

Supporting Information

C1 Polymerization of Fluorinated Aryl Diazomethanes

Songsu Kang,^{a,‡} Sherilyn J. Lu^{a,b,‡} and Christopher W. Bielawski^{a,b,}*

^a Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea

^b Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

[‡] These authors contributed equally to this work.

* To whom correspondence should be addressed.

Table of Contents

General Information	S2
Synthetic Procedures	S3
SEC Data	S21
TGA and DSC Data	S24
Contact Angle Measurement Data	S27
NMR Spectra	S30
References	S108

General Information

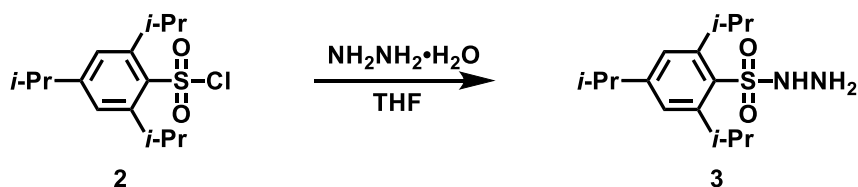
All solvents were purchased from Daejung Chemicals & Metals and used without additional purification unless otherwise noted. 1,3-Bis(trifluoromethyl)benzene was purchased from Alfa Aesar and used without additional purification. Poly(styrene) ($M_n = 9,370$ Da, $\bar{D} = 1.02$) was purchased from Agilent Technologies. All other chemicals were purchased from Aldrich, Alfa Aesar, or Tokyo Chemical Industry Co., LTD. and were used as received. Unless mentioned, all reactions were performed under a nitrogen atmosphere using standard Schlenk techniques.

^1H NMR and ^{13}C NMR spectra were recorded in THF- d_8 (^1H : 3.58 ppm; ^{13}C : 67.57 ppm), benzene- d_6 (^1H : 7.16 ppm; ^{13}C : 128.06 ppm), chloroform- d_1 (^1H : 7.26 ppm; ^{13}C : 77.2 ppm) or dichloromethane- d_2 (^1H : 5.32 ppm; ^{13}C : 54.00 ppm) using Bruker 400 MHz and 100 MHz spectrometers, respectively. ^{19}F NMR spectra were recorded using a Bruker 377 MHz spectrometer and calibrated to C_6F_6 as a reference (THF- d_8 : -164.51 ppm; benzene- d_6 : -163.16 ppm; dichloromethane- d_2 : -162.61; chloroform- d_1 : -161.64 ppm).¹ ^{11}B NMR spectra were recorded using a Bruker 128 MHz spectrometer and calibrated against $\text{BF}_3 \cdot \text{OEt}_2$ as a reference (benzene- d_6 : 0 ppm). Due to the overlap of $\text{BF}_3 \cdot \text{OEt}_2$ and poly(**1a**), $\text{BH}_3 \cdot \text{SMe}_2$ was used as a standard and calibrated against $\text{BF}_3 \cdot \text{OEt}_2$ in the ^{11}B NMR measurement of poly(**1a**). Splitting patterns are indicated as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; bs = broad singlet; br = broad; dd = doublet of doublet; dt = doublet of triplet; dm = doublet of multiplet; td = triplet of doublet; tt = triplet of triplet; tm = triplet of multiplet. Coupling constants (J) are expressed in Hertz. High-resolution mass spectra (HR-MS) data were obtained from a JMS-T100LP AccuTOF LC-plus 4G Atmospheric Pressure Ionization High Resolution Time-of-Flight Mass Spectrometer (Waters Inc.) Poly(phenyl methylene), poly(**1c**), poly(**1e**), poly(**1f**) and poly(2,3,4,5,6-pentafluorostyrene) were analyzed using a Malvern GPCmax Solvent/Sample Module chromatograph. Two fluorinated poly(styrene) columns (IMBMW-

3078) were used in series and maintained at 35 °C. THF was used as the mobile phase at a flow rate of 0.8 mL min⁻¹. Detection was performed using a Malvern Viscotek Triple Detector Array (TDA305) system. Molecular weight and polydispersity were obtained relative to poly(styrene) standards. For poly(**1a**), poly(**1b**), poly(**1d**) and poly(**1g**), SEC was performed on a customized YL9100 HPLC system. Three polystyrene columns (two HFIP3000 and one HFIP6000M) were used in series and maintained at 35 °C. Chloropentafluorobenzene was used as the mobile phase at a flow rate of 1.0 mL/min. Detection was performed using a YL9170 RI detector. Molecular weight and polydispersity data are reported related to poly(dimethylsiloxane) standards. Thermogravimetric analyses (TGA) were performed on a Thermal Advantages (TA) TGA 550 at a heating rate of 10 °C min⁻¹ and under an atmosphere of nitrogen by TA Instrument-Waters LLC (Seoul, South Korea). Differential scanning calorimetry (DSC) was performed on a Thermal Advantages DSC 2500 at a heating rate of 10 °C min⁻¹ and under an atmosphere of nitrogen by TA Instrument-Waters LLC (Seoul, South Korea). Elemental analyses were performed using a ThermoScientific Flash 2000 Organic Elemental Analyzer by the UNIST Central Research Facilities (Ulsan, South Korea). Analyses were performed in triplicate and averaged. Contact angles were measured on SEO-Phoenix 300 Touch Automatic Contact Angle Analyzer at 20 °C with a motor speed of 50% and frame interval of 300 ms for dynamic measurements. A Rhabdos HTSF-1000DH spin coater was used to coat silica wafers with polymer films; conditions: acceleration time of 10 s until 2000 rpm, and then hold for 1 min before deceleration.

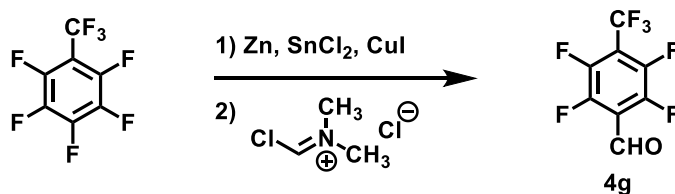
Synthetic Procedures

Synthesis of 2,4,6-triisopropylbenzenesulfonyl hydrazide 3



A previously reported procedure was modified to synthesize this compound.² Hydrazine monohydrate (4.13 g, 82.5 mmol) was added dropwise over a period of 15 min using a dropping funnel into a solution of 2,4,6-triisopropylbenzenesulfonyl chloride (10.0 g, 33.0 mmol) in THF (30 mL) at 0 °C. The resulting reaction mixture was stirred at 0 °C for 3 h. Water (15 mL) was added, and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed with brine (2 × 30 mL), dried over anhydrous sodium sulfate, filtered, and then concentrated under reduced pressure below 20 °C to afford a white solid. Pentane (250 mL) was added, and the resulting suspension was stirred vigorously at room temperature until fine solid was formed. The solid was collected by filtration and washed with cold pentane to afford the product as a white solid (8.30 g, 27.8 mmol) in 84% yield. Spectroscopic data recorded for the product were in accord with literature values. ¹H NMR (400 MHz, CDCl₃): δ 7.20 (s, 2H), 5.58 (bs, 1H), 4.20-4.10 (m, 2H), 3.61 (bs, 2H), 2.96-2.86 (m, 1H), 1.28-1.25 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 153.80, 151.88, 128.81, 124.07, 34.30, 29.86, 25.01, 23.62.

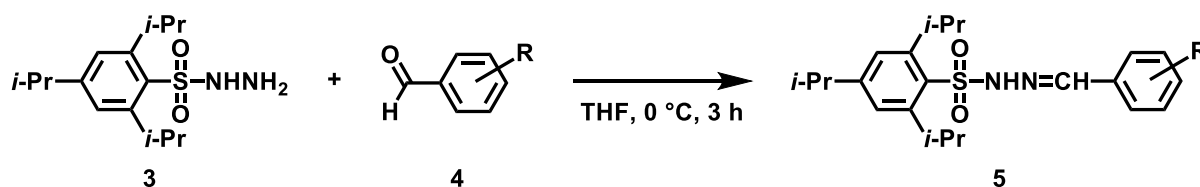
Synthesis of 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzaldehyde 4g



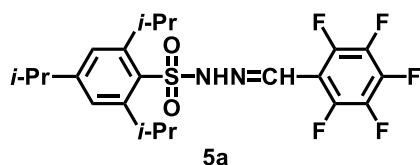
A previously reported procedure was modified to synthesize this compound.³ CuI (1.90 g, 9.97 mmol) was added to a mixture of octafluorotoluene (11.8 g, 50.0 mmol), Zn dust (9.85 g, 150 mmol) and SnCl₂ (0.95 g, 5.01 mmol) in DMF (27 mL) under an atmosphere of nitrogen. The

resulting reaction mixture was stirred at 90 °C for 1 h. The resulting solution was transferred into a dropping funnel, then added into the Vilsmeier-Haack reagent (10.24 g, 5.37 mmol) over 2.5 h at 0 °C. The reaction mixture was then stirred at 0 °C for additional 1 h. Water (80 mL) was added at 0 °C and the mixture was steam distilled at 130 °C. The organic layer was diluted with diethyl ether (150 mL) and washed with saturated ammonium chloride solution (3 × 100 mL). The organic solution was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The purification was accomplished by vacuum distillation (15 mmHg / 70 °C) to afford pale yellow liquid (7.10 g, 28.8 mmol) in 57% yield. ¹H NMR (400 MHz, CDCl₃): δ 10.34 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 181.52 (s), 146.88 (dm, *J* = 277 Hz), 144.52 (dm, *J* = 277 Hz), 120.44 (q, *J* = 275 Hz), 118.00 (t, *J* = 10 Hz), 114.79 (m). ¹⁹F NMR (377 MHz, CDCl₃): δ -56.66 (t, *J* = 22.5 Hz, 3F), -138.29 (m, 2F), -142.62 (m, 2F). HR-MS (ESI) calcd. for C₈H₂F₇O [M + H]⁺ 246.9994, found 246.9989.

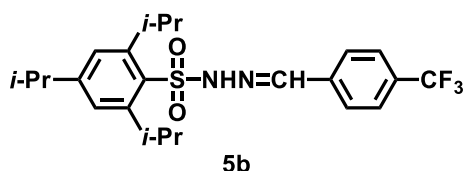
General procedure for the preparation of 2,4,6-triisopropylbenzenesulfonyl hydrazones 5a-5g and 2,4,6-triisopropylbenzenesulfonyl phenylhydrazones



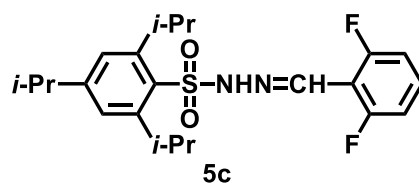
Benzaldehyde (4) (1 equiv.) was added dropwise into a solution of 2,4,6-triisopropylbenzenesulfonyl hydrazide (3) (1 equiv.) in THF (0.42 M) at 0 °C. The resulting reaction mixture was stirred at 0 °C for 3 h, and thereafter the solvent was removed under reduced pressure. The crude solid was purified by recrystallization in methanol to afford 2,4,6-triisopropylbenzenesulfonyl hydrazones 5a-5g.



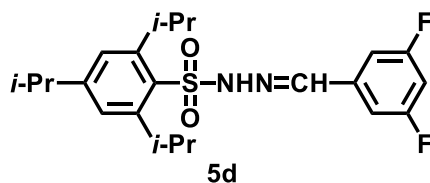
The hydrazone **5a** was prepared following the general procedure using 2,3,4,5,6-pentafluorobenzaldehyde (**4a**) (11.38 g, 58.0 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (17.32 g, 58.0 mmol). The resulting hydrazone **5a** was obtained as a white solid (23.31 g, 48.9 mmol) in 84% yield. ^1H NMR (400 MHz, $\text{THF-}d_8$): δ 10.92 (s, 1H), 7.86 (s, 1H), 7.25 (s, 2H), 4.34 - 4.24 (m, 2H), 2.95 - 2.88 (m, 1H), 1.27 - 1.24 (t, J = 6.8 Hz, 18H). ^{13}C NMR (100 MHz, $\text{THF-}d_8$): δ 154.08 (s), 152.36 (s), 146.02 (dm, J = 253 Hz), 142.27 (dm, J = 253 Hz), 138.84 (dm, J = 249 Hz), 133.77 (s), 132.24 (m), 124.65 (s), 111.04 (m), 35.27 (s), 30.86 (s), 25.34 (s), 24.04 (s). ^{19}F NMR (377 MHz, $\text{THF-}d_8$): δ -143.30 (dd, J = 11.3 Hz, 7.5 Hz, 2F), -153.87 (t, J = 22.5 Hz, 1F), -164.83 – -164.92 (m, 2F). HR-MS (ESI) calcd. for $\text{C}_{22}\text{H}_{26}\text{F}_5\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 477.1635, found 477.1659.



The hydrazone **5b** was prepared following the general procedure using 4-(trifluoromethyl)benzaldehyde (**4b**) (10.0 g, 57.4 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (17.14 g, 57.4 mmol). The resulting hydrazone **5b** was obtained as a white solid (17.82 g, 39.2 mmol) in 68% yield. ^1H NMR (400 MHz, $\text{THF-}d_8$): δ 10.69 (s, 1H), 7.87 (s, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.25 (s, 1H), 4.45 – 4.34 (m, 2H), 2.96 – 2.85 (m, 1H), 1.31 – 1.22 (m, 18H). ^{13}C NMR (100 MHz, $\text{THF-}d_8$): δ 153.96 (s), 152.23 (s), 143.34 (s), 139.37 (s), 134.13 (s), 131.73 (q, J = 32 Hz), 126.39 (m), 125.36 (q, J = 270 Hz), 124.67 (s), 35.25 (s), 30.88 (s), 25.43 (s), 24.06 (s). ^{19}F NMR (377 MHz, $\text{THF-}d_8$): δ -63.60 (s, 3F). HR-MS (ESI) calcd. for $\text{C}_{23}\text{H}_{30}\text{F}_3\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 455.1980, found 455.2009.

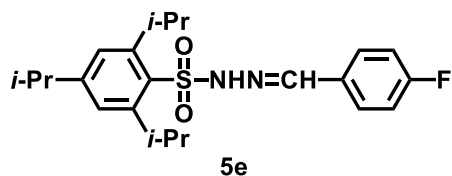


The hydrazone **5c** was prepared following the general procedure using 2,6-difluorobenzaldehyde (**4c**) (8.16 g, 57.4 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (17.14 g, 57.4 mmol). The resulting hydrazone **5c** was obtained as a white solid (16.31 g, 38.6 mmol) in 67% yield. ^1H NMR (400 MHz, THF- d_8): δ 10.61 (s, 1H), 7.95 (s, 1H), 7.33 – 7.26 (m, 1H), 7.23 (s, 2H), 6.95 – 6.90 (t, J = 8.6 Hz, 2H), 4.40 – 4.30 (m, 2H), 2.95 – 2.84 (m, 1H), 1.28 – 1.22 (m, 18H). ^{13}C NMR (100 MHz, THF- d_8): δ 161.90 (dd, J = 254 Hz, 7 Hz), 153.74 (s), 152.34 (s), 135.00 (s), 134.12 (s), 131.90 (t, J = 10 Hz), 124.53 (s), 112.87 (d, J = 27 Hz), 112.75 (m), 35.24 (s), 30.81 (s), 25.44 (s), 24.10 (s). ^{19}F NMR (377 MHz, THF- d_8): δ -113.38 (s, 2F). HR-MS (ESI) calcd. for $\text{C}_{22}\text{H}_{29}\text{F}_2\text{N}_2\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$ 423.1918, found 423.1922.

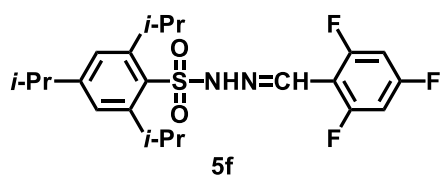


The hydrazone **5d** was prepared following the general procedure using 3,5-difluorobenzaldehyde (**4d**) (10.0 g, 70.3 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (21.0 g, 70.3 mmol). The resulting hydrazone **5d** was obtained as a white solid (22.37 g, 52.9 mmol) in 75% yield. ^1H NMR (400 MHz, THF- d_8): δ 10.70 (s, 1H), 7.76 (s, 1H), 7.25 – 7.17 (m, 4H), 6.95 – 6.89 (m, 1H), 4.41 – 4.31 (m, 2H), 2.96 – 2.86 (m, 1H), 1.30 – 1.23 (m, 18H). ^{13}C NMR (100 MHz, THF- d_8): δ 164.31 (dd, J = 233 Hz, 13 Hz), 154.02 (s), 152.25 (s), 142.45 (t, J = 3 Hz), 139.38 (t, J = 10 Hz), 134.06 (s), 124.69 (s), 110.34 (m), 105.36

(t, $J = 25$ Hz), 35.26 (s), 30.88 (s), 25.40 (s), 24.06 (s). ^{19}F NMR (377 MHz, $\text{THF-}d_8$): δ -110.97 (s, 2F). HR-MS (ESI) calcd. for $\text{C}_{22}\text{H}_{29}\text{F}_2\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 423.1918, found 423.1922.

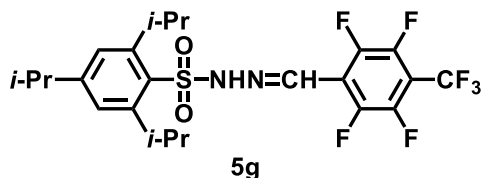


The hydrazone **5e** was prepared following the general procedure using 4-fluorobenzaldehyde (**4e**) (7.18 g, 57.8 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (17.27 g, 57.8 mmol). The resulting hydrazone **5e** was obtained as a white solid (15.95 g, 39.4 mmol) in 68% yield. ^1H NMR (400 MHz, $\text{THF-}d_8$): δ 10.37 (s, 1H), 7.80 (s, 1H), 7.62 – 7.58 (m, 2H), 7.23 (s, 2H), 7.09 – 7.04 (t, $J = 8.8$ Hz, 2H), 4.45 – 4.35 (m, 2H), 2.95 – 2.85 (m, 1H), 1.30 – 1.22 (m, 18H). ^{13}C NMR (100 MHz, $\text{THF-}d_8$): δ 164.67 (d, $J = 247$ Hz), 153.75 (s), 152.20 (s), 144.22 (s), 134.28 (s), 132.10 (d, $J = 3$ Hz), 129.76 (d, $J = 9$ Hz), 124.59 (s), 116.39 (d, $J = 22$ Hz), 35.24 (s), 30.83 (s), 25.45 (s), 24.09 (s). ^{19}F NMR (377 MHz, $\text{THF-}d_8$): δ -112.34 (s, 1F). HR-MS (ESI) calcd. for $\text{C}_{22}\text{H}_{30}\text{FN}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 405.2012, found 405.2012.

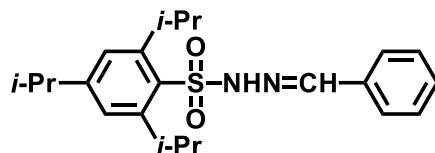


The hydrazone **5f** was prepared following the general procedure using 2,4,6-trifluorobenzaldehyde (**4f**) (8.17 g, 51.0 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (15.23 g, 51.0 mmol). The resulting hydrazone **5f** was obtained as a white solid (16.45 g, 37.3 mmol) in 73% yield. ^1H NMR (400 MHz, $\text{THF-}d_8$): δ 10.62 (s, 1H), 7.88 (s, 1H), 7.23 (s, 2H), 6.90 (t, $J = 8.8$ Hz, 2H), 4.38 – 4.28 (m, 2H), 2.95 – 2.85 (m, 1H), 1.27 – 1.22 (m, 18H). ^{13}C NMR (100 MHz, $\text{THF-}d_8$): δ 163.92 (dt, $J = 250$ Hz, 15 Hz), 162.30 (dm, $J = 256$ Hz), 153.78 (s), 152.35 (s), 134.15 (s), 134.09 (s), 124.54 (s), 109.95 (m), 101.76 (m), 35.26

(s), 30.82 (s), 25.42 (s), 24.09 (s). ^{19}F NMR (377 MHz, $\text{THF-}d_8$): δ -106.92 – -107.01 (m, 1F), -109.82 (t, J = 8.1 Hz, 2F). HR-MS (ESI) calcd. for $\text{C}_{22}\text{H}_{28}\text{F}_3\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 441.1824, found 441.1829.



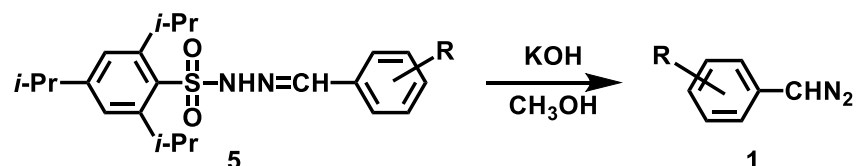
The hydrazone **5g** was prepared following the general procedure using 2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzaldehyde (**4g**) (11.70 g, 47.5 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (14.19 g, 47.5 mmol). The resulting hydrazone **5g** was obtained as a white solid (19.69 g, 37.3 mmol) in 78% yield. ^1H NMR (400 MHz, $\text{THF-}d_8$): δ 11.18 (s, 1H), 7.91 (s, 1H), 7.26 (s, 2H), 4.33 – 4.23 (m, 2H), 2.98 – 2.87 (m, 1H), 1.28 – 1.24 (m, 18H). ^{13}C NMR (100 MHz, $\text{THF-}d_8$): δ 154.29 (s), 152.41 (s), 145.82 (dm, J = 257 Hz), 145.28 (dm, J = 257 Hz), 133.60 (s), 131.67 (s), 124.73 (s), 122.17 (q, J = 272 Hz), 119.50 (t, J = 12 Hz), 109.26 (m), 35.28 (s), 30.91 (s), 25.32 (s), 24.03 (s). ^{19}F NMR (377 MHz, $\text{THF-}d_8$): δ -57.32 (t, J = 21.6 Hz, 3F), -142.00 (td, J = 17.0 Hz, 9.7 Hz, 2F), -143.55 – -143.83 (m, 2F). HR-MS (ESI) calcd. for $\text{C}_{23}\text{H}_{26}\text{F}_7\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 527.1603, found 527.1603.



Phenyl tosylhydrazone was prepared following the general procedure using phenyl benzaldehyde (7.11 g, 67.0 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazide (**3**) (20.0 g, 67.4 mmol). The resulting phenyl hydrazone was obtained as a white solid (19.70 g, 50.9 mmol) in 76% yield. ^1H NMR (400 MHz, $\text{THF-}d_8$): δ 10.35 (s, 1H), 7.80 (s, 1H), 7.57 – 7.55 (m, 2H), 7.29 – 7.23 (m, 5H), 4.47 – 4.36 (m, 2H), 2.95 – 2.86 (m, 1H), 1.31 – 1.22 (m, 18H).

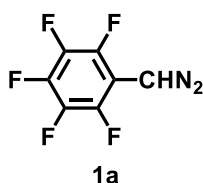
^{13}C NMR (100 MHz, $\text{THF-}d_8$): δ 153.69, 152.21, 145.41, 135.62, 134.33, 130.53, 129.38, 127.81, 124.55, 35.23, 30.82, 25.47, 24.10. HR-MS (ESI) calcd. for $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$ 387.2106, found 387.2106.

General procedure for the preparation of phenyl diazomethane 1a-1f and phenyl diazomethane

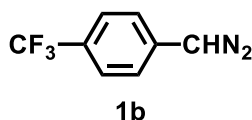


Potassium hydroxide (2 equiv.) was added into a solution of 2,4,6-triisopropylbenzenesulfonyl hydrazones (1 equiv.) in methanol (0.33 M) at room temperature. The resulting reaction mixture was stirred under reflux for 10 min until all of the starting material was consumed. After cooling to room temperature, the reaction mixture was poured into a beaker containing iced brine (50 mL). The resulting mixture was extracted with diethyl ether (3×50 mL) and the combined organic layer was washed with saturated aqueous NaHCO_3 (3×50 mL), brine (3×50 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure below 20 °C. The crude product was purified by vacuum distillation to afford pure phenyl diazomethane **1a-1f**.

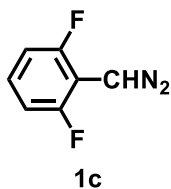
Caution: Diazo compounds are potentially explosive and toxic. It is recommended that all experiments using such compounds be conducted behind a blast shield and in a well-ventilated hood.



Phenyl diazomethane **1a** was synthesized following the general procedure using hydrazone **5a** (3.50 g, 7.34 mmol) and potassium hydroxide (0.823 g, 14.68 mmol). The phenyl diazomethane **1a** was obtained as a red liquid (0.887 g, 4.26 mmol) in 58% yield after vacuum distillation under 1.5 torr at 60 °C. ¹H NMR (400 MHz, C₆D₆): δ 3.82 (s, 1H). ¹³C NMR (100 MHz, C₆D₆): δ 140.85 (dm, *J* = 216 Hz), 138.28 (dm, *J* = 211 Hz), 137.44 (dm, *J* = 211 Hz), 107.00 (m), 37.94 (s). ¹⁹F NMR (377 MHz, C₆D₆): δ -147.58 – -147.66 (m, 2F), -163.47 (tt, *J* = 21.0 Hz, 3.2 Hz, 1F), -163.97 (td, *J* = 21.0 Hz, 6.3 Hz, 2F).

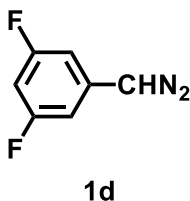


Phenyl diazomethane **1b** was synthesized following the general procedure using hydrazone **5b** (2.50 g, 5.50 mmol) and potassium hydroxide (0.62 g, 11.00 mmol). The phenyl diazomethane **1b** was obtained as a red liquid (0.96 g, 5.15 mmol) in 93% yield after vacuum distillation under 0.6 torr at 25 °C. ¹H NMR (400 MHz, C₆D₆): δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.27 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 1H). ¹³C NMR (100 MHz, C₆D₆): δ 135.04 (s), 126.06 (q, *J* = 4 Hz), 125.65 (q, *J* = 32 Hz), 125.17 (q, *J* = 269 Hz), 121.12 (s), 47.48 (s). ¹⁹F NMR (377 MHz, C₆D₆): δ -62.12 (s, 3F).

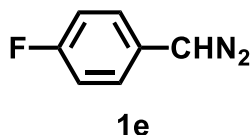


Phenyl diazomethane **1c** was synthesized following the general procedure using hydrazone **5c** (3.00 g, 7.10 mmol) and potassium hydroxide (0.796 g, 14.20 mmol). The phenyl diazomethane **1c** was obtained as a red liquid (0.45 g, 2.92 mmol) in 41% yield after vacuum distillation under 0.6 torr at 25 °C. ¹H NMR (400 MHz, C₆D₆): δ 6.41 – 6.24 (m, 3H), 4.24 (s, 1H). ¹³C

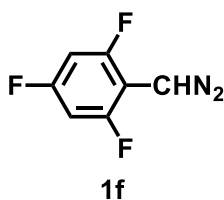
NMR (100 MHz, C₆D₆): δ 157.34 (dd, J = 237 Hz, 8 Hz), 123.99 (t, J = 9 Hz), 111.38 (m), 108.56 (t, J = 16 Hz), 38.19 (s). ¹⁹F NMR (377 MHz, C₆D₆): δ -117.29 – -117.34 (m, 2F).



Phenyl diazomethane **1d** was synthesized following the general procedure using hydrazone **5d** (3.00 g, 7.10 mmol) and potassium hydroxide (0.796 g, 14.20 mmol). The phenyl diazomethane **1d** was obtained as a red liquid (0.86 g, 5.58 mmol) in 78% yield after vacuum distillation under 0.6 torr at 25 °C. ¹H NMR (400 MHz, C₆D₆): δ 6.17 (tt, J = 9.0 Hz, 2.2 Hz, 1H), 5.96 – 5.93 (m, 2H), 3.81 (s, 1H). ¹³C NMR (100 MHz, C₆D₆): δ 164.05 (dd, J = 231 Hz, 14 Hz), 134.79 (t, J = 12 Hz), 103.91 (m), 98.89 (td, J = 26 Hz, 8 Hz), 47.96 (s). ¹⁹F NMR (377 MHz, C₆D₆): δ -110.04 (t, J = 8.4 Hz, 2F).

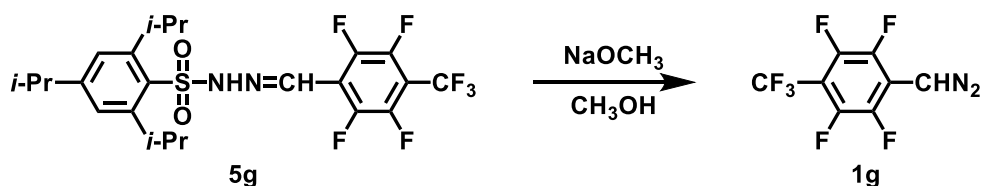


Phenyl diazomethane **1e** was synthesized following the general procedure using hydrazone **5e** (5.00 g, 12.36 mmol) and potassium hydroxide (1.38 g, 24.60 mmol). The phenyl diazomethane **1e** was obtained as a red liquid (0.900 g, 6.61 mmol) in 53% yield after vacuum distillation under 0.6 torr at 25 °C. ¹H NMR (400 MHz, C₆D₆): δ 6.68 (t, J = 8.7 Hz, 2H), 6.30 – 6.26 (m, 2H), 4.00 (s, 1H). ¹³C NMR (100 MHz, C₆D₆): δ 160.37 (d, J = 241 Hz), 125.73 (d, J = 3 Hz), 122.68 (d, J = 7 Hz), 116.28 (d, J = 23 Hz), 46.33 (s). ¹⁹F NMR (377 MHz, C₆D₆): δ -119.70 (s, 1F).



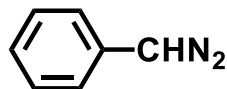
Phenyl diazomethane **1f** was synthesized following the general procedure using hydrazone **5f** (5.00 g, 11.35 mmol) and potassium hydroxide (1.27 g, 22.60 mmol). The phenyl diazomethane **1f** was obtained as a red liquid (0.790 g, 4.59 mmol) in 40% yield after vacuum distillation under 3 torr at 54 °C. ¹H NMR (400 MHz, C₆D₆): δ 6.18 (t, *J* = 8.8 Hz, 2H), 4.20 (s, 1H). ¹³C NMR (100 MHz, C₆D₆): δ 159.21 (dt, *J* = 275 Hz, 15 Hz), 156.85 (dm, *J* = 271 Hz), 104.73 (td, *J* = 16 Hz, 2 Hz), 100.53 (tm, *J* = 29 Hz), 37.44 (s). ¹⁹F NMR (377 MHz, C₆D₆): δ -114.68 (dd, *J* = 5.7 Hz, 2.8 Hz, 2F), -115.52 (tt, *J* = 8.7 Hz, 2.8 Hz, 1F).

Synthesis of phenyl diazomethane 1g



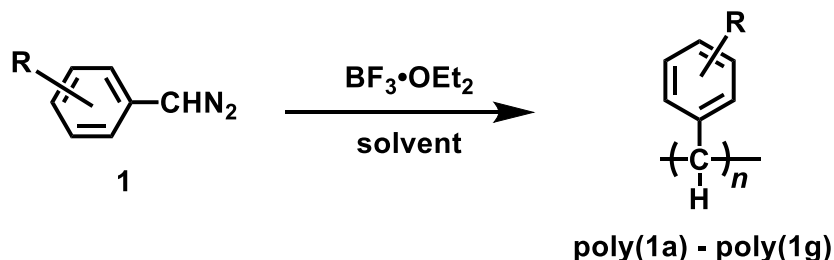
Under an atmosphere of nitrogen, freshly cut sodium (0.29 g, 12.61 mmol) was carefully added portion-wise into methanol (12.5 mL) at room temperature, and the resulting mixture was stirred at room temperature until sodium was dissolved. After hydrazone **5g** (6.50 g, 12.34 mmol) was added, the mixture was stirred at room temperature for 30 min. Cold brine (20 mL) was added and the mixture was extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed with brine (3 × 100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure below 20 °C. The purification was carried out by vacuum distillation under 0.6 torr at 70 °C to afford an orange liquid (2.23 g, 8.64 mmol) in 70% yield. ¹H NMR (400 MHz, C₆D₆): δ 3.95 (s, 1H). ¹³C NMR (100 MHz, C₆D₆): δ 144.29 (dm, *J* = 256 Hz), 142.28 (dm, *J* = 246 Hz), 121.95 (q, *J* = 272 Hz), 117.26 (t, *J* = 14 Hz), 102.62 (m), 40.11

(s). ^{19}F NMR (377 MHz, C_6D_6): δ -55.73 (t, J = 21.2 Hz, 3F), -143.33 – -143.61 (m, 2F), -146.26 – -146.37 (m, 2F).

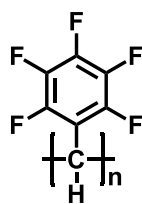


Phenyl diazomethane was synthesized following the general procedure using phenyl tosylhydrazone (3.0 g, 7.76 mmol) and potassium hydroxide (0.871 g, 15.52 mmol). Phenyl diazomethane was obtained as a red liquid (0.47 g, 3.97 mmol) in 51% yield after vacuum distillation under 1.5 torr at 25 °C. ^1H NMR (400 MHz, C_6D_6): δ 7.02 (t, J = 7.4 Hz, 2H), 6.82 (t, J = 7.4 Hz, 1H), 6.60 – 6.58 (m, 2H), 4.12 (s, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 130.10, 129.30, 124.04, 121.58, 47.00.

General procedure for the synthesis of poly(1a)-poly(1g) and poly(phenyl methylene)

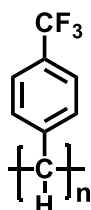


Under a nitrogen atmosphere, a solution of phenyl diazomethane **1** (0.48 M) was treated with $\text{BF}_3 \cdot \text{OEt}_2$ at room temperature. After stirring at room temperature for 10 min, the reaction mixture was poured into excess of methanol/water solution (200 mL) (methanol: water = 4:1). The precipitate was collected by filtration, and then washed with methanol (50 mL) to afford the desired homopolymer poly(**1a**) – poly(**1g**).



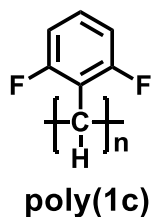
poly(1a)

Poly(**1a**) was synthesized following the general procedure using a solution of phenyl diazomethane **1a** (1.00 g, 4.80 mmol) in 1,3-bis(trifluoromethyl)benzene (10 mL) (0.48 M) and $\text{BF}_3 \cdot \text{OEt}_2$ (6 μl , 49 μmol). The resulting polymer was obtained as a white solid (0.639 g, 3.55 mmol) in 74% yield. ^1H NMR (400 MHz, C_6F_6): δ 3.96 (bs, 1H). ^{13}C NMR (100 MHz, C_6F_6): δ 147.38, 145.22, 142.88, 109.98, 43.03. ^{19}F NMR (377 MHz, C_6F_6): δ -133.97 (br, 2F), -149.90 (bs, 1F), -159.84 (bs, 2F). Anal. calcd for C_7HF_5 : C, 46.69; H, 0.56; Found: C, 48.24; H 0.82.

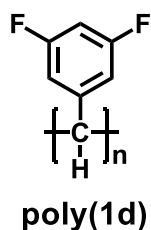


poly(1b)

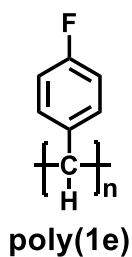
Poly(**1b**) was synthesized following the general procedure using a solution of phenyl diazomethane **1b** (0.70 g, 3.75 mmol) in 1,3-bis(trifluoromethyl)benzene (7.8 mL) (0.48 M) and $\text{BF}_3 \cdot \text{OEt}_2$ (6 μl , 49 μmol). The resulting polymer was obtained as a white solid (0.342 g, 2.16 mmol) in 57% yield. ^1H NMR (400 MHz, C_6F_6): δ 7.11 (bs, 4H), 3.00 (bs, 1H). ^{13}C NMR (100 MHz, C_6F_6): δ 141.21, 131.23, 131.23, 123.25, 123.25, 50.19. ^{19}F NMR (377 MHz, C_6F_6): δ -62.91 (bs, 3F). Anal. calcd for $\text{C}_8\text{H}_3\text{F}_3$: C, 60.77; H, 3.19; Found: C, 62.70; H 3.44.



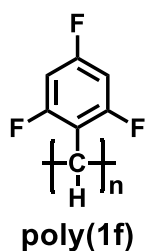
Poly(**1c**) was synthesized following the general procedure using a solution of phenyl diazomethane **1c** (0.75 g, 4.86 mmol) in benzene (10.1 mL) (0.48 M) and $\text{BF}_3 \cdot \text{OEt}_2$ (6 μl , 49 μmol). The resulting polymer was obtained as a white solid (0.321 g, 2.54 mmol) in 52% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.74 (br, 3H), 3.70 (br, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 163.00, 128.72, 116.48, 111.62, 43.91. ^{19}F NMR (377 MHz, CD_2Cl_2): δ -104.24 (br, 2F).



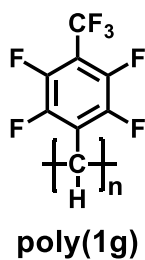
Poly(**1d**) was synthesized following the general procedure using a solution of phenyl diazomethane **1d** (0.86 g, 5.58 mmol) in 1,3-bis(trifluoromethyl)benzene (11.6 mL) (0.48 M) and $\text{BF}_3 \cdot \text{OEt}_2$ (6 μl , 49 μmol). The resulting polymer was obtained as a white solid (0.556 g, 4.41 mmol) in 79% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.78 (br, 2H), 5.59 (bs, 1H), 2.72 (bs, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.95, 140.44, 115.07, 104.04, 50.21. ^{19}F NMR (377 MHz, CD_2Cl_2): δ -110.23 (bs, 2F).



Poly(**1e**) was synthesized following the general procedure using a solution of phenyl diazomethane **1e** (0.67 g, 4.92 mmol) in benzene (10.2 mL) (0.48 M) and $\text{BF}_3 \cdot \text{OEt}_2$ (6 μl , 49 μmol). The resulting polymer was obtained as a white solid (0.298 g, 2.76 mmol) in 56% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.48 (bs, 4H), 2.76 (bs, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.90, 134.29, 134.29, 113.95, 49.61. ^{19}F NMR (377 MHz, CD_2Cl_2): δ -116.29 (bs, 1F).

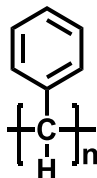


Poly(**1f**) was synthesized following the general procedure using a solution of phenyl diazomethane **1f** (0.67 g, 3.89 mmol) in toluene (8.1 mL) (0.48 M) and $\text{BF}_3 \cdot \text{OEt}_2$ (6 μl , 49 μmol). The resulting polymer was obtained as a white solid (0.283 g, 1.96 mmol) in 50% yield. ^1H NMR (400 MHz, CD_2Cl_2): δ 6.19 (br, 2H), 3.83 (br, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.73, 112.87, 111.69, 100.49, 42.70. ^{19}F NMR (377 MHz, CD_2Cl_2): δ -100.95 (br, 2F), -110.71 (bs, 1F).



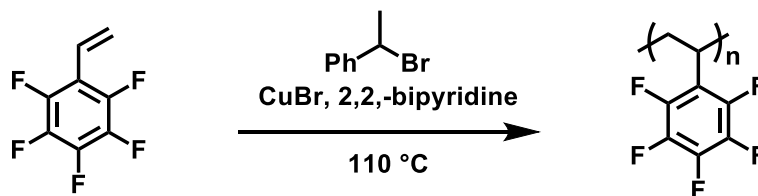
Poly(**1g**) was synthesized following the general procedure using a solution of phenyl diazomethane **1g** (0.56 g, 2.17 mmol) in 1,3-bis(trifluoromethyl)benzene (4.5 mL) (0.48 M) and $\text{BF}_3 \cdot \text{OEt}_2$ (6 μl , 49 μmol). The resulting polymer was obtained as a white solid (0.371 g, 1.61 mmol) in 74% yield. ^1H NMR (400 MHz, C_6F_6): δ 3.51 (br, 1H). ^{13}C NMR (100 MHz,

C₆F₆): δ 144.32, 144.32, 119.70, 112.54, 112.54, 42.72. ¹⁹F NMR (377 MHz, C₆F₆): δ -56.32 (bs, 3F), -135.35 (bs, 4F).



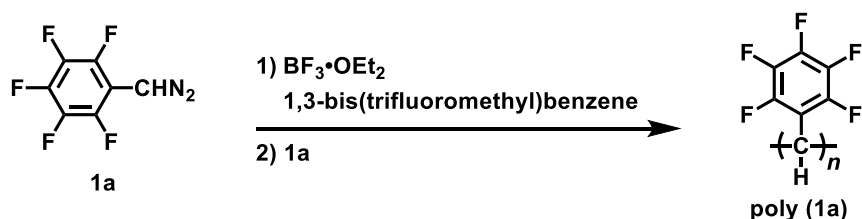
Poly(phenyl methylene) was synthesized following the general procedure using a solution of phenyl diazomethane (0.47 g, 3.97 mmol) in 1,3-bis(trifluoromethyl)benzene (8.2 mL) (0.48 M) and BF₃·OEt₂ (6 μ l, 49 μ mol). The resulting polymer was obtained as a white solid (0.219 g, 2.43 mmol) in 61% yield. ¹H NMR (400 MHz, CD₂Cl₂): δ 6.93 (bs, 5H), 3.20 (bs, 1H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 141.74, 139.83, 132.93, 126.54, 51.15.

Synthesis of poly(2,3,4,5,6-pentafluorostyrene)



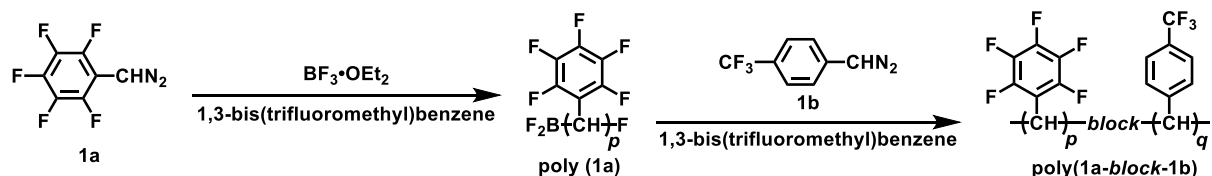
Poly(2,3,4,5,6-pentafluorostyrene) was prepared according to a literature procedure.⁴ To a 50 mL Schlenk flask, pentafluorostyrene (3.80 mL, 27.50 mmol), 1-phenylethyl bromide (0.070 mL, 0.513 mmol), CuBr (0.074 g, 0.515 mmol) and 2,2'-bipyridine (0.162 g, 1.03 mmol) were added. The reaction mixture was degassed by three freeze-pump-thaw cycles and stirred at 110 °C for 3 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, diluted with THF (20 mL), filtered through celite 245, and then precipitated into an excess of methanol (300 mL). The precipitate was collected by filtration, and then washed with methanol (100 mL) to afford poly(2,3,4,5,6-pentafluorostyrene) (4.72 g, 24.33 mmol) in 88% yield. Spectroscopic data recorded for the product were in accord with literature values.

Chain extension polymerization procedure



Under a nitrogen atmosphere, a solution of phenyl diazomethane **1a** (0.25 g, 1.20 mmol) and anisole (15 mg, 0.14 mmol) as internal standard in 1,3-bis(trifluoromethyl)benzene (2.5 mL) (0.48 M) was treated with $\text{BF}_3 \cdot \text{OEt}_2$ (6 μL , 49 μmol) at room temperature. The resulting reaction mixture was stirred for 10 min at room temperature, at which point an aliquot was removed for analysis. ^1H NMR and GPC analysis of the aliquot provided the following data: quantitative consumption of monomer, $M_n = 9.9$ kDa, $D = 1.09$. Another solution of phenyl diazomethane **1a** (0.50 g, 2.40 mmol) in 1,3-bis(trifluoromethyl)benzene (5.0 mL) (0.48 M) was then added into the reaction mixture via syringe, and then stirred for 30 min at room temperature. The reaction mixture was poured into excess of methanol/water solution (200 mL) (methanol: water = 4:1 v/v). The precipitate was collected by filtration, and then washed with methanol (50 mL) to afford the chain-extended poly(**1a**) as a white solid (0.40g, 2.22 mmol) in 66% yield.

Block copolymerization procedure



Under a nitrogen atmosphere, a solution of phenyl diazomethane **1** (0.25 g, 1.20 mmol) and anisole (15 mg, 0.14 mmol) as internal standard in 1,3-bis(trifluoromethyl)benzene (2.5 mL) (0.48 M) was treated with $\text{BF}_3 \cdot \text{OEt}_2$ (6 μL , 49 μmol) at room temperature. The resulting reaction mixture was stirred for 10 min at room temperature, at which point an aliquot was removed for

analysis. ^1H NMR and GPC analysis of the aliquot provided the following data: quantitative consumption of monomer, $M_n = 8.6$ kDa, $D = 1.17$. A solution of phenyl diazomethane **1b** (0.447 g, 2.40 mmol) in 1,3-bis(trifluoromethyl)benzene (5.0 mL) (0.48 M) was then added into the reaction mixture by syringe, and then stirred for 30 min at room temperature. The reaction mixture was poured into excess of methanol/water solution (200 mL) (methanol: water = 4:1 v/v). The precipitate was collected by filtration, and then washed with methanol (50 mL) to afford the block copolymer poly(**1a-block-1b**) as a white solid (0.362 g, 2.18 mmol) in 65% yield. Conversion of **1b** = 100%, $M_n = 10.8$ kDa, $D = 1.07$. ^1H NMR (400 MHz, C_6F_6): δ 7.02 (bs, 8H), 2.99 (bs, 3H). ^{13}C NMR (100 MHz, C_6F_6): δ 147.61, 145.26, 142.90, 141.20, 131.17, 123.36, 109.98, 50.61, 42.24. ^{19}F NMR (377 MHz, C_6F_6): -63.01, -134.10, -150.18, -160.06. Anal. calcd for $\text{C}_{22}\text{H}_7\text{F}_{13}$: C, 50.98; H, 1.36; Found: C, 57.04; H 2.18.

