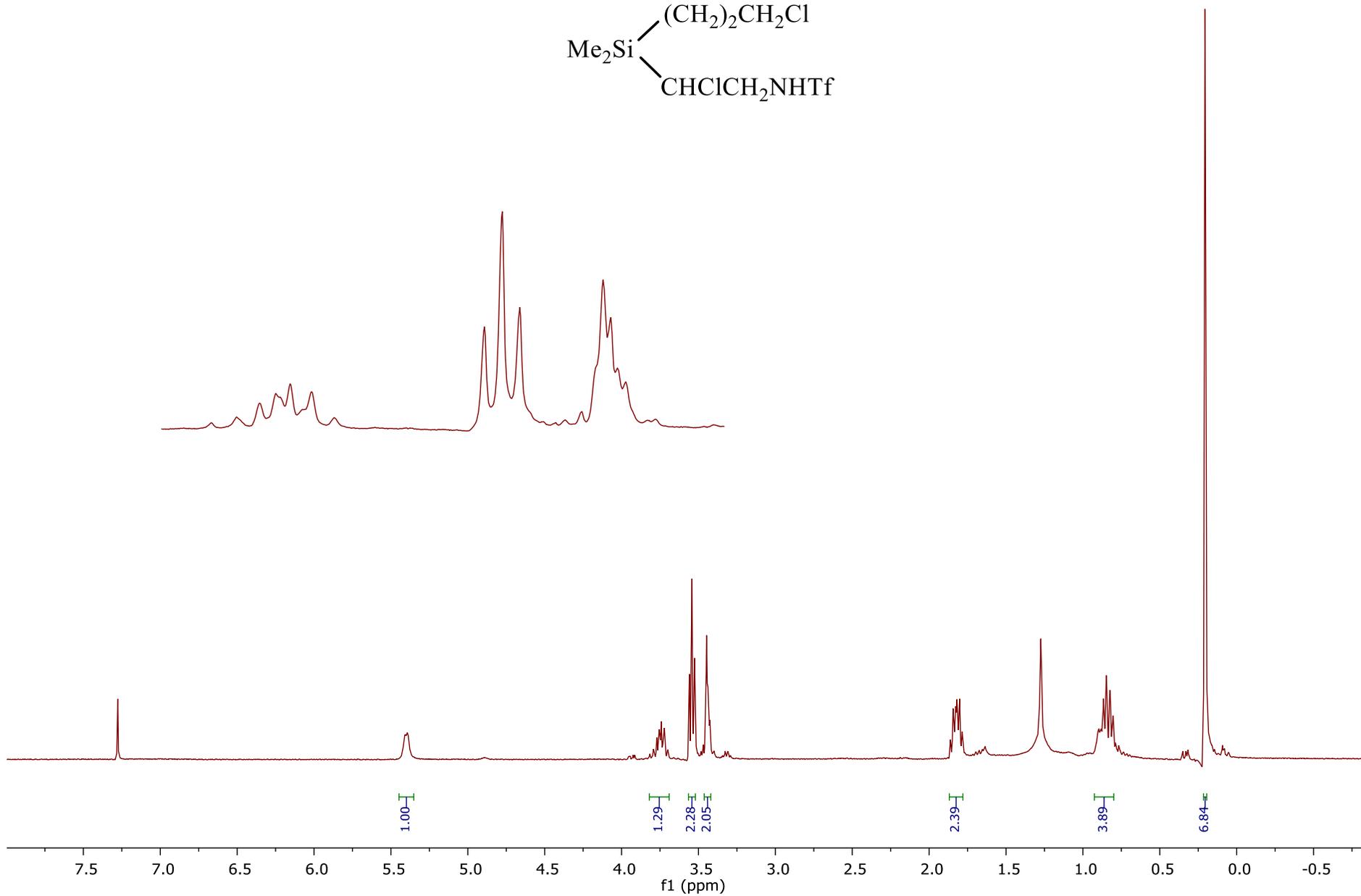
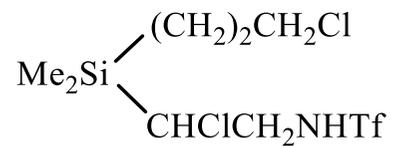


Figure S11. ^1H NMR spectrum of *N*-{2-chloro-2-[3-chloropropyl(dimethyl)silyl]ethyl}triflamide 5a

