Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information For

Intercepting the Banert Cascade with Nucleophilic Fluorine: Direct Access to α-Fluorinated *N*H-1,2,3-Triazoles.

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Azide Safety

Azides are known to be high energy materials and explosions have been reported when working with azides.[1] In the course of this work, no issues were encountered. All the azides synthesized in this report have C/N ratios equal to or above the recommended guideline of 3. Precautionary safety shields were used for all reactions using or producing more than 1 mmol of azide. Safety shields were used both in the fume hood and during rotary evaporation. All waste and aqueous solution which could be contaminated with azide were kept in individually labelled containers and were kept STRICTLY free of acid to avoid the accidental production on HN_3 – DO NOT use aqueous HCl during work up of any of the reactions reported herein. Further reading on azide safety is available.[2,3]

General Methods

All reactions conducted at elevated temperature used aluminium heating blocks with magnetic stirring (500 rpm). Reported temperatures were based on an external thermal couple. All commercially available chemicals were used without further purification. Dry tetrahydrofuran and dimethylformamide were obtained from a commercial solvent system utilizing activated alumina columns under a positive pressure of argon. Thin-layer chromatography (TLC) was used for monitoring reaction progress. Visualisation was conducted by using UV light, $KMnO_4$, or PMA stains. Organic solutions were concentrated using rotary evaporator under reduced pressure at or below 40 °C. Flash chromatography was performed on a Teledyne Isco CombiFlash R_f system utilizing normal phase precolumn load cartridges and gold high performance columns. Gas chromatography (GC) was performed on a Shimadzu GC-2010 Plus using an SHRxi-5ms 15 m column and a flame ionisation detector. The standard GC temperature ramp was as follows: Hold at 100 ºC (1 min), 30 ºC/min gradient (100-330 ºC), hold at 330 ºC (1.3 min). Yields reported based on GC analysis of product **3a** (Table S1) were determined by linear regression of a 5-point calibration curve with naphthalene as the internal standard. All proton (^{1}H) nuclear magnetic resonance spectra were recorded at 400 or 500 MHz. All carbon (^{13}C) nuclear magnetic resonance spectra were recorded at 100 or 125 MHz. The fluorine (^{19}F) nuclear magnetic resonance spectra were recorded at 376 or 470 MHz with proton decoupling. Chemical shifts are expressed in parts per million and are referenced to residual solvent ($CDCl_3$: 7.26 ppm), to the central carbon in the NMR solvent ($CDCl_3$: 77.0 ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, ad = apparent doublet–para disubstituted pattern, t = triplet, q = quartet and m = multiplet), integration, and coupling constant in Hertz (Hz). Infrared (IR) spectra were taken in a Nicolet Nexus 670 FT-IR with salt plates. IR spectra were reported in cm^{-1}.

Isomers of the Banert Cascade and Triazole Representation

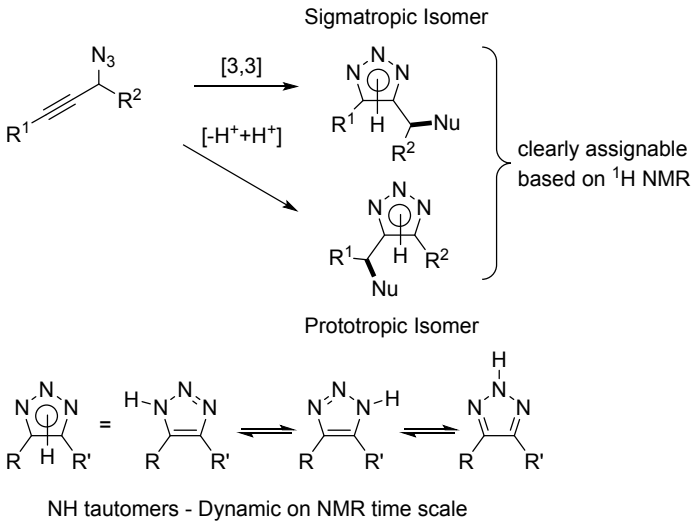
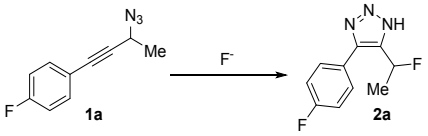


Figure S1 Isomers of the Banert Cascade and NH Tautomers

The Banert cascade can produce two independent regioisomers via two divergent mechanisms: the sigmatropic isomer and the prototropic isomer. It is important to note that the methodology reported within this report promotes only the sigmatropic isomer and no prototropic products were identified by ^{1}H NMR. The 1*H*-1,2,3-triazoles or *N*H-1,2,3-triazoles likely exist as a mixture of tautomeric structures. The NH tautomer structure depicted within this report has been arbitrarily chosen to represent this motif throughout. For a more thorough discussion, please see a detailed study on the tautomerisation.[4]

Triazole Optimisation



Example procedure given for solvent optimisation: A solution of azide **1a** (105 mg, 0.55 mmol) and anisonitrile (14.6 mg, 0.11 mmol, internal standard) was dissolved in CH_2Cl_2 (1.2 mL, ca. 0.9 mmol azide **1a**). The solution was transferred via syringe (0.2 mL portions) into 4 mL vials and the solvent evaporated. Each sample of azide was dissolved in a given solvent (0.1 M) and syringed into a separate 4 mL vial containing AgF (23 mg, 2 equiv) and a stirrer bar. The vial was sealed and heated to 60 °C. After 24h, the reaction was quenched by the addition of AcOH (0.1 ml, 1.0 M in brine). A sample was taken from the organic layer for HPLC-UV analysis.

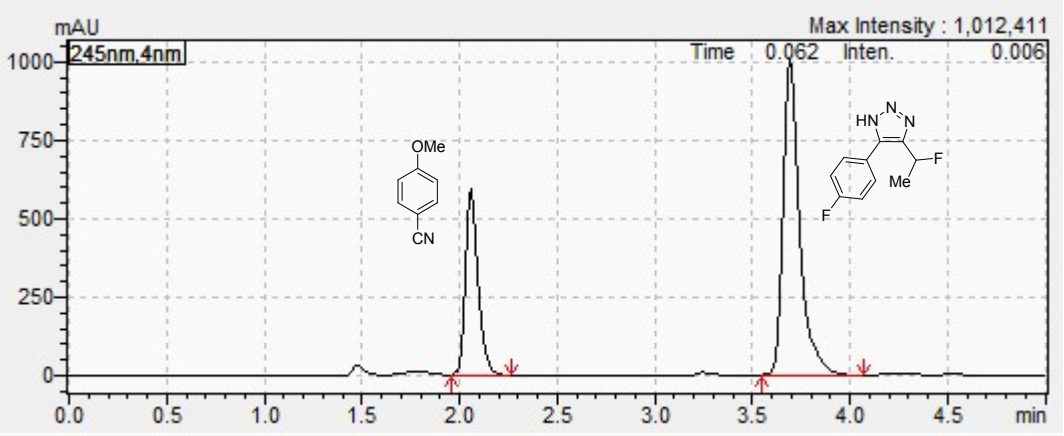
Entry	Fluoride source	Fluoride equiv	Solvent	°C	Yield 2a %
1	NH_4F	1-5	MeCN	60	-
2	NaF	1-5	MeCN	60	-
3	KF	1-5	MeCN	60	-
4	CsF	1-5	MeCN	60	-
5	ZnF_2	1-5	MeCN	60	-
6	TMAF	1-5	MeCN	60	-
7	TBAT	1-5	MeCN	60	-
8	DMPU-HF	1-5	MeCN	60	-
9	KHF_2	1-5	MeCN	60	-
10	HF-Et_3N	1-5	MeCN	60	-
11	AgF	2	DMF	60	9
12	AgF	2	CH_2Cl_2	60	15
13	AgF	2	propionitrile	60	83
14	AgF	2	Et_2O	60	0
15	AgF	2	chlorobenzene	60	7
16	AgF	2	THF	60	9
17	AgF	2	1,2-DCE	60	30
18	AgF	2	PhMe	60	3
19	AgF	2	1,4-dioxanes	60	17
20	AgF	0.5	MeCN	60	33
21	AgF	1	MeCN	60	56
22	AgF	1.5	MeCN	60	87
23	AgF	2	MeCN	60	>95
24	AgF	3	MeCN	60	>95
25	AgF	2	MeCN	40	58
26	AgF	2	MeCN	80	90

HPLC-UV conditions: Hypersil GOLD Silica 100 x 4.6 column, hexanes/IPA = 99: at 1.0 mL/min. T = 20 °C. λ = 245 nm. $T_{anisonitrile}$ = 2.06 min, T_{2a} = 3.69 min.

(-) no product or decomposition.

HPLC-UV Trace

Hypersil GOLD Silica 100 x 4.6 column, hexanes/IPA = 99: at 1.0 mL/min. T = 20 °C. λ = 245 nm. $T_{anisonitrile}$ = 2.06 min, T_{2a} = 3.69 min.

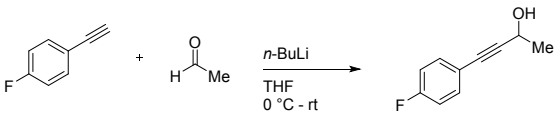


Peak#	Ret. Time	Area	Height	Mark	Conc.
1	2.056	2746770	591466	M	30.894
2	3.693	6144166	1011224	M	69.106
Total		8890936	1602690		100.000

Figure s1: Example HPLC-UV trace acquired during reaction optimisation

Propargyl Alcohol Synthesis

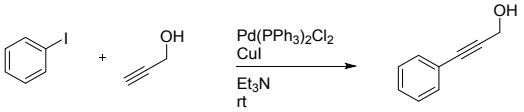
General Procedure 1



Example given for alcohol **S1a** A procedure was adapted from a known method.[5] To a solution of 4-fluorophenylacetlyene (1.50 g, 12.5 mmol) in THF (42 mL) cooled in an ice bath, *n*-butyllithium (5.9 mL, 2.5 M in hexanes, 14.9 mmol) was added dropwise. After 30 min, acetaldehyde (1.05 mL, 18.7 mmol) was added dropwise, and the ice bath was removed. After 1 h, the reaction mixture was poured onto NH_4Cl (15 mL, sat. aq.). The resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by column chromatography (0−40% EtOAc/ hexanes) afforded alcohol **S1a** (1.78 g, 87%) as a yellow oil. Characterisation data for this compound has been reported.[6]

Propargyl alcohols **S1a-S1l** and **S1p-S1q** were prepared using General procedure 1. Characterisation data for propargyl alcohols **S1a-S1l** and **S1p-S1q** have previously been reported.[6]

General Procedure 2

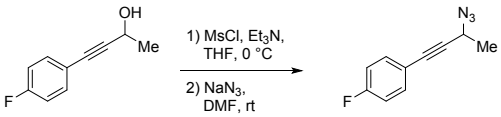


Example given for propargyl alcohol **S1n**. A procedure was adapted from a known method.[7] To a solution of iodobenzene (0.54 mL, 4.8 mmol) in triethylamine (12 mL, 0.34 M) was added $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) and CuI (15 mg, 0.08 mmol). The reaction was stirred for 5 min before the addition of propargyl alcohol (0.23 mL, 4.0 mmol). The resulting mixture was stirred for 18 hours. Then, the reaction was quenched by the addition of $NaHCO_3$ (15 mL, sat. aq.). The resulting mixture was extracted with EtOAc (3 × 20 mL) The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by column chromatography (0−40% EtOAc/ hexanes) afforded alcohol **2n** (438 mg, 83%) as an orange oil. Characterisation data for this compound has been reported.[7]

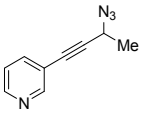
Propargyl alcohols **S1m-S1o** and **S1r** were prepared using General procedure 2

Propargyl Azide Synthesis

General Procedure 3

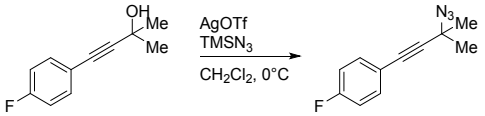


Example given for propargyl azide **1a**. A solution of alcohol **S1a** (800 mg, 4.9 mmol) in THF (8 mL) was cooled in an ice bath. Triethylamine (1.1 mL, 8.0 mmol) was added, followed by dropwise addition of methanesulfonyl chloride (0.45 mL, 5.9 mmol). After 5 min, the mixture was poured onto NH_4Cl (15 mL, sat. aq.). The resulting mixture was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The crude mesylate was immediately used without further purification. The residue was dissolved in DMF (6 mL). Sodium azide (476 mg, 7.3 mmol) was added as a solid at room temperature. After 1h, the mixture was poured onto NH_4Cl (15 mL, sat. aq.). The resulting mixture was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash chromatography (gradient elution 0−20% EtOAc in hexanes) afforded the product **1a** as a pale-yellow oil (785 mg, 85% over two steps).
Propargyl azides **1a-1q** were prepared using General procedure 3. Characterisation data for propargyl azides **1a-1q** have previously been reported.[6]



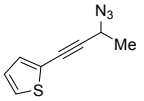
Compound **1n**. General procedure 3 was modified using 413 mg (2.8 mmol) of propargyl alcohol **S1n** heated to 40 °C for 1.5 h with NaN_3 (365 mg, 5.61 mmol) in DMF (8.0 mL). Product **1n** was isolated as a pale-yellow oil 50% (242 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (dd, J = 2.2, 0.9 Hz, 1H), 8.55 (dd, J = 4.9, 1.7 Hz, 1H), 7.74 (dt, J = 7.9, 1.9 Hz, 1H), 7.29 – 7.22 (m, 1H), 4.42 (q, J = 6.9 Hz, 1H), 1.54 (d, J = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.4, 149.1, 138.8, 123.0, 119.2, 89.0, 82.7, 48.8, 21.3.
IR (NaCl, thin film, cm^{-1}) 3320, 2989, 2135, 2102, 1477, 1408, 1363, 1168, 806, 728.
HRMS (EI-TOF) *m/z* $[M]^+$ calcd for $C_9H_8N_4^+$ 172.0743, found 172.0734.

General Procedure 4



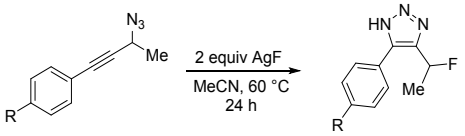
Example given for propargyl azide **1r**. To a solution of propargyl alcohol **s1r** (629 mg, 3.5 mmol) in CH_2Cl_2 (7.0 mL), cooled in an ice bath, AgOTf (180 mg, 0.7 mol) was added, followed by the addition of $TMSN_3$ (0.94 mL, 7.1 mmol). After 30 min, the reaction was quenched by the addition of Et_3N/MeOH (2:1, 2 mL). The resulting solution was filtered through basic Alumina and rinsed with CH_2Cl_2. The combined organic phases were concentrated under reduced pressure. Purification by column chromatography (EtOAc in hexanes, 5 - 20%) afforded the desired product **1r** (570 mg, 79%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.05 – 6.98 (m, 2H), 1.58 (s, 6H).
^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ -110.5.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 248.7 Hz),133.8 (d, $J_{C\text{-}F}$ = 9.1 Hz), 118.1 (d, $J_{C\text{-}F}$ = 3.9 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.6 Hz), 88.6, 83.7, 56.8, 29.1.
IR (NaCl, thin film, cm^{-1}) 2987, 2935, 2103, 1601, 1507, 1239, 1174, 1156, 1093, 869, 836.

HRMS (EI-TOF) *m/z* $[M]^+$ calcd for $C_{11}H_{10}FN_3^+$ 203.0853, found 203.0852.

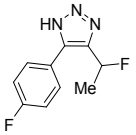


Compound **1m**. General procedure 4 was used and product **1m** was isolated as a yellow oil 53% (217 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, J = 5.1, 1.2 Hz, 1H), 7.25 (dd, J = 3.7, 1.2 Hz, 1H), 6.98 (dd, J = 5.2, 3.6 Hz, 1H), 4.42 (q, J = 6.9 Hz, 1H), 1.53 (d, J = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 132.8, 127.6, 127.0, 121.8, 89.4, 79.2, 49.1, 21.3.
IR (NaCl, thin film, cm^{-1}) 3322, 3107, 2988, 2935, 2223, 2111, 1445, 1355, 1240, 1196, 1082, 850, 703.
HRMS (EI-TOF) *m/z* $[M]^+$ calcd for $C_8H_7N_3S^+$ 177.0355, found 177.0353.

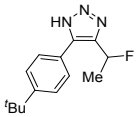
Triazole Synthesis



General procedure 5: Triazole Formation
Example given for compound 2a: In a nitrogen filled glovebox, a 20 mL vial was charged with AgF (122 mg, 0.96 mmol). The vial was sealed and removed from the glove box. Under air, a solution of azide **1a** (91 mg, 0.48 mmol) was prepared in MeCN (4.7 mL). The solution of azide **1a** was transferred to the vial containing AgF by syringe and rinsed with MeCN (0.1 mL). The vial was sealed and heated to 60 °C. After 24h, the reaction was quenched by the addition of AcOH (0.7 ml, 1.0 M in brine). The resulting solution was extracted with ethyl acetate (10 mL x 3). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash chromatography using a short plug of silica gel (gradient elution 0 – 60% EtOAc in hexanes) yielded the product as a colorless solid in 76% (76 mg) and 75% (75 mg) yield in duplicate trials. The average of 76% is reported.
NOTE: Triazole **2a** was unstable to silica gel chromatography if either AcOH or Et_3N was used as a 1% additive. Diminished mass recovery was observed with long column resonance times.



Compound **2a**
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.01 (br, 1H), 7.86 – 7.61 (m, 2H), 7.23 – 7.05 (m, 2H), 5.87 (dq, $J_{H\text{-}F}$ = 48.1, $J_{H\text{-}H}$ = 6.6 Hz, 1H), 1.84 (dd, $J_{H\text{-}F}$ = 23.2, $J_{H\text{-}H}$ = 6.6 Hz, 3H).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -112.0, -159.2.
^{13}C{^{1}H} NMR (125 MHz; $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 248.9 Hz), 144.3, 142.3 ($J_{C\text{-}F}$ = 22.1 Hz), 130.1 (dd, $J_{C\text{-}F}$ = 9.0 Hz, 3.7 Hz), 125.4, 116.0 (d, $J_{C\text{-}F}$ = 21.8 Hz), 82.9 (d, $J_{C\text{-}F}$ = 162.8 Hz), 19.4 (d, $J_{C\text{-}F}$ = 24.3 Hz).
IR (NaCl, thin film, cm^{-1}) 3143, 2990, 2927, 1610, 1507, 1230, 841, 764.
HRMS (EI-TOF) $[M]^+$ Calcd for $C_{10}H_9F_2N_3^+$ 209.0759; Found: 209.0755.



Compound **2b**. General procedure 5 was modified using azide **1b** and product **2b** was isolated as a brown, waxy solid in 82% (69 mg) and 86% (72 mg) yield in duplicate trials. The average of 84% is reported. This reaction was also conducted with azide **1b** ("scaled up", 1.06 mmol) and the product **2b** was isolated as a brown, waxy solid in 81% (212 mg) and 86% (225 mg) yield in duplicate trials. The average of 84% is reported.

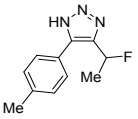
^{1}H NMR (500 MHz, C_6D_6) δ 11.78 (br, 1H), 7.90 – 7.83 (m, 2H), 7.36 – 7.30 (m, 2H), 5.71 (dq, $J_{H\text{-}F}$ = 48.4, $J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.71 (dd, $J_{H\text{-}F}$ = 22.9, $J_{H\text{-}H}$ = 6.5 Hz, 3H), 1.21 (s, 9H).

^{19}F {^{1}H} NMR (470 MHz, C_6D_6) δ -157.7.

^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 152.0, 145.3, 142.9 (d, $J_{C\text{-}F}$ = 23.8 Hz), 128.5, 128.4, 126.1, 83.1 (d, $J_{C\text{-}F}$ = 162.5 Hz), 34.7, 31.3, 19.5 (d, $J_{C\text{-}F}$ = 23.8 Hz).

IR (NaCl, thin film, cm^{-1}) 3149, 2963, 2868, 1484, 1103, 1072, 842.

HRMS (EI-TOF) $[M - F]^+$ calcd for $C_{14}H_{18}N_3^+$ 228.1495, found 228.1493.



Compound **2c**. General procedure 5 was modified using azide **1c** (70 mg, 0.38 mmol) and product **2c** was isolated as a colorless solid in 69% (54 mg) and 73% (57 mg) yield in duplicate trials. The average of 71% is reported.

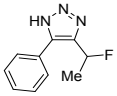
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.60 (br, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 5.88 (dq, $J_{H\text{-}F}$ = 48.0, $J_{H\text{-}H}$ = 6.5 Hz, 1H), 2.40 (s, 3H), 1.83 (dd, $J_{H\text{-}F}$ = 23.2, $J_{H\text{-}H}$ = 6.5 Hz, 3H).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -158.9

^{13}C{^{1}H} NMR (125 MHz; $CDCl_3$) δ 144.2, 142.0, 139.0, 129.6, 128.0, 125.9, 82.9 (d, $J_{C\text{-}F}$ = 163.6 Hz), 21.1, 19.5 (d, $J_{C\text{-}F}$ = 23.6 Hz).

IR (NaCl, thin film, cm^{-1}) 3405, 2936, 2863, 1620, 1510, 1021, 823.

HRMS (EI-TOF) $[M]^+$ Calculated for $C_{11}H_{12}FN_3^+$ 205.1010; Found: 205.1001.



Compound **2d**. General procedure 5 was modified using azide **1d** and product **2d** was isolated as a colorless amorphous solid in 73% (40 mg) and 84% (46 mg) yield in duplicate trials. The average of 79% is reported.

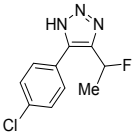
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.99 (br, 1H), 7.75 (dd, J = 6.4, 2.0 Hz, 2H), 7.47-7.38 (m, 3H), 5.89 (dq, $J_{H\text{-}F}$ = 47.8 Hz, $J_{H\text{-}H}$ = 6.8 Hz, 1H), 1.83 (dd, $J_{H\text{-}F}$ = 23.3 Hz, $J_{H\text{-}H}$ = 6.8 Hz, 3H).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.0.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.3, 142.2, 129.0, 128.9, 128.6, 128.2, 82.9 (d, $J_{C\text{-}F}$ = 162.8 Hz), 19.5 (d, $J_{C\text{-}F}$ = 24.9 Hz).

IR (NaCl, thin film, cm^{-1}) 3155, 2995, 2937, 2864, 1449, 1107, 1071, 864.

HRMS (EI-TOF) $[M]^+$ Calculated for $C_{10}H_{10}FN_3^+$ 191.0853; Found: 191.0850.



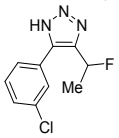
Compound **2e**. General procedure 5 was modified using azide **1e** (80 mg, 0.39 mmol) and product **2e** was isolated as a colorless solid in 76% (67 mg) and 80% (70 mg) yield in duplicate trials. The average of 78% is reported.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.50 – 7.42 (m, 2H), 5.87 (dq, $J_{H\text{-}F}$ = 48.1, $J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.83 (dd, $J_{H\text{-}F}$ = 23.3, $J_{H\text{-}H}$ = 6.5 Hz, 3H).

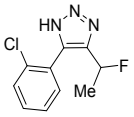
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.64.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.7, 142.8, 135.2, 129.5, 129.5, 129.1, 82.9 (d, $J_{C\text{-}F}$ = 163.4 Hz), 19.4 (d, $J_{C\text{-}F}$ = 25.4 Hz).

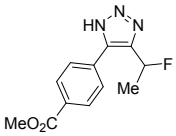
IR (NaCl, thin film, cm^{-1}) 3153 2994, 2927, 2854, 1608, 1490, 1094, 835.
HRMS (EI-TOF) $[M]^+$ Calculated for $C_{10}H_9ClFN_3^+$ 225.0464; Found: 225.0458.



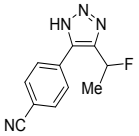
Compound **2f**. General procedure 5 was modified using azide **1f** and the product **2f** was isolated as a colorless oil in 63% (63 mg) and 59% (58 mg) yield in duplicate trials. The average of 61% is reported.
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.19 (br, 1H), 7.78 (br, 1H), 7.68 – 7.63 (m, 1H), 7.44 – 7.39 (m, 2H), 5.89 (dq, J_{H-F} = 48.1, J_{H-H} = 6.6 Hz, 1H), 1.84 (dd, J_{H-F} = 23.3, J_{H-H} = 6.5 Hz, 3H).
^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ -160.0.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.6, 142.9 (d, J_{C-F} = 23.2 Hz), 134.8, 131.1, 130.1, 129.1, 128.2 (d, J_{C-F} = 3.7 Hz), 126.3 (d, J_{C-F} = 3.5 Hz), 82.7 (d, J_{C-F} = 163.3 Hz), 19.4 (d, J_{C-F} = 24.0 Hz).
IR (NaCl, thin film, cm^{-1}) 3162, 2992, 2937, 1604, 1570, 1451, 1100, 1073, 1014, 867, 794, 778.
HRMS (EI-TOF) *m/z* $[M - F]^+$ calcd for $C_{10}H_9ClN_3^+$ 206.0480, found 206.0476.



Compound **2g**. General procedure 5 was modified using azide **1g** and product **2g** was isolated as a colorless oil in 72% (64 mg) and 72% (64 mg) yield in duplicate trials. The average of 72% is reported.
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.98 (br, 1H), 7.47 (dd, J = 7.7, 1.4 Hz, 1H), 7.45 (dd, J = 7.5, 1.9 Hz, 1H), 7.38 (td, J = 7.7, 1.9 Hz, 1H), 7.33 (td, J = 7.5, 1.4 Hz, 1H), 5.77 (dq, J_{H-F} = 47.6, J_{H-H} = 6.6 Hz, 1H), 1.73 (dd, J_{H-F} = 23.6, J_{H-H} = 6.6 Hz, 3H).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -163.4.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.6 (d, J_{C-F} = 22.5 Hz), 141.0, 133.6, 132.1, 130.7, 129.9, 128.0, 126.9, 83.0 (d, J_{C-F} = 163.8 Hz), 19.9 (d, J_{C-F} = 23.8 Hz).
IR (NaCl, thin film, cm^{-1}) 3135, 2991, 2928, 1474, 1432, 1071, 1036, 1003, 872, 757, 737.
HRMS (EI-TOF) *m/z* $[M - F]^+$ calcd for $C_{10}H_9ClN_3^+$ 206.0480, found 206.0475.

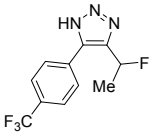


Compound **2h**. General procedure 5 was modified using azide **1h** (52 mg, 0.23 mmol) and product **2h** was isolated as a colorless solid in 88% (50 mg) and 84% (48 mg) yield in duplicate trials. The average of 86% is reported.
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (br, 1H), 8.17 – 8.12 (m, 2H), 7.89 – 7.83 (m, 2H), 5.91 (dq, J_{H-F} = 48.0, J_{H-H} = 6.6 Hz, 1H), 3.96 (s, 3H), 1.84 (dd, J_{H-F} = 23.3, J_{H-H} = 6.6 Hz, 3H).
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ -159.92.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 166.9, 144.7, 133.9, 130.3, 130.1, 128.1, 128.0, 82.8 (d, J_{C-F} = 162.0 Hz), 52.3, 19.4 (d, J_{C-F} = 25.5 Hz).
IR (NaCl, thin film, cm^{-1}) 3212, 2937, 1720, 1698, 1287, 1108.
HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{12}H_{12}FN_3NaO_2^+$ 272.0806, found 272.0804.

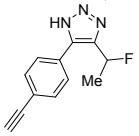


Compound **2i**. General procedure 5 was modified using azide **1i** and product **2i** was isolated as a brown, waxy solid in 71% (52 mg) and 70% (54 mg) yield in duplicate trials. The average of 71% is reported.
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.32 (br, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 5.92 (dq, J_{H-F} = 48.1 Hz, J_{H-H} = 6.6 Hz, 1H), 1.87 (dd, J_{H-F} = 23.4 Hz, J_{H-H} = 6.6 Hz, 3H).

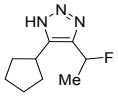
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -160.52.
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 134.4, 132.7, 128.8, 128.7, 118.5, 112.4, 82.9 (d, $J_{C\text{-}F}$ = 163.8 Hz), 19.4 (d, $J_{C\text{-}F}$ = 24.3 Hz).
IR (NaCl, thin film, cm^{-1}) 3190, 2995, 2231, 1614, 1072, 1005, 848.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{11}H_9FN_4Na^+$ 239.0703, found 239.0707.



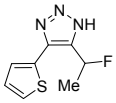
Compound **2j**. General procedure 5 was modified using azide **1j** (70 mg, 0.31 mmol) and product **2j** was isolated as a pale-yellow solid in 81% (91 mg) and 83% (92 mg) yield in duplicate trials. The average of 82% is reported.
^{1}H NMR (500 MHz, $CDCl_3$) δ 11.9 (br, 1H), 7.89 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 5.91 (dq, $J_{H\text{-}F}$ = 47.9, $J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.85 (dd, $J_{H\text{-}F}$ = 23.4, $J_{H\text{-}H}$ = 6.5 Hz, 3H).
^{19}F $\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -62.80 (3F), -160.13 (1F).
$^{13}C\{^{1}H\}$ NMR (125 MHz; $CDCl_3$) δ 144.3, 143.0, 132.8, 131.0 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.5, 125.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 123.9 (q, $J_{C\text{-}F}$ = 274.1 Hz), 82.8 (d, $J_{C\text{-}F}$ = 164.3 Hz), 19.5 (d, $J_{C\text{-}F}$ = 24.4 Hz),
IR (NaCl, thin film, cm^{-1}) 3149, 2999, 2935, 2857, 1624, 1329, 1131, 1073, 850.
HRMS (EI-TOF) $[M]^+$ Calculated for $C_{11}H_9F_4N_3^+$ 259.0727; Found: 259.0727.



Compound **2k**. General procedure 5 was modified using azide **1k** (90.0 mg, 0.46 mmol), with AgF (1.5 equiv) in MeCN (0.05 M) and product **2k** was isolated as a colorless solid in 48% (48 mg) and 48% (48 mg) yield in duplicate trials. The average of 48% is reported.
^{1}H NMR (500 MHz, CD_3CN) δ 13.01 (br, 1H), 7.78 – 7.67 (m, 2H), 7.63 – 7.57 (m, 2H), 5.92 (dq, $J_{H\text{-}F}$ = 48.2, $J_{H\text{-}H}$ 6.5 Hz, 1H), 3.48 (s, 1H), 1.77 (dd, $J_{H\text{-}F}$ = 23.6, $J_{H\text{-}H}$ 6.5 Hz, 3H).
^{19}F $\{^{1}H\}$ NMR (376 MHz, CD_3CN) δ -160.1.
$^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN) δ 146.0, 144.1, 133.4, 129.0, 123.3, 118.4, 84.1 (d, $J_{C\text{-}F}$ = 161.5 Hz), 83.8, 80.2, 19.7 (d, $J_{C\text{-}F}$ =25.5 Hz).
IR (NaCl, thin film, cm^{-1}) 3290, 3148, 2924, 2853, 1481, 1275, 1003, 844, 764.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{12}H_{10}FN_3Na^+$ 238.0751, found 238.0743.



Compound **2l**. General procedure 5 was modified using azide **1l** and product **2l** was isolated as a colorless solid in 50% (57 mg) and 32% (36 mg) yield in duplicate trials. The average of 41% is reported. Due to the low molar absorptivity of this product, the isolated yield was low. In a repeated experiment, the crude material was analyzed by ^{1}H NMR. Upon workup, the crude reaction mixture was submitted to ^{1}H NMR analysis in CD_3CN (0.55 mL) containing MTBE (0.093 mmol) as standard. The calculated yield of **2l** by NMR was 72%.
^{1}H NMR (500 MHz, C_6D_6) δ 11.11 (br, 1H), 5.60 (dq, $J_{H\text{-}F}$ = 48.6, $J_{H\text{-}H}$ = 6.5 Hz, 1H), 3.19 – 3.06 (m, 1H), 2.03 – 1.91 (m, 2H), 1.91 – 1.81 (m, 2H), 1.80 – 1.71 (m, 2H), 1.69 (dd, $J_{H\text{-}F}$ = 20.1, $J_{H\text{-}H}$ = 6.5 Hz, 3H). 1.55 – 1.45 (m, 2H).
$^{19}F\{^{1}H\}$ NMR (470 MHz, C_6D_6) δ -164.6.
$^{13}C\{^{1}H\}$ NMR (125 MHz, C_6D_6) δ 149.1, 143.8 (d, $J_{C\text{-}F}$ = 25.0 Hz), 83.4 (d, $J_{C\text{-}F}$ = 162.5 Hz), 56.7, 36.0, 33.5, 33.1, 25.7, 20.1 (d, $J_{C\text{-}F}$ = 25.1 Hz).
IR (NaCl, thin film, cm^{-1}) 3167, 2953, 2869, 1450, 1306, 1071, 1010, 979, 738.
HRMS (EI-TOF) *m/z* $[M - F]^+$ calcd for $C_9H_{14}N_3^+$ 164.1182, found 164.1176.



Compound **2m**. General procedure 5 was modified using azide **1m** (80 mg, 0.45 mmol) and product **2m** was isolated as a yellow oil in 73% (65 mg) and 71% (60 mg) yield in duplicate trials. The average of 72% is reported.

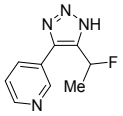
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.74 (bd, 1H), 7.49 (dd, J = 3.7, 1.2 Hz, 1H), 7.40 (dd, J = 5.2, 1.2 Hz, 1H), 7.12 (dd, J = 5.1, 3.6 Hz, 1H), 5.96 (dq, $J_{H\text{-}F}$ = 48.0, $J_{H\text{-}H}$ = 6.6 Hz, 1H), 1.86 (dd, $J_{H\text{-}F}$ = 23.3, $J_{H\text{-}H}$ = 6.6 Hz, 3H).

^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ -163.4.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.9 (d, $J_{C\text{-}F}$ = 23.7 Hz), 140.1, 130.5, 127.9, 127.4 (d, $J_{C\text{-}F}$ = 3.8 Hz), 126.9, 82.9 (d, $J_{C\text{-}F}$ = 162.5 Hz).19.28 (d, $J_{C\text{-}F}$ = 25.1 Hz).

IR (NaCl, thin film, cm^{-1}) 3157, 2991, 2919, 1700, 1379, 1329, 1074, 1021, 849, 737, 704.

HRMS (EI-TOF) m/z $[M\text{-}H\text{-}F]^+$ calcd for $C_8H_7N_3S^+$ 177.0355, found 177.0347.



Compound **2n**. General procedure 5 was modified using azide **1n** (78 mg, 0.45 mmol) and product **2n** was isolated as a pale-yellow waxy solid in 39% (33 mg) and 35% (30 mg) yield in duplicate trials. The average of 37% is reported.

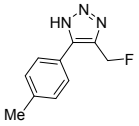
^{1}H NMR (500 MHz, CD_3CN) δ 8.93 (dd, J = 2.3, 0.9 Hz, 1H), 8.63 (dd, J = 4.8, 1.7 Hz, 1H), 8.08 (ddd, J = 7.9, 2.3, 1.7 Hz, 1H), 7.47 (ddd, J = 7.9, 4.8, 0.9 Hz, 1H), 5.94 (dq, $J_{H\text{-}F}$ = 48.3, $J_{H\text{-}H}$ = 6.5 Hz, 1H), 1.78 (dd, $J_{H\text{-}F}$ = 23.6, $J_{H\text{-}H}$ = 6.5 Hz, 3H).

^{19}F{^{1}H} NMR (376 MHz, CD_3CN) δ -160.0.

^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ 150.6, 149.5 (d, $J_{C\text{-}F}$ = 3.8 Hz), 142.7, 136.3, 136.2, 127.3, 124.7, 84.0 (d, $J_{C\text{-}F}$ = 158.8 Hz), 19.8 (d, $J_{C\text{-}F}$ = 23.7 Hz).

IR (NaCl, thin film, cm^{-1}) 3384, 3103, 2989, 2849, 1576, 1190, 1028, 983, 816, 708.

HRMS (EI-TOF) m/z $[M+H\text{-}F]^+$ calcd for $C_9H_{10}N_4^+$ 174.0900, found 174.0897.



Compound **2o**. General procedure 5 was modified using azide **1o** and the product **2o** was isolated as a yellow solid in 53% (62 mg) and 52% (59 mg) yield in duplicate trials. The average of 53% is reported.

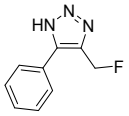
^{1}H NMR (500 MHz, **Acetic Acid-d_4)** δ 7.65 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 5.60 (d, $J_{H\text{-}F}$ = 48.8 Hz, 2H), 2.39 (s, 3H).

^{19}F {^{1}H} NMR (376 MHz, Acetic Acid-d_4) δ -204.6.

^{13}C{^{1}H} NMR (125 MHz, Acetic Acid-d_4) δ 145.0, 140.5, 138.9 (d, $J_{C\text{-}F}$ = 13.8 Hz), 130.7, 128.6, 126.4, 75.6 (d, $J_{C\text{-}F}$ = 161.2 Hz), 21.3.

IR (NaCl, thin film, cm^{-1}) 3403, 3001, 1461, 1275, 1260, 764, 749.

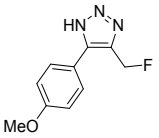
HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{10}H_{11}FN_3^+$ 192.0932, found 192.0932.



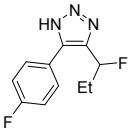
Compound **2p**. General procedure 5 was modified using azide **1p** and the product **2p** was isolated as a colorless solid in 54% (58 mg) and 52% (55 mg) yield in duplicate trials. The average of 53% is reported.

^{1}H NMR (500 MHz, Acetic Acid-d_4) δ 7.79 – 7.74 (m, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.42 (m, 1H), 5.61 (d, $J_{H\text{-}F}$ = 48.7 Hz, 2H).

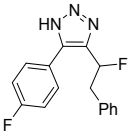
$^{19}F\{^1H\}$ NMR (376 MHz, Acetic Acid-d_4) δ -204.9.
$^{13}C\{^1H\}$ NMR (125 MHz, Acetic Acid-d_4) δ 145.3, 139.1 (d, $J_{C\text{-}F}$ = 21.3 Hz), 130.2, 130.0, 129.5, 128.6, 75.6 (d, $J_{C\text{-}F}$ = 161.3 Hz).
IR (NaCl, thin film, cm^{-1}) 3009, 2688, 1503, 1260, 956, 762, 750.
HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_9H_9FN_3^+$ 178.0775, found 178.0769.



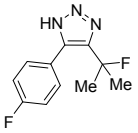
Compound **2q**. General procedure 5 was modified using azide **1q** and the product **2q** was isolated as a yellow solid in 65% (51 mg) and 58% (45 mg) yield in duplicate trials. The average of 62% is reported.
^1H NMR (400 MHz, Acetic Acid-d_4) δ 7.73 – 7.66 (m, 2H), 7.10 – 7.02 (m, 2H), 5.60 (d, $J_{H\text{-}F}$ = 48.8 Hz, 2H), 3.86 (s, 3H).
$^{19}F\{^1H\}$ NMR (376 MHz, Acetic Acid-d_4) δ -204.4.
$^{13}C\{^1H\}$ NMR (125 MHz, Acetic Acid-d_4) δ 161.7, 144.8, 138.7 (d, $J_{C\text{-}F}$ = 18.8 Hz), 130.2, 130.1, 115.5, 75.7 (d, $J_{C\text{-}F}$ = 161.3 Hz), 55.7.
IR (NaCl, thin film, cm^{-1}) 2934, 2836, 1615, 1510, 1302, 1264, 946, 829.
HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{10}H_{10}FN_3NaO^+$ 230.0700, found 230.0706.



