Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Rhodium(II)-catalyzed transannulation approach to N-fluoroalkylated indoles

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General information

All commercially available chemicals were used as received unless stated otherwise. Starting acetylenes and azides were prepared according to procedures published in the literature[1–3].

Automated flash column chromatography was performed on Teledyne ISCO CombiFlash Rf+ Lumen Automated Flash Chromatography System with UV/Vis detection.

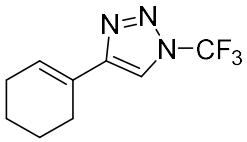
^{1}H, ^{13}C, and ^{19}F NMR spectra were measured at ambient temperature using 5 mm diameter NMR tubes. ^{13}C spectra were proton decoupled. The chemical shift values (δ) are reported in ppm relative to internal Me_4Si (0 ppm for ^{1}H and ^{13}C NMR) or residual solvents and internal $CFCl_3$ (0 ppm for ^{19}F NMR). Coupling constants (J) are reported in Hertz. Structural elucidation was aided by the additional acquisition of ^{13}C APT and/or various 2D spectra (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{13}C-^{19}F HMBC).

GC-MS spectra were recorded on Agilent 7890A GC (column HP-5MS, 30 m × 0.25 mm × 0.25 μm, 5% phenyl methylpolysiloxane) coupled with 5975C quadrupole mass selective electron impact (EI) detector (70 eV). High-resolution MS spectra (HRMS) were recorded on a Waters Micromass AutoSpec Ultima or Agilent 7890A GC coupled with Waters GCT Premier orthogonal acceleration time-of-flight detector using electron impact (EI) ionization or chemical ionization (CI). CEM Discover System (300 W power) was used for reactions carried out in a microwave reactor.

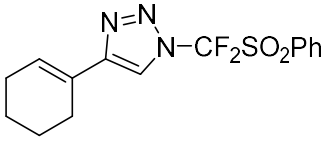
General procedures and spectroscopic data

General procedure A. Copper(I) 3-methylsalicylate (53.5 mg, 0.25 mmol) was placed in a 10 ml screw-cap glass tube and a cold solution of azide in THF (~6 mmol, 4-6 ml) was added. Subsequently, alkyne (5.0 mmol) in THF (1 ml) was added, and the flask was closed and stirred at rt for 18 h. The product was purified by flash column chromatography on silica gel (cyclohexane/EtOAc).

4-(cyclohex-1-en-1-yl)-1-(trifluoromethyl)-1H-1,2,3-triazole (**1a**): Prepared according to the **general procedure A** with trifluoromethyl azide as the starting azide. Yield: 79% (857 mg); colorless oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.41 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 6.71 (tt, *J* = 4.0, 1.8 Hz, 1H), 2.44 – 2.13 (m, 4H), 1.86 – 1.61 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 128.2, 125.7, 117.8 (q, $^{1}J_{C\text{-}F}$ = 267.4 Hz), 115.6, 26.4, 25.4, 22.4, 22.1; HRMS (APCI$^+$) *m/z* calcd for $C_9H_{11}F_3N_3$ $[M+H]^+$: 218.0905, found 218.0900.

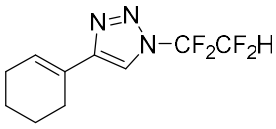


4-(cyclohex-1-en-1-yl)-1-(perfluoroethyl)-1H-1,2,3-triazole (**1b**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 60% (801 mg); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.44 (s, 3F), -99.19 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 6.73 (tt, *J* = 4.0, 1.8 Hz, 1H), 2.37 (tdd, *J* = 6.2, 2.7, 1.8 Hz, 2H), 2.24 (ddd, *J* = 6.1, 5.0, 3.1 Hz, 2H), 1.83 – 1.76 (m, 2H), 1.74 – 1.66 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 128.3, 125.7, 117.2 (qt, $^{1}J_{C\text{-}F}$ = 287.5 Hz, $^{2}J_{C\text{-}F}$ = 41.6 Hz, CF_3), 116.3, 110.3 (tq, $^{1}J_{C\text{-}F}$ = 269.9 Hz, $^{2}J_{C\text{-}F}$ = 43.0 Hz, CF_2), 26.3, 25.4, 22.3, 22.1; HRMS (APCI$^+$) *m/z* calcd for $C_{10}H_{11}F_5N_3$ $[M+H]^+$: 268.0873, found 268.0868.

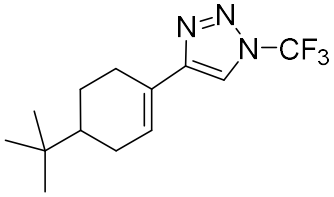


4-(cyclohex-1-en-1-yl)-1-(difluoro(phenylsulfonyl)methyl)-1H-1,2,3-triazole (**1c**): Prepared according to the **general procedure A** with ((azidodifluoromethyl)sulfonyl)benzene as the starting azide. Yield: 80% (1.36 g); colorless solid. The spectral data matched the published ones in literature[3].

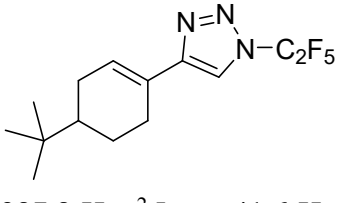
4-(cyclohex-1-en-1-yl)-1-(1,1,2,2-tetrafluoroethyl)-1H-1,2,3-triazole (**1d**): Prepared according to the **general procedure A** with 1,1,2,2-tetrafluoroethyl azide as the starting azide. Yield 91% (747 mg); pale-yellow oil; ^{19}F NMR (377 MHz, $CDCl_3$) δ -99.4 (td, *J* = 7.8, 4.7 Hz, 2F), -137.9 (dt, *J* = 52.4, 7.9 Hz, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.67 (tt, *J* = 3.9, 1.7 Hz, 1H), 6.60 (tt, *J* = 52.4, 4.6 Hz, 1H), 2.38 – 2.31 (m, 2H), 2.23 – 2.16 (m, 2H), 1.80 – 1.71 (m, 2H), 1.66 (t, *J* = 2.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 127.9, 125.9, 115.9, 112.2 (tt, $^{1}J_{C\text{-}F}$ = 265.5 Hz, $^{2}J_{C\text{-}F}$ 29.2 Hz, CF_2), 107.8 (tt, $^{1}J_{C\text{-}F}$ = 253.5 Hz, $^{2}J_{C\text{-}F}$ 35.5 Hz, CF_2H), 26.3, 25.3, 22.3, 22.0; HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{12}F_4N_3$ $[M+H]^+$: 250.0962, found 250.0964.



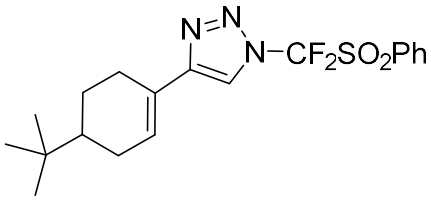
4-(4-(tert-butyl)cyclohex-1-en-1-yl)-1-(trifluoromethyl)-1H-1,2,3-triazole (**1e**): Prepared according to the **general procedure A** with trifluoromethyl azide as the starting azide. Yield: 91% (1.24 g); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.40 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 6.70 (dt, *J* = 5.2, 2.4 Hz, 1H), 2.49 (ddt, *J* = 18.3, 4.8, 2.4 Hz, 1H), 2.40 – 2.22 (m, 2H), 1.98 (dddd, *J* = 14.9, 8.1, 4.4, 2.3 Hz, 2H), 1.43 – 1.25 (m, 2H), 0.91 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 128.4, 125.5, 121.0, 117.8 (q, $J_{C\text{-}F}$ = 267.6 Hz), 43.9, 32.4, 27.8, 27.3, 27.1, 23.8; HRMS (ESI^+) *m/z* calcd for $C_{13}H_{19}F_3N_3$ $[M+H]^+$: 274.1526, found 274.1525.



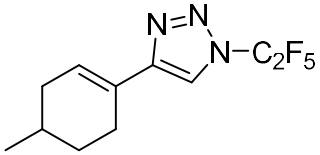
4-(4-(tert-butyl)cyclohex-1-en-1-yl)-1-(perfluoroethyl)-1H-1,2,3-triazole (**1f**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 82% (1.32 g); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.43 (s, 3F), -99.17 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.70 (s, 1H), 6.76 – 6.68 (m, 1H), 2.56 – 2.44 (m, 1H), 2.43 – 2.22 (m, 2H), 2.07 – 1.93 (m, 2H), 1.45 – 1.23 (m, 2H), 0.91 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 128.6, 125.5, 118.6 (qt, $^1J_{C\text{-}F}$ = 287.8 Hz, $^2J_{C\text{-}F}$ = 41.6 Hz, CF_3), 116.3, 111.6 (tq, $^1J_{C\text{-}F}$ = 270.0 Hz, $^2J_{C\text{-}F}$ = 43.1 Hz, CF_2), 43.9, 32.4, 27.9, 27.3, 27.2, 23.8; HRMS (EI^+) *m/z* calcd for $C_{14}H_{18}F_5N_3$ $[M]^+$: 323.1415, found 323.1421.

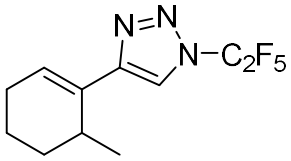


4-(4-(tert-butyl)cyclohex-1-en-1-yl)-1-(difluoro(phenylsulfonyl)methyl)-1H-1,2,3-triazole (**1g**): Prepared according to the **general procedure A** with ((azidodifluoromethyl)sulfonyl)benzene as the starting azide. Yield: 83% (1.64 g); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.94 (s); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.83 (td, *J* = 7.5, 1.2 Hz, 1H), 7.79 (s, 1H), 7.68 – 7.61 (m, 2H), 6.70 (dt, *J* = 5.4, 2.5 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.41 – 2.23 (m, 2H), 2.05 – 1.94 (m, 2H), 1.44 – 1.26 (m, 2H), 0.91 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 136.8, 131.1, 130.8, 130.0, 128.4, 125.6, 117.4, 116.2 (t, $J_{C\text{-}F}$ = 305.3 Hz), 43.9, 32.4, 27.8, 27.3, 27.1, 23.8; HRMS (ESI^+) *m/z* calcd for $C_{19}H_{24}O_2F_2N_3S$ $[M+H]^+$: 396.1552, found 396.1553; $C_{19}H_{23}O_2F_2N_3NaS$ $[M+Na]^+$: 418.1371, found 418.1373.



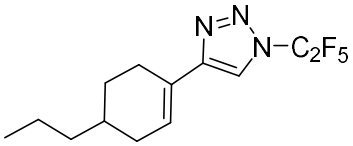
4-(4-methylcyclohex-1-en-1-yl)-1-(perfluoroethyl)-1H-1,2,3-triazole (**1h**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 64% (899 mg); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.43 (s, 3F), -99.19 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.71 (s, 1H), 6.79 – 6.45 (m, 1H), 2.57 – 2.21 (m, 3H), 1.93 – 1.82 (m, 3H), 1.46 – 1.31 (m, 1H), 1.02 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 127.9, 125.4, 117.2 (qt, $^1J_{C\text{-}F}$ = 287.8 Hz, $^2J_{C\text{-}F}$ = 41.6 Hz, CF_3), 116.3, 111.6 (tq, $^1J_{C\text{-}F}$ = 270.0 Hz, $^2J_{C\text{-}F}$ = 43.1 Hz, CF_2), 33.9, 30.5, 28.2, 26.4, 21.7; HRMS (EI^+) *m/z* calcd for $C_{11}H_{12}F_5N_3$ $[M]^+$: 281.0946, found 281.0944.



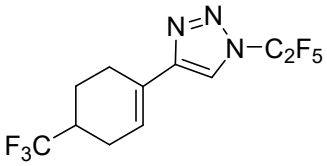


4-(6-methylcyclohex-1-en-1-yl)-1-(perfluoroethyl)-1H-1,2,3-triazole (**1i**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 76% (1.07 g); colorless oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.42 (s, 3F), -99.13 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.74 (s, 1H), 6.57 – 6.50 (m, 1H), 2.82 – 2.69 (m, 1H), 2.28 – 2.10 (m, 2H), 1.92 – 1.56 (m, 4H), 1.11 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 131.2, 128.6, 117.2 (qt, $^{1}J_{C\text{-}F}$ = 287.0 Hz, $^{2}J_{C\text{-}F}$ = 41.6 Hz, CF_3), 116.9, 110.3 (tq, $^{1}J_{C\text{-}F}$ = 270.7 Hz, $^{2}J_{C\text{-}F}$ = 43.0 Hz, CF_2), 29.9, 29.8, 25.8, 19.9, 17.8; HRMS (EI$^+$) *m/z* calcd for $C_{11}H_{12}F_5N_3$ $[M]^+$: 281.0946, found 281.0946.

1-(perfluoroethyl)-4-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-1H-1,2,3-triazole (**1j**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 66% (1.13 g); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.41 (s, 3F), -99.16 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.47 – 7.12 (m, 5H), 6.85 (tt, J = 3.3, 1.6 Hz, 1H), 3.04 – 2.84 (m, 1H), 2.65 – 2.54 (m, 3H), 2.50 – 2.35 (m, 1H), 2.23 – 2.11 (m, 1H), 2.05 – 1.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 146.3, 128.6, 127.7, 127.0, 126.4, 125.6, 117.2 (qt, $^{1}J_{C\text{-}F}$ = 287.6 Hz, $^{2}J_{C\text{-}F}$ = 41.5 Hz, CF_3), 116.5, 110.3 (tq, $^{1}J_{C\text{-}F}$ = 271.5 Hz, $^{2}J_{C\text{-}F}$ = 43.1 Hz, CF_2), 39.7, 33.5, 29.5, 27.0; HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{15}F_5N_3$ $[M]^+$: 344.1181, found 344.1181.

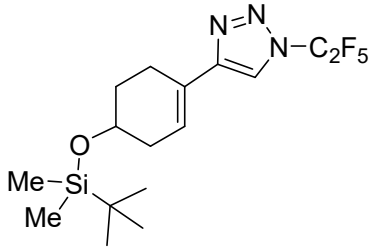


1-(perfluoroethyl)-4-(4-propylcyclohex-1-en-1-yl)-1H-1,2,3-triazole (**1k**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 78% (1.20 g); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.44 (s, 3F), -99.19 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 6.76 – 6.56 (m, 1H), 2.47 – 2.30 (m, 3H), 1.94 – 1.79 (m, 2H), 1.69 – 1.57 (m, 1H), 1.42 – 1.34 (m, 3H), 1.34 – 1.27 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 127.9, 125.6, 117.2 (qt, $^{1}J_{C\text{-}F}$ = 287.2 Hz, $^{2}J_{C\text{-}F}$ = 41.6 Hz, CF_3), 116.3, 110.3 (tq, $^{1}J_{C\text{-}F}$ = 269.4 Hz, $^{2}J_{C\text{-}F}$ = 43.0 Hz, CF_2), 38.7, 32.9, 32.1, 28.6, 26.4, 20.1, 14.4; HRMS (ESI$^+$) *m/z* calcd for $C_{13}H_{17}F_5N_3$ $[M+H]^+$: 310.1337, found 310.1336.



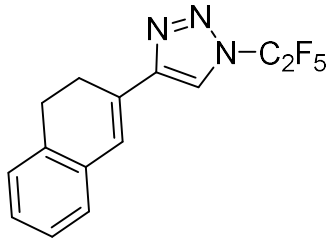
1-(perfluoroethyl)-4-(4-(trifluoromethyl)cyclohex-1-en-1-yl)-1H-1,2,3-triazole (**1l**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 75% (1.26 g); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.15 (d, J = 7.8 Hz, 3F), -84.41 (s, 3F), -99.18 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.71 – 6.62 (m, 1H), 2.73 – 2.56 (m, 1H), 2.55 – 2.25 (m, 4H), 2.24 – 2.11 (m, 1H), 1.80 – 1.64 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 127.8 (q, J = 278.3 Hz), 125.8, 124.8, 117.1 (qt, $^{1}J_{C\text{-}F}$ = 287.5, $^{2}J_{C\text{-}F}$ = 41.4 Hz, CF_3), 116.8, 110.3 (tq, $^{1}J_{C\text{-}F}$ = 270.6, $^{2}J_{C\text{-}F}$ = 43.2 Hz, CF_2), 38.3 (q, J = 27.5 Hz), 25.4, 24.4 (q, J = 2.9 Hz), 21.3 (q, J = 2.8 Hz); HRMS (ESI$^+$) *m/z* calcd for $C_{11}H_9F_8N_3$ $[M+H]^+$: 336.0742, found 336.0743.

4-(4-((tert-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)-1-(perfluoroethyl)-1H-1,2,3-triazole (**1m**):



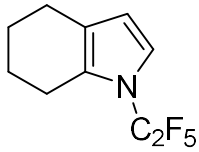
Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 85% (1.69 g); yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.43 (s, 3F), -99.17 (s, 2F); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 6.58 (ddt, *J* = 5.0, 3.4, 1.6 Hz, 1H), 4.05 – 3.96 (m, 1H), 2.62 – 2.52 (m, 1H), 2.51 – 2.35 (m, 2H), 2.28 – 2.15 (m, 1H), 1.97 – 1.88 (m, 1H), 1.83 – 1.72 (m, 1H), 0.89 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 125.4, 125.1, 116.9 (qt, $^{1}J_{C\text{-}F}$ = 287.0 Hz, $^{2}J_{C\text{-}F}$ = 41.6 Hz, CF_3), 116.3, 110.0 (tq, $^{1}J_{C\text{-}F}$ = 270.9 Hz, $^{2}J_{C\text{-}F}$ = 43.1 Hz, CF_2), 66.8, 34.9, 30.9, 25.7, 24.7, 18.1, -4.8; HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{25}OF_5N_3Si$ $[M+H]^+$: 398.1687, found 398.1683.

4-(3,4-dihydronaphthalen-2-yl)-1-(perfluoroethyl)-1H-1,2,3-triazole (**1n**): Prepared according to the **general procedure A** with pentafluoroethyl azide as the starting azide. Yield: 72% (1.13 g); colorless solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.35 (s, 3F), -99.12 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.24 – 7.04 (m, 4H), 2.99 (dd, *J* = 9.2, 7.2 Hz, 2H), 2.75 (ddd, *J* = 9.5, 7.3, 1.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 135.2, 133.5, 128.1, 127.6, 127.3, 127.0, 126.6, 126.2, 117.1 (qt, $^{1}J_{C\text{-}F}$ = 288.4 Hz, $^{2}J_{C\text{-}F}$ = 41.6 Hz, CF_3), 117.4, 110.3 (tq, $^{1}J_{C\text{-}F}$ = 270.4 Hz, $^{2}J_{C\text{-}F}$ = 43.1 Hz, CF_2), 27.6, 25.0; HRMS (ESI$^+$) *m/z* calcd for $C_{14}H_{11}F_5N_3$ $[M+H]^+$: 316.0873, found 316.0867.



General procedure B. *N*-(per)fluoroalkyl-triazole **1a-1i** (0.20 mmol) and bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] $Rh_2(esp)_2$ (1 mol%; 1.52 mg) were dissolved in dry DCE (2 ml) in a 10 ml microwave tube. The vial was flushed with nitrogen, capped and heated at 100 °C for 30 min in a microwave reactor. The resulting mixture was filtered through a pad of alumina, the solvent was evaporated under nitrogen flow or under vacuum. If necessary, purification using flash chromatography using silica gel (cyclohexane/EtOAc) was performed.

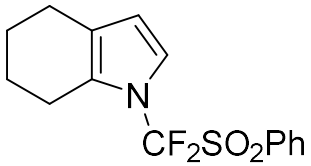
1-(trifluoromethyl)-4,5,6,7-tetrahydro-1H-indole **(2a)**: Prepared according to the **general procedure B**. ^{19}F NMR yield: 64%. To provide the NMR spectra, the reaction was repeated in $CDCl_3$ and worked up by filtering through alumina. ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.6 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.79 (m, 1H), 6.02 (d, *J* = 3.3 Hz, 1H), 2.65 (t, *J* = 6.0 Hz, 2H), 2.46 (t, *J* = 6.1 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.77 – 1.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.5, 121.9, 119.5 (q, $J_{C\text{-}F}$ = 260.1 Hz), 116.6, 110.7, 23.02, 23.00, 22.97, 22.3–22.1 (m); HRMS (EI$^+$) *m/z* calcd for $C_9H_{10}F_3N$ $[M]^+$: 189.0765, found 189.0760.



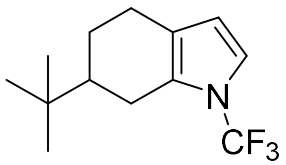
1-(perfluoroethyl)-4,5,6,7-tetrahydro-1H-indole (**2b**): Prepared according to the **general procedure B**. ^{19}F NMR yield: 92%, isolated yield: 10%; pale-yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (s, 3F), -96.3 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (ddt, *J* = 3.4, 1.7, 0.9 Hz, 1H), 6.08 (d, *J* = 3.3 Hz, 1H), 2.64 (t, *J* = 6.1 Hz, 2H), 2.48 (t, *J* = 6.1 Hz, 2H), 1.86 – 1.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.5, 122.2, 118.1 (qt, $^{1}J_{C\text{-}F}$ = 288.2, $^{2}J_{C\text{-}F}$ = 48.3 Hz, CF_3), 117.5 (t, *J* = 2.8 Hz), 111.9

(tq, $^{1}J_{C\text{-}F}$ = 263.3 Hz, $^{2}J_{C\text{-}F}$ = 41.6 Hz, CF_2), 111.5, 23.3, 23.24, 23.20, 23.0; HRMS (EI^+) *m/z* calcd for $C_{10}H_{10}F_5N$ $[M]^+$: 239.0728, found 239.0733.

1-(difluoro(phenylsulfonyl)methyl)-4,5,6,7-tetrahydro-1H-indole (**2c**): Prepared according to the **general procedure B**. Yield: 42%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.3 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.76 (ddt, *J* = 8.8, 7.3, 1.3 Hz, 1H), 7.65 – 7.54 (m, 2H), 6.71 (d, *J* = 3.3 Hz, 1H), 6.07 (d, *J* = 3.3 Hz, 1H), 2.56 – 2.41 (m, 4H), 1.76 – 1.60 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 132.8, 130.7, 129.6, 129.2 (t, *J* = 1.3 Hz), 122.6 – 122.4 (m), 118.7 (t, *J* = 2.9 Hz), 118.3 (t, *J* = 298.6 Hz), 112.0, 23.3, 23.2 – 23.0 (m), 22.9, 22.9 – 22.7 (m); HRMS (ESI^+) *m/z* calcd for $C_{15}H_{16}O_2F_2NS$ $[M+H]^+$: 312.0864, found 312.0866, $C_{15}H_{15}O_2F_2NNaS$ $[M+Na]^+$: 334.0689, found 334.0686.

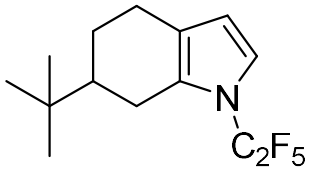


1-(1,1,2,2-tetrafluoroethyl)-4,5,6,7-tetrahydro-1H-indole (**2d**): Prepared according to the **general procedure B** (microwave heating to 140 °C for 30 min). Yield: 54%; pale yellow oil; ^{19}F NMR (377 MHz, $CDCl_3$) δ -94.9 (t, *J* = 5.6 Hz, 2F), -134.8 (dt, *J* = 53.4, 6.1 Hz, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 6.73 (d, *J* = 3.1 Hz, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 5.96 (tt, $^{2}J_{HF}$ = 53.4, $^{3}J_{HF}$ = 2.4 Hz, 1H), 2.66 (t, *J* = 5.8 Hz, 2H), 2.49 (t, *J* = 5.9 Hz, 2H), 1.88 – 1.67 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.8, 121.8, 117.1, 113.8 (tt, $^{1}J_{C\text{-}F}$ = 258.8 Hz, $^{2}J_{C\text{-}F}$ = 29.0 Hz, CF_2), 110.9, 108.9 (tt, $^{1}J_{C\text{-}F}$ = 253.6 Hz, $^{2}J_{C\text{-}F}$ = 46.9 Hz, CF_2H), 23.3, 23.2, 23.11, 23.05; HRMS ($APCI^+$) *m/z* calcd for $C_{10}H_{12}F_4N$ $[M+H]^+$: 222.0906, found 222.0901.

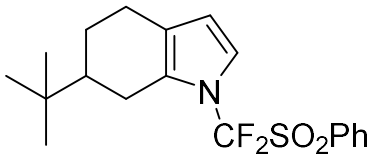


6-(tert-butyl)-1-(trifluoromethyl)-4,5,6,7-tetrahydro-1H-indole (**2e**): Prepared according to the **general procedure B**. Isolated yield: 62%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.5 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.76 (m, 1H), 6.02 (d, *J* = 3.3 Hz, 1H), 2.72 (dd, *J* = 16.1, 4.6 Hz, 1H), 2.56 (ddd, *J* = 14.1, 5.1, 1.8 Hz, 1H), 2.46 – 2.29 (m, 2H), 1.97 (dtd, *J* = 10.8, 3.4, 1.6 Hz, 1H), 1.56 – 1.44 (m, 1H), 1.36 – 1.17 (m, 1H), 0.95 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.2, 122.5–121.4 (m), 119.6 (q, $^{1}J_{C\text{-}F}$ = 260.1 Hz), 117.0 (q, *J* = 2.3 Hz), 110.3, 45.2, 32.7, 27.5, 24.8, 23.7, 23.7 (q, *J* = 1.9 Hz); HRMS (EI^+) *m/z* calcd for $C_{13}H_{18}F_3N$ $[M]^+$: 245.1386, found 245.1387.

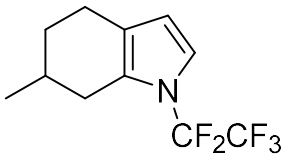
6-(tert-butyl)-1-(perfluoroethyl)-4,5,6,7-tetrahydro-1H-indole (**2f**): Prepared according to the **general procedure B**. ^{19}F NMR yield: 99%, isolated yield: 58%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.1 (s, 3F), -95.6 (d, ^{2}J = 222.4 Hz, 1F), -96.5 (d, ^{2}J = 222.4 Hz, 1F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 – 6.68 (m, 1H), 6.07 (d, *J* = 3.3 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.62 – 2.53 (m, 1H), 2.48 – 2.24 (m, 2H), 2.01 – 1.89 (m, 1H), 1.59 – 1.40 (m, 1H), 1.36 – 1.13 (m, 1H), 0.94 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.6 – 128.7 (m), 122.2, 118.1 (qt, $^{1}J_{C\text{-}F}$ = 288.2, $^{2}J_{C\text{-}F}$ = 48.4 Hz, CF_3), 111.9 (tq, $^{1}J_{C\text{-}F}$ = 262.9 Hz, $^{2}J_{C\text{-}F}$ = 41.8 Hz, CF_2), 118.0–117.5 (m), 111.1, 45.3, 32.7, 27.5, 24.7, 24.6–24.3 (m), 23.9; HRMS (EI^+) *m/z* calcd for $C_{14}H_{18}F_5N$ $[M]^+$: 295.1354, found 295.1361.



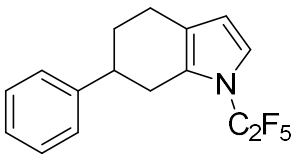
6-(tert-butyl)-1-(difluoro(phenylsulfonyl)methyl)-4,5,6,7-tetrahydro-1H-indole (**2g**): Prepared according to the **general procedure B**. ^{19}F NMR yield: 58%, isolated yield: 58%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.6 (d, ^2J = 187.7 Hz, 1F), -87.3 (d, ^2J = 187.6 Hz, 1F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.3 Hz, 2H), 7.75 (tt, J = 7.2, 1.2 Hz, 1H), 7.58 (ddd, J = 8.9, 7.7, 1.5 Hz, 2H), 6.72 (d, J = 3.3 Hz, 1H), 6.06 (d, J = 3.3 Hz, 1H), 2.57 – 2.48 (m, 2H), 2.42 – 2.31 (m, 1H), 2.13 – 1.98 (m, 1H), 1.93 – 1.74 (m, 1H), 1.31 (tdd, J = 11.5, 5.1, 1.9 Hz, 1H), 1.15 (qd, J = 12.2, 5.1 Hz, 1H), 0.88 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 132.7, 130.7, 129.9, 129.5, 122.4, 119.1 (t, J = 2.8 Hz), 118.3 (t, $J_{C\text{-}F}$ = 298.6 Hz), 111.6, 45.1, 32.6, 27.5, 24.5, 24.2 (t, J = 3.6 Hz), 23.9.; HRMS (EI$^+$) *m/z* calcd for $C_{19}H_{23}F_2NO_2S$ $[M]^+$: 367.1412, found 367.1413.



6-methyl-1-(perfluoroethyl)-4,5,6,7-tetrahydro-1H-indole (**2h**): Prepared according to the **general procedure B**. ^{19}F NMR yield: 99%, isolated yield: 38%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (s, 3F), -95.8 (d, ^2J = 222.4 Hz, 1F), -96.7 (d, ^2J = 222.5 Hz, 1F); ^{1}H NMR (401 MHz, $CDCl_3$) 6.73 (d, J = 3.2 Hz, 1H), 6.08 (d, J = 3.3 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.59 – 2.42 (m, 2H), 2.27 – 2.16 (m, 1H), 1.97 – 1.76 (m, 2H), 1.46 – 1.22 (m, 1H), 1.08 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.5 – 128.2 (m), 121.7, 118.0 (qt, $^1J_{C\text{-}F}$ = 288.3, $^2J_{C\text{-}F}$ = 48.4 Hz, CF_3), 117.6 (t, J = 3.3 Hz), 111.7 (tq, $^1J_{C\text{-}F}$ = 263.0 Hz, $^2J_{C\text{-}F}$ = 42.0 Hz, CF_2), 111.2, 31.2, 31.1–31.0 (m), 29.5, 22.6, 21.6; HRMS (EI$^+$) *m/z* calcd for $C_{11}H_{12}F_5N$ $[M]^+$: 253.0884, found 253.0890.



1-(perfluoroethyl)-4,5-dihydro-1H-benzo[g]indole (**2j**): Prepared according to the **general procedure B**. ^{19}F NMR yield: 80%, isolated yield: 65%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (s, 3F), -95.8 (d, ^2J = 222.7 Hz, 1F), -96.7 (d, ^2J = 222.7 Hz, 1F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 6.78 (d, J = 2.8 Hz, 1H), 6.14 (d, J = 3.3 Hz, 1H), 3.07 – 2.94 (m, 2H), 2.83 – 2.67 (m, 1H), 2.67 – 2.60 (m, 2H), 2.13 – 2.02 (m, 1H), 1.91 (ddt, J = 13.0, 11.6, 8.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 128.7, 128.4 – 127.9 (m), 127.1, 126.6, 122.0, 118.1 (qt, $^1J_{C\text{-}F}$ = 288.2, $^2J_{C\text{-}F}$ = 48.1 Hz, CF_3), 118.3 – 117.7 (m), 111.7 (tq, $^1J_{C\text{-}F}$ = 263.4 Hz, $^2J_{C\text{-}F}$ = 41.8 Hz, CF_2), 111.4, 41.2, 31.5 – 30.8 (m), 30.3, 23.3; HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{14}F_5N$ $[M]^+$: 315.1041, found 315.1043.



1-(perfluoroethyl)-6-propyl-4,5,6,7-tetrahydro-1H-indole (**2k**): Prepared according to the **general procedure B**. ^{19}F NMR yield: 64%, isolated yield: 61%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (s, 3F), -95.8 (d, ^2J = 222.4 Hz, 1F), -96.6 (d, ^2J = 222.4 Hz, 1F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 – 6.70 (m, 1H), 6.07 (d, J = 3.3 Hz, 1H), 2.75 (d, J = 16.3 Hz, 1H), 2.58 – 2.38 (m, 2H), 2.27 – 2.14 (m, 1H), 1.94 – 1.68 (m, 2H), 1.46 – 1.25 (m, 5H), 0.93 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.3 – 126.0 (m), 123.2 – 121.0 (m), 118.1 (qt, $^1J_{C\text{-}F}$ = 288.2, $^2J_{C\text{-}F}$ = 48.3 Hz, CF_3), 117.9 – 117.3 (m), 111.9 (tq, $^1J_{C\text{-}F}$ = 263.6 Hz, $^2J_{C\text{-}F}$ = 41.8 Hz, CF_2), 111.3, 38.5, 34.4, 29.4, 29.4–29.2 (m), 22.7, 20.3, 14.4; HRMS (EI$^+$) *m/z* calcd for $C_{13}H_{16}F_5N$ $[M]^+$: 281.1197, found 281.1200.

1-(perfluoroethyl)-4,5-dihydro-1H-benzo[g]indole (**2n**): Prepared according to the **general procedure B**. ^{19}F NMR yield: 58%, isolated yield: 38%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.3 (s, 3F), -89.3 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 1H), 7.26 – 7.19 (m, 2H), 7.20 – 7.09 (m, 1H), 6.96 – 6.90 (m, 1H), 6.28 (d, J = 3.3 Hz, 1H), 2.88 – 2.81 (m, 2H), 2.63 – 2.57 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 130.9 – 129.8 (m), 128.7, 128.5 – 128.2 (m), 128.2, 126.7, 126.2, 123.1 (t, J = 8.4 Hz), 121.9 – 120.8 (m), 118.1 (qt, $^{1}J_{C\text{-}F}$ = 288.4, $^{2}J_{C\text{-}F}$ = 45.8 Hz), 112.0 (tq, $^{1}J_{C\text{-}F}$ = 263.0 Hz, $^{2}J_{C\text{-}F}$ = 41.3 Hz, CF_2), 111.7, 30.7, 22.6.; HRMS (EI^+) *m/z* calcd for $C_{14}H_{10}F_5N$ $[M]^+$: 287.0728, found 287.0727.

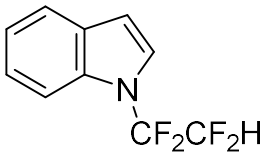
General procedure C. DDQ (2 equiv, 0.40 mmol) was added to the crude reaction mixture of **2a-2o** in dry DCE (2 ml) in a 10 ml microwave tube. The vial was flushed with nitrogen, capped, and heated at 100 °C for 30 min in a microwave reactor. The resulting mixture filtered through a pad of alumina, the solvent was evaporated under nitrogen flow or under vacuum. If necessary, purification using flash chromatography on silica gel (cyclohexane/EtOAc) was performed.

1-(trifluoromethyl)-1H-indole (**3a**): Prepared according to the **general procedure C**. ^{19}F NMR yield: 93%; To provide the NMR spectra, the reaction was performed in $CDCl_3$ and worked up by filtering through alumina. ^{19}F NMR (377 MHz, $CDCl_3$) δ -56.7 (s); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.73 – 7.51 (m, 2H), 7.39 – 7.20 (m, 3H), 6.66 (dd, J = 3.7, 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 129.9, 124.3, 123.2 – 123.0 (m), 122.7, 121.6, 119.5 (q, $J_{C\text{-}F}$ = 260.1 Hz), 112.0 (q, J = 2.5 Hz), 107.2 – 106.3 (m); HRMS (EI^+) *m/z* calcd for $C_9H_6F_3N$ $[M]^+$: 185.0447, found 185.0447.

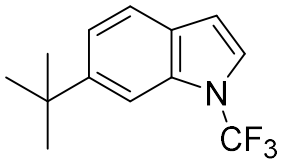
1-(perfluoroethyl)-1H-indole (**3b**): Prepared according to the **general procedure C**. ^{19}F NMR yield: 87%, isolated yield: 50%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0 (s, 3F), -97.8 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.64 (ddd, J = 7.7, 1.5, 0.8 Hz, 1H), 7.58 (dtt, J = 8.2, 2.0, 1.1 Hz, 1H), 7.36 – 7.19 (m, 2H), 7.22 (d, J = 3.5 Hz, 1H), 6.71 (dd, J = 3.7, 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 130.0 – 129.9 (m), 124.3, 123.6 (t, J = 2.9 Hz), 122.6, 121.6, 118.3 (qt, $^{1}J_{C\text{-}F}$ = 289.2, $^{2}J_{C\text{-}F}$ = 48.6 Hz, CF_3), 112.6 – 112.5 (m), 112.2 (tq, $^{1}J_{C\text{-}F}$ = 208.2 Hz, $^{2}J_{C\text{-}F}$ = 42.3 Hz, CF_2), 107.6 – 107.4 (m); HRMS ($APCI^+$) *m/z* calcd for $C_{10}H_6F_5N$ $[M]^+$: 235.0415, found 235.0416.

1-(difluoro(phenylsulfonyl)methyl)-1H-indole (**3c**): Prepared according to the **general procedure C**. ^{19}F NMR yield: 90%, isolated yield: 75%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.3 (s); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.75 – 7.66 (m, 1H), 7.61 – 7.55 (m, 1H), 7.54 – 7.46 (m, 3H), 7.24 – 7.17 (m, 2H), 7.17 – 7.11 (m, 1H), 6.66 (dd, J = 3.6, 0.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 135.0, 132.5, 130.7, 129.8, 129.6, 124.5 (t, J = 2.6 Hz), 124.2, 122.7, 121.3, 118.6 (t, $J_{C\text{-}F}$ = 299.3 Hz), 113.1 (t, J = 4.7 Hz), 107.9; HRMS ($APCI^+$) *m/z* calcd for $C_{15}H_{11}O_2F_2NS$ $[M]^+$: 307.0473, found 307.0475.

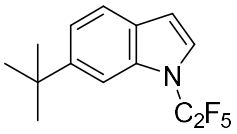
1-(1,1,2,2-tetrafluoroethyl)-1H-indole (**3d**): Prepared according to the **general procedure C**. ^{19}F NMR yield: 79%, isolated yield: 46%; pale yellow oil; ^{19}F NMR (377 MHz, $CDCl_3$) δ -96.9 (ddd, J = 8.0, 6.0, 1.9 Hz, 2F), -134.9 (dt, J = 53.2, 6.1 Hz, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 1H), 7.62 – 7.57 (m, 1H), 7.35 – 7.21 (m, 3H), 6.70 (dd, J = 3.6, 0.7 Hz, 1H), 6.11 (tt, $^{2}J_{HF}$ = 53.2, $^{3}J_{HF}$ = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 130.0, 124.0, 123.6, 122.3, 121.6, 114.3 (tt, $^{1}J_{C\text{-}F}$ = 259.8 Hz, $^{2}J_{C\text{-}F}$ = 29.3 Hz, CF_2), 112.4 (t, J = 4.2 Hz), 180.8 (tt, $^{1}J_{C\text{-}F}$ = 254.0 Hz, $^{2}J_{C\text{-}F}$ = 47.0 Hz, CF_2H), 106.8; HRMS (APCI$^+$) *m/z* calcd for $C_{10}H_7F_4N$ $[M]^+$: 217.0509, found 217.0510.



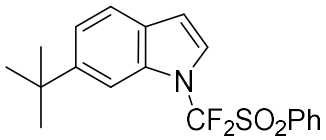
6-(tert-butyl)-1-(trifluoromethyl)-1H-indole (**3e**): Prepared according to the **general procedure C**, yield: 62%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.6 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 0.7 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.36 (dd, J = 8.4, 1.6 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 6.61 (dd, J = 3.6, 0.7 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 134.1, 127.4, 122.7 (q, J = 1.5 Hz), 120.8, 120.7, 119.0 (q, $J_{C\text{-}F}$ = 259.8 Hz), 108.1 (q, J = 2.6 Hz), 107.1 – 105.4 (m), 35.0, 31.7; HRMS (EI$^+$) *m/z* calcd $C_{13}H_{14}F_3N$ $[M]^+$: 241.1073, found 241.1075.



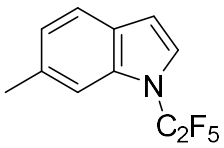
6-(tert-butyl)-1-(perfluoroethyl)-1H-indole (**3f**): Prepared according to the **general procedure C**. ^{19}F NMR yield: 99%, isolated yield: 70%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.8 (s, 3F), -97.4 (s, 2F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.35 (dd, J = 8.3, 1.7 Hz, 1H), 7.18 (d, J = 3.7 Hz, 1H), 6.71 – 6.59 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 134.9, 127.6, 123.3 (t, J = 2.9 Hz), 120.9, 120.8, 118.5 (qt, $^{1}J_{C\text{-}F}$ = 289.3, $^{2}J_{C\text{-}F}$ = 48.7 Hz, CF_3), 112.3 (tq, $^{1}J_{C\text{-}F}$ = 263.4 Hz, $^{2}J_{C\text{-}F}$ = 42.4 Hz, CF_2), 109.9 – 108.0 (m), 107.1, 35.2, 31.8.; HRMS (EI$^+$) *m/z* calcd for $C_{14}H_{14}F_5N$ $[M]^+$: 291.1041, found 291.1049.



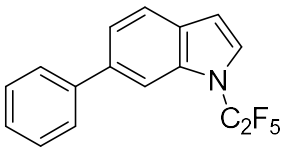
6-(tert-butyl)-1-(difluoro(phenylsulfonyl)methyl)-1H-indole (**3g**): Prepared according to the **general procedure C**, yield: 42%; pale yellow oil; ^{19}F NMR (377 MHz, $CDCl_3$) δ -88.2 (s); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.68 – 7.62 (m, 1H), 7.50 – 7.43 (m, 3H), 7.39 – 7.36 (m, 1H), 7.26 (dd, J = 8.4, 1.6 Hz, 1H), 7.12 (d, J = 3.7 Hz, 1H), 6.61 (d, J = 3.4 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 135.8, 135.3, 132.6, 130.6, 129.5, 127.3, 124.2 (t, J = 2.5 Hz), 120.8, 120.6, 118.6 (t, $J_{C\text{-}F}$ = 299.1 Hz), 109.4 (t, J = 5.0 Hz), 107.5, 35.0, 31.7; HRMS (EI$^+$) *m/z* calcd $C_{19}H_{19}F_2NO_2S$ $[M]^+$: 363.1099, found 363.1101.



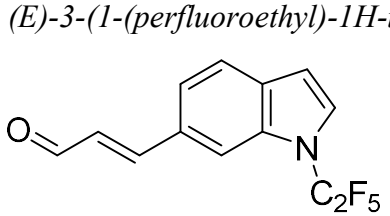
6-methyl-1-(perfluoroethyl)-1H-indole (**3h**): Prepared according to the **general procedure C**, yield: 45%; pale yellow oil; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.9 (s, 3F), -97.6 (s, 2F); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 1H), 7.37 – 7.35 (m, 1H), 7.14 (d, J = 3.4 Hz, 1H), 7.08 (dd, J = 8.1, 0.8 Hz, 1H), 6.64 (dd, J = 3.6, 0.6 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0, 134.3, 127.7, 124.2, 123.0 – 122.8 (m), 121.1, 118.4 (qt, $^{1}J_{C\text{-}F}$ = 289.3, $^{2}J_{C\text{-}F}$ = 48.7 Hz, CF_3), 112.8–112.4 (m), 112.2 (tq, $^{1}J_{C\text{-}F}$ = 263.9 Hz, $^{2}J_{C\text{-}F}$ = 42.3 Hz, CF_2), 107.3, 22.1; HRMS (EI$^+$) *m/z* calcd for $C_{11}H_8F_5N$ $[M]^+$: 249.0571, found 249.0570.



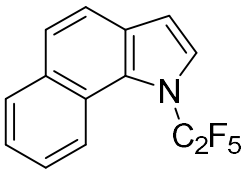
1-(perfluoroethyl)-6-phenyl-1H-indole (**3j**): Prepared according to the **general procedure C**, yield: 75%; pale-yellow oil; ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.8 (s, 3F), -97.6 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 1H), 7.73 – 7.69 (m, 1H), 7.68 – 7.60 (m, 2H), 7.57 – 7.44 (m, 3H), 7.43 – 7.32 (m, 1H), 7.29 – 7.18 (m, 1H), 6.79 – 6.65 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 141.6, 137.9, 135.1, 128.9, 127.6, 127.2, 123.9 (t, J = 2.9 Hz), 122.4, 121.6, 118.3 (qt, $^{1}J_{C\text{-}F}$ = 289.2, $^{2}J_{C\text{-}F}$ = 48.4 Hz, CF_3), 112.1 (tq, $^{1}J_{C\text{-}F}$ = 264.2 Hz, $^{2}J_{C\text{-}F}$ = 42.4 Hz, CF_2), 111.5 – 110.6 (m), 107.3; HRMS (EI$^+$) *m/z* calcd $C_{16}H_{10}F_5N$ $[M]^+$: 311.0728, found 311.0729.



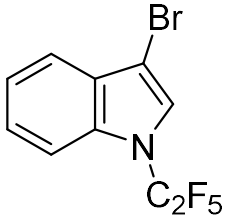
(E)-3-(1-(perfluoroethyl)-1H-indol-6-yl)acrylaldehyde (**3k**): DDQ (6 equiv., 1.2 mmol) was added to the crude reaction mixture of **2k** in dry DCE (2 ml) in a 10 ml microwave tube. The vial was flushed with nitrogen, capped, and heated at 100 °C for 30 min in a microwave reactor, then left at room temperature overnight to ensure full oxidation. The resulting mixture was filtered through a pad of alumina, the solvent was evaporated under nitrogen flow or under vacuum. Purified using flash chromatography on silica gel (cyclohexane/EtOAc). Yield 50%, pale yellow solid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0 (s, 3F), -97.9 (s, 2F); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (d, J = 7.6 Hz, 1H), 7.73 (s, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.59 (d, J = 15.9 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.34 – 7.31 (m, 1H), 6.78 (dd, J = 15.9, 7.7 Hz, 1H), 6.77 – 6.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 153.4, 134.8, 132.4, 130.5, 128.3, 126.1 – 126.0 (m), 122.35, 122.28, 118.2 (qt, $^{1}J_{C\text{-}F}$ = 289.3, $^{2}J_{C\text{-}F}$ = 48.0 Hz), 113.7 – 113.5 (m), 112.0 (tq, $^{1}J_{C\text{-}F}$ = 264.9 Hz, $^{2}J_{C\text{-}F}$ = 42.5 Hz, CF_2), 107.8; HRMS (EI$^+$) *m/z* calcd $C_{13}H_8F_5NO$ $[M]^+$: 289.0521, found 289.0520.



1-(perfluoroethyl)-1H-benzo[g]indole (**3n**): Prepared according to the **general procedure C**, yield: 38%; pale yellow oil; ^{19}F NMR (377 MHz, $CDCl_3$) δ -82.0 (s, 3F), -87.1 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.40 (d, J = 8.8 Hz, 1H), 7.97 (dd, J = 8.1, 1.4 Hz, 1H), 7.71 (q, J = 8.5 Hz, 2H), 7.60 (ddd, J = 8.7, 6.9, 1.5 Hz, 1H), 7.55 – 7.45 (m, 1H), 7.41 (tt, J = 4.0, 1.2 Hz, 1H), 6.84 (d, J = 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 129.8 (t, J = 2.2 Hz), 129.5, 128.5, 126.4 (t, J = 1.8 Hz), 125.3, 124.6, 123.9 (td, J = 4.1, 2.0 Hz), 122.4 (t, J = 11.3 Hz), 122.1, 120.3, 118.2 (qt, $^{1}J_{C\text{-}F}$ = 288.3, $^{2}J_{C\text{-}F}$ = 44.8 Hz, CF_3), 112.5 (tq, $^{1}J_{C\text{-}F}$ = 261.5 Hz, $^{2}J_{C\text{-}F}$ = 41.4 Hz, CF_2), 108.8–108.0 (m); HRMS (EI$^+$) *m/z* calcd $C_{14}H_8F_5N$ $[M]^+$: 285.0577, found 285.0572.

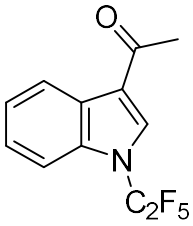


3-bromo-1-(perfluoroethyl)-1H-indole (**4**): Prepared according to literature procedure[4]: NBS (1.2 equiv., 0.25 mmol) was slowly added to a mixture of indole **3b** (0.2 mmol) and 2,4,6-trimethylaniline (2 mol%, 0.004 mmol) in DCM (2 ml). The reaction was stirred overnight at room temperature. Purified using flash chromatography on silica gel (cyclohexane/EtOAc). Yield: 64%; yellow oil; ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.0 (s, 3F), -98.0 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.58 – 7.53 (m, 1H), 7.37 (pd, J = 7.2, 1.4 Hz, 2H), 7.29 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 129.0, 125.5, 123.3, 122.3 (t, J = 3.1 Hz), 120.3, 118.2 (qt, $^{1}J_{C\text{-}F}$ = 289.0, $^{2}J_{C\text{-}F}$ = 48.1 Hz, CF_3), 112.7 (t, J = 4.6 Hz), 111.9 (tq, $^{1}J_{C\text{-}F}$ = 265.6

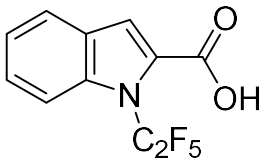


Hz, $^{2}J_{C\text{-}F}$ = 42.5 Hz, CF_2), 97.8; HRMS (APCI$^+$) *m/z* calcd $C_{10}H_5F_5NBr$ $[M]^+$: 312.9520, found 312.9519.

1-(1-(perfluoroethyl)-1H-indol-3-yl)ethan-1-one (**5**): To $FeCl_3$ (6 equiv., 1.2 mmol) in DCM (2 ml) was added acetic anhydride (3 equiv., 0.6 mmol) at 0 °C; then, indole **3a** (0.2 mmol) in DCM (2 ml) was added, the solution was allowed to reach room temperature and was stirred for 3 h. The resulting mixture was poured into ice water and extracted with DCM (3 × 10 ml). The combined organic phases were washed with brine (30 ml), dried over anhydrous $MgSO_4$, filtered, and purified using flash chromatography on silica gel. Yield: 89%; colorless crystals; ^{19}F NMR (377 MHz, $CDCl_3$) δ -84.4 (s, 3F), -98.1 (s, 2F); ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.43 (dt, *J* = 5.6, 3.3 Hz, 1H), 7.84 (s, 1H), 7.60 – 7.51 (m, 1H), 7.44 – 7.35 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 134.8, 129.4 (t, *J* = 3.3 Hz), 126.8, 125.6, 124.5, 123.2, 121.3, 117.9 (qt, $^{1}J_{C\text{-}F}$ = 289.0, $^{2}J_{C\text{-}F}$ = 47.0 Hz), 112.7–111.9 (m), 111.7 (tq, $^{1}J_{C\text{-}F}$ = 266.7 Hz, $^{2}J_{C\text{-}F}$ = 42.9 Hz, CF_2), 27.8; HRMS (EI$^+$) *m/z* calcd $C_{12}H_8F_5NO$ $[M]^+$: 277.0521, found 277.0518.



1-(perfluoroethyl)-1H-indole-2-carboxylic acid (**6**): The indole **3a** (0.2 mmol) prepared according to the **general procedure C** was dried under nitrogen flow, then THF (8 mL) was added. The solution was cooled down to -78 °C and *n*-BuLi (2.5M in hexane, 160 µL, 0.4 mmol, 2 equiv.) was added. The reaction was stirred for 30 minutes under nitrogen atmosphere. Then, excess of CO_2 (in the form of dry ice, ~2g) was added to the reaction mixture. After 15 minutes of stirring the reaction was quenched with acetic acid (1 mL). The reaction mixture was extracted with ether; the organic layer was washed with brine (3 × 20 mL) and then water (3 × 20 mL). Solvent evaporation afforded pure product. Yield: 91%; colorless crystals; ^{19}F NMR (377 MHz, $CDCl_3$) δ -83.2 (s, 3F), -90.2 (s, 2F); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.63 (s, 1H), 7.65 – 7.60 (m, 1H), 7.46 (ddd, *J* = 8.6, 7.2, 1.2 Hz, 1H), 7.32 (ddd, *J* = 7.9, 7.1, 0.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 138.5, 128.2, 128.0, 127.2, 123.6, 123.2, 120.4, 118.4 (qt, $^{1}J_{C\text{-}F}$ = 289.0, $^{2}J_{C\text{-}F}$ = 47.1 Hz), 114.7 – 114.0 (m), 112.5 (tq, $^{1}J_{C\text{-}F}$ = 271.3 Hz, $^{2}J_{C\text{-}F}$ = 43.6 Hz); HRMS (ESI$^-$) *m/z* calcd for $C_{11}H_5F_5NO_2$ $[M\text{-}H]^+$: 278.0246, found 278.0247.



X-ray crystallography

Single-crystal diffraction data of **6** were collected using Bruker D8 VENTURE system equipped with a Photon 100 CMOS detector, a multilayer monochromator, and a CuKα Incoatec microfocus sealed tube (λ = 1.54178 Å) at 180 K. The frames were integrated with the with Bruker SAINT[5] software package. The structure was solved by direct methods with SIR92[6] and refined by full-matrix least-squares on F with CRYSTALS.[7] The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. All hydrogen atoms were located in a difference Fourier map, but those attached to carbon atoms were repositioned geometrically. They were initially refined with soft restraints on the bond lengths and angles to regularise their geometry, then their positions were refined with riding constraints.

Crystal data for 6 (colourless, 0.090 × 0.137 × 0.254 mm): $C_{11}H_6F_5N_1O_2$, triclinic, space group *P*-1, $a = 7.6612(3)$ Å, $b = 8.6533(3)$ Å, $c = 8.7731(3)$ Å, $\alpha = 107.8102(12)°$, $\beta = 94.3444(13)°$, $\gamma = 95.6658(13)°$, $V = 547.57(3)$ Å^3, $Z = 2$, $M = 279.16$, 15955 reflections measured, 2004 independent reflections. Final $R = 0.044$, $wR = 0.055$, $GoF = 1.010$ for 1887 reflections with $I > 2\sigma(I)$ and 173 parameters. CCDC 2291313.

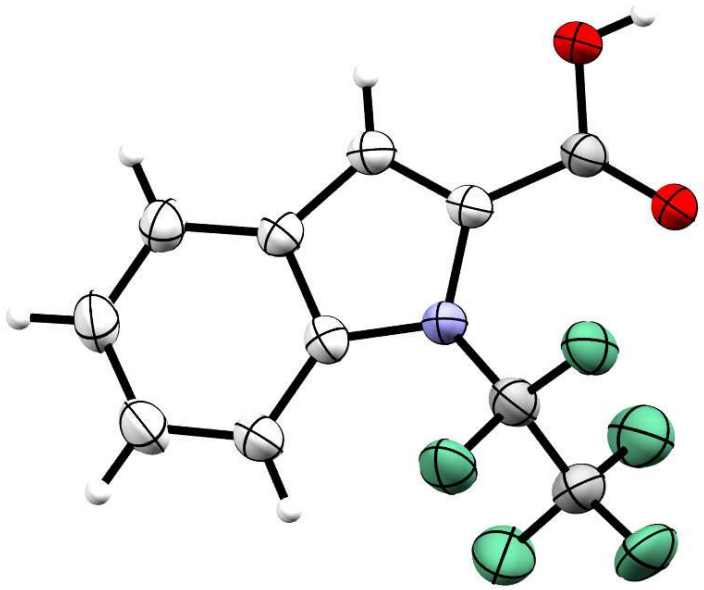
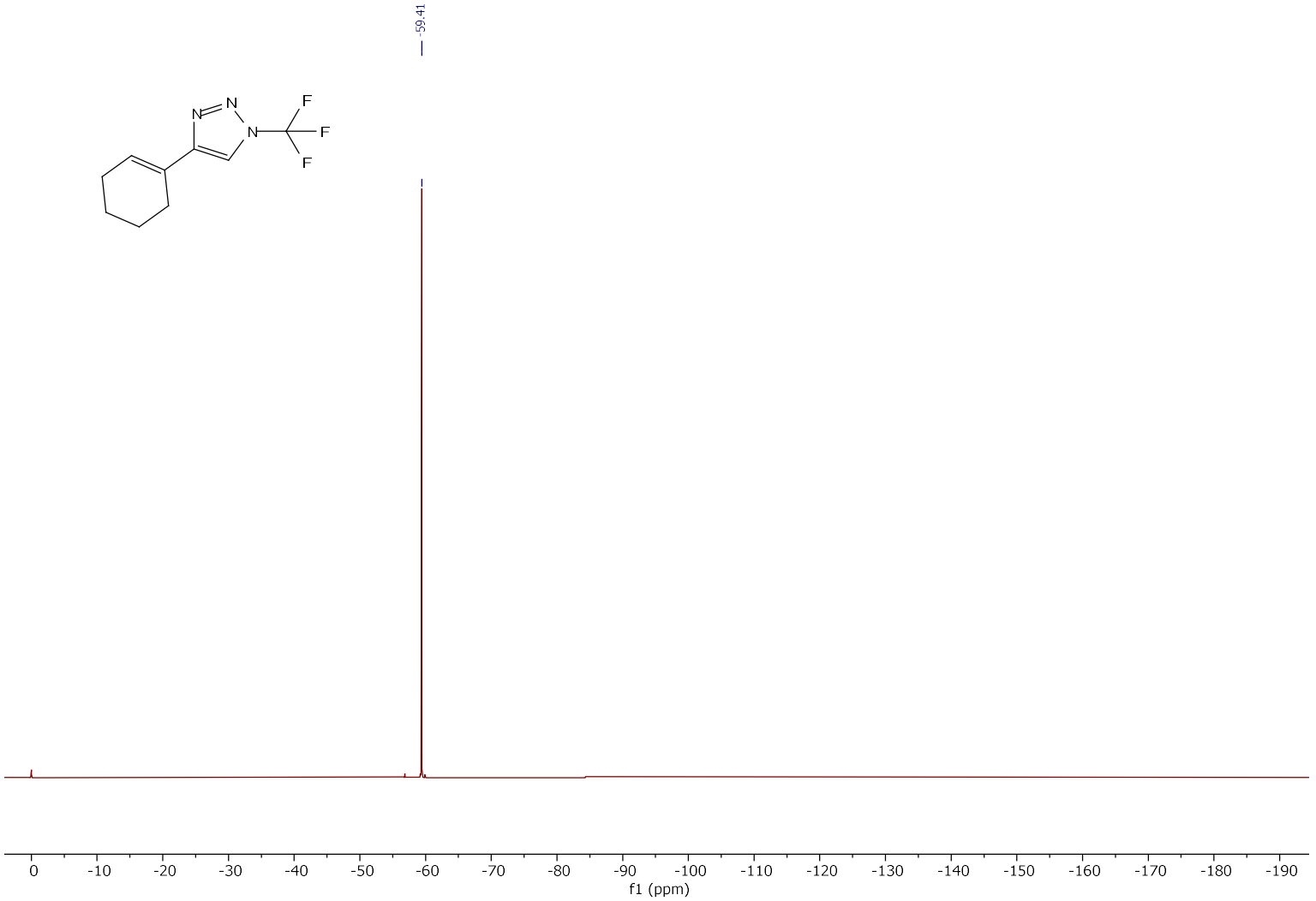


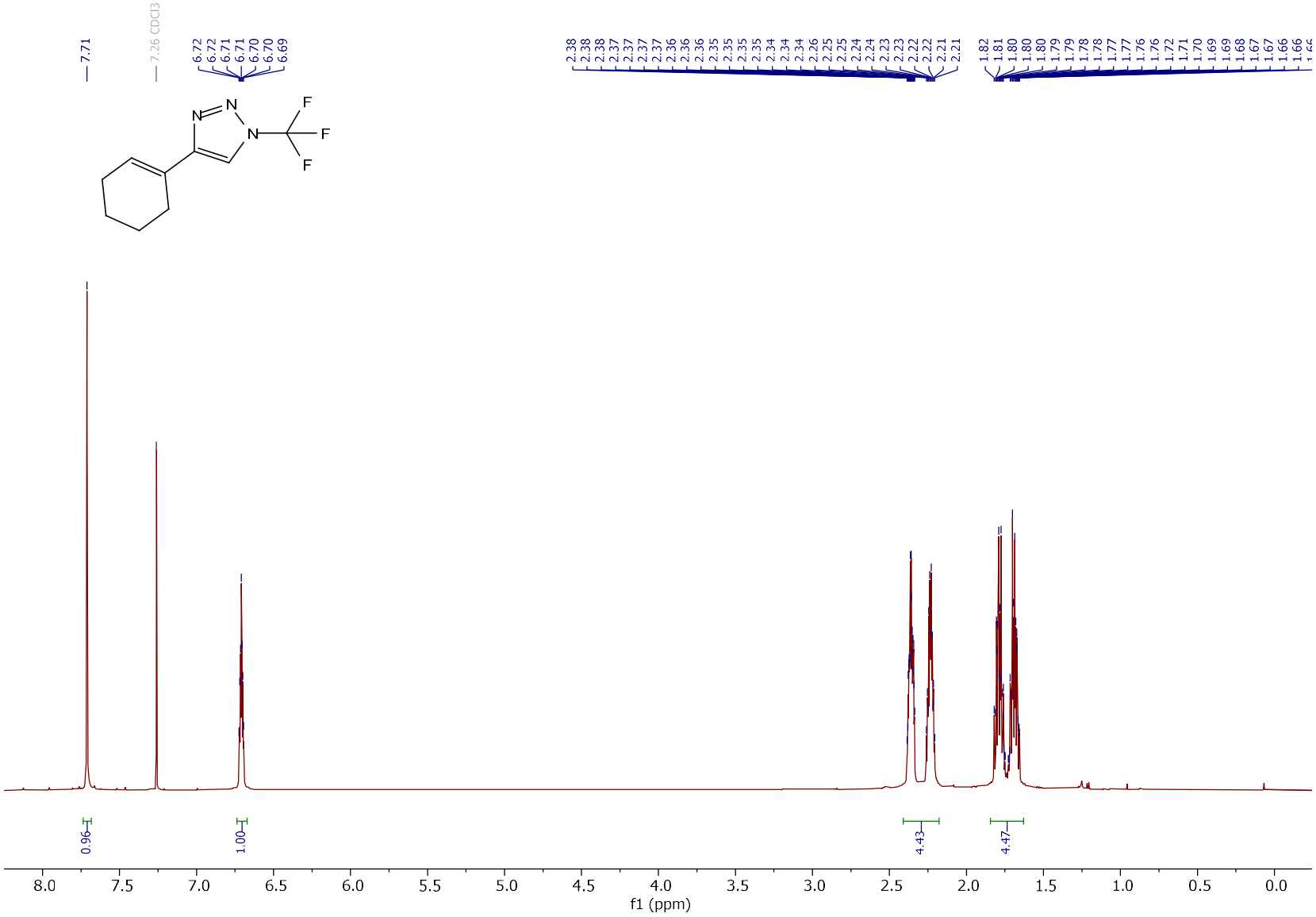
Figure 1. ORTEP diagram of **6**, displacement ellipsoids shown with 50 % probability.

