

Chlorotriflamidation of vinylsilanes with *N,N*-dichlorotriflamide

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General. IR spectra were taken on a Bruker Vertex 70 instrument in thin layer. NMR spectra were registered in CDCl₃ on a Bruker DPX 400 spectrometer with working frequencies 400 (¹H), 100 (¹³C), 386 (¹⁹F) and 79.5 (²⁹Si) MHz, respectively. Chemical shifts are referenced to TMS (¹H, ¹³C, ²⁹Si) and CCl₃F (¹⁹F), respectively. The signals were assigned using J_{mod} ¹³C spectra. Elemental analyses were done on a Thermo-Finnigan Flash EA analyzer. All solvents were purified by standard procedures. *N,N*-Dichlorotriflamide was prepared by chlorination of triflamide using the known procedure. Commercial or synthesized by the known procedures vinylsilanes were used. Pure products were isolated by column chromatography on silica.

Reaction of *N,N*-dichlorotriflamide with diphenyl(divinyl)silane. To the solution of 1.0 g (4.2 mmol) of diphenyl(divinyl)silane **3b** in 10 ml of CCl₄ the solution of 0.47 g (4.2 mmol) of TfNCl₂ in 10 ml of CCl₄ was added with stirring. The mixture was stirred for 1 h at –10 °C and for 4 h at room temperature. The solvent was removed, analytically pure products **4b** and **5** isolated by column chromatography on silica 0.063–0.2 mm, eluent hexane–chloroform 3:1.

[1-Chloro-2-(triflamido)ethyl](diphenyl)vinylsilane 4b. Yield 0.8 g (45%), colourless liquid. IR, ν , cm⁻¹: 3320, 2946, 2854, 1427, 1374, 1230, 1196, 1144, 1074, 969, 850. ¹H NMR, δ , ppm: 3.47 d.d.d (1H, NCH^A, J 14.4, 11.4, 3.0 Hz), 3.89 d.d.d (1H, NCH^B, J 14.4, 8.2, 3.0), 4.03 d.d (1H, CHCl, J 11.4, 3.0 Hz), 5.46 br.d (1H, NH, J 5.0 Hz), 5.94 d.d (1H, H^r, J 20.1, 3.4 Hz), 6.44 d.d (1H, H^{cis}, J 14.8, 3.4 Hz), 6.57 d.d (1H, SiCH=, J 20.1, 14.8 Hz), 7.24–7.49 m (4H, H^m), 7.49–7.55 m (2H, H^p), 7.61 d.d (1H, H^o, J 7.1, 1.1 Hz), 7.65 d.d (1H, H^o, J 7.8, 1.2 Hz). ¹³C NMR, δ , ppm: 47.89 (CH₂N), 48.24 (CHCl), 119.49 q (CF₃, J 320.4 Hz), 128.32 and 128.36 (C^m), 129.89 (SiCH=), 130.02 and 130.11 (C^{ipso}), 130.68 (C^p), 135.60 and 135.70 (C^o), 139.40 (=CH₂). ¹⁹F NMR, δ : –77.30 ppm. ²⁹Si NMR, δ : –5.61 ppm. Found, %: C, 21.15; H, 2.58; Cl 15.09; F, 24.01; N, 5.59; S, 9.15; Si, 6.16. Calcd. for C₁₇H₁₇ClF₃NO₂SSi (%): C, 20.05; H, 2.94; Cl, 14.79; F, 23.78; N, 5.84; S, 10.01; Si, 5.86.

(1,2-Dichloroethyl)(diphenyl)vinylsilane 5. Yield 0.4 g (30%), colourless liquid. IR, ν , cm⁻¹: 3058, 3013, 1645, 1427, 1113, 1007, 966, 703. ¹H NMR, δ , ppm: 3.75–3.83 m (1H, CHCl), 4.04–4.10 m (1H, CH₂Cl), 5.91 d.d (1H, =CH^r, J 20.2, 3.4 Hz), 6.40 d.d (1H, =CH^{cis}, J 14.9, 3.4 Hz), 6.60 m (1H, CH=, J 20.2, 14.8 Hz), 7.40–7.47 m (2H, H^m), 7.47–7.51 m (1H, H^p), 7.62 d (1H, H^o, J 6.6 Hz), 7.67 d (1H, H^o, J 6.6 Hz). ¹³C NMR, δ , ppm: 48.63 (CHCl), 49.27 (CH₂Cl), 128.20 and 128.23 (C^m), 130.46 (SiCH=), 130.57 and 130.75 (C^o), 134.73 (C^p), 138.88 (=CH₂). ²⁹Si NMR, δ : –16.71 ppm. Found, %: C, 63.01; H, 5.15; Cl, 23.16; Si, 8.68. Calcd. for C₁₆H₁₆Cl₂Si (%): C, 62.54, H, 5.25, Cl, 23.07, Si, 9.14.

