

Supporting Information

**Stereospecific and Chemoselective Copper-Catalyzed Deaminative
Silylation of Benzylic Ammonium Triflates**

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1. General Information

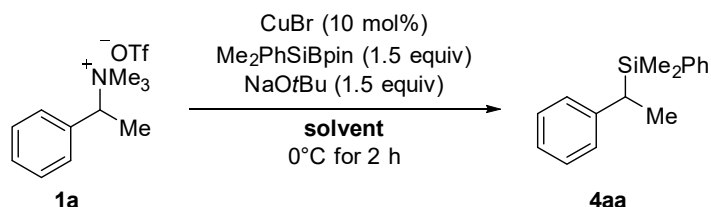
Reactions were performed in flame-dried glassware using conventional SCHLENK-techniques under a static pressure of nitrogen unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents (CH_2Cl_2 , *n*-hexane, THF, NMP) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (*tert*-butyl methyl ether, cyclohexane, CH_2Cl_2 , ethanol, ethyl acetate, *n*-pentane and MeOH) were distilled prior to use. Other chemicals were purchased from commercial sources and used as received. Compounds prepared according to literature procedures: Dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane^[S1]. The racemic dimethylamines were prepared using ESCHWEILER–CLARKE reactions^[S2], or by reductive amination of the corresponding acetophenone derivatives.^[S3] The following enantioenriched benzylic amines were commercially available and used as received: (*R*)-**S1a** (>99% ee), (*S*)-**S1f** (98% ee), (*R*)-**S1g** (98% ee), (*S*)-**S1h** (98% ee), (*R*)-**S1i** (99% ee), (*R*)-**S1m** (99% ee). Other enantioenriched benzylic amines were prepared by diastereoselective reduction of *tert*-butyl sulfinamides.^[S4] The enantiomeric excess of the synthesized amines was determined after derivatization to the respective amide with 4-Nitrobenzoyl chloride. *N,N*-dimethyl-4-phenylbut-3-yn-2-amine and (*R*)-*N,N*-dimethyl-4-phenylbut-3-yn-2-amine were synthesized according to a literature procedure.^[S5] Analytical thin layer chromatography (TLC) was performed on ALUGRAM® Xtra SIL G/UV₂₅₄ TLC-Sheets by *Macherey-Nagel*. Flash column chromatography was performed on silica gel 60 (40–63 μm , 230–400 mesh, ASTM) by *Grace* using the indicated solvents. ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ on Bruker AV400, AV500, or AV700 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (CHCl_3 : $\delta = 7.26$ ppm for ¹H NMR and CDCl_3 : $\delta = 77.16$ ppm for ¹³C NMR; $\text{DMSO}-d_6$: $\delta = 2.50$ ppm for ¹H NMR and $\text{DMSO}-d_6$: $\delta = 39.52$ ppm for ¹³C NMR). Data are reported as follows: chemical shift, multiplicity (br = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. Gas liquid chromatography (GLC) was performed on an *Agilent Technologies* 7820A gas chromatograph equipped with a HP-5 capillary column (30 m \times 0.32 mm, 0.25 μm film thickness) by *Agilent Technologies/CS-Chro-matographie Service* using the following program: N_2 carrier gas, injection temperature 250 °C, detector temperature 300 °C, flow rate: 1.7 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630 FT-IR spectrometer equipped with an ATR unit and the signals are reported in wavenumbers (cm^{-1}). Melting points (m.p.) were determined with a *Stuart Scientific* SMP20 melting point apparatus and are not corrected. The solvent used for precipitation and washing is quoted in parentheses. High resolution mass spectrometry (HRMS) analysis was performed by the Analytical Facility at the *Institut für Chemie, Technische Universität Berlin*. The compound names were generated by the computer program *ChemDraw* according to the guidelines specified by the *International Union of Pure and Applied Chemistry* (IUPAC).

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2. Optimization Study

General procedure for the optimization reactions: In a nitrogen-filled glove box, the copper salt (25 μ mol, 10 mol%), the base (0.38 mmol, 1.5 equiv), and a magnetic stir bar are subsequently added to a flame-dried Schlenk tube. The tube is transferred to a Schlenk line outside the glove box, and the corresponding benzylic ammonium triflate is added, followed by tetracosane as the internal standard. The tube is evacuated and backfilled with N_2 (3 times). The solvent (1 mL) is added, and the resulting suspension is stirred for 15 min at rt. The mixture is cooled to 0 $^{\circ}C$ and dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (1.5 equiv) is added dropwise. The reaction mixture is kept at 0 $^{\circ}C$ for 2 h and, after this time, an aliquot of the reaction mixture is subjected to GLC analysis.

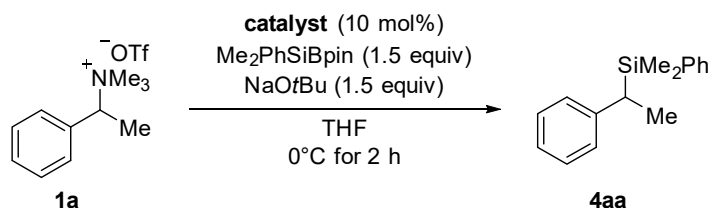
Table S1: Screening of solvents in the silylation of **1a**.



entry	solvent	yield ^[a]
1	Et ₂ O	50 (68 after 18 h)
2	THF	92
3	1,4-Dioxane	77 (84 after 18 h)
4	toluene	30 (46 after 18 h)
5	CH ₂ Cl ₂	n.d.
6	THF/NMP (9:1)	12
7	THF/DMSO (9:1)	45
8	THF/1,4-dioxane	75

[a] Determined by GLC analysis using tetracosane as internal standard. n.d. = not determined.

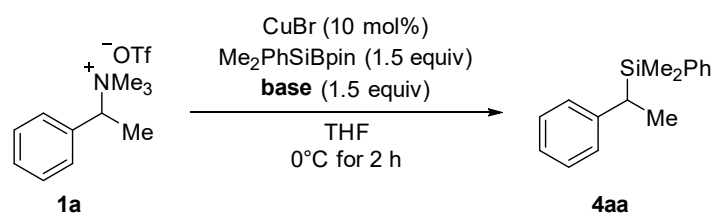
Table S2: Screening of copper salts in the silylation of **1a**.



entry	catalyst	yield ^[a]
1	CuCl	78
2	CuBr	92
3	CuI	71
4	CuOTf	84
5	CuCN	65
6	CUSCN	56
7	Cu(Tc)	64
8	CuOAc	52
9	Cu(acac) ₂	45

[a] Determined by GLC analysis using tetracosane as internal standard.

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Table S3: Screening of bases in the silylation of **1a**.

entry	catalyst	yield ^[a]
1	LiOMe	n.d.
2	NaOMe	46
3	KOMe	7
4	LiOtBu	69
5	NaOtBu	92
6	KOtBu	n.d.

[a] Determined by GLC analysis using tetracosane as internal standard.

3. General Procedures

3.1 General Procedure for the Synthesis of Ammonium Triflates (GP1)

According to a modified literature procedure,^[S5] the corresponding dimethylamine was dissolved in Et₂O (1.0M), and the resulting solution was cooled to 0 °C with an icewater bath. At this temperature, methyl triflate was slowly added dropwise. The suspension was stirred 15 min at 0 °C, the ice bath was removed, and the mixture was stirred for another 15 min at rt. The solvent was removed carefully with a pipette, and the residue was washed with Et₂O (2 × 3 mL) and then covered with Et₂O to complete the precipitation of the salt (if it had not occurred yet). In some cases the salts were purified by flash column chromatography on silica gel using the indicated mixture of CH₂Cl₂ and MeOH. The precipitate was filtered over a sintered funnel, washed with Et₂O and dried under oil pump vacuum. The ammonium salts were obtained as white or yellowish microcrystalline solids, that were grinded to powders with mortar and pestle for better solubility.

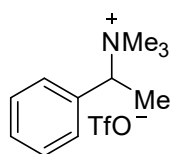
3.2 General Procedure for the Nucleophilic Silylation (GP2)

In a nitrogen-filled glove box, CuBr (3.6 mg, 25 μmol, 10 mol%), NaOtBu (36 mg, 0.38 mmol, 1.5 equiv), and a magnetic stir bar are subsequently added to a flame-dried Schlenk tube. The tube is transferred to a SCHLENK-line outside the glove box, and THF (1 mL) is added. The resulting suspension is stirred for 15 min at rt and then cooled to 0 °C. Dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (1.5 equiv) is added dropwise, followed by the corresponding ammonium triflate. The walls of the SCHLENK-tube are washed with THF (0.5 mL), and the reaction mixture is kept at 0 °C for 2 h. After this time, the reaction mixture is diluted with cyclohexane (2 mL), filtered through a short plug of silica gel, and the reaction tube and silica gel are rinsed with ethyl acetate (3 × 5 mL). The collected filtrate is concentrated under reduced pressure, and the residue is purified by flash column chromatography on silica gel using the indicated mixture of cyclohexane and ethyl acetate.

3.3 General Procedure for the Oxidation of the 1,1,2,2-Tetramethyl-1,2-diphenyldisilane Byproduct (GP3)

According to a modified literature procedure,^[S6] Au/TiO₂ (100 mg, ~2.0 mol% in Au) and a magnetic stir bar are added to a glass vial (6 mL) in a nitrogen-filled glove box. Outside the glove box, the crude mixture of the preceding silylation is transferred to this vial with ethyl acetate (3 × 0.3 mL), and one drop of H₂O (3–5 mg) is added. The reaction is stirred for 3 h at rt and after this time the reaction mixture is diluted with cyclohexane (3 mL), filtered through a short plug of silica gel, and the reaction tube and silica gel are rinsed with a solution of ethyl acetate in cyclohexane (20%, 3 × 5 mL). The collected filtrate is concentrated under reduced pressure, and the residue is purified by flash column chromatography on silica gel using the indicated mixture of cyclohexane and ethyl acetate.

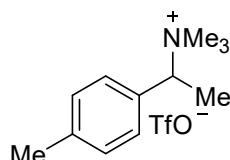
4. Preparation and Characterization Data for the Ammonium Triflates

**1a**

$C_{12}H_{18}F_3NO_3S$
 M = 313.34 g/mol

***N,N,N*-Trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate (1a).** Prepared from *N,N*-dimethyl-1-phenylethan-1-amine (2.55 mg, 17.1 mmol, 1.00 equiv) according to **GP1**, using MeOTf (2.08 mL, 18.8 mmol, 1.1 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 25 mL) afforded the title compound **1a** (4.60 g, 14.7 mmol, 86%) as a white powder. **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = 1.72 (d, *J* = 7.0 Hz, 3H), 2.97 (s, 9H), 4.76 (q, *J* = 7.0 Hz, 1H), 7.45–7.55 (m, 3H), 7.56–7.64 (m, 2H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 14.5, 50.5 (t, *J* = 3.8 Hz, [H₃C]₃N), 72.6, 120.7 (q, *J* = 322 Hz, CF₃), 128.9, 130.2, 130.5, 133.5. **¹⁹F {¹H} NMR** (659 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3037, 2294, 2104, 1478, 1249, 1154, 1026, 954, 841, 774, 710. **HRMS** (ESI) calculated for C₁₁H₁₈N⁺ [M–OTf]⁺: 164.1434; found: 164.1434. The spectroscopic data are in accordance with those reported.^[S7]

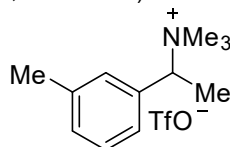
***(R)*-*N,N,N*-Trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate [(*R*)-1a].** Prepared from (*R*)-*N,N*-dimethyl-1-phenylethan-1-amine (336 mg, 2.25 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.30 mL, 2.7 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound (*R*)-**1a** (684 mg, 2.18 mmol, 97%) as a white powder. **Optical rotation**: [α] = +0.60 (*c* = 1.00, CHCl₃, >99% ee). The enantiomeric excess was indicated by a label on the bottle of the corresponding amine.

**1b**

$C_{13}H_{20}F_3NO_3S$
 M = 327.36 g/mol

***N,N,N*-Trimethyl-1-(*p*-tolyl)ethan-1-aminium trifluoromethanesulfonate (1b).** Prepared from *N,N*-dimethyl-1-(*p*-tolyl)ethan-1-amine (303 mg, 1.86 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.25 mL, 2.23 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1b** (514 mg, 1.57 mmol, 84%) as a white powder. **¹H NMR** (400 MHz, DMSO-*d*₆): δ/ppm = 1.69 (d, *J* = 7.0 Hz, 3H), 2.35 (s, 3H), 2.95 (s, 9H), 4.71 (q, *J* = 7.0 Hz, 1H), 7.28–7.33 (m, 2H), 7.43–7.51 (m, 2H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 14.5, 20.7, 50.4 (t, *J* = 4.0 Hz, [H₃C]₃N), 72.4, 120.7 (q, *J* = 322 Hz, CF₃), 129.4, 130.4, 130.5, 139.8. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3034, 1477, 1254, 1151, 1027, 953, 825, 756. **HRMS** (ESI) calculated for C₁₂H₂₀N⁺ [M–OTf]⁺: 178.1590; found: 178.1588.

***(R)*-*N,N,N*-Trimethyl-1-(*p*-tolyl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-1b].** Prepared from (*R*)-*N,N*-dimethyl-1-(*p*-tolyl)ethan-1-amine (120 mg, 0.735 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.10 mL, 0.88 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound (*R*)-**1b** (167 mg, 0.51 mmol, 69%) as a white powder. **Optical rotation**: [α] = –14.3 (*c* = 0.10, CHCl₃, 98% ee). The enantiomeric excess of (*R*)-**1b** was determined at the stage of the 4-nitrobenzoyl amide (See Ch9 for HPLC traces). HPLC analysis on a chiral stationary phase (Daicel Chiralcel IA column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 80:20, flow rate 1 mL/min, λ = 210 nm): *t*_R = 8.8 min for (*S*)-**1b**, *t*_R = 12.0 min for (*R*)-**1b**.

**1c**

$C_{13}H_{20}F_3NO_3S$
 M = 327.36 g/mol

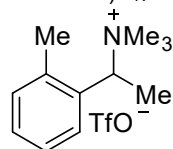
***N,N,N*-Trimethyl-1-(*m*-tolyl)ethan-1-aminium trifluoromethanesulfonate (1c).** Prepared from *N,N*-dimethyl-1-(*m*-tolyl)ethan-1-amine (464 mg, 2.84 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.39 mL, 3.4 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1c** (822 mg, 2.51 mmol, 88%) as a white powder. **¹H NMR** (400 MHz, DMSO-*d*₆): δ/ppm = 1.70 (d, *J* = 7.0 Hz, 3H), 2.36 (s, 3H), 2.97 (s, 9H), 4.70 (q, *J* = 7.0 Hz, 1H), 7.29–7.43 (m, 4H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 14.5, 20.9, 50.5 (t, *J* = 3.7 Hz, [H₃C]₃N), 72.7, 120.7 (q, *J* = 322 Hz, CF₃), 127.6, 128.7, 130.7, 130.9, 133.4, 138.2. **¹⁹F**

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¹H NMR (471 MHz, DMSO-*d*₆): δ/ppm = -77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3041, 1676, 1607, 1477, 1251, 1149, 1027, 953, 834, 796, 724. **HRMS** (ESI) calculated for C₁₂H₂₀N⁺ [M-OTf]⁺: 178.1590; found: 178.1588.

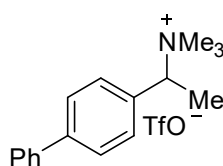
(*R*)-*N,N,N*-Trimethyl-1-(*m*-tolyl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-1c**]**. Prepared from (*R*)-*N,N*-dimethyl-1-(*m*-tolyl)-ethan-1-amine (160 mg, 0.980 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.14 mL, 1.2 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 5 mL) afforded the title compound (*R*)-**1c** (284 mg, 0.868 mmol, 89%) as a white powder.

Optical rotation: [α] = +5.63 (*c* = 1.00, CHCl₃, 98% ee). The enantiomeric excess of (*R*)-**1c** was determined at the stage of the 4-nitrobenzoyl amide (See Ch9 for HPLC traces). HPLC analysis on a chiral stationary phase (Daicel Chiralcel IA column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 80:20, flow rate 1 mL/min, λ = 210 nm): *t*_R = 7.2 min for (*S*)-**1c**, *t*_R = 8.8 min for (*R*)-**1c**.

**1d**

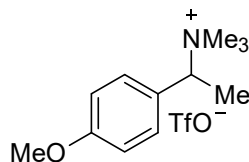
C₁₃H₂₀F₃NO₃S
M = 327.36 g/mol

***N,N,N*-Trimethyl-1-(*o*-tolyl)ethan-1-aminium trifluoromethanesulfonate (**1d**)**. Prepared from *N,N*-dimethyl-1-(*o*-tolyl)ethan-1-amine (313 mg, 1.92 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.26 mL, 2.3 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1d** (541 mg, 1.65 mmol, 86%) as a white powder. **¹H NMR** (400 MHz, DMSO-*d*₆): δ/ppm = 1.68 (d, *J* = 6.9 Hz, 3H), 2.45 (s, 3H), 3.00 (s, 9H), 5.00 (q, *J* = 6.9 Hz, 1H), 7.31–7.41 (m, 3H), 7.58–7.65 (m, 1H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 15.6, 19.9, 50.4 (t, *J* = 3.8 Hz, [H₃C]₃N), 68.2, 121.2 (q, *J* = 322 Hz, CF₃), 126.4, 128.9, 129.7, 131.4, 132.2, 138.5. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = -77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3035, 2980, 1480, 1251, 1142, 1027, 956, 842, 771, 734. **HRMS** (ESI) calculated for C₁₂H₂₀N⁺ [M-OTf]⁺: 178.1590; found: 178.1588. The spectroscopic data are in accordance with those reported.^[S7]

**1e**

C₁₈H₂₂F₃NO₃S
M = 389.43 g/mol

1-([1,1'-Biphenyl]-4-yl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1e**)**. Prepared from 1-([1,1'-biphenyl]-4-yl)-*N,N*-dimethylethan-1-amine (335 mg, 1.49 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.20 mL, 1.8 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1e** (523 mg, 1.34 mmol, 90%) as a white powder. **¹H NMR** (400 MHz, DMSO-*d*₆): δ/ppm = 1.75 (d, *J* = 7.0 Hz, 3H), 3.02 (s, 9H), 4.82 (q, *J* = 7.0 Hz, 1H), 7.38–7.45 (m, 1H), 7.46–7.54 (m, 2H), 7.66–7.76 (m, 4H), 7.77–7.84 (m, 2H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 14.5, 50.5, 72.3, 120.7 (q, *J* = 320 Hz, CF₃), 126.8, 127.0, 128.0, 129.1, 131.1, 132.5, 139.0, 141.7. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = -77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3036, 2306, 2106, 1484, 1255, 1153, 1028, 956, 836, 756, 699. **HRMS** (ESI) calculated for C₁₇H₂₂N⁺ [M-OTf]⁺: 240.1747 found: 240.1745. The spectroscopic data are in accordance with those reported.^[S8]

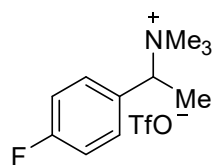
**1f**

C₁₃H₂₀F₃NO₄S
M = 343.36 g/mol

1-(4-Methoxyphenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1f**)**. Prepared from 1-(4-methoxyphenyl)-*N,N*-dimethylethan-1-amine (1.36 mL, 7.28 mmol, 1.00 equiv) according to **GP1**, using MeOTf (1.0 mL, 9.0 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1f** (2.259 g, 6.579 mmol, 90%) as a white powder. **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = 1.68 (d, *J* = 7.0 Hz, 3H), 2.94 (s, 9H), 3.80 (s, 3H), 4.70 (q, *J* = 7.0 Hz, 1H), 7.00–7.07 (m, 2H), 7.48–7.55 (m, 2H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 14.6, 50.2 (t, *J* = 3.9 Hz, [H₃C]₃N), 72.3, 114.1, 120.1 (q, *J* = 322 Hz, CF₃), 125.3, 131.9, 160.4. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = -77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2323, 2130, 1883, 1519, 1249, 1158, 1032, 838, 764. **HRMS** (ESI) calculated for C₁₂H₂₀NO⁺ [M-OTf]⁺: 194.1539; found: 194.1534. The spectroscopic data are in accordance with those reported.^[S9]

SUPPORTING INFORMATION

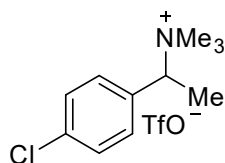
(S)-1-(4-Methoxyphenyl)-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate [(S)-1f]. Prepared from (S)-1-(4-methoxyphenyl)-N,N-dimethylethan-1-amine (300 mg, 1.67 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.21 mL, 1.8 mmol, 1.1 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 5 mL) afforded the title compound (S)-**1f** (540 mg, 1.67 mmol, 93%) as a white powder. **Optical rotation:** [α] = -28.7 (c = 1.00, CHCl₃, 98% ee). The enantiomeric excess was indicated by a label on the bottle of the corresponding amine.

**1g**

C₁₂H₁₇F₄NO₃S
M = 331.33 g/mol

1-(4-Fluorophenyl)-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate (1g). Prepared from 1-(4-fluorophenyl)-N,N-dimethylethan-1-amine (397 mg, 2.37 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.32 mL, 2.9 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1g** (722 mg, 2.18 mmol, 92%) as a white powder. **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = 1.70 (d, *J* = 7.0 Hz, 3H), 2.97 (s, 9H), 4.79 (q, *J* = 7.0 Hz, 1H), 7.30–7.38 (m, 2H), 7.62–7.70 (m, 2H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 14.6, 50.4 (t, *J* = 3.5 Hz, [H₃C]₃N), 71.8, 115.8 (d, *J* = 21 Hz), 120.7 (q, *J* = 322 Hz, CF₃), 129.8 (d, *J* = 3.5 Hz), 132.8, 162.9 (d, *J* = 248 Hz). **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = -111.1 (CF), -77.7 (CF₃). **IR** (ATR): $\tilde{\nu}$ /cm⁻¹ = 3579, 2313, 2099, 1920, 1609, 1516, 1491, 1234, 1159, 1066, 1025, 954, 839, 756, 699. **HRMS** (ESI) calculated for C₁₁H₁₇FN⁺ [M-OTf]⁺: 182.1340; found: 182.1337. The spectroscopic data are in accordance with those reported.^[S8]

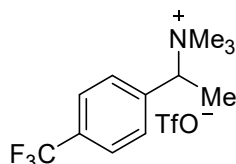
(R)-1-(4-Fluorophenyl)-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate [(R)-1g]. Prepared from (R)-1-(4-fluorophenyl)-N,N-dimethylethan-1-amine (200 mg, 1.20 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.15 mL, 1.4 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 5 mL) afforded the title compound (R)-**1g** (371 mg, 1.11 mmol, 93%) as a white powder. **Optical rotation:** [α] = +17.3 (c = 1.00, CHCl₃, 98% ee). The enantiomeric excess was indicated by a label on the bottle of the corresponding amine.

**1h**

C₁₂H₁₇ClF₃NO₃S
M = 347.78 g/mol

1-(4-Chlorophenyl)-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate (1h). Prepared from 1-(4-chlorophenyl)-N,N-dimethylethan-1-amine (400 mg, 2.18 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.43 mL, 4.1 mmol, 1.9 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1h** (725 mg, 2.09 mmol, 96%) as an off-white powder. **¹H NMR** (700 MHz, DMSO-*d*₆): δ/ppm = 1.70 (d, *J* = 7.0 Hz, 3H), 2.97 (s, 9H), 4.70 (q, *J* = 7.0 Hz, 1H), 7.56–7.59 (m, 2H), 7.61–7.65 (m, 2H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 14.4, 50.5, 71.7, 120.7 (q, *J* = 322 Hz, CF₃), 128.9, 132.3, 132.4, 135.0. **¹⁹F {¹H} NMR** (659 MHz, DMSO-*d*₆): δ/ppm = -77.7 (CF₃). **IR** (ATR): $\tilde{\nu}$ /cm⁻¹ = 3035, 2290, 2092, 1915, 1596, 1491, 1256, 1153, 1028, 954, 832, 755. **HRMS** (ESI) calculated for C₁₁H₁₇ClN⁺ [M-OTf]⁺: 198.1044; found: 198.1044.

(S)-1-(4-Chlorophenyl)-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate [(S)-1h]. Prepared from (S)-1-(4-chlorophenyl)-N,N-dimethylethan-1-amine (422 mg, 2.30 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.31 mL, 2.8 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1h** (745 mg, 2.14 mmol, 97%) as a white powder. **Optical rotation:** [α] = -23.6 (c = 1.00, CHCl₃, 98% ee). The enantiomeric excess was indicated by a label on the bottle of the corresponding amine.

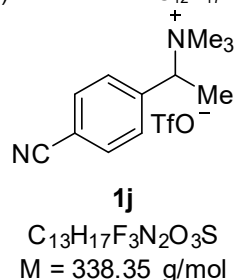
**1i**

C₁₃H₁₇F₆NO₃S
M = 381.33 g/mol

N,N,N-Trimethyl-1-[4-(trifluoromethyl)phenyl]ethan-1-aminium trifluoromethanesulfonate (1i). Prepared from N,N-dimethyl-1-[4-(trifluoromethyl)phenyl]ethan-1-amine (357 mg, 1.64 mmol, 1.00 equiv) according to **GP1**, using MeOTf (125 μL, 1.97 mmol, 1.20 equiv).

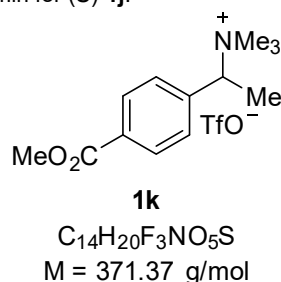
SUPPORTING INFORMATION

Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1i** (480 mg, 1.26 mmol, 77%) as a white powder. ¹H NMR (400 MHz, DMSO-*d*₆): δ/ppm = 1.74 (d, *J* = 6.9 Hz, 3H), 3.01 (s, 9H), 4.89 (q, *J* = 6.9 Hz, 1H), 7.79–7.92 (m, 4H). ¹³C {¹H} NMR (126 MHz, DMSO-*d*₆): δ/ppm = 14.4, 50.7, 71.8, 120.7 (q, *J* = 322 Hz, CF₃), 123.9 (q, *J* = 273 Hz, CF₃), 125.8 (q, *J* = 4.0 Hz), 130.4 (q, *J* = 32.0 Hz), 131.5, 138.0. ¹⁹F {¹H} NMR (471 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 1621, 1475, 1328, 1251, 1160, 1070, 1028, 951, 844, 756, 700. HRMS (ESI) calculated for C₁₂H₁₇F₃N⁺ [M–OTf]⁺: 232.1308; found: 232.1305.

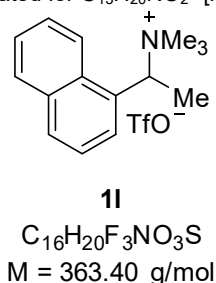


1-(4-Cyanophenyl)-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate (1j). Prepared from 4-(1-(dimethylamino)ethyl)benzotrile (470 mg, 2.70 mmol, 1.00 equiv) according to **GP1**, using MeOTf (367 μ L, 3.24 mmol, 1.20 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1j** (754 mg, 2.23 mmol, 83%) as a white powder. ¹H NMR (500 MHz, DMSO-*d*₆): δ/ppm = 1.73 (d, *J* = 7.0 Hz, 3H), 3.00 (s, 9H), 4.86 (q, *J* = 7.0 Hz, 1H), 7.77–7.86 (m, 2H), 7.96–8.02 (m, 2H). ¹³C {¹H} NMR (126 MHz, DMSO-*d*₆): δ/ppm = 14.3, 50.7, 71.8, 112.9, 118.2, 120.7 (q, *J* = 322 Hz, CF₃), 131.5, 132.7, 138.5. ¹⁹F {¹H} NMR (471 MHz, DMSO-*d*₆): δ/ppm = –77.8 (CF₃). IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2227, 1490, 1422, 1259, 1150, 1063, 1029, 964, 845, 690. HRMS (ESI) calculated for C₁₂H₁₇N₂⁺ [M–OTf]⁺: 189.1386; found: 189.1385.

(R)-1-(4-Cyanophenyl)-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate [(R)-1j]. Prepared from (*R*)-4-(1-(dimethylamino)ethyl)benzotrile (178 mg, 1.02 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.14 μ L, 1.2 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 5 mL) afforded the title compound (*R*)-**1j** (312 mg, 0.922 mmol, 90%) as an off-white powder. **Optical rotation:** [α] = –17.0 (*c* = 0.10, CHCl₃, 97% ee). The enantiomeric excess of (*R*)-**1j** could only reliably be determined after silylation. Derivatization of the free amine to the 4-nitrobenzoyl amide led to partial racemization (e.r. = 95:5, see Ch9). HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 99.5:0.5, flow rate 0.8 mL/min, λ = 210 nm): *t*_R = 9.8 min for (*R*)-**1j**, *t*_R = 10.9 min for (*S*)-**1j**.



1-[4-(Methoxycarbonyl)phenyl]-N,N,N-trimethylethan-1-aminium trifluoromethanesulfonate (1k). Prepared from 4-(1-(dimethylamino)ethyl)benzotrile (420 mg, 2.03 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.25 mL, 2.2 mmol, 1.1 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1k** (730 mg, 1.97 mmol, 97%) as a white powder. ¹H NMR (500 MHz, DMSO-*d*₆): δ/ppm = 1.74 (d, *J* = 7.0 Hz, 3H), 3.00 (s, 9H), 3.88 (s, 3H), 4.86 (q, *J* = 7.0 Hz, 1H), 7.72–7.79 (m, 2H), 8.03–8.08 (m, 2H). ¹³C {¹H} NMR (126 MHz, DMSO-*d*₆): δ/ppm = 14.4, 50.6, 52.4, 71.9, 120.7 (q, *J* = 322 Hz, CF₃), 129.5, 131.0, 131.1, 138.4, 165.7. ¹⁹F {¹H} NMR (659 MHz, DMSO-*d*₆): δ/ppm = –77.8 (CF₃). IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3042, 2959, 2300, 2106, 1716, 1475, 1438, 1253, 1144, 1027, 959, 847, 776, 716. HRMS (ESI) calculated for C₁₃H₂₀NO₂⁺ [M–OTf]⁺: 222.1489; found: 222.1489.

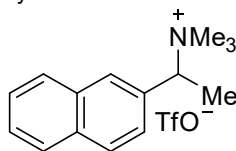


N,N,N-Trimethyl-1-(naphthalen-1-yl)ethan-1-aminium trifluoromethanesulfonate (1l). Prepared from *N,N*-dimethyl-1-(naphthalen-1-yl)ethan-1-amine (500 mg, 2.51 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.40 mL, 3.5 mmol, 1.4 equiv). During the reaction, no precipitate, but a second liquid layer was formed. Purification by flash column chromatography on silica gel (MeOH:CH₂Cl₂ = 1:19 → 1:9) afforded the title compound **1l** (733 mg, 2.02 mmol, 80%) as a white powder. *R*_f = 0.25 (MeOH:CH₂Cl₂ = 1:9). **M.P.** = 77–80 °C (MeOH:CH₂Cl₂ = 1:9). ¹H NMR (400 MHz, DMSO-*d*₆): δ/ppm = 1.84 (d, *J* = 6.8 Hz, 3H), 3.04 (s, 9H), 5.76 (q, *J* = 6.8 Hz, 1H), 7.59–7.73 (m, 3H), 7.92–7.98 (m, 1H), 8.03–8.08 (m, 1H), 8.09–8.14 (m, 1H), 8.55–8.62 (m, 1H). ¹³C {¹H} NMR (101 MHz, DMSO-*d*₆): δ/ppm = 15.8, 50.6, 66.1, 120.7 (q,

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$J = 322$ Hz, CF_3), 123.3, 125.3, 126.2, 127.3, 128.4, 129.2, 129.8, 130.8, 132.2, 133.5. ^{19}F { 1H } NMR (471 MHz, DMSO- d_6): $\delta/ppm = -77.7$ (CF_3). IR (ATR): $\tilde{\nu}/cm^{-1} = 3038, 1484, 1394, 1247, 1154, 1026, 951, 857, 830, 780$. HRMS (ESI) calculated for $C_{15}H_{20}N^+$ [M-OTf] $^+$: 214.1590; found: 214.1588. The spectroscopic data are in accordance with those reported.^[S8]

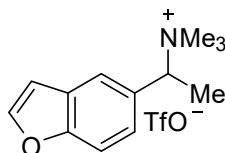
(*R*)-*N,N,N*-Trimethyl-1-(naphthalen-1-yl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-1l**]**. Prepared from (*R*)-*N,N*-dimethyl-1-(naphthalene-1-yl)ethan-1-amine (500 mg, 2.51 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.40 mL, 3.5 mmol, 1.4 equiv). During the reaction, no precipitate, but a second liquid layer was formed. Purification by flash column chromatography on silica gel (MeOH:CH₂Cl₂ = 1:19 → 1:9) afforded the title compound (*R*)-**1l** (699 mg, 1.93 mmol, 77%) as a white-pink powder. **Optical rotation**: $[\alpha] = -43.9$ ($c = 1.00$, CHCl₃, 99% ee). The enantiomeric excess was indicated by a label on the bottle of the corresponding amine.

**1m**

$C_{16}H_{20}F_3NO_3S$
M = 363.40 g/mol

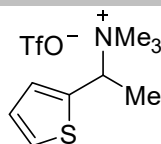
***N,N,N*-Trimethyl-1-(naphthalen-2-yl)ethan-1-aminium trifluoromethanesulfonate (1m)**. Prepared from *N,N*-dimethyl-1-(naphthalen-2-yl)ethan-1-amine (500 mg, 2.51 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.34 mL, 3.0 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. The layer was washed with Et₂O (2 × 5 mL) and cyclohexane (1 × 5 mL). Then the waxy solid was covered with cyclohexane and subjected to an ultrasonic bath for 5 min. During this time, the product solidified and the solvent was removed with a pipette. Drying of the residue at oil pump vacuum at rt afforded the title compound **1m** (734 mg, 2.03 mmol, 81%) as a white powder. **M.P.** = 56–59 °C (cyclohexane). 1H NMR (400 MHz, DMSO- d_6): $\delta/ppm = 1.82$ (d, $J = 6.6$ Hz, 3H), 3.04 (s, 9H), 4.94 (q, $J = 6.9$ Hz, 1H), 7.58–7.66 (m, 2H), 7.67–7.74 (m, 1H), 7.95–8.08 (m, 3H), 8.15–8.22 (m, 1H). ^{13}C { 1H } NMR (101 MHz, DMSO- d_6): $\delta/ppm = 14.7, 50.6, 72.8, 120.7$ (q, $J = 322$ Hz, CF_3), 126.8, 127.2, 127.4, 127.6, 128.4 (2C), 130.6, 130.9, 132.4, 133.4. ^{19}F { 1H } NMR (471 MHz, DMSO- d_6): $\delta/ppm = -77.7$ (CF_3). IR (ATR): $\tilde{\nu}/cm^{-1} = 3040, 2297, 2112, 1623, 1481, 1412, 1248, 1153, 1027, 955, 828, 750$. HRMS (ESI) calculated for $C_{15}H_{20}N^+$ [M-OTf] $^+$: 214.1590; found: 214.1588. The spectroscopic data are in accordance with those reported.^[S8]

(*R*)-*N,N,N*-Trimethyl-1-(naphthalen-2-yl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-1m**]**. Prepared from *N,N*-dimethyl-1-(naphthalen-2-yl)ethan-1-amine (500 mg, 2.51 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.34 mL, 3.0 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. The layer was washed with Et₂O (2 × 5 mL) and cyclohexane (1 × 5 mL). Then the waxy solid was covered with cyclohexane and subjected to an ultrasonic bath for 5 min. During this time, the product solidified and the solvent was removed with a pipette. Drying of the residue at oil pump vacuum at rt afforded the title compound (*R*)-**1m** (808 mg, 2.23 mmol, 89%) as a white powder. **Optical rotation**: $[\alpha] = +14.4$ ($c = 1.00$, CHCl₃, 99% ee). The enantiomeric excess was indicated by a label on the bottle of the corresponding amine.

**1n**

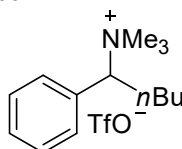
$C_{14}H_{18}F_3NO_4S$
M = 353.36 g/mol

1-(Benzofuran-5-yl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1n). Prepared from 1-(benzofuran-5-yl)-*N,N,N*-dimethylethan-1-amine (263 mg, 1.39 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.19 mL, 1.7 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. Purification of the bottom layer by flash column chromatography on silica gel (MeOH:CH₂Cl₂ = 1:9) afforded the title compound **1n** (808 mg, 2.23 mmol, 89%) as a colorless waxy residue, which slowly solidified. $R_f = 0.24$ (MeOH:CH₂Cl₂ = 1:9). **M.P.** = 46–47 °C (MeOH:CH₂Cl₂ = 1:9). 1H NMR (500 MHz, DMSO- d_6): $\delta/ppm = 1.77$ (d, $J = 6.7$ Hz, 3H), 3.00 (s, 9H), 4.89 (q, $J = 6.9$ Hz, 1H), 7.04 (d, $J = 1.2$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 8.6$ Hz, 1H), 7.93 (s, 1H), 8.09 (d, $J = 2.0$ Hz, 1H). ^{13}C { 1H } NMR (126 MHz, DMSO- d_6): $\delta/ppm = 15.0, 50.4$ (t, $J = 3.6$ Hz, [H₃C]₃N), 72.7, 107.0, 111.6, 120.7 (q, $J = 322$ Hz, CF_3), 123.7, 126.8, 127.6, 128.2, 147.3, 154.8. ^{19}F { 1H } NMR (471 MHz, DMSO- d_6): $\delta/ppm = -77.7$ (CF_3). IR (ATR): $\tilde{\nu}/cm^{-1} = 3511, 3116, 1612, 1471, 1253, 1156, 1026, 950, 902, 836$. HRMS (ESI) calculated for $C_{13}H_{18}NO^+$ [M-OTf] $^+$: 204.1383; found: 204.1382. The spectroscopic data are in accordance with those reported.^[S9]

**1o**

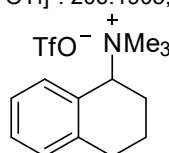
$C_{10}H_{16}F_3NO_3S_2$
 M = 319.36 g/mol

***N,N,N*-Trimethyl-1-(thiophen-2-yl)ethan-1-aminium trifluoromethanesulfonate (1o).** Prepared from *N,N*-dimethyl-1-(thiophen-2-yl)ethan-1-amine (144 mg, 0.928 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.12 mL, 1.1 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. Purification of the bottom layer by flash column chromatography on silica gel (MeOH:CH₂Cl₂ = 1:9) afforded the title compound **1o** (212 mg, 0.664 mmol, 72%) as a colorless waxy residue, which did not solidify even at low temperatures (−30 °C, freezer). *R_f* = 0.14 (MeOH:CH₂Cl₂ = 1:9). ¹H NMR (500 MHz, DMSO-*d*₆): δ/ppm = 1.74 (d, *J* = 7.0 Hz, 3H), 3.02 (s, 9H), 5.12 (q, *J* = 7.0 Hz, 1H), 7.18 (dd, *J* = 5.1 Hz, 3.5 Hz, 1H), 7.46 (dd, *J* = 3.5 Hz, 0.88 Hz, 1H), 7.79 (dd, *J* = 5.1 Hz, 0.88 Hz, 1H). ¹³C {¹H} NMR (126 MHz, DMSO-*d*₆): δ/ppm = 16.5, 50.3 (t, *J* = 3.2 Hz, [H₃C]₃N), 67.8, 120.7 (q, *J* = 322 Hz, CF₃), 127.5, 129.2, 131.7, 135.5. ¹⁹F {¹H} NMR (569 MHz, DMSO-*d*₆): δ/ppm = −77.7 (CF₃). IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2312, 2112, 1604, 1487, 1249, 1159, 1029, 955, 831, 712. HRMS (ESI) calculated for C₉H₁₆NS⁺ [M-OTf]⁺: 170.0998; found: 170.0995.

**1p**

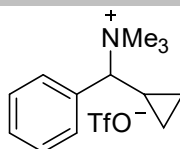
$C_{15}H_{24}F_3NO_3S$
 M = 355.42 g/mol

***N,N,N*-Trimethyl-1-phenylpentan-1-aminium trifluoromethanesulfonate (1p).** Prepared from *N,N*-dimethyl-1-phenylpentan-1-amine (500 mg, 2.62 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.35 mL, 3.1 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. The layer was washed with Et₂O (2 × 5 mL) and cyclohexane (1 × 5 mL). Then the waxy solid was covered with cyclohexane and subjected to an ultrasonic bath for 5 min. During this time, no product solidified and the solvent was removed with a pipette. Drying of the residue at oil pump vacuum at rt afforded the title compound **1p** (513 mg, 1.44 mmol, 55%) as a colorless waxy residue, which did not solidify even at low temperatures (−30 °C, freezer). ¹H NMR (400 MHz, DMSO-*d*₆): δ/ppm = 0.79 (t, *J* = 7.4 Hz, 3H), 0.77–0.87 (m, 1H), 0.92–1.04 (m, 1H), 1.18–1.38 (m, 1H), 2.15–2.27 (m, 2H), 2.97 (s, 9H), 4.53 (dd, *J* = 11.0 Hz, 4.6 Hz, 1H), 7.33–7.78 (m, 5H). ¹³C {¹H} NMR (101 MHz, DMSO-*d*₆): δ/ppm = 13.6, 21.5, 26.1, 28.2, 50.9, 71.2, 120.7 (q, *J* = 322 Hz, CF₃), 129.0, 129.6, 130.2, 131.7. ¹⁹F {¹H} NMR (471 MHz, DMSO-*d*₆): δ/ppm = −77.7 (CF₃). IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3052, 2959, 2866, 2102, 1987, 1675, 1467, 1252, 1155, 1024, 950, 854, 796, 732. HRMS (ESI) calculated for C₁₄H₂₄N⁺ [M-OTf]⁺: 206.1903; found: 206.1900.

**1q**

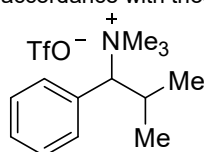
$C_{14}H_{20}F_3NO_3S$
 M = 339.37 g/mol

***N,N,N*-Trimethyl-1,2,3,4-tetrahydronaphthalen-1-aminium trifluoromethanesulfonate (1q).** Prepared from *N,N*-dimethyl-1,2,3,4-tetrahydronaphthalen-1-amine (677 mg, 3.86 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.52 mL, 4.6 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1q** (508 mg, 1.50 mmol, 39%) as a white powder. **M.P.** 87–89 °C (Et₂O). ¹H NMR (400 MHz, DMSO-*d*₆): δ/ppm = 1.39–1.54 (m, 1H), 2.00–2.10 (m, 1H), 2.11–2.24 (m, 1H), 2.34–2.47 (m, 1H), 2.70–2.80 (m, 2H), 2.98 (s, 9H), 4.89 (dd, *J* = 8.3 Hz, 4.1 Hz, 1H), 7.28–7.35 (m, 2H), 7.40–7.46 (m, 1H), 7.47–7.51 (m, 1H). ¹³C {¹H} NMR (176 MHz, DMSO-*d*₆): δ/ppm = 21.0, 22.8, 27.9, 50.6 (t, *J* = 3.4 Hz, [H₃C]₃N), 71.7, 120.7 (q, *J* = 322 Hz, CF₃), 125.9, 127.0, 129.6, 130.1, 133.5, 142.7. ¹⁹F {¹H} NMR (659 MHz, DMSO-*d*₆): δ/ppm = −77.7 (CF₃). IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3040, 2943, 1484, 1248, 1149, 1028, 958, 881, 837, 753, 690. HRMS (ESI) calculated for C₁₃H₂₀N⁺ [M-OTf]⁺: 190.1590; found: 190.1589. The spectroscopic data are in accordance with those reported.^[S7]

**1r**

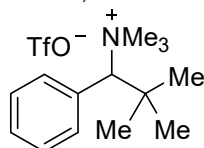
$C_{14}H_{20}F_3NO_3S$
 M = 339.37 g/mol

1-Cyclopropyl-*N,N,N*-trimethyl-1-phenylmethanaminium trifluoromethanesulfonate (1r). Prepared from 1-cyclopropyl-*N,N*-dimethyl-1-phenylmethanamine (155 mg, 0.884 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.12 mL, 1.1 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 5 mL) afforded the title compound **1r** (252 mg, 0.743 mmol, 84%) as a white powder. **M.P.** 93–95 °C (Et₂O). **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = –0.12–{–0.04} (m, 1H), 0.54–0.63 (m, 1H), 0.80–0.88 (m, 1H), 0.96–1.05 (m, 1H), 1.82–1.93 (m, 1H), 3.05 (s, 9H), 3.95 (d, *J* = 10.8 Hz, 1H), 7.37–7.72 (m, 5H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 3.3, 10.0 (2C), 51.0 (t, *J* = 3.0 Hz, [H₃C]₃N), 80.8, 120.7 (q, *J* = 322 Hz, CF₃), 128.7, 129.8, 130.9, 133.1. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3059, 1476, 1248, 1159, 1025, 970, 915, 857, 727. **HRMS** (ESI) calculated for C₁₃H₂₀N⁺ [M–OTf]⁺: 190.1590; found: 190.1588. The spectroscopic data are in accordance with those reported.^[S7]

**1s**

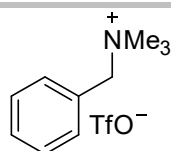
$C_{14}H_{22}F_3NO_3S$
 M = 341.39 g/mol

***N,N,N,2*-Tetramethyl-1-phenylpropan-1-aminium trifluoromethanesulfonate (1s).** Prepared from *N,N,2*-trimethyl-1-phenylpropan-1-amine (200 mg, 1.13 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.14 mL, 1.3 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. The layer was washed with Et₂O (2 × 3 mL). Then the waxy solid was covered with cyclohexane and subjected to an ultrasonic bath for 5 min. During this time, no product solidified and the solvent was removed with a pipette. Drying of the residue at oil pump vacuum at rt afforded the title compound **1s** (230 mg, 0.674 mmol, 60%) as a colorless waxy residue, which solidified over 2 h. Both, ¹H NMR and ¹³C NMR show minor impurities, which could not be identified. **M.P.** 44–46 °C (decomposition, Et₂O). **¹H NMR** (400 MHz, DMSO-*d*₆): δ/ppm = 0.94 (dd, *J* = 10.6 Hz, 6.7 Hz, 6H), 2.79 (ds, *J* = 6.7 Hz, 4.4 Hz, 1H), 3.07 (s, 9H), 4.50 (d, *J* = 4.4 Hz, 1H), 7.30–7.77 (m, 5H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 20.2, 23.0, 27.2, 52.5, 82.7, 120.7 (q, *J* = 322 Hz, CF₃), 128.8, 129.8, 131.3, 133.7. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2973, 2106, 1473, 1252, 1152, 1025, 969, 854, 747, 708. **HRMS** (ESI) calculated for C₁₃H₂₂N⁺ [M–OTf]⁺: 192.1747; found: 192.1746.

**1t**

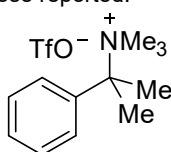
$C_{15}H_{24}F_3NO_3S$
 M = 355.42 g/mol

***N,N,N,2,2*-Pentamethyl-1-phenylpropan-1-aminium trifluoromethanesulfonate (1t).** Prepared from *N,N,2,2*-tetramethyl-1-phenylpropan-1-amine (360 mg, 1.88 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.25 mL, 2.3 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. The layer was washed with Et₂O (2 × 5 mL). Then the waxy solid was covered with cyclohexane and subjected to an ultrasonic bath for 5 min. During this time, no product solidified and the solvent was removed with a pipette. Drying of the residue at oil pump vacuum at rt afforded the title compound **1t** (600 mg, 1.69 mmol, 90%) as a colorless waxy residue, which solidified very slowly. **M.P.** 43–45 °C (decomposition, Et₂O). **¹H NMR** (400 MHz, DMSO-*d*₆): δ/ppm = 0.92 (s, 9H), 2.90 (s, 9H), 4.40 (s, 1H), 7.09–7.15 (m, 1H), 7.21–7.30 (m, 3H), 7.50–7.56 (m, 1H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 30.6, 36.9, 54.7, 86.2, 120.7 (q, *J* = 322 Hz, CF₃), 128.0, 128.5, 128.8, 129.6, 133.7, 134.1. **¹⁹F {¹H} NMR** (659 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2976, 1626, 1483, 1415, 1249, 1170, 1022, 957, 853, 827, 739. **HRMS** (ESI) calculated for C₁₄H₂₄N⁺ [M–OTf]⁺: 206.1903; found: 206.1903.

**1u**

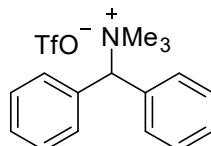
$C_{11}H_{16}F_3NO_3S$
 M = 299.31 g/mol

***N,N,N*-Trimethyl-1-phenylmethanaminium trifluoromethanesulfonate (1u).** Prepared from *N,N*-dimethyl-1-phenylmethanamine (2.75 mL, 18.3 mmol, 1.00 equiv) according to **GP1**, using MeOTf (2.75 mL, 25.1 mmol, 1.4 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound **1u** (5.04 g, 16.8 mmol, 92%) as a white powder. **M.P.** 72–74 °C (Et₂O). **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = 3.02 (s, 9H), 4.51 (s, 2H), 7.48–7.57 (m, 5H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 51.8 (t, *J* = 3.7 Hz, [H₃C]₃N), 67.9, 120.7 (q, *J* = 322 Hz, CF₃), 128.3, 128.9, 130.3, 132.8. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 1480, 1375, 1255, 1150, 1028, 989, 888, 779, 725. **HRMS** (ESI) calculated for C₁₀H₁₆N⁺ [M–OTf]⁺: 150.1277; found: 150.1276. The spectroscopic data are in accordance with those reported.^[S8]

**1v**

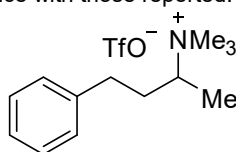
$C_{13}H_{20}F_3NO_3S$
 M = 327.36 g/mol

***N,N,N*-Trimethyl-2-phenylpropan-2-aminium trifluoromethanesulfonate (1v).** Prepared from *N,N*-dimethyl-2-phenylpropan-2-amine (327 mg, 2.00 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.25 mL, 2.2 mmol, 1.1 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (2 × 5 mL) afforded the title compound **1v** (594 mg, 1.81 mmol, 91%) as a white powder. **M.P.** 84–86 °C (Et₂O). **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = 1.90 (s, 6H), 2.93 (s, 9H), 7.48–7.53 (m, 3H), 7.74–7.80 (m, 2H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 22.5, 49.3 (t, *J* = 3.2 Hz, [H₃C]₃N), 74.4, 120.7 (q, *J* = 322 Hz, CF₃), 128.4, 129.6, 129.7, 135.4. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 1823, 1476, 1250, 1155, 1028, 965, 814, 756, 703. **HRMS** (ESI) calculated for C₁₂H₂₀N⁺ [M–OTf]⁺: 178.1590; found: 178.1589. The spectroscopic data are in accordance with those reported.^[S7]

**1w**

$C_{17}H_{20}F_3NO_3S$
 M = 375.41 g/mol

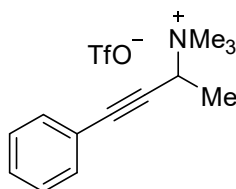
***N,N,N*-Trimethyl-1,1-diphenylmethanaminium trifluoromethanesulfonate (1w).** Prepared from *N,N*-dimethyl-1,1-diphenylmethan-amine (500 mg, 2.37 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.32 mL, 2.8 mmol, 1.2 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (2 × 5 mL) afforded the title compound **1w** (839 mg, 2.24 mmol, 94%) as a white powder. **M.P.** 126–128 °C (Et₂O). **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = 3.08 (s, 9H), 5.92 (s, 1H), 7.50–7.56 (m, 6H), 7.84–7.92 (m, 4H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 51.8, 80.6, 120.7 (q, *J* = 322 Hz, CF₃), 129.3, 130.0, 130.9, 132.7. **¹⁹F {¹H} NMR** (659 MHz, DMSO-*d*₆): δ/ppm = –77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 1824, 1664, 1473, 1253, 1150, 1025, 962, 855, 740, 702. **HRMS** (ESI) calculated for C₁₂H₂₀N⁺ [M–OTf]⁺: 226.1590; found: 226.1590. The spectroscopic data are in accordance with those reported.^[S10]

**1x**

$C_{14}H_{22}F_3NO_3S$
 M = 341.39 g/mol

SUPPORTING INFORMATION

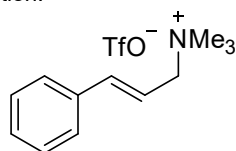
***N,N,N*-Trimethyl-4-phenylbutan-2-aminium trifluoromethanesulfonate (1x)**. Prepared from *N,N*-dimethyl-4-phenylbutan-2-amine (500 mg, 2.37 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.32 mL, 2.8 mmol, 1.2 equiv). During the reaction, no precipitate, but a second liquid layer was formed. The layer was washed with Et₂O (2 × 5 mL). The waxy solid was covered with cyclohexane and subjected to an ultrasonic bath for 5 min. During this time, no product solidified and the solvent was removed with a pipette. Drying of the residue at oil pump vacuum at rt afforded the title compound **1x** (435 mg, 1.27 mmol, 89%) as a colorless waxy residue, which did not solidify even at low temperatures (−30 °C, freezer). **¹H NMR** (400 MHz, DMSO-*d*₆): δ/ppm = 1.34–1.41 (m, 3H), 1.62–1.75 (m, 1H), 2.19–2.30 (m, 1H), 2.52–2.60 (m, 1H), 2.69–2.79 (m, 1H), 2.99 (s, 9H), 3.35–3.45 (m, 1H), 7.19–7.26 (m, 1H), 7.27–7.35 (m, 4H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 13.3, 31.0, 32.1, 50.1 (t, *J* = 3.8 Hz, [H₃C]₃N), 69.9, 120.7 (q, *J* = 322 Hz, CF₃), 126.2, 128.3, 128.4, 140.5. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = −77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2123, 1818, 1476, 1251, 1149, 1027, 954, 848, 754, 701. **HRMS** (ESI) calculated for C₁₃H₂₂N⁺ [M–OTf]⁺: 192.1747; found: 192.1746.

**5**

C₁₄H₁₈F₃NO₃S
M = 337.36 g/mol

***N,N,N*-Trimethyl-4-phenylbut-3-yn-2-aminium (5)**. Prepared from *N,N*-dimethyl-4-phenylbut-3-yn-2-amine (314 mg, 1.81 mmol, 1.00 equiv) according to **GP1**, using MeOTf (225 μL, 1.96 mmol, 1.1 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 5 mL) afforded the title compound **7** (526 mg, 1.56 mmol, 86%) as a white powder. **¹H NMR** (500 MHz, DMSO-*d*₆): δ/ppm = 1.67 (d, *J* = 6.9 Hz, 3H), 3.17 (s, 9H), 4.87 (q, *J* = 6.9 Hz, 1H), 7.41–7.52 (m, 3H), 7.56–7.62 (m, 2H). **¹³C {¹H} NMR** (101 MHz, DMSO-*d*₆): δ/ppm = 15.7, 50.3, 62.4, 82.1, 89.5, 120.3, 120.7 (q, *J* = 322 Hz, CF₃), 128.7, 129.8, 131.8. **¹⁹F {¹H} NMR** (471 MHz, DMSO-*d*₆): δ/ppm = −77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3041, 2231, 1487, 1250, 1146, 1026, 954, 841, 760, 693. **HRMS** (ESI) calculated for C₁₃H₁₈N⁺ [M–OTf]⁺: 188.1434; found: 188.1432. The spectroscopic data are in accordance with those reported.^[S5]

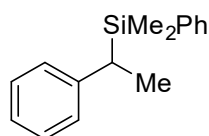
(*S*)-*N,N,N*-Trimethyl-4-phenylbut-3-yn-2-aminium [(*S*)-5]. Prepared from (*S*)-*N,N*-dimethyl-4-phenylbut-3-yn-2-amine (2.75 g, 15.9 mmol, 1.00 equiv) according to **GP1**, using MeOTf (1.82 mL, 16.1 mmol, 1.01 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (3 × 10 mL) afforded the title compound (*R*)-**7** (1.00 g, 3.08 mmol, 99%) as a white powder. **Optical rotation**: [α] = +20 (c = 1.00, CHCl₃, >95% ee). This value is consistent with literature ([α] = + 18.6 for 99% ee)^[S5]. The enantiomeric excess was indicated by a label on the bottle of the corresponding alcohol, prior to dimethylation.

**7**

C₁₃H₁₈F₃NO₃S
M = 325.35 g/mol

(*E*)-*N,N,N*-Trimethyl-3-phenylprop-2-en-1-aminium trifluoromethanesulfonate (7). Prepared from (*E*)-*N,N*-dimethyl-3-phenylprop-2-en-1-amine (500 mg, 3.10 mmol, 1.00 equiv) according to **GP1**, using MeOTf (0.39 mL, 3.4 mmol, 1.1 equiv). Vacuum filtration and subsequent rinsing of the precipitate with Et₂O (2 × 5 mL) afforded the title compound **7** (1.00 g, 3.08 mmol, 99%) as a white powder. **¹H NMR** (700 MHz, DMSO-*d*₆): δ/ppm = 3.07 (s, 9H), 4.10 (d, *J* = 7.5 Hz, 1H), 6.49 (dt, *J* = 15.7 Hz, 7.5 Hz, 1H), 6.88 (d, *J* = 15.7 Hz, 1H), 7.34–7.38 (m, 1H), 7.39–7.43 (m, 2H), 7.57–7.61 (m, 2H). **¹³C {¹H} NMR** (126 MHz, DMSO-*d*₆): δ/ppm = 51.9 (t, *J* = 4.0 Hz, [H₃C]₃N), 67.0 (t, *J* = 2.7 Hz, H₂CN), 116.7, 120.7 (q, *J* = 322 Hz, CF₃), 127.2, 128.7, 128.9, 135.2, 140.9. **¹⁹F {¹H} NMR** (659 MHz, DMSO-*d*₆): δ/ppm = −77.7 (CF₃). **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3035, 1652, 1480, 1249, 1150, 1026, 971, 891, 737, 689. **HRMS** (ESI) calculated for C₁₂H₁₈N⁺ [M–OTf]⁺: 176.1434; found: 176.1434. The spectroscopic data are in accordance with those reported.^[S10]

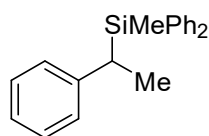
5. Experimental Details of the Nucleophilic Silylation and Characterization Data

**4aa**C₁₆H₂₀Si

M = 240.42 g/mol

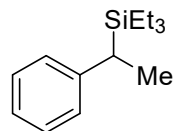
Dimethyl(phenyl)(1-phenylethyl)silane (4aa). Prepared from *N,N,N*-trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate (**1a**, 78 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4aa** (51 mg, 0.20 mmol, 81%) as a colorless oil. *R_f* = 0.55 (cyclohexane). ¹H NMR (500 MHz, CDCl₃): δ/ppm = 0.19 (s, 3H), 0.24 (s, 3H), 1.33 (d, *J* = 7.5 Hz, 3H), 2.38 (q, *J* = 7.5 Hz, 1H), 6.91–6.98 (m, 2H), 7.05–7.12 (m, 1H), 7.16–7.23 (m, 2H), 7.29–7.41 (m, 5H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ/ppm = –5.4, –4.2, 15.2, 29.6, 124.5, 127.4, 127.7, 128.0, 129.1, 134.3, 137.7, 145.3. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ/ppm = –1.05. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3032, 2954, 2869, 1945, 1597, 1248, 1110, 812, 774, 696. HRMS (EI) calculated for C₁₆H₂₀Si⁺ [*M*]⁺: 240.1329; found: 240.1328. The spectroscopic data are in accordance with those reported.^[S11]

(S)-Dimethyl(phenyl)(1-phenylethyl)silane [(S)-4aa]. Prepared from (*R*)-*N,N,N*-trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate [(*R*)-**1a**, 78 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound (*S*)-**4aa** (48 mg, 0.20 mmol, 79%) as a colorless oil. **Optical rotation:** [α] = +1.2 (*c* = 1.00, CHCl₃, >99% ee). The enantiomeric excess of (*S*)-**4aa** was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 98:2, flow rate 0.8 mL/min, λ = 210 nm): *t_R* = 24.9 min for (*S*)-**4aa**, *t_R* = 30.0 min for (*R*)-**4aa**.

**4ab**C₂₁H₂₂Si

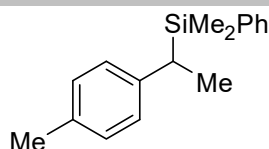
M = 302.49 g/mol

Methyldiphenyl(1-phenylethyl)silane (4ab). Prepared from *N,N,N*-trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate (**1a**, 78 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ab** (30 mg, 0.099 mmol, 40%) as an off-white oil. *R_f* = 0.37 (cyclohexane). ¹H NMR (500 MHz, CDCl₃): δ/ppm = 0.45 (s, 3H), 1.42 (d, *J* = 7.5 Hz, 3H), 2.81 (q, *J* = 7.5 Hz, 1H), 6.86–6.93 (m, 2H), 7.04–7.10 (m, 1H), 7.11–7.17 (m, 2H), 7.25–7.31 (m, 2H), 7.32–7.44 (m, 6H), 7.49–7.54 (m, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ/ppm = –5.7, 16.1, 28.2, 124.8, 127.7, 127.9 (2C), 128.0, 129.3, 129.4, 135.1, 135.4, 136.1, 144.7. One carbon atom is missing. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ/ppm = –6.25. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3032, 2922, 2868, 1952, 1596, 1425, 1250, 1106, 995, 788, 694. HRMS (APCI) calculated for C₁₅H₁₇Si⁺ [*M*-C₆H₅]⁺: 225.1094; found: 225.1106.

**4ac**C₁₄H₂₄Si

M = 220.43 g/mol

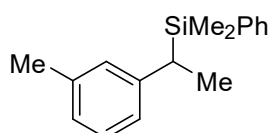
Triethyl(1-phenylethyl)silane (4ac). Prepared from *N,N,N*-trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate (**1a**, 78 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ac** (35 mg, 0.16 mmol, 64%) as a colorless oil. *R_f* = 0.81 (cyclohexane). ¹H NMR (500 MHz, CDCl₃): δ/ppm = 0.52 (q, *J* = 8.0 Hz, 6H), 0.89 (t, *J* = 8.0 Hz, 9H), 1.38 (d, *J* = 7.6 Hz, 3H), 2.31 (d, *J* = 7.6 Hz, 1H), 7.04–7.11 (m, 3H), 7.20–7.25 (m, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ/ppm = 2.2, 7.6, 15.6, 27.0, 124.3, 127.3, 128.1, 146.5. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ/ppm = 7.46. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2950, 2873, 1598, 1492, 1451, 1237, 1009, 762, 697. HRMS (EI) calculated for C₁₄H₂₄Si⁺ [*M*]⁺: 220.1642; found: 220.1645. The spectroscopic data are in accordance with those reported.^[S12]

**4ba**C₁₇H₂₂Si

M = 254.45 g/mol

Dimethyl(phenyl)[1-(p-tolyl)ethyl]silane (4ba). Prepared from *N,N,N*-trimethyl-1-(p-tolyl)ethan-1-aminium trifluoromethanesulfonate (**1b**, 82 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ba** (50 mg, 0.20 mmol, 79%) as a colorless oil. *R_f* = 0.60 (cyclohexane). ¹H NMR (500 MHz, CDCl₃): δ/ppm = 0.20 (s, 3H), 0.24 (s, 3H), 1.32 (d, *J* = 7.6 Hz, 3H), 2.31 (s, 3H), 2.35 (q, *J* = 7.6 Hz, 1H), 6.83–6.88 (m, 2H), 6.99–7.05 (m, 2H), 7.30–7.40 (m, 3H), 7.40–7.44 (m, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ/ppm = –5.4, –4.1, 15.4, 21.1, 29.0, 127.3, 127.7, 128.8, 129.1, 133.8, 134.3, 137.9, 142.2. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ/ppm = –1.29. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2953, 2867, 1892, 1509, 1425, 1247, 1111, 1006, 809, 770, 697. HRMS (EI) calculated for C₁₇H₂₂Si⁺ [M]⁺: 254.1485; found: 254.1483.

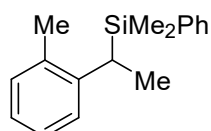
(S)-Dimethyl(phenyl)[1-(p-tolyl)ethyl]silane [(S)-4ba]. Prepared from (*S*)-*N,N,N*-trimethyl-1-(p-tolyl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-**1b**, 82 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ba** (49 mg, 0.19 mmol, 77%) as a colorless oil. **Optical rotation:** [α] = +2.5 (*c* = 0.10, CHCl₃, 98% ee). The enantiomeric excess of (*S*)-**4ba** was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 98:2, flow rate 0.8 mL/min, λ = 210 nm): *t_R* = 24.3 min for (*R*)-**4ba**, *t_R* = 28.8 min for (*S*)-**4ba**.

**4ca**C₁₇H₂₂Si

M = 254.45 g/mol

Dimethyl(phenyl)[1-(m-tolyl)ethyl]silane (4ca). Prepared from *N,N,N*-trimethyl-1-(m-tolyl)ethan-1-aminium trifluoromethanesulfonate (**1c**, 82 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ca** (48 mg, 0.19 mmol, 75%) as a colorless oil. *R_f* = 0.60 (cyclohexane). ¹H NMR (500 MHz, CDCl₃): δ/ppm = 0.19 (s, 3H), 0.24 (s, 3H), 1.31 (d, *J* = 7.5 Hz, 3H), 2.26 (s, 3H), 2.35 (q, *J* = 7.5 Hz, 1H), 6.72 (s, 1H), 6.74–6.77 (m, 1H), 6.88–6.92 (m, 1H), 7.06–7.11 (m, 1H), 7.29–7.41 (m, 5H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ/ppm = –5.4, –4.2, 15.2, 21.6, 29.5, 124.5, 125.3, 127.6, 127.9, 128.4, 129.1, 134.3, 137.4, 137.8, 145.2. ²⁹Si{¹H} DEPT NMR (99 MHz, CDCl₃): δ/ppm = –1.18. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3019, 2953, 2867, 1602, 1426, 1247, 1111, 811, 769, 697. HRMS (EI) calculated for C₁₇H₂₂Si⁺ [M]⁺: 254.1485; found: 254.1485.

(S)-Dimethyl(phenyl)[1-(m-tolyl)ethyl]silane [(S)-4ca]. Prepared from (*R*)-*N,N,N*-trimethyl-1-(m-tolyl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-**1c**, 82 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound (*S*)-**4ca** (48 mg, 0.19 mmol, 76%) as a colorless oil. **Optical rotation:** [α] = +2.7 (*c* = 0.10, CHCl₃, 98% ee). The enantiomeric excess of (*S*)-**4ca** was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 98:2, flow rate 0.8 mL/min, λ = 210 nm): *t_R* = 20.5 min for (*R*)-**4ca**, *t_R* = 22.7 min for (*S*)-**4ca**.

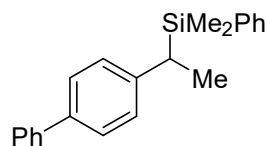
**4da**C₁₇H₂₂Si

M = 254.45 g/mol

Dimethyl(phenyl)[1-(o-tolyl)ethyl]silane (4da). Prepared from *N,N,N*-trimethyl-1-(o-tolyl)ethan-1-aminium trifluoromethanesulfonate (**1d**, 82 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4da** (25 mg, 0.098 mmol, 39%) as an off-white oil. *R_f* = 0.60

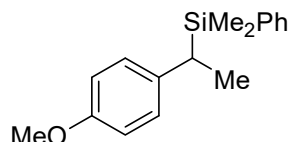
SUPPORTING INFORMATION

(cyclohexane). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ/ppm = 0.18 (s, 3H), 0.30 (s, 3H), 1.33 (d, J = 7.5 Hz, 3H), 2.09 (s, 3H), 2.60 (q, J = 7.5 Hz, 1H), 6.95–7.02 (m, 2H), 7.04–7.08 (m, 1H), 7.09–7.14 (m, 1H), 7.28–7.33 (m, 2H), 7.34–7.39 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ/ppm = –5.3, –4.1, 16.0, 20.4, 24.1, 124.3, 125.9, 126.5, 127.7, 129.1, 130.1, 134.2, 135.0, 138.1, 144.0. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): δ/ppm = –0.96. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3065, 2954, 2868, 1733, 1600, 1457, 1248, 1109, 1034, 808, 697. HRMS (ESI) calculated for $\text{C}_{17}\text{H}_{22}\text{Si}^+ [\text{M}-\text{C}_6\text{H}_5]^+$: 177.1094; found: 177.1090.

**4ea** $\text{C}_{22}\text{H}_{24}\text{Si}$

M = 316.52 g/mol

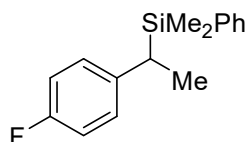
{1-[(1,1'-biphenyl)-4-yl]ethyl}dimethyl(phenyl)silane (4ea). Prepared from 1-[(1,1'-biphenyl)-4-yl]-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (**1e**, 97 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ea** (36 mg, 0.11 mmol, 46%) as an off-white solid. R_f = 0.20 (cyclohexane). **M.P.** 48–50 °C (cyclohexane). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ/ppm = 0.24 (s, 3H), 0.28 (s, 3H), 1.37 (d, J = 7.6 Hz, 3H), 2.44 (q, J = 7.6 Hz, 1H), 6.98–7.05 (m, 2H), 7.28–7.48 (m, 10H), 7.57–7.63 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ/ppm = –5.3, –4.2, 15.2, 29.4, 126.7, 126.9, 127.0, 127.7, 127.8, 128.8, 129.2, 134.3, 137.4, 137.6, 141.3, 144.6. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): δ/ppm = –1.02. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3020, 2951, 1484, 1425, 1245, 1110, 1006, 811, 760, 689. HRMS (APCI) calculated for $\text{C}_{16}\text{H}_{19}\text{Si}^+ [\text{M}-\text{C}_6\text{H}_5]^+$: 239.1251; found: 239.1250.

**4fa** $\text{C}_{17}\text{H}_{22}\text{OSi}$

M = 270.45 g/mol

[1-(4-Methoxyphenyl)ethyl]dimethyl(phenyl)silane (4fa). Prepared from 1-(4-methoxyphenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (**1f**, 86 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. Purification by flash column chromatography on silica gel using *tert*-butyl methyl ether in cyclohexane (0%→2%) afforded the title compound **4fa** (52 mg, 0.19 mmol, 77%) as a colorless oil. R_f = 0.45 (*tert*-butyl methyl ether:cyclohexane = 1:49). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ/ppm = 0.19 (s, 3H), 0.23 (s, 3H), 1.30 (d, J = 7.6 Hz, 3H), 2.31 (q, J = 7.6 Hz, 1H), 3.78 (s, 3H), 6.73–6.78 (m, 2H), 6.83–6.88 (m, 2H), 7.30–7.41 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ/ppm = –5.4, –4.2, 15.5, 28.4, 55.4, 113.5, 127.7, 128.2, 129.1, 134.3, 137.3, 137.9, 156.9. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): δ/ppm = –1.31. IR (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2952, 1727, 1608, 1506, 1458, 1242, 1111, 1037, 807, 733. HRMS (EI) calculated for $\text{C}_{17}\text{H}_{22}\text{OSi}^+ [\text{M}]^+$: 270.1434; found: 270.1428.

(*R*)-[1-(4-Methoxyphenyl)ethyl]dimethyl(phenyl)silane [(*R*)-4fa]. Prepared from (*S*)-1-(4-methoxyphenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate [(*S*)-**1f**, 86 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. Purification by flash column chromatography on silica gel using *tert*-butyl methyl ether in cyclohexane (0%→2%) afforded the title compound **4fa** (50 mg, 0.19 mmol, 75%) as a colorless oil. **Optical rotation**: $[\alpha]_D^{20}$ = +11.2 (c = 0.5, CHCl_3 , 97% ee). The enantiomeric excess of (*R*)-**4fa** was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 95:5, flow rate 0.8 mL/min, λ = 210 nm): t_R = 22.4 min for (*S*)-**4fa**, t_R = 24.1 min for (*R*)-**4fa**.

**4ga** $\text{C}_{16}\text{H}_{19}\text{FSi}$

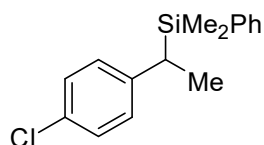
M = 258.41 g/mol

[1-(4-fluorophenyl)ethyl]dimethyl(phenyl)silane (4ga). Prepared from 1-(4-fluorophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (**1g**, 83 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ga** (48 mg, 0.19 mmol, 74%) as a colorless oil. R_f = 0.43 (cyclohexane). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ/ppm = 0.20 (s, 3H), 0.24 (s, 3H), 1.31 (d, J = 7.6 Hz, 3H), 2.35 (q, J = 7.6 Hz, 1H), 6.82–6.91 (m, 4H), 7.29–7.39 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ/ppm = –5.3, –4.5, 15.4, 28.9, 114.7 (d, J = 20.8 Hz), 127.7, 128.4

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(d, $J = 7.6$ Hz), 129.2, 134.3, 137.3, 140.9, 160.5 (d, $J = 241$ Hz). $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): $\delta/\text{ppm} = -1.07$. IR (ATR): $\tilde{\nu}/\text{cm}^{-1} = 3067, 2955, 2869, 1878, 1599, 1503, 1426, 1315, 1220, 1110, 1009, 809, 771, 697$. HRMS (EI) calculated for $\text{C}_{16}\text{H}_{19}\text{FSi}^+$ $[\text{M}]^+$: 258.1235; found: 258.1230.

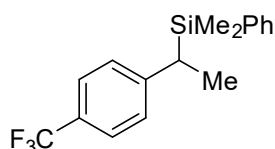
(S)-[1-(4-fluorophenyl)ethyl]dimethyl(phenyl)silane [(S)-4ga]. Prepared from 1-(4-fluorophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate [(*R*)-1g, 83 mg, 0.25 mmol, 1.00 equiv] according to GP2. The crude material was purified according to GP3. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound (S)-4ga (46 mg, 0.18 mmol, 71%) as a colorless oil. **Optical rotation**: $[\alpha] = -20.9$ ($c = 1.0$, CHCl_3 , 98% ee). The enantiomeric excess of (S)-4ga was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 98:2, flow rate 0.8 mL/min, $\lambda = 210$ nm): $t_{\text{R}} = 25.9$ min for (S)-4ga, $t_{\text{R}} = 27.8$ min for (R)-4ga.

**4ha**

$\text{C}_{16}\text{H}_{19}\text{ClSi}$
M = 274.86 g/mol

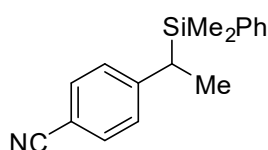
[1-(4-Chlorophenyl)ethyl]dimethyl(phenyl)silane (4ha). Prepared from 1-(4-chlorophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1h, 87 mg, 0.25 mmol, 1.00 equiv) according to GP2. The crude material was purified according to GP3. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound 4ha (43 mg, 0.16 mmol, 62%) as a colorless oil. $R_{\text{f}} = 0.47$ (cyclohexane). ^1H NMR (500 MHz, CDCl_3): $\delta/\text{ppm} = 0.20$ (s, 3H), 0.24 (s, 3H), 1.31 (d, $J = 7.6$ Hz, 3H), 2.35 (q, $J = 7.6$ Hz, 1H), 6.80–6.87 (m, 2H), 7.12–7.18 (m, 2H), 7.29–7.40 (m, 5H). ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta/\text{ppm} = -5.3, -4.5, 15.1, 29.2, 127.8, 128.1, 128.6, 129.3, 130.1, 134.3, 137.1, 143.9$. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): $\delta/\text{ppm} = -0.99$. IR (ATR): $\tilde{\nu}/\text{cm}^{-1} = 3067, 2954, 2869, 1889, 1487, 1248, 1111, 1009, 830, 770, 698$. HRMS (APCI) calculated for $\text{C}_{16}\text{H}_{18}\text{FSi}^+$ $[\text{M}-\text{H}]^+$: 273.0861; found: 273.0859.

(R)-[1-(4-Chlorophenyl)ethyl]dimethyl(phenyl)silane [(R)-4ha]. Prepared from (S)-1-(4-chlorophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate [(S)-1h, 87 mg, 0.25 mmol, 1.00 equiv] according to GP2. The crude material was purified according to GP3. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound (R)-4ha (44 mg, 0.16 mmol, 64%) as a colorless oil. **Optical rotation**: $[\alpha] = +18.5$ ($c = 1.0$, CHCl_3 , 98% ee). The enantiomeric excess of (R)-4ha was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 98:2, flow rate 0.8 mL/min, $\lambda = 210$ nm): $t_{\text{R}} = 24.8$ min for (S)-4ha, $t_{\text{R}} = 27.8$ min for (R)-4ha.

**4ia**

$\text{C}_{17}\text{H}_{19}\text{F}_3\text{Si}$
M = 308.42 g/mol

Dimethyl(phenyl){1-[4-(trifluoromethyl)phenyl]ethyl}silane (4ia). Prepared from 1-[4-(trifluoromethyl)phenyl]-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1i, 87 mg, 0.25 mmol, 1.00 equiv) according to GP2. The crude material was purified according to GP3. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound 4ia (50 mg, 0.16 mmol, 65%) as an off-white oil. $R_{\text{f}} = 0.63$ (cyclohexane). ^1H NMR (400 MHz, CDCl_3): $\delta/\text{ppm} = 0.21$ (s, 3H), 0.25 (s, 3H), 1.35 (d, $J = 7.5$ Hz, 3H), 2.45 (q, $J = 7.5$ Hz, 1H), 6.97–7.02 (m, 2H), 7.29–7.40 (m, 5H), 7.40–7.45 (m, 2H). ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta/\text{ppm} = -5.4, -4.5, 15.0, 30.1, 124.6$ (q, $J = 272$ Hz, CF_3), 124.9 (q, $J = 3.8$ Hz), 127.5, 127.8, 129.4, 134.2, 134.3, 136.8, 149.8. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): $\delta/\text{ppm} = -1.26$. IR (ATR): $\tilde{\nu}/\text{cm}^{-1} = 2956, 1614, 1426, 1322, 1251, 1112, 1067, 829, 791, 731, 697$. HRMS (APCI) calculated for $\text{C}_{17}\text{H}_{20}\text{F}_3\text{Si}^+$ $[\text{M}+\text{H}]^+$: 308.1208; found: 308.1214.

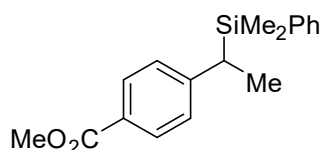
**4ia**

$\text{C}_{17}\text{H}_{19}\text{NSi}$
M = 265.43 g/mol

SUPPORTING INFORMATION

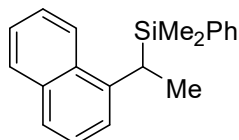
4-{1-[Dimethyl(phenyl)silyl]ethyl}benzonitrile (4ja). Prepared from 1-(4-cyanophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (**1j**, 85 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. Purification by flash column chromatography on silica gel using CH₂Cl₂ in cyclohexane (0% →10%) afforded the title compound **4ja** (33 mg, 0.12 mmol, 50%) as an off-white solid. *R_f* = 0.08 (CH₂Cl₂:Cyclohexane = 1:19). **M.P.** 46–48 °C. **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.22 (s, 3H), 0.26 (s, 3H), 1.35 (d, *J* = 7.4 Hz, 3H), 2.46 (q, *J* = 7.4 Hz, 1H), 6.94–6.98 (m, 2H), 7.29–7.41 (m, 5H), 7.43–7.47 (m, 2H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –5.2, –4.8, 14.7, 31.0, 108.1, 119.6, 127.9 (2C), 129.6, 131.8, 134.2, 136.3, 151.7. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –0.29. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3067, 2956, 2875, 2220, 1600, 1412, 1248, 1109, 1009, 804, 772, 698. **HRMS** (APCI) calculated for C₁₇H₁₉NSi⁺ [M]⁺: 265.1281; found: 265.1277.

(S)-4-{1-[Dimethyl(phenyl)silyl]ethyl}benzonitrile [(S)-4ja]. Prepared from (*R*)-1-(4-cyanophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate [(*R*)-**1j**, 85 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. Purification by flash column chromatography on silica gel using CH₂Cl₂ in cyclohexane (0% →10%) afforded the title compound (*S*)-**4ja** (32 mg, 0.12 mmol, 48%) as an off-white solid. **Optical rotation:** [α] = +7.1 (*c* = 0.5, CHCl₃, 99% ee). The enantiomeric excess of (*S*)-**4ja** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OD-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 99.5:0.5, flow rate 0.8 mL/min, λ = 210 nm): *t_R* = 9.8 min for (*S*)-**4ja**, *t_R* = 10.9 min for (*R*)-**4ja**.

**4ka**

C₁₈H₂₂O₂Si
M = 298.46 g/mol

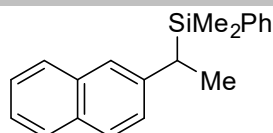
Methyl 4-{1-[dimethyl(phenyl)silyl]ethyl}benzoate (4ka). Prepared from 1-[4-(methoxycarbonyl)phenyl]-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (**1k**, 93 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. Purification by flash column chromatography on silica gel using *tert*-butyl methyl ether in cyclohexane (0%→2%) afforded the title compound **4ka** (56 mg, 0.19 mmol, 75%) as an off-white oil. *R_f* = 0.25 (*tert*-butyl methyl ether:cyclohexane = 1:39). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.20 (s, 3H), 0.24 (s, 3H), 1.35 (d, *J* = 7.4 Hz, 3H), 2.47 (q, *J* = 7.4 Hz, 1H), 3.89 (s, 3H), 6.94–7.00 (m, 2H), 7.28–7.40 (m, 5H), 7.83–7.89 (m, 2H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –5.3, –4.5, 14.9, 30.5, 52.0, 126.7, 127.3, 127.8, 129.4 (2C), 134.3, 136.9, 151.5, 167.5. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –0.62. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2952, 2870, 1716, 1604, 1431, 1273, 1178, 1106, 812, 699. **HRMS** (APCI) calculated for C₁₈H₂₃O₂Si⁺ [M]⁺: 299.1462; found: 299.1459.

**4la**

C₂₀H₂₂Si
M = 290.48 g/mol

Dimethyl[1-(naphthalen-1-yl)ethyl](phenyl)silane (4la). Prepared from *N,N,N*-trimethyl-1-(naphthalen-1-yl)ethan-1-aminium trifluoromethanesulfonate (**1l**, 87 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4la** (59 mg, 0.20 mmol, 81%) as an off-white oil. *R_f* = 0.35 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.12 (s, 3H), 0.22 (s, 3H), 1.47 (d, *J* = 7.0 Hz, 3H), 3.31 (q, *J* = 7.0 Hz, 1H), 7.09–7.14 (m, 1H), 7.28–7.46 (m, 8H), 7.59–7.64 (m, 1H), 7.80–7.84 (m, 1H), 7.96–8.02 (m, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –5.3, –3.5, 16.3, 23.1, 123.5, 124.0, 125.0, 125.1, 125.2, 125.6, 127.7, 128.9, 129.2, 131.8, 134.0, 134.3, 137.8, 142.2. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –0.11. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3045, 2953, 2923, 2869, 1591, 1459, 1392, 1248, 1110, 811, 771, 697. **HRMS** (APCI) calculated for C₂₀H₂₃Si⁺ [M+H]⁺: 291.1564; found: 291.1575.

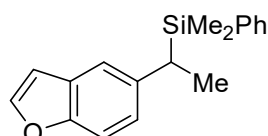
(S)-Dimethyl[1-(naphthalen-1-yl)ethyl](phenyl)silane [(S)-4la]. Prepared from (*R*)-*N,N,N*-trimethyl-1-(naphthalen-1-yl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-**1l**, 87 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound (*S*)-**4la** (60 mg, 0.21 mmol, 81%) as an off-white oil. **Optical rotation:** [α] = +69.8 (*c* = 1.0, CHCl₃, 99% ee). The enantiomeric excess of (*S*)-**4la** was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 95:5, flow rate 0.8 mL/min, λ = 210 nm): *t_R* = 31.1 min for (*S*)-**4la**, *t_R* = 42.0 min for (*R*)-**4la**.

**4ma**C₂₀H₂₂Si

M = 290.48 g/mol

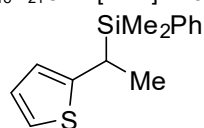
Dimethyl[1-(naphthalen-2-yl)ethyl](phenyl)silane (4ma). Prepared from *N,N,N*-trimethyl-1-(naphthalen-2-yl)ethan-1-aminium trifluoromethanesulfonate (**1m**, 91 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ma** (54 mg, 0.19 mmol, 75%) as a colorless oil. *R_f* = 0.40 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.22 (s, 3H), 0.27 (s, 3H), 1.43 (d, *J* = 7.5 Hz, 3H), 2.55 (q, *J* = 7.5 Hz, 1H), 7.06–7.12 (m, 1H), 7.29–7.45 (m, 8H), 7.64–7.72 (m, 2H), 7.75–7.80 (m, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –5.3, –4.2, 15.3, 29.9, 124.7 (2C), 125.8, 127.3, 127.4 (2C), 127.7 (2C), 129.2, 131.5, 133.8, 134.3, 137.6, 143.1. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –0.82. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3048, 2953, 2867, 1628, 1596, 1425, 1247, 1111, 810, 733, 698. **HRMS** (APCI) calculated for C₂₀H₂₃Si⁺ [M+H]⁺: 291.1564; found: 291.1575.

(S)-Dimethyl[1-(naphthalen-2-yl)ethyl](phenyl)silane [(S)-4ma]. Prepared from (*R*)-*N,N,N*-trimethyl-1-(naphthalen-2-yl)ethan-1-aminium trifluoromethanesulfonate [(*R*)-**1m**, 91 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound (*S*)-**4ma** (56 mg, 0.19 mmol, 77%) as a colorless oil. **Optical rotation:** [α] = –46.1 (*c* = 1.0, CHCl₃, 97% ee). The enantiomeric excess of (*S*)-**4ma** was determined at the stage of the alcohol after TAMAO-Oxidation of the corresponding silane. HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 95:5, flow rate 0.8 mL/min, λ = 210 nm): *t_R* = 30.9 min for (*S*)-**4ma**, *t_R* = 42.0 min for (*R*)-**4ma**.

**4na**C₁₈H₂₀OSi

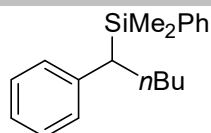
M = 280.44 g/mol

[1-(Benzofuran-5-yl)ethyl]dimethyl(phenyl)silane (4na). Prepared from 1-(Benzofuran-5-yl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (**1n**, 93 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. Purification by flash column chromatography on silica gel using *tert*-butyl methyl ether in cyclohexane (0%→1%) afforded the title compound **4na** (51 mg, 0.18 mmol, 73%) as a yellow oil. *R_f* = 0.25 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.20 (s, 3H), 0.25 (s, 3H), 1.38 (d, *J* = 7.5 Hz, 3H), 2.47 (q, *J* = 7.5 Hz, 1H), 6.66 (dd, *J* = 2.2 Hz, 0.95 Hz, 1H), 6.87 (dd, *J* = 8.5 Hz, 1.9 Hz, 1H), 7.14 (d, *J* = 1.9 Hz, 1H), 7.29–7.34 (m, 3H), 7.34–7.37 (m, 1H), 7.37–7.41 (m, 2H), 7.56 (d, *J* = 2.2 Hz, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –5.4, –4.2, 15.9, 29.3, 106.5, 110.6, 119.0, 124.4, 127.4, 127.7, 129.1, 134.3, 137.8, 139.8, 144.9, 153.9. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –1.15. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3066, 2953, 2867, 1462, 1248, 1109, 1030, 810, 731, 698. **HRMS** (APCI) calculated for C₁₈H₂₁OSi⁺ [M+H]⁺: 281.1356; found: 281.1355.

**4oa**C₁₄H₁₈SSi

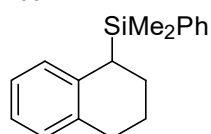
M = 246.44 g/mol

Dimethyl(phenyl)(1-(thiophen-2-yl)ethyl)silane (4oa). Prepared from *N,N,N*-trimethyl-1-(thiophen-2-yl)ethan-1-aminium trifluoromethanesulfonate (**1o**, 80 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4oa** (39 mg, 0.16 mmol, 63%) as a colorless oil. *R_f* = 0.54 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.26 (s, 3H), 0.31 (s, 3H), 1.37 (d, *J* = 7.5 Hz, 3H), 2.69 (q, *J* = 7.5 Hz, 1H), 6.53 (dt, *J* = 3.5 Hz, 0.95 Hz, 1H), 6.88 (dd, *J* = 5.1 Hz, 3.5 Hz, 1H), 6.99 (dd, *J* = 5.1 Hz, 1.0 Hz, 1H), 7.29–7.47 (m, 2H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –5.3, –4.3, 17.1, 25.2, 121.1, 122.1, 126.7, 127.8, 129.3, 134.2, 137.4, 149.3. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –1.05. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3067, 2953, 2867, 1454, 1426, 1248, 1110, 991, 810, 772, 731. **HRMS** (APCI) calculated for C₂₀H₂₃Si⁺ [M+H]⁺: 247.0971; found: 247.0969.

**4pa**C₁₉H₂₆Si

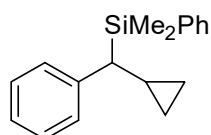
M = 282.50 g/mol

Dimethyl(phenyl)(1-phenylpentyl)silane (4pa). Prepared from *N,N,N*-trimethyl-1-phenylpentan-1-aminium trifluoromethanesulfonate (**1p**, 89 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4pa** (31 mg, 0.11 mmol, 44%) as a colorless oil. *R*_f = 0.48 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.16 (s, 3H), 0.24 (s, 3H), 0.77 (t, *J* = 7.1 Hz, 3H), 1.05–1.28 (m, 4H), 1.66–1.80 (m, 2H), 2.22 (dd, *J* = 11.8 Hz, 3.8 Hz, 1H), 6.90–6.94 (m, 2H), 7.05–7.11 (m, 1H), 7.15–7.22 (m, 2H), 7.29–7.42 (m, 5H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –5.1, –3.7, 14.0, 22.6, 29.1, 31.5, 36.7, 124.5, 127.7, 128.1 (2C), 129.0, 134.3, 138.0, 143.3. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –2.22. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 2954, 2923, 2854, 1598, 1488, 1450, 1247, 1111, 905, 826, 731, 696. **HRMS** (APCI) calculated for C₁₃H₂₁Si⁺ [M–C₆H₅]⁺: 205.1407; found: 205.1408.

**4qa**C₁₈H₂₂Si

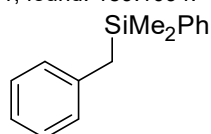
M = 266.46 g/mol

Dimethyl(phenyl)(1,2,3,4-tetrahydronaphthalen-1-yl)silane (4qa). Prepared from *N,N,N*-trimethyl-1,2,3,4-tetrahydronaphthalen-1-aminium trifluoromethanesulfonate (**1q**, 85 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4qa** (33 mg, 0.12 mmol, 50%) as an off-white oil. *R*_f = 0.53 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = 0.27 (s, 3H), 0.29 (s, 3H), 1.58–1.96 (m, 4H), 2.49–2.74 (m, 3H), 6.79–6.86 (m, 1H), 6.94–7.04 (m, 3H), 7.29–7.43 (m, 5H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –3.3, –3.0, 22.1, 25.1, 29.0, 29.6, 124.2, 125.2, 127.8, 128.6, 129.0, 129.3, 134.2, 136.7, 138.9 (2C). **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –0.77. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3012, 2927, 2852, 1597, 1485, 1426, 1247, 1110, 809, 730, 697. **HRMS** (APCI) calculated for C₁₈H₂₁Si⁺ [M–H]⁺: 265.1407; found: 265.1405.

**4ra**C₁₈H₂₂Si

M = 266.46 g/mol

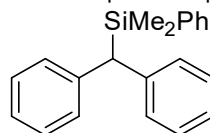
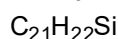
[Cyclopropyl(phenyl)methyl]dimethyl(phenyl)silane (4ra). Prepared from 1-cyclopropyl-*N,N,N*-trimethyl-1-phenylmethanaminium trifluoromethanesulfonate (**1r**, 85 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ra** (28 mg, 0.11 mmol, 42%) as a colorless oil. *R*_f = 0.55 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ/ppm = –0.07 (m, 1H), 0.11 (m, 1H), 0.28 (s, 3H), 0.30 (s, 3H), 0.43 (m, 1H), 0.61 (m, 1H), 1.12 (m, 1H), 1.48 (d, *J* 11.0 Hz, 1H), 6.88–6.94 (m, 2H), 7.05–7.11 (m, 1H), 7.14–7.20 (m, 2H), 7.28–7.32 (m, 2H), 7.33–7.40 (m, 3H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ/ppm = –4.2, –3.8, 5.3, 7.8, 12.1, 42.3, 124.5, 127.5, 127.8, 127.9, 129.1, 134.4, 137.8, 144.4. **²⁹Si{¹H} DEPT NMR** (99 MHz, CDCl₃): δ/ppm = –1.88. **IR** (ATR): $\tilde{\nu}/\text{cm}^{-1}$ = 3012, 2927, 2852, 1597, 1485, 1426, 1247, 1110, 809, 730, 697. **HRMS** (APCI) calculated for C₁₂H₁₇Si⁺ [M–C₆H₅]⁺: 189.1101; found: 189.1094.

**4ua**C₁₅H₁₈Si

M = 226.39 g/mol

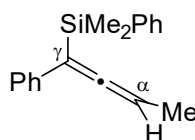
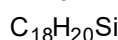
SUPPORTING INFORMATION

Benzylidimethyl(phenyl)silane (4ua). Prepared from *N,N,N*-trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate (**1u**, 85 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4ua** (42 mg, 0.18 mmol, 73%) as a colorless oil. $R_f = 0.43$ (cyclohexane). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta/\text{ppm} = 0.26$ (s, 6H), 2.32 (s, 2H), 6.91–6.98 (m, 2H), 7.04–7.11 (m, 1H), 7.15–7.22 (m, 2H), 7.32–7.40 (m, 3H), 7.44–7.50 (m, 2H). $^{13}\text{C } \{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta/\text{ppm} = -3.3$, 26.3, 124.2, 127.9, 128.2, 128.5, 129.2, 133.9, 138.6, 139.8. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): $\delta/\text{ppm} = -3.77$. IR (ATR): $\tilde{\nu}/\text{cm}^{-1} = 3022$, 2954, 2890, 1598, 1491, 1425, 1247, 1111, 903, 823, 694. HRMS (APCI) calculated for $\text{C}_9\text{H}_{13}\text{Si}^+$ [$\text{M}-\text{C}_6\text{H}_5$] $^+$: 149.0781; found: 149.0781. The spectroscopic data are in accordance with those reported.^[S13]

**4ua**

M = 302.49 g/mol

Benzhydryldimethyl(phenyl)silane (4wa). Prepared from *N,N,N*-trimethyl-1-(naphthalen-2-yl)ethan-1-aminium trifluoromethane-sulfonate (**1w**, 94 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **4wa** (38 mg, 0.13 mmol, 50%) as a colorless oil. $R_f = 0.18$ (cyclohexane). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta/\text{ppm} = 0.30$ (s, 6H), 3.74 (s, 1H), 6.03–7.15 (m, 6H), 7.18–7.23 (m, 4H), 7.27–7.30 (m, 4H), 7.32–7.37 (m, 1H). $^{13}\text{C } \{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta/\text{ppm} = -3.0$, 45.9, 125.3, 127.7, 128.3, 129.1, 129.2, 134.6, 137.7, 142.4. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): $\delta/\text{ppm} = -2.89$. IR (ATR): $\tilde{\nu}/\text{cm}^{-1} = 3022$, 2955, 1595, 1491, 1446, 1248, 1111, 1031, 806, 734, 696. HRMS (APCI) calculated for $\text{C}_{15}\text{H}_{17}\text{Si}^+$ [$\text{M}-\text{C}_6\text{H}_5$] $^+$: 225.1094; found: 225.1102.

**6**

M = 264.44 g/mol

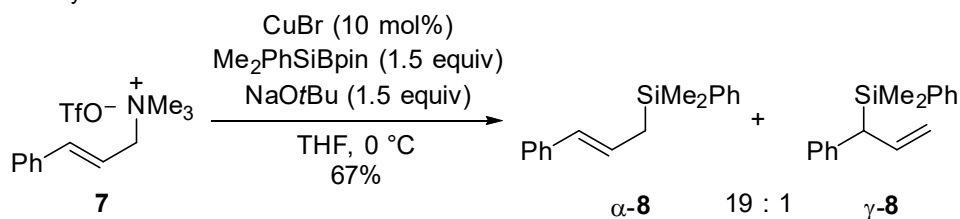
Dimethyl(phenyl)(1-phenylbuta-1,2-dien-1-yl)silane (6). Prepared from *N,N,N*-trimethyl-4-phenylbut-3-yn-2-aminium (**5**, 84 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **6** (32 mg, 0.12 mmol, 48%, $\alpha:\gamma = 1:>99$) as a yellow oil. $R_f = 0.38$ (cyclohexane). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta/\text{ppm} = 0.45$ (s, 6H), 1.76 (d, $J = 7.0$ Hz, 3H), 5.19 (q, $J = 7.0$ Hz, 1H), 7.09–7.14 (m, 1H), 7.17–7.24 (m, 4H), 7.33–7.39 (m, 3H), 7.56–7.63 (m, 2H). $^{13}\text{C } \{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta/\text{ppm} = -1.8$, -1.7 , 13.4, 82.2, 98.0, 126.0, 127.7, 127.8, 128.3, 129.1, 133.9, 137.6, 138.7, 210.7. $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3): $\delta/\text{ppm} = -9.02$. IR (ATR): $\tilde{\nu}/\text{cm}^{-1} = 3050$, 2955, 1925, 1733, 1593, 1426, 1250, 1116, 1048, 788, 728, 695. HRMS (APCI) calculated for $\text{C}_{12}\text{H}_{15}\text{Si}^+$ [$\text{M}-\text{C}_6\text{H}_5$] $^+$: 187.0938; found: 187.0940. The spectroscopic data are in accordance with those reported.^[S14]

(R)-Dimethyl(phenyl)(1-phenylbuta-1,2-dien-1-yl)silane [(R)-6]. Prepared from (*S*)-*N,N,N*-trimethyl-4-phenylbut-3-yn-2-aminium [(*S*)-**5**, 84 mg, 0.25 mmol, 1.00 equiv] according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound (*S*)-**6** (37 mg, 0.14 mmol, 56%) as a light-yellow oil. **Optical rotation:** $[\alpha] = +10$ ($c = 0.6$, CHCl_3 , 20% ee). The enantiomeric excess of (*S*)-**6** was determined by HPLC analysis on a chiral stationary phase (Daicel Chiralcel OJ-H column, column temperature 20 °C, solvent *n*-heptane:isopropanol = 99:1, flow rate 0.7 mL/min, $\lambda = 230$ nm): $t_R = 7.2$ min for (*R*)-**6**, $t_R = 9.3$ min for (*S*)-**6**. The absolute configuration was assigned by comparison with the reported optical rotation of (*R*)-**6**.^[S14]

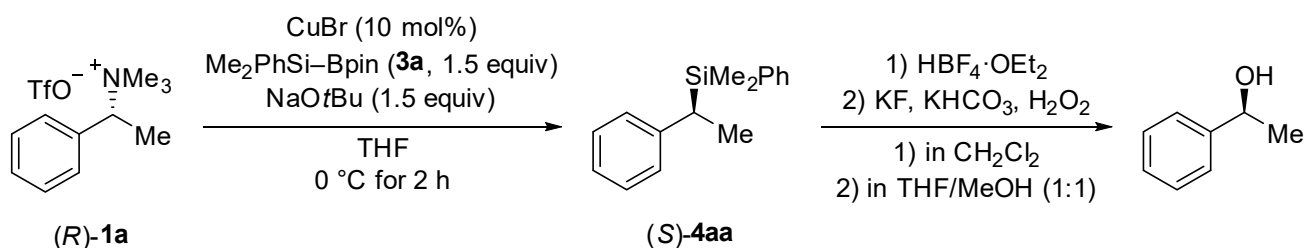
SUPPORTING INFORMATION

6. Silylation of an Allylic Ammonium Salt

The following reaction was not included in the original manuscript. Hence we were only able to synthesize primary allylic ammonium salts, the stereospecificity of this reaction could not be investigated yet. Efforts to synthesize an enantioenriched secondary allylic substrate are still ongoing in our laboratory.