SEC Data

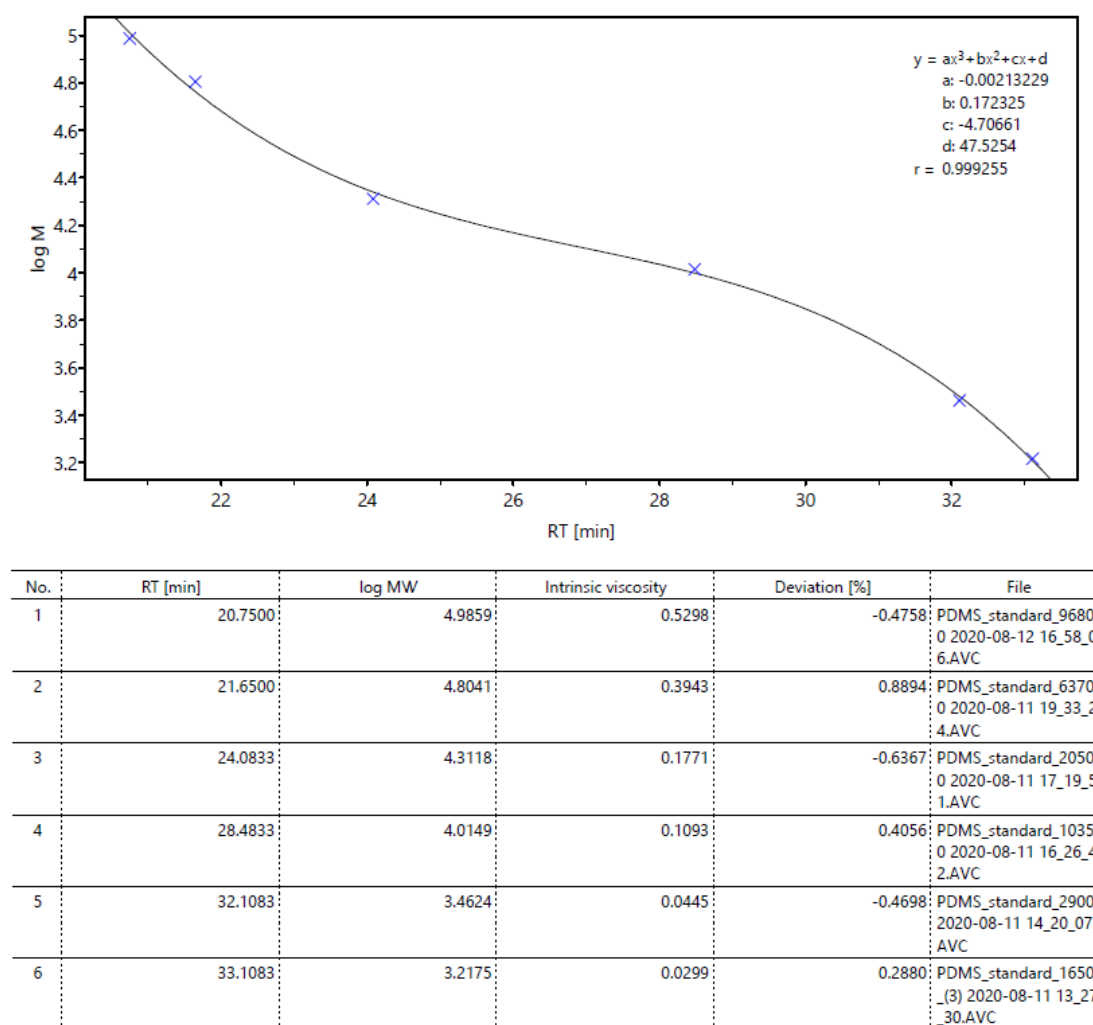


Figure S1. Calibration curve used for SEC analysis. Chloropentafluorobenzene was used as the eluent and the data are reported against poly(dimethylsiloxane) standards.

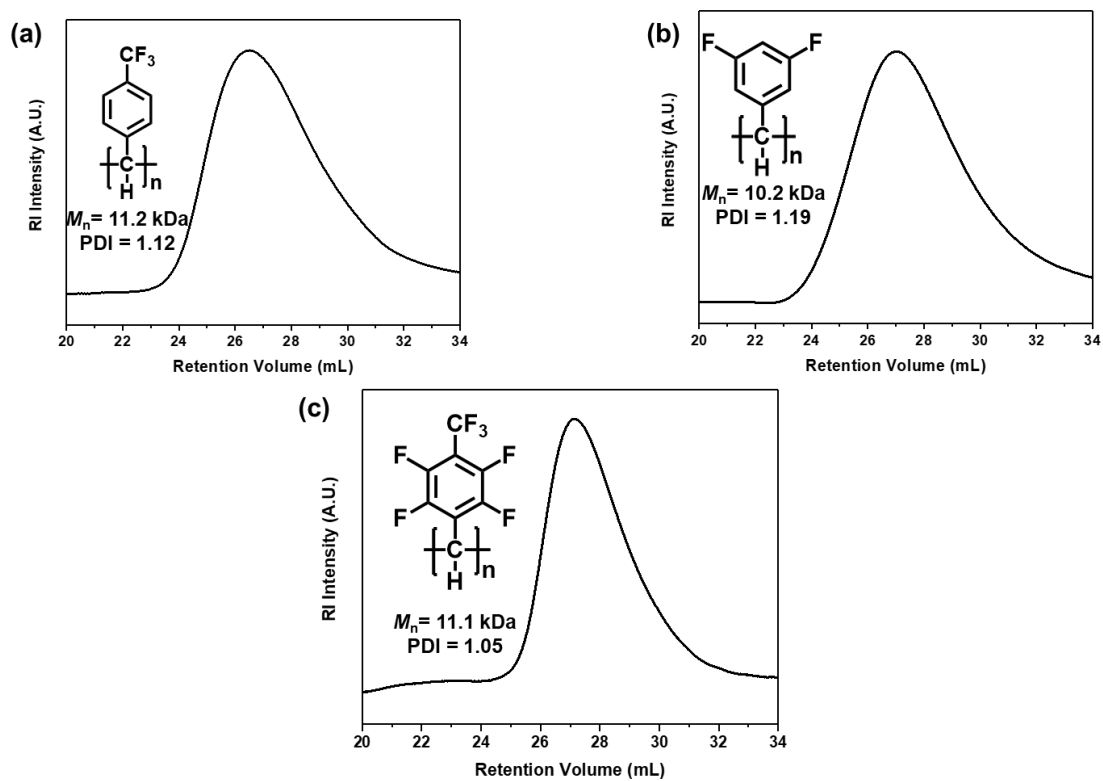


Figure S2. SEC data recorded for (a) poly(**1b**), (b) poly(**1d**) and (c) poly(**1g**) obtained with chloropentafluorobenzene as the eluent with a flow rate of 1.0 mL min^{-1} against poly(dimethylsiloxane) standards.

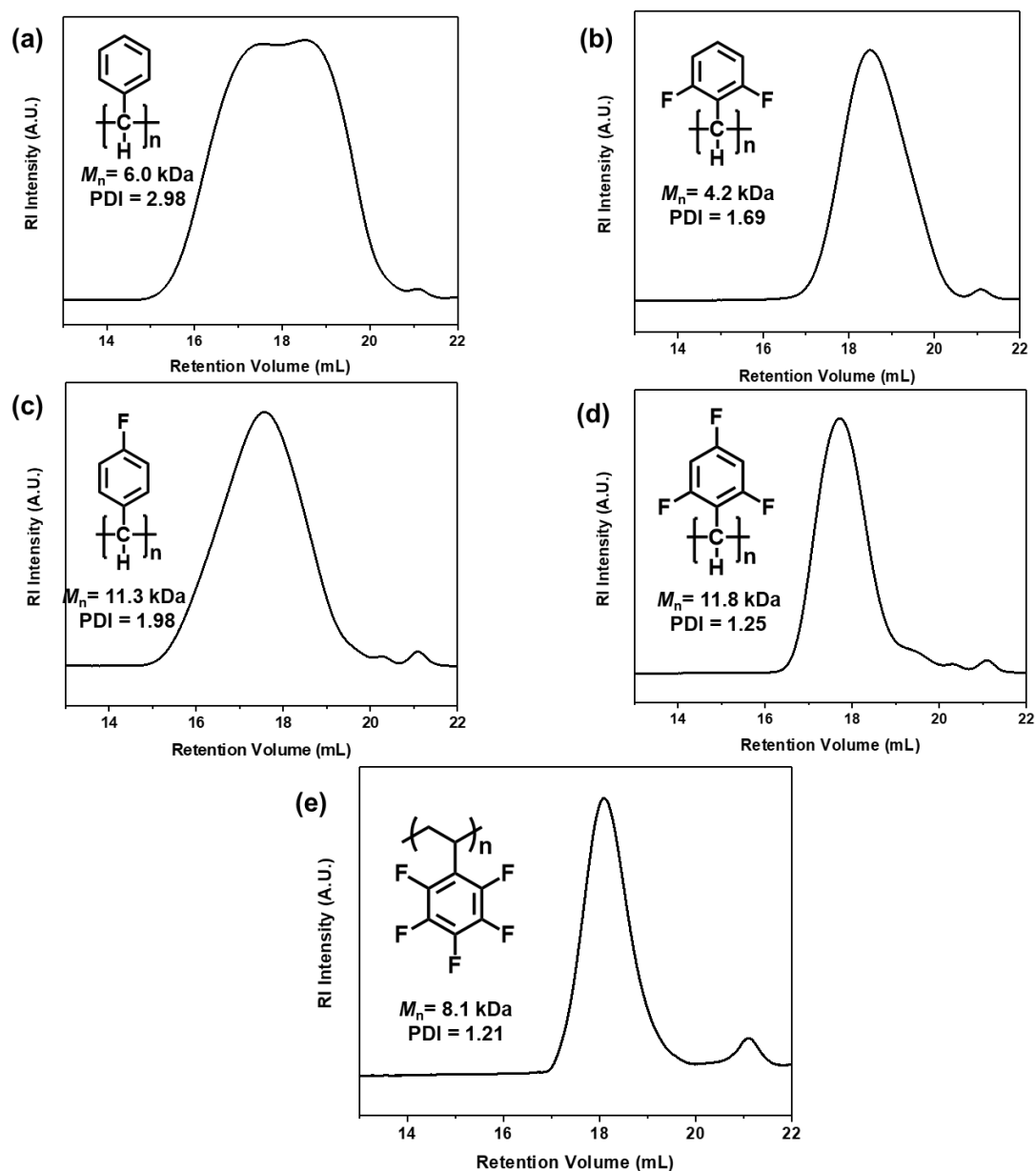


Figure S3. SEC data recorded for (a) poly(phenyl methylene), (b) poly(**1c**), (c) poly(**1e**), (d) poly(**1f**) and (e) poly(2,3,4,5,6-pentafluorostyrene) obtained with THF as the eluent with a flow rate of 0.8 mL min^{-1} against poly(styrene) standards.

TGA and DSC Data

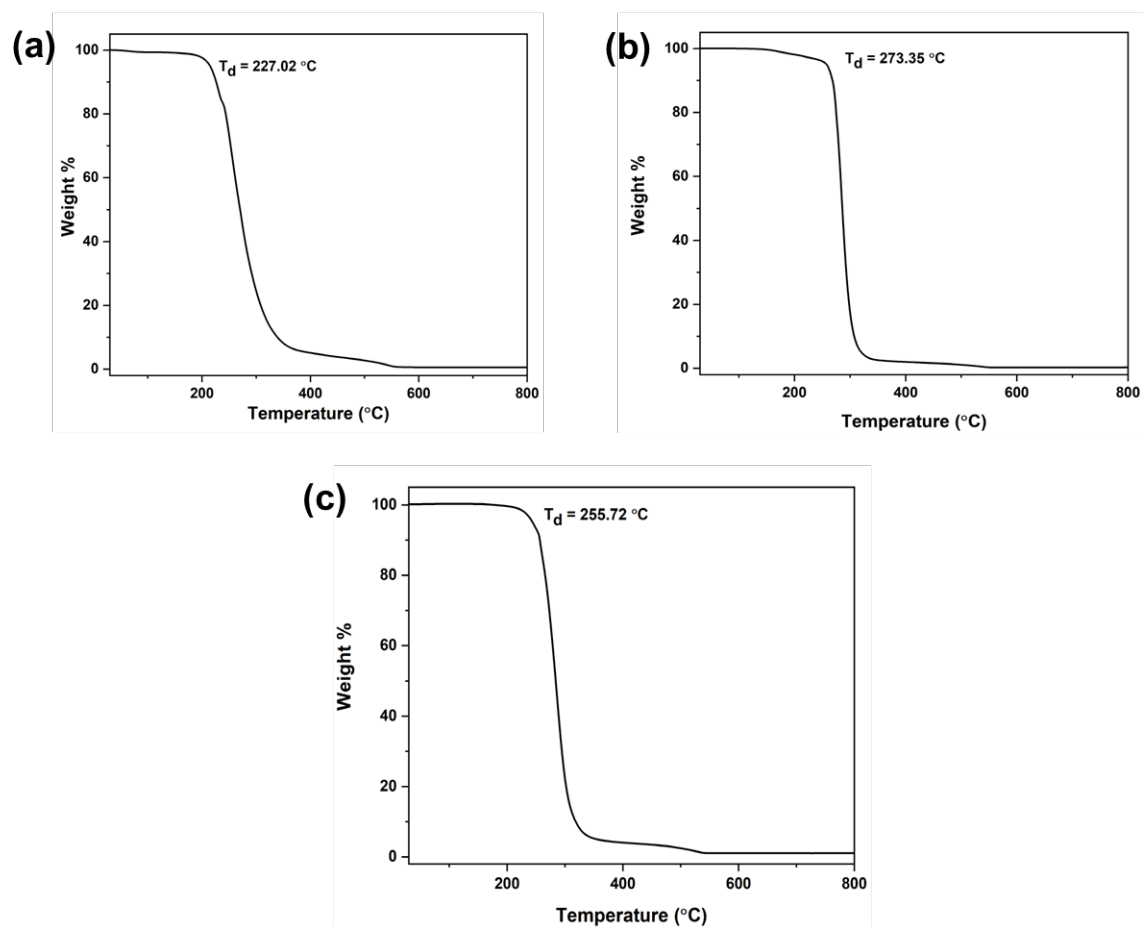


Figure S4. TGA data recorded for (a) poly(**1a**), (b) poly(**1b**) and (c) poly(**1a-block-1b**) as obtained under an atmosphere of nitrogen and at a heating rate of 10 °C min⁻¹. The T_d value was determined from the onset of mass loss.

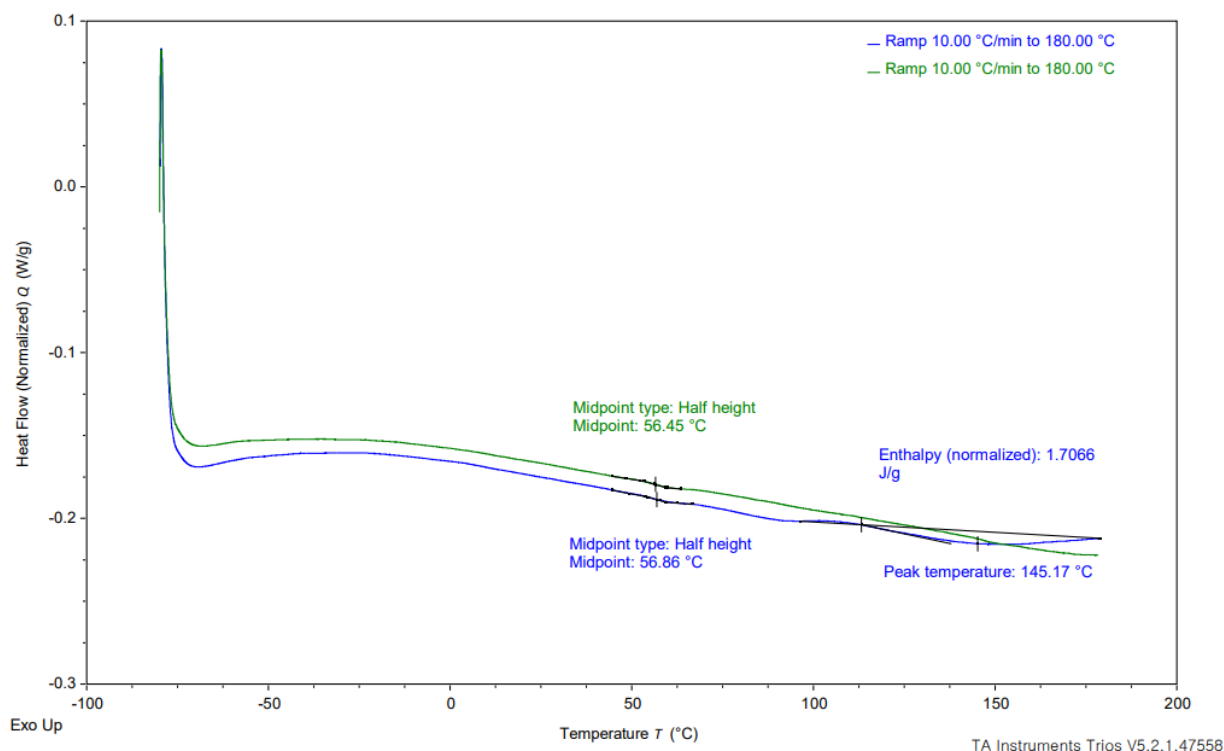


Figure S5. DSC thermogram recorded for poly(**1a**) (blue line: first heating, green line: second heating). Data were recorded at a heating rate of 10 °C min⁻¹ under an atmosphere of nitrogen.

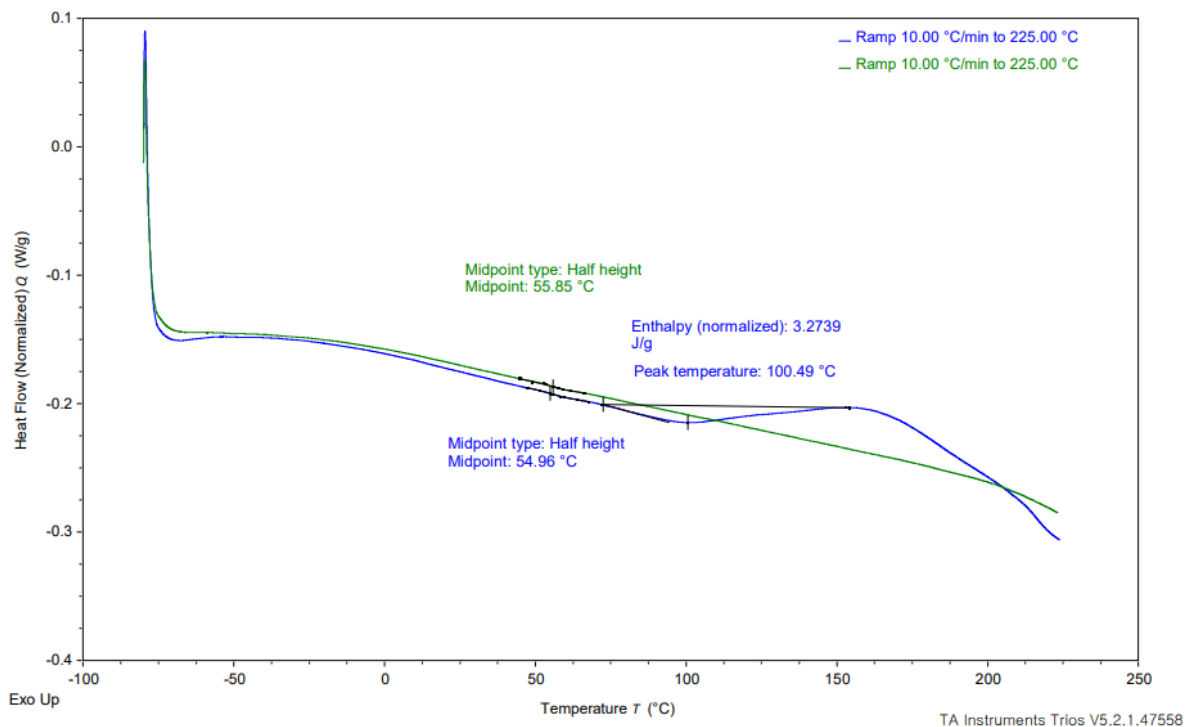


Figure S6. DSC thermogram recorded for poly(**1b**) (blue line: first heating, green line: second heating). Data were recorded at a heating rate of 10 °C min⁻¹ under an atmosphere of nitrogen.

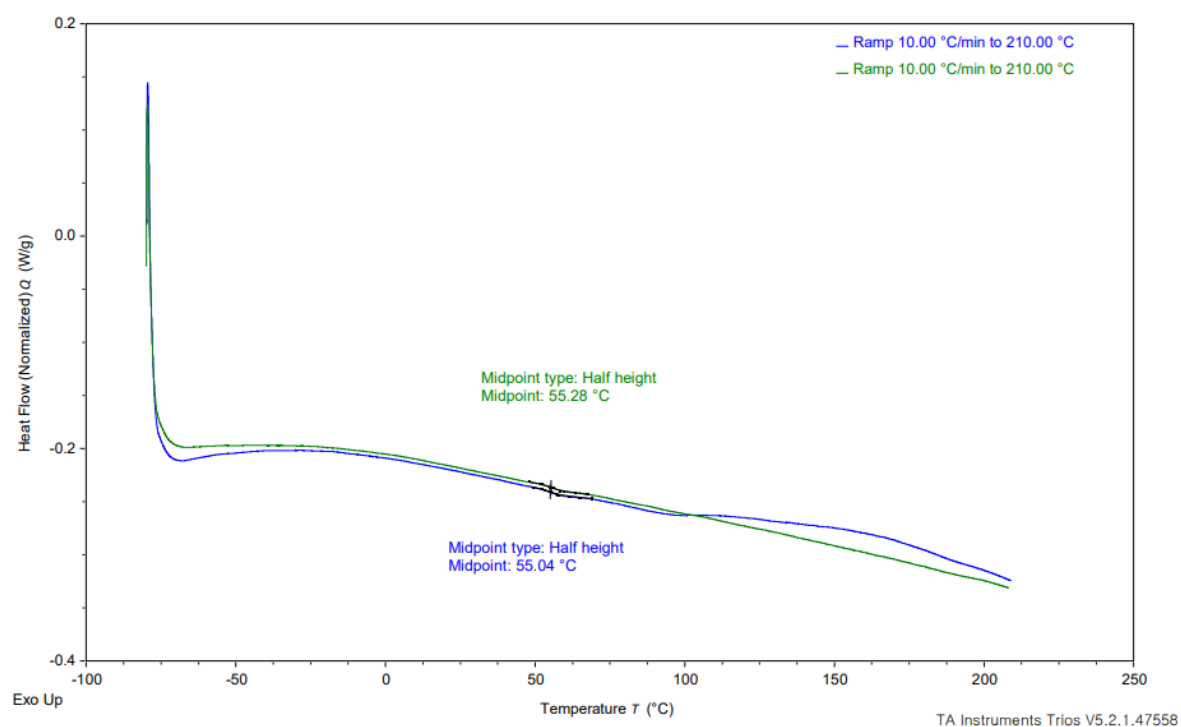


Figure S7. DSC thermogram recorded for poly(**1a-block-1b**) (blue line: first heating, green line: second heating). Data were recorded at a heating rate of 10 °C min⁻¹ under an atmosphere of nitrogen

Contact Angle Measurement Data

The thin films which were used for contact angle measurements were prepared via spin coating. A solution of the polymer in their respective solvents was prepared (5 mg mL⁻¹), dropped onto a silica wafer, and spin-coated. The film was then dried under vacuum for 18 h for conditioning. The contact angles were then measured at 20 °C with water or diiodomethane using the sessile drop method. For the dynamic contact angle measurements, the needle tip was kept in contact with the water droplet. In a separate set of experiments, poly (**1a**), poly (**1b**), and poly (**1a-block-1b**) were separately spin-coated and then annealed at 80 °C for 3 h prior to conducting the contact angle measurements. All measurements were repeated, and average values are reported.

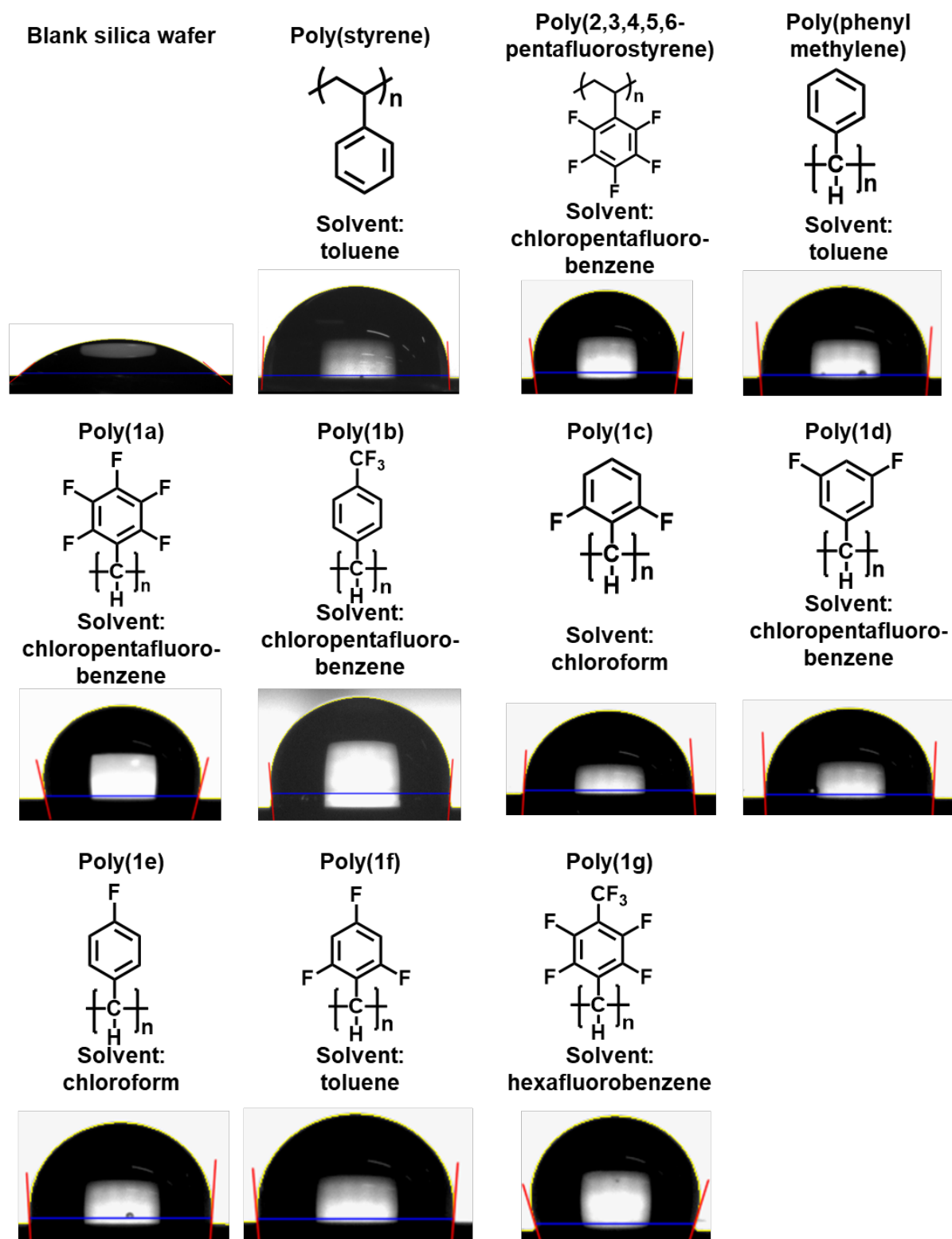


Figure S8. Photographs of the water droplets that were used to measure the static contact angles of a blank silica wafer, poly(styrene), poly(2,3,4,5,6-pentafluorostyrene), poly(phenyl methylene), and poly(1a – g).

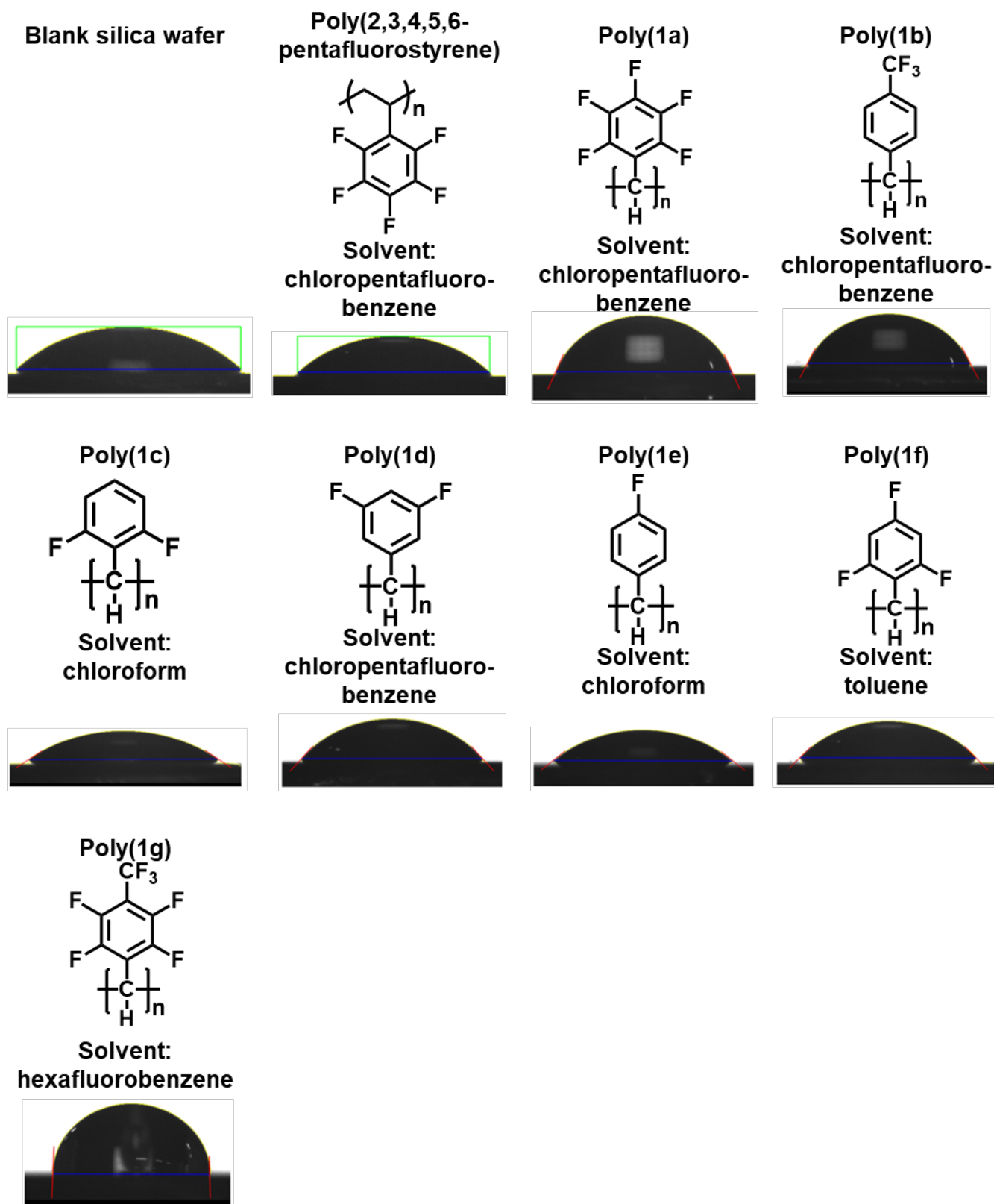


Figure S9. Photographs of the diiodomethane droplets that were used to measure the static contact angles of a blank silica wafer, poly(2,3,4,5,6-pentafluorostyrene), and poly(1a – 1g).

NMR Spectra

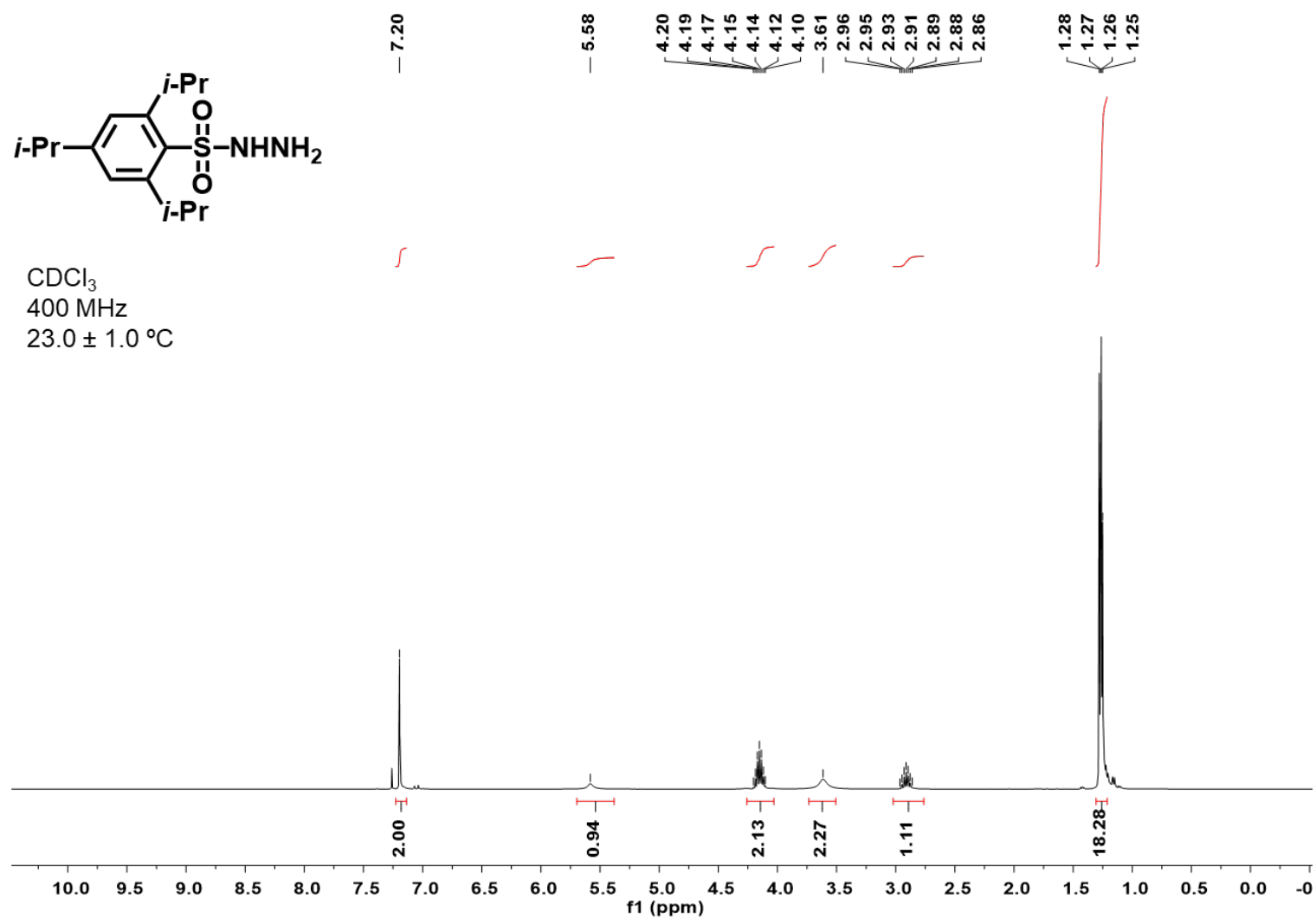


Figure S10. ¹H NMR spectrum of **3** as recorded in CDCl₃ at 23 °C.

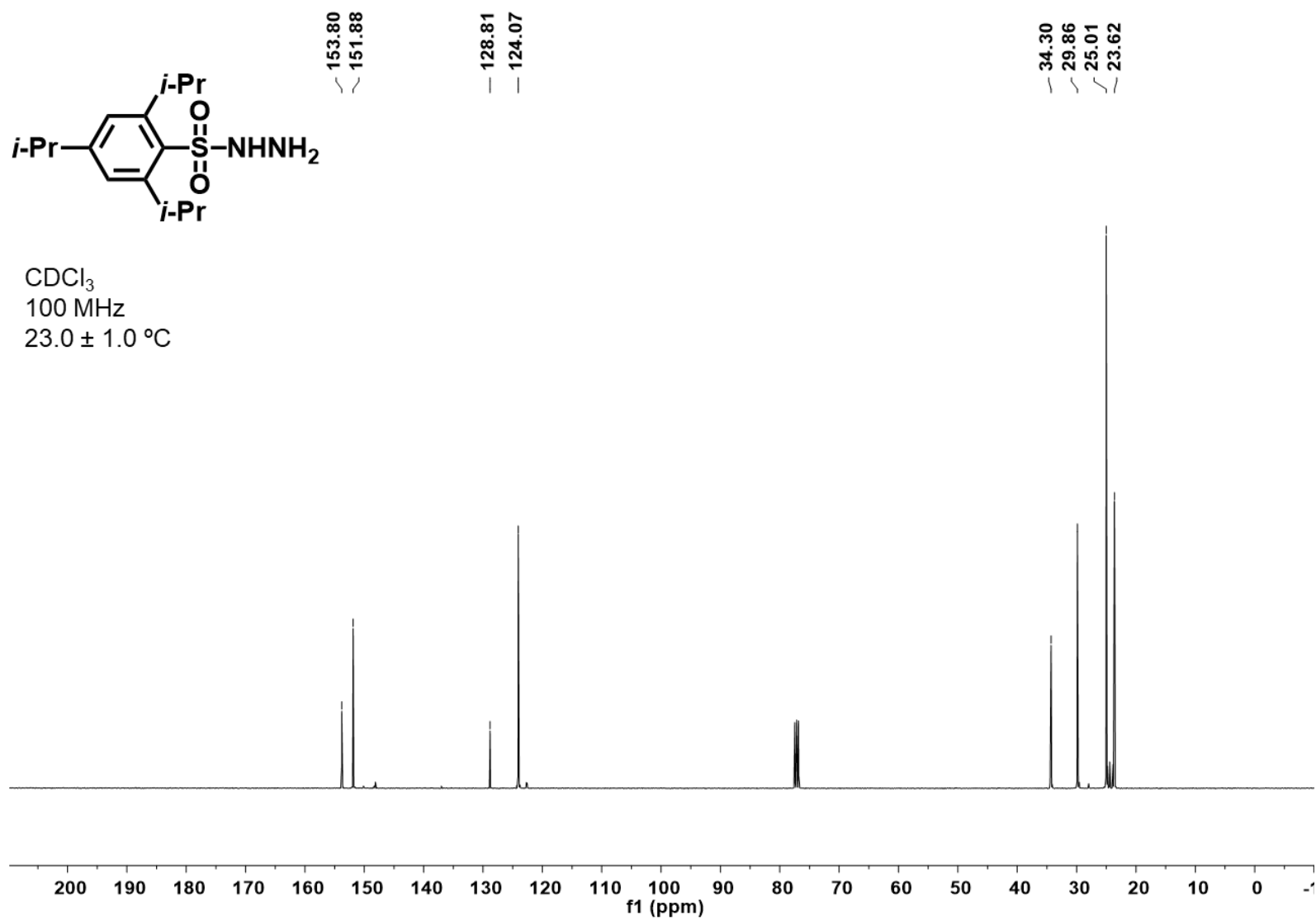


Figure S11. ¹³C NMR spectrum of **3** as recorded in CDCl₃ at 23 °C.

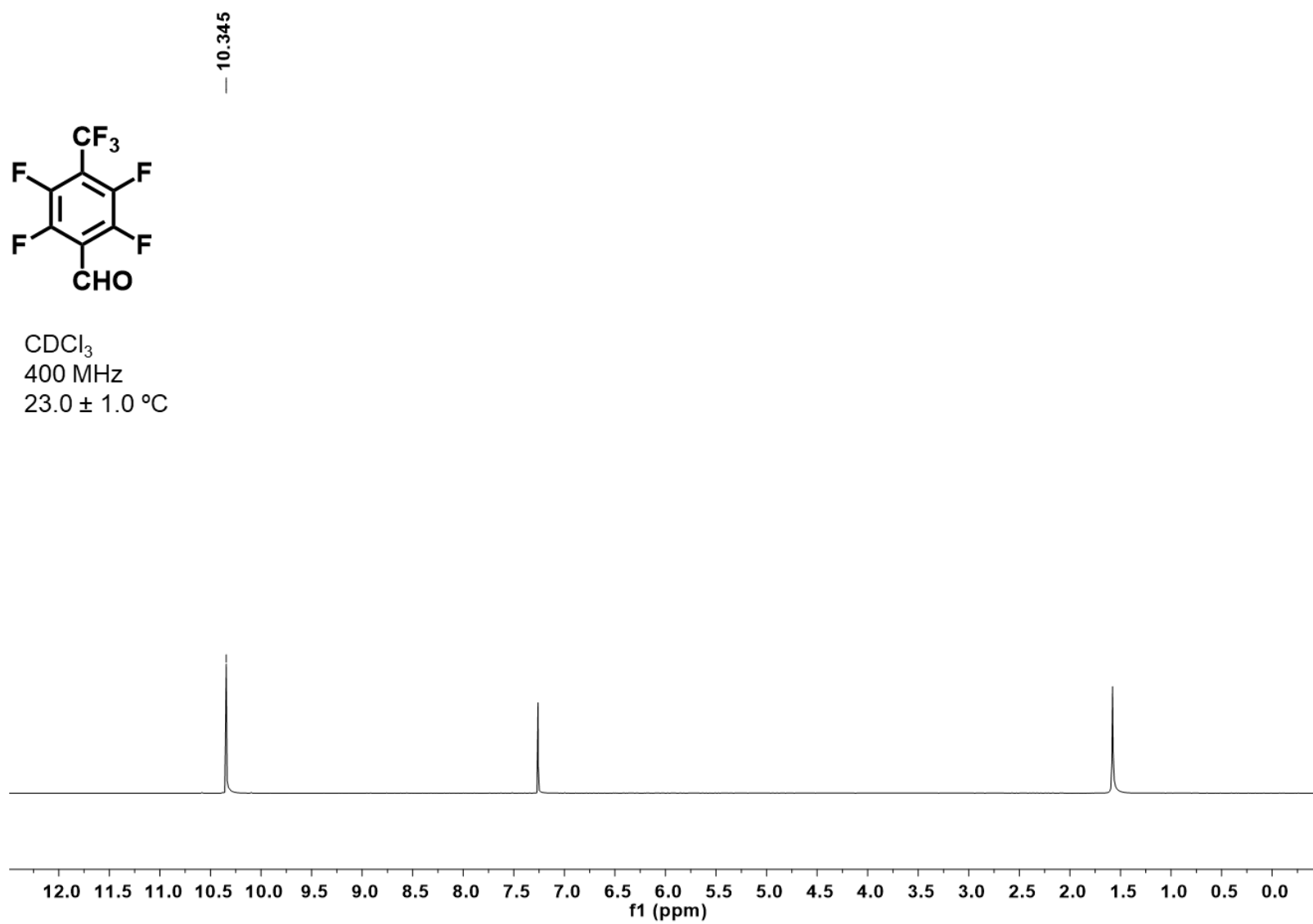


Figure S12. ¹H NMR spectrum of **4g** as recorded in CDCl₃ at 23 °C.

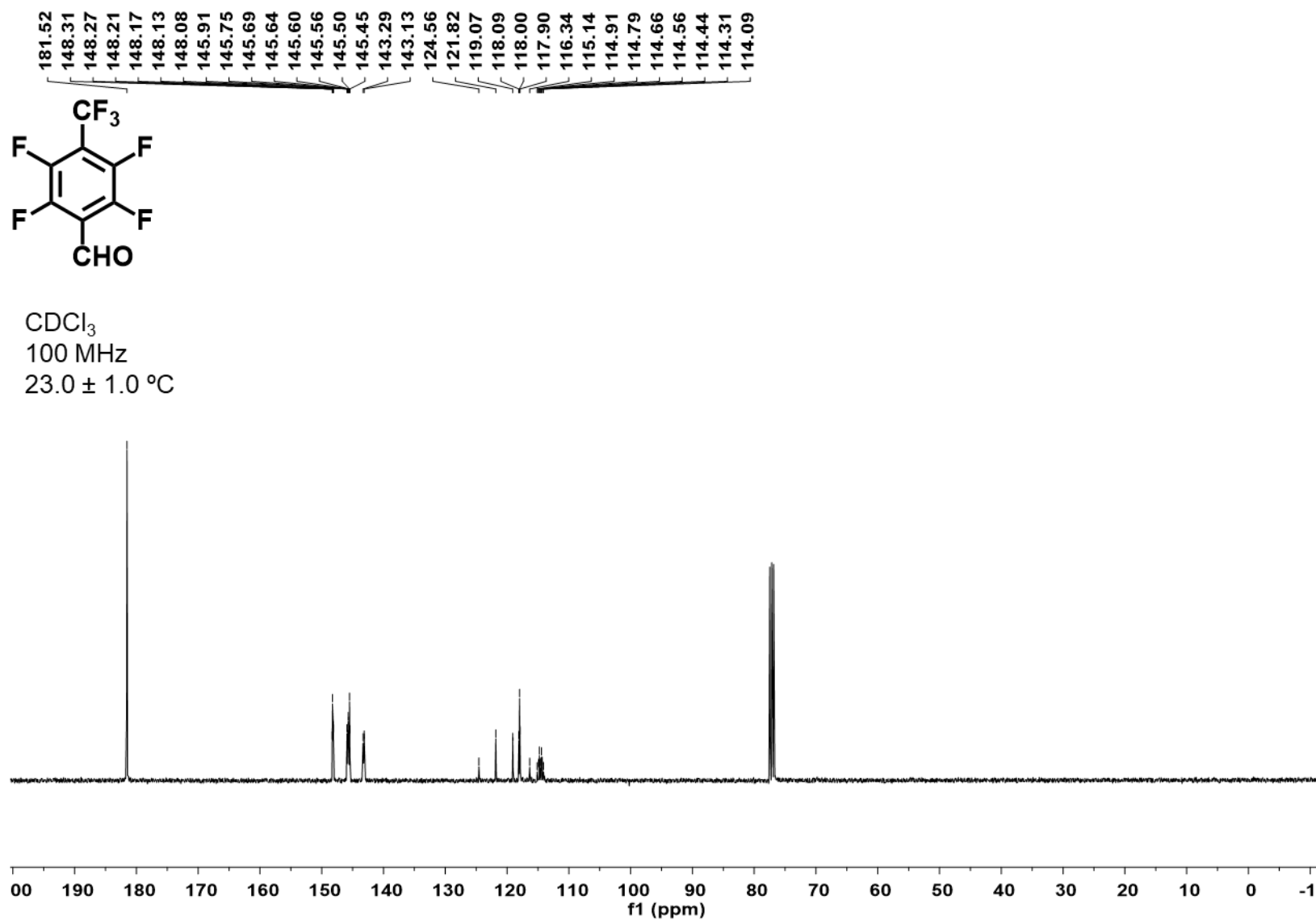


Figure S13. ¹³C NMR spectrum of **4g** as recorded in CDCl₃ at 23 °C.

