Electronic Supplementary Material (ESI) for Chemical Science.

Chemo- and Regio-divergent Access to Fluorinated 1-Alkyl and 1-Acyl Triazenes from Alkynyl Triazenes

Jin-Fay Tan,[a] Carl Thomas Bormann,[b] Kay Severin[b] and Nicolai Cramer*[a]

a. Laboratory of Asymmetric Catalysis and Synthesis, EPFL SB ISIC LCSA, BCH 430, CH-1015 Lausanne
(Switzerland). E-mail: nicolai.cramer@epfl.ch
b. Laboratory of Supramolecular Chemistry, EPFL SB ISIC LCS, BCH 3307, CH-1015 Lausanne (Switzerland).

Supporting Information

Table of Content:

1. General Methods:

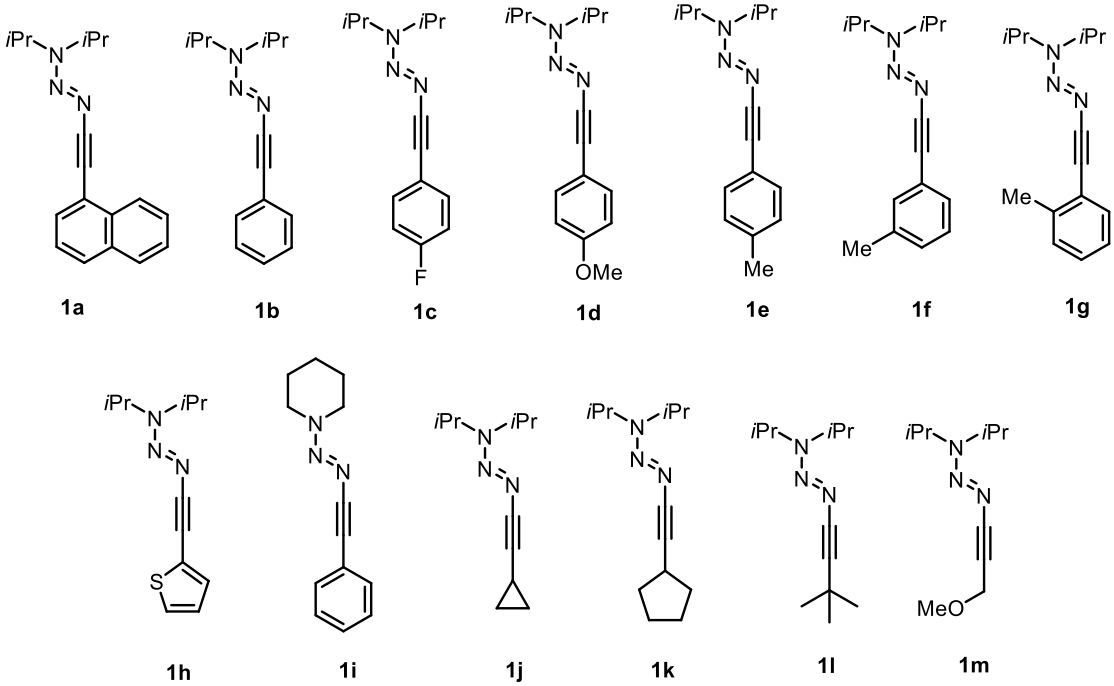
All reactions were were carried out under an atmosphere of dry nitrogen or nitrous oxide (purity: 99.999%, Messer Schweiz AG) using standard Schlenk or glovebox techniques in oven-dried glassware with magnetic stirring, unless otherwise indicated. Reagents and solvents were purchased from Aldrich, Acros, Alfa Aesar, Abcr, or TCI. Chemicals were used as obtained from the suppliers. Dry THF was obtained using a solvent purification system with an aluminum oxide column (Innovative Technologies). Falcon tubes used are 14 mL non-pyrogenic polypropylene round-bottomed tubes, (17 x 100 mm), purchased from Corning Science México S.A. De C.V.

Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade) or basic alumina (Acros, Brockmann activity 1, 50-200 μm, 60A). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualised under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. For the purification of acid sensitive compounds, silicagel 230-400 mesh particle size (100 g) was deactivated prior to use by adding dichloromethane containing 5 vol% triethylamine (300 mL), removal of the solvent under reduced pressure, and drying of the silica at room temperature under oil pump vacuum overnight.

NMR spectra were recorded on a Bruker Avance 400 spectrometer with a BBFOz ATMA probe and Bruker DRX600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; brs, broad singlet. Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 101 MHz on a Bruker AV400 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (77.16 ppm).

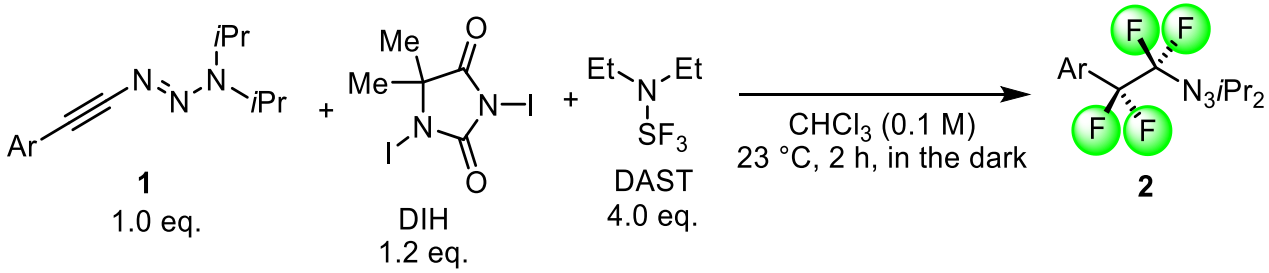
Electrospray–ionisation HRMS data were acquired on a Q–Tof Ultima mass spectrometer (Waters) or an Agilent LC-MS TOF. High resolution mass are given in *m/z*. Data from the Lock–Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

2. Preparation of 1-Alkynyl Triazenes Substrates



All 1-alkynyl triazenes were previously reported and synthesized by reaction of lithium amides with N_2O and alkynyl Grignard reagents as described in the literature.[1,2] The spectra were in good agreement with the reported data.

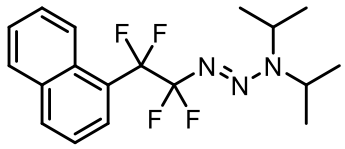
3. General Procedure A for the Synthesis of 1,1,2,2-Tetrafluoroethyl Triazenes 2:



General Procedure A: Alkynyl triazene **1** (0.10 mmol, 1.0 eq.) and DIH (0.12 mmol, 45.6 mg. 1.2 eq.) were weighed in Falcon tube containing a magnetic stirring bar. Addition of $CHCl_3$ (1.0 mL) at RT was immediately followed by addition of DAST (0.40 mmol, 52.8 µL, 4.0 eq.) *via* a micro pipette. The mixture was stirred at RT for 2 h, in the dark with aluminium foil.

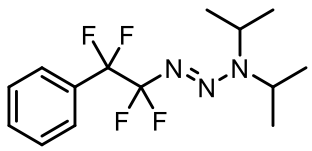
After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the 1,1,2,2-tetrafluoroethyl triazene product **2**.

(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-(naphthalen-1-yl)ethyl)triaz-1-ene (**2a**):



Obtained as yellow solid in 87 % yield (28.9 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.38–8.30 (m, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.55–7.45 (m, 3H), 4.95 (m, 1H), 3.82 (m, 1H), 1.08 (d, *J* = 6.8 Hz, 6H), 1.02 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 134.2, 132.0, 130.6, 128.7, 127.9 (t, $^2J_{C\text{-}F}$ = 22.5 Hz), 127.8 (t, $^3J_{C\text{-}F}$ = 9.5 Hz), 126.8, 126.3 (t, $^3J_{C\text{-}F}$ = 6.4 Hz), 125.8, 124.3, 118.8 (tt, $^1J_{C\text{-}F}$ = 261.1, 31.9 Hz), 118.4 (tt, $^1J_{C\text{-}F}$ = 254.1, 38.3 Hz), 50.0, 47.2, 23.0, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -97.8 (t, *J* = 7.8 Hz), -105.7 (t, *J* = 7.9 Hz); **IR (ATR):** $\tilde{\nu}$ 1755, 1539, 1358, 1210, 867, 770, 700, 582 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}F_4N_3^+$ 356.1744; Found 356.1738; **R_f:** 0.60 (1:9 EtOAc/pentane).

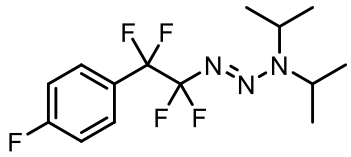
(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-phenylethyl)triaz-1-ene (**2b**):



Obtained as yellow oil in 82 % yield (25.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.59–7.54 (m, 2H), 7.46–7.36 (m,

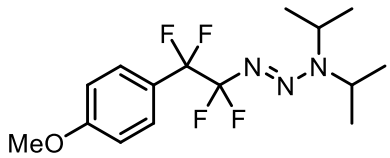
3H), 4.98 (m, 1H), 3.94 (m, 1H), 1.19 (d, *J* = 6.6 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 132.1 (t, $^2J_{C\text{-}F}$ = 24.4 Hz), 130.5, 128.0, 126.9, 118.1 (tt, $^1J_{C\text{-}F}$ = 261.6, 32.0 Hz), 116.3 (tt, $^1J_{C\text{-}F}$ = 254.9, 39.0 Hz), 50.3, 47.2, 23.01, 18.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.0 (t, *J* = 6.5 Hz), -112.6 (t, *J* = 6.5 Hz); **IR (ATR):** $\tilde{\nu}$ 1743, 1545, 1360, 1210, 866, 770, 705, 580 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}F_4N_3^+$ 306.1588; Found 306.1587; **R_f:** 0.29 (1:9 EtOAc/pentane).

(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-(4-fluorophenyl)ethyl)triaz-1-ene (**2c**):



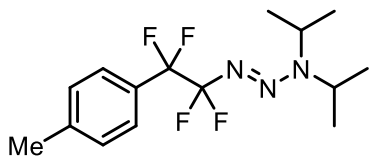
5.0 eq. DAST used. Obtained as yellow oil in 80 % yield (26.0 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.55 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 4.97 (m, 1H), 3.96 (m, 1H), 1.22 (d, *J* = 6.6 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 164.20 (d, $^1J_{C\text{-}F}$ = 250.2 Hz), 129.38–129.16 (m), 128.3 (t, $^2J_{C\text{-}F}$ = 25.5 Hz), 118.0 (tt), 116.2 (tt), 115.3 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 50.5, 47.4, 23.1, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -98.9 (t, *J* = 6.4 Hz), -110.2, -112.0 (t, *J* = 6.6 Hz); **IR (ATR):** $\tilde{\nu}$ 2930, 1514, 1468, 1429, 1224, 1160, 1127, 1090, 1069, 839 cm^{-1}; **HRMS (ESI/QTOF** m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}F_5N_3^+$ 324.1494; Found 324.1494; **R_f:** 0.61 (1:9 EtOAc/pentane).

(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-(4-methoxyphenyl)ethyl)triaz-1-ene (**2d**):



Obtained as yellow oil in 93 % yield (31.3 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.48 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.99 (m, 1H), 3.95 (m, 1H), 3.83 (s, 3H), 1.22 (d, *J* = 6.6 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 161.4, 128.5 (t, $^3J_{C\text{-}F}$ = 6.4 Hz), 124.4 (t, $^2J_{C\text{-}F}$ = 25.2 Hz), 118.2 (tt, $^1J_{C\text{-}F}$ = 261.5Hz, $^2J_{C\text{-}F}$ = 32.7 Hz), 116.8 (tt, $^1J_{C\text{-}F}$ = 253.6 Hz, $^2J_{C\text{-}F}$ = 38.6 Hz), 113.5, 55.5, 50.4, 47.3, 23.1, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.1 (t, *J* = 6.7 Hz), -111.5 (t, *J* = 6.7 Hz).; **IR (ATR):** $\tilde{\nu}$ 1518, 1427, 1247, 1223, 1179, 1158, 1128, 1092, 1025, 958, 906, 831 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}F_4N_3O^+$ 336.1694; Found 336.1698; **R_f:** 0.39 (1:9 EtOAc/pentane).

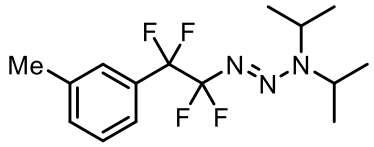
(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-(*p*-tolyl)ethyl)triaz-1-ene (**2e**):



Obtained as yellow oil in 90 % yield (28.6 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.44 (d, *J* = 7.9 Hz, 2H), 7.21

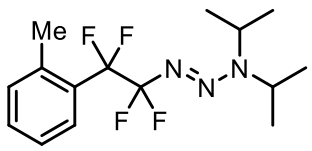
(d, *J* = 7.9 Hz, 2H), 4.99 (m, 1H), 3.94 (m, 1H), 2.37 (s, 3H), 1.20 (d, *J* = 6.7 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 140.7, 129.4 (t, $^2J_{C-F}$ = 24.8 Hz), 128.8, 126.9 (t, $^3J_{C-F}$ = 6.4 Hz), 118.2 (tt, $^1J_{C-F}$ = 261.2, 32.2 Hz), 116.6 (tt, $^1J_{C-F}$ = 253.9, 38.6 Hz), 50.4, 47.3, 23.1, 21.5, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.0 (t, *J* = 6.4 Hz), -112.2 (t, *J* = 6.3 Hz); **IR (ATR):** $\tilde{\nu}$ 1680, 1223, 1158, 1123, 1092, 1028, 881, 812, 704, 676 cm^{-1}; **HRMS (ESI/QTOF** m/z: [M + H]$^+$ Calcd for $C_{15}H_{22}F_4N_3^+$ 320.1744; Found 320.1743; **R_f:** 0.58 (1:9 EtOAc/pentane).

(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-(*m*-tolyl)ethyl)triaz-1-ene (**2f**):



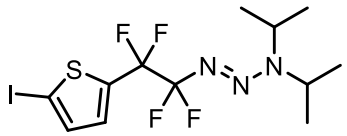
10 eq. DAST was used. Obtained as yellow oil in 56 % yield (17.9 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.40–7.33 (m, 2H), 7.32–7.23 (m, 2H), 4.99 (m, 1H), 3.94 (m, 1H), 2.38 (s, 3H), 1.20 (d, *J* = 6.6 Hz, 6H), 1.17 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 137.8, 132.1 (t, $^2J_{C-F}$ = 24.3 Hz), 131.3, 128.0, 127.6 (t, $^3J_{C-F}$ = 6.3 Hz), 124.1 (t, $^3J_{C-F}$ = 6.3 Hz), 118.3 (tt, $^1J_{C-F}$ = 261.1, 31.9 Hz), 116.5 (tt, $^1J_{C-F}$ = 254.1, 38.3 Hz), 50.4, 47.3, 23.1, 21.5, 18.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.0 (t, *J* = 6.6 Hz), -112.4 (t, *J* = 6.7 Hz); **IR (ATR):** $\tilde{\nu}$ 1745, 1661, 1537, 1358, 1209, 865, 768, 700, 580 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{15}H_{22}F_4N_3^+$ 320.1744; Found 320.1744; **R_f:** 0.55 (1:9 EtOAc/pentane).

(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-(*o*-tolyl)ethyl)triaz-1-ene (**2g**):



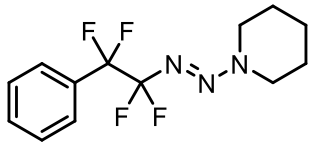
Obtained as yellow oil in 77 % yield (24.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.46 (d, *J* = 7.9 Hz, 1H), 7.31 (m, 1H), 7.19 (m, 2H), 5.04 (m, 1H), 3.94 (m, 1H), 2.49 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 137.8 (t, $^3J_{C-F}$ = 2.6 Hz), 132.1, 130.5, 130.1 (t, $^2J_{C-F}$ = 22.8 Hz), 128.8 (t, $^3J_{C-F}$ = 8.5 Hz), 125.4, 118.7 (tt, $^1J_{C-F}$ = 261.9, 32.3 Hz), 118.0 (tt, $^1J_{C-F}$ = 255.5, 39.6 Hz), 50.2, 47.2, 23.2, 20.9 (m, *J* = 4.9, 2.4 Hz), 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -98.2 (t, *J* = 6.5 Hz), -107.8 (t, *J* = 6.8 Hz); **IR (ATR):** $\tilde{\nu}$ 1680, 1223, 1158, 1123, 1092, 1028, 881, 812, 704, 676 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{15}H_{22}F_4N_3^+$ 320.1744; Found 320.1753; **R_f:** 0.52 (1:9 EtOAc/pentane).

(*E*)-3,3-diisopropyl-1-(1,1,2,2-tetrafluoro-2-(5-iodothiophen-2-yl)ethyl)triaz-1-ene (**2h**):



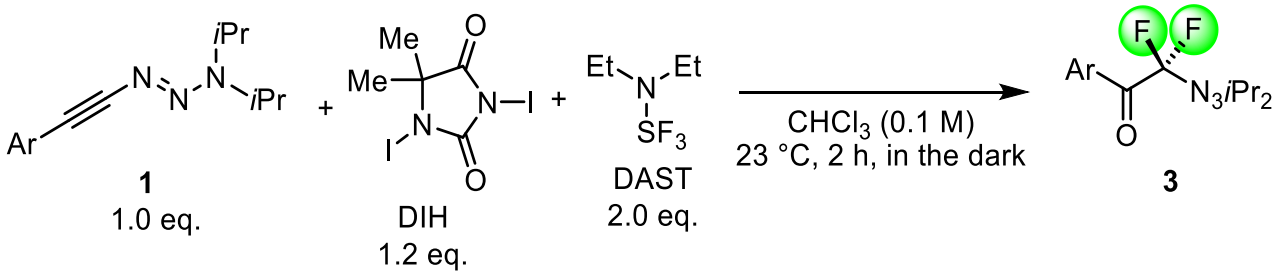
2.4 eq. DIH used. Obtained as yellow oil in 53 % yield (23.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.19 (dt, *J* = 3.8, 1.2 Hz, 1H), 7.05 (dt, *J* = 3.9, 1.2 Hz, 1H), 5.06 (hept, *J* = 6.8 Hz, 1H), 3.99 (hept, *J* = 6.6 Hz, 1H), 1.26 (d, *J* = 6.6 Hz, 6H), 1.21 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 139.2 (t, $^{2}J_{C\text{-}F}$ = 29.6 Hz), 136.6, 130.6 (t, $^{3}J_{C\text{-}F}$ = 5.7 Hz), 117.7 (tt, $^{1}J_{C\text{-}F}$ = 262.2, 31.3 Hz), 114.5 (tt, $^{1}J_{C\text{-}F}$ = 253.8, 40.0 Hz), 78.0, 50.5, 47.6, 23.2, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.0 (t, *J* = 8.0 Hz), -103.3 (t, *J* = 8.2 Hz); **IR (ATR):** $\tilde{\nu}$ 2978, 1468, 1427, 1370, 1246, 1161, 1132, 1112, 1065, 1044, 923, 803 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{12}H_{17}F_4IN_3S^+$ 438.0119; Found 438.0113; **R_f:** 0.73 (1:9 EtOAc/pentane).

(*E*)-1-((1,1,2,2-tetrafluoro-2-phenylethyl)diazenyl)piperidine (**2i**):



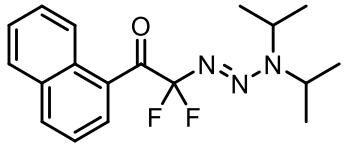
Obtained as yellow oil in 78 % yield (22.5 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.59 (d, *J* = 7.5 Hz, 2H), 7.50–7.41 (m, 3H), 3.74 (dt, *J* = 14.2, 5.7 Hz, 4H), 1.77–1.66 (m, 4H), 1.64–1.60 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 132.0 (t, $^{2}J_{C\text{-}F}$ = 24.4 Hz), 130.7, 128.1, 127.1 (t, $^{3}J_{C\text{-}F}$ = 6.6 Hz), 117.8 (tt, $^{1}J_{C\text{-}F}$ = 261.4, 32.2 Hz), 116.3 (tt, $^{1}J_{C\text{-}F}$ = 255.1, 38.2 Hz), 53.7, 43.6, 26.3, 24.3, 24.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.3 (t, *J* = 5.3 Hz), -112.8 (t, *J* = 5.5 Hz); **IR (ATR):** $\tilde{\nu}$ 1745, 1661, 1537, 1358, 1209, 865, 768, 700, 580 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}F_4N_3^+$ 290.1275; Found 290.1265; **R_f:** 0.44 (1:9 EtOAc/pentane).