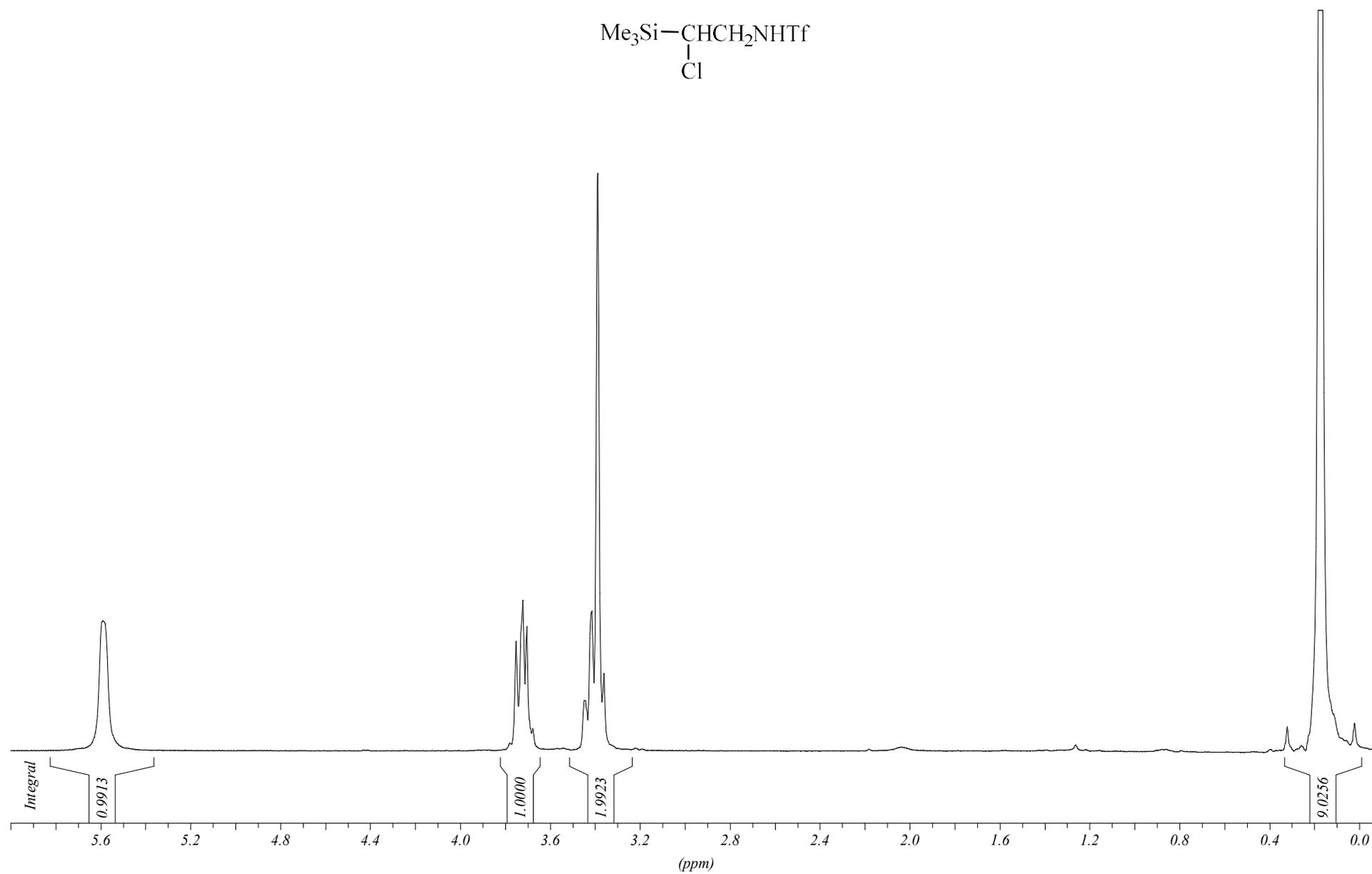
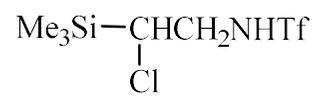


Figure S1. ^1H NMR spectrum of *N*-[(2-chloro-2-trimethylsilyl)ethyl]triflamide **2**

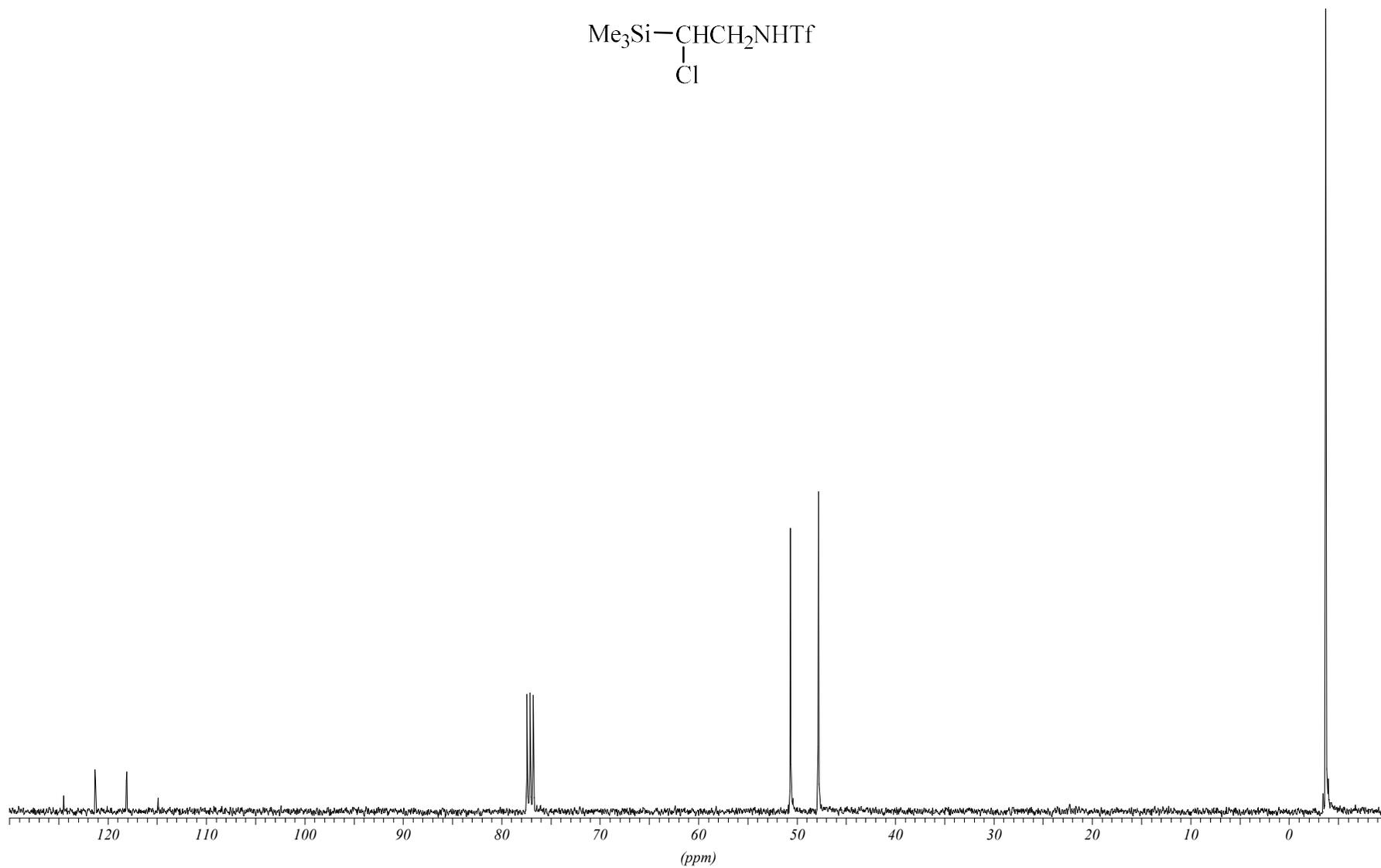


Figure S2. ^{13}C NMR spectrum of *N*-[(2-chloro-2-trimethylsilyl)ethyl]triflamide **2**