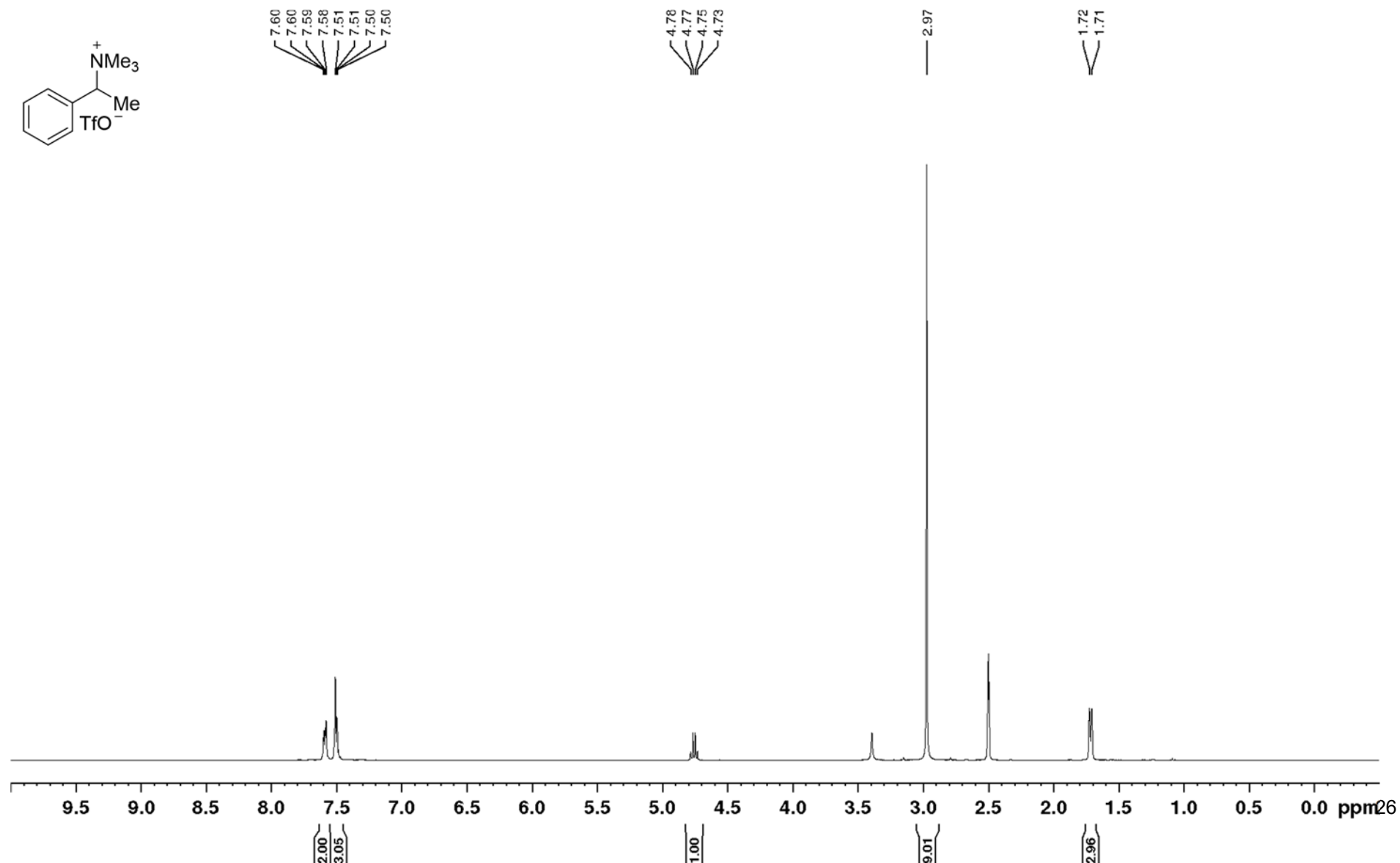
Cinnamyl dimethyl(phenyl)silane (8). Prepared from (*E*)-*N,N,N*-trimethyl-3-phenylprop-2-en-1-aminium trifluoromethanesulfonate (**7**, 81 mg, 0.25 mmol, 1.00 equiv) according to **GP2**. The crude material was purified according to **GP3**. Purification by flash column chromatography on silica gel using cyclohexane afforded the title compound **7** (42 mg, 0.17 mmol, 67%, α : γ = 19:1) as an off-white oil. *R_f* = 0.42 (cyclohexane). **¹H NMR** (500 MHz, CDCl₃): δ /ppm = 0.31 (s, 6H), 1.89 (d, *J* = 6.9 Hz, 2H), 6.15–6.28 (m, 2H), 7.11–7.19 (m, 1H), 7.23–7.28 (m, 4H), 7.33–7.39 (m, 3H), 7.49–7.56 (m, 2H). Selected signals for the γ -isomer: δ /ppm = 0.24 (s, 3H), 0.26 (s, 3H), 3.14 (d, *J* = 9.6 Hz, 1H), 4.86–4.96 (m, 2H), 6.03–6.14 (m, 1H). **¹³C {¹H} NMR** (126 MHz, CDCl₃): δ /ppm = -3.2, 23.2, 125.7, 126.4, 127.3, 128.0, 128.5, 129.1, 129.2, 133.8, 138.5, 138.7. **²⁹Si {¹H} DEPT NMR** (99 MHz, CDCl₃): δ /ppm = -4.06. **IR** (ATR): $\tilde{\nu}$ /cm⁻¹ = 2953, 2921, 2850, 1702, 1596, 1425, 1249, 1113, 826, 729, 693. **HRMS** (APCI) calculated for C₁₇H₂₀Si⁺ [M+H]⁺: 253.1407; found: 253.1404. The spectroscopic data are in accordance with those reported.^[S15]

7. Assignment of the Absolute Configuration of Dimethyl(phenyl)(1-phenylethyl)silane (**4aa**)

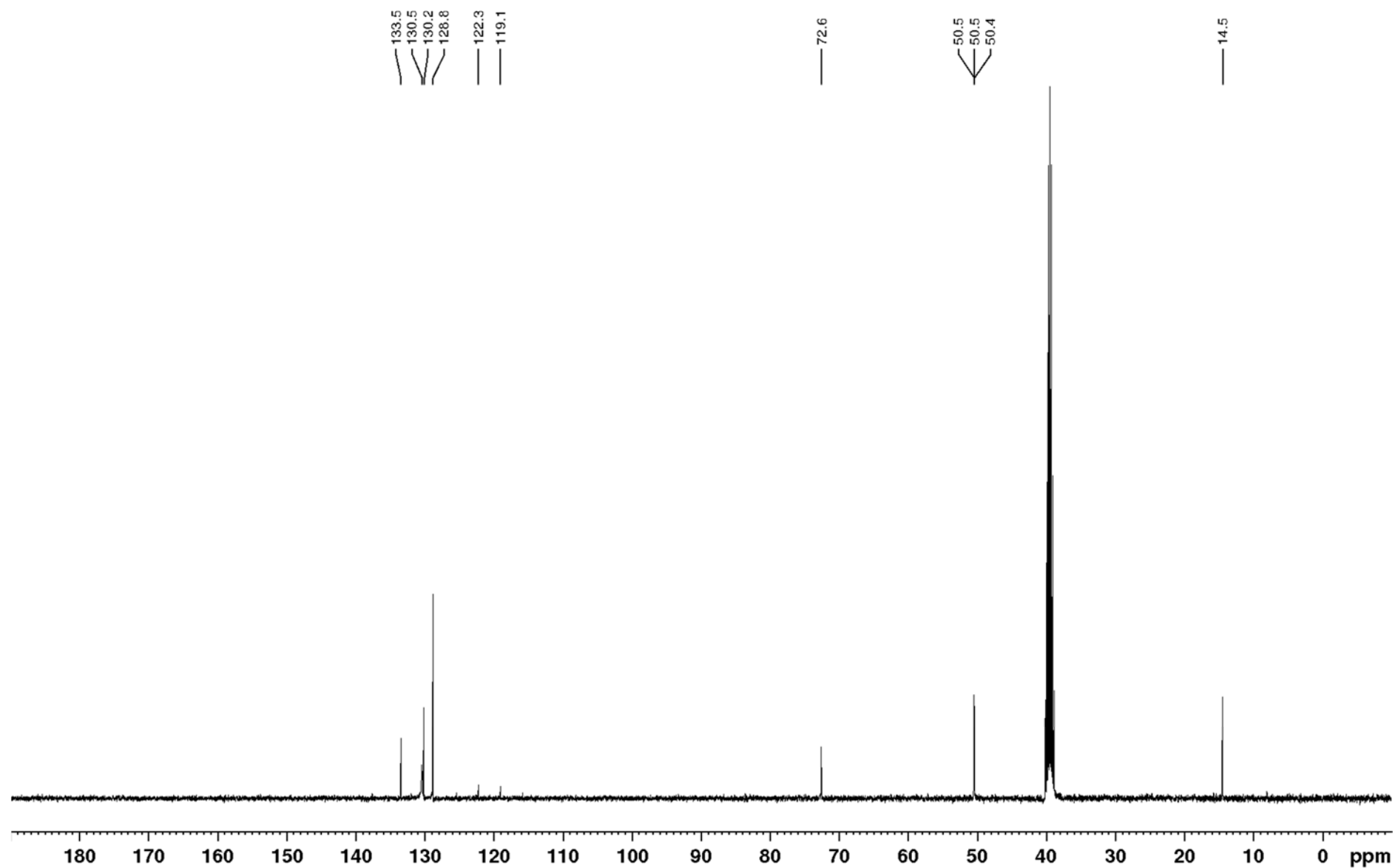
The TAMAO-FLEMING oxidation was conducted according to a modified literature procedure.^[S16] A flame-dried SCHLENK-tube charged with crude **4aa** [24 mg, 0.10 mmol, resulting from reaction of enantioenriched (*R*)-**1a** under our standard conditions] was filled with nitrogen gas. At 25 °C, CH₂Cl₂ (1.0 mL) and HBF₄·OEt₂ (0.23 mL, 0.28 mmol) were sequentially added. The mixture was allowed to stir at rt for 16 h and was then quenched with water (5 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL), dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. To the crude product in a 6-mL glass vial, THF (0.4 mL), MeOH (0.4 mL), KF (23, 0.40 mmol), KHCO₃ (100 mg, 1.00 mmol), and H₂O₂ (113 mg, 1 mmol) were sequentially added at rt. The mixture was stirred for 24 h at 40 °C and then quenched by addition of saturated aqueous Na₂S₂O₃ solution (2 mL). The phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography, and the optical rotation value was measured: [α] = –35.2 (c = 0.5, CHCl₃, e.r. 99.8:0.2). The reported optical rotation for (*S*)-phenylethanol is α = –39.0 (c = 1.0, CHCl₃, e.r. 98.5:1.5).^[S17] Therefore the absolute configuration of the silane is *S*, in accordance with the postulated S_N2 mechanism.

SUPPORTING INFORMATION

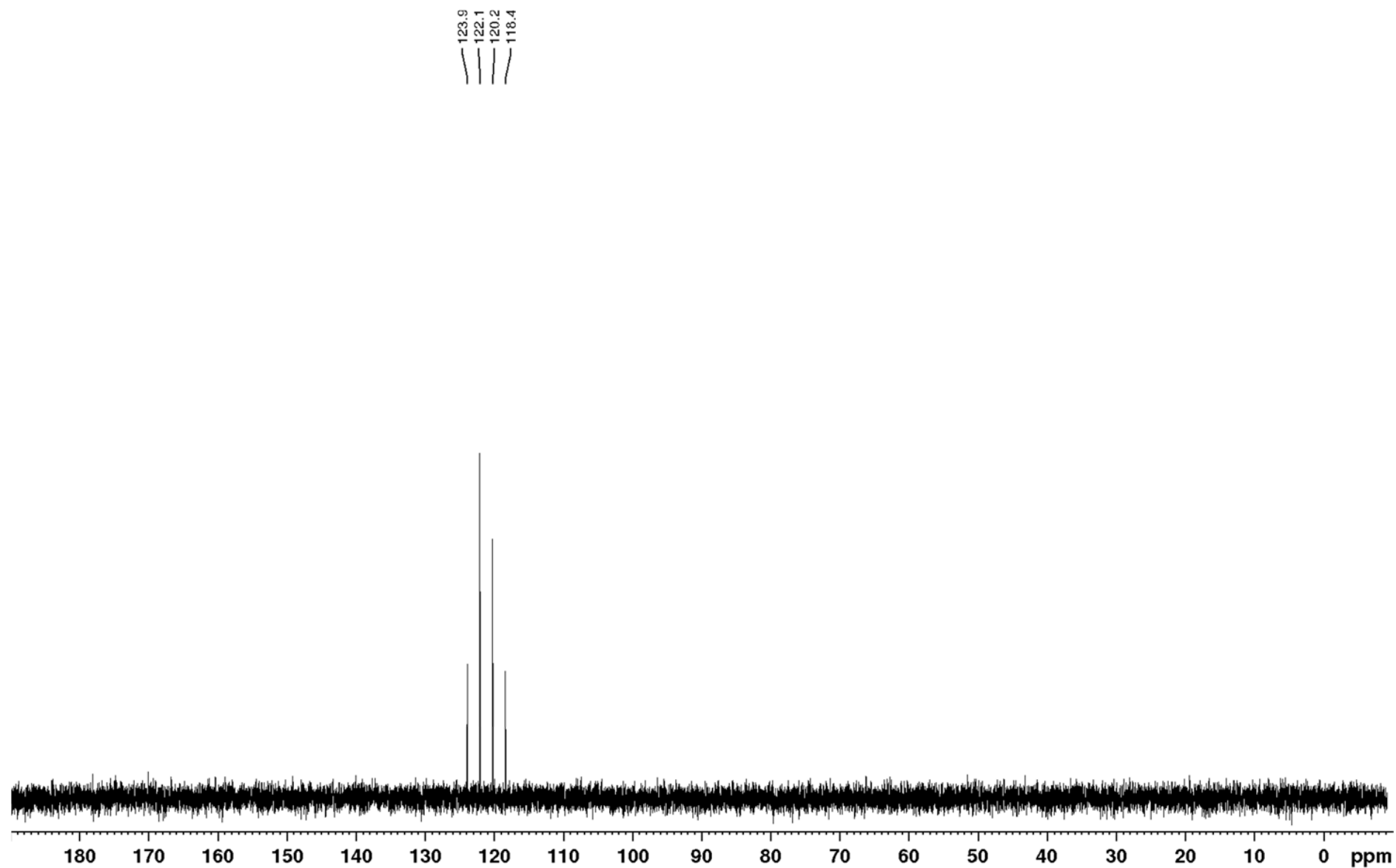
8. NMR Spectra

N,N,N-trimethyl-1-phenylethan-1-aminium trifluoromethanesulfonate (1a)¹H NMR (500 MHz, DMSO-*d*₆):

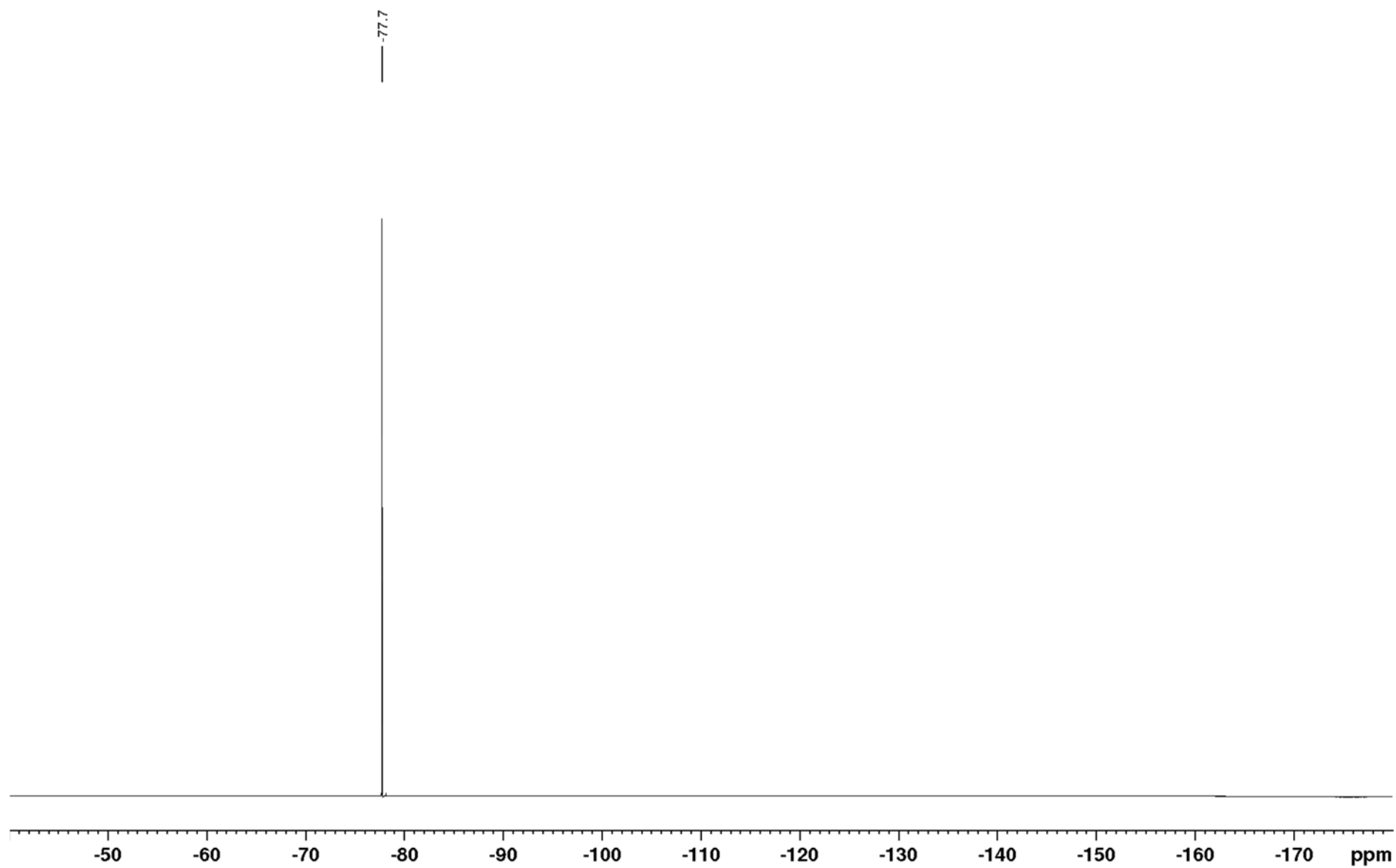
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

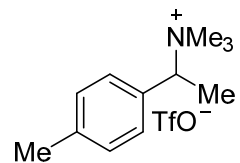
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

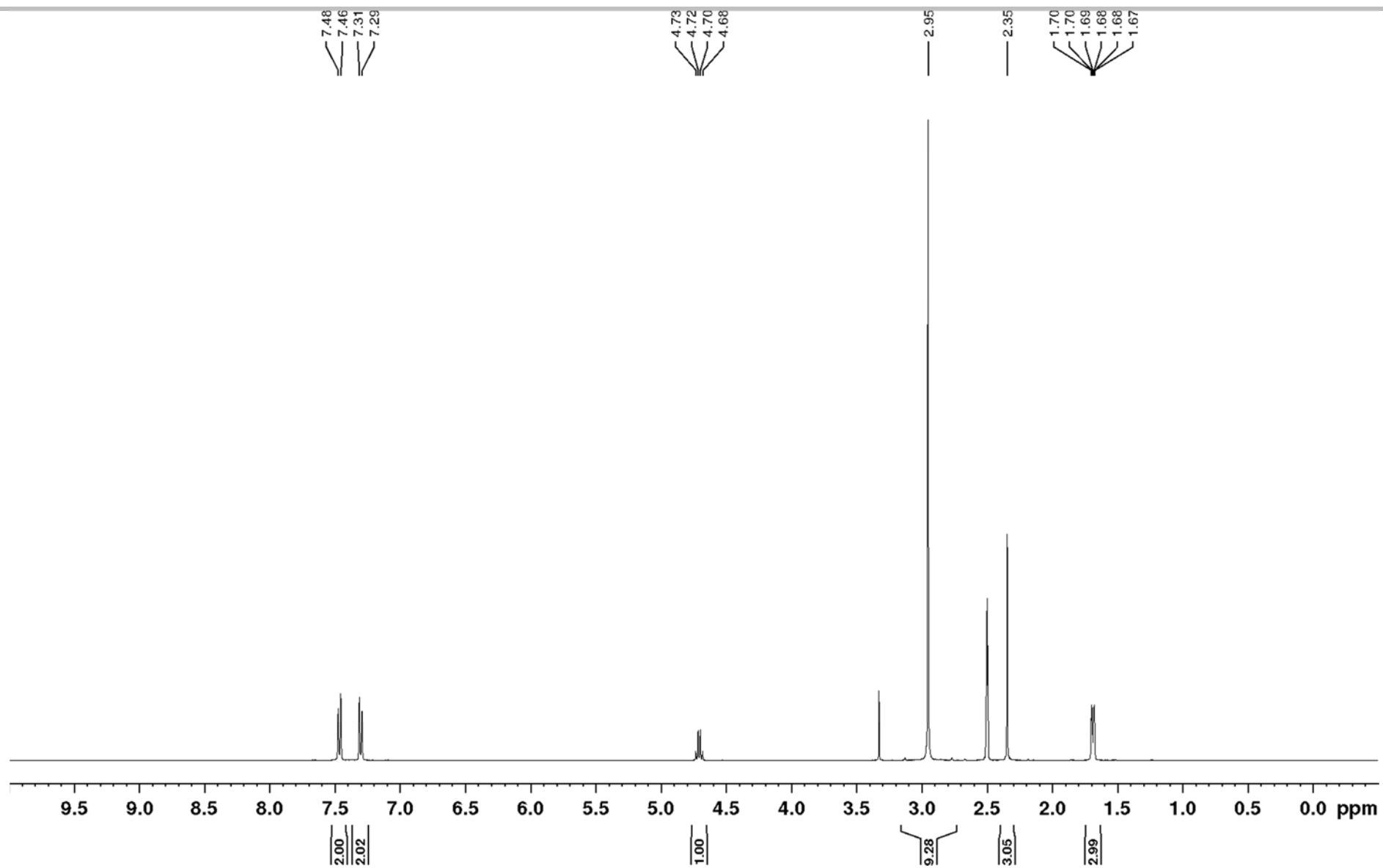
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

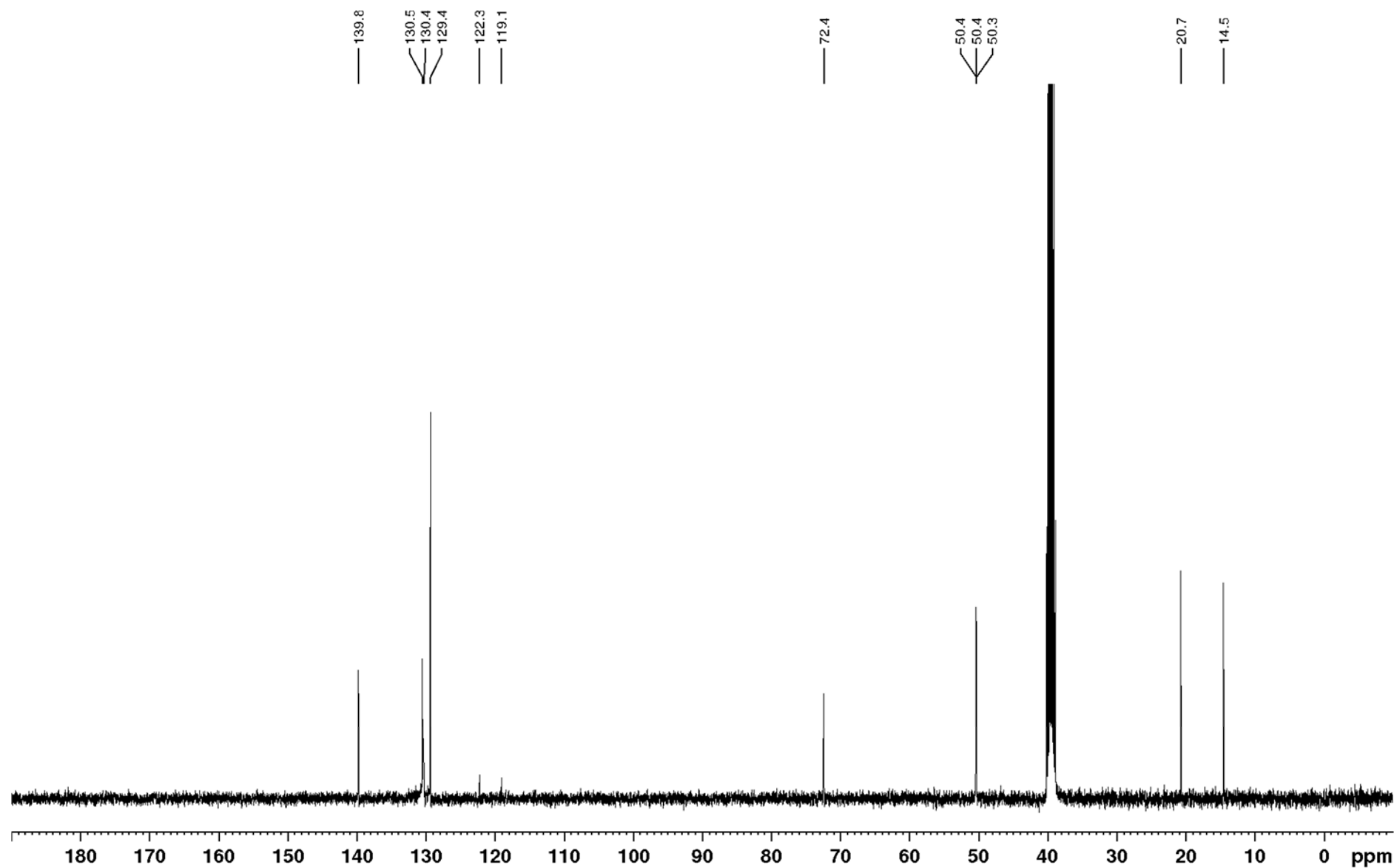
SUPPORTING INFORMATION

***N,N,N*-trimethyl-1-(*p*-tolyl)ethan-1-aminium trifluoromethanesulfonate (1b)**¹H NMR (400 MHz, DMSO-*d*₆):

SUPPORTING INFORMATION



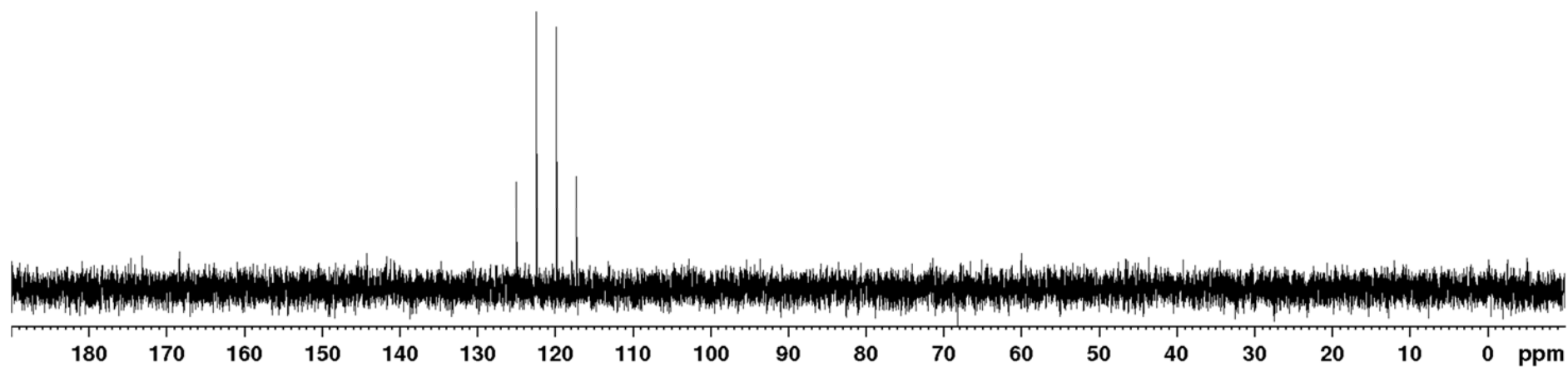
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO- d_6):

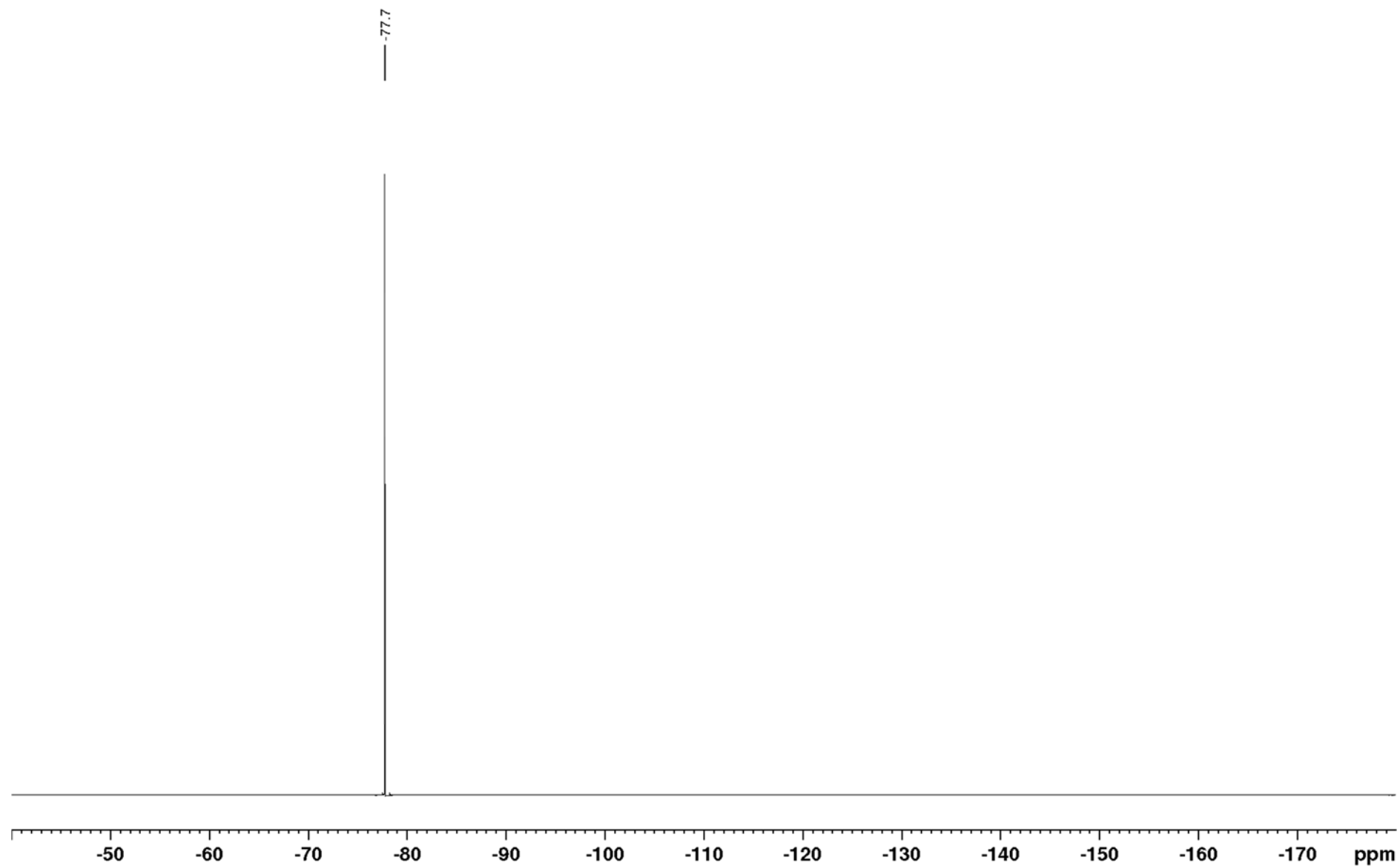
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

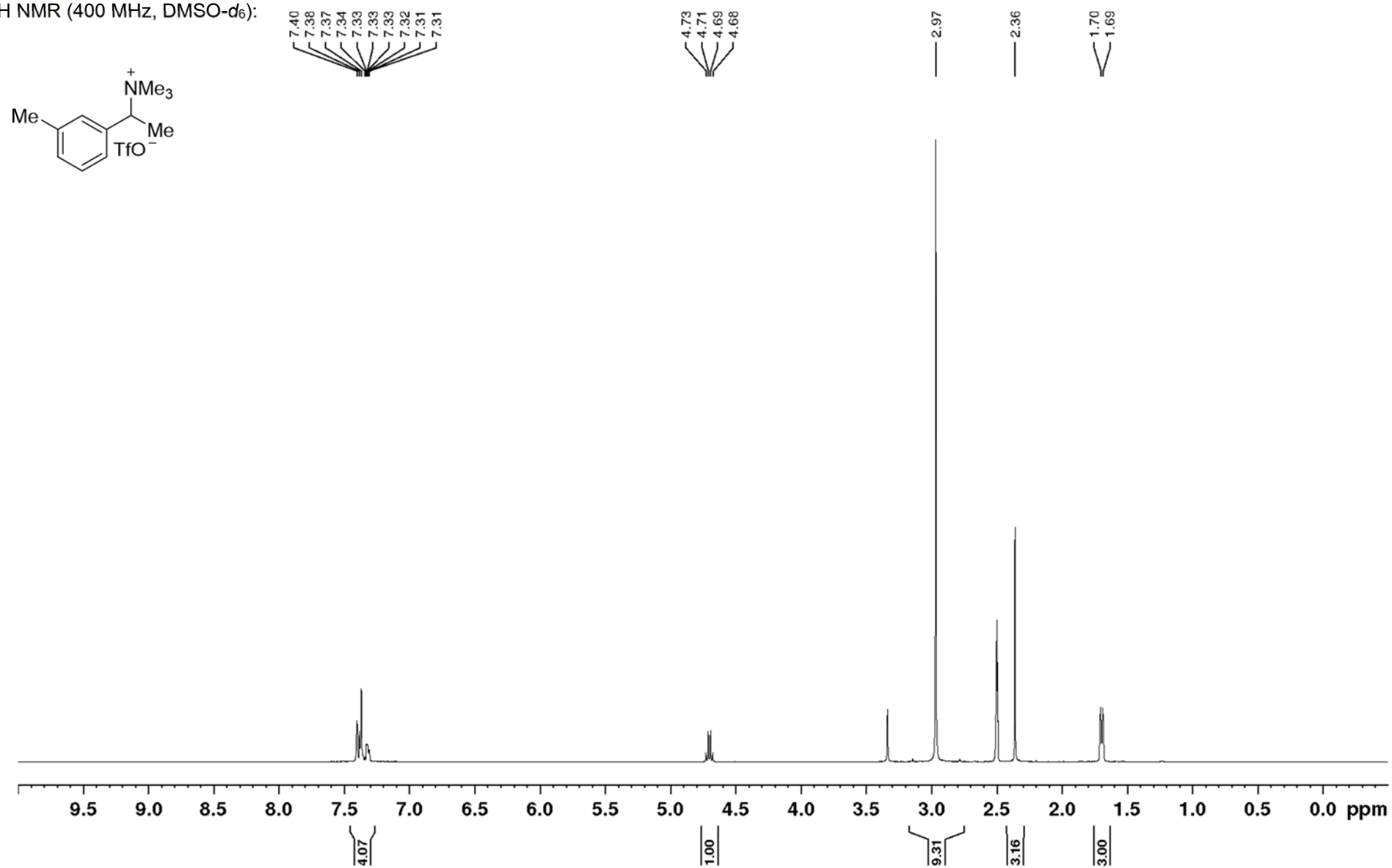
125.0
122.4
119.9
117.3



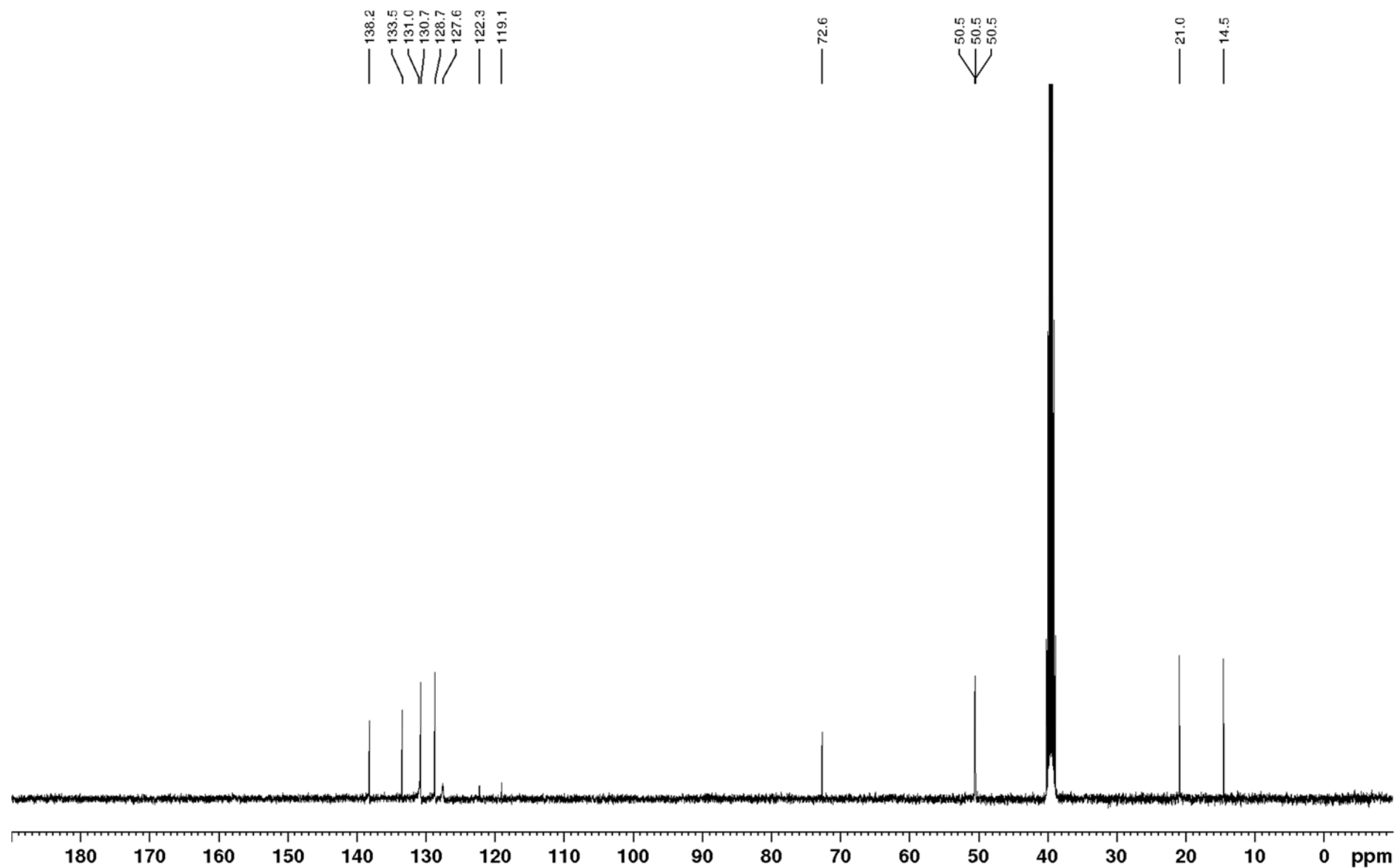
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

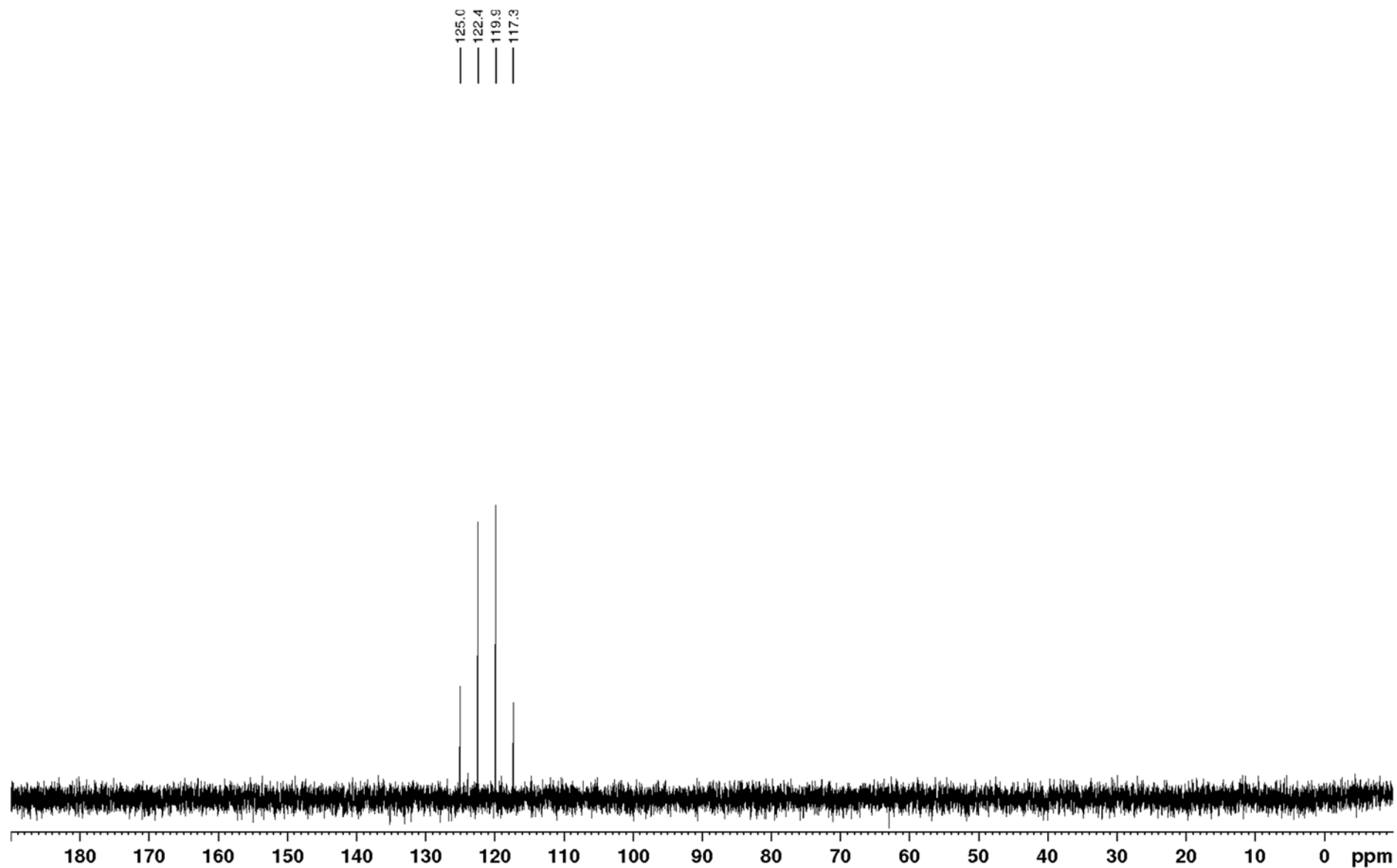
SUPPORTING INFORMATION

***N,N,N*-trimethyl-1-(*m*-tolyl)ethan-1-aminium trifluoromethanesulfonate (1c)**¹H NMR (400 MHz, DMSO-*d*₆):

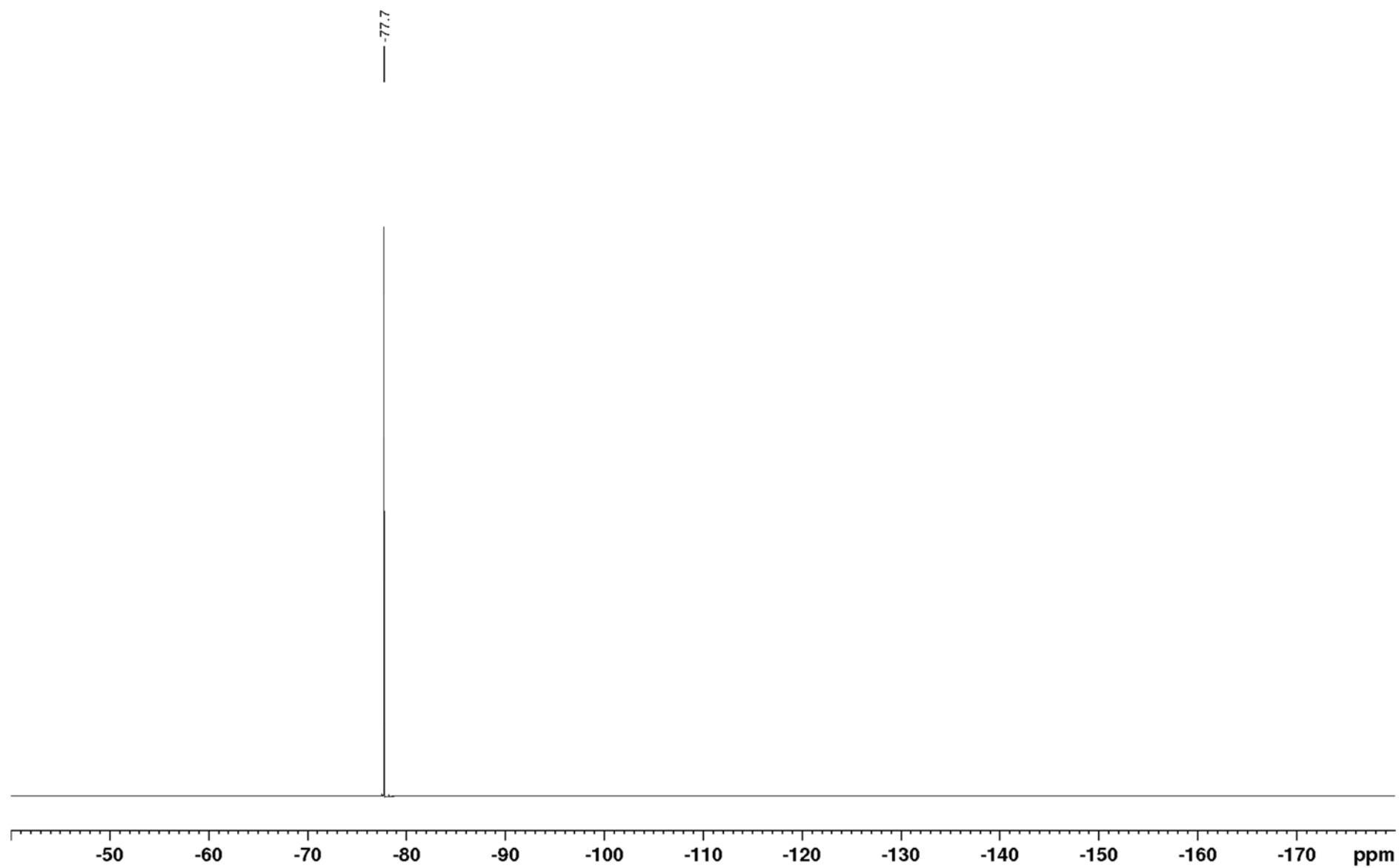
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO- d_6):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

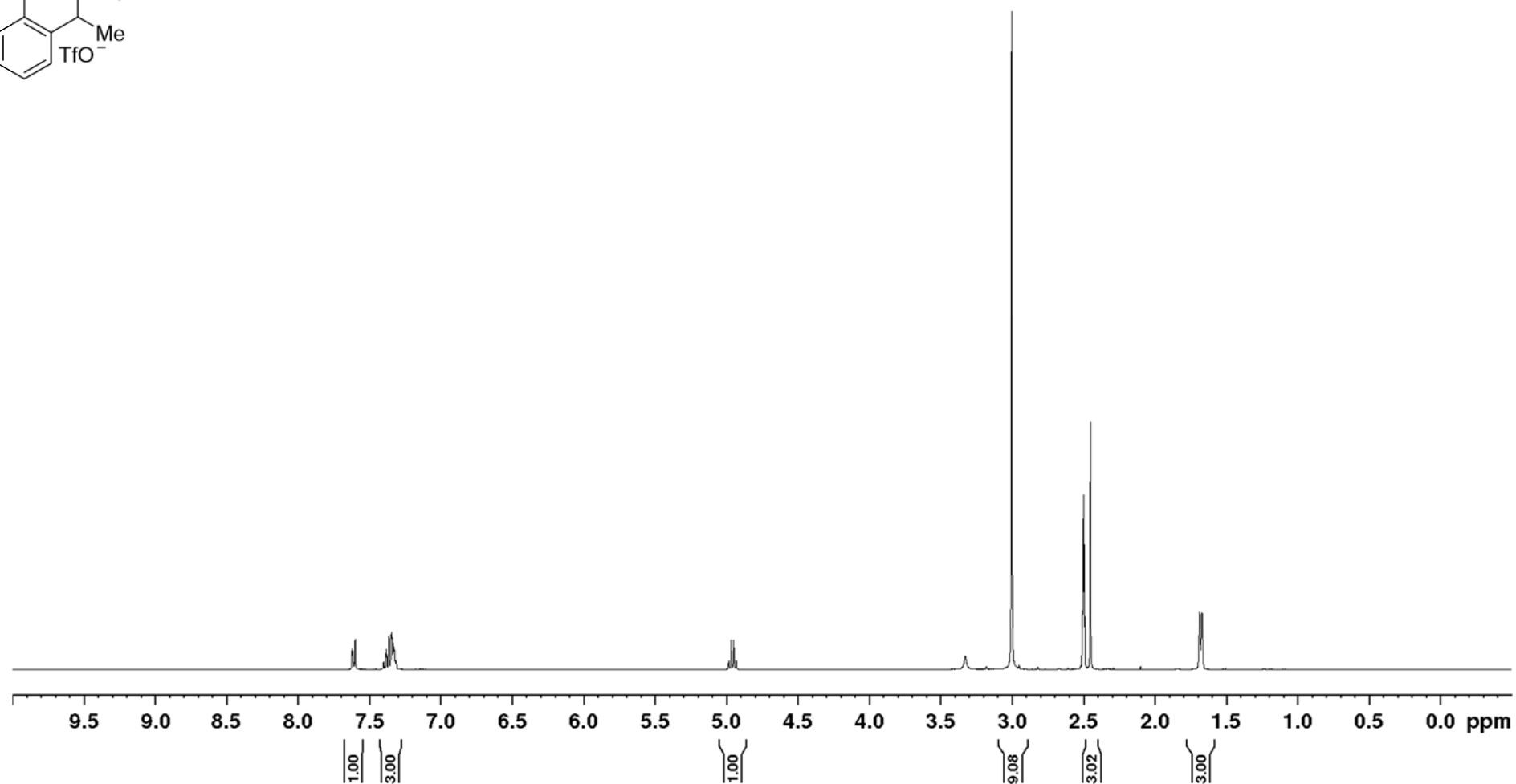
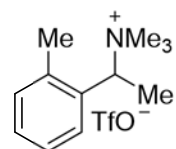
***N,N,N*-trimethyl-1-(*m*-tolyl)ethan-1-aminium trifluoromethanesulfonate (1c)**¹H NMR (400 MHz,7.62
7.62
7.60
7.40
7.40
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.314.98
4.97
4.95
4.93

3.00

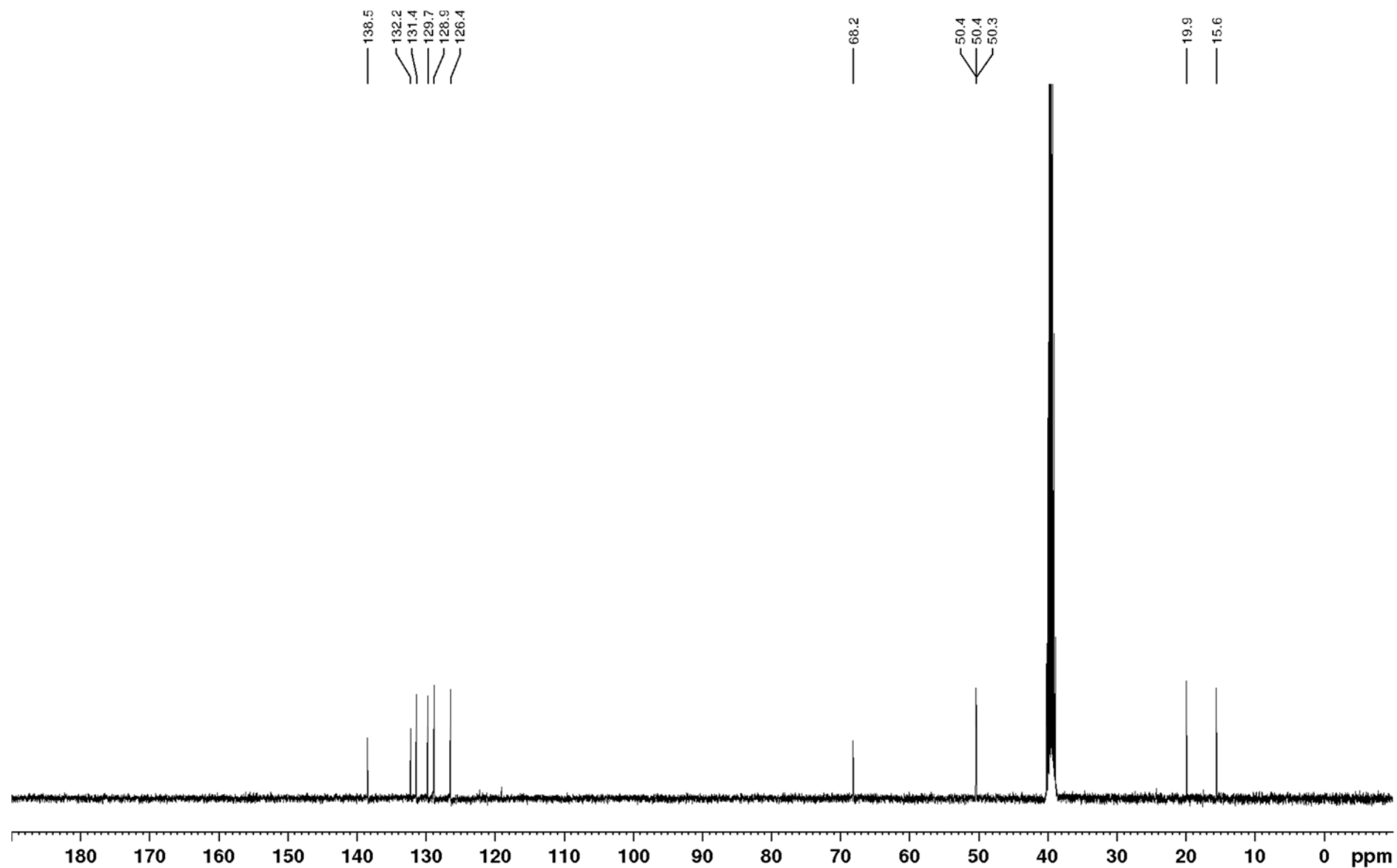
2.45

1.69

1.67

DMSO-*d*₆):

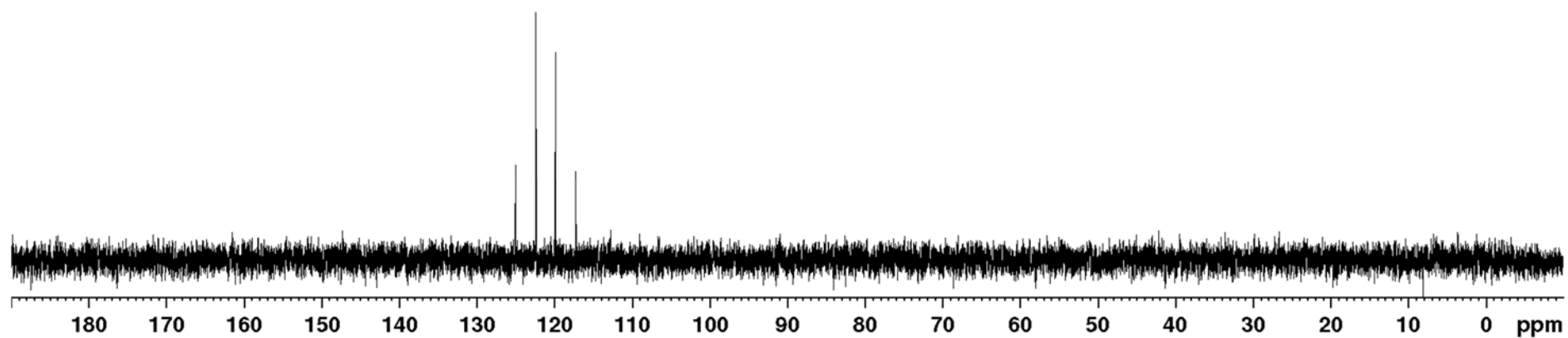
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

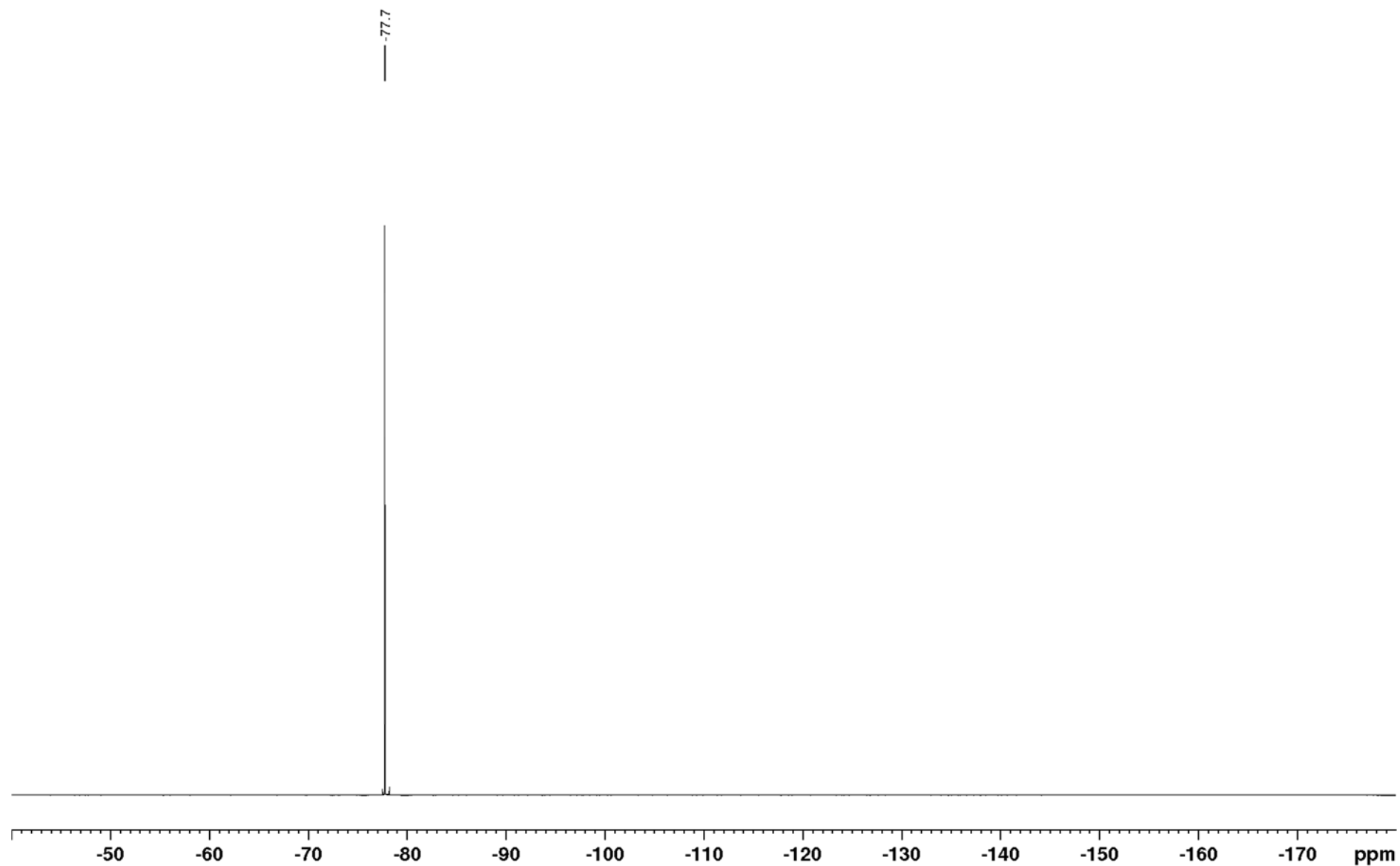
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

125.0
122.4
119.9
117.3



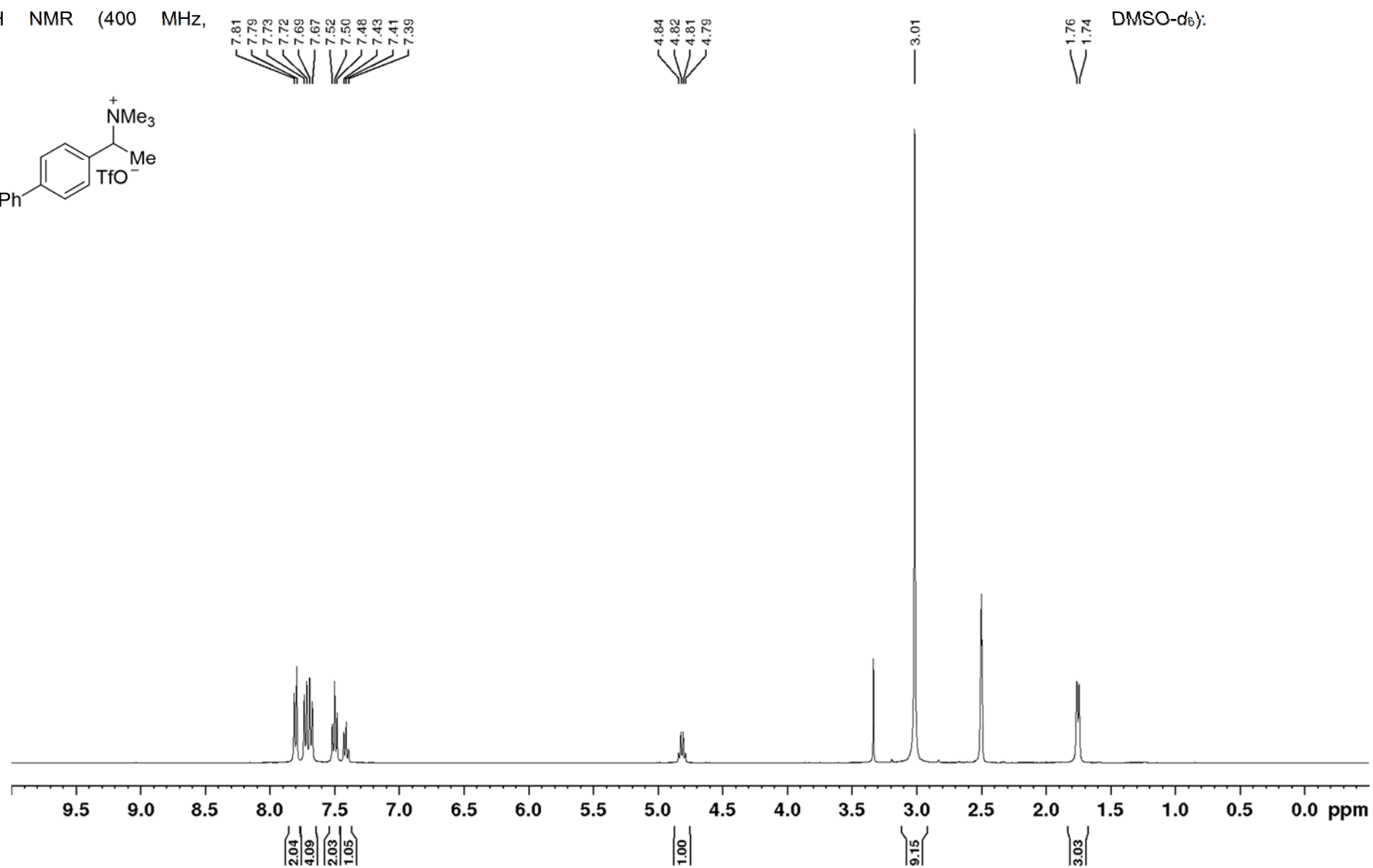
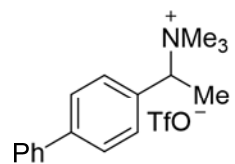
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

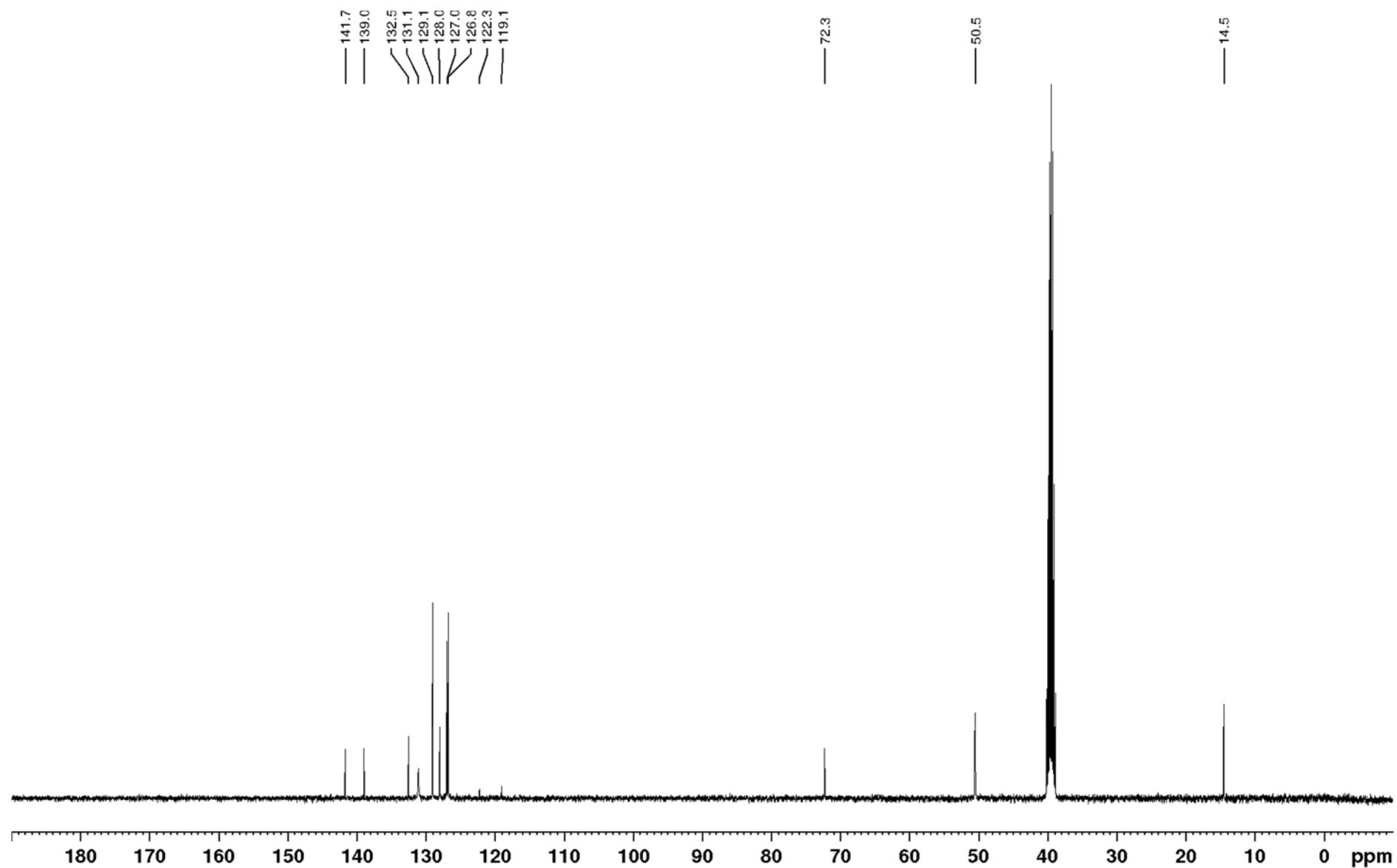
SUPPORTING INFORMATION

([1,1'-Biphenyl]-4-yl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1e)¹H NMR (400 MHz,7.81
7.79
7.73
7.72
7.69
7.67
7.52
7.50
7.48
7.43
7.41
7.394.84
4.82
4.81
4.79

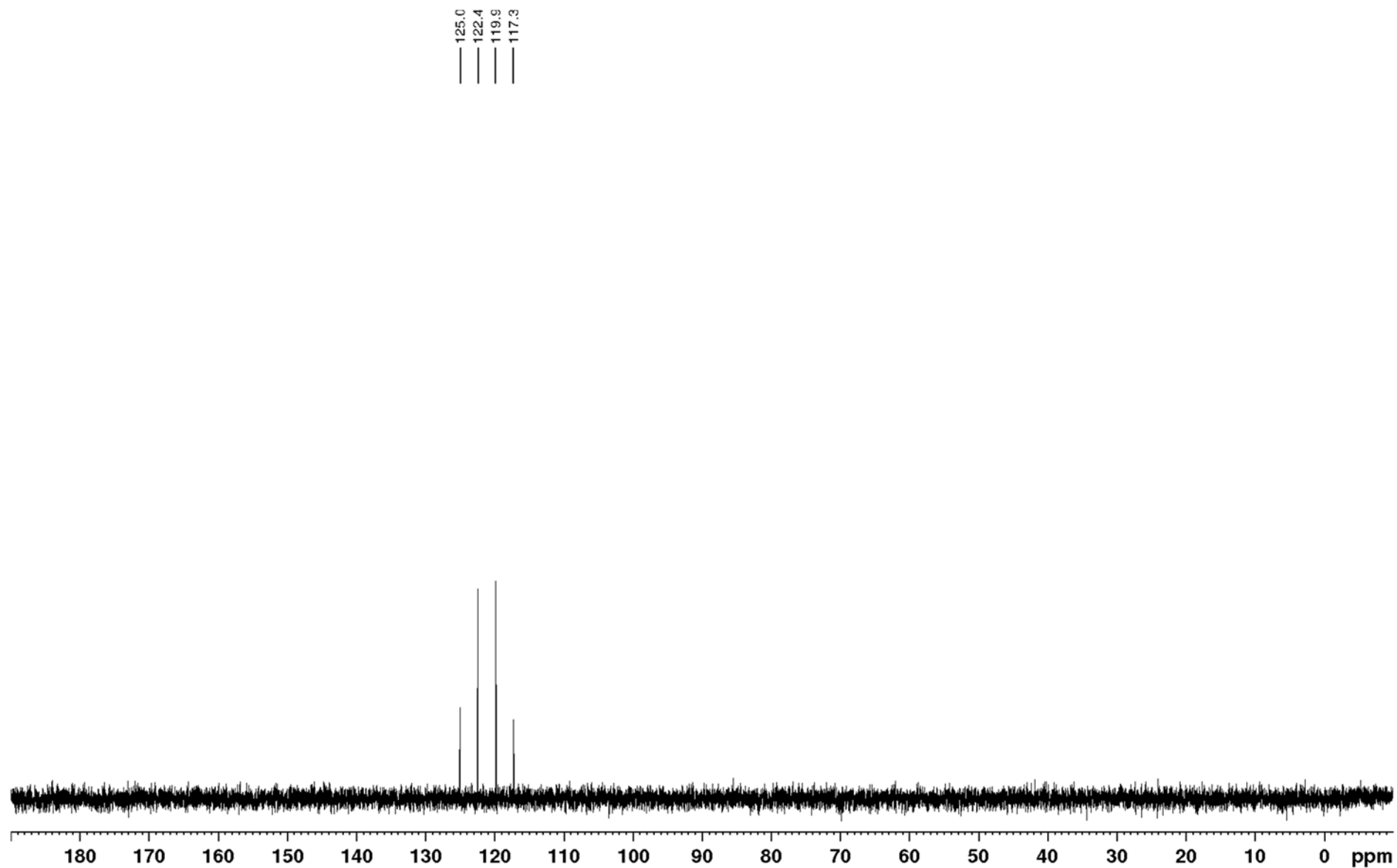
3.01

1.76
1.74DMSO-*d*₆):

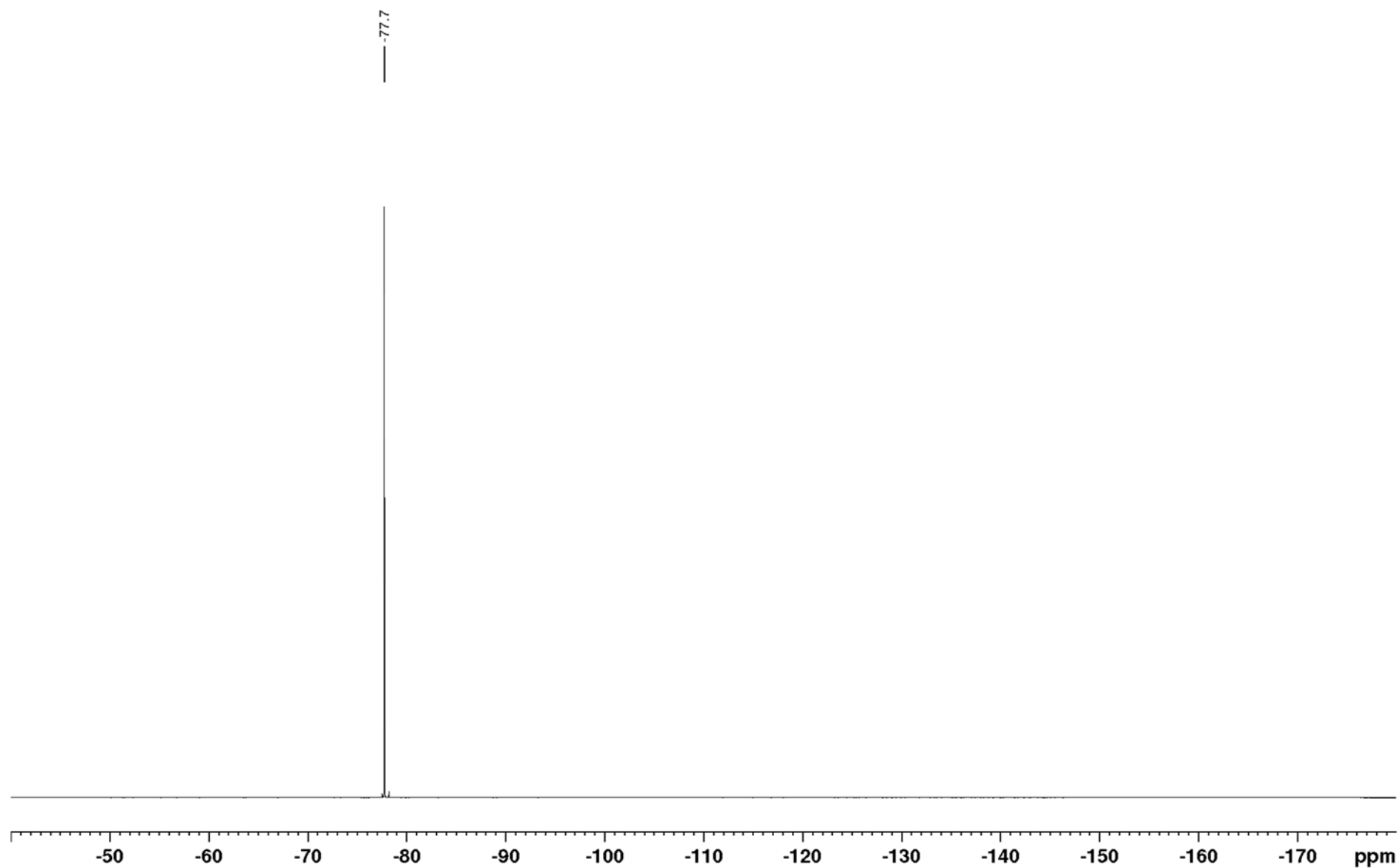
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

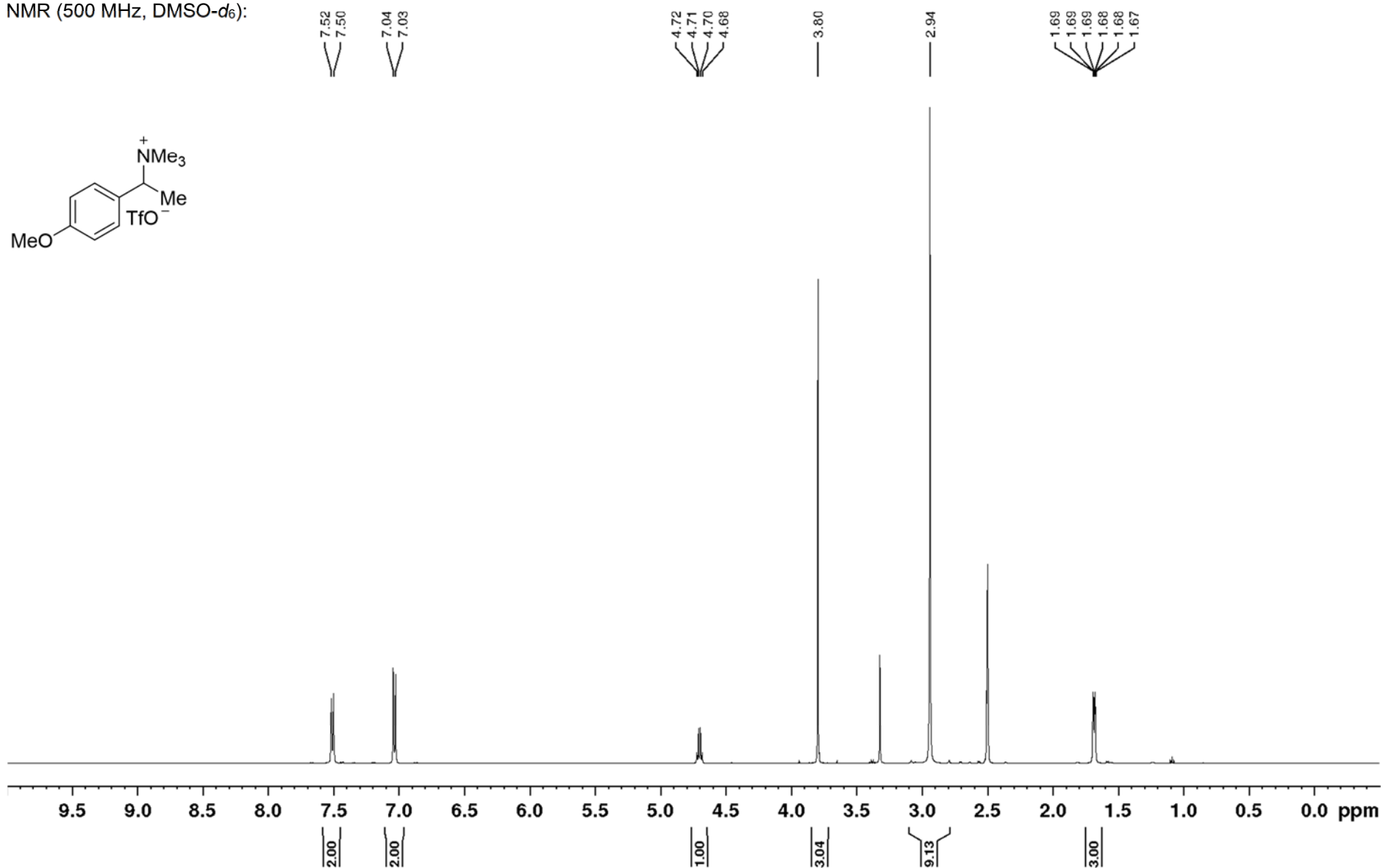
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

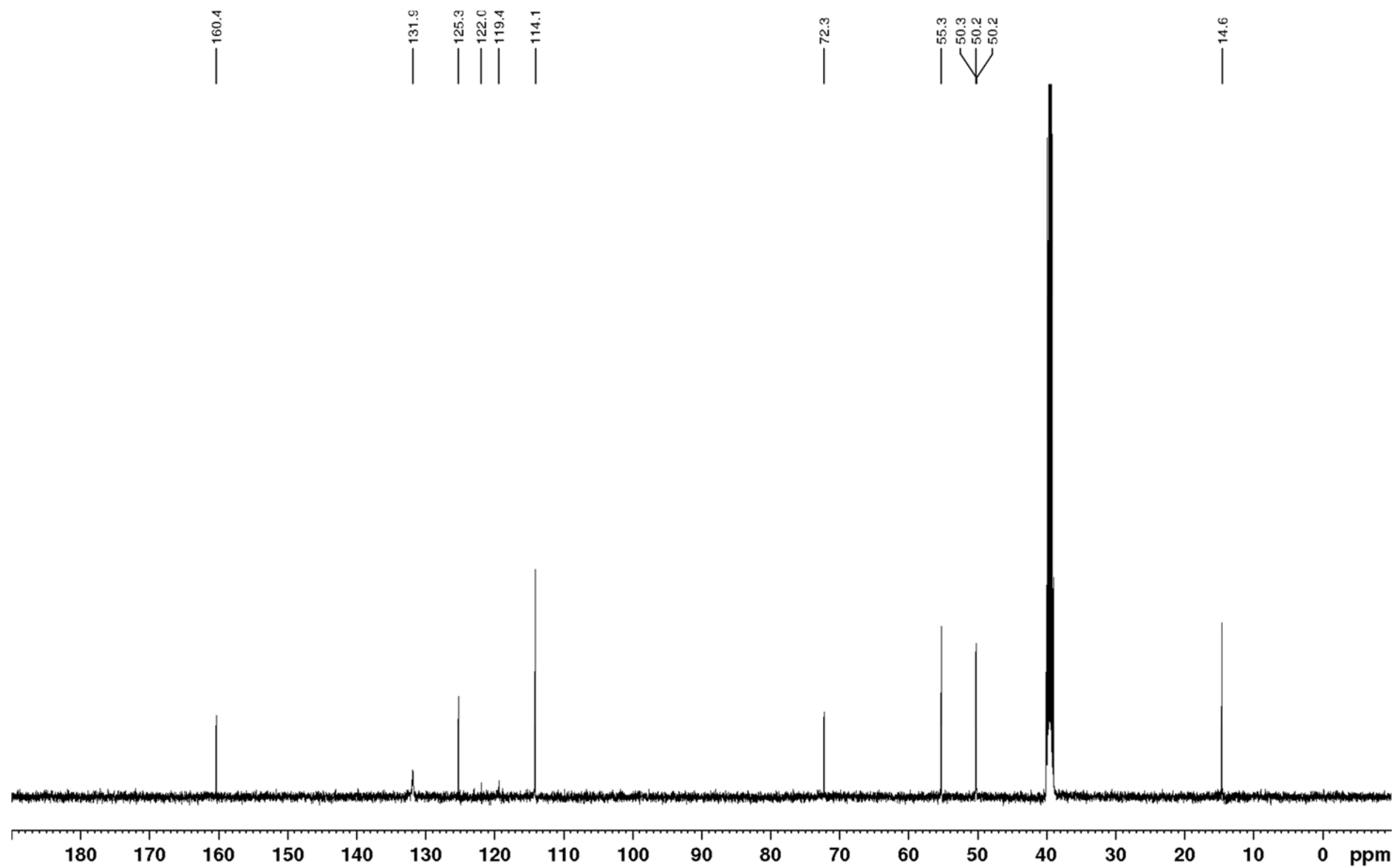
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

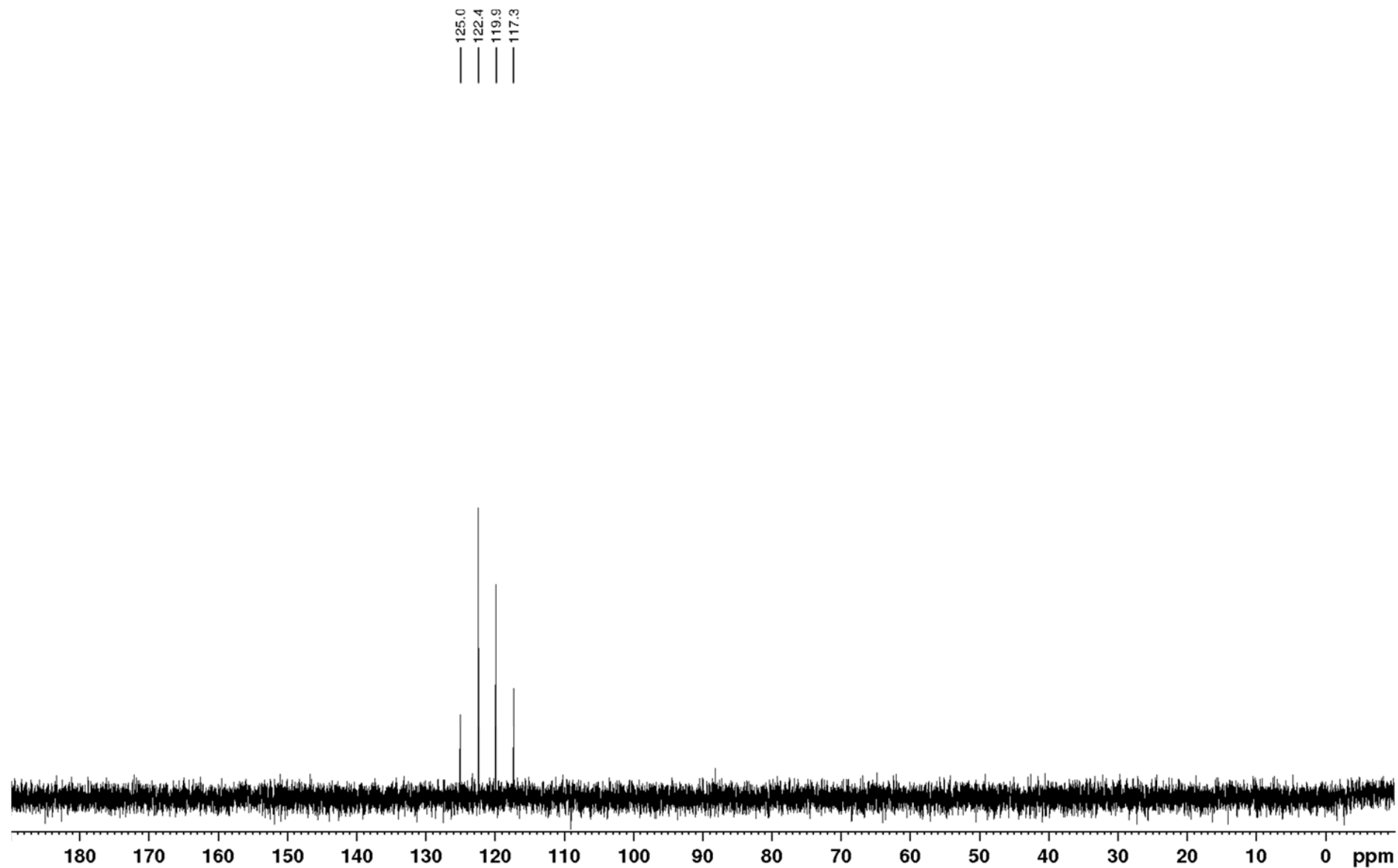
SUPPORTING INFORMATION

1-(4-Methoxyphenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1f)¹H NMR (500 MHz, DMSO-*d*₆):

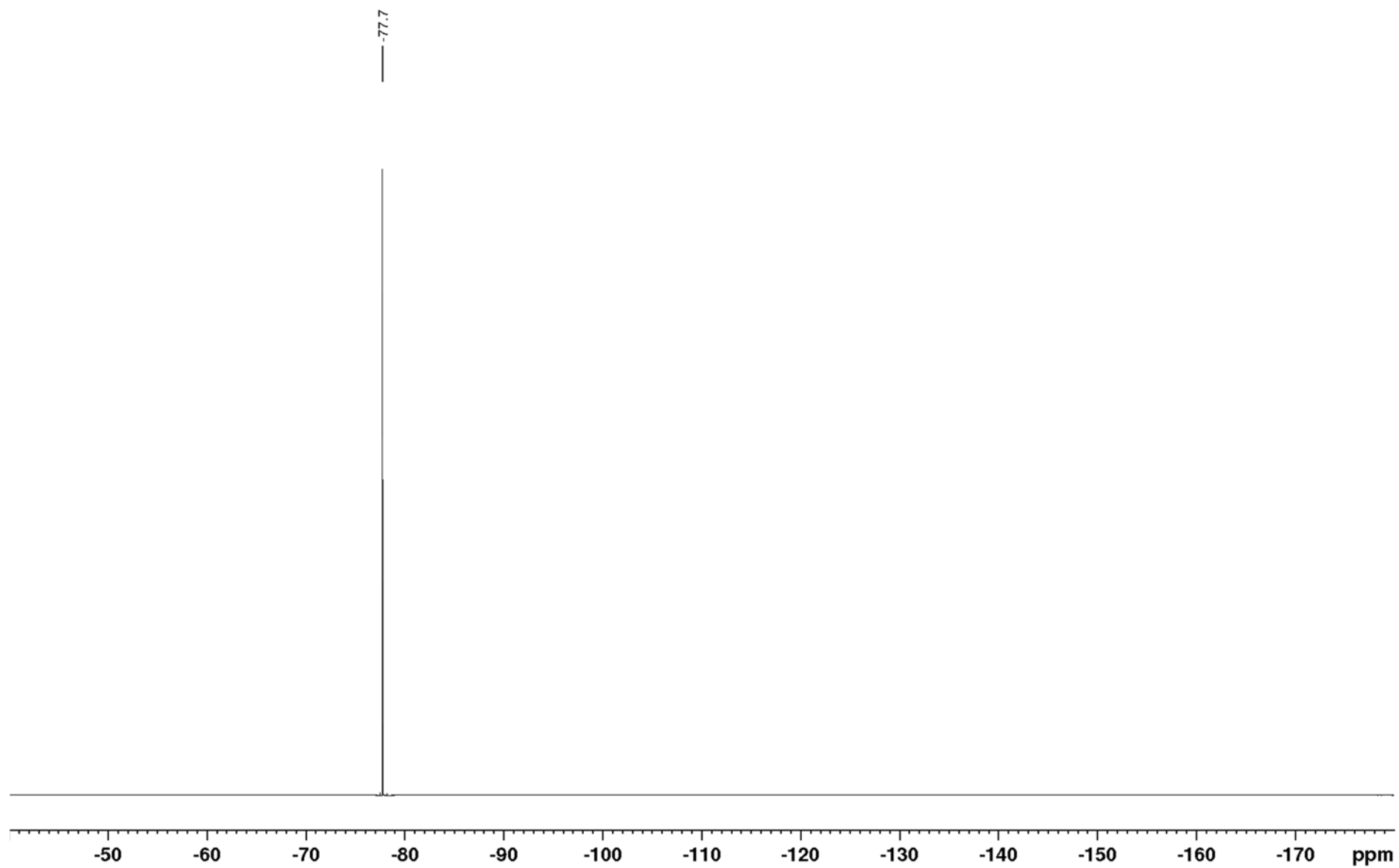
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

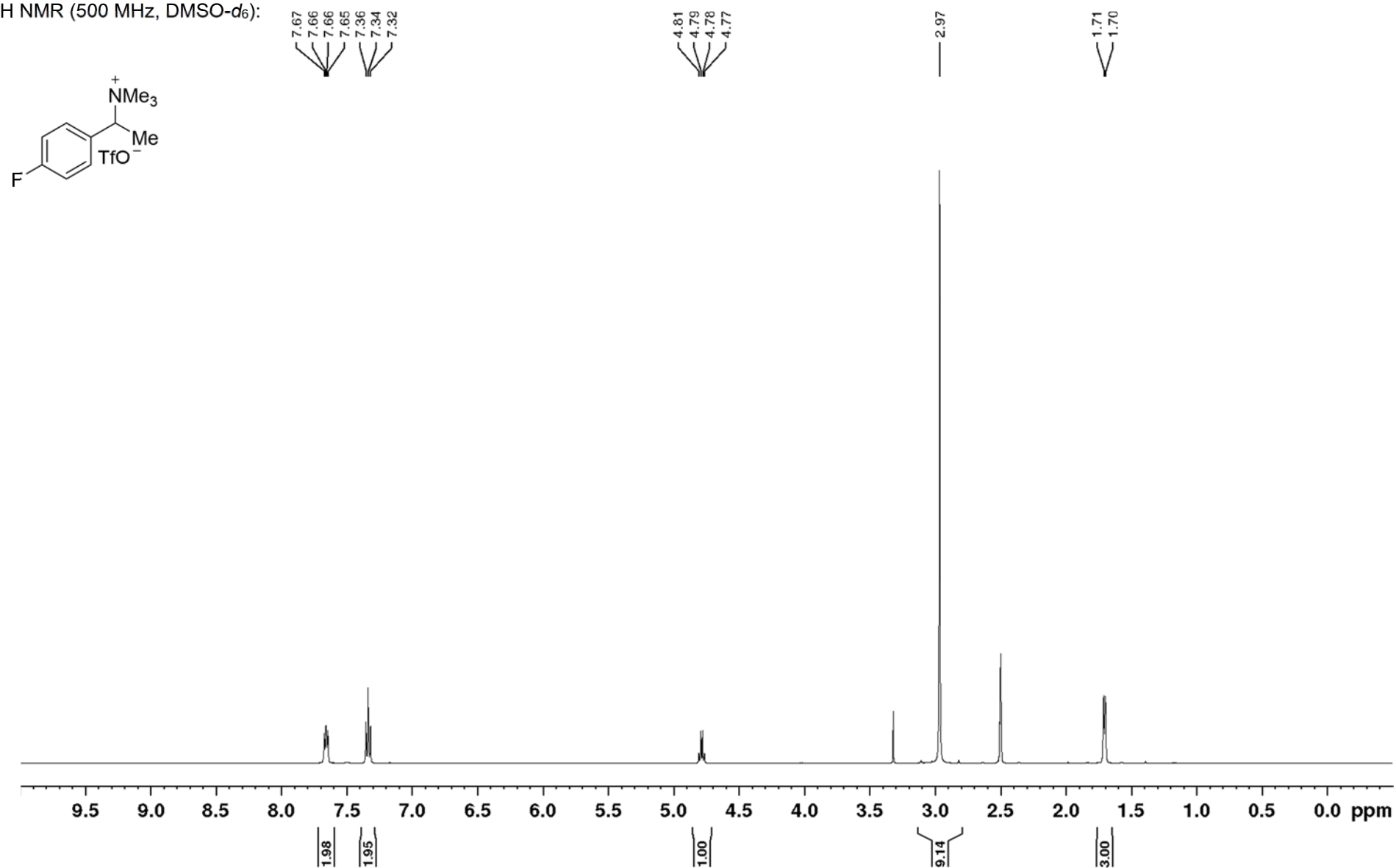
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

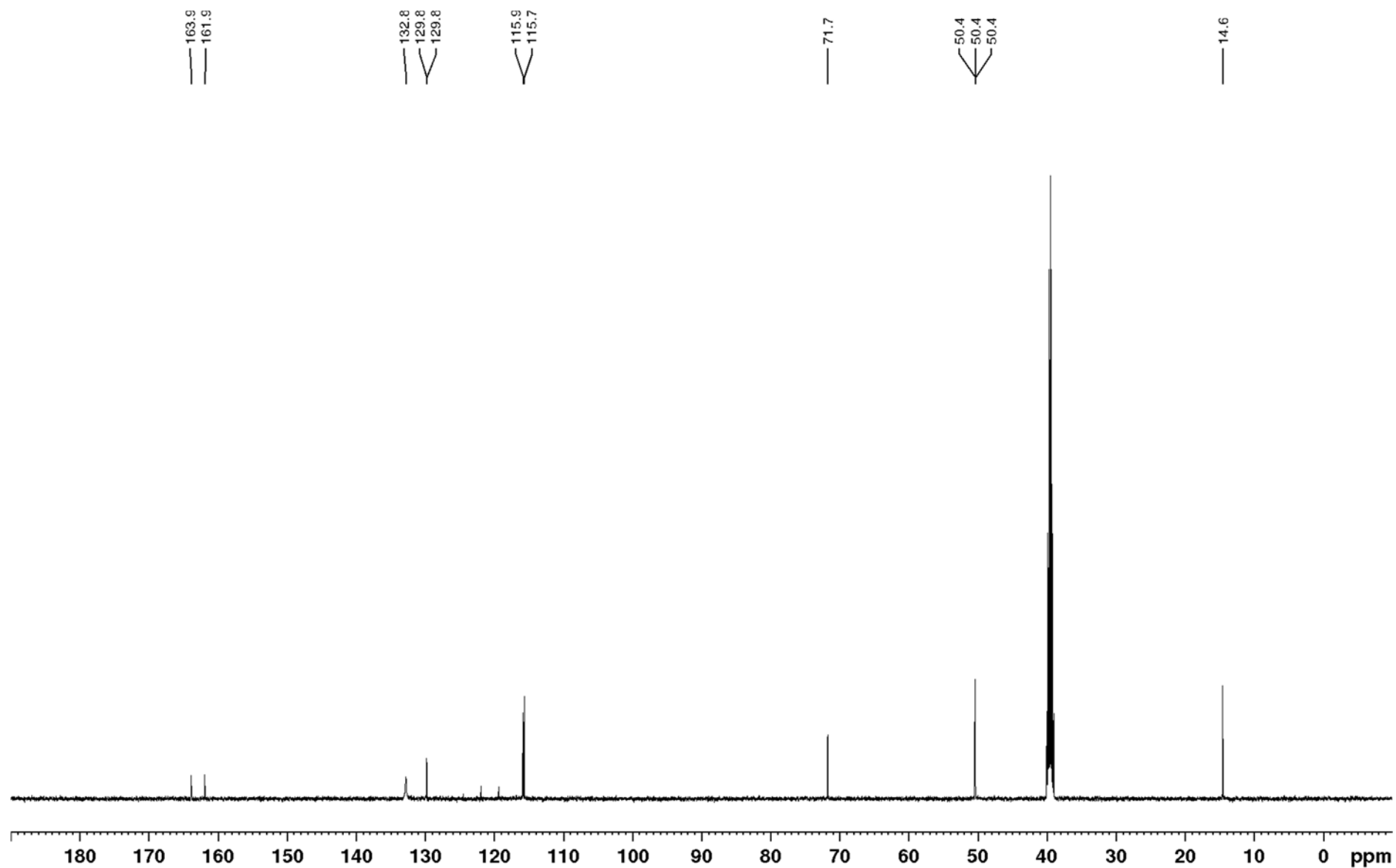
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

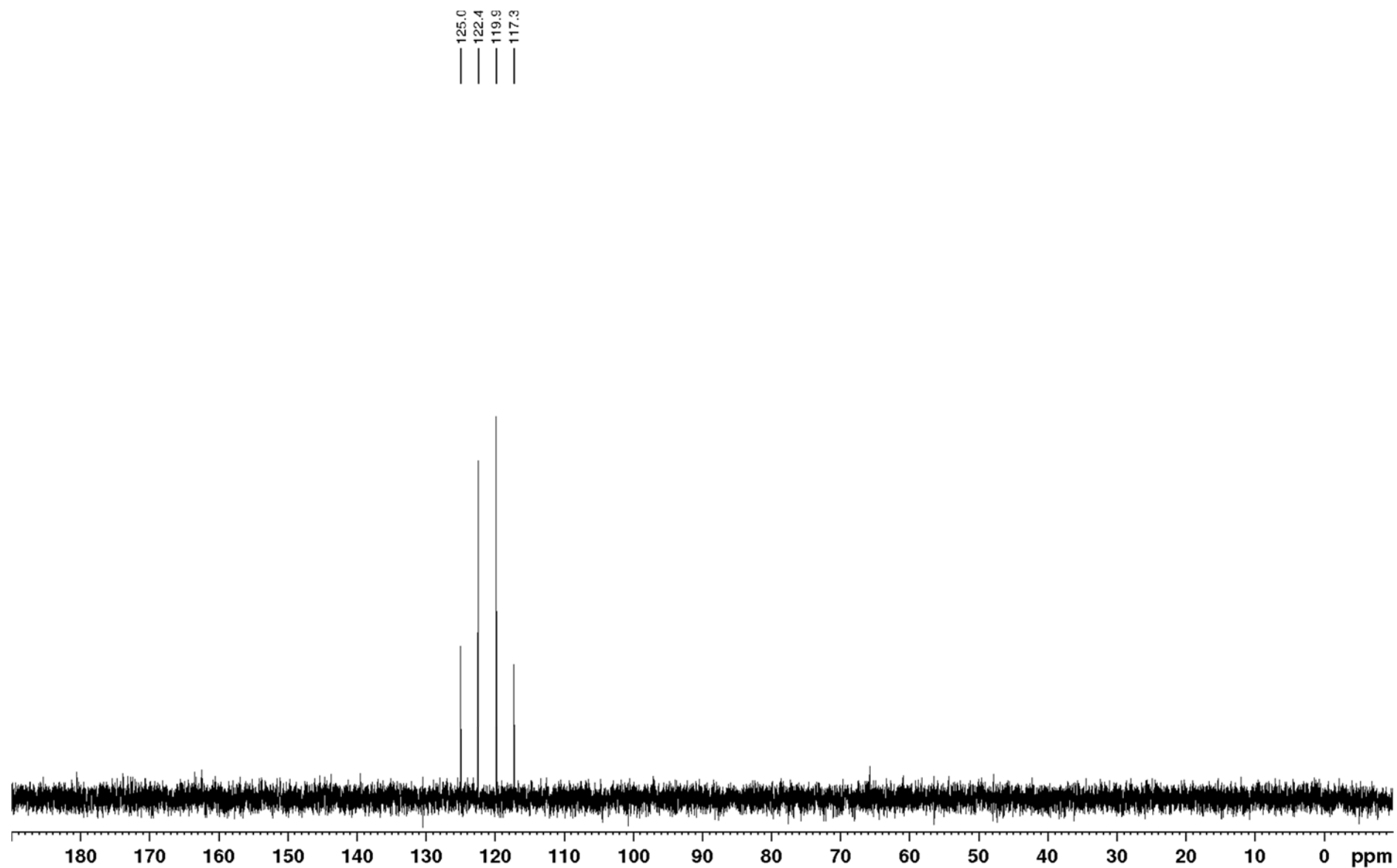
SUPPORTING INFORMATION

1-(4-Fluorophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1g)¹H NMR (500 MHz, DMSO-*d*₆):

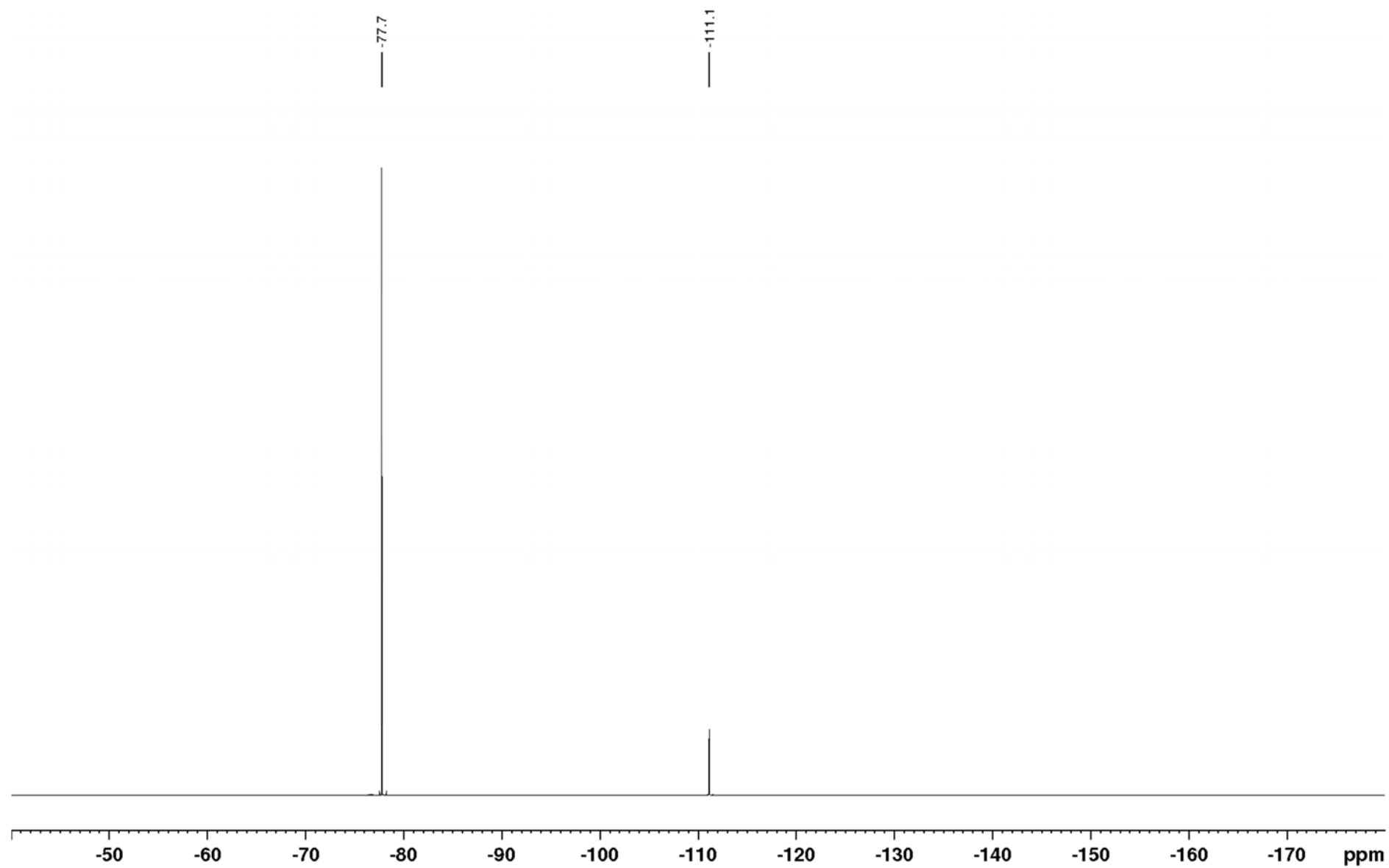
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