4. General Procedure B for the Synthesis of α-Difluoro Triazenyl Ketones 3:



General Procedure B: Alkynyl triazene **1** (0.10 mmol, 1.0 eq.) and DIH (0.12 mmol, 45.6 mg. 1.2 eq.) were weighed in Falcon tube containing a magnetic stirring bar. Addition of $CHCl_3$ (1.0 mL) at RT was immediately followed by addition of DAST (0.20 mmol, 26.4 µL, 2.0 eq.) *via* a micro pipette. The mixture was stirred at RT for 2 h, in the dark with aluminium foil.

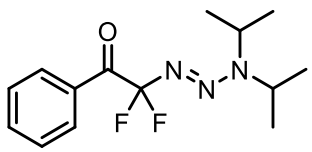
After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the α-difluoro triazenyl ketone product **3**.



(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-(naphthalen-1-yl)ethan-1-one (**3a**):

Obtained as yellow oil in 92 % yield (30.8 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.79 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.06–7.97 (m, 2H), 7.87 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.63 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.47 (dd, *J* = 8.2, 7.4 Hz, 1H), 5.14 (m, 1H), 3.83 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 191.6 (t, $^2J_{C\text{-}F}$ = 35.2 Hz), 134.0, 133.9, 131.6 (t, $^3J_{C\text{-}F}$ = 3.7 Hz), 131.3, 129.9, 128.7, 128.6, 126.6, 125.8, 124.1, 119.0 (t, $^1J_{C\text{-}F}$ = 248.7 Hz), 50.2, 47.3, 23.1, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -82.8; **IR (ATR):** $\tilde{\nu}$ 2923, 2852, 1680, 1598, 1453, 1408, 1260, 1227, 1196, 1175, 720 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{18}H_{21}F_2N_3NaO^+$ 356.1545; Found 356.1541; **R_f:** 0.44 (1:9 EtOAc/pentane).

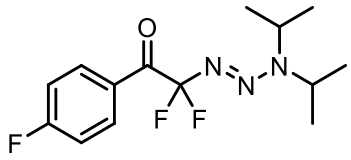
(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-phenylethan-1-one (**3b**):



Obtained as yellow oil in 89 % yield (25.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.97 (d, *J* = 7.4 Hz, 2H), 7.58–7.50 (m, 1H), 7.48–7.40 (m, 2H), 5.14 (m, 1H), 3.82 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 189.2 (t, $^2J_{C\text{-}F}$ = 34.8 Hz), 133.6, 132.7, 130.6 (t, $^3J_{C\text{-}F}$ = 2.1 Hz), 128.5, 119.2 (t, $^1J_{C\text{-}F}$ = 245.9

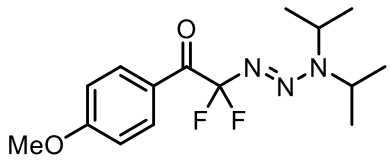
Hz), 50.1, 47.2, 23.1, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -83.7; **IR (ATR):** $\tilde{\nu}$ 2926, 1696, 1679, 1469, 1449, 1281, 1211, 1170, 1134, 1098, 709, 666 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}F_2N_3O^+$ 284.1569; Found 284.1364; **R_f:** 0.18 (1:9 EtOAc/pentane).

(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-(4-fluorophenyl)ethan-1-one (**3c**):



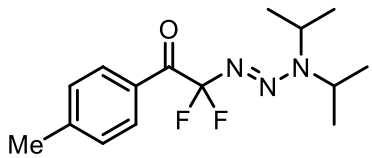
Obtained as yellow oil in 86 % yield (26.0 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.06–7.97 (m, 2H), 7.14–7.07 (m, 2H), 5.14 (m, 1H), 3.85 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 187.7 (t, $^2J_{C-F}$ = 35.1 Hz), 165.96 (d, $^1J_{C-F}$ = 256.3 Hz), 133.4 (dt, $^3J_{C-F}$ = 9.6, 2.4 Hz), 129.1 (d, $^3J_{C-F}$ = 3.1 Hz), 119.1 (t, $^1J_{C-F}$ = 246.0 Hz), 115.7 (d, $^2J_{C-F}$ = 22.0 Hz), 50.2, 47.4, 23.1, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -83.67, -103.83; **IR (ATR):** $\tilde{\nu}$ 1713, 1600, 1432, 1410, 1223, 1158, 1130, 1025, 941, 853, 744, 619 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}F_3N_3NaO^+$ 324.1294; Found 324.1293; **R_f:** 0.18 (1:9 EtOAc/pentane).

(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-phenylethan-1-one (**3d**):



0.3 eq. DAST. Obtained as yellow oil in 47 % yield (14.8 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.95 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 5.14 (t, *J* = 7.8 Hz, 1H), 3.89 (d, *J* = 2.7 Hz, 1H), 3.86 (s, 3H), 1.25–1.17 (m, 6H), 1.00–0.94 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 187.7 (t, $^2J_{C-F}$ = 34.3 Hz), 163.9, 133.0, 125.7, 119.3 (t, $^1J_{C-F}$ = 246.4 Hz), 113.7, 55.6, 50.1, 47.2, 23.2, 19.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -83.5; **IR (ATR):** $\tilde{\nu}$ 2925, 2853, 1702, 1602, 1512, 1602, 1512, 1433, 1262, 1162, 1133, 1026, 940 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{15}H_{21}F_2N_3NaO_2^+$ 336.1494; Found 336.1486; **R_f:** 0.12 (1:9 EtOAc/pentane).

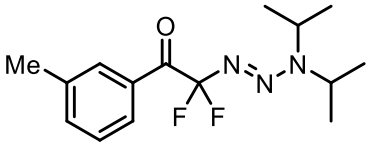
(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-(*p*-tolyl)ethan-1-one (**3e**):



Obtained as colourless solid in 93 % yield (27.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.86 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.14 (m, 1H), 3.83 (m, 1H), 2.40 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 188.8 (t, $^2J_{C-F}$ = 34.5 Hz), 144.6, 130.7, 130.2, 129.2, 119.2 (t, $^1J_{C-F}$ = 246.3 Hz), 50.1, 47.2, 23.1, 21.9, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -83.7; **IR**

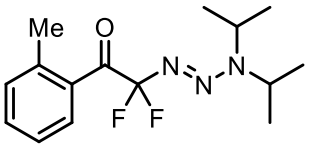
(ATR): $\tilde{\nu}$ 1676, 1605, 1314, 1282, 1217, 1208, 1173, 1098, 735, 712 cm^{-1}; **HRMS (ESI/QTOF)** $[M + Na]^+$ Calcd for $C_{15}H_{21}F_2N_3NaO^+$ 320.1545; Found 320.1538; **R_f:** 0.27 (1:9 EtOAc/pentane).

(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-(*m*-tolyl)ethan-1-one (**3f**):



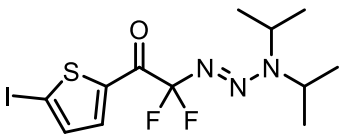
5 hour reaction time. Obtained as colourless oil in 64 % yield (19.0 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.82–7.72 (m, 2H), 7.38–7.28 (m, 2H), 7.26 (s, 1H), 5.15 (m, 1H), 3.83 (m, 1H), 2.38 (s, 3H), 1.21 (dd, *J* = 6.8, 1.3 Hz, 6H), 0.95 (dd, *J* = 6.6, 1.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 189.3 (t, $^2J_{C\text{-}F}$ = 35.1 Hz), 138.2, 134.4, 132.6, 131.0, 128.3, 127.9, 119.2 (t, $^1J_{C\text{-}F}$ = 247.2 Hz), 50.1, 47.2, 23.1, 21.4, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -83.7; **IR (ATR):** $\tilde{\nu}$ 1676, 1608, 1314, 1292, 1219, 1208, 1173, 1100, 967, 735, 712 cm^{-1}; **HRMS (ESI/QTOF)** $[M + Na]^+$ Calcd for $C_{15}H_{21}F_2N_3NaO^+$ 320.1545; Found 320.1542; **R_f:** 0.28 (1:9 EtOAc/pentane).

(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-(o-tolyl)ethan-1-one (**3g**):



5 hour reaction time. Obtained as yellow oil in 67 % yield (19.8 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.71 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 5.1 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 5.13 (m, 1H), 3.87 (m, 1H), 2.58 (s, 3H), 1.20 (d, *J* = 6.1 Hz, 6H), 1.02 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 191.1 (t, $^2J_{C\text{-}F}$ = 34.7 Hz), 141.0, 132.05, 132.03, 132.02, 131.6 (t, $^3J_{C\text{-}F}$ = 3.3 Hz), 125.2, 118.7 (t, $^1J_{C\text{-}F}$ = 248.2 Hz), 50.0, 47.1, 23.0, 21.9, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -83.3; **IR (ATR):** $\tilde{\nu}$ 1680, 1605, 1315, 1286, 1217, 1208, 1173, 1098, 733, 712 cm^{-1}; **HRMS (ESI/QTOF)** $[M + Na]^+$ Calcd for $C_{15}H_{21}F_2N_3NaO^+$ 320.1545; Found 320.1538; **R_f:** 0.34 (1:9 EtOAc/pentane).

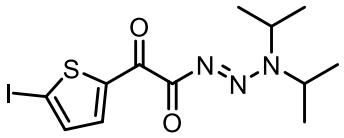
(*E*)-2-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-1-(5-iodothiophen-2-yl)ethan-1-one (**3h**):



2.4 eq. DIH used. Obtained as yellow oil in 33 % yield (13.6 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.38 (dt, *J* = 4.1, 1.2 Hz, 1H), 7.30 (d, *J* = 4.0 Hz, 1H), 5.11 (hept, *J* = 6.8 Hz, 1H), 3.90 (hept, *J* = 6.6 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 7H), 1.05 (d, *J* = 6.6 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -84.5; **IR (ATR):** $\tilde{\nu}$ 2978, 2929, 1687, 1469, 1434, 1401, 1370, 1223, 1132, 1061, 1024, 956, 860, 792, 736, 720 cm^{-1}; **HRMS**

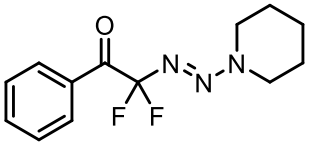
(ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}F_2IN_3NaOS^+$ 437.9919; Found 437.9923; **R_f:** 0.27 (1:9 EtOAc/pentane). No successful **^{13}C NMR** spectrum was recorded as **3h** rapidly converts to diketone **4h** within 15 minutes.

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2-(5-iodothiophen-2-yl)ethane-1,2-dione (**4h**):



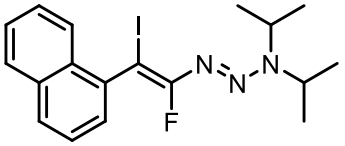
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31 (d, *J* = 3.9 Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 1H), 5.51 (hept, *J* = 6.8 Hz, 1H), 4.17 (hept, *J* = 6.6 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 185.9, 178.9, 147.0, 138.5, 136.1, 87.5, 52.7, 50.6, 23.2, 19.0; **IR (ATR):** $\tilde{\nu}$ 2970, 2929, 1680, 1477, 1400, 1370, 1138, 1000, 996, cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}IN_3NaO_2S^+$ 415.9900; Found 415.9905; **R_f:** 0.38 (1:2 EtOAc/pentane).

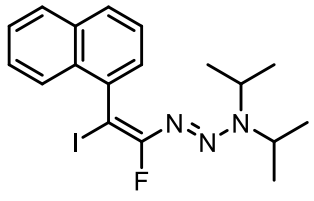
(*E*)-2,2-difluoro-1-phenyl-2-(piperidin-1-yldiazenyl)ethan-1-one (**3i**):



Obtained as yellow oil in 80 % yield (21.3 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.99 (d, *J* = 7.8 Hz, 2H), 7.57 (td, *J* = 7.2, 1.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 3.84 (t, *J* = 5.6 Hz, 2H), 3.58 (t, *J* = 5.7 Hz, 2H), 1.63 (m 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 188.4 (t, $^2J_{C\text{-}F}$ = 35.2 Hz), 133.9, 132.4, 130.7 (t, $^3J_{C\text{-}F}$ = 2.2 Hz), 128.6, 118.8 (t, $^1J_{C\text{-}F}$ = 249.6 Hz), 53.6, 43.5, 26.3, 24.4, 23.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -84.8; **IR (ATR):** $\tilde{\nu}$ 2923, 2852, 1680, 1598, 1453, 1408, 1260, 1227, 1196, 1175, 720 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{16}F_2N_3O^+$ 268.1256; Found 268.1056; **R_f:** 0.25 (1:9 EtOAc/pentane).

(*E*)-1-((*E*)-1-fluoro-2-iodo-2-(naphthalen-1-yl)vinyl)-3,3-diisopropyltriaz-1-ene, (*E*)-1-((*Z*)-1-fluoro-2-iodo-2-(naphthalen-1-yl)vinyl)-3,3-diisopropyltriaz-1-ene (**5a**):

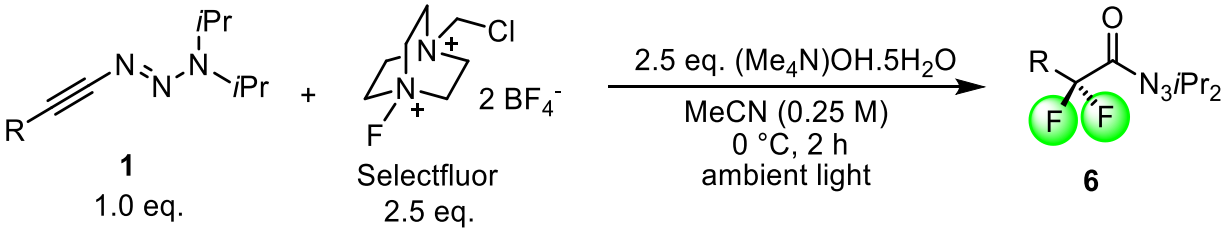




Isolated from reaction crude during optimizations. Obtained as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = **Trans isomer**: 8.10 (d, *J* = 8.3 Hz, 1H), 7.89–7.85 (m, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.62–7.39 (m, 4H, overlapped), 5.09 (hept, *J* = 6.8 Hz, 1H), 4.09 (hept, *J* = 6.6 Hz, 1H), 1.40 (dd, *J* = 6.8, 3.7 Hz, 6H), 1.36 (dd, *J* = 6.7, 2.7 Hz, 6H); **Cis isomer**: 8.04 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H, overlapped), 7.75 (d, *J* = 8.2 Hz, 1H), 7.61–7.38 (m, 4H, overlapped), 4.32 (hept, *J* = 6.8 Hz, 1H), 3.78 (hept, *J* = 6.6 Hz, 1H), 1.00 (t, *J* = 6.8 Hz, 6H), 0.79 (dd, *J* = 6.8, 3.4 Hz,

6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.0 (d, $^1J_{C-F}$ = 277.3 Hz), 154.5 (d, $^1J_{C-F}$ = 298.5 Hz), 137.4 (d, $^3J_{C-F}$ = 4.0 Hz), 136.9, 136.3, 135.5, 134.0, 133.9, 131.7, 131.5, 129.3, 128.7, 128.7 (d, $^3J_{C-F}$ = 3.1 Hz), 128.4, 128.3, 128.2, 126.4, 126.2, 126.0, 125.9, 125.6, 125.5, 63.2 (d, $^2J_{C-F}$ = 40.5 Hz), 59.3 (d, $^2J_{C-F}$ = 40.0 Hz), 51.5, 51.1, 48.7, 47.9, 23.3, 23.2, 22.8, 22.8, 19.1, 19.0, 18.6, 18.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -92.7; **IR (ATR):** $\tilde{\nu}$ 2972, 2930, 1718, 1688, 1625, 1574, 1467, 1399, 1379, 1367, 1249, 1221, 1195, 1157, 1129, 1099732, 695 cm^{-1}; **HRMS (ESI/QTOF)** $[M + H]^+$ Calcd for $C_{18}H_{22}FIN_3^+$ 426.0837; Found 426.0831; **R_f:** 0.84 (1:9 EtOAc/pentane).

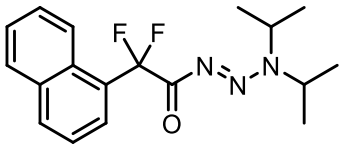
5. General Procedure C for the Synthesis of α-Difluoro Acyl Triazenes 6:



General Procedure C: Alkynyl triazene **1** (0.10 mmol, 1.0 eq.), Selectfluor (0.25 mmol, 88.6 mg. 2.5 eq.) and $(Me_4N)OH.5H_2O$ (0.25 mmol, 45.3 mg. 2.5 eq.) were weighed in a test tube containing a magnetic stirring bar. MeCN (0.25 mL) pre-cooled at 0 ˚C was added to the test tube. The mixture was stirred at 0 ˚C for 2 h under ambient light.

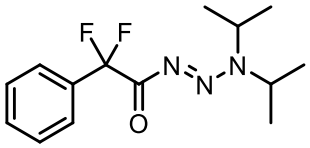
After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the α-difluoro acyl triazene product **6**.

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-(naphthalen-1-yl)ethan-1-one (**6a**):



Obtained as white solid in 86 % yield (28.8 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.39–8.27 (m, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.88–7.83 (m, 1H), 7.56–7.45 (m, 3H), 4.88 (m, 1H), 4.16 (m, 1H), 1.27 (d, *J* = 6.7 Hz, 6H), 1.08 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.2 (t, $^2J_{C\text{-}F}$ = 29.4 Hz), 133.9, 131.1, 130.9 (t, $^2J_{C\text{-}F}$ = 23.6 Hz), 129.8, 128.6, 127.1, 126.1, 125.3 (t, $^4J_{C\text{-}F}$ = 3.0 Hz), 124.9 (t, $^3J_{C\text{-}F}$ = 9.3 Hz), 124.6, 116.5 (t, $^1J_{C\text{-}F}$ = 251.2 Hz), 54.4, 51.4, 22.6, 18.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.8; **IR (ATR):** $\tilde{\nu}$ 1645, 1450, 1400, 1260, 1120, 1048, 822, 695, 679 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{18}H_{21}F_2N_3NaO^+$ 356.1545; Found 356.1540; **R_f:** 0.30 (1:7 EtOAc/pentane).

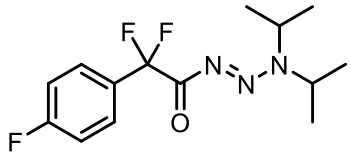
(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-phenylethan-1-one (**6b**):



Obtained as yellow oil in 85 % yield (24.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.70–7.61 (m, 2H), 7.41 (dd, *J* = 5.0, 1.9 Hz, 3H), 5.16 (m, 1H), 4.21 (m, 1H), 1.30 (d, *J* = 6.6 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.1 (t, $^2J_{C\text{-}F}$ = 29.2 Hz), 135.0 (t, $^2J_{C\text{-}F}$ = 25.7 Hz), 130.3, 128.4, 125.7 (t, $^3J_{C\text{-}F}$ = 6.1 Hz), 115.8 (t, $^1J_{C\text{-}F}$ = 251.4 Hz), 53.9, 51.0, 22.8, 18.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -102.6; **IR (ATR):** $\tilde{\nu}$ 2960, 1644, 1453,

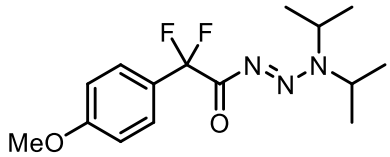
1397, 1262, 1060, 812, 699 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{14}H_{19}F_2N_3NaO^+$ 306.1388; Found 306.1389; **R_f:** 0.17 (1:7 EtOAc/pentane).