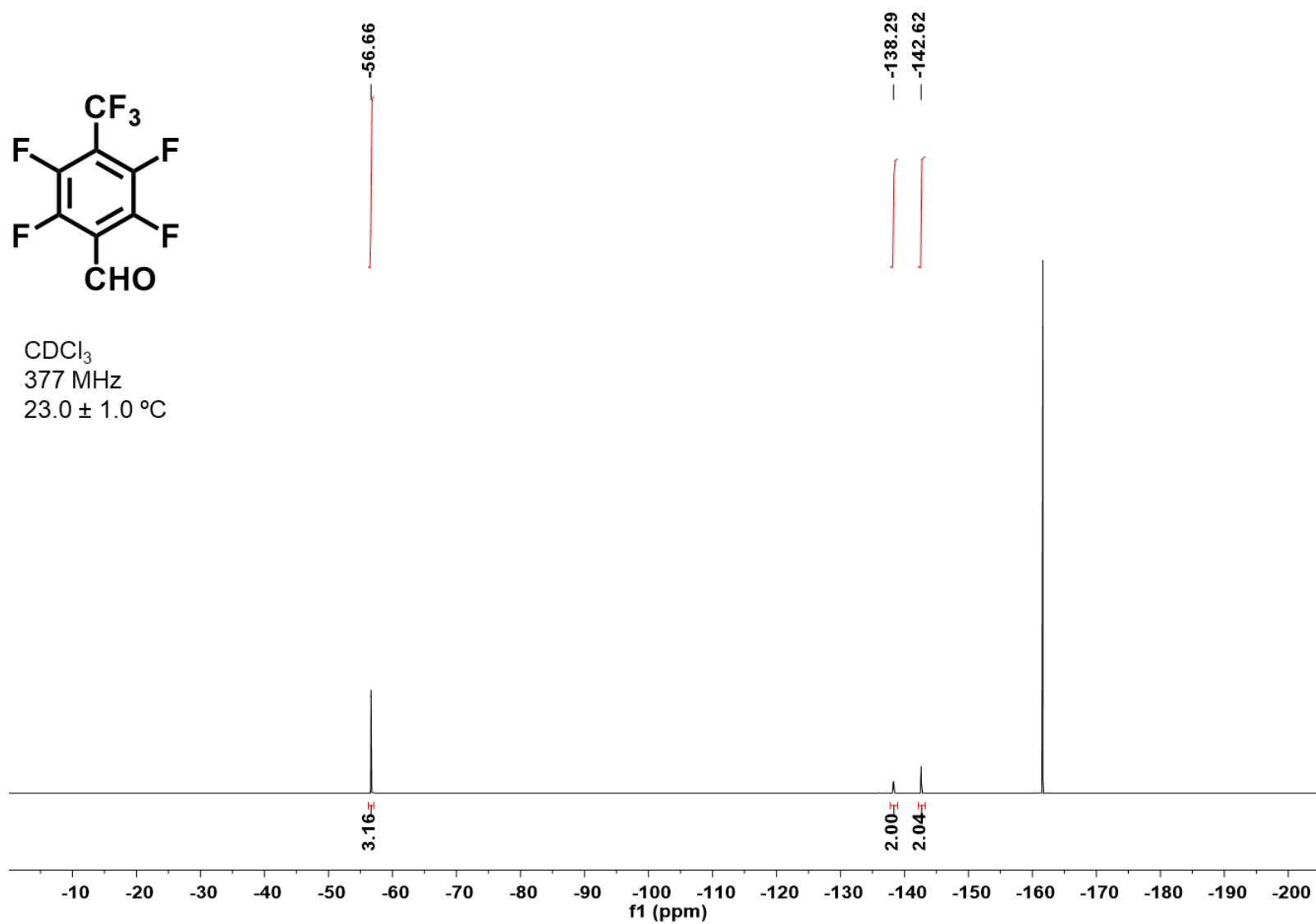


Figure S14. ¹⁹F NMR spectrum of **4g** as recorded in CDCl₃ with hexafluorobenzene as a reference at 23 °C.

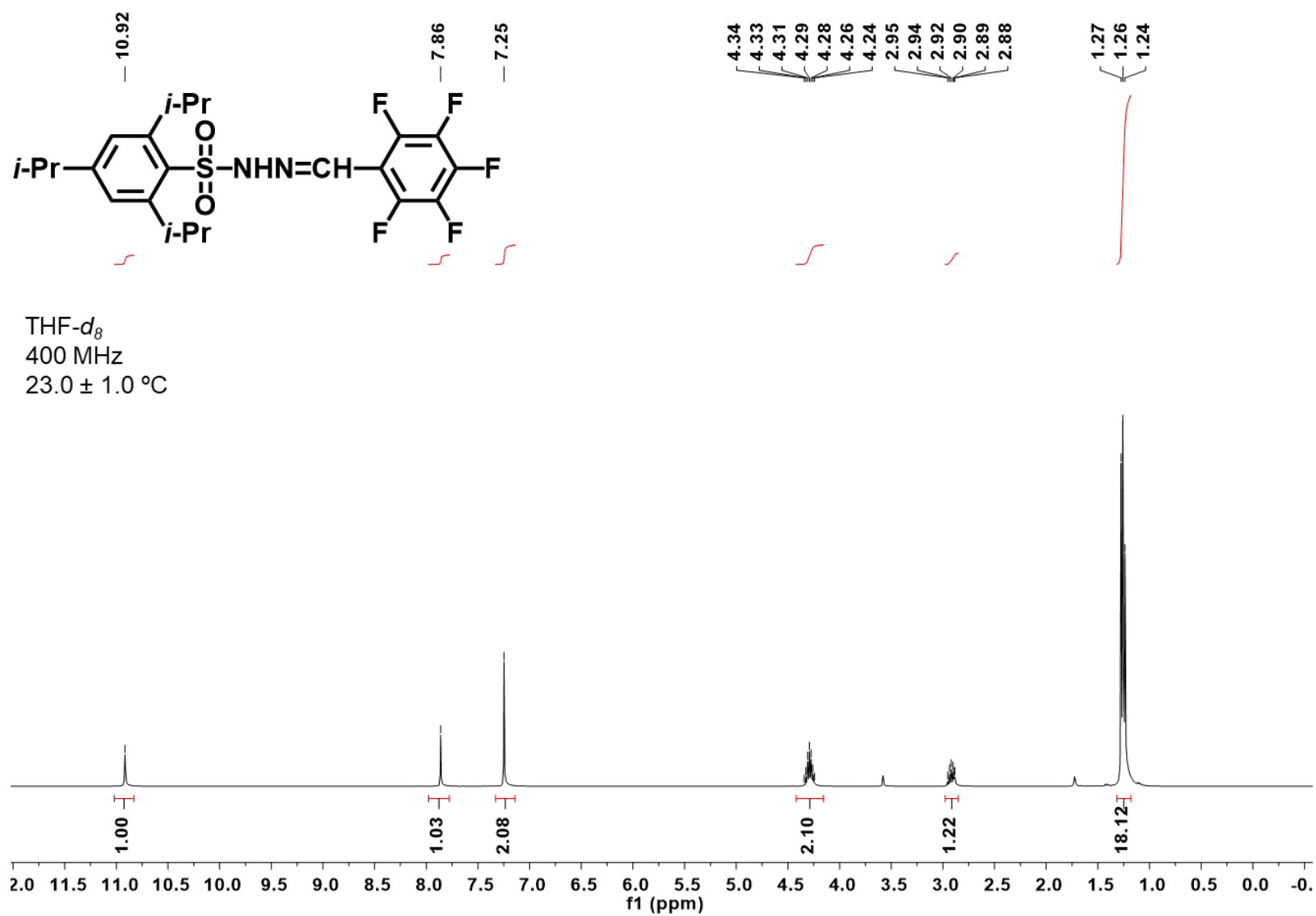


Figure S15. ¹H NMR spectrum of **5a** as recorded in THF-*d*₈ at 23 °C.

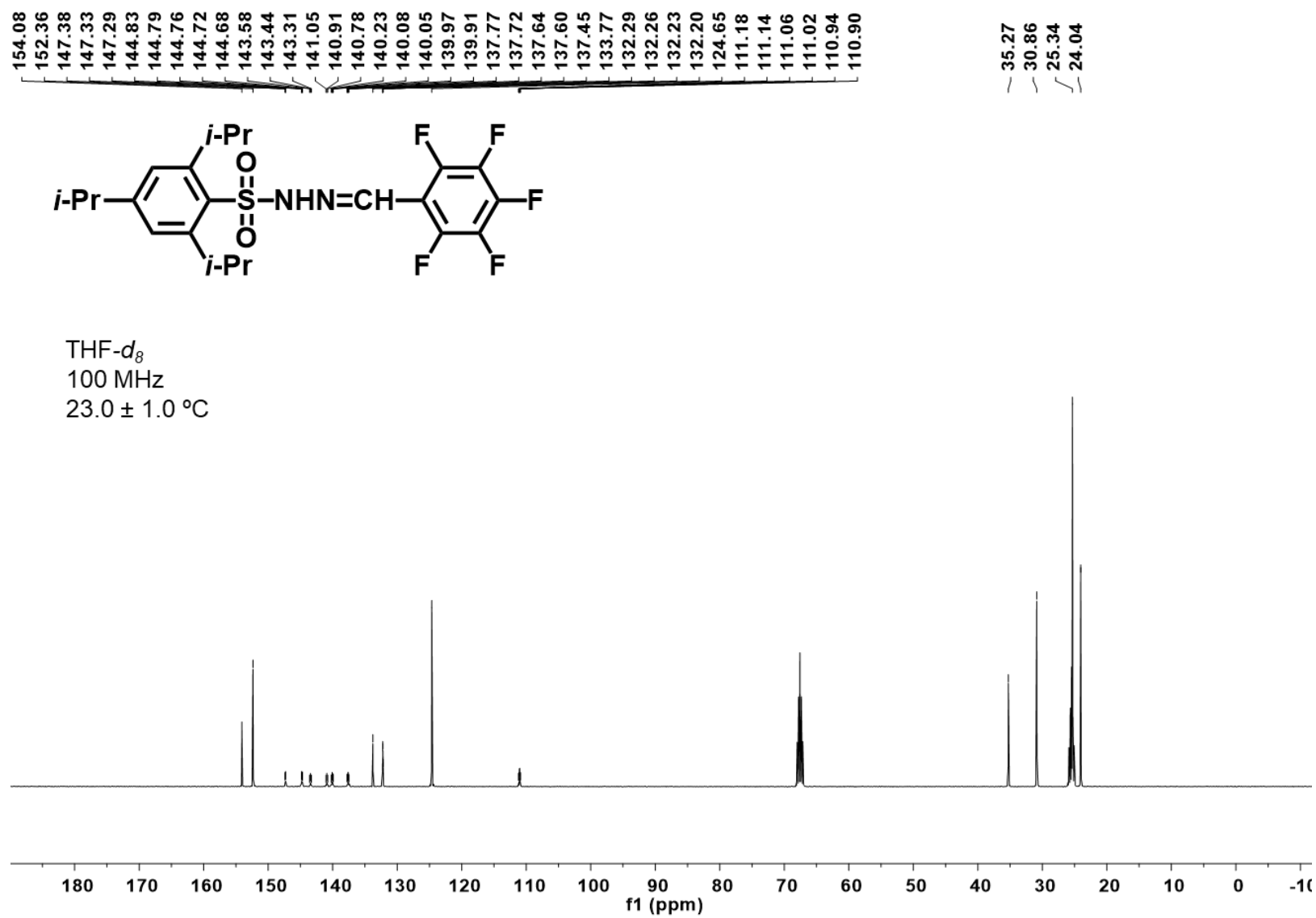


Figure S16. ^{13}C NMR spectrum of **5a** as recorded in THF- d_8 at 23 $^{\circ}$ C.

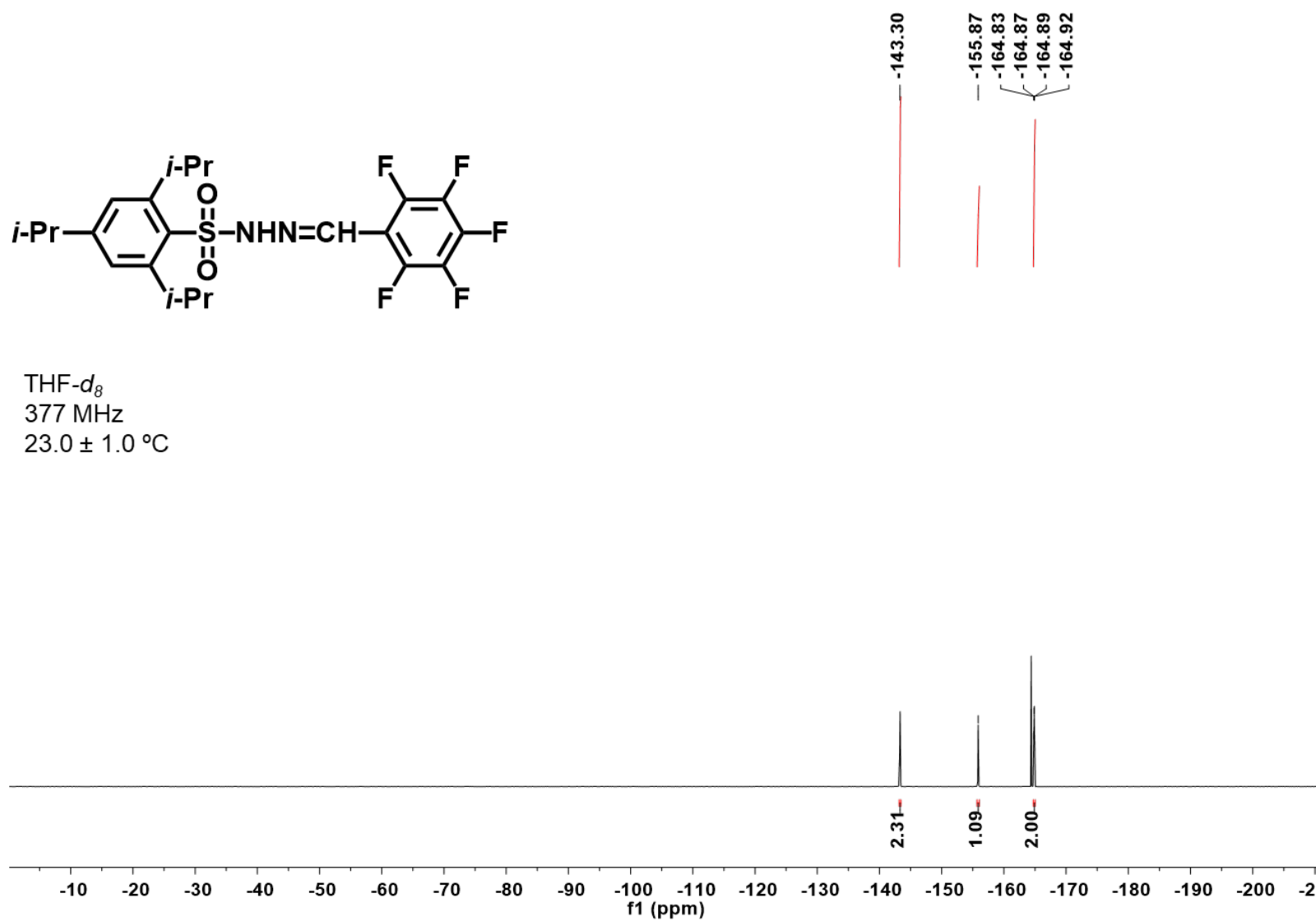


Figure S17. ^{19}F NMR spectrum of **5a** as recorded in THF- d_8 with hexafluorobenzene as a reference at 23 °C.

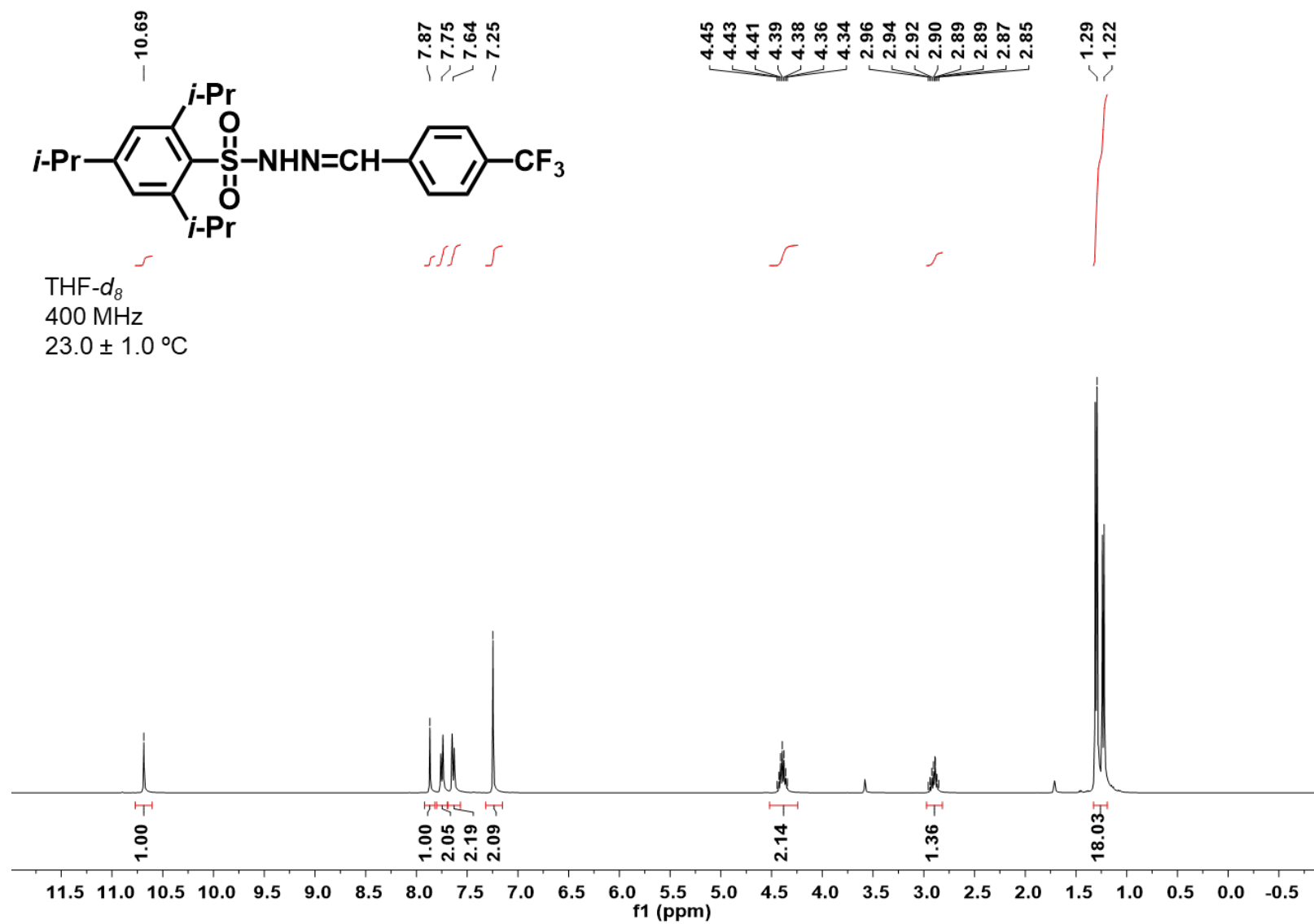


Figure S18. ^1H NMR spectrum of **5b** as recorded in THF- d_8 at 23 °C.

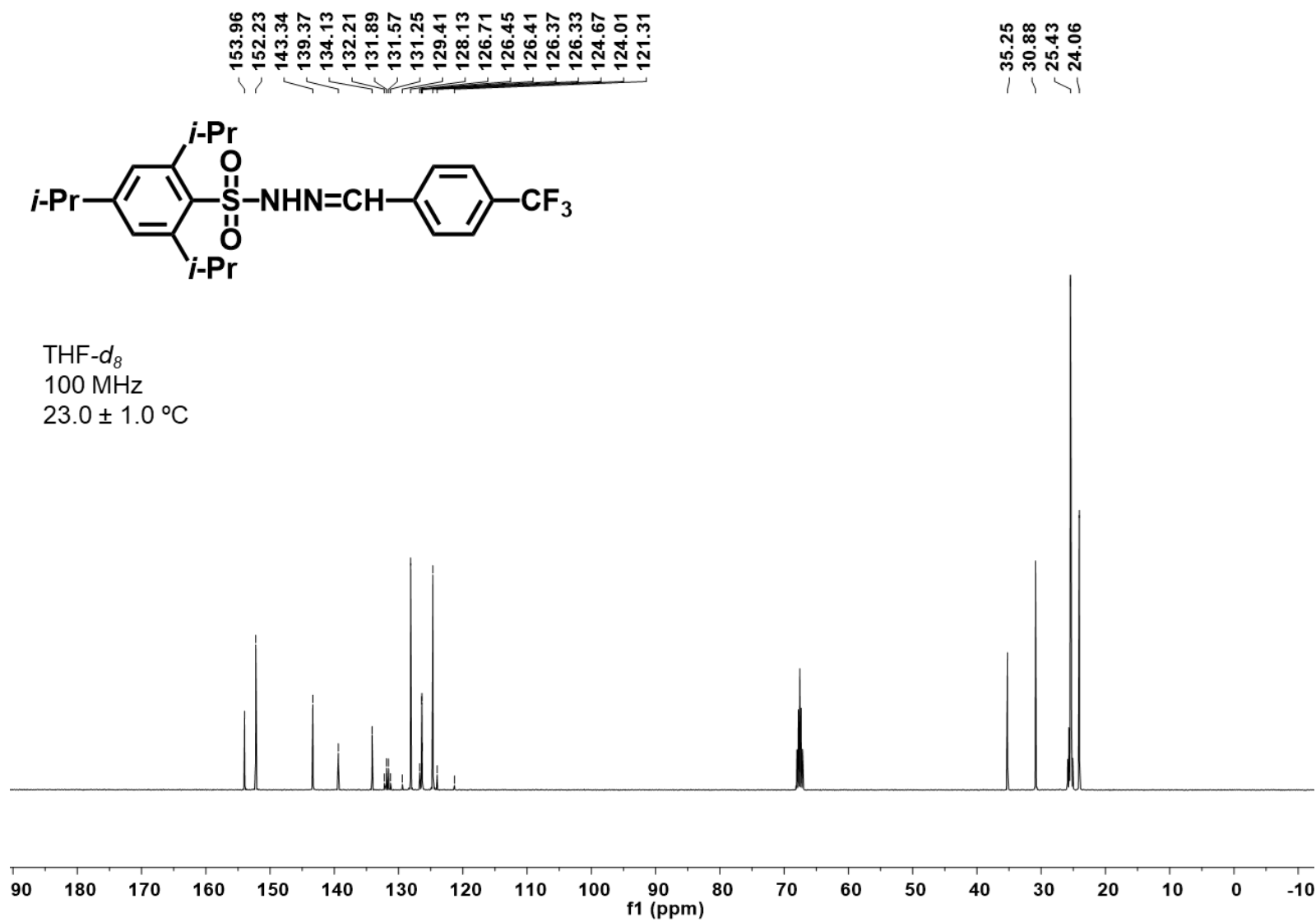


Figure S19. ¹³C NMR spectrum of **5b** as recorded in THF-*d*₈ at 23 °C.

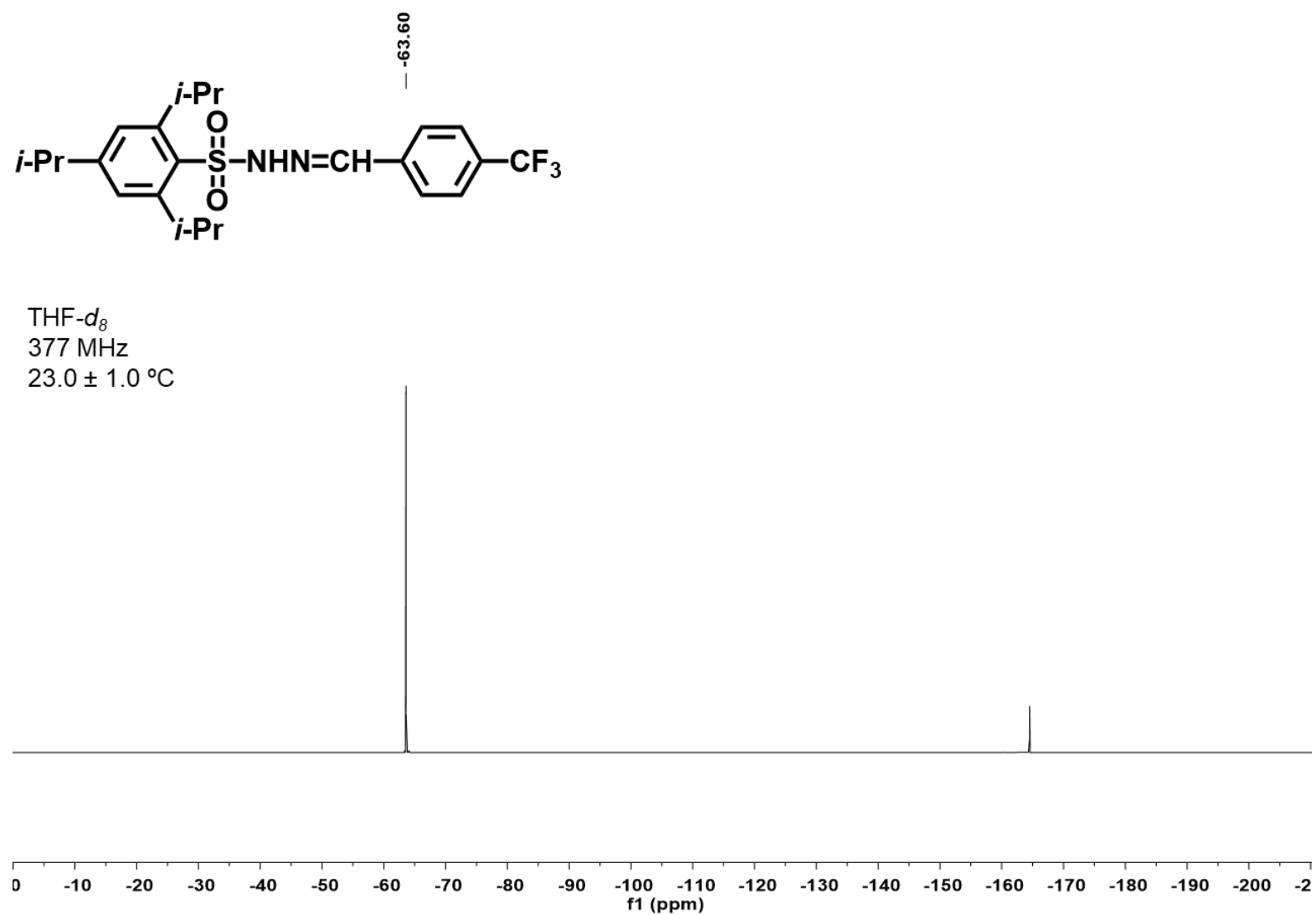


Figure S20. ^{19}F NMR spectrum of **5b** as recorded in THF- d_8 with hexafluorobenzene as a reference at 23 °C.

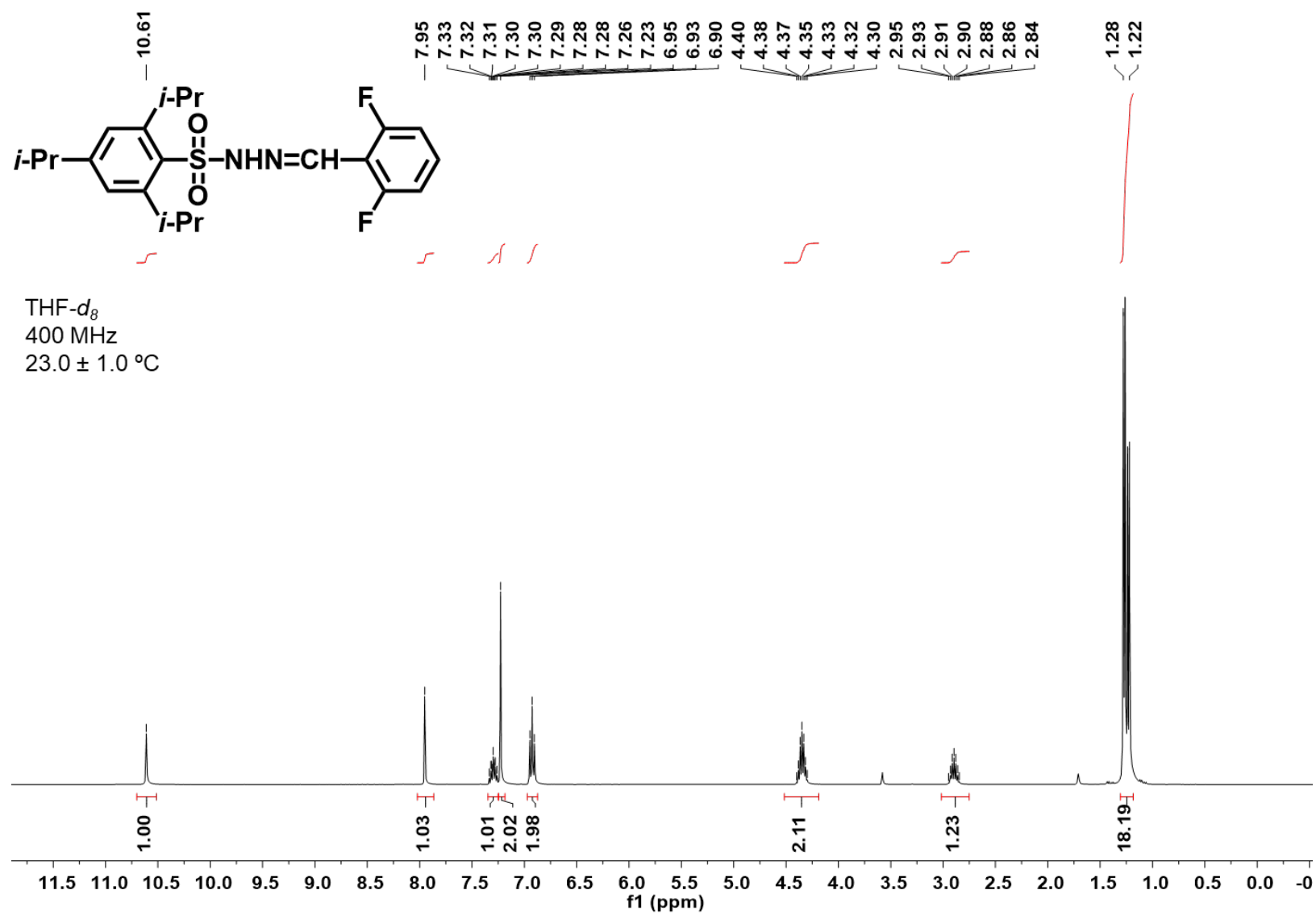


Figure S21. ^1H NMR spectrum of **5c** as recorded in THF- d_8 at 23 $^{\circ}$ C.

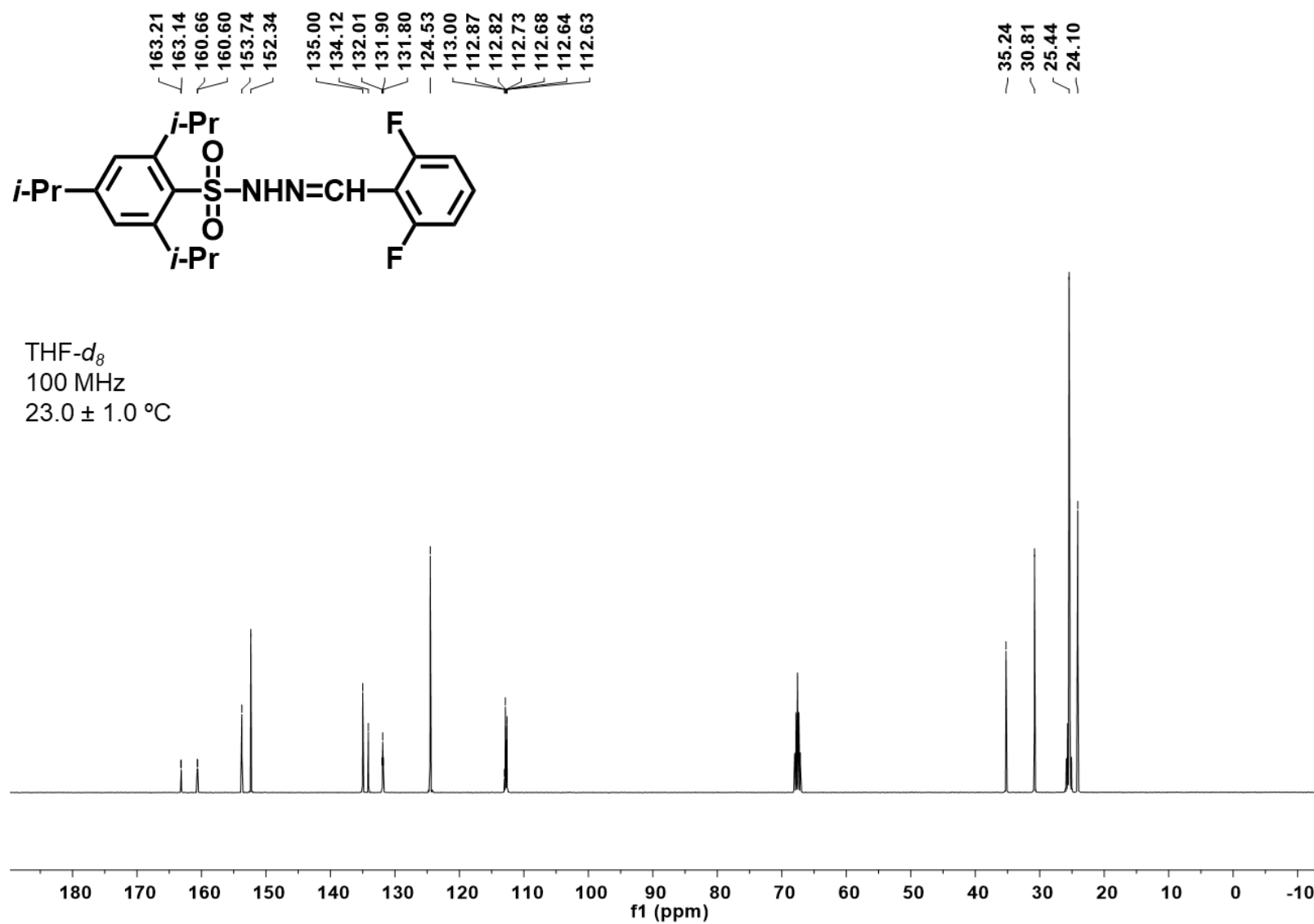


Figure S22. ^{13}C NMR spectrum of **5c** as recorded in THF- d_8 at 23 °C.

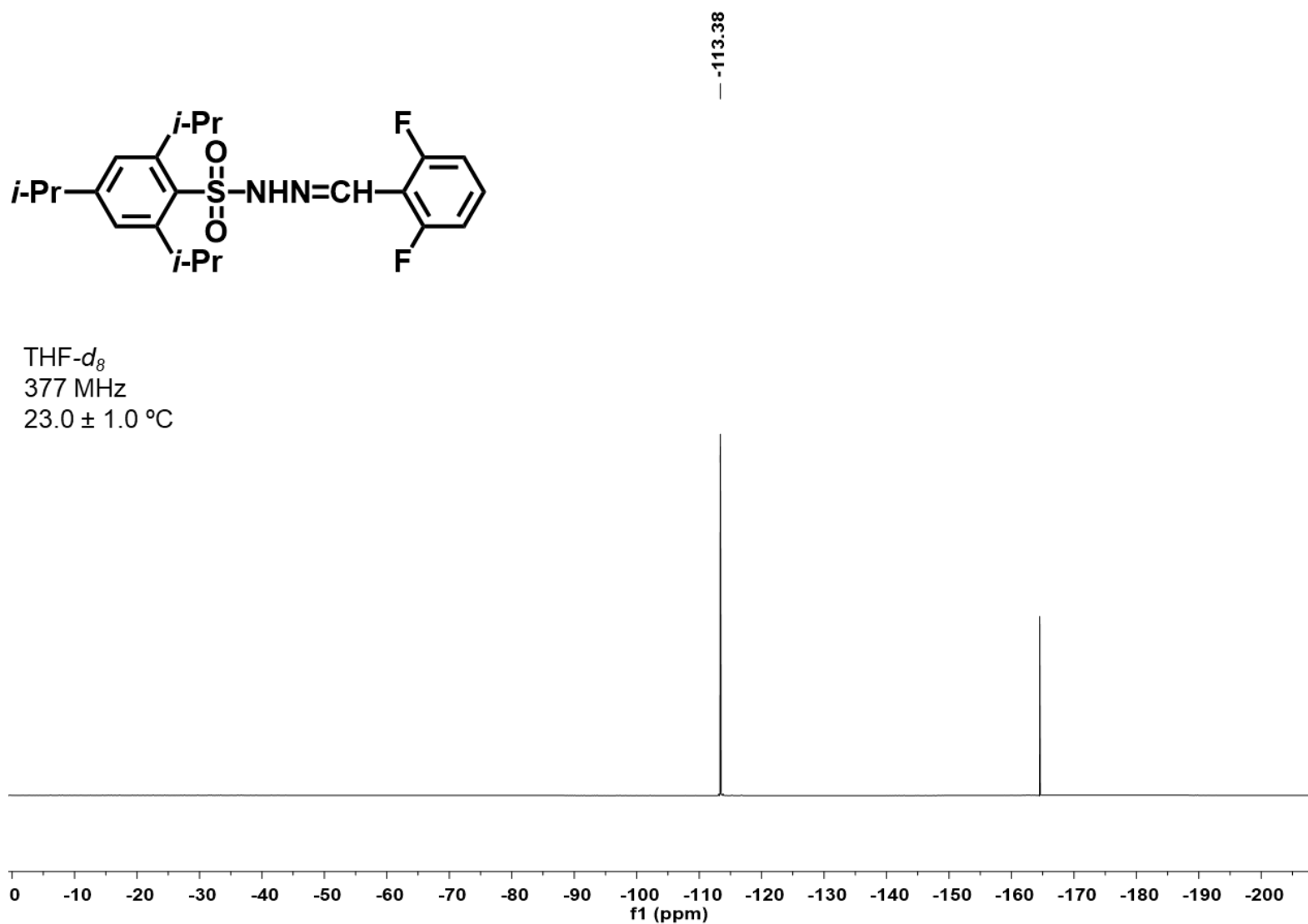


Figure S23. ^{19}F NMR spectrum of **5c** as recorded in THF- d_8 with hexafluorobenzene as a reference at 23 °C.

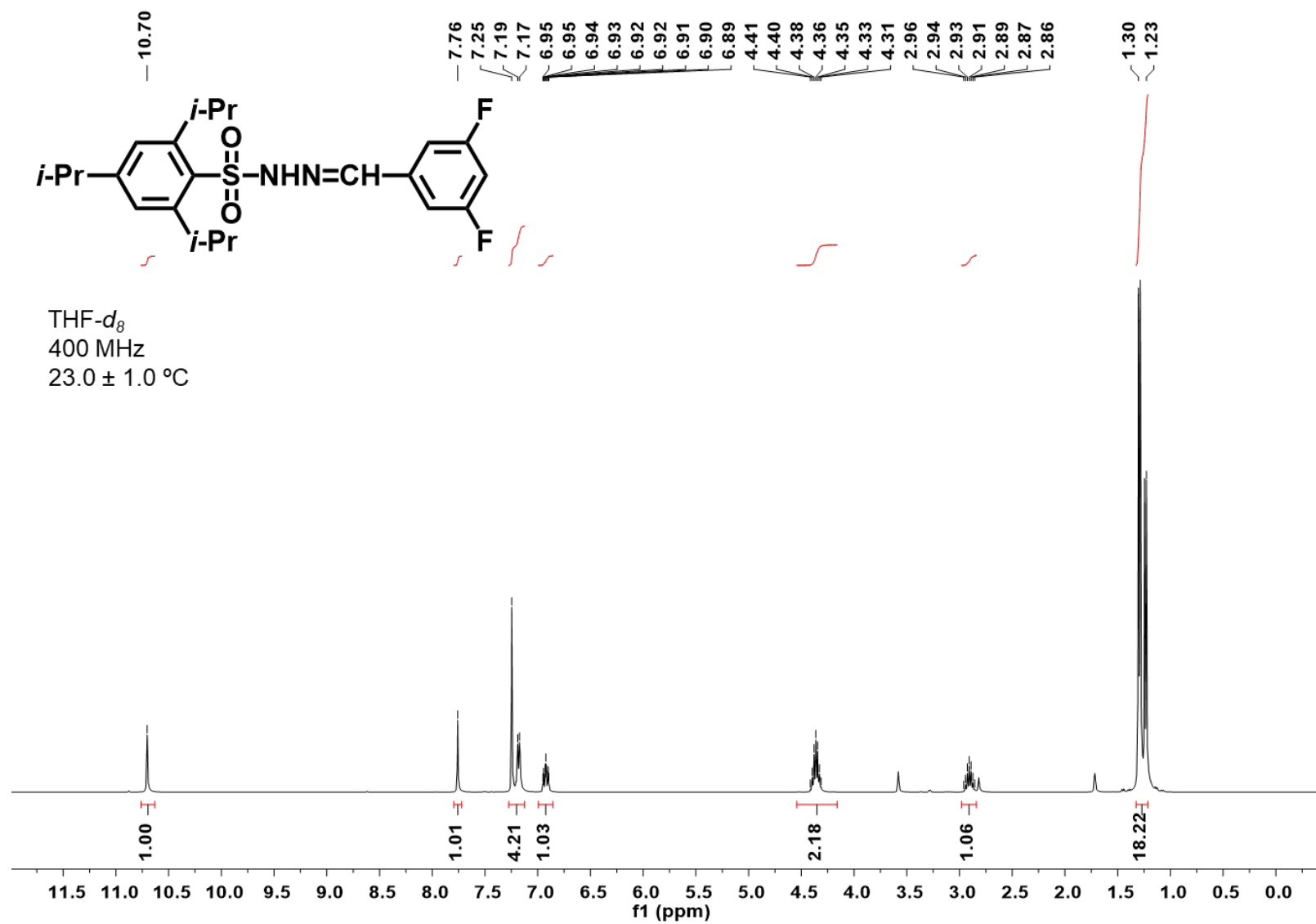


Figure S24. ^1H NMR spectrum of **5d** as recorded in THF- d_8 at 23 °C.

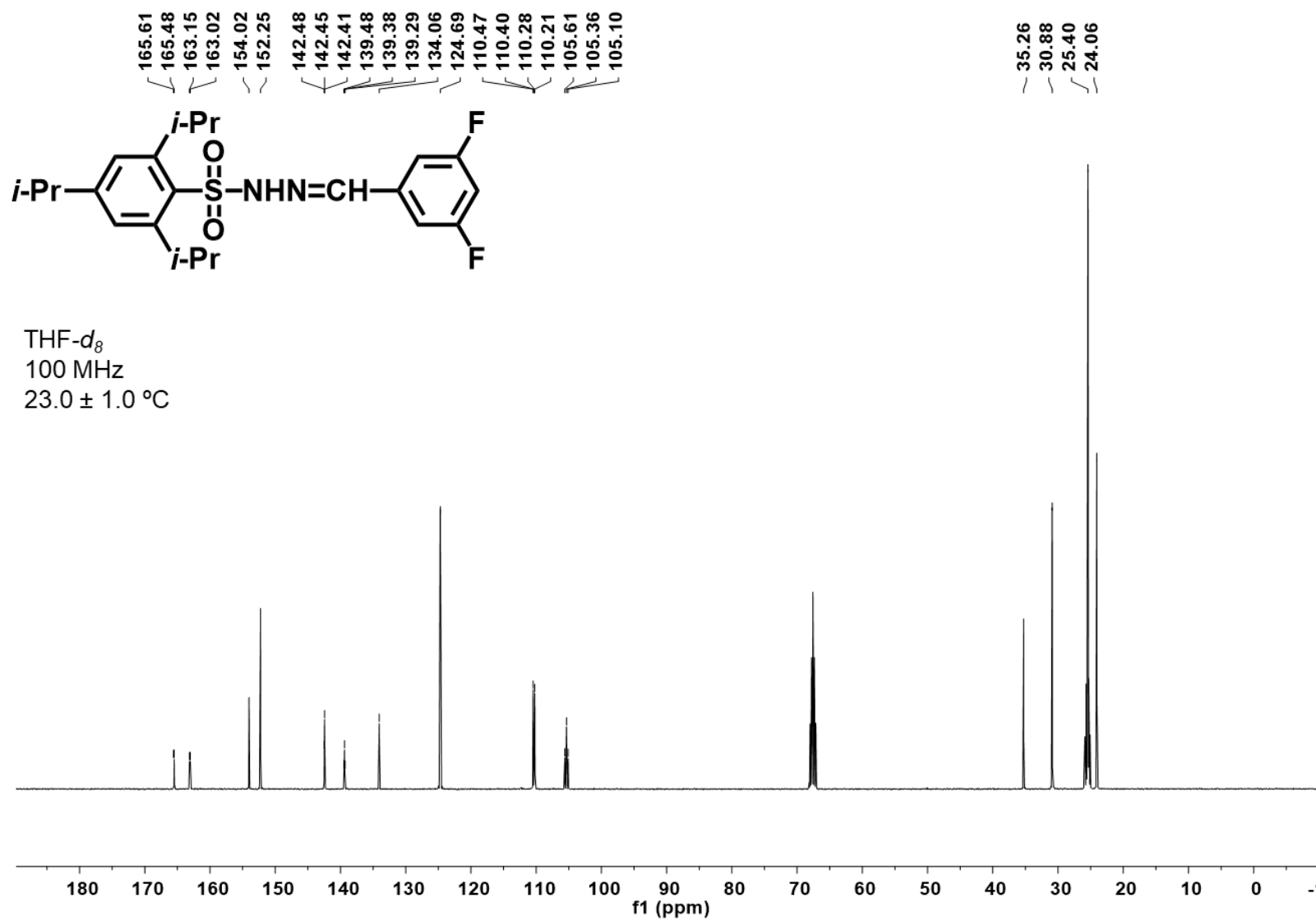


Figure S25. ¹³C NMR spectrum of **5d** as recorded in THF-*d*₈ at 23 °C.

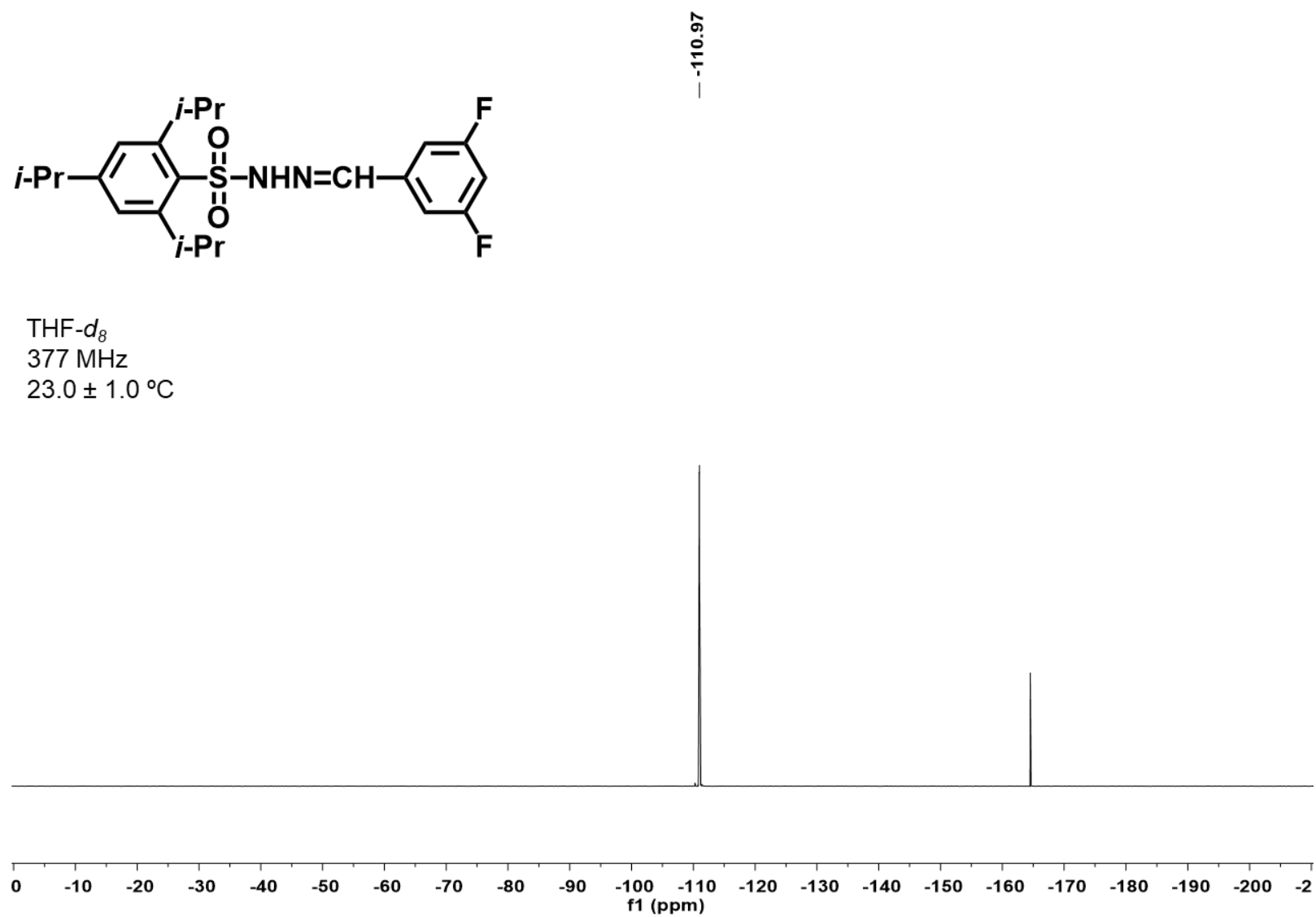


Figure S26. ^{19}F NMR spectrum of **5d** as recorded in THF- d_8 with hexafluorobenzene as a reference at 23 $^{\circ}$ C.