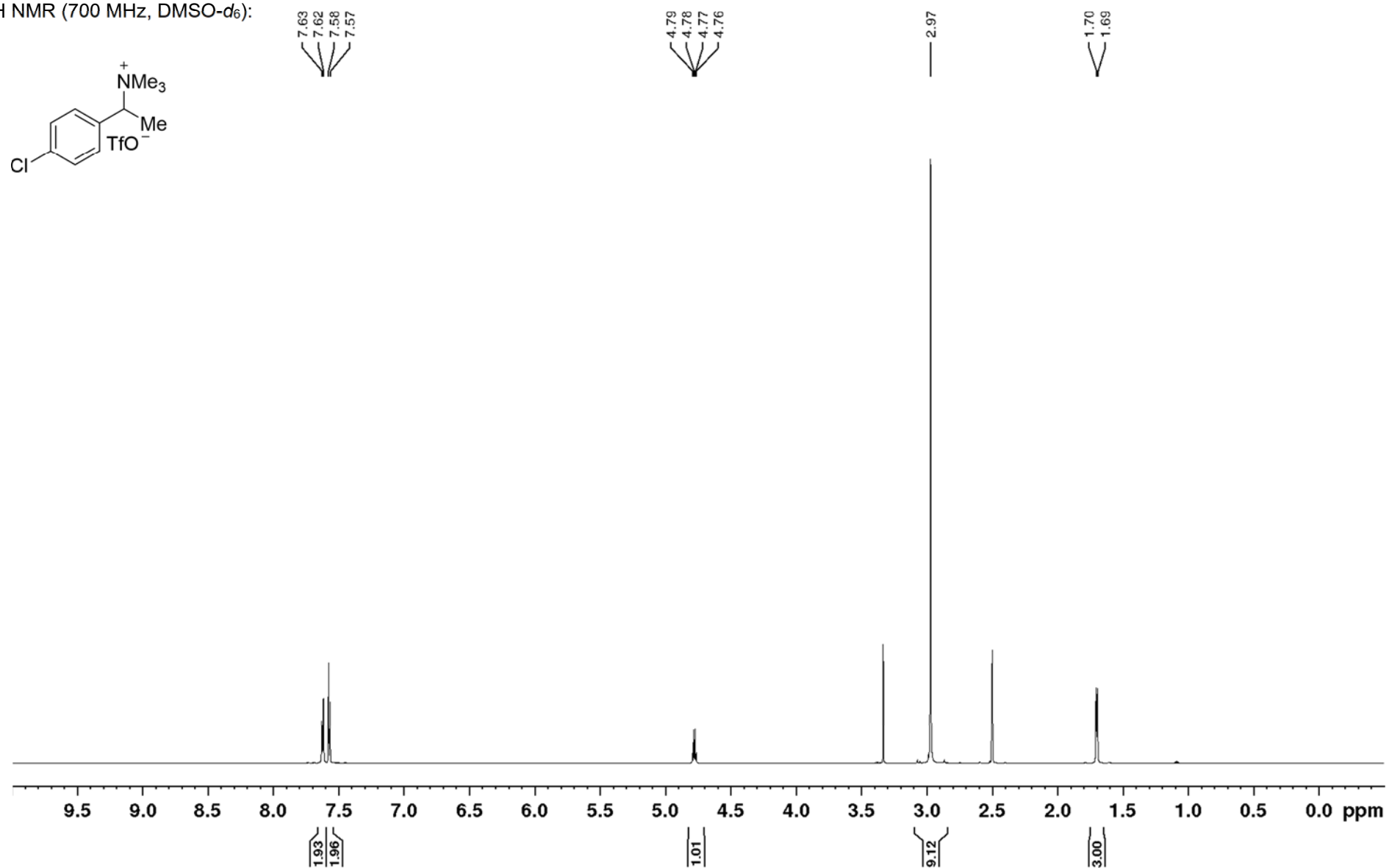
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

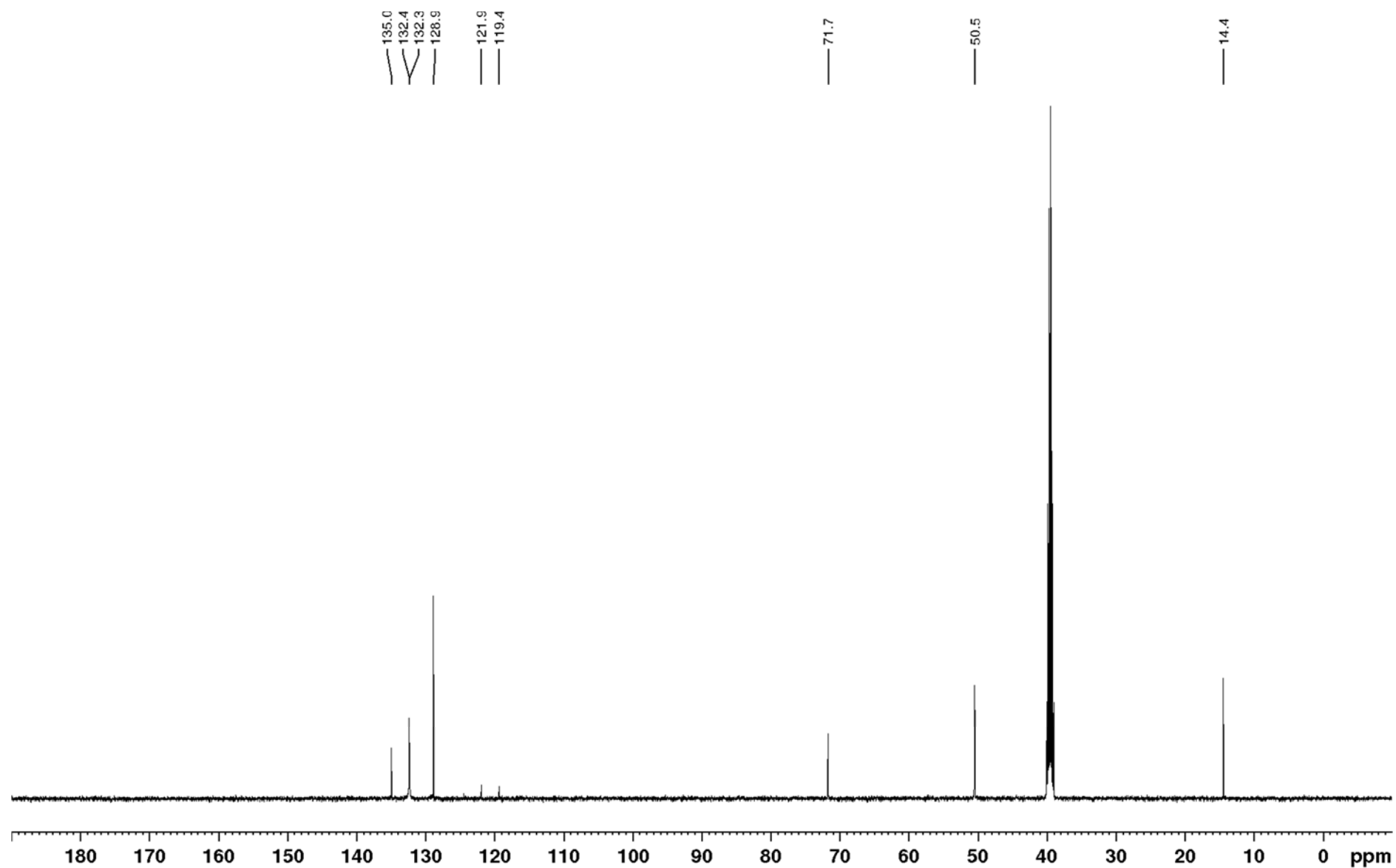
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

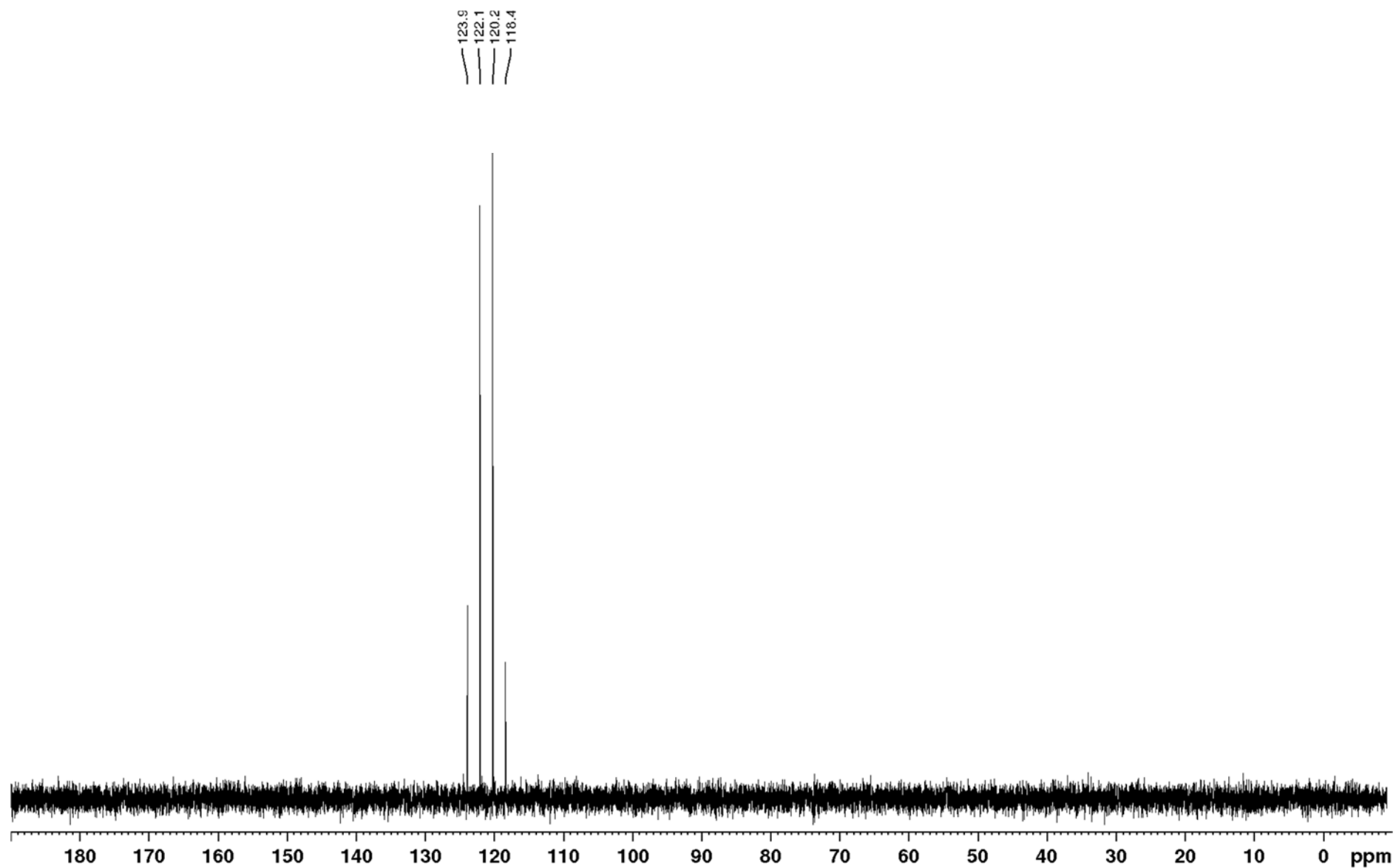
SUPPORTING INFORMATION

1-(4-Chlorophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1h)¹H NMR (700 MHz, DMSO-*d*₆):

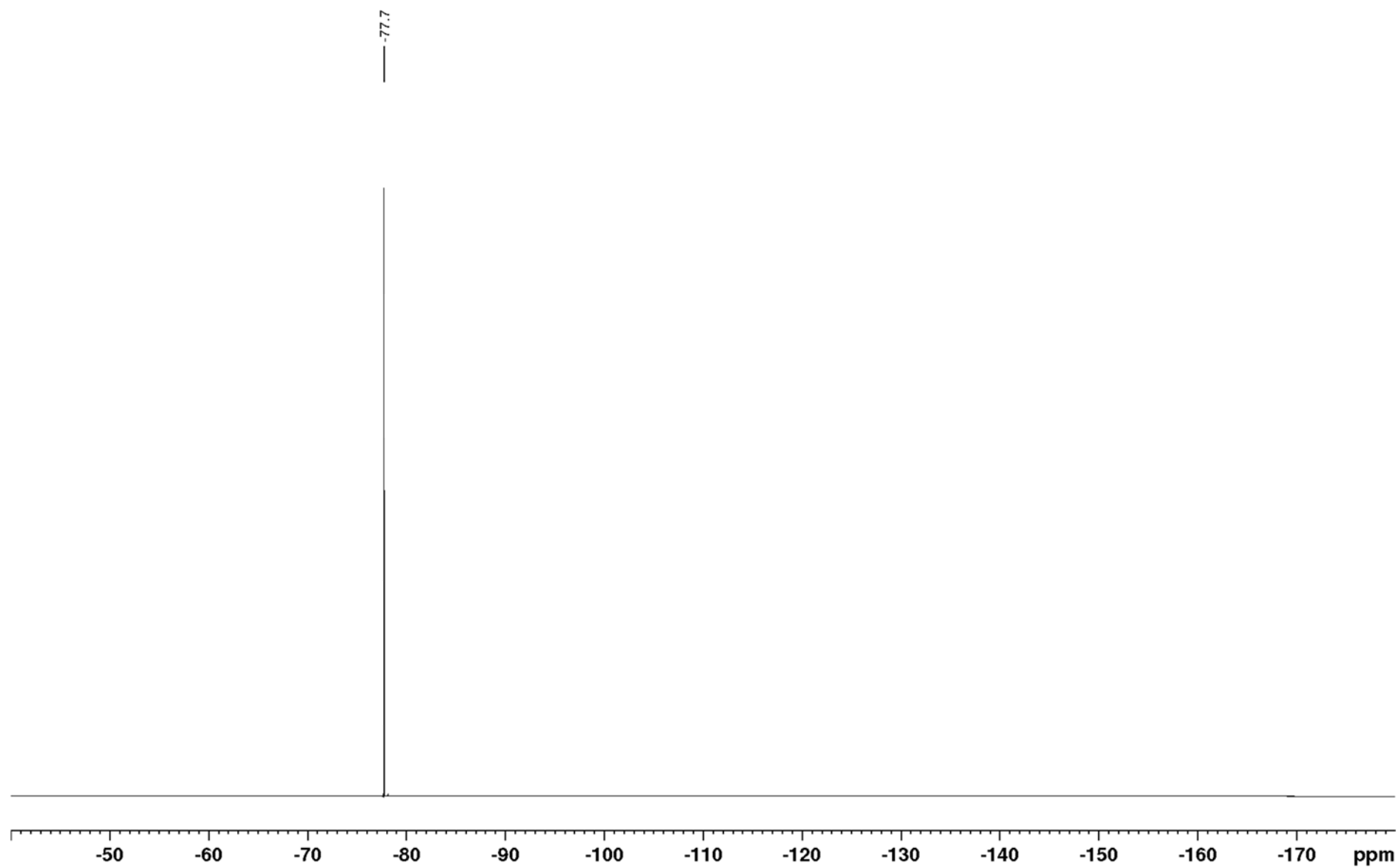
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

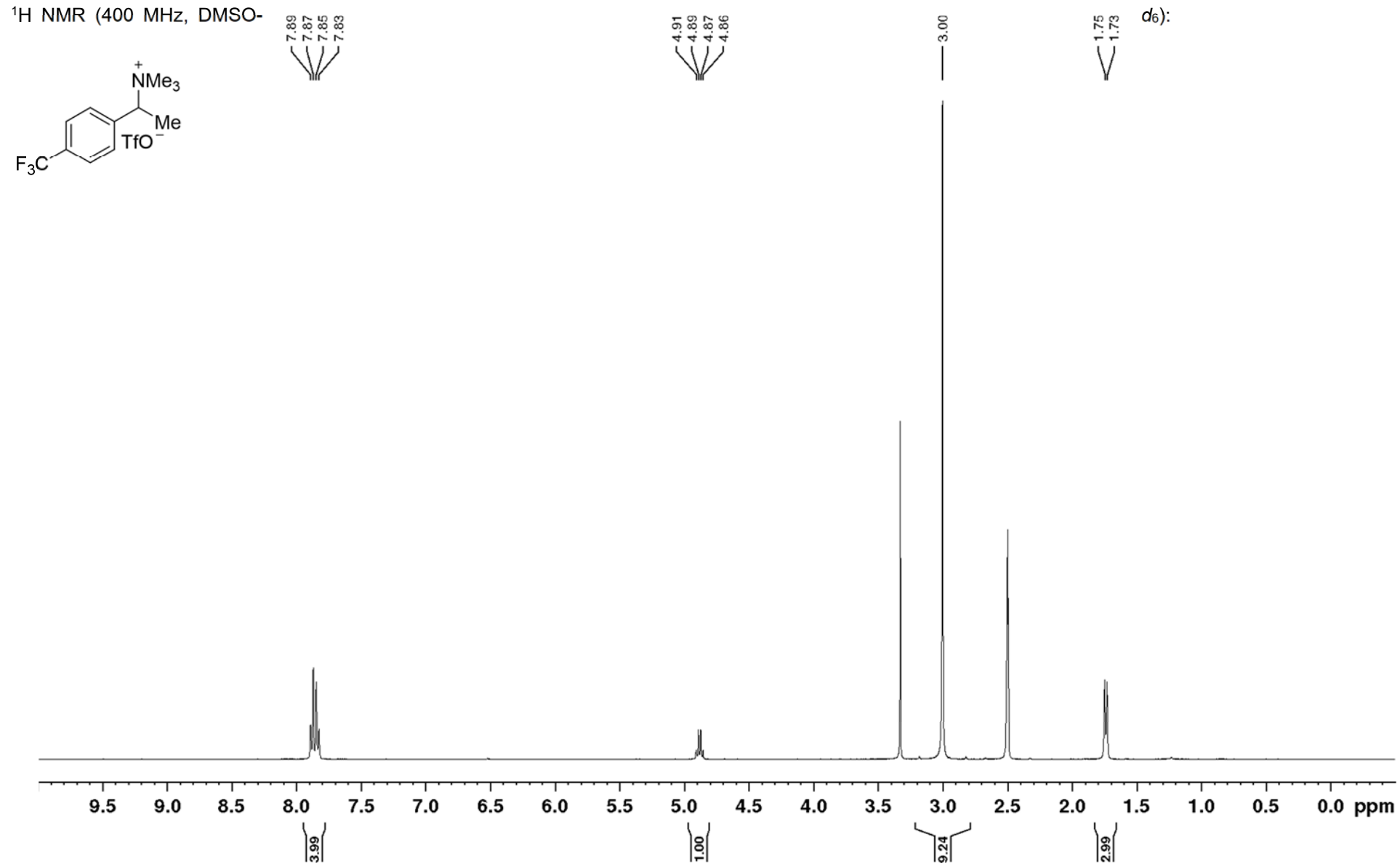
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

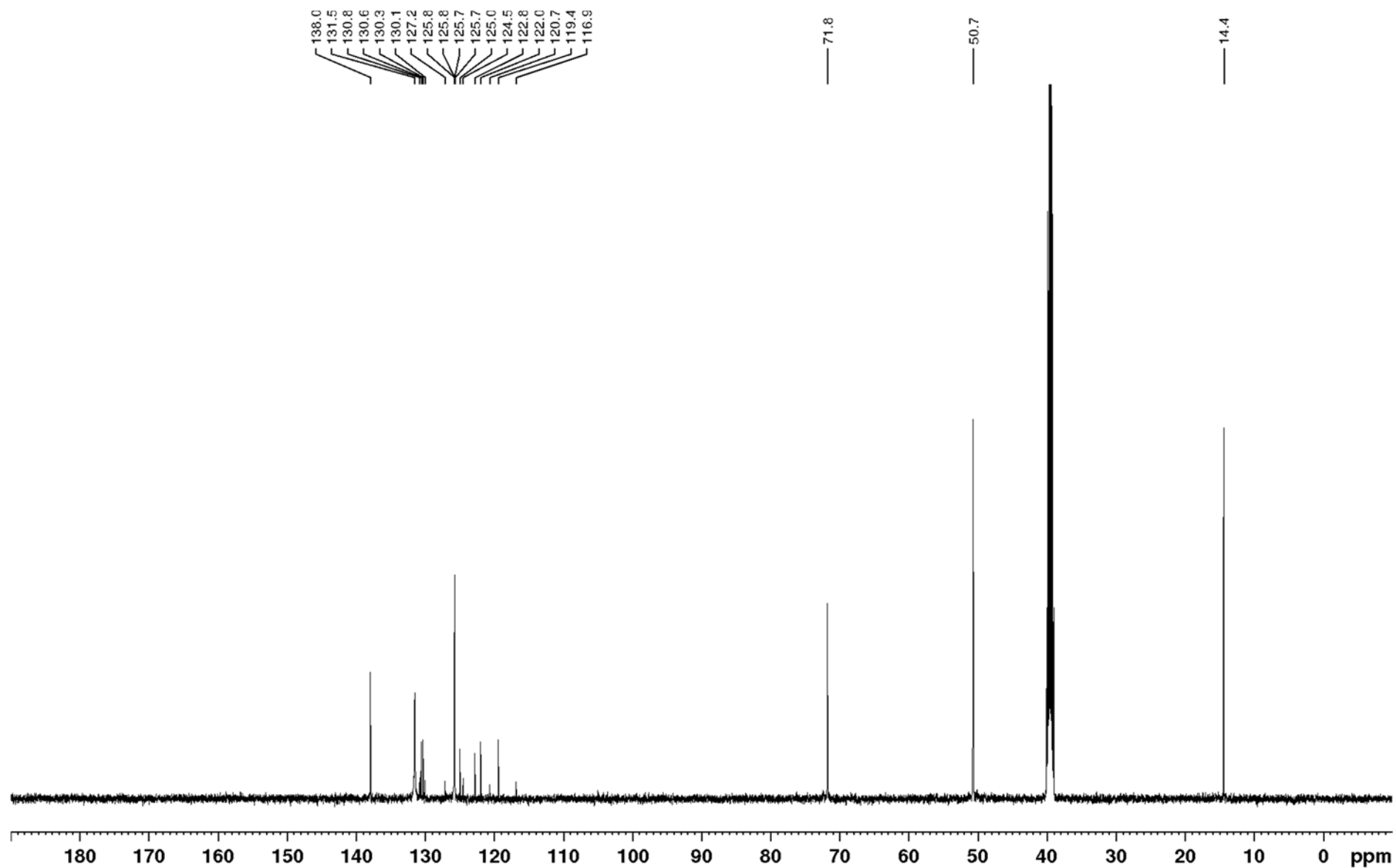
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

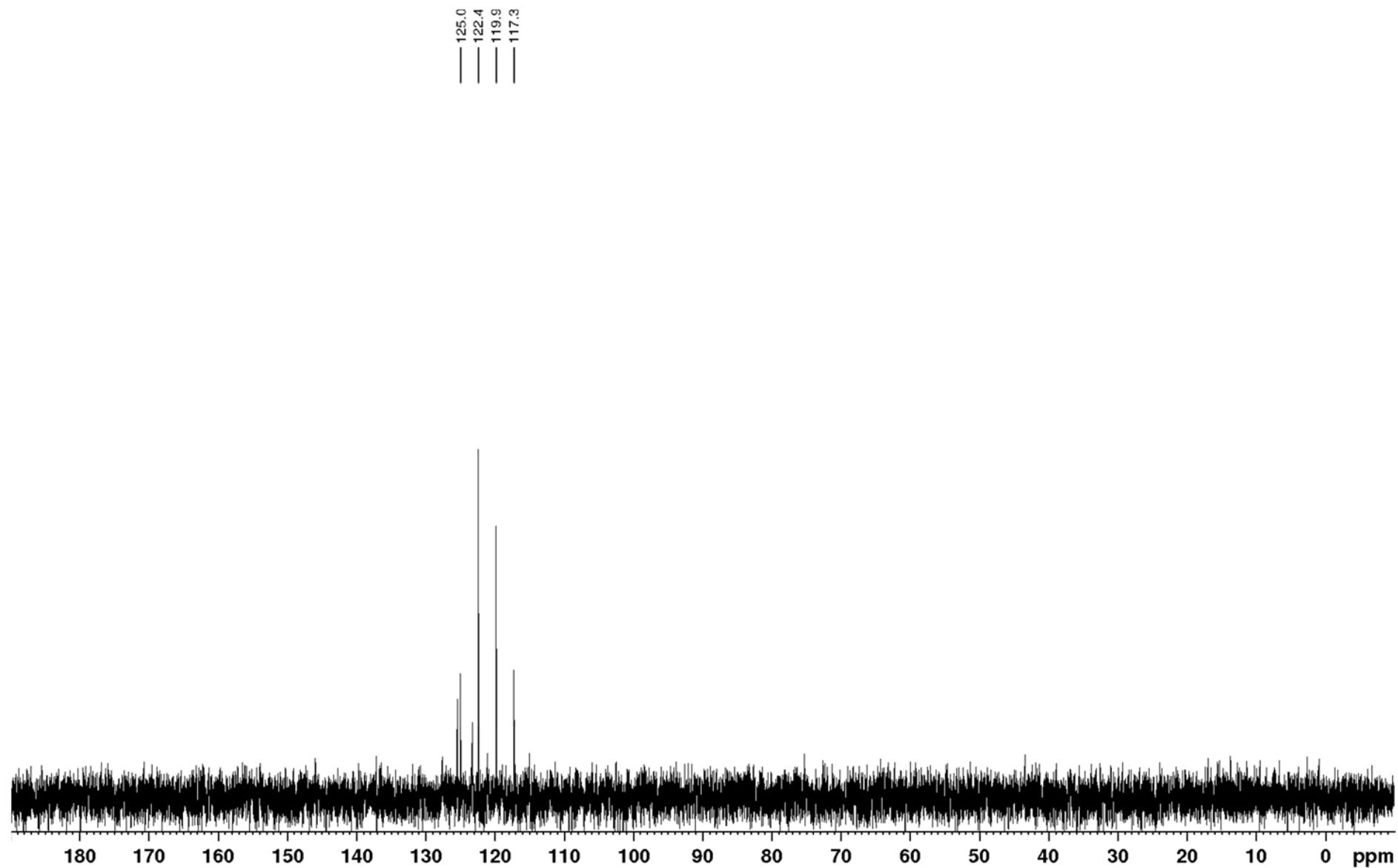
SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1-[4-(trifluoromethyl)phenyl]ethan-1-aminium trifluoromethanesulfonate (1i)**¹H NMR (400 MHz, DMSO-

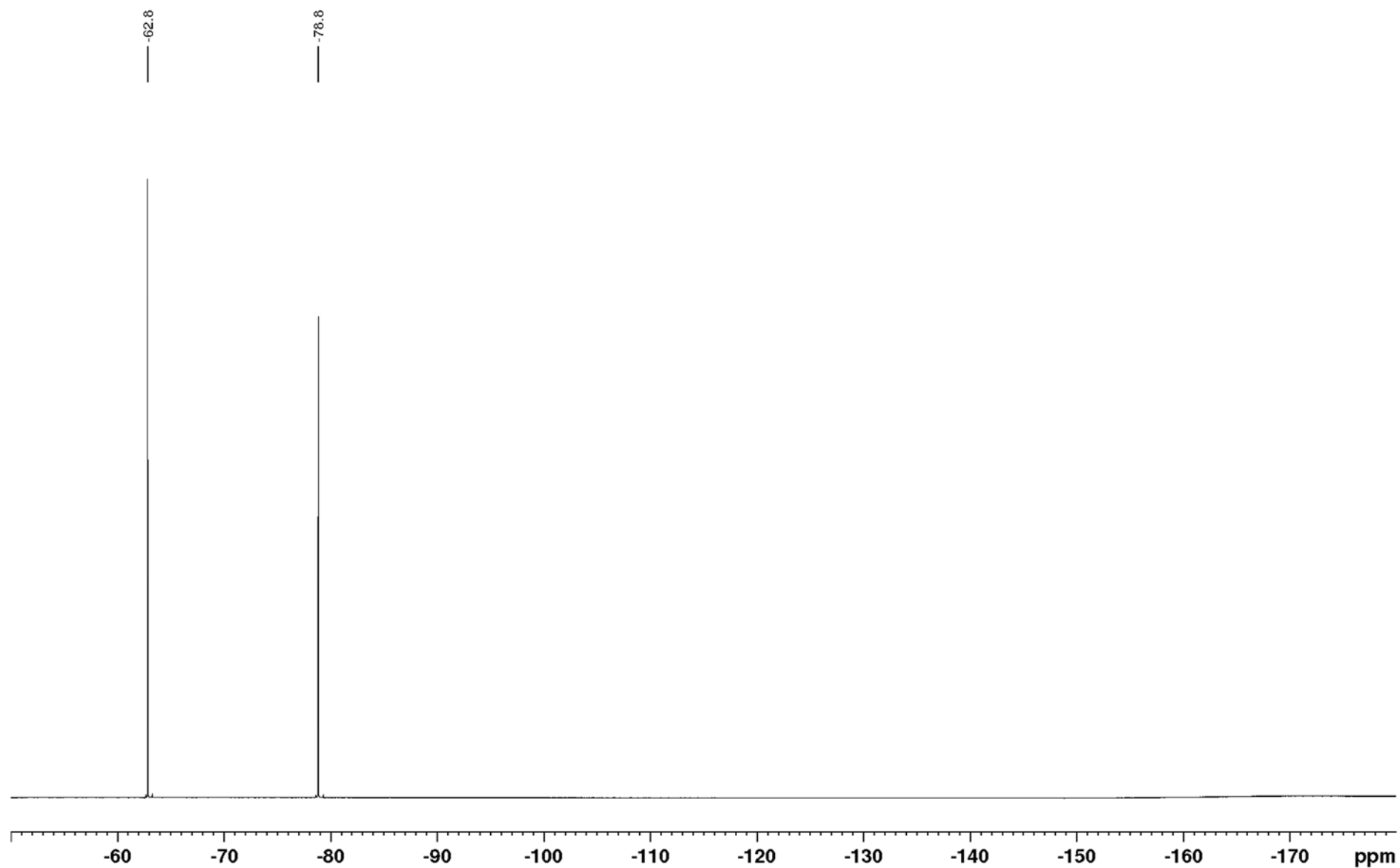
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

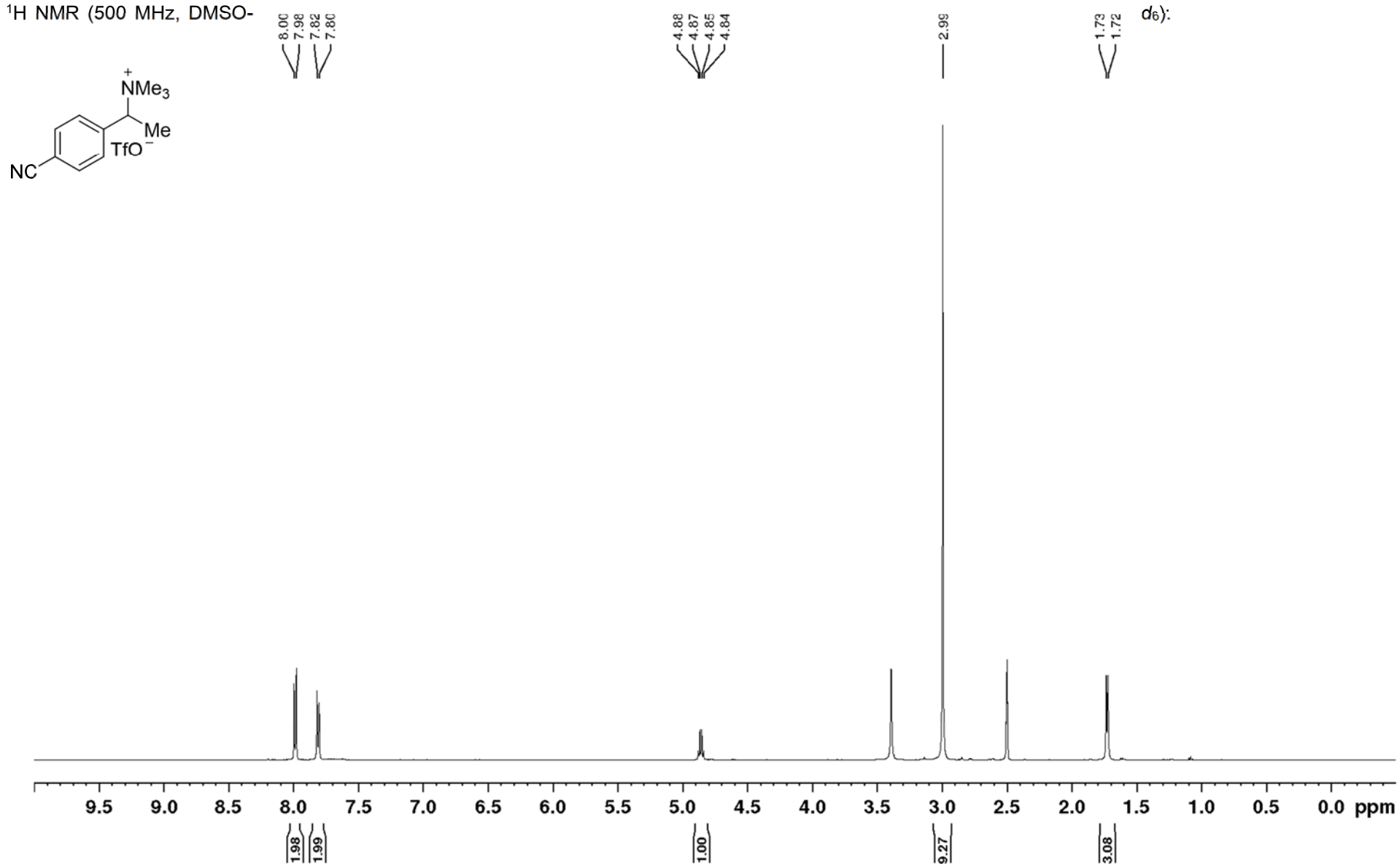
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

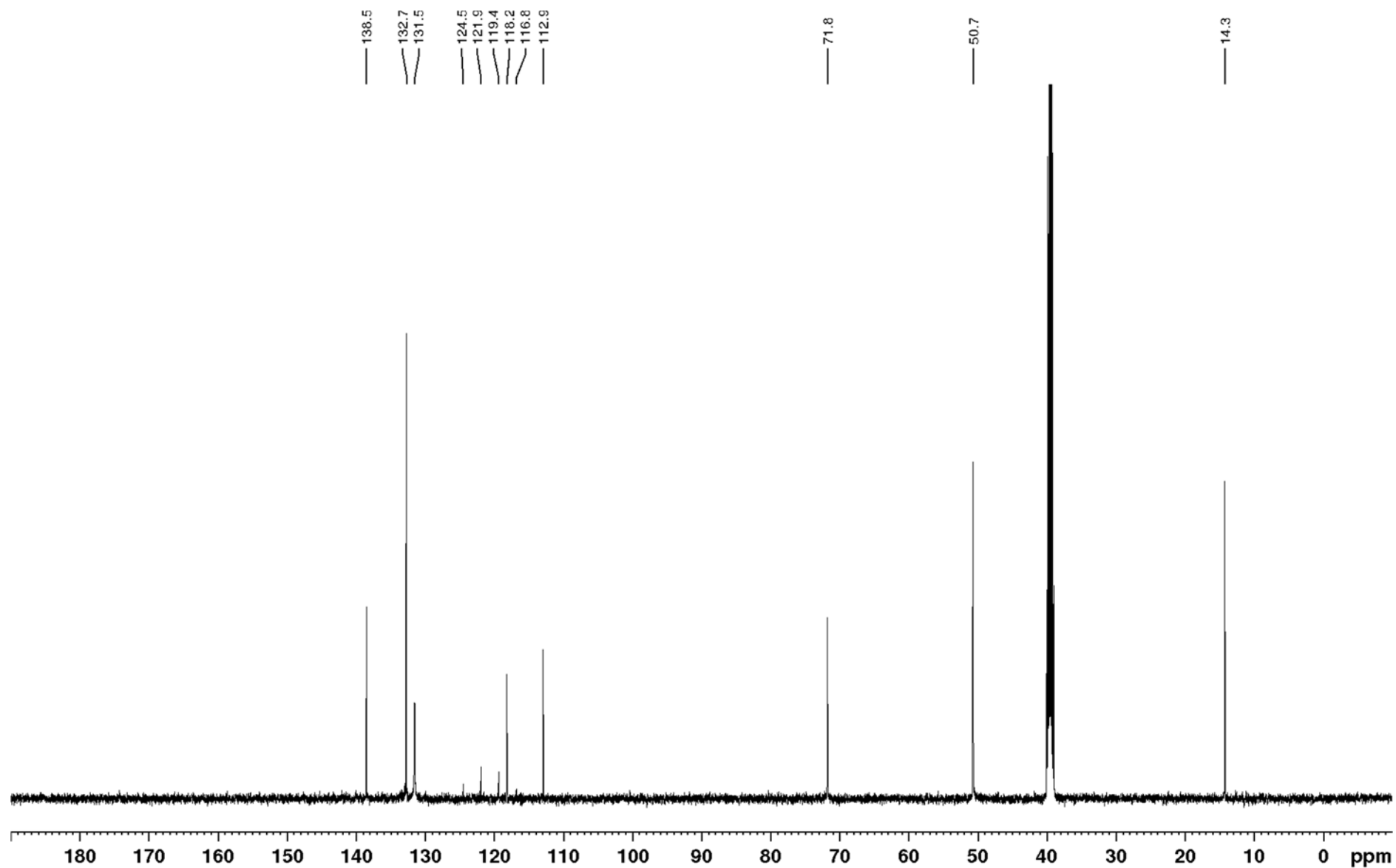
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

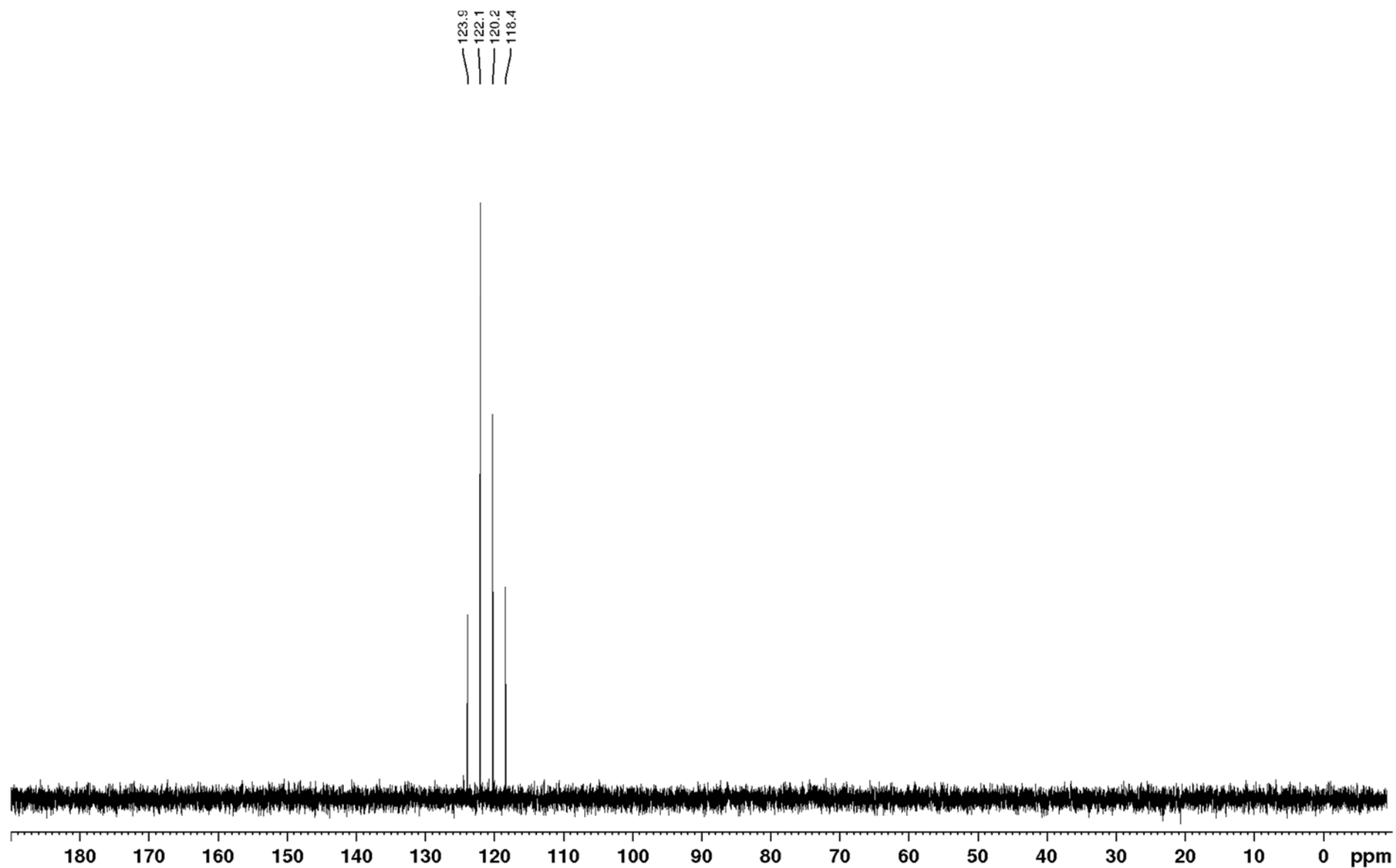
SUPPORTING INFORMATION

1-(4-Cyanophenyl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1j) ^1H NMR (500 MHz, DMSO-

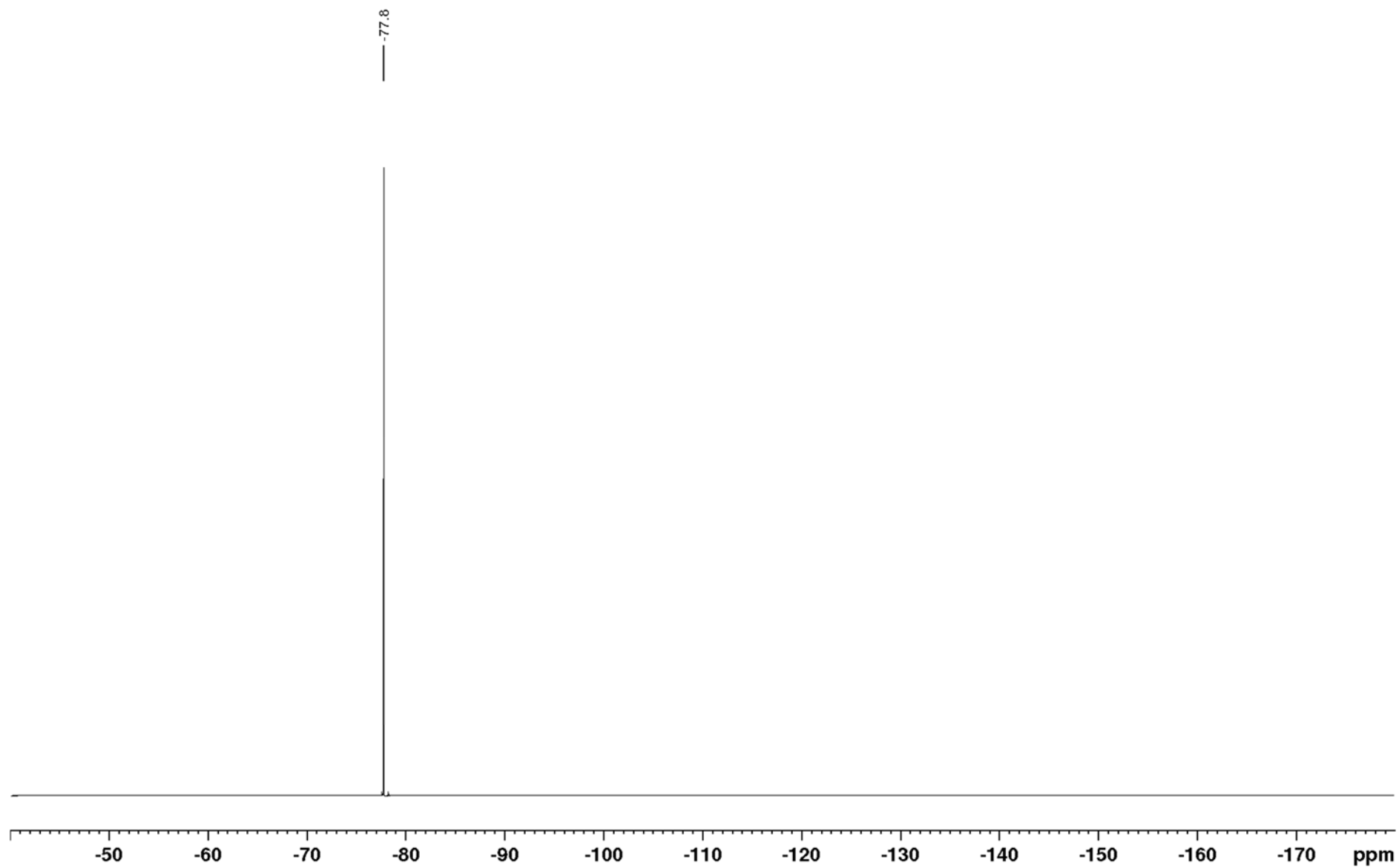
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

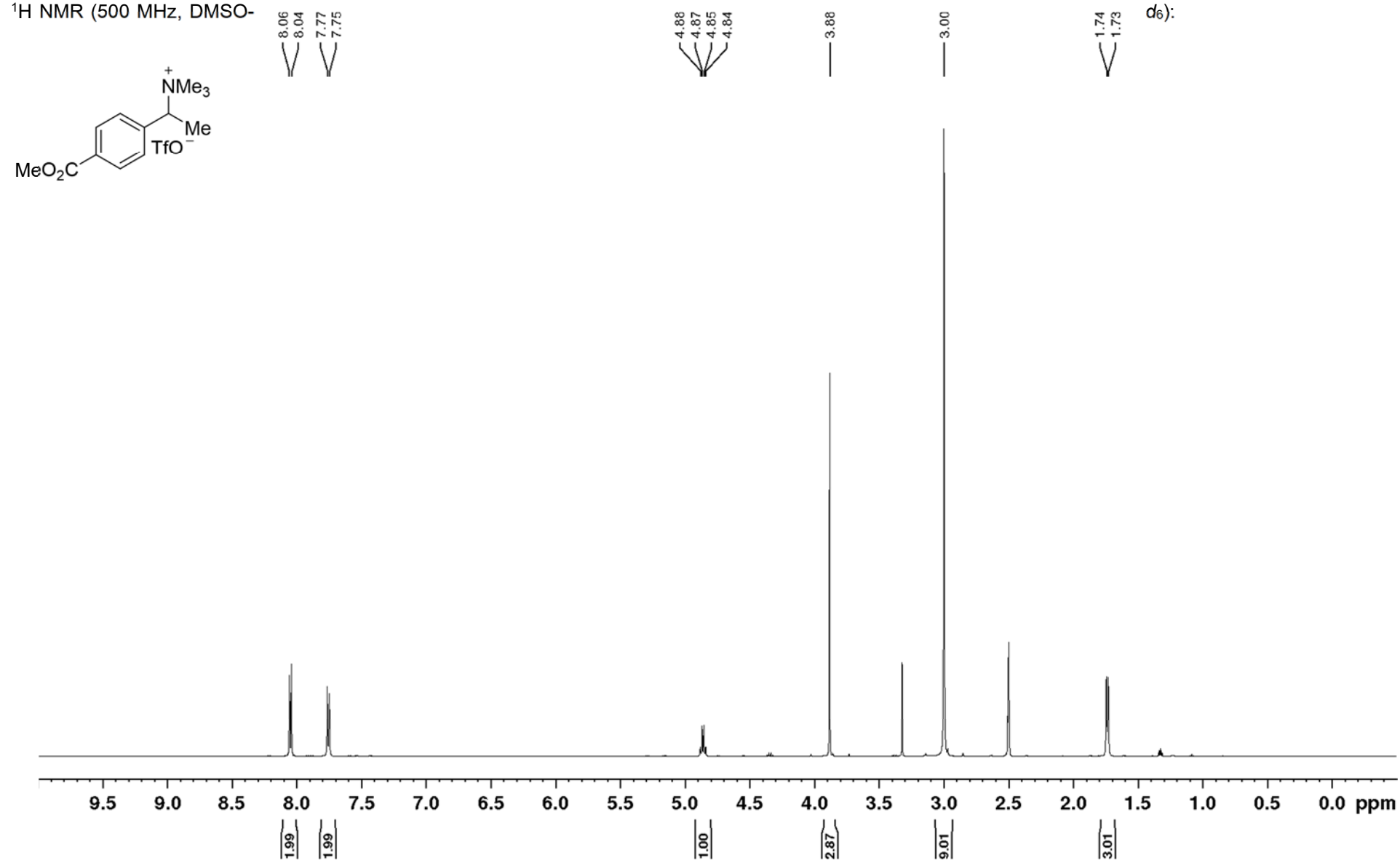
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

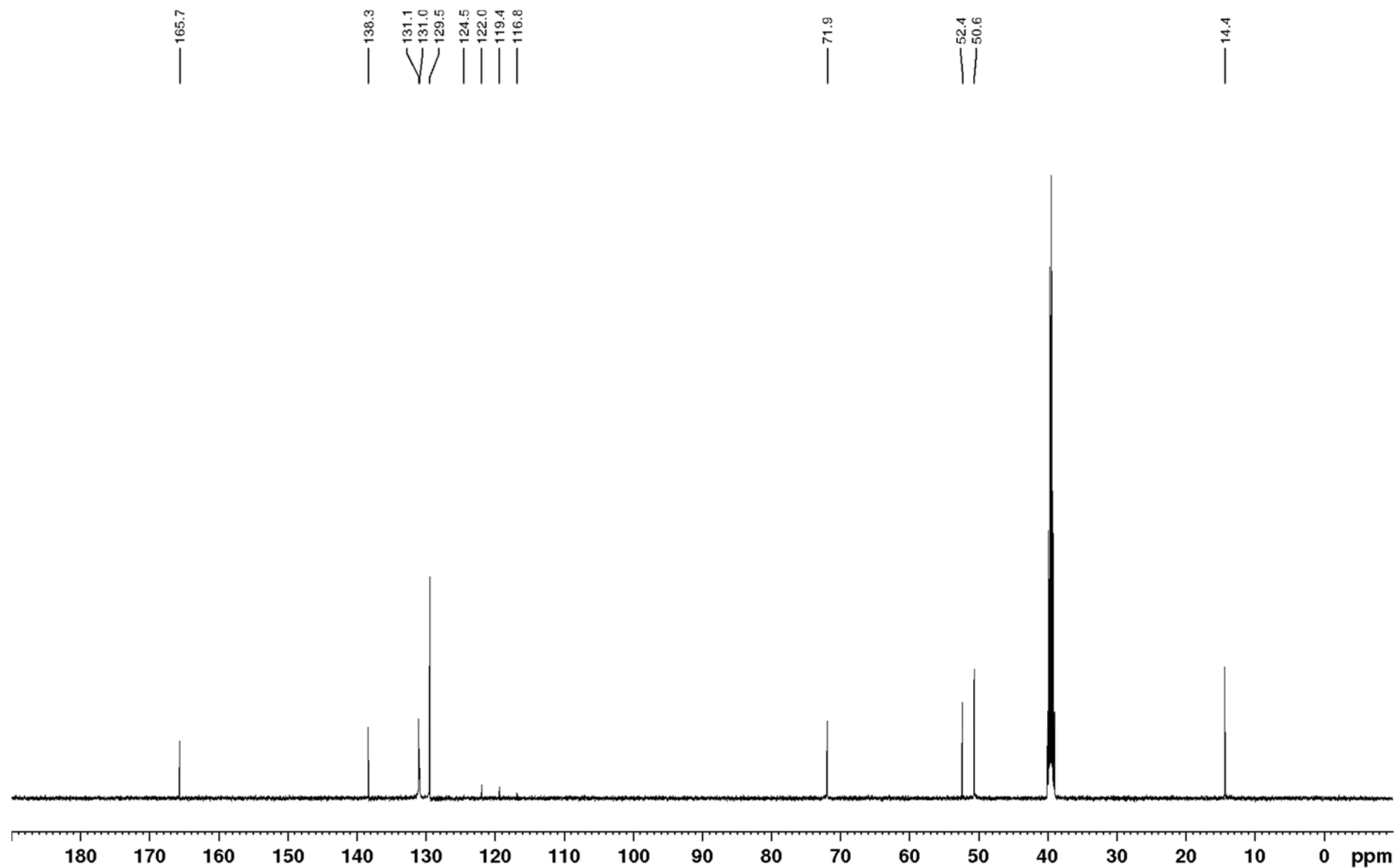
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

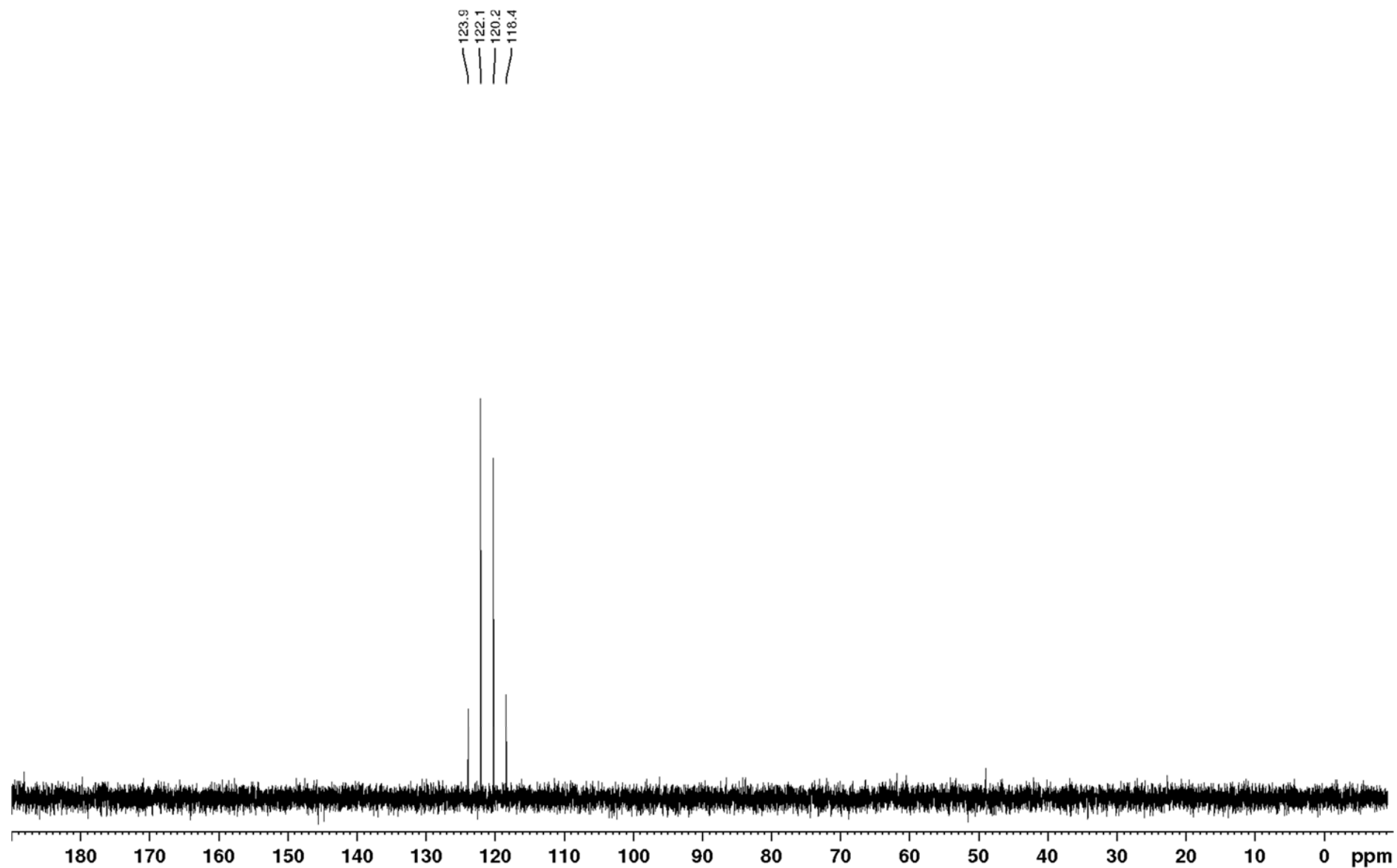
SUPPORTING INFORMATION

1-[4-(Methoxycarbonyl)phenyl]-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1k)¹H NMR (500 MHz, DMSO-

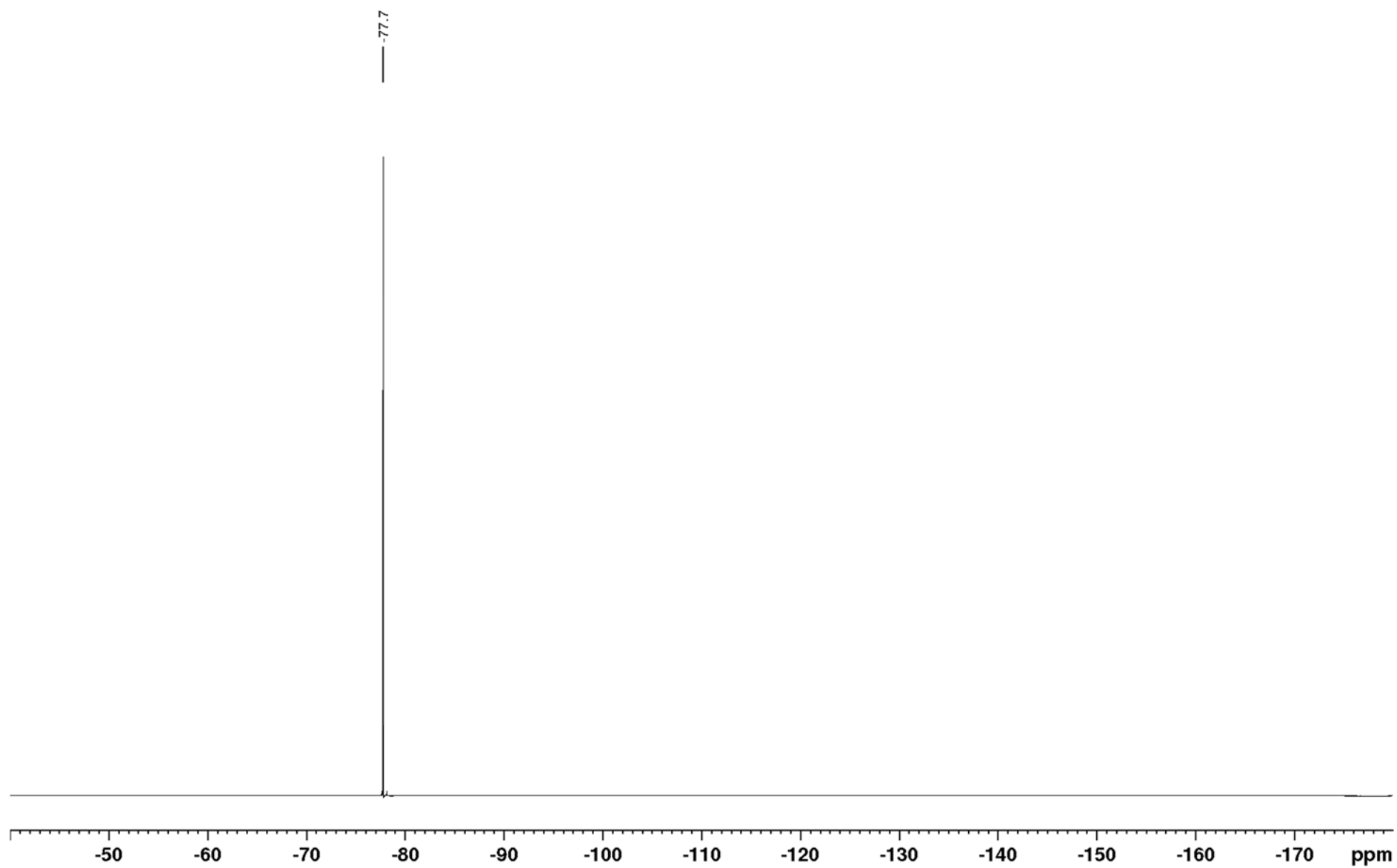
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

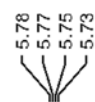
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

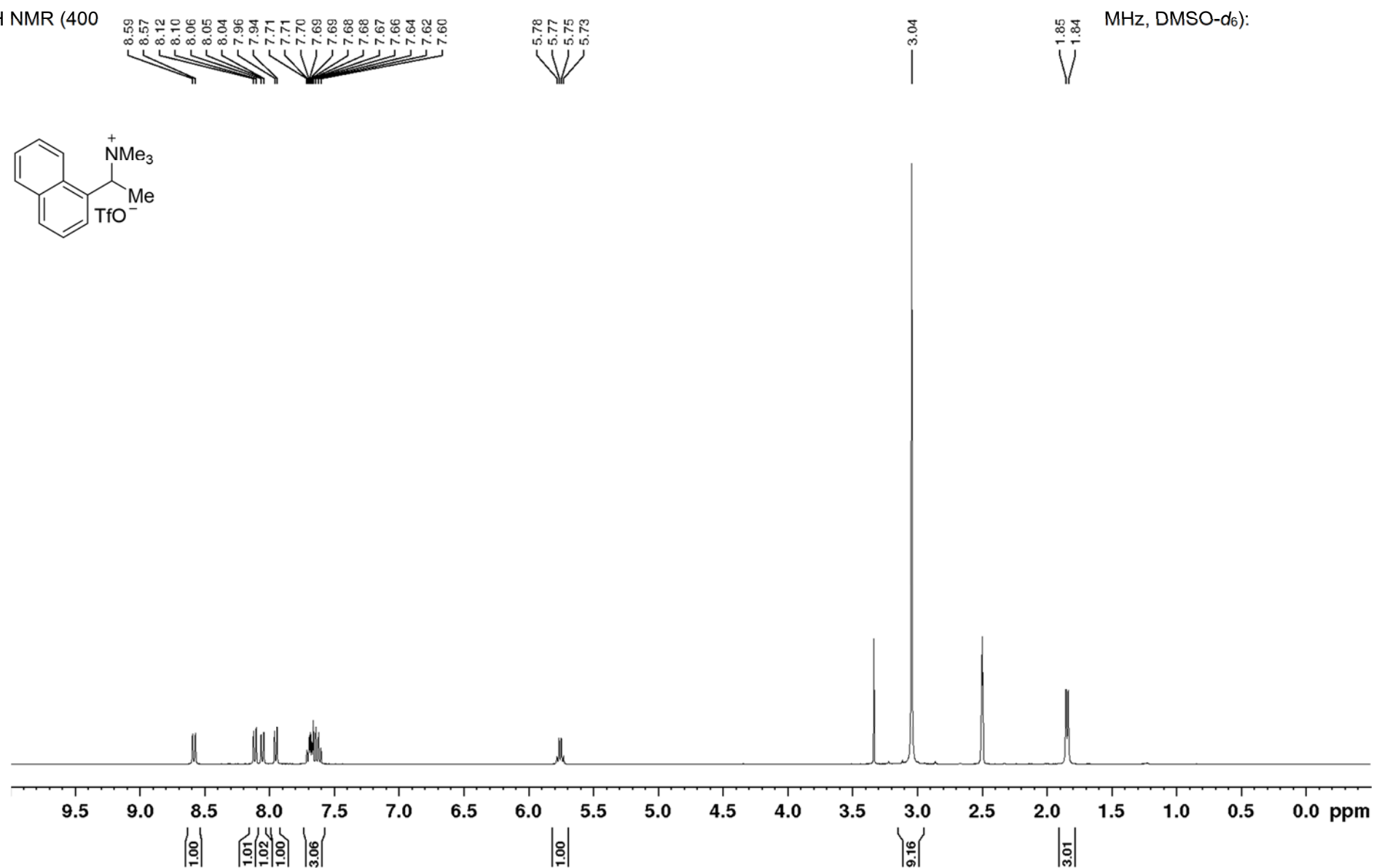
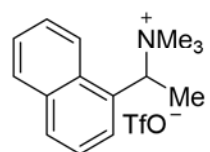
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

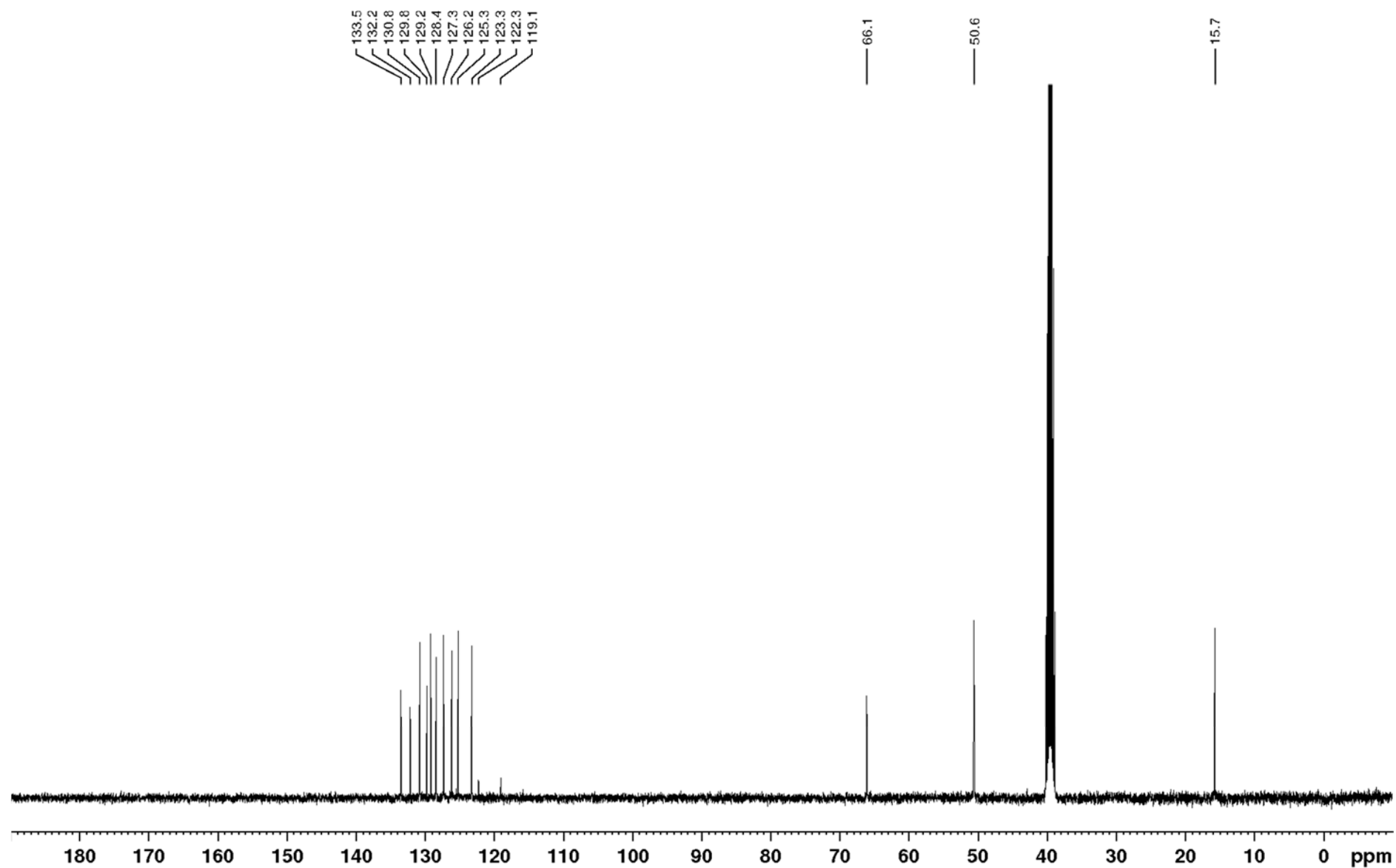
SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1-(naphthalen-1-yl)ethan-1-aminium trifluoromethanesulfonate (1I).**¹H NMR (400

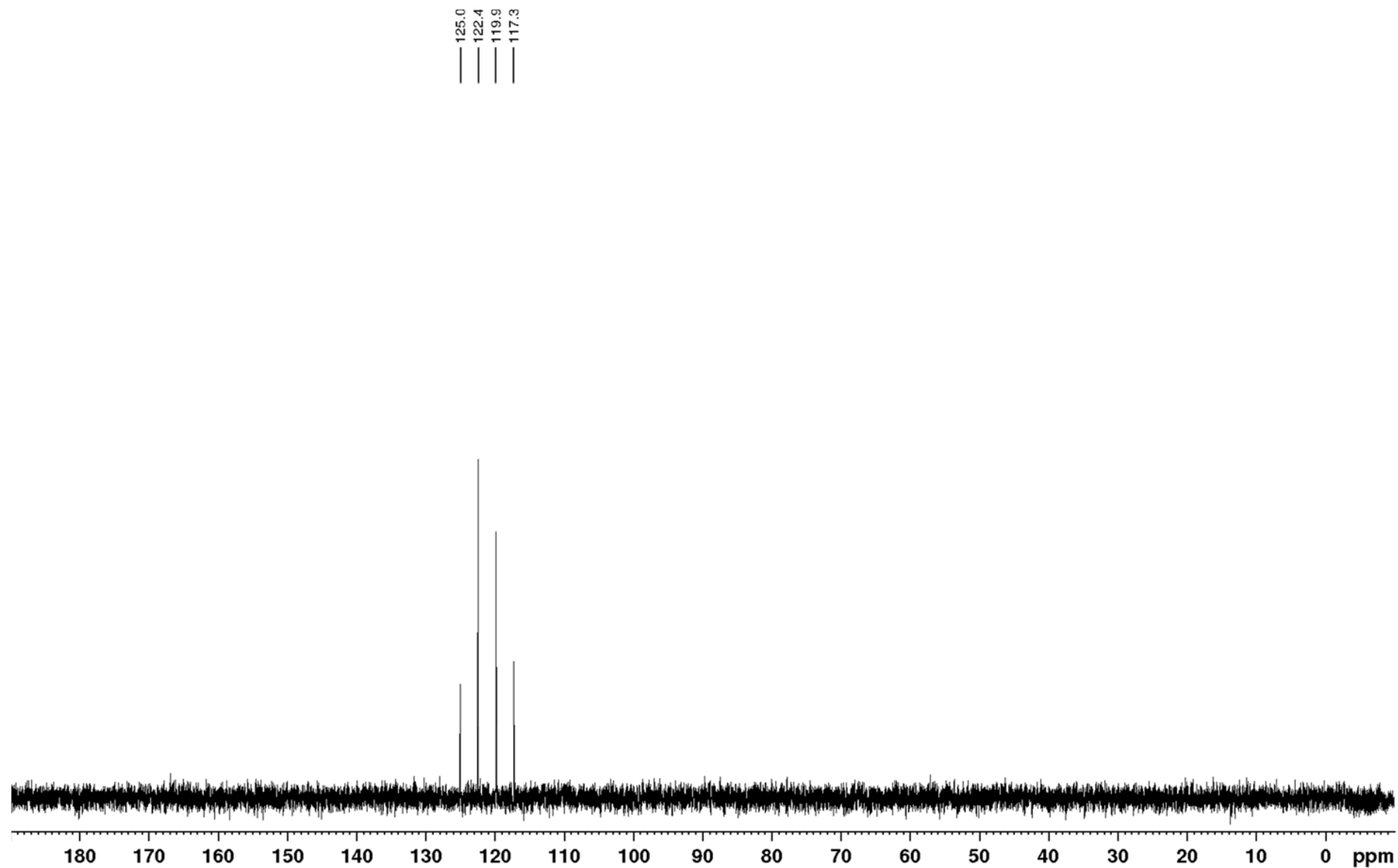
3.04

1.85
1.84MHz, DMSO-d₆):

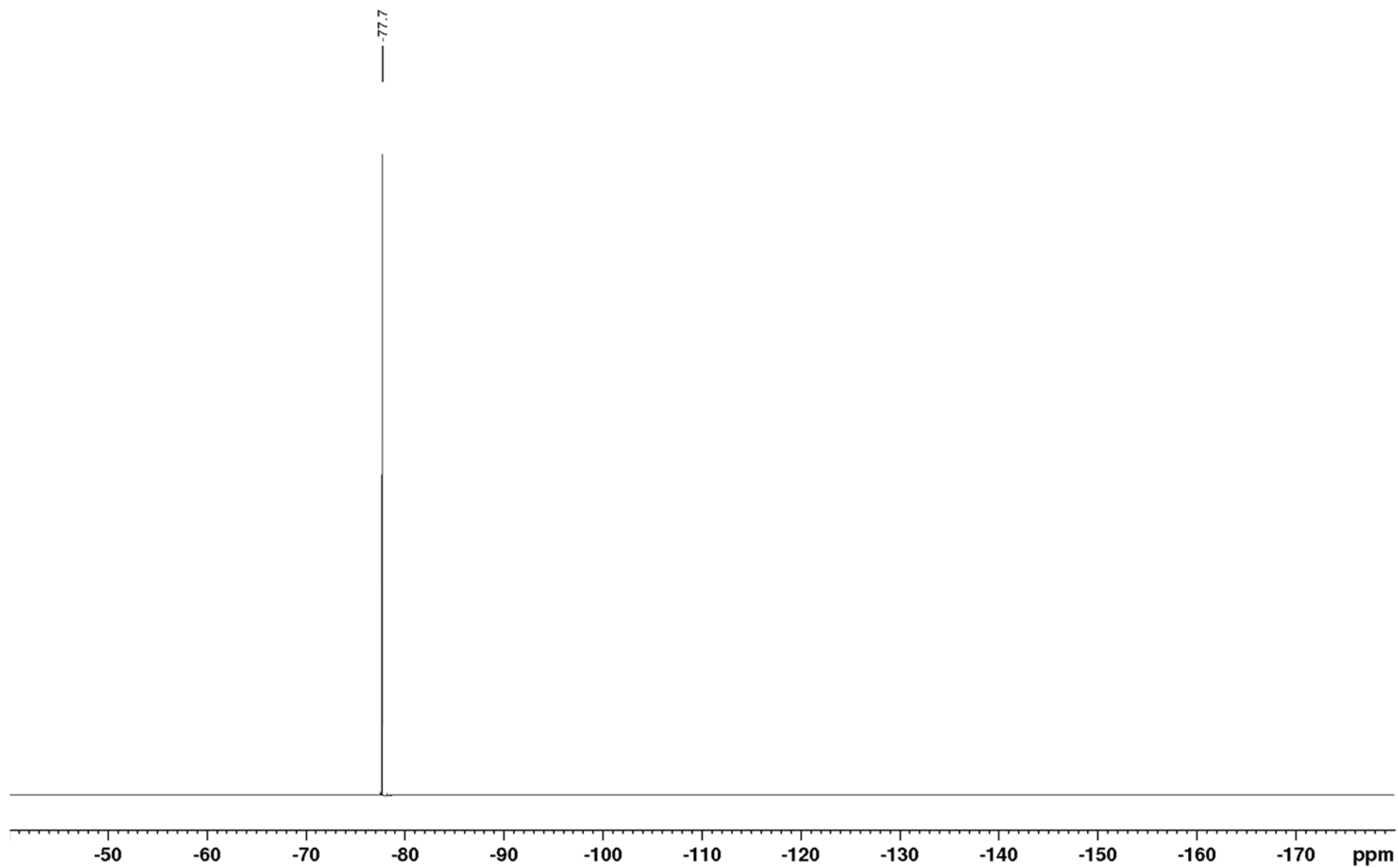
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO- d_6):

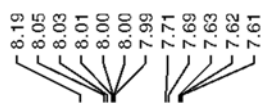
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

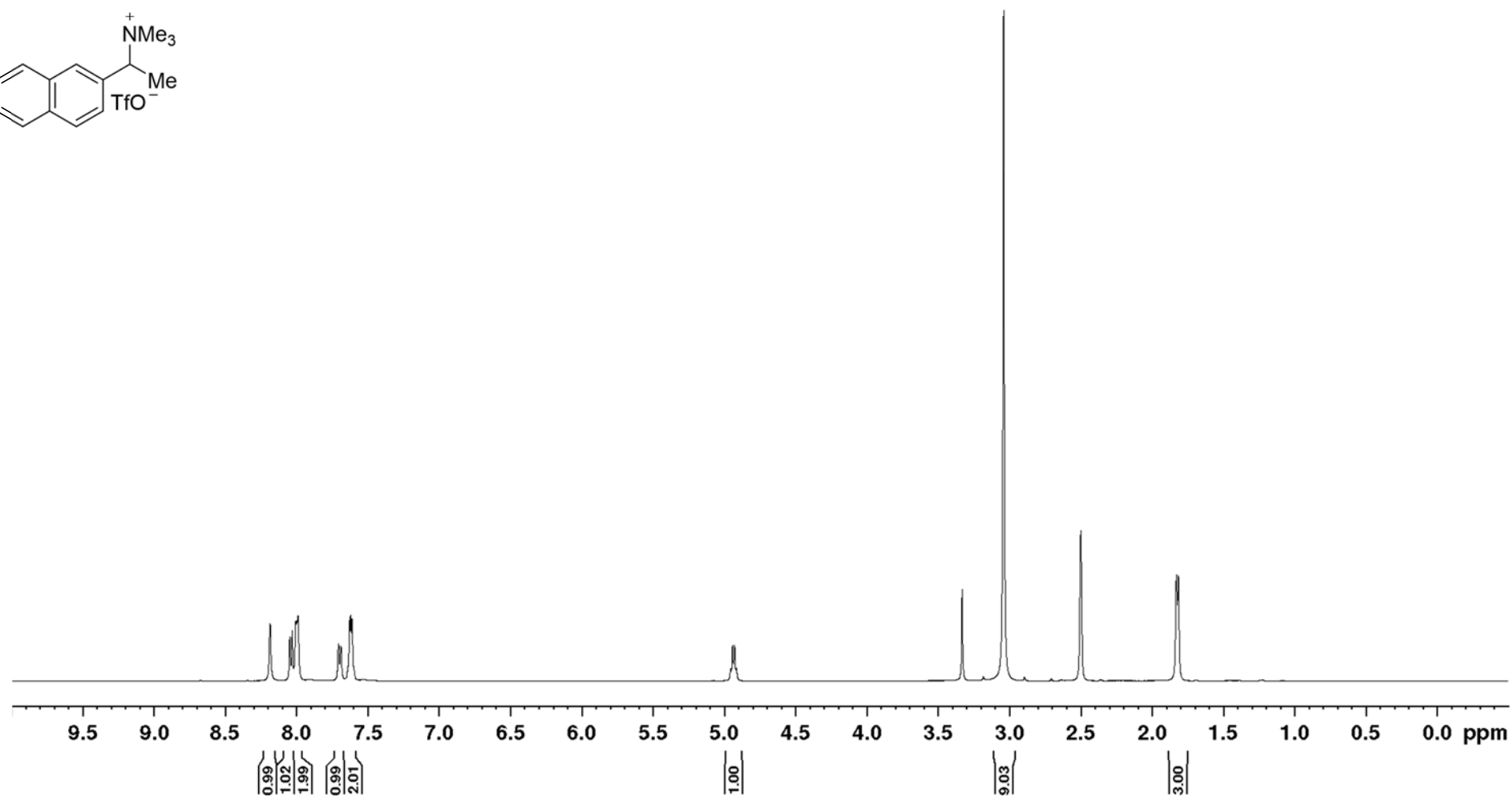
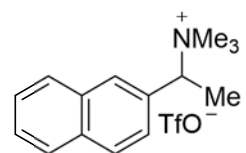
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

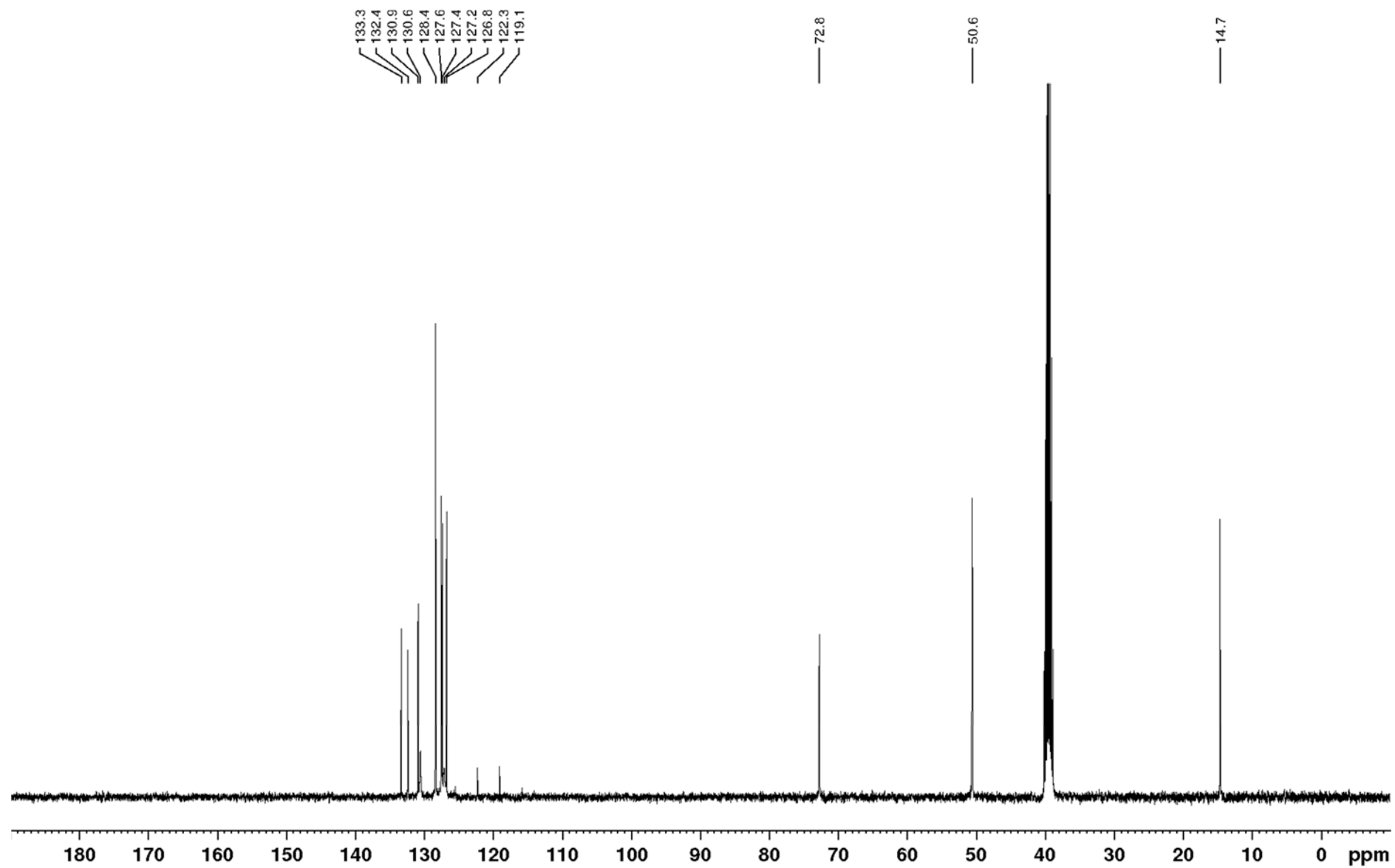
SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1-(naphthalen-2-yl)ethan-1-aminium trifluoromethanesulfonate (1m).**¹H NMR (400 MHz,

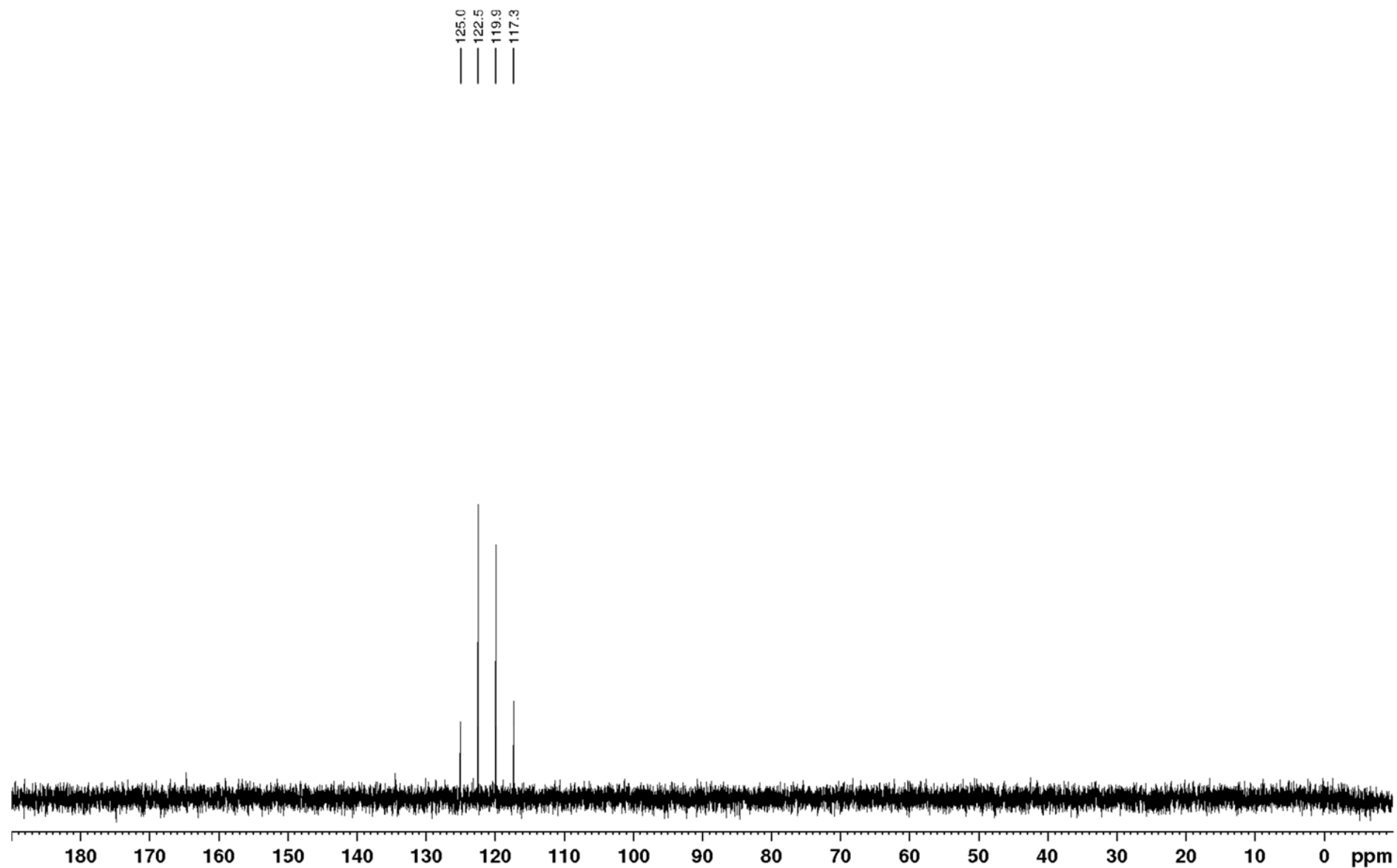
3.04

1.83
1.82DMSO-*d*₆:

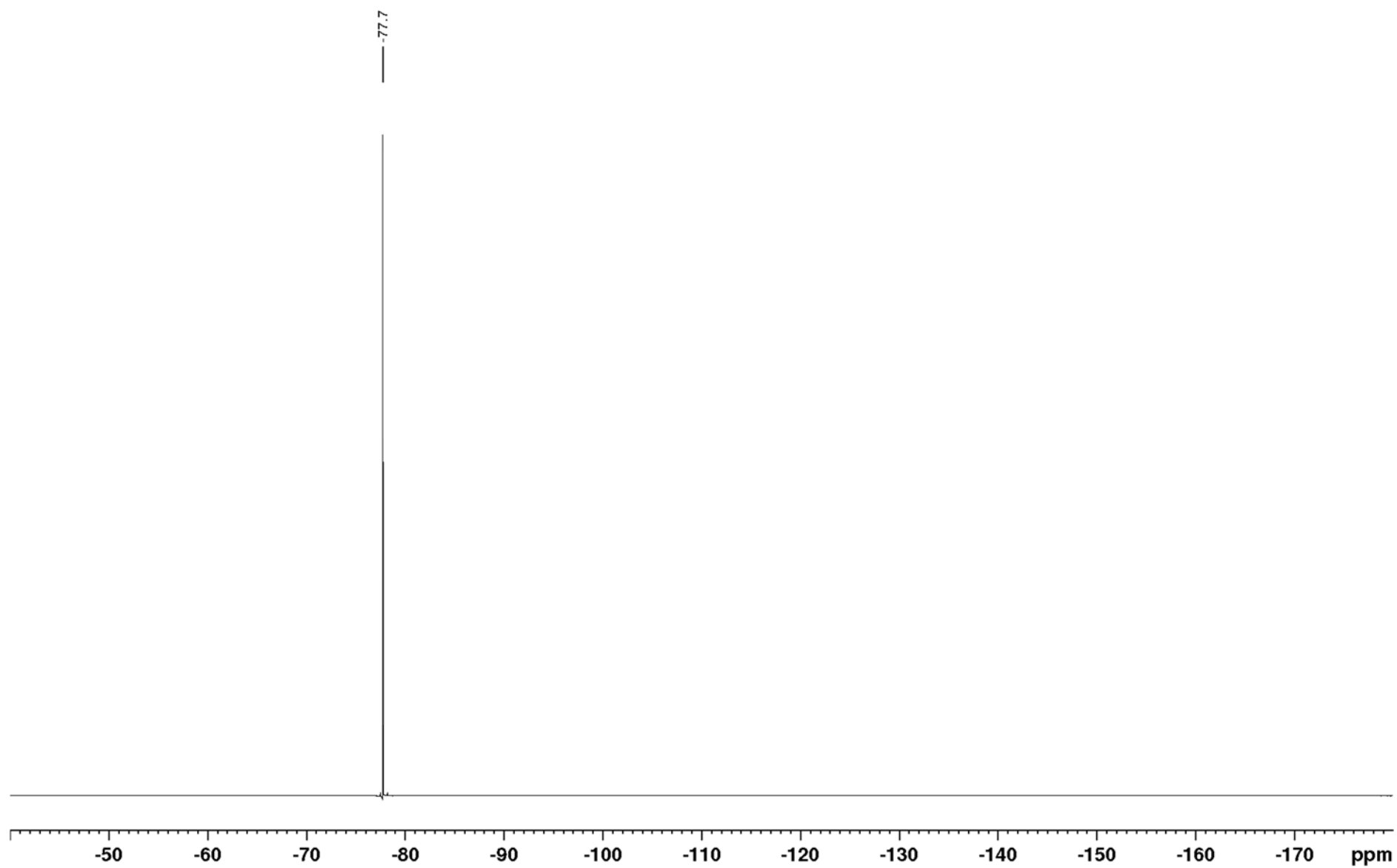
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

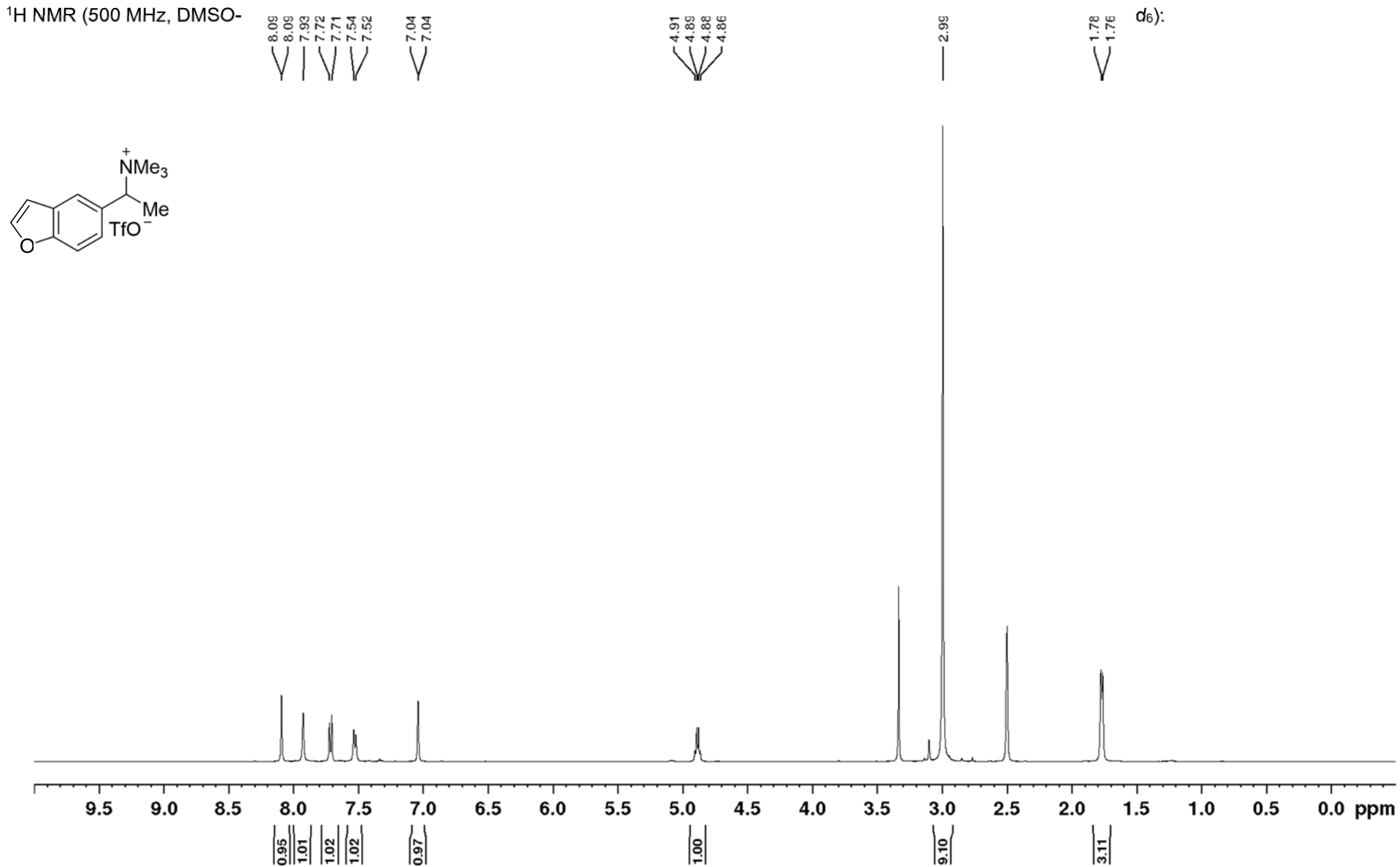
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

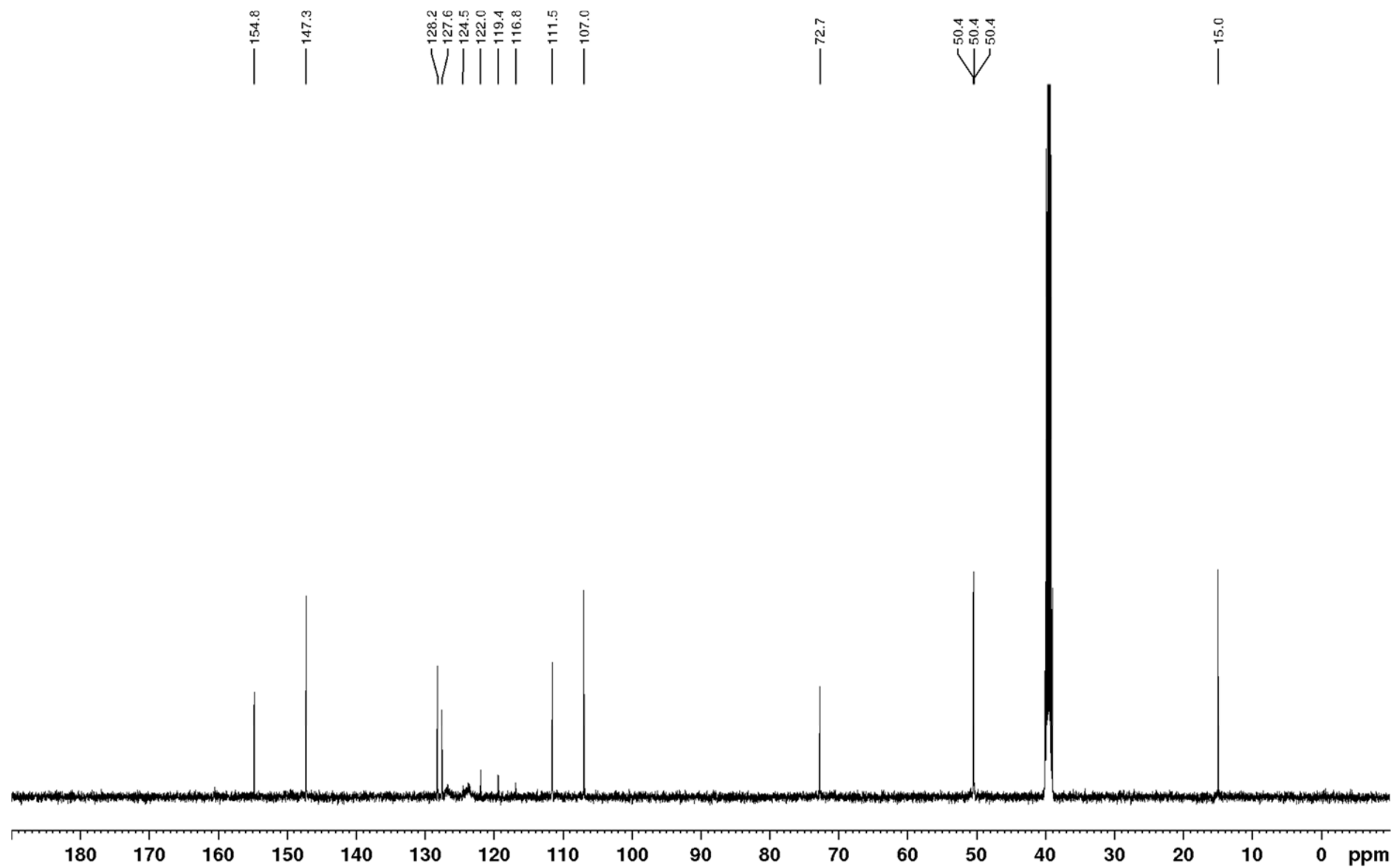
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

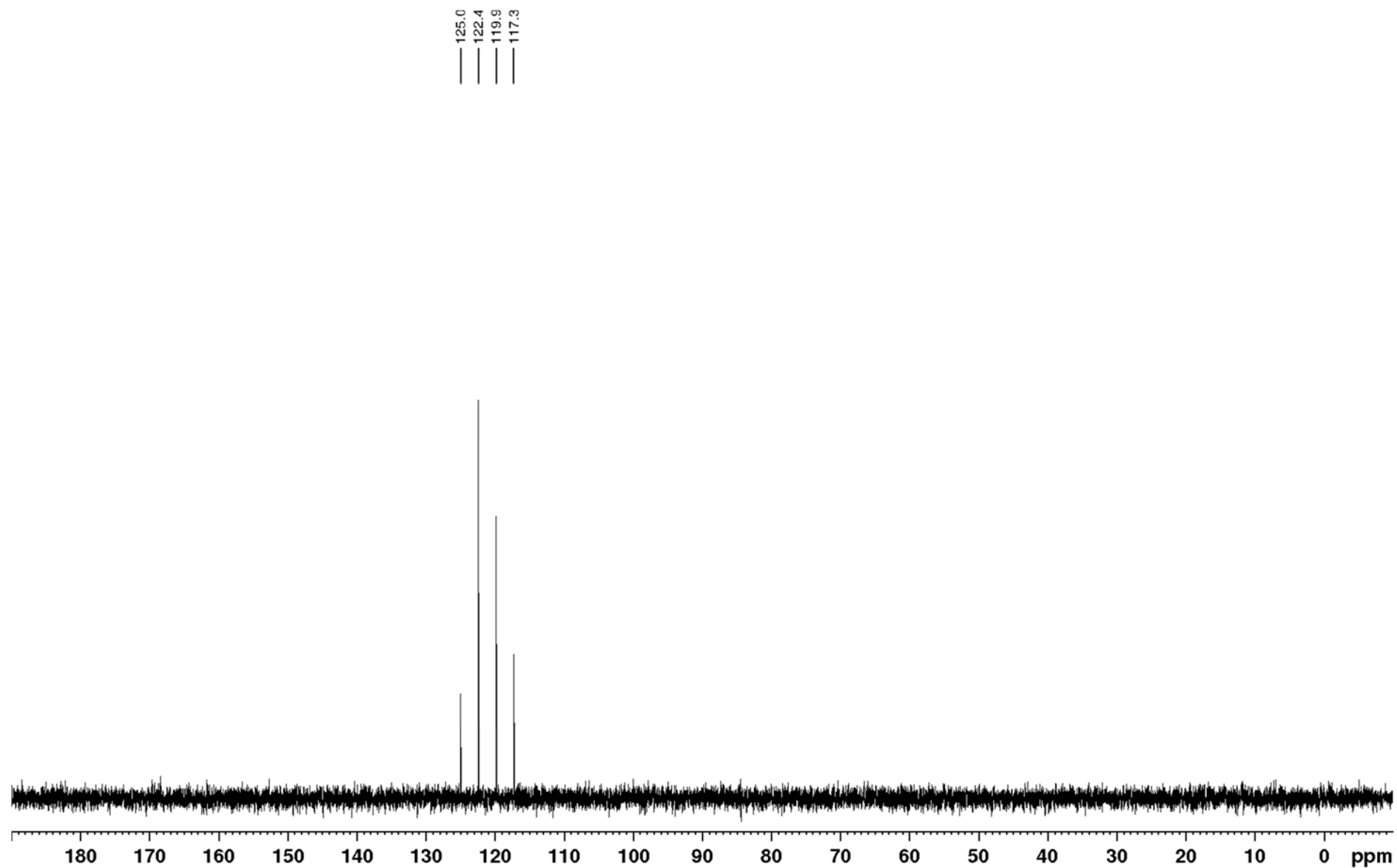
SUPPORTING INFORMATION

1-(Benzofuran-5-yl)-*N,N,N*-trimethylethan-1-aminium trifluoromethanesulfonate (1n).¹H NMR (500 MHz, DMSO-