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-(4-fluorophenyl)ethan-1-one (**6c**):

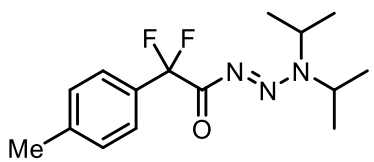


Obtained as yellow oil in 90 % yield (27.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.71–7.53 (m, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 5.16 (m, 1H), 4.23 (m, 1H), 1.34 (d, *J* = 6.7 Hz, 6H), 1.27 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) 173.8 (t, $^2J_{C\text{-}F}$ = 29.4 Hz), 163.9 (d, $^1J_{C\text{-}F}$ = 249.5 Hz), 133.6 (d, $^3J_{C\text{-}F}$ = 9.2 Hz), 131.65–130.52 (m), 128.0 (dt, $^3J_{C\text{-}F}$ = 8.8, 6.0 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 54.0, 51.2, 22.9, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -102.2, -110.6 (t, *J* = 3.0 Hz).; **IR (ATR):** $\tilde{\nu}$ 1699, 1655, 1608, 1511, 1396, 1299, 1261, 1234, 1159, 1122, 1096, 842 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{14}H_{18}F_3N_3NaO^+$ 324.1294; Found 324.1284; **R_f:** 0.55 (1:3 EtOAc/pentane).

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-(4-methoxyphenyl)ethan-1-one (**6d**):



Obtained as yellow oil in 64 % yield (20.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.57 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.17 (m, 1H), 4.22 (m, 1H), 3.82 (s, 3H), 1.33 (d, *J* = 6.6 Hz, 6H), 1.27 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.3 (t, $^2J_{C\text{-}F}$ = 30.0 Hz), 161.1, 127.4 (t, $^3J_{C\text{-}F}$ = 5.9 Hz), 127.1 (d, $^2J_{C\text{-}F}$ = 26.4 Hz), 115.9 (t, $^1J_{C\text{-}F}$ = 251.3 Hz), 113.8, 55.5, 53.8, 51.0, 22.9, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -101.6; **IR (ATR):** $\tilde{\nu}$ 1697, 1654, 1614, 1515, 1302, 1250, 1177, 1096, 1024, 988, 837 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{15}H_{21}F_2N_3NaO_2^+$ 336.1494; Found 336.1499; **R_f:** 0.70 (1:3 EtOAc/pentane).

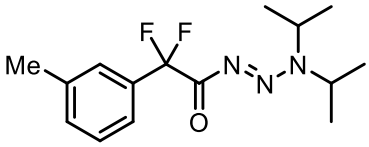


(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-(p-tolyl)ethan-1-one (**6e**):

Obtained as yellow oil in 83 % yield (24.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.53 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 5.17 (m, 1H), 4.21 (m, 1H), 2.36 (s, 3H), 1.32 (d, *J* = 6.7 Hz, 6H), 1.26 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.3 (t, $^2J_{C\text{-}F}$ = 29.5 Hz), 140.3, 132.1 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 129.1, 125.7 (t, $^3J_{C\text{-}F}$ = 6.0 Hz), 116.0 (t, $^1J_{C\text{-}F}$ = 251.3 Hz), 53.8, 50.9, 22.8, 21.5, 18.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -102.2; **IR (ATR):** $\tilde{\nu}$ 1702, 1650, 1396, 1337, 1299, 1270, 1234, 1186, 1099,

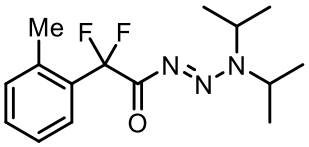
1078, 999, 808 cm^{-1}; **HRMS (ESI/QTOF)** [M + Na]$^+$ Calcd for $C_{15}H_{21}F_2N_3NaO^+$ 320.1545; Found 320.1540; **R_f:** 0.29 (1:9 EtOAc/pentane).

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-(m-tolyl)ethan-1-one (**6f**):



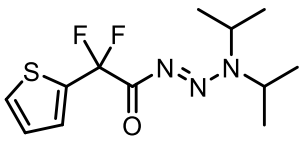
Obtained as yellow oil in 77 % yield (22.9 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.48–7.41 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24–7.20 (m, 1H), 5.17 (hept, *J* = 6.8 Hz, 1H), 4.21 (hept, *J* = 6.6 Hz, 1H), 2.37 (s, 3H), 1.31 (d, *J* = 6.6 Hz, 6H), 1.26 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.3 (t, $^2J_{C\text{-}F}$ = 29.3 Hz), 138.2, 134.9 (t, $^2J_{C\text{-}F}$ = 25.4 Hz), 131.0, 128.3, 126.3 (t, $^3J_{C\text{-}F}$ = 6.0 Hz), 122.8 (t, $^3J_{C\text{-}F}$ = 6.1 Hz), 115.9 (t, $^1J_{C\text{-}F}$ = 251.6 Hz), 53.9, 50.98, 22.8, 21.5, 18.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -102.6; **IR (ATR):** $\tilde{\nu}$ 1698, 1650, 1395, 1336, 1296, 1277, 1234, 1185, 1155, 1095, 1079, 1003, 809, 797, 747 cm^{-1}; **HRMS (ESI/QTOF)** [M + Na]$^+$ Calcd for $C_{15}H_{21}F_2N_3NaO^+$ 320.1545; Found 320.1539; **R_f:** 0.39 (1:4 EtOAc/pentane).

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-(o-tolyl)ethan-1-one (**6g**):



Obtained as yellow oil in 80 % yield (23.8 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.66–7.59 (m, 1H), 7.32–7.27 (m, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 5.00 (m, 1H), 4.19 (m, 1H), 2.42 (t, *J* = 2.1 Hz, 3H), 1.28 (d, *J* = 6.6 Hz, 6H), 1.18 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.1 (t, $^2J_{C\text{-}F}$ = 29.4 Hz), 136.4 (t, $^3J_{C\text{-}F}$ = 3.3 Hz), 133.5 (t, $^2J_{C\text{-}F}$ = 23.6 Hz), 131.6, 130.0, 126.40 (t, $^3J_{C\text{-}F}$ = 8.7 Hz), 125.6, 116.3 (t, $^1J_{C\text{-}F}$ = 251.1 Hz), 54.2, 51.2, 22.7, 20.0 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 18.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -100.9; **IR (ATR):** $\tilde{\nu}$ 1698, 1655, 1326, 1295, 1274, 1233, 1156, 1078, 809, 797, 748 cm^{-1}; **HRMS (ESI/QTOF)** [M + Na]$^+$ Calcd for $C_{15}H_{21}F_2N_3NaO^+$ 320.1545; Found 320.1544; **R_f:** 0.70 (1:3 EtOAc/pentane).

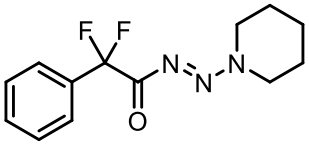
(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-2-(thiophen-2-yl)ethan-1-one (**6h**):



Obtained as yellow oil in 59 % yield (17.0 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.42 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.39 (dt, *J* = 2.9, 1.5 Hz, 1H), 7.05–7.01 (m, 1H), 5.30 (m, 1H), 4.26 (m, 1H), 1.39 (d, *J* = 6.6 Hz, 6H), 1.32 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 173.0 (t, $^2J_{C\text{-}F}$ = 29.1 Hz), 136.5 (t, $^2J_{C\text{-}F}$ = 30.6 Hz), 128.3, 128.1 (t, $^3J_{C\text{-}F}$ = 5.6 Hz), 126.9, 114.0 (t, $^1J_{C\text{-}F}$ = 250.1 Hz), 53.9, 51.2, 23.0, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -92.3; **IR (ATR):** $\tilde{\nu}$ 2930, 1698, 1432, 1335, 1260, 1241, 1098, 1042,

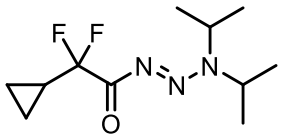
1012, 717, 456, 418 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{12}H_{17}F_2N_3NaOS^+$ 312.0953; Found 312.0958; **R_f:** 0.70 (1:3 EtOAc/pentane).

(*E*)-2,2-difluoro-2-phenyl-1-(piperidin-1-yldiazenyl)ethan-1-one (**6i**):



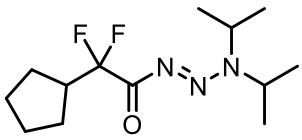
Obtained as yellow oil in 79 % yield (21.0 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.66 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.45–7.37 (m, 3H), 4.08–4.03 (m, 2H), 4.00–3.93 (m, 2H), 1.88–1.81 (m, 2H), 1.77 (ddd, *J* = 10.6, 8.3, 4.6 Hz, 2H), 1.71 (q, *J* = 6.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.8 (t, $^2J_{C\text{-}F}$ = 30.1 Hz), 134.6 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 130.4, 128.4, 125.9 (t, $^3J_{C\text{-}F}$ = 6.1 Hz), 115.6 (t, $^1J_{C\text{-}F}$ = 251.4 Hz), 55.9, 46.5, 26.6, 25.1, 23.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -104.0; **IR (ATR):** $\tilde{\nu}$ 2950, 1644, 1452, 1397, 1261, 1123, 1058, 814, 700, 677 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{14}H_{15}F_2O_3^+$ 268.1256; Found 268.1256; **R_f:** 0.18 (1:3 EtOAc/pentane).

(*E*)-2-cyclopropyl-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoroethan-1-one (**6j**):



Obtained as yellow oil in 89 % yield (22.0 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 5.27 (hept, *J* = 6.8 Hz, 1H), 4.29 (hept, *J* = 6.6 Hz, 1H), 1.72–1.55 (m, 1H), 1.44 (d, *J* = 6.7 Hz, 6H), 1.34 (d, *J* = 6.9 Hz, 6H), 0.86–0.77 (m, 2H), 0.69–0.58 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.4 (t, $^2J_{C\text{-}F}$ = 29.5 Hz), 117.0 (t, $^1J_{C\text{-}F}$ = 248.7 Hz), 53.8, 50.9, 23.1, 18.8, 14.6 (t, $^2J_{C\text{-}F}$ = 28.2 Hz), 1.55 (t, $^3J_{C\text{-}F}$ = 4.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -110.4; **IR (ATR):** $\tilde{\nu}$ 2982, 1698, 1653, 1470, 1444, 1385, 1372, 1337, 1302, 1262, 1216, 1187, 1157, 1134, 1095, 1071, 1004, 920, 857 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{11}H_{19}F_2N_3NaO^+$ 270.1388; Found 270.1398; **R_f:** 0.60 (1:4 EtOAc/pentane).

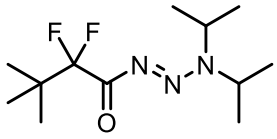
(*E*)-2-cyclopentyl-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoroethan-1-one (**6k**):



Obtained as yellow oil in 84 % yield (23.2 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 5.25 (m, 1H), 4.27 (m, 1H), 2.75 (m, 1H), 1.81–1.62 (m, 6H), 1.61–1.51 (m, 2H), 1.44 (d, *J* = 6.6 Hz, 6H), 1.33 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.8 (t, $^2J_{C\text{-}F}$ = 28.3 Hz), 119.5 (t, $^1J_{C\text{-}F}$ = 250.9 Hz), 53.7, 50.9, 43.6 (t, $^2J_{C\text{-}F}$ = 22.9 Hz), 26.2, 26.0 (t, $^3J_{C\text{-}F}$ = 3.8 Hz), 23.0, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -111.8; **IR (ATR):** $\tilde{\nu}$ 2965, 1697, 1444, 1371, 1336, 1300, 1250, 1207, 1156, 1133,

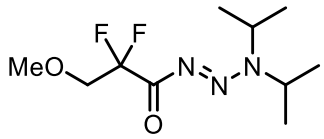
1099, 1061, 1002, 925 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{13}H_{23}F_2N_3NaO^+$ 298.1701; Found 298.1708; **R_f:** 0.54 (1:3 EtOAc/pentane).

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-3,3-dimethylbutan-1-one (**6l**):



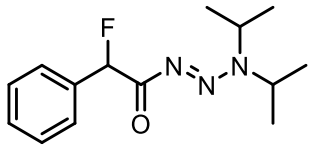
Obtained as white solid in 63 % yield (16.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 5.16 (hept, *J* = 6.8 Hz, 1H), 4.28 (hept, *J* = 6.6 Hz, 1H), 1.44 (d, *J* = 6.6 Hz, 6H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.13 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 174.7 (t, $^2J_{C\text{-}F}$ = 28.3 Hz), 120.8 (t, $^1J_{C\text{-}F}$ = 255.1 Hz), 54.0, 51.1, 37.8 (t, $^2J_{C\text{-}F}$ = 22.5 Hz), 24.2 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 23.0, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -115.5; **IR (ATR):** $\tilde{\nu}$ 2968, 1699, 1445, 1370, 1250, 1156, 1120, 1096, 1061, 929 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{12}H_{23}F_2N_3NaO^+$ 286.1701; Found 286.1709; **R_f:** 0.41 (1:4 EtOAc/pentane).

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2,2-difluoro-3-methoxypropan-1-one (**6m**):



Obtained as yellow oil in 39 % yield (9.9 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 5.32 (m, 1H), 4.29 (m, 1H), 3.95 (t, *J* = 13.3 Hz, 2H), 3.48 (s, 3H), 1.44 (d, *J* = 6.6 Hz, 6H), 1.34 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 173.1 (t, $^2J_{C\text{-}F}$ = 25.9 Hz), 115.9 (t, $^1J_{C\text{-}F}$ = 253.3 Hz), 72.5 (t, $^2J_{C\text{-}F}$ = 27.8 Hz), 60.4, 53.8, 51.0, 23.1, 18.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -112.5; **IR (ATR):** $\tilde{\nu}$ 2093, 2926, 2854, 1703, 1647, 1469, 1397, 1339, 1297, 1260, 1208, 1153, 1100, 1016 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{10}H_{19}F_2N_3NaO_2^+$ 274.1338; Found 274.1344; **R_f:** 0.68 (1:4 EtOAc/pentane).

(*E*)-1-(3,3-diisopropyltriaz-1-en-1-yl)-2-fluoro-2-phenylethan-1-one (**8b**):

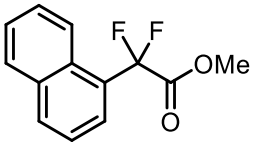


Isolated from reaction crude during optimizations. Obtained as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.46 (dt, *J* = 7.7, 1.9 Hz, 2H), 7.40–7.31 (m, 3H), 6.38 (d, *J* = 49.6 Hz, 1H), 5.34 (hept, *J* = 6.8 Hz, 1H), 4.12 (hept, *J* = 6.5 Hz, 1H), 1.36 (d, *J* = 6.6 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 180.4 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 135.8 (d, $^2J_{C\text{-}F}$ = 19.6 Hz), 129.3 (d, $^3J_{C\text{-}F}$ = 2.9 Hz), 128.7, 128.0 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 91.2 (d, $^1J_{C\text{-}F}$ = 180.5 Hz), 52.0, 49.5, 23.4, 23.1, 18.90; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -174.2; **IR (ATR):** $\tilde{\nu}$ 2978, 1702, 1468, 1455, 1431, 1343, 1328, 1285, 1268, 1219, 1170, 1134, 1098, 1041, 1012, 767,

739, 698, 609 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}FN_3NaO^+$ 288.1483; Found 288.1483; **R_f:** 0.33 (2:3 EtOAc/pentane).

6. Product Derivatizations:

Methyl 2,2-difluoro-2-(naphthalen-1-yl)acetate (**11a**):

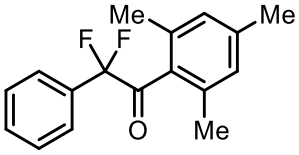


6a (0.10 mmol, 35.5 mg. 1.0 eq.) was dissolved in 1.0 mL MeOH, followed by 0.12 mL $BF_3.OEt_2$ (10.0 eq.). Reaction mixuture was stirred at 60 ˚C for 2 h. After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the product.

Obtained as white solid in 80 % yield (18.9 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.18 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.93–7.89 (m, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.56 (tt, *J* = 10.0, 6.6 Hz, 3H), 3.82 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 165.1 (t, $^2J_{C\text{-}F}$ = 35.2 Hz), 134.0, 132.2, 129.5, 129.1, 128.4 (t, $^2J_{C\text{-}F}$ = 23.2 Hz), 127.6, 126.5, 125.04 (t, $^3J_{C\text{-}F}$ = 9.4 Hz), 124.7, 124.3, 114.5 (t, $^1J_{C\text{-}F}$ = 251.5 Hz), 53.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -99.96. The spectra obtained fit with reported literature.[3]

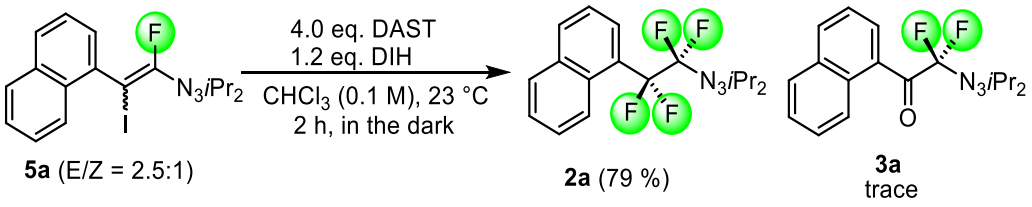
2,2-Difluoro-1-mesityl-2-phenylethan-1-one (**12b**):

6a (0.10 mmol, 35.5 mg. 1.0 eq.) was dissolved in 1.0 mL *p*-xylene, followed by 0.12 mL $BF_3.OEt_2$ (10.0 eq.). Reaction mixuture was stirred at 60 ˚C for 2 h. After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the product.



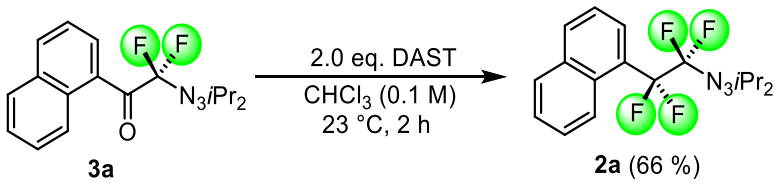
Obtained a colourless oil in 92 % yield (28.4 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.10 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 6.90 (s, 2H), 2.33 (t, *J* = 4.0 Hz, 6H), 2.30 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -89.9. The spectra obtained fit with reported literature.[4]

7. Control Experiments:



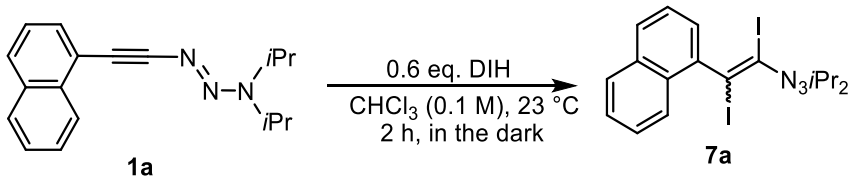
5a (E/Z = 2.5:1) **2a** (79 %) **3a** trace

5a (0.10 mmol, 42.5 mg, 1.0 eq.) and DIH (0.12 mmol, 45.6 mg. 1.2 eq.) were weighed in Falcon tube containing a magnetic stirring bar. Addition of $CHCl_3$ (1.0 mL) at RT was immediately followed by addition of DAST (0.40 mmol, 52.8 µL, 4.0 eq.) *via* a micro pipette. The mixture was stirred at RT for 2 h, in the dark with aluminium foil. After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford product **2a** in 79 % yield (28.0 mg). Trace amount of **3a** was observed on crude NMR.



3a **2a** (66 %)

3a (0.10 mmol, 33.3 mg, 1.0 eq.) was weighed in Falcon tube containing a magnetic stirring bar. Addition of $CHCl_3$ (1.0 mL) at RT was immediately followed by addition of DAST (0.20 mmol, 26.4 µL, 2.0 eq.) *via* a micro pipette. The mixture was stirred at RT for 2 h. After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford product **2a** in 66 % yield (23.4 mg).