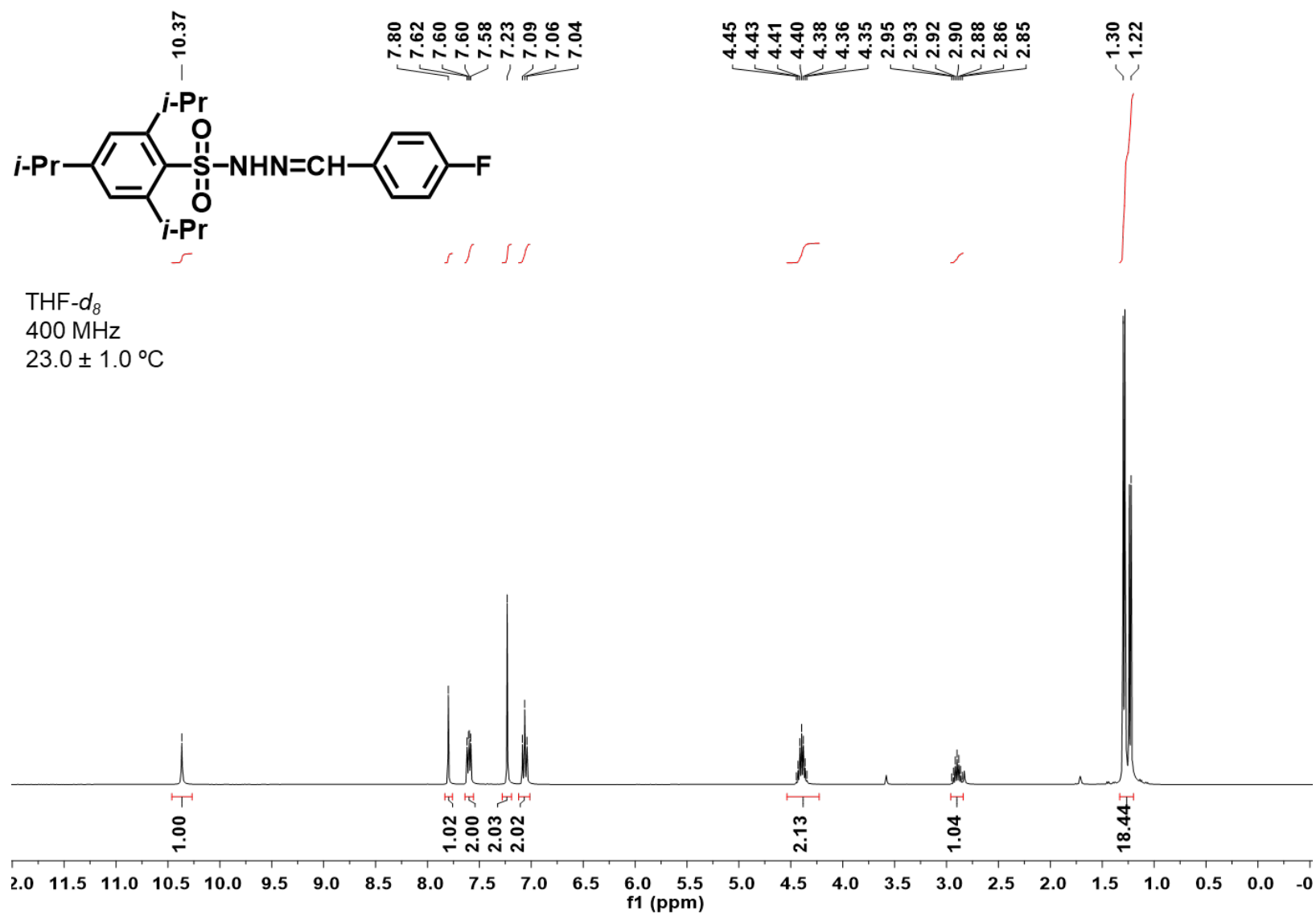


Figure S27. ^1H NMR spectrum of **5e** as recorded in THF- d_8 at 23 $^{\circ}$ C.

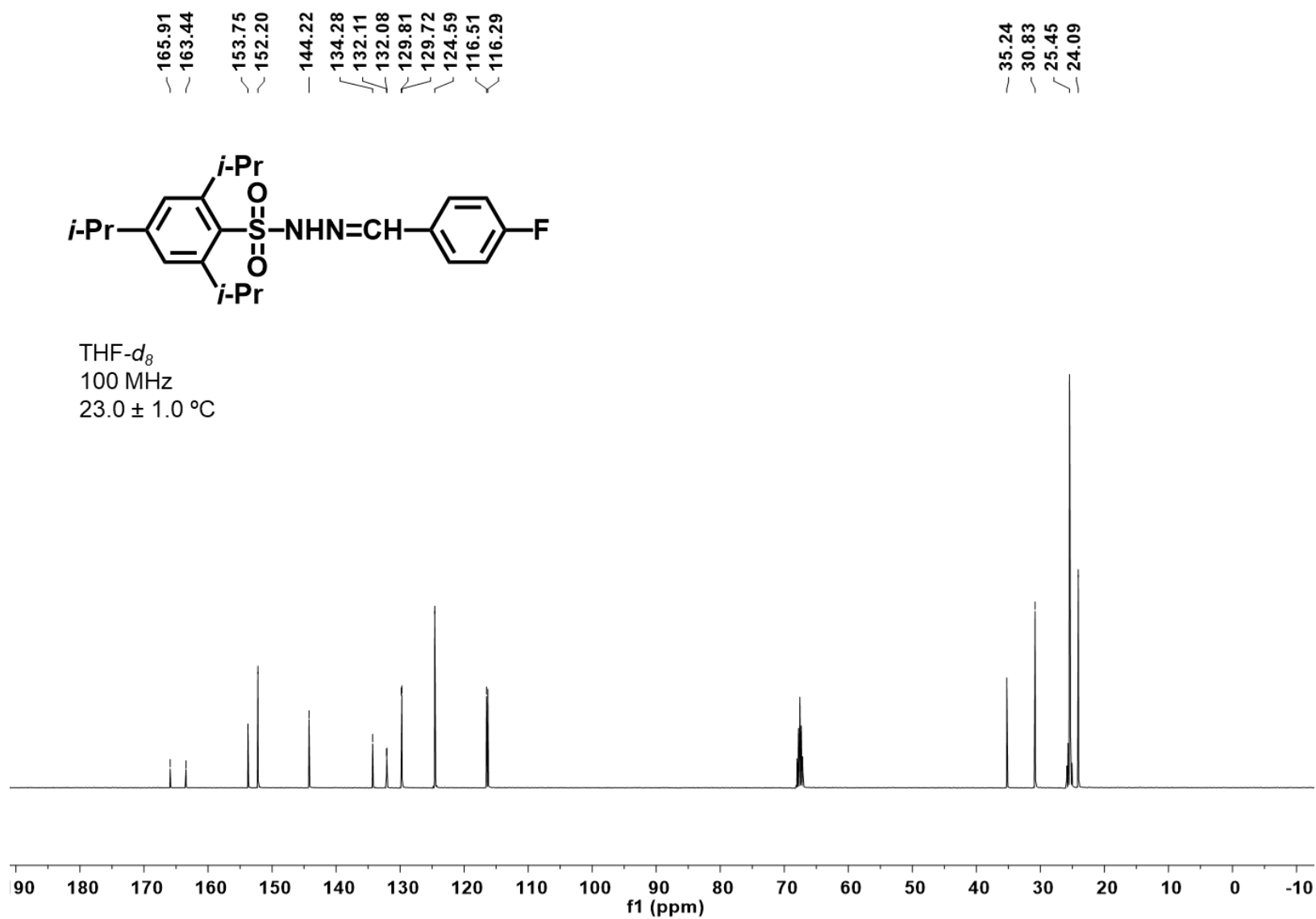


Figure S28. ^{13}C NMR spectrum of **5e** as recorded in THF- d_8 at 23 °C.

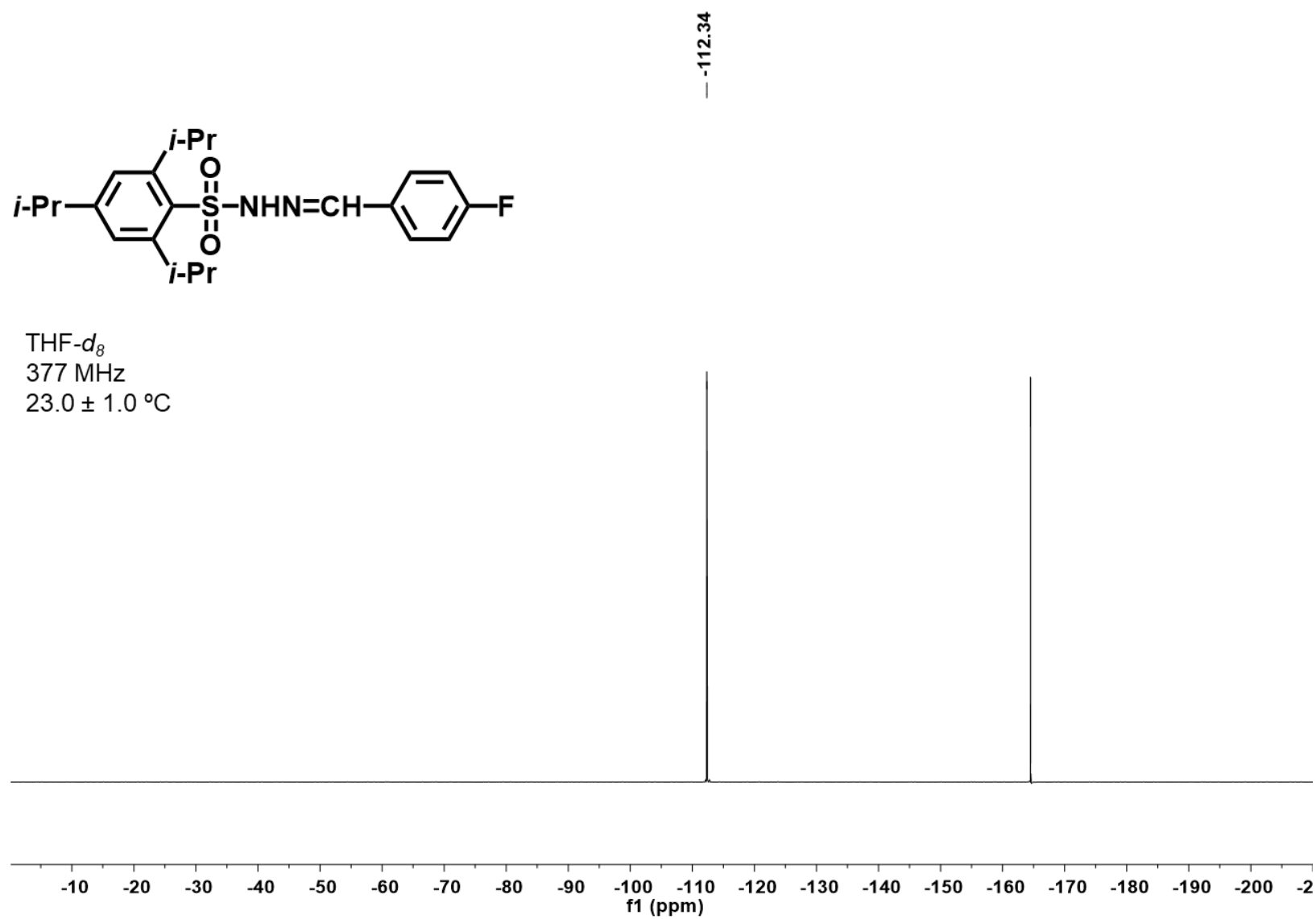


Figure S29. ^{19}F NMR spectrum of **5e** as recorded in THF- d_8 with hexafluorobenzene as a reference at 23 °C.

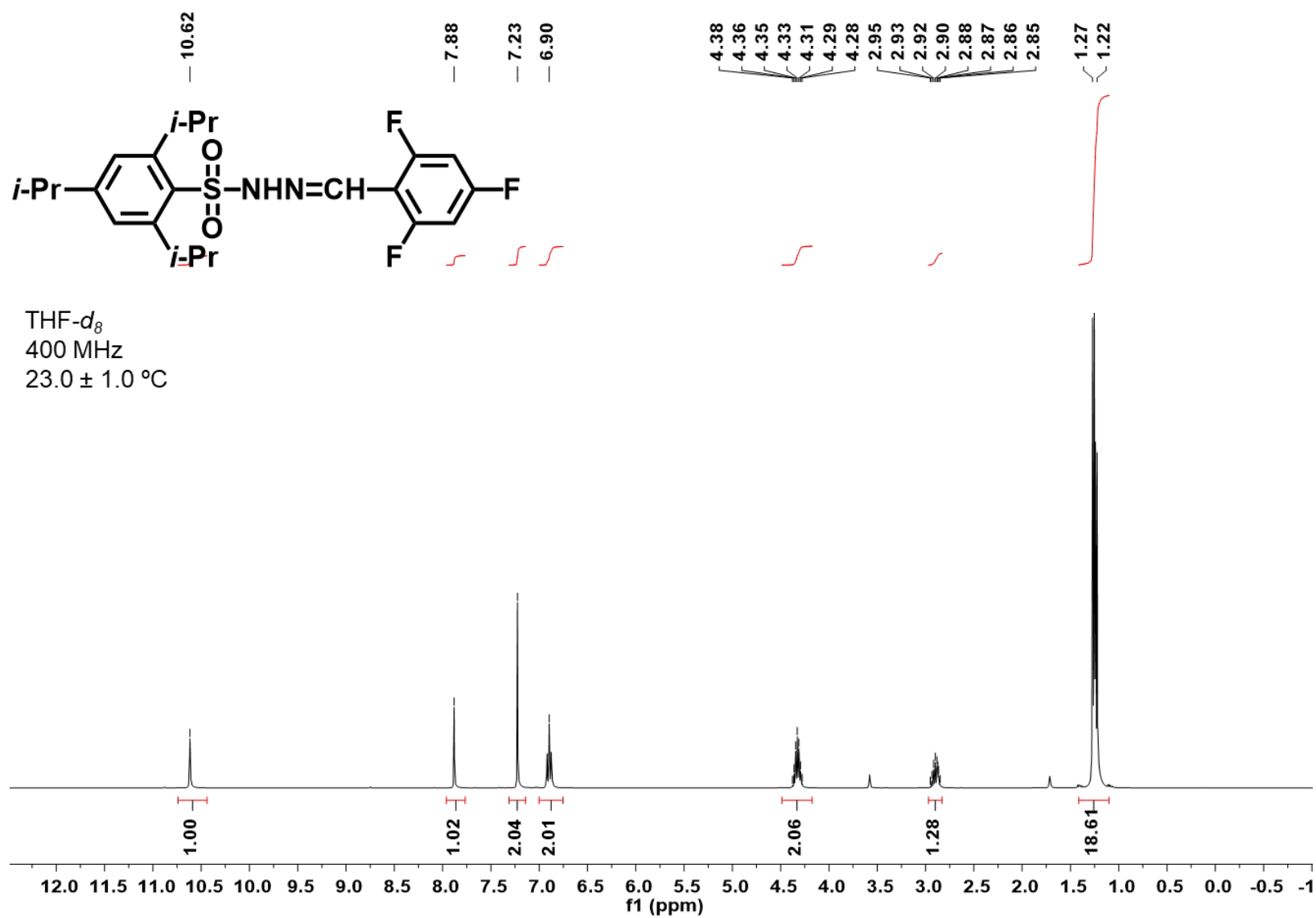


Figure S30. ¹H NMR spectrum of **5f** as recorded in THF-*d*₈ at 23 °C.

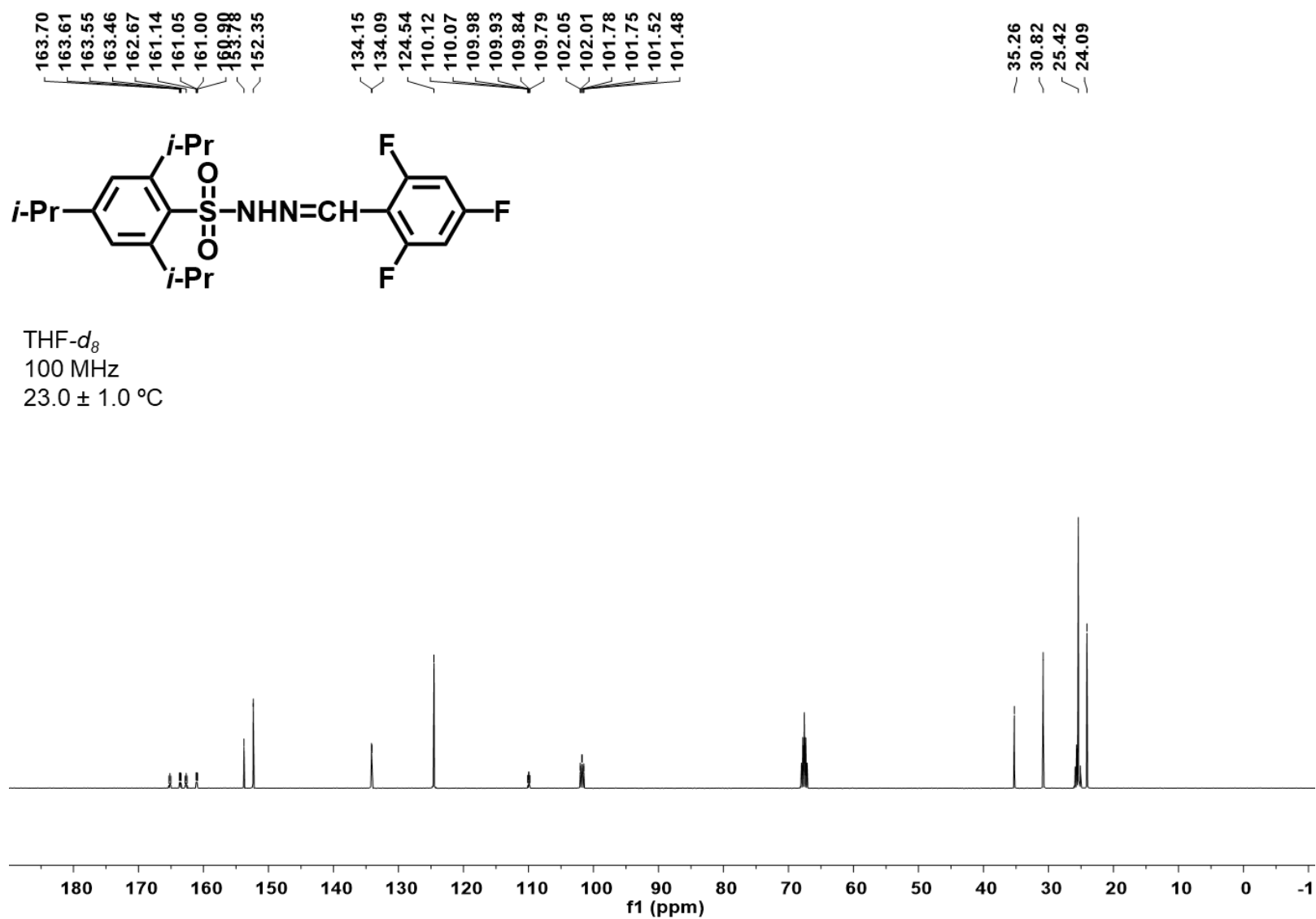


Figure S31. ^{13}C NMR spectrum of **5f** as recorded in THF- d_8 at 23 °C.

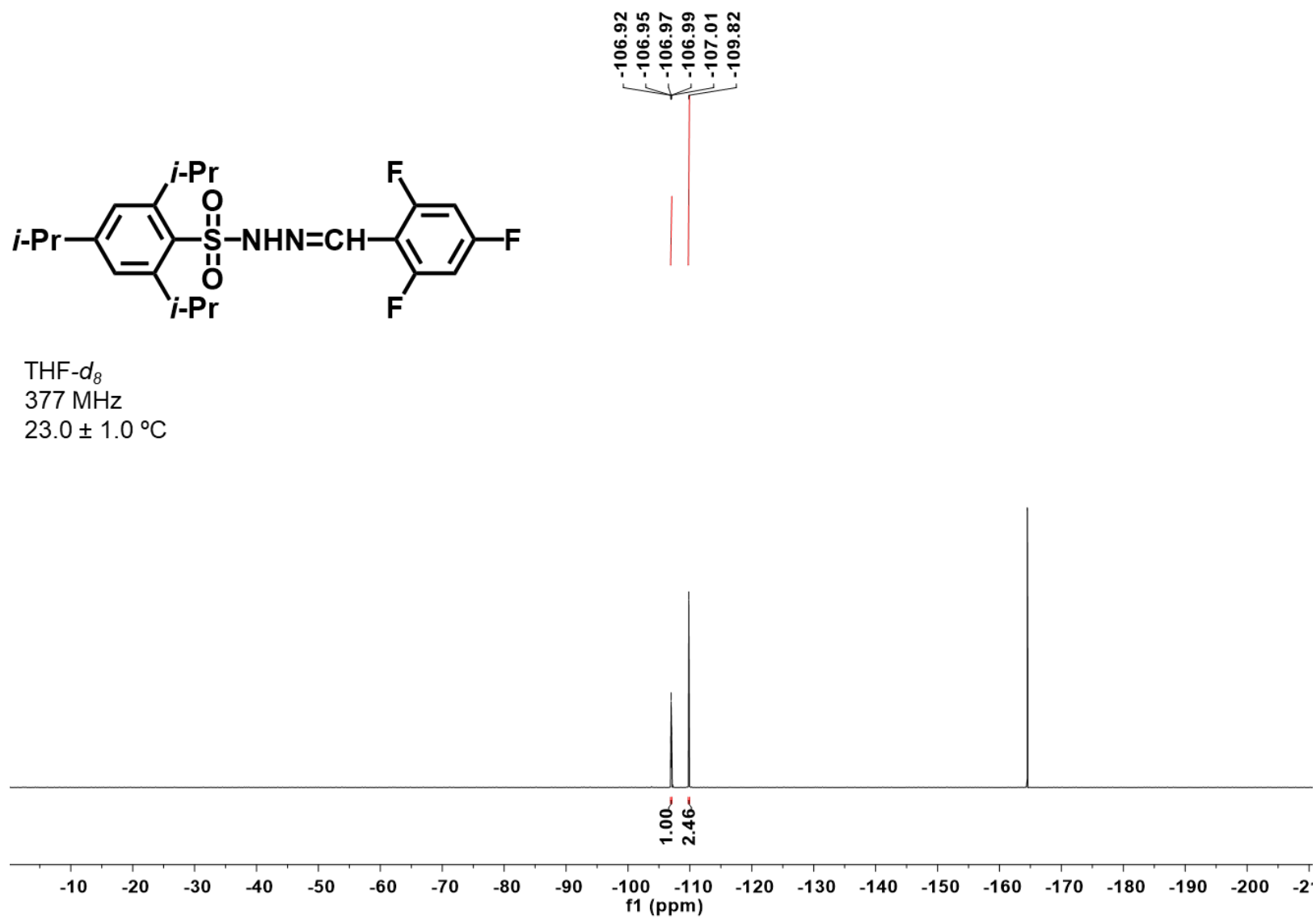


Figure S32. ^{19}F NMR spectrum of **5f** as recorded in THF- d_8 with hexafluorobenzene as a reference at 23 $^{\circ}$ C.

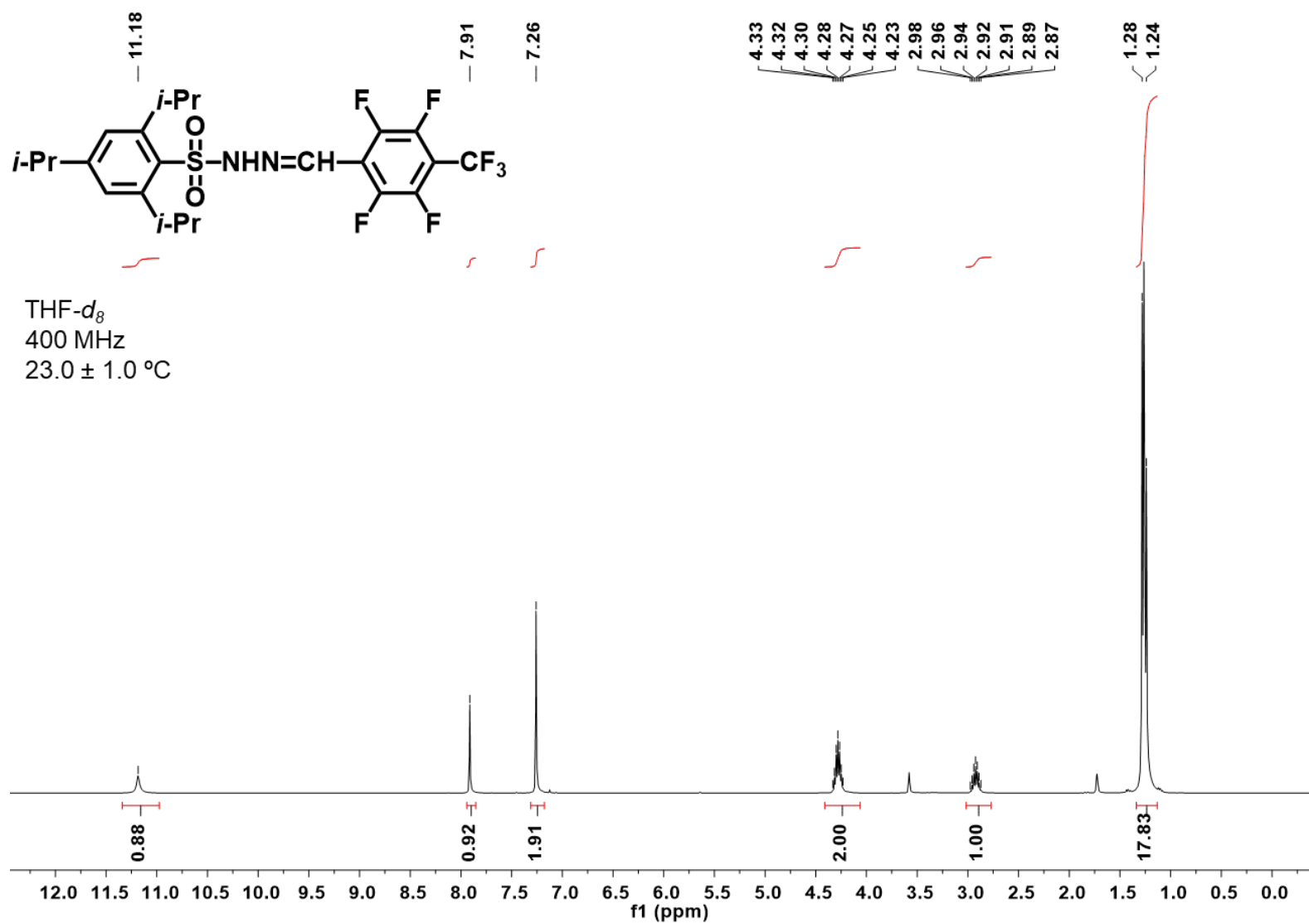


Figure S33. ^1H NMR spectrum of **5g** as recorded in THF- d_8 at 23 $^{\circ}$ C.

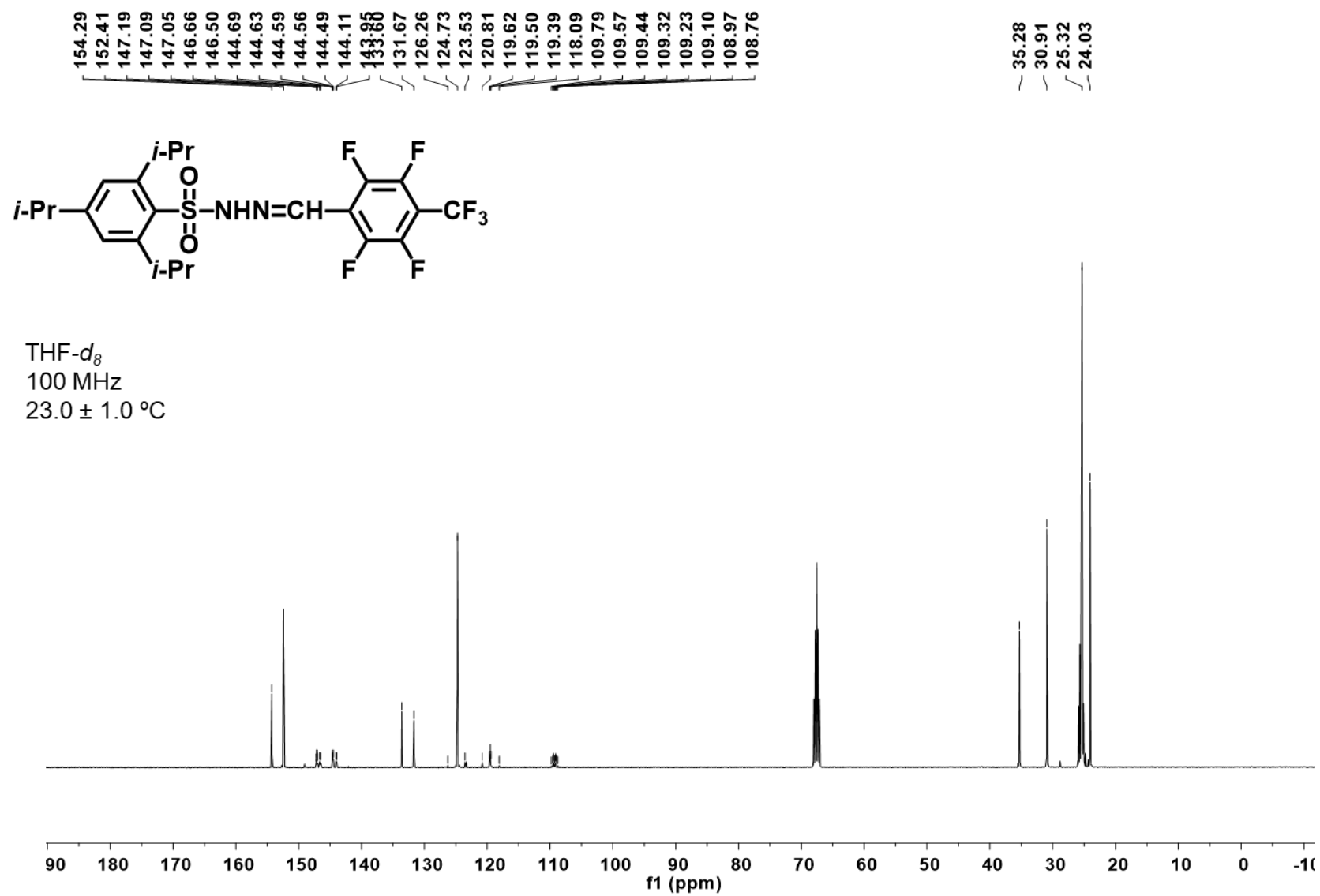


Figure S34. ^{13}C NMR spectrum of **5g** as recorded in THF- d_8 at 23 $^\circ\text{C}$.

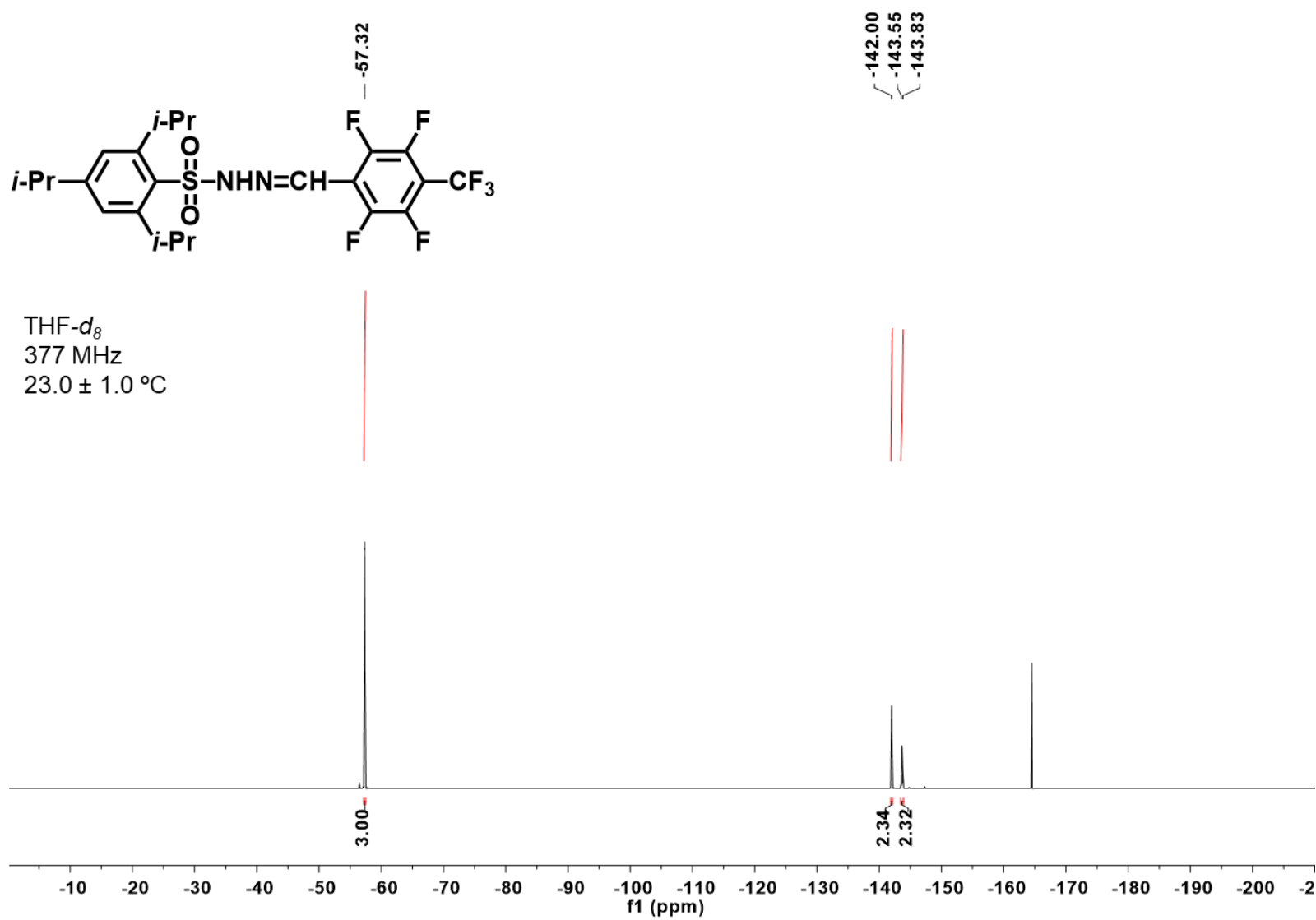


Figure S35. ^{19}F NMR spectrum of **5g** as recorded in THF- d_8 with hexafluorobenzene as a reference at 23 $^{\circ}$ C.

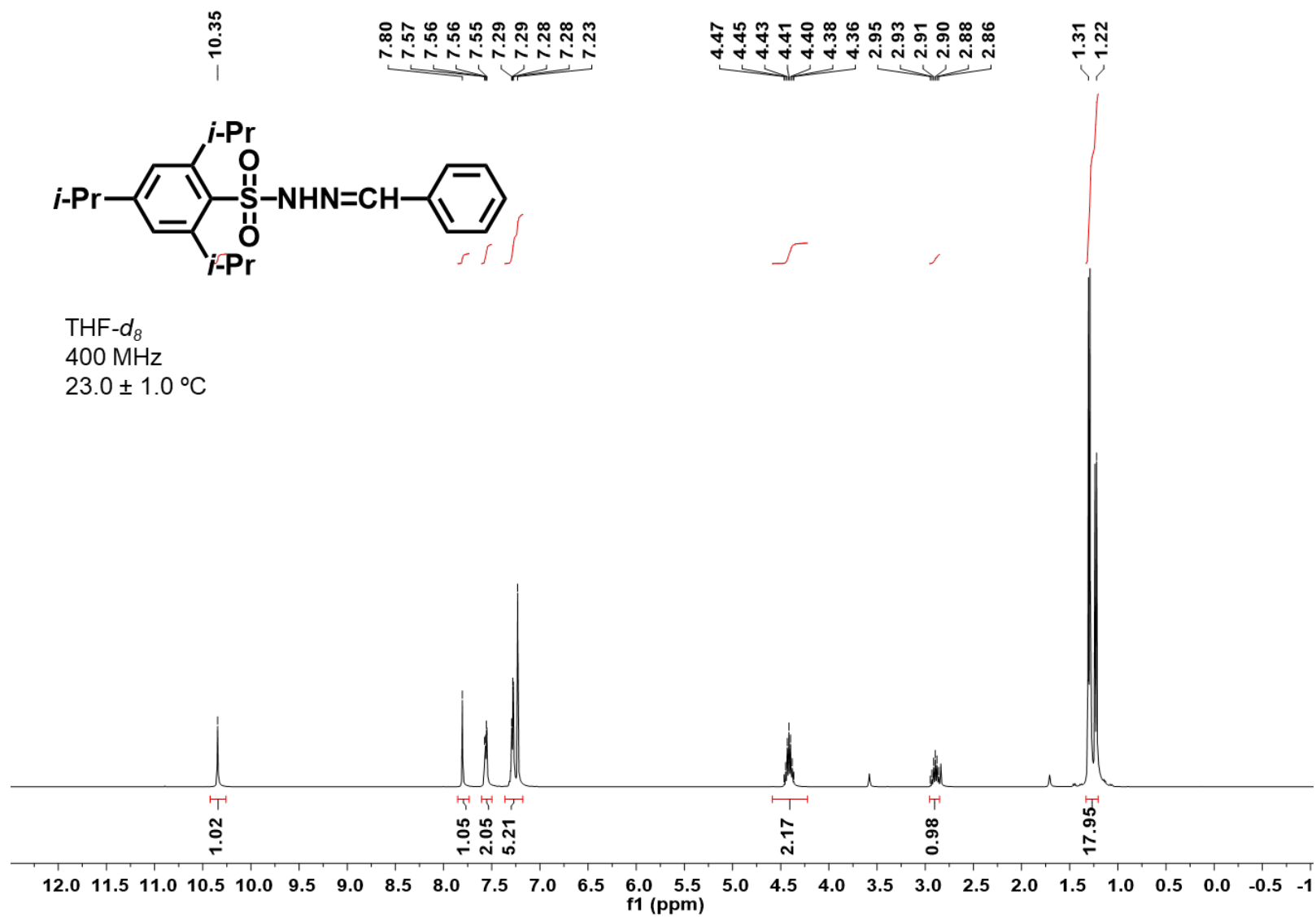


Figure S36. ^1H NMR spectrum of 2,4,6-triisopropylbenzenesulfonyl phenylhydrazone as recorded in THF- d_8 at 23 $^{\circ}$ C.

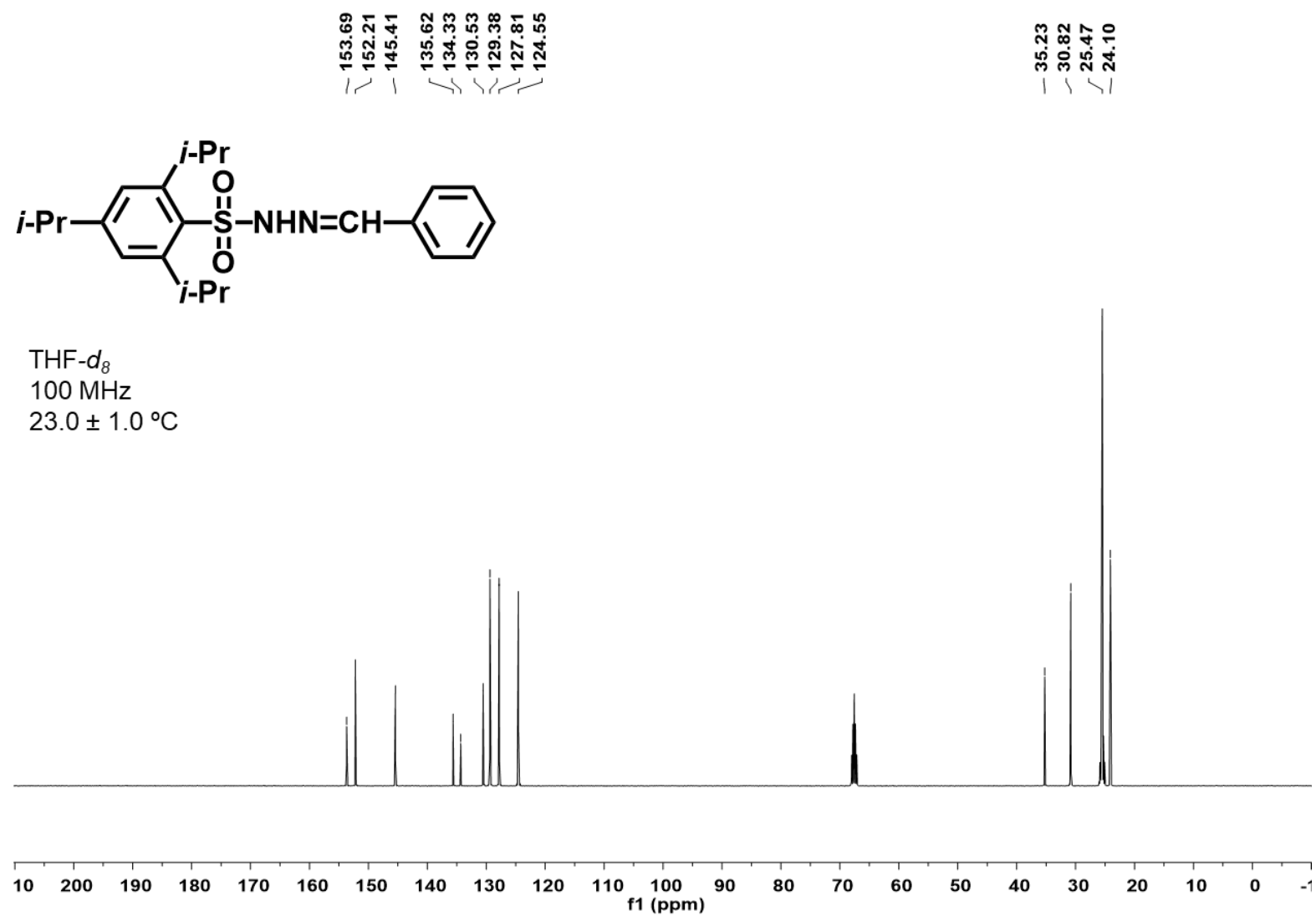


Figure S37. ^{13}C NMR spectrum of 2,4,6-triisopropylbenzenesulfonyl phenylhydrazone as recorded in THF- d_8 at 23 $^{\circ}$ C.