^{19}F NMR, ^{1}H NMR and ^{13}C NMR spectra for spectroscopic data

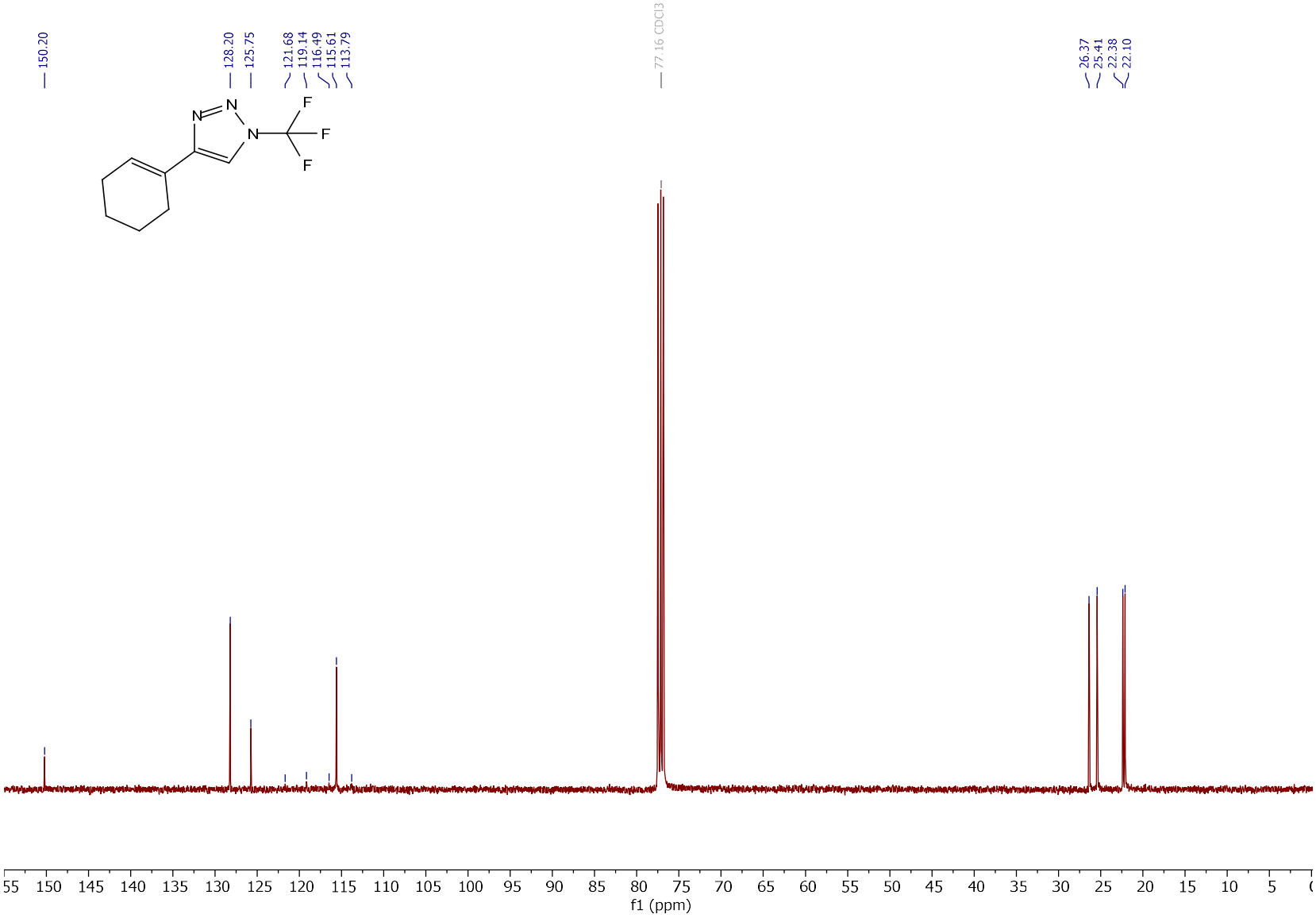
^{19}F NMR (376 MHz, $CDCl_3$) of **1a**



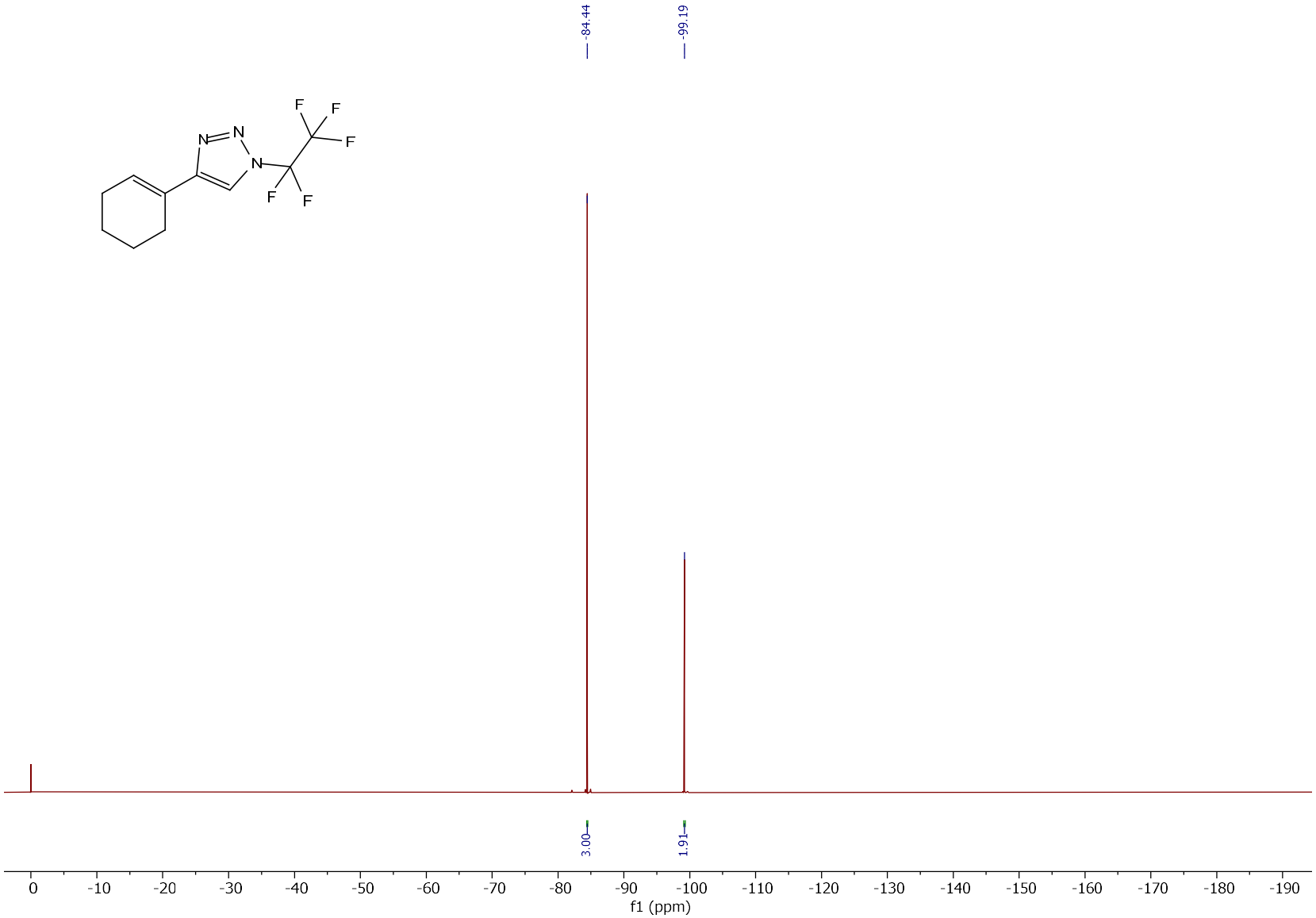
^{1}H NMR (400 MHz, $CDCl_3$) if **1a**



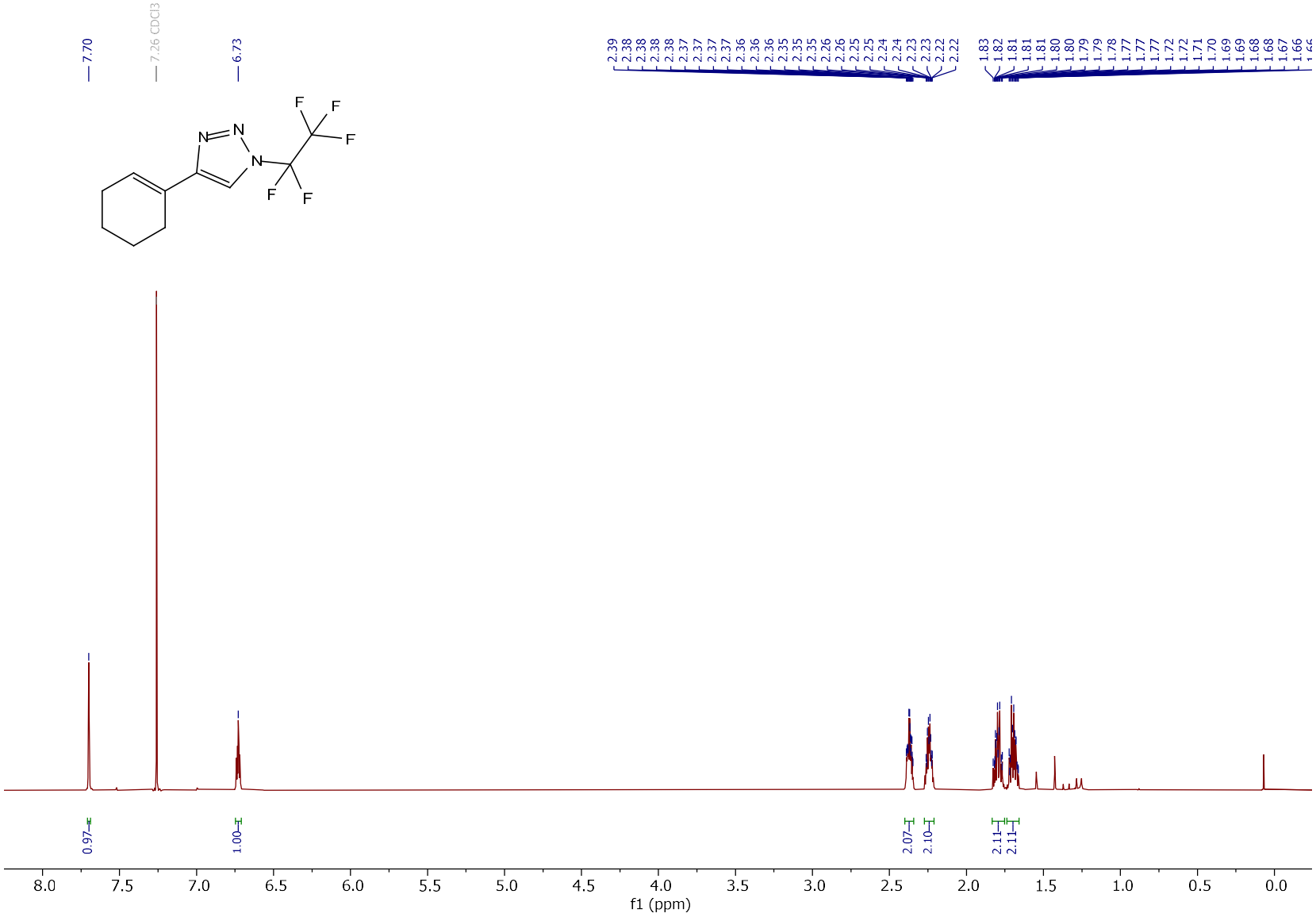
^{13}C NMR (101 MHz, $CDCl_3$) of **1a**



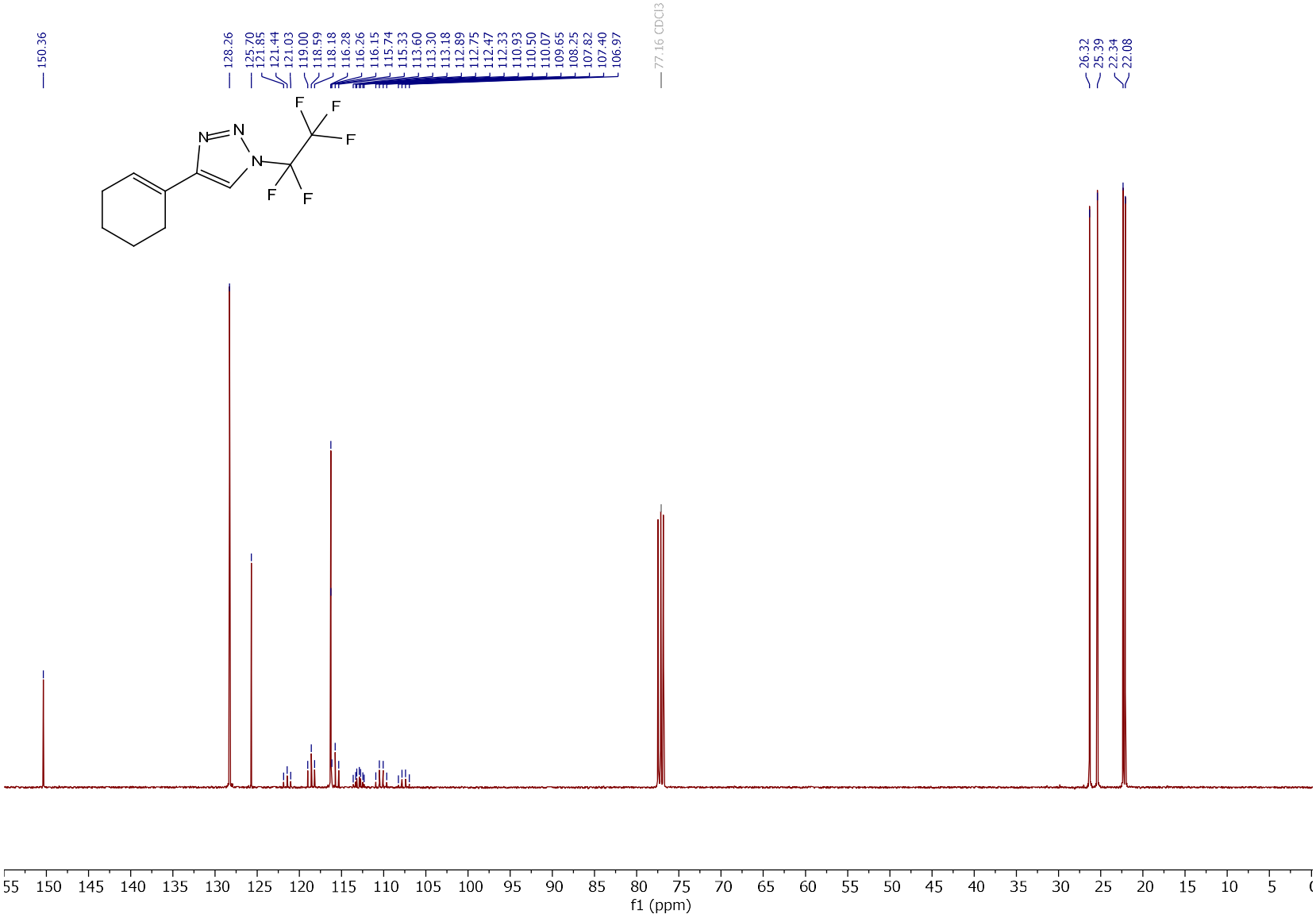
^{19}F NMR (376 MHz, $CDCl_3$) of **1b**



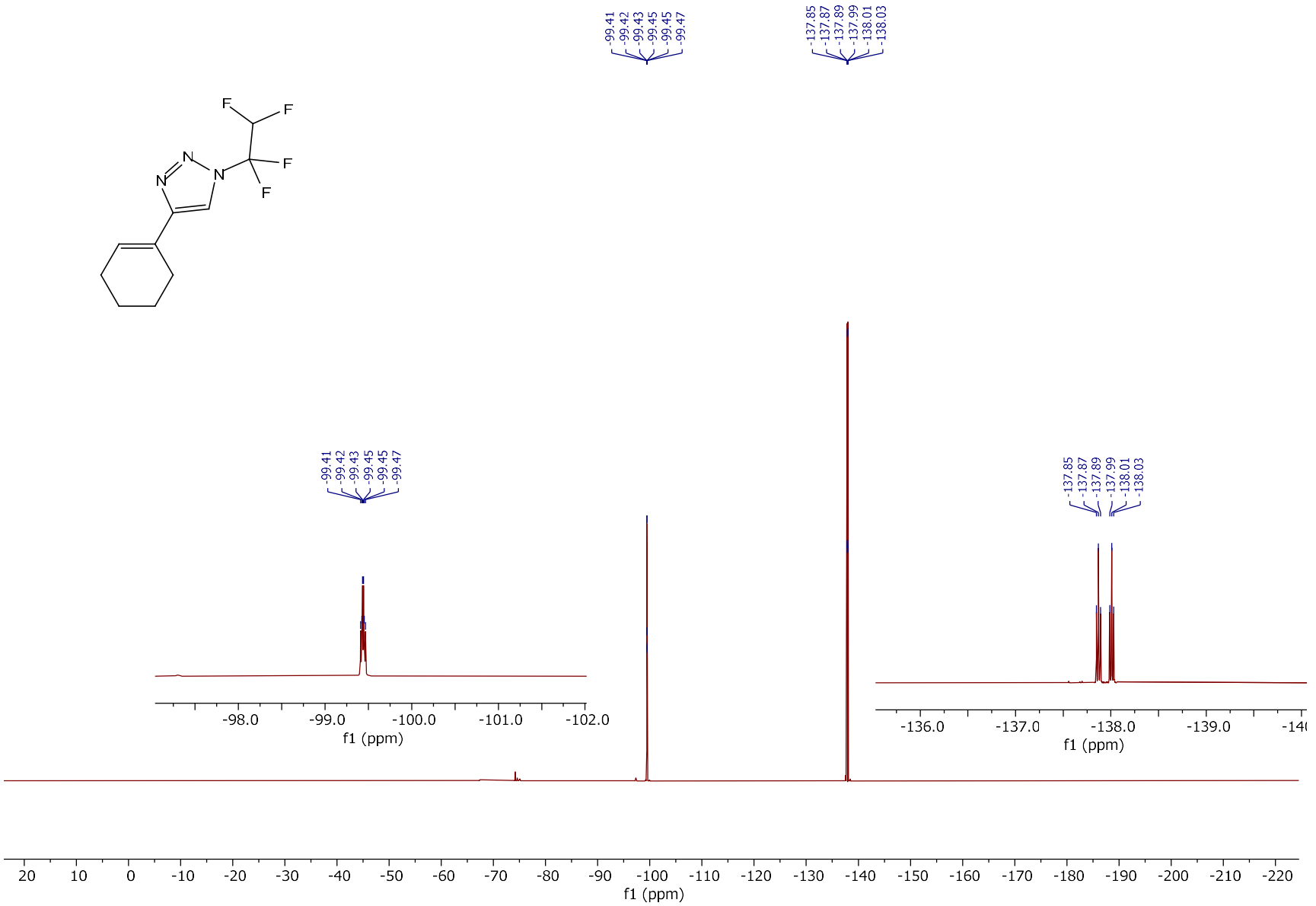
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



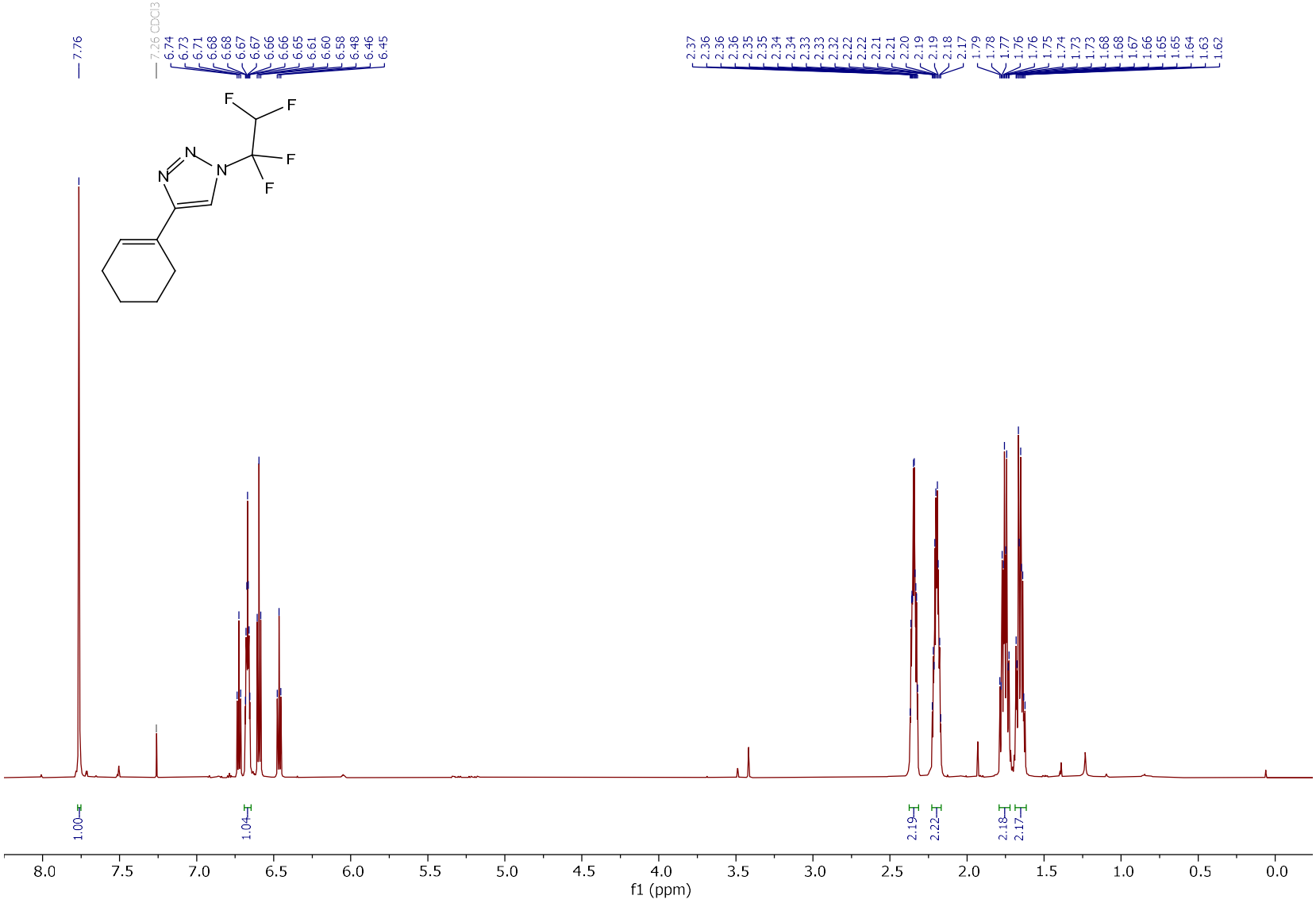
^{13}C NMR (101 MHz, $CDCl_3$) of **1b**



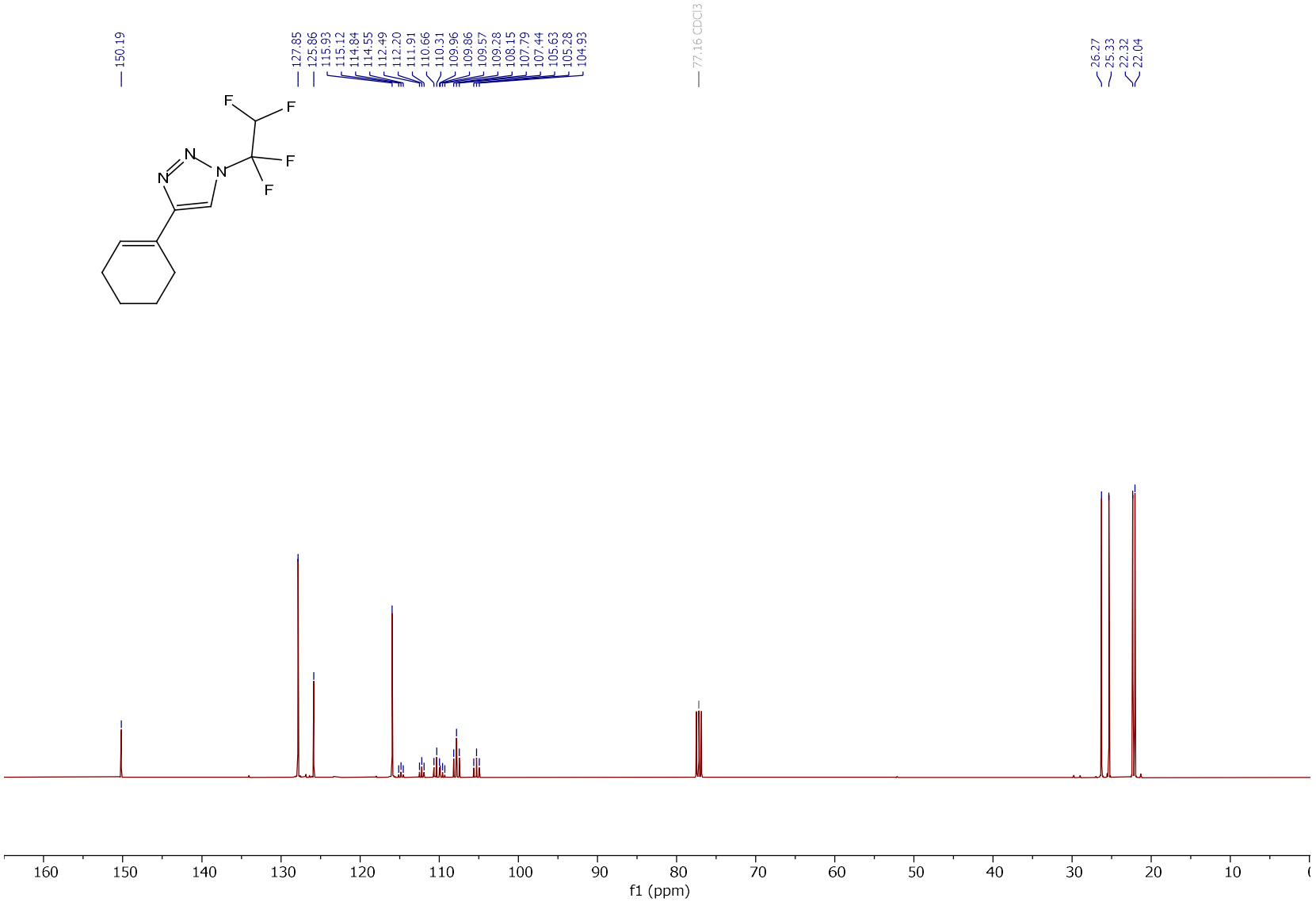
^{19}F NMR (376 MHz, $CDCl_3$) of **1d**



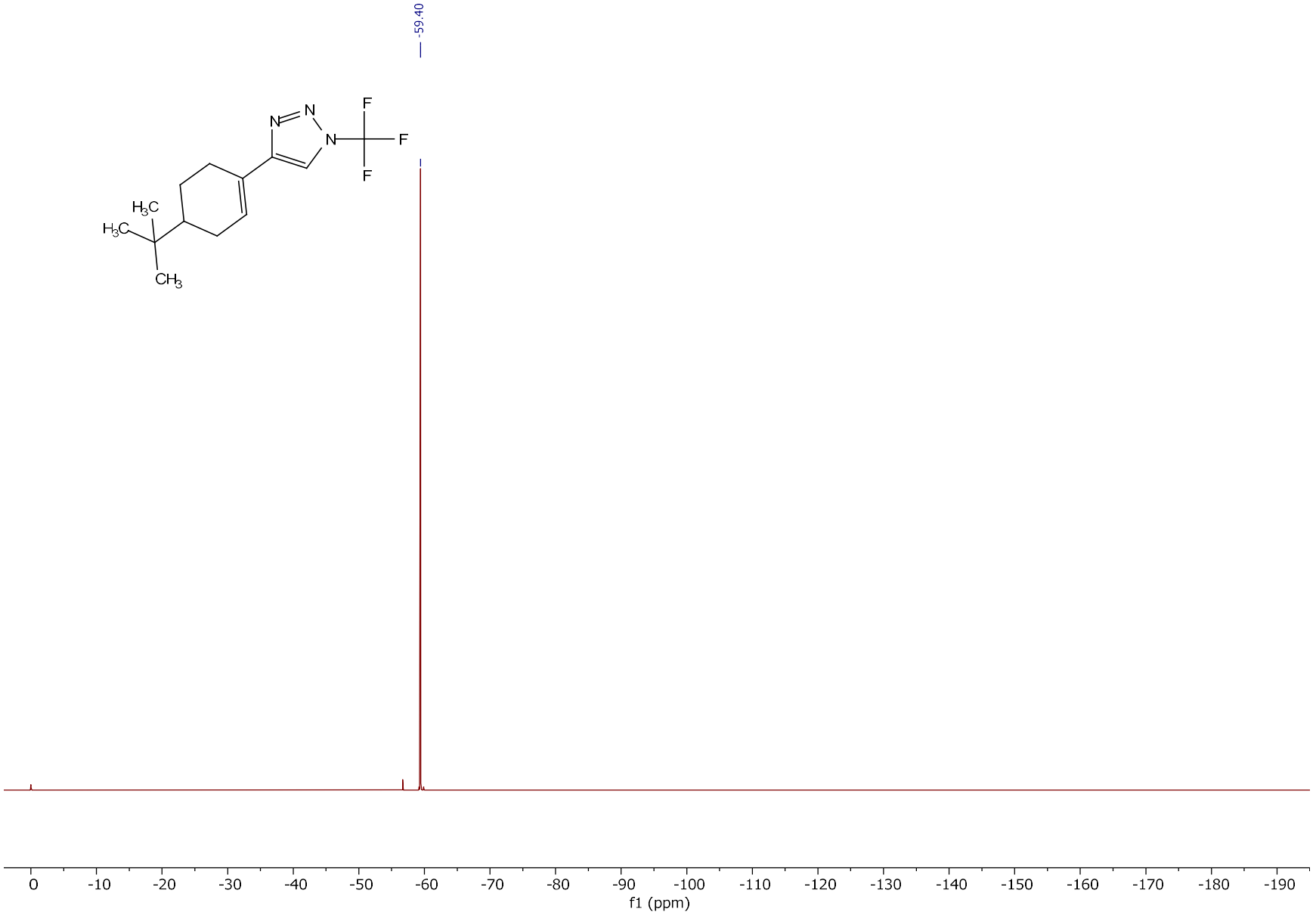
^{1}H NMR (401 MHz, $CDCl_3$) of **1d**



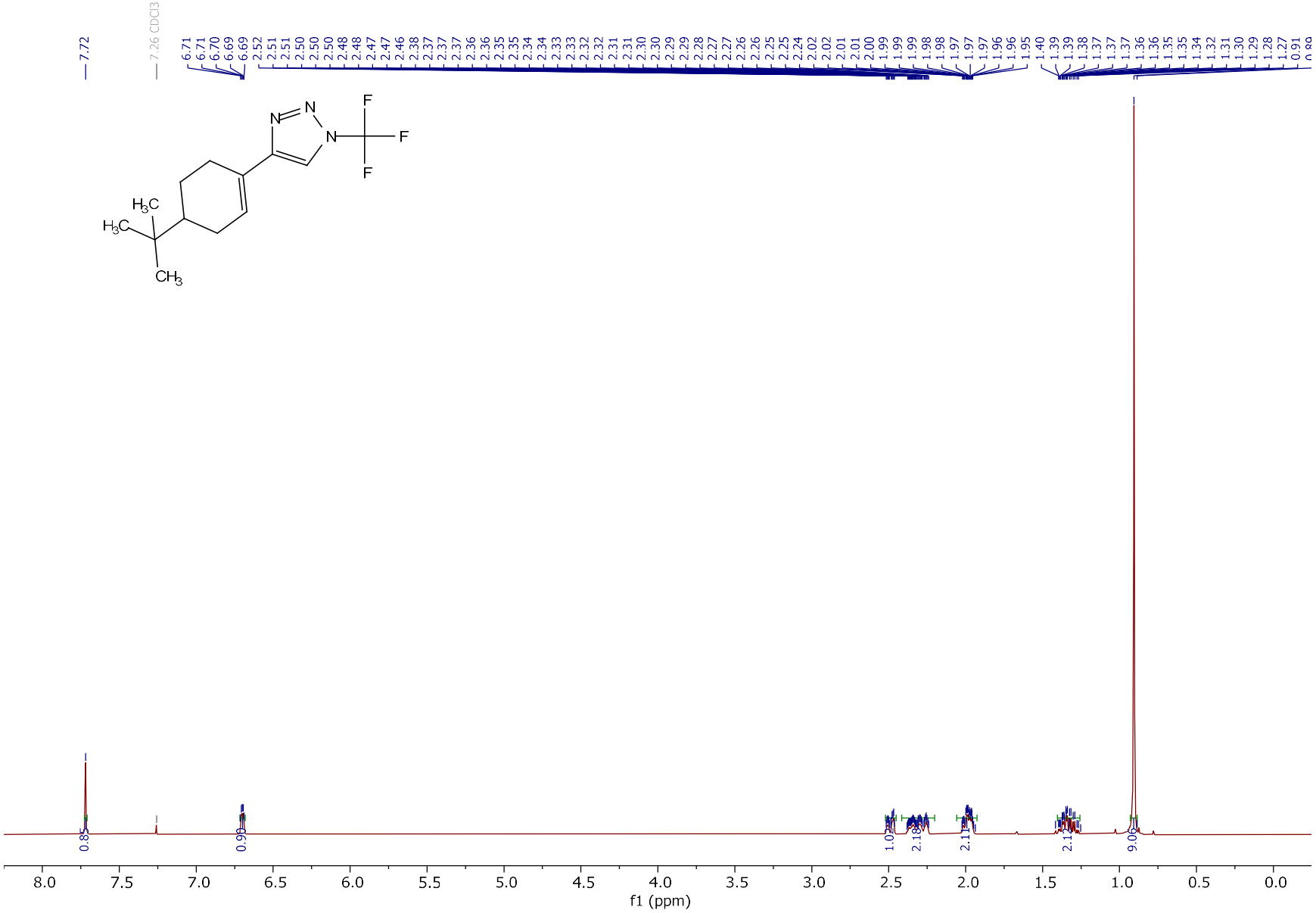
^{13}C NMR (101 MHz, $CDCl_3$) of **1d**



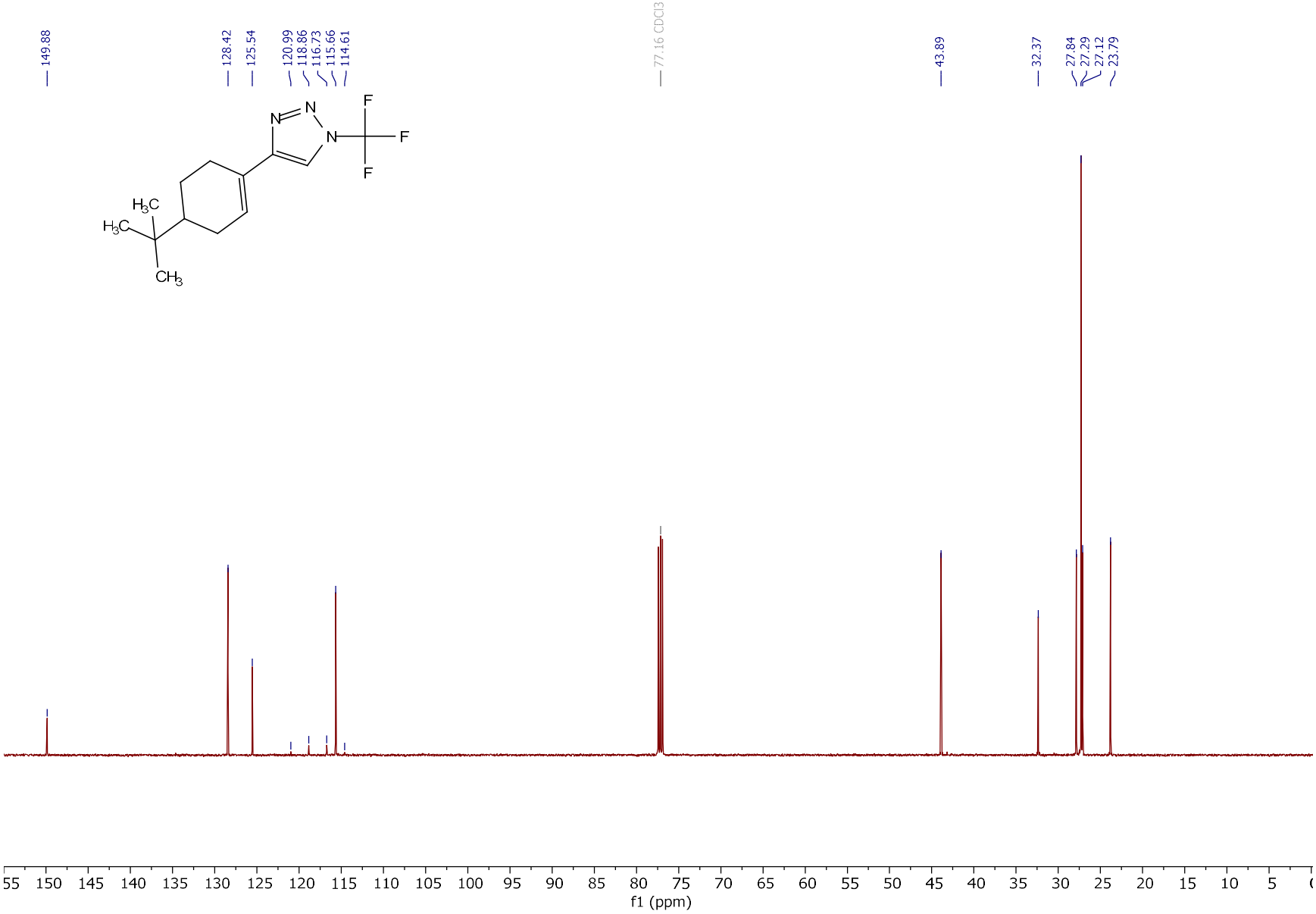
^{19}F NMR (376 MHz, $CDCl_3$) of **1e**



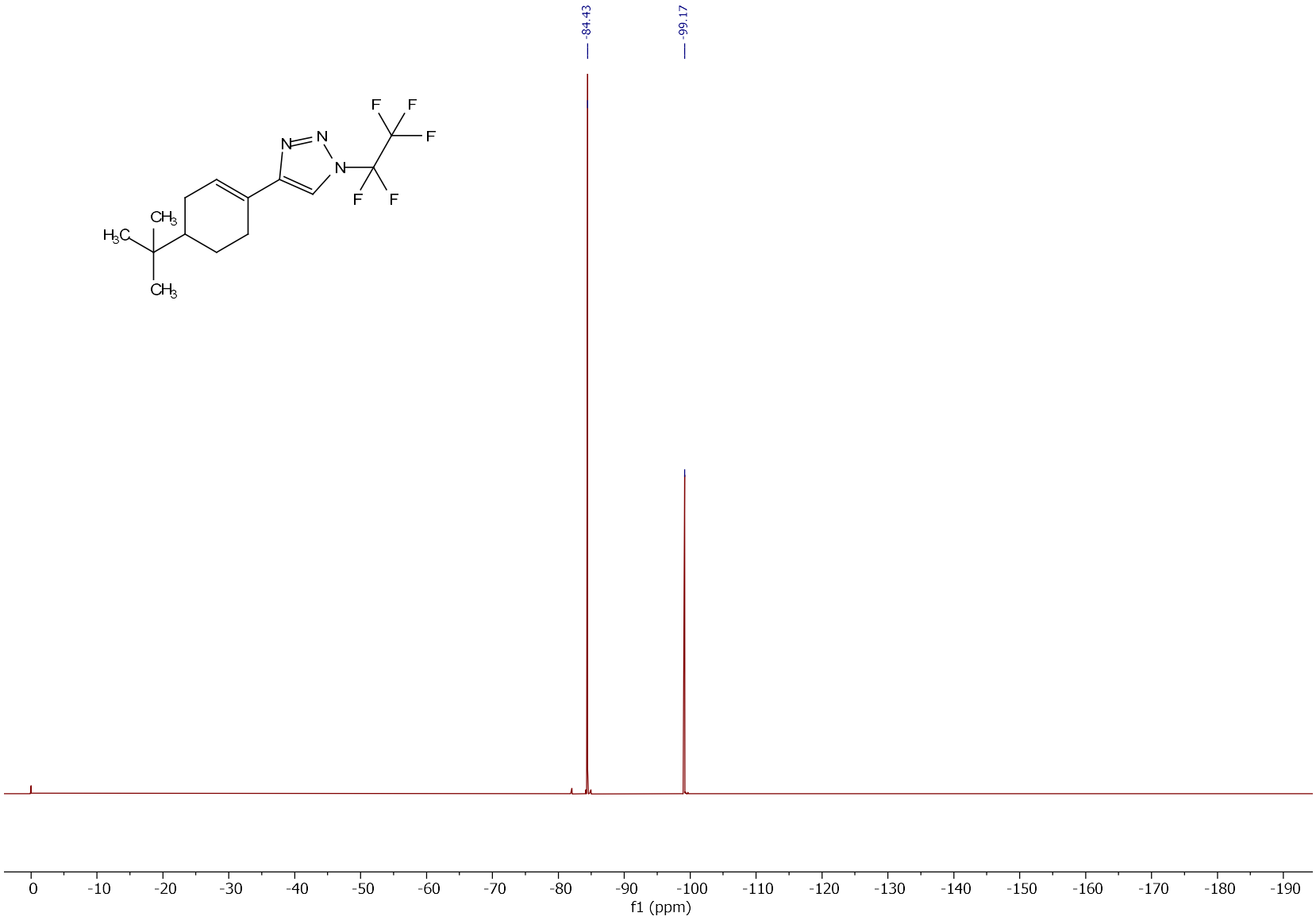
^{1}H NMR (500 MHz, $CDCl_3$) of **1e**



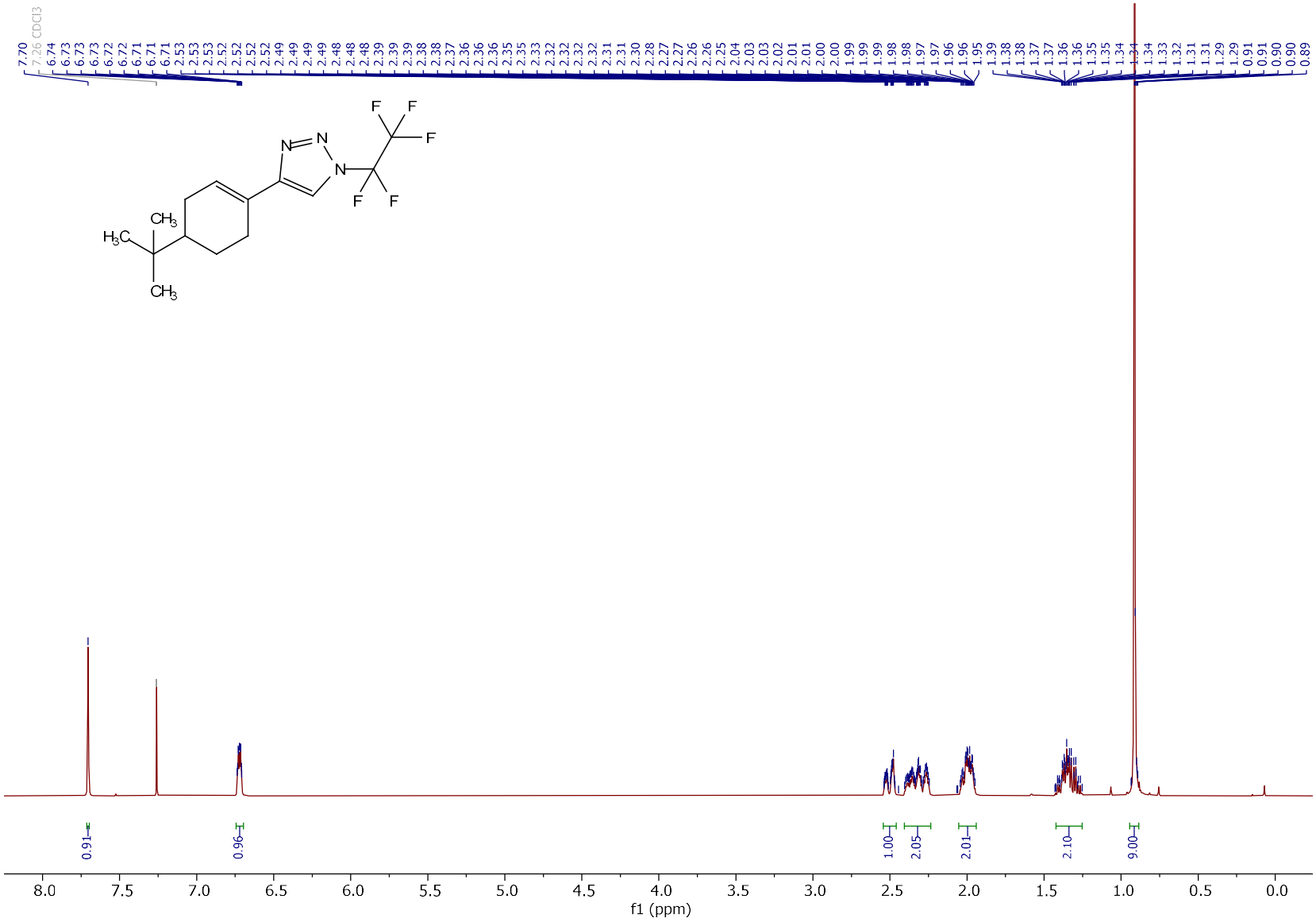
^{13}C NMR (126 MHz, $CDCl_3$) of **1e**



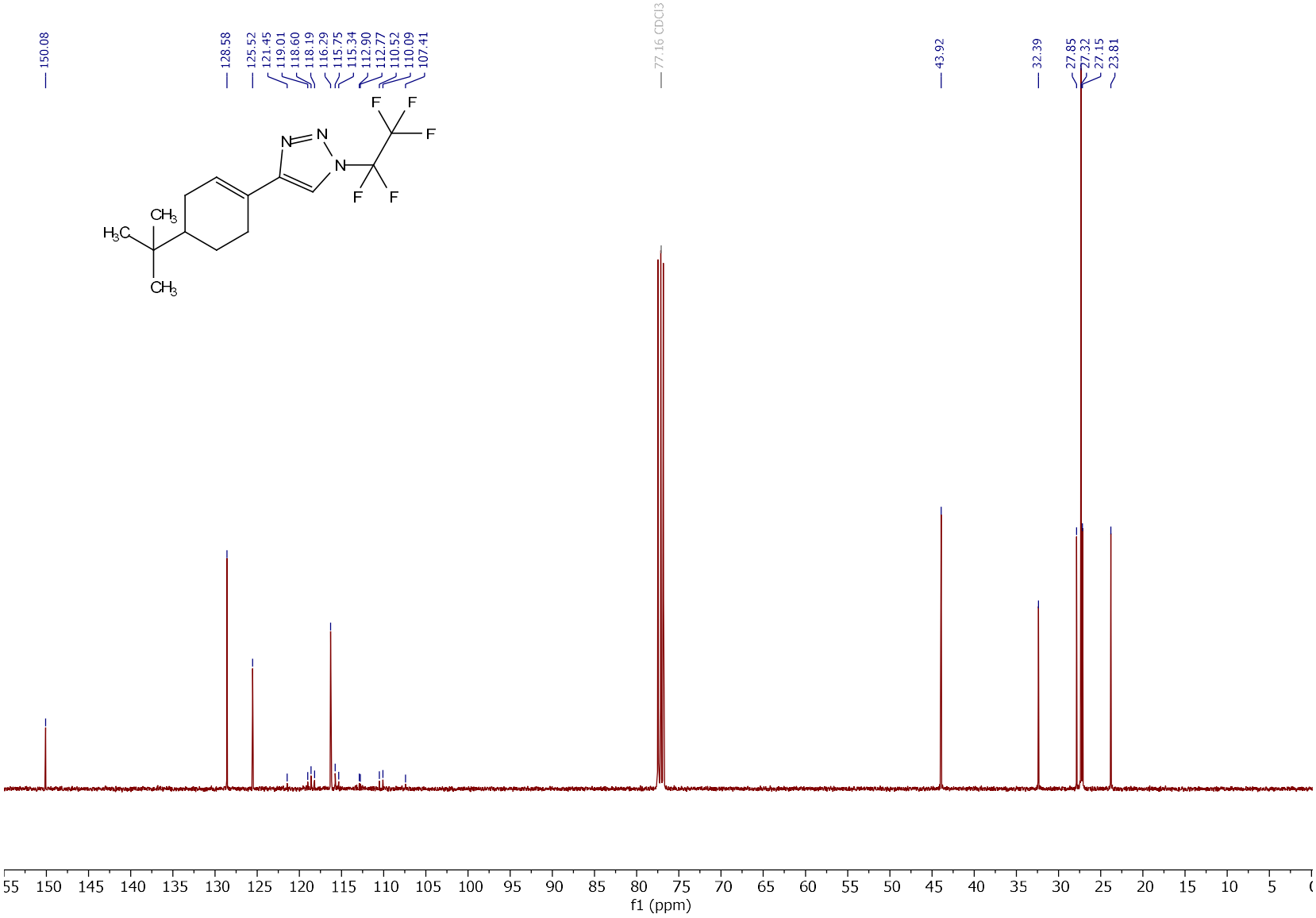
^{19}F NMR (376 MHz, $CDCl_3$) of **1f**



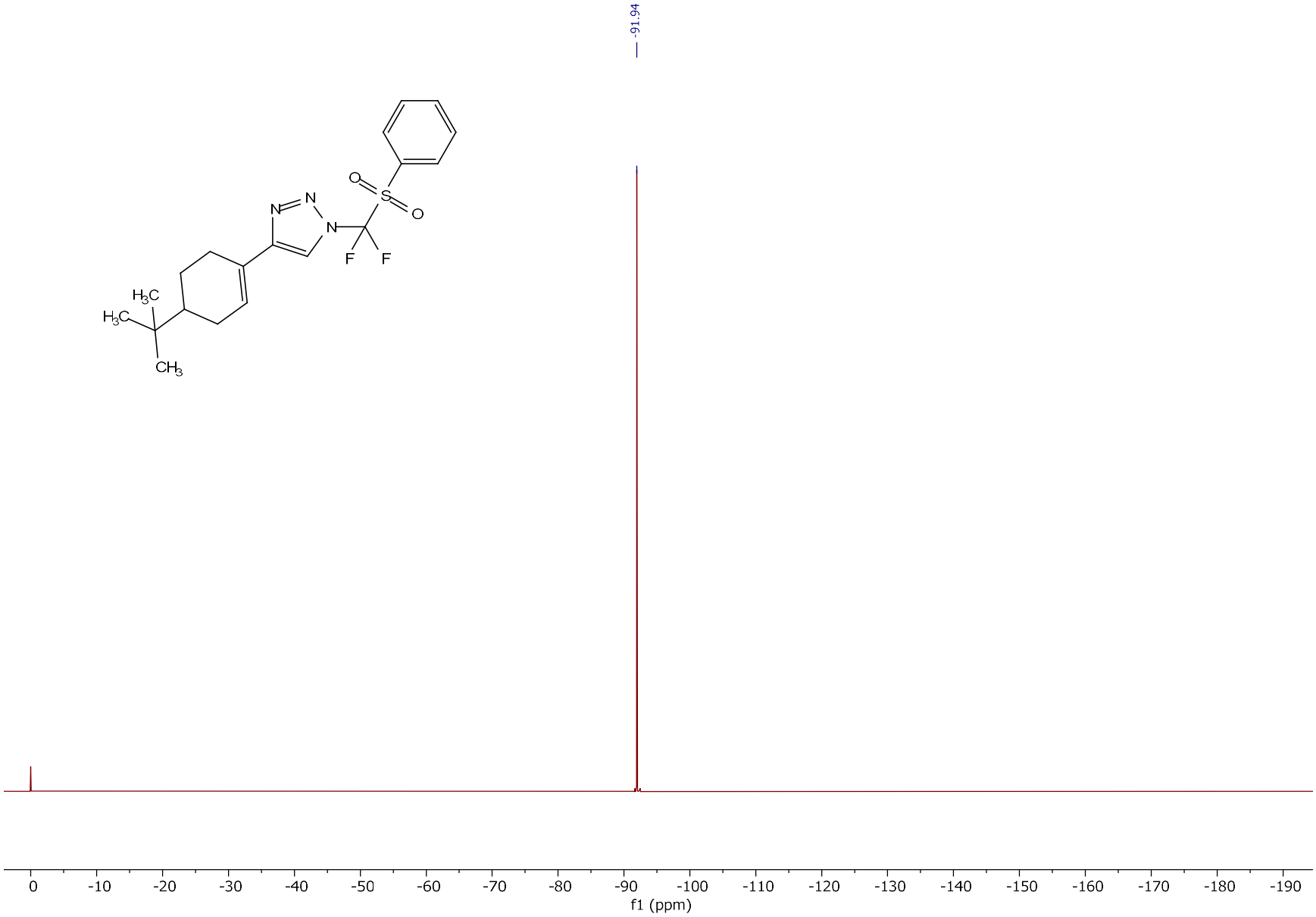
^{1}H NMR (401 MHz, $CDCl_3$) of **1f**



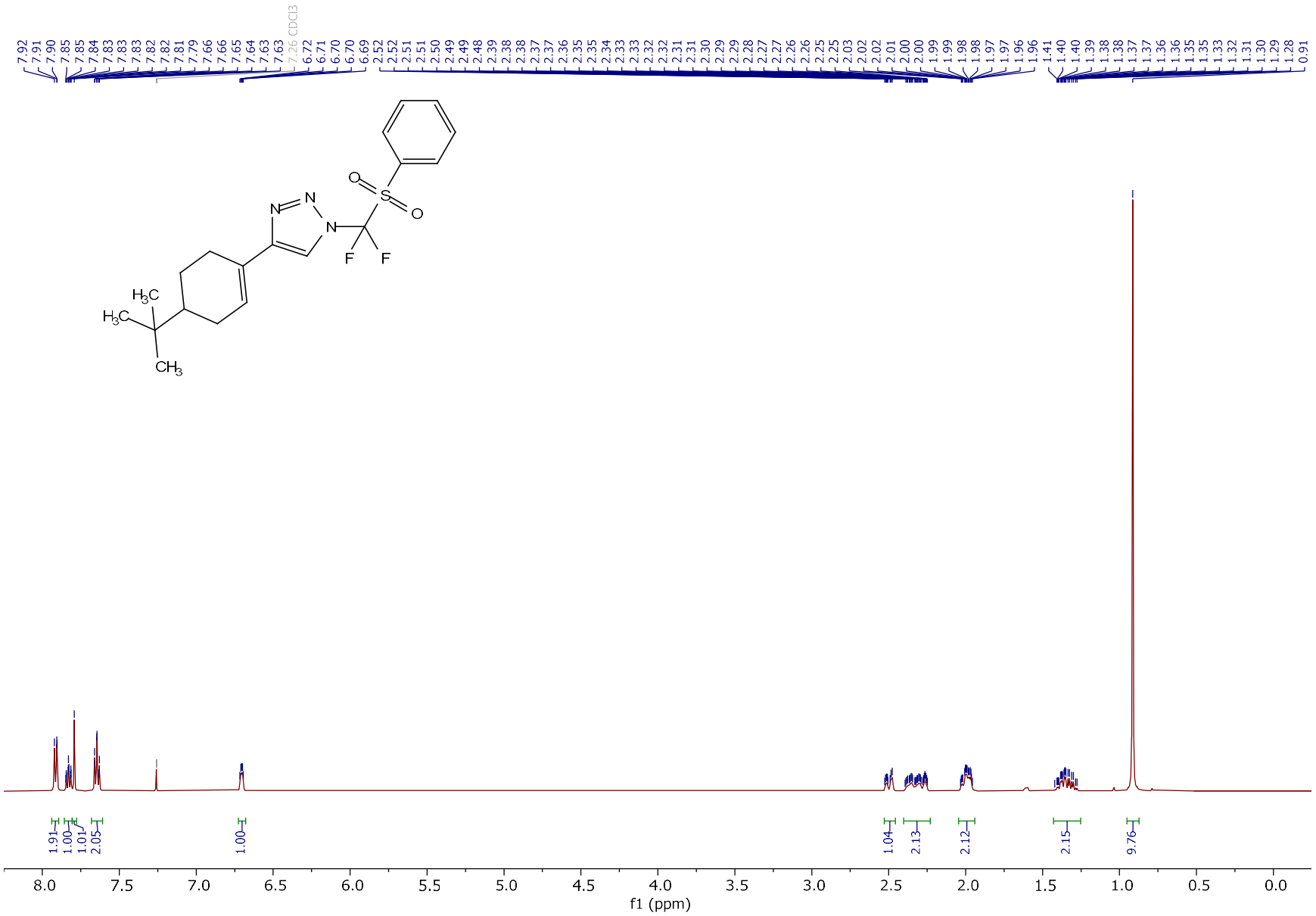
^{13}C NMR (101 MHz, $CDCl_3$) of **1f**



