Supporting Information

Azidofluoromethane: Synthesis, Stability and Reactivity in [3 + 2] Cycloadditions

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General information

Reactions with air-sensitive materials were carried out under nitrogen atmosphere using standard Schlenk techniques. THF was dried with sodium and distilled under nitrogen. All other solvents were dried by activated molecular sieves (3 Å) and stored under argon. All commercially available chemicals were used as received unless stated otherwise. Automated flash column chromatography was performed on Teledyne ISCO CombiFlash Rf+ Lumen Automated Flash Chromatography System with UV/Vis detection using standard manufacturer's RediSep Rf columns, eluent cyclohexane-ethyl acetate. The melting points are uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured at ambient temperature using 5 mm diameter NMR tubes. ^{13}C NMR 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. UPLC-MS analyses were performed on Acquity UPLC Instrument (Waters Corporation). High resolution MS spectra (HRMS) were recorded on an LTQ Orbitrap XL using electrospray ionization (ESI), 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, and on a Bruker solariX 94 ESI/MALDI-FT-ICR using dual ESI/MALDI ionization.

Preparation of azidofluoromethane 1

Bromofluoromethane (0.826 g, 7.31 mmol) was dissolved in degassed NMP (2.558 g) and cooled to 10 °C. Sodium azide (0.951 g, 14.62 mmol) was suspended in NMP (3.141 g) in a 10 mL round-bottomed flask with glass cup and stirred at rt. Safety shield and metal safety clamp was used. The cooled bromide solution was added at once to the sodium azide suspension, the reaction vessel was closed and stirred for 2 h to complete conversion (NMR control). No overpressure was observed. Then THF (5 mL) was added to the reaction flask and co-distilled with the azide (temp. up to rt, 4 Torr, 20 min). The distillate (2.902 g) was collected in a cold trap cooled to -70 °C and contained azidofluoromethane **1** (6.17 mmol, 84% yield) dissolved in THF. Other solvents (DCE, DCM, $CDCl_3$ etc.) were used similarly. Fresh (10-30 min) azidofluoromethane-containing $CDCl_3$ distillate was used for NMR analysis. ^1H NMR (401 MHz, $CDCl_3$) δ 5.15 (d, *J* = 51.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 91.40 (d, *J* = 211.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.28 (t, *J* = 52.0 Hz); HRMS (EI$^+$) *m/z* calcd for CH_2N_3F $[M]^+$: 75.0233, found 75.0234.

Optimization of the synthesis of 1 (Table 1)

Bromofluoromethane (approximately 1 mmol) was dissolved in degassed solvent (2.0 g) and weighed. Sodium azide (1.5 eq.) was suspended in water and the mixture was stirred at rt. The bromofluoromethane solution was added to the azide suspension, the reaction vessel was closed and stirred at a given temperature for a given time.

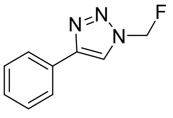
Azidofluoromethane stability studies

To the NMP solution of the crude azidofluoromethane, $CDCl_3$ (1.0 mL) was added and co-distilled with the azide to a trap cooled to -70 °C. The solution was transferred to NMR tube and warmed to rt. After storage for 60 min at rt all ^1H, ^{19}F and ^{13}C NMR signals corresponding to the azide disappeared. Signals at 6.6 ppm (^1H NMR) and 108.7 ppm (^{13}C NMR) were assigned to HCN (see spectrum - p. SI14).

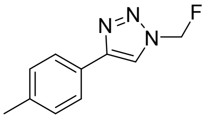
Synthesis of 4-substituted 1-fluoromethyl triazoles **2a-2h** *by azide-alkyne cycloaddition*

Method A. DMF (0.4 mL) was saturated with FCH_2Br (0.5 mmol) and cooled. Alkyne (0.5 mmol), NaN_3 (65 mg, 1.0 mmol) in H_2O (1.0 mL) and copper(I) 3-methylsalicylate (2.1 mg, 0.01 mmol, 2 mol%) were placed in a 10 mL screw-cap glass tube and the DMF solution of the bromide was added. The flask was closed and stirred at 40 °C for 20 h. Et_2O (20 mL) was added and the organic phase was washed with water (10 mL), aqueous LiCl solution (1M, 10 mL) and brine (6 x 10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by automated flash column chromatography on silica gel.

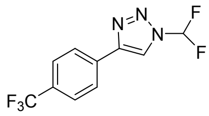
Method B. Alkyne (1.0 mmol) in THF (1 mL) was placed in a 10 mL screw-cap glass tube and a cold solution of FCH_2N_3 (1.0 mmol) in THF (approx. 0.5 mL) was added. Subsequently, copper(I) 3-methylsalicylate (4.2 mg, 0.02 mmol, 2 mol%) was added, the flask was closed and stirred at 40 °C for 20 h. THF was removed under reduced pressure, Et_2O (20 mL) was added and the organic phase was washed with aqueous $NaHCO_3$ solution (5%, 2 × 10 mL), water (10 mL), aqueous LiCl solution (1M, 10 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by automated flash column chromatography on silica gel.



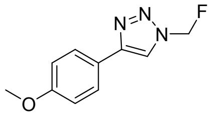
*1-(Fluoromethyl)-4-phenyl-1*H*-1,2,3-triazole (***2a***):* Method A, yield: 93%, colorless crystalline solid, m.p. 106–107 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.86 (d, *J* = 6.3 Hz, 2H), 7.51 – 7.42 (m, 2H), 7.42 – 7.35 (m, 1H), 6.33 (d, *J* = 51.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.26, 129.84, 129.12, 128.90, 126.12, 120.23, 85.36 (d, *J* = 205.7 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -167.52 (t, *J* = 51.2 Hz); HRMS (EI) *m/z* calcd for $C_9H_8N_3F$ $[M]^+$: 177.0702, found 177.0703.



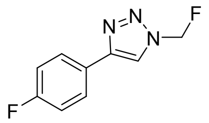
*1-(Fluoromethyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (***2b***):* Method A, yield: 64%, colorless crystalline solid, m.p. 133–134 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.30 (d, *J* = 51.2 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.25, 138.79, 129.75, 126.97, 125.96, 119.95, 85.30 (d, *J* = 205.5 Hz), 21.42; ^{19}F NMR (377 MHz, $CDCl_3$) δ -167.38 (t, *J* = 51.2 Hz); HRMS (EI) *m/z* calcd for $C_{10}H_{10}N_3F$ $[M]^+$: 191.0859, found 191.0862.



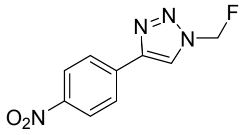
*1-(Fluoromethyl)-4-(*p*-trifluoromethyl)-1*H*-1,2,3-triazole (***2c***):* Method A, yield: 89%, light-yellow crystalline solid, m.p. 126–127 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 6.34 (d, *J* = 50.9 Hz, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.70, 133.12, 132.19, 130.62 (q, *J* = 32.5 Hz), 126.14, 125.99 (q, *J* = 3.7 Hz), 121.01, 85.25 (d, *J* = 206.5 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.72 (s, 3F), -167.38 (t, *J* = 50.9 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{10}H_7N_3F_4$ $[M]^+$: 245.0576, found 245.0578.



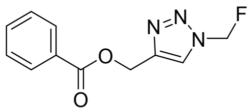
*1-(Fluoromethyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (***2d***):* Method A, yield: 93%, method B, yield: 77%, white crystalline solid, m.p. 121–123 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.83 – 7.72 (m, 2H), 7.02 – 6.90 (m, 2H), 6.30 (d, *J* = 51.2 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.15, 149.08, 127.42, 122.47, 119.41, 114.50, 85.33 (d, *J* = 205.6 Hz), 55.48; ^{19}F NMR (377 MHz, $CDCl_3$) δ -167.37 (t, *J* = 51.3 Hz); HRMS (ESI) *m/z* calcd for $C_{10}H_{10}N_3OF$ $[M]^+$: 207.0808, found 207.0807.



*1-(Fluoromethyl)-4-(*p*-fluorophenyl)-1*H*-1,2,3-triazole (***2e***):* Method A, yield: 51%, white crystalline solid, m.p. 120–122 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.87 – 7.78 (m, 2H), 7.18 – 7.11 (m, 2H), 6.32 (d, *J* = 51.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.16 (d, *J* = 248.3 Hz), 148.39, 127.92 (d, *J* = 8.3 Hz), 126.09, 119.99, 116.17 (d, *J* = 21.9 Hz), 85.37 (d, *J* = 206.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.08 (tt, *J* = 8.6, 5.3 Hz, 1F), -167.65 (t, *J* = 51.1 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_9H_7N_3F_2$ $[M]^+$: 195.0605, found 195.0608.

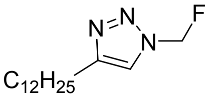


*1-(Fluoromethyl)-4-(*p*-nitrophenyl)-1*H*-1,2,3-triazole (***2f***):* Method A, yield: 59%, method B, yield 71%, yellow crystalline solid, m.p. 198–199 °C; ^{1}H NMR (401 MHz, DMSO-*d*$_6$) δ 9.16 (s, 1H), 8.35 – 8.31 (m, 2H), 8.19 – 8.15 (m, 2H), 6.55 (d, *J* = 50.7 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 146.99, 145.33, 136.25, 126.34, 124.87, 124.42, 85.62 (d, *J* = 199.2 Hz); ^{19}F NMR (377 MHz, DMSO-*d*$_6$) δ -166.97 (t, *J* = 50.7 Hz); HRMS (ESI) *m/z* calcd for $C_9H_7N_4O_2F$ $[M]^+$: 222.0553, found 222.0552.



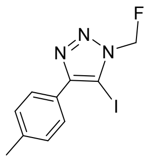
*(1-(Fluoromethyl)-1*H*-1,2,3-triazol-4-yl)methyl benzoate (*2g*):* Method B, yield: 81%, white crystalline solid, m.p. 72–73 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.98 (s, 1H), 7.56 – 7.51 (m, 1H), 7.43 – 7.37 (m, 2H), 6.26 (d, *J* = 50.9 Hz, 2H), 5.48 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.42, 144.31, 133.40, 129.77, 129.57,

128.50, 125.02, 85.14 (d, *J* = 205.9 Hz), 57.76; ^{19}F NMR (377 MHz, $CDCl_3$) δ -167.63 (t, *J* = 50.8 Hz); HRMS (ESI+) *m/z* calcd for $C_{11}H_{11}N_3O_2F$ $[M + H]^+$: 236.08298, found 236.08313.

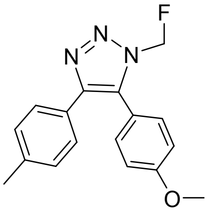


*4-Dodecyl-1-(fluoromethyl)-1*H*-1,2,3-triazole (***2h***):* Method B, yield: 89%, white crystalline solid, m.p. 71–72 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.52 (s, 1H), 6.21 (d, *J* = 51.4 Hz, 2H), 2.75 – 2.69 (m, 2H), 1.66 (p, *J* = 7.8 Hz, 2H), 1.36 – 1.27 (m, 4H), 1.24 (s, 14H), 0.89 – 0.81 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.93, 121.42, 85.10 (d, *J* = 204.5 Hz), 32.00, 29.75, 29.72 (2xC), 29.62, 29.44 (2xC), 29.30, 29.29, 25.58, 22.77, 14.19; ^{19}F NMR (377 MHz, $CDCl_3$) δ - 166.82 (t, *J* = 51.4 Hz); HRMS (EI) *m/z* calcd for $C_{15}H_{28}N_3F$ $[M]^+$: 269.2267, found 269.2273.

*Synthesis of 4,5-disubstituted 1*H*-1,2,3-triazoles* **4** *via 5-iodotriazole* **3**



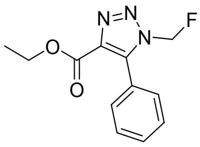
*1-(Fluoromethyl)-5-iodo-4-(*p*-tolyl)-1*H*-1,2,3-triazole (***3***):* To the THF solution of azidofluoromethane (**1**) (0.5 mmol, approx. 0.3 mL), 4-ethynyl toluene (58 mg, 0.5 mmol) in THF (1.0 mL), Et_3N (60 mg, 0.6 mmol, 1.2 equiv.), ICl (81 mg, 0.5 mmol) and CuI (95 mg, 0.5 mmol) were added. The reaction mixture was stirred at rt under nitrogen for 20 h (UPLC-MS control). The reaction mixture was then poured into water (10 mL) and extracted with Et_2O. The organic solution was dried over $MgSO_4$, filtered and evaporated to dryness, and purified by flash column chromatography to obtain white crystalline compound (142 mg, 90%), m.p. 164–165 °C. ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.32 – 7.28 (m, 2H), 6.37 (d, *J* = 51.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.20, 151.26, 139.23, 129.52, 127.56, 126.66, 85.37 (d, *J* = 207.7 Hz), 21.52; ^{19}F NMR (377 MHz, $CDCl_3$) δ -170.19 (t, *J* = 51.0 Hz); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{10}N_3FI$ $[M]^+$: 317.98980, found 317.98955.



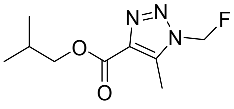
*1-(Fluoromethyl)-5-(4-methoxyphenyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (***4***):* To a 10 mL screw-cap glass tube were added the iodo derivative **3** (43 mg, 0.13 mmol), 4-methoxyphenylboronic acid (27 mg, 0.17 mmol), K_2CO_3 (90 mg, 0.65 mmol), and wet THF (1.5 mL). Then $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) was added and the reaction mixture was stirred at 50 °C under N_2 for 18 h (UPLC-MS control). The reaction mixture was then poured into water (10 mL) and extracted with Et_2O (3 × 10 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated to dryness, and purified by flash column chromatography to obtain yellow crystalline compound (22 mg, 58%), m.p. 96–98 °C. ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.50–7.48 (m, 2H), 7.35–7.33 (m, 2H), 7.13–7.11 (m, 2H), 7.03–7.01 (m, 2H), 6.10 (d, *J* = 51.4 Hz, 2H), 3.88 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.06, 144.95, 138.12, 134.50, 131.50, 129.40, 127.59, 127.11, 118.27, 114.99, 83.47 (d, *J* = 204.3 Hz), 55.52, 21.37; ^{19}F NMR (377 MHz, $CDCl_3$) δ -164.60 (t, *J* = 51.4 Hz); HRMS (ESI$^+$) *m/z* calcd for ($C_{17}H_{17}ON_3F$) $[M+H]^+$: 298.13502, found 298.13508.

*Synthesis of 4,5-disubstituted 1*H*-1,2,3-triazoles* **5a-5h** *by the azide-ketone [3+2] cycloaddition*

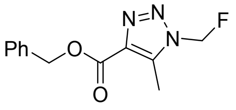
In a 10 mL screw-cap glass tube containing a cold solution of crude azidofluoromethane (**1**) in NMP (1.5 mmol, approx. 1 mL), ketone (1.5 mmol) and pyrrolidine (21 mg, 0.3 mmol) were added and the mixture was stirred at 45 °C for 20 h (UPLC-MS control). After reaching the complete conversion, the crude reaction mixture was purified by automated flash column chromatography on silica gel.



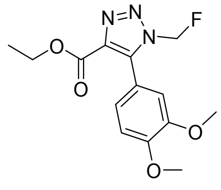
*Ethyl 1-(fluoromethyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (***5a***):* Yield: 67%, colorless oil, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 5H), 6.10 (d, J = 50.7 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.57, 142.79, 130.93, 130.21, 128.80, 124.39, 83.43 (d, J = 206.5 Hz), 61.44, 14.15; ^{19}F NMR (377 MHz, $CDCl_3$) δ -165.51 (t, J = 50.6 Hz); HRMS (ESI) *m/z* calcd for $C_{12}H_{13}N_3O_2F$ $[M + H]^+$: 250.0992, found 250.0993.



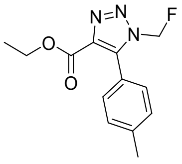
*Isobutyl 1-(fluoromethyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate (***5b***):* Yield: 70%, colorless oil, ^{1}H NMR (401 MHz, $CDCl_3$) δ 6.25 (d, J = 50.9 Hz, 2H), 4.10 (d, J = 6.8 Hz, 2H), 2.64 (s, 3H), 2.07 (dp, J = 13.4, 6.7 Hz, 1H), 0.97 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) 161.17, 139.57, 137.35, 83.41 (d, J = 204.8 Hz), 71.10, 27.70, 19.06, 8.50; ^{19}F NMR (377 MHz, $CDCl_3$) δ -172.20 (t, J = 50.8 Hz); HRMS (ESI$^+$) *m/z* calcd for $C_9H_{15}N_3O_2F$ $[M + H]^+$: 216.11428, found 216.11424.



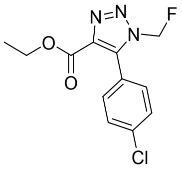
*Benzyl 1-(fluoromethyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate (***5c***):* Yield: 76%, colorless crystalline solid, m.p. 62–64 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.30 (m, 3H), 6.25 (d, J = 50.9 Hz, 2H), 5.40 (s, 2H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.10, 140.07, 137.27, 135.53, 128.72, 128.57, 128.54, 83.41 (d, J = 205.6 Hz), 66.92, 8.62; ^{19}F NMR (377 MHz, $CDCl_3$) δ -172.60 (t, J = 50.8 Hz); HRMS (EI) *m/z* calcd for $C_{12}H_{12}N_3O_2F$ $[M]^+$: 249.0914, found 249.0915.



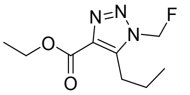
*Ethyl 5-(3,4-dimethoxyphenyl)-1-(fluoromethyl)- 1*H*-1,2,3-triazole-4-carboxylate (***5d***):* Yield: 89%, colorless crystalline solid, m.p. 111–112 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.10 (dd, J = 8.3, 2.0 Hz, 1H), 7.04 (d, J = 1.9 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.12 (d, J = 50.8 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.75, 151.16, 148.97, 142.87, 136.76, 123.46, 116.19, 113.22, 111.10, 83.49 (d, J = 205.6 Hz), 61.44, 56.13, 56.09, 14.29; ^{19}F NMR (377 MHz, $CDCl_3$) δ -164.87 (t, J = 50.6 Hz); HRMS (EI) *m/z* calcd for $C_{14}H_{16}N_3O_4F$ $[M]^+$: 309.1125, found 309.1123.



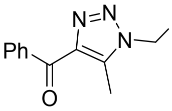
*Ethyl 1-(fluoromethyl)-5-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (***5e***):* Yield: 63%, colorless crystalline solid, m.p. 30–32 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.38 (dt, J = 8.3, 1.9 Hz, 2H), 7.31 (dt, J = 8.0, 1.8 Hz, 2H), 6.08 (d, J = 50.7 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.64, 142.98, 141.30, 136.94, 130.06, 129.49, 121.22, 83.38 (d, J = 206.0 Hz), 61.37, 21.54, 14.17; ^{19}F NMR (377 MHz, $CDCl_3$) δ -165.42 (t, J = 50.7 Hz); HRMS (ESI$^+$) *m/z* calcd for $C_{13}H_{15}N_3O_2F$ $[M + H]^+$: 264.11428, found 264.11401.



*Ethyl 5-(4-chlorophenyl)-1-(fluoromethyl)- 1*H*-1,2,3-triazole-4-carboxylate (***5f***):* Yield: 52%, colorless crystalline solid, m.p. 77–78 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.48 – 7.45 (m, 2H), 6.11 (d, J = 50.7 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 1.40 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.39, 141.65, 137.42, 137.25, 131.57, 129.14, 122.67, 83.39 (d, J = 206.6 Hz), 61.55, 14.13; ^{19}F NMR (377 MHz, $CDCl_3$) δ - 164.79 (t, J = 50.6 Hz); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{12}N_3O_2ClF$ $[M + H]^+$: 284.05966, found 284.05924.



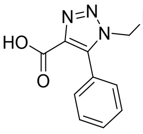
*Ethyl 1-(fluoromethyl)-5-propyl-1*H*-1,2,3-triazole-4-carboxylate (***5g***):* Yield: 71%, colorless oil, ^{1}H NMR (401 MHz, $CDCl_3$) δ 6.24 (d, *J* = 50.9 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.04 – 2.93 (m, 2H), 1.72 – 1.58 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.07, 143.90, 137.09, 83.29 (d, *J* = 205.5 Hz), 61.20, 24.71, 22.43, 14.25, 13.73; ^{19}F NMR (377 MHz, $CDCl_3$) δ -169.95 (t, *J* = 50.9 Hz); HRMS (EI) *m/z* calcd for $C_9H_{14}N_3O_2F$ $[M]^+$: 215.1070, found 215.1072.



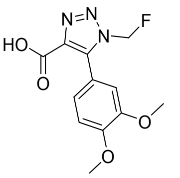
*(1-(Fluoromethyl)-5-methyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone (***5h***):* Yield: 90%, yellowish oil, ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.32 – 8.29 (m, 2H), 7.63 – 7.57 (m, 1H), 7.54 – 7.48 (m, 2H), 6.32 (d, *J* = 50.9 Hz, 2H), 2.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) 187.32, 144.14, 140.91 (d, *J* = 1.5 Hz), 137.10, 133.29, 130.66, 128.45, 83.35 (d, *J* = 205.6 Hz), 9.12; ^{19}F NMR (377 MHz, $CDCl_3$) δ -172.70 (t, *J* = 50.9 Hz); HRMS (EI) *m/z* calcd for $C_{11}H_{10}N_3OF$ $[M]^+$: 219.0808, found 219.0807.

***Synthesis of 5-substituted 1*H*-1,2,3-triazole-4-carboxylic acids* 6a,d,e,f**

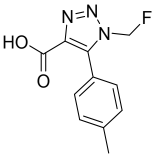
Ester **5** (0.2 mmol) was dissolved in THF (1 mL) and the solution of LiOH·H_2O (16.8 mg, 0.4 mmol) in water (0.5 mL) was slowly added. The reaction mixture was stirred at rt for 45 min. 1M HCl solution (0.6 mL) was then added, the mixture was stirred for 10 min (UPLC control), poured to 1M LiCl solution (15 mL) and Et_2O (15 mL) in a separatory funnel. After vigorous shaking, the organic layer was separated and dried with $MgSO_4$ overnight. After evaporation to dryness, white crystals of the acid were obtained.



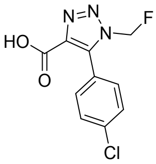
*1-(Fluoromethyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid (***6a***):* Yield: 86%, colorless crystals, m.p. 172-174 °C (dec.), ^{1}H NMR (401 MHz, DMSO-*d*$_6$) δ 7.61 – 7.50 (m, 5H), 6.26 (d, *J*=50.8, 2H), 3.36 (br s, 1H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 161.44, 141.82, 137.39, 130.34, 130.09, 128.51, 124.75, 84.12 (d, *J* = 199.9 Hz); ^{19}F NMR (377 MHz, DMSO-*d*$_6$) δ -166.31 (t, *J* = 50.8 Hz); HRMS (ESI-) *m/z* calcd for $C_{10}H_7N_3O_2F$ $[M - H]^+$: 220.05278, found 220.05283.



*5-(3,4-Dimethoxyphenyl)-1-(fluoromethyl)-1*H*-1,2,3-triazole-4-carboxylic acid (***6d***):* Yield: 60%, colorless crystals, m.p. 168-169 °C (dec.), ^{1}H NMR (401 MHz, Acetone-*d*$_6$) δ 7.21 – 7.13 (m, 3H), 6.33 (d, *J* = 51.0 Hz, 2H), 3.90 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 161.89, 152.08, 149.98, 137.55, 124.05, 117.68, 114.76, 114.75, 112.23, 85.01 (d, *J* = 200.6 Hz), 56.20, 56.10; ^{19}F NMR (377 MHz, DMSO-*d*$_6$) δ -166.31 (t, *J* = 50.8 Hz); HRMS (ESI$^-$) *m/z* calcd for $C_{12}H_{11}N_3O_4F$ $[M - H]^+$: 280.07391, found 280.07394.



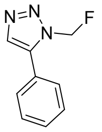
*1-(Fluoromethyl)-5-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylic acid (***6e***):* Yield: 88%, colorless crystals, m.p. 204-205 °C (dec.), ^{1}H NMR (401 MHz, DMSO-*d*$_6$) δ 7.45 – 7.33 (m, 4H), 6.25 (d, *J* = 50.9 Hz, 2H), 3.39 (br s, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 161.97, 142.38, 140.63, 137.69, 130.44, 129.57, 122.17, 84.54 (d, *J* = 199.9 Hz), 21.43; ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -166.16 (t, *J* = 50.8 Hz); HRMS (ESI$^-$) *m/z* calcd for $C_{11}H_9N_3O_2F$ $[M - H]^+$: 280.07391, found 280.07394.



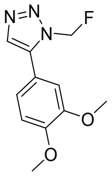
*5-(4-Chlorophenyl)-1-(fluoromethyl)-1*H*-1,2,3-triazole-4-carboxylic acid* (**6f**)*:* Yield: 91%, colorless crystals, m.p. 178–180 °C (dec.), ^{1}H NMR (401 MHz, Acetone-d_6) δ 7.63 (s, 4H), 6.34 (d, *J* = 50.9 Hz, 2H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 161.65, 142.32, 138.18, 137.03, 132.94, 129.59, 124.86, 85.03 (d, *J* = 201.3 Hz).; ^{19}F NMR (377 MHz, Acetone-d_6) δ -166.58 (t, *J* = 50.9 Hz); HRMS (ESI$^-$) *m/z* calcd for $C_{10}H_6N_3O_2ClF$ [M – H]$^+$: 254.01381, found 254.01386.

Synthesis of 1-fluoromethyl-5-substituted 1H-1,2,3-triazoles 7a,d,e,f

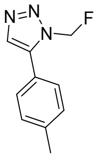
Carboxylic acid **6** (0.1 mmol) was heated for 10 min above its m.p. (180-215 °C) in an open 2 mL sample vial (oil bath). CO_2 evolution was observed. The obtained light brown oil was dried at low vacuum overnight and purified by automated flash column chromatography on silica gel.



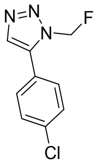
*1-(Fluoromethyl)-5-phenyl-1*H*-1,2,3-triazole* (**7a**)*:* Yield: 97%, colorless crystals, m.p. 58–60 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.53 (s, 5H), 6.24 (d, *J* = 51.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.68, 133.28, 130.31, 129.49, 128.81, 125.66, 83.49 (d, *J* = 204.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -163.96 (t, *J* = 51.2 Hz); HRMS (CI$^+$) *m/z* calcd for $C_9H_9N_3F$ [M + H]$^+$: 178.0781, found 178.0782.



*5-(3,4-Dimethoxyphenyl)-1-(fluoromethyl)-1*H*-1,2,3-triazole* (**7d**)*:* Yield: 63%, colorless crystals, m.p. 138–140 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.10 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.23 (d, *J* = 51.4 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.76, 149.63, 139.75, 132.91, 121.78, 118.01, 111.75, 111.67, 83.53 (d, *J* = 203.5 Hz), 56.17; ^{19}F NMR (377 MHz, $CDCl_3$) δ -163.62 (t, *J* = 51.4 Hz); HRMS (CI$^+$) *m/z* calcd for $C_{11}H_{13}N_3O_2F$ [M + H]$^+$: 238.0992, found 238.0990.



*1-(Fluoromethyl)-5-(*p*-tolyl)-1*H*-1,2,3-triazole* (**7e**)*:* Yield: 81%, colorless crystals, m.p. 44–46 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.42 – 7.40 (m, 2H), 7.33 – 7.31 (m, 2H), 6.22 (d, *J* = 51.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.60, 139.74, 133.06, 130.17, 128.67, 122.69, 83.46 (d, *J* = 203.9 Hz), 21.46; ^{19}F NMR (377 MHz, $CDCl_3$) δ -163.96 (t, *J* = 51.3 Hz); HRMS (CI$^+$) *m/z* calcd for $C_{10}H_{11}N_3F$ [M + H]$^+$: 192.0937, found 192.0939.



*5-(4-Chlorophenyl)-1-(fluoromethyl)-1*H*-1,2,3-triazole* (**7f**)*:* Yield: 85%, colorless crystals, m.p. 62–63 °C, ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.54 – 7.44 (m, 4H), 6.22 (d, *J* = 51.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.58, 136.70, 133.42, 130.06, 129.82, 124.08, 83.48 (d, *J* = 204.3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -163.84 (t, *J* = 51.3 Hz); HRMS (CI$^+$) *m/z* calcd for $C_9H_8N_3ClF$ [M + H]$^+$: 212.0391, found 212.0387.

Computational studies

Cartesian coordinates of transition states and ground state minima of the fluorinated azidomethanes localized at the PBE0/6-31+g* level. Gaussian 09, revision D.01 was used for the calculations.

CH_3N_3 *Azidomethane*

TS

7

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.364307
N	1.910072	0.000000	2.055970
N	2.566234	0.000000	2.944375
H	-1.130257	0.000000	0.095884
H	0.261762	0.919655	-0.557338
H	0.261762	-0.919655	-0.557338

S0 minimum

7

C	-0.049040	0.000000	0.039257
N	0.171604	0.000000	1.485723
H	0.936731	0.000000	-0.426200
H	-0.594347	-0.894414	-0.287129
H	-0.594347	0.894414	-0.287129
N	-0.841737	0.000000	2.177554
N	-1.702670	0.000000	2.922257

CFH_2N_3 *Azidofluoromethane*

TS

7

C	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.407152
N	1.143361	0.000000	-0.666548
N	1.886934	-1.763797	-0.620117
N	2.760955	-2.417214	-0.789096
H	-0.144427	1.065952	-0.359437
H	-0.874309	-0.596434	-0.296444

S0 minimum

7

C	0.035601	-0.046825	-0.054628
H	0.091132	-0.031637	1.033623
H	1.032269	-0.121400	-0.505172
F	-0.505877	1.157878	-0.475324
N	-0.812521	-1.152768	-0.409912
N	-0.870309	-1.405121	-1.619539
N	-1.023446	-1.738317	-2.690789

CF_2HN_3 *Azidodifluoromethane*

TS

7

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.312210
F	1.143402	0.000000	-0.740861
F	-0.888339	0.719876	-0.740861

N	0.615320	1.736647	1.855376
N	0.875128	2.469916	2.637341
H	-0.381850	-1.077714	0.164048

S0 minimum
7

C	-0.056022	-0.059327	0.013986
H	-0.180225	-0.116063	1.101201
F	1.250823	-0.010631	-0.282989
F	-0.626967	1.104136	-0.406814
N	-0.599034	-1.179038	-0.696921
N	-1.773640	-1.442523	-0.417761
N	-2.838972	-1.787829	-0.256910

CF_3N_3 Azidotrifluoromethane
TS
7

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.360192
F	1.398058	0.000000	0.165941
F	-0.371628	-1.066991	-0.701278
F	-0.371974	1.066963	-0.701060
N	-3.464767	0.002454	-0.411204
N	-4.353862	0.002922	-1.062177

S0 minimum
7

C	0.085007	0.157289	-0.115471
F	-0.160853	-0.588693	0.951682
F	1.381202	0.518330	-0.097270
F	-0.632993	1.290991	-0.022277
N	-0.250827	-0.606892	-1.265922
N	-0.063791	-0.018002	-2.341510
N	0.054796	0.389984	-3.386505

Cartesian coordinates of transition states and ground state minima of the fluorinated azidomethanes localized at the CASPT2/6-31g* level. We have considered an active space of 6 electrons in 5 orbitals. The transition states were localized with MOLPRO2012 package (www.molpro.net).
CH_3N_3 Azidomethane
TS
7

C	-0.3835302327	0.0000012924	-1.8037612282
N	0.6618617987	-0.0000001660	-0.8650113208
N	-0.1670291654	-0.0000052510	0.8790166972
N	-0.0435897600	0.0000037024	1.9966435449
H	0.3031331684	0.0000115566	-2.6789377829
H	-1.0017321465	-0.9065426970	-1.8837357478
H	-1.0017422407	0.9065395670	-1.8837222224

S0 minimum
7

C	0.0000000946	0.3629563809	-1.6241505002

N	0.0000007241	-0.6153829767	-0.5171838341
N	-0.0000000278	-0.0908714949	0.6173410284
N	-0.0000006438	0.2599216149	1.7159295700
H	-0.0000004905	-0.2224328612	-2.5416450603
H	-0.8927046372	0.9960259432	-1.6010894570
H	0.8927049805	0.9960257623	-1.6010904933

CFH_2N_3 Azidofluoromethane
TS
7

C	-0.3484839193	-0.4297708003	1.2094120032
F	0.1400742808	0.7881744492	1.7196688900
N	0.3181629610	-1.0202858895	0.1818121642
N	-0.1242686907	0.0377312805	-1.3557109471
N	0.0245368016	0.3954527123	-2.4177004760
H	-0.0847206469	-1.2495516020	1.9194003324
H	-1.4382328784	-0.3266519437	1.1653499209

S0 minimum
7

C	-0.5014505409	0.3741751299	-1.0806647940
F	0.7246631398	-0.1174702979	-1.5141810169
N	-0.9054730587	-0.2336129093	0.1735480563
N	-0.0737125316	-0.0417610266	1.1025101955
N	0.5905569013	0.0315715636	2.0347605942
H	-1.2674437209	0.1043319393	-1.8059517864
H	-0.4048622498	1.4614731541	-0.9966875219

CF_2HN_3 Azidodifluoromethane
TS
7

C	0.0007858997	-0.3560727471	-0.9881073673
F	1.0826305567	0.4530311852	-1.2216325302
N	0.0055020991	-1.2305762972	0.0233251920
F	-1.0876333207	0.4455458965	-1.2175766116
N	0.0024954925	0.0187993962	1.5935878807
N	-0.0020531456	0.3879056273	2.6605585573
H	0.0023245552	-1.2451356126	-1.6906026300

S0 minimum
7

C	0.0002710032	-0.4236309980	-0.9178394995
F	1.0944531038	0.3742871521	-1.1147432873
N	0.0001092026	-1.0023534986	0.3923239679
N	-0.0001271634	-0.1179806378	1.3048470863
N	-0.0003580303	0.5448347423	2.2358911036
F	-1.0941435465	0.3738457897	-1.1152109358
H	0.0005907173	-1.2302534535	-1.6474509952

CF_3N_3 Azidotrifluoromethane
TS

S0 minimum

7

C	0.0000357107	-0.0338503446	-0.6396408912
N	0.0007153405	-0.9011939561	0.4954688651
N	0.0002472328	-0.2494733520	1.5869199993
N	-0.0000731771	0.1740334096	2.6477694850
F	-0.0002673585	-0.8024955778	-1.7288705393
F	-1.0848295656	0.7726837874	-0.6757774399
F	1.0845276349	0.7731324542	-0.6767431044

Table S1: Activation energies $\Delta E^{\#}$ for the thermal decomposition of fluorinated azidomethanes calculated at different electronic structure levels. All activation energies are shown in eV units.

	CH_3N_3	CFH_2N_3	CF_2HN_3	CF_3N_3
PBE0/6-31+g*	2.29	1.83	2.01	2.92
CCSD(T)/aug-cc-pVQZ [a]	1.84	1.48	1.65	2.42
CASPT2(6,5)/6-31g*	2.11	1.56	1.73	– [b]
CCSD(T)/aug-cc-pVTZ [c]	1.82	1.47	1.64	– [b]

[a] energies for structures optimized at the PBE0/6-31+g* level

[b] We were not able to localize the transition state for CF_3N_3 at the CASPt2 level.

[c] energies for structures optimized at the CASPT2/6-31g* level

Table S2: Energy position of singlet-triplet crossing points with respect to the ground singlet electronic state of the azidomethanes. All energies are shown in eV units.

	CH_3N_3	CFH_2N_3	CF_2HN_3	CF_3N_3
CASSCF(6,5)/6-31g*	1.92	1.86	2.72	2.98
CCSD(T)/aug-cc-pVTZ (S) [c]	1.50	1.34	1.90	1.84
CCSD(T)/aug-cc-pVTZ (T) [d]	1.31	1.43	2.07	2.16

[c] energies for singlet MECI structures optimized on CASSCF/6-31g* level

[d] energies for triplet MECI structures optimized on CASSCF/6-31g* level

The Cartesian coordinates of the minimum energy crossing points between singlet and triplet states were localized at the CASSCF/6-31g* level, using and active space comprising of 6 electrons in 5 orbitals. We have considered averaging over one singlet and one triplet state.

