Supporting Information

Synthesis of tetrafluoroethylene- and tetrafluoroethyl-containing azides and their 1,3-dipolar cycloaddition as synthetic application

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General experimental procedures. All solvents were dried by activated molecular sieves (3 Å) and stored under argon. The NMR chemical shift values (δ) are reported in ppm relative to internal Me_4Si (0 ppm for ^1H and ^{13}C NMR) or residual solvents and internal $CFCl_3$ (0 ppm for ^{19}F NMR). ^{13}C NMR spectra were proton decoupled. *p*-Toluenesulfonyl azide (tosyl azide),[1] perfluorobutanesulfonyl azide (nonaflyl azide),[2] trimethyl-(1,1,2,2-tetrafluoro-2-phenylthio)ethyl)silane[3] and 2-substituted 1-bromo-1,1,2,2-tetrafluoroethanes[4] **1** were prepared according to literature reports. Other bromides **1** are commercially available from CF Plus Chemicals (www.cfplus.cz).

Synthesis of azides 2a–h. Bromide **1** (0.57 mmol) was dissolved in anhydrous THF (2 mL) and cooled to –78 °C. A solution of *i*-PrMgCl·LiCl in THF (1.3 M, 0.46 mL, 0.60 mmol), was added dropwise. After 45 min, a solution of *p*-toluenesulfonyl azide (225 mg, 1.14 mmol; General Procedure A) or perfluorobutanesulfonyl azide (370 mg, 1.14 mmol, General Procedure B) in THF (1 mL) was introduced dropwise at –78 °C, and the mixture was stirred for 3 h while warming up to rt. Saturated aqueous NH_4Cl (5 mL) was added, the product was extracted with Et_2O, dried ($MgSO_4$), and concentrated. The crude product was purified by flash column chromatography (hexane), affording a colorless liquid.

*1-(2-Azido-1,1,2,2-tetrafluoroethoxy)benzene (**2a**).*[4] General Procedure A; yield: 92 %; colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.19-7.15 (m, 1H), 7.12-7.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.99, 129.90, 126.92, 121.76, 115.99 (tt, $^1J_{C\text{-}F}$ = 274.2 Hz, $^2J_{C\text{-}F}$ = 32.3 Hz, CF_2), 113.85 (tt, $^1J_{C\text{-}F}$ = 313.1 Hz, $^2J_{C\text{-}F}$ = 45.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.00 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -94.24 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (EI^+) *m/z* calcd for $C_8H_5F_4N_3O$ $[M]^+$: 235.0369, found 235.0367.

*1-(2-Azido-1,1,2,2-tetrafluoroethoxy)-4-fluorobenzene (**2b**).* General Procedure A; yield: 79 %; colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.19 (m, 2H), 7.11-7.06 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.10 (d, $^1J_{C\text{-}F}$ = 246.4 Hz), 144.64, 123.59 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 116.63 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 115.91 (tt, $^1J_{C\text{-}F}$ = 275.7 Hz, $^2J_{C\text{-}F}$ = 32.3 Hz, CF_2), 113.68 (tt, $^1J_{C\text{-}F}$ = 313.1 Hz, $^2J_{C\text{-}F}$ = 44.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.08 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -86.30 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -115.12 (tt, $^3J_{H\text{-}F}$ = 11.3 Hz, $^4J_{H\text{-}F}$ = 3.8 Hz, 1F); HRMS (EI^+) *m/z* calcd for $C_8H_4F_5N_3O$ $[M]^+$: 253.0275, found 253.0274.

*1-(2-Azido-1,1,2,2-tetrafluoroethoxy)-4-bromobenzene (**2c**).* General Procedure A; yield: 76%; general method B; yield: 72%; colorless oil, R_f (petroleum ether) = 0.77; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.13-7.11 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.93, 132.92, 123.53, 120.37, 115.84 (tt, $^{1}J_{C\text{-}F}$ = 276.7 Hz, $^{2}J_{C\text{-}F}$ = 32.3 Hz, CF_2), 113.57 (tt, $^{1}J_{C\text{-}F}$ = 313.1 Hz, $^{2}J_{C\text{-}F}$ = 44.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.39 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F), -93.95 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (EI^+) *m/z* calcd for $C_8H_4BrF_4N_3O$ $[M]^+$: 312.9474, found 312.9476.

*1-(2-Azido-1,1,2,2-tetrafluoroethoxy)-4-methoxybenzene (**2d**).* General Procedure B; yield: 84%; colorless oil, R_f (petroleum ether/EtOAc, 95:5) = 0.64; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.12 (m, 2H), 6.90-6.88 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.27, 142.06, 123.06, 116.25 (tt, $^{1}J_{C\text{-}F}$ = 275.7 Hz, $^{2}J_{C\text{-}F}$ = 38.3 Hz, CF_2), 114.76, 114.49 (tt, $^{1}J_{C\text{-}F}$ = 272.7 Hz, $^{2}J_{C\text{-}F}$ = 41.4 Hz, CF_2), 55.67; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.33 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F), -94.16 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_9H_7N_3O_2F_4$ $[M + H]^+$: 265.0475, found 265.0474.

*3-(2-Azido-1,1,2,2-tetrafluoroethoxy)-*N,N-*dimethylaniline (**2e**).* General Procedure B; yield: 87%; colorless oil, R_f (petroleum ether/EtOAc, 90:10) = 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.19 (m, 1H), 6.63-6.62 (m, 1H), 6.61-6.60 (m, 1H), 6.49-6.48 (m, 1H), 2.96 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.83, 149.98, 129.96, 116.27 (tt, $^{1}J_{C\text{-}F}$ = 275.7 Hz, $^{2}J_{C\text{-}F}$ = 38.3 Hz, CF_2), 114.48 (tt, $^{1}J_{C\text{-}F}$ = 231.7 Hz, $^{2}J_{C\text{-}F}$ = 41.4 Hz, CF_2), 110.62, 108.92, 105.44, 40.50; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.91 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F), -94.35 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{10}H_{10}N_3OF_4$ $[M + H]^+$: 278.0791, found 278.0792.

*1-(2-Azido-1,1,2,2-tetrafluoroethoxy)-3-(trifluoromethyl)benzene (**2f**).* General Procedure B; yield: 73%; colorless oil, R_f (petroleum ether/EtOAc, 97:3) = 0.55; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.52 (m, 2H), 7.48 (s, 1H), 7.43-7.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.99, 132.49 (q, $^{1}J_{C\text{-}F}$ = 124.1 Hz, CF_3), 130.66, 125.12, 124.76, 123.83, 119.04, 116.27 (tt, $^{1}J_{C\text{-}F}$ = 281.8 Hz, $^{2}J_{C\text{-}F}$ = 37.4 Hz, CF_2), 114.41 (tt, $^{1}J_{C\text{-}F}$ = 274.7 Hz, $^{2}J_{C\text{-}F}$ = 41.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.36, -87.39, -93.87; HRMS (ESI) *m/z* calcd for $C_9H_4N_3OF_7$ $[M + H]^+$: 303.0244, found 303.0243.

*1-(2-Azido-1,1,2,2-tetrafluoroethoxy)-2,4-di-*tert-*butylbenzene (**2g**).* General Procedure B; yield: 71%; colorless oil, R_f (petroleum ether/EtOAc, 98:2) = 0.77; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.41 (m, 1H), 7.28-7.25 (m, 1H), 7.22-7.19 (m, 1H), 1.39 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.09, 146.52, 139.66, 125.03, 124.02, 118.68, 116.55 (tt, $^{1}J_{C\text{-}F}$ = 276.7 Hz, $^{2}J_{C\text{-}F}$ = 39.4 Hz, CF_2), 114.77 (tt, $^{1}J_{C\text{-}F}$ = 271.7 Hz, $^{2}J_{C\text{-}F}$ = 42.4 Hz, CF_2), 35.14, 34.75, 31.56, 30.23; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.82 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F), -92.91 (t, $^{3}J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{16}H_{21}N_3OF_4$ $[M + H]^+$: 347.1616, found 347.1621.

*1-(2-Azido-1,1,2,2-tetrafluoroethyl)-4-bromo-1H-pyrazole (**2h**).* General Procedure B; yield: 44%; colorless oil, R_f (petroleum ether/EtOAc, 94:6) = 0.58; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.74 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.43, 129.08, 117.89 (tt, $^1J_{C-F}$ = 279.8 Hz, $^2J_{C-F}$ = 42.4 Hz, CF_2), 115.12 (tt, $^1J_{C-F}$ = 287.8 Hz, $^2J_{C-F}$ = 43.4 Hz, CF_2), 97.48; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.12 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -99.52 (t, $^3J_{F-F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_5H_2N_5BrF_4$ $[M + H]^+$: 286.9429, found 286.9430.

Synthesis of (2-azido-1,1,2,2-tetrafluoroethyl)(phenyl)sulfane (2i). CsF (0.98 g, 6.4 mmol) was dried for 72 h at 135 °C under high vacuum in a screw-capped vial with silicon septum. The vial was cooled to rt, backfilled with argon, dry DMF (4 mL) was added and the mixture was cooled to –60 °C while being stirred. Cold solutions of $PhSCF_2CF_2SiMe_3$ (1.412 g, 5 mmol) in dry DMF (1 mL) and nonaflyl azide (1.625 g, 5 mmol, Method A) or tosyl azide (0.985 g, 5 mmol, Method B) in dry DMF (1 mL) were added dropwise over 20 min. The reaction mixture was stirred at –60 °C for 1 h and 3 h to warm up to rt. Saturated aqueous NH_4Cl (5 mL) was added, the product was extracted with Et_2O, the combined organic phase was washed with brine, dried ($MgSO_4$), and concentrated. The crude product was purified by flash column chromatography (hexane), affording a colorless liquid. Method A, yield: 89%; Method B, yield: 72%; colorless oil, R_f (petroleum ether/EtOAc, 98:2) = 0.64; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 2H), 7.52-7.48 (m, 1H), 7.44-7.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.32, 130.99, 129.49, 123.47, 122.65 (tt, $^1J_{C-F}$ = 290.9 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 116.57 (tt, $^1J_{C-F}$ = 275.7 Hz, $^2J_{C-F}$ = 34.3 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.70 (t, $^3J_{F-F}$ = 7.5 Hz, 2F), -89.83 (t, $^3J_{F-F}$ = 7.6 Hz, 2F); HRMS (EI) *m/z* calcd for $C_8H_5N_3SF_4$ $[M]^+$: 251.0140, found 251.0141.

Synthesis of 1-(1,1,2,2-tetrafluoroalkyl)triazoles (4). Copper(I) 3-methylsalicylate (2.1 mg, 0.01 mmol) was added to a solution of **2** (1.0 mmol) in THF (2 mL) in a 10 mL screw-cap glass tube. Subsequently alkyne **3** (1.0 mmol) in THF (0.5 mL) was added, the flask was closed and stirred at rt for 18 h (UPLC-MS control). THF was removed under reduced pressure, Et_2O (20 mL) was added and the organic phase was washed with aqueous $NaHCO_3$ solution, water and brine, dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by crystallization from hexane or by column chromatography on silica gel (hexane/EtOAc, 99:1).

*1-(1,1,2,2-Tetrafluoro-2-phenoxyethyl)-4-*p*-tolyl-1*H*-1,2,3-triazole (**4aj**).* Yield: 85%; white solid, mp 65–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.71-7.69 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.18 (m, 3H), 7.08-7.06 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

148.53, 148.50, 139.28, 129.93, 129.84, 127.16, 126.22, 126.14, 121.76, 118.00, 115.90 (tt, $^1J_{C-F}$ = 276.7 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 111.59 (tt, $^1J_{C-F}$ = 271.6 Hz, $^2J_{C-F}$ = 45.4 Hz, CF_2), 21.46; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.24 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -99.35 (t, $^3J_{F-F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{17}H_{14}N_3OF_4$ [M + H]$^+$: 352.10675, found 352.10681.

*4-(4-Nitrophenyl)-1-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1*H-*1,2,3-triazole (**4ak**)*. Yield: 78%; white solid, mp 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.35-8.33 (m, 2H), 8.11-8.09 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.28 (m, 1H), 7.17-7.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.42, 148.14, 146.26, 135.18, 130.02, 127.33, 126.90, 124.57, 121.70, 120.07, 115.79 (tt, $^1J_{C-F}$ = 276.7 Hz, $^2J_{C-F}$ = 37.3 Hz, CF_2), 111.58 (tt, $^1J_{C-F}$ = 273.7 Hz, $^2J_{C-F}$ = 41.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.65 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -98.80 (t, $^3J_{F-F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{16}H_{11}N_4O_3F_4$ [M + H]$^+$: 383.07618, found 383.07629.

*3-(1-(1,1,2,2-Tetrafluoro-2-phenoxyethyl)-1*H-*1,2,3-triazol-4-yl)pyridine (**4al**)*. Yield: 78%; white solid, mp 70–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (br s, 1H), 8.65 (br s, 1H), 8.33 (s, 1H), 8.29-8.27 (m, 1H), 7.43 (br s, 1H), 7.38-7.35 (m, 2H), 7.30-7.26 (m, 1H), 7.16-7.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.09, 148.41, 147.25, 145.37, 133.71, 129.95, 129.72, 127.23, 124.08, 121.67, 119.02, 115.78 (tt, $^1J_{C-F}$ = 277.8 Hz, $^2J_{C-F}$ = 36.4 Hz, CF_2), 111.55 (tt, $^1J_{C-F}$ = 272.7 Hz, $^2J_{C-F}$ = 42.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.16 (br t, 2F), -99.28 (br t, $^3J_{F-F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{15}H_{11}N_4OF_4$ [M + H]$^+$: 339.08635, found 339.08642.

*1-(1,1,2,2-Tetrafluoro-2-(4-fluorophenoxy)ethyl)-4-(*p-*tolyl)-1*H-*1,2,3-triazole (**4bj**)*. Yield: 72%; white solid, mp 83–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.82-7.80 (m, 2H), 7.31-7.29 (m, 2H), 7.10 (br s, 2H), 7.08-7.06 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.15 (d, $^1J_{C-F}$ = 246.4 Hz), 148.53, 144.19, 139.34, 129.86, 128.80, 126.14, 123.64 (d, $^3J_{C-F}$ = 9.1 Hz), 117.92, 116.68 (d, $^2J_{C-F}$ = 24.2 Hz), 115.84 (tt, $^1J_{C-F}$ = 277.8 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 111.52 (tt, $^1J_{C-F}$ = 271.7 Hz, $^2J_{C-F}$ = 43.4 Hz, CF_2), 21.47; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.51 (br t, 2F), -99.14 (br t, $^3J_{F-F}$ = 3.8 Hz, 2F), -115.16 to -115.21 (br m, 1F); HRMS (ESI) *m/z* calcd for $C_{17}H_{13}N_3OF_5$ [M + H]$^+$: 370.09733, found 370.09740.

*4-(4-Nitrophenyl)-1-(1,1,2,2-tetrafluoro-2-(4-fluorophenoxy)ethyl)-1*H-*1,2,3-triazole (**4bk**)*. Yield: 69%; white solid, mp 116–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.34-8.42 (m, 2H), 8.11-8.08 (m, 2H), 7.16-7.13 (m, 2H), 7.08-7.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.21 (d, $^1J_{C-F}$ = 246.4 Hz), 148.15, 146.28, 144.03, 135.09, 126.90, 124.57, 123.58 (d, $^3J_{C-F}$ = 9.1 Hz), 120.03, 116.77 (d, $^2J_{C-F}$ = 24.2 Hz), 115.72 (tt, $^1J_{C-F}$ = 277.7 Hz, $^2J_{C-F}$ = 38.4

Hz, CF_2), 111.50 (tt, $^1J_{C-F}$ = 272.7 Hz, $^2J_{C-F}$ = 41.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.93 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -98.60 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -114.31 to -114.37 (br m, 1F); HRMS (ESI) *m/z* calcd for $C_{16}H_{10}N_4O_3F_5$ $[M + H]^+$: 401.06676, found 401.06668.

*3-(1-(1,1,2,2-Tetrafluoro-2-(4-fluorophenoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)pyridine* ***(4bl)***. Yield: 41%; white solid, mp 61–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (br s, 1H), 8.87 (br s, 1H), 8.32 (s, 1H), 8.28 (br s, 1H), 7.49 (br s, 1H), 7.14-7.10 (m, 2H), 7.05-7.01 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.12 (d, $^1J_{C-F}$ = 246.7 Hz), 149.97, 147.25, 145.67, 144.05, 144.02, 133.28, 125.29, 123.50 (d, $^3J_{C-F}$ = 8.7 Hz), 118.97, 116.67 (d, $^2J_{C-F}$ = 23.8 Hz), 115.71 (tt, $^1J_{C-F}$ = 276.7 Hz, $^2J_{C-F}$ = 36.4 Hz, CF_2), 111.47 (tt, $^1J_{C-F}$ = 272.7 Hz, $^2J_{C-F}$ = 41.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.63 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -99.05 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -114.91 to -114.97 (br m, 1F); HRMS (ESI) *m/z* calcd for $C_{15}H_{10}N_4OF_5$ $[M + H]^+$: 357.07693, found 357.07695.

*1-(2-(4-Bromophenoxy)-1,1,2,2-tetrafluoroethyl)-4-phenyl-1*H*-1,2,3-triazole* ***(4cm)***. Yield: 92%; white solid, mp 83–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.91-7.89 (m, 2H), 7.51-7.46 (m, 4H), 7.43-7.39 (m, 1H), 7.07-7.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.47, 133.08, 129.34, 129.20, 128.96, 126.25, 123.59, 120.65, 118.29, 115.79 (tt, $^1J_{C-F}$ = 277.8 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 111.49 (tt, $^1J_{C-F}$ = 272.7 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.37 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -99.12 (t, $^3J_{F-F}$ = 3.8 Hz, 2F); HRMS (EI) *m/z* calcd for $C_{16}H_{11}N_3OBrF_4$ $[M]^+$: 416.00161, found 416.00164.

*1-(2-(4-Bromophenoxy)-1,1,2,2-tetrafluoroethyl)-4-*p*-tolyl-1*H*-1,2,3-triazole* ***(4cj)***. Yield: 81%; white solid, mp 87–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.79-7.77 (m, 2H), 7.51-7.48 (m, 2H), 7.29-7.27 (m, 2H), 7.07-7.05 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.55, 147.51, 139.36, 133.06, 129.87, 129.15, 126.15, 123.60, 120.62, 117.88, 115.80 (tt, $^1J_{C-F}$ = 277.8 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 111.48 (tt, $^1J_{C-F}$ = 271.7 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 21.50; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.36 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -99.11 (t, $^3J_{F-F}$ = 3.8 Hz, 2F); HRMS (EI) *m/z* calcd for $C_{17}H_{13}N_3OBrF_4$ $[M]^+$: 430.01726, found 430.01731.

*1-(2-(4-Bromophenoxy)-1,1,2,2-tetrafluoroethyl)-4-(4-nitrophenyl)-1*H*-1,2,3-triazole* ***(4ck)***. Yield: 48%; white solid, mp 137–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.35-8.33 (m, 2H), 8.11-8.08 (m, 2H), 7.52-7.50 (m, 2H), 7.07-7.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.19, 147.39, 146.30, 135.07, 133.15, 126.91, 124.60, 123.52, 120.80, 119.95, 115.69 (tt, $^1J_{C-F}$ = 277.8 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 111.47 (tt, $^1J_{C-F}$ = 272.7 Hz, $^2J_{C-F}$ = 44.4 Hz,

CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.25 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -99.03 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (EI) *m/z* calcd for $C_{16}H_{10}N_4O_3BrF_4$ $[M]^+$: 460.98669, found 460.98672.

*3-(1-(2-(4-Bromophenoxy)-1,1,2,2-tetrafluoroethyl)-1*H*-1,2,3-triazol-4-yl)pyridine* ***(4cl)***. Yield: 95%; white solid, mp 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (br s, 1H), 8.76 (br s, 1H), 8.29 (s, 1H), 8.28-8.26 (m, 1H), 7.51-7.47 (m, 2H), 7.47 (br s, 1H), 7.06-7.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.26, 147.76, 147.39, 147.34, 145.60, 133.46, 133.08, 124.67, 123.51, 120.70, 118.87, 115.70 (tt, $^1J_{C\text{-}F}$ = 277.8 Hz, $^2J_{C\text{-}F}$ = 35.3 Hz, CF_2), 111.45 (tt, $^1J_{C\text{-}F}$ = 272.7 Hz, $^2J_{C\text{-}F}$ = 39.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.27 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -99.01 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (EI) *m/z* calcd for $C_{15}H_{10}N_4OBrF_4$ $[M]^+$: 416.99686, found 416.99693.

*4-Phenyl-1-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)-1*H*-1,2,3-triazole* ***(4dm)***. Yield: 82%; white solid, mp 71–72 °C; R_f (petroleum ether/EtOAc, 95:5) = 0.45; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.91-7.89 (m, 2H), 7.50-7.46 (m, 2H), 7.43-7.39 (m, 1H), 7.09-7.07 (m, 2H), 6.87-6.85 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.39, 148.39, 141.72, 129.25, 129.17, 129.07, 126.24, 123.05, 118.41, 115.88 (tt, $^1J_{C\text{-}F}$ = 277.8 Hz, $^2J_{C\text{-}F}$ = 37.4 Hz, CF_2), 114.80, 111.62 (tt, $^1J_{C\text{-}F}$ = 270.7 Hz, $^2J_{C\text{-}F}$ = 40.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.57 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -99.31 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{17}H_{14}O_2N_3F_4$ $[M + H]^+$: 368.1016, found 368.1017.

*4-(4-Methoxyphenyl)-1-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)-1*H*-1,2,3-triazole* ***(4dn)***. Yield: 86%; white solid, mp 83–84 °C; R_f (petroleum ether/EtOAc, 9:1) = 0.61; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 9.1 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 9.1 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.43, 158.38, 148.27, 141.76, 127.62, 123.07, 121.71, 117.46, 115.94 (tt, CF_2), 114.79, 114.57, 111.60 (tt, CF_2), 55.73, 55.49; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.54 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -99.28 (t, $^3J_{F\text{-}F}$ = 3.7 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{18}H_{16}O_3N_3F_4$ $[M + H]^+$: 398.1123, found 398.1122.

*4-(4-Nitrophenyl)-1-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)-1*H*-1,2,3-triazole* ***(4dk)***. Yield: 77%; white solid, mp 121–123 °C; R_f (petroleum ether/EtOAc, 9:1) = 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.34 (m, 2H), 8.34 (s, 1H), 8.11-8.09 (m, 2H), 7.09-7.07 (m, 2H), 6.88-6.86 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.47, 148.12, 146.22, 141.59, 135.20, 126.88, 124.56, 122.98, 120.08, 115.77 (tt, $^1J_{C\text{-}F}$ = 276.7 Hz, $^2J_{C\text{-}F}$ = 37.4 Hz, CF_2), 114.84, 111.60 (tt, $^1J_{C\text{-}F}$ = 271.7 Hz, $^2J_{C\text{-}F}$ = 38.4 Hz, CF_2), 55.74; ^{19}F NMR (376 MHz, $CDCl_3$)

δ -86.48 (t, $^3J_{F-F}$ = 3.6 Hz, 2F), -99.24 (t, $^3J_{F-F}$ = 3.6 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{17}H_{13}O_4N_4F_4$ [M + H]$^+$: 413.0867, found 413.0868.

N,N-*Dimethyl-3-(1,1,2,2-tetrafluoro-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethoxy)aniline* ***(4em)****.* Yield: 79%; white solid, mp 80–82 °C; R_f (petroleum ether/EtOAc, 9:1) = 0.61; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.91-7.89 (m, 2H), 7.49 – 7.46 (m, 2H), 7.42 – 7.39 (m, 1H), 7.20-7.16 (m, 1H), 6.61-6.58 (m, 1H), 6.50-6.48 (m, 1H), 6.42-6.40 (m, 1H), 2.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.82, 149.71, 148.38, 130.00, 129.23, 129.18, 129.15, 126.26, 118.49, 115.63 (tt, CF_2), 110.81, 110.62 (tt, CF_2), 108.82, 105.33, 40.48; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.19 (t, $^3J_{F-F}$ = 3.8 Hz, 2F), -99.49 (t, $^3J_{F-F}$ = 3.7 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{18}H_{17}ON_4F_4$ [M + H]$^+$: 381.1334, found 381.1333.

N,N-*Dimethyl-3-(1,1,2,2-tetrafluoro-2-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-ethoxy)aniline* ***(4en)****.* Yield: 81%; white solid, mp 64–66 °C. R_f (petroleum ether/EtOAc, 9:1) = 0.51; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.84-7.81 (m, 2H), 7.20-7.16 (m, 1H), 7.01-6.98 (m, 2H), 6.61-6.59 (m, 1H), 6.50 – 6.47 (m, 1H), 6.42-6.41 (m, 1H), 3.86 (s, 3H), 2.93 (s, 6H);^{13}C NMR (101 MHz, $CDCl_3$) δ 160.40, 151.80, 149.71, 148.24, 129.98, 127.61, 121.76, 117.55, 115.93 (tt, $^1J_{C-F}$ = 275.7 Hz, $^2J_{C-F}$ = 43.4 Hz, CF_2), 114.56, 111.65 (tt, $^1J_{C-F}$ = 278.7 Hz, $^2J_{C-F}$ = 46.4 Hz, CF_2), 110.79, 108.84, 105.34, 55.50, 40.47; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.16 (t, $^3J_{F-F}$ = 3.7 Hz, 2F), -99.47 (t, $^3J_{F-F}$ = 3.6 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{19}H_{19}O_2N_4F_4$ [M + H]$^+$: 411.1440, found 411.1439.

N,N-*Dimethyl-3-(1,1,2,2-tetrafluoro-2-(4-(4-nitrophenyl)-1*H*-1,2,3-triazol-1-yl)ethoxy)-aniline* ***(4ek)****.* Yield: 84%; white solid, mp 122–123 °C; R_f (petroleum ether/EtOAc, 9:1) = 0.37; ^{1}H NMR (400 MHz, $CDCl_3$) 8.36-8.34 (m, 2H), 8.34 (s, 1H), 8.11-8.08 (m, 2H), 7.21-7.16 (m, 1H), 6.62-6.59 (m, 1H), 6.49 – 6.46 (m, 1H), 6.42-6.41 (m, 1H), 2.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.81, 149.59, 148.10, 146.20, 135.25, 130.03, 126.87, 124.54, 120.16, 115.80 (tt, $^1J_{C-F}$ = 277.8 Hz, $^2J_{C-F}$ = 36.4 Hz, CF_2), 111.64 (tt, $^1J_{C-F}$ = 2745.7 Hz, $^2J_{C-F}$ = 43.4 Hz, CF_2), 110.86, 108.63, 105.13, 40.42; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.10 (t, $^3J_{F-F}$ = 3.7 Hz, 2F), -99.44 (t, $^3J_{F-F}$ = 3.7 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{18}H_{16}O_3N_5F_4$ [M + H]$^+$: 426.1184, found 426.1184.

4-(4-Nitrophenyl)-1-(1,1,2,2-tetrafluoro-2-(3-(trifluoromethyl)phenoxy)ethyl)-1H-1,2,3-triazole ***(4fk)****.* Yield: 70%; white solid, mp 102–103 °C; R_f (petroleum ether/EtOAc, 9:1) = 0.44; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37-8.35 (m, 2H), 8.34 (s, 1H), 8.11-8.09 (m, 2H), 7.61-7.59 (m, 1H), 7.57-7.53 (m, 1H), 7.45 (br s, 1H), 7.41 – 7.39 (m, 1H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 148.47, 148.21, 146.36, 135.04, 132.75 (q, $^1J_{C-F}$ = 33.3 Hz, CF_3), 130.84, 126.93, 125.16, 124.60, 124.28 (q, $^3J_{C-F}$ = 4.0 Hz), 121.86, 119.96, 119.02 (q, $^2J_{C-F}$ = 4.0 Hz), 119.00, 115.81 (tt, $^1J_{C-F}$ = 281.8 Hz, $^2J_{C-F}$ = 37.4 Hz, CF_2), 111.43 (tt, $^1J_{C-F}$ = 272.7 Hz, $^2J_{C-F}$ = 40.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.36 (s, 3F), -86.17 (t, $^3J_{F-F}$ = 3.7 Hz, 2F), -98.96 (t, $^3J_{F-F}$ = 3.7 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{17}H_{10}O_3N_4F_7$ $[M + H]^+$: 451.0636, found 451.0636.

*1-(1,1,2,2-Tetrafluoro-2-(3-(trifluoromethyl)phenoxy)ethyl)-4-(4-(trifluoromethyl)-phenyl)-1*H*-1,2,3-triazole (**4fo**).* Yield: 48%; white solid, mp 81–82 °C; R_f (petroleum ether/EtOAc, 9:1) = 0.47; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.05-8.03 (m, 2H), 7.76-7.74 (m, 2H), 7.61-7.59 (m, 1H), 7.56-7.52 (m, 1H), 7.45 (br s, 1H), 7.41 – 7.38 (m, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 148.53, 147.17, 132.76 (q, $^1J_{C-F}$ = 33.3 Hz, CF_3), 132.37, 132.36, 131.26 (q, $^1J_{C-F}$ = 33.3 Hz, CF_3), 130.80, 126.52, 126.25 (q, $^2J_{C-F}$ = 4.0 Hz), 125.20, 124.24 (q, $^3J_{C-F}$ = 4.0 Hz), 121.89, 119.19, 119.07 (q, $^2J_{C-F}$ = 4.0 Hz), 115.87 (tt, $^1J_{C-F}$ = 279.8 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 111.45 (tt, $^1J_{C-F}$ = 273.7 Hz, $^2J_{C-F}$ = 42.4 Hz, CF_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.30 (s, 3F), -63.35 (s, 3F), -86.21 (t, $^3J_{F-F}$ = 3.3 Hz, 2F), -98.98 (t, $^3J_{F-F}$ = 3.3 Hz, 2F).; HRMS (ESI) *m/z* calcd for $C_{18}H_{10}ON_3F_{10}$ $[M + H]^+$: 474.0659, found 474.0658.

*Ethyl 1-(1,1,2,2-tetrafluoro-2-(3-(trifluoromethyl)phenoxy)ethyl)-1*H*-1,2,3-triazole-4-carboxylate (**4fp**).* Yield: 73%; colorless oil; R_f (petroleum ether/EtOAc, 9:1) = 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.61-7.59 (m, 1H), 56-7.52 (m, 1H), 7.42 (br s, 1H), 7.38-7.35 (m, 1H), 4.48 (q, $^3J_{H-H}$ = 7.2 Hz, 2H), 1.44 (t, $^3J_{H-H}$ = 7.1 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.55, 148.33, 140.97, 132.69 (q, $^1J_{C-F}$ = 33.3 Hz, CF_3), 130.83, 126.91, 125.10, 124.28 (q, $^3J_{C-F}$ = 4.0 Hz), 118.94 (q, $^2J_{C-F}$ = 4.0 Hz), 115.62 (tt, $^1J_{C-F}$ = 278.8 Hz, $^2J_{C-F}$ = 37.4 Hz, CF_2), 111.31 (tt, $^1J_{C-F}$ = 272.8 Hz, $^2J_{C-F}$ = 46.4 Hz, CF_2), 62.11, 14.28.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.37 (s, 3F), -86.35 (t, $^3J_{F-F}$ = 3.3 Hz, 2F), -99.23 (t, $^3J_{F-F}$ = 3.3 Hz, 2F).; HRMS (ESI) *m/z* calcd for $C_{14}H_{11}N_3O_3F_7$ $[M + H]^+$: 402.0683, found 402.0683.

*4-Butyl-1-(2-(2,4-di-*tert*-butylphenoxy)-1,1,2,2-tetrafluoroethyl)-1*H*-1,2,3-triazole (**4fq**).* Yield: 81%; colorless oil; R_f (petroleum ether) = 0.87; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.59-7.57 (m, 1H), 7.55-7.53 (m, 1H), 7.42 (br s, 1H), 7.38-7.36 (m, 1H), 2.81 (t, $^3J_{H-H}$ = 7.4 Hz, 2H), 1.76-1.68 (m, 2H), 1.46-1.38 (m, 2H), 0.95 (t, $^3J_{H-H}$ = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.26, 148.64, 132.66 (q, $^1J_{C-F}$ = 33.3 Hz, CF_3), 130.71, 125.19, 124.06 (q, $^3J_{C-F}$ = 4.0 Hz), 121.91, 119.58, 119.05 (q, $^2J_{C-F}$ = 4.0 Hz), 115.92 (tt, $^1J_{C-F}$ = 278.8 Hz, $^2J_{C-F}$ = 38.4 Hz, CF_2), 111.37 (tt, $^1J_{C-F}$ = 271.7 Hz, $^2J_{C-F}$ = 41.4 Hz, CF_2), 31.22, 25.18, 22.36, 13.87;

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.37 (s, 3F), -86.38 (t, $^3J_{F\text{-}F}$ = 3.4 Hz, 2F), -98.99 (t, $^3J_{F\text{-}F}$ = 3.3 Hz, 2F).; HRMS (EI) *m/z* calcd for $C_{15}H_{14}ON_3F_7$ $[M]^+$: 385.1025, found 385.1029.

1-(2-(2,4-Di-tert-*butylphenoxy)-1,1,2,2-tetrafluoroethyl)-4-phenyl-1*H-*1,2,3-triazole* ***(4gm)***. Yield: 90%;white solid, mp 102–103 °C; R_f (petroleum ether) = 0.78; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.89-7.87 (m, 2H), 7.49 – 7.45 (m, 2H), 7.41-7.39 (m, 2H), 7.25-7.24 (m, 1H), 7.21-7.18 (m, 1H), 1.31 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.50, 148.48, 146.39, 139.70, 129.25, 129.18, 129.09, 126.27, 125.13, 124.13, 118.88, 118.42, 116.43 (tt, $^1J_{C\text{-}F}$ = 280.6 Hz, $^2J_{C\text{-}F}$ = 38.3 Hz, CF_2), 111.72 (tt, $^1J_{C\text{-}F}$ = 272.8 Hz, $^2J_{C\text{-}F}$ = 42.3 Hz, CF_2), 35.06, 34.74, 31.51, 30.19; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.47 (t, $^3J_{F\text{-}F}$ = 3.4 Hz, 2F), -98.60 (t, $^3J_{F\text{-}F}$ = 3.4 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{24}H_{28}ON_3F_4$ $[M + H]^+$: 450.2163, found 450.2163.

1-(2-(2,4-Di-tert-*butylphenoxy)-1,1,2,2-tetrafluoroethyl)-4-(4-methoxyphenyl)-1*H-*1,2,3 triazole* ***(4gn)***. Yield: 85%; white solid, mp 85–86 °C; R_f (petroleum ether/EtOAc, 96:4) = 0.57; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.82-7.80 (m, 2H), 7.41-7.40 (m, 1H), 7.27-7.24 (m, 1H), 7.21-7.18 (m, 1H), 7.01-6.98 (m, 2H), 3.86 (s, 3H), 1.31 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.43, 148.47, 148.35, 146.40, 139.70, 127.63, 125.12, 124.12, 121.72, 118.88, 117.48, 116.44 (tt, $^1J_{C\text{-}F}$ = 279.8 Hz, $^2J_{C\text{-}F}$ = 38.4 Hz, CF_2), 114.59, 111.70 (tt, $^1J_{C\text{-}F}$ = 303.0 Hz, $^2J_{C\text{-}F}$ = 43.2 Hz, CF_2), 55.51, 35.06, 34.75, 31.51, 30.19; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.49 (t, $^3J_{F\text{-}F}$ = 3.4 Hz, 2F), -98.61 (t, $^3J_{F\text{-}F}$ = 3.4 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{25}H_{30}O_2N_3F_4$ $[M + H]^+$: 480.2269, found 480.2268.

1-(2-(2,4-Di-tert-*butylphenoxy)-1,1,2,2-tetrafluoroethyl)-4-(4-nitrophenyl)-1*H-*1,2,3-triazole* ***(4gk)***. Yield: 83%; white solid, mp 116117 °C; R_f (petroleum ether/EtOAc, 95:5) = 0.64; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36-8.34 (m, 2H), 8.34 (s, 1H), 8.09-8.07 (m, 2H), 7.41-7.40 (m, 1H), 7.26-7.23 (m, 1H), 7.21-7.18 (m, 1H), 1.31 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.70, 148.18, 146.31, 139.65, 135.18, 126.90, 125.21, 124.61, 124.20, 120.04, 118.87, 118.84, 116.32 (tt, $^1J_{C\text{-}F}$ = 274.7 Hz, $^2J_{C\text{-}F}$ = 36.4 Hz, CF_2), 111.71 (tt, $^1J_{C\text{-}F}$ = 276.7 Hz, $^2J_{C\text{-}F}$ = 44.4 Hz, CF_2), 35.06, 34.76, 31.50, 30.21; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.31 (t, $^3J_{F\text{-}F}$ = 2.5 Hz, 2F), -98.61 (t, $^3J_{F\text{-}F}$ = 2.5 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{24}H_{27}O_3N_4F_4$ $[M + H]^+$: 495.2014, found 495.2014.

Ethyl 1-(2-(2,4-di-tert-*butylphenoxy)-1,1,2,2-tetrafluoroethyl)-1*H-*1,2,3-triazole-4-carboxylate* ***(4gp)***. Yield: 85%; colorless oil; R_f (petroleum ether/EtOAc, 9:1) = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.41-7.40 (m, 1H), 7.21-7.19 (m, 2H), 4.47 (q, $^3J_{H\text{-}H}$ = 7.2

Hz, 2H), 1.43 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H), 1.31 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.63, 148.68, 146.23, 140.92, 139.68, 126.97, 125.18, 124.16, 118.85, 116.14 (tt, $^1J_{C\text{-}F}$ = 279.9 Hz, $^2J_{C\text{-}F}$ = 37.4 Hz, CF_2), 111.60 (tt, $^1J_{C\text{-}F}$ = 274.7 Hz, $^2J_{C\text{-}F}$ = 43.4 Hz, CF_2), 62.07, 35.02, 34.72, 31.46, 30.19, 14.35; ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.78 (t, $^3J_{F\text{-}F}$ = 3.3 Hz), -98.10 (t, $^3J_{F\text{-}F}$ = 3.3 Hz); HRMS (ESI) *m/z* calcd for $C_{21}H_{28}O_3N_3F_4$ $[M + H]^+$: 446.2061, found 446.2062.

*1-(2-(4-Bromo-1*H*-pyrazol-1-yl)-1,1,2,2-tetrafluoroethyl)-4-phenyl-1*H*-1,2,3-triazole* ***(4hm)****.* Yield: 64%; white solid, mp 102–105 °C; R_f (petroleum ether/EtOAc, 8:2) = 0.54; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.87 – 7.81 (m, 3H), 7.67 (d, *J* = 1.4 Hz, 1H), 7.51 – 7.38 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.56, 144.87, 129.41, 129.25, 129.20, 128.75, 126.27, 118.27, 112.11 (tt, $^1J_{C\text{-}F}$ = 273.7 Hz, $^2J_{C\text{-}F}$ = 42.4 Hz), 111.71(tt, $^1J_{C\text{-}F}$ = 270.7 Hz, $^2J_{C\text{-}F}$ = 42.4 Hz), 97.91; ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.05 (t, $^3J_{F\text{-}F}$ = 4.8 Hz, 2F), -98.40 (t, $^3J_{F\text{-}F}$ = 4.8 Hz, 2F).; HRMS (ESI) *m/z* calcd for $C_{13}H_9N_5BrF_4$ $[M + H]^+$: 389.9972, found 389.9973.

*1-(1,1,2,2-Tetrafluoro-2-(phenylthio)ethyl)-4-*p*-tolyl-1*H*-1,2,3-triazole (****4ij****).* Yield: 59%; white solid, mp 68–71 °C; R_f (petroleum ether/EtOAc, 9:1) = 0.60; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.67-7.65 (m, 2H), 7.56-7.54 (m, 2H), 7.41-7.37 (m, 1H), 7.33-7.29 (m, 2H), 7.20-7.18 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.55, 139.24, 137.31, 131.18, 129.82, 129.55, 126.21, 126.13, 122.86, 122.14 (tt, $^1J_{C\text{-}F}$ = 300.9 Hz, $^2J_{C\text{-}F}$ = 37.4 Hz, CF_2), 117.96, 113.68 (tt, $^1J_{C\text{-}F}$ = 274.7 Hz, $^2J_{C\text{-}F}$ = 41.4 Hz, CF_2), 21.49; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.63 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -95.58 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{17}H_{14}N_3F_4S$ $[M + H]^+$: 368.08397, found 368.08391.

Synthesis of 1-(1,1,2,2-tetrafluoroethyl)-4-*p*-tolyl-1*H*-1,2,3-triazole (5). 4ij (40 mg, 0.11 mmol) was dissolved in dry xylene (1 mL) and heated to 120 °C in a 10 mL screw-cap tube equipped with magnetic stirrer and septum. AIBN (3 mg, 0.02 mmol) and *n*-Bu_3SnH (55 mg, 0.19 mmol) in dry xylene (1 mL) were added dropwise over 20 min. After 10 min of further heating, the reaction mixture was cooled to rt, evaporated and purified by flash column chromatography (pentane/EtOAc, 9:1). Alternatively **5** was prepared from **2i**. **2i** (0.338 g, 1.349 mmol) was dissolved in dry xylene (5 mL) and heated to 100 °C in a 20 mL round-bottomed flask equipped with magnetic stirrer, septum and connected to cold-trap receiver filled with dry THF (2 mL) cooled to –78 °C. AIBN (33 mg, 0.202 mmol) and *n*-Bu_3SnH (0.687 g, 2.361 mmol) in dry xylene (2 mL) were added dropwise over 40 min. Stirring at 100 °C together with cold-trap distillation (–78 °C) was continued for 5 h. THF solution of the product containing 2-azido-1,1,2,2-tetrafluoroethane (13% GC yield) was directly used for click reaction. To the cold colution of the azide, **3j** (20 mg, 0.17 mmol) and copper(I) 3-methylsalicylate (1 mg, 0.005 mmol) were added, and the reaction mixture was stirred at rt for 18 h (UPLC-MS control). After evaporation of the solvent and crystallization from hexane, pure **5** was obtained. Yield: 73% from **4ij**, 6% (21 mg) from **2i**; white solid, mp 68–71 °C; R_f (pentane/EtOAc, 9:1) = 0.55; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.77-7.75 (m, 2H), 7.29-7.27 (m, 2H), 6.66 (tt, $^2J_{H\text{-}F}$ = 52.4 Hz, $^3J_{H\text{-}F}$ = 4.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.82, 139.48, 129.89, 126.18, 125.99, 117.10, 112.30 (tt, $^1J_{C\text{-}F}$ = 266.6 Hz, $^2J_{C\text{-}F}$ = 29.3 Hz, CF_2), 107.82 (tt, $^1J_{C\text{-}F}$ = 253.5 Hz, $^2J_{C\text{-}F}$ = 35.3 Hz, CF_2), 21.49; ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.44 (td, $^3J_{F\text{-}F}$ = 7.6 Hz, $^3J_{F\text{-}H}$ = 3.8 Hz, 2F), -137.85 (dt, $^2J_{F\text{-}H}$ = 52.6 Hz, $^3J_{F\text{-}F}$ = 7.6 Hz, 2F); HRMS (EI) *m/z* calcd for $C_{11}H_9N_3F_4$ $[M]^+$: 259.0733, found 259.0735.

Synthesis of 5-iodo-1-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (7aj). To a 10 mL screw-cap glass tube cooled to 0 °C, containing copper(I) *p*-tolylacetylide **6j** (0.196 g, 1.1 mmol) and azide **2a** (0.235 g, 1 mmol) in THF (4 mL), a solution of I_2 (0.254 g, 1 mmol) and Et_3N (0.202 g, 2 mmol) in THF (1 mL) was slowly added. After slow warming to rt and stirring under Ar for 16 h, the reaction mixture was poured into water and extracted with Et_2O. The organic phase was dried ($MgSO_4$), concentrated and the residue chromatographed on silica gel (hexane/EtOAc, 99:1) to obtain white crystalline compound (0.252 g, 62% yield), mp 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.72 (m, 2H), 7.30–7.28 (m, 2H), 7.23–7.20 (m, 3H), 7.17-7.15 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.32, 148.74, 139.56, 129.91, 129.46, 128.49, 127.03, 126.08, 121.77, 115.95 (tt, $^1J_{C\text{-}F}$ = 278.8 Hz, $^2J_{C\text{-}F}$ = 36.4 Hz), 112.41 (tt, $^1J_{C\text{-}F}$ = 273.7 Hz, $^2J_{C\text{-}F}$ = 39.4 Hz), 71.54, 21.53; ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.63 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -94.01 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{17}H_{13}N_3F_4IO$ $[M + H]^+$: 478.00339, found 478.00325.

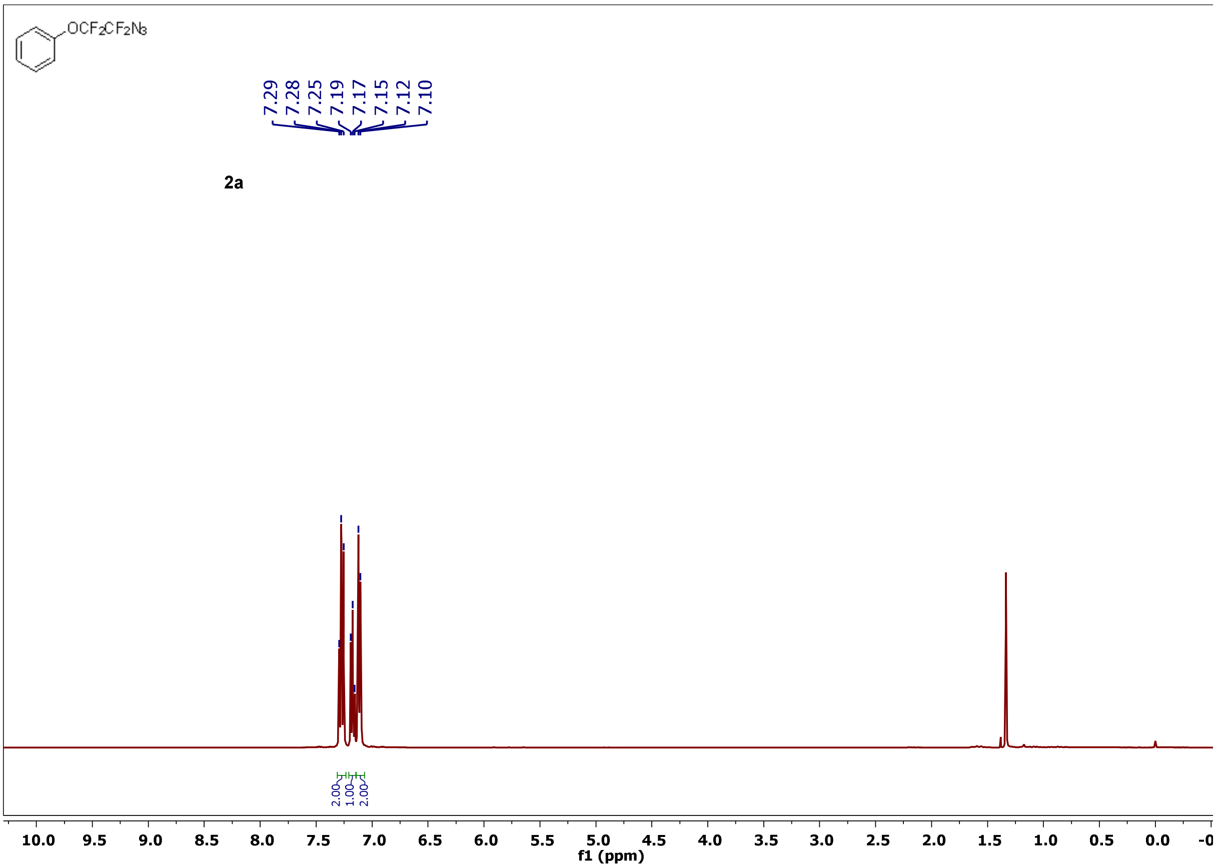
Synthesis of 5-iodo-4-phenyl-1-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)- 1*H*-1,2,3-triazole (7dm). To a 10 mL screw-cap glass tube cooled to 0 °C, containing copper(I) phenylacetylide (**6m**) (0.181 g, 1.1 mmol) and azide **2d** (0.265 g, 1 mmol) in THF (4 mL), a solution of I_2 (0.254 g, 1 mmol) and Et_3N (0.202 g, 2 mmol) in THF (1 mL) was slowly added. After slow warming to rt and stirring under Ar for 16 h, the reaction mixture was poured into water (10 mL) and extracted with Et_2O. The organic phase was dried ($MgSO_4$), concentrated and the residue chromatographed on silica gel (hexane/EtOAc, 99:1) to obtain white crystalline compound (0.438 g, 89% yield), mp 96–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.51–7.47 (m, 3H), 7.18–7.16 (m, 2H), 6.90-6.87 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.32, 152.24, 141.95, 129.51, 129.01, 128.77, 128.64, 123.09, 115.95 (tt, $^1J_{C\text{-}}$

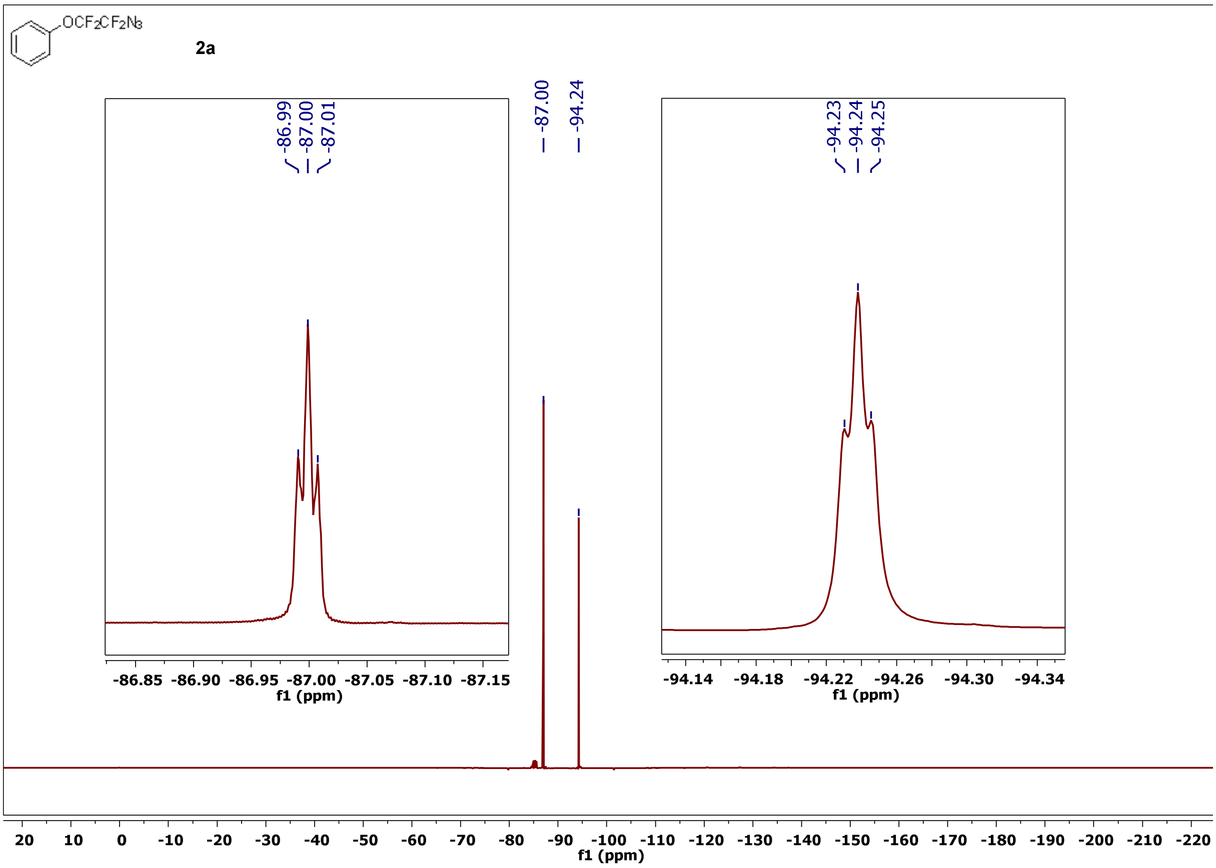
$_F$ = 276.7 Hz, $^2J_{C\text{-}F}$ = 38.4 Hz), 114.80, 112.46 (tt, $^1J_{C\text{-}F}$ = 272.7 Hz, $^2J_{C\text{-}F}$ = 42.4 Hz), 71.82, 55.76; ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.87 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -94.94 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{17}H_{13}N_3F_4IO_2$ [M + H]$^+$: 493.99833, found 493.99831.

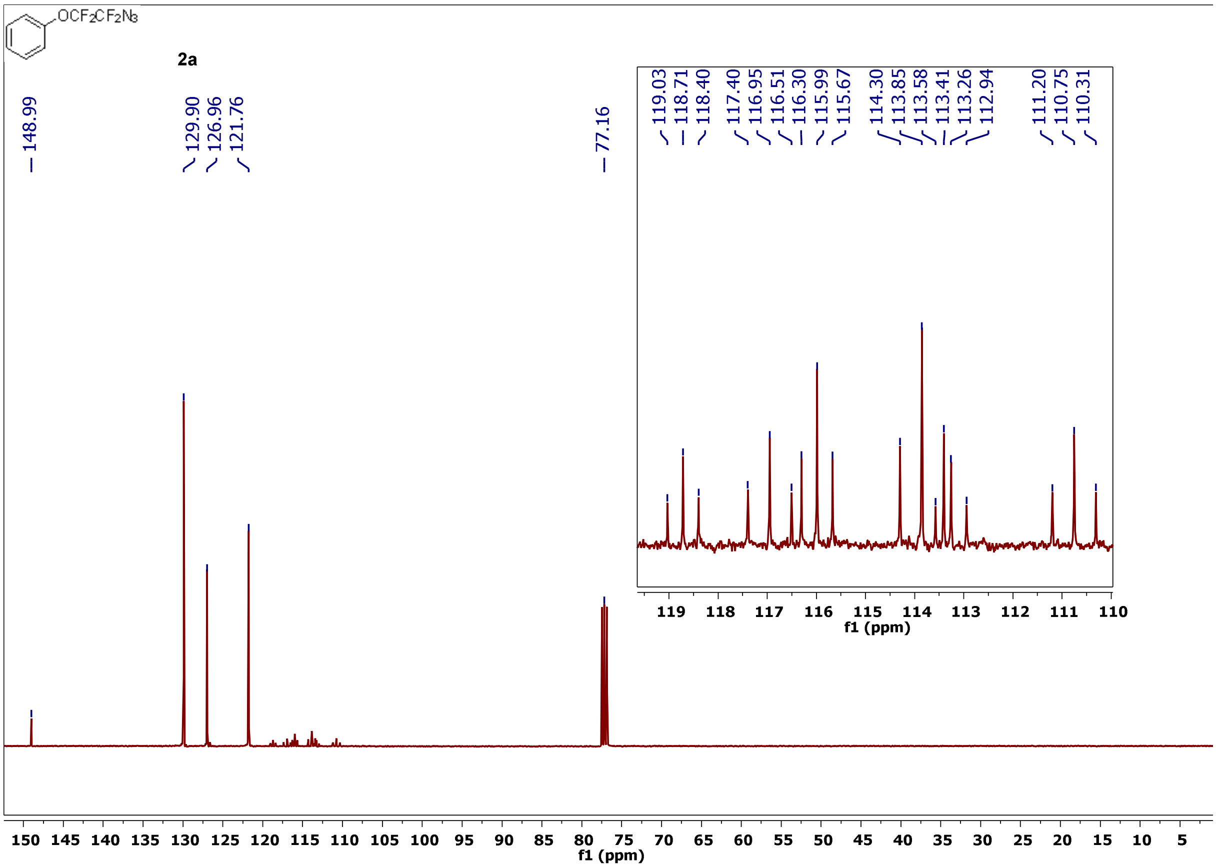
Synthesis of 5-((4-fluorophenyl)ethynyl)-1-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (8). Iodotriazole **7aj** (0.145 g, 0.3 mmol), 1-ethynyl-4-fluorobenzene (37 mg, 0.3 mmol), and K_2CO_3 (0.138 g, 1 mmol) were suspended in dry DMF (1 mL) and degassed. $Pd(OAc)_2$ (2 mg, 0.009 mmol, 0.03 equiv.) and copper(I) 3-methylsalicylate (2 mg, 0.009 mmol, 0.03 equiv.) were added and the reaction mixture was stirred at 50 °C for 24 h under UPLC-MS control. Water (5 mL) was added, the product was extracted with Et_2O, the combined organic phase was washed with brine, dried ($MgSO_4$), and concentrated. The crude product was purified by flash column chromatography (hexane). Yield: 43%; yellow solid, mp 89–93 °C; ^{1}H NMR (500.0 MHz, $CDCl_3$): δ 8.13-8.11 (m, 2H), 7.58-7.54 (m, 2H), 7.37-7.35 (m, 2H), 7.33-7.31 (m, 2H), 7.29-7.27 (m, 1H), 7.21-7.19 (m, 2H), 7.14-7.10 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 163.46 (d, $^1J_{C\text{-}F}$ = 252.6), 148.86, 148.61, 139.58, 133.76 (d, $^3J_{C\text{-}F}$ = 8.7), 129.75, 129.52, 126.82, 126.65, 126.07, 123.37, 121.51, 117.33 (d, $^4J_{C\text{-}F}$ = 3.6), 116.17 (d, $^2J_{C\text{-}F}$ = 22.3), 115.97 (tt, $^1J_{C\text{-}F}$ = 277.6, $^2J_{C\text{-}F}$ = 37.1, CF_2), 112.07 (tt, $^1J_{C\text{-}F}$ = 273.1, $^2J_{C\text{-}F}$ = 42.2, CF_2), 102.14, 73.94, 21.45; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.90 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -97.71 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -108.14 (tt, $^3J_{H\text{-}F}$ = 8.3 Hz, $^4J_{H\text{-}F}$ = 5.3 Hz, 1F); HRMS (ESI) *m/z* calcd for $C_{25}H_{17}F_5N_3O$ [M + H]$^+$: 470.12863, found 470.12864.

Synthesis of 4-(phenyl)-1-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)-5-(*p*-tolyl)-1*H*-1,2,3-triazole (9). To a 5 mL screw-cap glass tube containing **7dm** (88 mg, 0.18 mmol, 1.0 equiv.), *p*-tolylboronic acid (36.7 mg, 0.27 mmol, 1.5 equiv.), and K_2CO_3 (69 mg, 0.5 mmol, 2.8 equiv.), dry DMF (2.0 mL) and $Pd(OAc)_2$ (1.2 mg, 0.01 mmol, 2.8 mol%) were added. The reaction mixture was stirred at rt in the closed vial for 16 h (UPLC-MS control), then poured into 5% HCl (10 mL) and extracted with Et_2O. The organic phase was dried ($MgSO_4$), concentrated, chromatographed on silica gel (hexane/EtOAc, 99:1), and triturated with cold hexane to obtain white crystalline product **9** (43 mg). Yield: 52%; white solid, mp 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2H), 7.26–7.24 (m, 7H), 7.11–7.08 (m, 2H), 6.86-6.84 (m, 2H), 3.78 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.26, 145.58, 141.99, 140.38, 134.62, 130.34, 129.69, 129.19, 128.65, 128.50, 127.28, 123.38, 123.21, 115.99 (tt, $^1J_{C\text{-}F}$ = 276.7 Hz, $^2J_{C\text{-}F}$ = 37.4 Hz), 114.73, 112.55 (tt, $^1J_{C\text{-}F}$ = 271.7 Hz, $^2J_{C\text{-}F}$ = 41.4 Hz), 55.75, 21.66; ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.53 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F), -93.96 (t, $^3J_{F\text{-}F}$ = 3.8 Hz, 2F); HRMS (ESI) *m/z* calcd for $C_{24}H_{20}F_4N_3O_2$ [M + H]$^+$: 458.14862, found 458.14862.