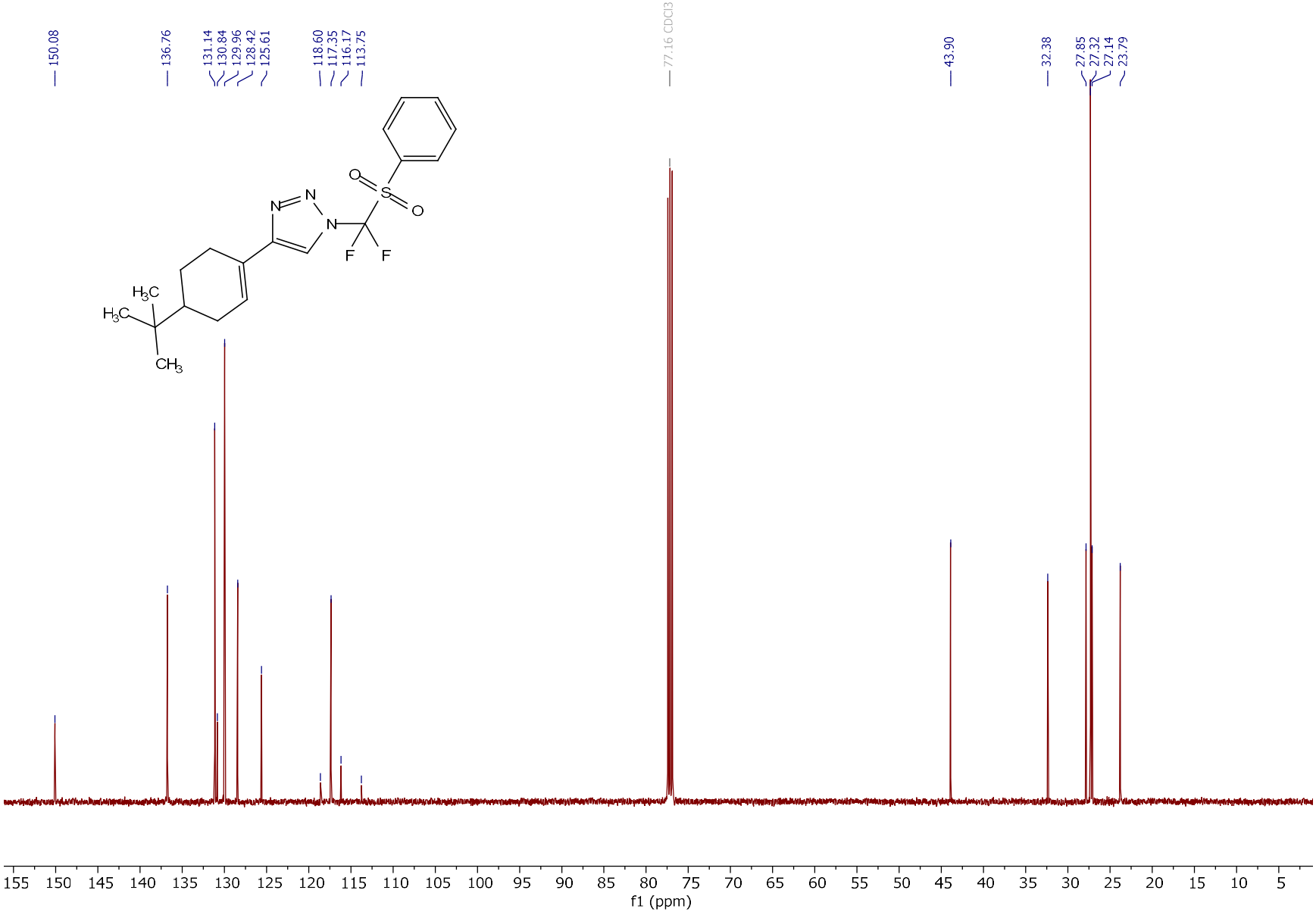
^{19}F NMR (376 MHz, $CDCl_3$) of **1g**



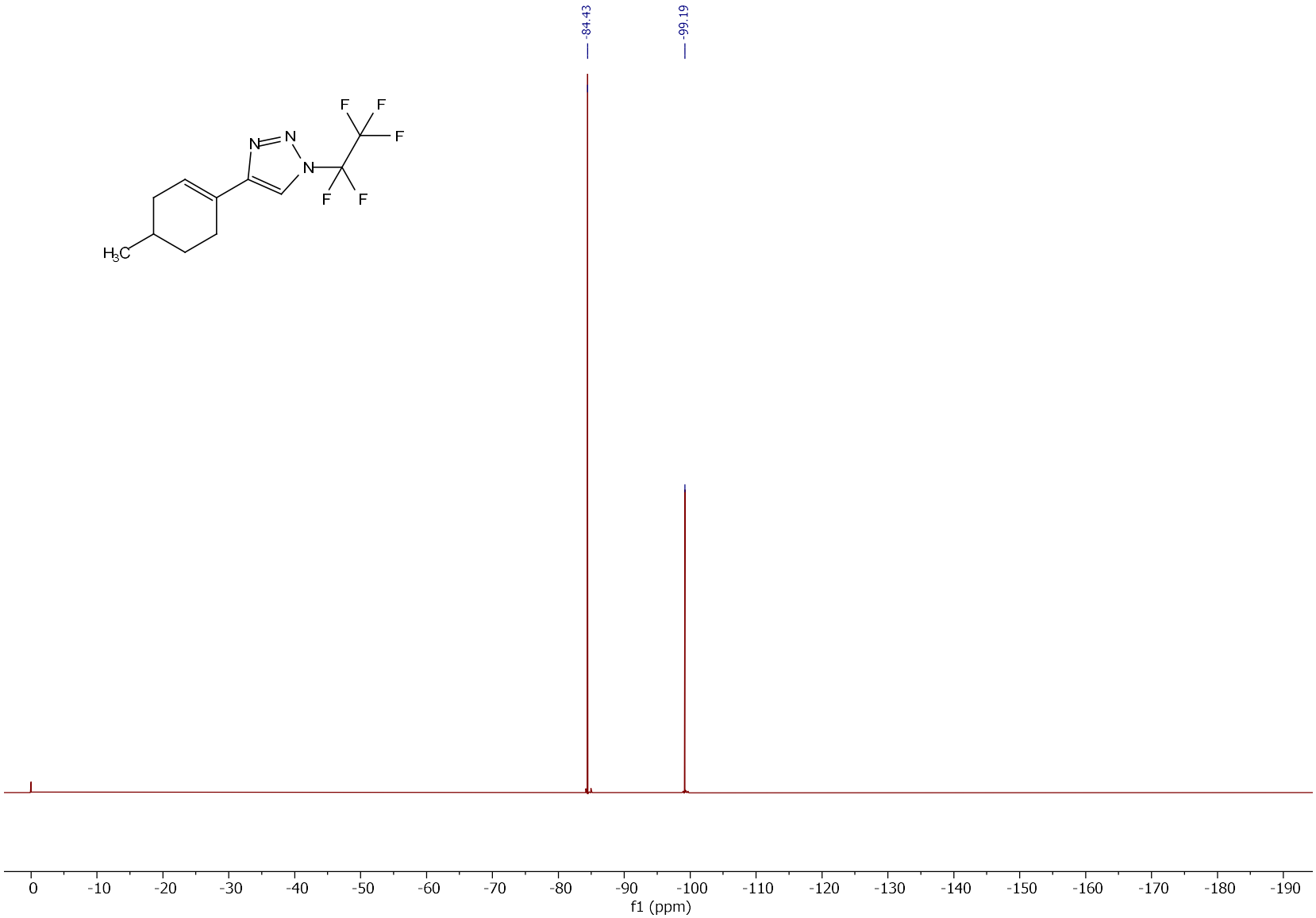
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



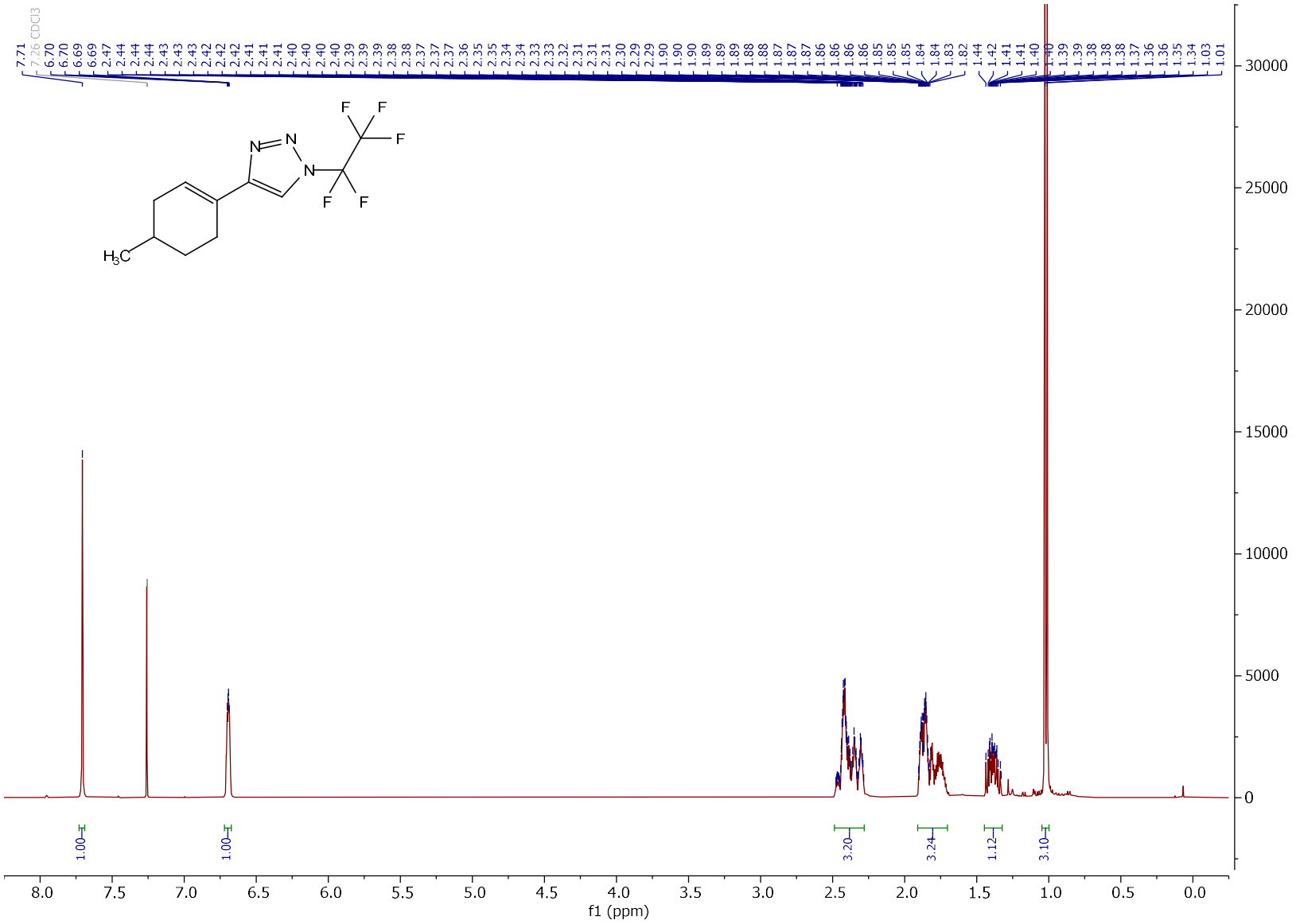
^{13}C NMR (101 MHz, $CDCl_3$) of **1g**



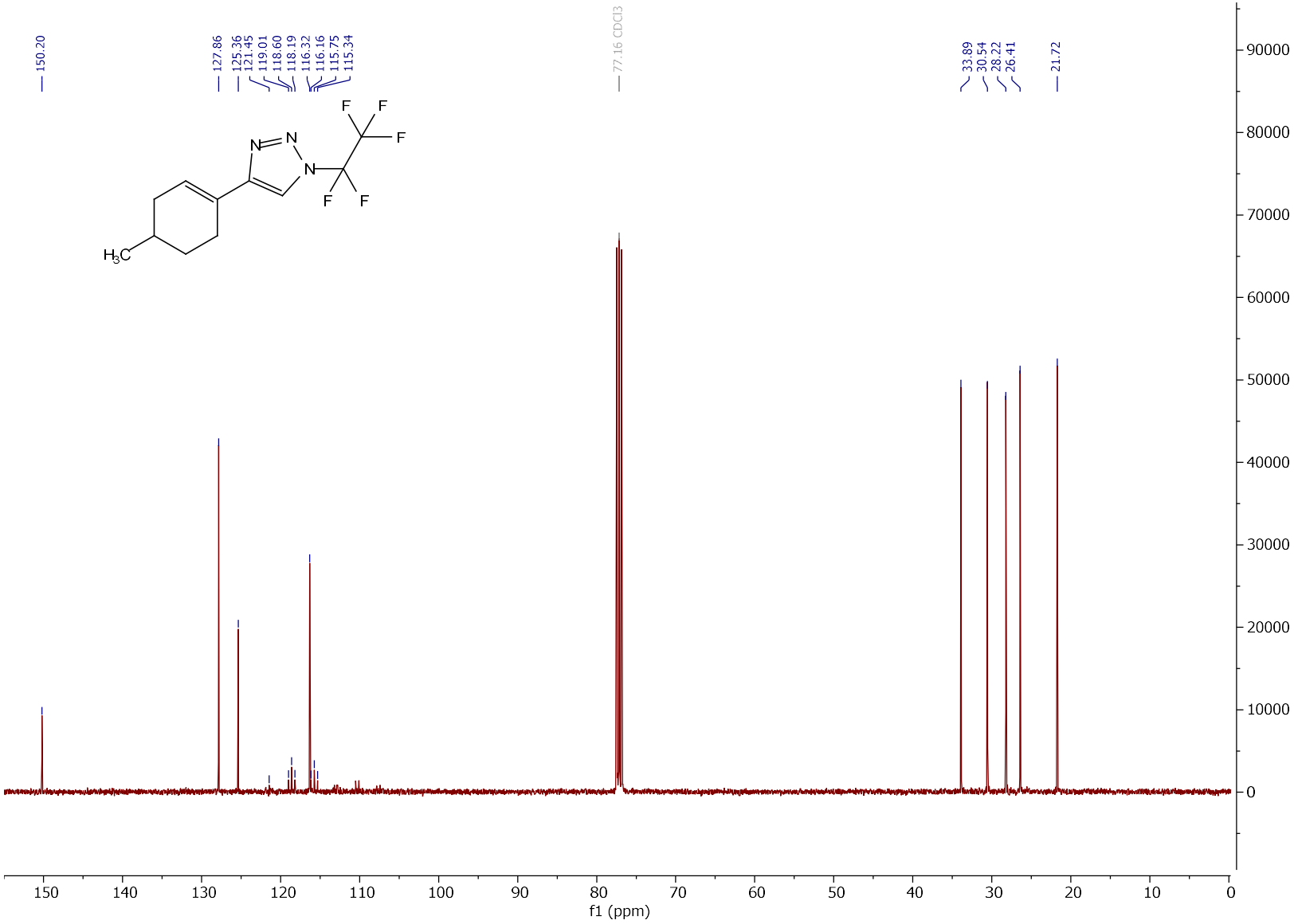
^{19}F NMR (376 MHz, $CDCl_3$) of **1h**



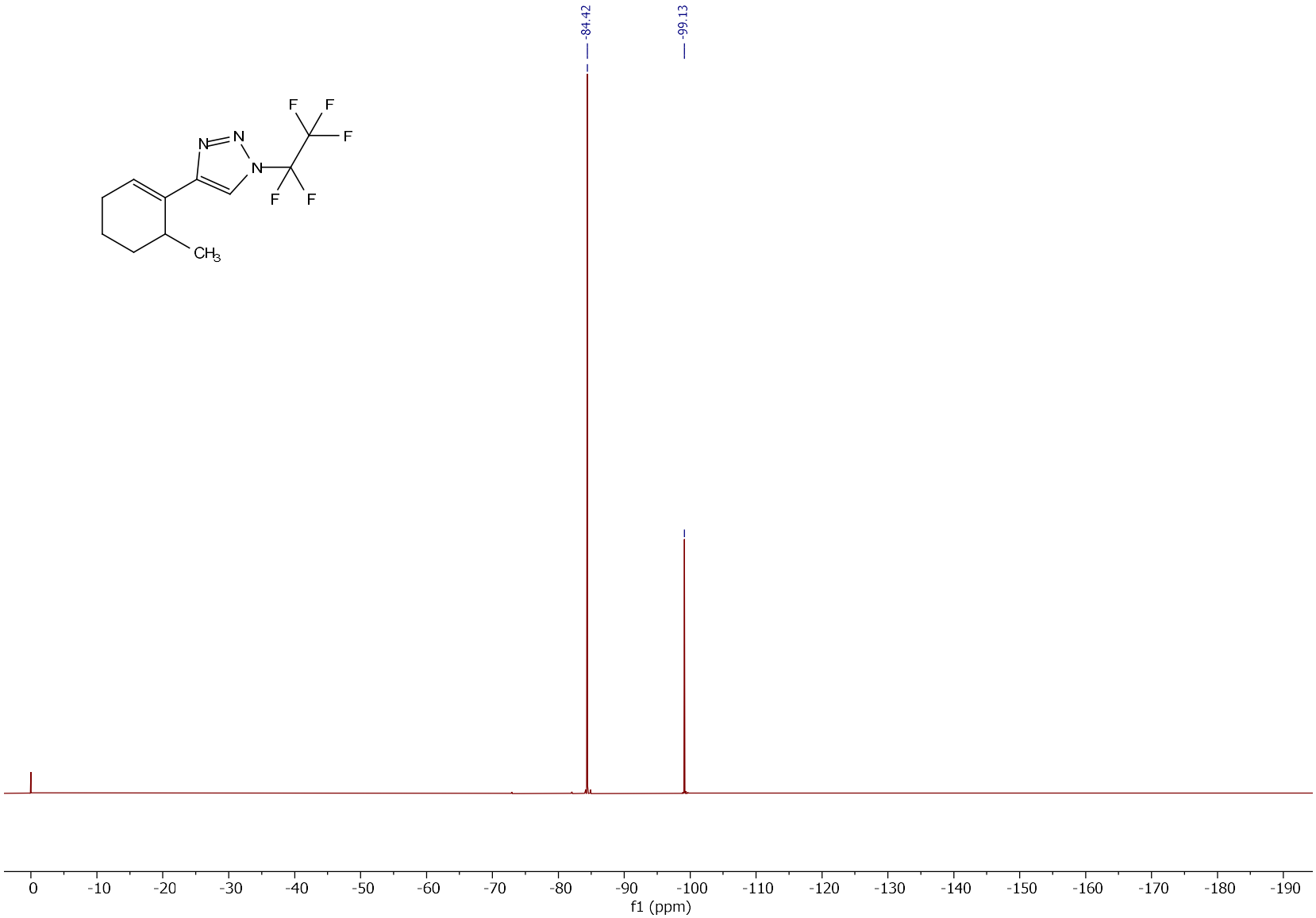
^{1}H NMR (401 MHz, $CDCl_3$) of **1h**



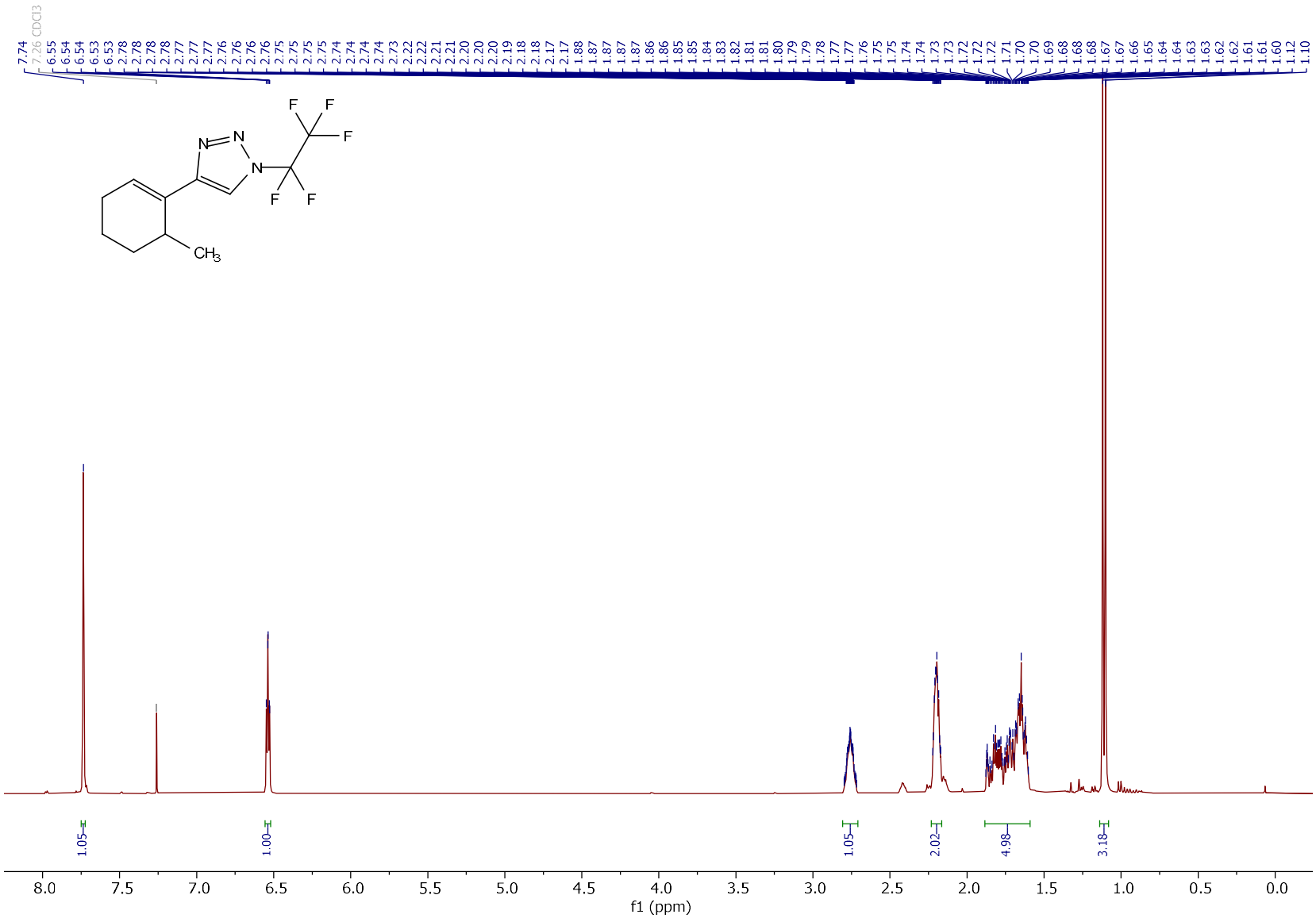
^{13}C NMR (101 MHz, $CDCl_3$) of **1h**



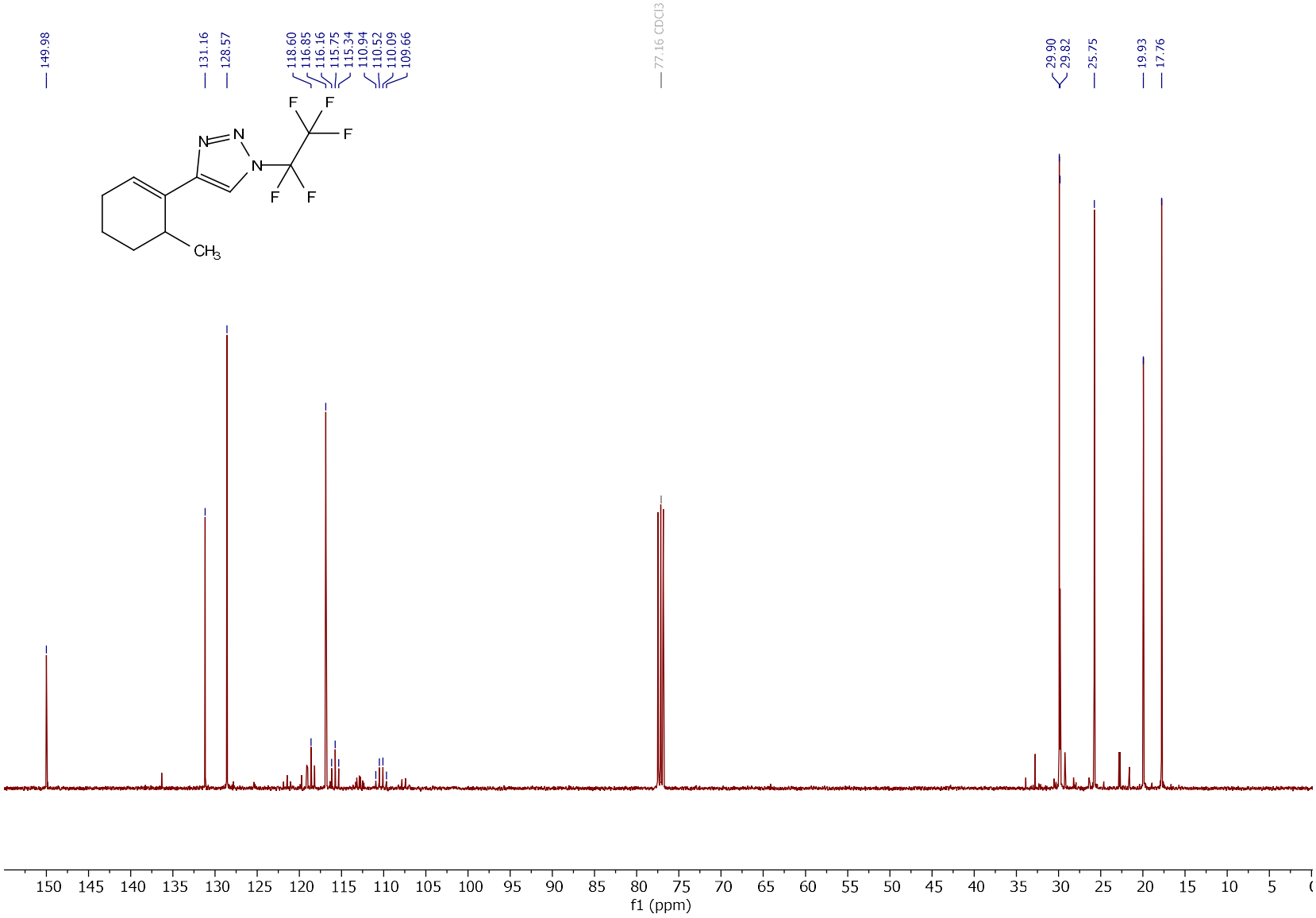
^{19}F NMR (376 MHz, $CDCl_3$) of **1i**



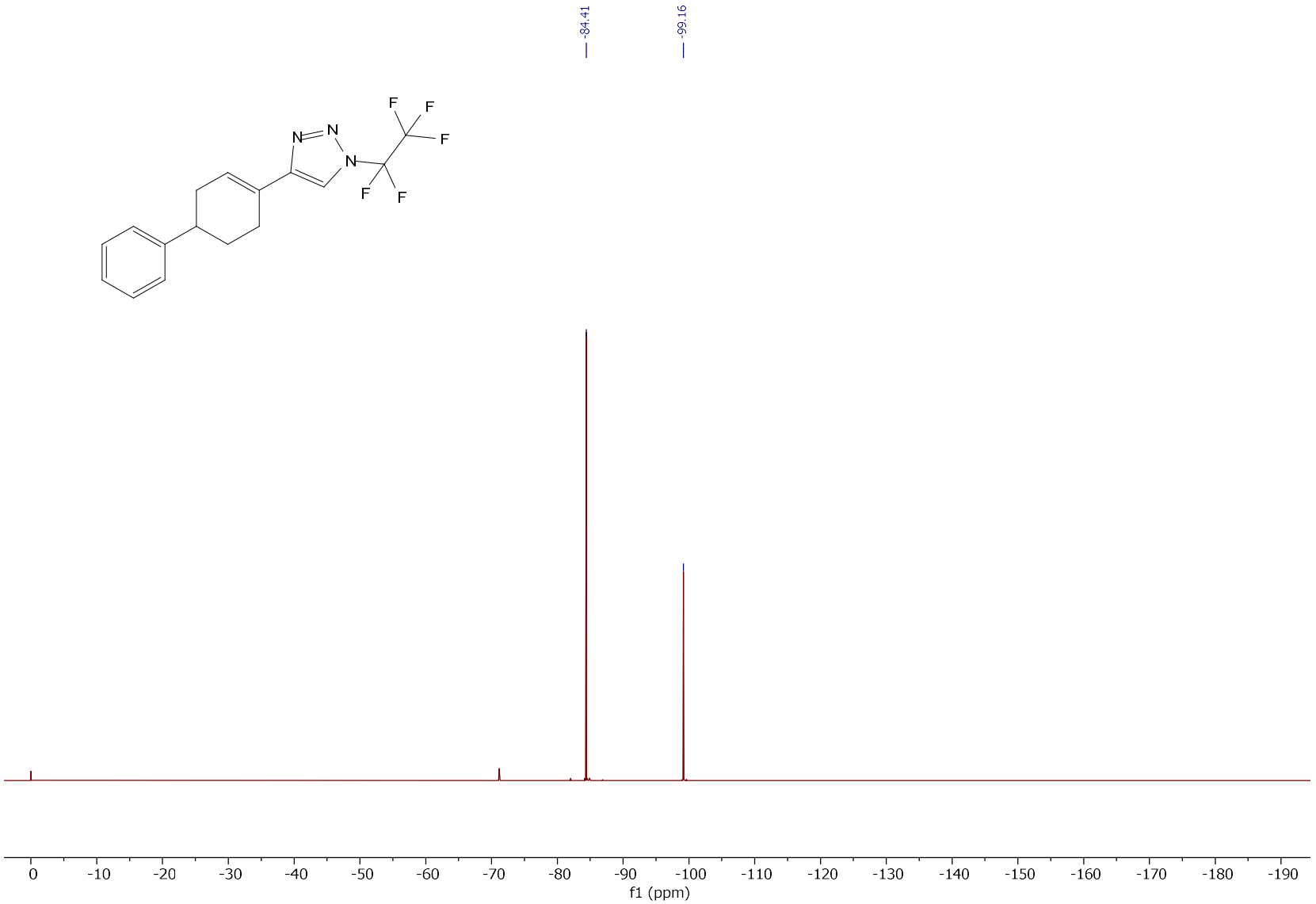
^{1}H NMR (401 MHz, $CDCl_3$) of **1i**



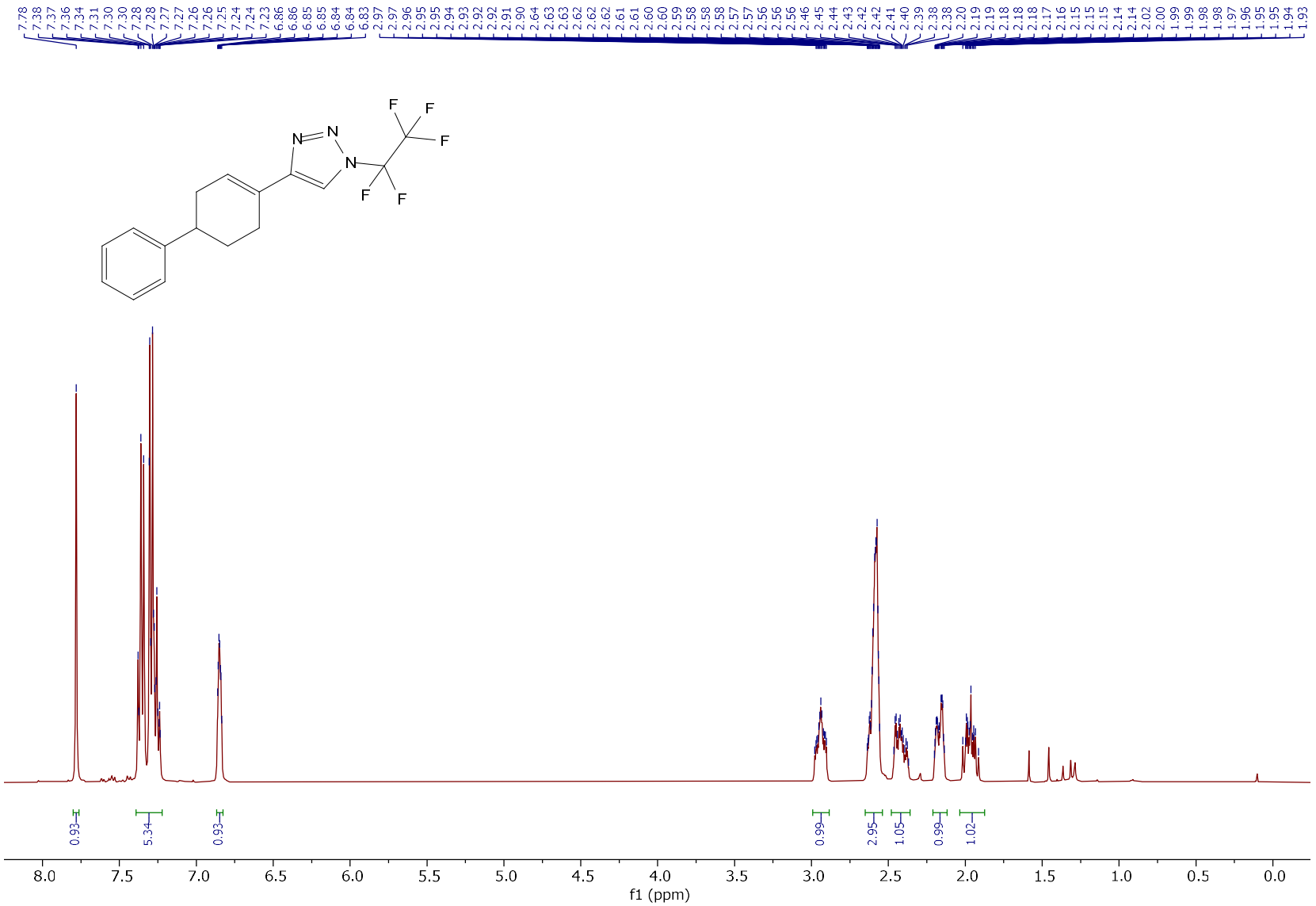
^{13}C NMR (101 MHz, $CDCl_3$) of **1i**



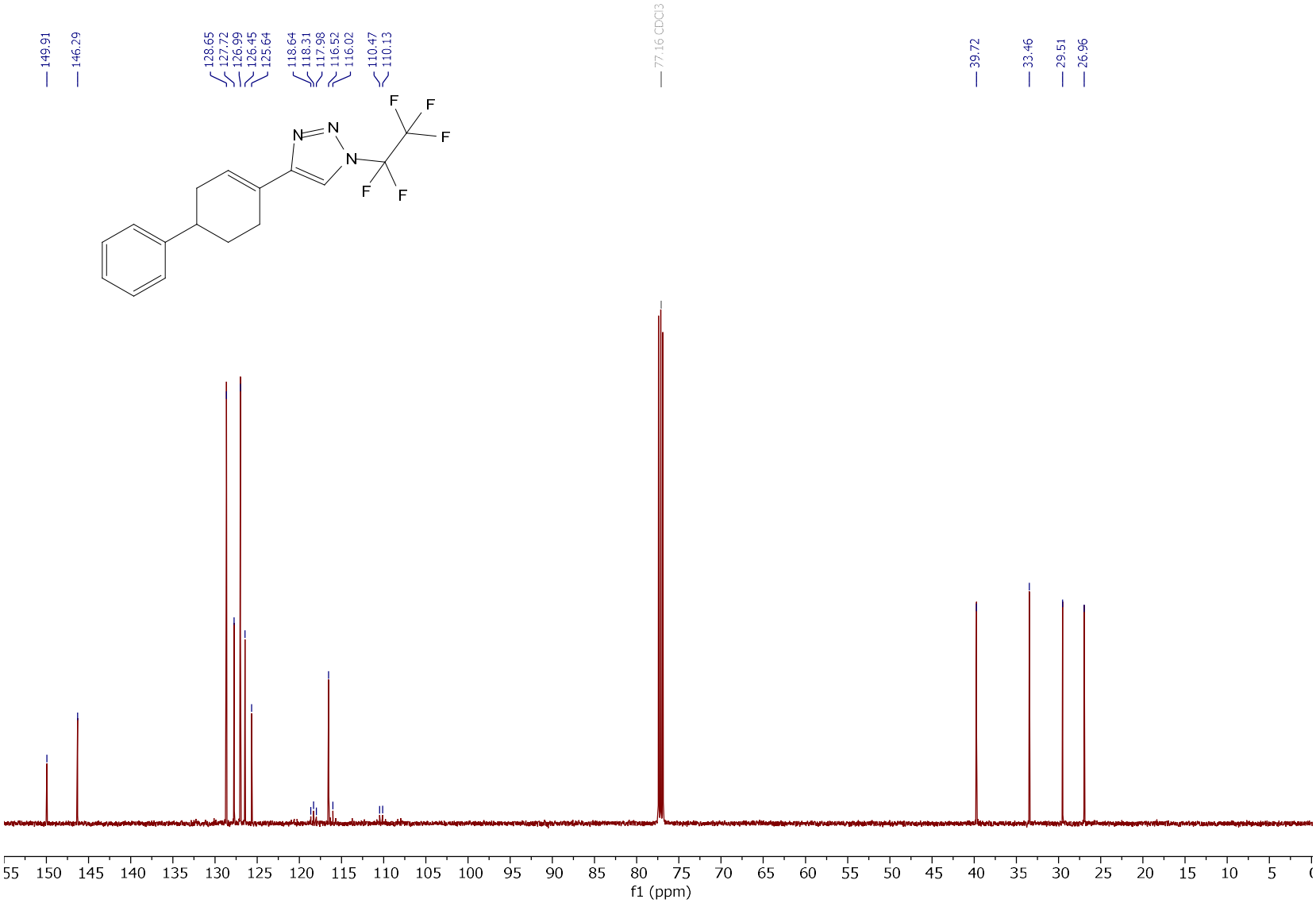
^{19}F NMR (376 MHz, $CDCl_3$) of **1j**



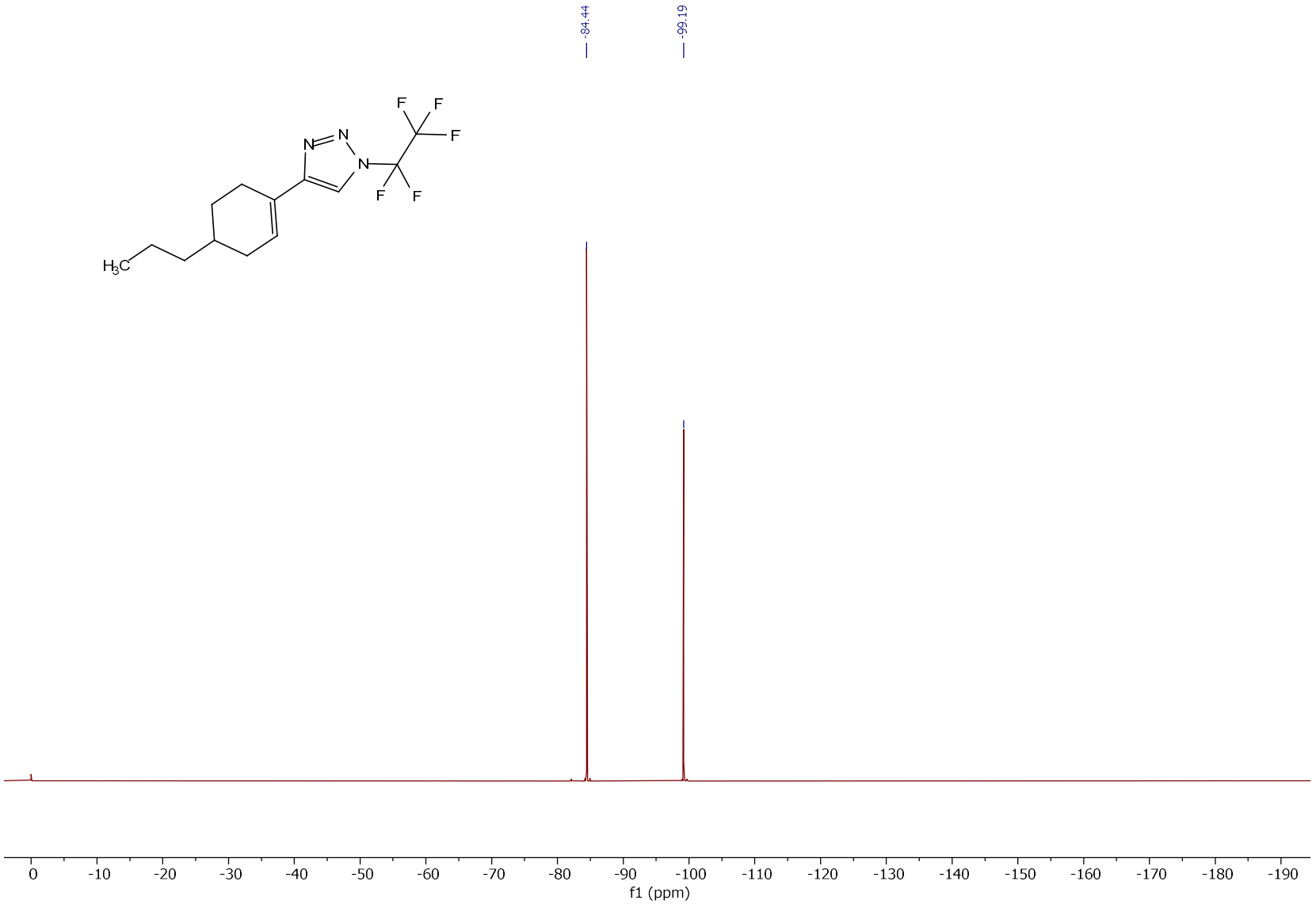
^{1}H NMR (400 MHz, $CDCl_3$) of **1j**



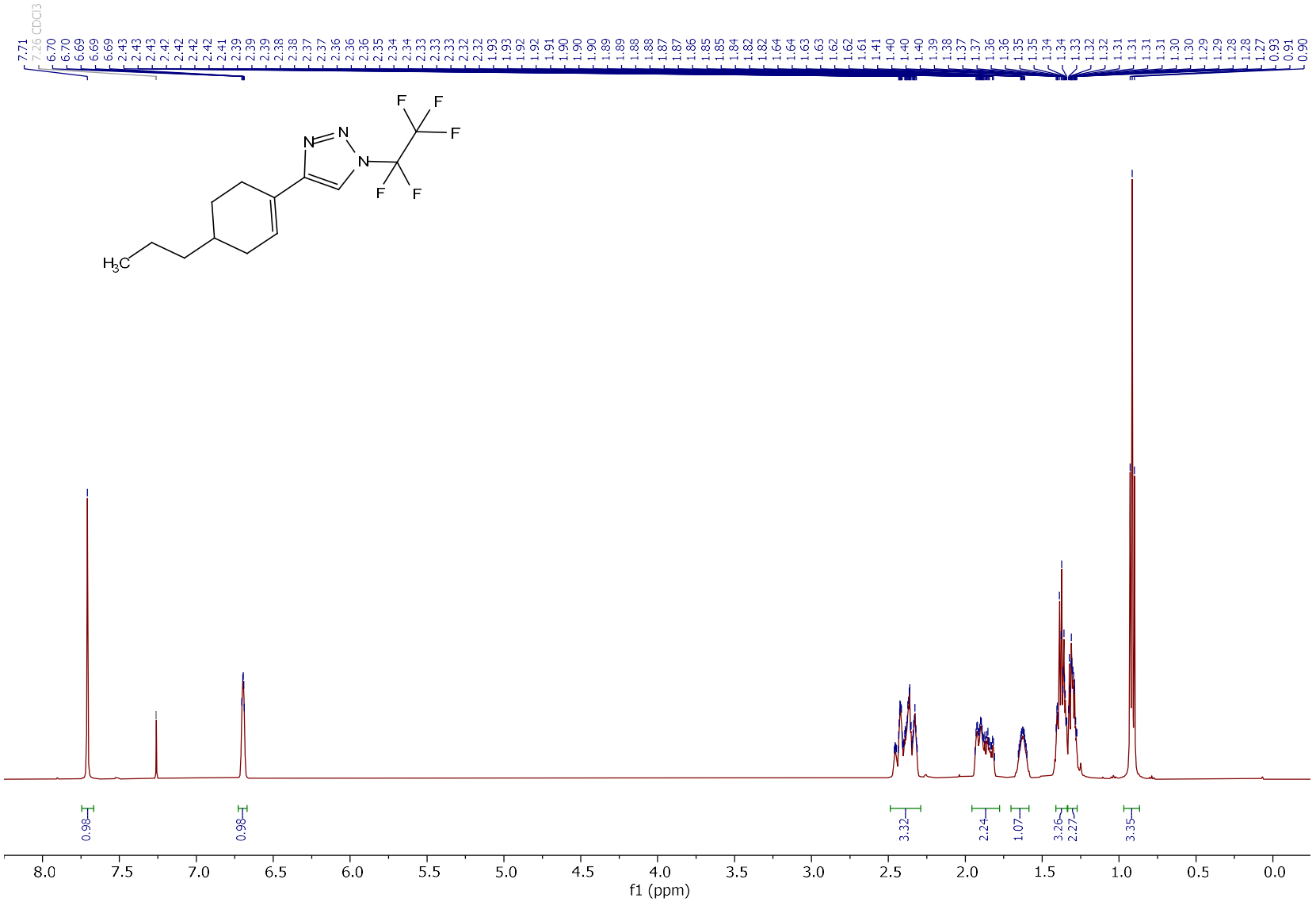
^{13}C NMR (126 MHz, $CDCl_3$) of **1j**



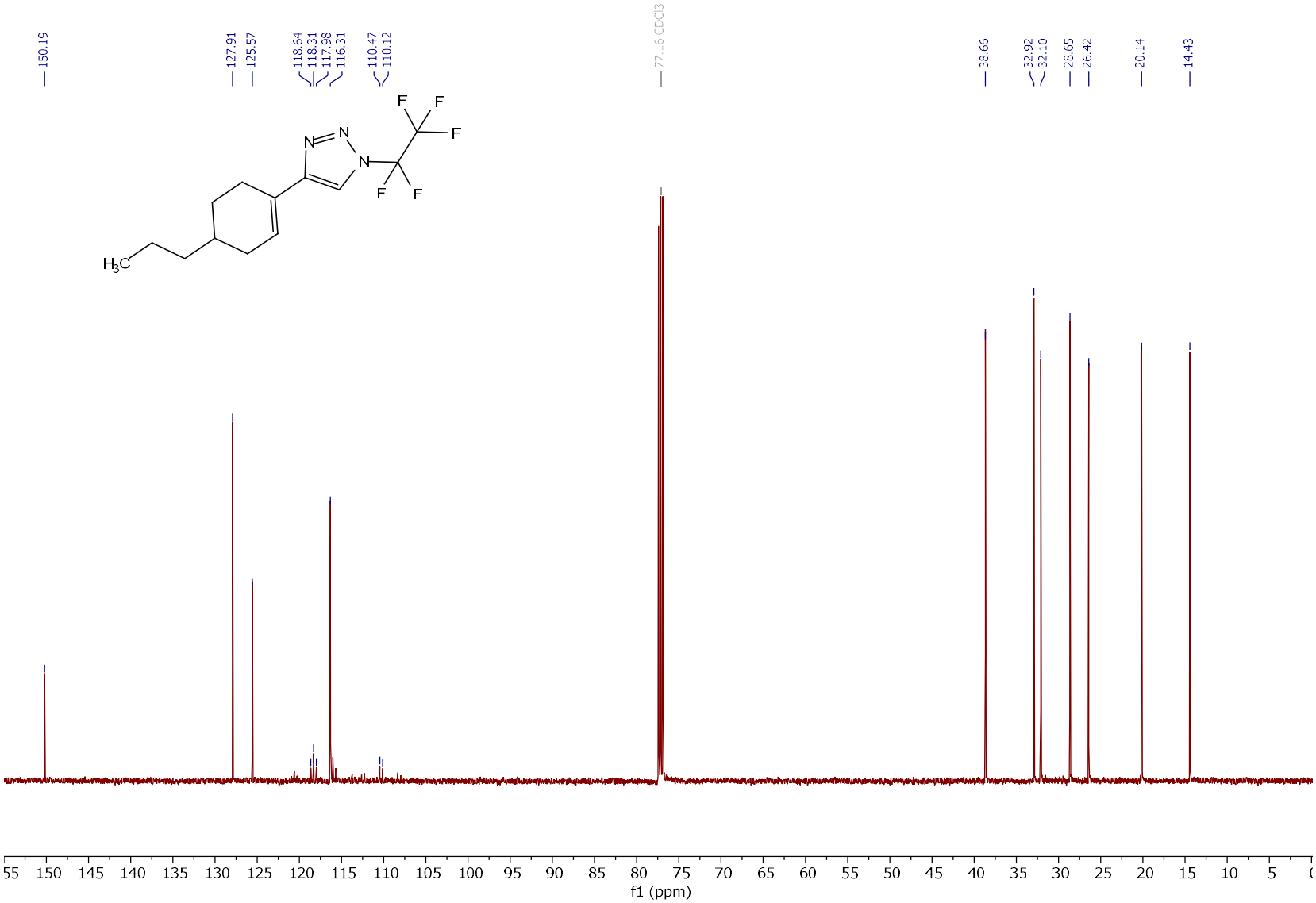
^{19}F NMR (376 MHz, $CDCl_3$) of **1k**



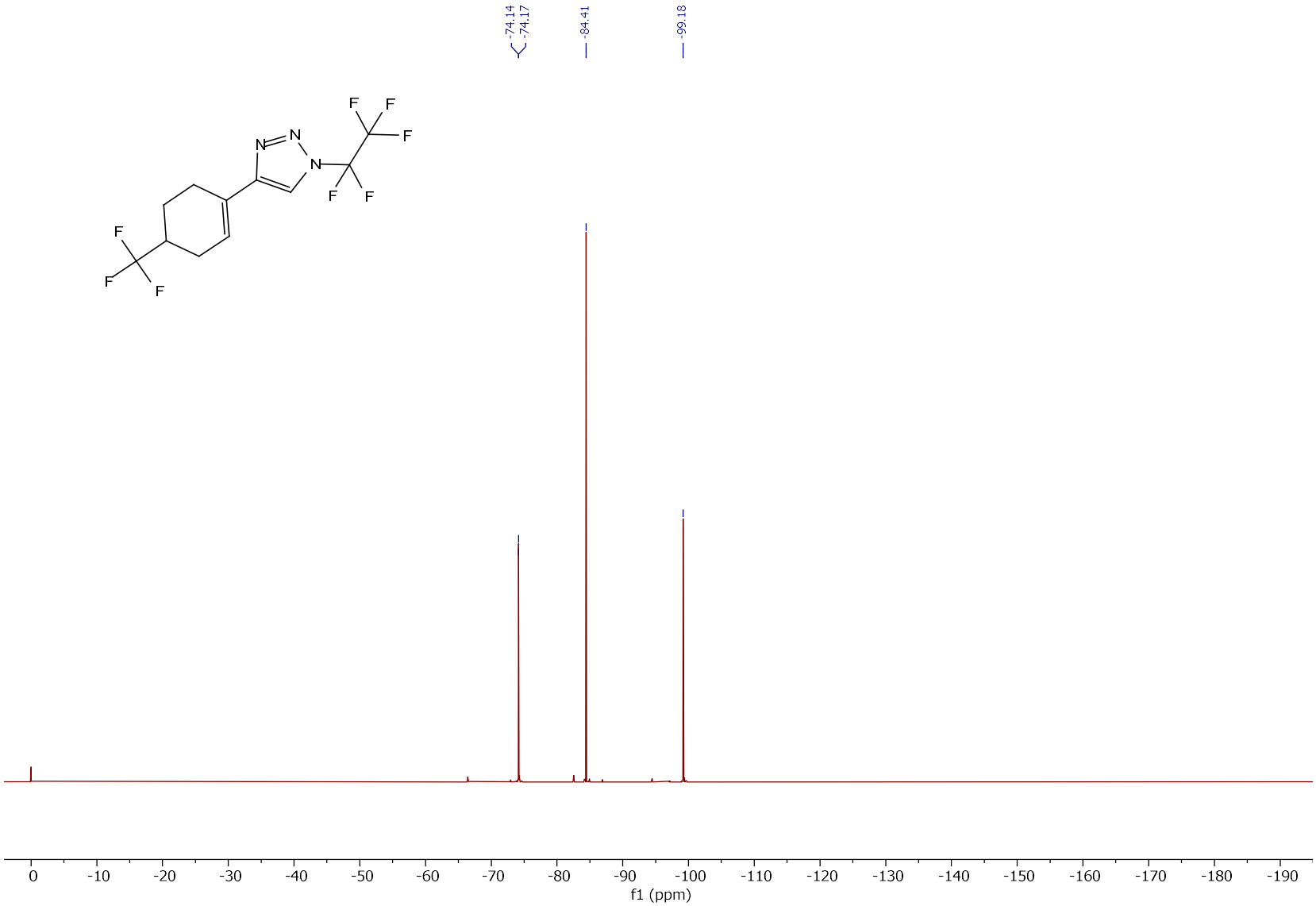
^{1}H NMR (500 MHz, $CDCl_3$) of **1k**



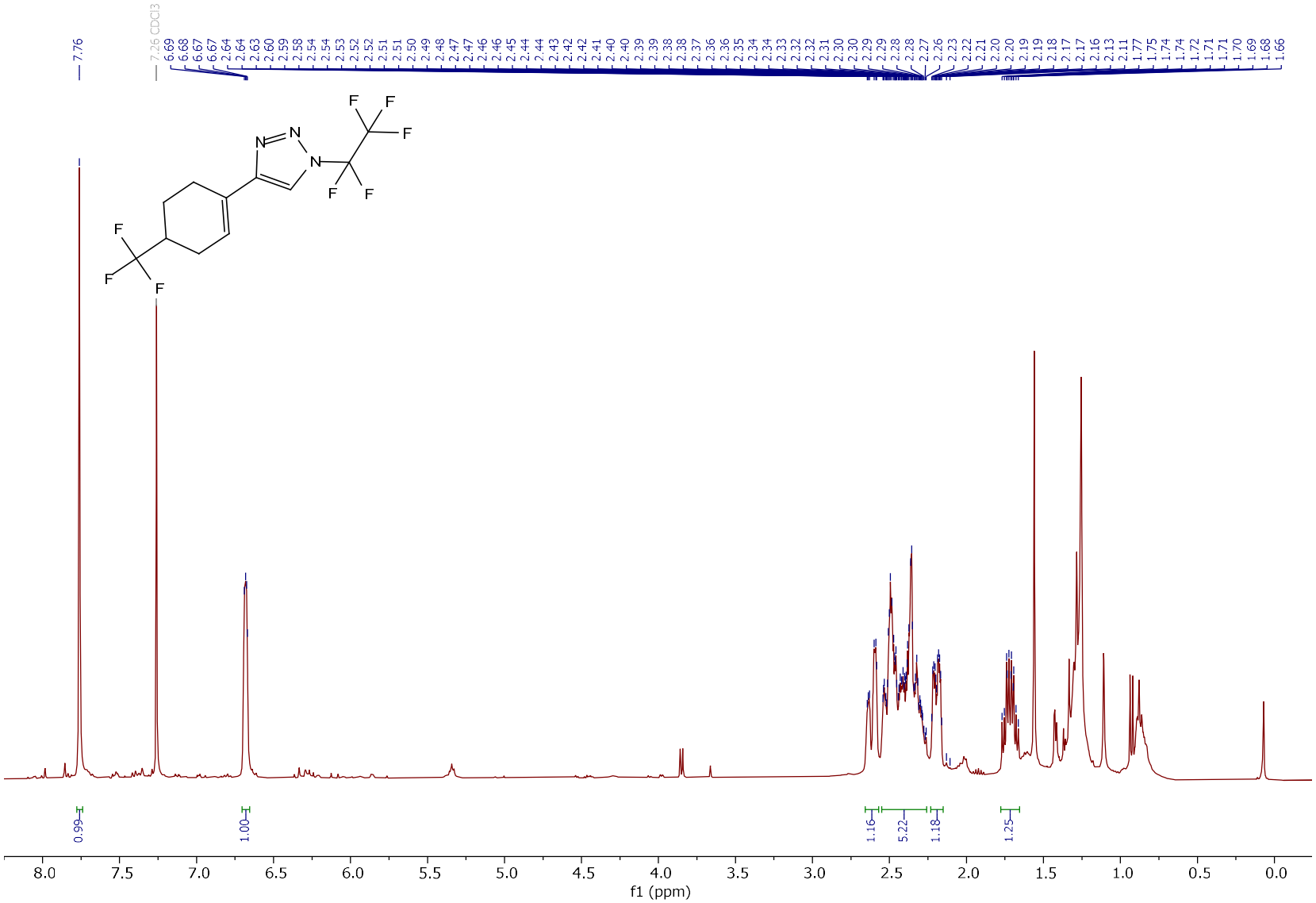
^{13}C NMR (126 MHz, $CDCl_3$) of **1k**



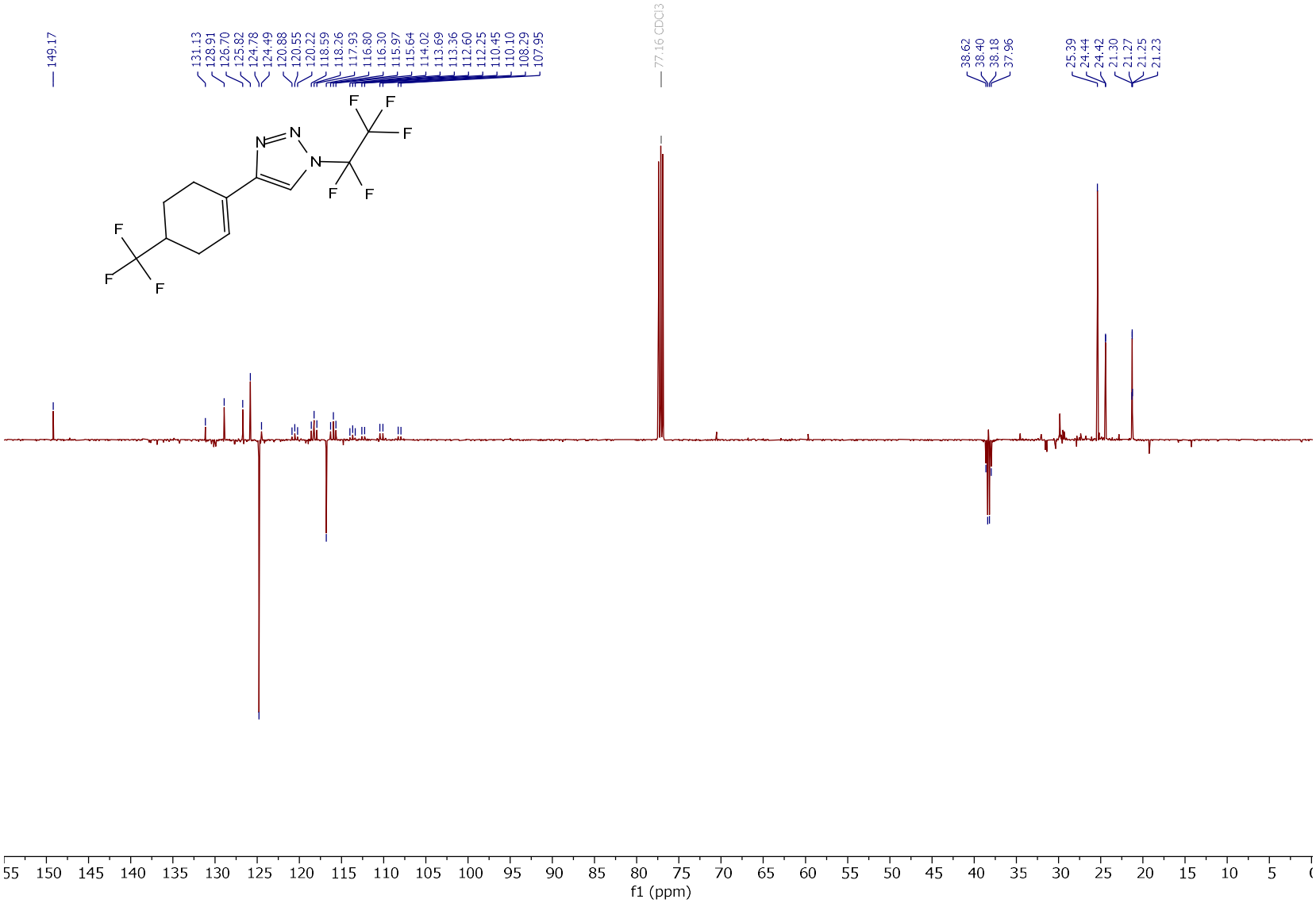
^{19}F NMR (376 MHz, $CDCl_3$) of **1l**



