Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Light-Promoted Copper-Catalyzed Cage C-Arylation of *o*-Carboranes: Facile Synthesis of 1-Aryl-*o*-Carborane and *o*-Carborane-Fused Cyclics

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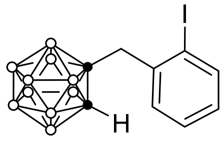
General Procedures.

All reactions were carried out in flame-dried glassware under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox. ^{1}H NMR spectra were recorded on a Bruker DPX400 spectrometer at 400 MHz or a Bruker 500 spectrometer at 500 MHz. ^{19}F NMR spectra were recorded on a Bruker DPX400 spectrometer at 376 MHz or a Bruker 500 spectrometer at 470 MHz. ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer at 100 MHz or a Bruker 500 spectrometer at 126 MHz. ^{11}B NMR spectra were recorded on a Bruker DPX 400 spectrometer at 128 MHz or a Bruker 500 spectrometer at 160 MHz. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3\cdot OEt_2$ (0.00 ppm) for boron chemical shifts, and to external $CFCl_3$ (0.00 ppm) for fluorine chemical shifts. GC analyses were performed on Thermo Scientific Trace 1310. GC-MS analyses were performed on Agilent GC-MS 6890N. Mass spectra were obtained on a Thermo Finnigan MAT 95 XL spectrometer. Compounds **1b**,[1] **1c**[2] and **1y**[2] were prepared according to literature methods. All chemicals were purchased from commercial corporations and used as received unless otherwise specified.

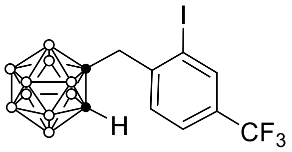
Experimental Section

Preparation of Starting Materials (1d, 1f, 1g). A typical procedure for 1d. To a stirring solution of *o*-carborane (144 mg, 1.0 mmol) in diethyl ether (8 mL) at 0 °C in an ice-water bath was added dropwise a solution of *n*-butyllithium in hexane (0.63 mL, 1.60 M, 1.0 mmol) under argon atmosphere. The suspension was stirred at room temperature for 1 h, then cooled again to 0 °C, to which was added 1-(bromomethyl)-2-iodobenzene (297 mg, 1.0 mmol). The resulting solution was stirred at room temperature overnight. Then, the reaction was quenched with water. The organic phase was separated, and the aqueous solution was extracted with diethyl ether (2 x 15 mL). The ether solutions were combined and dried over Na_2SO_4. The organic phase was concentrated to dryness in vacuo, and the residue was subjected to flash column chromatography on silica gel (230-400 mesh) using n-hexane as eluent to give **1d**.

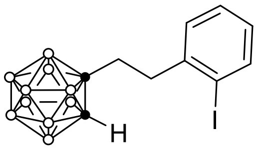


1d: White solid. Yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J_{HH} = 8.0, 1.3 Hz, 1H), 7.37 (td, J_{HH} = 7.5, 1.3 Hz, 1H), 7.23 (dd, J_{HH} = 7.7, 1.7 Hz, 1H), 7.02 (td, J_{HH} = 7.7, 1.7 Hz, 1H) (aromatic *H*), 3.82 (s, 1H) (cage

H), 3.75 (s, 2H) (C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 140.33, 138.73, 131.63, 130.16, 128.81, 101.77 (aromatic *C*), 74.35, 59.80 (cage *C*), 46.78 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.52 (1B), -5.74 (1B), -9.98 (2B), -11.42 (2B), -12.77 (2B), -13.44 (2B). HRMS (APCI): *m/z* calcd for $C_9H_{17}B_{10}I$ [M]$^+$: 360.1377. Found: 360.1364.

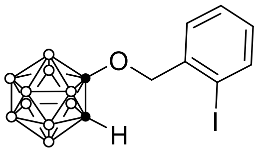


1f: White solid. Yield: 28%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.01 (d, J_{HH} = 8.3 Hz, 1H), 7.44 (d, J_{HH} = 2.2 Hz, 1H), 7.28 (dd, J_{HH}= 8.2, 2.0 Hz, 1H) (aromatic *H*), 3.85 (s, 1H) (cage *H*), 3.80 (s, 2H) (C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 140.96, 139.82, 131.41 (d, $^2J_{C\text{-}F}$ = 33.2 Hz), 128.15 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 126.57 (q, $^3J_{C\text{-}F}$ = 3.7 Hz) (aromatic *C*), 123.55 (d, $^1J_{C\text{-}F}$ = 272.6 Hz) (*C*F$_3$), 105.98 (aromatic *C*), 73.44, 60.43 (cage *C*), 46.75 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.20 (1B), -5.39 (1B), -9.61 (2B), -11.42 (2B), -13.00 (4B). ^{19}F NMR (377 MHz, CDCl$_3$): δ -63.06. HRMS (APCI): *m/z* calcd for $C_{10}H_{16}B_{10}F_3I$ [M-H]$^-$: 427.1184. Found: 427.1174.



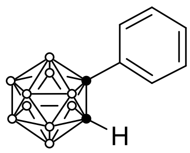
1g: White solid. Yield: 13%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80 (dd, J_{HH} = 7.9, 1.3 Hz, 1H), 7.29 (td, J_{HH} = 7.4, 1.3 Hz, 1H), 7.17 (dd, J_{HH} = 7.7, 1.7 Hz, 1H), 6.93 (td, J_{HH}= 7.6, 1.8 Hz, 1H) (aromatic *H*), 3.67 (s, 1H) (cage *H*), 3.09 – 2.77 (m, 2H), 2.60 – 2.20 (m, 2H) (C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 141.33, 139.92, 129.55, 128.99, 128.92, 100.09 (aromatic *C*), 74.36, 61.39 (cage *C*), 40.68, 38.30 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.58 (1B), -5.98 (1B), -9.59 (2B), -11.91 (2B), -12.49 (2B), -13.42 (2B). HRMS (APCI): *m/z* calcd for $C_{10}H_{19}B_{10}I$ [M-H]$^-$: 373.1467. Found: 373.1466.

Preparation of Starting Material (1e). A Schlenk tube was charged with 1-OH-*o*-carborane (160 mg, 1.0 mmol), 1-(bromomethyl)-2-iodobenzene (297 mg, 1.0 mmol), potassium carbonate (138 mg, 1.0 mmol), and acetone (5 mL). The suspension was stirred at 80 °C overnight. After removal of the solvent, diethyl ether and water were added to the mixture. The resulting solution was extracted with diethyl ether (15 mL) for three times. The organic phase was concentrated to dryness in vacuo, and the residue was subjected to flash column chromatography on silica gel (230-400 mesh) using n-hexane as eluent to give **1e**.

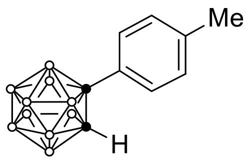


1e: White solid. Yield: 60%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85 (d, J = 7.9 Hz, 1H), 7.36 (t, J_{HH}= 7.4 Hz, 1H), 7.30 (dd, J_{HH}= 7.7, 1.8 Hz, 1H), 7.06 (td, J_{HH}= 7.6, 1.8 Hz, 1H) (aromatic *H*), 4.76 (s, 2H) (C*H*$_2$), 4.05 (s, 1H) (cage *H*). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 139.82, 136.77, 130.83, 130.10, 128.70, 102.79 (aromatic *C*), 98.76 (cage *C*), 80.66 (*C*H$_2$), 63.46 (cage *C*). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -4.93 (1B), -12.48 (5B), -13.95 (2B), -15.43 (2B). HRMS (APCI): *m/z* calcd for $C_9H_{17}B_{10}IO$ [M]$^+$: 377.1405. Found: 377.1404.

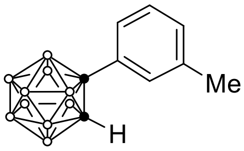
Preparation of 1-Aryl-*o*-Carboranes 3. *o*-Carborane (**1**; 43.2 mg, 0.30 mmol), aryl iodide (pre-dried with molecular sieves, 0.90 mmol), LiO^{t}Bu (36.0 mg, 0.45 mmol), Ag_2CO_3 (126.0 mg, 0.45 mmol) and CuI (8.4 mg, 0.045 mmol) were mixed in dry DME (3 mL) in a 10 mL quartz tube equipped with a magnetic stirring bar. The reaction mixture was irradiated with 8 W UV lamp (254 nm) and stirred at room temperature for 24 h. After quenching with aqueous acetyl acid solution, the mixture was extracted with diethyl ether (15 mL×3). The ether solutions were combined and dried over Na_2SO_4. After filtration, the clear solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using n-hexane as eluent to give the desired products **3**.



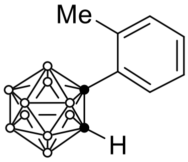
3a: White solid. Yield: 83%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, J_{HH} = 7.3 Hz, 2H), 7.40 (t, J_{HH} = 7.3 Hz, 1H), 7.34 (t, J_{HH} = 7.3 Hz, 2H) (aromatic *H*), 3.97 (s, 1H) (cage *H*). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.56 (1B), -4.88 (1B), -9.49 (2B), -11.36 (2B), -11.79 (2B), -13.34 (2B). This is a known compound and these data are very similar to the reported ones.[3]



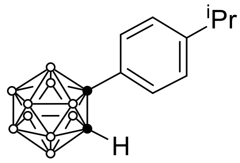
3b: White solid. Yield: 78%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37 (d, J_{HH} = 8.4 Hz, 2H), 7.13 (d, J_{HH} = 8.1 Hz, 2H) (aromatic *H*), 3.93 (s, 1H) (cage *H*), 2.34 (s, 3H) (C*H*$_3$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -1.82 (1B), -4.32 (1B), -8.81 (2B), -10.56 (2B), -11.05 (2B), -12.58 (2B). This is a known compound and these data are very similar to the reported ones.[3]



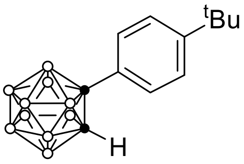
3c: White solid. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.27 (s, 2H), 7.24 – 7.18 (m, 2H) (aromatic *H*), 3.97 (s, 1H) (cage *H*), 2.35 (s, 3H) (CH_3). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): *δ* -1.35 (1B), -3.63 (1B), -8.22 (2B), -10.07 (4B), -12.09 (2B). This is a known compound and these data are very similar to the reported ones.[3]



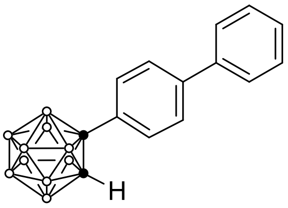
3d: White solid. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.56 (d, J_{HH} = 7.9 Hz, 1H), 7.28 – 7.17 (m, 2H), 7.12 (d, J_{HH} = 7.4 Hz, 1H) (aromatic *H*), 4.57 (s, 1H) (cage *H*), 2.57 (s, 3H) (CH_3). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): *δ* -2.29 (2B), -8.19 (2B), -8.79 (2B), -10.59 (2B), -12.60 (2B). This is a known compound and these data are very similar to the reported ones.[3]



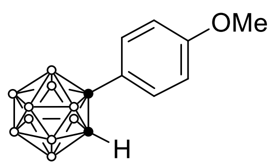
3e: White solid. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.40 (d, J_{HH} = 8.5 Hz, 2H), 7.17 (d, J_{HH} = 8.4 Hz, 2H) (aromatic *H*), 3.93 (s, 1H) (cage *H*), 2.93 – 2.86 (m, 1H) (C*H*), 1.24 (s, 3H) (CH_3), 1.22 (s, 3H) (CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): *δ* 151.08, 130.97, 127.77, 127.00 (aromatic *C*), 60.51 (cage *C*H, another cage C was not observed), 33.81 (*C*H), 23.83 (*C*H_3). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): *δ* -2.58 (1B), -5.07 (1B), -9.60 (2B), -11.34 (2B), -11.87 (2B), -13.37 (2B). HRMS (EI): *m/z* calcd for $C_{11}H_{22}B_{10}$ $[M]^{+}$: 262.2725. Found: 262.2723.



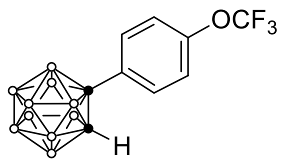
3f: White solid. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.40 (d, J_{HH} = 8.7 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H) (aromatic *H*), 3.93 (s, 1H) (cage *H*), 1.30 (s, 9H) (^{t}Bu *H*). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): *δ* -2.58 (1B), -5.06 (1B), -9.60 (2B), -11.31 (2B), -11.87 (2B), -13.36 (2B). This is a known compound and these data are very similar to the reported ones.[3]



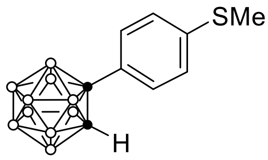
3g: White solid. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.56 – 7.55 (m, 6H), 7.46 (t, J_{HH} = 7.5 Hz, 2H), 7.39 (t, J_{HH} = 7.3 Hz, 1H) (aromatic *H*), 3.99 (s, 1H) (cage *H*). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): *δ* -2.18 (1B), -4.60 (1B), -9.17 (2B), -11.54 (4B), -12.91 (2B). This is a known compound and these data are very similar to the reported ones.[3]



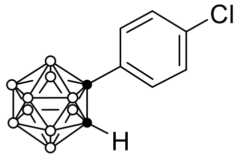
3h: White solid. Yield: 65%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42 (d, J_{HH} = 9.0 Hz, 2H), 6.82 (d, J_{HH} = 9.0 Hz, 2H) (aromatic H), 3.87 (s, 1H) (cage H), 3.81 (s, 3H) (OCH_3). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.42 (1B), -5.21 (1B), -9.66 (2B), -11.19 (2B), -11.98 (2B), -13.27 (2B). This is a known compound and these data are very similar to the reported ones.[3]



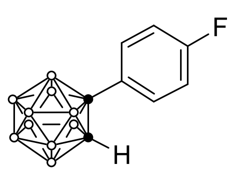
3i: White solid. Yield: 72%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.54 (d, J_{HH} = 9.0 Hz, 2H), 7.18 (d, J_{HH} = 8.3 Hz, 2H) (aromatic H), 3.93 (s, 1H) (cage H). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.02 (1B), -4.35 (1B), -9.08 (2B), -11.04 (2B), -11.65 (2B), -12.90 (2B). This is a known compound and these data are very similar to the reported ones.[3]



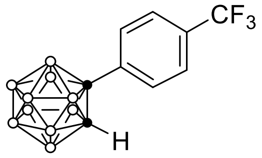
3j: White solid. Yield: 42%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39 (d, J_{HH} = 8.7 Hz, 2H), 7.16 (d, J_{HH} = 8.7 Hz, 2H) (aromatic H), 3.90 (s, 1H) (cage H), 2.48 (s, 3H) (SCH_3). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): -2.31 (1B), -4.85 (1B), -9.36 (2B), -11.13 (2B), -11.78 (2B), -13.10 (2B). This is a known compound and these data are very similar to the reported ones.[3]



3k: White solid. Yield: 65%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H) (aromatic H), 3.92 (s, 1H) (cage H). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.43 (1B), -4.75 (1B), -9.41 (2B), -11.34 (2B), -11.98 (2B), -13.23 (2B). This is a known compound and these data are very similar to the reported ones.[3]

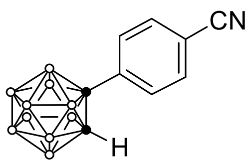


3l: White solid. Yield: 71%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 – 7.46 (m, 2H), 7.06 – 6.98 (m, 2H) (aromatic H), 3.90 (s, 1H) (cage H). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.19 (1B), -4.71 (1B), -9.35 (2B), -11.14 (2B), -11.83 (2B), -13.06 (2B). This is a known compound and these data are very similar to the reported ones.[3]



3m: White solid. Yield: 76%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62 (s, 4H) (aromatic H), 3.99 (s, 1H) (cage H). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.21 (1B), -4.16 (1B), -9.12 (2B), -11.68 (4B), -13.09 (2B).

This is a known compound and these data are very similar to the reported ones.[4]



3n: White solid. Yield: 63%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66 (d, J_{HH} = 8.8 Hz, 2H), 7.60 (d, J_{HH} = 8.7 Hz, 2H) (aromatic *H*), 3.99 (s, 1H) (cage *H*). ^{13}C{^{1}H} NMR (400 MHz, CDCl$_3$): δ 138.14, 132.70, 128.43, 117.55, 114.21 (aromatic *C* & *C*N), 74.72, 59.75 (cage *C*). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.27 (1B), -4.01 (1B), -9.09 (2B), -11.46 (4B), -13.14 (2B). HRMS (EI): *m/z* calcd for $C_9H_{15}B_{10}N$ [M]$^+$: 245.2207. Found: 245.2204. This is a reported compound with ^{1}H NMR data only.[5]

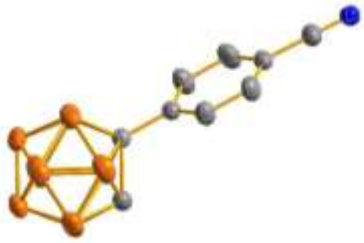
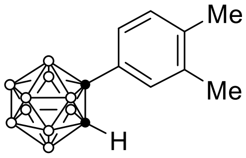
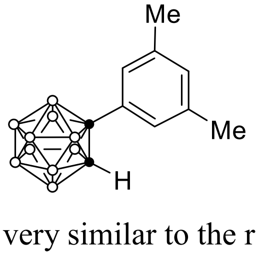


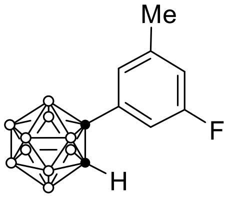
Figure S1. Molecular structure of **3n**.



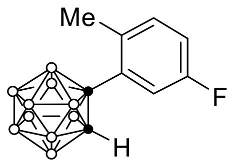
3o: White solid. Yield: 67%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.24 (d, J_{HH} = 2.3 Hz, 1H), 7.20 (dd, J_{HH} = 8.0, 2.4 Hz, 1H), 7.08 (d, J_{HH} = 8.0 Hz, 1H) (aromatic *H*), 3.95 (s, 1H) (cage *H*), 2.27 (s, 3H), 2.26 (s, 3H) (C*H*$_3$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -1.76 (1B), -4.24 (1B), -8.68 (2B), -10.38 (2B), -10.90 (2B), -12.45 (2B). This is a known compound and these data are very similar to the reported ones.[4]



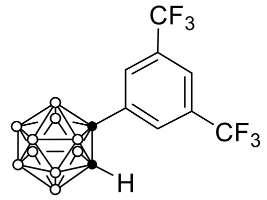
3p: White solid. Yield: 74%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.07 (s, 2H), 7.02 (s, 1H) (aromatic *H*), 3.97 (s, 1H) (cage *H*), 2.31 (s, 6H) (C*H*$_3$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.74 (1B), -5.00 (1B), -9.56 (2B), -11.45 (4B), -13.44 (2B). This is a known compound and these data are very similar to the reported ones.[4]



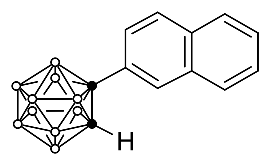
3q: White solid. Yield: 70%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.05 (s, 1H), 7.00 (dt, J_{HH}= 9.7, 2.3 Hz, 1H), 6.92 (d, J_{HH} = 9.0 Hz, 1H) (aromatic *H*), 3.94 (s, 1H) (cage *H*), 2.36 (s, 3H) (C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 162.49 (d, $^1J_{C\text{-}F}$ = 247.5 Hz), 141.38 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 135.33, 124.05 (d, $^{4}J_{\text{C-F}}$ = 2.7 Hz), 117.73 (d, $^{2}J_{\text{C-F}}$ = 20.8 Hz), 112.43 (d, $^{2}J_{\text{C-F}}$ = 24.9 Hz) (aromatic *C*), 75.46, 60.10 (cage *C*), 21.58 ($\mathit{C}\mathrm{H}_3$). ^{19}F NMR (377 MHz, $CDCl_3$): *δ* -112.3. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): *δ* -2.60 (1B), -4.72 (1B), -9.45 (2B), -11.41 (4B), -13.34 (2B). HRMS (APCI): *m/z* calcd for $C_9H_{17}B_{10}F$ [M]$^-$: 252.2328. Found: 252.2324.



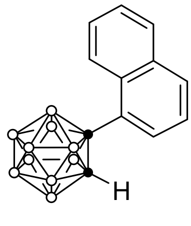
3r: White solid. Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.31 (dd, J_{HH} = 10.9, 2.7 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.00 – 6.92 (m, 1H) (aromatic *H*), 4.54 (s, 1H) (cage *H*), 2.52 (s, 3H) ($\mathrm{C}\mathit{H}_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 160.99 (d, $^{1}J_{\text{C-F}}$ = 245.8 Hz). 135.36 (d, $^{3}J_{\text{C-F}}$ = 7.7 Hz), 133.47 (d, $^{3}J_{\text{C-F}}$ = 7.3 Hz), 130.50 (d, $^{4}J_{\text{C-F}}$ = 3.4 Hz), 118.62 (d, $^{2}J_{\text{C-F}}$ = 25.3 Hz), 116.47 (d, $^{2}J_{\text{C-F}}$ = 20.4 Hz) (aromatic *C*), 77.04, 59.35 (cage *C*), 22.58 ($\mathit{C}\mathrm{H}_3$). ^{19}F NMR (377 MHz, $CDCl_3$): *δ* -115.1. ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): *δ* -3.39 (2B), -9.30 (2B), -10.05 (2B), -11.95 (2B), -13.76 (2B). HRMS (APCI): *m/z* calcd for $C_9H_{17}B_{10}F$ [M]$^+$: 252.2317. Found: 252.2309.



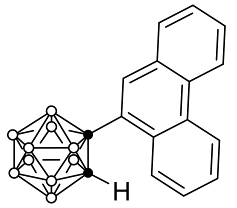
3s: White solid. Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.93 (s, 3H) (aromatic *H*), 4.02 (s, 1H) (cage *H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 136.16, 132.88 (q, $^{2}J_{\text{C-F}}$ = 34.0 Hz), 127.96 (d, $^{3}J_{\text{C-F}}$ = 3.1 Hz) (aromatic *C*), 122.68 (q, $^{1}J_{\text{C-F}}$ = 273.2 Hz) ($\mathit{C}\mathrm{F}_3$), 73.85, 60.13 (cage *C*). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): *δ* -1.85 (1B), -3.71 (1B), -8.83 (2B), -11.23 (2B), -11.86 (2B), -12.81 (2B). ^{19}F NMR (377 MHz, $CDCl_3$): *δ* -62.9. HRMS (APCI): *m/z* calcd for $C_{10}H_{14}B_{10}F_6$ [M-H]$^-$: 355.1935. Found: 355.1934.



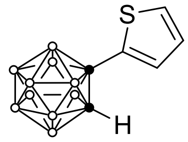
3t: White solid. Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.98 (d, J_{HH} = 1.8 Hz, 1H), 7.86 – 7.79 (m, 3H), 7.57 – 7.53 (m, 3H) (aromatic *H*), 4.09 (s, 1H) (cage *H*). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): *δ* -2.14 (1B), -4.39 (1B), -9.02 (2B), -11.30 (4B), -12.85 (2B). This is a known compound and these data are very similar to the reported ones.[4]



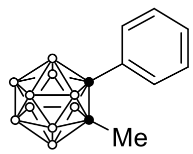
3u: White solid. Yield: 59%. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.71 (d, J_{HH} = 8.9 Hz, 1H), 7.90 (d, J_{HH} = 8.1 Hz, 2H), 7.79 (dd, J_{HH} = 7.7, 1.2 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.55 – 7.51 (m, 1H), 7.41 (t, J_{HH} = 7.9 Hz, 1H) (aromatic *H*), 4.64 (s, 1H) (cage *H*). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): *δ* -3.15 (2B), -9.31 (2B), -10.40 (4B), -13.72 (2B). This is a known compound and these data are very similar to the reported ones.[3]



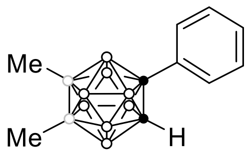
3v: White solid. Yield: 47%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.88 – 8.71 (m, 2H), 8.64 (d, J_{HH} = 8.4 Hz, 1H), 8.08 (s, 1H), 7.87 (d, J_{HH} = 7.6 Hz, 1H), 7.81 – 7.55 (m, 4H) (aromatic *H*), 4.72 (s, 1H) (cage *H*). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -3.01 (2B), -9.25 (2B), -10.37 (4B), -13.70 (2B). This is a known compound and these data are very similar to the reported ones.[3]



3w: Colorless oil. Yield: 15%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26 – 7.23 (m, 1H), 7.20 (dd, J_{HH} = 3.7, 1.2 Hz, 1H), 6.91 (dd, J_{HH} = 5.2, 3.7 Hz, 1H) (aromatic *H*), 3.85 (s, 1H) (cage *H*). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -1.75 (1B), -5.01 (1B), -9.70 (2B), -10.38 (2B), -11.65 (2B), -13.00 (2B). This is a known compound and these data are very similar to the reported one.[6]

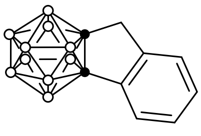


3x: White solid. Yield: 20%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, J_{HH} = 7.9 Hz, 2H), 7.46 (t, J_{HH} = 7.3 Hz, 1H), 7.39 (t, J_{HH} = 7.5 Hz, 2H) (aromatic *H*), 1.69 (s, 3H) (C*H*$_3$). ^{11}B NMR (128 MHz, CDCl$_3$): δ -3.48 (1B), -4.90 (1B), -9.70 (4B), -10.56 (4B). This is a known compound and these data are very similar to the reported one.[3]

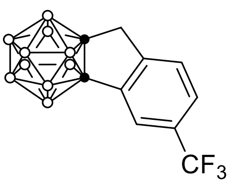


3y: White solid. Yield: 70%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50 (d, J_{HH} = 7.5 Hz, 2H), 7.38 (t, J_{HH} = 7.1 Hz, 1H), 7.32 (t, J_{HH} = 7.4 Hz, 2H) (aromatic *H*), 3.78 (s, 1H) (cage *H*), 0.28 (s, 3H), 0.24 (s, 3H) (C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 133.56, 129.73, 128.84, 127.88 (aromatic *C*), 69.50, 53.64 (cage *C*), two B-*C*H$_3$ carbons were not observed. ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ 7.36 (2B), 5.19 (2B), -7.44 (2B), -11.24 (2B), -13.31 (2B). HRMS (APCI): *m/z* calcd for $C_{10}H_{20}B_{10}$ [M]$^+$: 248.2568. Found: 248.2599.

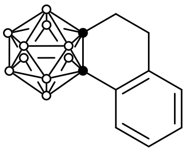
Preparation of *o*-Carborane-Fused Cyclics 4. Cage C-substituted *o*-carboranes (**1d**-**1g**; 0.30 mmol), LiO^{t}Bu (36.0 mg, 0.45 mmol), Ag$_2$CO$_3$ (126.0 mg, 0.45 mmol) and CuI (8.4 mg, 0.045 mmol) were mixed in DME (3 mL) in a 10 mL quartz tube equipped with a magnetic stirring bar. The reaction mixture was irradiated under 8 W UV lamp (254 nm) and stirred at room temperature for 24 h. Afterwards, the reaction was quenched with aqueous acetyl acid, and extracted with diethyl ether (15 mL×3). The ether solutions were combined and dried over Na$_2$SO$_4$. After filtration, the clear solution was concentrated to dryness in vacuo. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) using n-hexane as eluent to give the products **4**.



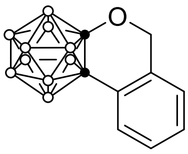
4a: White solid. Yield: 57%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 (d, J_{HH} = 7.7 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.18 (d, J_{HH} = 7.5 Hz, 1H) (aromatic *H*), 3.66 (s, 2H) (C*H*$_2$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -6.88 (4B), -8.92 (2B), -11.82 (2B), -13.12 (2B). This is a known compound and these data are very similar to the reported ones.[7,8]



4b: White solid. Yield: 36%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.57 (d, J_{HH} = 8.6 Hz, 1H), 7.49 – 7.47 (m, 2H) (aromatic *H*), 3.74 (s, 2H) (C*H*$_2$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 145.34, 142.38, 131.71 (d, $^2J_{C\text{-}F}$ = 32.8 Hz), 125.48 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 122.86 (q, $^3J_{C\text{-}F}$ = 3.7 Hz) (aromatic *C*), 123.64 (d, $^1J_{C\text{-}F}$ = 282.0 Hz), 122.12 (aromatic *C*), 83.40, 77.29 (cage *C*), 41.00 (*C*H$_2$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -5.50 (2B), -6.78 (2B), -7.73 (2B), -10.74 (2B), -12.08 (2B). ^{19}F NMR (377 MHz, CDCl$_3$): δ -61.6. HRMS (APCI): *m/z* calcd for $C_{10}H_{15}B_{10}F_3$ [M-H]$^-$: 299.2061. Found: 299.2057.



4c: White solid. Yield: 29%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52 (dd, J_{HH} = 7.3, 1.9 Hz, 1H), 7.33 – 7.18 (m, 2H), 7.10 (dd, J_{HH} = 7.4, 1.6 Hz, 1H) (aromatic *H*), 2.95 (t, J_{HH} = 7.0 Hz, 2H), 2.68 (t, J_{HH} = 7.0 Hz, 2H) (C*H*$_2$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -4.08 (1B), -6.23 (1B), -9.27 (2B), -10.64 (6B). This is a known compound and these data are very similar to the reported ones.[7]



4d: White solid. Yield: 20%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.57 – 7.42 (m, 1H), 7.43 – 7.28 (m, 2H), 7.12 – 6.91 (m, 1H) (aromatic *H*), 5.01 (s, 2H) (C*H*$_2$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -6.25 (1B), -9.55 (2B), -11.11 (1B), -12.23 (2B), -12.95 (4B). This is a known compound and these data are very similar to the reported ones.[7]

Radical Trapping Experiment. *o*-Carborane (**1a**; 14.4 mg, 0.10 mmol), iodobenzene (61.2 mg, 0.30 mmol), LiO^{t}Bu (12.0 mg, 0.15 mmol), Ag_2CO_3 (42.0 mg, 0.15 mmol), CuI (2.8 mg, 0.015 mmol) and TEMPO (0.1 or 0.2 mmol) were mixed in dry DME (1 mL) in a 10 mL quartz tube equipped with a magnetic stirring bar. The reaction mixture was irradiated under 8 W UV lamp (254 nm) and stirred at room temperature for 12 h. Afterwards, the reaction was quenched with aqueous acetyl acid, and examined by GC-MS analysis.

$CuCl_2$ Catalyzed Reaction. *o*-Carborane (**1a**; 14.4 mg, 0.10 mmol), iodobenzene (**2a**; 20.4 mg, 0.10 mmol), LiO^{t}Bu (12.0 mg, 0.15 mmol), Ag_2CO_3 (42.0 mg, 0.15 mmol) and $CuCl_2$ (2.0 mg, 0.015 mmol) were mixed in dry DME (1 mL) in a 5 mL quartz tube equipped with a magnetic stirring bar. The reaction mixture was irradiated with 8 W UV lamp (254 nm) and stirred at room temperature for 12 h. After quenching with aqueous acetyl acid solution, the mixture was examined by GC-MS analysis.

X-ray Structure Determination. X-ray data were collected at 296 K on a BRUKER D8VENTURE DIFFRACTOMETE using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[9] The structure was solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[10] All hydrogen atoms were geometrically fixed using the riding model. Details of the crystal structure were deposited in the Cambridge Crystallographic Data Centre with the following deposit number CCDC-1996712 for **3n.**

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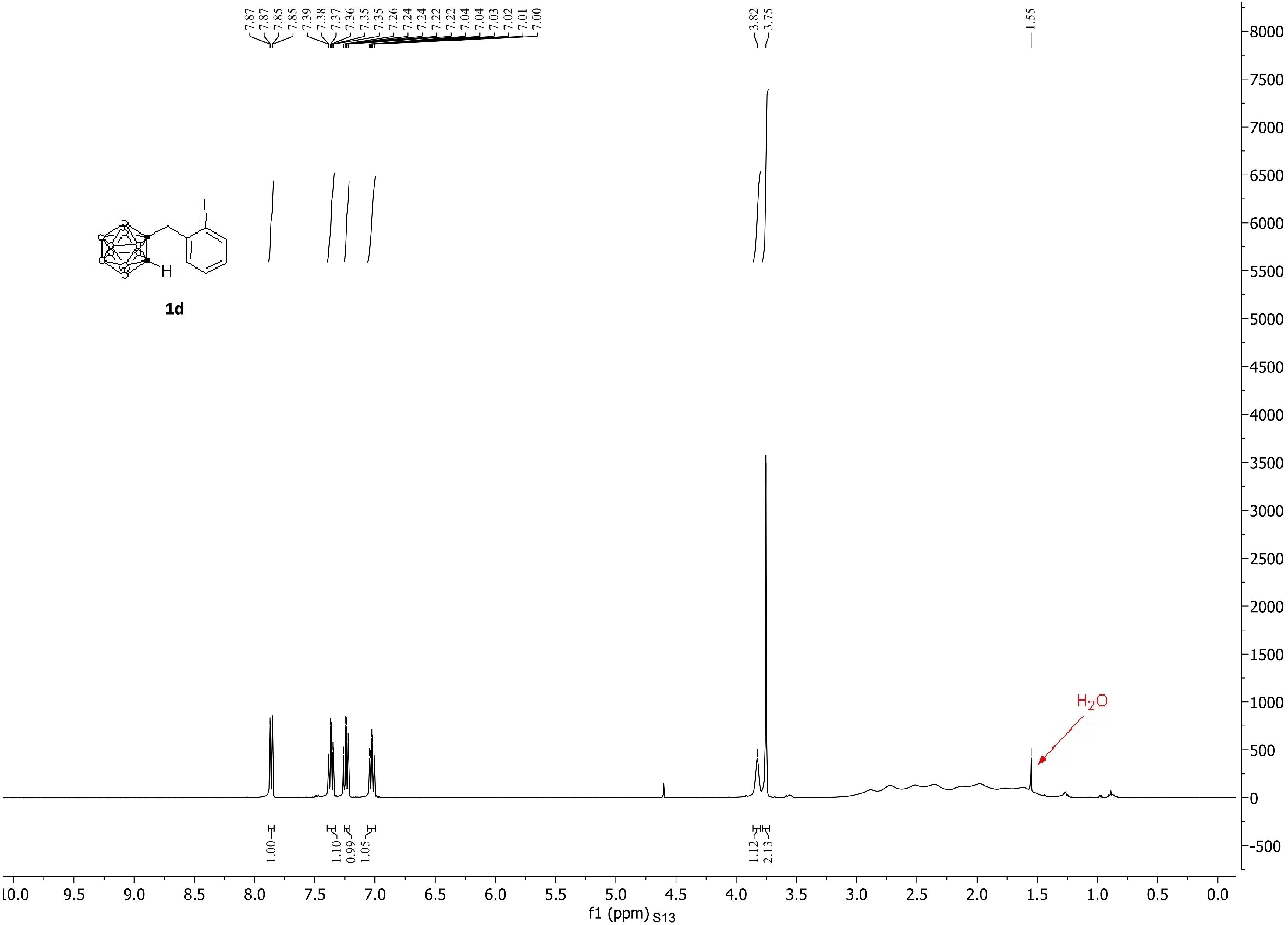
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H
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1.00
1.10
0.99
1.05
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2.13
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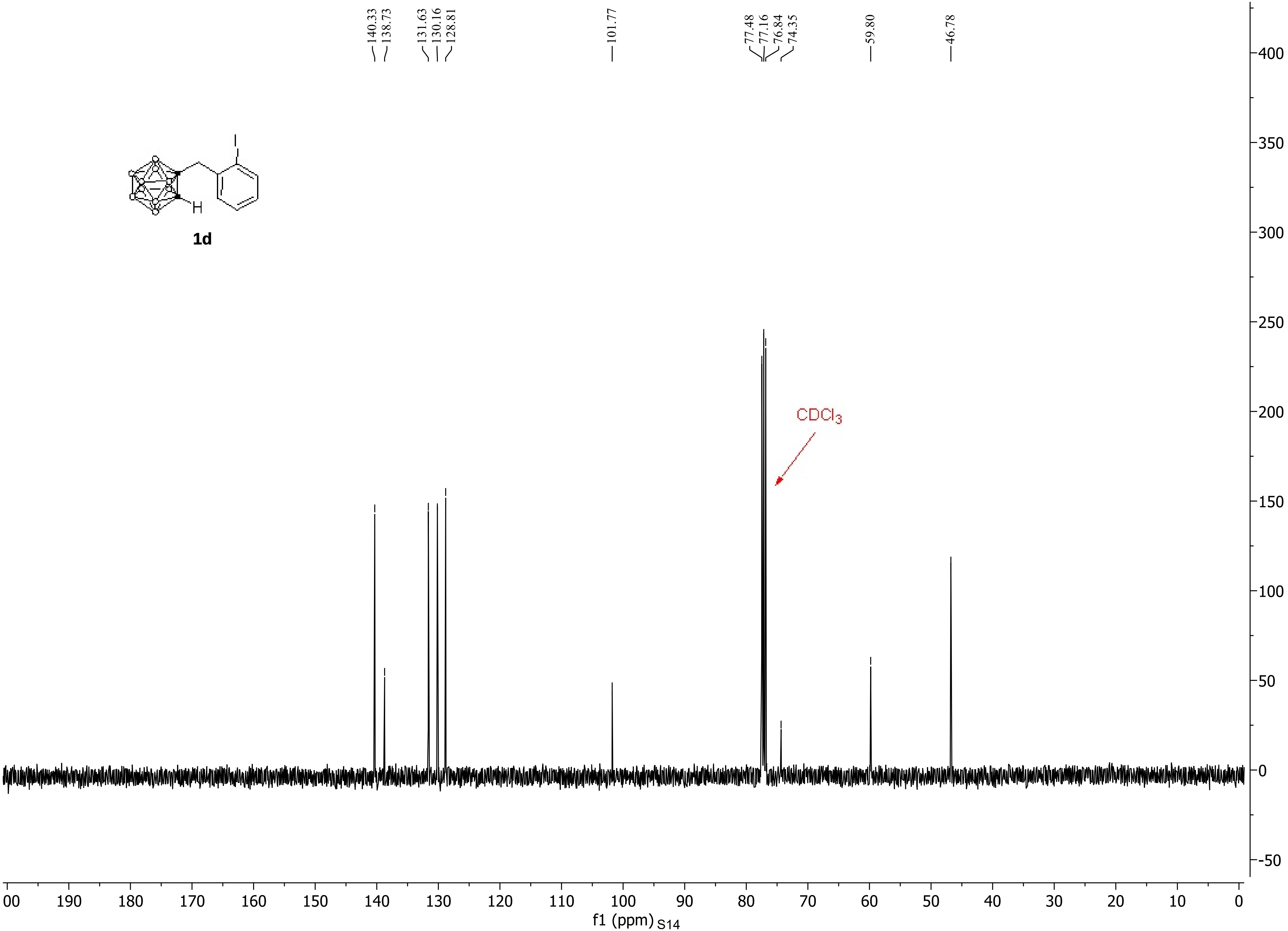
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H
1d
CDCl$_3$
400
350
300
250
200
150
100
50
0
-50
00
190
180
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10
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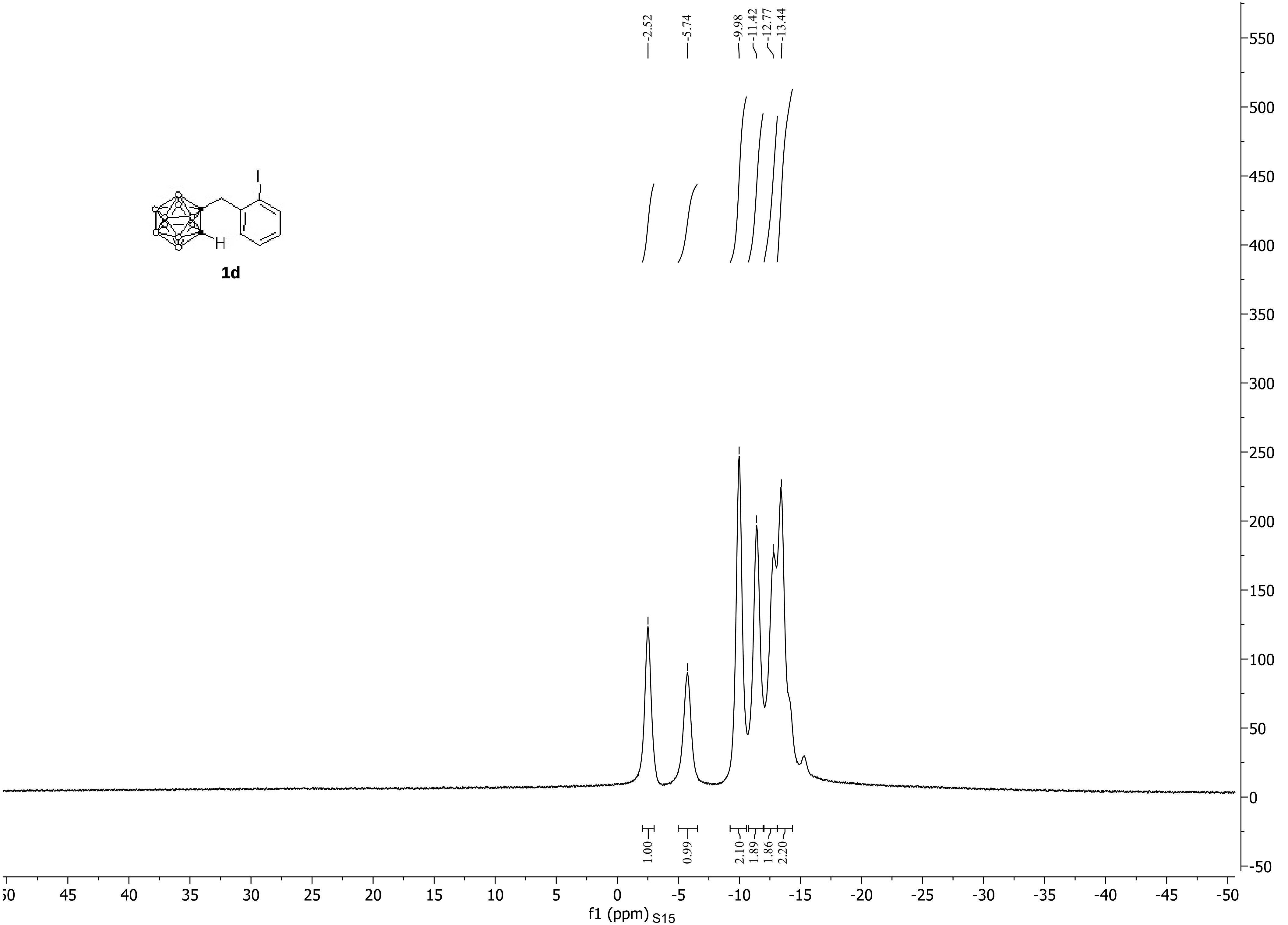
f1 (ppm)