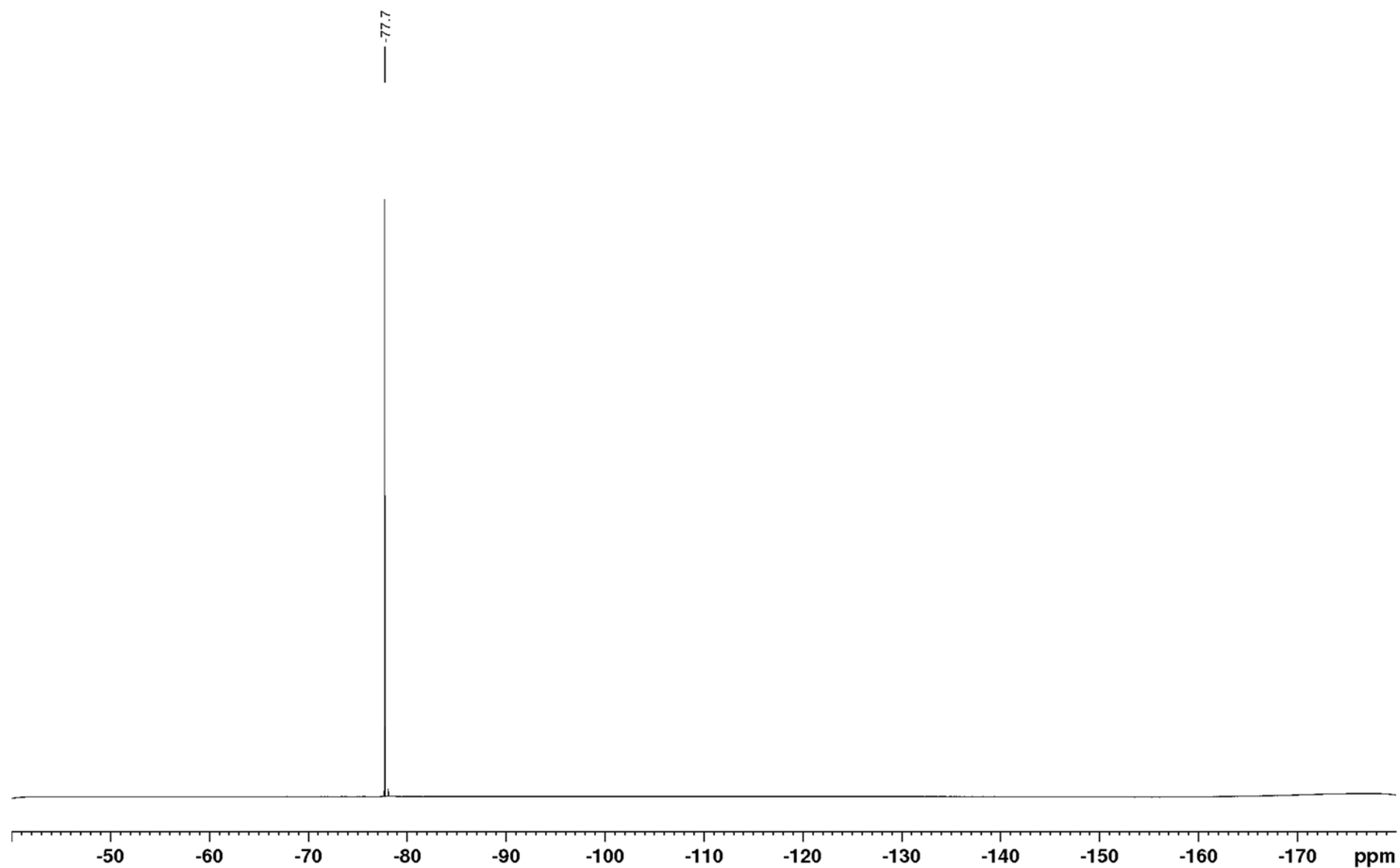
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

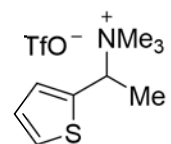
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1-(thiophen-2-yl)ethan-1-aminium trifluoromethanesulfonate (1o).**¹H NMR (500 MHz, DMSO-

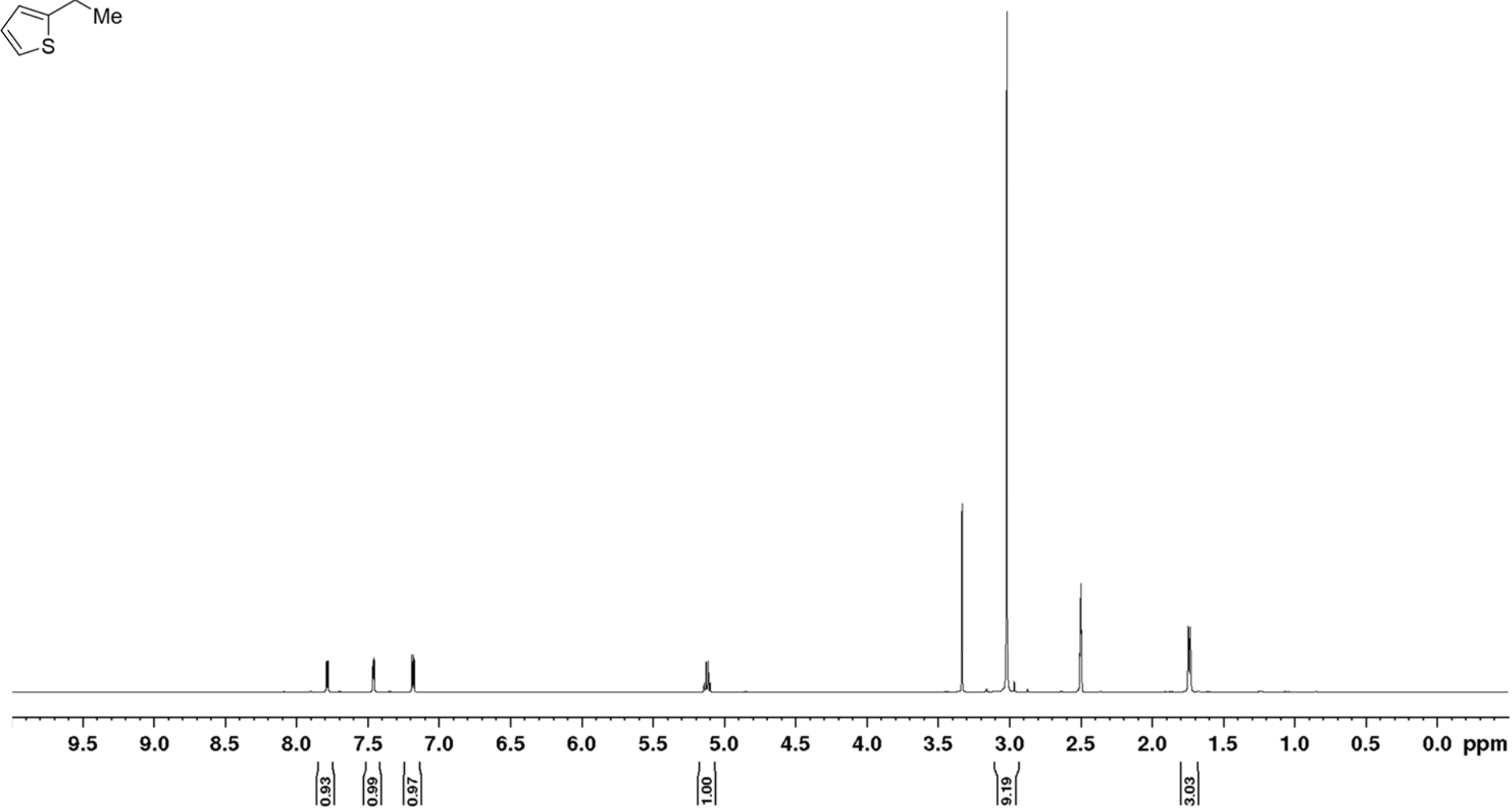
7.79
7.79
7.78
7.78
7.46
7.46
7.46
7.46
7.19
7.18
7.17

5.14
5.13
5.11
5.10

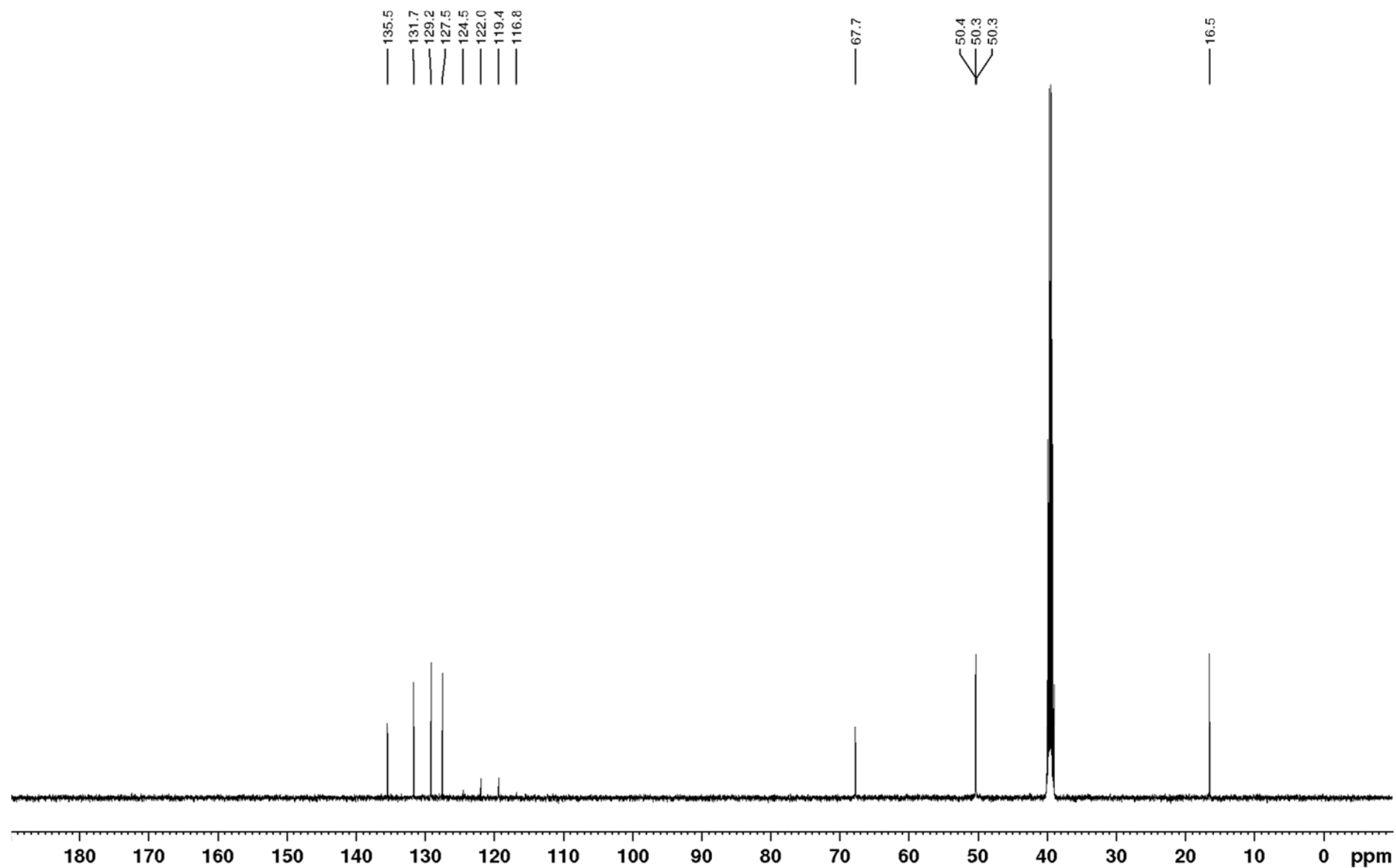
3.02

1.74
1.73

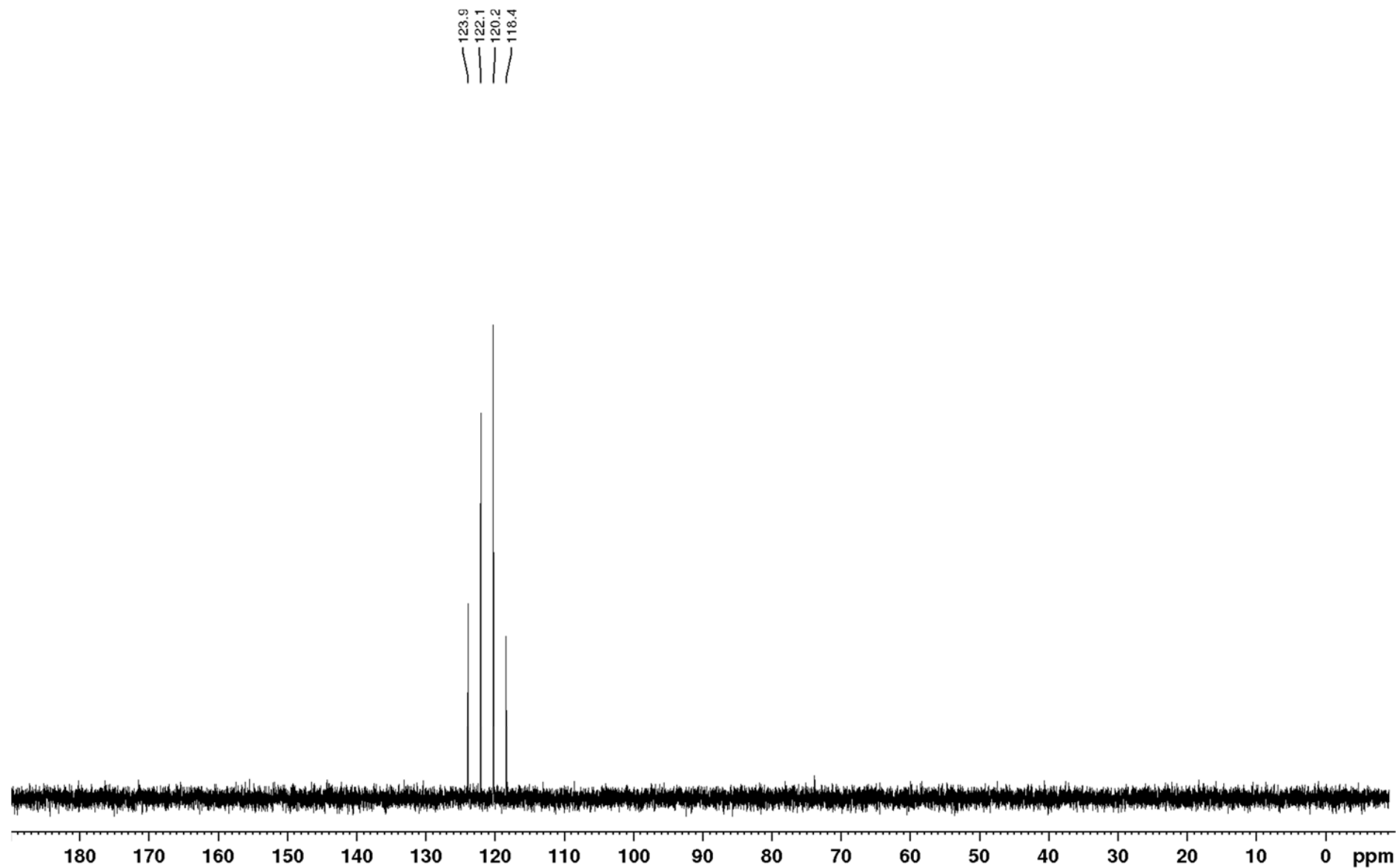
d₆):



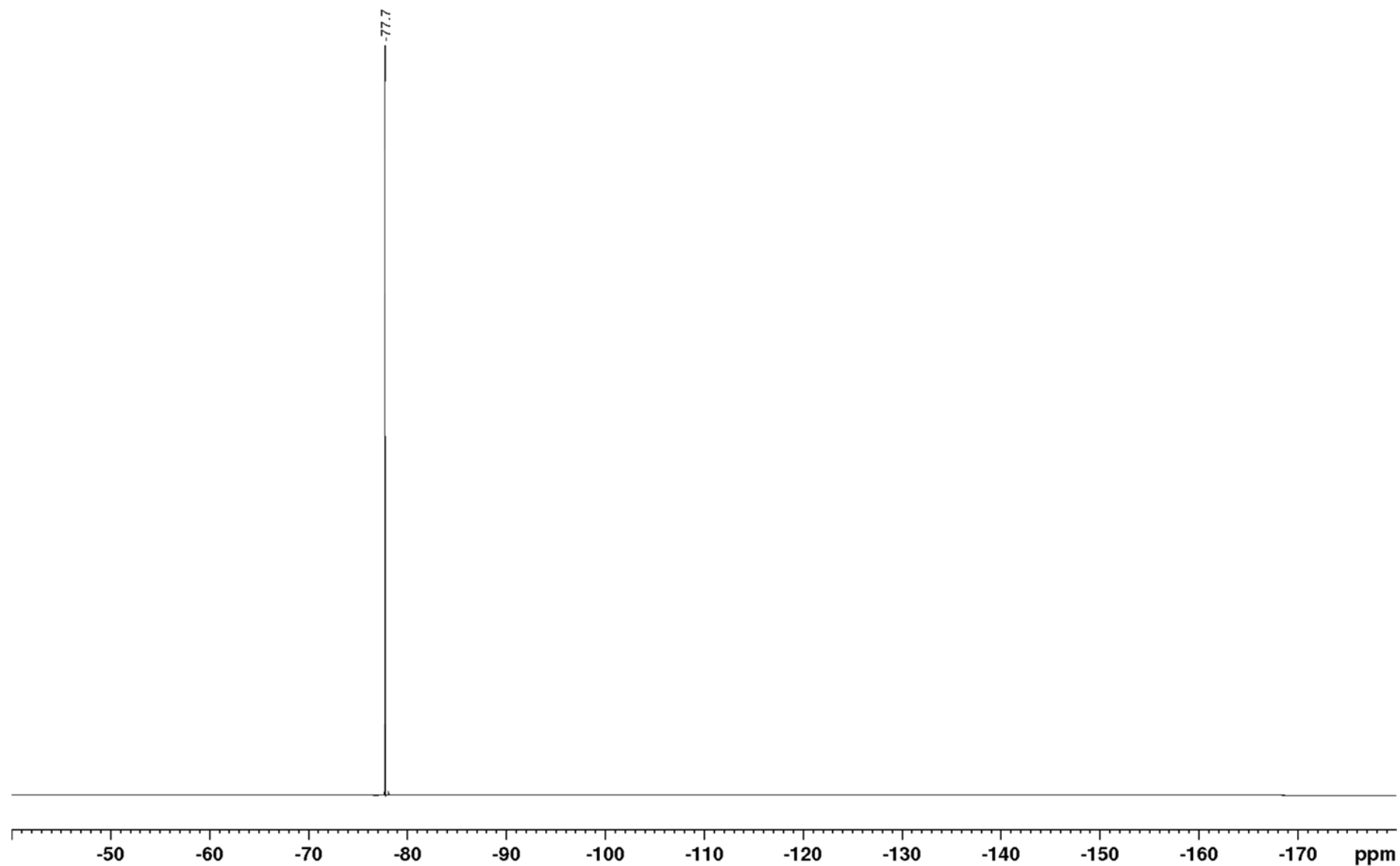
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1-phenylpentan-1-aminium trifluoromethanesulfonate (1p).**

¹H NMR (400 MHz, DMSO-

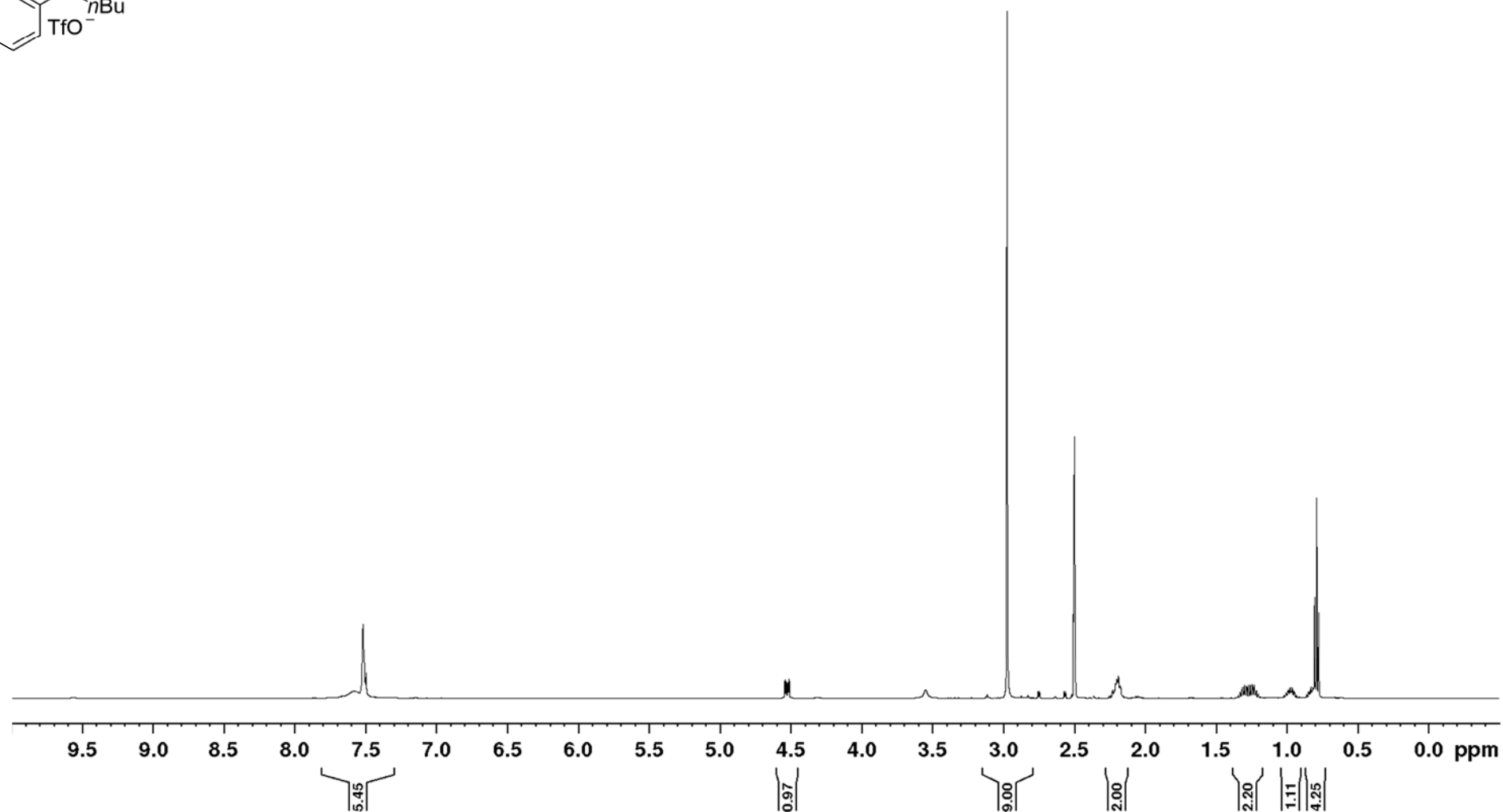


7.65
7.60
7.58
7.57
7.55
7.52
7.51
7.50
7.49
7.48

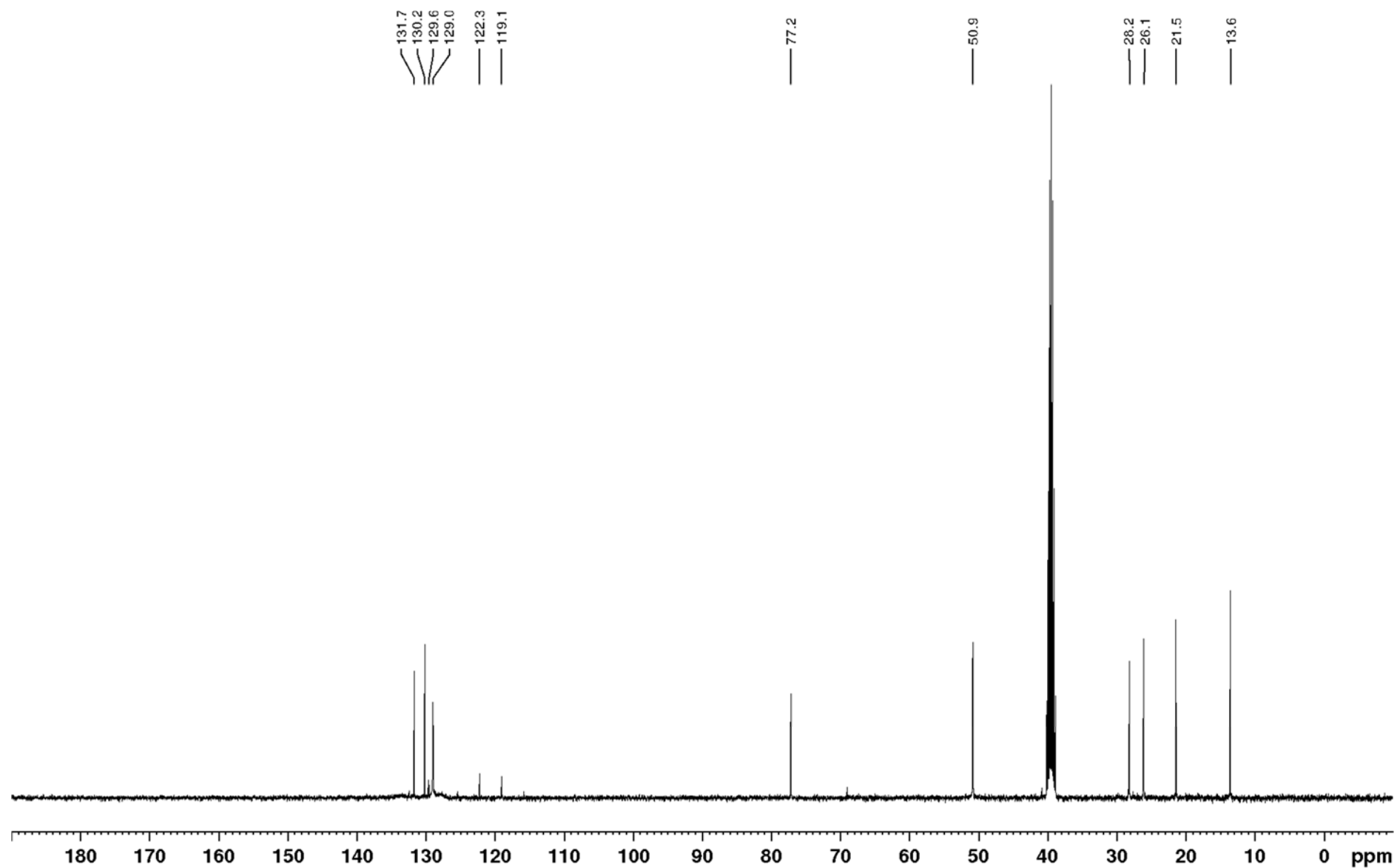
4.54
4.53
4.52
4.51

2.97
2.21
2.20
2.19
2.19
2.18
2.18
2.17
1.32
1.31
1.30
1.30
1.29
1.29
1.28
1.27
1.26
1.25
1.24
1.23
1.21
0.99
0.98
0.96
0.80
0.79
0.77

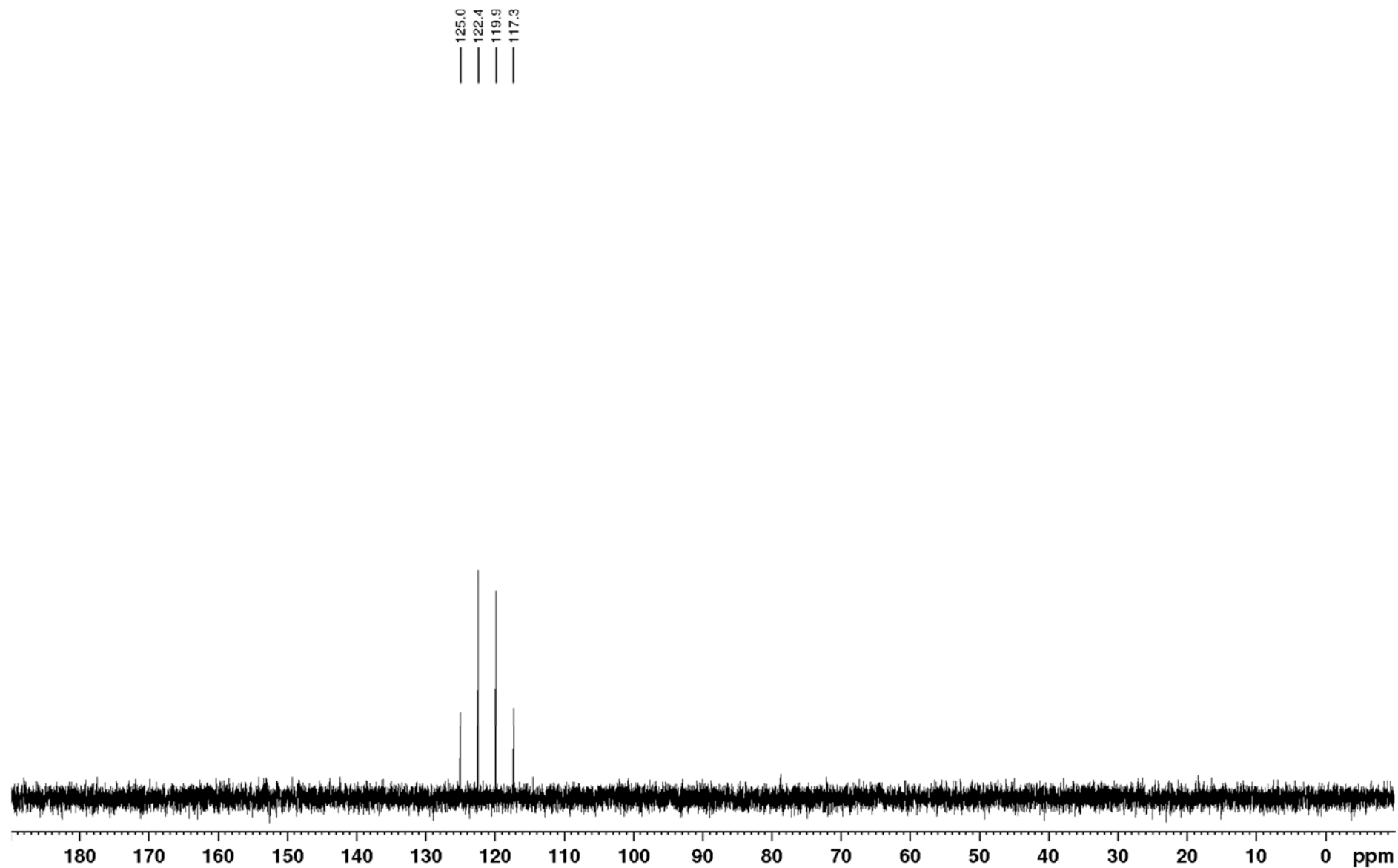
d₆):



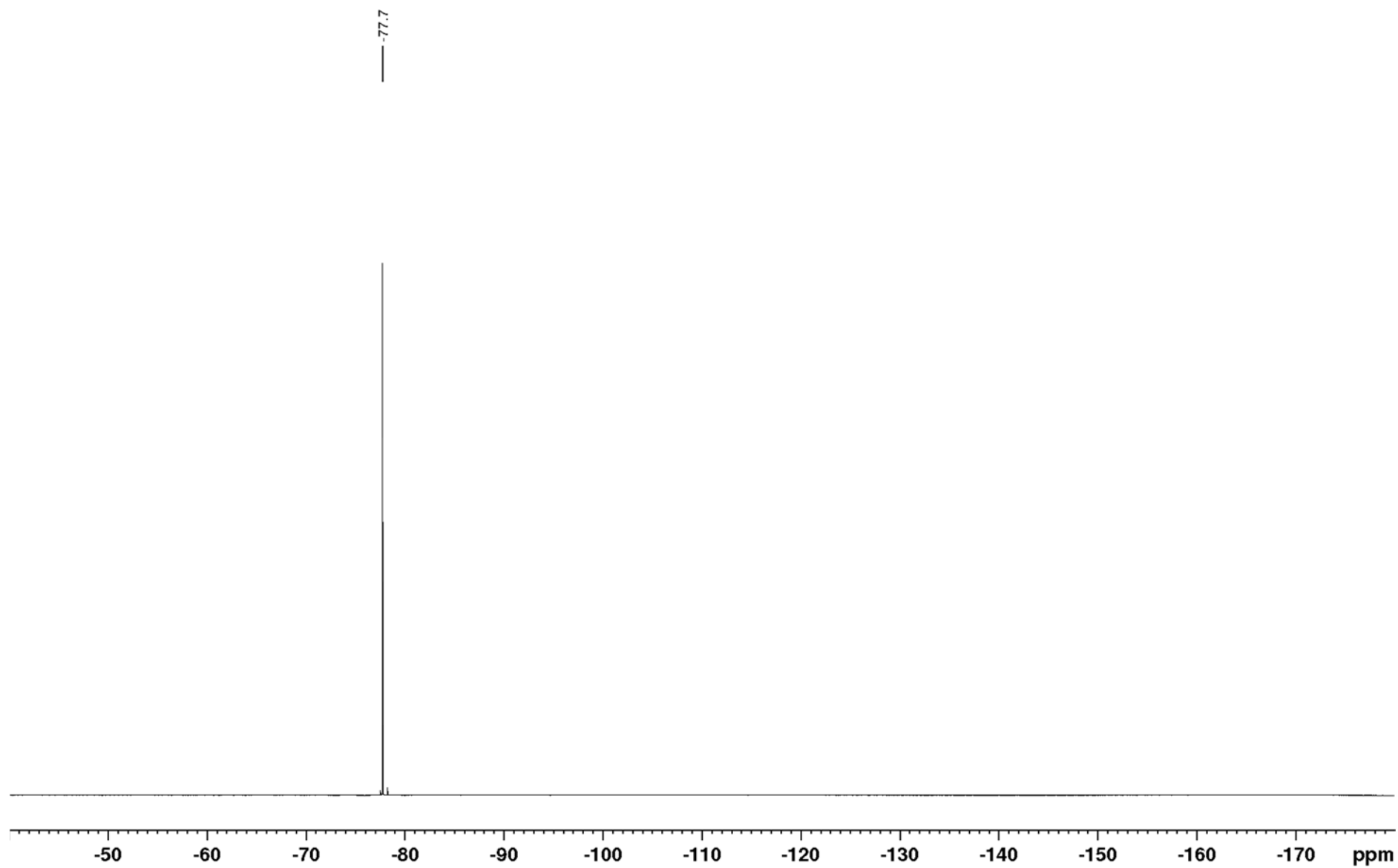
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

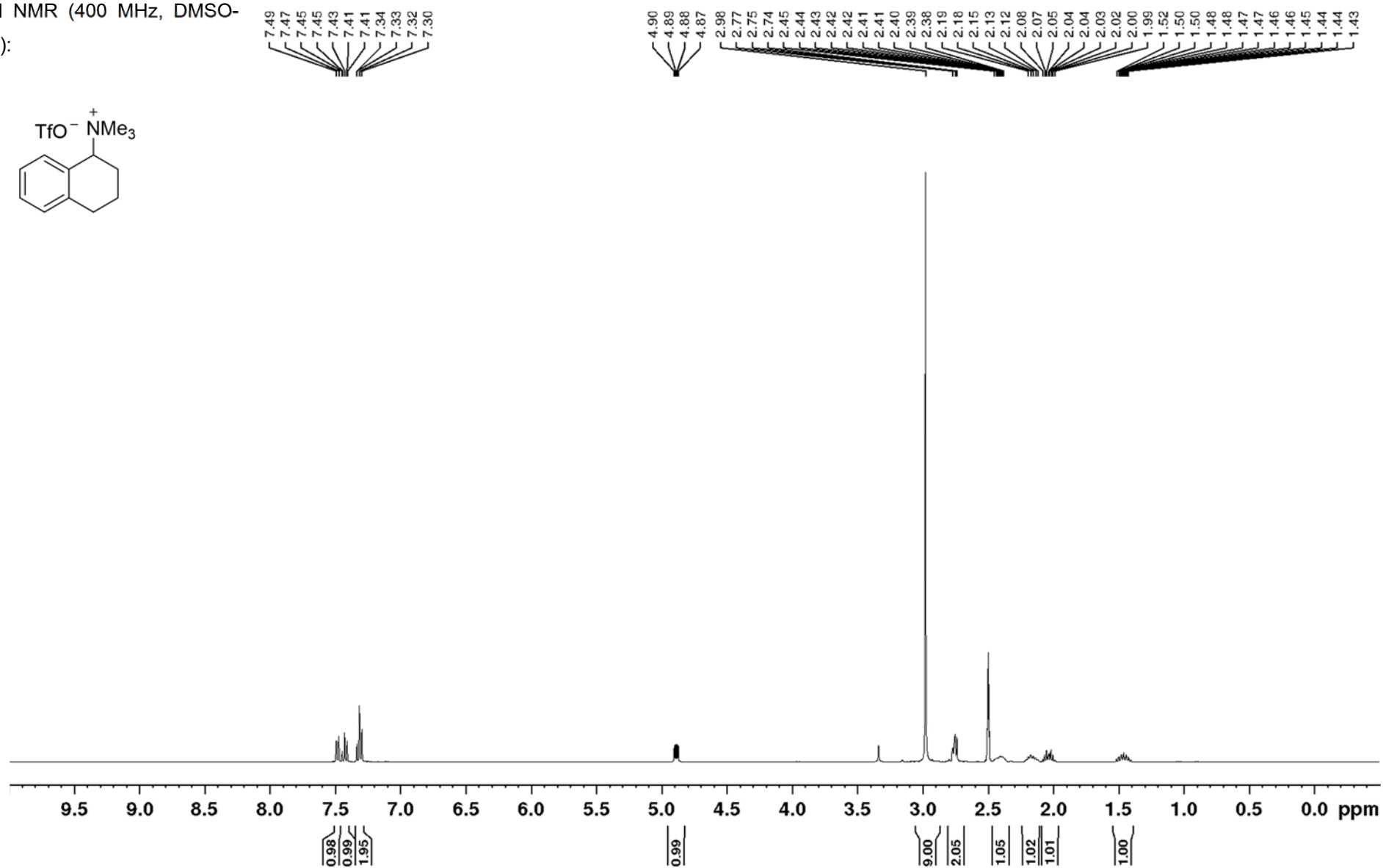
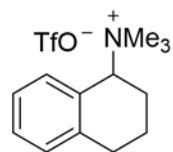
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

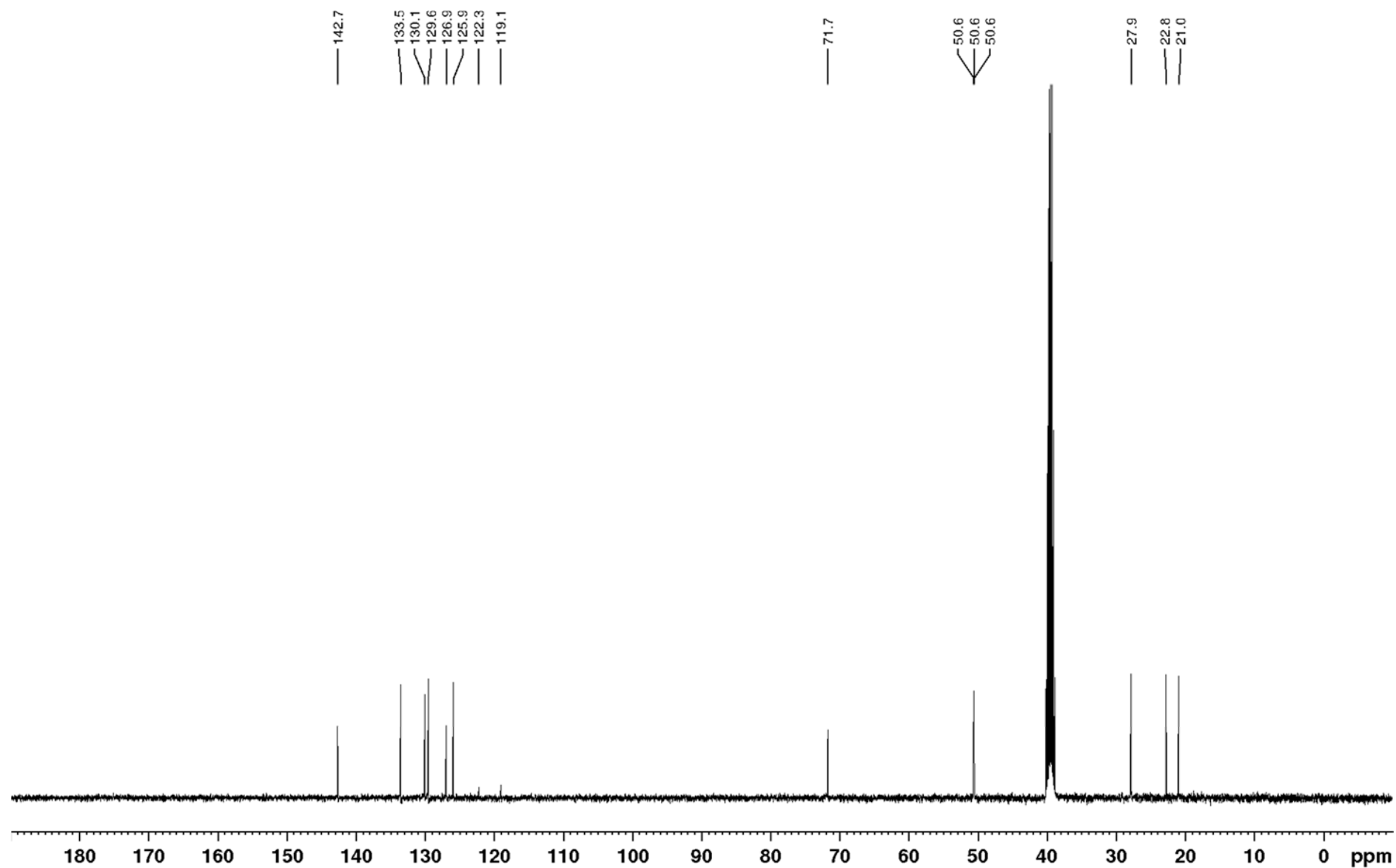
SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1,2,3,4-tetrahydronaphthalen-1-aminium trifluoromethanesulfonate (1q).**

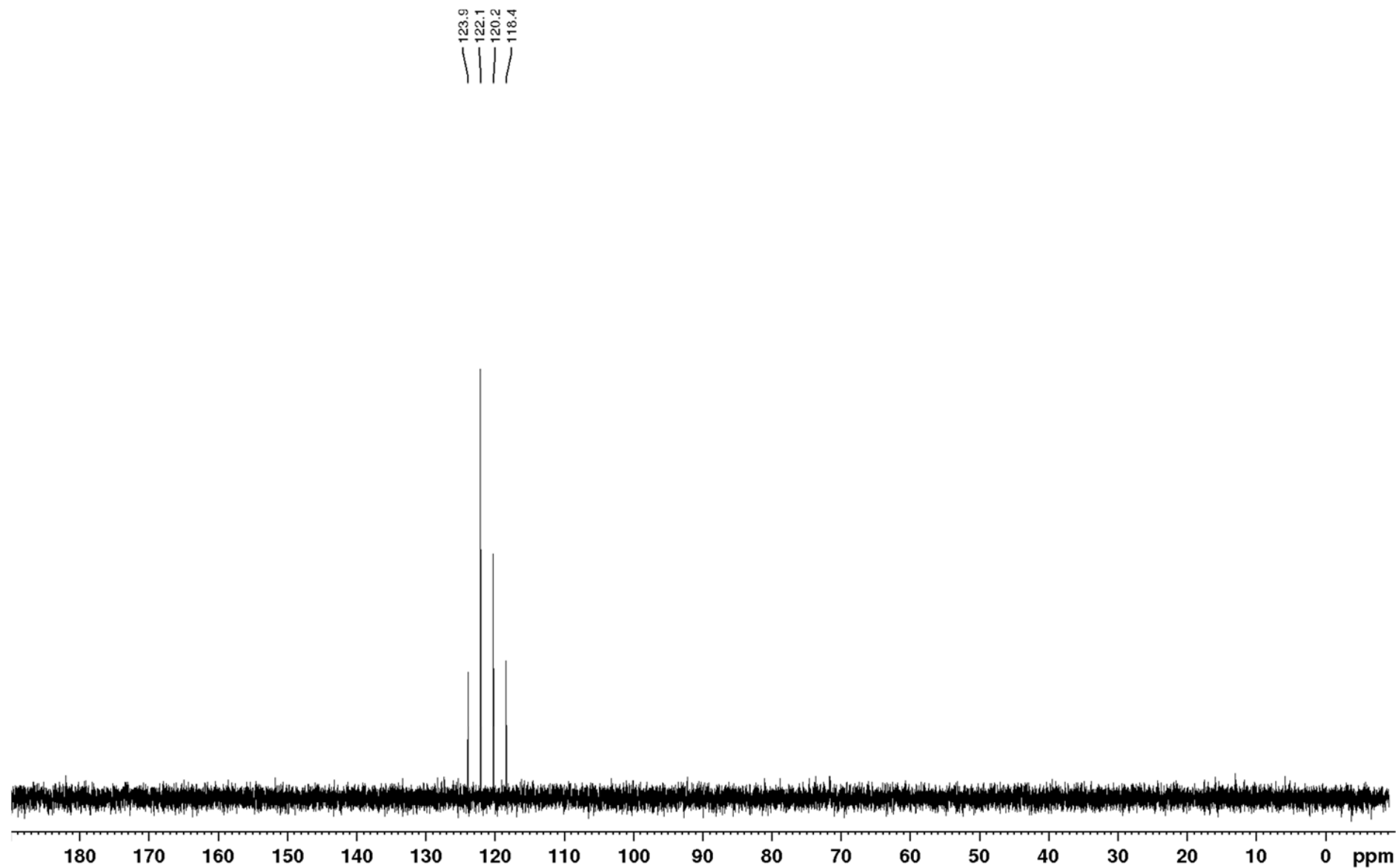
¹H NMR (400 MHz, DMSO-
d₆):



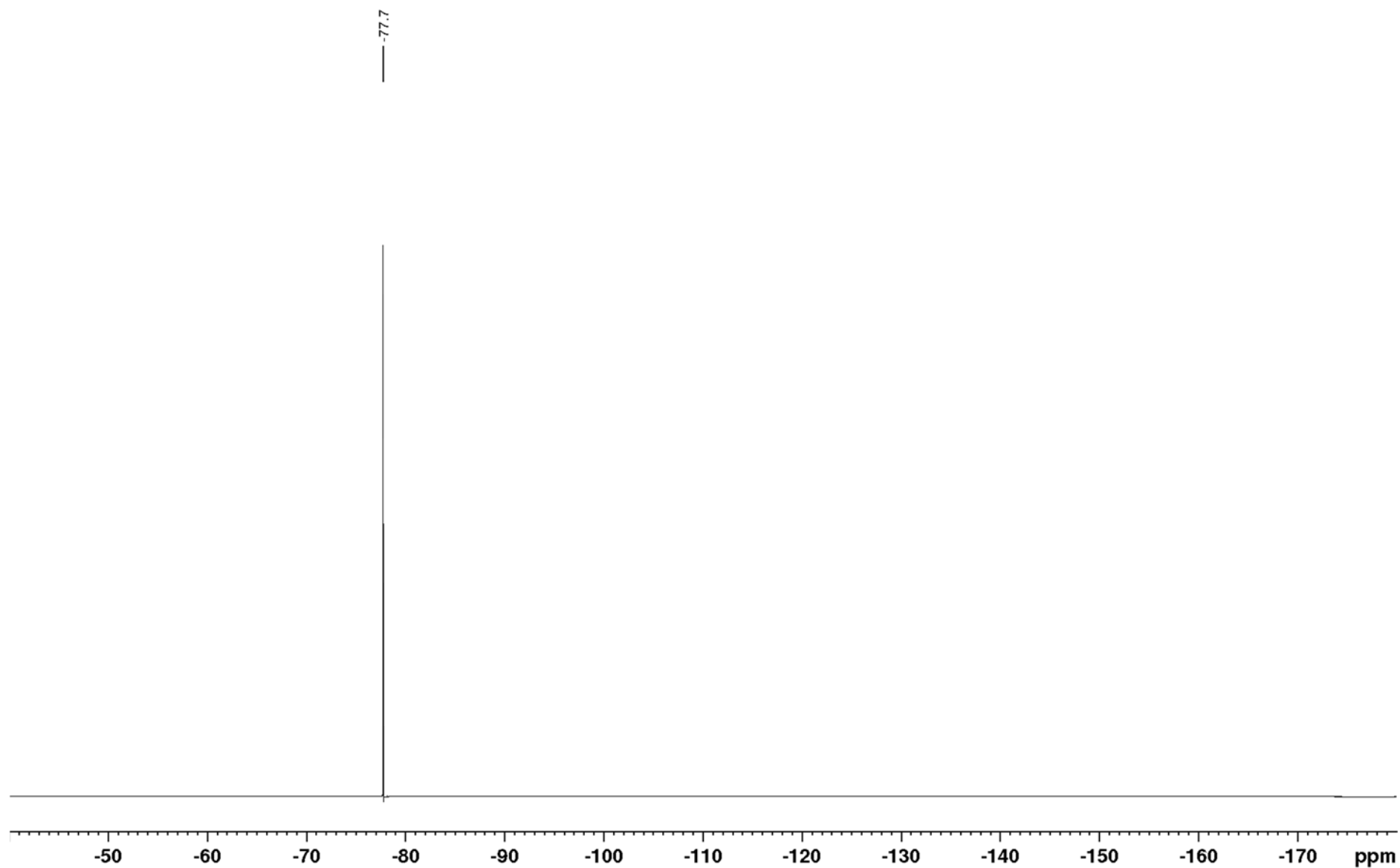
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

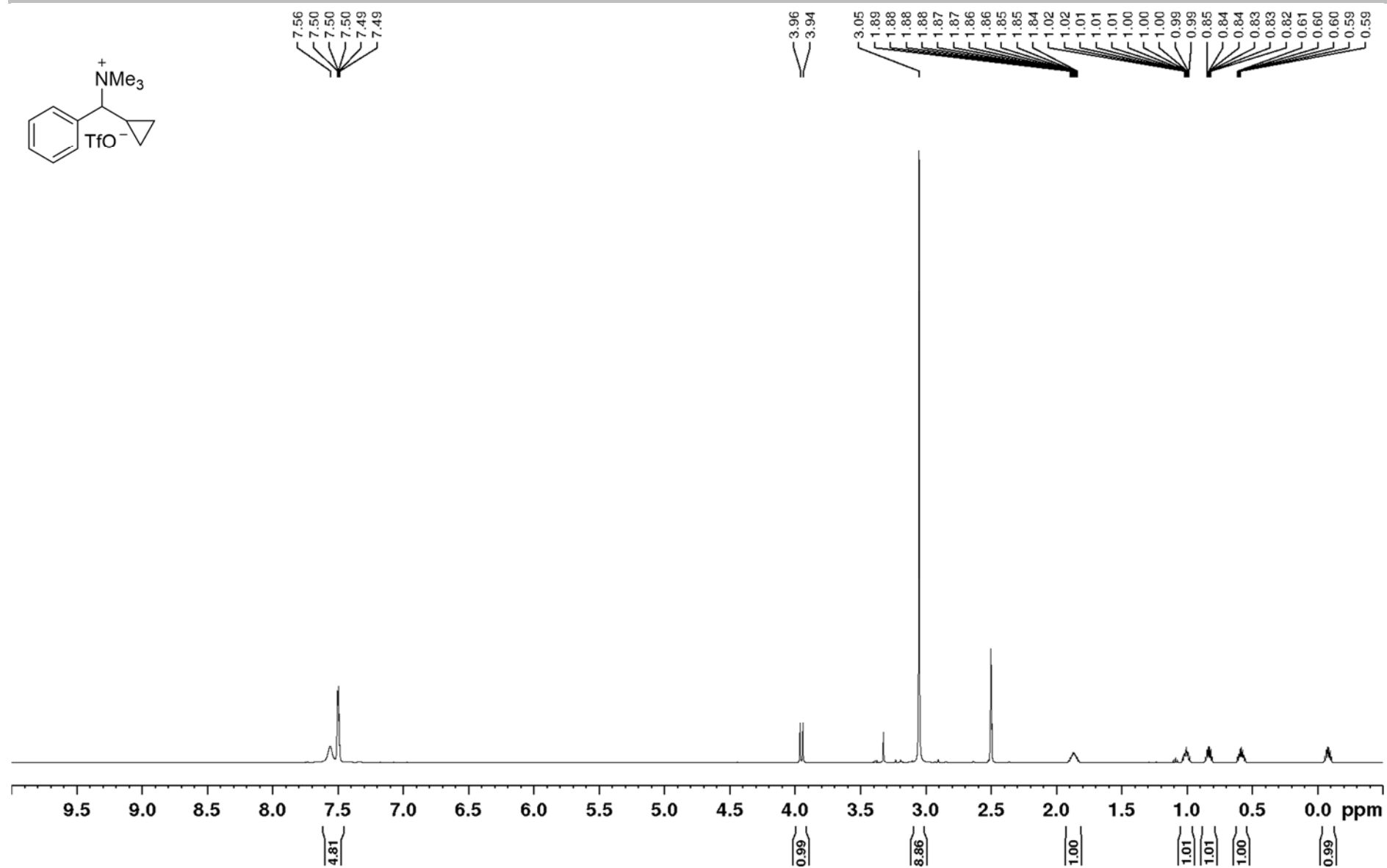
 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

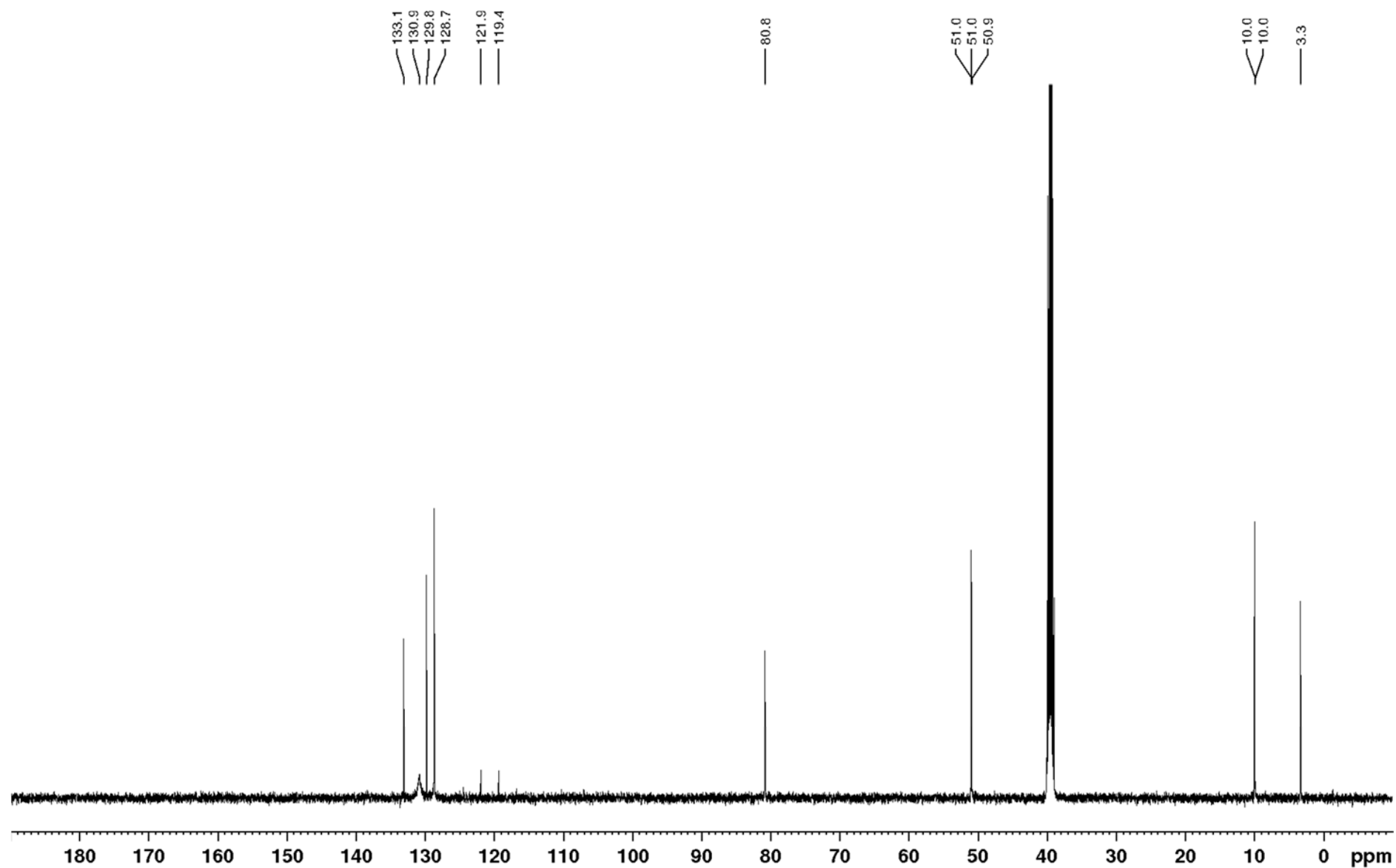
1-Cyclopropyl-*N,N,N*-trimethyl-1-phenylmethanaminium trifluoromethanesulfonate (1r)

¹H NMR (500 MHz, DMSO-*d*₆):

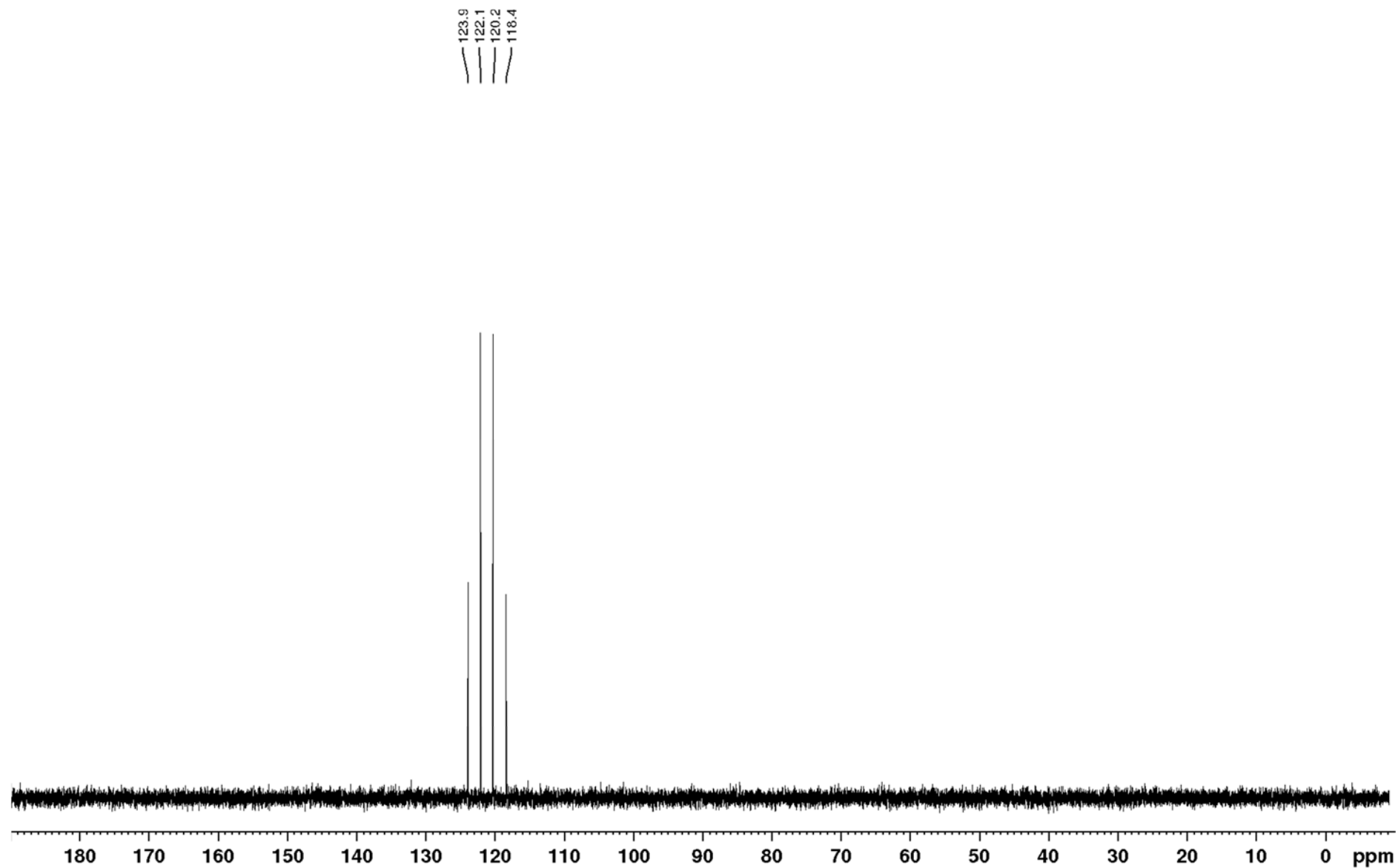
SUPPORTING INFORMATION



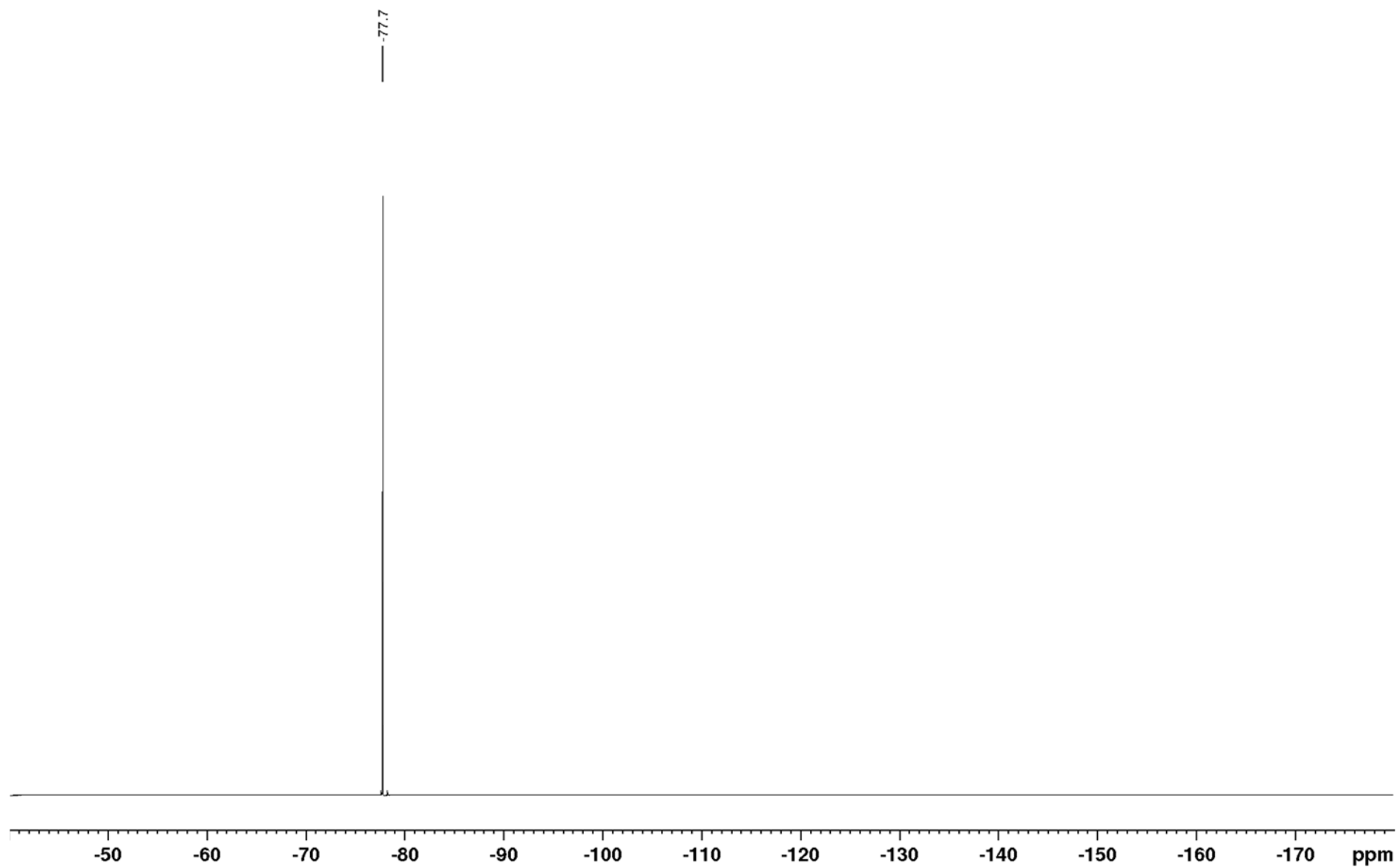
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

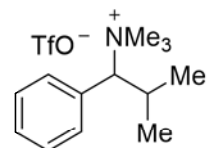
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

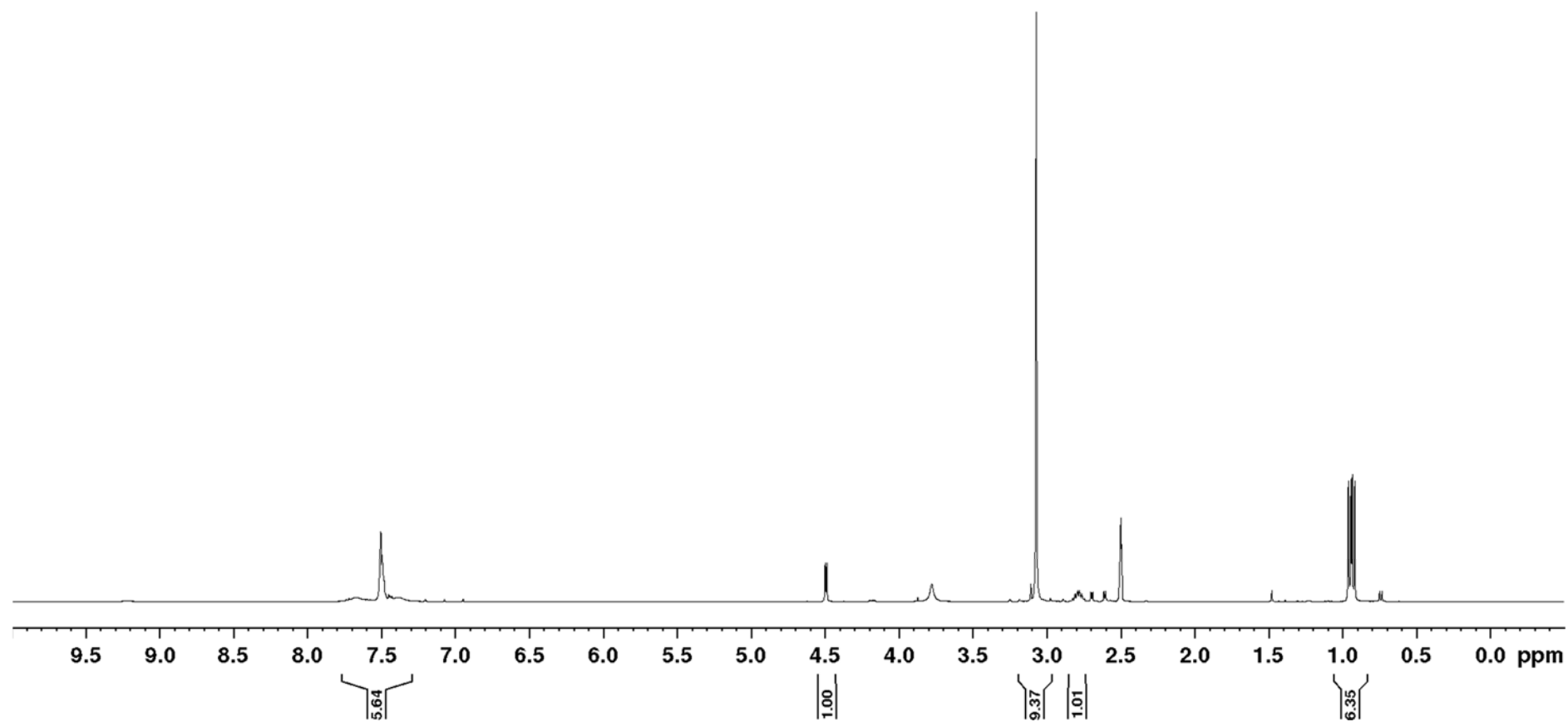
***N,N,N,2*-Tetramethyl-1-phenylpropan-1-aminium trifluoromethanesulfonate (1s)**¹H NMR (400 MHz,

7.74
7.72
7.72
7.67
7.61
7.60
7.50
7.48
7.45
7.44
7.43
7.43
7.39

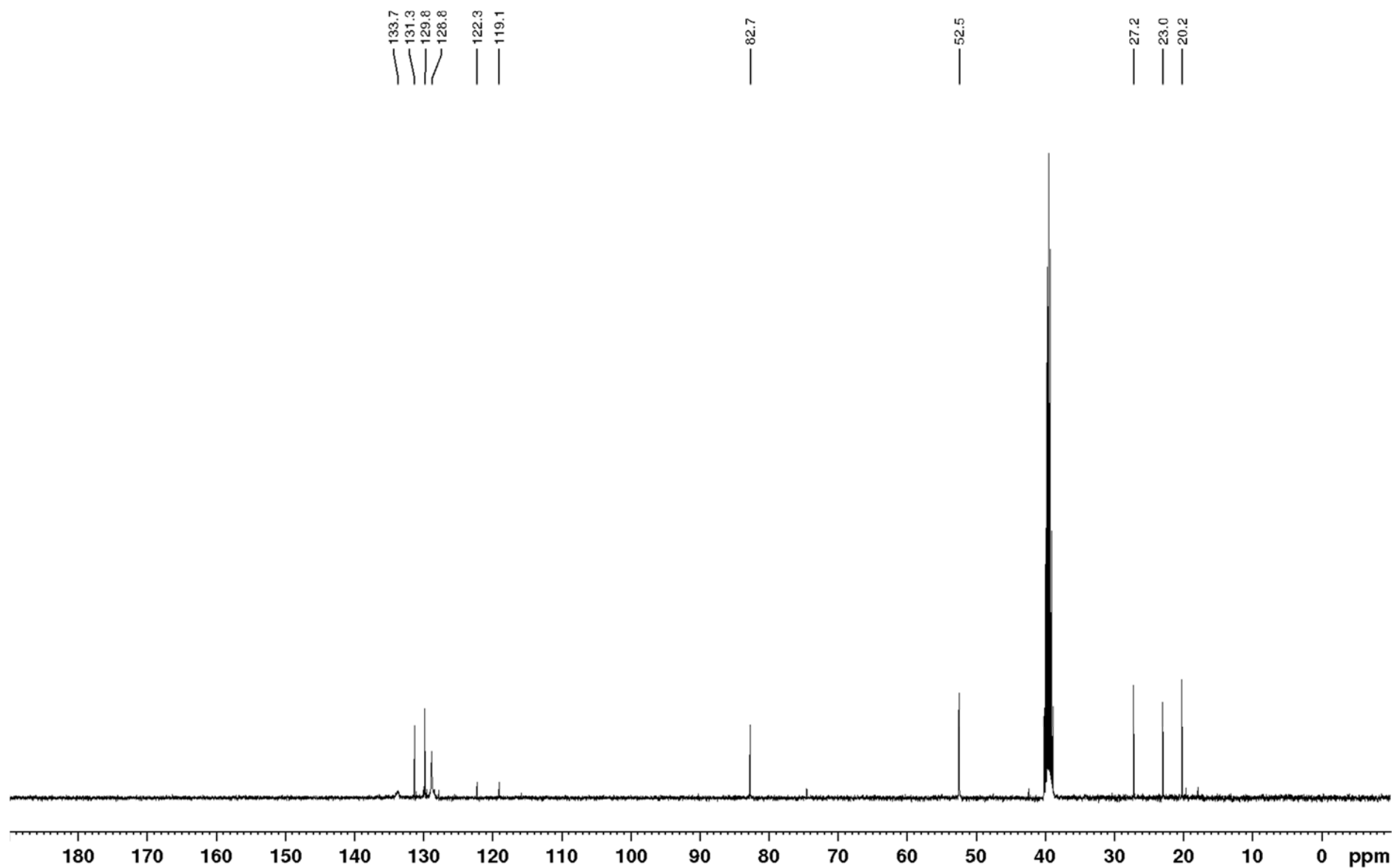
4.50
4.49

3.07
2.82
2.81
2.80
2.79
2.78
2.76
2.76
2.75

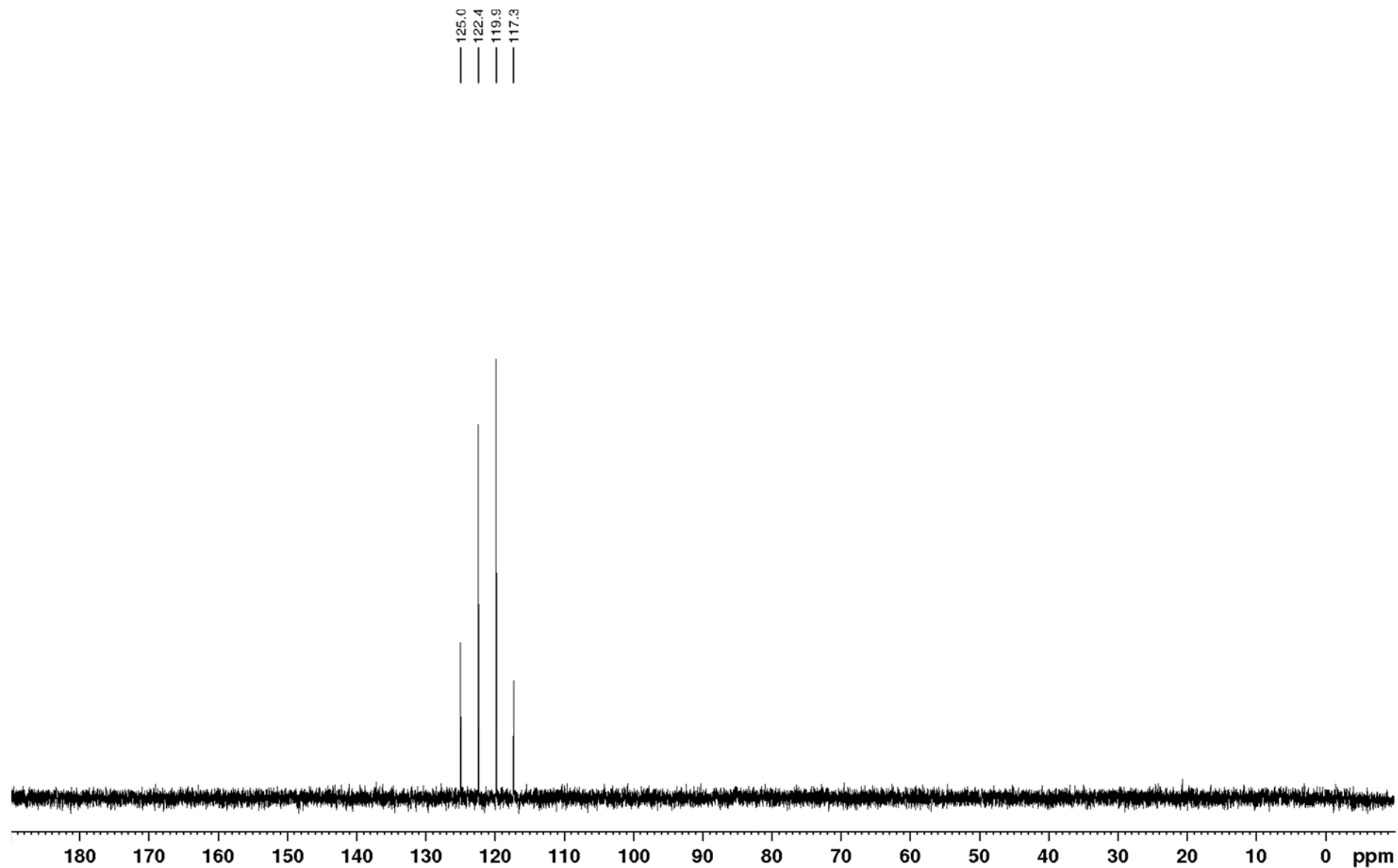
0.96
0.94
0.93
0.92

DMSO-*d*₆):

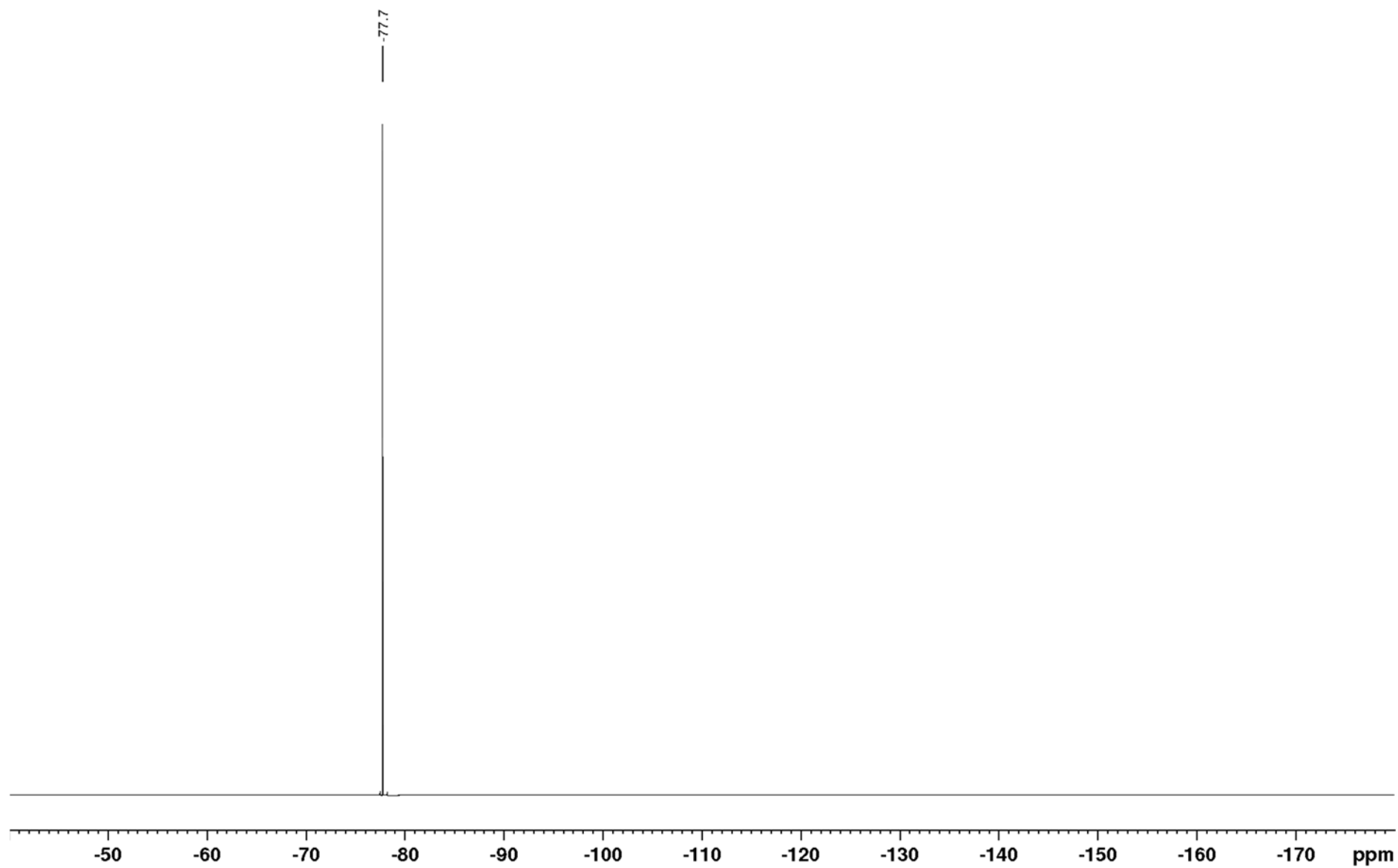
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

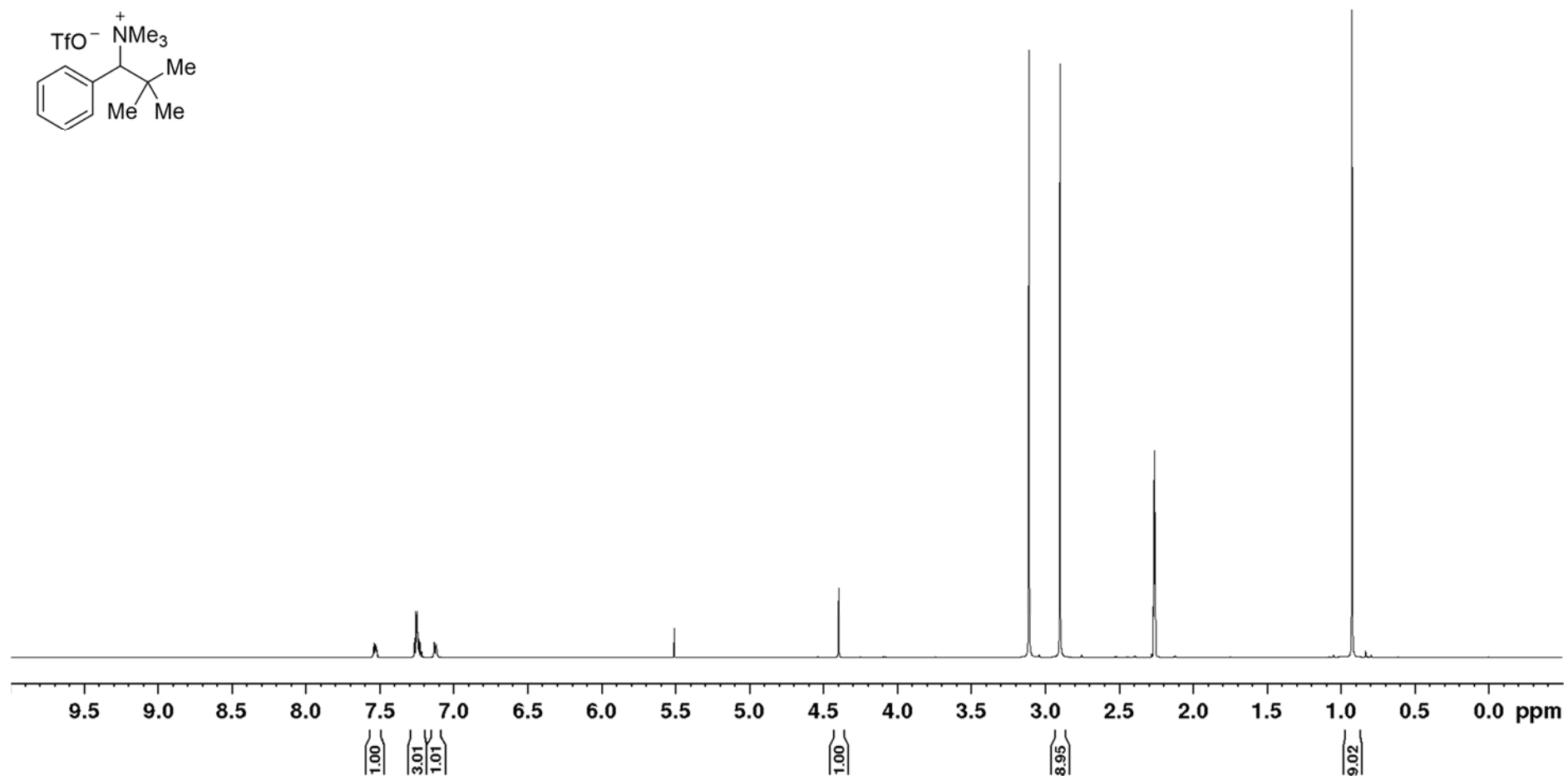
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

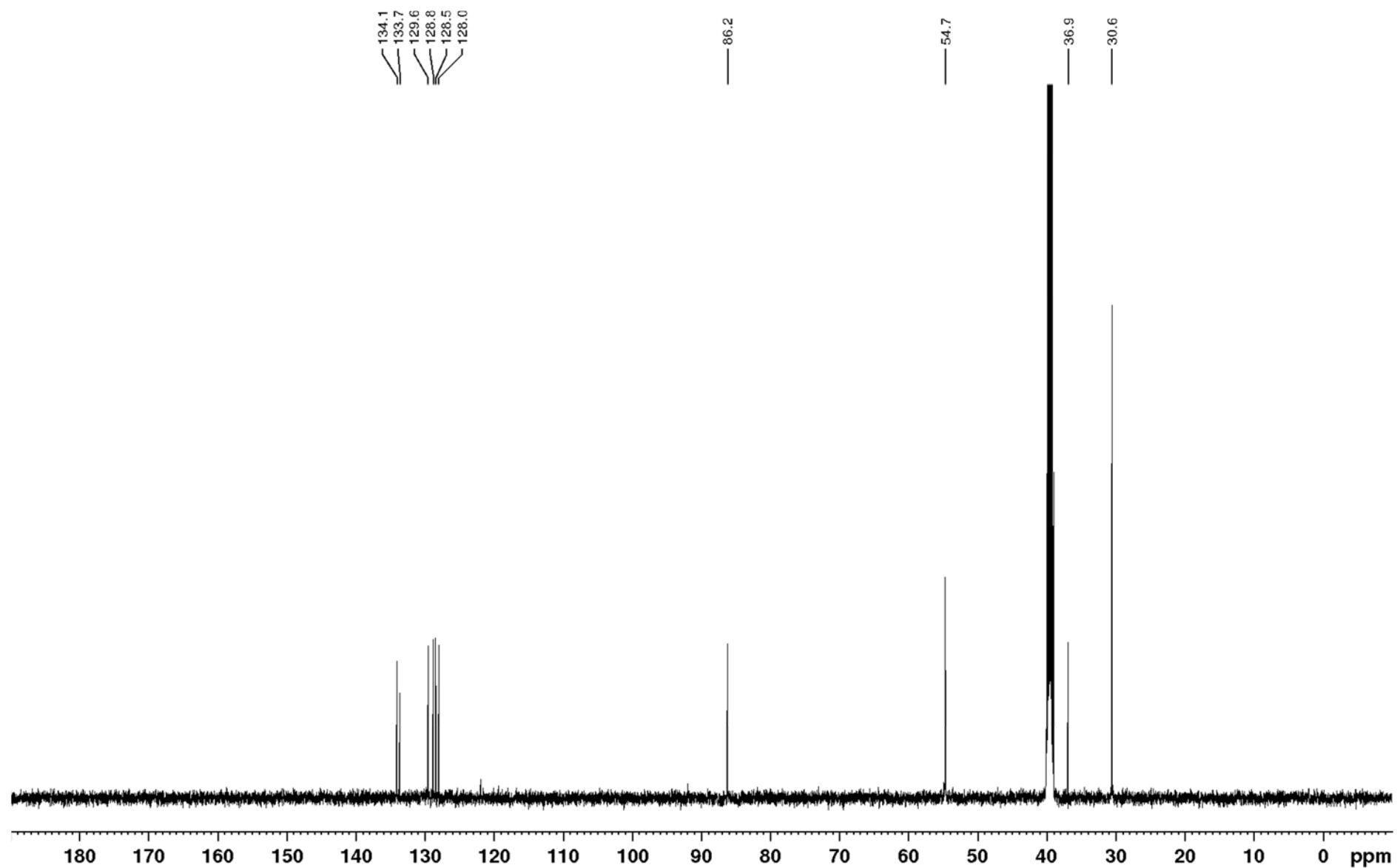
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

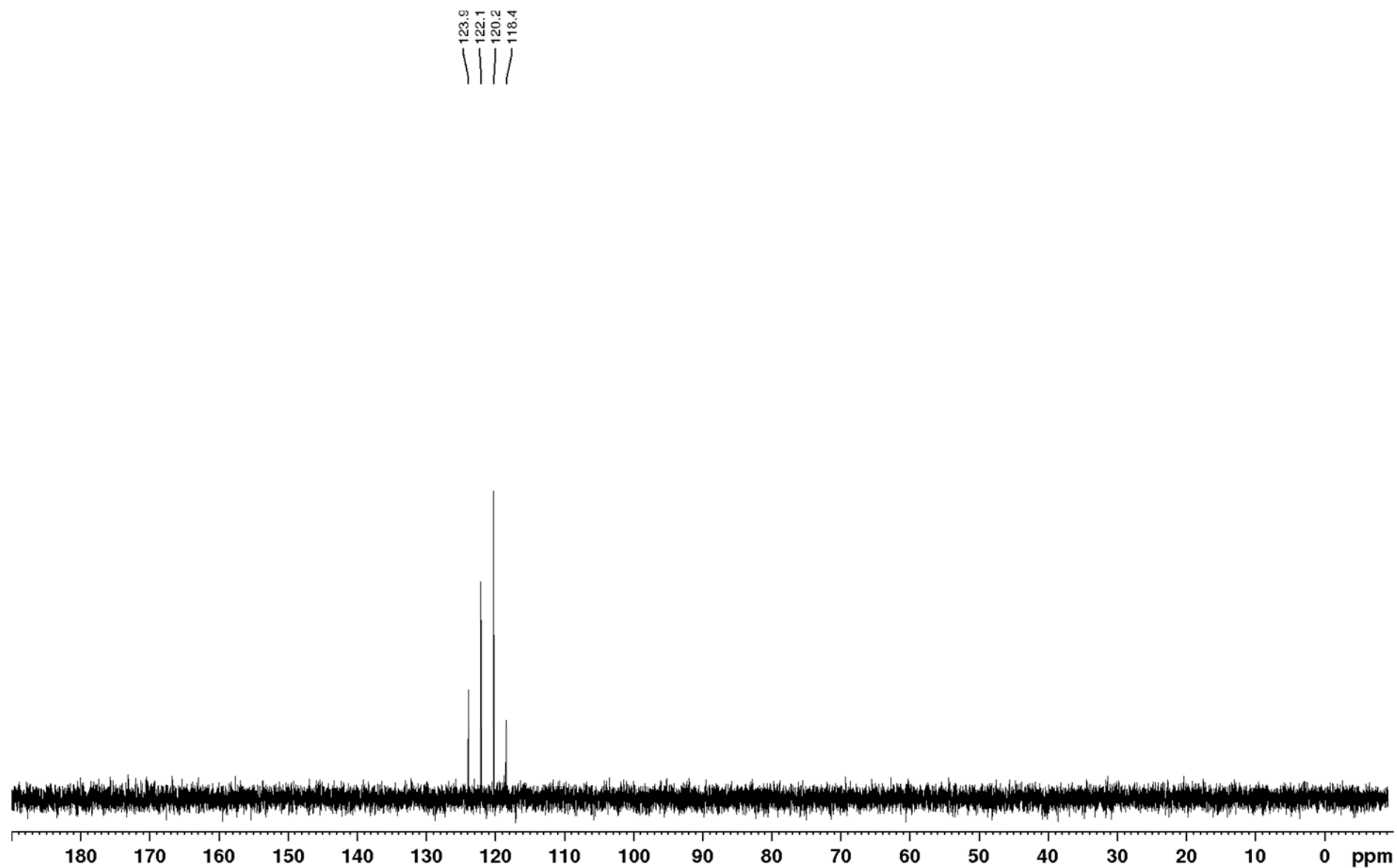
SUPPORTING INFORMATION

***N,N,N,2,2*-Pentamethyl-1-phenylpropan-1-aminium trifluoromethanesulfonate (1t).**¹H NMR (400 MHz,DMSO-*d*₆):

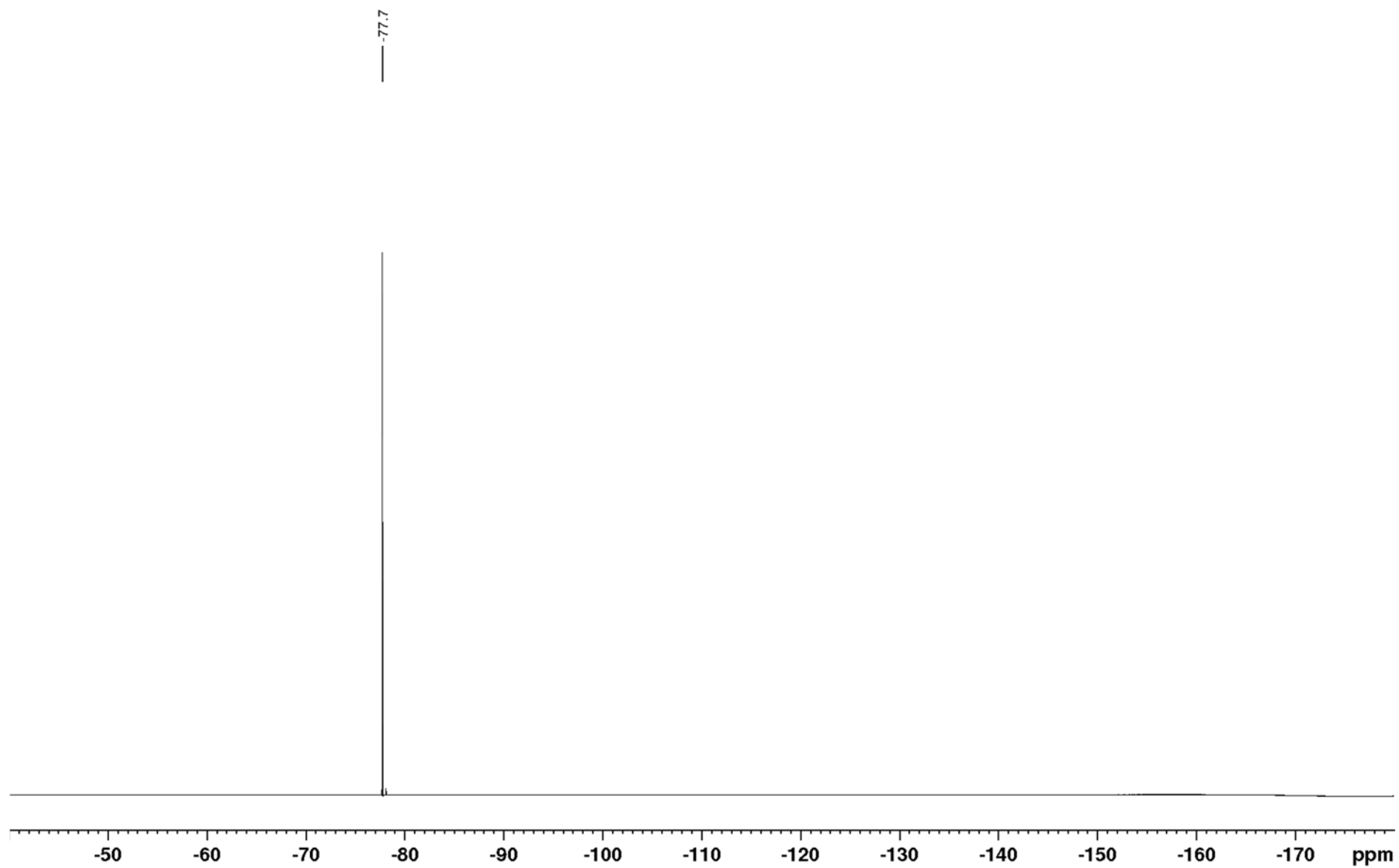
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

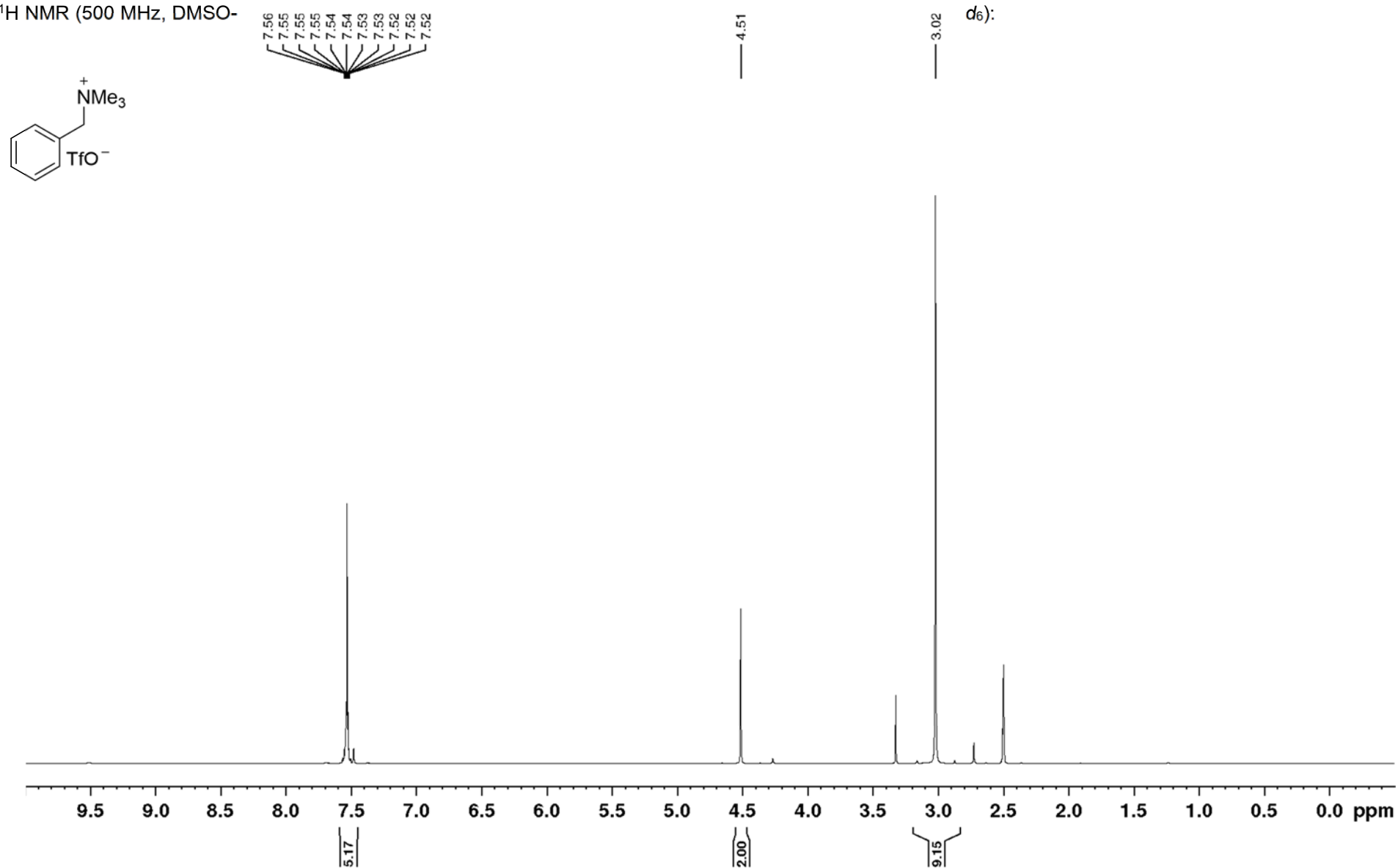
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

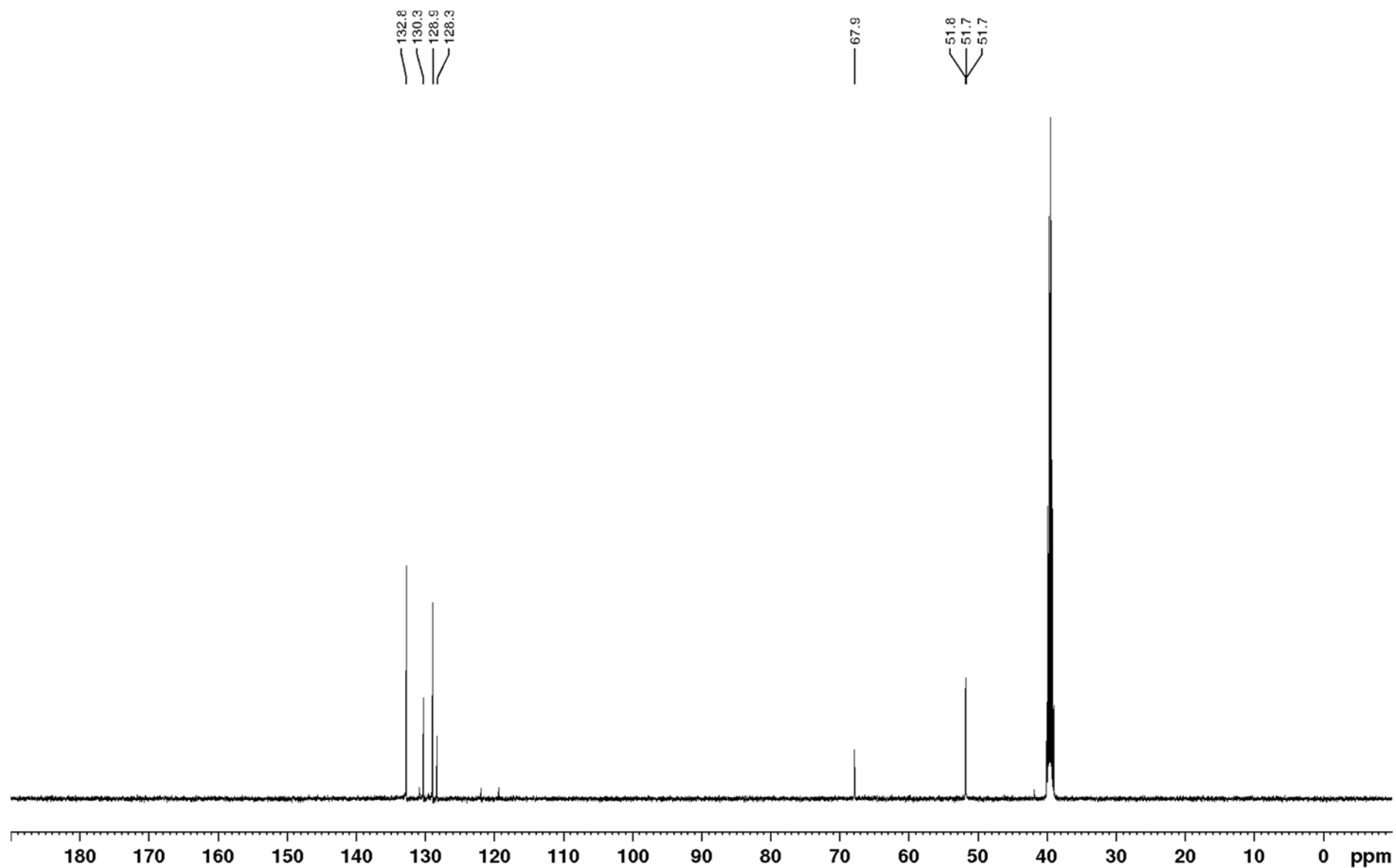
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