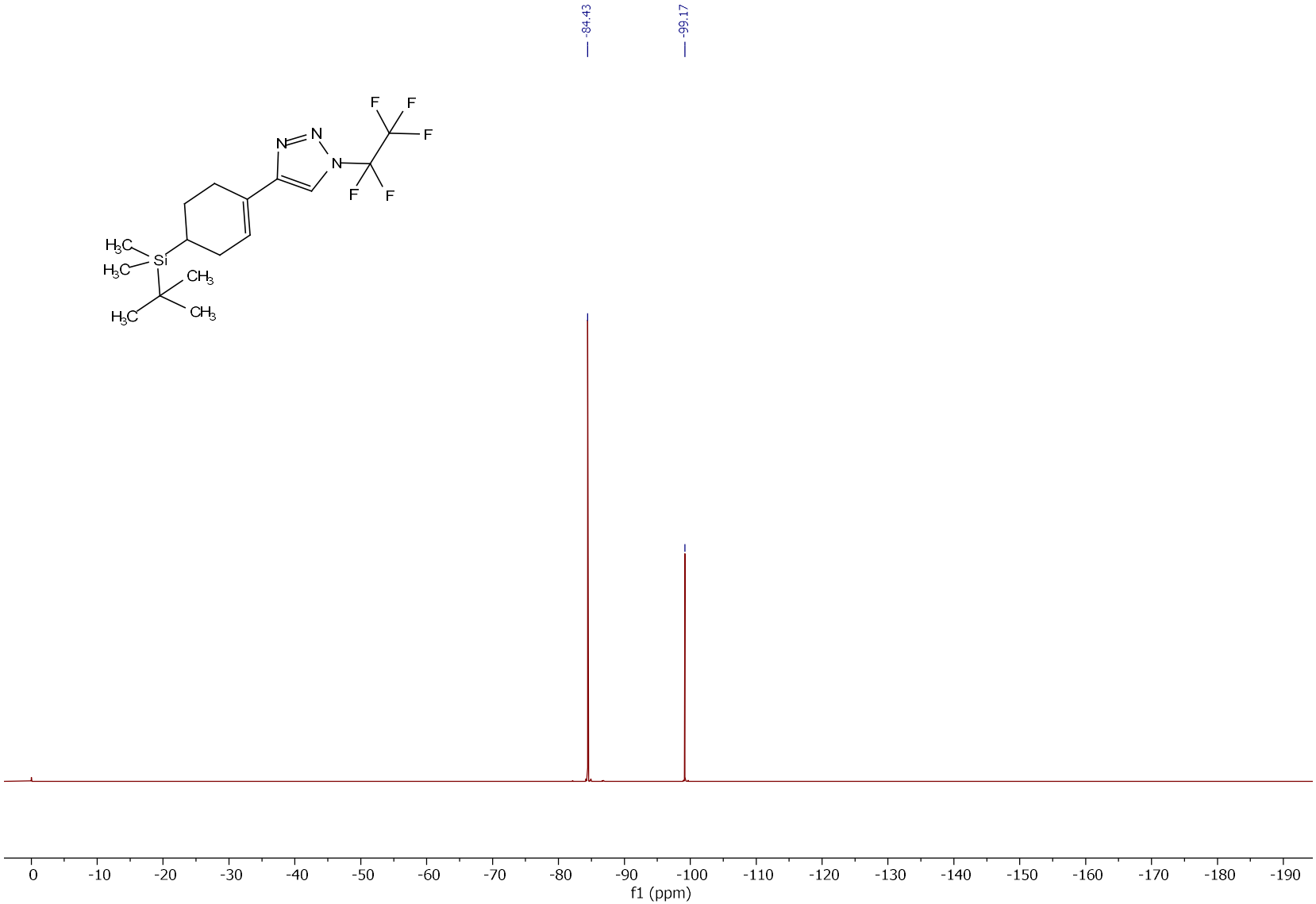
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



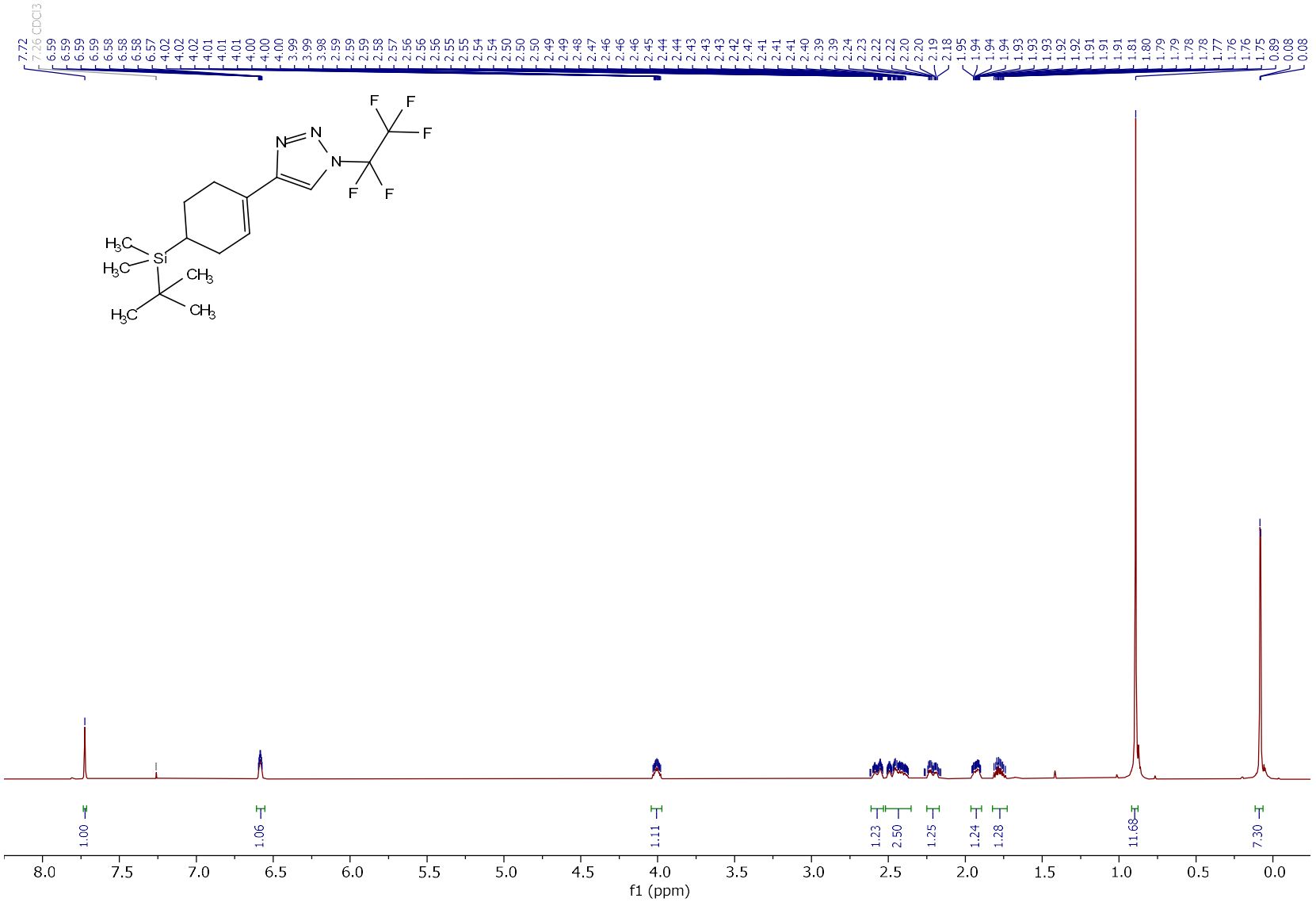
^{13}C NMR (126 MHz, $CDCl_3$) of **11**



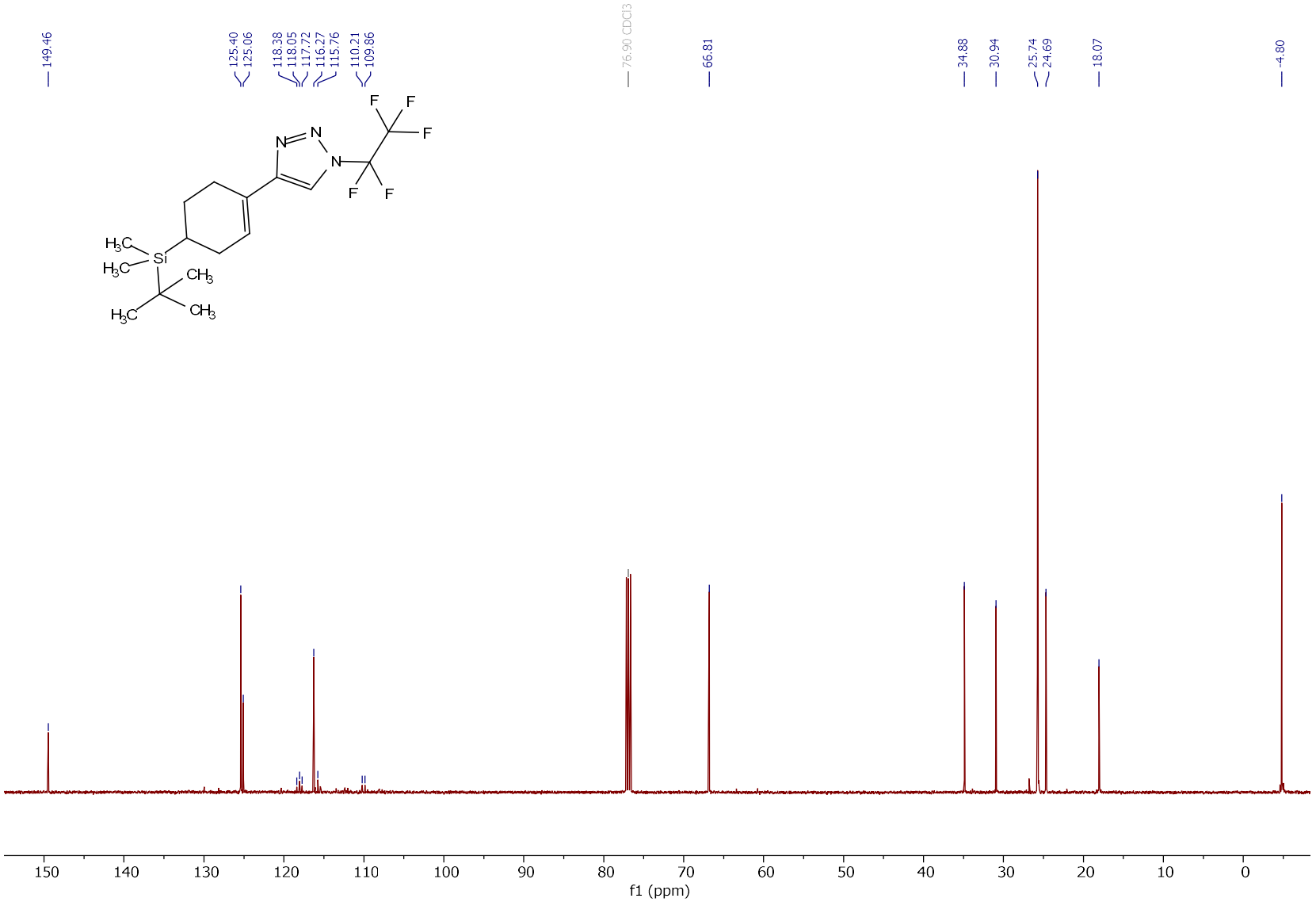
^{19}F NMR (376 MHz, $CDCl_3$) of **1m**



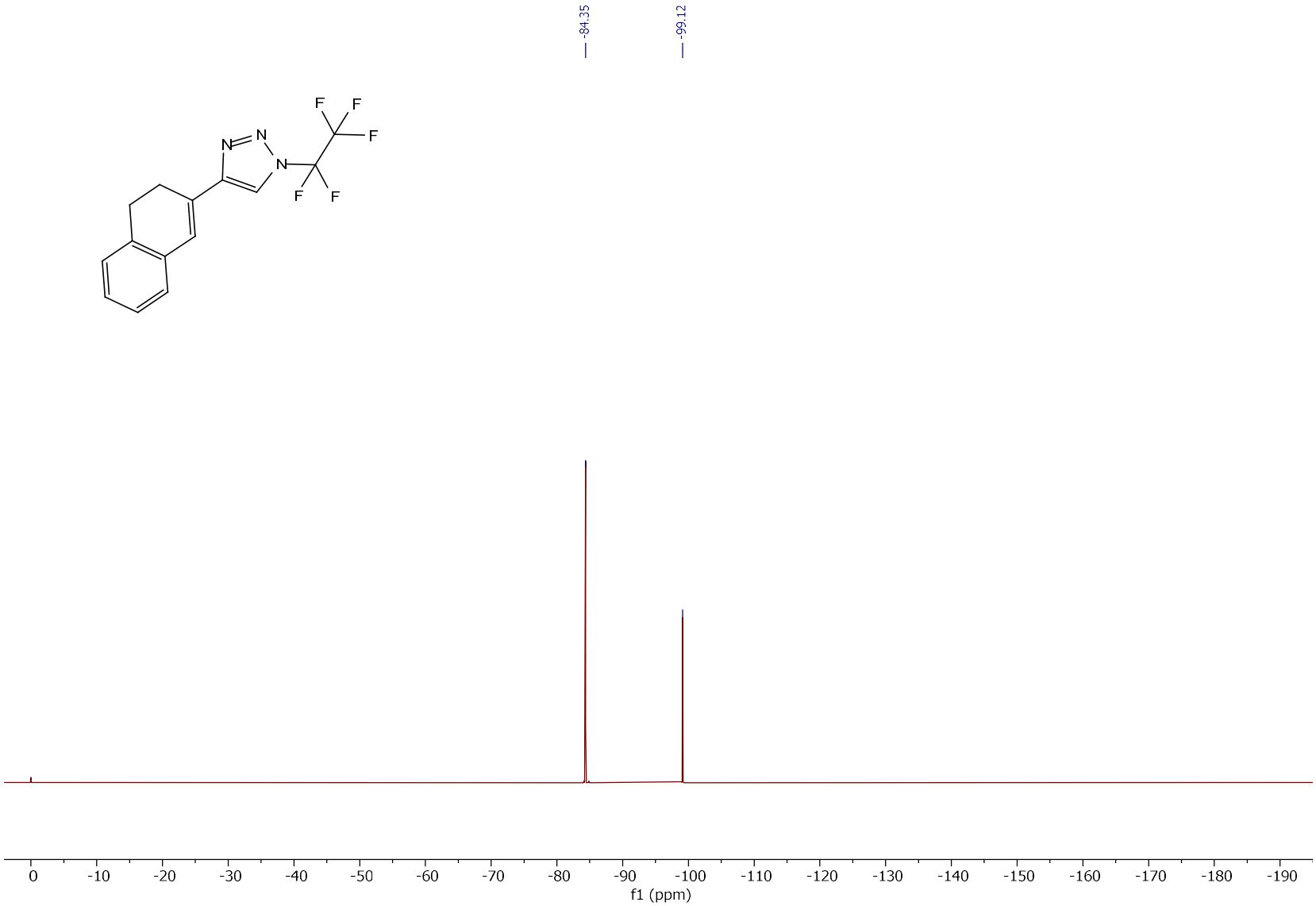
^{1}H NMR (500 MHz, $CDCl_3$) of **1m**



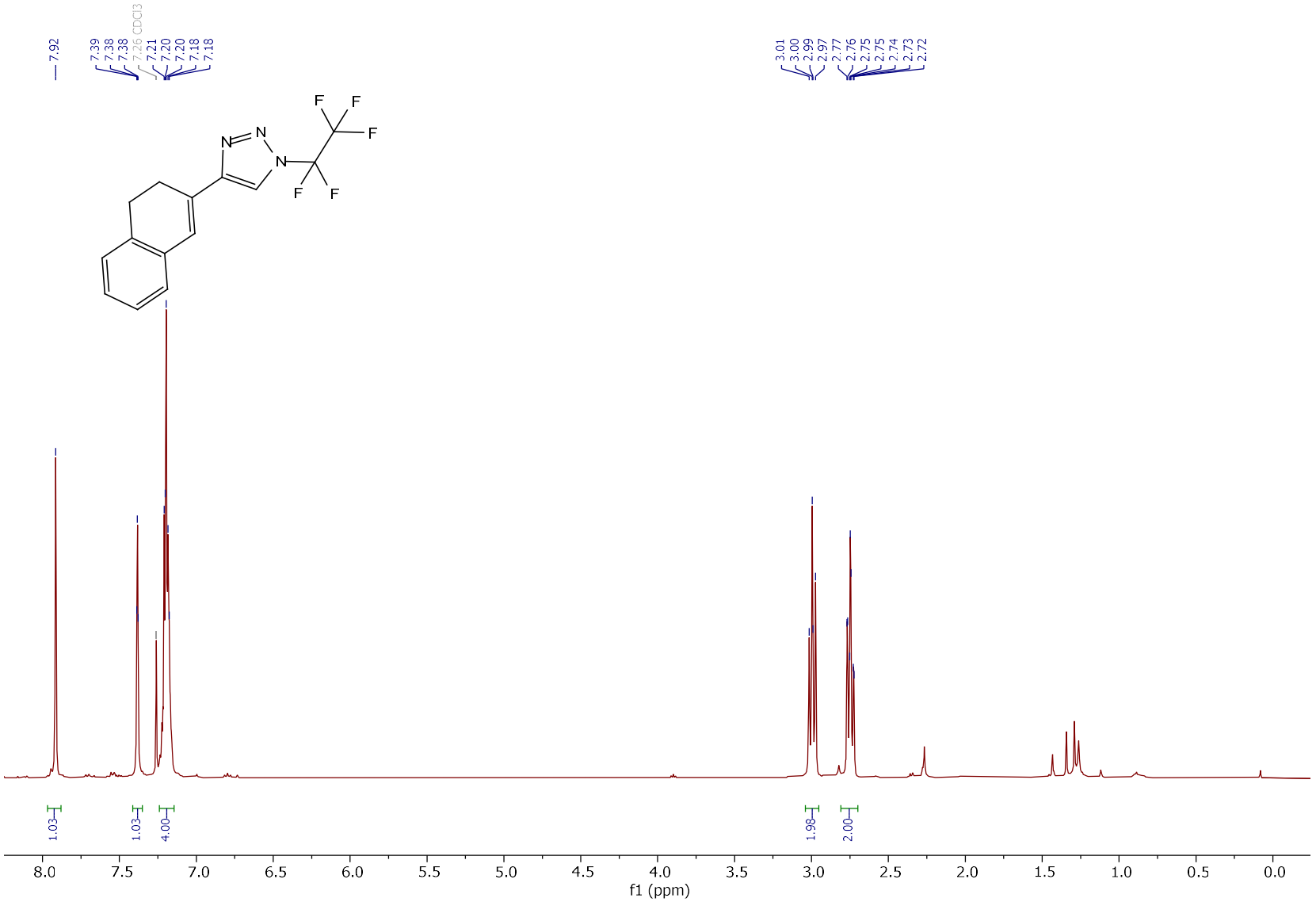
^{13}C NMR (126 MHz, $CDCl_3$) of **1m**



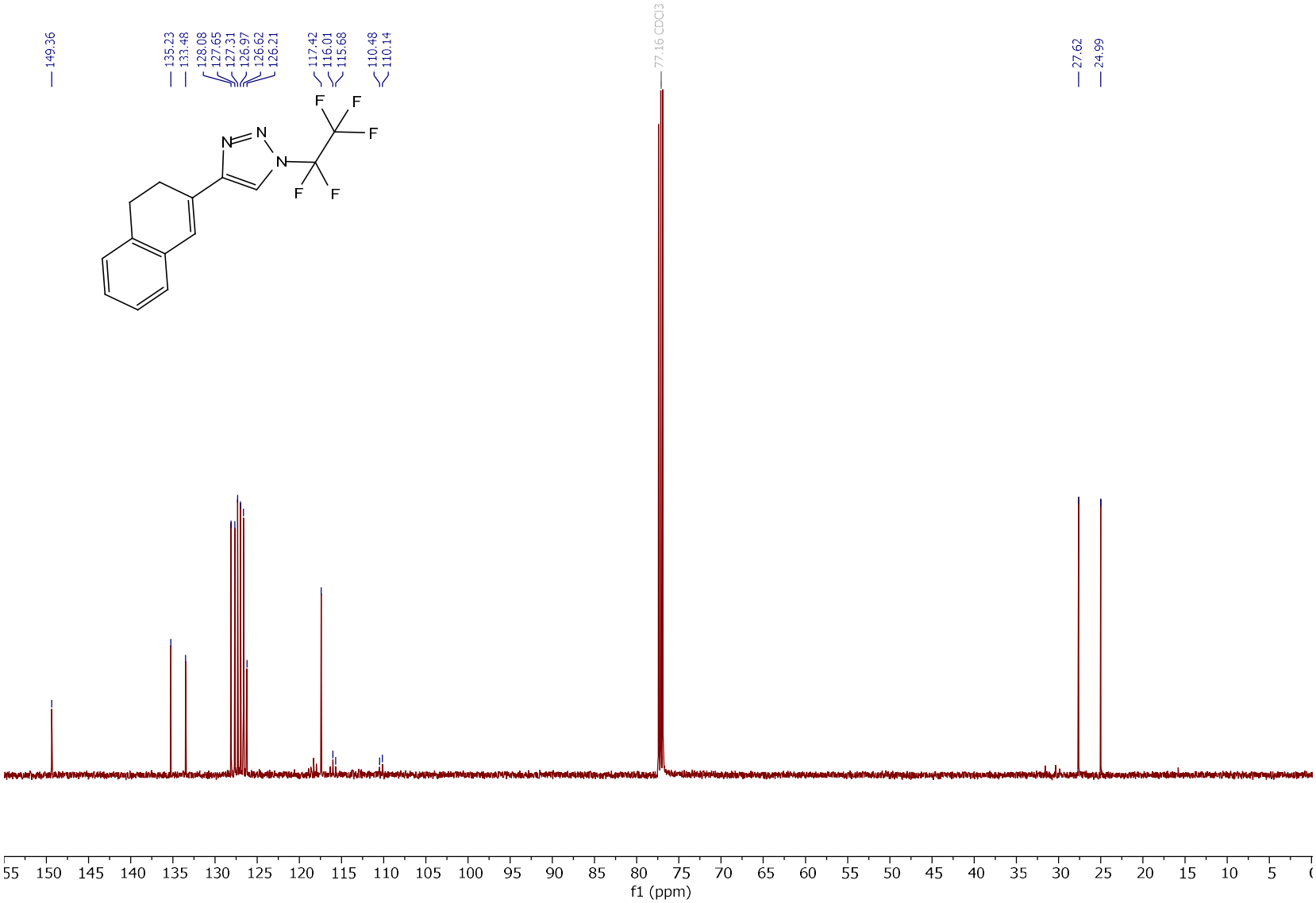
^{19}F NMR (376 MHz, $CDCl_3$) of **1n**



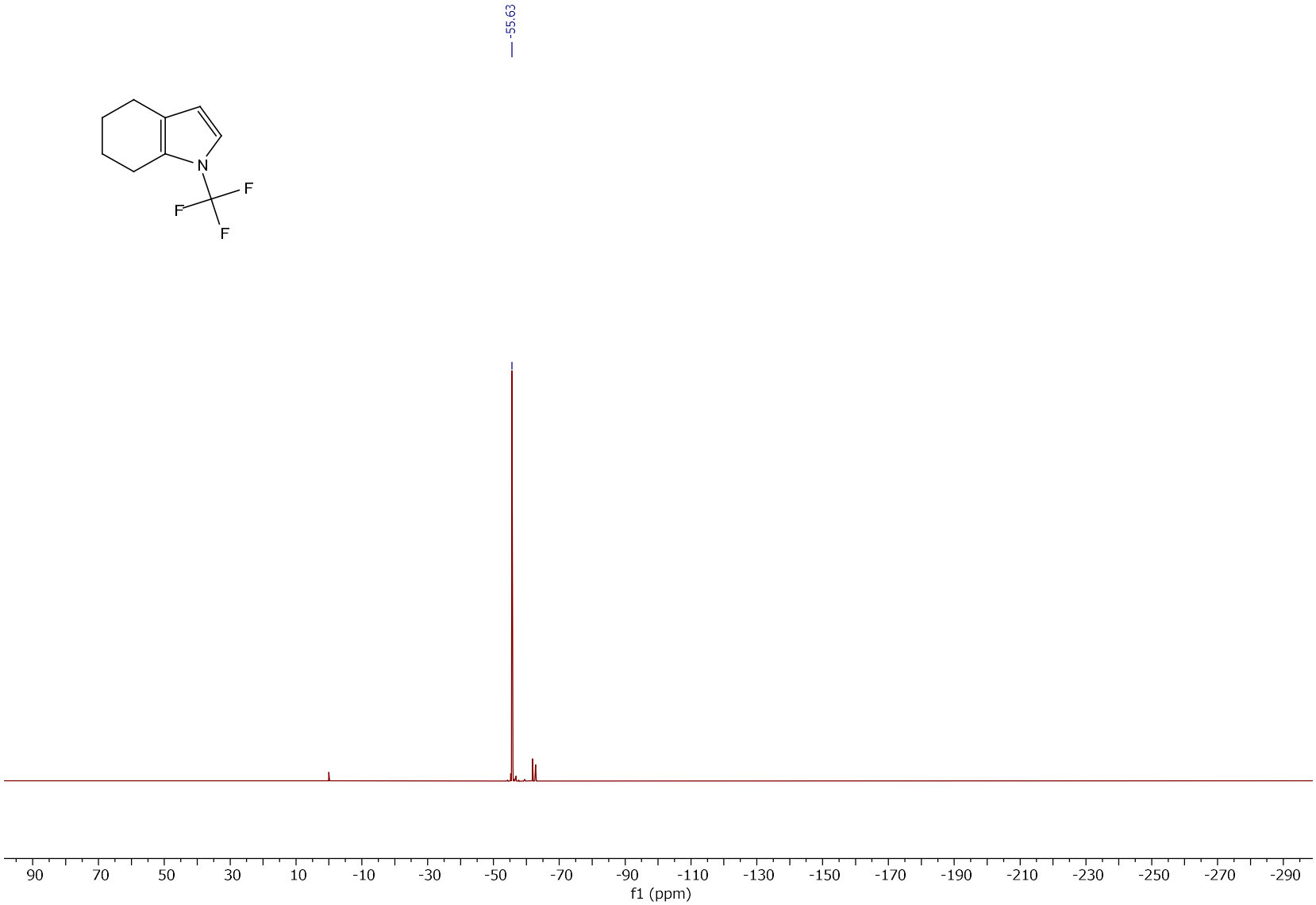
^{1}H NMR (400 MHz, $CDCl_3$) of **1n**



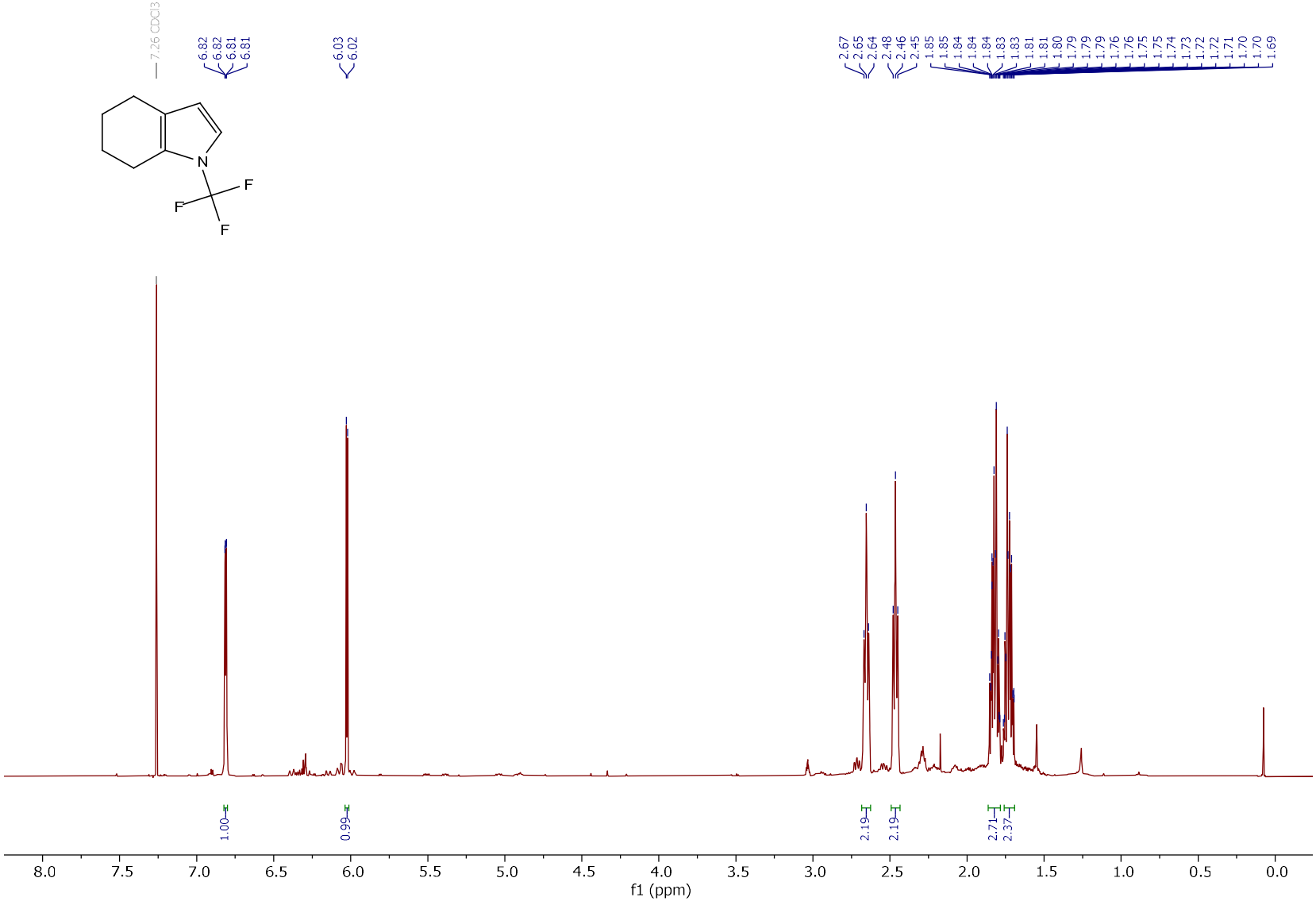
^{13}C NMR (126 MHz, $CDCl_3$) of **1n**



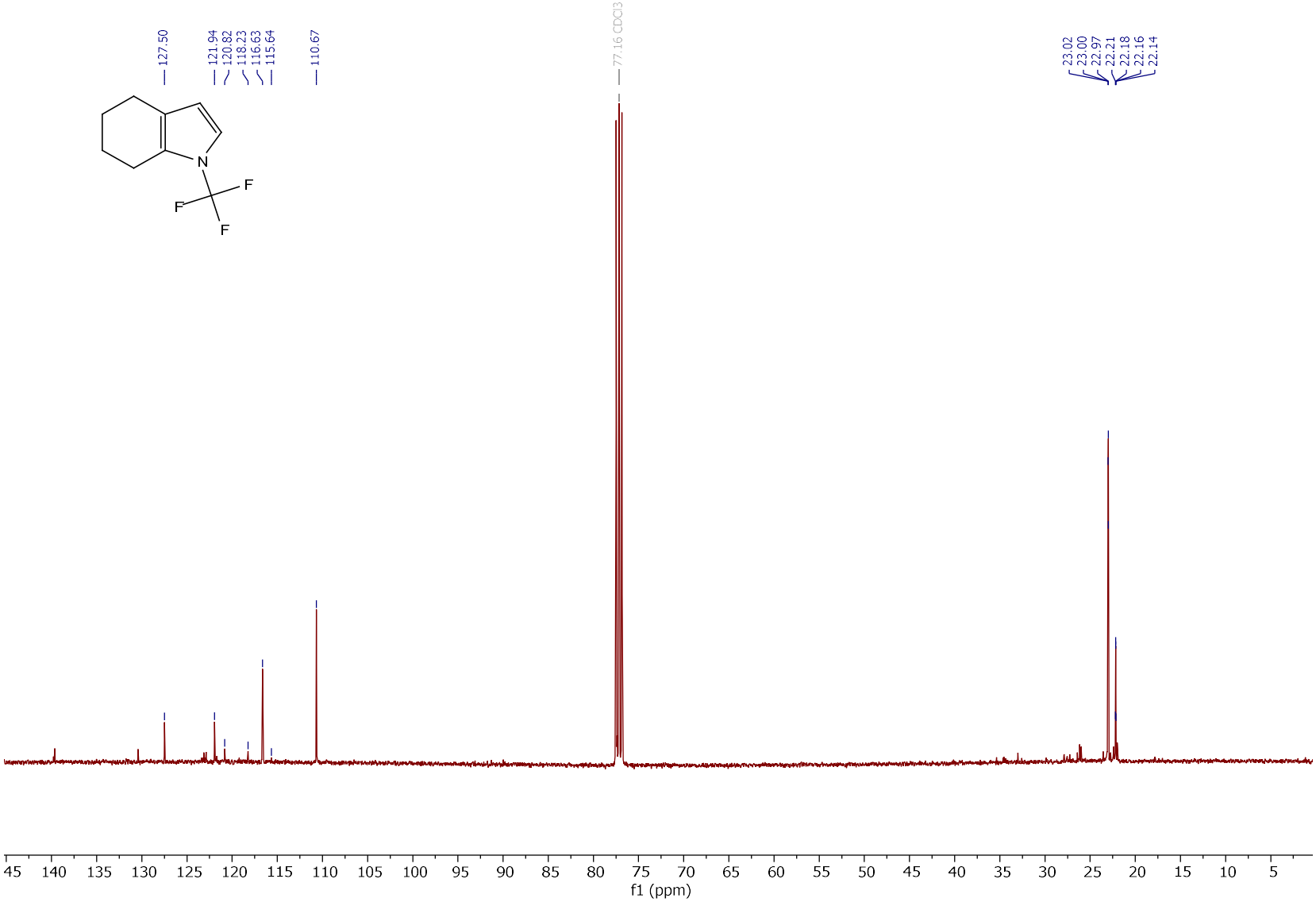
^{19}F NMR (376 MHz, $CDCl_3$) of **2a**



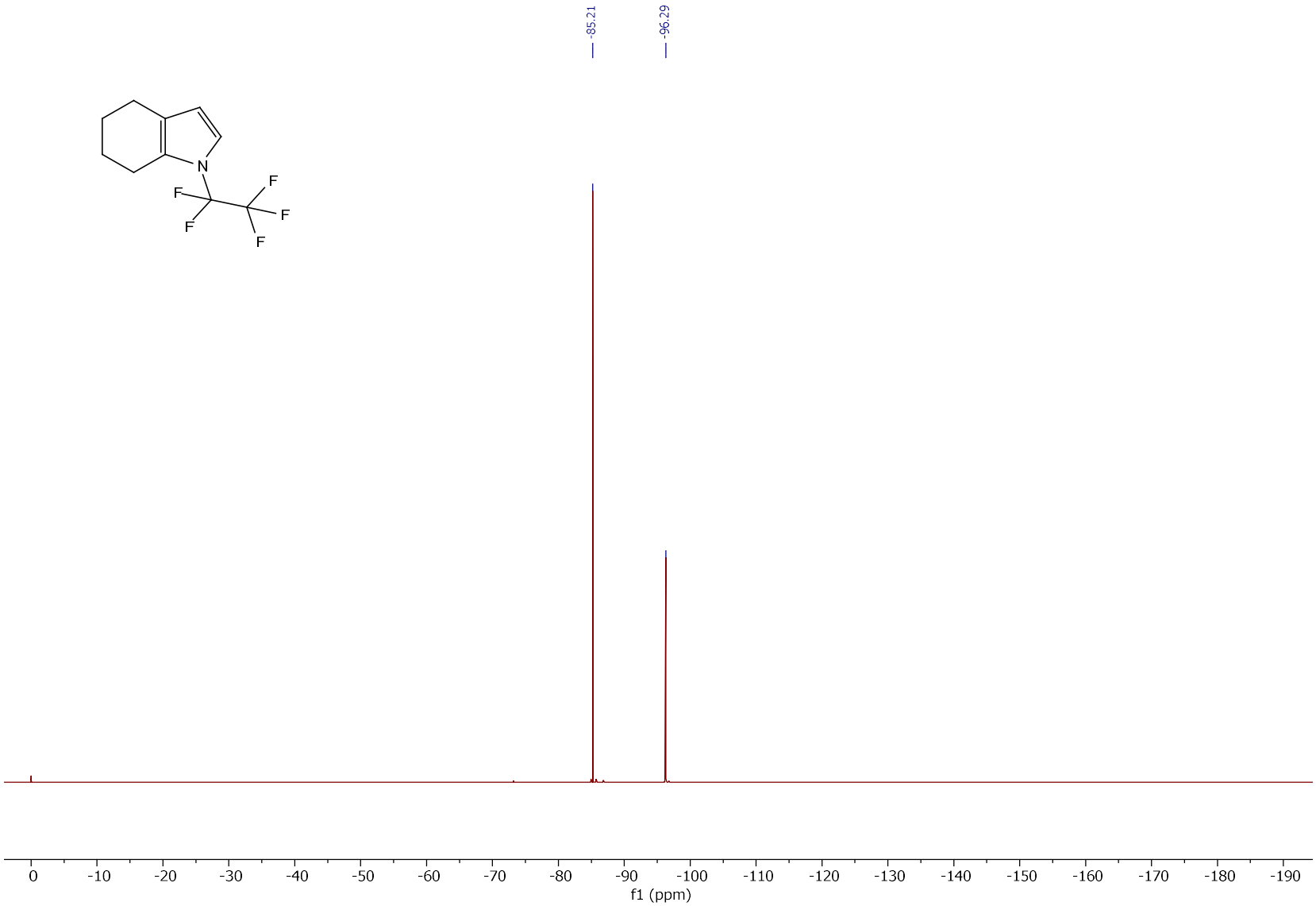
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



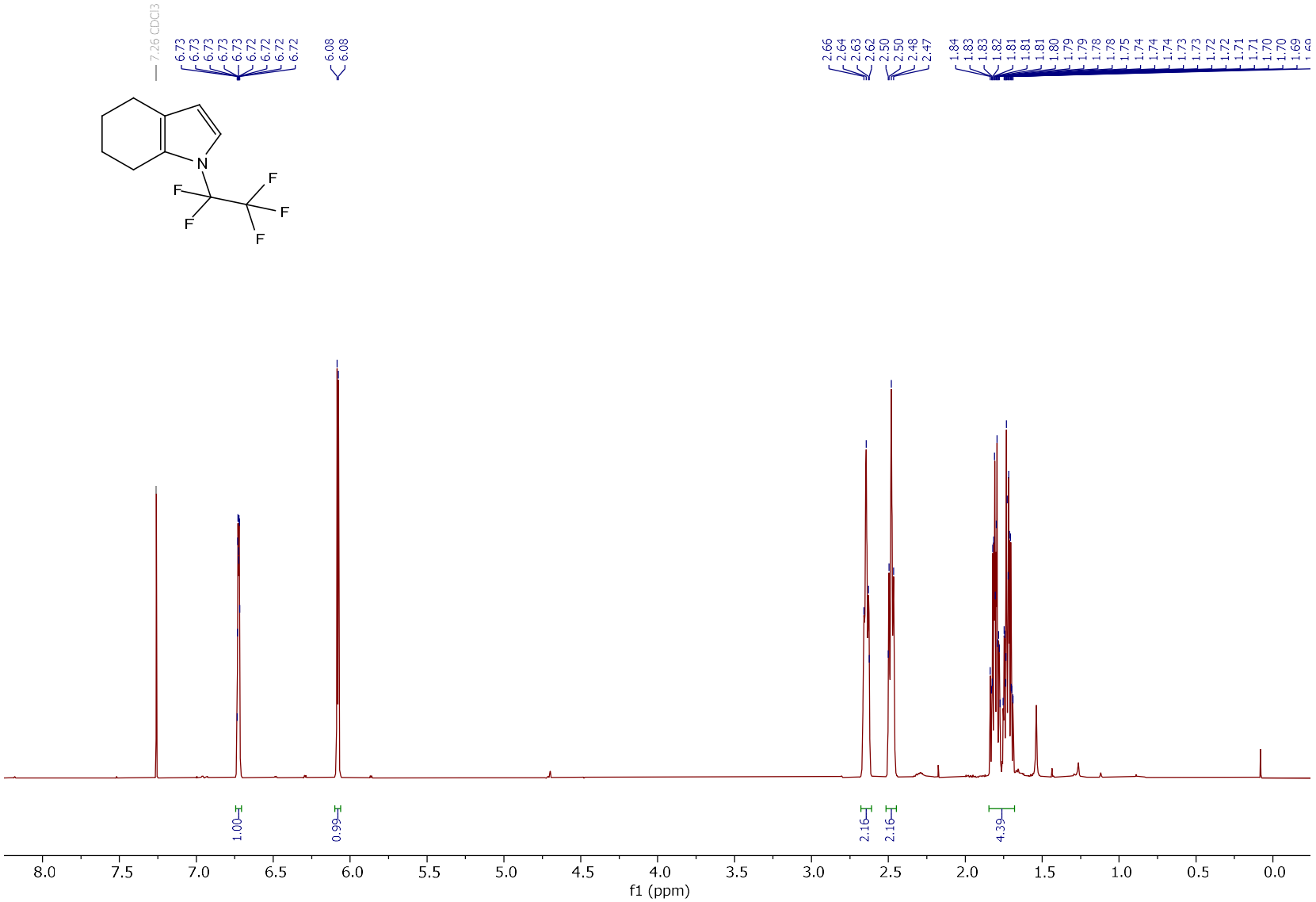
^{13}C NMR (101 MHz, $CDCl_3$) of **2a**



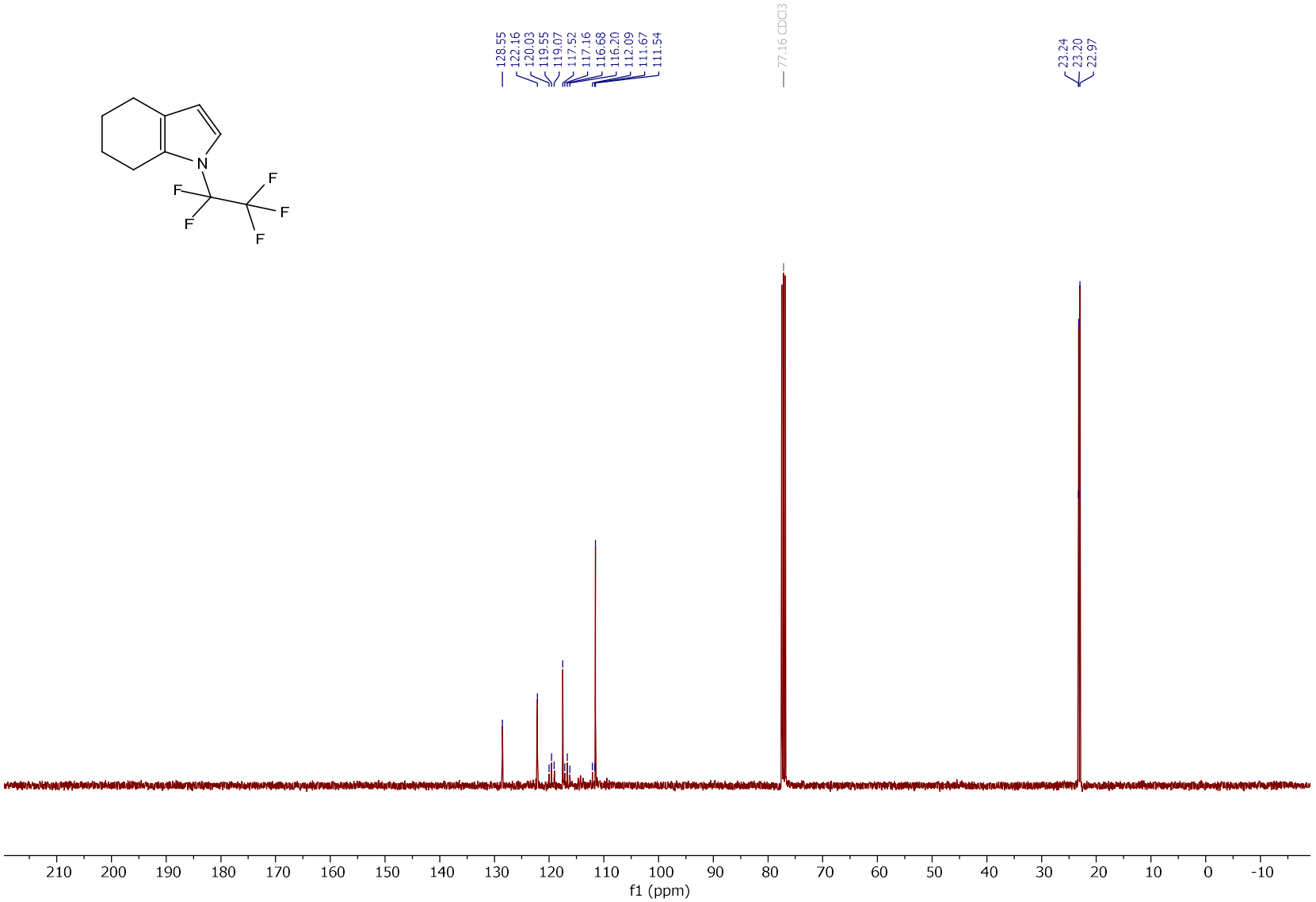
^{19}F NMR (376 MHz, $CDCl_3$) of **2b**



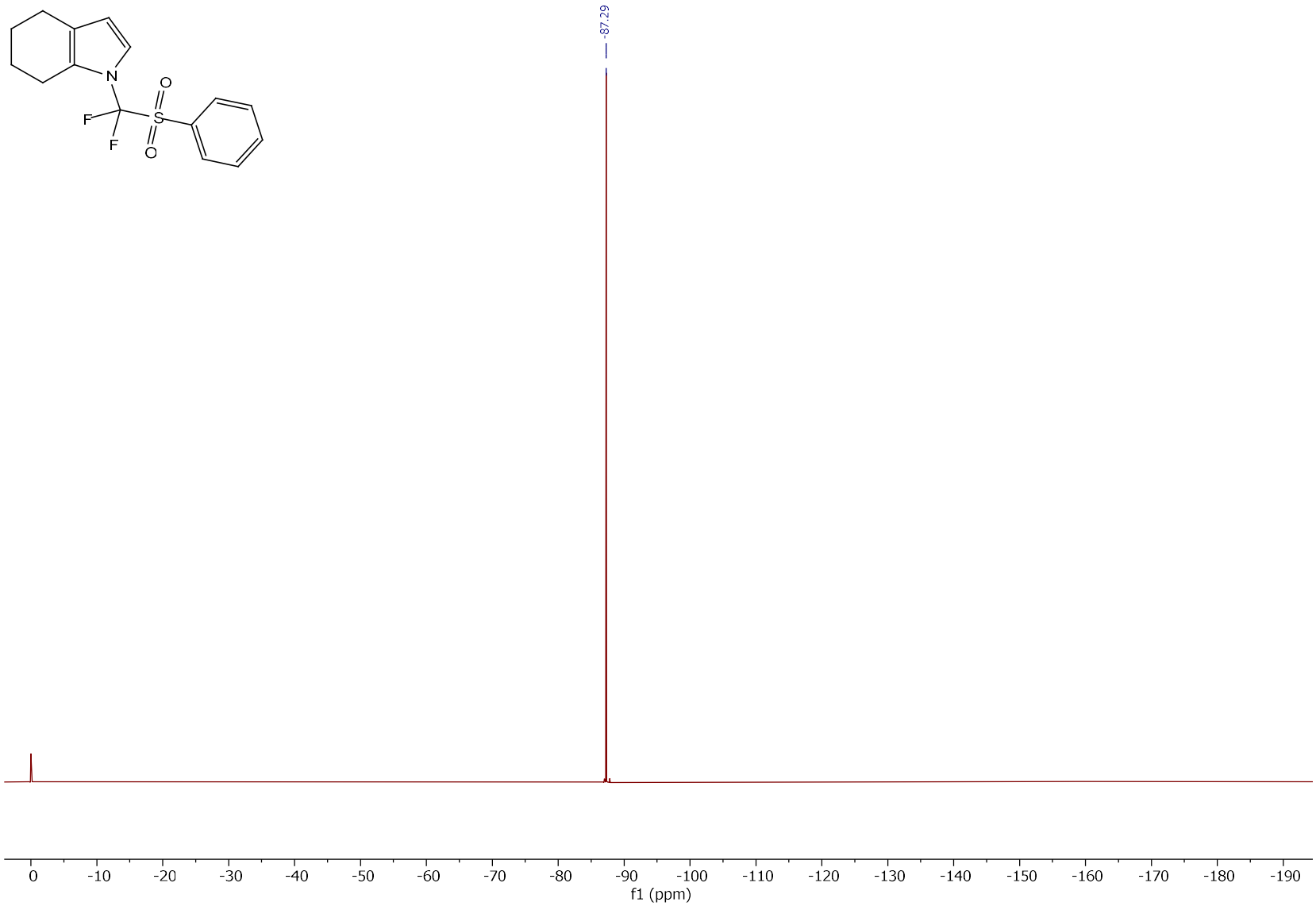
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



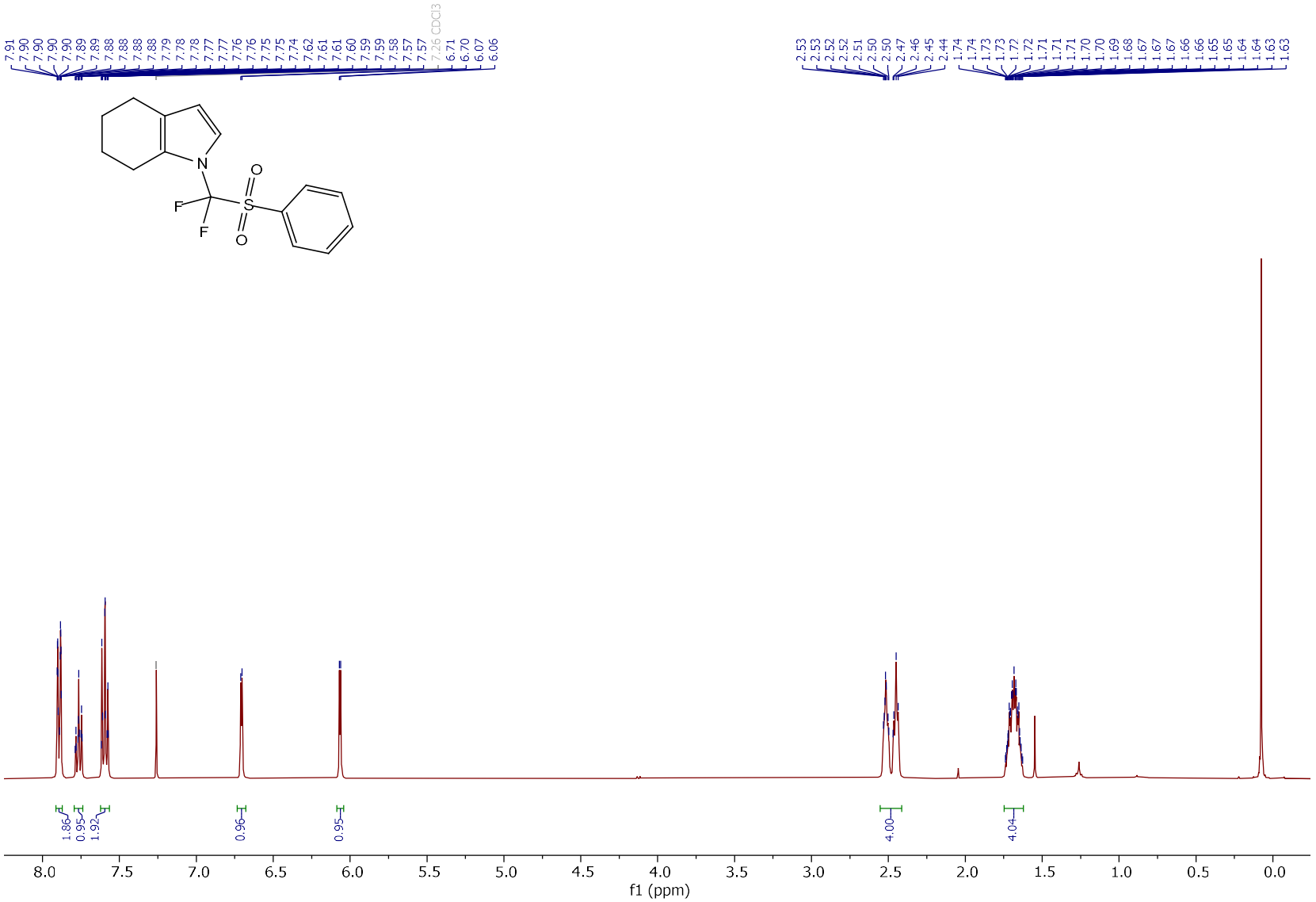
^{13}C NMR (101 MHz, $CDCl_3$) of **2b**



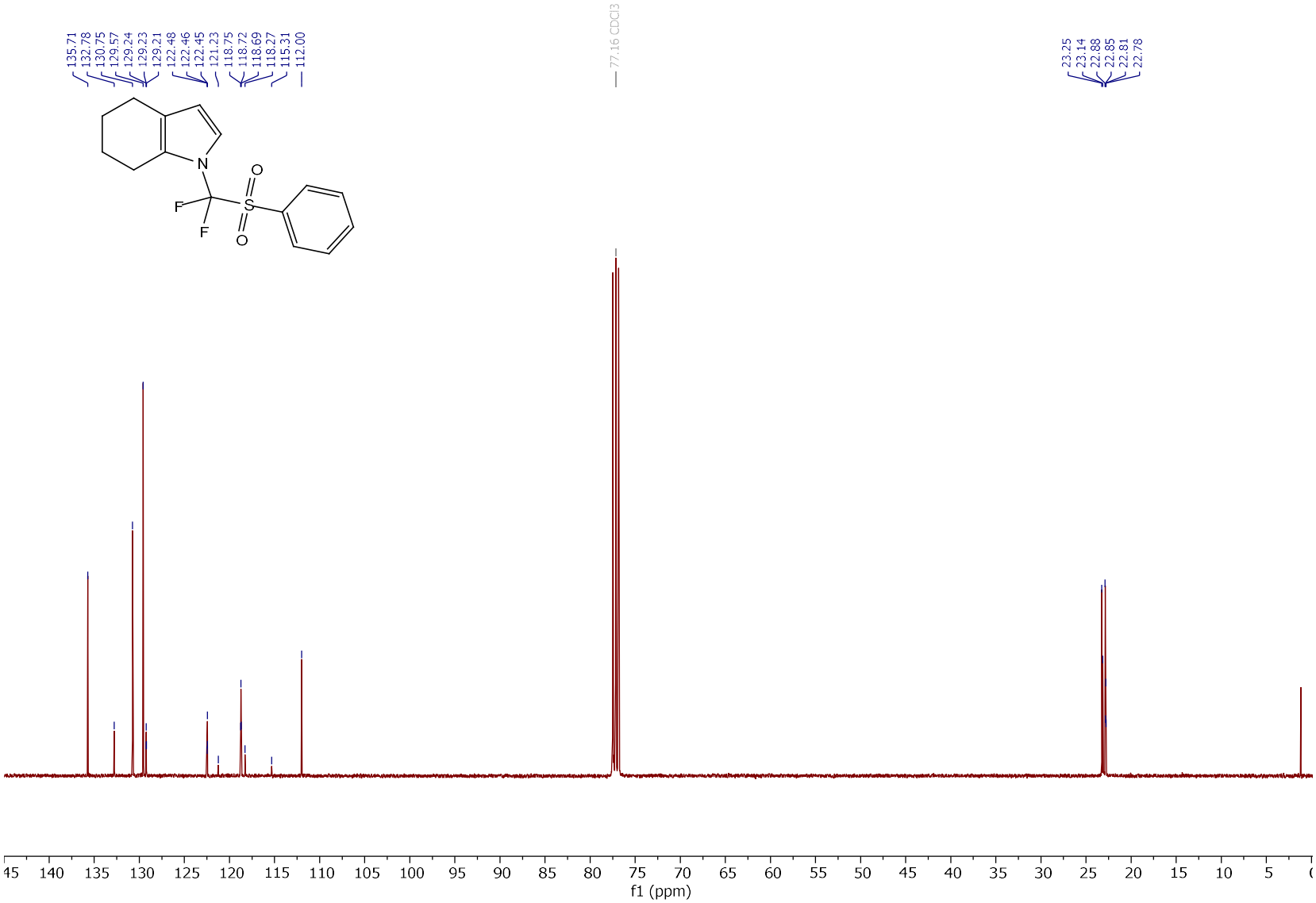
^{19}F NMR (376 MHz, $CDCl_3$) of **2c**



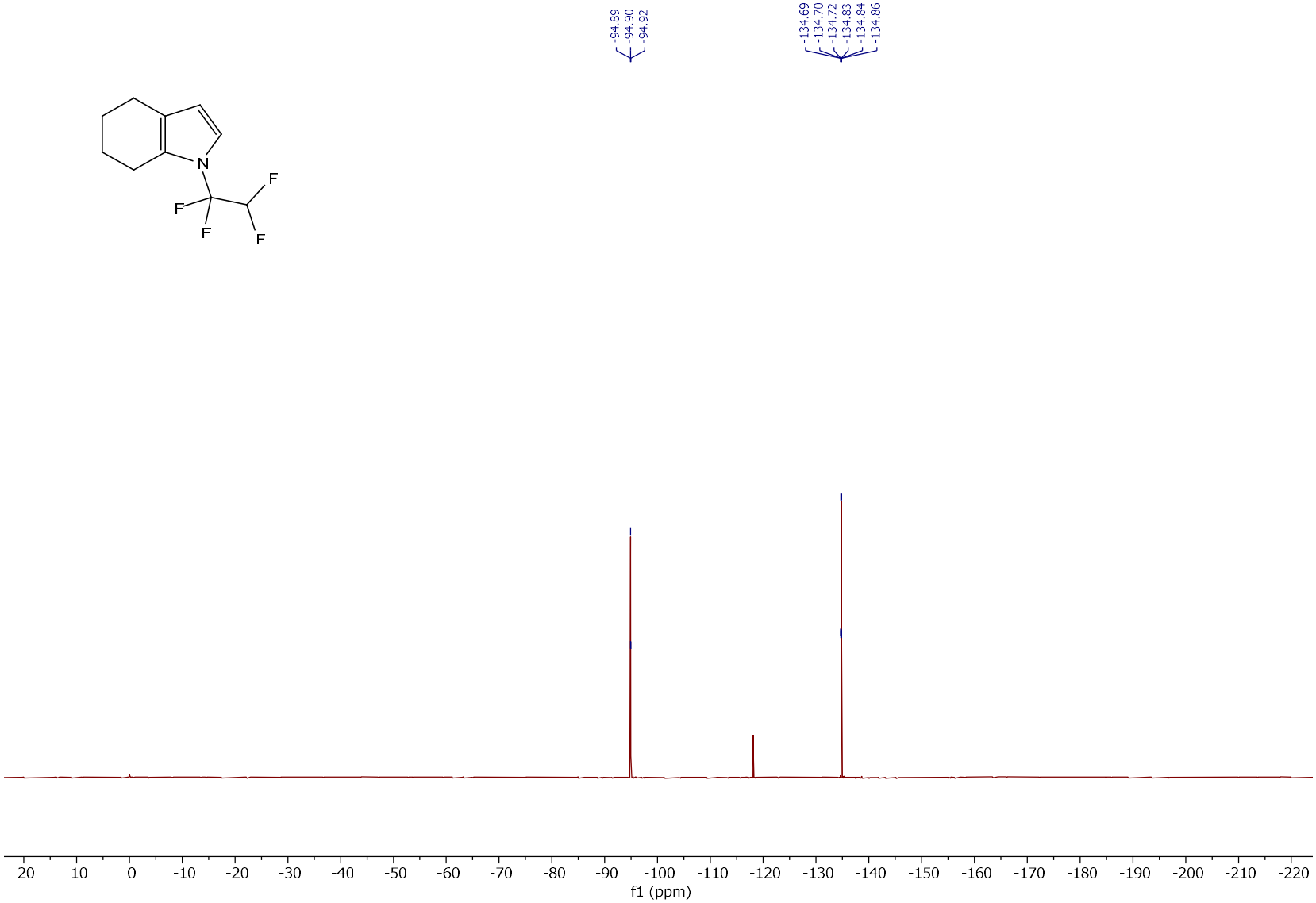
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