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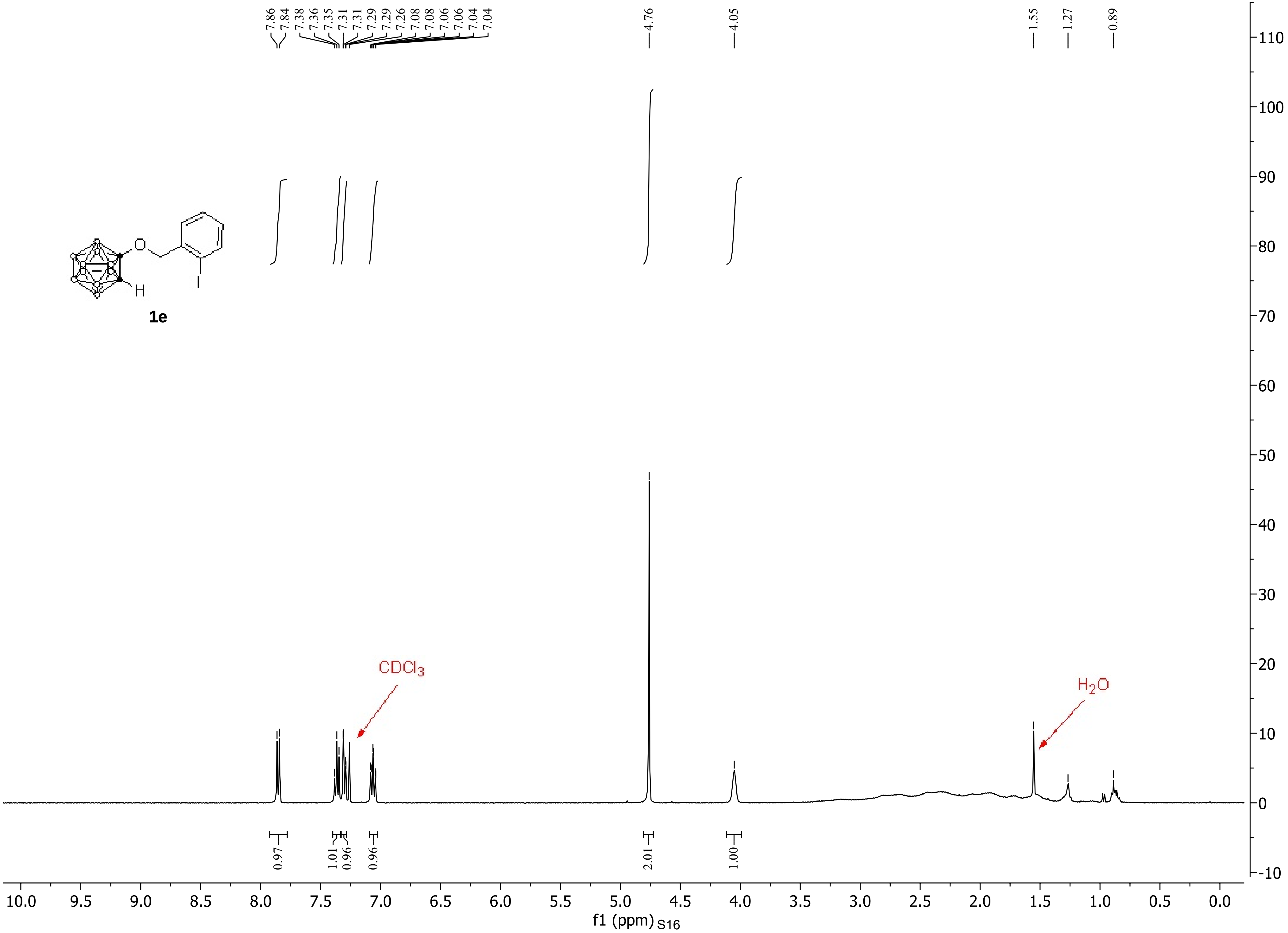
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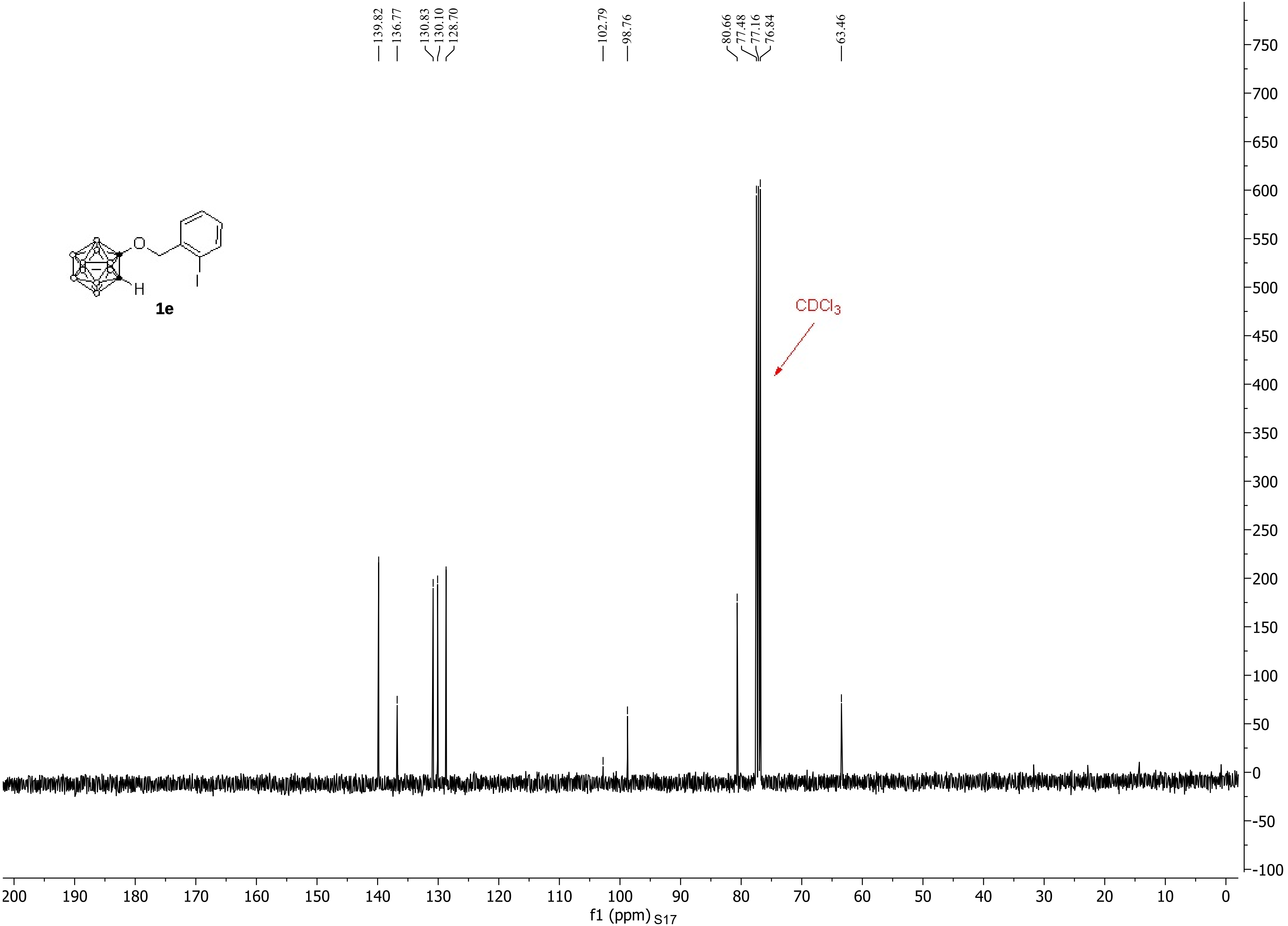
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H
I
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CDCl$_3$
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700
650
600
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500
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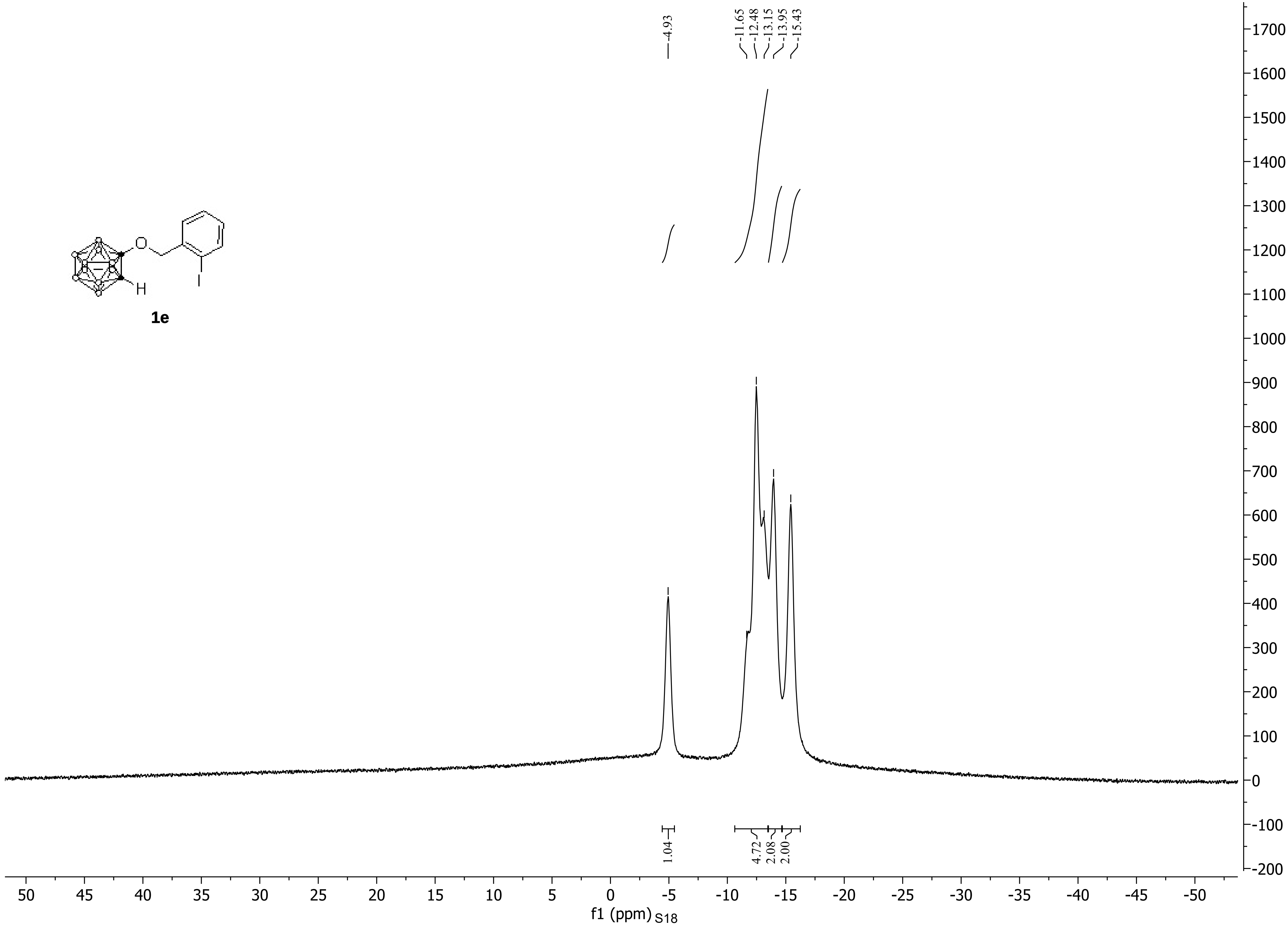
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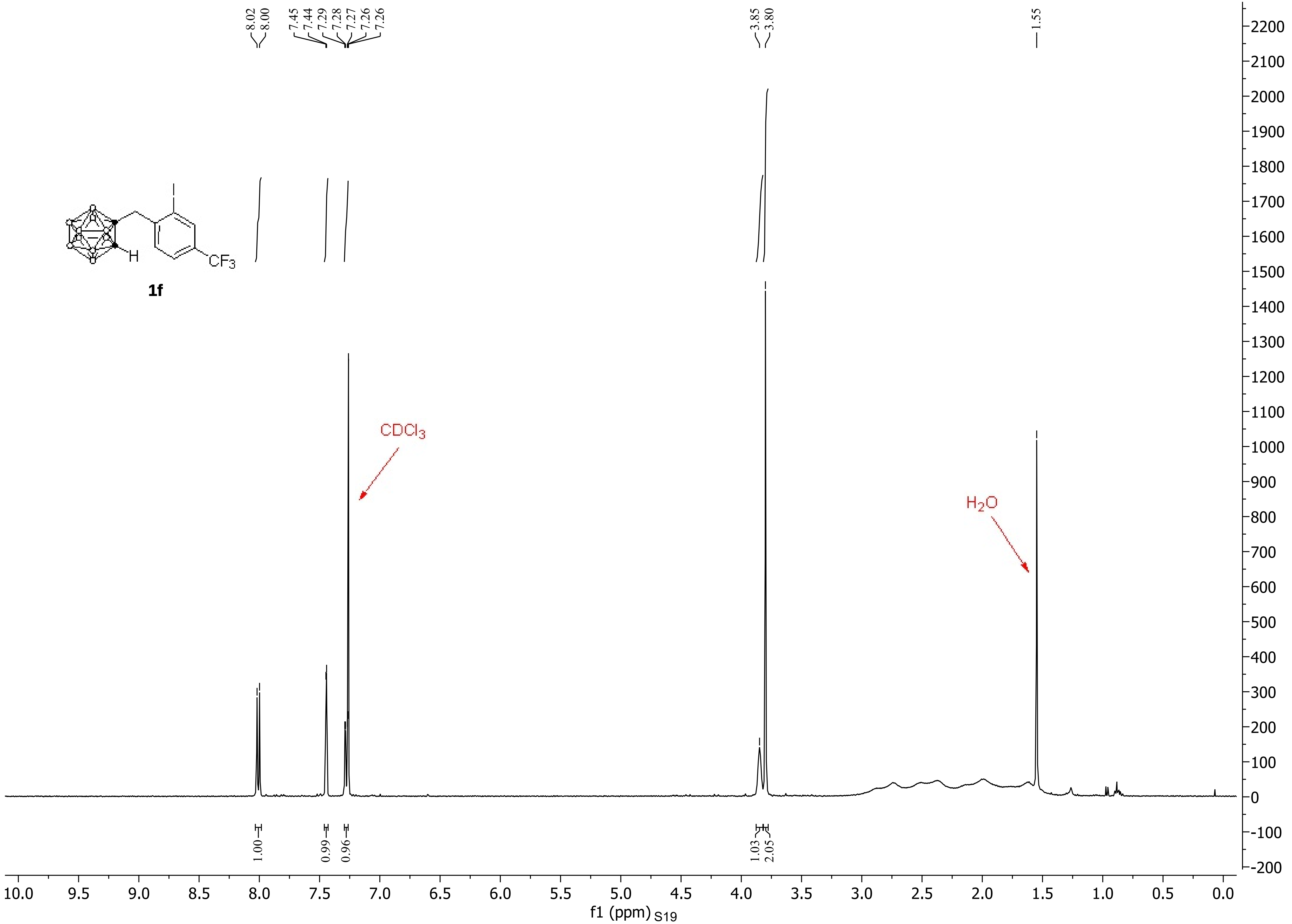
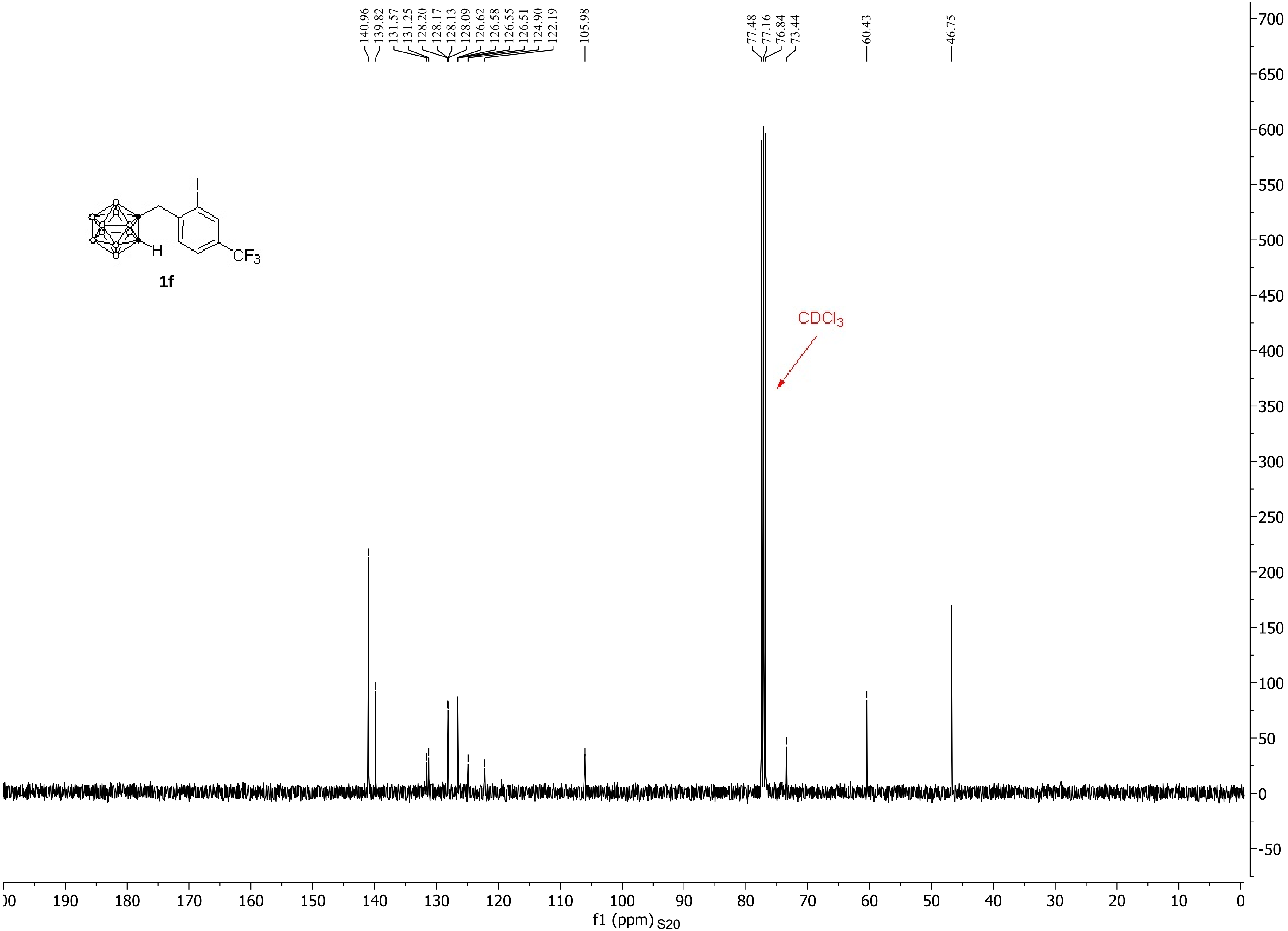
-100
-200
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

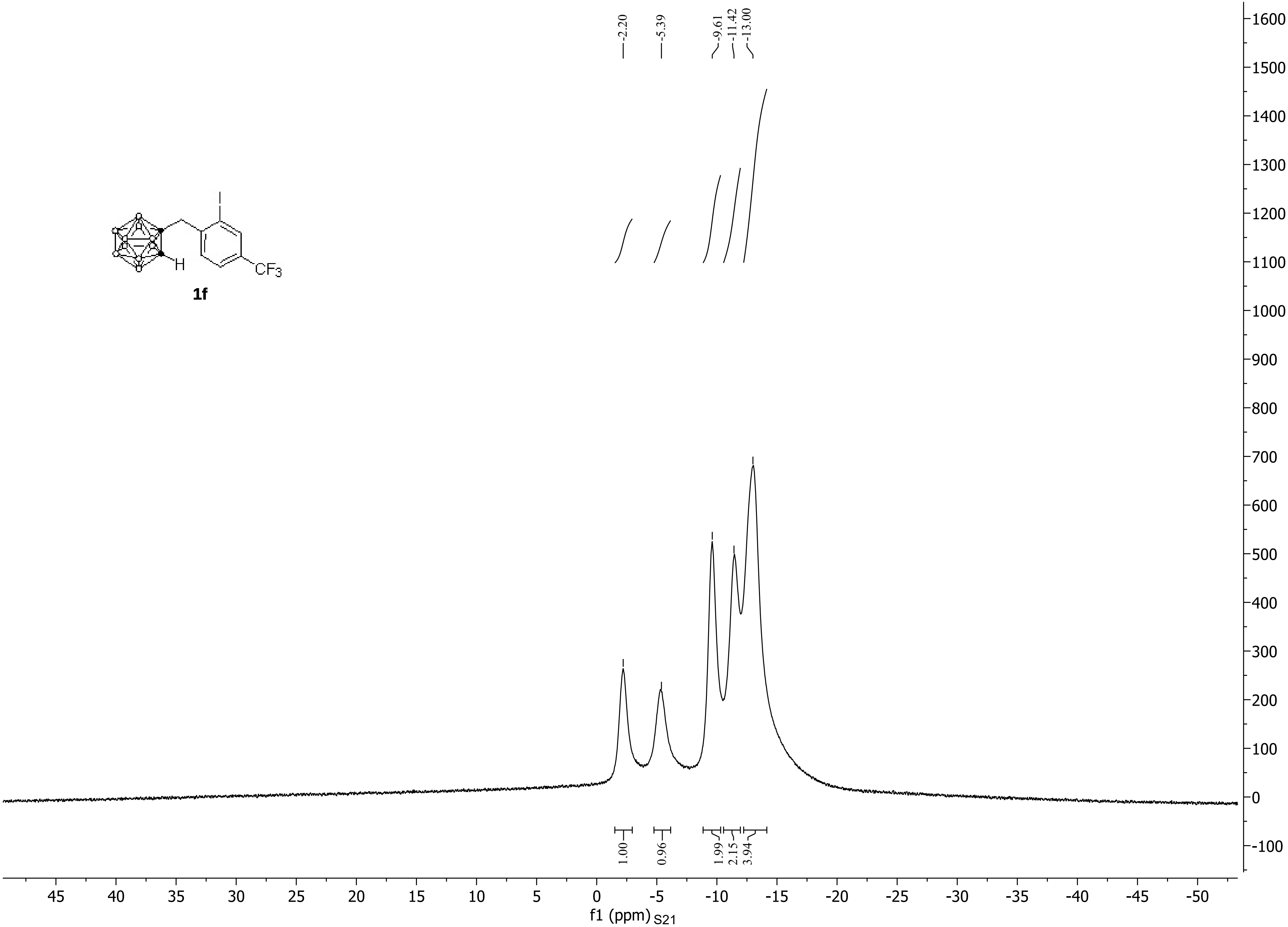


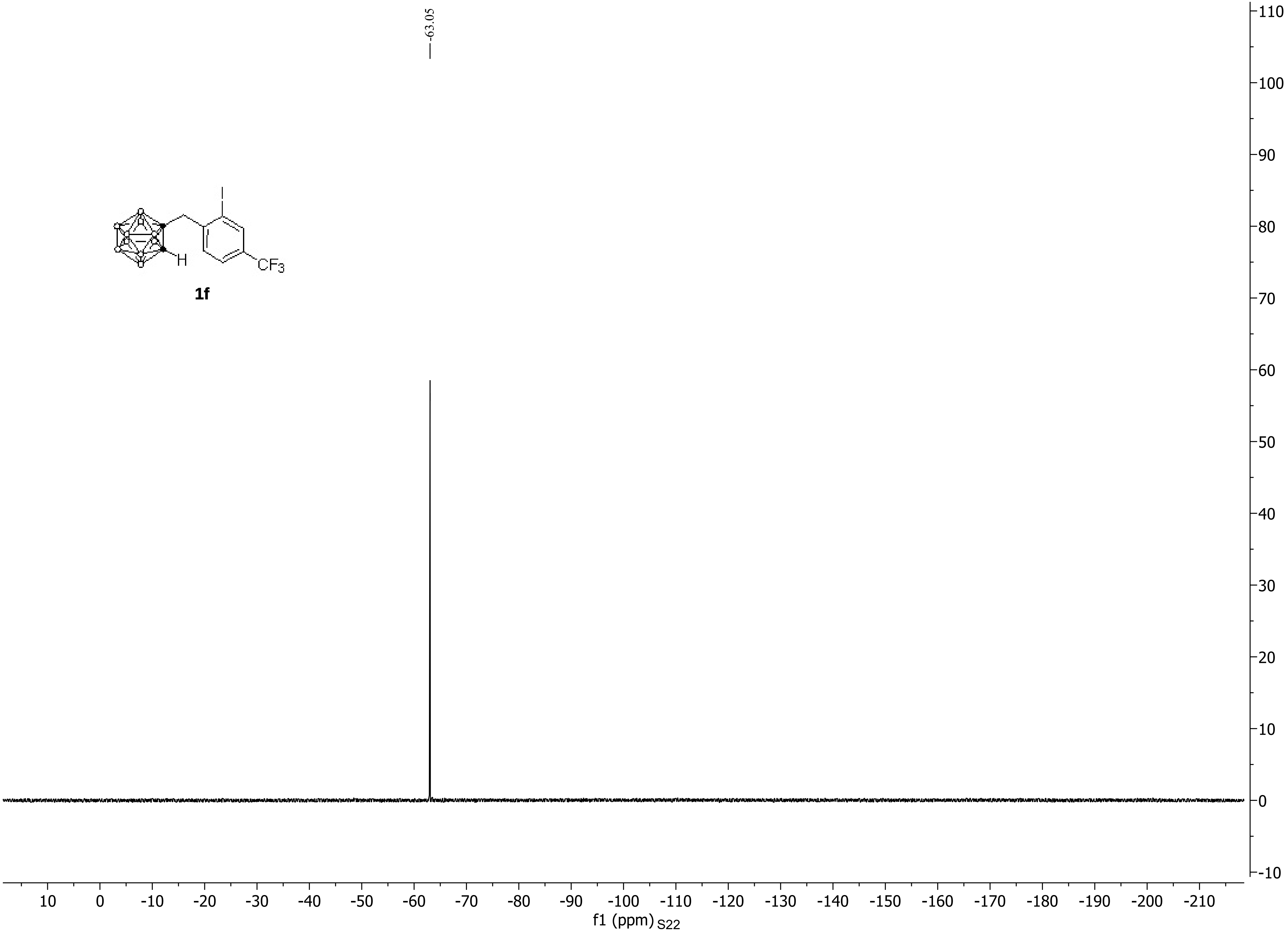
8.02
8.00
7.45
7.44
7.29
7.28
7.27
7.26
7.26
3.85
3.80
1.55
H
CF3
CDCl3
H2O
1.00
0.99
0.96
1.03
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

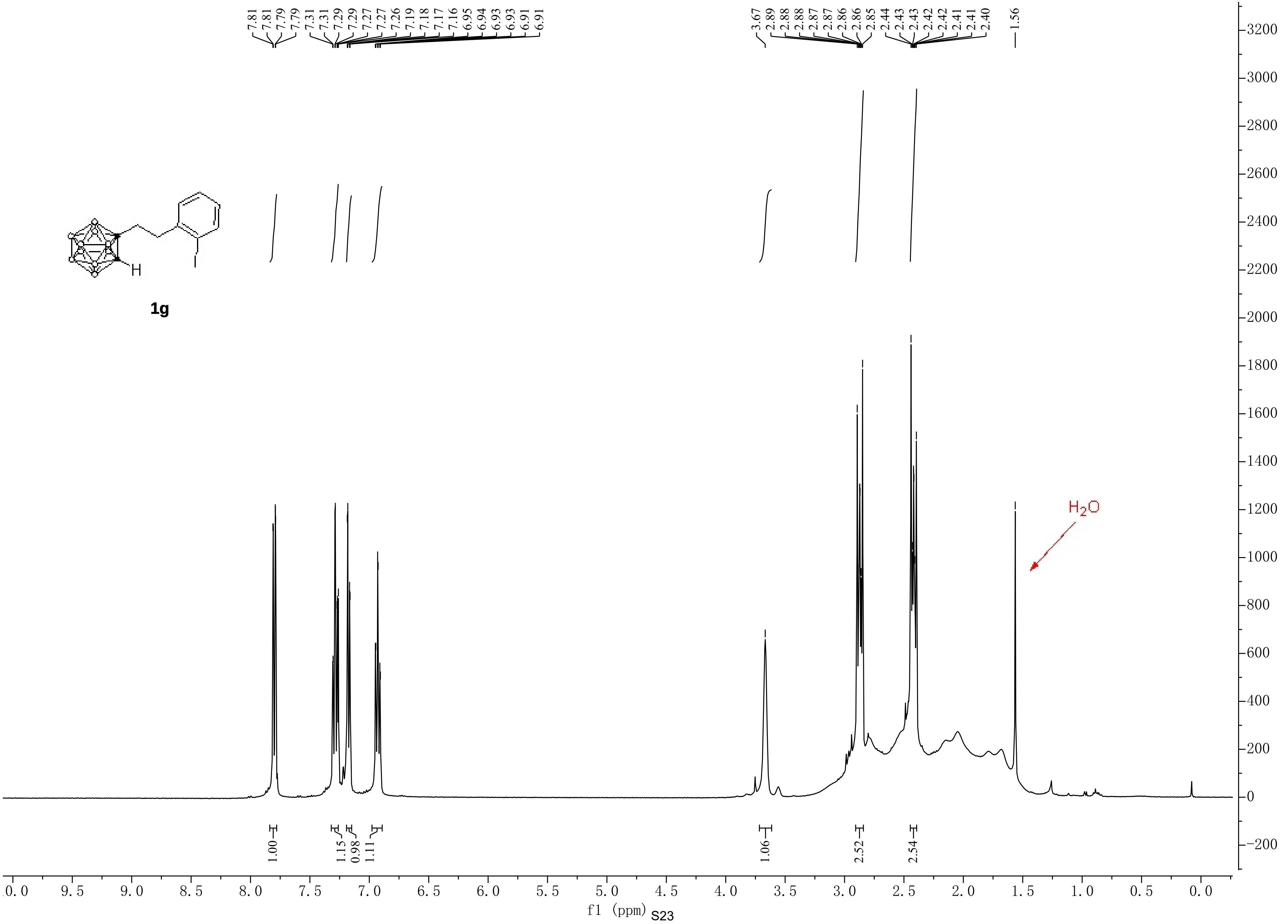
1f


1f

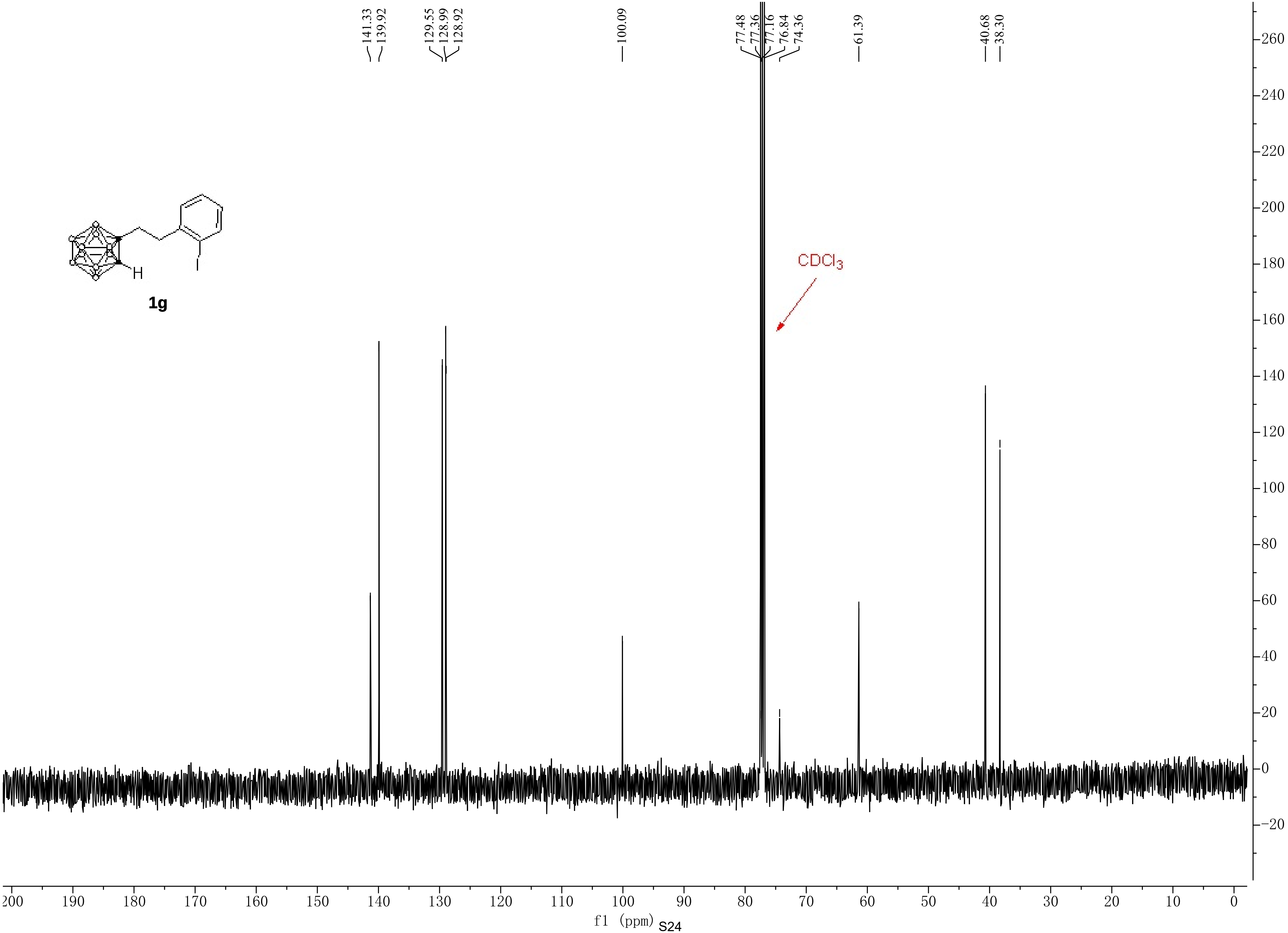
140.96
139.82
131.57
131.25
128.20
128.17
128.13
128.09
126.62
126.58
126.55
126.51
124.90
122.19
105.98
77.48
77.16
76.84
73.44
60.43
46.75
CDCl3
H
I
CF3
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

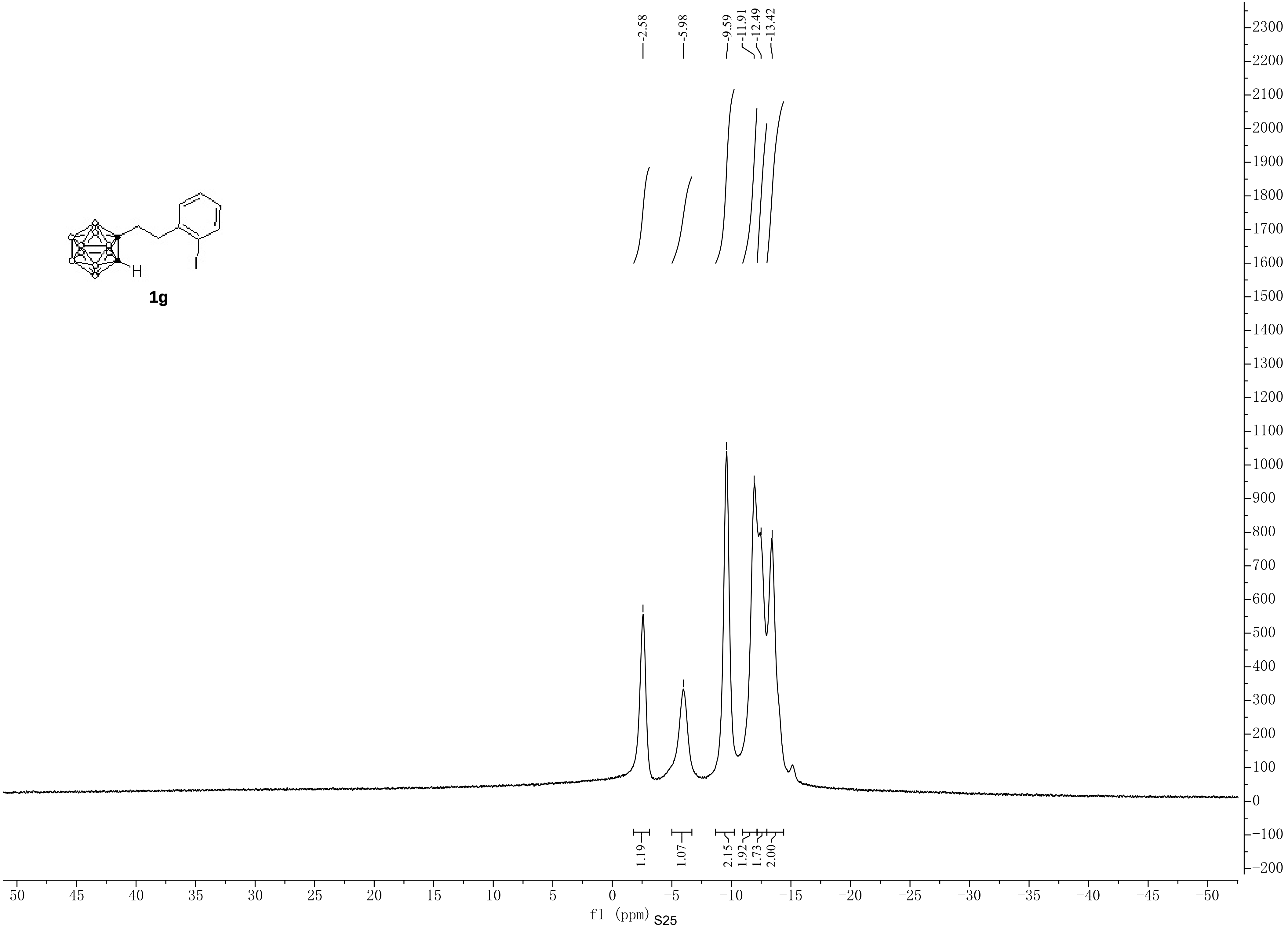

-2.20
-5.39
-9.61
-11.42
-13.00
H
I
CF3
1f
1.00
0.96
1.99
2.15
3.94
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


1f
-63.05
I
H
CF3
110
100
90
80
70
60
50
40
30
20
10
0
-10
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.81
7.81
7.79
7.79
7.31
7.31
7.29
7.29
7.27
7.27
7.26
7.19
7.18
7.17
7.16
6.95
6.94
6.93
6.93
6.91
6.91
3.67
2.89
2.88
2.88
2.87
2.87
2.86
2.86
2.85
2.44
2.43
2.43
2.42
2.42
2.41
2.41
2.40
1.56
H
I
H₂O
1.00
1.15
0.98
1.11
1.06
2.52
2.54
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

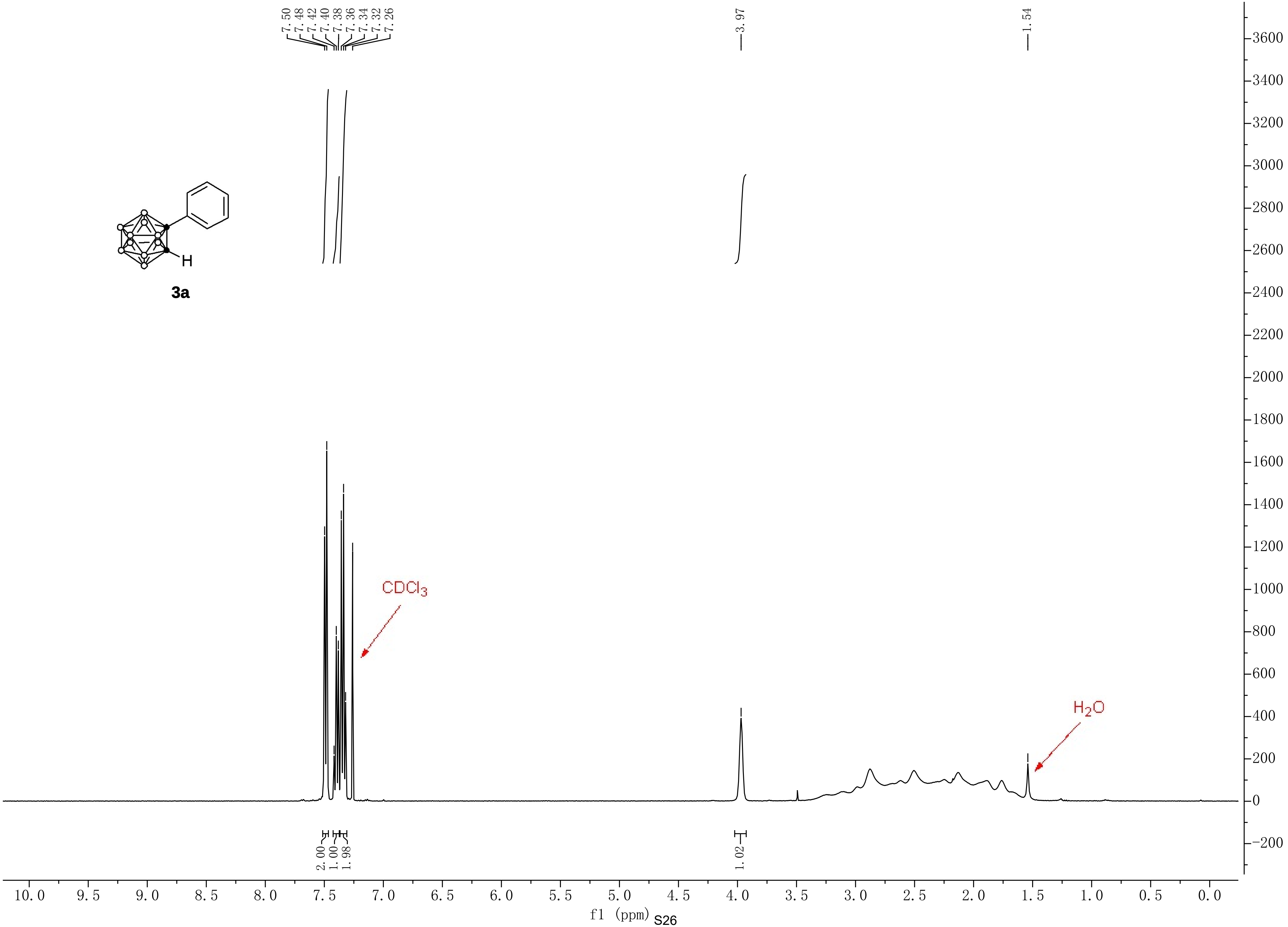
1g


141.33
139.92
129.55
128.99
128.92
100.09
77.48
77.36
77.16
76.84
74.36
61.39
40.68
38.30
CDCl3
H
I
1g
260
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