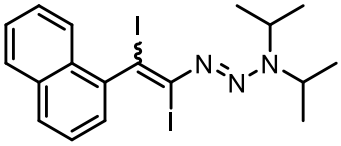
1a **7a**

With 1.2 eq. (nBu$_4$N)I: 92 %
Without (nBu$_4$N)I : No product

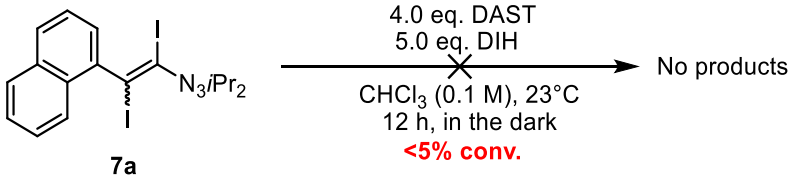
Alkynyl triazene **1a** (0.10 mmol, 27.9 mg, 1.0 eq.), (nBu$_4$N)I (0.12 mmol, 44.3 mg. 1.2 eq.) and DIH (0.06 mmol, 22.8 mg. 0.6 eq.) were weighed in Falcon tube containing a magnetic stirring bar. $CHCl_3$ (1.0 mL) was added at RT. The mixture was stirred at RT for 2 h in the dark with aluminium foil. After completion of reaction, the mixture was

concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **7a** in 92 % yield (48.8 mg). When no (*n*Bu$_4$N)I was added, full decomposition of **1a** was observed with no defined product formed.

1-(1,2-diiodo-2-(naphthalen-1-yl)vinyl)-3,3-diisopropyltriaz-1-ene (**7a**):

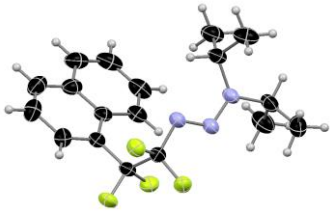


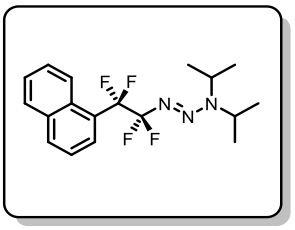
Obtained as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.98 (d, *J* = 8.3 Hz, 1H), 7.92–7.83 (m, 2H), 7.58–7.41 (m, 4H), 5.14 (hept, *J* = 6.8 Hz, 1H), 4.10 (hept, *J* = 6.6 Hz, 1H), 1.44 (dd, *J* = 6.6, 2.9 Hz, 6H), 1.40 (dd, *J* = 6.8, 3.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 143.0, 134.0, 130.8, 128.6, 128.5, 127.9, 126.3, 126.3, 126.2, 125.8, 118.8, 82.0, 51.5, 51.4, 23.8, 23.8, 19.2, 19.1; **IR (ATR):** $\tilde{\nu}$ 2974, 1463, 1415, 1382, 1365, 1275, 801, 781, cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{18}H_{22}I_2N_3^+$ 533.9898; Found 533.9910; **R_f:** 0.88 (1:9 EtOAc/pentane).



7a (0.08 mmol, 42.7 mg, 1.0 eq.), and DIH (0.40 mmol, 152.0 mg. 5.0 eq.) were weighed in Falcon tube containing a magnetic stirring bar. Addition of $CHCl_3$ (1.0 mL) at RT was immediately followed by addition of DAST (0.32 mmol, 42.3 µL, 4.0 eq.) *via* a micro pipette. The mixture was stirred at RT for 12 h, in the dark with aluminium foil. After completion of reaction, the mixture was concentrated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to recover >95 % **7a**.

8. X-ray Structures:





Compound	**2a**
Formula	$C_{18}H_{21}F_4N_3$
$D_{calc.}$/ g cm^{-3}	1.340
μ /mm^{-1}	0.941
Formula Weight	355.38
Colour	colourless
Shape	prism
Size/mm^3	0.36×0.25×0.11
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	9.21581(8)
b/Å	14.44752(14)
c/Å	13.23644(14)
α/°	90
β/°	91.4811(9)
γ/°	90
V/Å^3	1761.79(3)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu$K\alpha$
Θ_{min}/°	4.531
Θ_{max}/°	76.037
Measured Refl's.	18746
Indep't Refl's	3665
Refl's I≥2σ(I)	3433
R_{int}	0.0214
Parameters	230
Restraints	0
Largest Peak/e Å^{-3}	0.285
Deepest Hole/e Å^{-3}	-0.213
GooF	1.019
wR_2 (all data)	0.1065
wR_2	0.1043
R_1 (all data)	0.0397
R_1	0.0378

Reflection Statistics

Total reflections (after filtering)	19120	Unique reflections	3665
Completeness	0.994	Mean I/σ	37.26
hkl_{max} collected	(11, 17, 16)	hkl_{min} collected	(-9, -18, -16)
hkl_{max} used	(11, 18, 16)	hkl_{min} used	(-11, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	14.45	d_{min} used	0.79
Friedel pairs	2692	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0214
R_{sigma}	0.0148	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(5105, 2803, 1133, 398, 216, 108, 56, 55, 29, 26, 11, 9, 4, 4)	Maximum multiplicity	19
Removed systematic absences	374	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
F1	8272.3(7)	5216.0(5)	8664.7(5)	43.59(19)
F2	7384.6(8)	4308.7(5)	7491.6(5)	41.87(18)
F3	8510.5(7)	6614.7(5)	7396.5(5)	42.82(18)
F4	9523.7(7)	5352.5(6)	6876.9(6)	46.8(2)
N1	5953.0(10)	5473.3(7)	7954.3(7)	34.0(2)
N2	5856.0(10)	6078.5(7)	8656.7(7)	34.1(2)
N3	4546.0(10)	6369.7(7)	8832.6(8)	38.1(2)
C1	7417.8(12)	5206.4(8)	7812.8(8)	34.4(2)
C2	8199.5(11)	5768.7(8)	6995.9(9)	35.1(2)
C3	7398.9(12)	5821.5(8)	5989.0(8)	34.7(2)
C4	7661.9(15)	5113.1(9)	5328.1(10)	43.7(3)
C5	6946.6(18)	5063.4(11)	4375.8(10)	54.6(3)
C6	5974.2(17)	5725.7(11)	4097.2(10)	52.6(3)
C7	5665.6(13)	6470.3(9)	4751.4(10)	43.2(3)
C8	4646.9(14)	7156.6(11)	4450.0(11)	52.5(3)
C9	4350.2(14)	7885.7(11)	5056.8(13)	57.1(4)
C10	5059.0(15)	7962.1(10)	6012.6(12)	51.2(3)
C11	6033.0(13)	7305.4(9)	6343.3(10)	41.4(3)
C12	6376.5(11)	6534.8(8)	5721.1(9)	35.4(2)
C13	4439.6(13)	7060.4(9)	9651.6(10)	43.9(3)
C14	5161.8(17)	7959.0(10)	9360.8(14)	60.1(4)
C15	5040.6(17)	6683.3(11)	10649.7(11)	55.6(4)
C16	3229.1(12)	6028.0(10)	8286.9(10)	43.8(3)
C17	2436.5(15)	6816.7(12)	7755.2(12)	56.1(4)
C18	2255.7(15)	5509.2(11)	9015.5(13)	55.7(4)

Table 2: Anisotropic Displacement Parameters (×10^4) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	36.1(3)	57.8(4)	36.7(4)	-0.3(3)	-2.8(3)	9.2(3)
F2	42.7(4)	35.9(4)	47.2(4)	-1.3(3)	5.3(3)	6.2(3)
F3	36.5(4)	45.5(4)	46.4(4)	-5.3(3)	-1.0(3)	-8.5(3)
F4	26.0(3)	65.3(5)	49.3(4)	-2.2(3)	5.6(3)	8.6(3)
N1	28.9(4)	38.4(5)	35.0(4)	-1.4(4)	4.6(3)	1.5(3)
N2	29.3(4)	36.4(5)	37.0(5)	-0.6(4)	6.9(3)	0.7(3)
N3	27.9(4)	43.4(5)	43.3(5)	-7.0(4)	7.9(4)	0.6(4)
C1	30.7(5)	38.3(6)	34.0(5)	-2.5(4)	0.6(4)	4.5(4)
C2	24.3(5)	41.2(6)	39.8(6)	-3.9(4)	3.3(4)	1.9(4)
C3	30.1(5)	39.2(6)	34.8(5)	0.0(4)	4.0(4)	-2.6(4)
C4	47.9(6)	43.5(6)	39.8(6)	-2.8(5)	4.6(5)	2.6(5)
C5	69.6(9)	53.9(8)	40.1(7)	-8.7(6)	0.8(6)	-4.2(7)
C6	57.4(8)	62.3(8)	37.6(6)	1.2(6)	-5.7(5)	-13.8(6)
C7	34.9(6)	50.8(7)	43.9(6)	10.9(5)	-1.1(5)	-9.8(5)
C8	37.2(6)	63.2(8)	56.6(8)	22.0(7)	-4.7(5)	-6.3(6)
C9	34.7(6)	59.6(8)	77.3(10)	30.3(7)	7.3(6)	4.3(6)
C10	43.1(6)	41.9(7)	69.4(9)	10.6(6)	15.0(6)	5.0(5)
C11	35.2(6)	40.0(6)	49.4(6)	3.3(5)	7.6(5)	-0.5(4)
C12	27.8(5)	38.3(6)	40.4(6)	4.3(4)	4.1(4)	-5.2(4)
C13	35.2(5)	43.9(6)	53.3(7)	-12.3(5)	13.8(5)	0.0(5)
C14	55.1(8)	42.1(7)	84.0(11)	-11.5(7)	21.3(8)	-2.4(6)
C15	57.6(8)	62.7(9)	47.1(7)	-15.4(6)	11.2(6)	-1.1(6)
C16	27.9(5)	53.9(7)	49.7(7)	-8.7(5)	3.4(5)	1.1(5)
C17	36.8(6)	73.2(10)	58.5(8)	15.2(7)	3.8(6)	-1.6(6)
C18	37.8(6)	52.1(8)	77.2(10)	9.1(7)	0.9(6)	-6.5(5)

Table 3: Bond Lengths in Å for **2a**.

Atom	Atom	Length/Å
F1	C1	1.3587(13)
F2	C1	1.3649(13)
F3	C2	1.3599(13)
F4	C2	1.3732(12)
N1	N2	1.2812(13)
N1	C1	1.4210(13)
N2	N3	1.3051(13)
N3	C13	1.4785(15)
N3	C16	1.4809(15)
C1	C2	1.5455(16)
C2	C3	1.5085(15)
C3	C4	1.3720(17)
C3	C12	1.4347(16)
C4	C5	1.4091(19)

Atom	Atom	Length/Å
C5	C6	1.356(2)
C6	C7	1.415(2)
C7	C8	1.4156(19)
C7	C12	1.4290(17)
C8	C9	1.357(2)
C9	C10	1.413(2)
C10	C11	1.3701(18)
C11	C12	1.4252(17)
C13	C14	1.5132(19)
C13	C15	1.520(2)
C16	C17	1.517(2)
C16	C18	1.5302(19)

Table 4: Bond Angles in ° for **2a**.

Atom	Atom	Atom	Angle/°
N2	N1	C1	111.42(9)
N1	N2	N3	115.57(9)
N2	N3	C13	115.31(9)
N2	N3	C16	123.76(10)

Atom	Atom	Atom	Angle/°
C13	N3	C16	120.90(9)
F1	C1	F2	106.03(9)
F1	C1	N1	114.84(9)
F1	C1	C2	107.74(9)

Atom	Atom	Atom	Angle/°
F2	C1	N1	106.57(9)
F2	C1	C2	106.77(9)
N1	C1	C2	114.27(9)
F3	C2	F4	105.03(9)
F3	C2	C1	107.28(9)
F3	C2	C3	113.11(9)
F4	C2	C1	106.36(9)
F4	C2	C3	109.67(9)
C3	C2	C1	114.74(9)
C4	C3	C2	115.80(10)
C4	C3	C12	120.26(11)
C12	C3	C2	123.90(10)
C3	C4	C5	121.48(13)
C6	C5	C4	119.87(13)
C5	C6	C7	120.82(12)
C6	C7	C8	120.17(13)
C6	C7	C12	120.31(12)
C8	C7	C12	119.52(13)
C9	C8	C7	121.29(13)
C8	C9	C10	119.67(12)
C11	C10	C9	121.05(14)
C10	C11	C12	120.65(13)
C7	C12	C3	117.26(11)
C11	C12	C3	124.93(11)
C11	C12	C7	117.80(11)
N3	C13	C14	110.77(11)
N3	C13	C15	111.45(11)
C14	C13	C15	112.07(13)
N3	C16	C17	110.77(11)
N3	C16	C18	110.02(11)
C17	C16	C18	112.17(11)

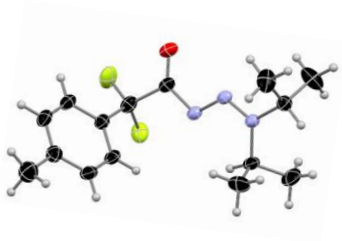
Table 5: Torsion Angles in ° for **2a**.

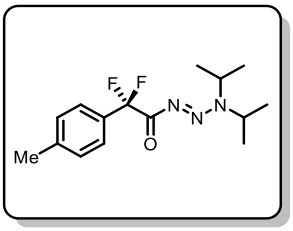
Atom	Atom	Atom	Atom	Angle/°
F1	C1	C2	F3	-53.96(11)
F1	C1	C2	F4	58.03(11)
F1	C1	C2	C3	179.47(9)
F2	C1	C2	F3	-167.48(8)
F2	C1	C2	F4	-55.50(11)
F2	C1	C2	C3	65.94(11)
F3	C2	C3	C4	148.93(10)
F3	C2	C3	C12	-33.36(14)
F4	C2	C3	C4	32.07(14)
F4	C2	C3	C12	-150.23(10)
N1	N2	N3	C13	179.36(10)
N1	N2	N3	C16	1.12(16)
N1	C1	C2	F3	74.95(11)
N1	C1	C2	F4	-173.07(9)
N1	C1	C2	C3	-51.63(13)
N2	N1	C1	F1	32.44(13)
N2	N1	C1	F2	149.52(9)
N2	N1	C1	C2	-92.79(11)
N2	N3	C13	C14	66.62(15)
N2	N3	C13	C15	-58.89(14)
N2	N3	C16	C17	-120.88(13)
N2	N3	C16	C18	114.54(13)
C1	N1	N2	N3	179.46(9)
C1	C2	C3	C4	-87.55(12)
C1	C2	C3	C12	90.15(13)
C2	C3	C4	C5	177.85(12)
C2	C3	C12	C7	-177.72(10)
C2	C3	C12	C11	3.11(17)
C3	C4	C5	C6	0.0(2)
C4	C3	C12	C7	-0.11(16)
C4	C3	C12	C11	-179.29(11)
C4	C5	C6	C7	0.0(2)
C5	C6	C7	C8	-179.97(13)
C5	C6	C7	C12	-0.1(2)
C6	C7	C8	C9	-178.89(12)

Atom	Atom	Atom	Atom	Angle/°
C6	C7	C12	C3	0.13(17)
C6	C7	C12	C11	179.37(11)
C7	C8	C9	C10	-0.52(19)
C8	C7	C12	C3	-179.99(10)
C8	C7	C12	C11	-0.75(16)
C8	C9	C10	C11	-0.69(19)
C9	C10	C11	C12	1.16(19)
C10	C11	C12	C3	178.76(11)
C10	C11	C12	C7	-0.42(17)
C12	C3	C4	C5	0.05(19)
C12	C7	C8	C9	1.24(19)
C13	N3	C16	C17	60.98(15)
C13	N3	C16	C18	-63.61(15)
C16	N3	C13	C14	-115.09(13)
C16	N3	C13	C15	119.41(13)

Table 6: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H4	8341.38	4645.67	5516.71	52
H5	7145.42	4566.65	3929.92	65
H6	5494.07	5689.22	3454.62	63
H8	4161.64	7105.55	3810.47	63
H9	3669.27	8342.56	4840.11	68
H10	4856.92	8476.98	6432.6	61
H11	6483.92	7364.27	6993.64	50
H13	3385.9	7193.8	9740.73	53
H14A	6199.68	7851.48	9267.17	90
H14B	5035.48	8416.83	9897.69	90
H14C	4718.11	8190.6	8729.22	90
H15A	4589.44	6084.06	10789.04	83
H15B	4825.99	7118.16	11194.11	83
H15C	6093.72	6604.63	10609.44	83
H16	3543.45	5579.81	7760.01	53
H17A	2110.71	7264.28	8257.3	84
H17B	1593.96	6572.36	7375.06	84
H17C	3092.62	7122.91	7289.64	84
H18A	2811.53	5011.3	9346.74	84
H18B	1425.42	5244.52	8638.99	84
H18C	1906.75	5939.47	9527.52	84





Compound	**6e**
Formula	$C_{15}H_{21}F_2N_3O$
$D_{calc.}$/ g cm^{-3}	1.215
μ/mm^{-1}	0.783
Formula Weight	297.35
Colour	colourless
Shape	prism-shaped
Size/mm^3	0.31×0.07×0.04
T/K	140.00(10)
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	9.5957(2)
b/Å	9.9111(3)
c/Å	10.2433(2)
α/°	104.216(2)
β/°	114.117(2)
γ/°	101.164(2)
V/Å^3	812.95(4)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu$K\alpha$
Θ_{min}/°	4.880
Θ_{max}/°	75.125
Measured Refl's.	12419
Indep't Refl's	3276
Refl's I≥2σ(I)	3033
R_{int}	0.0085
Parameters	196
Restraints	0
Largest Peak/e Å^{-3}	0.232
Deepest Hole/e Å^{-3}	-0.183
GooF	1.060
wR_2 (all data)	0.0948
wR_2	0.0931
R_1 (all data)	0.0378
R_1	0.0356

Table 7: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6e**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
F1	4983.2(8)	2835.2(8)	8173.3(9)	40.6(2)
F2	3189.6(10)	729.2(8)	6420.5(10)	47.5(2)
O1	2035.5(12)	2115.2(9)	4565.5(10)	42.3(2)
N1	3478.0(11)	4398.2(10)	6618.7(10)	25.6(2)
N2	2894.0(10)	5010.5(9)	5615.0(10)	24.8(2)
N3	3392.5(10)	6429.4(9)	6152.8(10)	24.2(2)
C1	2869.7(13)	2875.1(12)	5909.6(13)	28.1(2)
C2	3348.0(14)	2154.9(12)	7130.2(14)	32.1(3)
C3	2368.0(13)	2201.9(12)	7958.7(13)	27.7(2)
C4	1061.6(14)	984.4(12)	7550.2(14)	32.5(3)
C5	151.2(14)	1078.5(13)	8302.7(14)	35.5(3)
C6	510.2(15)	2372.2(13)	9470.6(14)	34.6(3)
C7	1810.3(14)	3589.8(13)	9852.9(13)	33.2(3)
C8	2724.5(13)	3512.4(12)	9107.2(13)	29.8(2)
C9	-462.3(19)	2467.2(17)	10308.1(19)	51.9(4)
C10	4548.7(14)	7346.6(12)	7783.8(13)	32.3(3)
C11	3625(2)	7932.5(17)	8554.8(16)	52.9(4)
C12	5909.2(17)	8549.5(15)	7928.8(17)	48.8(4)
C13	2624.3(13)	7118.2(12)	5039.1(13)	29.1(2)
C14	3259(2)	6979(2)	3899.8(18)	56.7(4)
C15	797.0(16)	6474.9(18)	4274.8(19)	51.7(4)

Table 8: Anisotropic Displacement Parameters (×10^4) for **6e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	26.3(3)	49.3(4)	50.5(4)	26.3(4)	17.4(3)	13.6(3)
F2	67.1(5)	27.3(4)	68.9(5)	20.7(4)	44.9(5)	26.1(4)
O1	50.5(5)	26.0(4)	34.2(5)	1.3(4)	14.7(4)	4.6(4)
N1	24.4(4)	21.5(4)	27.7(5)	7.1(4)	10.7(4)	7.4(3)
N2	21.7(4)	22.7(4)	26.7(4)	5.7(3)	10.9(4)	6.7(3)
N3	22.7(4)	21.2(4)	24.6(4)	6.2(3)	9.1(4)	6.5(3)
C1	25.4(5)	22.8(5)	32.7(6)	5.3(4)	14.1(5)	6.8(4)
C2	31.3(6)	22.8(5)	41.8(6)	10.3(5)	16.8(5)	11.2(4)
C3	24.7(5)	24.2(5)	30.9(6)	10.9(4)	9.7(4)	8.3(4)
C4	32.7(6)	21.0(5)	35.6(6)	6.8(4)	12.7(5)	5.1(4)
C5	30.2(6)	27.2(6)	41.4(7)	11.4(5)	14.5(5)	1.6(4)
C6	32.7(6)	34.8(6)	35.9(6)	13.4(5)	16.5(5)	9.1(5)
C7	32.9(6)	27.8(6)	28.3(6)	4.3(4)	10.2(5)	5.8(5)
C8	23.1(5)	24.6(5)	30.0(6)	6.8(4)	6.3(4)	2.3(4)
C9	55.9(9)	50.1(8)	59.4(9)	18.0(7)	39.6(8)	12.9(7)
C10	34.7(6)	22.7(5)	24.5(5)	4.8(4)	4.9(5)	5.0(4)
C11	71.6(10)	48.9(8)	34.7(7)	6.2(6)	28.3(7)	18.2(7)
C12	35.0(7)	37.6(7)	44.7(8)	9.2(6)	3.5(6)	-4.0(5)
C13	28.4(5)	29.3(5)	29.4(6)	13.2(4)	11.5(5)	11.1(4)
C14	64.1(10)	86.3(12)	46.7(8)	39.3(8)	35.6(8)	40.1(9)
C15	29.1(6)	60.3(9)	66.1(10)	39.9(8)	12.5(6)	17.4(6)

Table 9: Bond Lengths in Å for **6e**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C2	1.3873(14)	N1	N2	1.3064(13)
F2	C2	1.3675(13)	N1	C1	1.3860(13)
O1	C1	1.2084(14)	N2	N3	1.2859(12)

Atom	Atom	Length/Å
N3	C10	1.4823(13)
N3	C13	1.4836(14)
C1	C2	1.5426(16)
C2	C3	1.5022(16)
C3	C4	1.3929(15)
C3	C8	1.3916(16)
C4	C5	1.3830(17)
C5	C6	1.3902(17)
C6	C7	1.3970(17)
C6	C9	1.5047(18)
C7	C8	1.3798(17)
C10	C11	1.5144(19)
C10	C12	1.5164(18)
C13	C14	1.5119(17)
C13	C15	1.5146(17)

Table 10: Bond Angles in ° for **6e**.