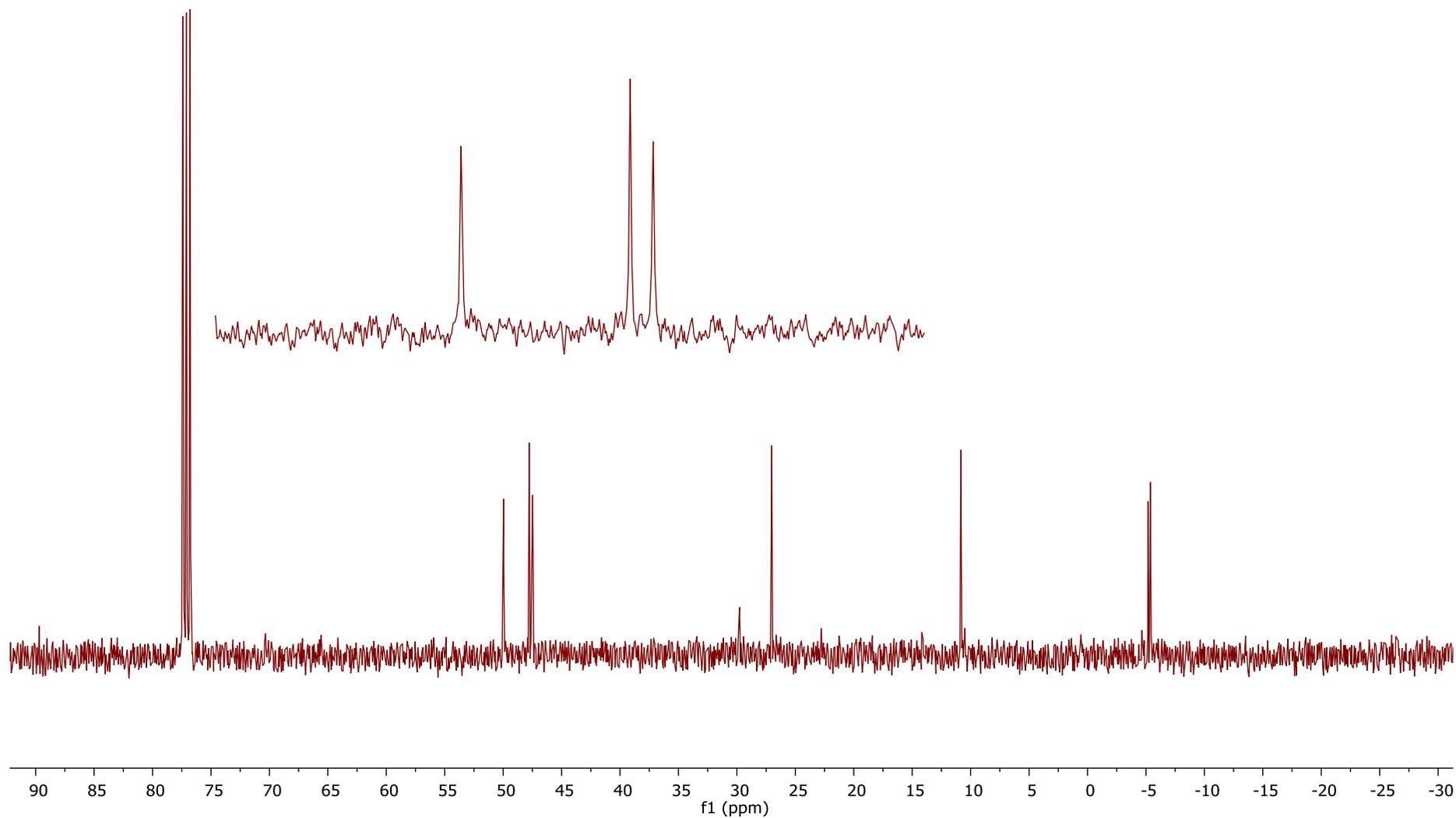
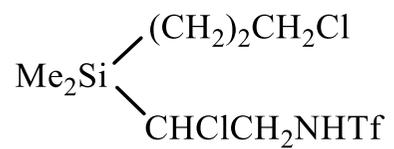


Figure S12. ^{13}C NMR spectrum of *N*-{2-chloro-2-[3-chloropropyl(dimethyl)silyl]ethyl}triflamide 5a