Compound **2r**. General procedure 5 was modified using azide **1r** and the product **2r** was isolated as a colorless solid in 77% (60 mg) and 68% (53 mg) yield in duplicate trials. The average of 73% is reported.
^1H NMR (500 MHz, $CDCl_3$) δ 12.37 (br, 1H), 7.75 – 7.67 (m, 2H), 7.19 – 7.12 (m, 2H), 5.60 (ddd, $J_{H\text{-}F}$ = 48.1, $J_{H\text{-}H}$ = 8.2, 5.7 Hz, 1H), 2.28 (m, 1H), 2.08 (m, 1H), 1.02 (t, J = 7.4 Hz, 3H).
$^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ -112.0, -166.8.
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 249.6 Hz), 144.5, 141.6 (d, $J_{C\text{-}F}$ = 22.6 Hz), 130.2 (dd, $J_{C\text{-}F}$ = 8.8, 3.7 Hz), 125.3 (d, $J_{C\text{-}F}$ = 3.6 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.7 Hz), 87.7 (d, $J_{C\text{-}F}$ = 166.9 Hz), 26.7 (d, $J_{C\text{-}F}$ = 22.8 Hz), 9.7 (d, $J_{C\text{-}F}$ = 5.5 Hz).
IR (NaCl, thin film, cm^{-1}) 3133, 2975, 2936, 2879, 1610, 1505, 1474, 1265, 1231, 1160, 842, 739.
HRMS (EI-TOF) *m/z* $[M - F]^+$ calcd for $C_{11}H_{11}FN_3^+$ 204.0932, found 204.0926.



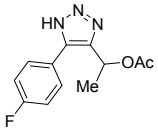
Compound **2s**. General procedure 5 was modified using azide **1s** and the product **2s** was isolated as a colorless solid in 70% (39 mg) and 83% (46 mg) yield in duplicate trials. The average of 77% is reported.
^1H NMR (500 MHz, $CDCl_3$) δ 11.7 (br, 1H), 7.65 – 7.57 (m, 2H), 7.31 – 7.18 (m, 5H), 7.17 – 7.10 (m, 2H), 5.85 (ddd, $J_{H\text{-}F}$ = 47.9, $J_{H\text{-}H}$ = 8.2, 5.7 Hz, 1H), 3.61 (ddd, $J_{H\text{-}F}$ = 14.4, $J_{H\text{-}H}$ = 14.4, 8.2 Hz, 1H), 3.40 (ddd, $J_{H\text{-}F}$ = 26.4, $J_{H\text{-}H}$ = 14.4, 5.7 Hz, 1H).
$^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ -111.9, -163.8.
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 250.2 Hz), 144.9, 141.4 (d, $J_{C\text{-}F}$ = 23.6 Hz), 136.0 (d, $J_{C\text{-}F}$ = 5.3 Hz), 130.2 (dd, $J_{C\text{-}F}$ = 8.8, 3.6 Hz), 129.4, 128.5, 126.9, 125.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 86.6 (d, $J_{C\text{-}F}$ = 168.5 Hz), 39.8 (d, $J_{C\text{-}F}$ = 23.6 Hz).
IR (NaCl, thin film, cm^{-1}) 3157, 3028, 2927, 1507, 1486, 1260, 1160, 840, 764, 750.
HRMS (EI-TOF) *m/z* $[M - F]^+$ calcd for $C_{16}H_{13}FN_3^+$ 266.1088, found 266.1089.



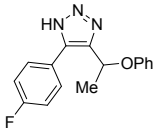
Compound **2t**. General procedure 5 was modified using azide **1t** and the product **2t** was isolated as a colorless oil in 62% (56 mg) and 61% (54 mg) yield in duplicate trials. The average of 62% is reported.
^{1}H NMR (500 MHz, C_6D_6) δ 11.04 (br, 1H), 7.67 (dd, J = 8.6, 5.4 Hz, 2H), 6.86 – 6.74 (m, 2H), 1.63 (d, $J_{H\text{-}F}$ = 20.9 Hz, 6H).
^{19}F {^{1}H} NMR (470 MHz, C_6D_6) δ -112.6, -126.3.
^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ163.5(d, $J_{C\text{-}F}$ = 246.3 Hz), 146.7, 144.1, 131.6 (dd, $J_{C\text{-}F}$ = 8.8, 3.6 Hz), 127.3, 115.7 (d, $J_{C\text{-}F}$ = 21.3 Hz), 91.9 (d, $J_{C\text{-}F}$ = 162.5 Hz), 27.4 (d, $J_{C\text{-}F}$ = 27.4 Hz),
IR (NaCl, thin film, cm^{-1}) 3399, 3186, 3056, 2977, 2929, 1710, 1460, 1423, 1265, 1224, 839, 743.
HRMS (EI-TOF) *m/z* $[M - F]^+$ calcd for $C_{11}H_{11}FN_3^+$ 204.0932, found 204.0927.

Additional Nucleophiles

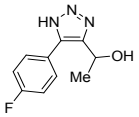
General Procedure 6. A 20 mL vial was charged with silver salt (equiv as noted) and any additional additives. Under air, a solution of azide **1a** (1 equiv) was prepared in MeCN (0.1 M). The solution of azide **1a** was transferred to the vial containing silver salt and any additional additives by syringe and rinsed with MeCN (0.1 mL). The vial was sealed and heated to 60 °C. After 24h, the reaction was quenched by the addition of AcOH (0.7 ml, 1.0 M in brine). The resulting solution was extracted with ethyl acetate (10 mL x 3). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash chromatography using a short plug of silica gel (gradient elution 0 – 60% EtOAc in hexanes) yielded the product.
Note: for compounds **3a**, **3b** and **3d** triazole carbon(s) were not readily detected (very broad and weak signal). This is likely due to the dynamic behavior of the triazole products.



General procedure 6 was modified using AgOAc (90.1 mg, 0.54 mmol, 2 equiv) and the product **3a** was isolated as a yellow oil in 75% (50 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 13.60 (br, 1H), 7.67 – 7.58 (m, 2H), 7.16 – 7.10 (m, 2H), 6.24 (q, J = 6.6 Hz, 1H), 2.03 (s, 3H), 1.65 (d, J = 6.6 Hz, 3H).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -112.3.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.6, 163.0 (d, $J_{C\text{-}F}$ = 247.5 Hz), 143.1, 130.0 (d, $J_{C\text{-}F}$ = 8.8 Hz), 125.8, 115.9 (d, $J_{C\text{-}F}$ = 22.5 Hz), 64.7, 21.0, 19.9.
IR (NaCl, thin film, cm^{-1}) 3173, 2990, 2936, 1739, 1373, 1236, 841.
HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{12}H_{12}FN_3NaO_2^+$ 272.0806, found 272.0818.

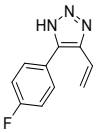


General procedure 6 was modified using Ag_2CO_3 (159 mg, 0.57 mmol, 1 equiv), KOH (42 mg, 0.76 mmol, 1.3 equiv) and phenol (71.1 mg, 0.76 mmol, 1.3 equiv) and the product **3b** was isolated as a waxy oil in 92% (108 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.32 (br, 1H), 7.75 – 7.68 (m, 2H), 7.25 – 7.19 (m, 2H), 7.16 – 7.10 (m, 2H), 6.97 – 6.88 (m, 3H), 5.74 (q, J = 6.6 Hz, 1H), 1.74 (d, J = 6.6 Hz, 3H).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -112.6.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 247.5 Hz), 156.9, 143.7, 130.2 (d, $J_{C\text{-}F}$ = 7.5 Hz), 129.5, 126.1, 121.5, 115.9, 115.8 (d, $J_{C\text{-}F}$ = 22.8 Hz), 68.2, 20.1.
IR (NaCl, thin film, cm^{-1}) 3145, 2986, 2929, 1597, 1507, 1429, 1229, 841, 753.
HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{16}H_{14}FN_3NaO^+$ 306.1013, found 306.1027.



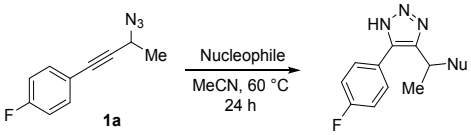
General procedure 6 was modified using AgOTf (104 mg, 0.36 mmol, 2 equiv) and water (20 mg, 1.1 mmol, 3 equiv) and the product **3c** was isolated as a colorless solid in 27% (21 mg).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.16 – 7.08 (m, 2H), 5.21 (q, J = 6.6 Hz, 1H), 1.62 (d, J = 6.6 Hz, 3H).
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -112.6.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.9 (d, $J_{C\text{-}F}$ = 247.5 Hz), 145.2, 142.5, 129.8 (d, $J_{C\text{-}F}$ = 8.8 Hz), 125.9 (d, $J_{C\text{-}F}$ = 2.5 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.2 Hz), 62.3, 22.8.
IR (NaCl, thin film, cm^{-1}) 3166, 3023, 2979, 2931, 1610, 1507, 1482, 1229, 1098, 840.

HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{10}H_{10}FN_3NaO^+$ 230.0700, found 230.0695.



General procedure 6 was modified using AgTFA (186 mg, 0.84 mmol, 2 equiv) and the product **3d** was isolated as a colorless solid in 66% (34 mg).
^{1}H NMR (500 MHz, Acetic Acid-d_4) δ 7.72 – 7.64 (m, 2H), 7.26 – 7.17 (m, 2H), 6.81 (dd, J = 17.7, 11.3 Hz, 1H), 6.05 (dd, J = 17.7, 1.1 Hz, 1H), 5.51 (dd, J = 11.3, 1.2 Hz, 1H).
^{19}F{^{1}H} NMR (376 MHz, Acetic Acid-d_4) δ -113.8.
^{13}C{^{1}H} NMR (125 MHz, Acetic Acid-d_4) δ 164.2 (d, $J_{C\text{-}F}$ = 245 Hz), 131.1 (d, $J_{C\text{-}F}$ = 8.8 Hz), 126.9 (d, $J_{C\text{-}F}$ = 2.5 Hz), 124.2, 119.8, 116.8 (d, $J_{C\text{-}F}$ = 22.5 Hz).
IR (NaCl, thin film, cm^{-1}) 3148, 3014, 2930, 1783, 1670, 1533, 1508, 1476, 1226, 1159, 840.
HRMS (ESI-TOF) *m/z* [M + Na]$^+$ calcd for $C_{10}H_8FN_3Na^+$ 212.0594, found 212.0604.

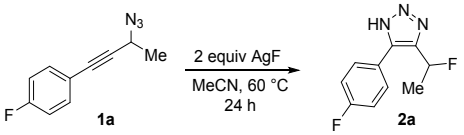
The use of silver salts was advantageous for all of these nucleophiles. Under the same conditions, using other salt/reagents, the results varied:



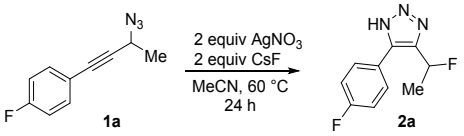
Nucleophile	Desired product	% Yield[a]
AgOAc (2 equiv)	3a	70
Bu_4NOAc (2 equiv)	3a	n.d.
Acetic Acid (2 equiv)	3a	23
Ag_2CO_3 (1 equiv), KOH (2 equiv), phenol (1.5 equiv)	3b	98
K_2CO_3 (1 equiv), KOH (2 equiv), phenol (1.5 equiv)	3b	73
K_2CO_3 (1 equiv), phenol (1.5 equiv)	3b	n.d.
AgOTf (1 equiv), H_2O (5 equiv)	3c	24
H_2O (5 equiv)	3c	n.d.
LiOH (5 equiv)	3c	n.d.
AgTFA (2 equiv)	3d	51
Trifluoroacetic acid (2 equiv)	3d	n.d.
KTFA (2 equiv)	3d	n.d.

[a]Reactions conducted with azide **1a** (0.1 mmol) at 0.1 M in MeCN at 60 °C. Yield determined from the quenched reaction mixture against anisonitrile as an internal standard via ^{1}H-NMR. All yield values are single trials. Abbreviation n.d. = not detected (less than 5%).

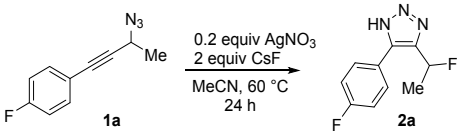
Reactions Conducted With One Gram of Substrate 1a



In a nitrogen filled glovebox, a 100 mL round bottomed flask was charged with AgF (1.34 g, 10.6 mmol) and a stir bar. The round bottomed flask was sealed and removed from the glove box. Under air, a solution of azide **1a** (1.00 g, 5.29 mmol) was prepared in MeCN (51 mL). The solution of azide **1a** was transferred to the flask containing AgF by syringe and rinsed with MeCN (2 mL). The flask was sealed and heated to 60 °C. After 24h, the reaction was quenched by the addition of AcOH (15 ml, 1.0 M in brine). The resulting solution was extracted with ethyl acetate (20 mL x 3). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash chromatography using a short plug of silica gel (gradient elution 0 – 60% EtOAc in hexanes) yielded the product as a colorless solid in 74% (817 mg).



In a nitrogen filled glovebox, a 100 mL round bottomed flask was charged with $AgNO_3$ (1.79 g, 10.6 mmol), CsF (1.60 g, 10.6 mmol) and a stirrer bar. The round bottomed flask was sealed and removed from the glove box. Under air, a solution of azide **1a** (1.00 g, 5.29 mmol) was prepared in MeCN (51 mL). The solution of azide **1a** was transferred to the flask containing $AgNO_3$ and CsF by syringe and rinsed with MeCN (2 mL). The flask was sealed and heated to 60 °C. After 24h, the reaction was quenched by the addition of AcOH (20 ml, 1.0 M in brine). The resulting solution was extracted with ethyl acetate (20 mL x 3). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash chromatography using a short plug of silica gel (gradient elution 0 – 60% EtOAc in hexanes) yielded the product as a colorless solid in 57% (634 mg).



In a nitrogen filled glovebox, a 100 mL round bottomed flask was charged with $AgNO_3$ (181 mg, 1.06 mmol), CsF (1.60 g, 10.6 mmol) and a stirrer bar. The round bottomed flask was sealed and removed from the glove box. Under air, a solution of azide **1a** (1.00 g, 5.29 mmol) was prepared in MeCN (51 mL). The solution of azide **1a** was transferred to the flask containing $AgNO_3$ and CsF by syringe and rinsed with MeCN (2 mL). The flask was sealed and heated to 60 °C. After 24h, the reaction was quenched by the addition of AcOH (20 ml, 1.0 M in brine). The resulting solution was extracted with ethyl acetate (20 mL x 3). The combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by flash chromatography using a short plug of silica gel (gradient elution 0 – 60% EtOAc in hexanes) yielded the product as a colorless solid in 11% (121 mg).

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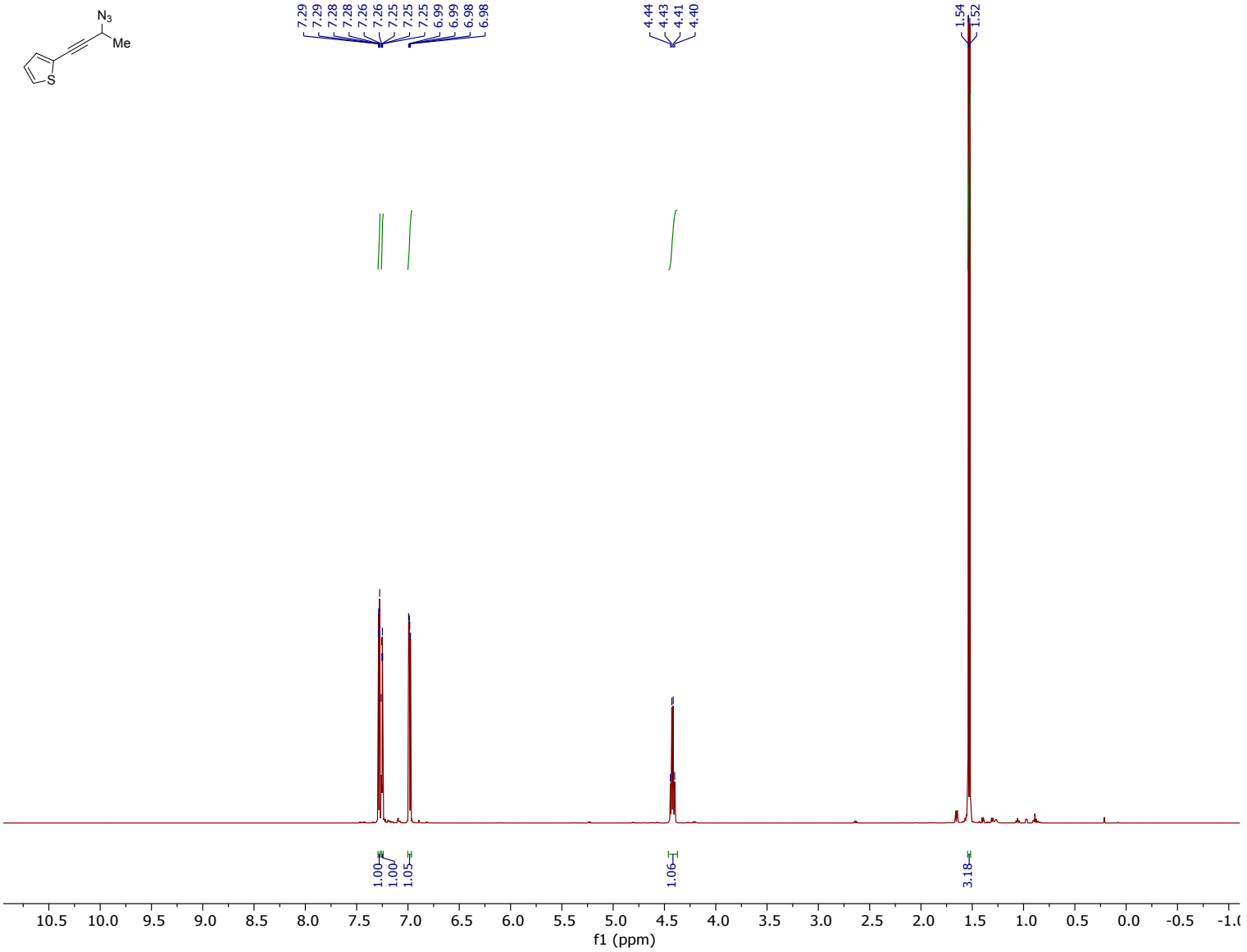
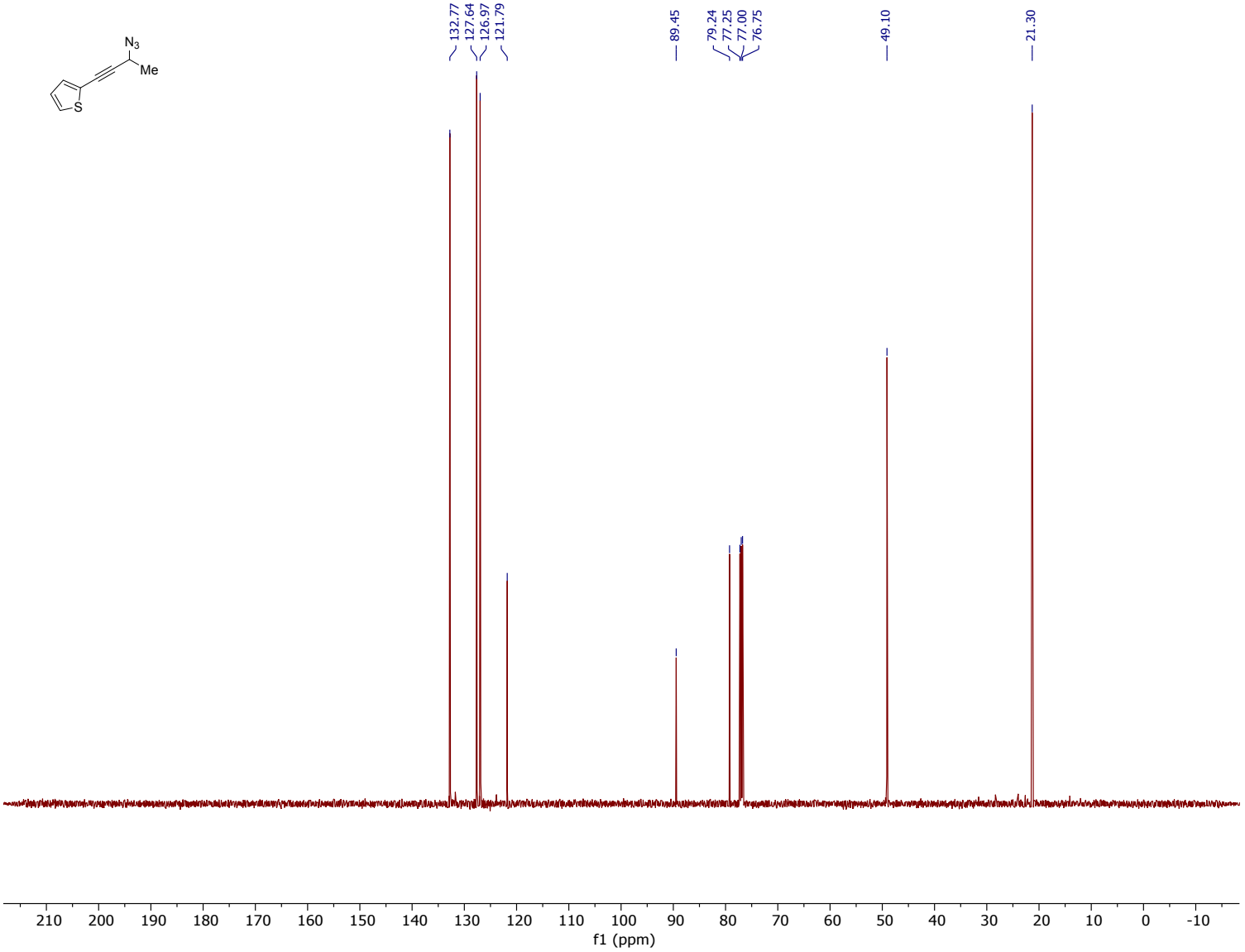
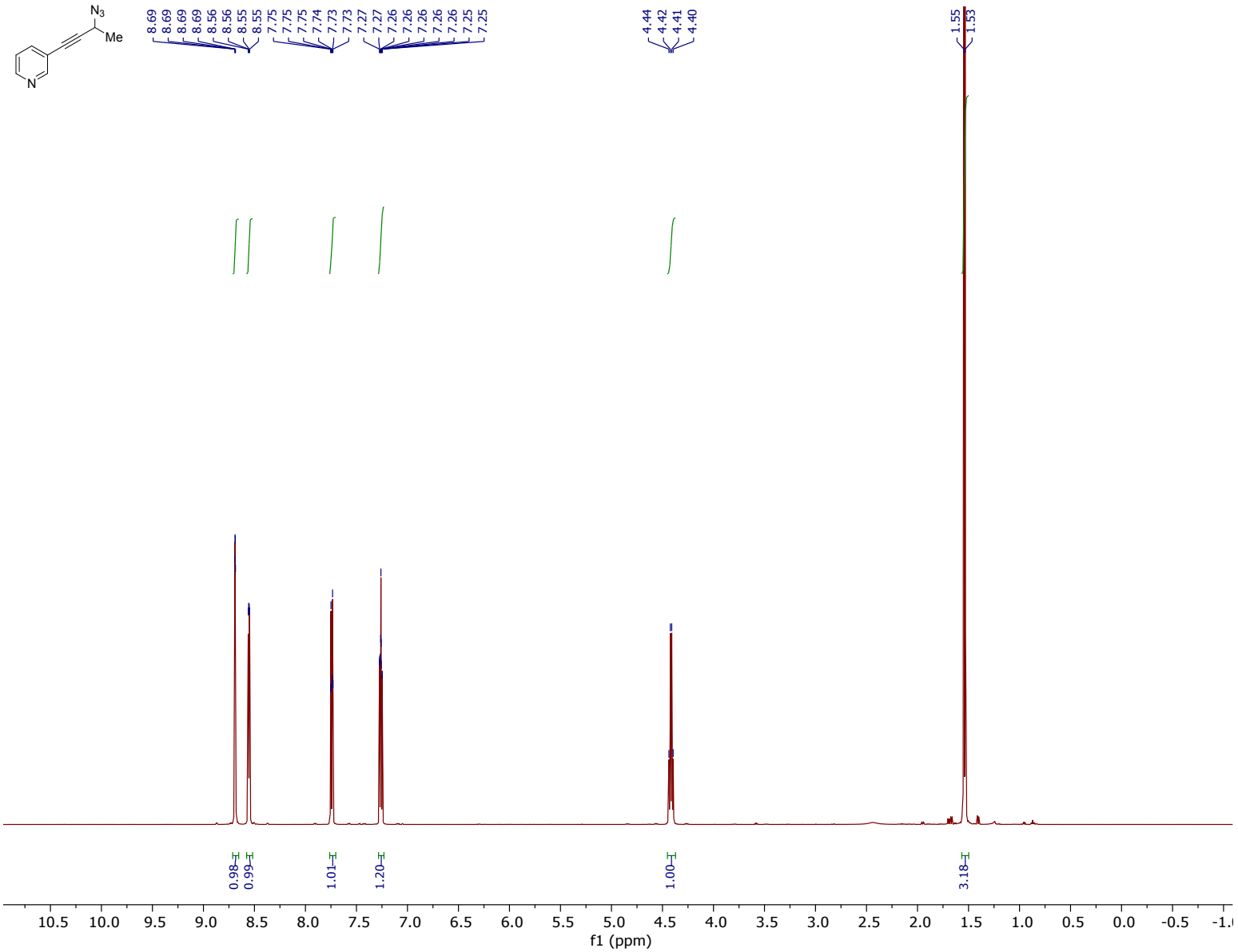


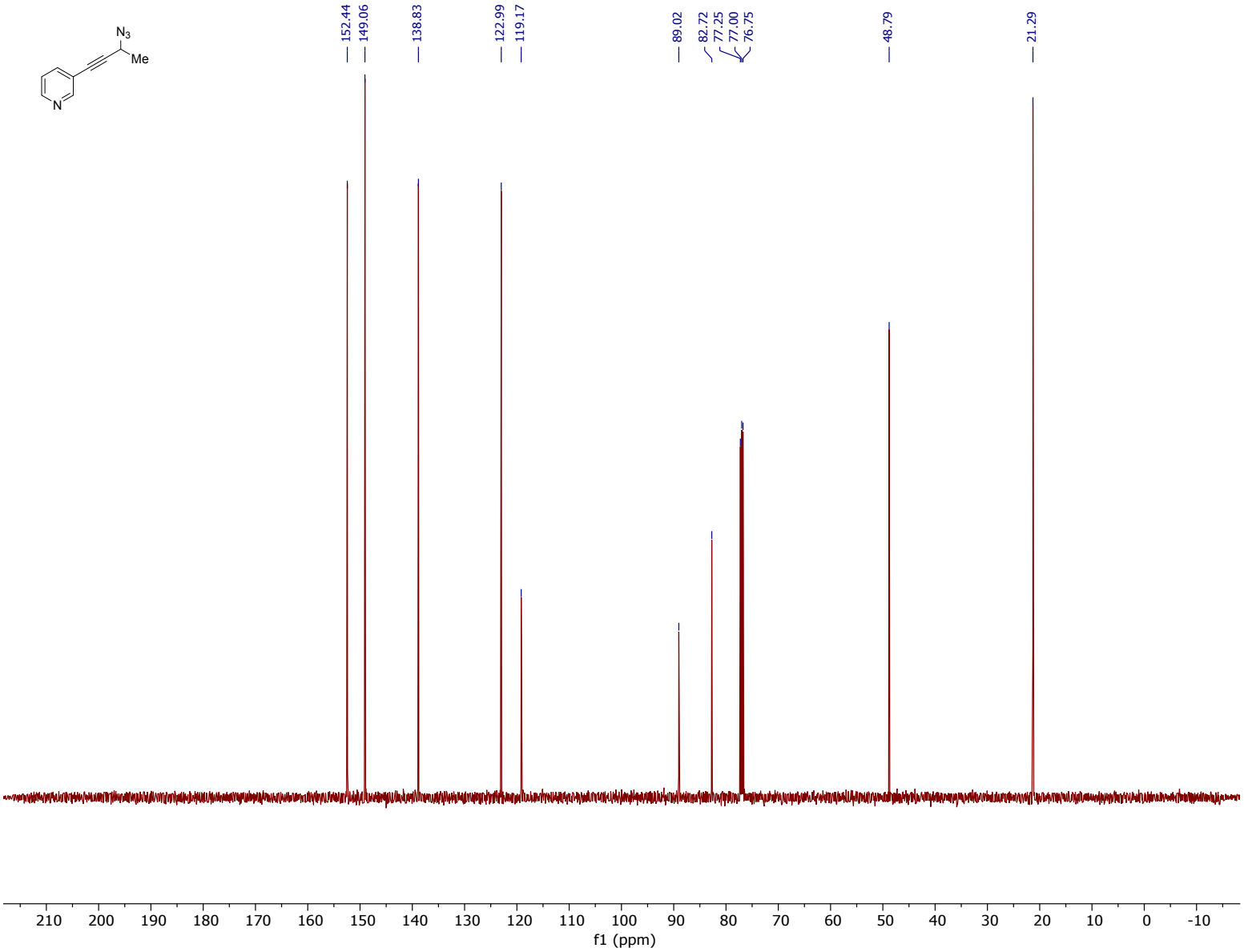
Compound **S1** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



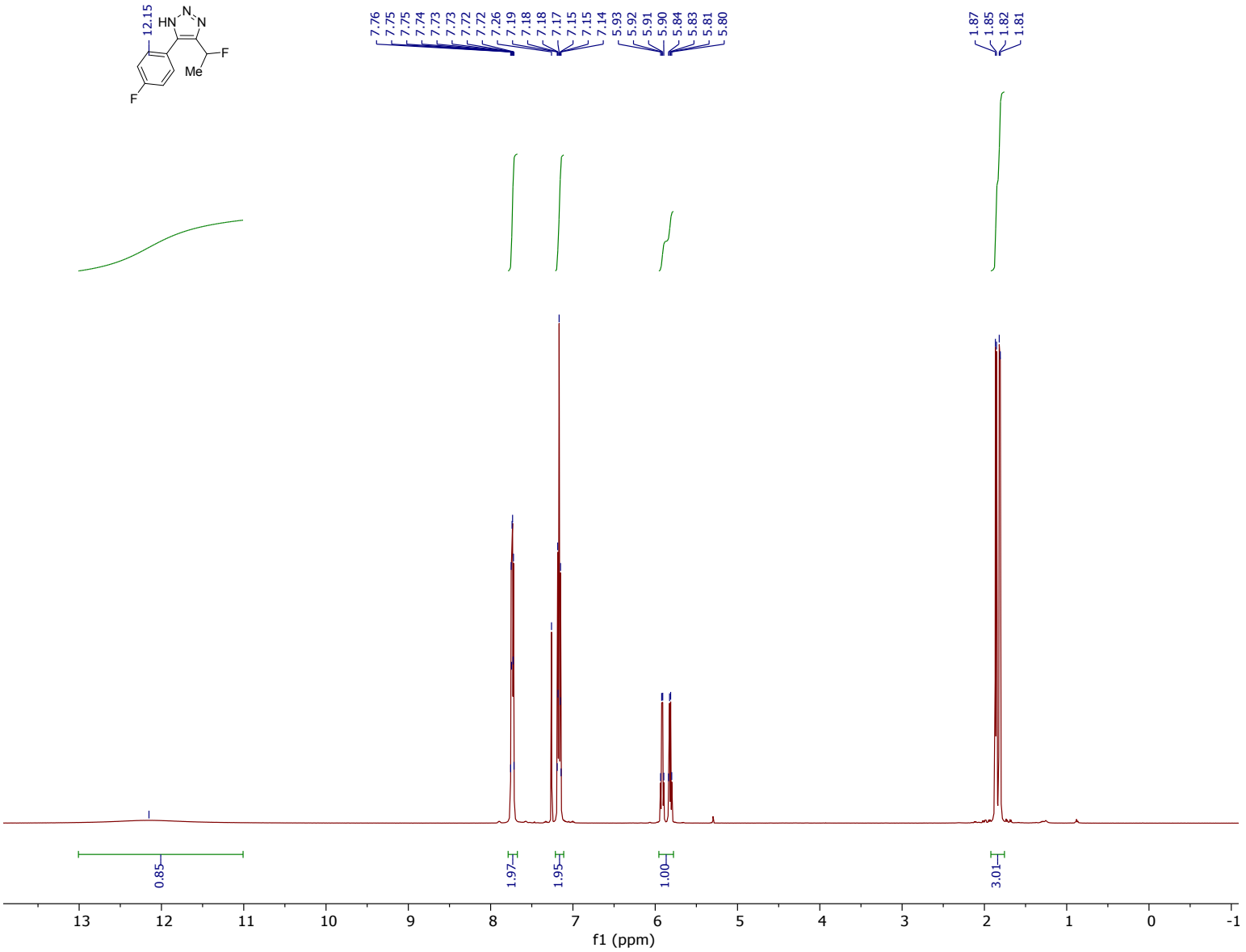
Compound **S1** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



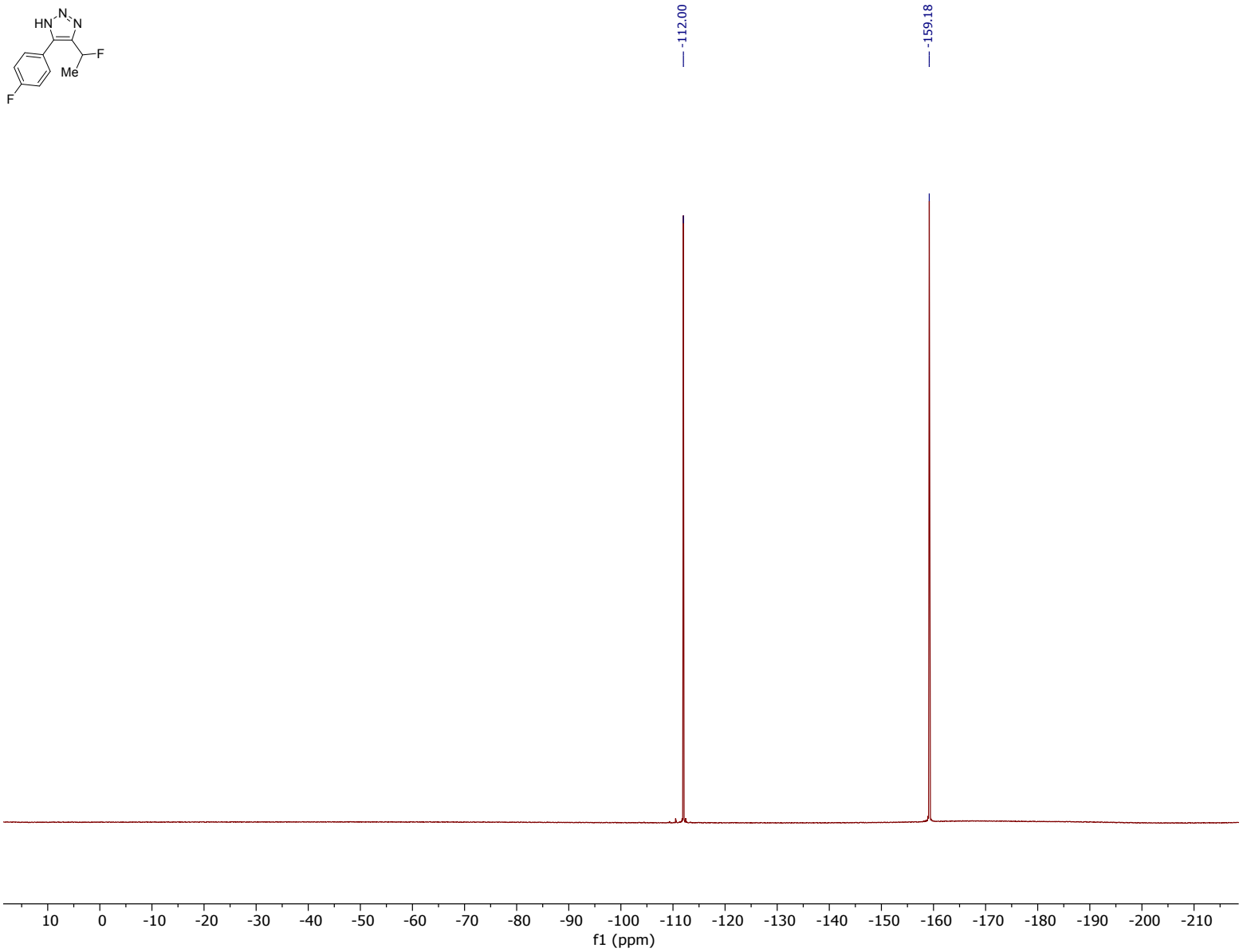
Compound **S2** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



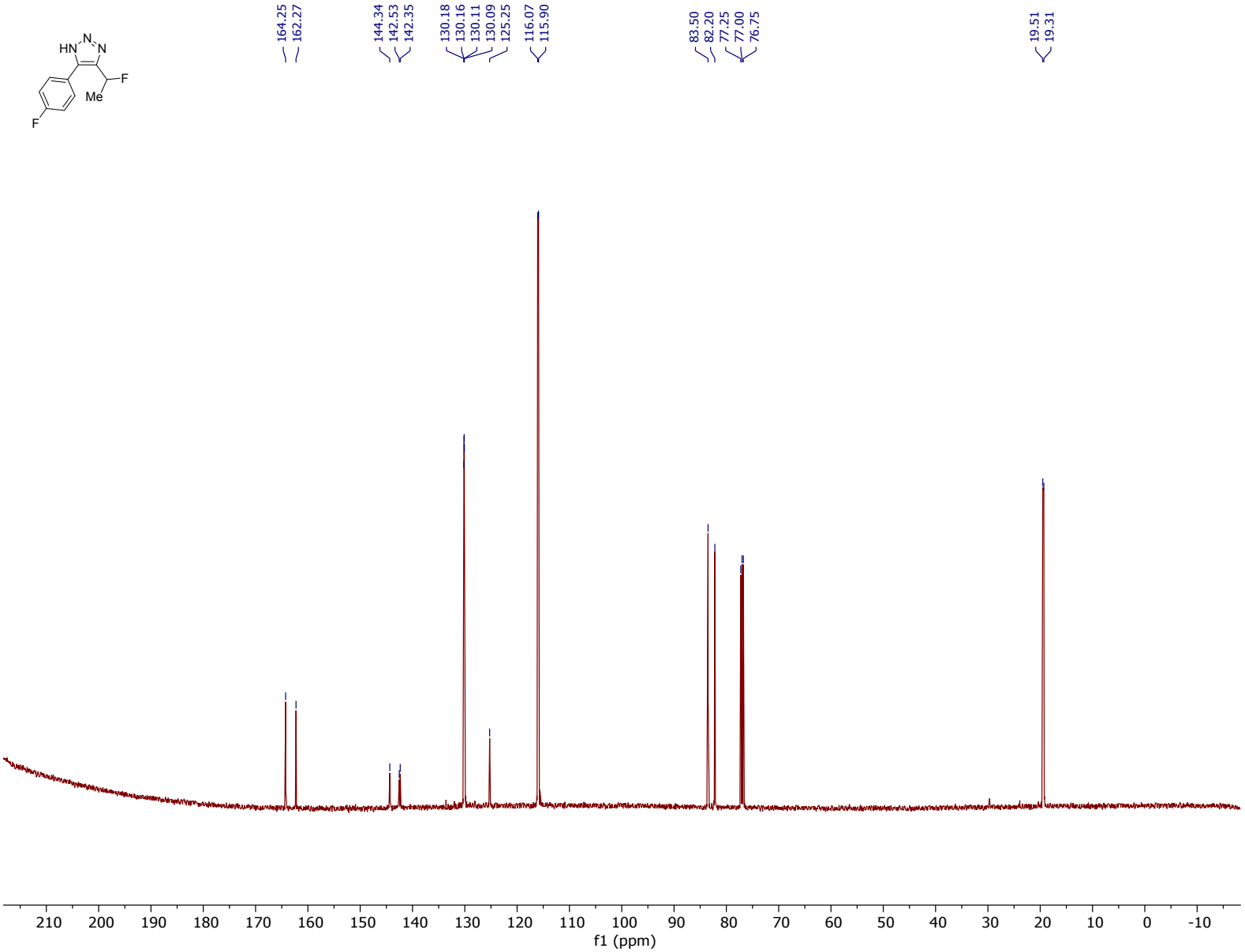
Compound **S2** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