Atom	Atom	Atom	Angle/°
N2	N1	C1	110.08(9)
N3	N2	N1	115.20(8)
N2	N3	C10	124.04(9)
N2	N3	C13	115.03(8)
C10	N3	C13	120.77(8)
O1	C1	N1	129.90(11)
O1	C1	C2	120.21(10)
N1	C1	C2	109.84(9)
F1	C2	C1	109.37(9)
F1	C2	C3	110.07(9)
F2	C2	F1	105.13(9)
F2	C2	C1	108.08(9)
F2	C2	C3	110.50(9)
C3	C2	C1	113.34(9)
C4	C3	C2	121.37(10)
C8	C3	C2	119.20(10)
C8	C3	C4	119.35(11)
C5	C4	C3	119.96(11)
C4	C5	C6	121.34(11)
C5	C6	C7	118.03(11)
C5	C6	C9	121.36(11)
C7	C6	C9	120.61(12)
C8	C7	C6	121.21(11)
C7	C8	C3	120.09(10)
N3	C10	C11	108.91(10)
N3	C10	C12	111.22(10)
C11	C10	C12	113.34(11)
N3	C13	C14	110.28(10)
N3	C13	C15	110.60(9)
C14	C13	C15	112.82(12)

Table 11: Torsion Angles in ° for **6e**.

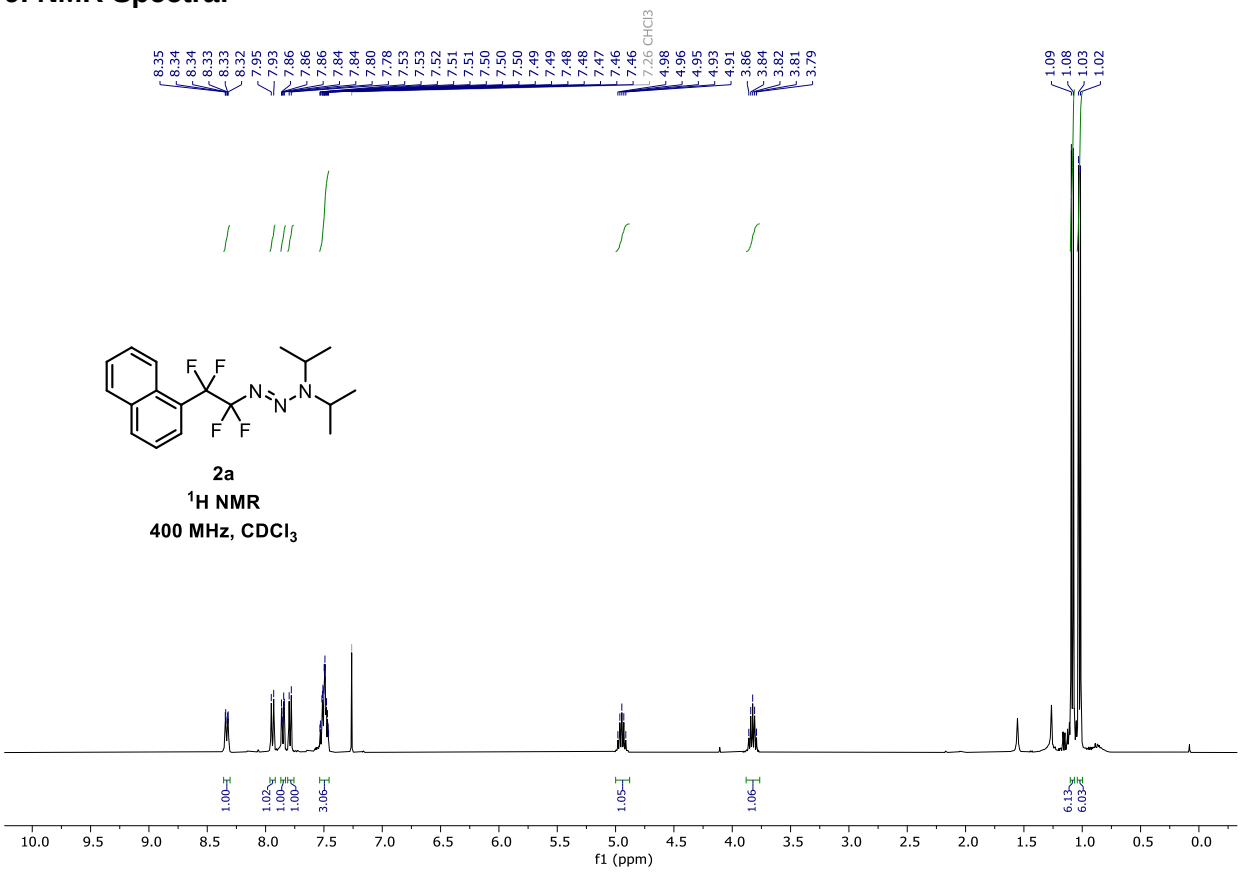
Atom	Atom	Atom	Atom	Angle/°
F1	C2	C3	C4	-137.95(11)
F1	C2	C3	C8	45.26(13)
F2	C2	C3	C4	-22.27(15)
F2	C2	C3	C8	160.94(10)
O1	C1	C2	F1	134.86(11)
O1	C1	C2	F2	20.91(14)
O1	C1	C2	C3	-101.92(12)
N1	N2	N3	C10	0.18(14)
N1	N2	N3	C13	-175.15(8)
N1	C1	C2	F1	-47.42(12)
N1	C1	C2	F2	-161.37(9)
N1	C1	C2	C3	75.80(11)
N2	N1	C1	O1	6.16(16)
N2	N1	C1	C2	-171.28(8)
N2	N3	C10	C11	-103.47(12)
N2	N3	C10	C12	130.91(11)
N2	N3	C13	C14	-73.44(13)
N2	N3	C13	C15	52.05(13)
C1	N1	N2	N3	-179.50(8)
C1	C2	C3	C4	99.21(12)
C1	C2	C3	C8	-77.58(13)
C2	C3	C4	C5	-177.90(11)
C2	C3	C8	C7	178.22(10)
C3	C4	C5	C6	-0.01(19)
C4	C3	C8	C7	1.37(17)
C4	C5	C6	C7	0.87(19)
C4	C5	C6	C9	-178.94(12)
C5	C6	C7	C8	-0.61(18)

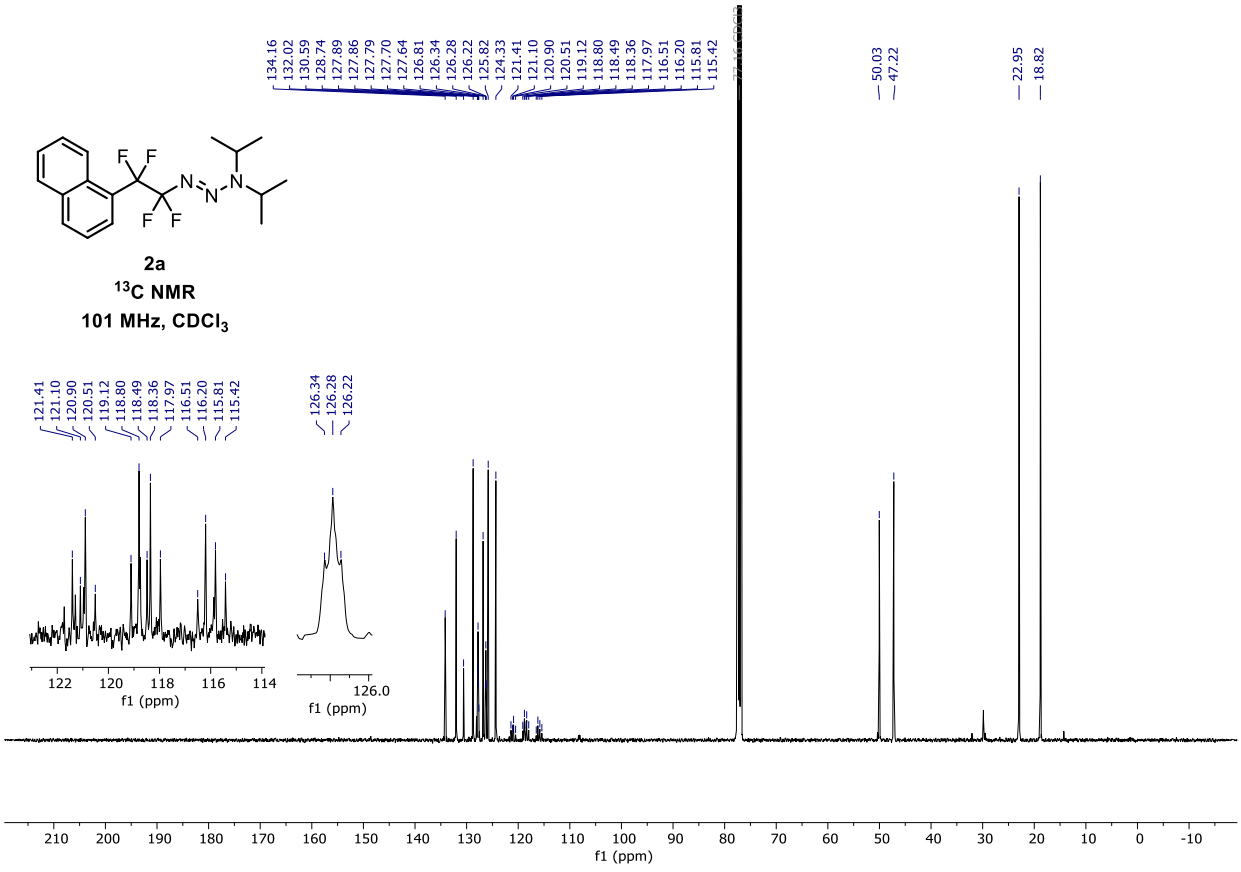
Atom	Atom	Atom	Atom	Angle/°
C6	C7	C8	C3	-0.50(18)
C8	C3	C4	C5	-1.12(17)
C9	C6	C7	C8	179.19(12)
C10	N3	C13	C14	111.07(13)
C10	N3	C13	C15	-123.44(12)
C13	N3	C10	C11	71.60(13)
C13	N3	C10	C12	-54.02(14)

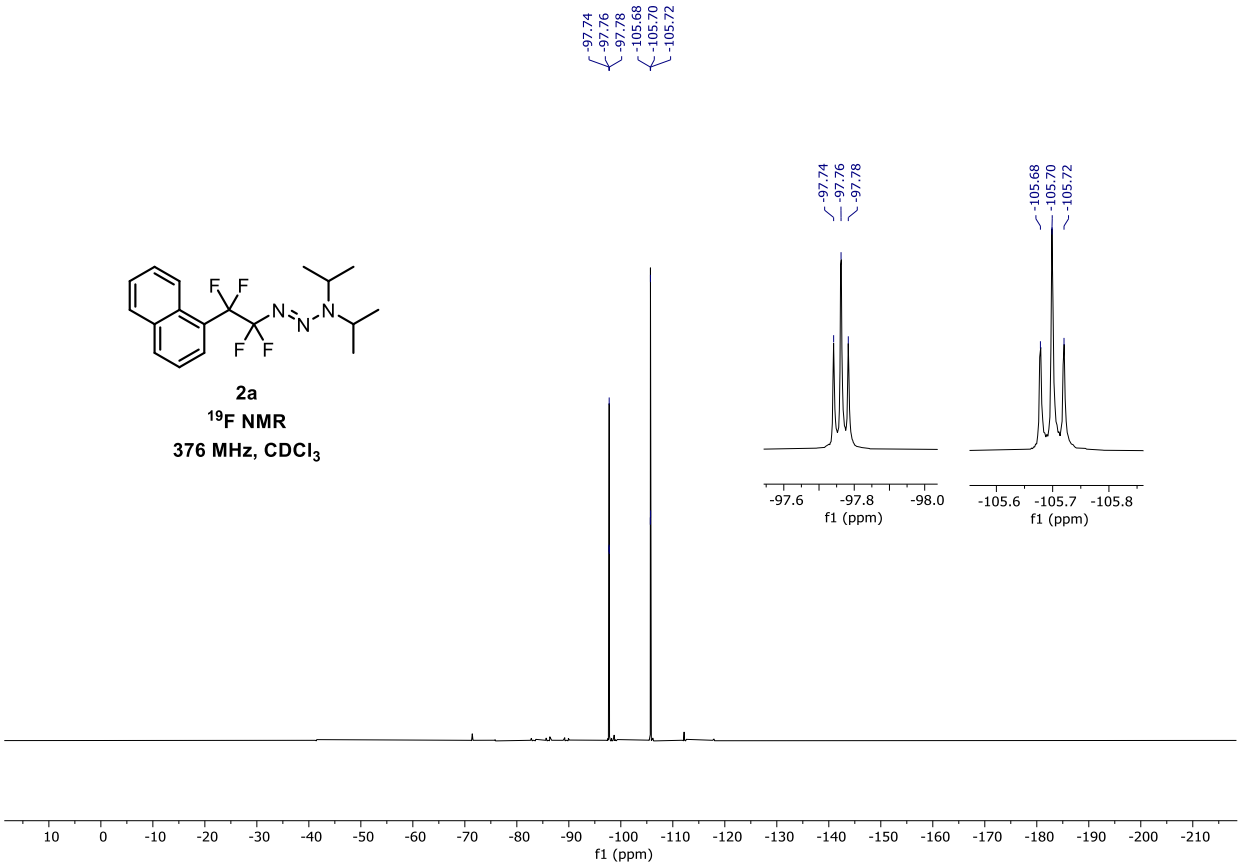
Table 12: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6e**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

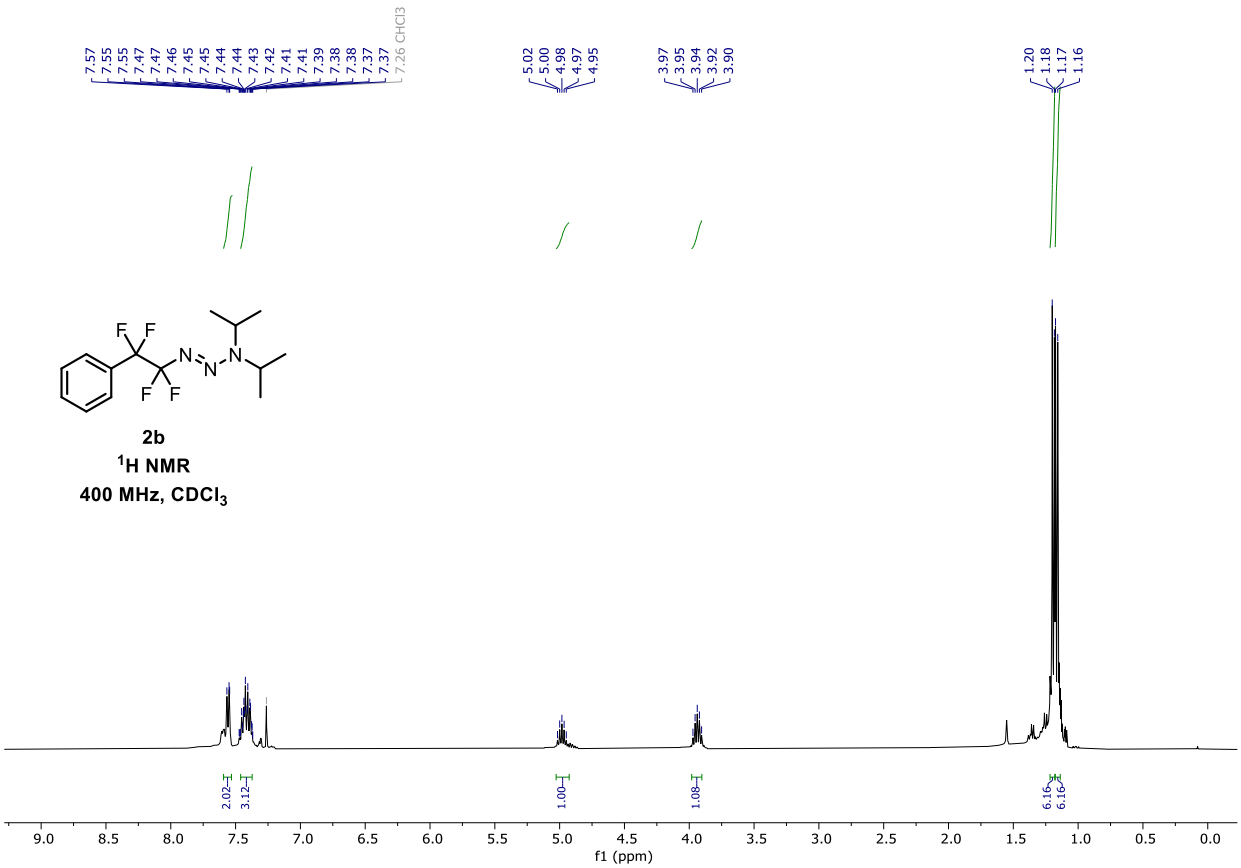
Atom	x	y	z	U_{eq}
H4	796.23	89.88	6755.12	39
H5	-737.53	242.15	8015.72	43
H7	2069.66	4487.67	10640.81	40
H8	3598.52	4354.94	9378.13	36
H9A	131.03	2376.61	11302.37	78
H9B	-1506.32	1667.15	9696.38	78
H9C	-644.92	3419.73	10470.84	78
H10	5040.16	6690.8	8291.86	39
H11A	3141.34	8591.59	8087.59	79
H11B	4367.06	8478.8	9651.42	79
H11C	2767.8	7106.15	8424.35	79
H12A	6414.35	8108.55	7354.78	73
H12B	6720.12	9062.2	9012.9	73
H12C	5472.42	9255.03	7512.55	73
H13	2942.81	8193.71	5626.09	35
H14A	4435.87	7461.93	4448.86	85
H14B	2755.92	7451.96	3181.78	85
H14C	2996.03	5932.87	3330.17	85
H15A	447.48	5421.12	3677.48	77
H15B	310.71	6984.08	3591.23	77
H15C	450.46	6603.22	5061.07	77