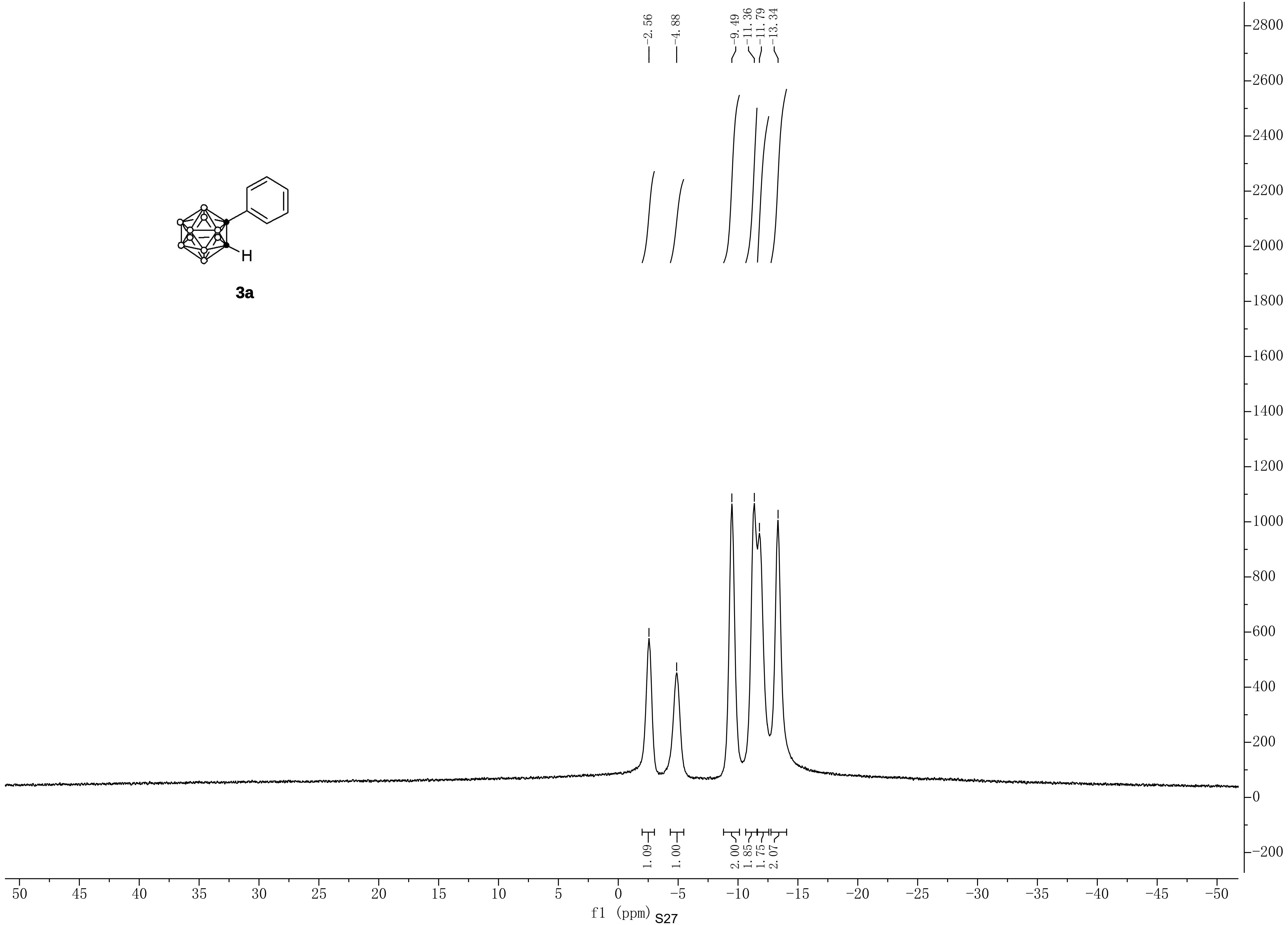
1g

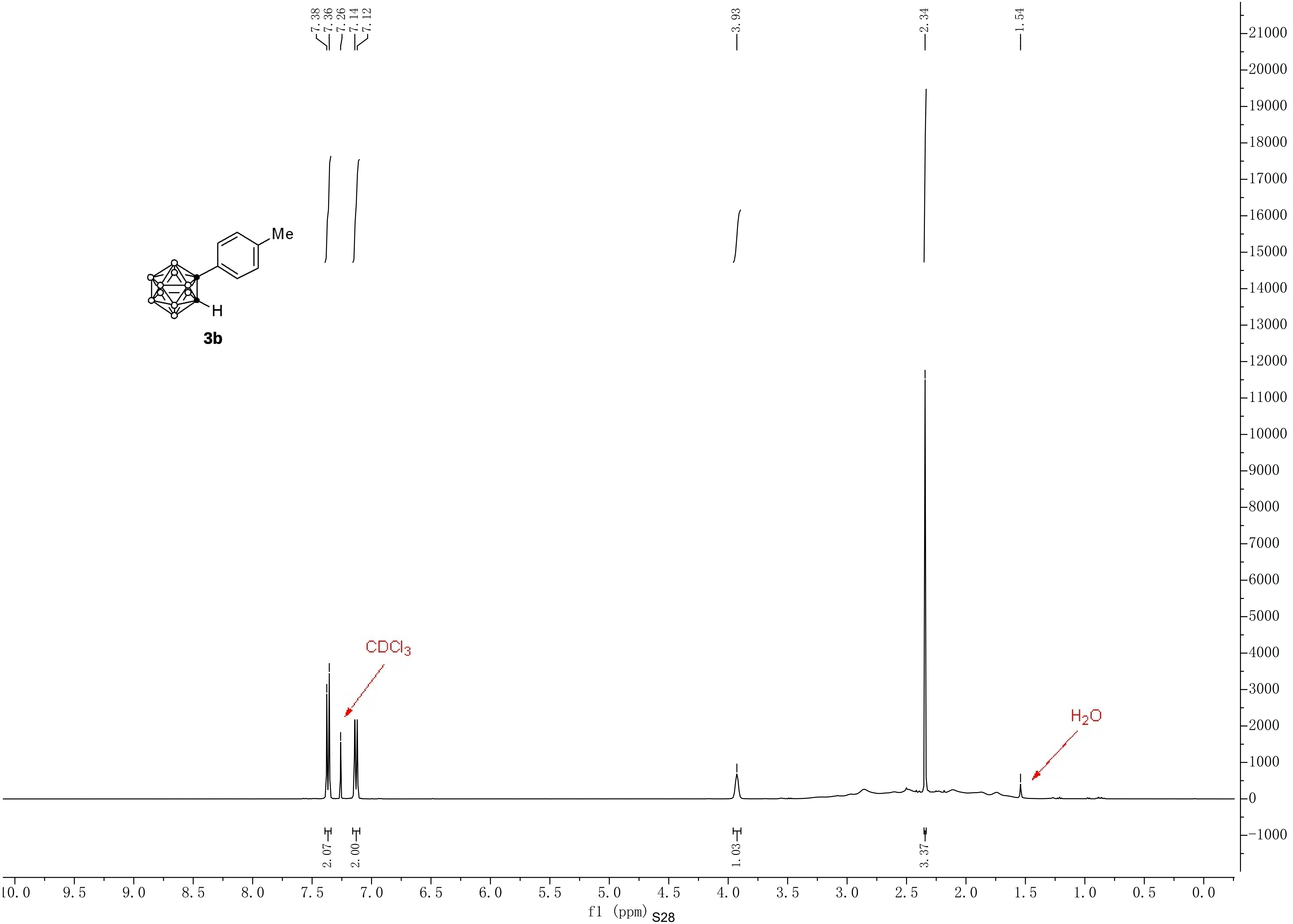
-2.58
-5.98
-9.59
-11.91
-12.49
-13.42
H
I
1.19
1.07
2.15
1.92
1.73
2.00
50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)
2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 −100 −200



3a

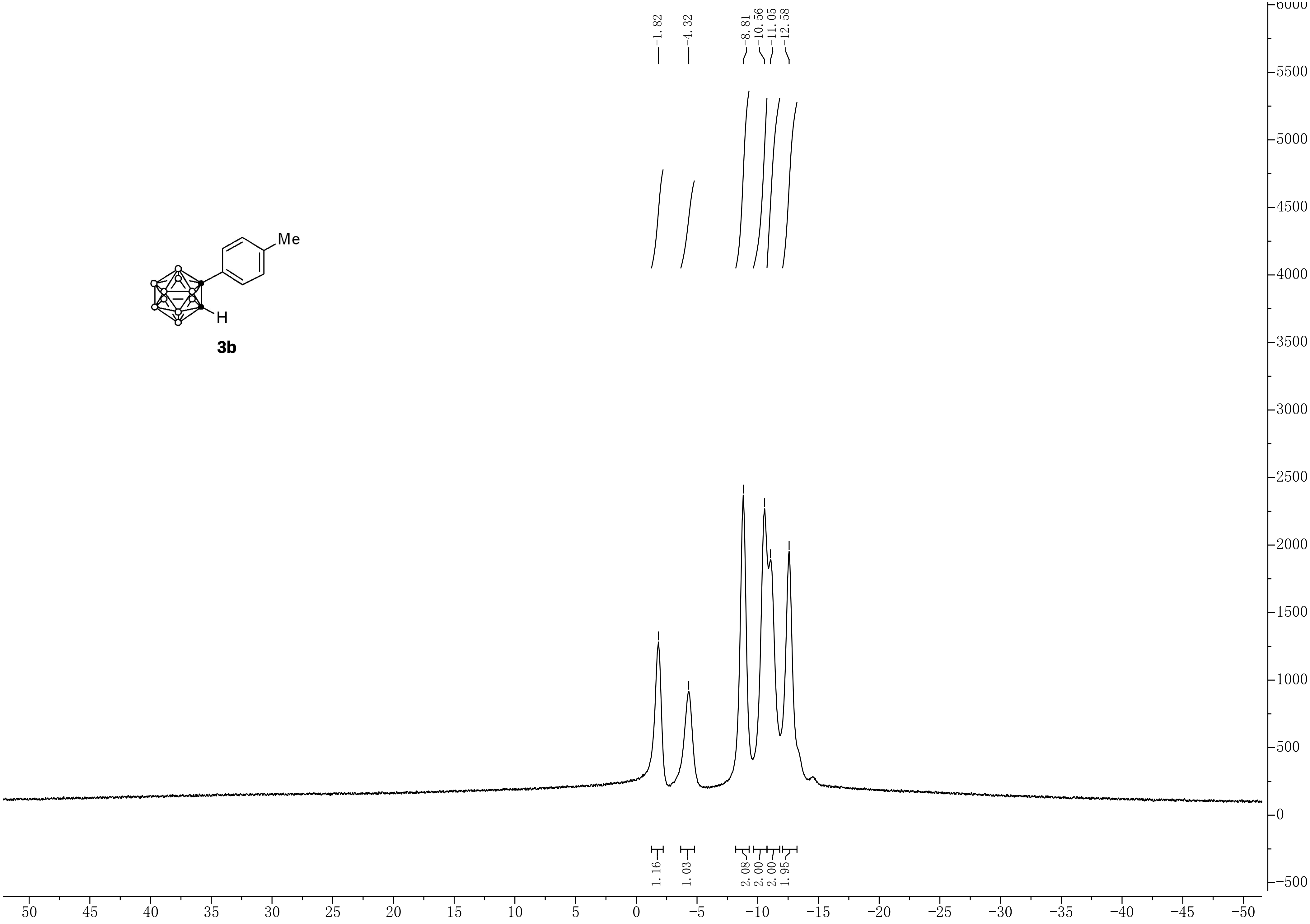
7.50
7.48
7.42
7.40
7.38
7.36
7.34
7.32
7.26
3.97
1.54
H
CDCl$_3$
H$_2$O
2.00
1.00
1.98
1.02
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

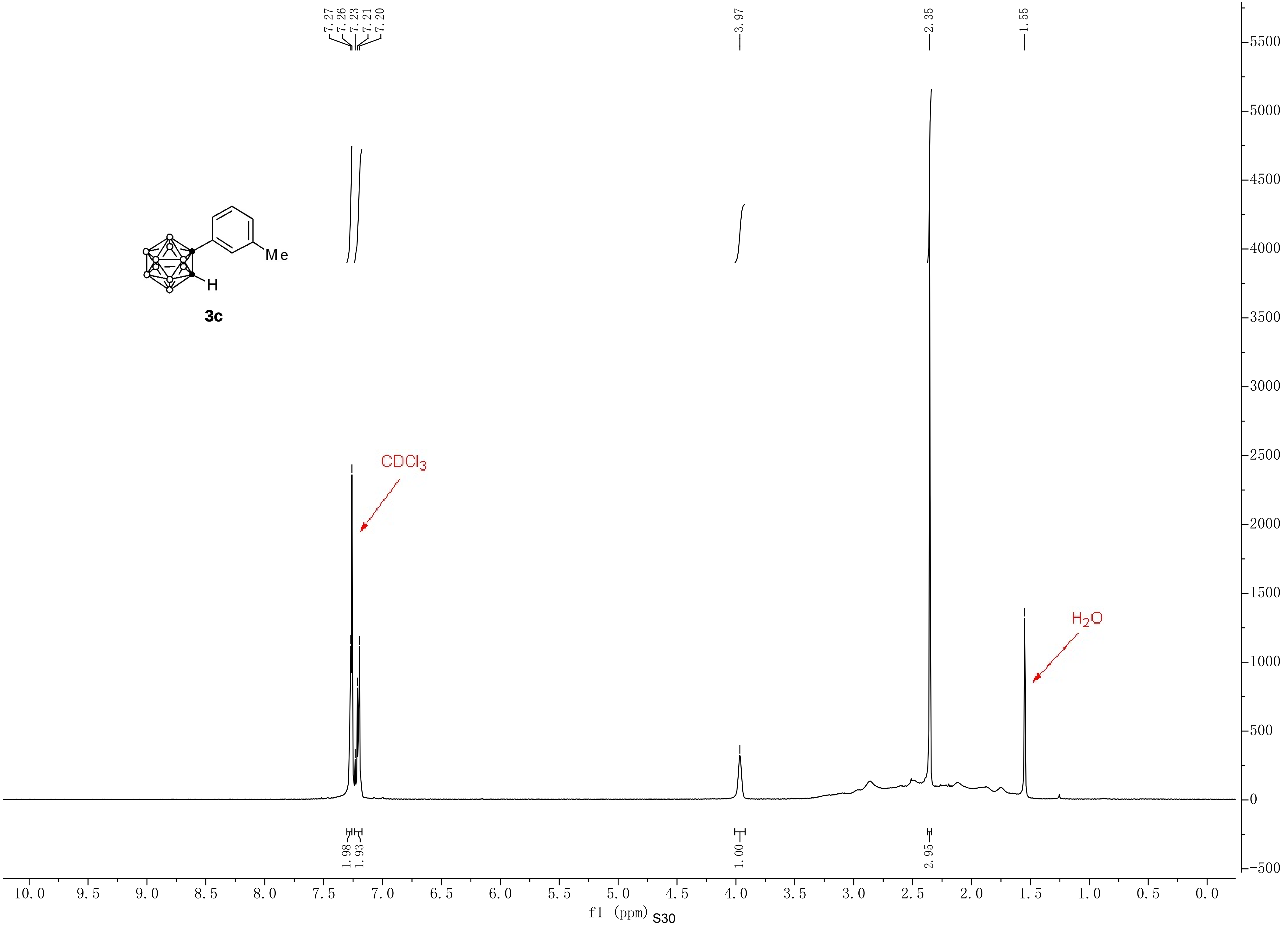

-2.56
-4.88
-9.49
-11.36
-11.79
-13.34
H
3a
1.09
1.00
2.00
1.85
1.75
2.07
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

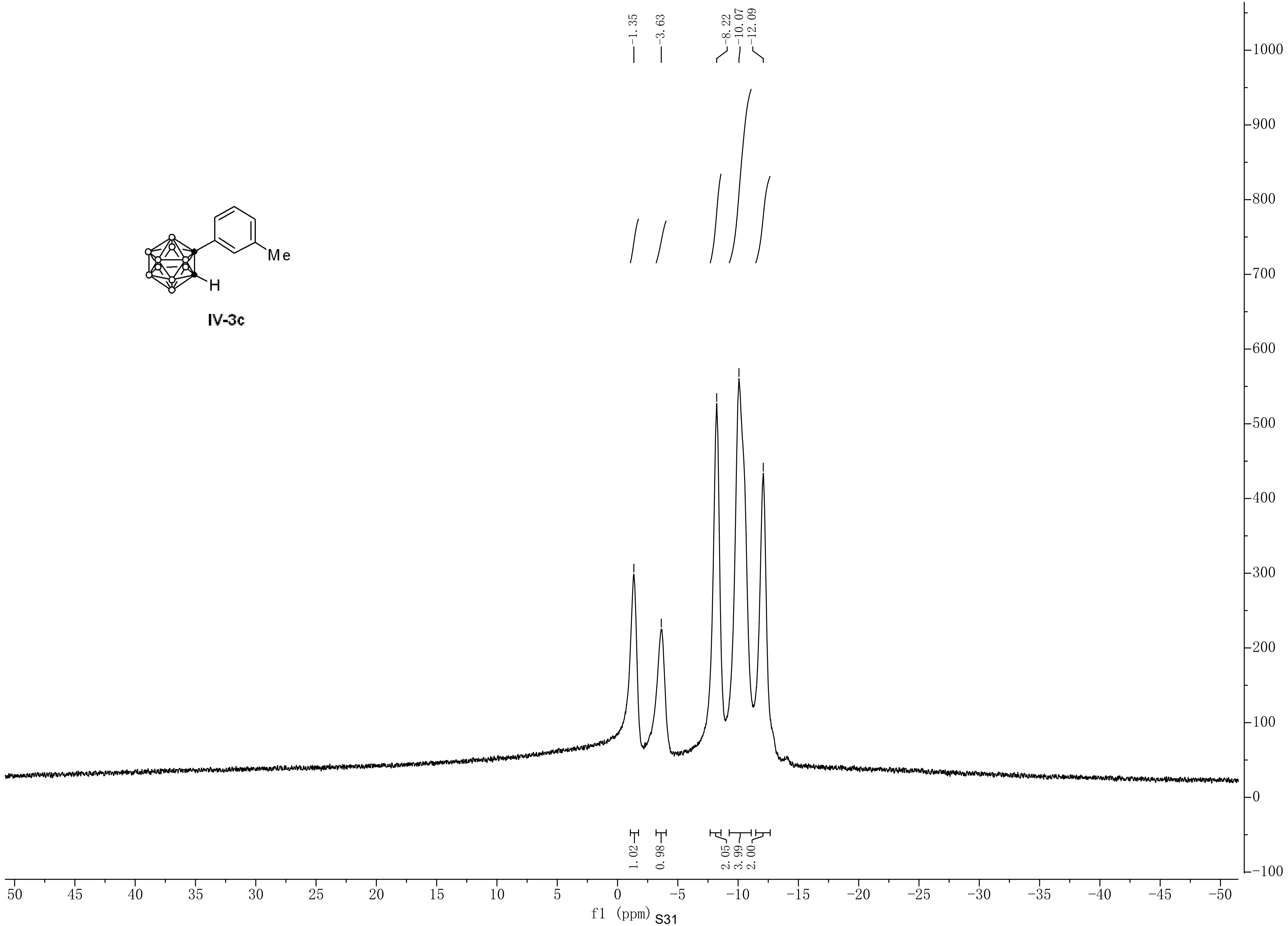


3b

7.38
7.36
7.26
7.14
7.12
3.93
2.34
1.54
Me
H
CDCl$_3$
H$_2$O
2.07
2.00
1.03
3.37
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

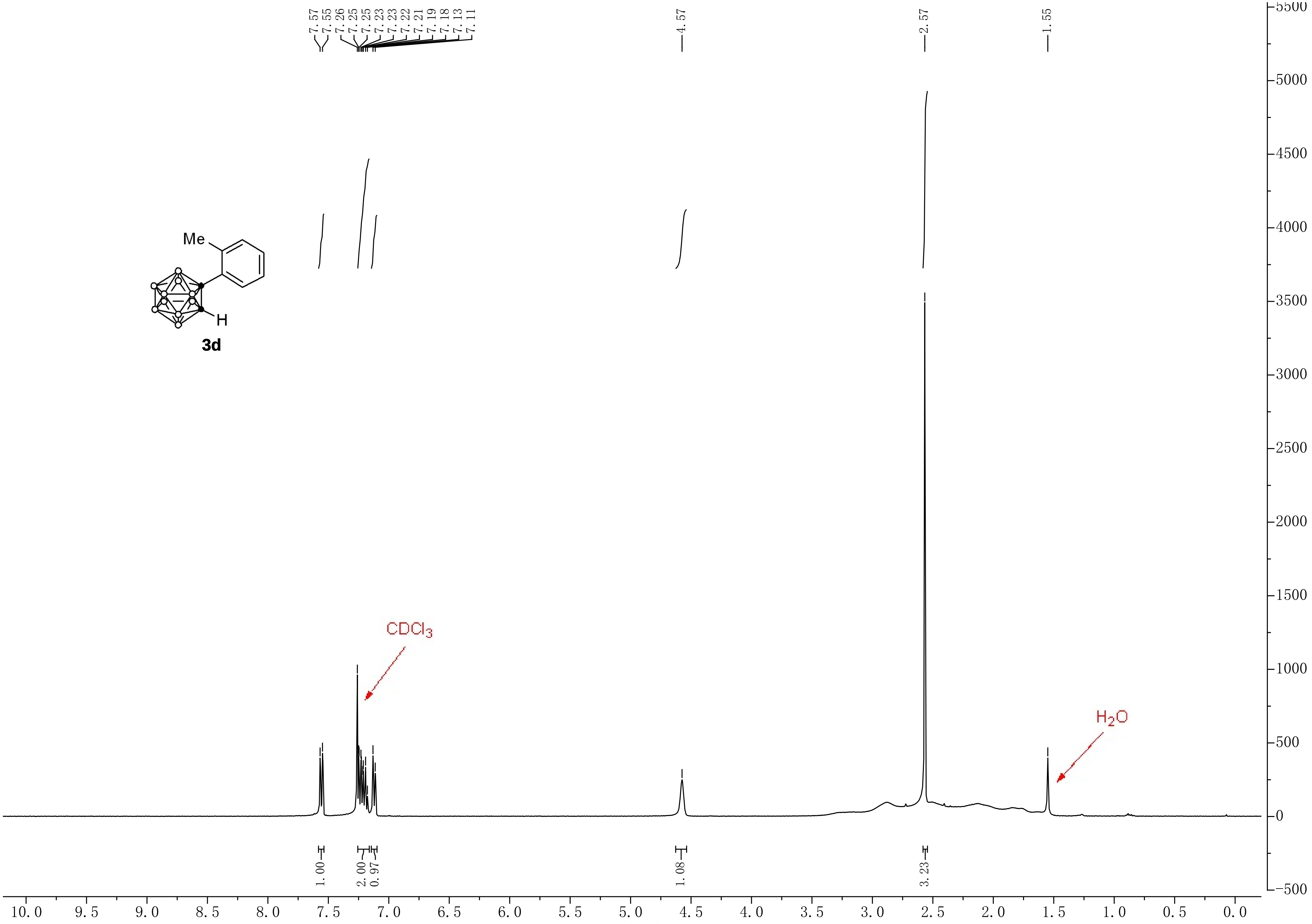

-1.82
-4.32
-8.81
-10.56
-11.05
-12.58
Me
H
3b
1.16
1.03
2.08
2.00
2.00
1.95
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

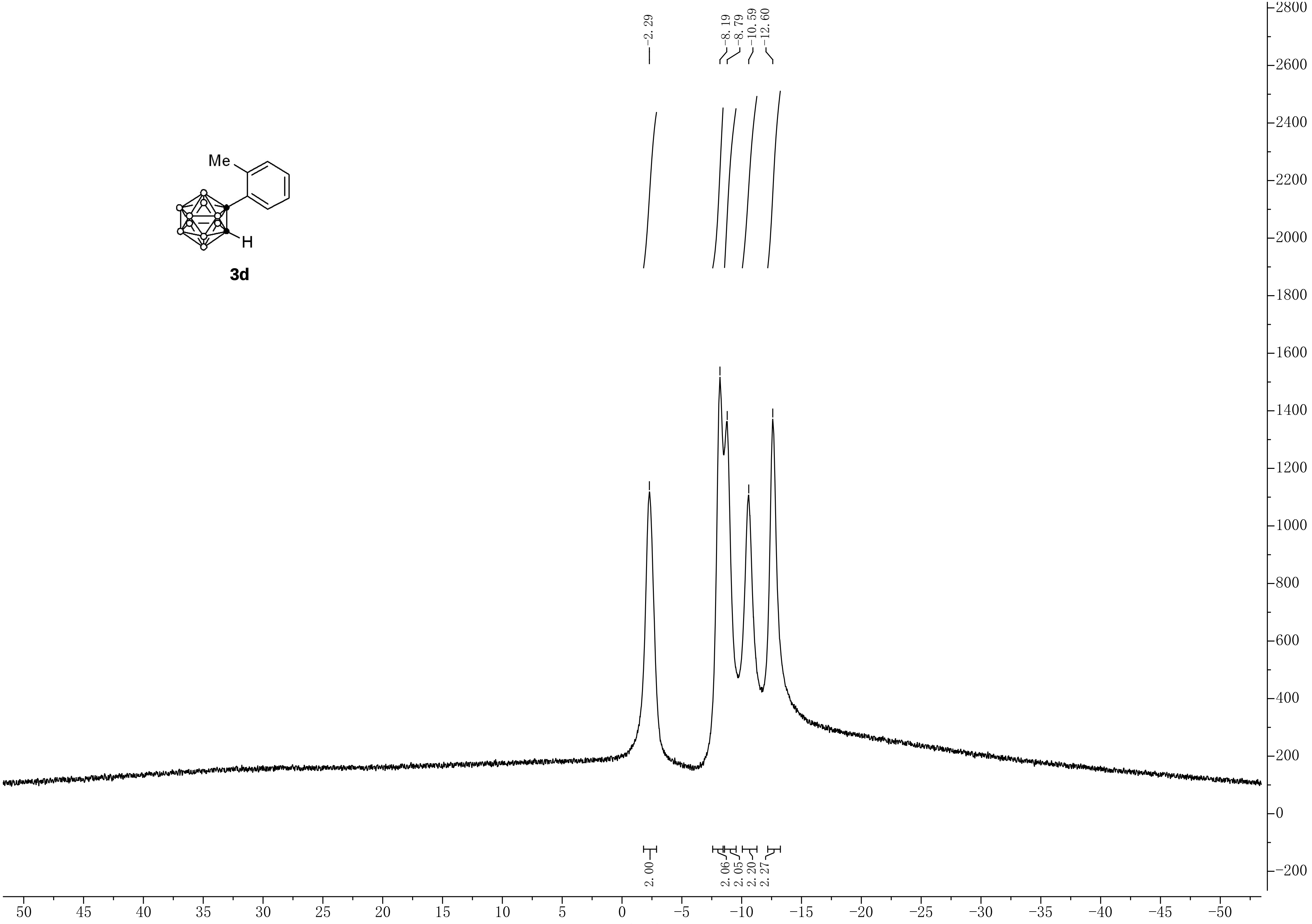

7.27
7.26
7.23
7.21
7.20
3.97
2.35
1.55
Me
H
3c
CDCl$_3$
H$_2$O
1.98
1.93
1.00
2.95
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



Me
H
-1.35
-3.63
-8.22
-10.07
-12.09
1.02
0.98
2.05
3.99
2.00
1000
900
800
700
600
500
400
300
200
100
0
−100
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)

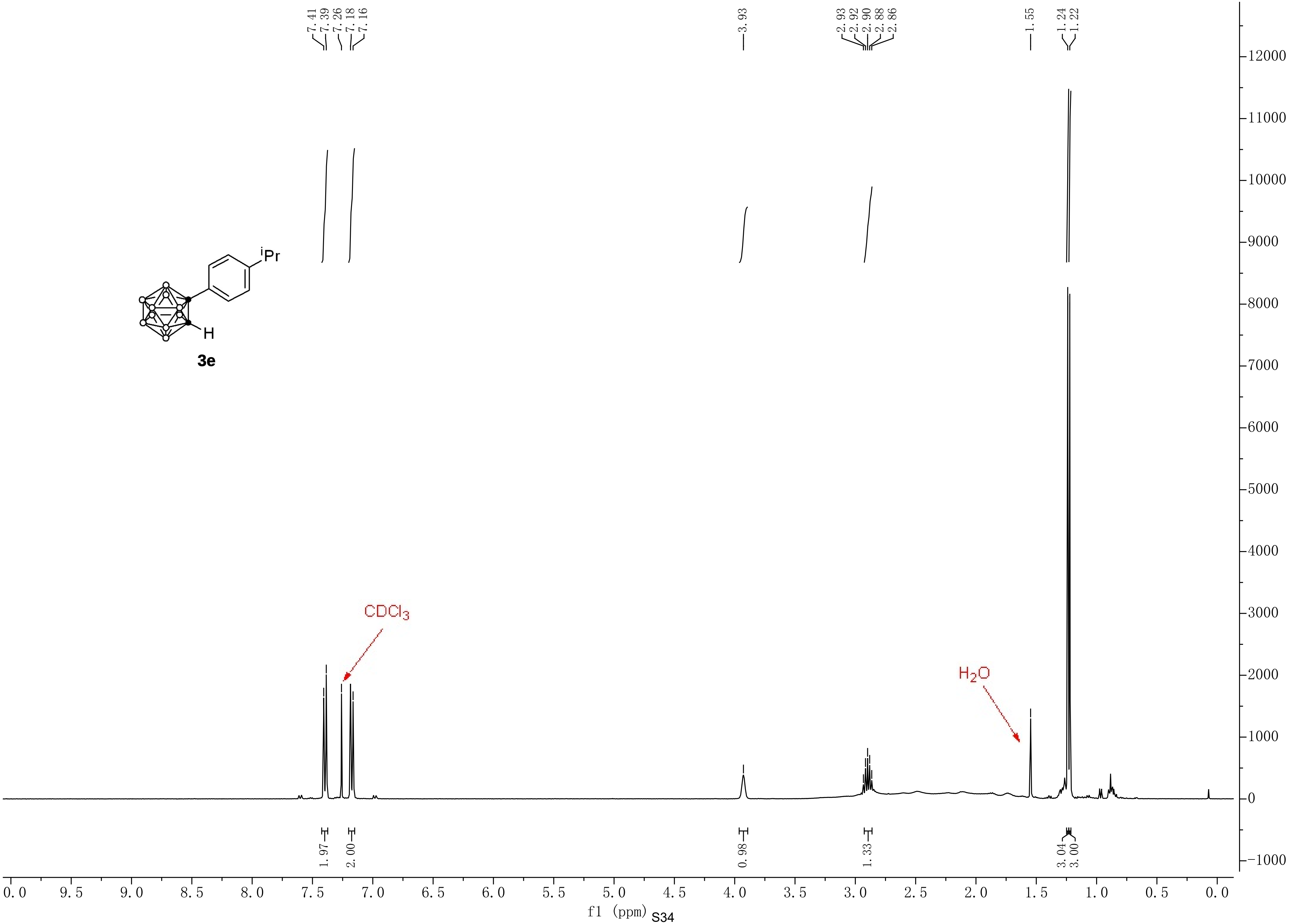
IV-3c

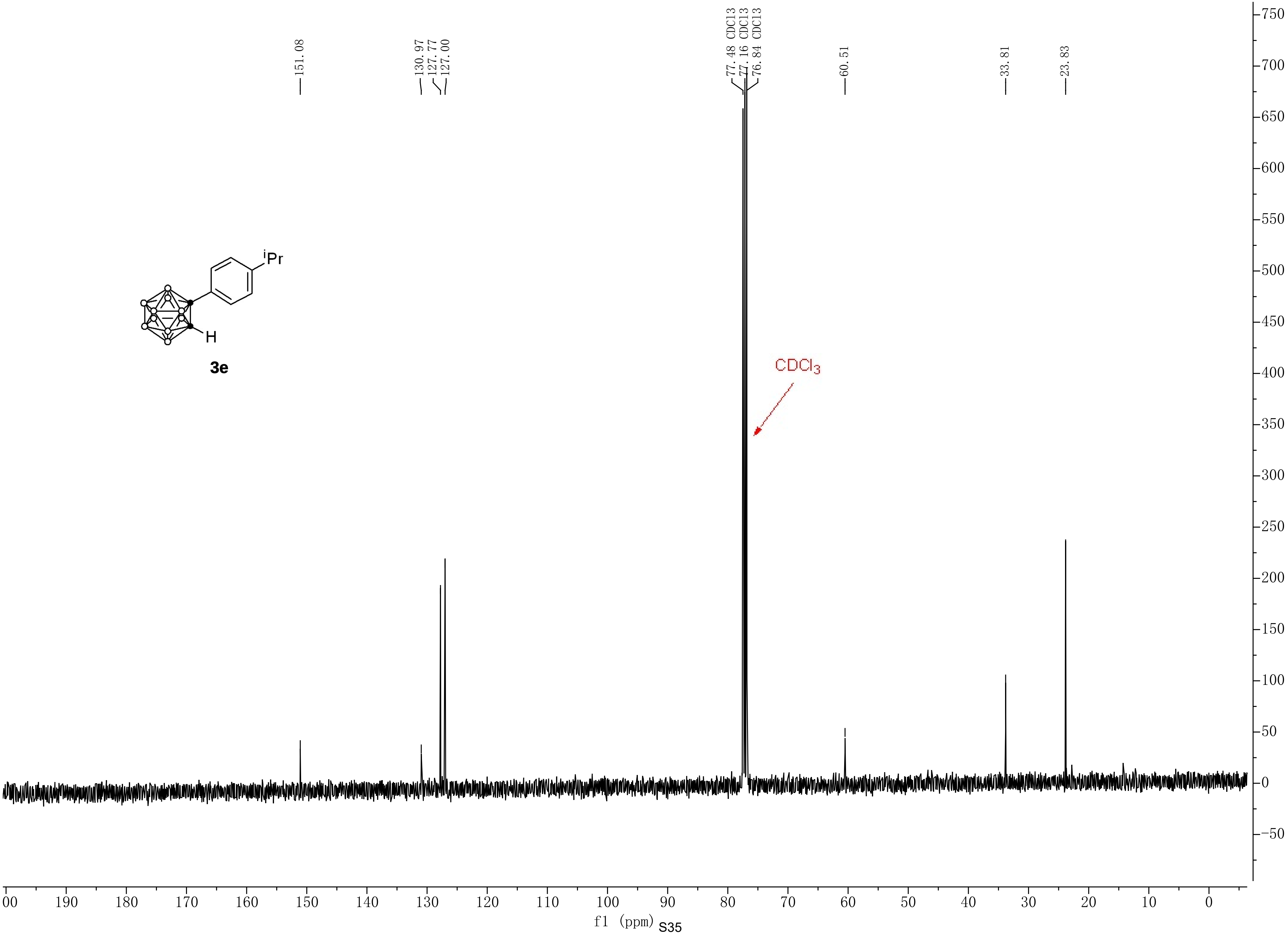

7.57
7.55
7.26
7.25
7.25
7.23
7.23
7.22
7.21
7.19
7.18
7.13
7.11
4.57
2.57
1.55
Me
H
3d
CDCl$_3$
H$_2$O
1.00
2.00
0.97
1.08
3.23
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

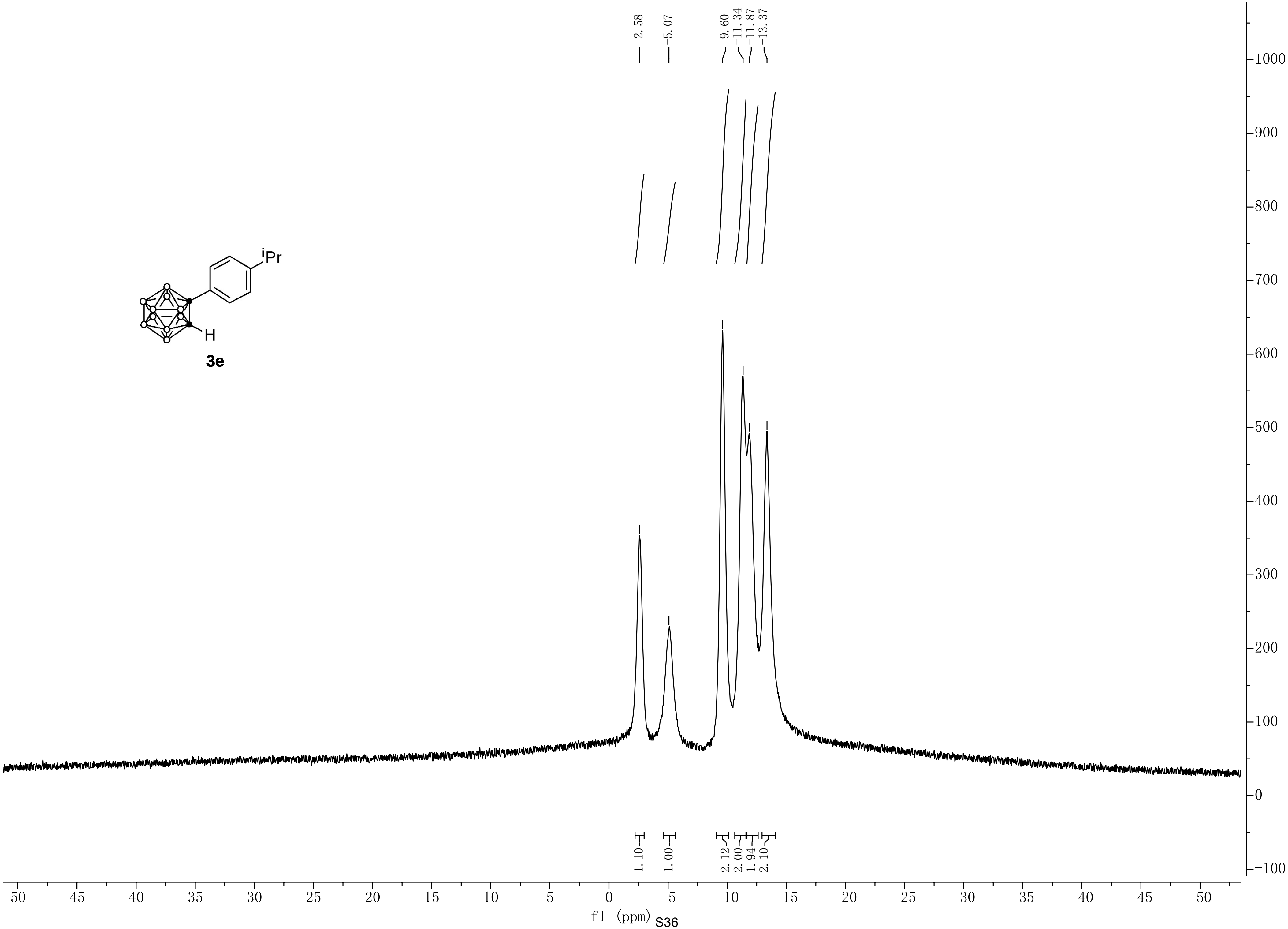


3d

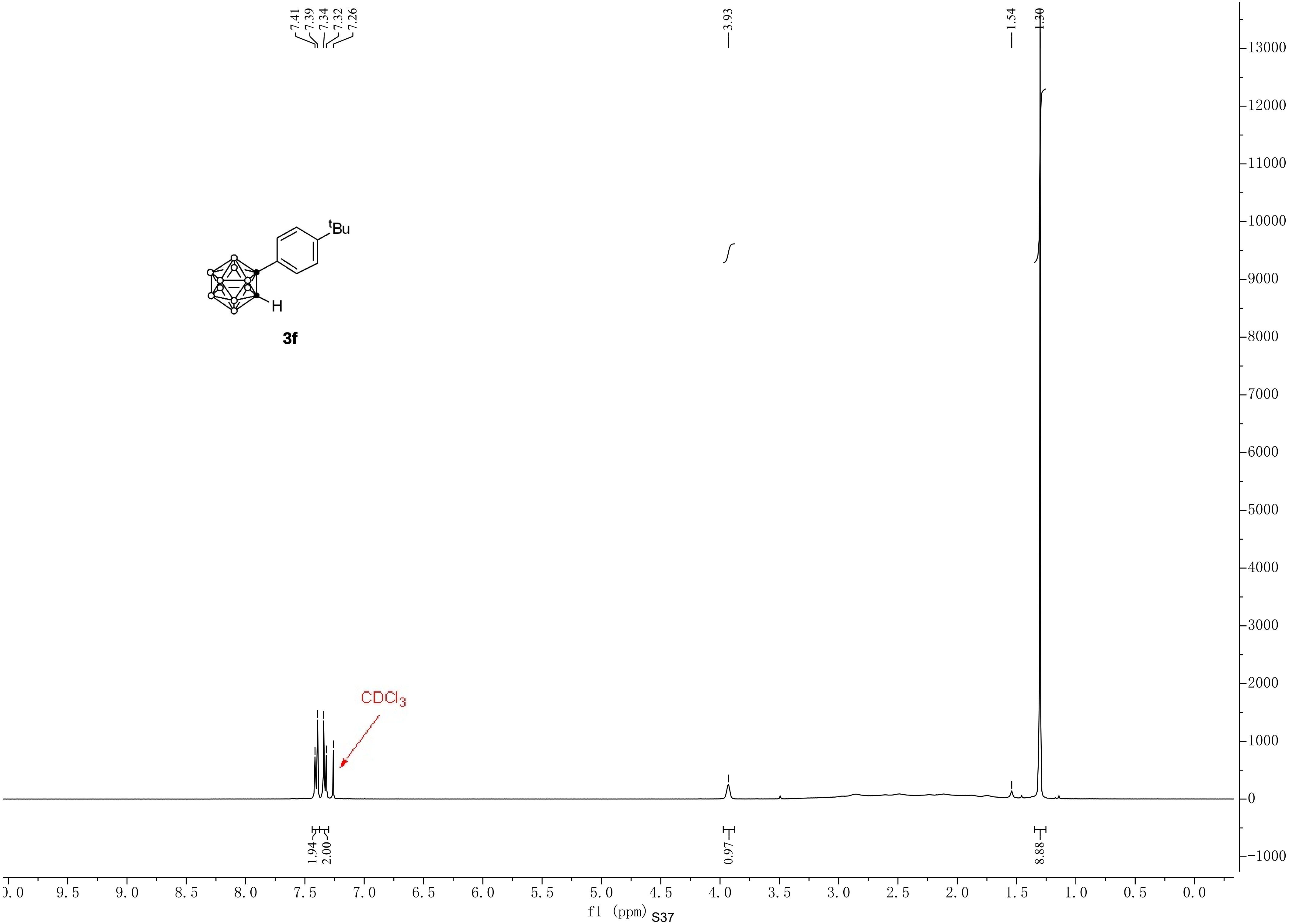
Me
H
-2.29
-8.19
-8.79
-10.59
-12.60
2.00
2.06
2.05
2.20
2.27
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


7.41
7.39
7.26
7.18
7.16
3.93
2.93
2.92
2.90
2.88
2.86
1.55
1.24
1.22
iPr
H
3e
CDCl3
H2O
1.97
2.00
0.98
1.33
3.04
3.00
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

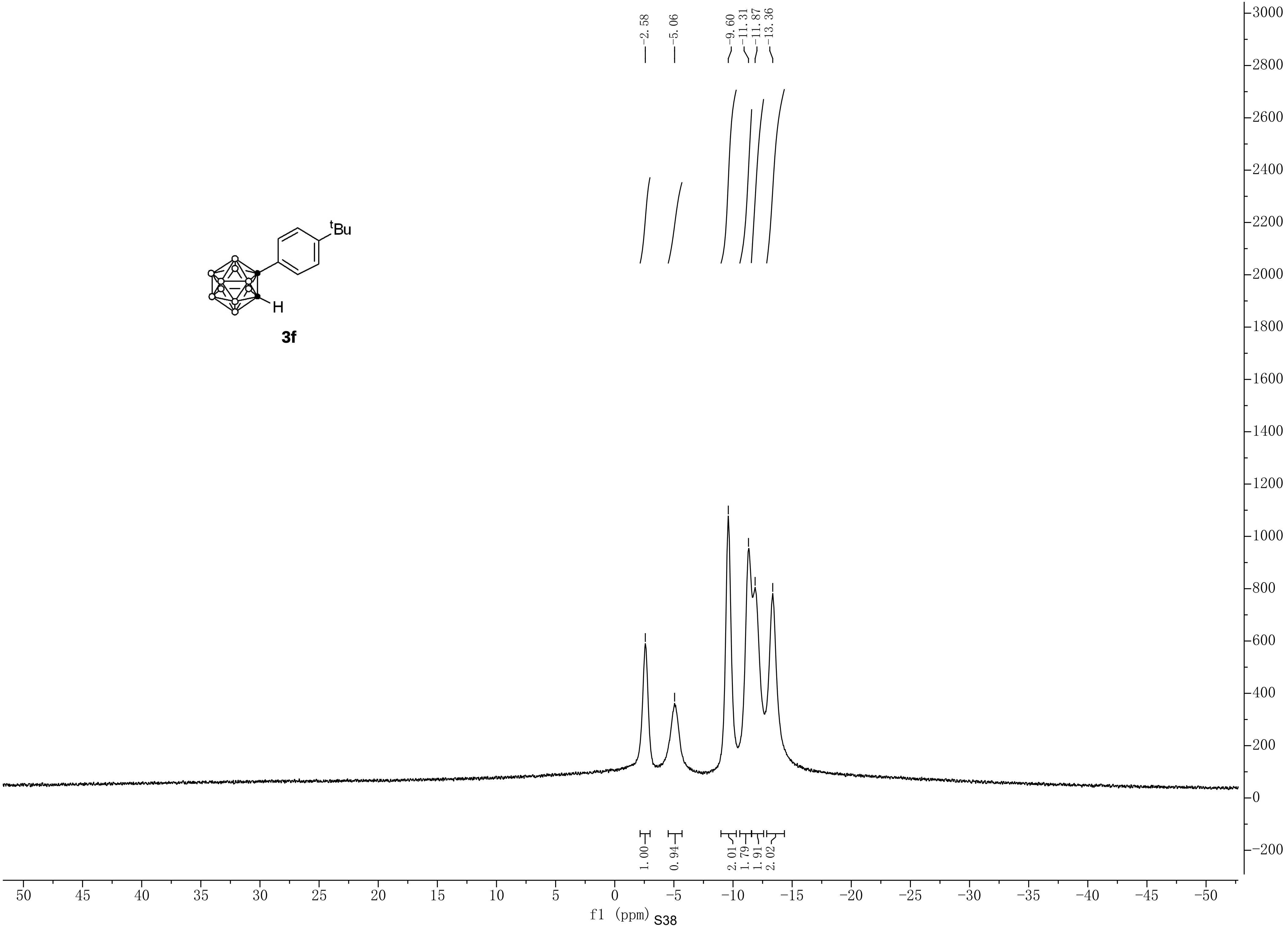

151.08
130.97
127.77
127.00
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
60.51
33.81
23.83
CDCl$_3$
^{i}Pr
H
3e
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