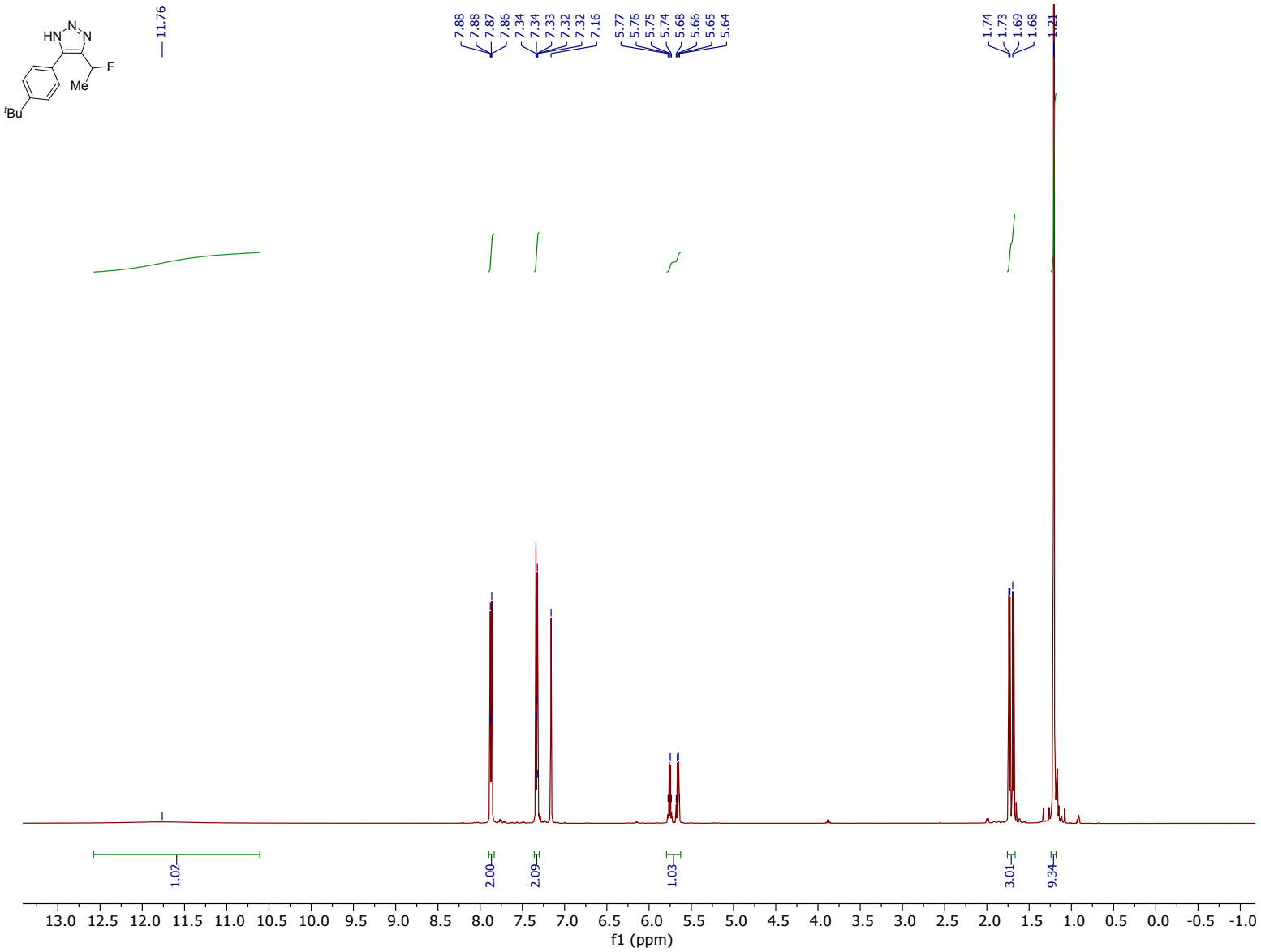
Compound **2a** 400 MHz ^{1}H NMR spectrum in $CDCl_3$



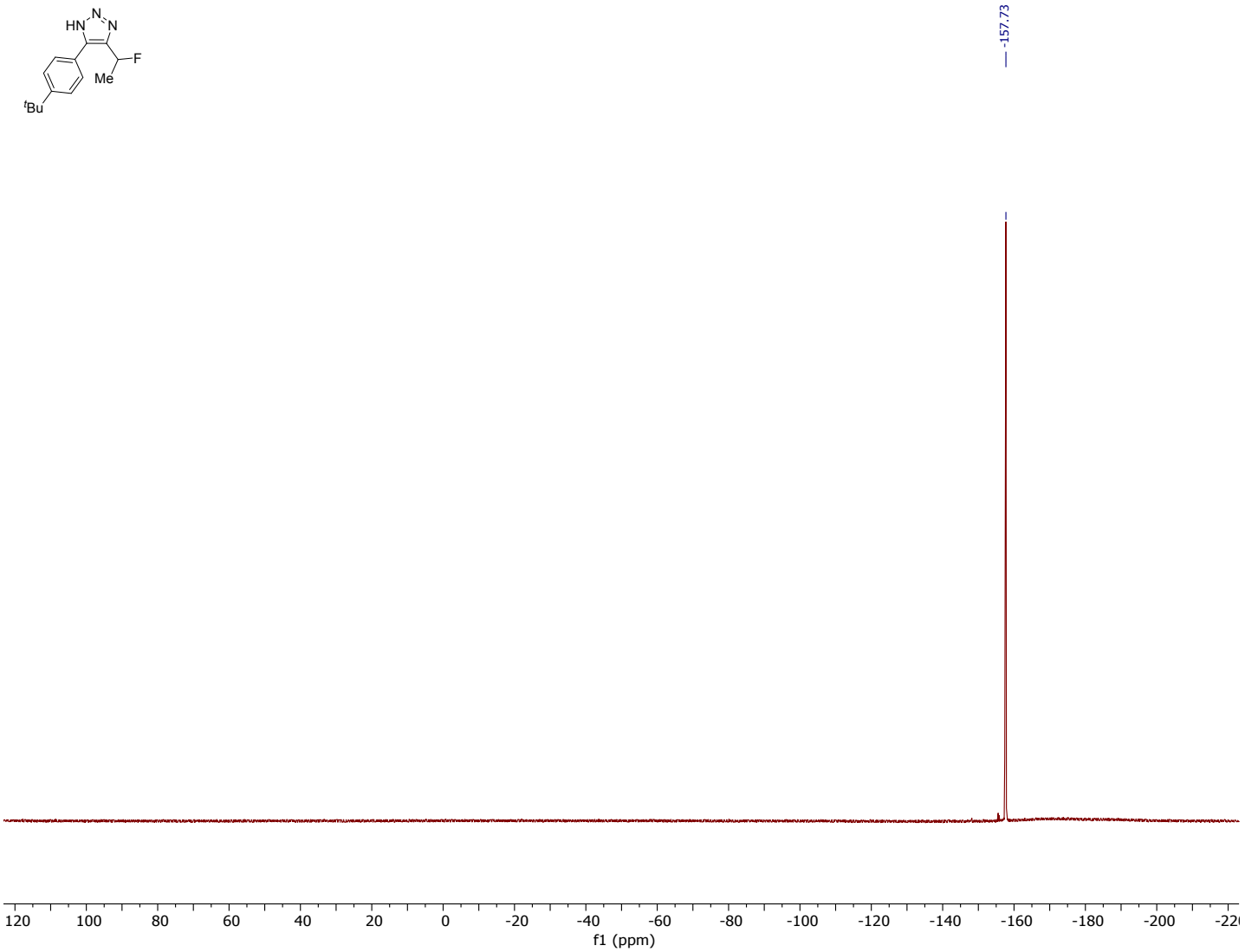
Compound **2a** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



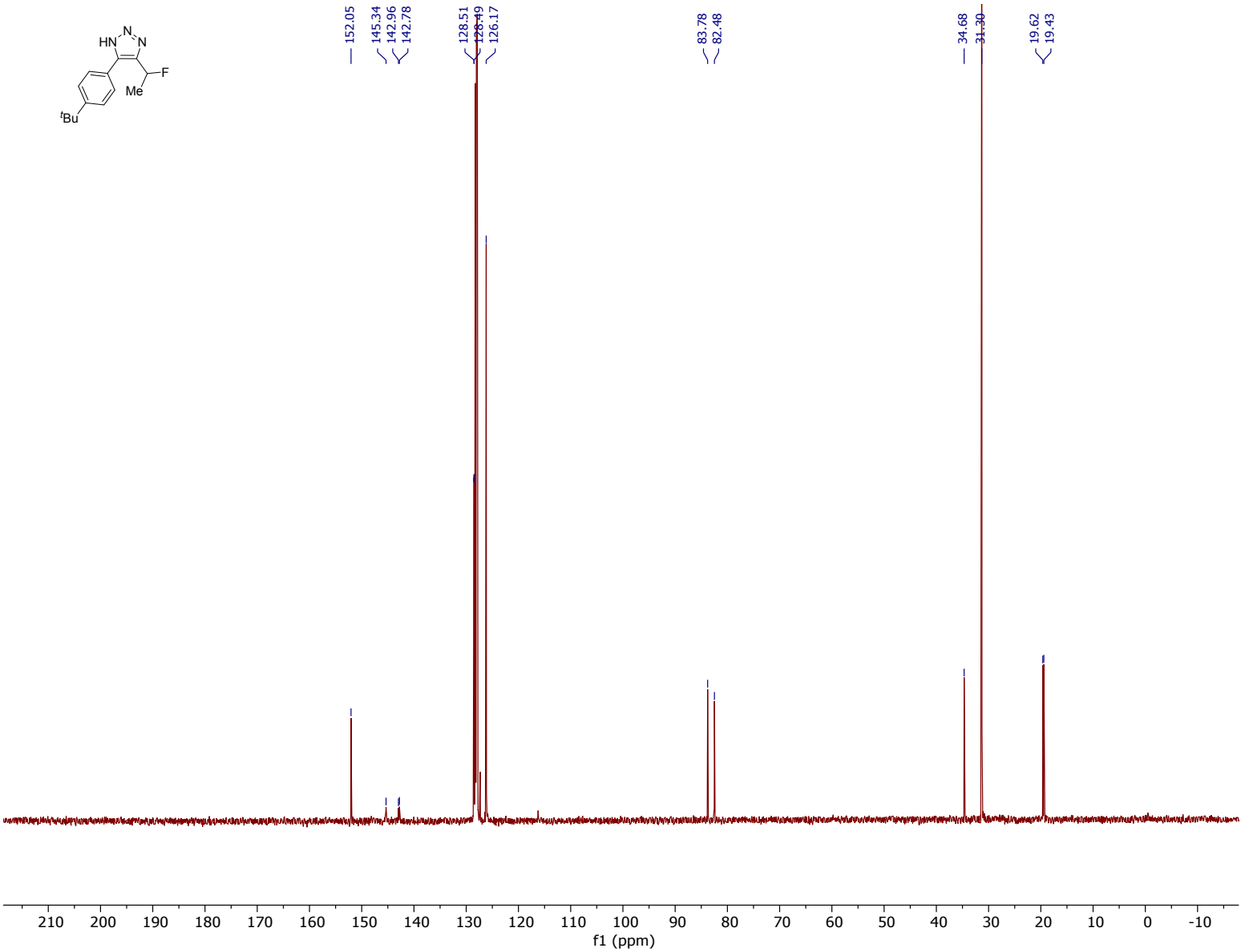
Compound **2a** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



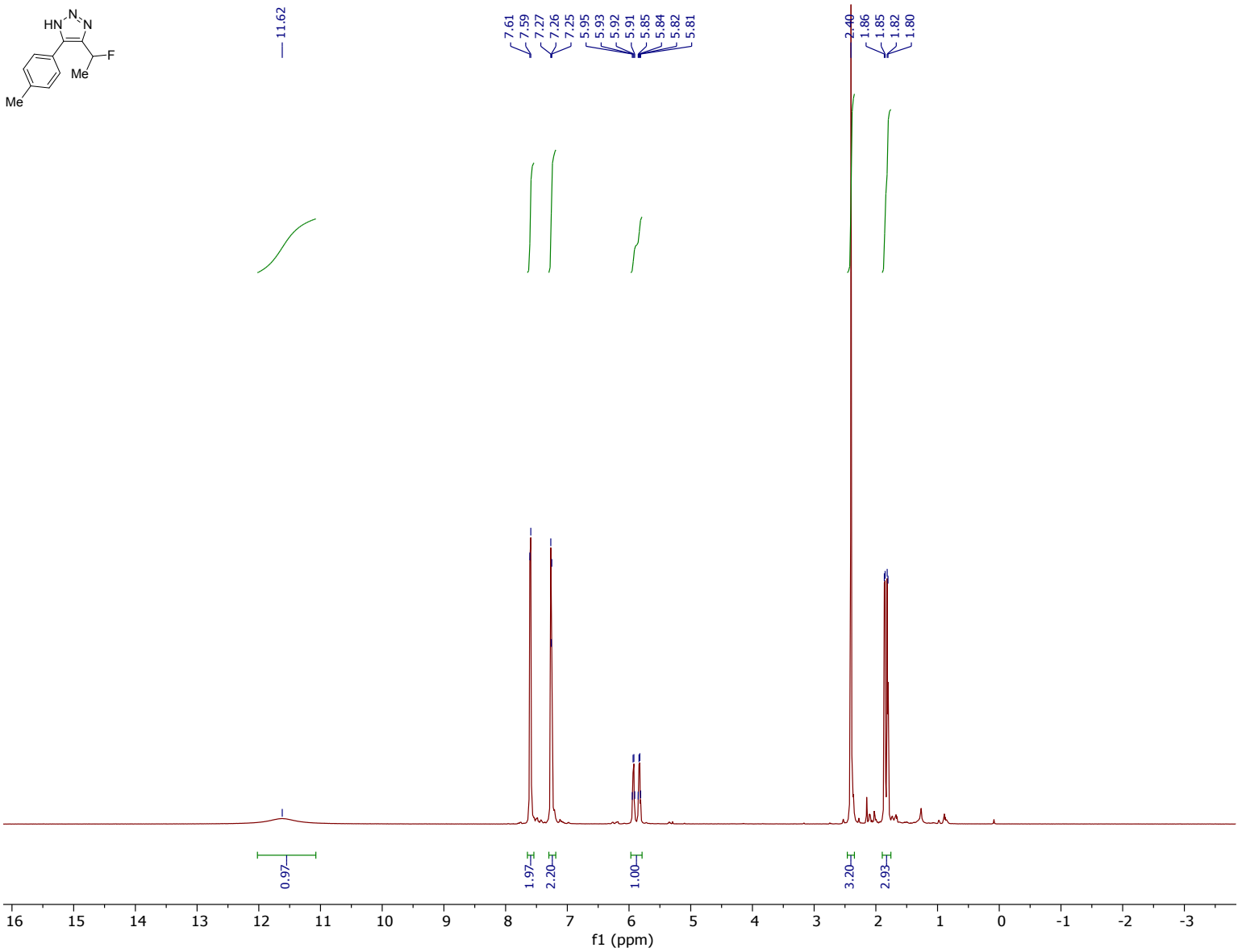
Compound **2b** 500 MHz ^{1}H NMR spectrum in C_6D_6



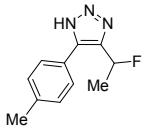
Compound **2b** 470 MHz ^{19}F NMR spectrum in C_6D_6



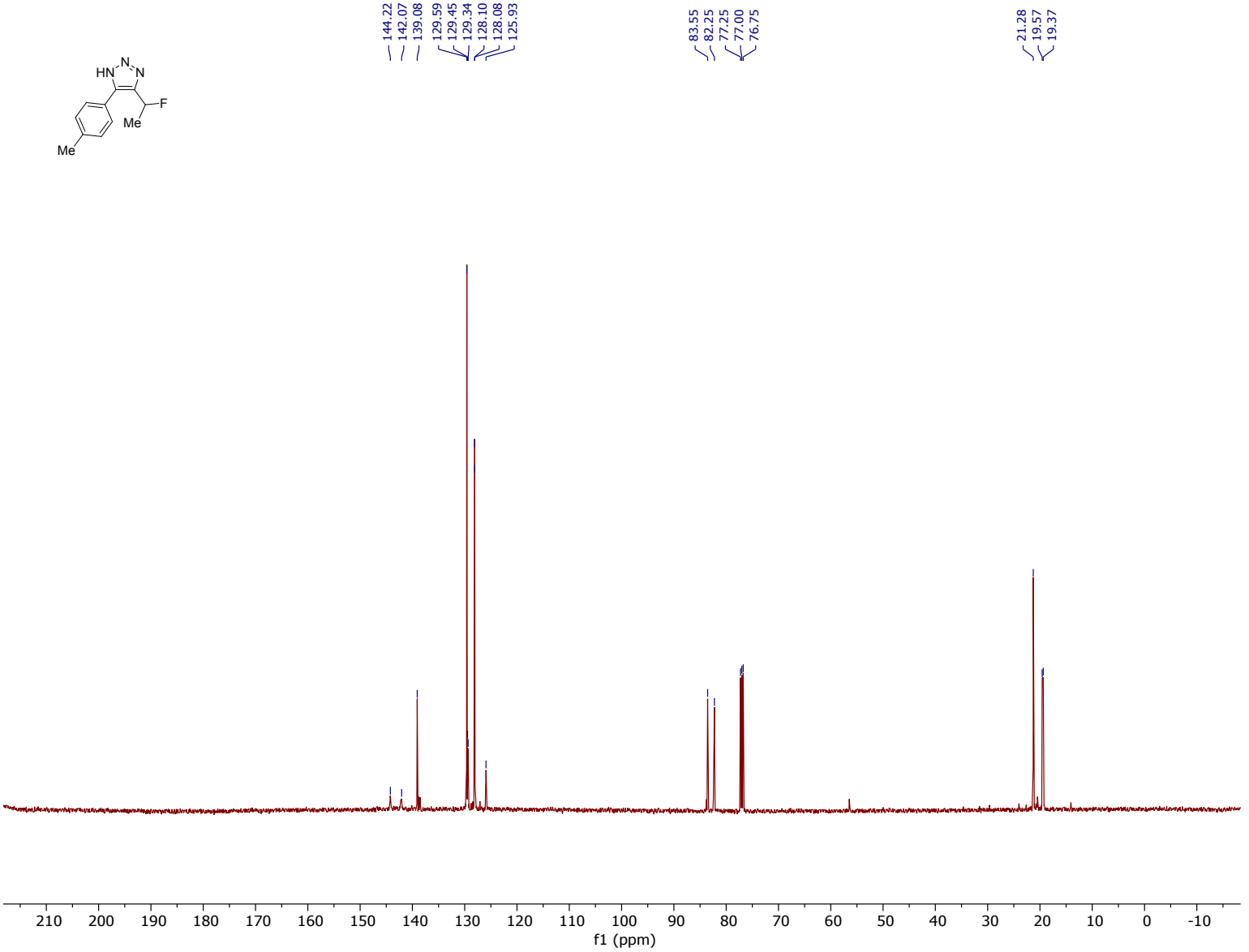
Compound **2b** 125 MHz ^{13}C NMR spectrum in C_6D_6



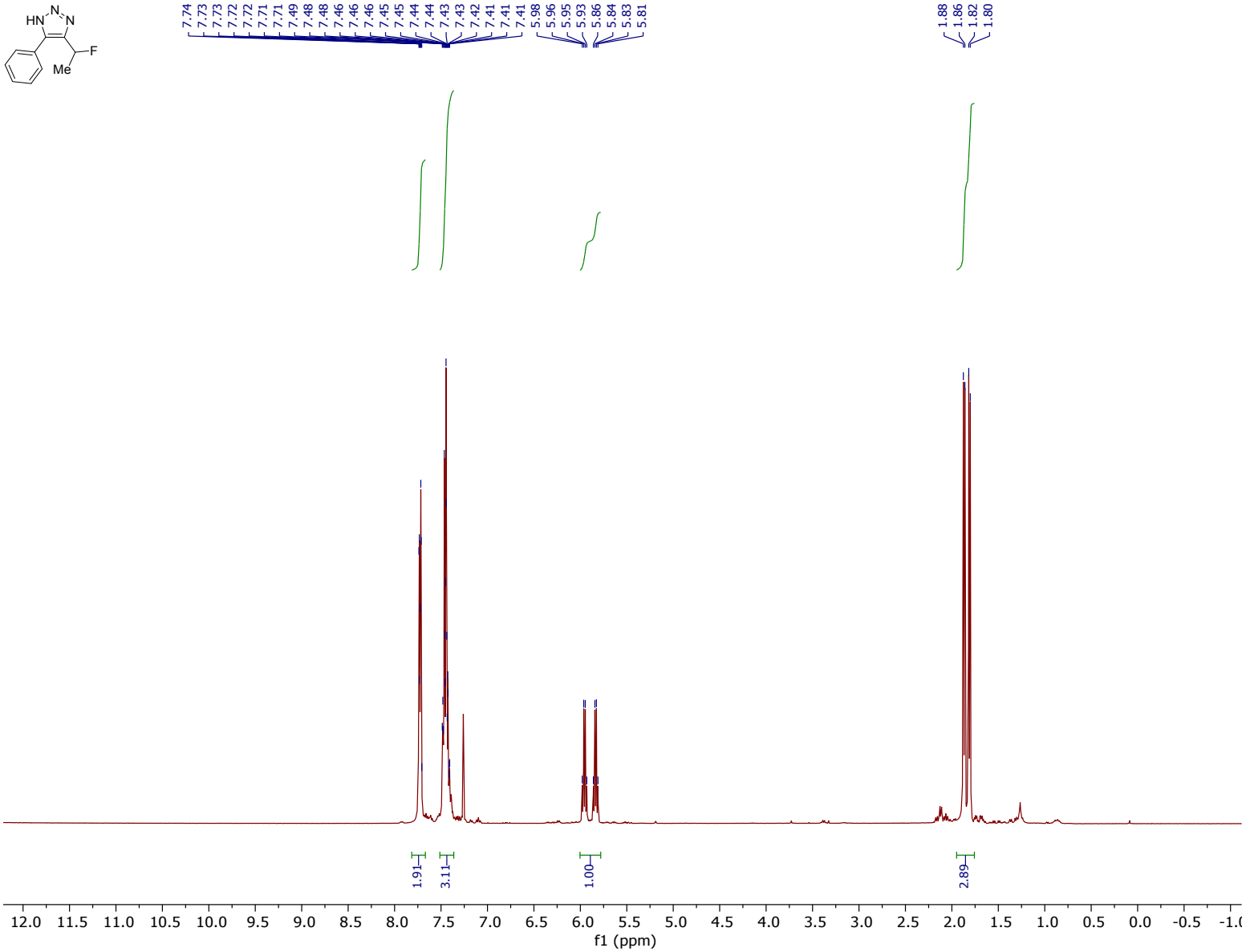
Compound **2c** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



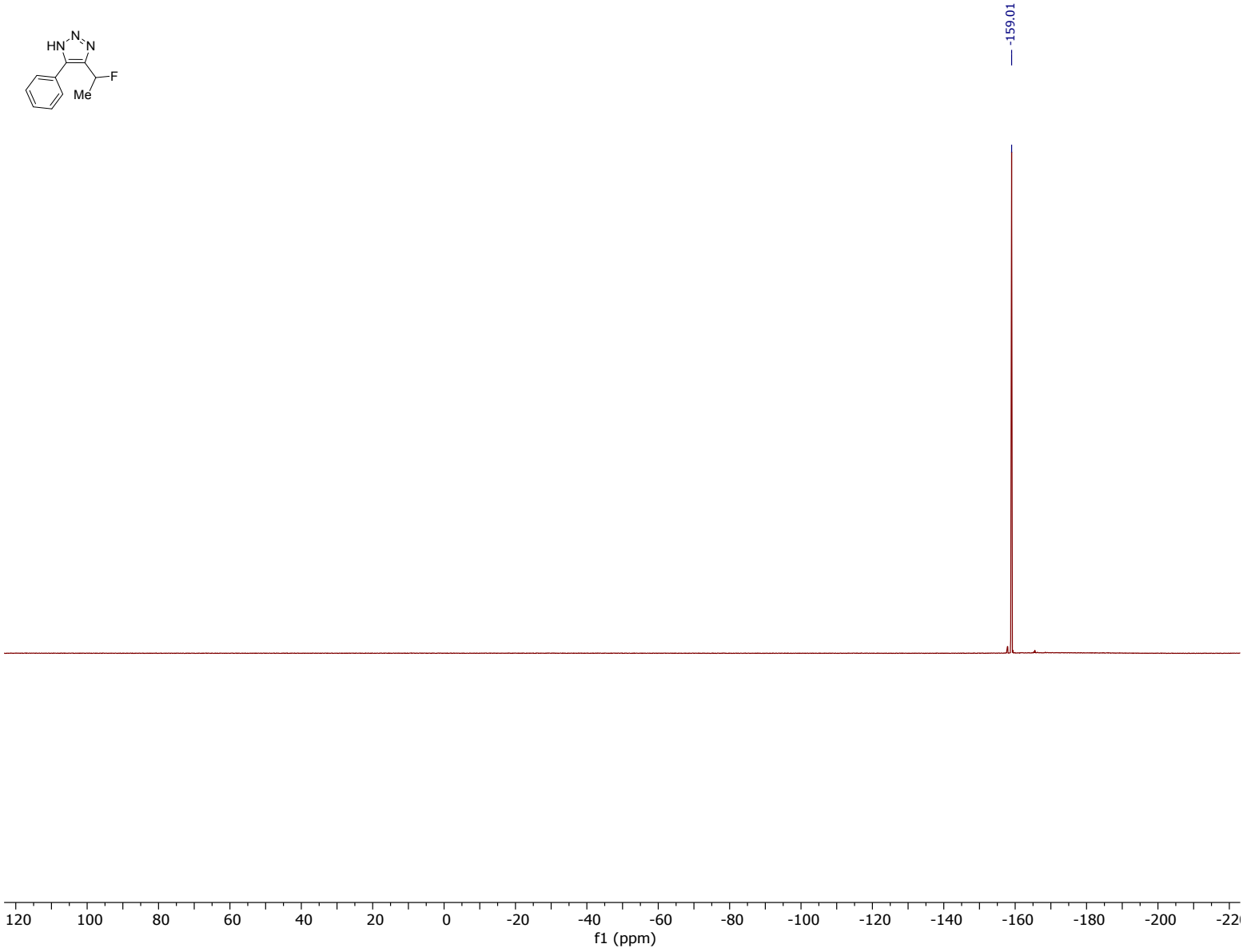
Compound **2c** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



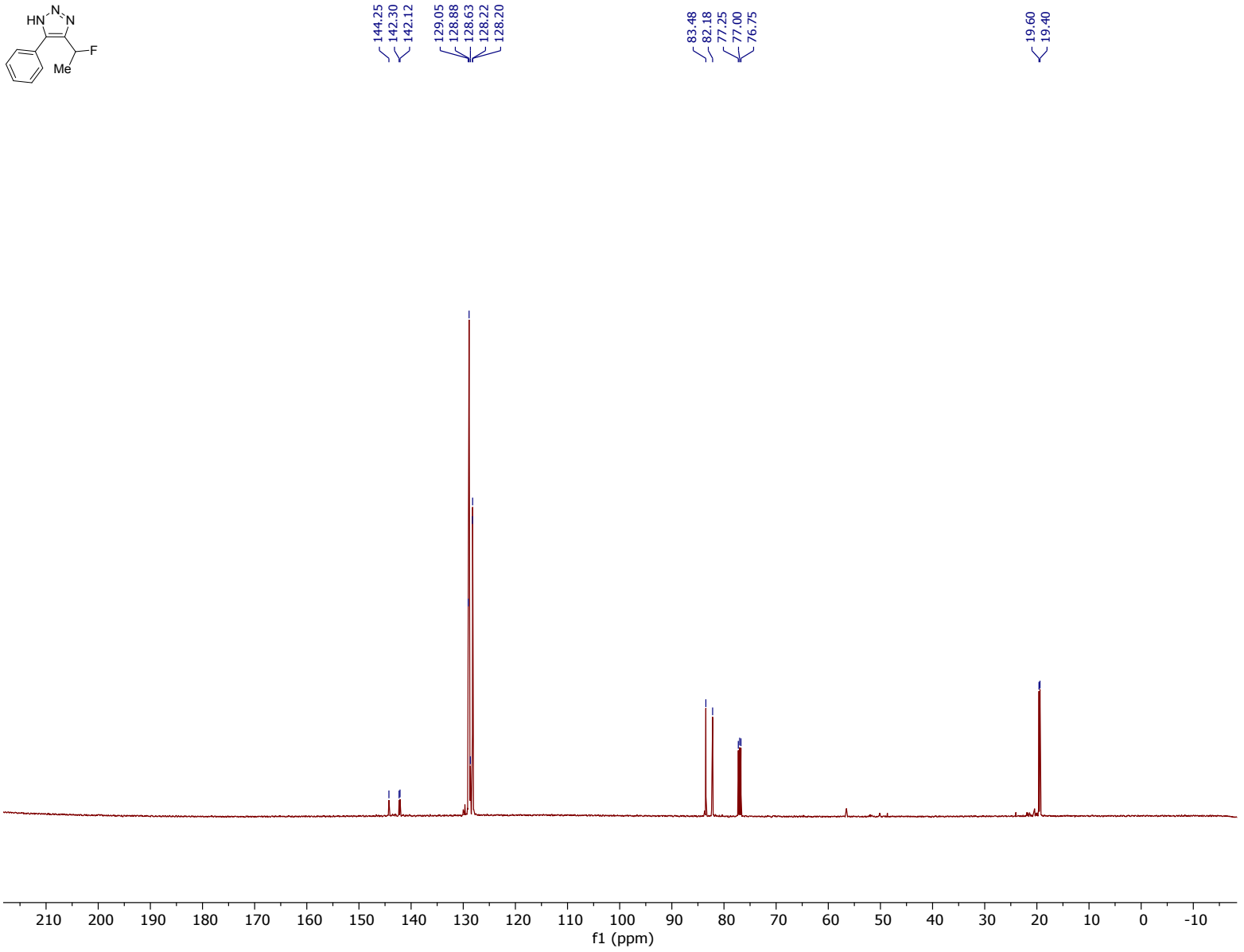
Compound **2c** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



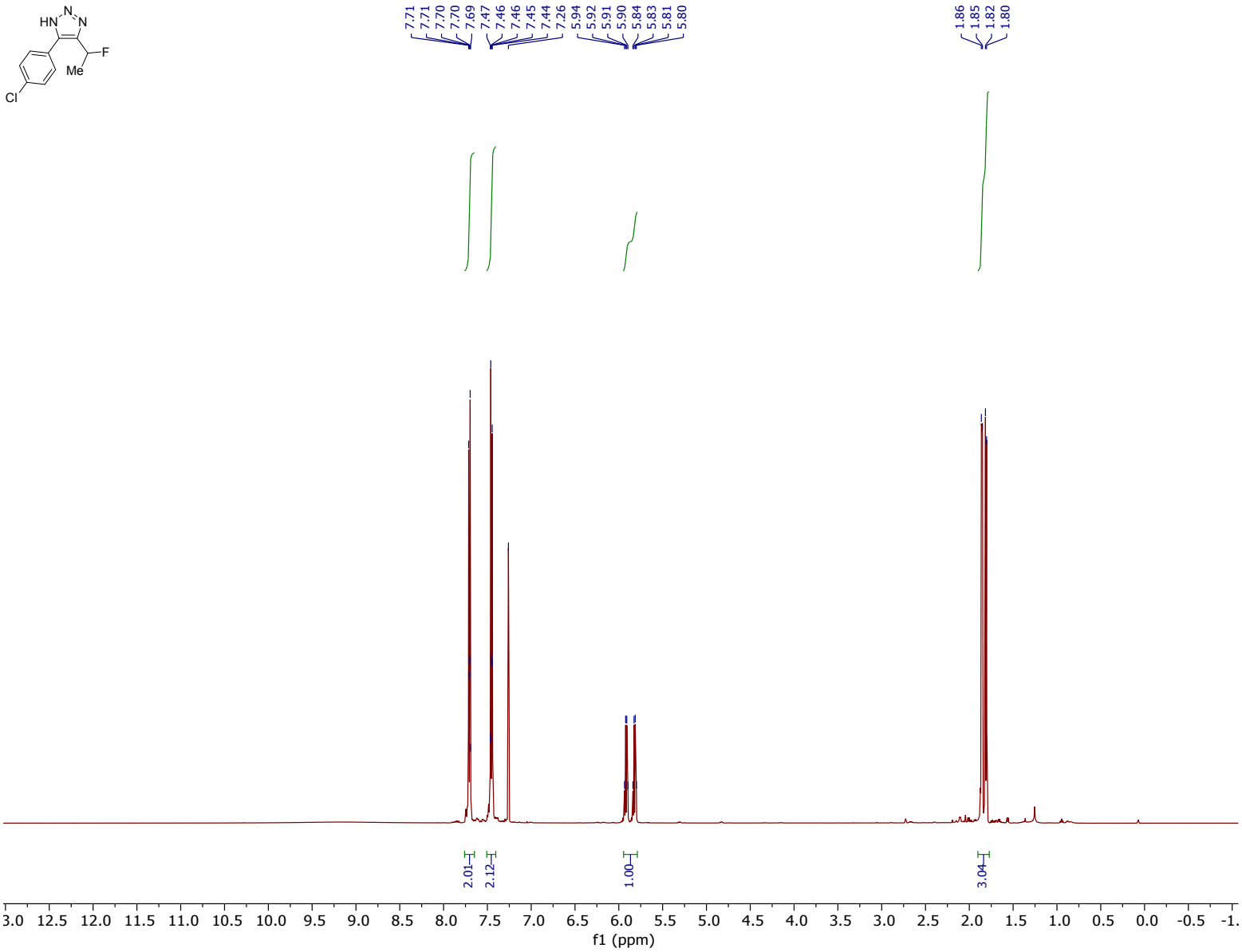
Compound **2d** 400 MHz ^{1}H NMR spectrum in $CDCl_3$



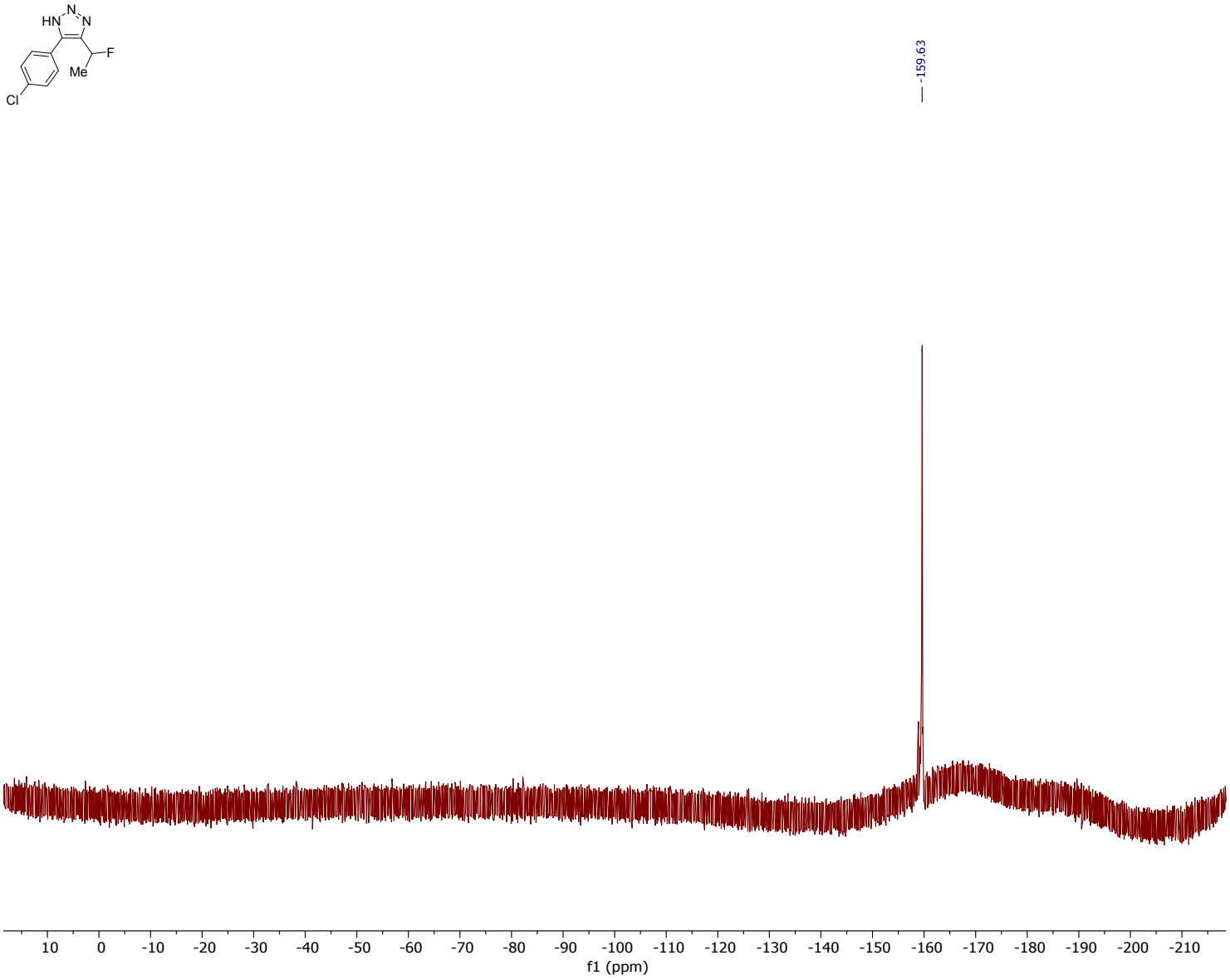
Compound **2d** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



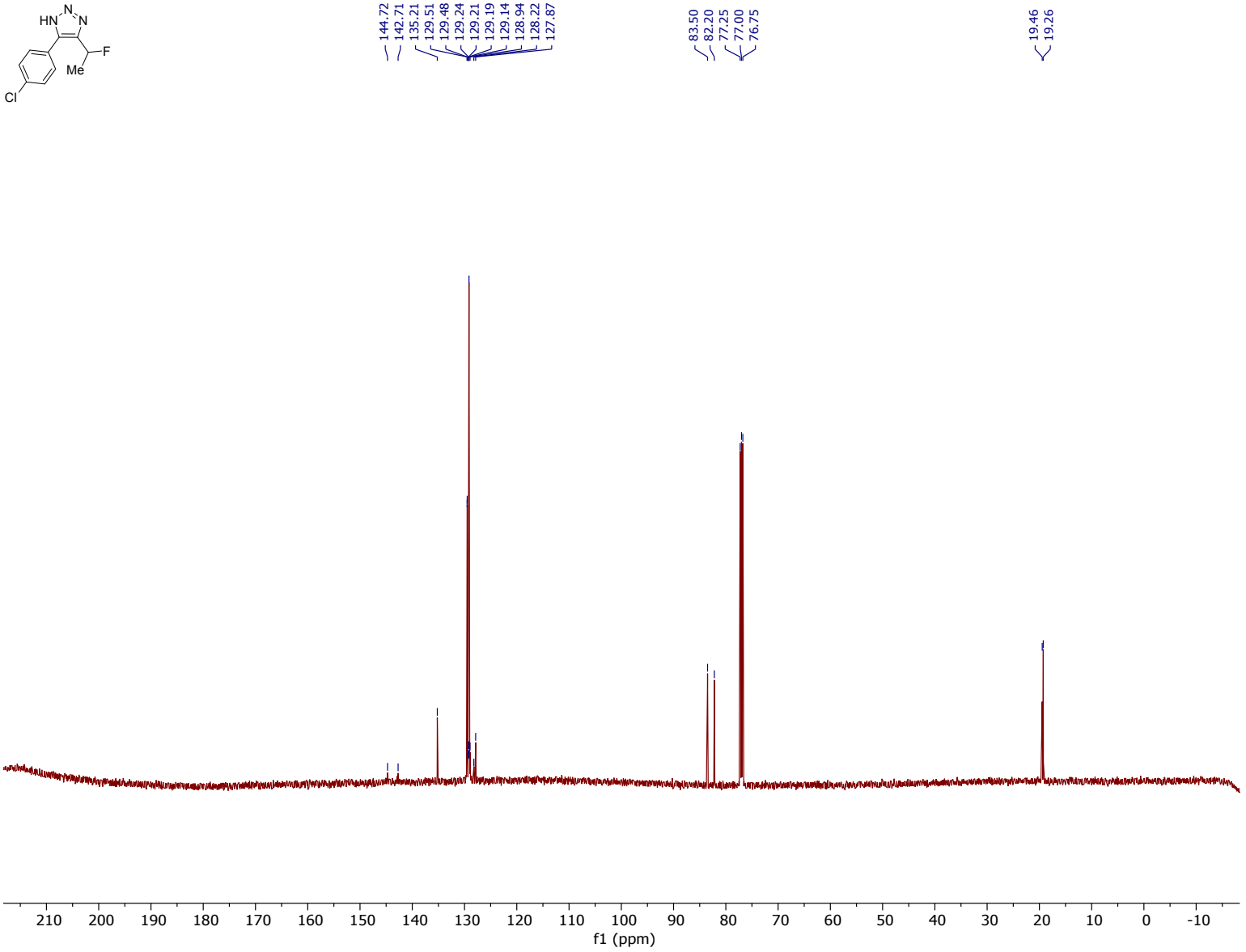
Compound **2d** 500MHz ^{13}C NMR spectrum in $CDCl_3$