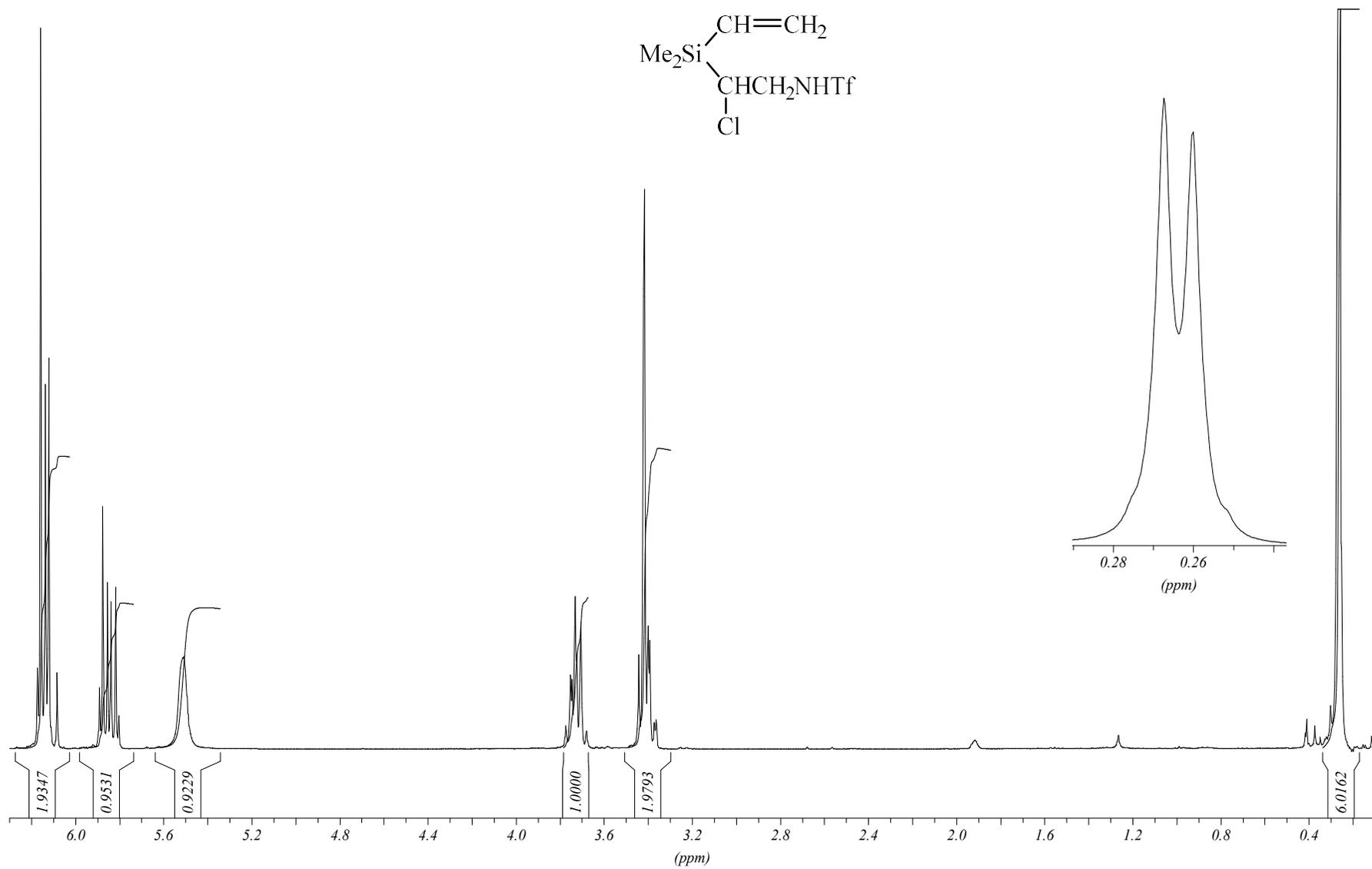


Figure S3. ¹H NMR spectrum of [1-chloro-2-(triflamido)ethyl](dimethyl)vinylsilane **4a**