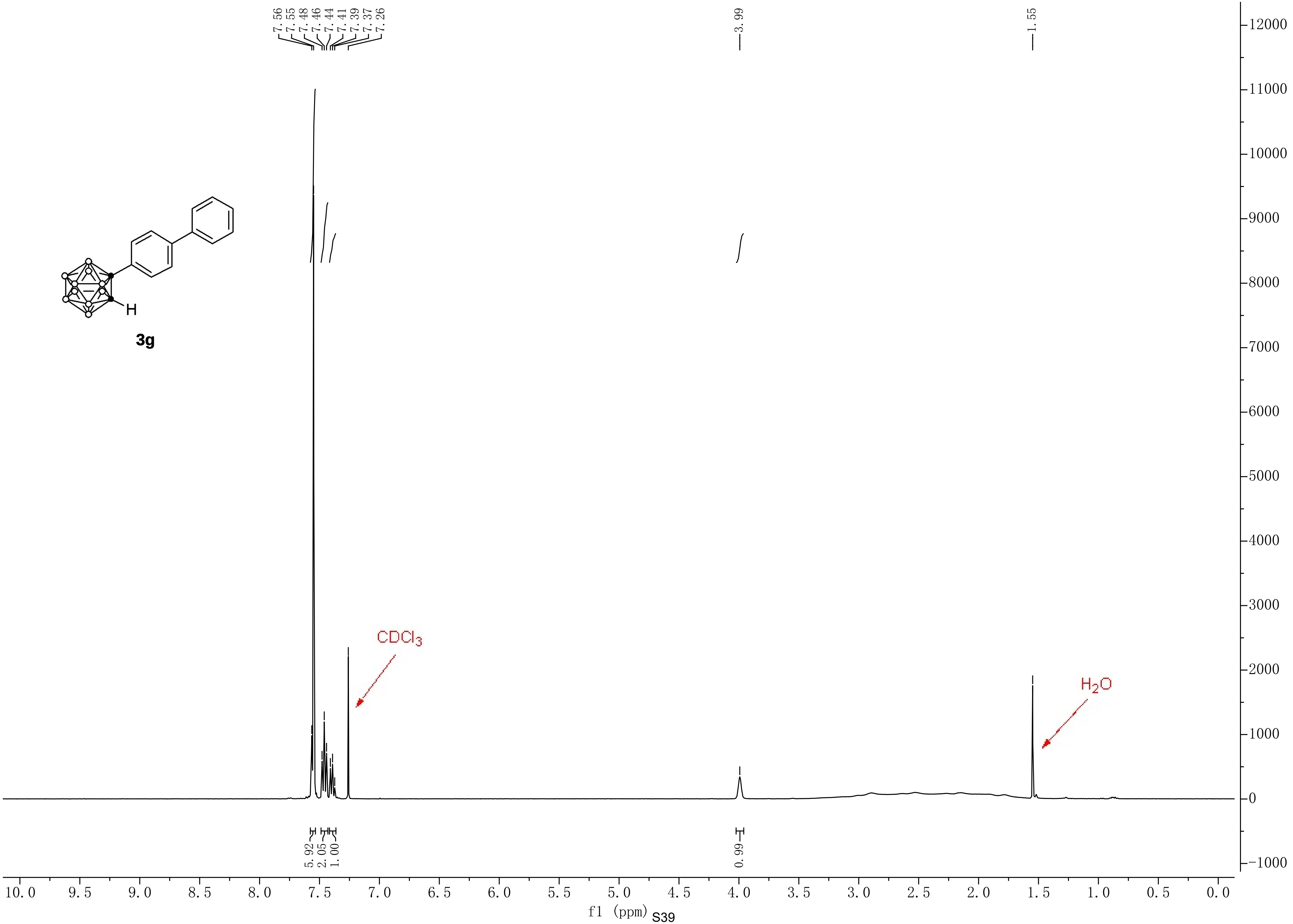


-2.58
-5.07
-9.60
-11.34
-11.87
-13.37
iPr
H
3e
1.10
1.00
2.12
2.00
1.94
2.10
1000
900
800
700
600
500
400
300
200
100
0
-100
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

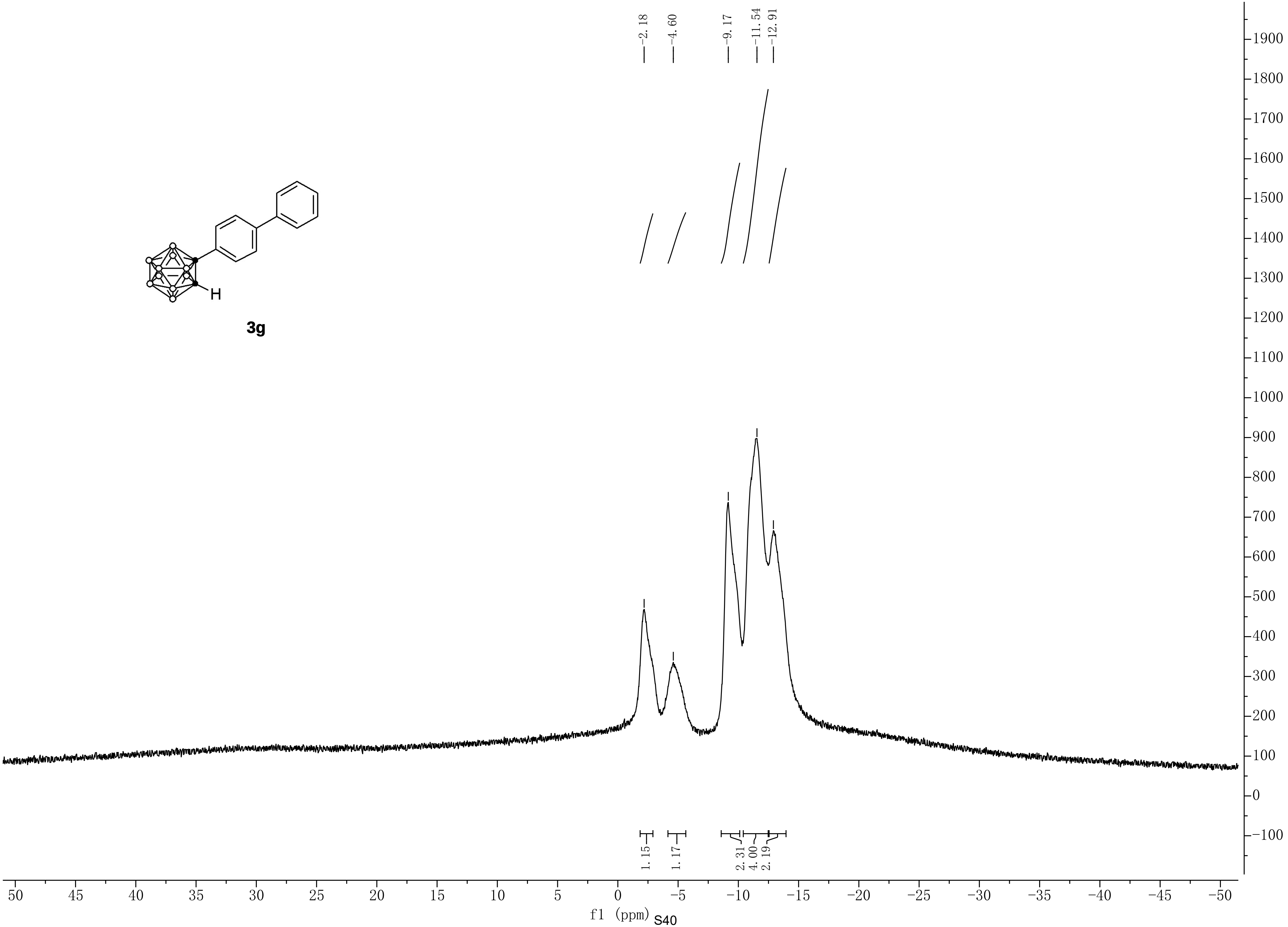

7.41
7.39
7.34
7.32
7.26
3.93
1.54
1.30
^{t}Bu
H
CDCl$_3$
1.94
2.00
0.97
8.88
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

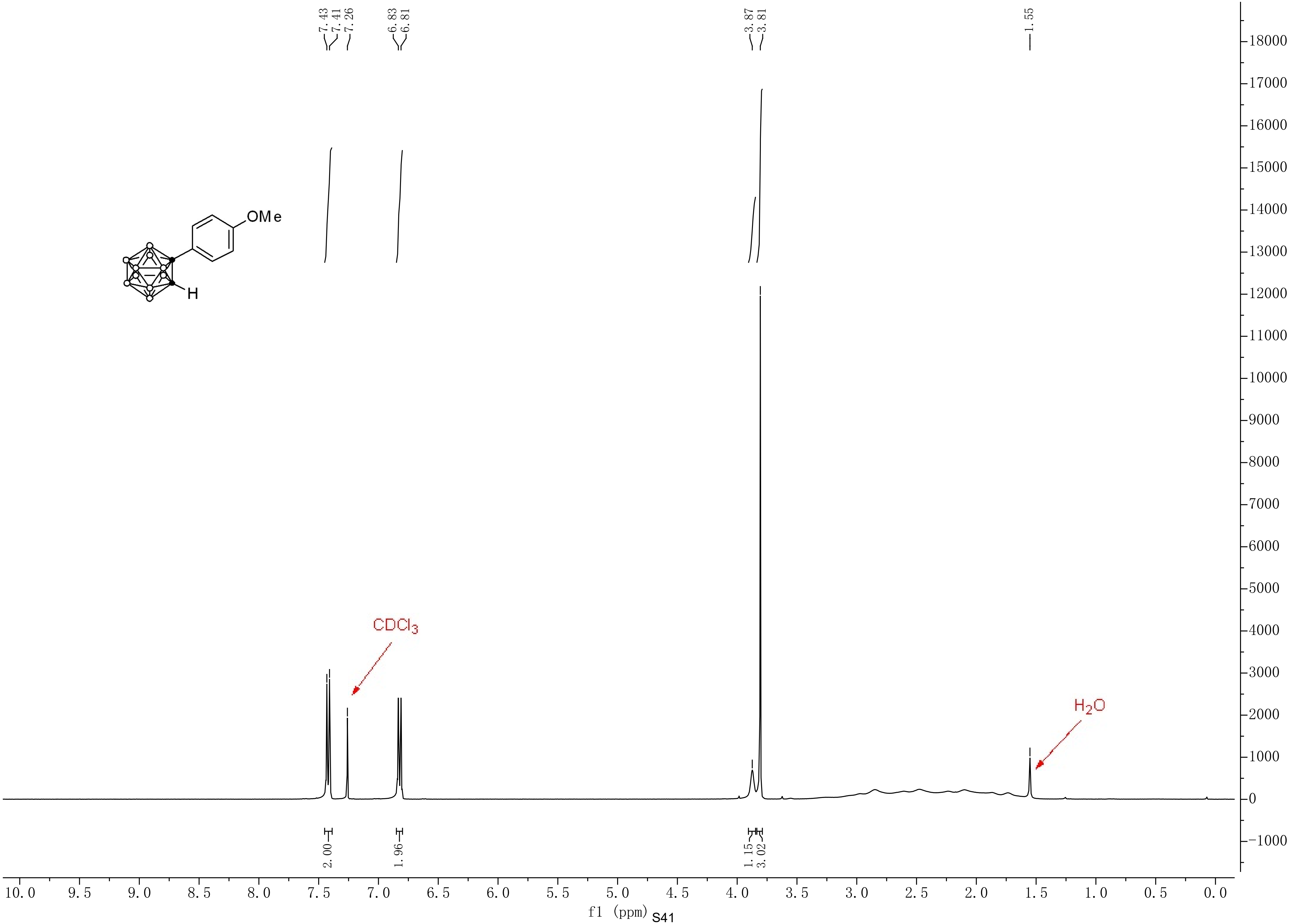
3f

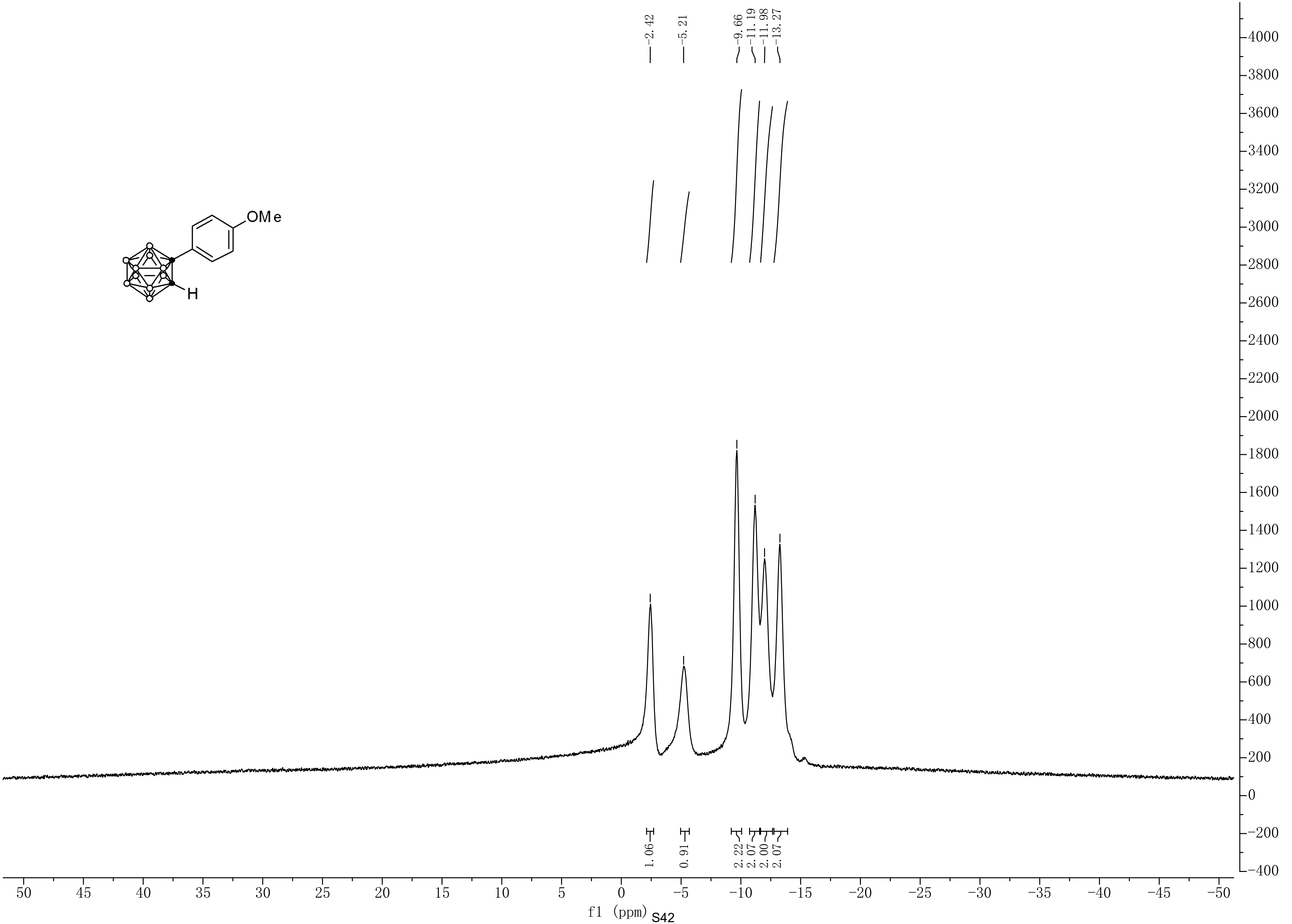

-2.58
-5.06
-9.60
-11.31
-11.87
-13.36
1.00
0.94
2.01
1.79
1.91
2.02
tBu
H
3f
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200

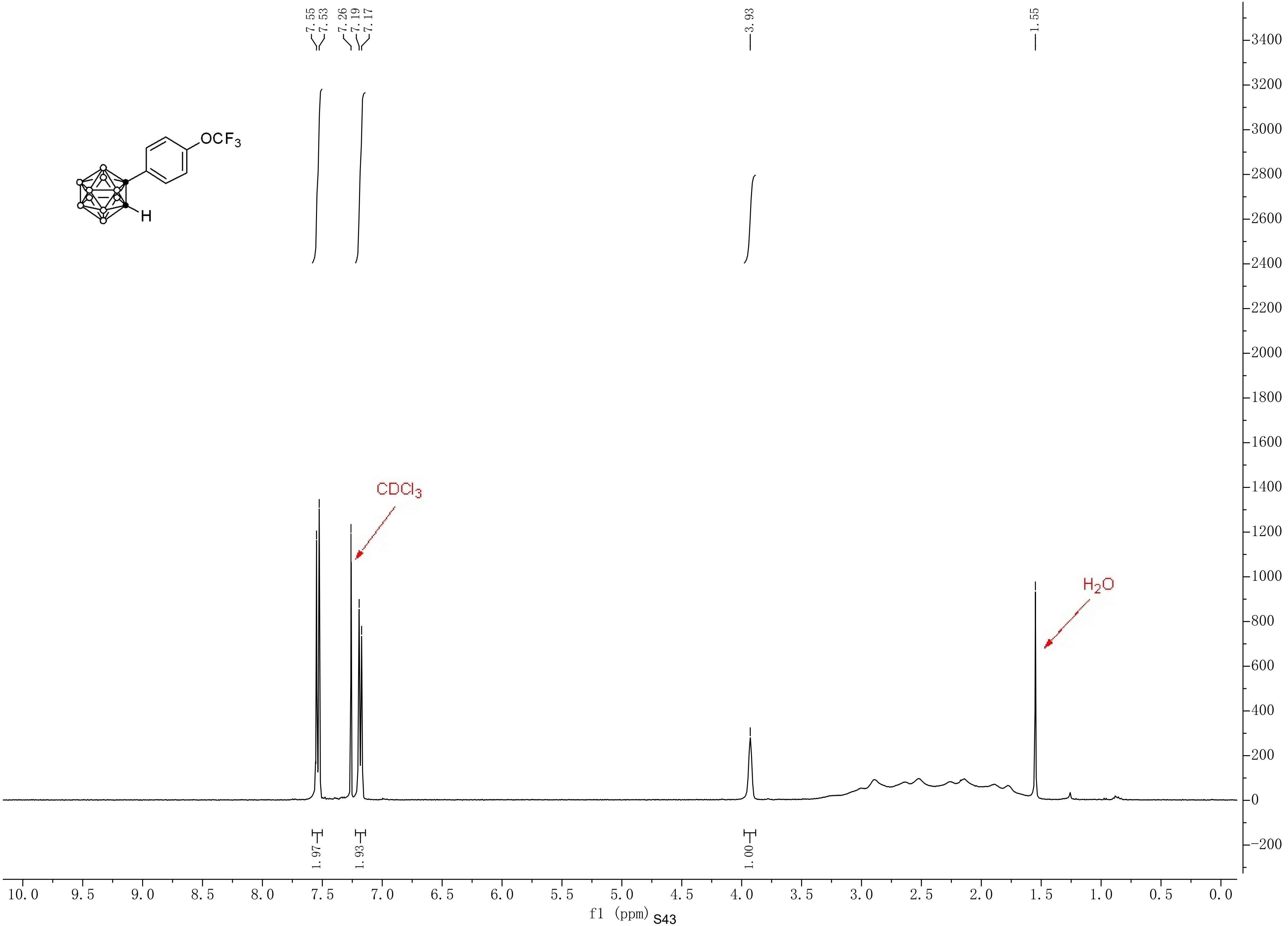

7.56
7.55
7.48
7.46
7.44
7.41
7.39
7.37
7.26
3.99
1.55
H
CDCl₃
H₂O
5.92
2.05
1.00
0.99
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

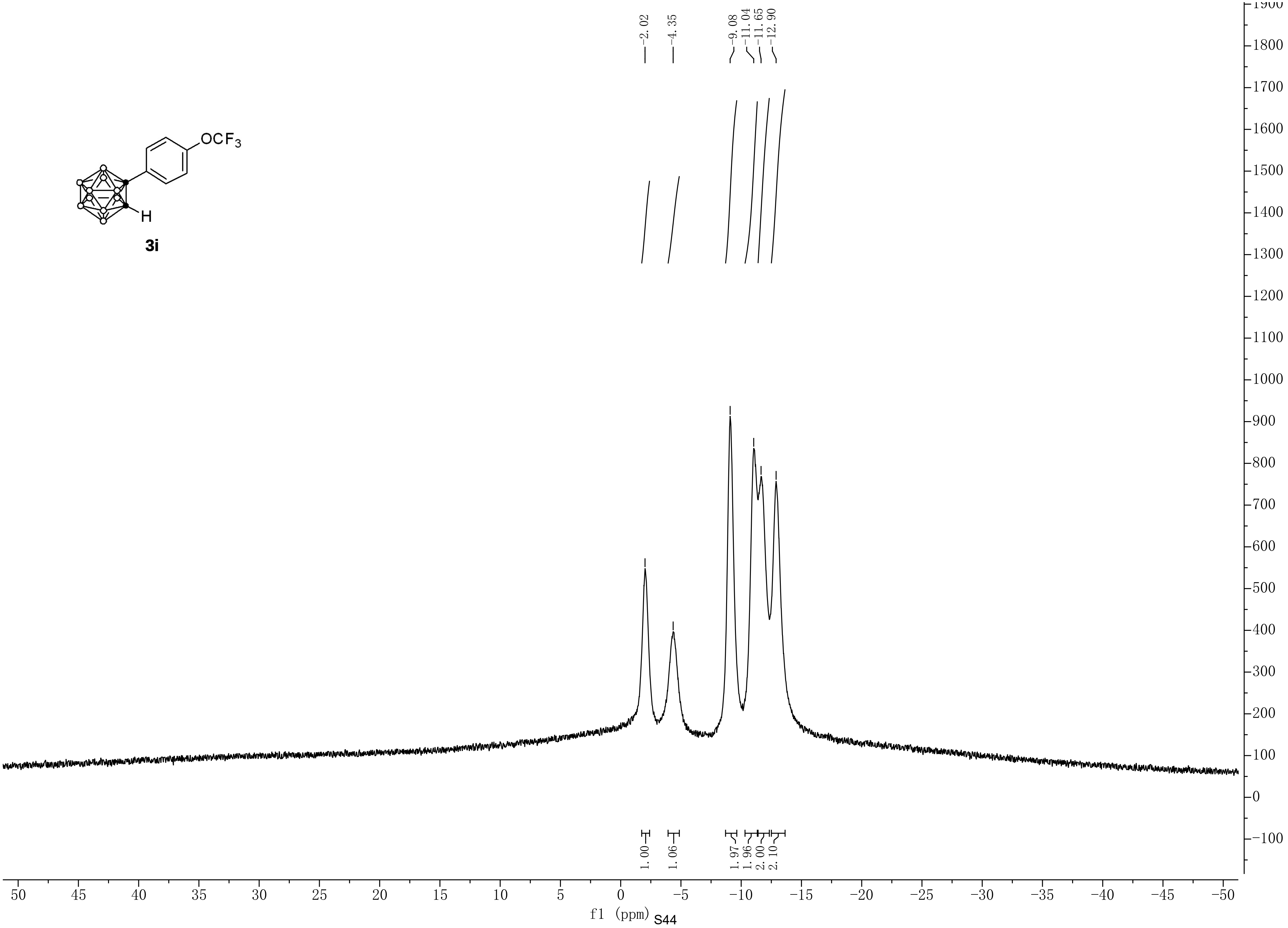
3g


3g
H
−2.18
−4.60
−9.17
−11.54
−12.91
1.15
1.17
2.31
4.00
2.19
50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)
1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 −100

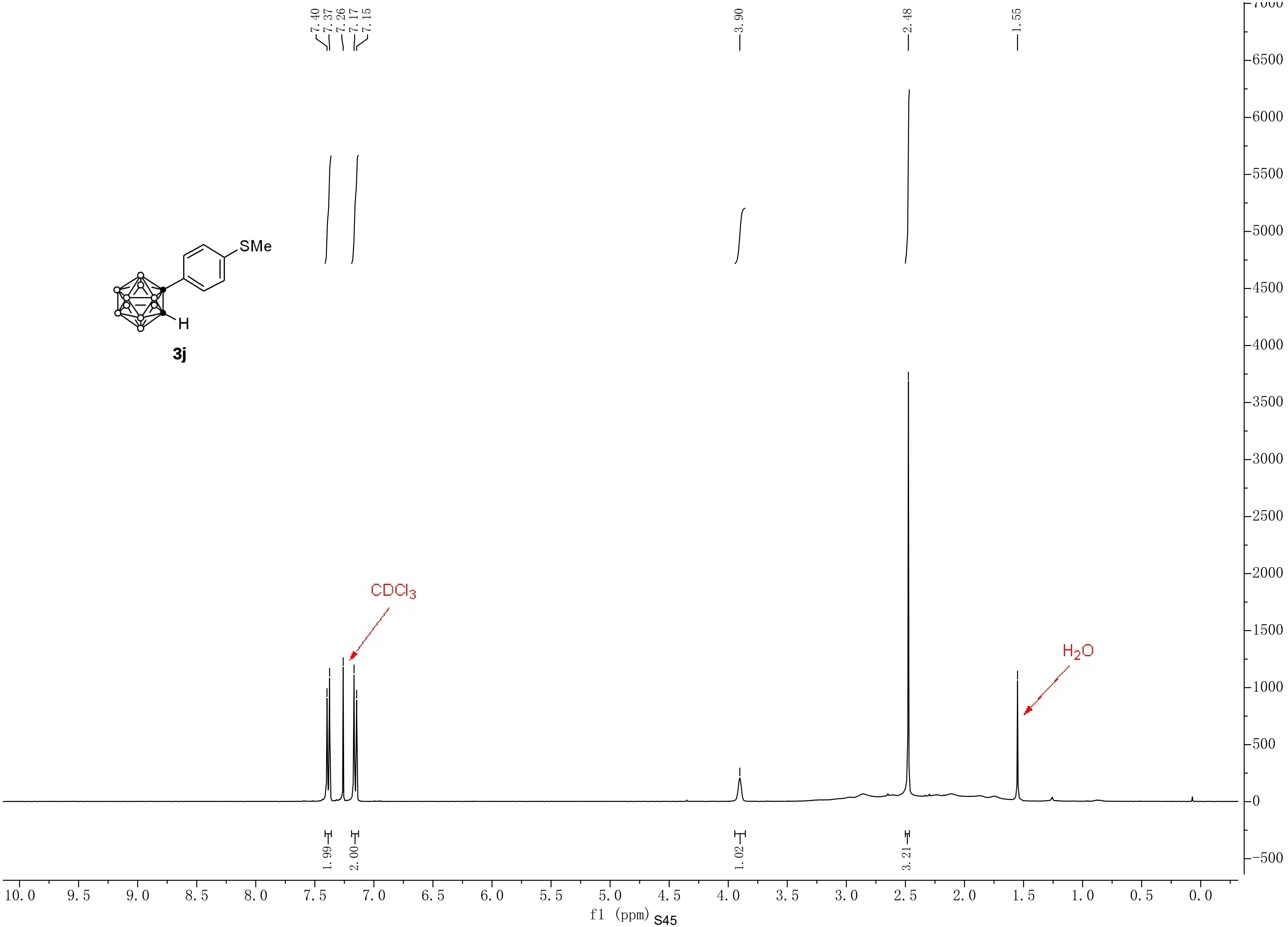

7.43
7.41
7.26
6.83
6.81
3.87
3.81
1.55
OMe
H
CDCl$_3$
H$_2$O
2.00
1.96
1.15
3.02
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

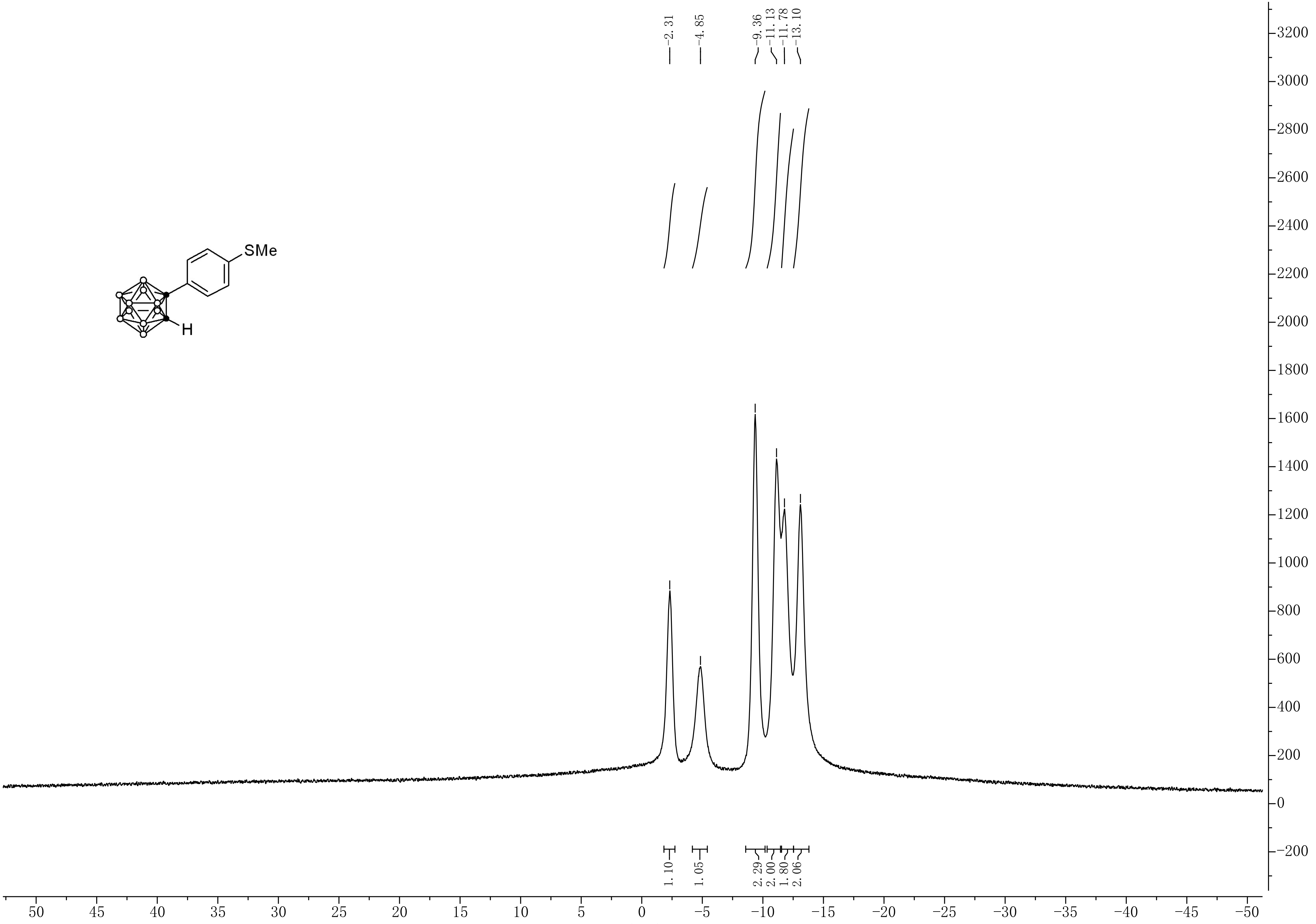

OMe
H
-2.42
-5.21
-9.66
-11.19
-11.98
-13.27
1.06
0.91
2.22
2.07
2.00
2.07
f1 (ppm)
50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 −200 −400

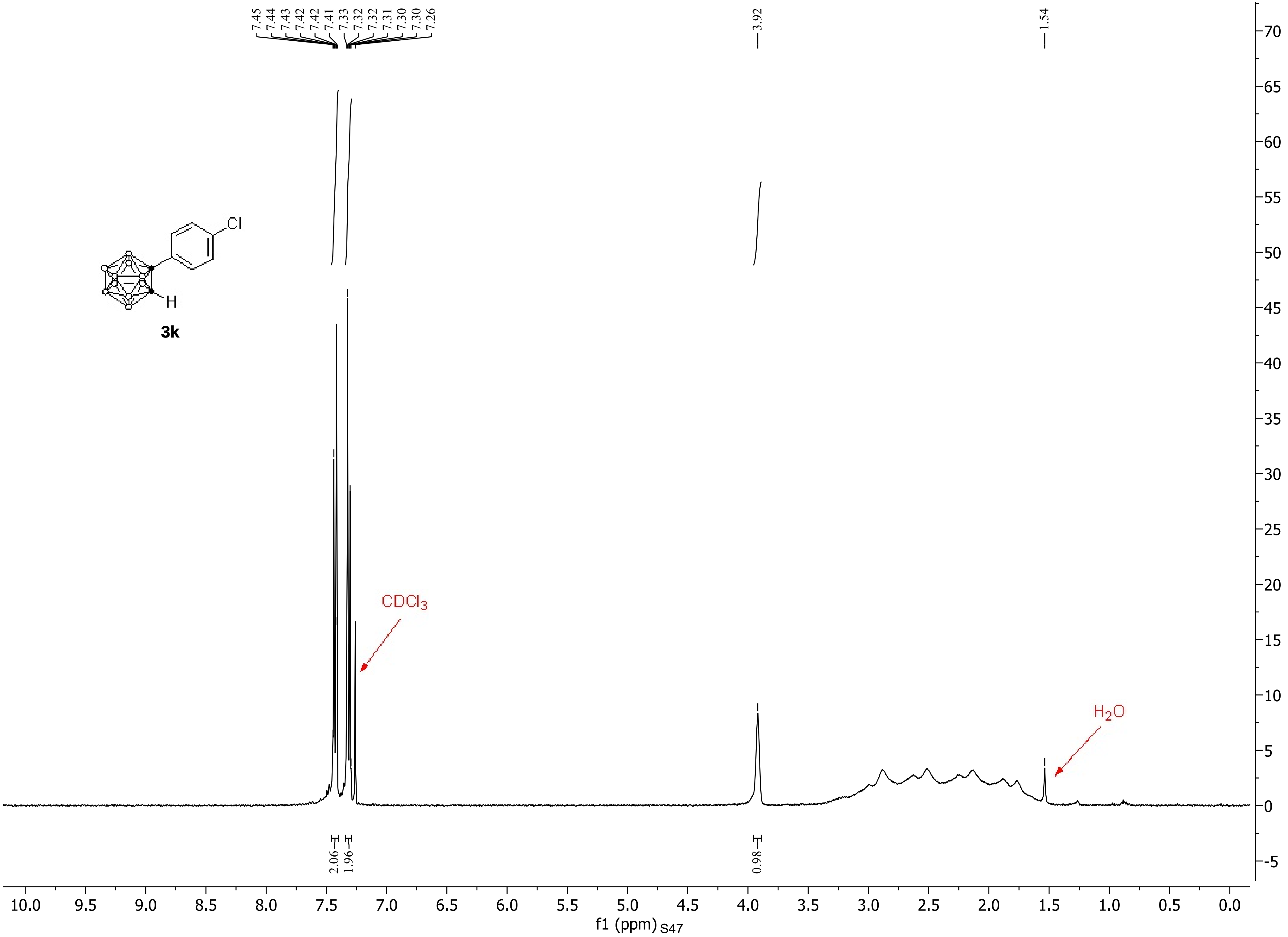

7.55
7.53
7.26
7.19
7.17
3.93
1.55
OCF3
H
CDCl3
H2O
1.97
1.93
1.00
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

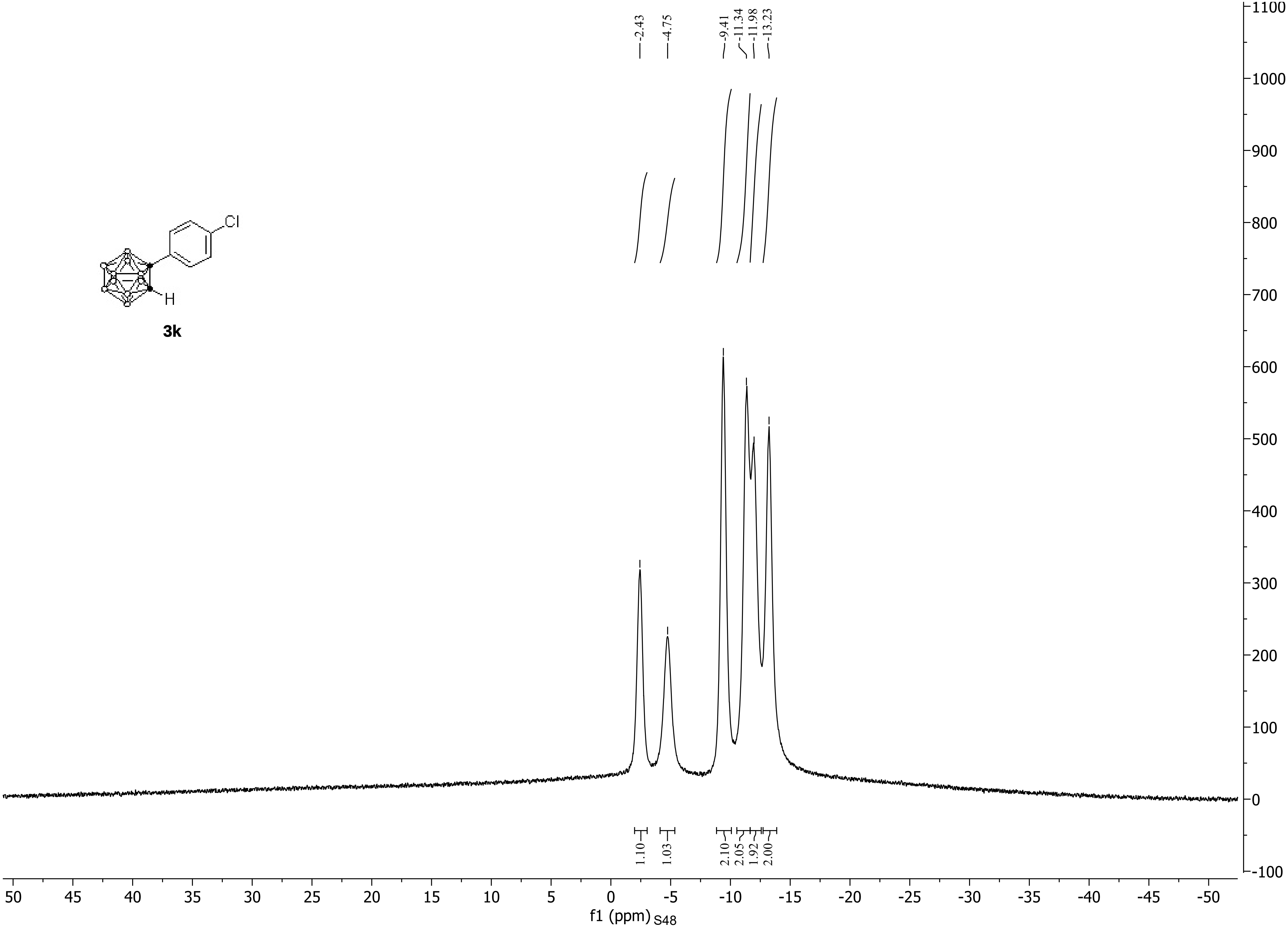

OCF3
H
-2.02
-4.35
-9.08
-11.04
-11.65
-12.90
1.00
1.06
1.97
1.96
2.00
2.10
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)

3i

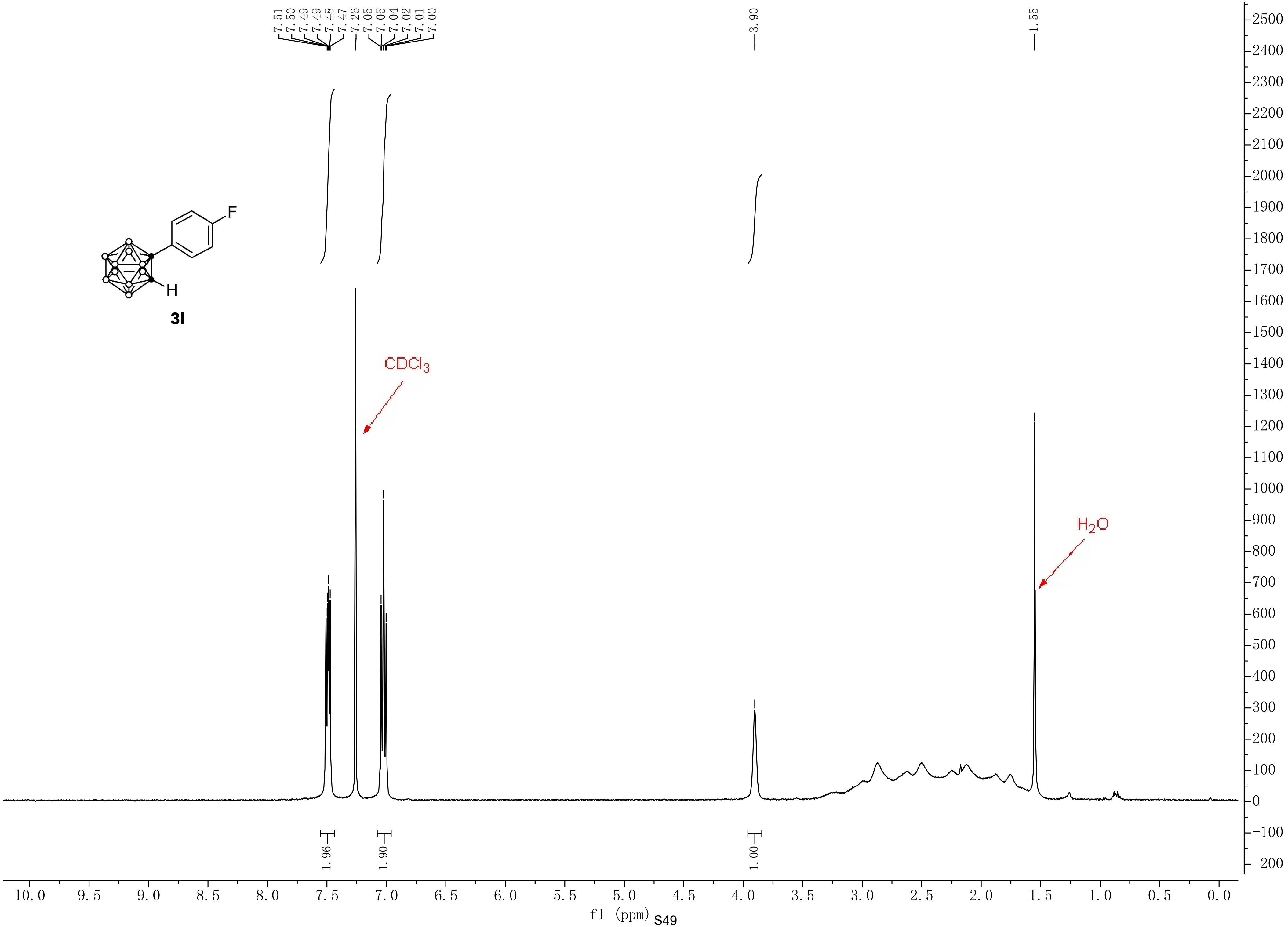

7.40
7.37
7.26
7.17
7.15
3.90
2.48
1.55
SMe
H
3j
CDCl$_3$
H$_2$O
1.99
2.00
1.02
3.21
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