NMR spectra collection



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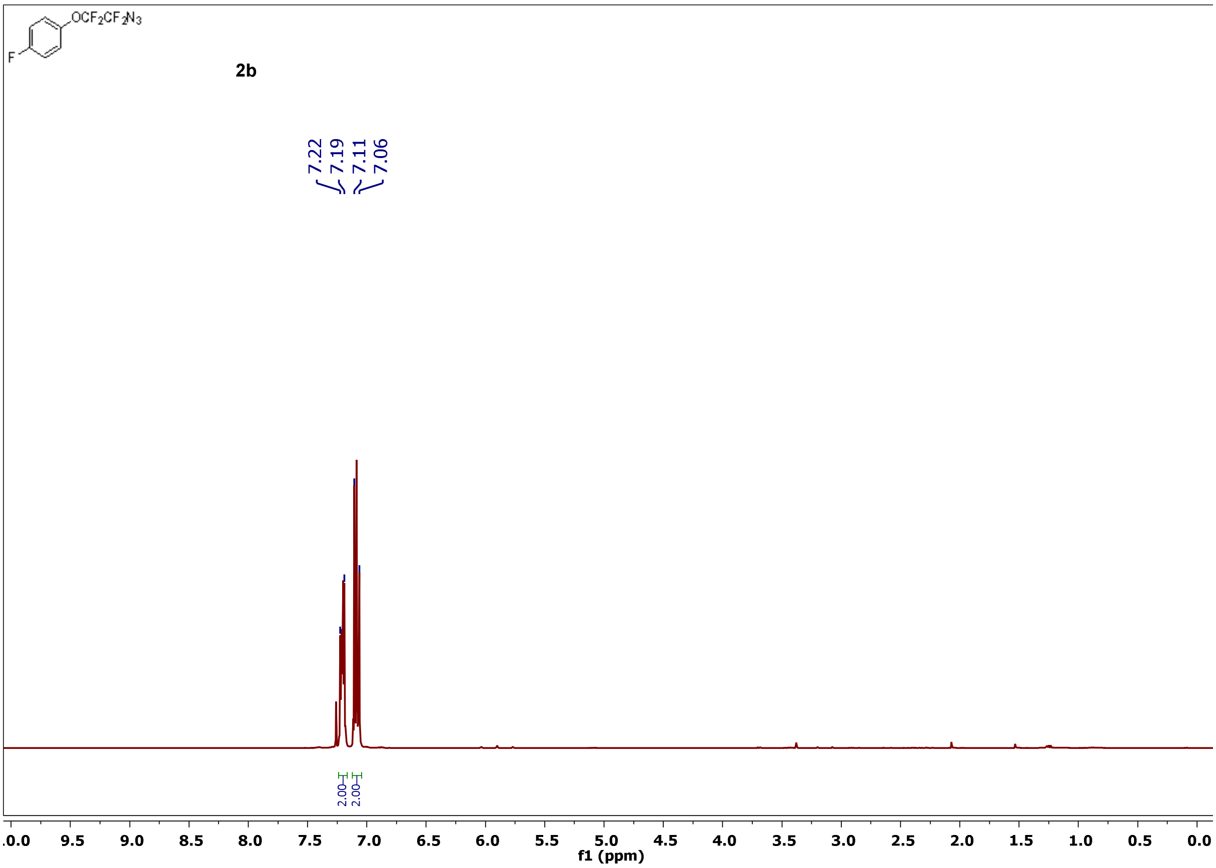
f1 (ppm)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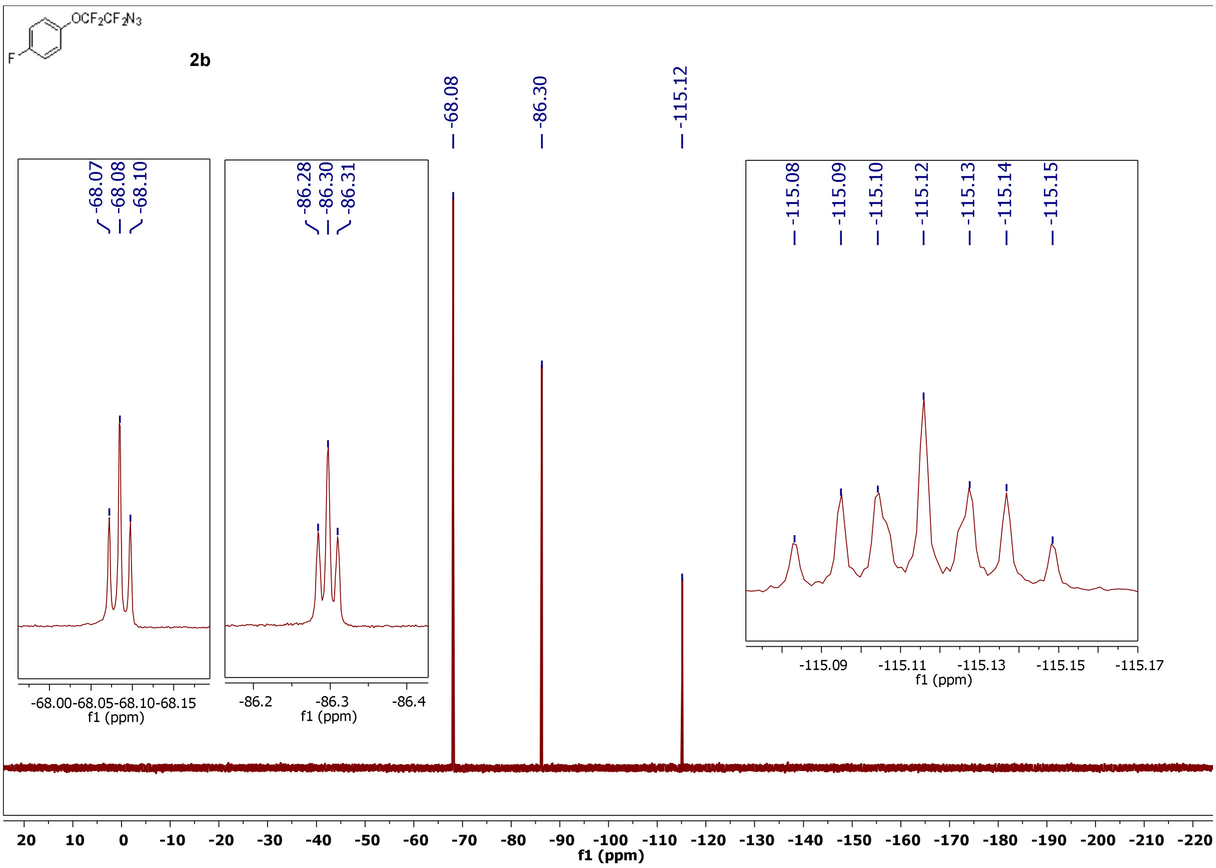
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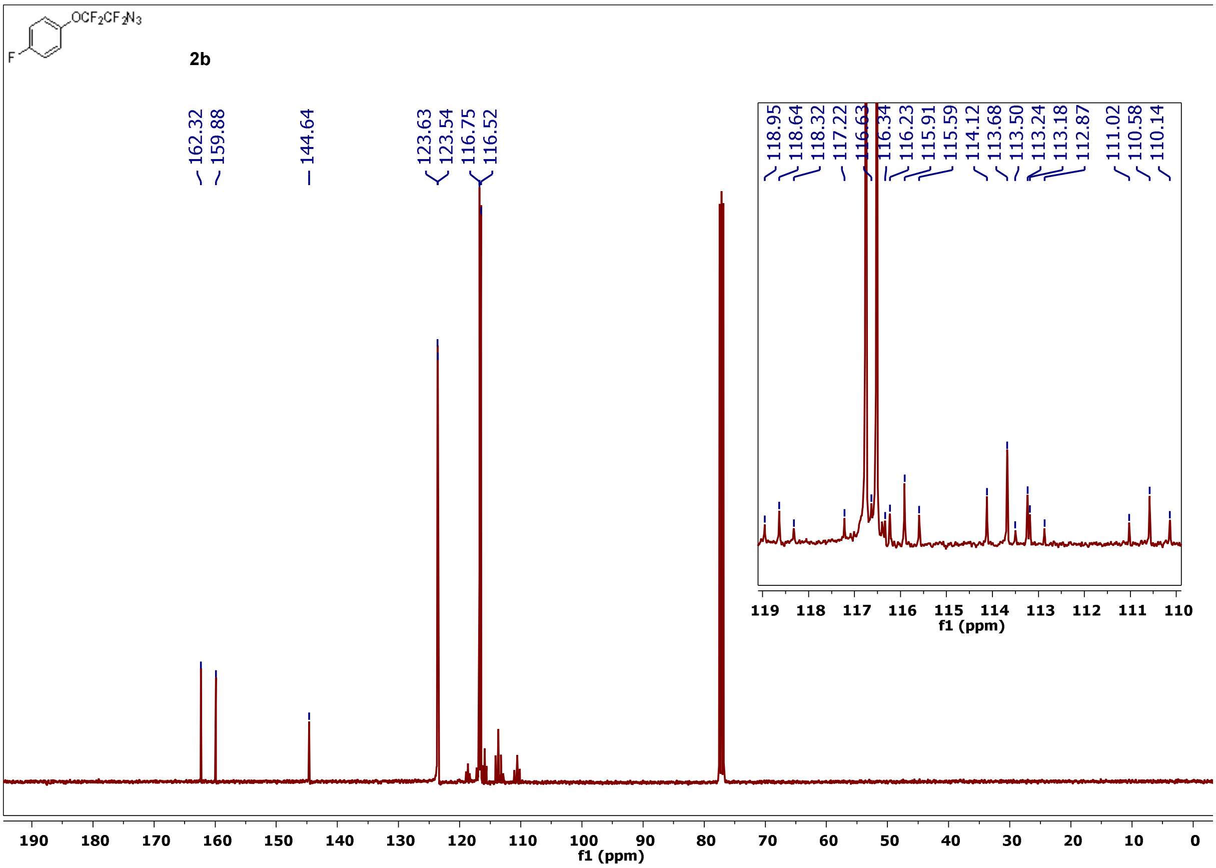
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114.12
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113.24
113.18
112.87
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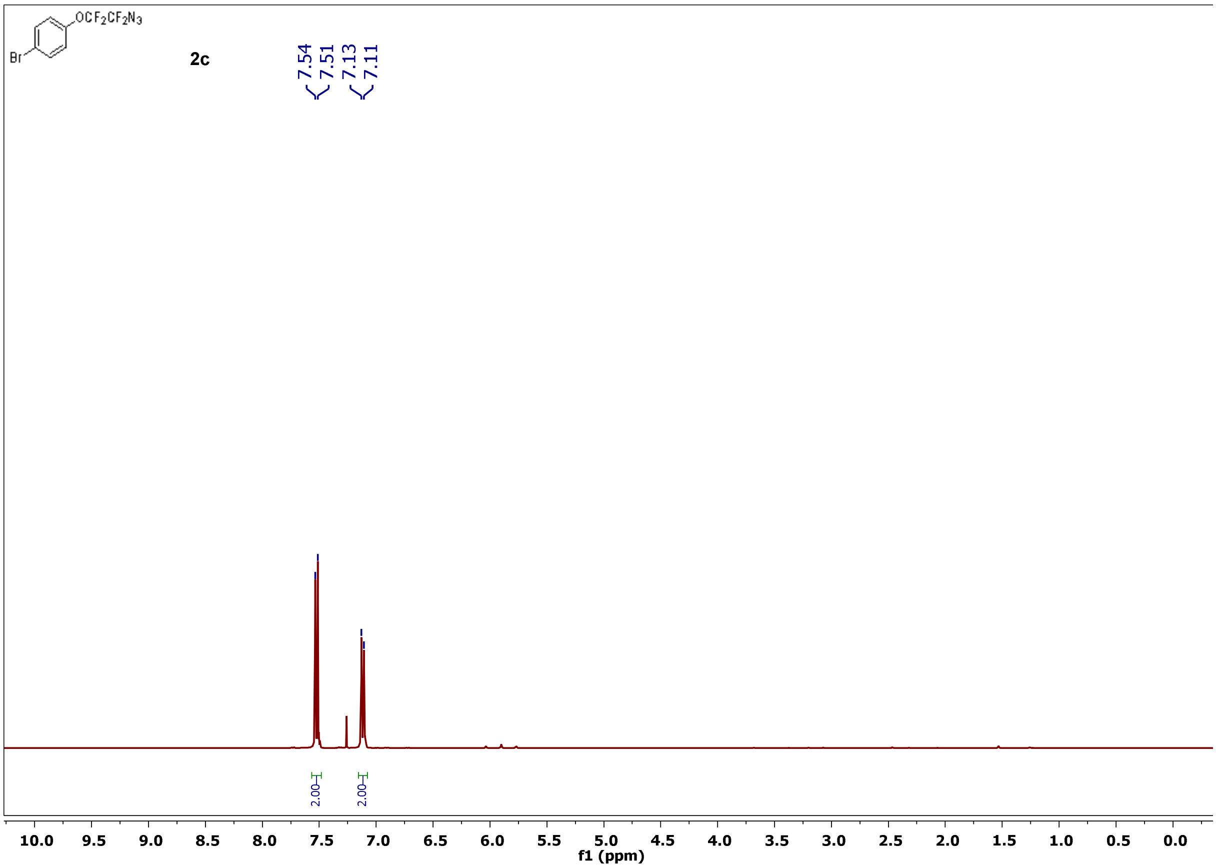
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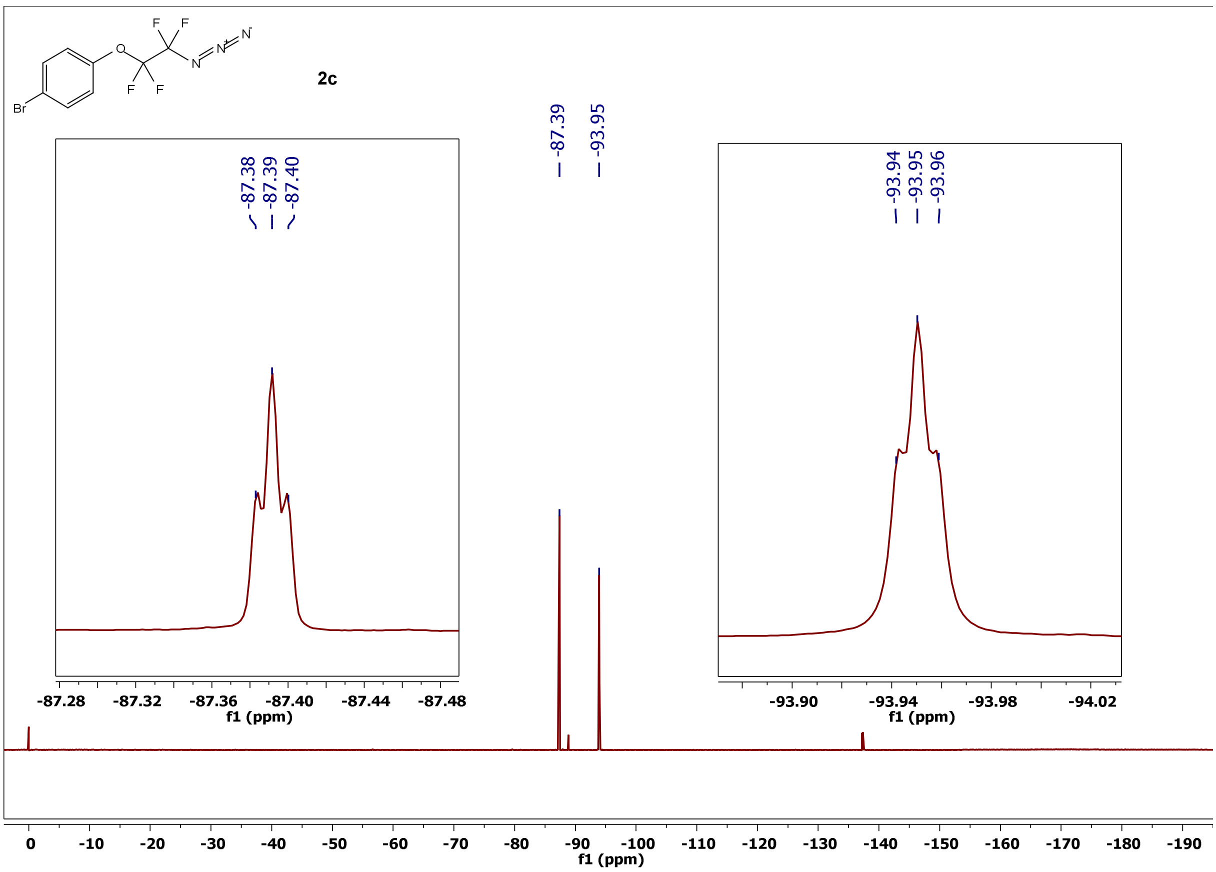
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N N N
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-93.95
-93.96
-93.90 -93.94 -93.98 -94.02
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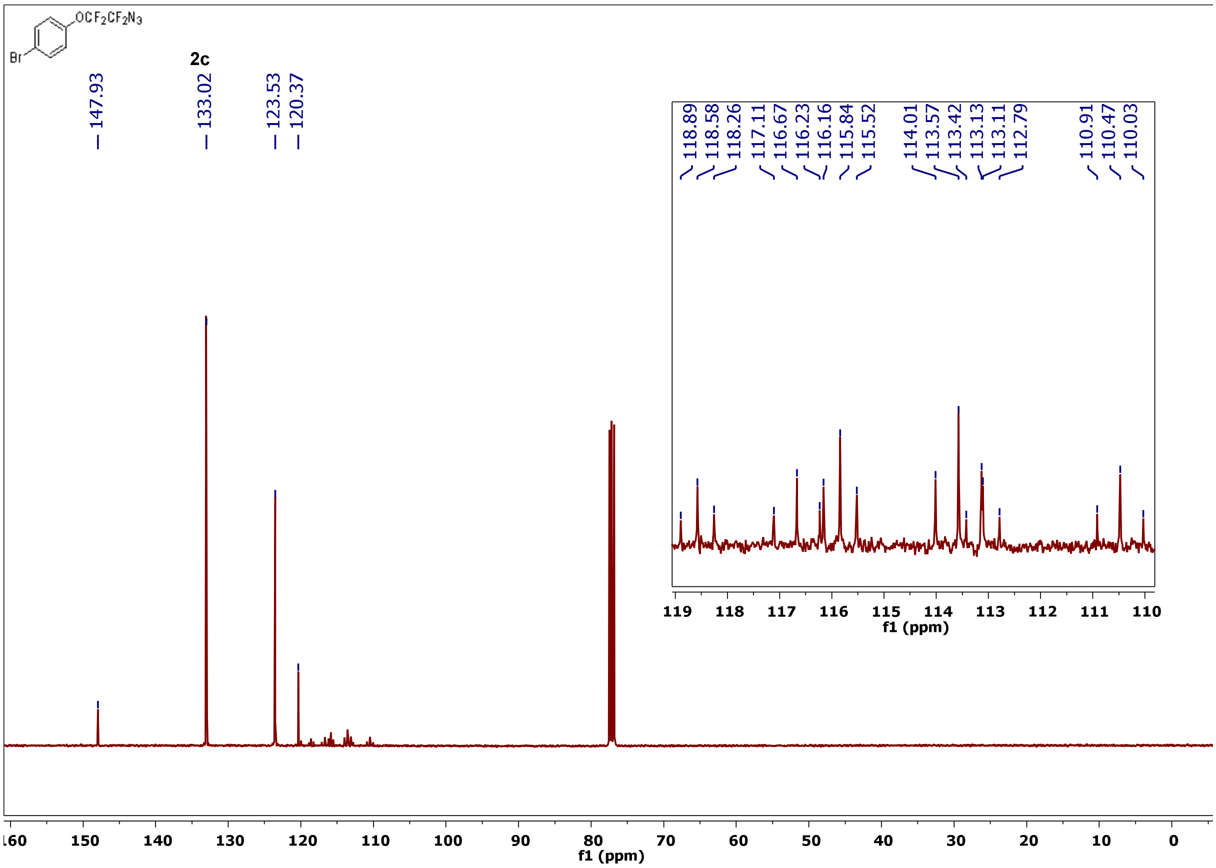
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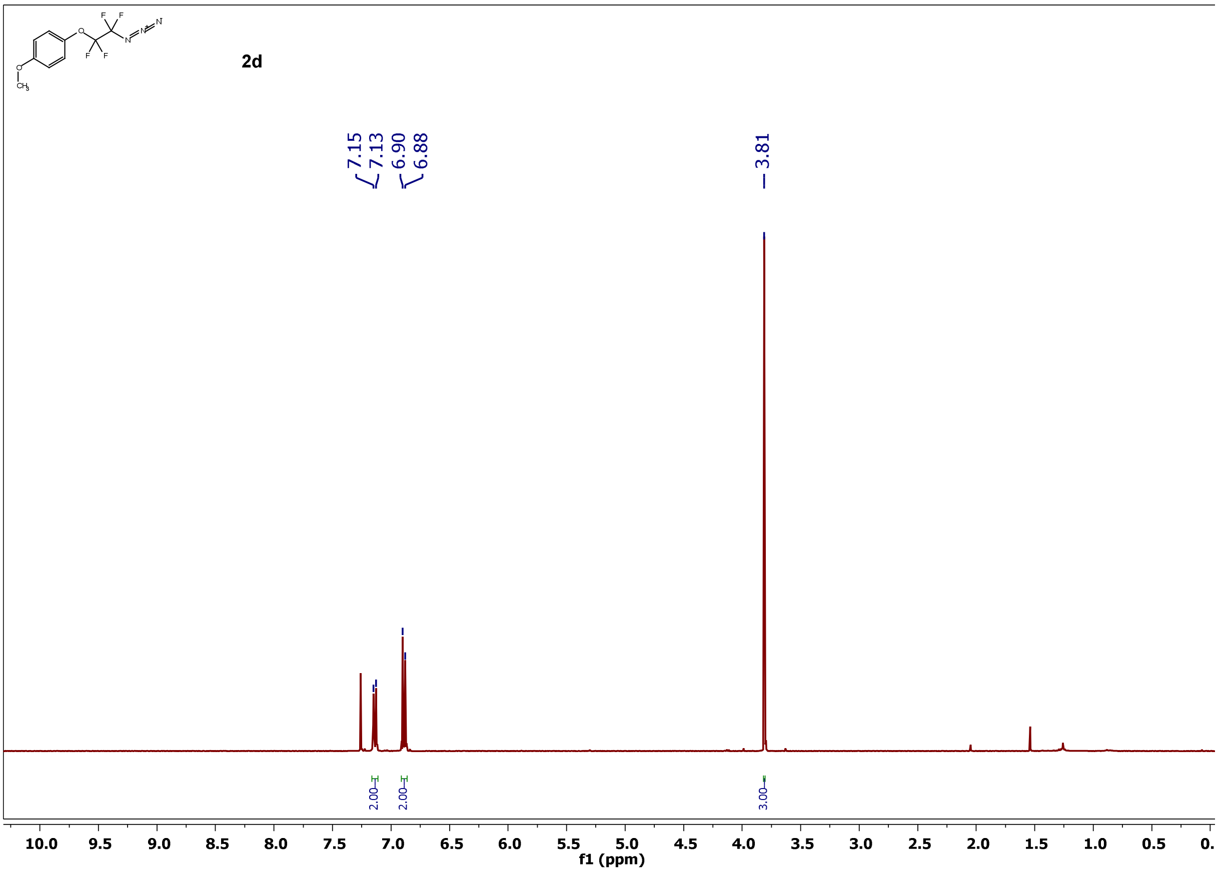
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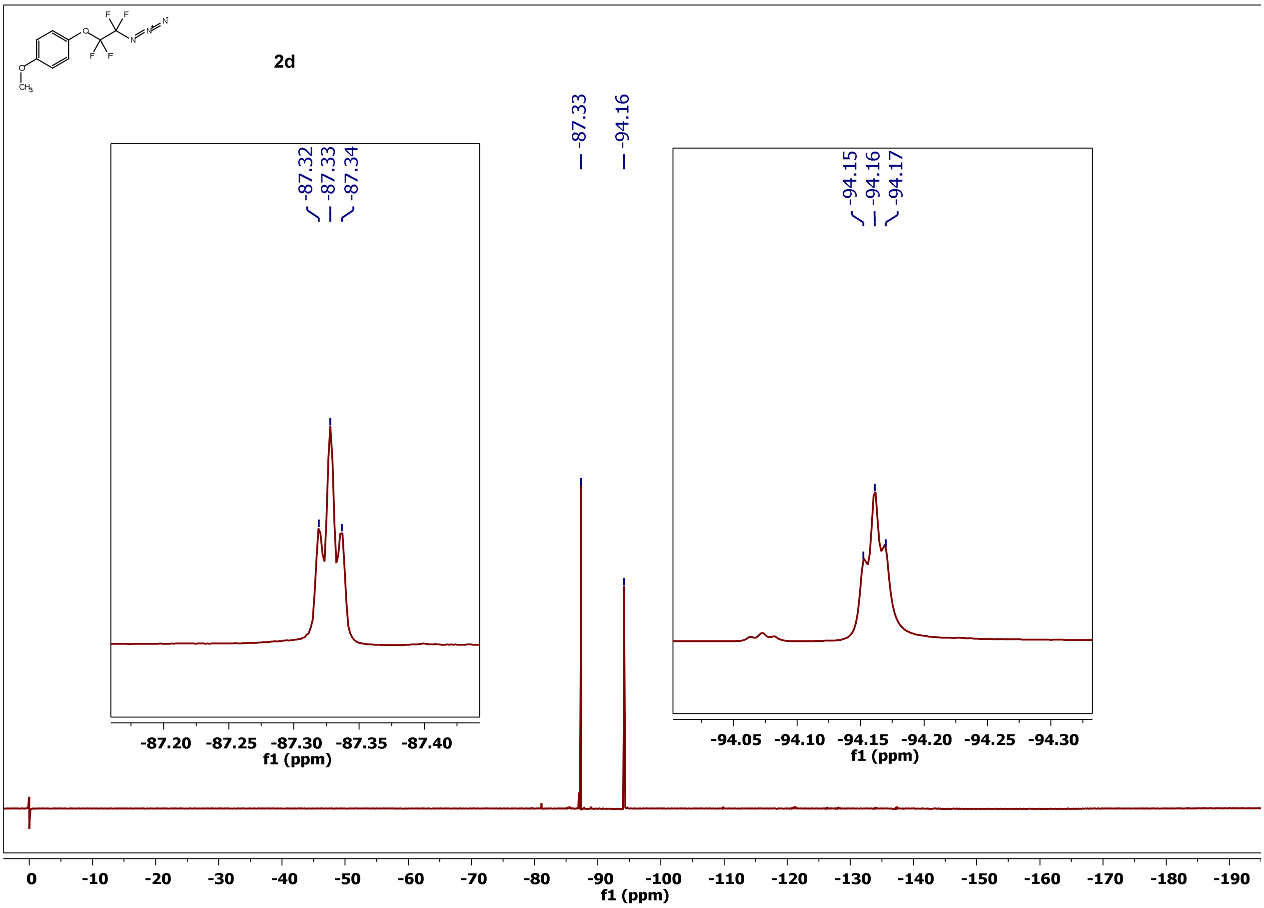
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f1 (ppm)
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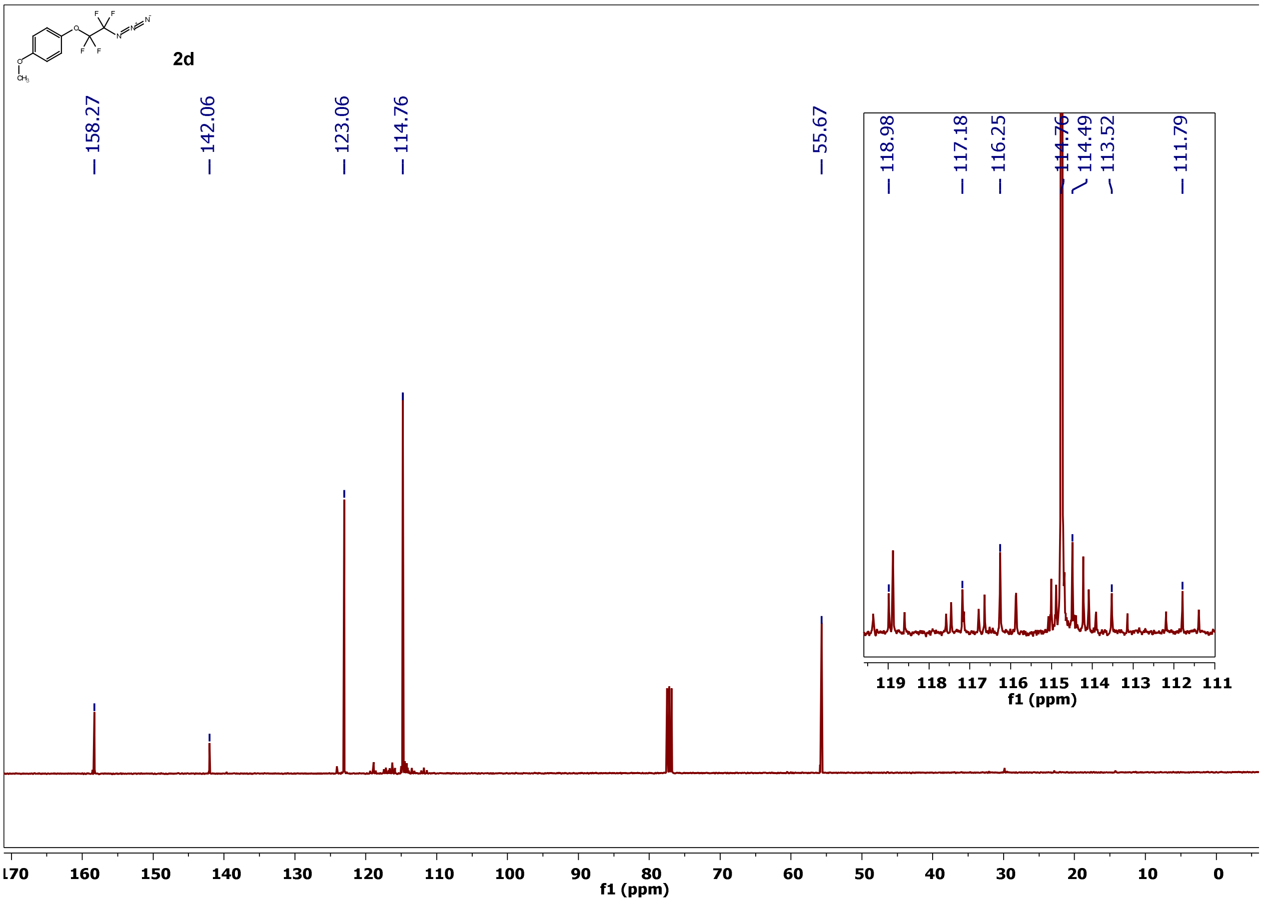
f1 (ppm)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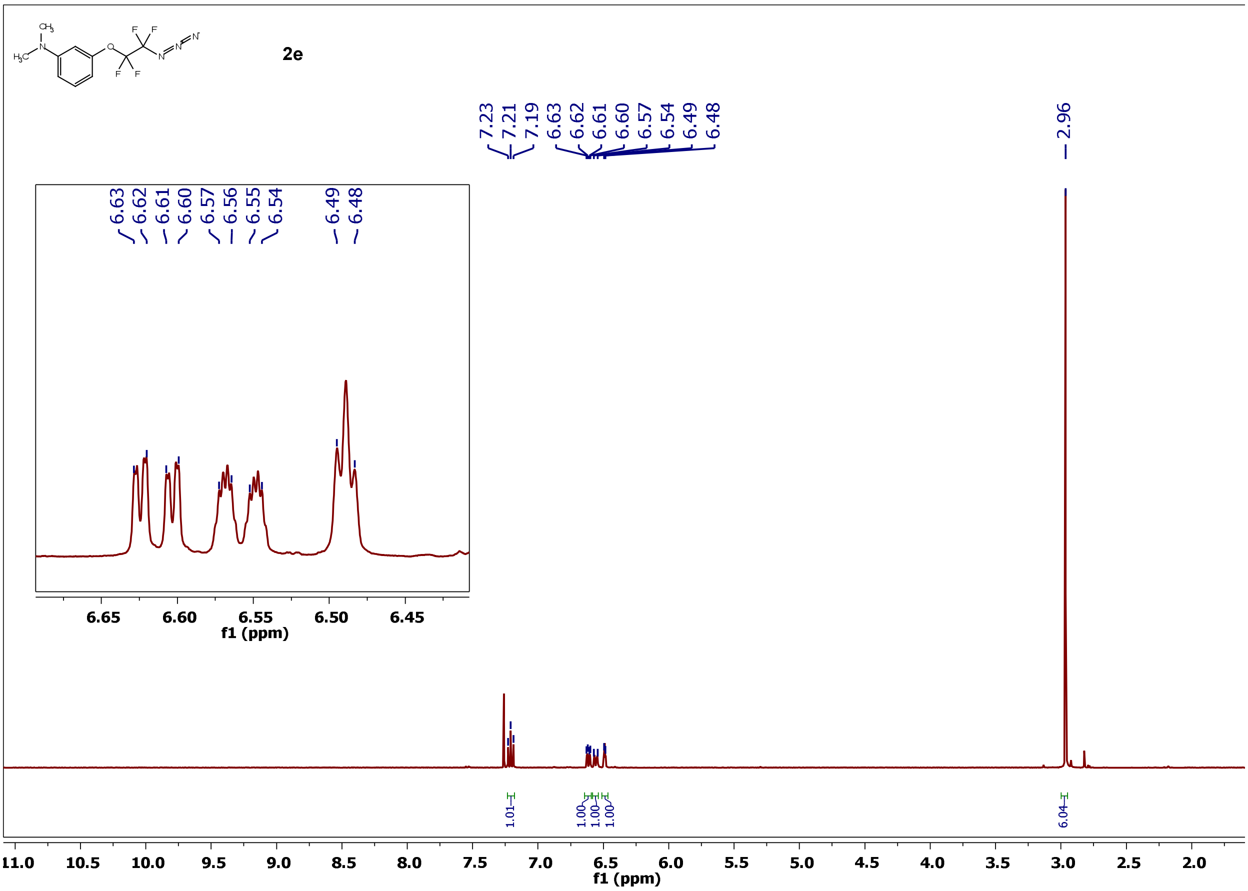
f1 (ppm)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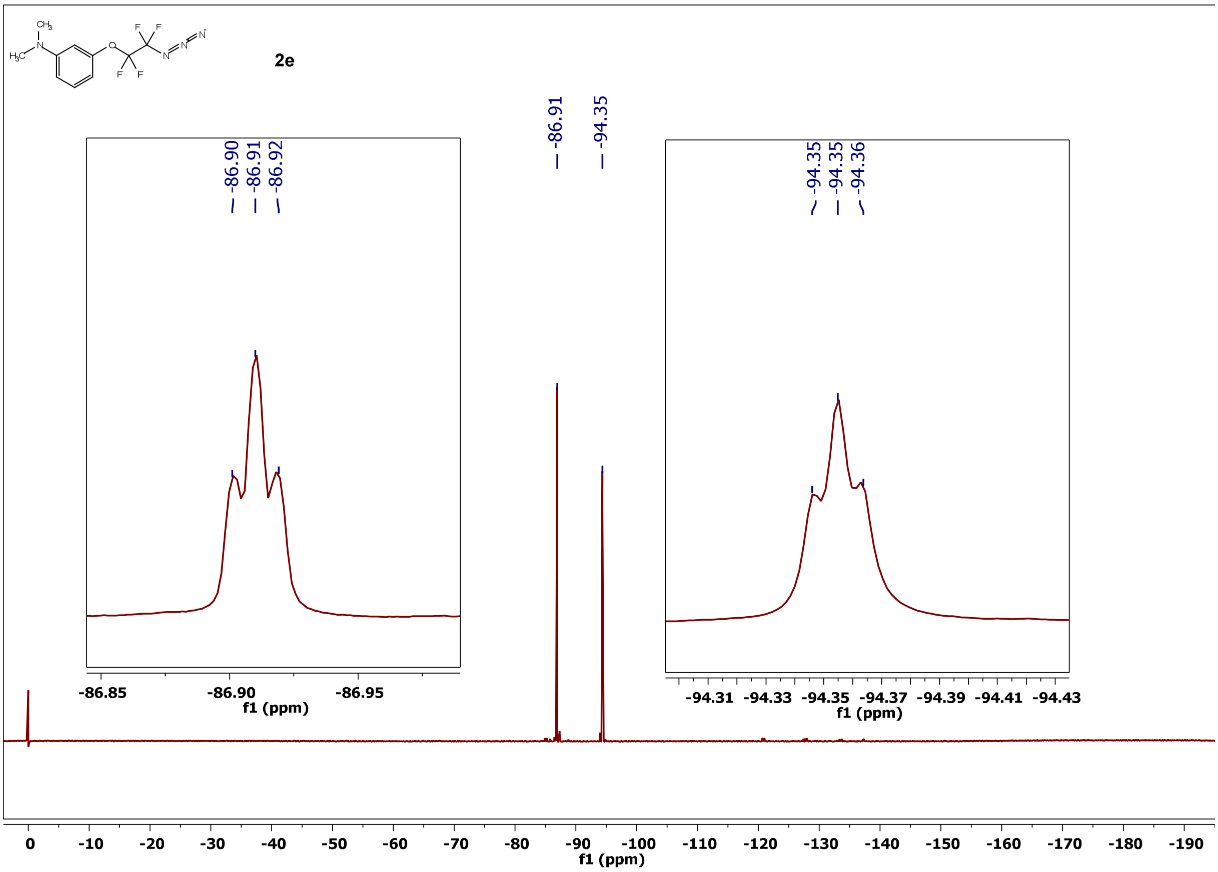

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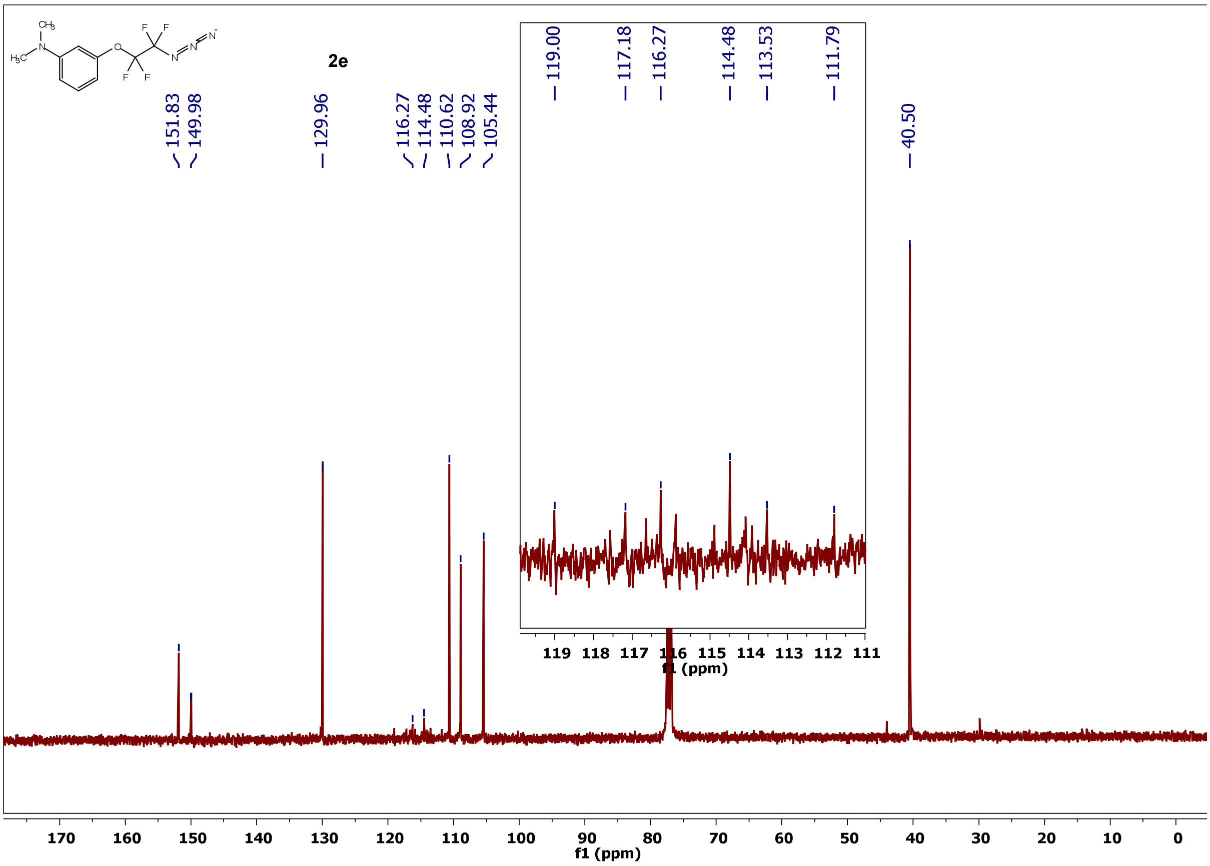
f1 (ppm)



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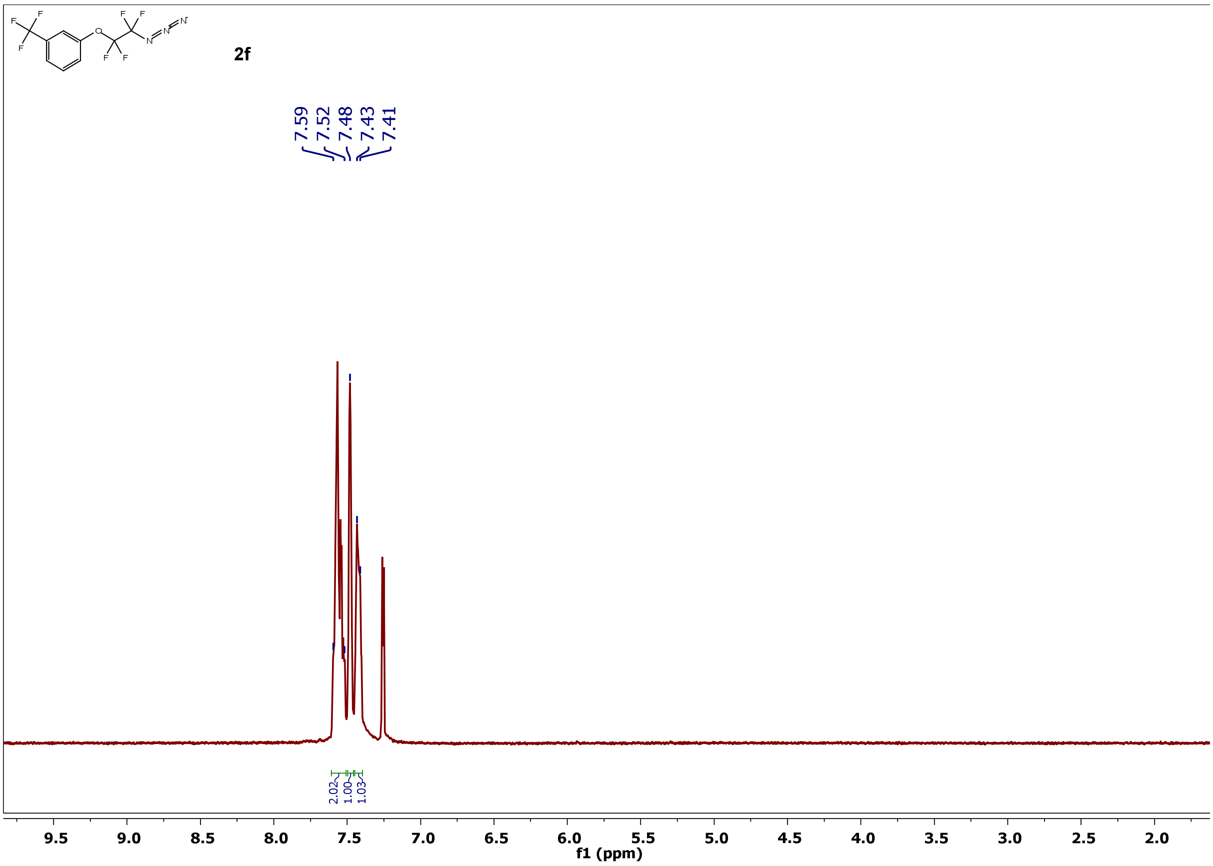
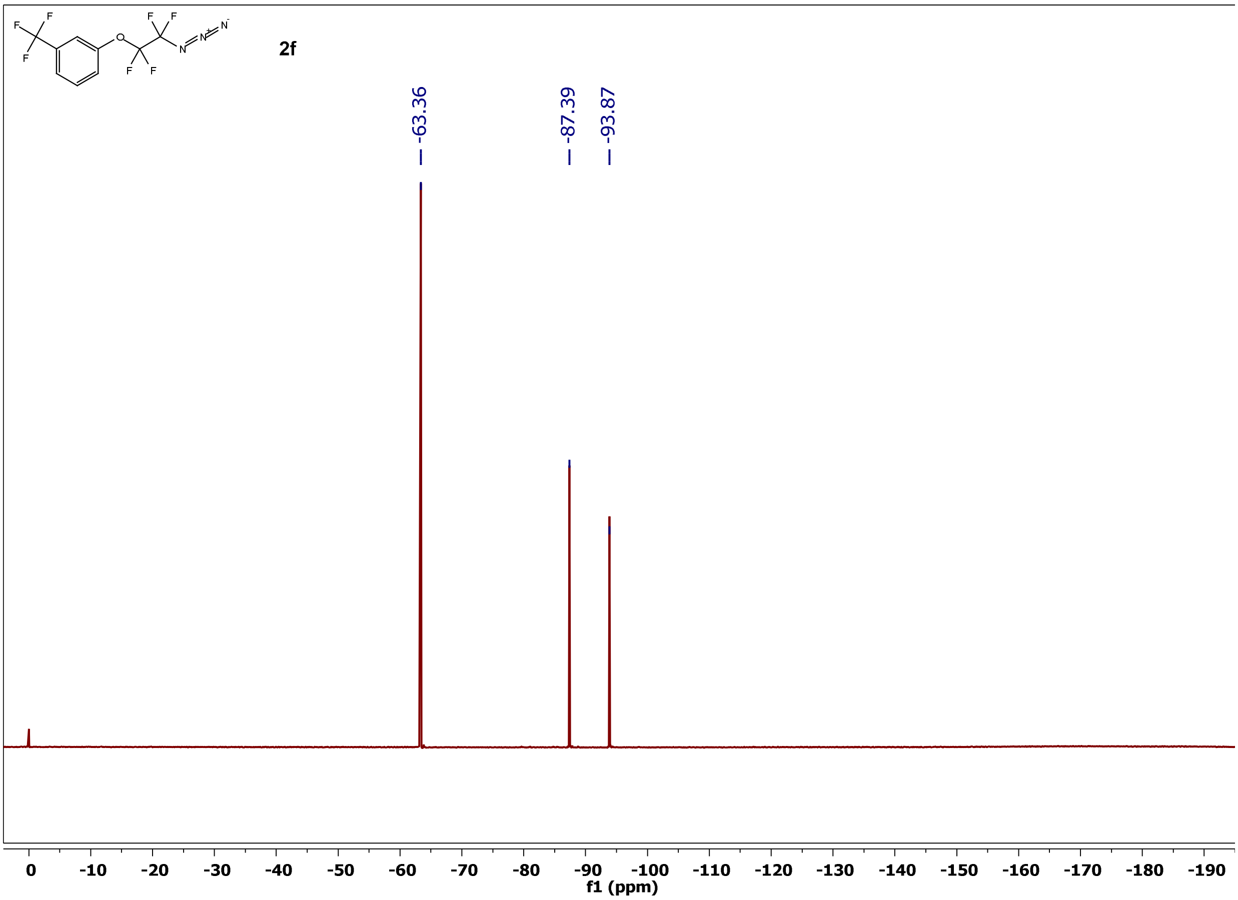
f1 (ppm)

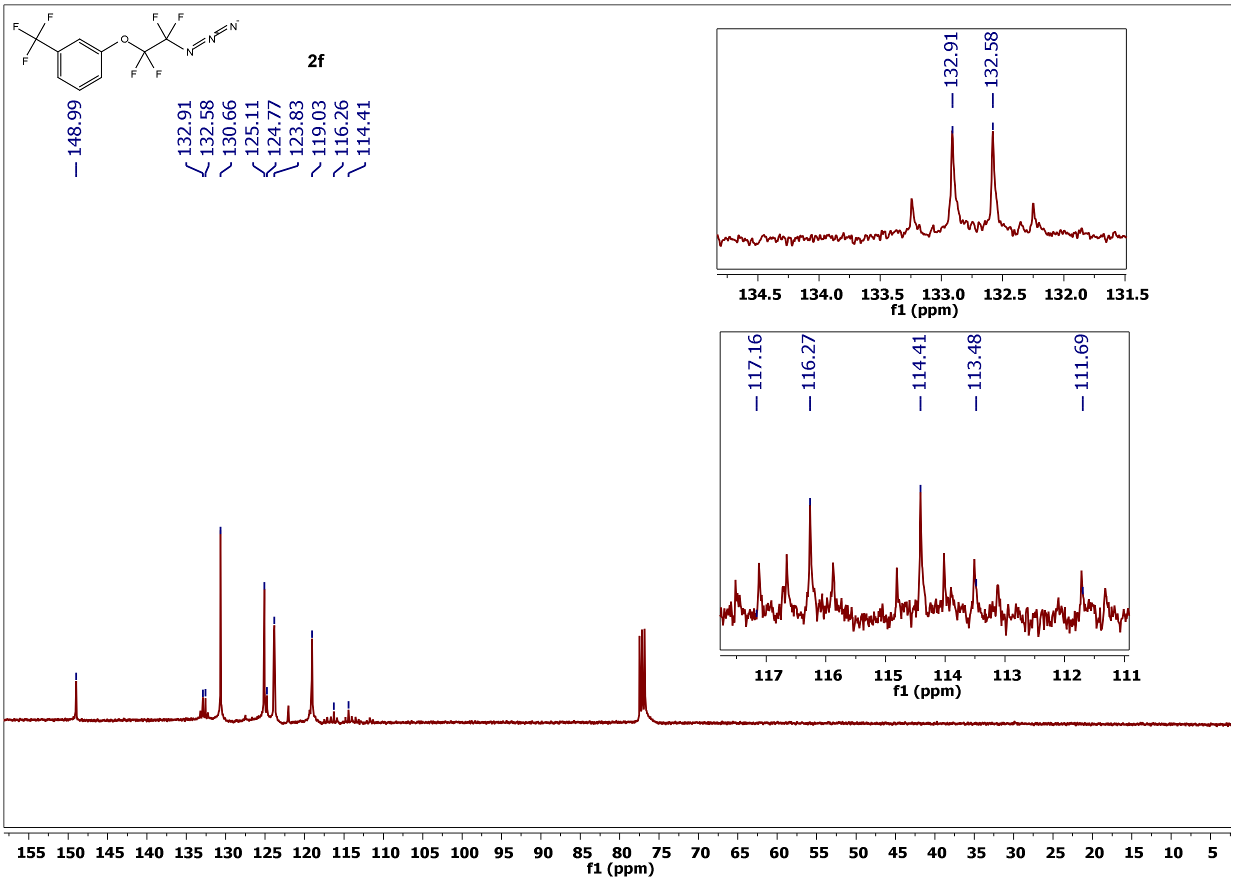
2e

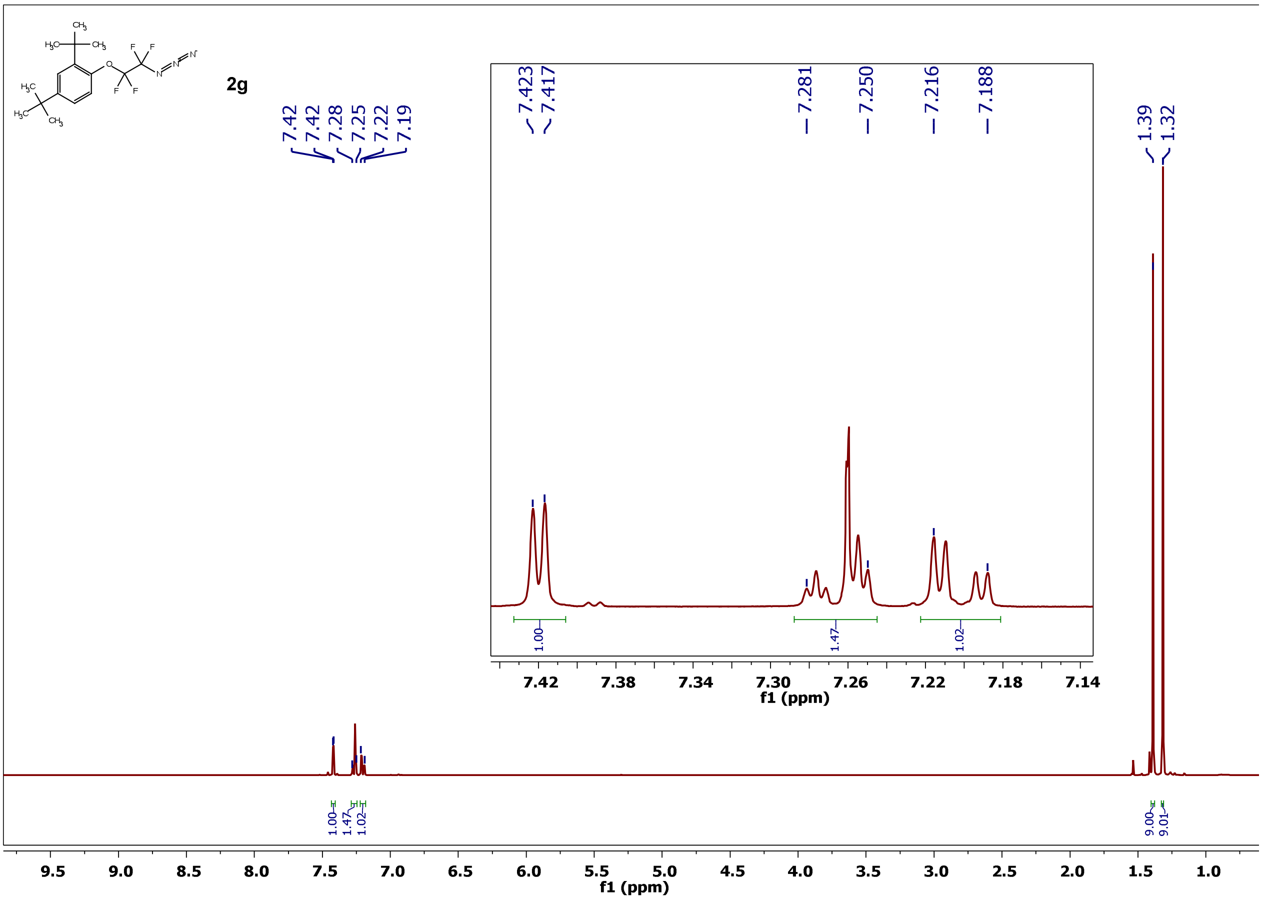


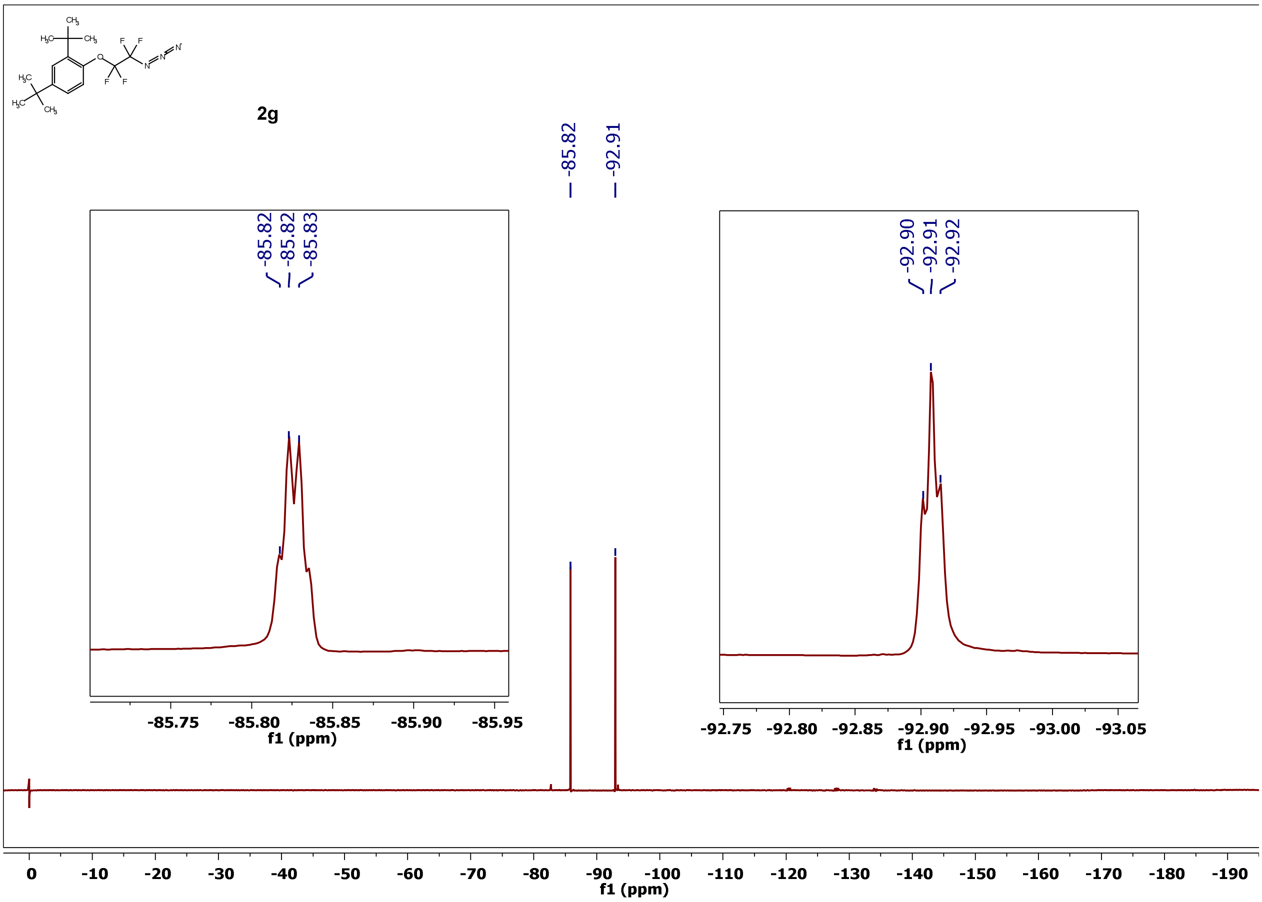
7.59
7.52
7.48
7.43
7.41
2.02
1.00
1.03
f1 (ppm)

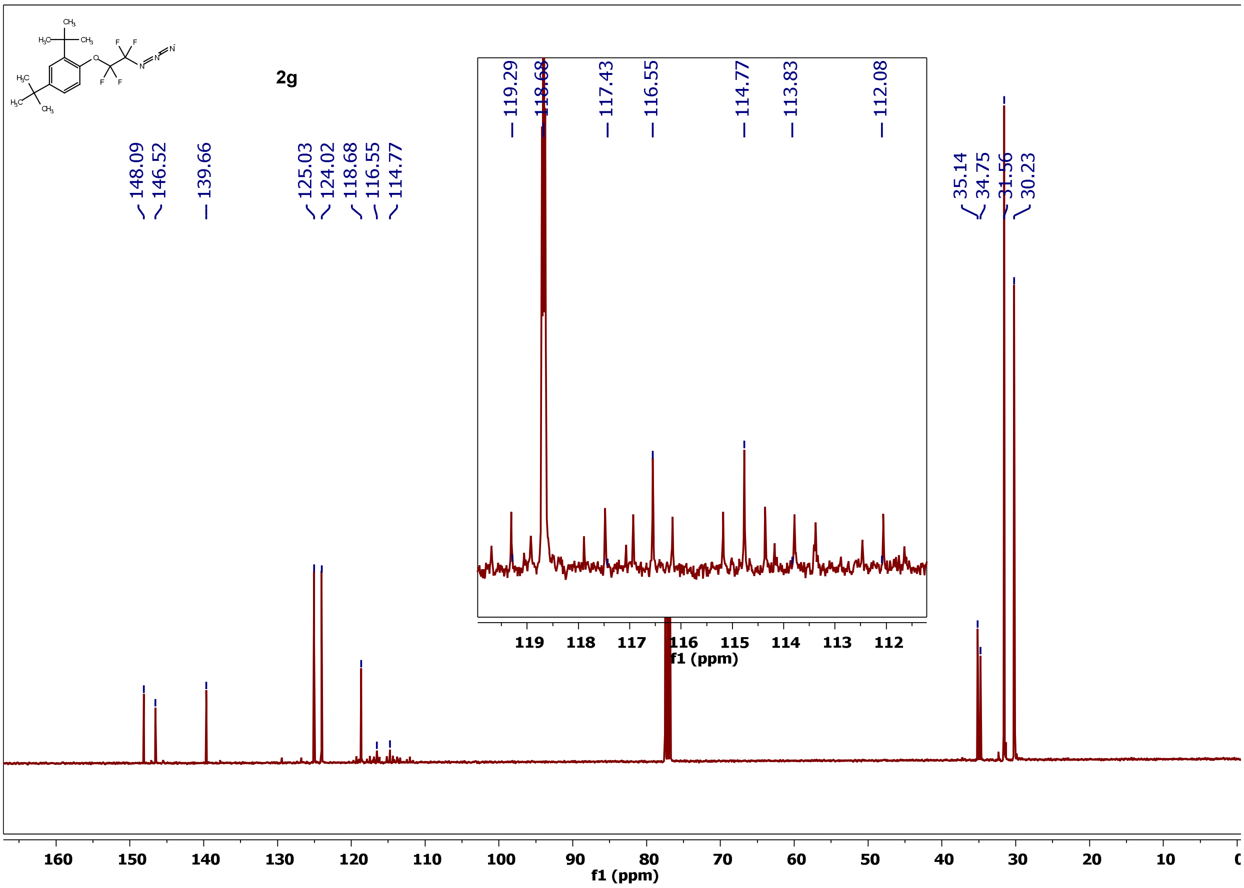
2f

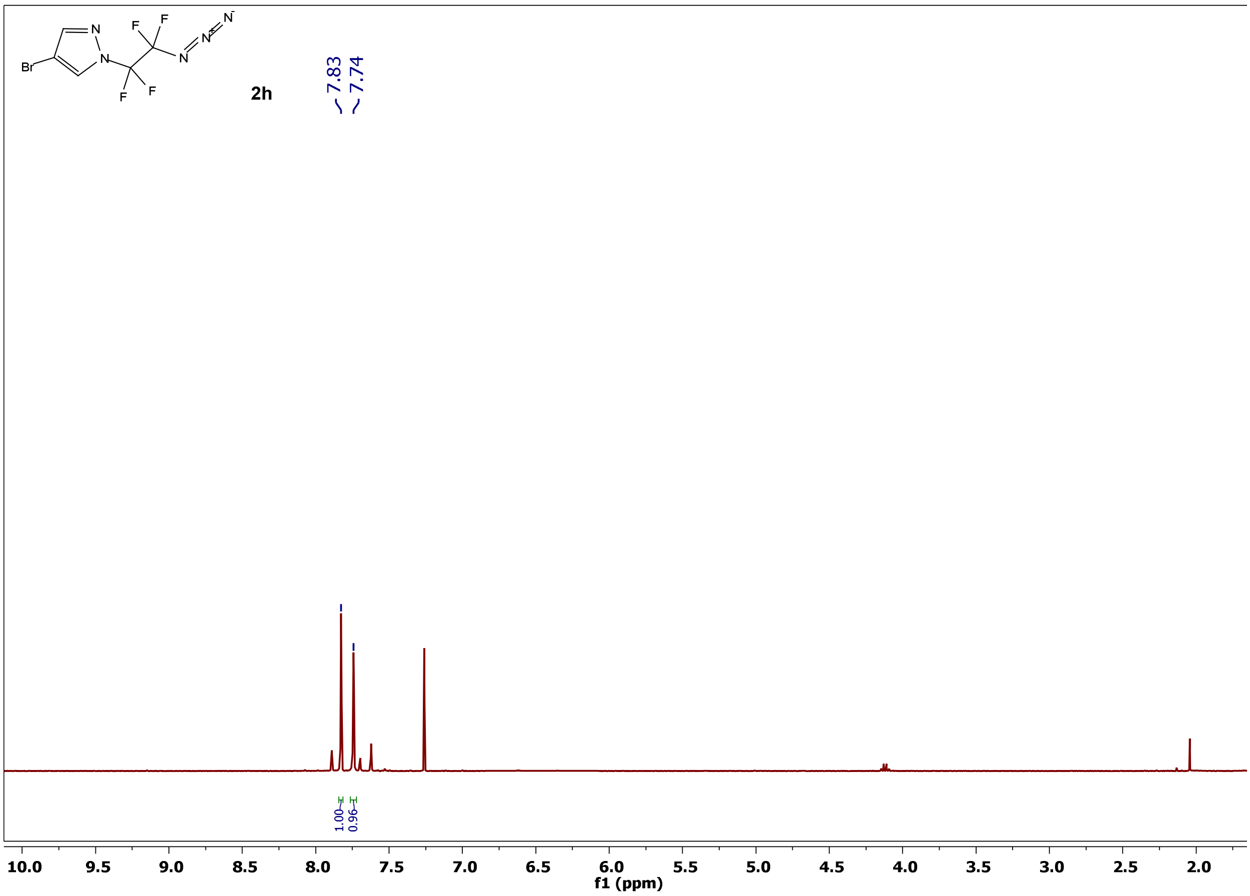

2f
-63.36
-87.39
-93.87
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


2f
148.99
132.91
132.58
130.66
125.11
124.77
123.83
119.03
116.26
114.41
117.16
116.27
114.41
113.48
111.69
f1 (ppm)