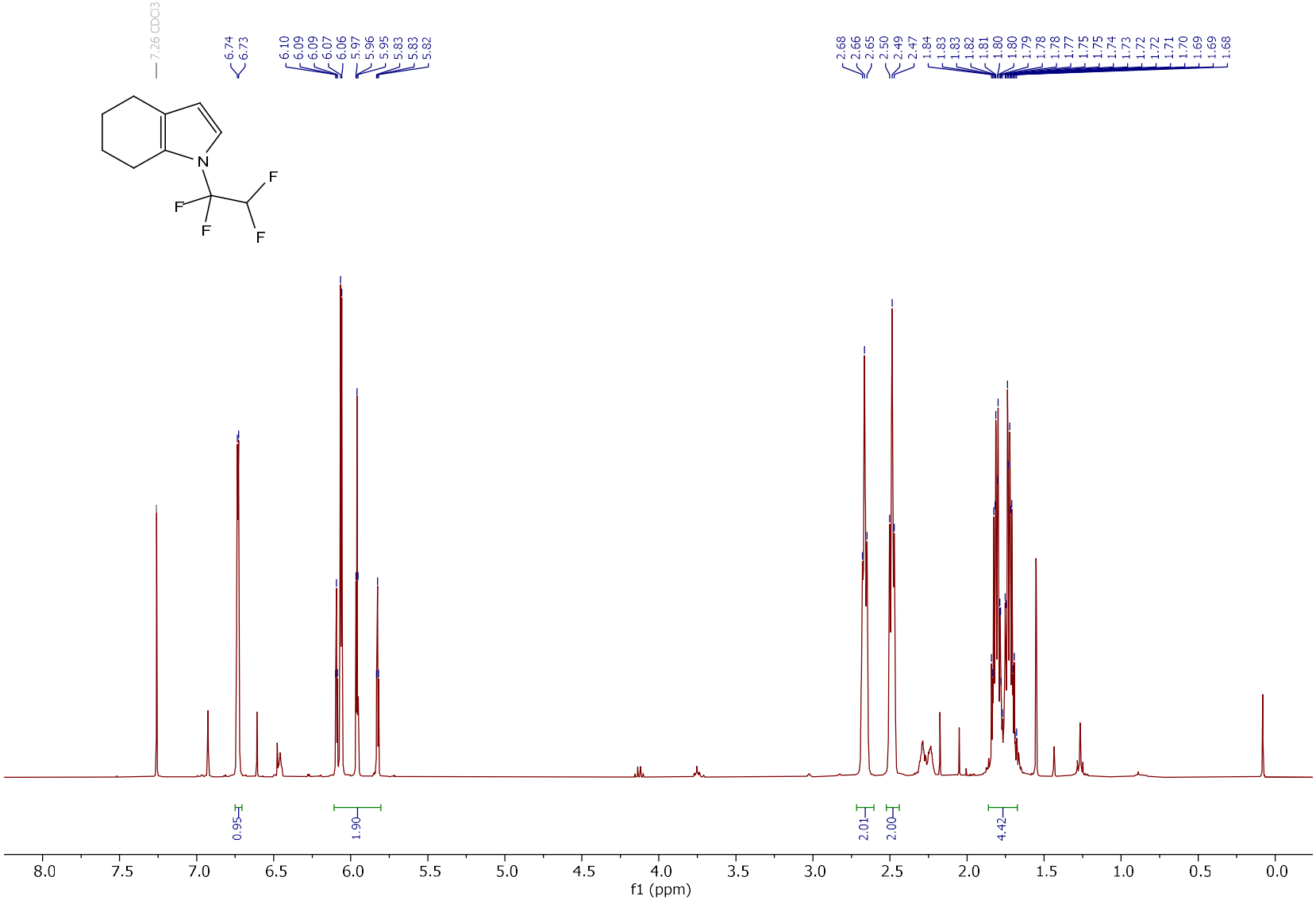
^{13}C NMR (101 MHz, $CDCl_3$) of **2c**



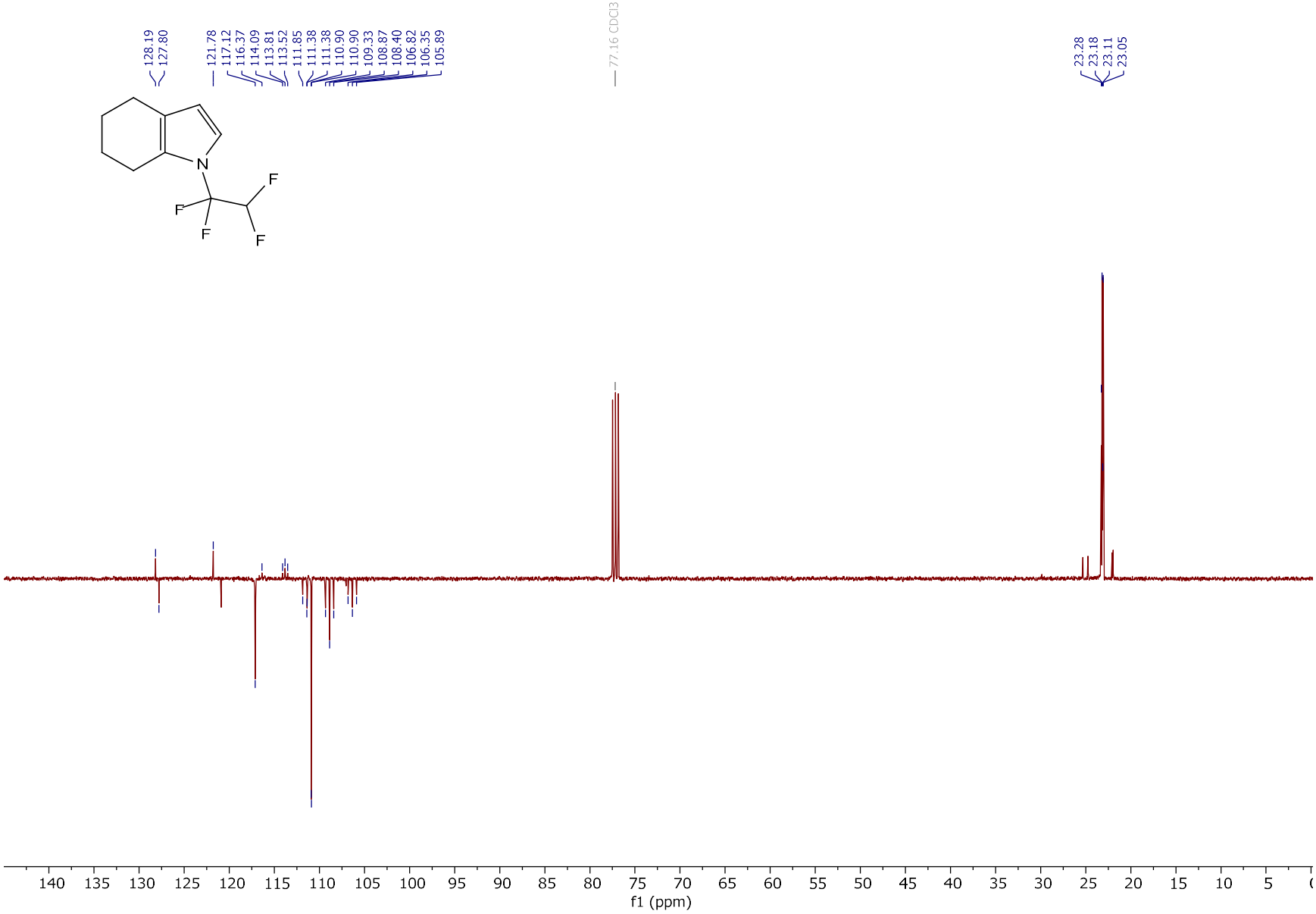
^{19}F NMR (377 MHz, $CDCl_3$) of **2d**



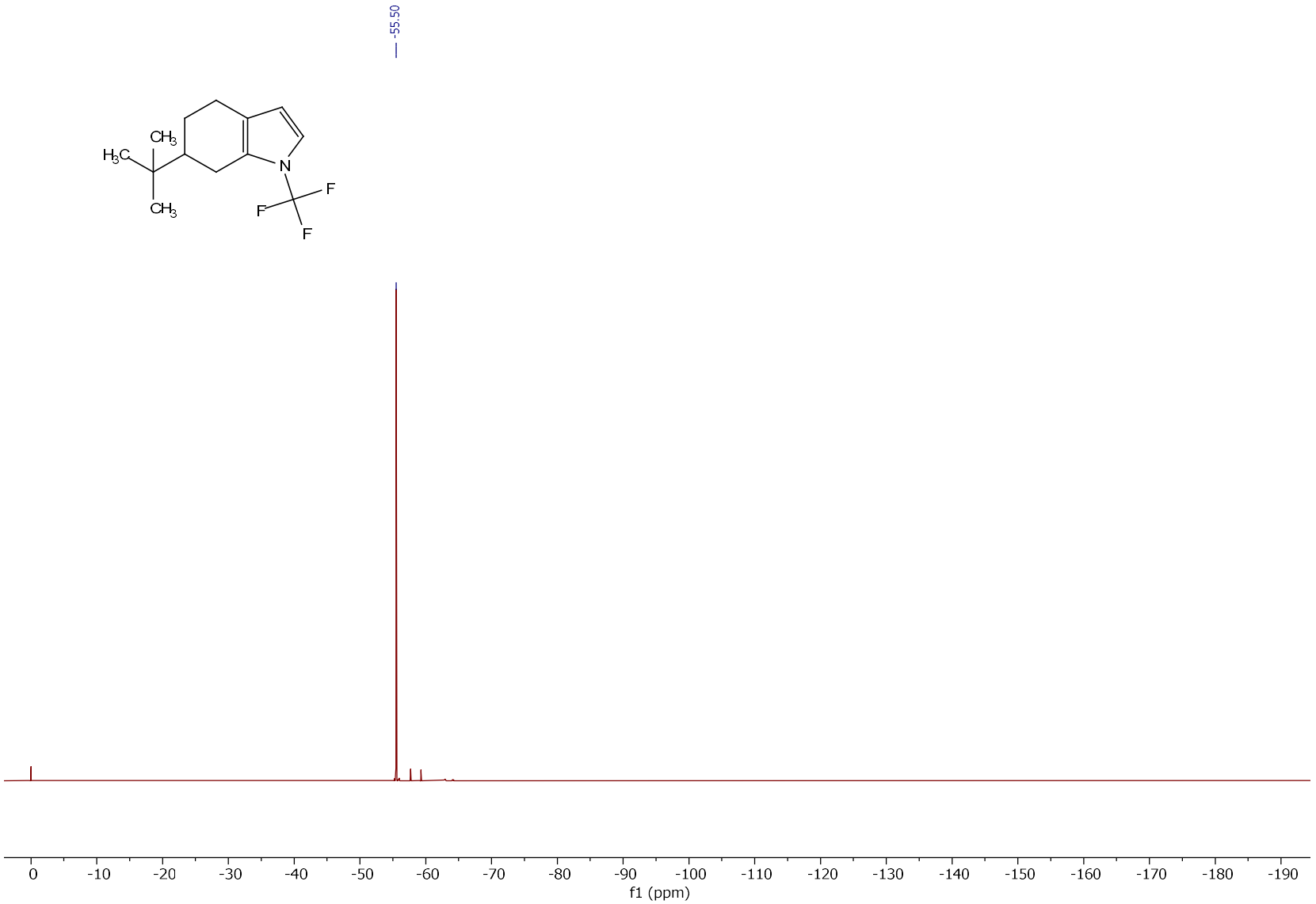
^{1}H NMR (401 MHz, $CDCl_3$) of **2d**



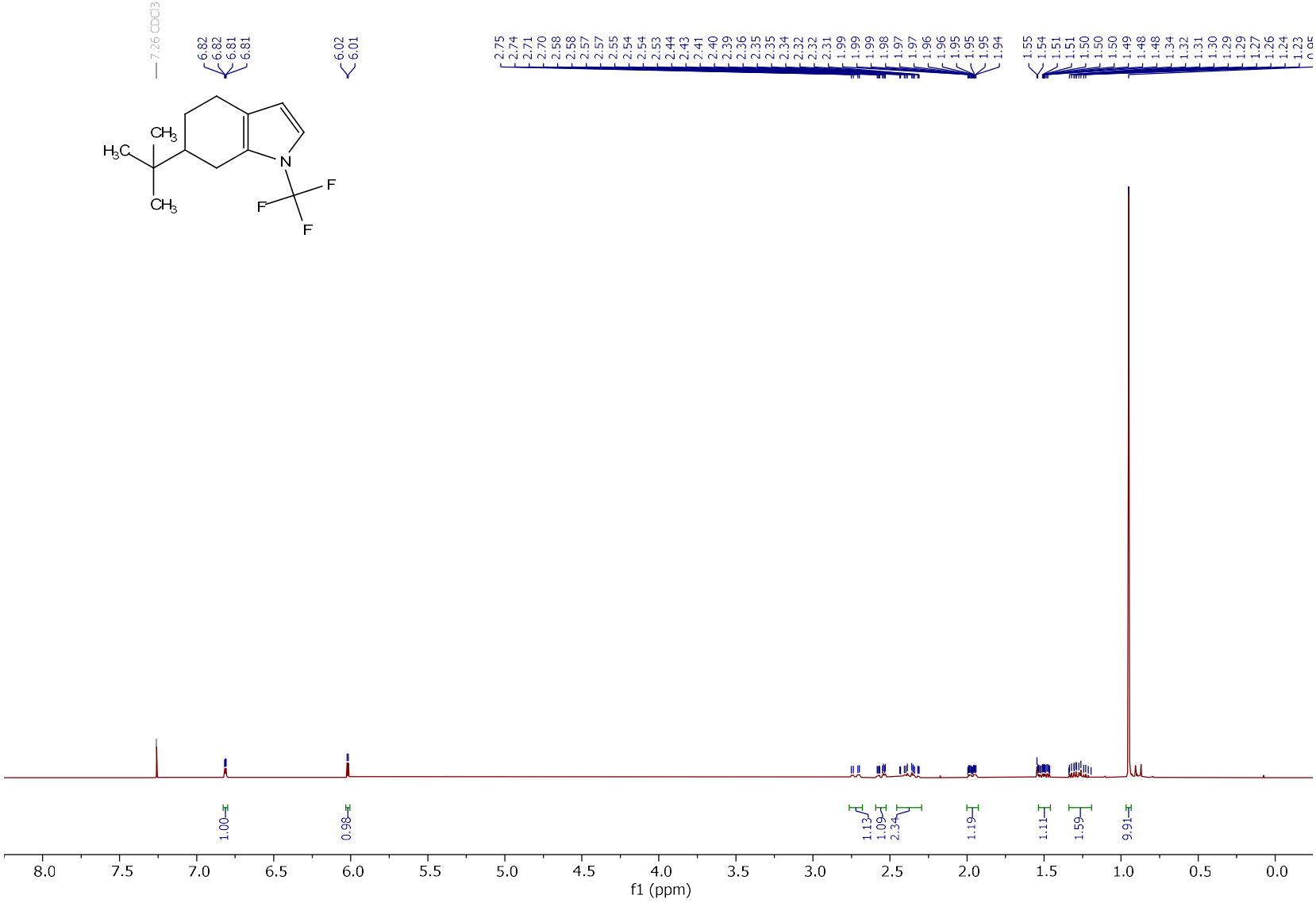
^{13}C NMR (101 MHz, $CDCl_3$) of **2d**



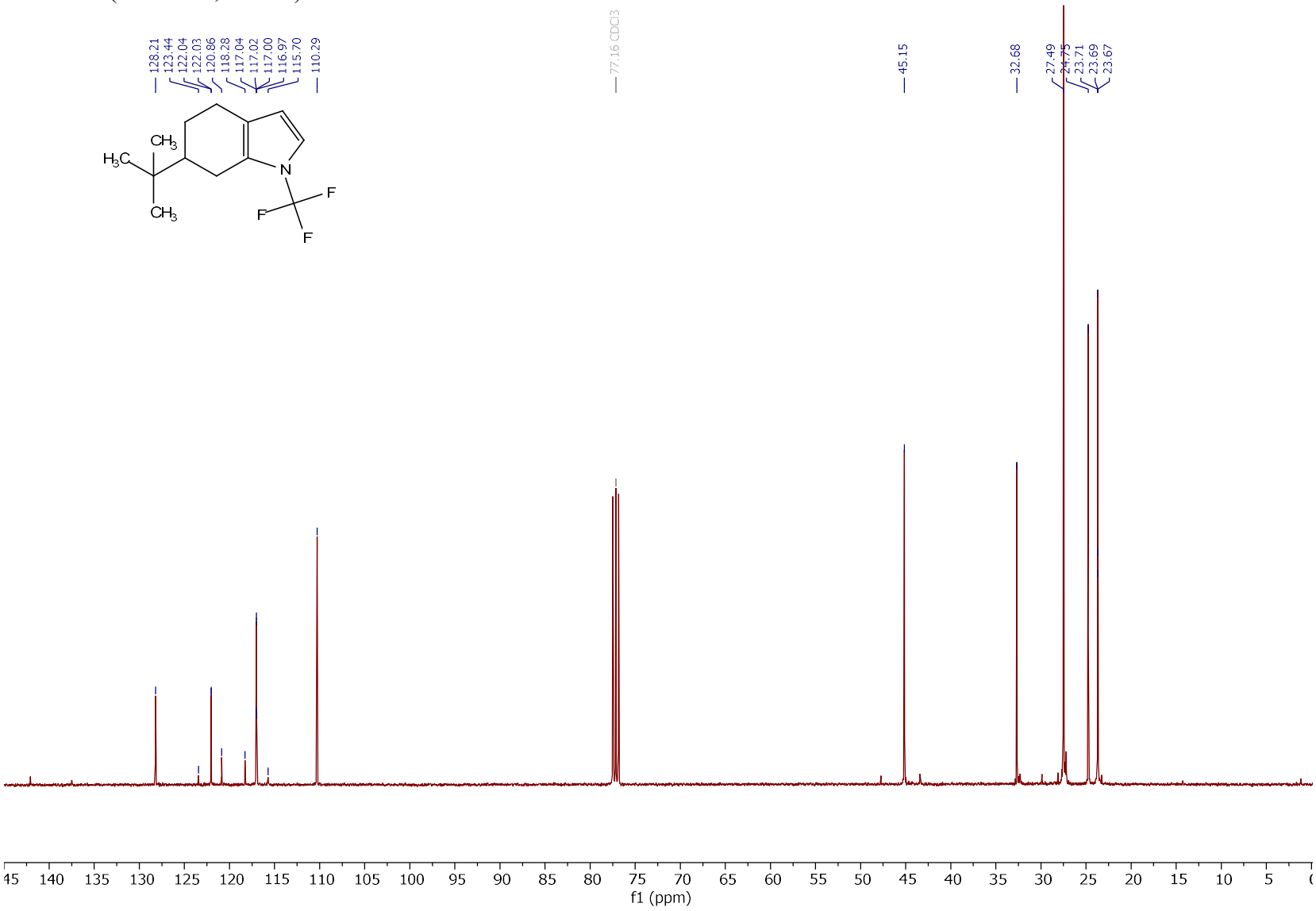
^{19}F NMR (376 MHz, $CDCl_3$) of **2e**



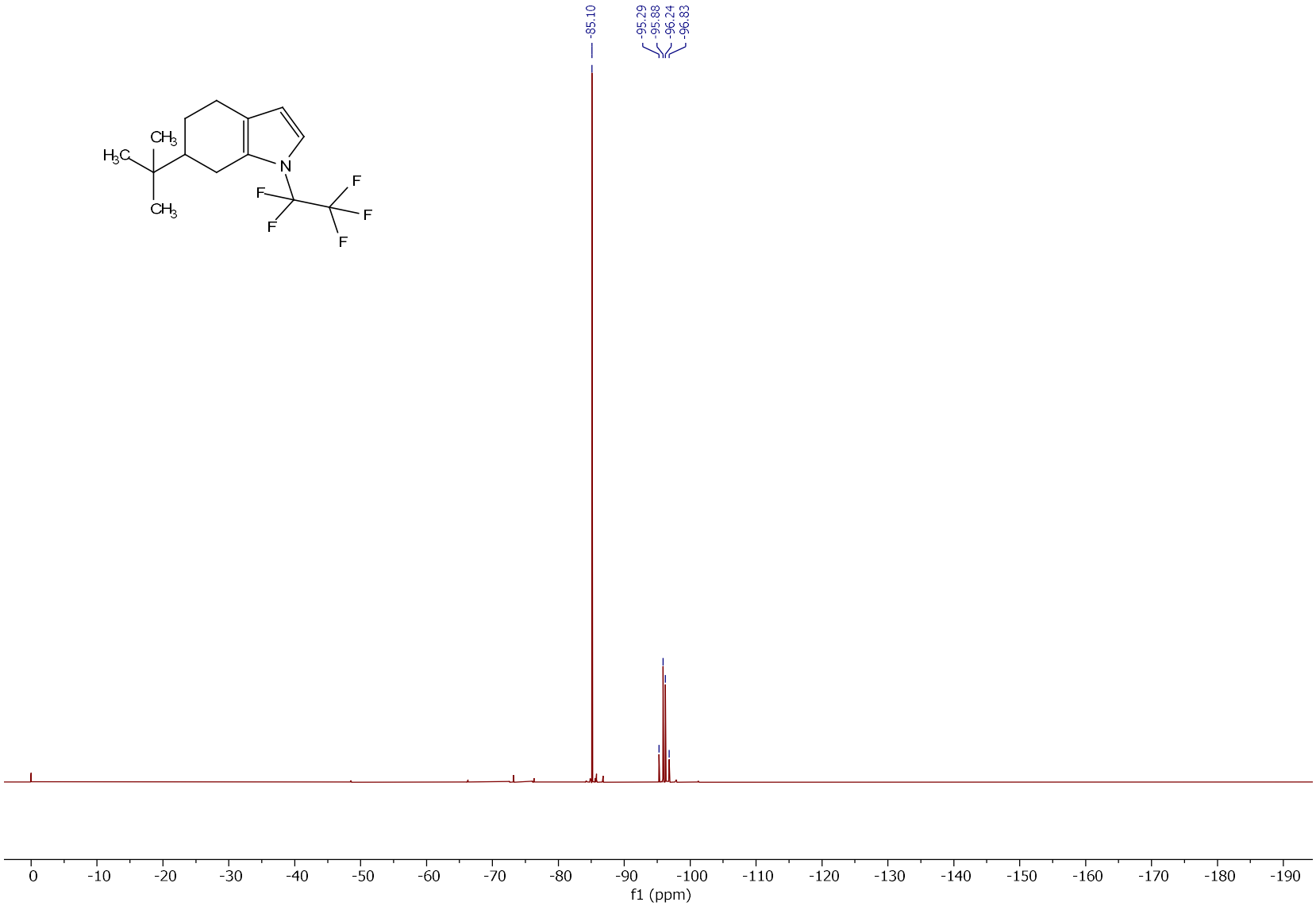
^{1}H NMR (400 MHz, $CDCl_3$) of **2e**



^{13}C NMR (101 MHz, $CDCl_3$) of **2e**



^{19}F NMR (376 MHz, $CDCl_3$) of **2f**



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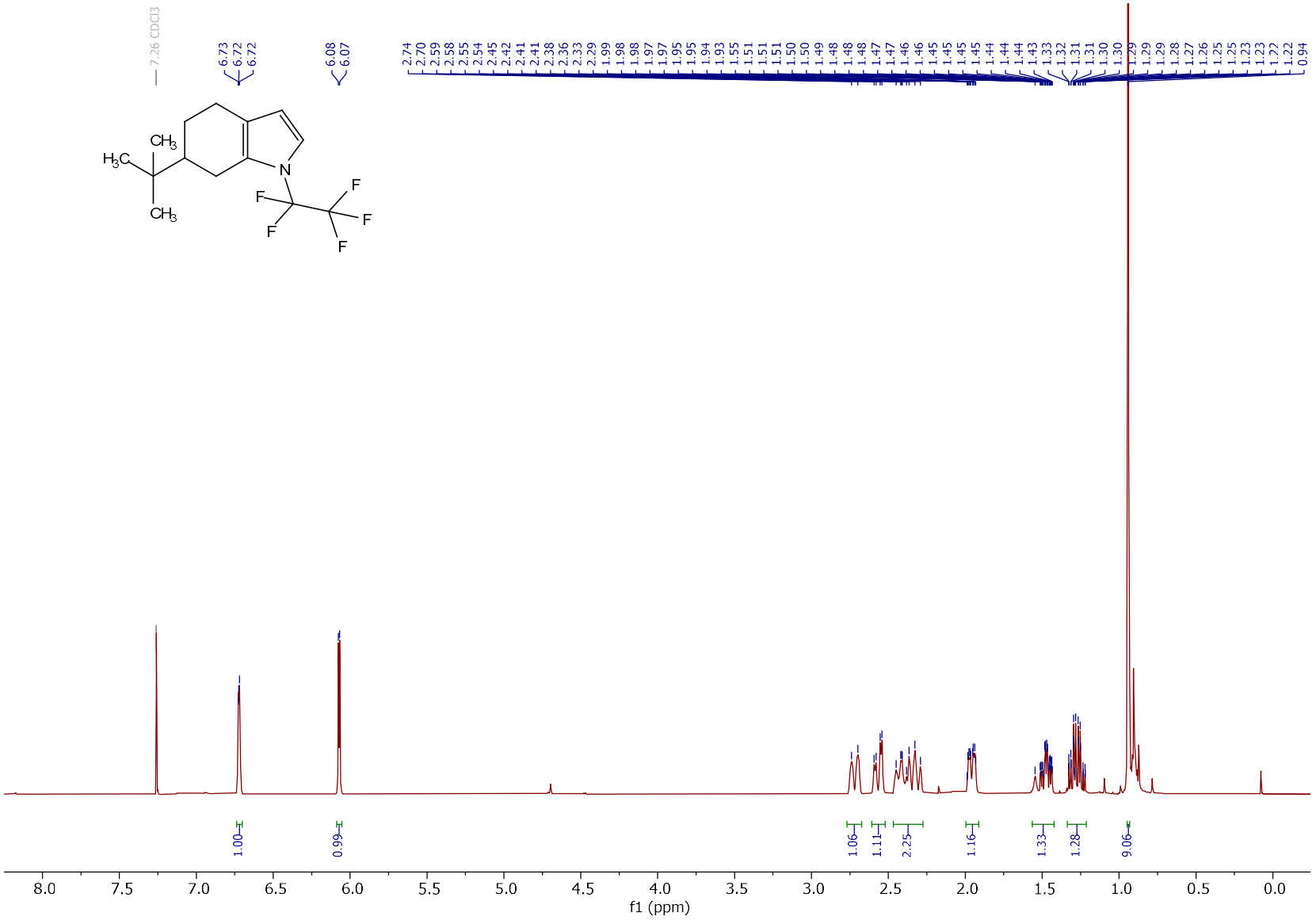
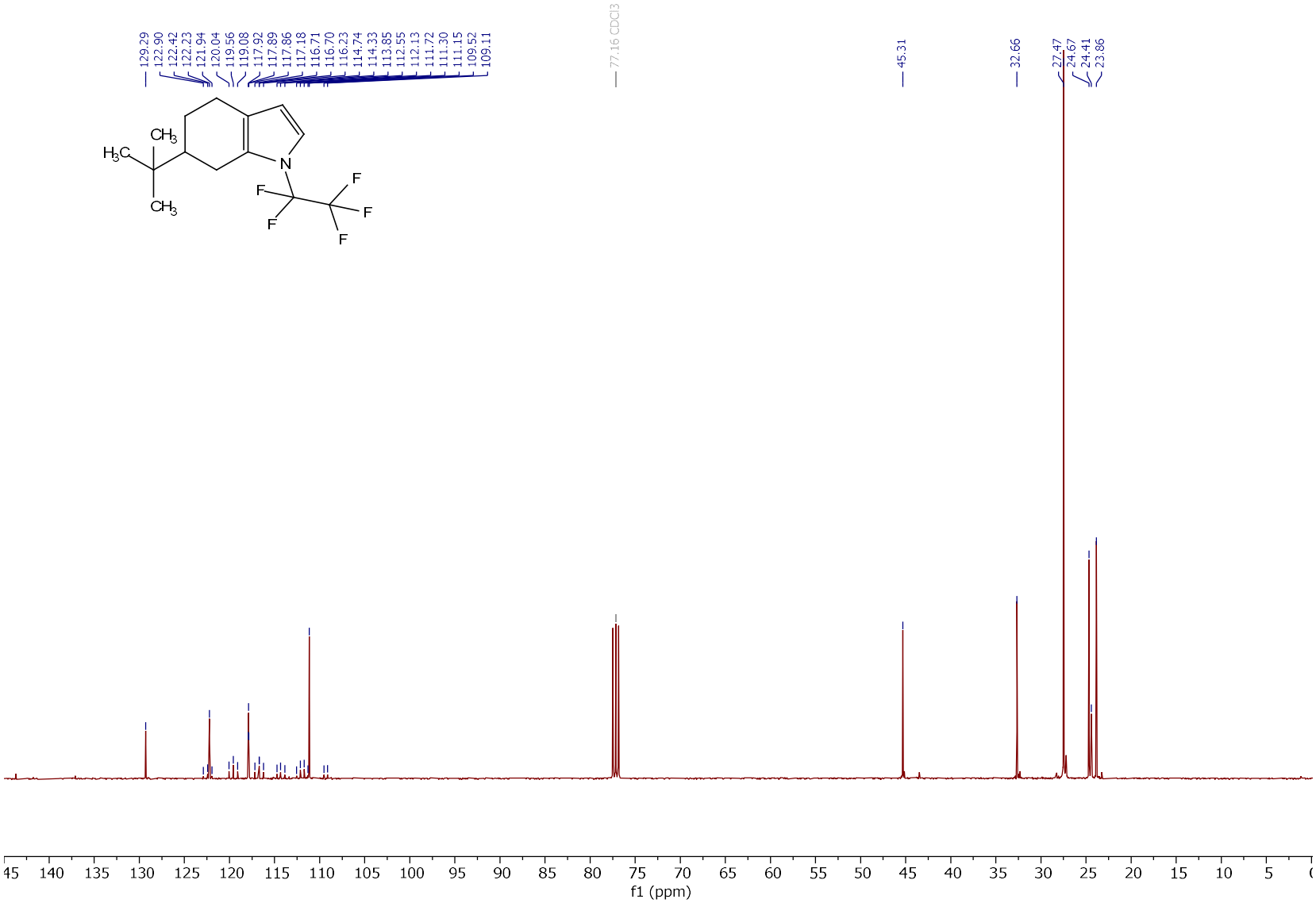
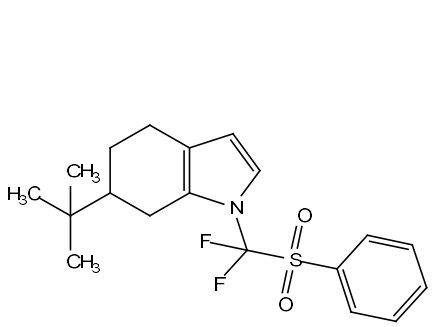


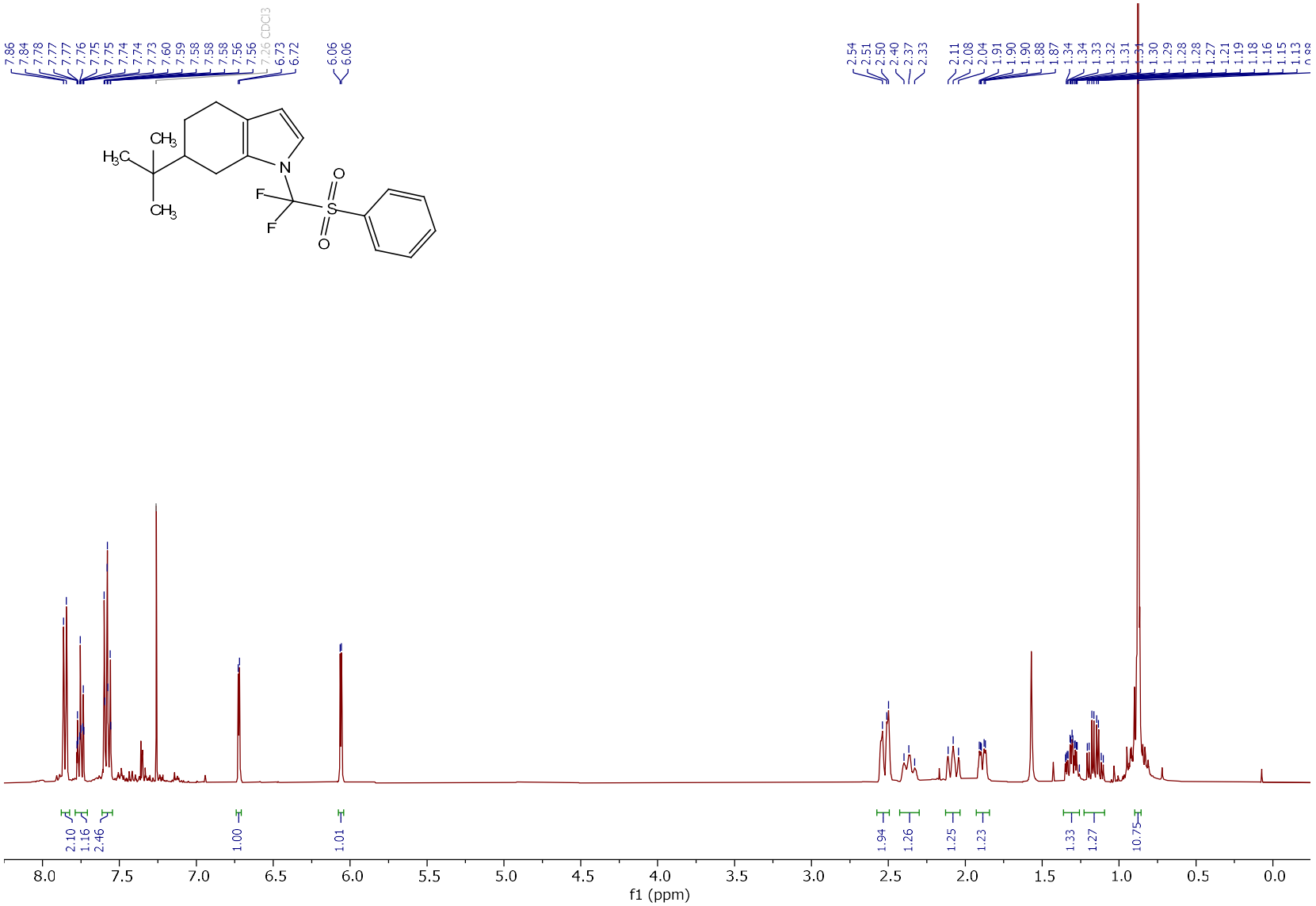
^{13}C NMR (101 MHz, $CDCl_3$) of **2f**



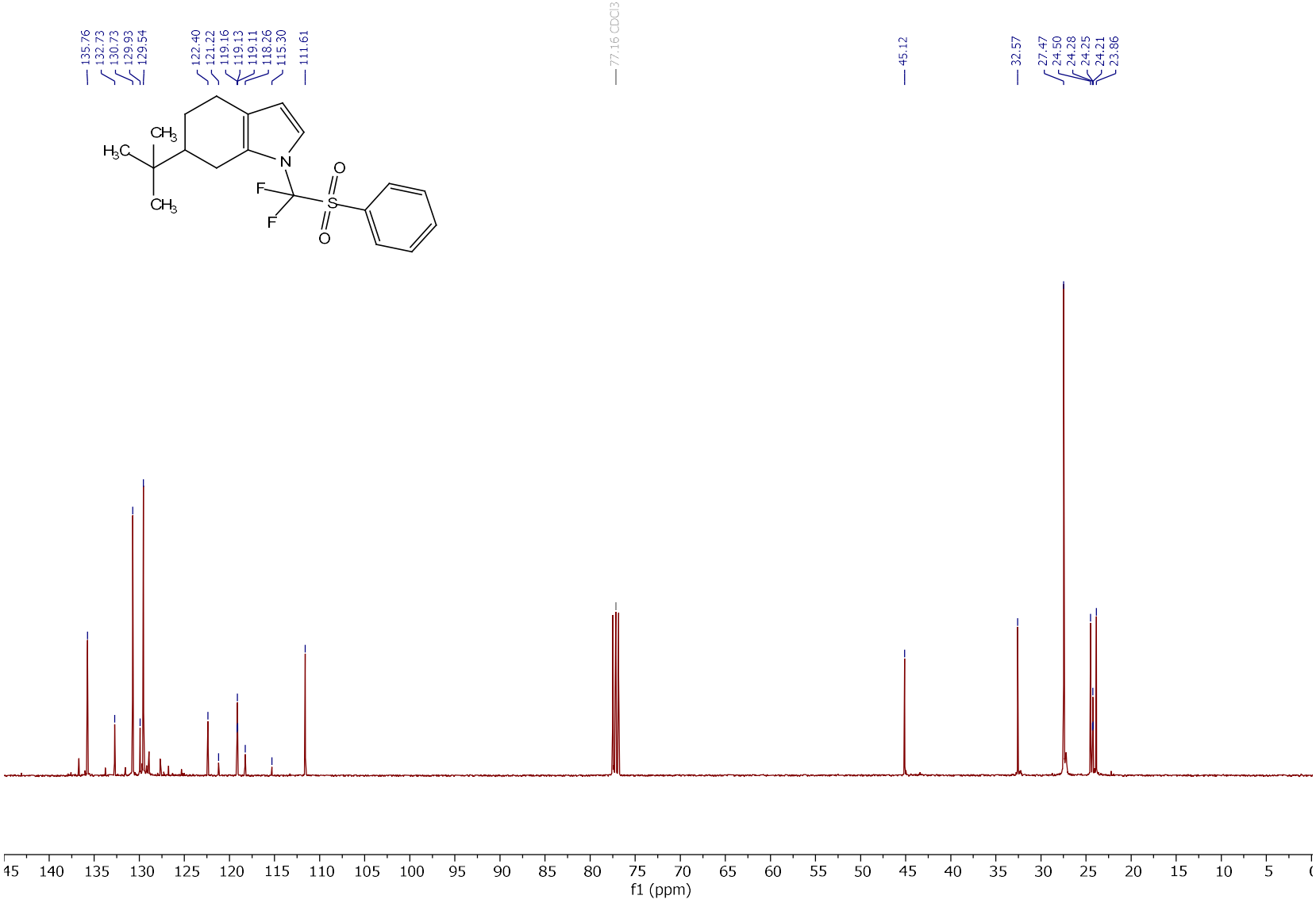
^{19}F NMR (376 MHz, $CDCl_3$) of **2g**



^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



^{13}C NMR (101 MHz, $CDCl_3$) of **2g**



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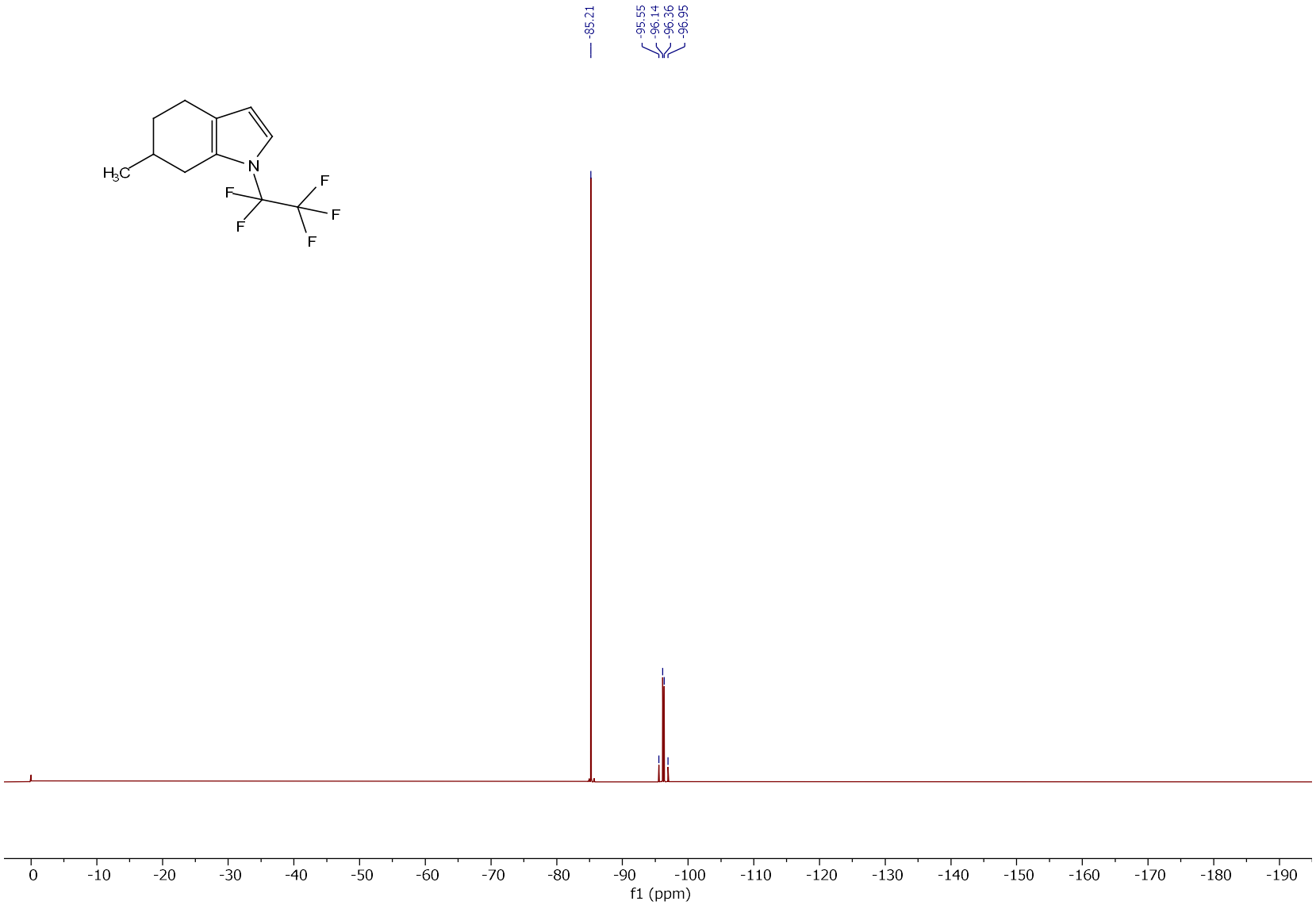
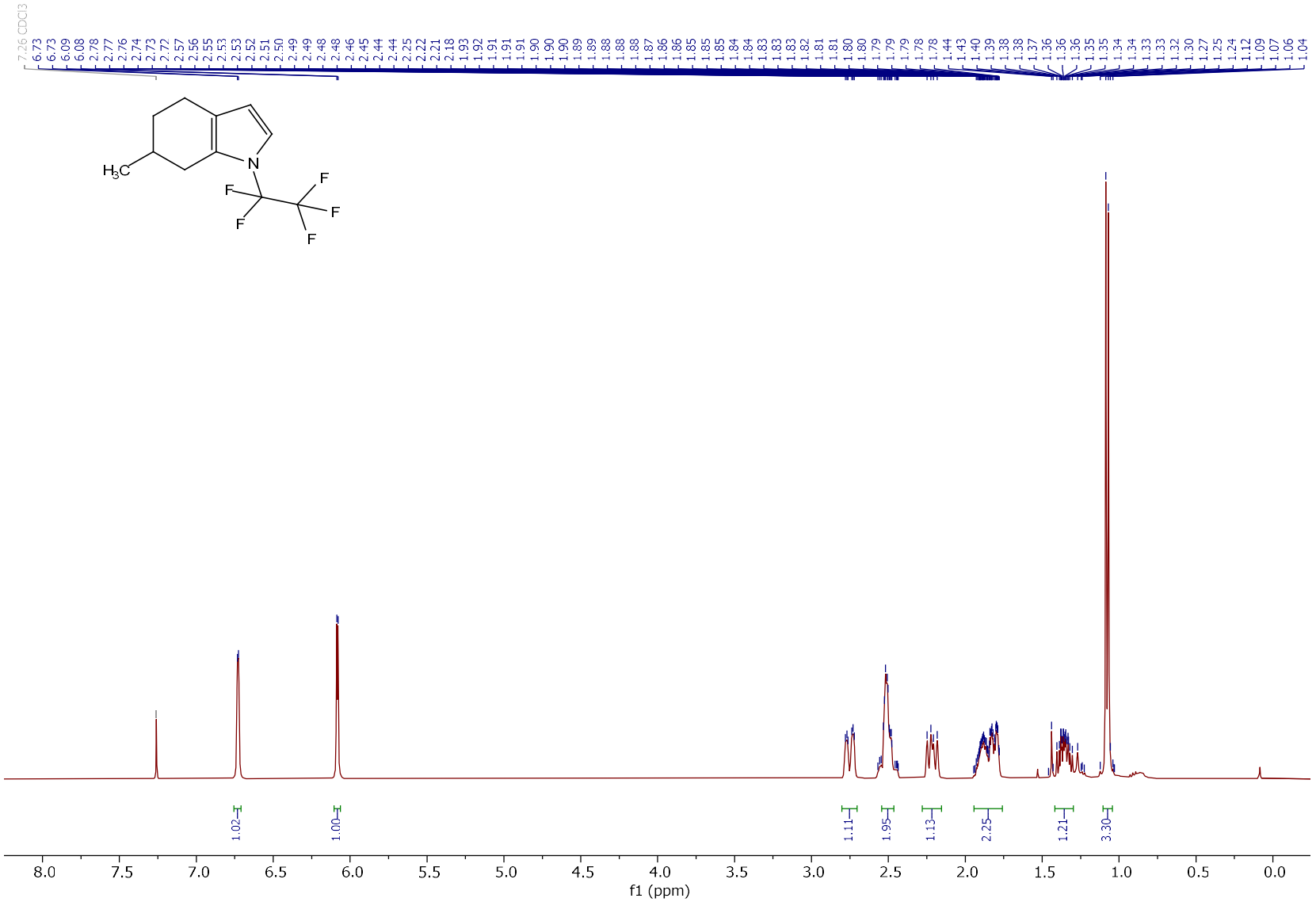


^{1}H NMR (401 MHz, $CDCl_3$) of **2h**



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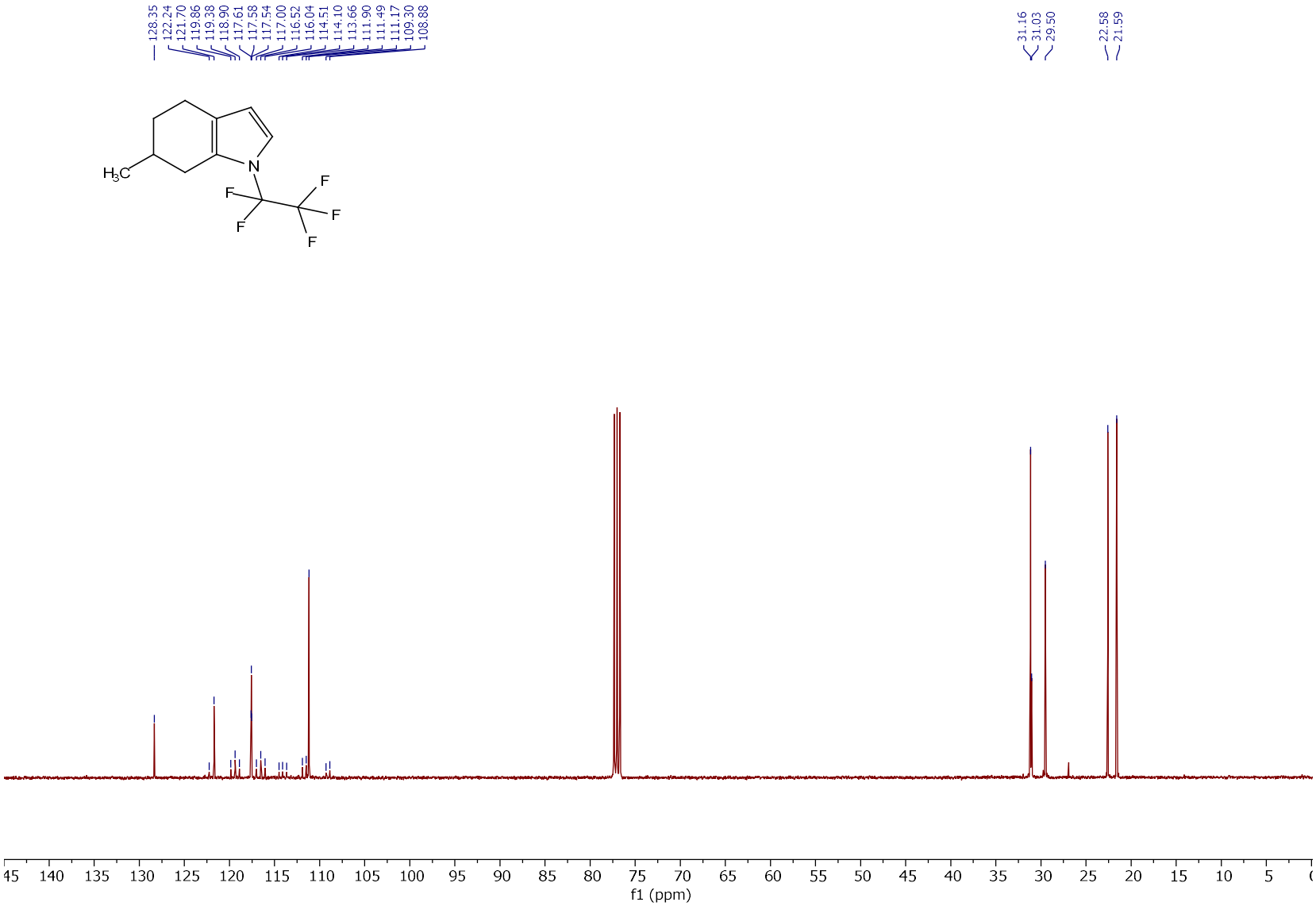

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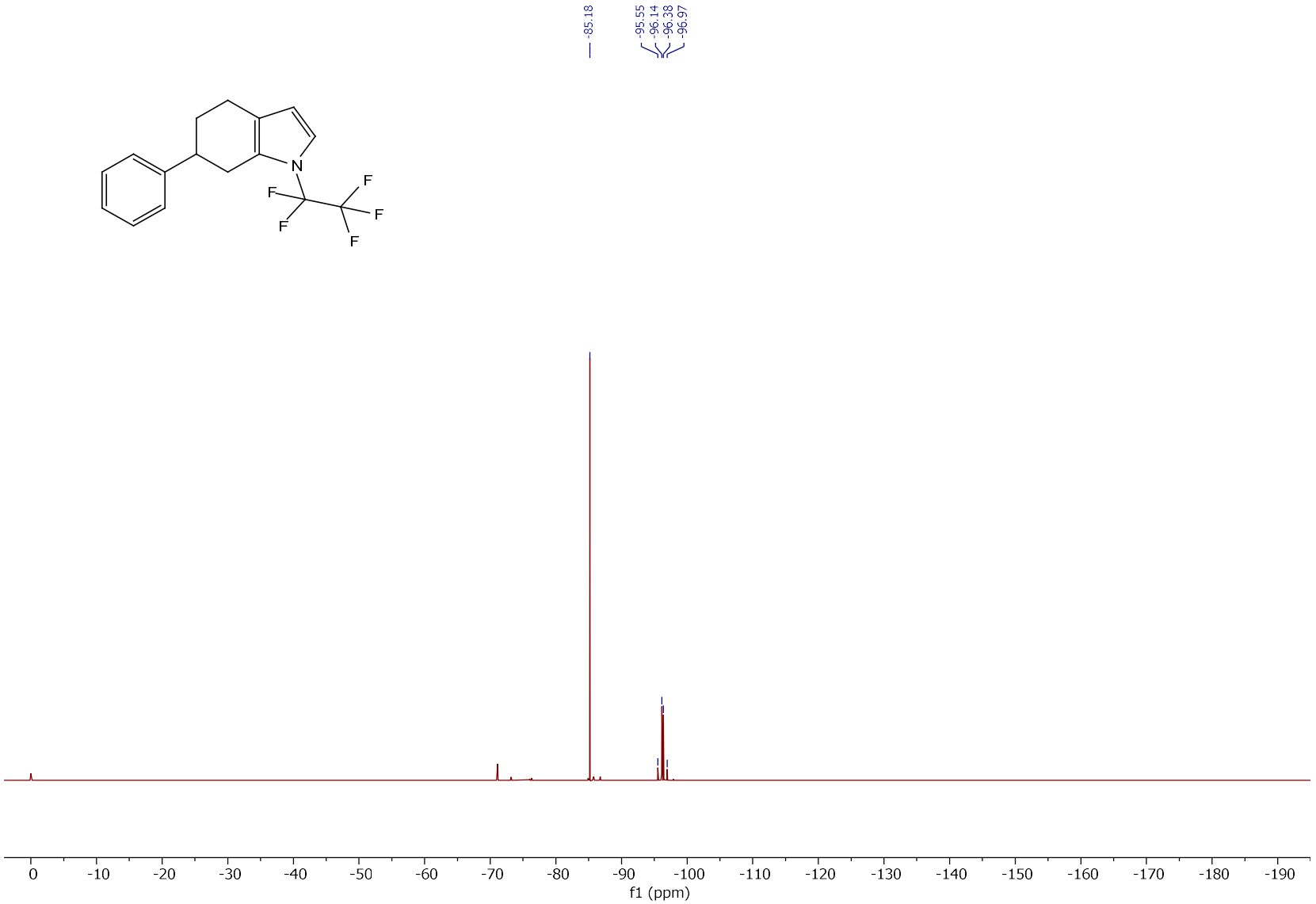

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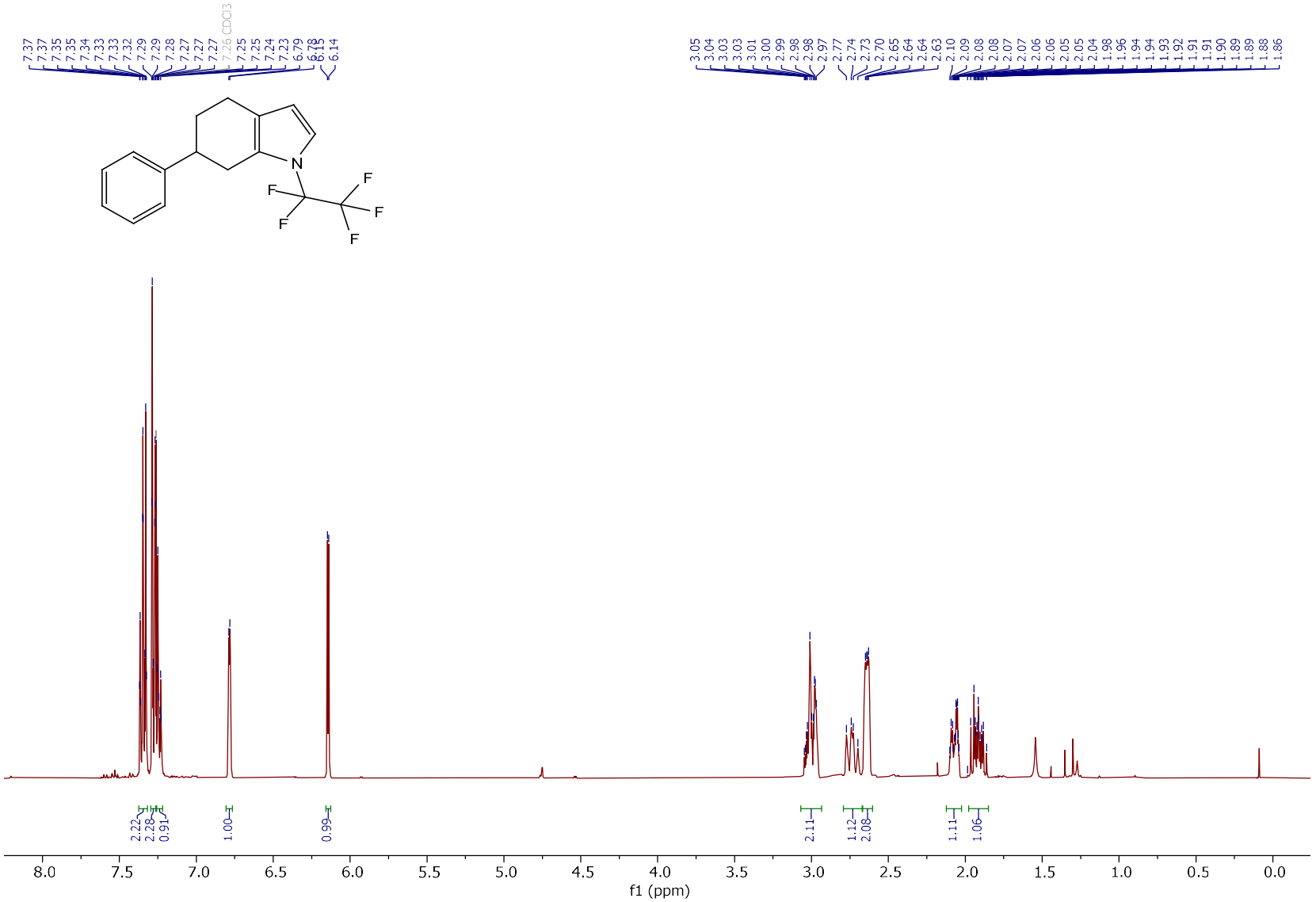
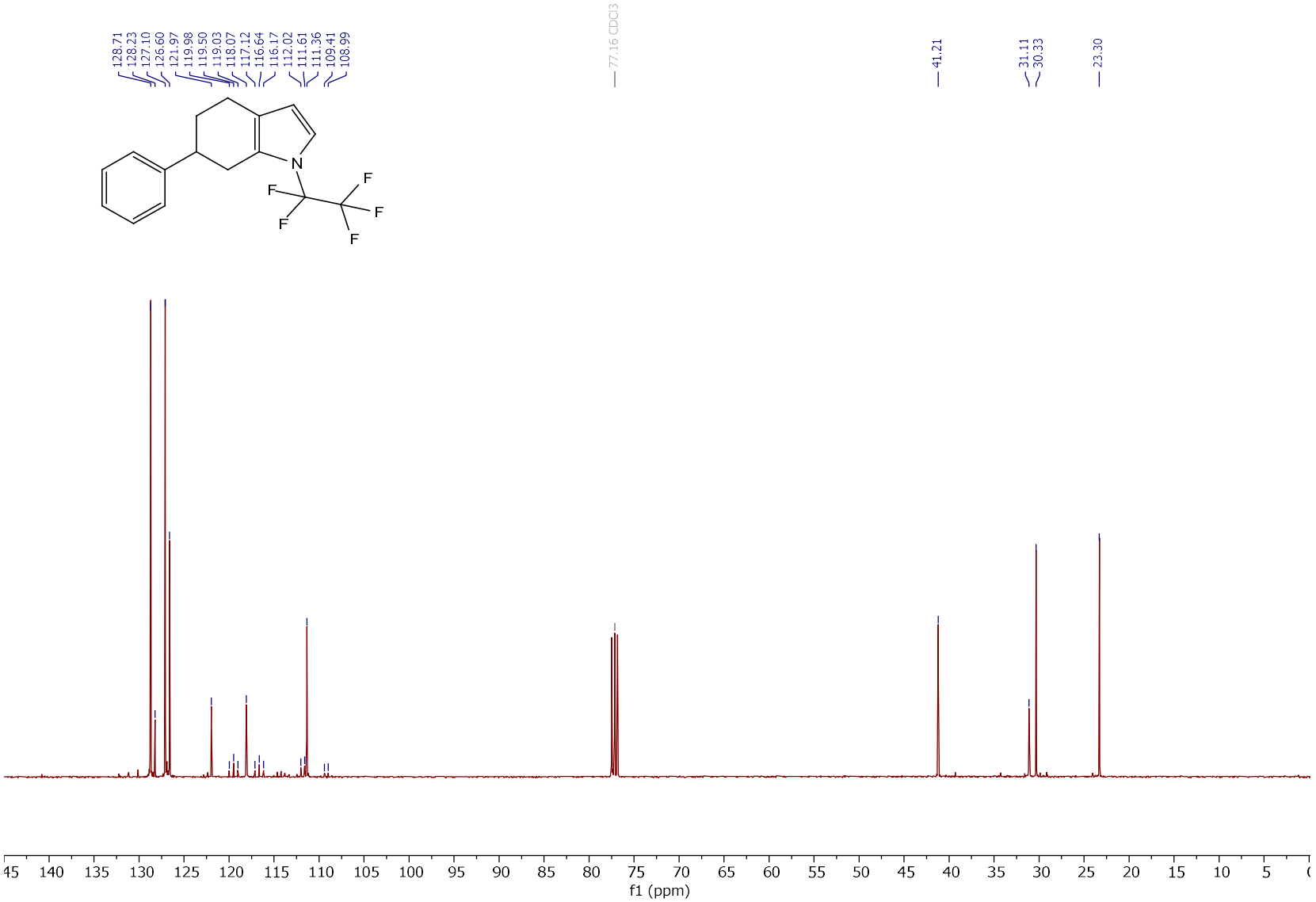
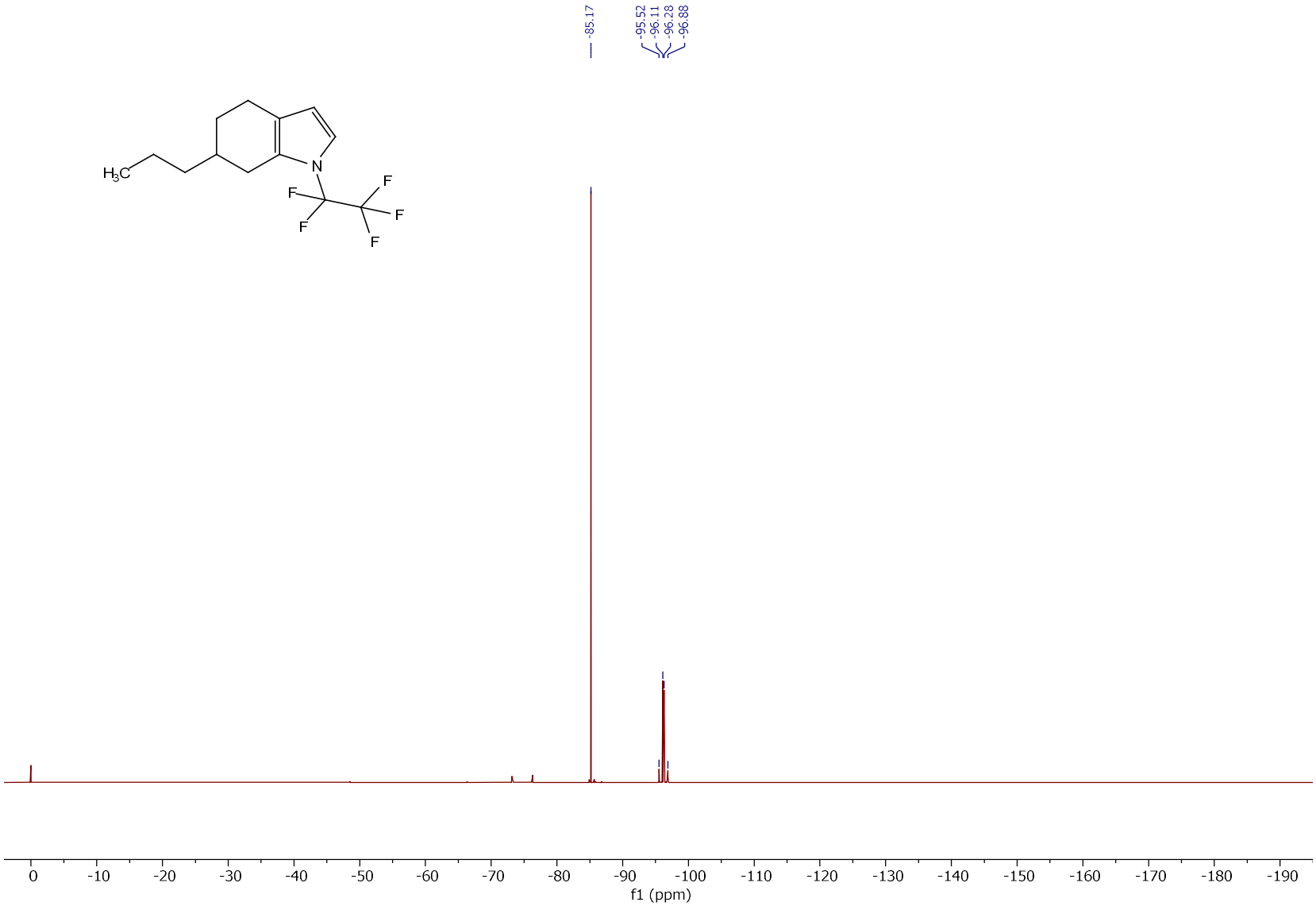