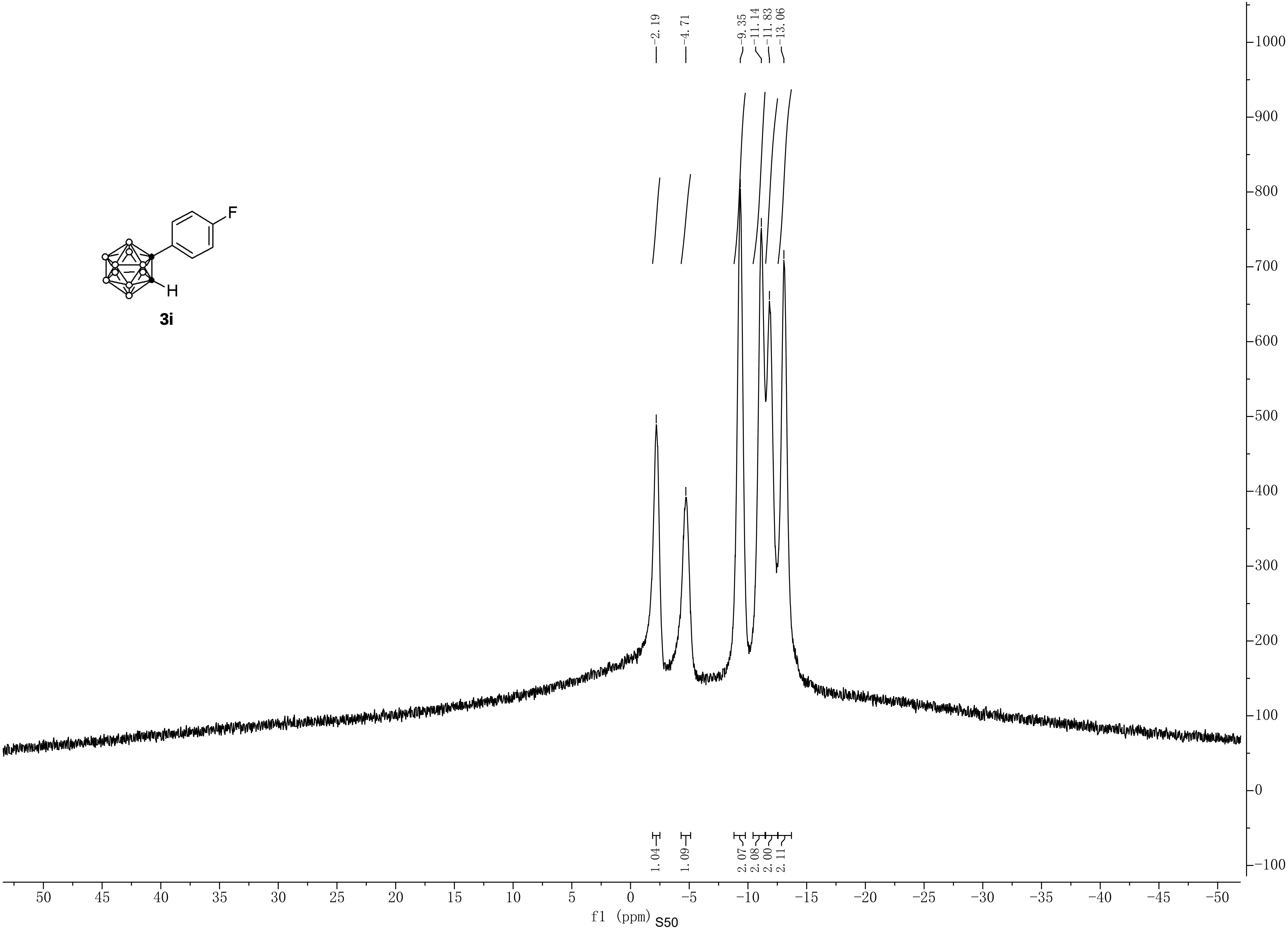

SMe
H
-2.31
-4.85
-9.36
-11.13
-11.78
-13.10
1.10
1.05
2.29
2.00
1.80
2.06
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)

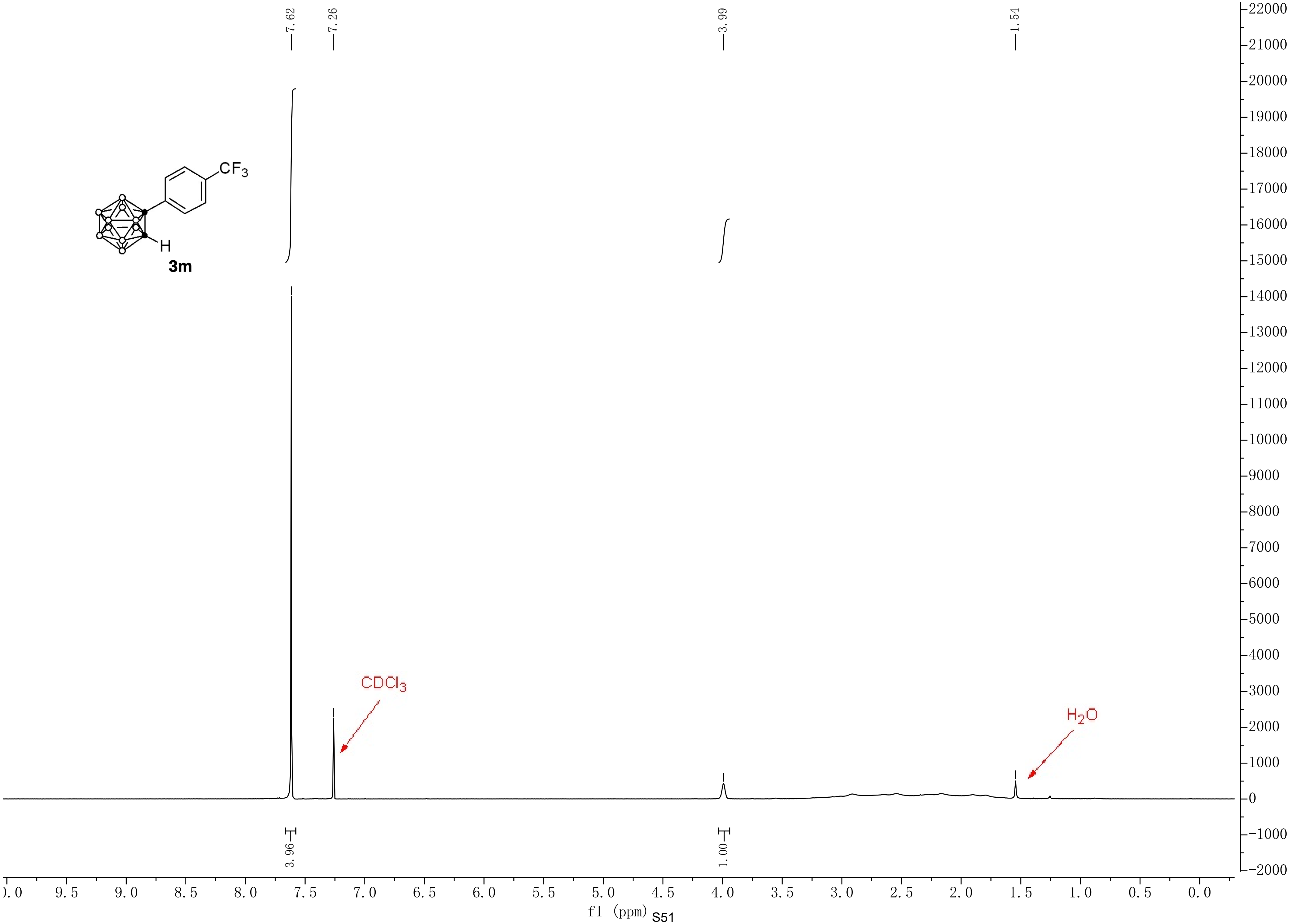

7.45
7.44
7.43
7.42
7.42
7.41
7.33
7.32
7.32
7.31
7.30
7.30
7.26
3.92
1.54
Cl
H
3k
CDCl3
H2O
2.06
1.96
0.98
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

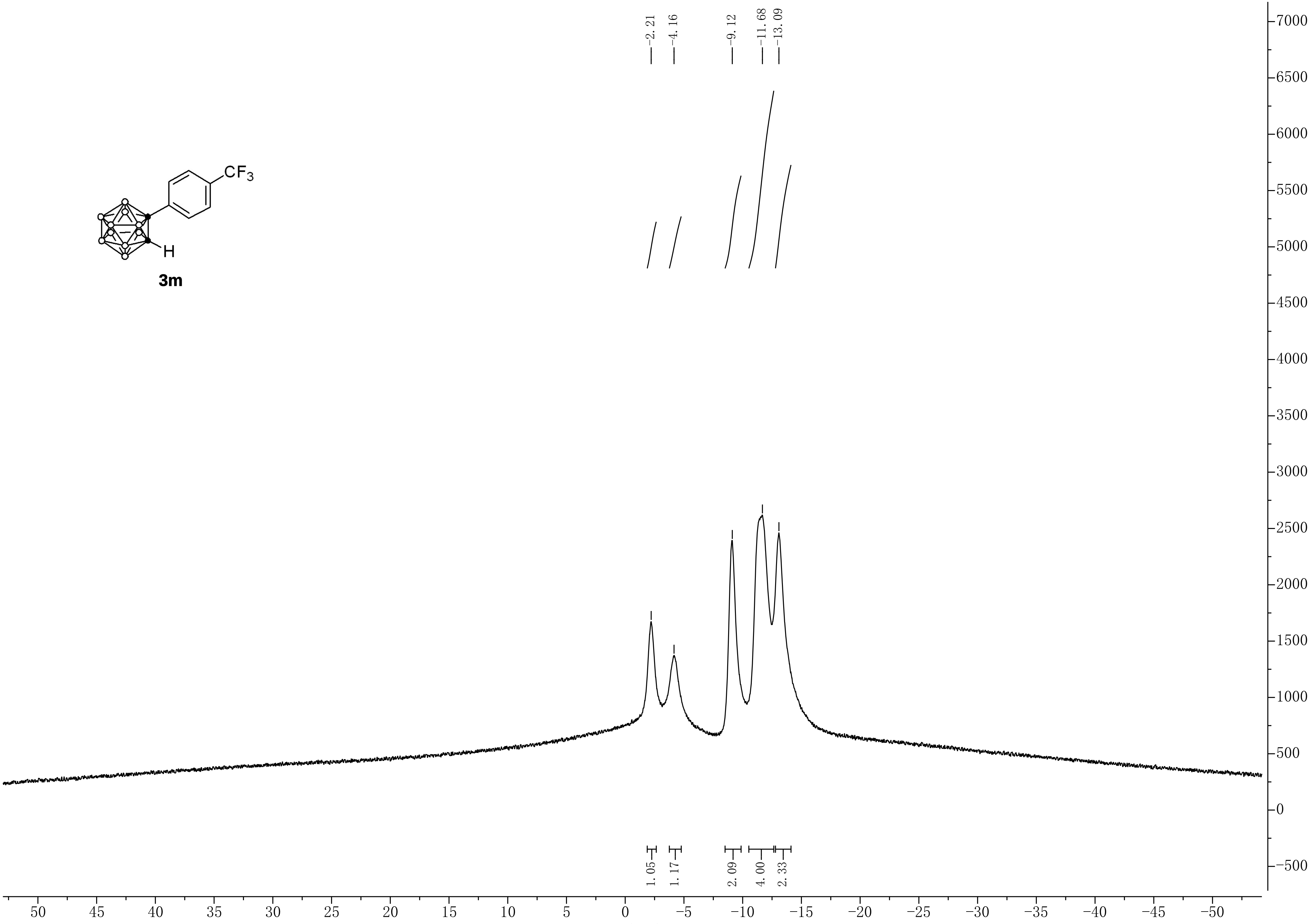

-2.43
-4.75
-9.41
-11.34
-11.98
-13.23
Cl
H
1.10
1.03
2.10
2.05
1.92
2.00
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

3k


7.51
7.50
7.49
7.49
7.48
7.47
7.26
7.05
7.05
7.04
7.02
7.01
7.00
3.90
1.55
F
H
3l
CDCl$_3$
H$_2$O
1.96
1.90
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200

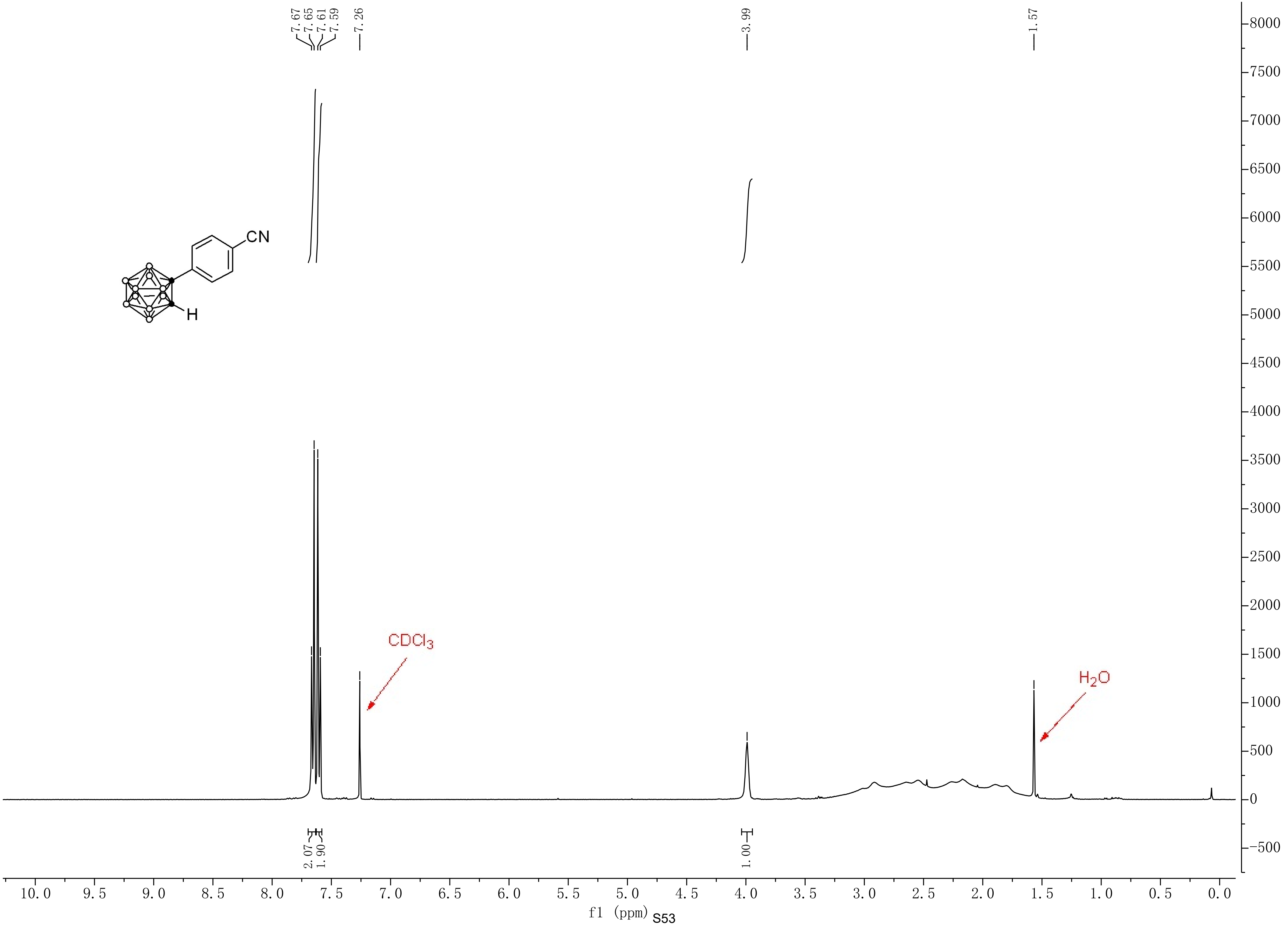

3i
F
H
-2.19
-4.71
-9.35
-11.14
-11.83
-13.06
1.04
1.09
2.07
2.08
2.00
2.11
1000
900
800
700
600
500
400
300
200
100
0
−100
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)

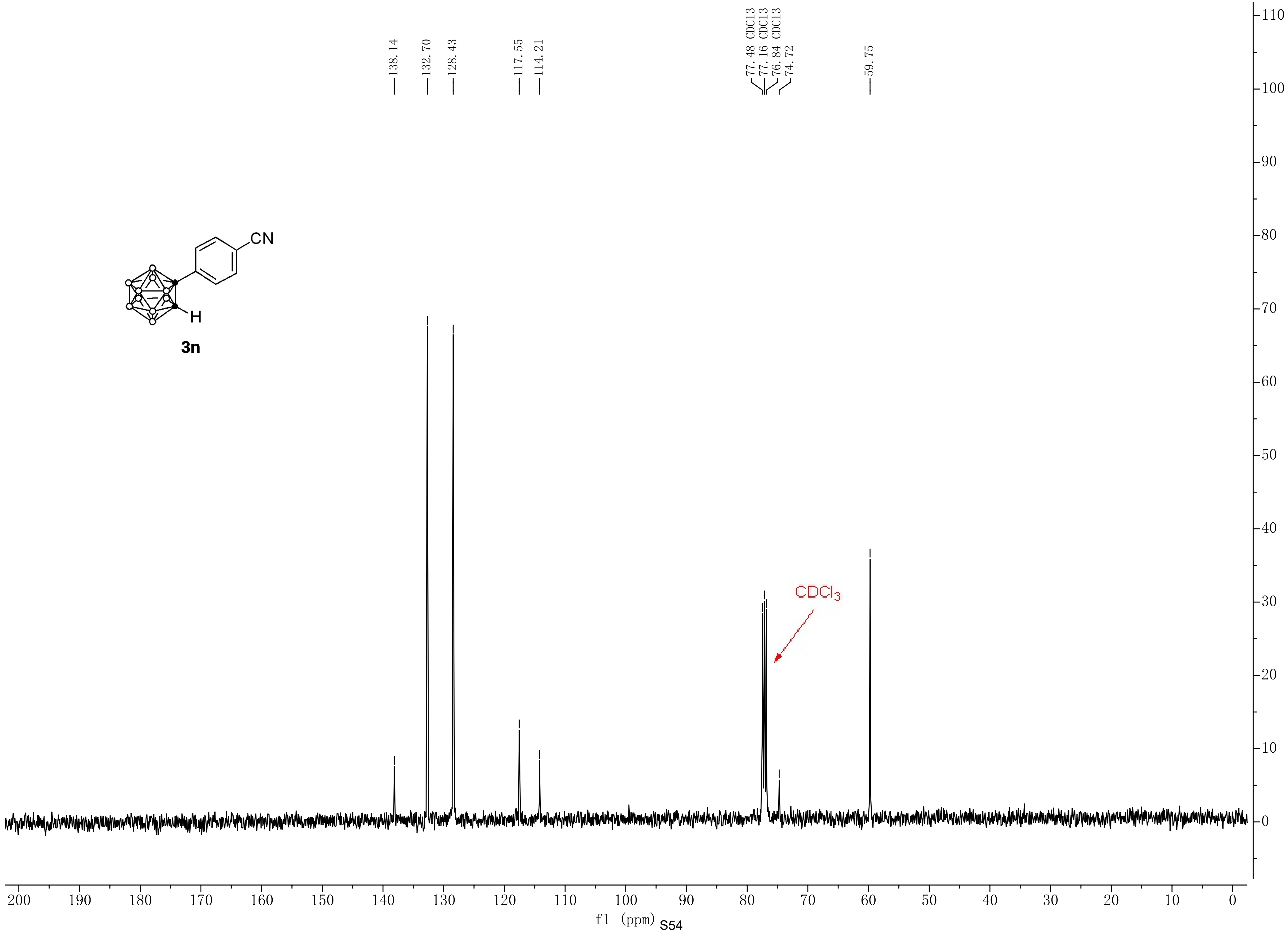

7.62
7.26
3.99
1.54
CF$_3$
H
3m
CDCl$_3$
H$_2$O
3.96
1.00
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

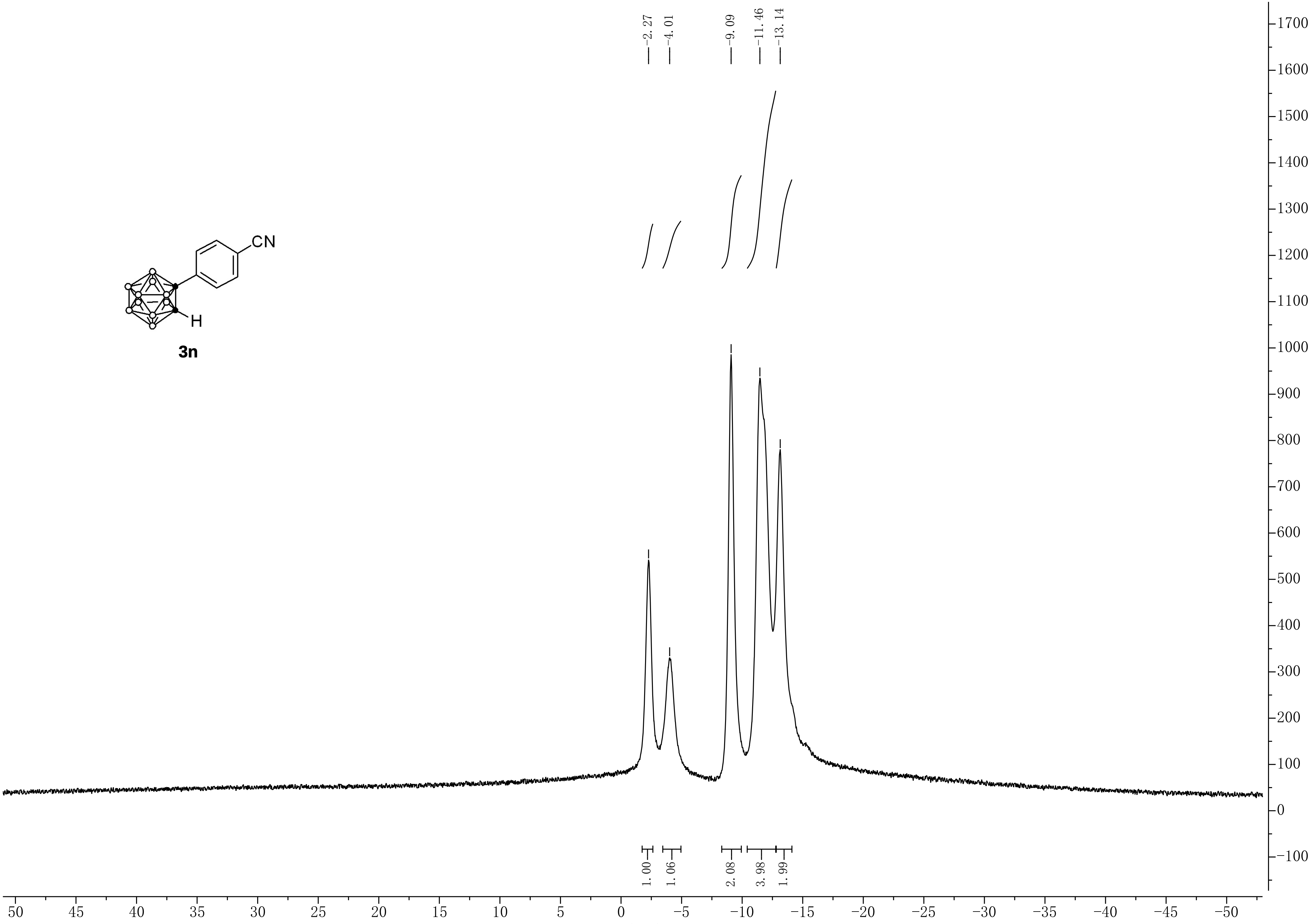


3m

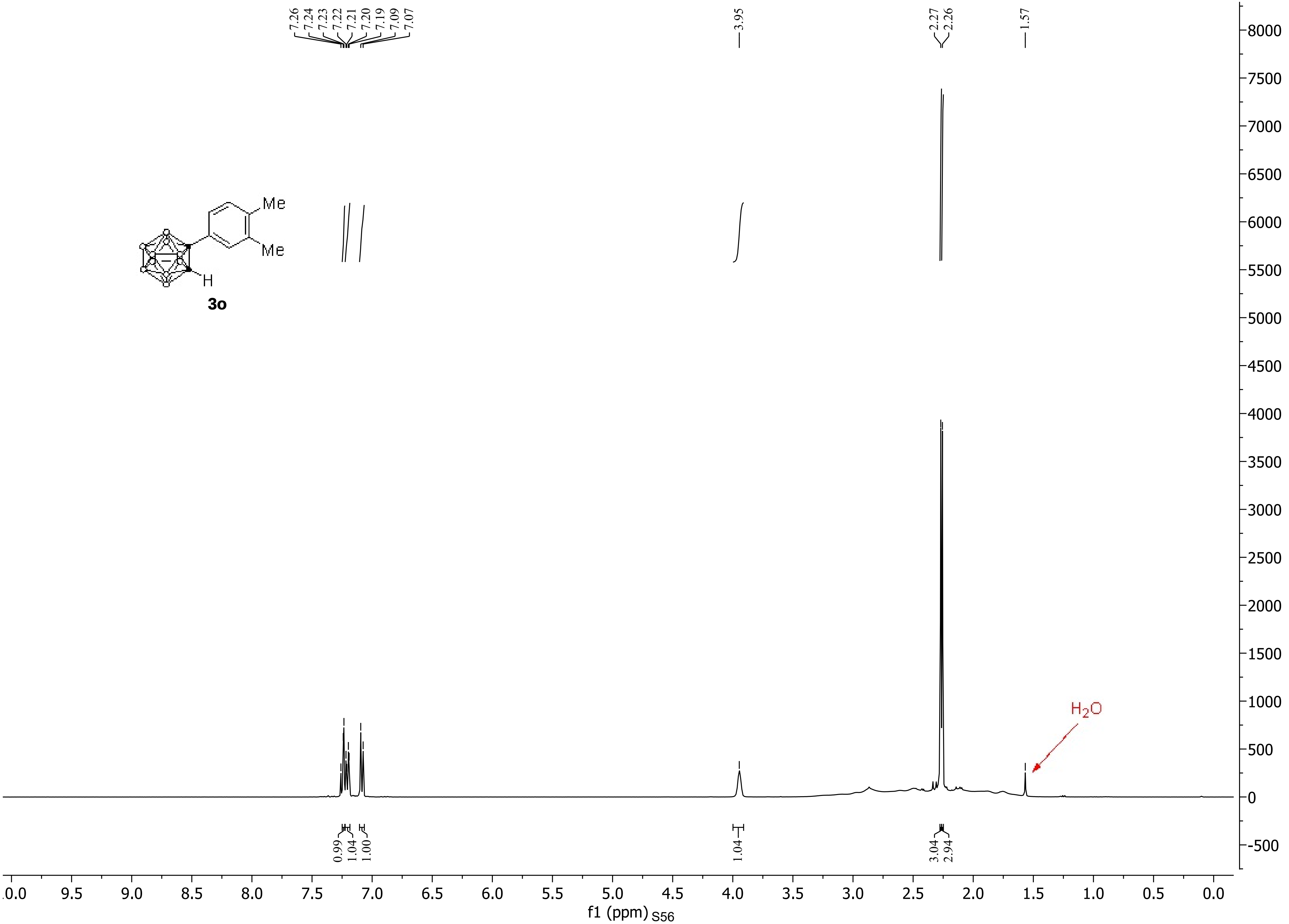
CF3
H
-2.21
-4.16
-9.12
-11.68
-13.09
1.05
1.17
2.09
4.00
2.33
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

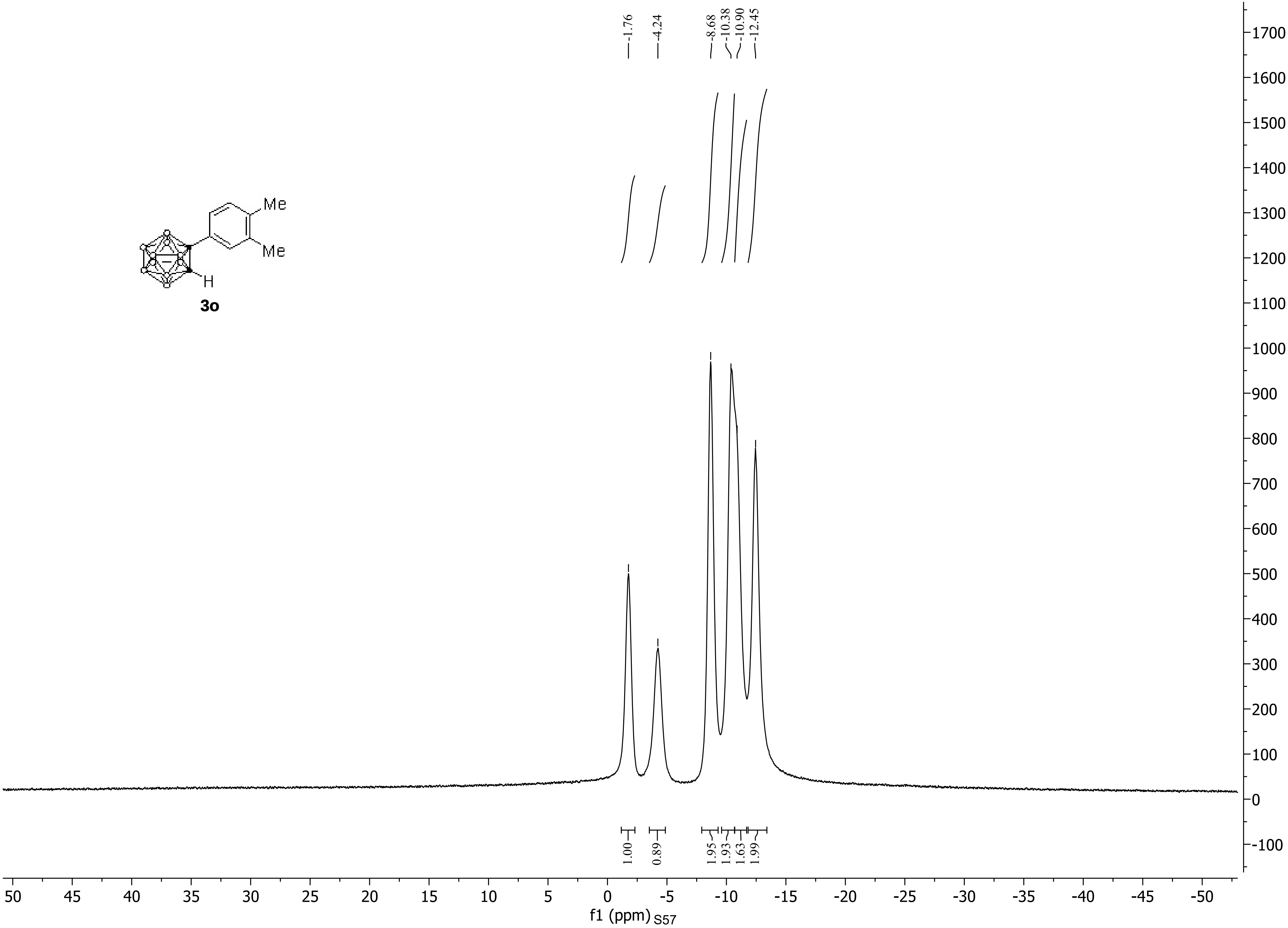

7.67
7.65
7.61
7.59
7.26
3.99
1.57
CN
H
CDCl3
H2O
2.07
1.90
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500

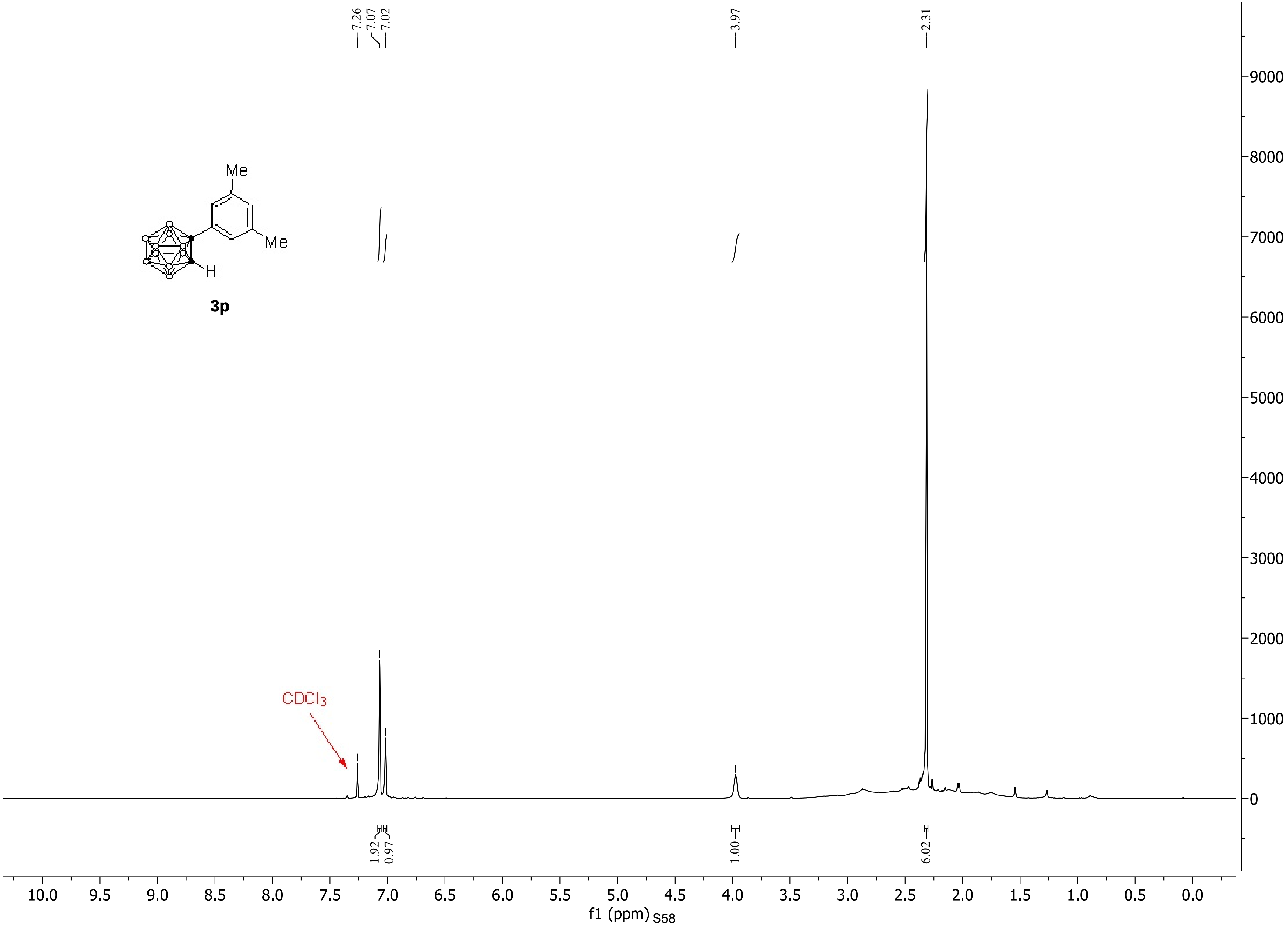

138.14
132.70
128.43
117.55
114.21
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.72
59.75
CN
H
3n
CDCl3
110
100
90
80
70
60
50
40
30
20
10
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

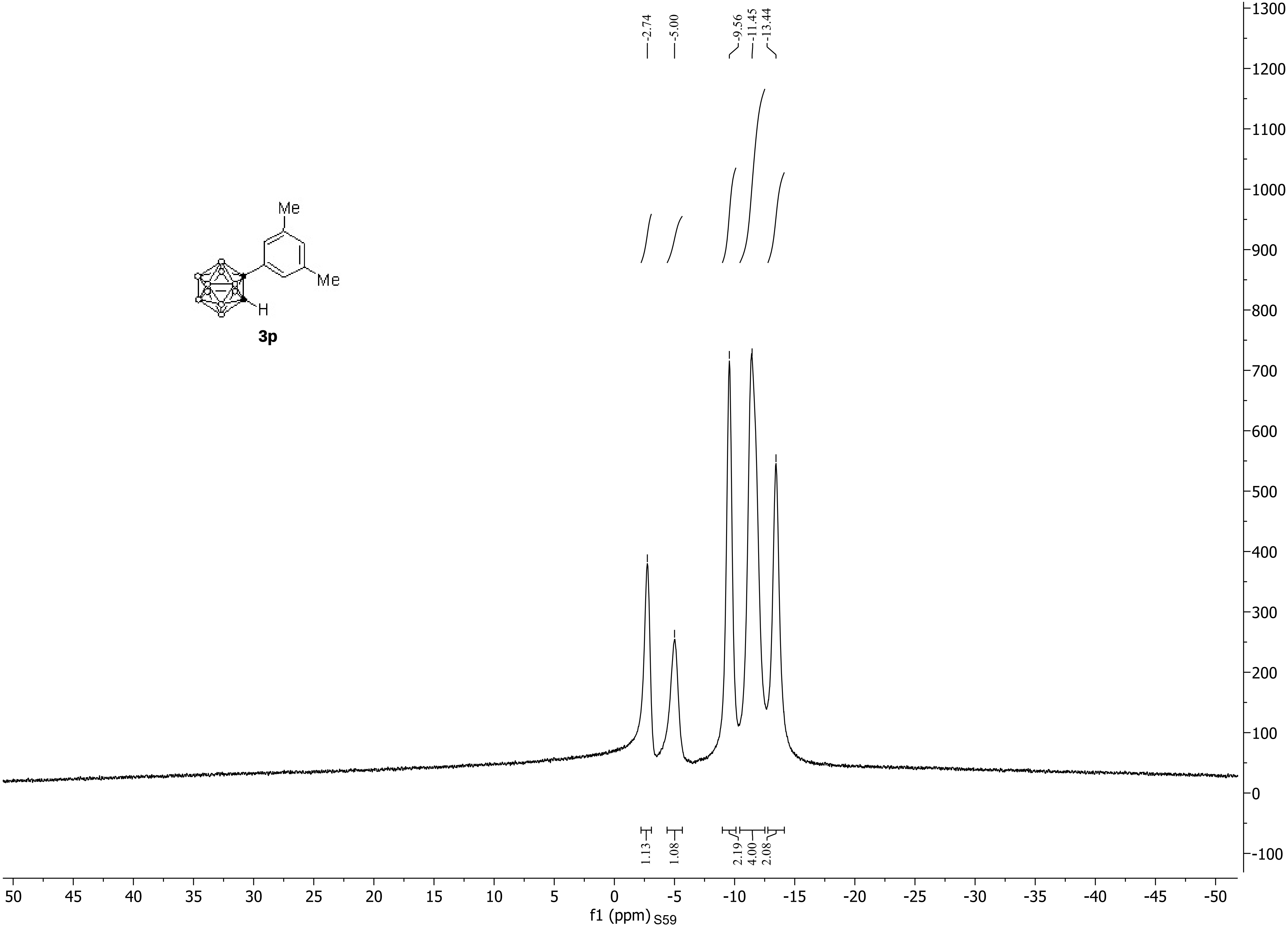

CN
H
-2.27
-4.01
-9.09
-11.46
-13.14
1.00
1.06
2.08
3.98
1.99
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)