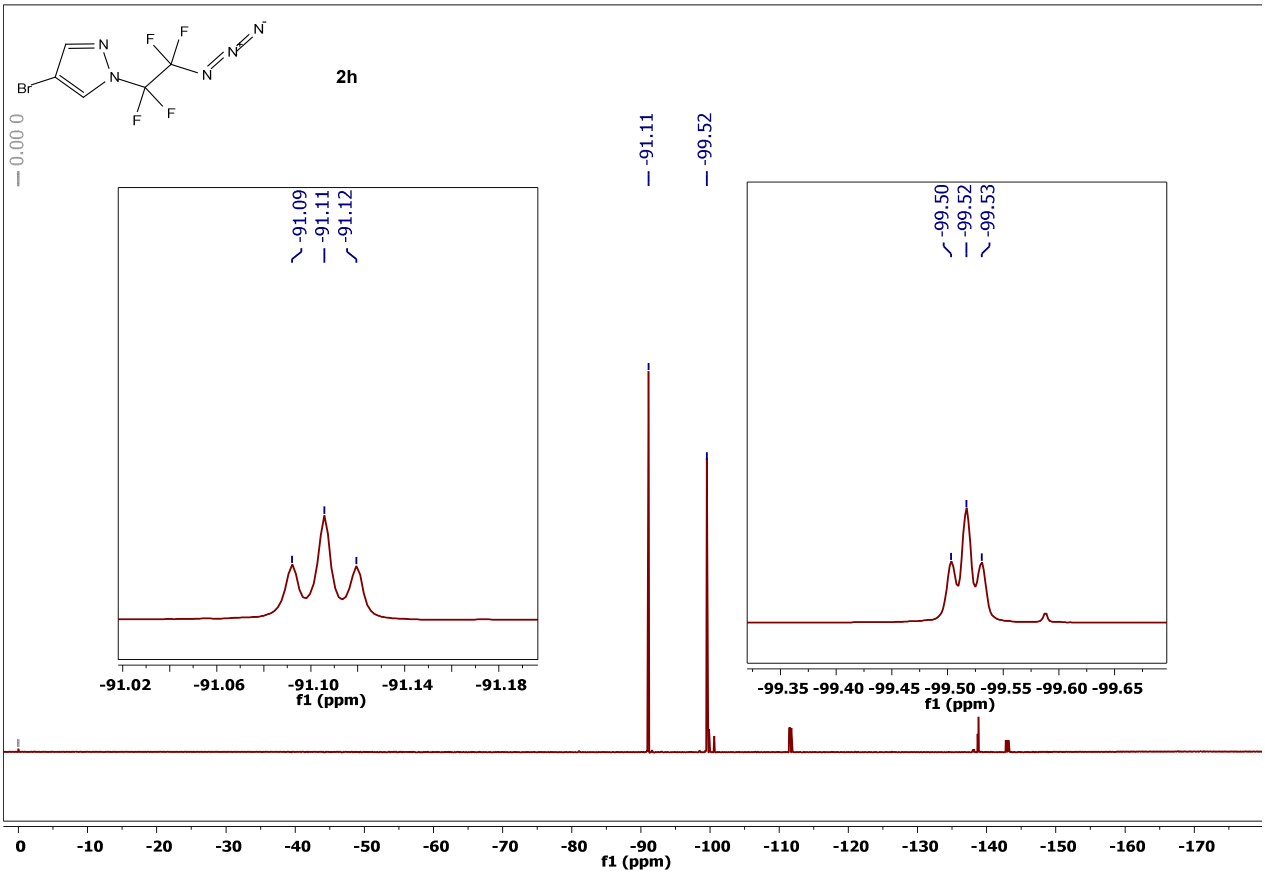

2g
7.42
7.42
7.28
7.25
7.22
7.19
7.423
7.417
7.281
7.250
7.216
7.188
1.39
1.32
1.00
1.47
1.02
9.00
9.01
f1 (ppm)

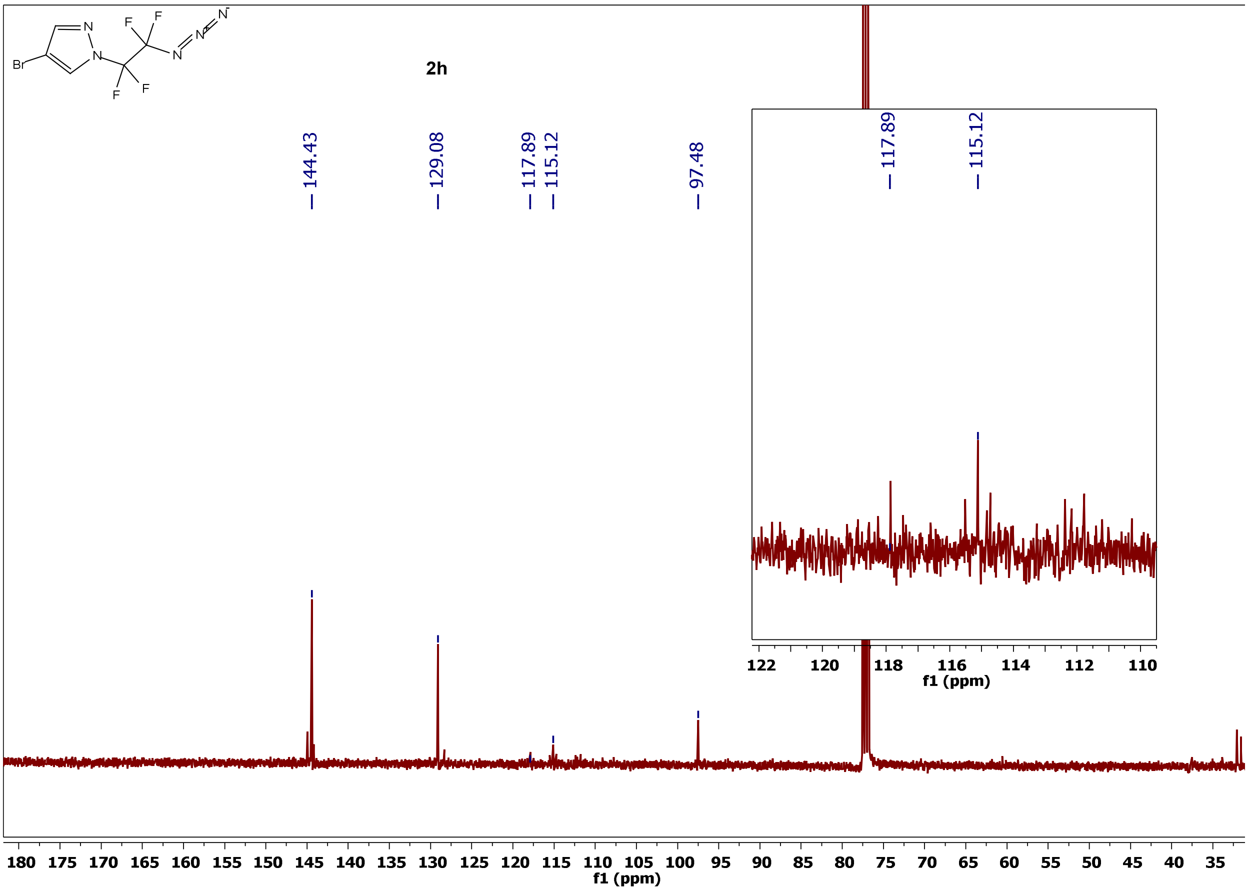

2g
-85.82
-92.91
-85.82
-85.82
-85.83
-92.90
-92.91
-92.92
f1 (ppm)

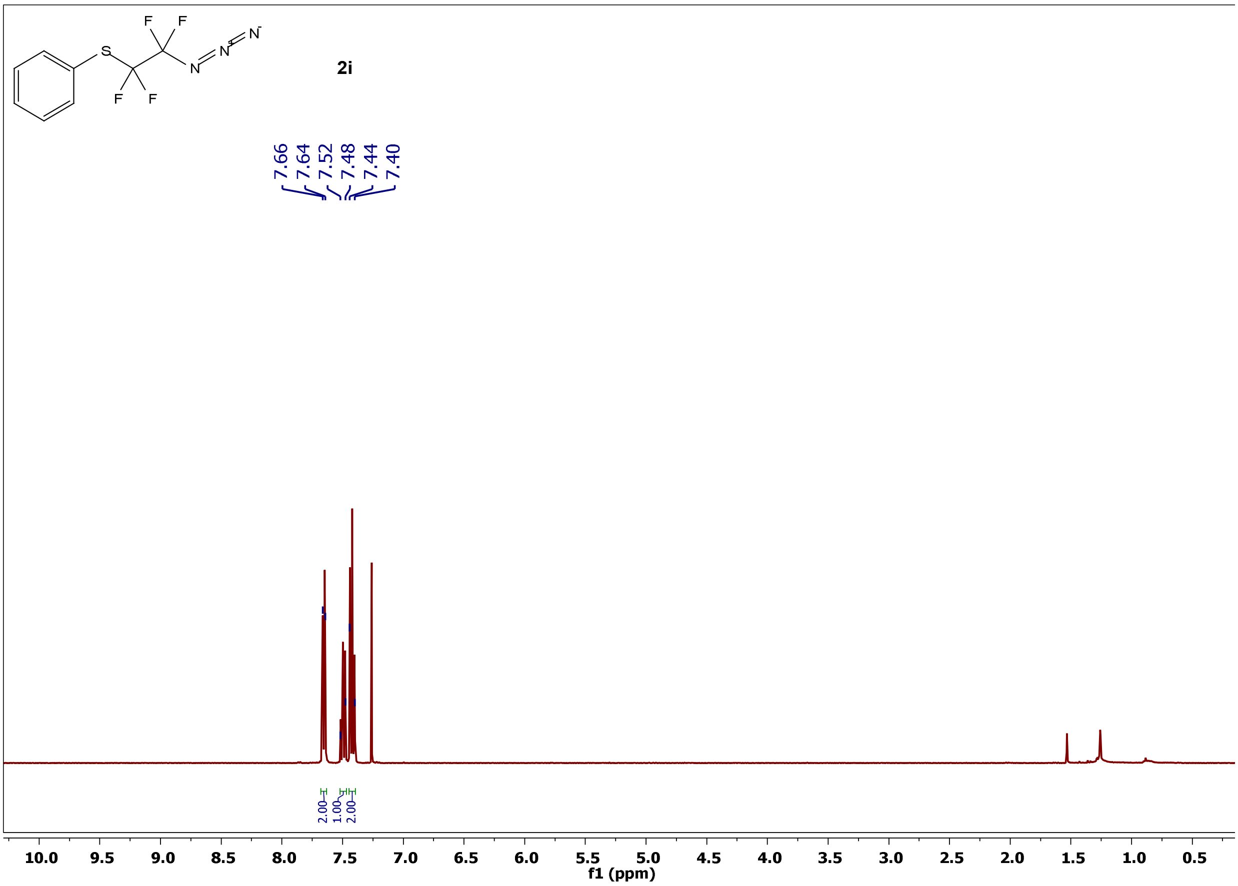

2g
148.09
146.52
139.66
125.03
124.02
118.68
116.55
114.77
35.14
34.75
31.56
30.23
119.29
118.68
117.43
116.55
114.77
113.83
112.08
f1 (ppm)
f1 (ppm)



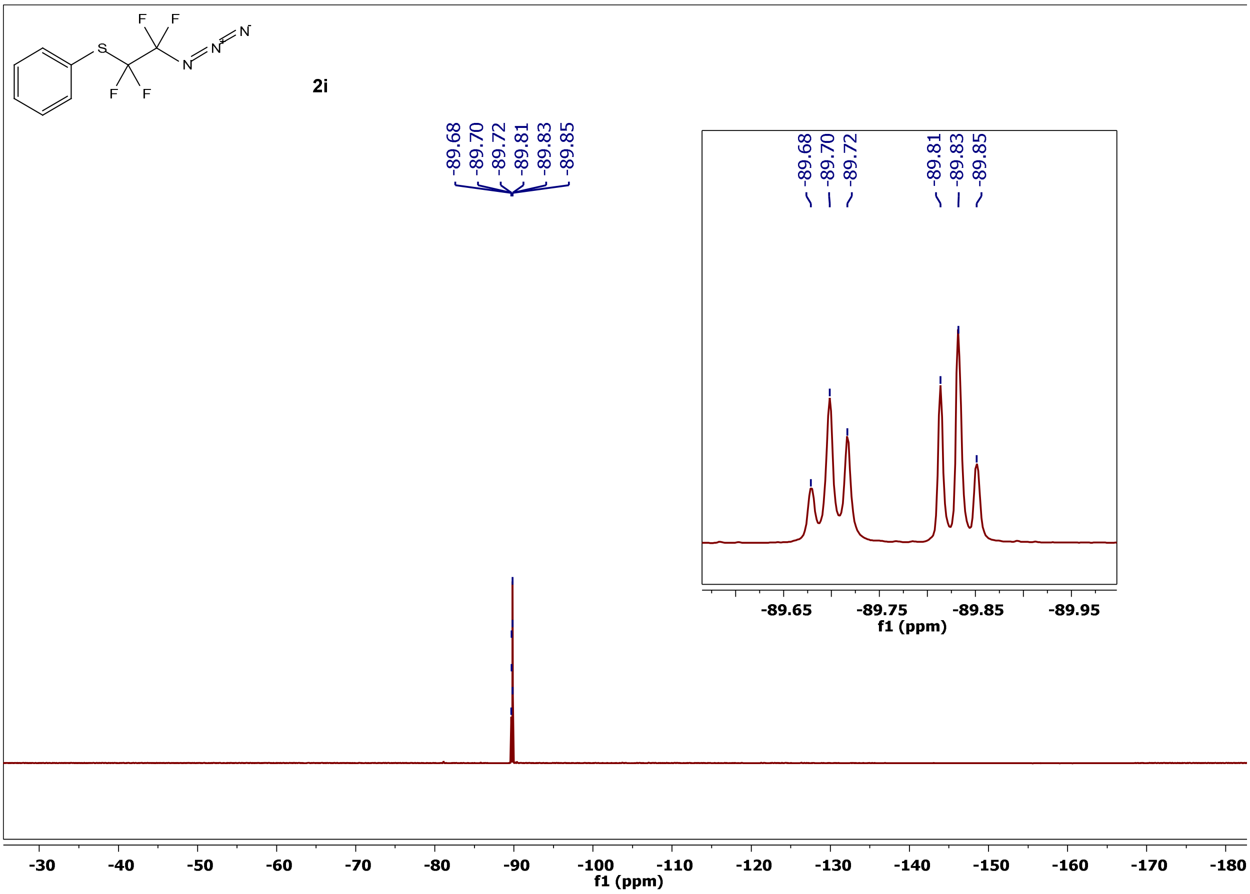
2h
7.83
7.74
1.00
0.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)


2h
-91.11
-99.52
-91.09
-91.11
-91.12
-99.50
-99.52
-99.53
f1 (ppm)

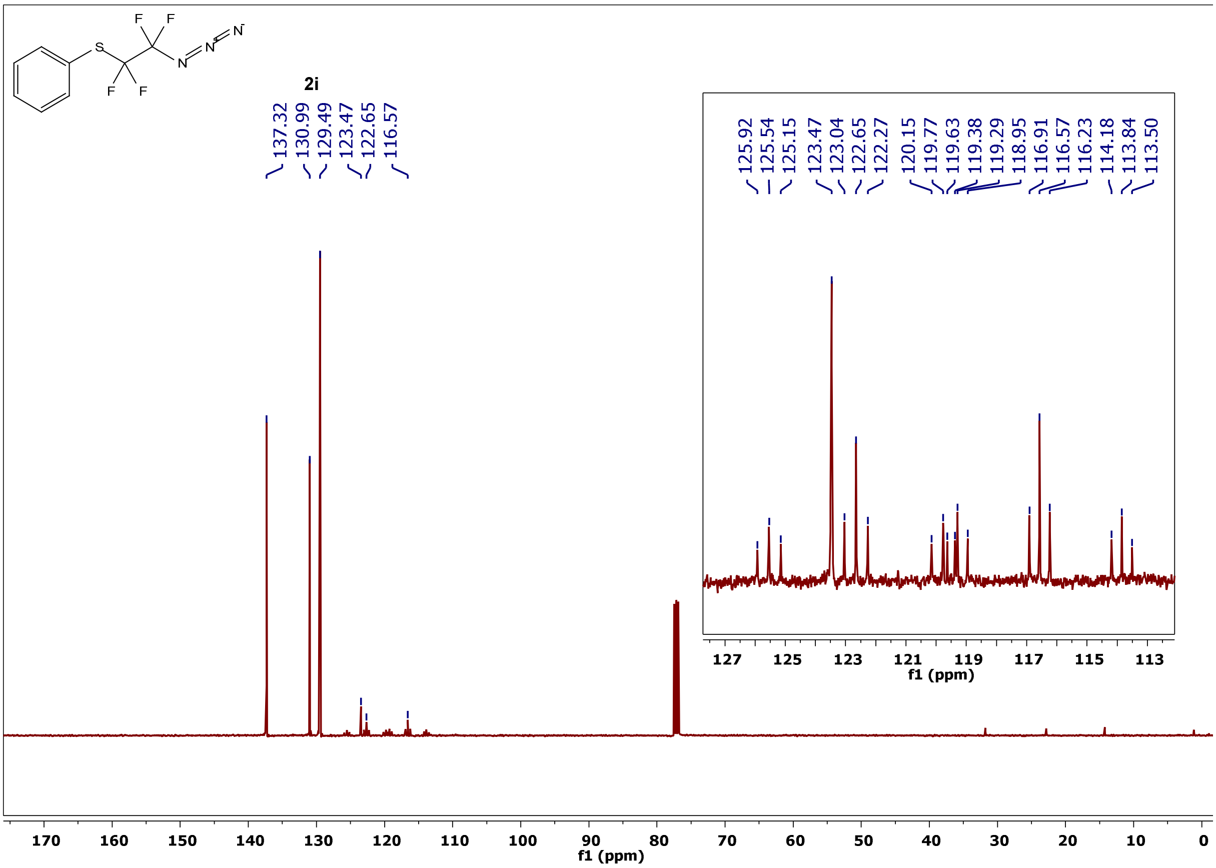

2h
144.43
129.08
117.89
115.12
97.48
f1 (ppm)

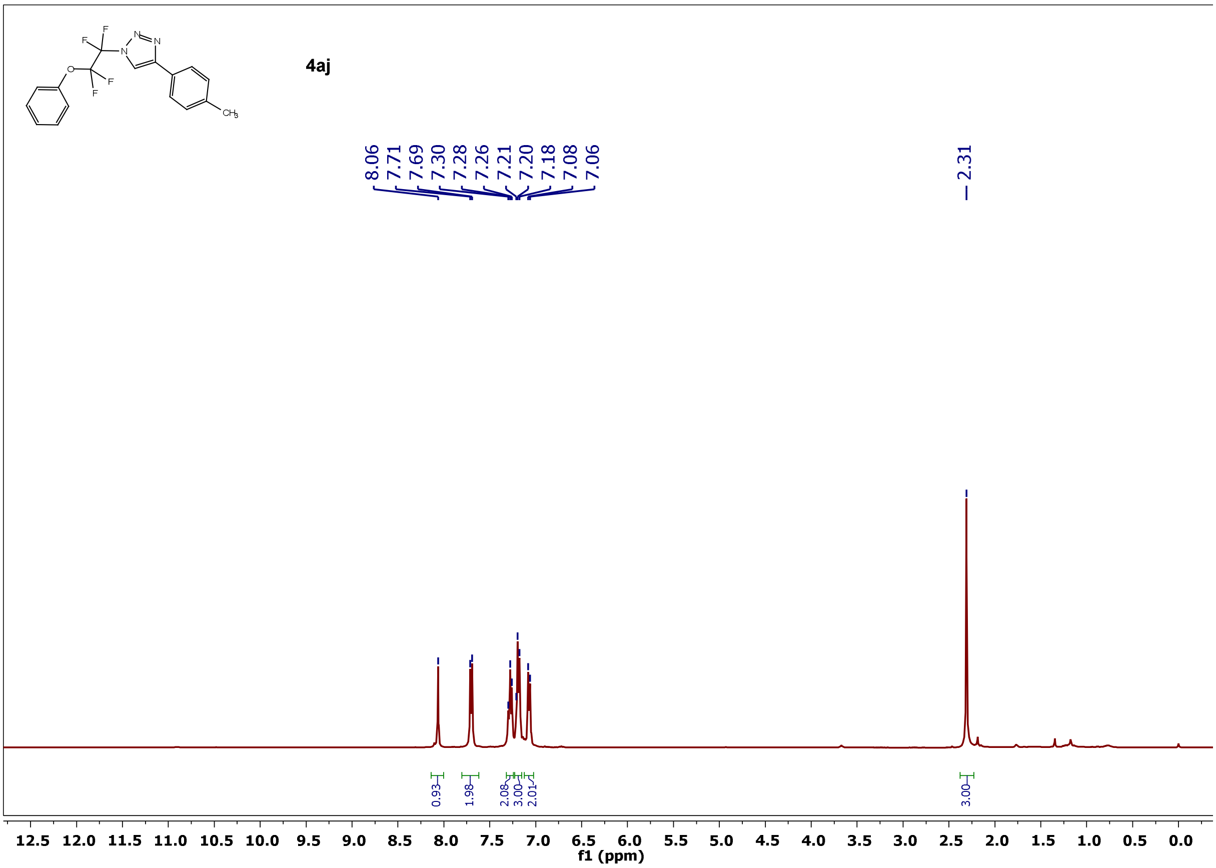


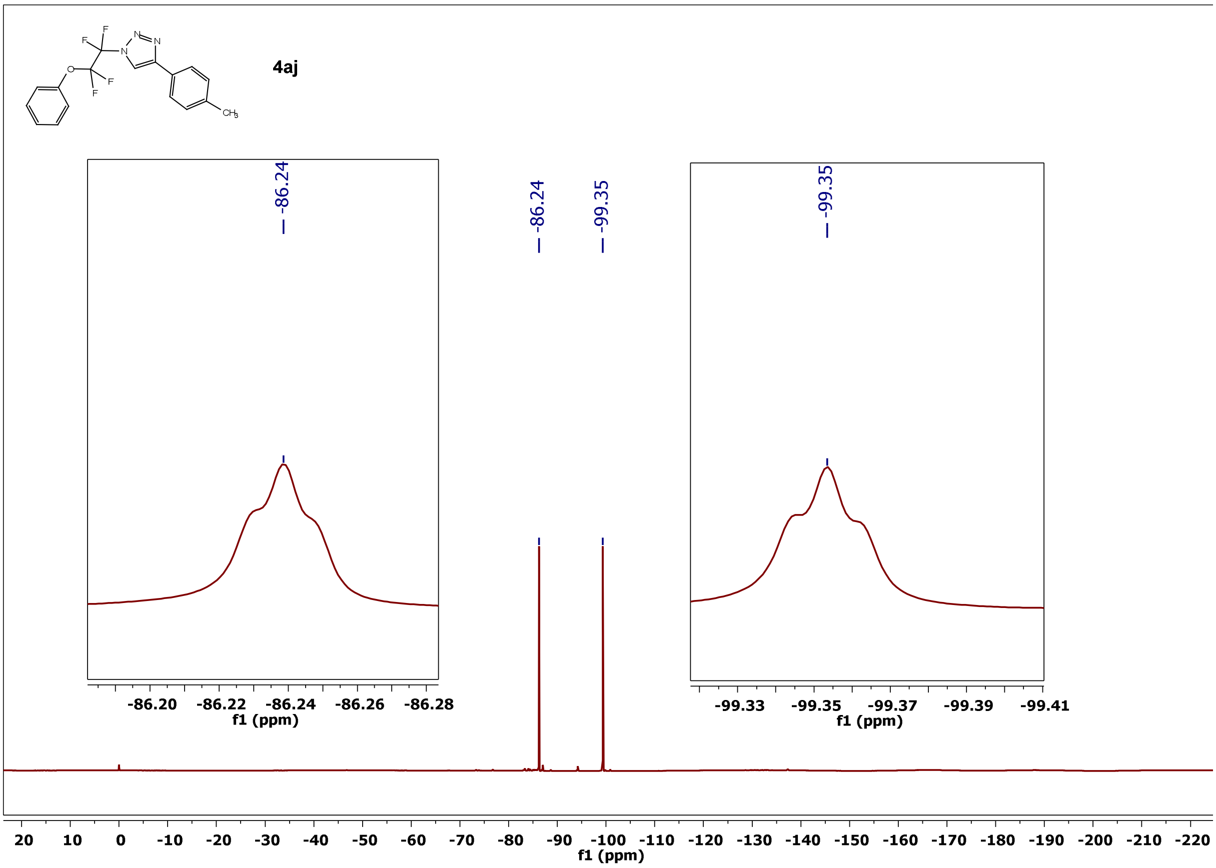
2i
7.66
7.64
7.52
7.48
7.44
7.40
2.00
1.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

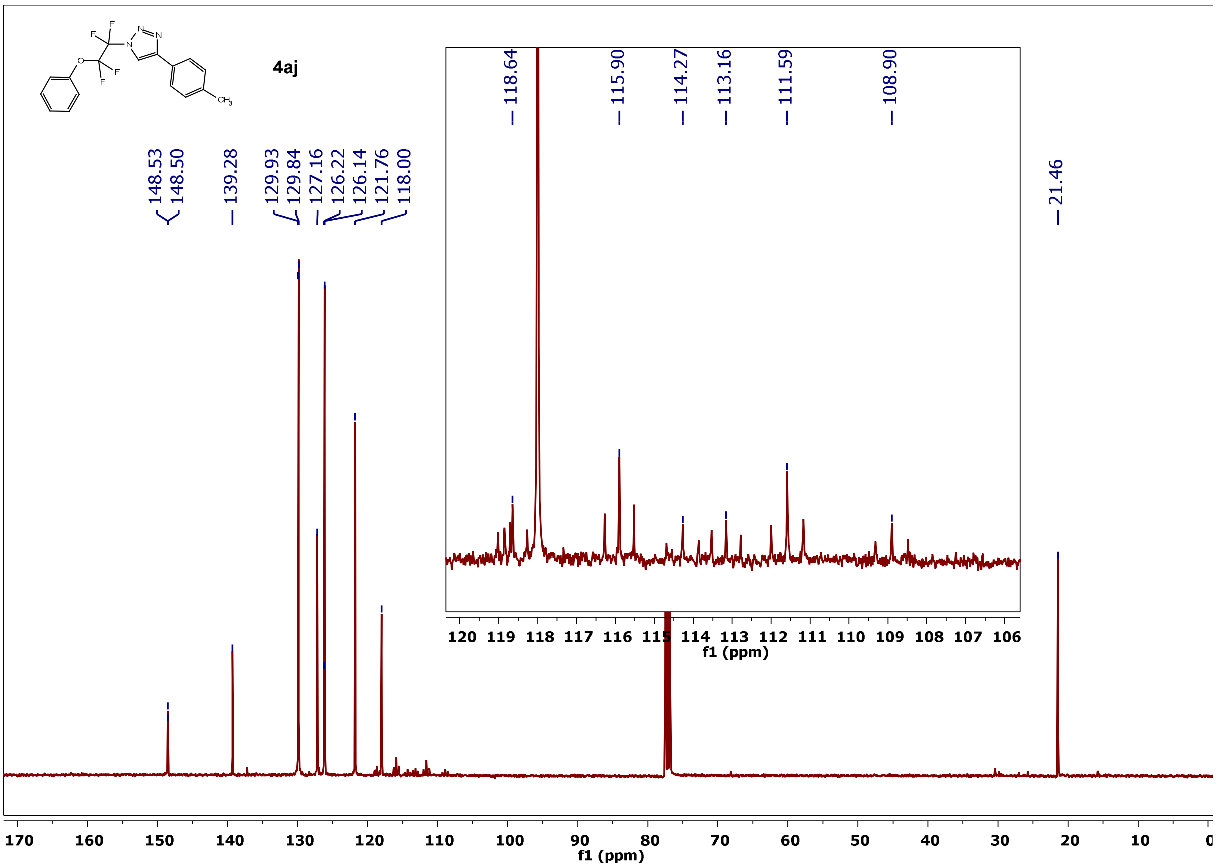


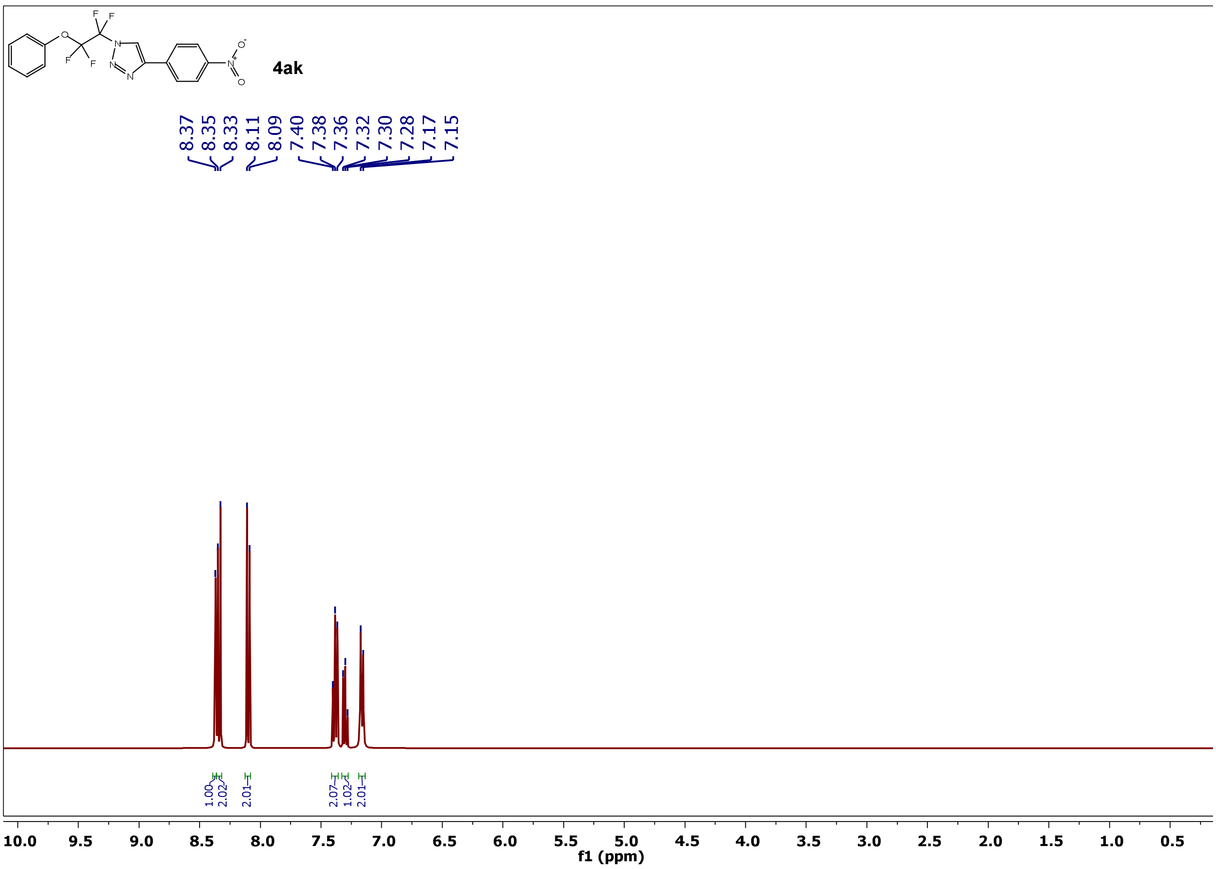
2i
-89.68
-89.70
-89.72
-89.81
-89.83
-89.85
-89.65
-89.75
-89.85
-89.95
f1 (ppm)
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

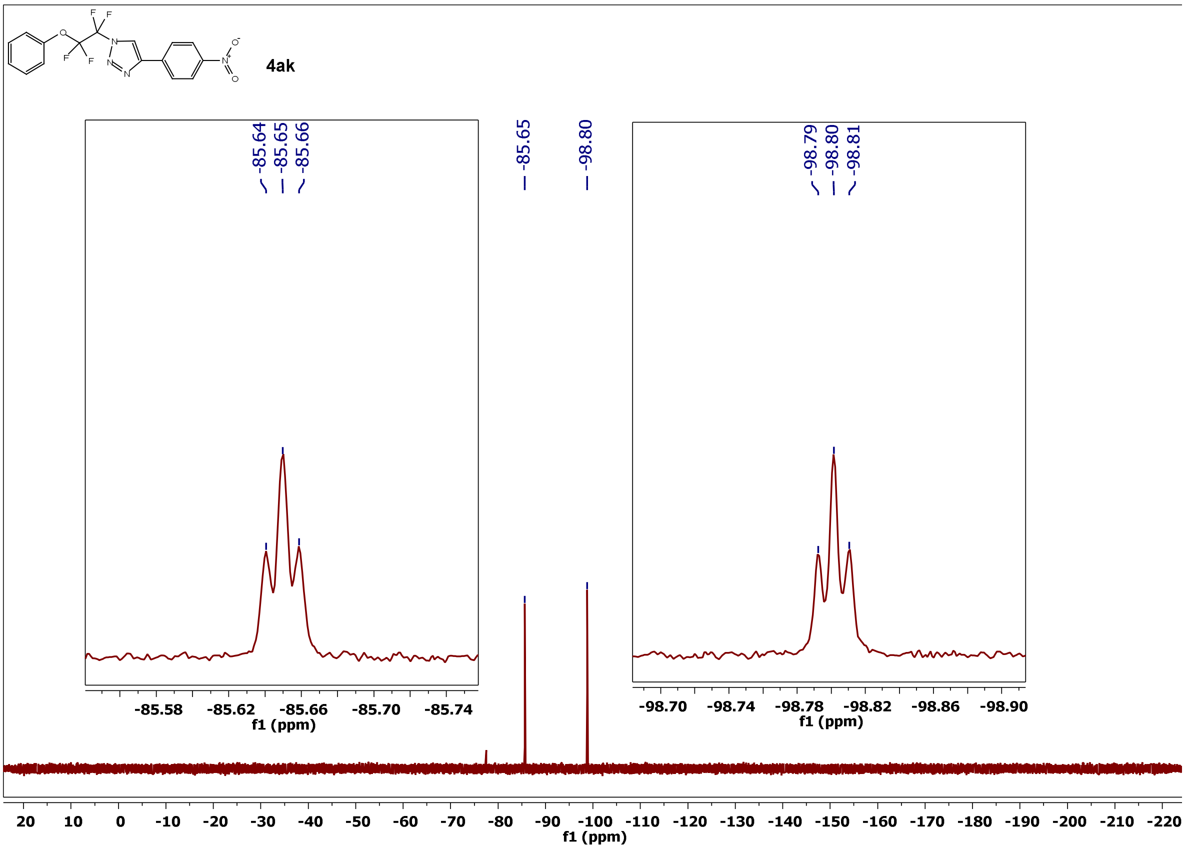

2i
137.32
130.99
129.49
123.47
122.65
116.57
125.92
125.54
125.15
123.47
123.04
122.65
122.27
120.15
119.77
119.63
119.38
119.29
118.95
116.91
116.57
116.23
114.18
113.84
113.50
127
125
123
121
119
117
115
113
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

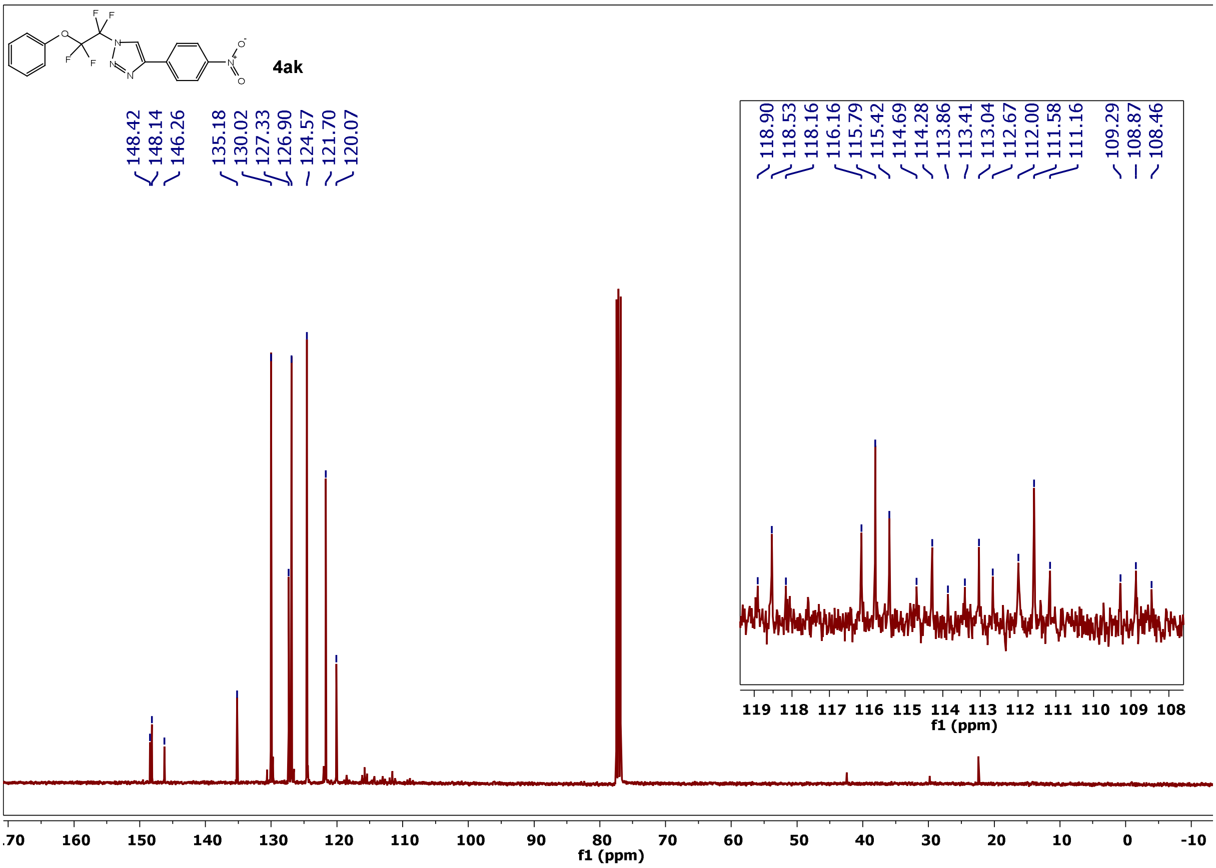

4aj
8.06
7.71
7.69
7.30
7.28
7.26
7.21
7.20
7.18
7.08
7.06
2.31
0.93
1.98
2.08
3.00
2.01
3.00
f1 (ppm)

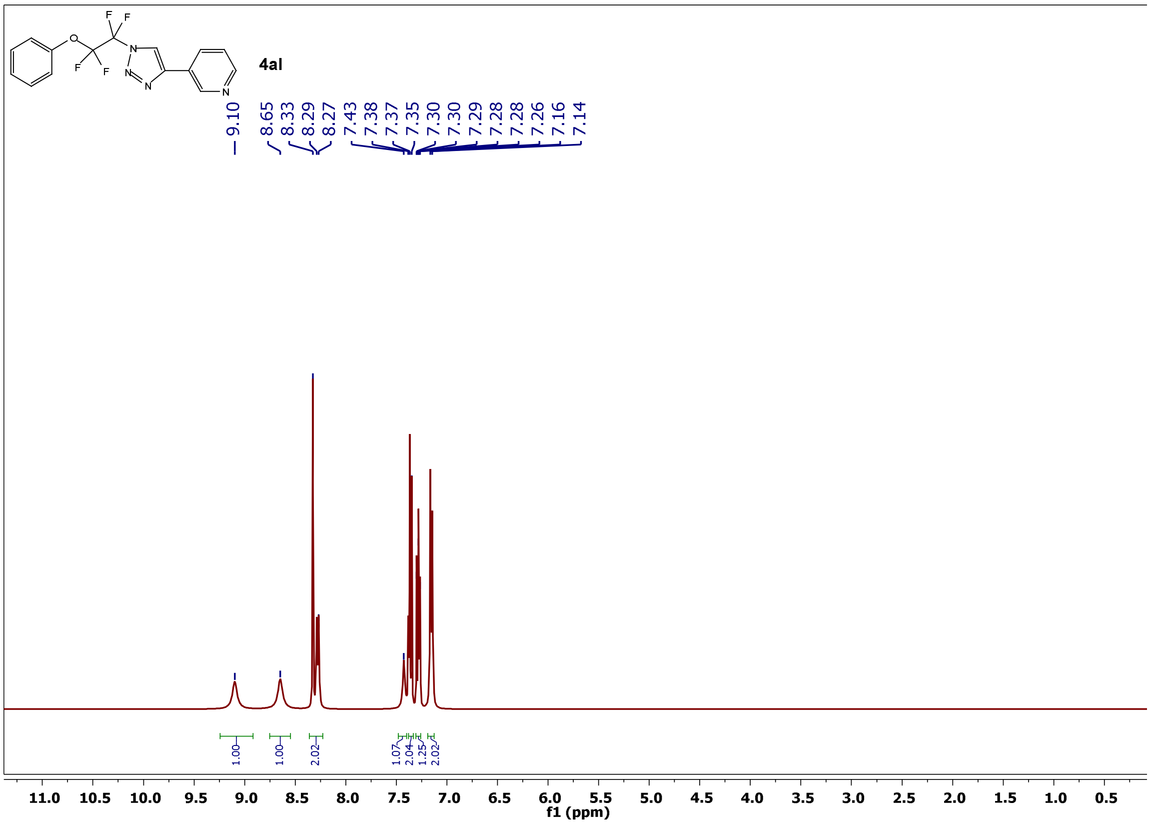

4aj
-86.24
-99.35
f1 (ppm)

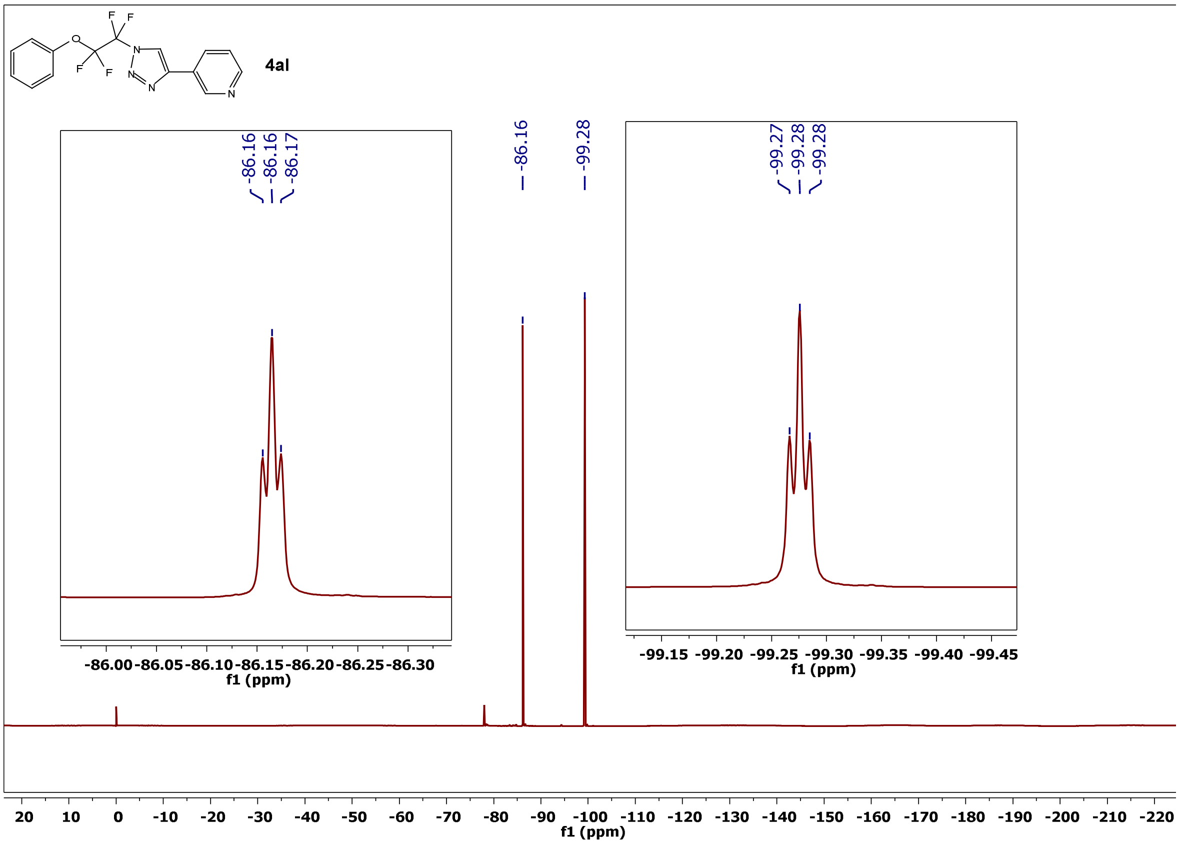

4aj
148.53
148.50
139.28
129.93
129.84
127.16
126.22
126.14
121.76
118.00
21.46
118.64
115.90
114.27
113.16
111.59
108.90
f1 (ppm)

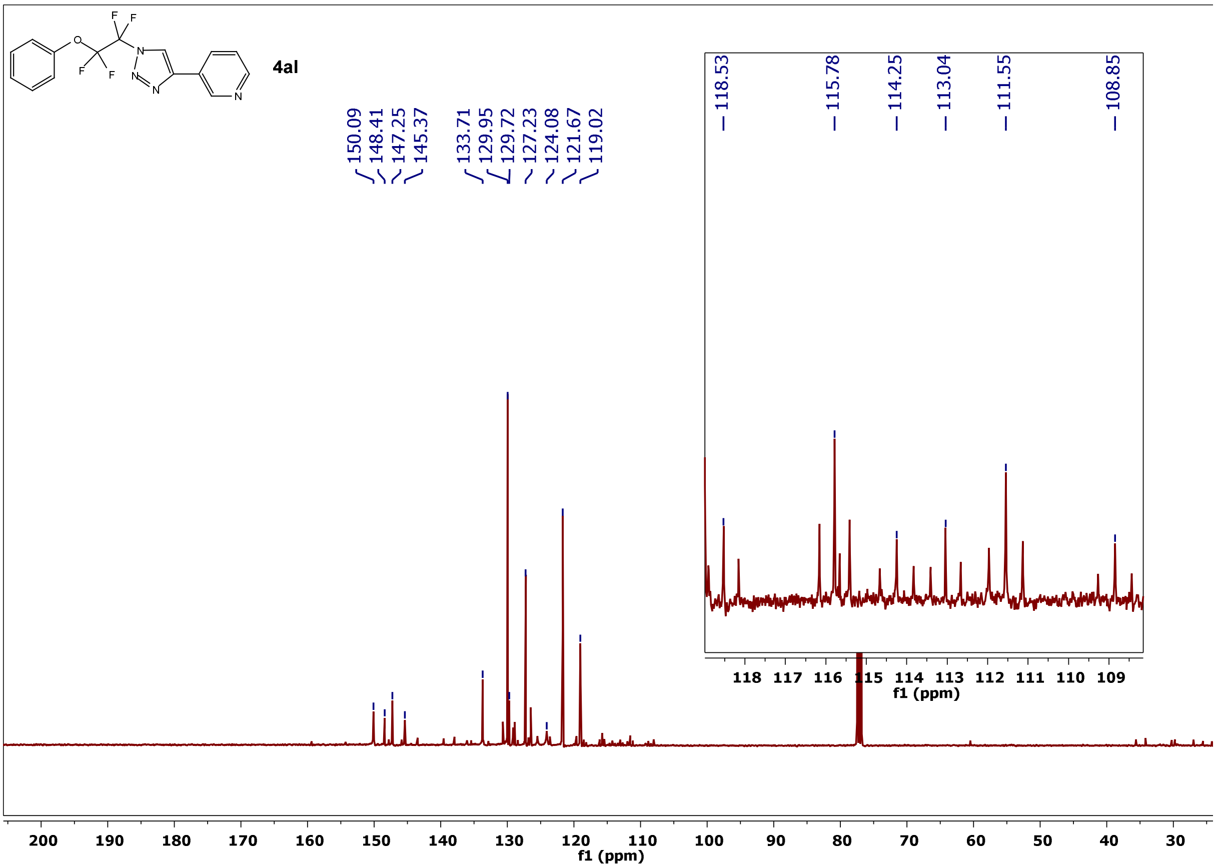

4ak
8.37
8.35
8.33
8.11
8.09
7.40
7.38
7.36
7.32
7.30
7.28
7.17
7.15
1.00
2.02
2.01
2.07
1.02
2.01
f1 (ppm)


4ak
-85.64
-85.65
-85.66
-85.65
-98.80
-98.79
-98.80
-98.81
-85.58 -85.62 -85.66 -85.70 -85.74
f1 (ppm)
-98.70 -98.74 -98.78 -98.82 -98.86 -98.90
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)

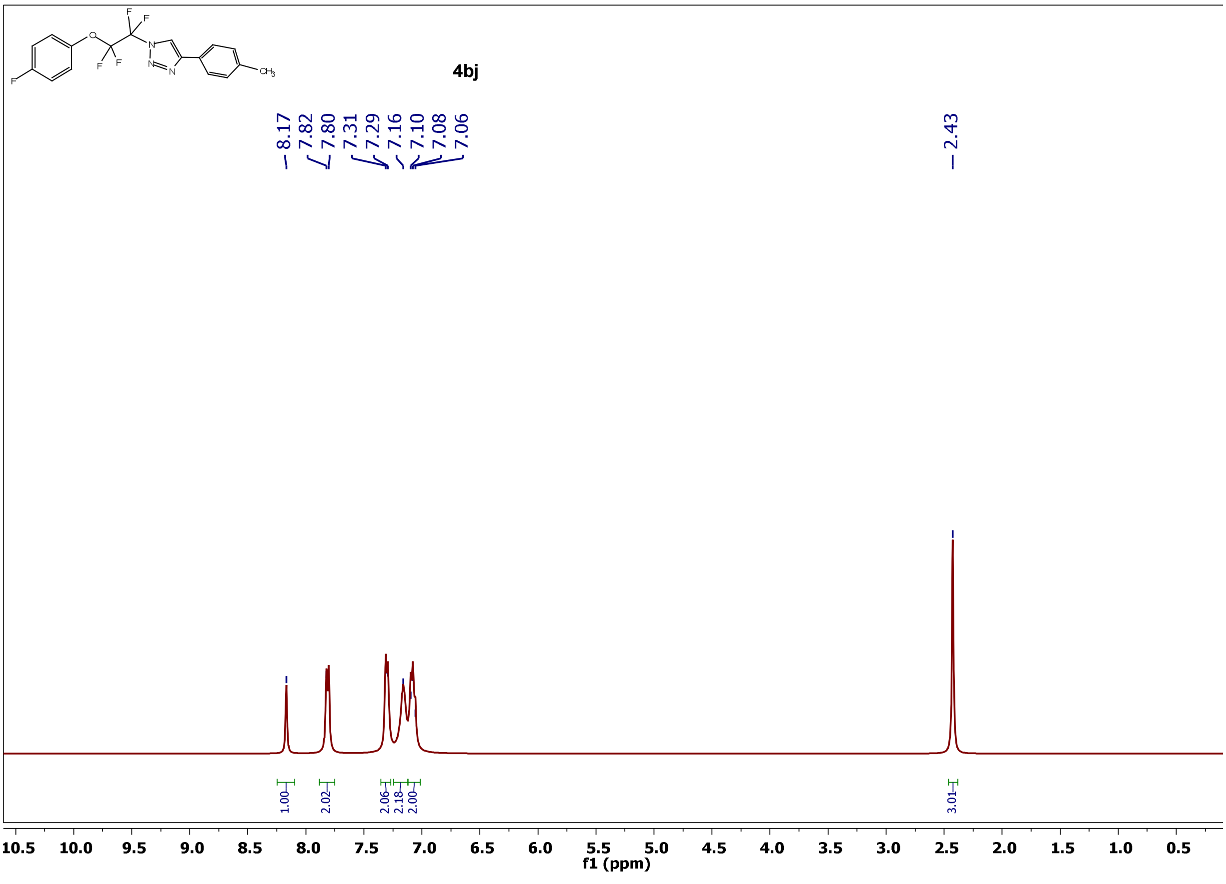

4ak
148.42
148.14
146.26
135.18
130.02
127.33
126.90
124.57
121.70
120.07
118.90
118.53
118.16
116.16
115.79
115.42
114.69
114.28
113.86
113.41
113.04
112.67
112.00
111.58
111.16
109.29
108.87
108.46
119 118 117 116 115 114 113 112 111 110 109 108
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4al
9.10
8.65
8.33
8.29
8.27
7.43
7.38
7.37
7.35
7.30
7.30
7.29
7.28
7.28
7.26
7.16
7.14
1.00
1.00
2.02
1.07
2.04
1.25
2.02
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
f1 (ppm)

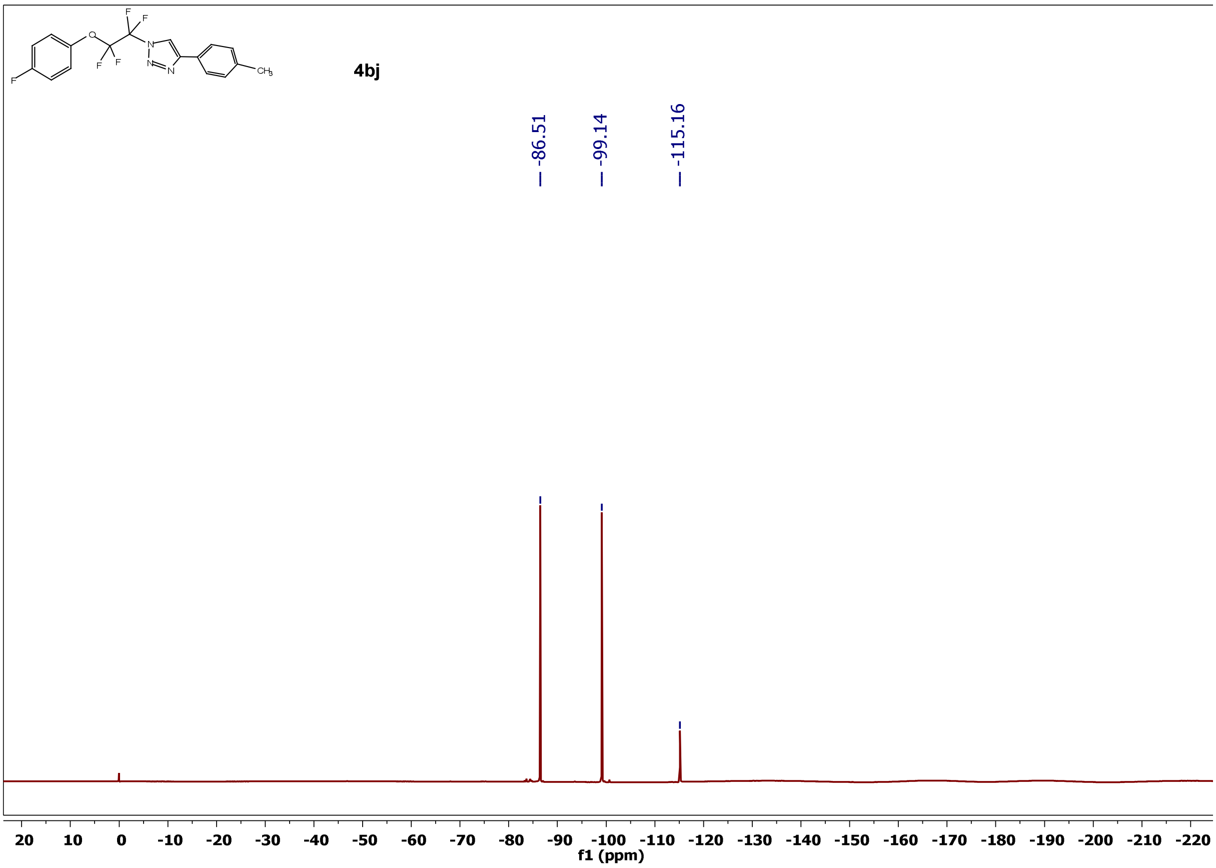

4al
-86.16
-86.16
-86.17
-86.16
-99.28
-99.27
-99.28
-99.28
-86.00 -86.05 -86.10 -86.15 -86.20 -86.25 -86.30
f1 (ppm)
-99.15 -99.20 -99.25 -99.30 -99.35 -99.40 -99.45
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

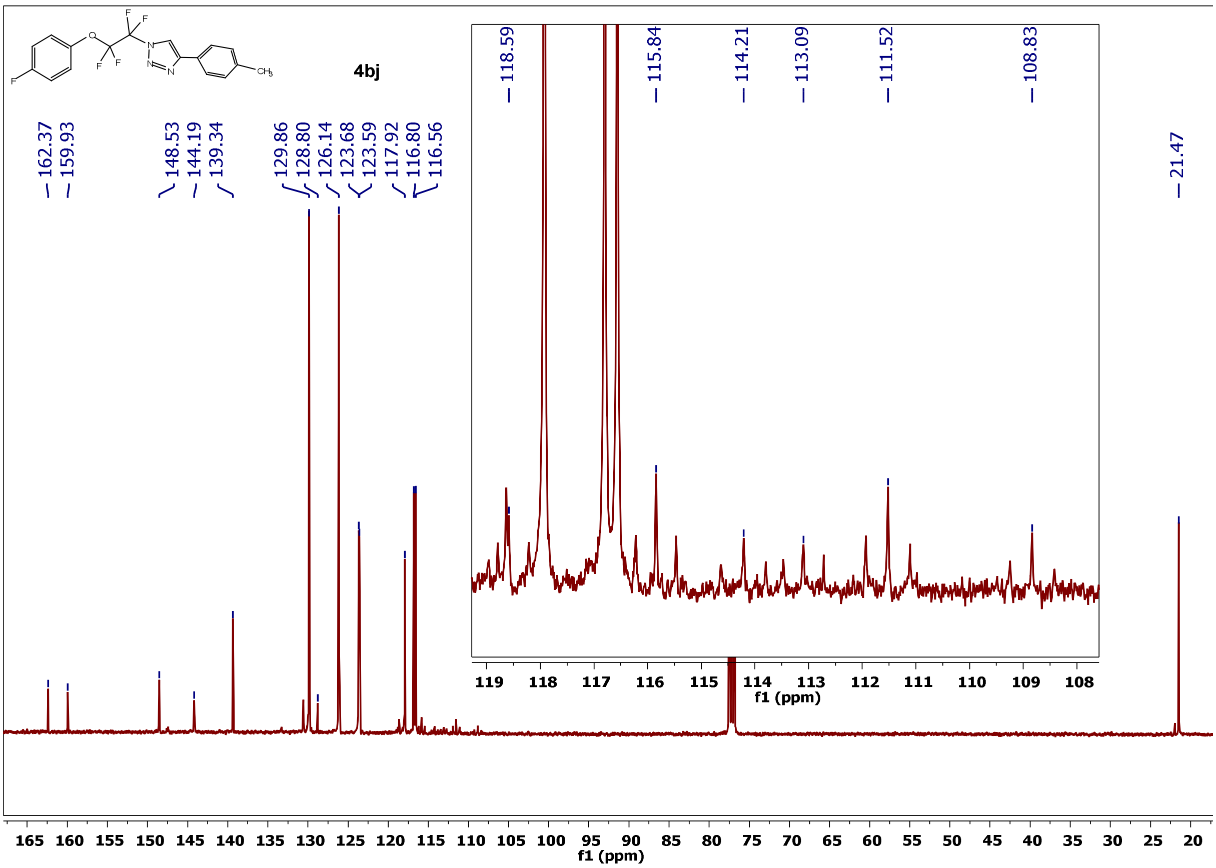


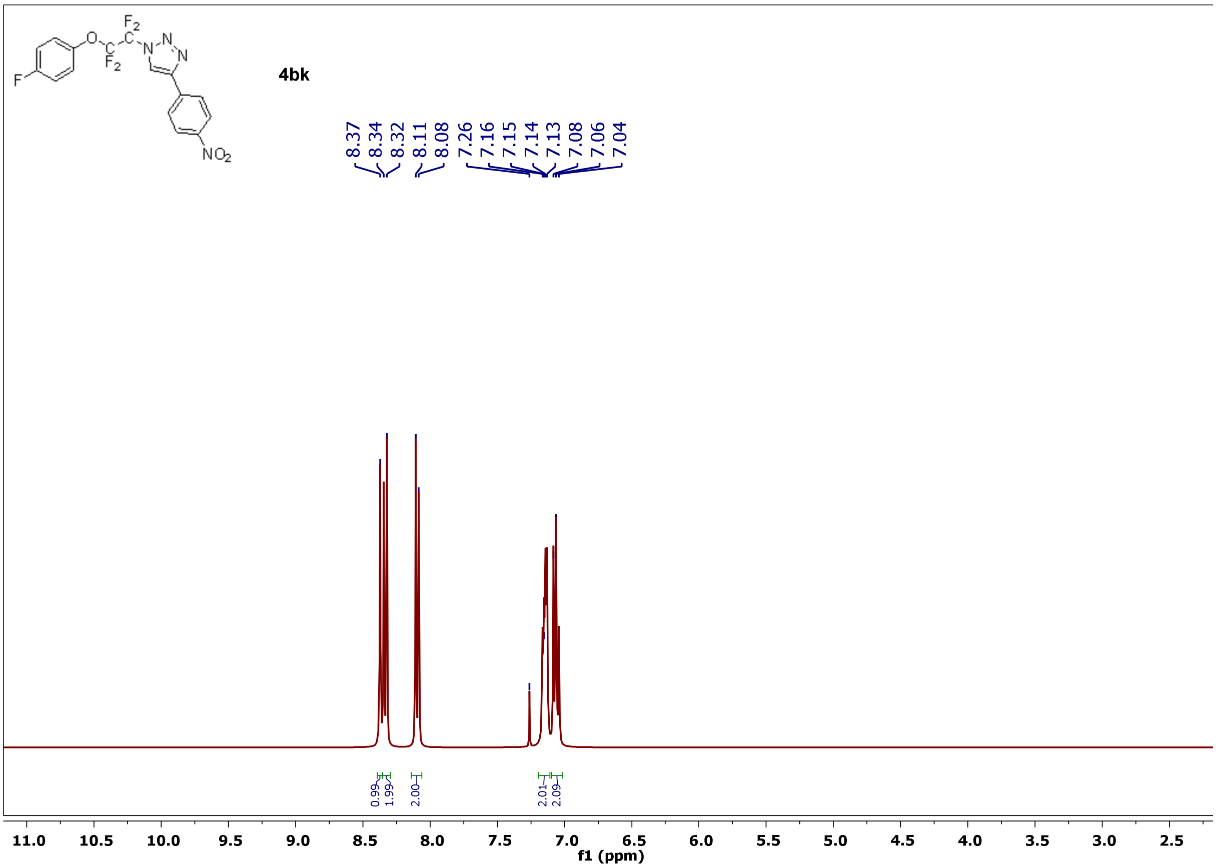
4al
150.09
148.41
147.25
145.37
133.71
129.95
129.72
127.23
124.08
121.67
119.02
118.53
115.78
114.25
113.04
111.55
108.85
f1 (ppm)