CH_3N_3 Azidomethane

MECP

7

C	-0.0084114012	0.0243481665	-0.2283267089
N	-0.8022320578	0.0608155269	0.8529945572
N	2.3596832893	-0.3150353636	2.7572435652
N	2.6812523142	0.2394763801	3.6400049966
H	-1.0726140798	0.0953291816	-0.6754458631
H	0.4125684323	-0.9142984683	-0.5964267015
H	0.5236145031	0.9093645769	-0.5833378455

CFH_2N_3 Azidofluoromethane

MECP

7

C	1.8425131782	-0.2956572620	0.0456795920
N	1.4551464655	0.9137028306	0.1421523941
N	-1.6605138034	-0.1294170063	0.0320493013
N	-2.6981535267	-0.2489701564	-0.2285083621

H	2.9003435406	0.0734278517	-0.1277367520
H	1.5661697704	-0.8979653850	-0.7968667426
F	1.8487123755	-1.1302858727	1.1490825694

CF_2HN_3 Azidodifluoromethane
MECP
7

C	1.6246456942	-0.3383915972	0.0021850793
F	1.5773767587	-1.0875735128	1.1139352817
N	0.7918219511	0.8105884023	0.0393930815
N	-0.8871518552	-0.0417140551	-0.0355861271
N	-1.9482810841	-0.2193871286	-0.0557991359
F	2.8244611520	0.2470847911	-0.0514346025
H	1.5011473832	-1.0055908997	-0.8345155771

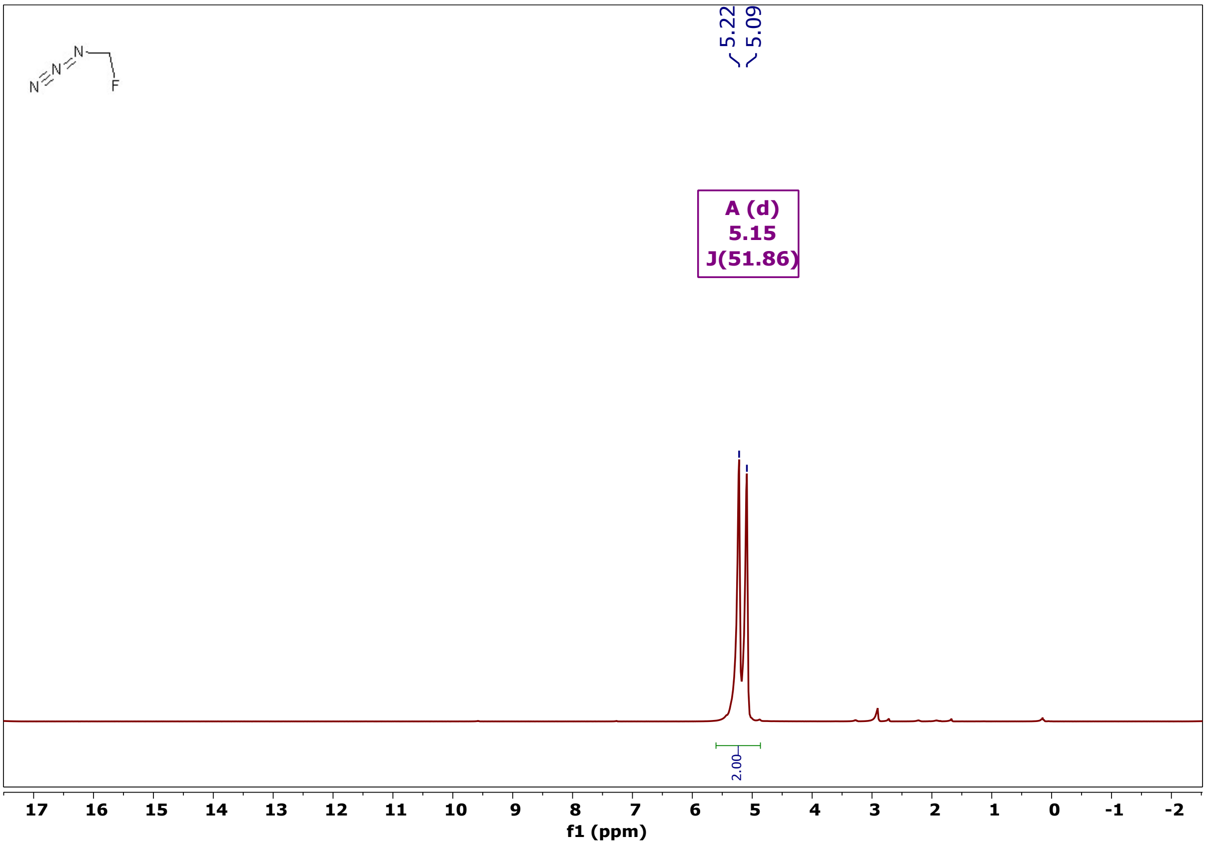
CF_3N_3 Azidotrifluoromethane
MECP
7

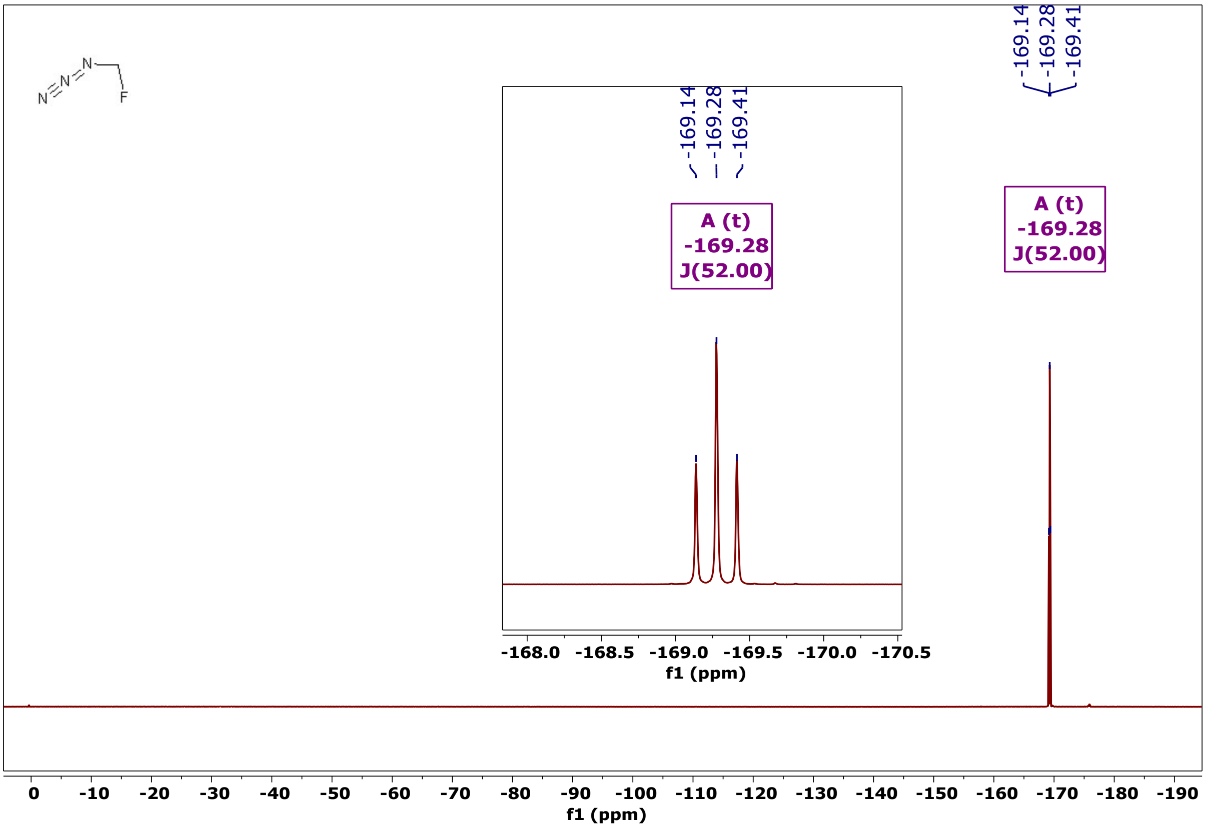
C	1.6217041971	-0.3319340447	-0.0033160893
F	2.8224458939	0.2103341769	-0.0094847114
F	1.4969979168	-1.0920993761	1.0682572157
N	0.8038495092	0.8181981929	-0.0333395707
N	-0.8657652231	-0.0364158799	-0.0224962067
N	-1.9191010394	-0.2518541432	-0.0229462628
F	1.5076167454	-1.1396039259	-1.0407773748

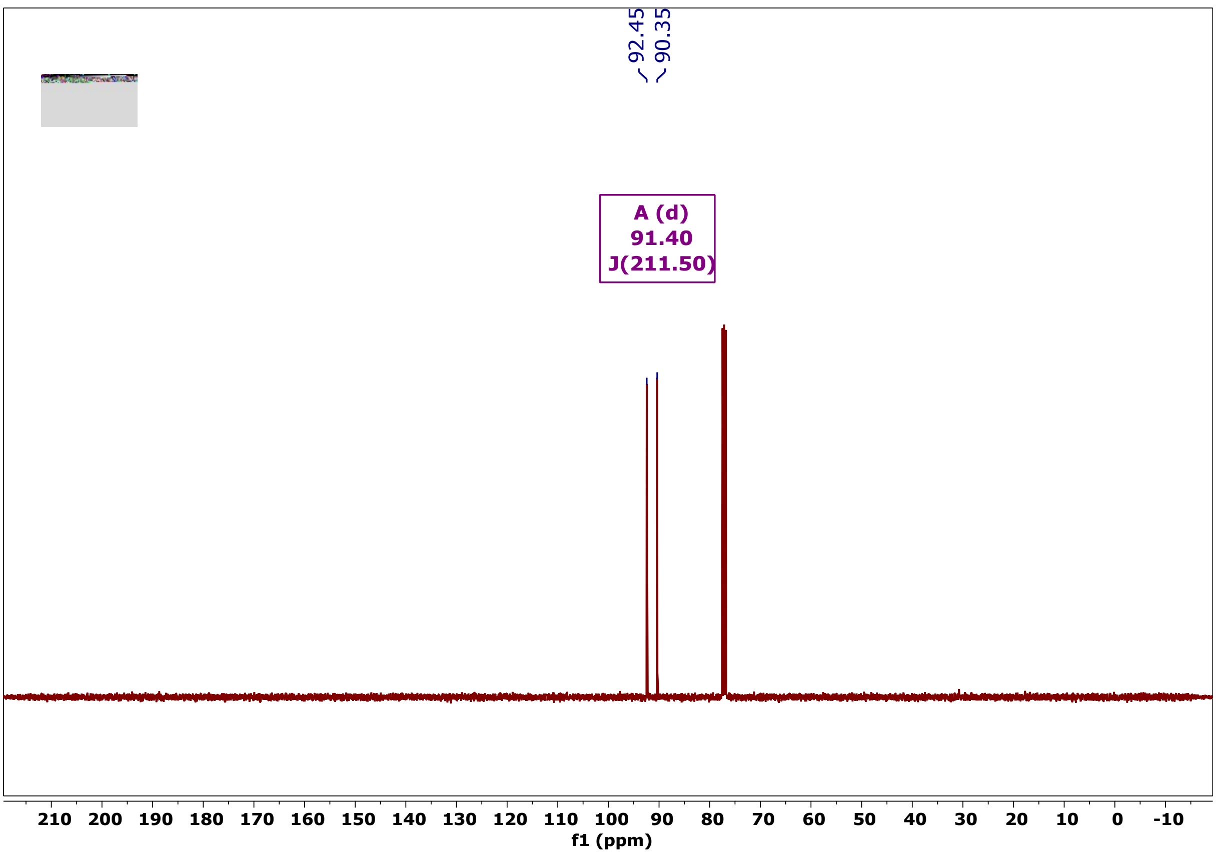
Table S3: Energetics for a subsequent decomposition of azidomethanes. Nitrene intermediate and imine products are considered. All structures were optimized at the PBE0/6-31+g* level and recalculated with the CCSD(T)/aug-cc-pVTZ level. Nitrene intermediate is stable in a triplet state and also in a singlet state for azidotrifluoromethane. The energies of singlet states of methylnitrene, fluoromethylnitrene and difluoromethylnitrene are shown for structures optimized with fixed N_α-C-H angle; the angle was fixed to a value found in singlet trifluoromethylnitrene. All energies are shown in eV units.

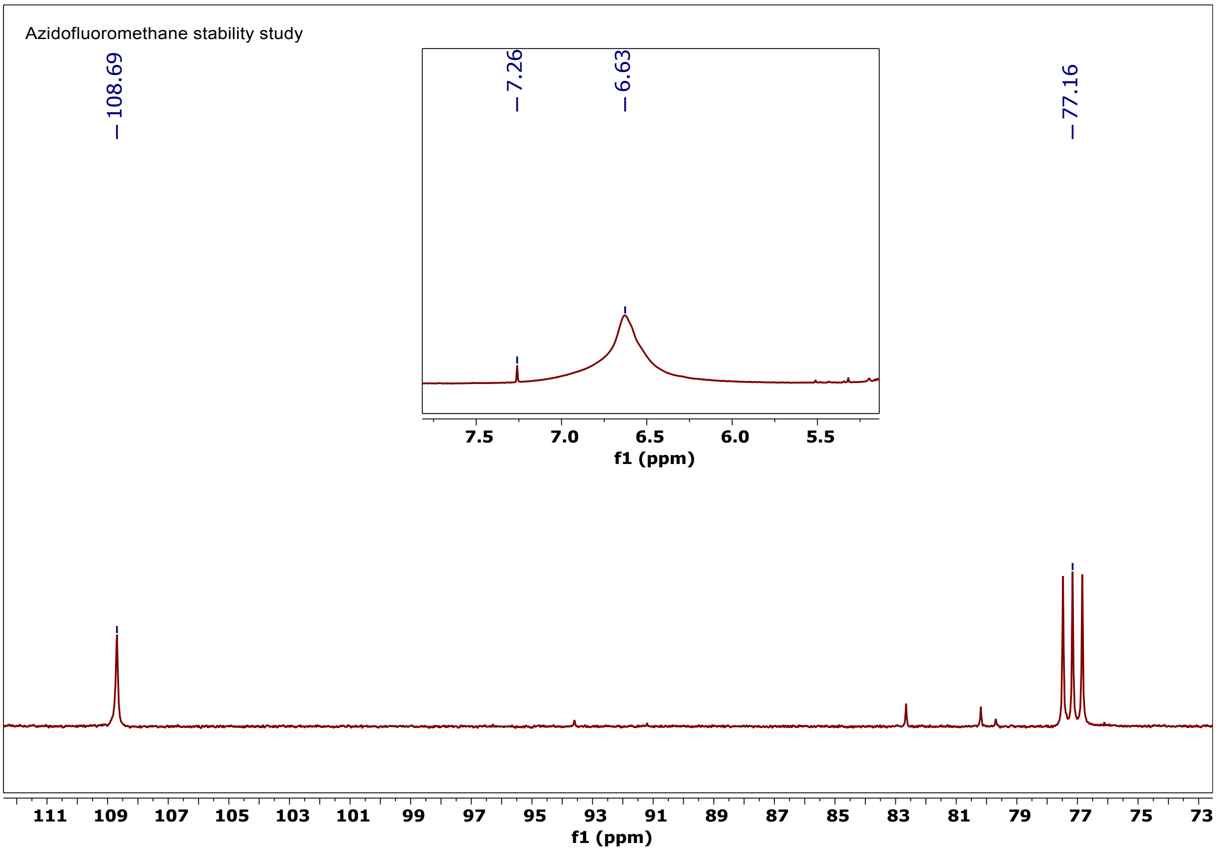
	nitrene (S_0) + N_2	nitrene (T_1) + N_2	imine (S_0) + N_2	imine (T_1) + N_2
CH_3N_3	1.99	0.22	-2.11	1.74
CFH_2N_3	1.21	0.47	-2.46	3.37
CF_2HN_3	1.52	0.57	-2.40	2.49
CF_3N_3	2.44	0.63	0.33	6.48

Copies of NMR spectra Compound **1** (azidofluoromethane)

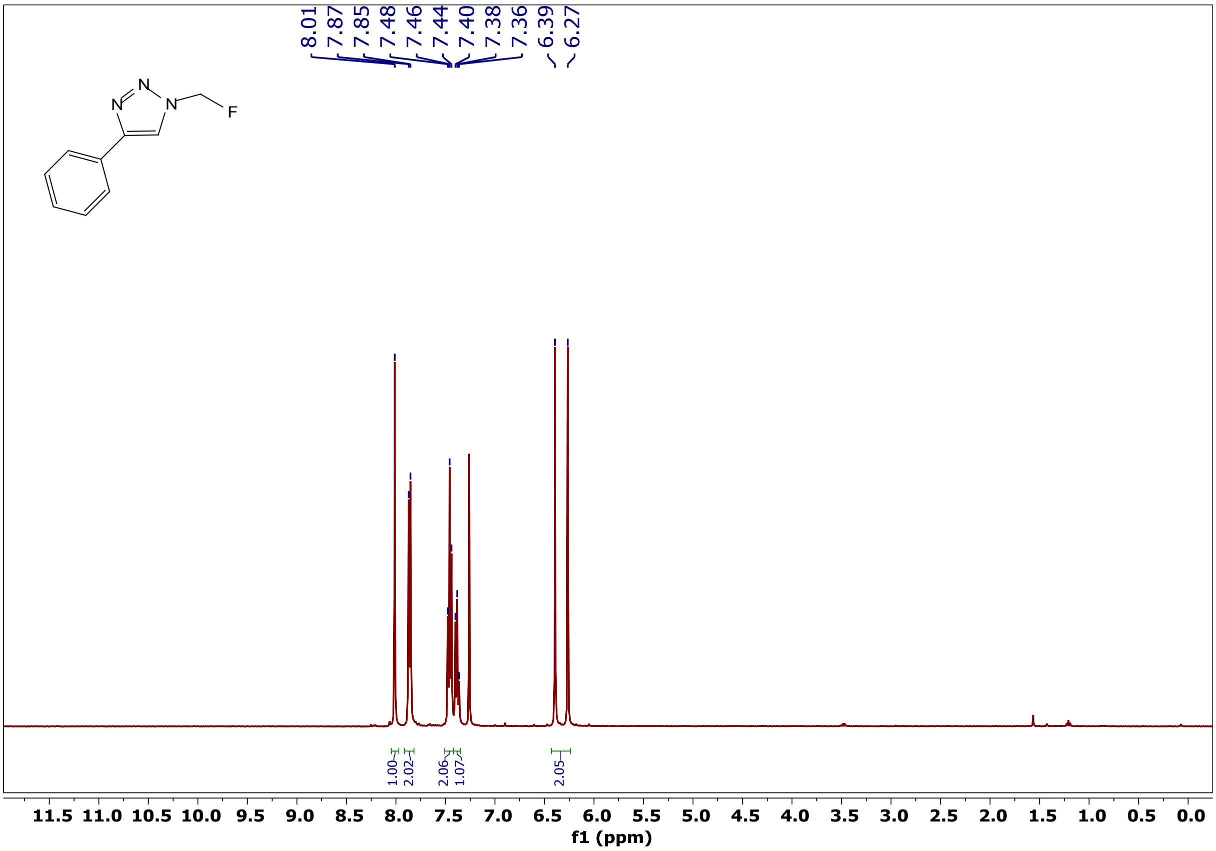




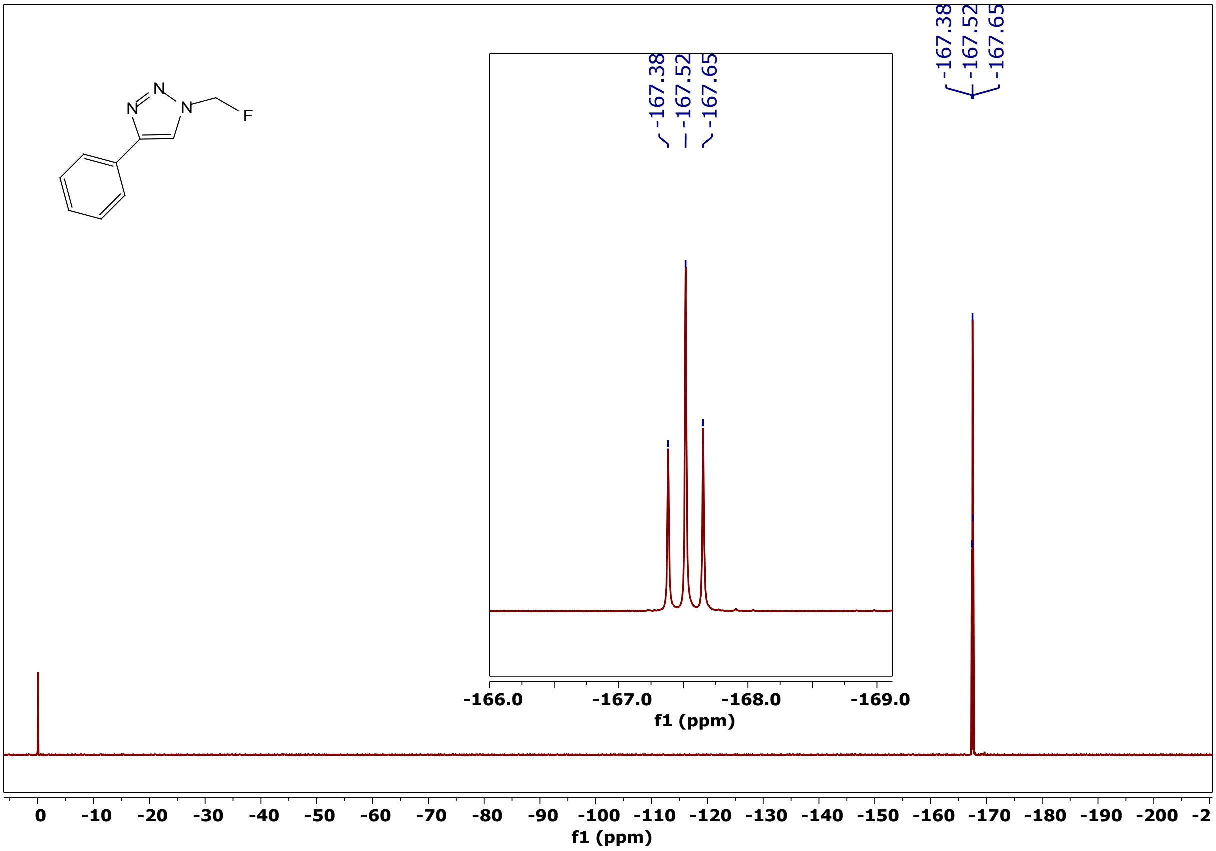

92.45
90.35
A (d)
91.40
J(211.50)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Azidofluoromethane stability study
108.69
7.26
6.63
77.16
7.5 7.0 6.5 6.0 5.5
f1 (ppm)
111 109 107 105 103 101 99 97 95 93 91 89 87 85 83 81 79 77 75 73
f1 (ppm)

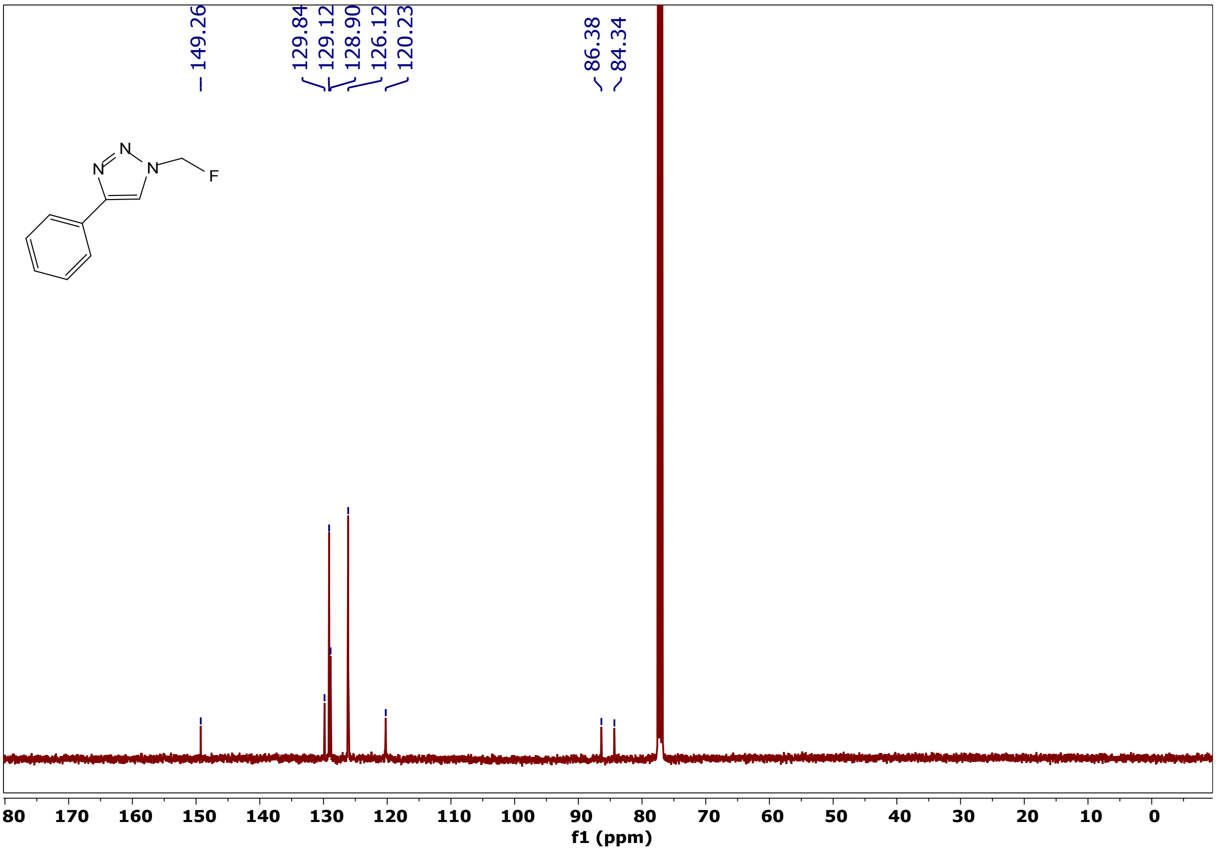
Compound **2a**



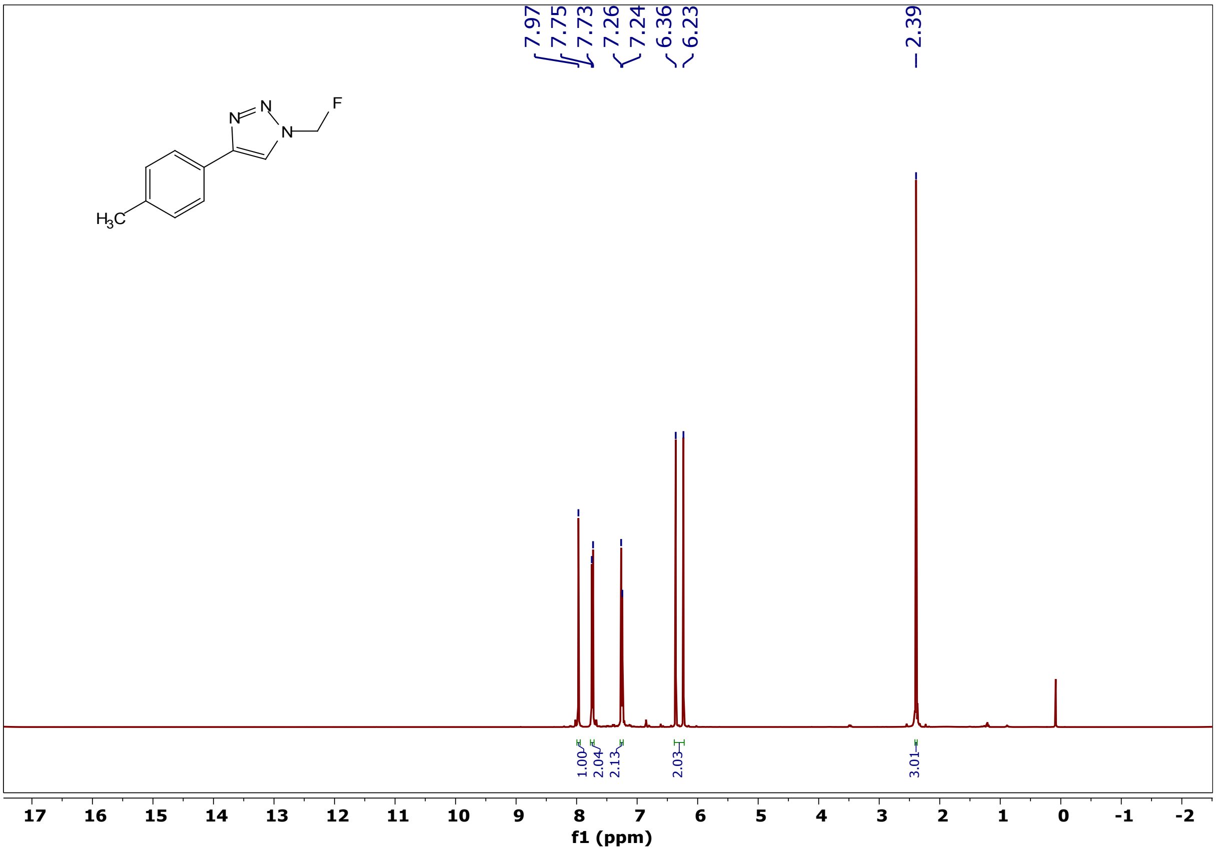
N
N
N
F
8.01
7.87
7.85
7.48
7.46
7.44
7.40
7.38
7.36
6.39
6.27
1.00
2.02
2.06
1.07
2.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

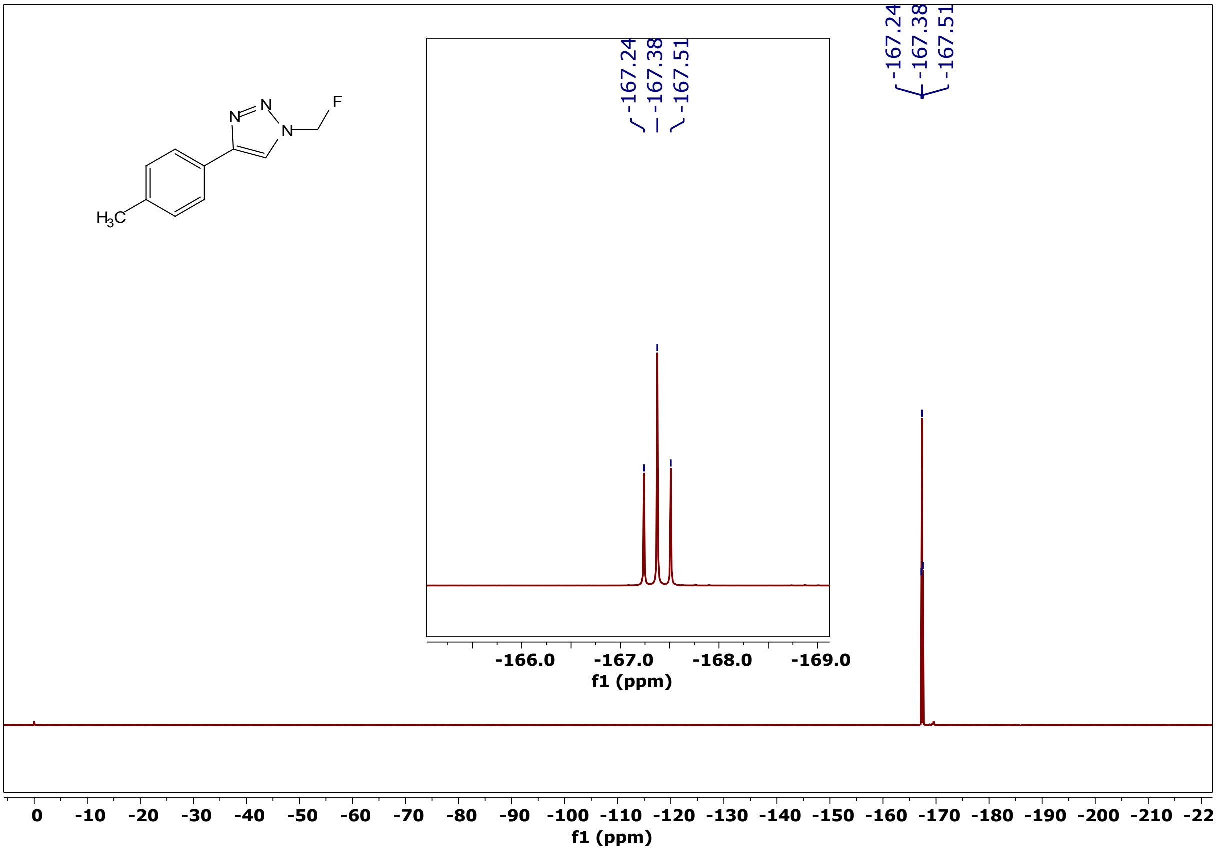


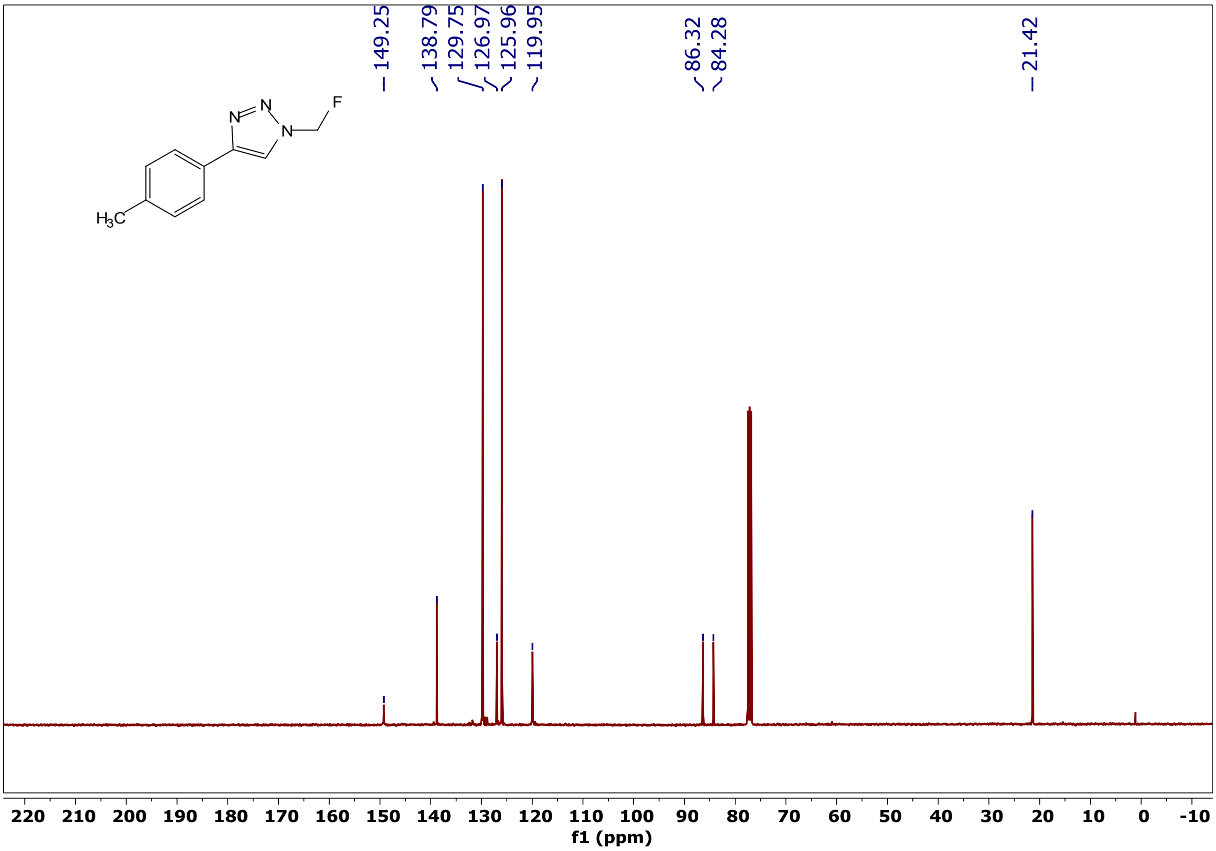
N
N
N
F
-167.38
-167.52
-167.65
-167.38
-167.52
-167.65
-166.0 -167.0 -168.0 -169.0
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)


149.26
129.84
129.12
128.90
126.12
120.23
86.38
84.34
N
N
N
F
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

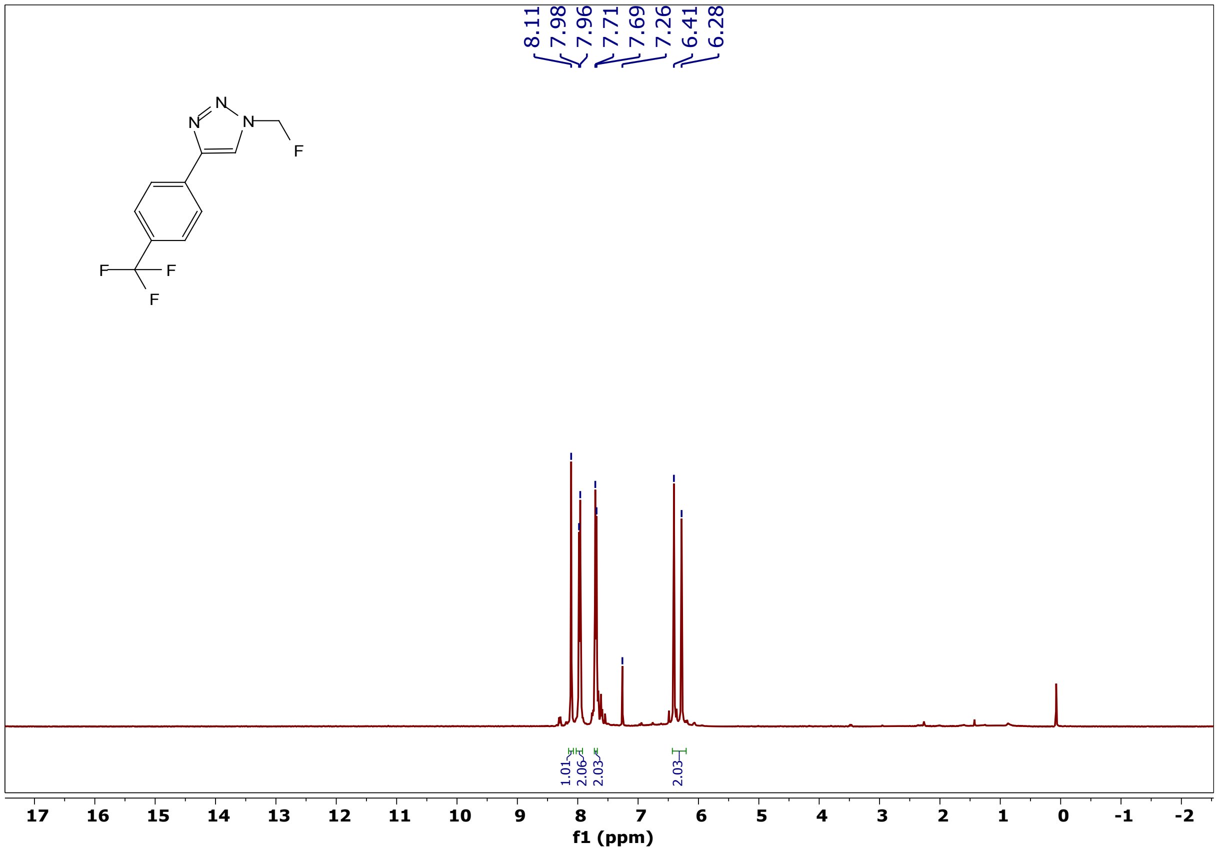
Compound **2b**


7.97
7.75
7.73
7.26
7.24
6.36
6.23
2.39
1.00
2.04
2.13
2.03
3.01
N
N
N
F
H_3C
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

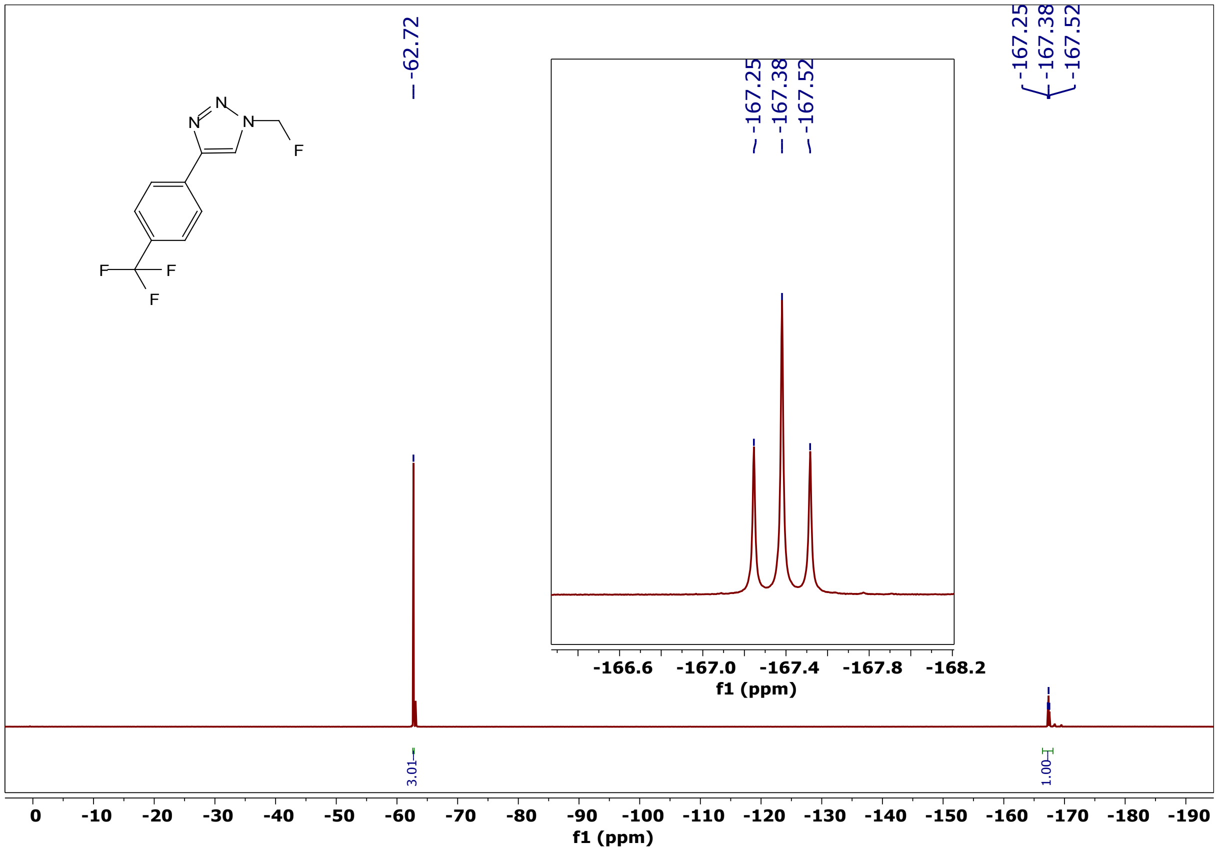

-167.24
-167.38
-167.51
-166.0 -167.0 -168.0 -169.0
f1 (ppm)
N
N
N
F
H_3C
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)


149.25
138.79
129.75
126.97
125.96
119.95
86.32
84.28
21.42
N
N
N
F
H3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