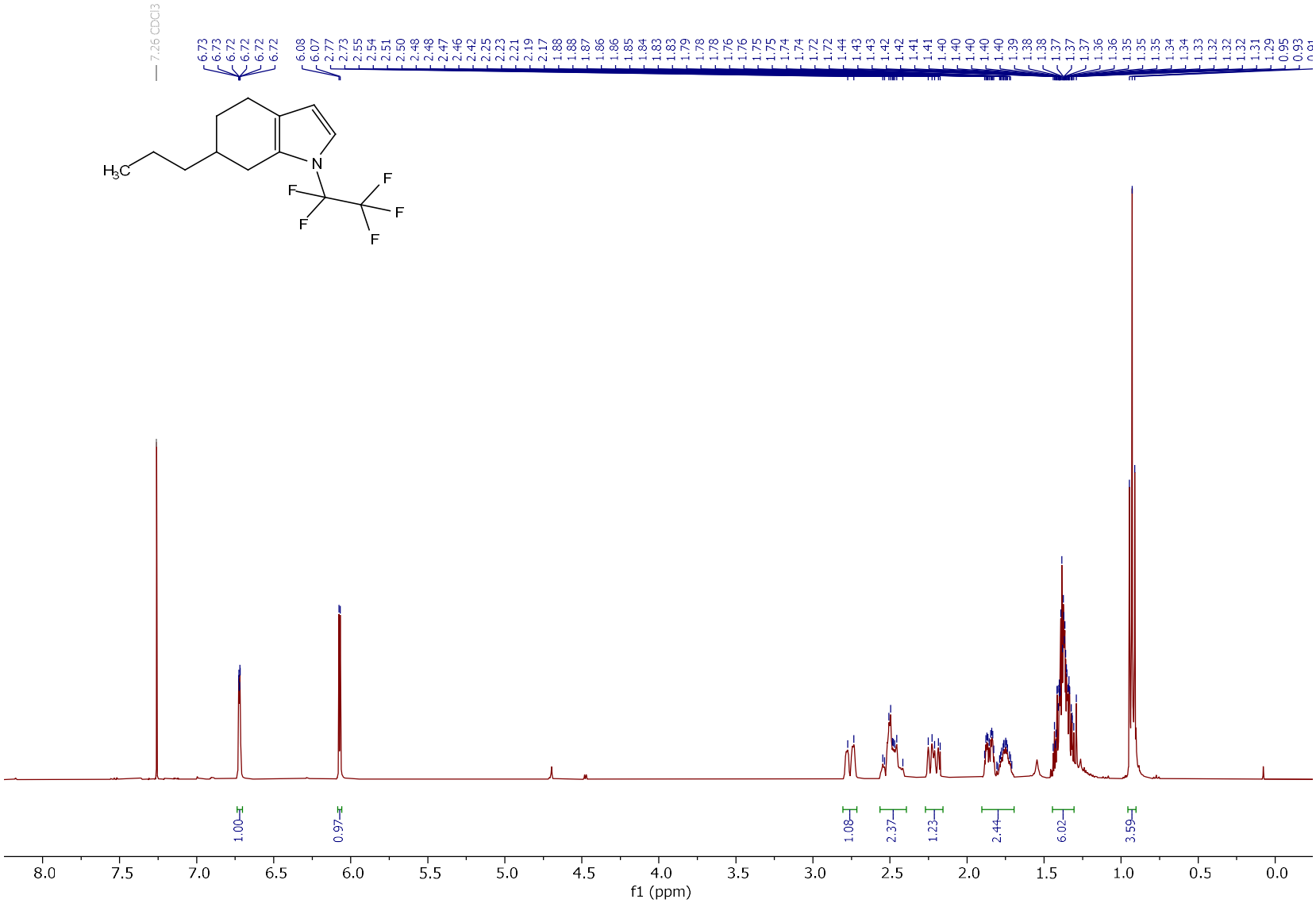
^{13}C NMR (101 MHz, $CDCl_3$) of **2j**



^{19}F NMR (376 MHz, $CDCl_3$) of **2k**



^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



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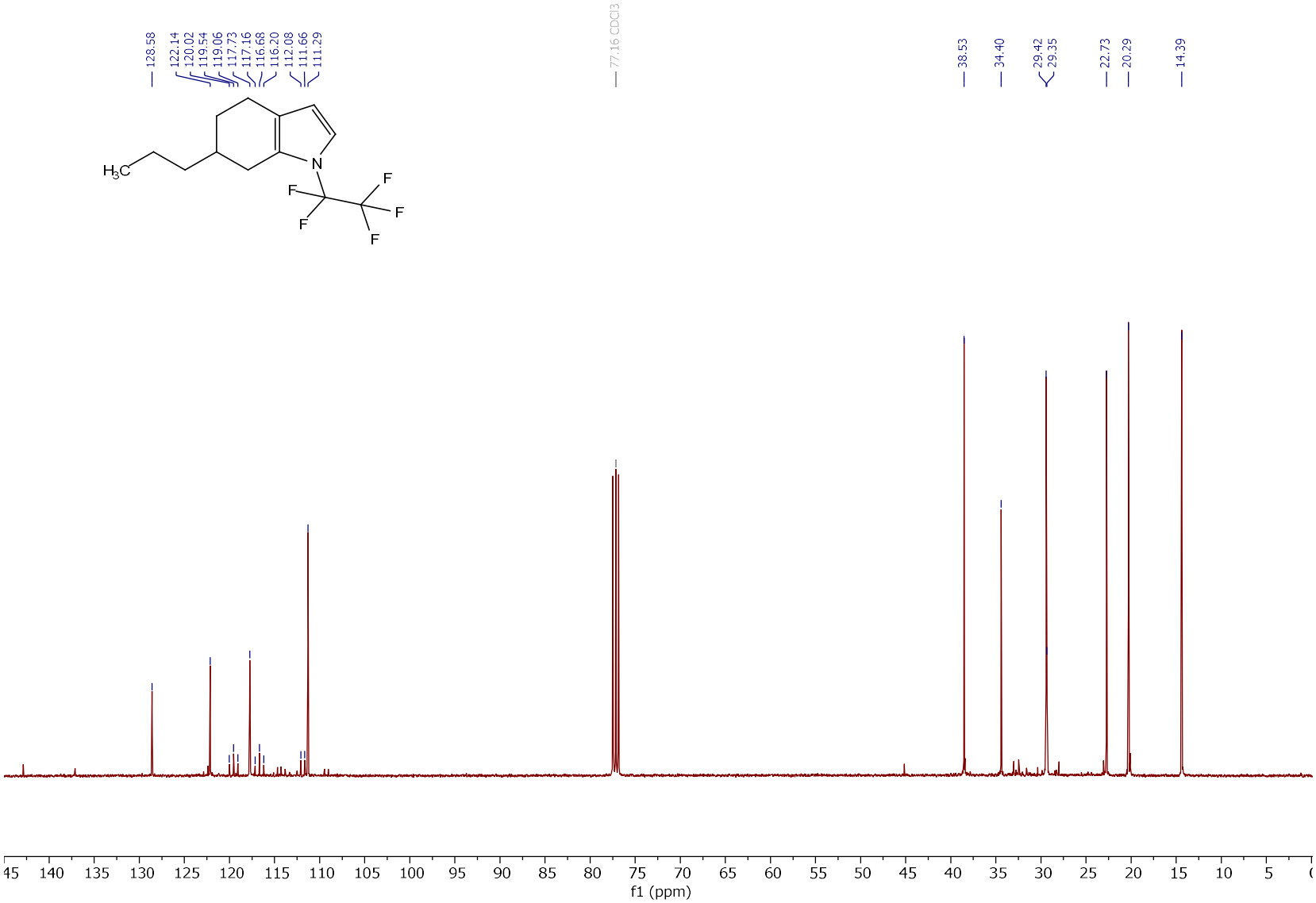
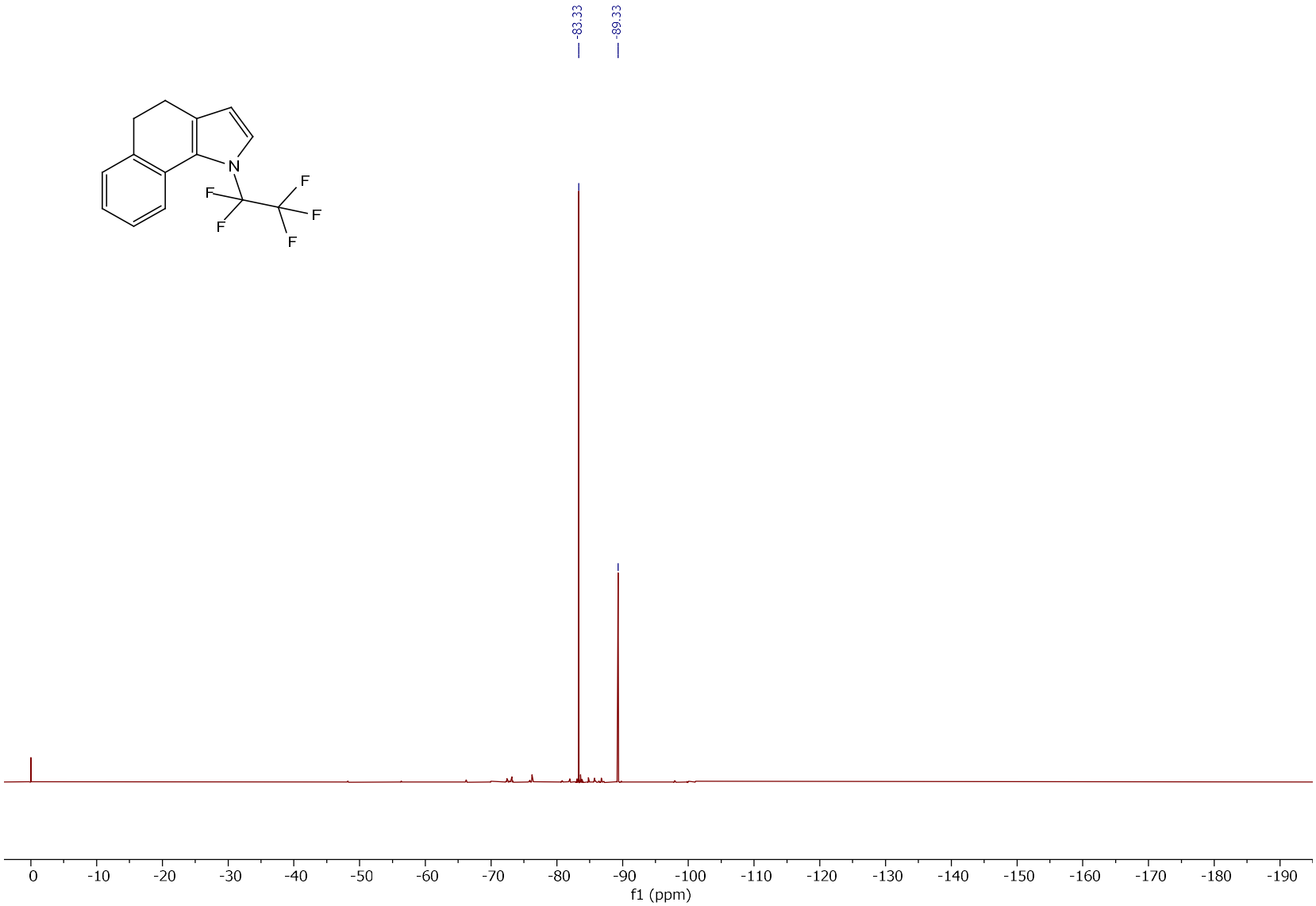


^{19}F NMR (376 MHz, $CDCl_3$) of **2n**



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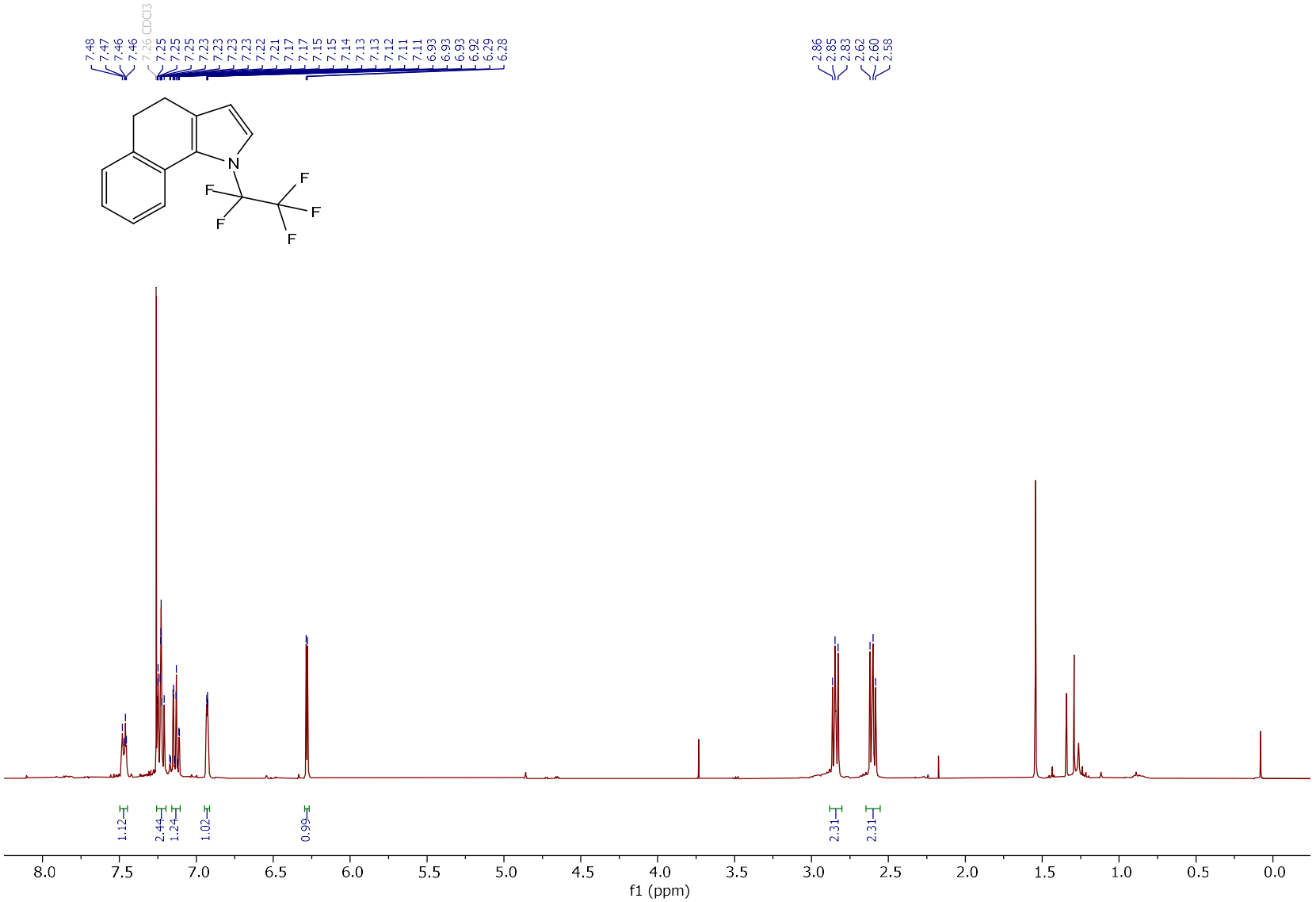

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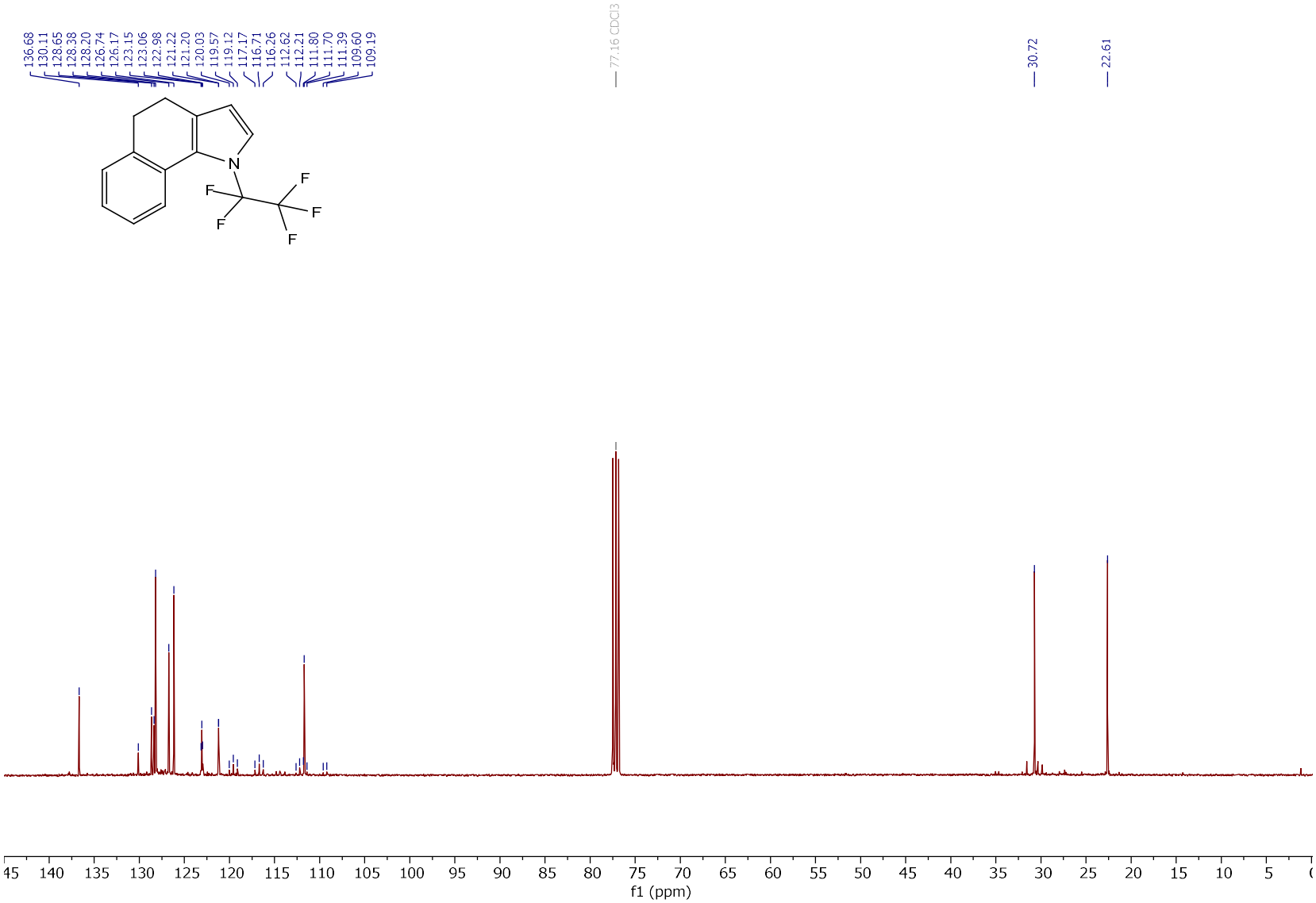
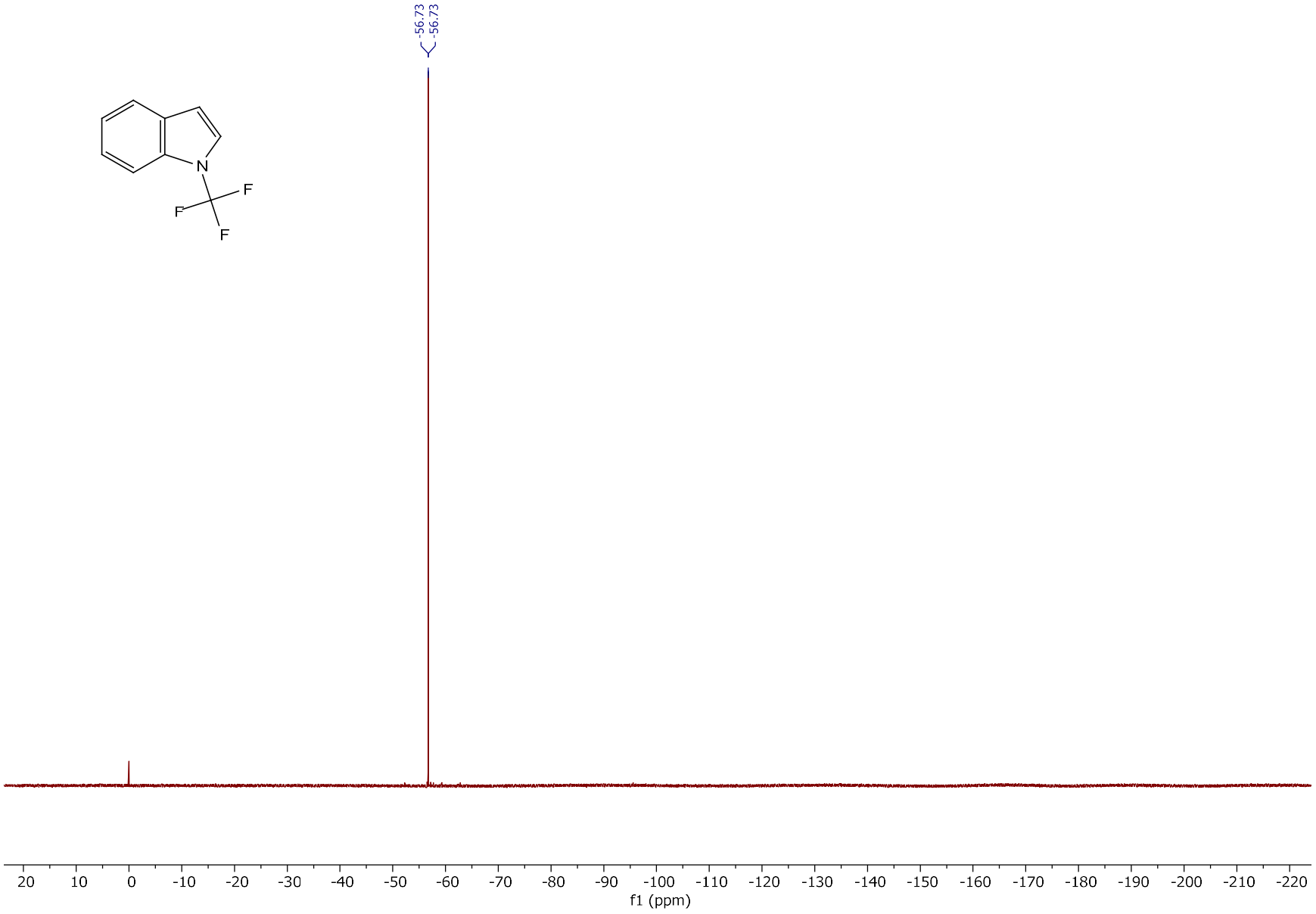
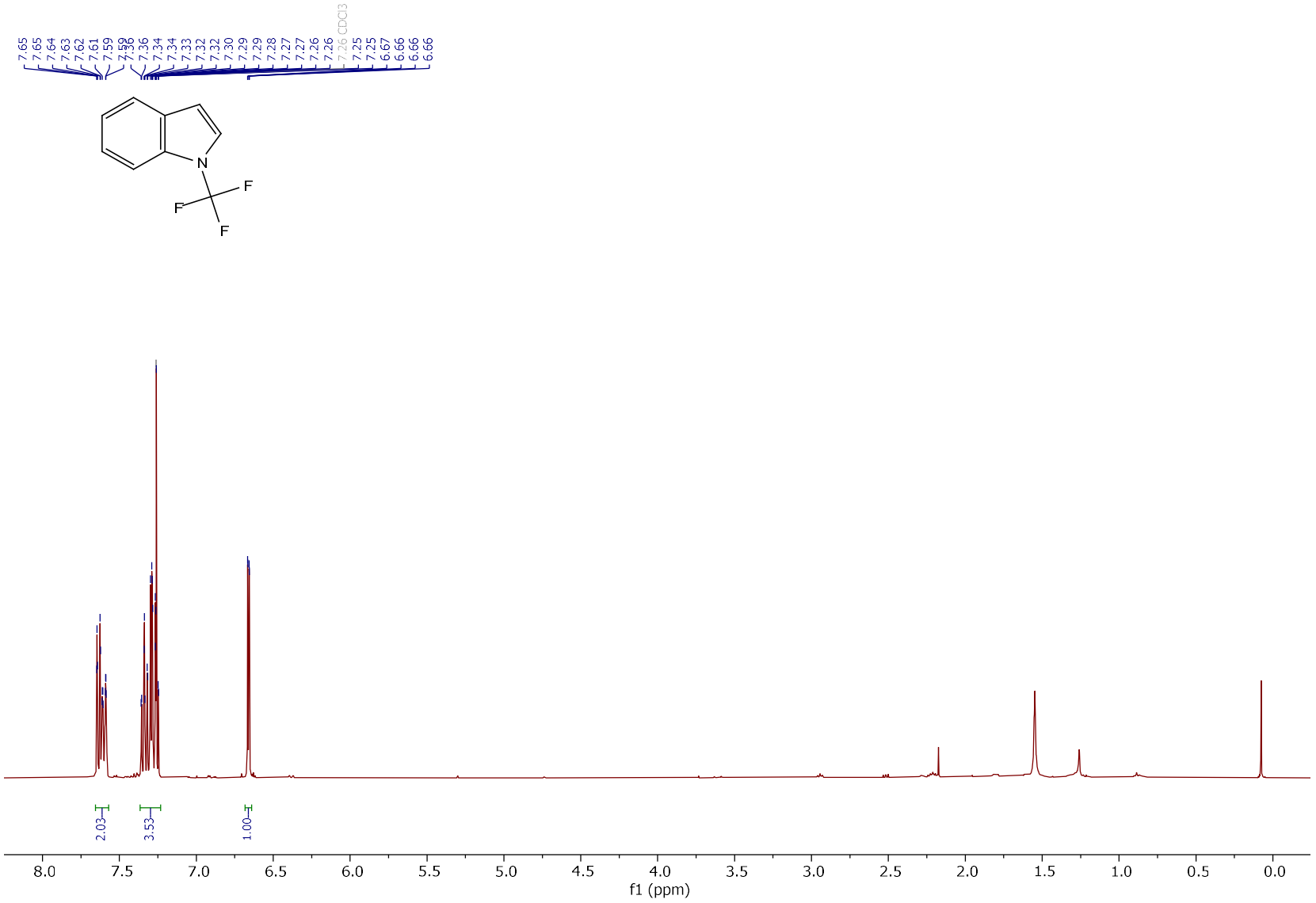


^{19}F NMR (377 MHz, $CDCl_3$) of **3a**



^{1}H NMR (401 MHz, $CDCl_3$) of **3a**



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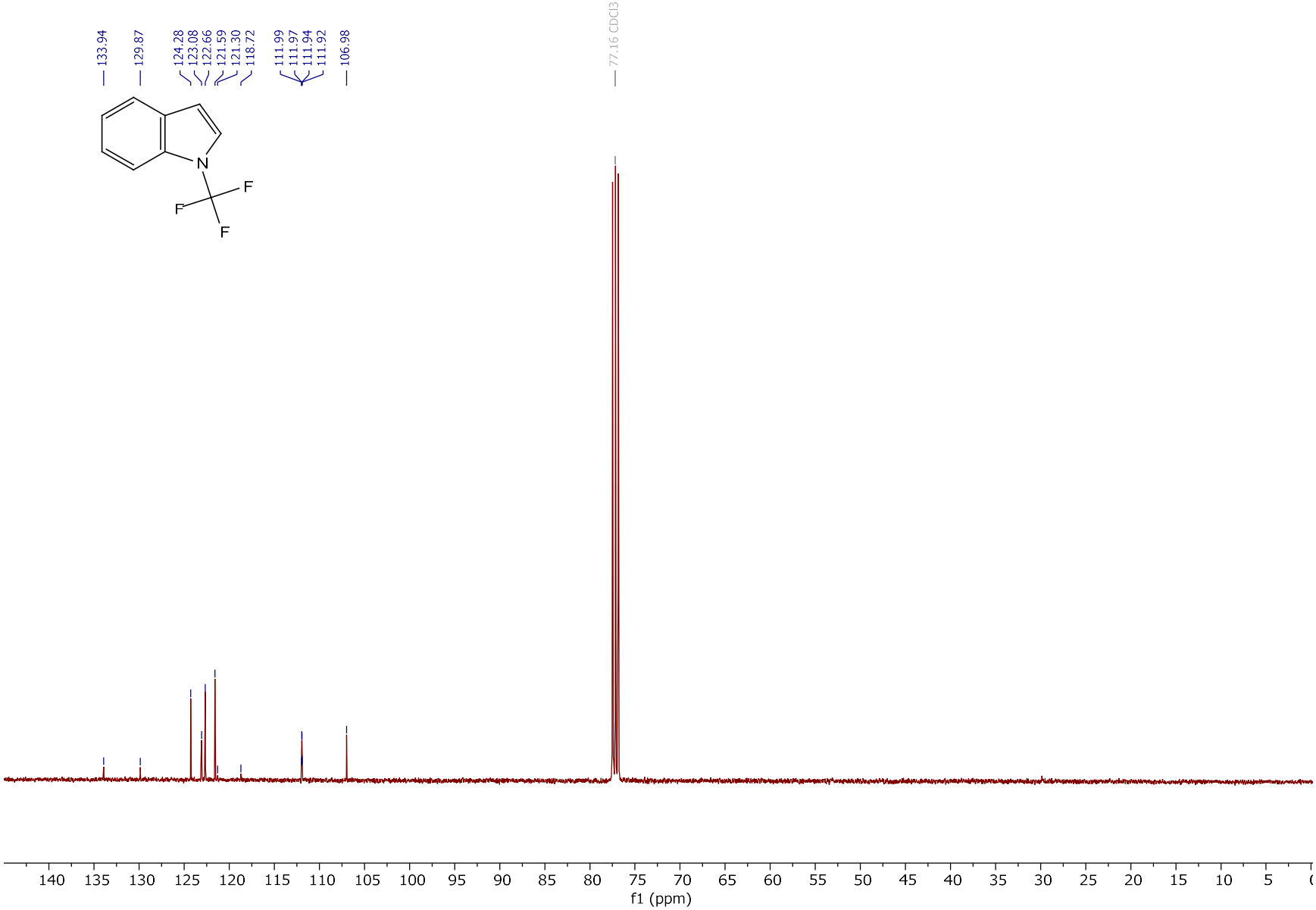
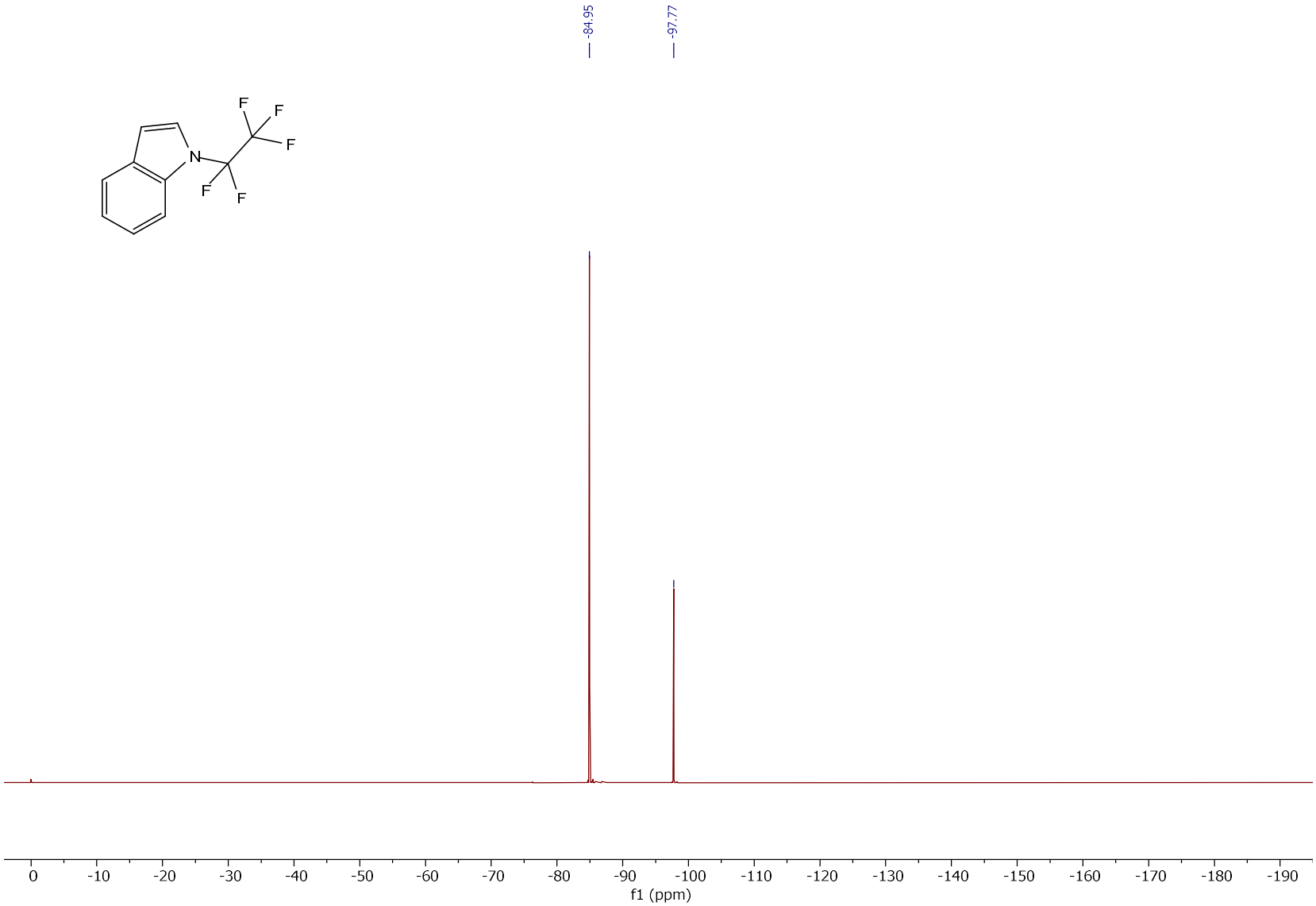


^{19}F NMR (376 MHz, $CDCl_3$) of **3b**



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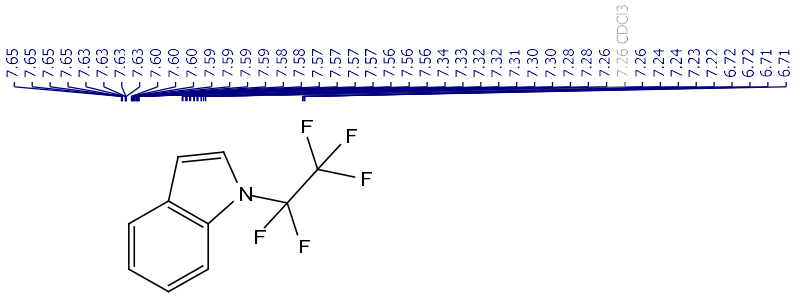
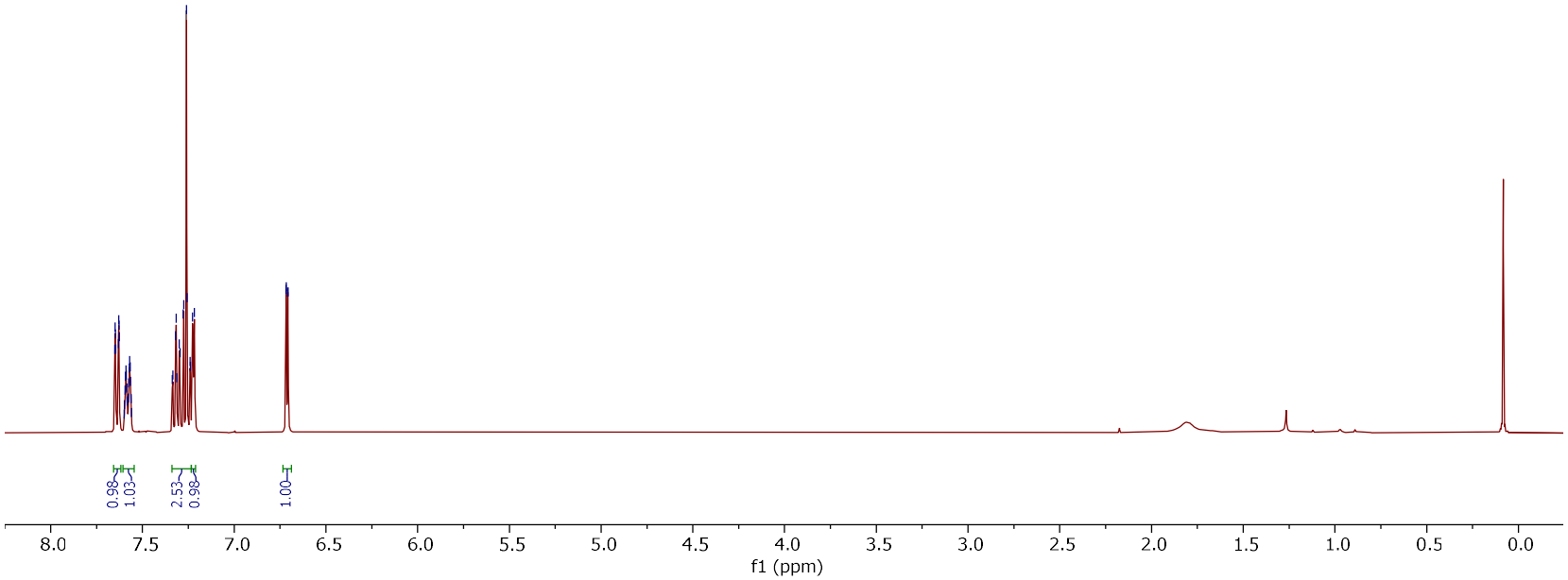
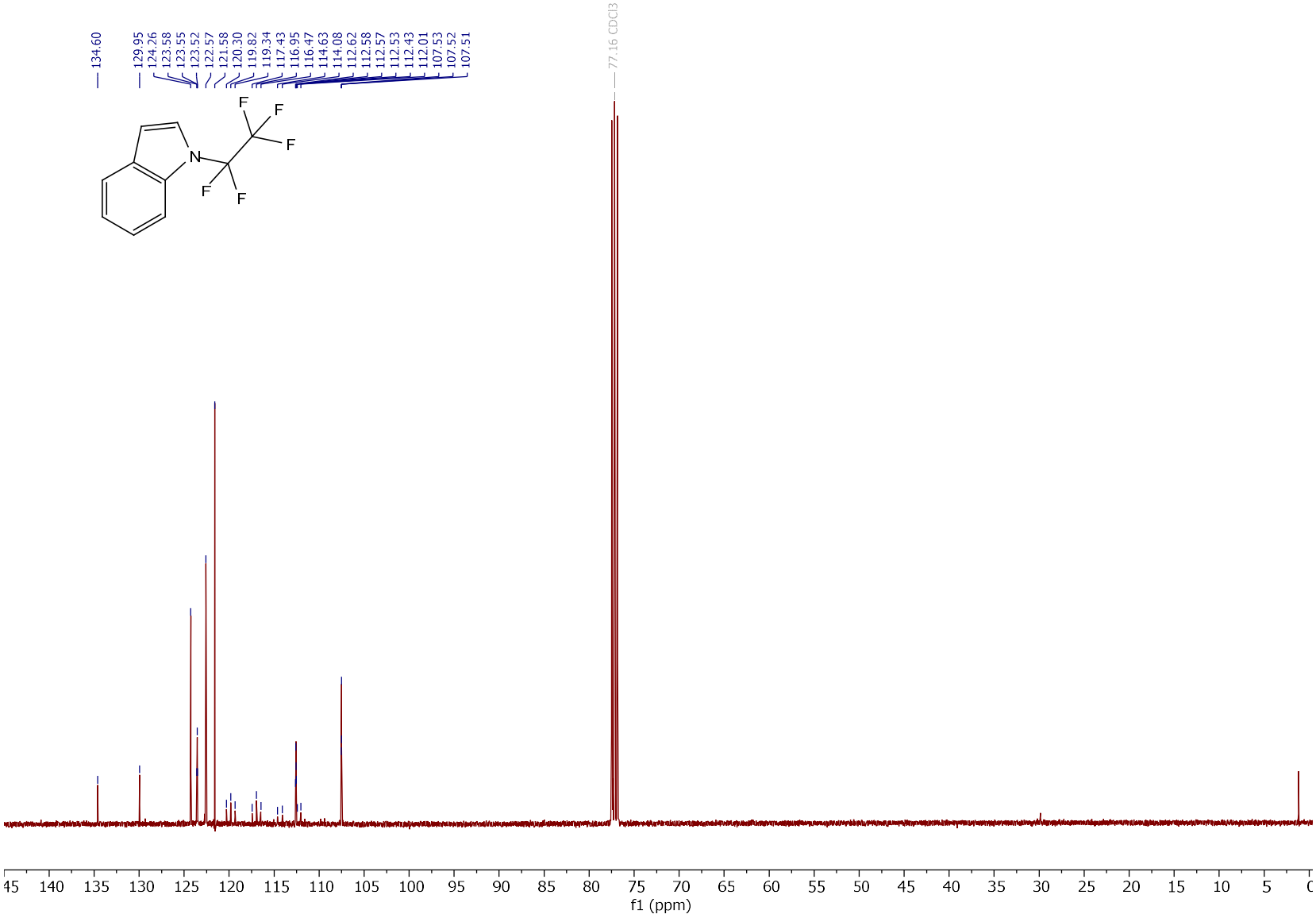




^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



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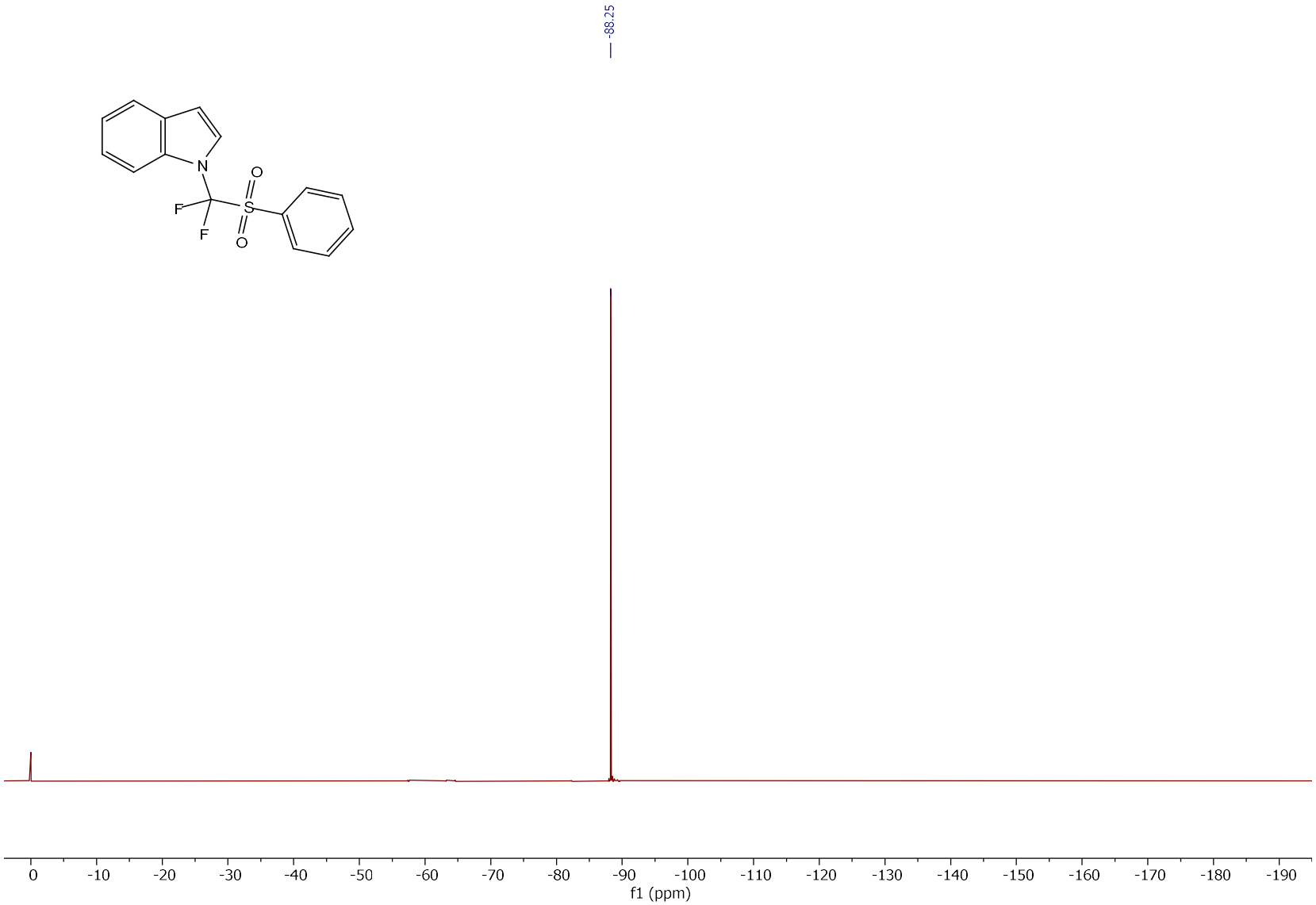
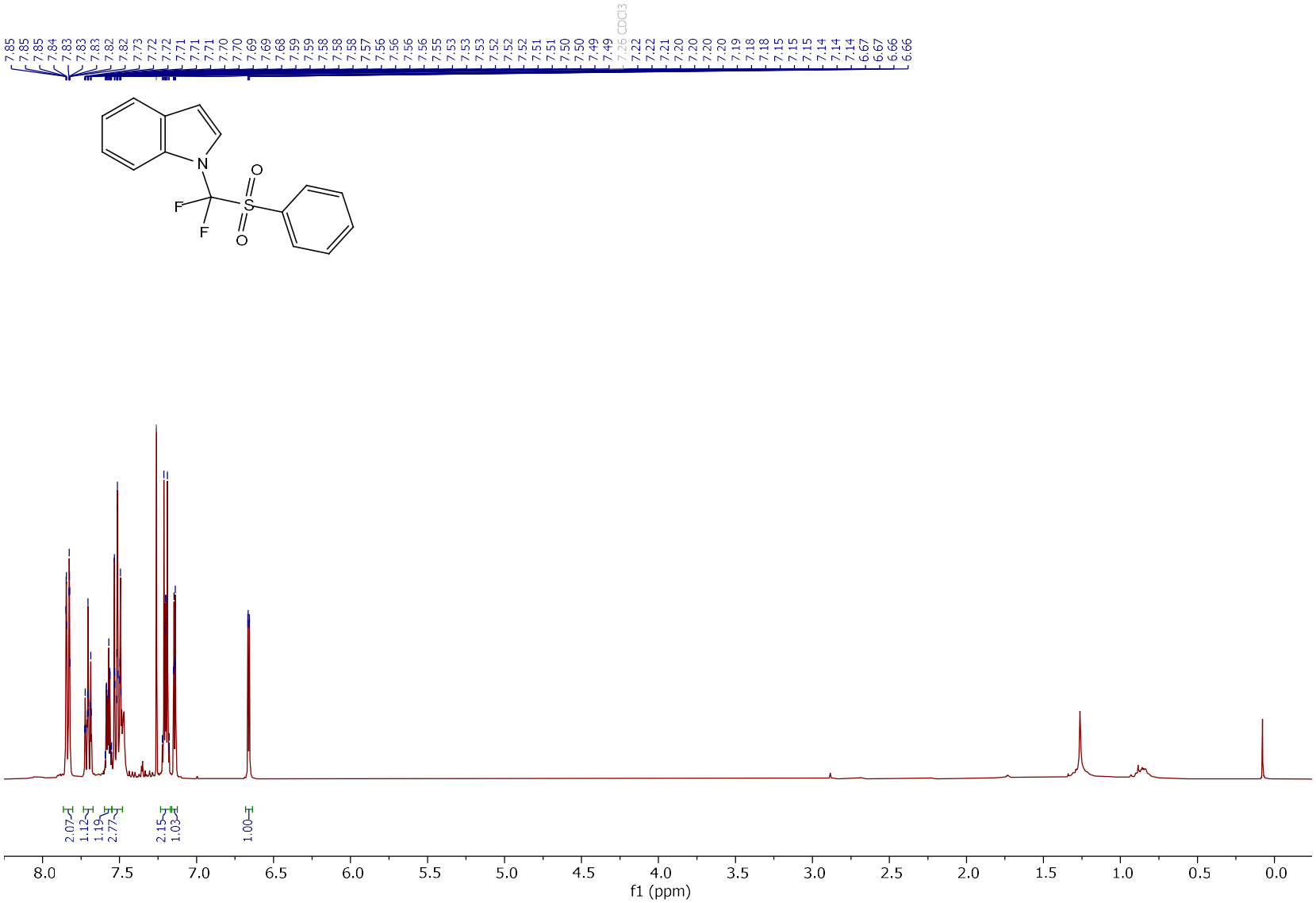
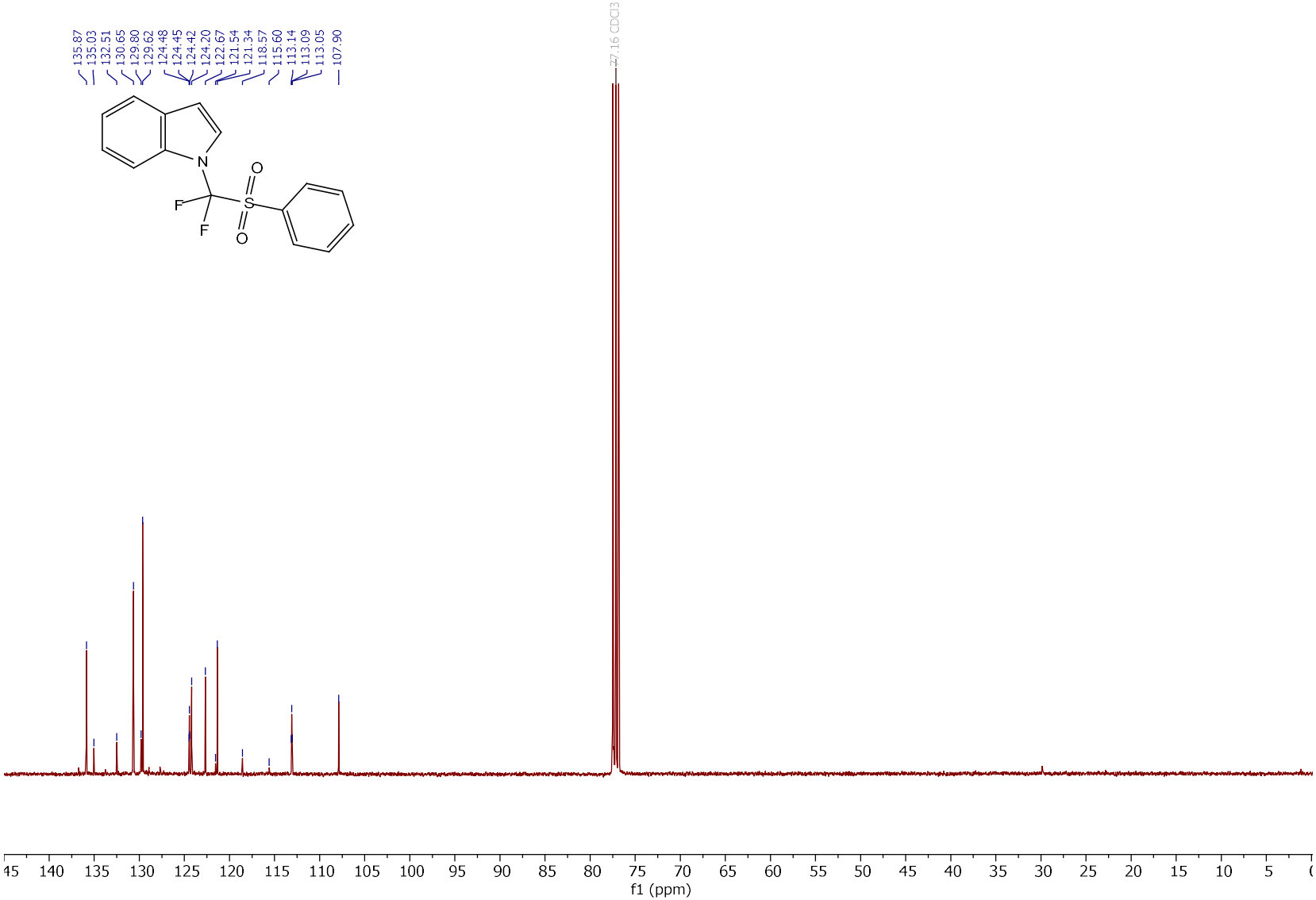