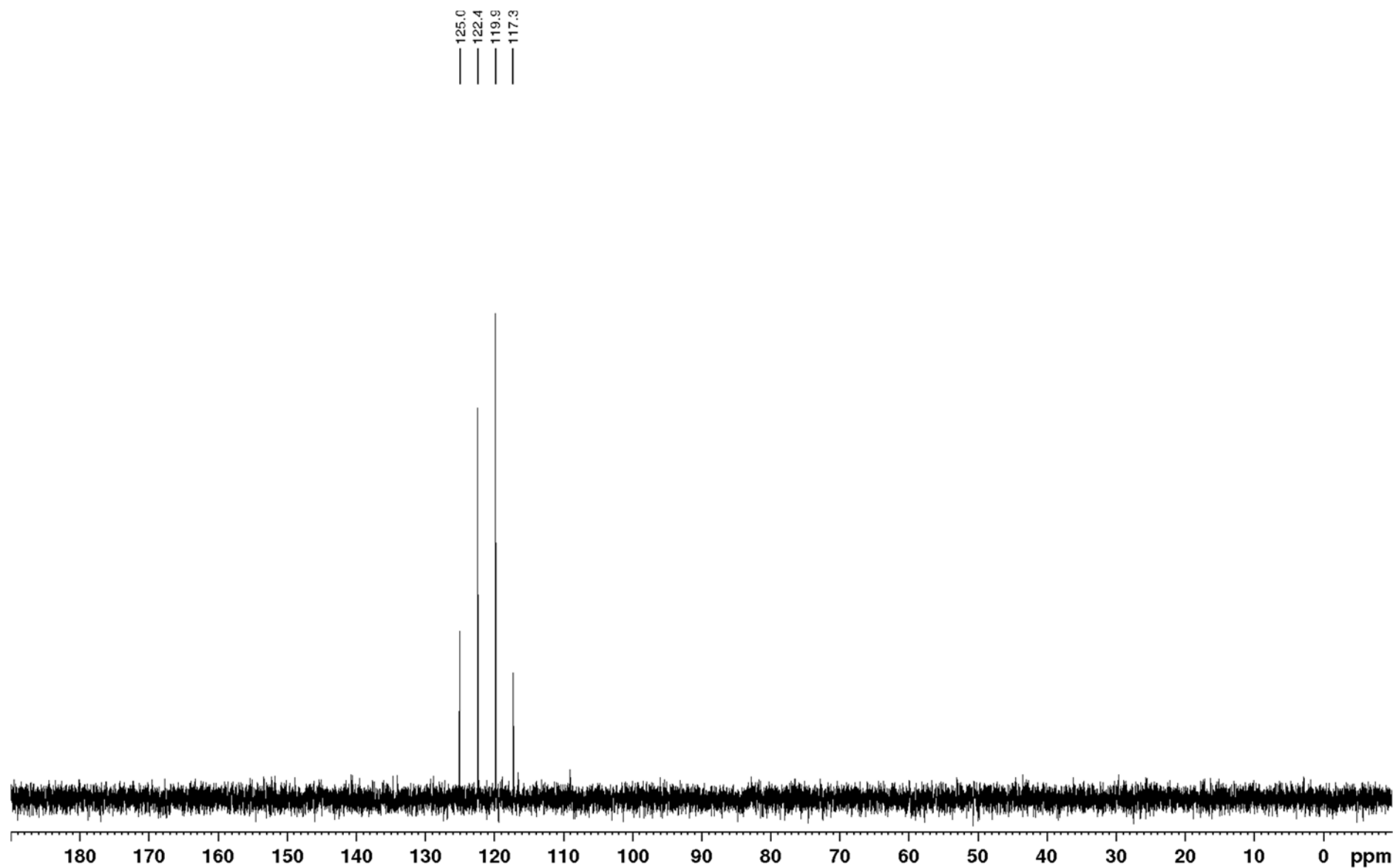
SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1-phenylmethanaminium trifluoromethanesulfonate (1u).**¹H NMR (500 MHz, DMSO-

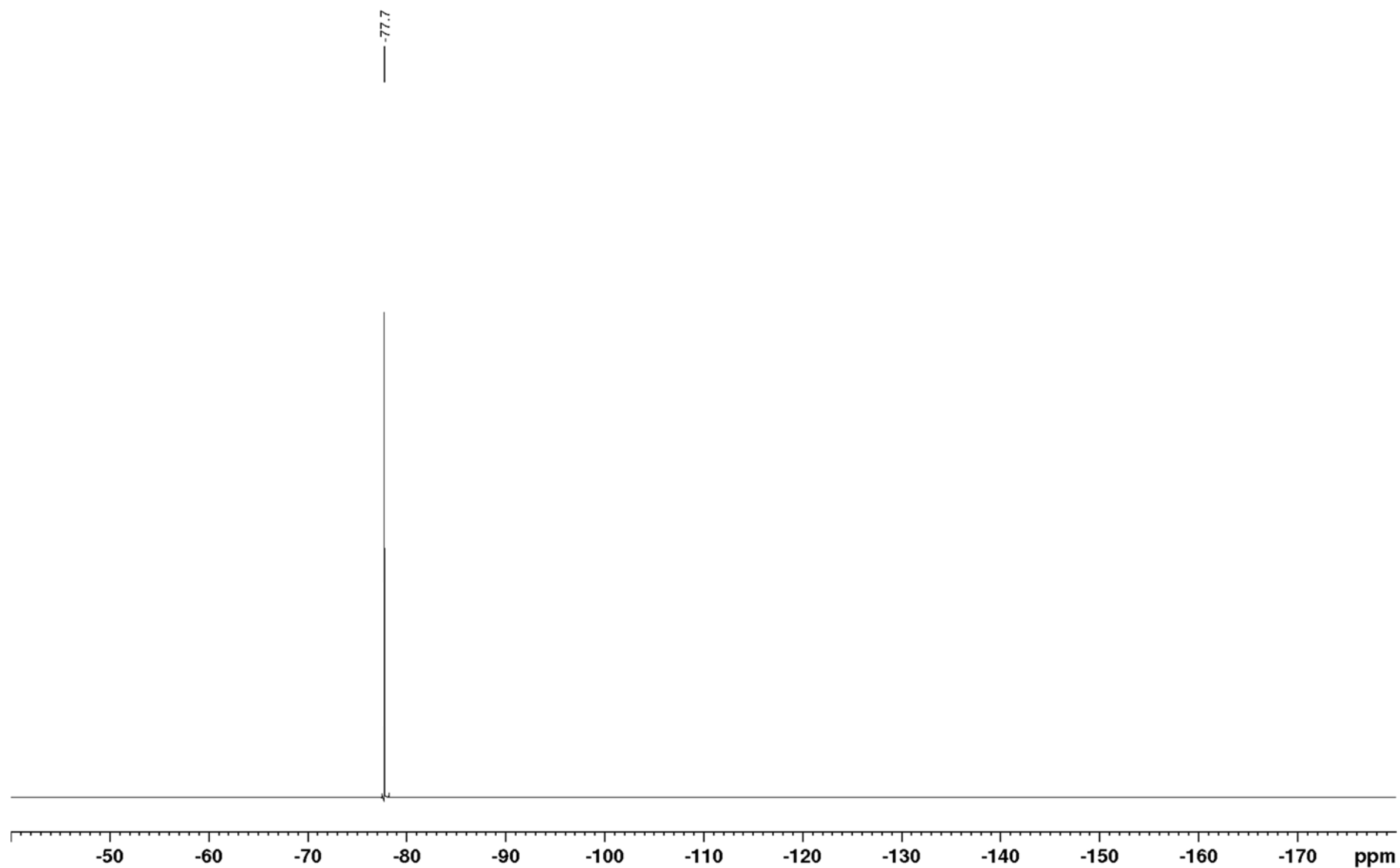
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

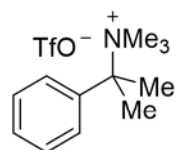
 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO}-d_6$):

SUPPORTING INFORMATION

***N,N,N*-Trimethyl-2-phenylpropan-2-aminium trifluoromethanesulfonate (1v).**

¹H NMR (500 MHz,

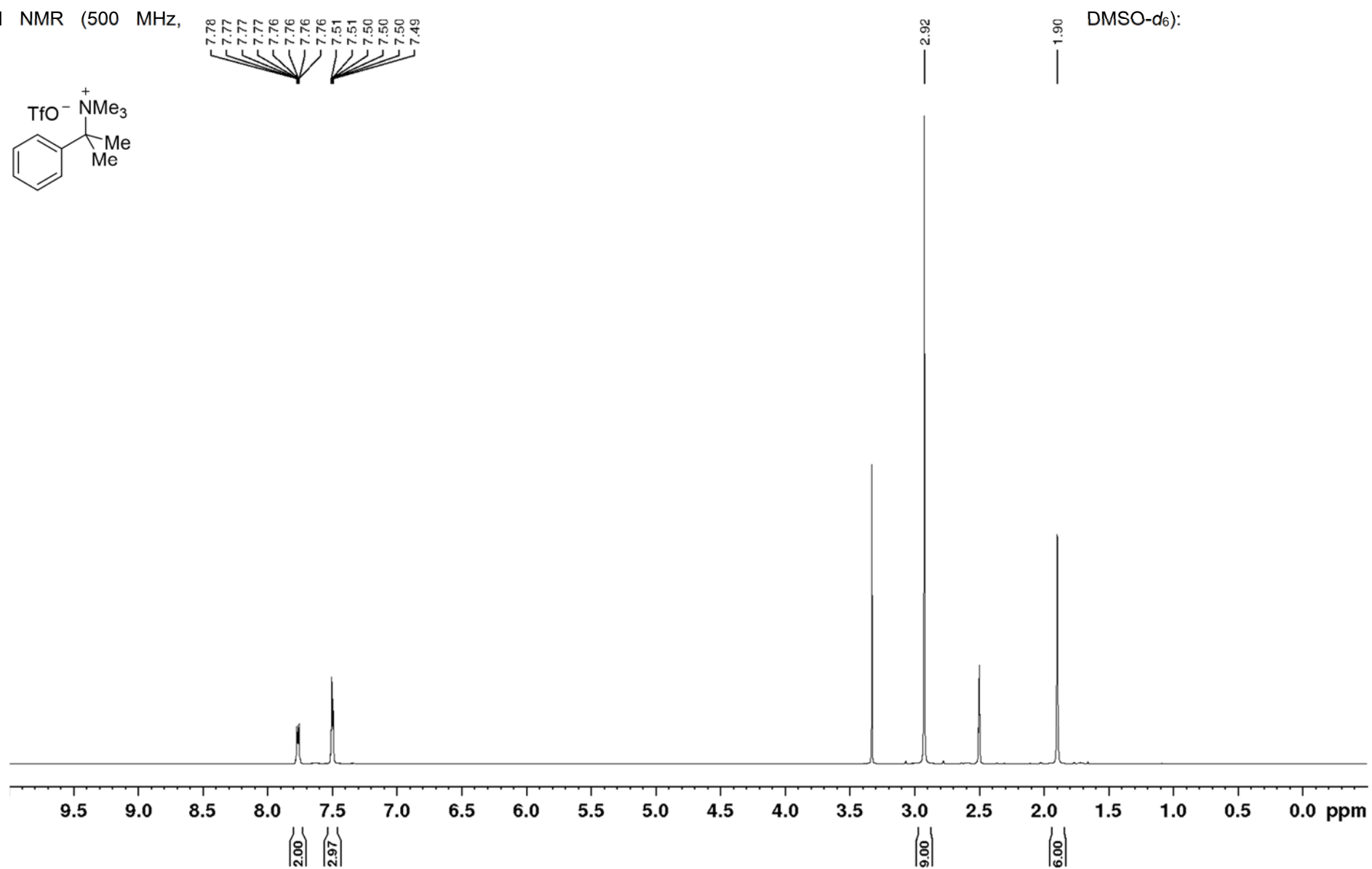
7.78
7.77
7.77
7.77
7.76
7.76
7.76
7.51
7.51
7.50
7.50
7.49



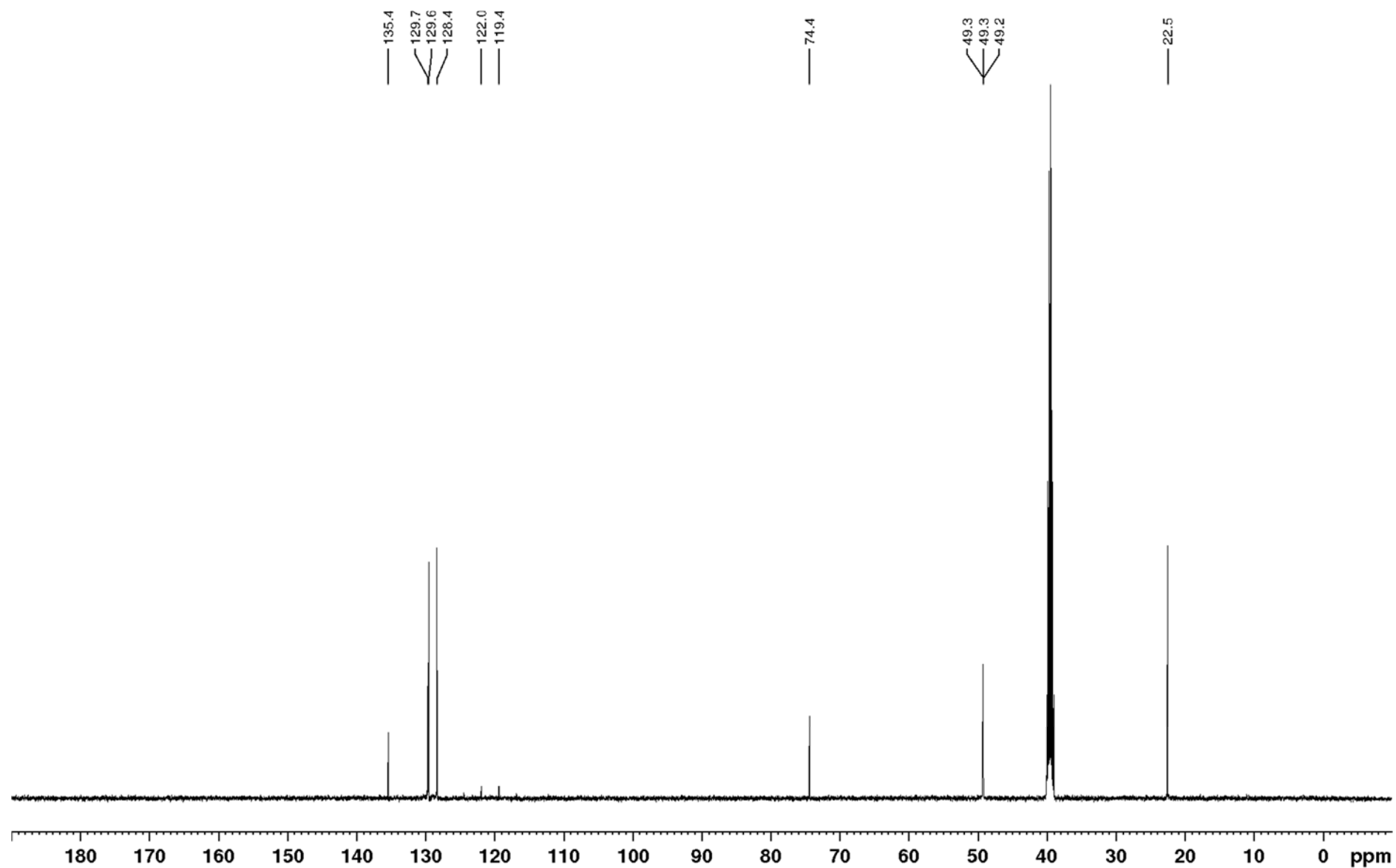
DMSO-*d*₆):

2.92

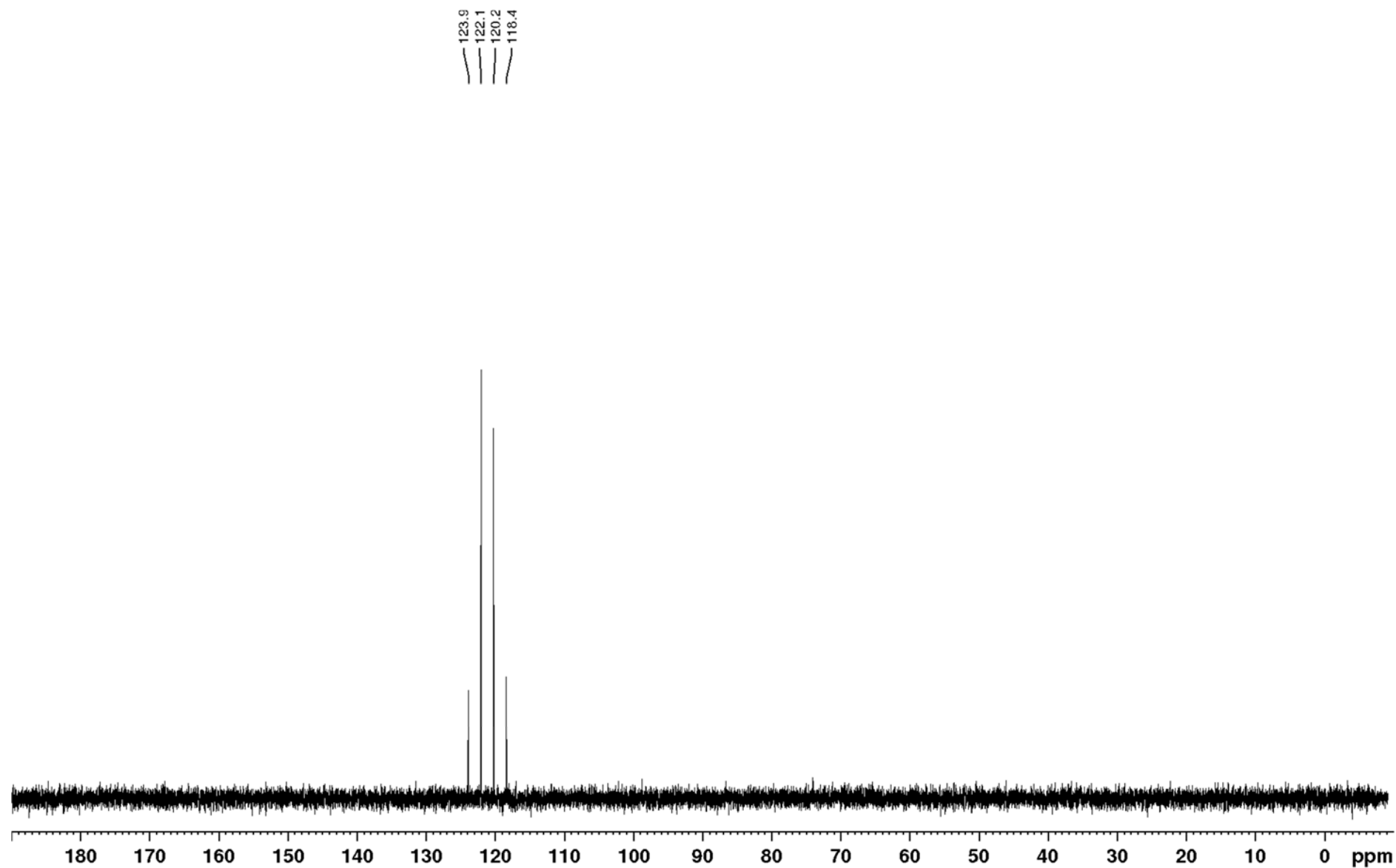
1.90



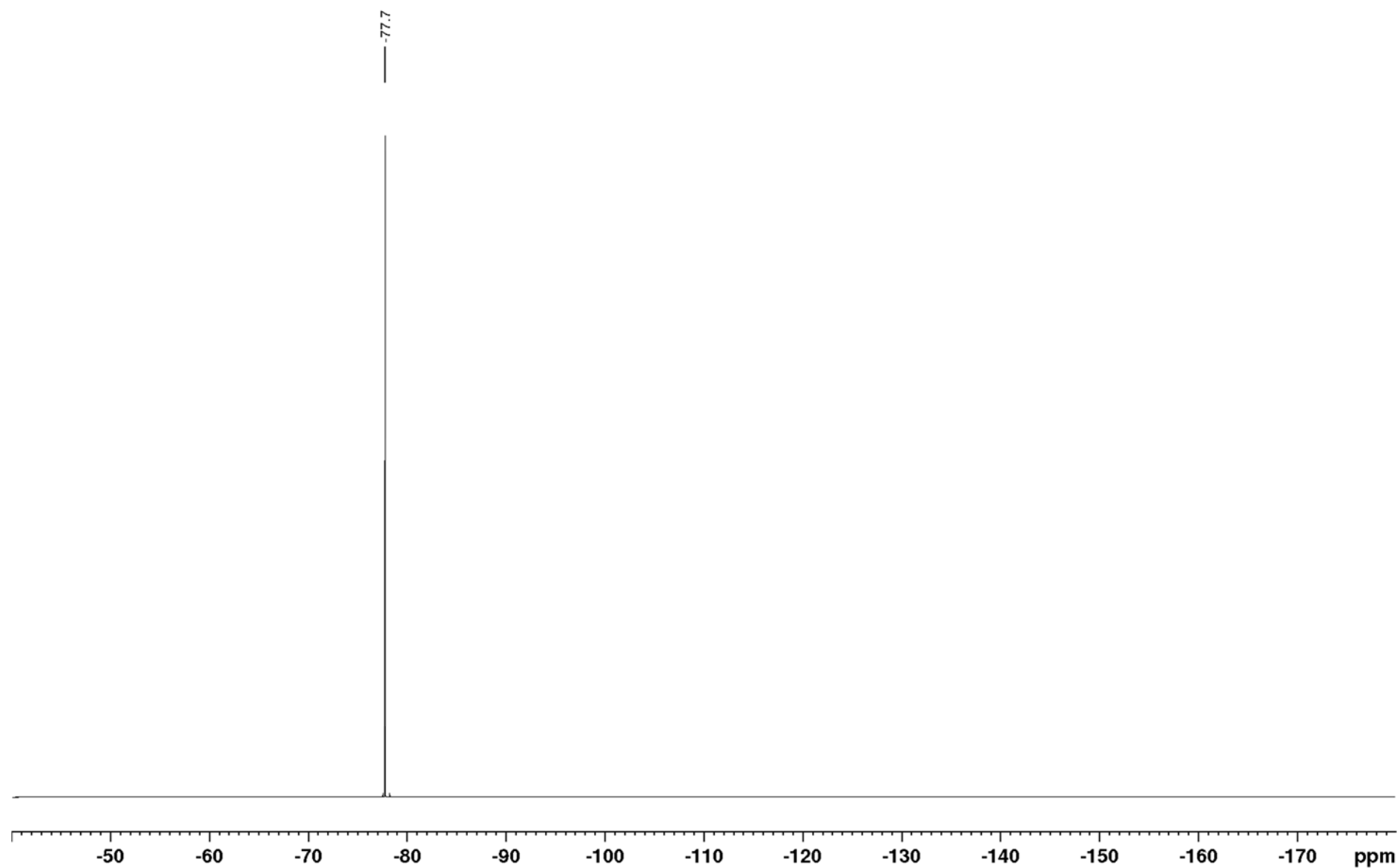
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

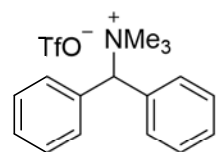
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

***N,N,N*-Trimethyl-1,1-diphenylmethanaminium trifluoromethanesulfonate (1w).**

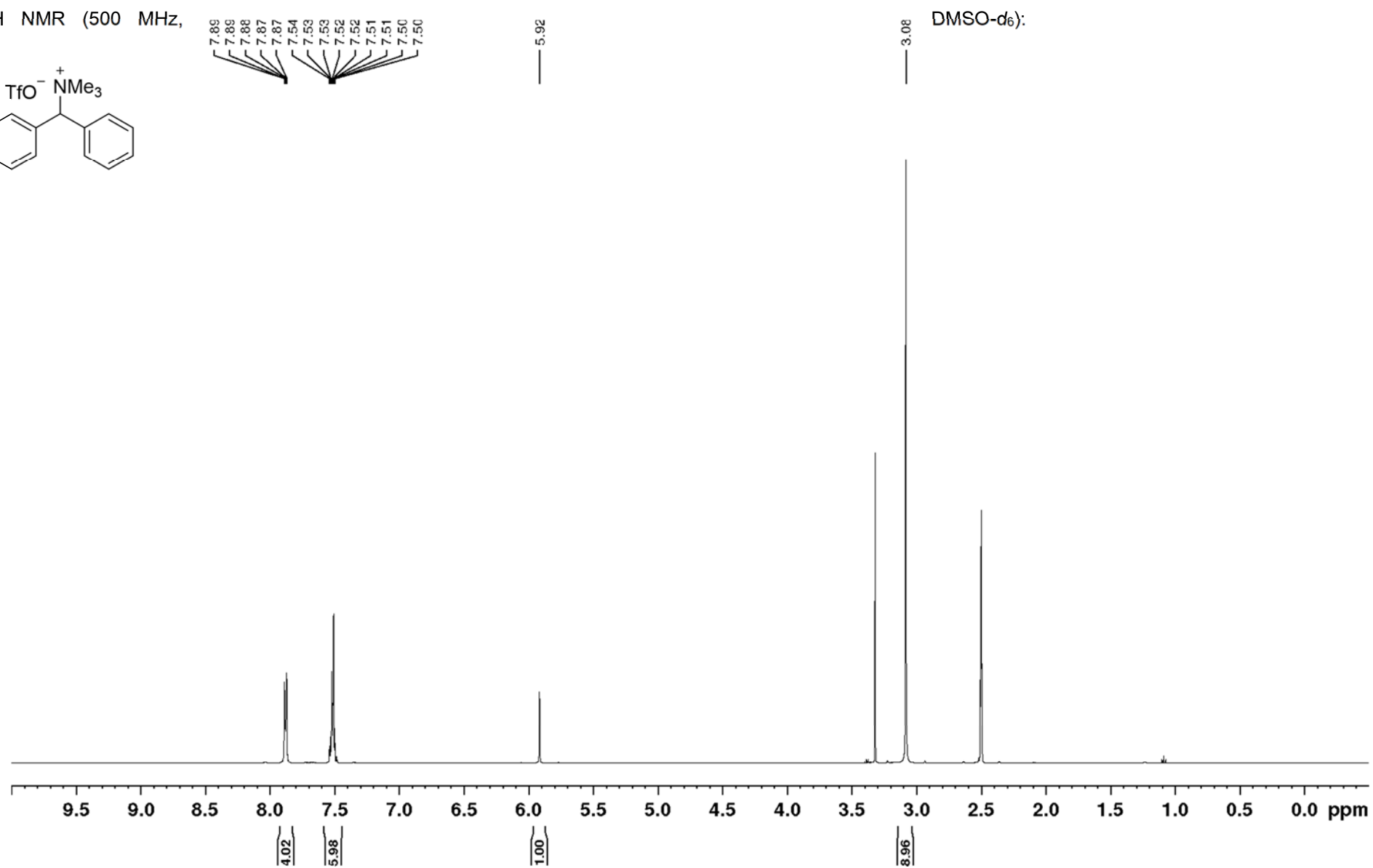
¹H NMR (500 MHz,



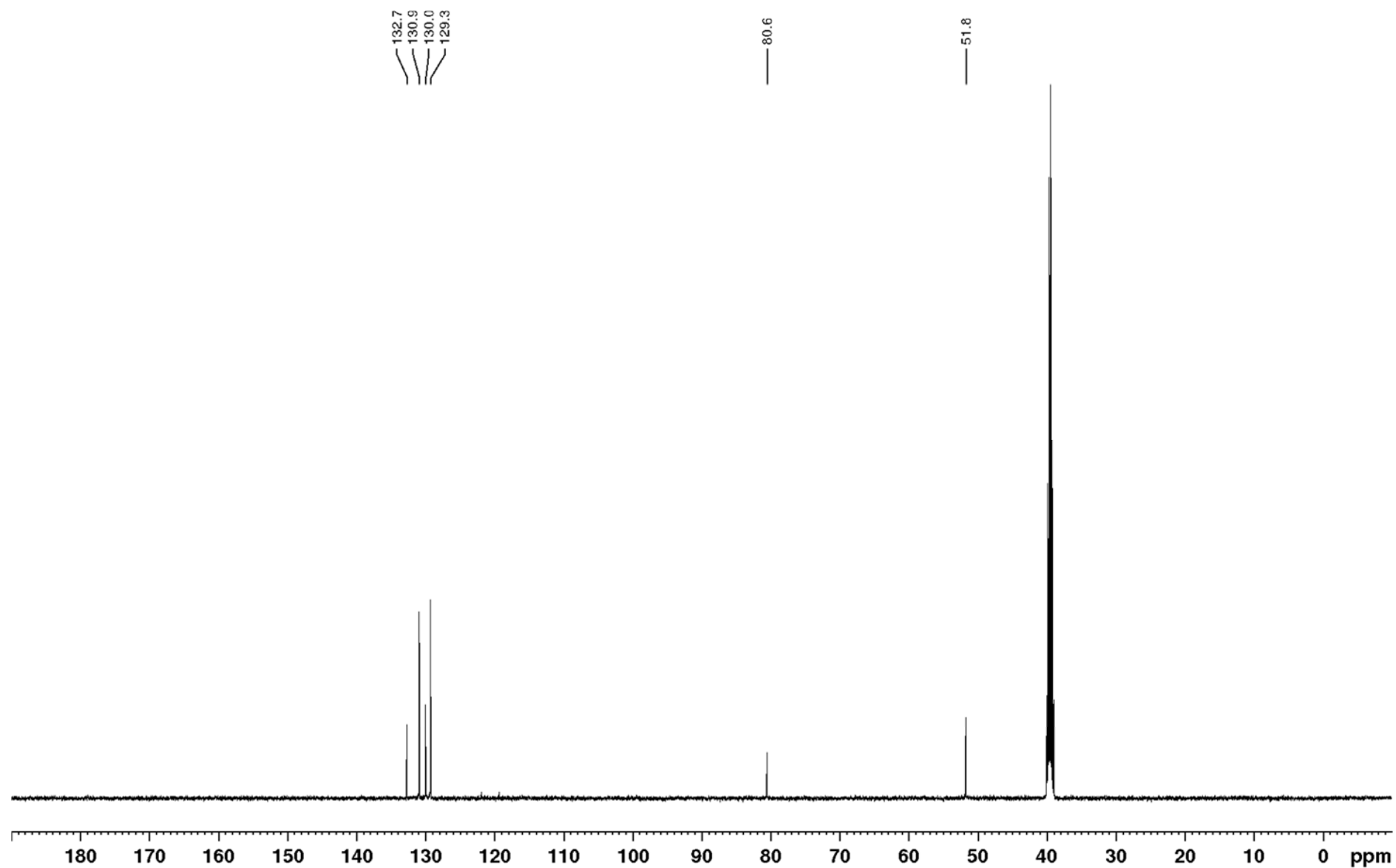
7.89
7.88
7.88
7.87
7.87
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50

5.92

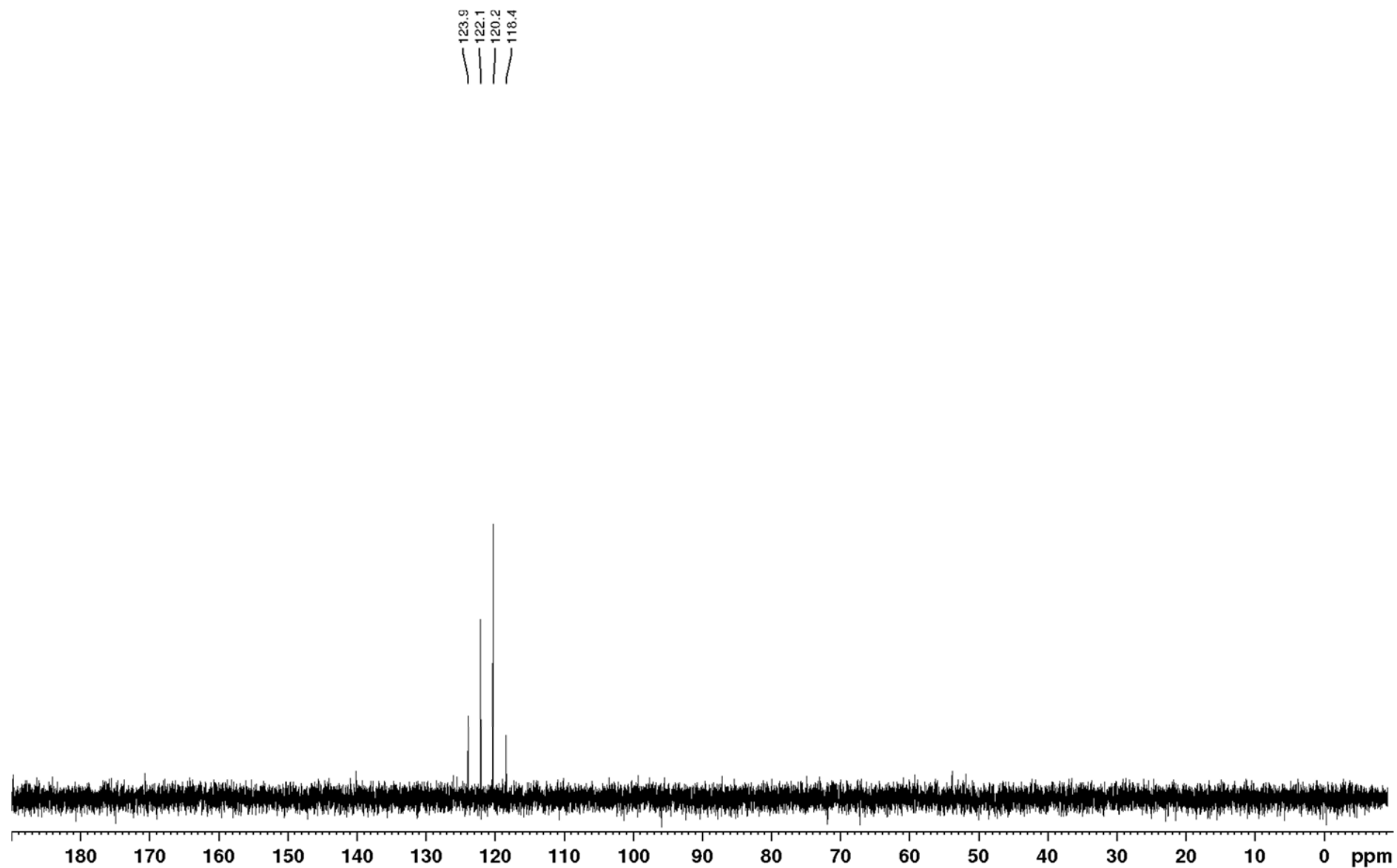
3.08 DMSO-d₆:



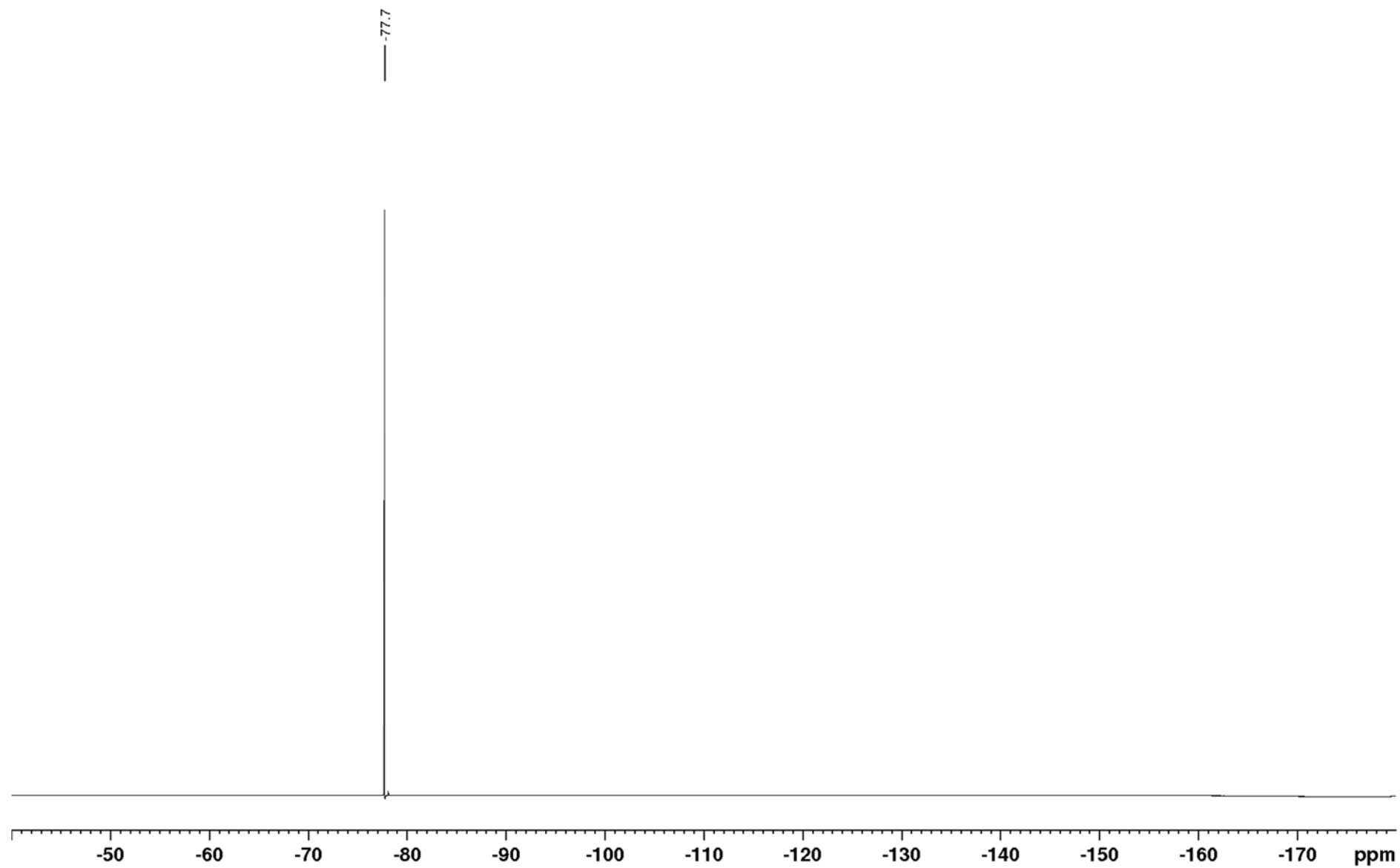
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

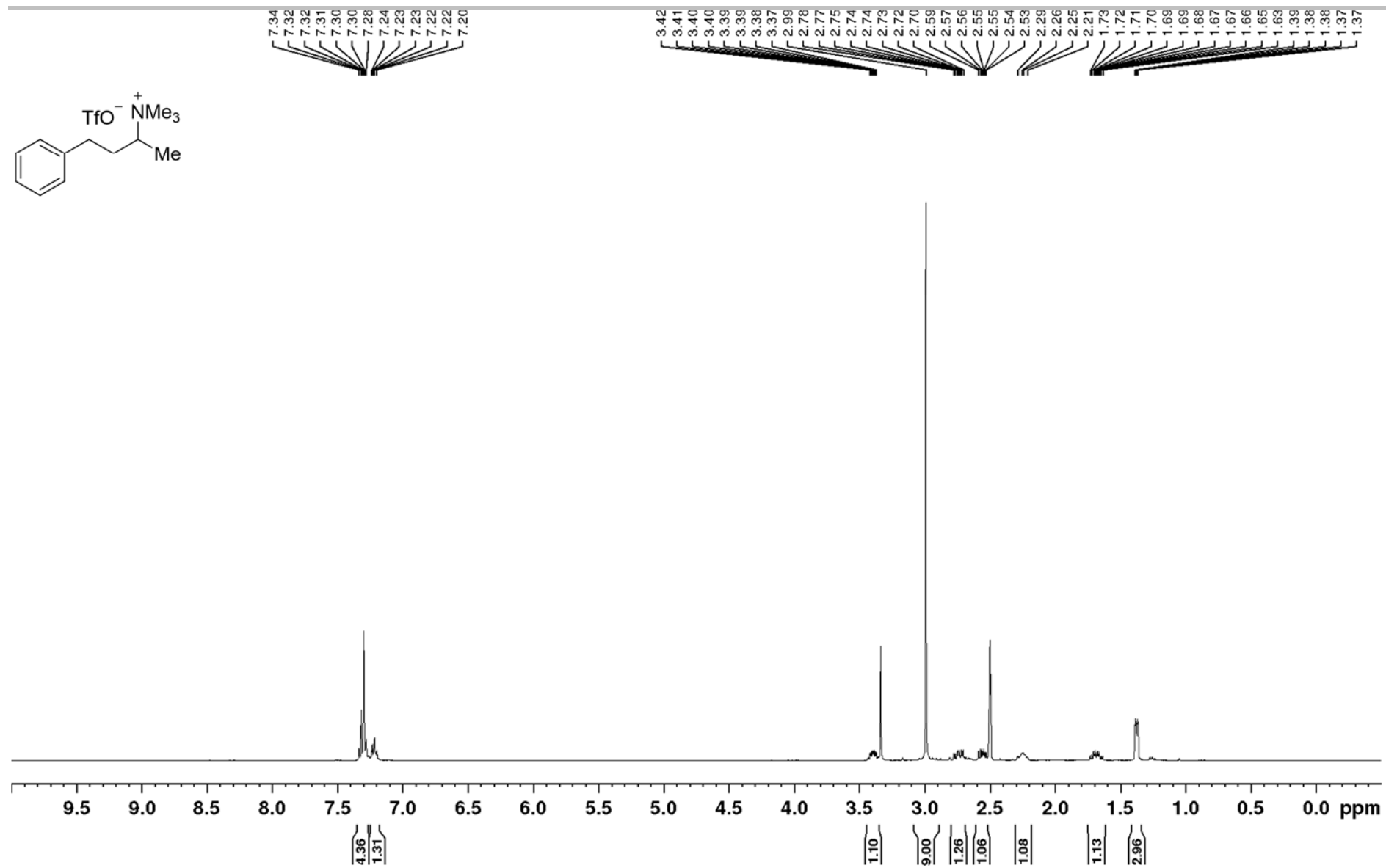
 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

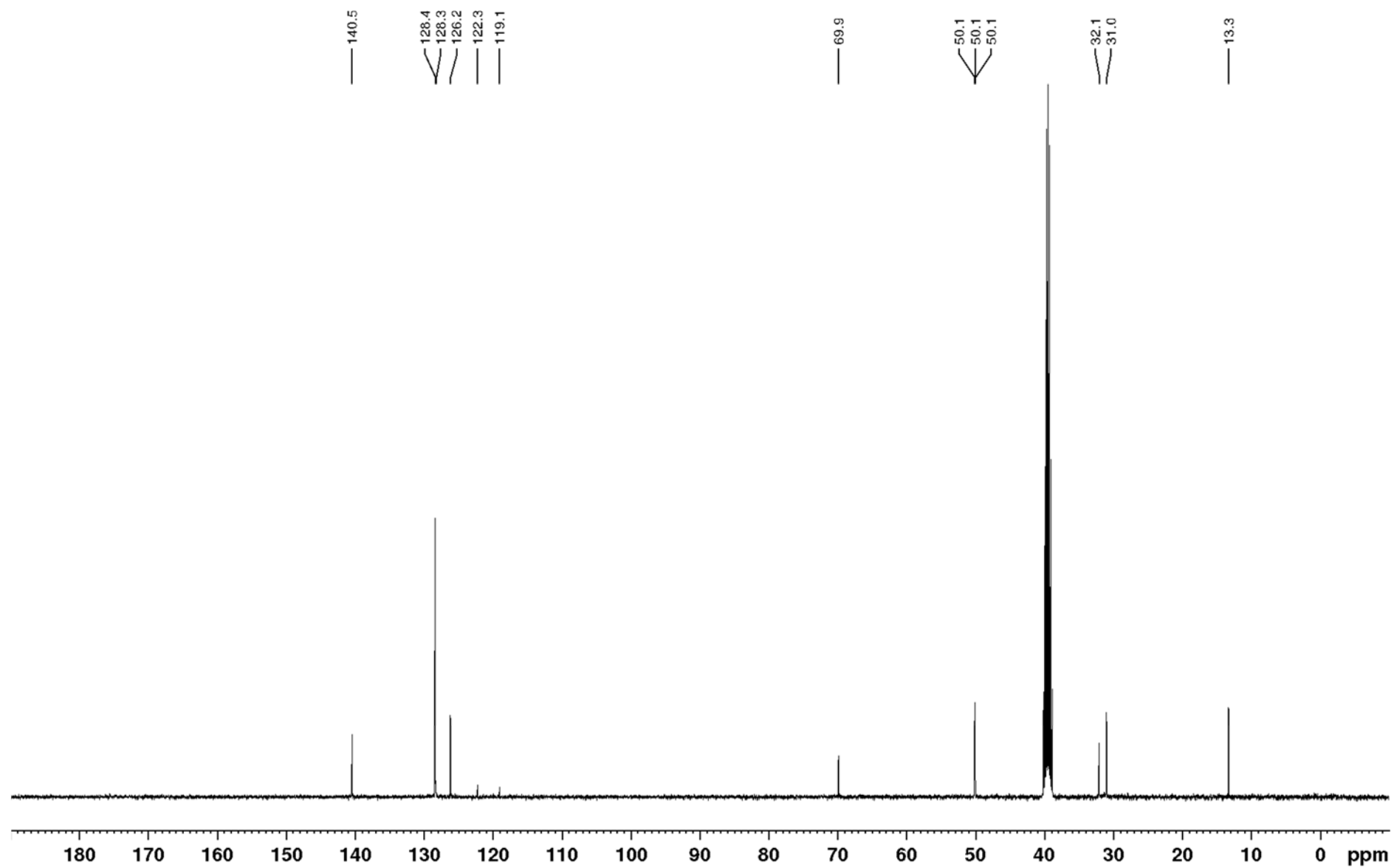
***N,N,N*-Trimethyl-4-phenylbutan-2-aminium trifluoromethanesulfonate (1x).**

¹H NMR (400 MHz, DMSO-*d*₆):

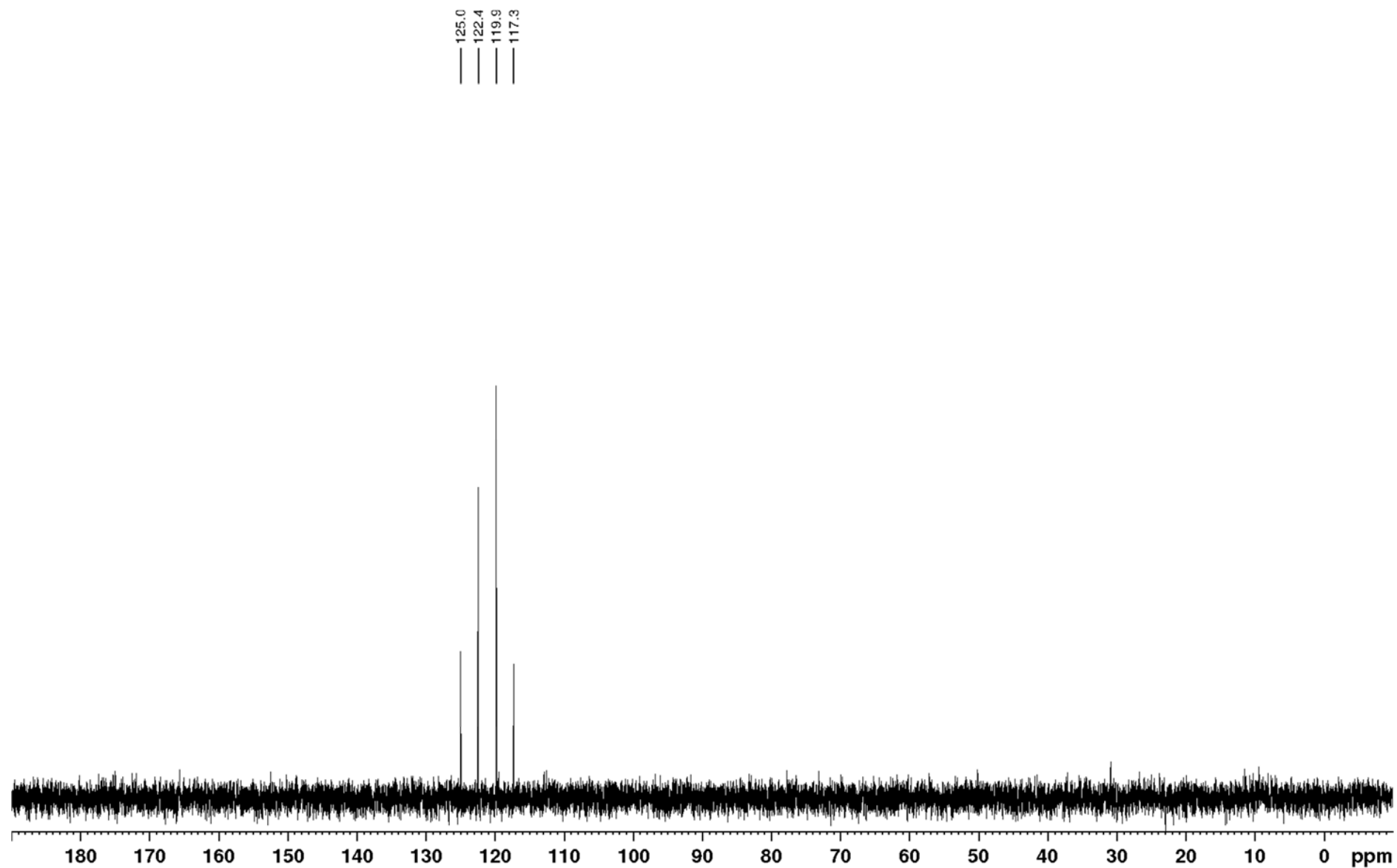
SUPPORTING INFORMATION



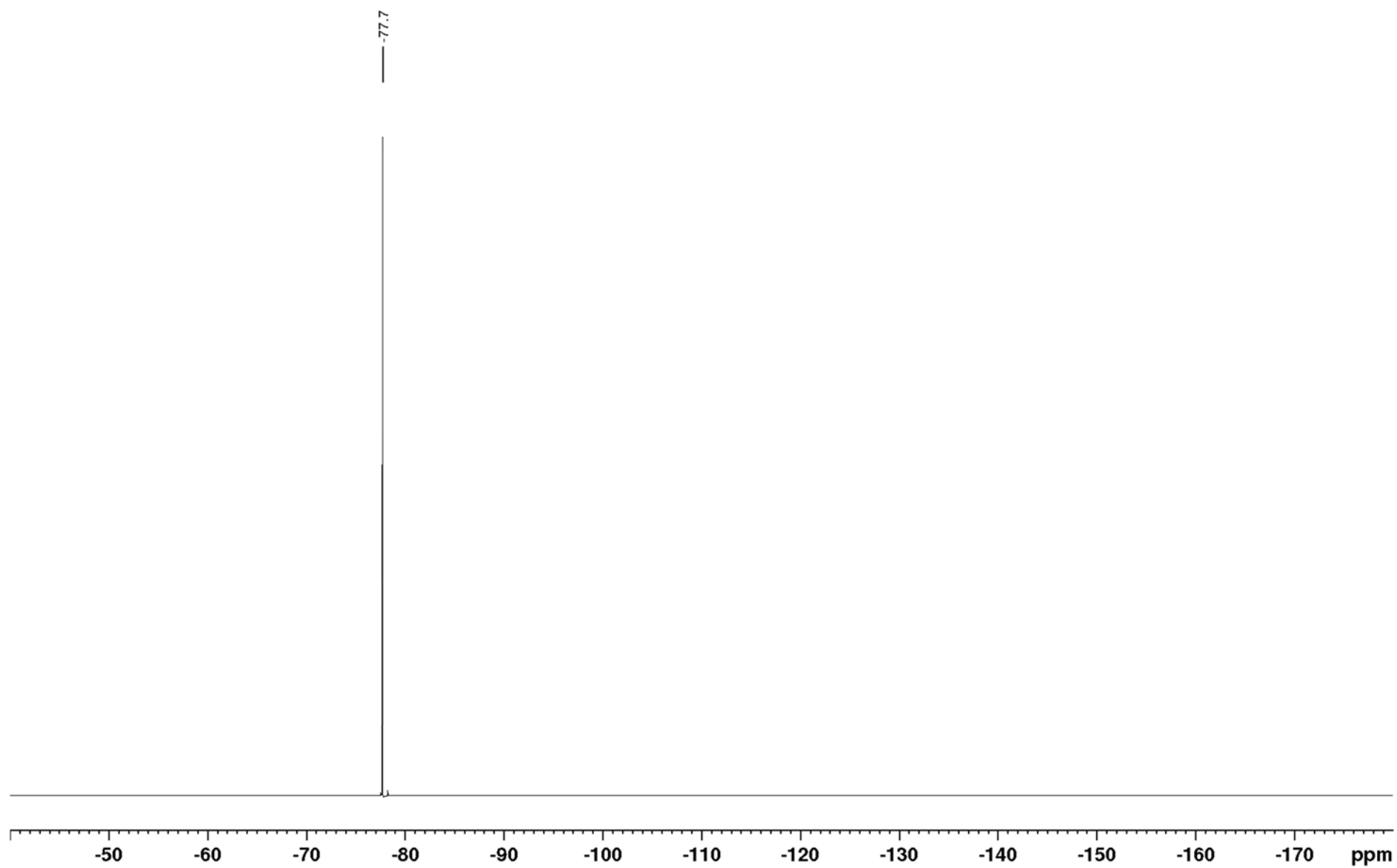
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

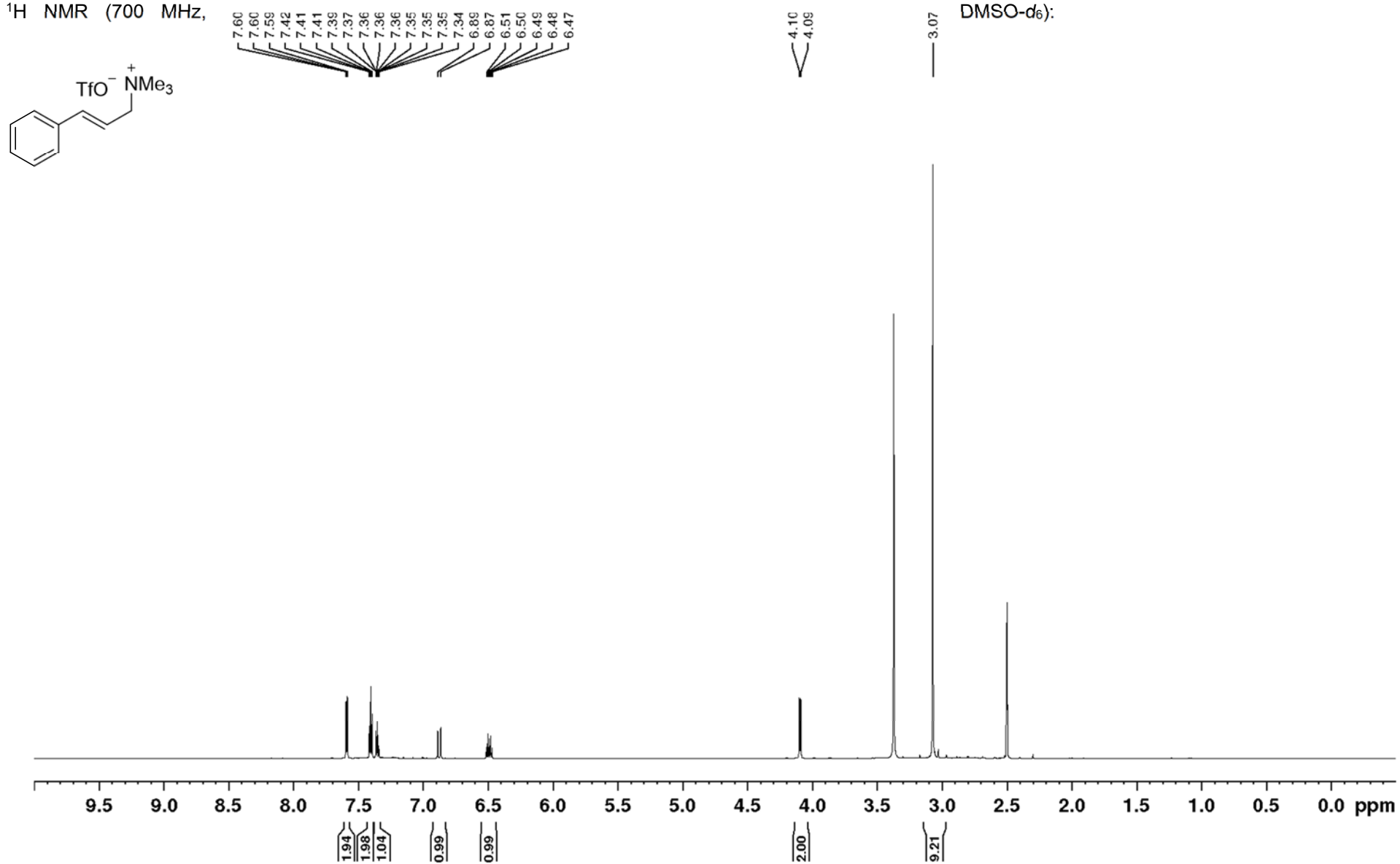
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

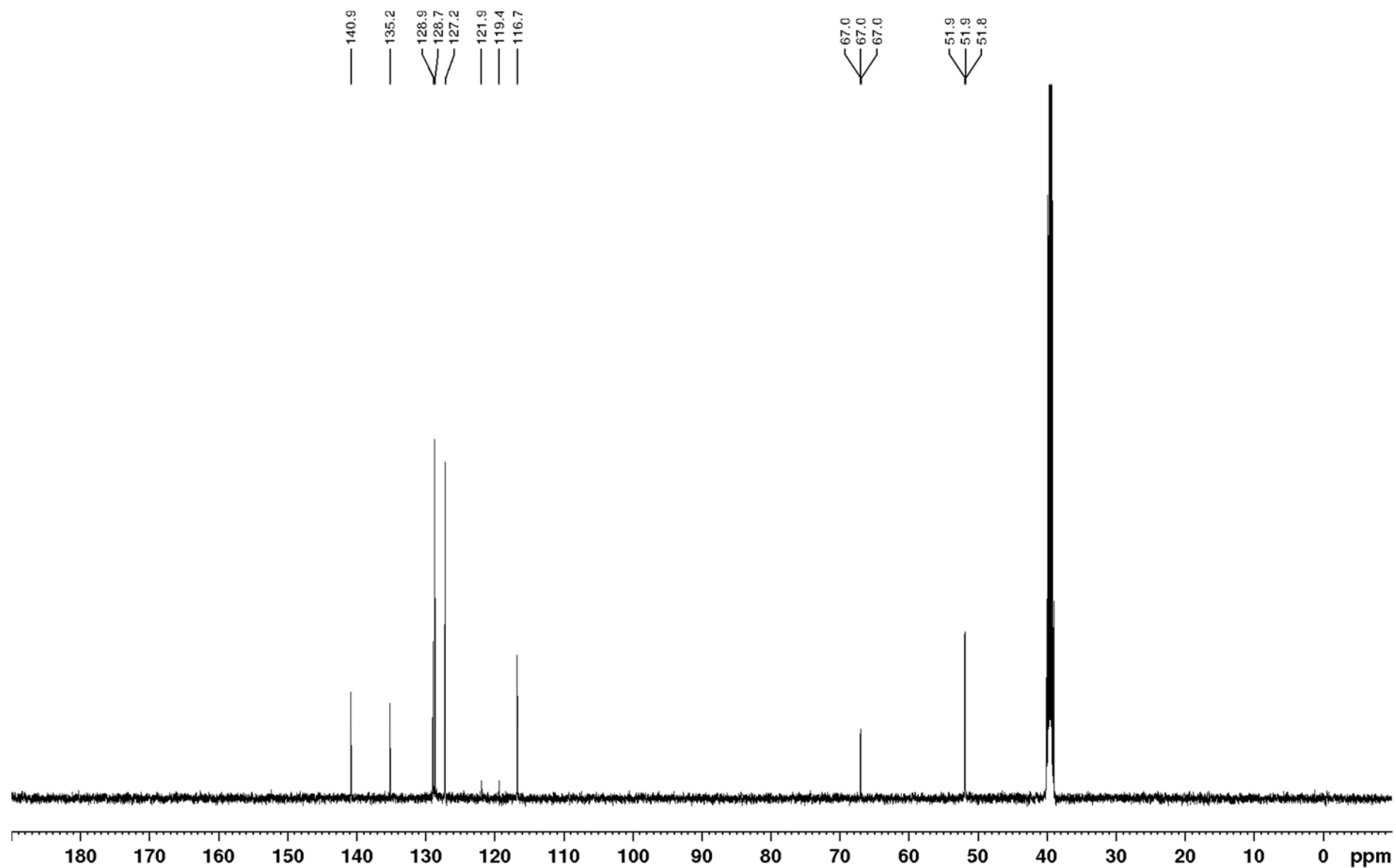
SUPPORTING INFORMATION

(*E*)-*N,N,N*-Trimethyl-3-phenylprop-2-en-1-aminium trifluoromethanesulfonate (5).

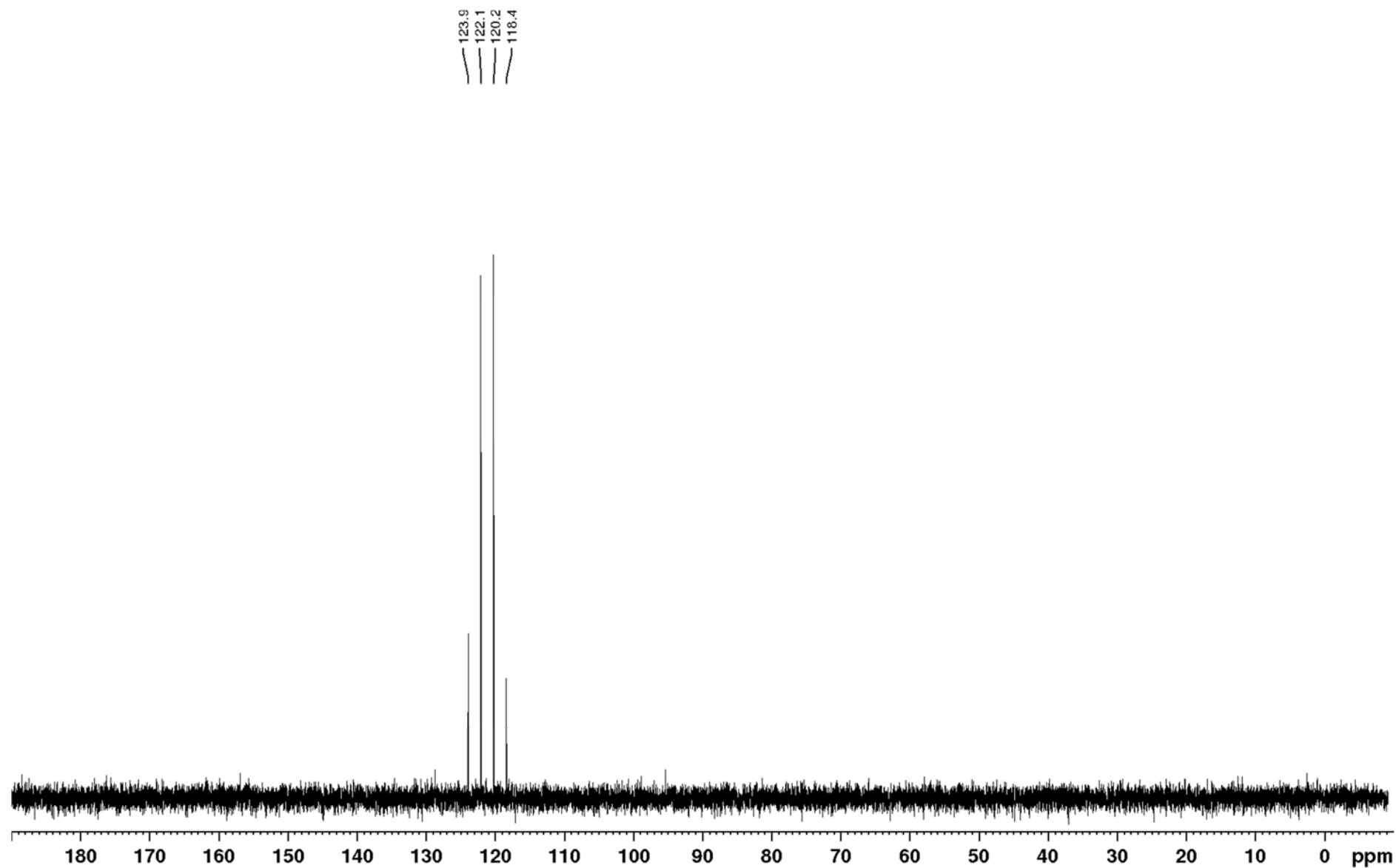
¹H NMR (700 MHz,



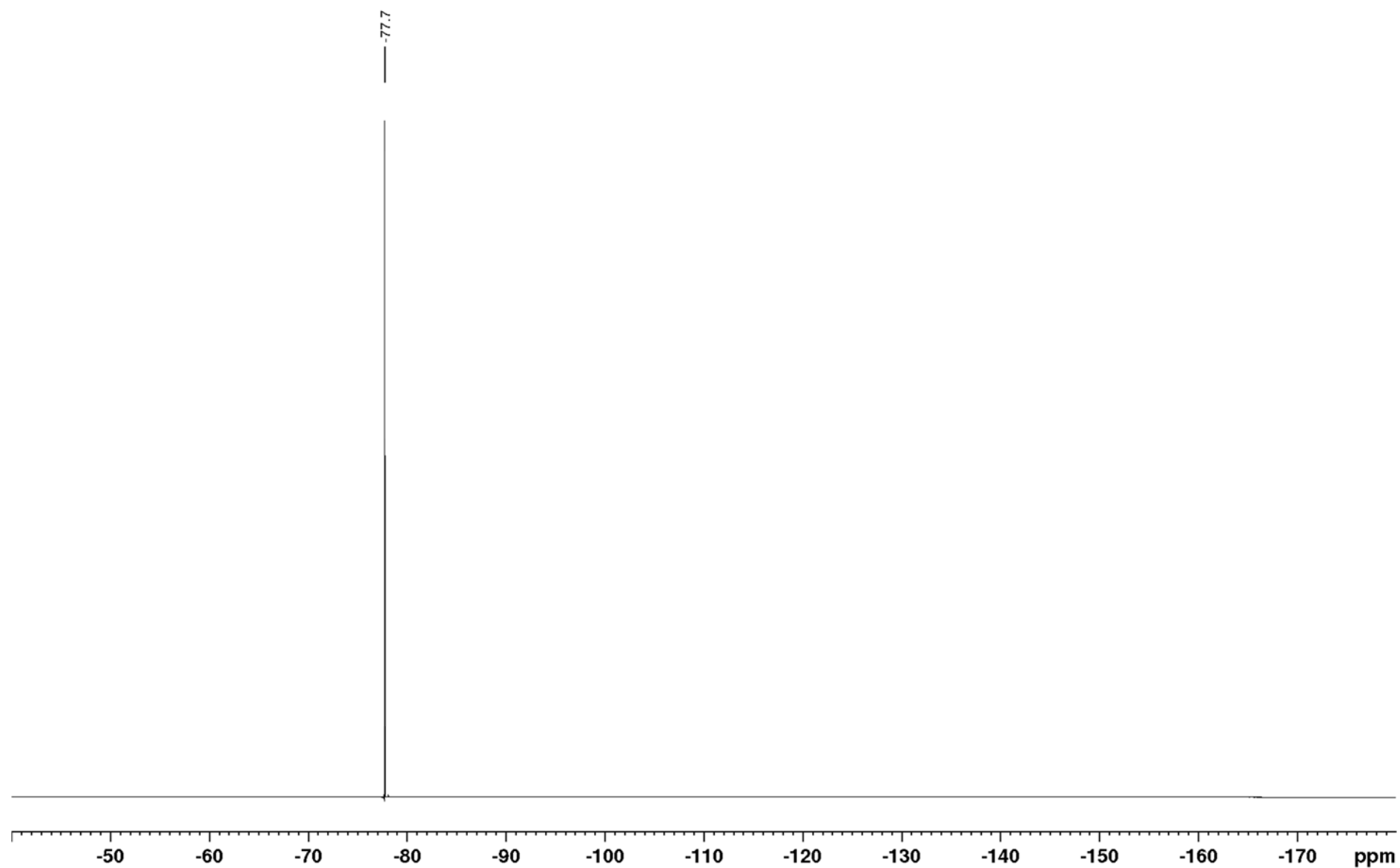
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$):

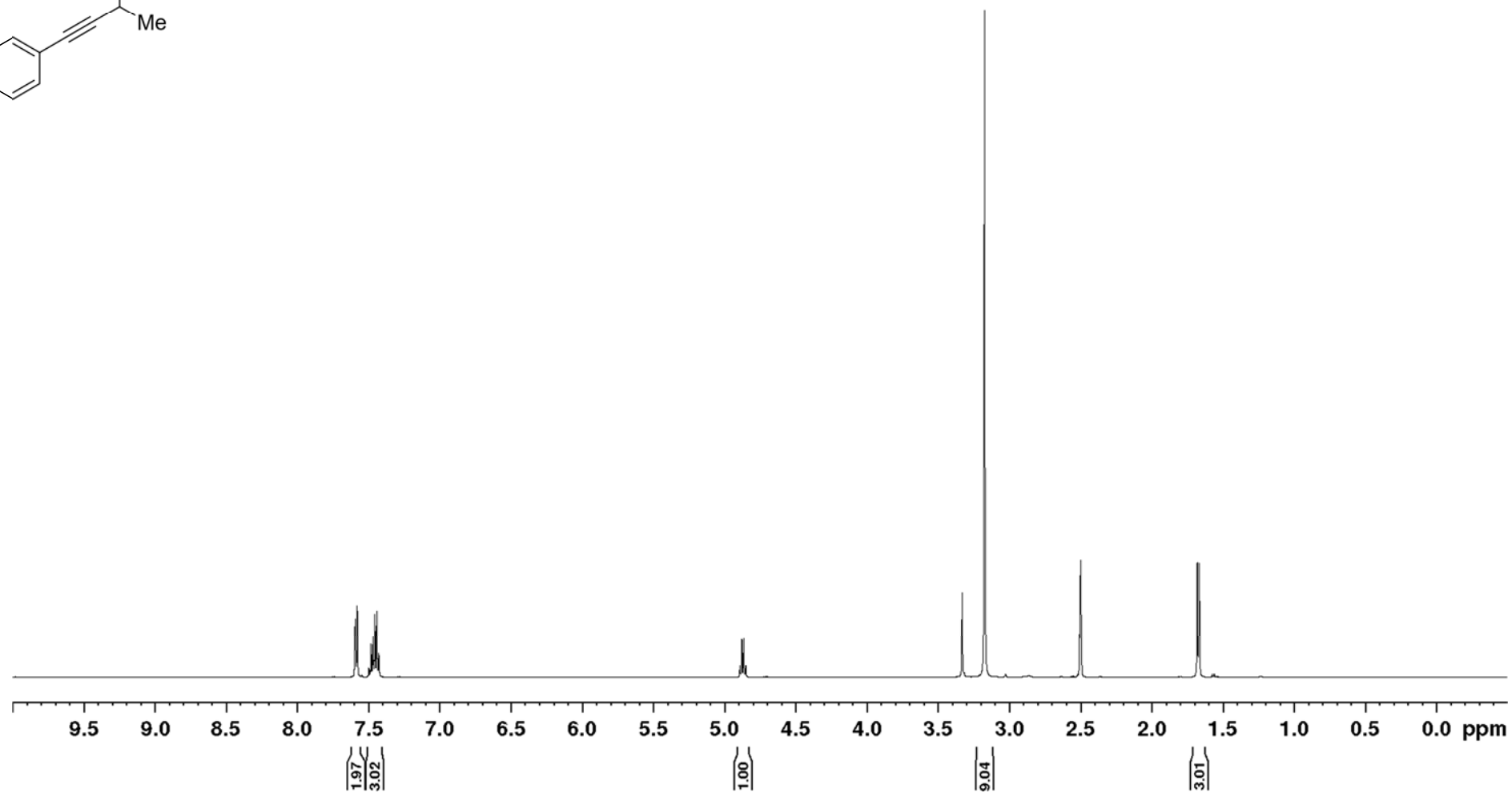
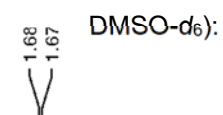
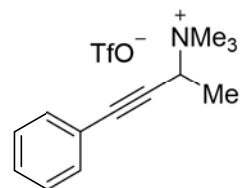
SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (176 MHz, $\text{DMSO-}d_6$):

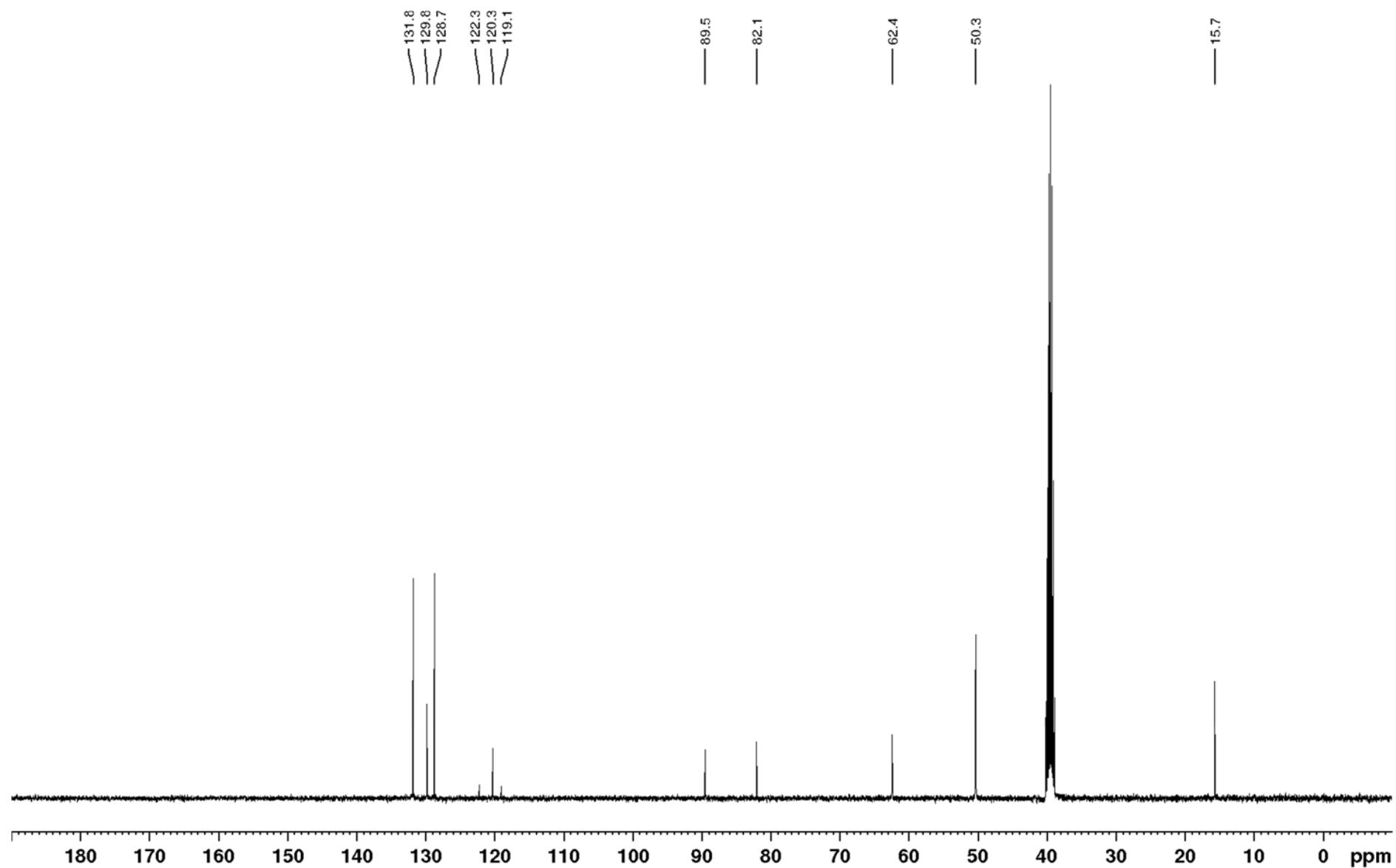
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (659 MHz, $\text{DMSO-}d_6$):

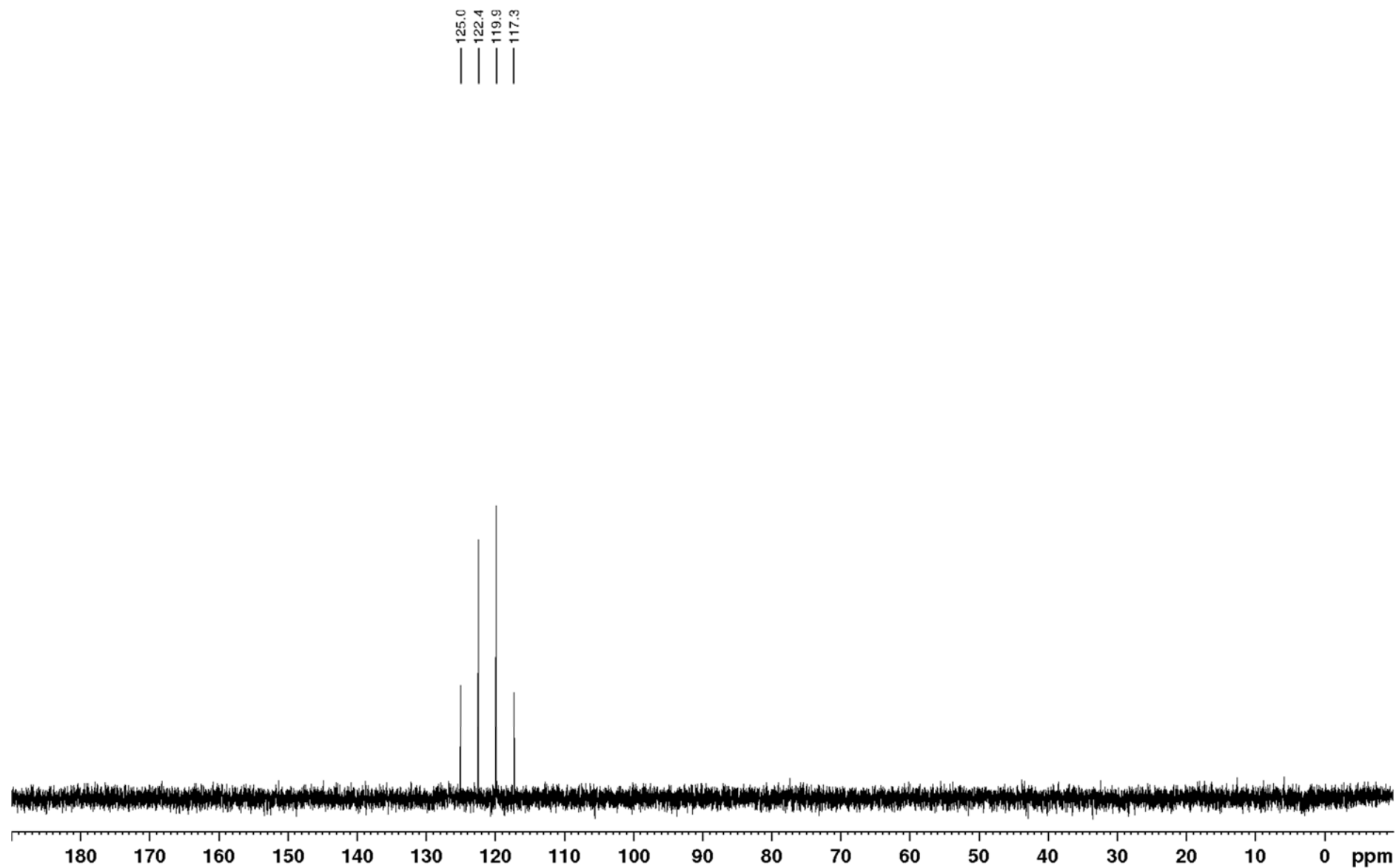
SUPPORTING INFORMATION

***N,N,N*-Trimethyl-4-phenylbut-3-yn-2-aminium (7)**¹H NMR (500 MHz,

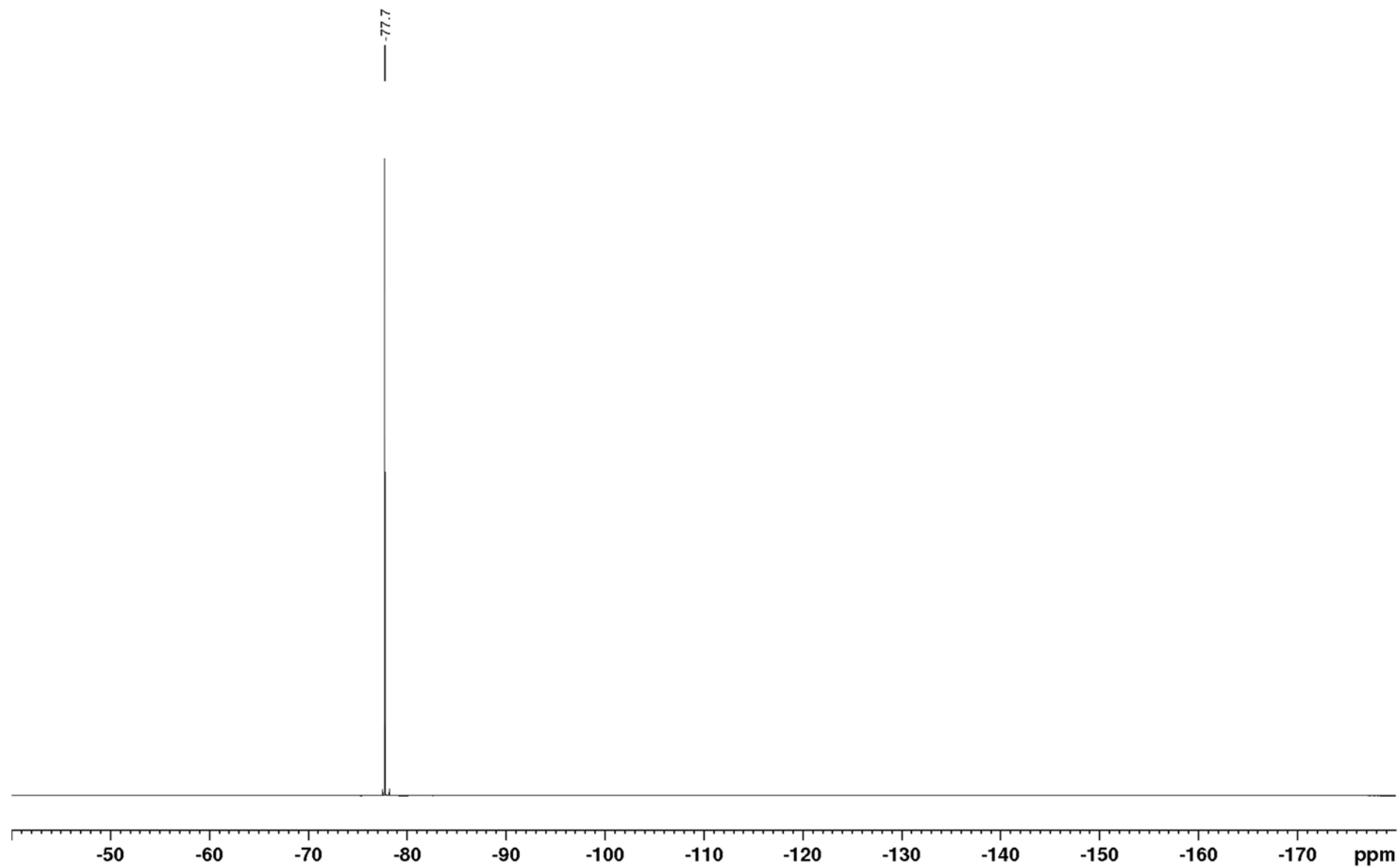
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

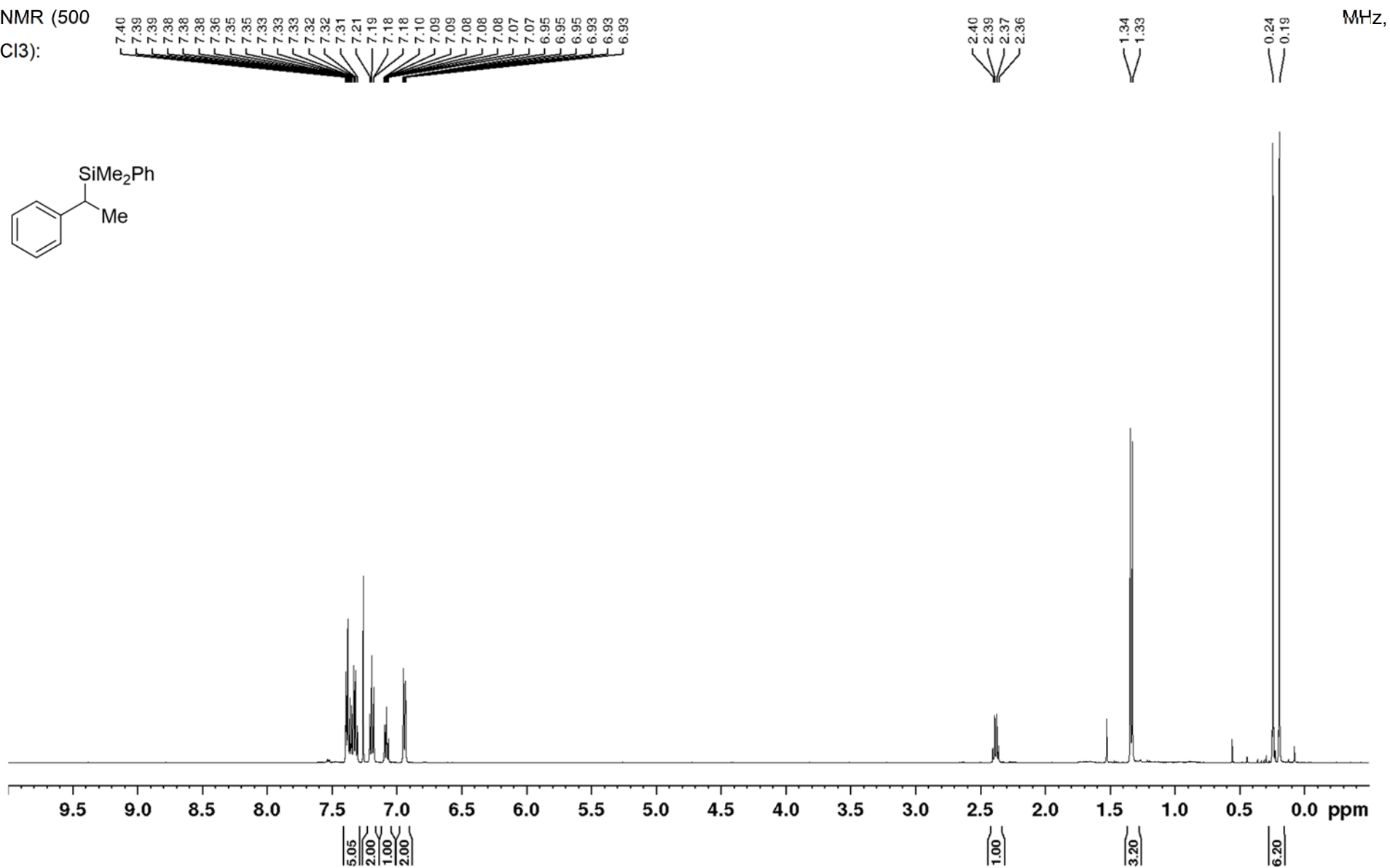
SUPPORTING INFORMATION

 $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, $\text{DMSO-}d_6$):

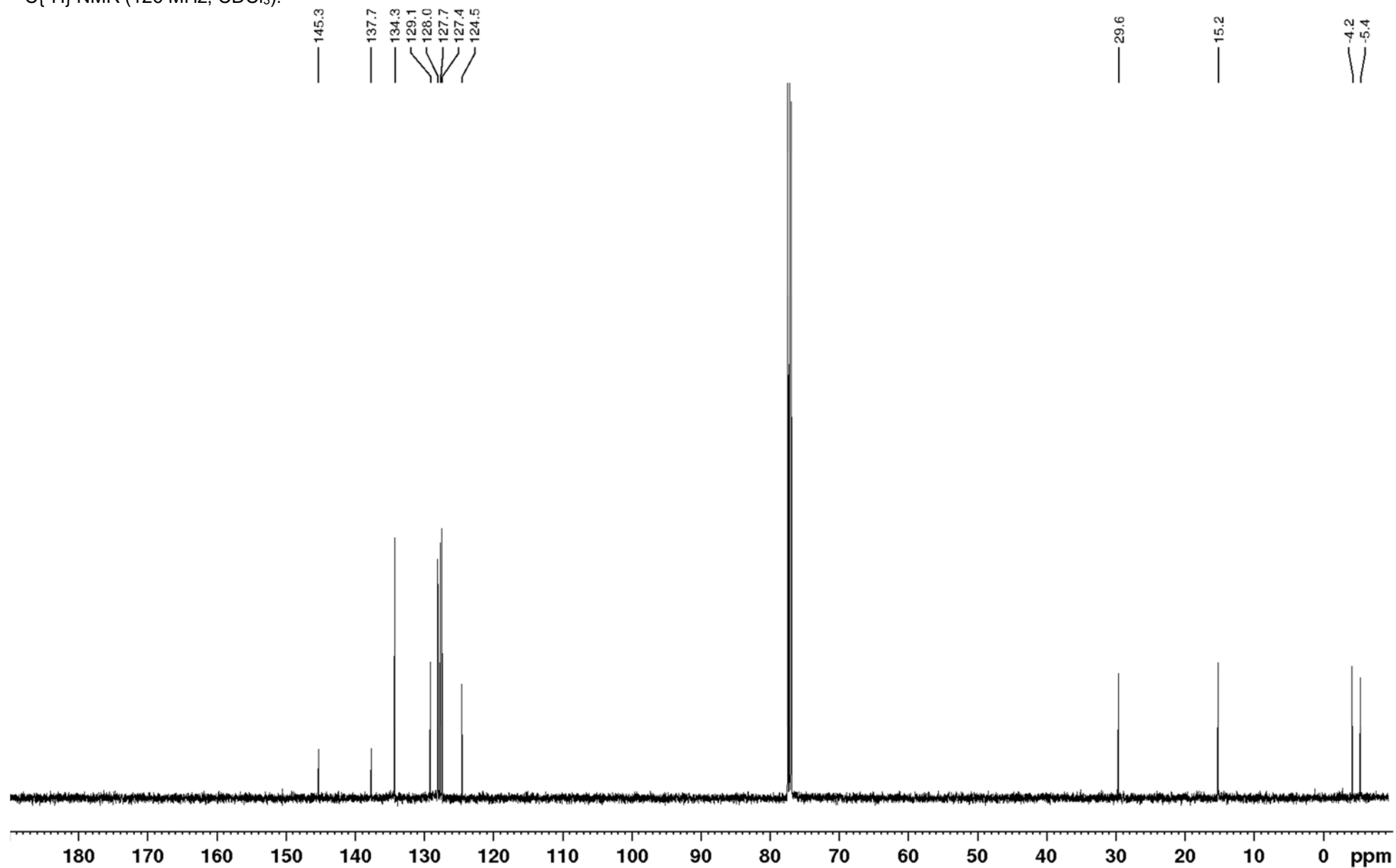
SUPPORTING INFORMATION

Dimethyl(phenyl)(1-phenylethyl)silane (4aa)

¹H NMR (500
CDCl₃):

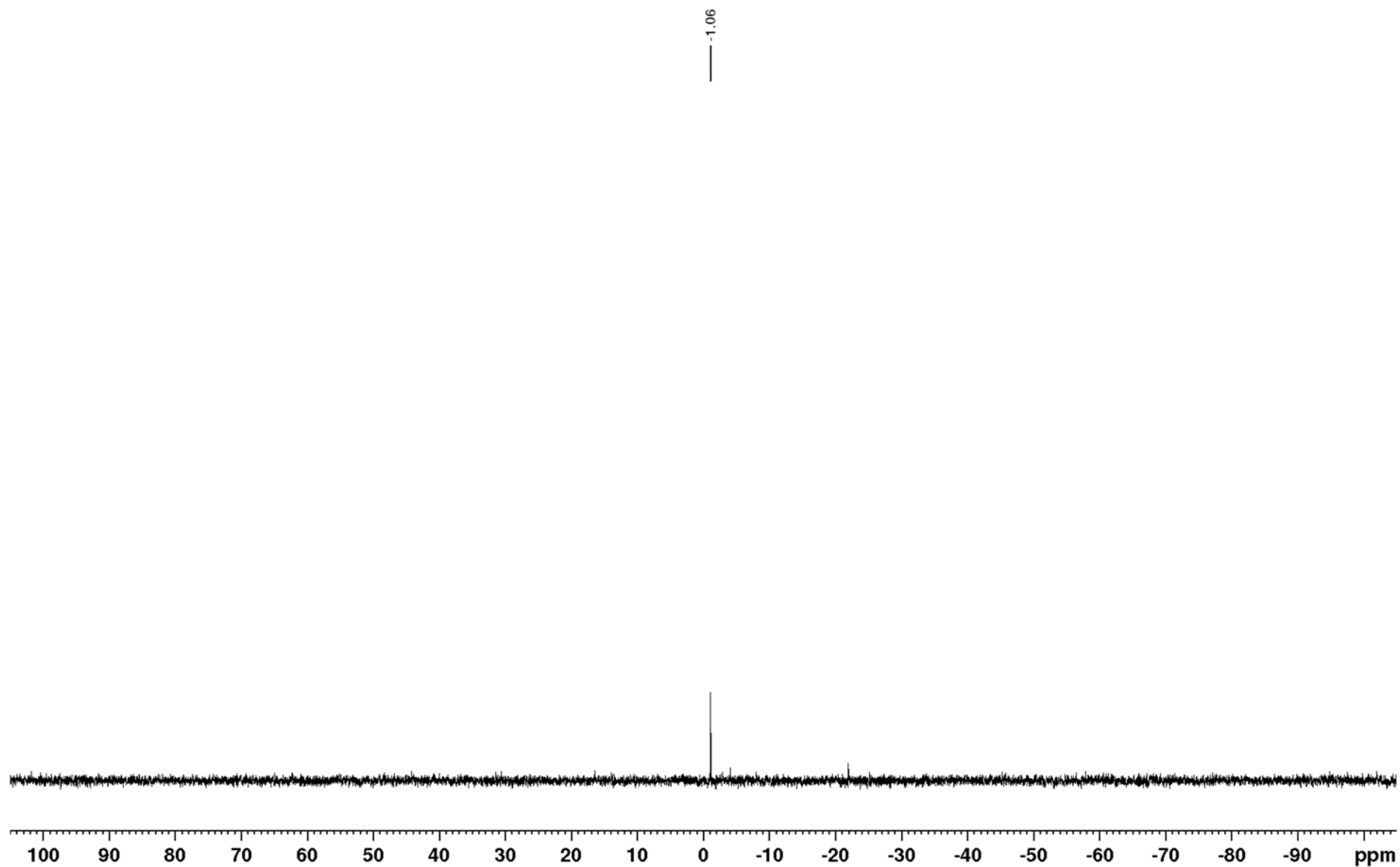


SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

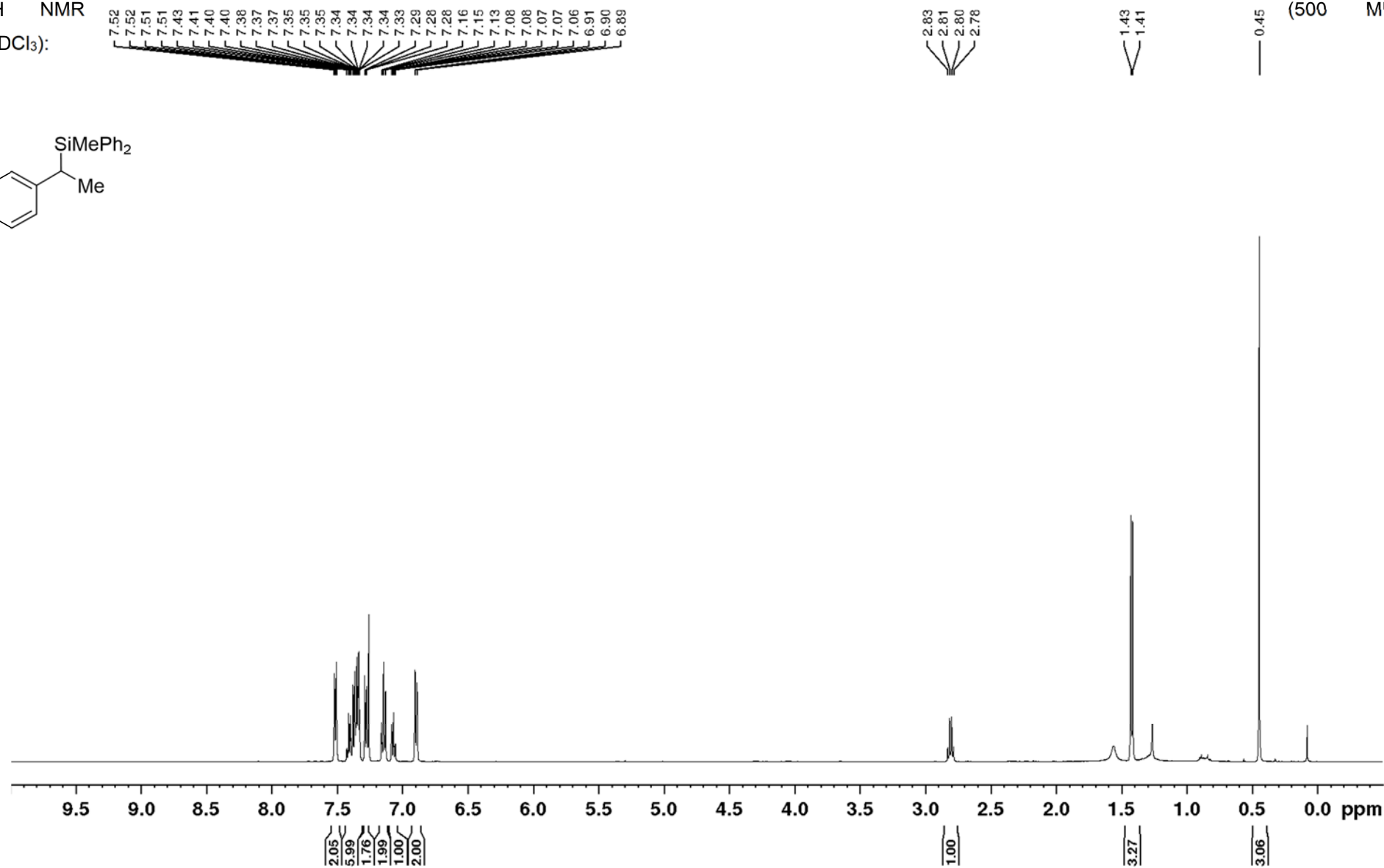
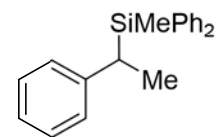
$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):



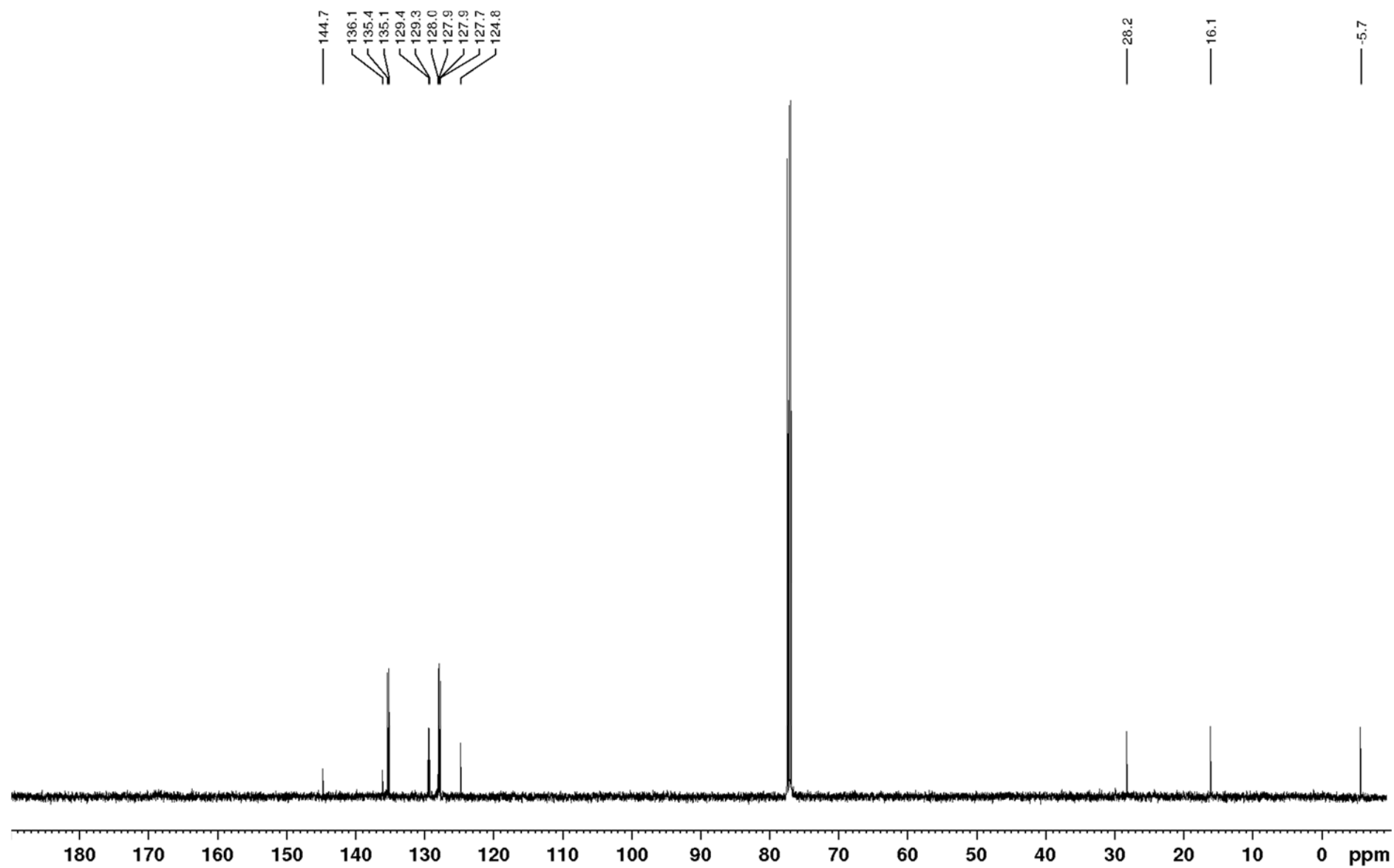
SUPPORTING INFORMATION

Methyldiphenyl(1-phenylethyl)silane (4ab)