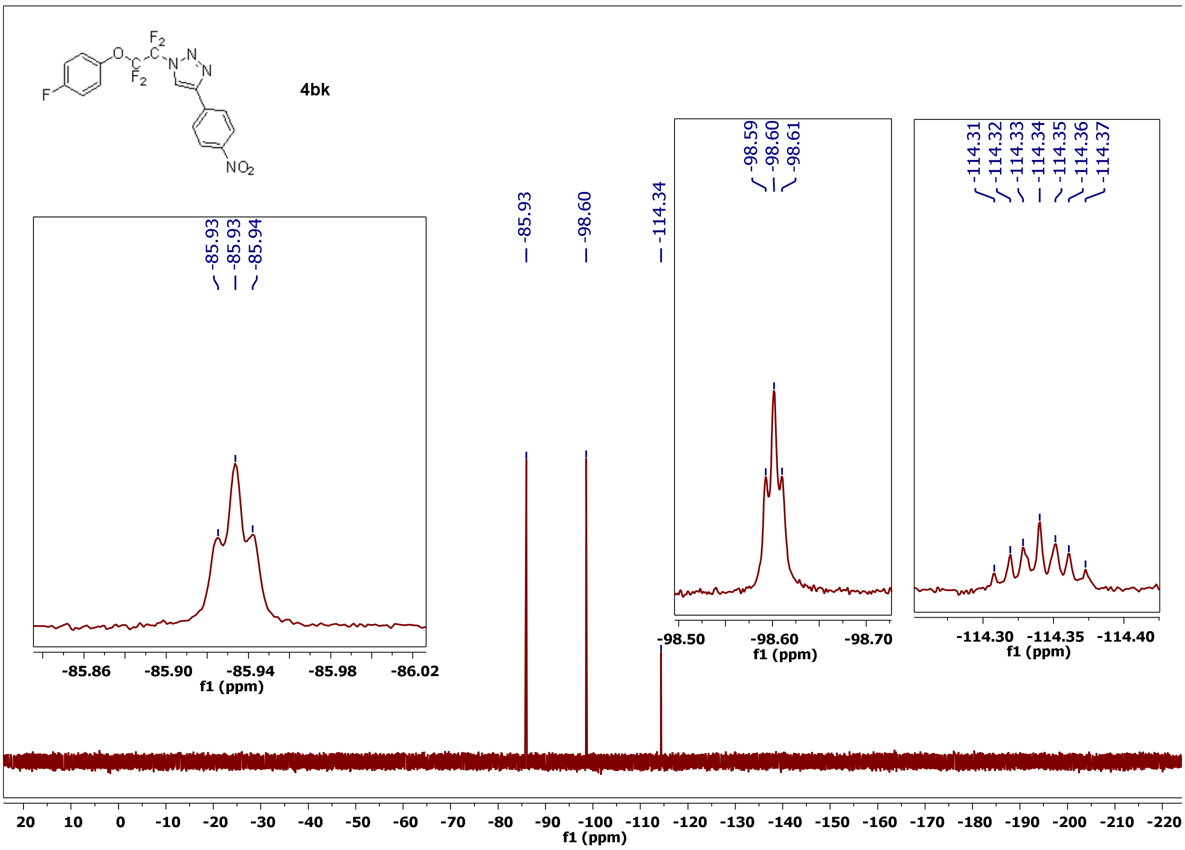


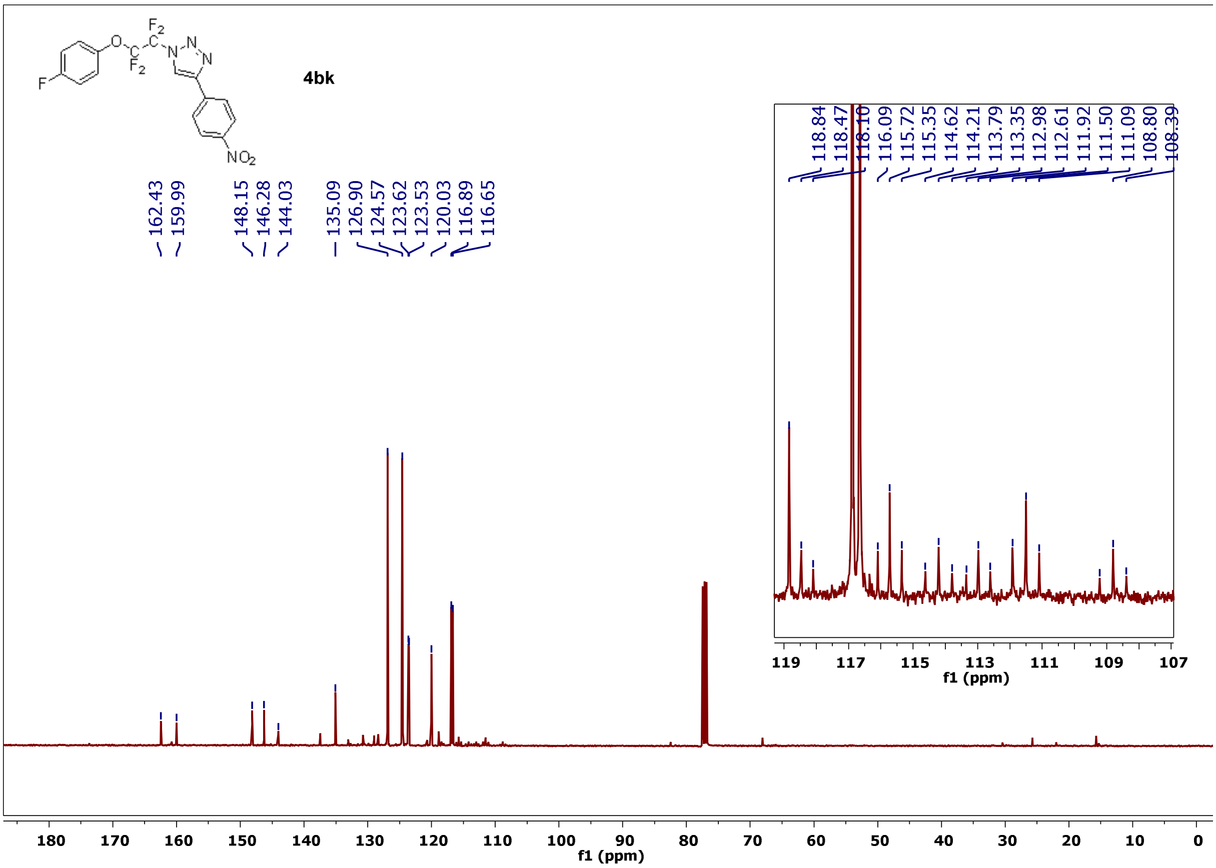
4bj
8.17
7.82
7.80
7.31
7.29
7.16
7.10
7.08
7.06
2.43
1.00
2.02
2.06
2.18
2.00
3.01
f1 (ppm)


4bj
-86.51
-99.14
-115.16
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)

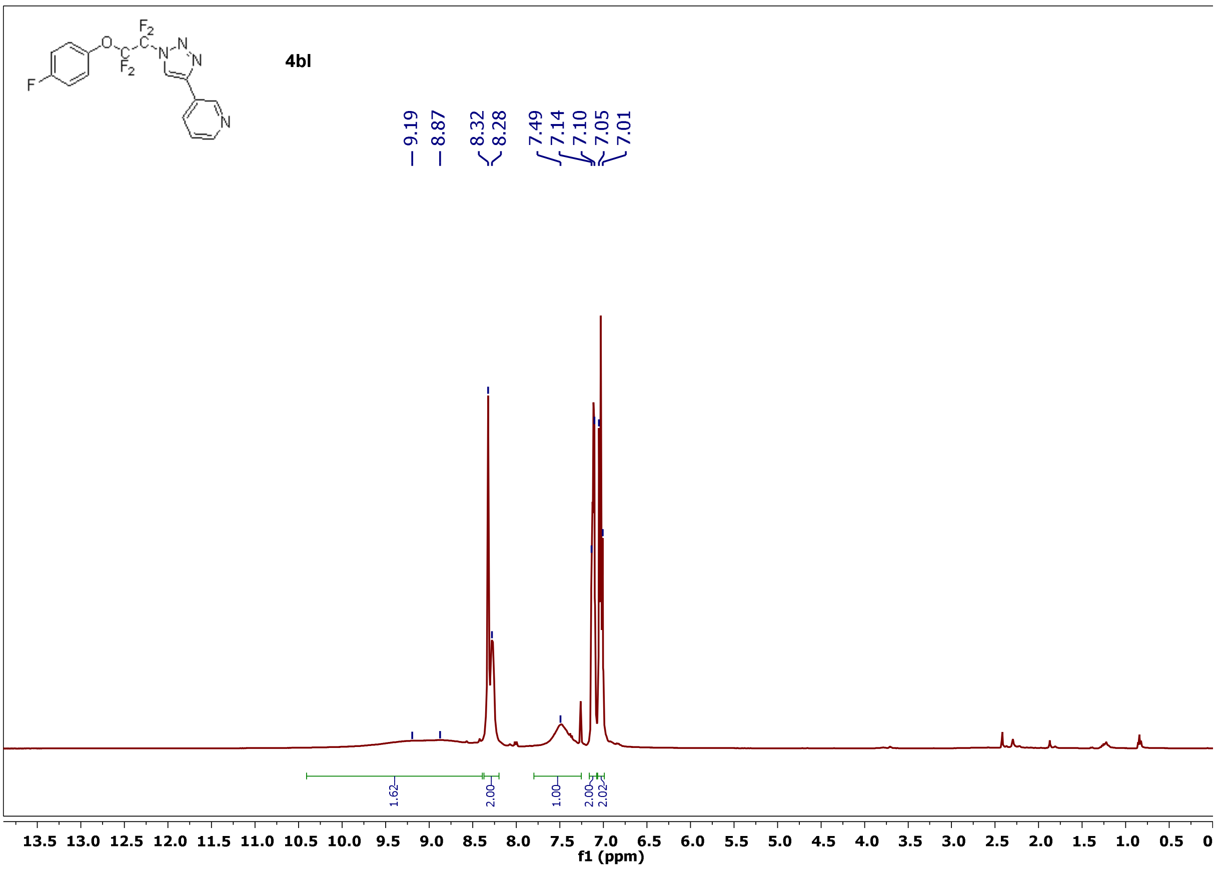

4bj
162.37
159.93
148.53
144.19
139.34
129.86
128.80
126.14
123.68
123.59
117.92
116.80
116.56
21.47
118.59
115.84
114.21
113.09
111.52
108.83
119 118 117 116 115 114 113 112 111 110 109 108
f1 (ppm)
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)


4bk
8.37
8.34
8.32
8.11
8.08
7.26
7.16
7.15
7.14
7.13
7.08
7.06
7.04
0.99
1.99
2.00
2.01
2.09
f1 (ppm)

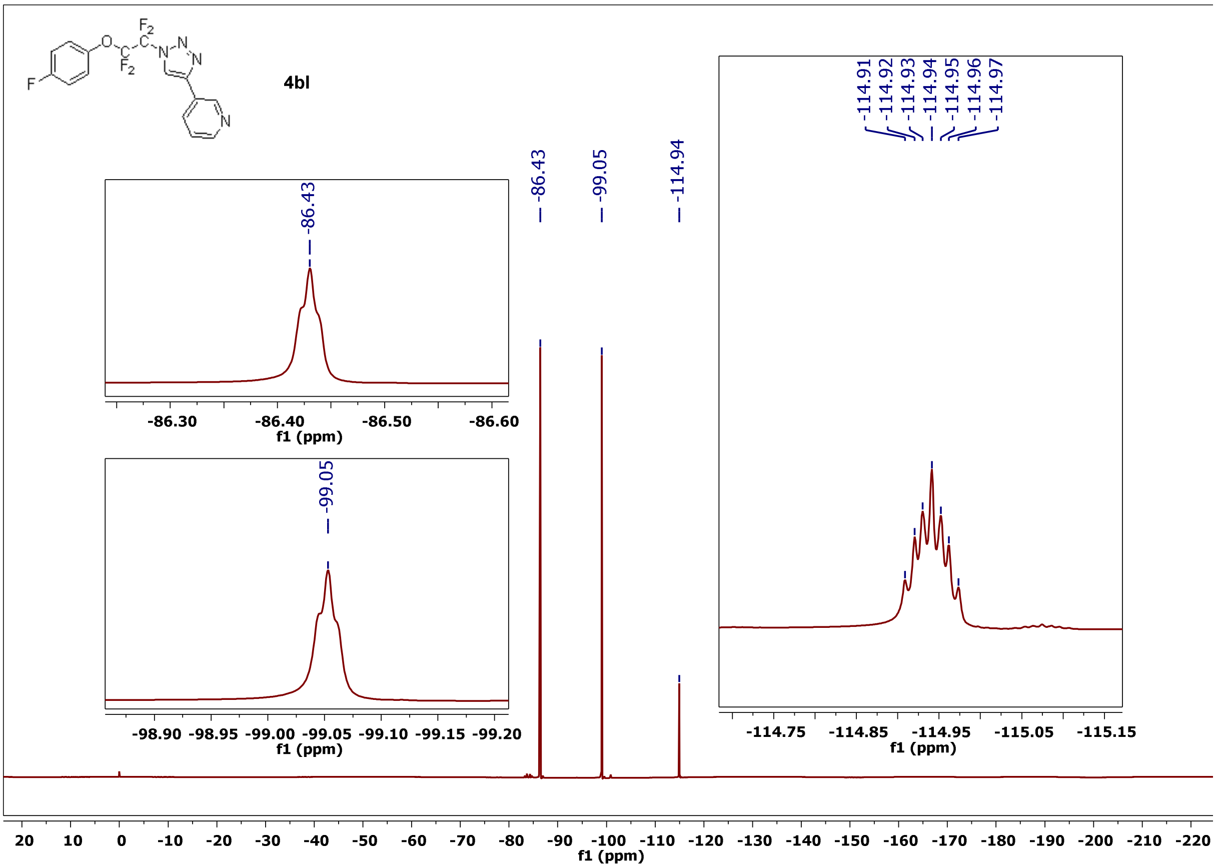

4bk
-85.93
-98.60
-114.34
-85.93
-85.93
-85.94
-98.59
-98.60
-98.61
-114.31
-114.32
-114.33
-114.34
-114.35
-114.36
-114.37
f1 (ppm)

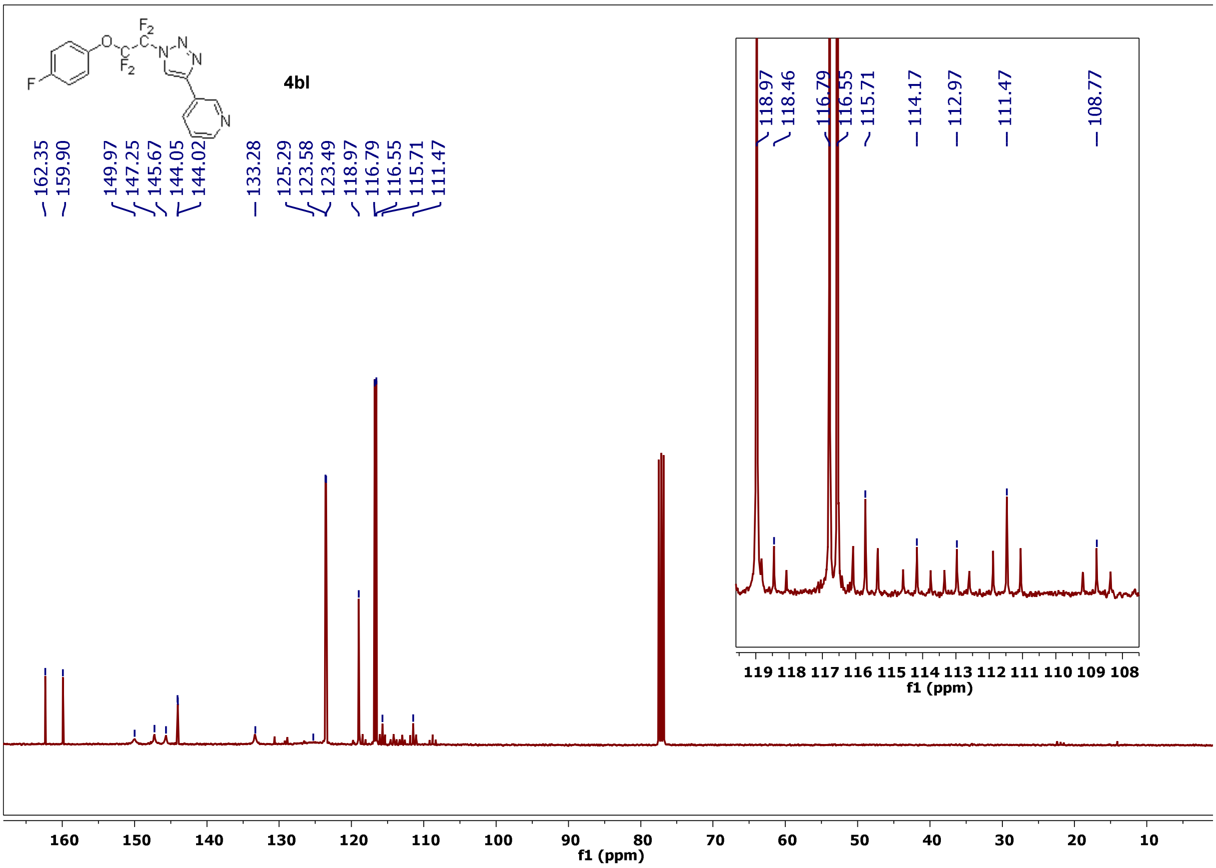


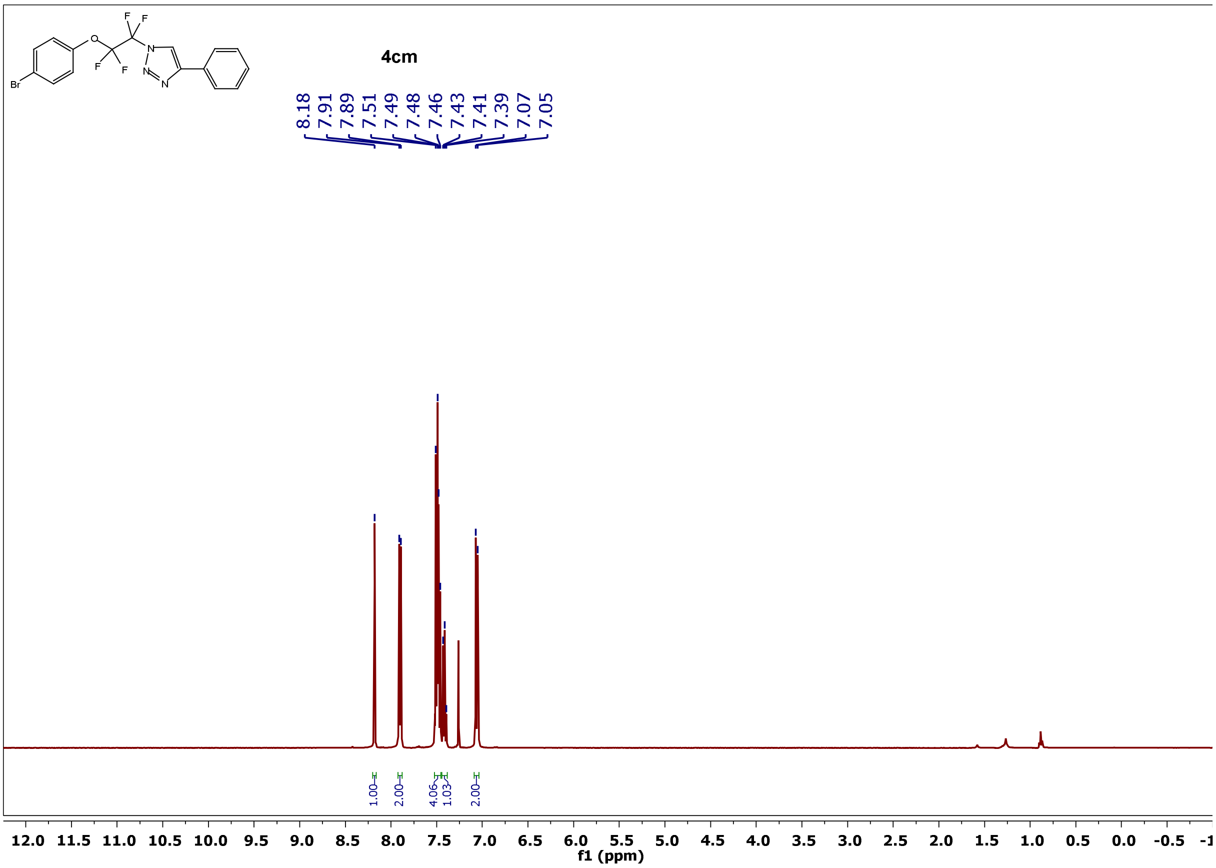
4bk
162.43
159.99
148.15
146.28
144.03
135.09
126.90
124.57
123.62
123.53
120.03
116.89
116.65
118.84
118.47
118.10
116.09
115.72
115.35
114.62
114.21
113.79
113.35
112.98
112.61
111.92
111.50
111.09
108.80
108.39
f1 (ppm)

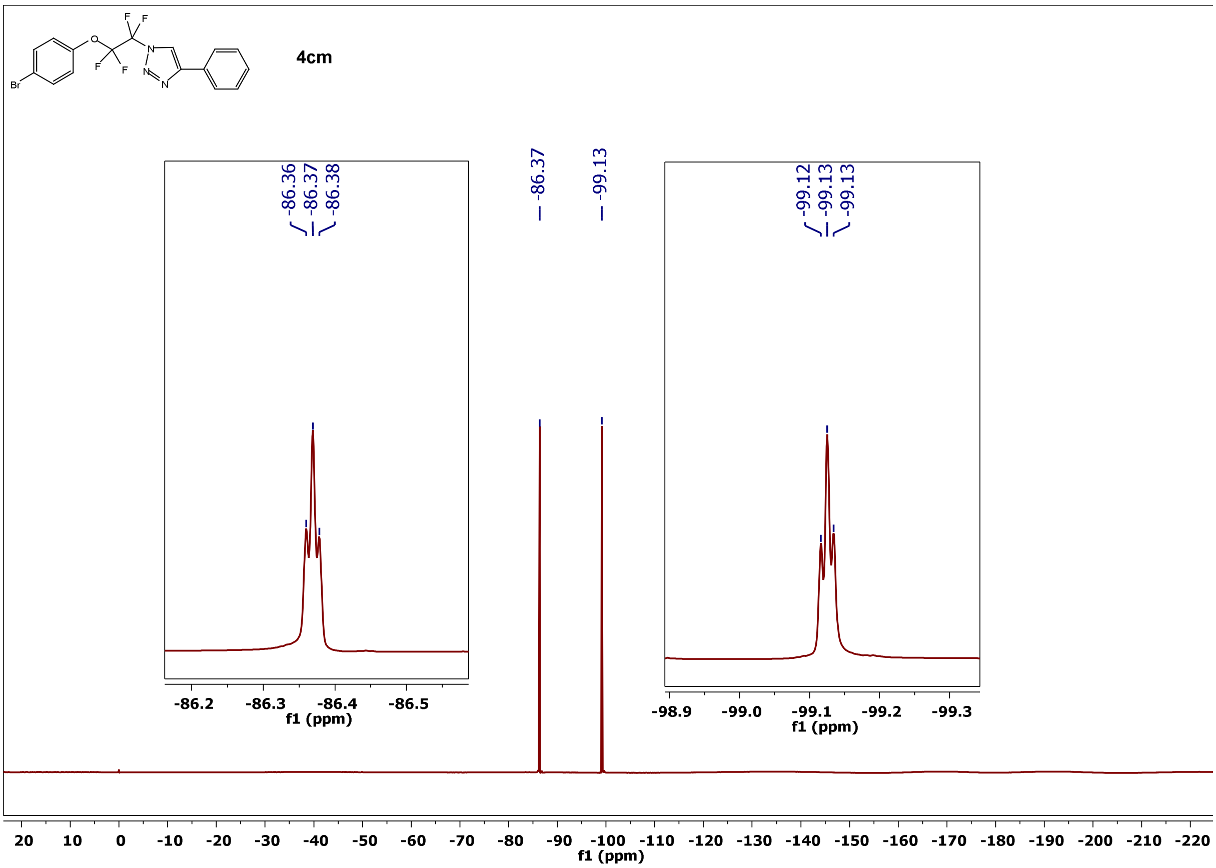


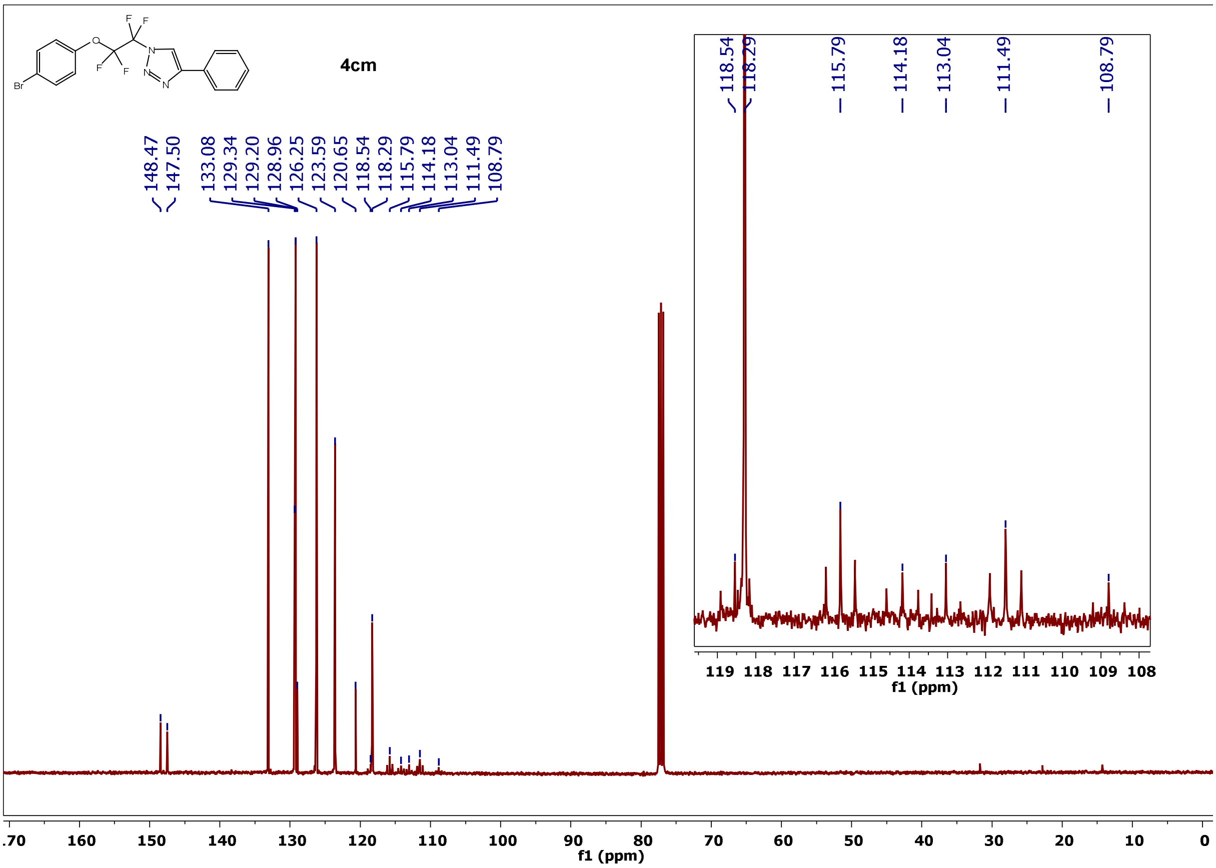
4bl
9.19
8.87
8.32
8.28
7.49
7.14
7.10
7.05
7.01
1.62
2.00
1.00
2.00
2.02
f1 (ppm)

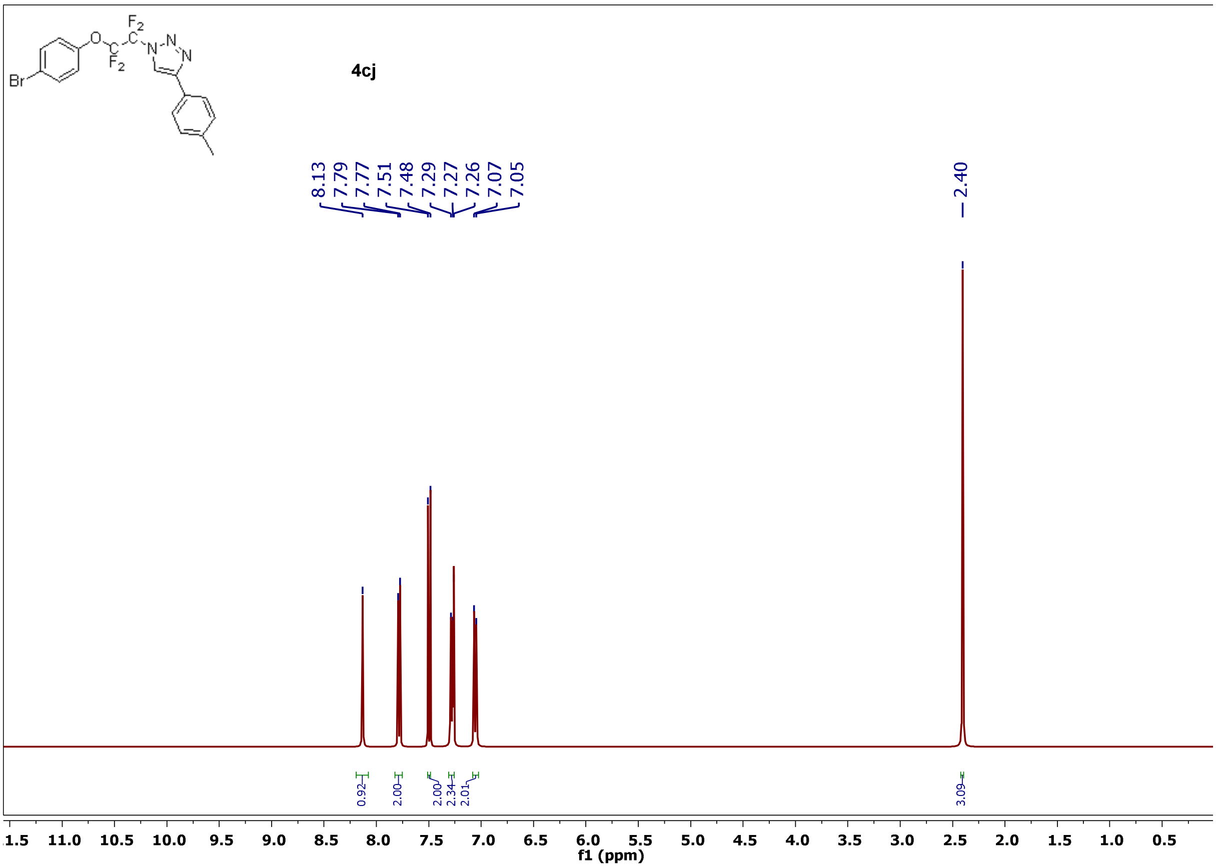

4bl
-86.43
-99.05
-114.94
-114.91
-114.92
-114.93
-114.94
-114.95
-114.96
-114.97
f1 (ppm)

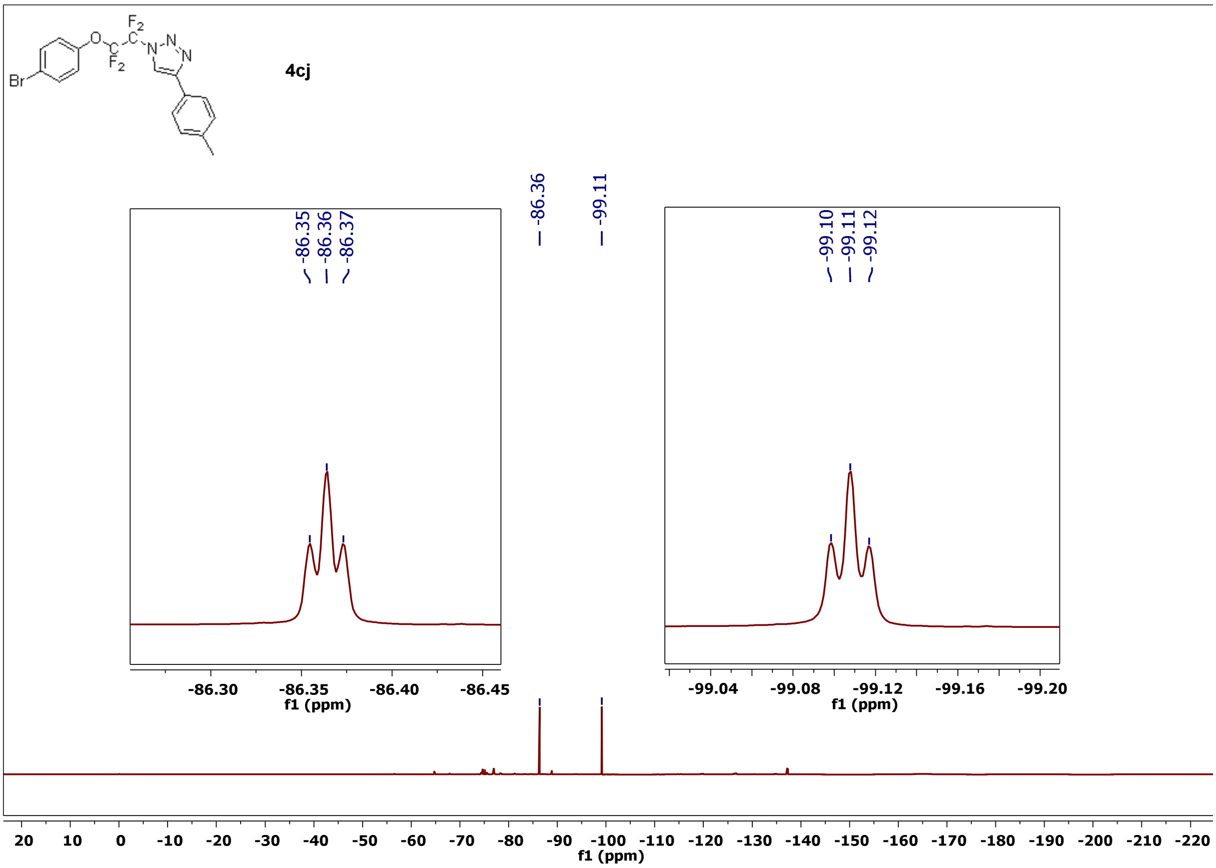

4bl
162.35
159.90
149.97
147.25
145.67
144.05
144.02
133.28
125.29
123.58
123.49
118.97
116.79
116.55
115.71
111.47
118.46
114.17
112.97
108.77
f1 (ppm)

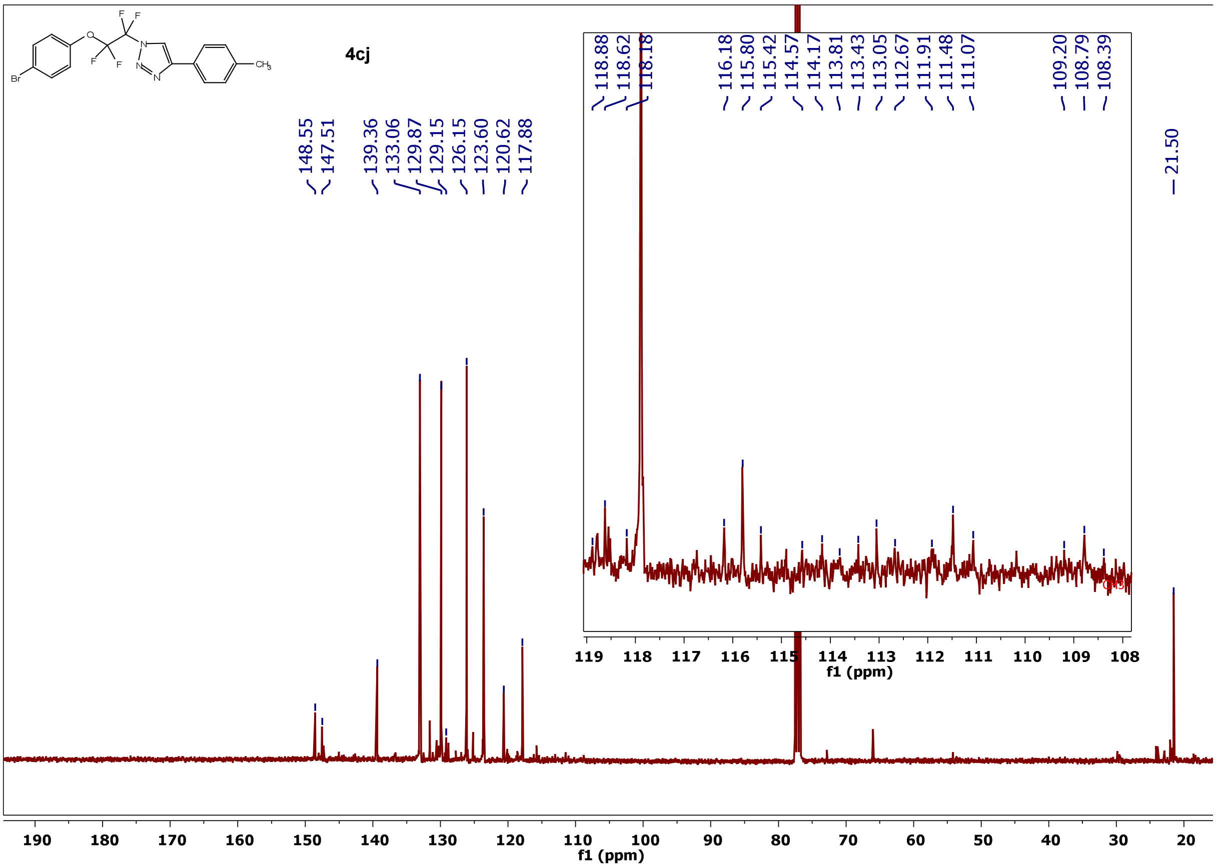

4cm
8.18
7.91
7.89
7.51
7.49
7.48
7.46
7.43
7.41
7.39
7.07
7.05
1.00
2.00
4.06
1.03
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

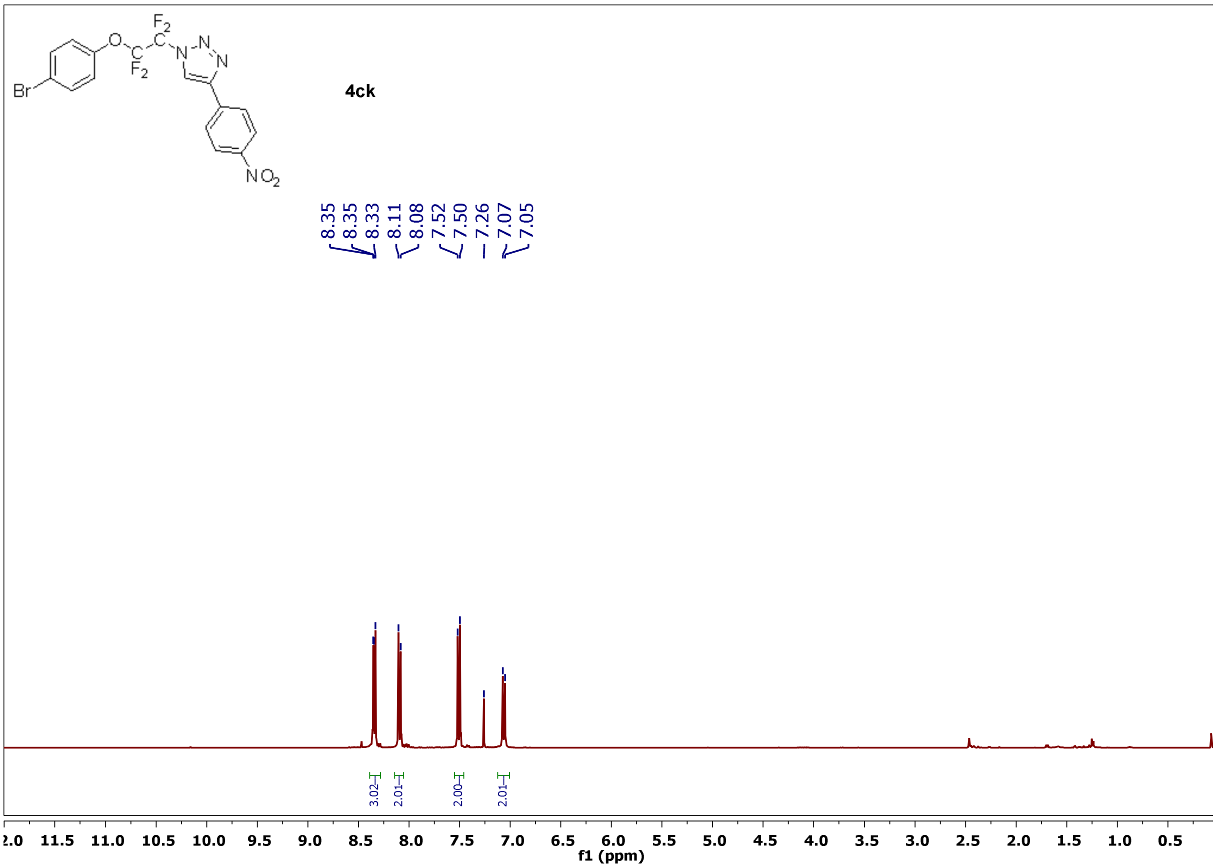

4cm
-86.36
-86.37
-86.38
-86.37
-99.13
-99.12
-99.13
-99.13
-86.2 -86.3 -86.4 -86.5
f1 (ppm)
-98.9 -99.0 -99.1 -99.2 -99.3
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

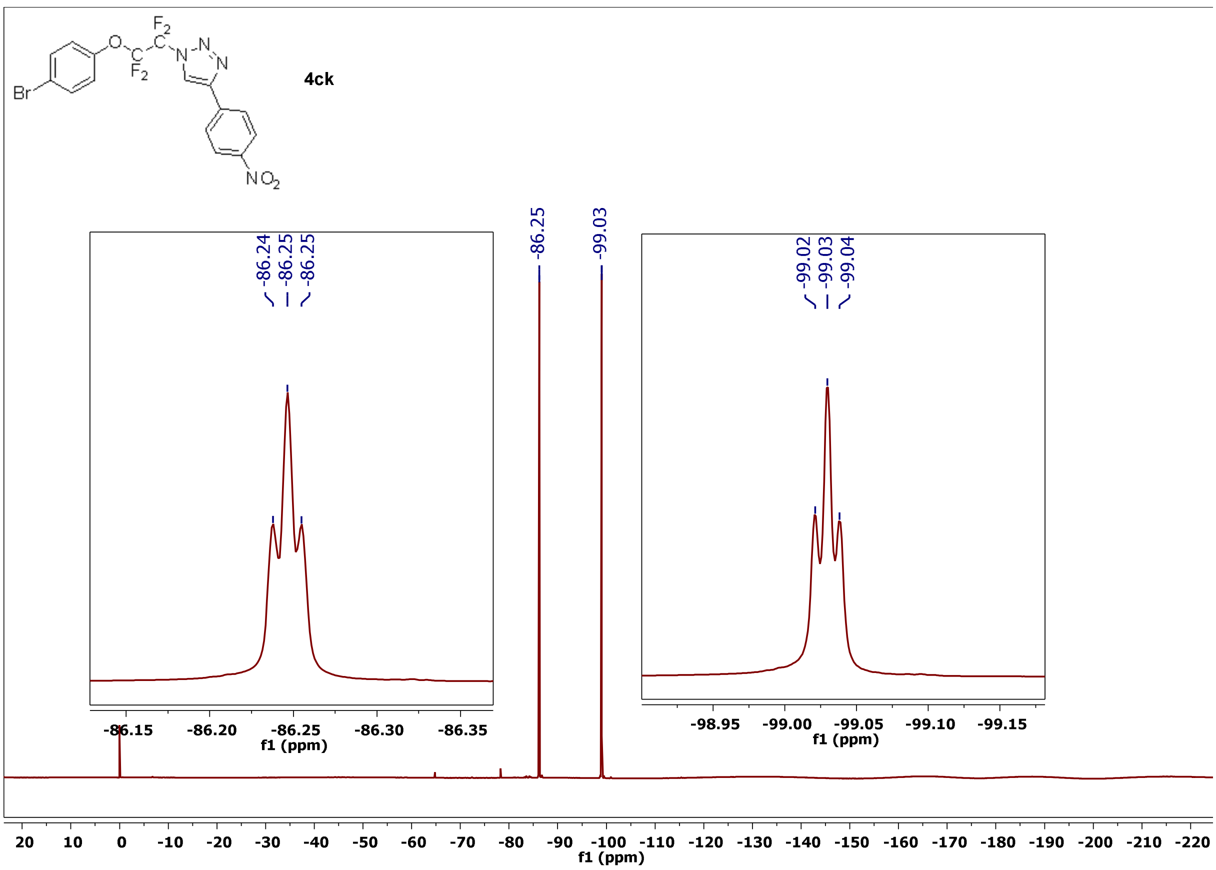

4cm
148.47
147.50
133.08
129.34
129.20
128.96
126.25
123.59
120.65
118.54
118.29
115.79
114.18
113.04
111.49
108.79
f1 (ppm)

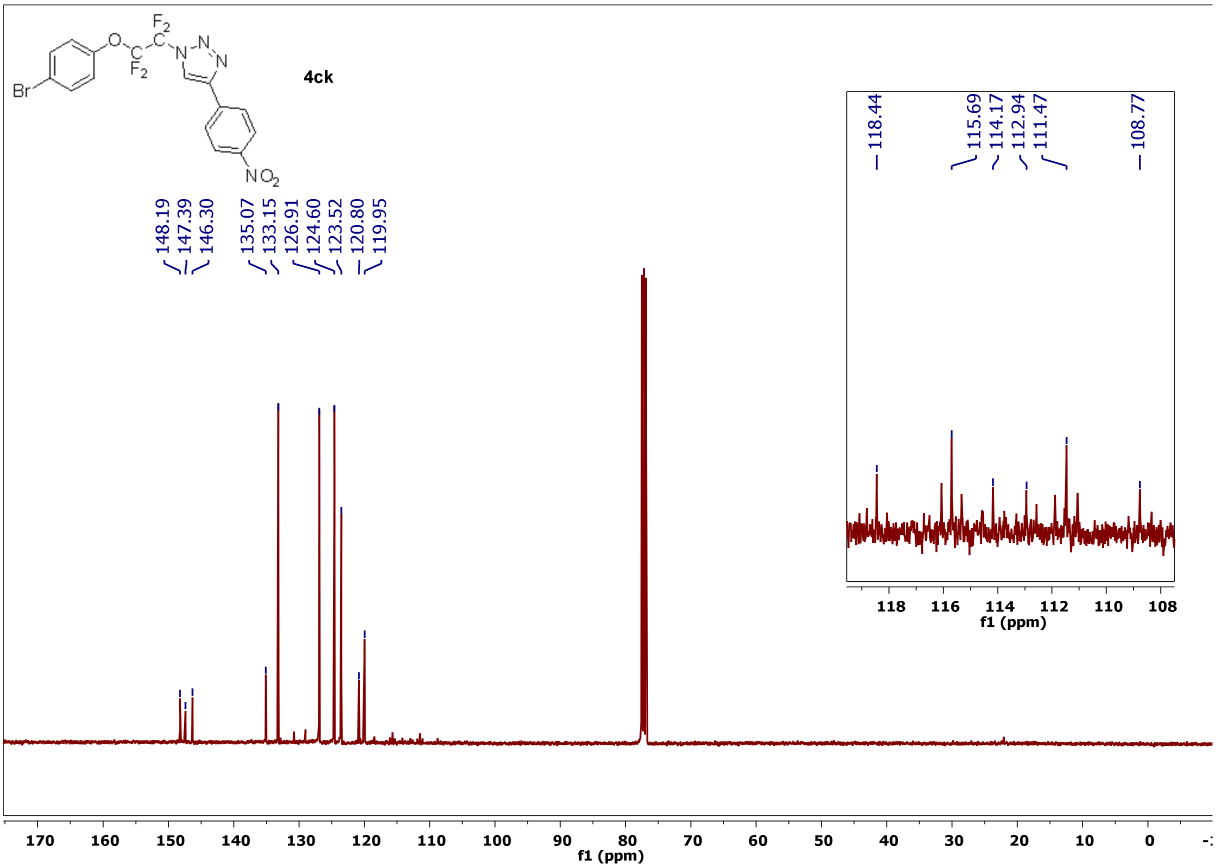

4cj
8.13
7.79
7.77
7.51
7.48
7.29
7.27
7.26
7.07
7.05
2.40
0.92
2.00
2.00
2.34
2.01
3.09
f1 (ppm)

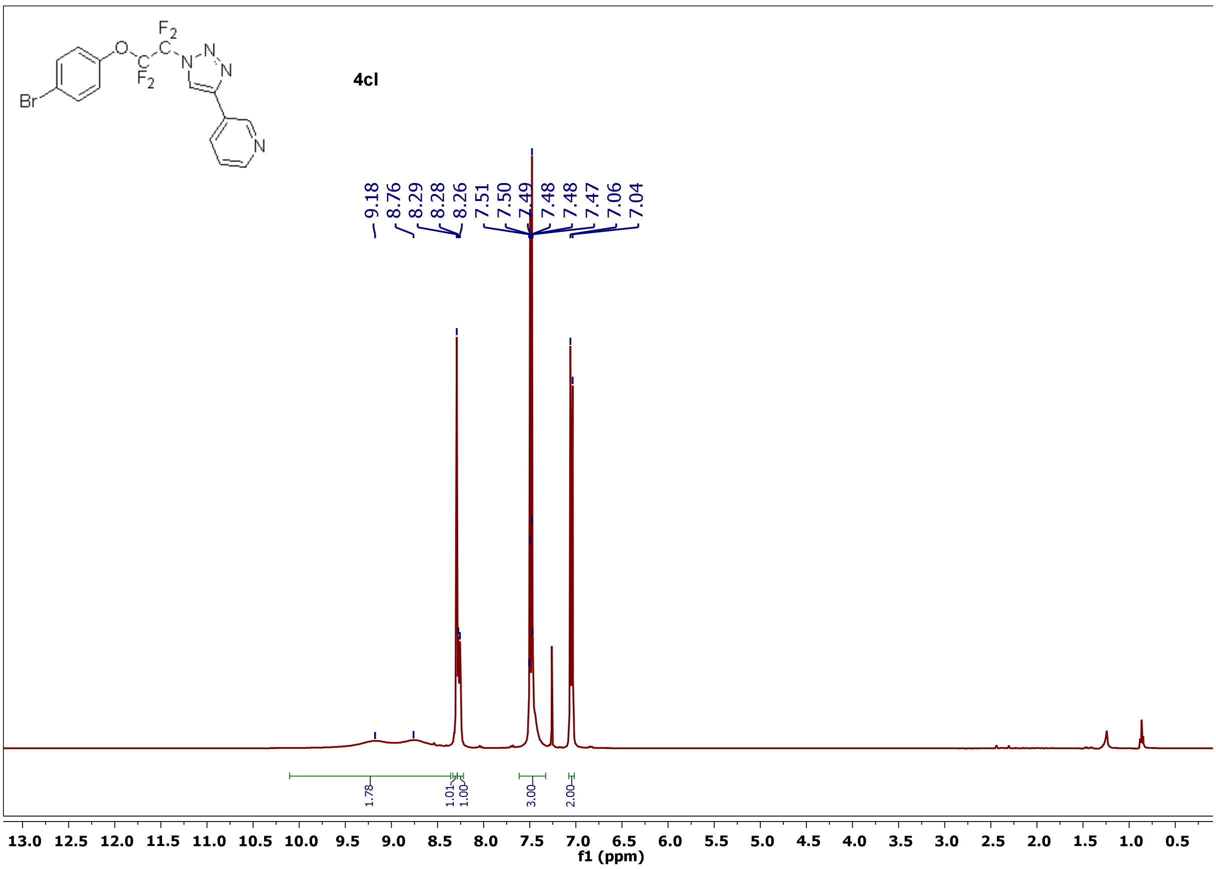

4cj
-86.36
-99.11
-86.35
-86.36
-86.37
-99.10
-99.11
-99.12
-86.30 -86.35 -86.40 -86.45
f1 (ppm)
-99.04 -99.08 -99.12 -99.16 -99.20
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

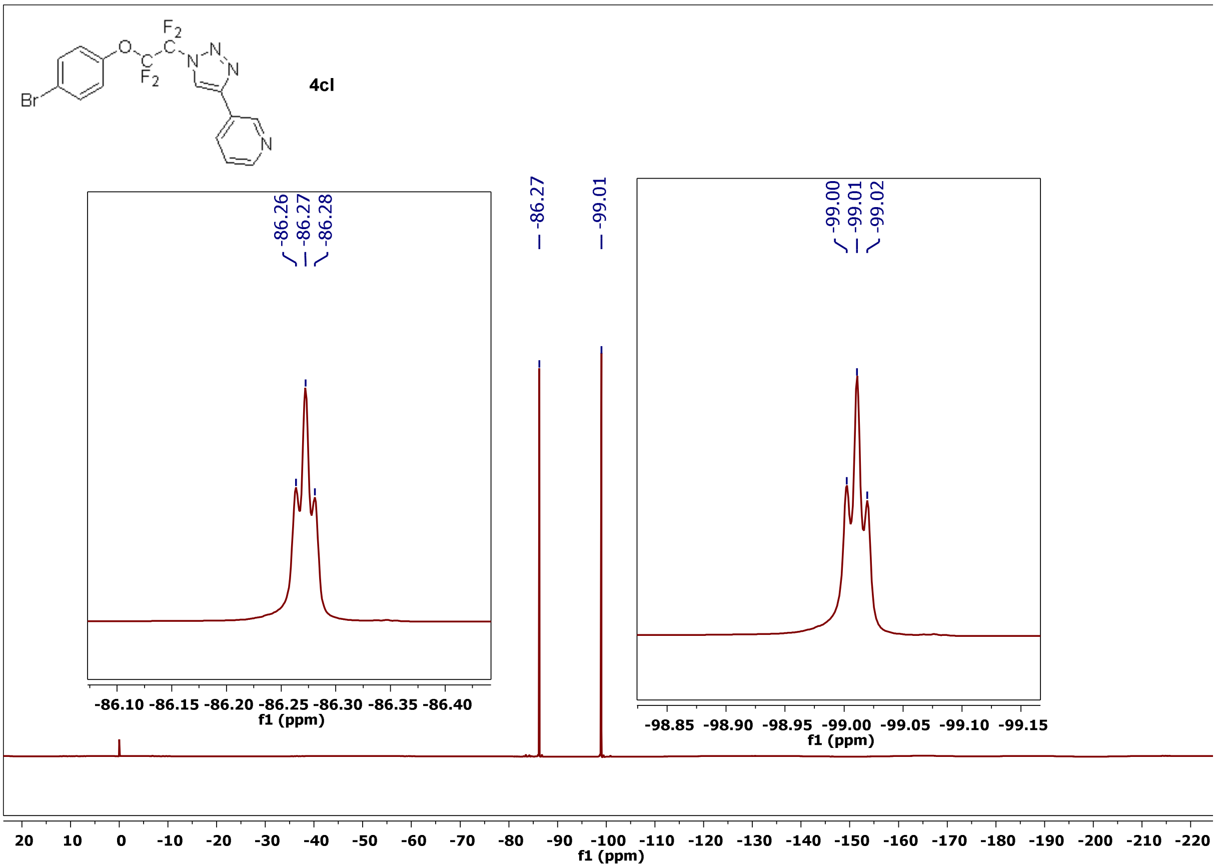

4cj
148.55
147.51
139.36
133.06
129.87
129.15
126.15
123.60
120.62
117.88
21.50
118.88
118.62
118.18
116.18
115.80
115.42
114.57
114.17
113.81
113.43
113.05
112.67
111.91
111.48
111.07
109.20
108.79
108.39
119 118 117 116 115 114 113 112 111 110 109 108
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

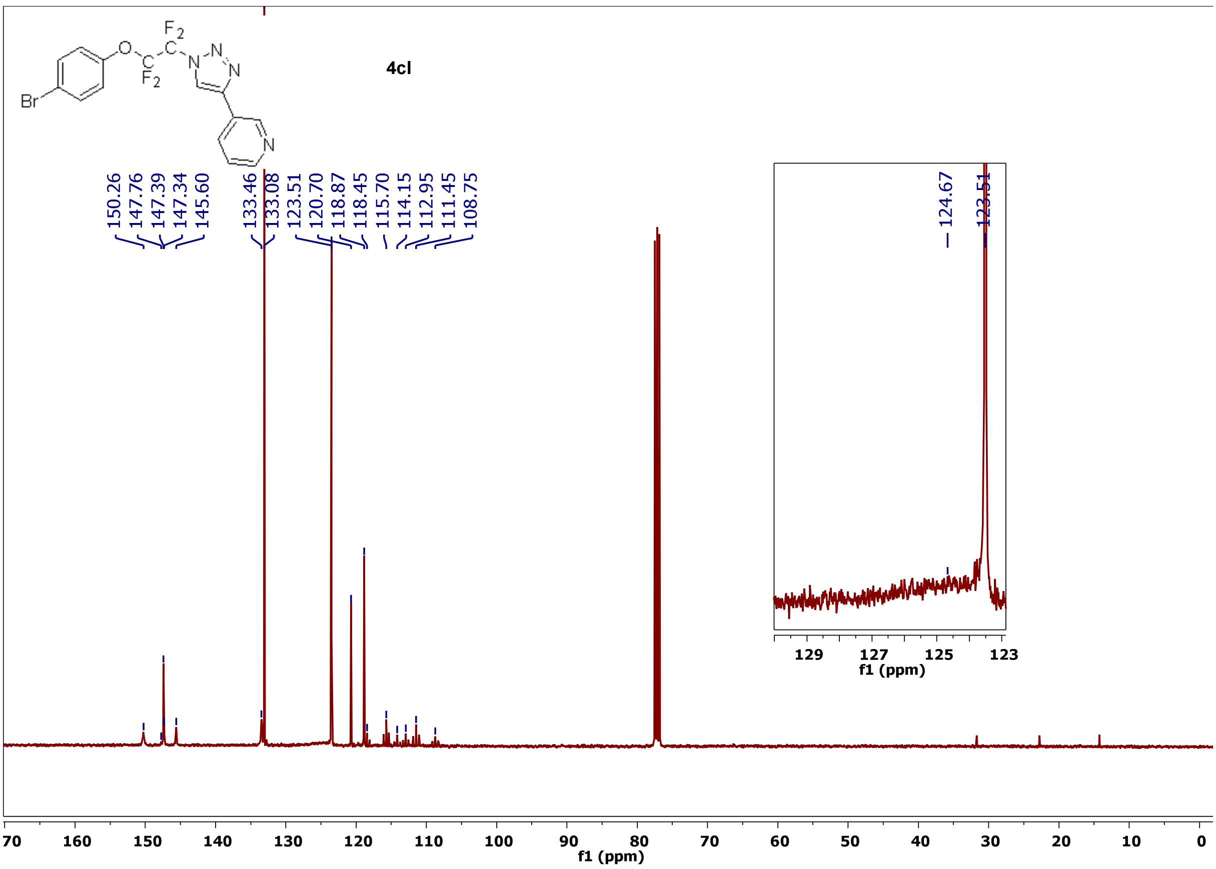

4ck
8.35
8.35
8.33
8.11
8.08
7.52
7.50
7.26
7.07
7.05
f1 (ppm)