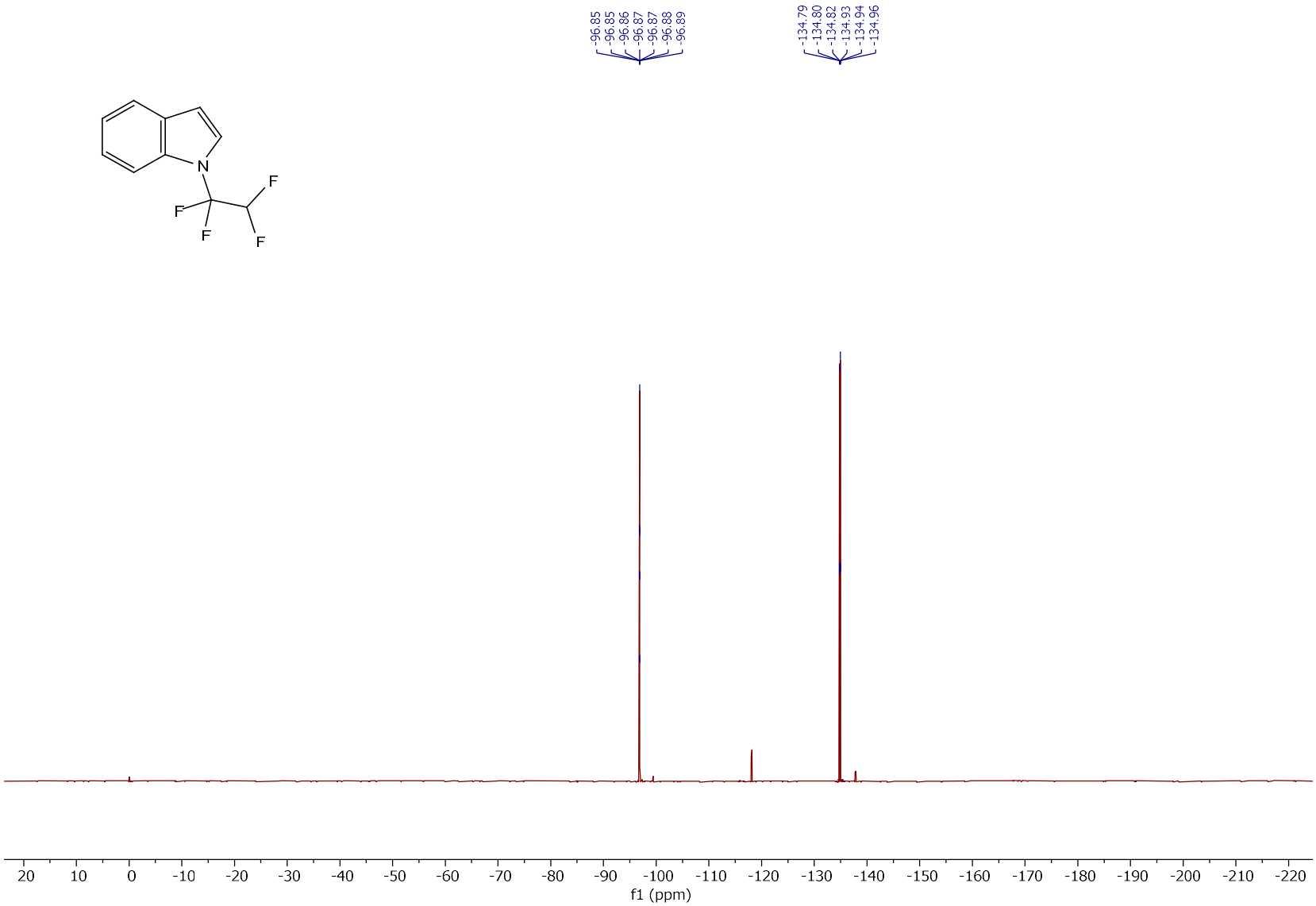
^{1}H NMR (401 MHz, $CDCl_3$) of **3c**



^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



^{19}F NMR (377 MHz, $CDCl_3$) of **3d**



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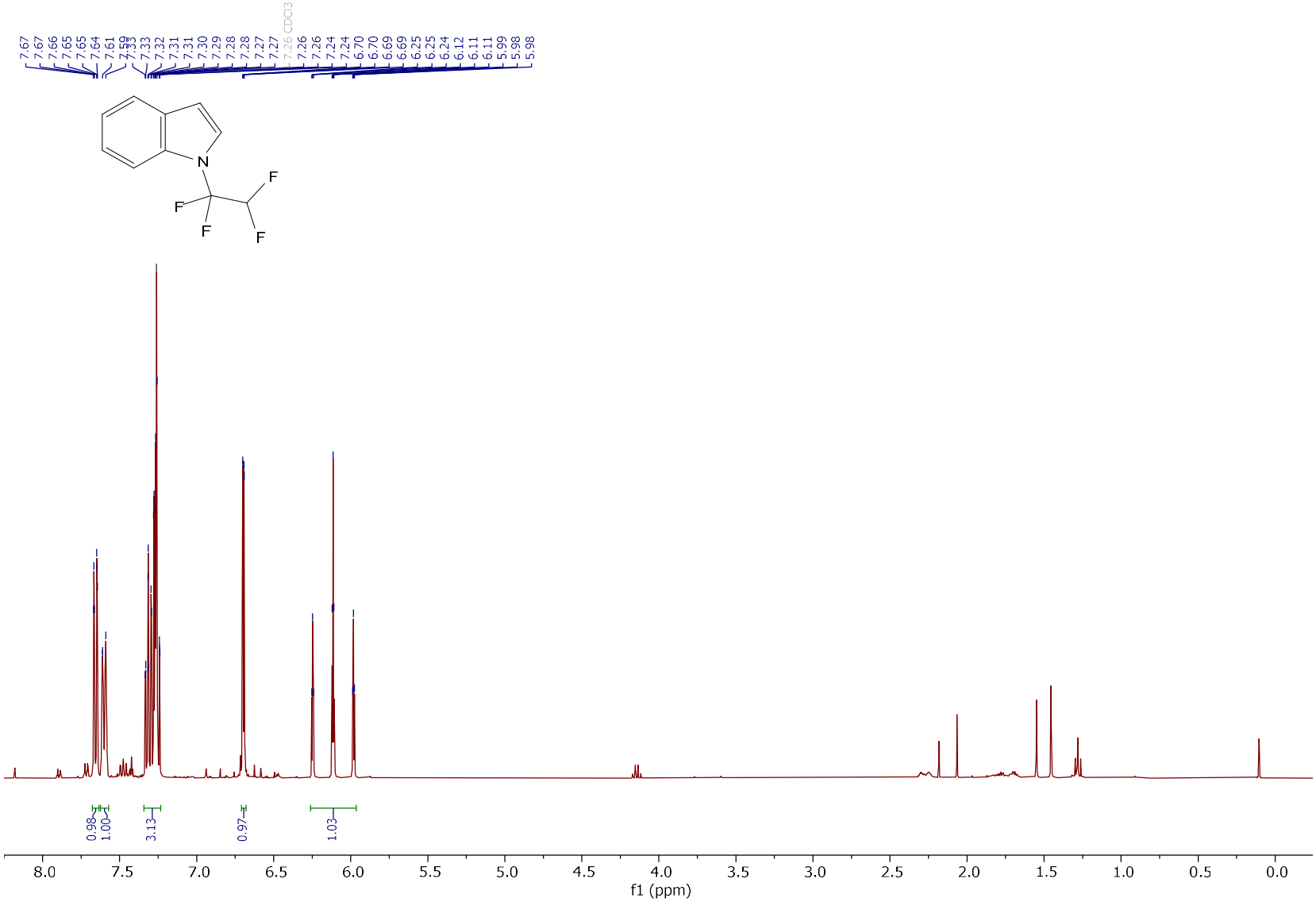

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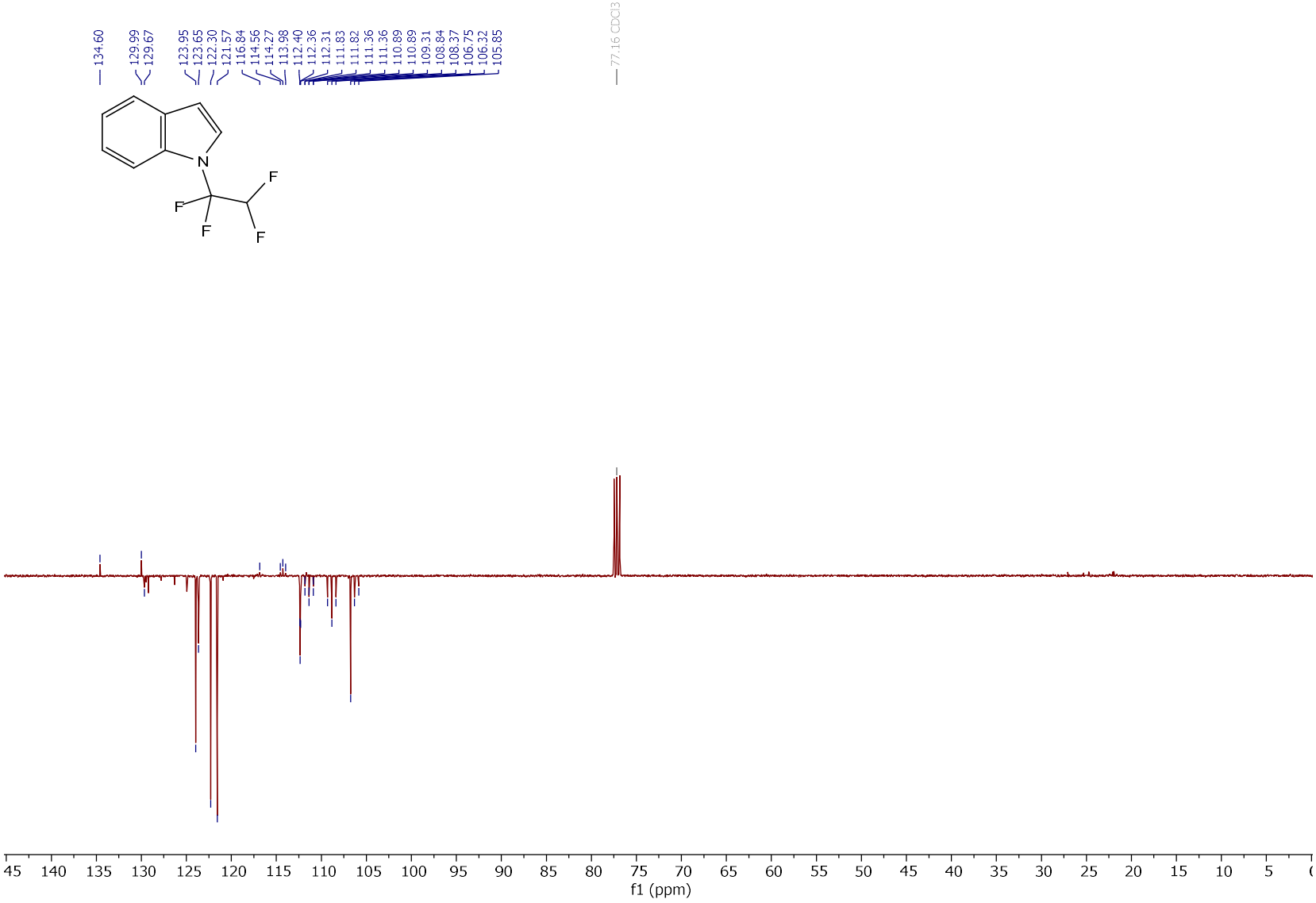

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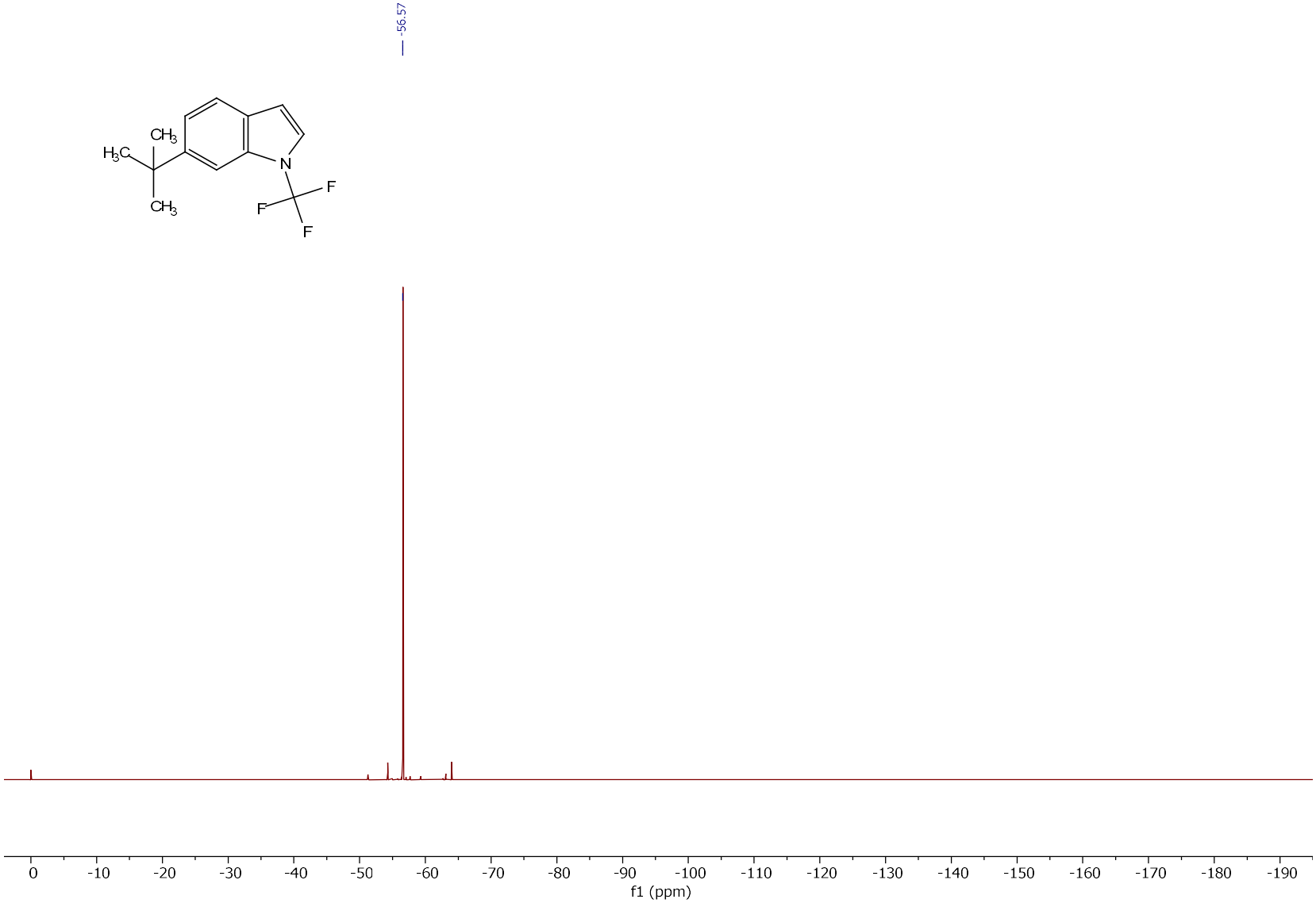

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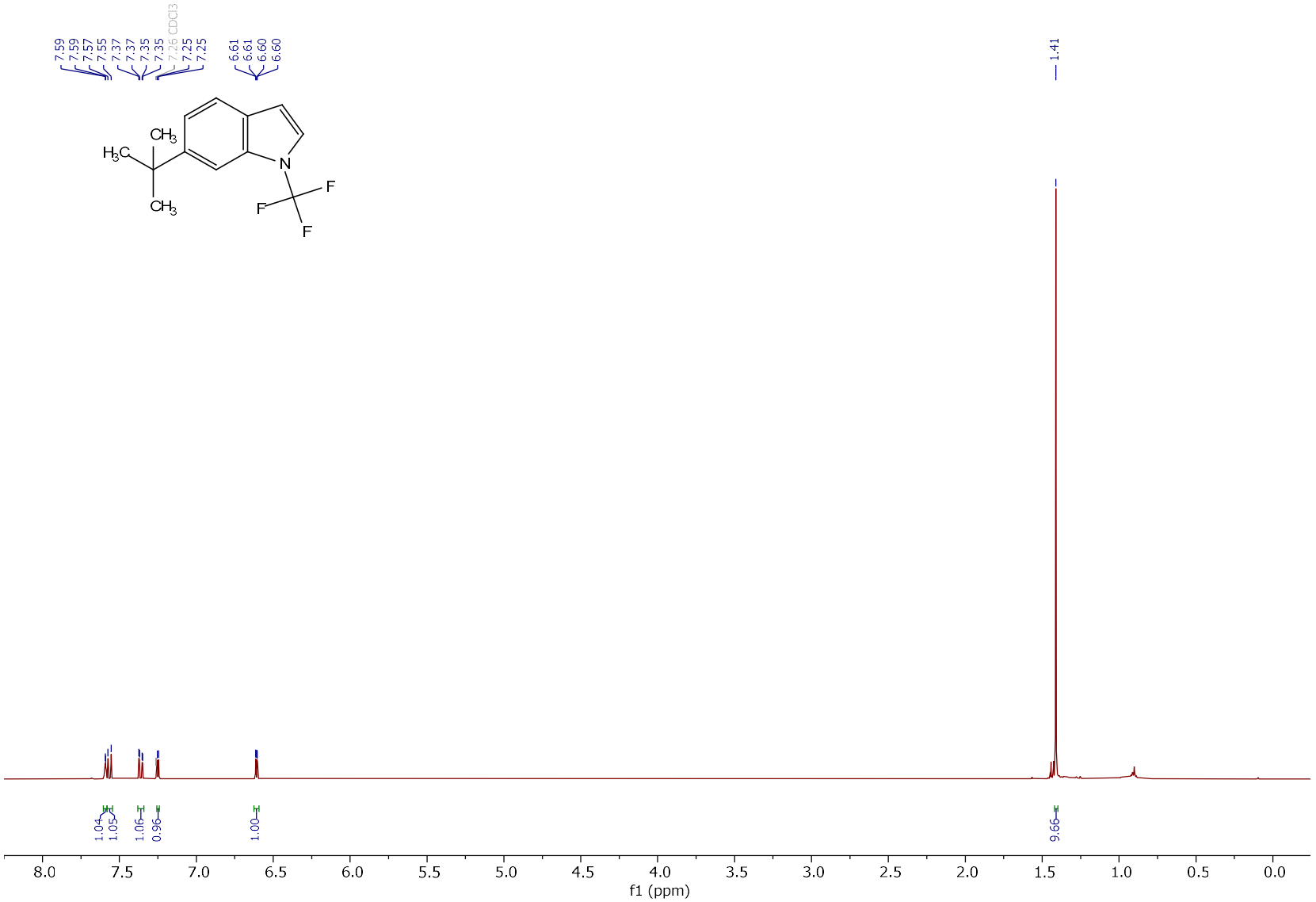

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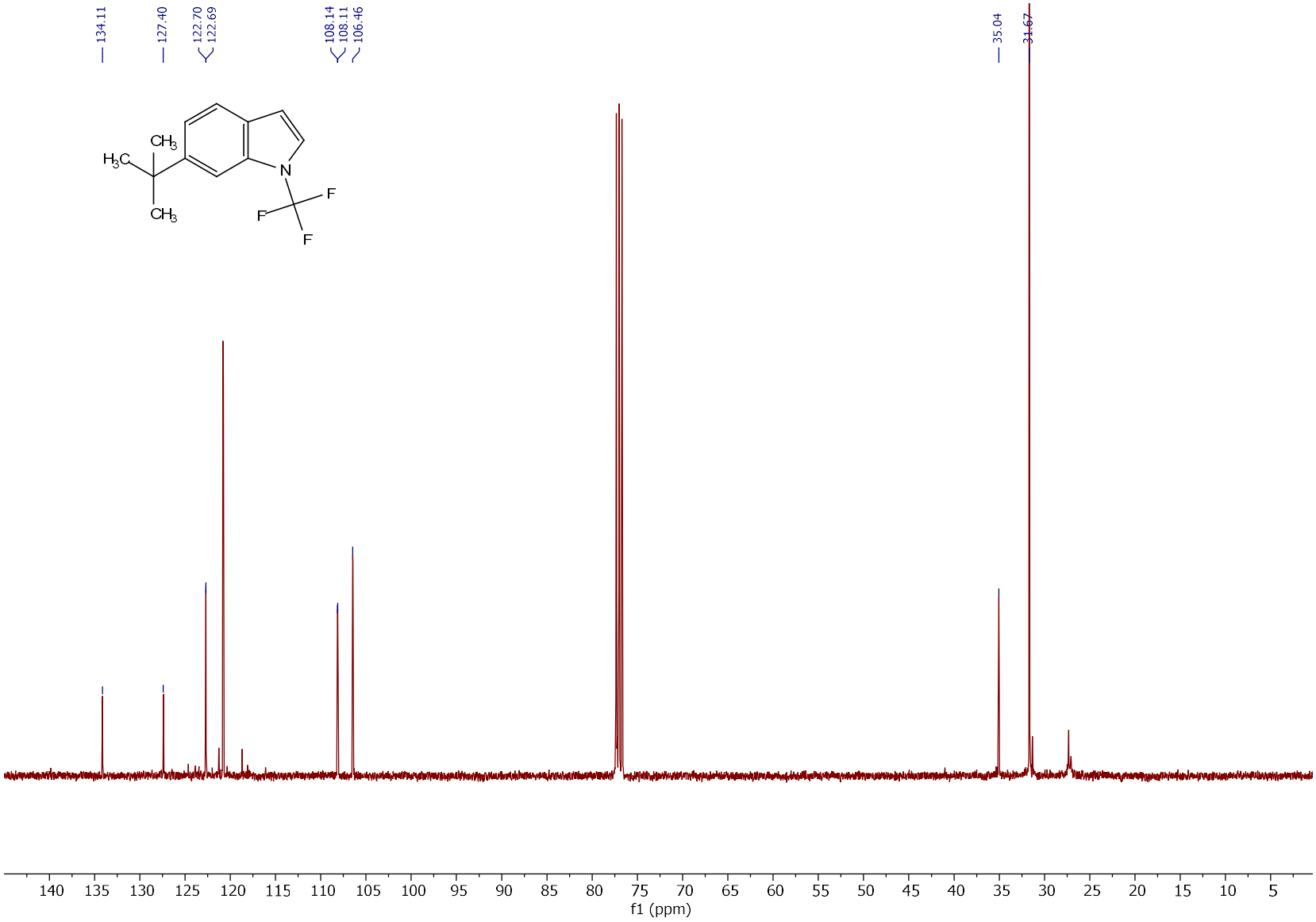
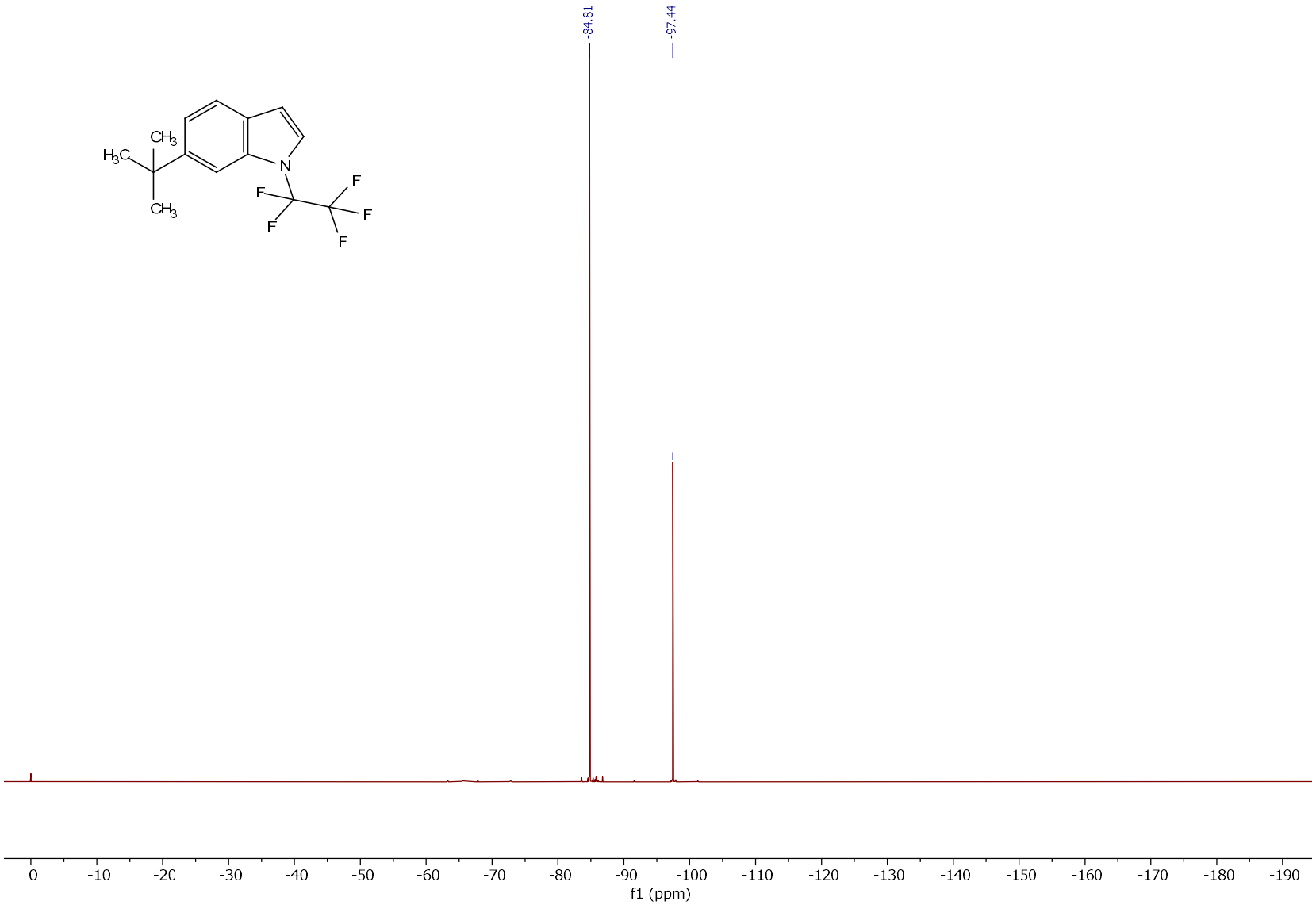


^{19}F NMR (376 MHz, $CDCl_3$) of **3f**



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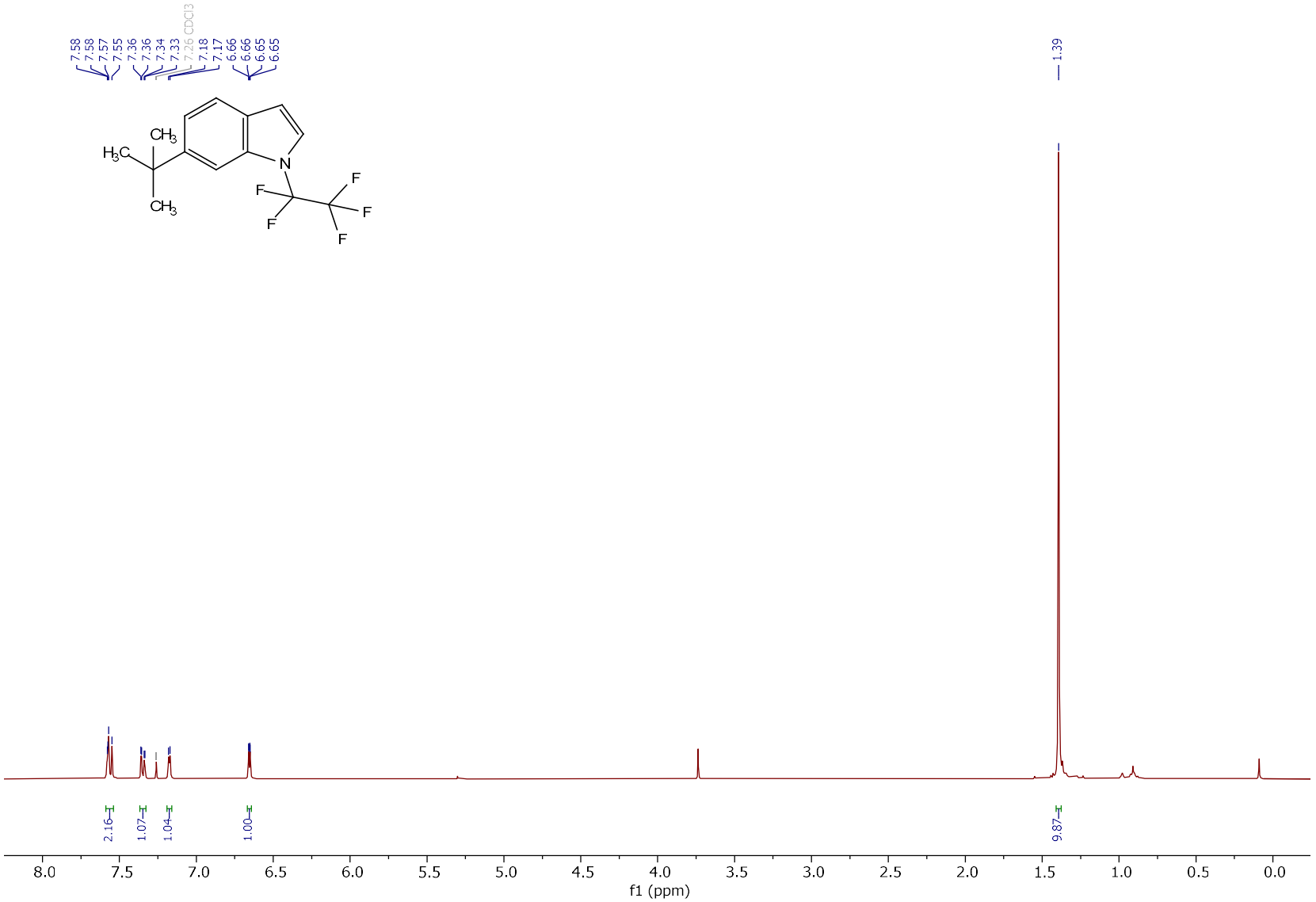
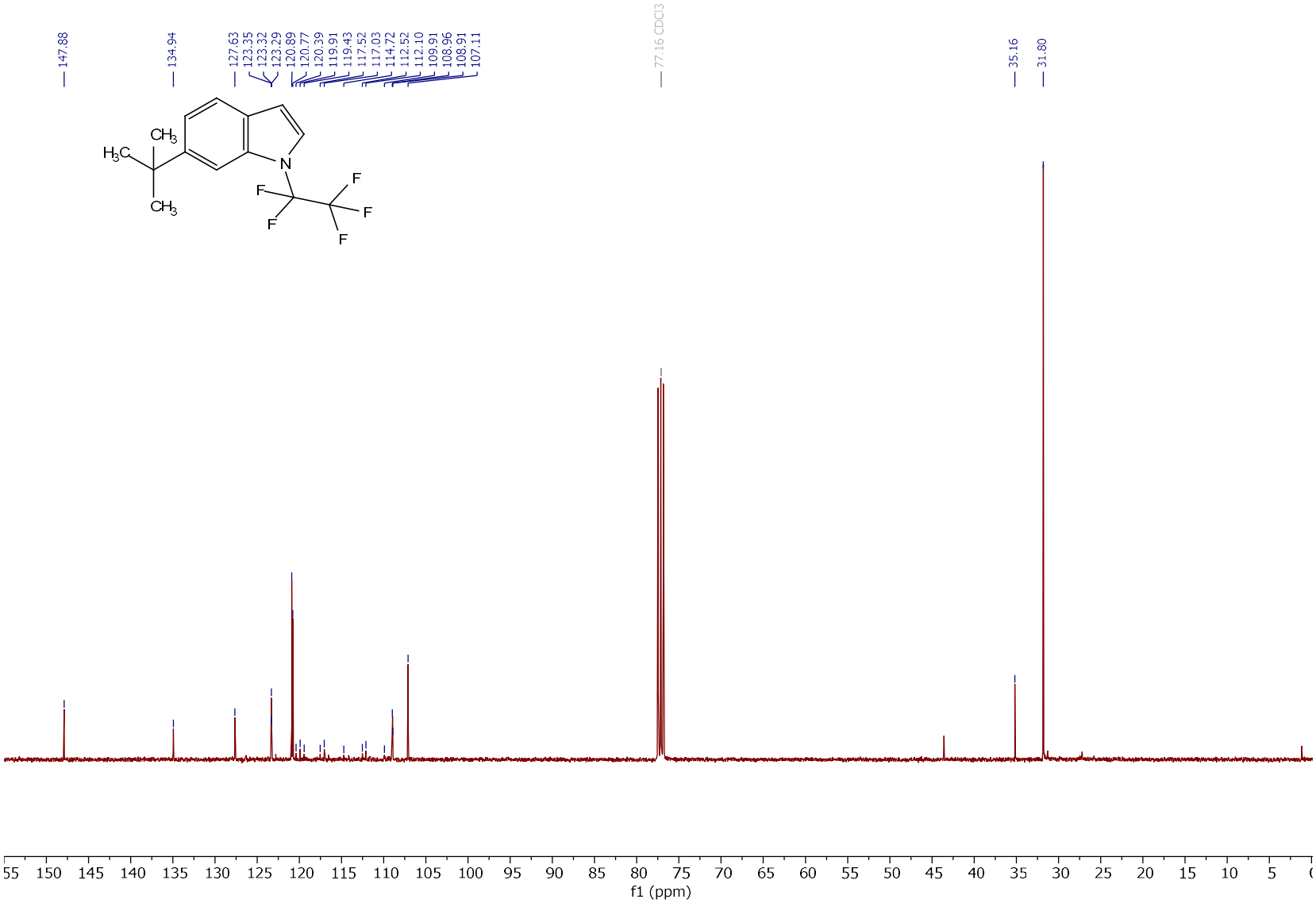
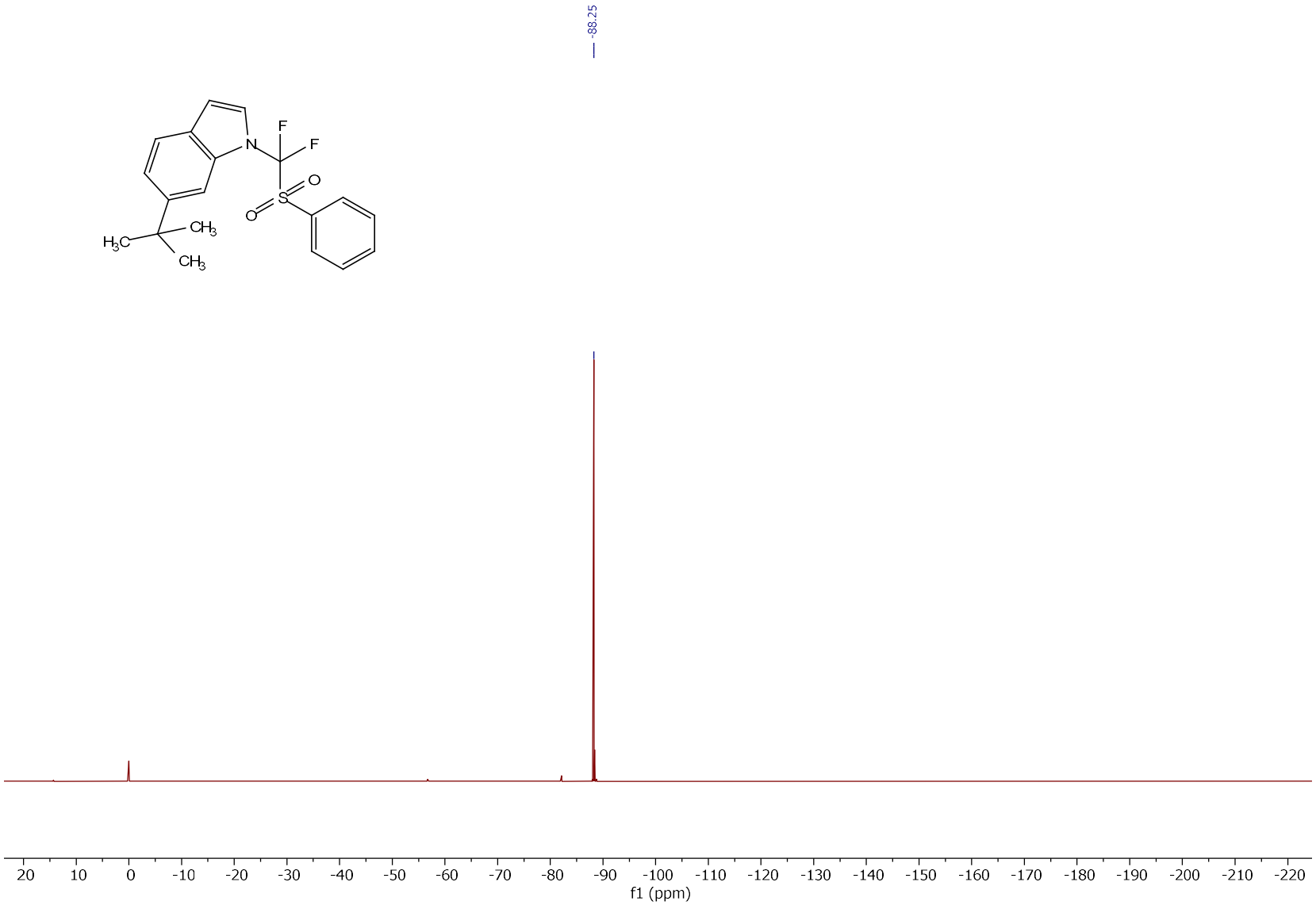


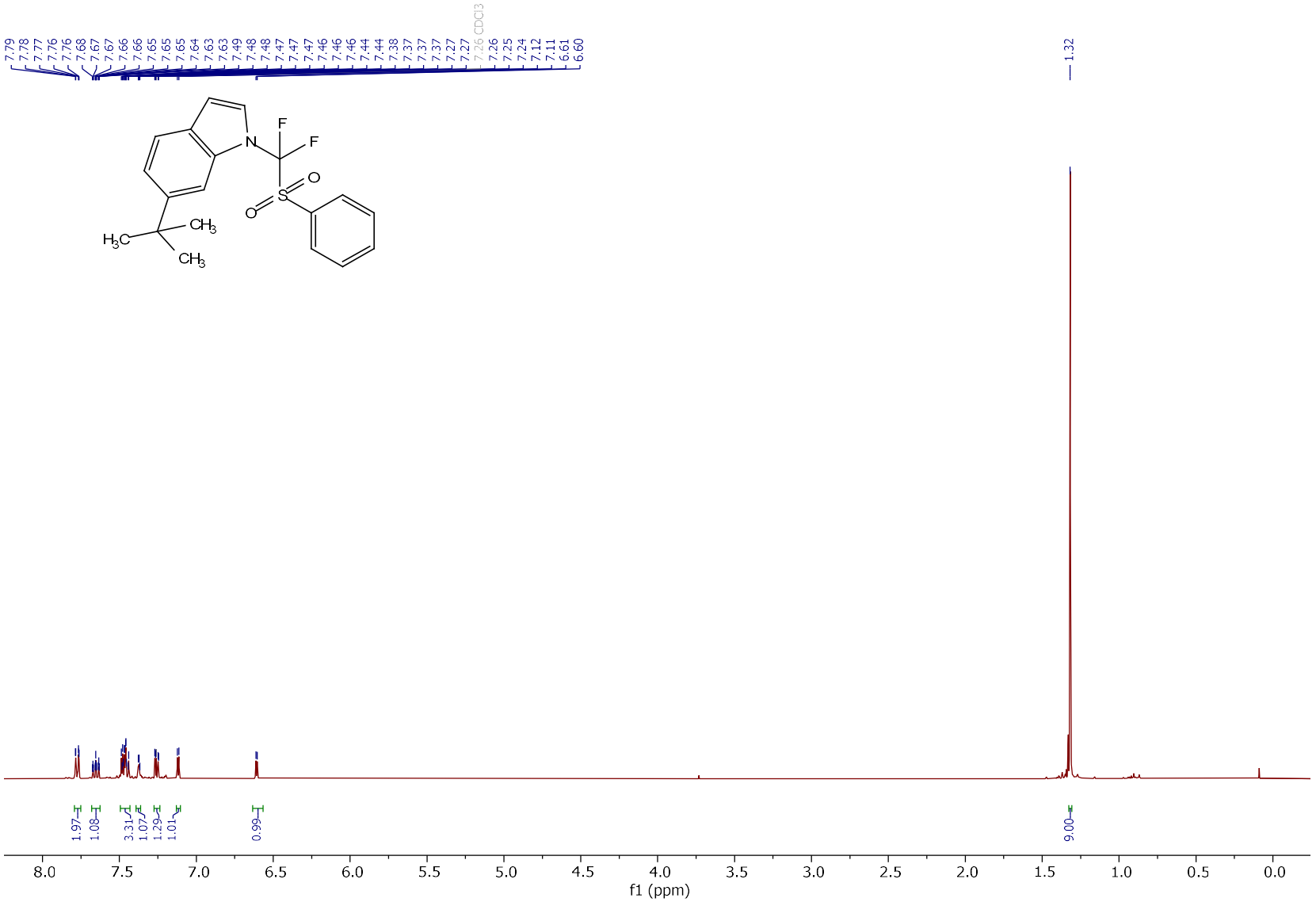
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



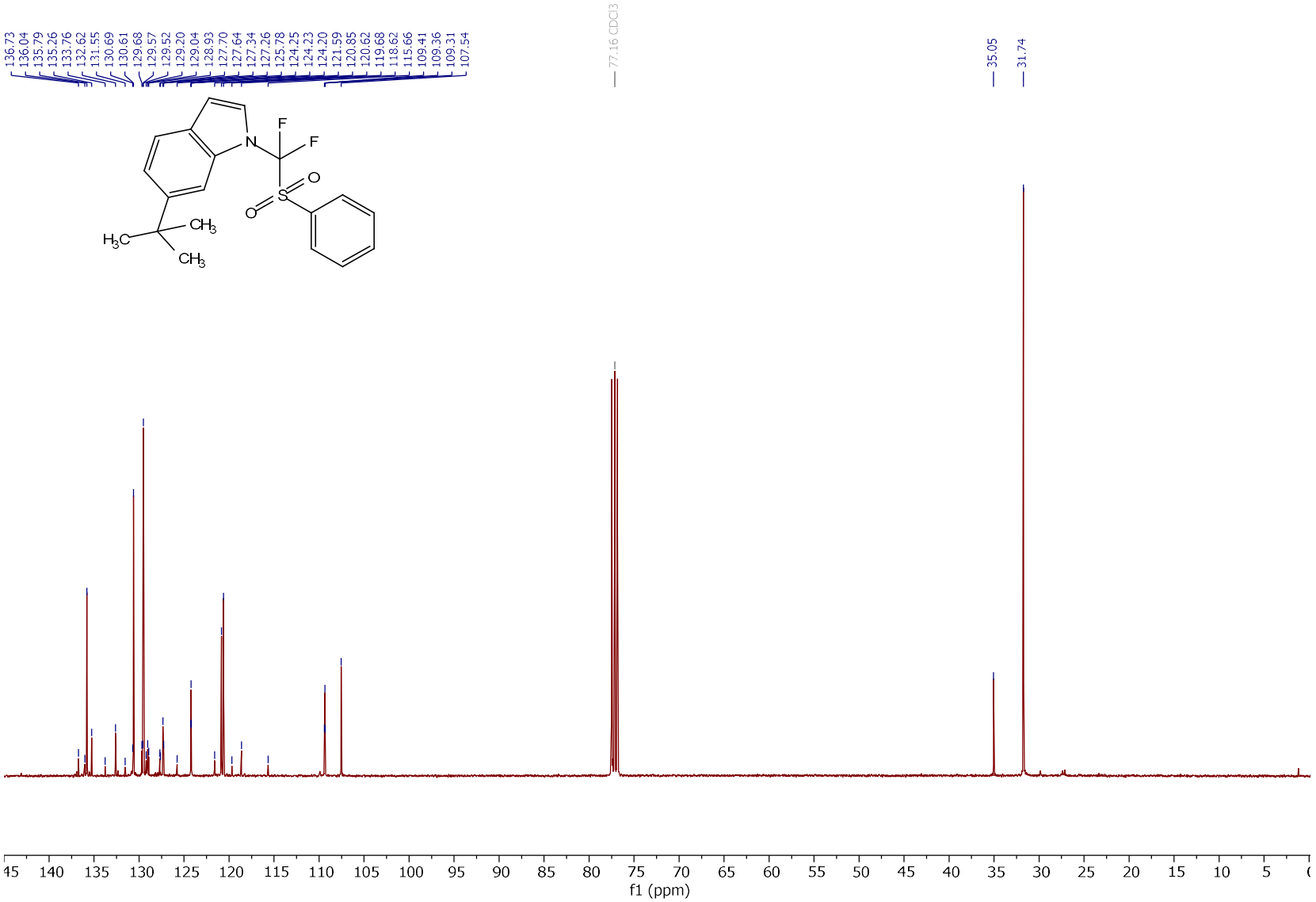
^{19}F NMR (377 MHz, $CDCl_3$) of **3g**



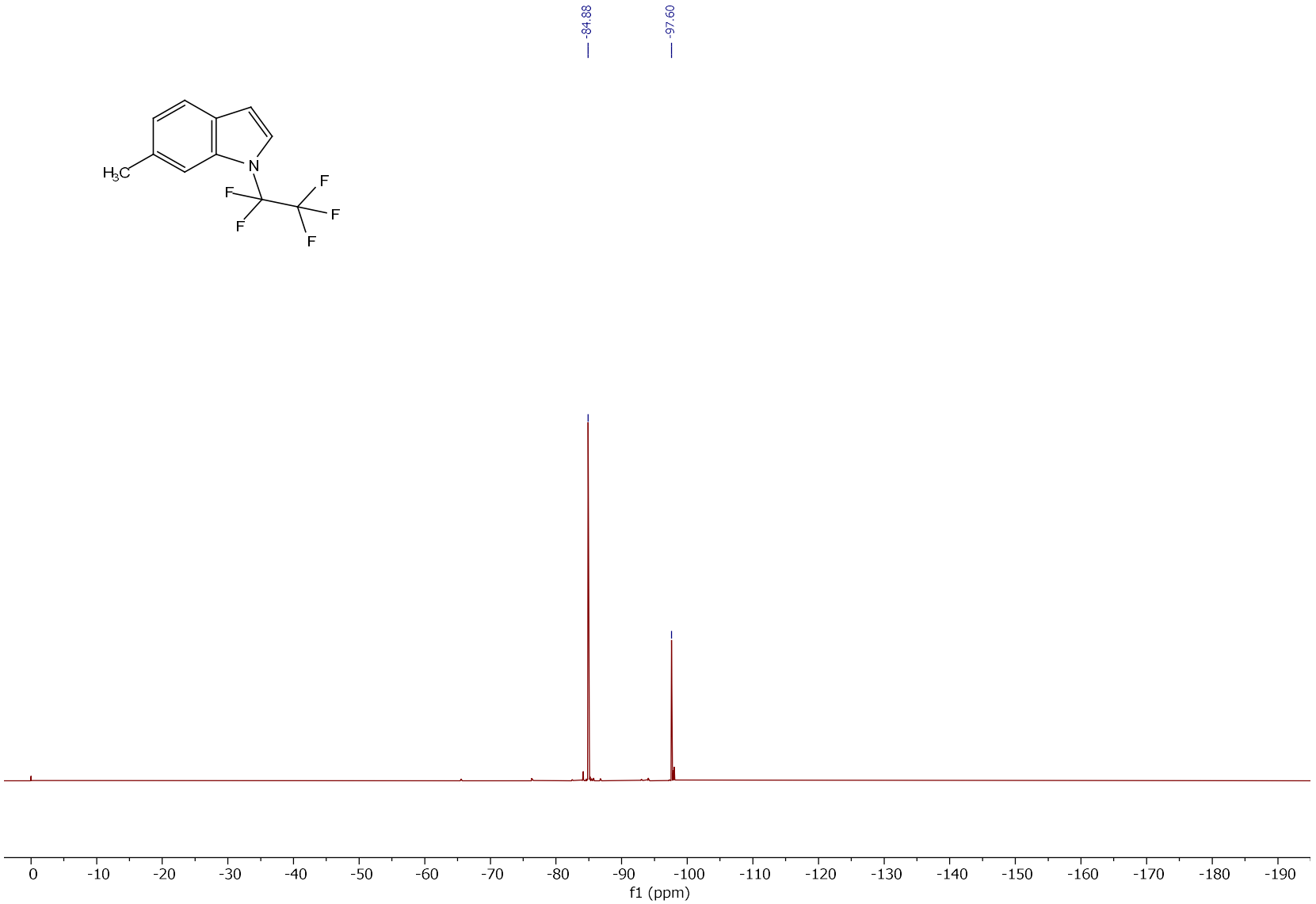
^{1}H NMR (401 MHz, $CDCl_3$) of **3g**



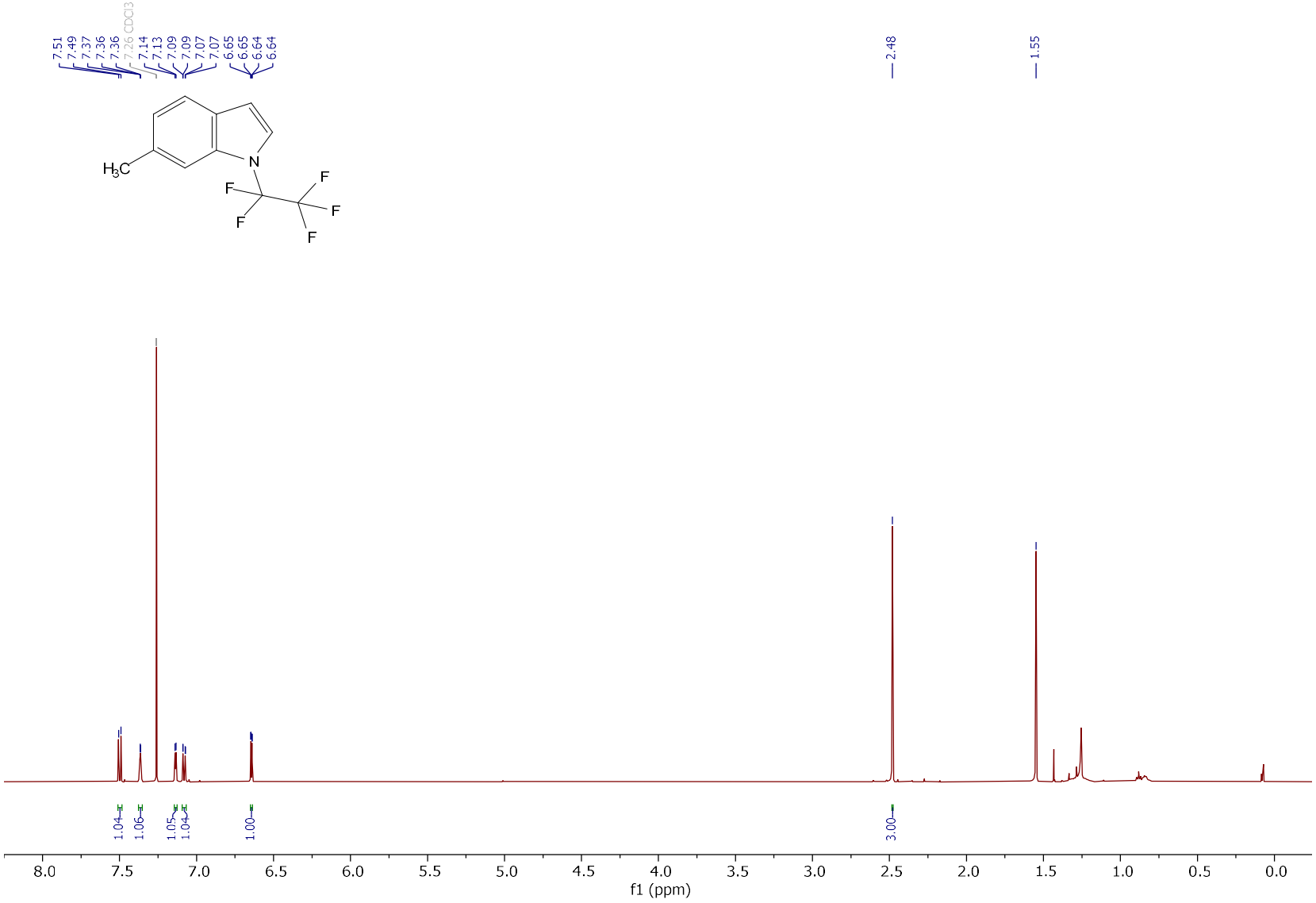
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



^{19}F NMR (376 MHz, $CDCl_3$) of **3h**



^{1}H NMR (500 MHz, $CDCl_3$) of **3h**



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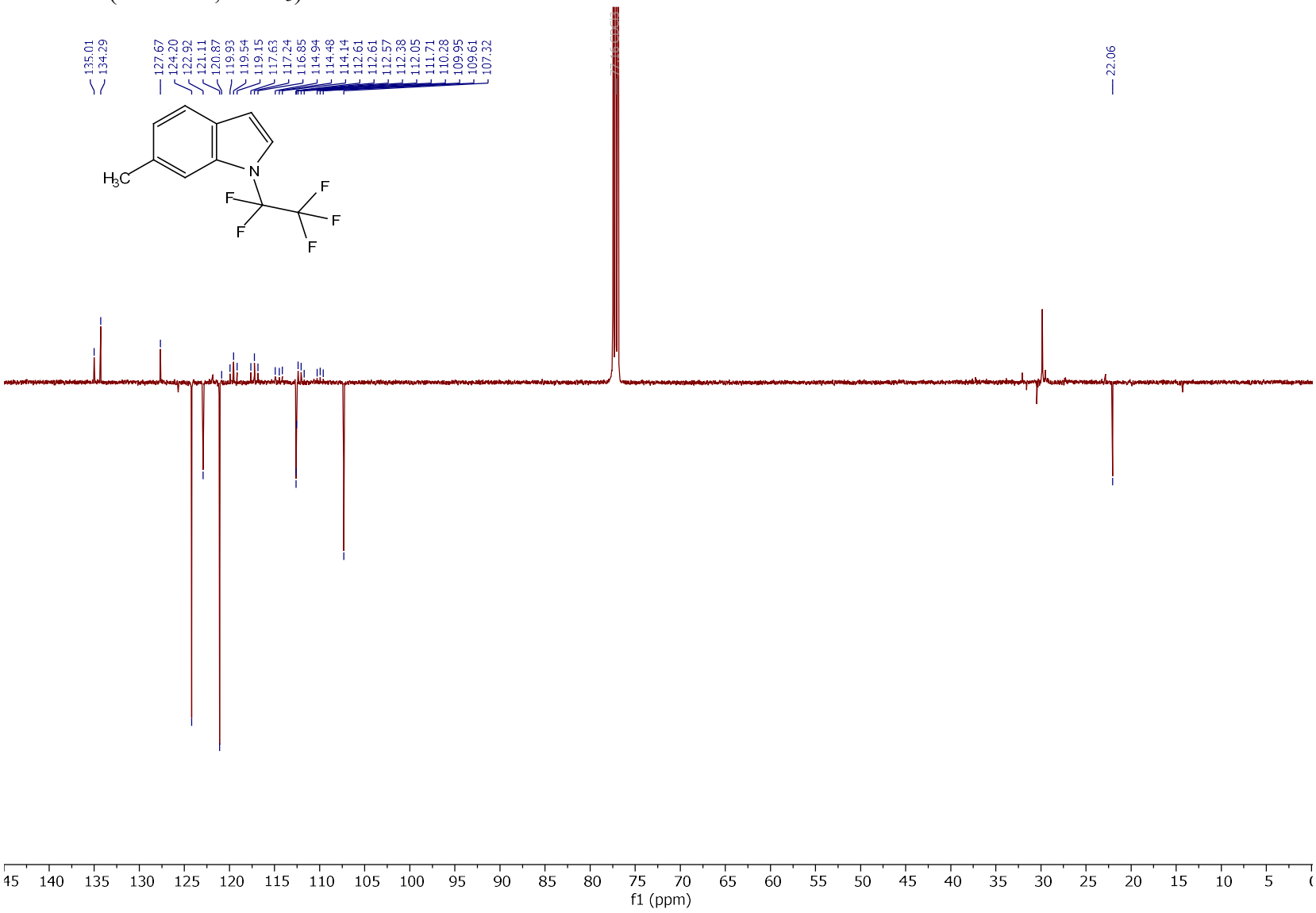
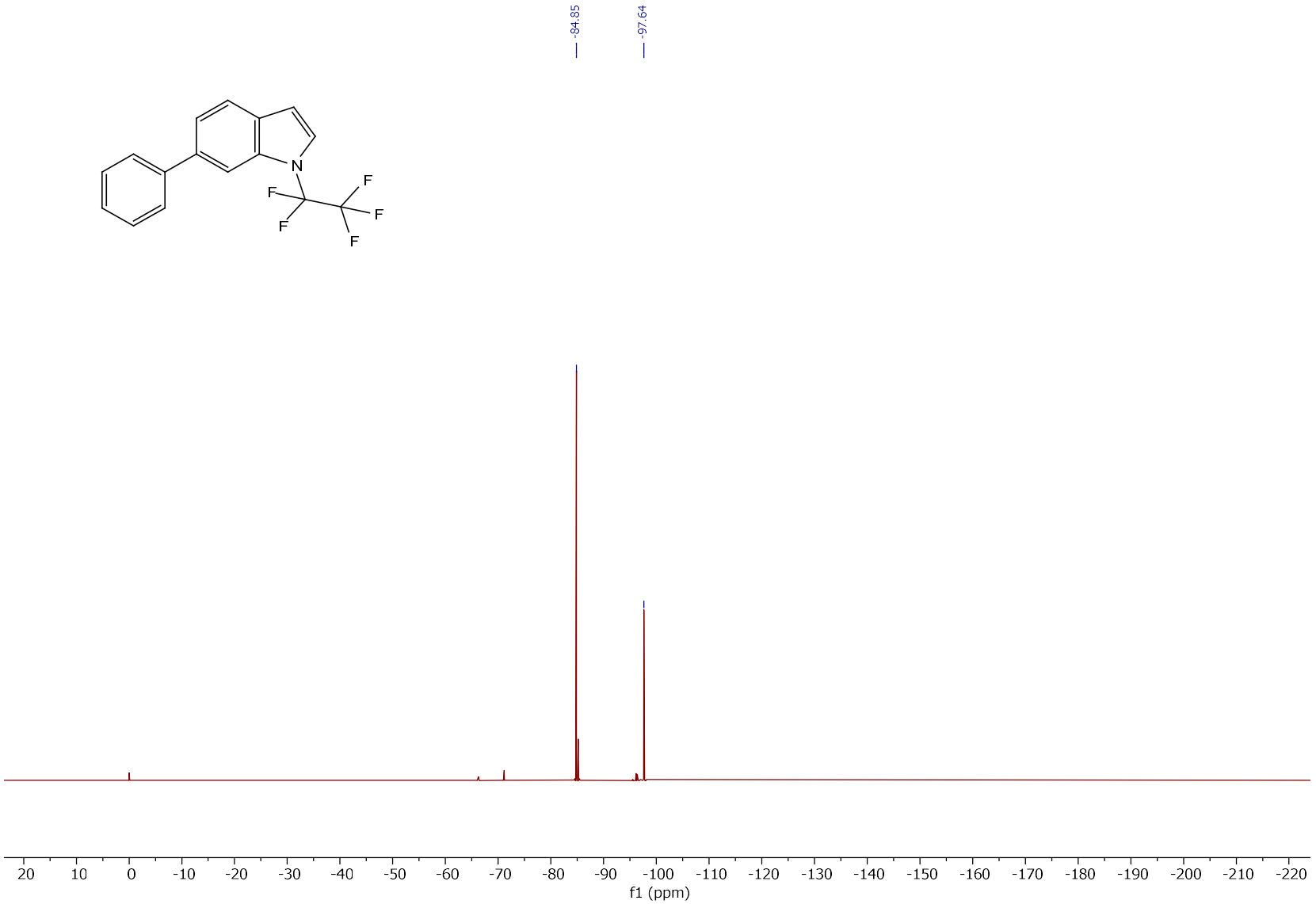
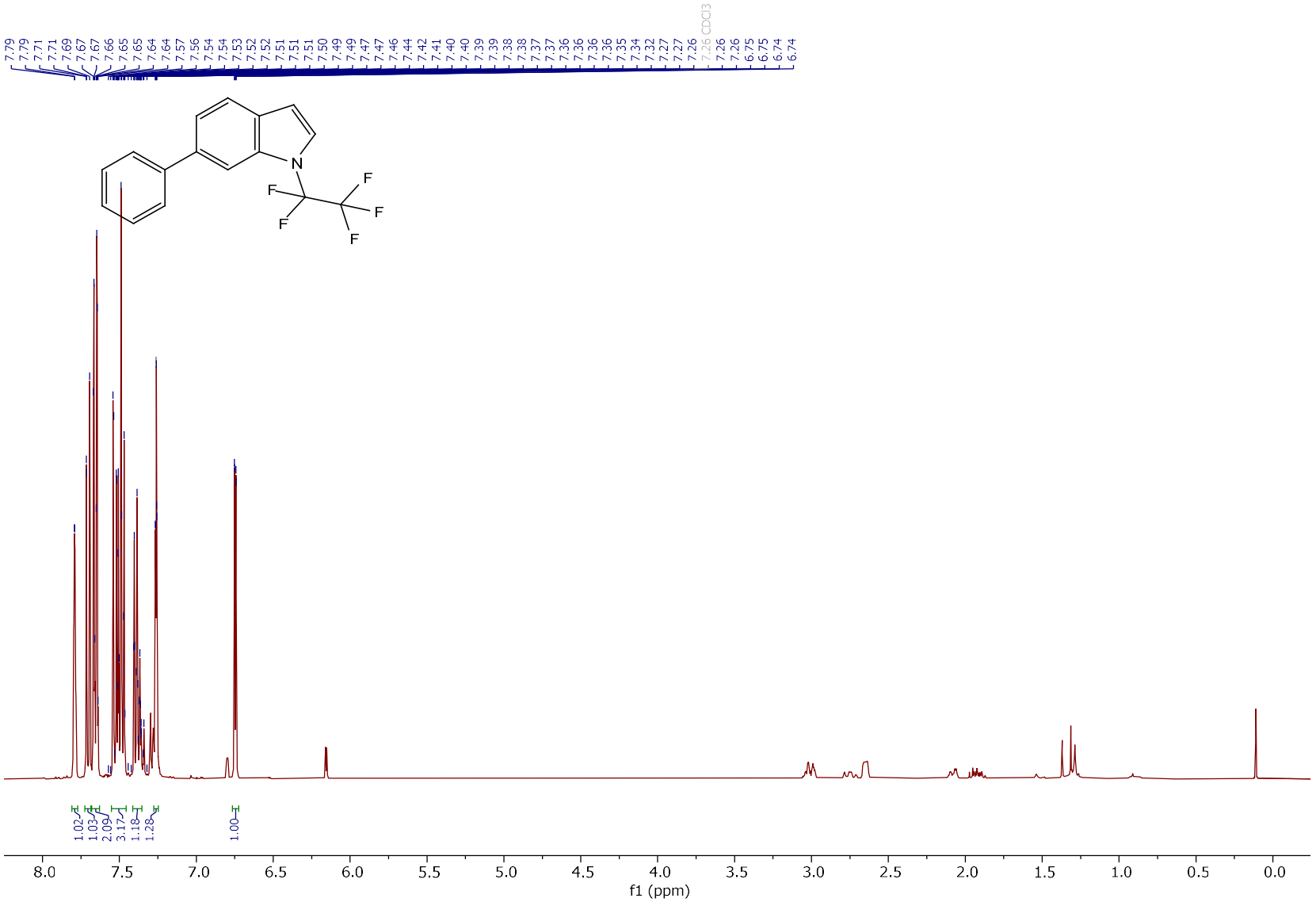