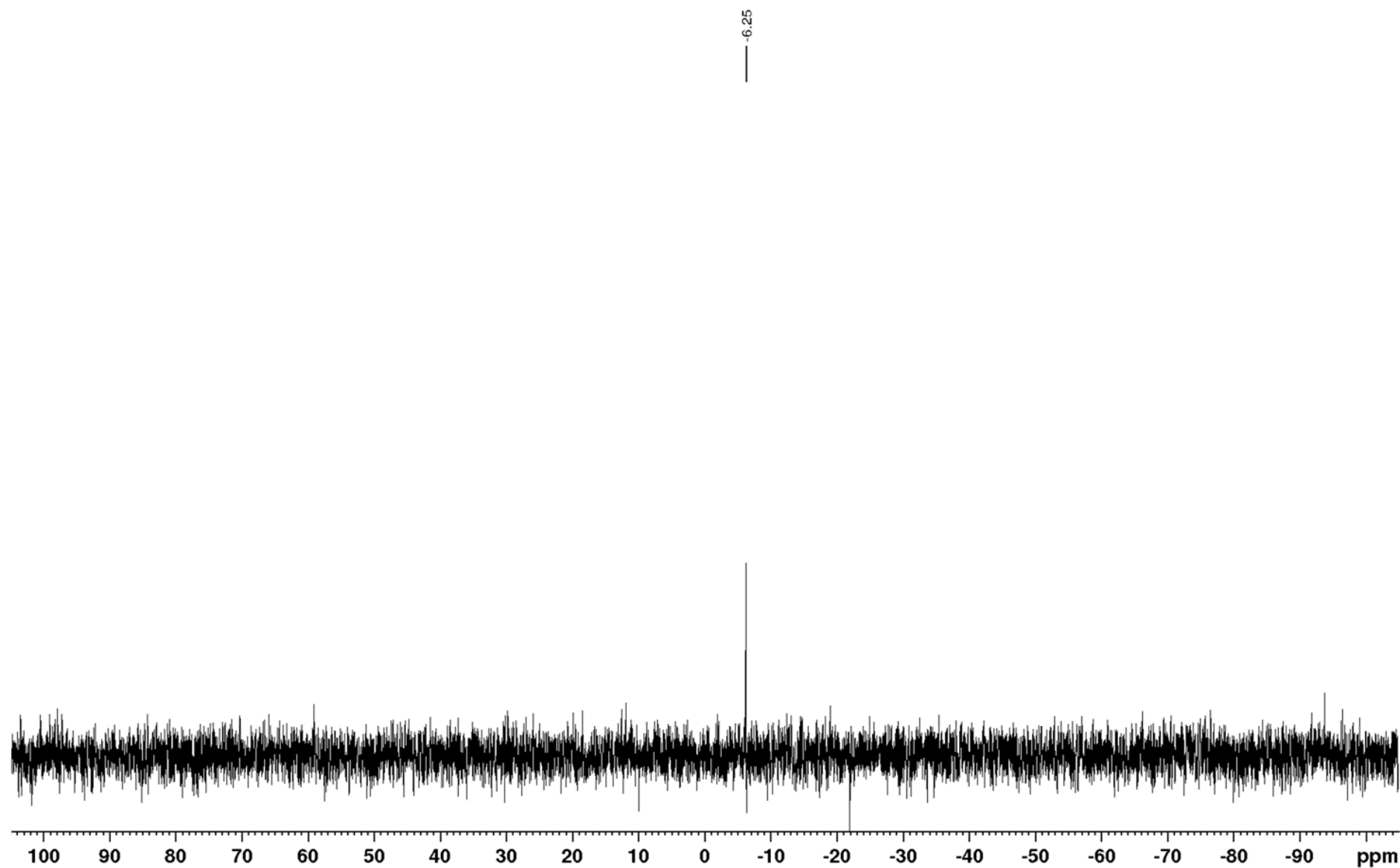
^1H NMR
 CDCl_3 : (500 MHz,



SUPPORTING INFORMATION

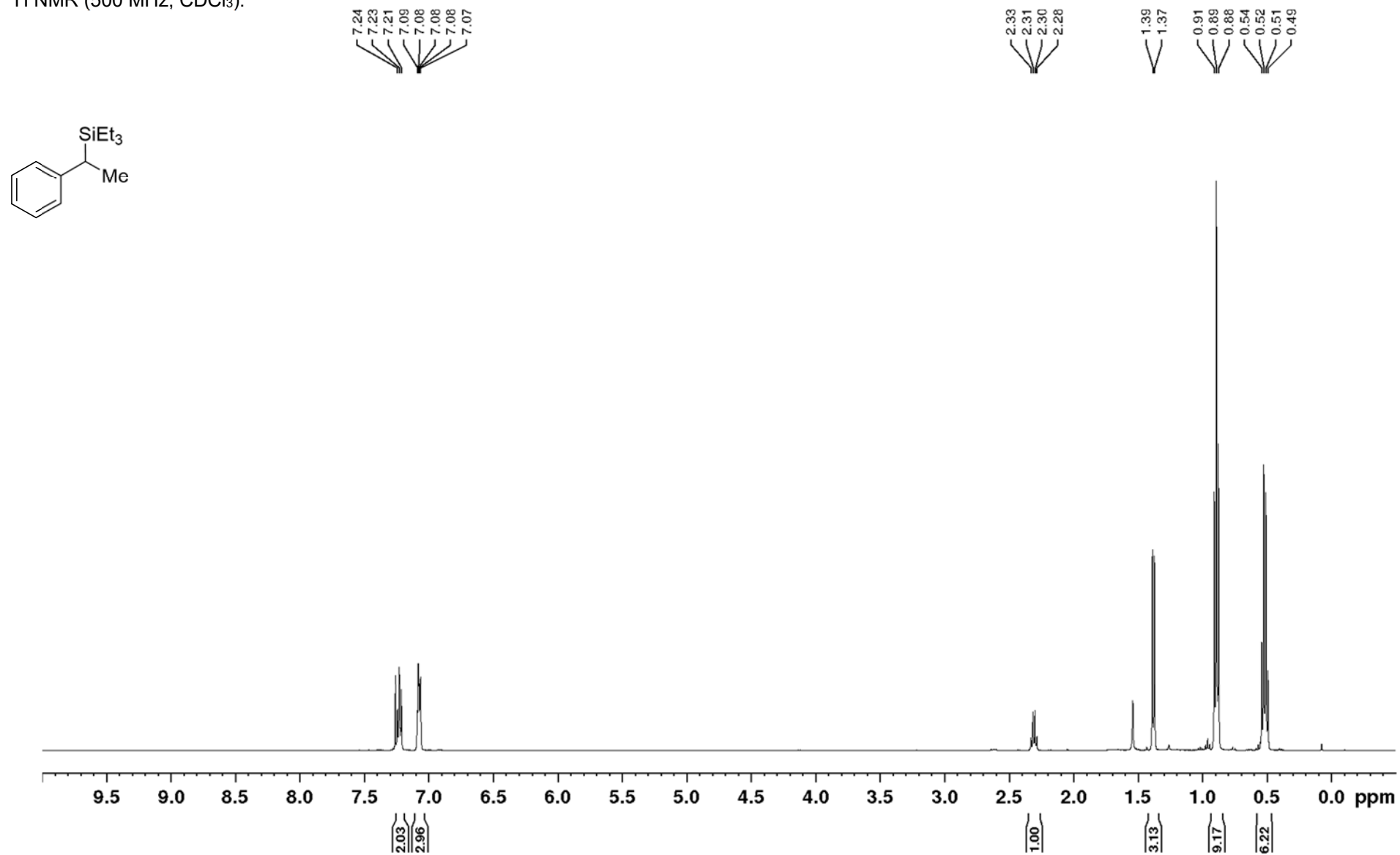
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

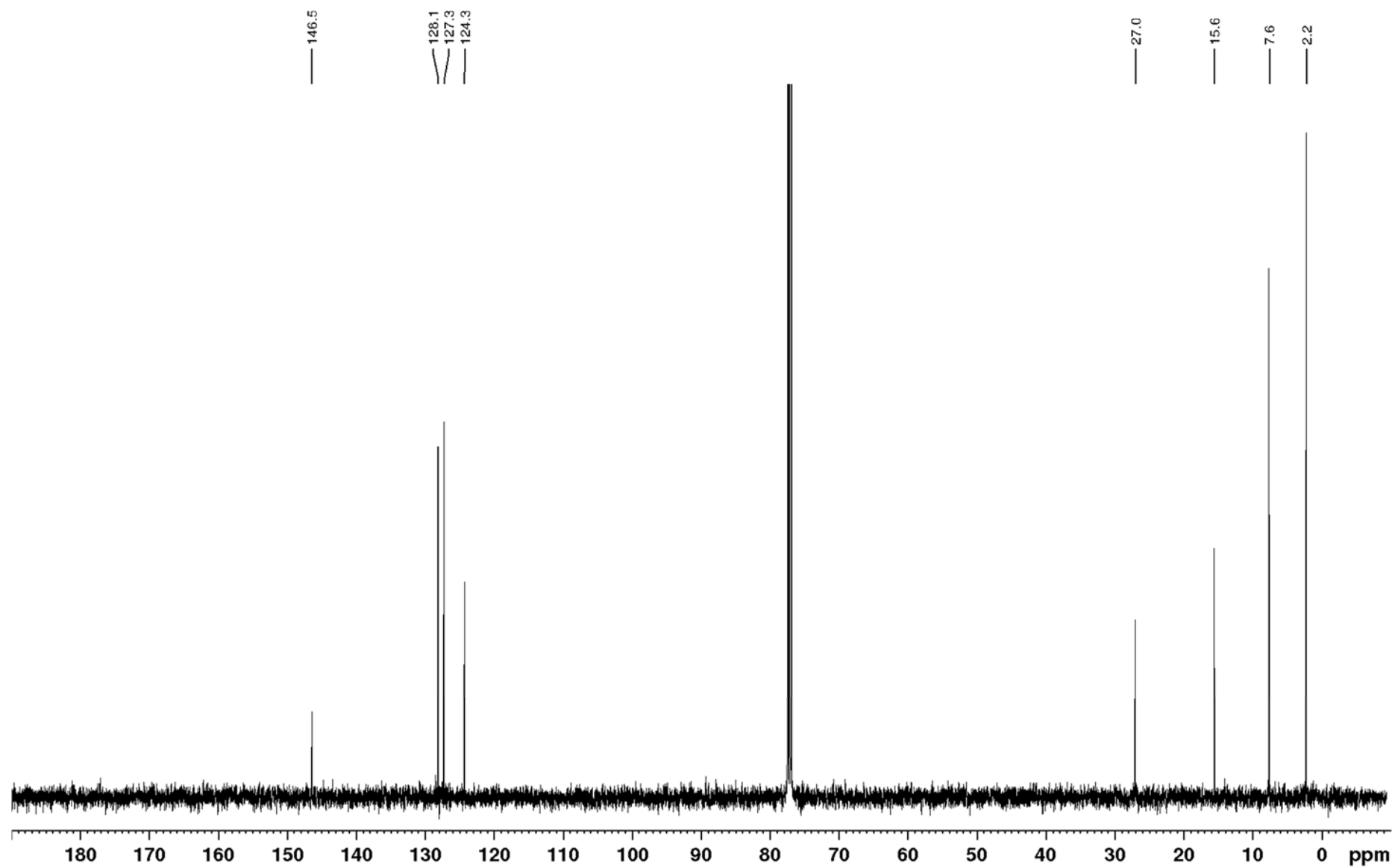
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

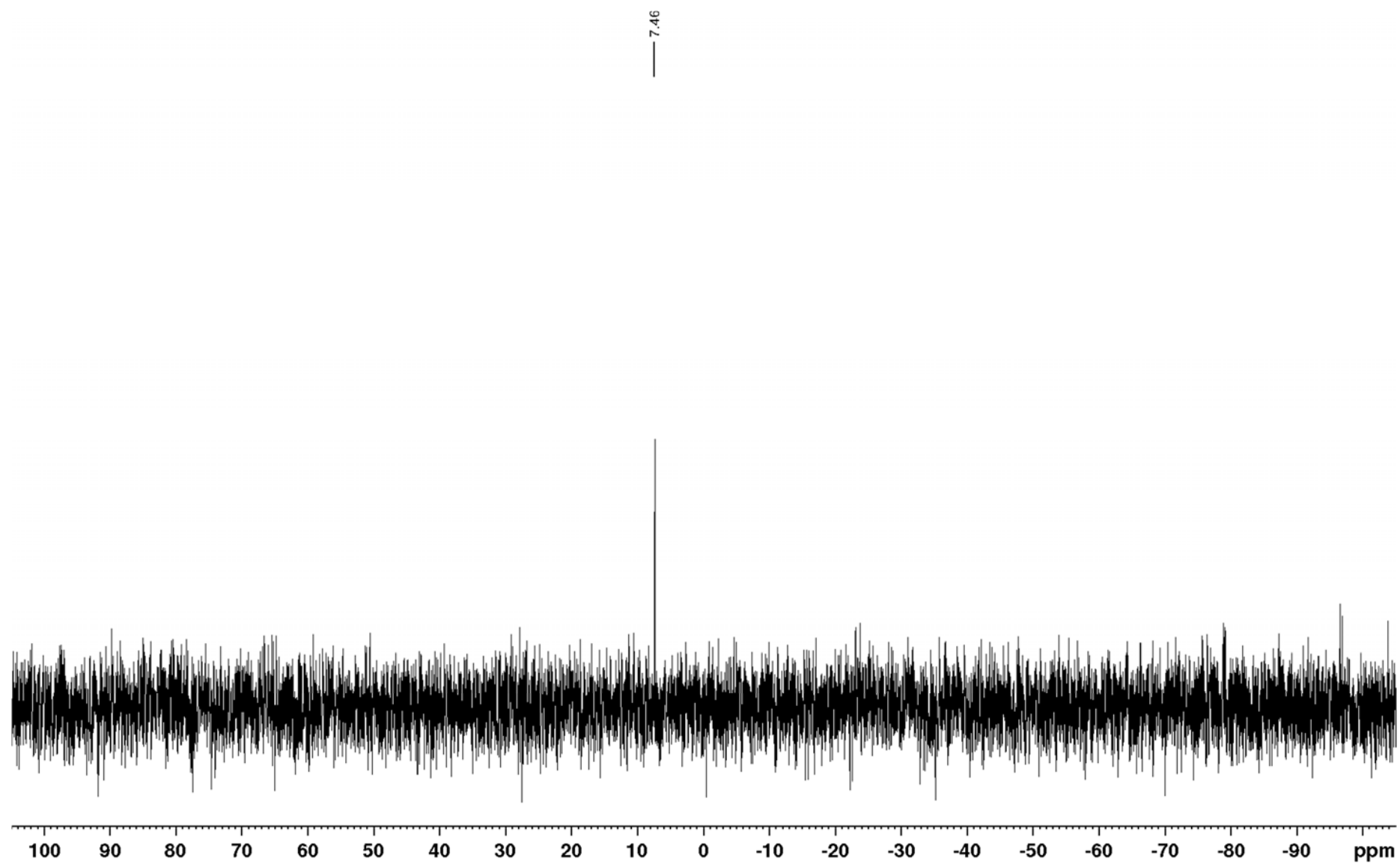
Triethyl(1-phenylethyl)silane (4ac)

 ^1H NMR (500 MHz, CDCl_3):

SUPPORTING INFORMATION

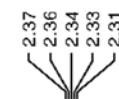
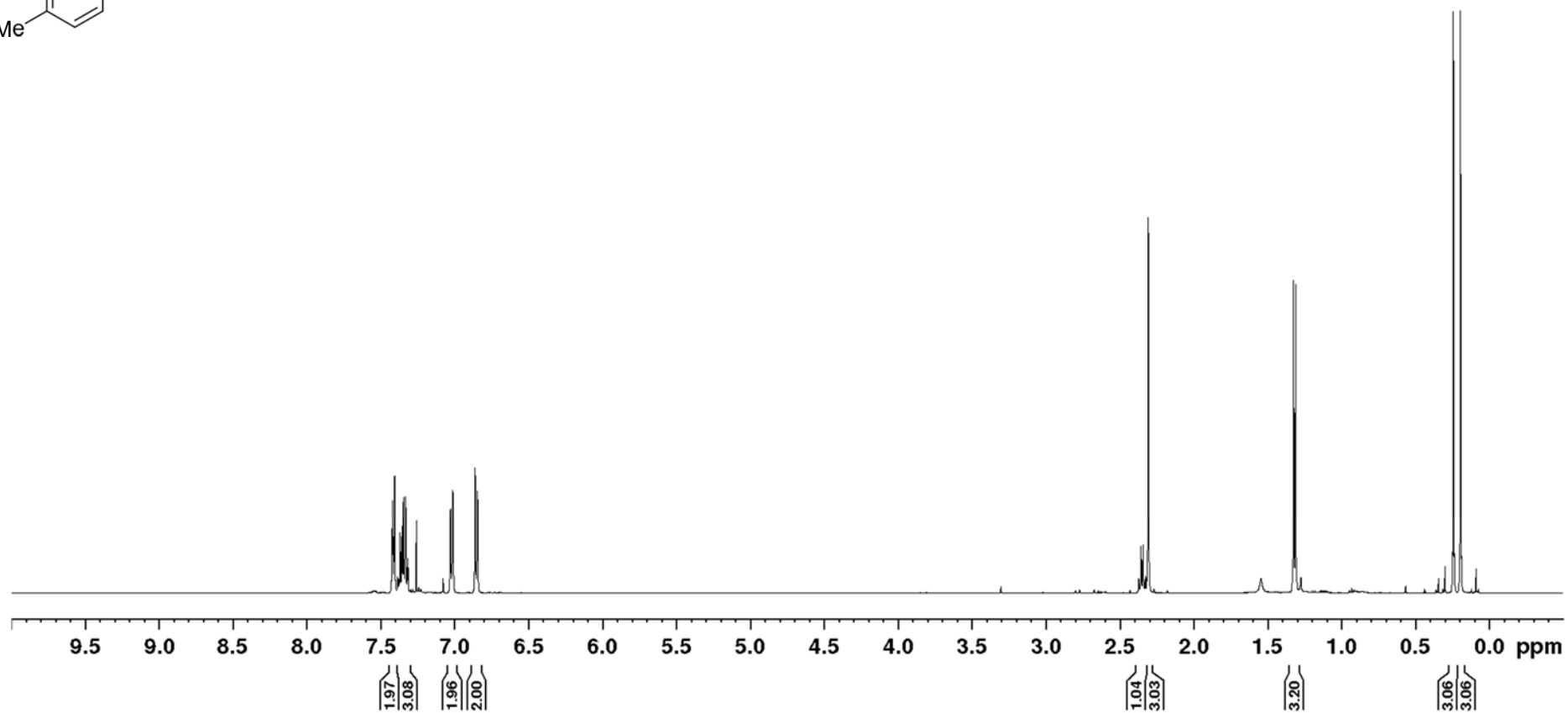
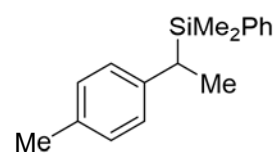
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

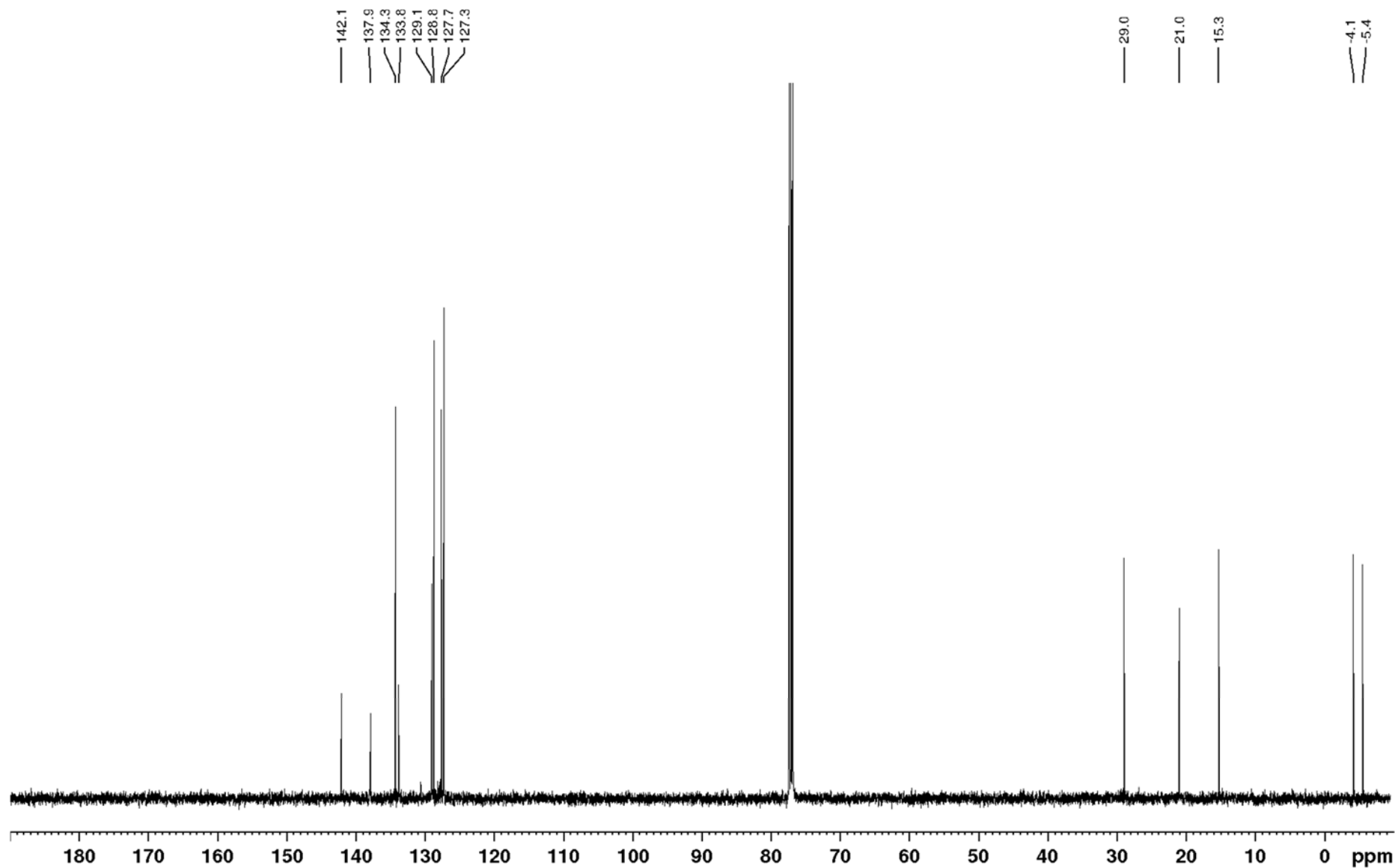
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

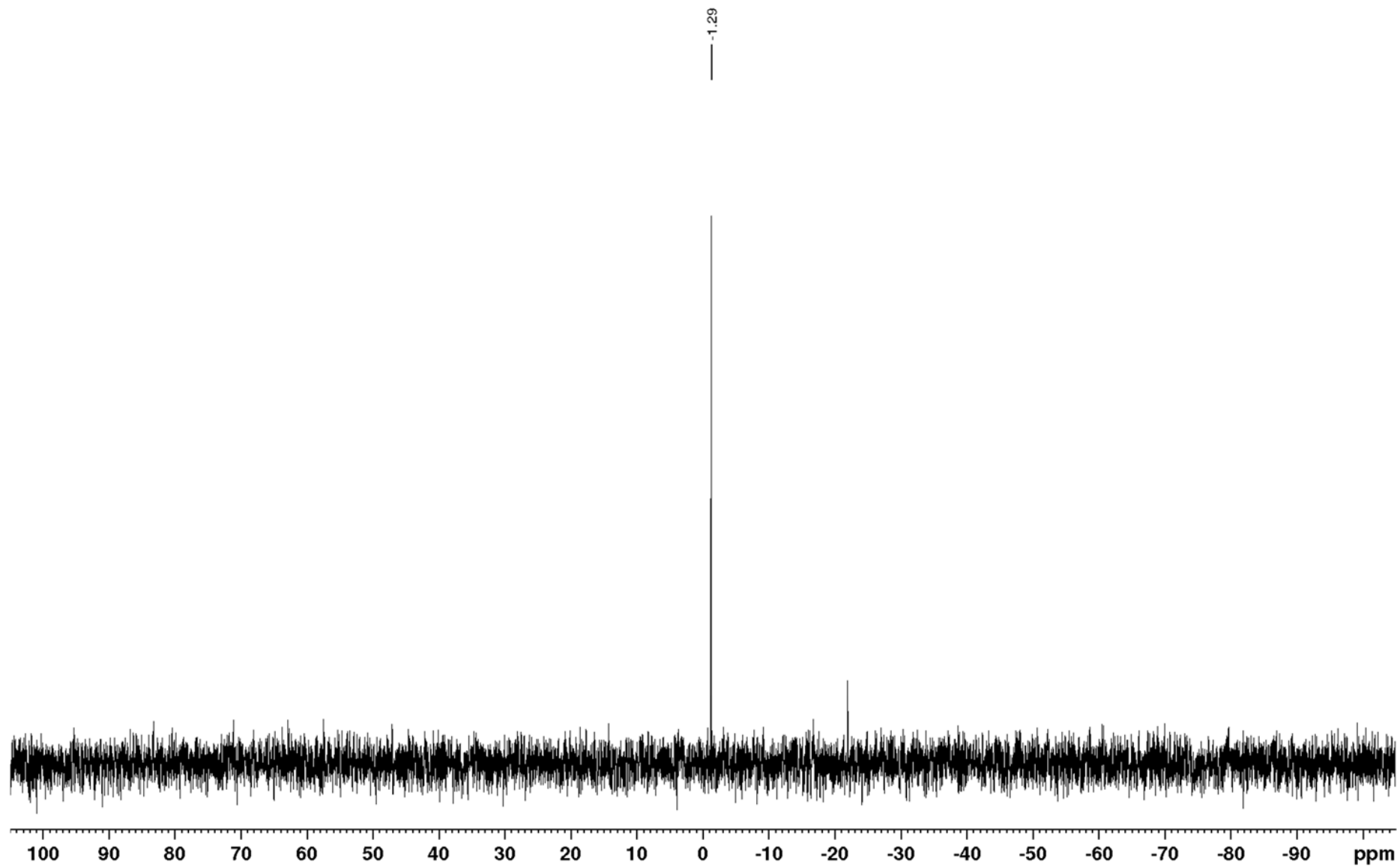
Dimethyl(phenyl)[1-(p-tolyl)ethyl]silane (4ba)

 ^1H NMR (500 MHz, CDCl_3 :

SUPPORTING INFORMATION

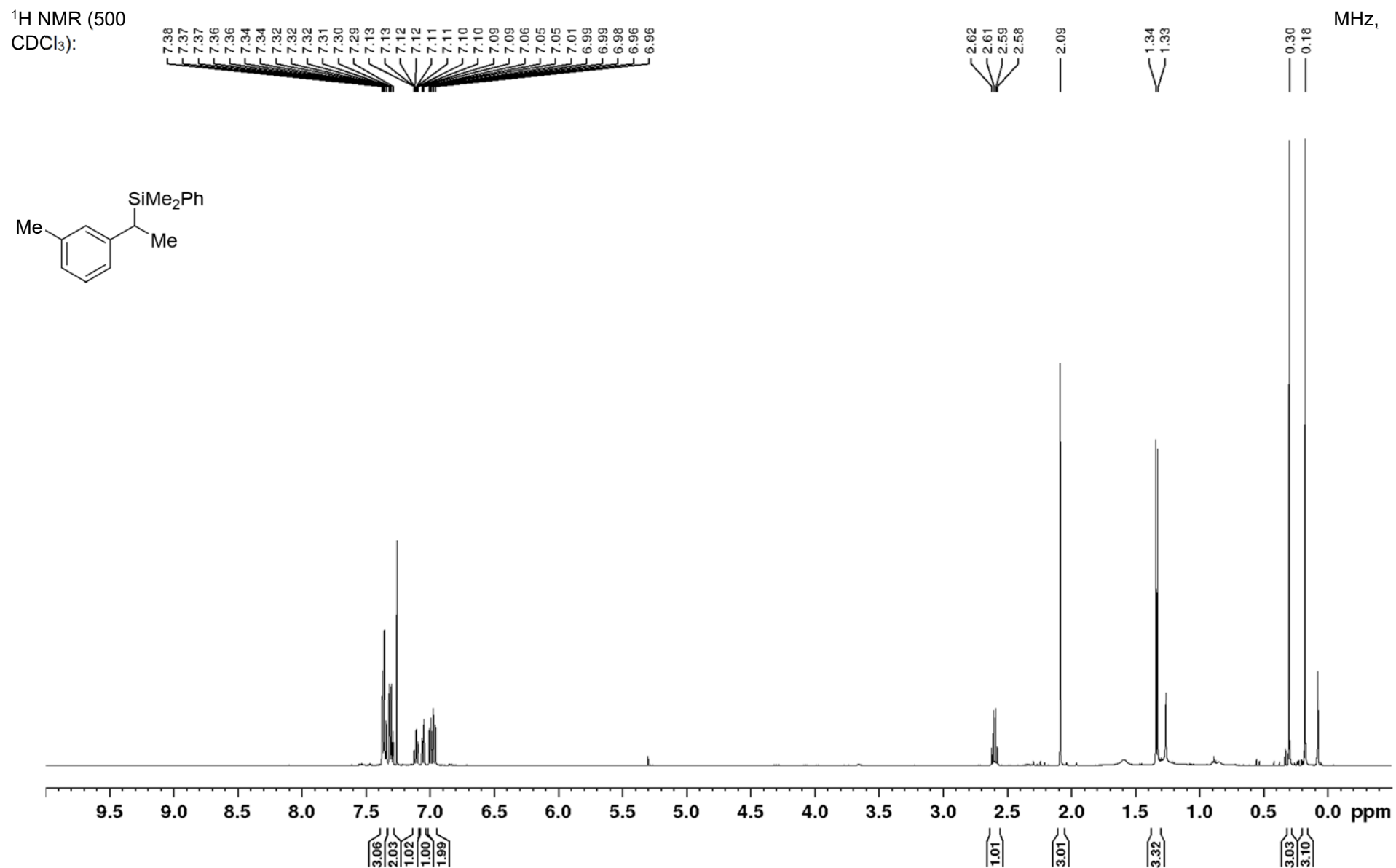
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

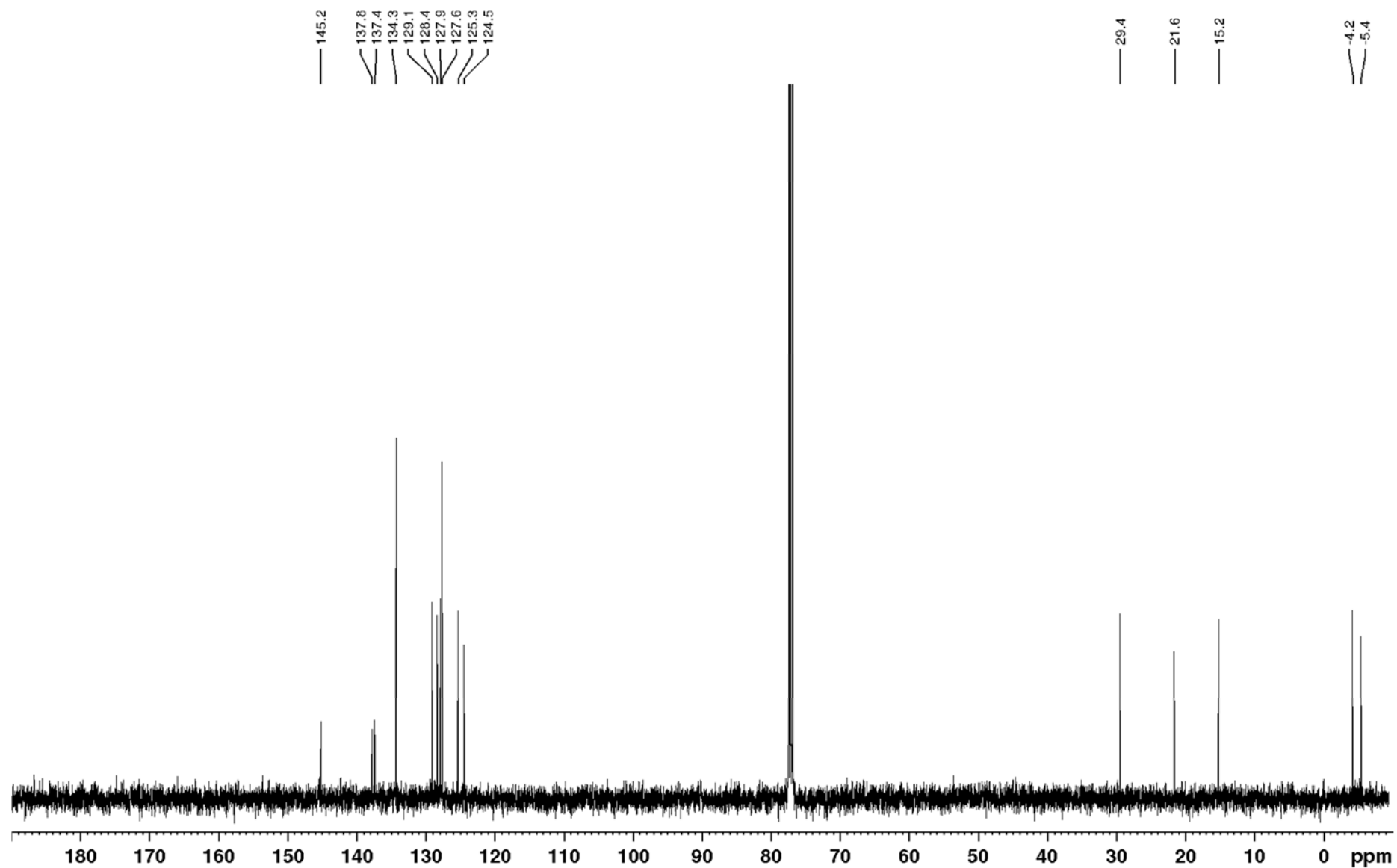
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

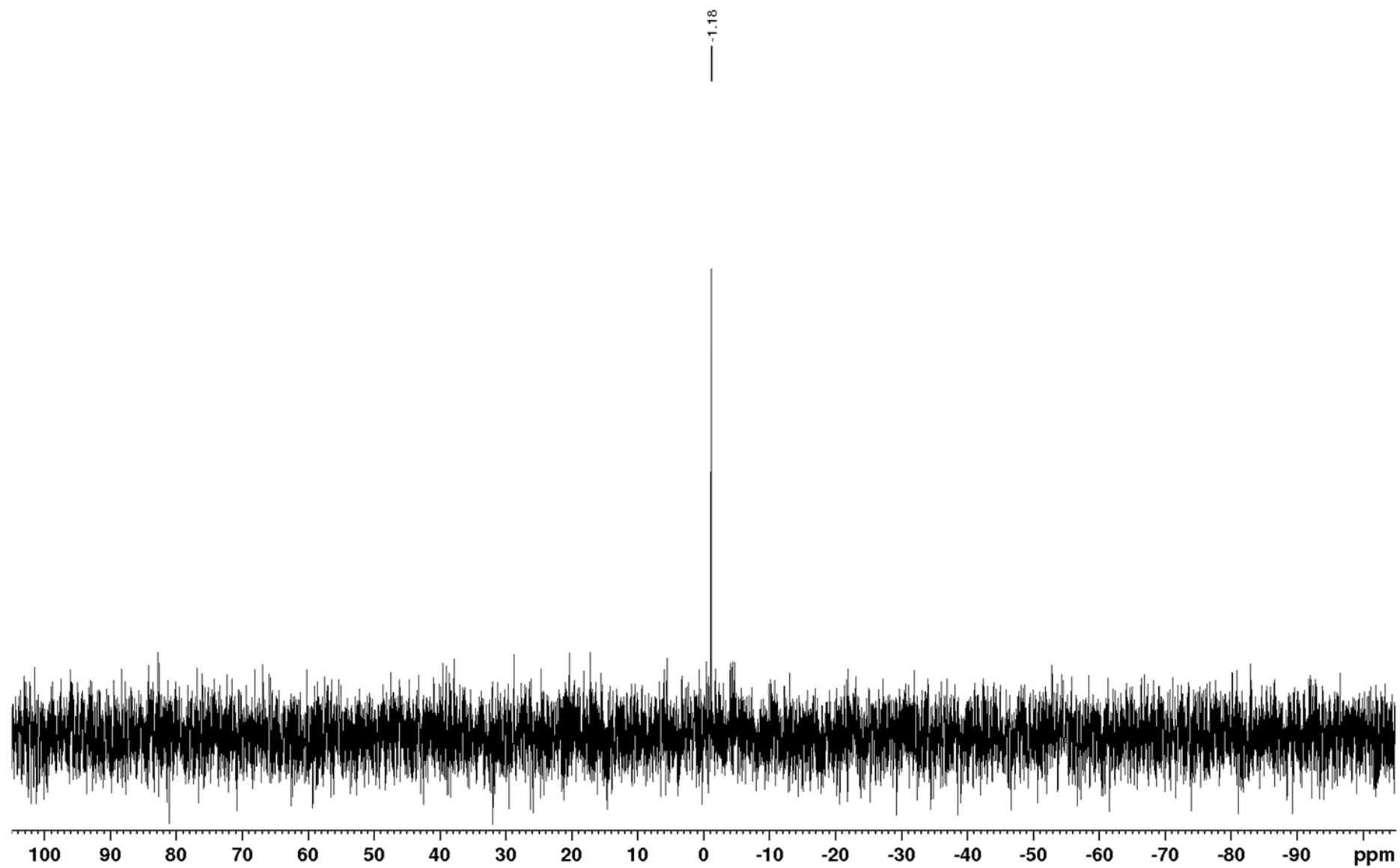
Dimethyl(phenyl)[1-(m-tolyl)ethyl]silane (4ca)

 ^1H NMR (500
 CDCl_3):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

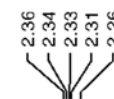
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

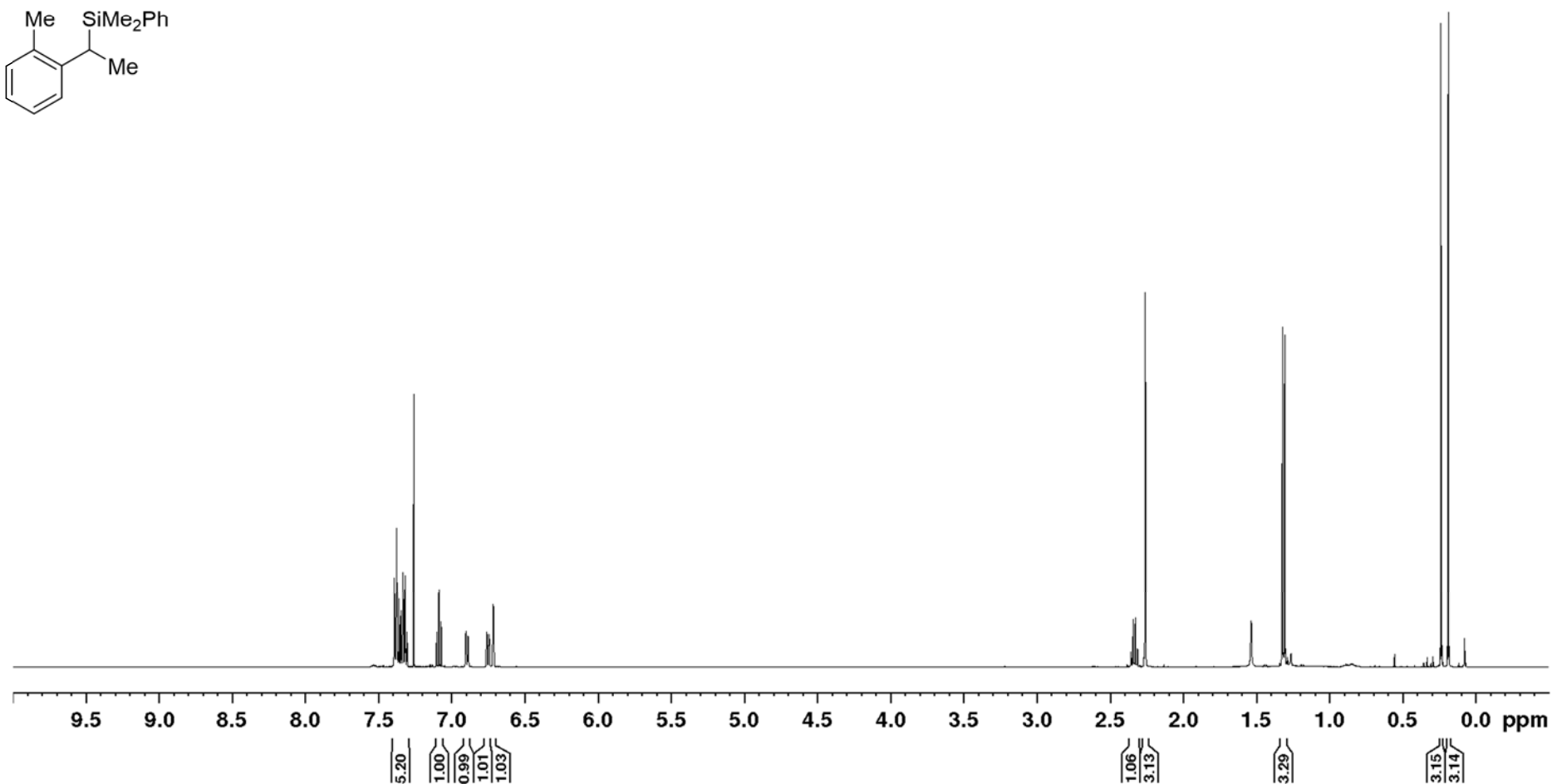
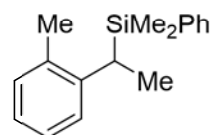
SUPPORTING INFORMATION

Dimethyl(phenyl)[1-(o-tolyl)ethyl]silane (4da)

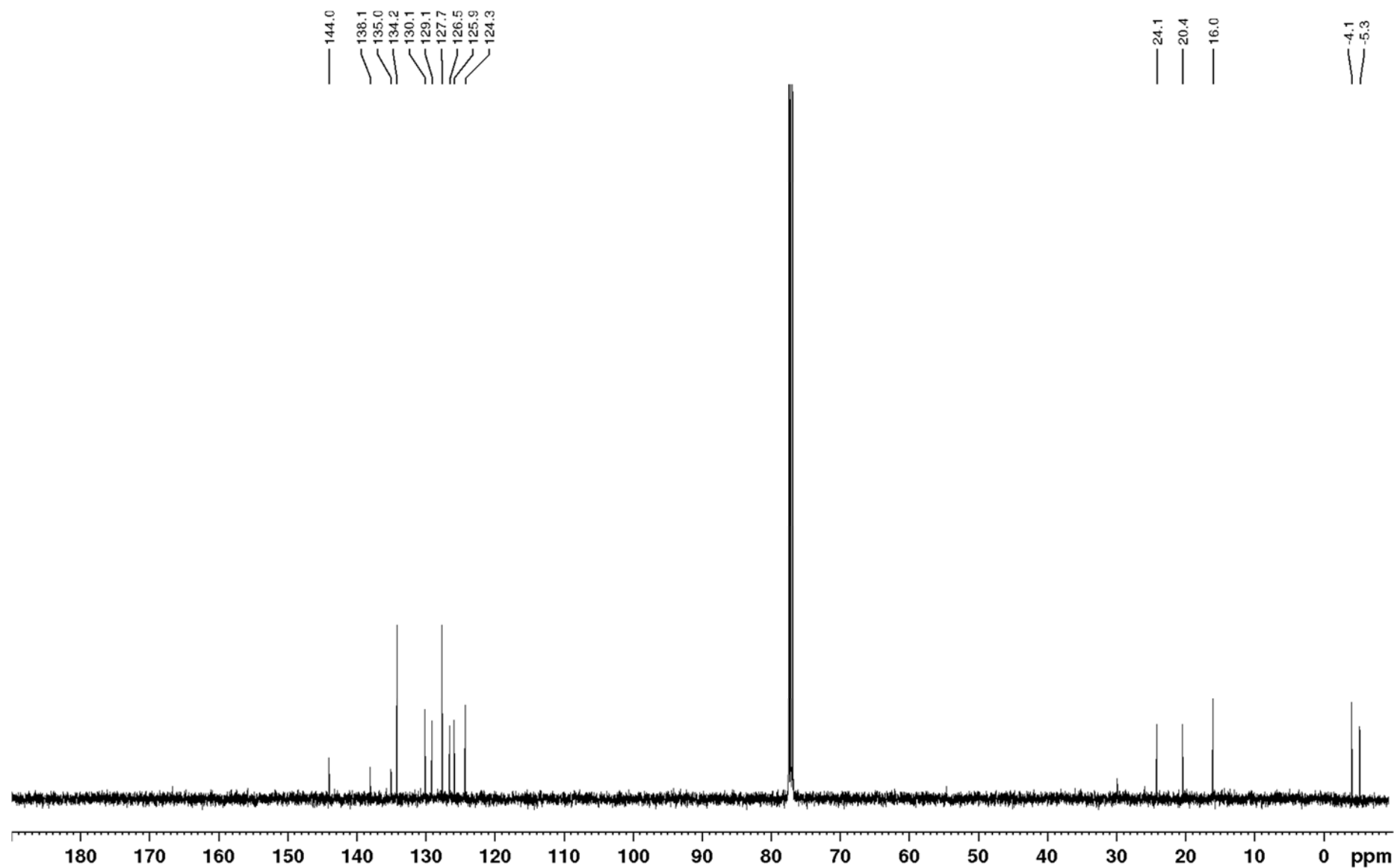
¹H NMR (500
CDCl₃):



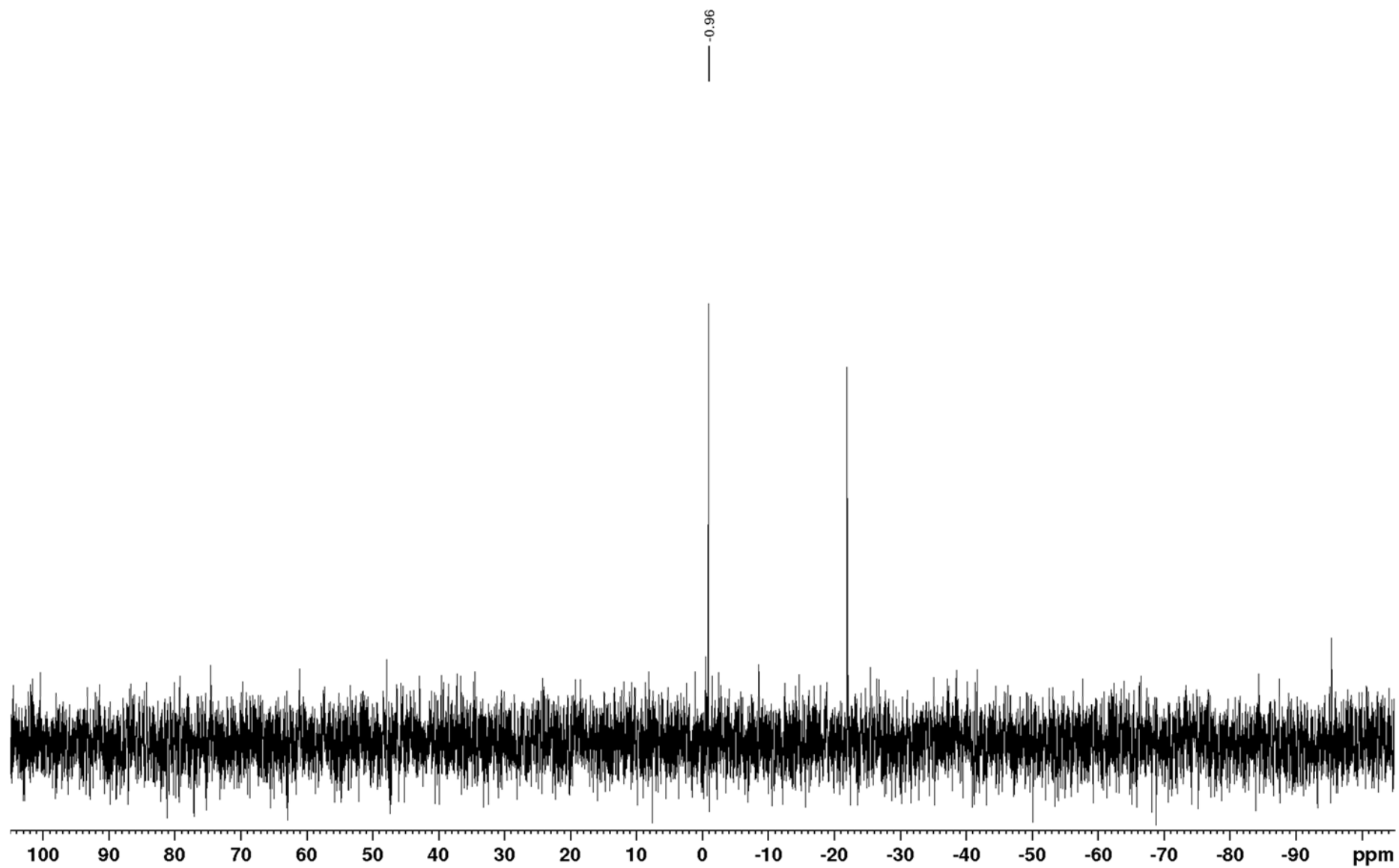
MHz,



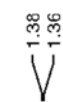
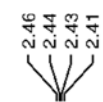
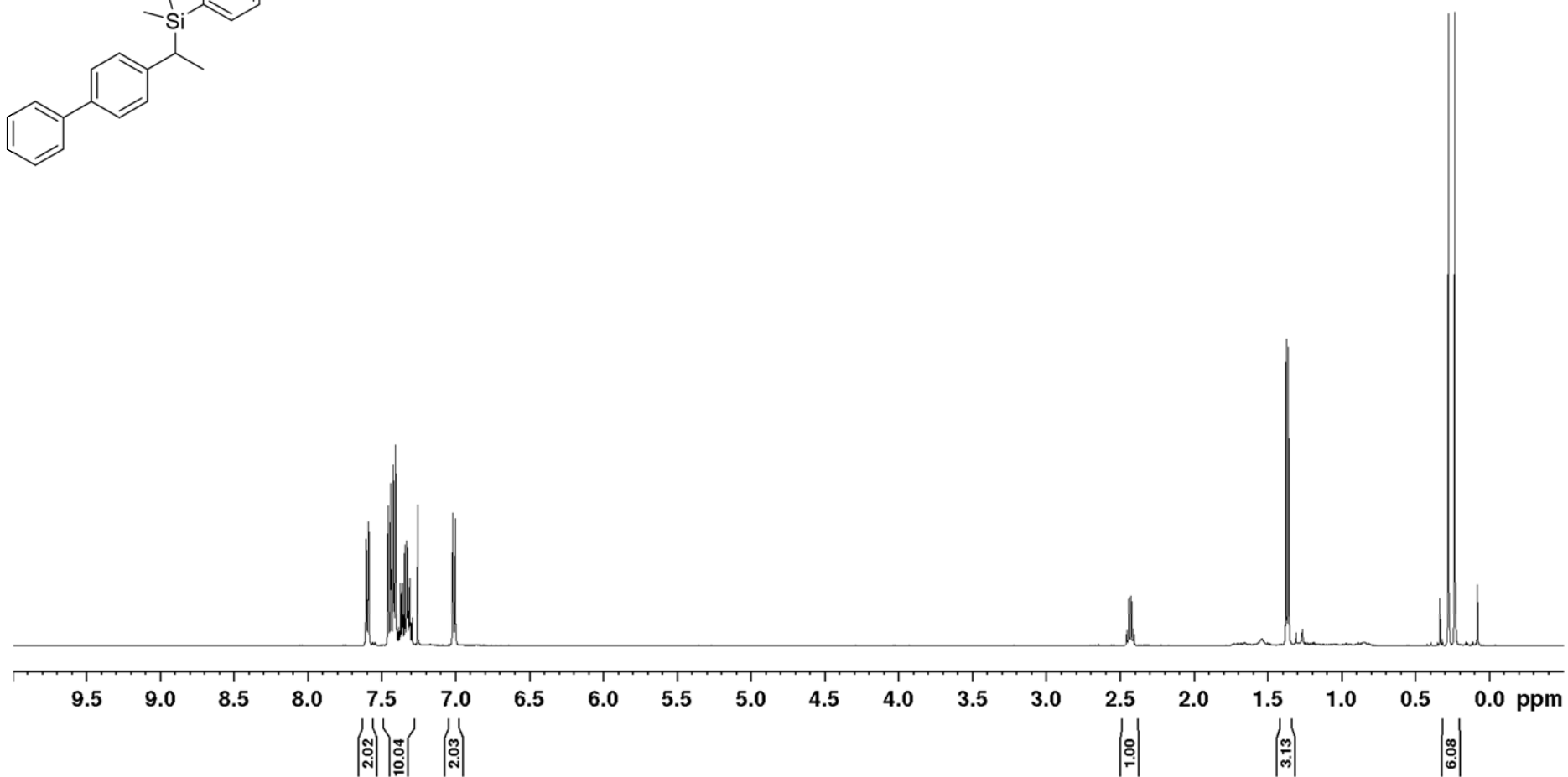
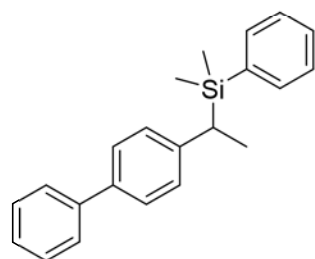
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

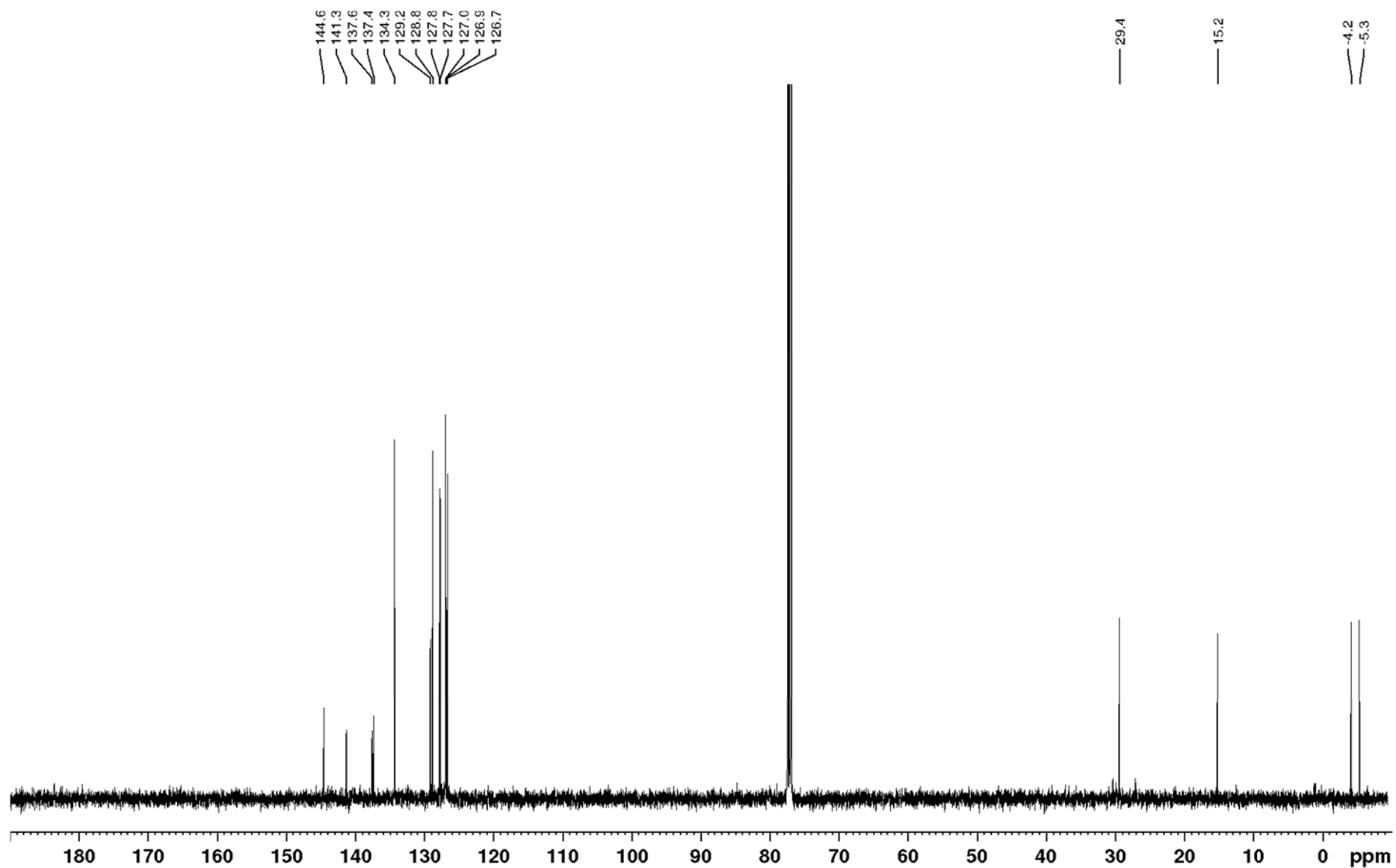
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

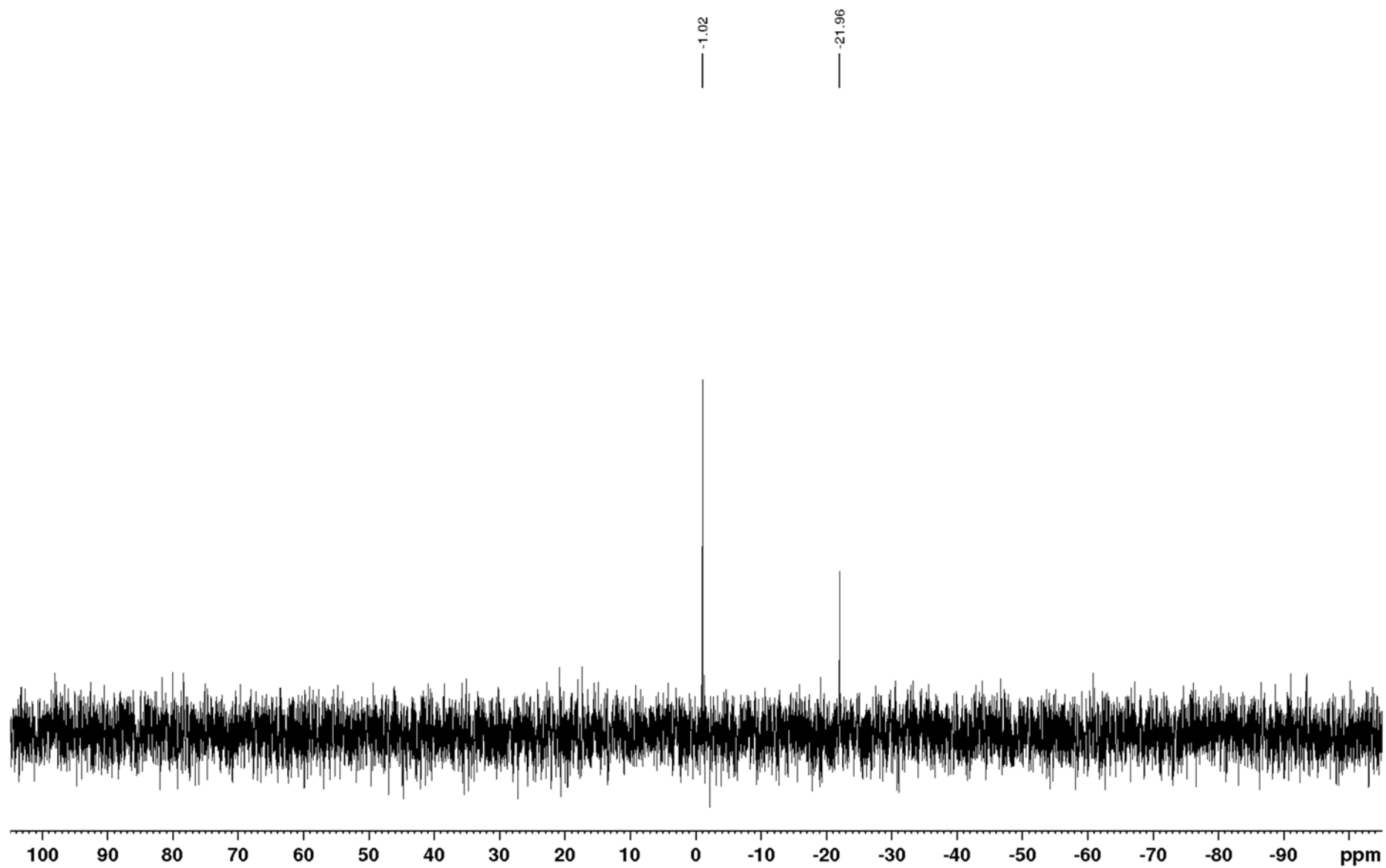
SUPPORTING INFORMATION

{1-[(1,1'-Biphenyl)-4-yl]ethyl}dimethyl(phenyl)silane (4ea)¹H NMR (500 MHz,CDCl₃):

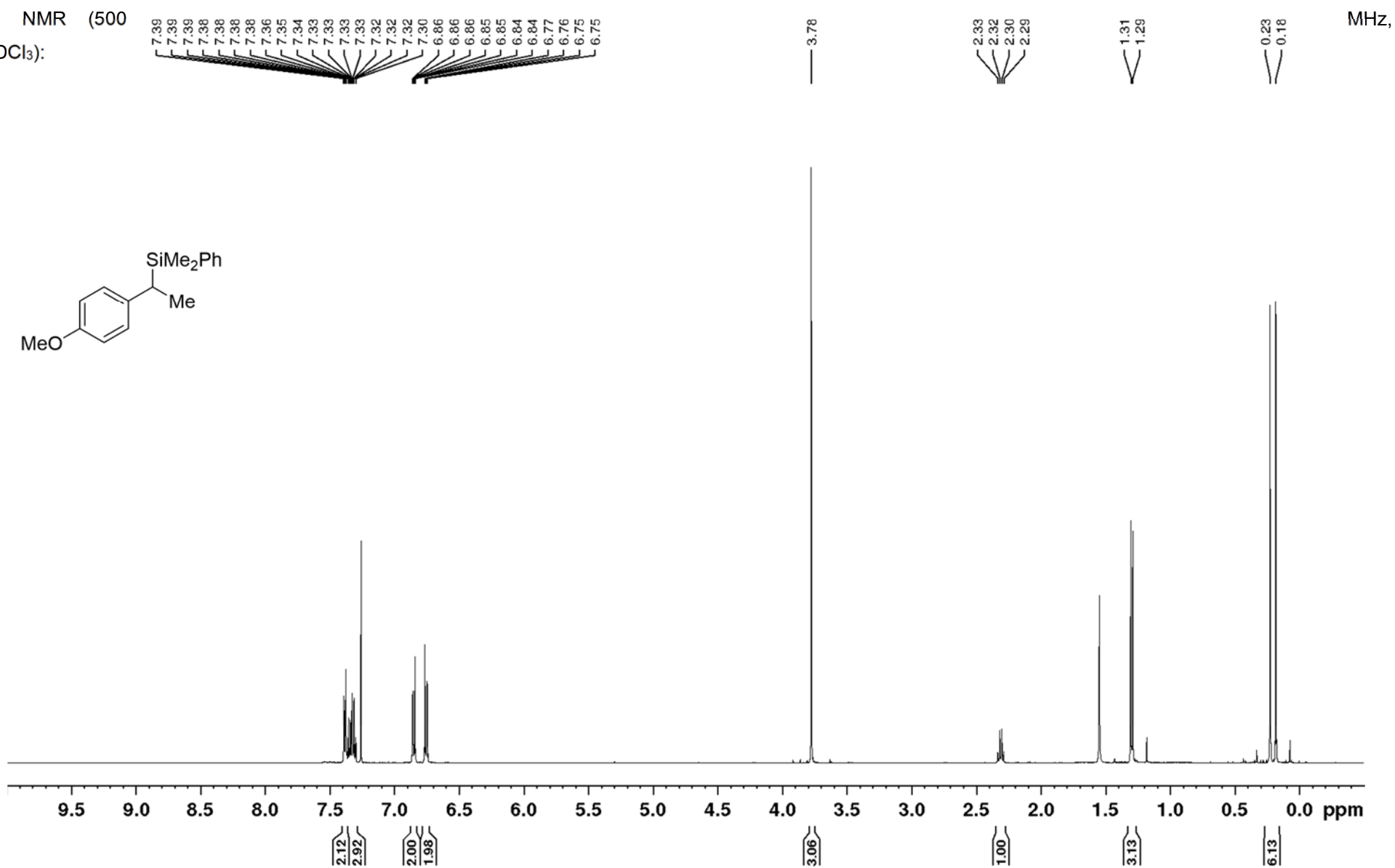
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

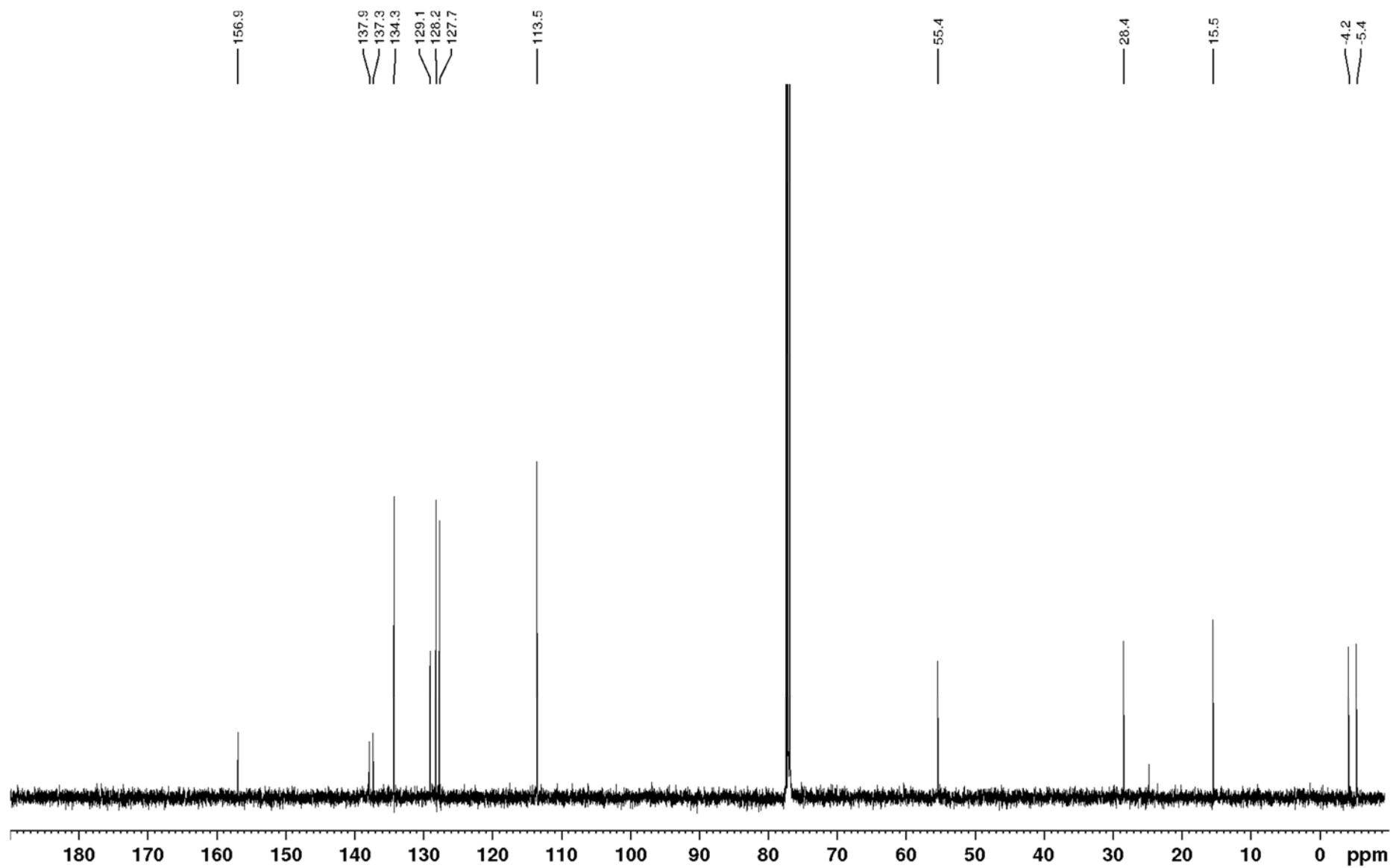
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

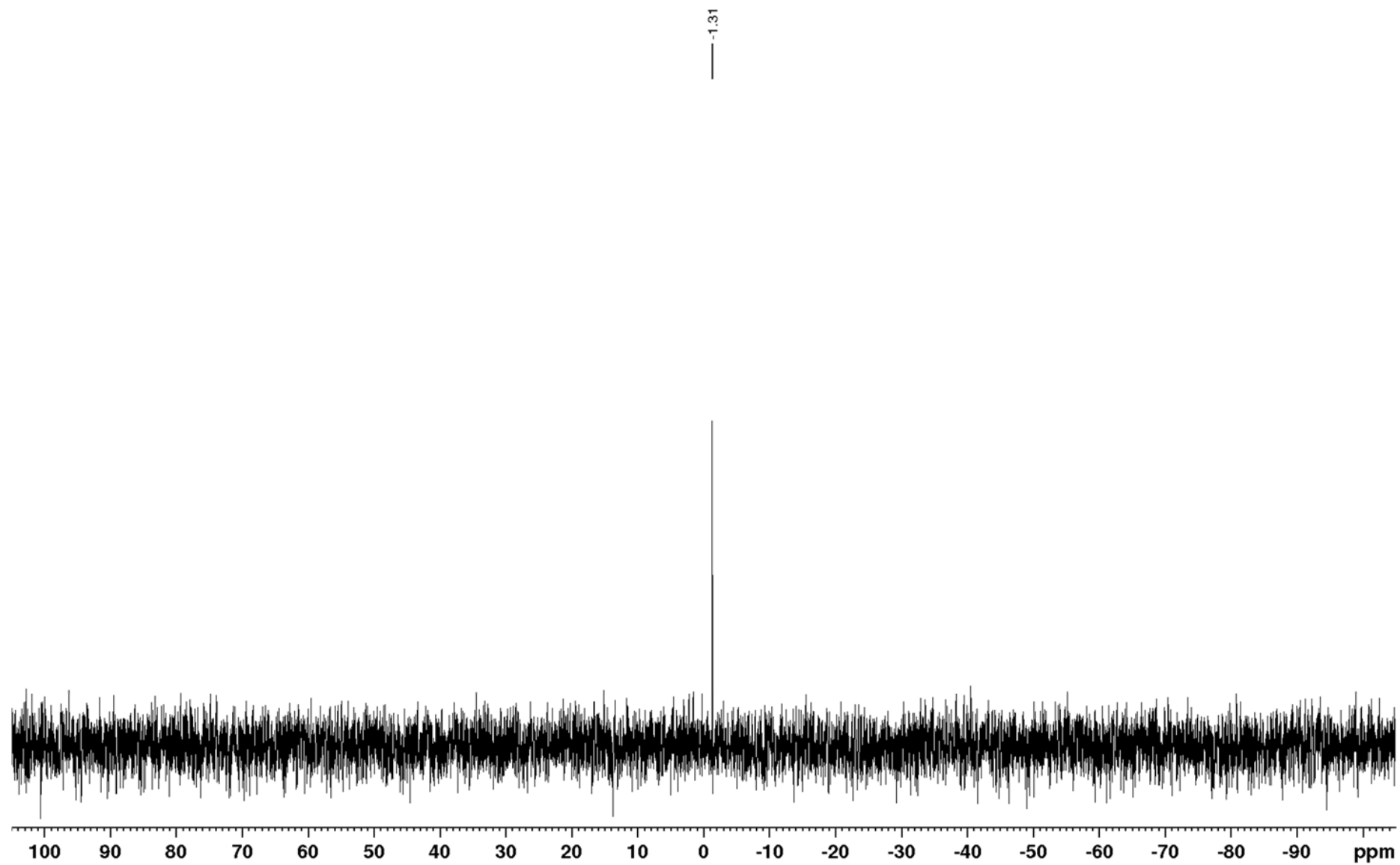
SUPPORTING INFORMATION

[1-(4-Methoxyphenyl)ethyl]dimethyl(phenyl)silane (4fa)¹H NMR (500
CDCl₃):

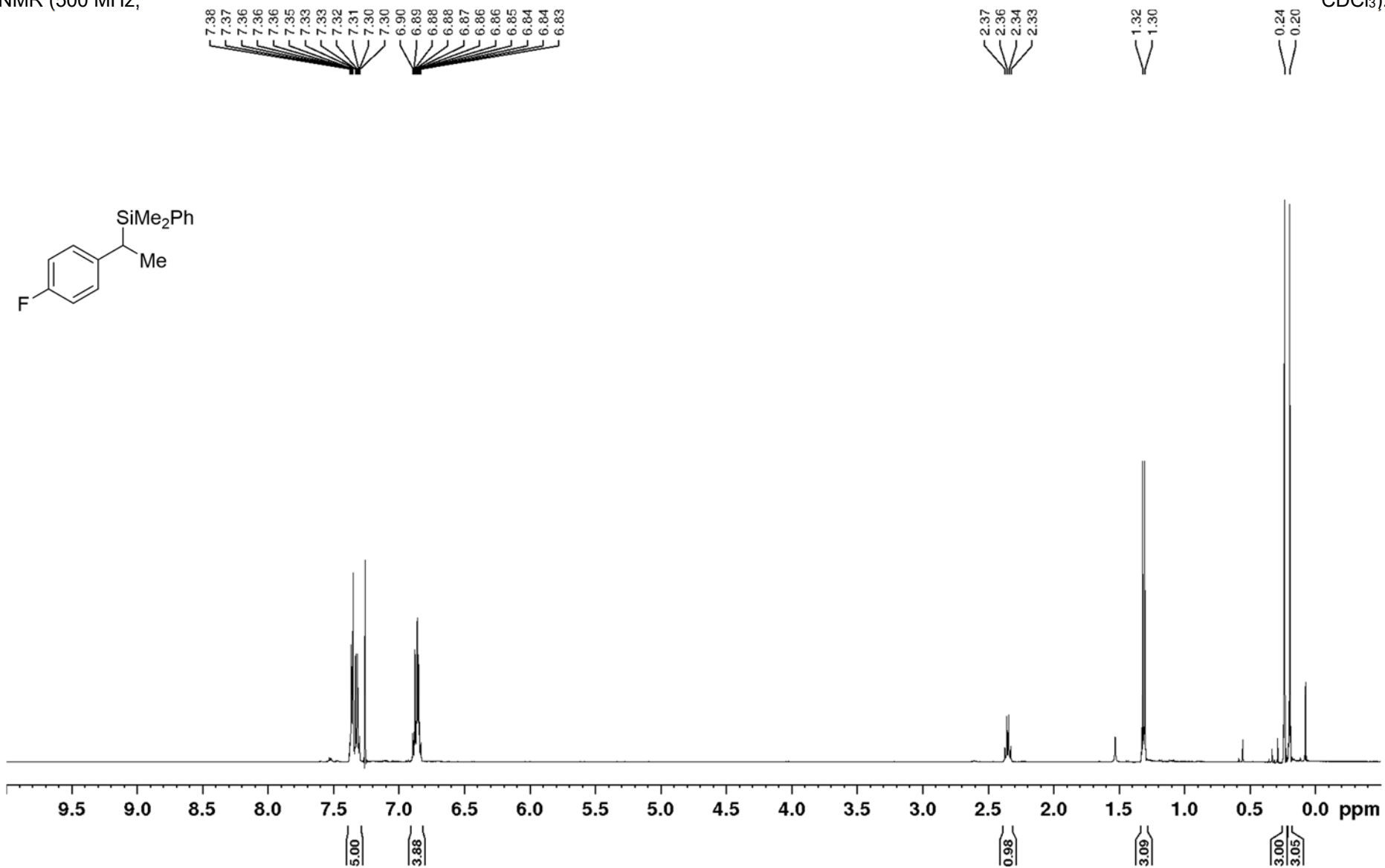
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

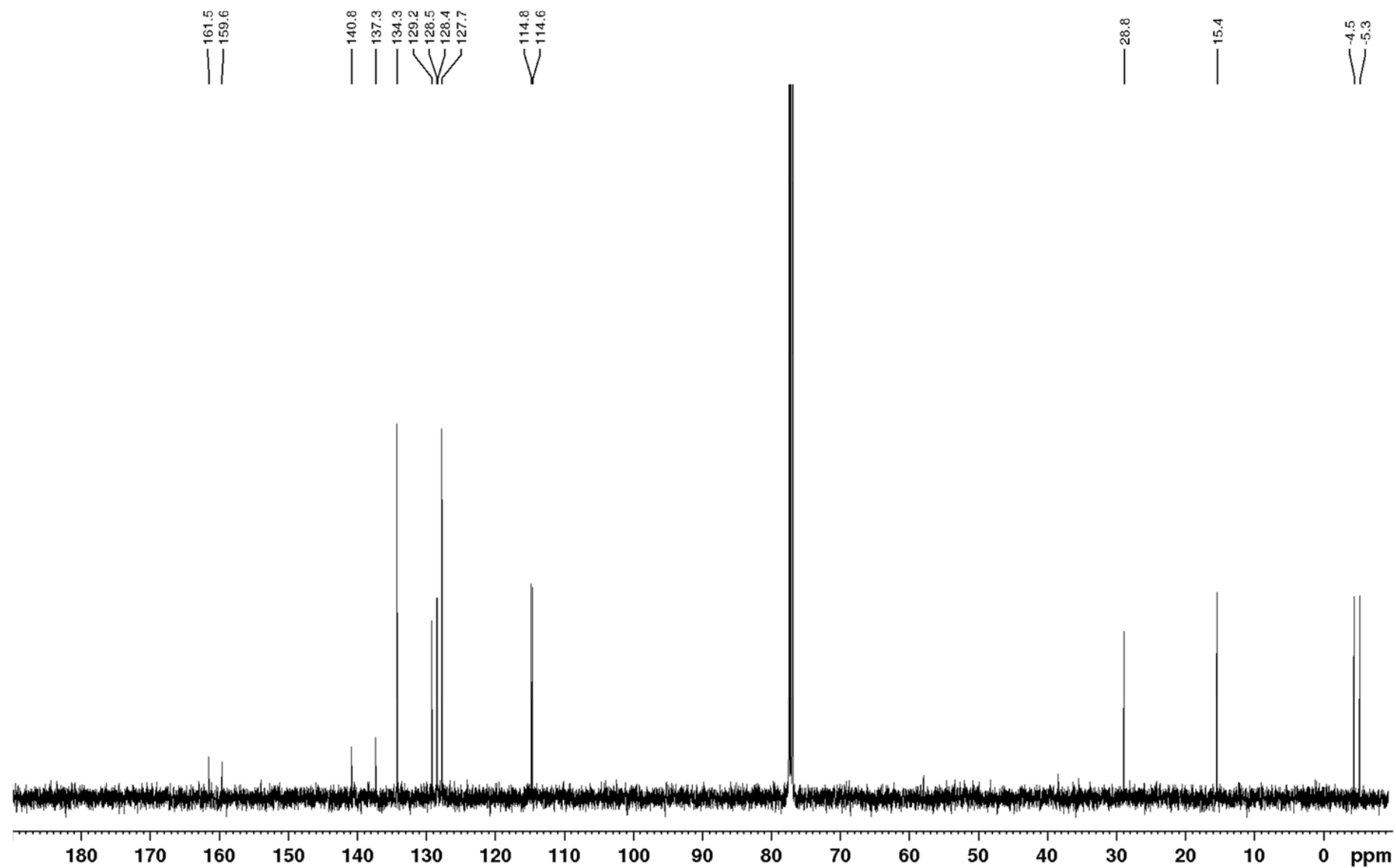
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

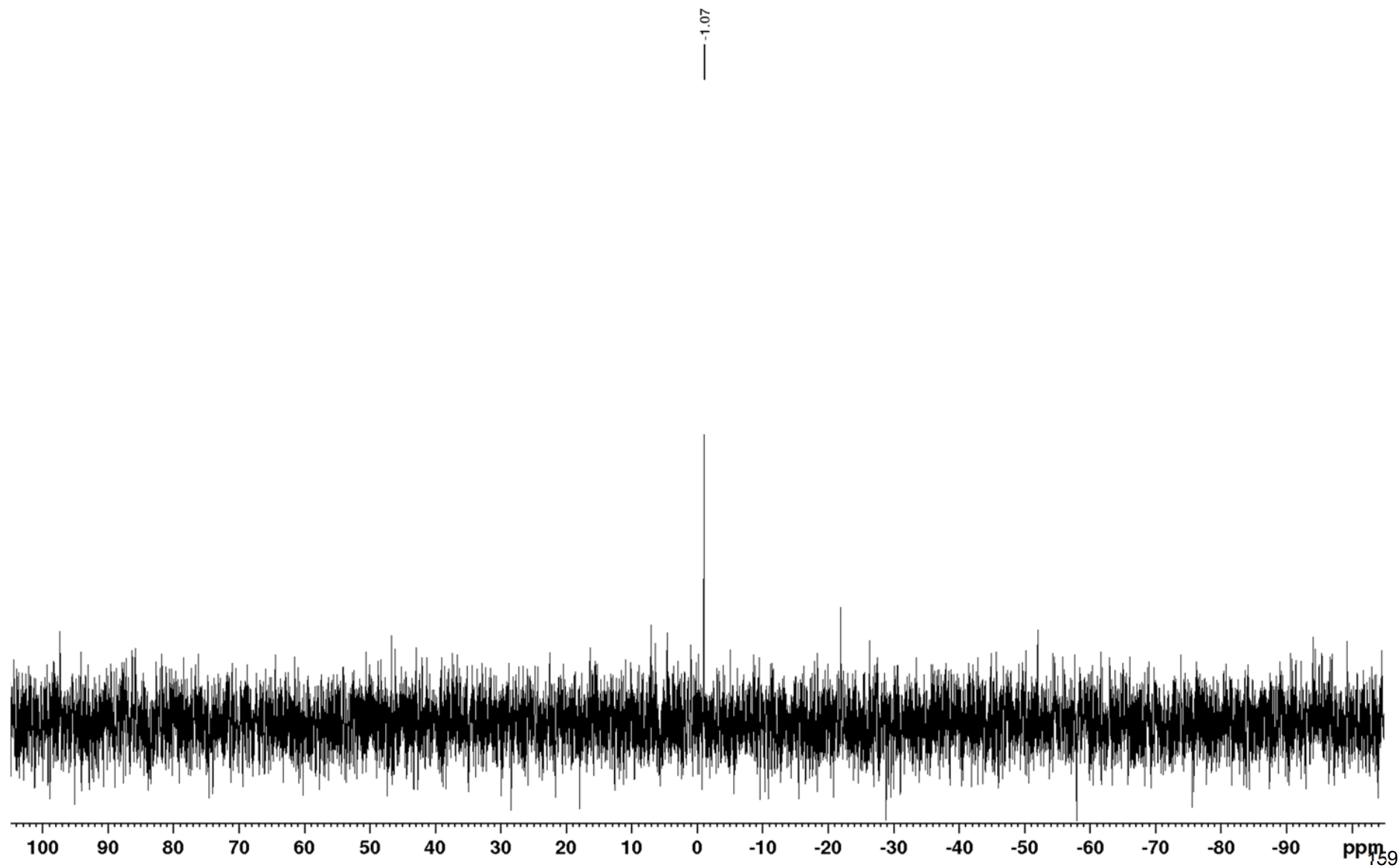
[1-(4-Fluorophenyl)ethyl]dimethyl(phenyl)silane (4ga)¹H NMR (500 MHz,CDCl₃):

SUPPORTING INFORMATION

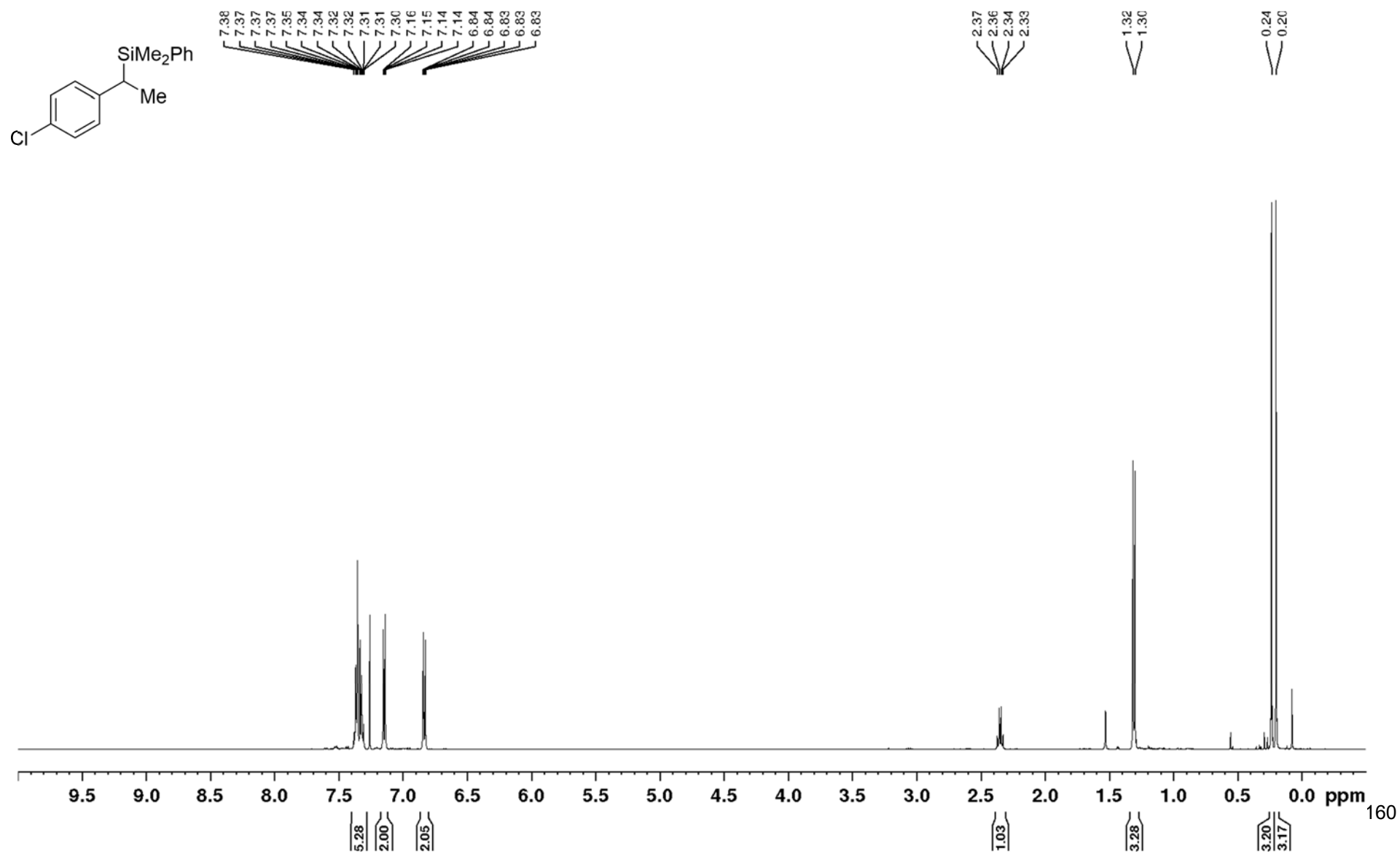
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

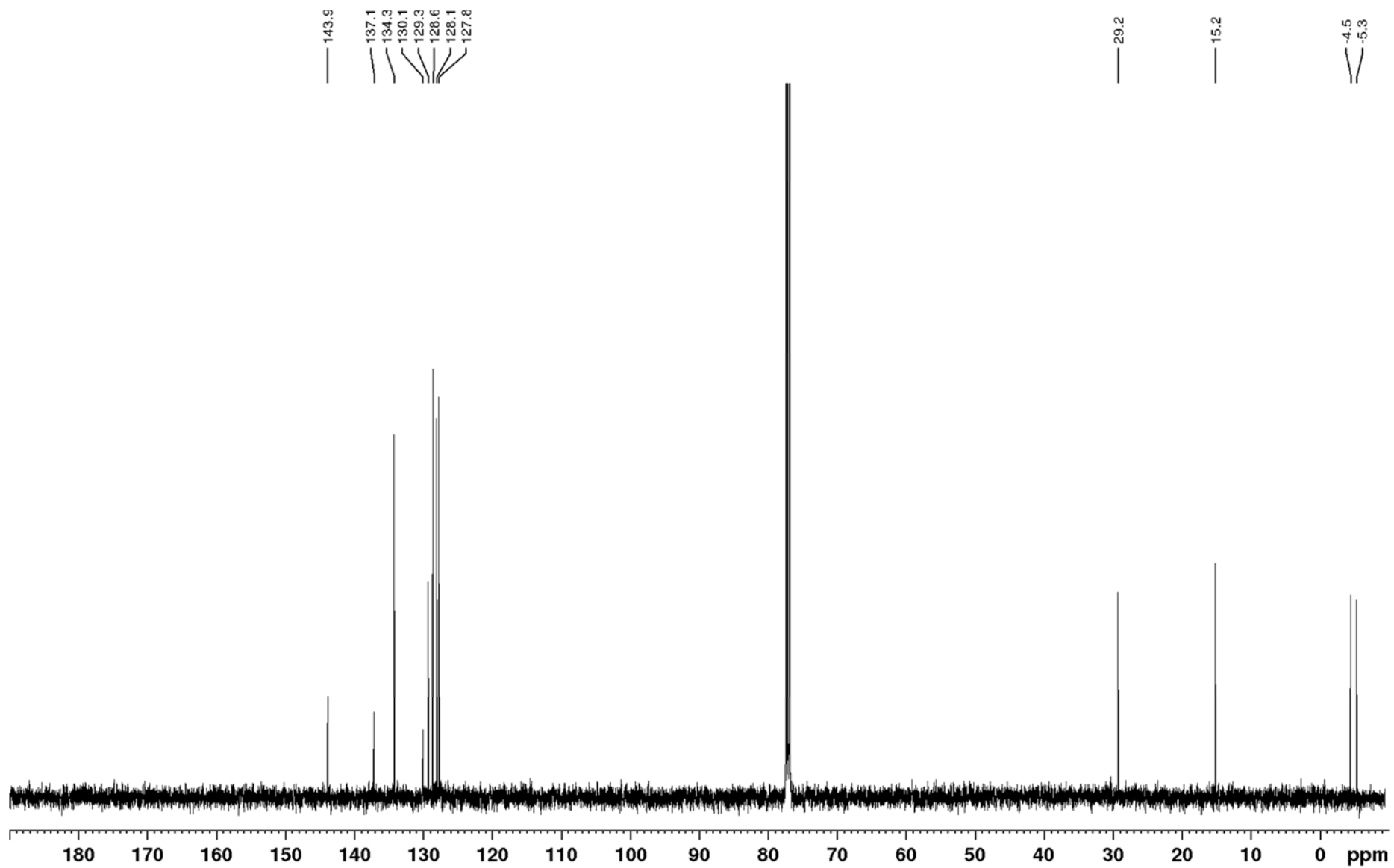
$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):



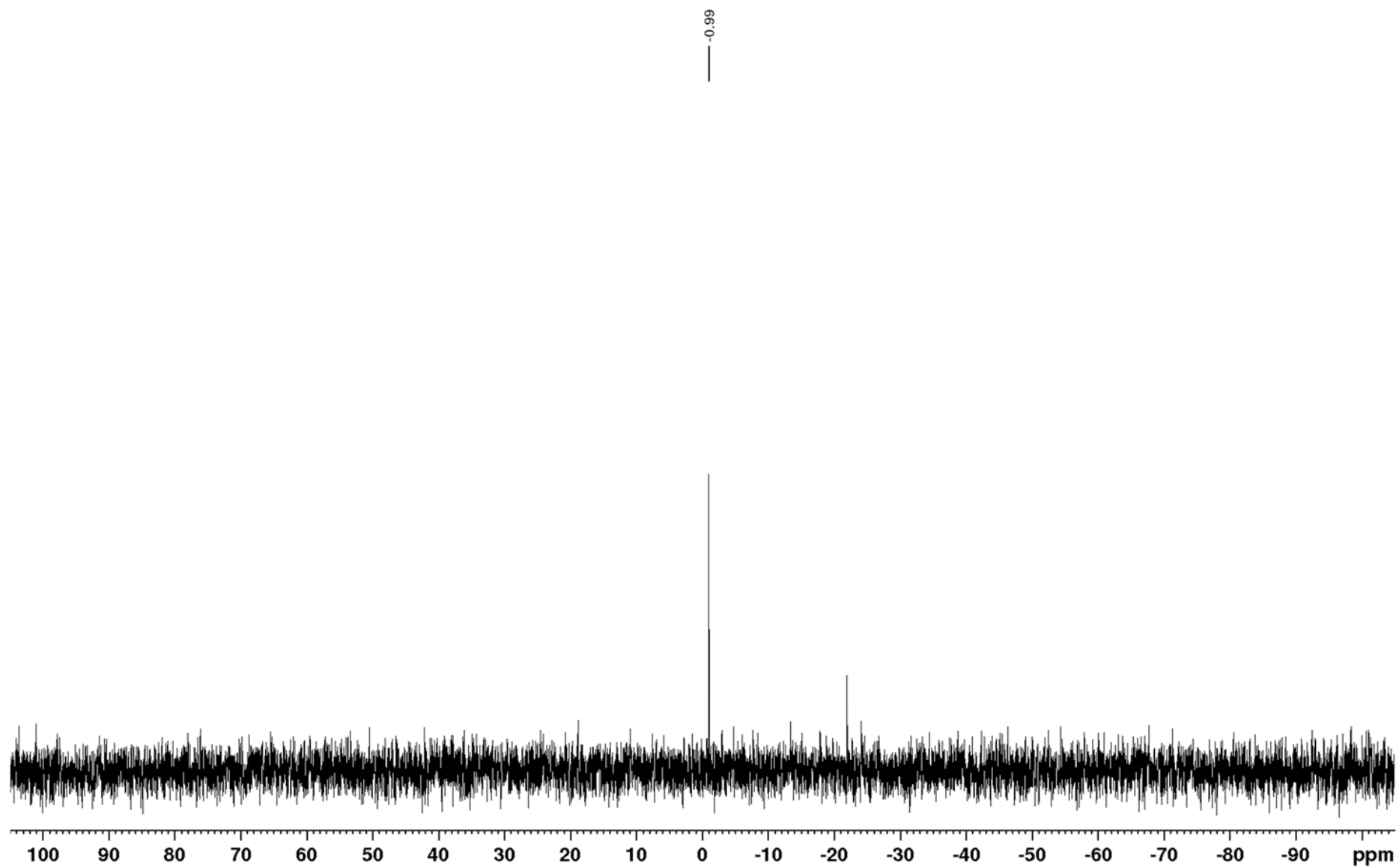
SUPPORTING INFORMATION

[1-(4-Chlorophenyl)ethyl]dimethyl(phenyl)silane (4ha)¹H NMR (500 MHz, CDCl₃):

SUPPORTING INFORMATION

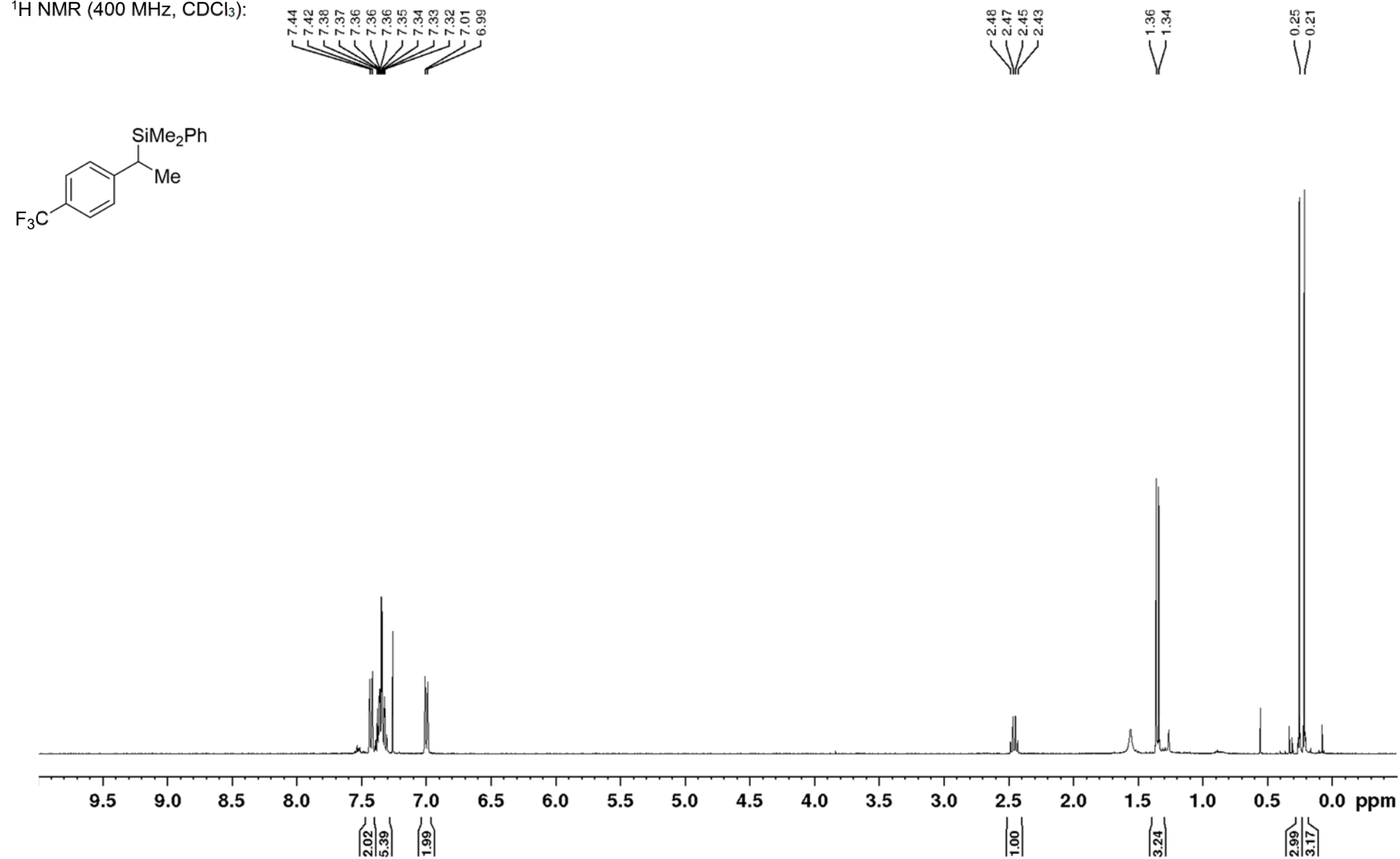
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

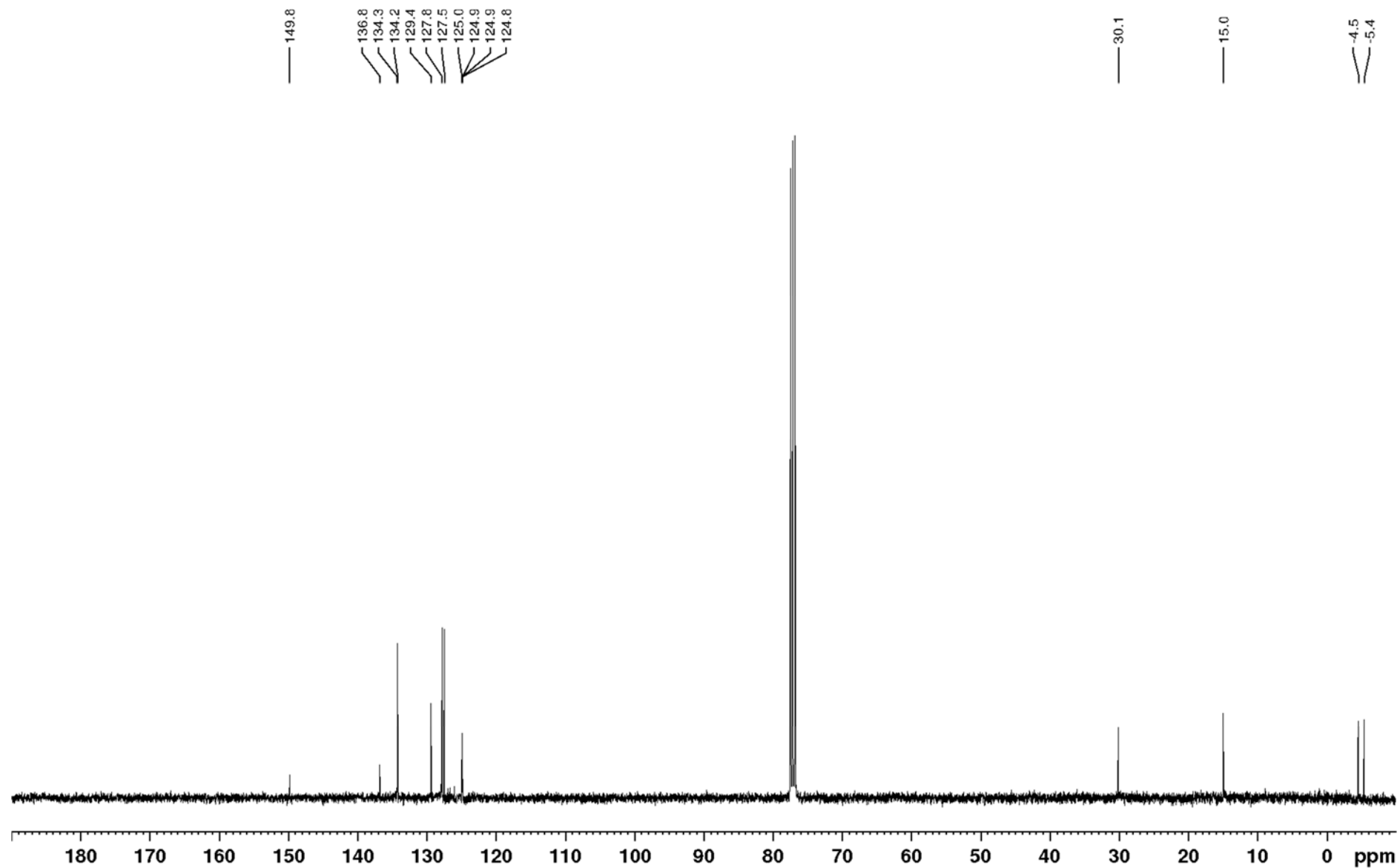
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