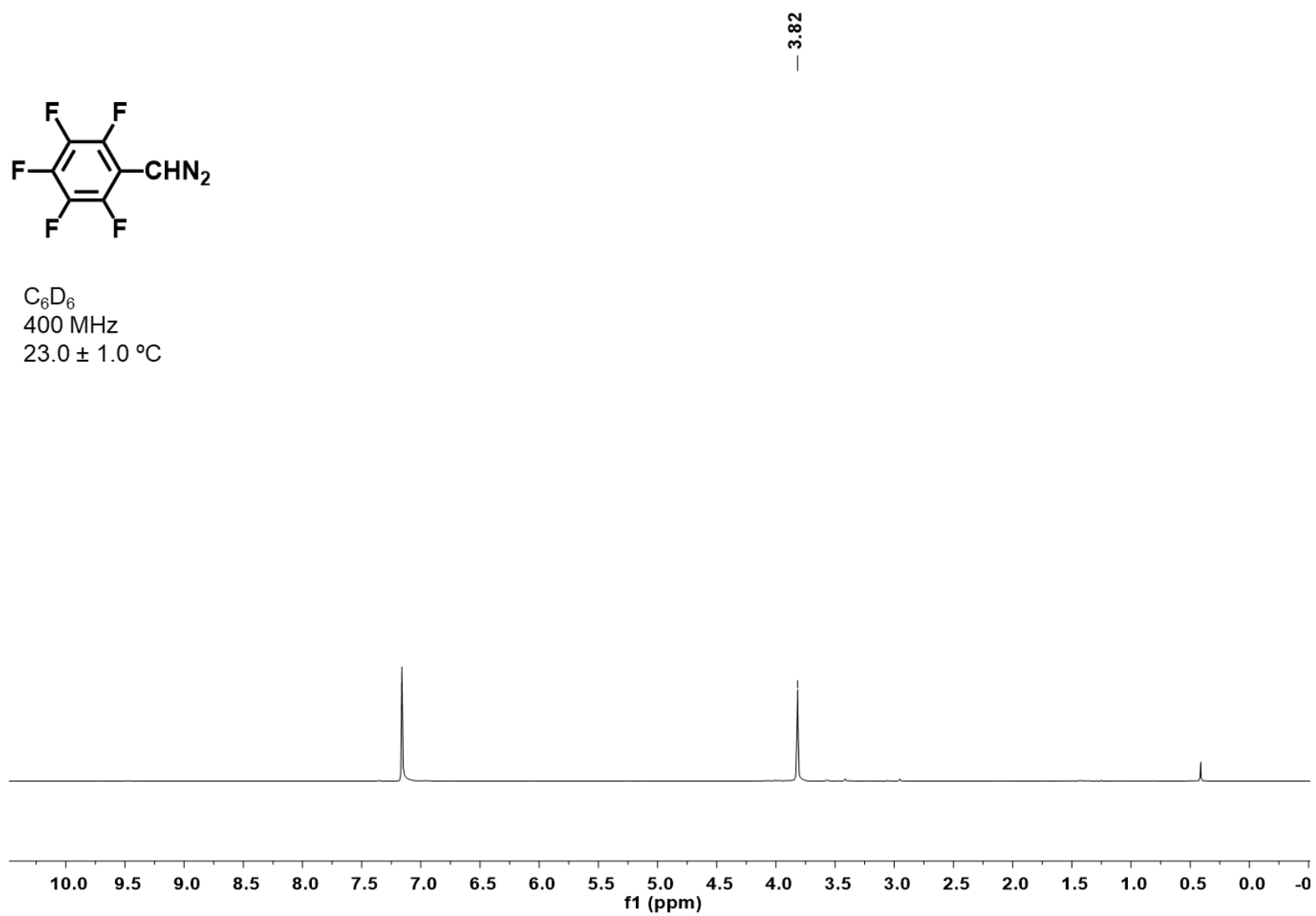


Figure S38. ^1H NMR spectrum of **1a** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

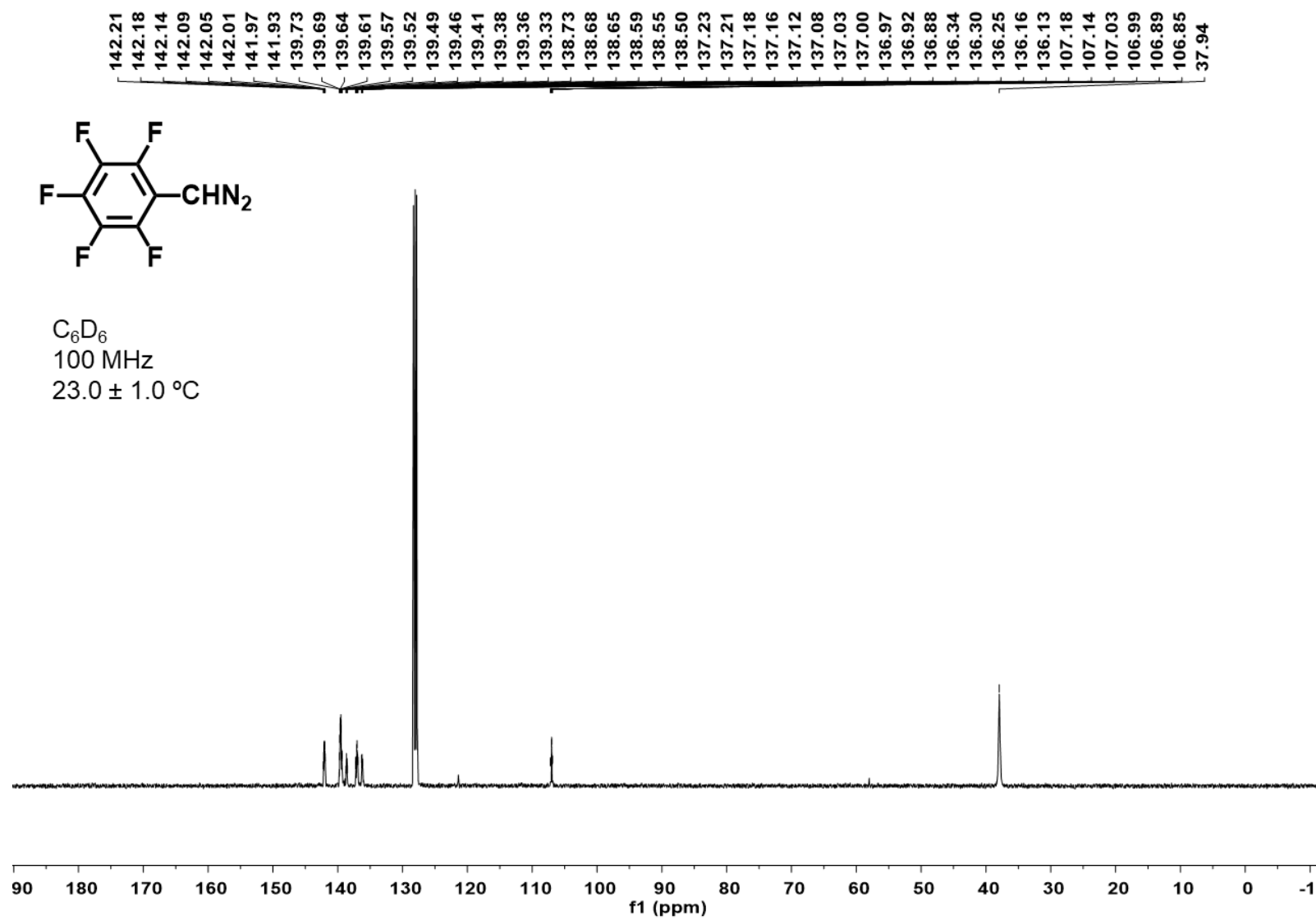


Figure S39. ^{13}C NMR spectrum of **1a** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

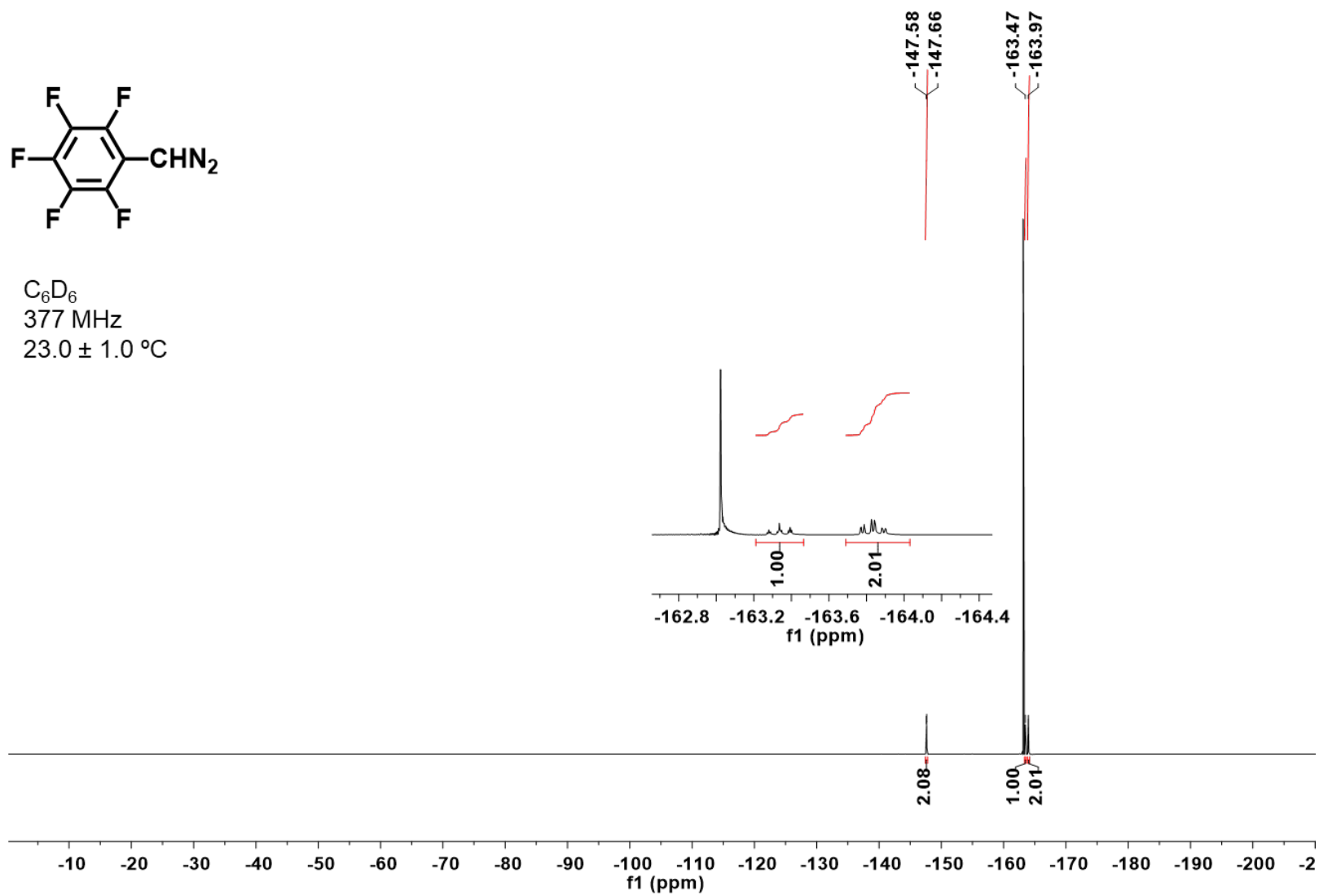


Figure S40. ^{19}F NMR spectrum of **1a** as recorded in C_6D_6 with hexafluorobenzene as a reference at $23\text{ }^\circ\text{C}$.

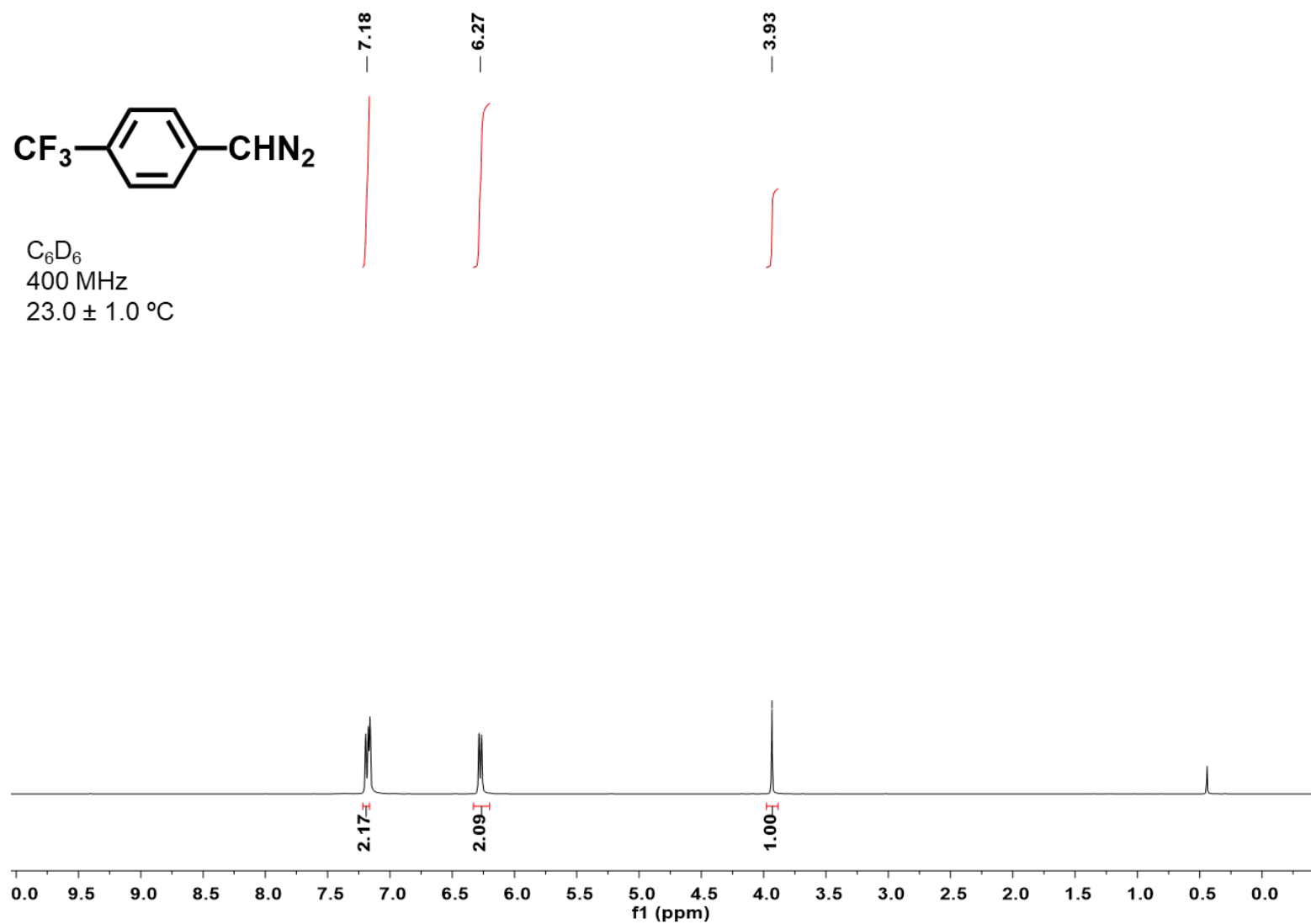


Figure S41. ^1H NMR spectrum of **1b** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

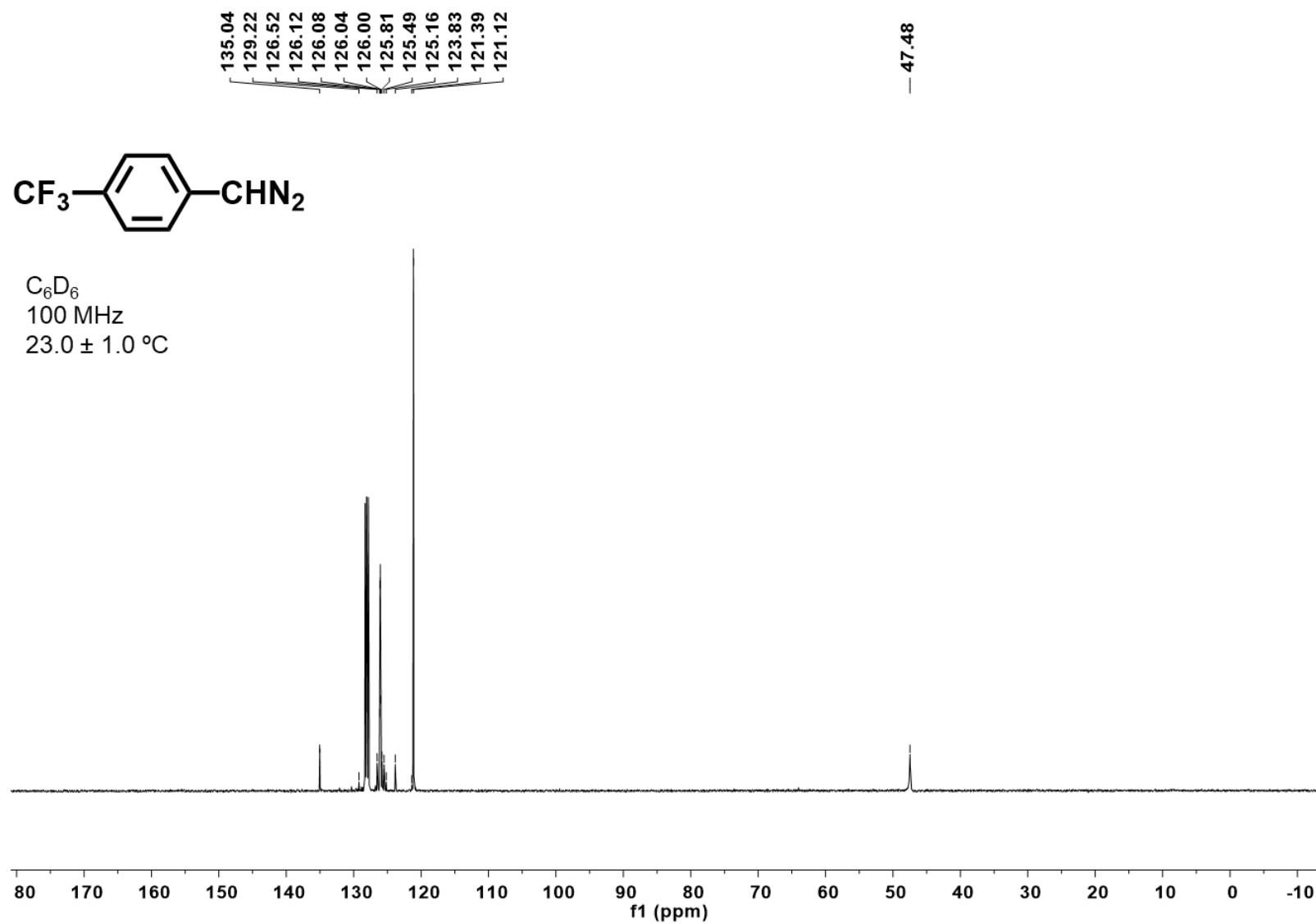


Figure S42. ^{13}C NMR spectrum of **1b** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

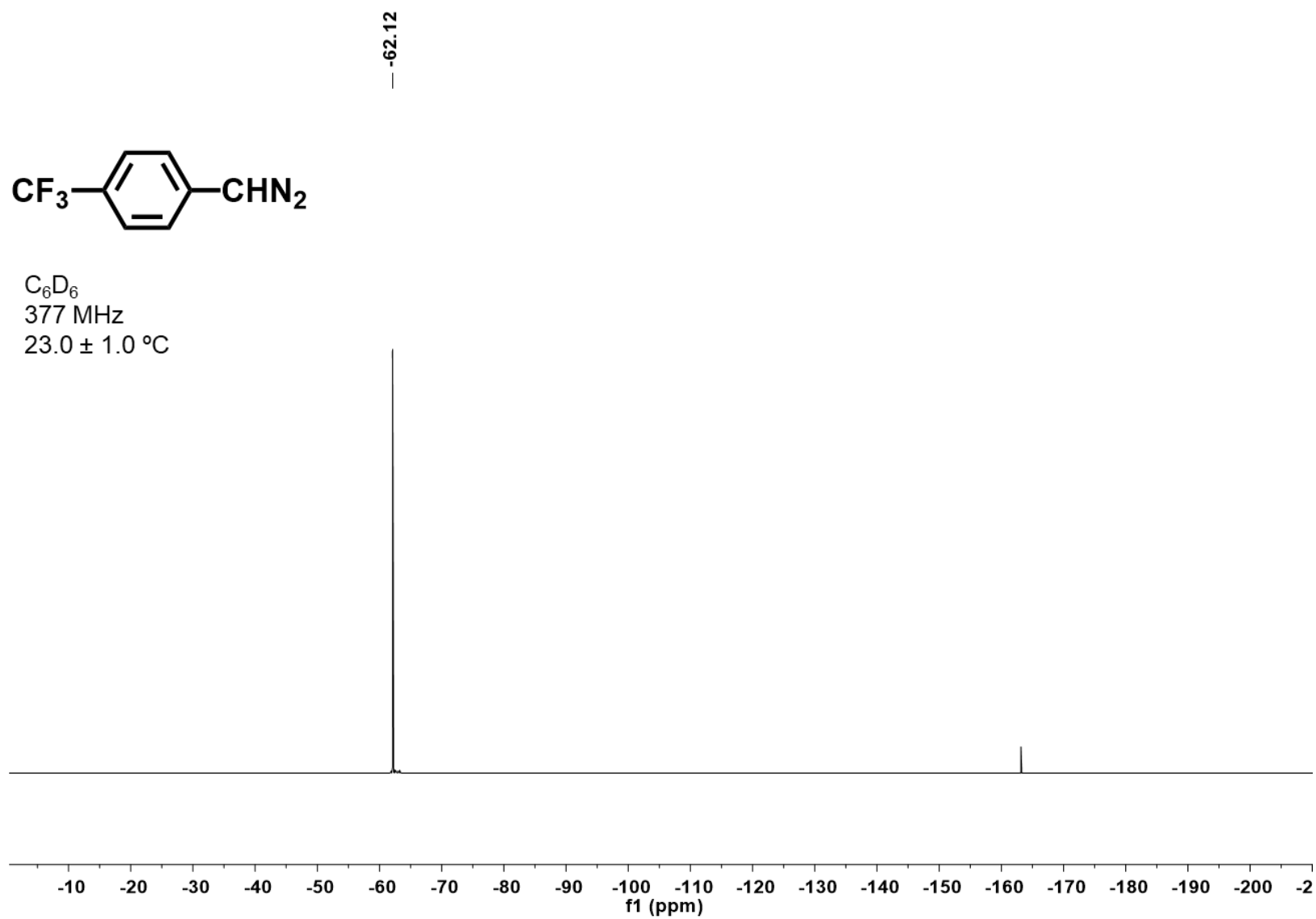


Figure S43. ^{19}F NMR spectrum of **1b** as recorded in C_6D_6 with hexafluorobenzene as a reference at $23\text{ }^\circ\text{C}$.

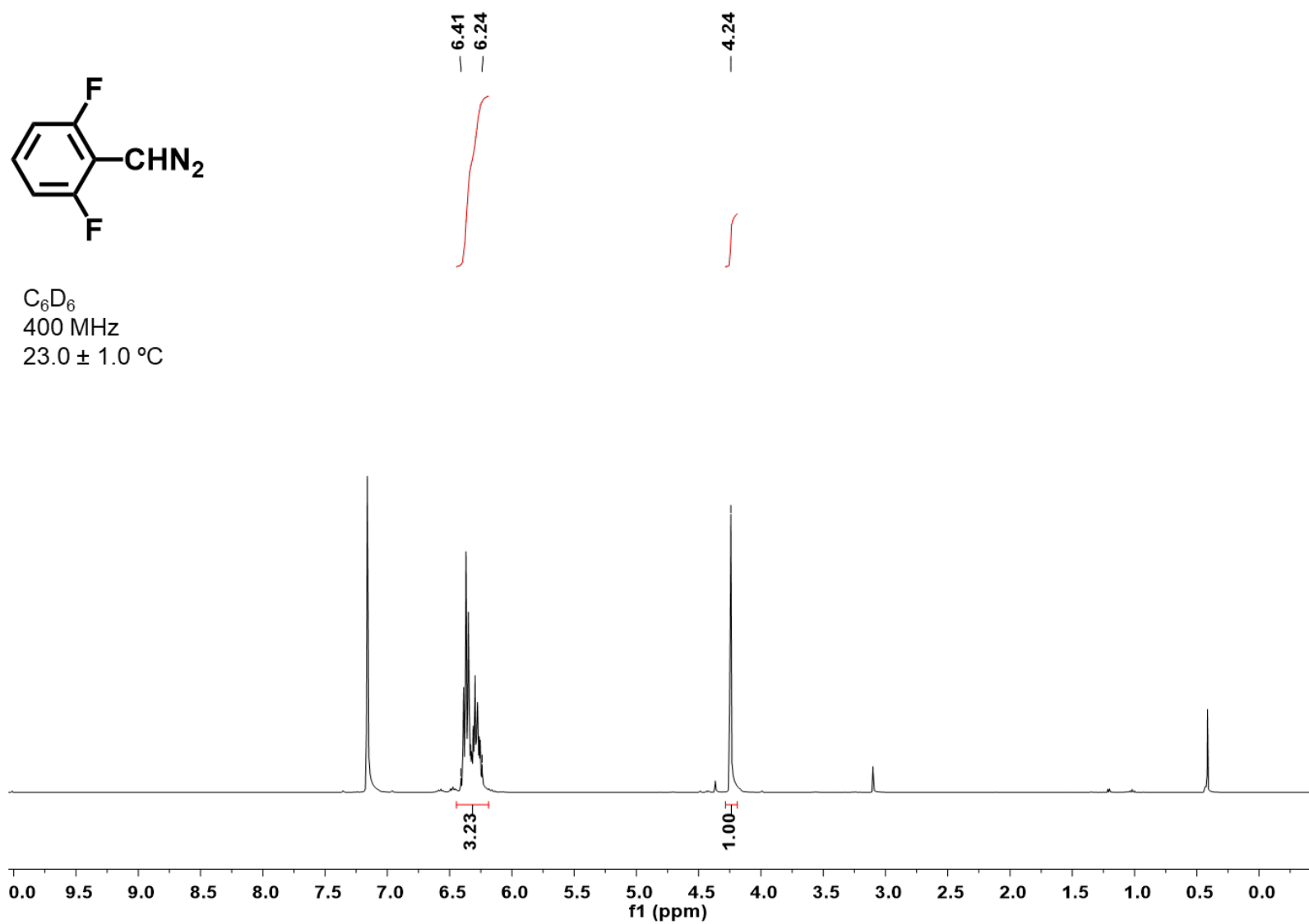


Figure S44. ^1H NMR spectrum of **1c** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

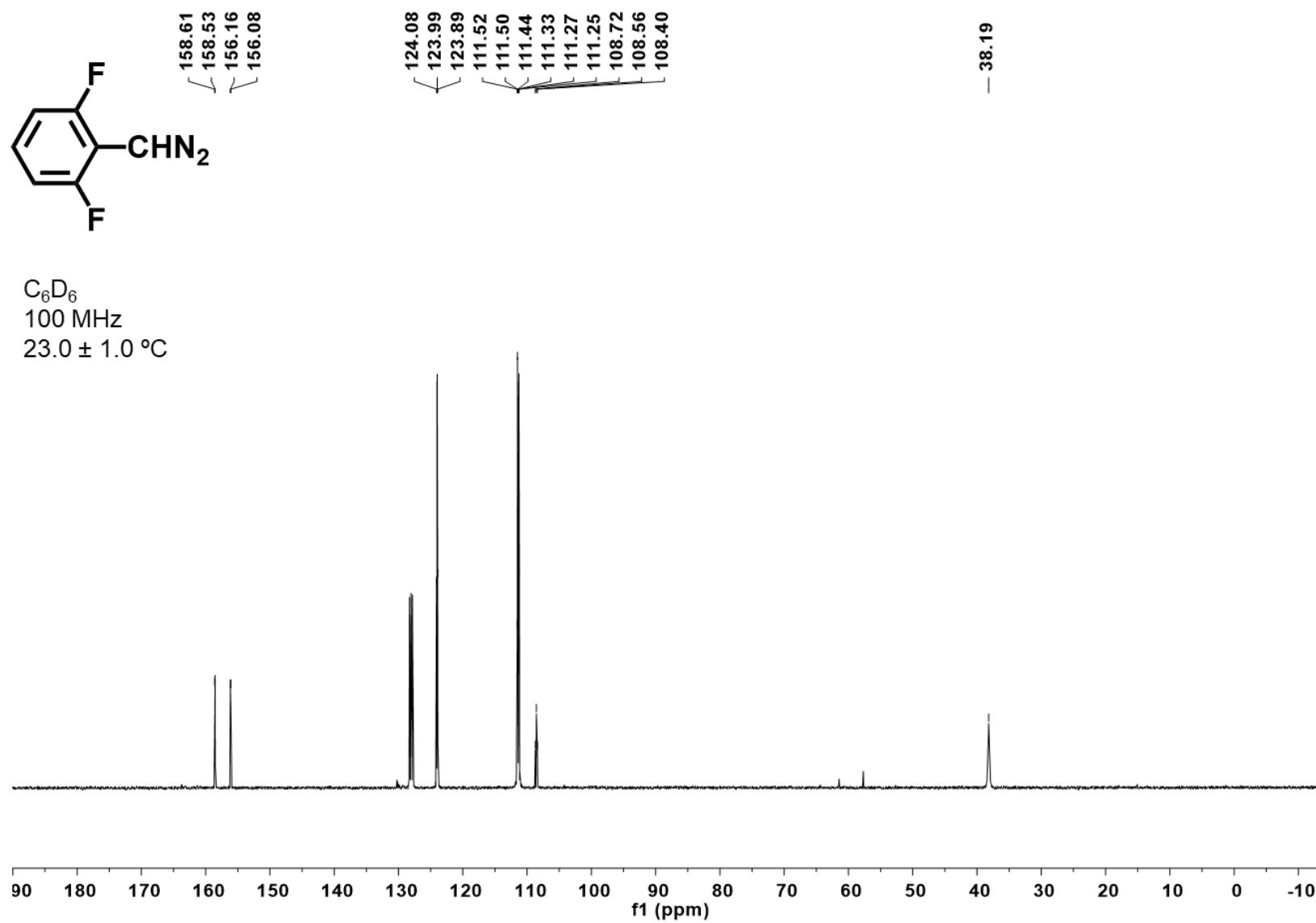


Figure S45. ^{13}C NMR spectrum of **1c** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

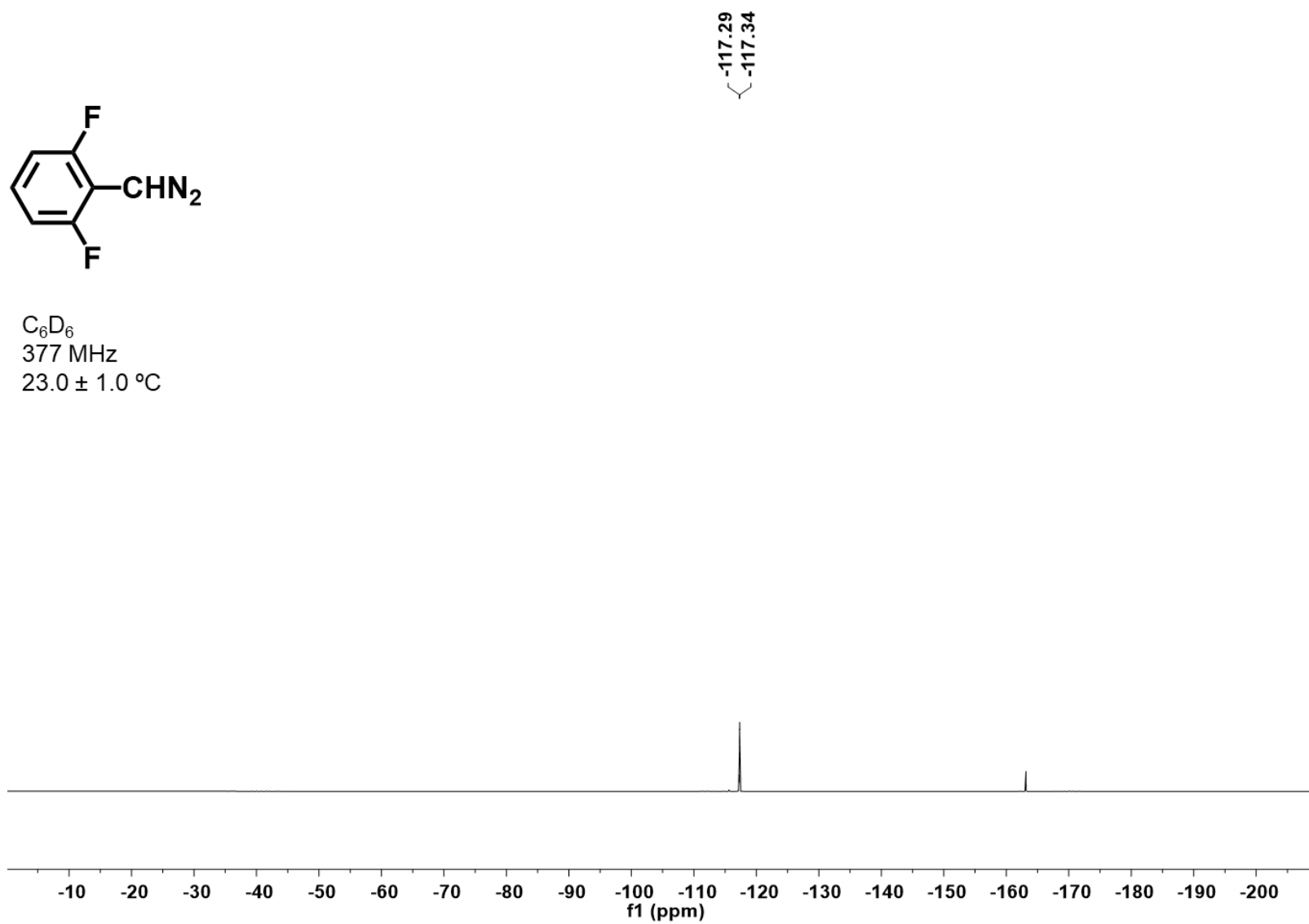


Figure S46. ^{19}F NMR spectrum of **1c** as recorded in C_6D_6 with hexafluorobenzene as a reference at $23\text{ }^\circ\text{C}$.

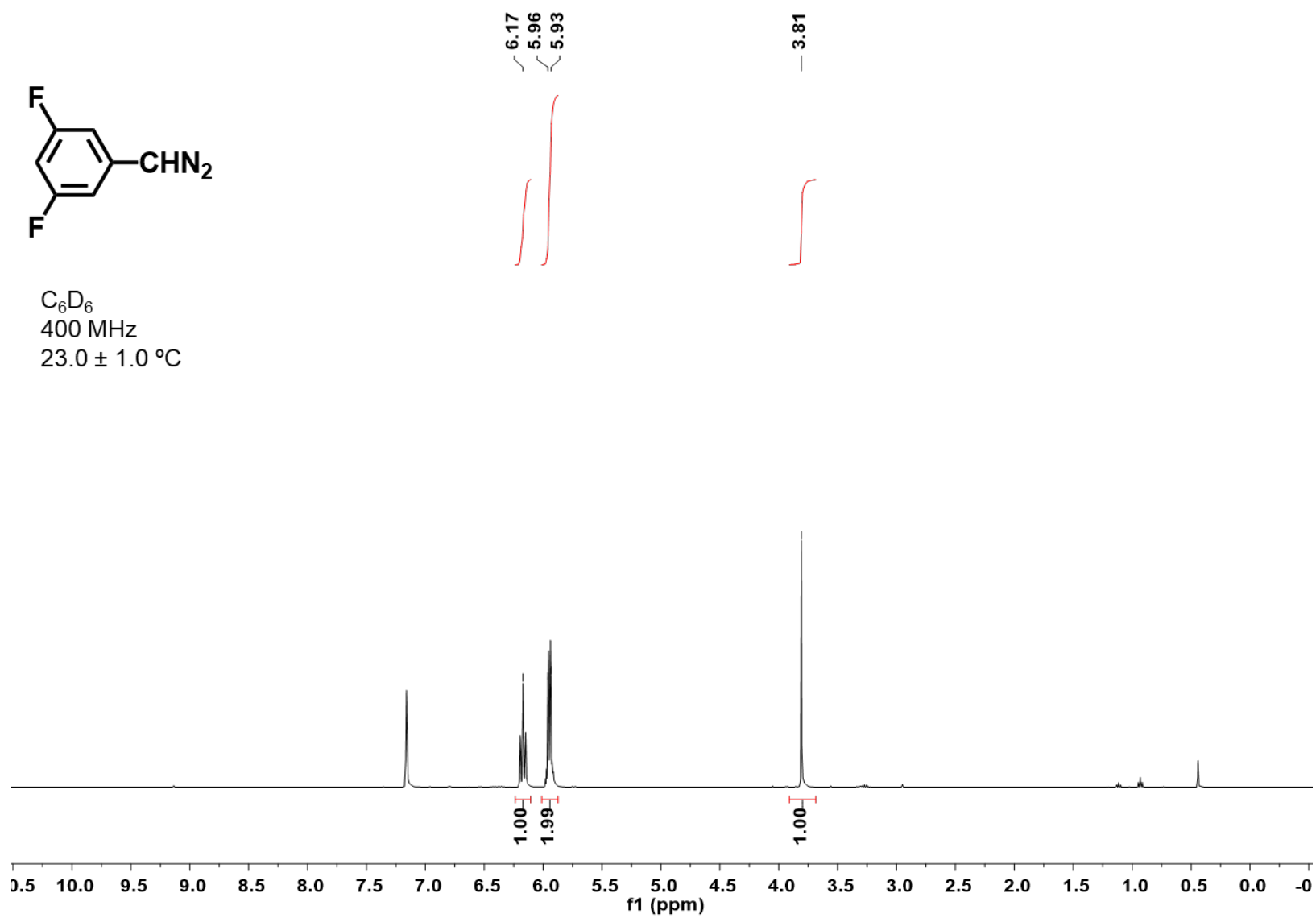


Figure S47. ¹H NMR spectrum of **1d** as recorded in C₆D₆ at 23 °C.

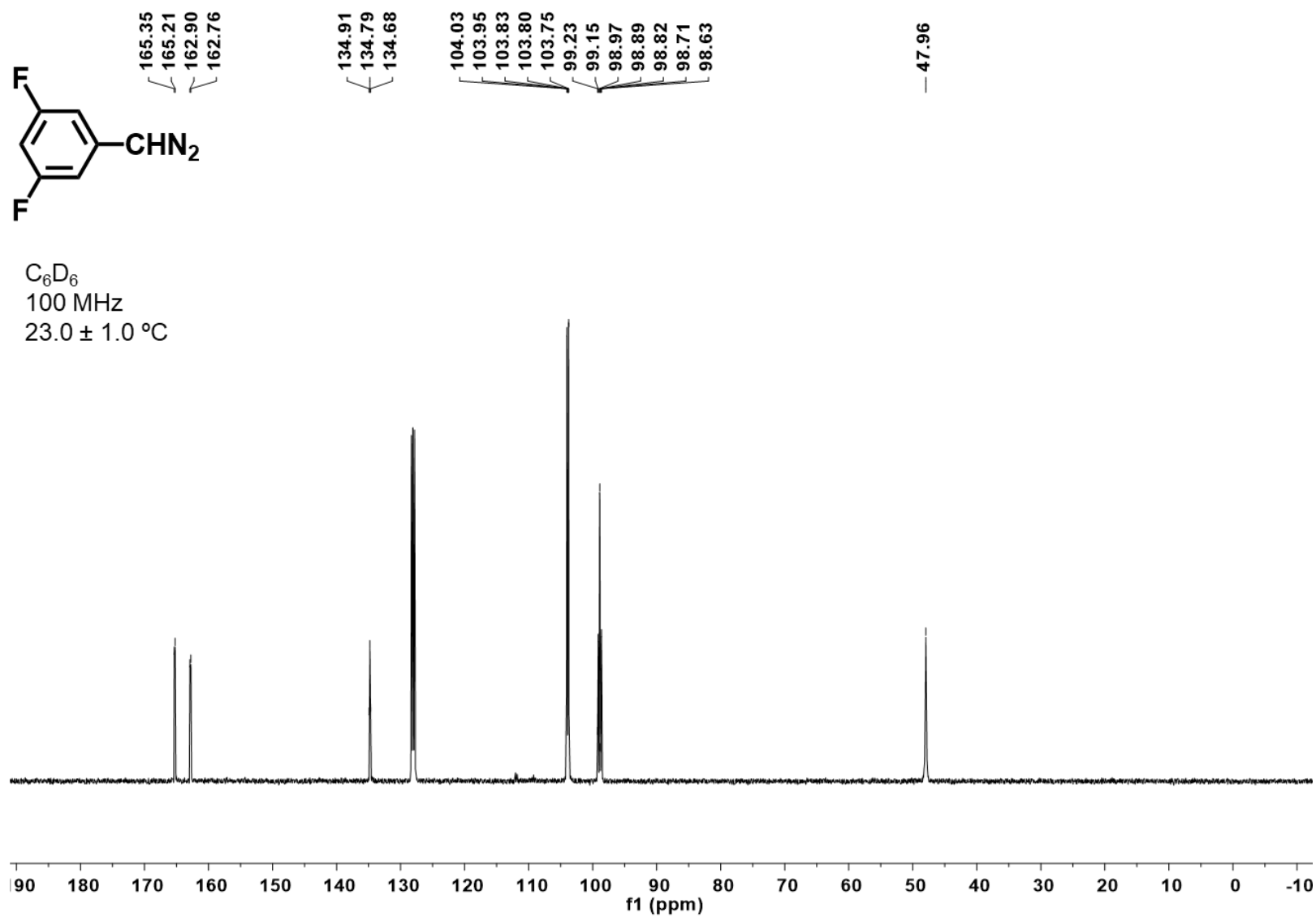


Figure S48. ^{13}C NMR spectrum of **1d** as recorded in C_6D_6 at 23°C .

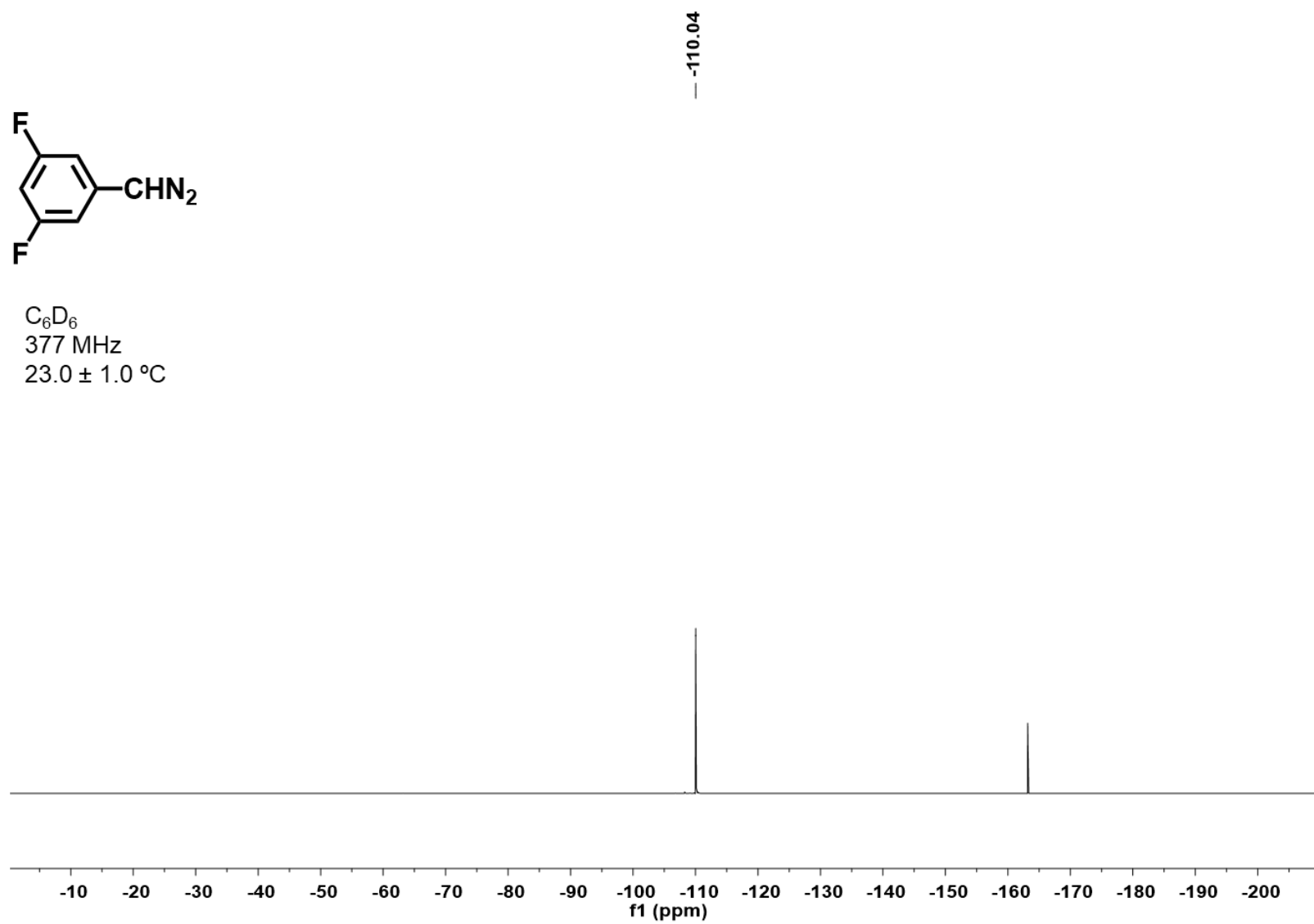


Figure S49. ^{19}F NMR spectrum of **1d** as recorded in C_6D_6 with hexafluorobenzene as a reference at $23\text{ }^\circ\text{C}$.

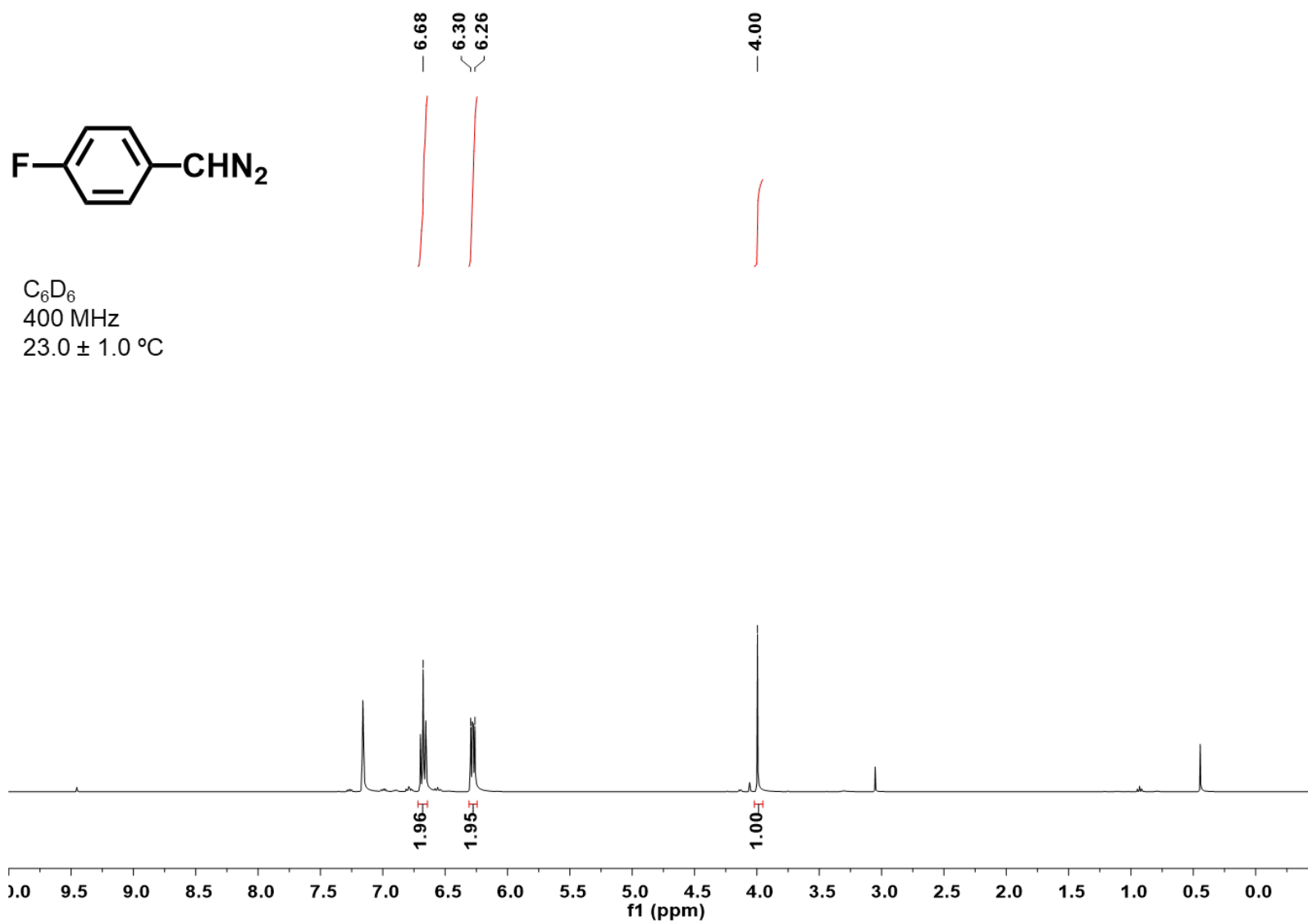


Figure S50. ^1H NMR spectrum of **1e** as recorded in C_6D_6 at 23°C .