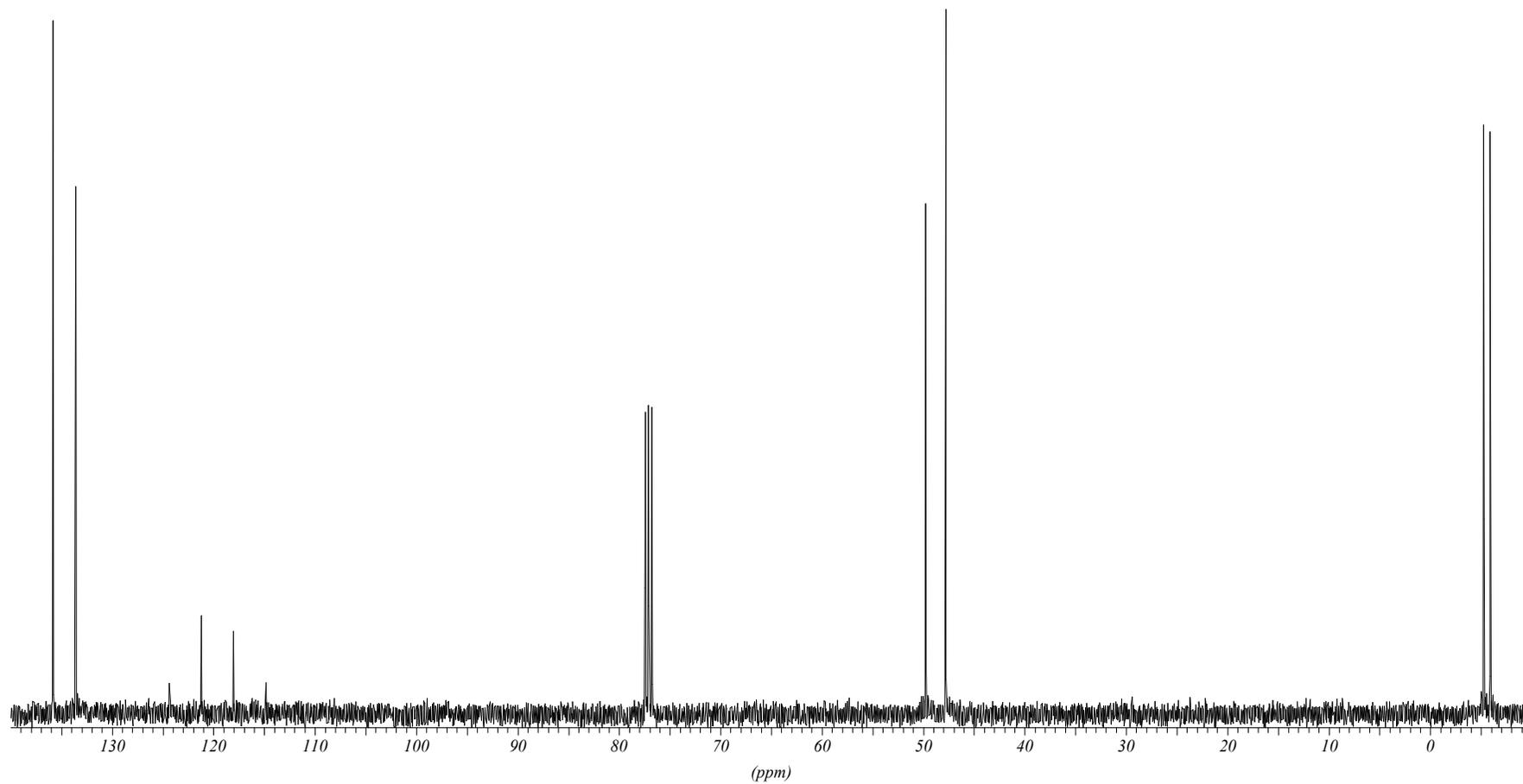
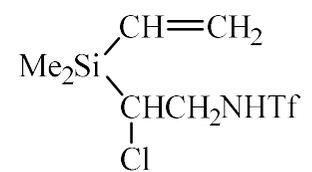


Figure S4. ¹³C NMR spectrum of [1-chloro-2-(triflamido)ethyl](dimethyl)vinylsilane **4a**

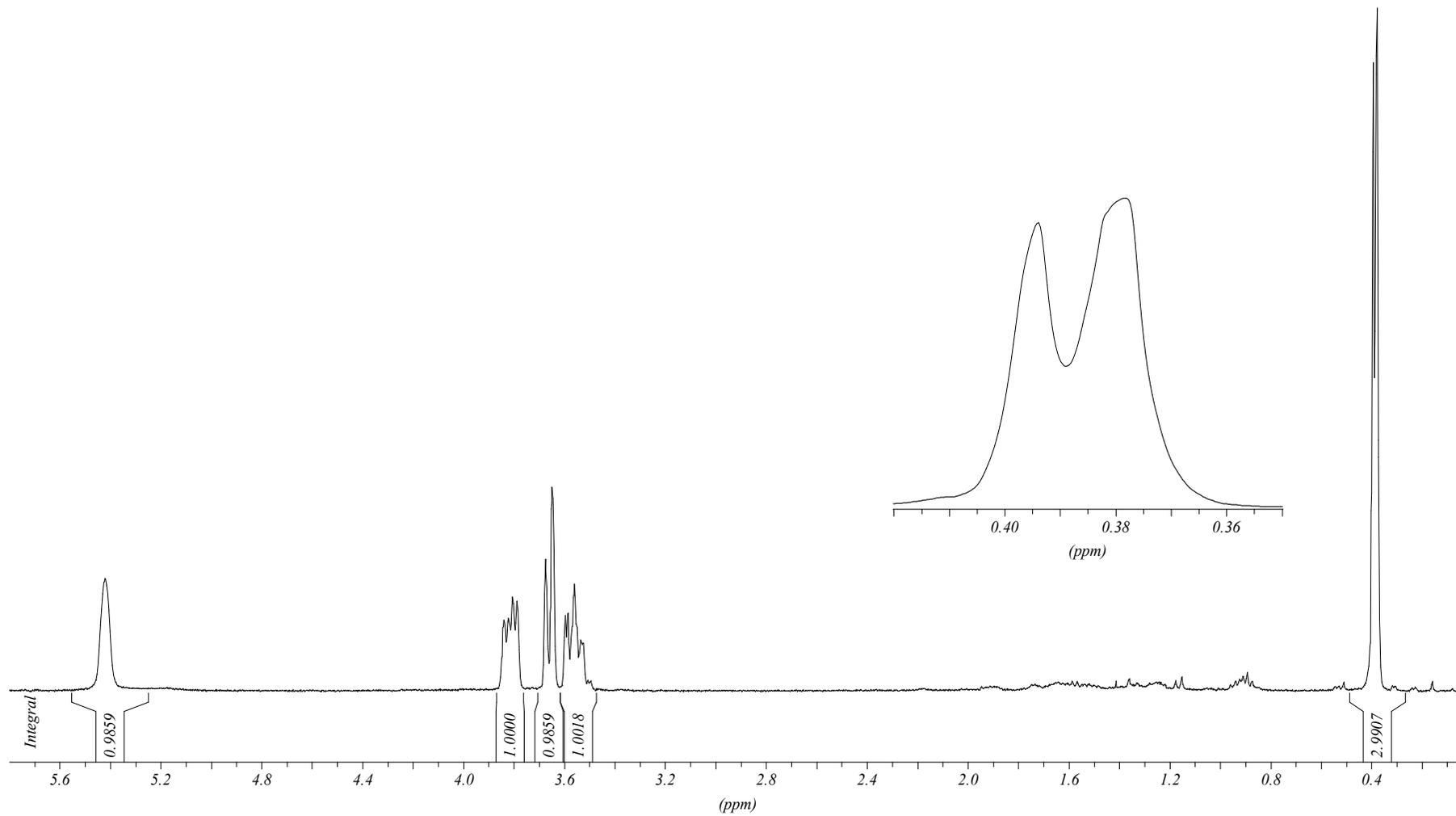


Figure S5. ¹H NMR spectrum of bis[1-chloro-2-(triflamido)ethyl](dimethyl)silane **6**