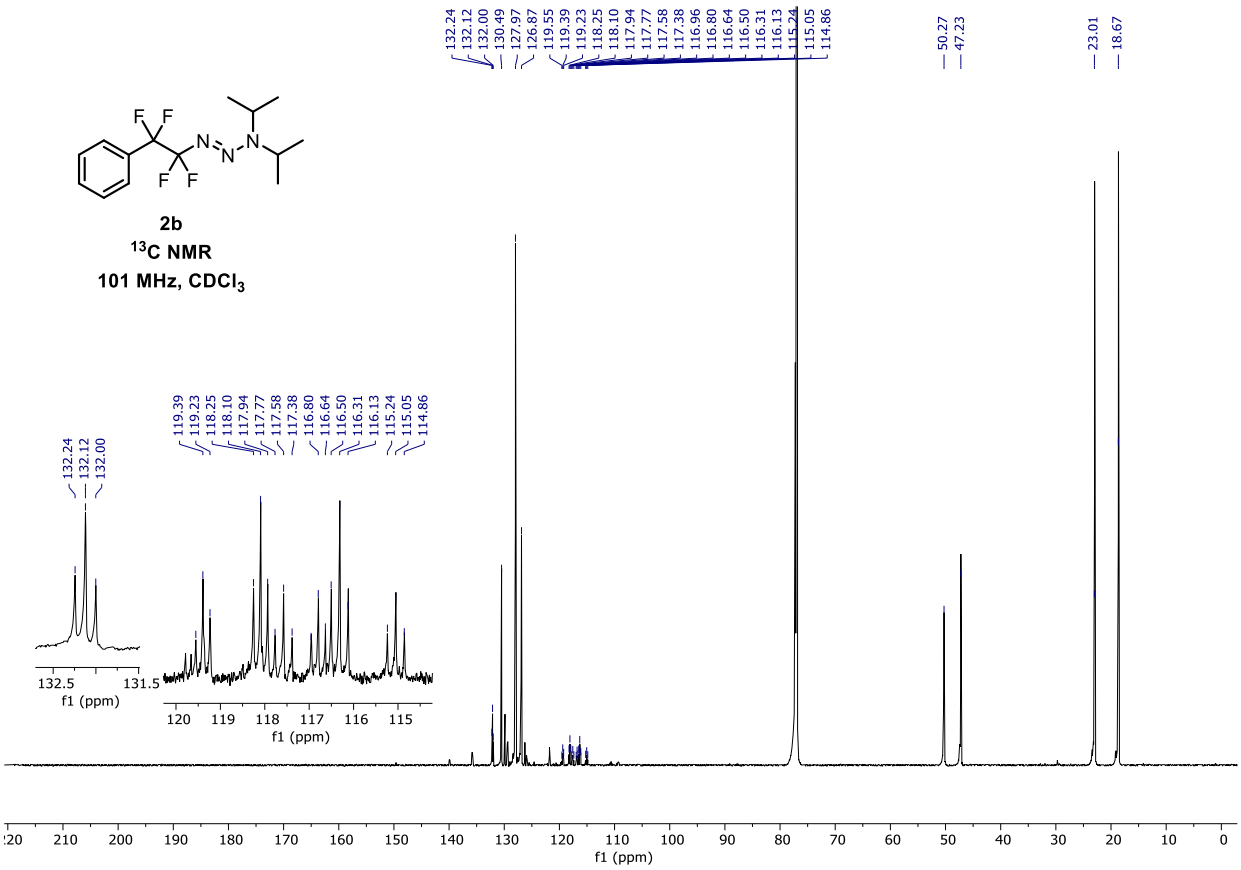
9. NMR Spectra:

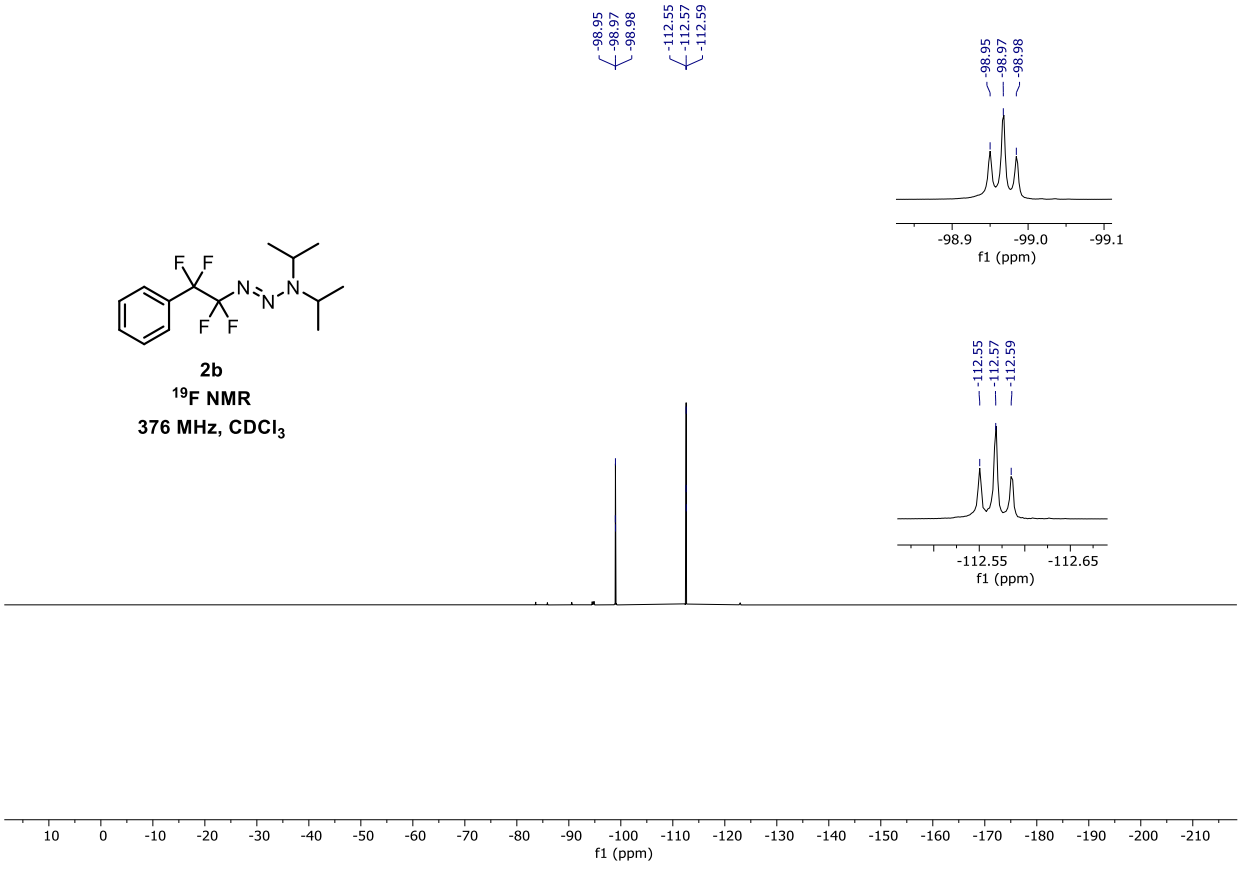


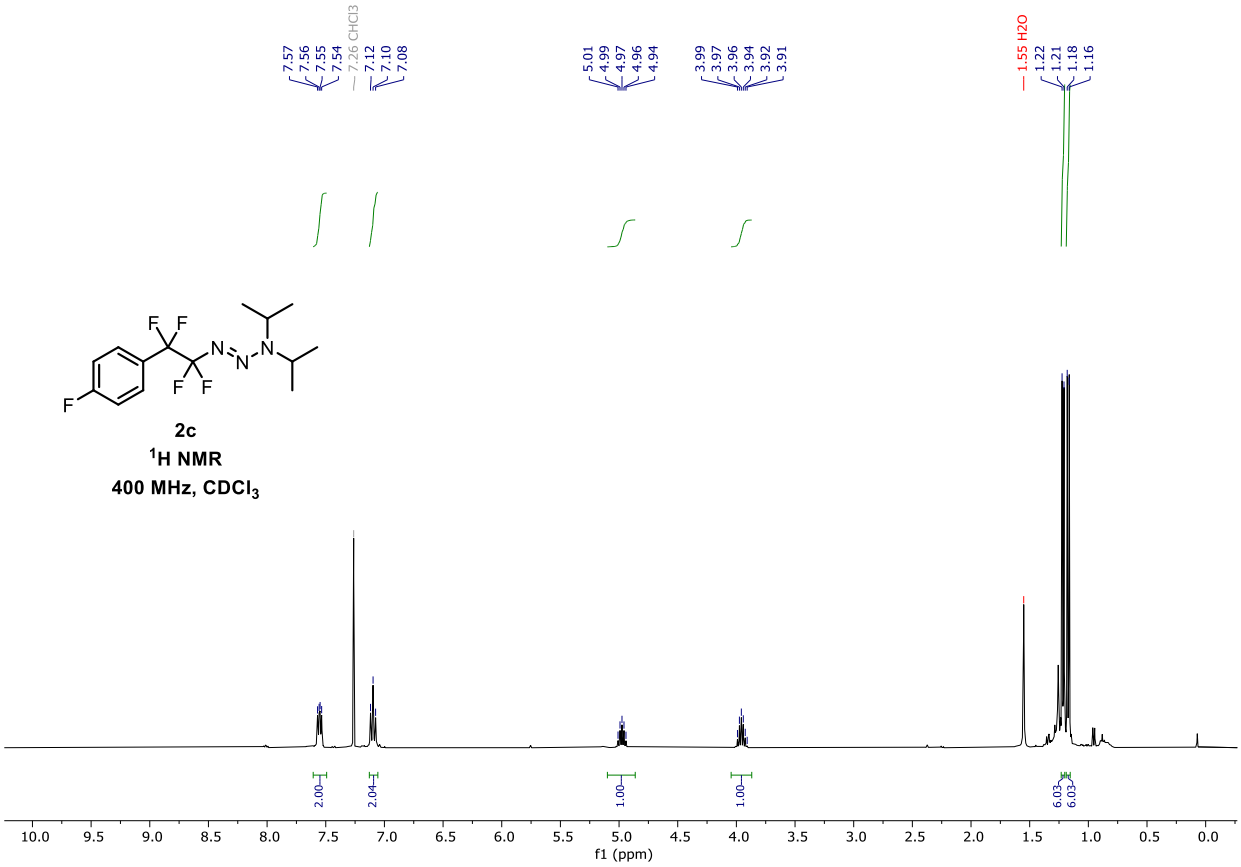


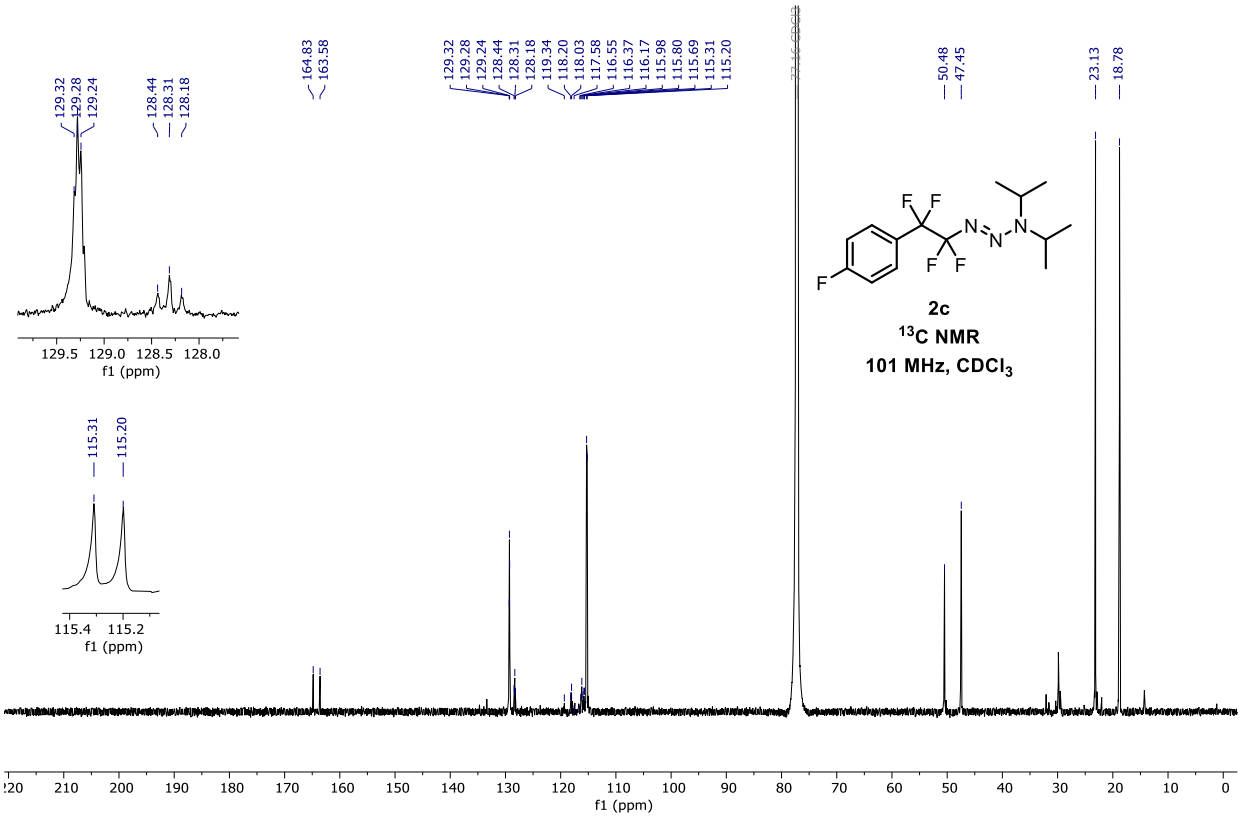

-97.74
-97.76
-97.78
-105.68
-105.70
-105.72
F F
N
N
N
F F
2a
19F NMR
376 MHz, CDCl3
-97.6
-97.8
-98.0
f1 (ppm)
-105.6
-105.7
-105.8
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

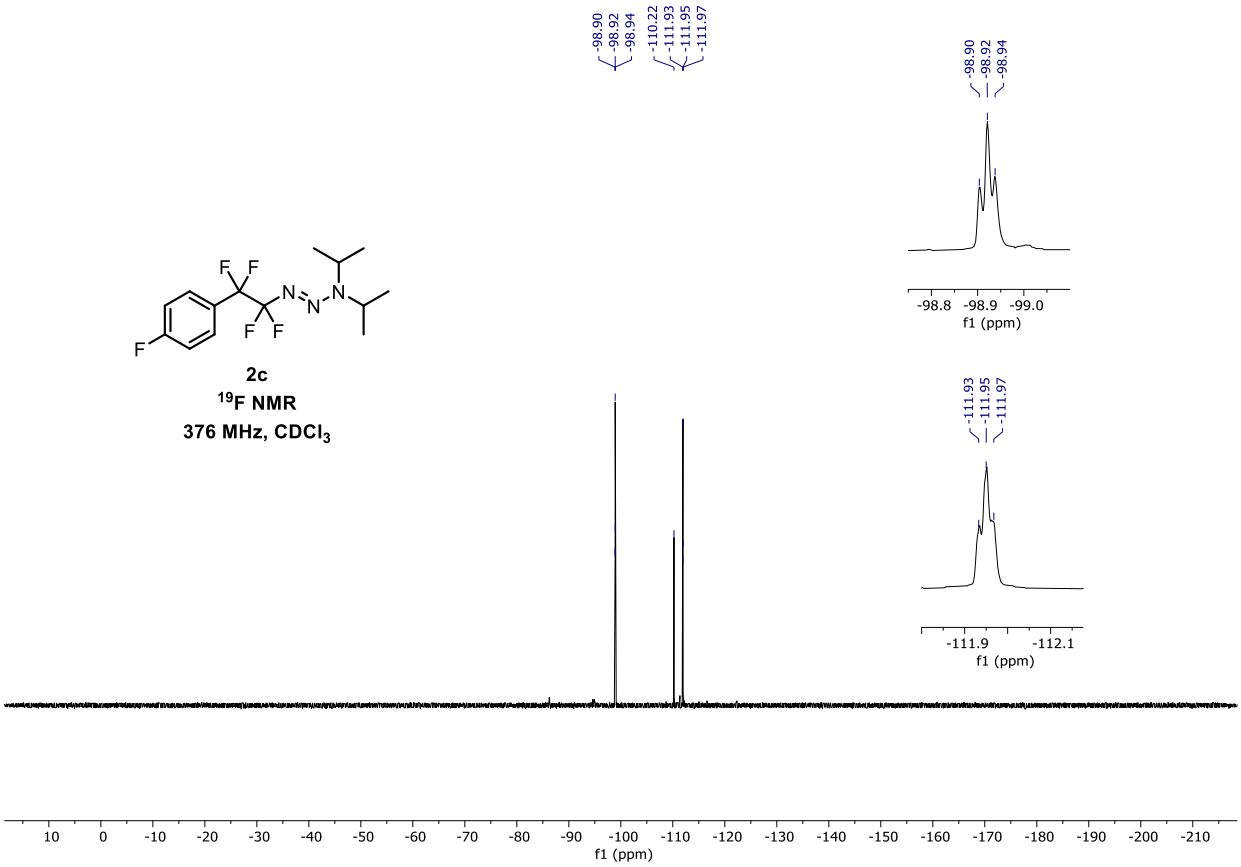

7.57
7.55
7.55
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.41
7.41
7.39
7.38
7.38
7.37
7.37
7.26 CHCl3
5.02
5.00
4.98
4.97
4.95
3.97
3.95
3.94
3.92
3.90
1.20
1.18
1.17
1.16
F F
N
N
N
F F
2b
1H NMR
400 MHz, CDCl3
2.02
3.12
1.00
1.08
6.16
6.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2b
13C NMR
101 MHz, CDCl3
f1 (ppm)

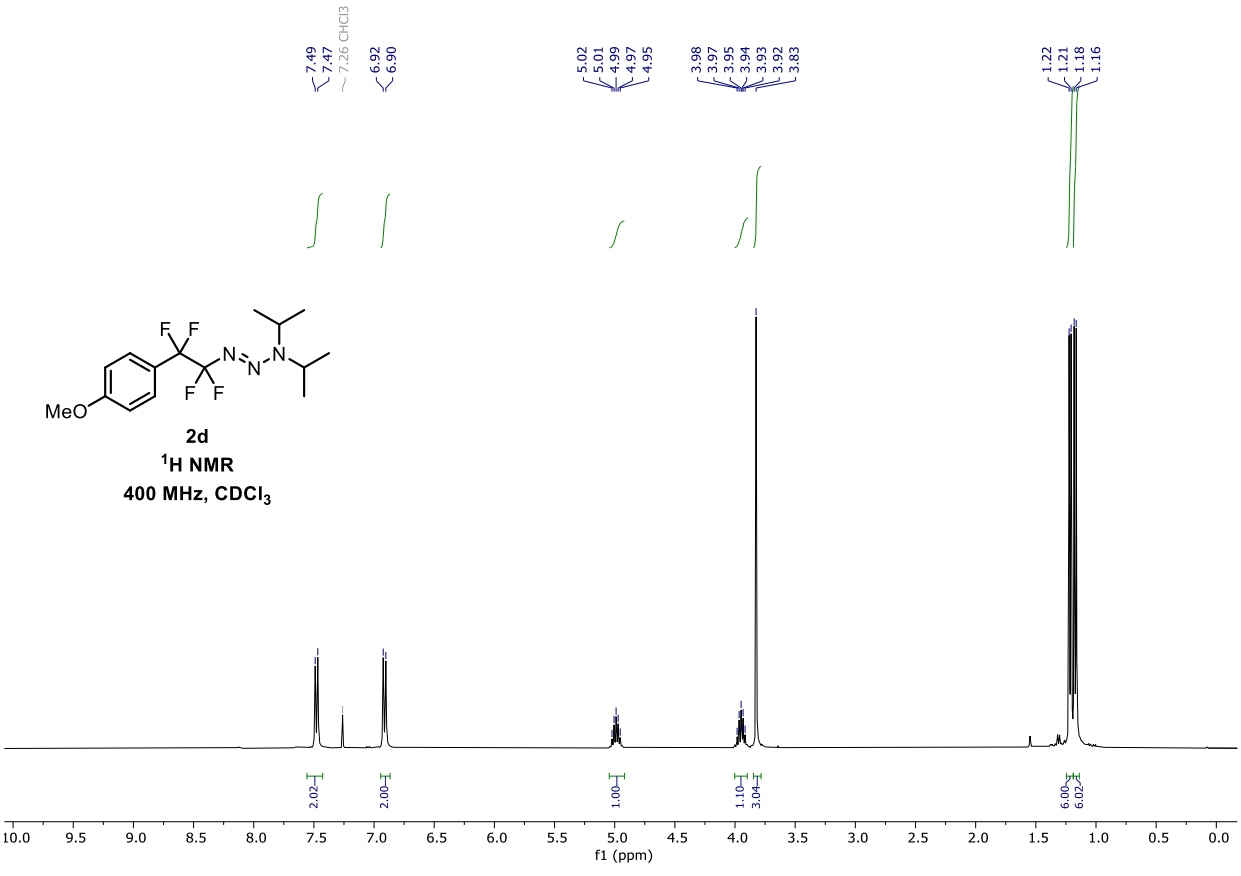

2b
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.57
7.56
7.55
7.54
7.26 CHCl3
7.12
7.10
7.08
5.01
4.99
4.97
4.96
4.94
3.99
3.97
3.96
3.94
3.92
3.91
1.55 H2O
1.22
1.21
1.18
1.16
F F
N
N
N
F F
F
2c
1H NMR
400 MHz, CDCl3
2.00
2.04
1.00
1.00
6.03
6.03
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)