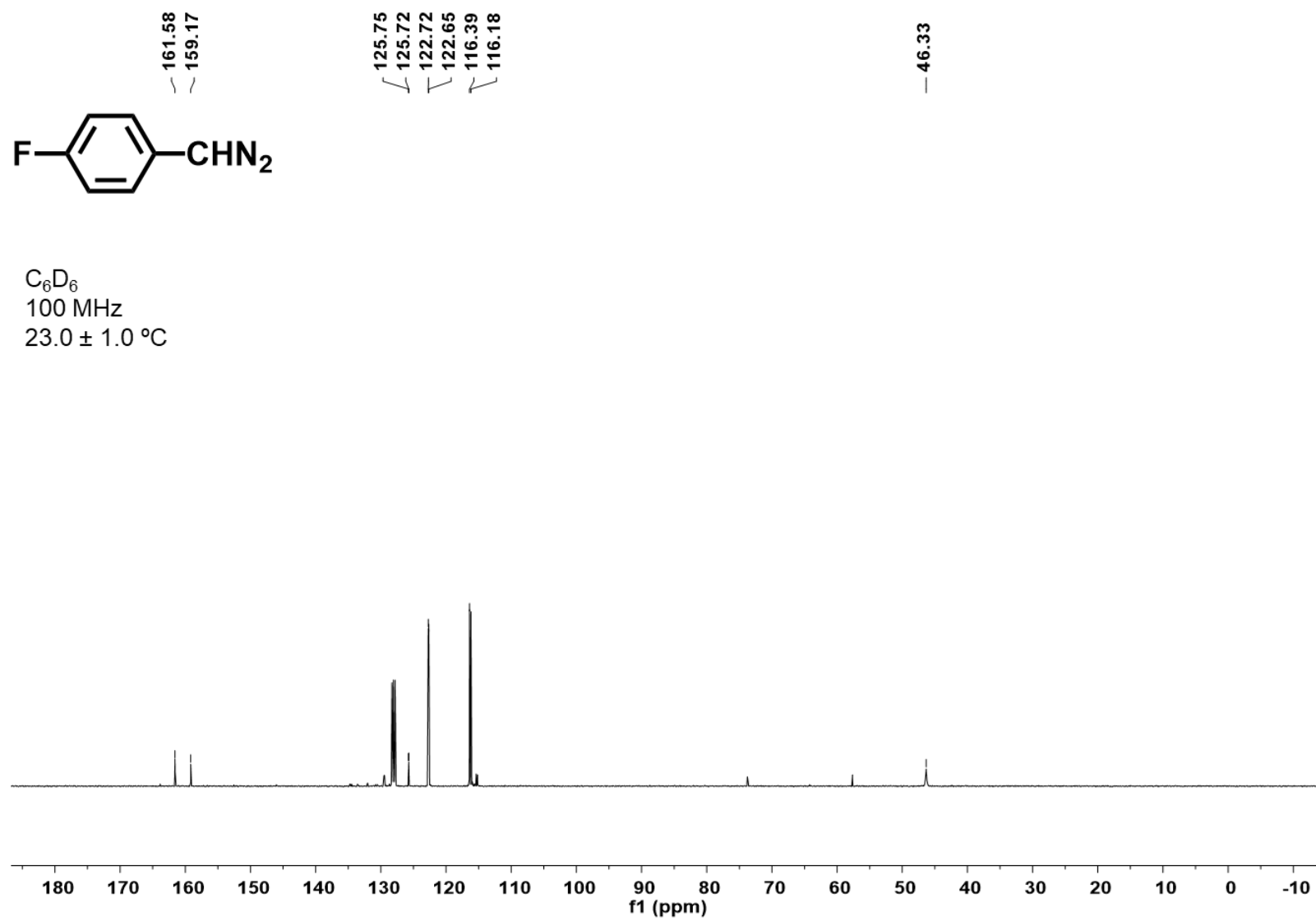


Figure S51. ^{13}C NMR spectrum of **1e** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

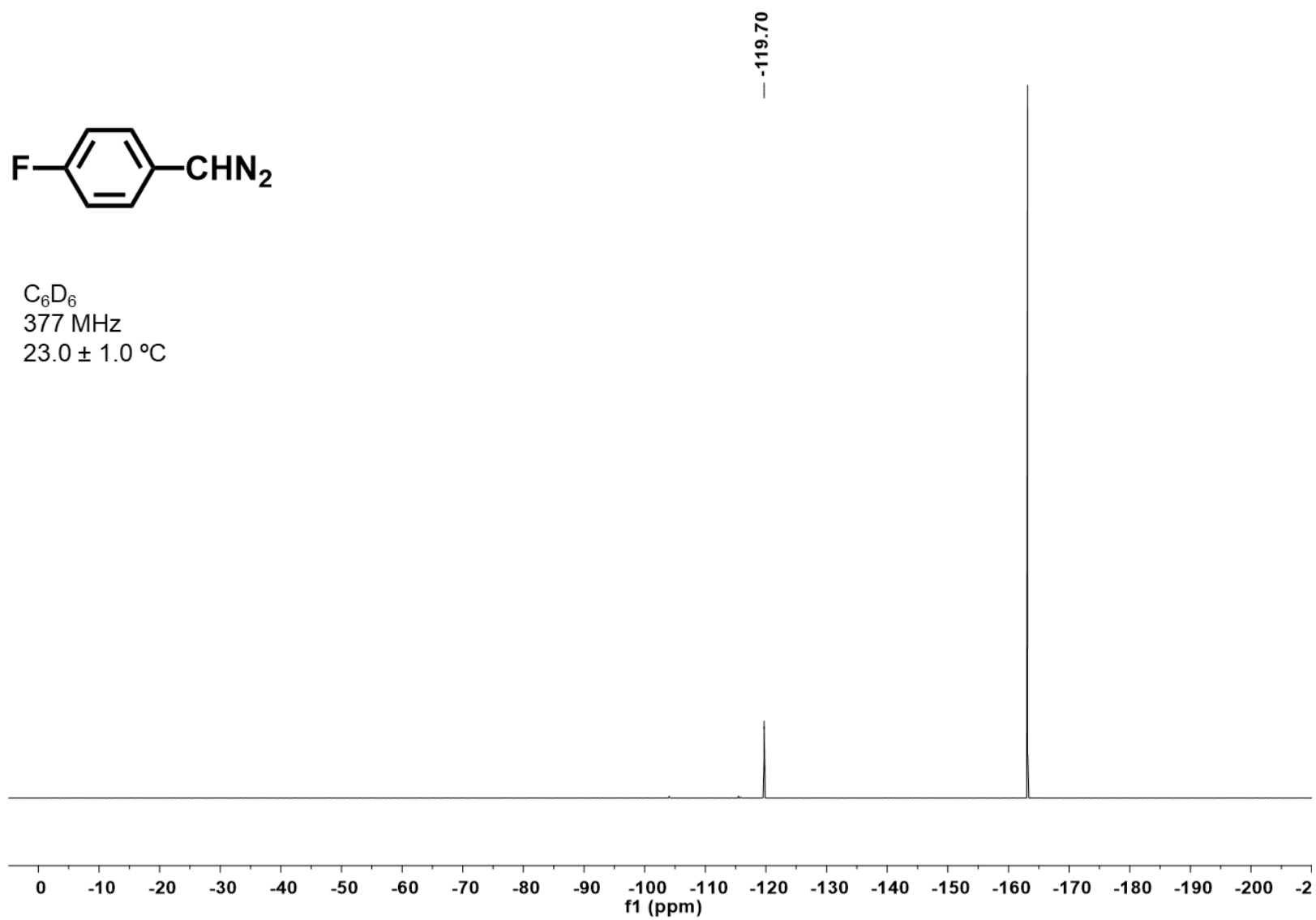


Figure S52. ^{19}F NMR spectrum of **1e** as recorded in C_6D_6 with hexafluorobenzene as a reference at $23\text{ }^\circ\text{C}$.

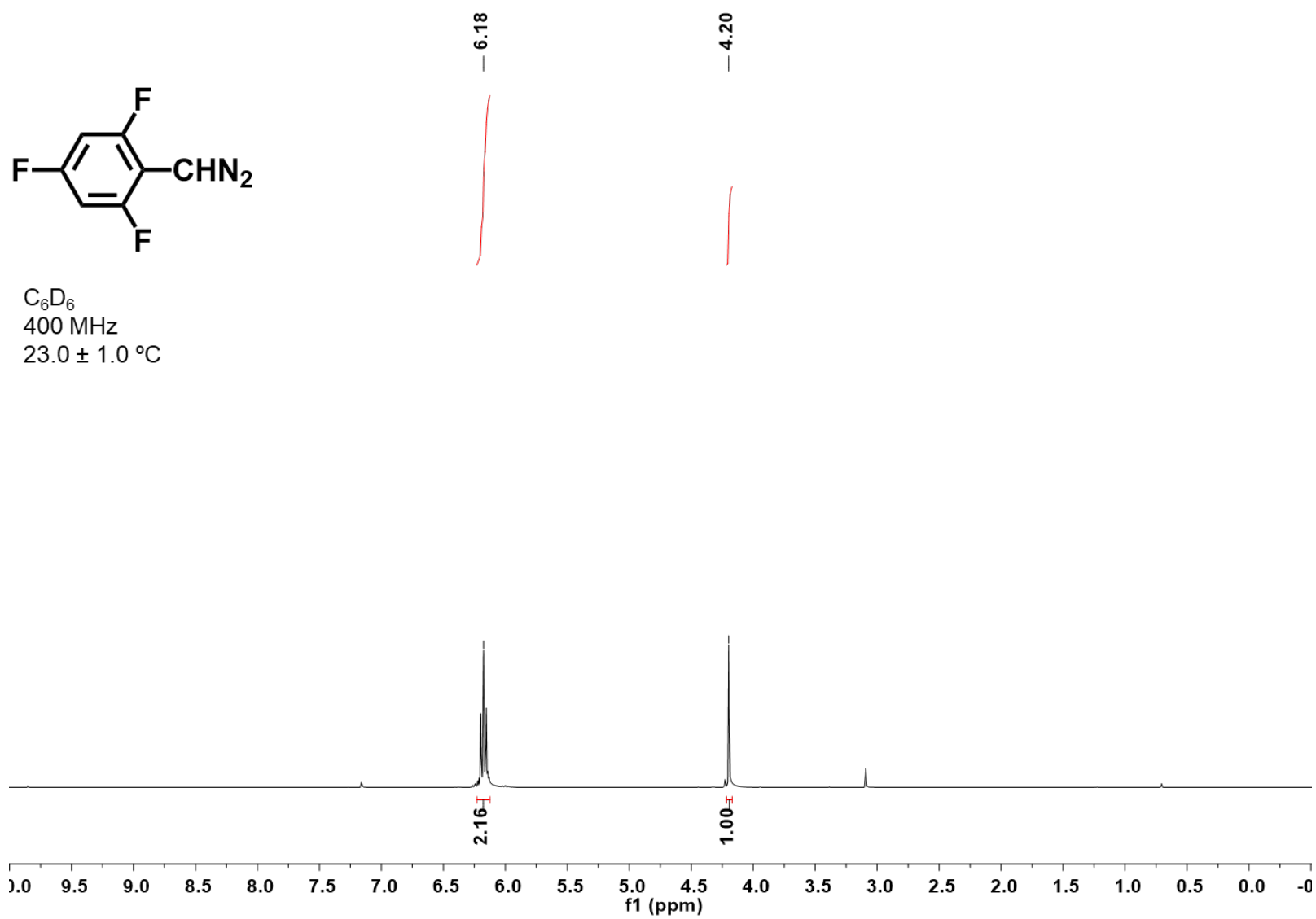


Figure S53. ^1H NMR spectrum of **1f** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

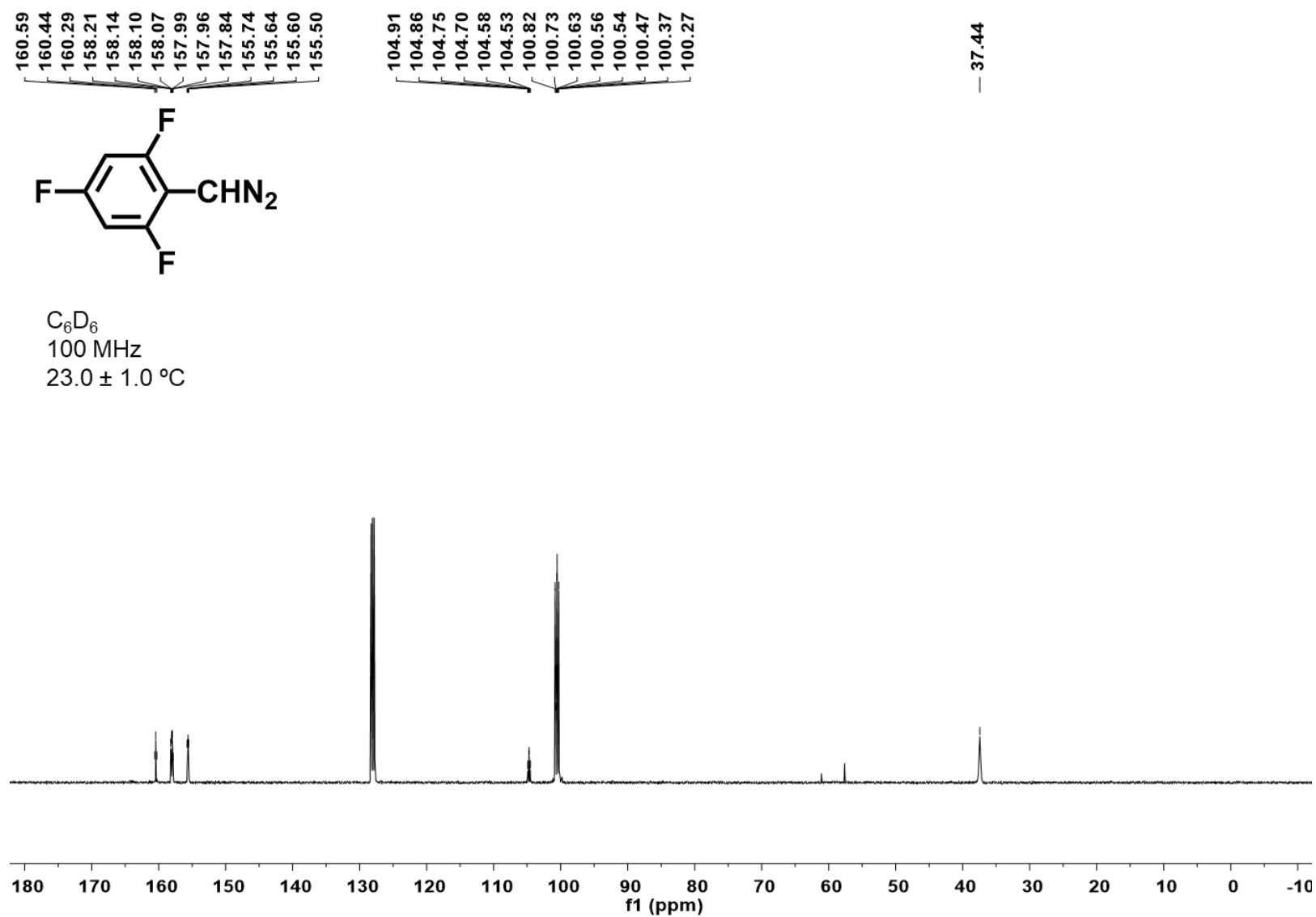


Figure S54. ^{13}C NMR spectrum of **1f** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

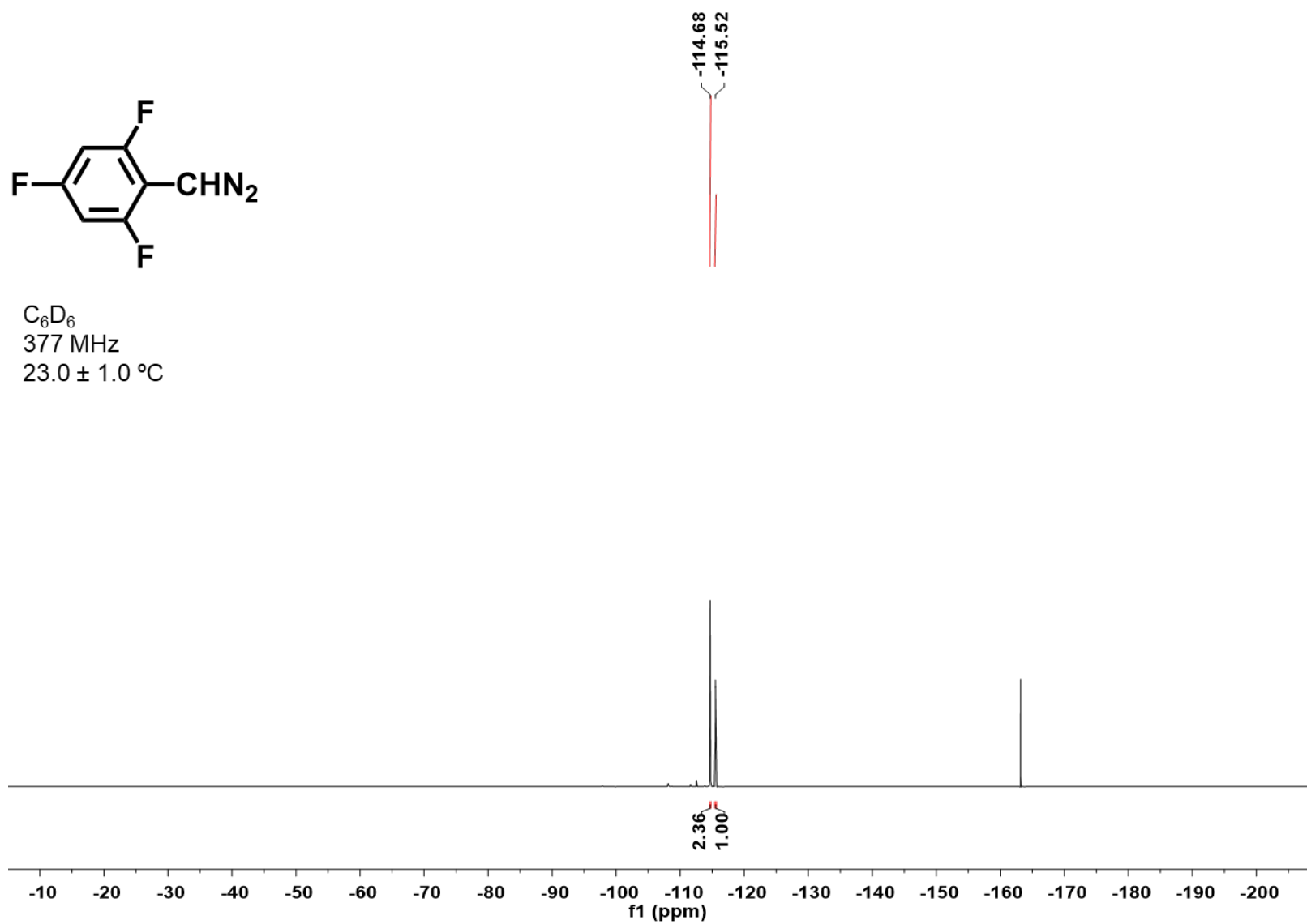


Figure S55. ^{19}F NMR spectrum of **1f** as recorded in C_6D_6 with hexafluorobenzene as a reference at $23\text{ }^\circ\text{C}$.

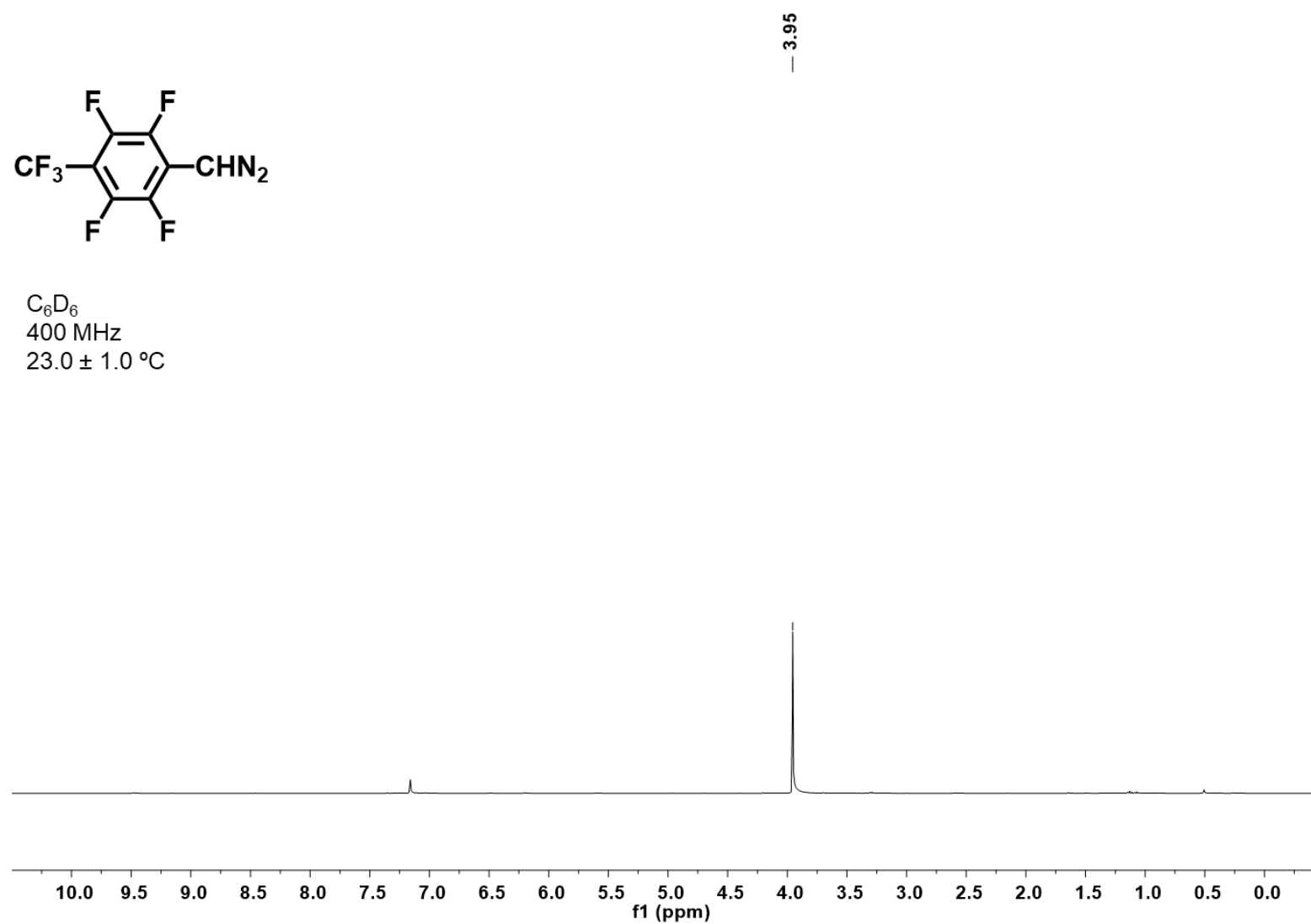


Figure S56. ^1H NMR spectrum of **1g** as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

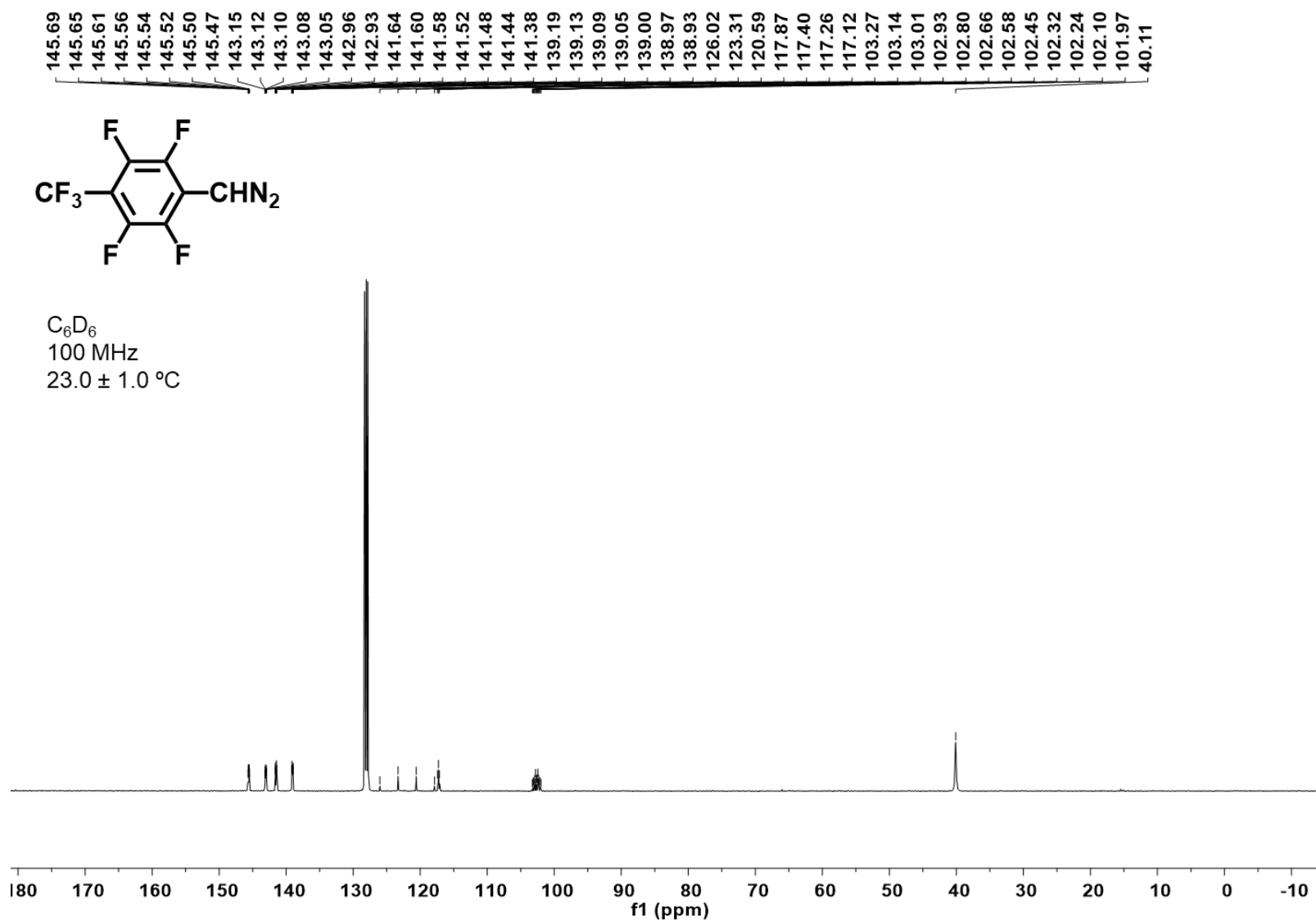


Figure S57. ^{13}C NMR spectrum of **1g** as recorded in C_6D_6 at 23°C .

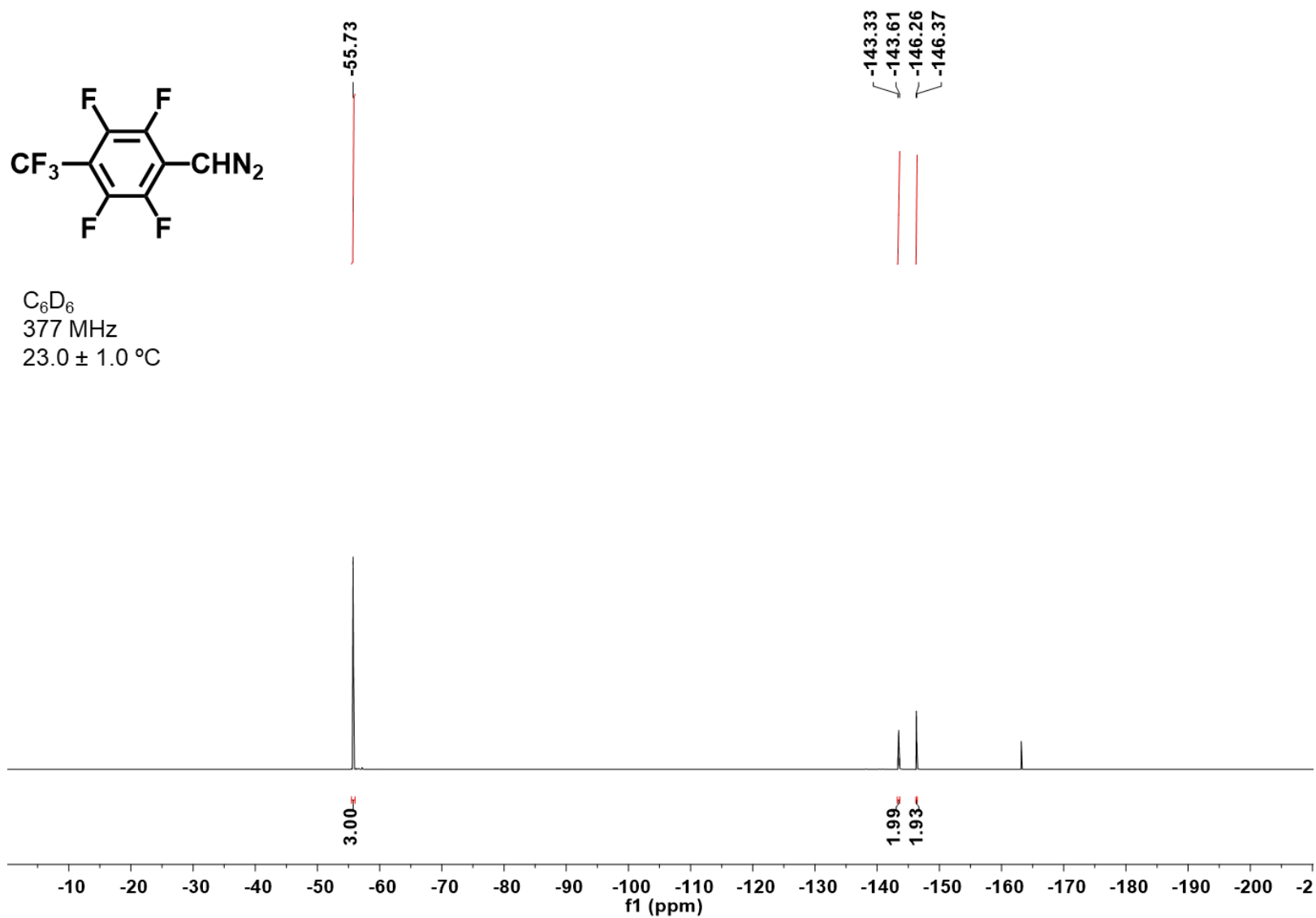


Figure S58. ^{19}F NMR spectrum of **1g** as recorded in C_6D_6 with hexafluorobenzene as a reference at $23\text{ }^\circ\text{C}$.

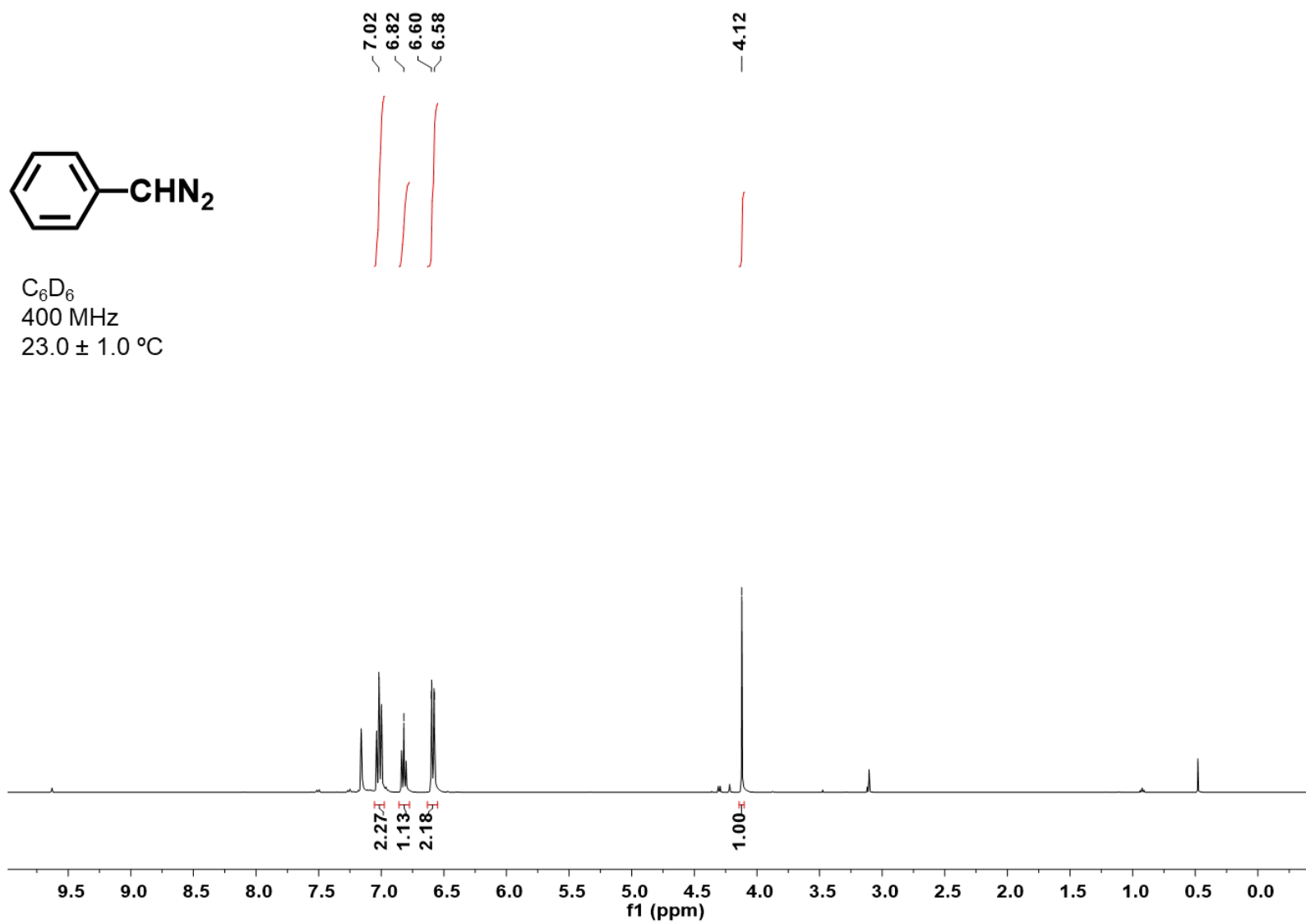


Figure S59. ^1H NMR spectrum of phenyl diazomethane as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.

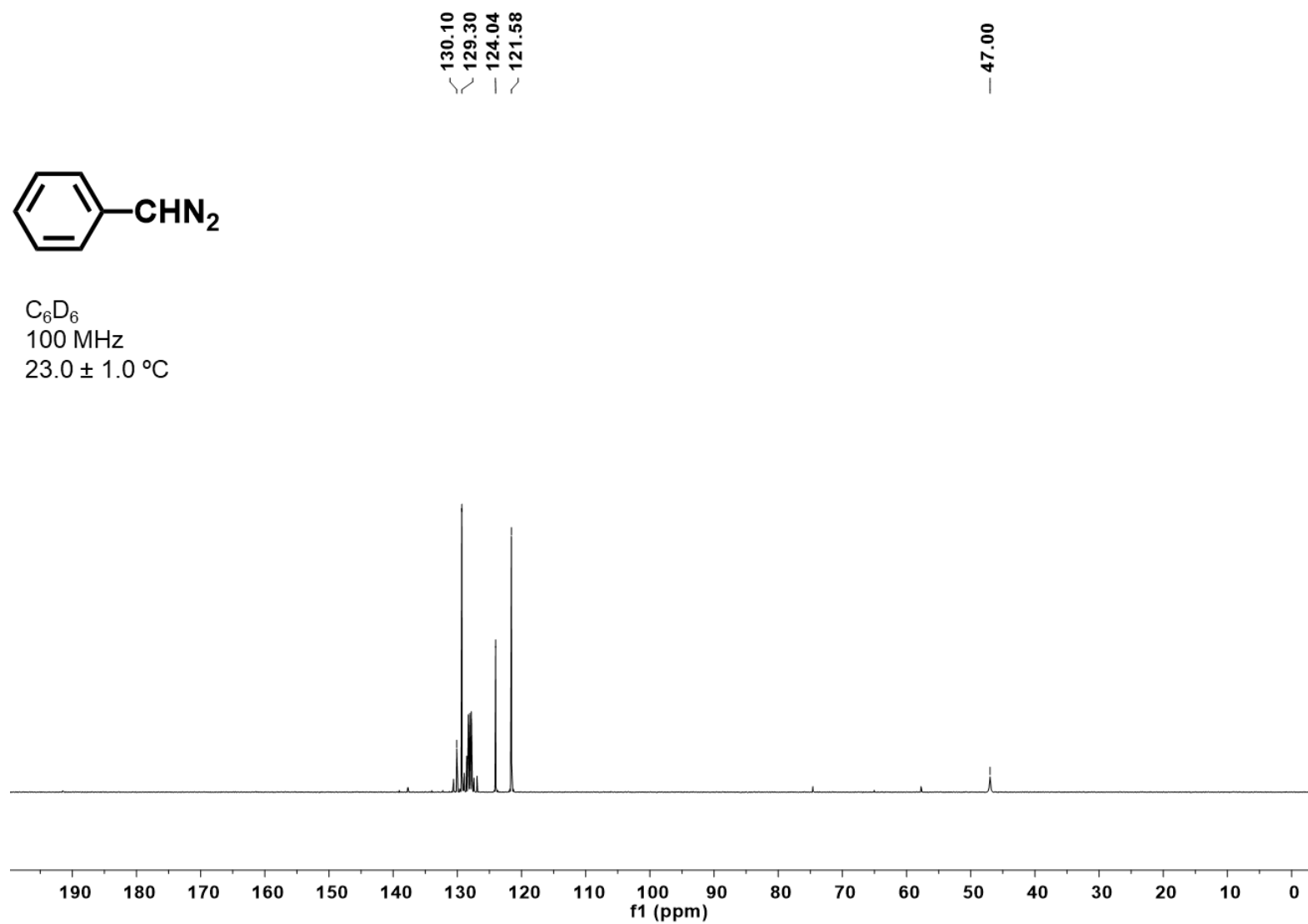
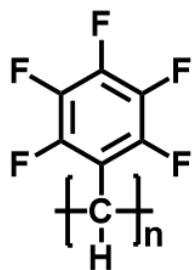


Figure S60. ^{13}C NMR spectrum of phenyl diazomethane as recorded in C_6D_6 at $23\text{ }^\circ\text{C}$.



hexafluorobenzene
400 MHz
 23.0 ± 1.0 °C

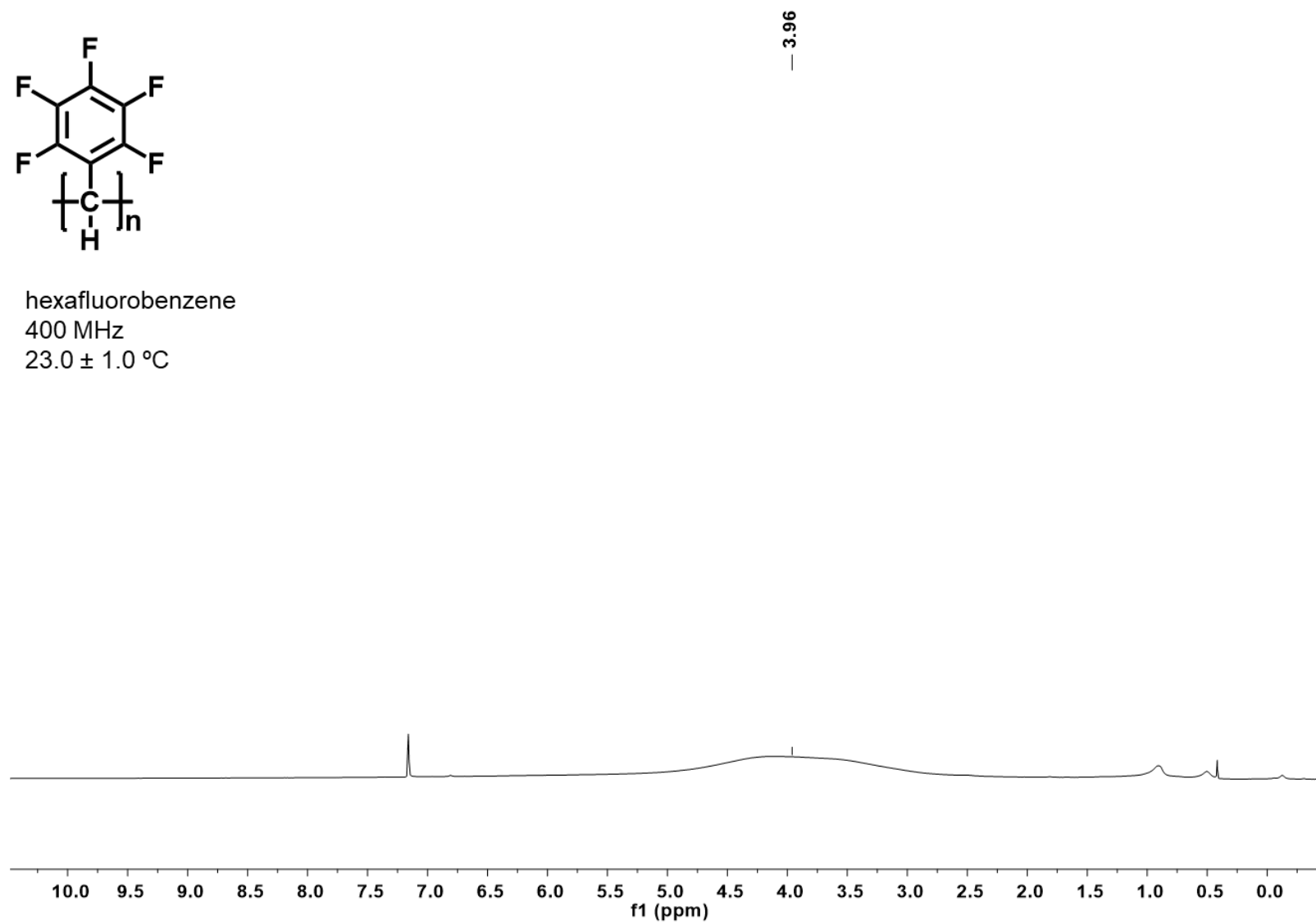


Figure S61. ^1H NMR spectrum of poly(**1a**) as recorded in hexafluorobenzene with C_6D_6 as a reference at 23 °C.

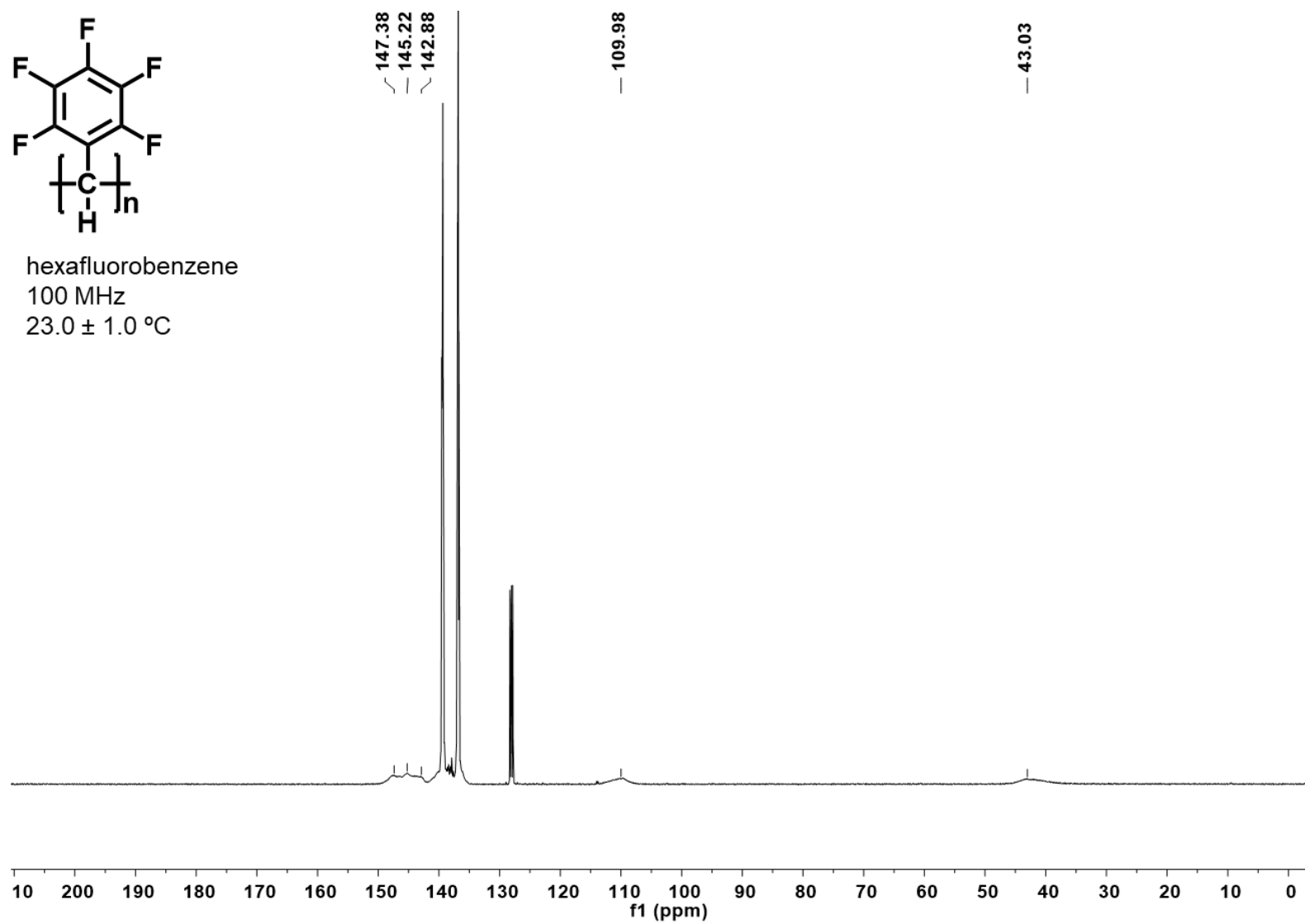


Figure S62. ^{13}C NMR spectrum of poly(**1a**) as recorded in hexafluorobenzene with C_6D_6 as a reference at 23 °C.

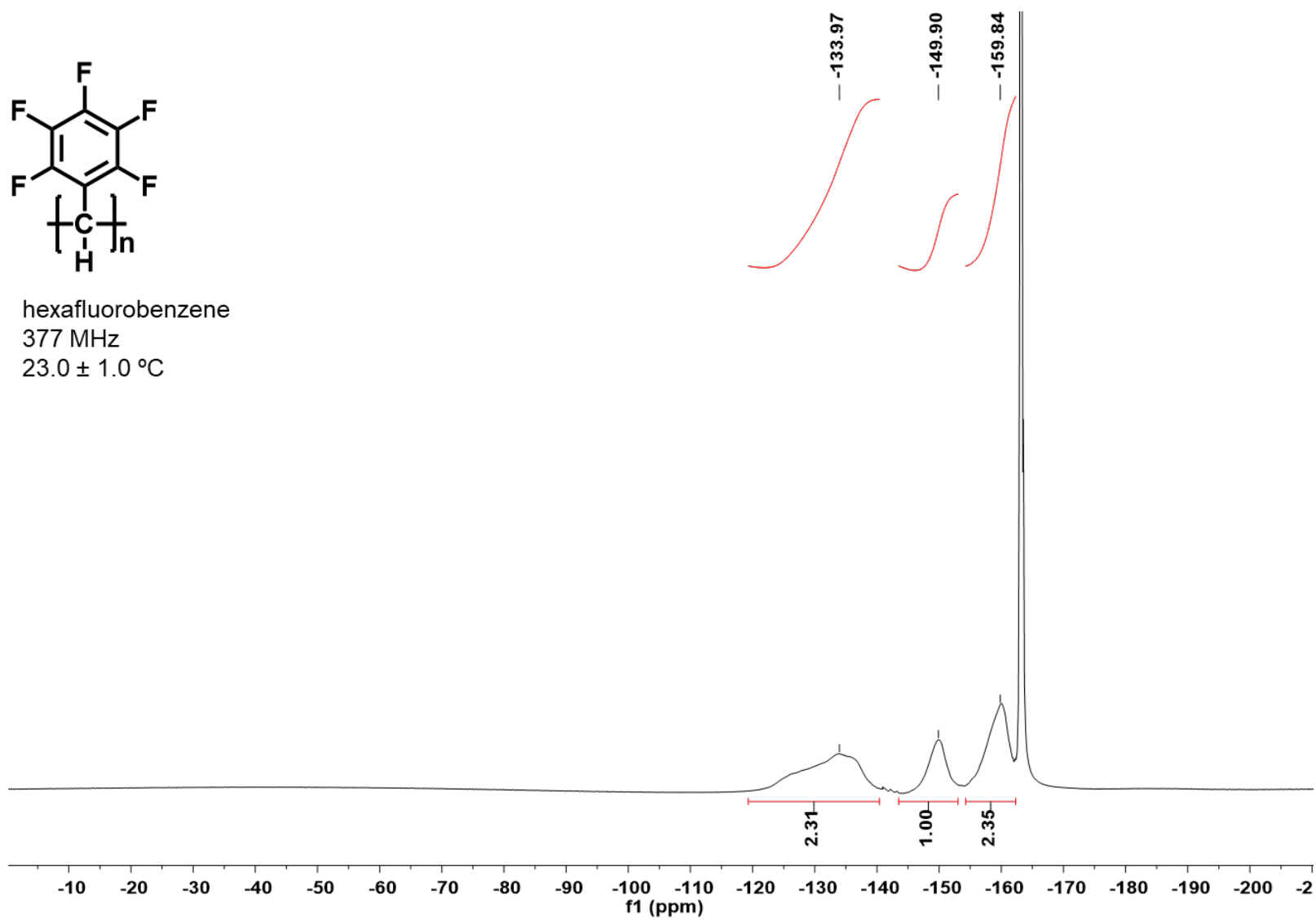


Figure S63. ^{19}F NMR spectrum of poly(**1a**) as recorded in hexafluorobenzene at 23 °C.