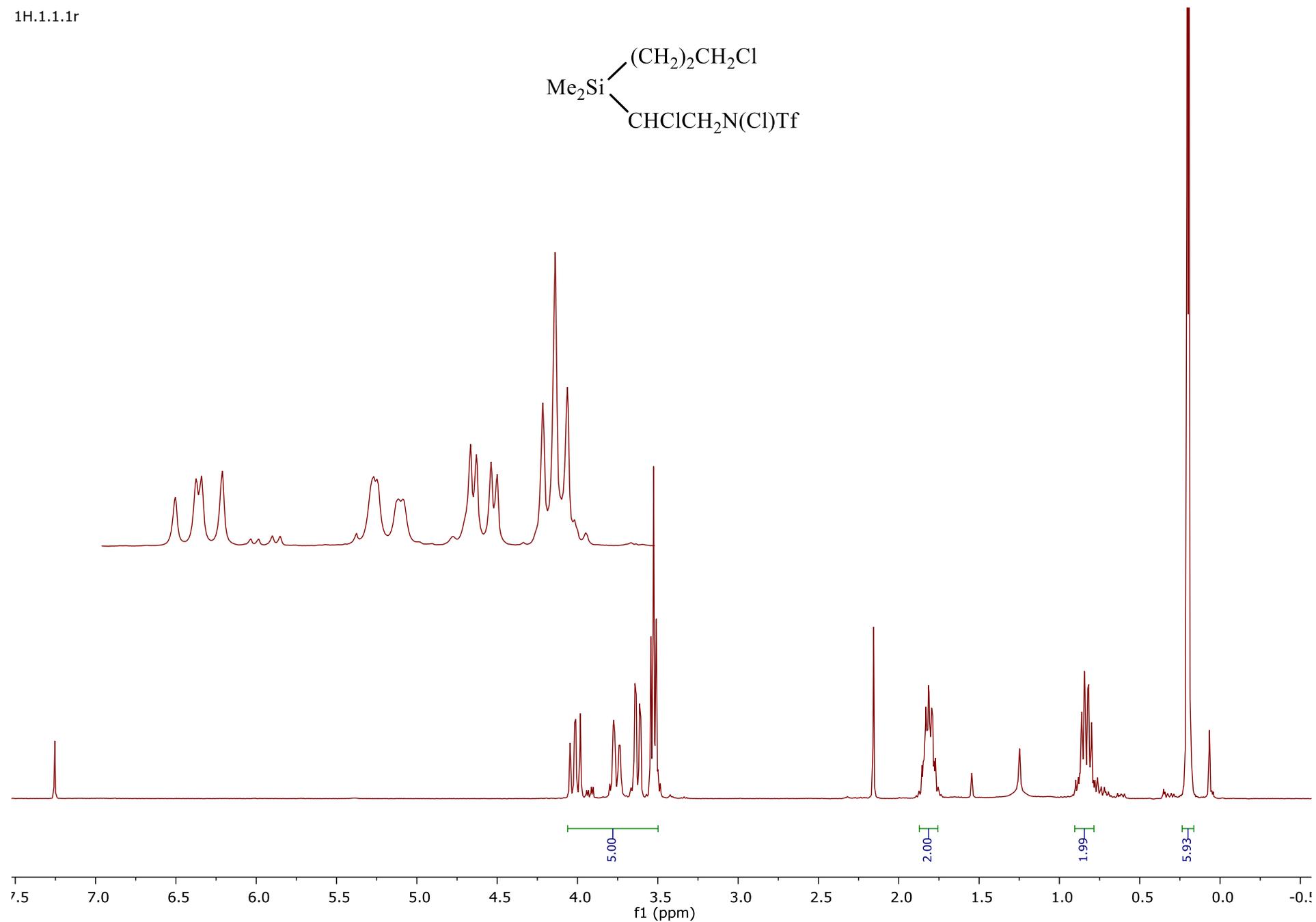
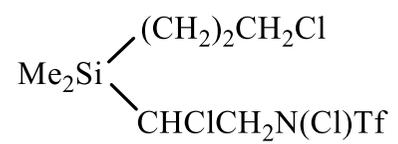


Figure S13. ^1H NMR spectrum of N-chloro-N-{2-chloro-2-[(3-chloropropyl)(dimethyl)silyl]ethyl}triflamide 5b