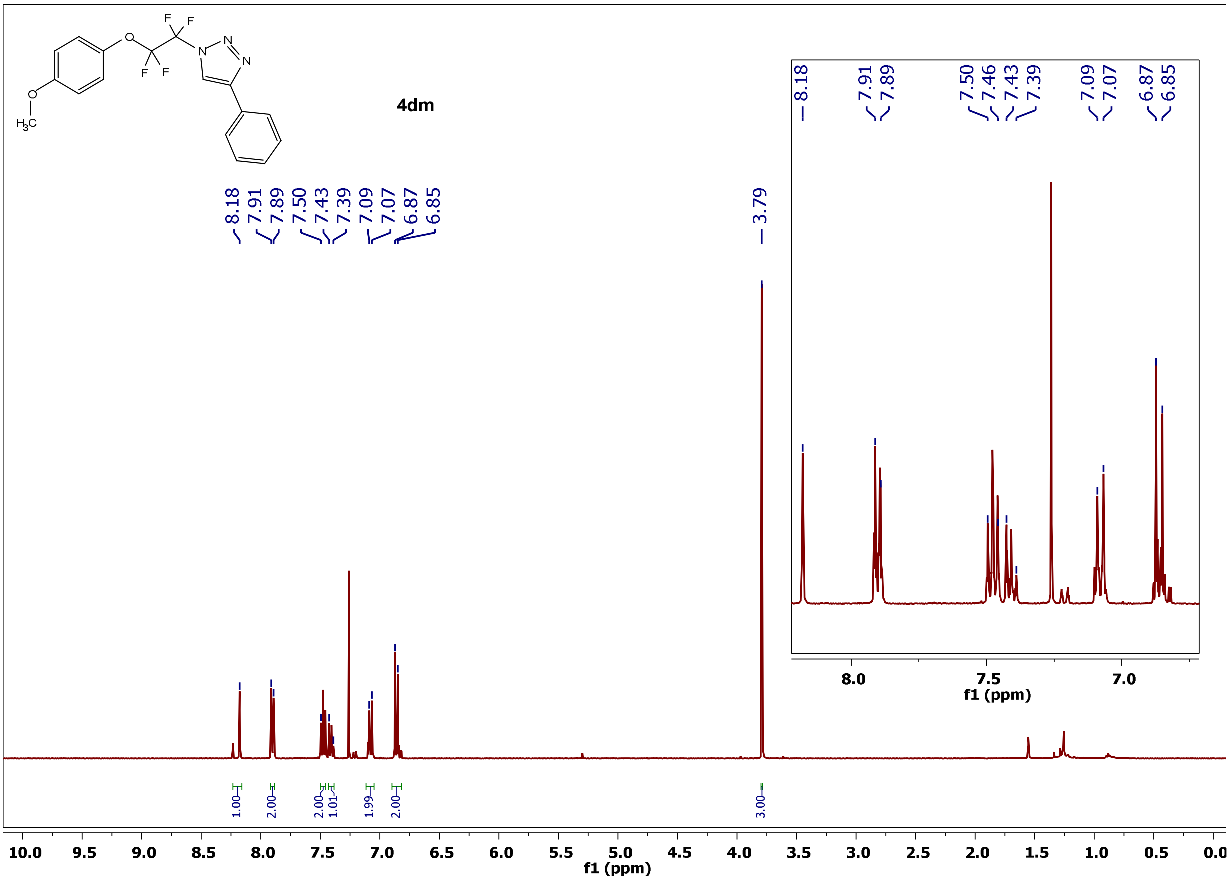

4ck
-86.25
-99.03
-86.24
-86.25
-86.25
-99.02
-99.03
-99.04
f1 (ppm)


Br
O
F2
C
C
F2
N
N
N
NO2
4ck
148.19
147.39
146.30
135.07
133.15
126.91
124.60
123.52
120.80
119.95
118.44
115.69
114.17
112.94
111.47
108.77
118
116
114
112
110
108
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

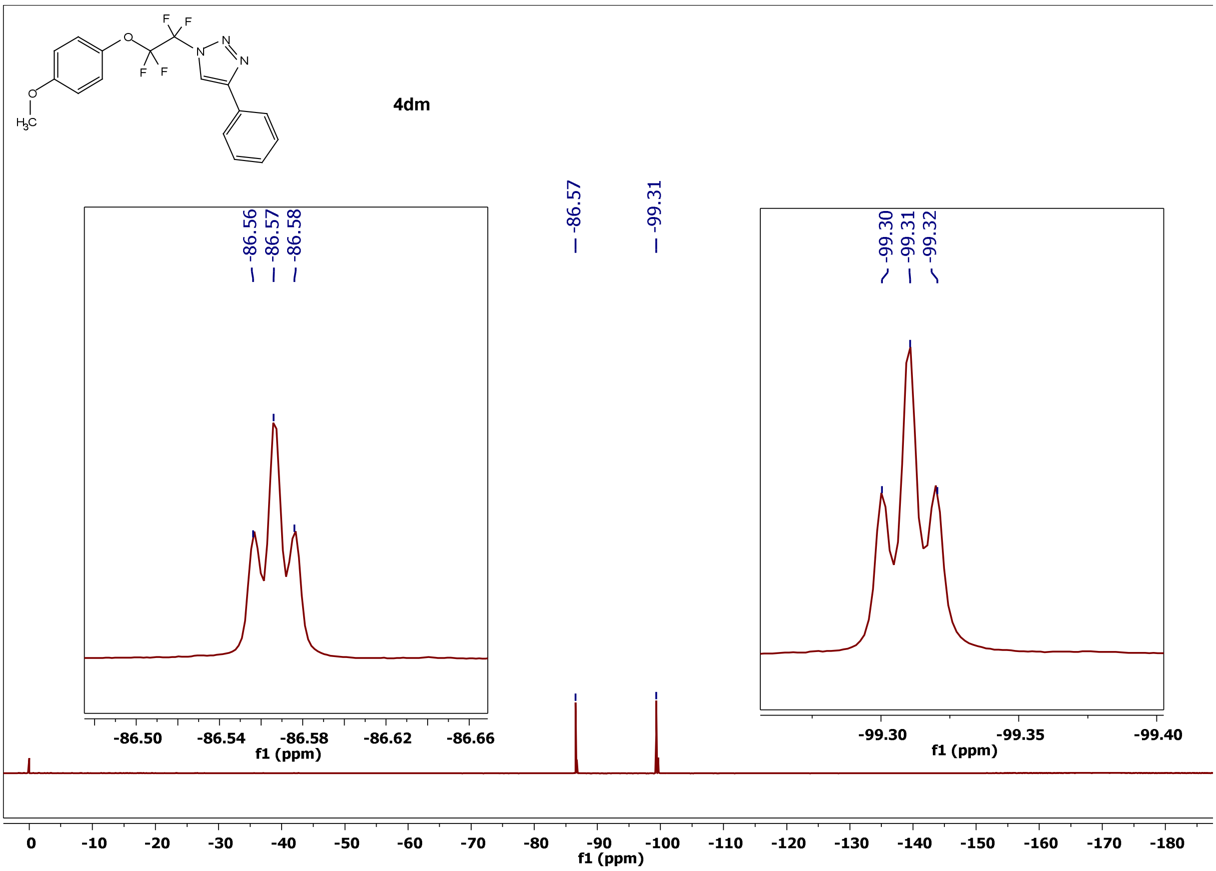

Br
O
F2
C
C
F2
N
N
N
N
4cl
9.18
8.76
8.29
8.28
8.26
7.51
7.50
7.49
7.48
7.48
7.47
7.06
7.04
1.78
1.01
1.00
3.00
2.00
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


4cl
-86.26
-86.27
-86.28
-86.27
-99.01
-99.00
-99.01
-99.02
-86.10 -86.15 -86.20 -86.25 -86.30 -86.35 -86.40
f1 (ppm)
-98.85 -98.90 -98.95 -99.00 -99.05 -99.10 -99.15
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)

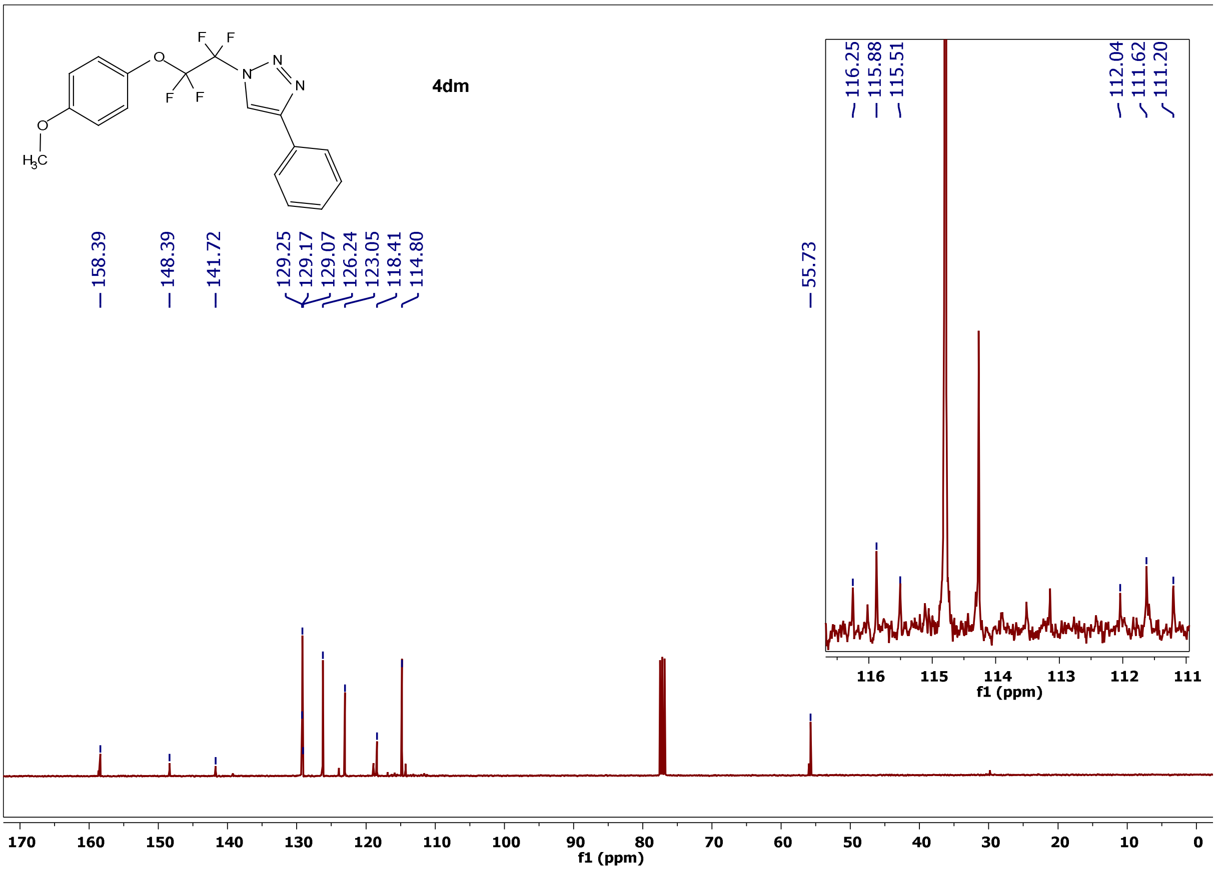

4cl
150.26
147.76
147.39
147.34
145.60
133.46
133.08
123.51
120.70
118.87
118.45
115.70
114.15
112.95
111.45
108.75
124.67
123.51
129 127 125 123
f1 (ppm)
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

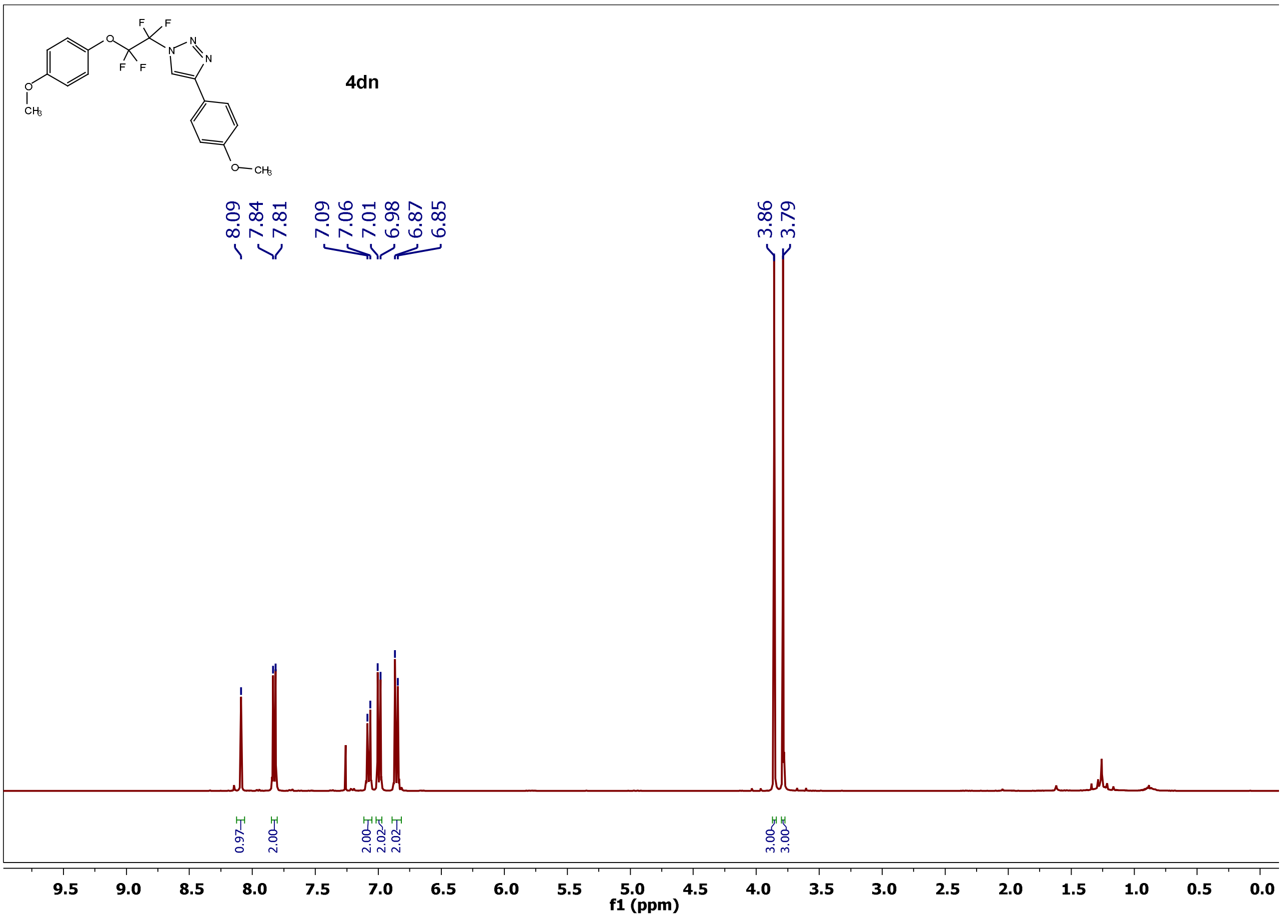


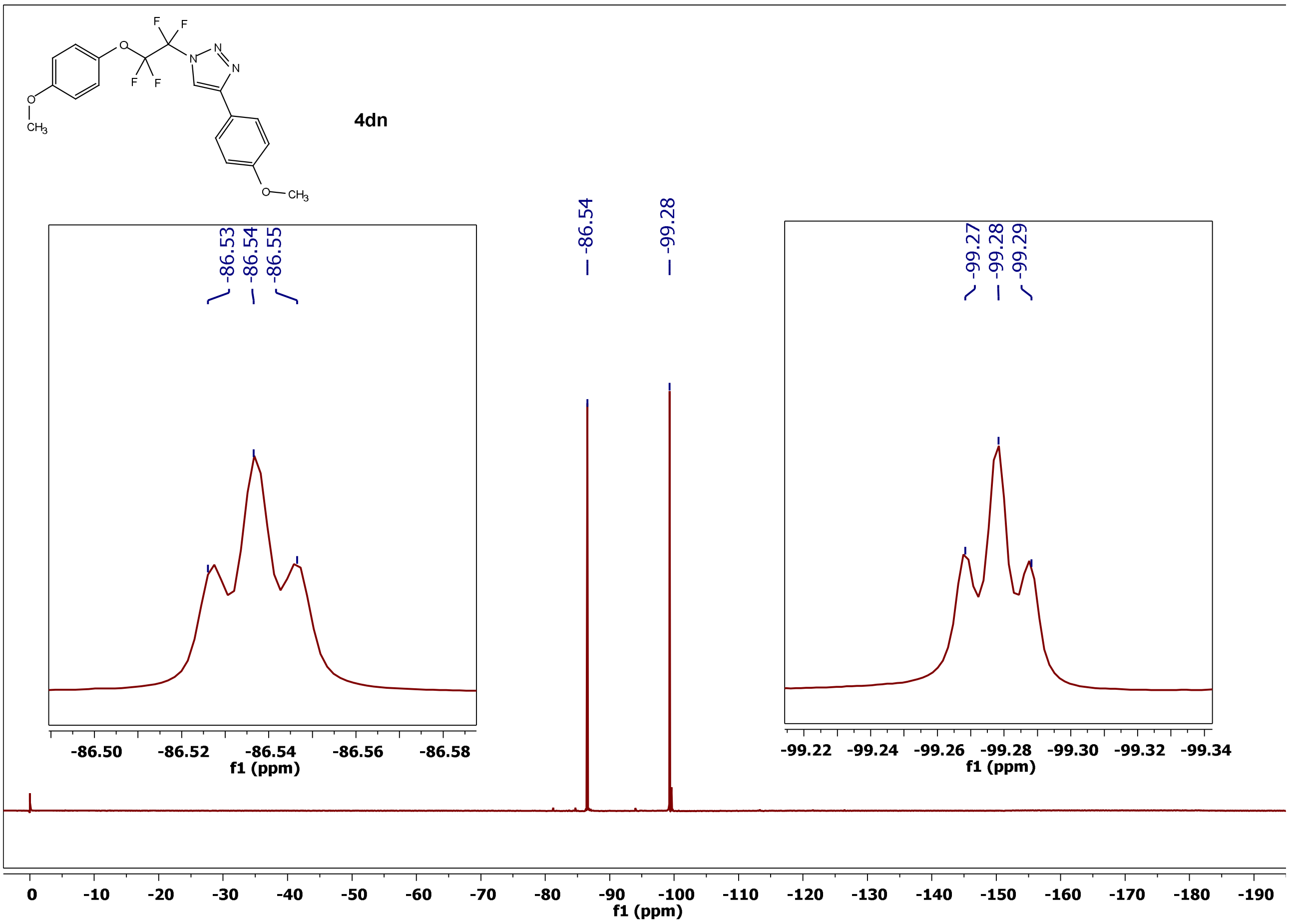
4dm
8.18
7.91
7.89
7.50
7.43
7.39
7.09
7.07
6.87
6.85
3.79
7.46
1.00
2.00
2.00
1.01
1.99
2.00
3.00
f1 (ppm)



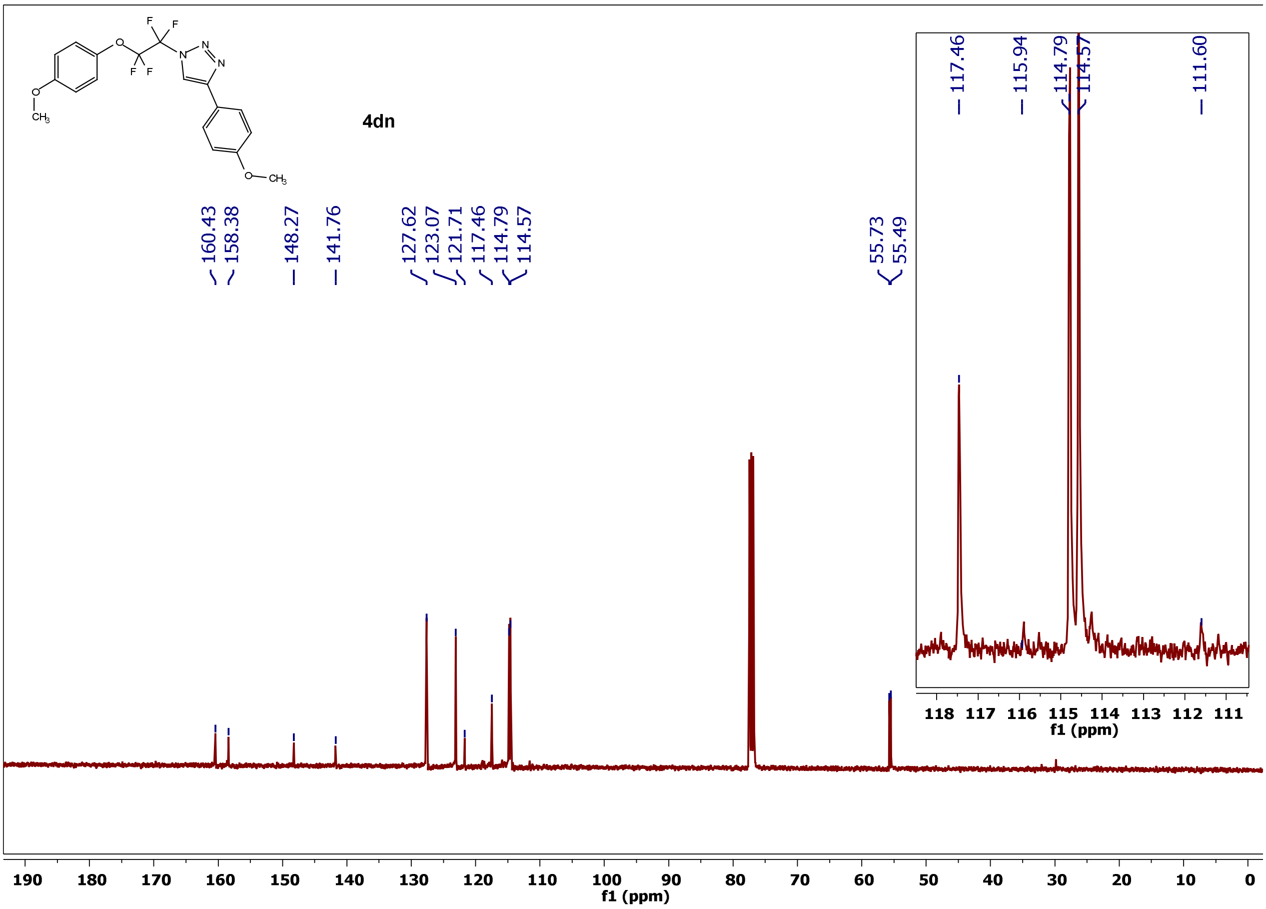
4dm
-86.57
-99.31
-86.56
-86.57
-86.58
-99.30
-99.31
-99.32
f1 (ppm)

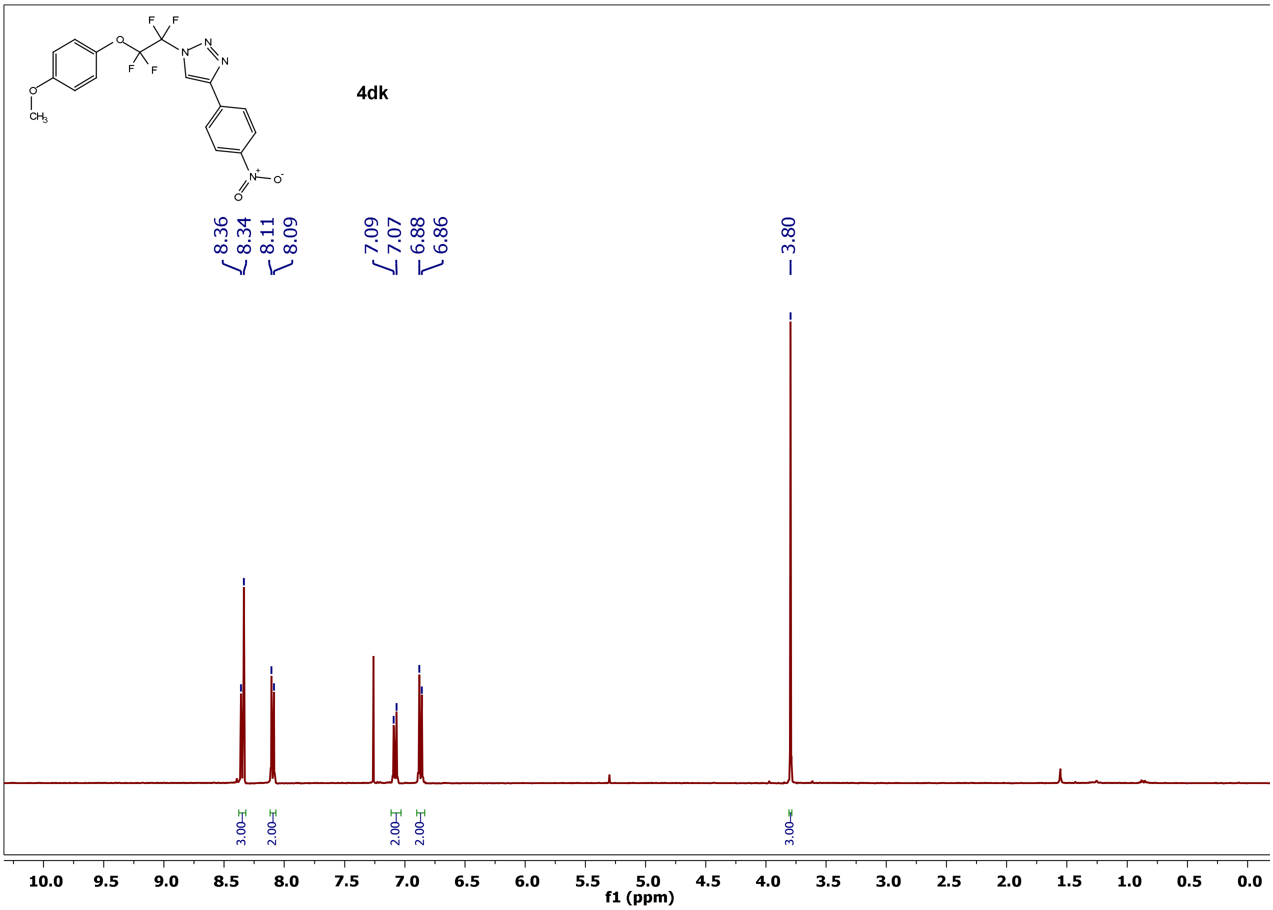

4dm
158.39
148.39
141.72
129.25
129.17
129.07
126.24
123.05
118.41
114.80
55.73
116.25
115.88
115.51
112.04
111.62
111.20
f1 (ppm)

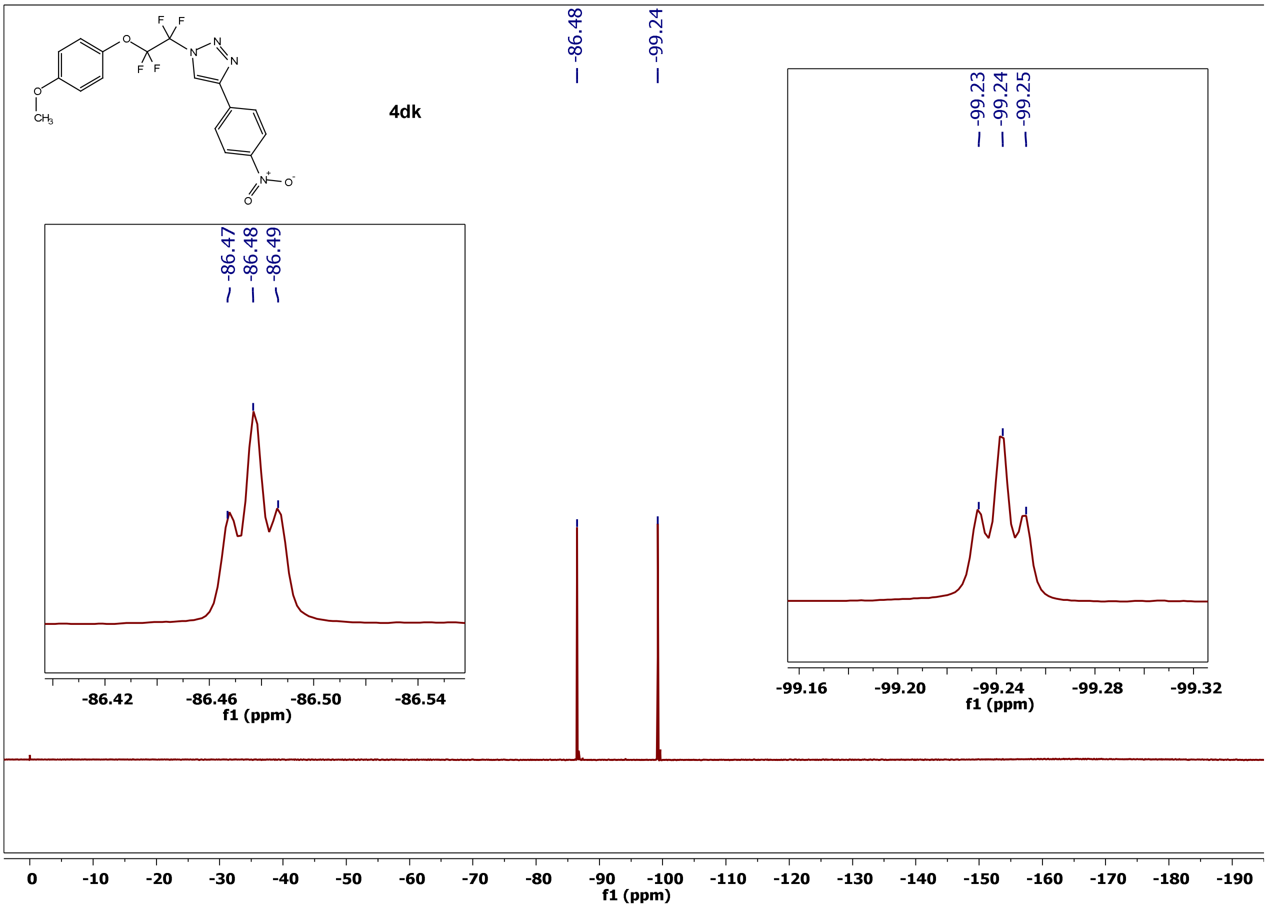

4dn
8.09
7.84
7.81
7.09
7.06
7.01
6.98
6.87
6.85
3.86
3.79
0.97
2.00
2.00
2.02
2.02
3.00
3.00
f1 (ppm)



4dn
-86.54
-99.28
-86.53
-86.54
-86.55
-99.27
-99.28
-99.29
f1 (ppm)

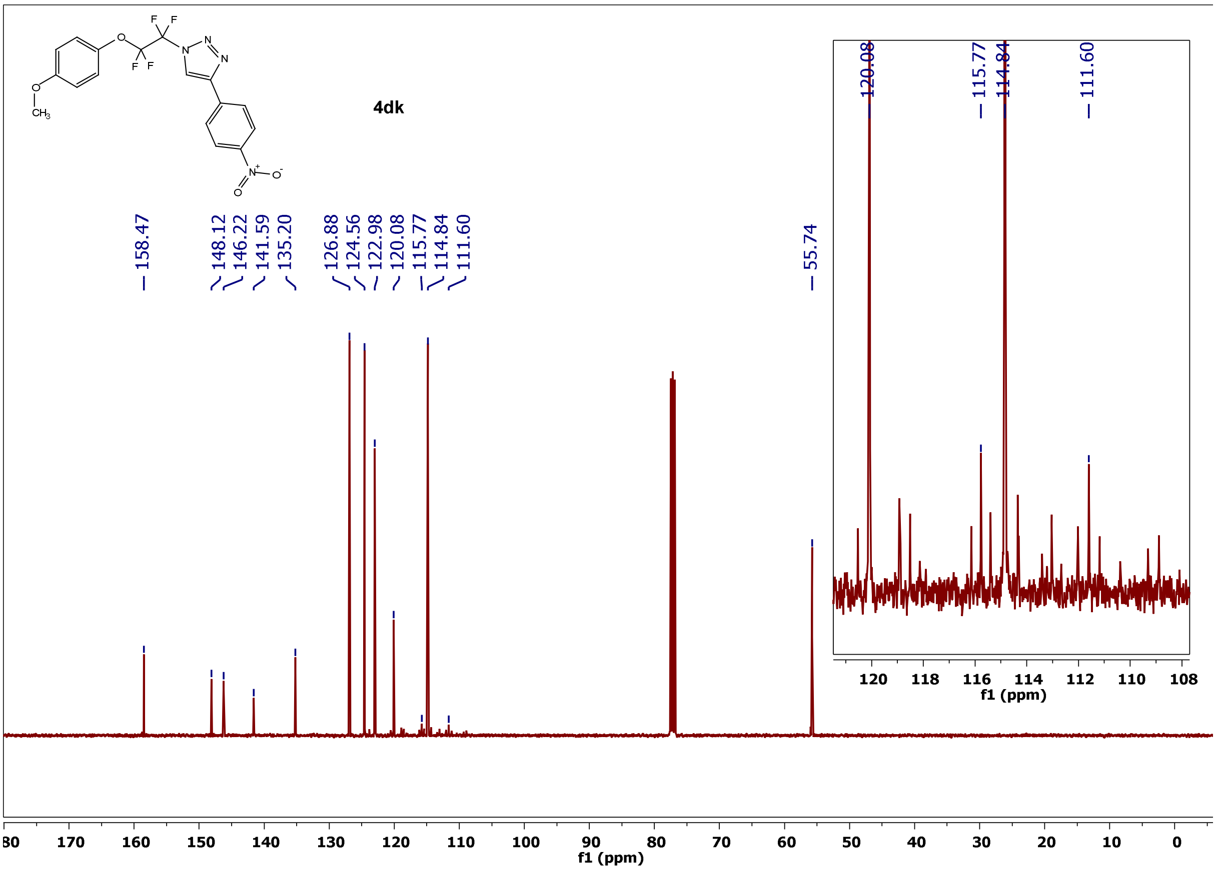

4dn
160.43
158.38
148.27
141.76
127.62
123.07
121.71
117.46
114.79
114.57
55.73
55.49
117.46
115.94
114.79
114.57
111.60
118 117 116 115 114 113 112 111
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


4dk
8.36
8.34
8.11
8.09
7.09
7.07
6.88
6.86
3.80
3.00
2.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

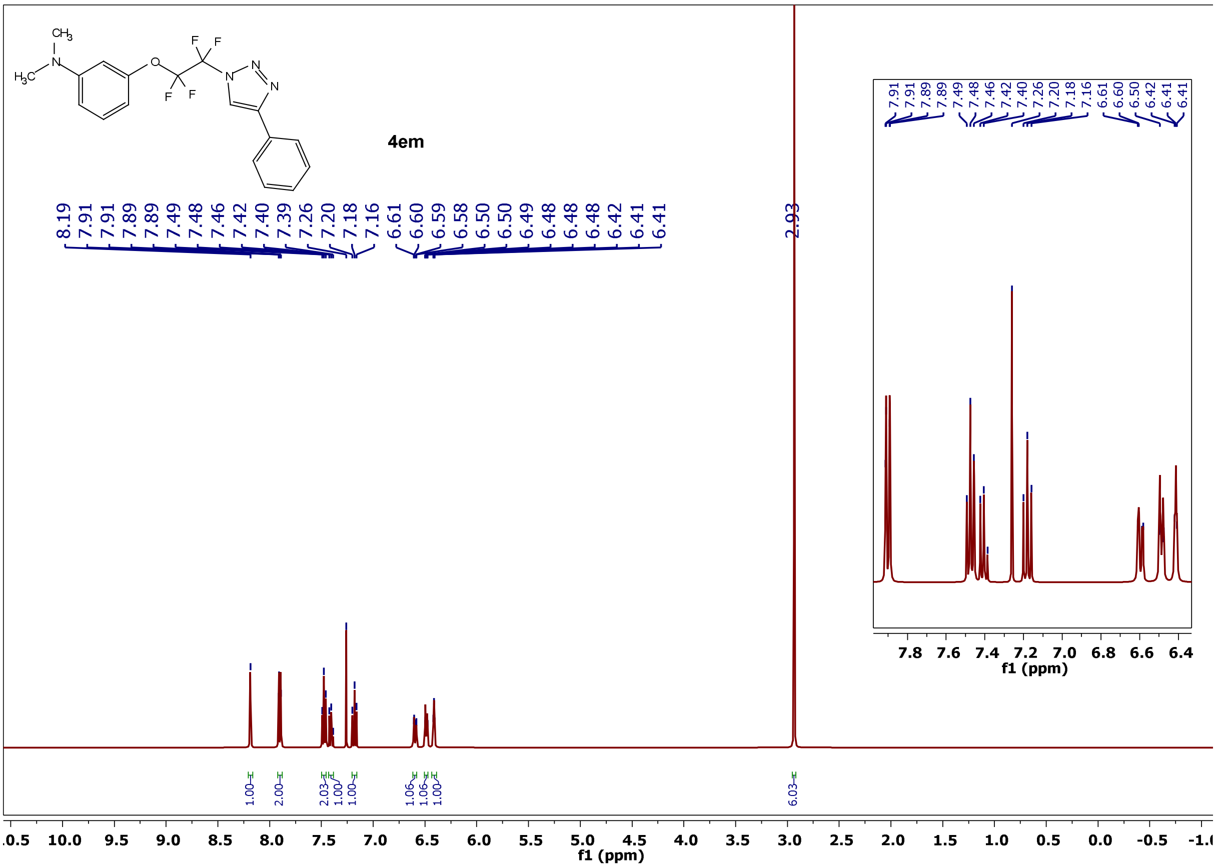


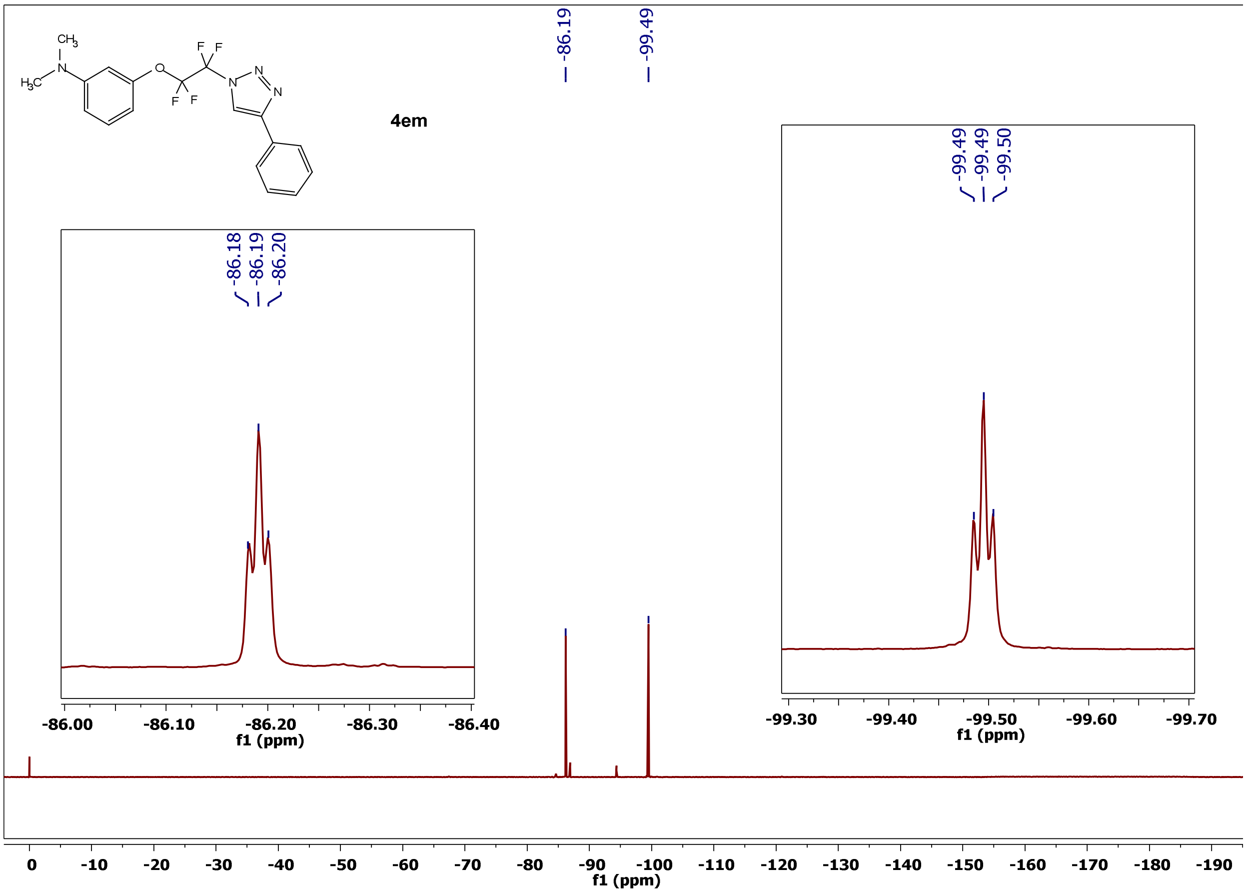
4dk
-86.48
-99.24
-86.47
-86.48
-86.49
-99.23
-99.24
-99.25
f1 (ppm)

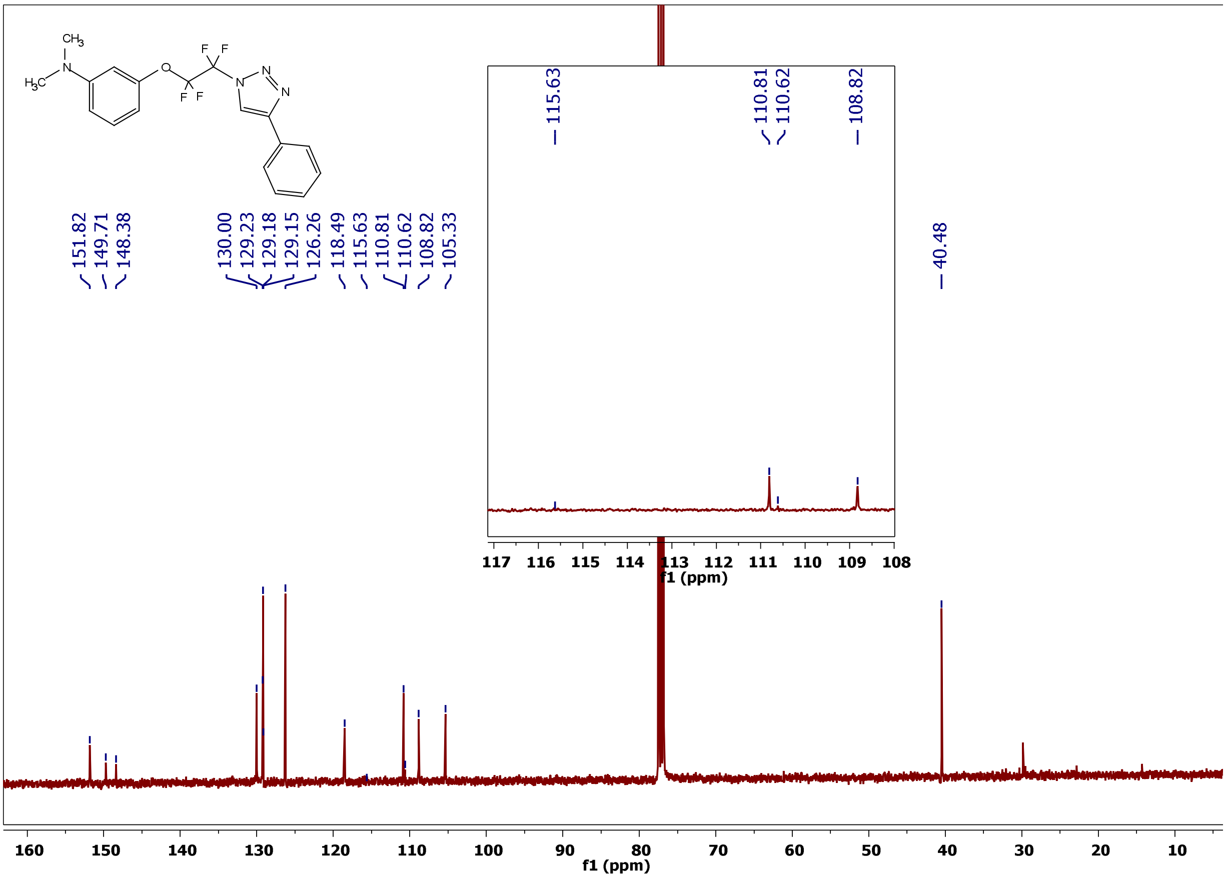
4dk

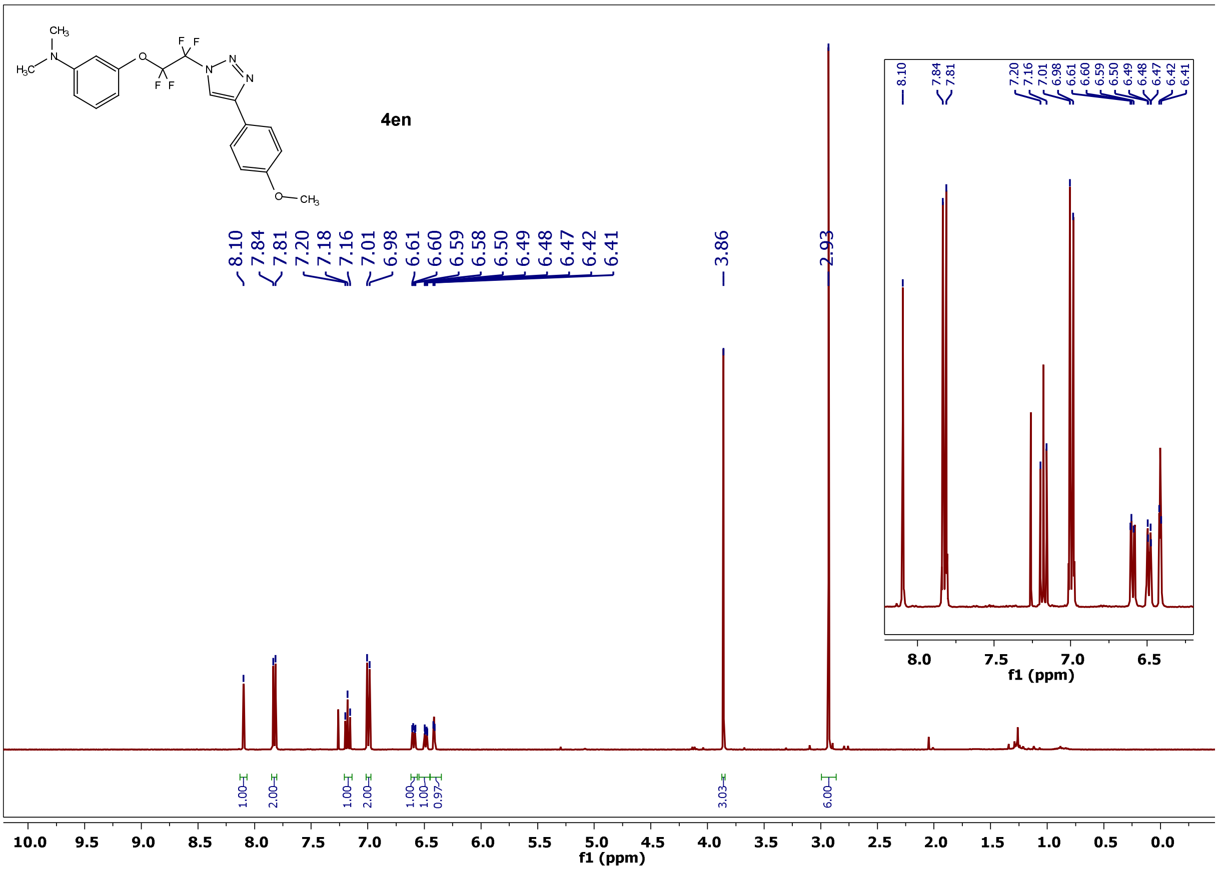


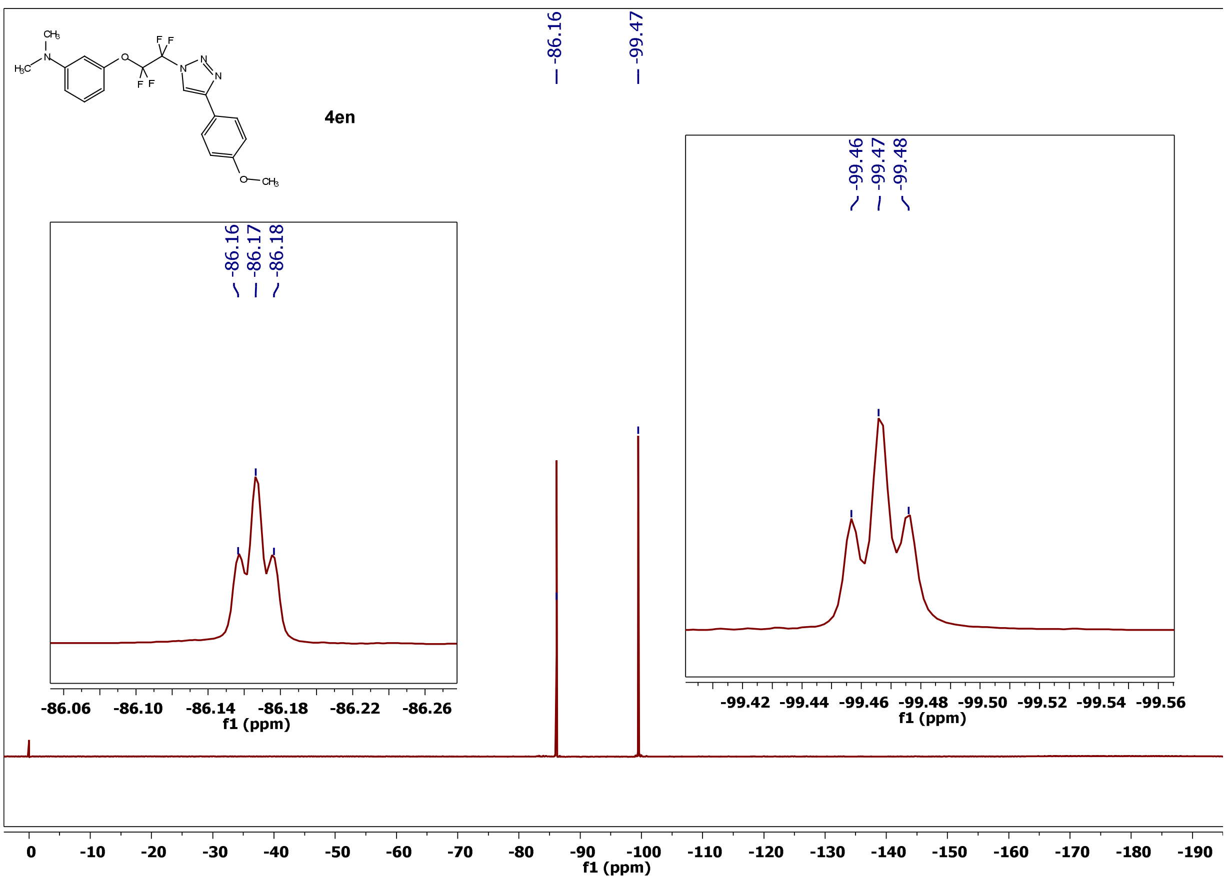
4em



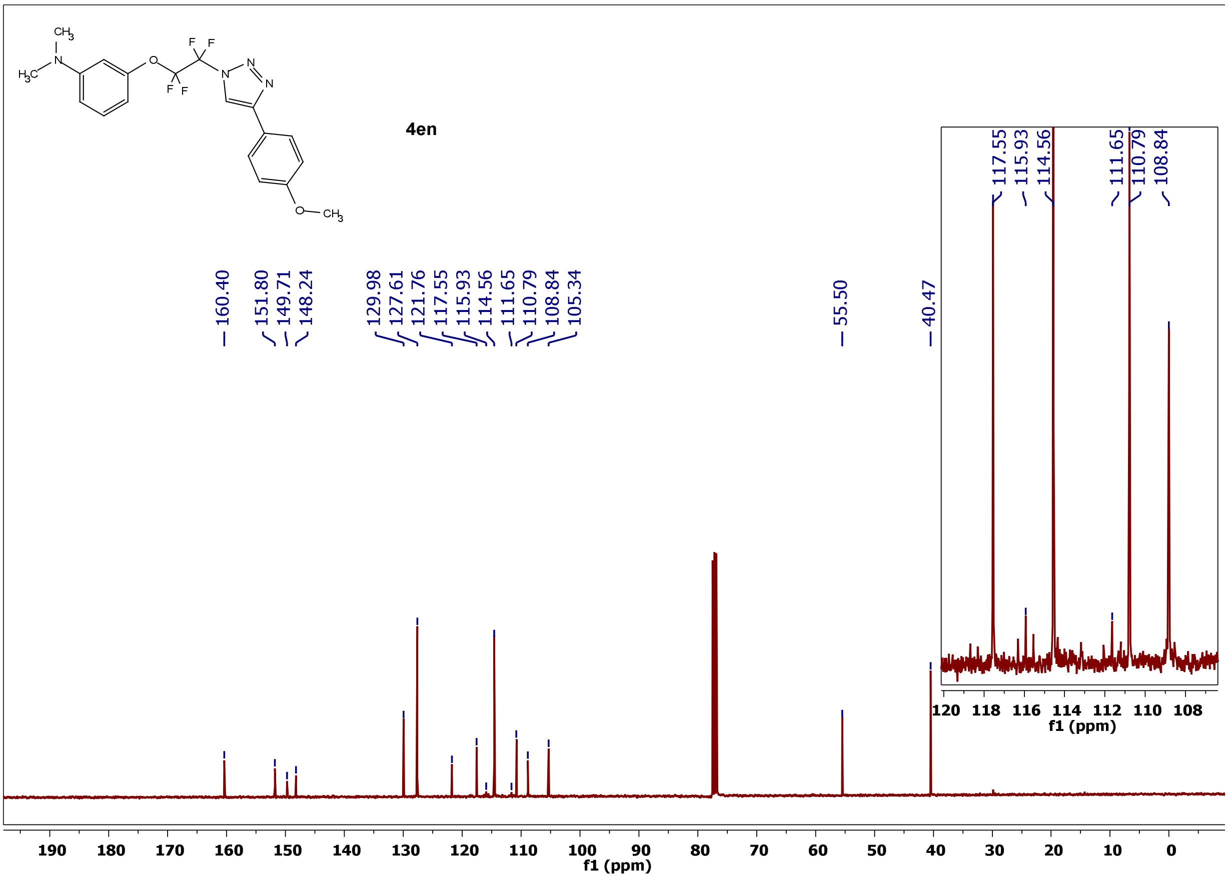

4em
-86.19
-99.49
-86.18
-86.19
-86.20
-99.49
-99.49
-99.50
-86.00 -86.10 -86.20 -86.30 -86.40
f1 (ppm)
-99.30 -99.40 -99.50 -99.60 -99.70
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


CH3
H3C
N
O
F F
F F
N
N
N
151.82
149.71
148.38
130.00
129.23
129.18
129.15
126.26
118.49
115.63
110.81
110.62
108.82
105.33
40.48
115.63
110.81
110.62
108.82
117 116 115 114 113 112 111 110 109 108
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

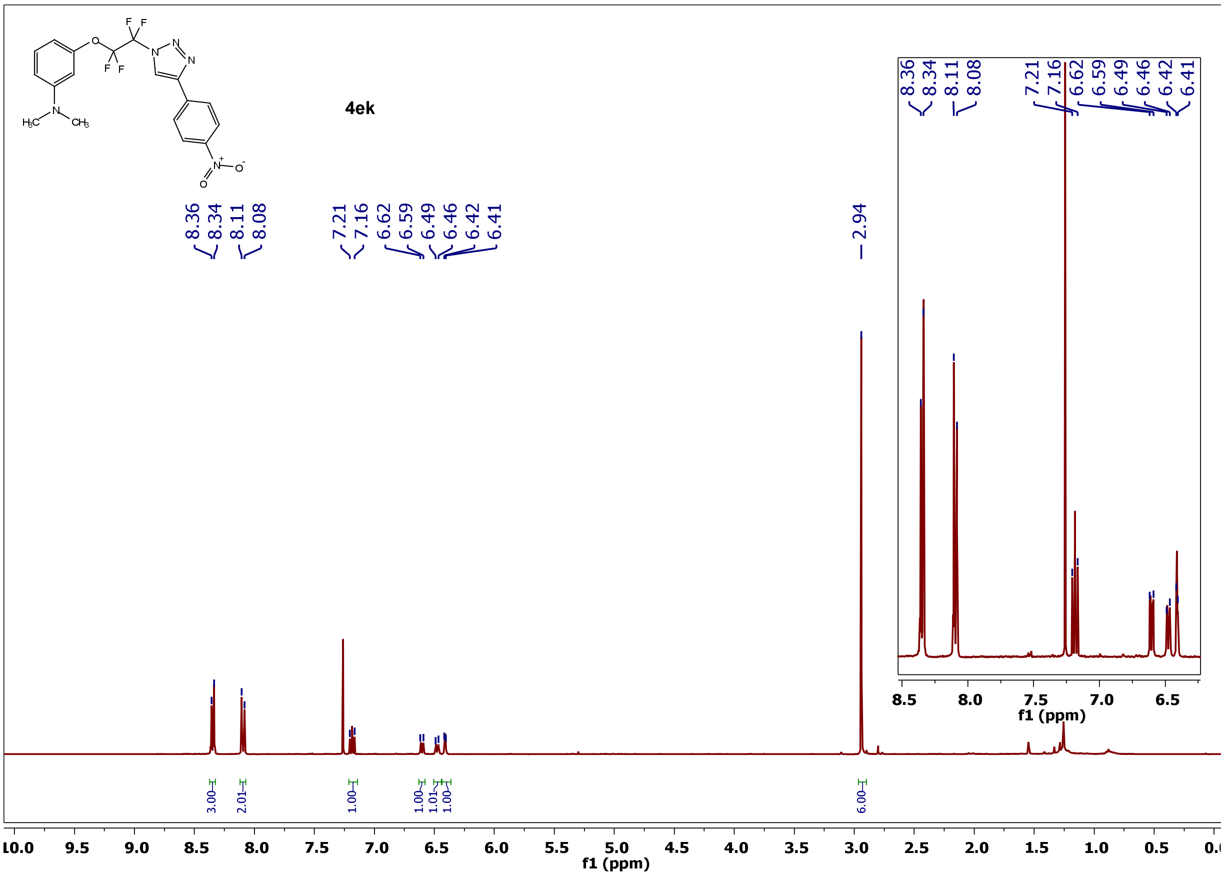

4en
8.10
7.84
7.81
7.20
7.18
7.16
7.01
6.98
6.61
6.60
6.59
6.58
6.50
6.49
6.48
6.47
6.42
6.41
3.86
2.93
1.00
2.00
1.00
2.00
1.00
1.00
0.97
3.03
6.00
f1 (ppm)

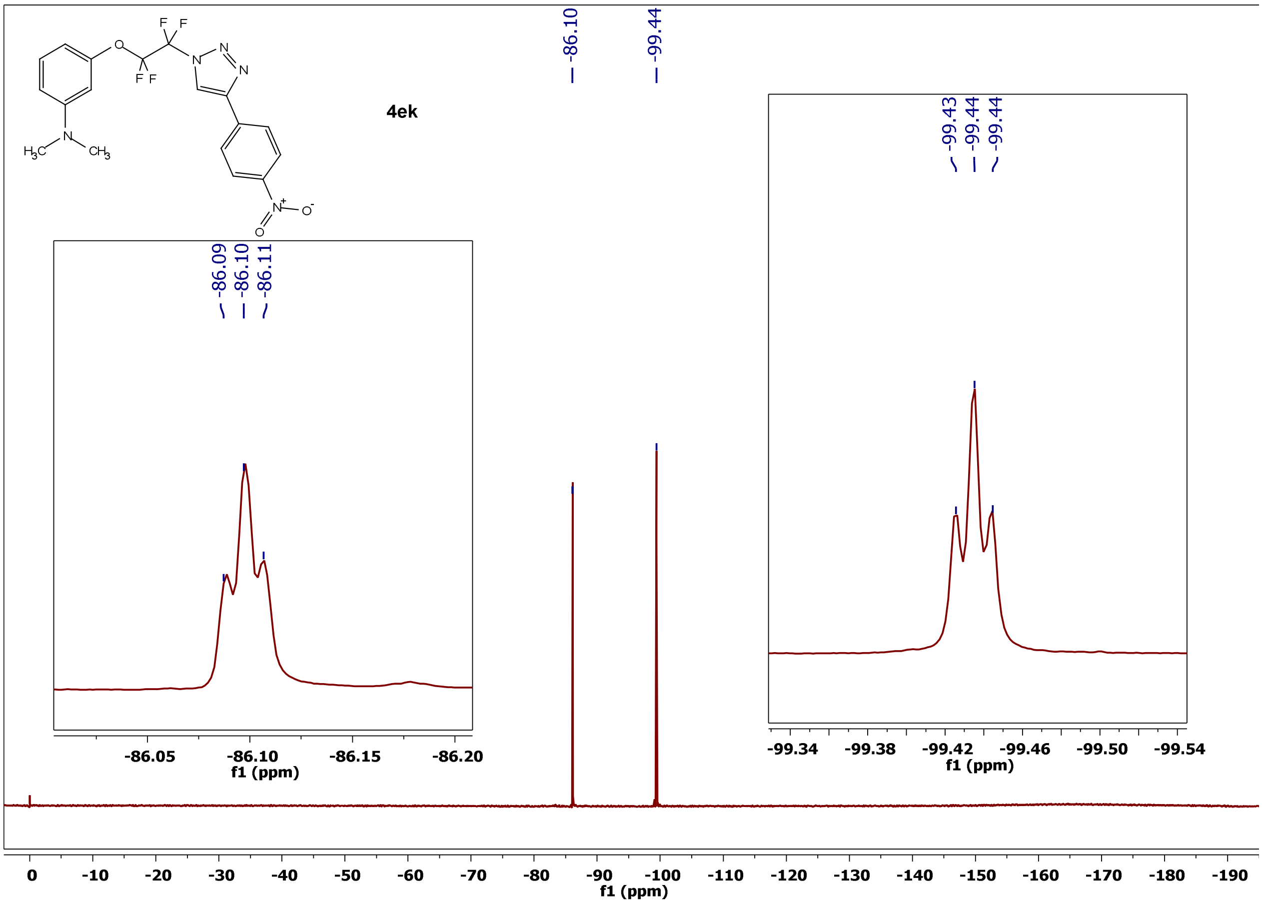


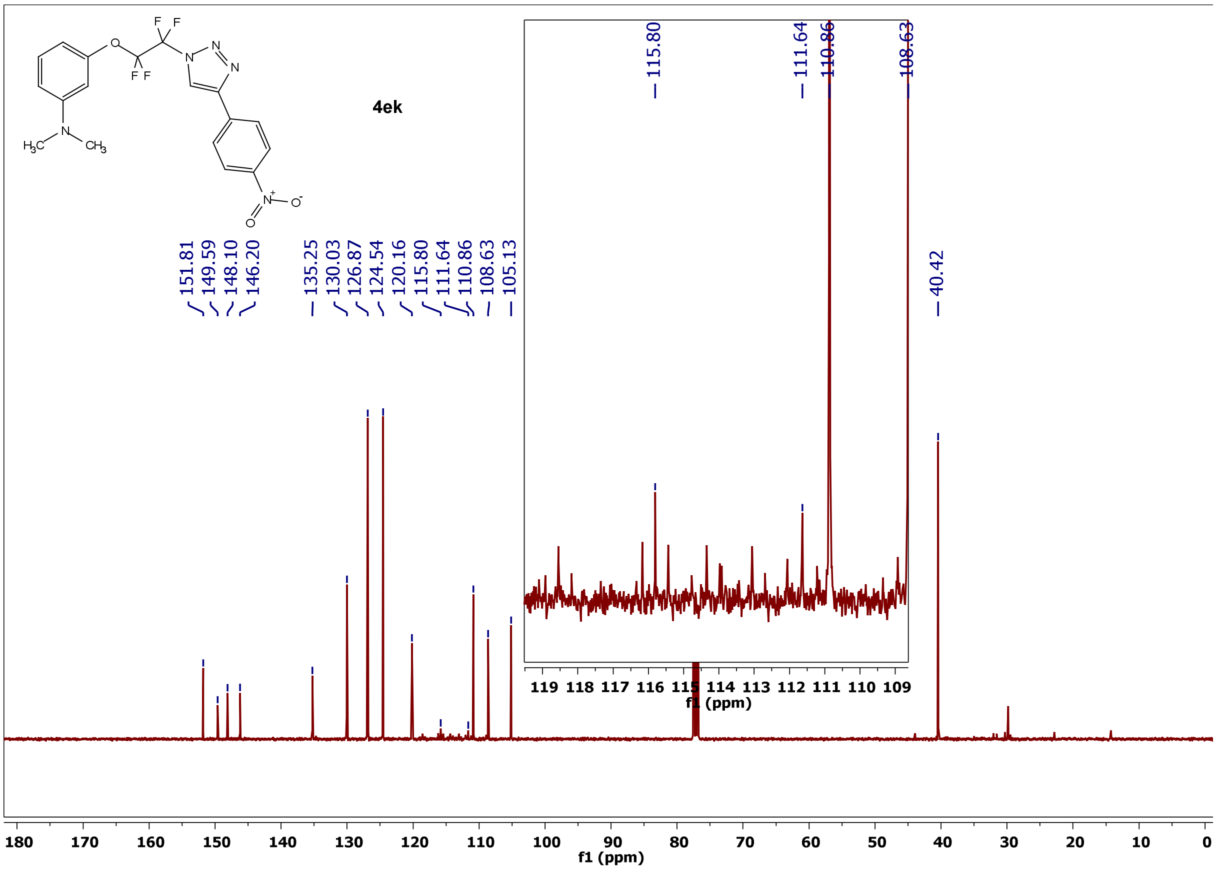
4en
-86.16
-99.47
-86.16
-86.17
-86.18
-99.46
-99.47
-99.48
-86.06 -86.10 -86.14 -86.18 -86.22 -86.26
f1 (ppm)
-99.42 -99.44 -99.46 -99.48 -99.50 -99.52 -99.54 -99.56
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