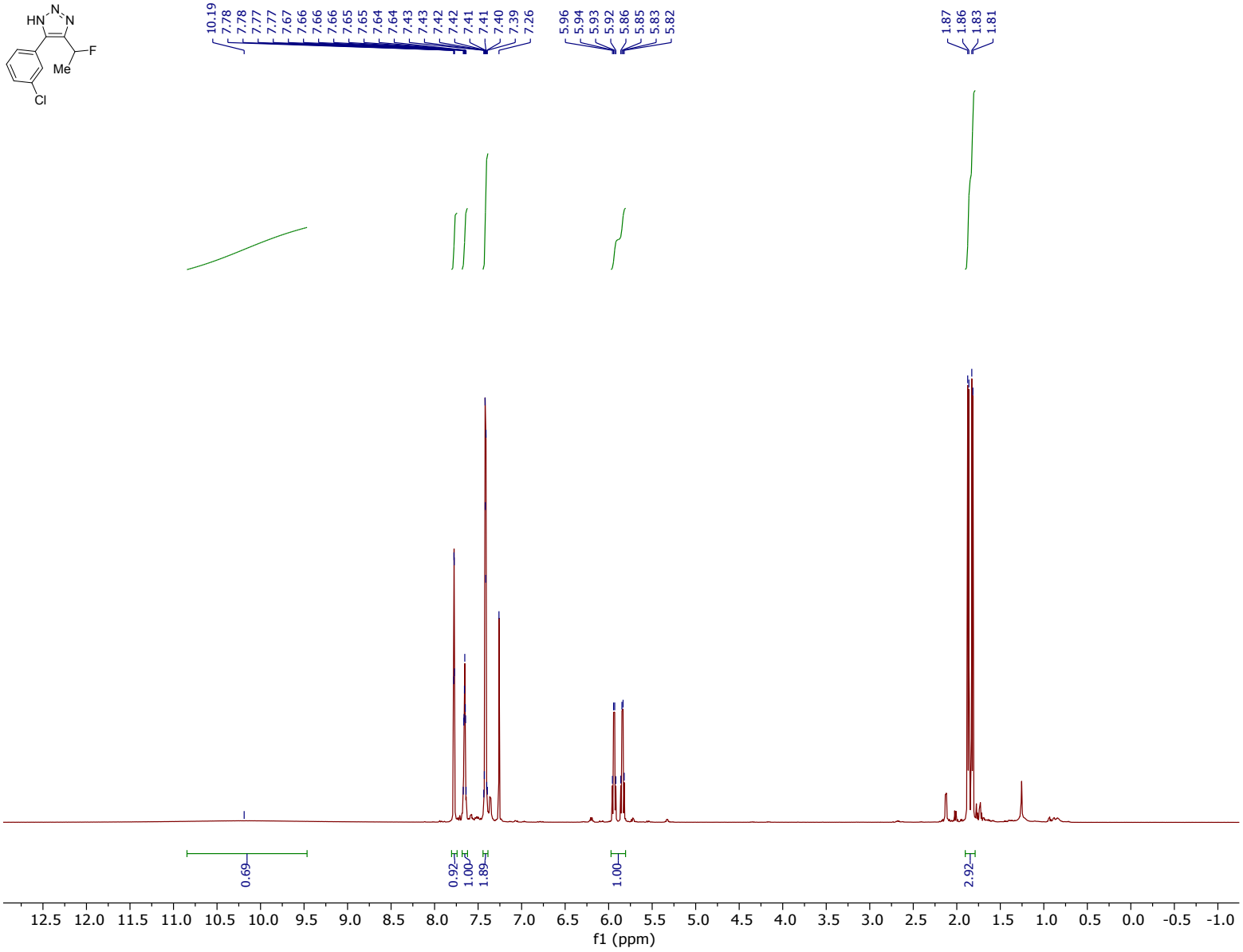
Compound **2e** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



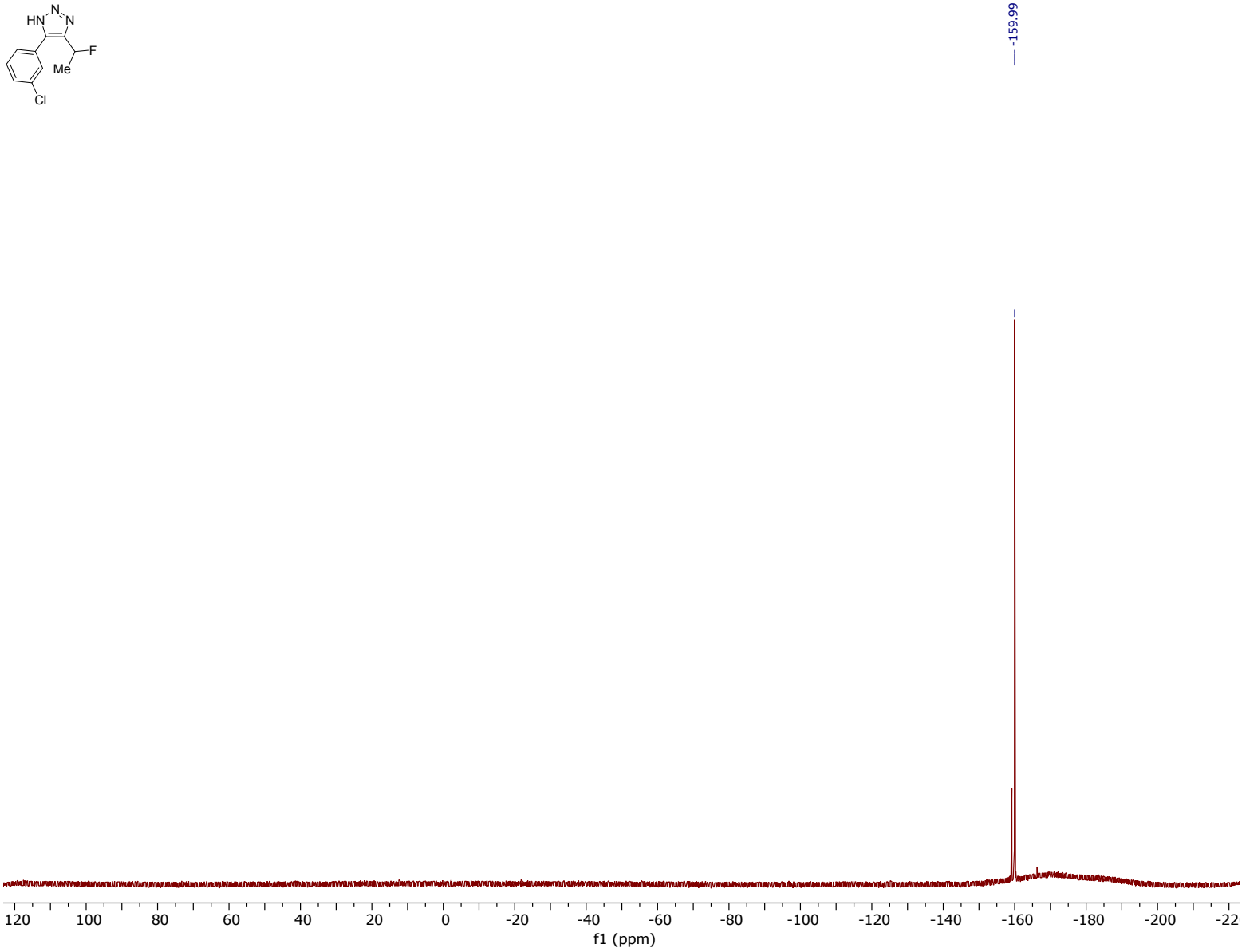
Compound **2e** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



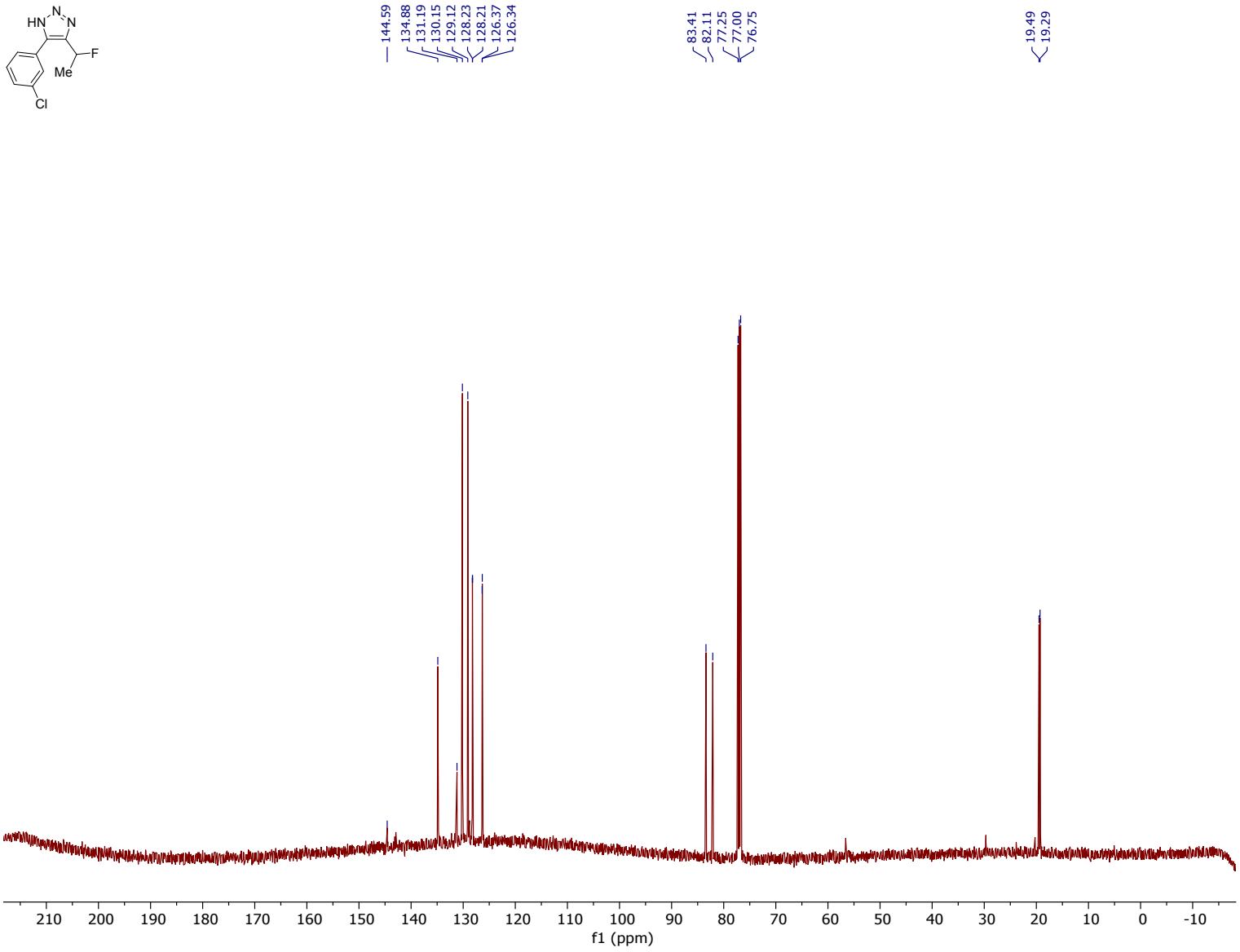
Compound **2e** 500MHz ^{13}C NMR spectrum in $CDCl_3$



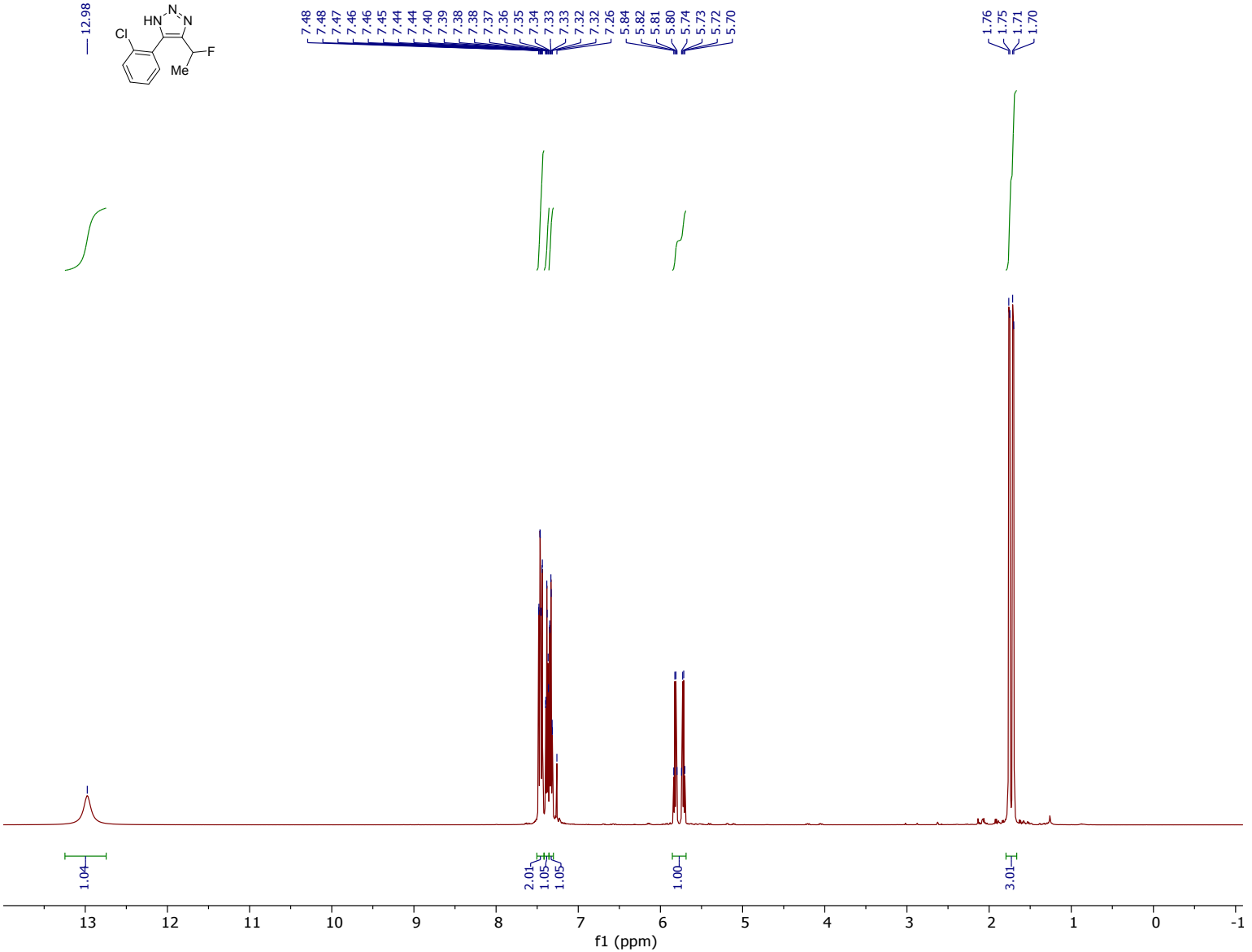
Compound **2f** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



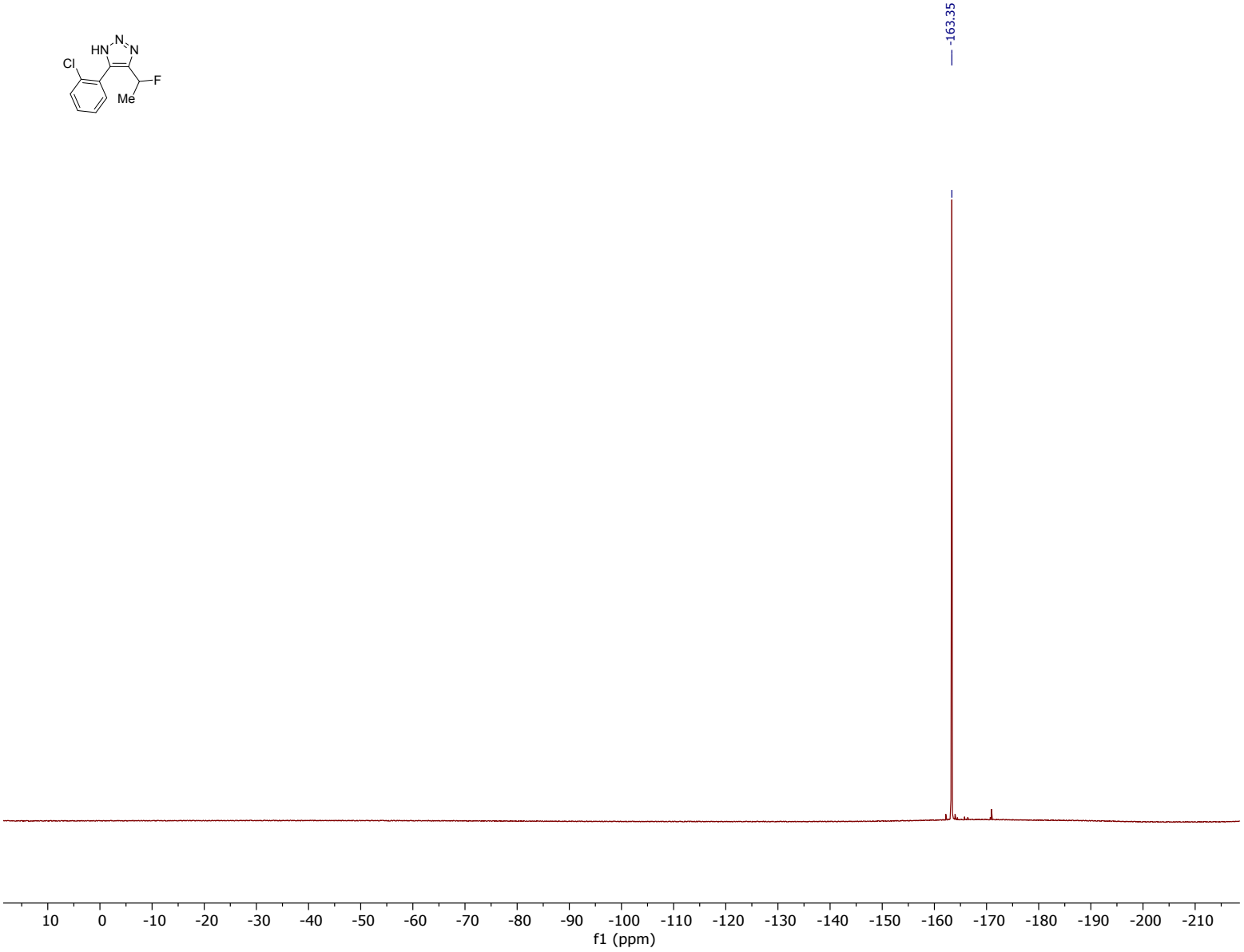
Compound **2f** 470 MHz ^{19}F NMR spectrum in $CDCl_3$



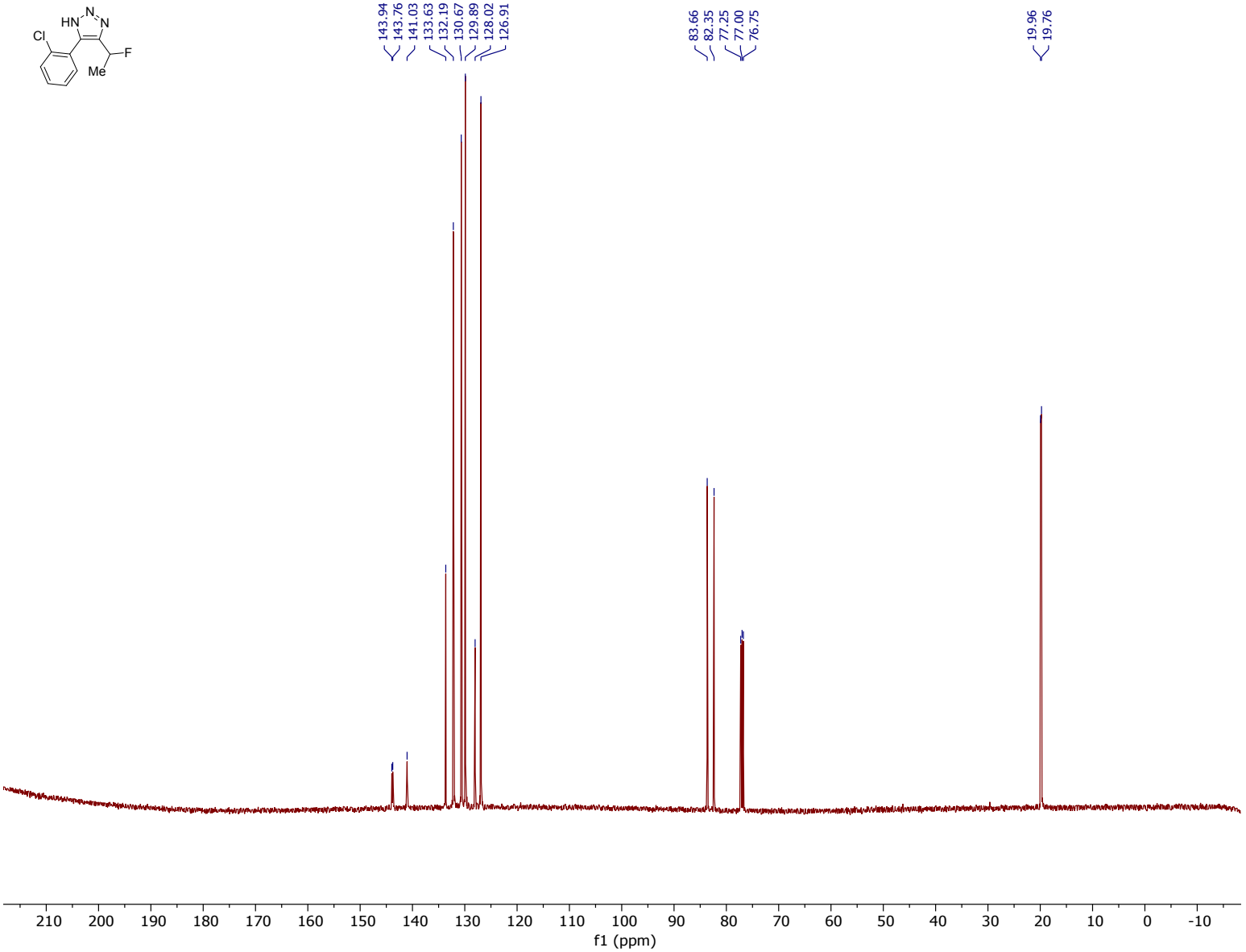
Compound **2f** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



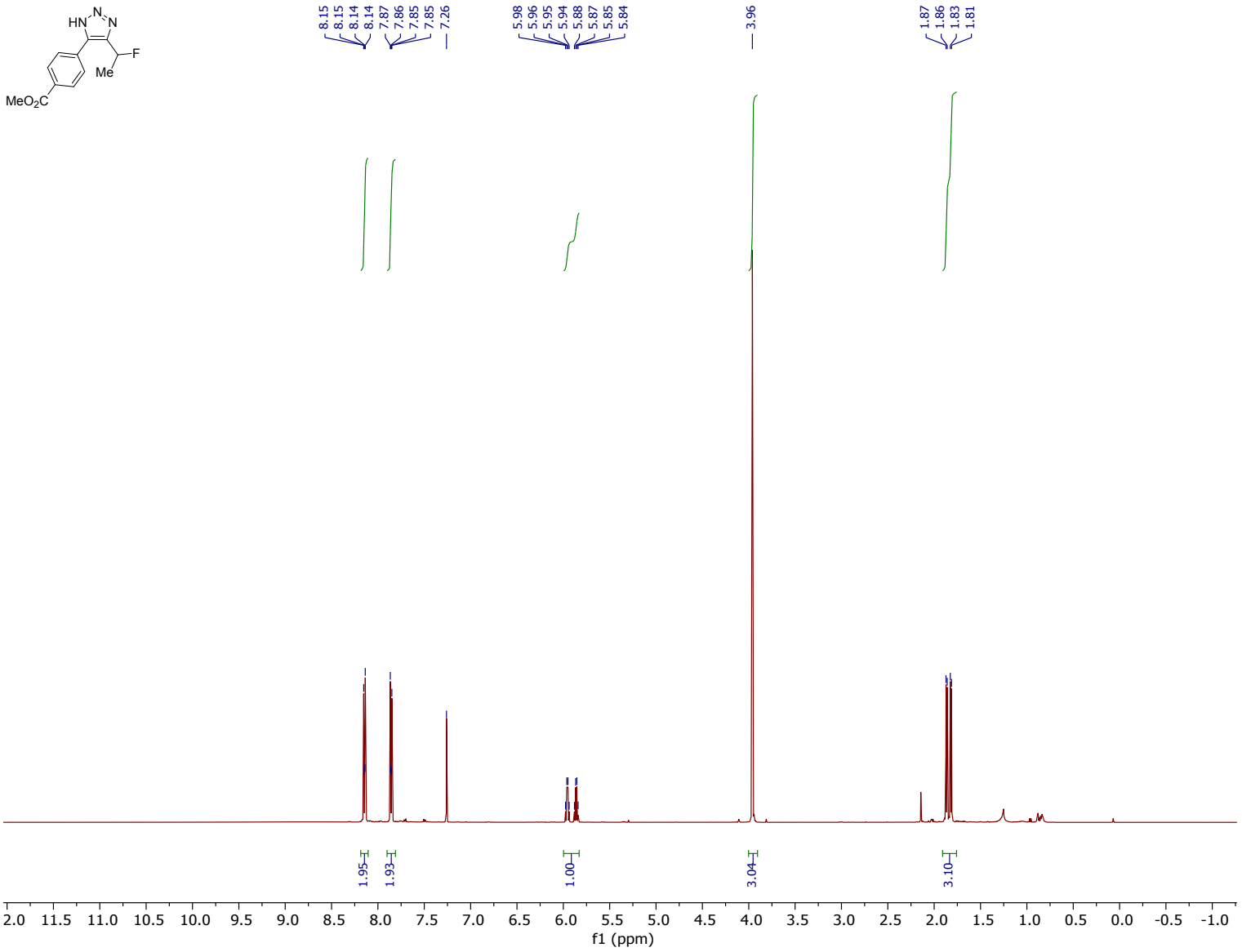
Compound **2g** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



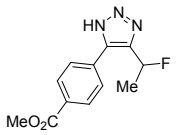
Compound **2g** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



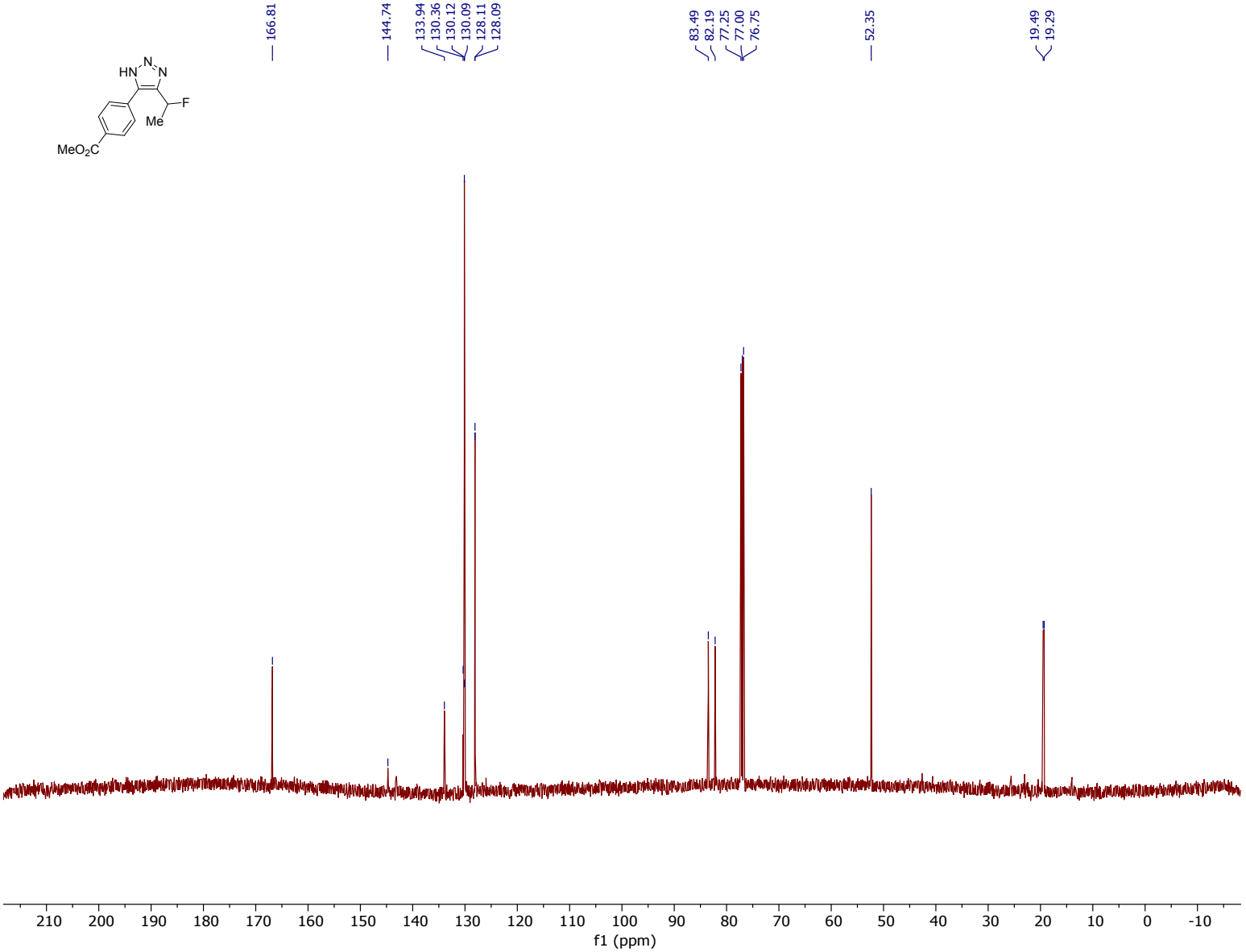
Compound **2g** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



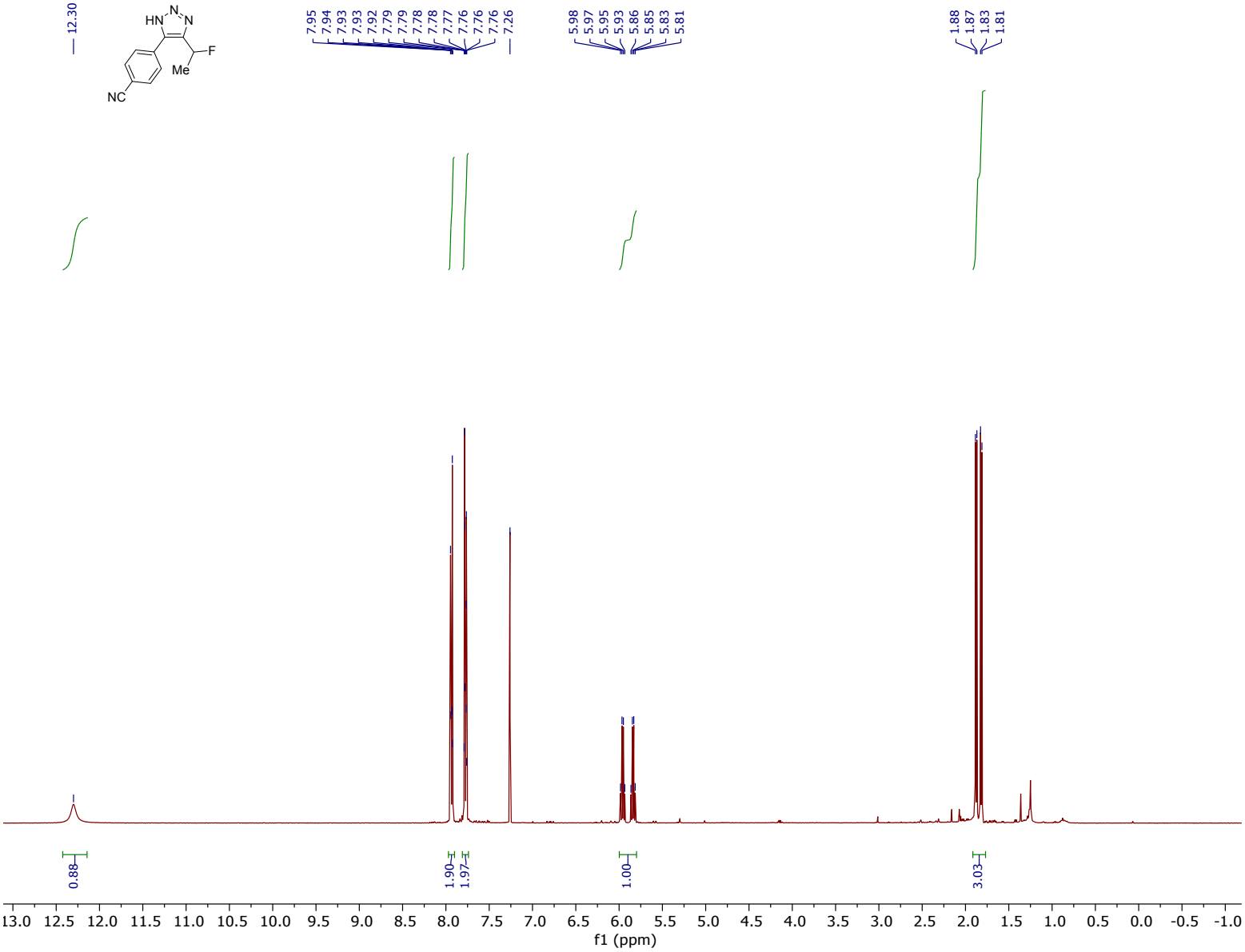
Compound **2h** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



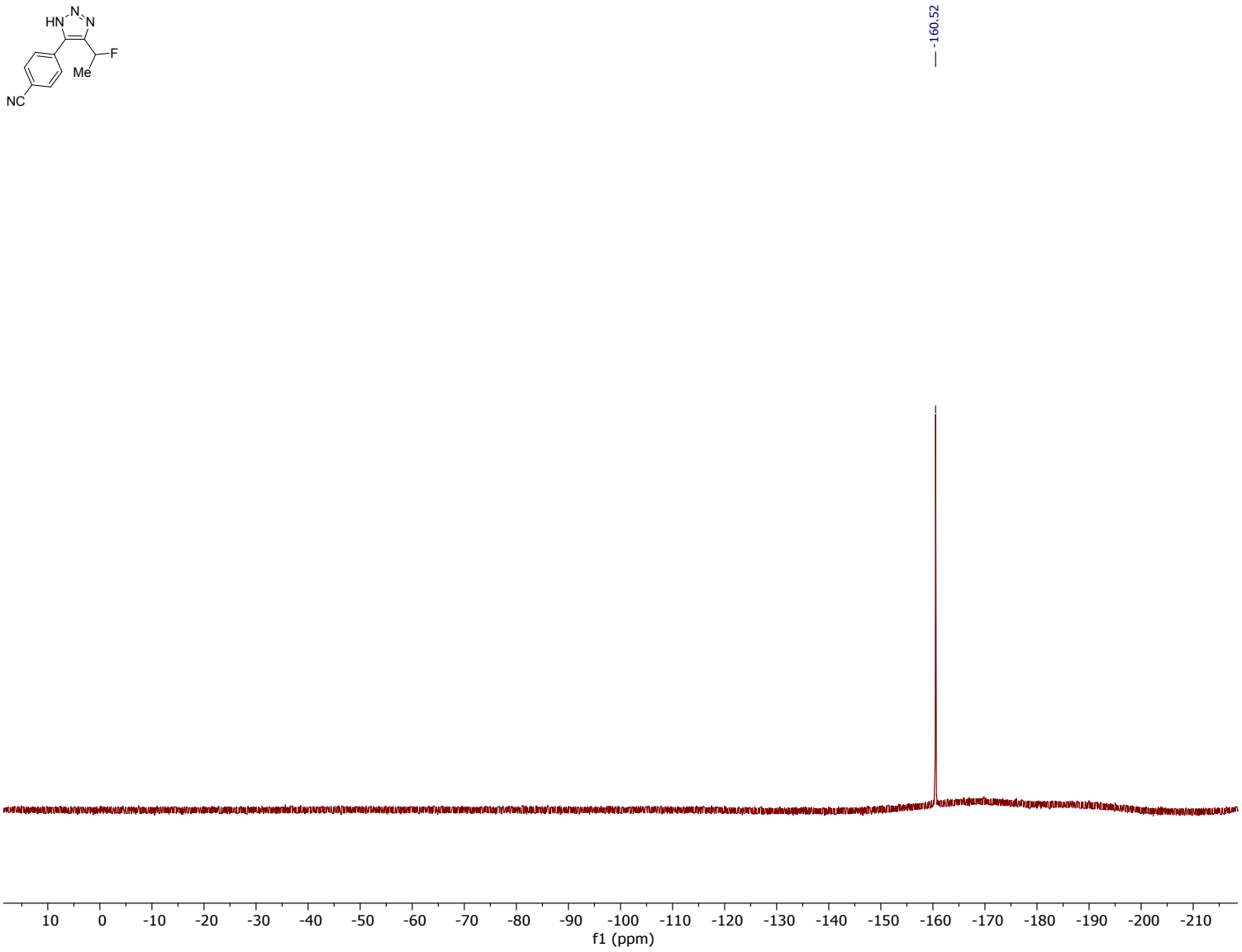
Compound **2h** 376 MHz ^{19}F spectrum in $CDCl_3$