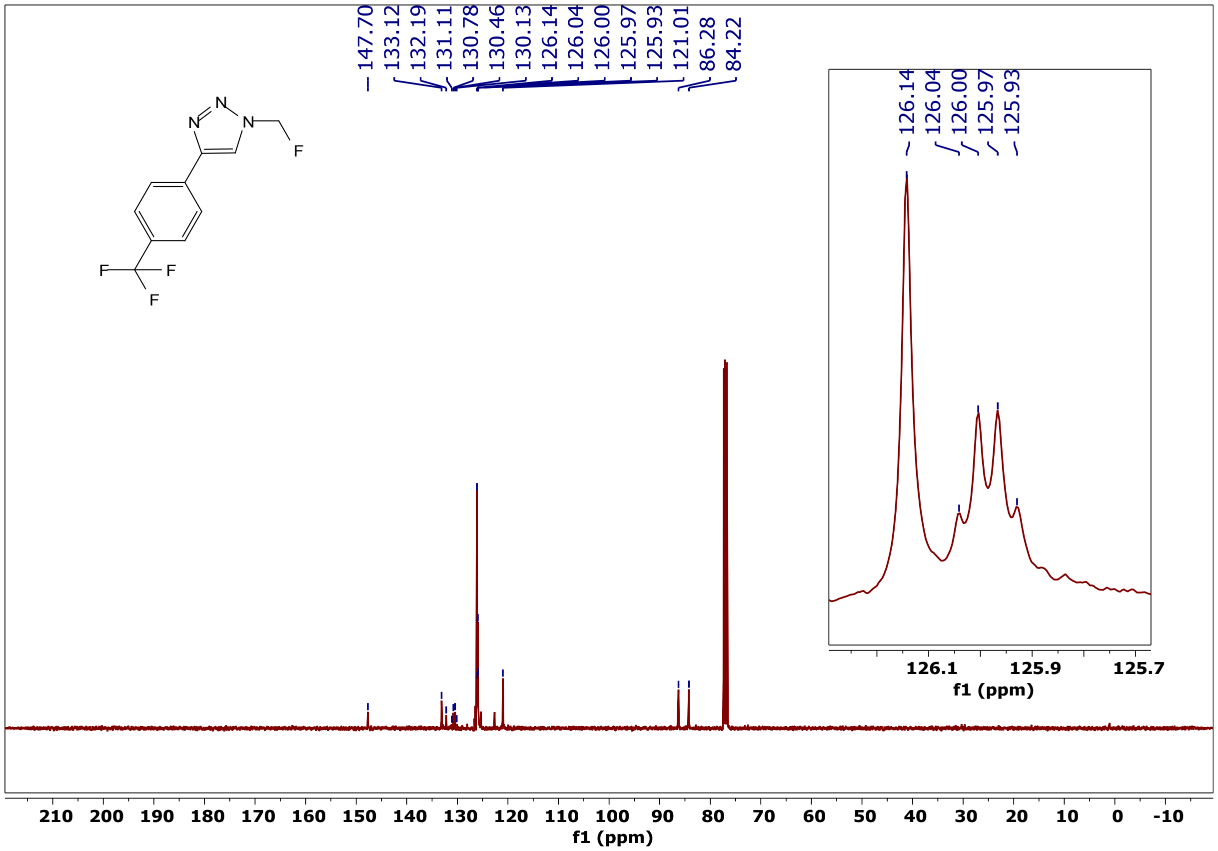
Compound **2c**



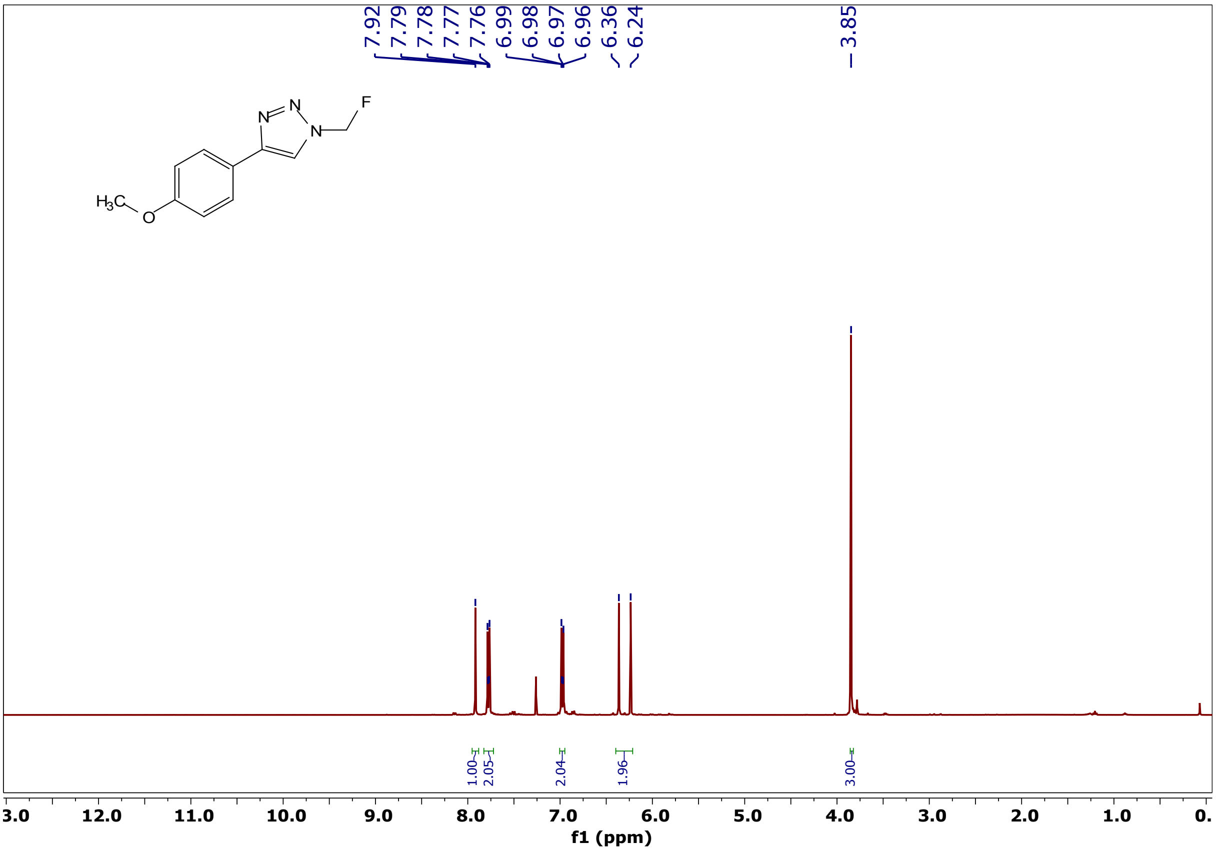
8.11
7.98
7.96
7.71
7.69
7.26
6.41
6.28
N
N
N
F
F
F
F
1.01
2.06
2.03
2.03
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

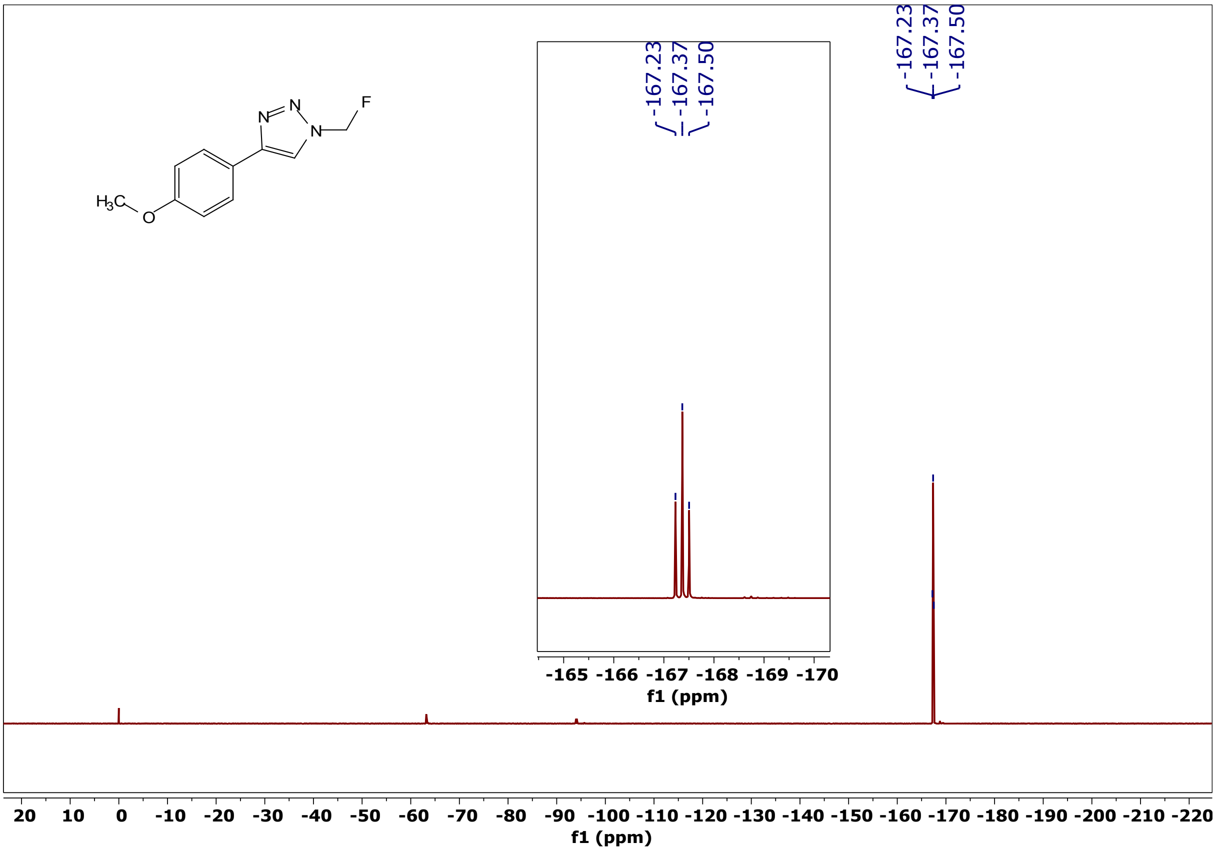


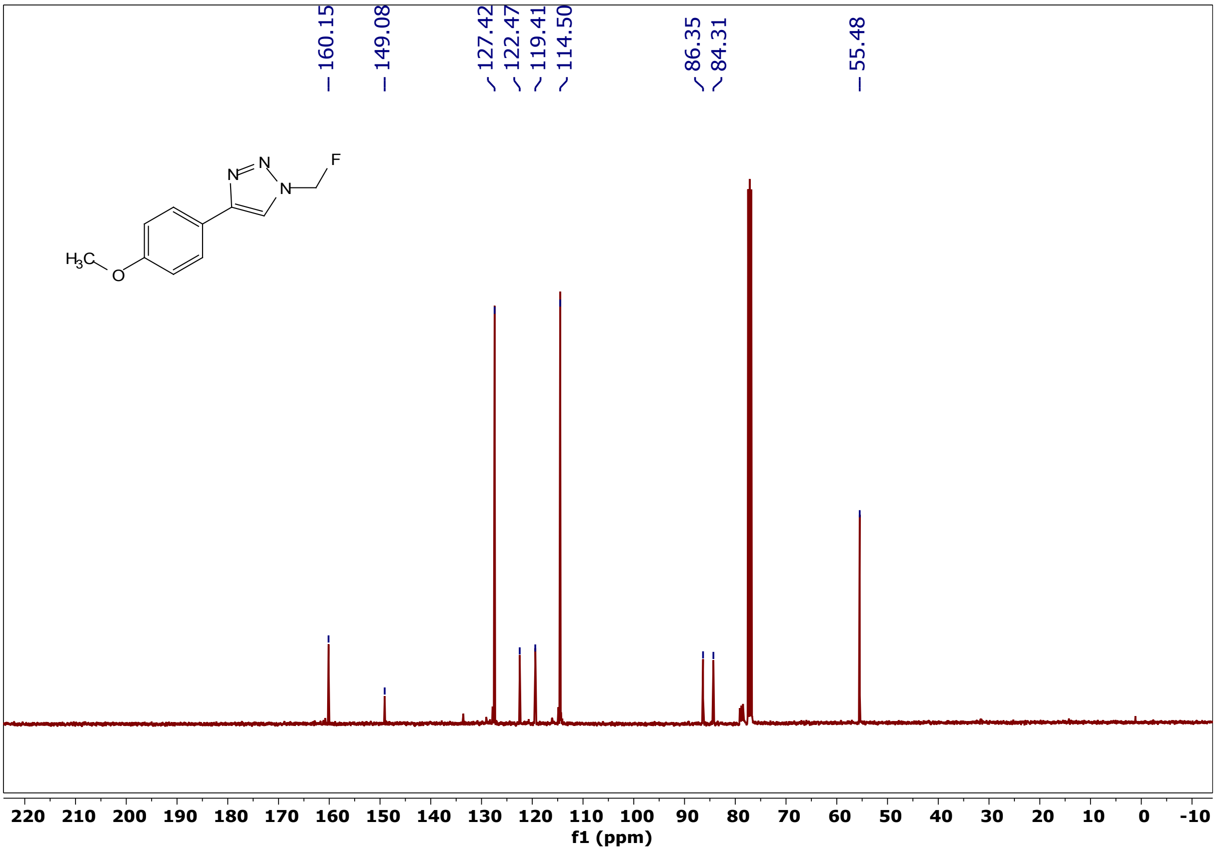
-62.72
-167.25
-167.38
-167.52
N
N
N
F
F
F
F
-166.6 -167.0 -167.4 -167.8 -168.2
f1 (ppm)
3.01
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


147.70
133.12
132.19
131.11
130.78
130.46
130.13
126.14
126.04
126.00
125.97
125.93
121.01
86.28
84.22
N
N
N
F
F
F
F
126.14
126.04
126.00
125.97
125.93
126.1
125.9
125.7
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

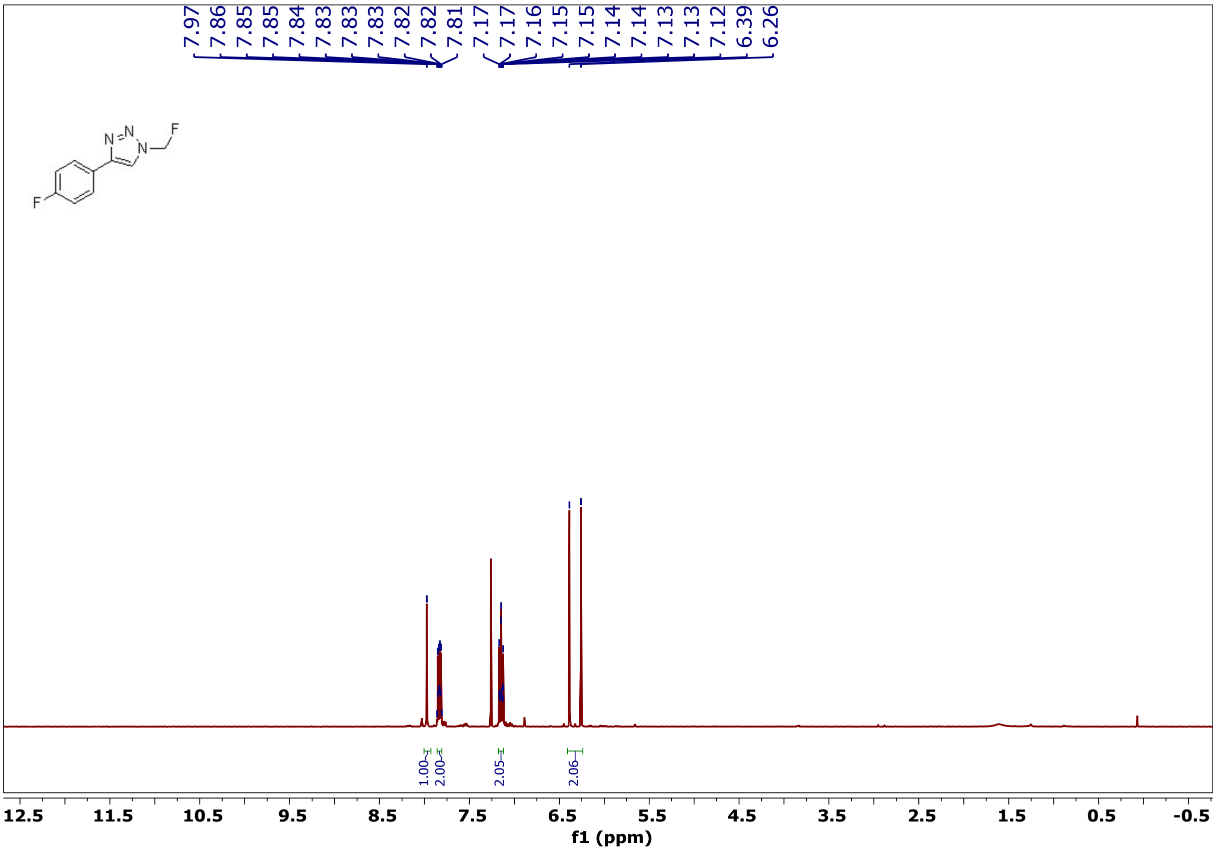
Compound **2d**

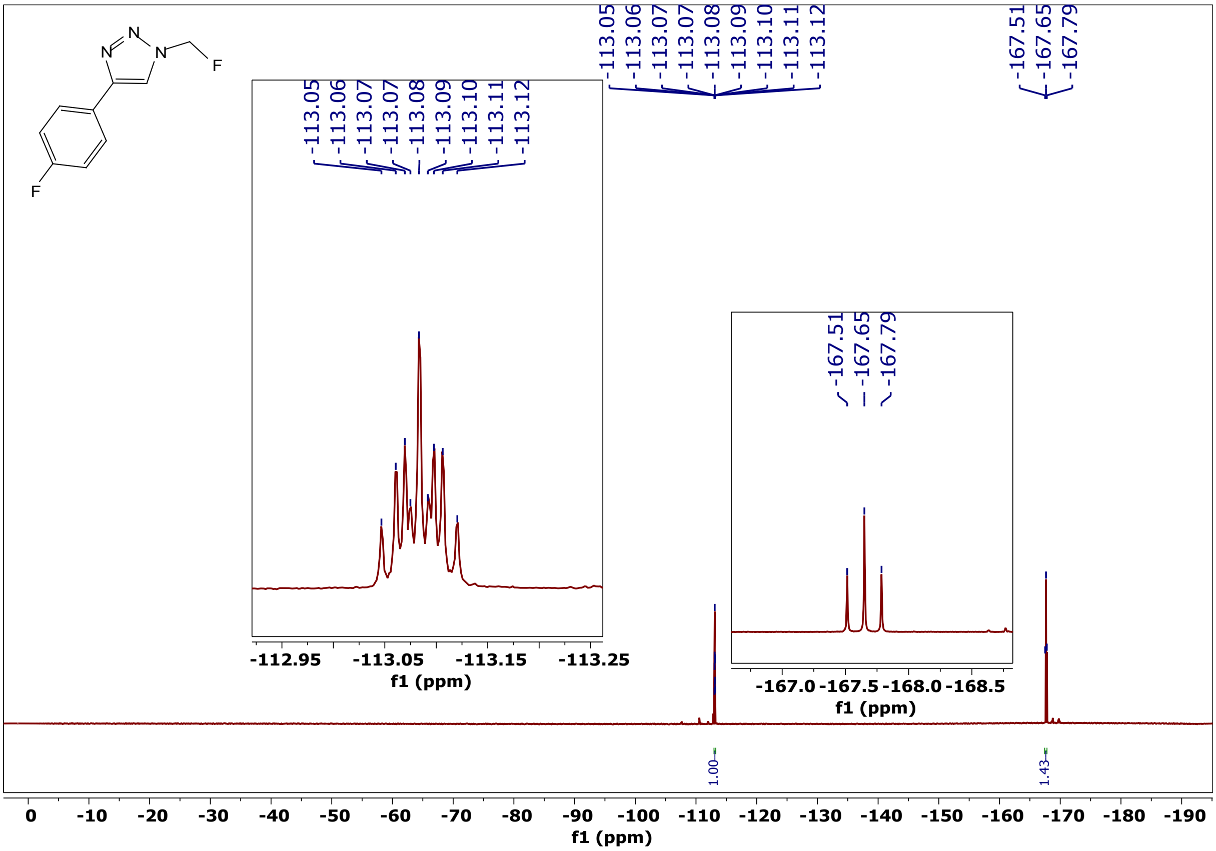

7.92
7.79
7.78
7.77
7.76
6.99
6.98
6.97
6.96
6.36
6.24
3.85
N
N
N
F
H3C
O
1.00
2.05
2.04
1.96
3.00
3.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.
f1 (ppm)

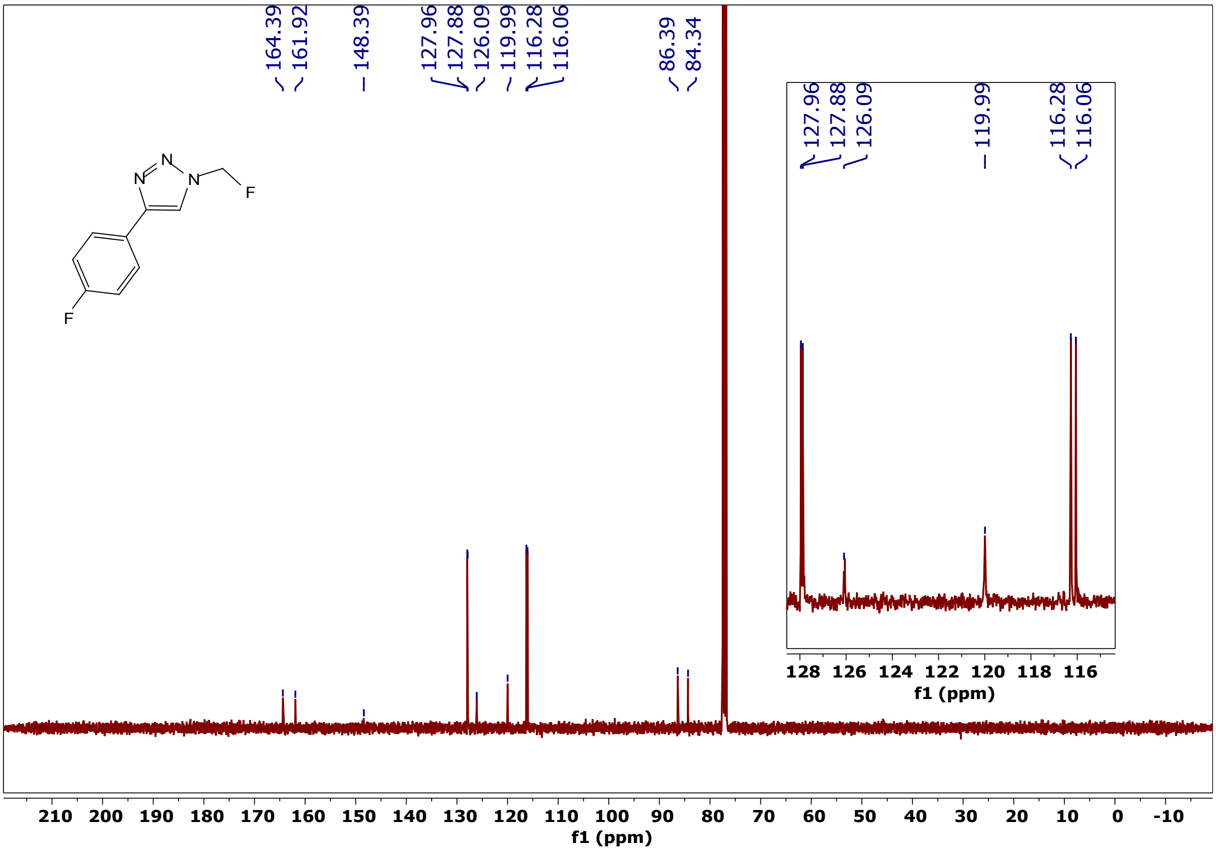

-167.23
-167.37
-167.50
-167.23
-167.37
-167.50
N
N
N
F
H3C
O
-165 -166 -167 -168 -169 -170
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


160.15
149.08
127.42
122.47
119.41
114.50
86.35
84.31
55.48
N
N
N
F
H3C
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

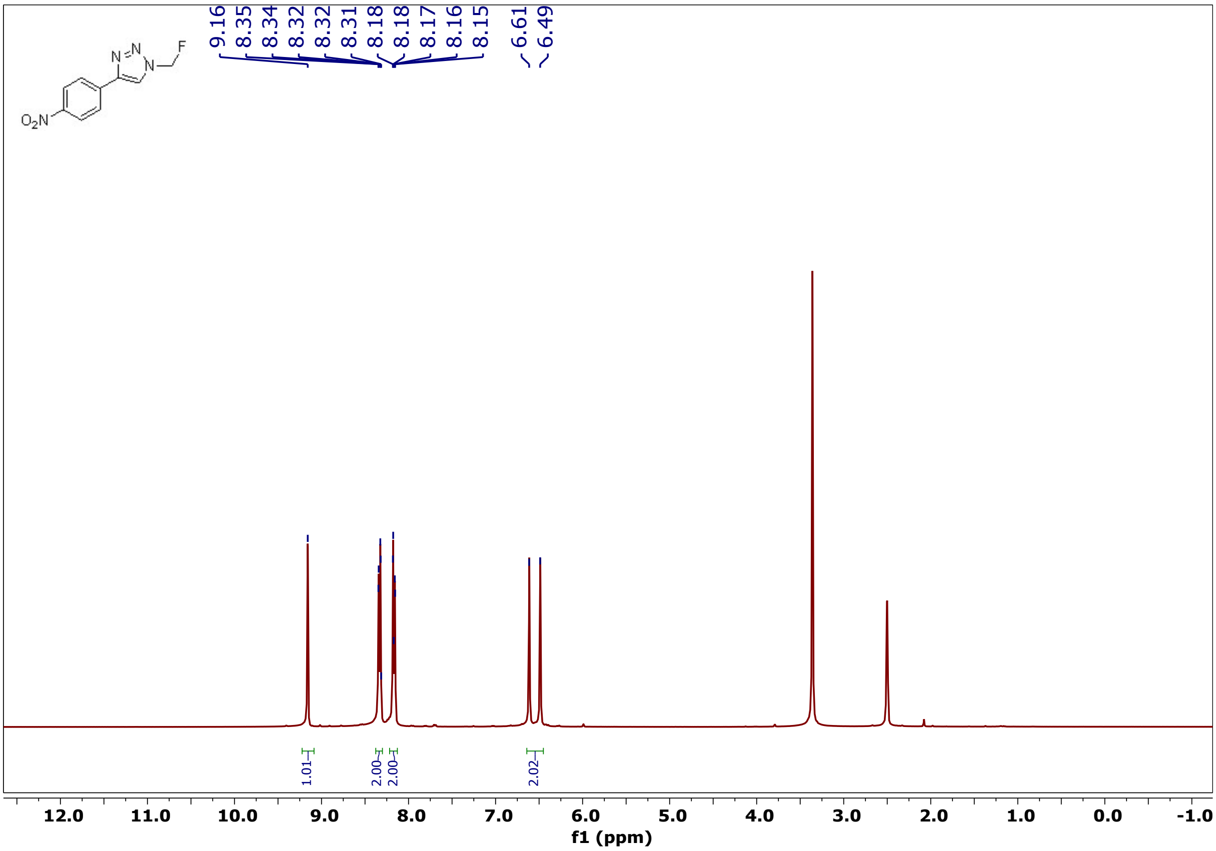
Compound **2e**

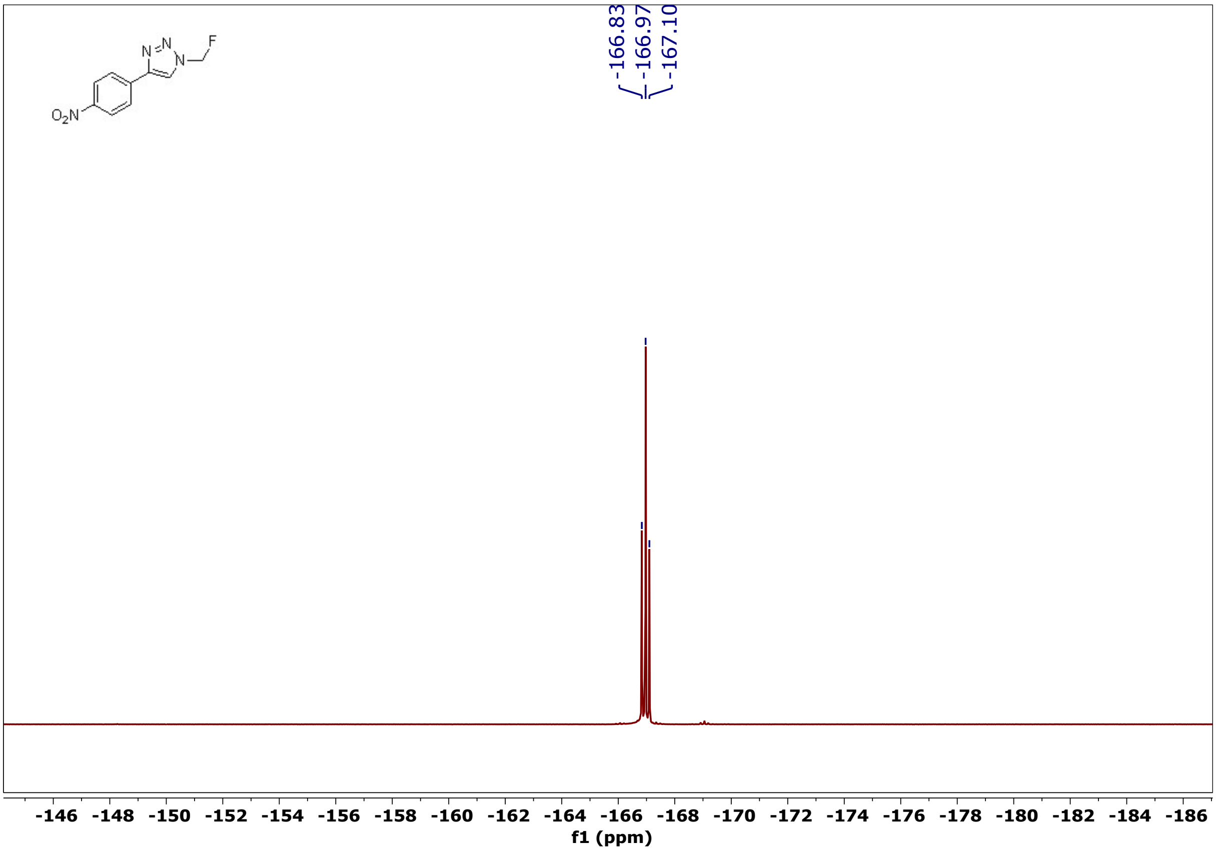

7.97
7.86
7.85
7.85
7.84
7.83
7.83
7.83
7.82
7.82
7.81
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.12
6.39
6.26
N
N
N
F
F
1.00
2.00
2.05
2.06
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

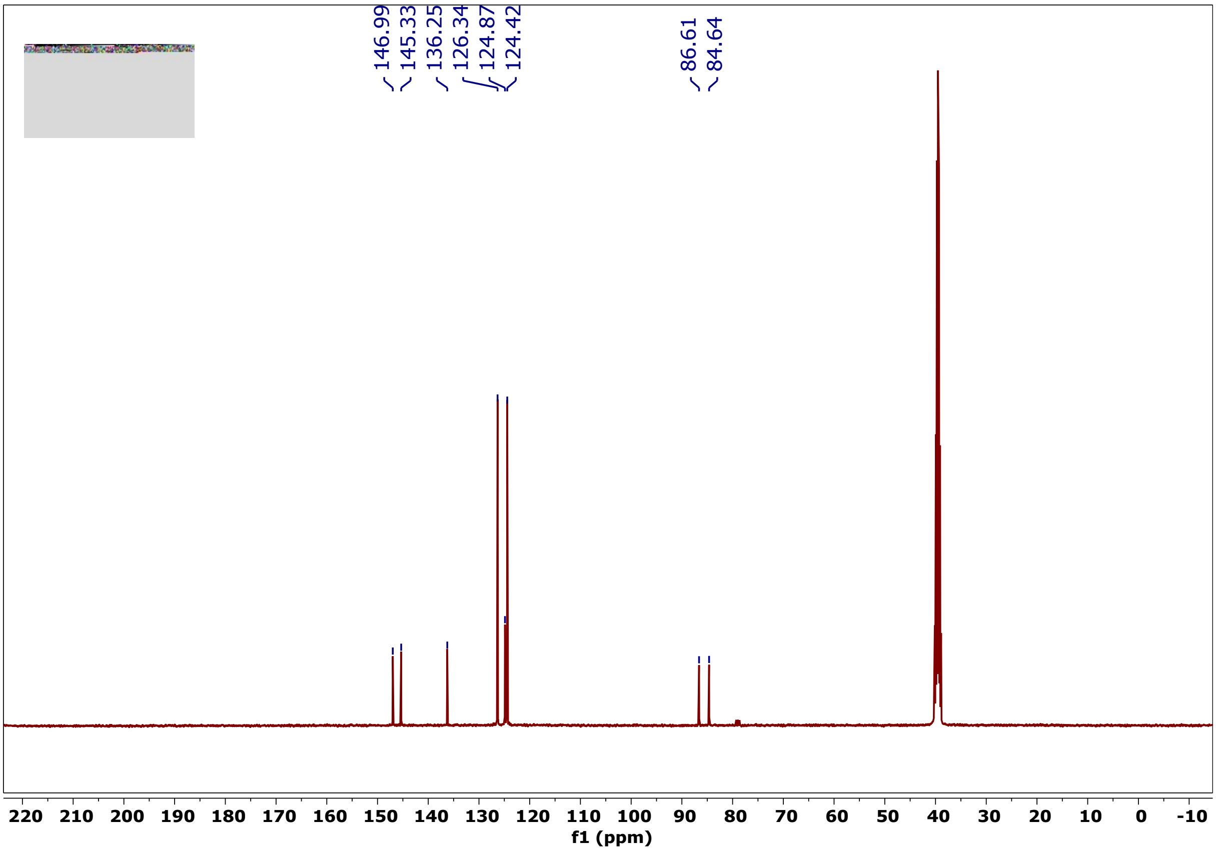

N
N
N
F
F
-113.05
-113.06
-113.07
-113.07
-113.08
-113.09
-113.10
-113.11
-113.12
-167.51
-167.65
-167.79
-112.95
-113.05
-113.15
-113.25
f1 (ppm)
-167.0
-167.5
-168.0
-168.5
f1 (ppm)
1.00
1.43
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


164.39
161.92
148.39
127.96
127.88
126.09
119.99
116.28
116.06
86.39
84.34
N
N
N
F
F
127.96
127.88
126.09
119.99
116.28
116.06
128 126 124 122 120 118 116
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

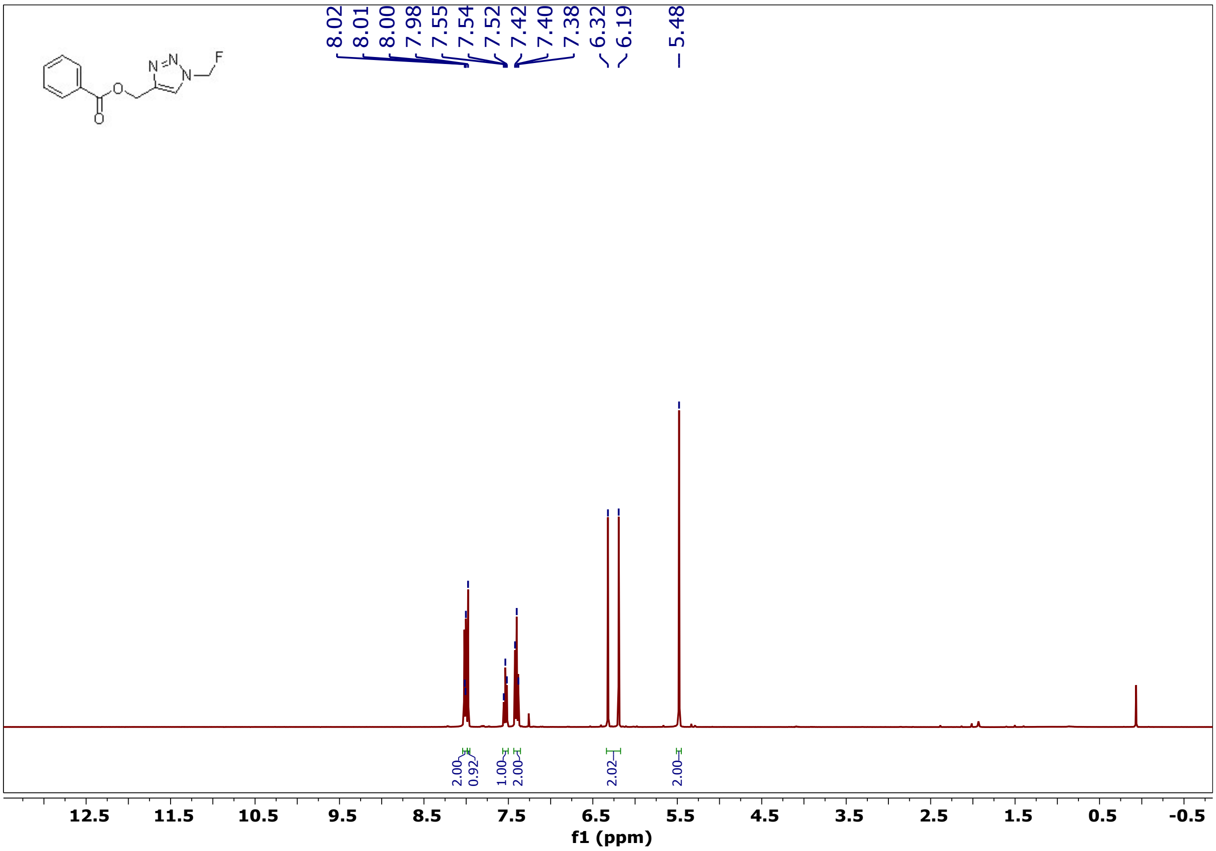
Compound **2f**

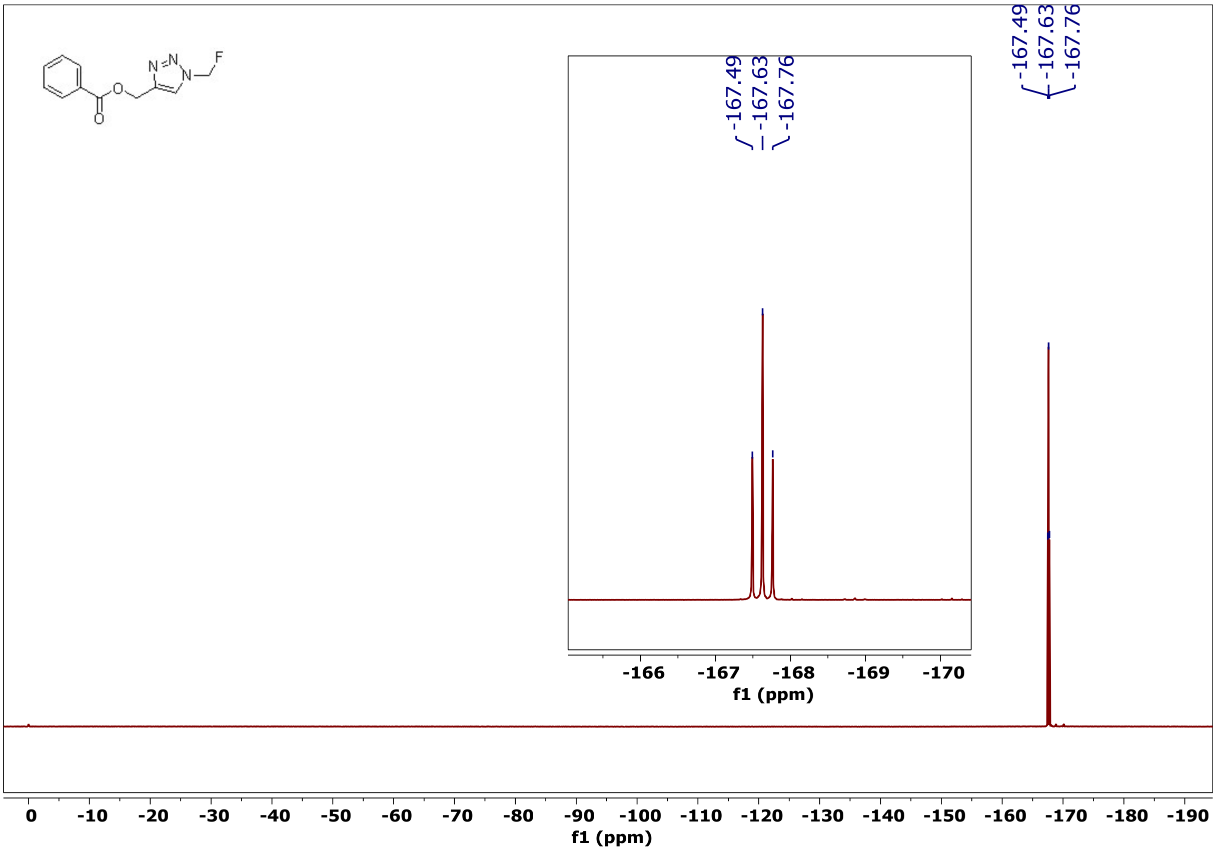

N=N
N
F
O$_2$N
9.16
8.35
8.34
8.32
8.32
8.31
8.18
8.18
8.17
8.16
8.15
6.61
6.49
1.01
2.00
2.00
2.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