^{19}F NMR (377 MHz, $CDCl_3$) OF **3j**



^{1}H NMR (401 MHz, $CDCl_3$) of **3j**



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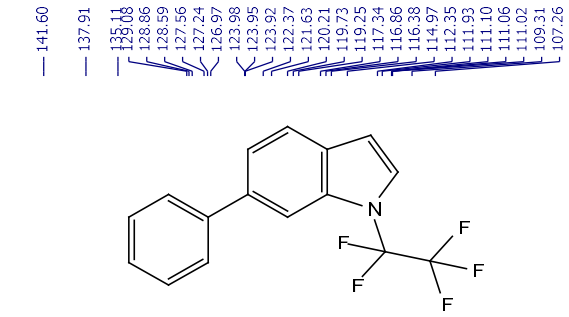
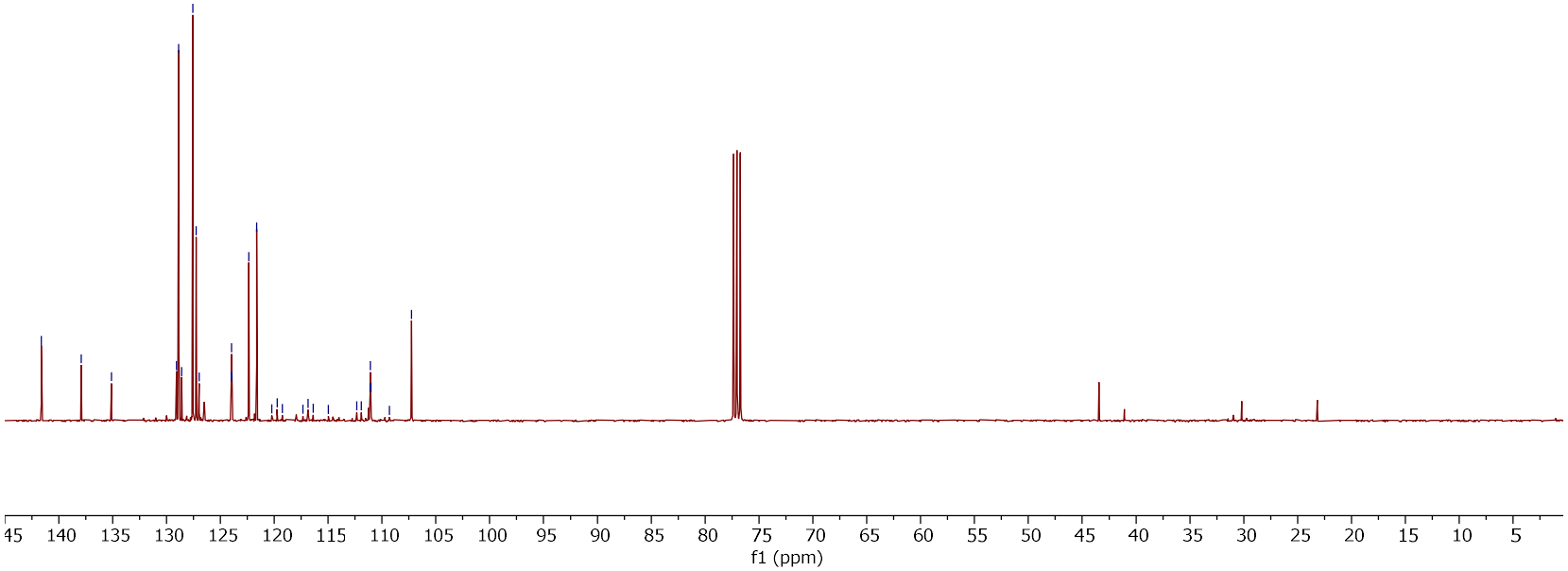
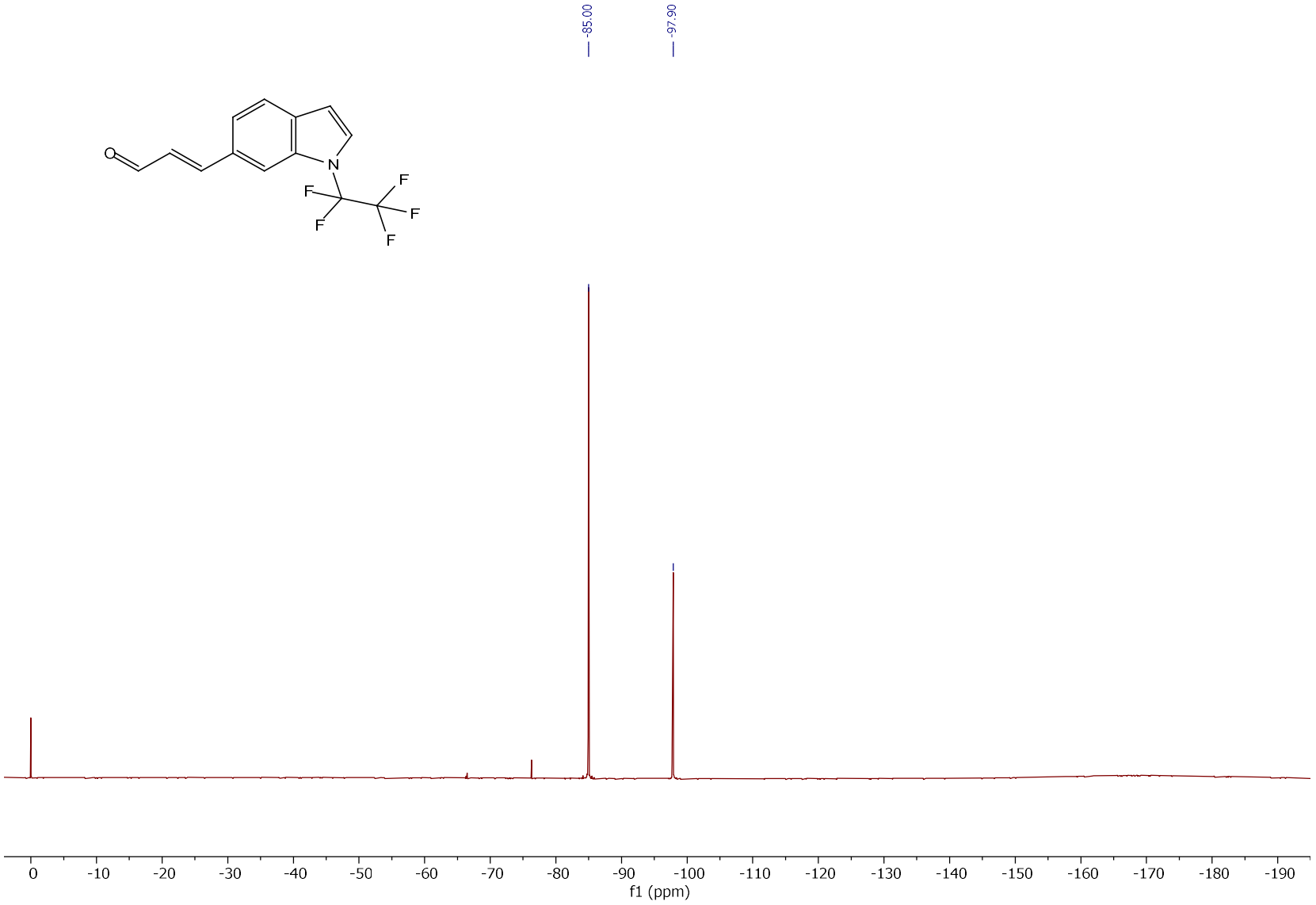
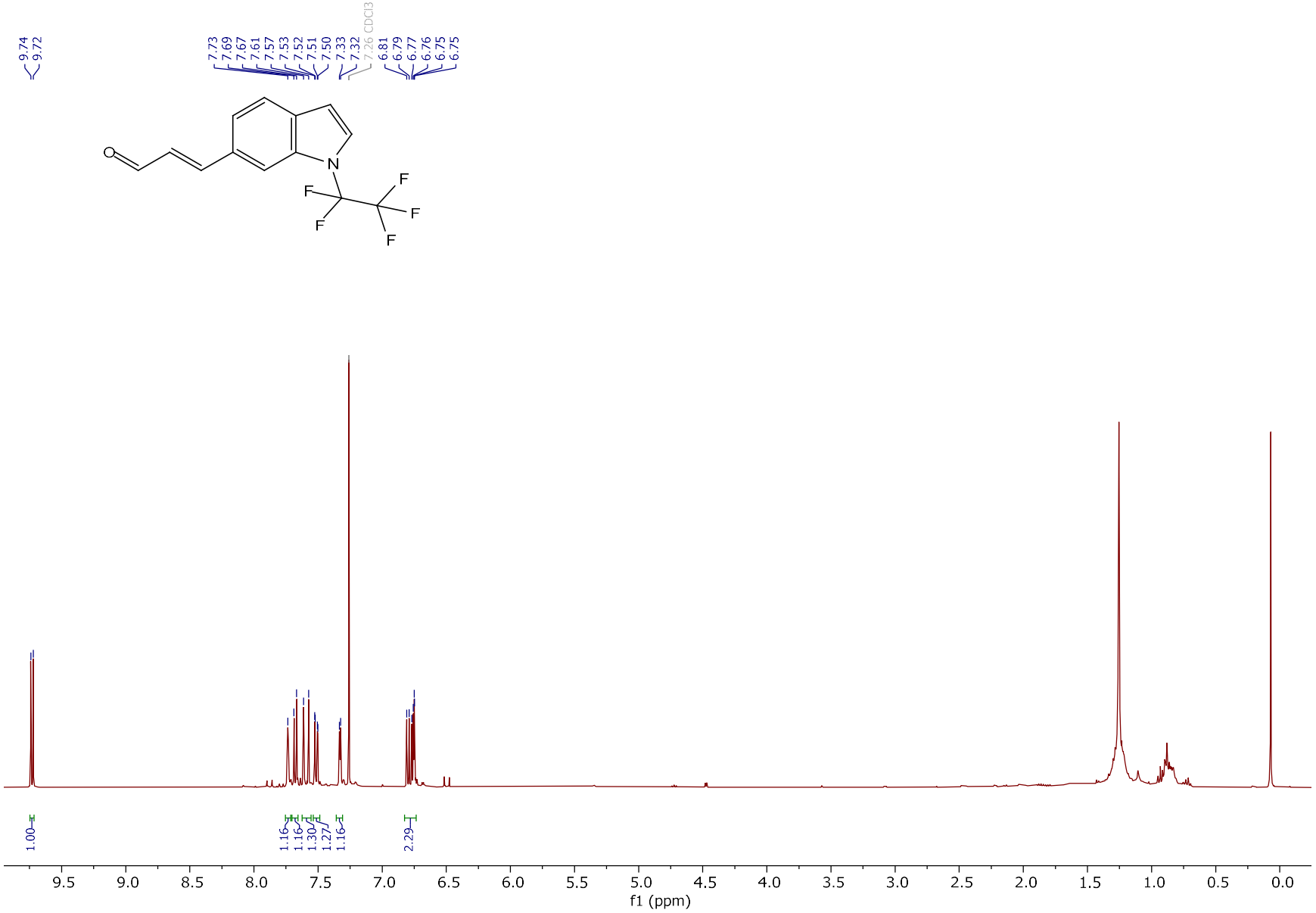




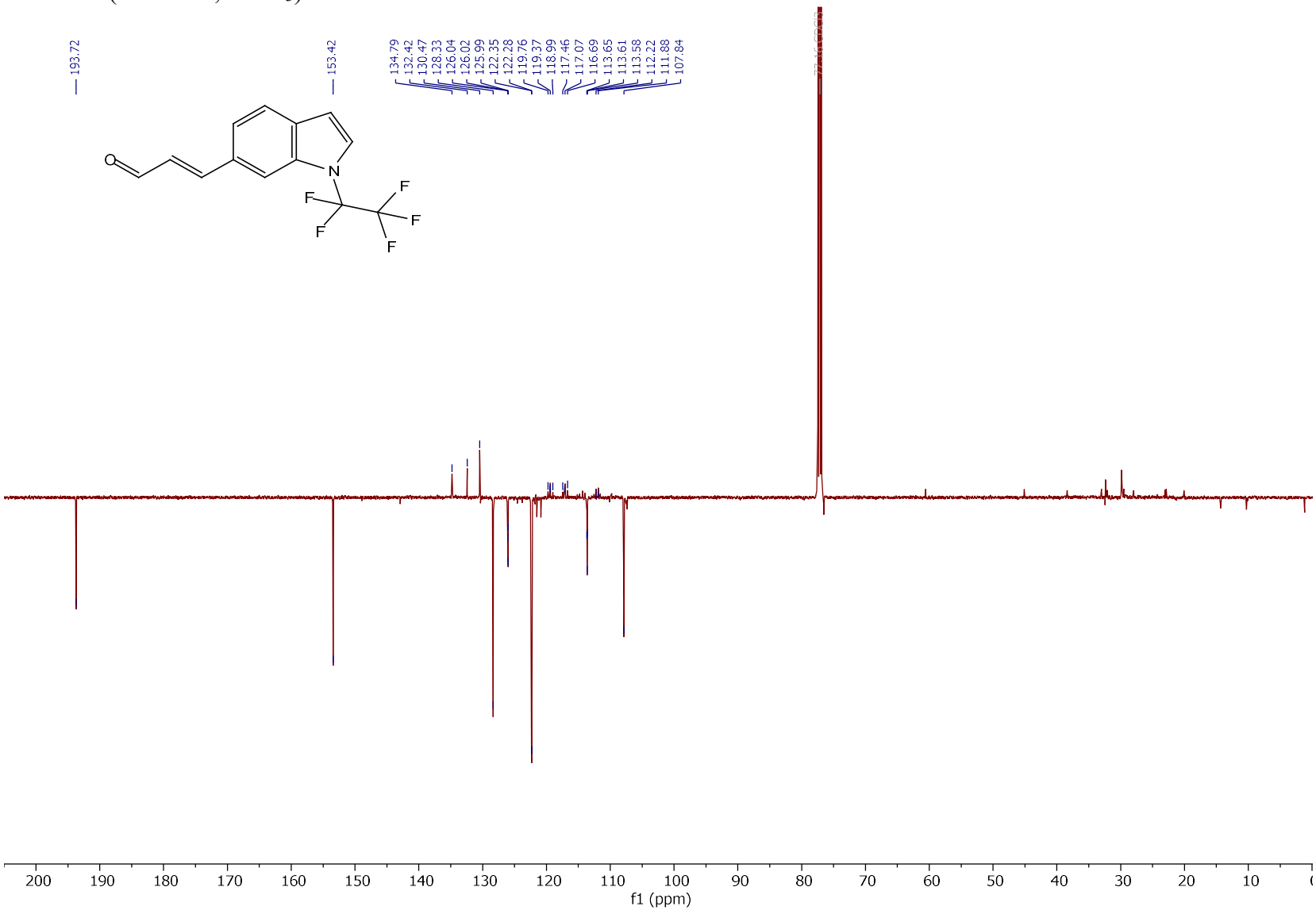
^{19}F NMR (376 MHz, $CDCl_3$) of **3k**



^{1}H NMR (401 MHz, $CDCl_3$) of **3k**



^{13}C NMR (126 MHz, $CDCl_3$) of **3k**



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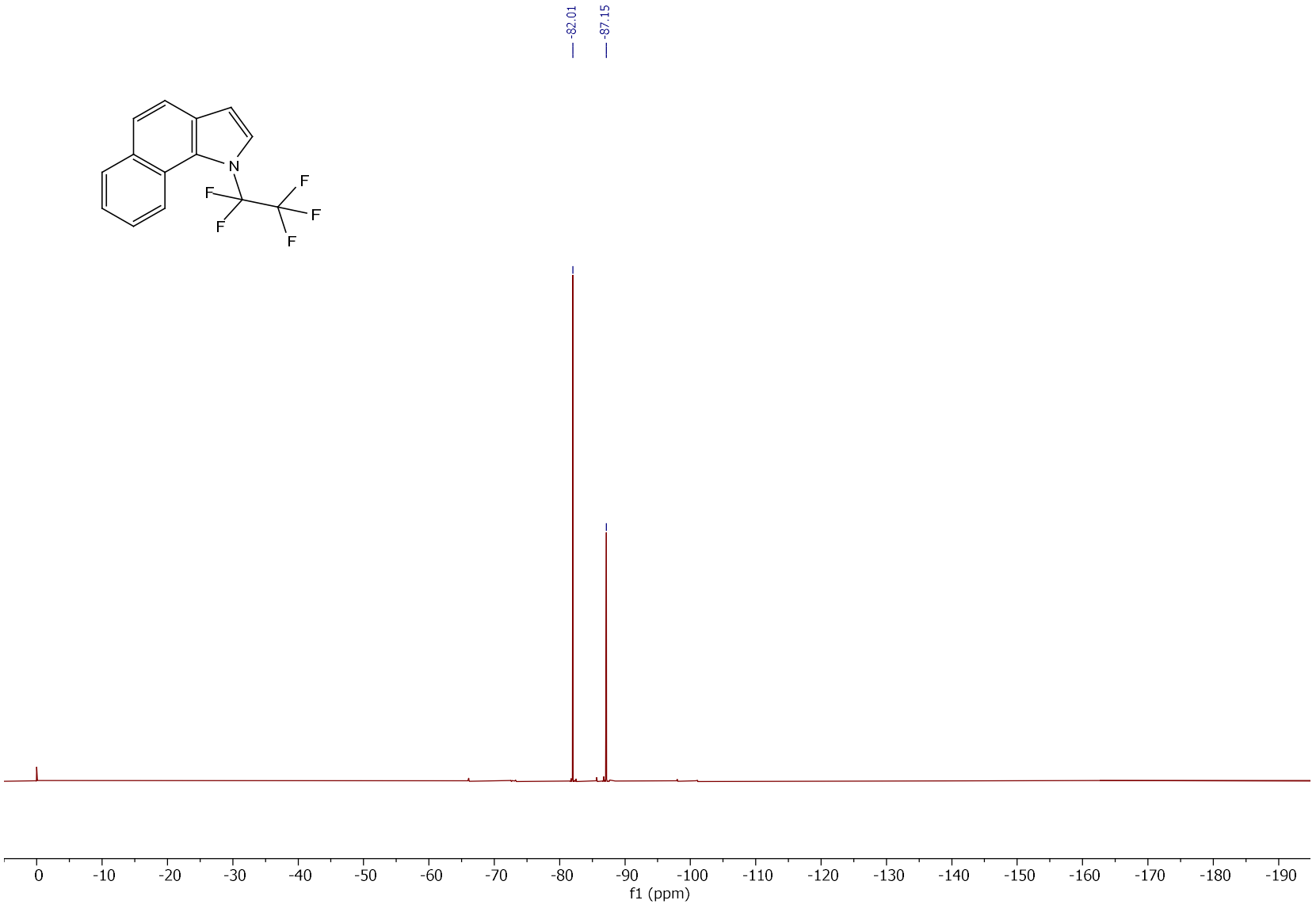
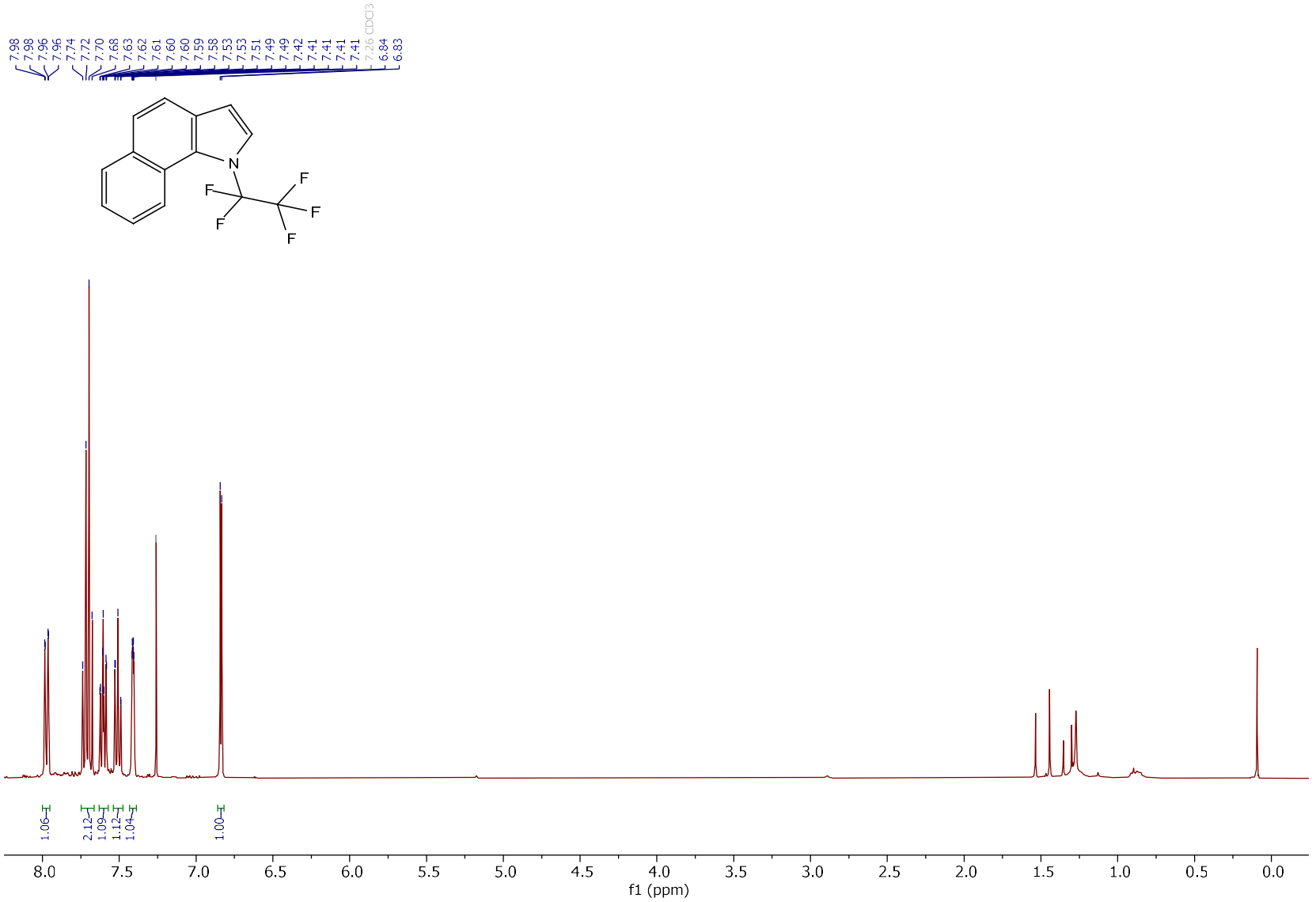
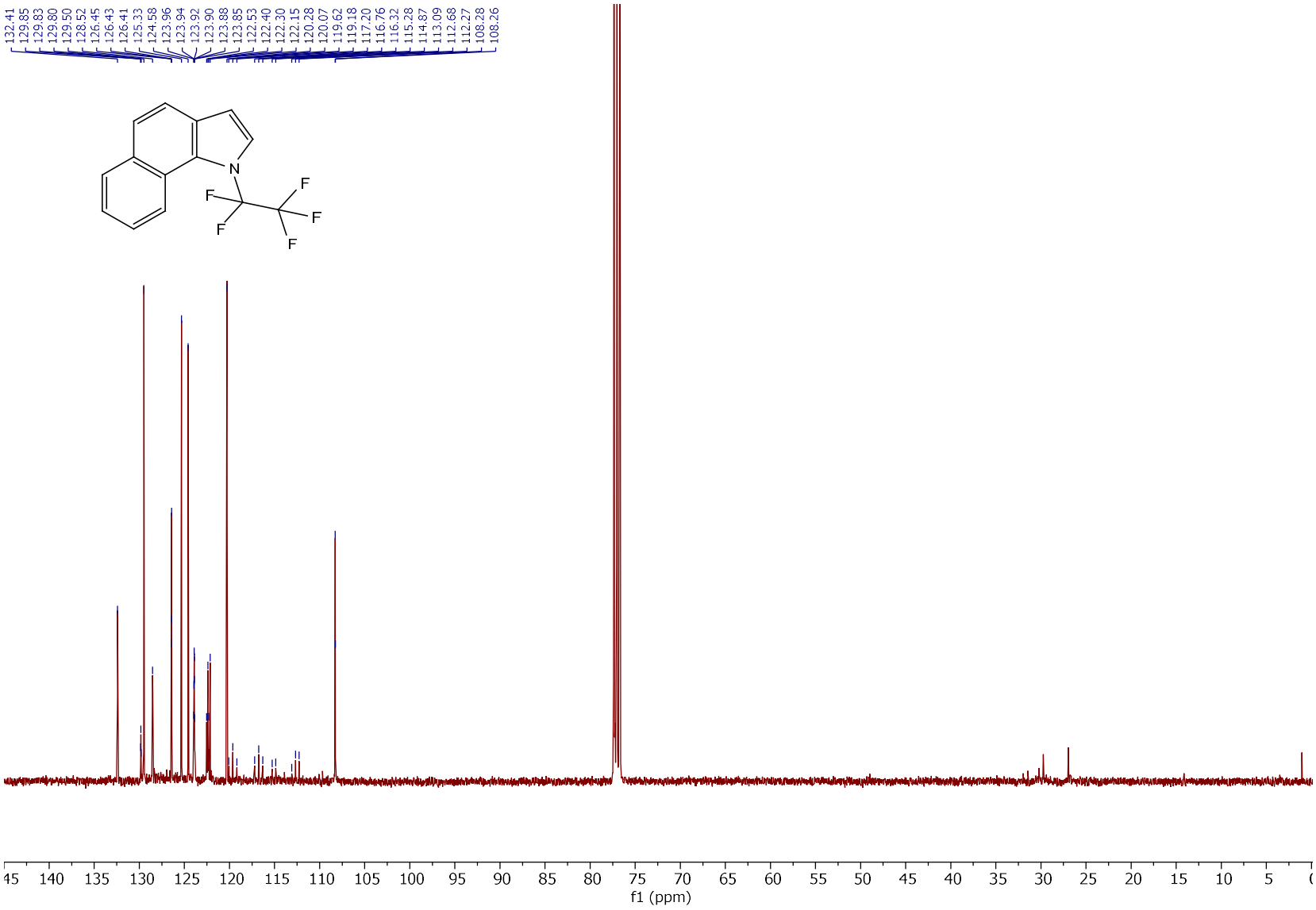


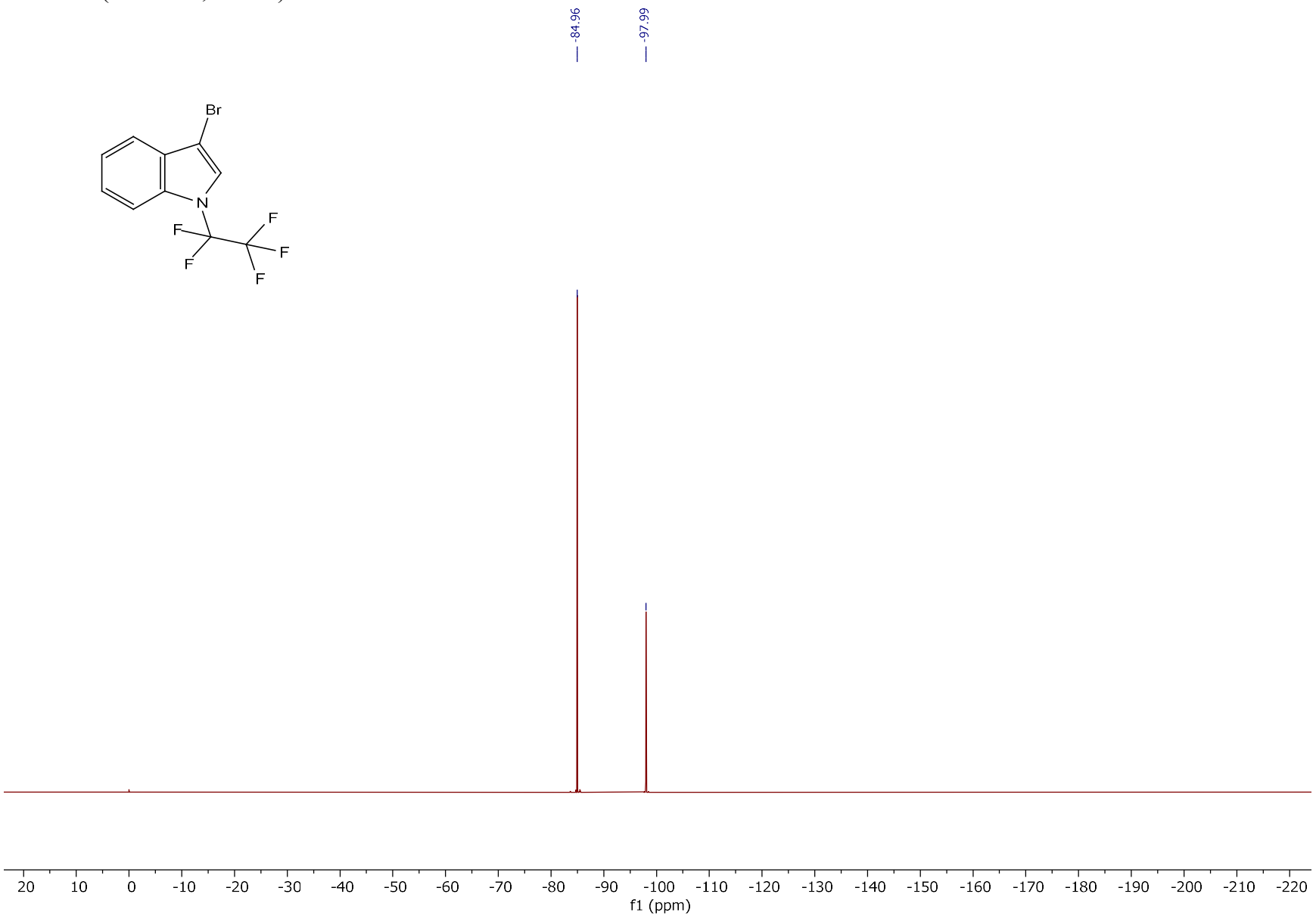
^{1}H NMR (401 MHz, $CDCl_3$) of **3n**



^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



^{19}F NMR (377 MHz, $CDCl_3$) of **4**



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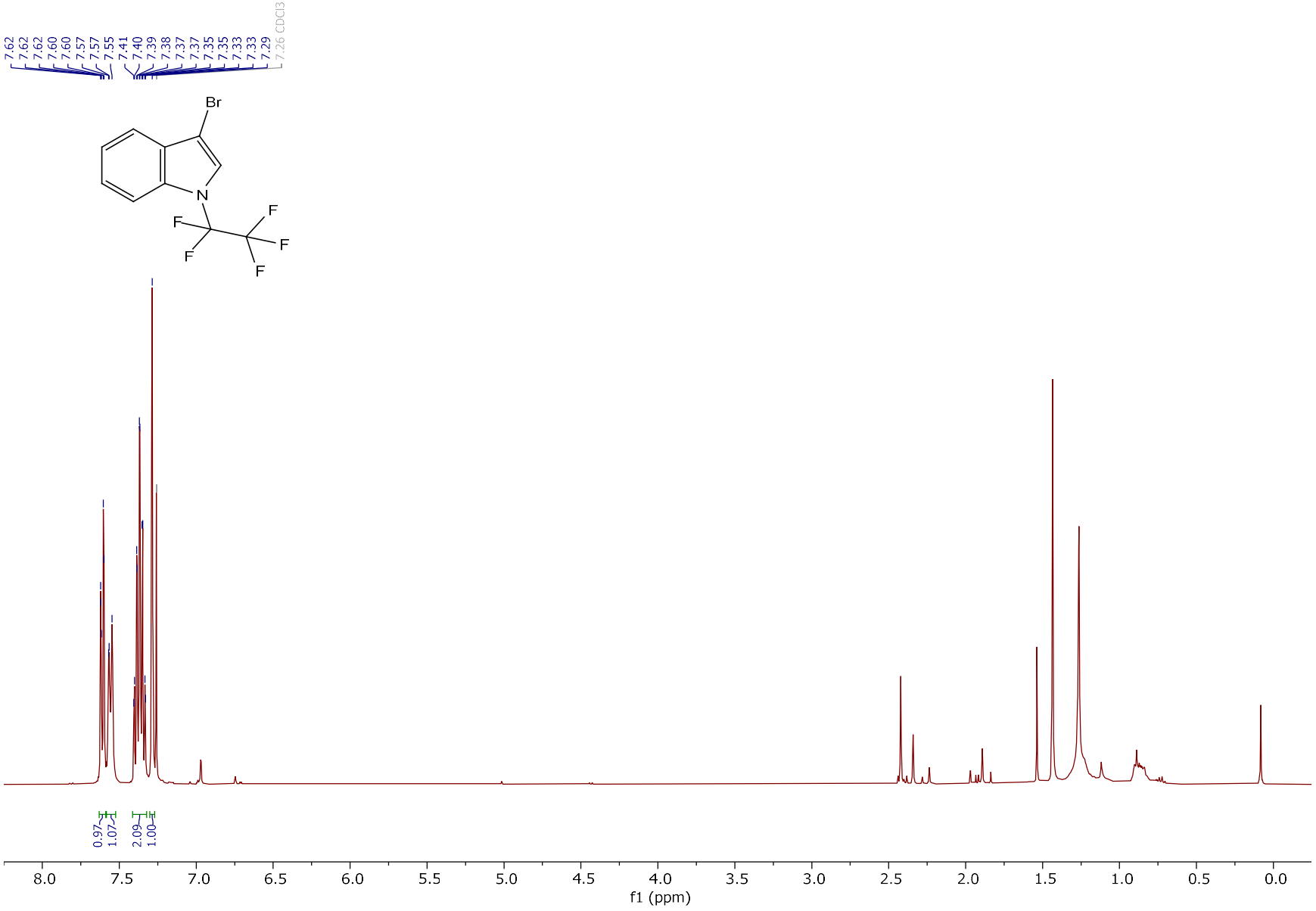

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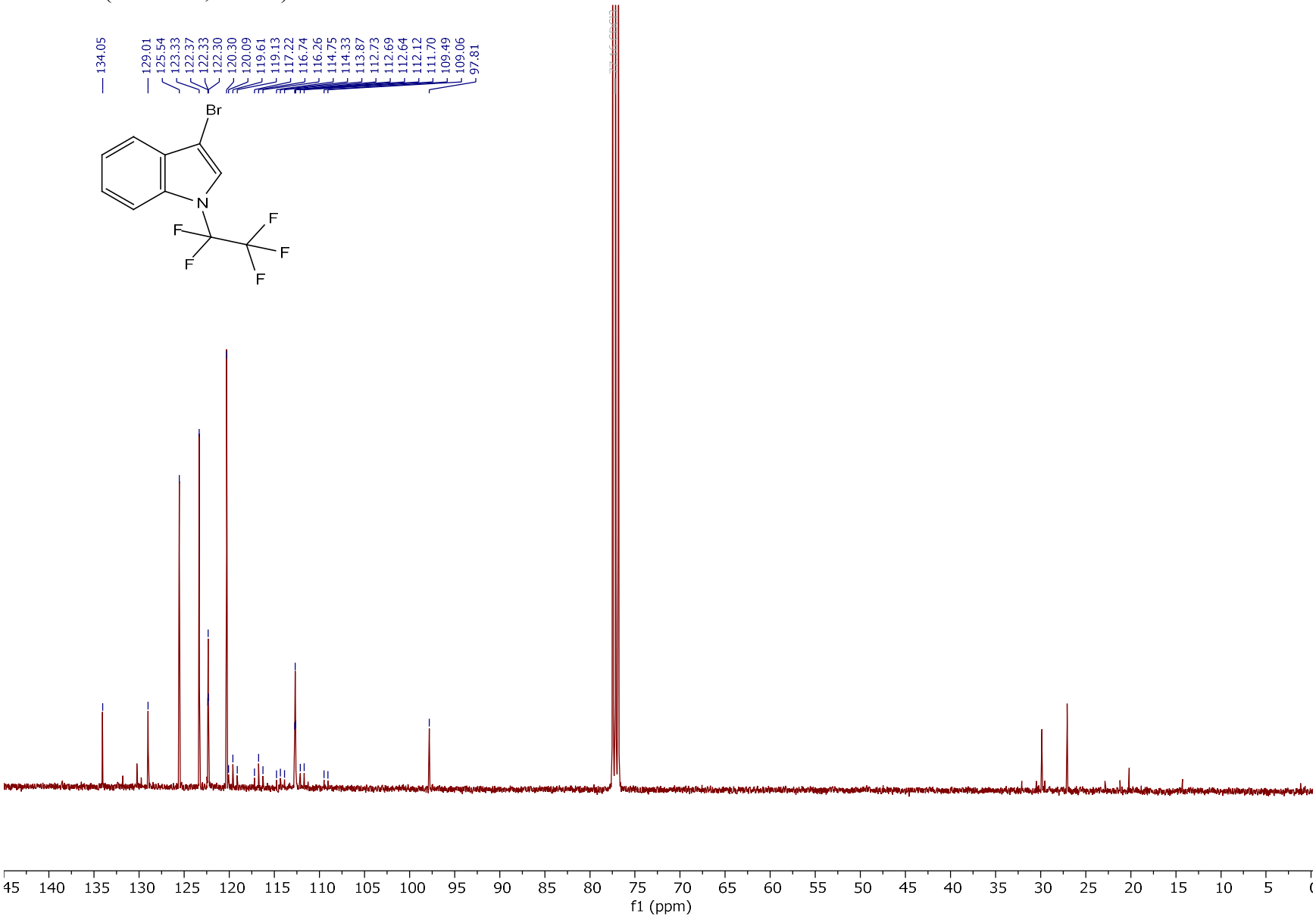
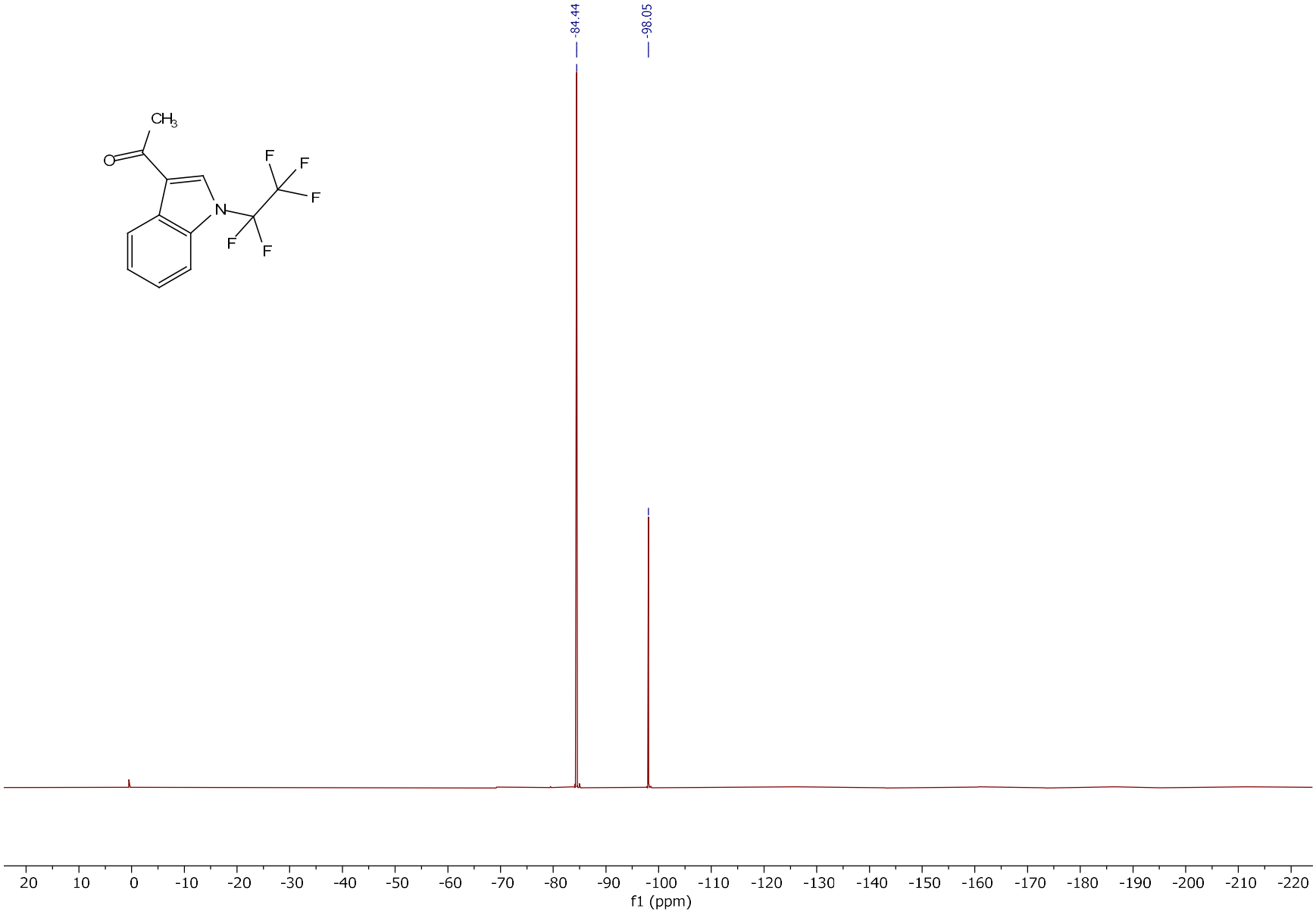
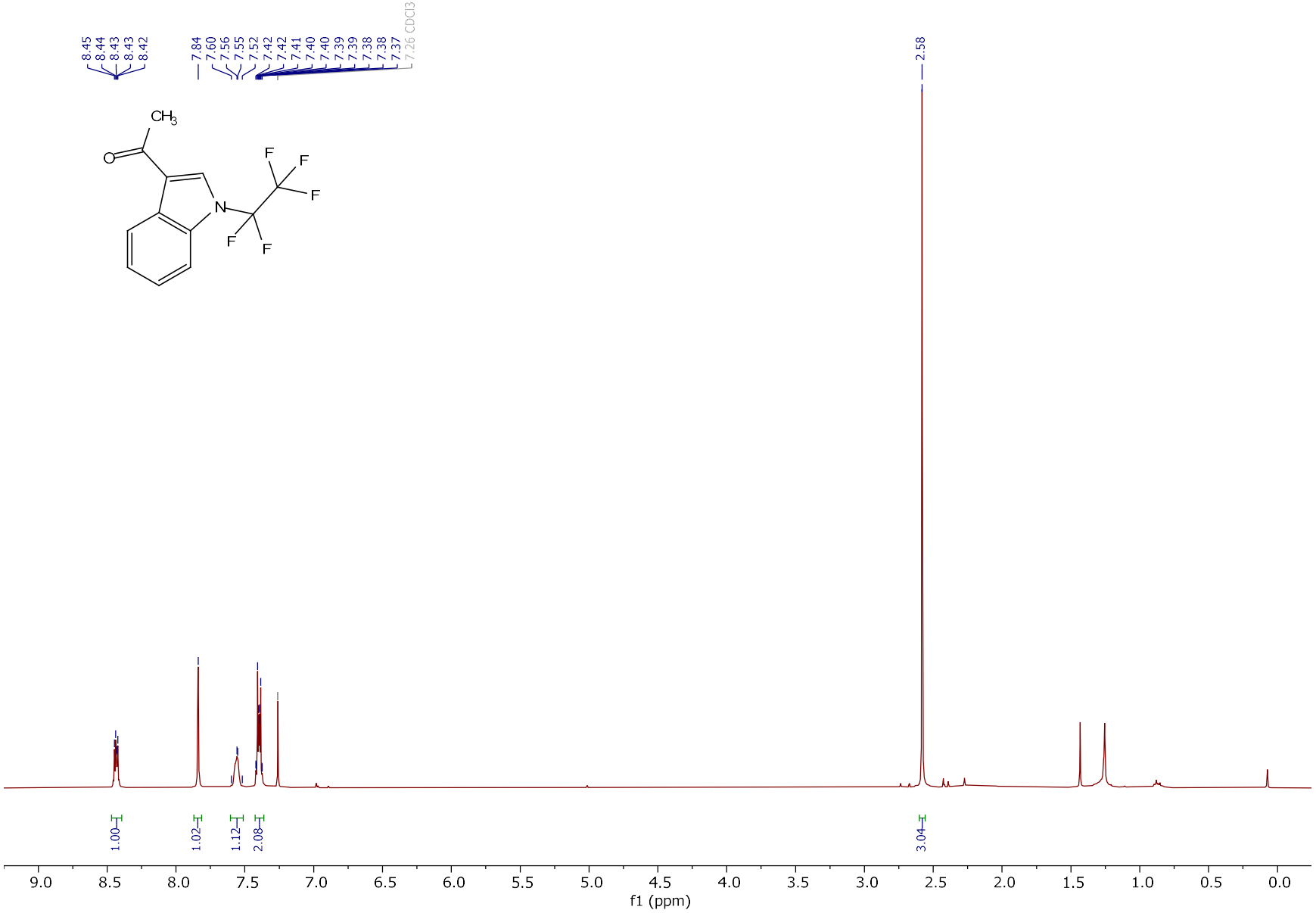


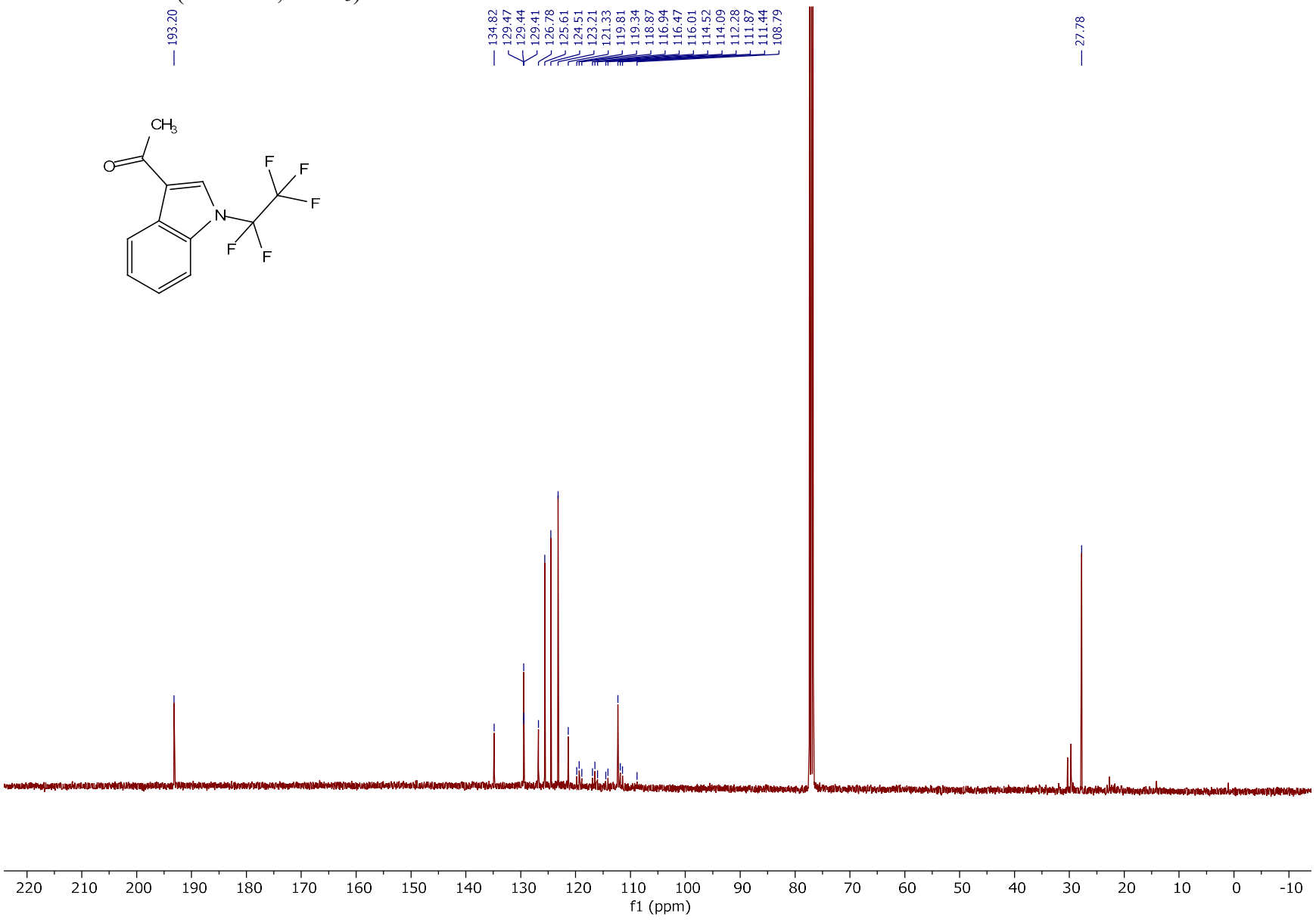
^{19}F NMR (377 MHz, $CDCl_3$) of **5**



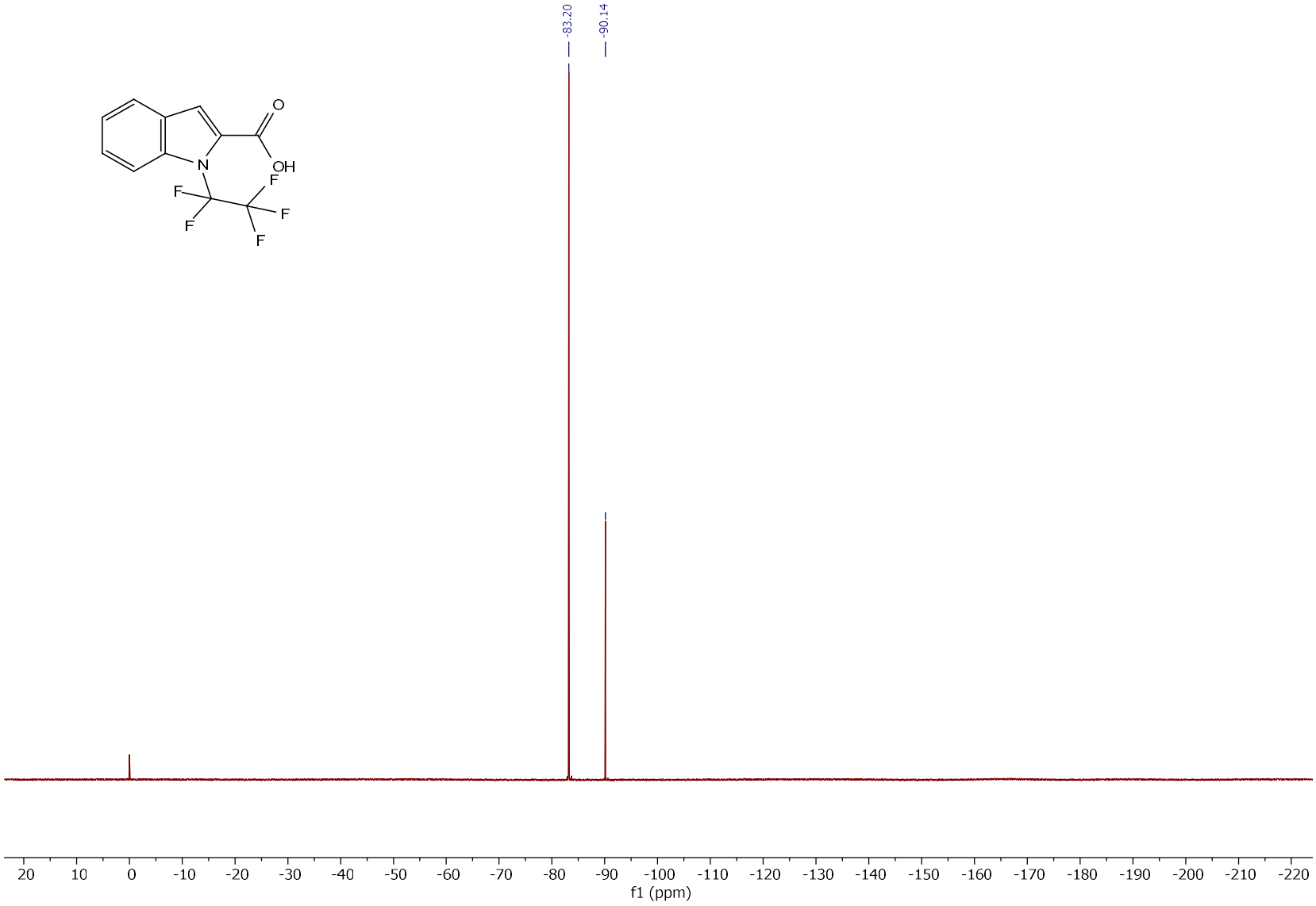
^{1}H NMR (401 MHz, $CDCl_3$) of **5**



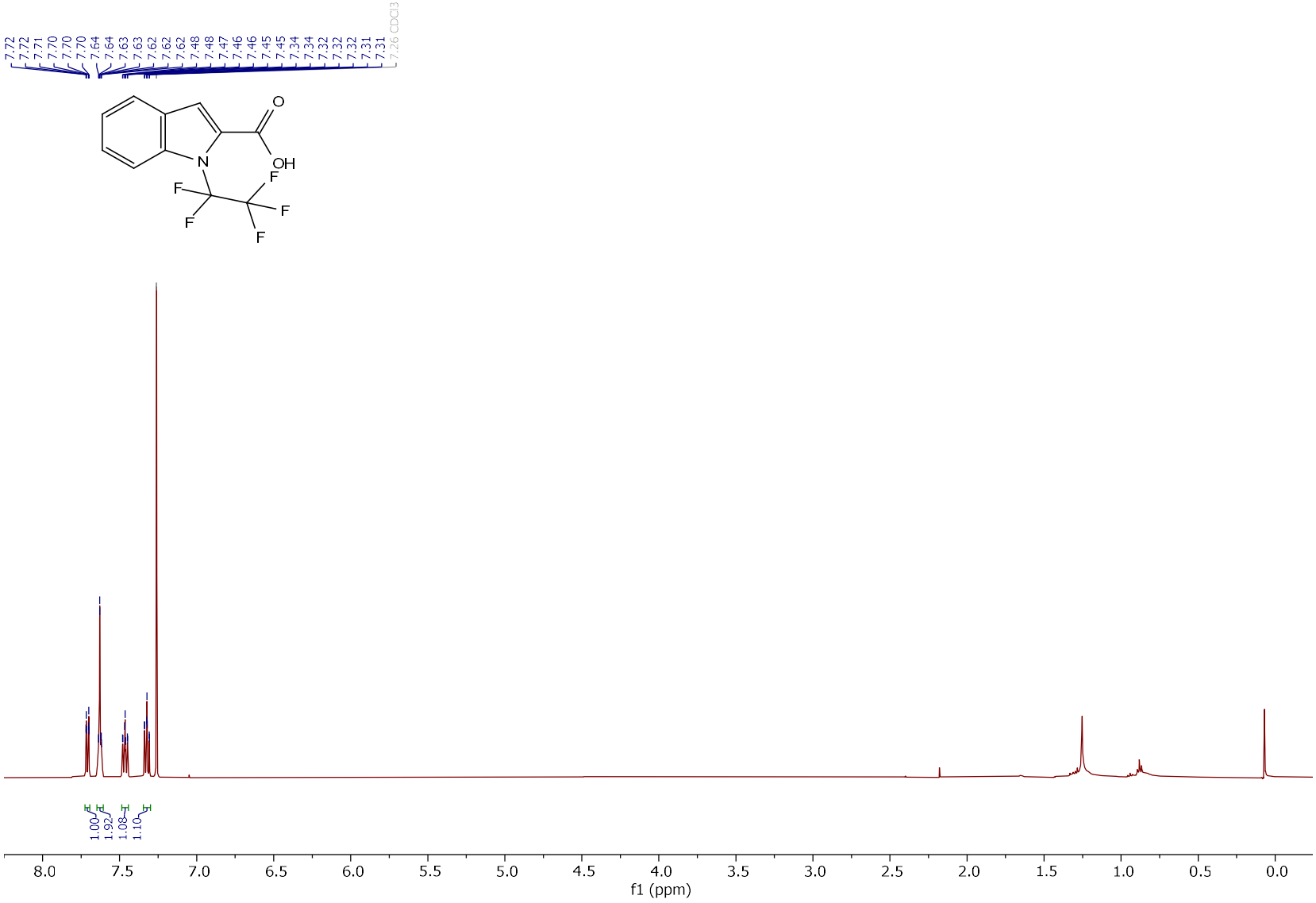
^{13}C NMR (101 MHz, $CDCl_3$) of **5**



^{19}F NMR (377 MHz, $CDCl_3$) of **6**



^{1}H NMR (500 MHz, $CDCl_3$) of **6**



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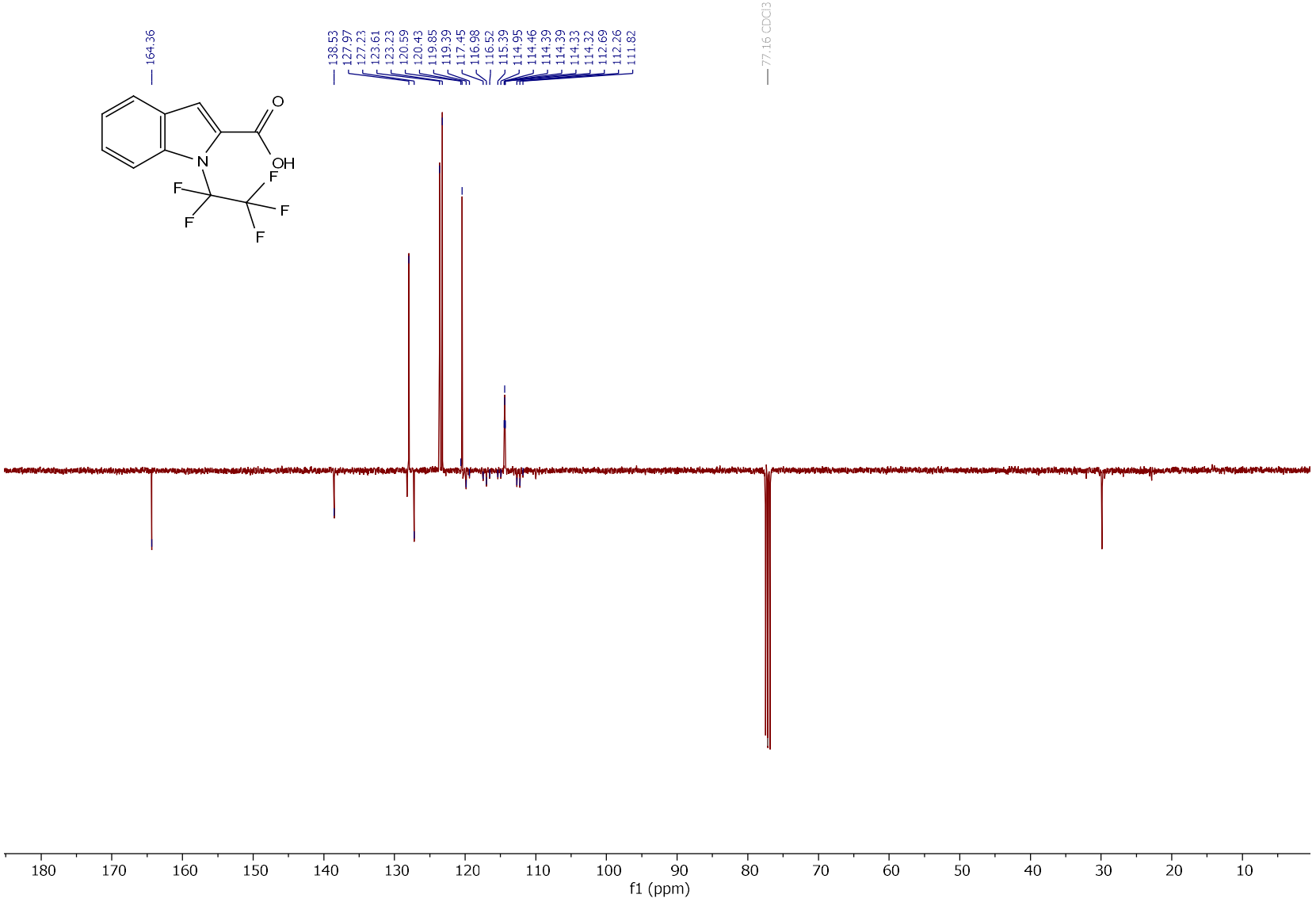

References and notes

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