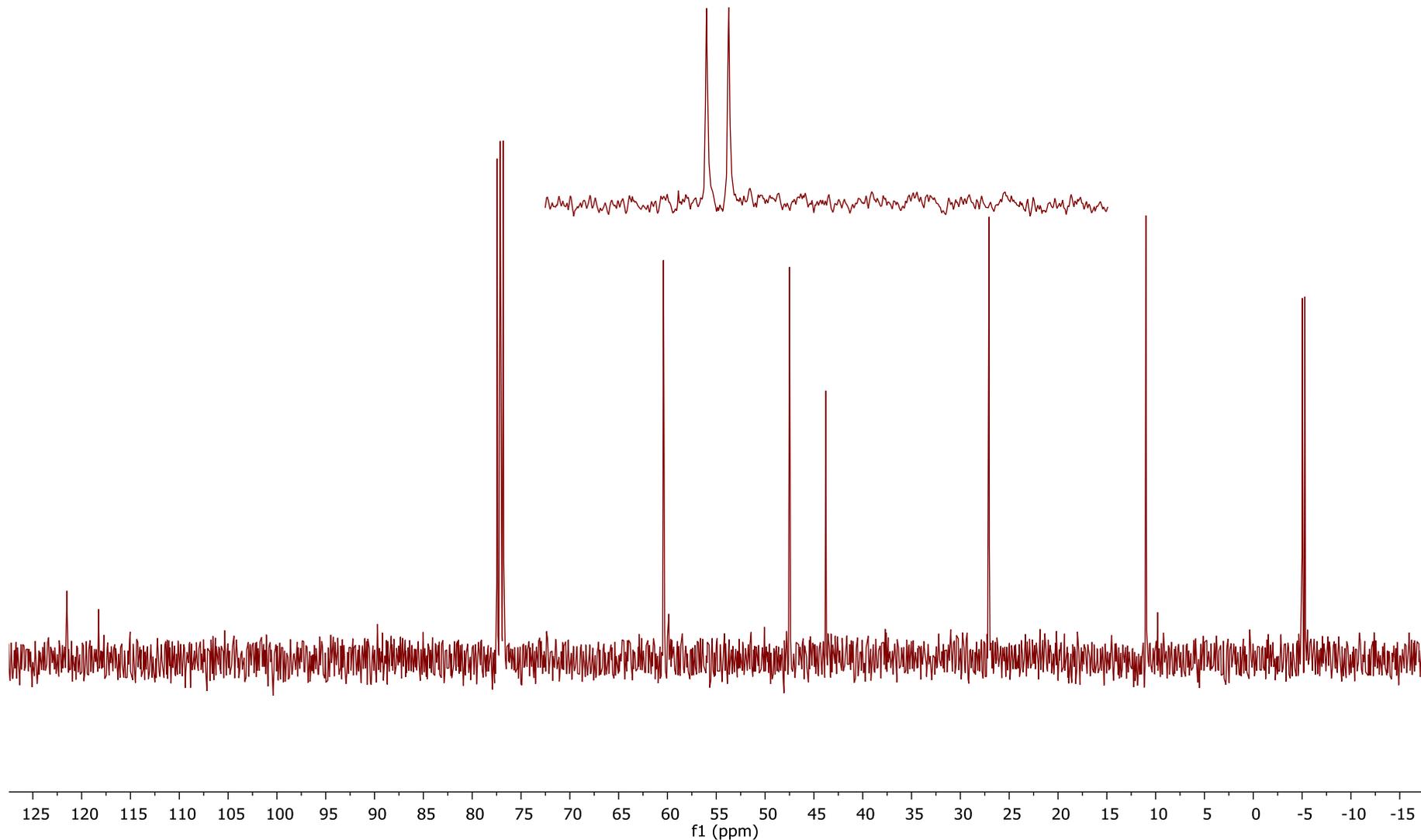
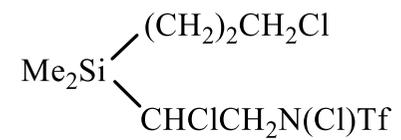


Figure S14. ^{13}C NMR spectrum of *N*-chloro-*N*-{2-chloro-2-[(3-chloropropyl)(dimethyl)silyl]ethyl}triflamide **5b**