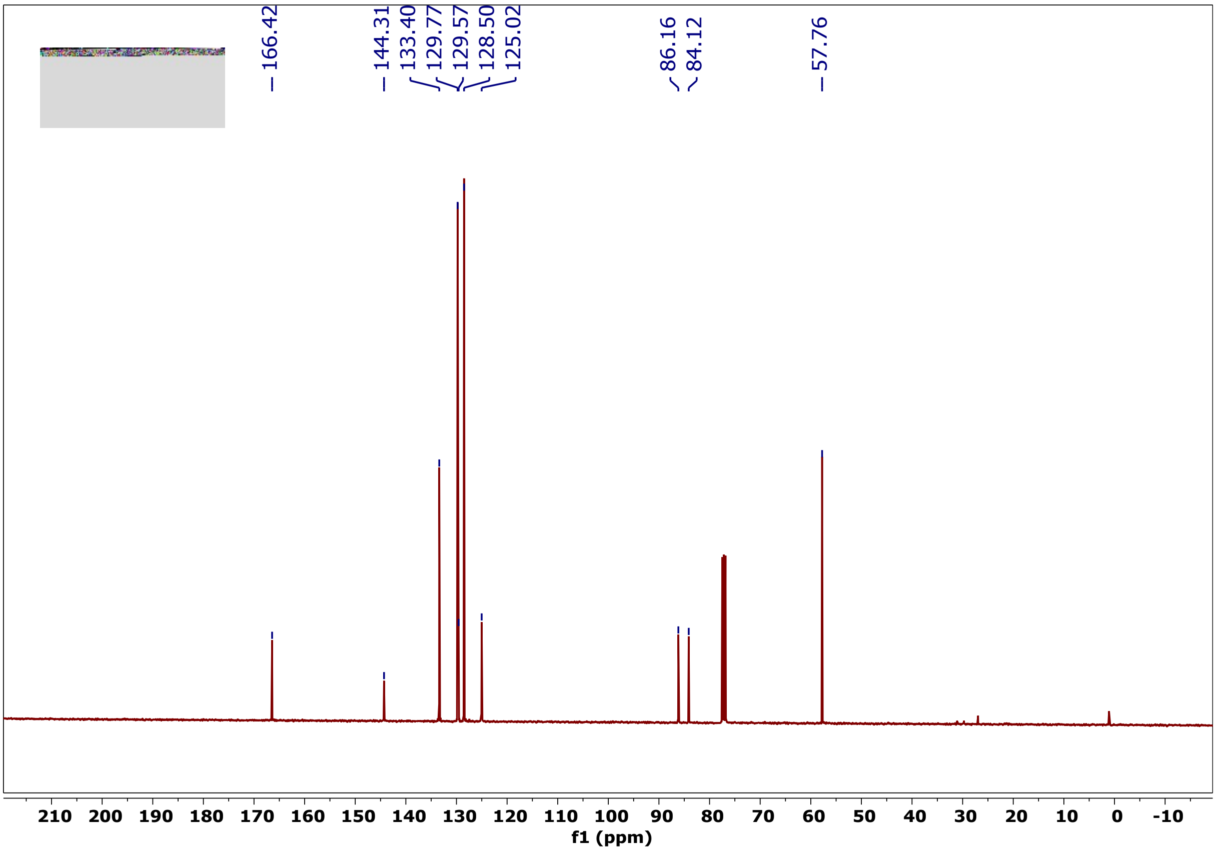

N=N
N
F
O$_2$N
-166.83
-166.97
-167.10
-146
-148
-150
-152
-154
-156
-158
-160
-162
-164
-166
-168
-170
-172
-174
-176
-178
-180
-182
-184
-186
f1 (ppm)


146.99
145.33
136.25
126.34
124.87
124.42
86.61
84.64
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

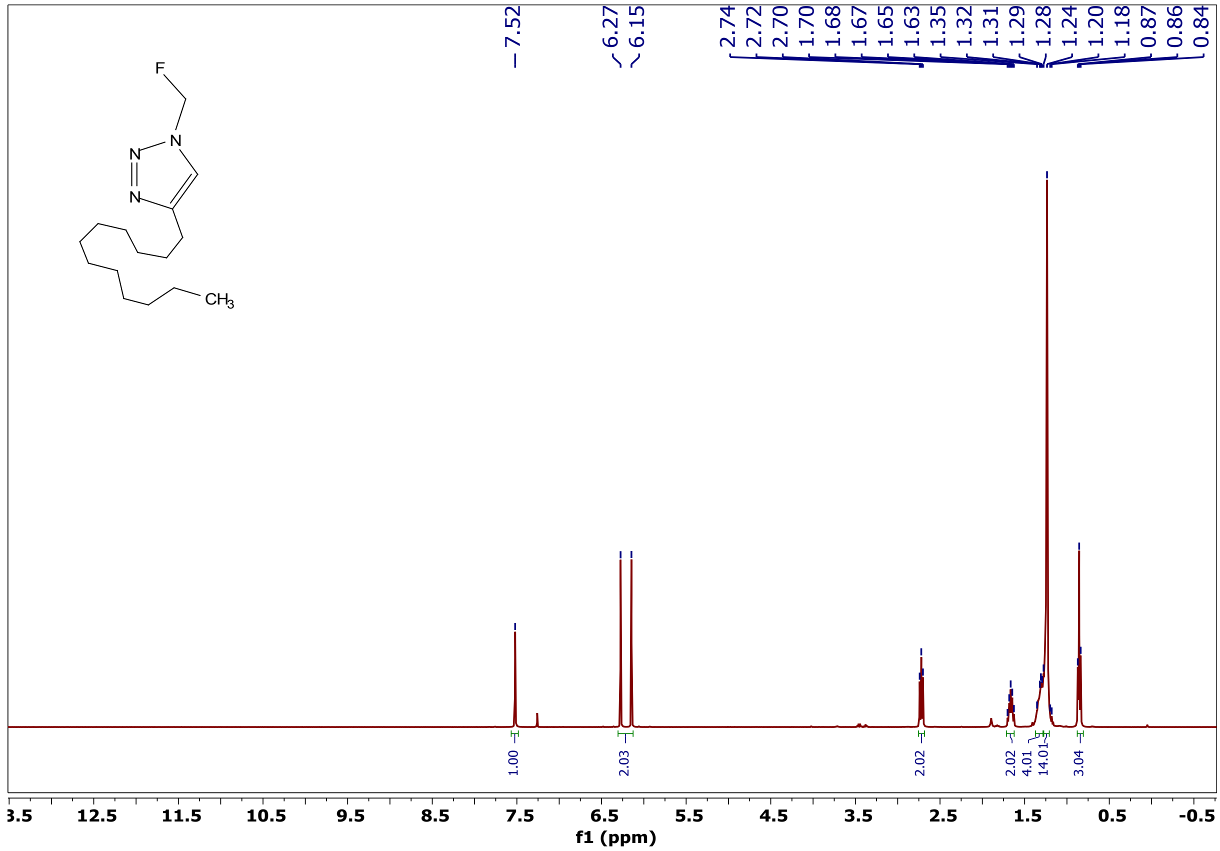
Compound **2g**

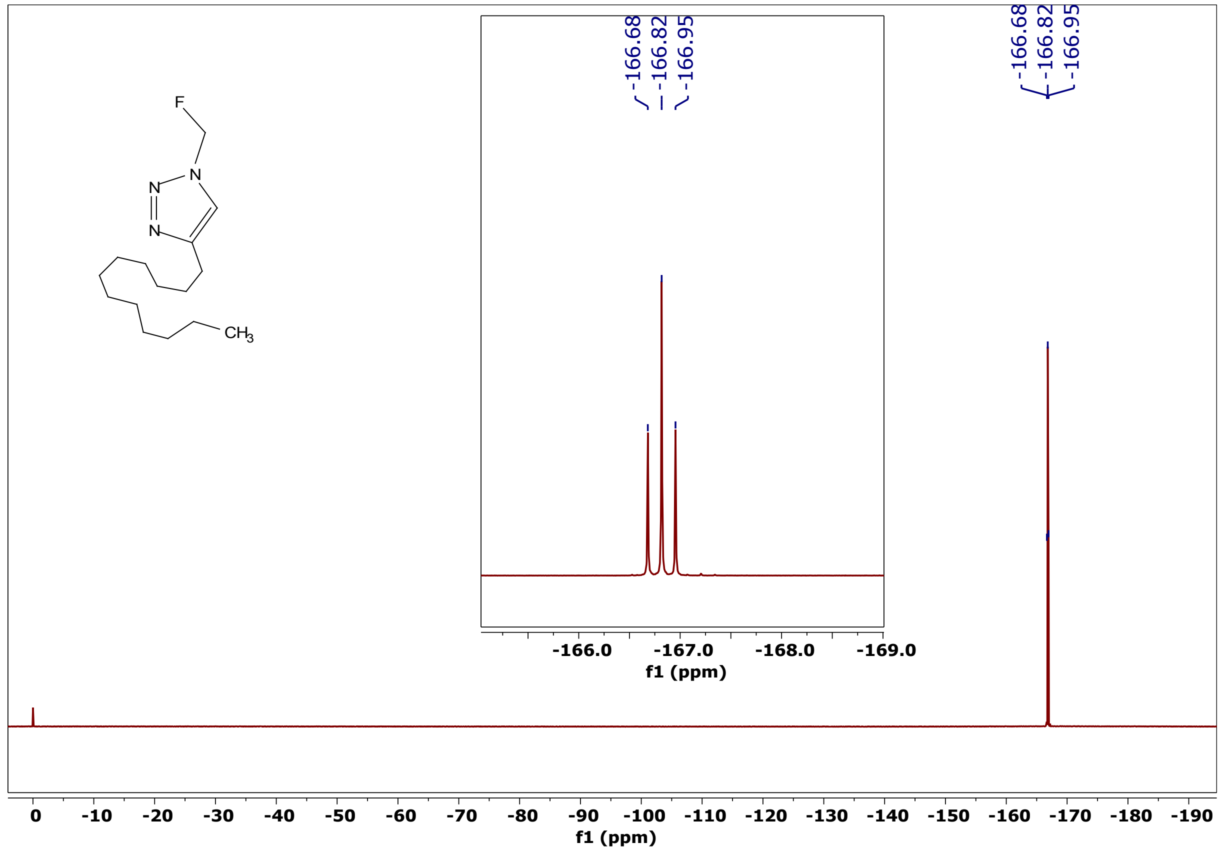

8.02
8.01
8.00
7.98
7.55
7.54
7.52
7.42
7.40
7.38
6.32
6.19
5.48
2.00
0.92
1.00
2.00
2.02
2.00
N
N
N
F
O
O
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

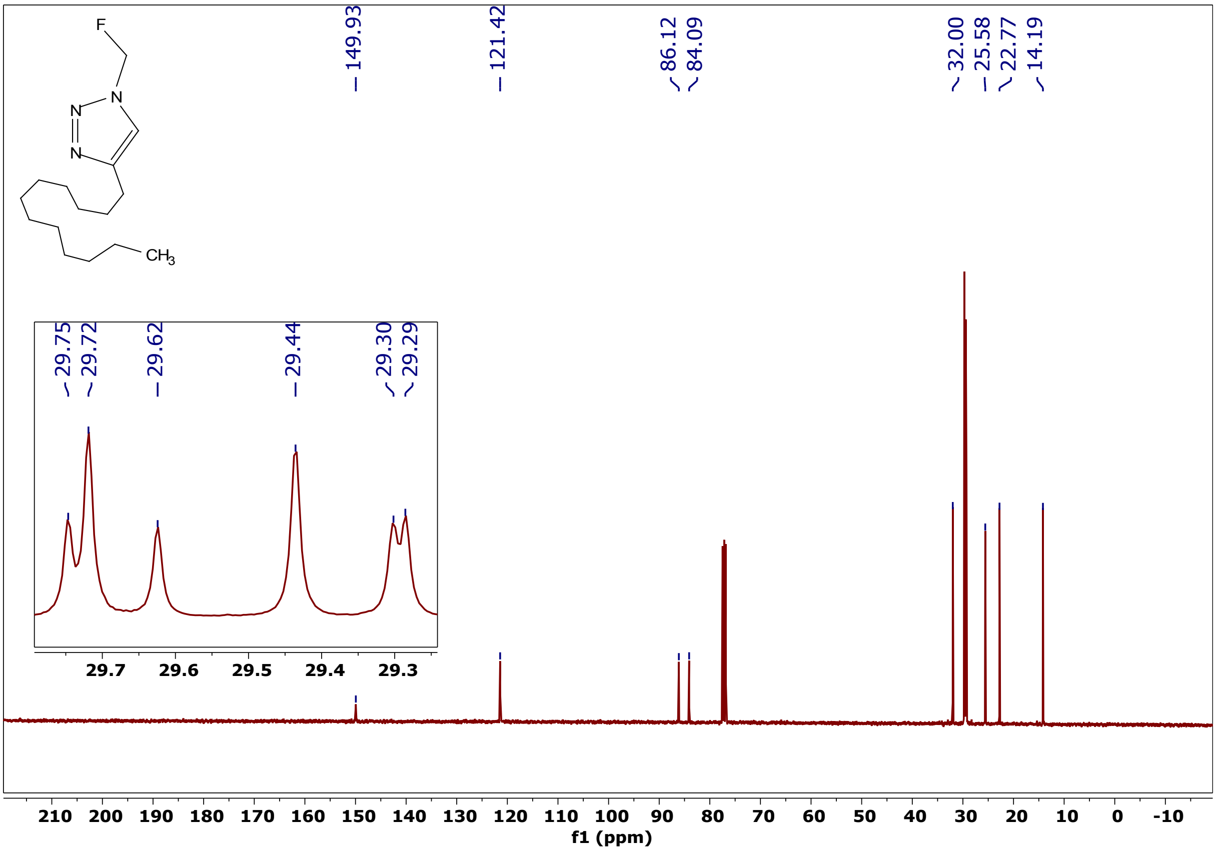

-167.49
-167.63
-167.76
-167.49
-167.63
-167.76
N
N
N
F
O
O
-166
-167
-168
-169
-170
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


166.42
144.31
133.40
129.77
129.57
128.50
125.02
86.16
84.12
57.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

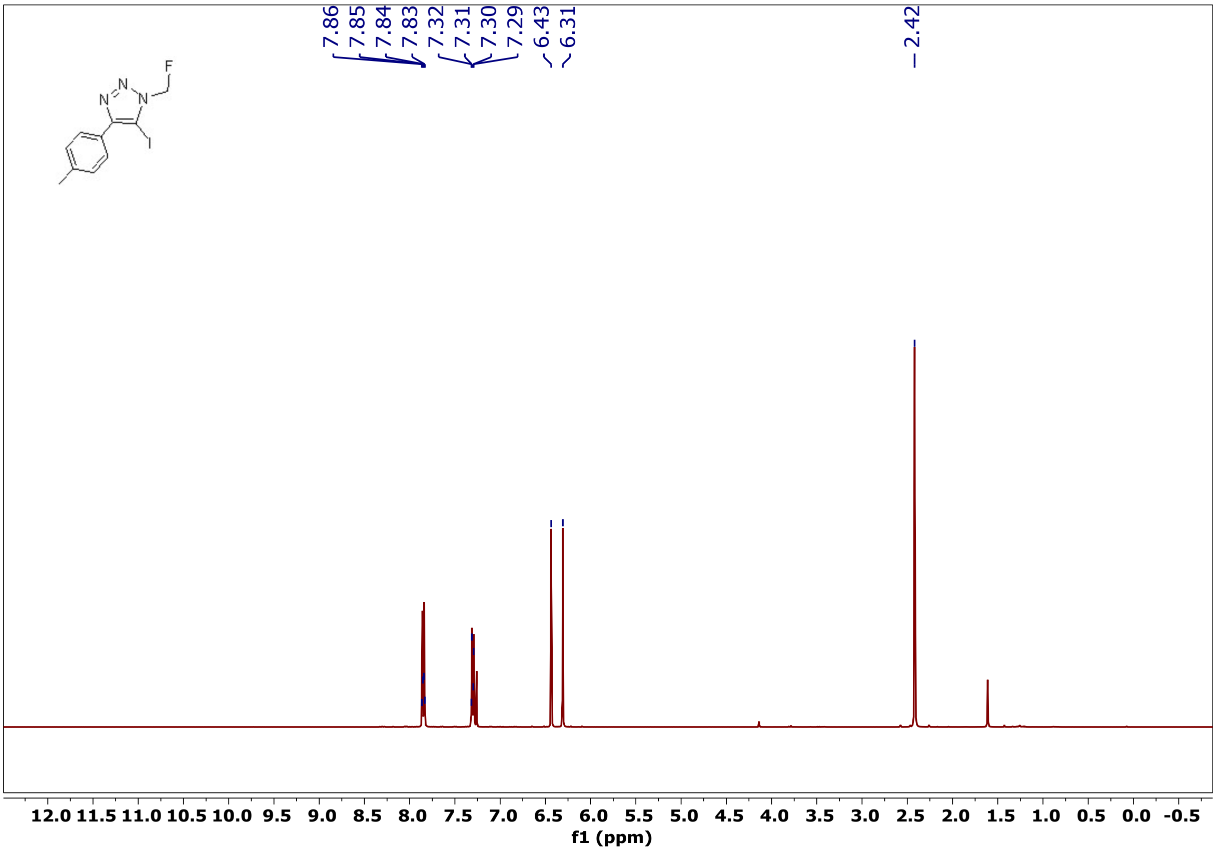
Compound **2h**

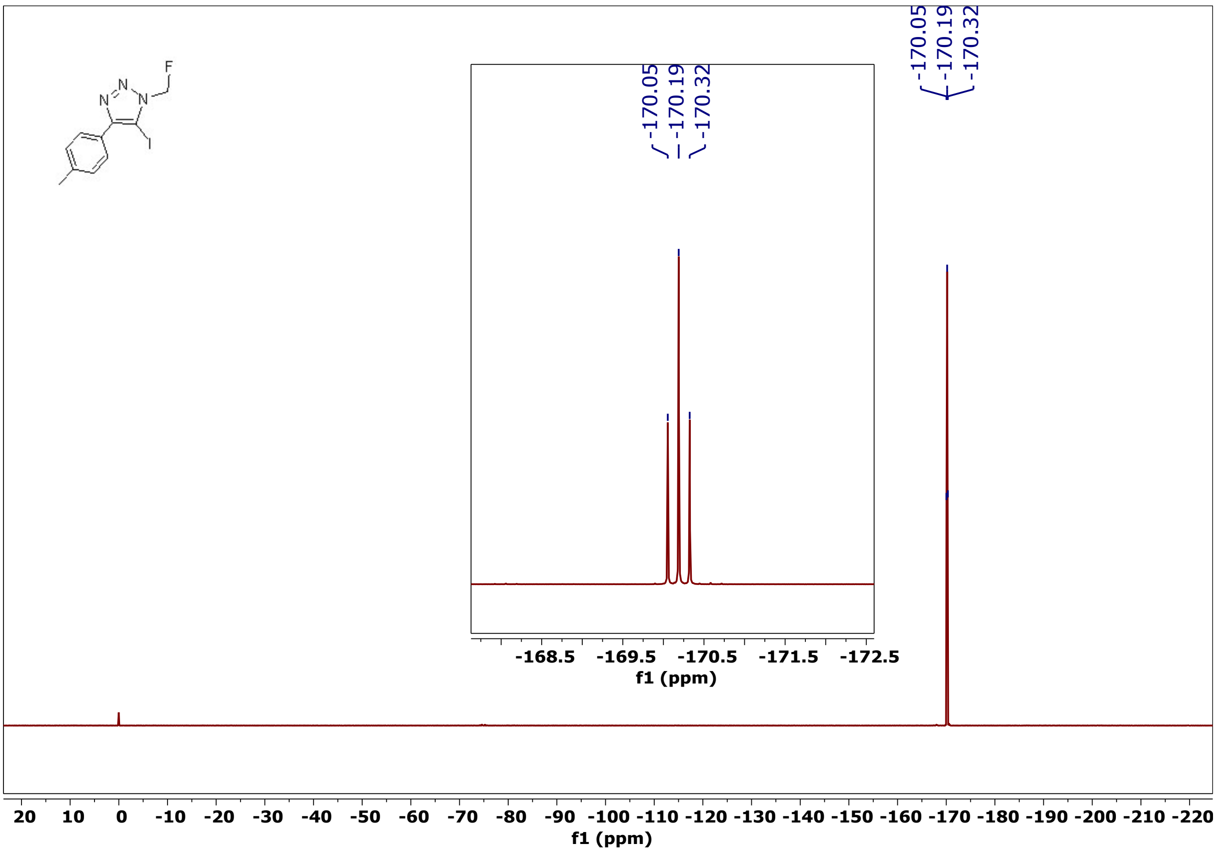

7.52
6.27
6.15
2.74
2.72
2.70
1.70
1.68
1.67
1.65
1.63
1.35
1.32
1.31
1.29
1.28
1.24
1.20
1.18
0.87
0.86
0.84
F
N
N
N
CH_3
1.00
2.03
2.02
2.02
4.01
14.01
3.04
3.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

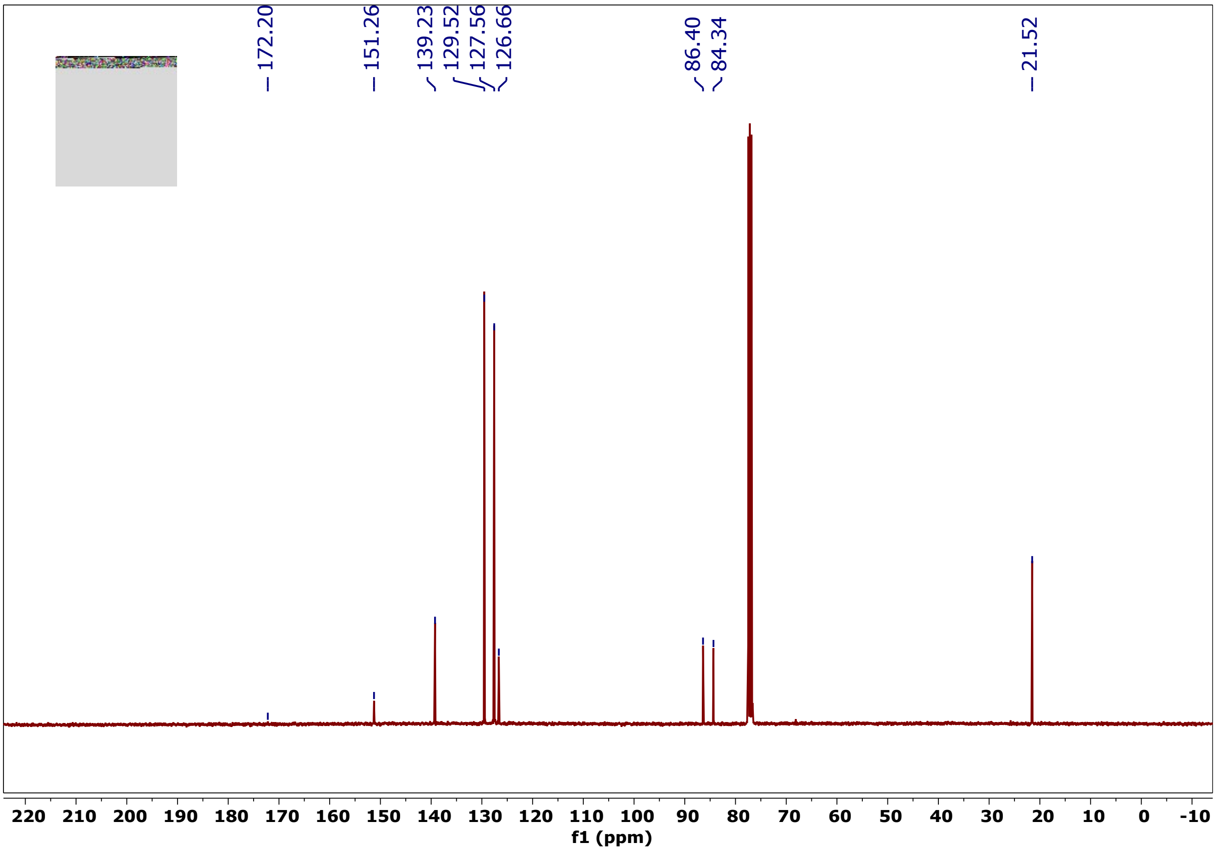

-166.68
-166.82
-166.95
-166.68
-166.82
-166.95
F
N
N
N
CH_3
-166.0
-167.0
-168.0
-169.0
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


F
N
N
N
CH3
149.93
121.42
86.12
84.09
32.00
25.58
22.77
14.19
29.75
29.72
29.62
29.44
29.30
29.29
29.7
29.6
29.5
29.4
29.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

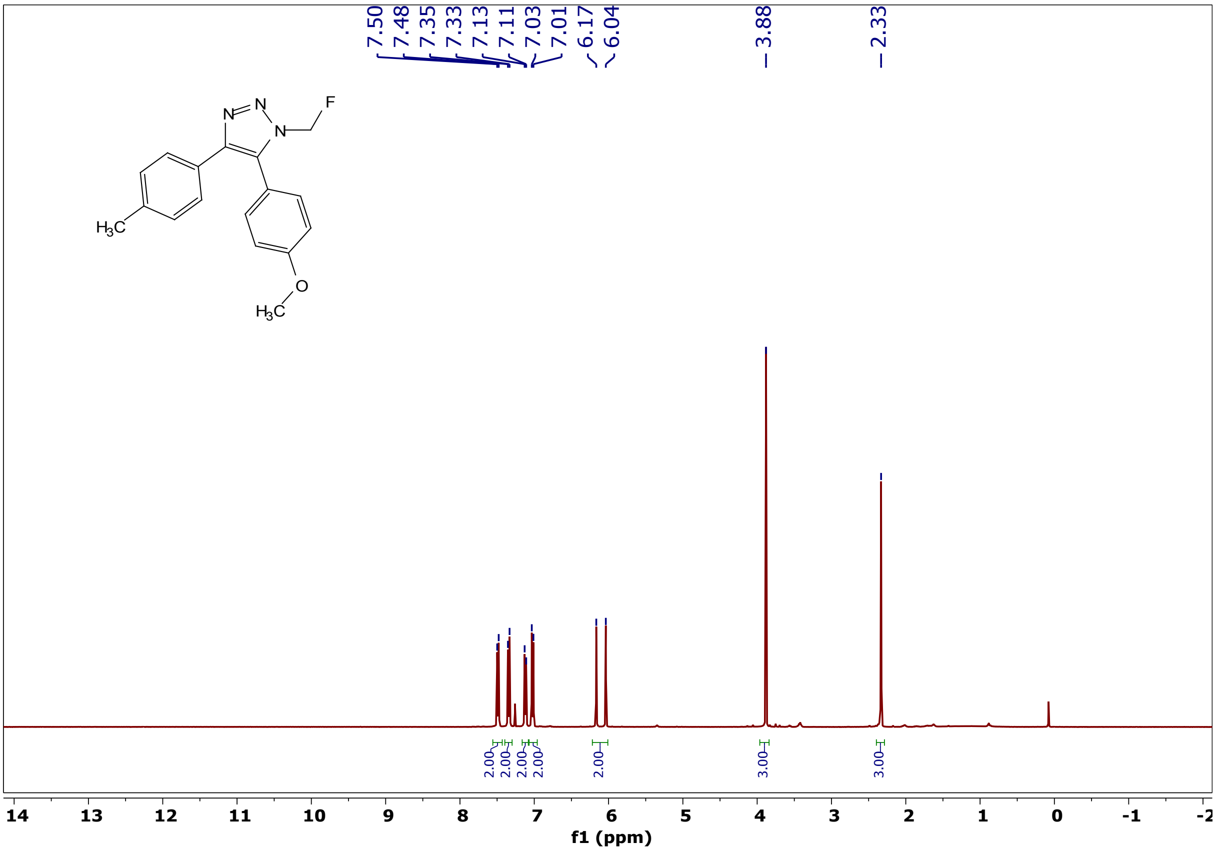
Compound **3**

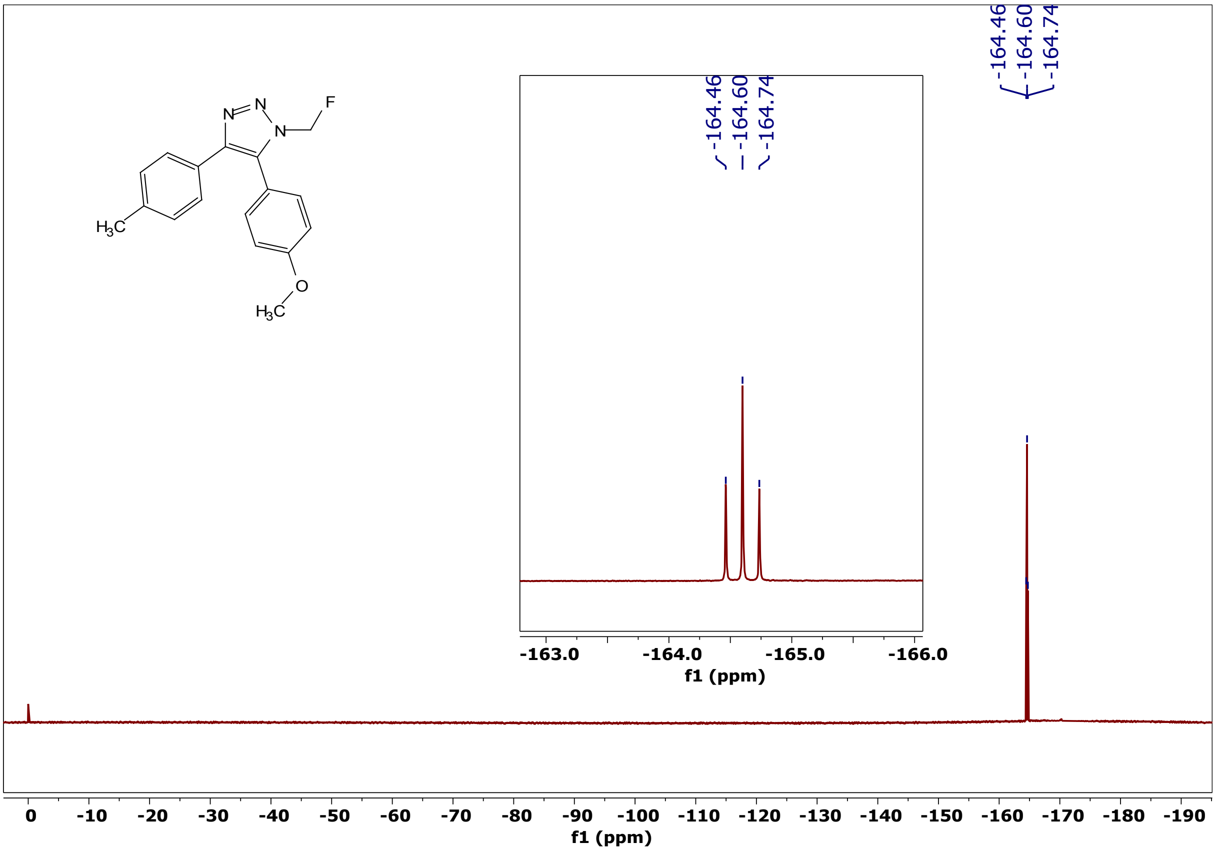

7.86
7.85
7.84
7.83
7.32
7.31
7.30
7.29
6.43
6.31
2.42
F
N
N
N
I
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

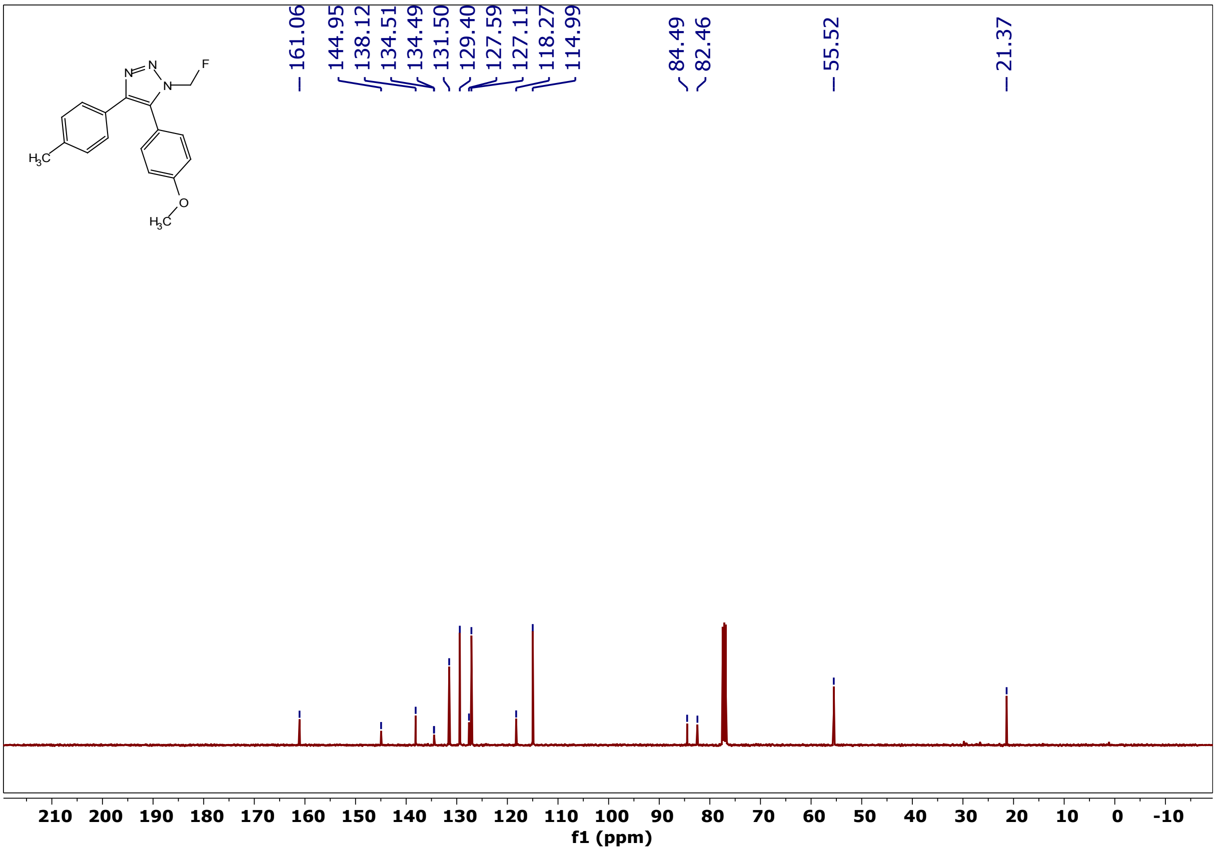

-170.05
-170.19
-170.32
F
N
N
N
I
-168.5 -169.5 -170.5 -171.5 -172.5
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


172.20
151.26
139.23
129.52
127.56
126.66
86.40
84.34
21.52
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

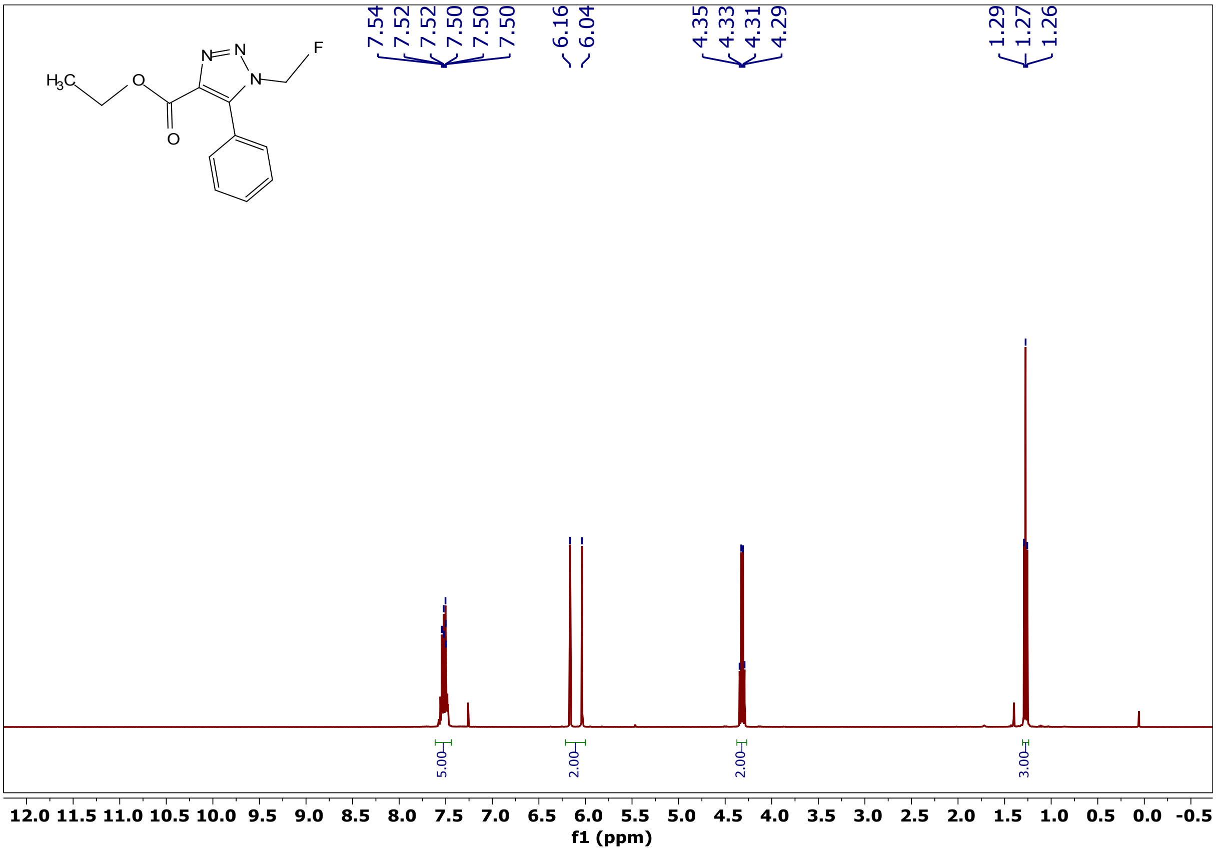
Compound **4**

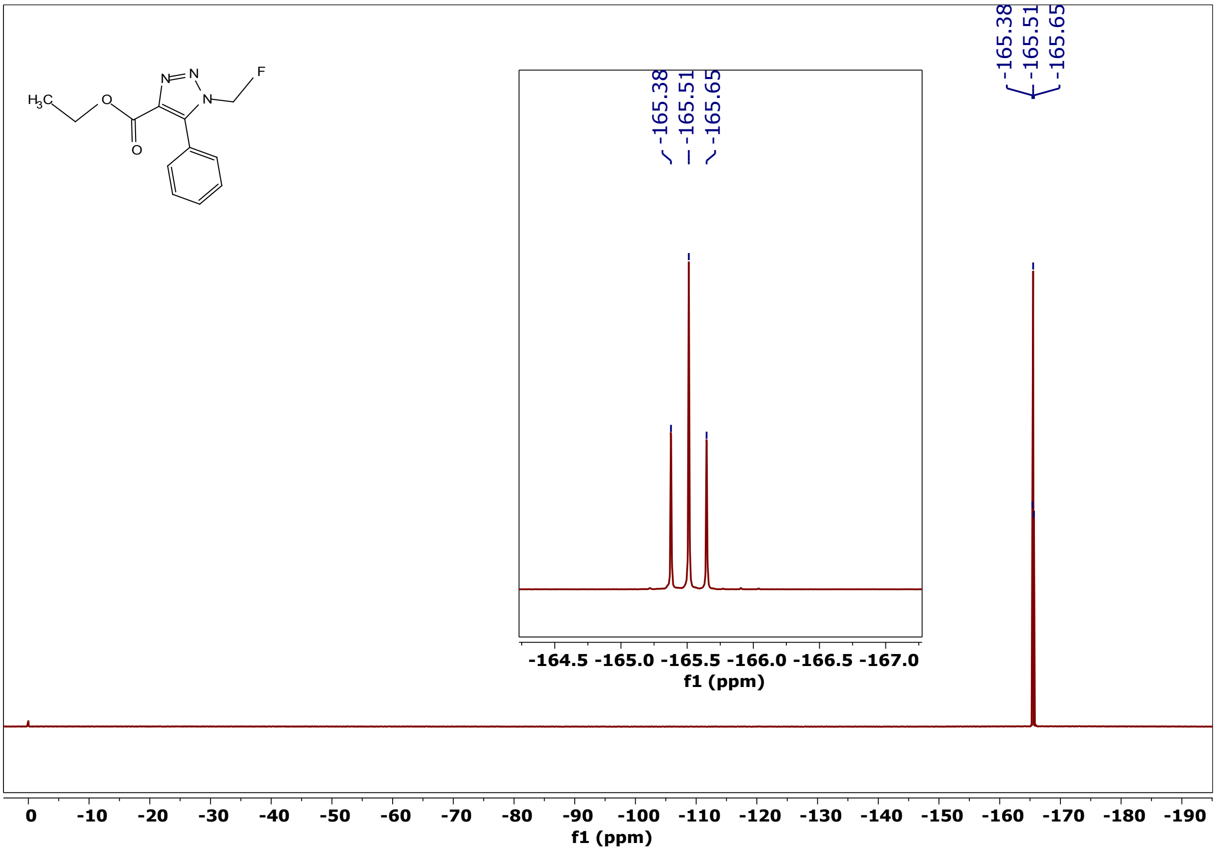

7.50
7.48
7.35
7.33
7.13
7.11
7.03
7.01
6.17
6.04
3.88
2.33
2.00
2.00
2.00
2.00
2.00
3.00
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
N
N
N
F
H3C
O
H3C