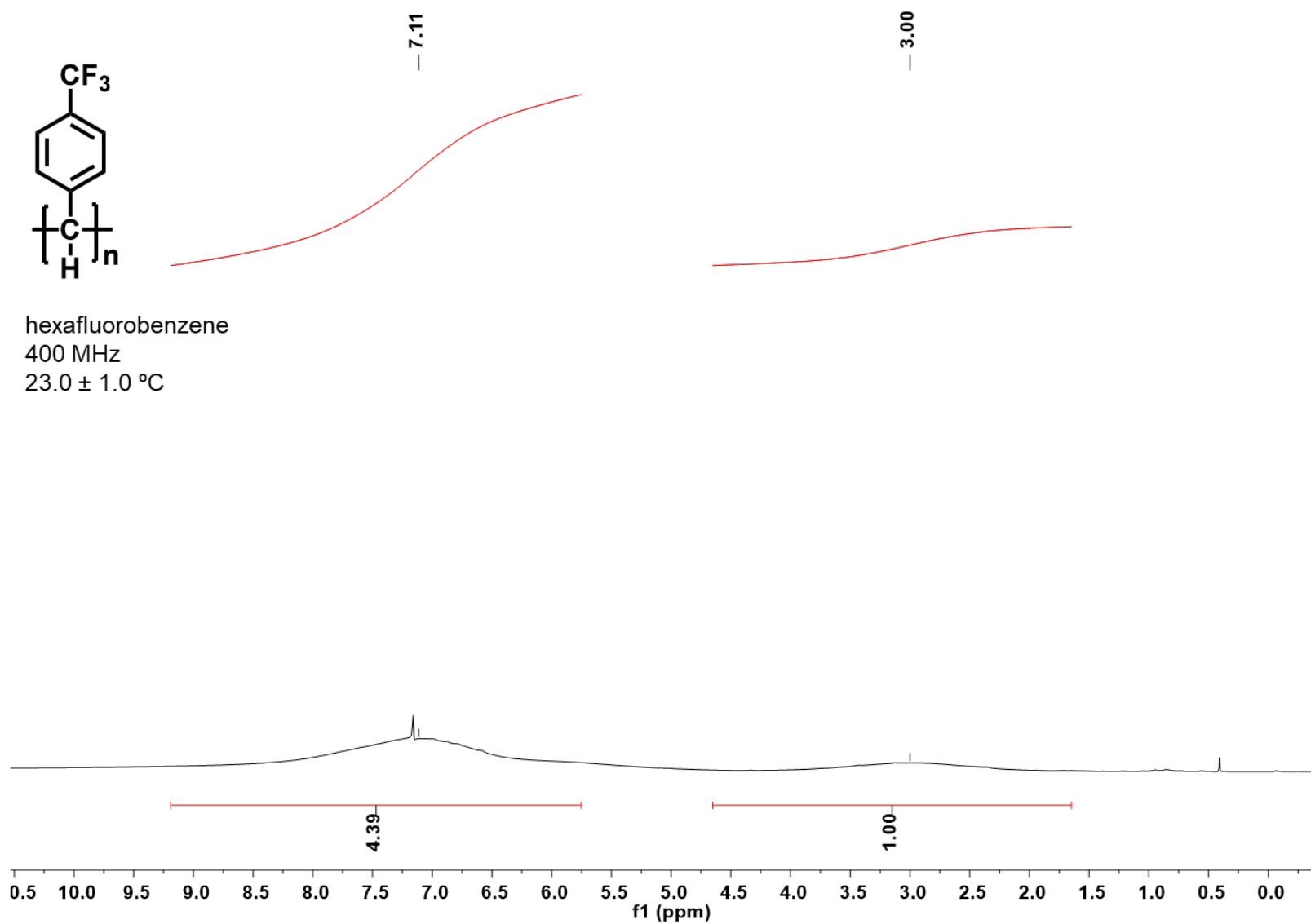


Figure S64. ^1H NMR spectrum of poly(**1b**) as recorded in hexafluorobenzene with C_6D_6 as a reference at 23 °C.

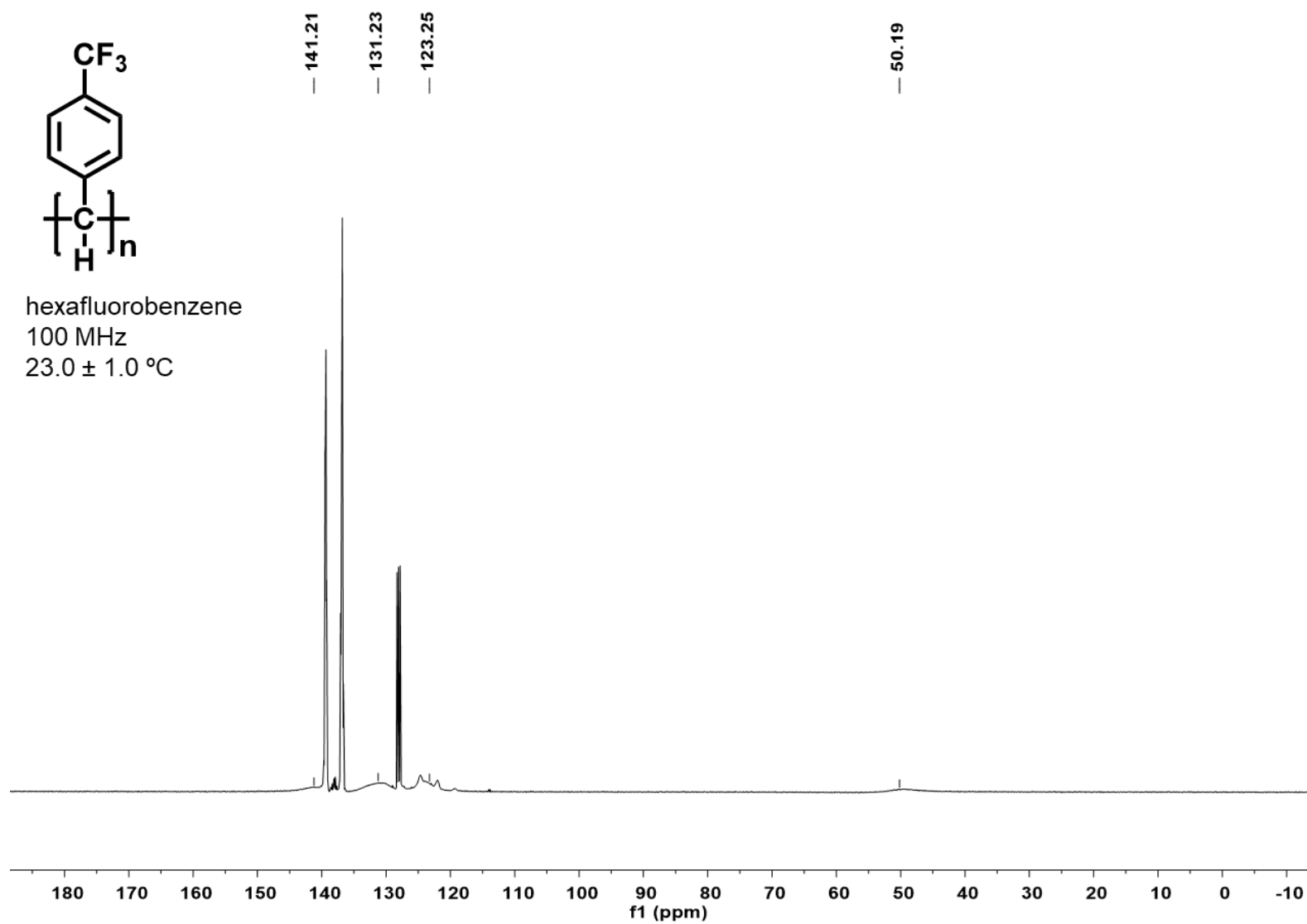


Figure S65. ¹³C NMR spectrum of poly(1b) as recorded in hexafluorobenzene with C₆D₆ as a reference at 23 °C.

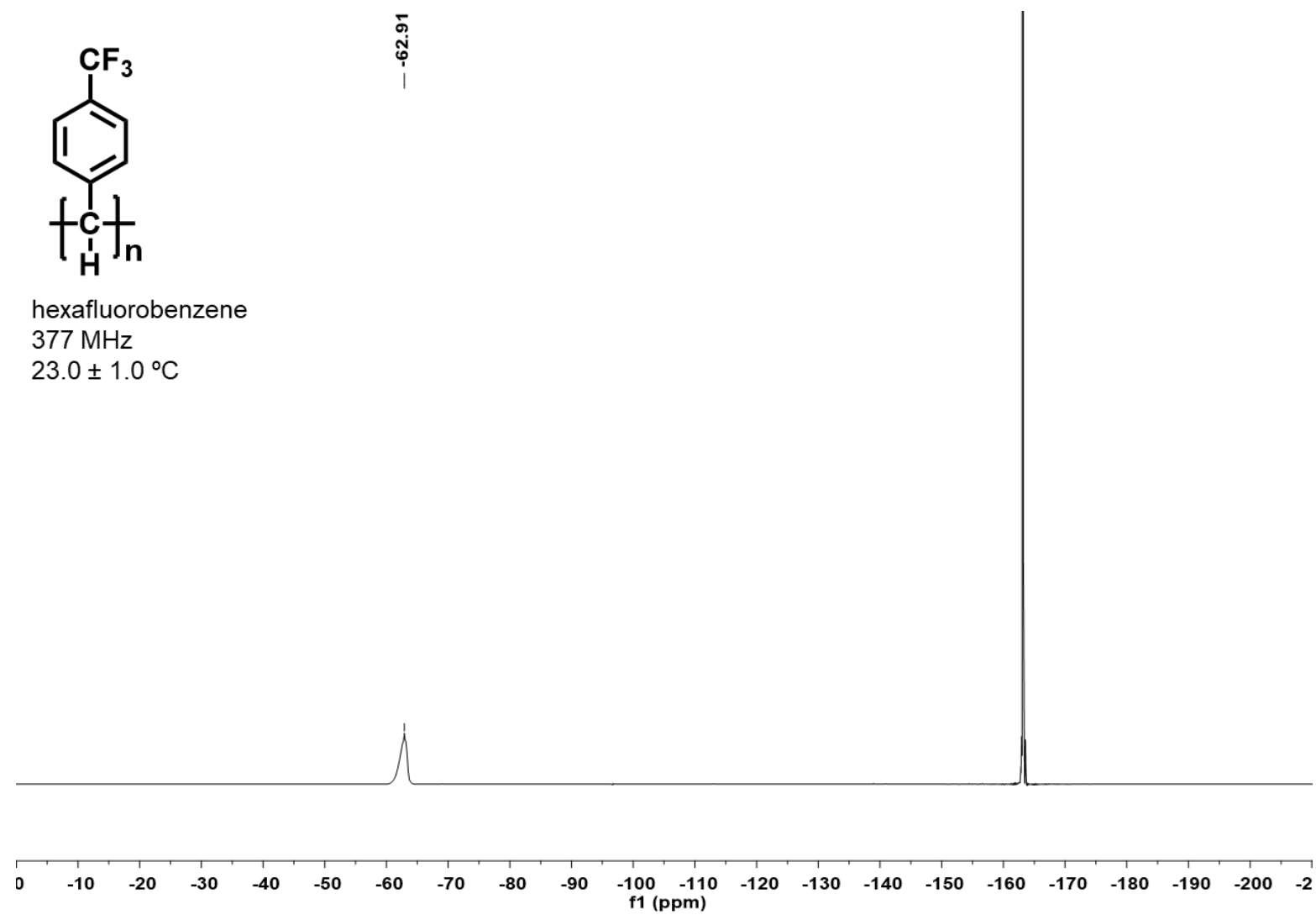


Figure S66. ¹⁹F NMR spectrum of poly(**1b**) as recorded in hexafluorobenzene at 23 °C.

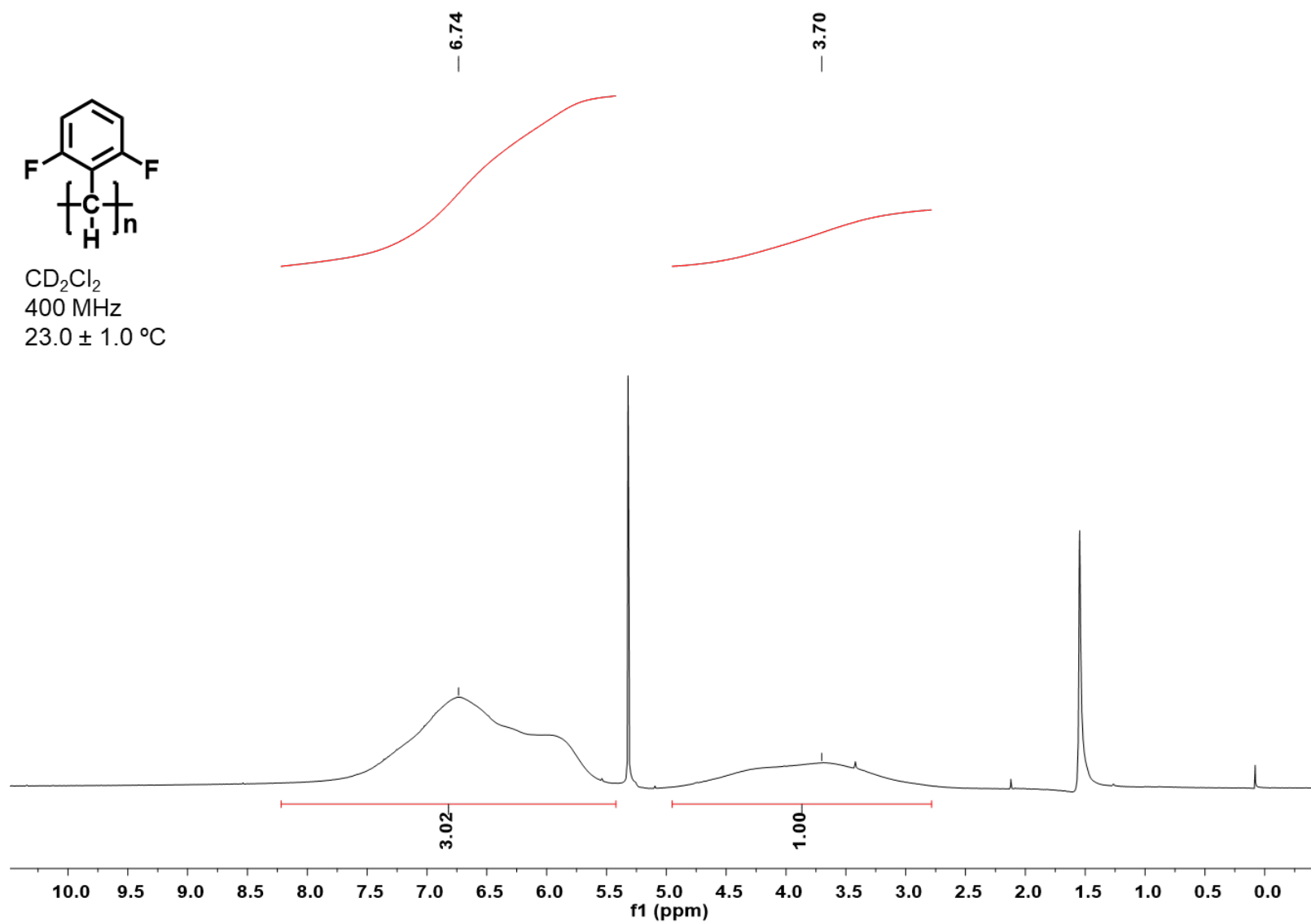


Figure S67. ^1H NMR spectrum of poly(1c) as recorded in CD_2Cl_2 at 23°C .

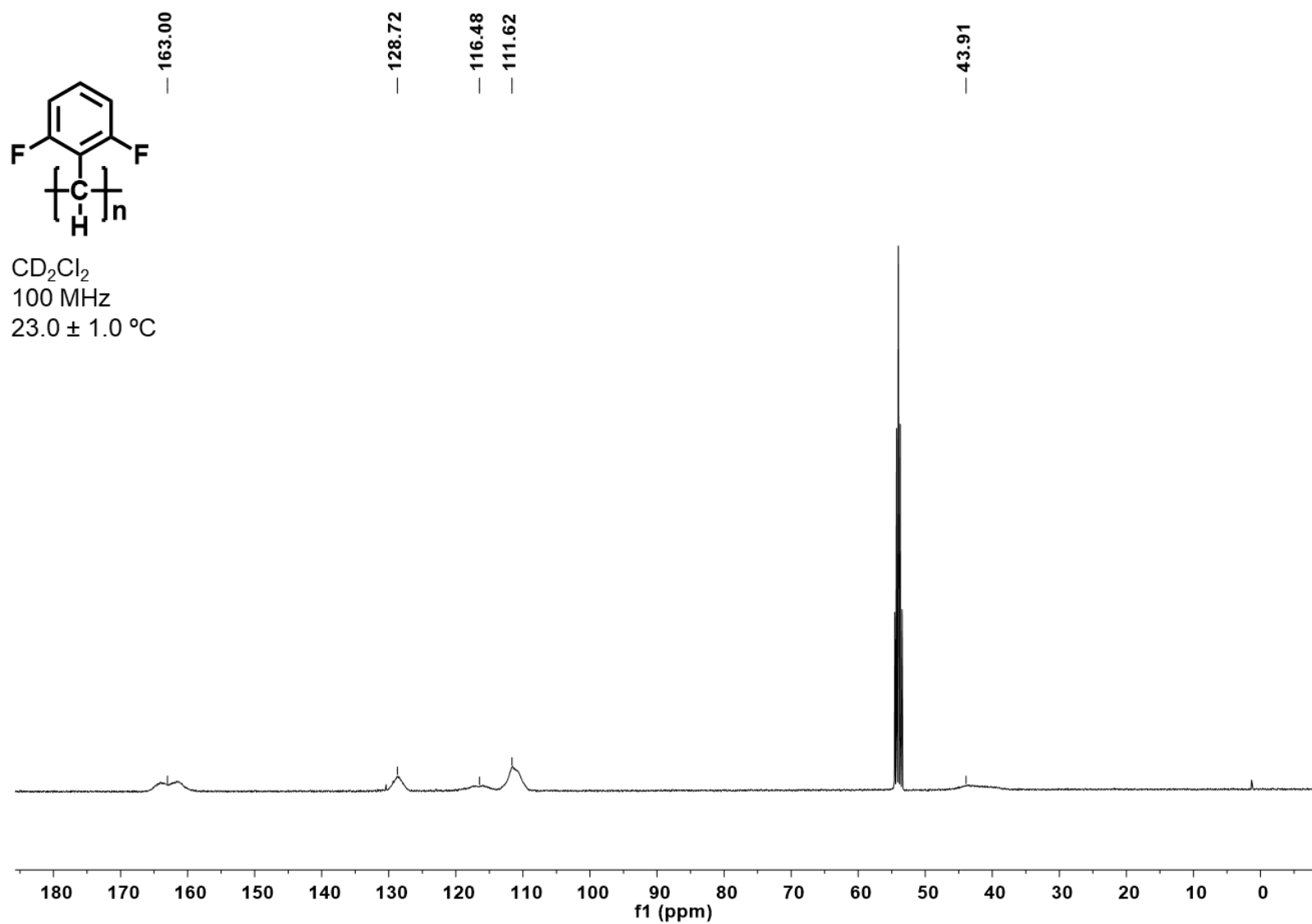


Figure S68. ^{13}C NMR spectrum of poly(1c) as recorded in CD_2Cl_2 at 23 °C.

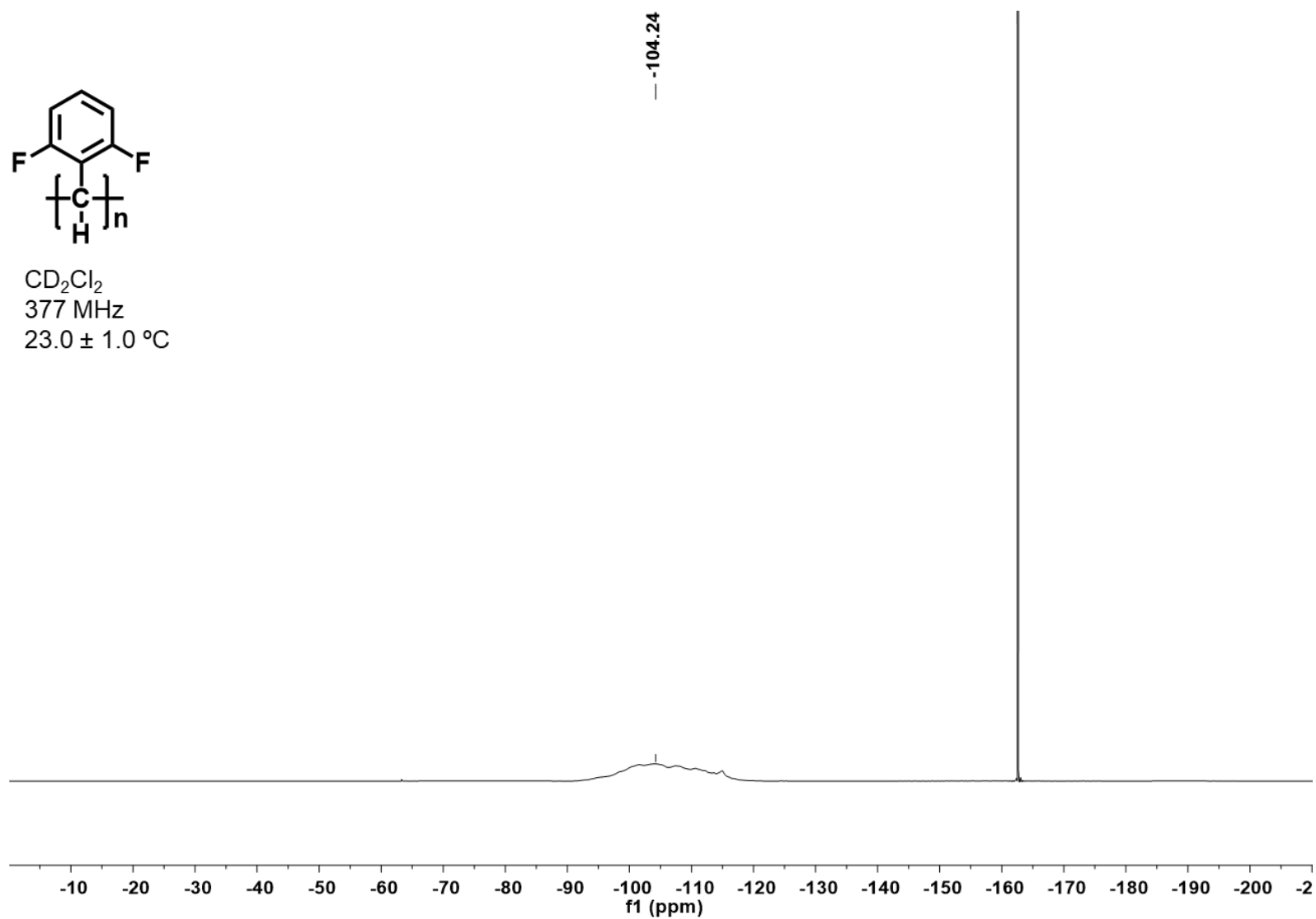


Figure S69. ¹⁹F NMR spectrum of poly(**1c**) as recorded in CD₂Cl₂ with hexafluorobenzene as a reference at 23 °C.

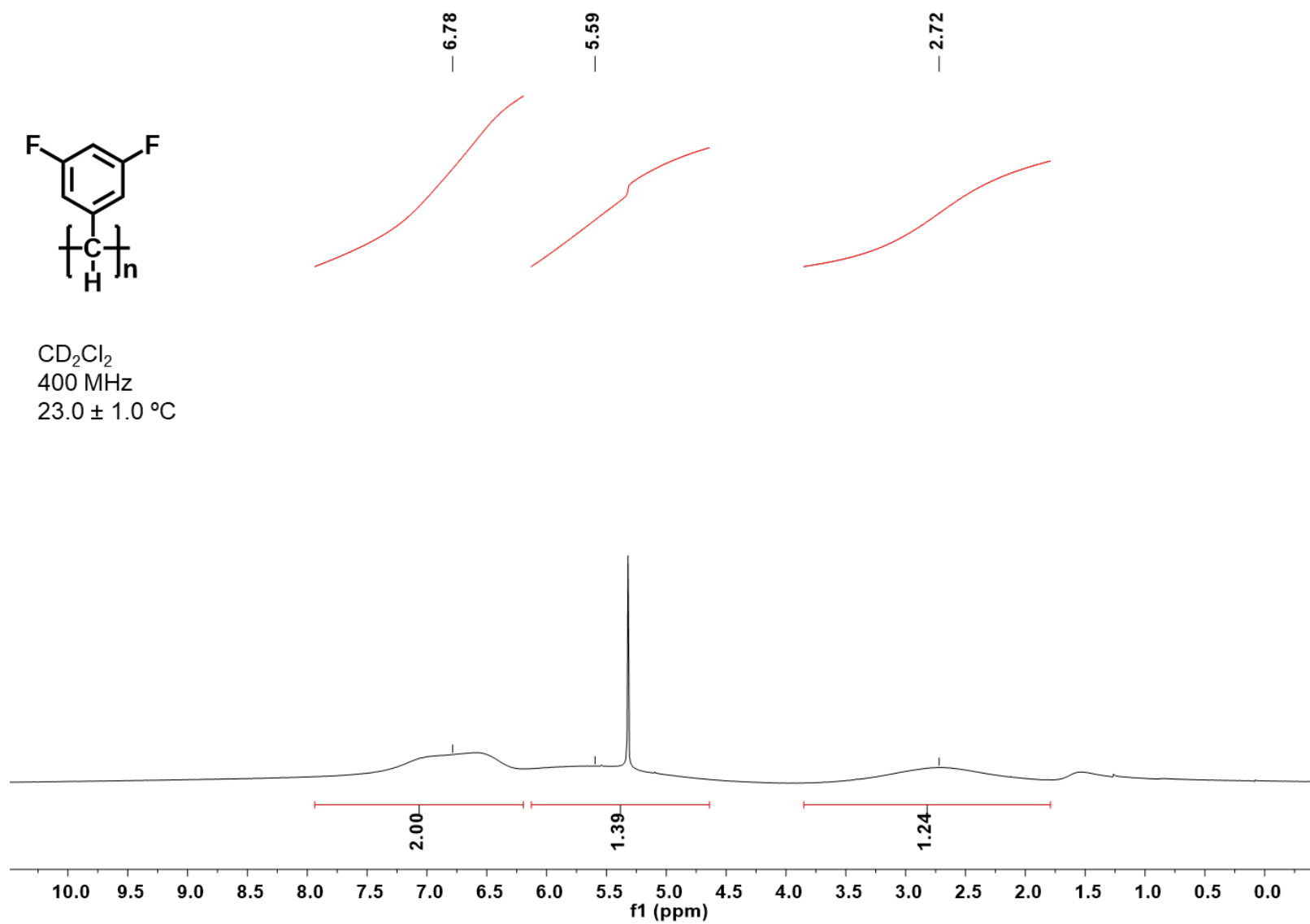


Figure S70. ¹H NMR spectrum of poly(**1d**) as recorded in CD₂Cl₂ at 23 °C.

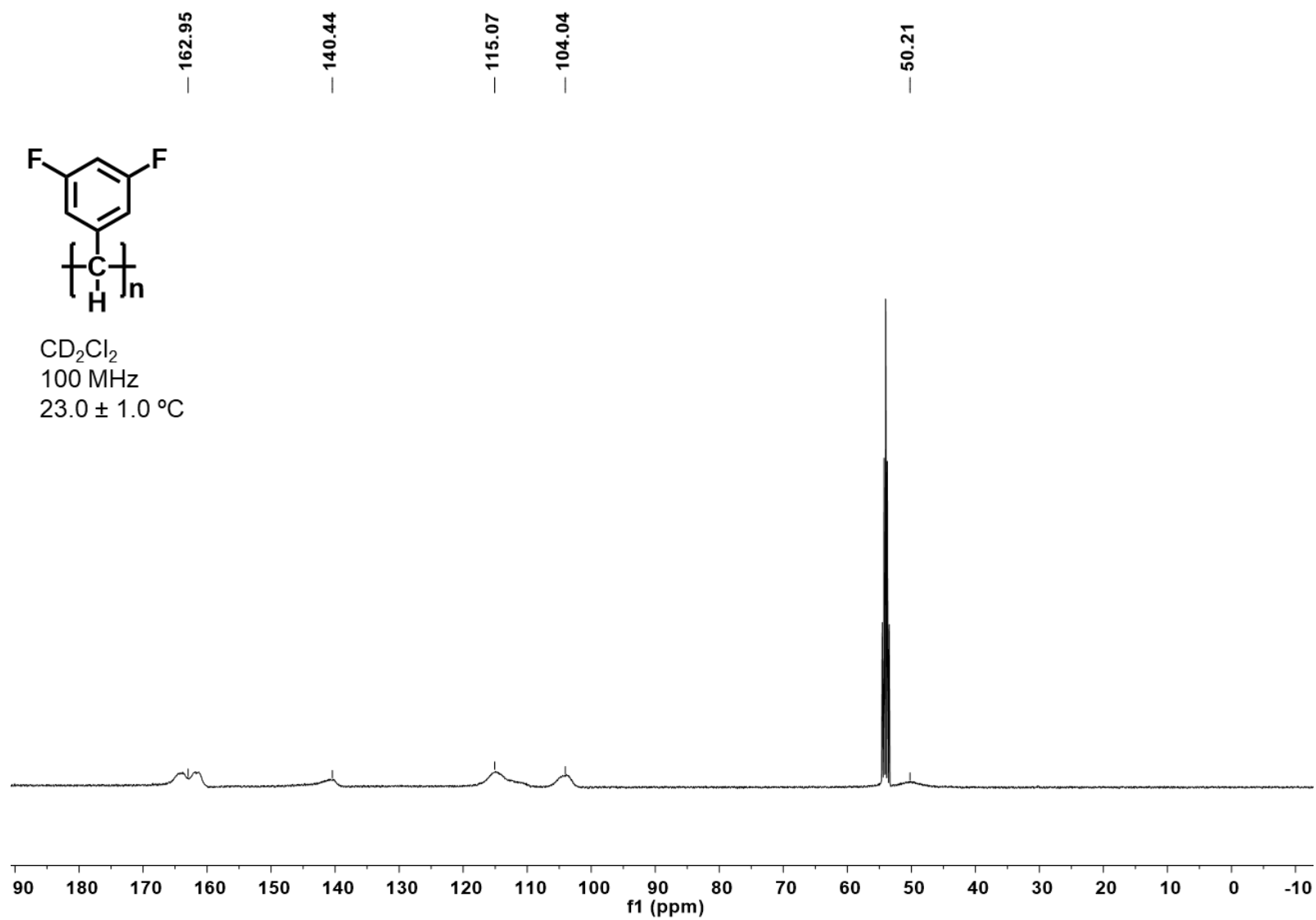


Figure S71. ¹³C NMR spectrum of poly(**1d**) as recorded in CD₂Cl₂ at 23 °C.

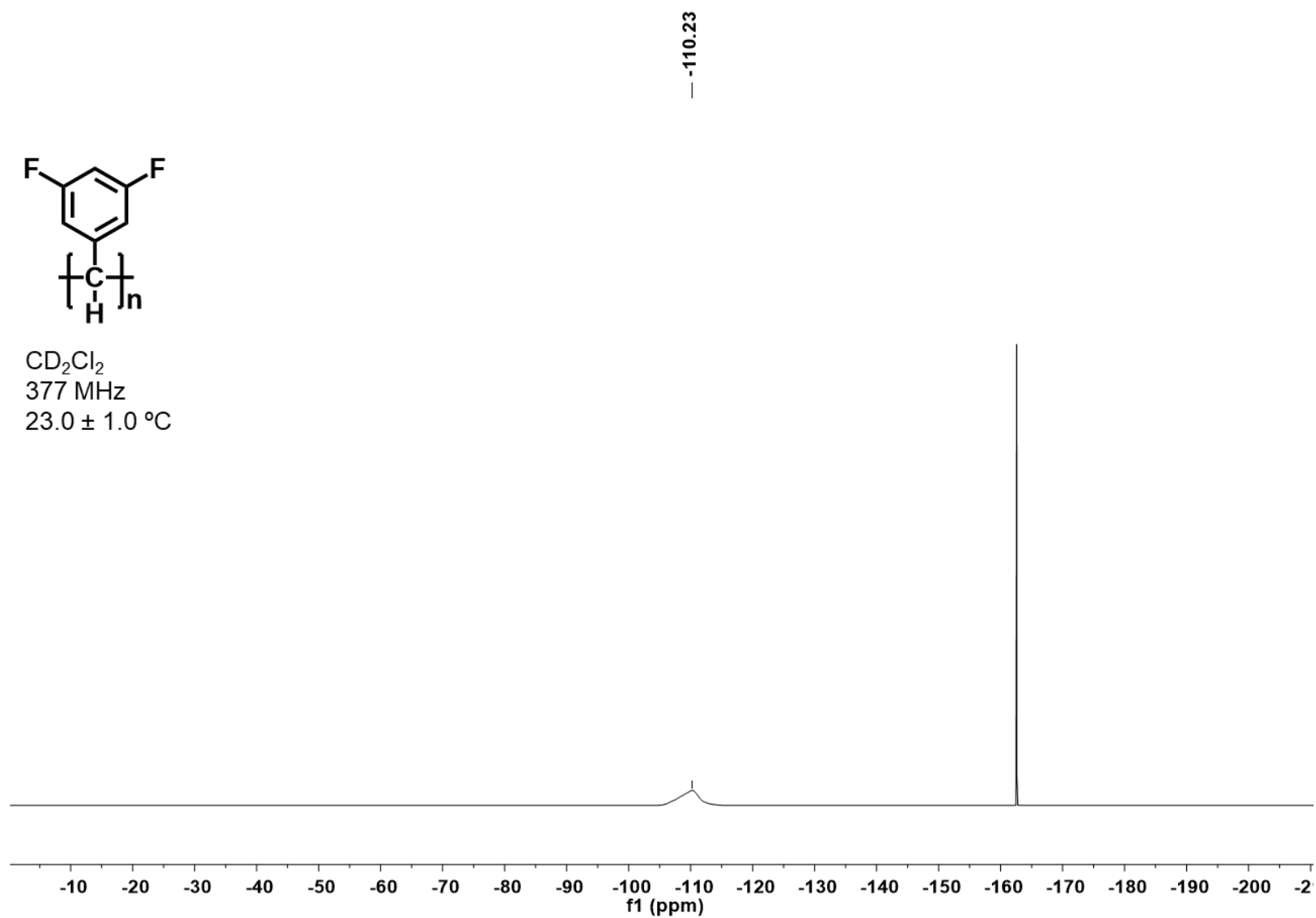


Figure S72. ¹⁹F NMR spectrum of poly(**1d**) as recorded in CD₂Cl₂ with hexafluorobenzene as a reference at 23 °C.

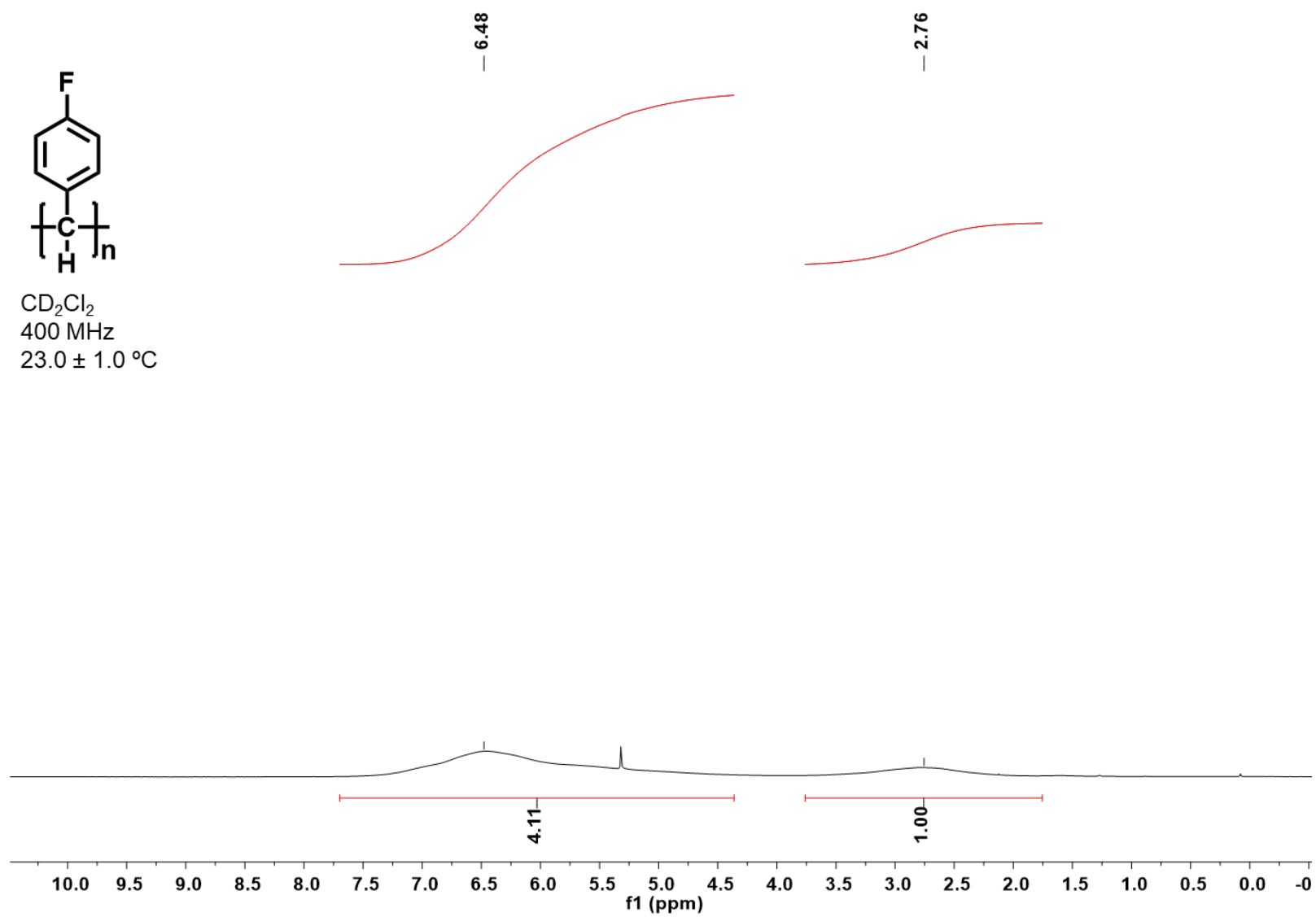


Figure S73. ^1H NMR spectrum of poly(**1e**) as recorded in CD_2Cl_2 at 23 °C.

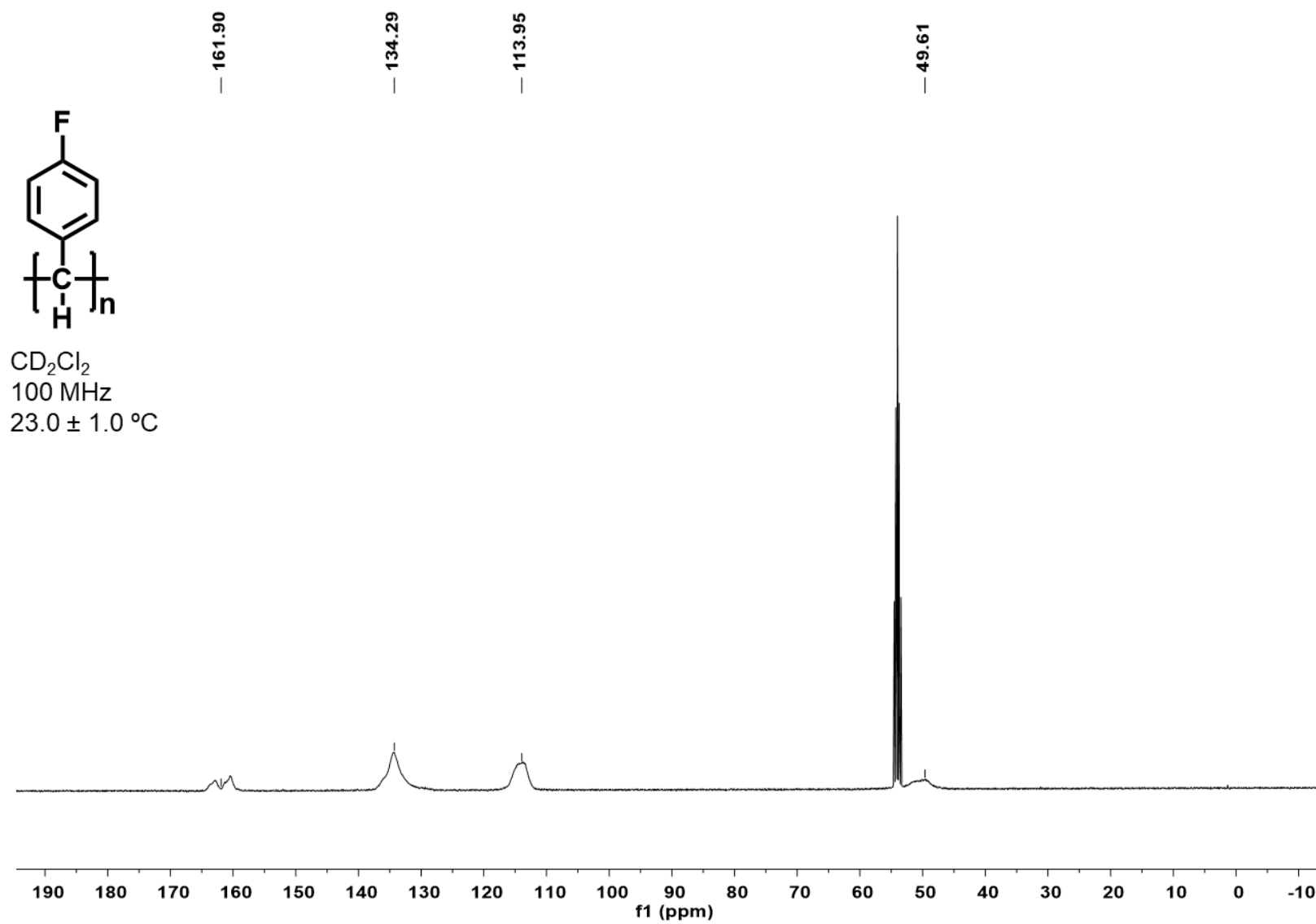


Figure S74. ¹³C NMR spectrum of poly(**1e**) as recorded in CD₂Cl₂ at 23 °C.

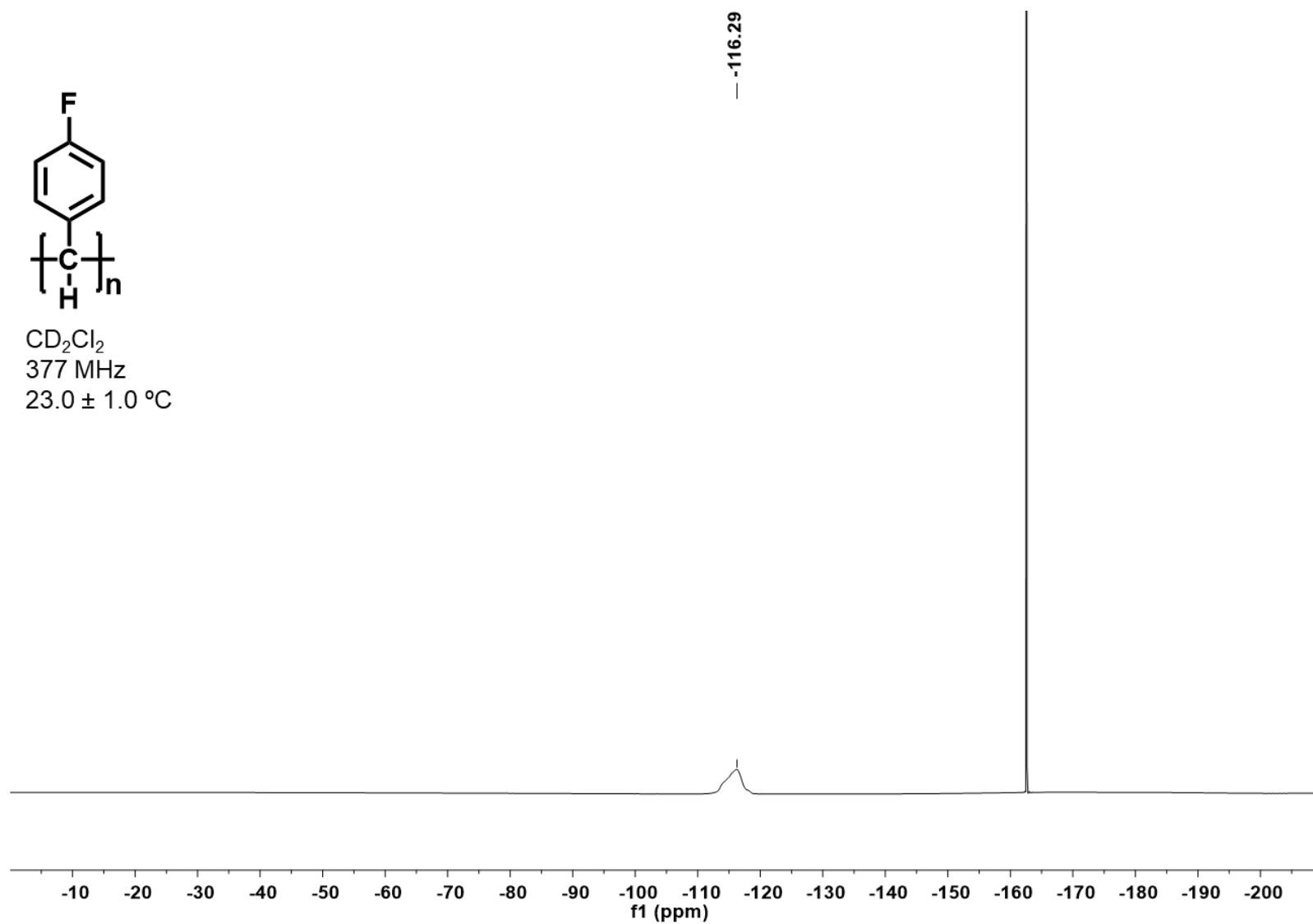


Figure S75. ¹⁹F NMR spectrum of poly(**1e**) as recorded in CD₂Cl₂ with hexafluorobenzene as a reference at 23 °C.