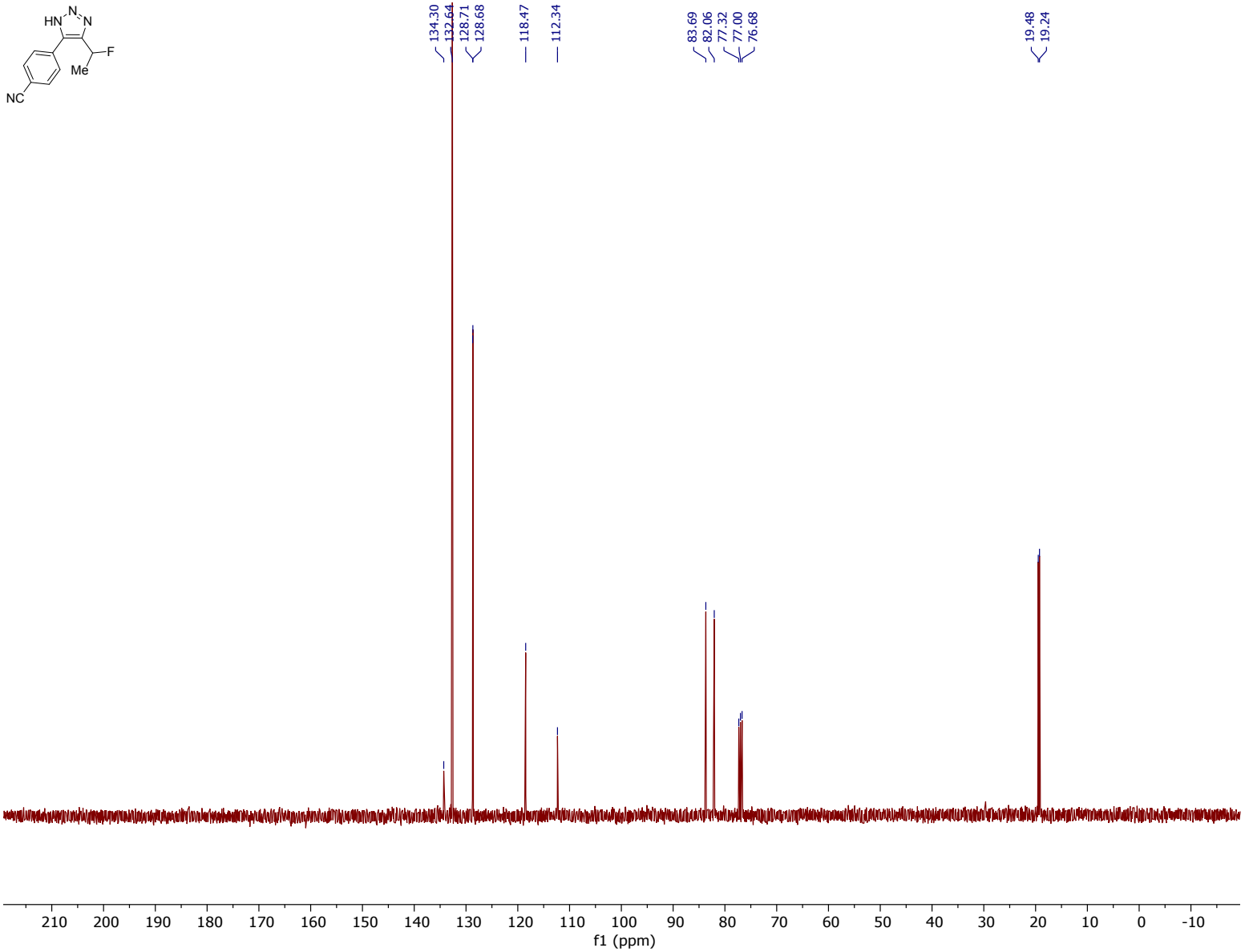
Compound **2h** 125 MHz ^{13}C NMR spectrum in$CDCl_3$



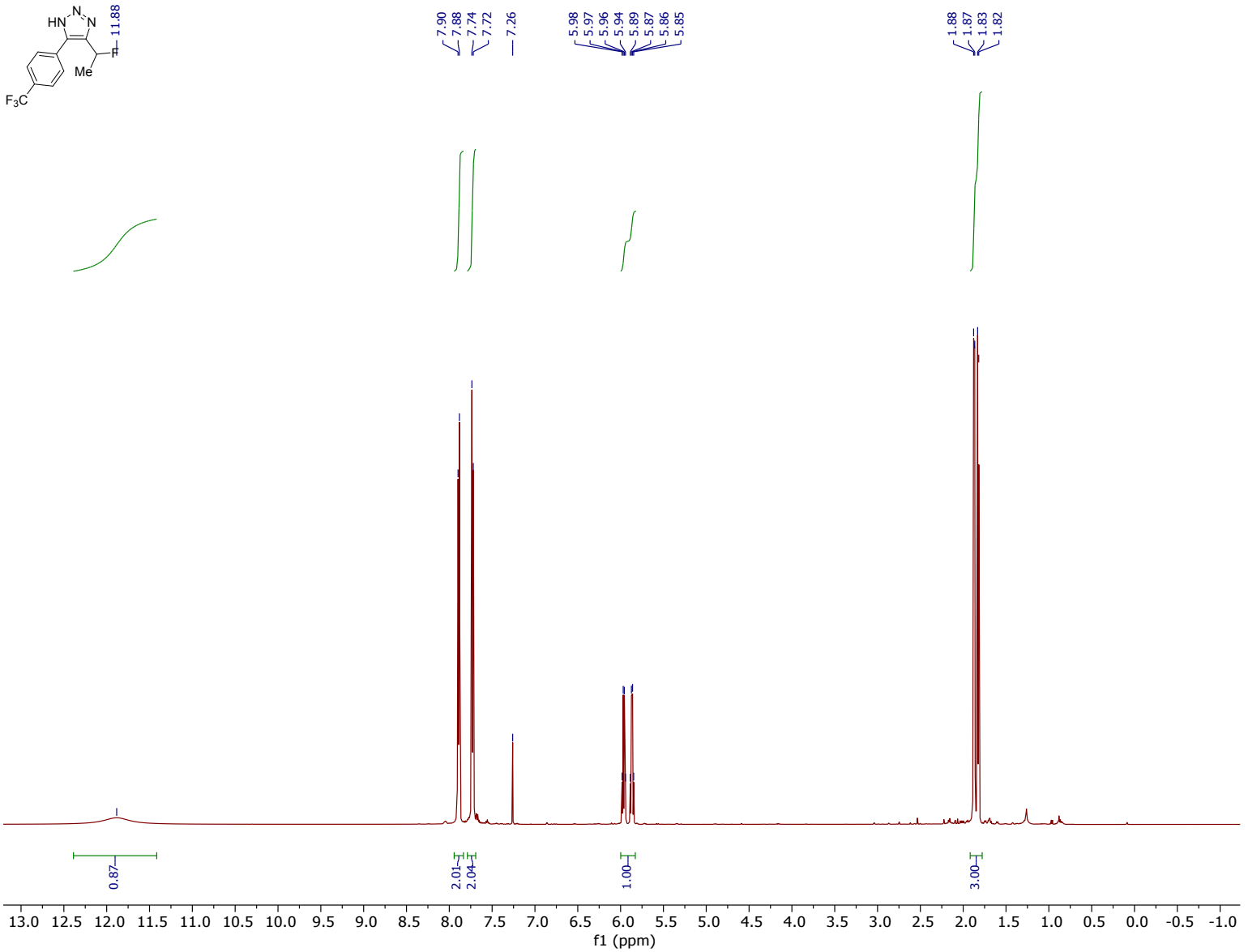
Compound **2i** 400 MHz ^{1}H NMR spectrum in $CDCl_3$



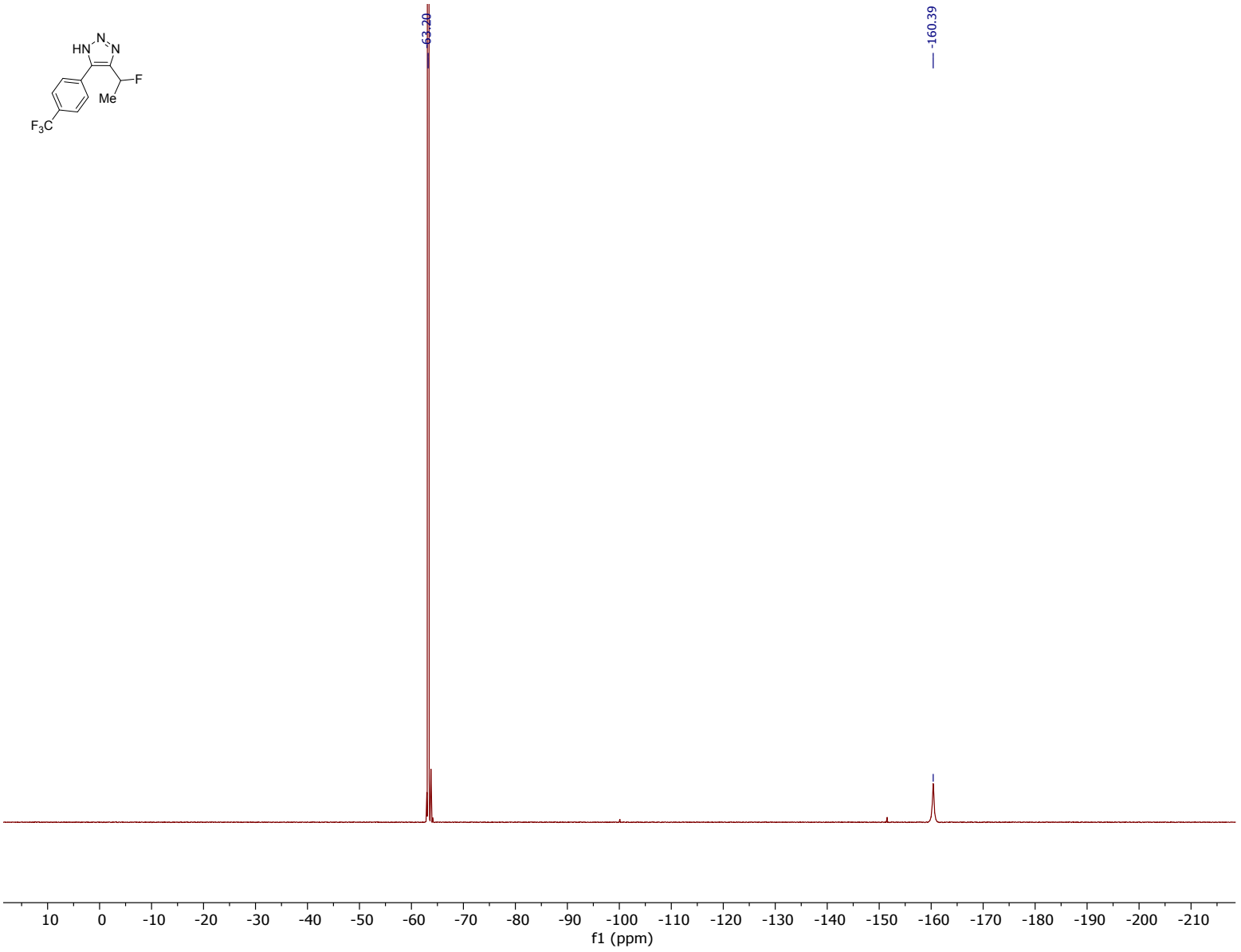
Compound **2i** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



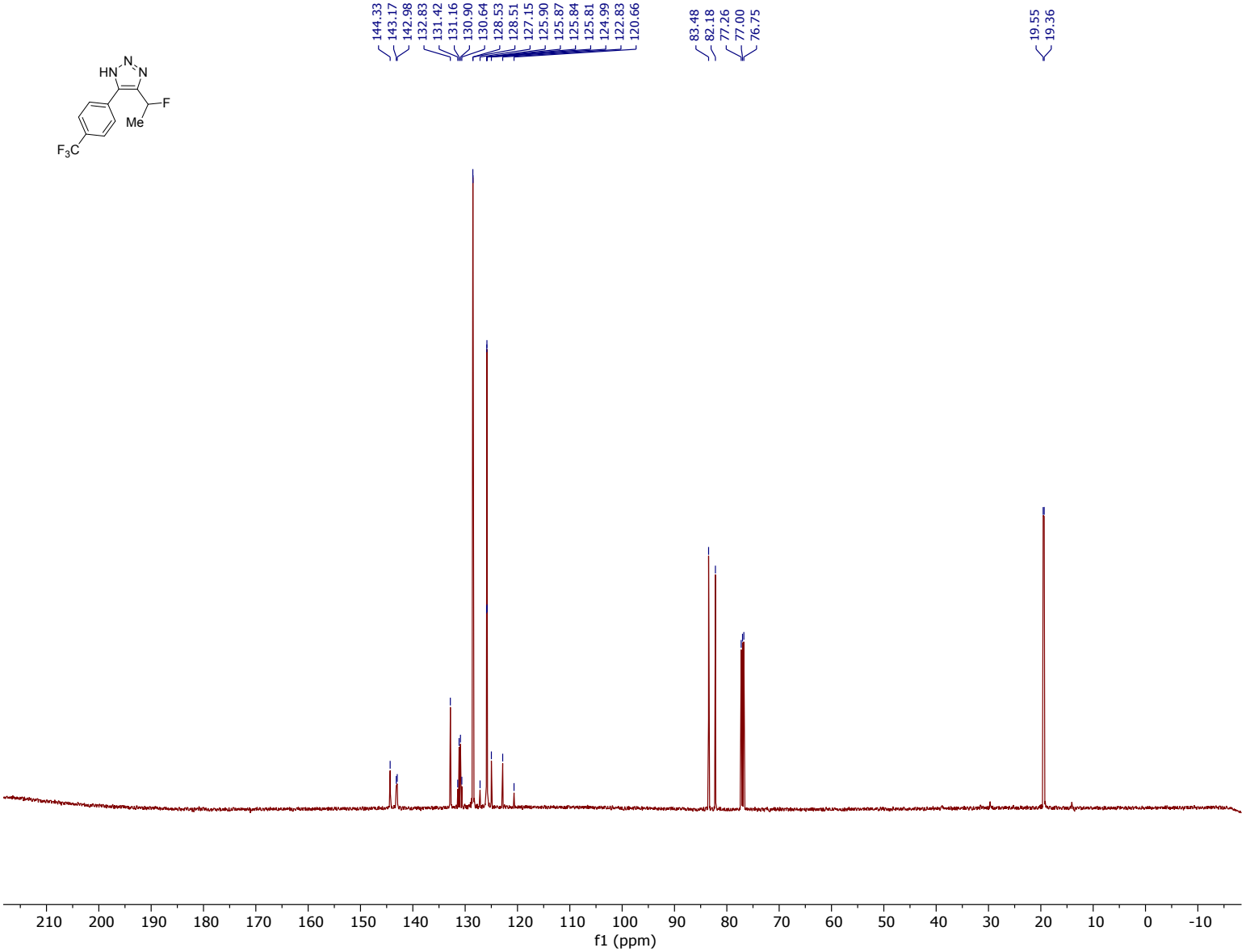
Compound **2i** 100 MHz ^{13}C NMR spectrum in $CDCl_3$



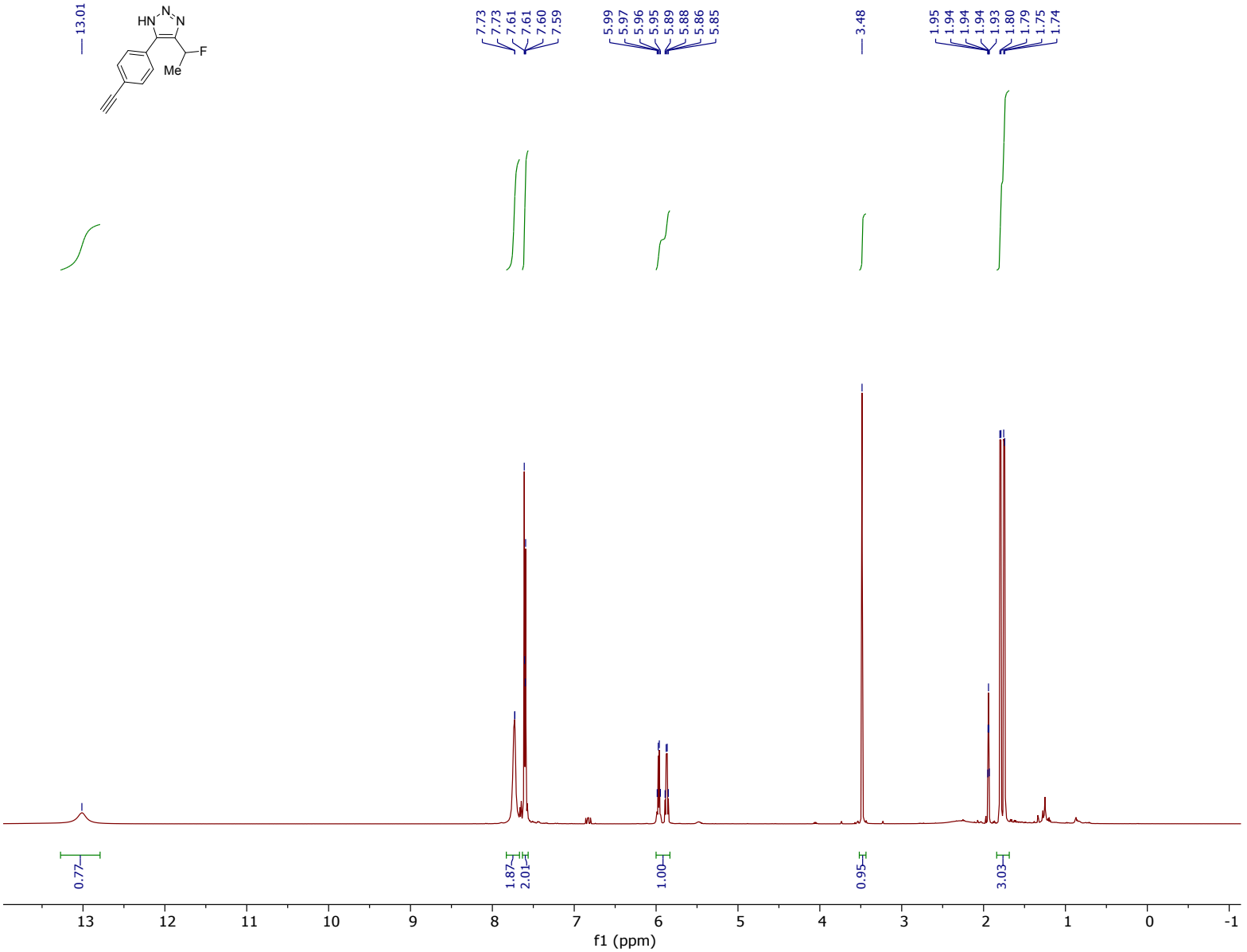
Compound **2j** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



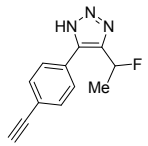
Compound **2j** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



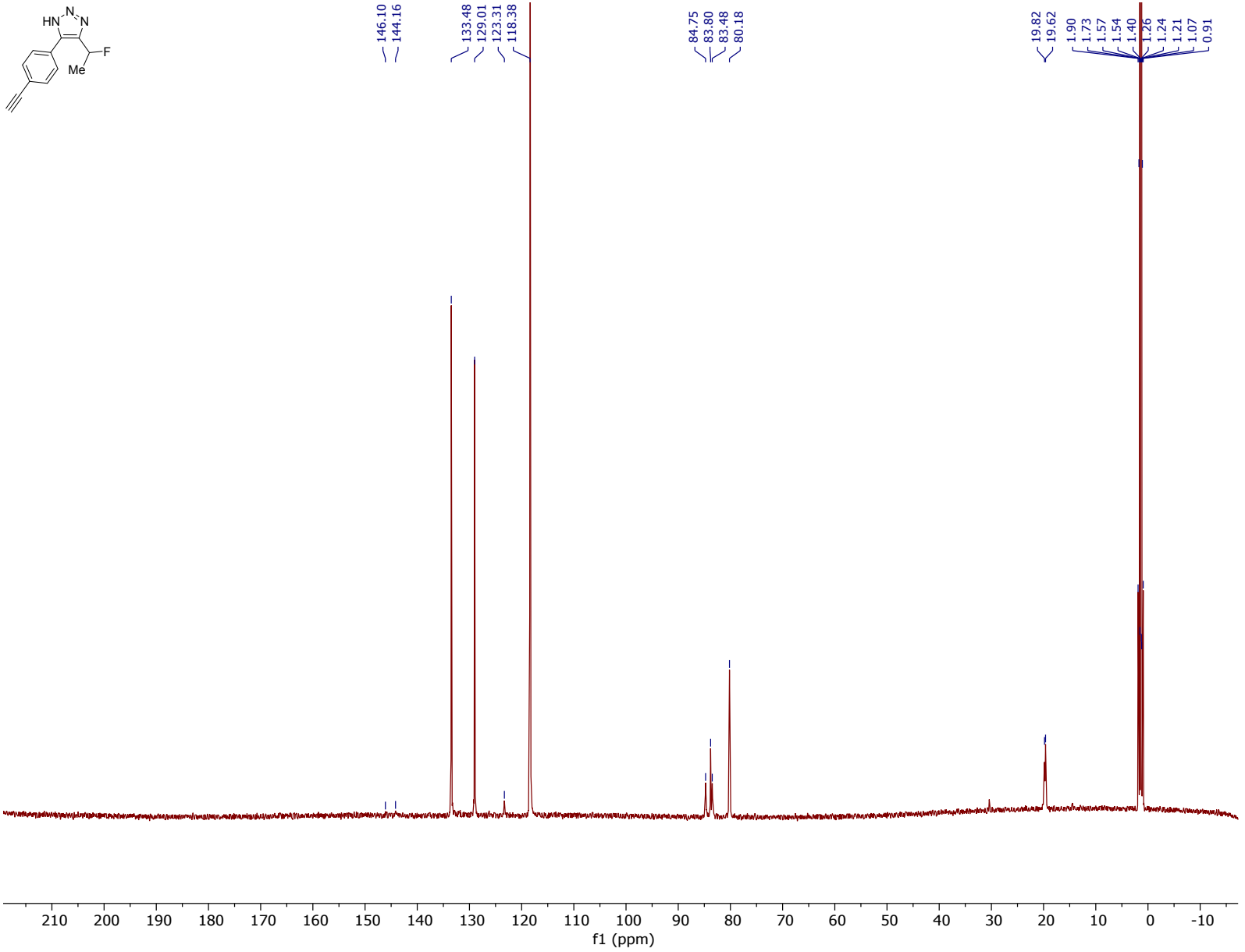
Compound **2j** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



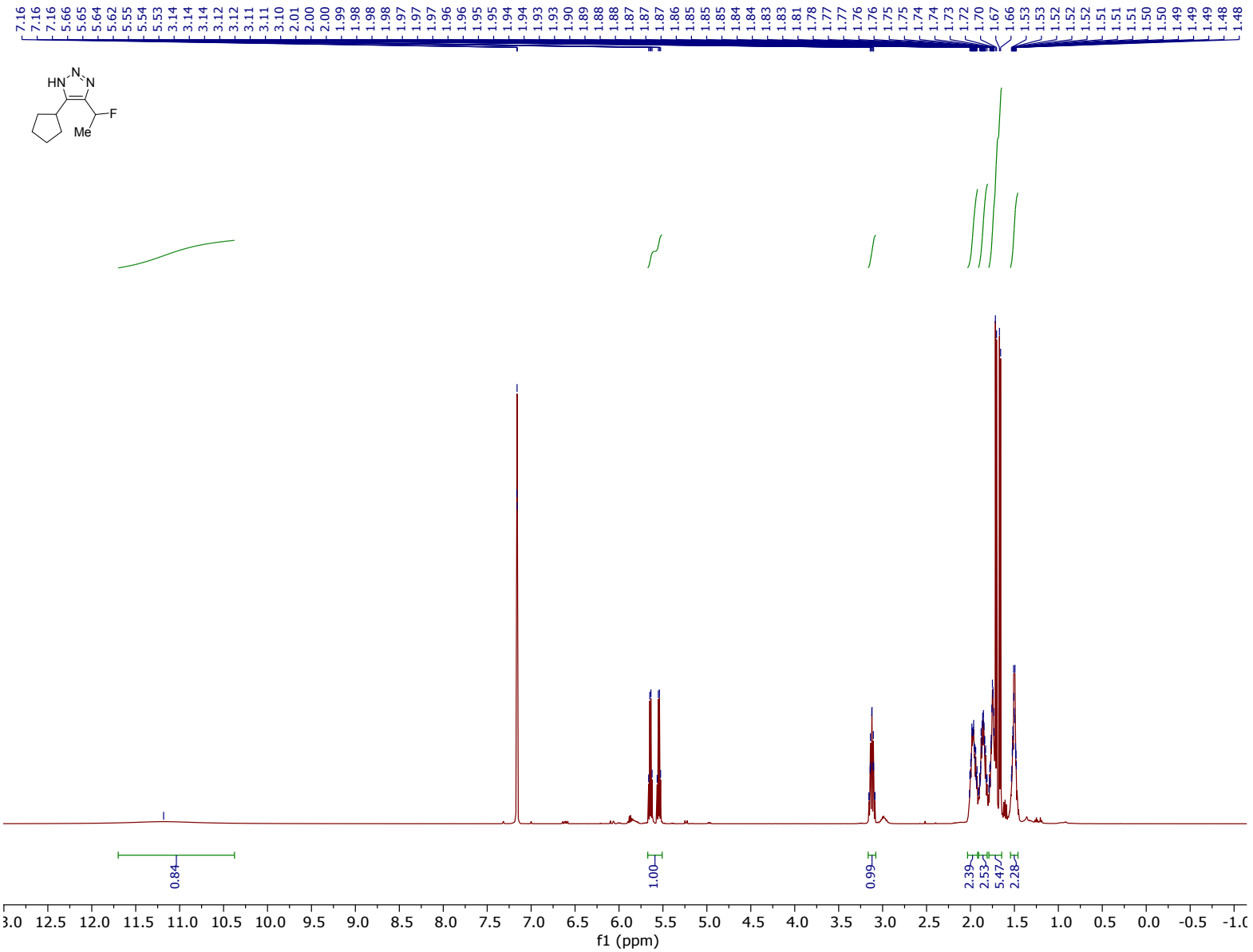
Compound **2k** 500 MHz ^{1}H NMR spectrum in CD_3CN



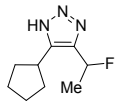
Compound **2k** 376 MHz ^{19}F NMR spectrum in CD_3CN



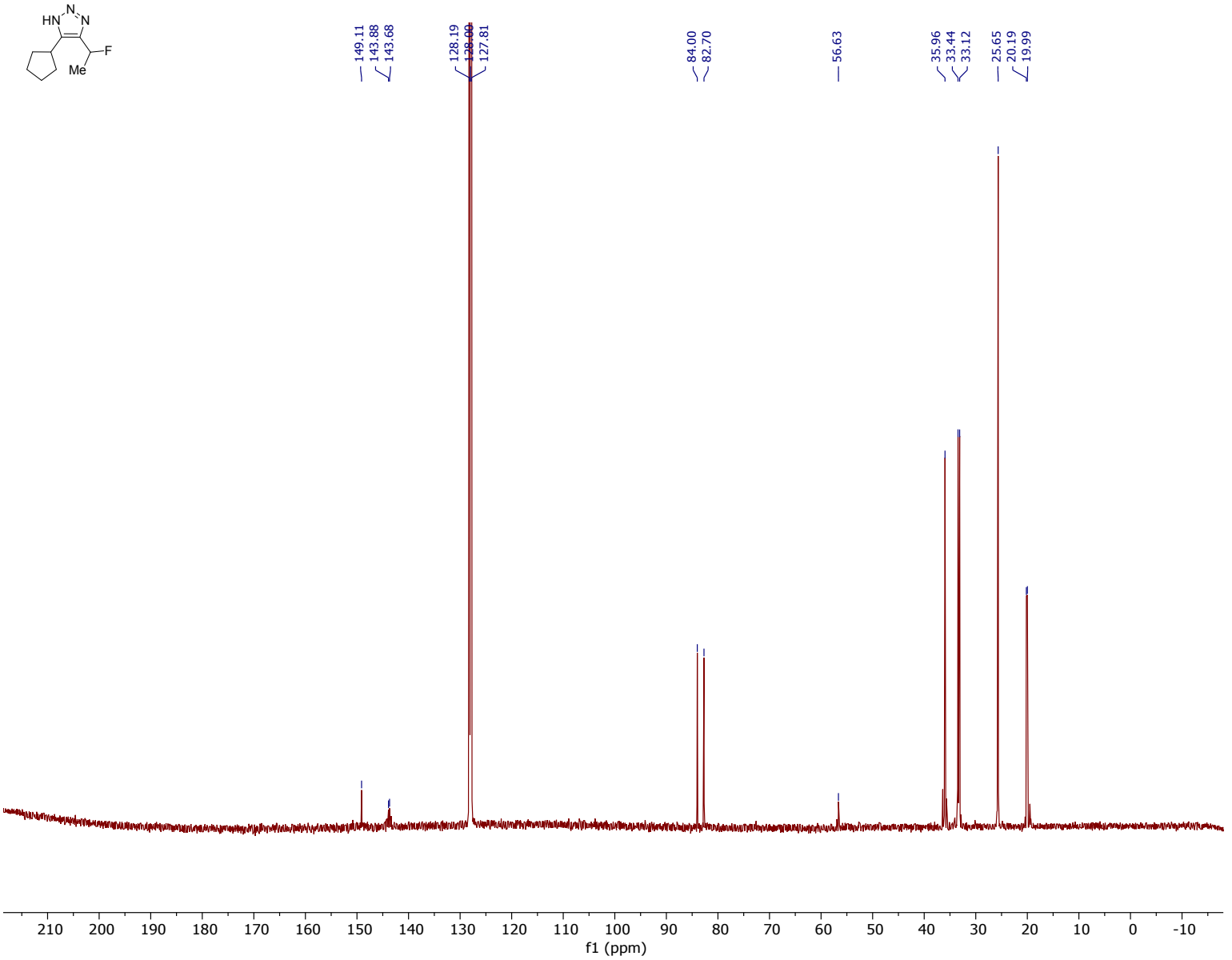
Compound **2k** 125 MHz ^{13}C NMR spectrum in CD_3CN



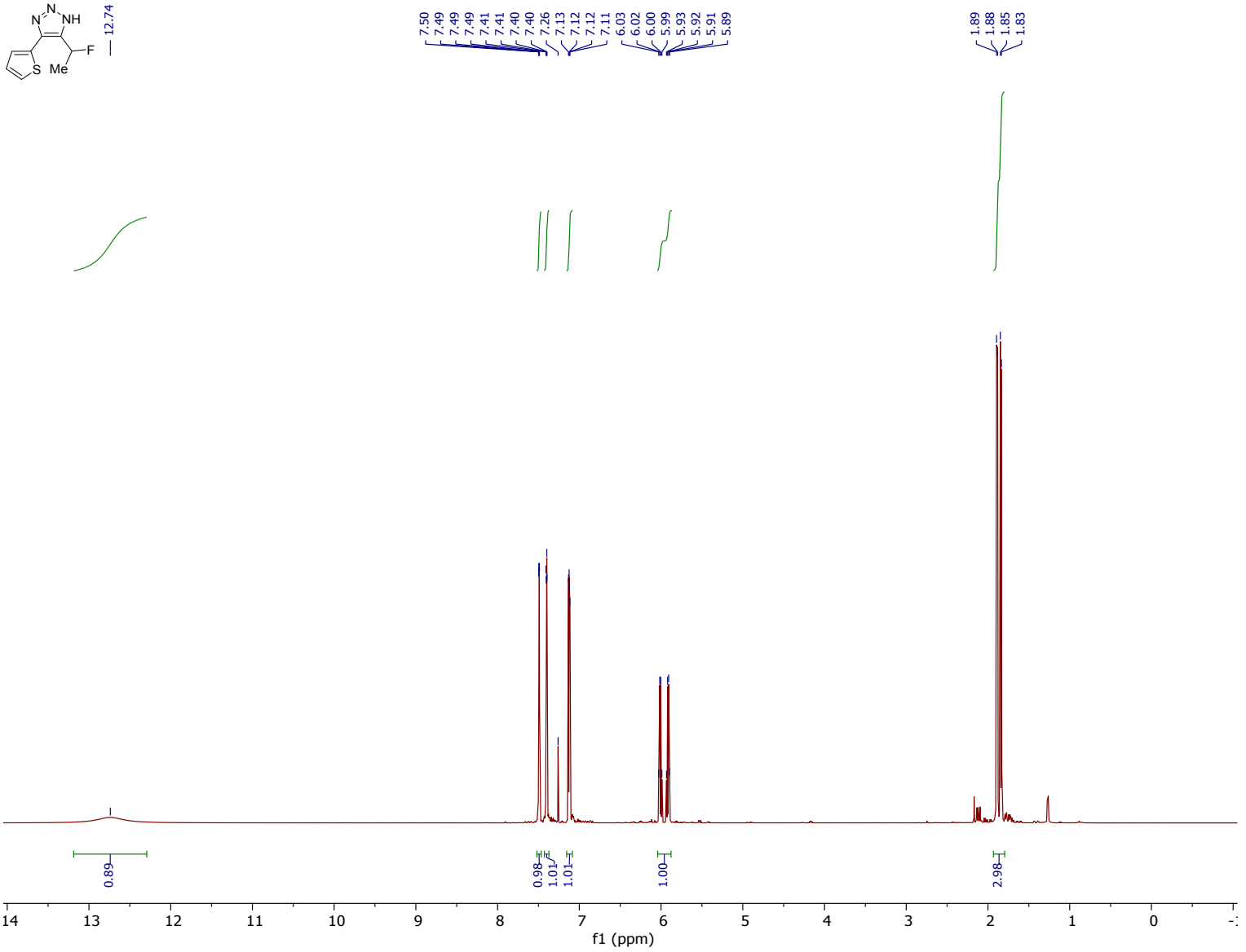
Compound **2l** 500 MHz ^{1}H NMR spectrum in C_6D_6



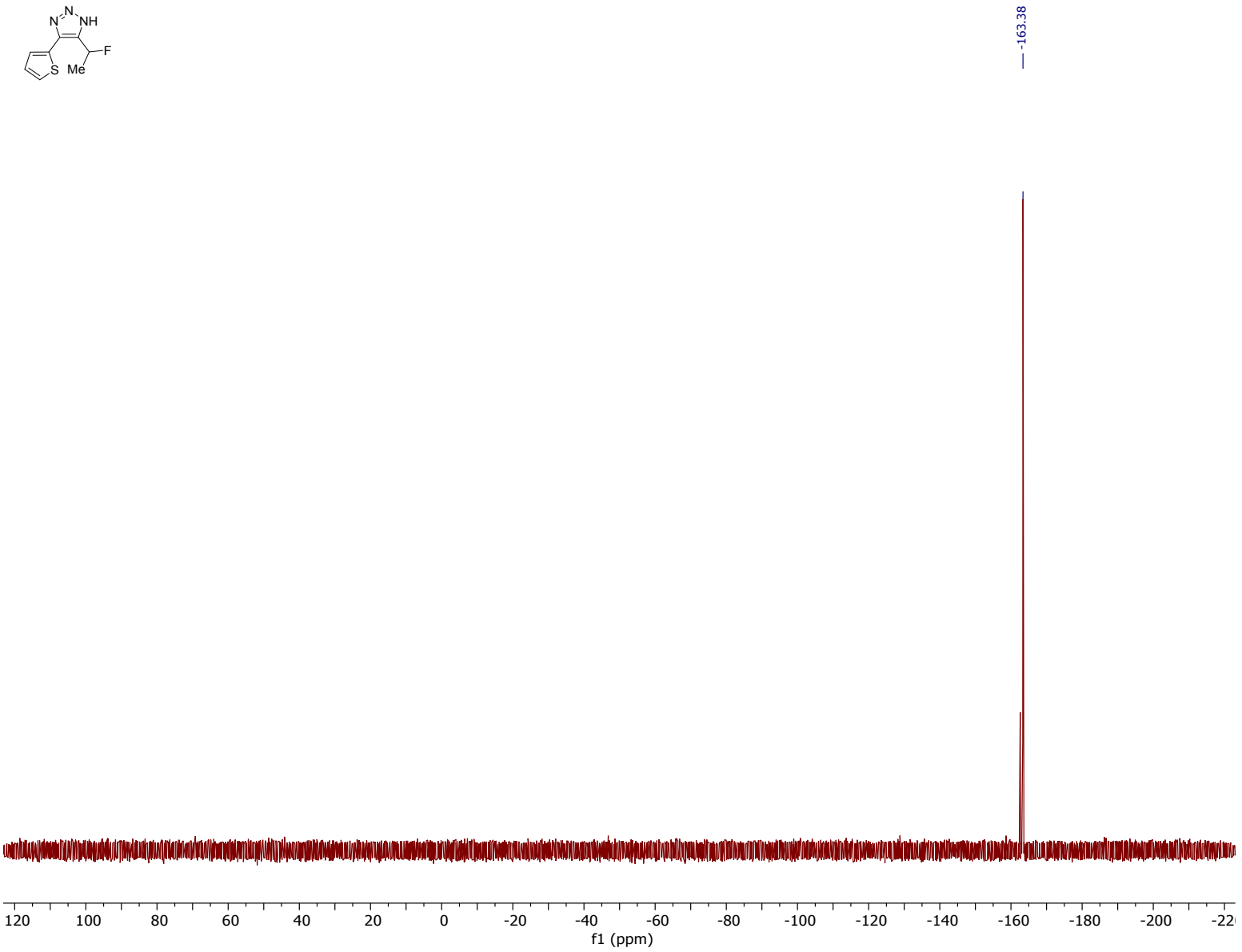
Compound **2l** 470 MHz ^{19}F NMR spectrum in C_6D_6



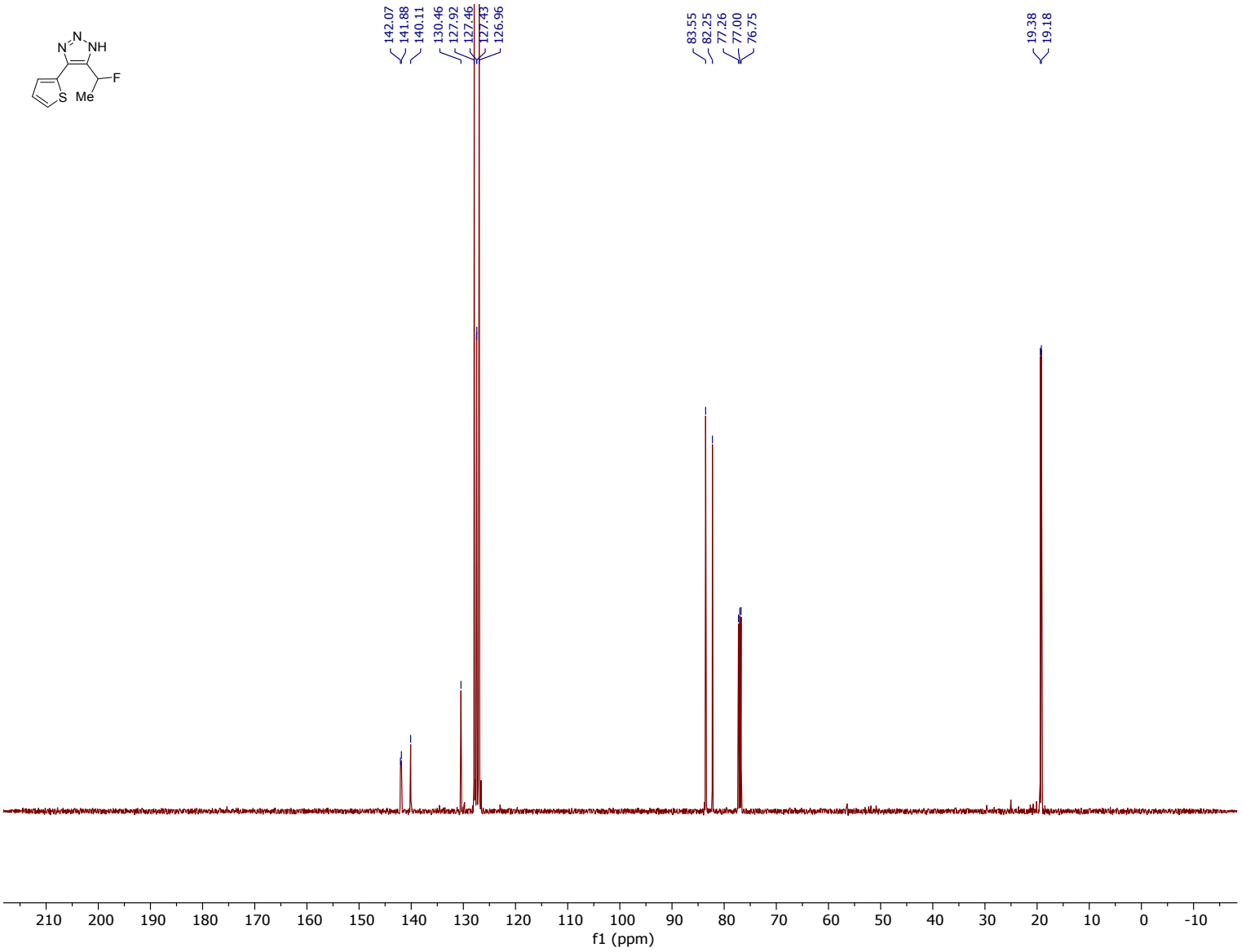
Compound **2l** 125 MHz ^{13}C NMR spectrum in C_6D_6