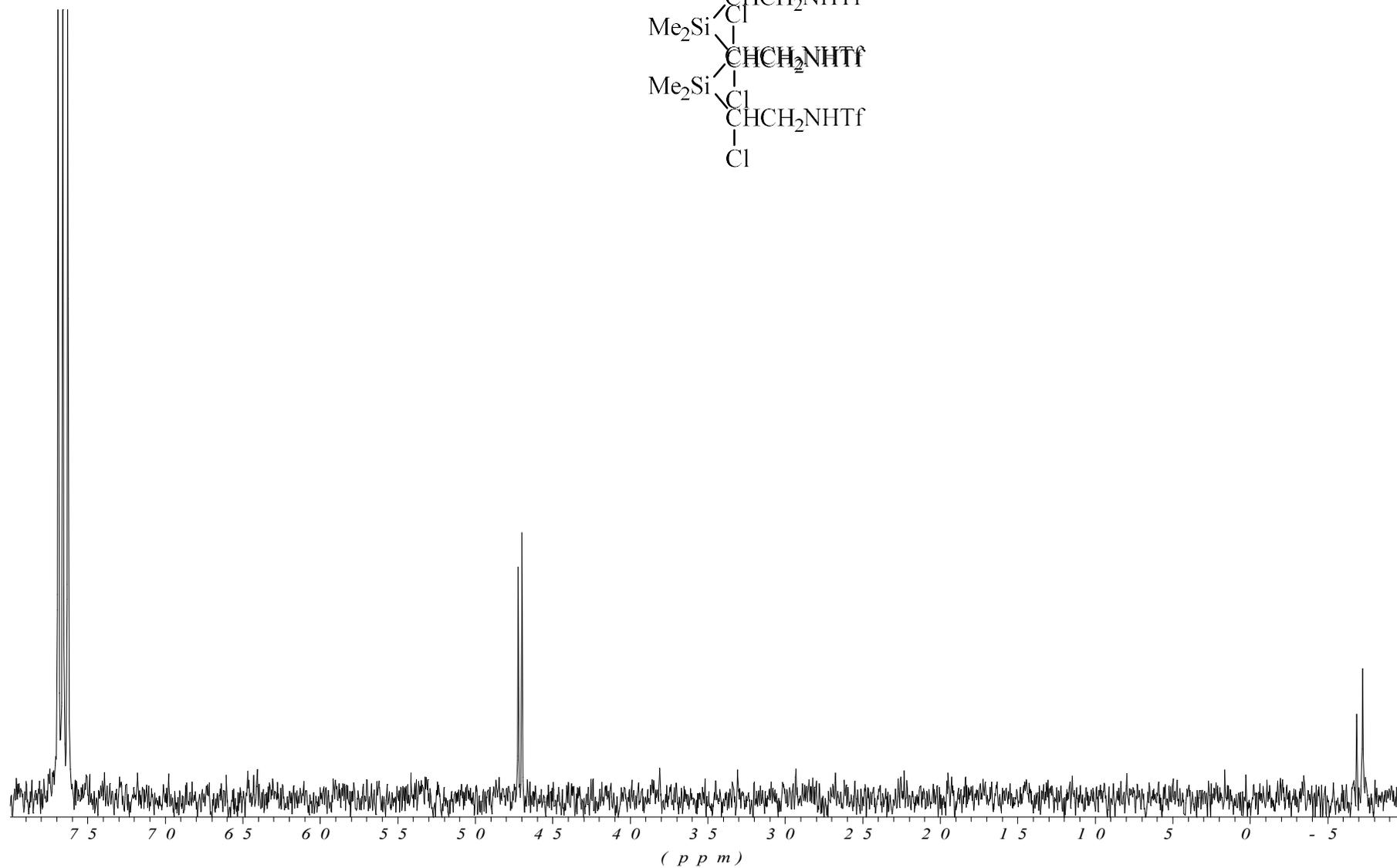
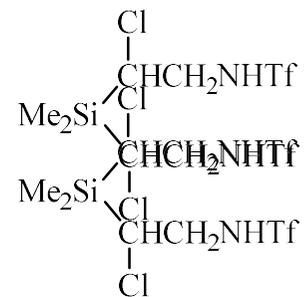


Figure S6. ¹³C NMR spectrum of bis[1-chloro-2-(triflamido)ethyl](dimethyl)silane **6**