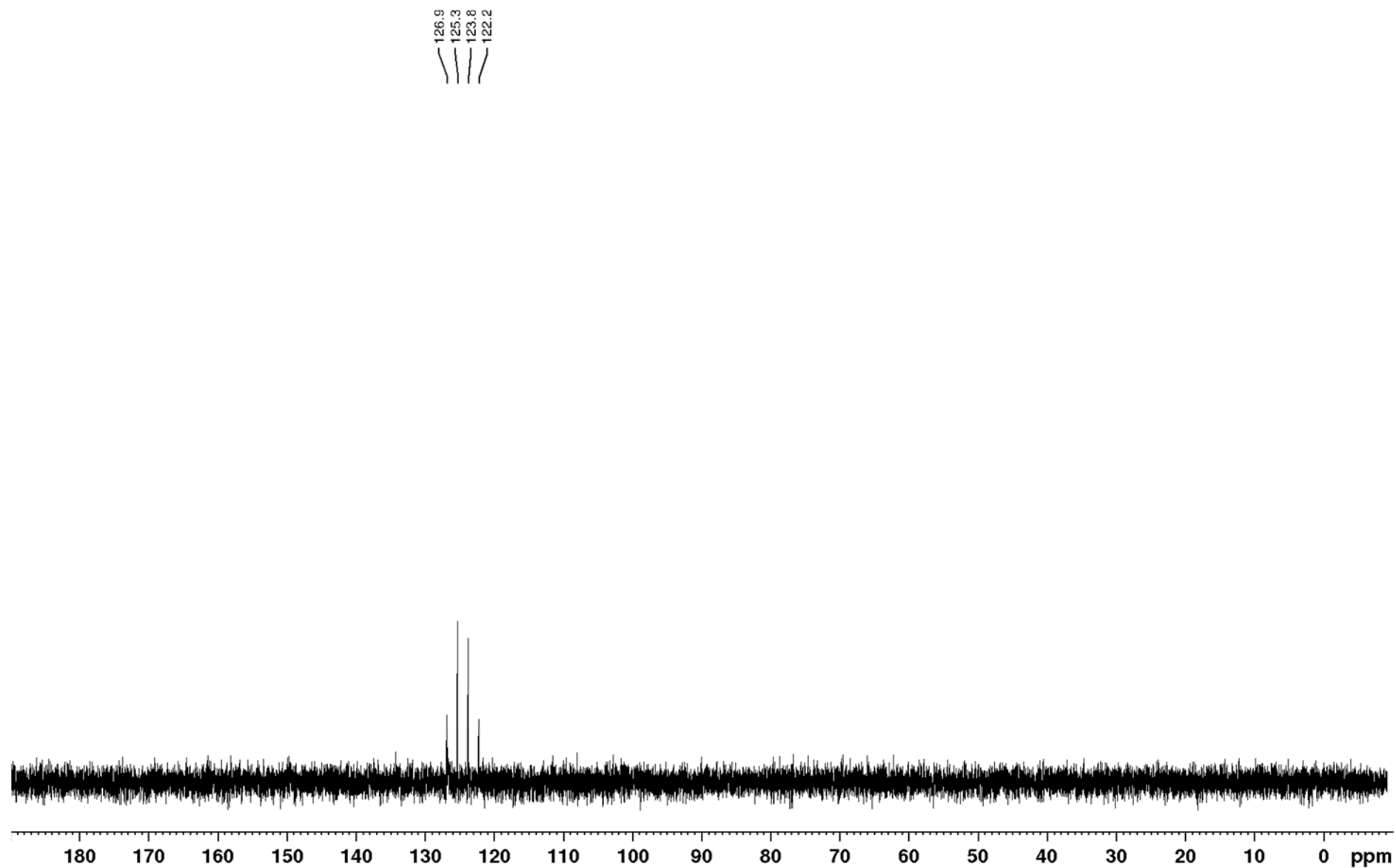
Dimethyl(phenyl){1-[4-(trifluoromethyl)phenyl]ethyl}silane (4ia)

 ^1H NMR (400 MHz, CDCl_3):

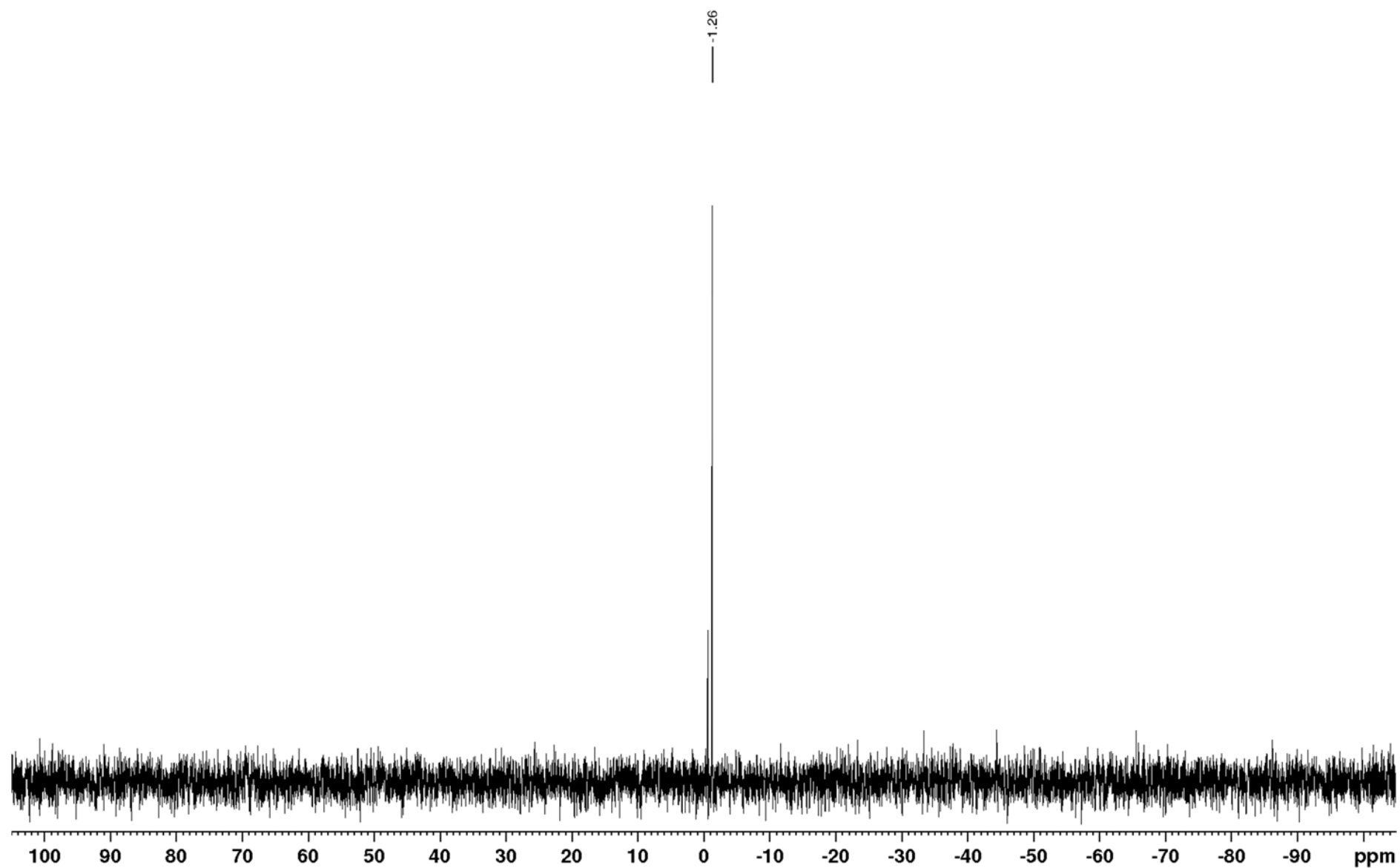
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^{19}\text{F}\}$ DEPT NMR (126 MHz, $\text{DMSO-}d_6$):

SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

4-{1-[Dimethyl(phenyl)silyl]ethyl}benzonitrile (4ja)

 ^1H NMR CDCl_3 :

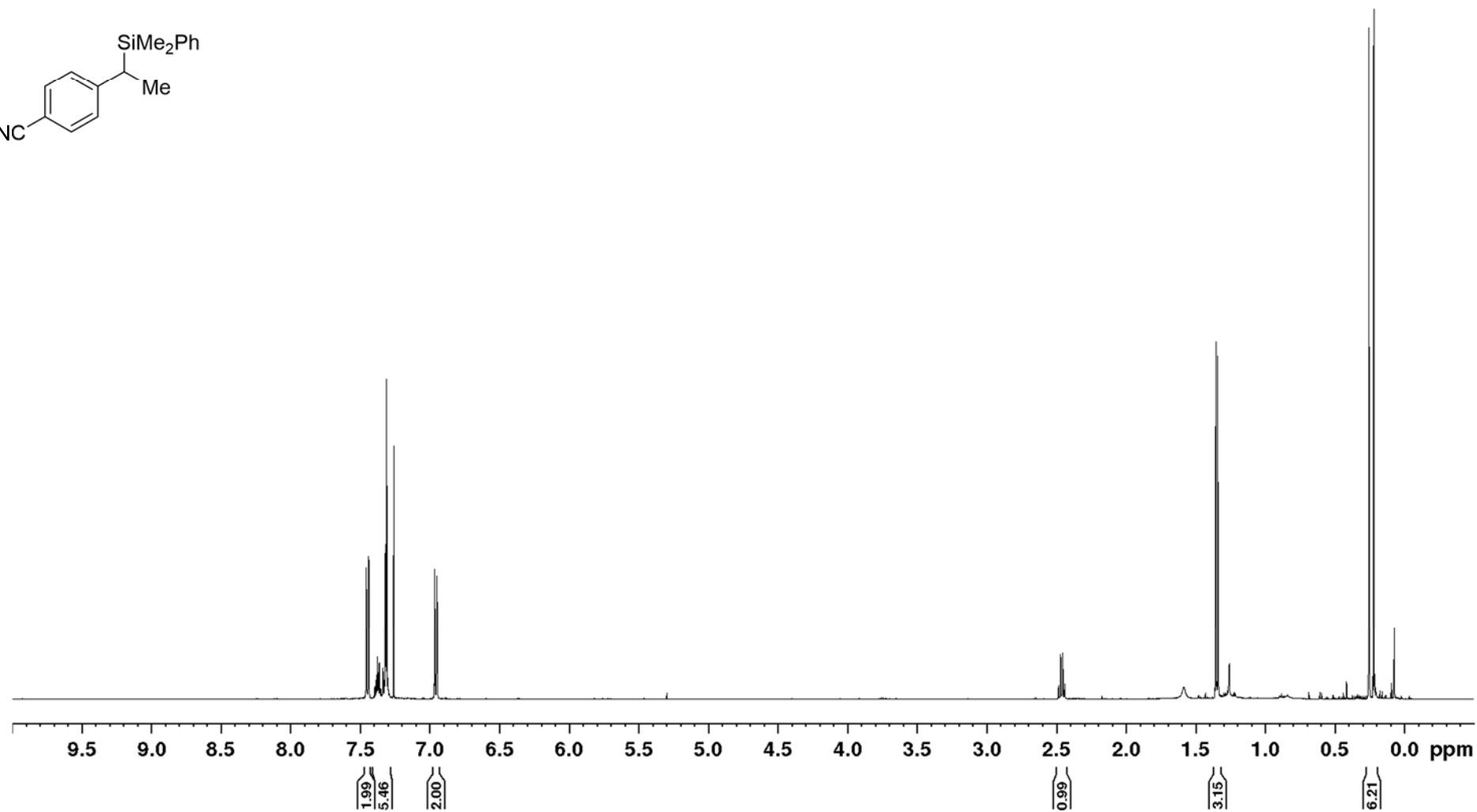
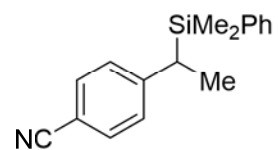
7.46
7.46
7.45
7.44
7.44
7.44
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.30
6.97
6.97
6.96
6.96
6.95
6.95
6.94

2.48
2.47
2.45
2.44

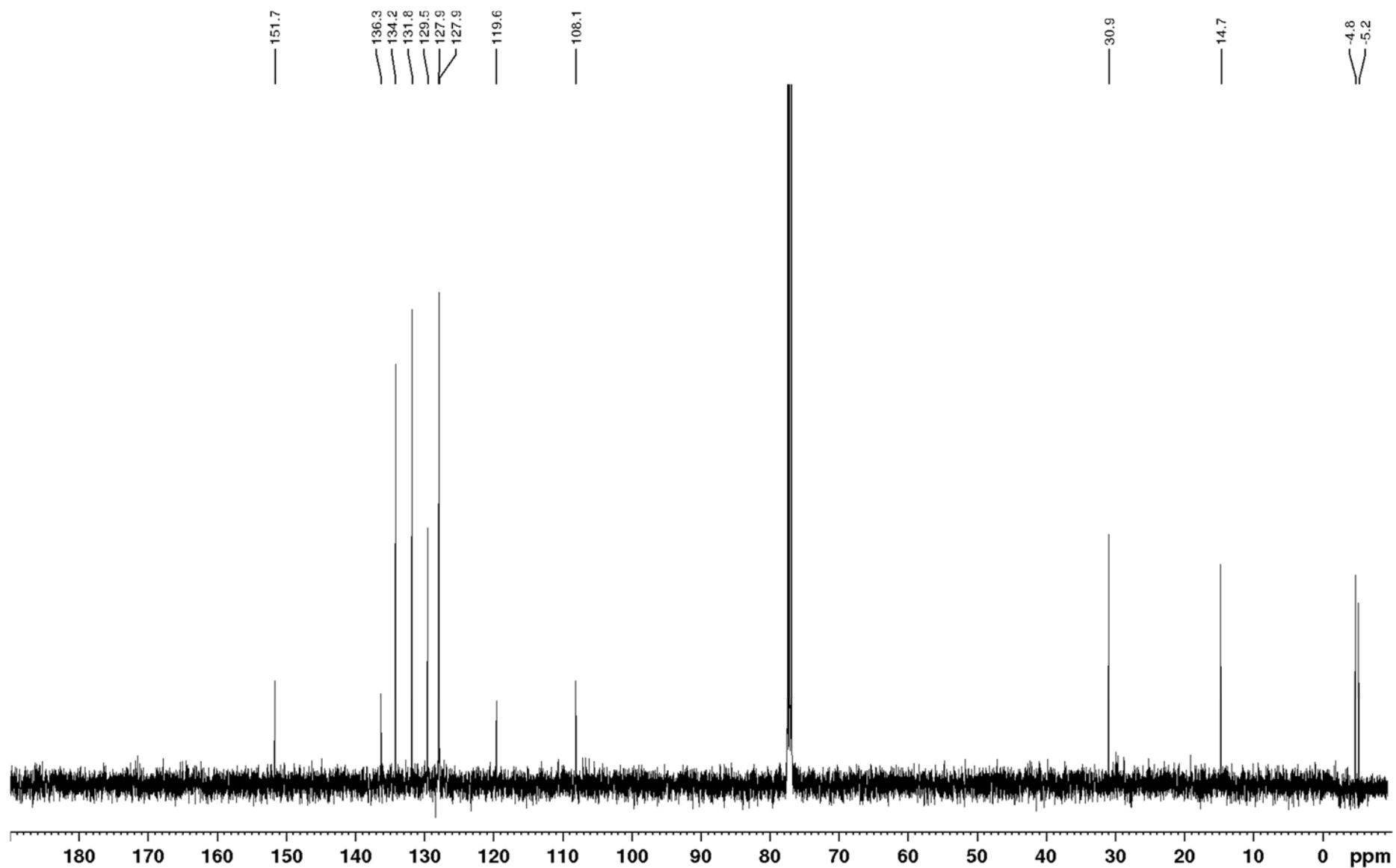
1.35
1.34

0.26
0.22

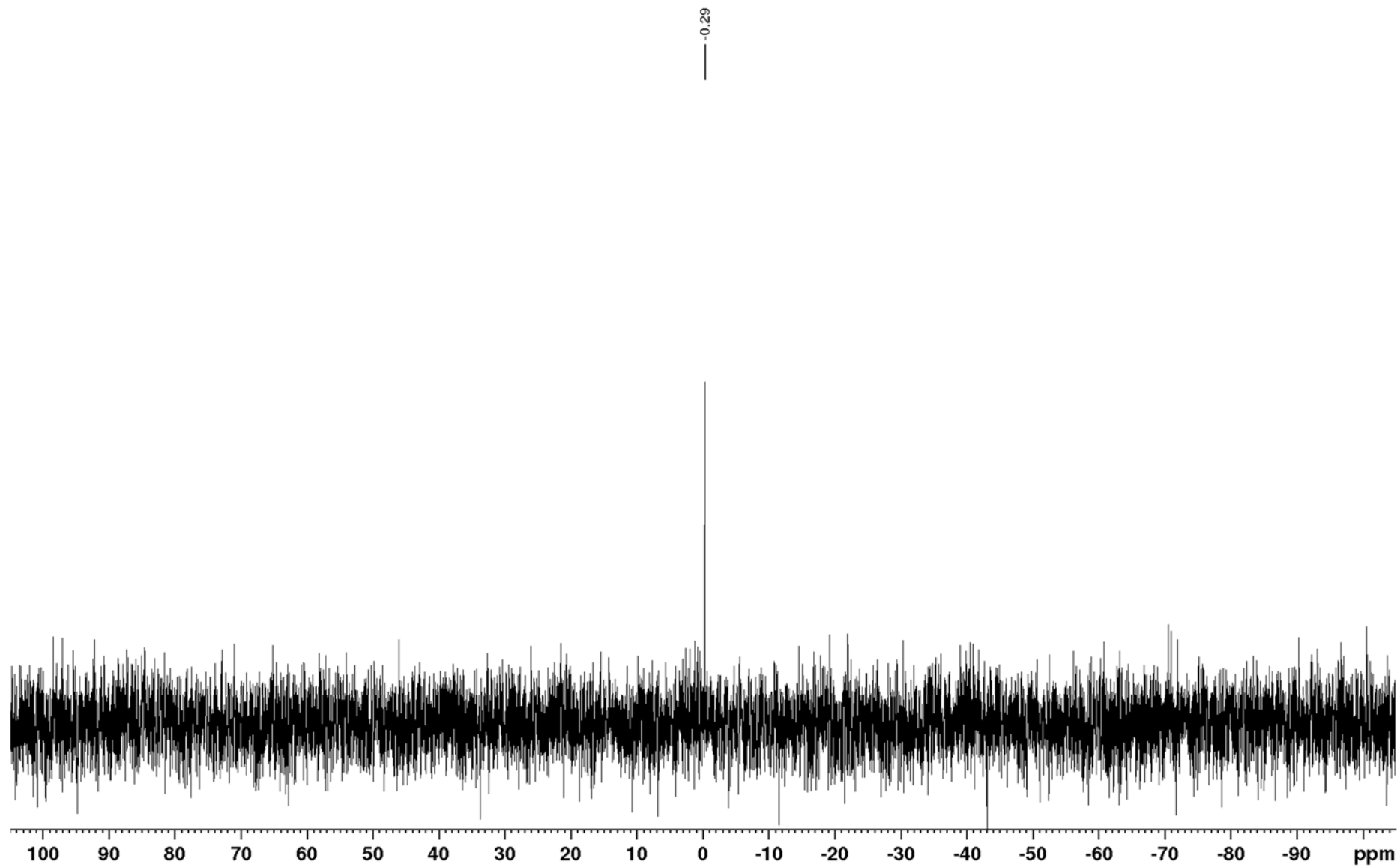
(500 MHz,



SUPPORTING INFORMATION

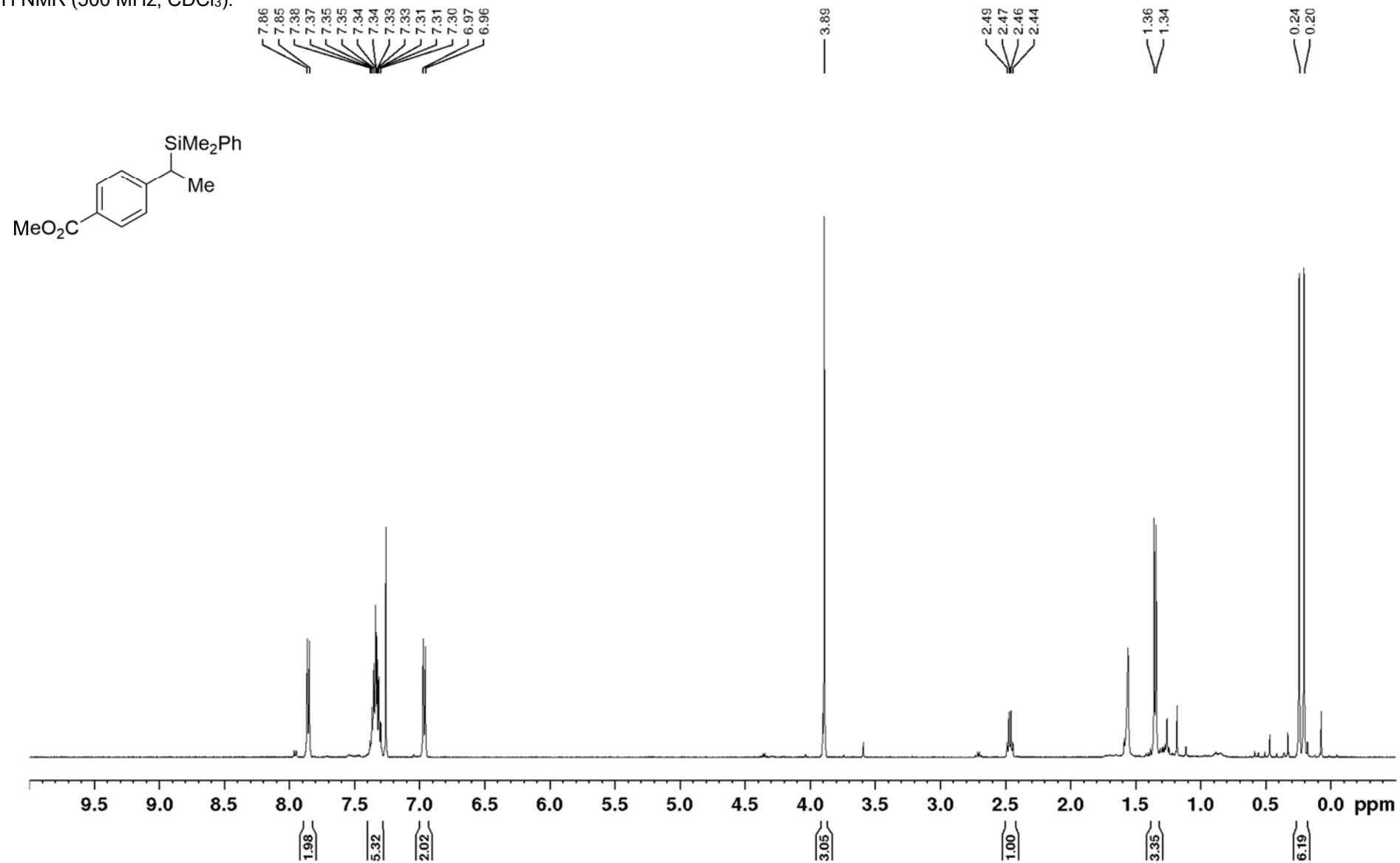
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

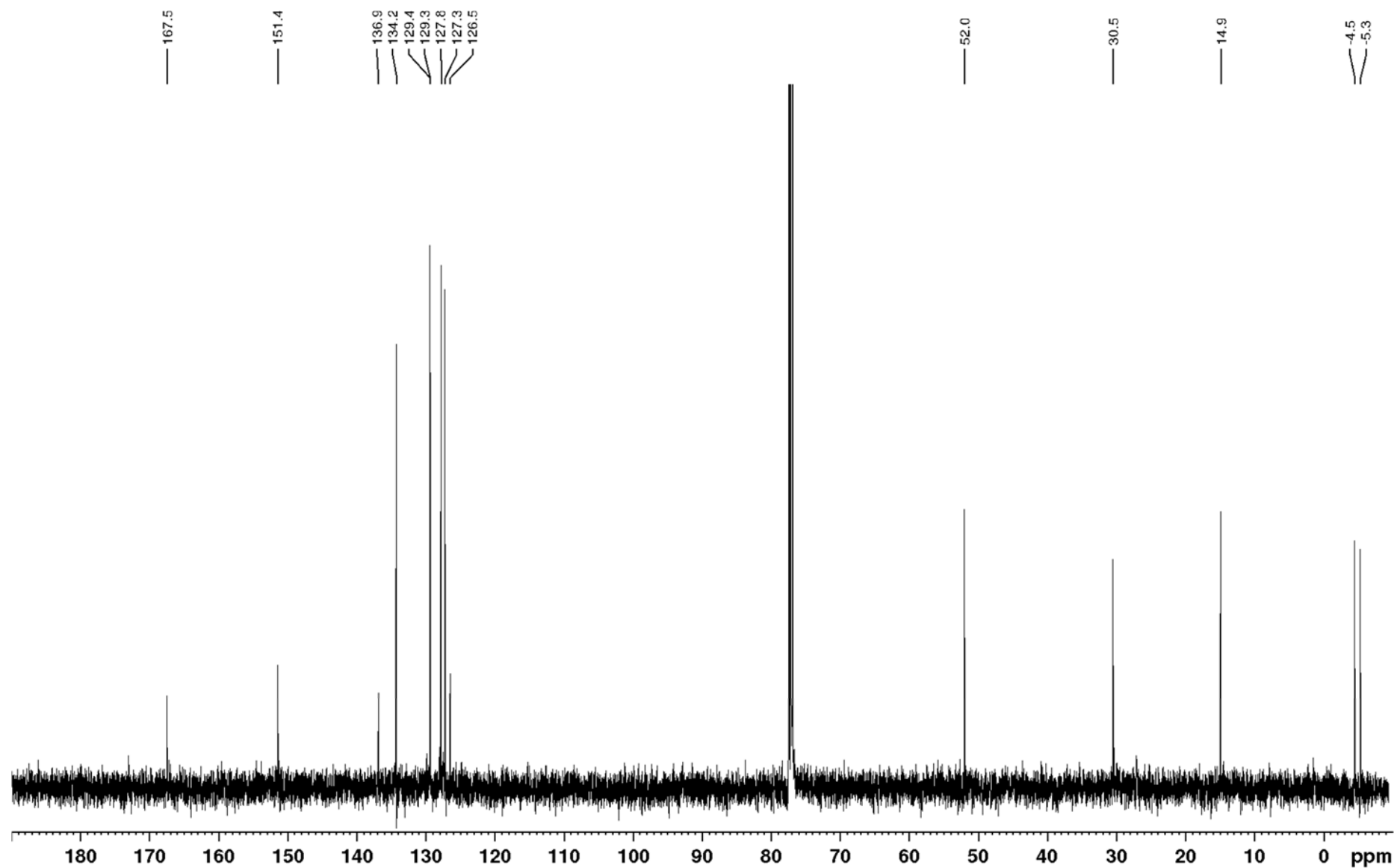
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

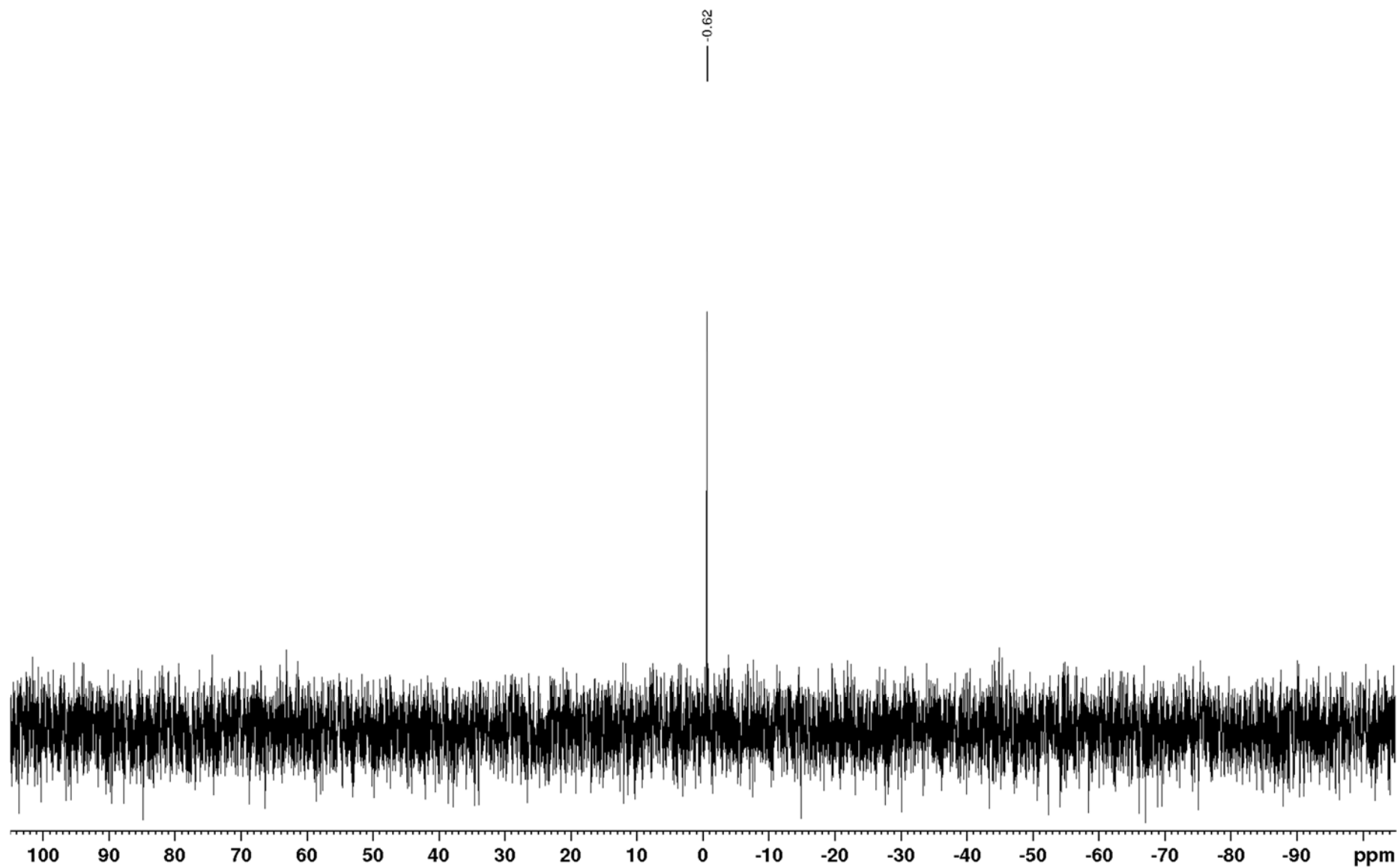
Methyl 4-{1-[dimethyl(phenyl)silyl]ethyl}benzoate (4ka)

 ^1H NMR (500 MHz, CDCl_3):

SUPPORTING INFORMATION

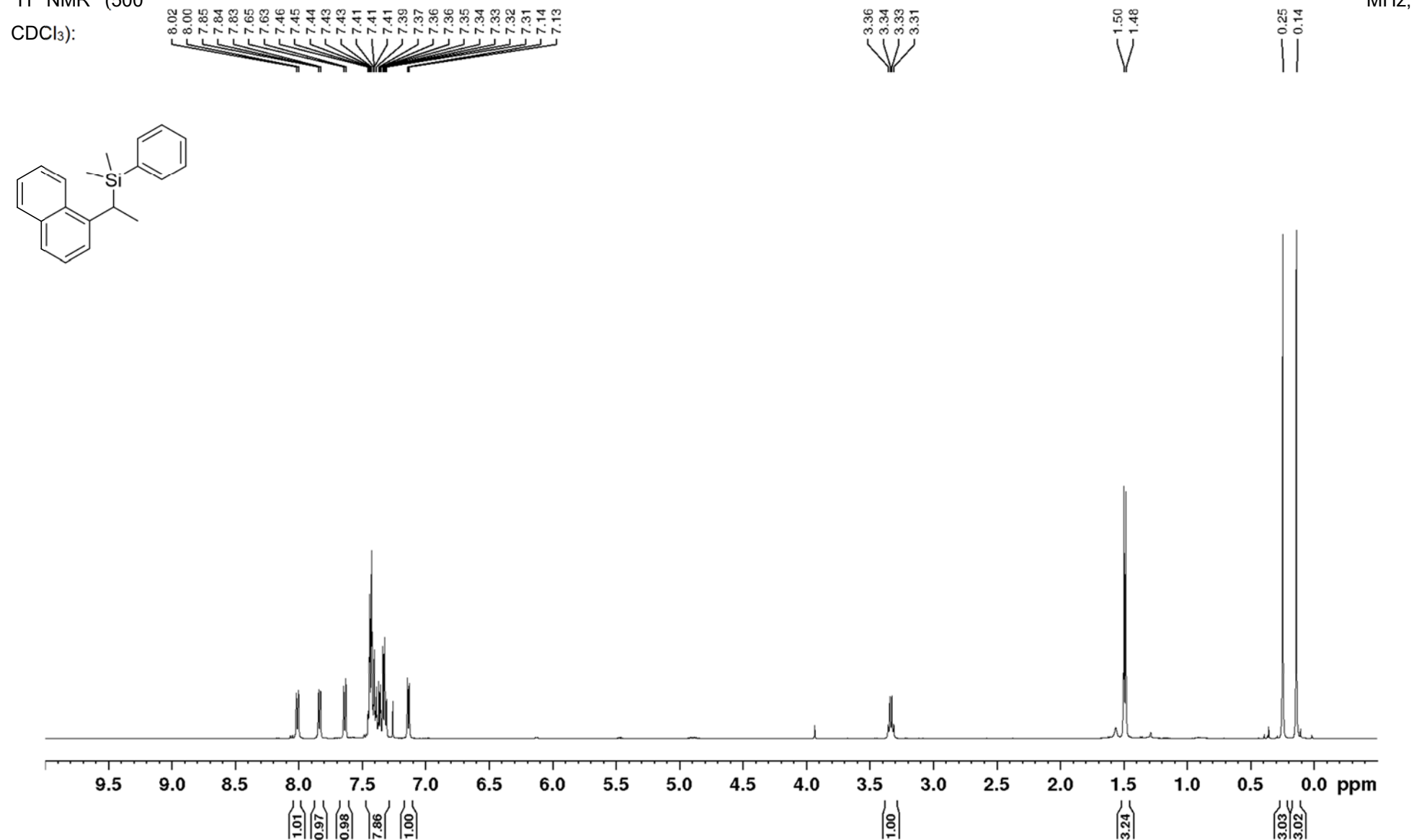
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

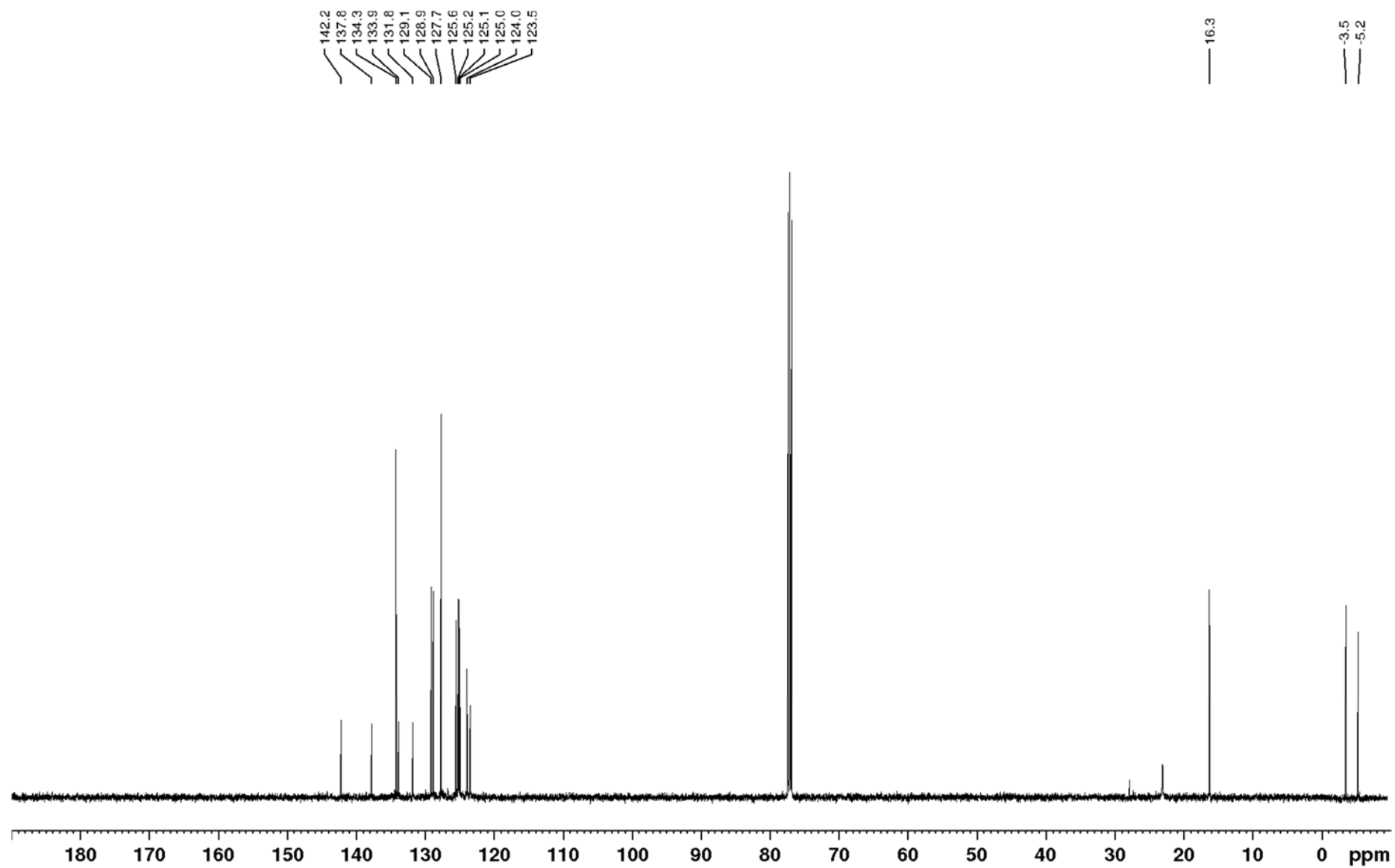
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

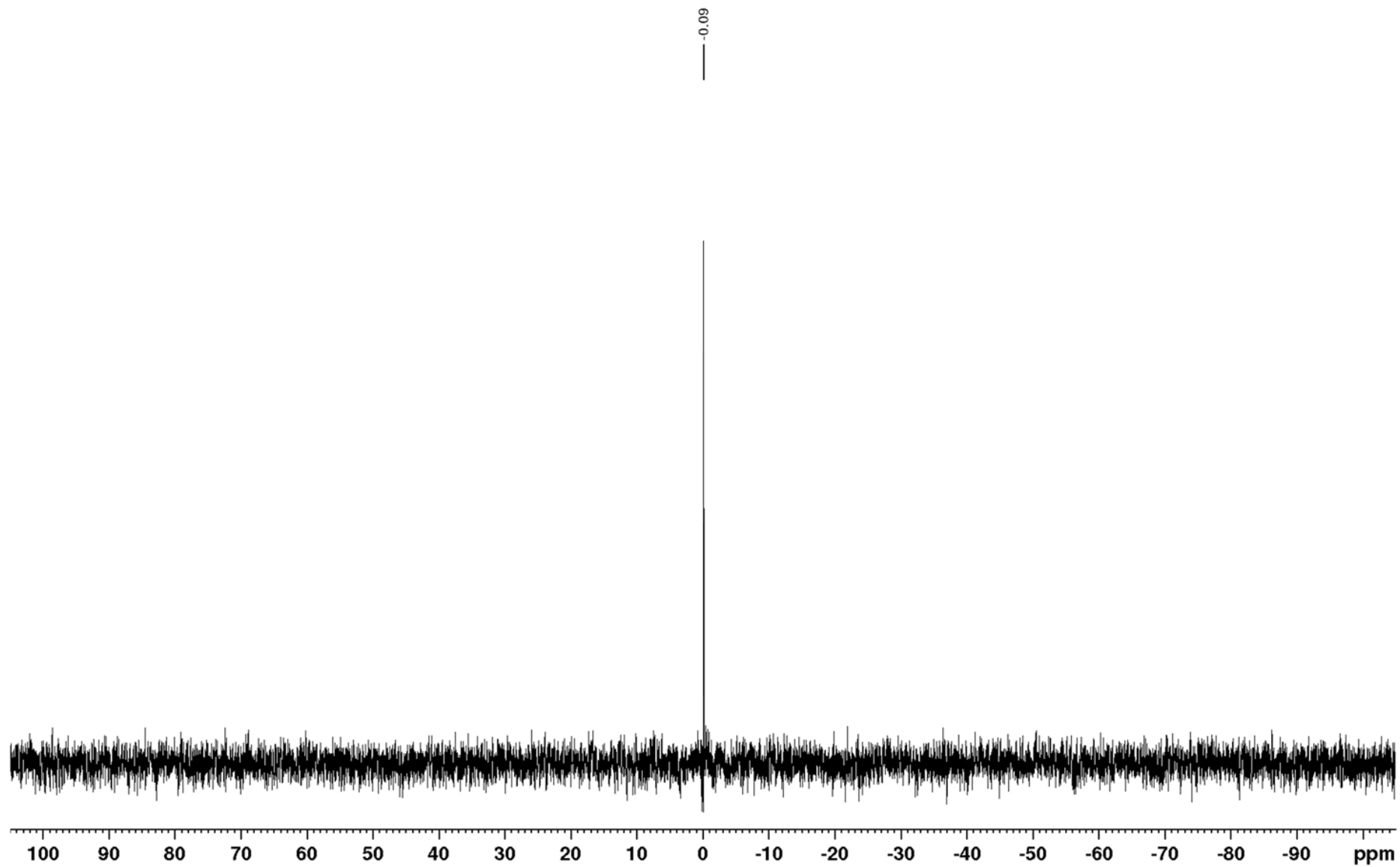
Dimethyl[1-(naphthalen-1-yl)ethyl](phenyl)silane (41a)

 ^1H NMR (500
 CDCl_3):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

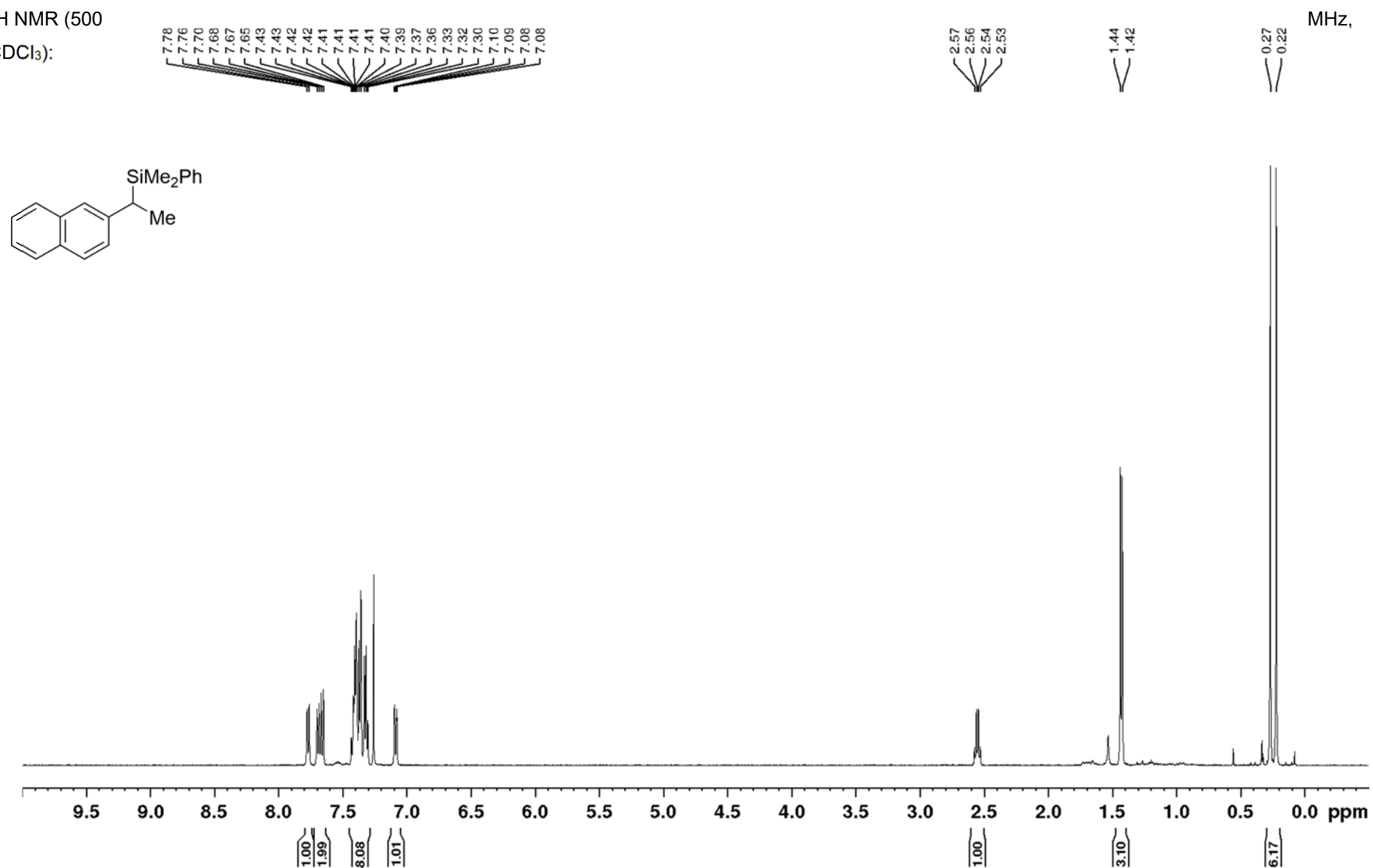
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

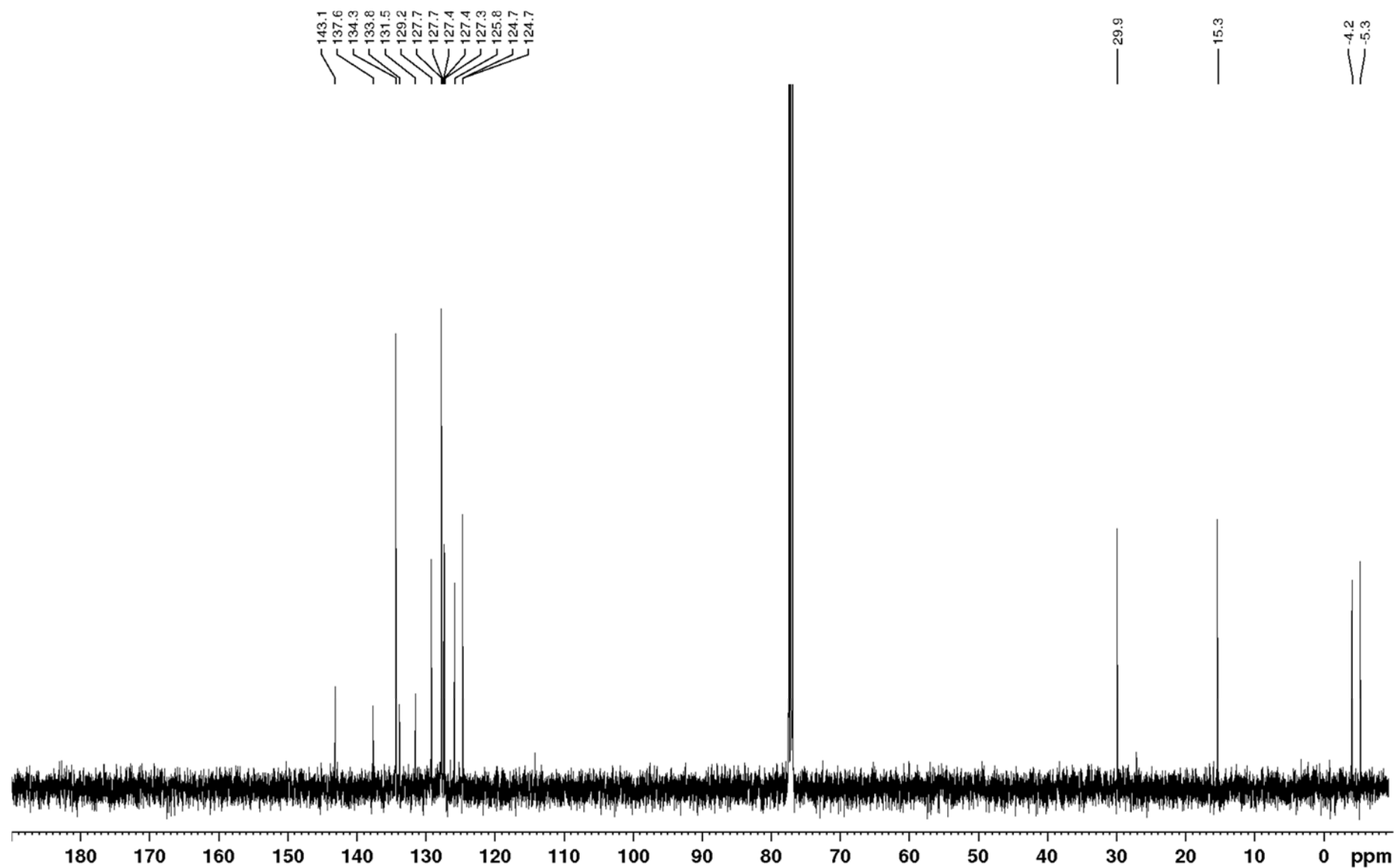
SUPPORTING INFORMATION

Dimethyl[1-(naphthalen-2-yl)ethyl](phenyl)silane (4ma)

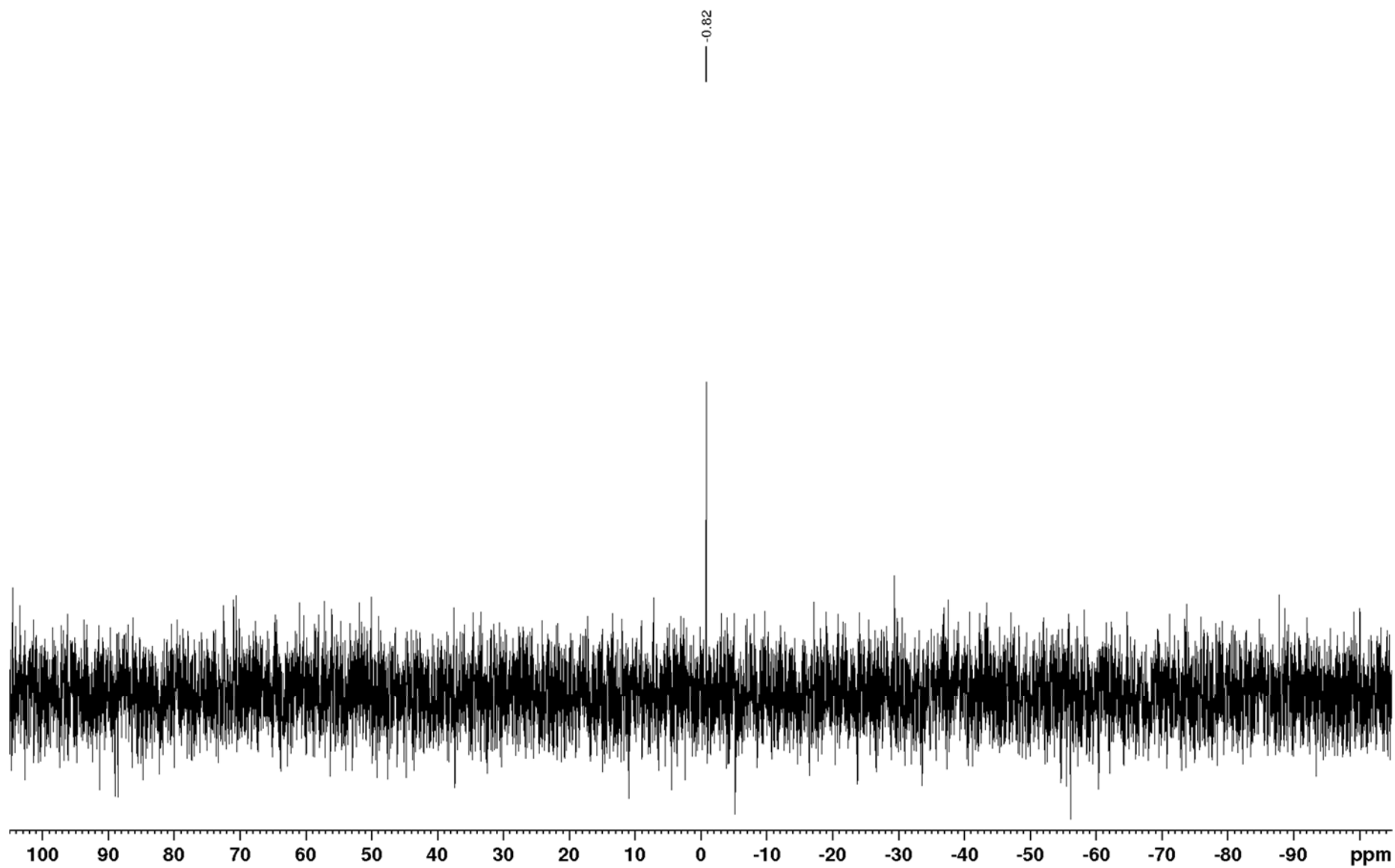
^1H NMR (500
 CDCl_3):



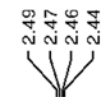
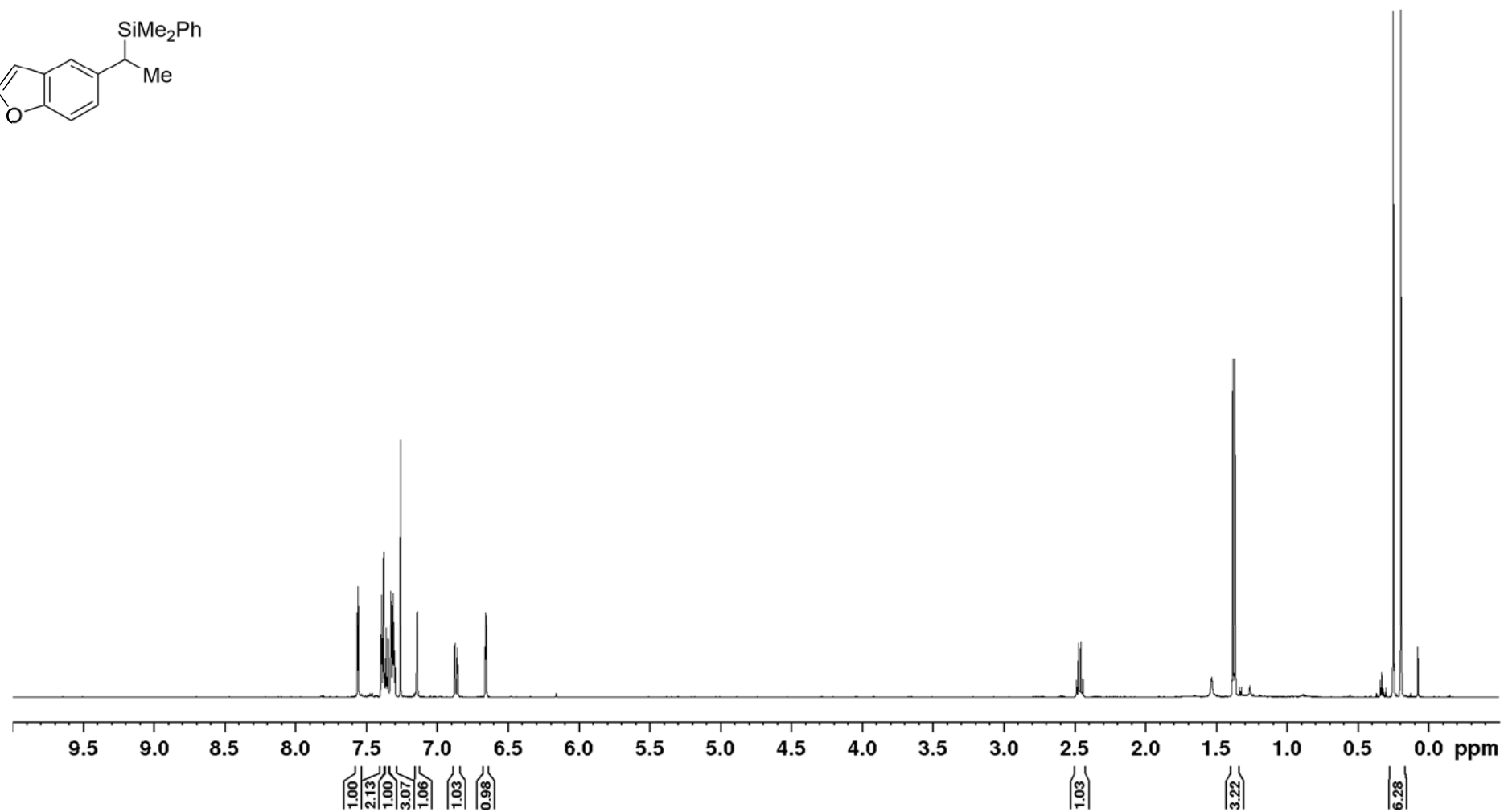
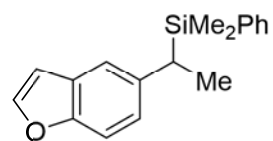
SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

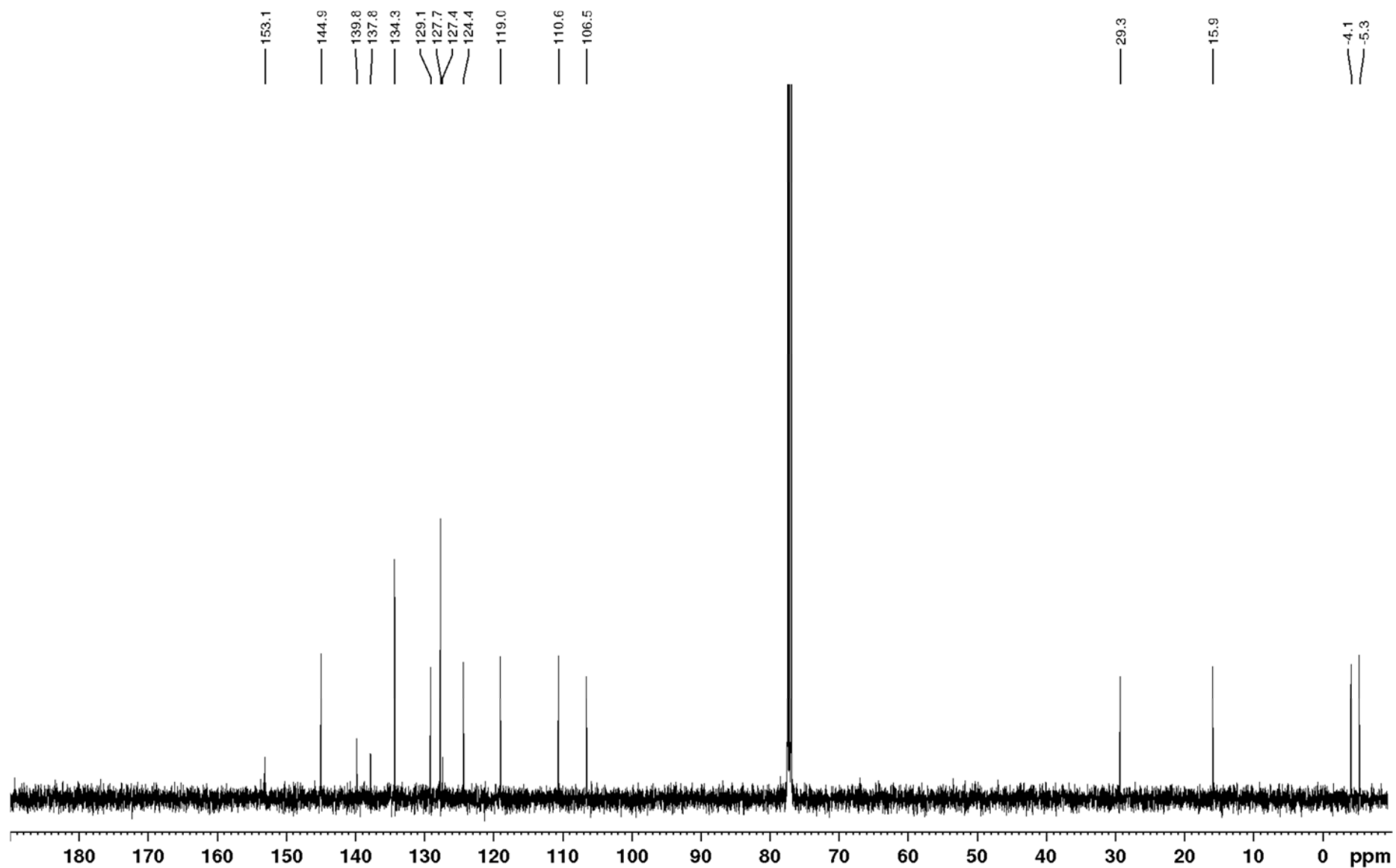
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

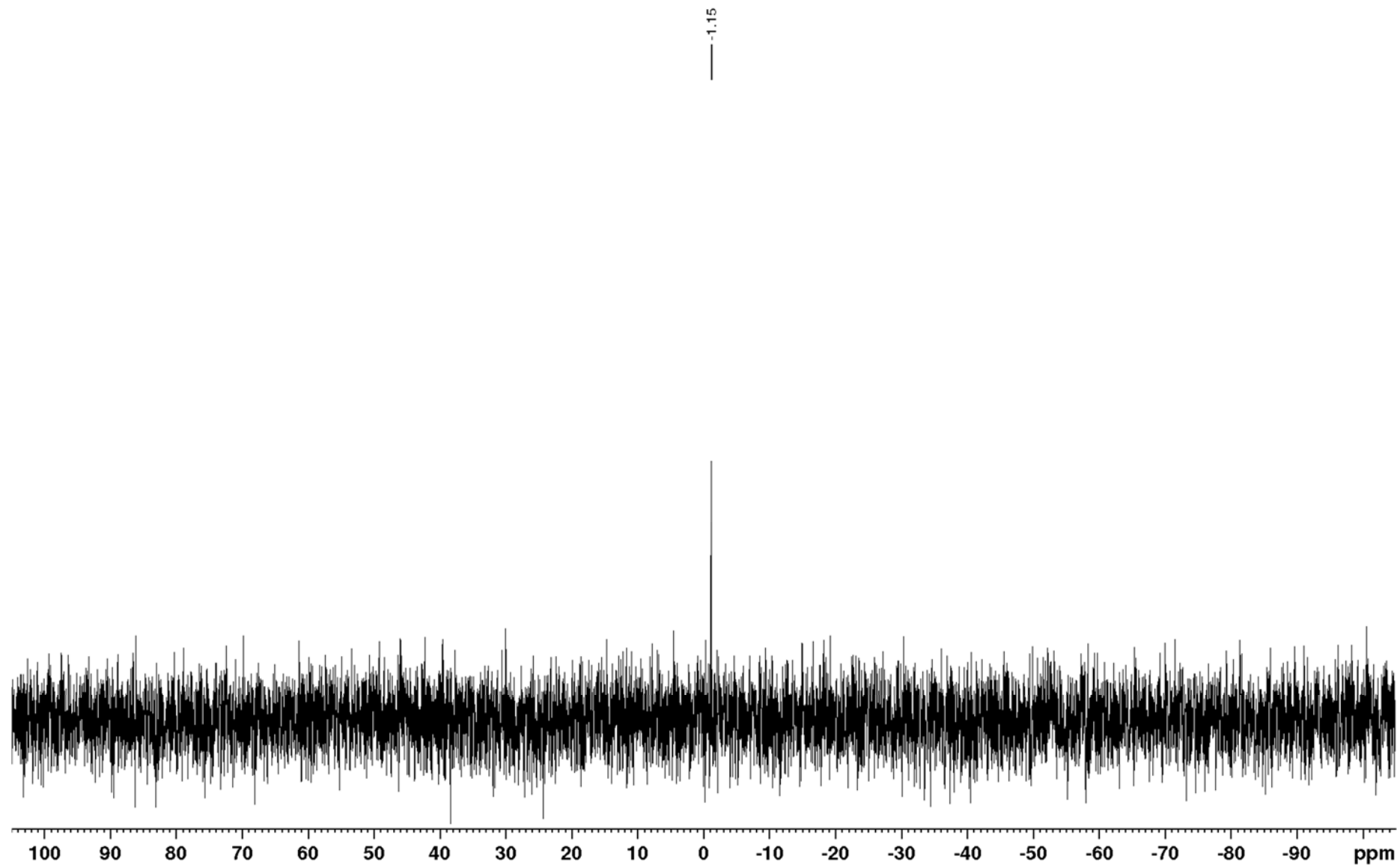
[1-(Benzofuran-5-yl)ethyl]dimethyl(phenyl)silane (4na)¹H NMR (500 MHz,CDCl₃):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

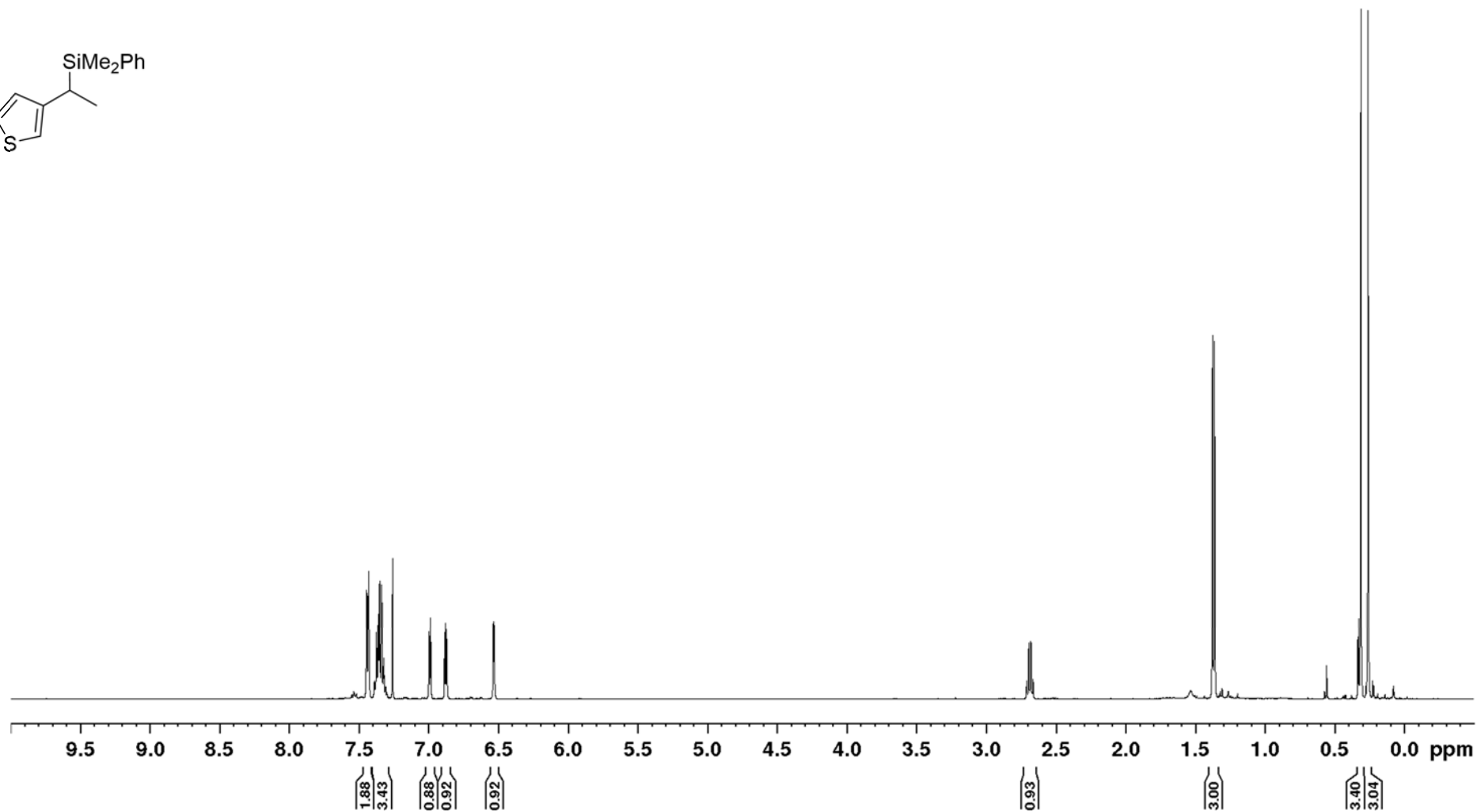
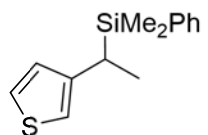
SUPPORTING INFORMATION

$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

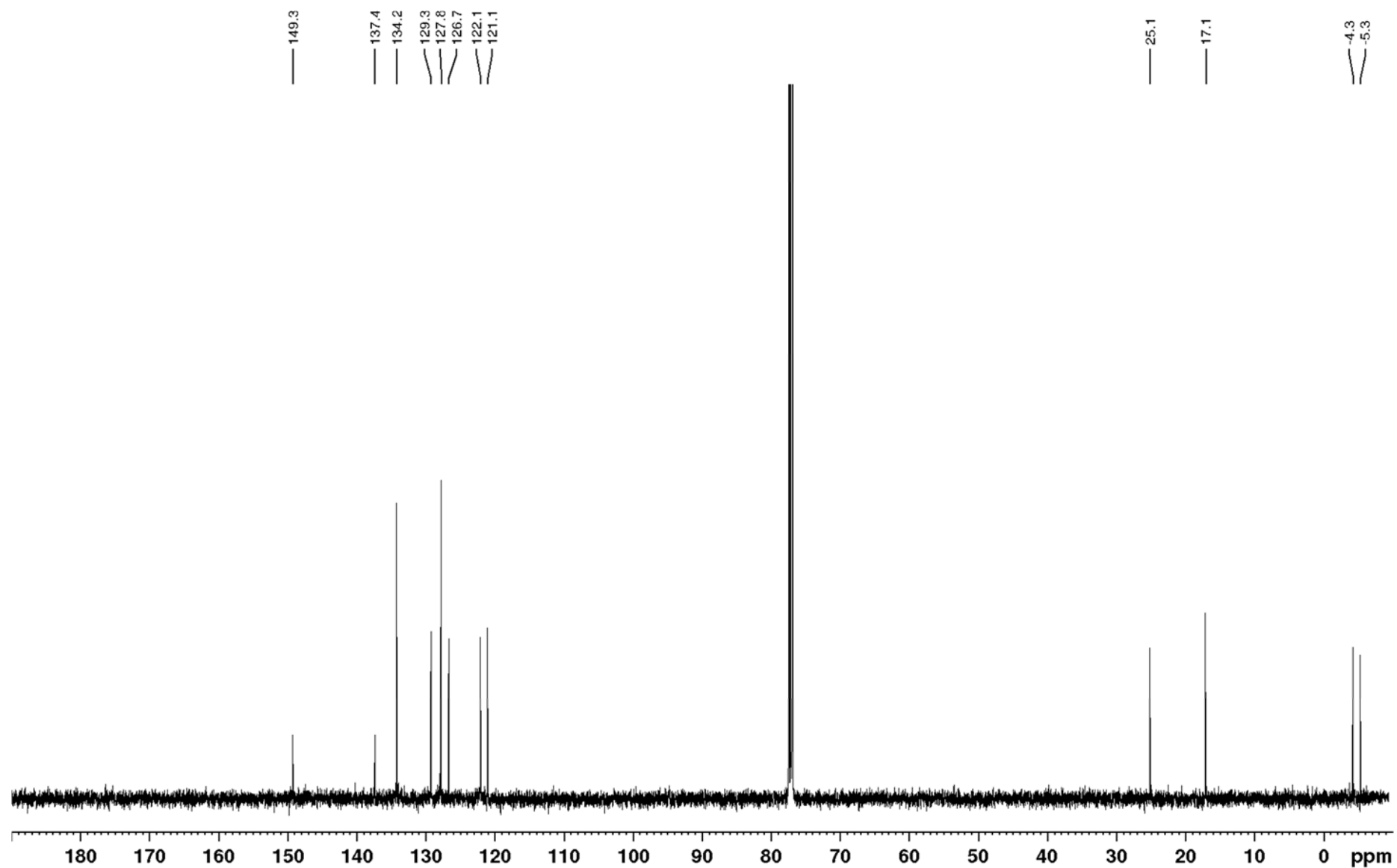


SUPPORTING INFORMATION

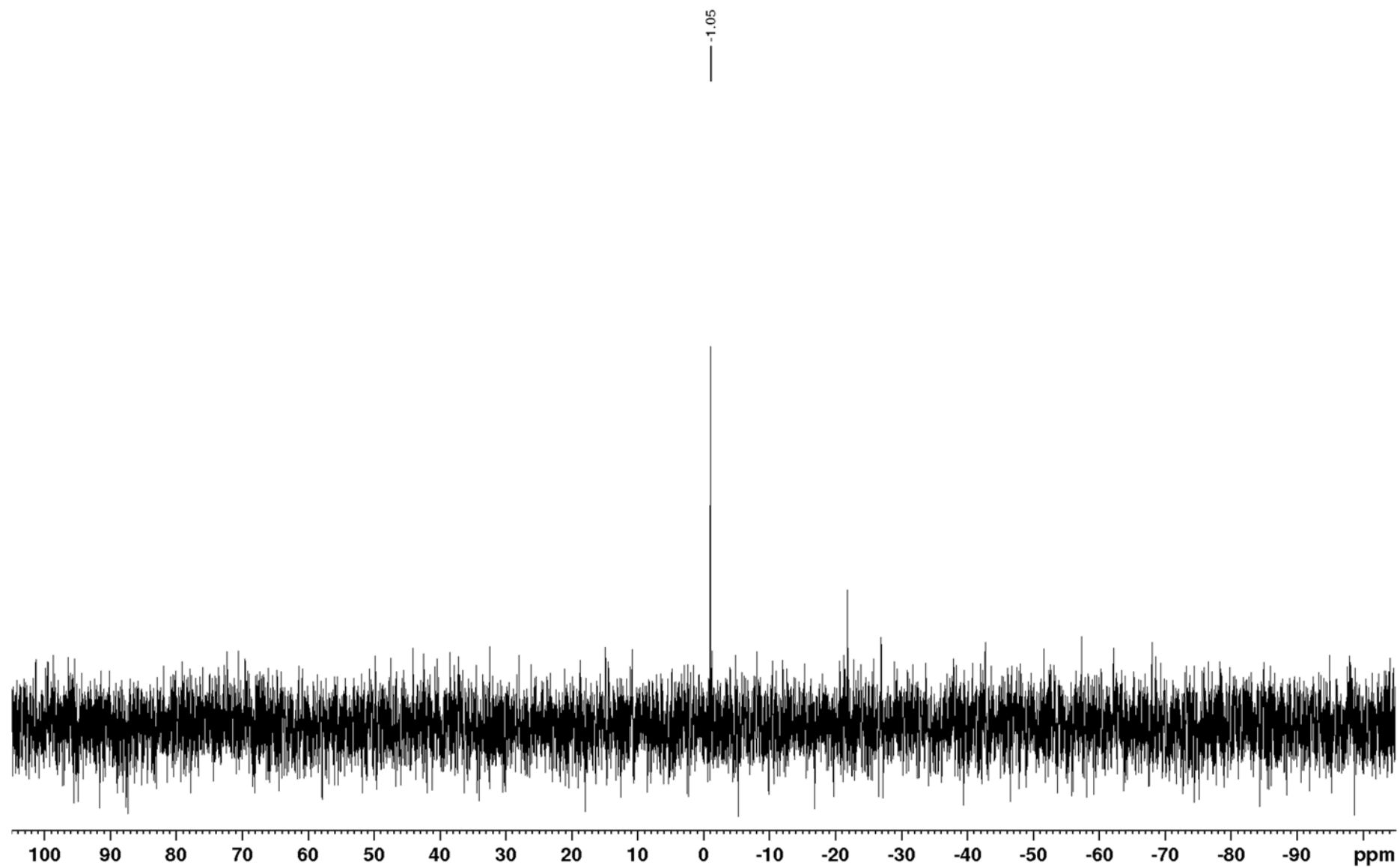
Dimethyl(phenyl)[1-(thiophen-3-yl)ethyl]silane (4oa)

 ^1H NMR
 CDCl_3 :

SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

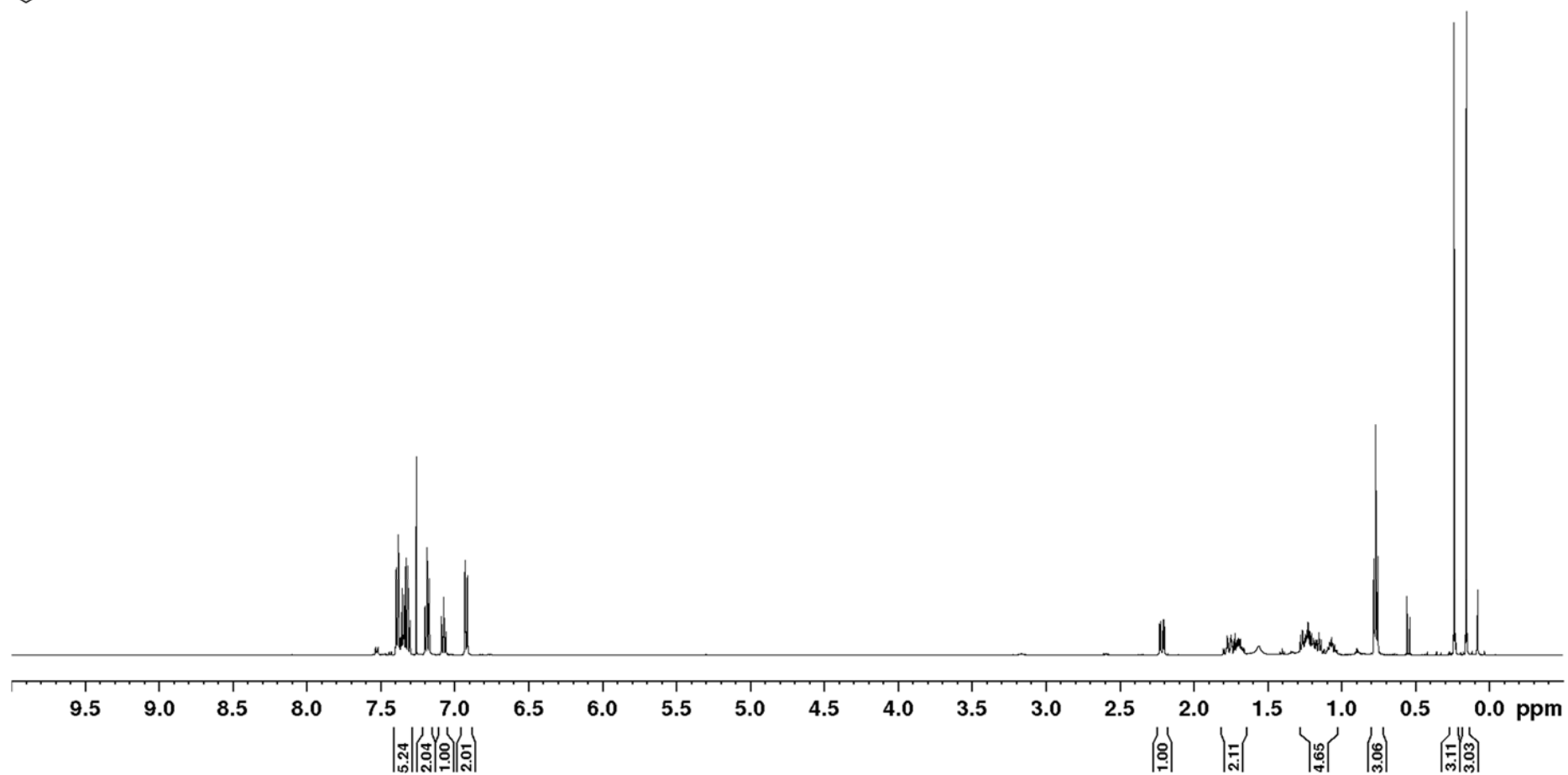
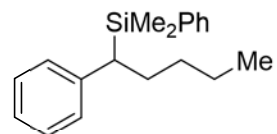
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

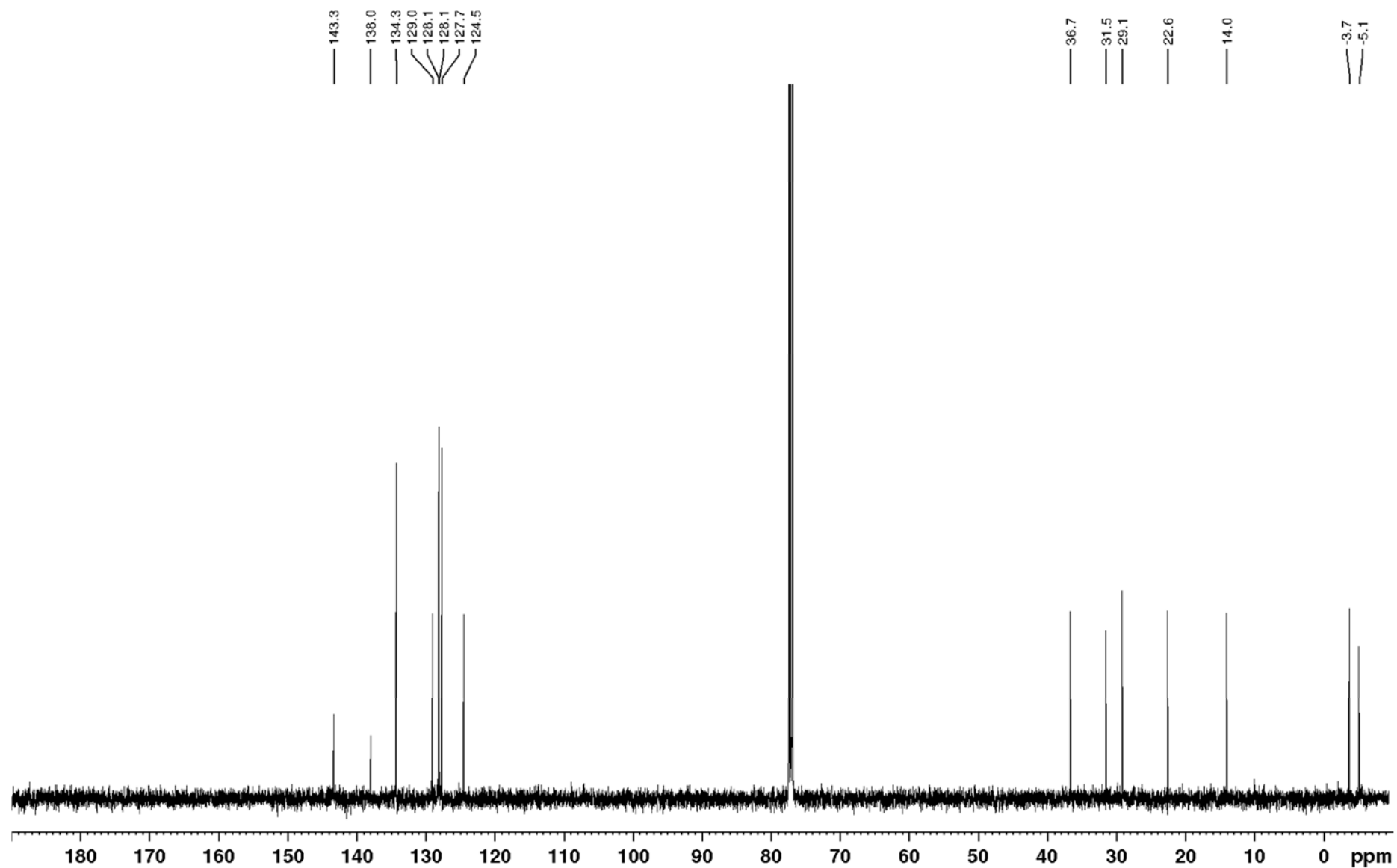
SUPPORTING INFORMATION

Dimethyl(phenyl)(1-phenylpentyl)silane (4pa)

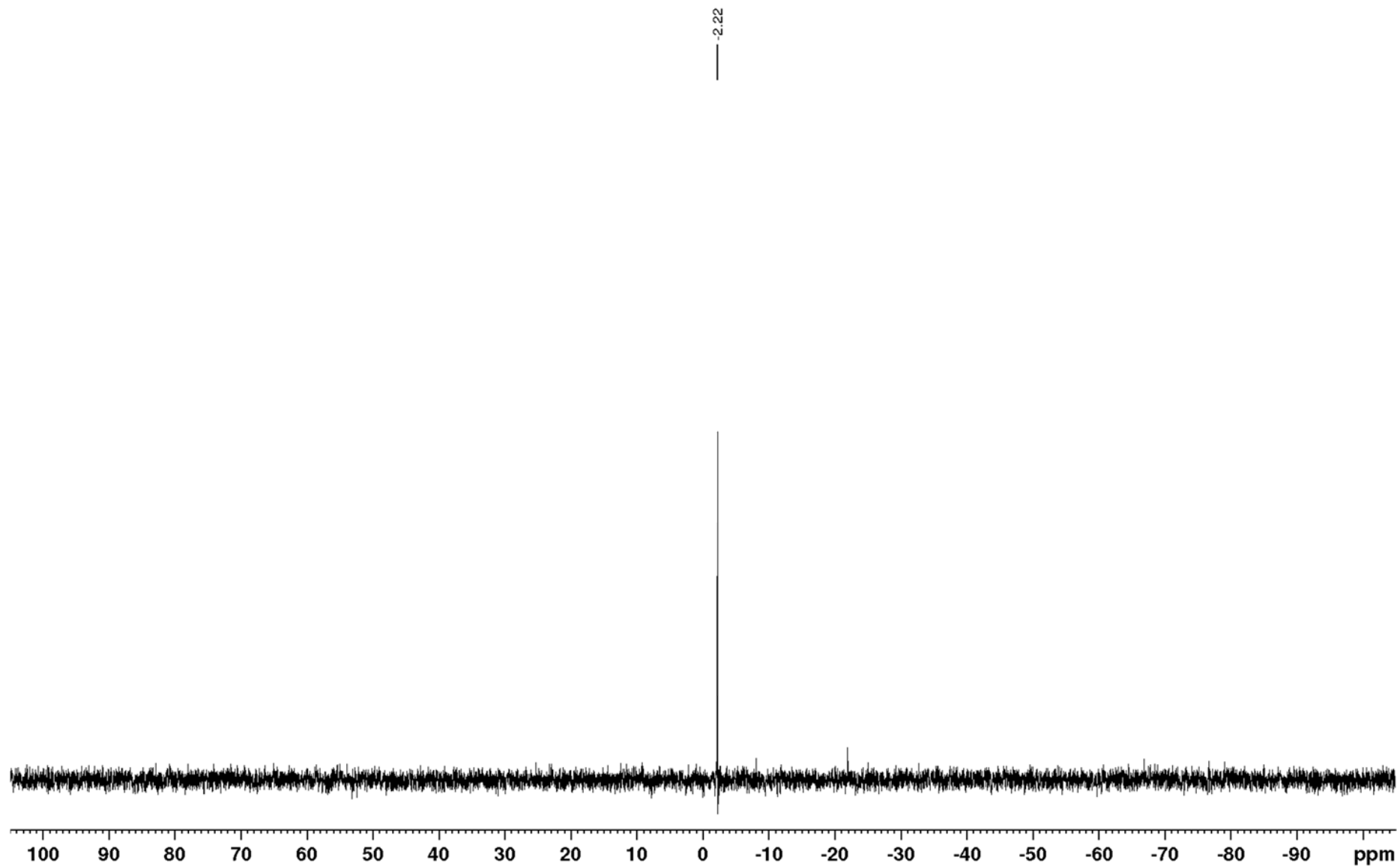
^1H NMR (500 MHz,
 CDCl_3):



SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

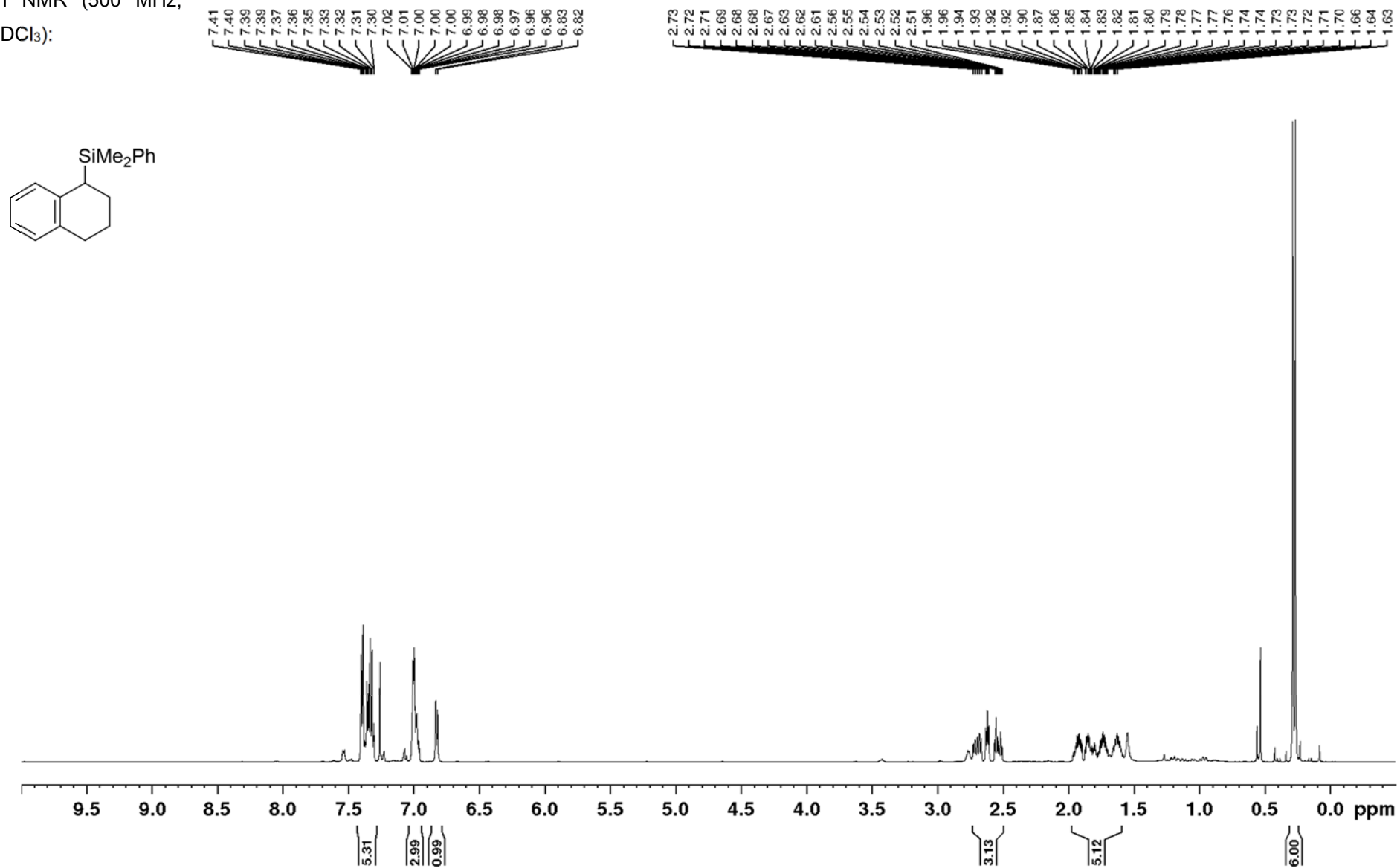
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

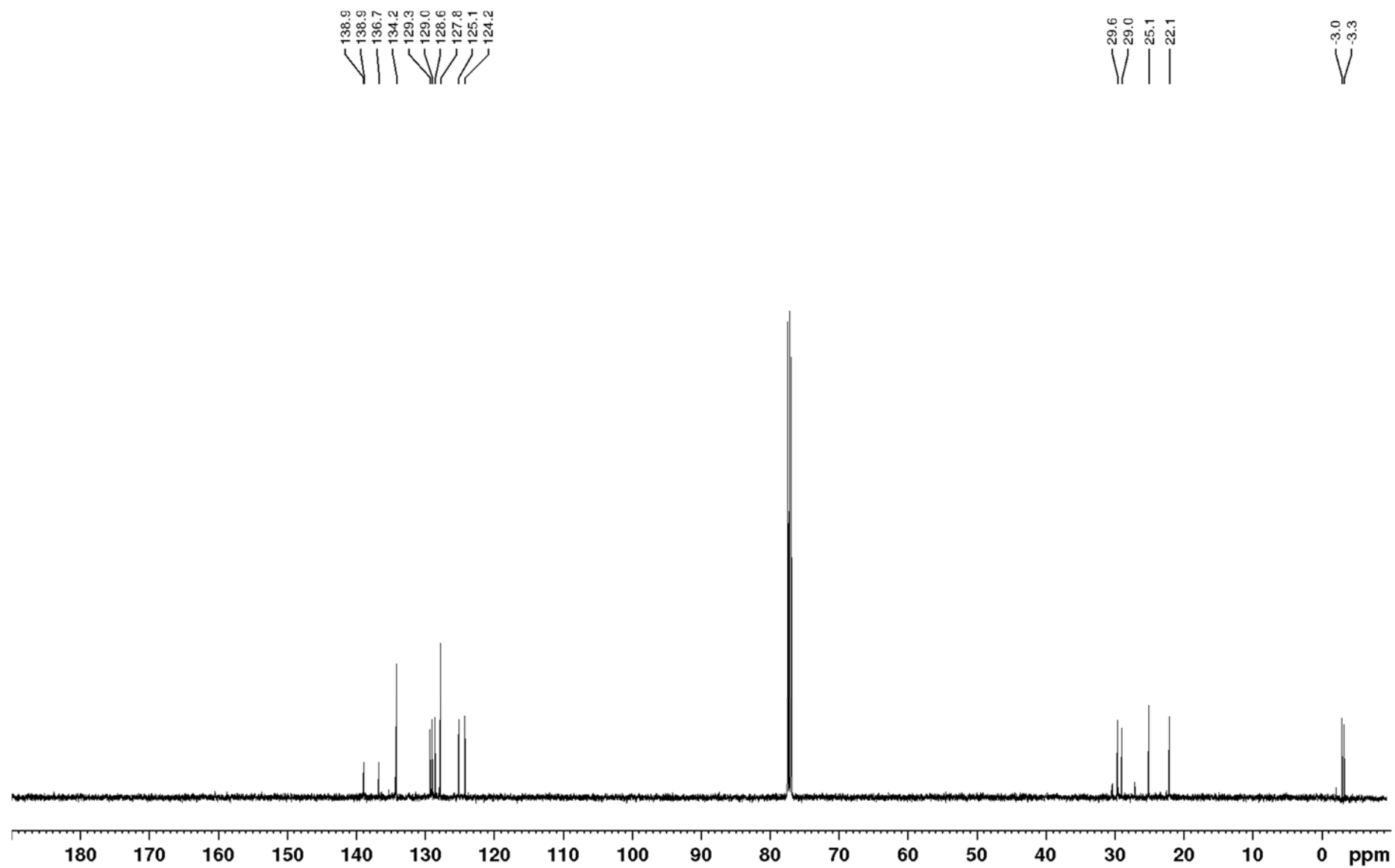
SUPPORTING INFORMATION

Dimethyl(phenyl)(1,2,3,4-tetrahydronaphthalen-1-yl)silane (4qa)

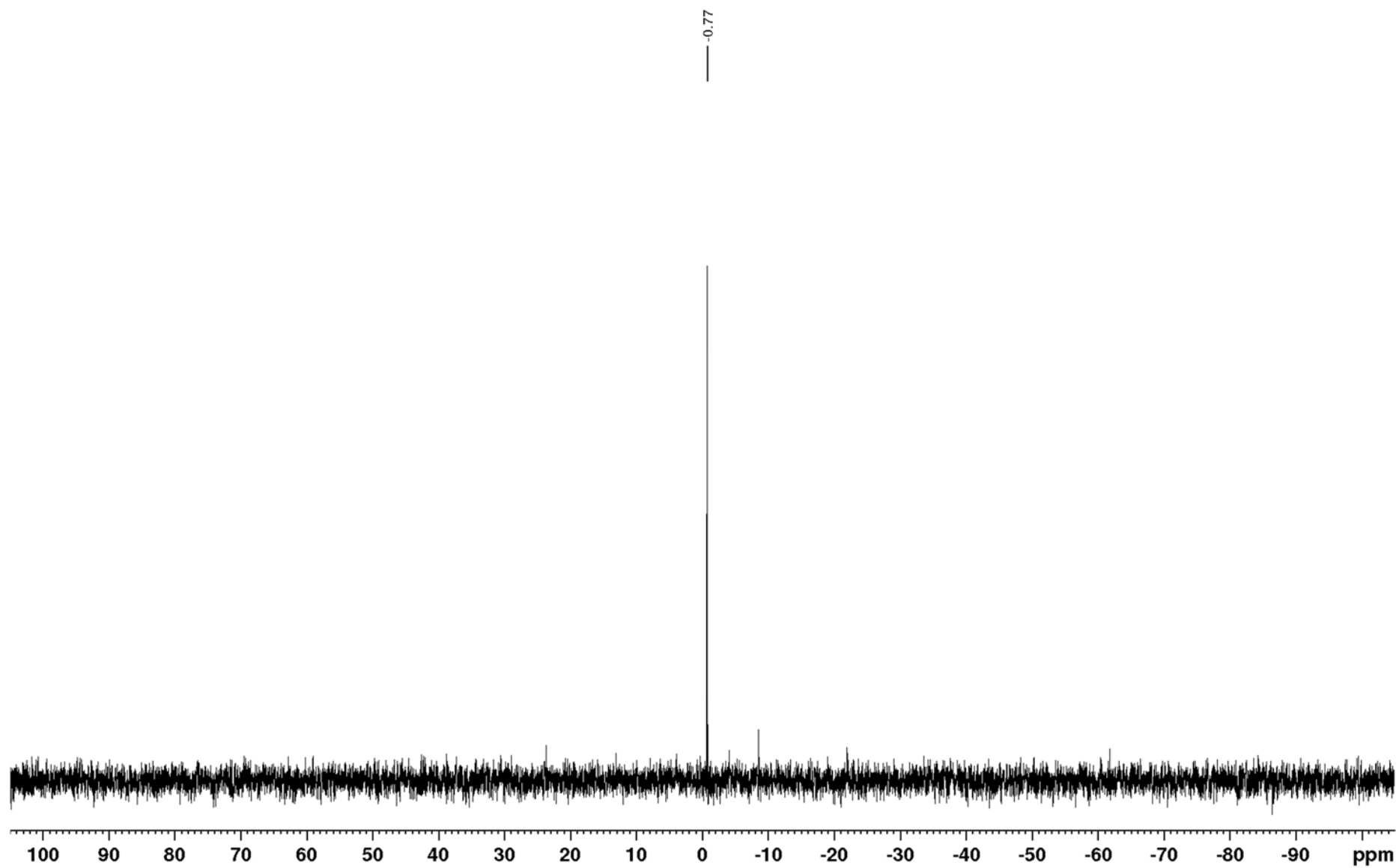
^1H NMR (500 MHz,
 CDCl_3):



SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

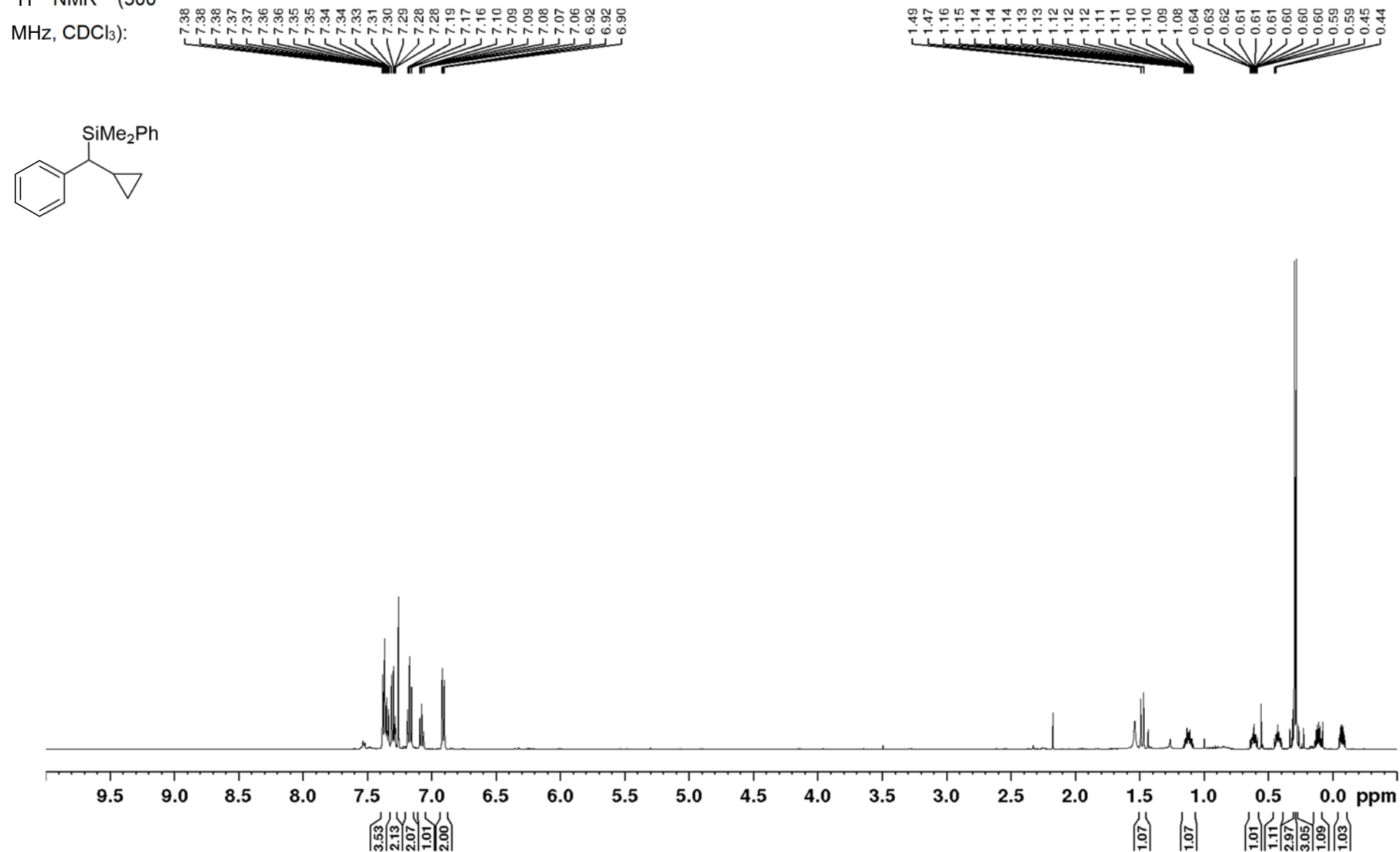
SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