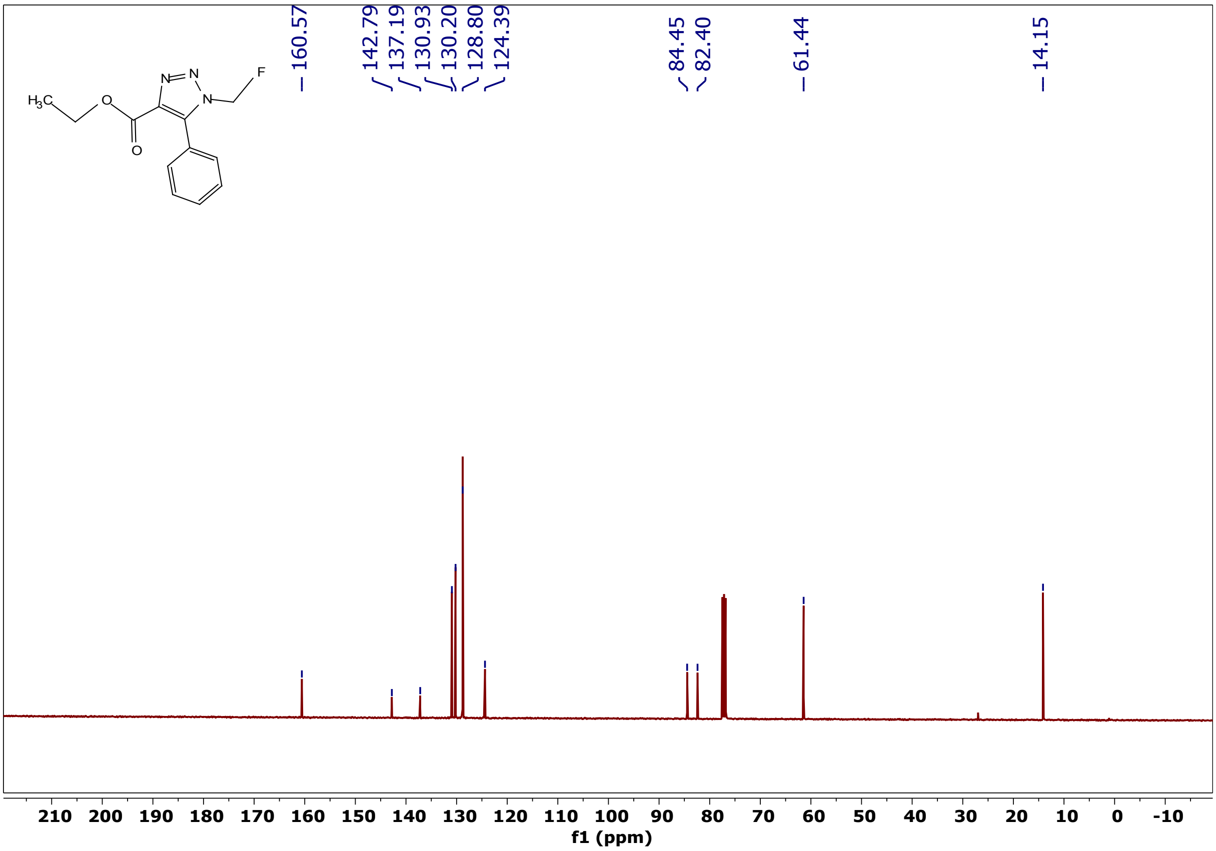

-164.46
-164.60
-164.74
-163.0
-164.0
-165.0
-166.0
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)
N
N
N
F
H3C
O
H3C


161.06
144.95
138.12
134.51
134.49
131.50
129.40
127.59
127.11
118.27
114.99
84.49
82.46
55.52
21.37
N
N
N
F
H3C
O
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound **5a**

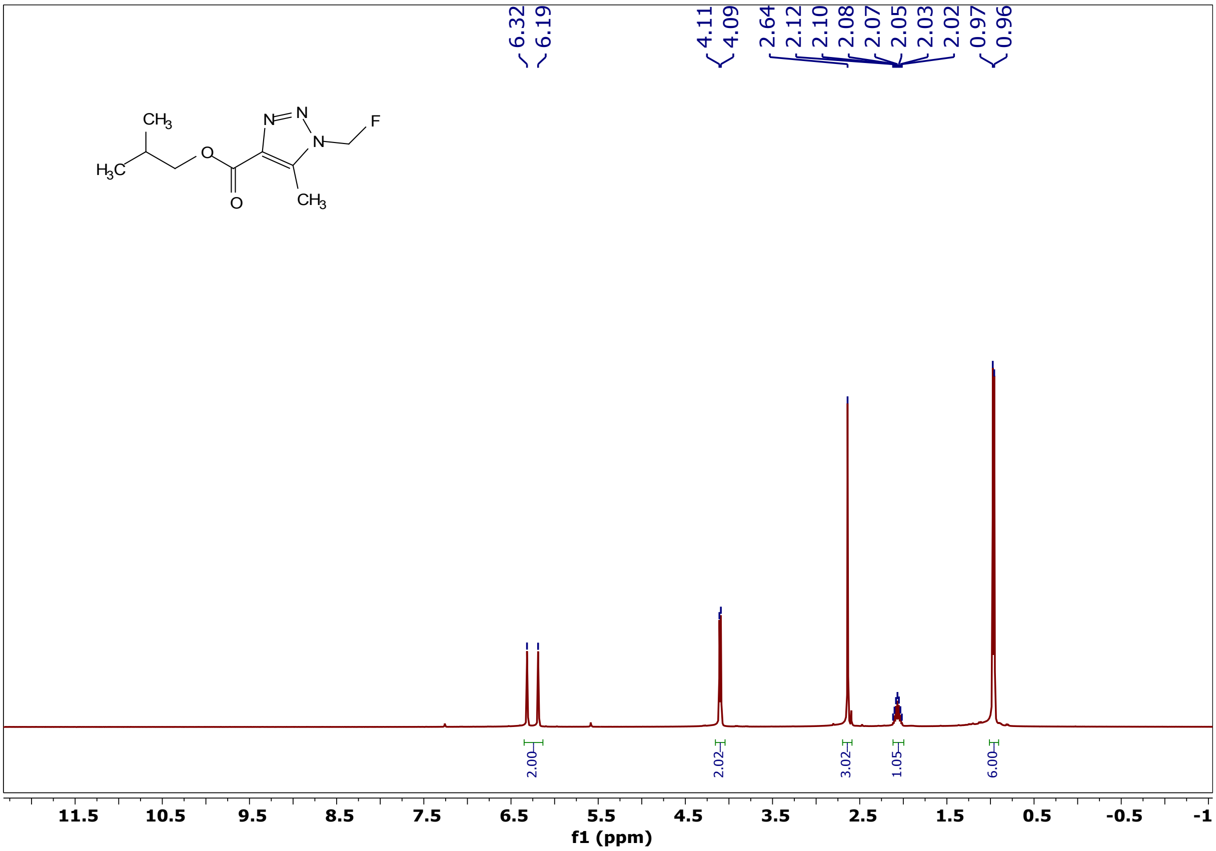

7.54
7.52
7.52
7.50
7.50
7.50
6.16
6.04
4.35
4.33
4.31
4.29
1.29
1.27
1.26
5.00
2.00
2.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-165.38
-165.51
-165.65
-164.5 -165.0 -165.5 -166.0 -166.5 -167.0
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

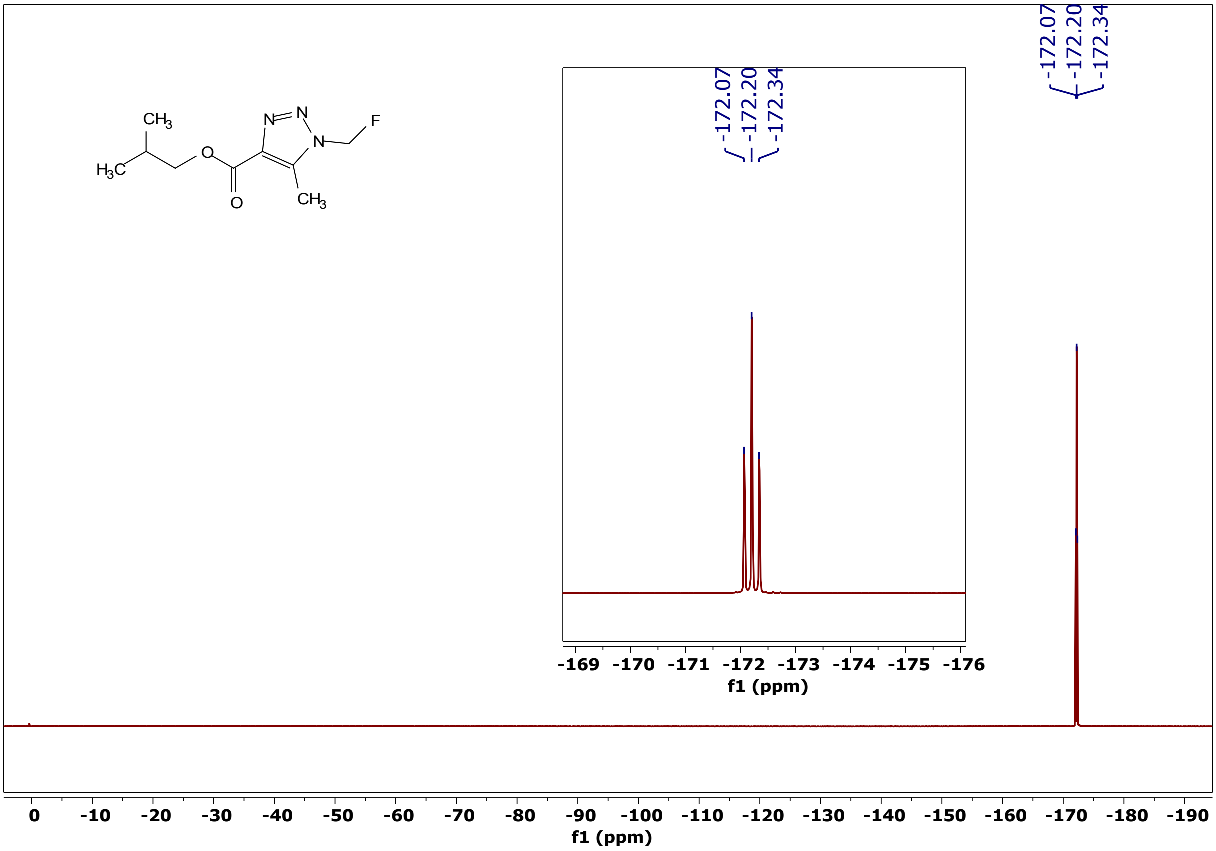


160.57
142.79
137.19
130.93
130.20
128.80
124.39
84.45
82.40
61.44
14.15
H3C
O
O
N
N
N
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

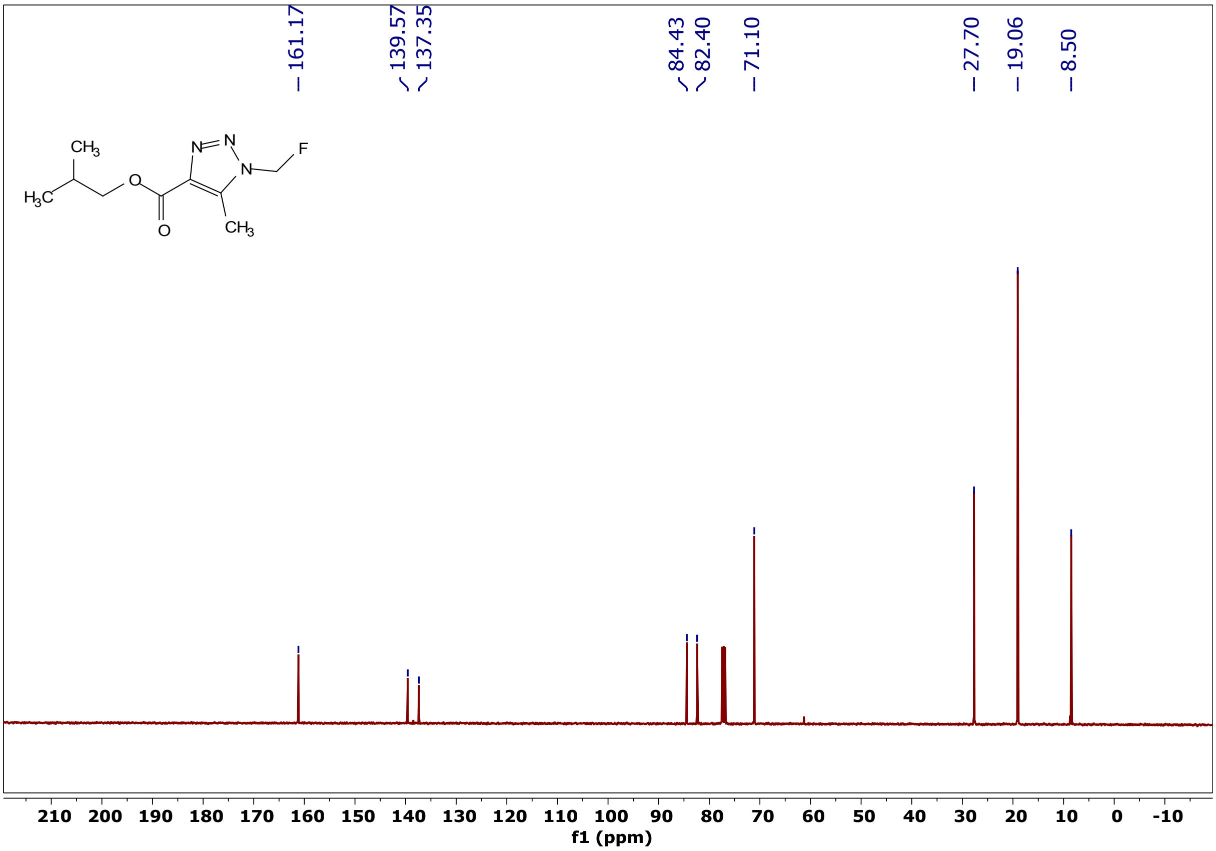
Compound **5b**



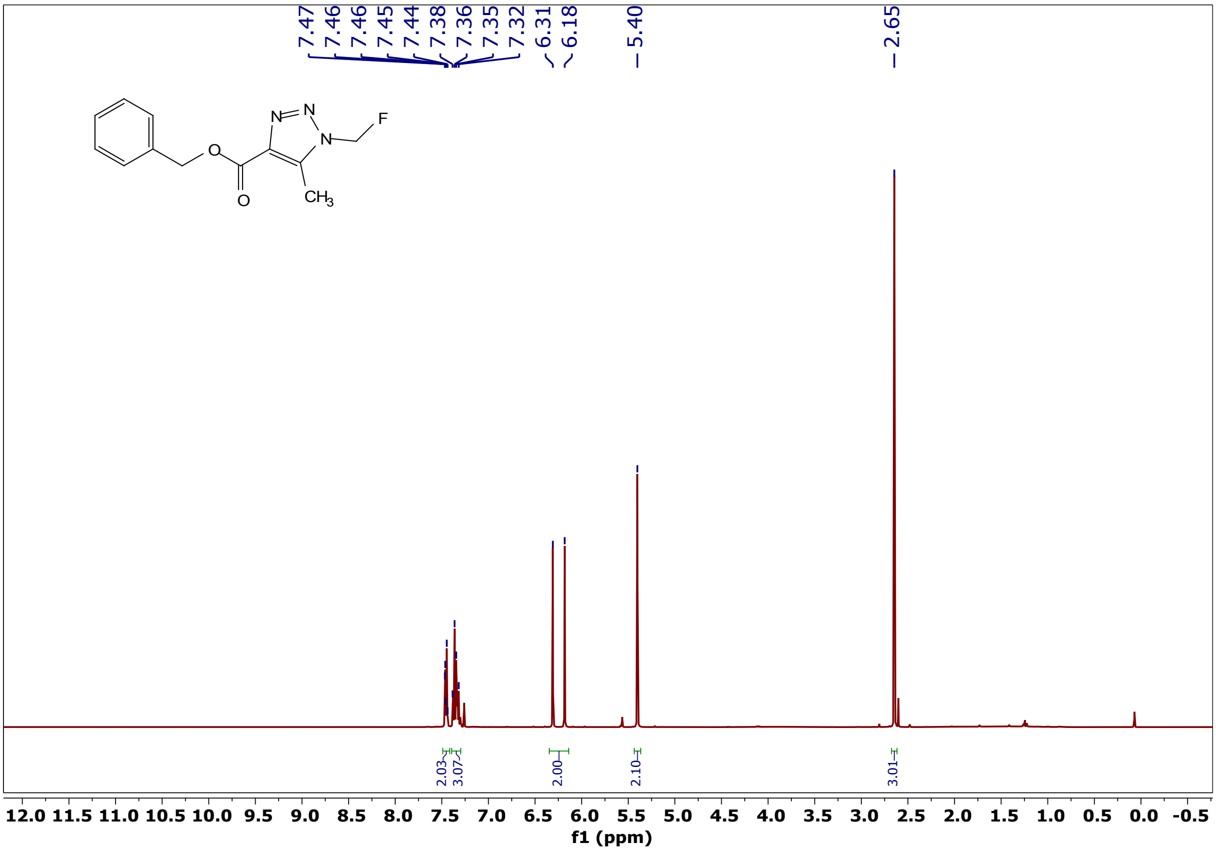
6.32
6.19
4.11
4.09
2.64
2.12
2.10
2.08
2.07
2.05
2.03
2.02
0.97
0.96
CH3
H3C
O
O
N
N
N
F
CH3
2.00
2.02
3.02
1.05
6.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1
f1 (ppm)

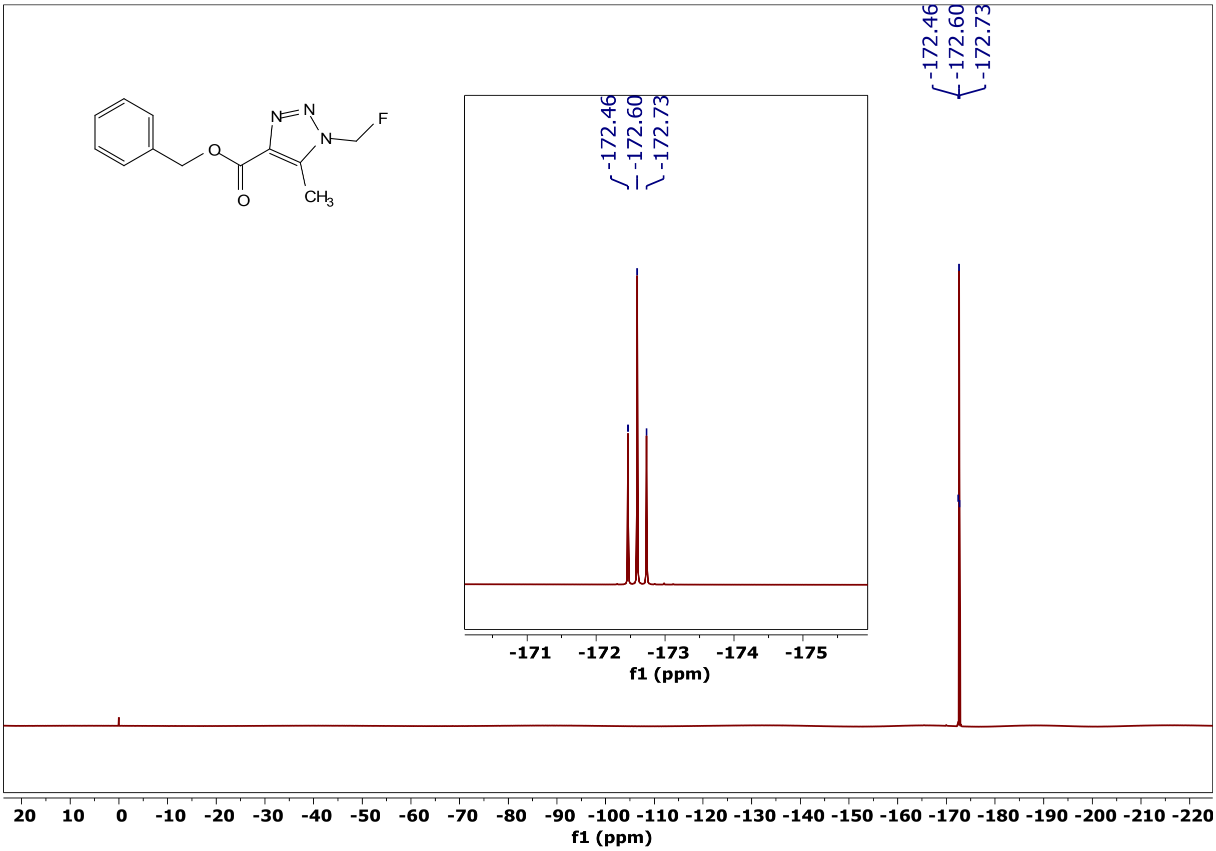


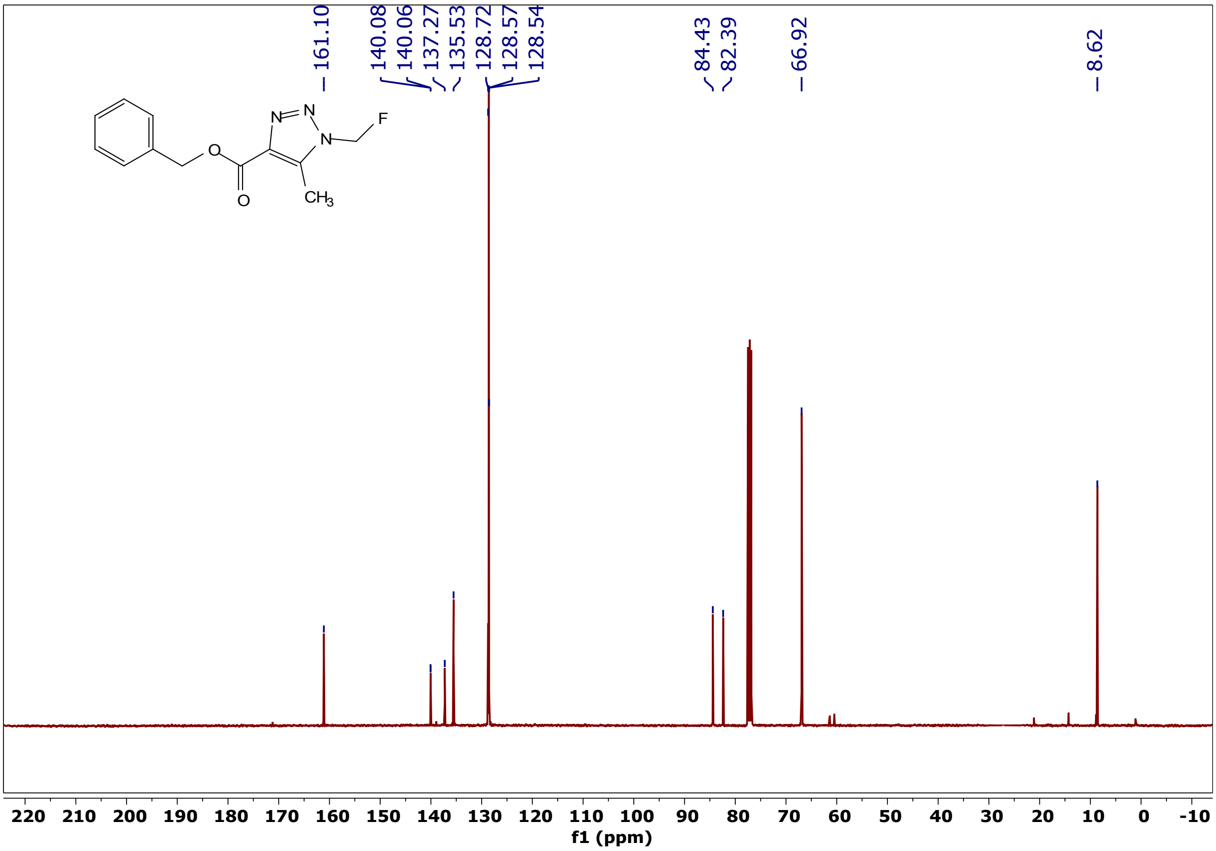
-172.07
-172.20
-172.34
CH3
H3C
O
O
N
N
N
F
CH3
-169
-170
-171
-172
-173
-174
-175
-176
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


161.17
139.57
137.35
84.43
82.40
71.10
27.70
19.06
8.50
CH3
H3C
O
O
N
N
N
F
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound **5c**

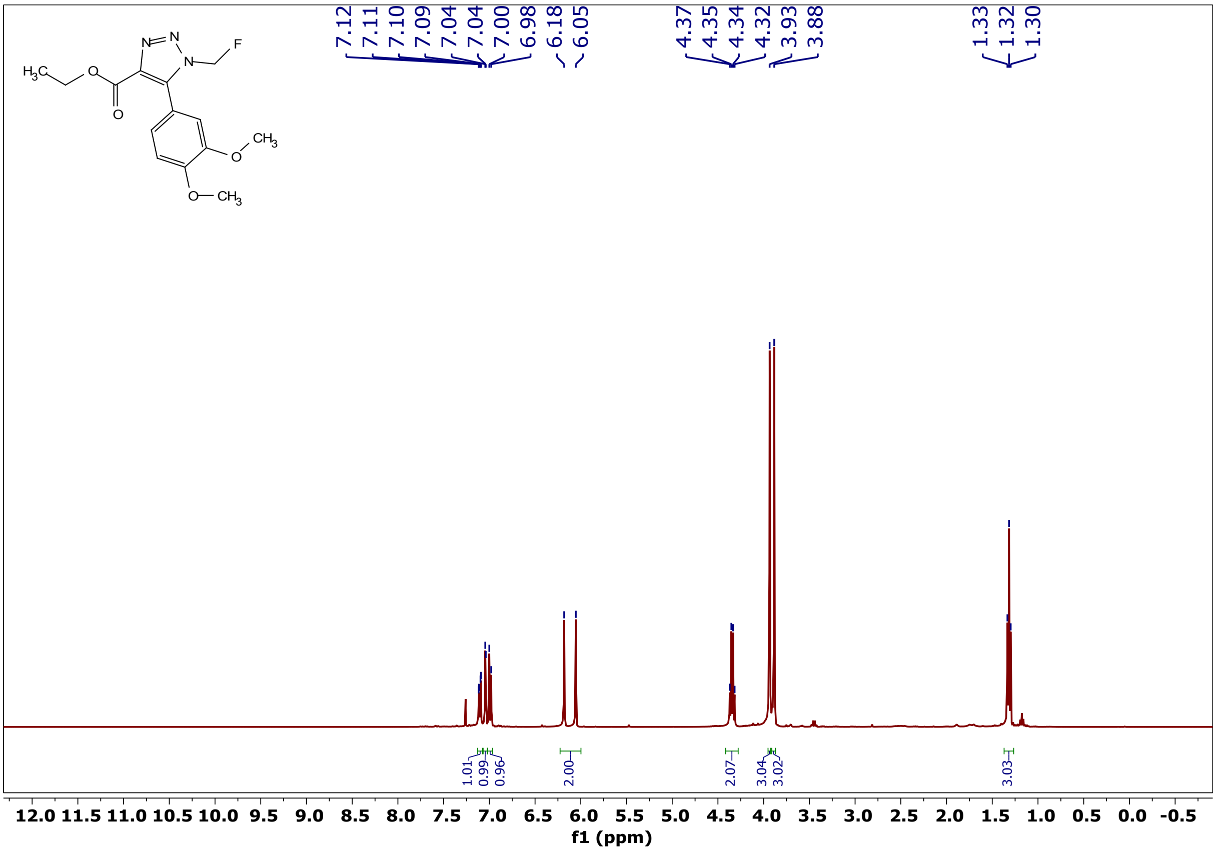

7.47
7.46
7.46
7.45
7.44
7.38
7.36
7.35
7.32
6.31
6.18
5.40
2.65
N
N
N
F
O
O
CH3
2.03
3.07
2.00
2.10
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

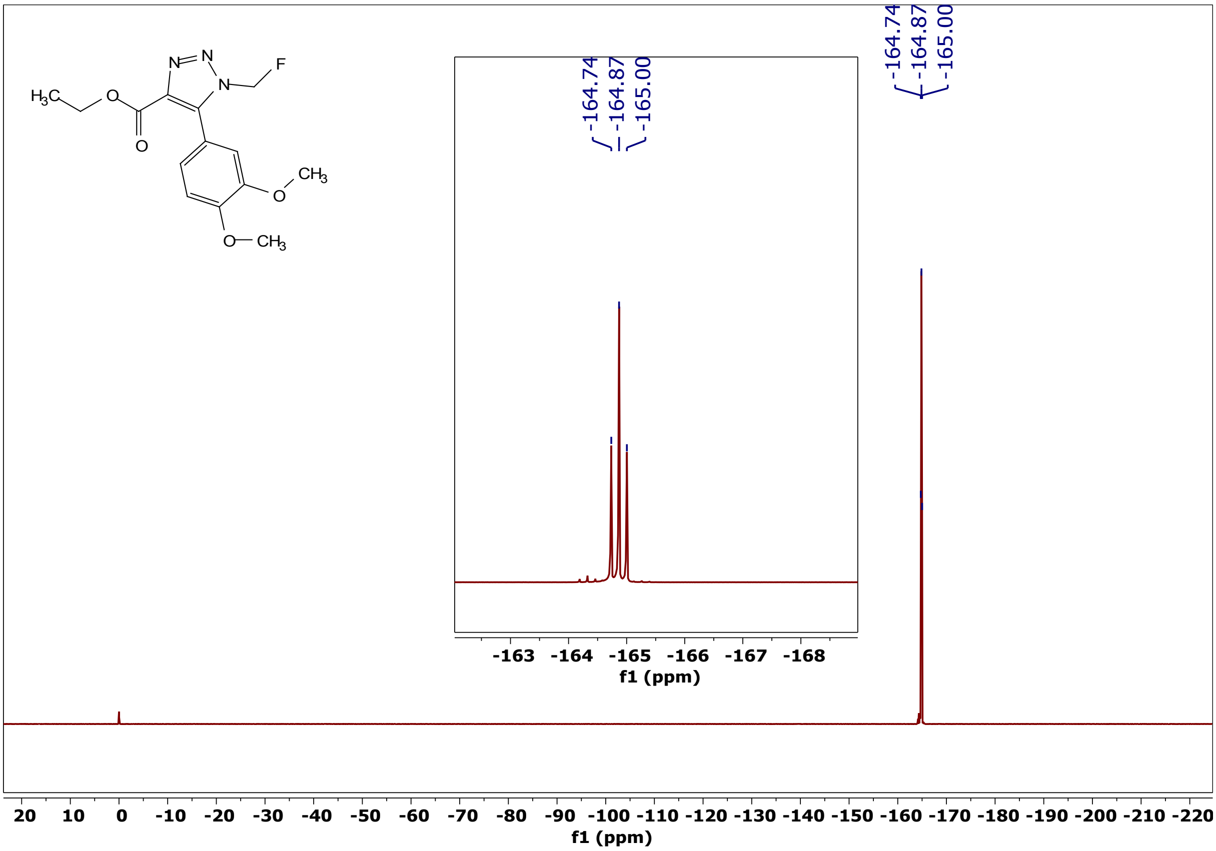

-172.46
-172.60
-172.73
N
N
N
F
O
O
CH3
-171 -172 -173 -174 -175
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

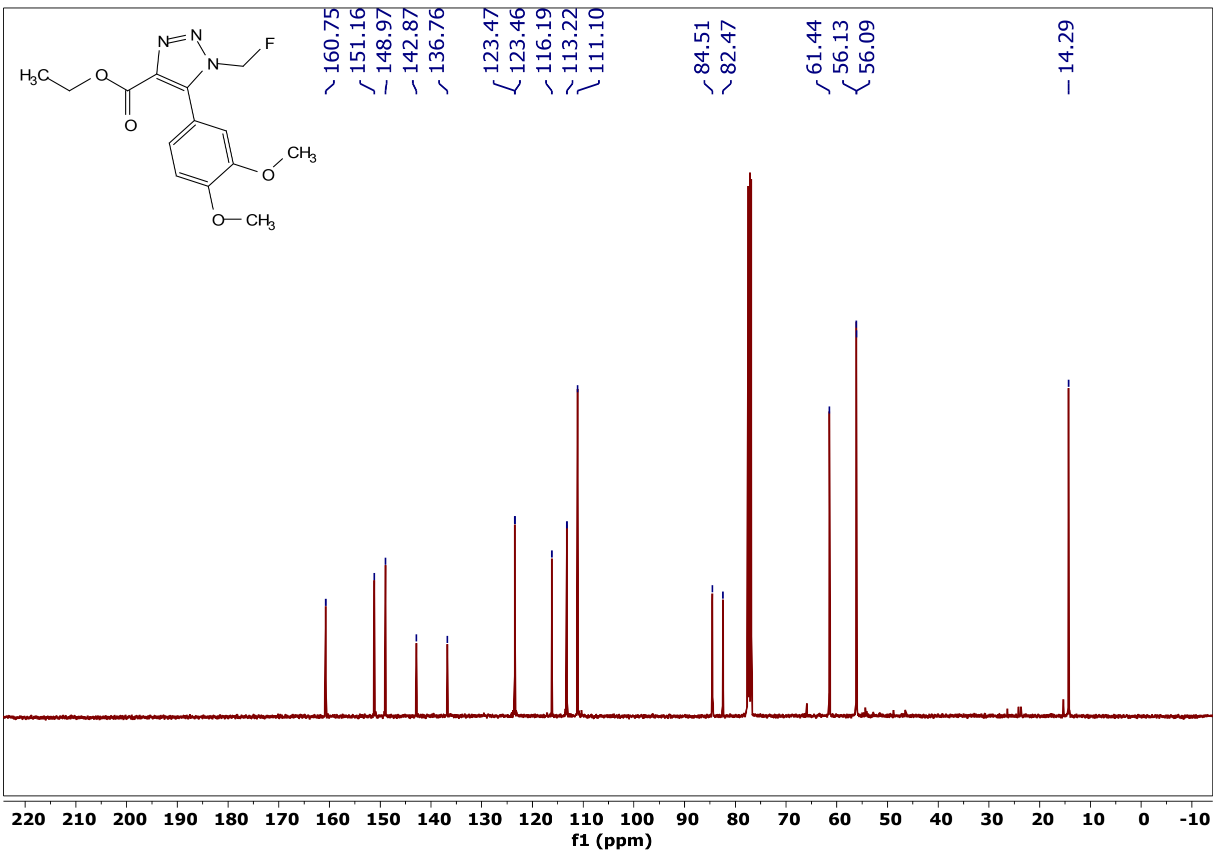


161.10
140.08
140.06
137.27
135.53
128.72
128.57
128.54
84.43
82.39
66.92
8.62
N
N
N
F
O
O
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

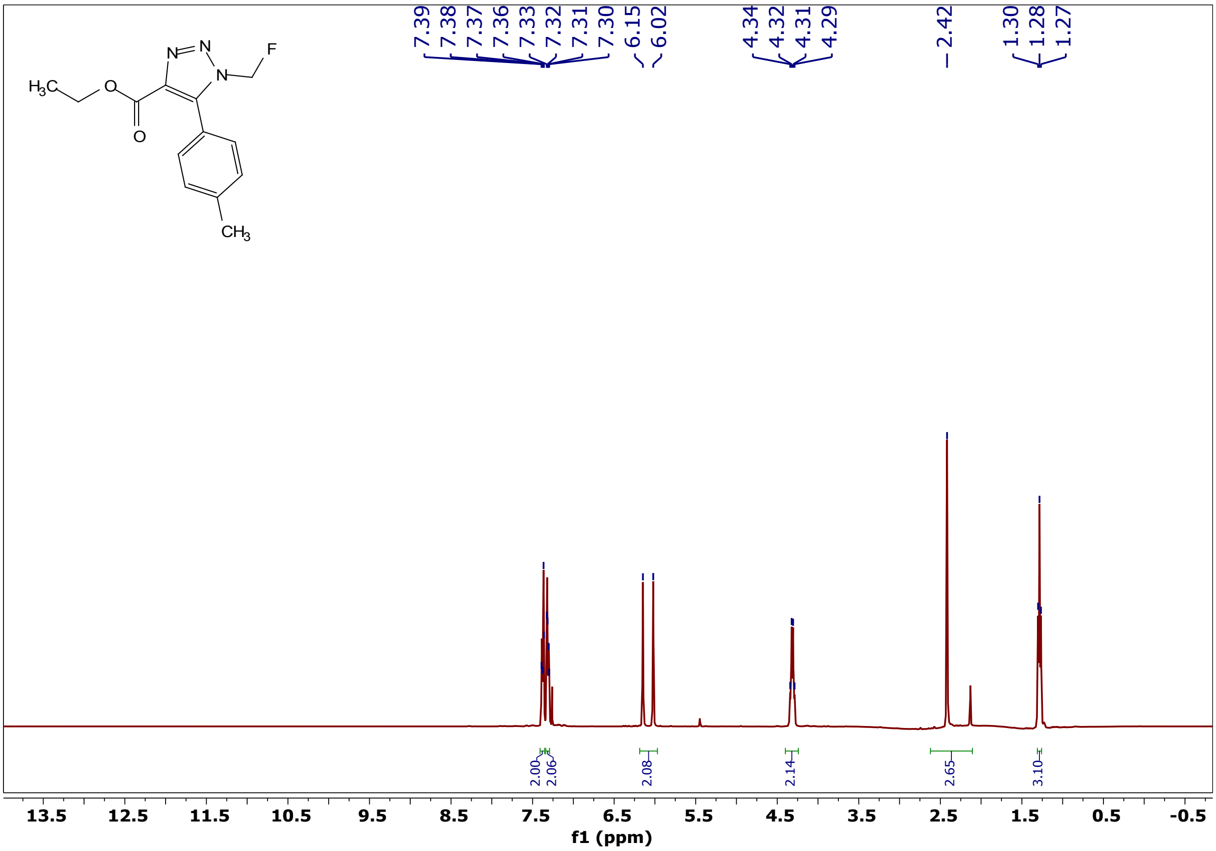
Compound **5d**

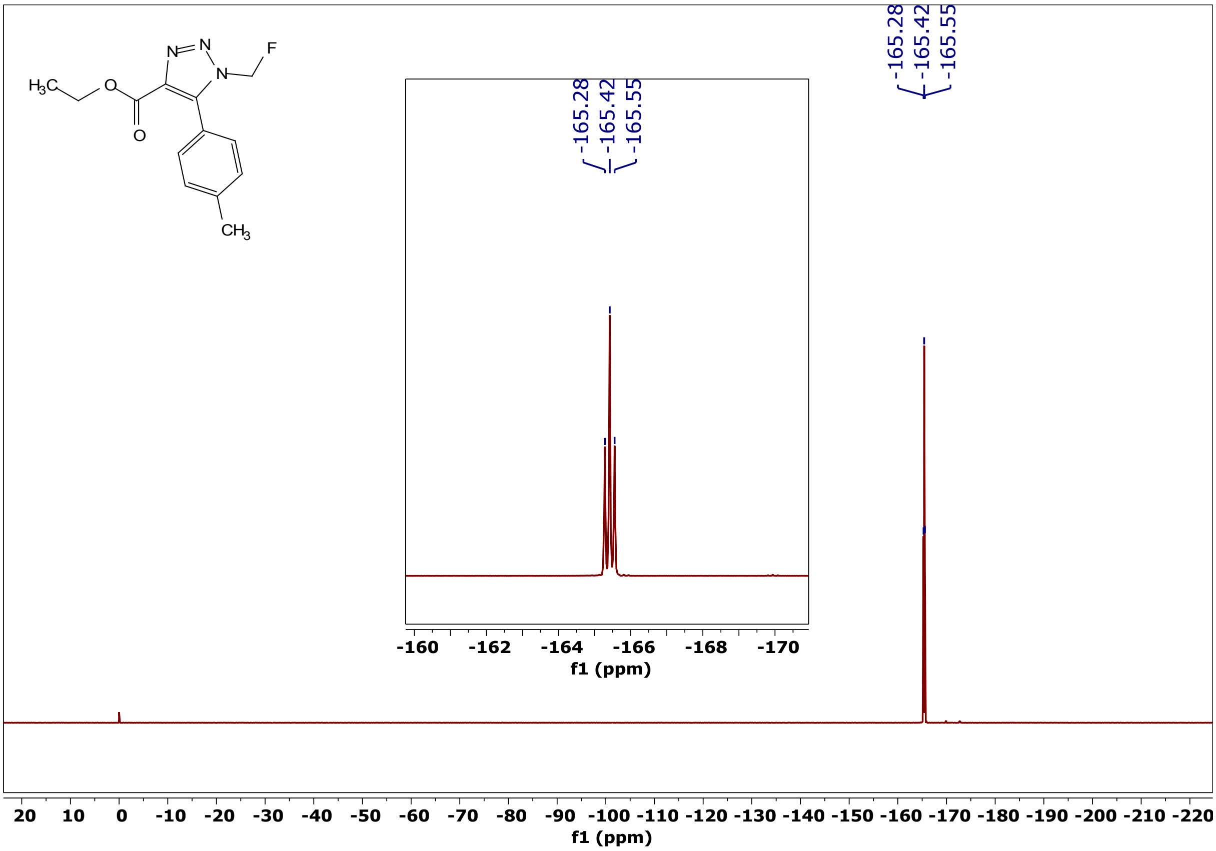

7.12
7.11
7.10
7.09
7.04
7.04
7.00
6.98
6.18
6.05
4.37
4.35
4.34
4.32
3.93
3.88
1.33
1.32
1.30
1.01
0.99
0.96
2.00
2.07
3.04
3.02
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