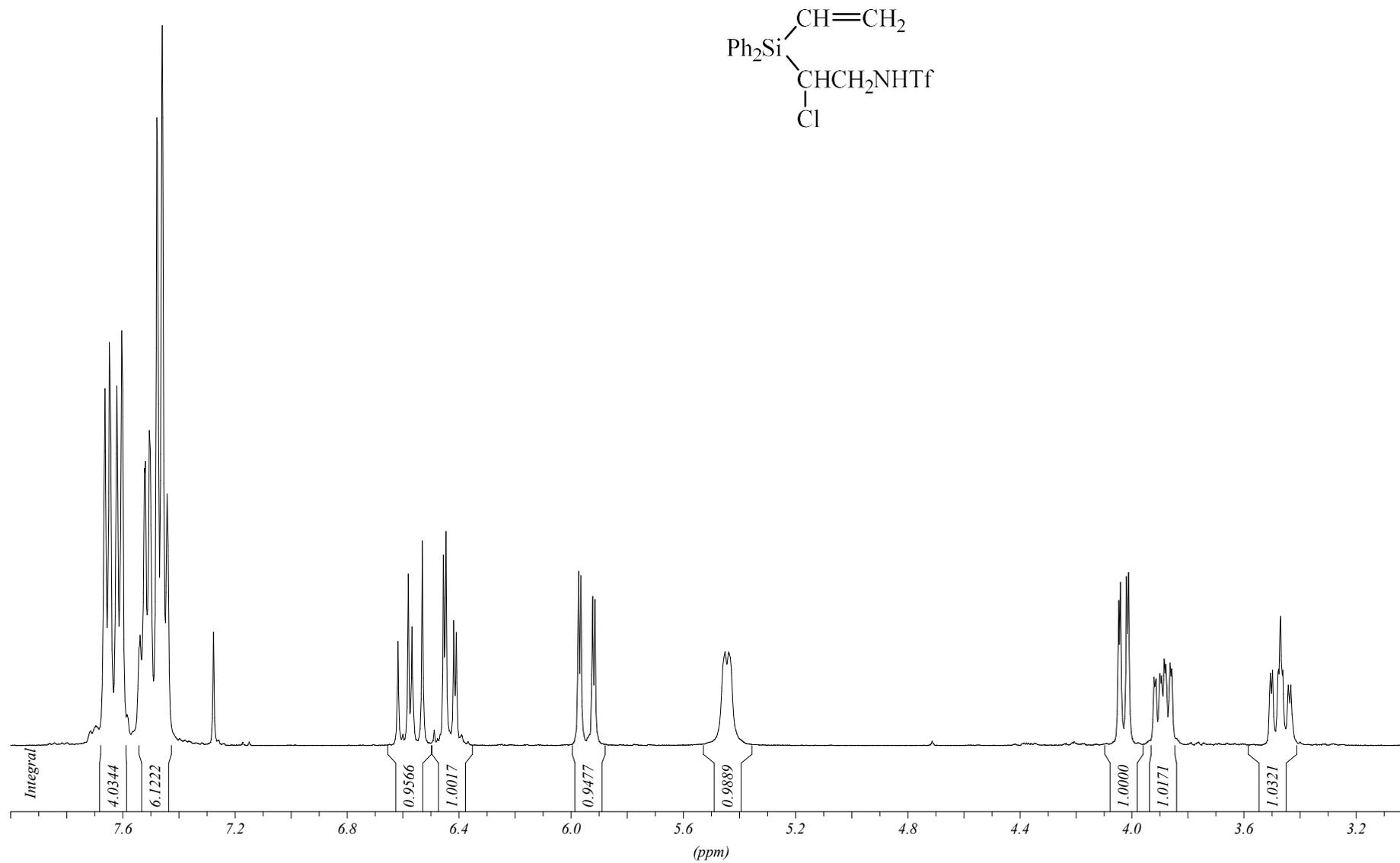


Figure S7. ¹H NMR spectrum of [1-chloro-2-(triflamido)ethyl](diphenyl)vinylsilane **4b**

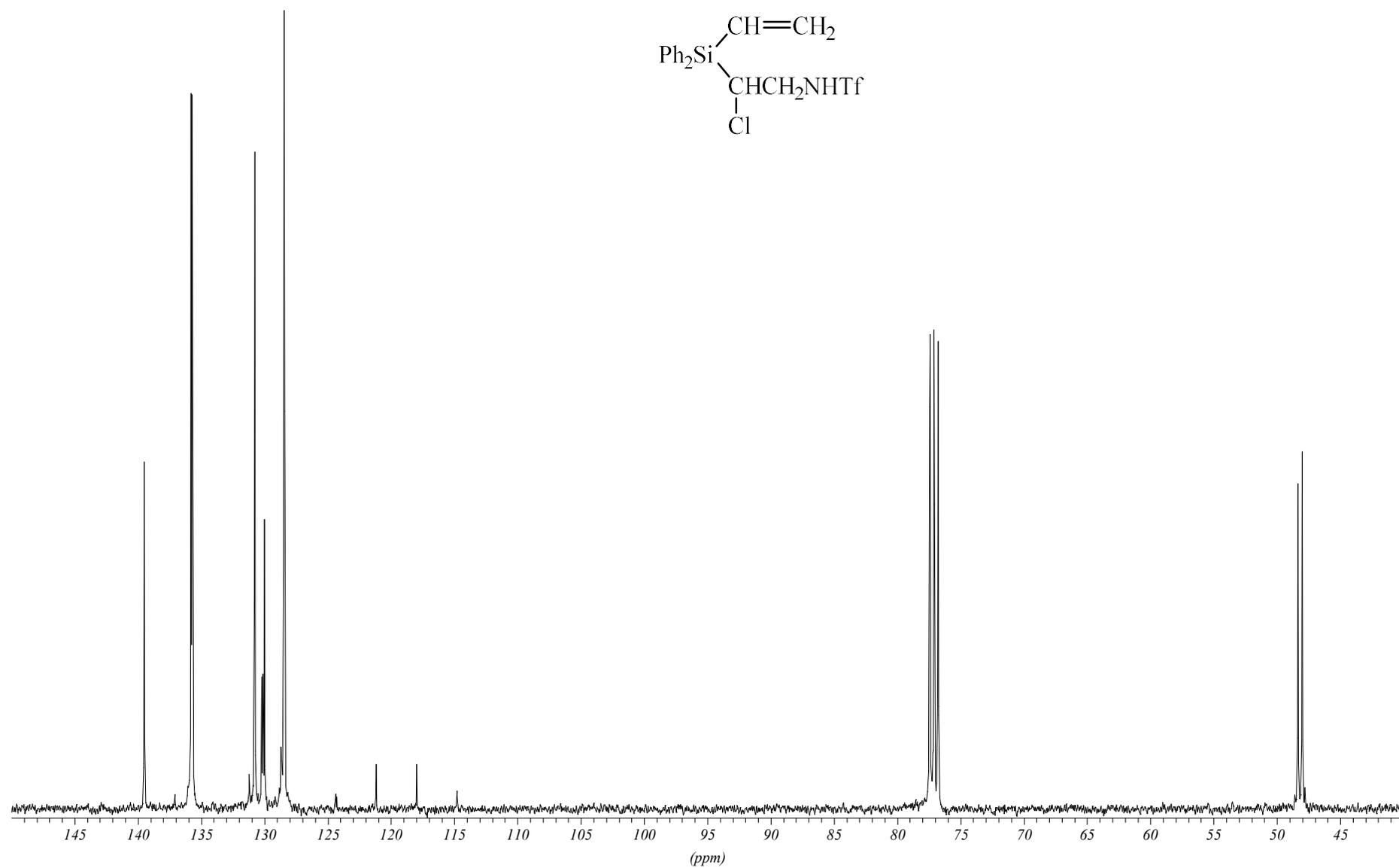
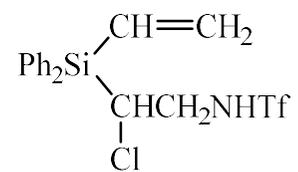