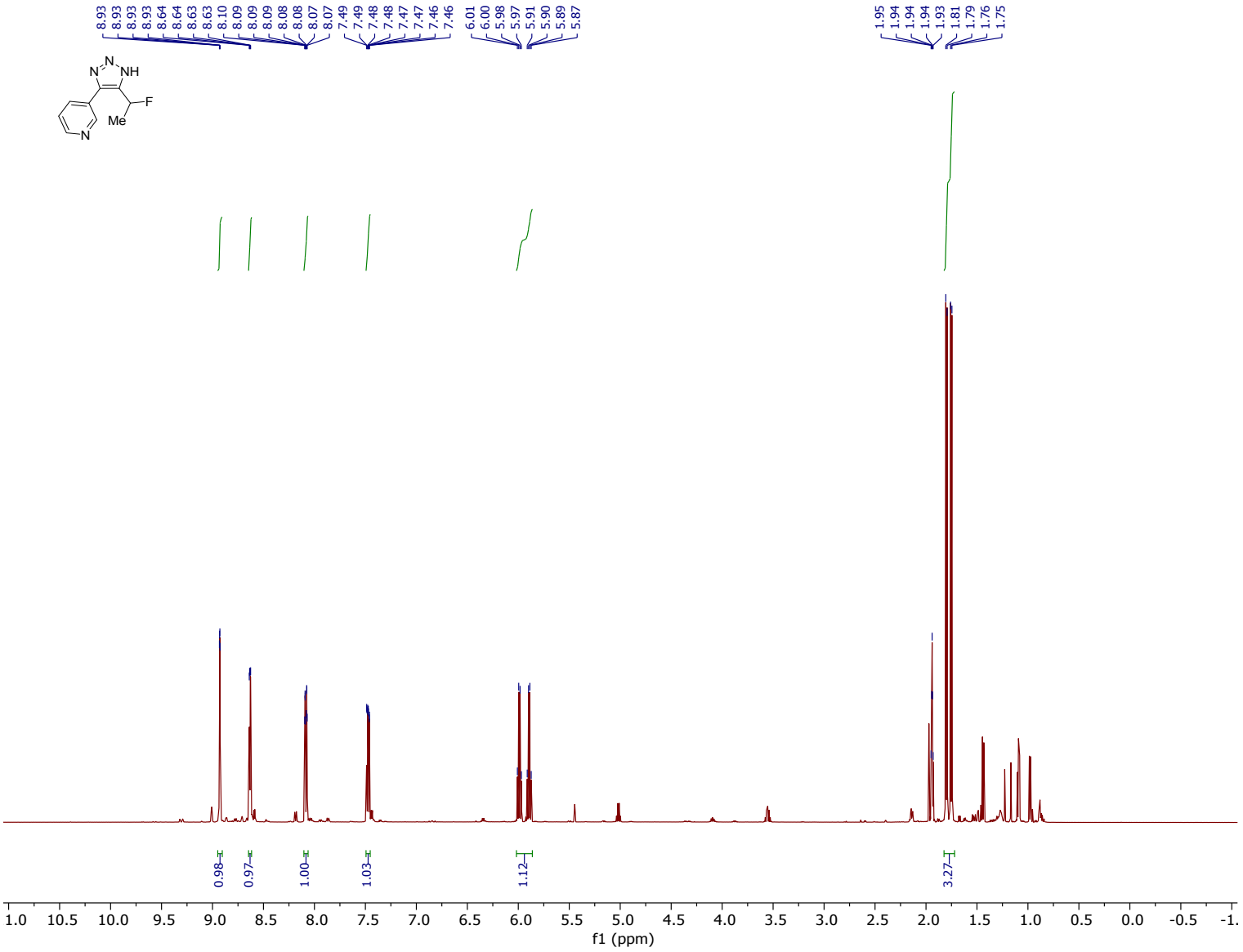
Compound **2m** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



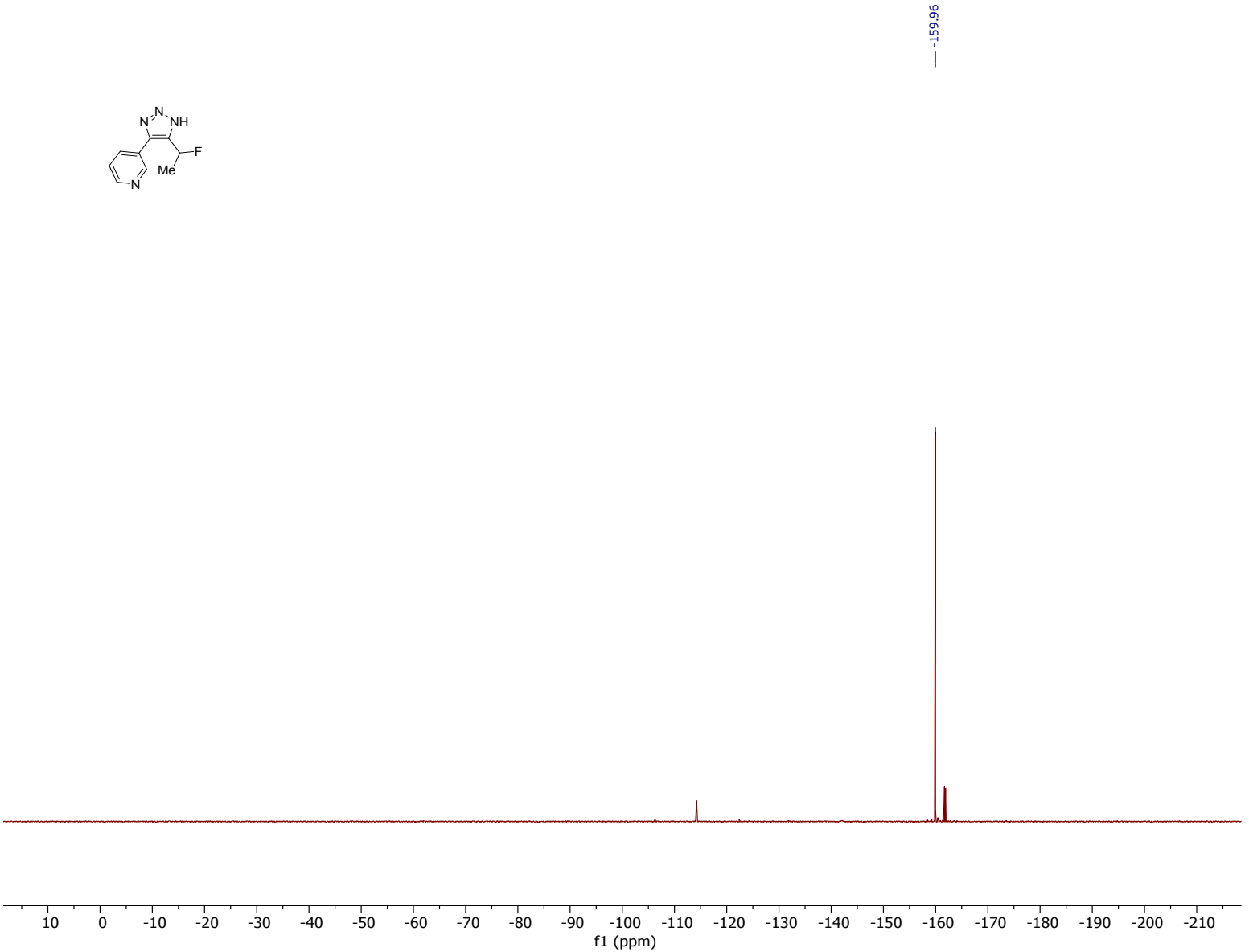
Compound **2m** 470 MHz ^{19}F NMR spectrum in $CDCl_3$



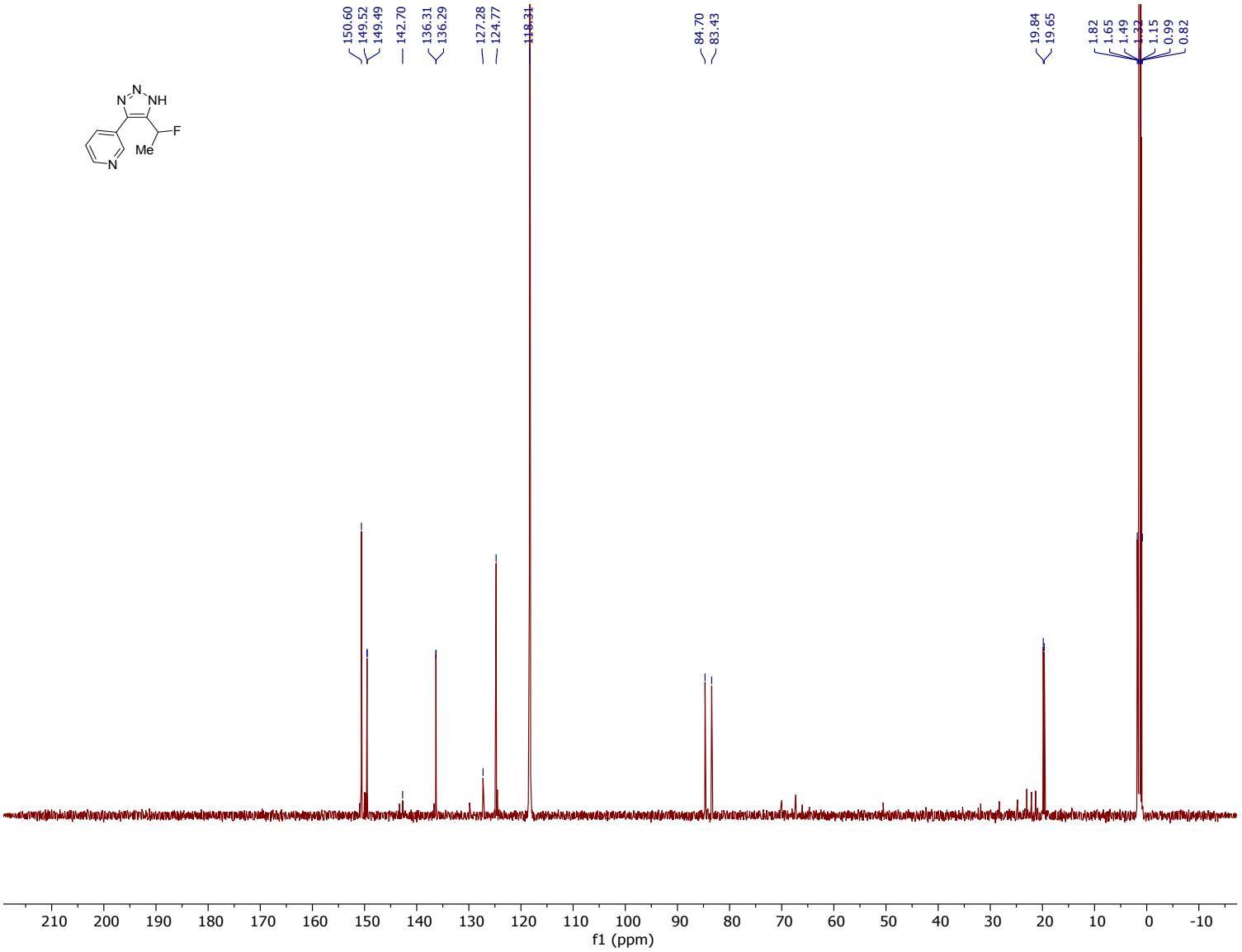
Compound **2m** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



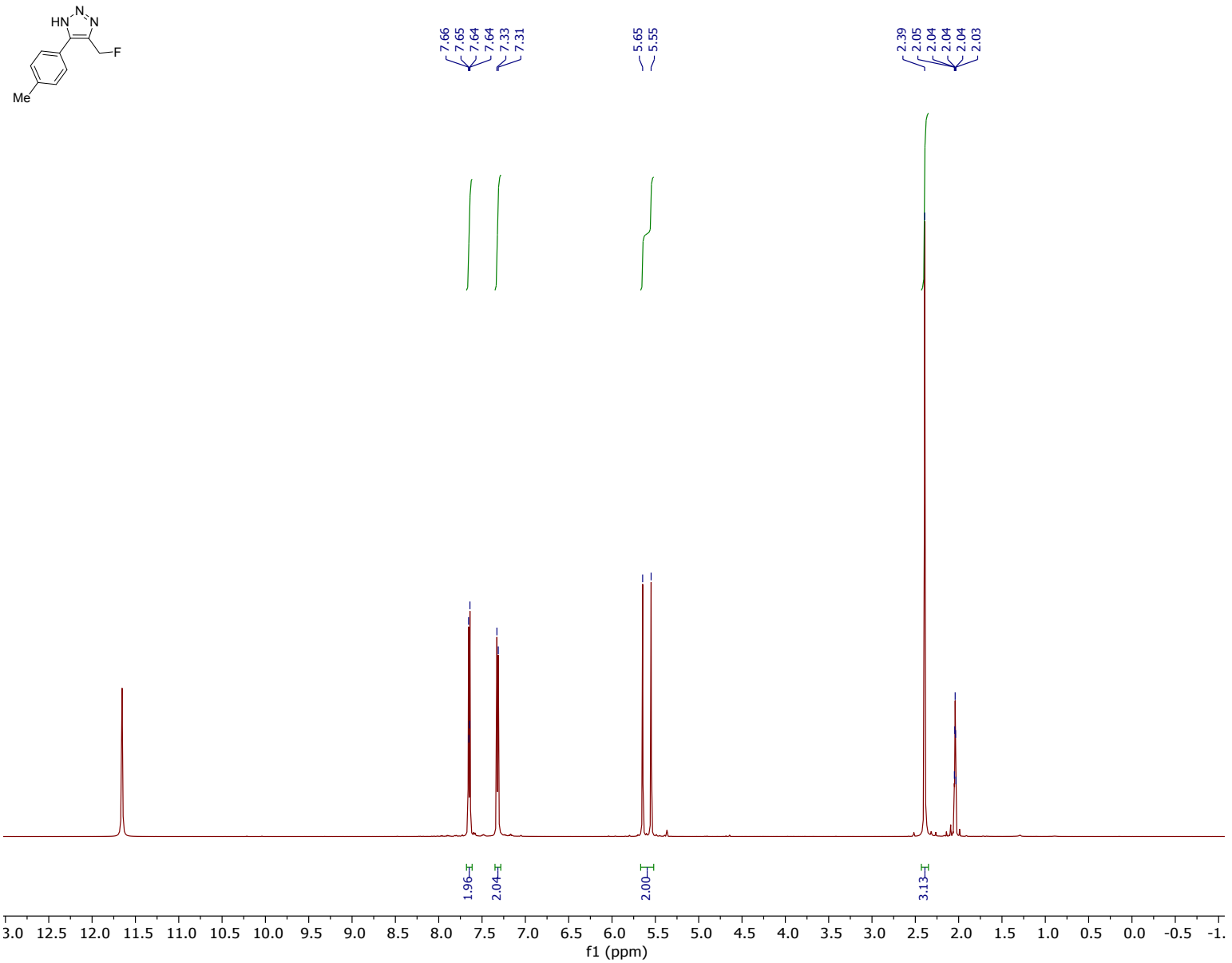
Compound **2n** 500 MHz ^{1}H NMR spectrum in CD_3CN



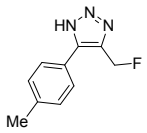
Compound **2n** 470 MHz ^{19}F NMR spectrum in CD_3CN



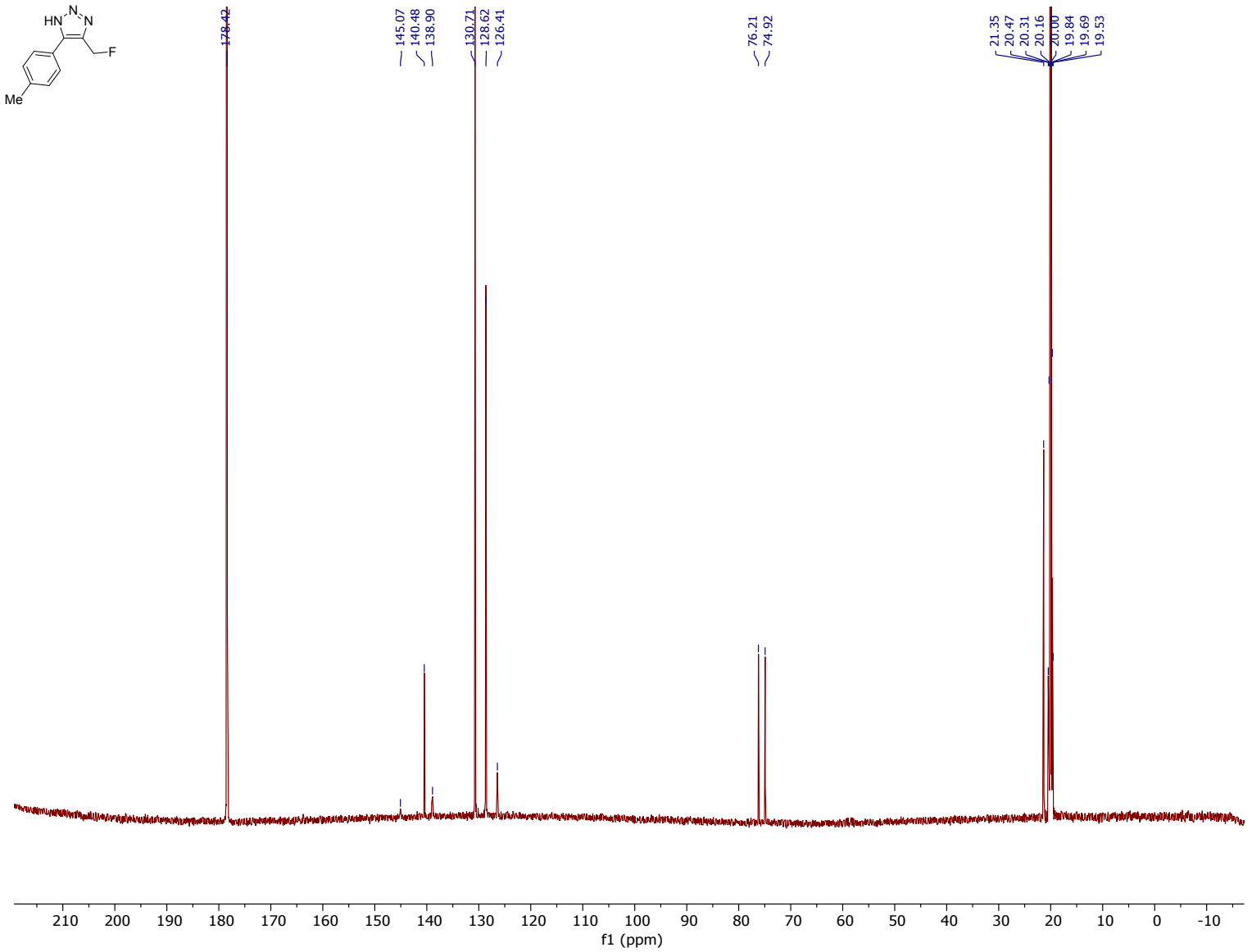
Compound **2n** 125 MHz ^{13}C NMR spectrum in CD_3CN



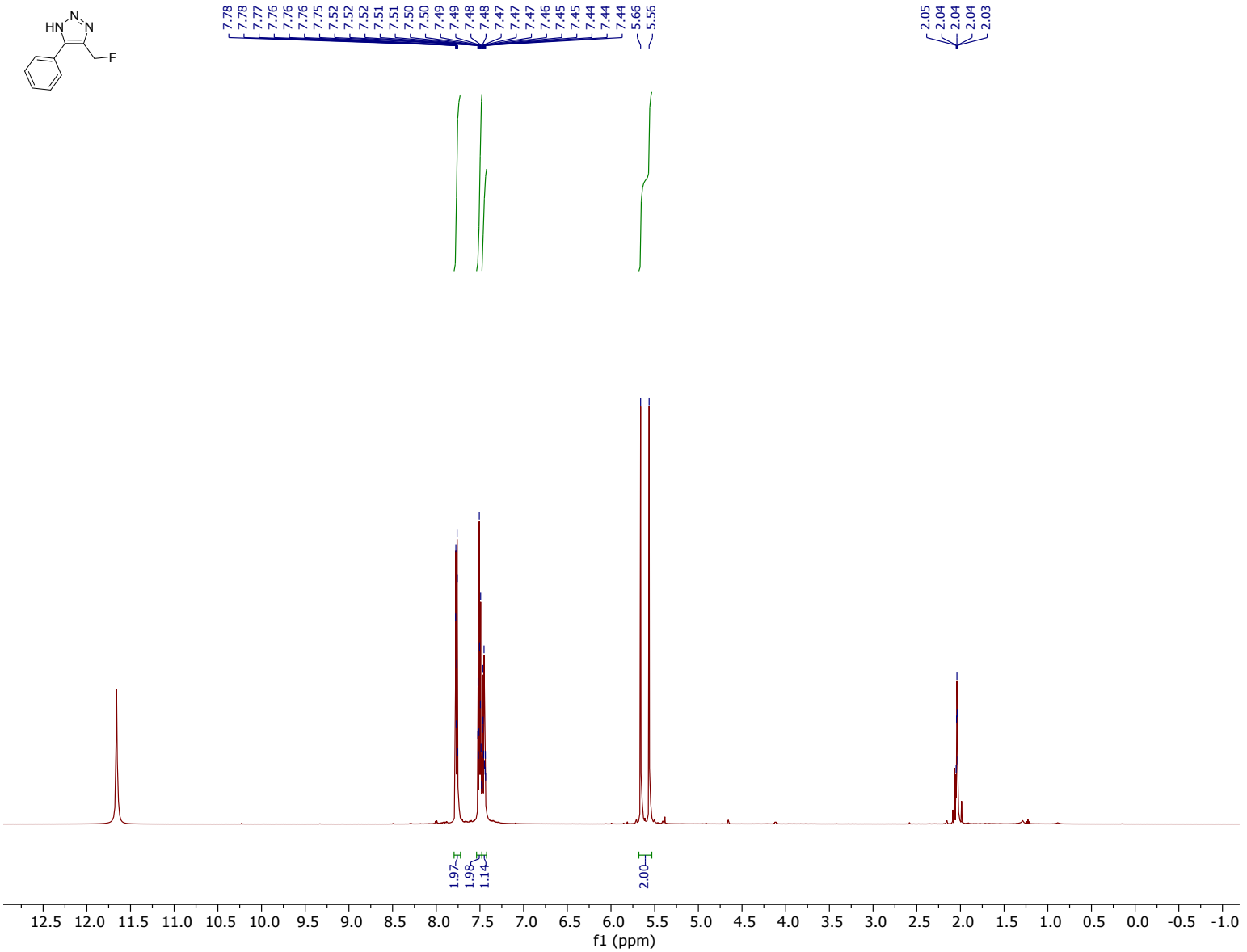
Compound **2o** 500 MHz ^{1}H NMR spectrum in Acetic acid-d_4



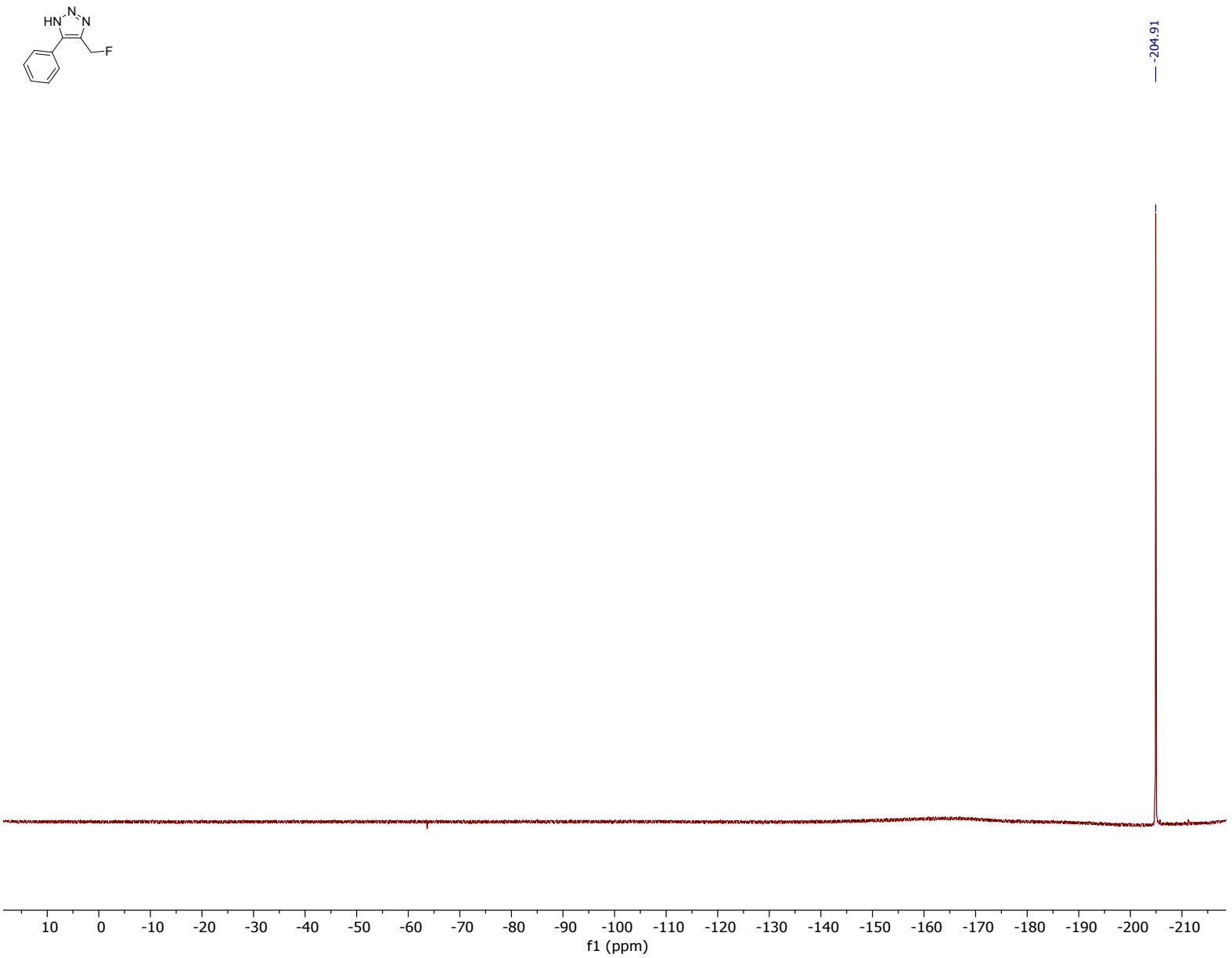
Compound **2o** 376 MHz ^{19}F NMR spectrum in Acetic acid-d_4



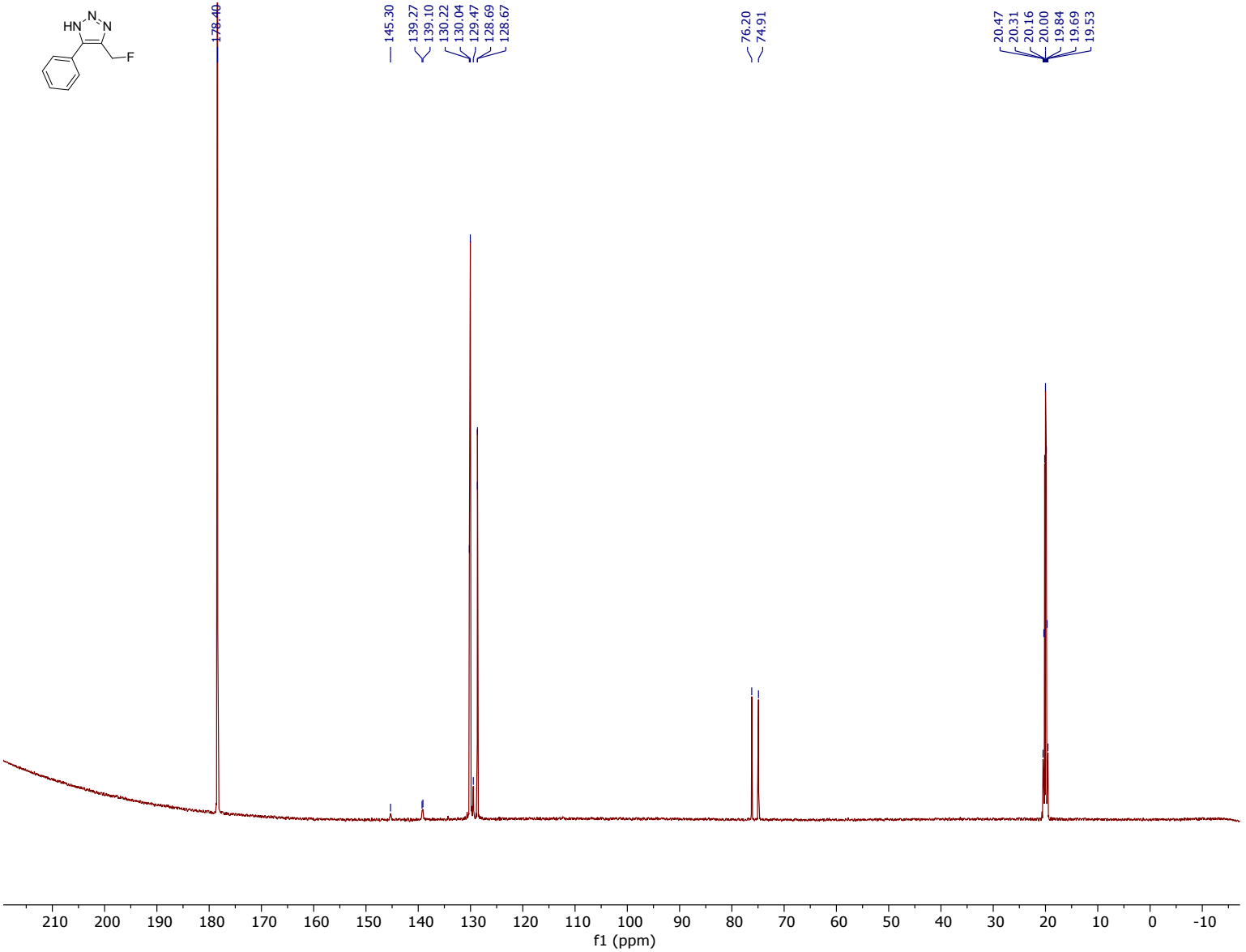
Compound **2o** 125 MHz ^{13}C NMR spectrum in Acetic acid-d_4



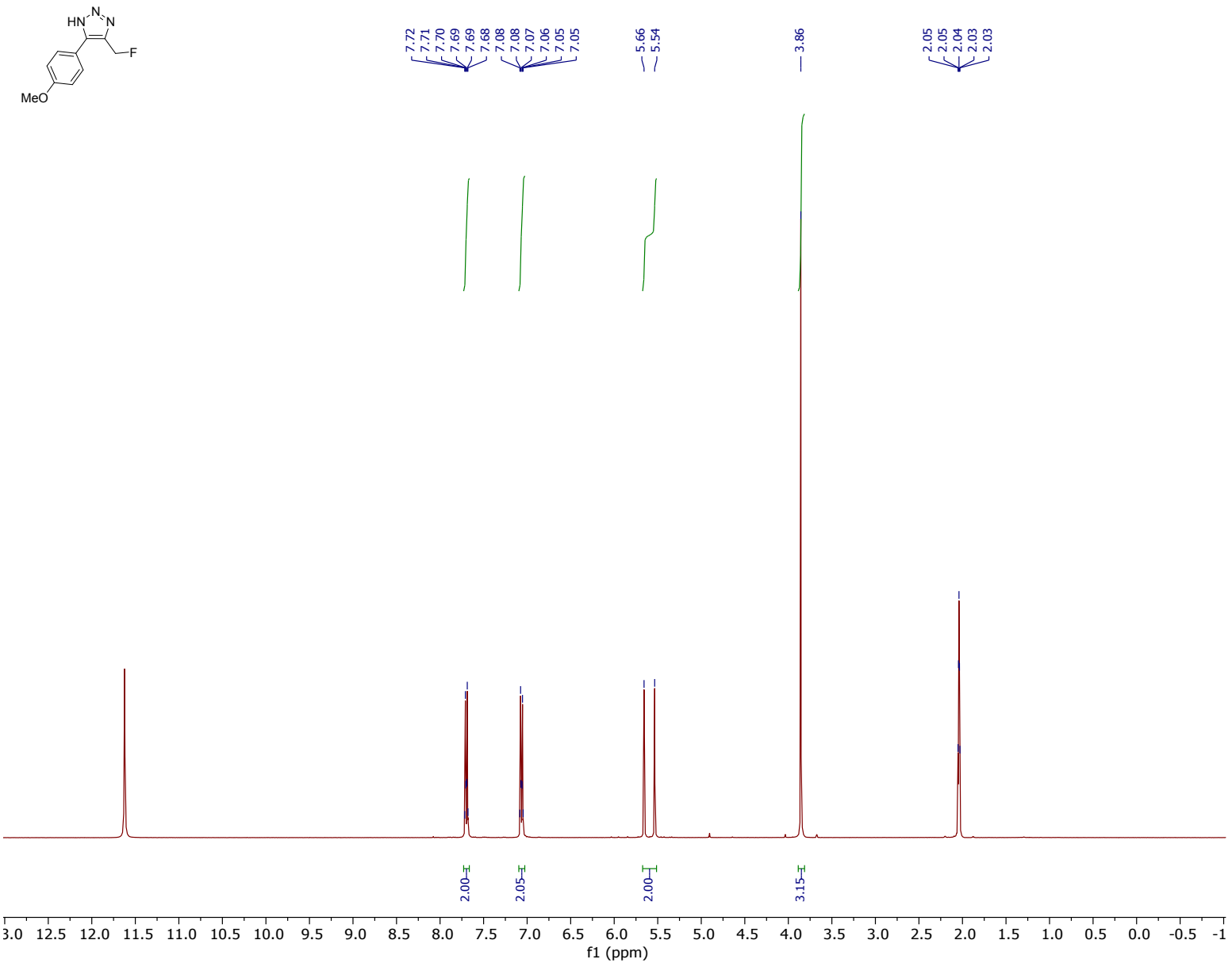
Compound **2p** 500 MHz ^{1}H NMR spectrum in Acetic acid-d_4



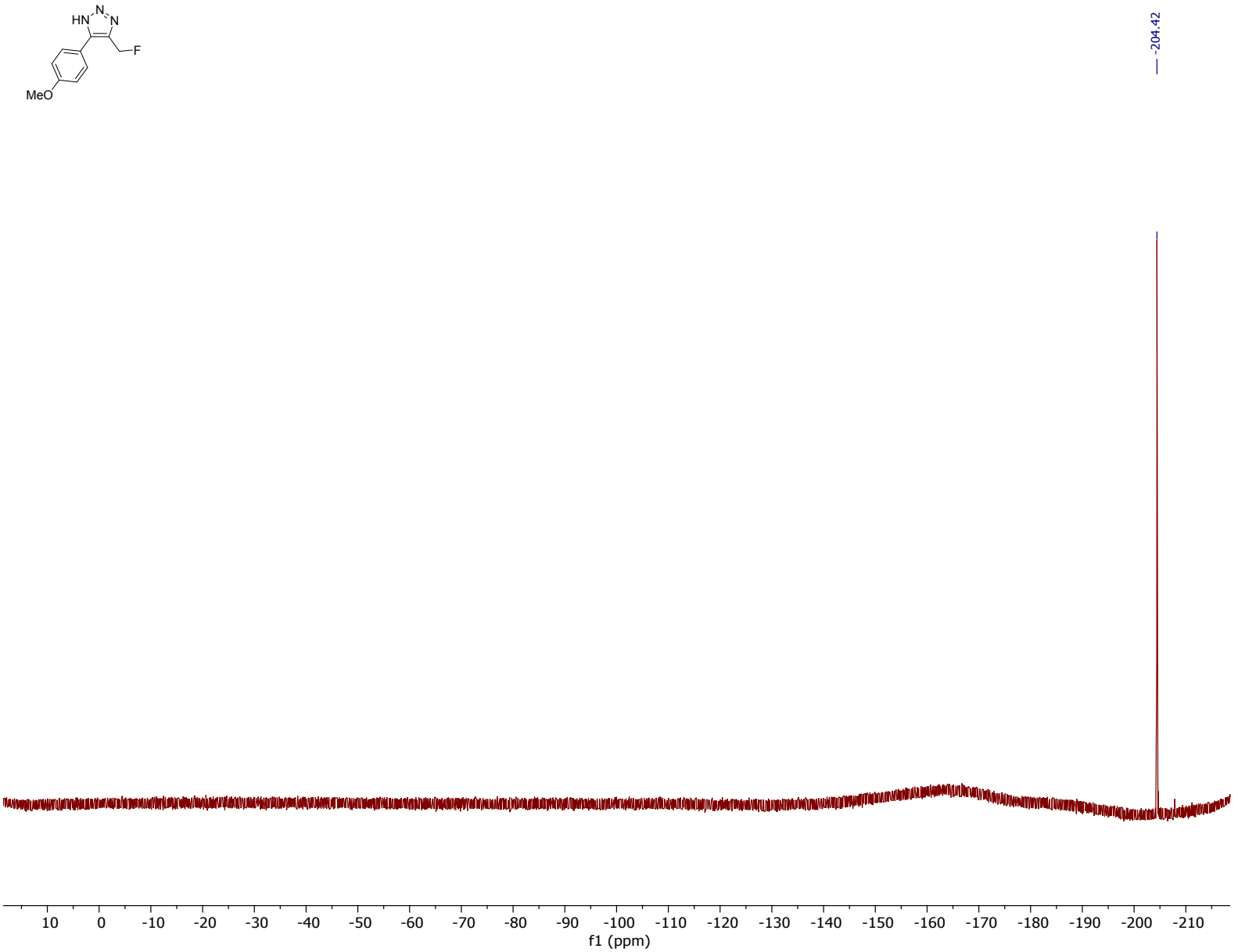
Compound **2p** 376 MHz ^{19}F NMR spectrum in Acetic acid-d_4



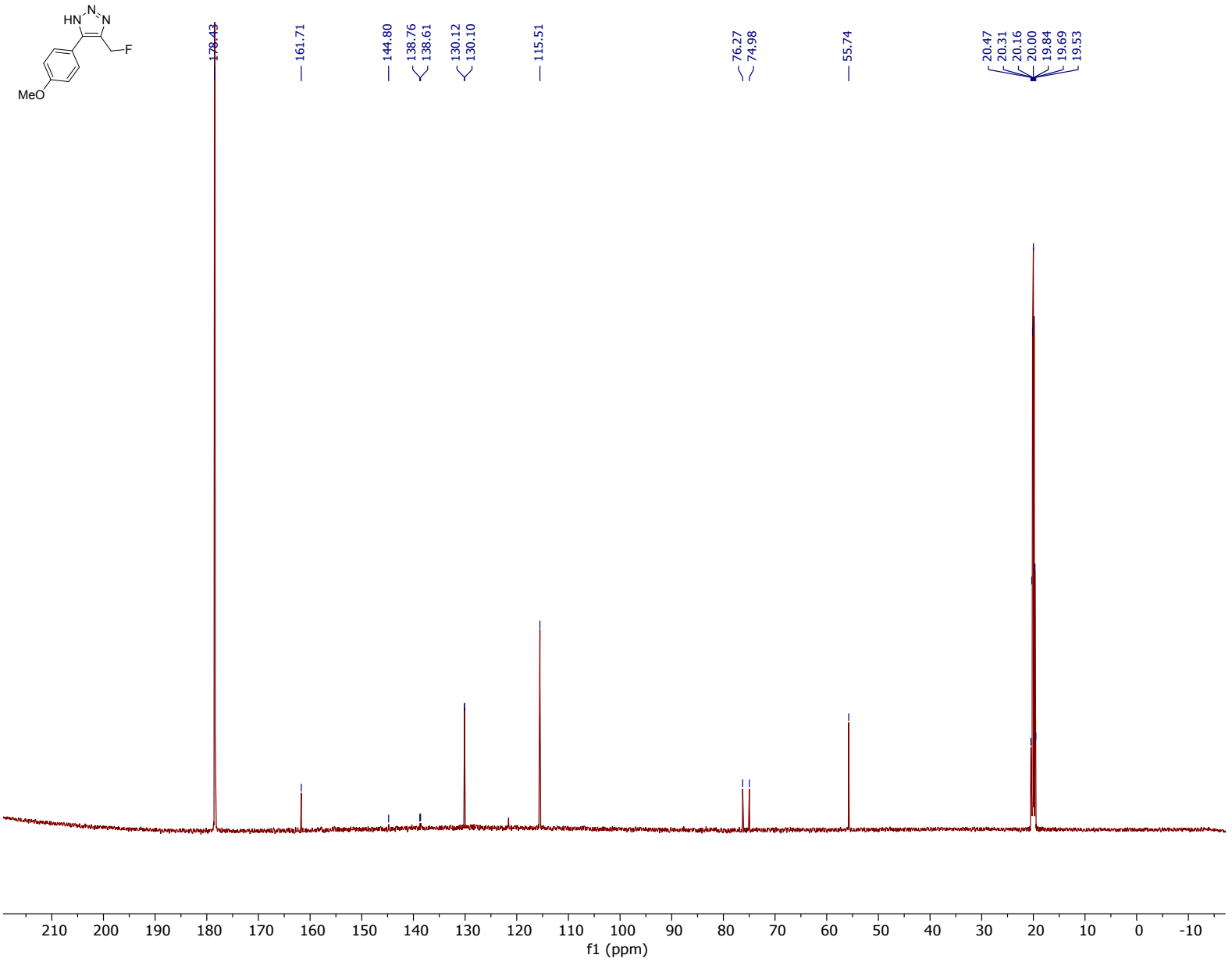
Compound **2p** 125 MHz ^{13}C NMR spectrum in Acetic acid-d_4