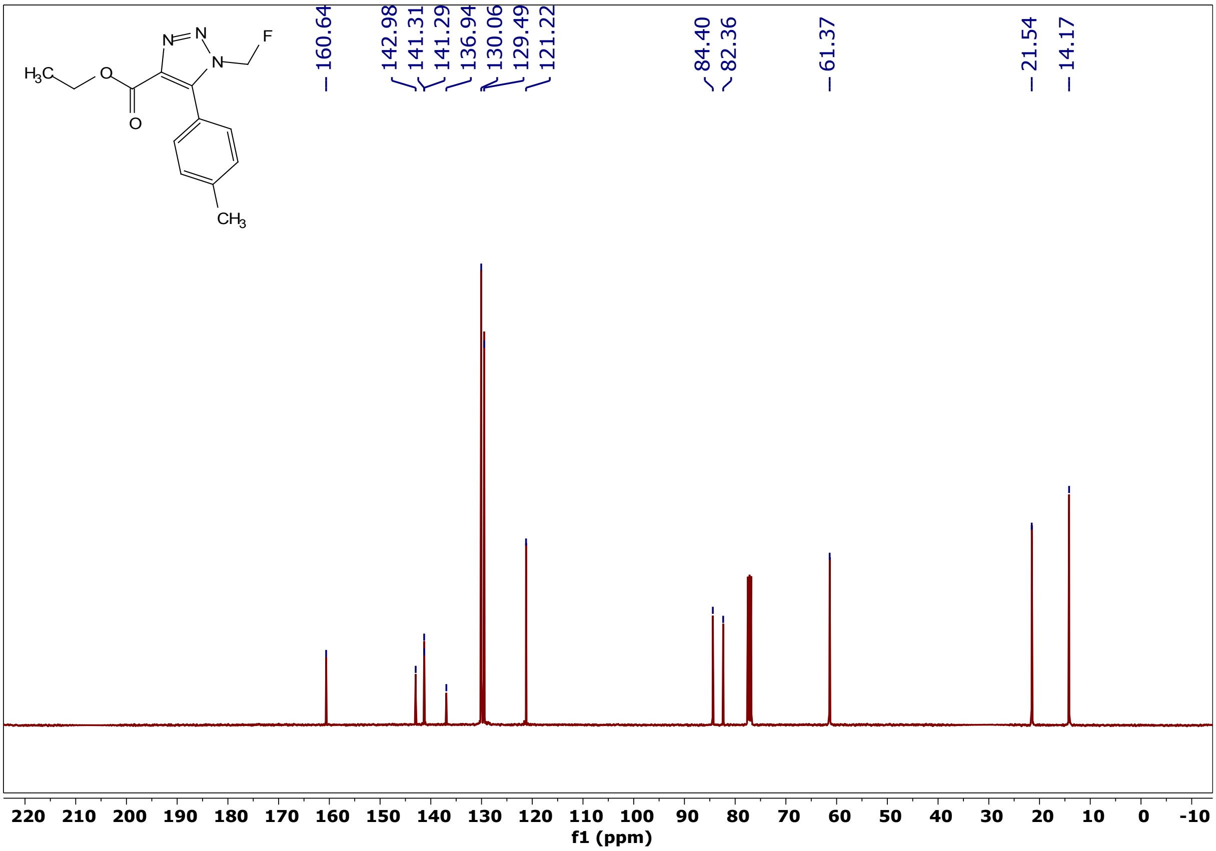

-164.74
-164.87
-165.00
-164.74
-164.87
-165.00
-163 -164 -165 -166 -167 -168
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


160.75
151.16
148.97
142.87
136.76
123.47
123.46
116.19
113.22
111.10
84.51
82.47
61.44
56.13
56.09
14.29
N
N
N
F
H_3C
O
O
O
CH_3
O
CH_3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

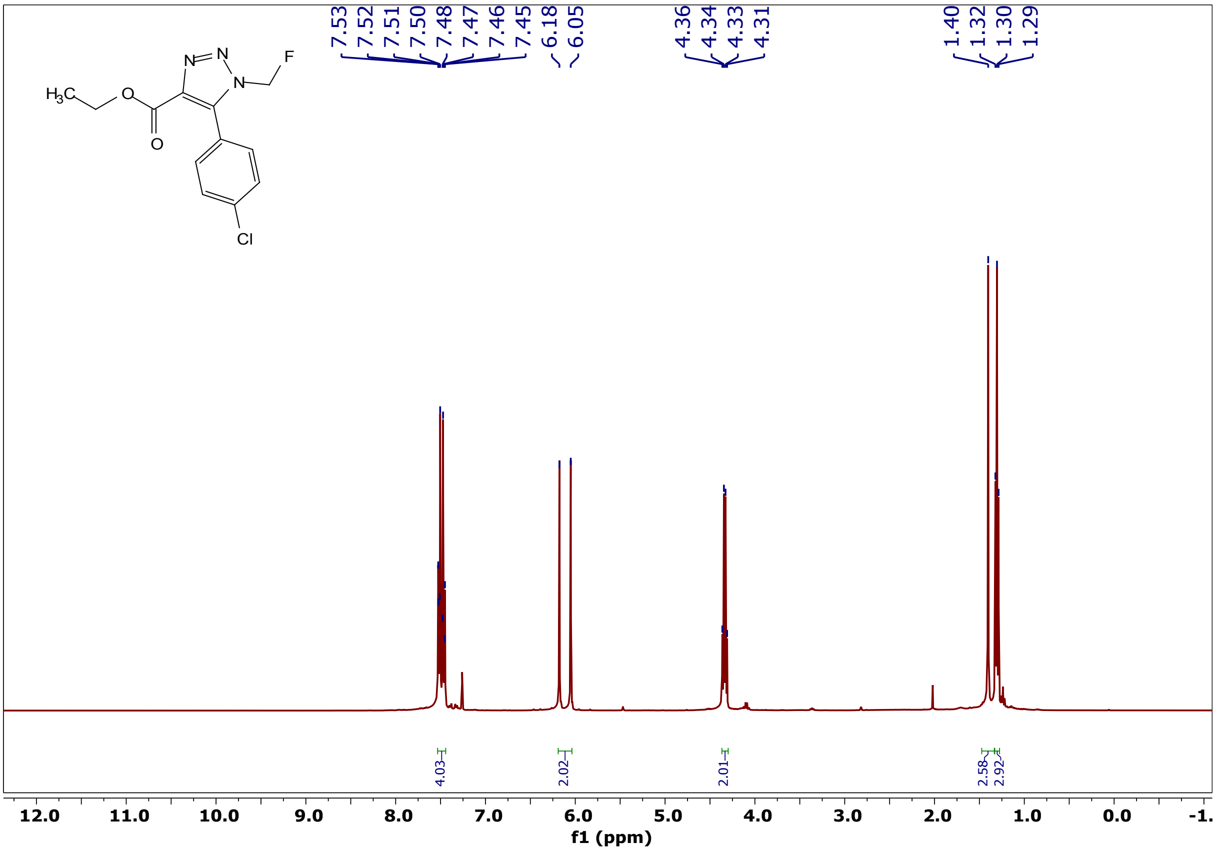
Compound **5e**

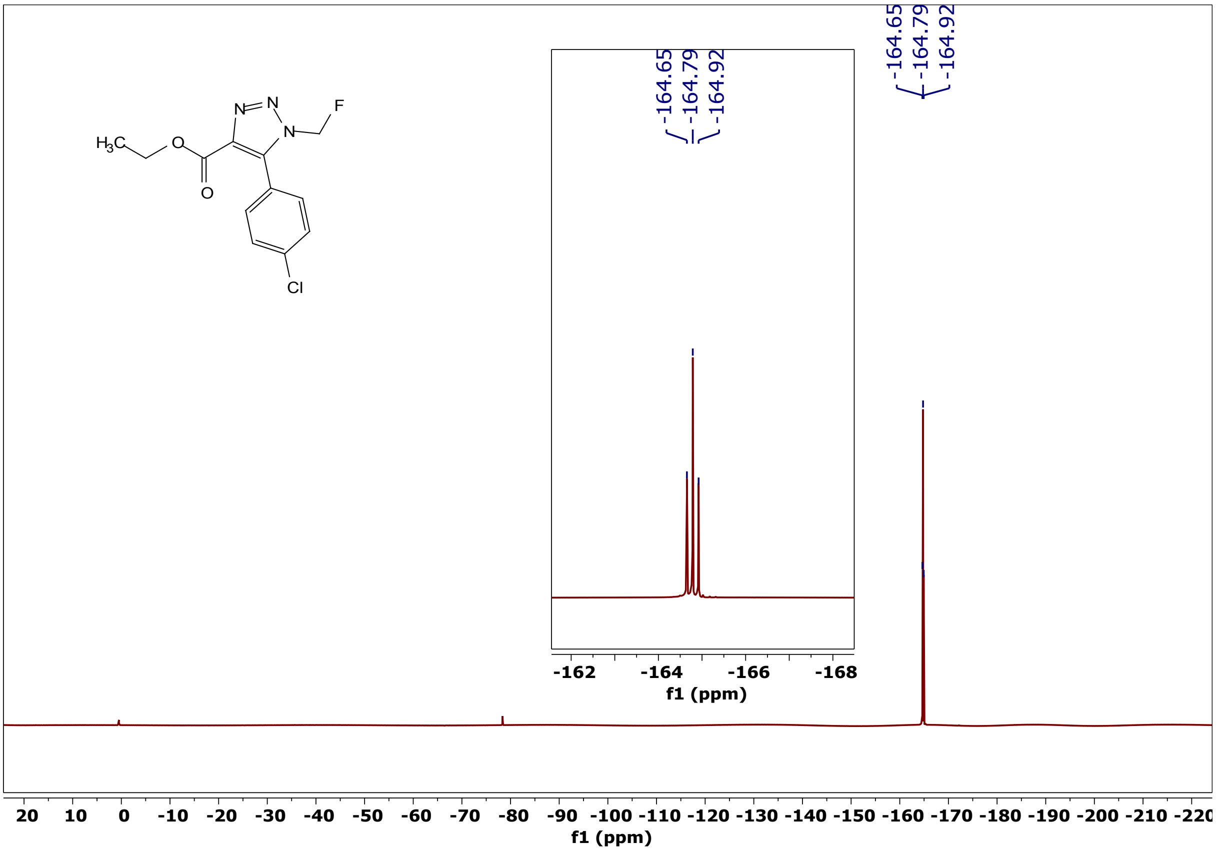

H$_3$C
O
O
N
N
N
F
CH$_3$
7.39
7.38
7.37
7.36
7.33
7.32
7.31
7.30
6.15
6.02
4.34
4.32
4.31
4.29
2.42
1.30
1.28
1.27
2.00
2.06
2.08
2.14
2.65
3.10
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

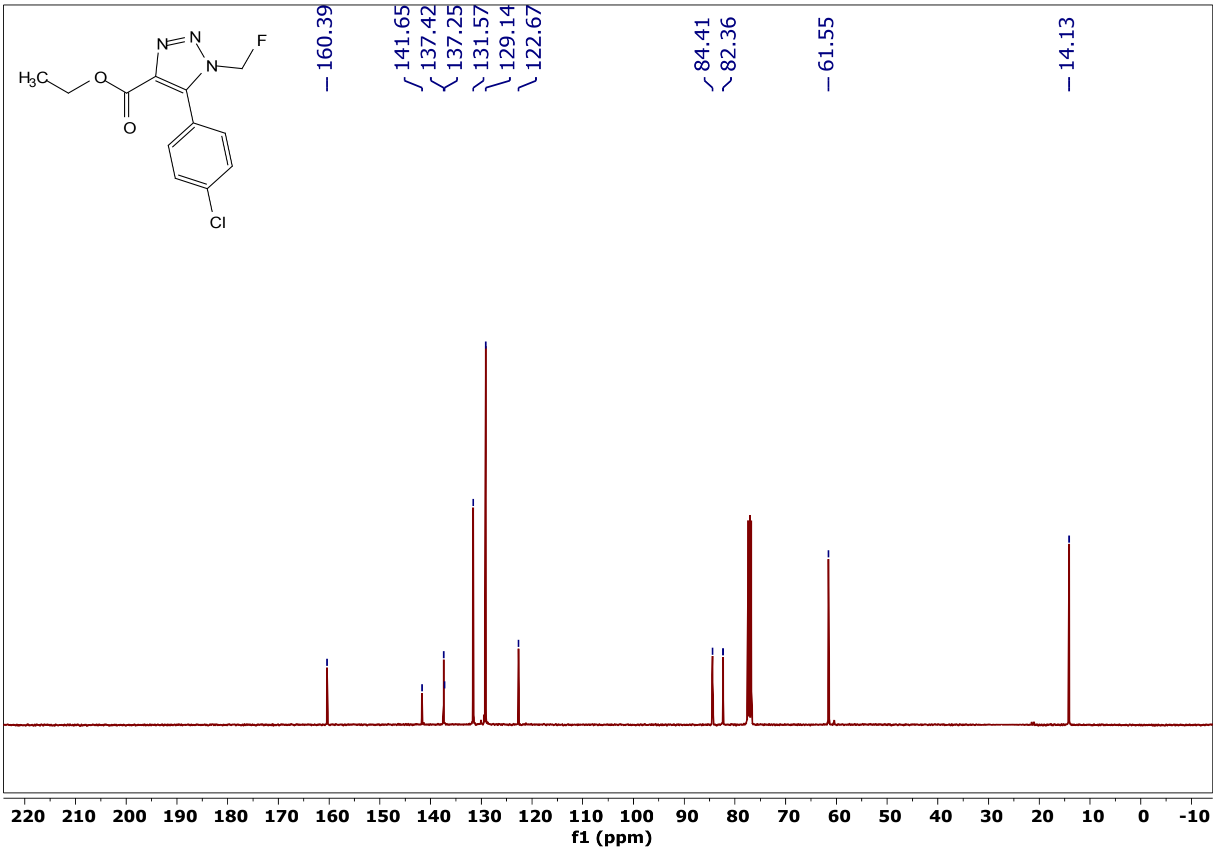

H$_3$C
O
O
N
N
N
F
CH$_3$
-165.28
-165.42
-165.55
-165.28
-165.42
-165.55
-160
-162
-164
-166
-168
-170
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


160.64
142.98
141.31
141.29
136.94
130.06
129.49
121.22
84.40
82.36
61.37
21.54
14.17
H3C
O
O
N
N
N
F
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound **5f**

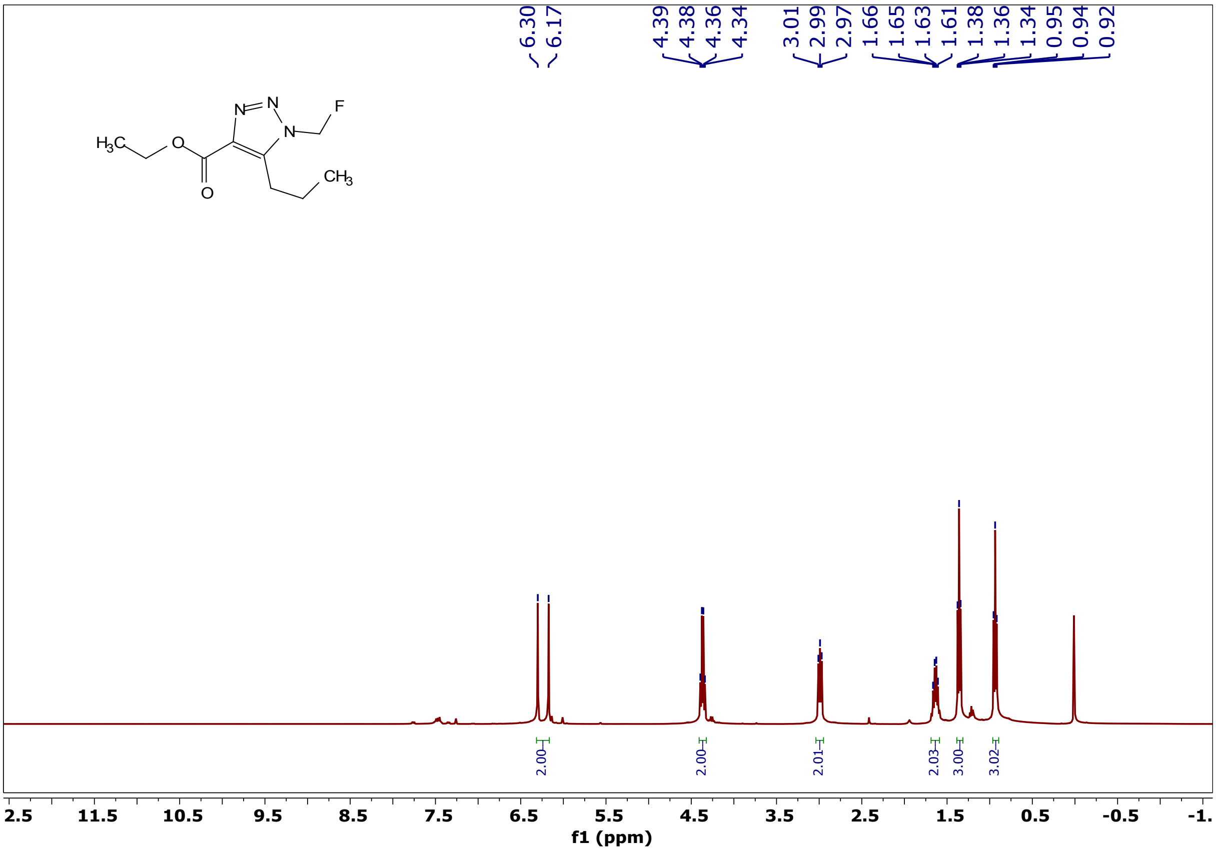

7.53
7.52
7.51
7.50
7.48
7.47
7.46
7.45
6.18
6.05
4.36
4.34
4.33
4.31
1.40
1.32
1.30
1.29
H3C
O
O
N
N
N
F
Cl
4.03
2.02
2.01
2.58
2.92
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.
f1 (ppm)

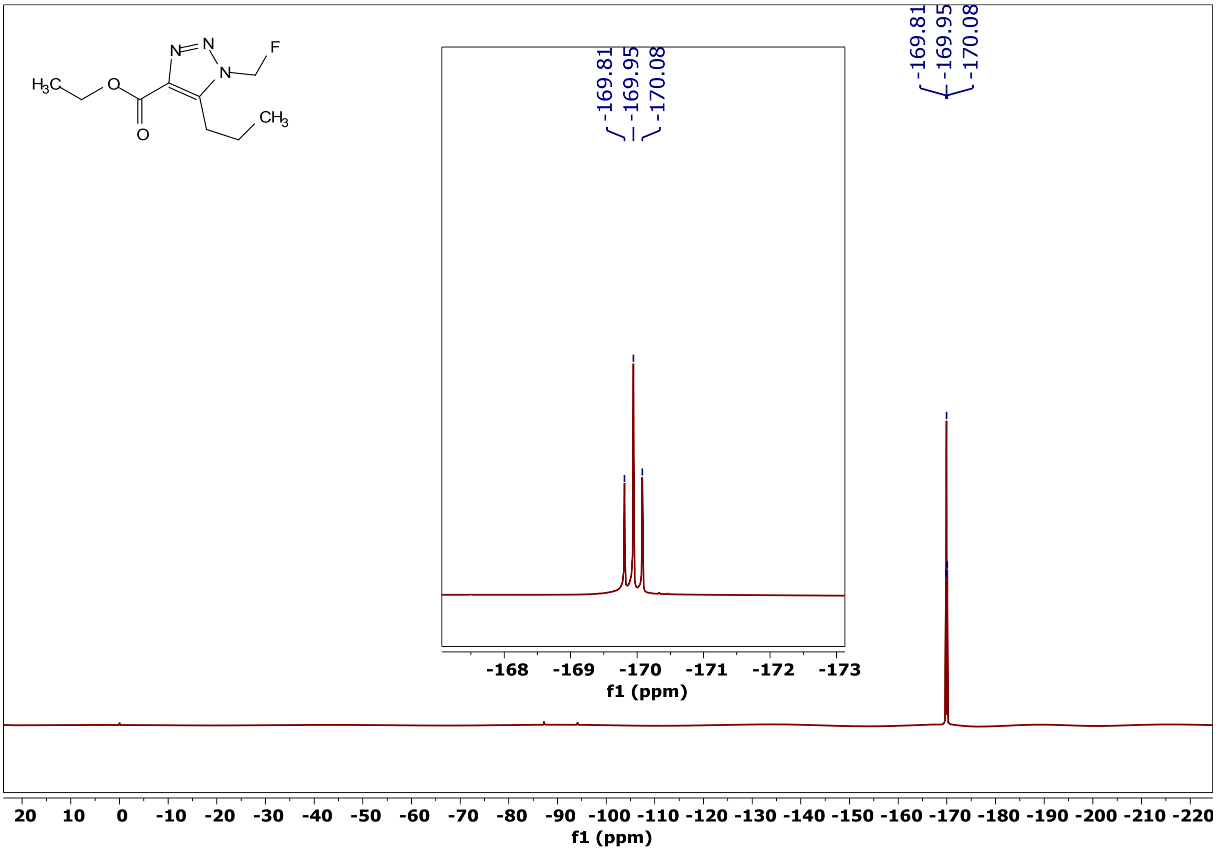

-164.65
-164.79
-164.92
-164.65
-164.79
-164.92
H3C
O
O
N
N
N
F
Cl
-162
-164
-166
-168
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

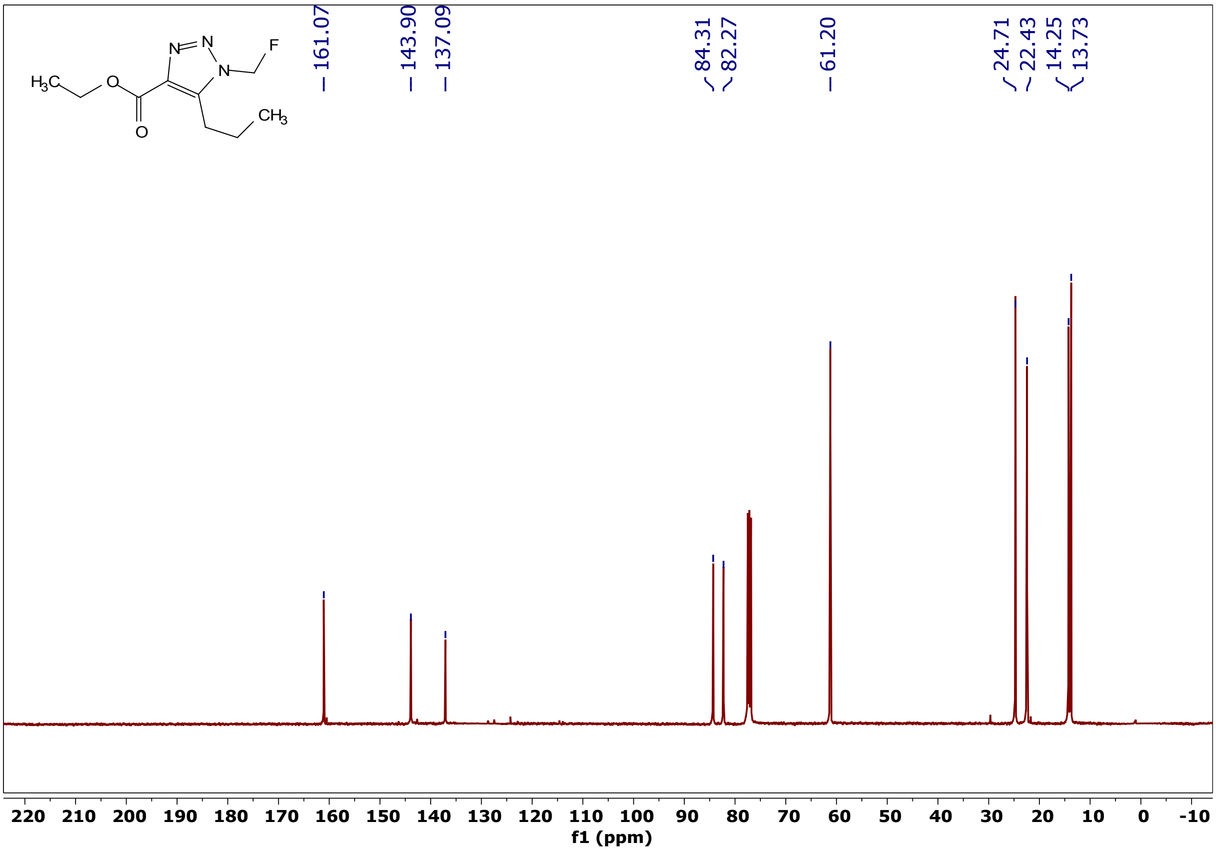


H3C
O
O
N
N
N
F
Cl
160.39
141.65
137.42
137.25
131.57
129.14
122.67
84.41
82.36
61.55
14.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound **5g**

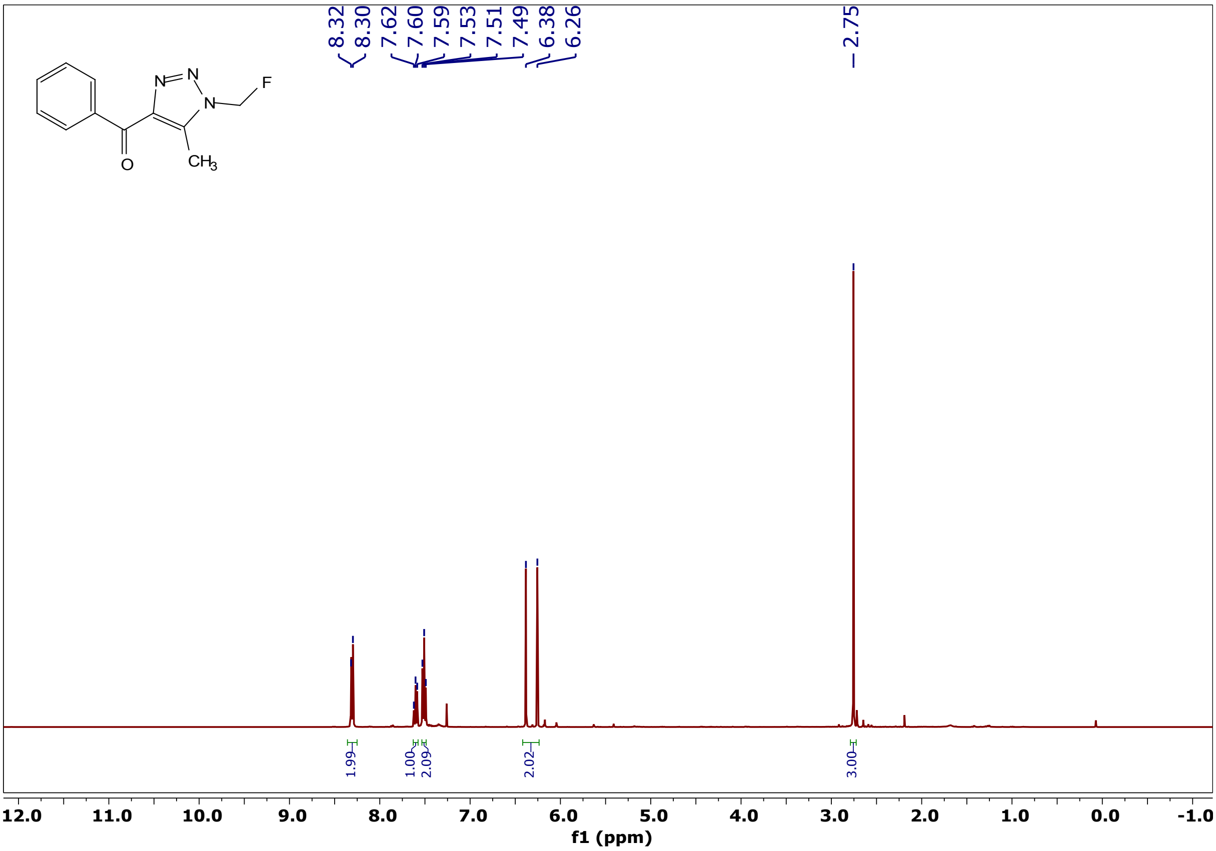

6.30
6.17
4.39
4.38
4.36
4.34
3.01
2.99
2.97
1.66
1.65
1.63
1.61
1.38
1.36
1.34
0.95
0.94
0.92
H3C
O
N
N
N
F
CH3
O
2.00
2.00
2.01
2.03
3.00
3.02
2.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.
f1 (ppm)

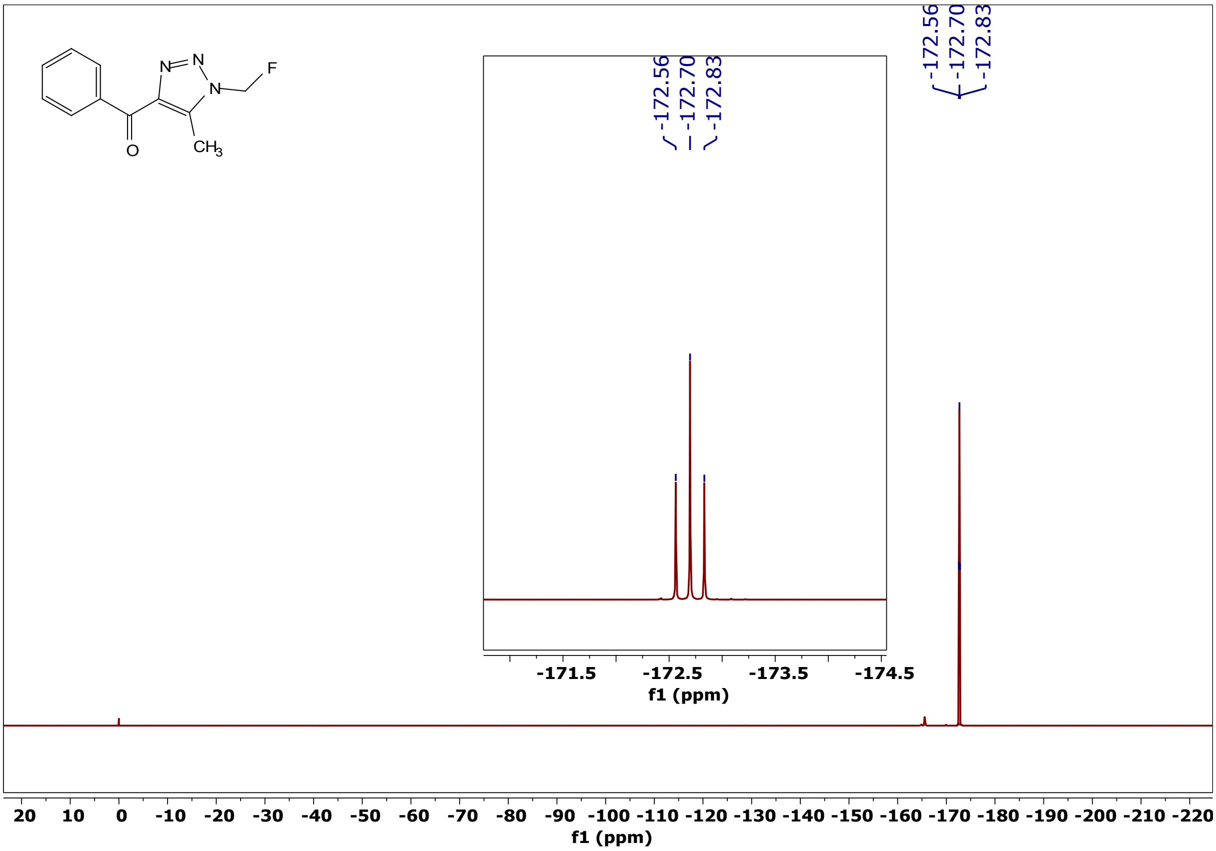

-169.81
-169.95
-170.08
H3C
O
N
N
N
F
CH3
O
-168
-169
-170
-171
-172
-173
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

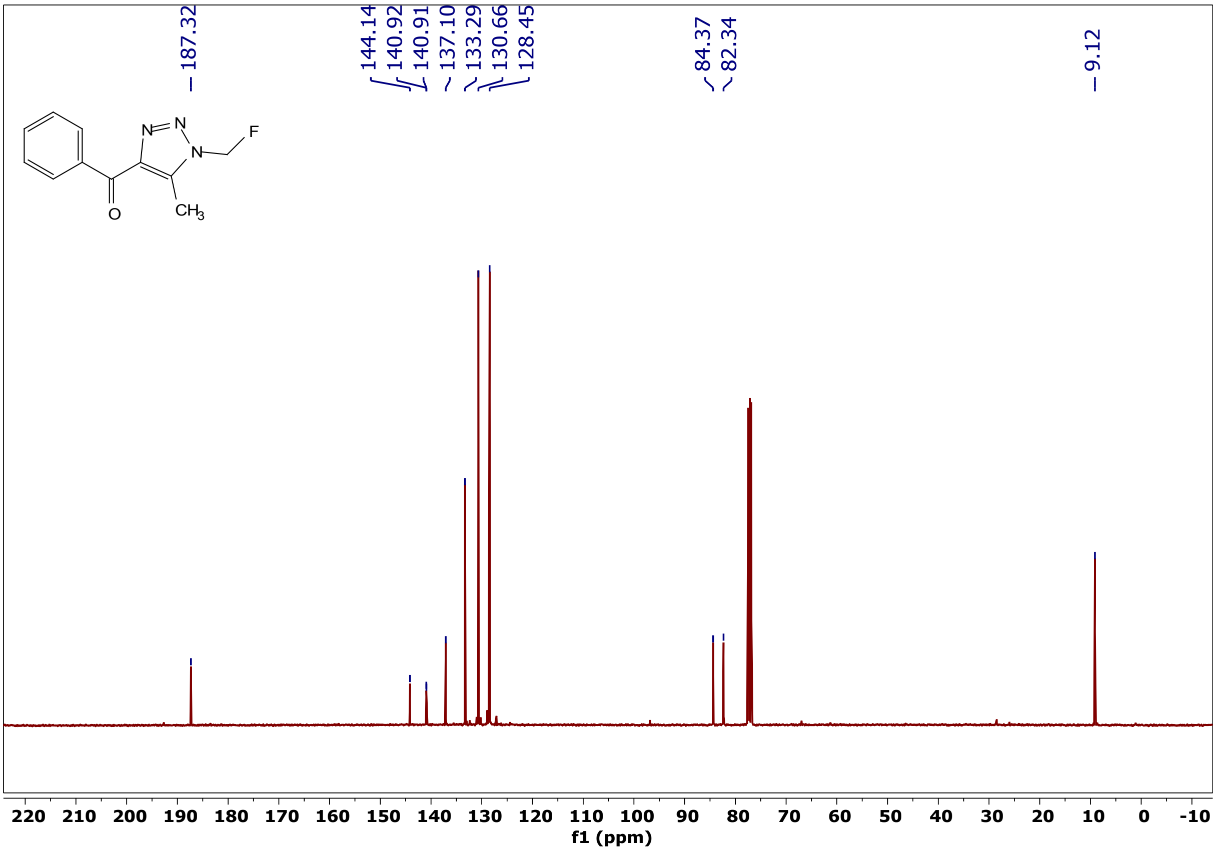


H3C
O
O
N
N
N
F
CH3
161.07
143.90
137.09
84.31
82.27
61.20
24.71
22.43
14.25
13.73
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

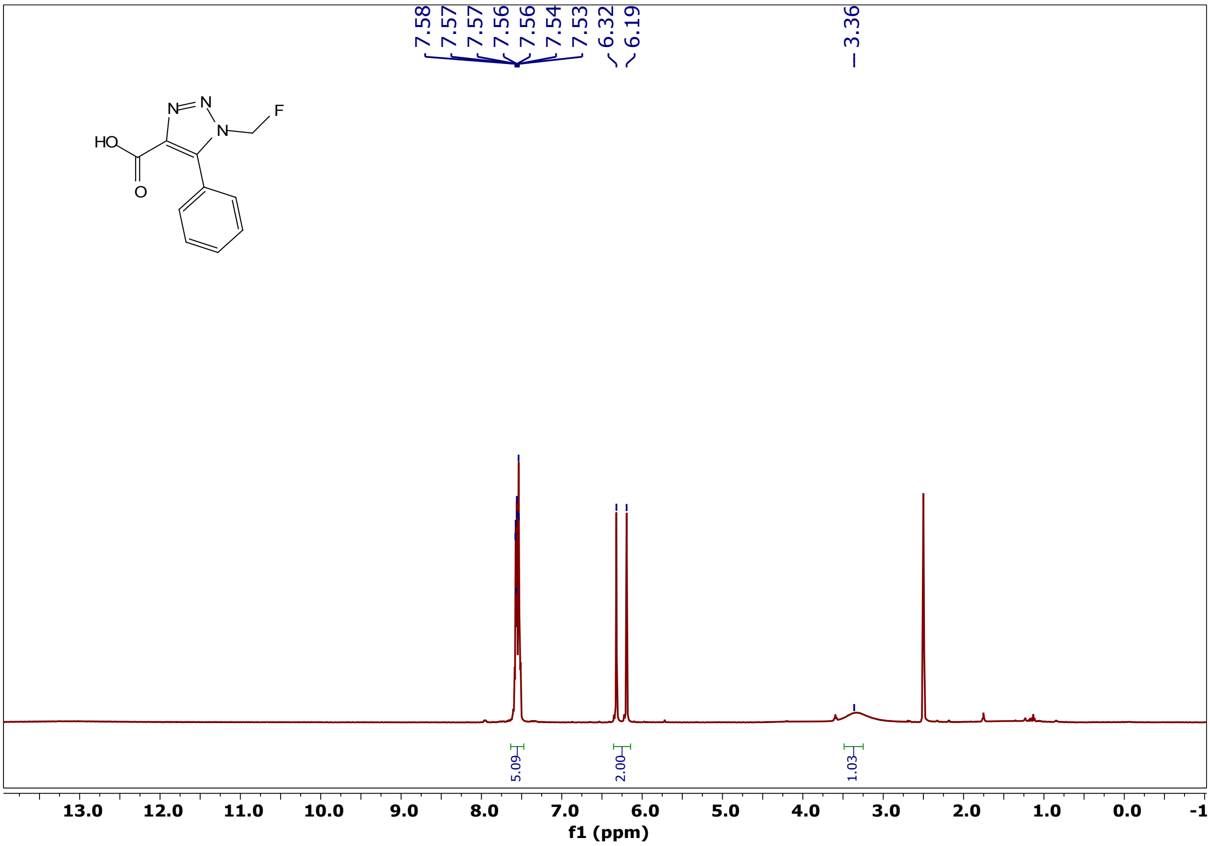
Compound **5h**


8.32
8.30
7.62
7.60
7.59
7.53
7.51
7.49
6.38
6.26
2.75
N
N
N
F
O
CH3
1.99
1.00
2.09
2.02
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