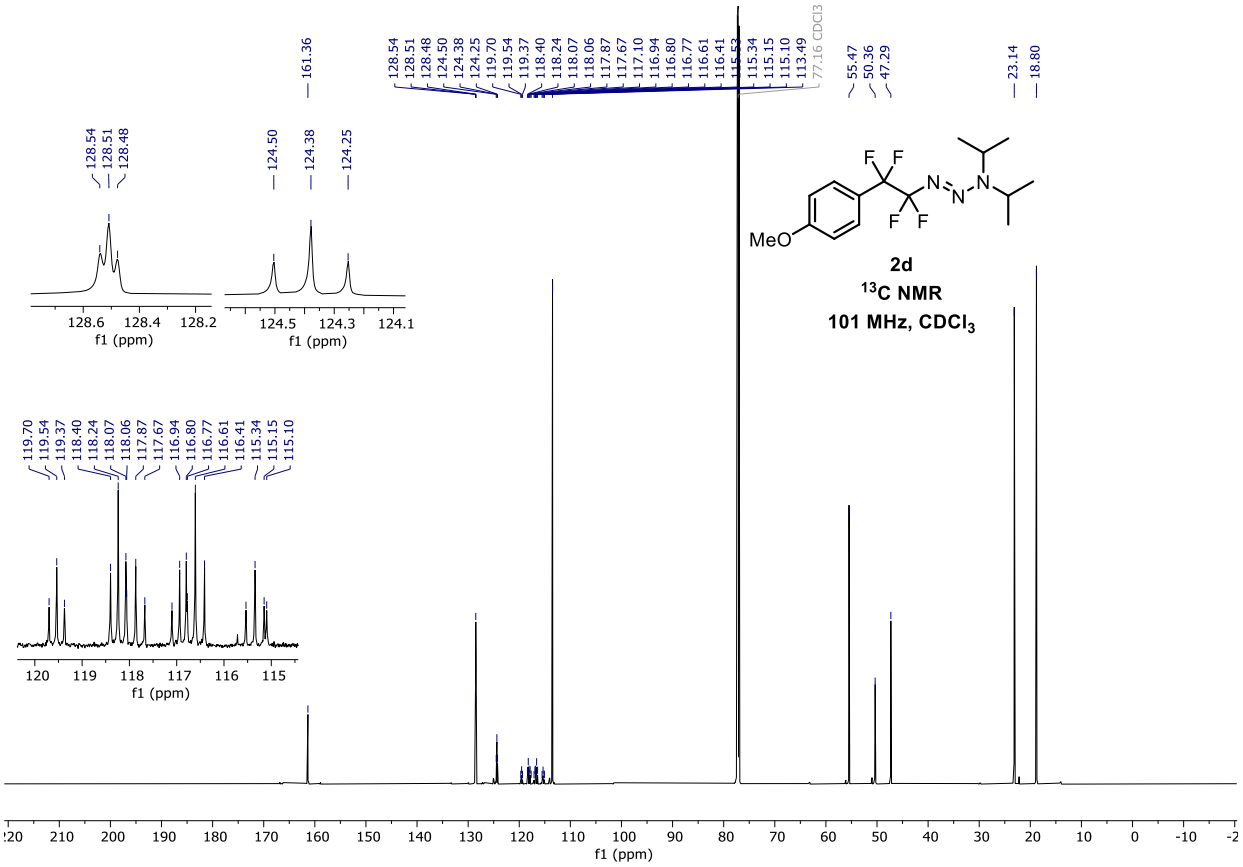

129.32
129.28
129.24
128.44
128.31
128.18
129.5 129.0 128.5 128.0
f1 (ppm)
115.31
115.20
115.4 115.2
f1 (ppm)
164.83
163.58
129.32
129.28
129.24
128.44
128.31
128.18
119.34
118.20
118.03
117.58
116.55
116.37
116.17
115.98
115.80
115.69
115.31
115.20
77.46 CDCl3
50.48
47.45
23.13
18.78
F F
N
N
N
F F
F
2c
13C NMR
101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

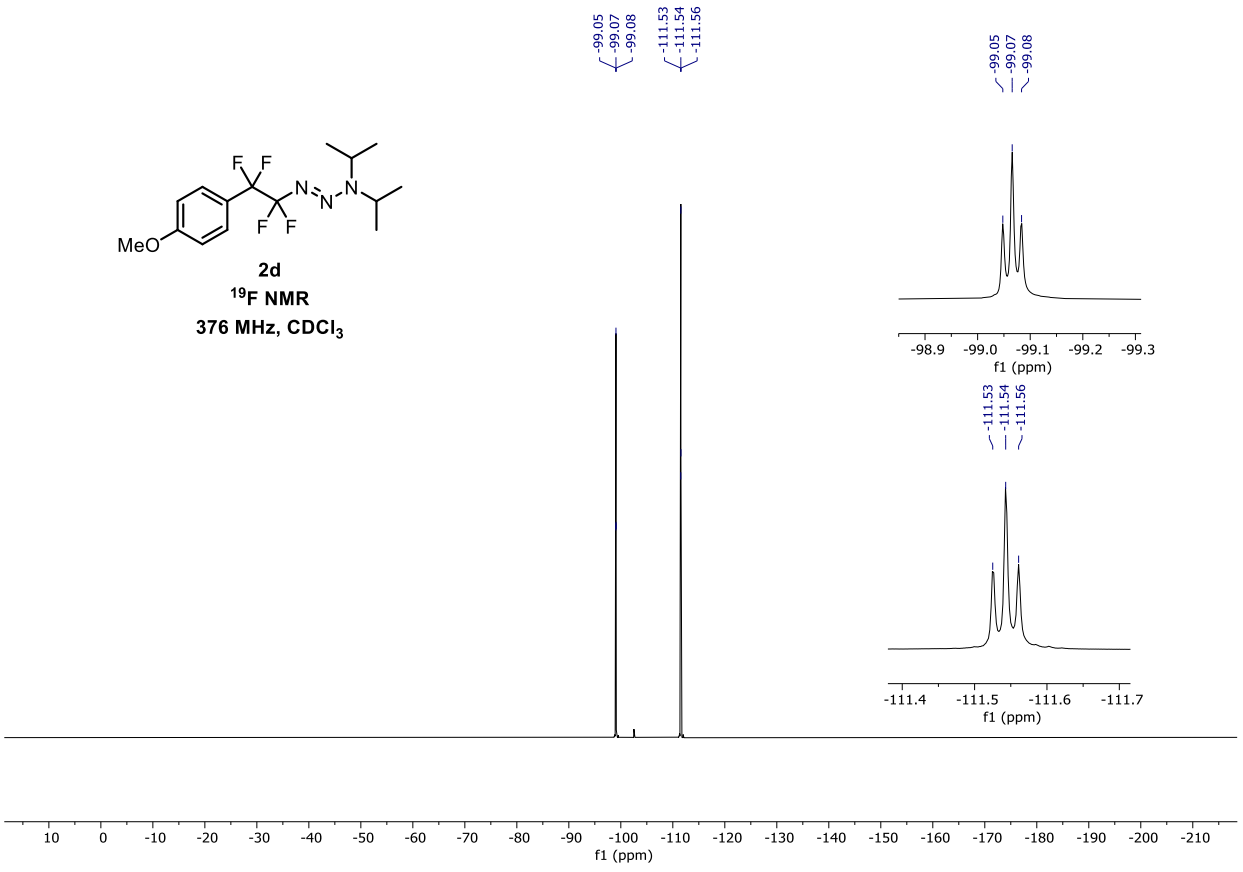


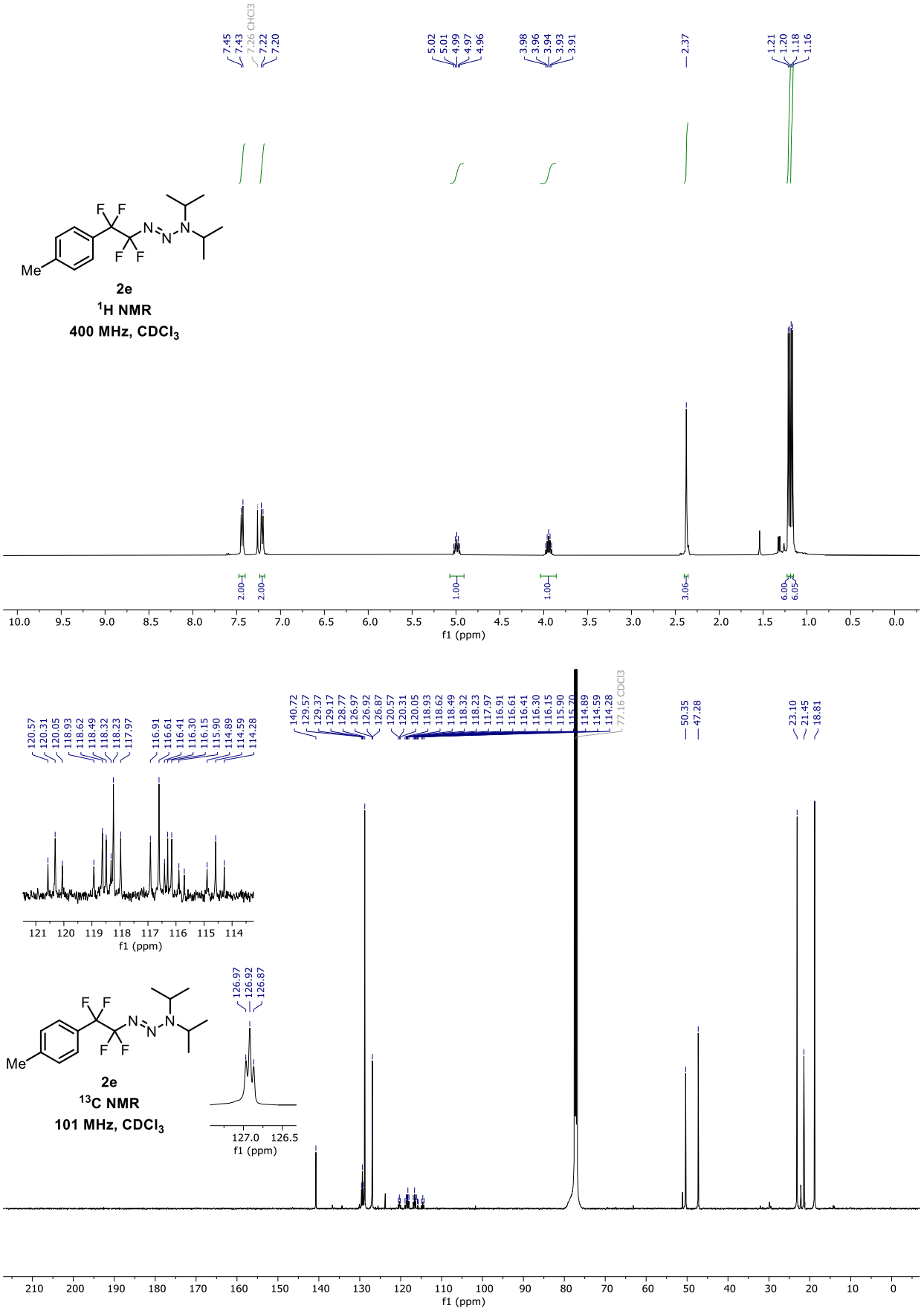
2c
^{19}F NMR
376 MHz, $CDCl_3$

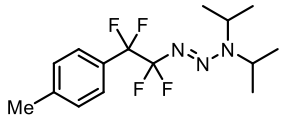


2d
^{1}H NMR
400 MHz, $CDCl_3$


2d
13C NMR
101 MHz, CDCl3
MeO
f1 (ppm)


2d
19F NMR
376 MHz, CDCl3
MeO
f1 (ppm)

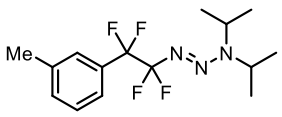

7.45
7.43
7.26 CHCl3
7.22
7.20
5.02
5.01
4.99
4.97
4.96
3.98
3.96
3.94
3.93
3.91
2.37
1.21
1.20
1.18
1.16
F F
N
N
N
F F
Me
2e
1H NMR
400 MHz, CDCl3
2.00
2.00
1.00
1.00
3.06
6.00
6.05
f1 (ppm)
140.72
129.57
129.37
129.17
128.77
126.97
126.92
126.87
120.57
120.31
120.05
118.93
118.62
118.49
118.32
118.23
117.97
116.91
116.61
116.41
116.30
116.15
115.90
114.89
114.59
114.28
77.16 CDCl3
50.35
47.28
23.10
21.45
18.81
f1 (ppm)
f1 (ppm)
126.97
126.92
126.87
f1 (ppm)
2e
13C NMR
101 MHz, CDCl3