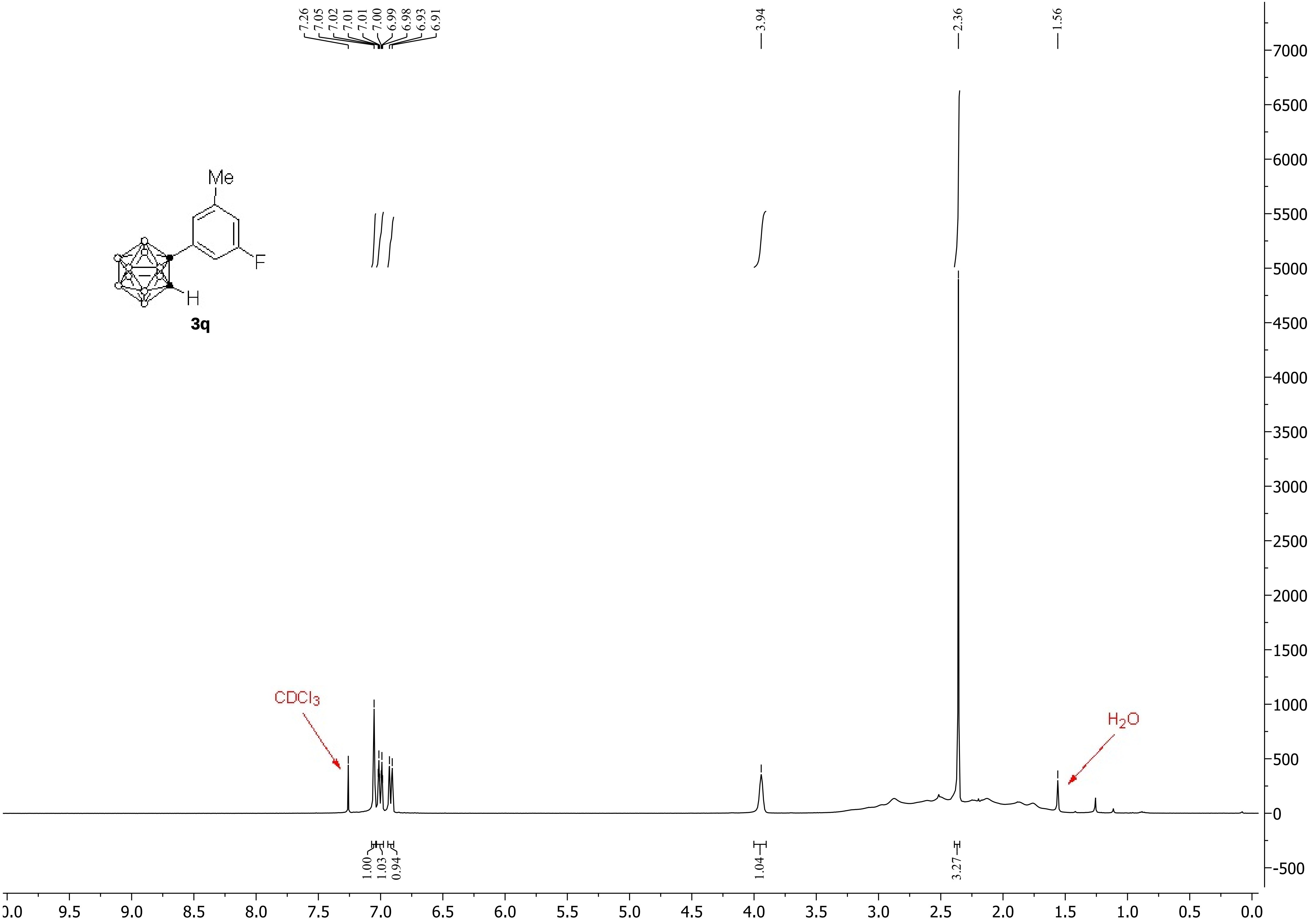
3n

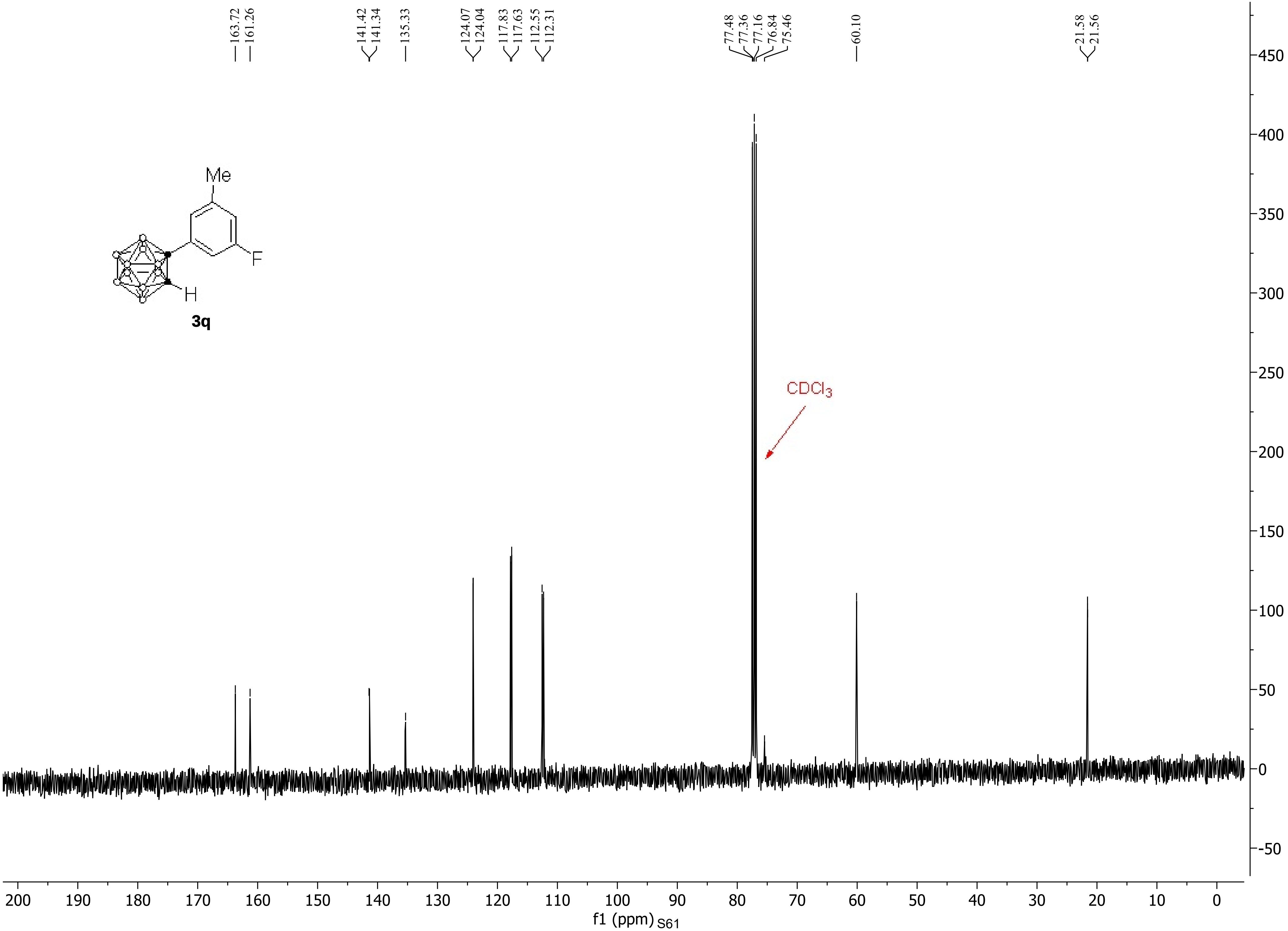

7.26
7.24
7.23
7.22
7.21
7.20
7.19
7.09
7.07
3.95
2.27
2.26
1.57
Me
Me
H
3o
H$_2$O
0.99
1.04
1.00
1.04
3.04
2.94
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

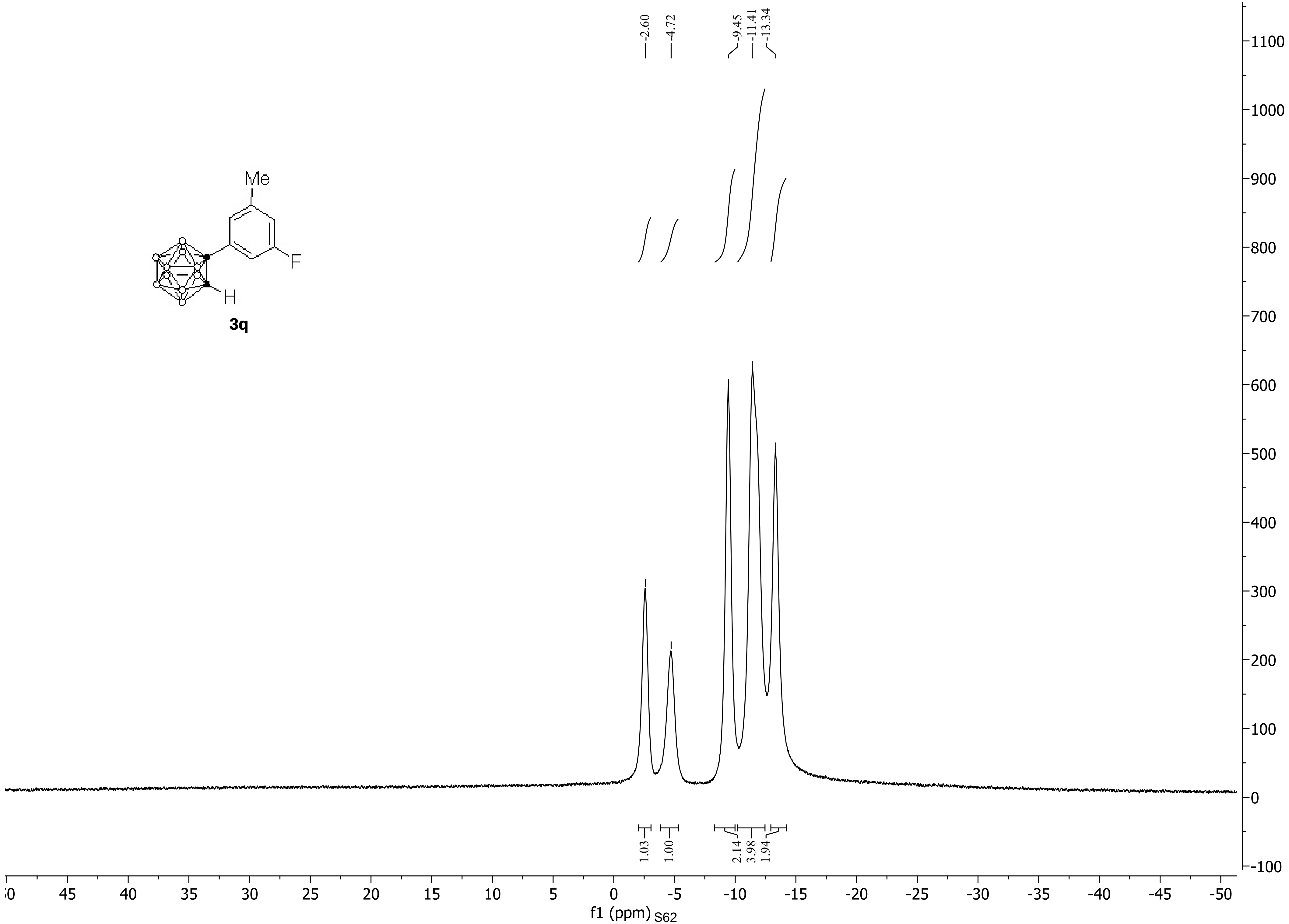

-1.76
-4.24
-8.68
-10.38
-10.90
-12.45
Me
Me
H
3o
1.00
0.89
1.95
1.93
1.63
1.99
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

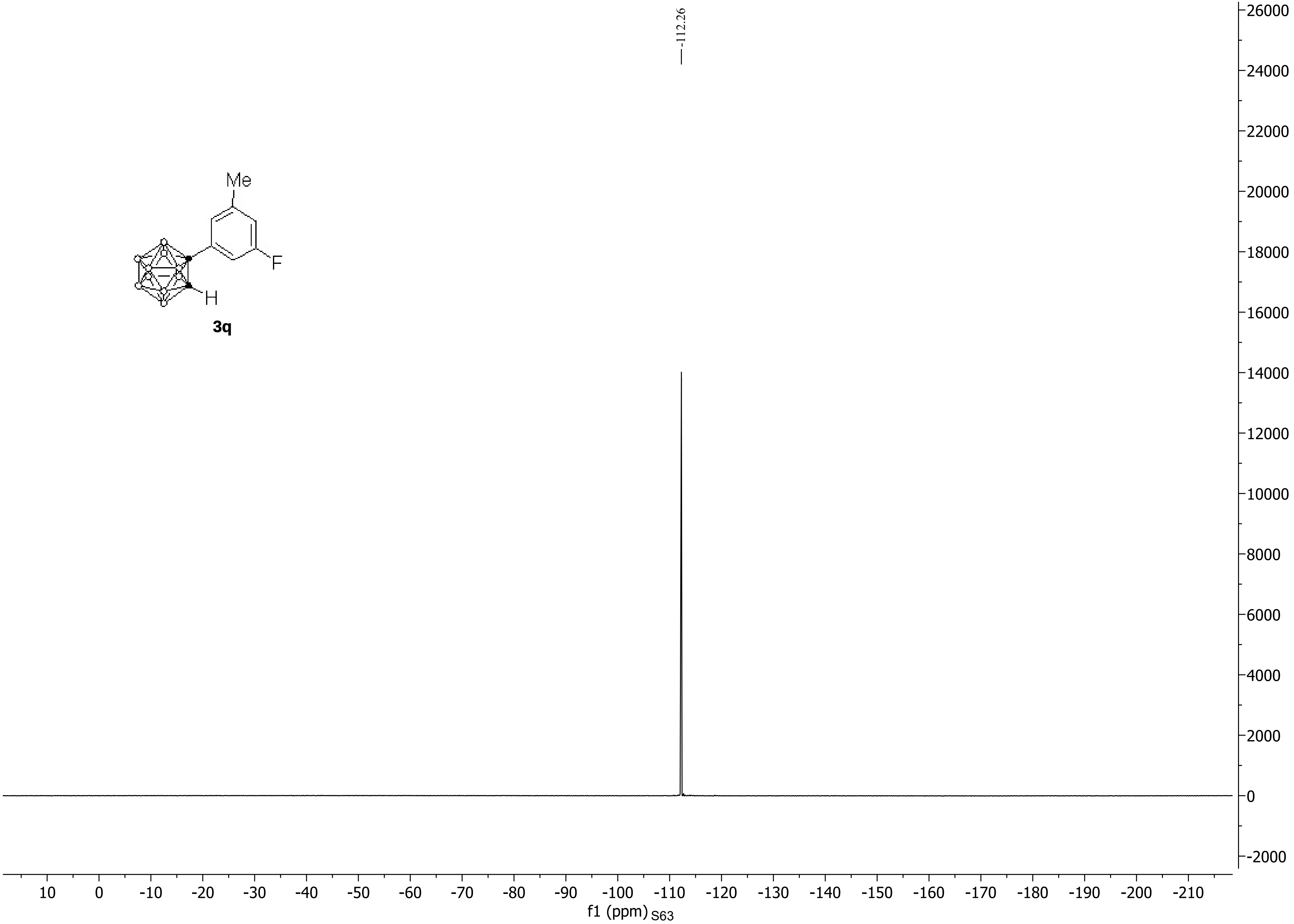

7.26
7.07
7.02
3.97
2.31
Me
Me
H
3p
$CDCl_3$
1.92
0.97
1.00
6.02
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

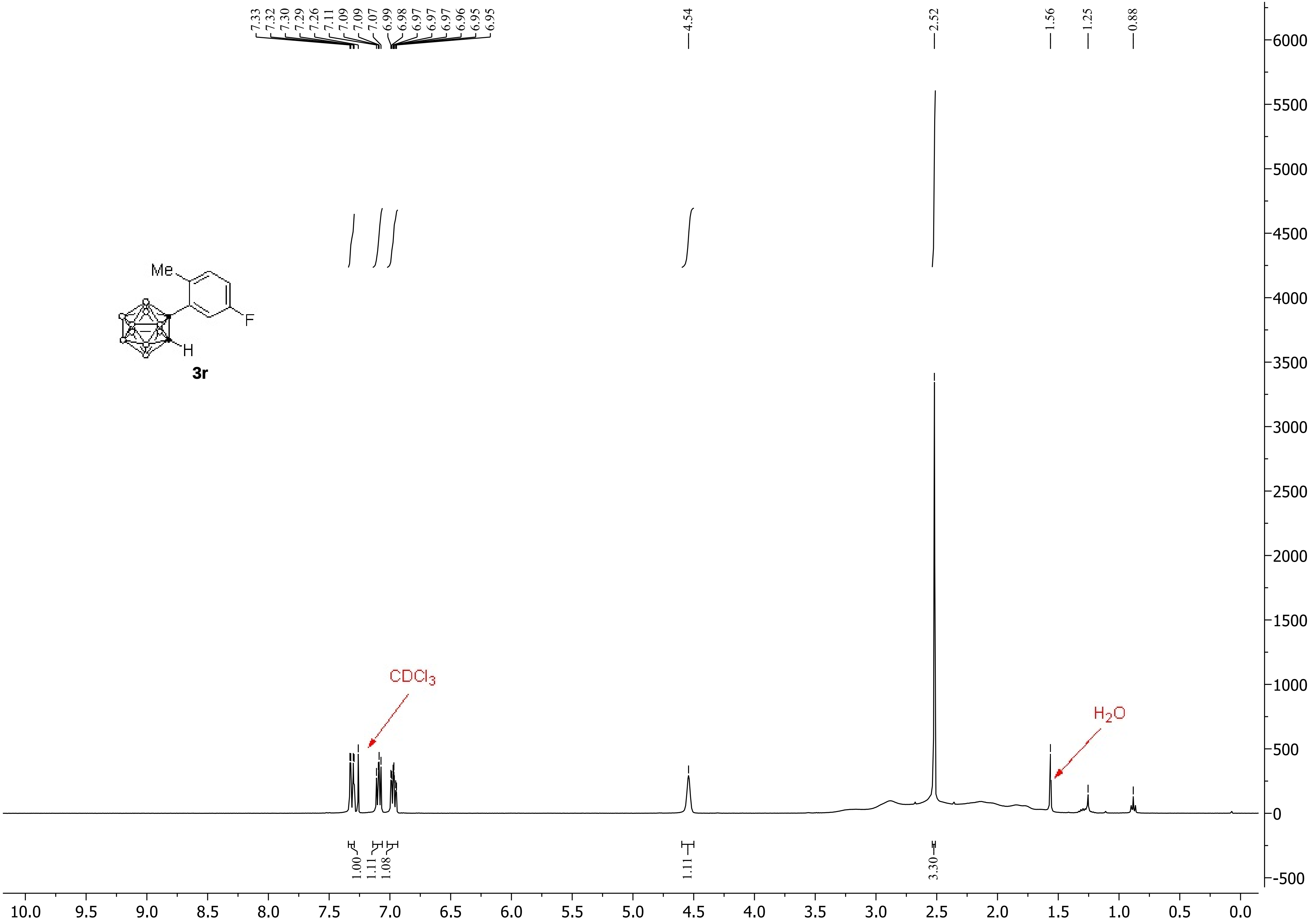

-2.74
-5.00
-9.56
-11.45
-13.44
Me
Me
H
3p
1.13
1.08
2.19
4.00
2.08
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

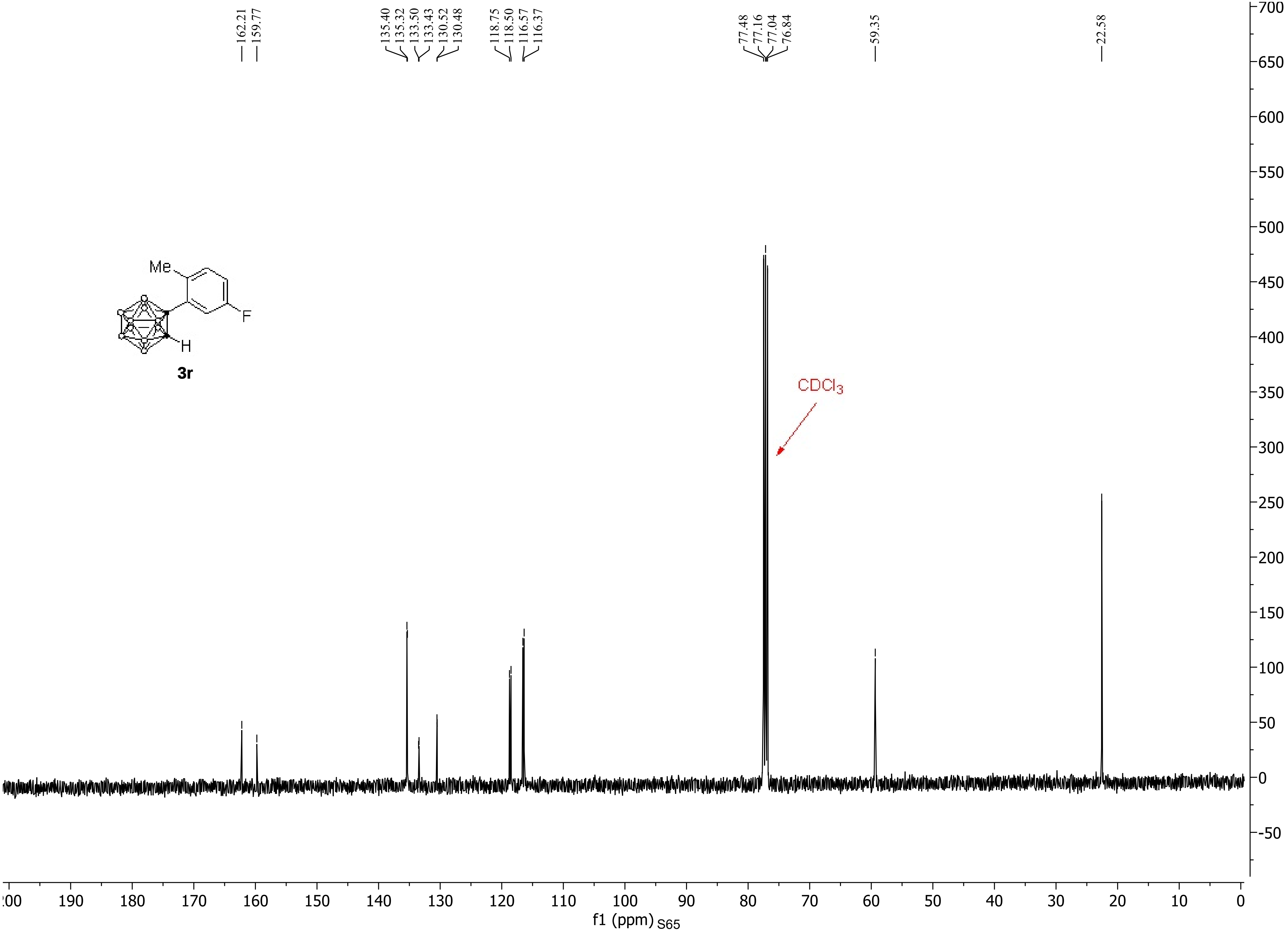

7.26
7.05
7.02
7.01
7.01
7.00
6.99
6.98
6.93
6.91
3.94
2.36
1.56
Me
F
H
3q
CDCl3
H2O
1.00
1.03
0.94
1.04
3.27
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

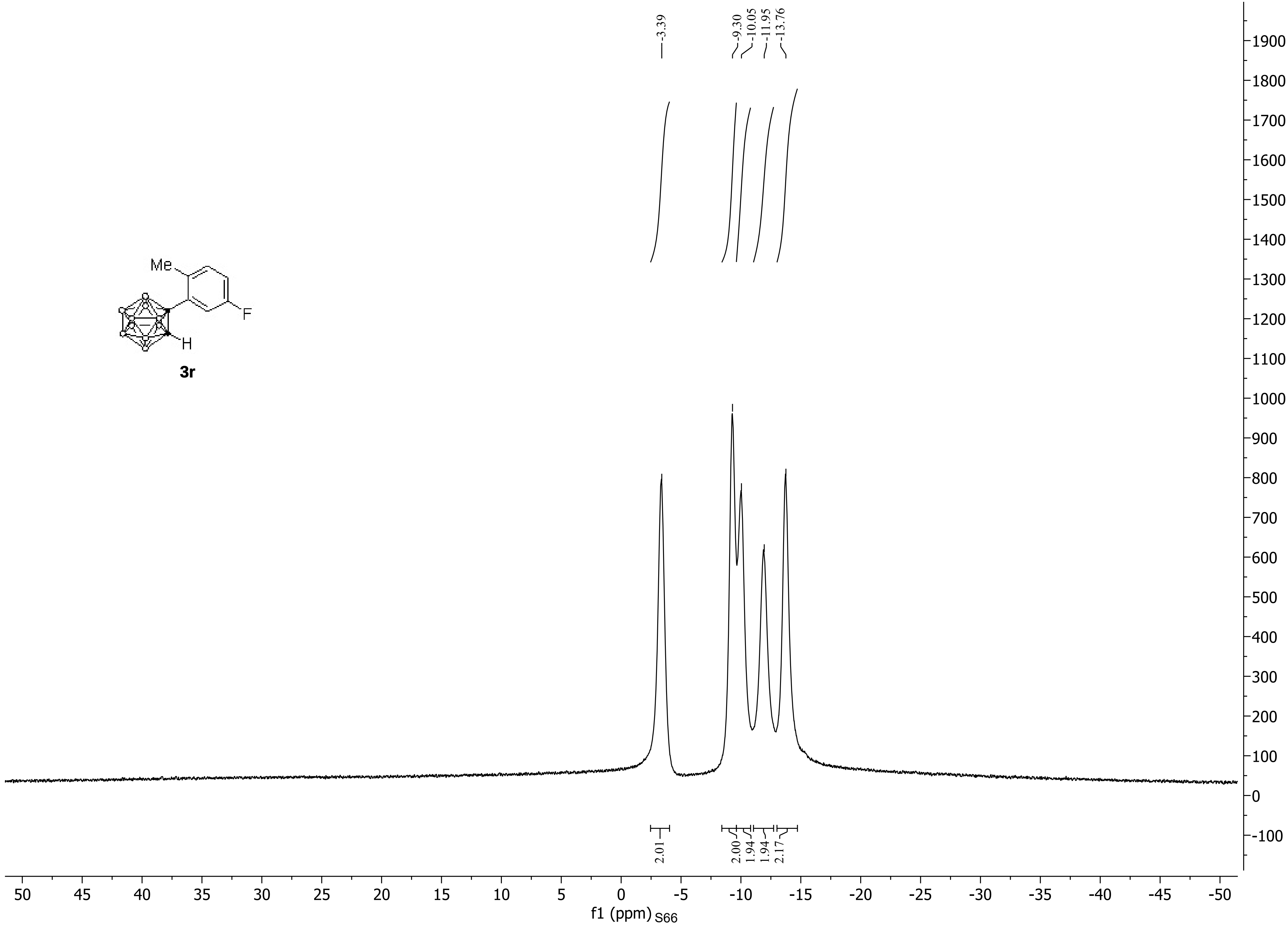

163.72
161.26
141.42
141.34
135.33
124.07
124.04
117.83
117.63
112.55
112.31
77.48
77.36
77.16
76.84
75.46
60.10
21.58
21.56
Me
F
H
3q
$CDCl_3$
450
400
350
300
250
200
150
100
50
0
-50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-2.60
-4.72
-9.45
-11.41
-13.34
Me
F
H
3q
1.03
1.00
2.14
3.98
1.94
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

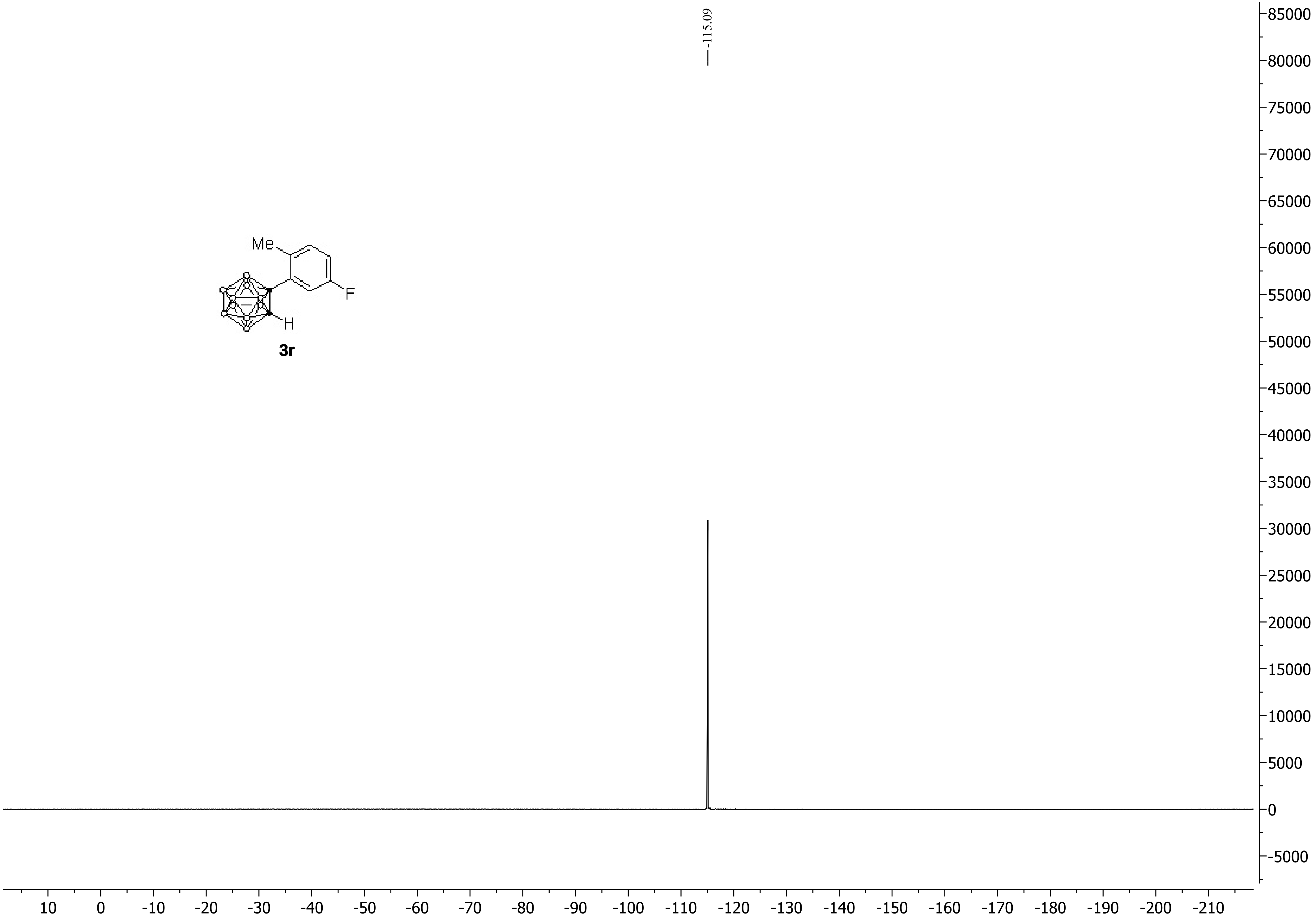

-112.26
Me
F
H
3q
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

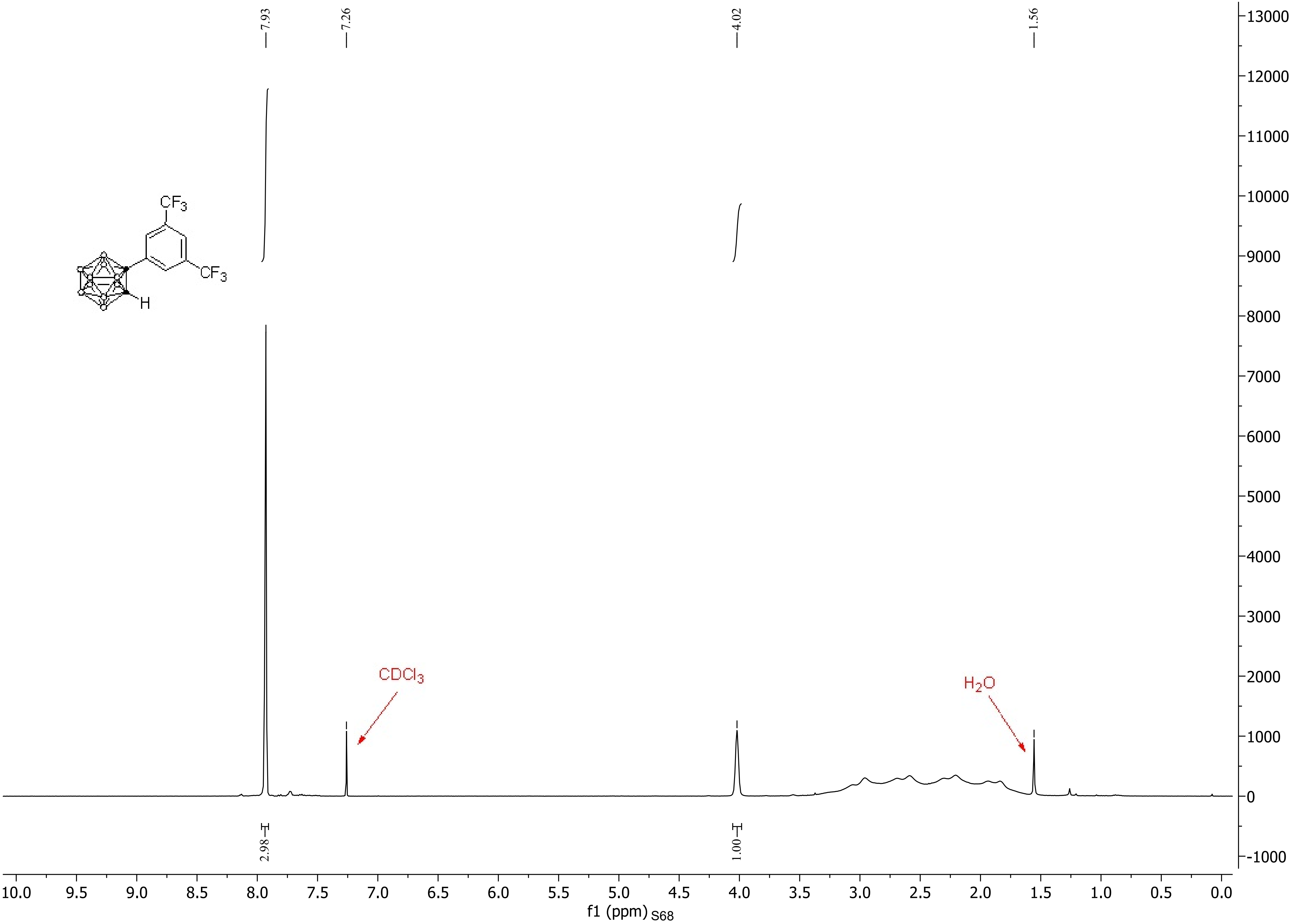

7.33
7.32
7.30
7.29
7.26
7.11
7.09
7.09
7.07
6.99
6.98
6.97
6.97
6.97
6.96
6.95
6.95
4.54
2.52
1.56
1.25
0.88
Me
F
H
3r
CDCl$_3$
H$_2$O
1.00
1.11
1.08
1.11
3.30
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

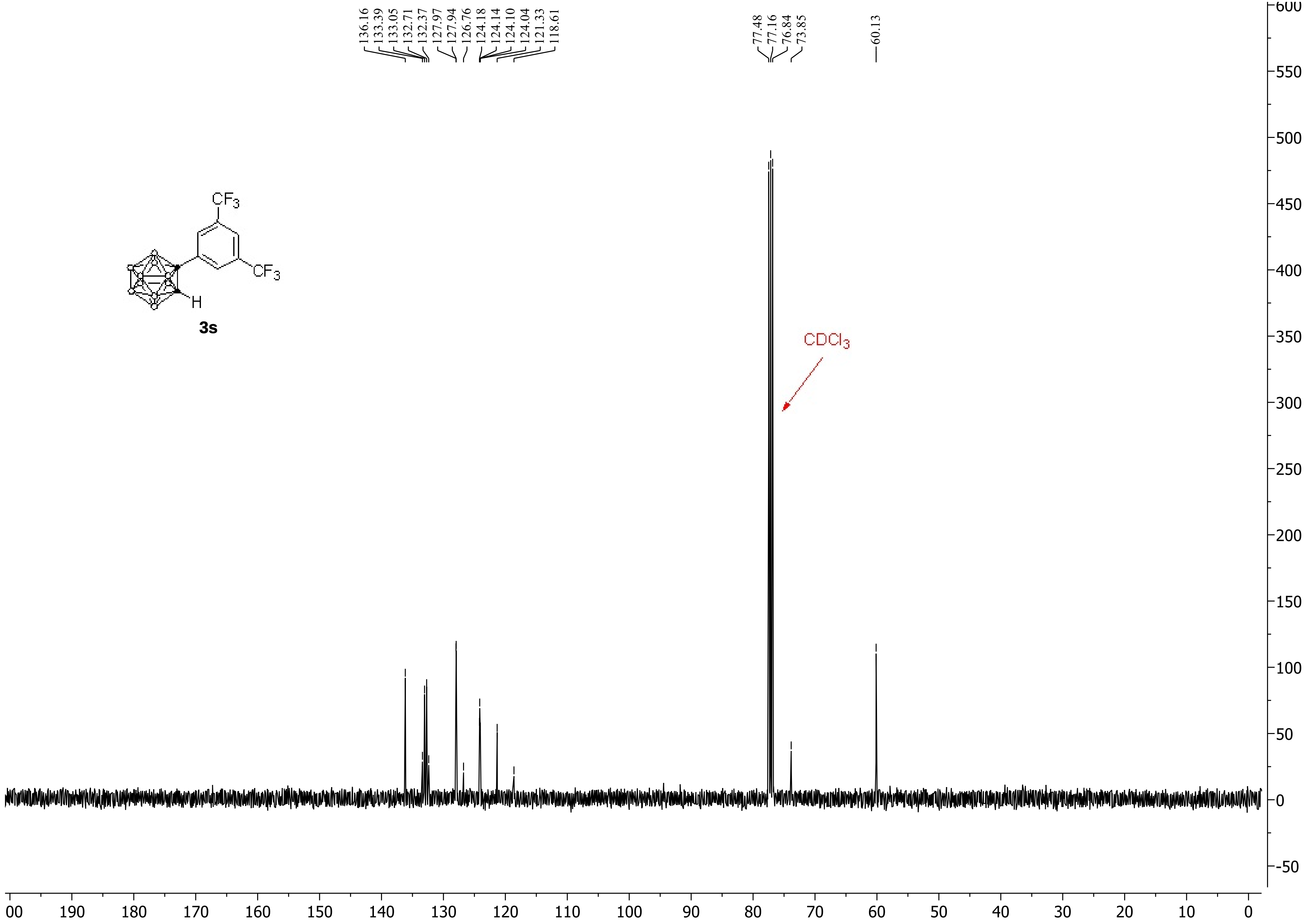

162.21
159.77
135.40
135.32
133.50
133.43
130.52
130.48
118.75
118.50
116.57
116.37
77.48
77.16
77.04
76.84
59.35
22.58
Me
F
H
3r
CDCl3
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

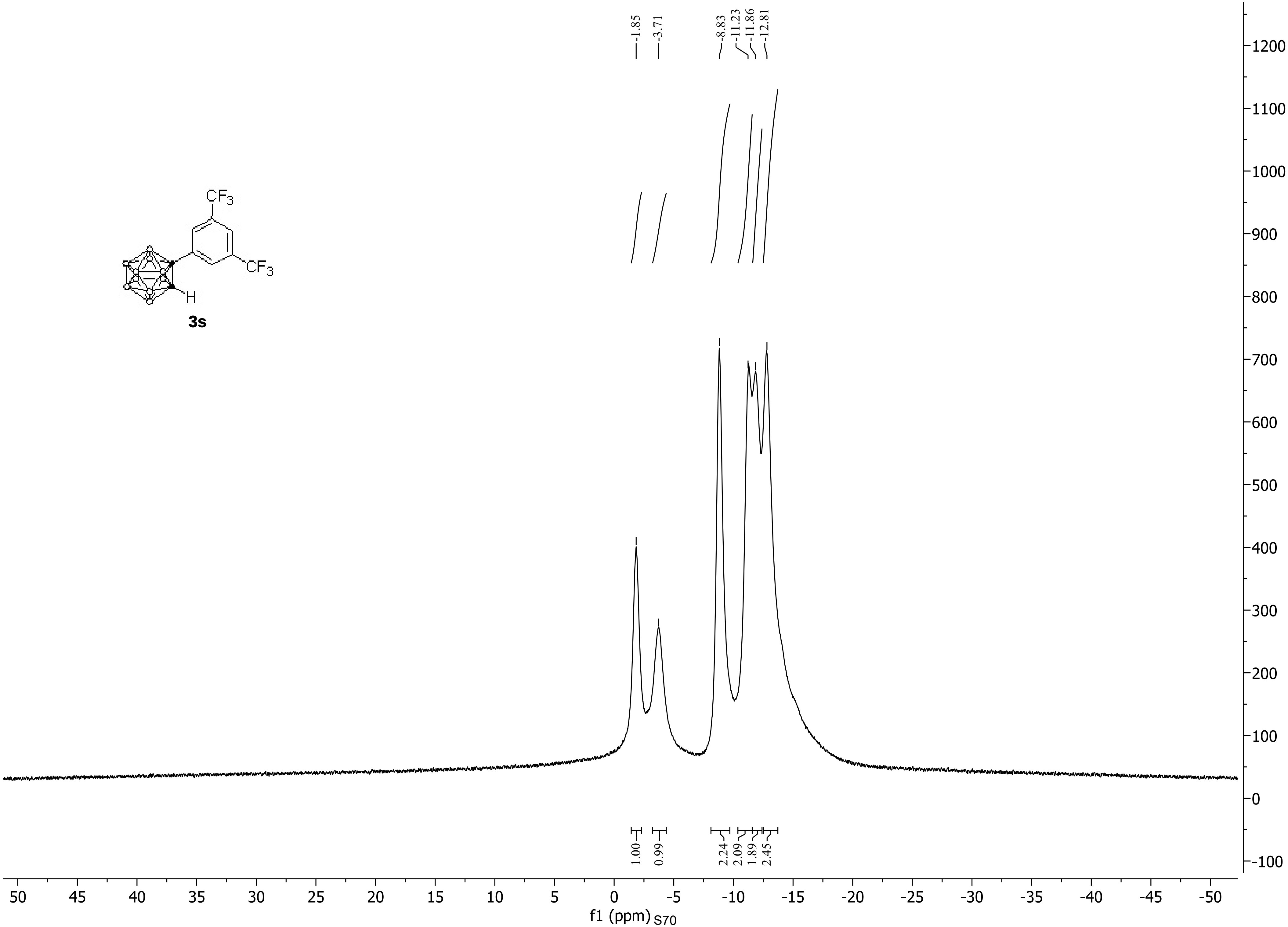

-3.39
-9.30
-10.05
-11.95
-13.76
Me
F
H
2.01
2.00
1.94
1.94
2.17
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

3r


-115.09
Me
F
H
3r
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

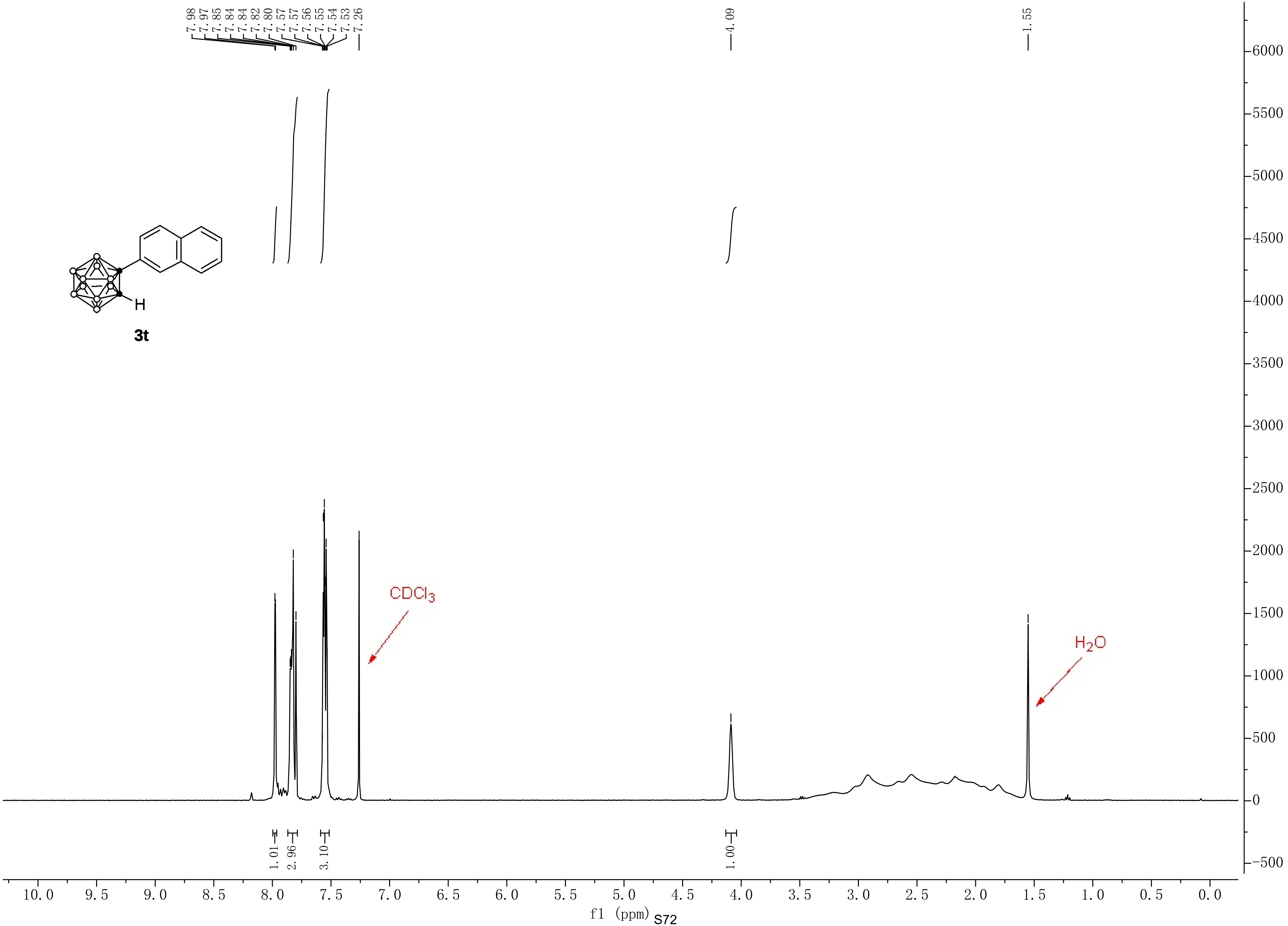

7.93
7.26
4.02
1.56
CF3
CF3
H
CDCl3
H2O
2.98
1.00
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