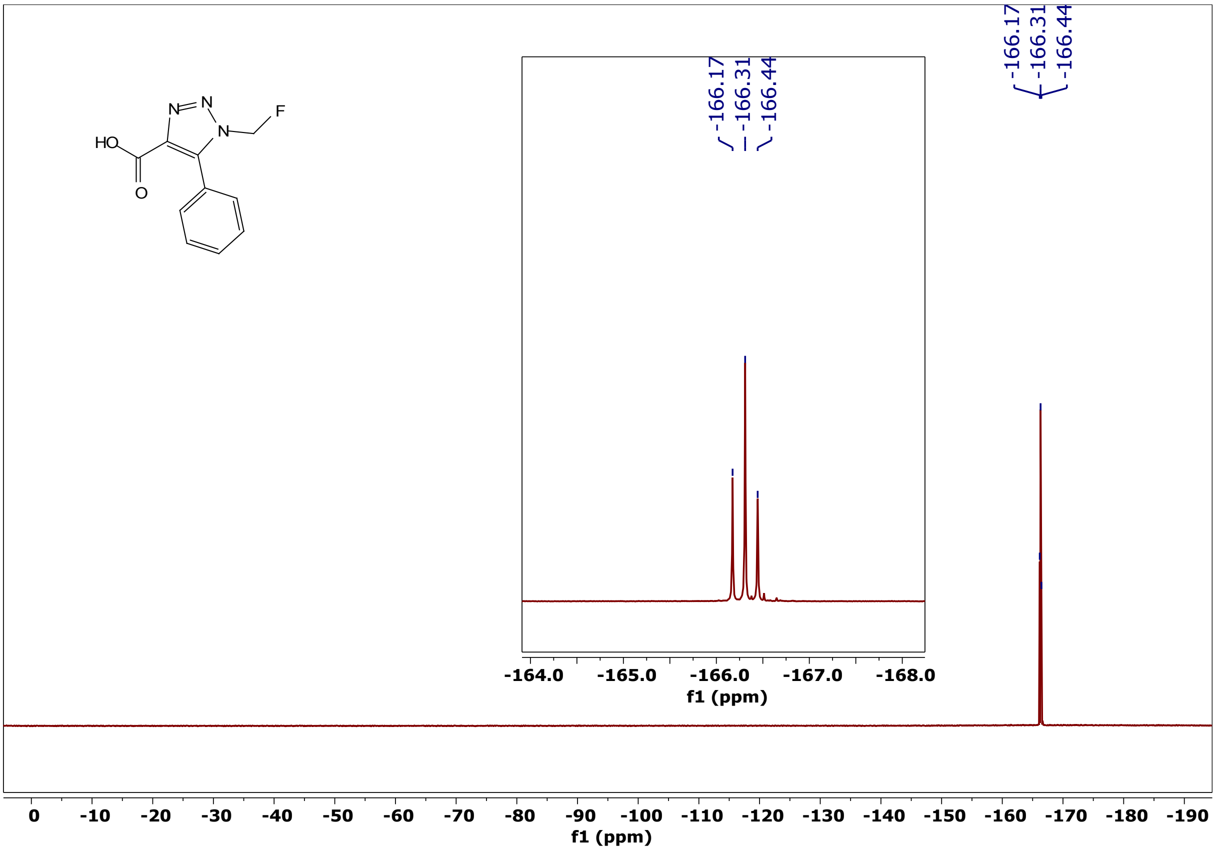

-172.56
-172.70
-172.83
N
N
N
F
O
CH3
-172.56
-172.70
-172.83
-171.5
-172.5
-173.5
-174.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


187.32
144.14
140.92
140.91
137.10
133.29
130.66
128.45
84.37
82.34
9.12
N
N
N
F
O
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

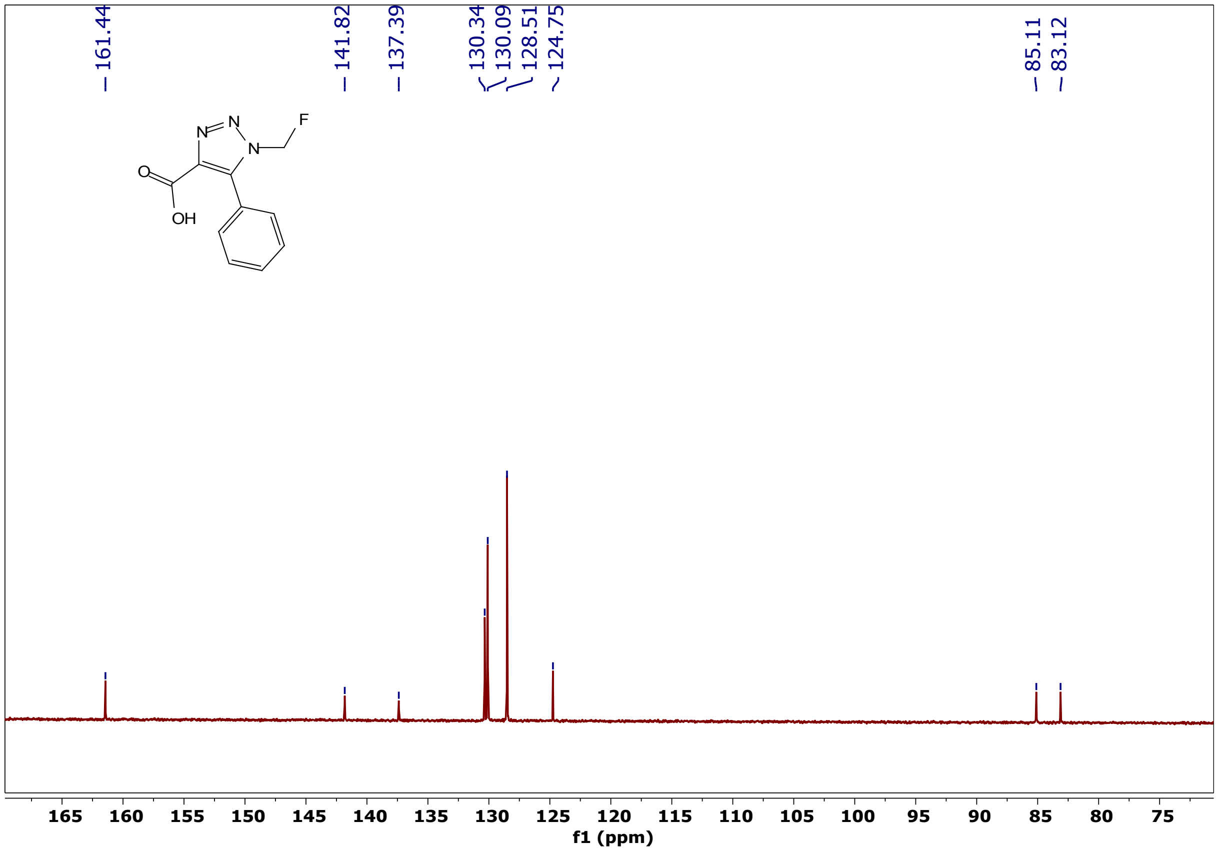
Compound **6a**



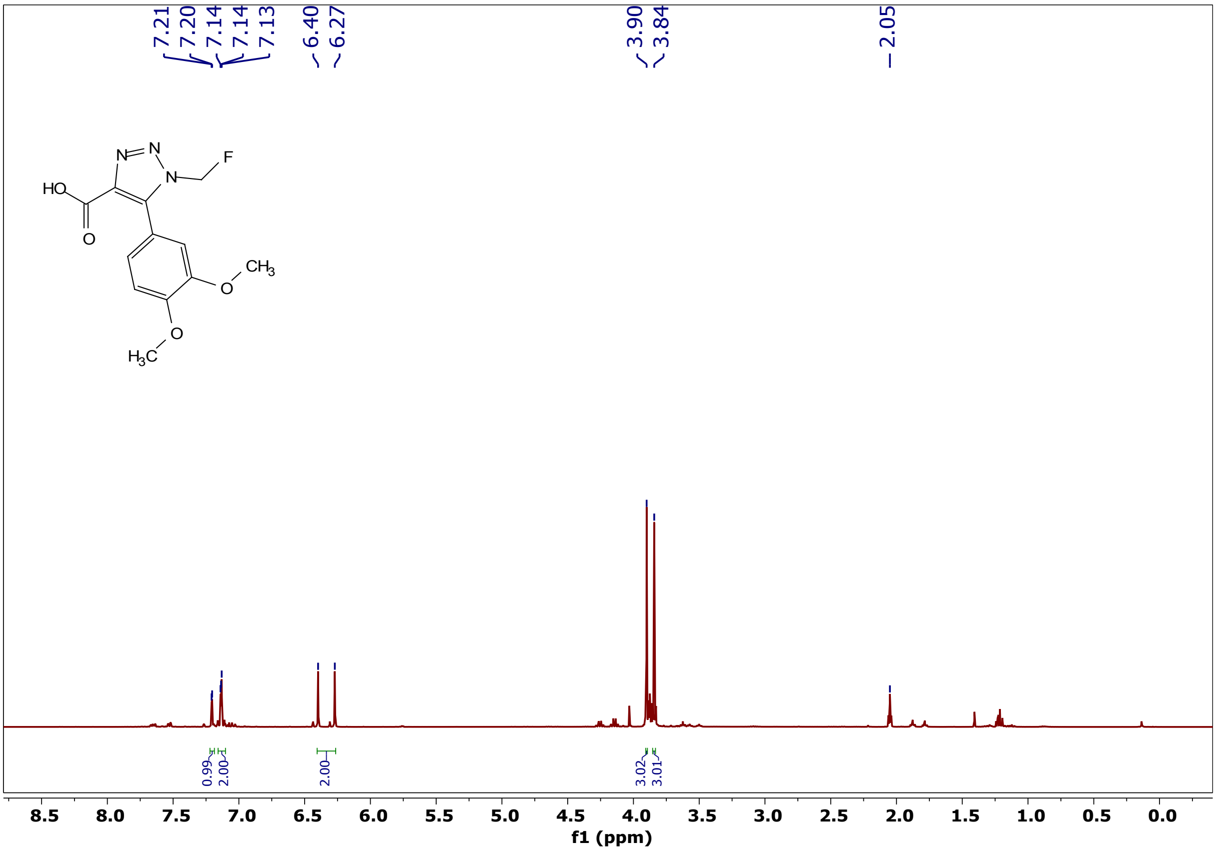
7.58
7.57
7.57
7.56
7.56
7.54
7.53
6.32
6.19
3.36
HO
O
N
N
N
F
5.09
2.00
1.03
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)

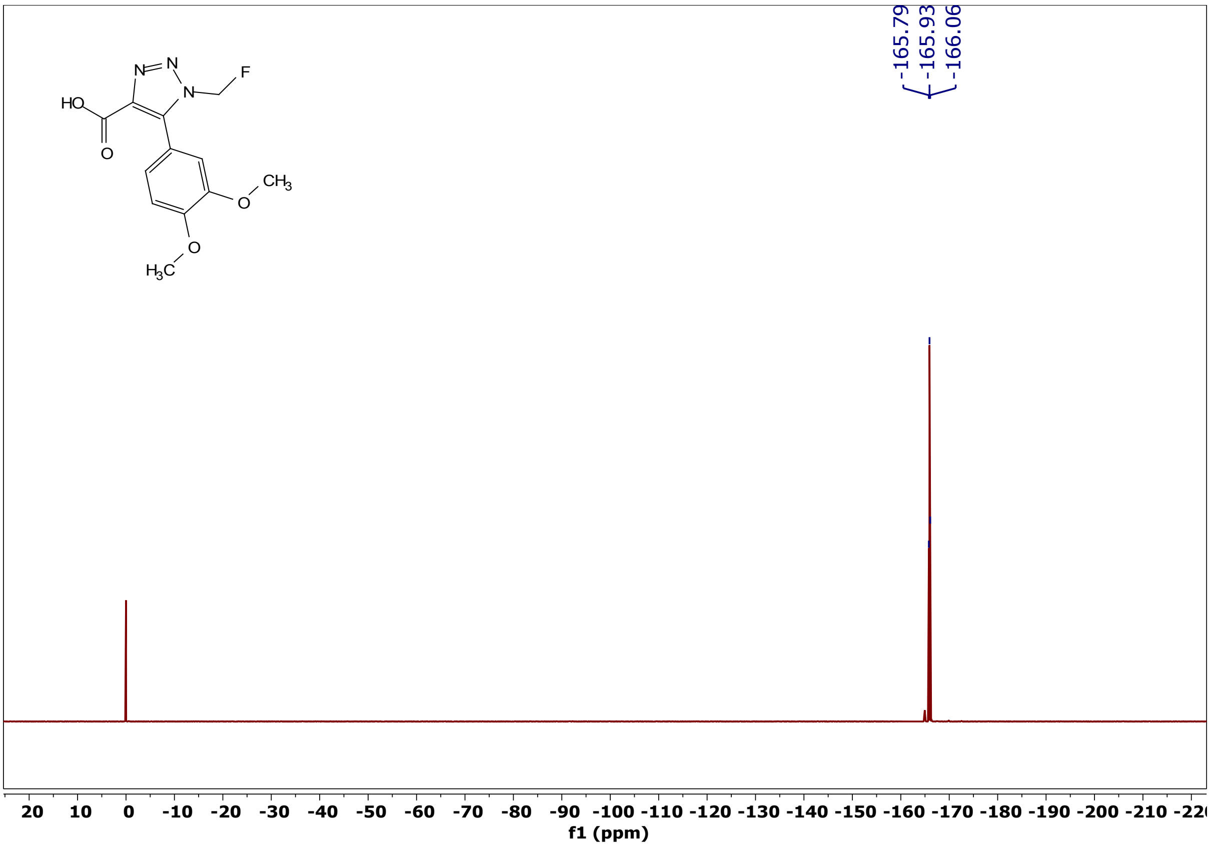


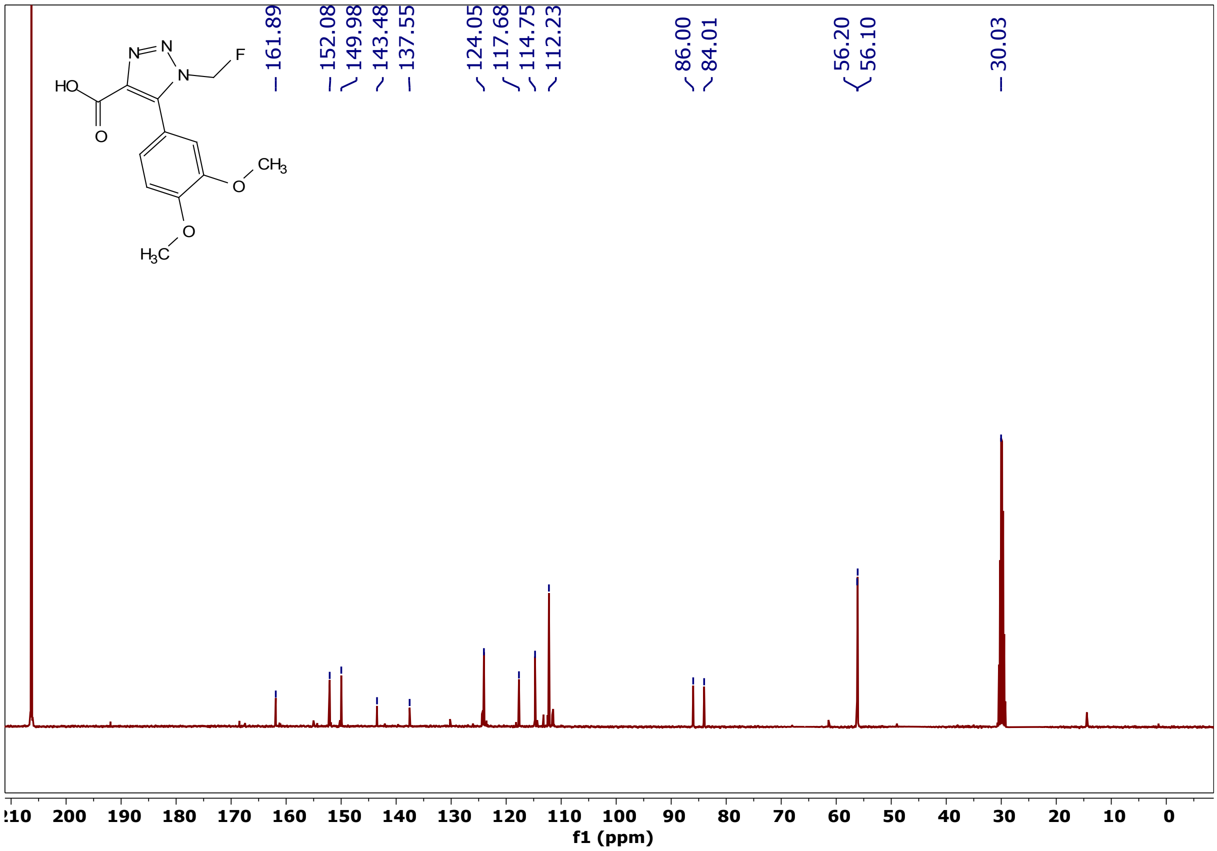
-166.17
-166.31
-166.44
HO
O
N
N
N
F
-164.0
-165.0
-166.0
-167.0
-168.0
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


161.44
141.82
137.39
130.34
130.09
128.51
124.75
85.11
83.12
N
N
N
F
O
OH
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
f1 (ppm)

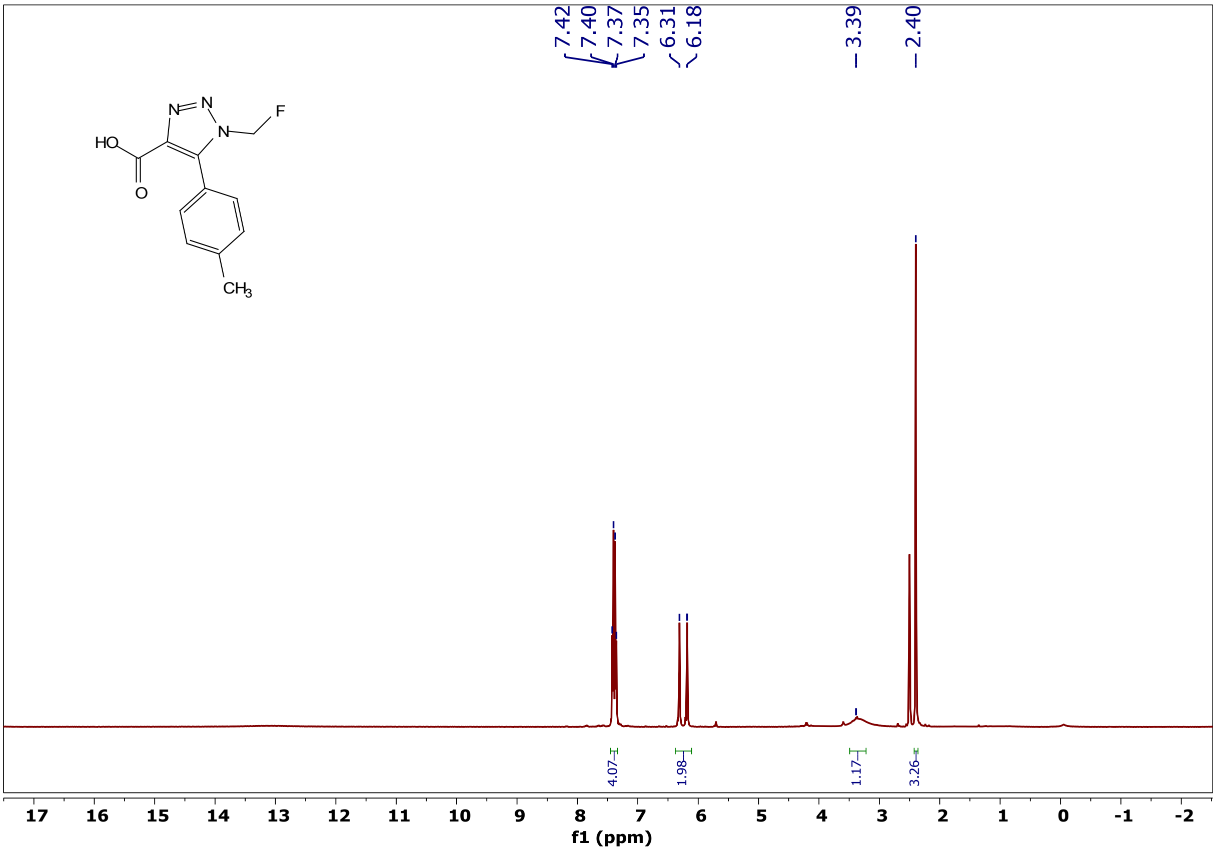
Compound **6d**

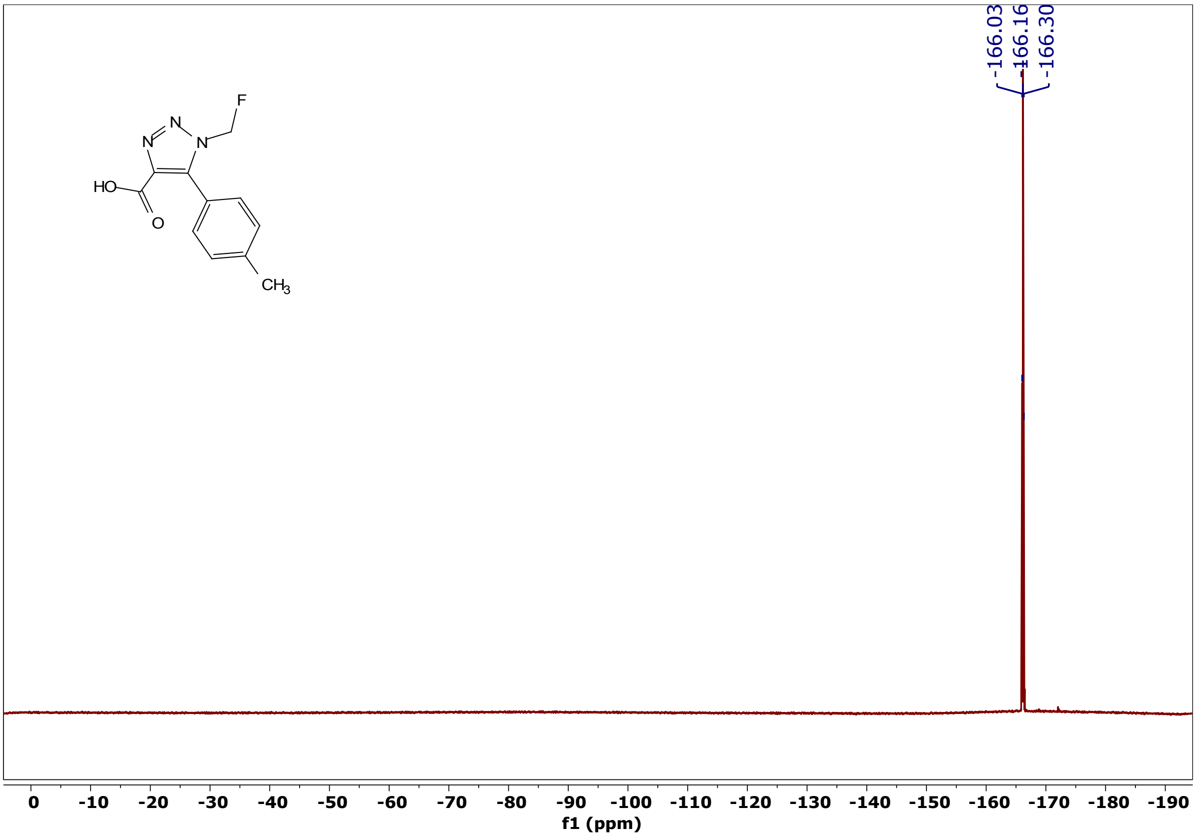

7.21
7.20
7.14
7.14
7.13
6.40
6.27
3.90
3.84
2.05
0.99
2.00
2.00
3.02
3.01
HO
O
N
N
N
F
O
CH3
O
H3C
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

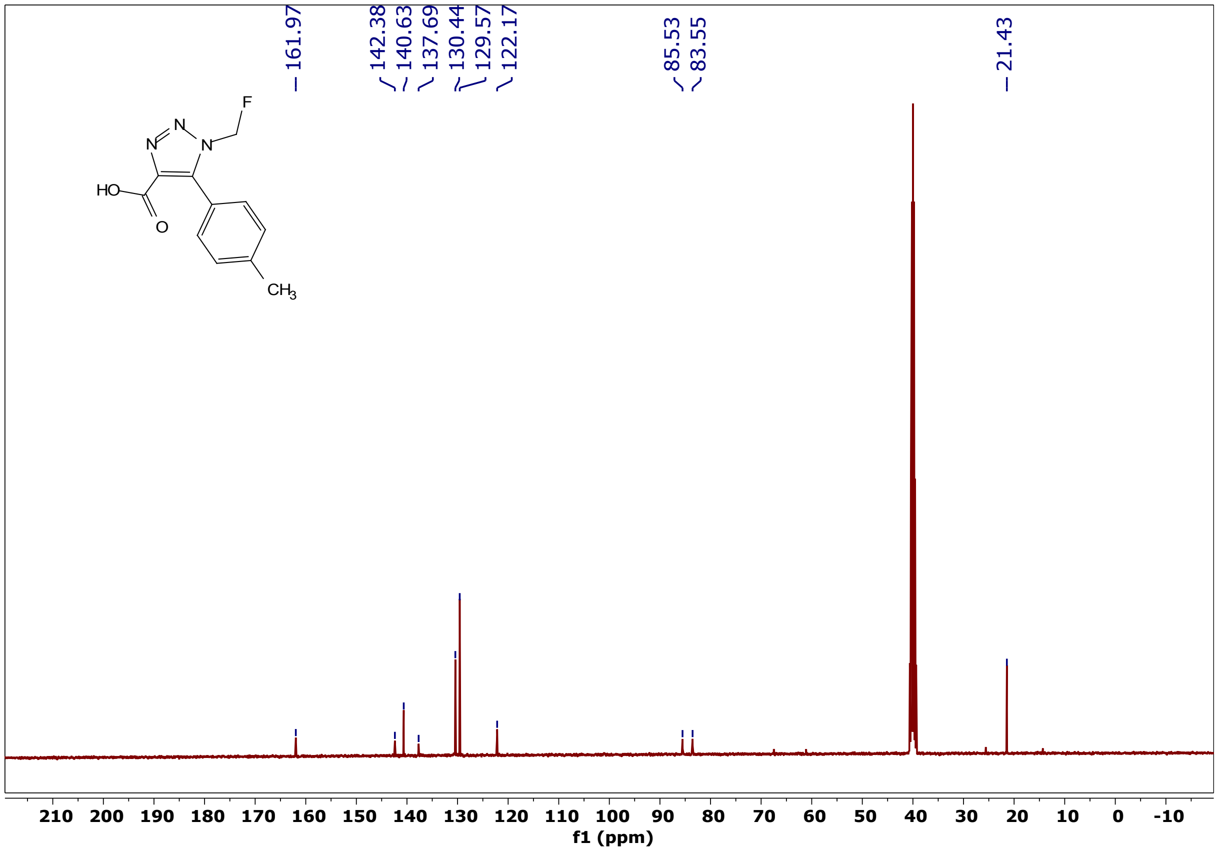

-165.79
-165.93
-166.06
HO
O
N
N
N
F
O
CH3
O
H3C
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


161.89
152.08
149.98
143.48
137.55
124.05
117.68
114.75
112.23
86.00
84.01
56.20
56.10
30.03
N
N
N
F
HO
O
O
CH3
O
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

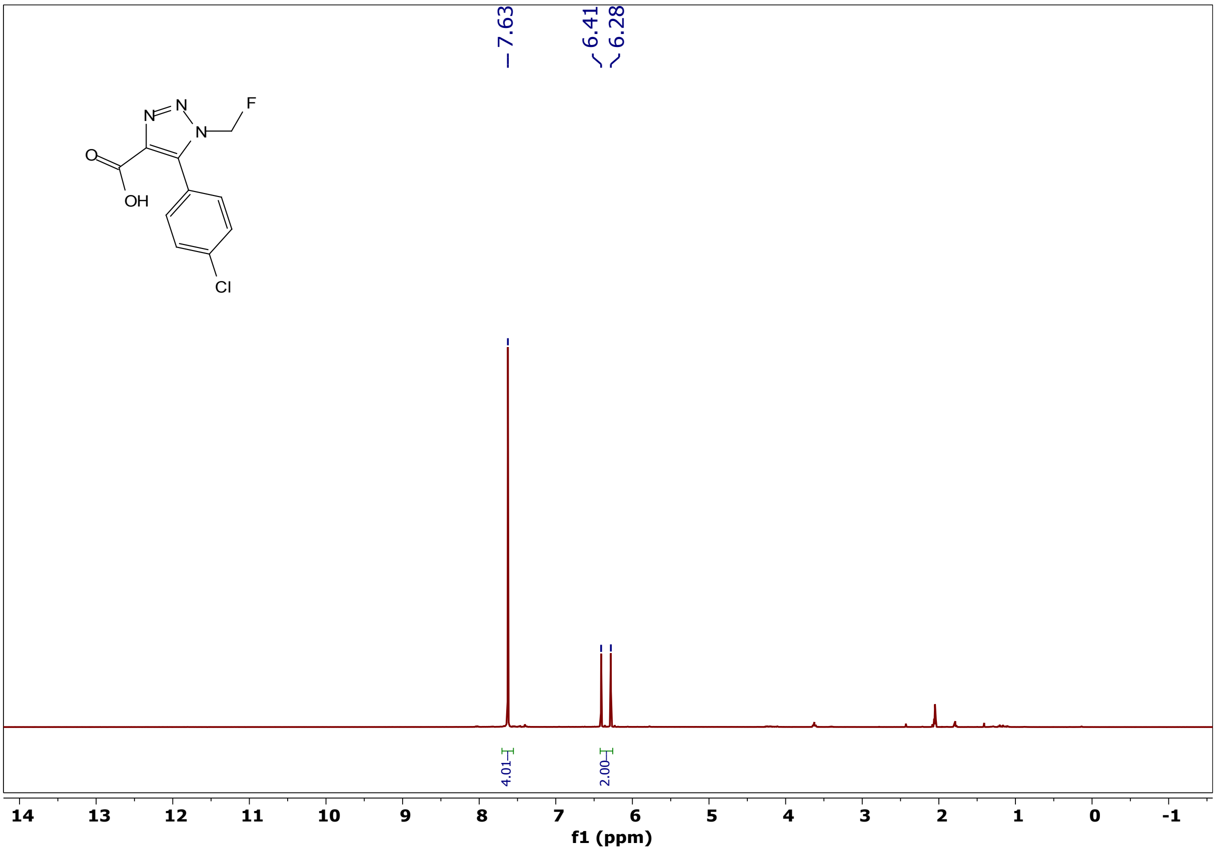
Compound **6e**

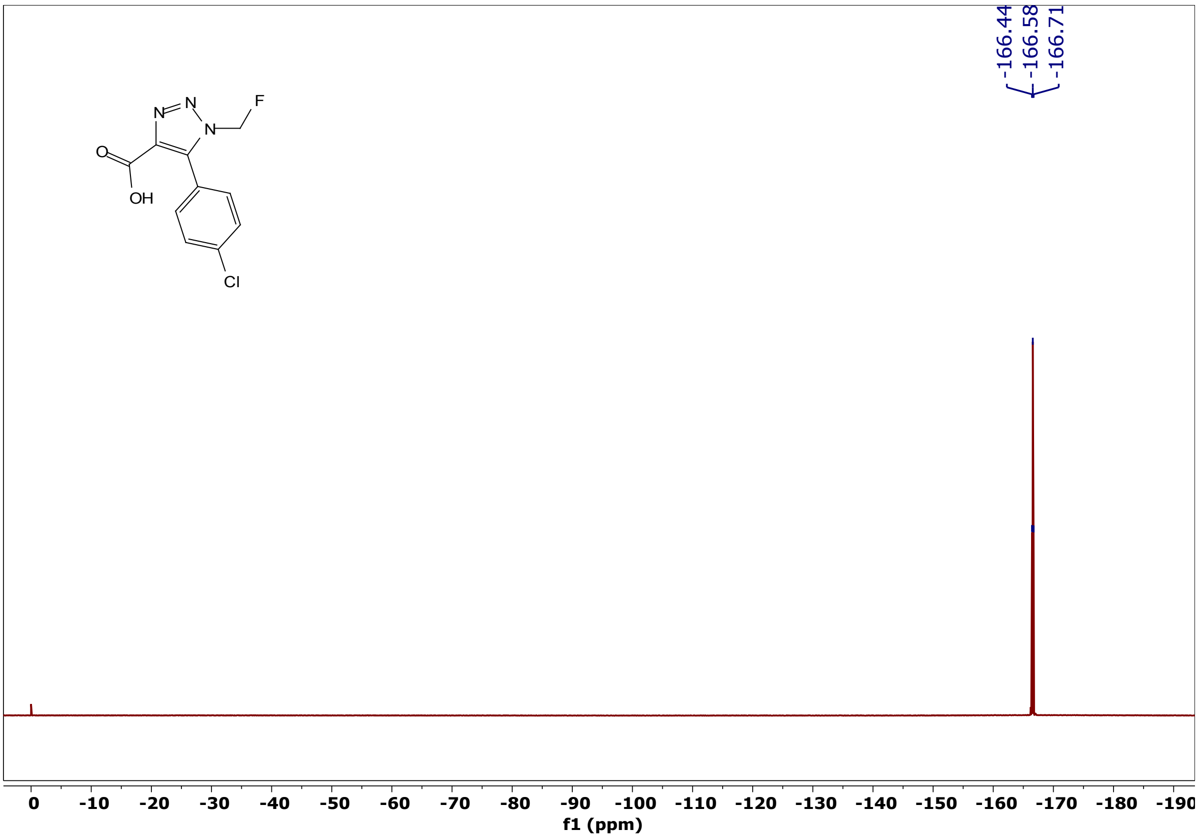

7.42
7.40
7.37
7.35
6.31
6.18
3.39
2.40
N
N
N
F
HO
O
CH3
4.07
1.98
1.17
3.26
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

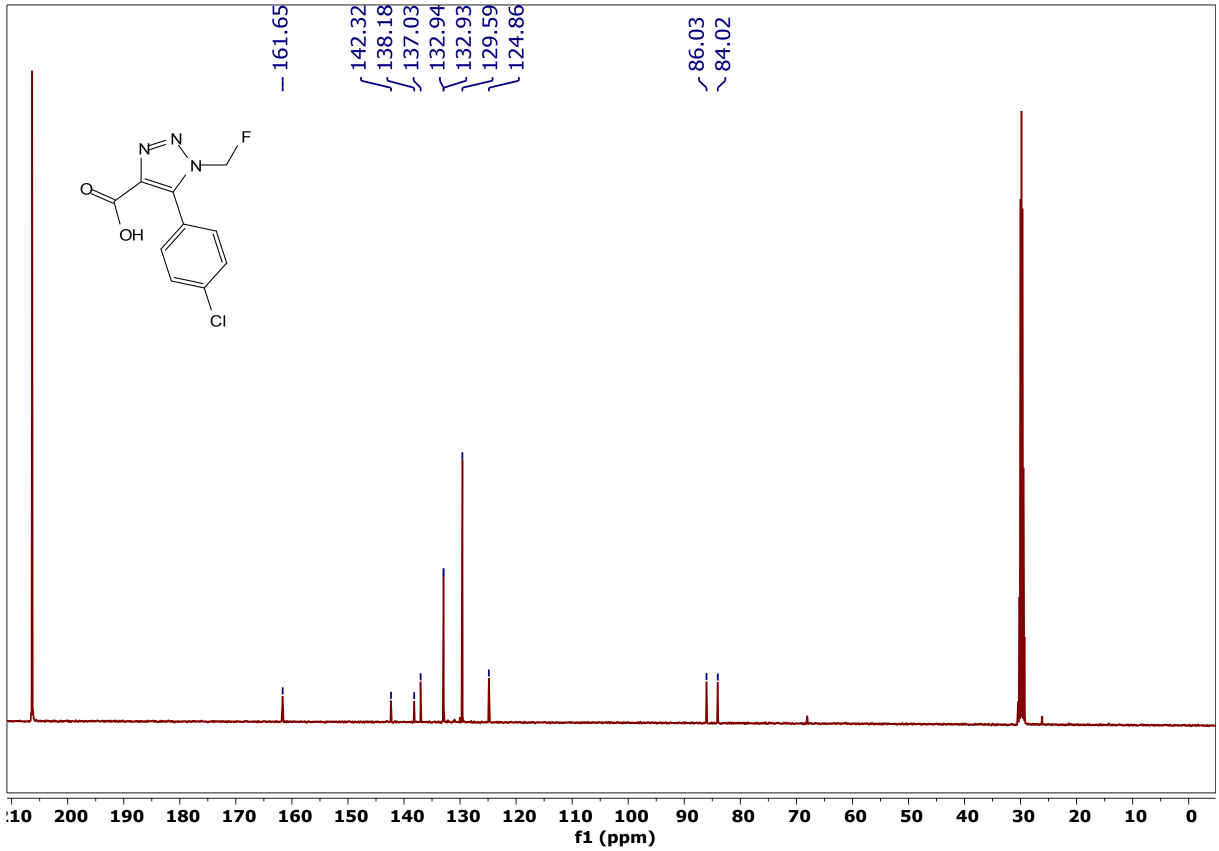

-166.03
-166.16
-166.30
N
N
N
F
HO
O
CH3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


161.97
142.38
140.63
137.69
130.44
129.57
122.17
85.53
83.55
21.43
F
N
N
N
HO
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