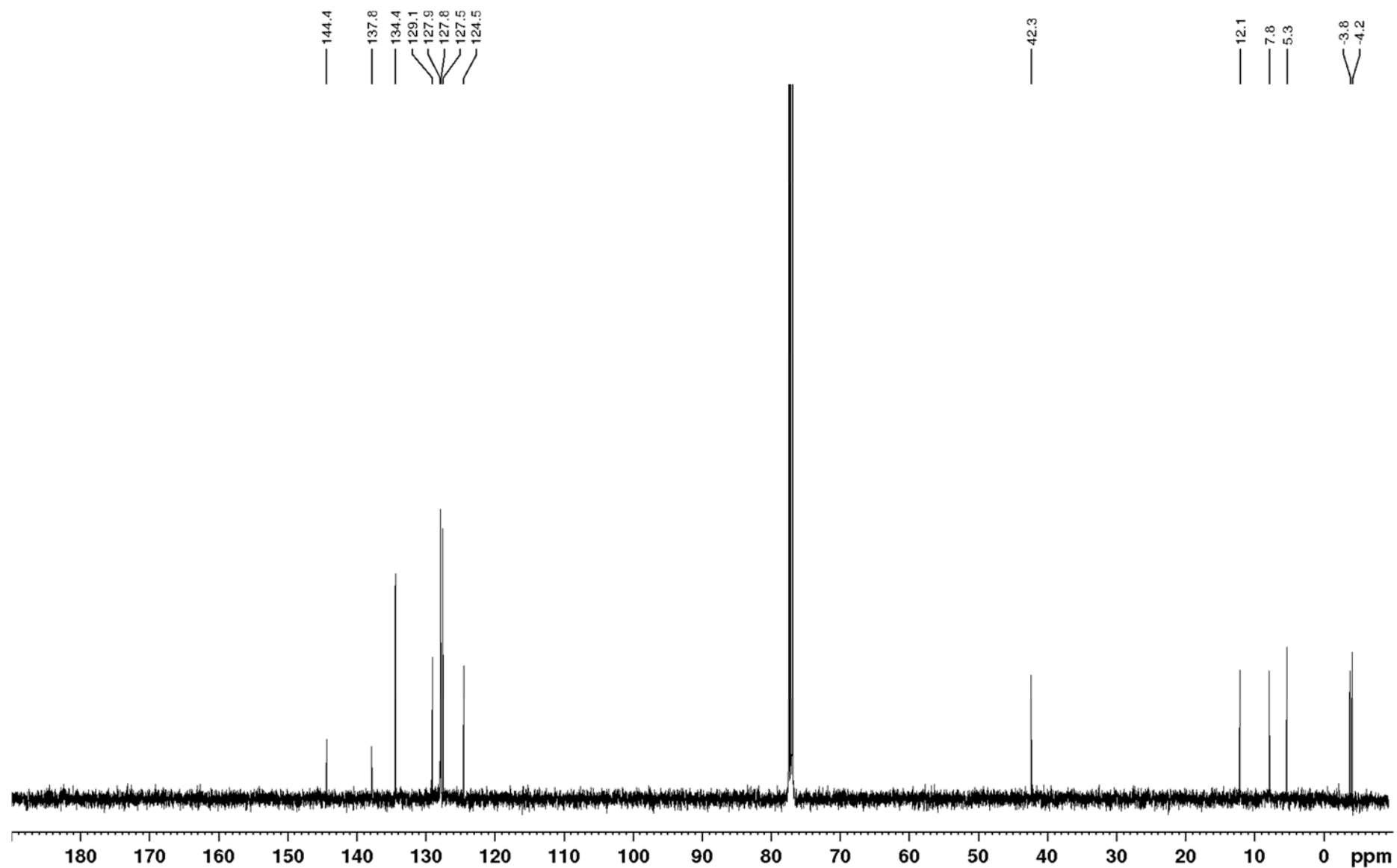
SUPPORTING INFORMATION

[Cyclopropyl(phenyl)methyl]dimethyl(phenyl)silane (4ra)

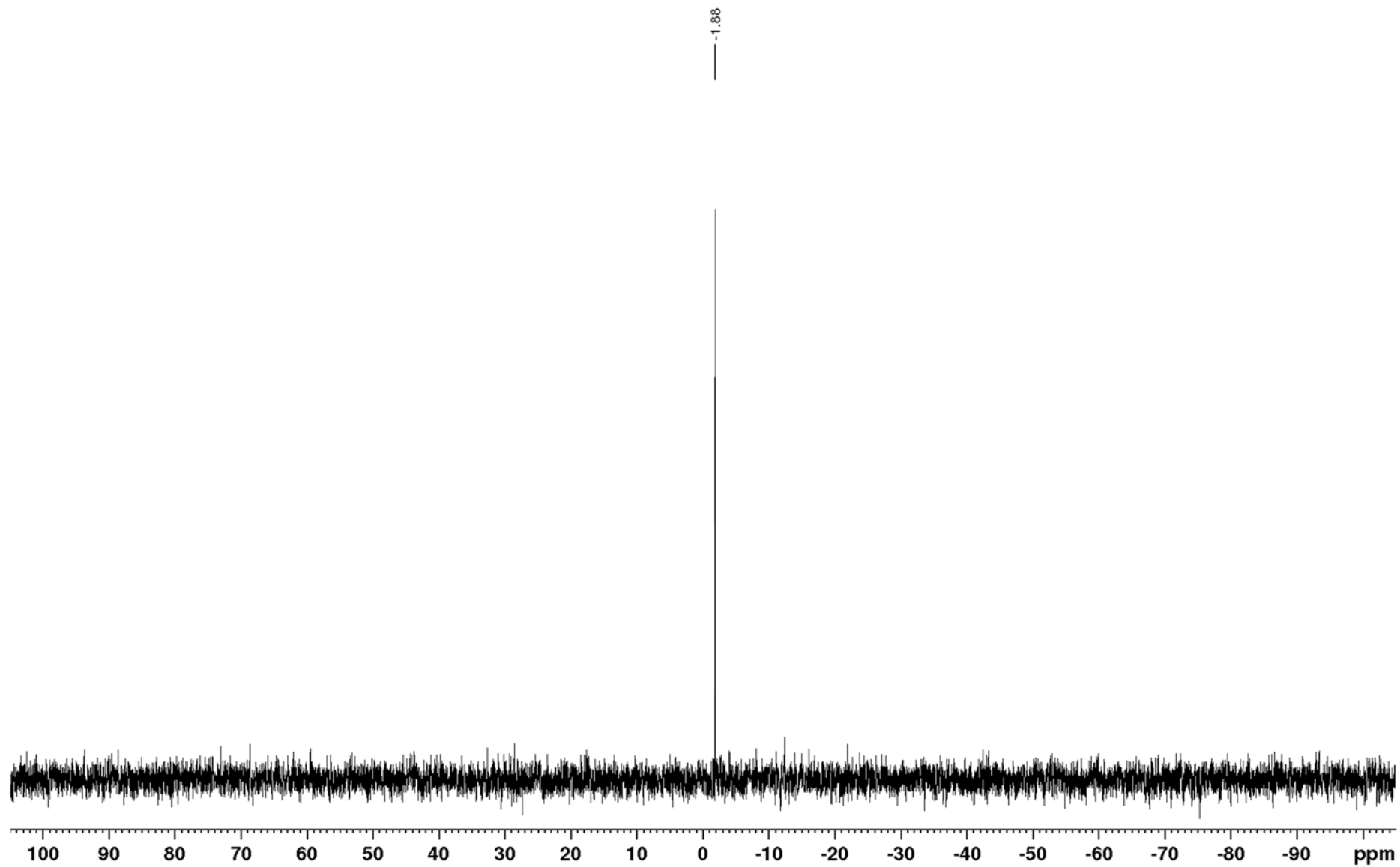
¹H NMR (500
MHz, CDCl₃):



SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

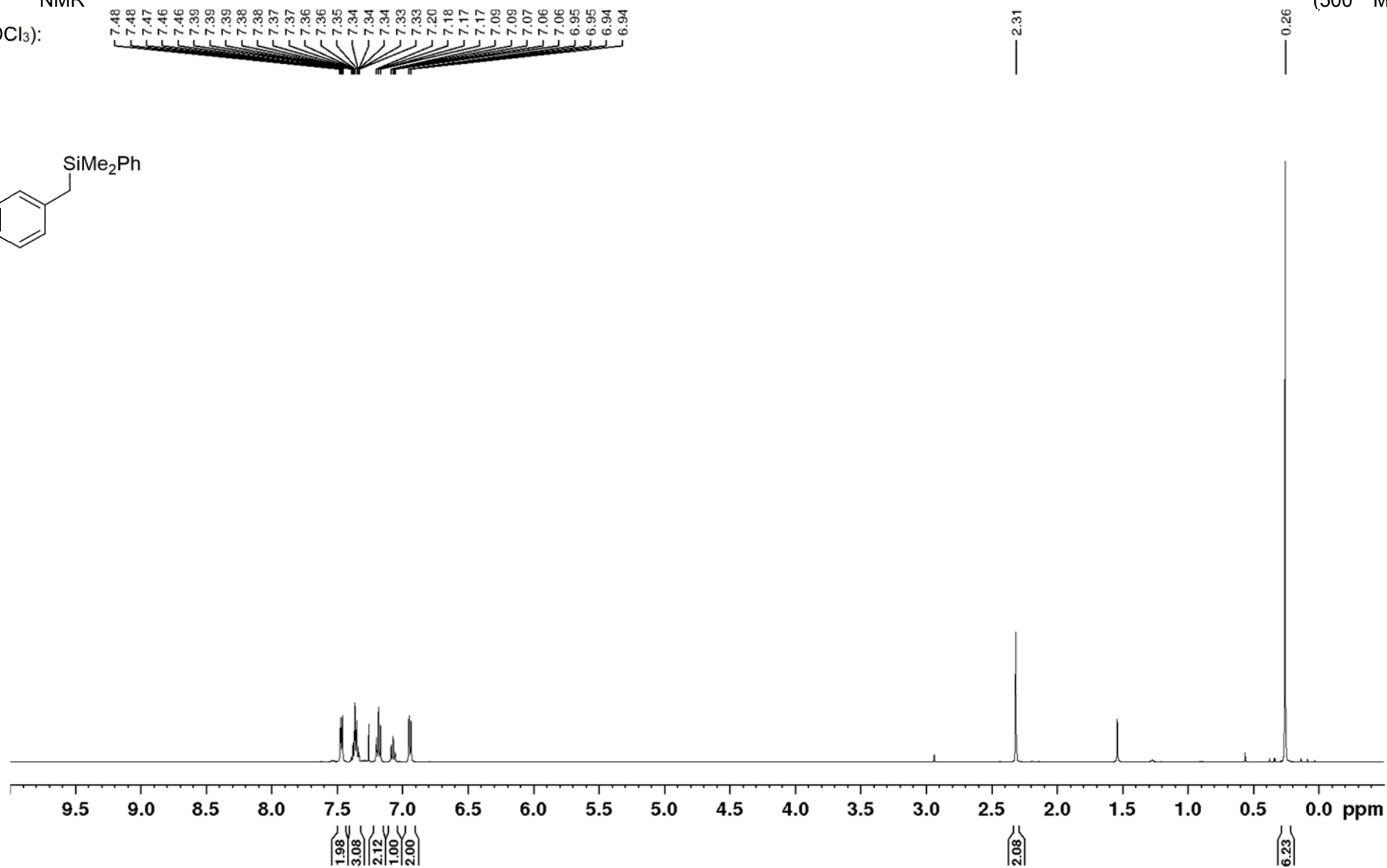
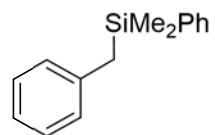
Benzyldimethyl(phenyl)silane (4ua)

¹H NMR
CDCl₃:7.48
7.47
7.46
7.46
7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.20
7.16
7.17
7.17
7.09
7.09
7.07
7.06
7.06
6.95
6.95
6.94
6.94

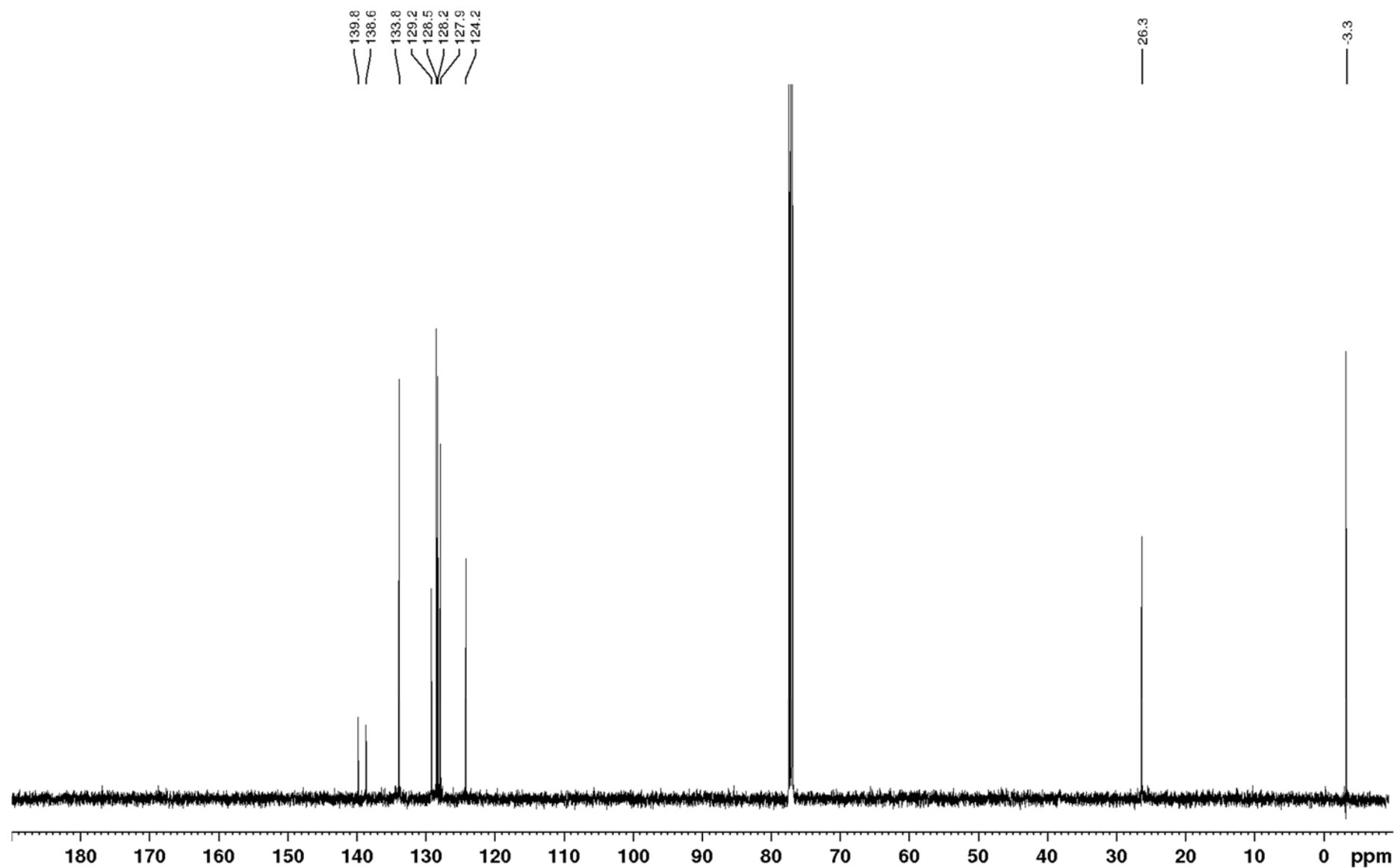
2.31

0.26

(500 MHz,

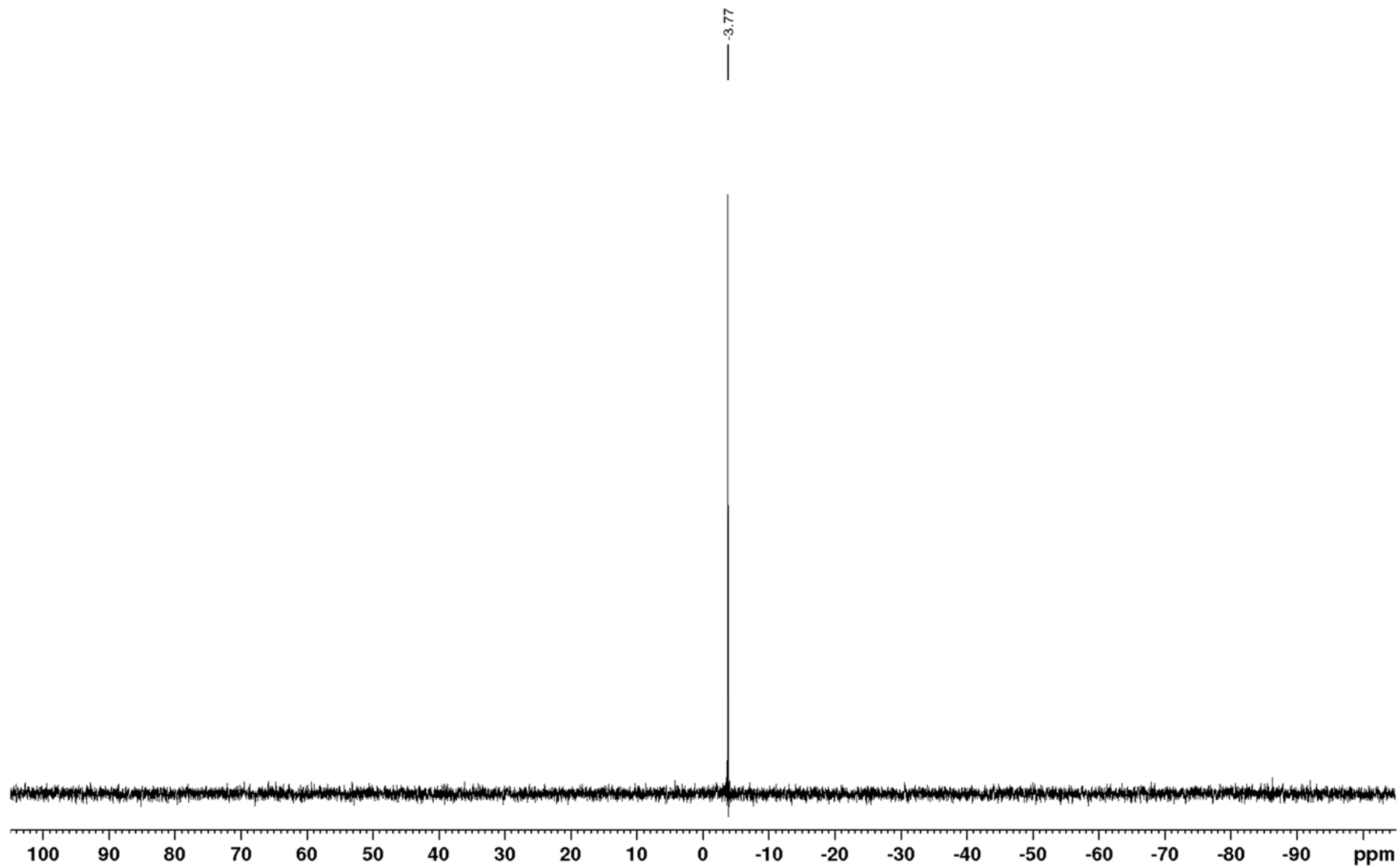


SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

$^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):



SUPPORTING INFORMATION

Benzhydryldimethyl(phenyl)silane (4wa)

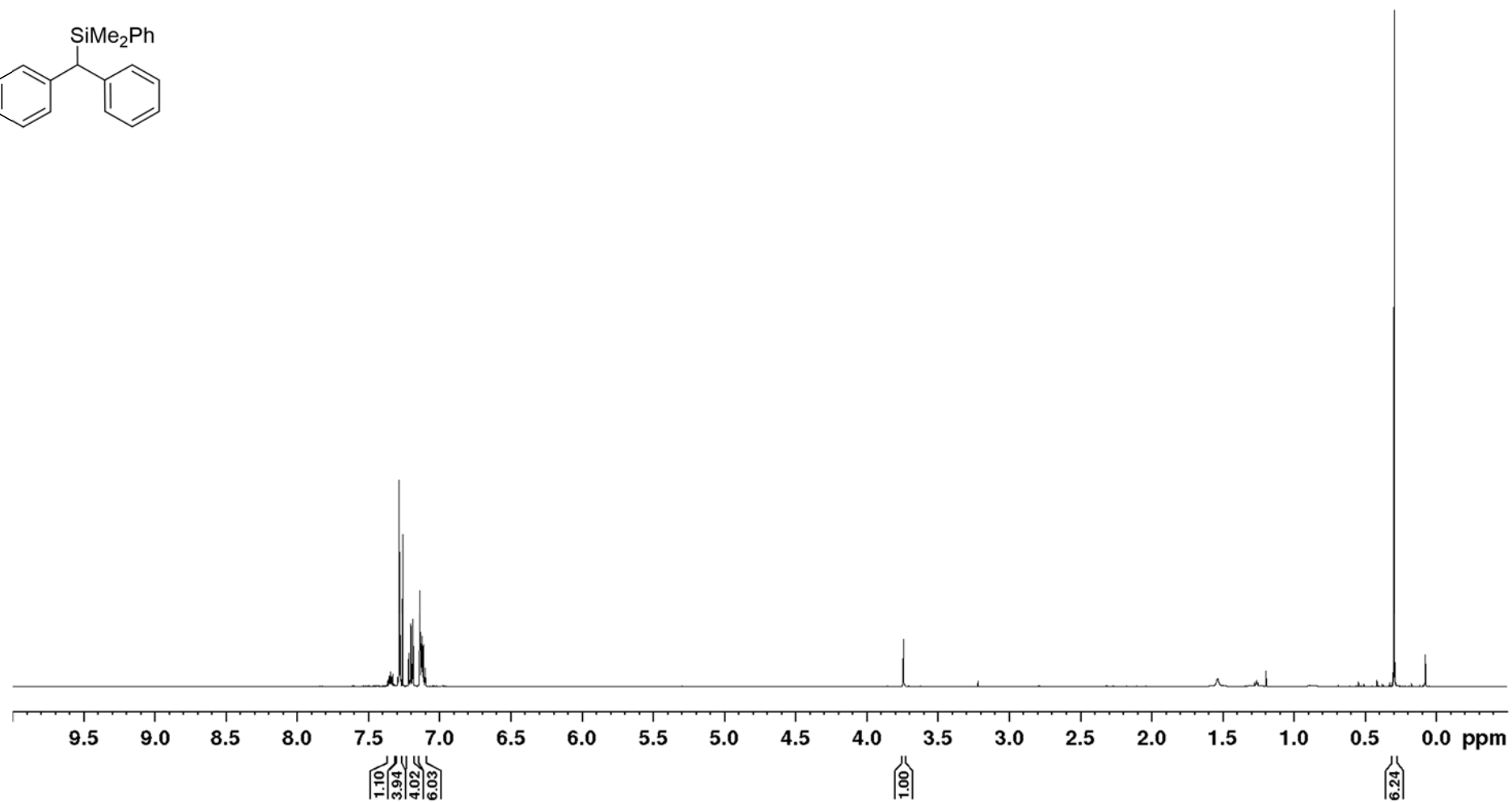
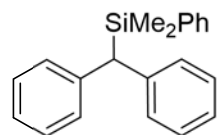
 ^1H NMR CDCl_3 :

7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.29
7.29
7.28
7.27
7.27
7.26
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.14
7.14
7.13
7.12
7.12
7.12
7.11
7.10
7.10

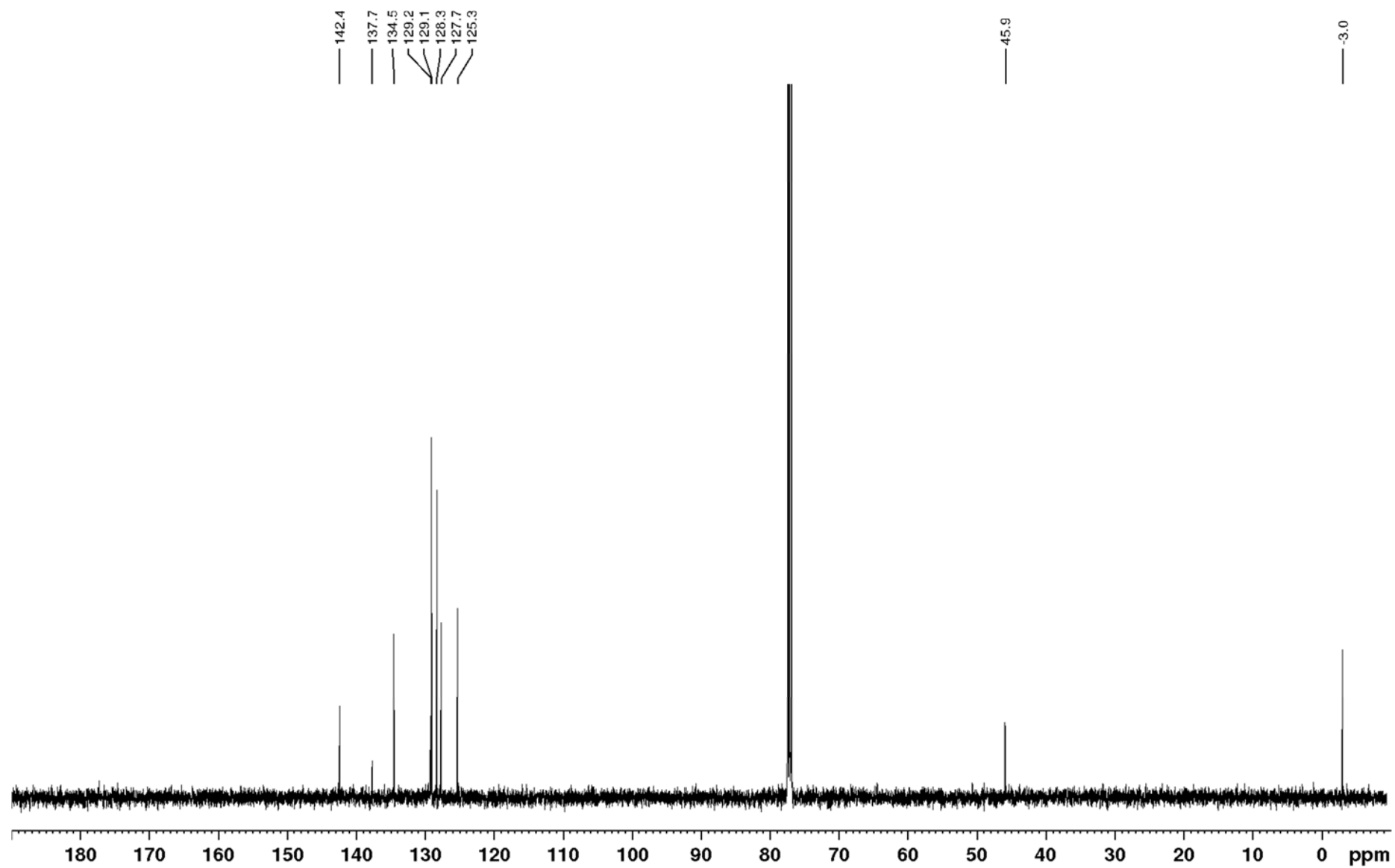
3.74

0.30

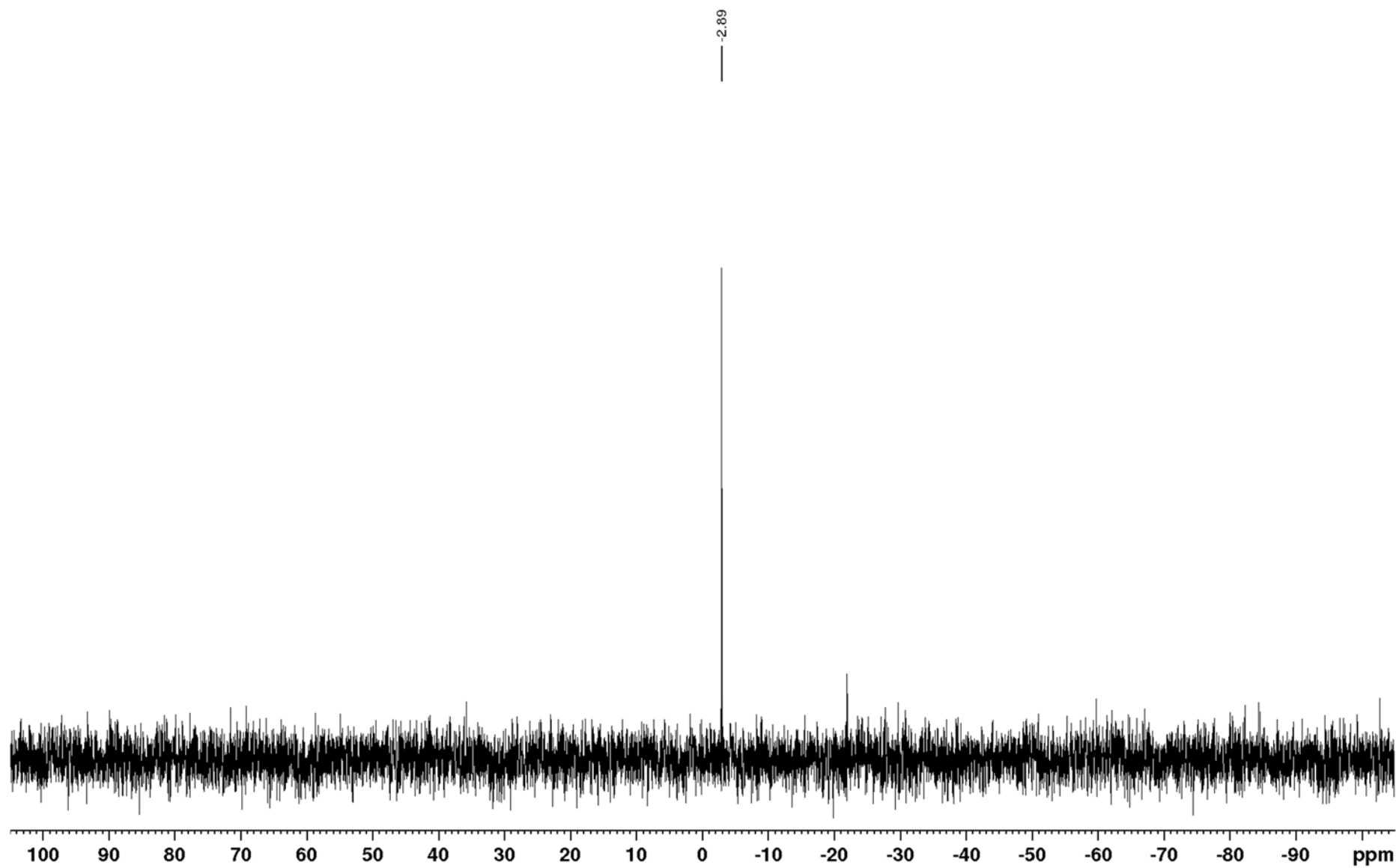
(500 MHz,



SUPPORTING INFORMATION

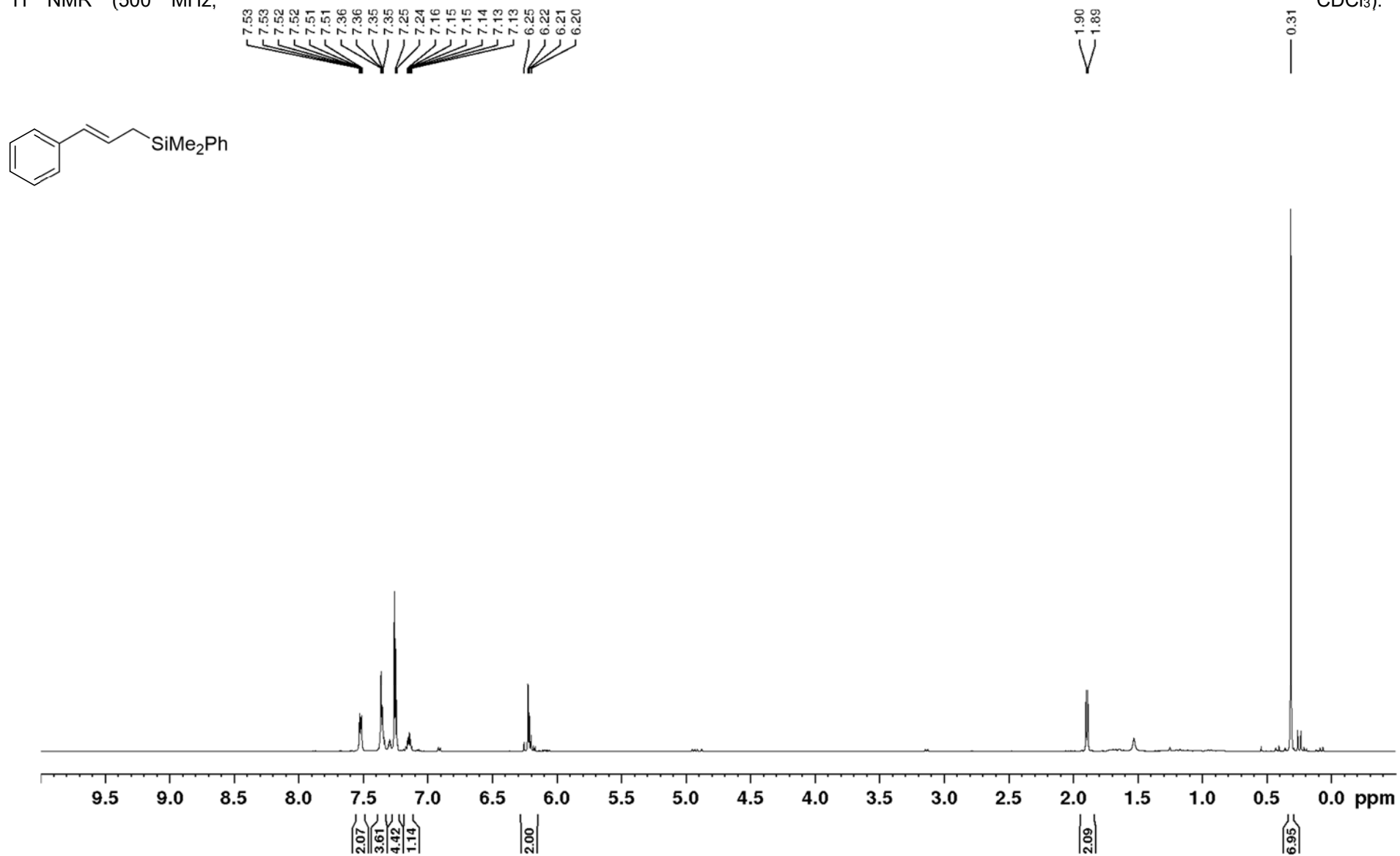
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

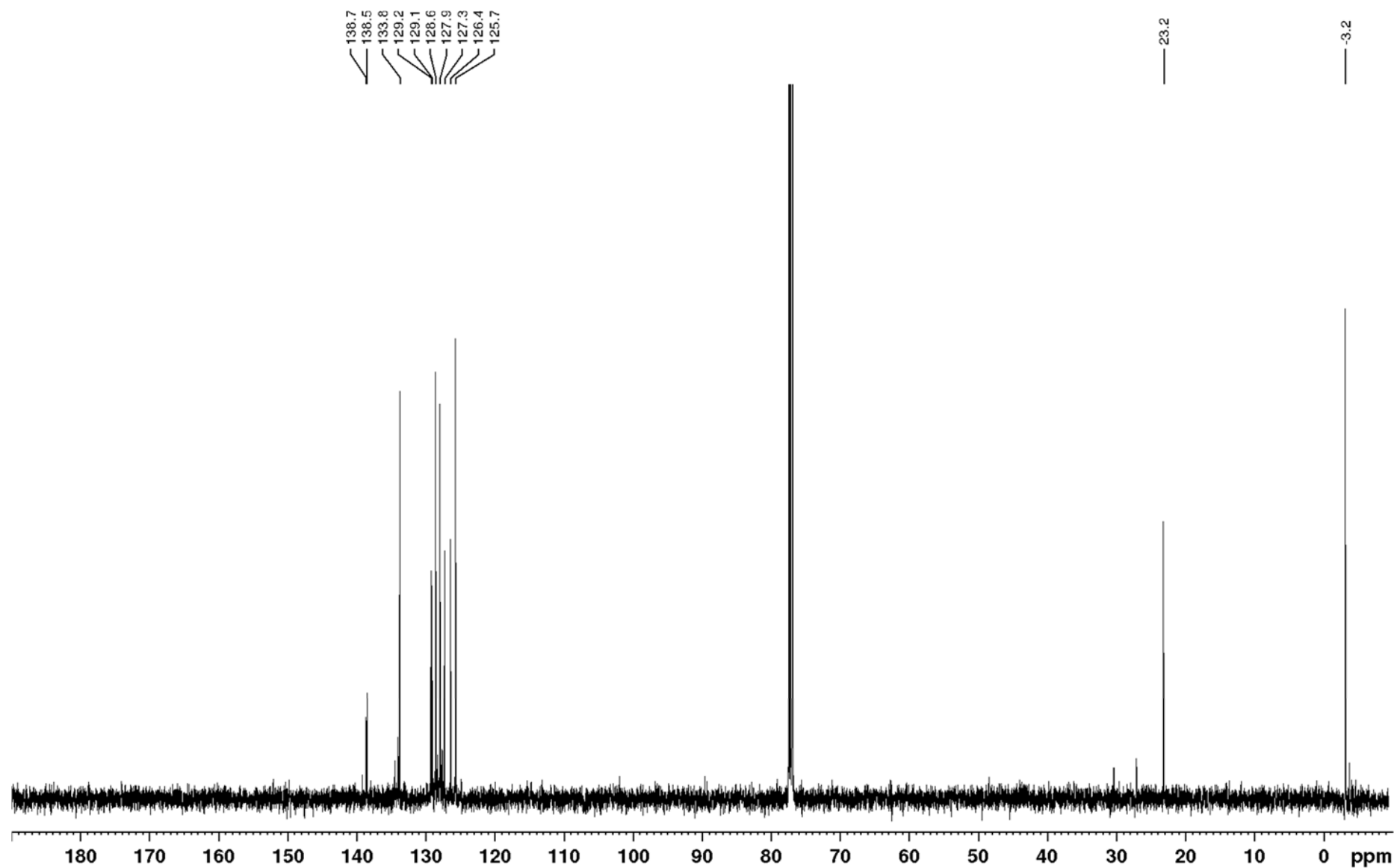
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

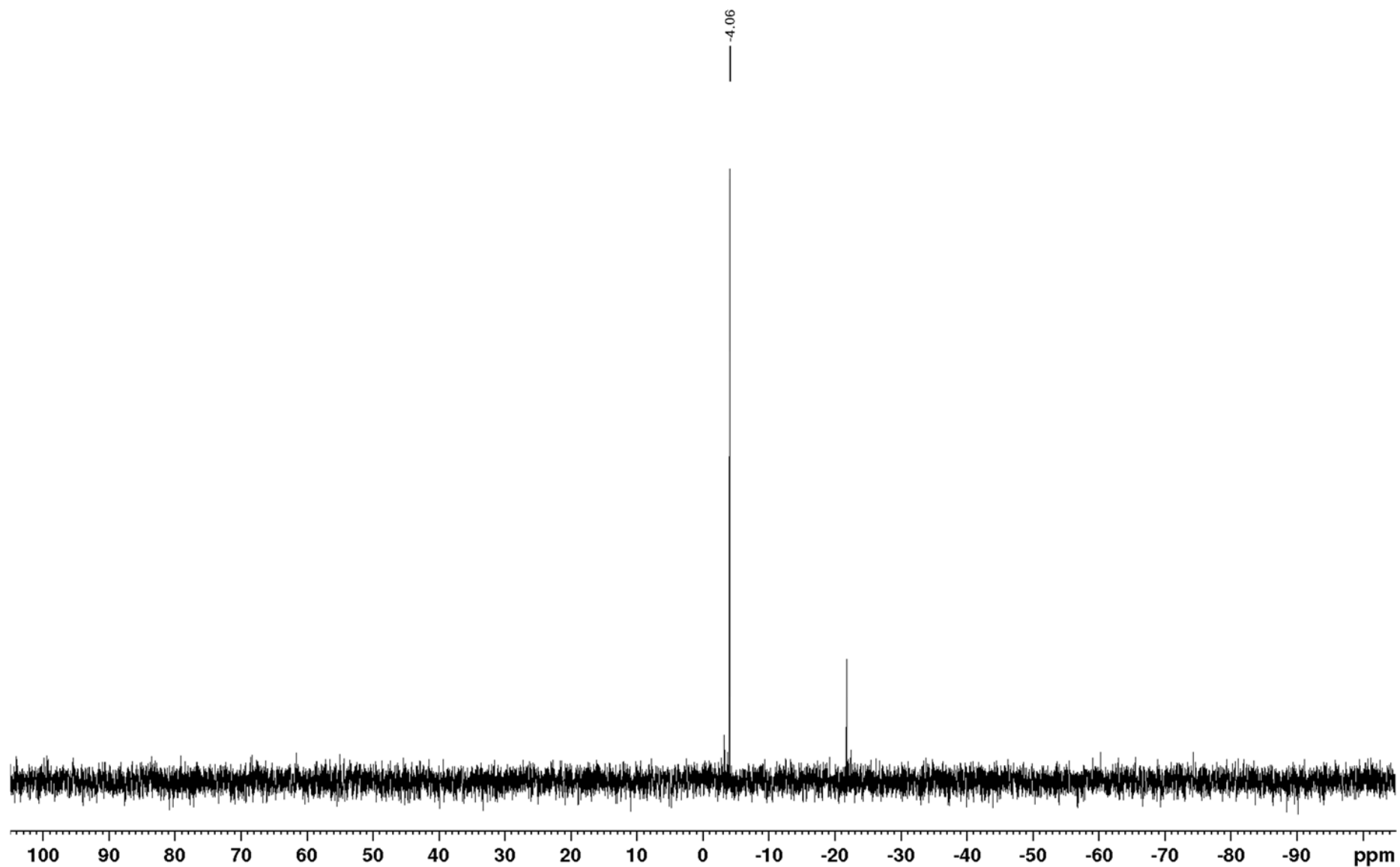
Cinnamyl dimethyl(phenyl)silane (6)

 ^1H NMR (500 MHz, CDCl_3):

SUPPORTING INFORMATION

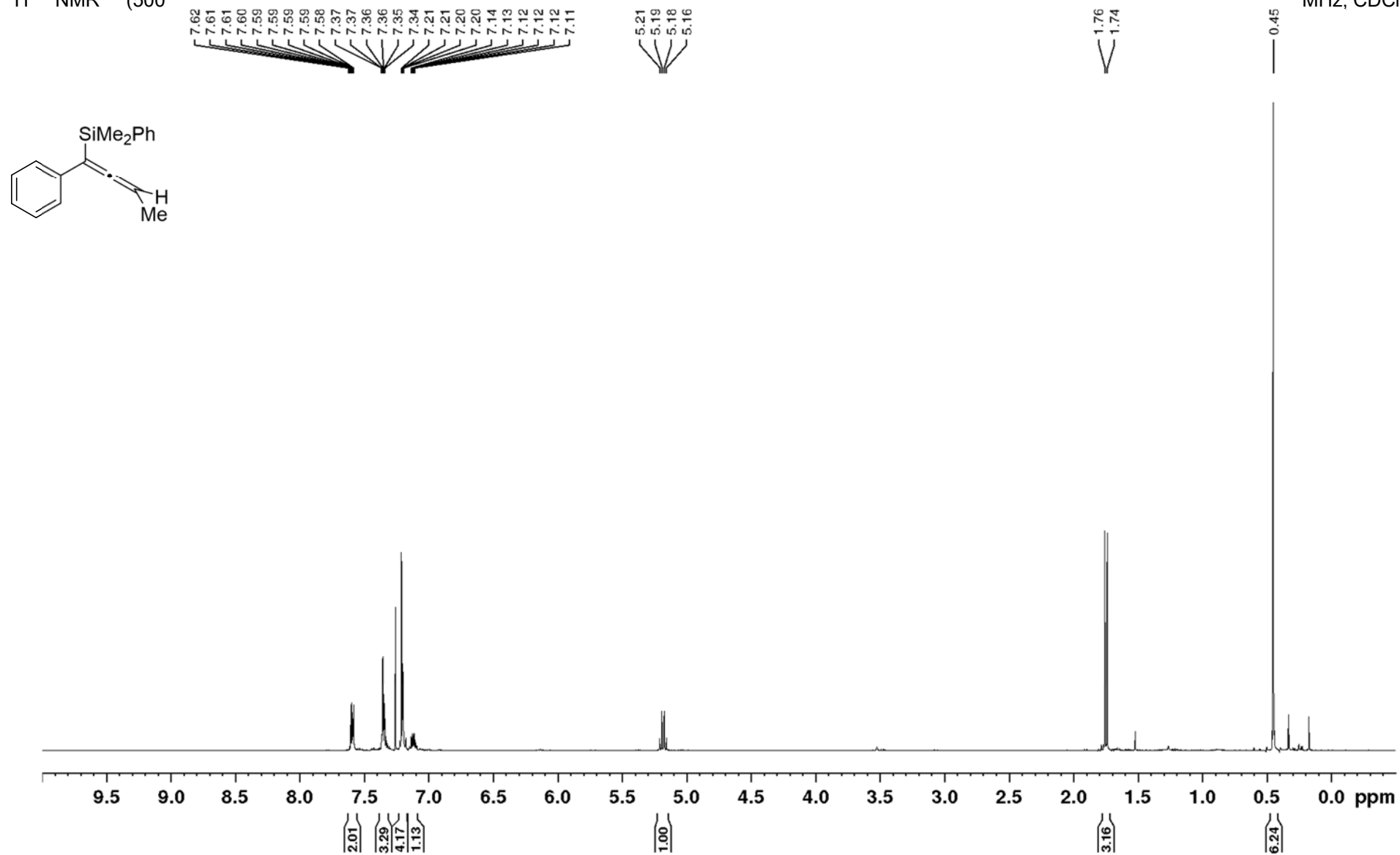
 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

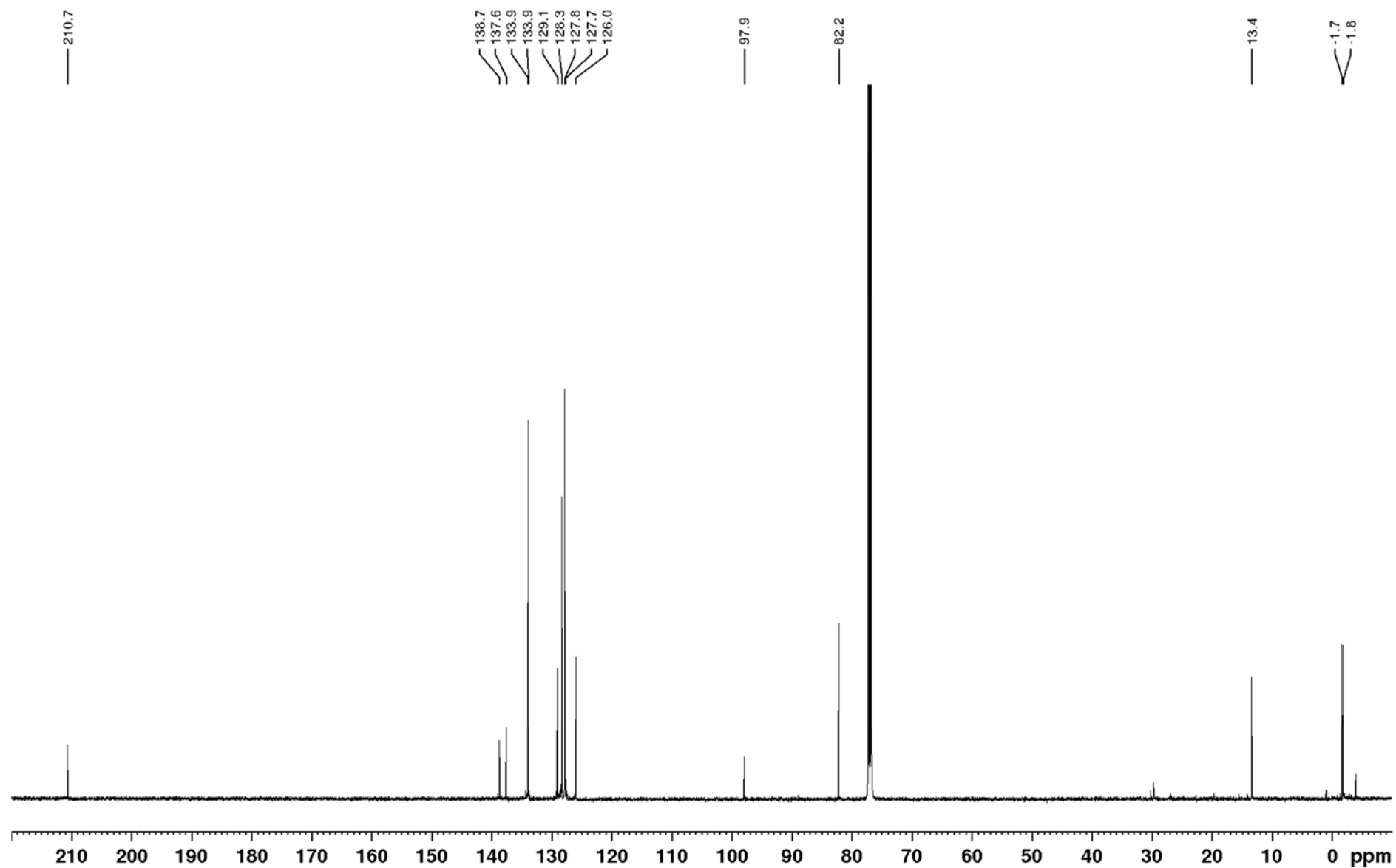
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

SUPPORTING INFORMATION

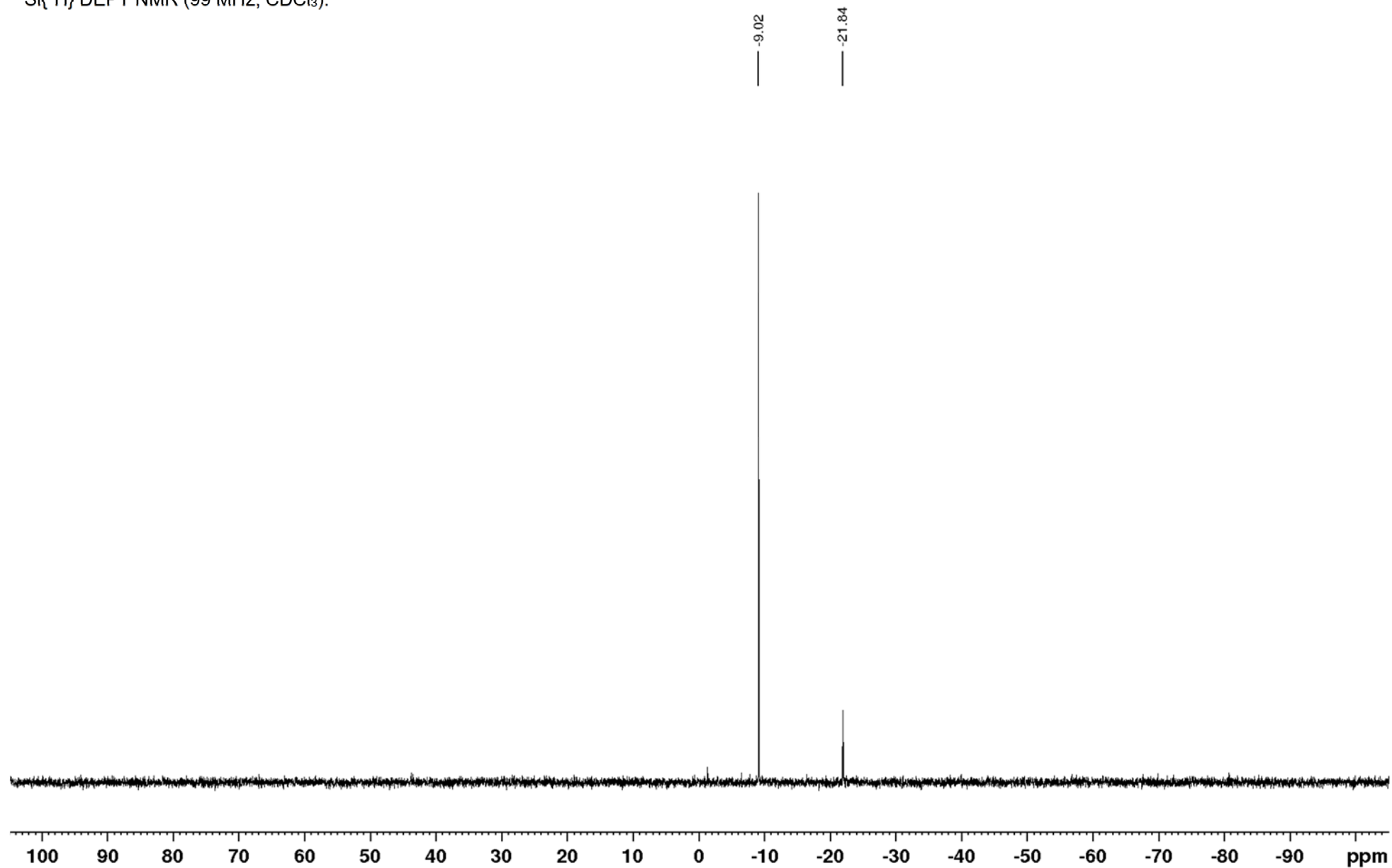
Dimethyl(3-methyl-1-phenylbuta-1,2-dien-1-yl)(phenyl)silane (8)

 ^1H NMR (500MHz, CDCl_3):

SUPPORTING INFORMATION

 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3):

SUPPORTING INFORMATION

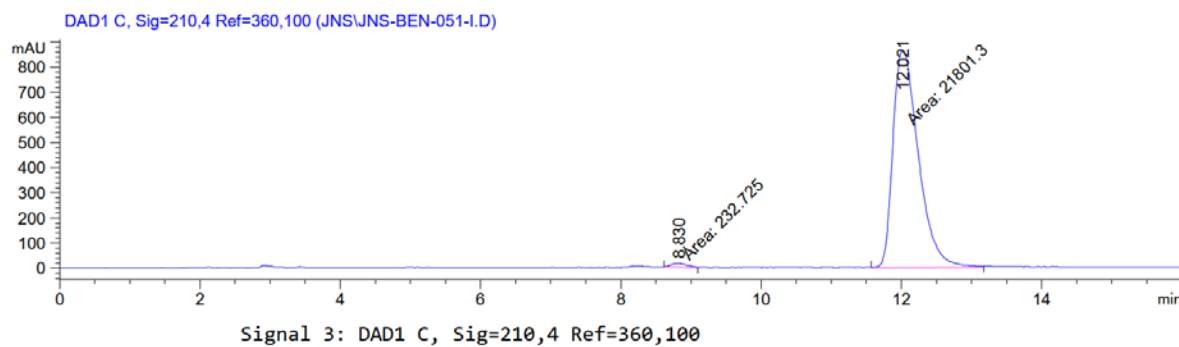
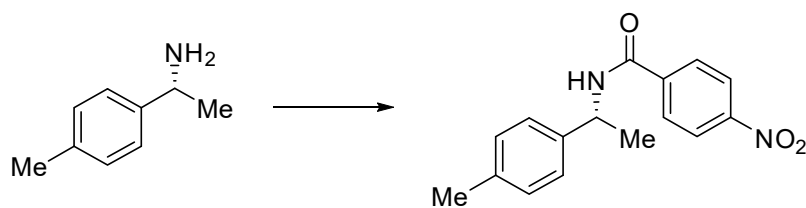
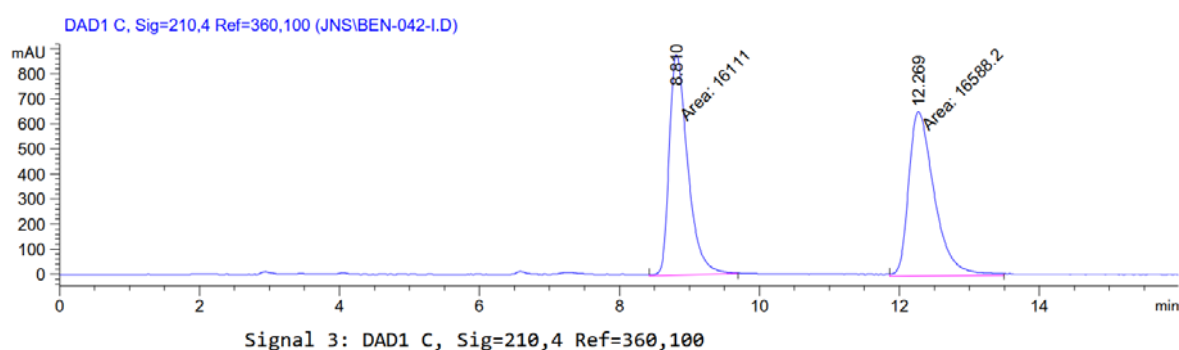
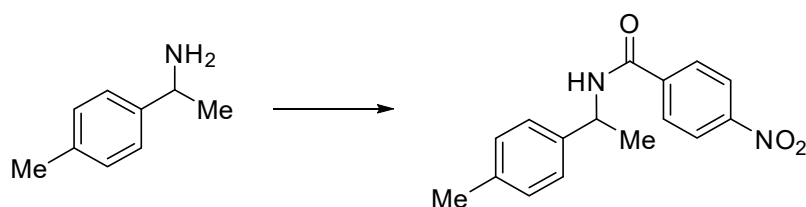
 $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (99 MHz, CDCl_3):

9. HPLC Traces of Synthesized Chiral Substrates

Selected HPLC Traces of Starting materials

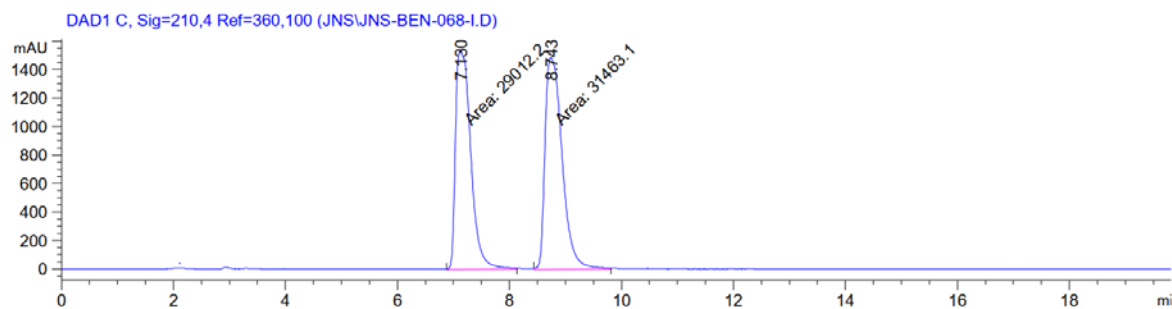
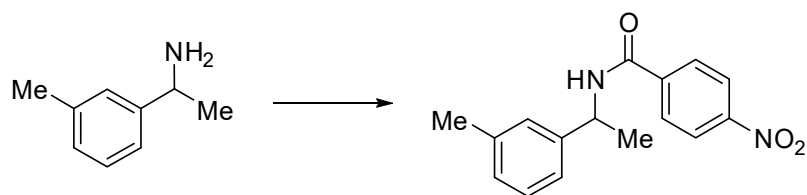
The enantiomeric excess of the free amines was determined after derivatization to the corresponding 4-nitrobenzoyl amides, using 4-nitrobenzoyl chloride (1.5 equiv) and Et₃N (2.0 equiv) in CH₂Cl₂ at rt.

1-(p-tolyl)ethan-1-amine (S1b)



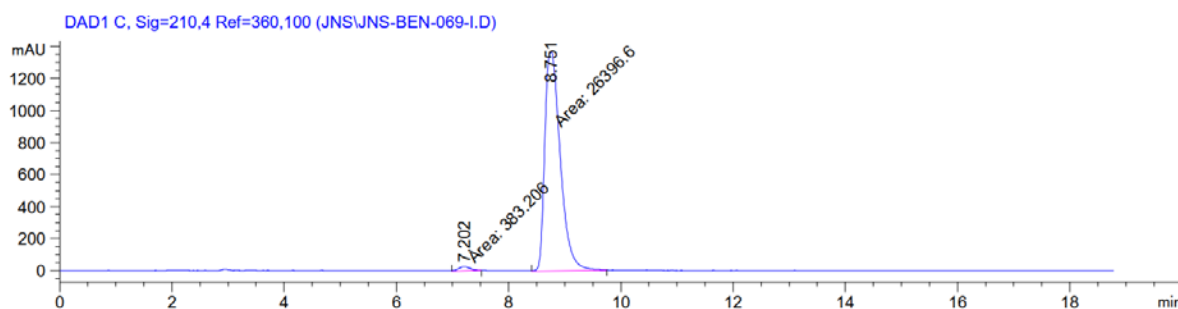
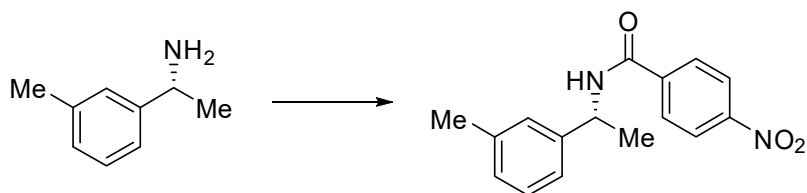
SUPPORTING INFORMATION

1-(m-tolyl)ethan-1-amine (S1c)



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.130	MM	0.3136	2.90122e4	1541.67126	47.9736
2	8.743	MM	0.3527	3.14631e4	1486.74390	52.0264

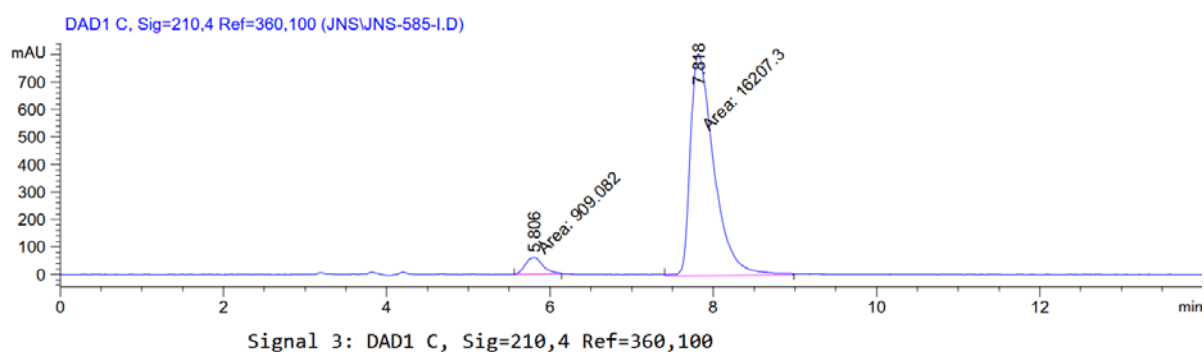
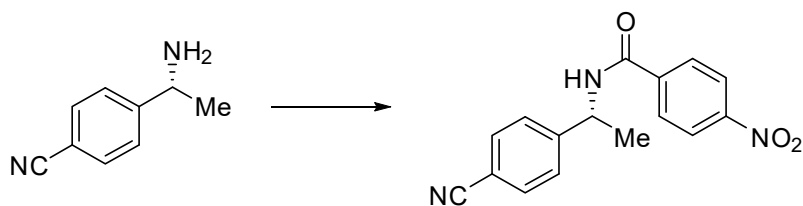
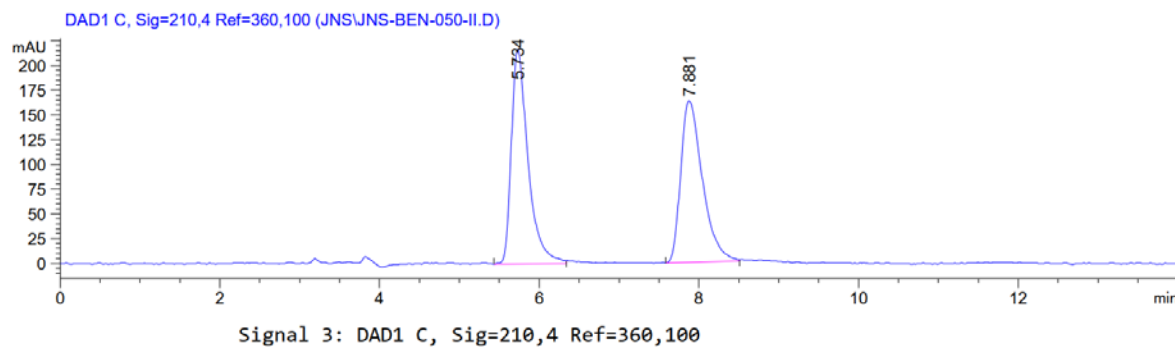
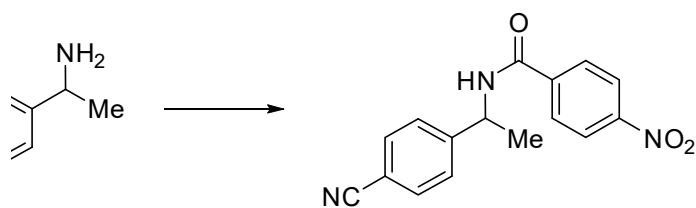


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.202	MM	0.2414	383.20621	26.45647	1.4310
2	8.751	MM	0.3207	2.63966e4	1371.63818	98.5690

SUPPORTING INFORMATION

4-(1-aminoethyl)benzoinitrile (S1j)

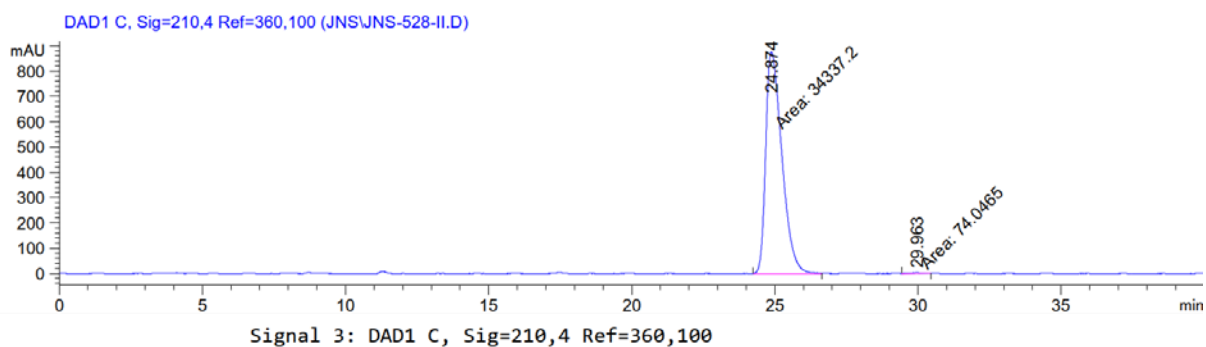
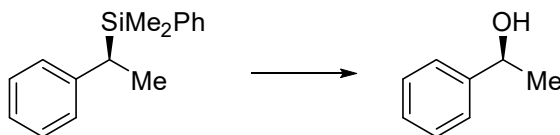
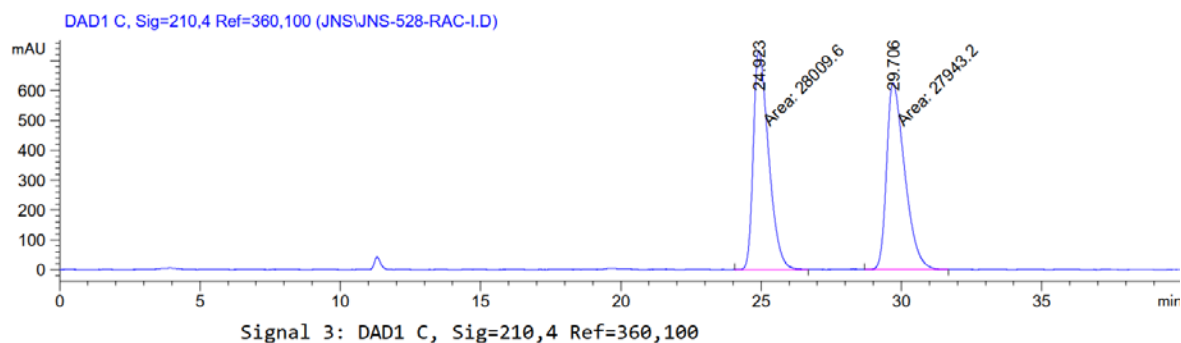
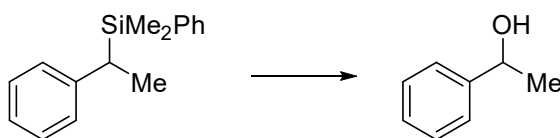


The enantiomeric ratio of 95:5 is a result of slow racemization during the derivatization. The enantiomeric ratio of the corresponding silane (S)-4ja, was determined to be 98.5:1.5 at the stage of the alcohol. The ee of the amine therefore is estimated to be in the same range.

SUPPORTING INFORMATION

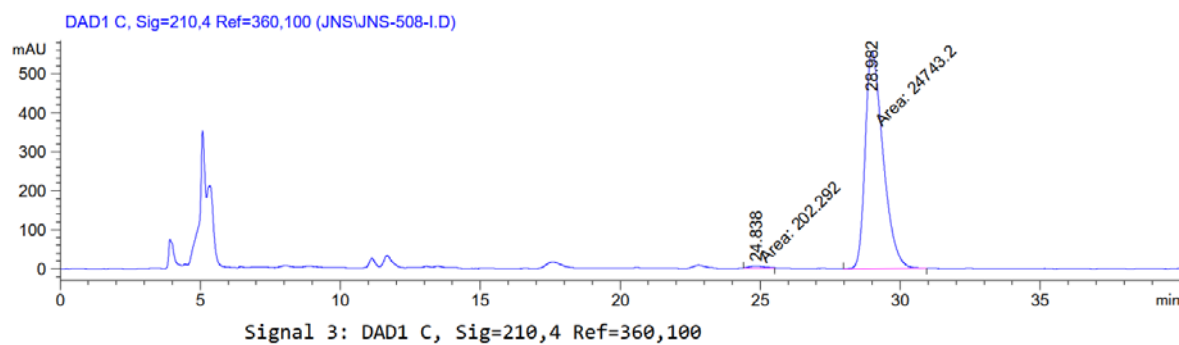
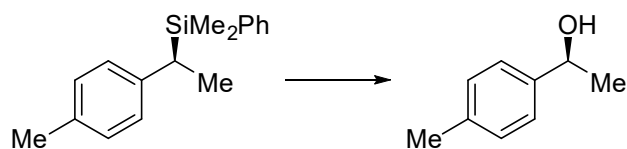
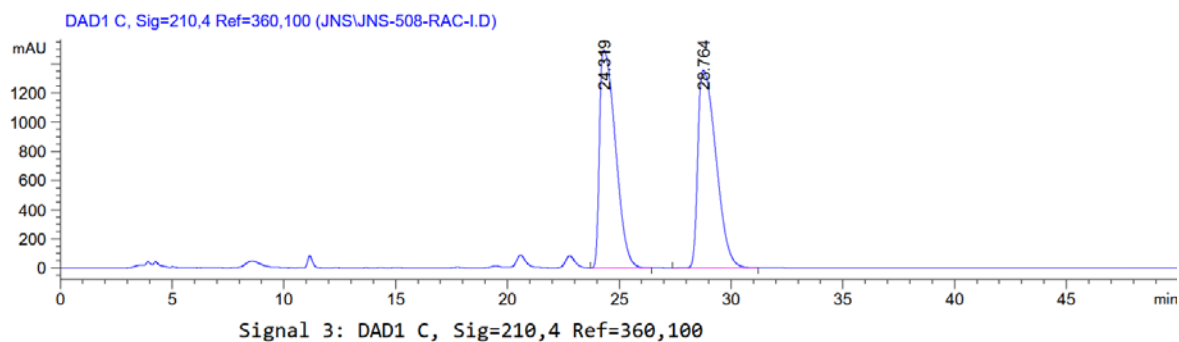
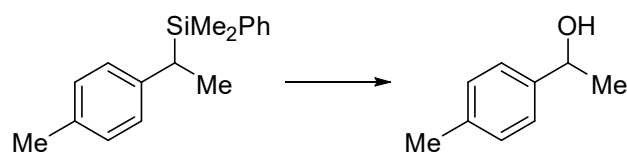
10. HPLC Traces of Chiral Silanes

The enantiomeric excess of the silanes was determined after conversion to the corresponding alcohol, except for silane **4ja**, as it was polar enough for normal phase HPLC. (See Ch7 for the standard procedure).

Dimethyl(phenyl)(1-phenylethyl)silane (**4aa**)

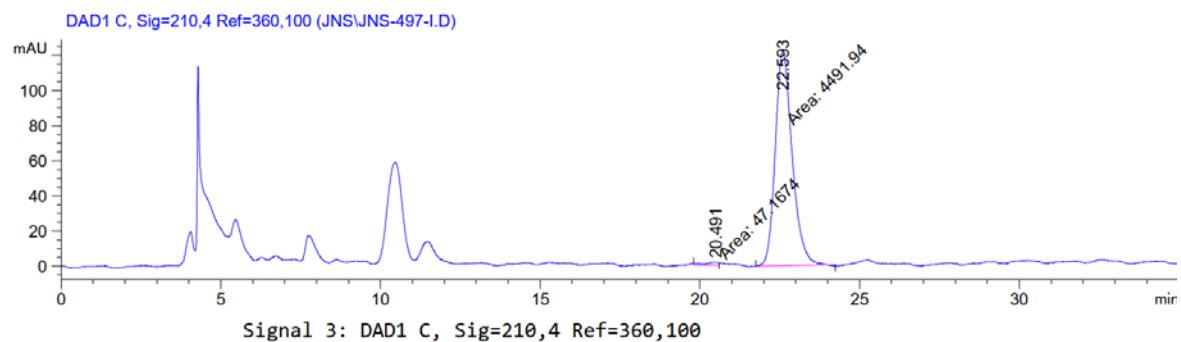
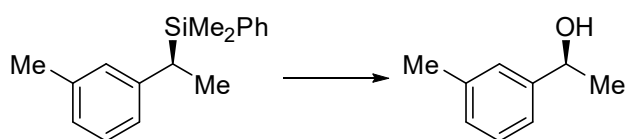
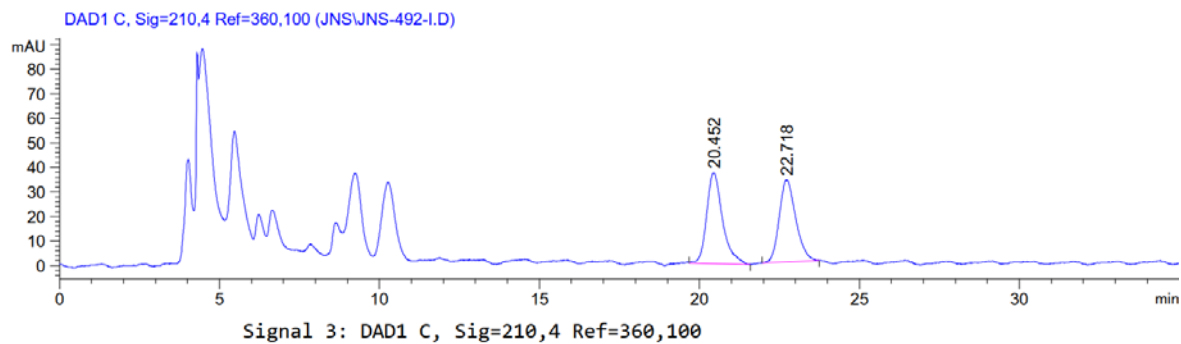
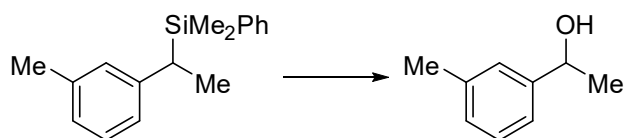
SUPPORTING INFORMATION

Dimethyl(phenyl)[1-(p-tolyl)ethyl]silane (4ba)

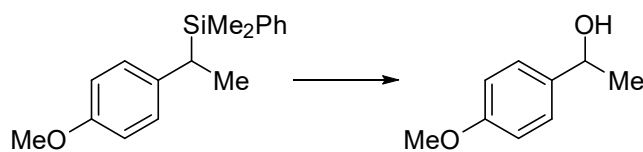


SUPPORTING INFORMATION

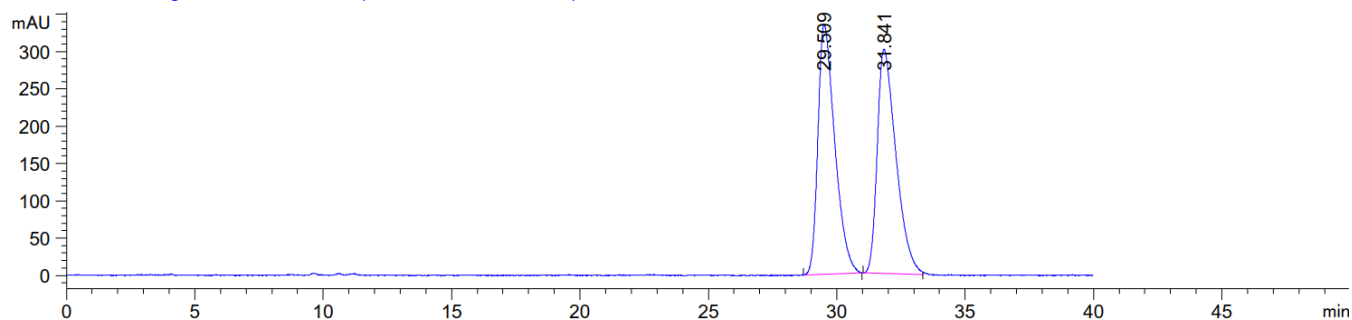
Dimethyl(phenyl)[1-(m-tolyl)ethyl]silane (4ca)



SUPPORTING INFORMATION

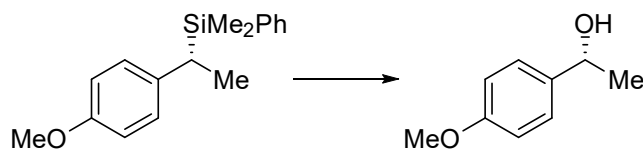
[1-(4-Methoxyphenyl)ethyl]dimethyl(phenyl)silane (4fa)

DAD1 C, Sig=210,4 Ref=360,100 (JNSJNS-547-RAC-III.D)

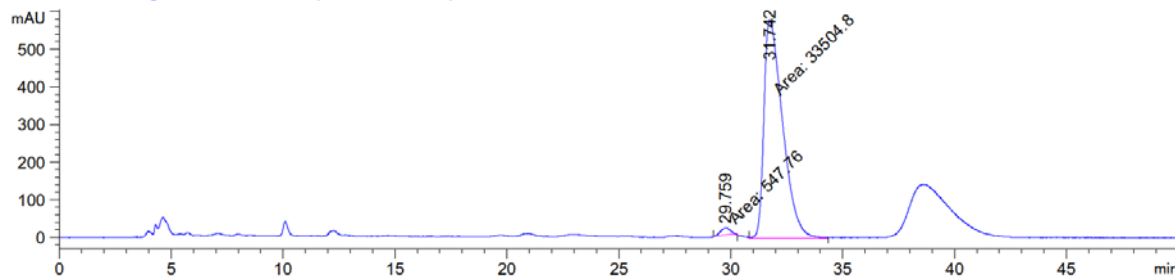


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.509	BB	0.6294	1.53093e4	334.82629	50.0540
2	31.841	BV	0.6967	1.52763e4	300.70102	49.9460



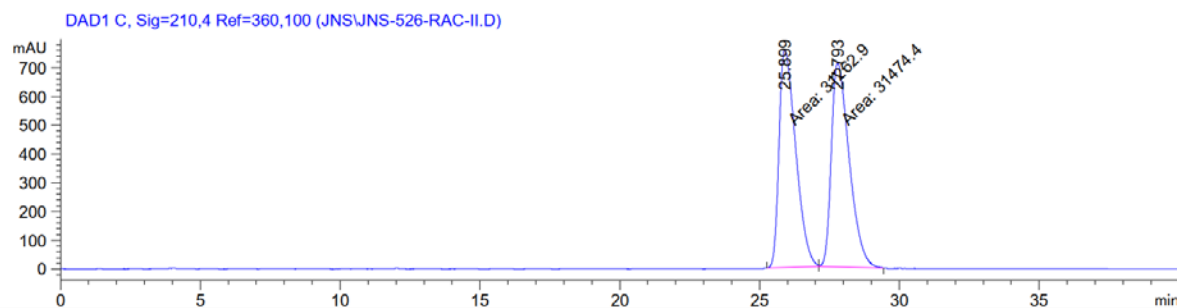
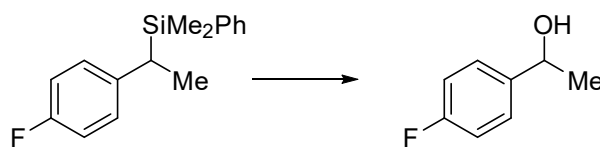
DAD1 C, Sig=210,4 Ref=360,100 (JNSJNS-584-I.D)



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

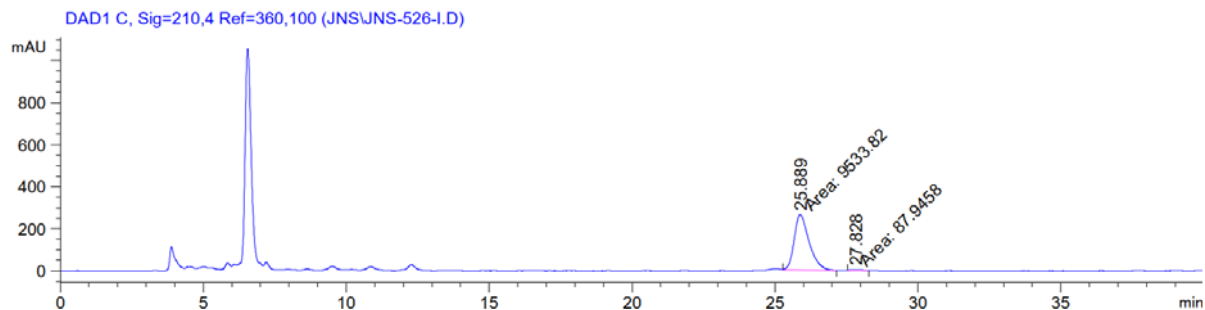
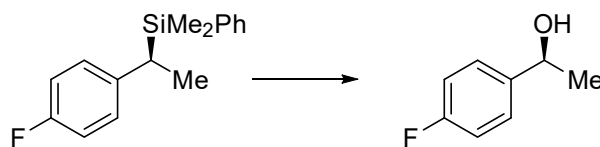
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.759	MM	0.4983	547.76031	18.32254	1.6086
2	31.742	MM	0.9635	3.35048e4	579.59424	98.3914

SUPPORTING INFORMATION

[1-(4-Fluorophenyl)ethyl]dimethyl(phenyl)silane (4ga)

Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.899	MM	0.6888	3.12629e4	756.48669	49.8314
2	27.793	MM	0.7413	3.14744e4	707.66315	50.1686

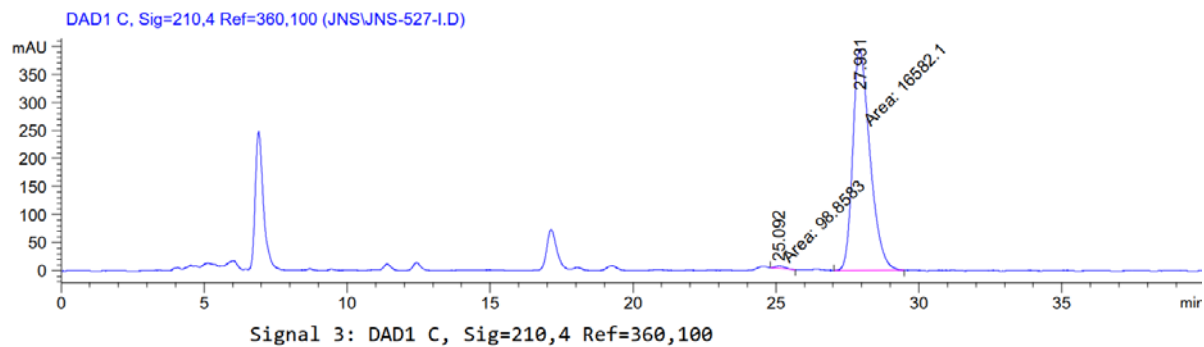
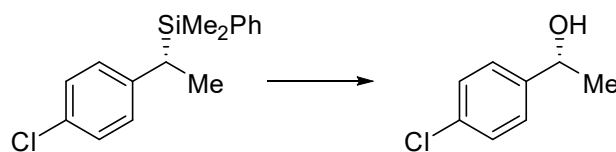
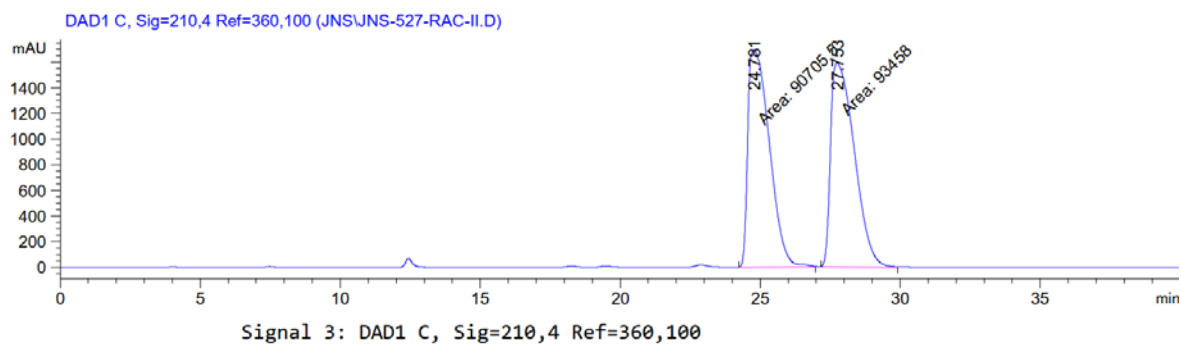
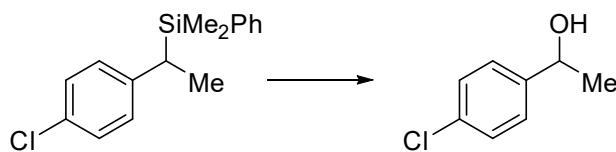


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.889	MM	0.6031	9533.81934	263.45593	99.0860
2	27.828	MM	0.4313	87.94580	3.39850	0.9140

SUPPORTING INFORMATION

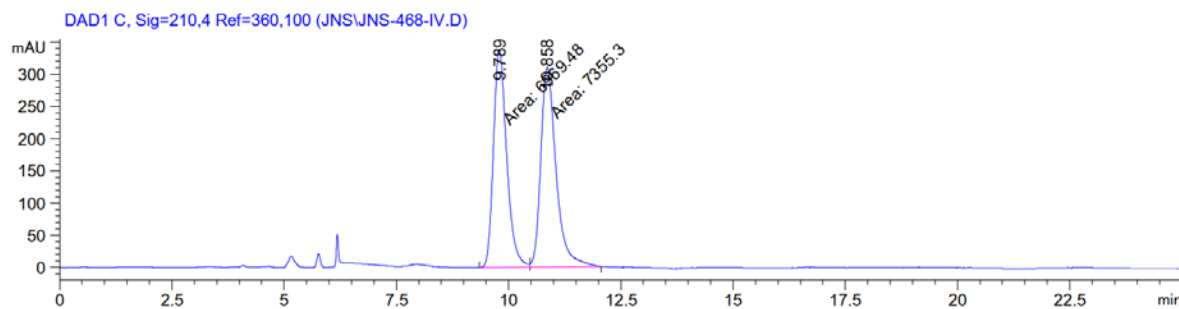
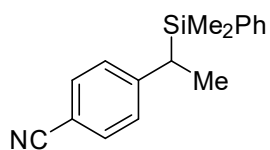
[1-(4-Chlorophenyl)ethyl]dimethyl(phenyl)silane (4ha)



SUPPORTING INFORMATION

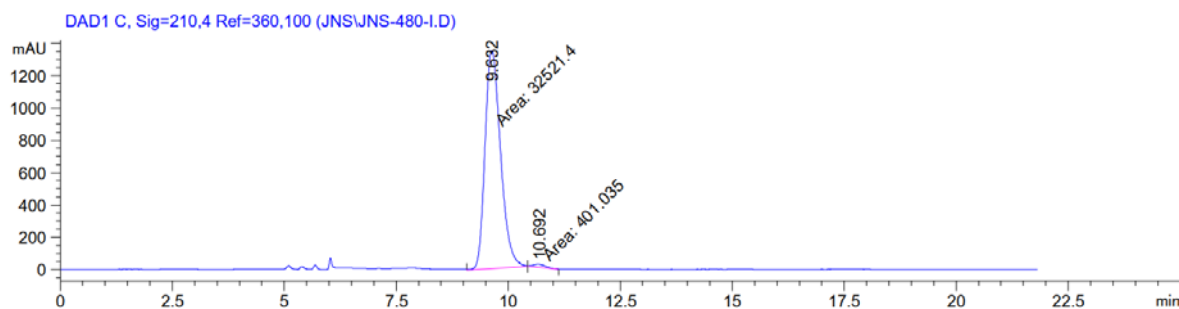
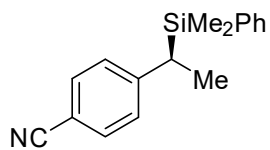
4-{1-[Dimethyl(phenyl)silyl]ethyl}benzonitrile (4ja)

This rather polar compound could be resolved without prior derivatization to the alcohol.



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.789	MM	0.3426	6969.47949	339.02939	48.6533
2	10.858	MM	0.3955	7355.30225	309.94904	51.3467

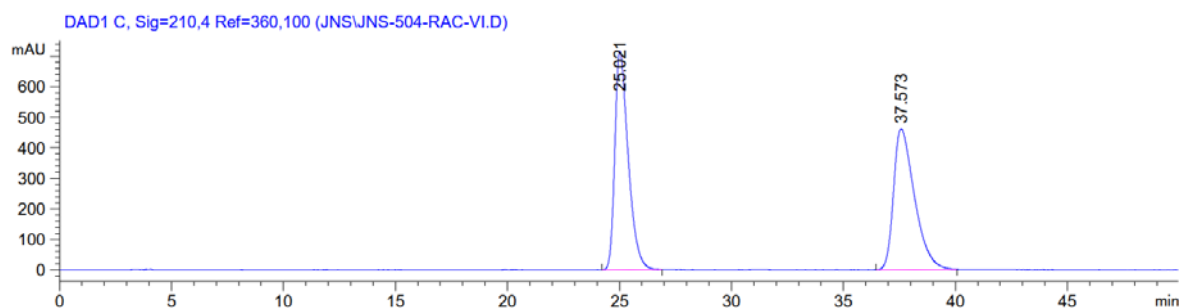
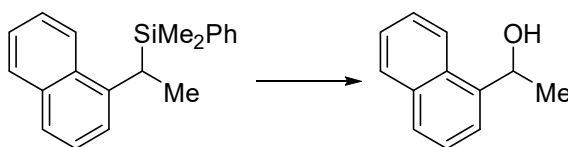


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.632	MM	0.4020	3.25214e4	1348.40576	98.7819
2	10.692	MM	0.3328	401.03516	20.08642	1.2181

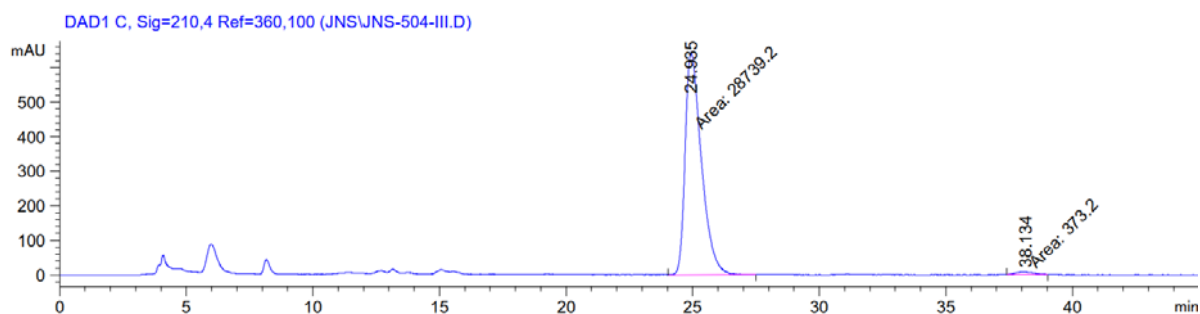
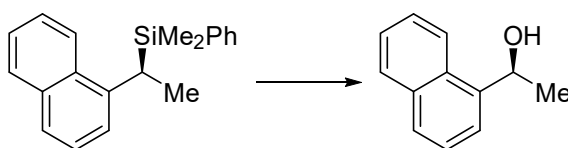
SUPPORTING INFORMATION

Dimethyl[1-(naphthalen-1-yl)ethyl](phenyl)silane (4Ia)



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.021	BB	0.6038	2.96568e4	715.17938	49.7083
2	37.573	VV	0.8586	3.00049e4	461.44684	50.2917

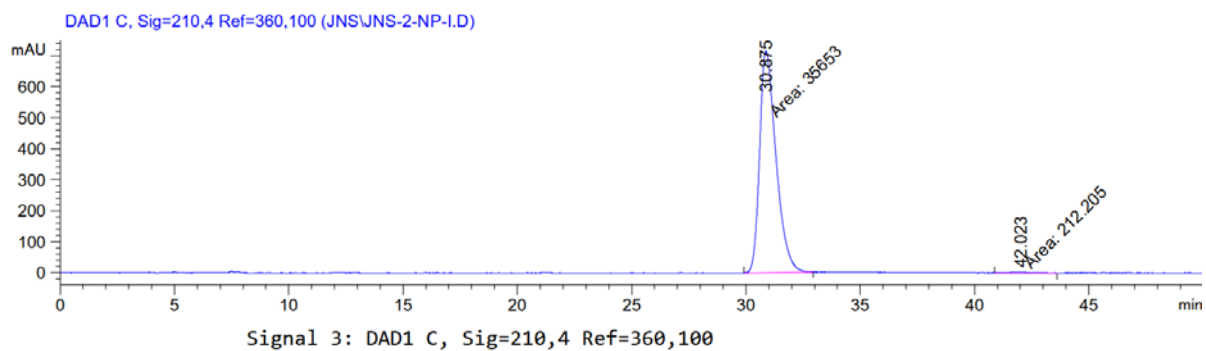
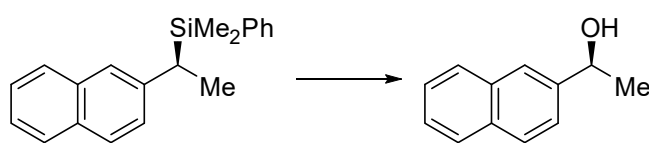
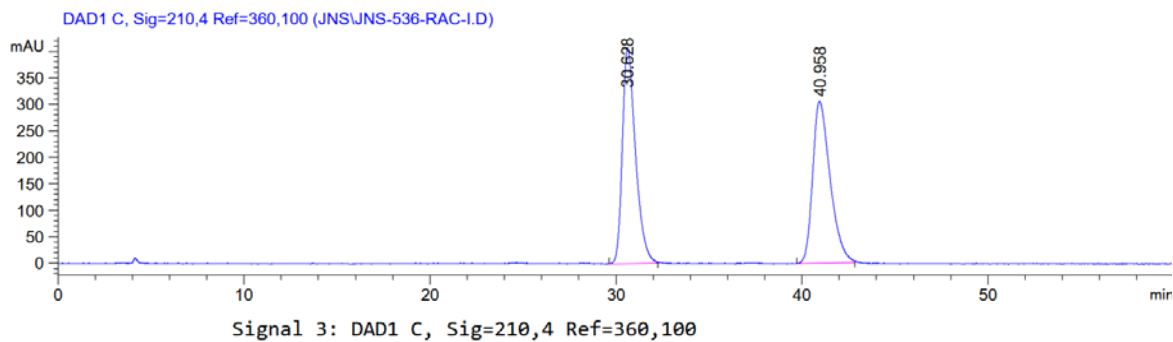
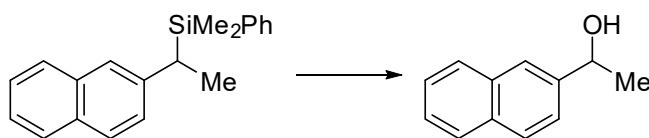


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.935	MM	0.7424	2.87392e4	645.18597	98.7181
2	38.134	MM	0.8170	373.19971	7.61338	1.2819

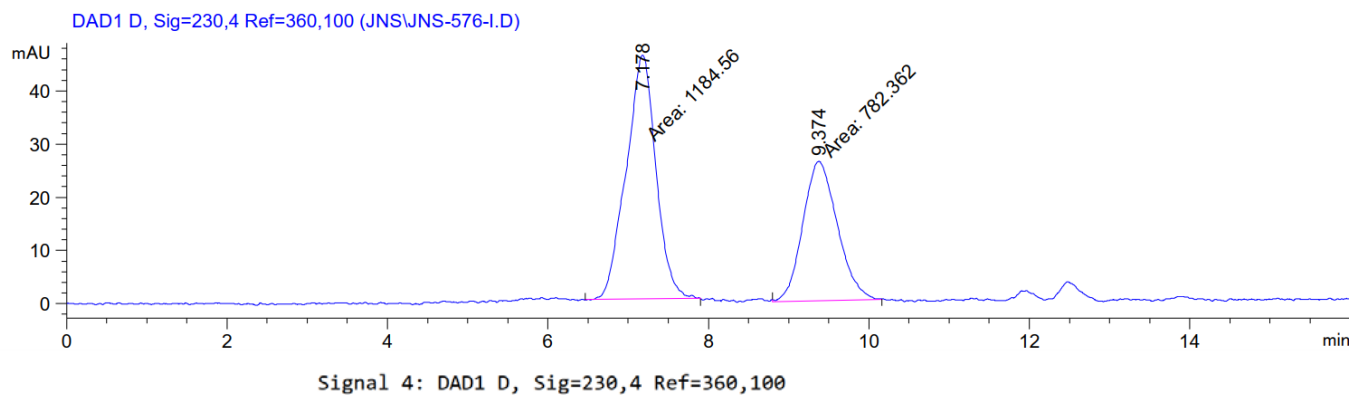
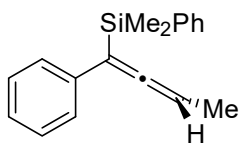
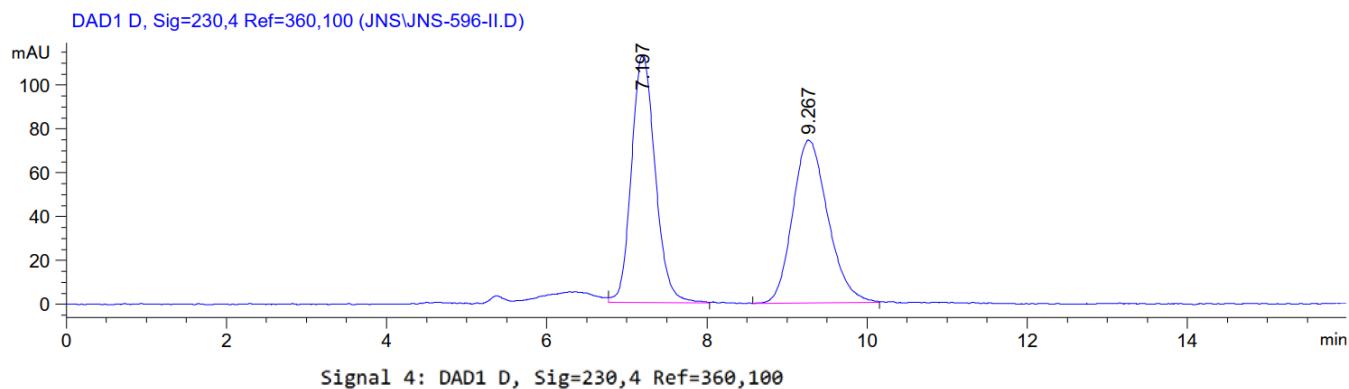
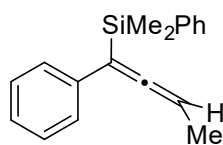
SUPPORTING INFORMATION

Dimethyl[1-(naphthalen-2-yl)ethyl](phenyl)silane (4ma)



SUPPORTING INFORMATION

Dimethyl(3-methyl-1-phenylbuta-1,2-dien-1-yl)(phenyl)silane (6)



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