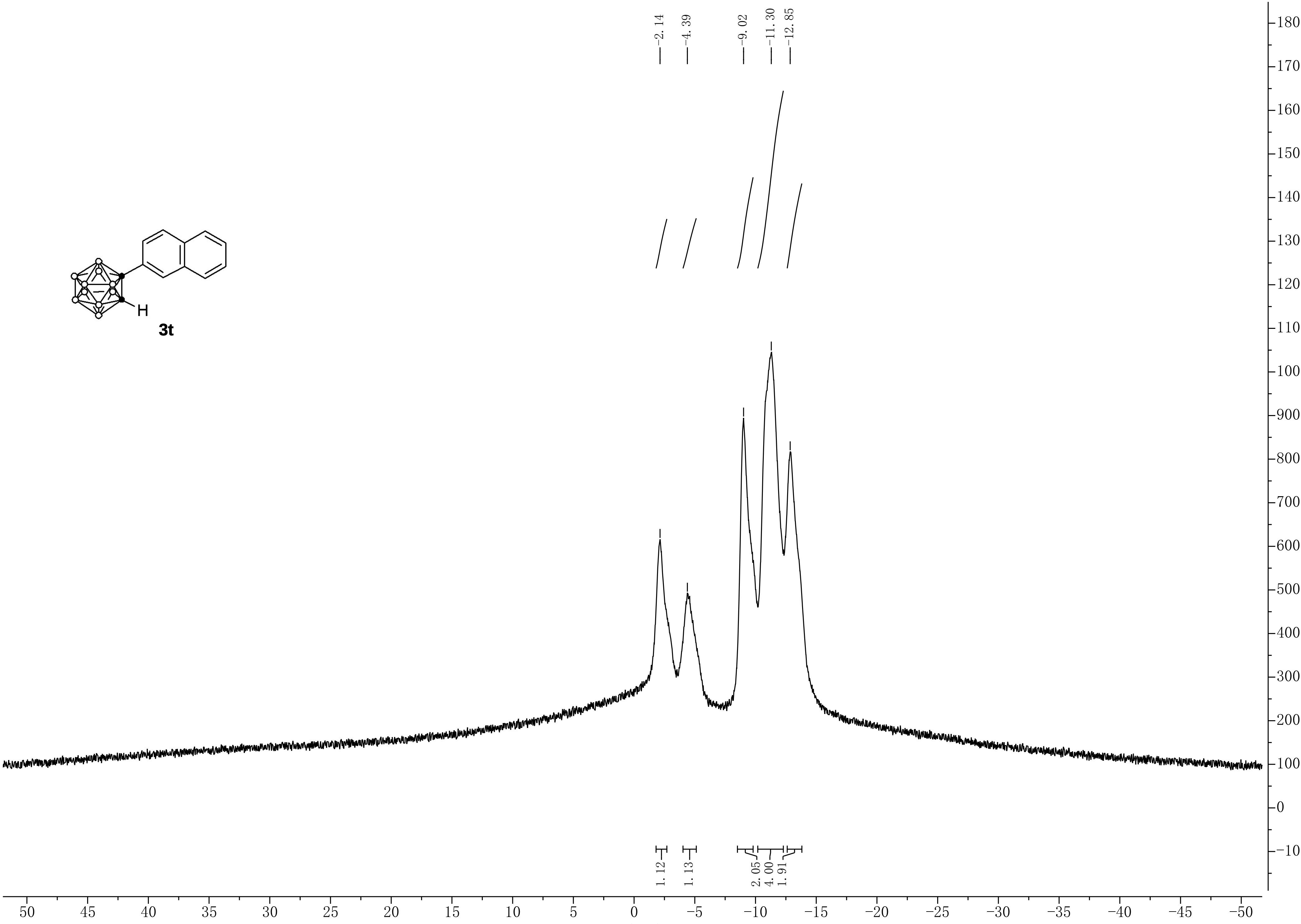

136.16
133.39
133.05
132.71
132.37
127.97
127.94
126.76
124.18
124.14
124.10
124.04
121.33
118.61
77.48
77.16
76.84
73.85
60.13
CF3
CF3
H
3s
CDCl3
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



-1.85
-3.71
-8.83
-11.23
-11.86
-12.81
CF3
CF3
H
3s
1.00
0.99
2.24
2.09
1.89
2.45
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

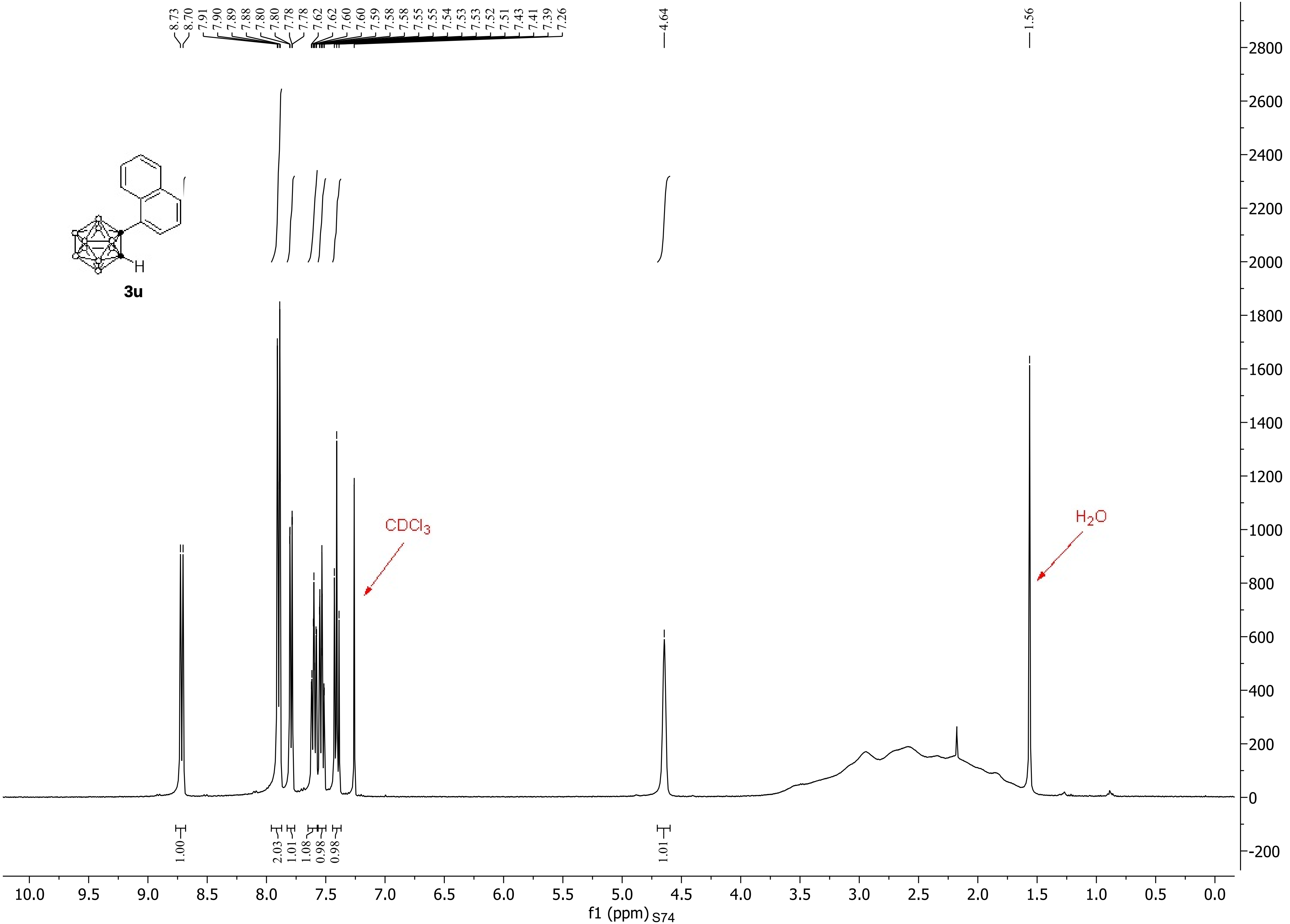

-62.94
CF3
CF3
H
3s
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

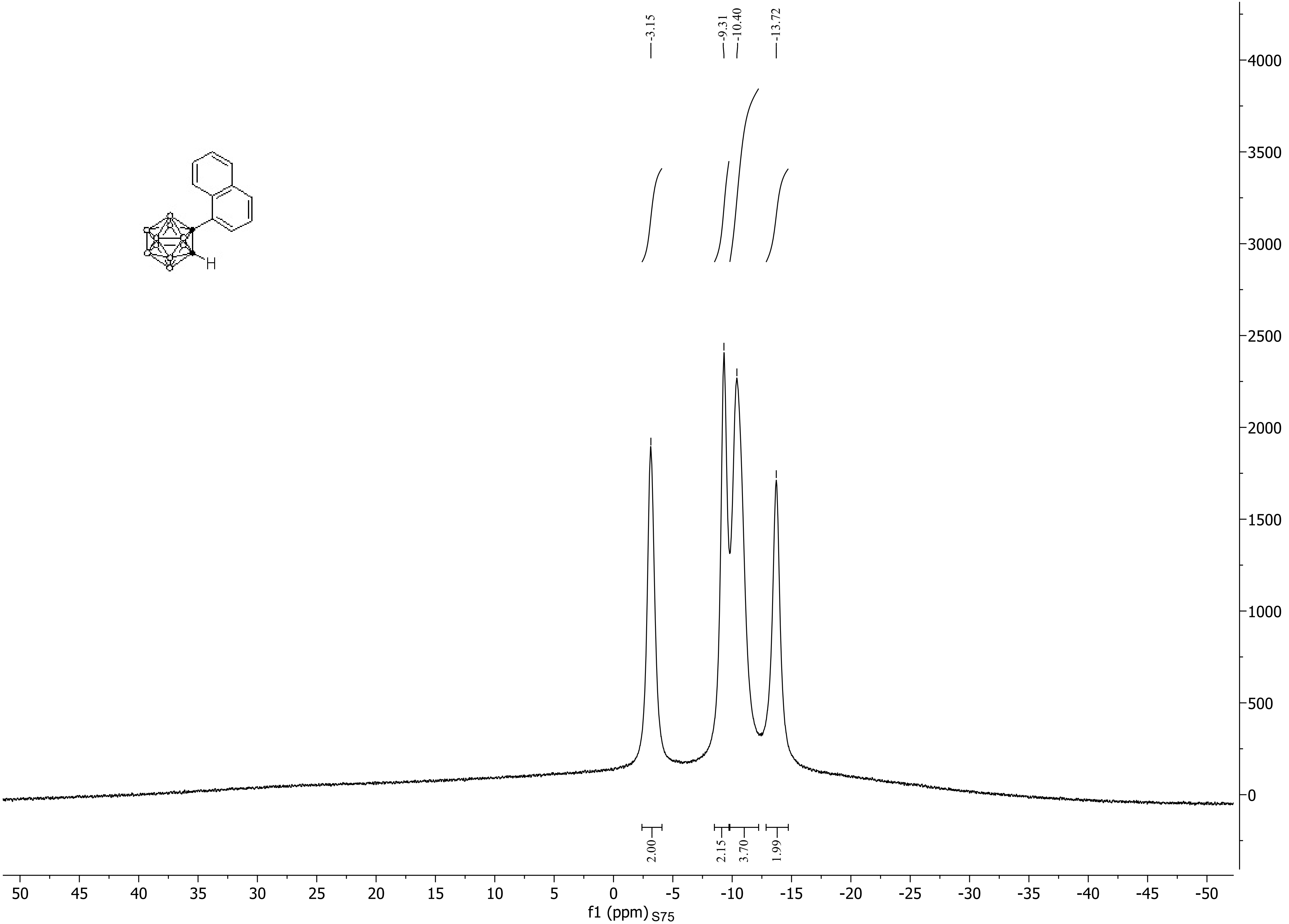

7.98
7.97
7.85
7.84
7.84
7.82
7.80
7.57
7.57
7.56
7.55
7.54
7.53
7.26
4.09
1.55
H
3t
CDCl3
H2O
1.01
2.96
3.10
1.00
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



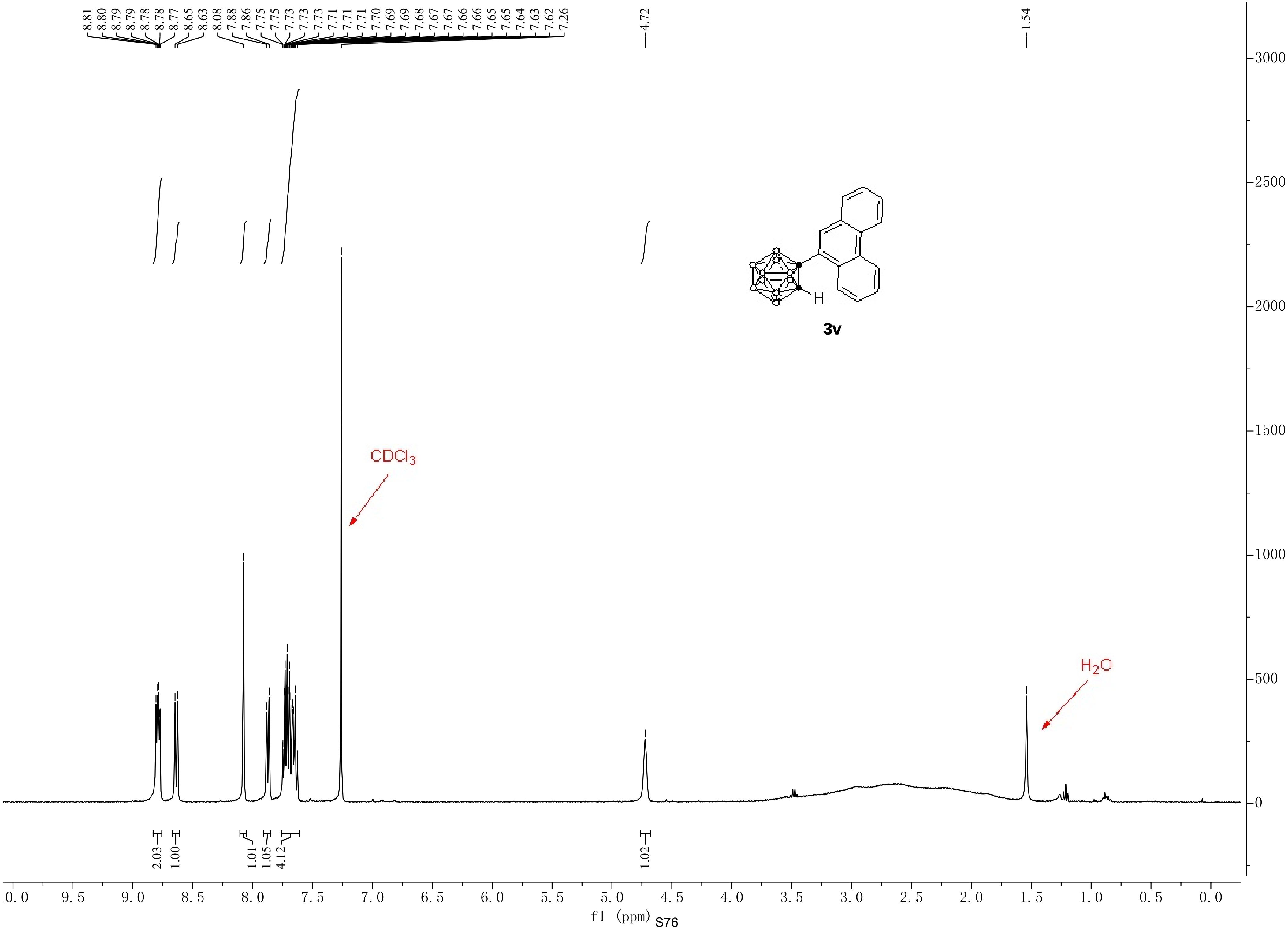
-2.14
-4.39
-9.02
-11.30
-12.85
1.12
1.13
2.05
4.00
1.91
H
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)

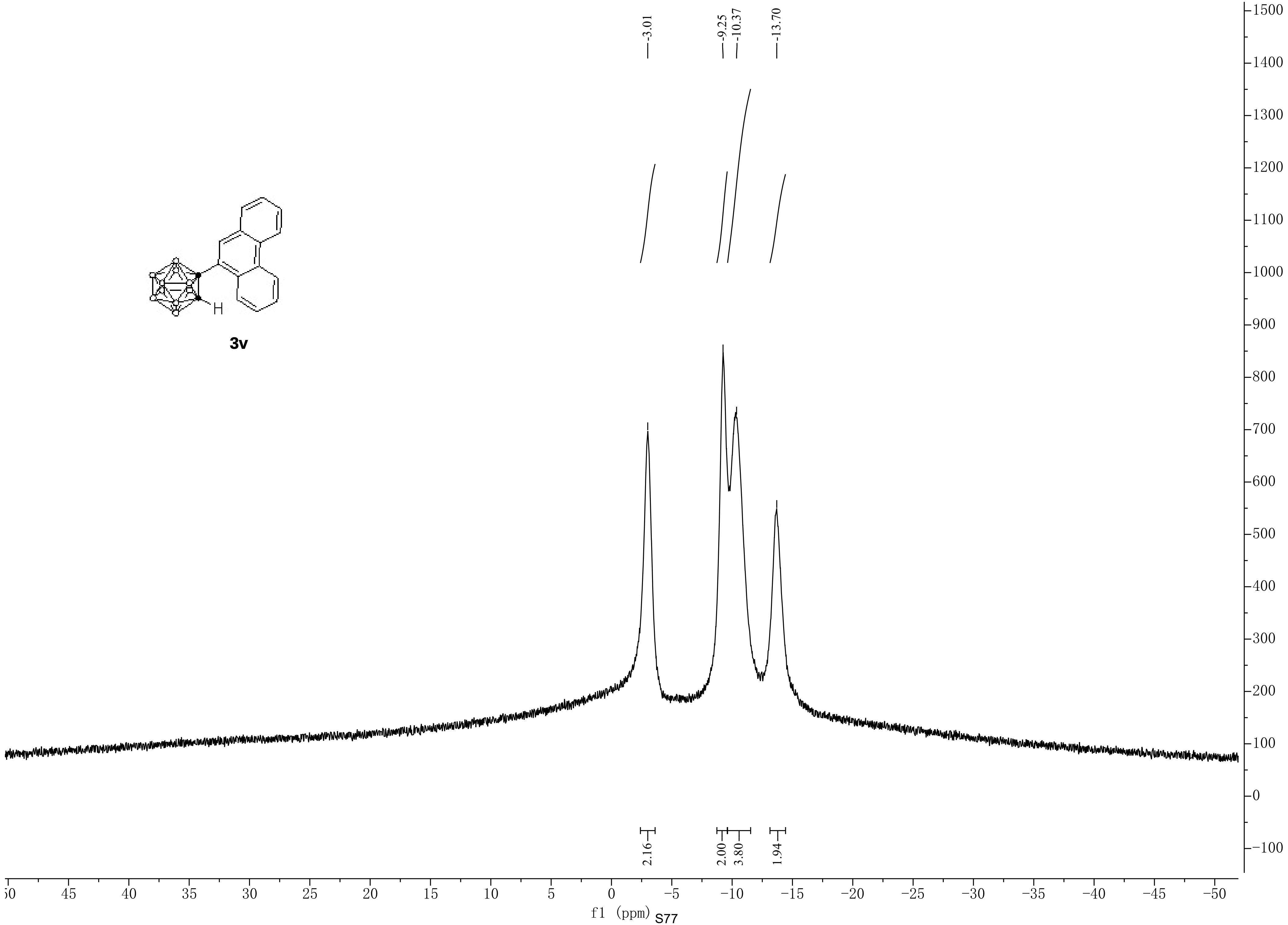
3t

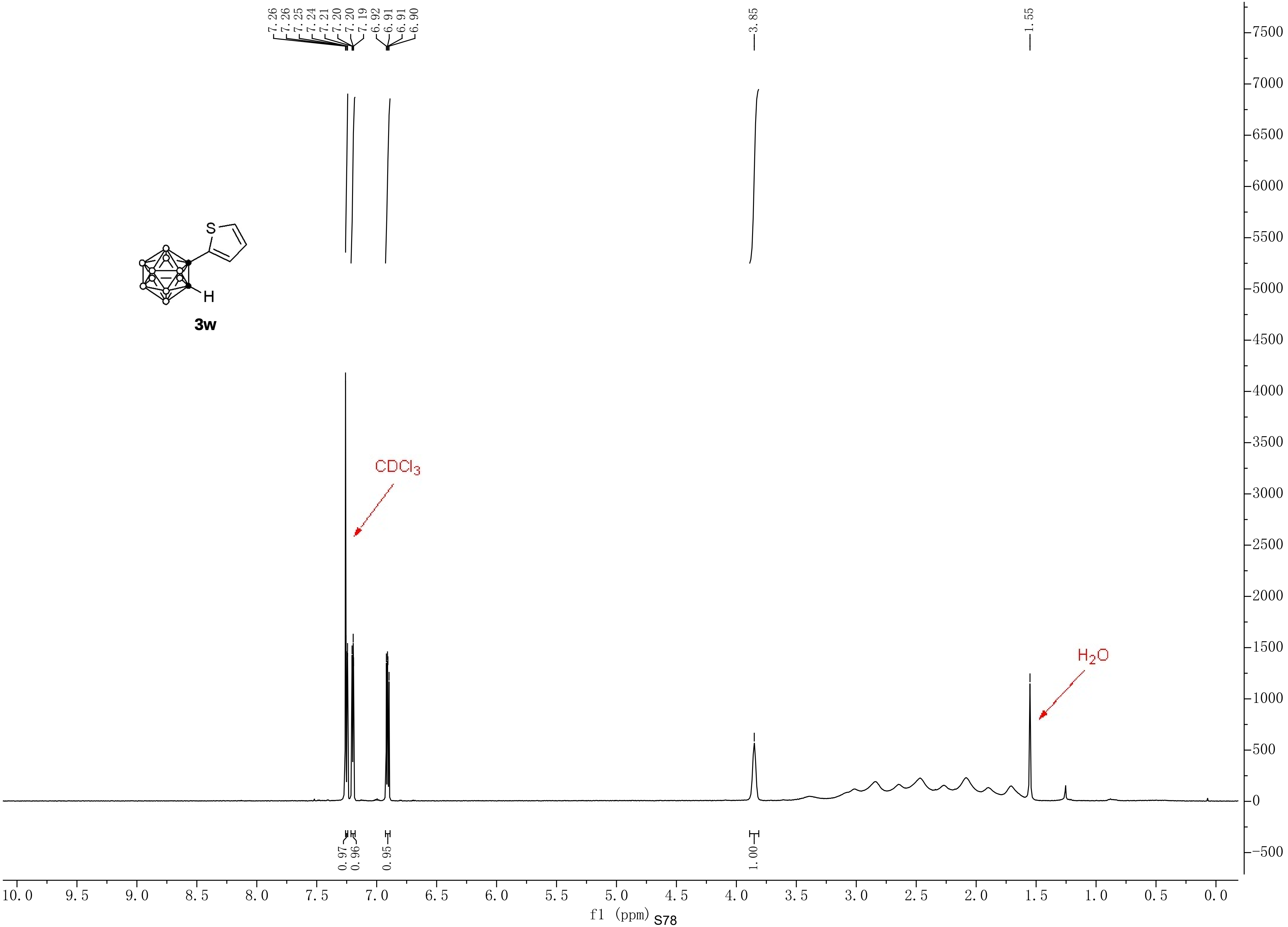

8.73
8.70
7.91
7.90
7.89
7.88
7.80
7.80
7.78
7.78
7.62
7.62
7.60
7.60
7.59
7.58
7.58
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.43
7.41
7.39
7.26
4.64
1.56
H
3u
CDCl$_3$
H$_2$O
1.00
2.03
1.01
1.08
0.98
0.98
1.01
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

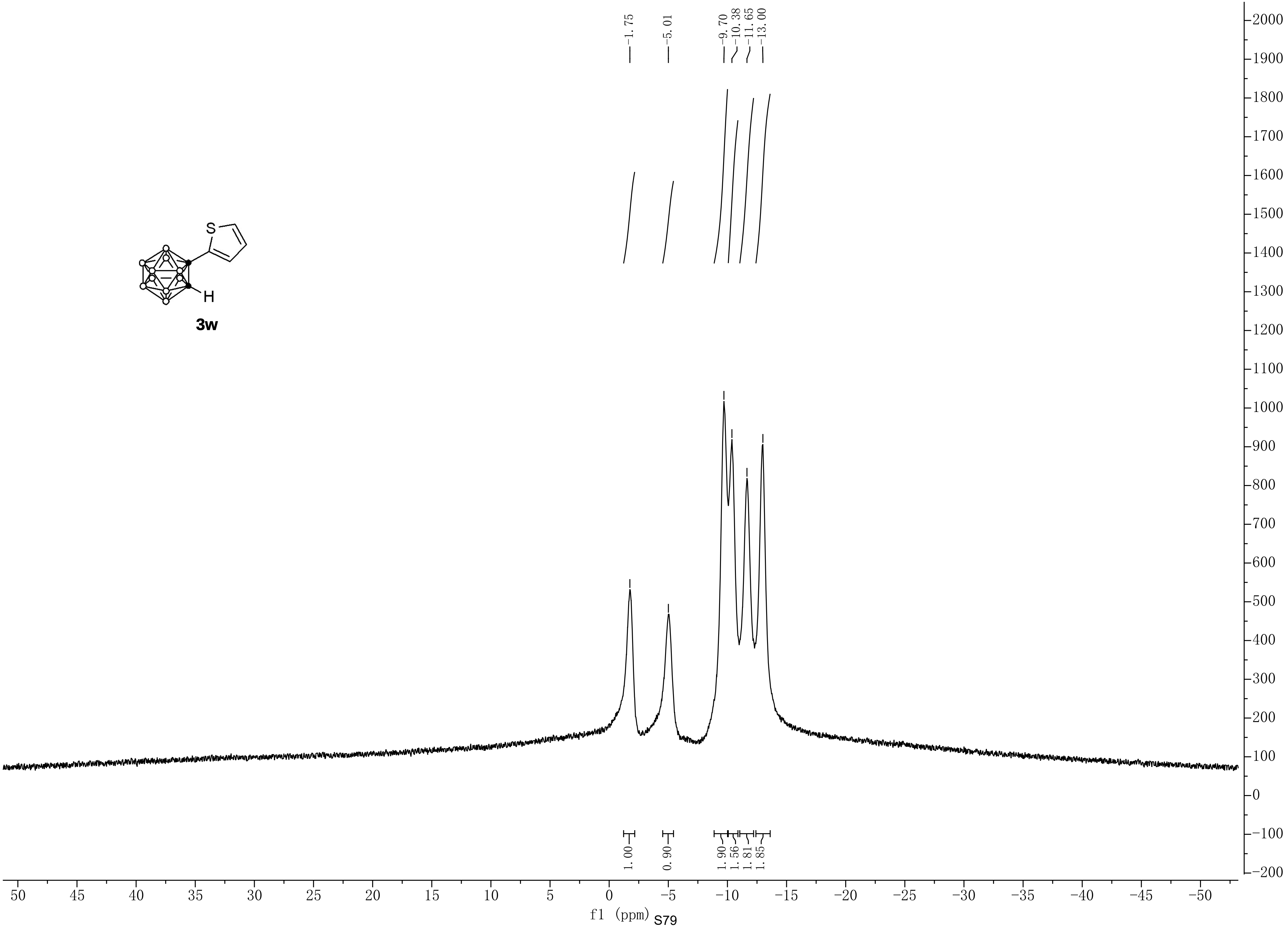


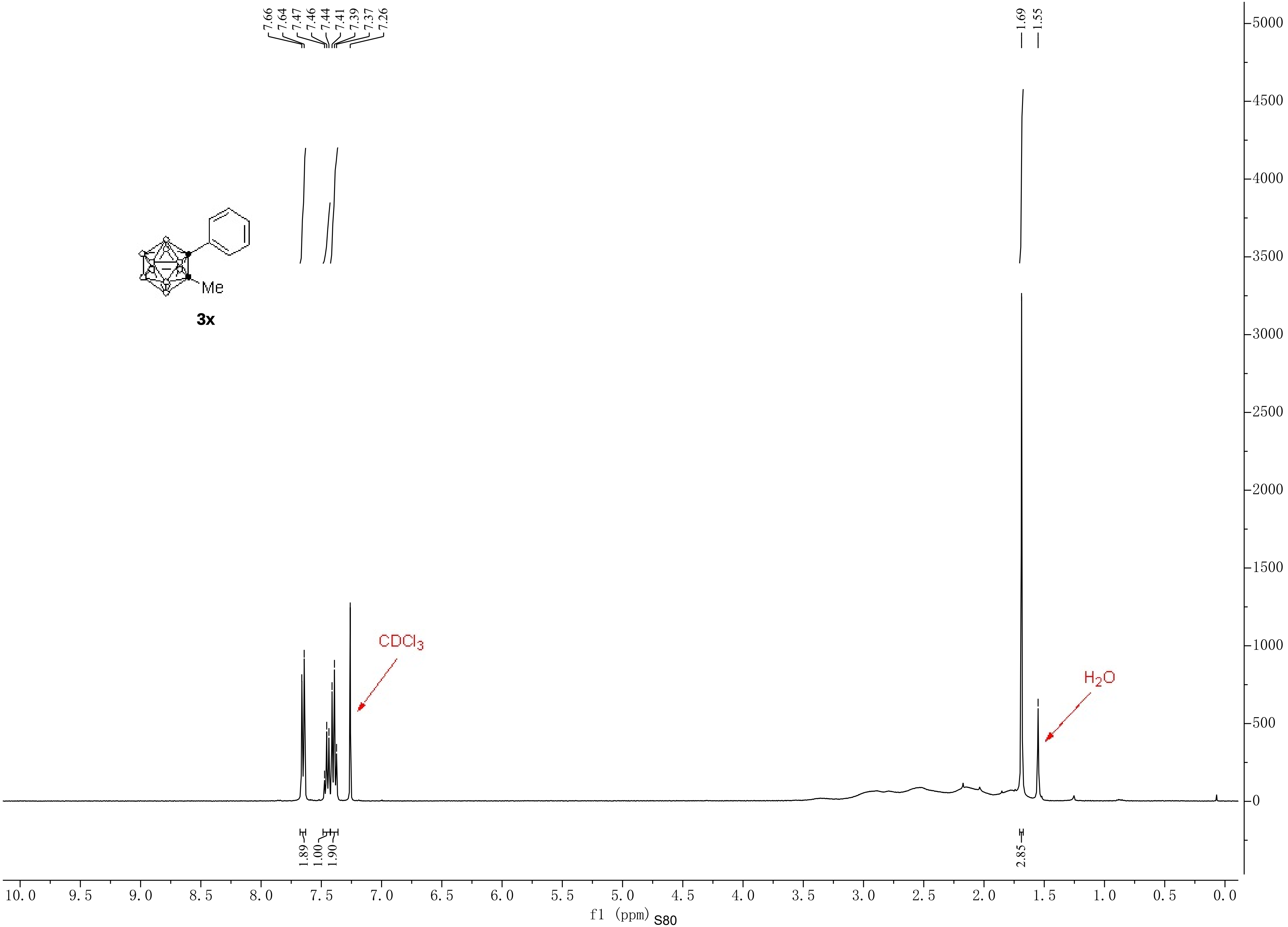
-3.15
-9.31
-10.40
-13.72
H
2.00
2.15
3.70
1.99
4000
3500
3000
2500
2000
1500
1000
500
0
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


8.81
8.80
8.79
8.79
8.78
8.78
8.77
8.65
8.63
8.08
7.88
7.86
7.75
7.75
7.73
7.73
7.73
7.71
7.71
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.66
7.65
7.65
7.64
7.63
7.62
7.26
4.72
1.54
H
3v
CDCl3
H2O
2.03
1.00
1.01
1.05
4.12
1.02
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

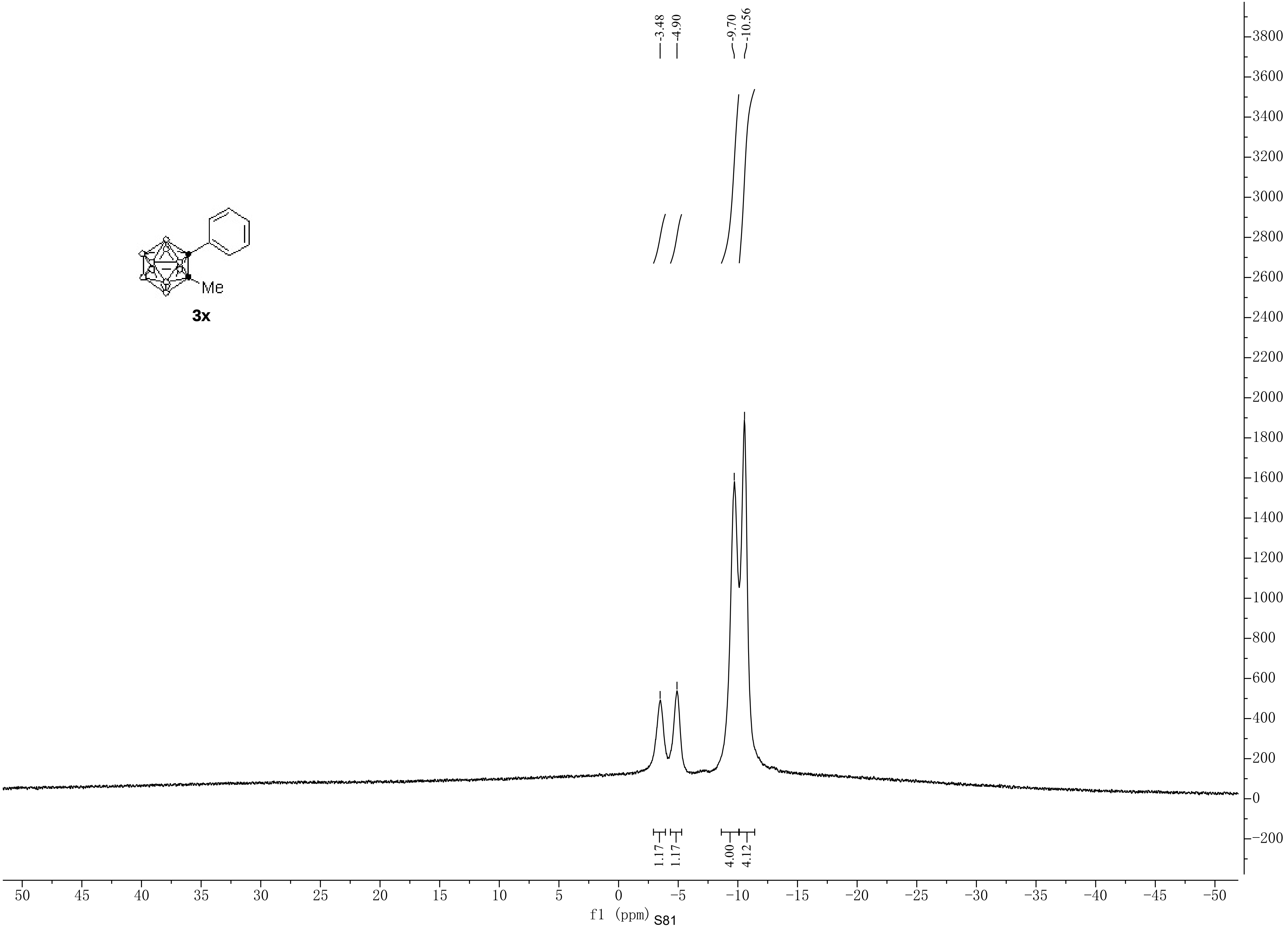

-3.01
-9.25
-10.37
-13.70
H
3v
2.16
2.00
3.80
1.94
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100


7.26
7.26
7.25
7.24
7.21
7.20
7.20
7.19
6.92
6.91
6.91
6.90
3.85
1.55
S
H
3w
CDCl3
H2O
0.97
0.96
0.95
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


3w
S
H
1.75
5.01
9.70
10.38
11.65
13.00
1.00
0.90
1.90
1.56
1.81
1.85
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200

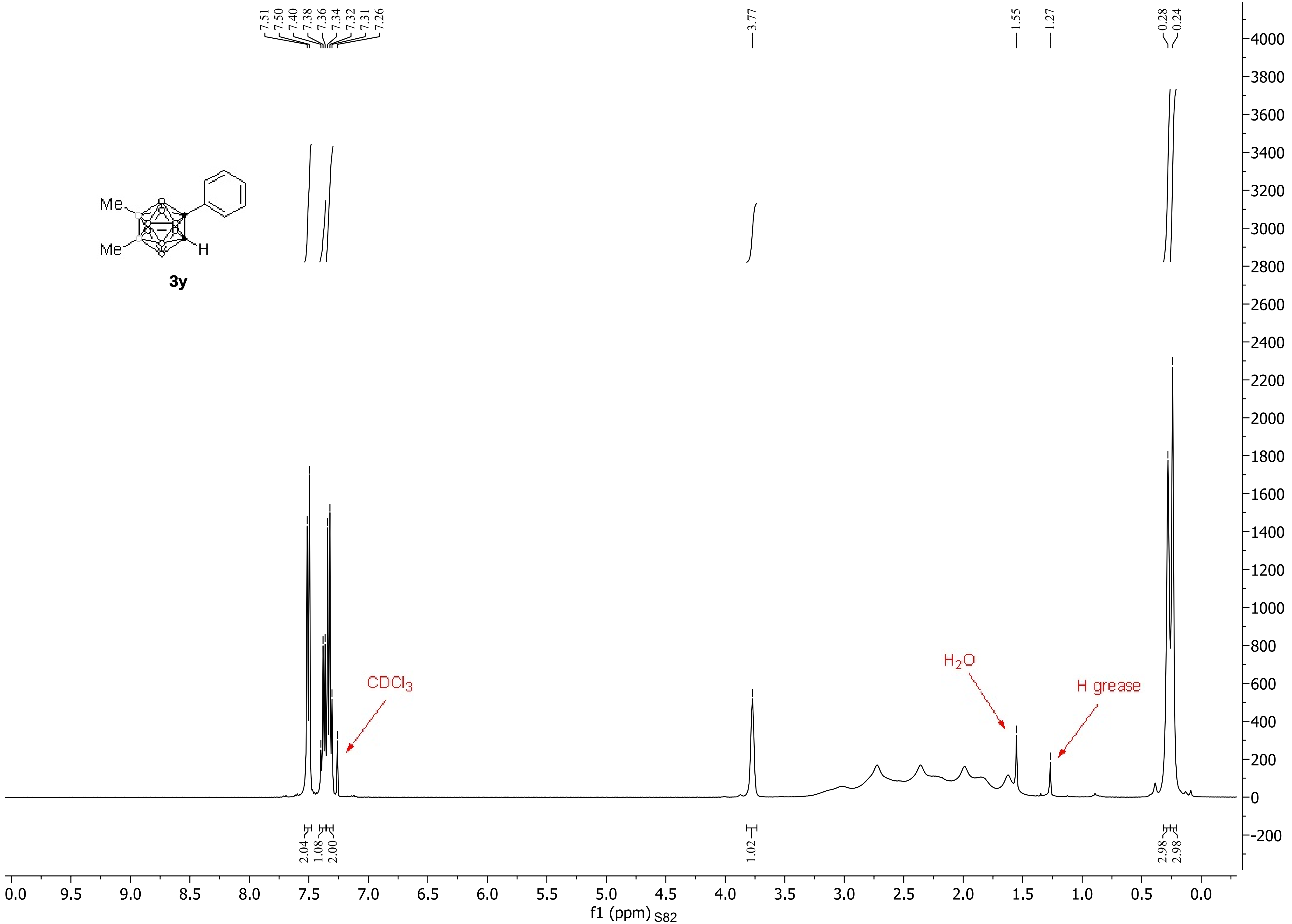


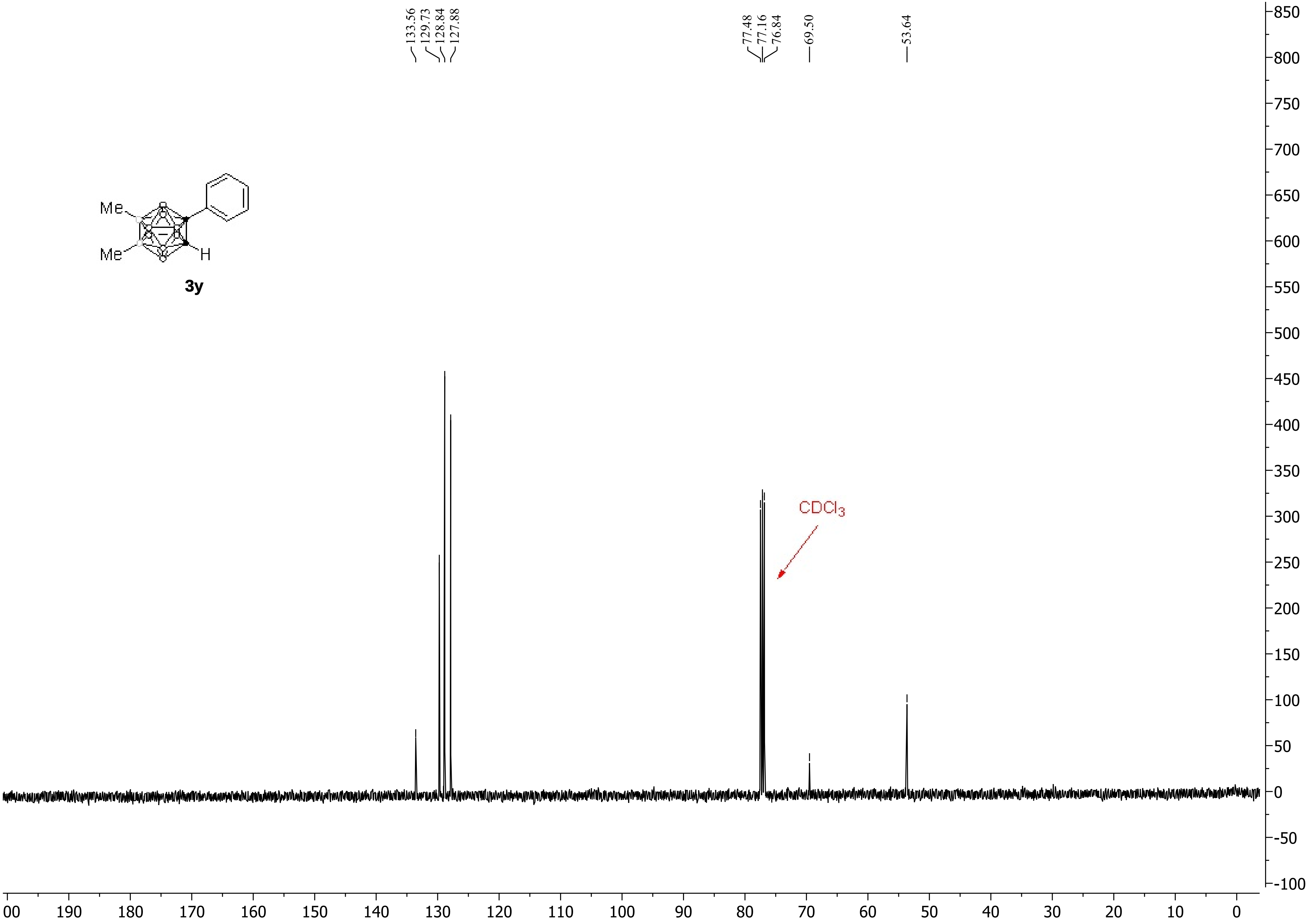
7.66
7.64
7.47
7.46
7.44
7.41
7.39
7.37
7.26
1.69
1.55
Me
3x
CDCl$_3$
H$_2$O
1.89
1.00
1.90
2.85
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