Figure S8. ¹³C NMR spectrum of [1-chloro-2-(triflamido)ethyl](diphenyl)vinylsilane **4b**

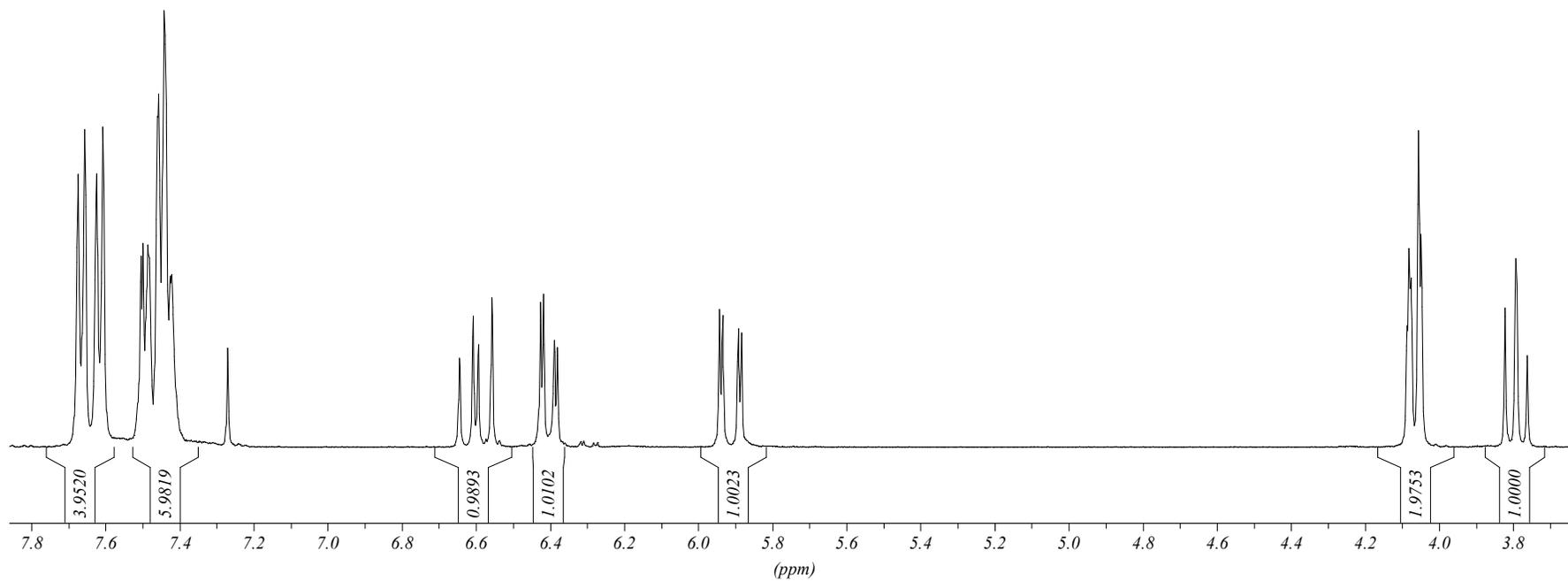
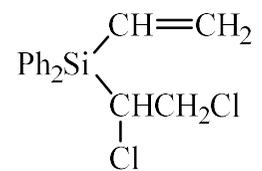