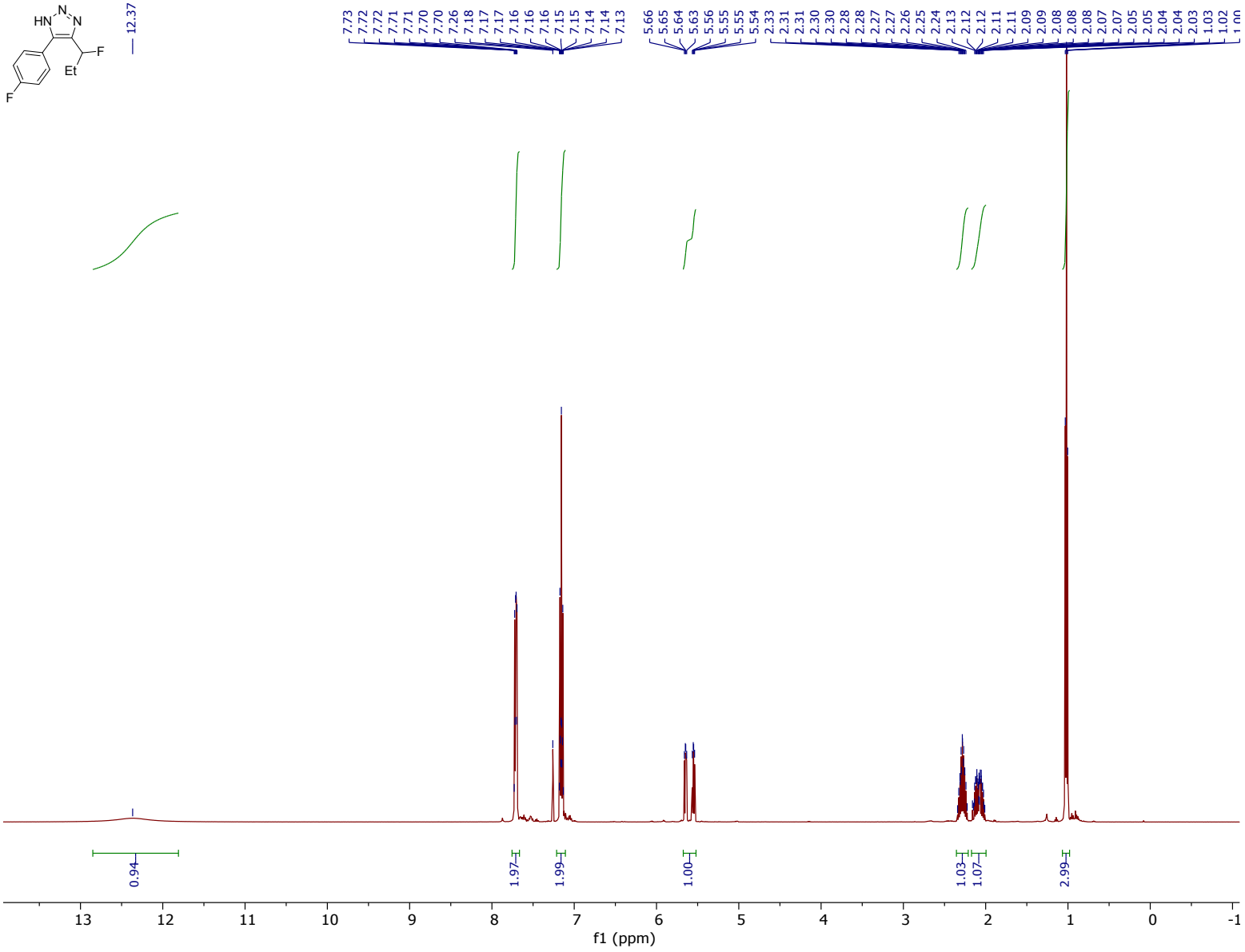
Compound **2q** 400 MHz ^{1}H NMR spectrum in Acetic acid-d_4



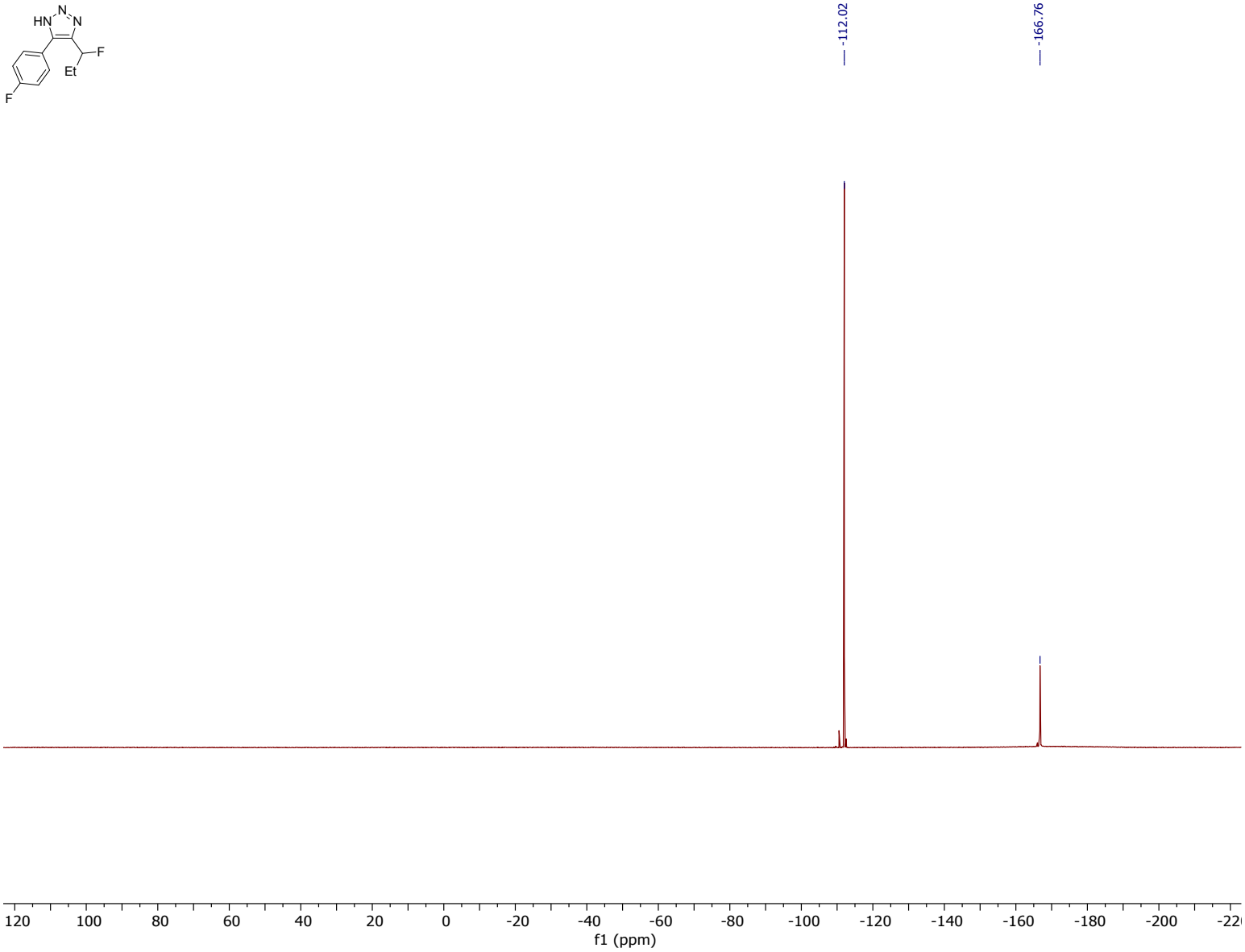
Compound **2q** 376 MHz ^{19}F NMR spectrum in Acetic acid-d_4



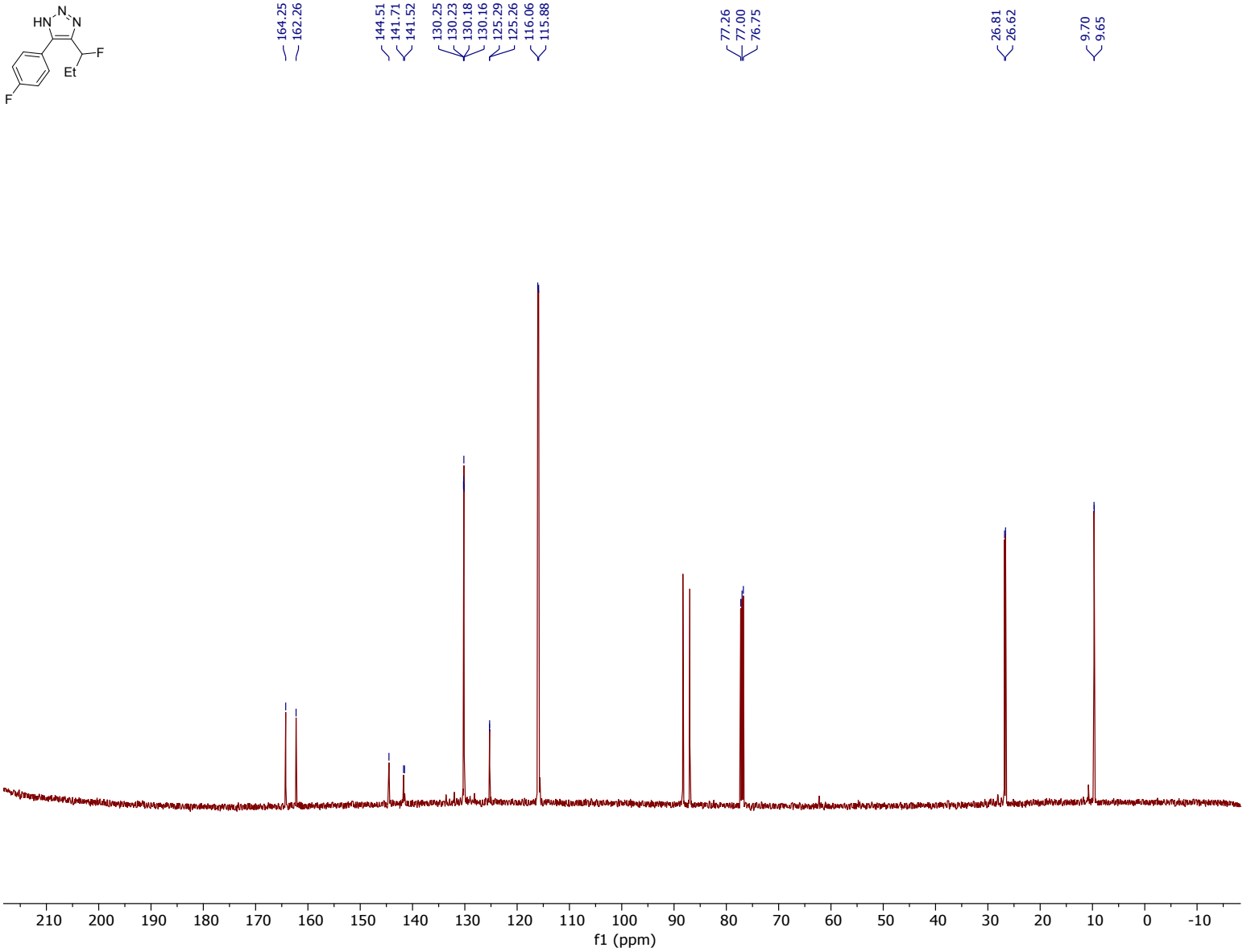
Compound **2q** 125 MHz ^{13}C NMR spectrum in Acetic acid-d_4



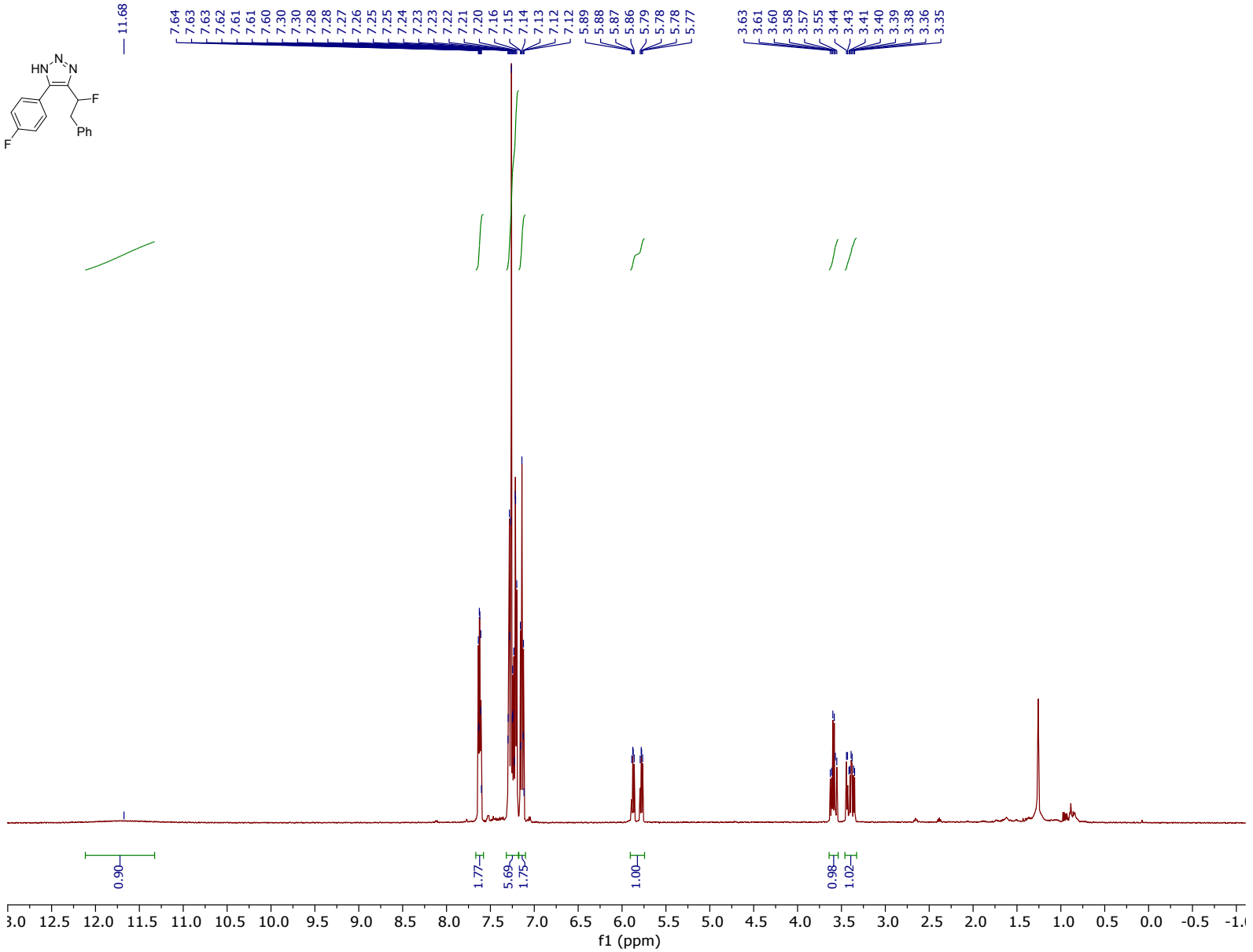
Compound **2r** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



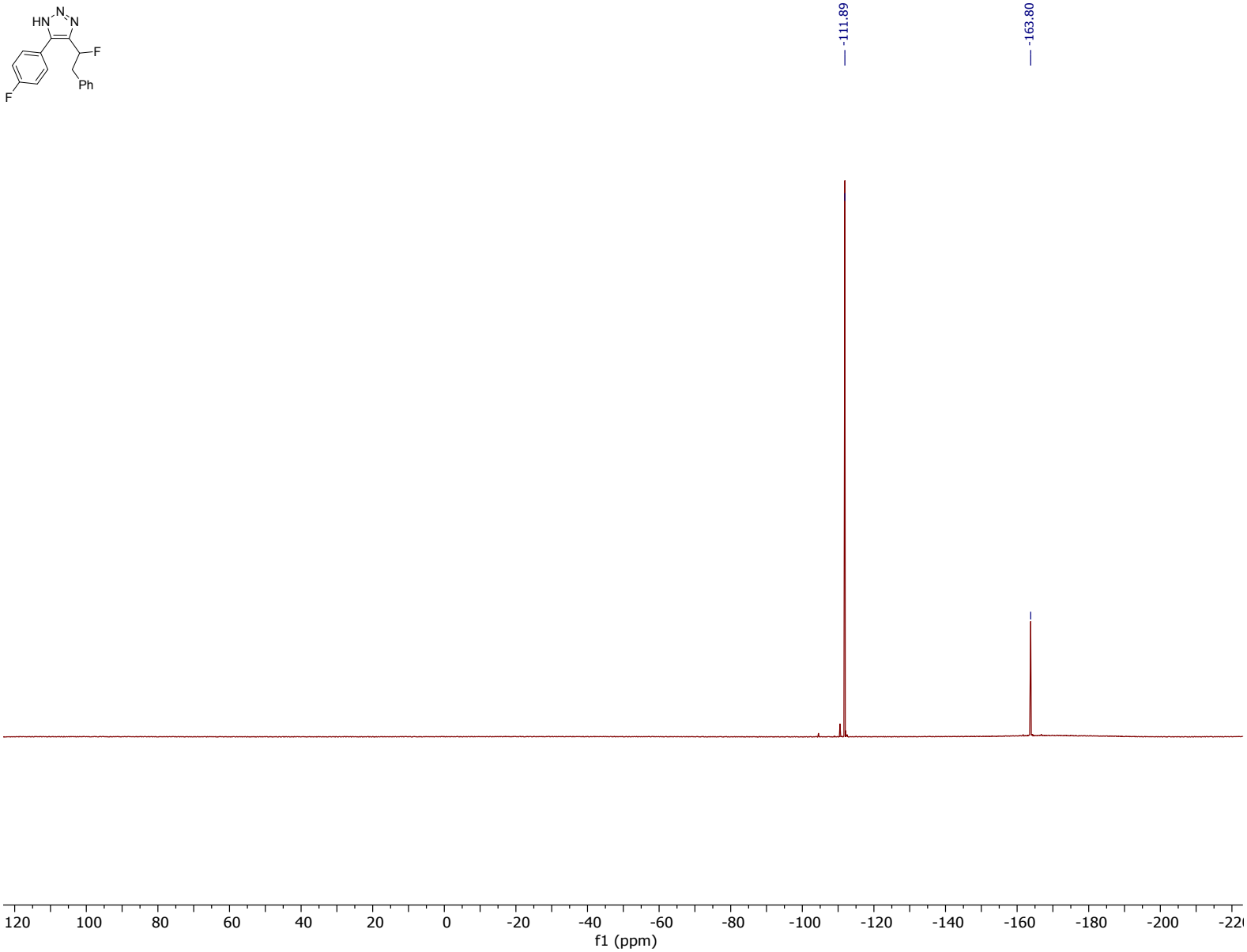
Compound **2r** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



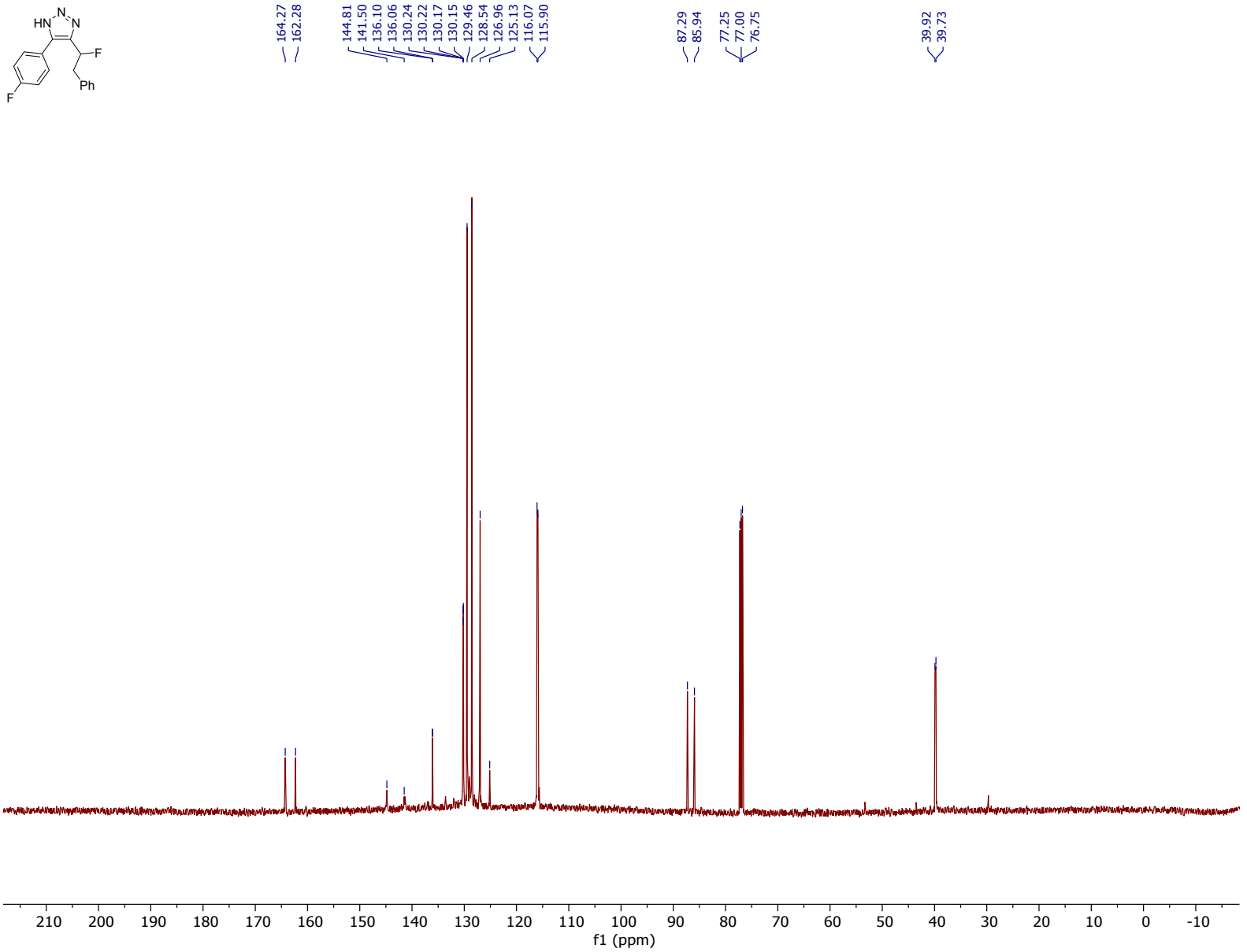
Compound **2r** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



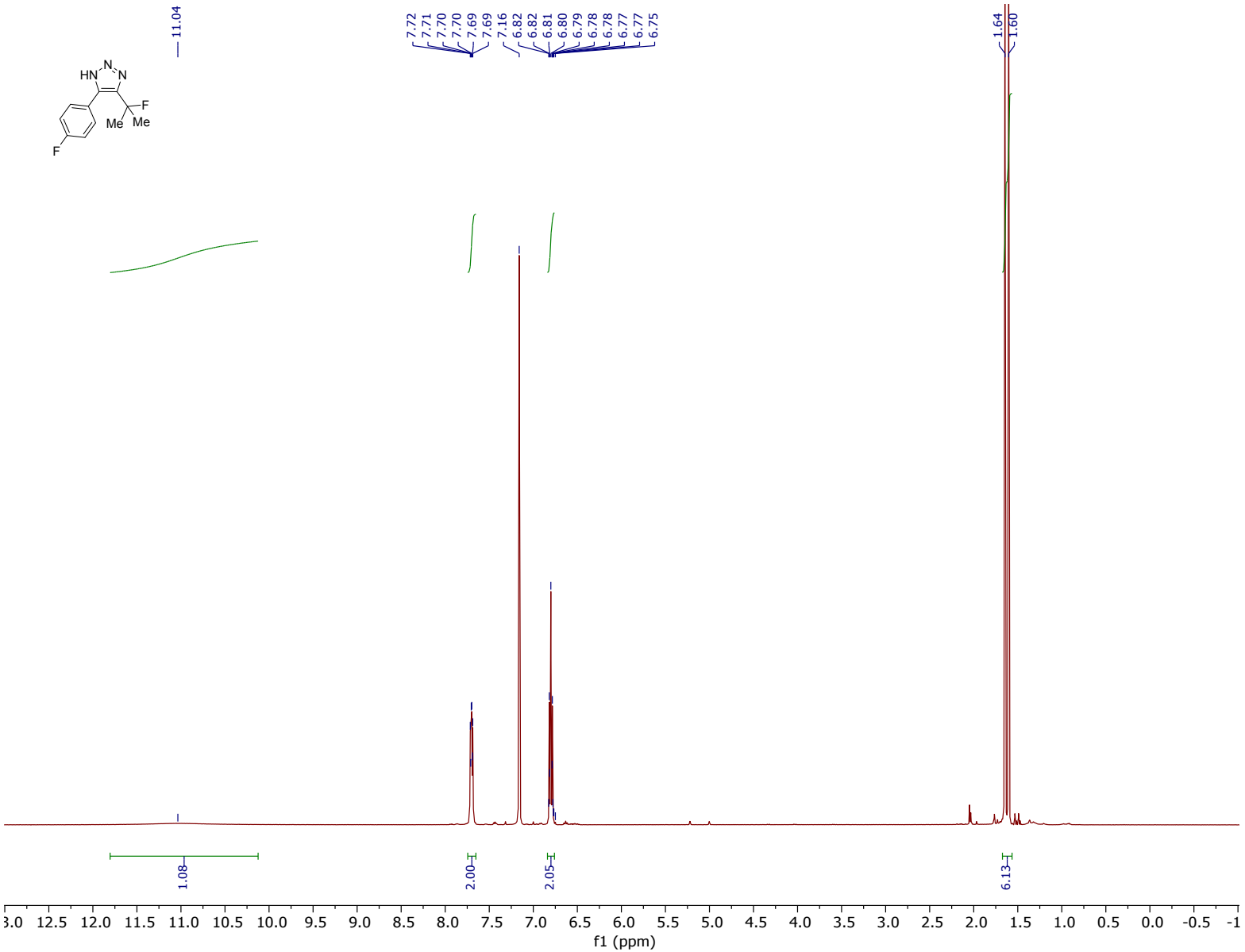
Compound **2s** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



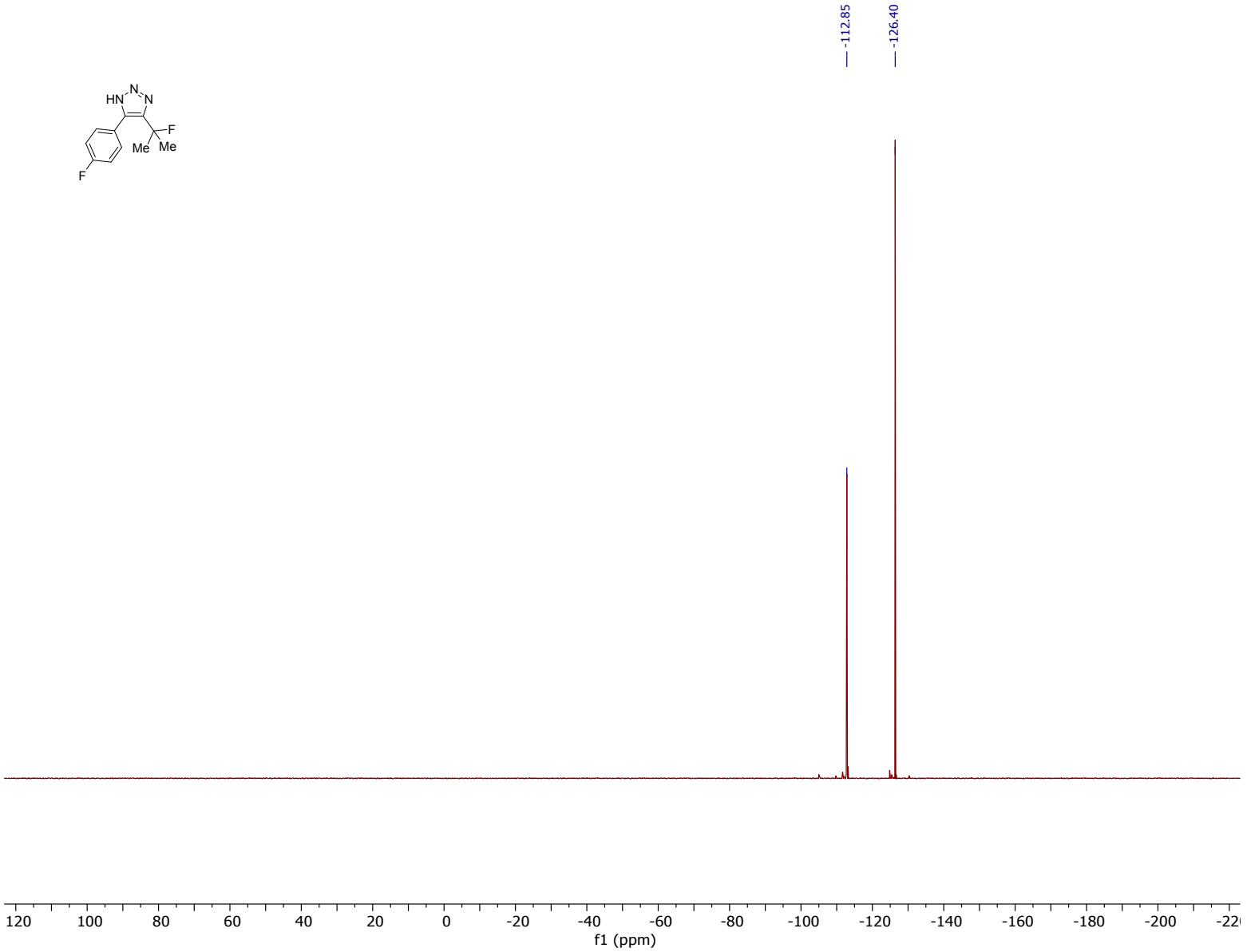
Compound **2s** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



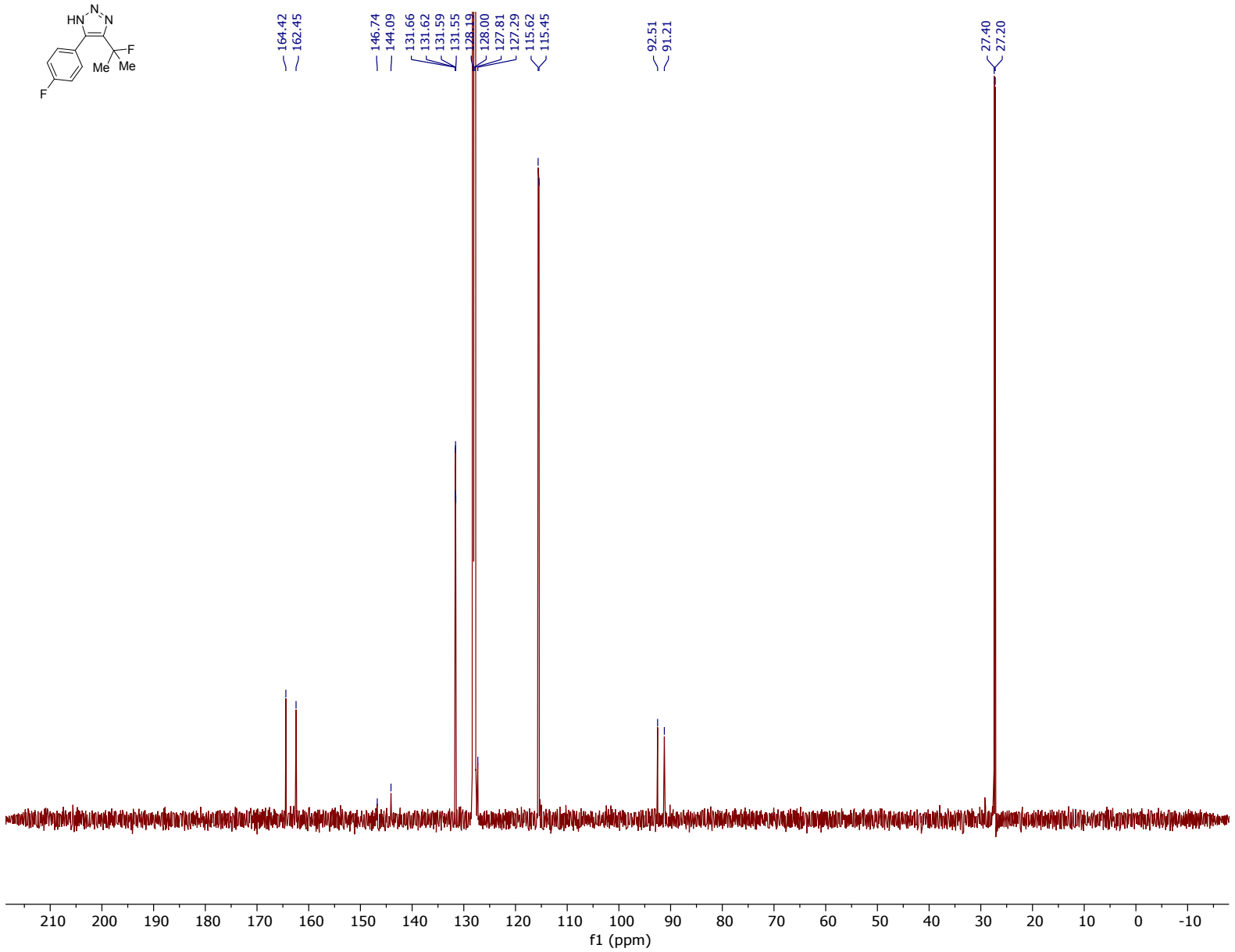
Compound **2s** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



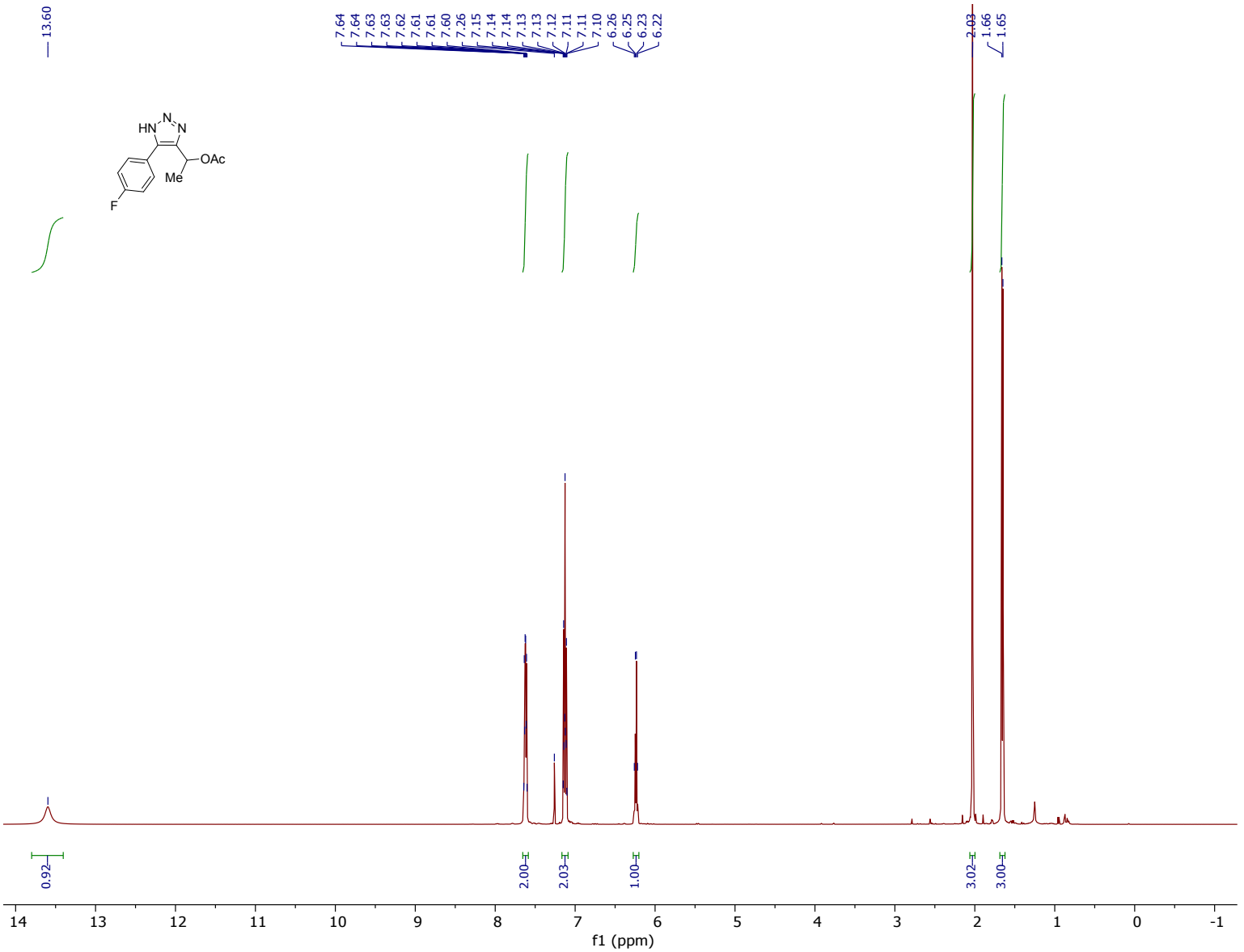
Compound **2t** 500 MHz ^{1}H NMR spectrum in C_6D_6