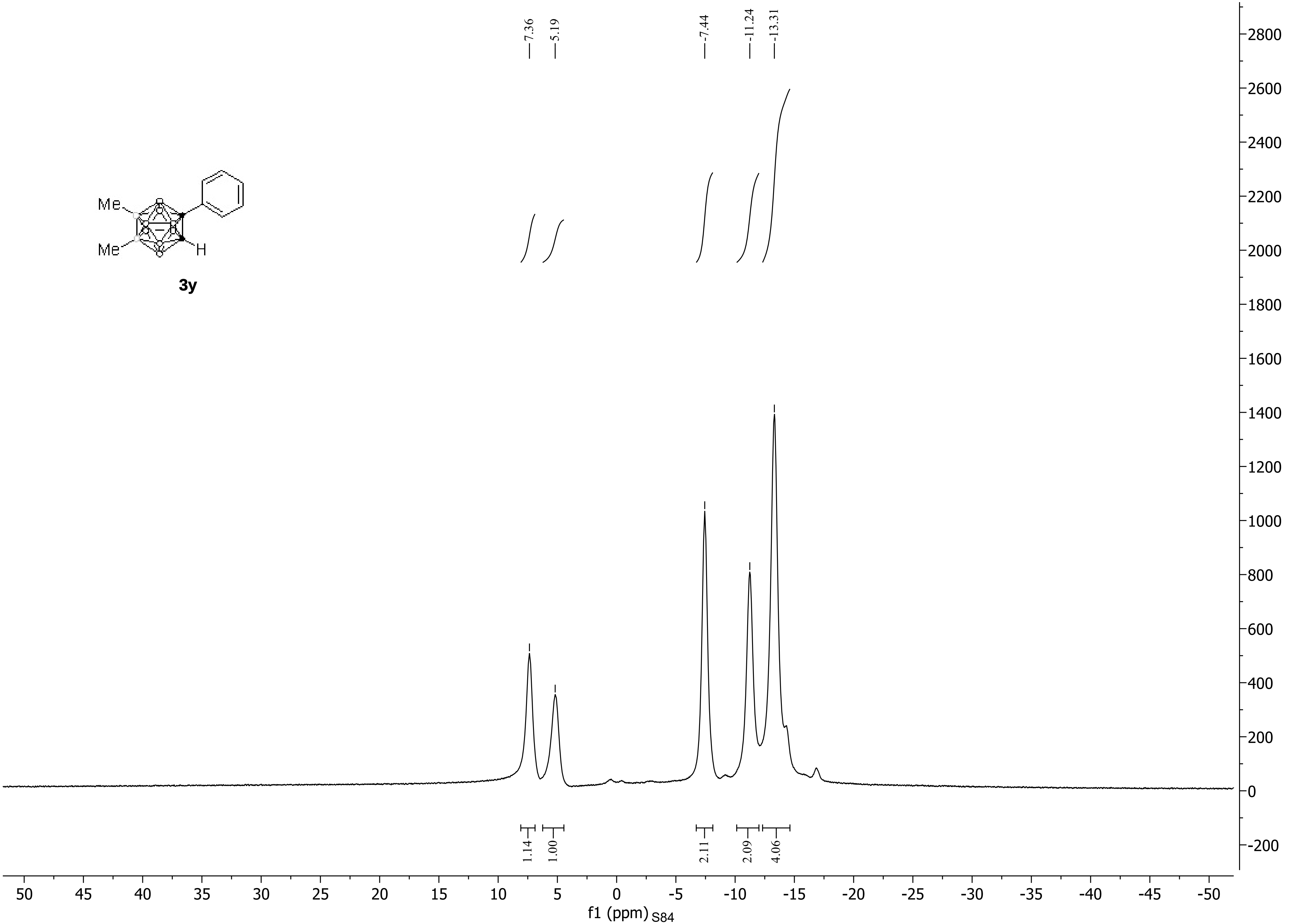


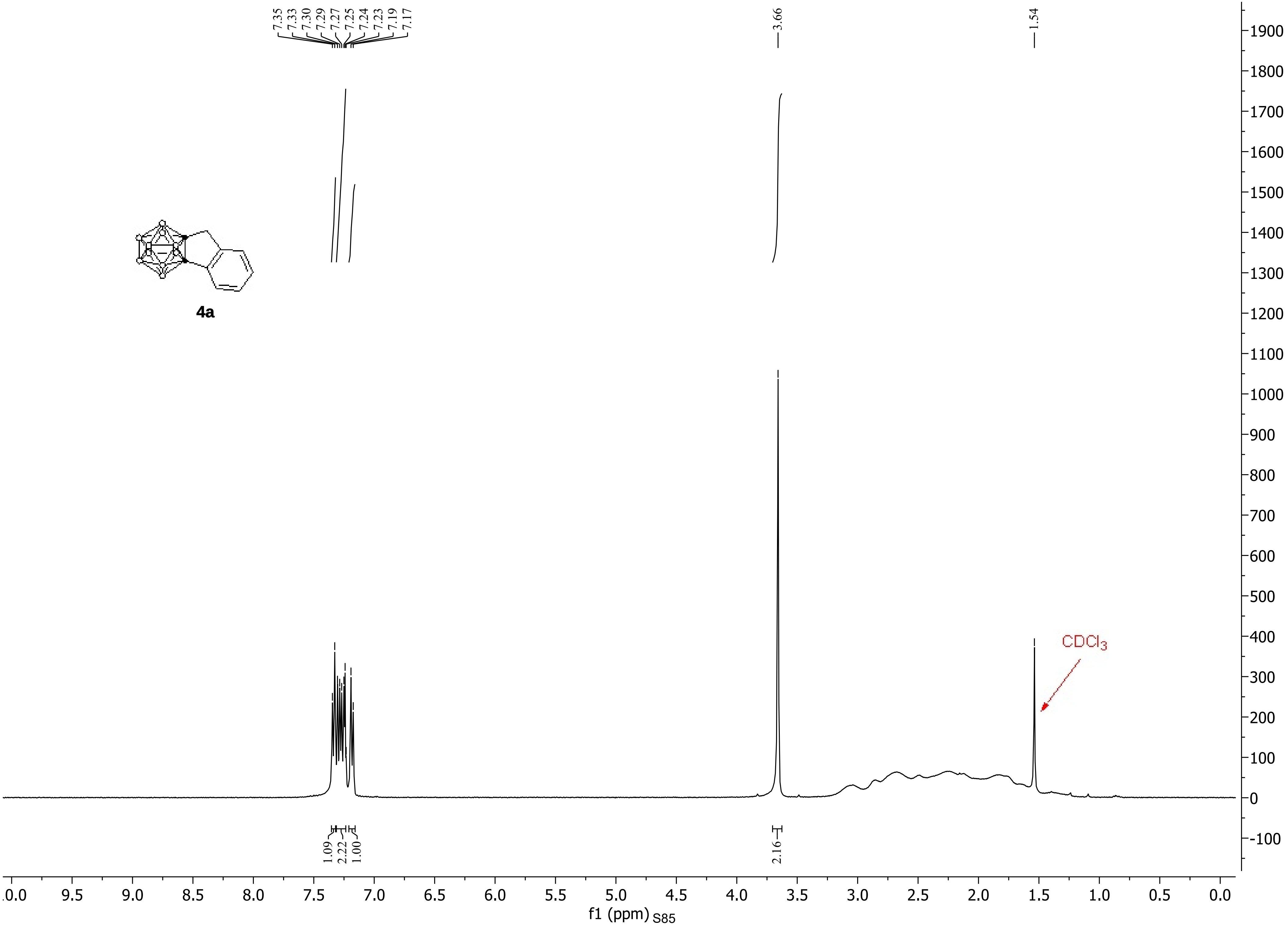
-3.48
-4.90
-9.70
-10.56
Me
1.17
1.17
4.00
4.12
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)

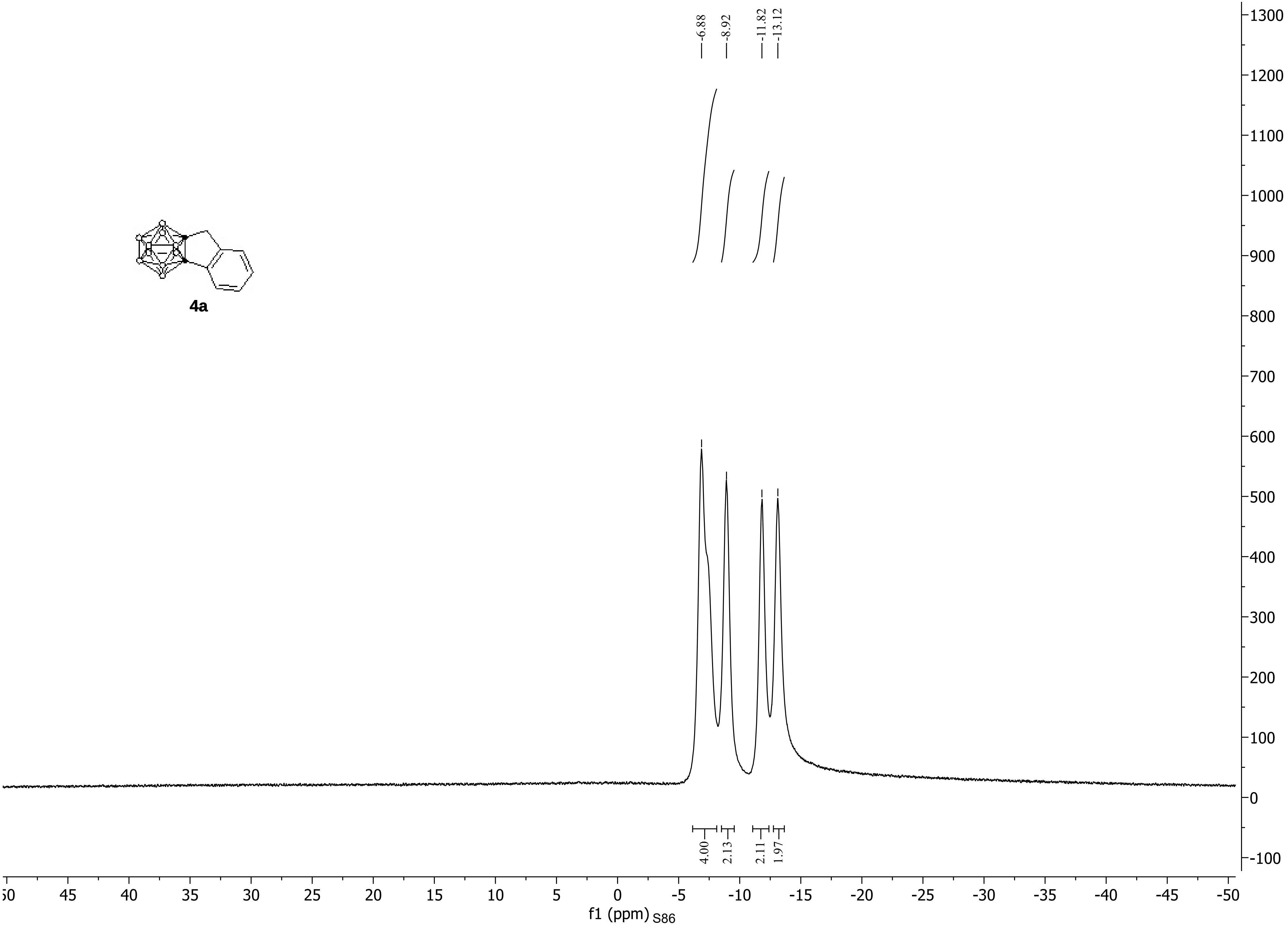
3x

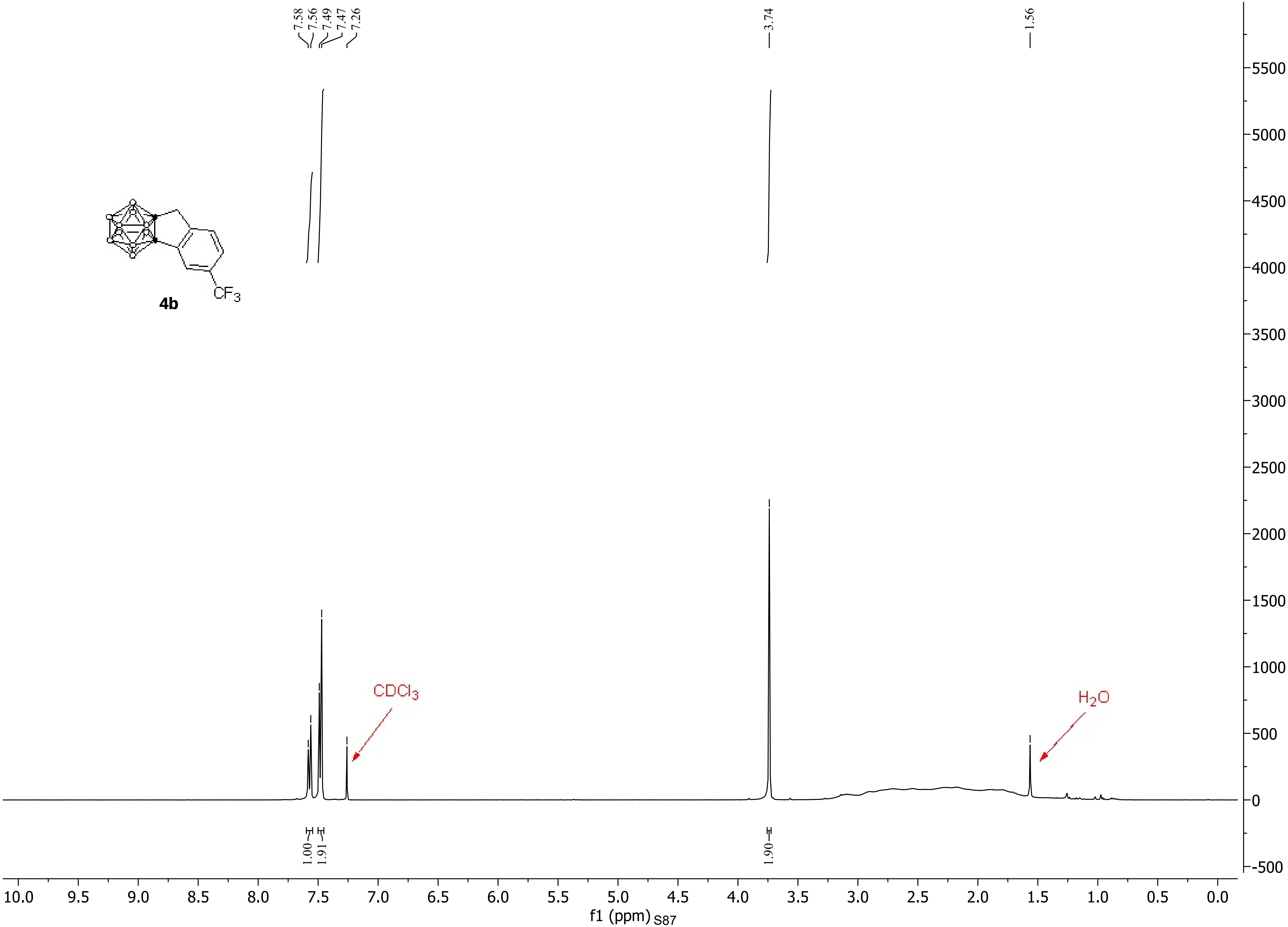

7.51
7.50
7.40
7.38
7.36
7.34
7.32
7.31
7.26
3.77
1.55
1.27
0.28
0.24
Me
Me
H
3y
CDCl$_3$
H$_2$O
H grease
2.04
1.08
2.00
1.02
2.98
2.98
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

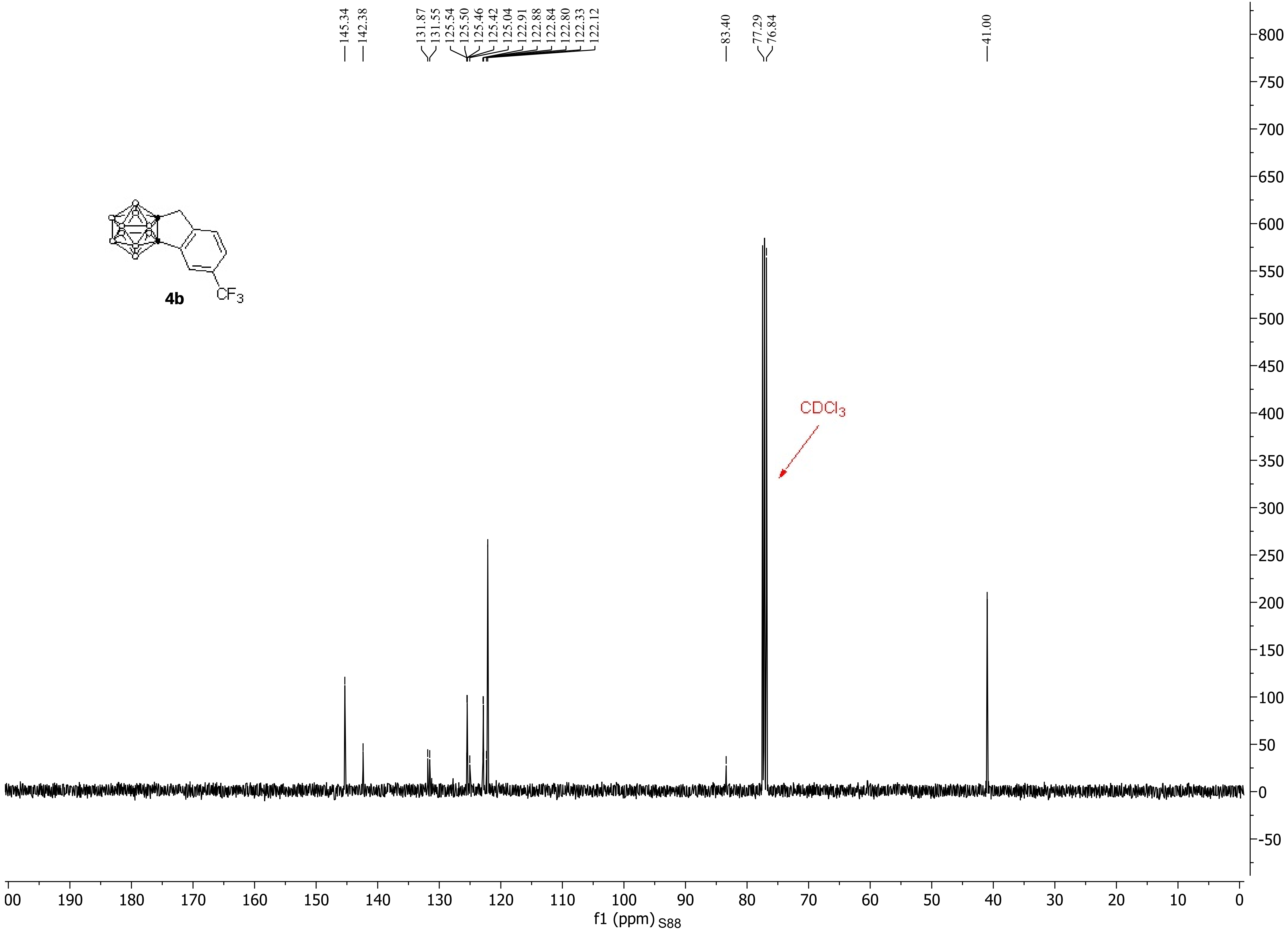

133.56
129.73
128.84
127.88
77.48
77.16
76.84
69.50
53.64
Me
Me
H
3y
CDCl$_3$
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

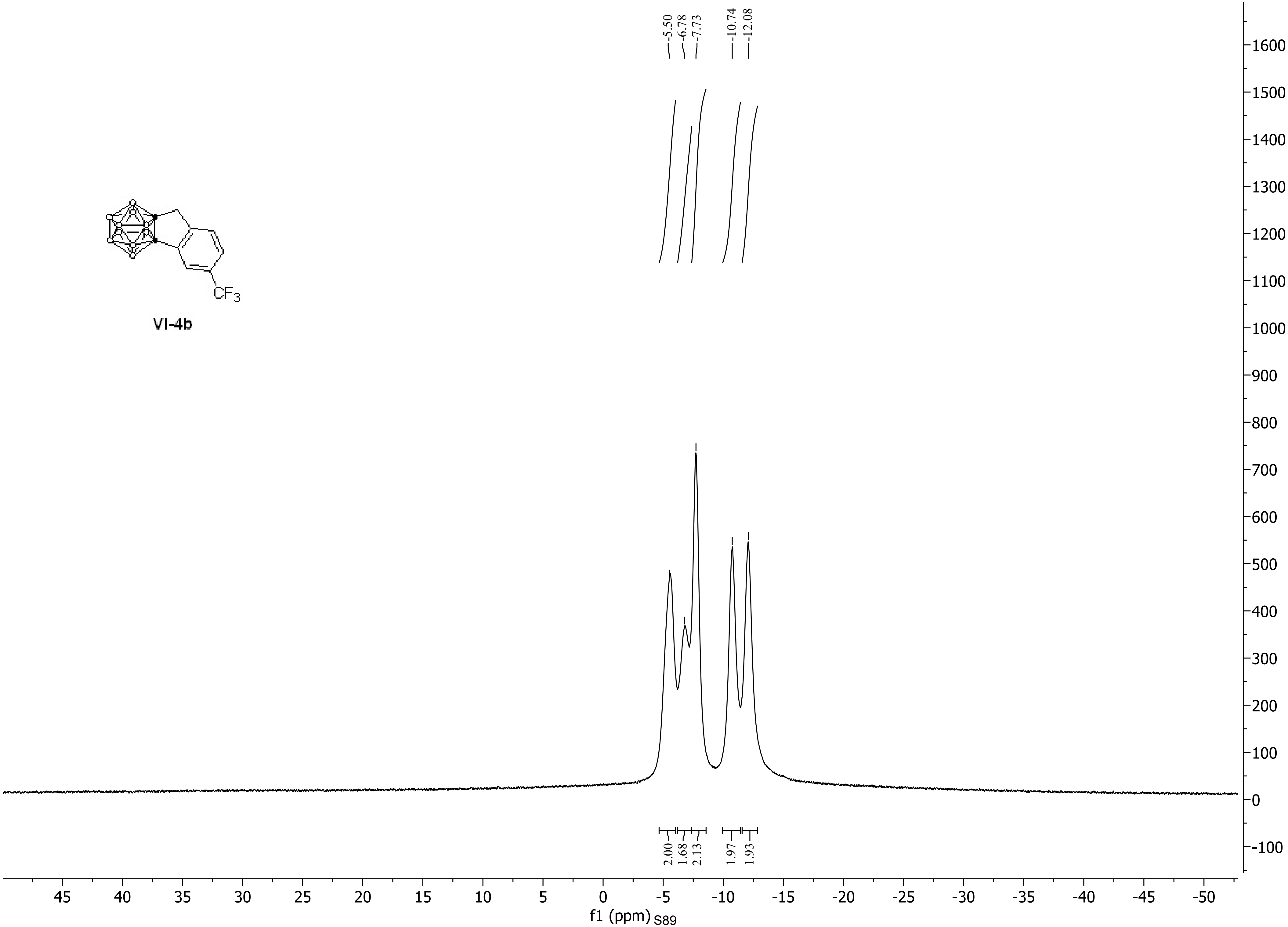

7.36
5.19
-7.44
-11.24
-13.31
Me
Me
H
3y
1.14
1.00
2.11
2.09
4.06
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


7.35
7.33
7.30
7.29
7.27
7.25
7.24
7.23
7.19
7.17
3.66
1.54
4a
CDCl$_3$
1.09
2.22
1.00
2.16
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
.0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

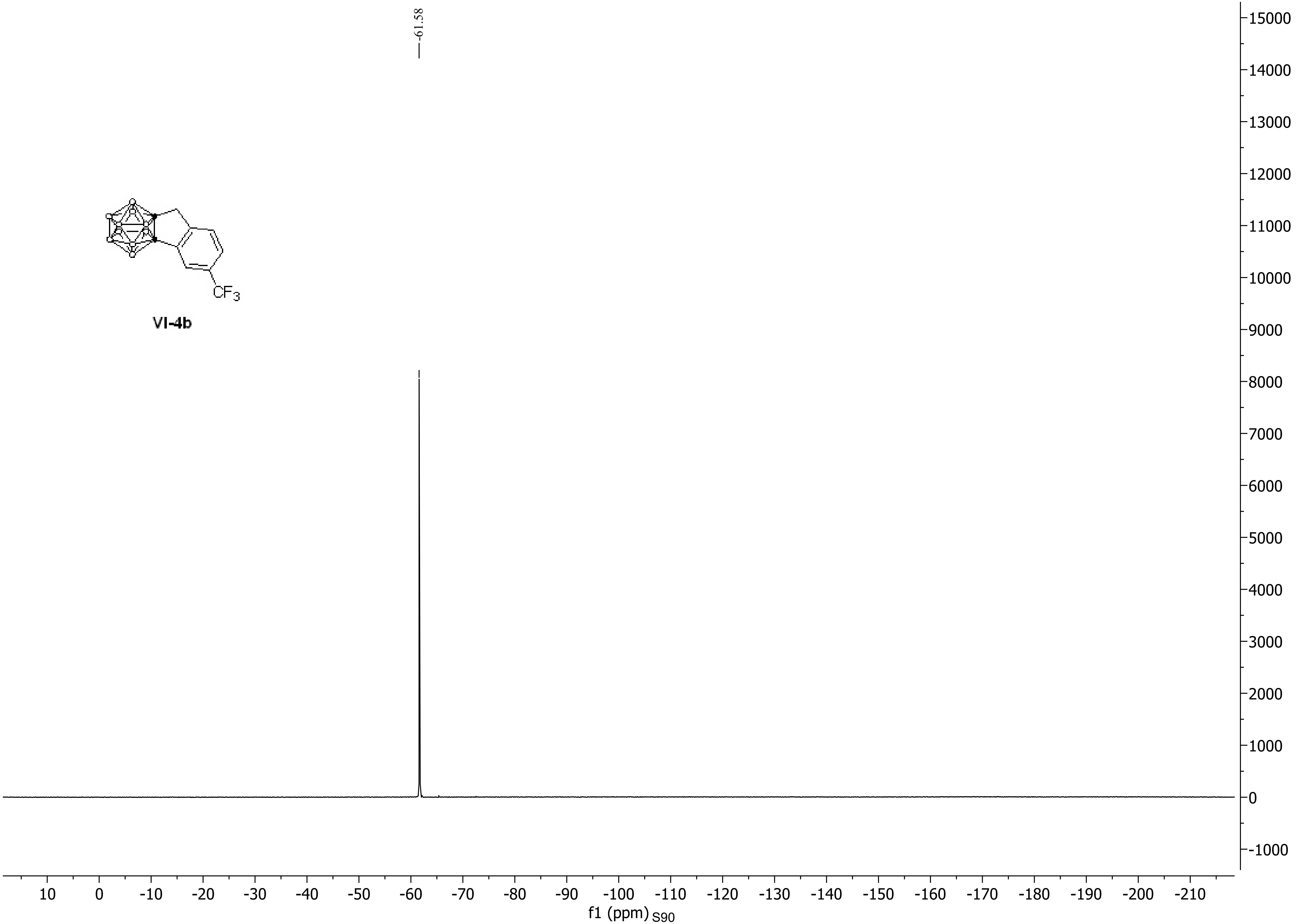

-6.88
-8.92
-11.82
-13.12
4a
4.00
2.13
2.11
1.97
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

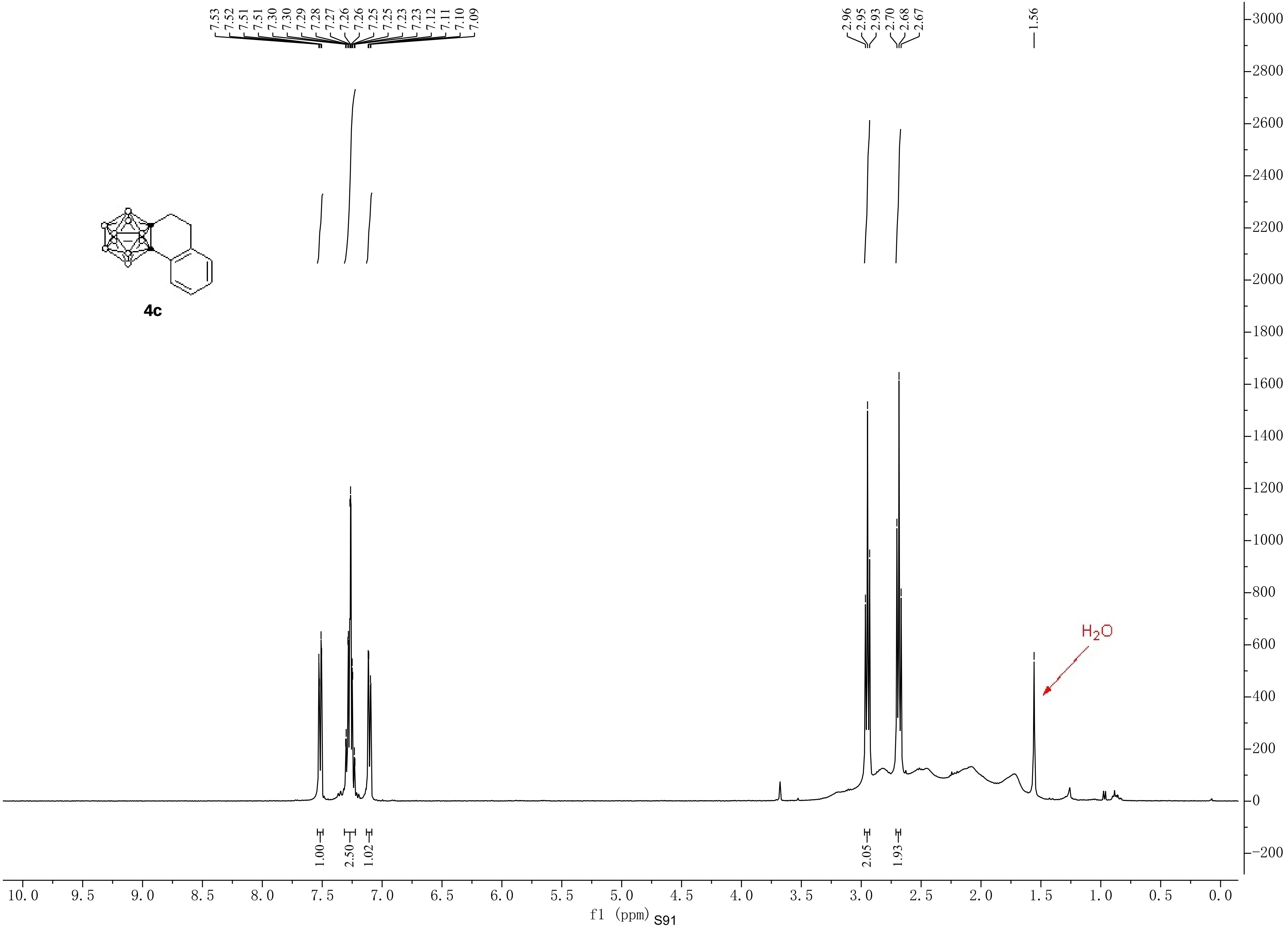

7.58
7.56
7.49
7.47
7.26
3.74
1.56
CF_3
4b
$CDCl_3$
H_2O
1.00
1.91
1.90
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

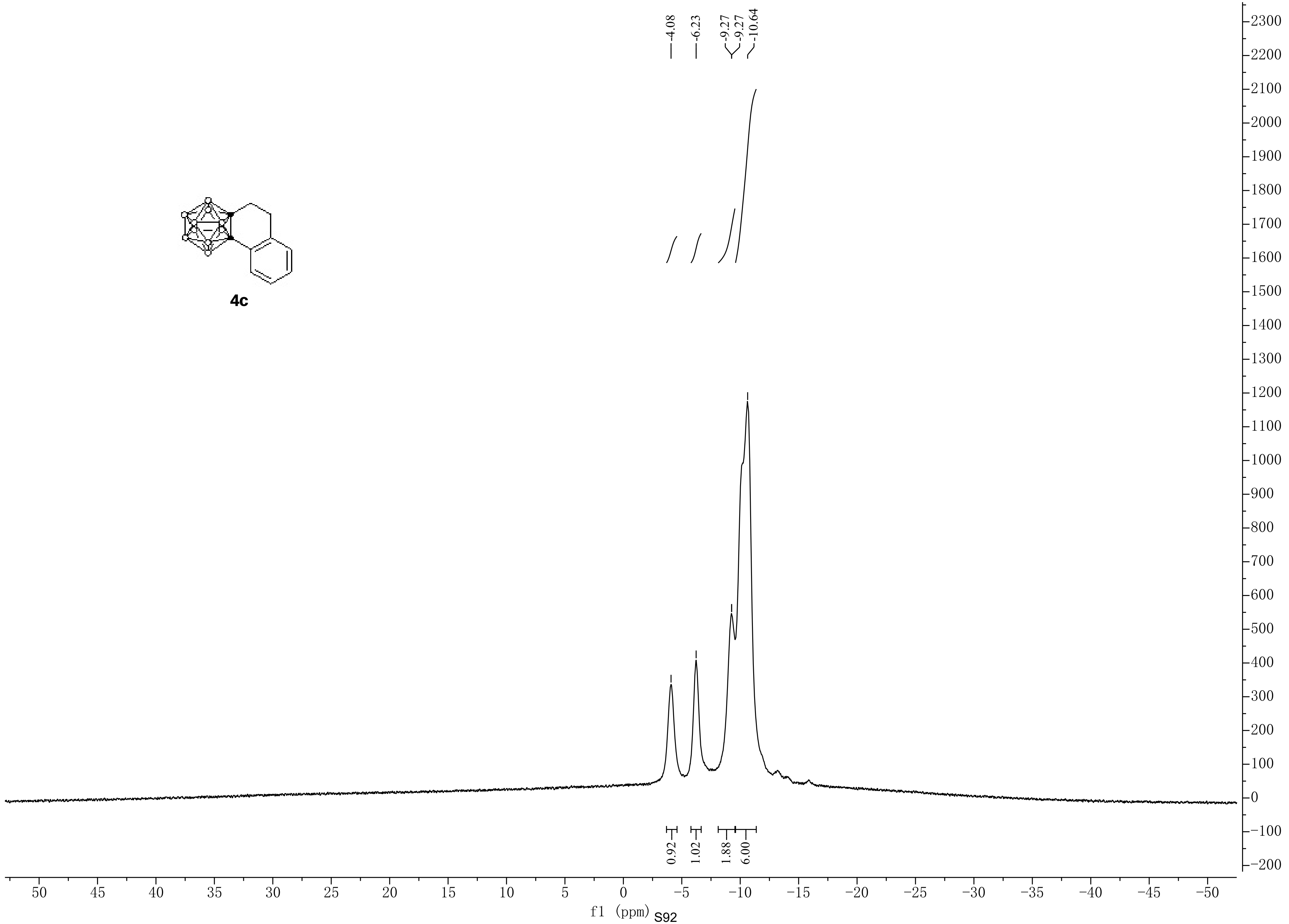

145.34
142.38
131.87
131.55
125.54
125.50
125.46
125.42
125.04
122.91
122.88
122.84
122.80
122.33
122.12
83.40
77.29
76.84
41.00
CF3
4b
CDCl3
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

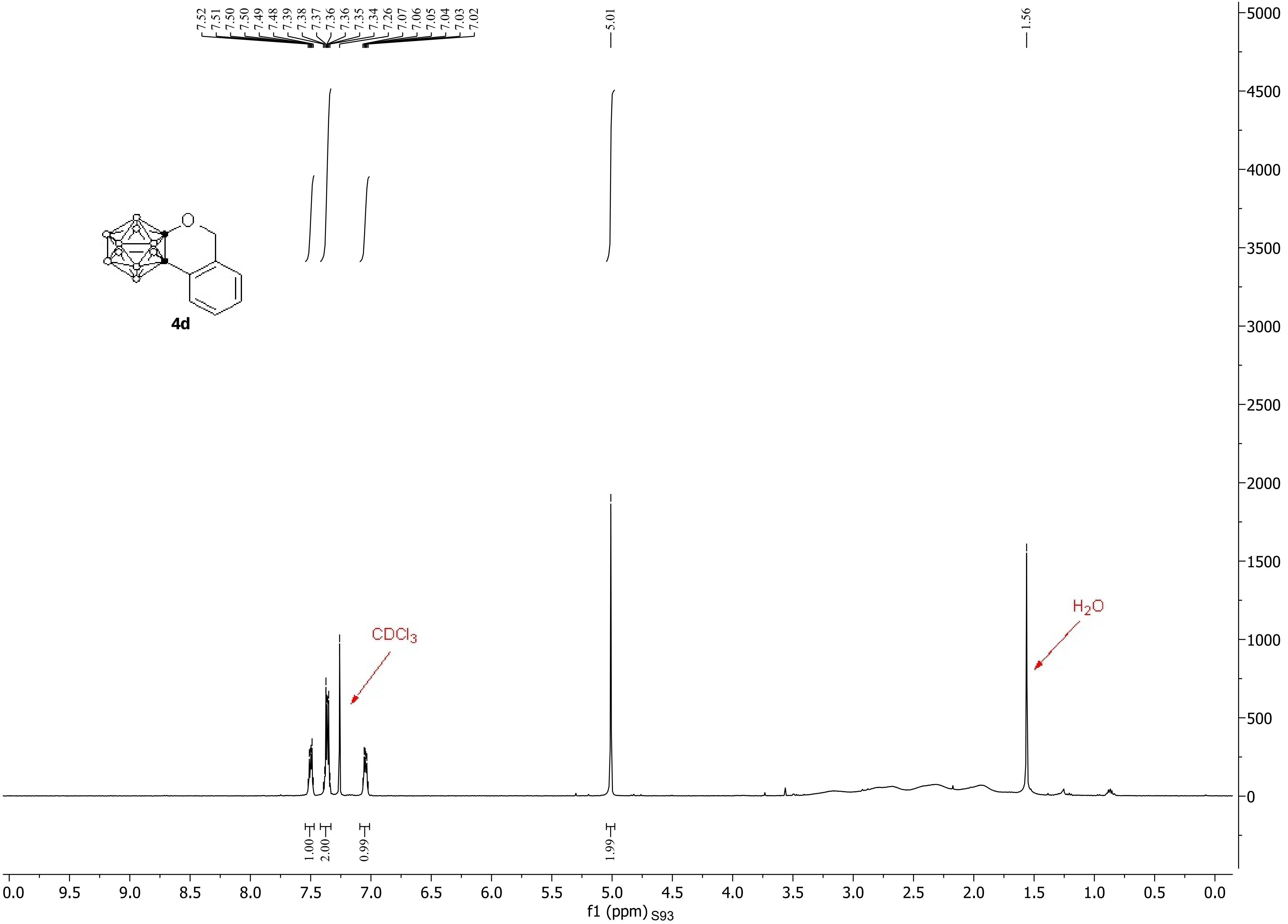

-5.50
-6.78
-7.73
-10.74
-12.08
CF$_3$
2.00
1.68
2.13
1.97
1.93
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

VI-4b


-61.58
CF$_3$
VI-4b
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

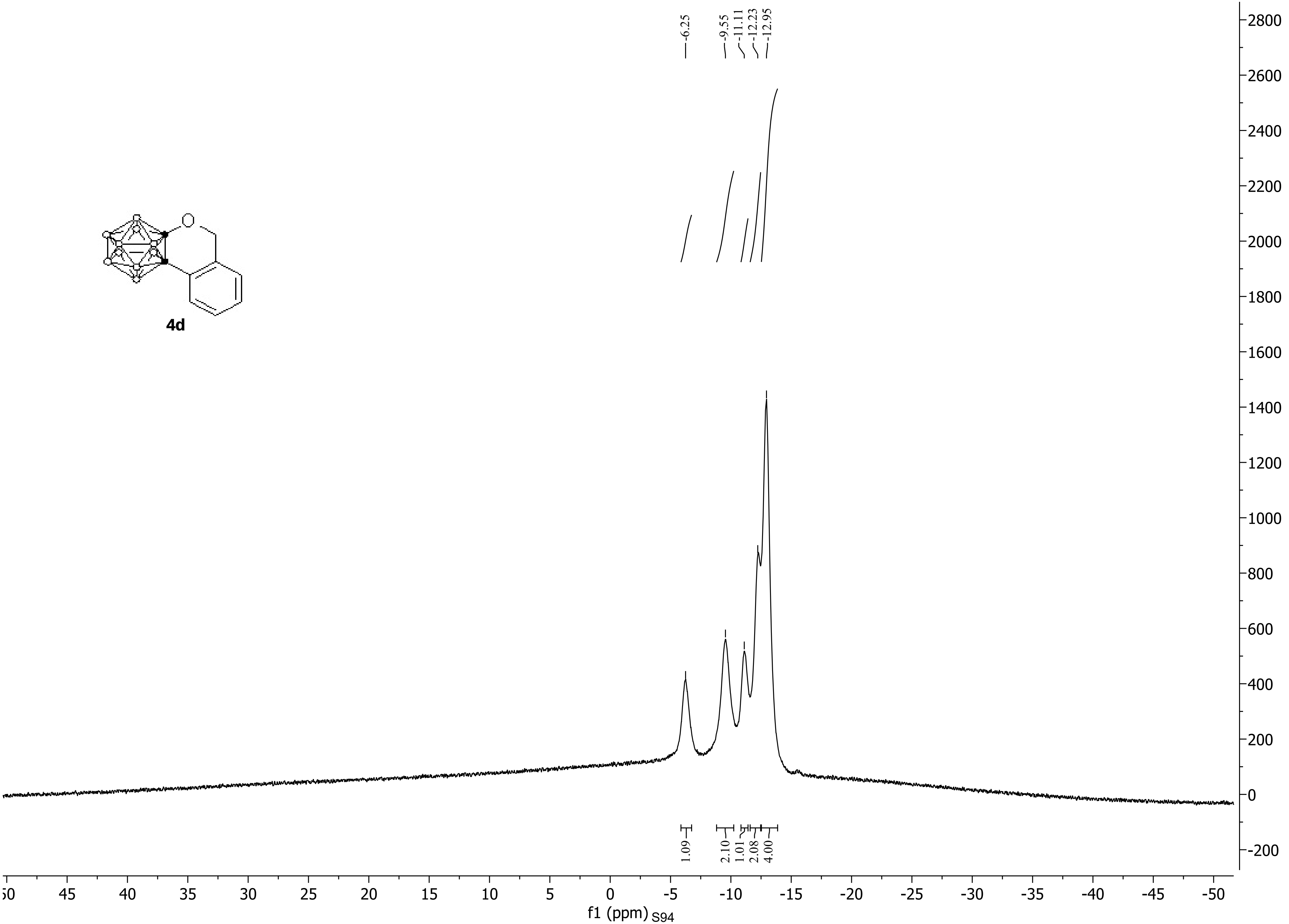

7.53
7.52
7.51
7.51
7.30
7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.25
7.23
7.23
7.12
7.11
7.10
7.09
2.96
2.95
2.93
2.70
2.68
2.67
1.56
4c
H2O
1.00
2.50
1.02
2.05
1.93
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-4.08
-6.23
-9.27
-9.27
-10.64
4c
0.92
1.02
1.88
6.00
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
50
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
−50
f1 (ppm)



4d

7.52
7.51
7.50
7.50
7.49
7.48
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.26
7.07
7.06
7.05
7.04
7.03
7.02
5.01
1.56
O
CDCl$_3$
H$_2$O
1.00
2.00
0.99
1.99
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4d
-6.25
-9.55
-11.11
-12.23
-12.95
1.09
2.10
1.01
2.08
4.00
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200