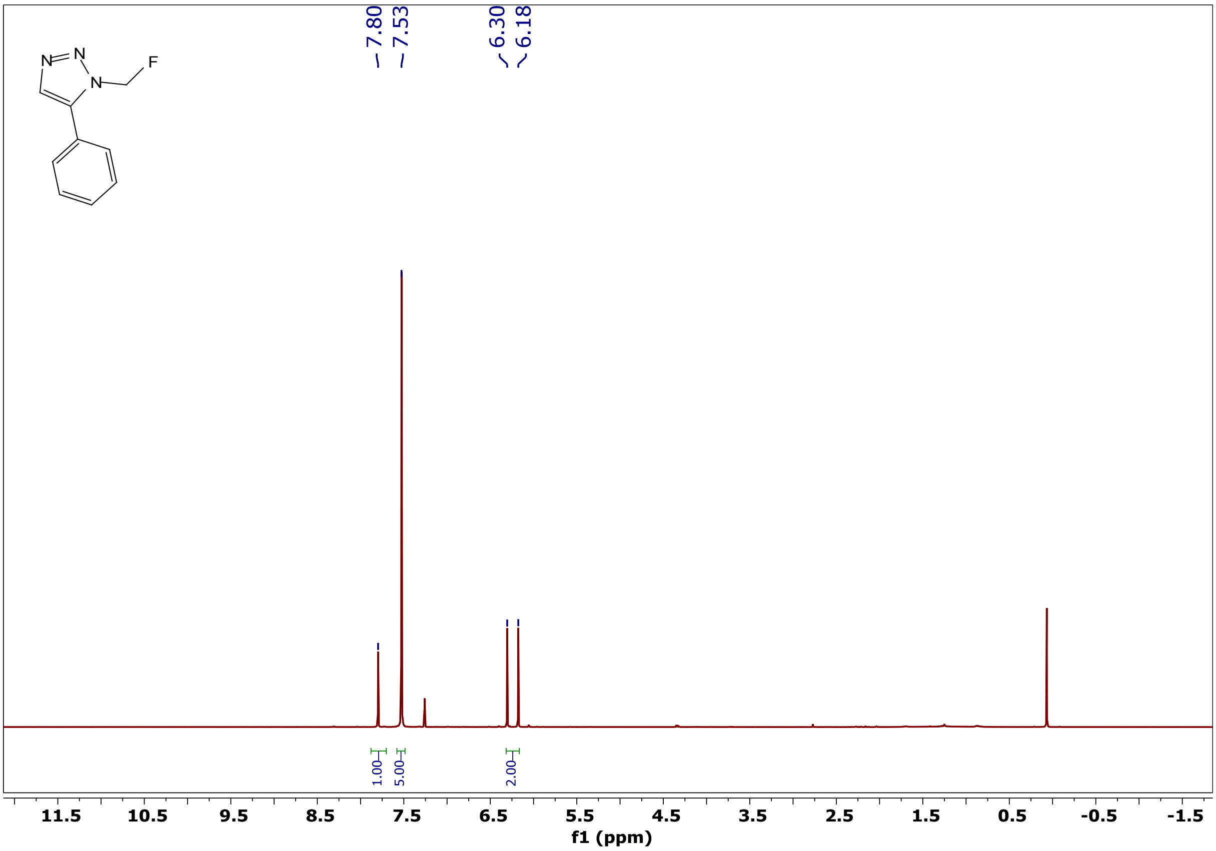
Compound **6f**


7.63
6.41
6.28
F
N
N
N
O
OH
Cl
4.01
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

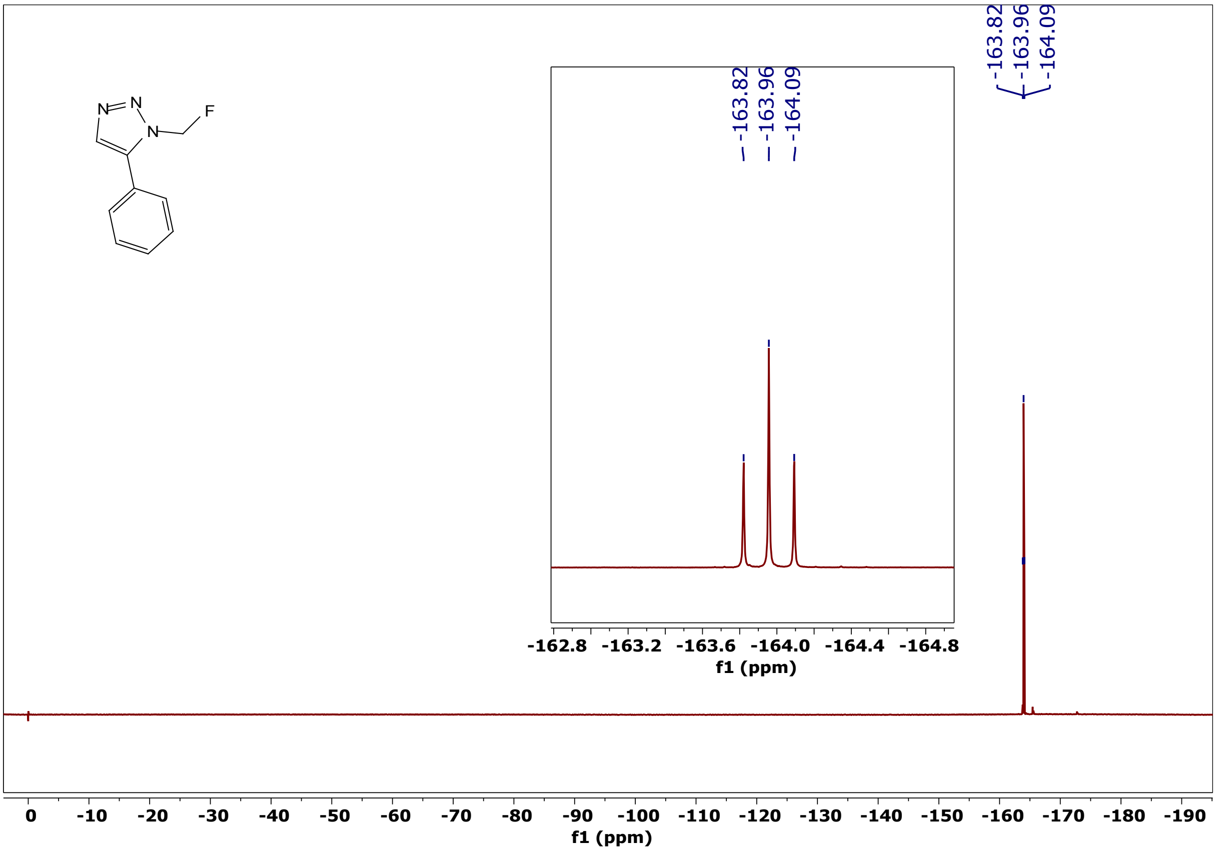

-166.44
-166.58
-166.71
F
N
N
N
O
OH
Cl
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


161.65
142.32
138.18
137.03
132.94
132.93
129.59
124.86
86.03
84.02
N
N
N
F
O
OH
Cl
:10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

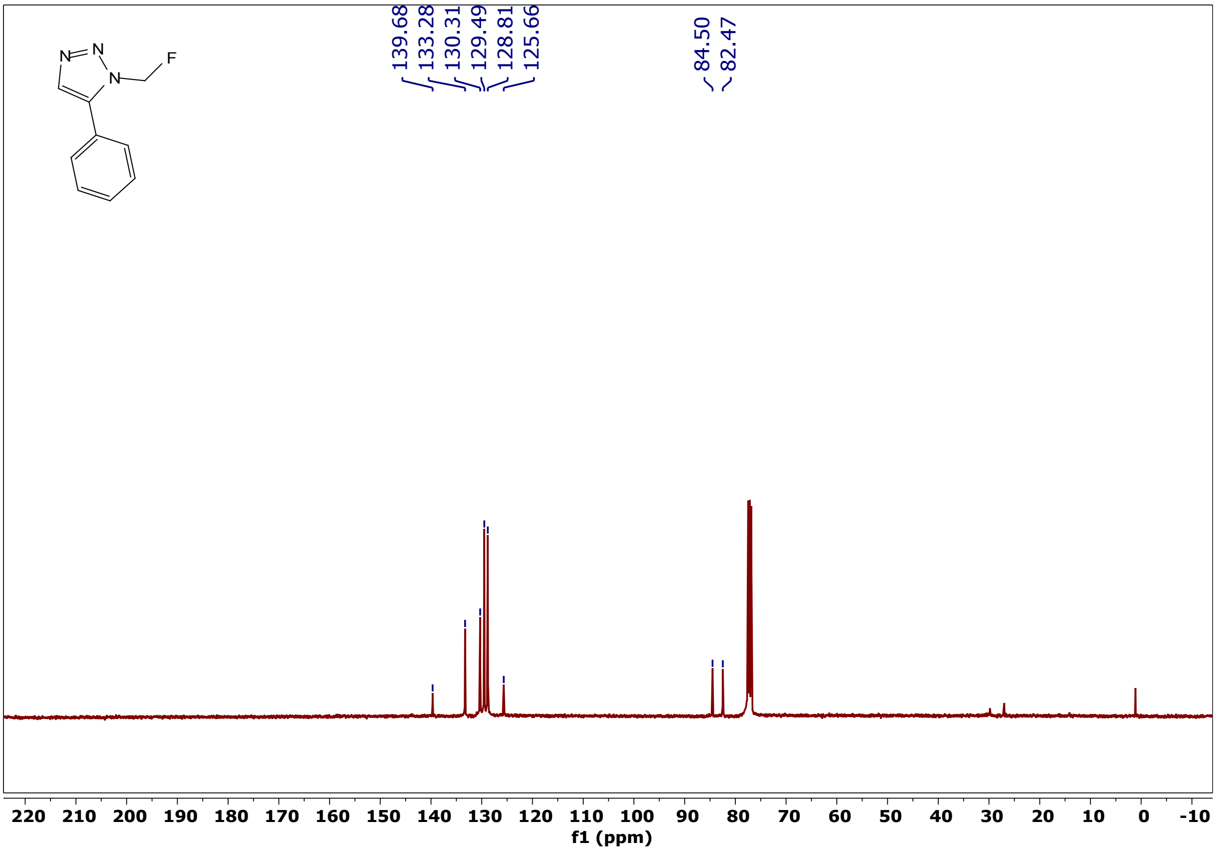
Compound **7a**



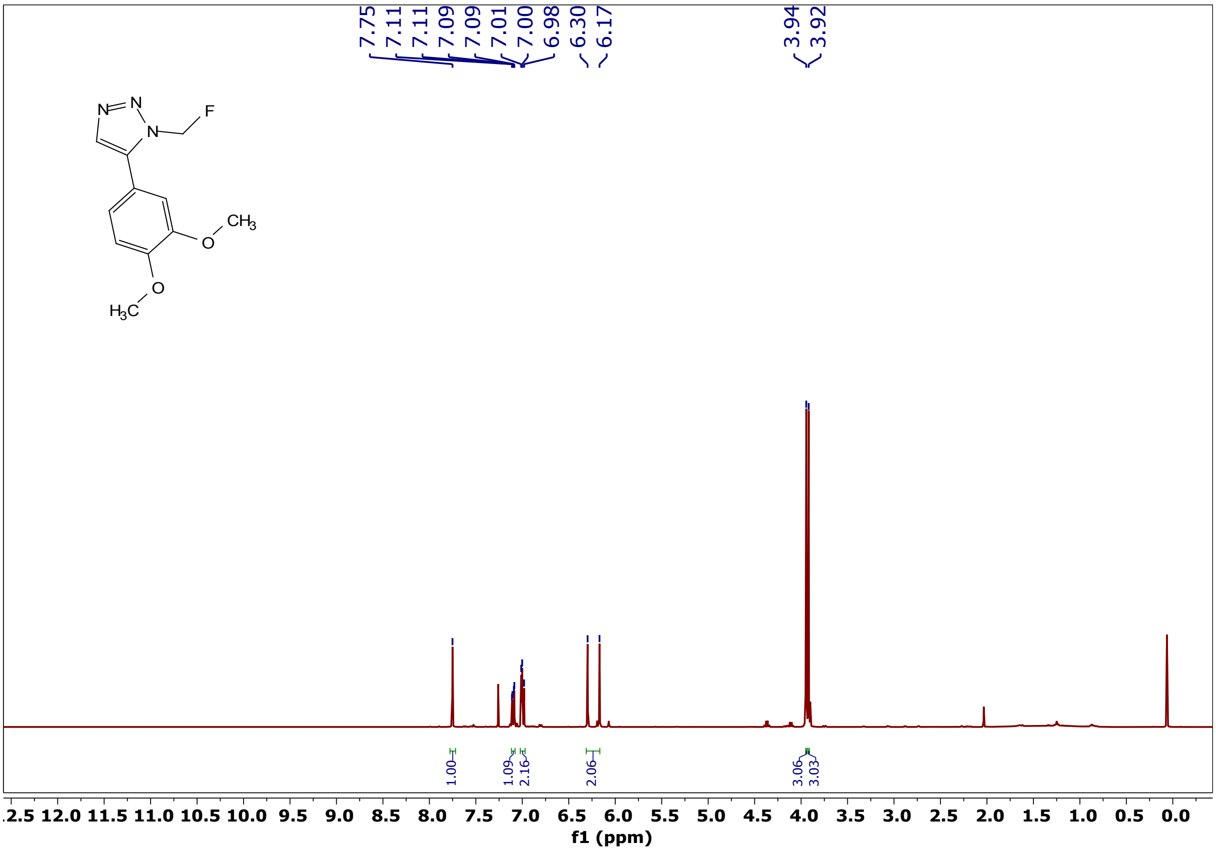
7.80
7.53
6.30
6.18
1.00
5.00
2.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)
N
N
N
F

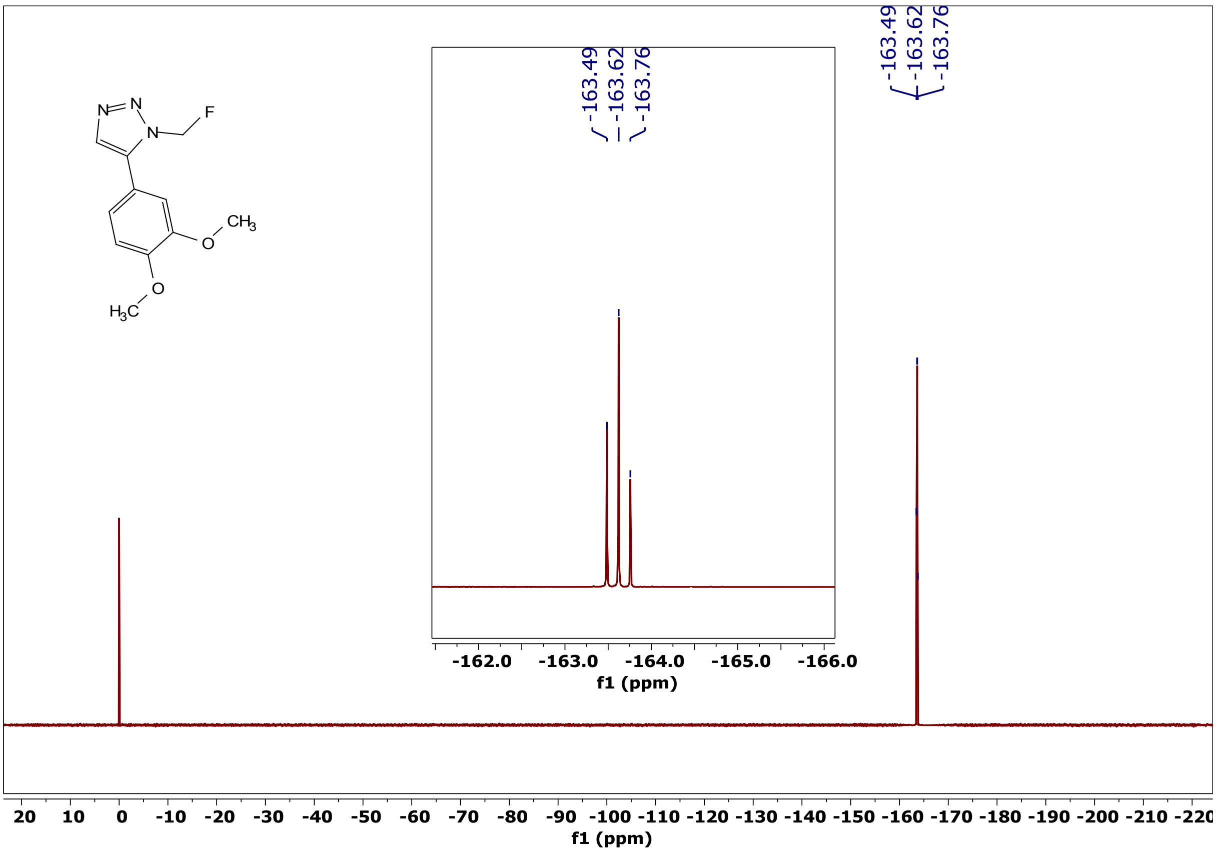


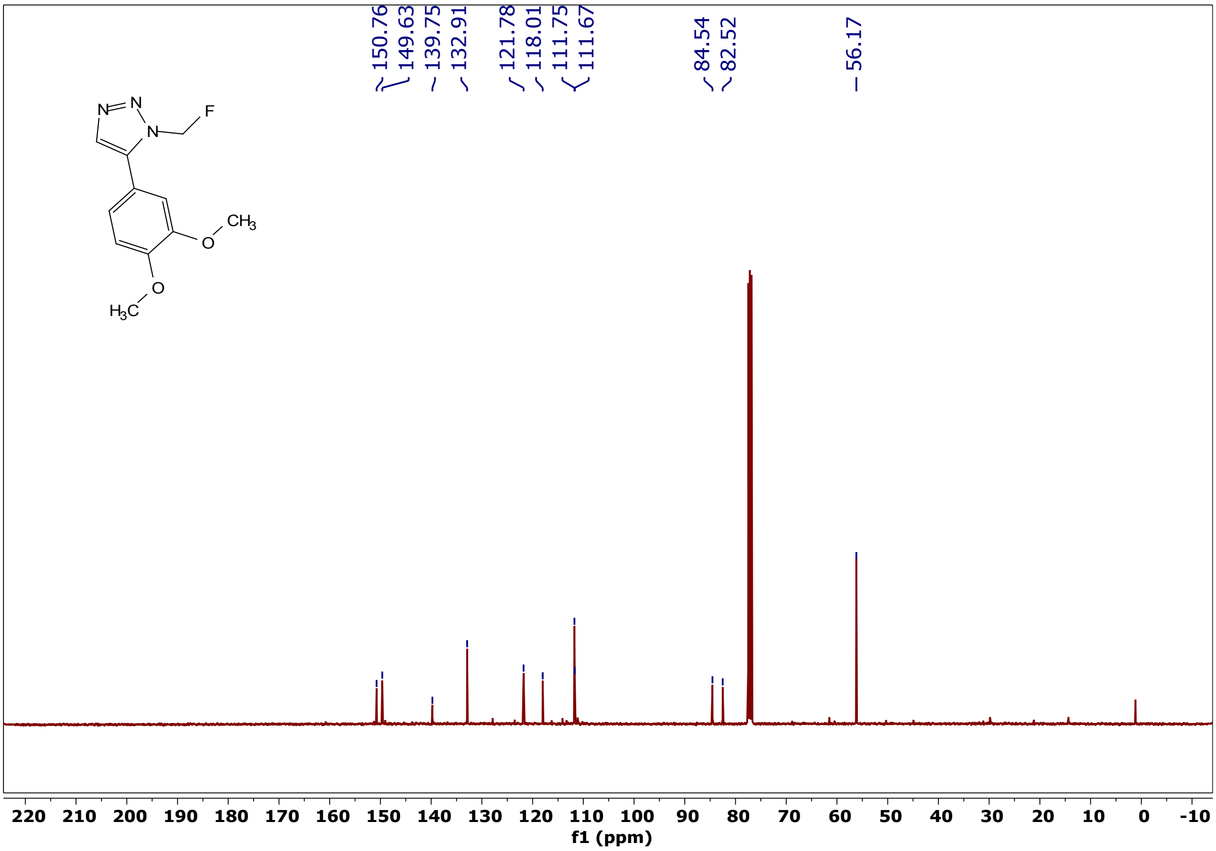
-163.82
-163.96
-164.09
-162.8
-163.2
-163.6
-164.0
-164.4
-164.8
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)
N
N
N
F


139.68
133.28
130.31
129.49
128.81
125.66
84.50
82.47
N
N
N
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

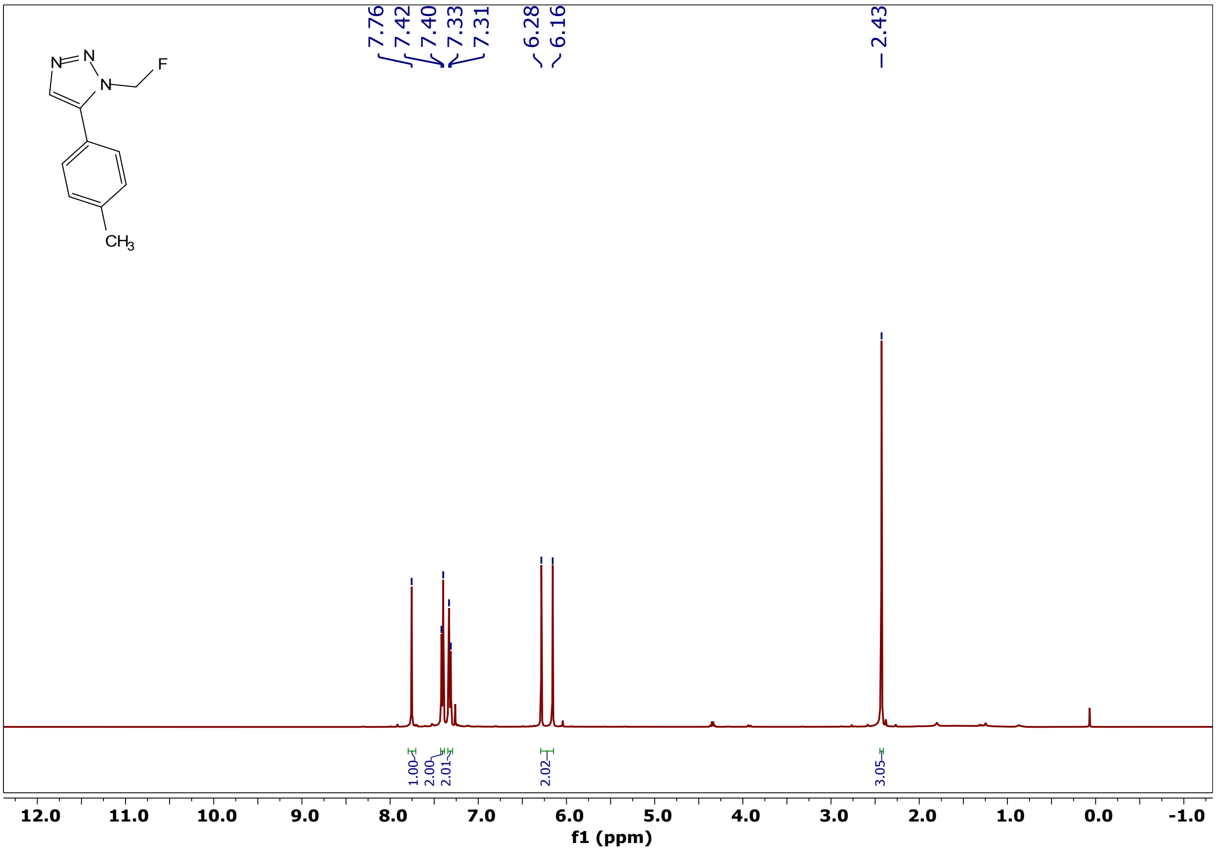
Compound **7d**

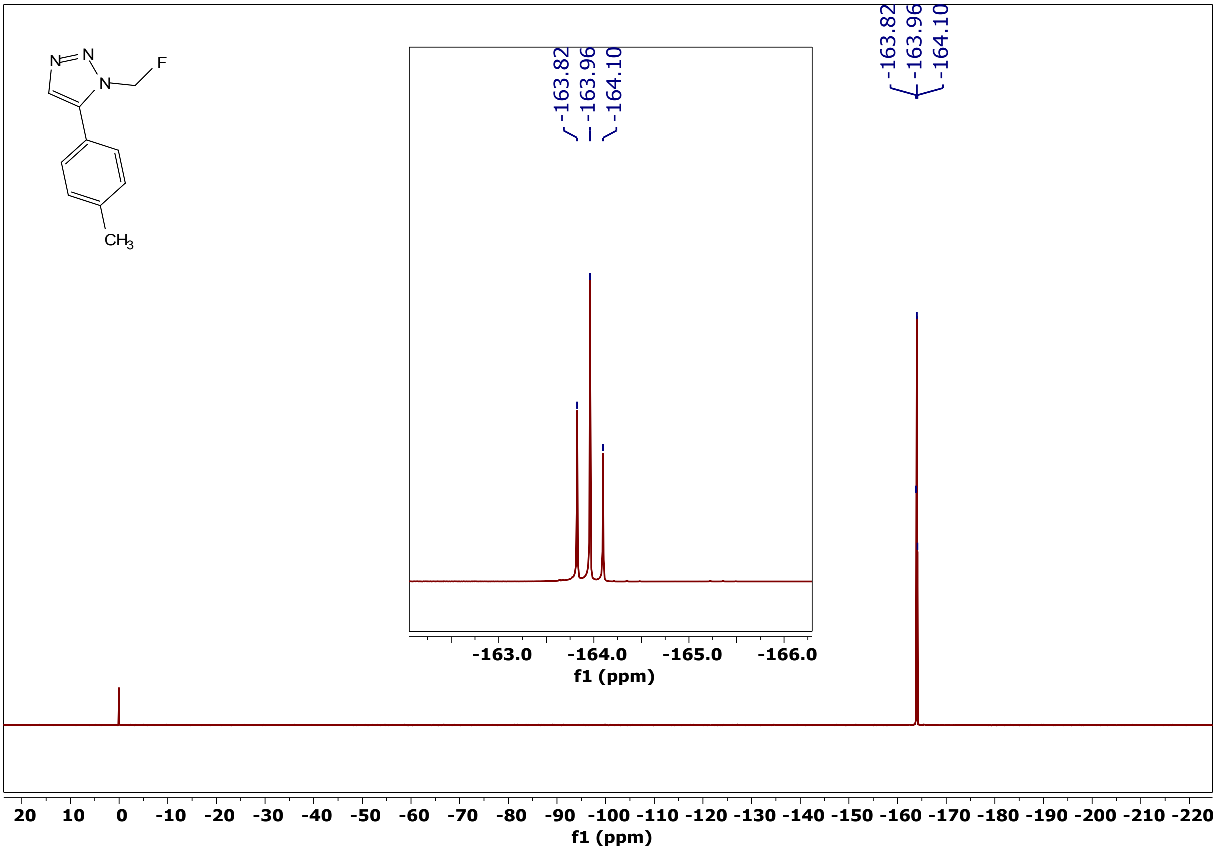

7.75
7.11
7.11
7.09
7.09
7.01
7.00
6.98
6.30
6.17
3.94
3.92
N
N
N
F
CH3
O
O
H3C
1.00
1.09
2.16
2.06
3.06
3.03
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

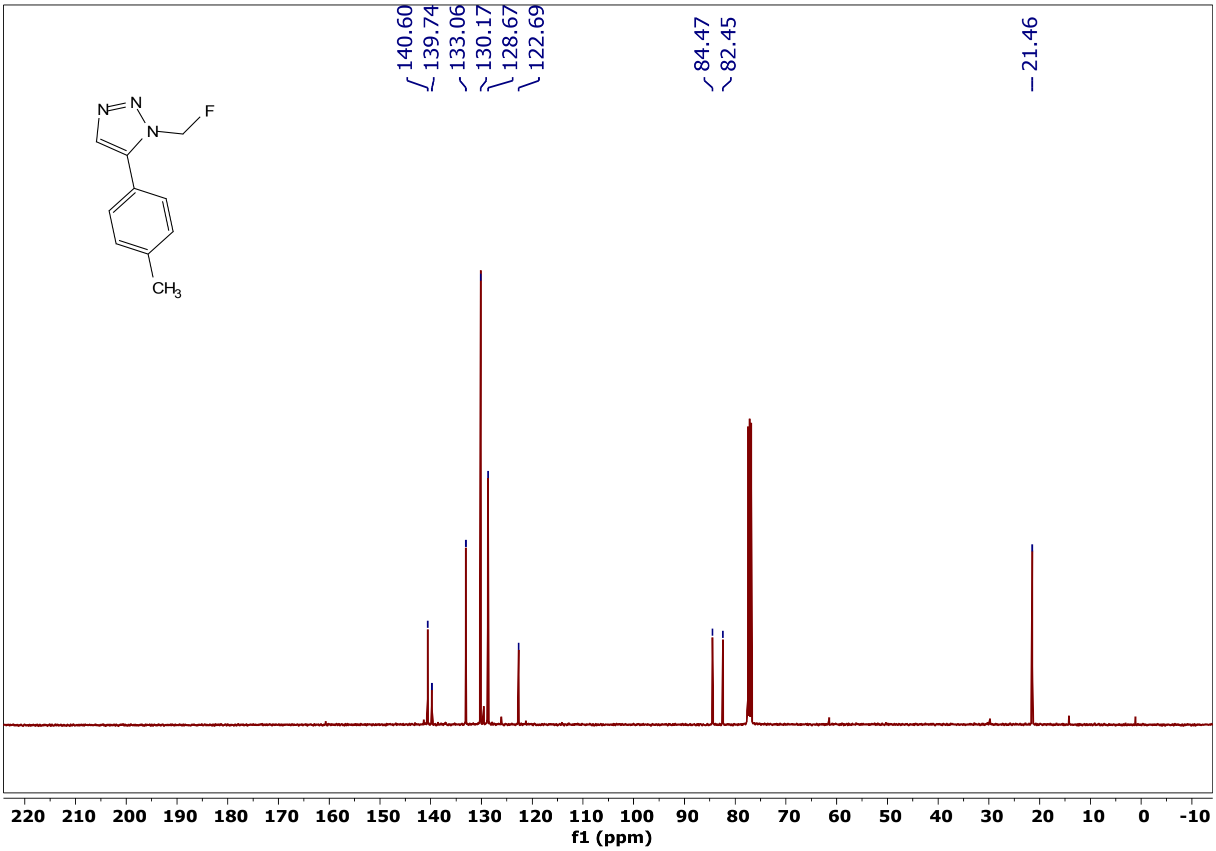

-163.49
-163.62
-163.76
-163.49
-163.62
-163.76
N
N
N
F
CH3
O
O
H3C
-162.0 -163.0 -164.0 -165.0 -166.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


150.76
149.63
139.75
132.91
121.78
118.01
111.75
111.67
84.54
82.52
56.17
N
N
N
F
O
CH3
O
H3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

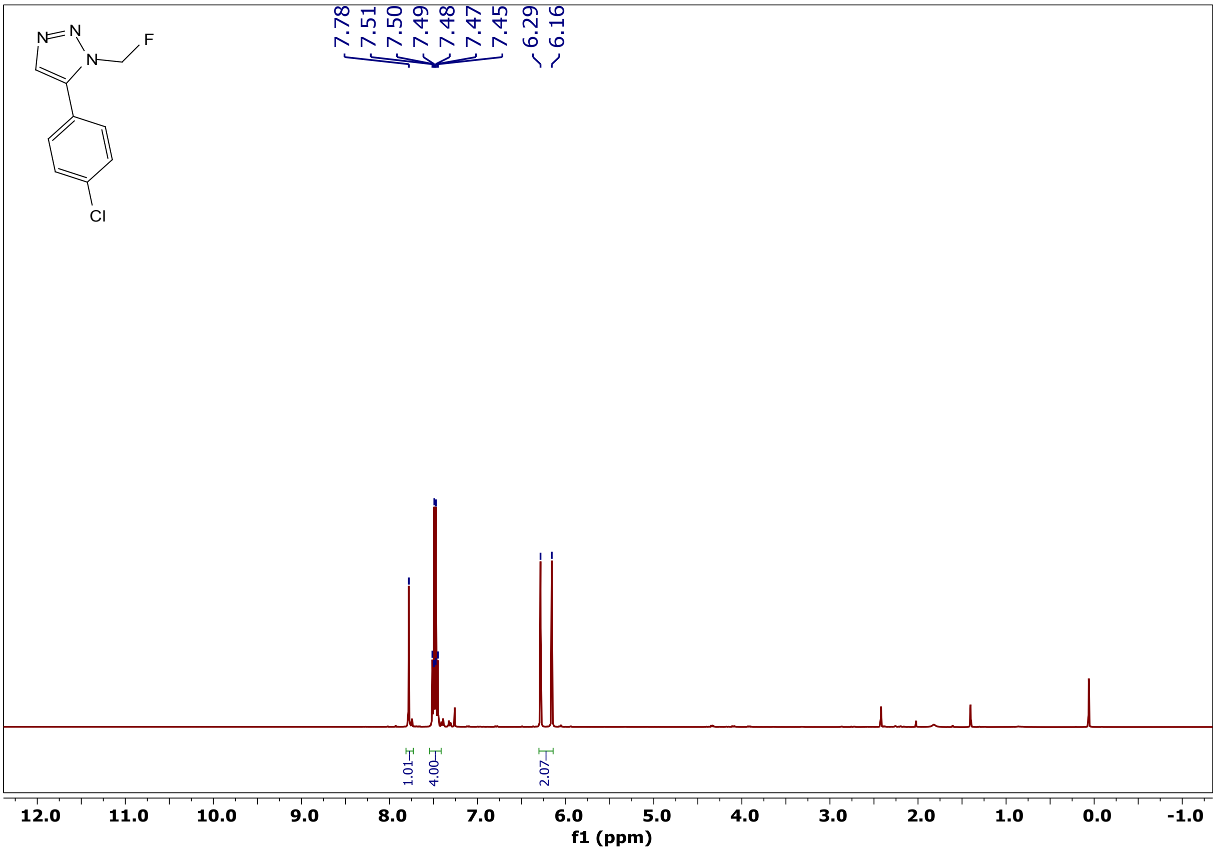
Compound **7e**

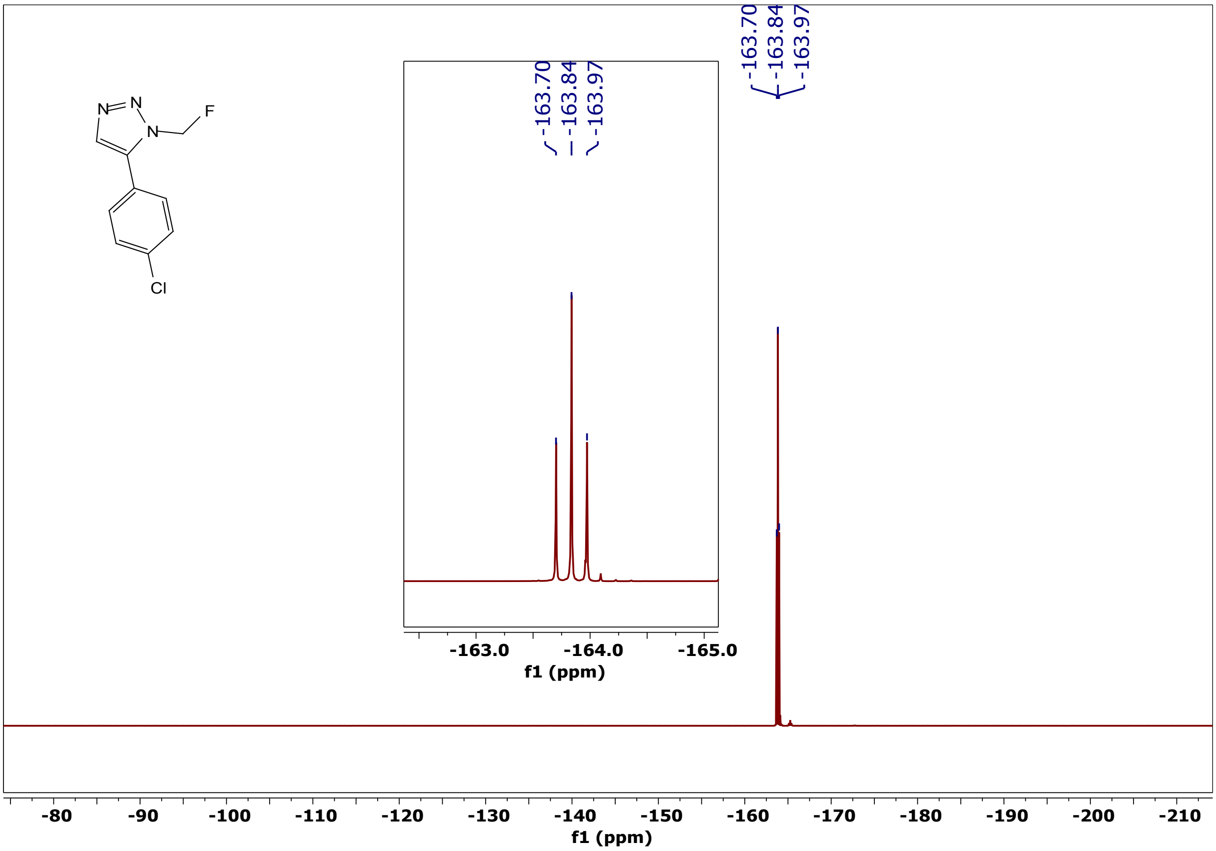

7.76
7.42
7.40
7.33
7.31
6.28
6.16
2.43
N
N
N
F
CH3
1.00
2.00
2.01
2.02
3.05
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

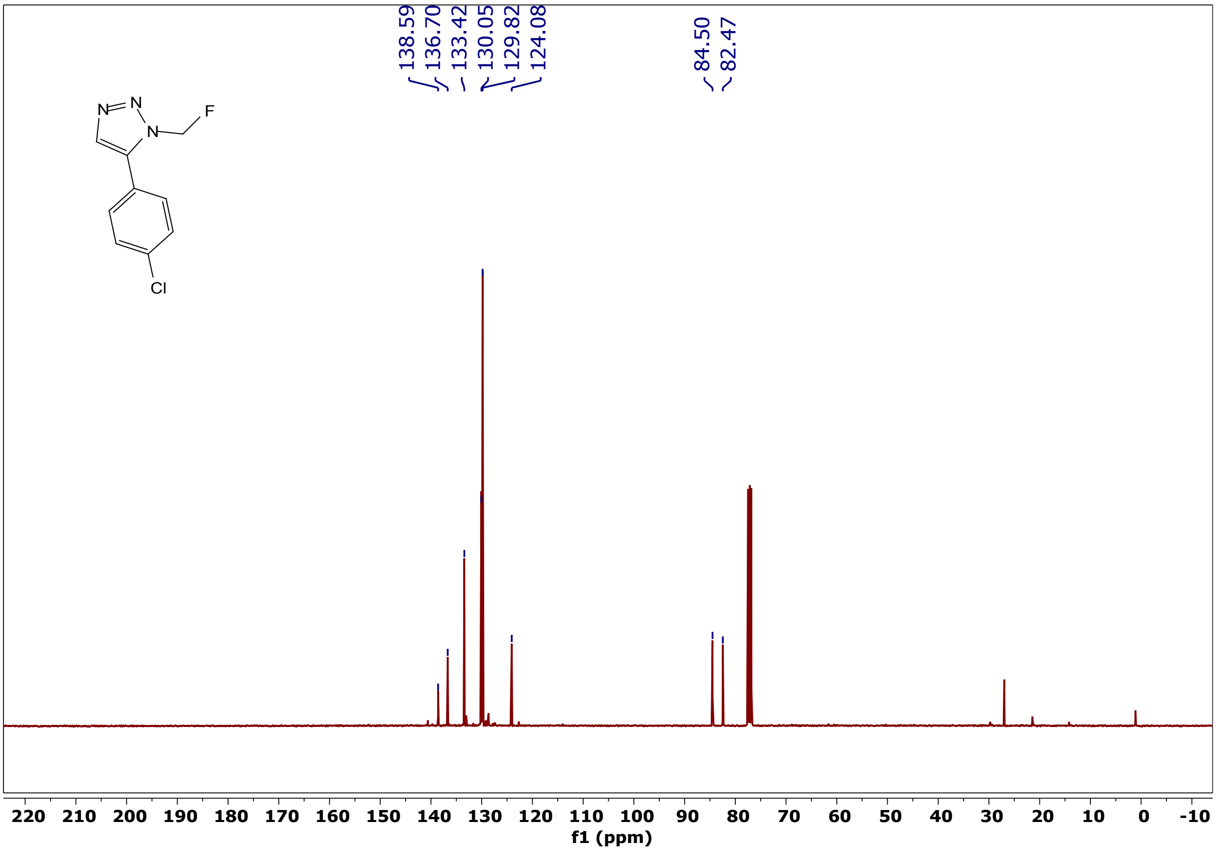

-163.82
-163.96
-164.10
N
N
N
F
CH3
-163.82
-163.96
-164.10
-163.0
-164.0
-165.0
-166.0
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


140.60
139.74
133.06
130.17
128.67
122.69
84.47
82.45
21.46
N
N
N
F
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound **7f**


N
N
N
F
Cl
7.78
7.51
7.50
7.49
7.48
7.47
7.45
6.29
6.16
1.01
4.00
2.07
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


N
N
N
F
Cl
-163.70
-163.84
-163.97
-163.70
-163.84
-163.97
-163.0
-164.0
-165.0
f1 (ppm)
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


138.59
136.70
133.42
130.05
129.82
124.08
84.50
82.47
N
N
N
F
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)