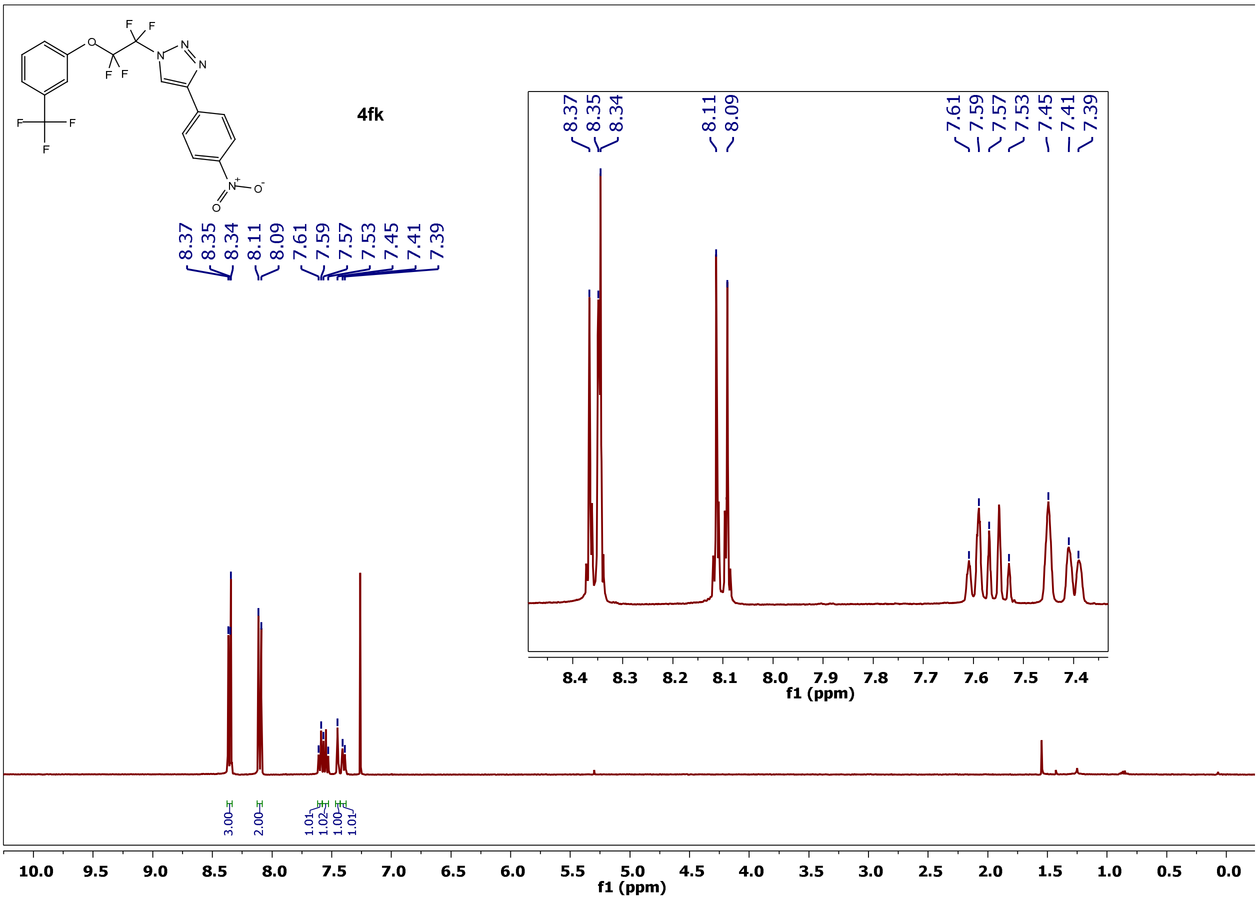


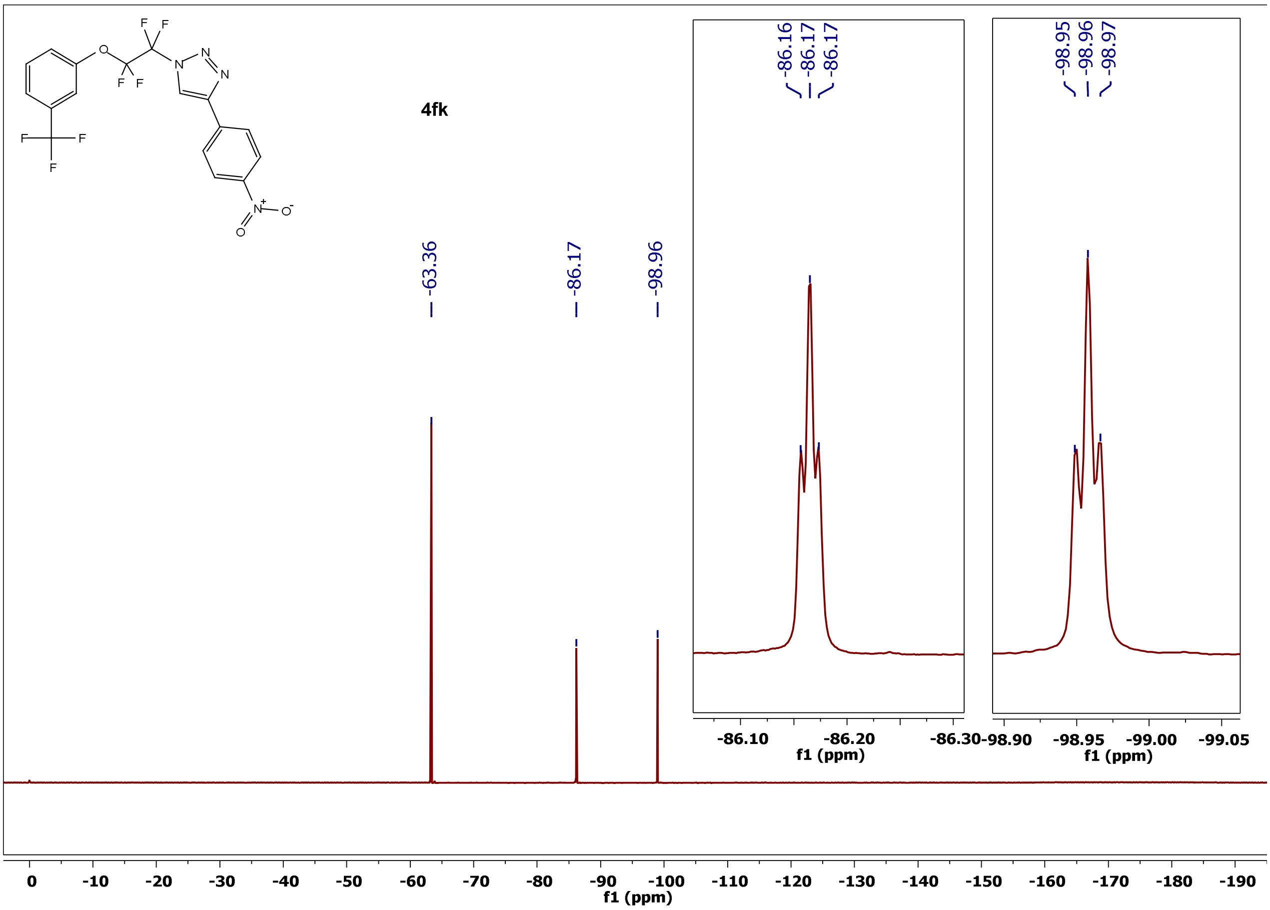
4en
160.40
151.80
149.71
148.24
129.98
127.61
121.76
117.55
115.93
114.56
111.65
110.79
108.84
105.34
55.50
40.47
117.55
115.93
114.56
111.65
110.79
108.84
120 118 116 114 112 110 108
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

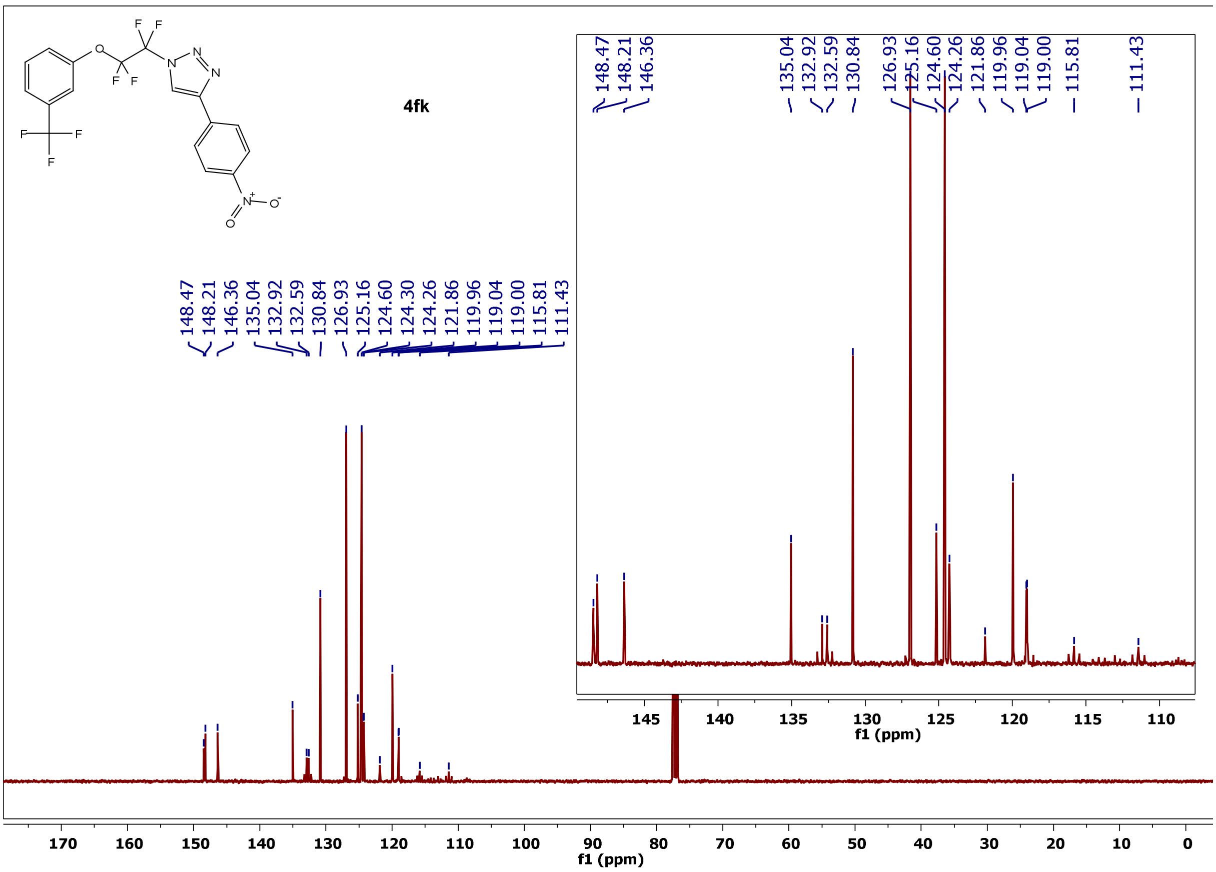

4ek
8.36
8.34
8.11
8.08
7.21
7.16
6.62
6.59
6.49
6.46
6.42
6.41
2.94
3.00
2.01
1.00
1.00
1.01
1.00
6.00
f1 (ppm)

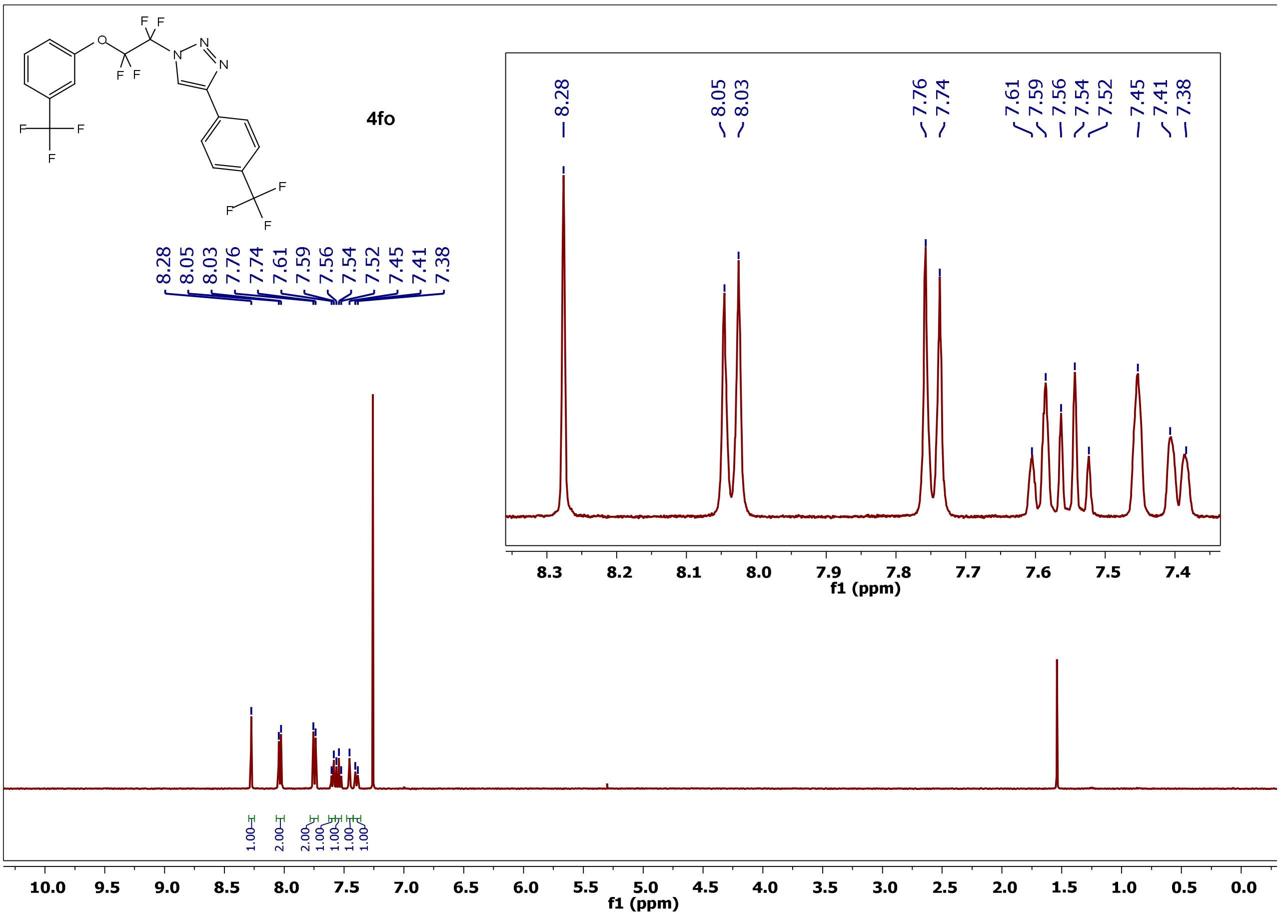

4ek
-86.10
-99.44
-86.09
-86.10
-86.11
-99.43
-99.44
-99.44
f1 (ppm)


4ek
151.81
149.59
148.10
146.20
135.25
130.03
126.87
124.54
120.16
115.80
111.64
110.86
108.63
105.13
40.42
f1 (ppm)


4fk
8.37
8.35
8.34
8.11
8.09
7.61
7.59
7.57
7.53
7.45
7.41
7.39
3.00
2.00
1.01
1.02
1.00
1.01
f1 (ppm)


4fk
-63.36
-86.17
-98.96
-86.16
-86.17
-86.17
-98.95
-98.96
-98.97
f1 (ppm)


4fk
148.47
148.21
146.36
135.04
132.92
132.59
130.84
126.93
125.16
124.60
124.30
124.26
121.86
119.96
119.04
119.00
115.81
111.43
f1 (ppm)


4fo
8.28
8.05
8.03
7.76
7.74
7.61
7.59
7.56
7.54
7.52
7.45
7.41
7.38
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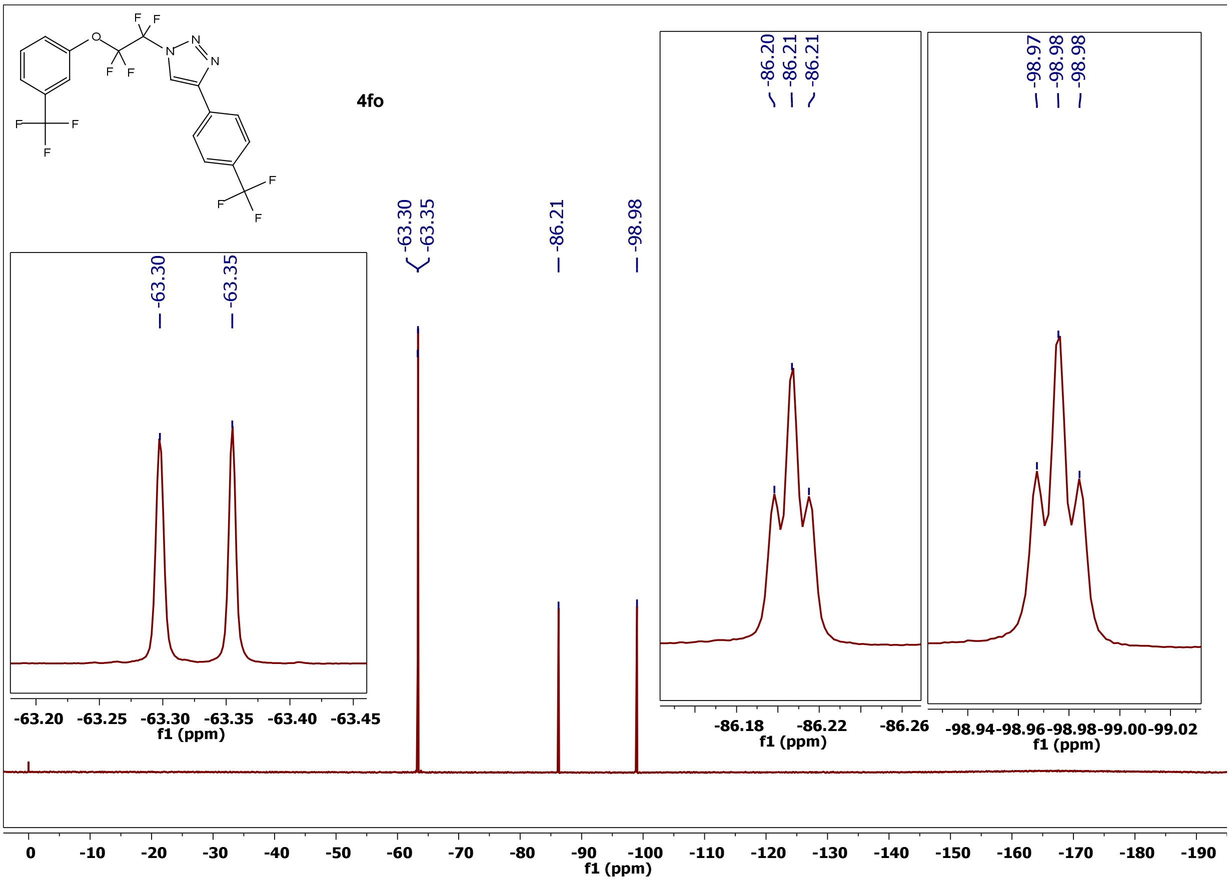
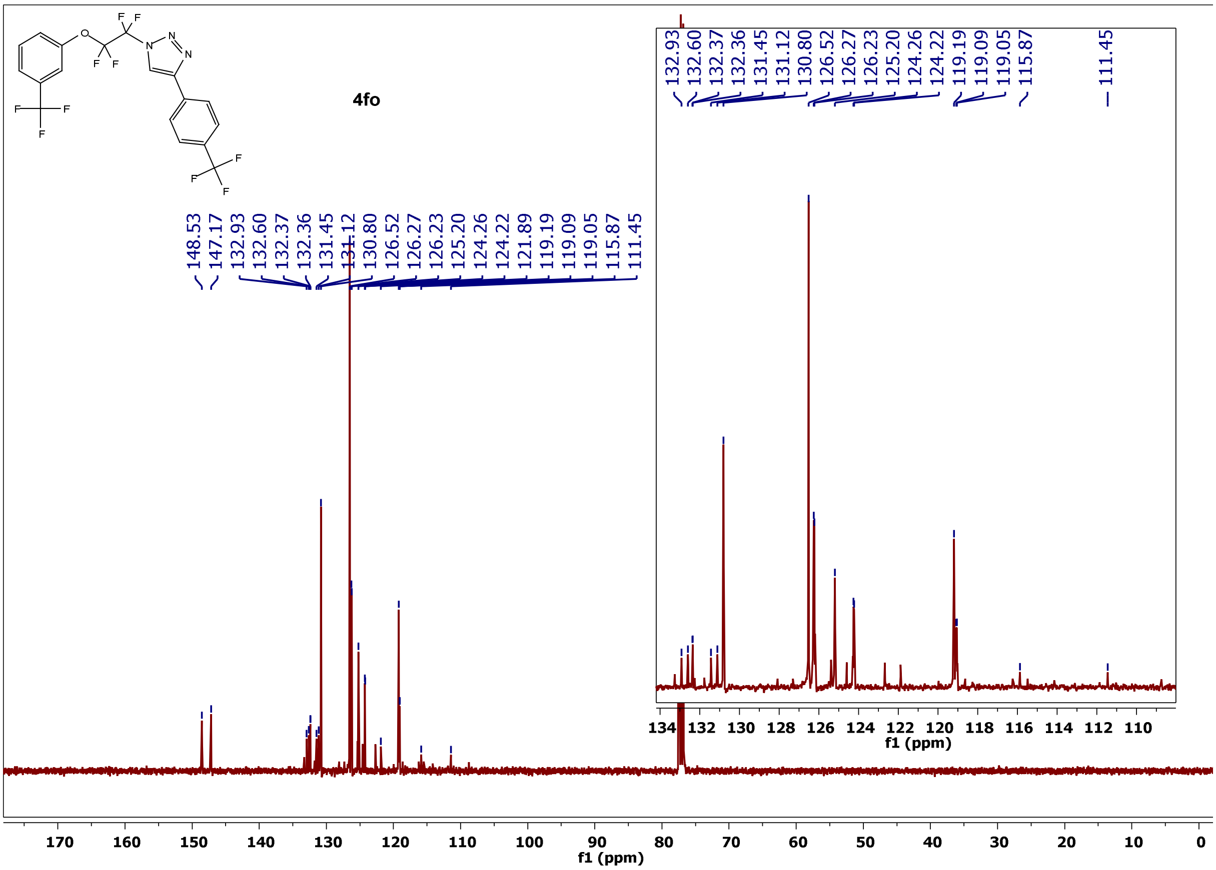
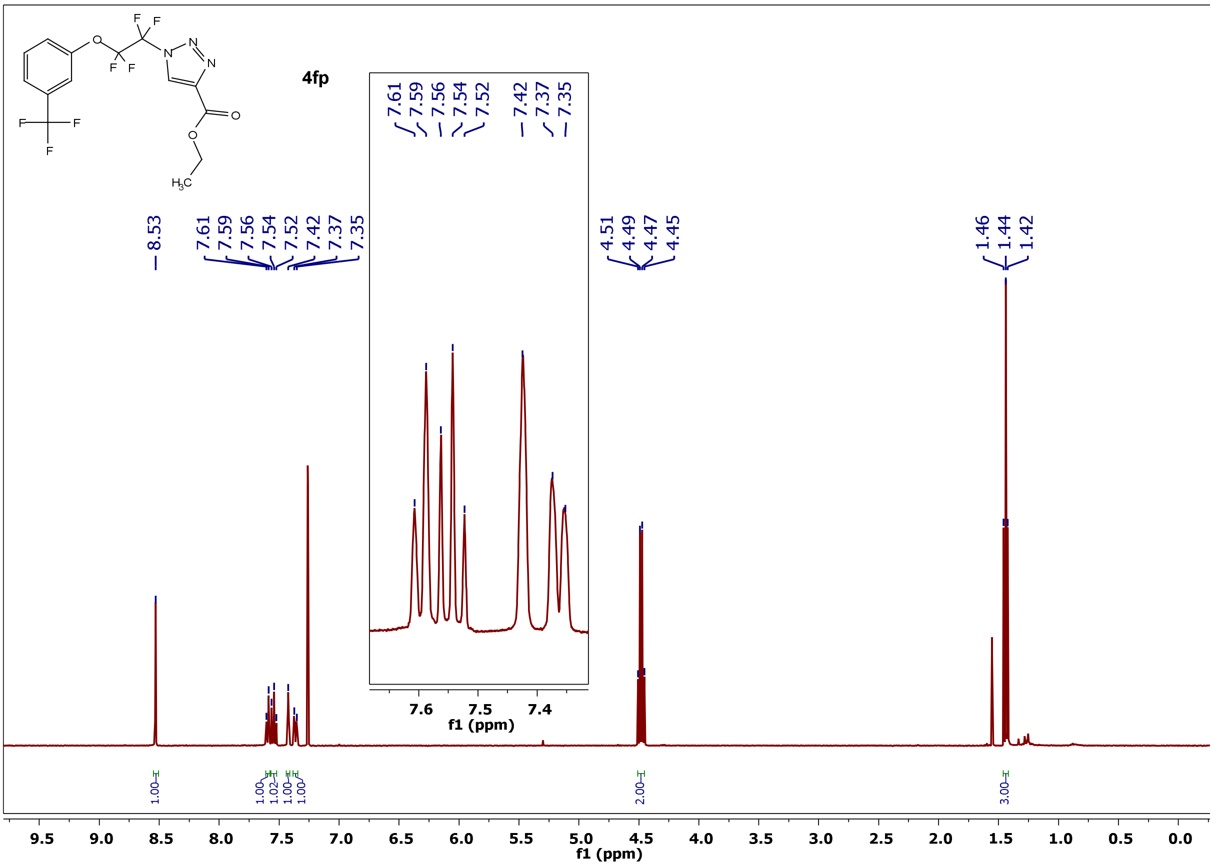
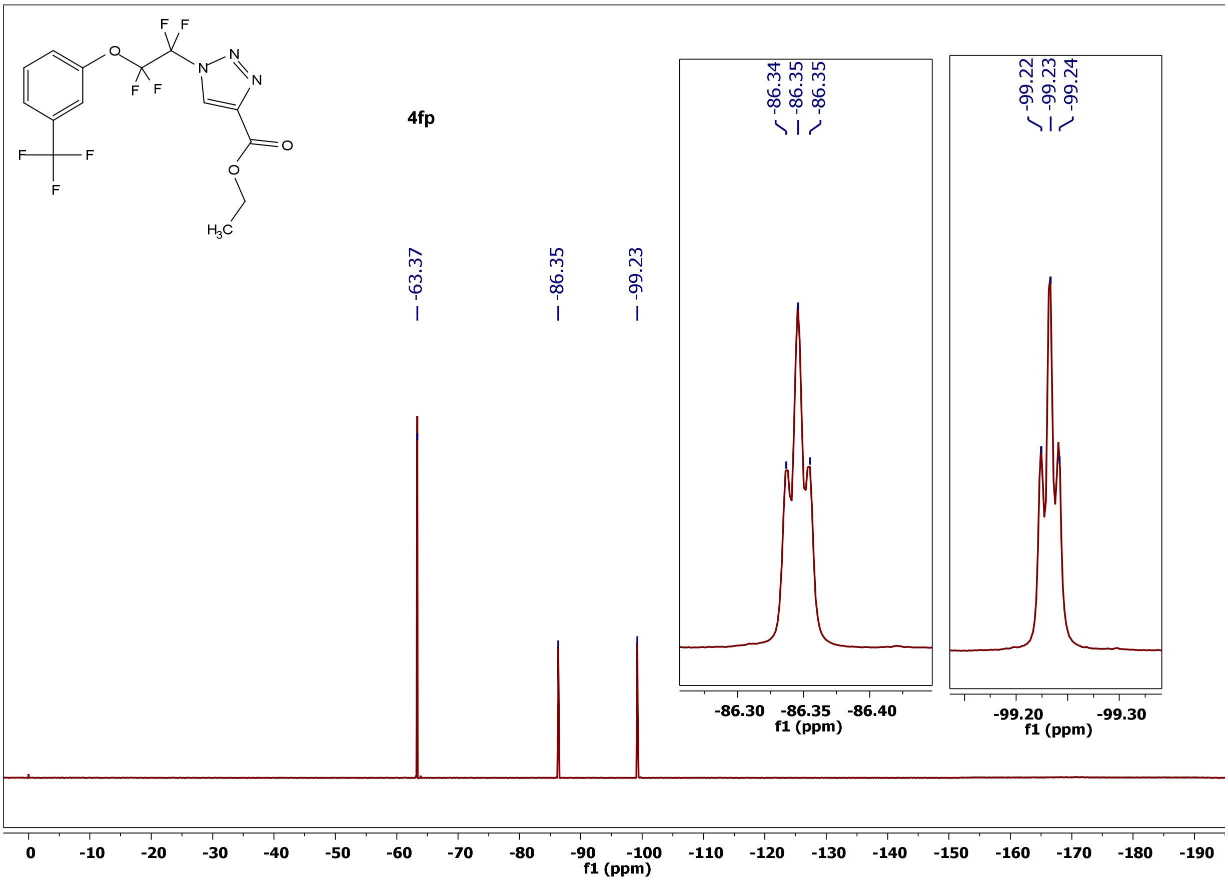
1.00
1.00
f1 (ppm)

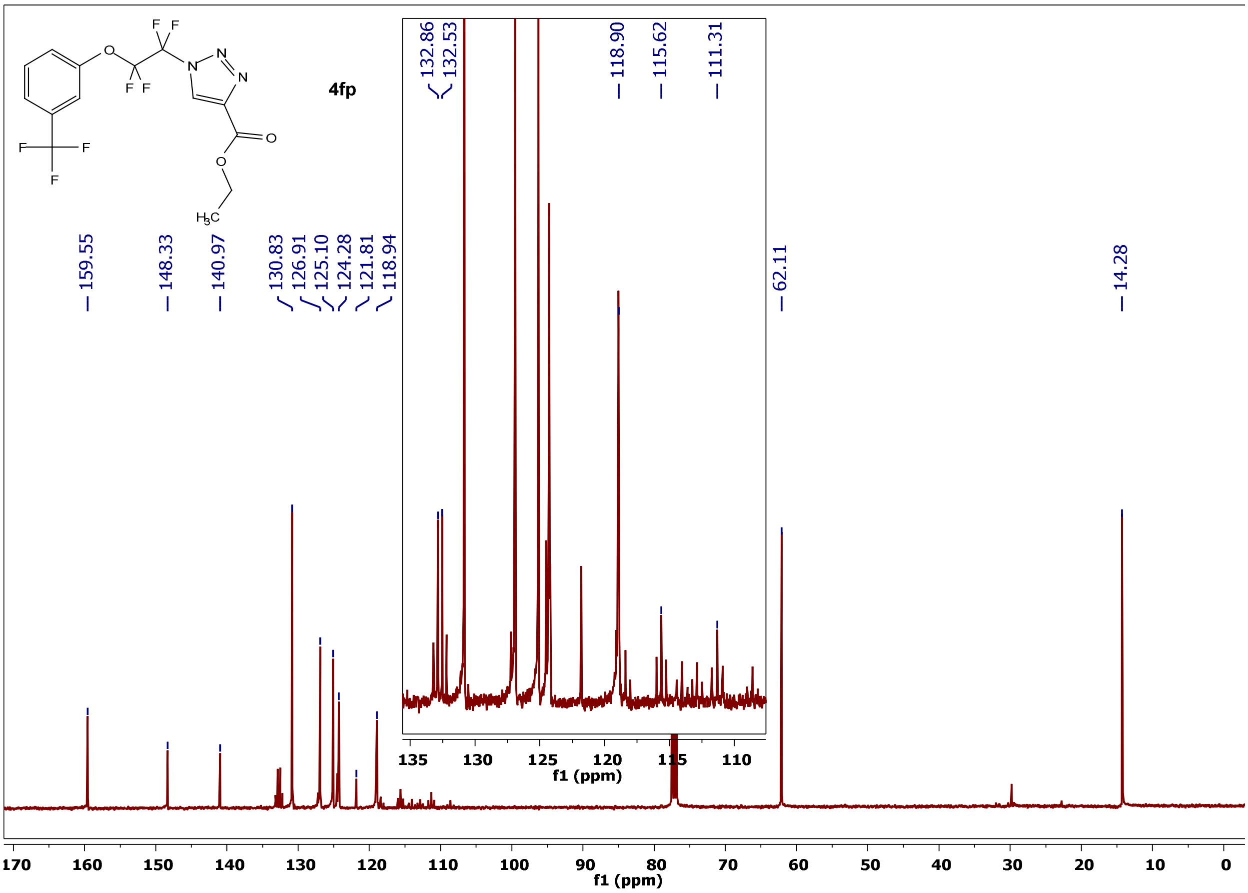

4fo
-63.30
-63.35
-86.21
-98.98
-86.20
-86.21
-86.21
-98.97
-98.98
-98.98
-63.20 -63.25 -63.30 -63.35 -63.40 -63.45
f1 (ppm)
-86.18 -86.22 -86.26
f1 (ppm)
-98.94 -98.96 -98.98 -99.00 -99.02
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

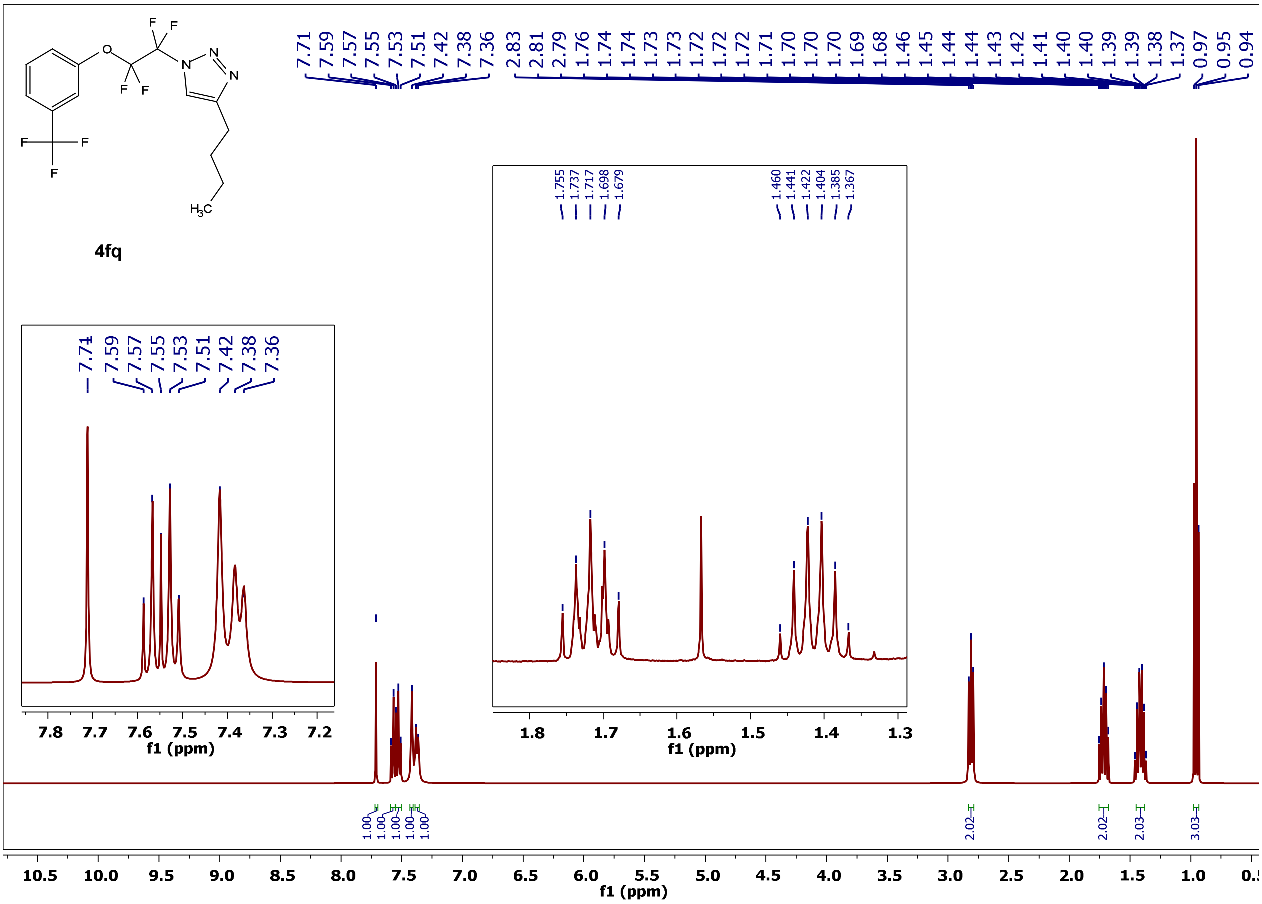

4fo
148.53
147.17
132.93
132.60
132.37
132.36
131.45
131.12
130.80
126.52
126.27
126.23
125.20
124.26
124.22
121.89
119.19
119.09
119.05
115.87
111.45
134 132 130 128 126 124 122 120 118 116 114 112 110
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



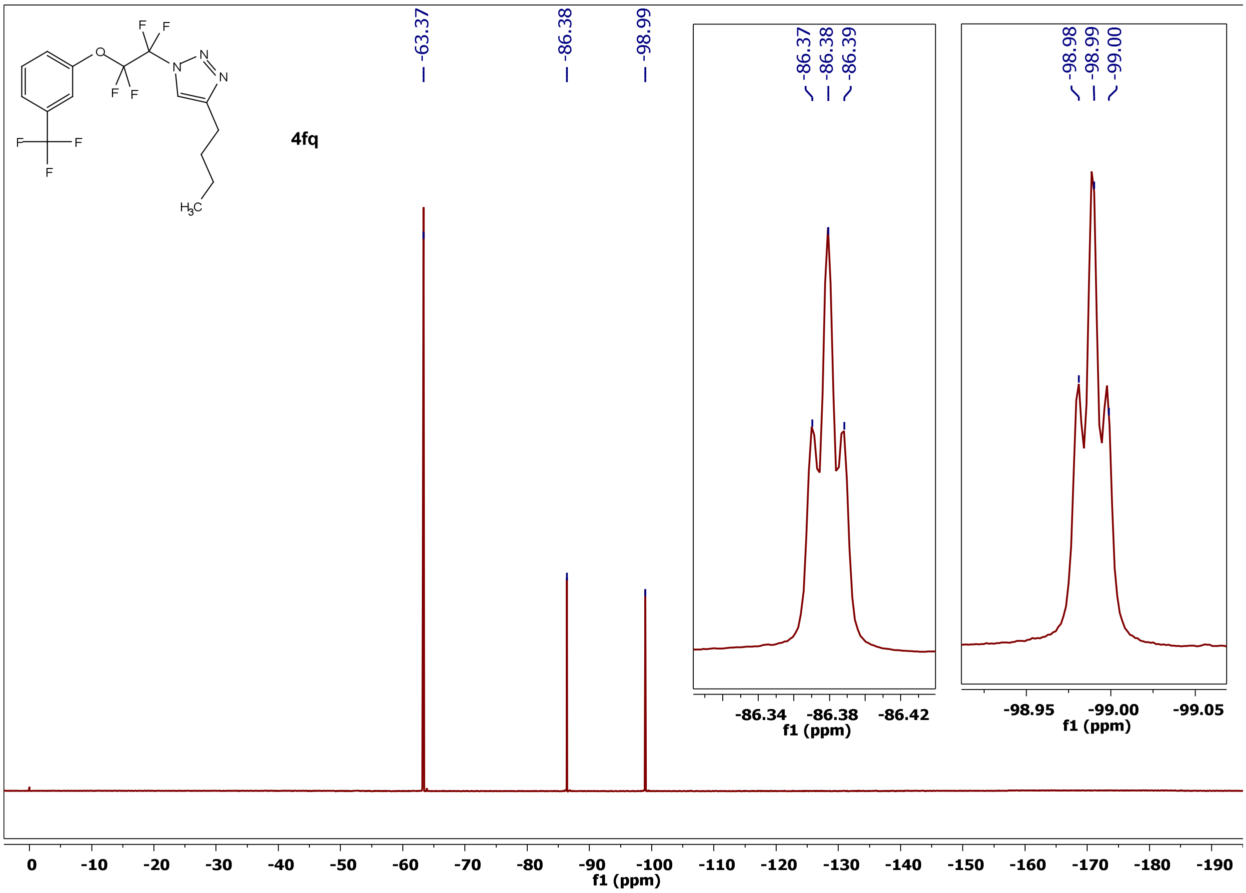
4fp
8.53
7.61
7.59
7.56
7.54
7.52
7.42
7.37
7.35
4.51
4.49
4.47
4.45
1.46
1.44
1.42
1.00
1.00
1.02
1.00
1.00
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.6 7.5 7.4
f1 (ppm)

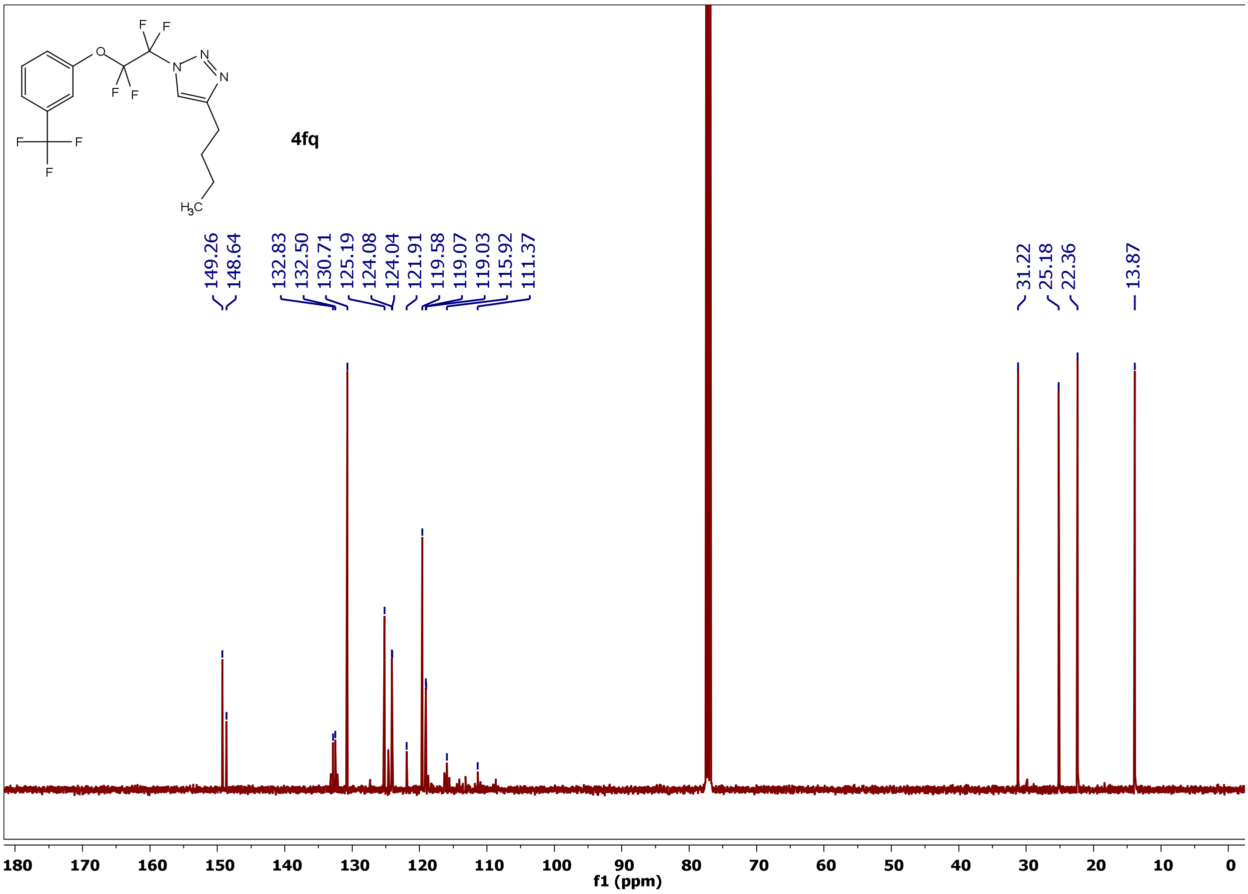

4fp
-63.37
-86.35
-99.23
-86.34
-86.35
-86.35
-86.30 -86.35 -86.40
f1 (ppm)
-99.22
-99.23
-99.24
-99.20 -99.30
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

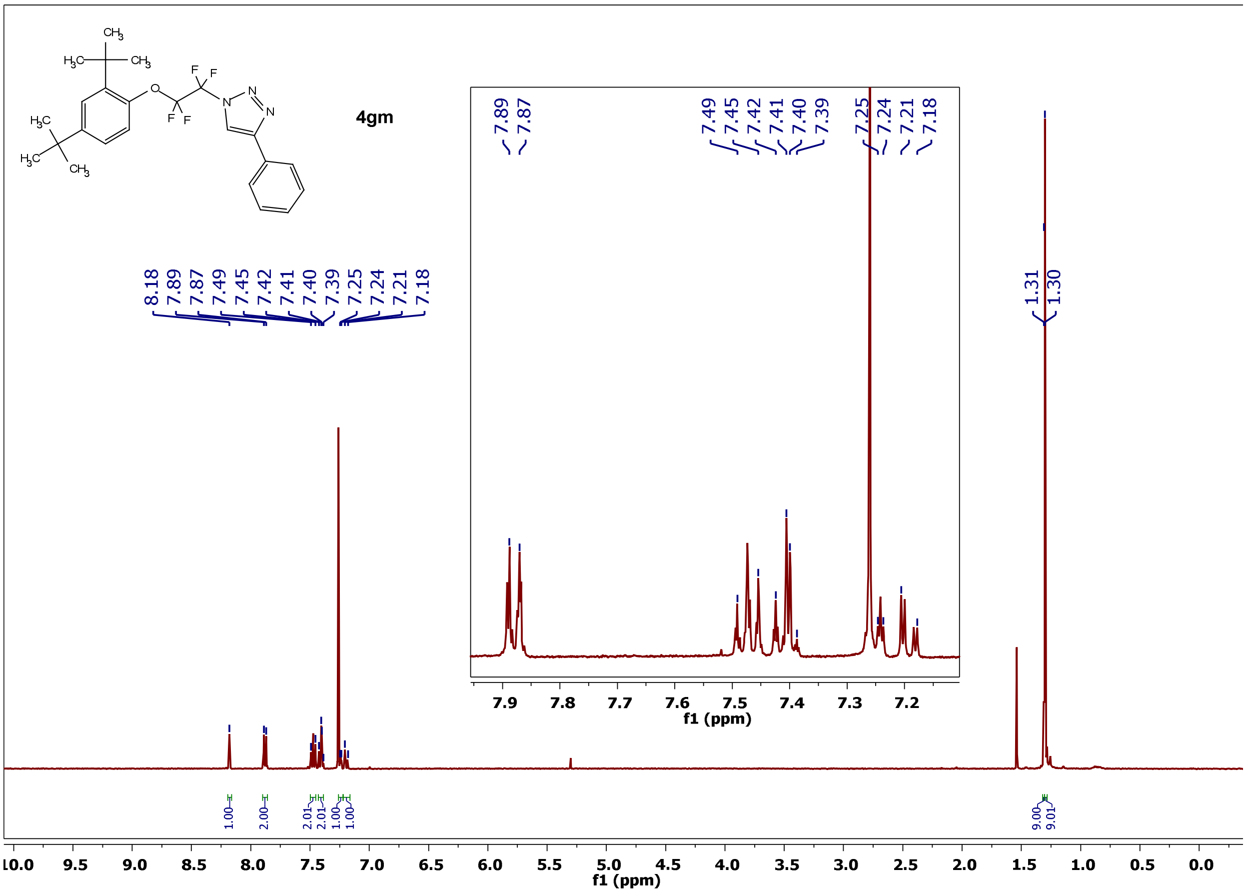

4fp
159.55
148.33
140.97
130.83
126.91
125.10
124.28
121.81
118.94
62.11
14.28
132.86
132.53
118.90
115.62
111.31
f1 (ppm)
f1 (ppm)

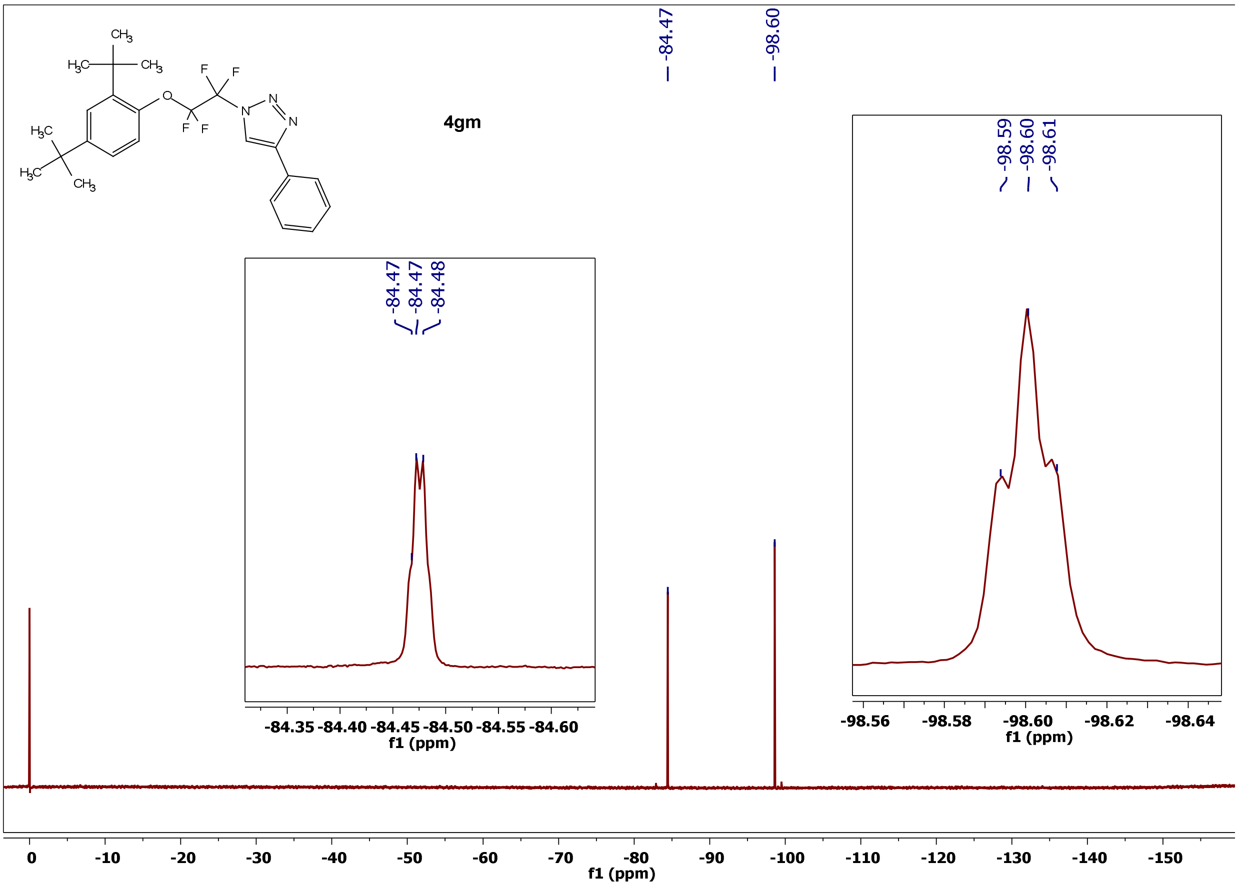


4fq

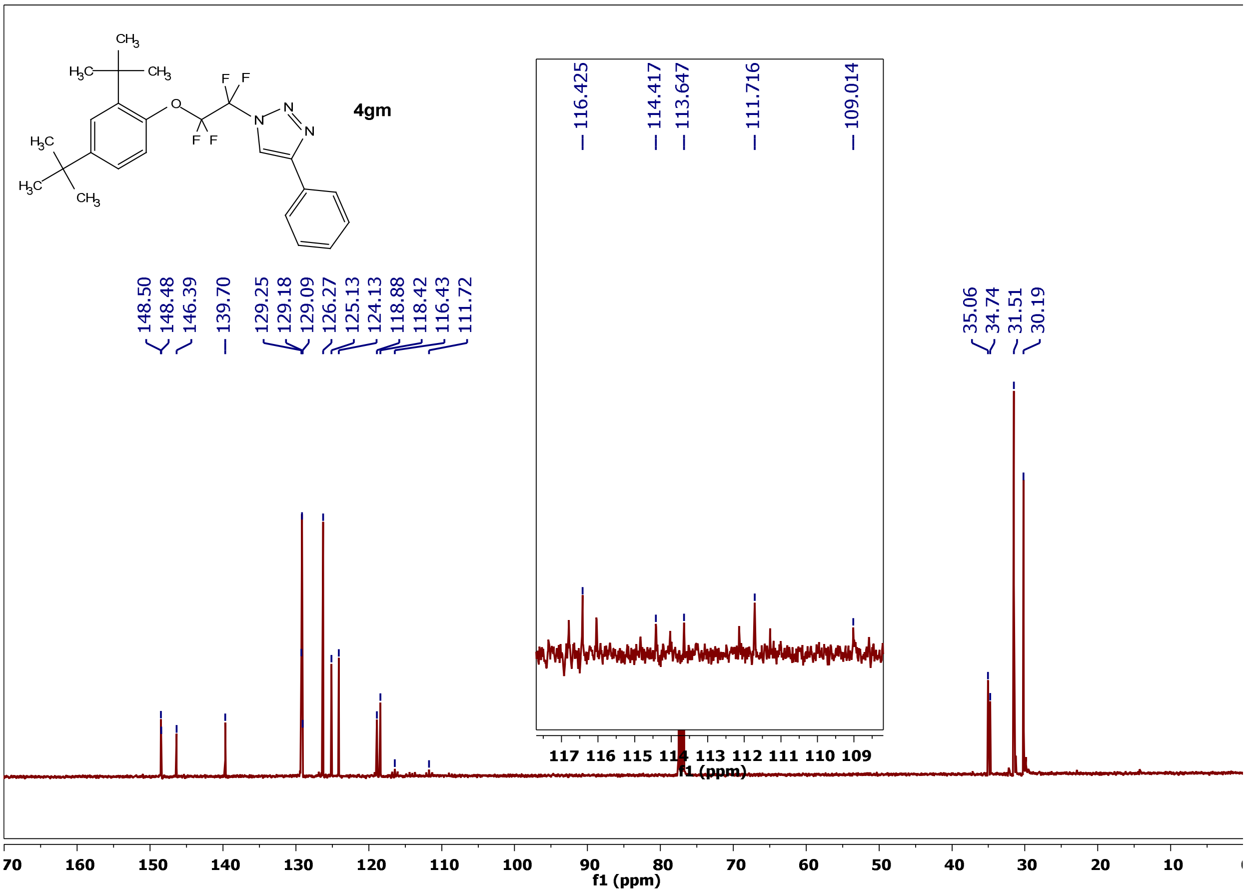

4fq
-63.37
-86.38
-98.99
-86.37
-86.38
-86.39
-98.98
-98.99
-99.00
-86.34
-86.38
-86.42
f1 (ppm)
-98.95
-99.00
-99.05
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

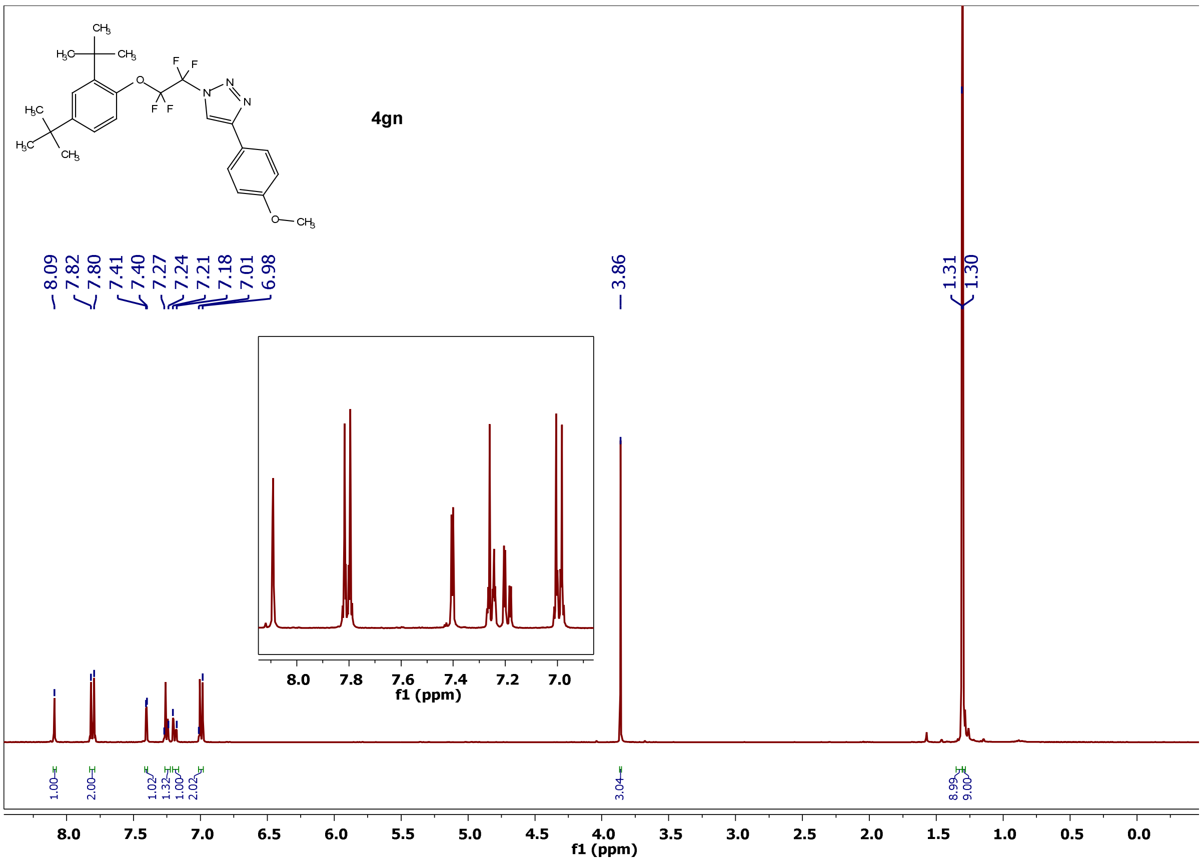

4fq
149.26
148.64
132.83
132.50
130.71
125.19
124.08
124.04
121.91
119.58
119.07
119.03
115.92
111.37
31.22
25.18
22.36
13.87
f1 (ppm)