Figure S9. ¹H NMR spectrum of (1,2-dichloroethyl)(diphenyl)vinylsilane **5**

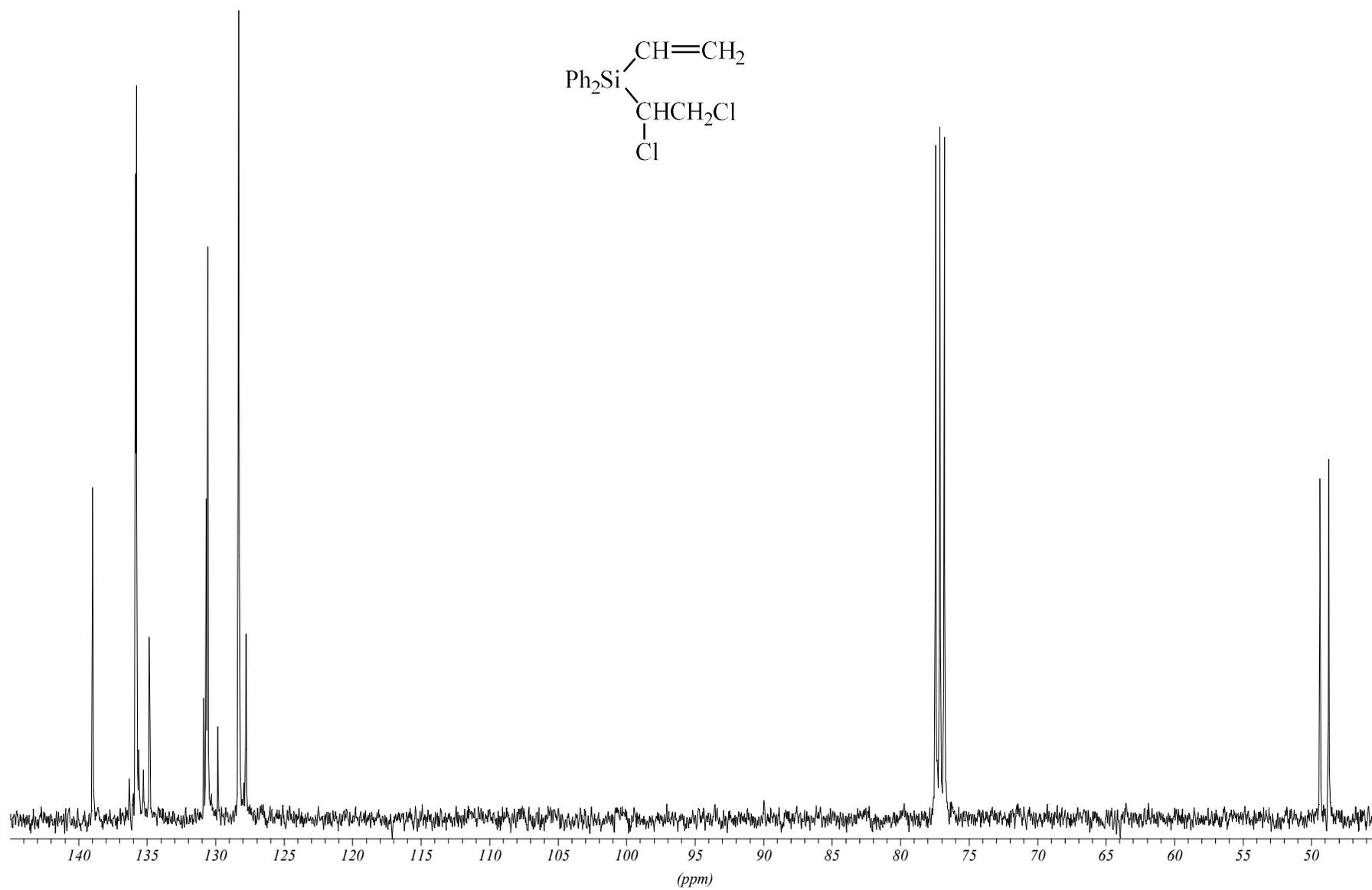


Figure S10. ^{13}C NMR spectrum of (1,2-dichloroethyl)(diphenyl)vinylsilane **5**

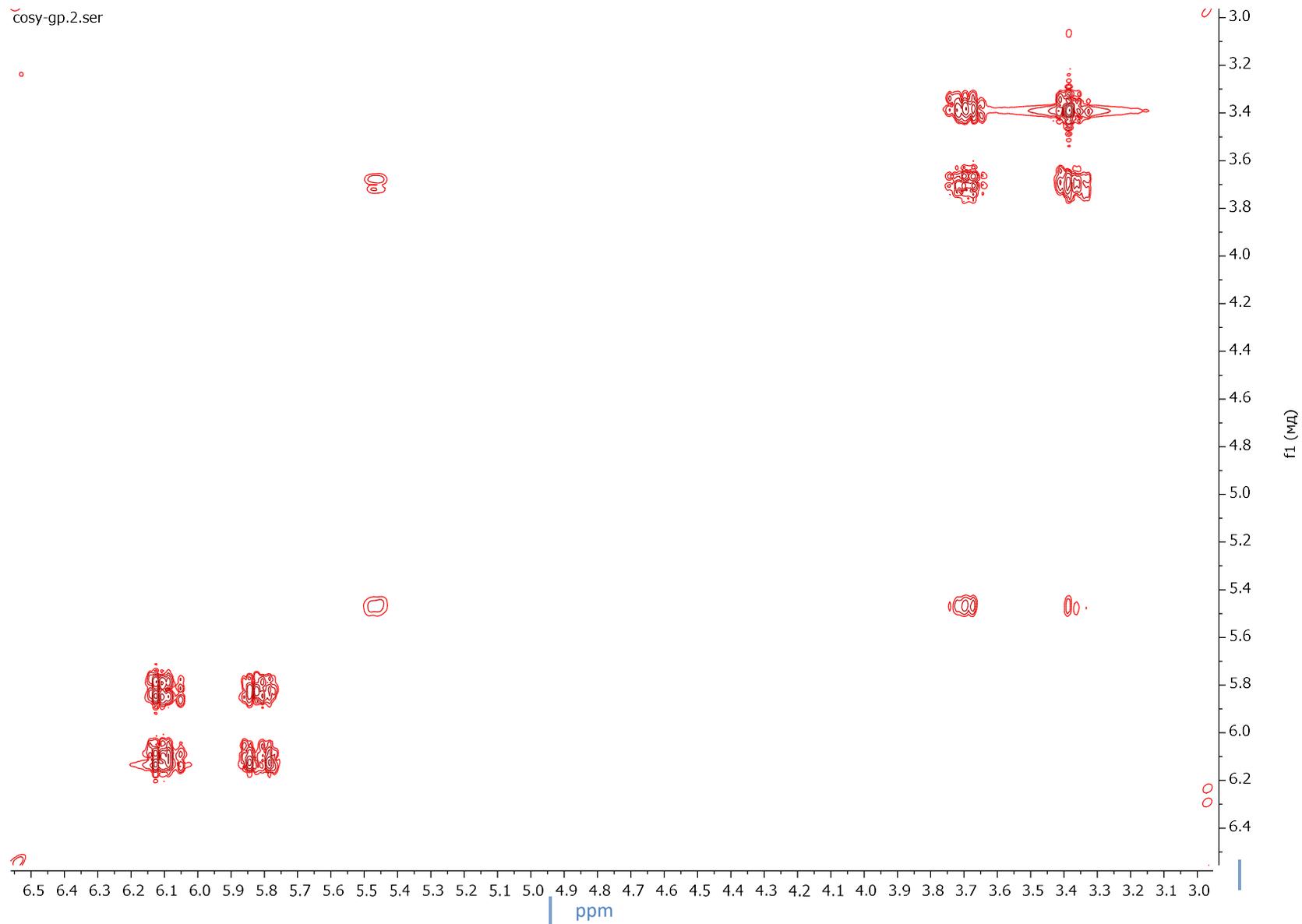


Figure S11. $\{^1\text{H}-^1\text{H}\}$ COSY spectrum of [1-chloro-2-(triflamido)ethyl](dimethyl)vinylsilane **4a**