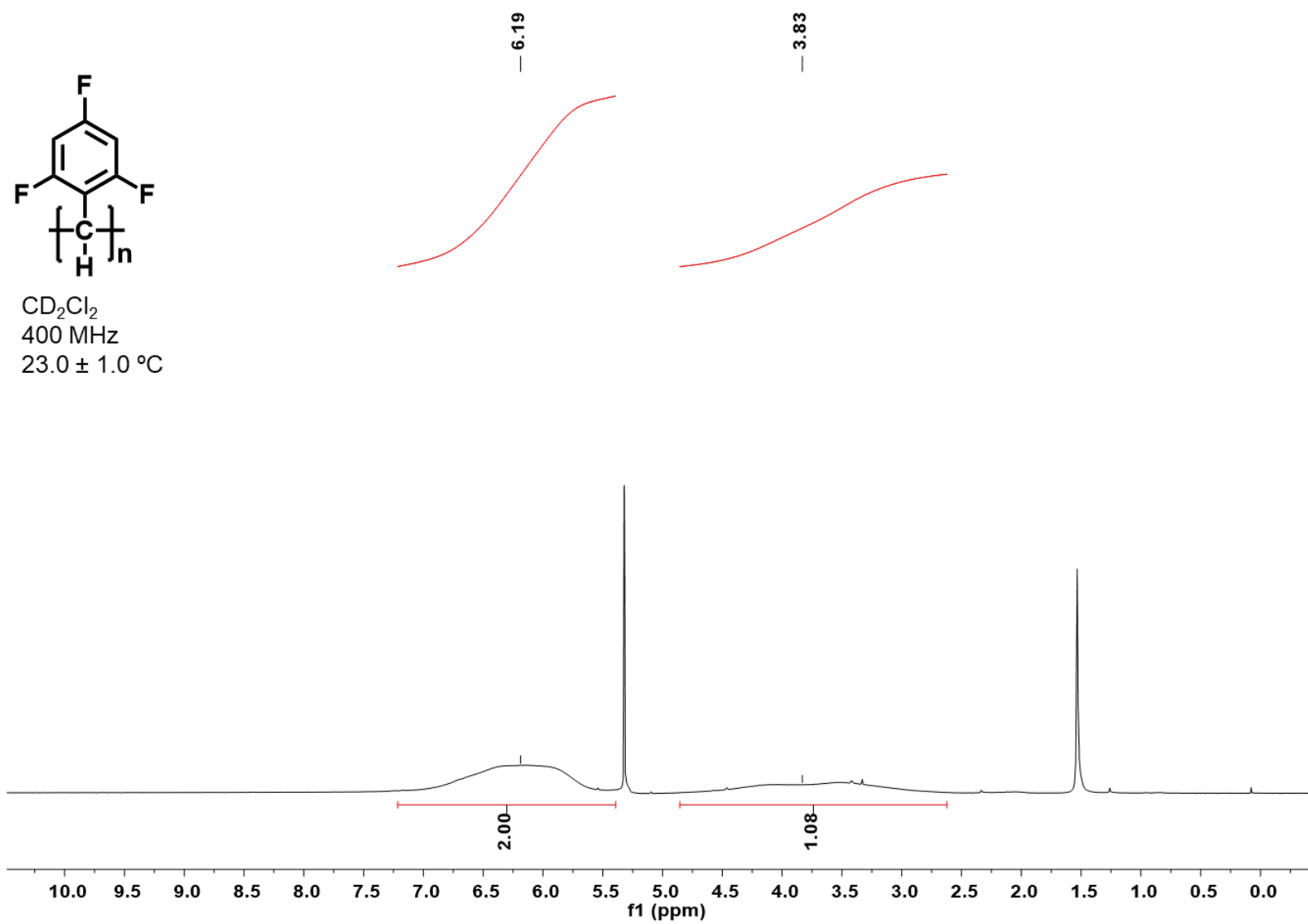


Figure S76. ^1H NMR spectrum of poly(1f) as recorded in CD_2Cl_2 at 23°C .

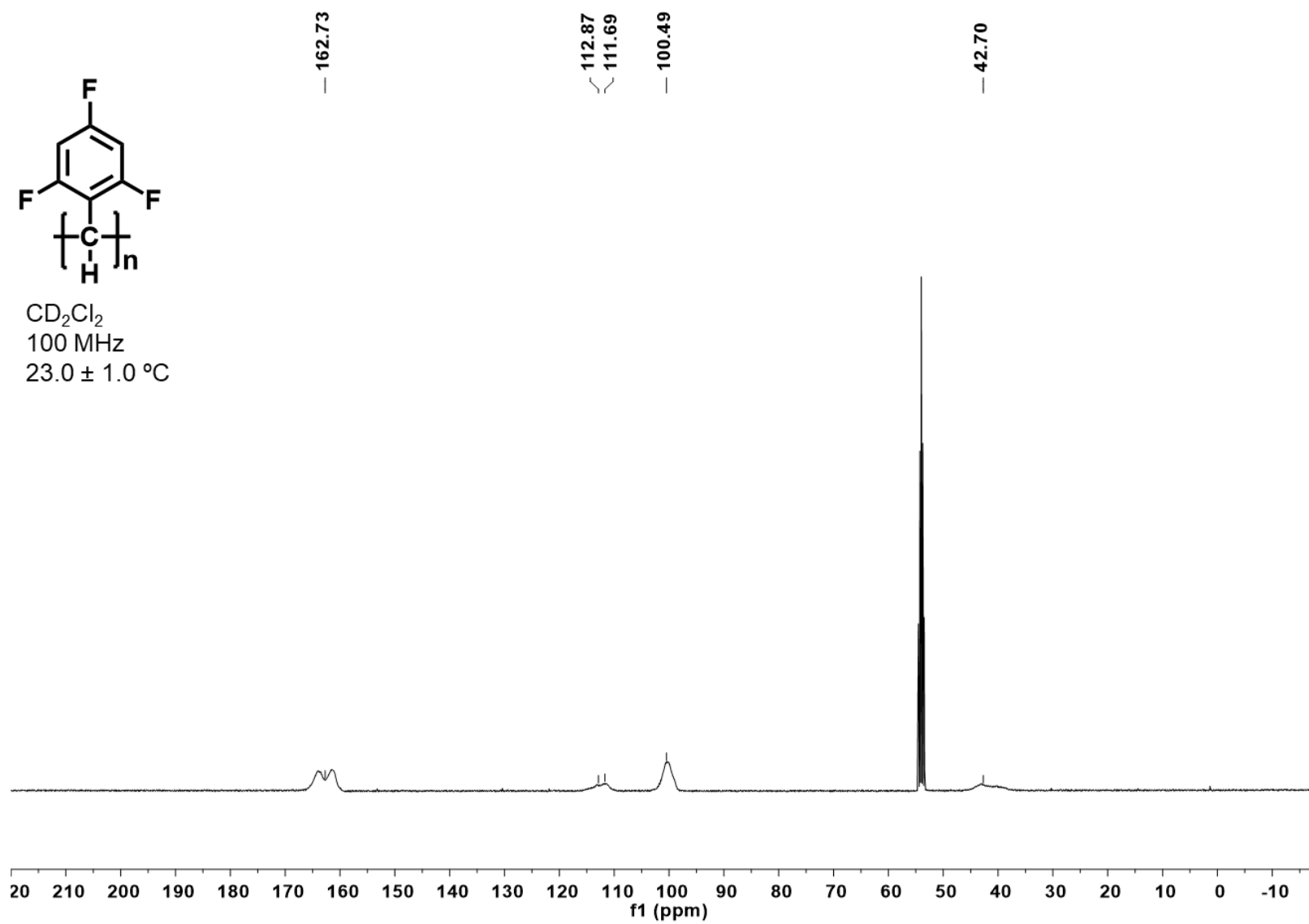


Figure S77. ^{13}C NMR spectrum of poly(**1f**) as recorded in CD_2Cl_2 at 23°C .

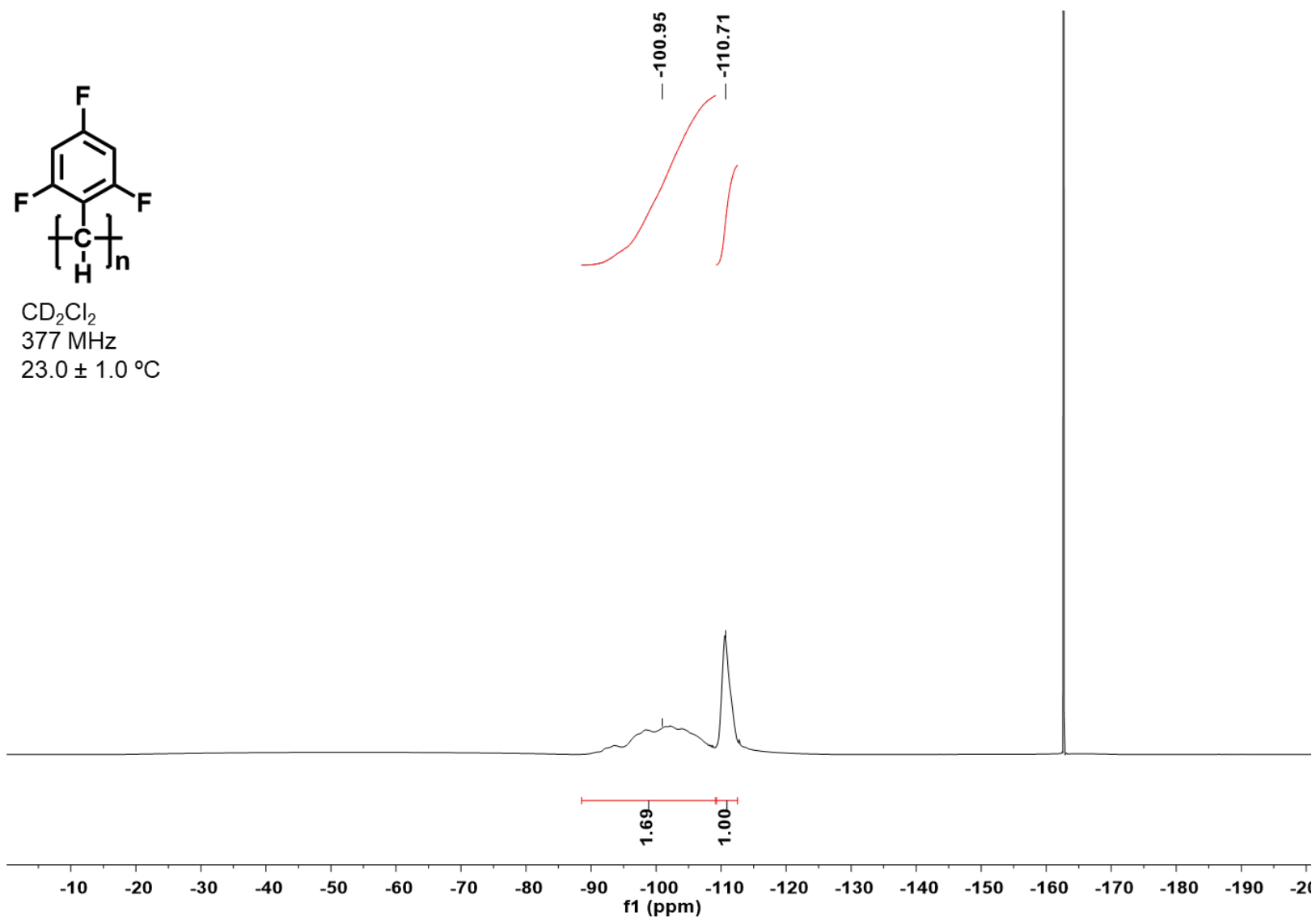


Figure S78. ¹⁹F NMR spectrum of poly(1f) as recorded in CD₂Cl₂ with hexafluorobenzene as a reference at 23 °C.

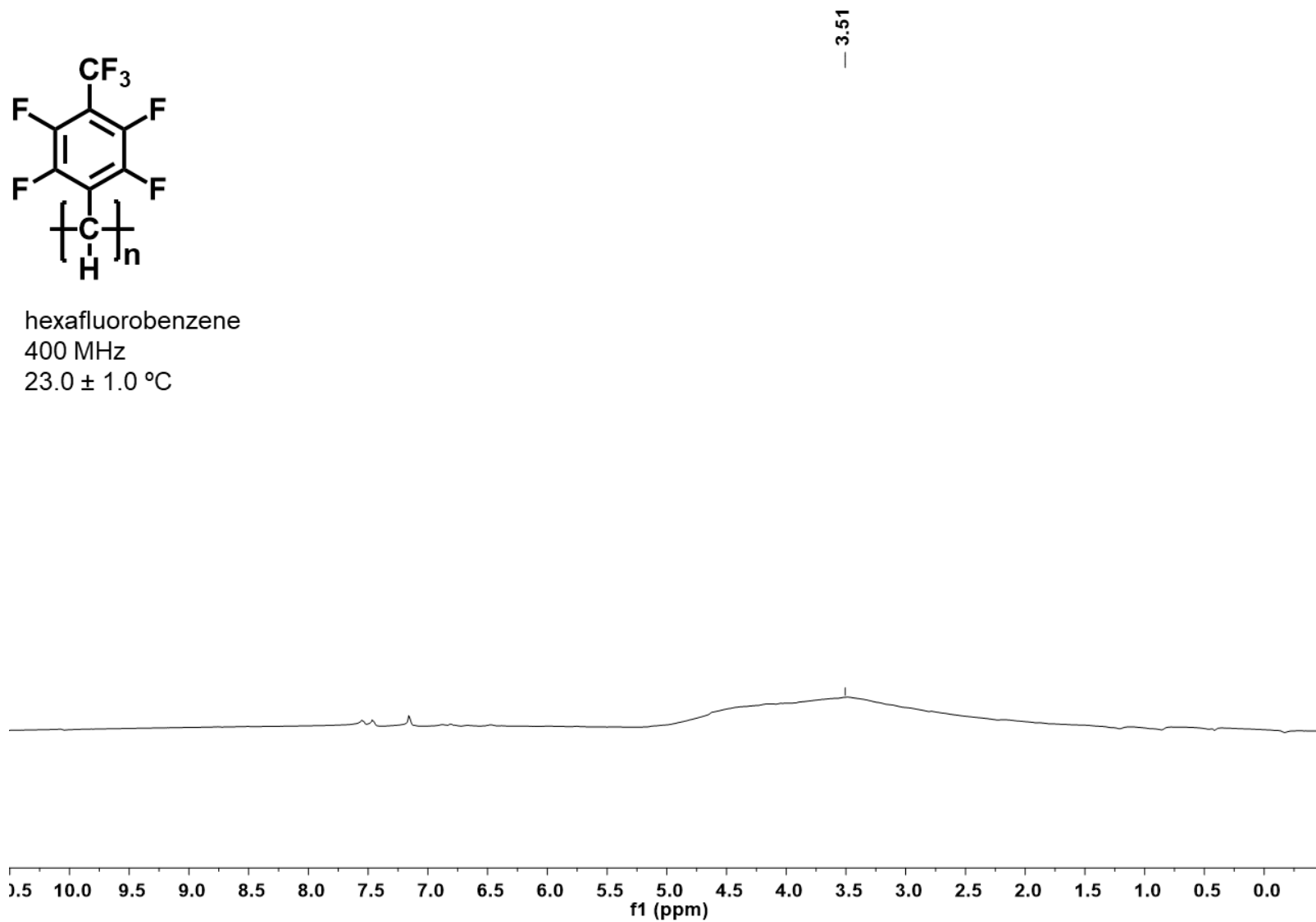


Figure S79. ^1H NMR spectrum of poly(**1g**) as recorded in hexafluorobenzene with C_6D_6 as a reference at 23 °C.

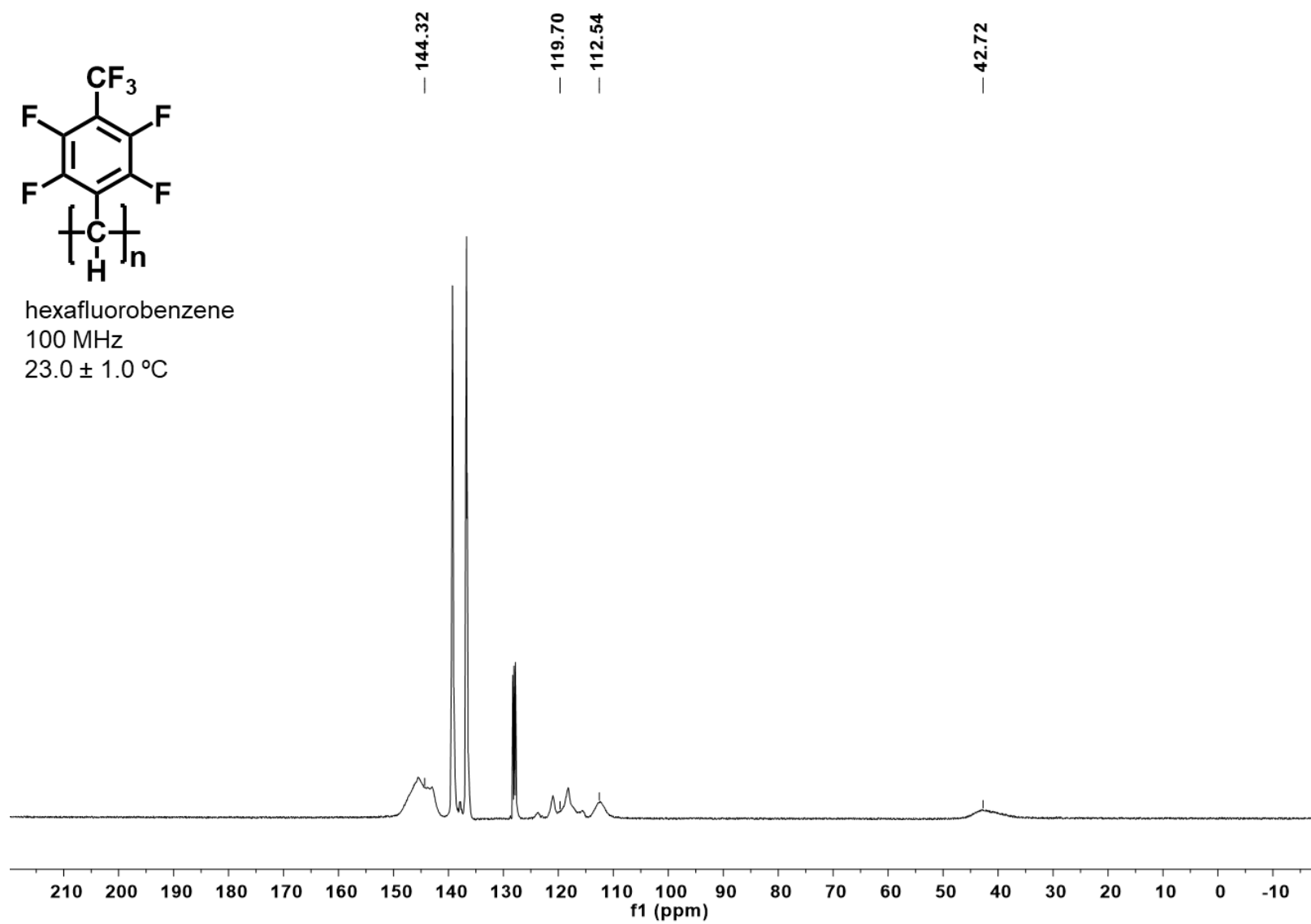


Figure S80. ^{13}C NMR spectrum of poly(**1g**) as recorded in hexafluorobenzene with C_6D_6 as a reference at 23 °C.

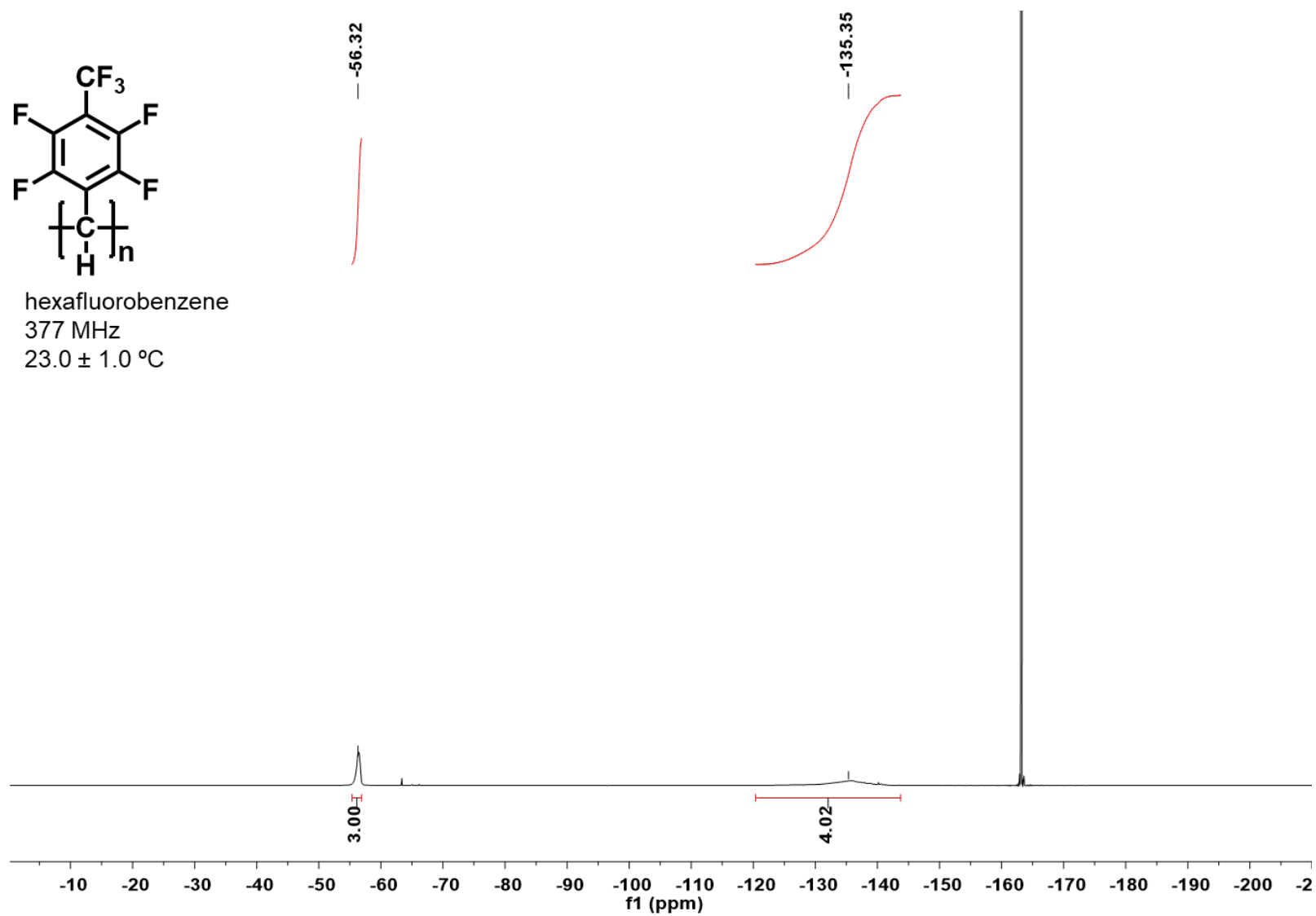


Figure S81. ^{19}F NMR spectrum of poly(**1g**) as recorded in hexafluorobenzene at 23°C .

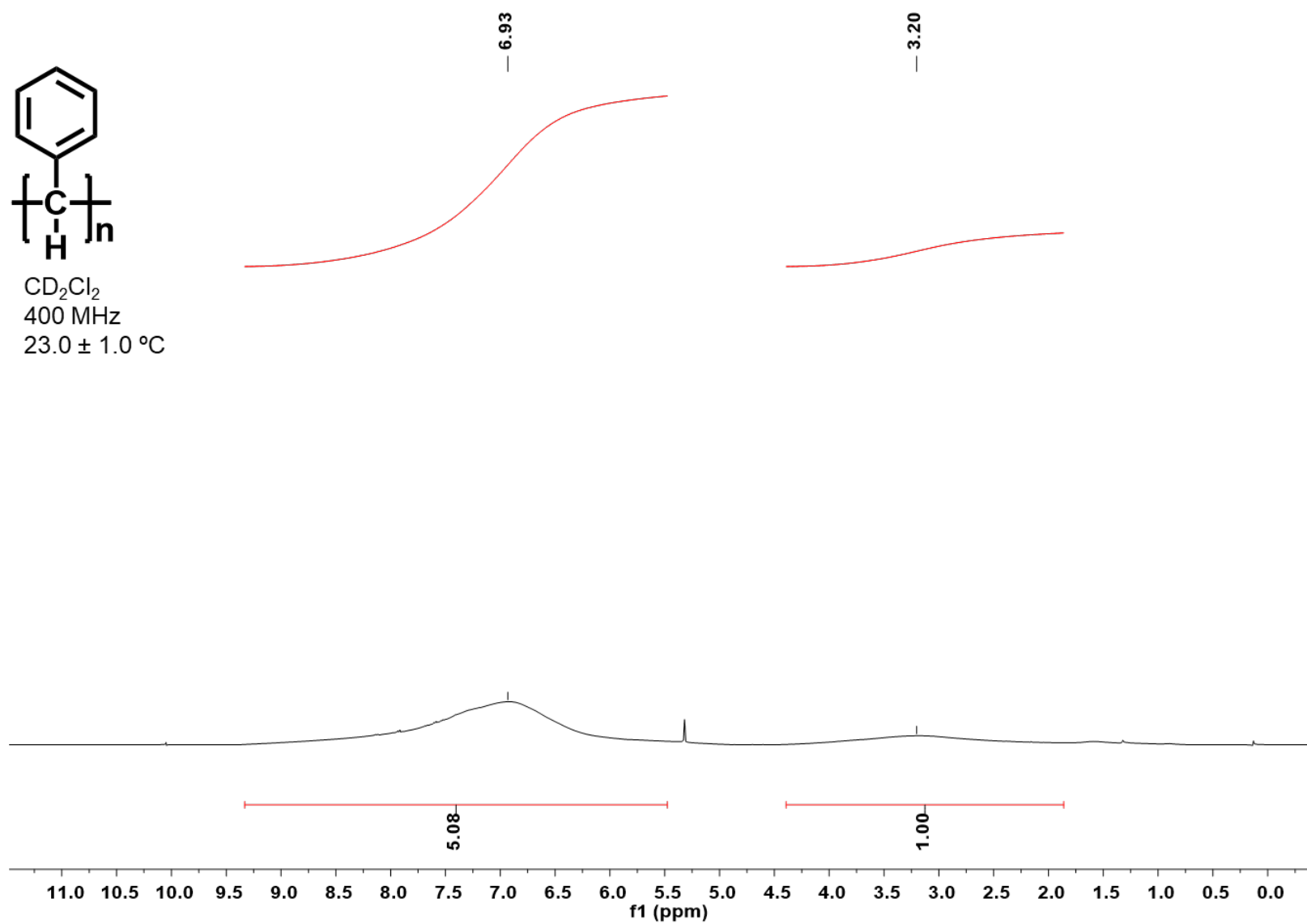


Figure S82. ¹H NMR spectrum of poly(phenyl methylene) as recorded in CD₂Cl₂ at 23 °C.

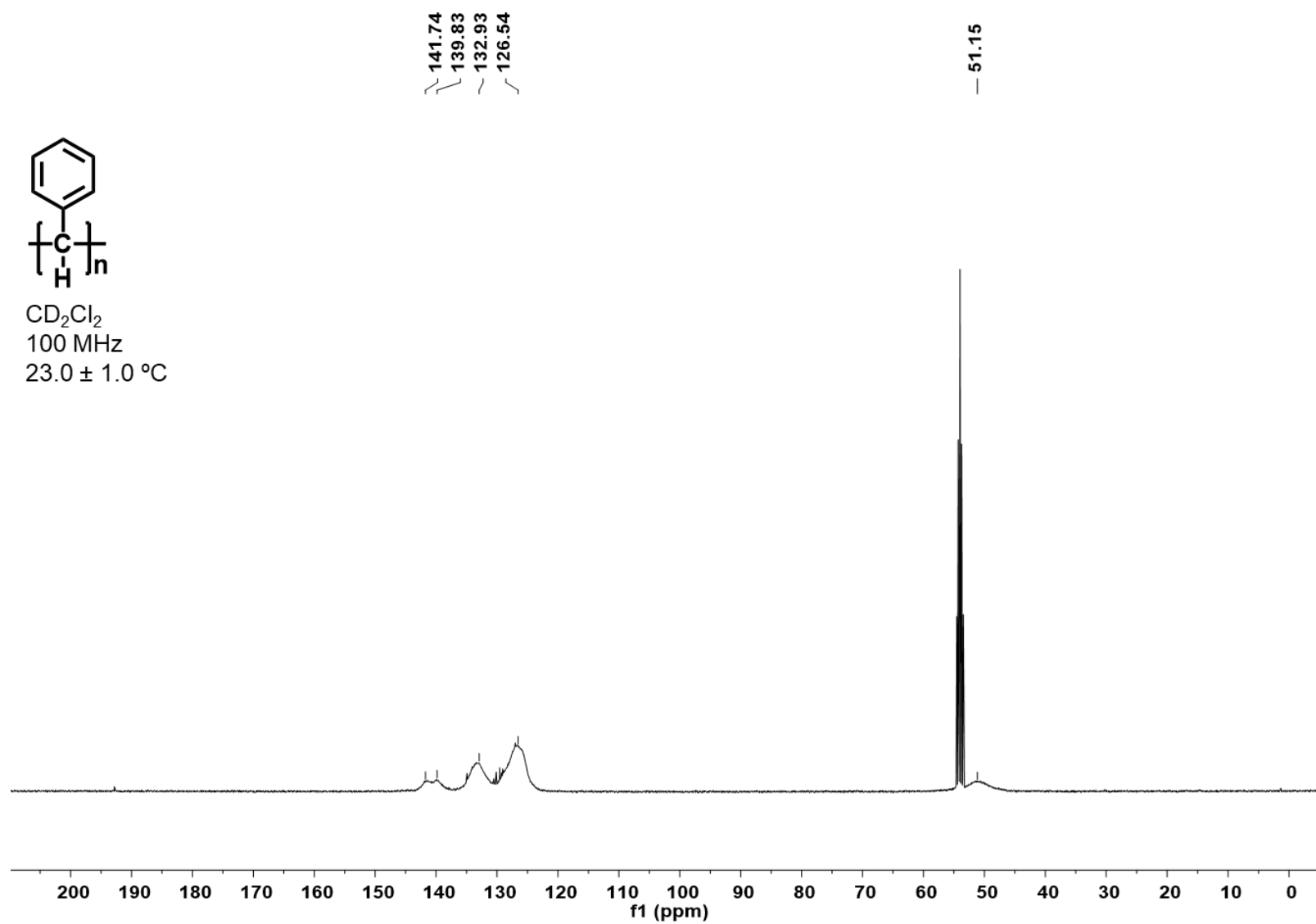


Figure S83. ¹³C NMR spectrum of poly(phenyl methylene) as recorded in CD₂Cl₂ at 23 °C.

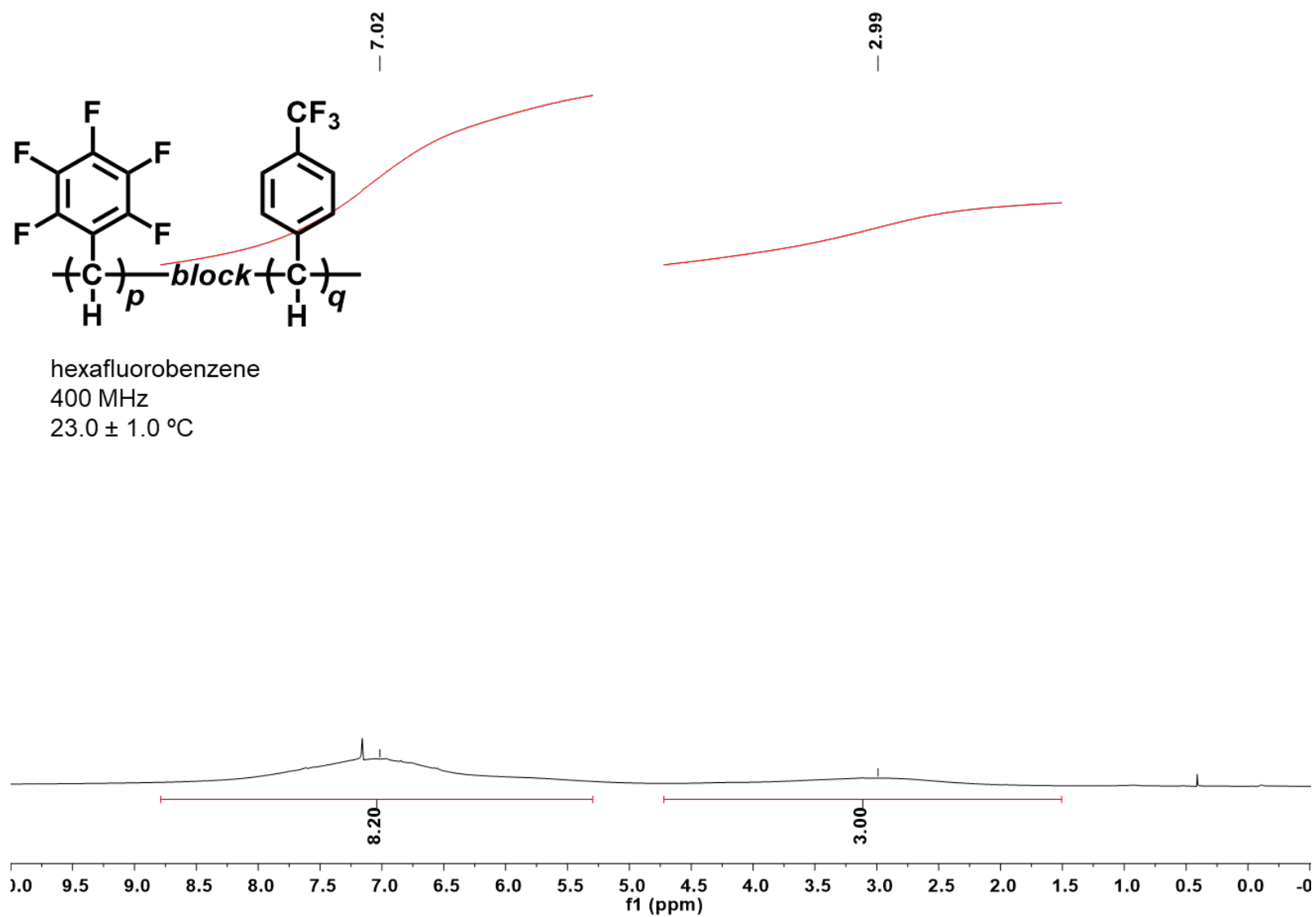


Figure S84. ^1H NMR spectrum of poly(**1a-block-1b**) as recorded in hexafluorobenzene with C_6D_6 as a reference at 23 °C.

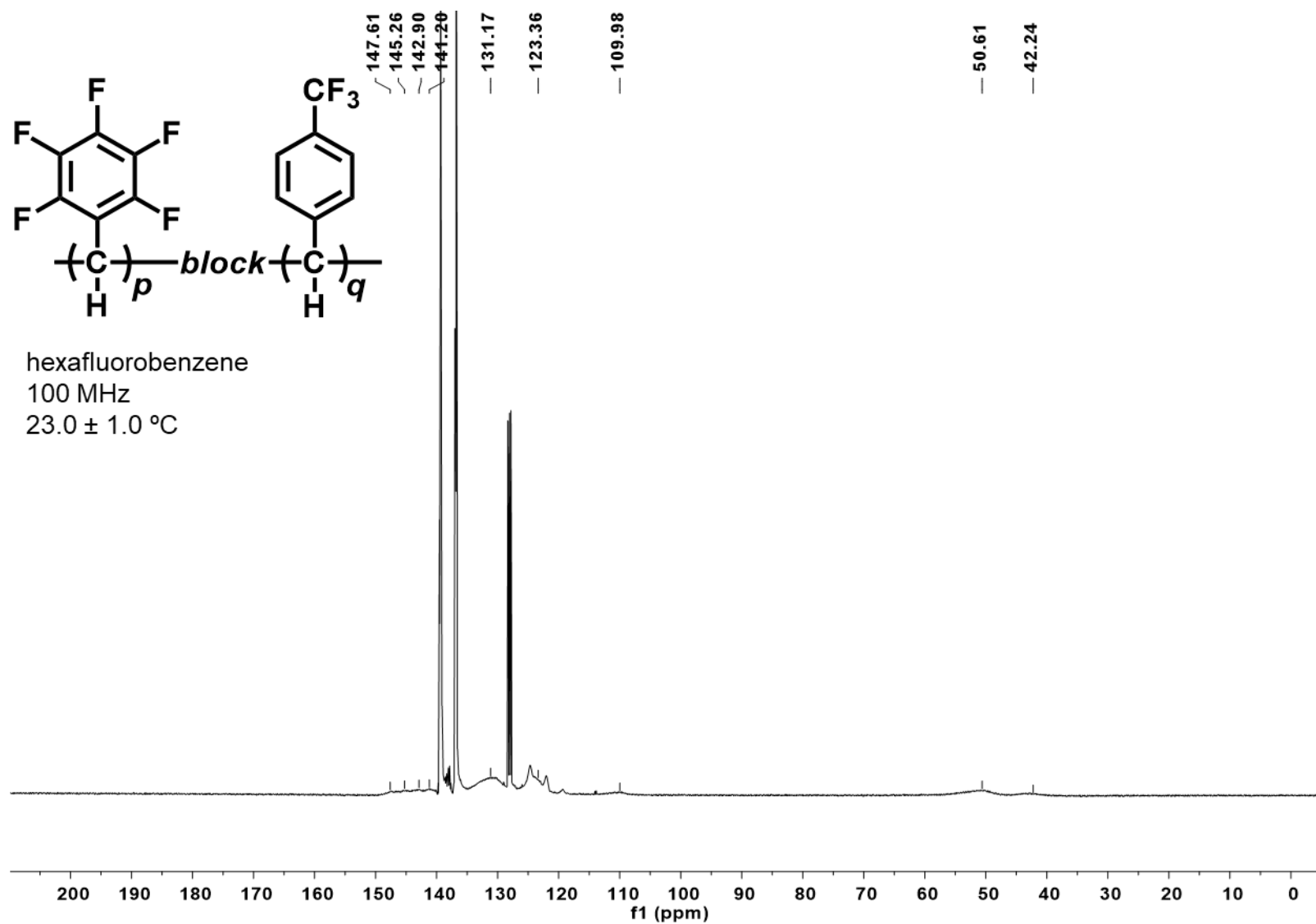


Figure S85. ^{13}C NMR spectrum of poly(**1a-block-1b**) as recorded in hexafluorobenzene with C_6D_6 as a reference at 23 °C.

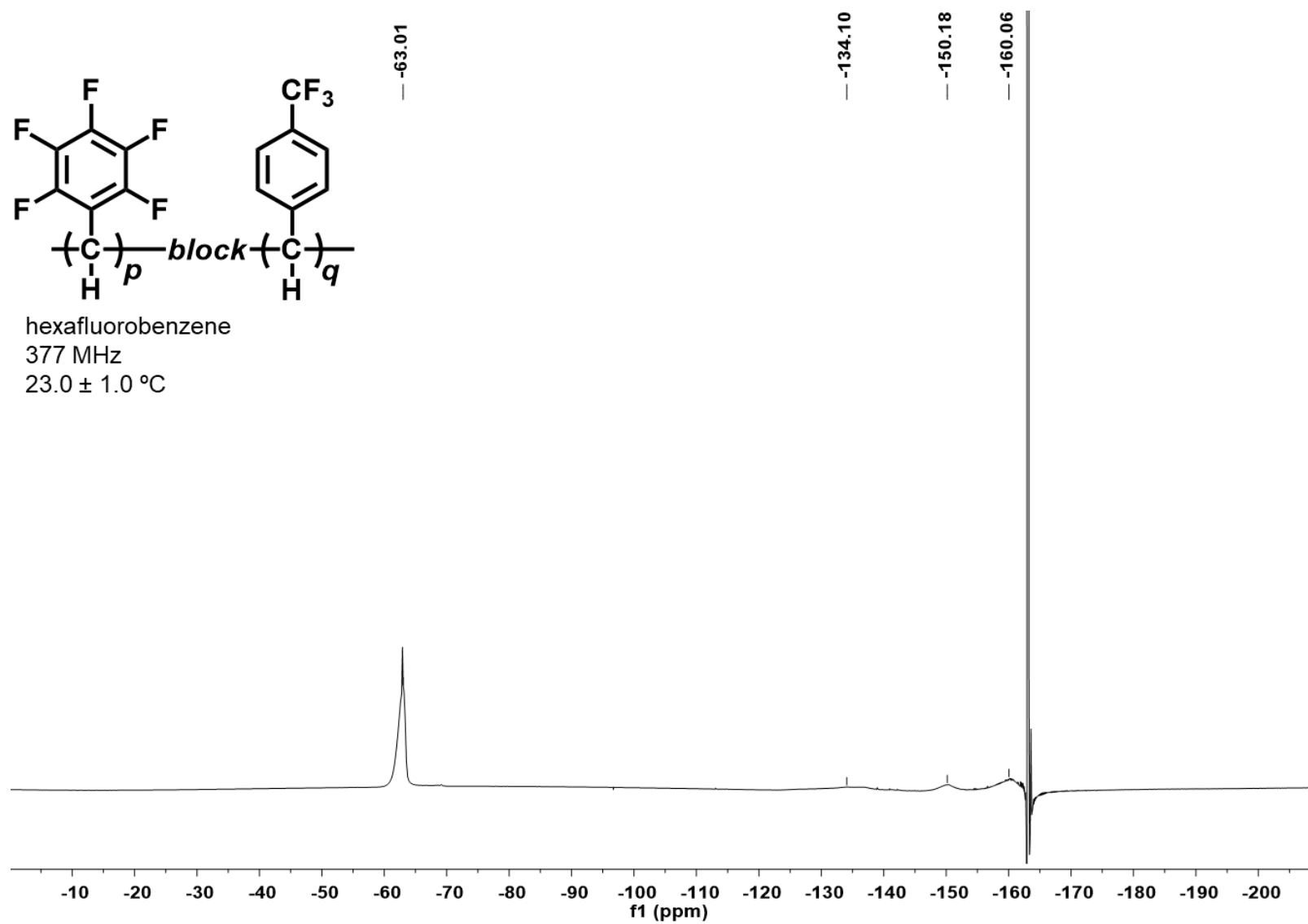


Figure S86. ^{19}F NMR spectrum of poly(**1a**-*block*-**1b**) as recorded in hexafluorobenzene at 23 °C.

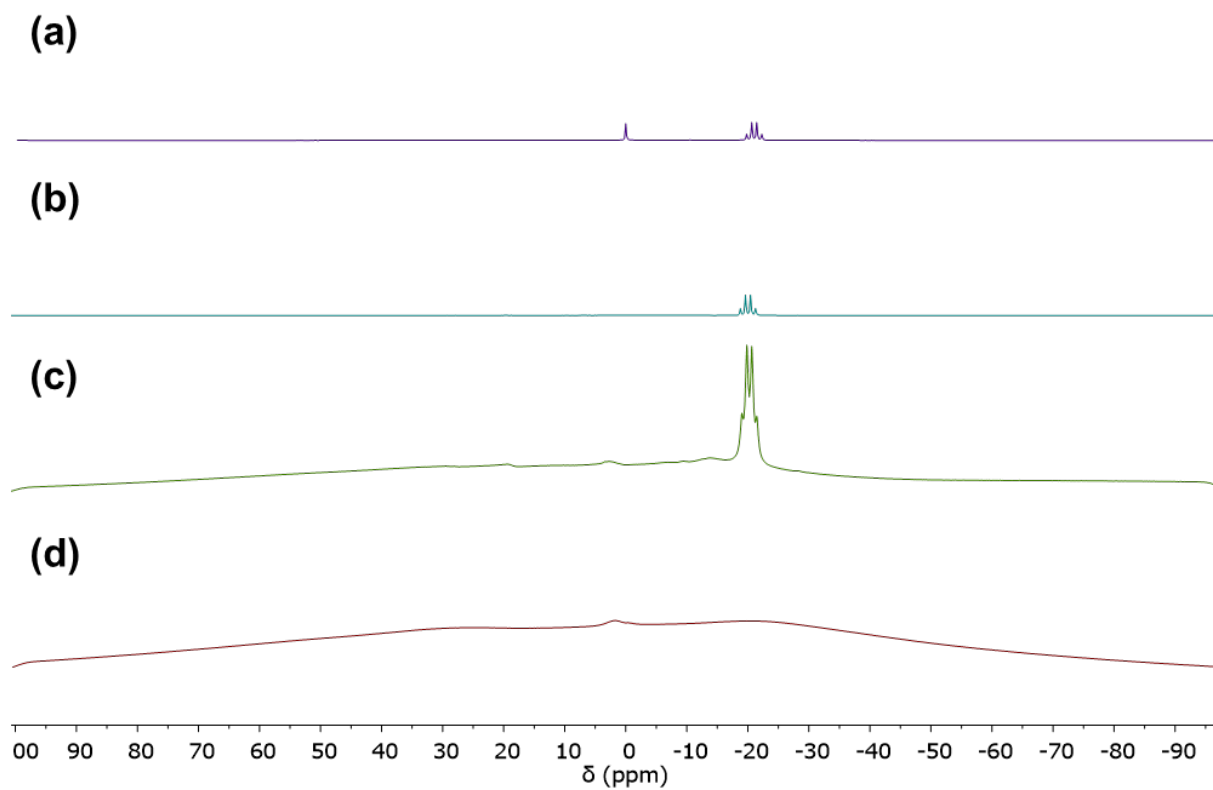


Figure S87. ^{11}B NMR spectra of (a) $\text{BH}_3\cdot\text{SMe}_2$ with $\text{BF}_3\cdot\text{OEt}_2$, (b) $\text{BH}_3\cdot\text{SMe}_2$, (c) poly(**1a**) with $\text{BH}_3\cdot\text{SMe}_2$, and (d) poly(**1a**) as recorded in hexafluorobenzene at 23 °C.

References

1. Rosenau, C. P.; Jelier, B. J.; Gossert, A. D.; Togni, A., Exposing the Origins of Irreproducibility in Fluorine NMR Spectroscopy. *Angew. Chem. Int. Ed.* **2018**, *57*, 9528–9533.
2. Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P., Asymmetric Radical Cyclopropanation of Alkenes with In Situ-Generated Donor-Substituted Diazo Reagents via Co(II)-Based Metalloradical Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 1049–1052.
3. Vinogradov, A. S.; Platonov, V. E. In *Reactions of polyfluoroarylzinc compounds with Vilsmeier-Haack reagent; new synthesis of polyfluorinated aromatic aldehydes and acetals*, 15th Int. Electron. Conf. Synth. Org. Chem., MDPI: 2011; pp 1–10.
4. Jankova, K.; Hvilsted, S., Preparation of poly(2,3,4,5,6-pentafluorostyrene) and block copolymers with styrene by ATRP. *Macromolecules* **2003**, *36*, 1753–1758.