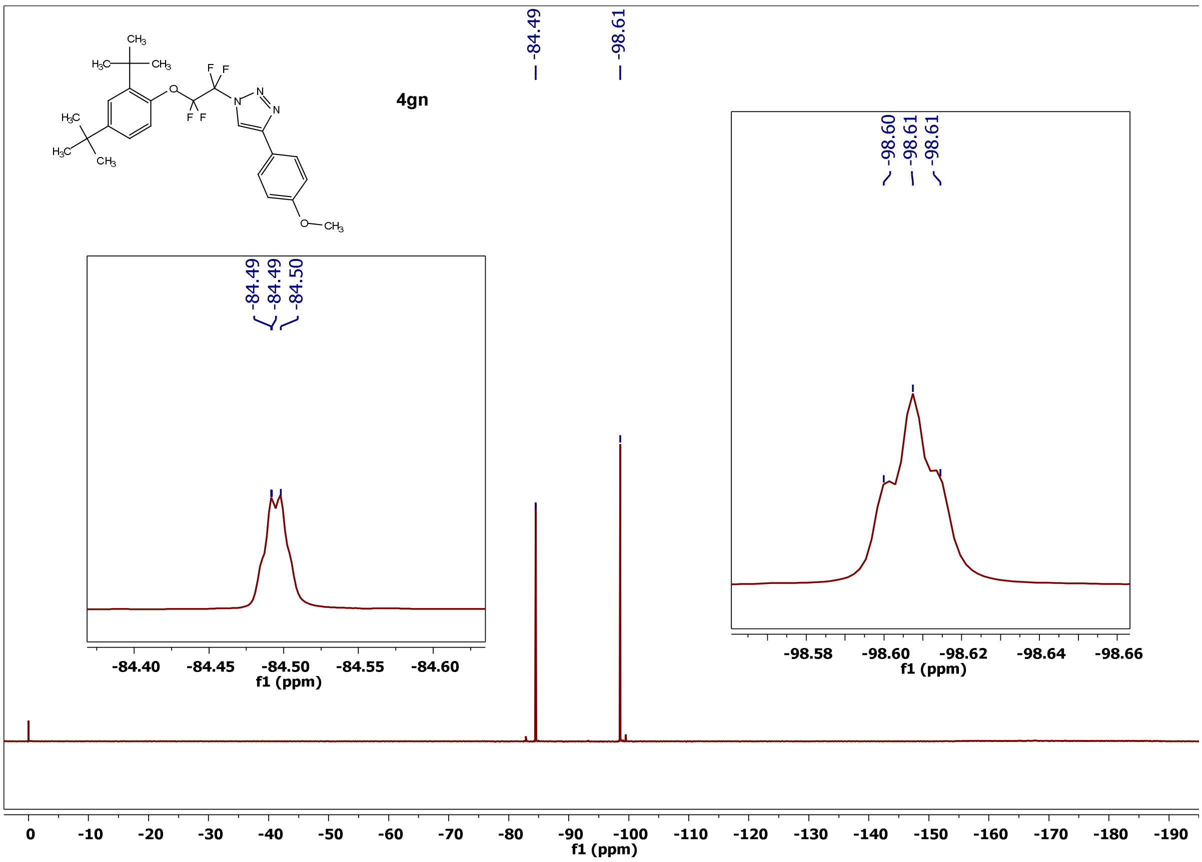

4gm
8.18
7.89
7.87
7.49
7.45
7.42
7.41
7.40
7.39
7.25
7.24
7.21
7.18
1.31
1.30
1.00
2.00
2.01
2.01
1.00
1.00
9.00
9.01
f1 (ppm)

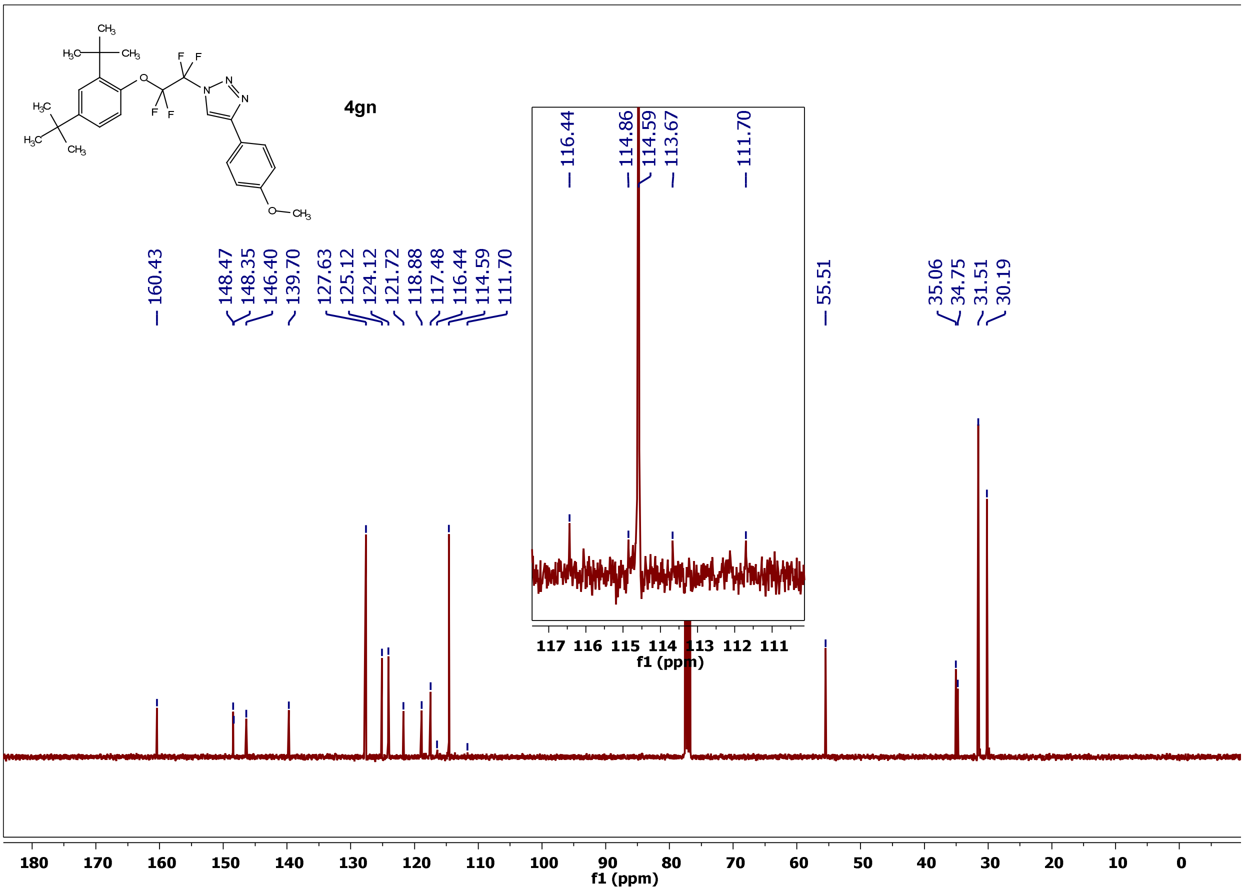


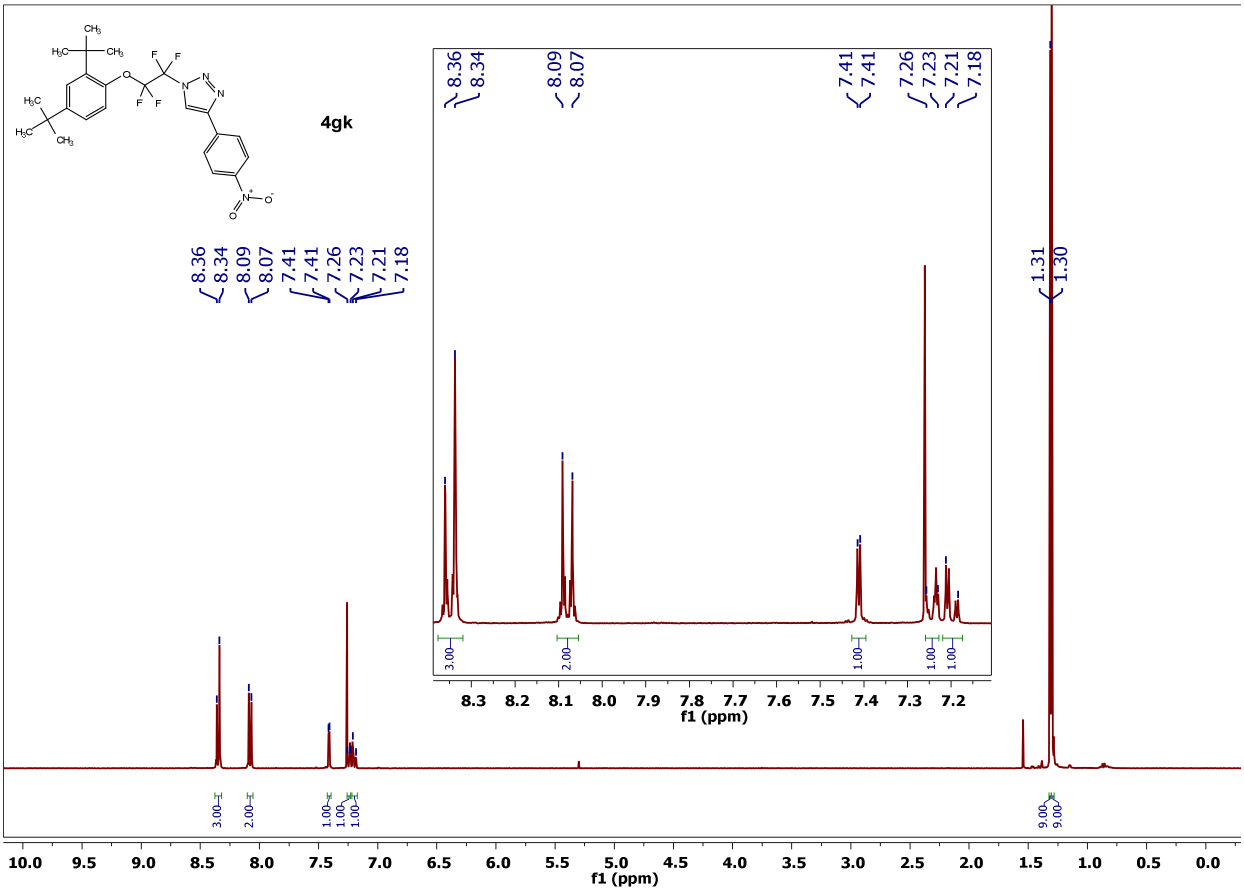
4gm
-84.47
-98.60
-84.47
-84.47
-84.48
-98.59
-98.60
-98.61
-84.35 -84.40 -84.45 -84.50 -84.55 -84.60
f1 (ppm)
-98.56 -98.58 -98.60 -98.62 -98.64
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


4gm
148.50
148.48
146.39
139.70
129.25
129.18
129.09
126.27
125.13
124.13
118.88
118.42
116.43
111.72
35.06
34.74
31.51
30.19
116.425
114.417
113.647
111.716
109.014
f1 (ppm)

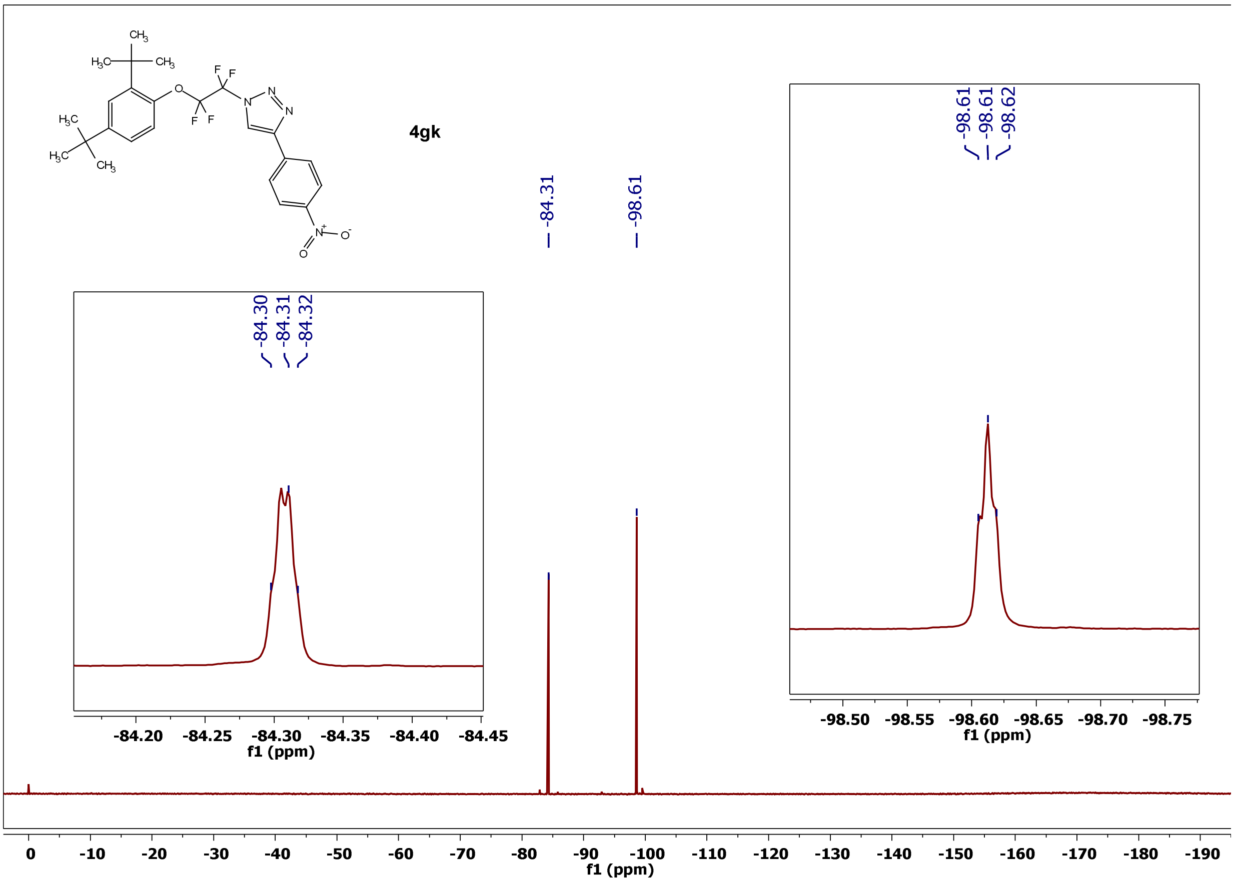

4gn
8.09
7.82
7.80
7.41
7.40
7.27
7.24
7.21
7.18
7.01
6.98
3.86
1.31
1.30
f1 (ppm)

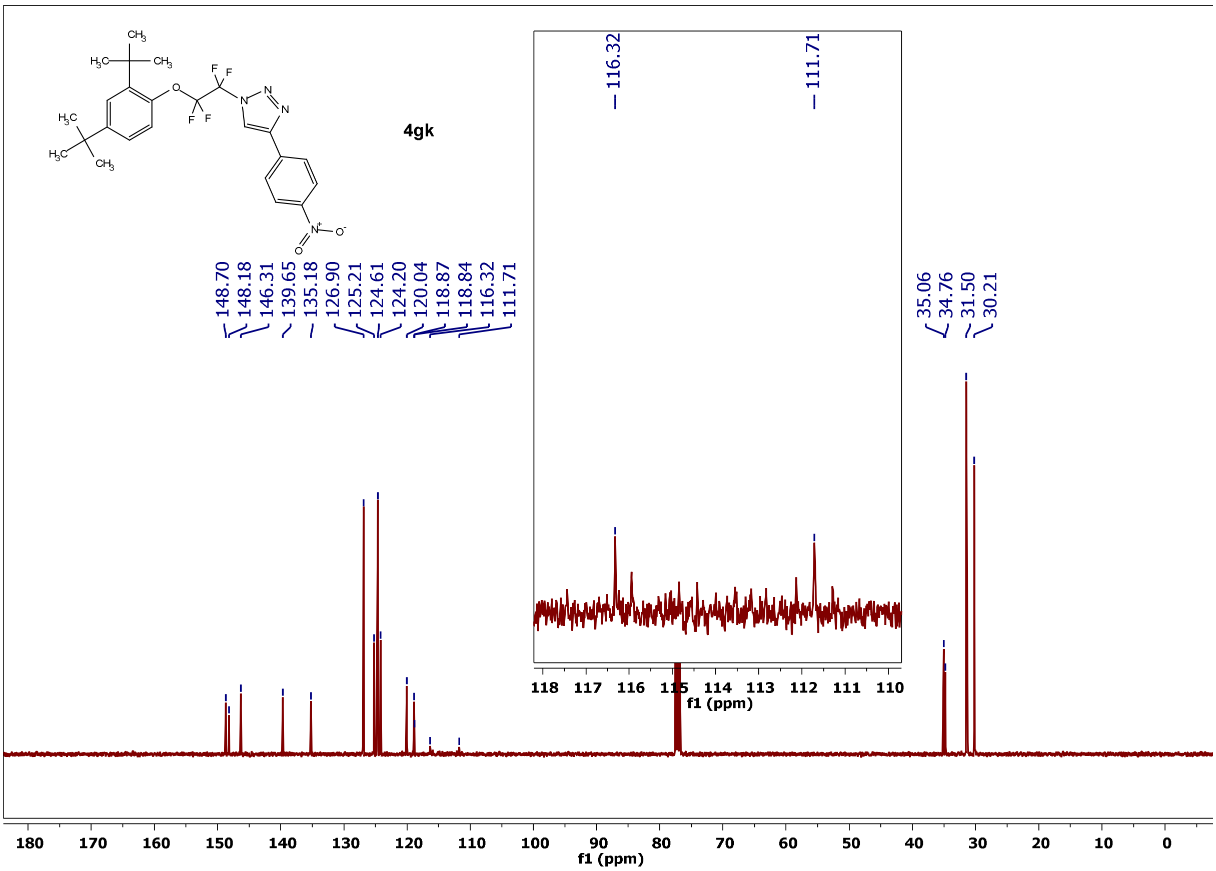

4gn
-84.49
-98.61
-84.49
-84.49
-84.50
-98.60
-98.61
-98.61
-84.40 -84.45 -84.50 -84.55 -84.60
f1 (ppm)
-98.58 -98.60 -98.62 -98.64 -98.66
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

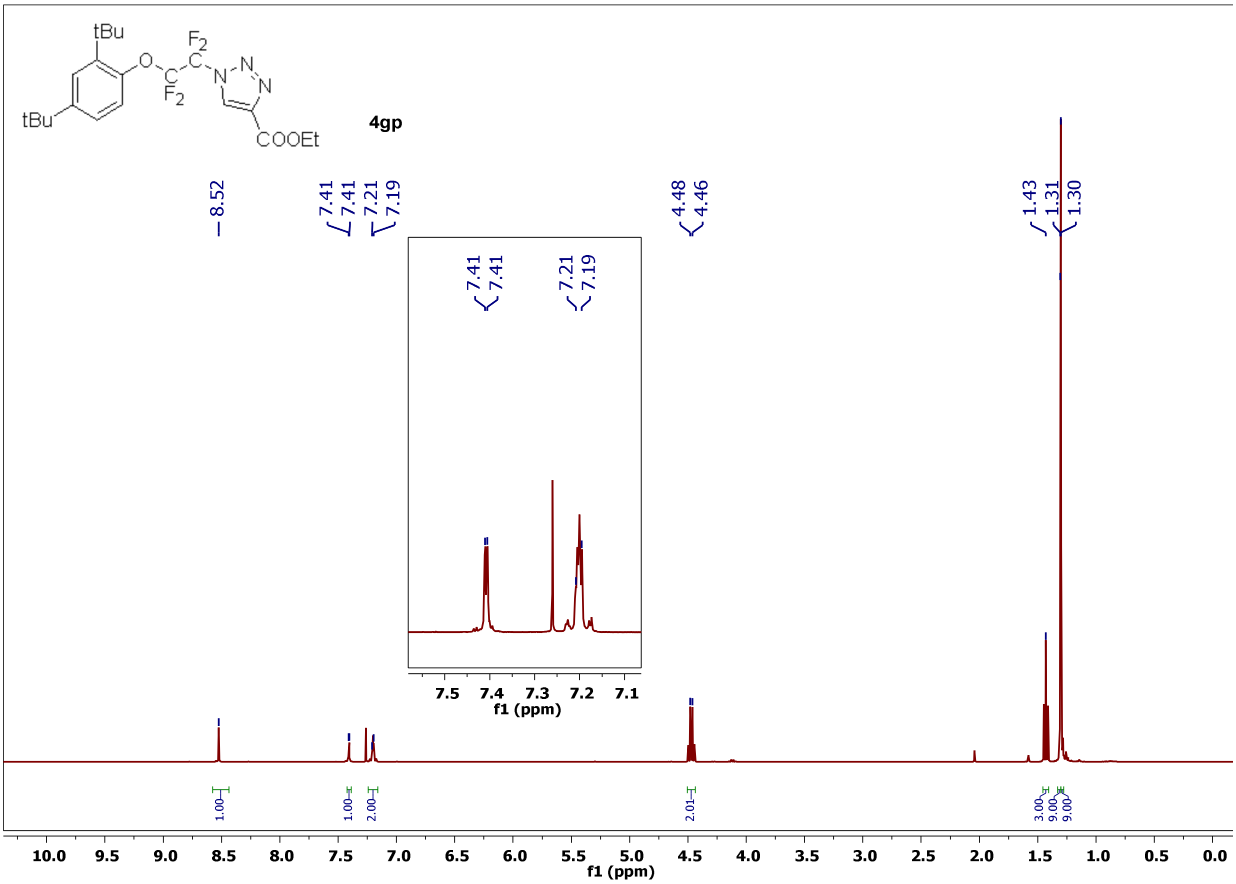

4gn
160.43
148.47
148.35
146.40
139.70
127.63
125.12
124.12
121.72
118.88
117.48
116.44
114.59
111.70
55.51
35.06
34.75
31.51
30.19
116.44
114.86
114.59
113.67
111.70
f1 (ppm)
f1 (ppm)

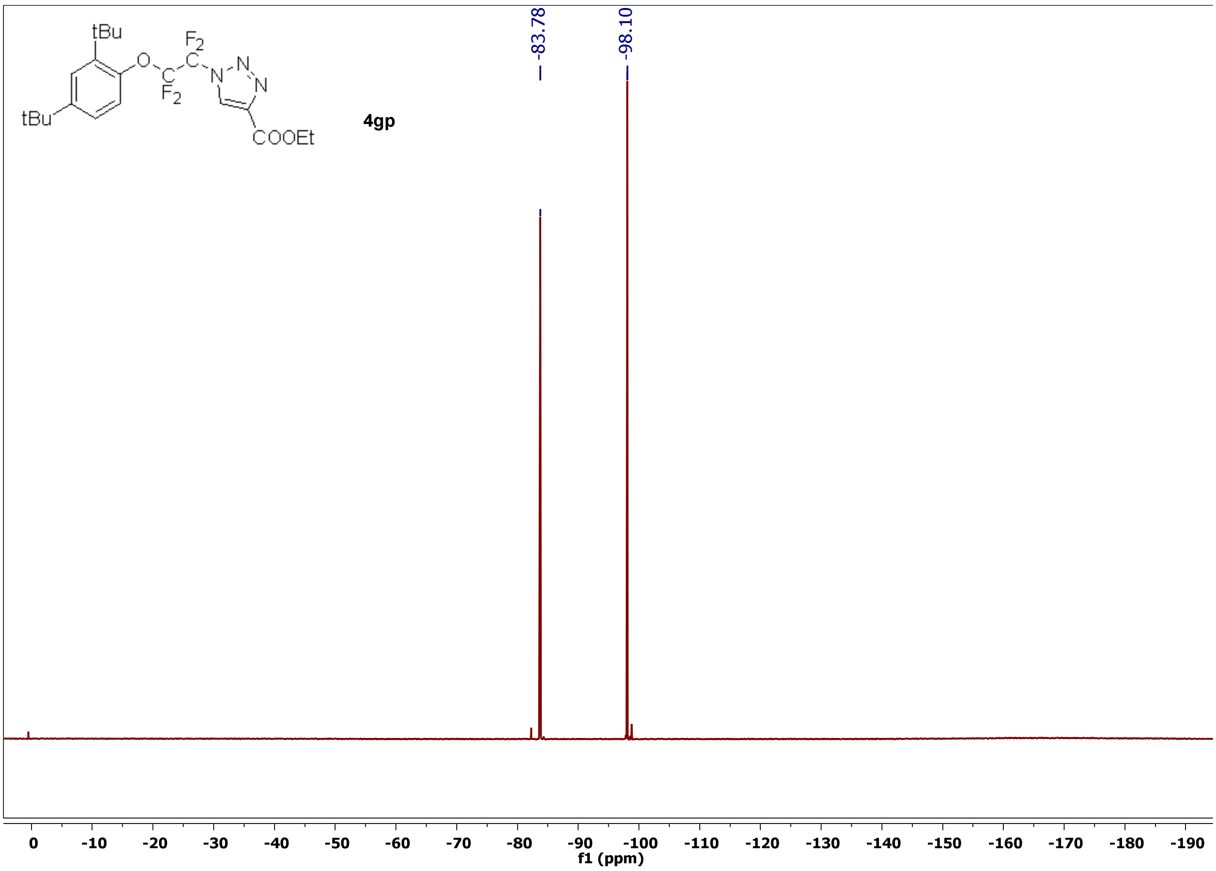


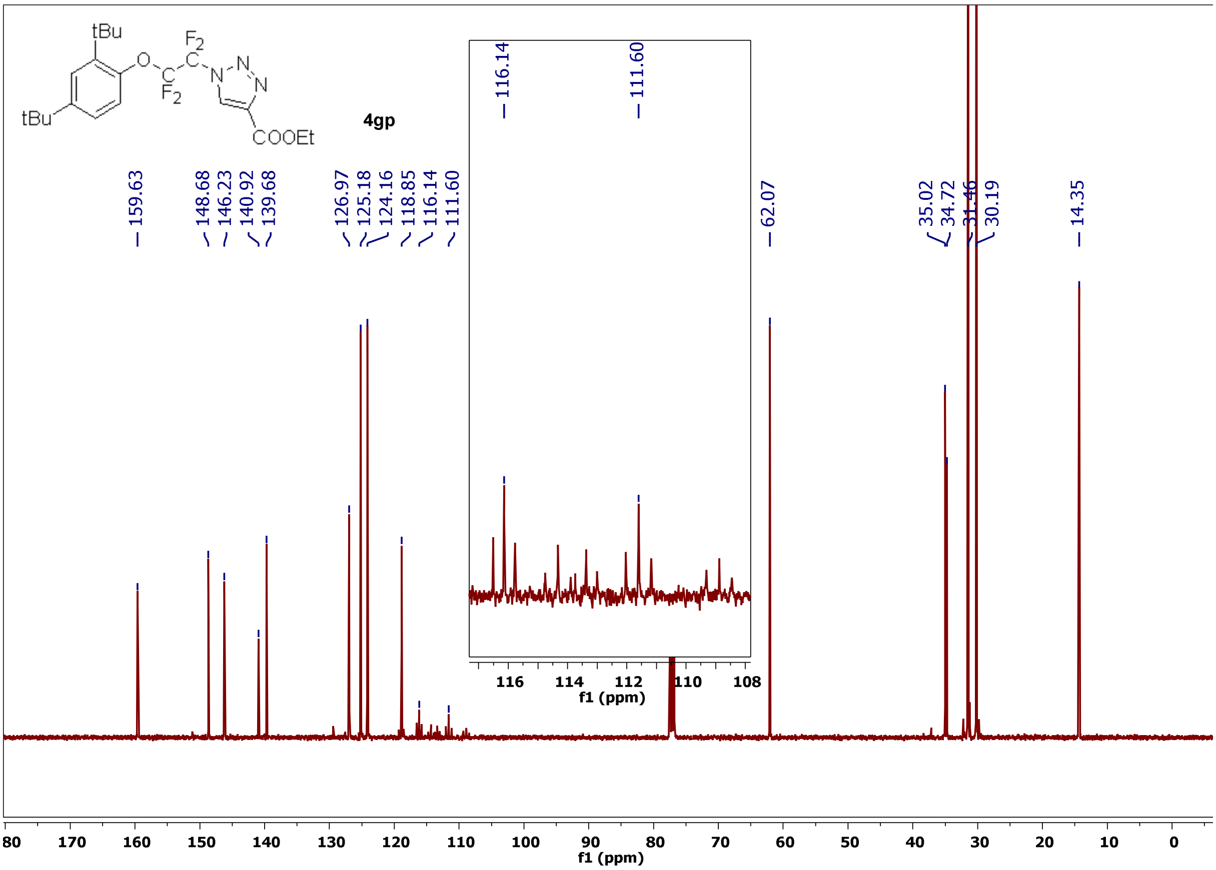
4gk
8.36
8.34
8.09
8.07
7.41
7.41
7.26
7.23
7.21
7.18
1.31
1.30
3.00
2.00
1.00
1.00
1.00
9.00
9.00
f1 (ppm)

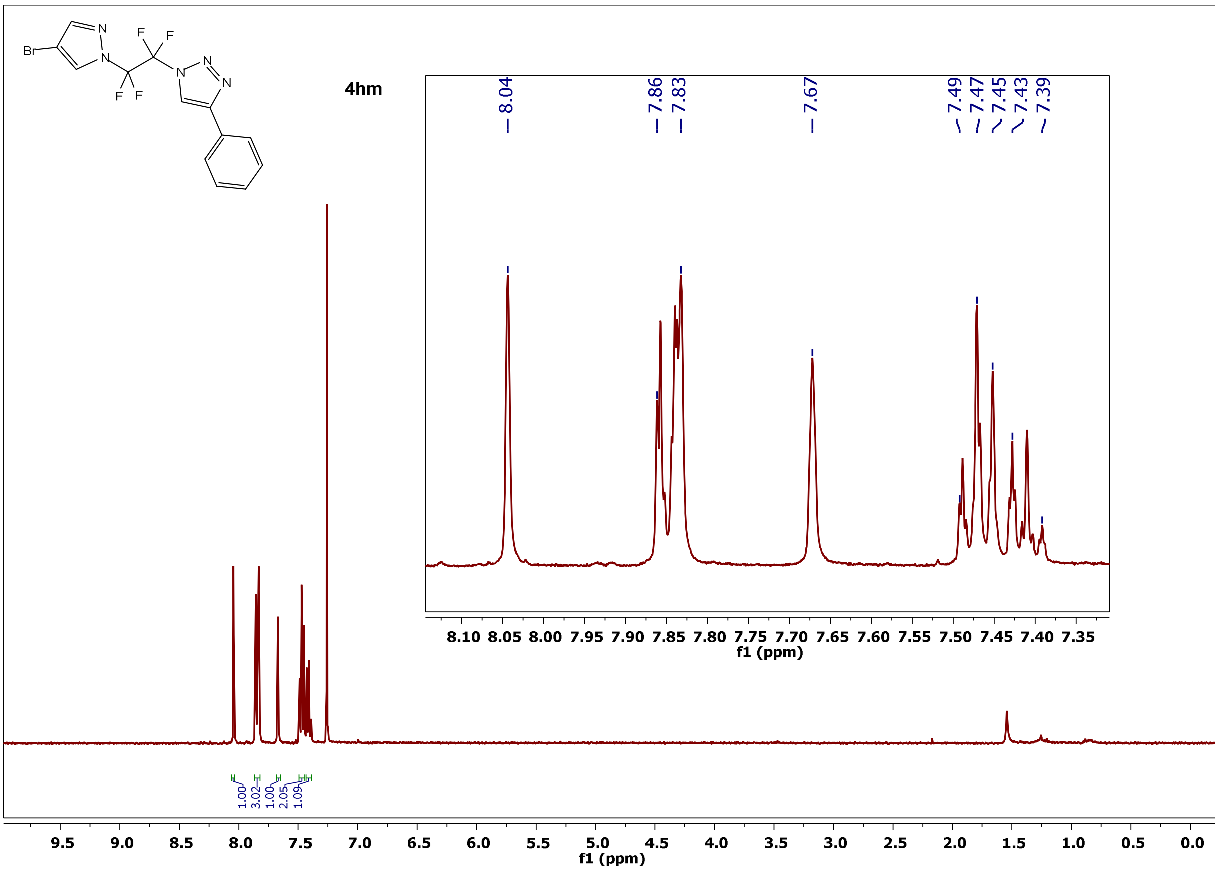

4gk
-84.31
-98.61
-84.30
-84.31
-84.32
-98.61
-98.61
-98.62
f1 (ppm)


4gk
148.70
148.18
146.31
139.65
135.18
126.90
125.21
124.61
124.20
120.04
118.87
118.84
116.32
111.71
35.06
34.76
31.50
30.21
116.32
111.71
f1 (ppm)

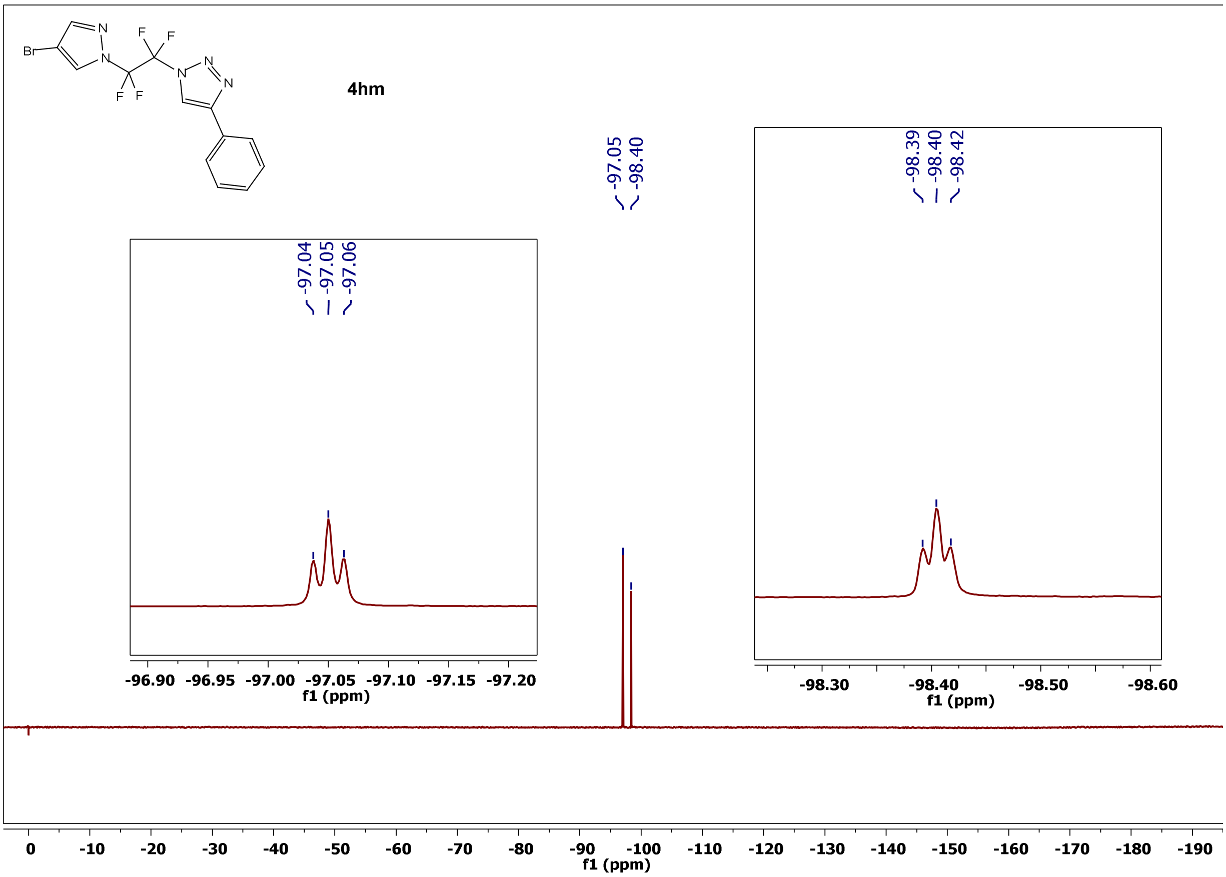

tBu
tBu
F2
F2
O
C
C
N
N
N
COOEt
4gp
8.52
7.41
7.41
7.21
7.19
4.48
4.46
1.43
1.31
1.30
1.00
1.00
2.00
2.01
3.00
9.00
9.00
7.5 7.4 7.3 7.2 7.1
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

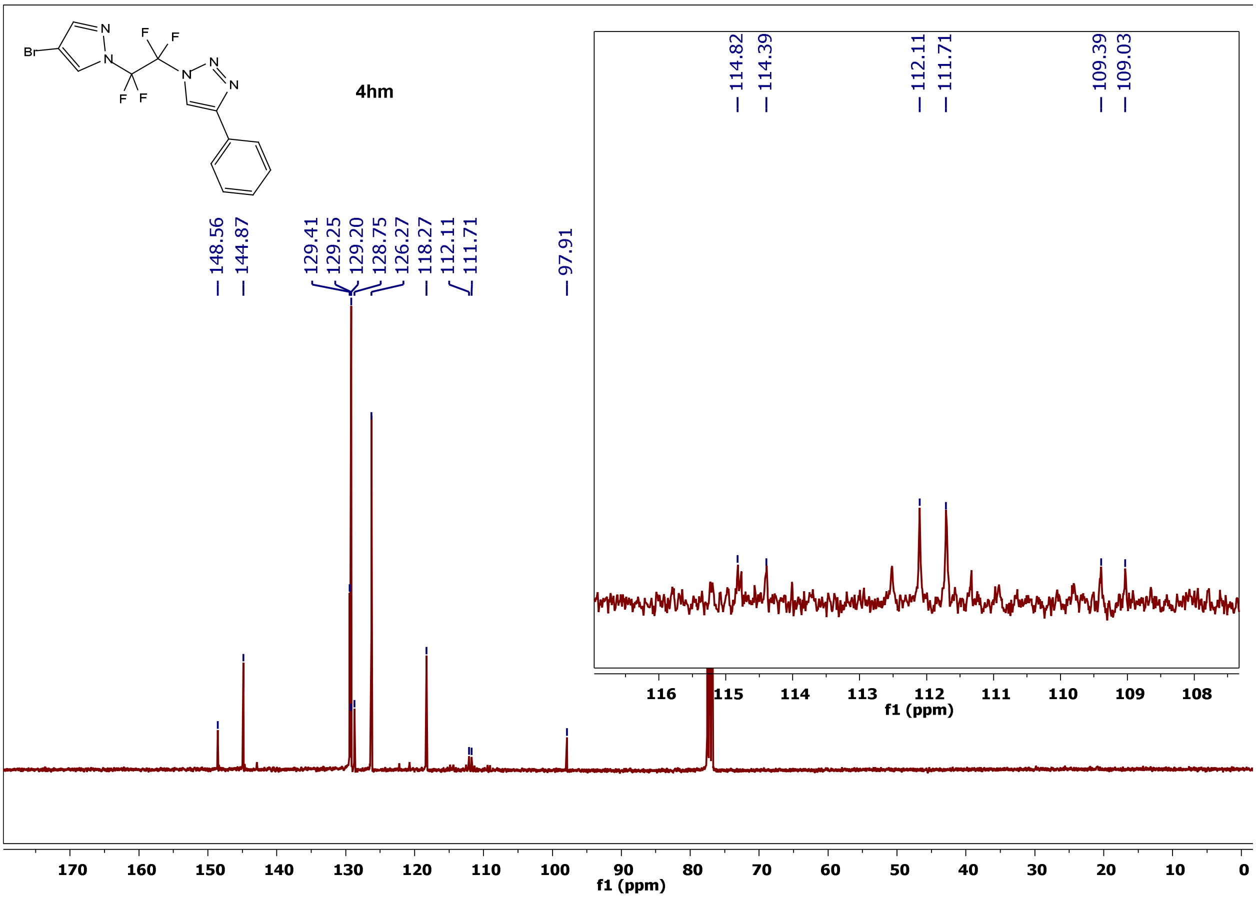

tBu
tBu
F2
F2
O
C
C
N
N
N
COOEt
4gp
-83.78
-98.10
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

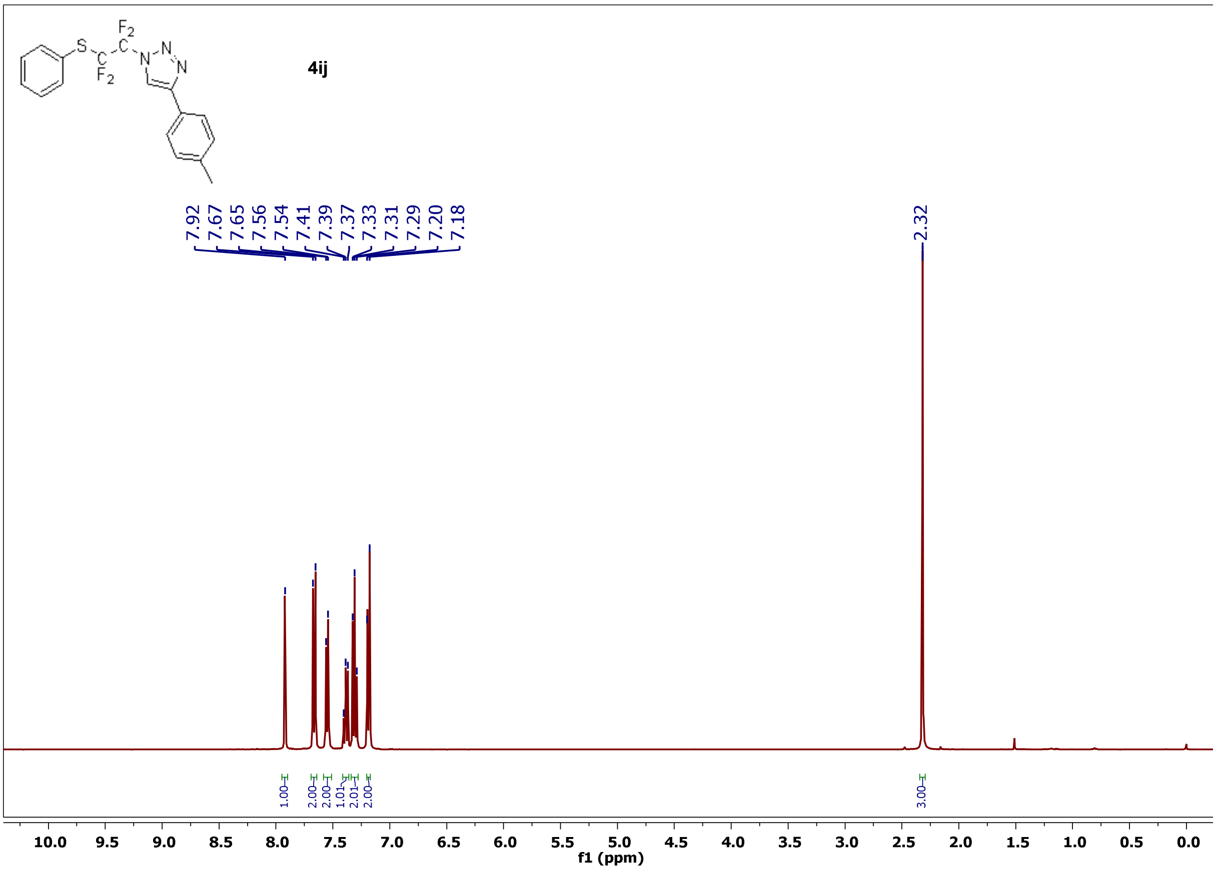

tBu
O
F2
C
N
N
N
tBu
C
F2
COOEt
4gp
159.63
148.68
146.23
140.92
139.68
126.97
125.18
124.16
118.85
116.14
111.60
62.07
35.02
34.72
31.46
30.19
14.35
116.14
111.60
f1 (ppm)
f1 (ppm)

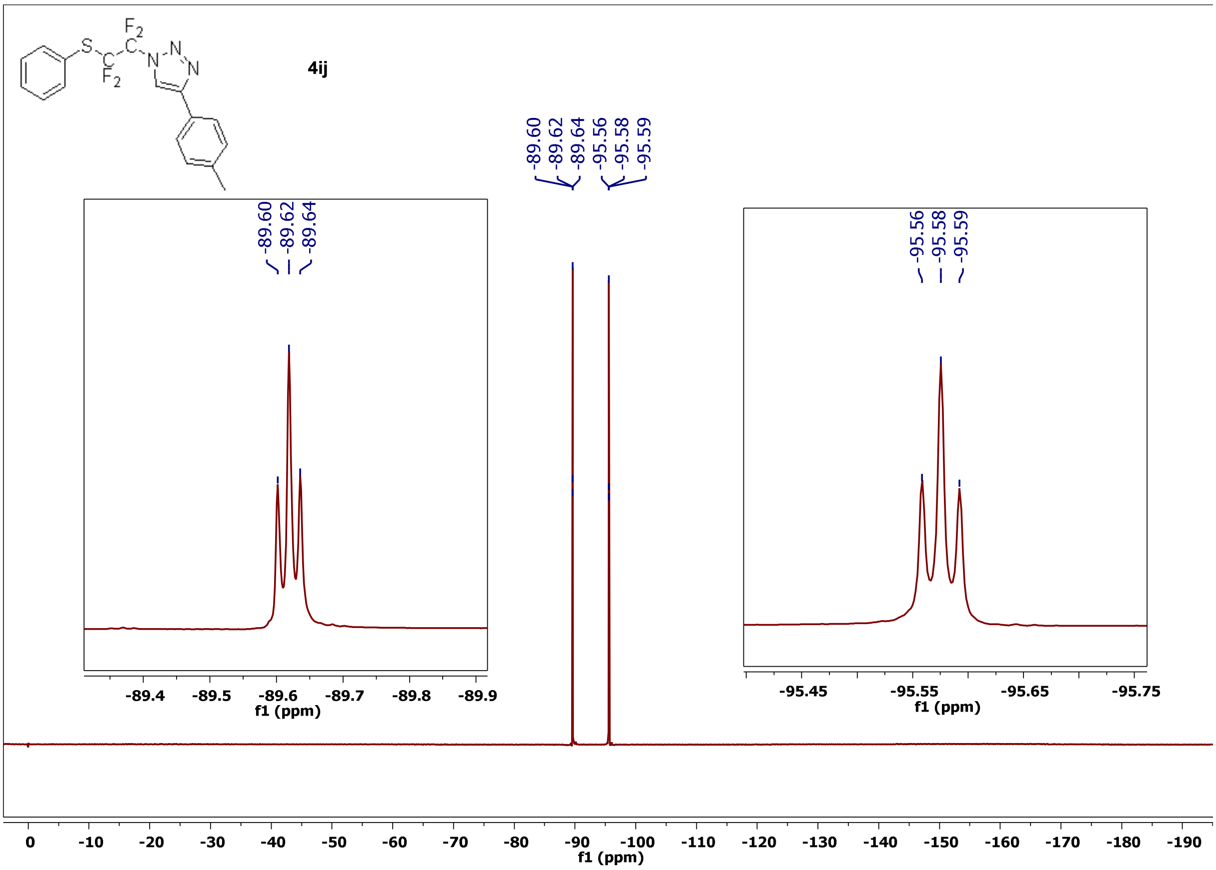

Br
N
N
F
F
F
F
N
N
N
4hm
8.04
7.86
7.83
7.67
7.49
7.47
7.45
7.43
7.39
1.00
3.02
1.00
2.05
1.09
f1 (ppm)
f1 (ppm)

4hm

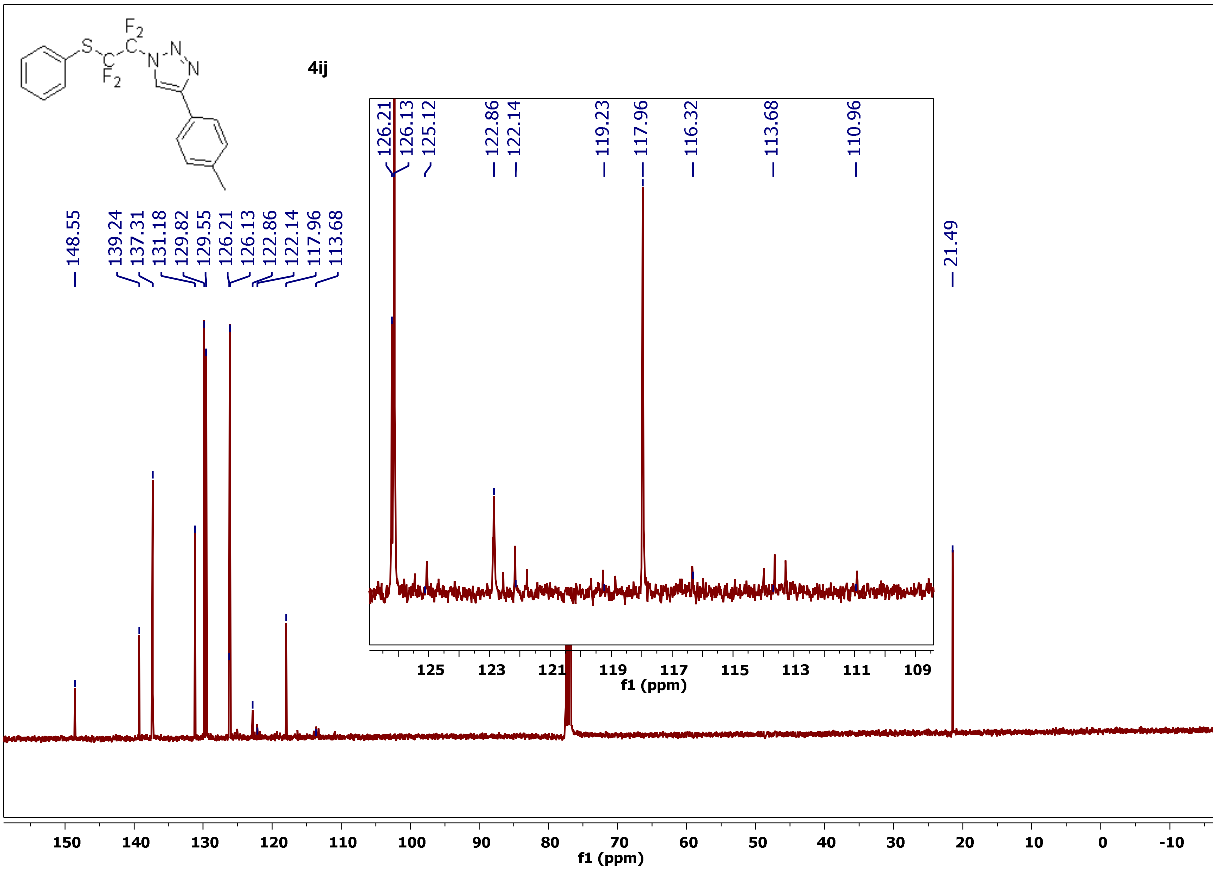

-97.05
-98.40
-97.04
-97.05
-97.06
-98.39
-98.40
-98.42
-96.90 -96.95 -97.00 -97.05 -97.10 -97.15 -97.20
f1 (ppm)
-98.30 -98.40 -98.50 -98.60
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


4hm
148.56
144.87
129.41
129.25
129.20
128.75
126.27
118.27
112.11
111.71
97.91
114.82
114.39
112.11
111.71
109.39
109.03
f1 (ppm)
f1 (ppm)

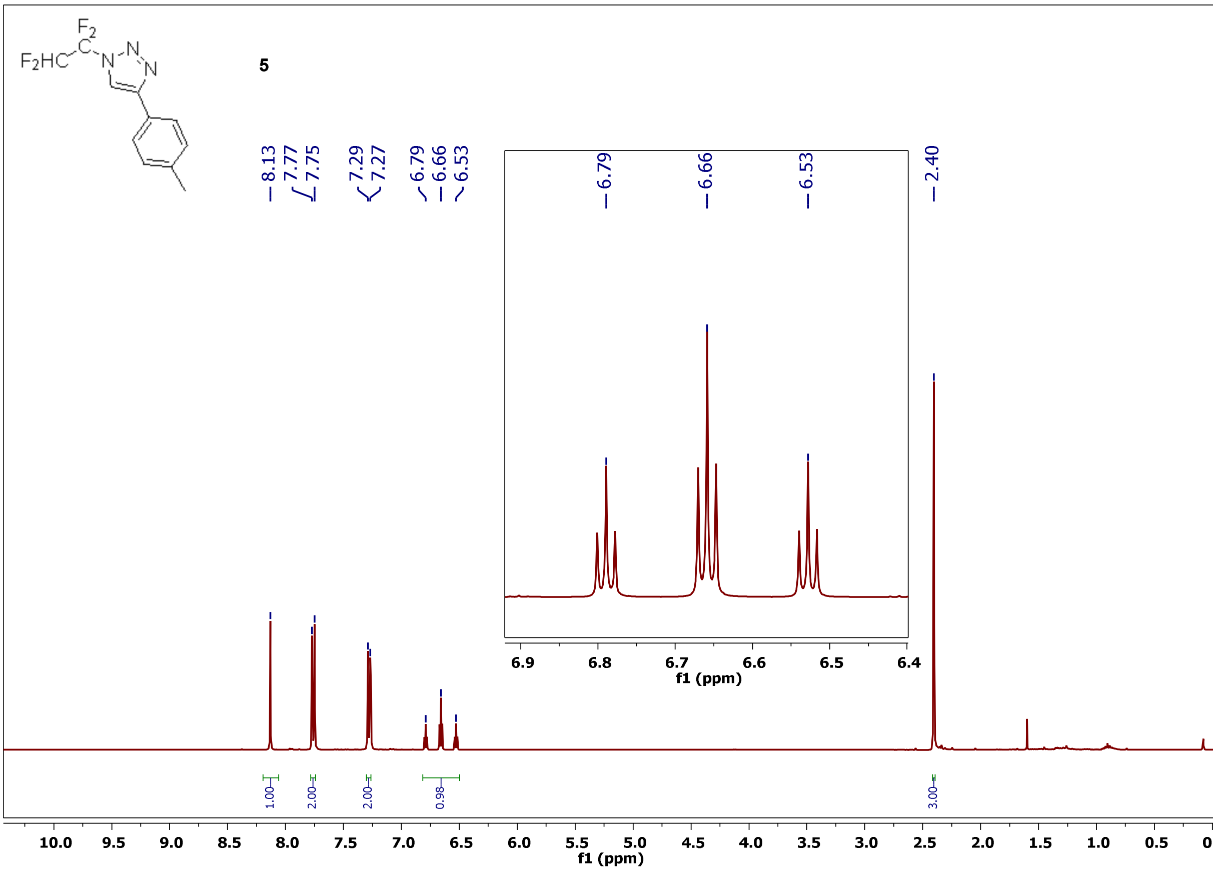

4ij
7.92
7.67
7.65
7.56
7.54
7.41
7.39
7.37
7.33
7.31
7.29
7.20
7.18
2.32
1.00
2.00
2.00
1.01
2.01
2.00
3.00
f1 (ppm)

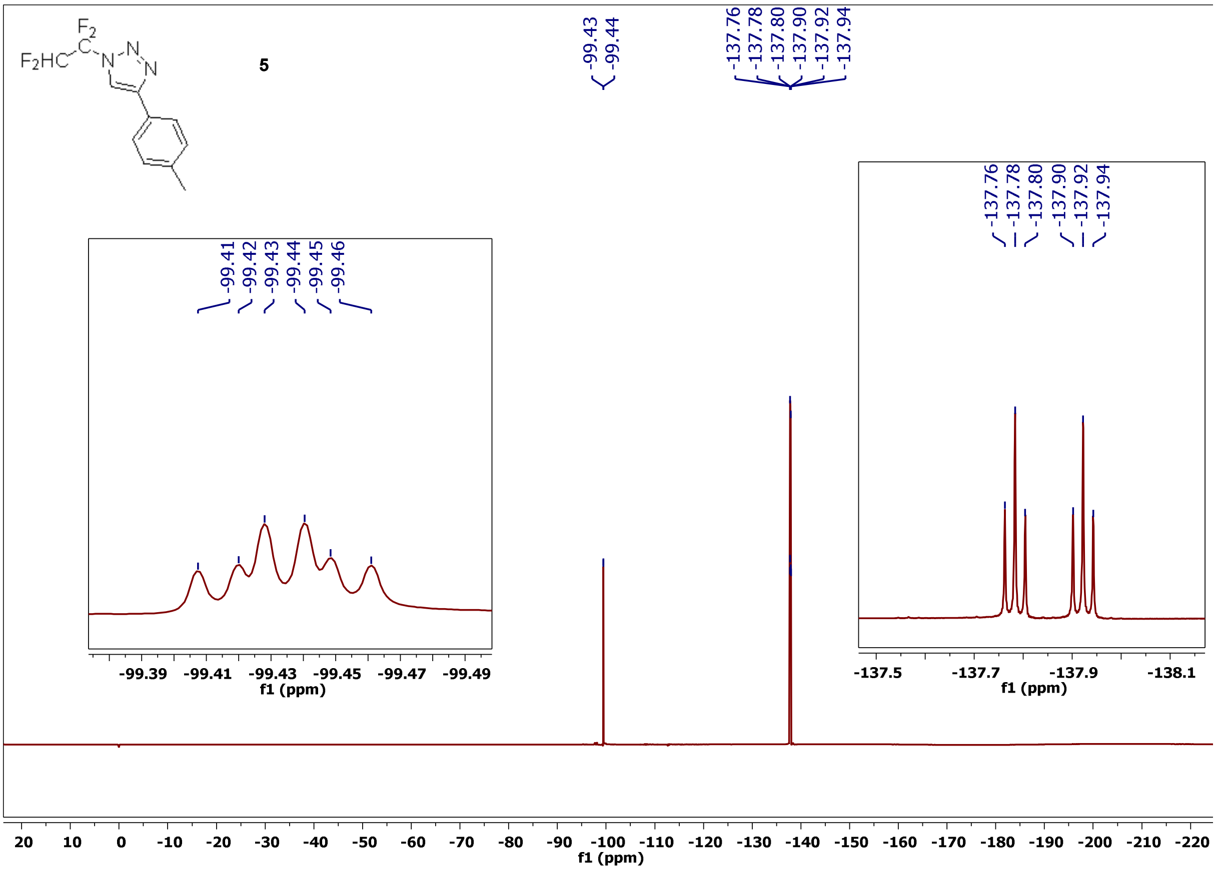

4ij
-89.60
-89.62
-89.64
-95.56
-95.58
-95.59
f1 (ppm)

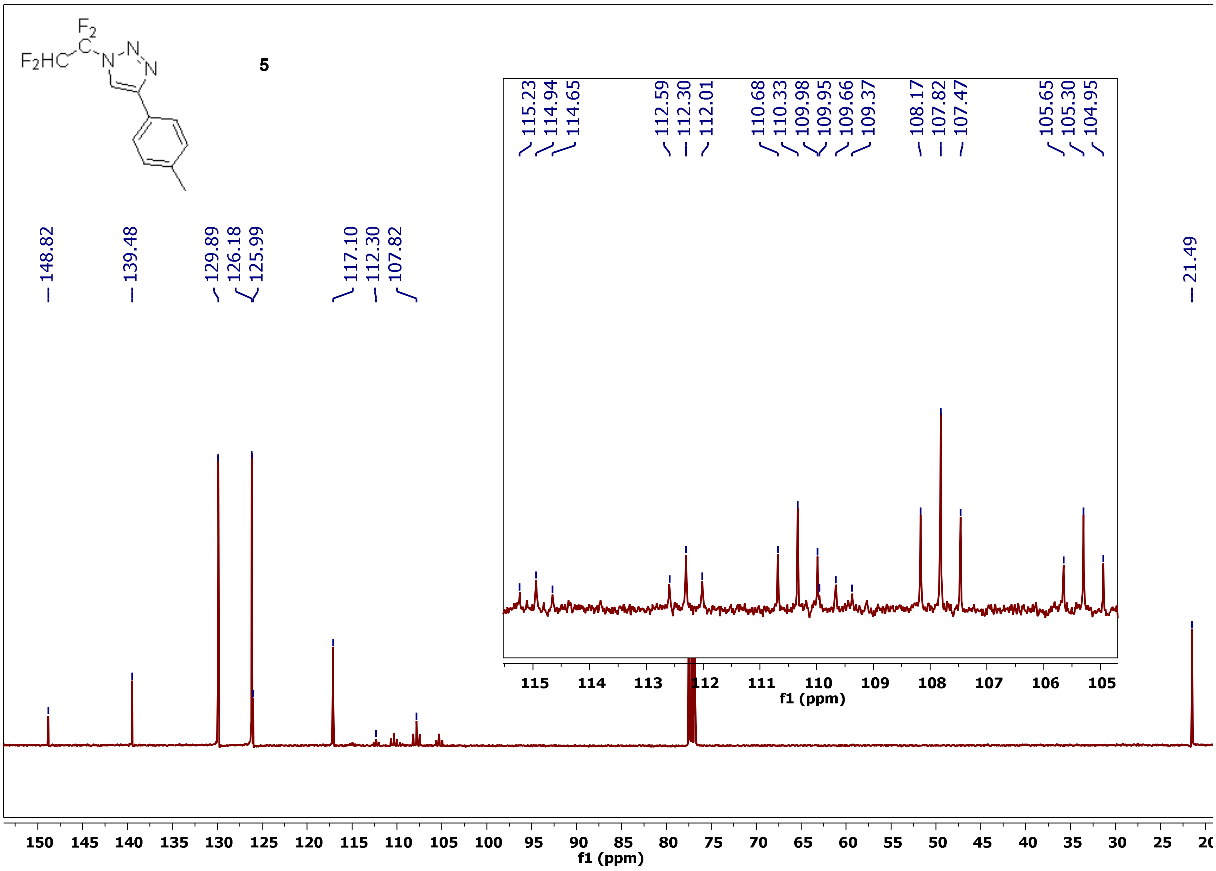
4ij

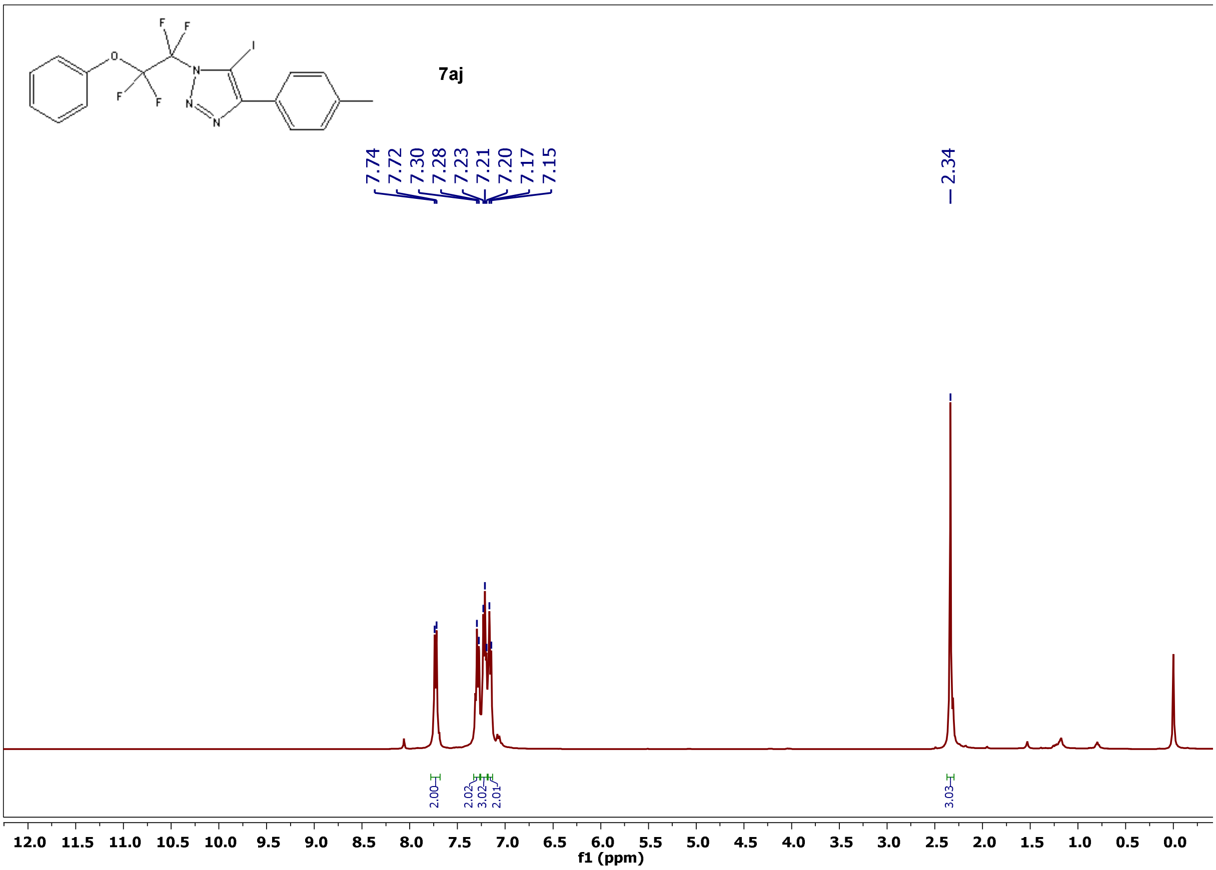

148.55
139.24
137.31
131.18
129.82
129.55
126.21
126.13
122.86
122.14
117.96
113.68
21.49
126.21
126.13
125.12
122.86
122.14
119.23
117.96
116.32
113.68
110.96
f1 (ppm)