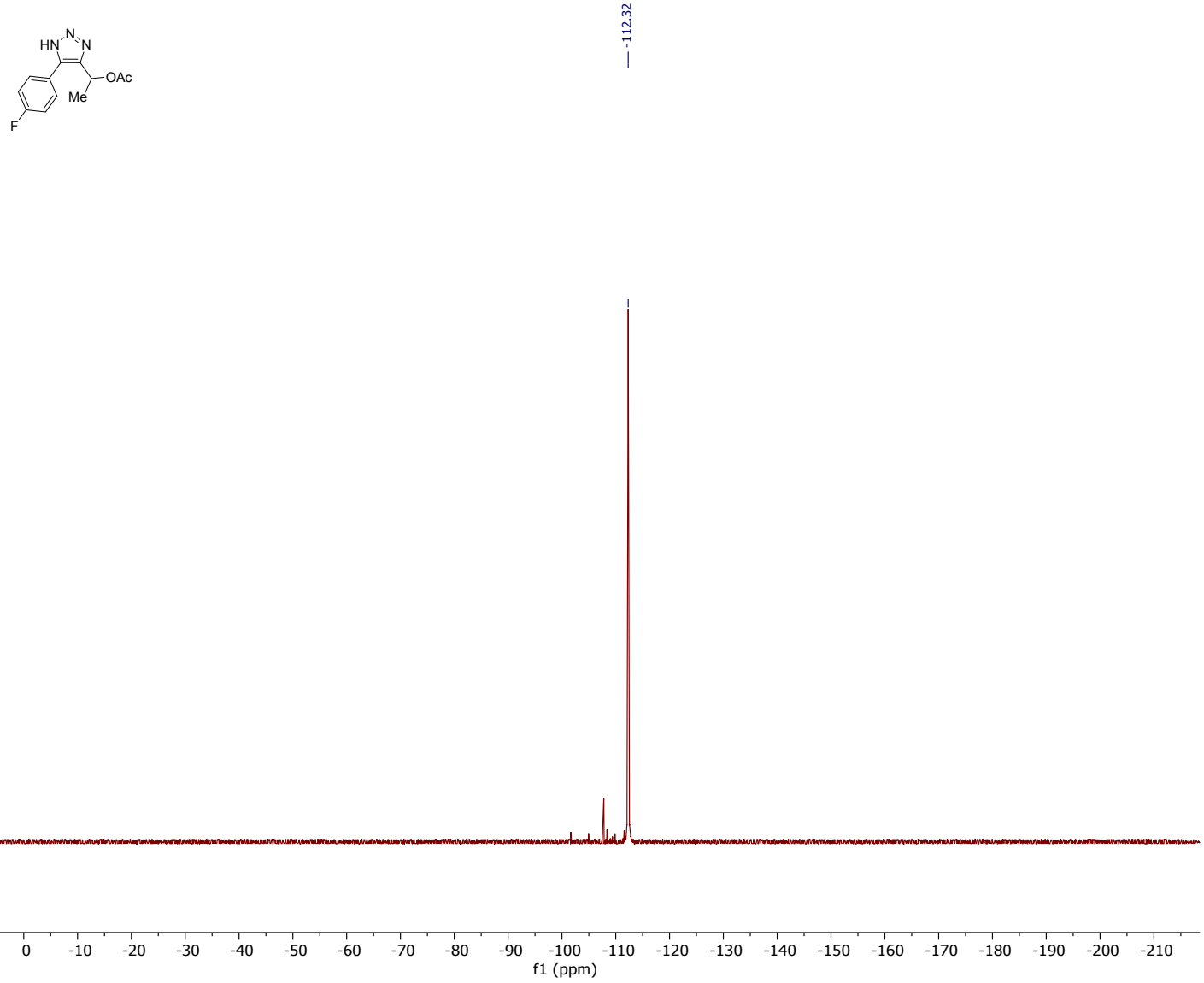
Compound **2t** 470 MHz ^{19}F NMR spectrum in C_6D_6



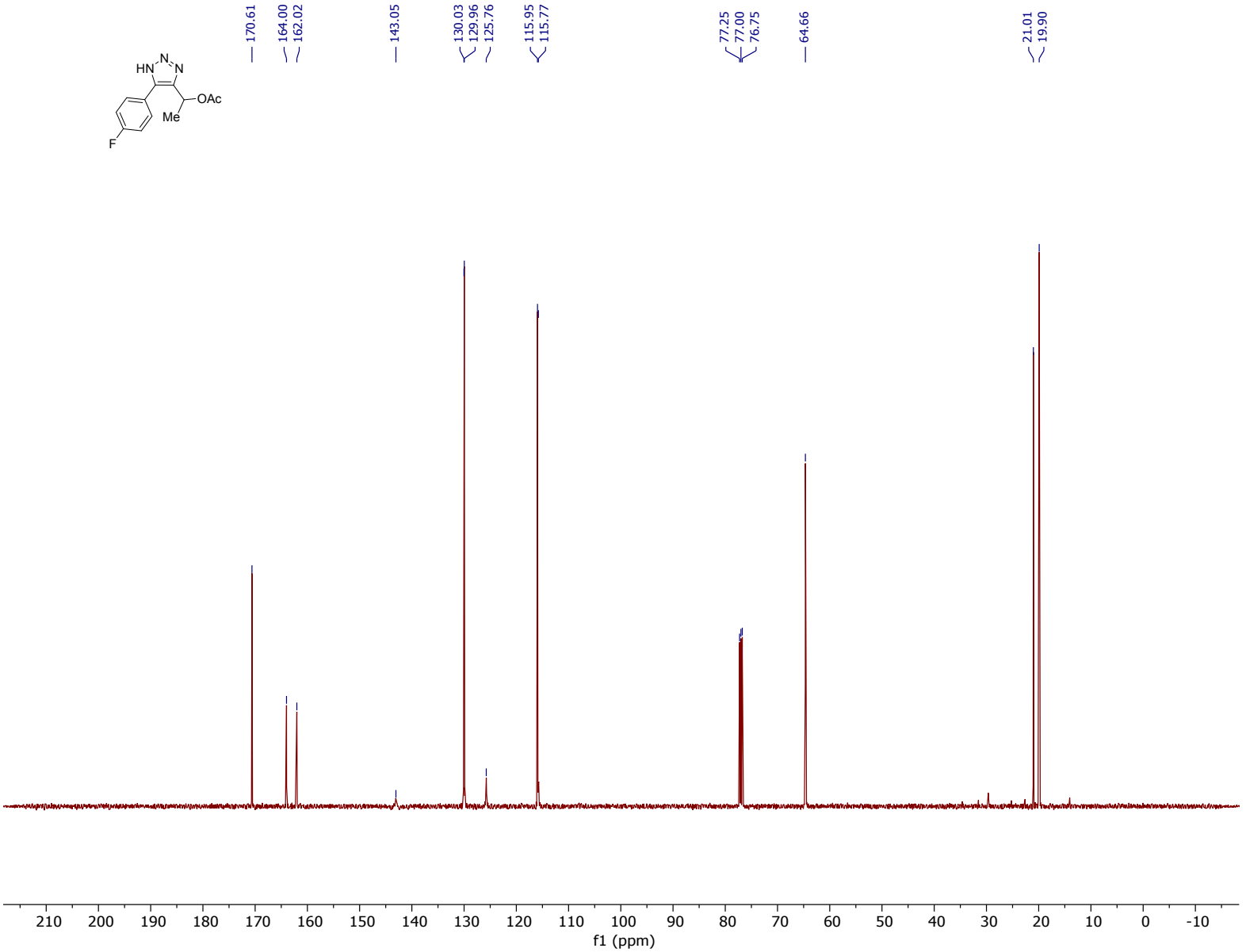
Compound **2t** 125 MHz ^{13}C NMR spectrum in C_6D_6



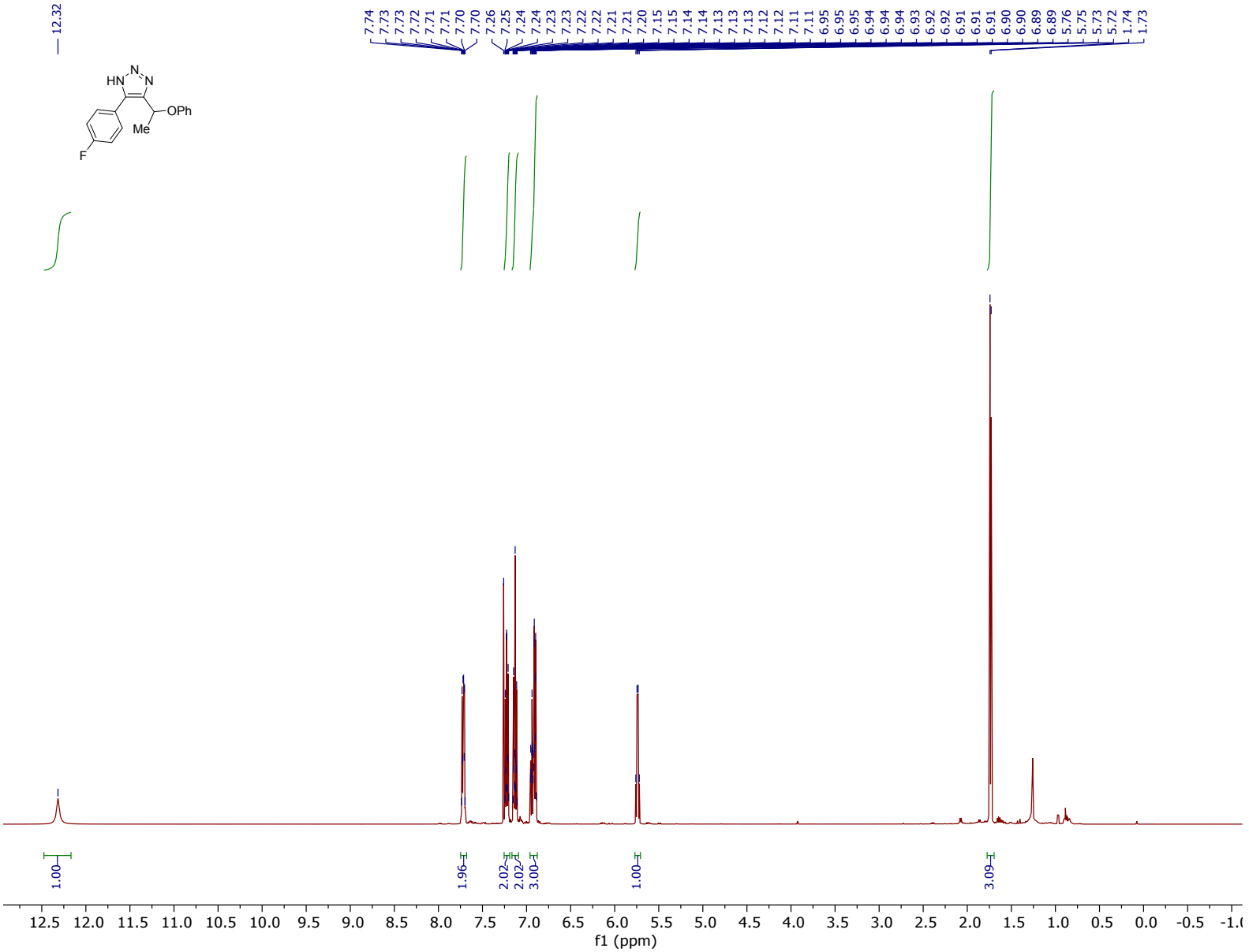
Compound **3a** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



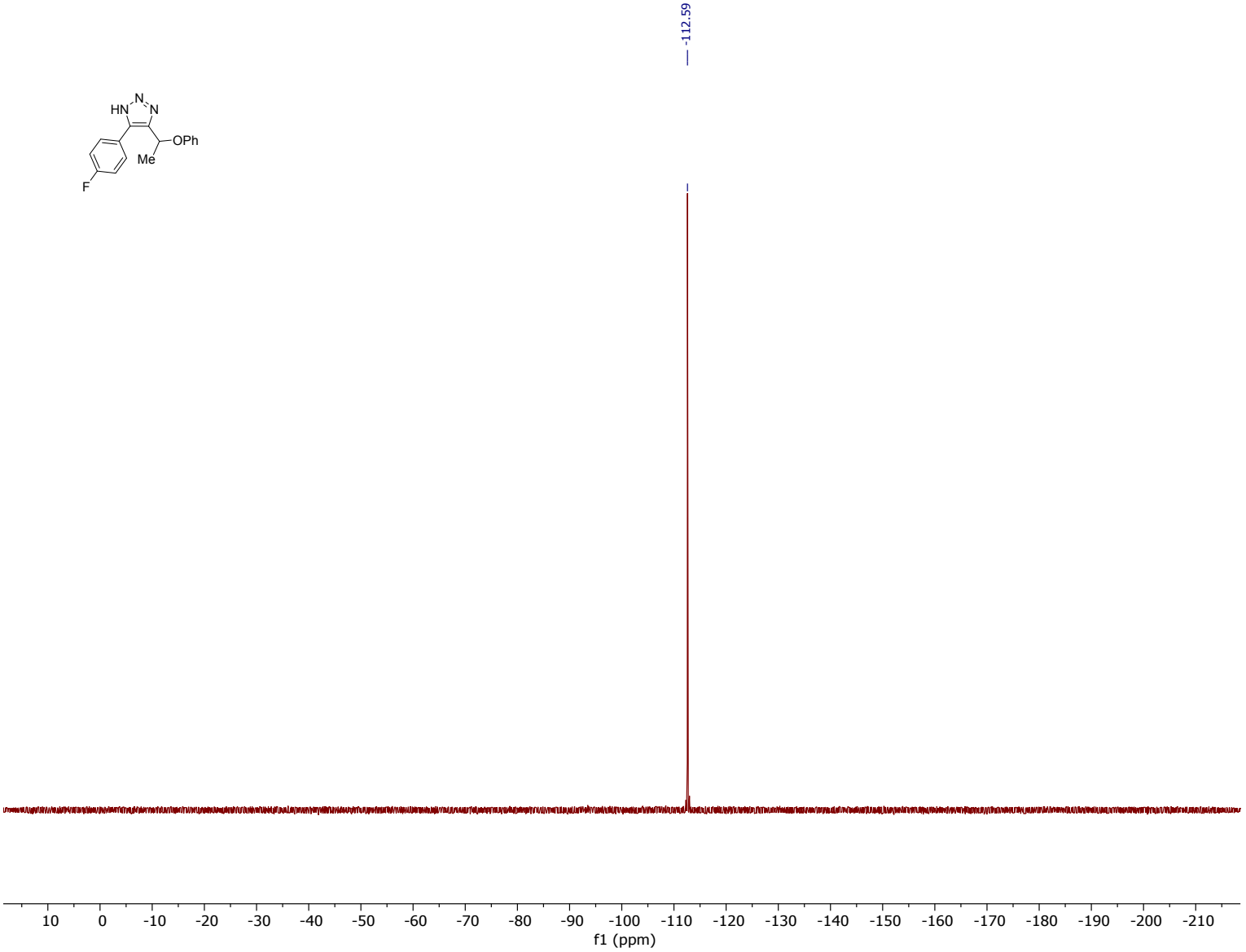
Compound **3a** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



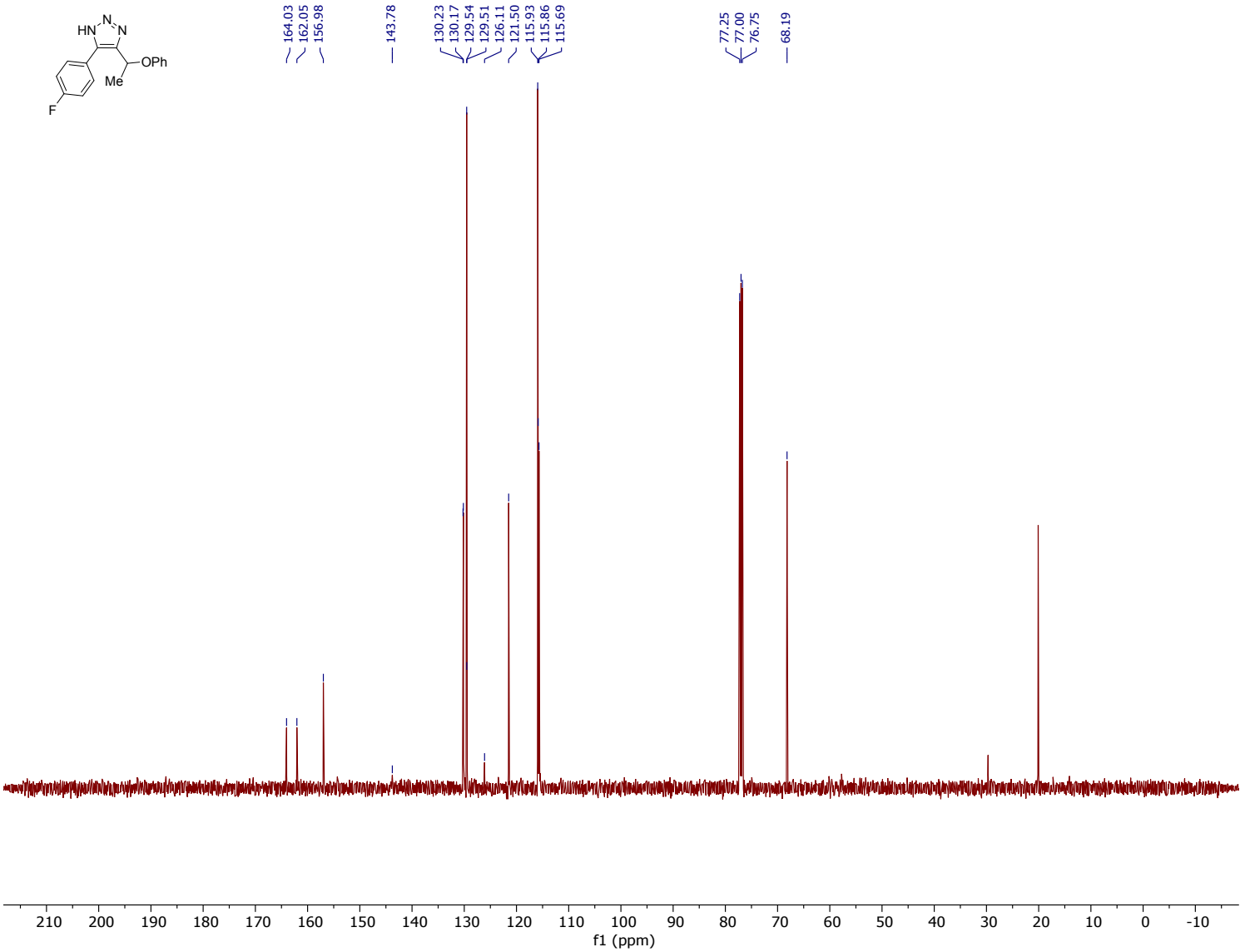
Compound **3a** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



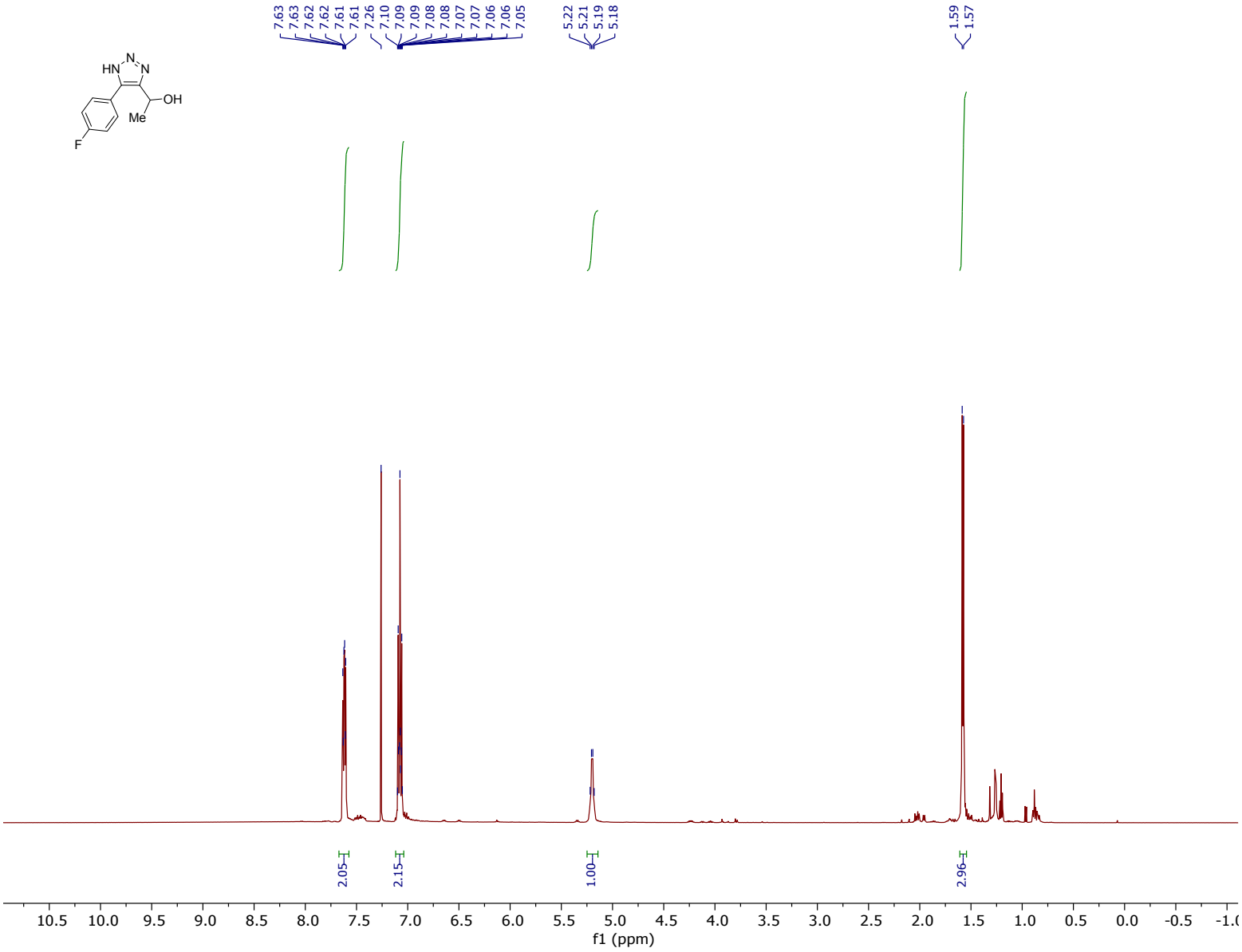
Compound **3b** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



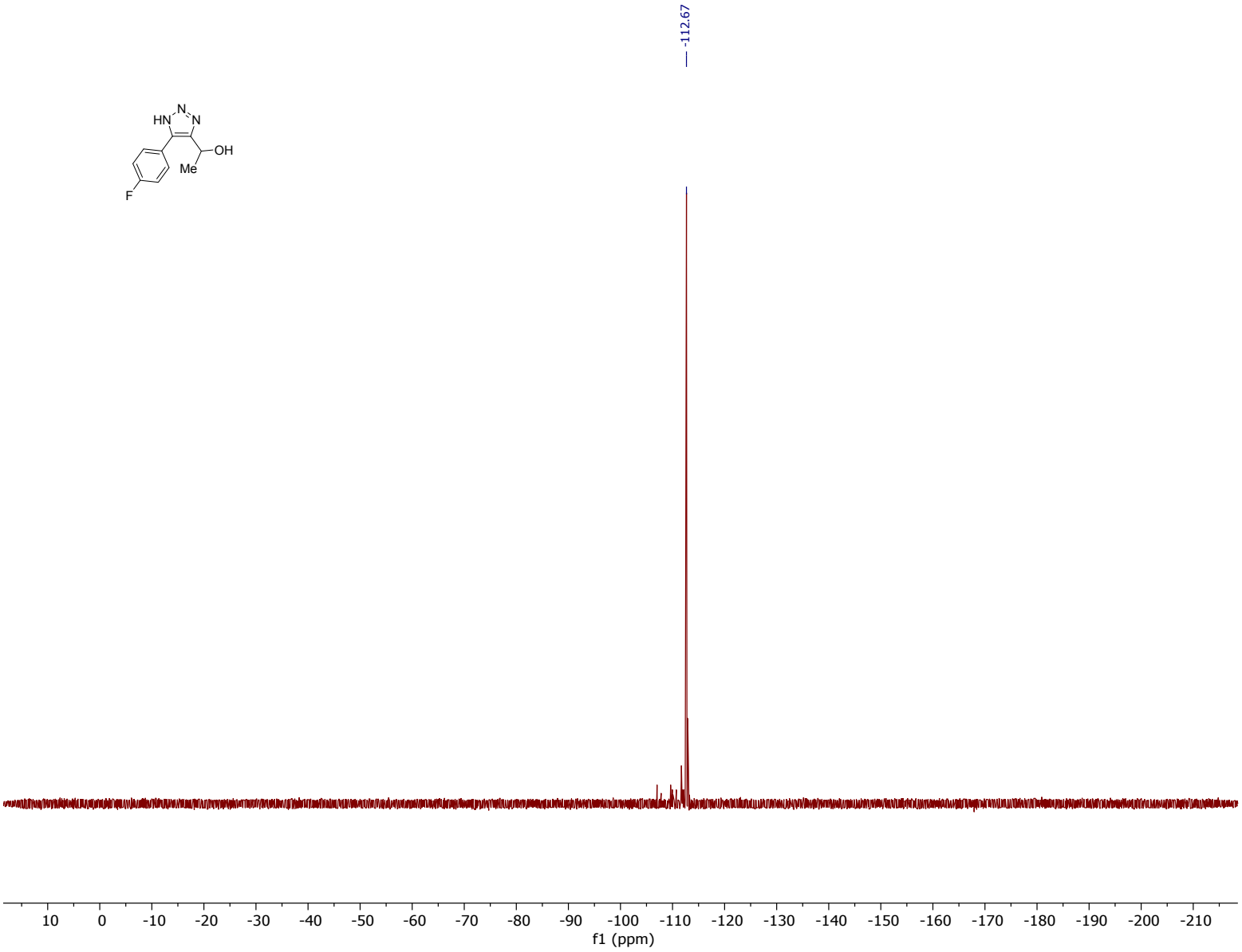
Compound **3b** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



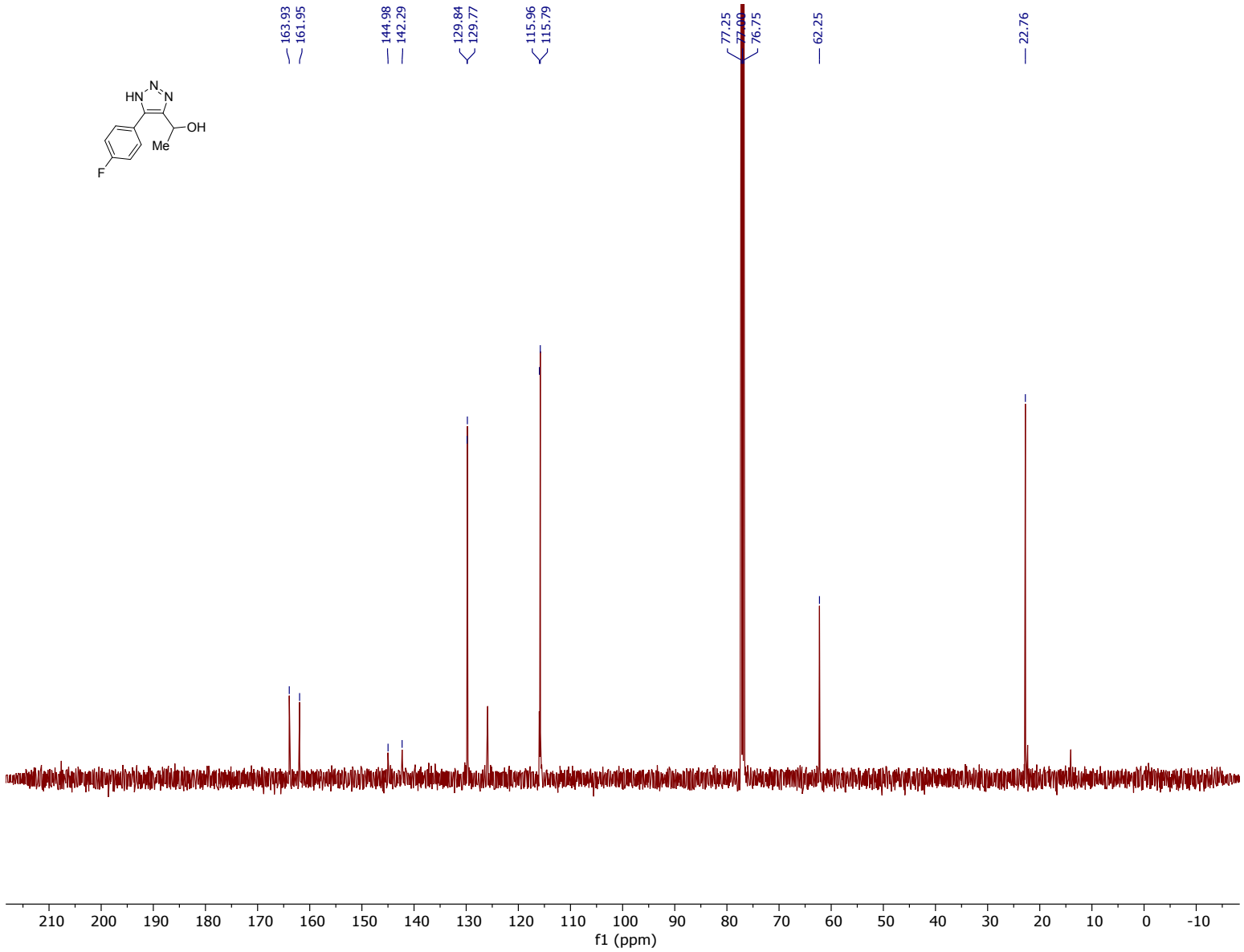
Compound **3b** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



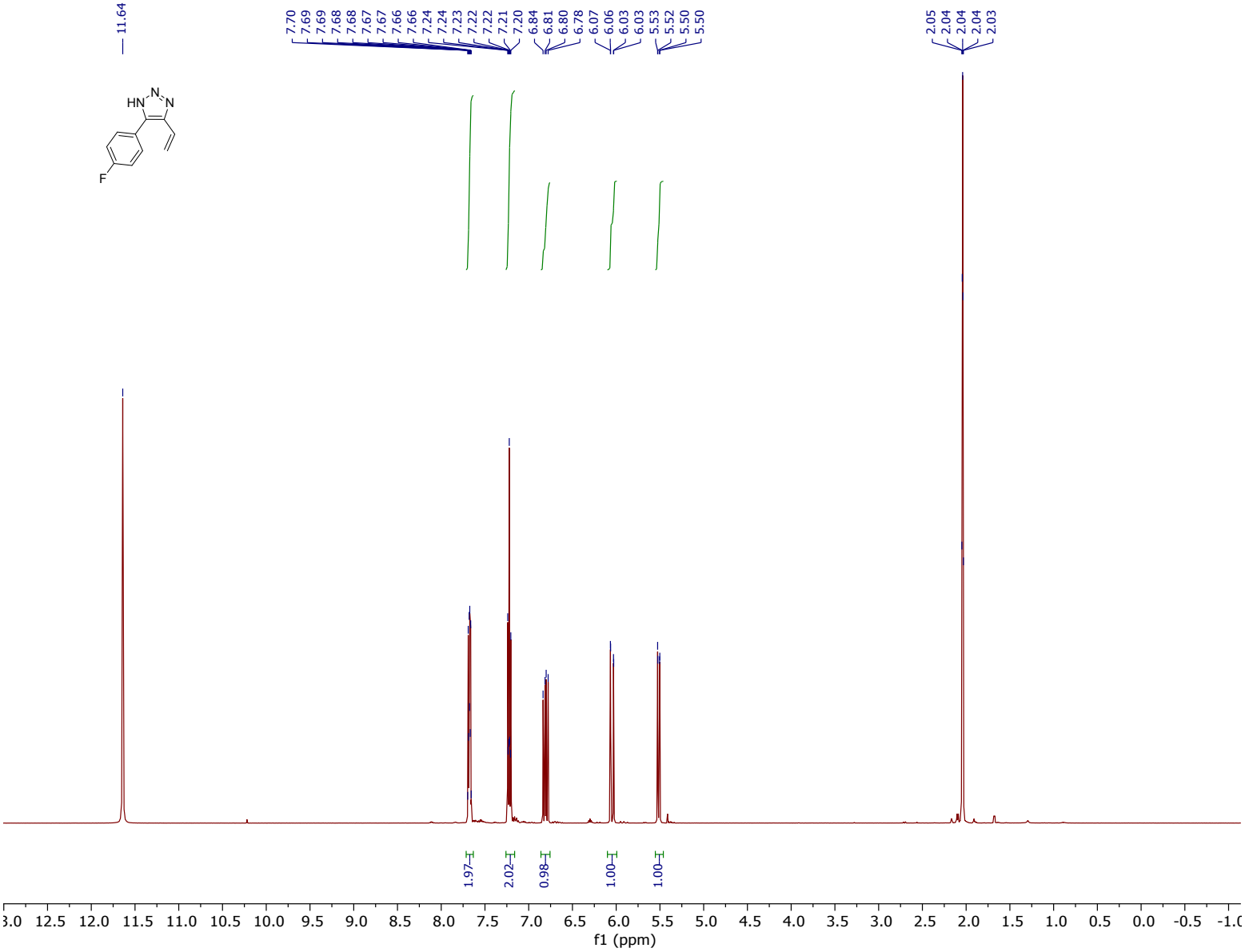
Compound **3c** 500 MHz ^{1}H NMR spectrum in $CDCl_3$



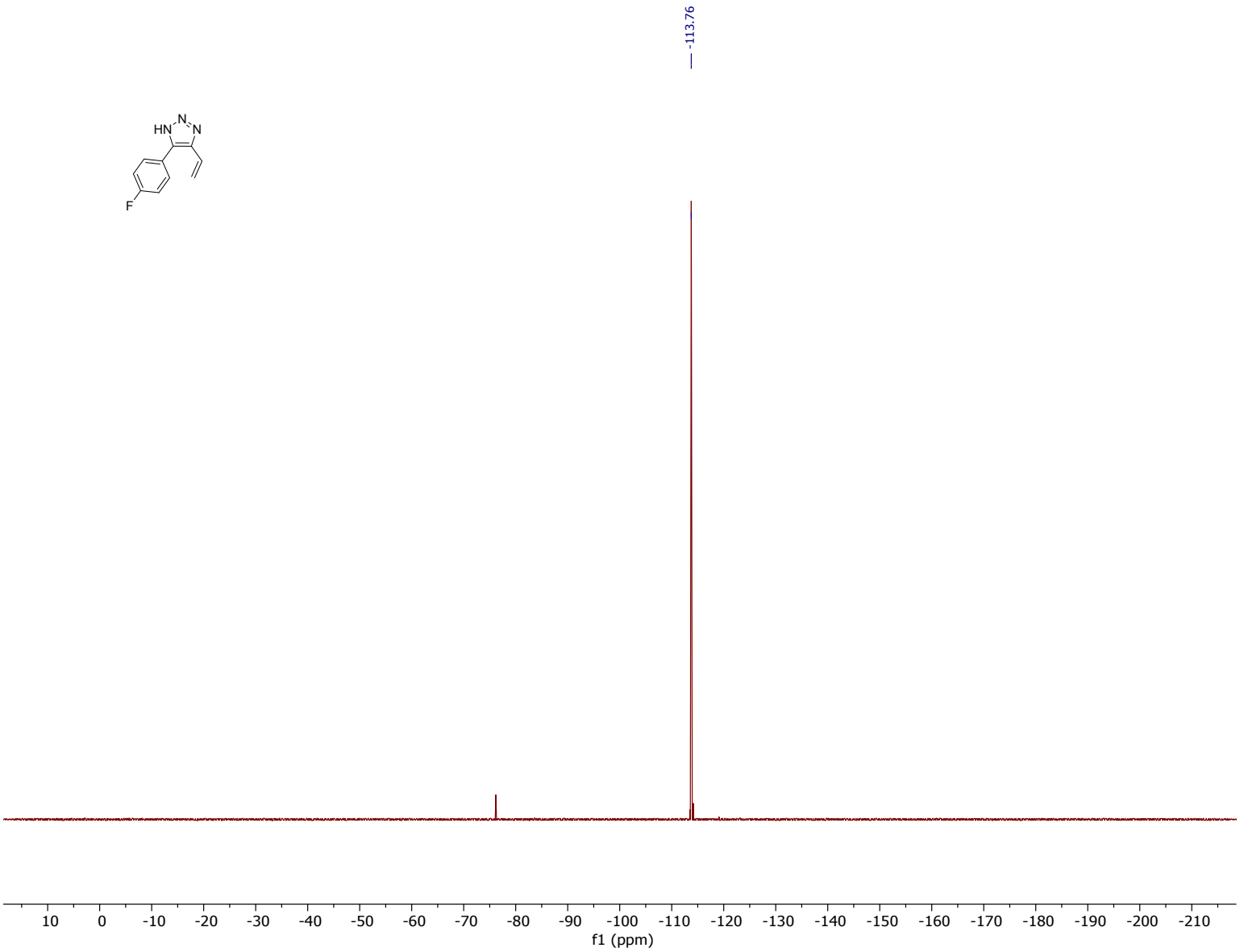
Compound **3c** 376 MHz ^{19}F NMR spectrum in $CDCl_3$



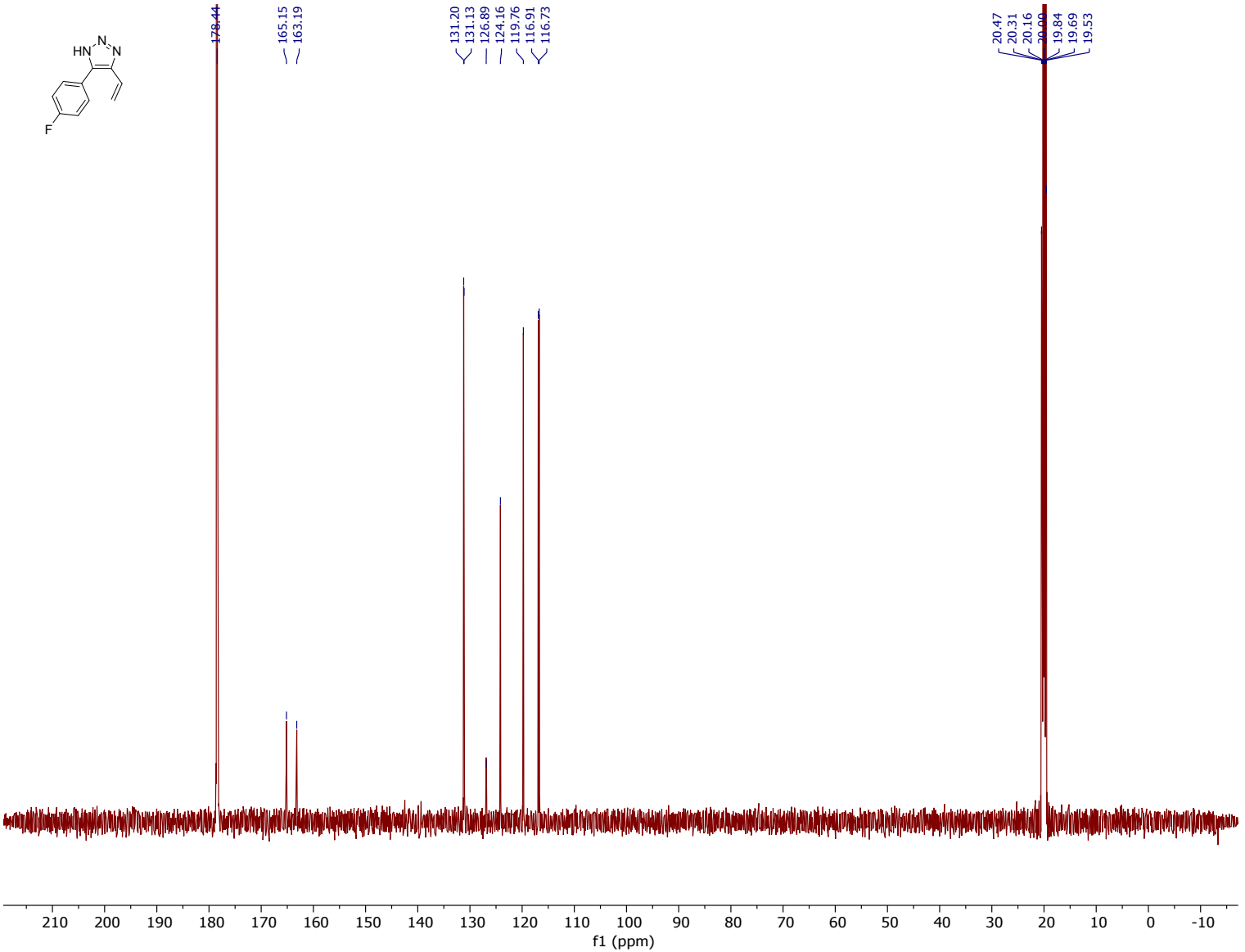
Compound **3c** 125 MHz ^{13}C NMR spectrum in $CDCl_3$



Compound **3d** 500 MHz ^{1}H NMR spectrum in Acetic acid-d_4



Compound **3d** 376 MHz ^{19}F NMR spectrum in Acetic acid-d_4



Compound **3d** 125 MHz ^{13}C NMR spectrum in Acetic acid-d_4