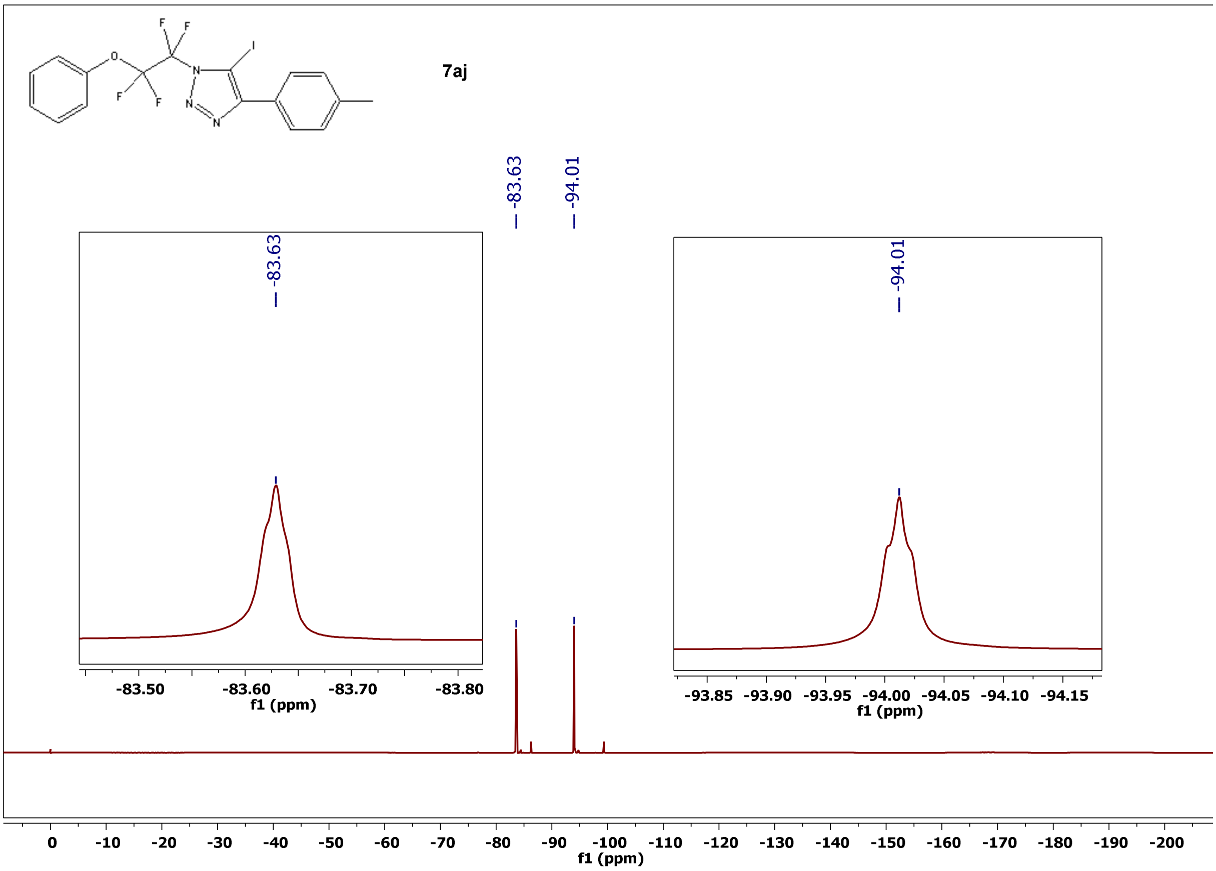
5

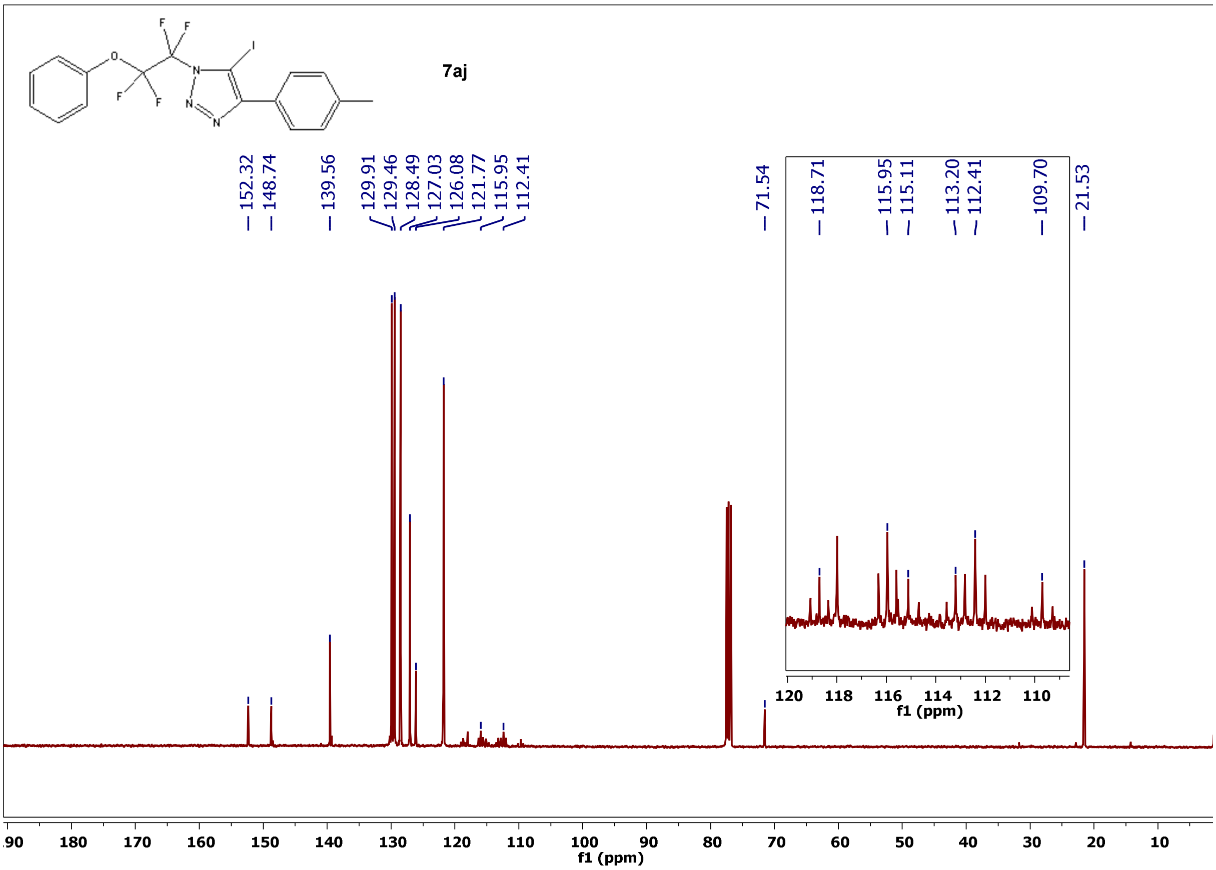

8.13
7.77
7.75
7.29
7.27
6.79
6.66
6.53
2.40
1.00
2.00
2.00
0.98
3.00
f1 (ppm)

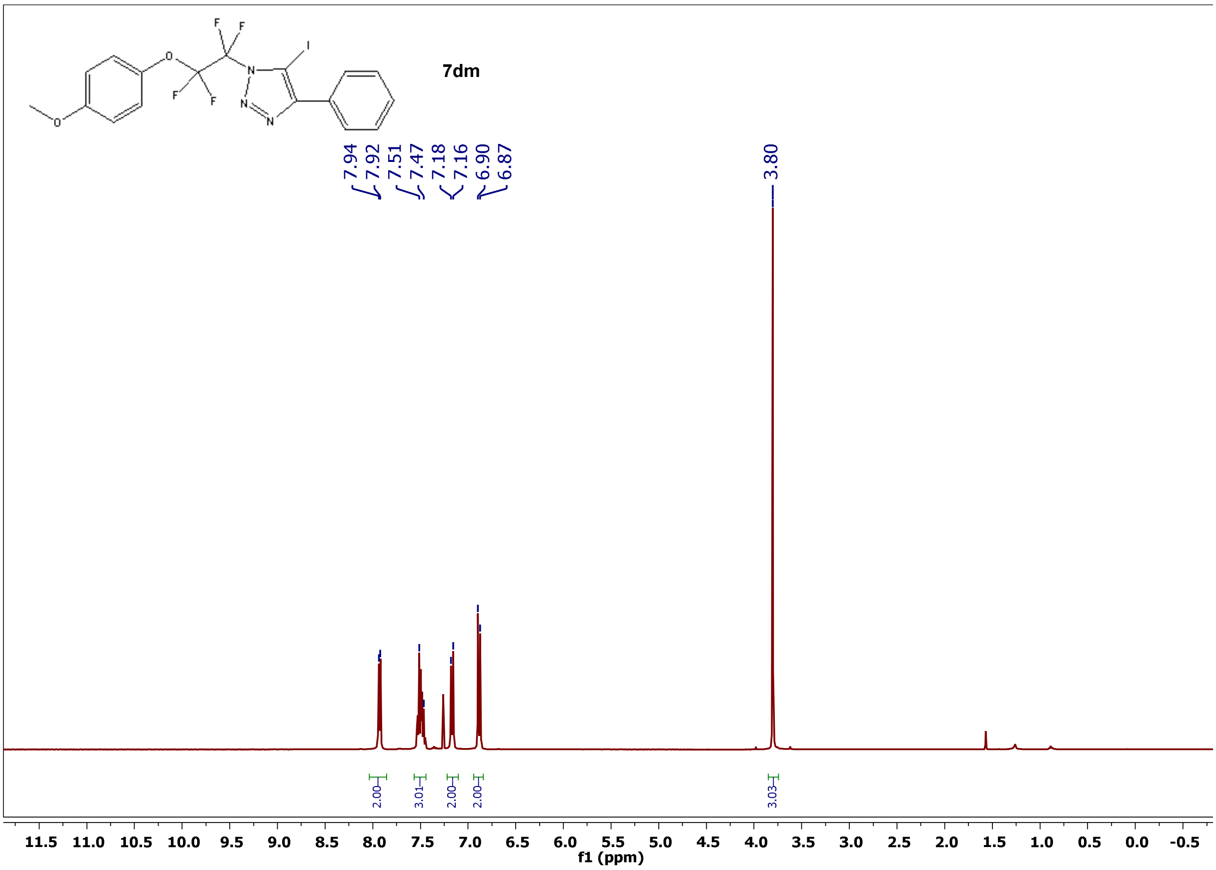

5
-99.43
-99.44
-137.76
-137.78
-137.80
-137.90
-137.92
-137.94
-99.41
-99.42
-99.43
-99.44
-99.45
-99.46
f1 (ppm)
f1 (ppm)
f1 (ppm)


5
148.82
139.48
129.89
126.18
125.99
117.10
112.30
107.82
21.49
115.23
114.94
114.65
112.59
112.30
112.01
110.68
110.33
109.98
109.95
109.66
109.37
108.17
107.82
107.47
105.65
105.30
104.95
f1 (ppm)
f1 (ppm)


7aj
7.74
7.72
7.30
7.28
7.23
7.21
7.20
7.17
7.15
2.34
2.00
2.02
3.02
2.01
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
f1 (ppm)


7aj
-83.63
-94.01
-83.63
-83.50 -83.60 -83.70 -83.80
f1 (ppm)
-94.01
-93.85 -93.90 -93.95 -94.00 -94.05 -94.10 -94.15
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


7aj
152.32
148.74
139.56
129.91
129.46
128.49
127.03
126.08
121.77
115.95
112.41
71.54
118.71
115.95
115.11
113.20
112.41
109.70
21.53
f1 (ppm)


7dm
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7.92
7.51
7.47
7.18
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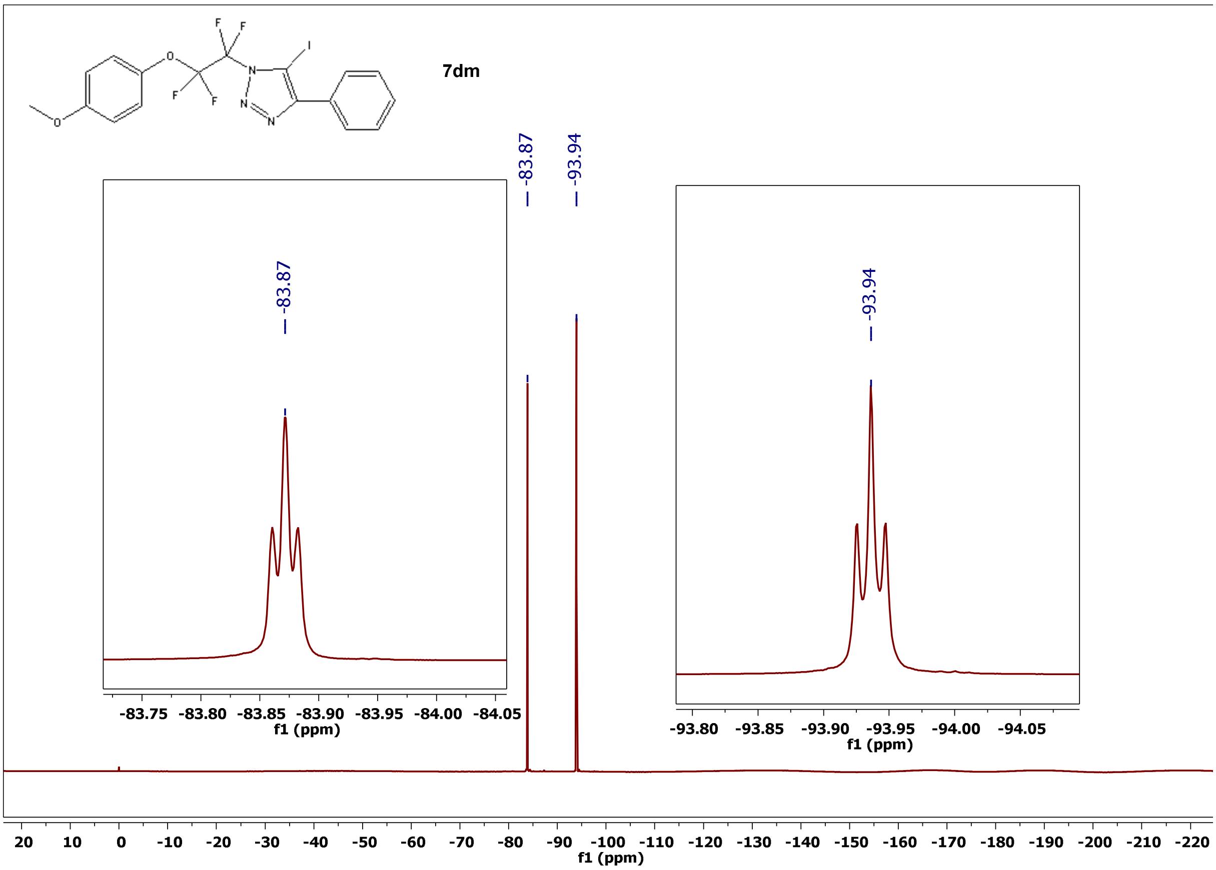
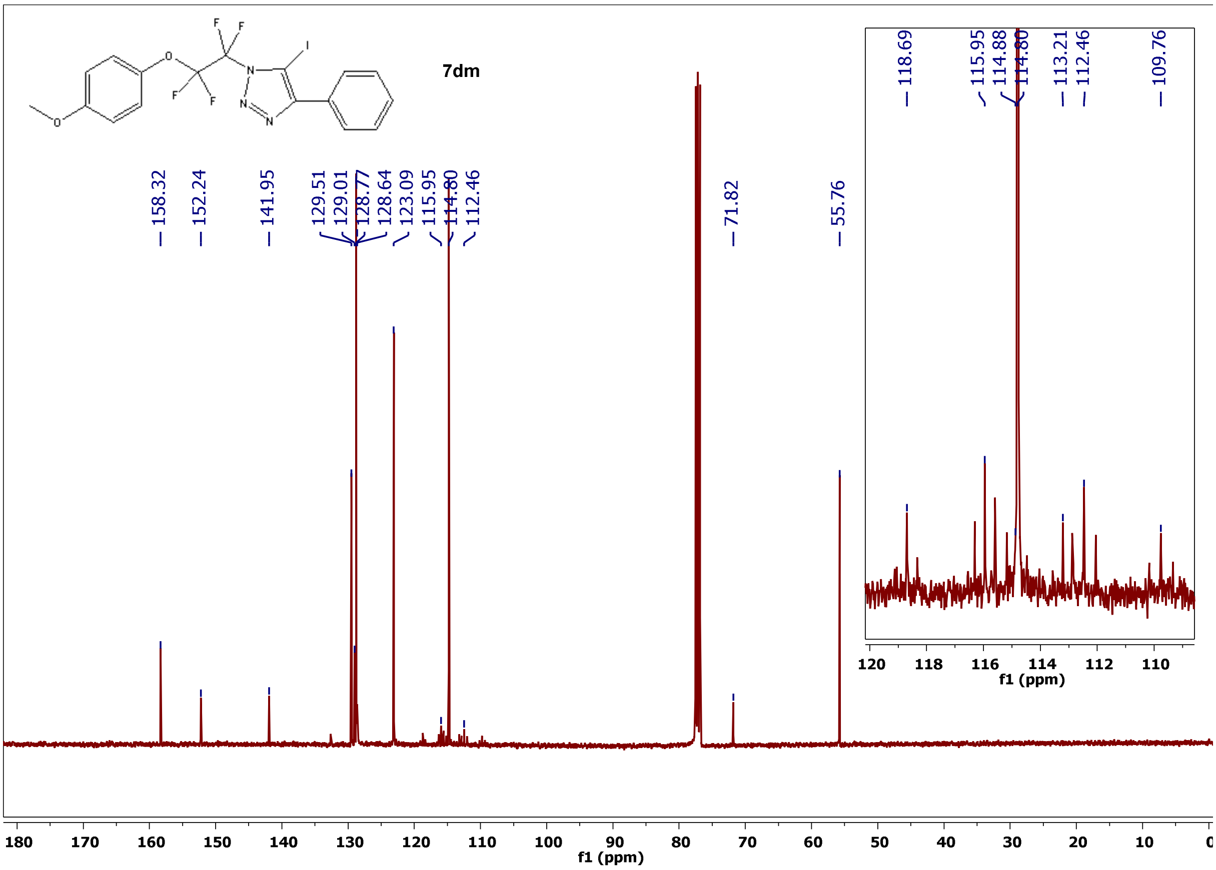
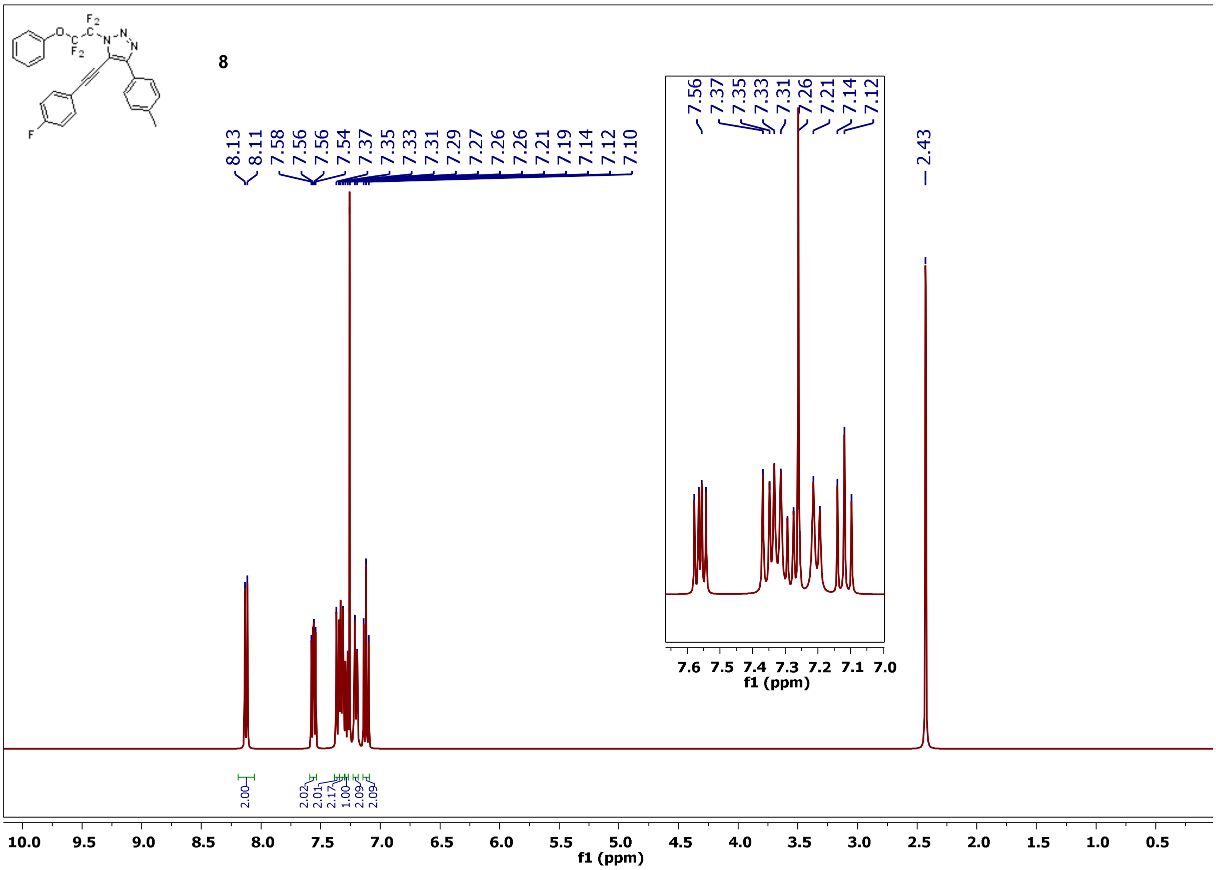
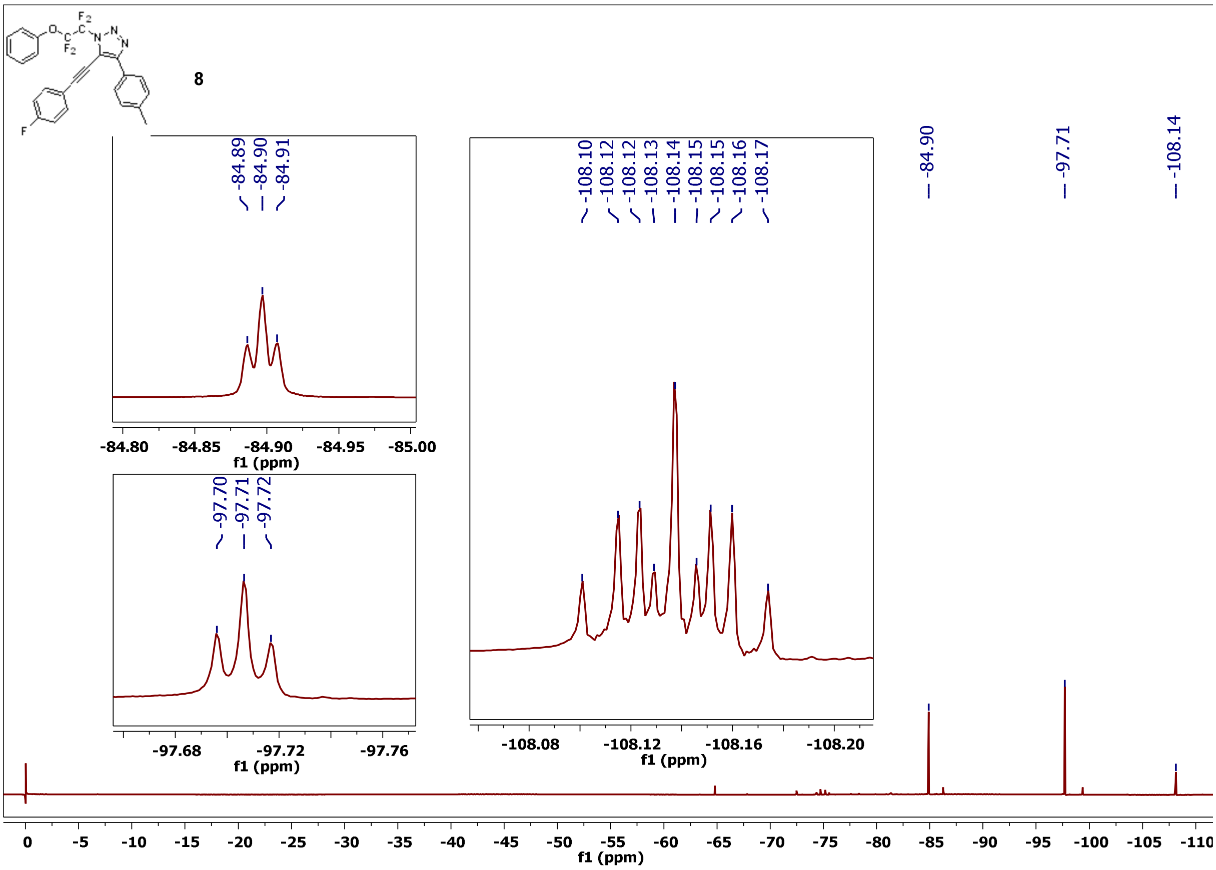
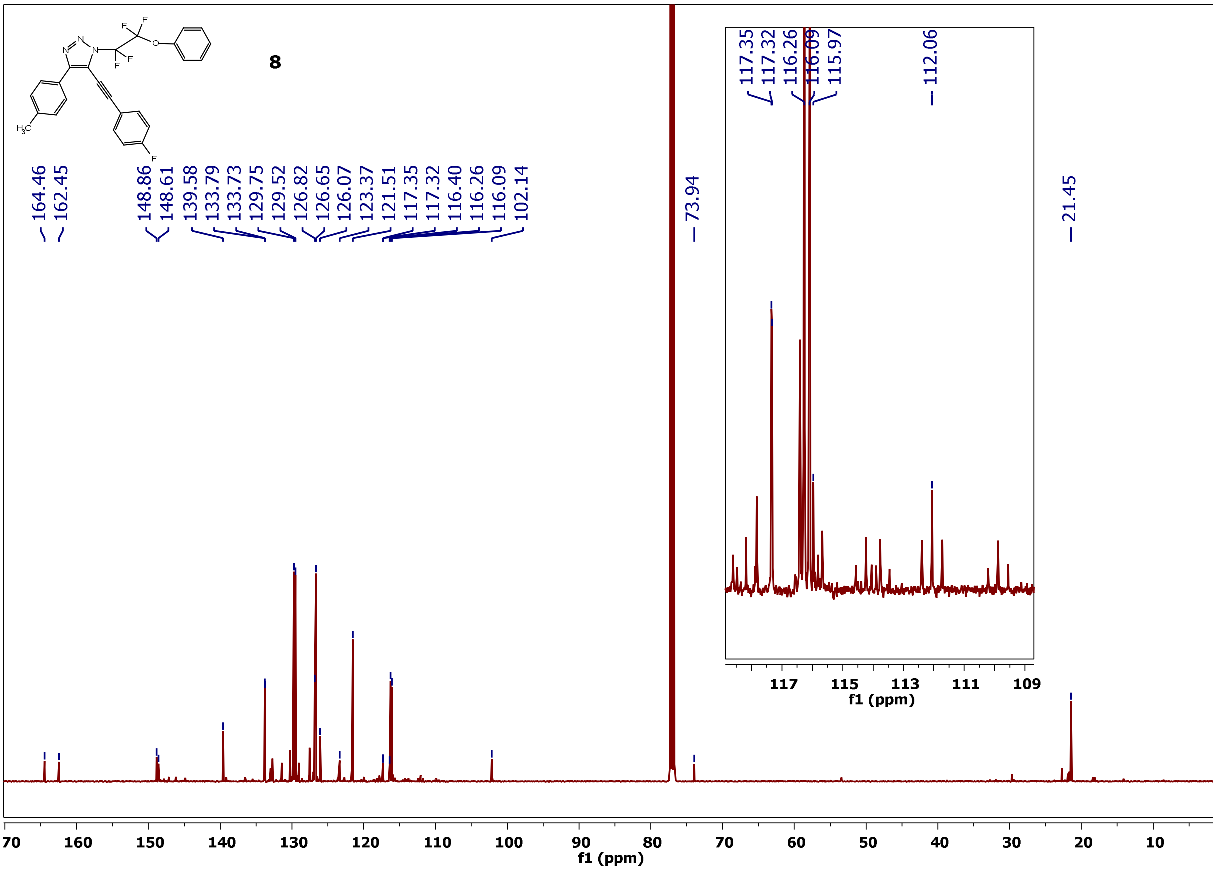
6.90
6.87
3.80
2.00
3.01
2.00
2.00
3.03
f1 (ppm)


7dm
-83.87
-93.94
-83.87
-93.94
f1 (ppm)


7dm
158.32
152.24
141.95
129.51
129.01
128.77
128.64
123.09
115.95
114.80
112.46
71.82
55.76
118.69
115.95
114.88
114.80
113.21
112.46
109.76
f1 (ppm)


8
8.13
8.11
7.58
7.56
7.56
7.54
7.37
7.35
7.33
7.31
7.29
7.27
7.26
7.26
7.21
7.19
7.14
7.12
7.10
2.43
f1 (ppm)


8
-84.90
-97.71
-108.14
f1 (ppm)


8
164.46
162.45
148.86
148.61
139.58
133.79
133.73
129.75
129.52
126.82
126.65
126.07
123.37
121.51
117.35
117.32
116.40
116.26
116.09
102.14
73.94
21.45
117.35
117.32
116.26
116.09
115.97
112.06
117
115
113
111
109
f1 (ppm)
70
160
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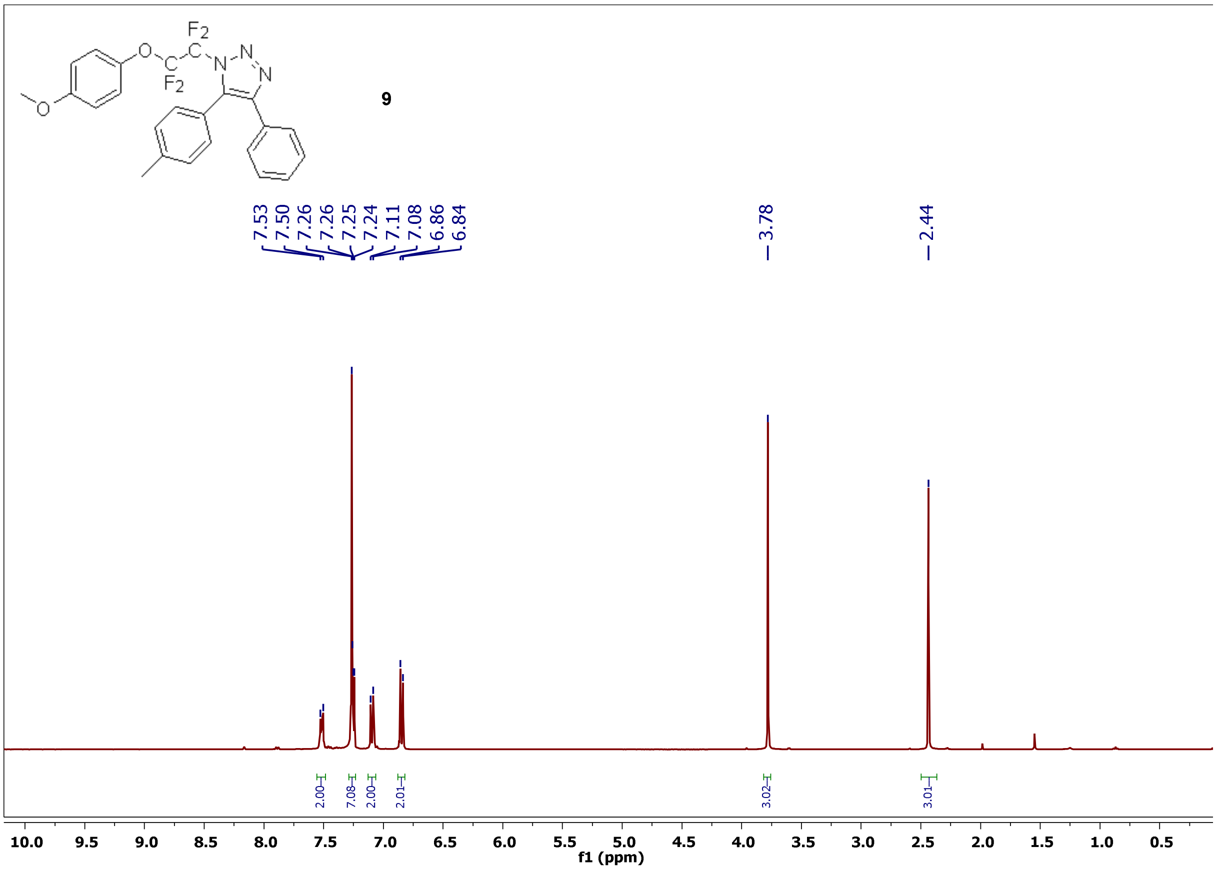
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


9
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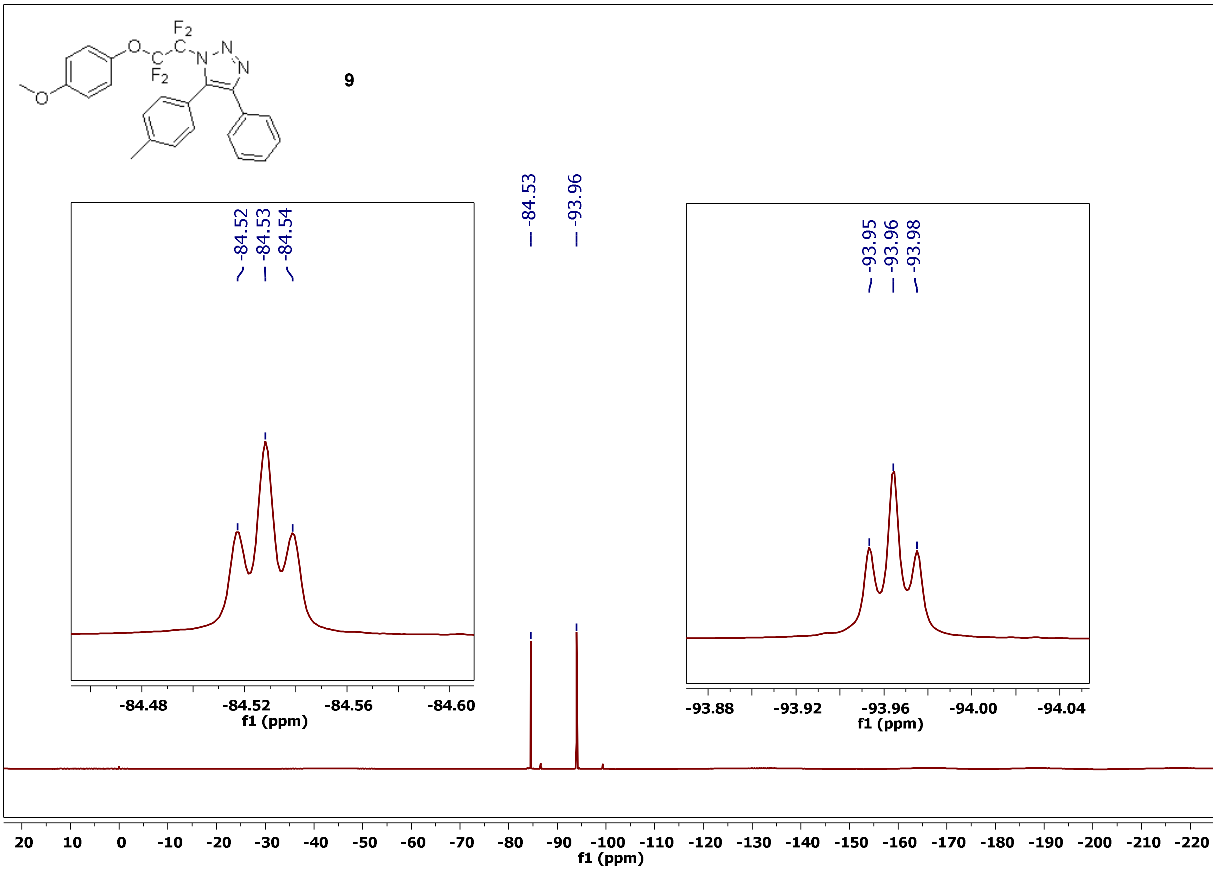
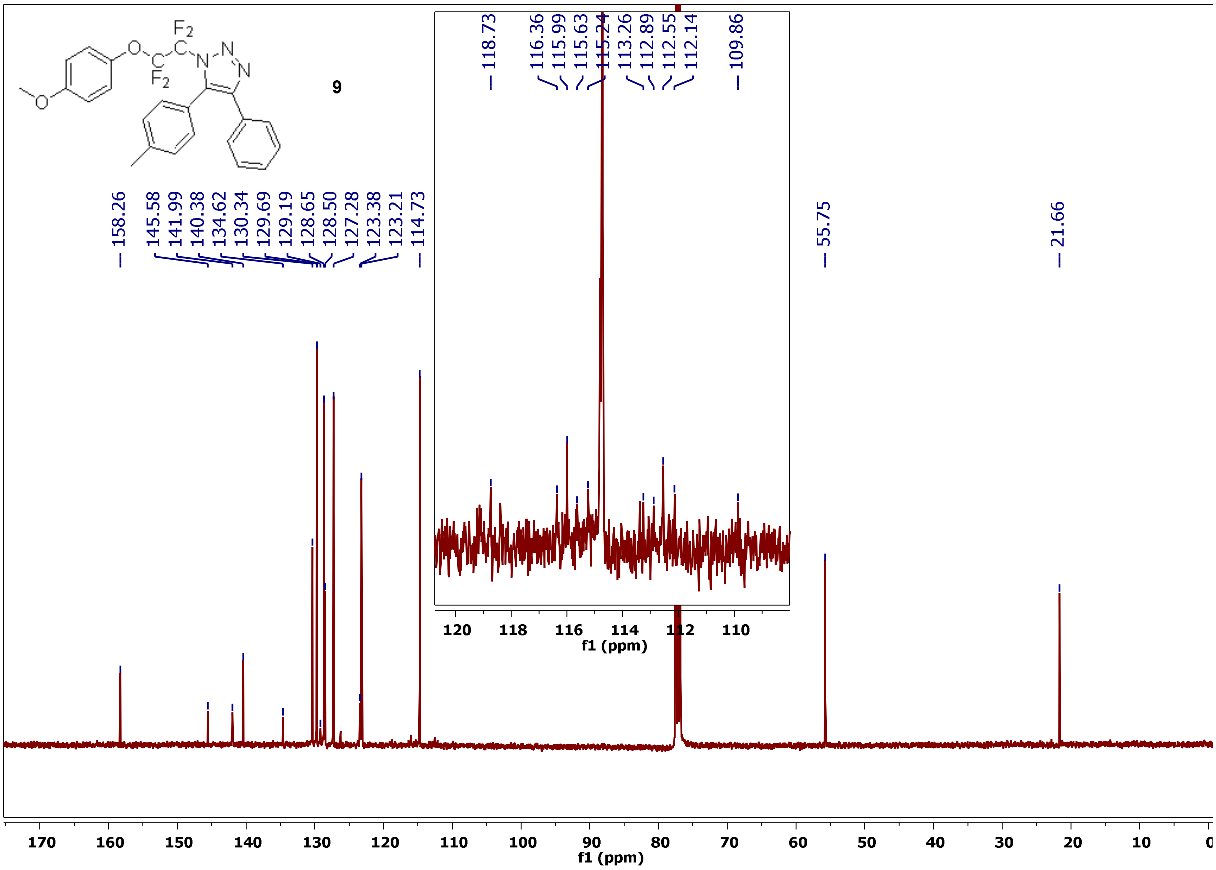
7.50
7.26
7.25
7.24
7.11
7.08
6.86
6.84
3.78
2.44
2.00
7.08
2.00
2.01
3.02
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


9
-84.53
-93.96
-84.52
-84.53
-84.54
-93.95
-93.96
-93.98
f1 (ppm)


9
158.26
145.58
141.99
140.38
134.62
130.34
129.69
129.19
128.65
128.50
127.28
123.38
123.21
114.73
118.73
116.36
115.99
115.63
115.24
113.26
112.89
112.55
112.14
109.86
55.75
21.66
f1 (ppm)

Crystallographic data collection

The crytal data were collected on an Xcalibur PX system equipped with Onyx CCD detector and a Cu Kα sealed tube (λ = 1.54178 Å) with an enhanced monochromator using combined φ and ω scans at 180 K. CrysAlisProCCD[5] was used for data collection, cell refinement and data reduction. All structures were solved by direct methods with SIR92[6] and refined by full-matrix least-squares on F with CRYSTALS.[7] The positional and anisotropical thermal parameters of all non-hydrogen atoms were refined. All hydrogen atoms were found from a Fourier difference map and then recalculated into idealized positions and refined with riding constraints.

Crystal data for ***4dm*** *(0.15 × 0.30 × 0.62 mm):* $C_{17}H_{13}F_4N_3O_2$, monoclinic, space group $P2_1/c$, a = 18.5871(12) Å, b = 5.6567(4) Å, c = 15.3181(11) Å, β = 95.884(6)°, V = 1602.08(19) $Å^3$, Z = 4, M = 367.30, 6578 reflections measured, 3165 independent reflections. Final R = 0.048, wR = 0.048, GoF = 1.145 for 2402 reflections with $I > 2\sigma(I)$ and 236 parameters. CCDC 1545038.

Crystal data for ***4hm*** *(0.07 × 0.08 × 0.31 mm):* $C_{13}H_8Br_1F_4N_5$, orthorhombic, space group $Pna2_1$, a = 18.6519(9) Å, b = 5.6223(3) Å, c = 27.0706(13) Å, V = 2838.8(2) $Å^3$, Z = 8, M = 780.27, 19763 reflections measured, 4630 independent reflections. Final R = 0.028, wR = 0.029, GoF = 1.111 for 4020 reflections with $I > 2\sigma(I)$ and 416 parameters. Flack parameter x = 0.058(15). The asymmetric unit contains two crystallographically independent molecules of **4hm.** CCDC 1545040.

Crystal data for ***4ij*** *(0.06 × 0.36 × 0.63 mm):* $C_{17}H_{13}F_4N_3S_1$, orthorhombic, space group $P2_12_12_1$, a = 5.3006(6) Å, b = 8.6660(10) Å, c = 35.753(4) Å, V = 1642.3(3) $Å^3$, Z = 4, M = 367.37, 19043 reflections measured, 3016 independent reflections. Final R = 0.062, wR = 0.059, GoF = 0.969 for 2465 reflections with $I > 2\sigma(I)$ and 227 parameters. Flack parameter x = 0.14(3). CCDC 1545041.

Crystal data for ***5*** *(0.05 × 0.10 × 0.81 mm):* $C_{11}H_9F_4N_3$, monoclinic, space group $P2_1$, a = 7.1098(10) Å, b = 5.6455(8) Å, c = 14.581(2) Å, β = 90.522(7)°, V = 585.25(14) $Å^3$, Z = 2, M = 259.20, 7865 reflections measured, 2147 independent reflections. Final R = 0.082, wR = 0.092, GoF = 1.040 for 1878 reflections with $I > 2\sigma(I)$ and 165 parameters. Flack parameter x = -0.1(5). The data collection was considerably affected by the poor crystal quality, which resulted in a slightly lower precision of the structure determination. Nevertheless, all the main structural features of this compound are still described reasonably well. The investigated crystal was found to be a twin with the twin law (1 0 0, 0 -1 0, 0 0 -1), as determined by ROTAX[8] and a refined component ratio of 0.937(3):0.063(3) Several restraints were used to regularize the geometry and the thermal motion of the tetrafluoroethyl chain. CCDC 1545042.

Crystal data for ***7dm*** *(0.14 × 0.16 × 0.37 mm):* $C_{17}H_{12}F_4I_1N_3O_2$, monoclinic, space group *C*2/*c*, *a* = 16.0915(14) Å, *b* = 7.1728(6) Å, *c* = 31.911(3) Å, *β* = 104.303(3)°, *V* = 3569.0(5) Å^3, *Z* = 8, *M* = 493.20, 27846 reflections measured, 3282 independent reflections. Final *R* = 0.089, *wR* = 0.092, *GoF* = 1.010 for 2184 reflections with $I > 2\sigma(I)$ and 244 parameters. CCDC 1545039.

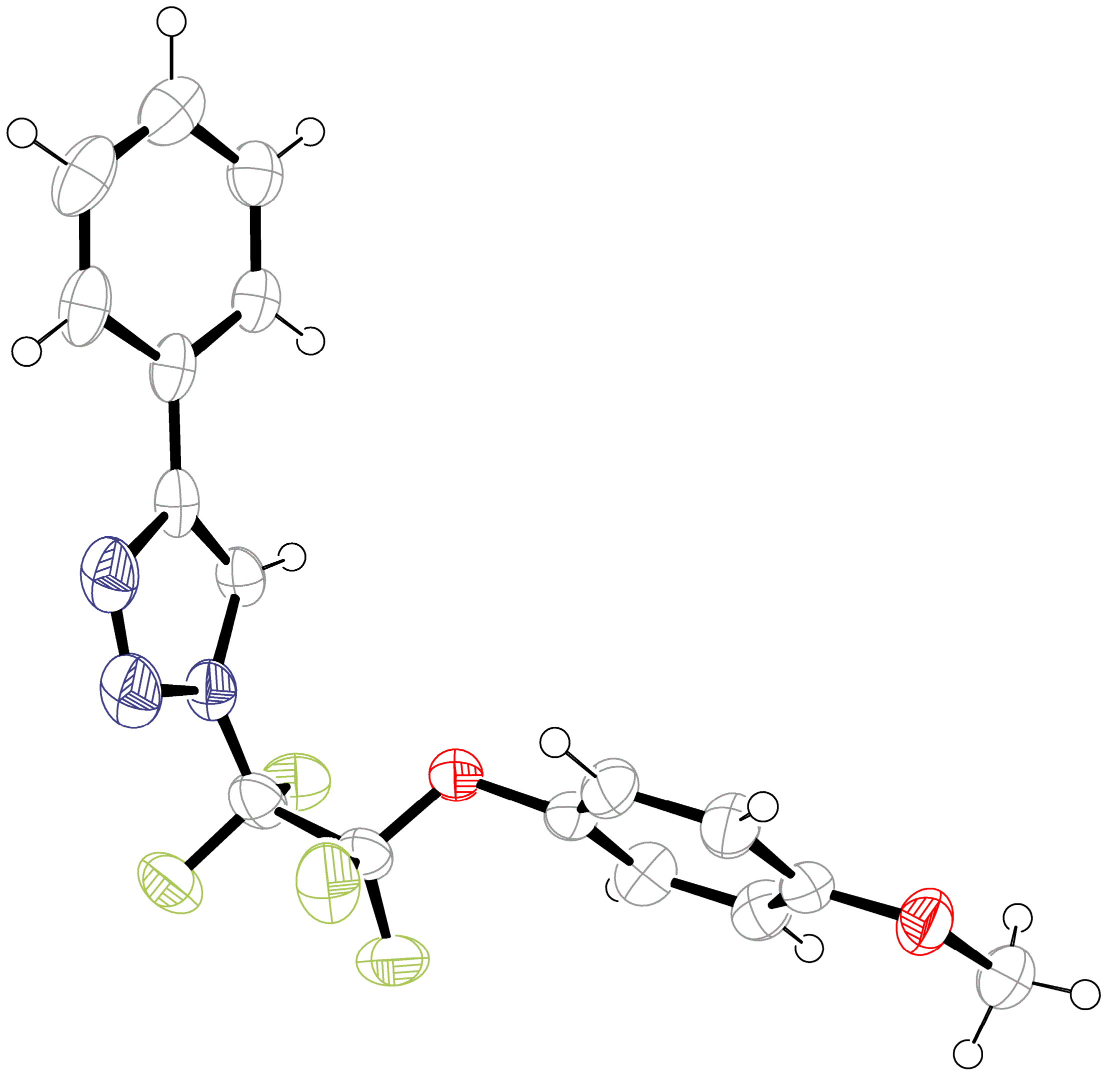


Figure SI1 An ORTEP[9] view of **4dm**, displacement ellipsoids shown with 50 % probability.

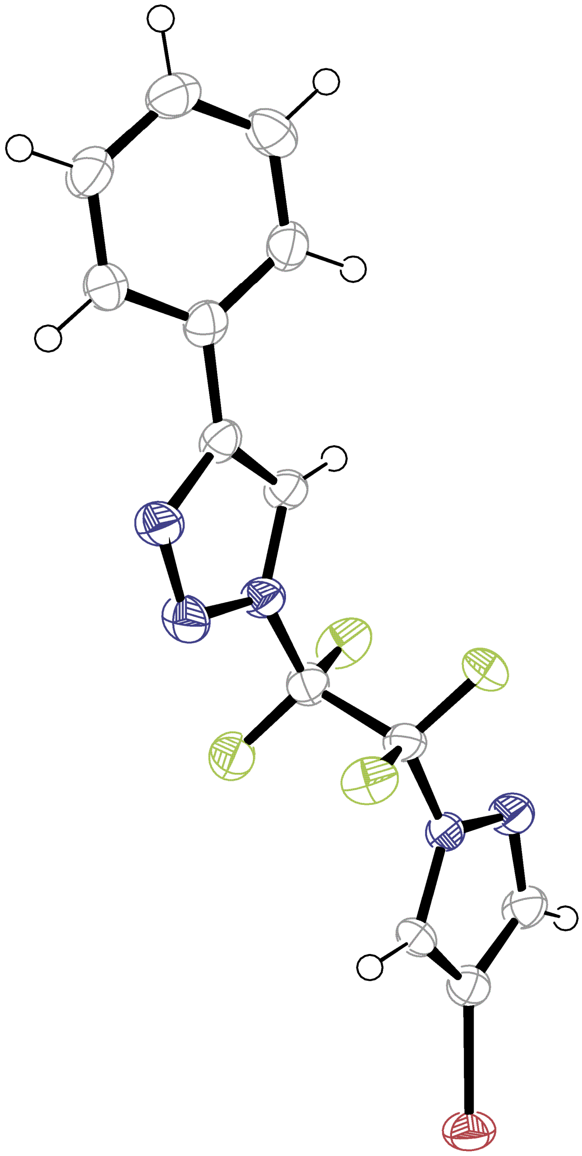


Figure SI2 An ORTEP[9] view of **4hm**, displacement ellipsoids shown with 50 % probability. Only one of the molecules contained in the asymmetric unit is depicted.

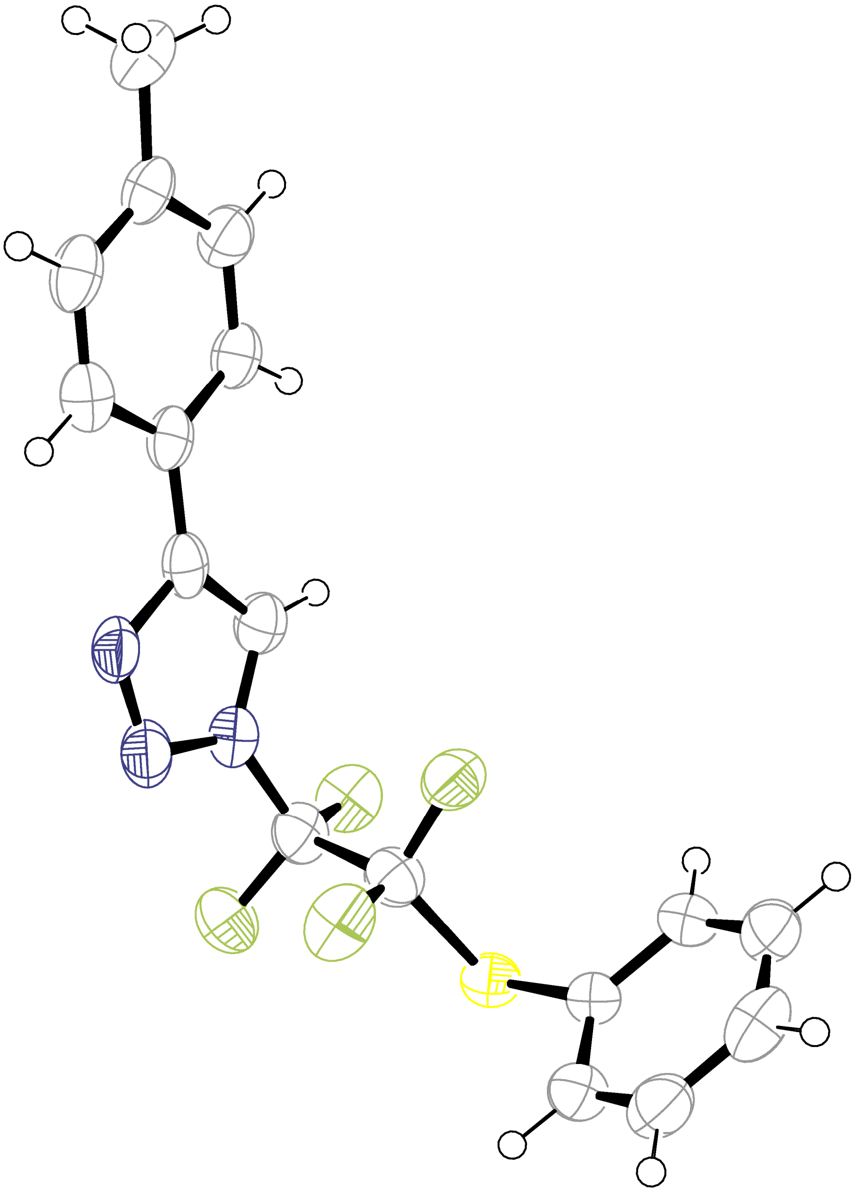


Figure SI3 An ORTEP[9] view of **4ij**, displacement ellipsoids shown with 50 % probability.

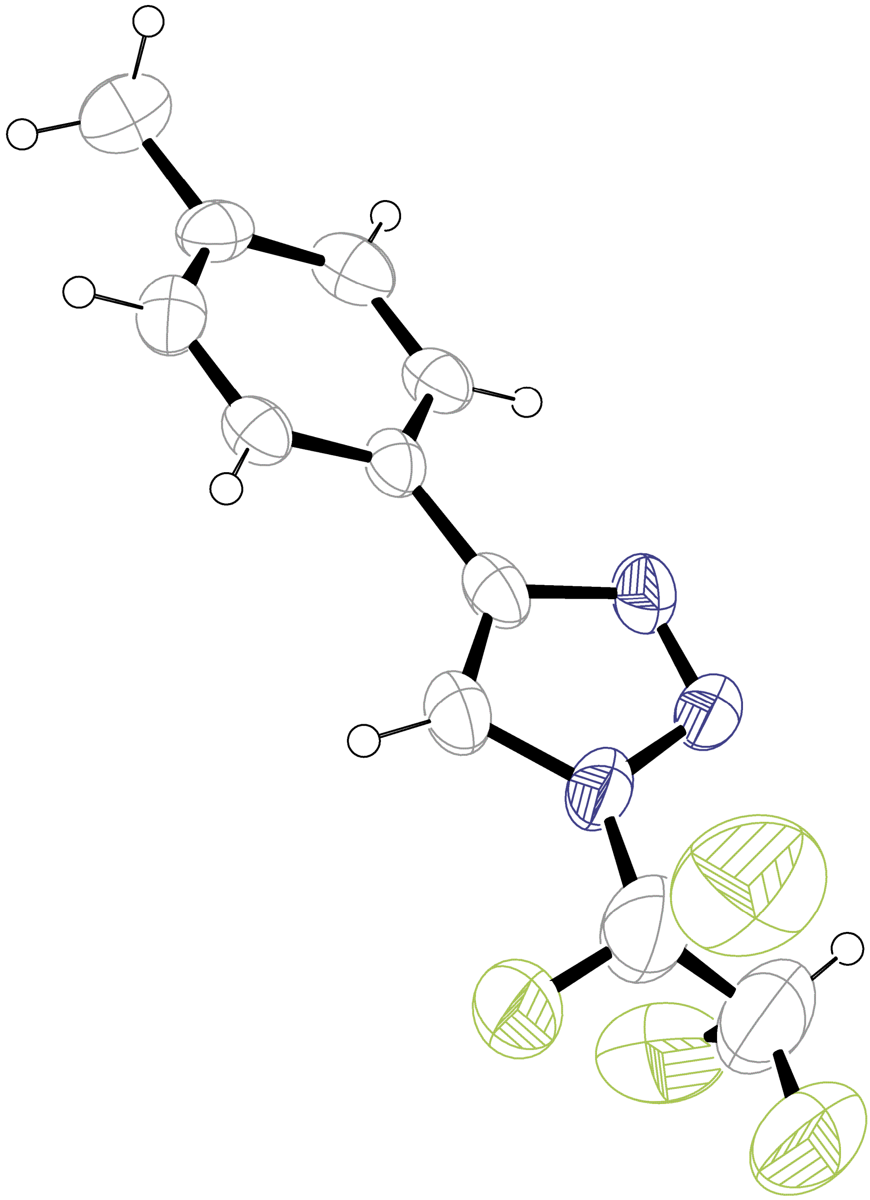


Figure SI4 An ORTEP[9] view of **5**, displacement ellipsoids shown with 40 % probability.

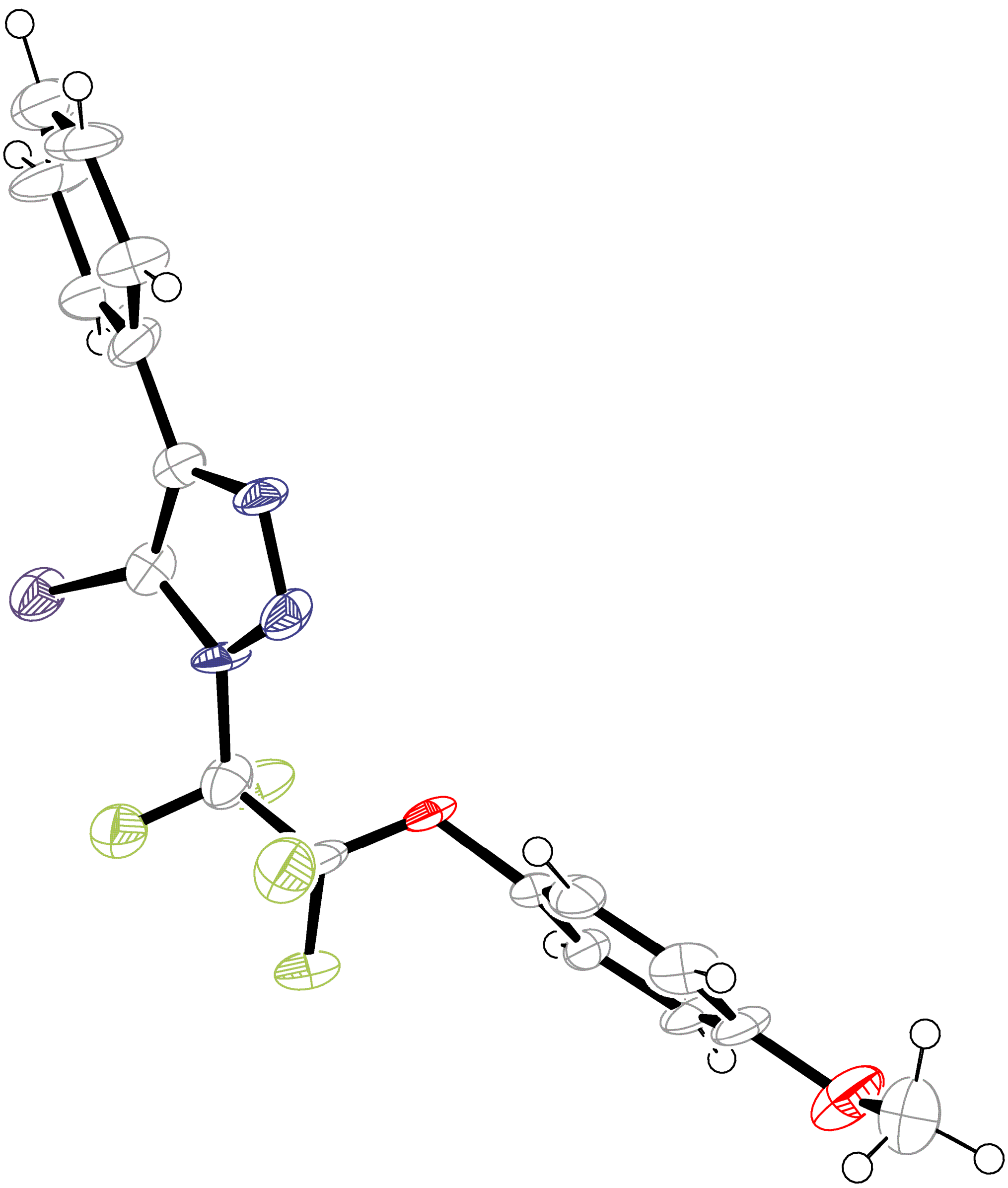


Figure SI5 An ORTEP[9] view of **7dm**, displacement ellipsoids shown with 50 % probability.

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