2e

^{19}F NMR

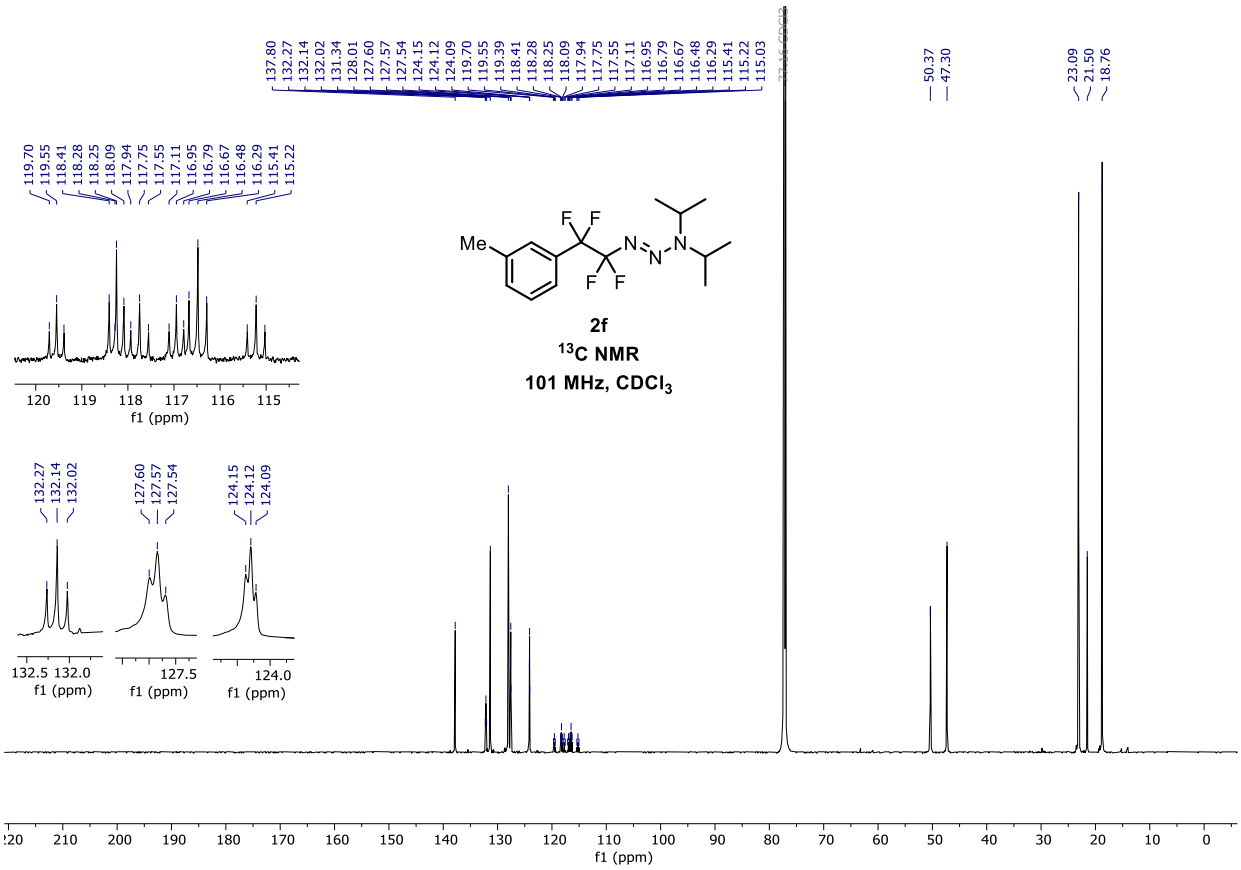
376 MHz, $CDCl_3$

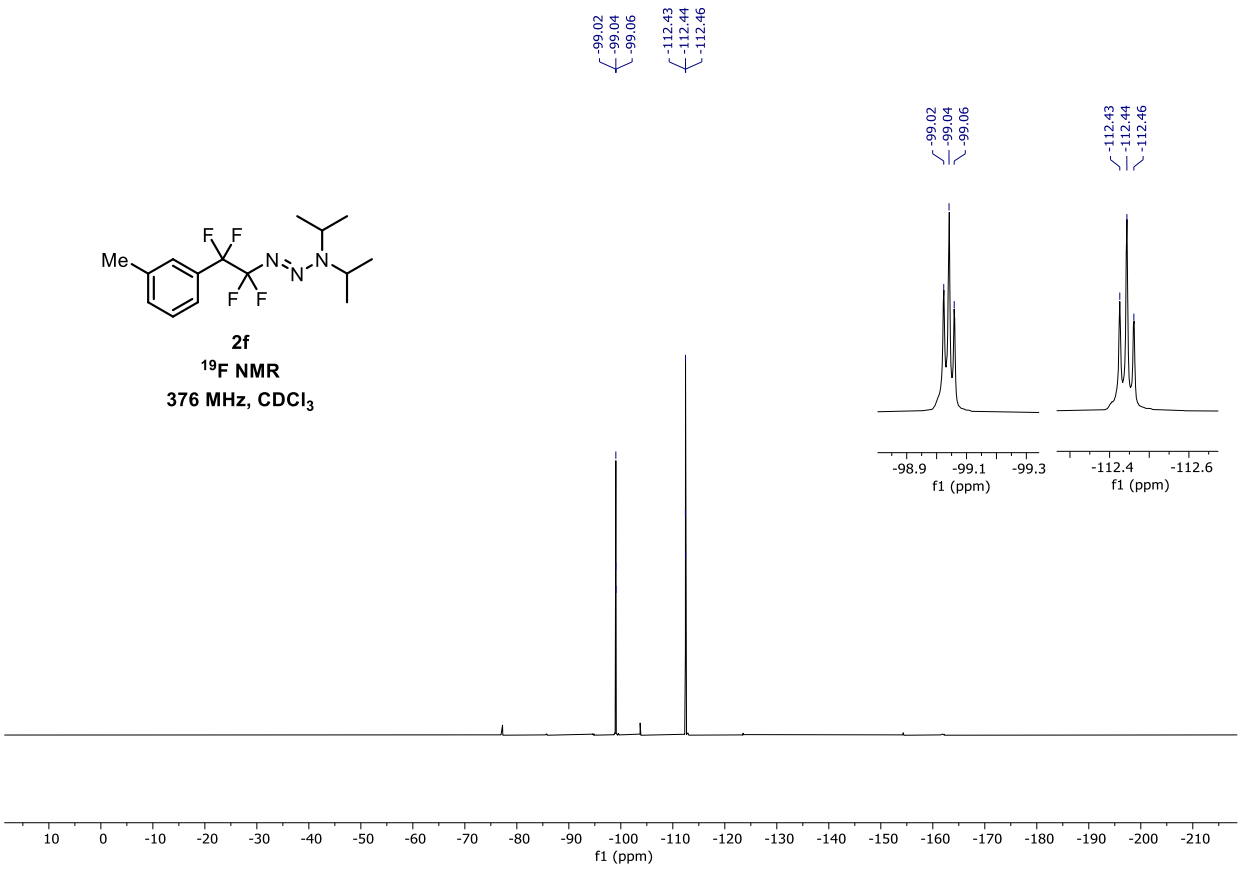


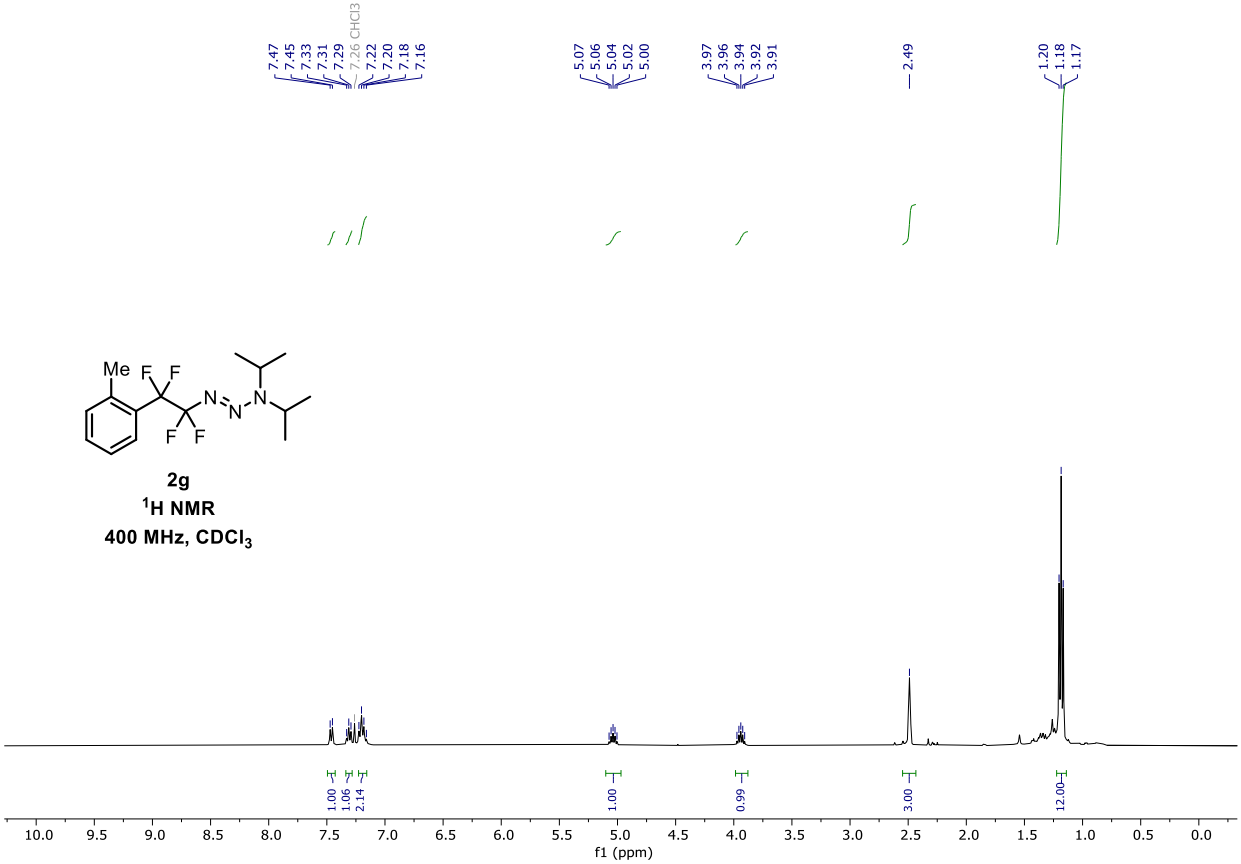
2f

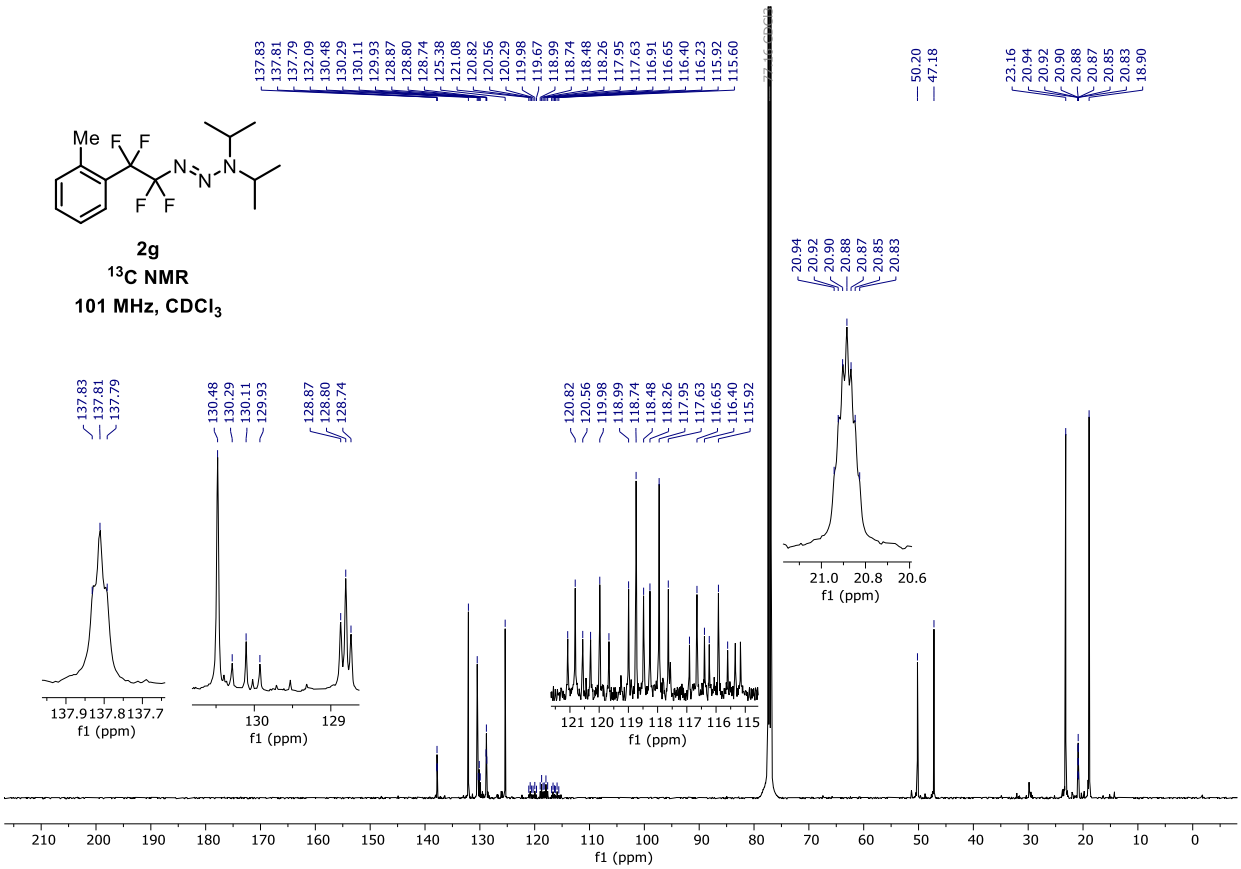
^{1}H NMR

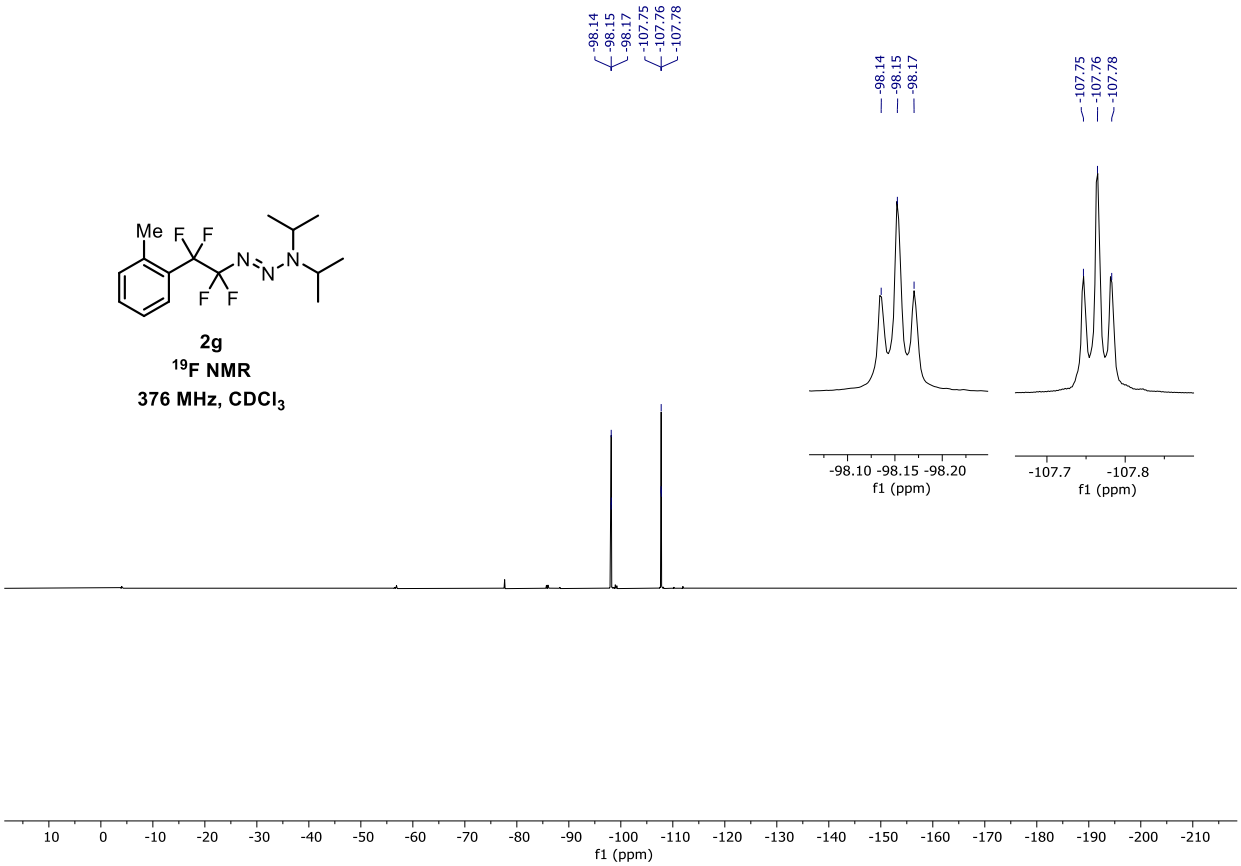
400 MHz, $CDCl_3$


137.80
132.27
132.14
132.02
131.34
128.01
127.60
127.57
127.54
124.15
124.12
124.09
119.70
119.55
119.39
118.41
118.28
118.25
118.09
117.94
117.75
117.55
117.11
116.95
116.79
116.67
116.48
116.29
115.41
115.22
115.03
77.16 CDCl3
50.37
47.30
23.09
21.50
18.76
119.70
119.55
118.41
118.28
118.25
118.09
117.94
117.75
117.55
117.11
116.95
116.79
116.67
116.48
116.29
115.41
115.22
120 119 118 117 116 115
f1 (ppm)
Me
F F
F F
N
N
2f
13C NMR
101 MHz, CDCl3
132.27
132.14
132.02
127.60
127.57
127.54
124.15
124.12
124.09
132.5 132.0
f1 (ppm)
127.5
f1 (ppm)
124.0
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

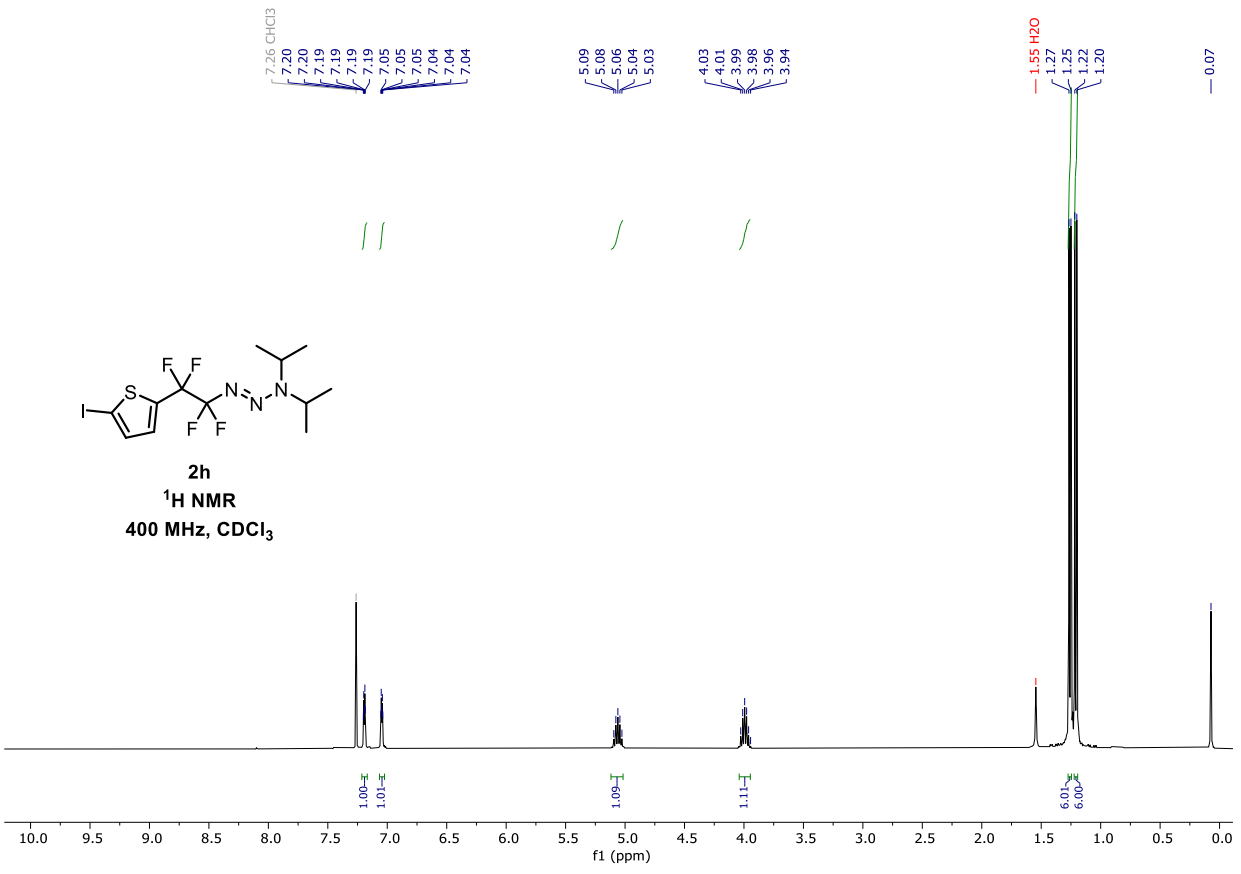

-99.02
-99.04
-99.06
-112.43
-112.44
-112.46
Me
F F
F F
N
N
2f
19F NMR
376 MHz, CDCl3
-98.9 -99.1 -99.3
f1 (ppm)
-112.4 -112.6
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.47
7.45
7.33
7.31
7.29
7.26 CHCl3
7.22
7.20
7.18
7.16
5.07
5.06
5.04
5.02
5.00
3.97
3.96
3.94
3.92
3.91
2.49
1.20
1.18
1.17
Me
F
F
N
N
N
F
F
2g
1H NMR
400 MHz, CDCl3
1.00
1.06
2.14
1.00
0.99
3.00
12.00
f1 (ppm)

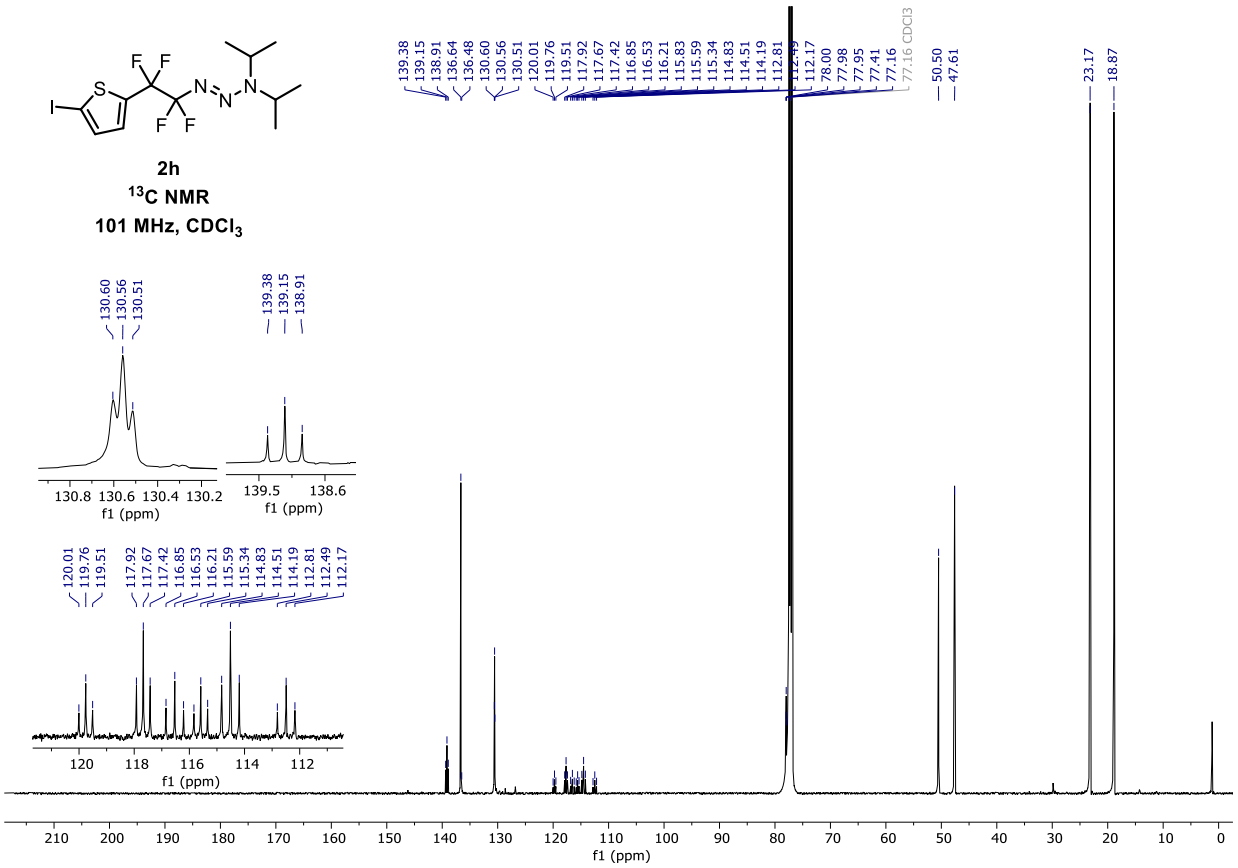

137.83
137.81
137.79
132.09
130.48
130.29
130.11
129.93
128.87
128.80
128.74
125.38
121.08
120.82
120.56
120.29
119.98
119.67
118.99
118.74
118.48
118.26
117.95
117.63
116.91
116.65
116.40
116.23
115.92
115.60
77.16
50.20
47.18
23.16
20.94
20.92
20.90
20.88
20.87
20.85
20.83
18.90
Me
F
F
N
N
N
F
F
2g
13C NMR
101 MHz, CDCl3
f1 (ppm)

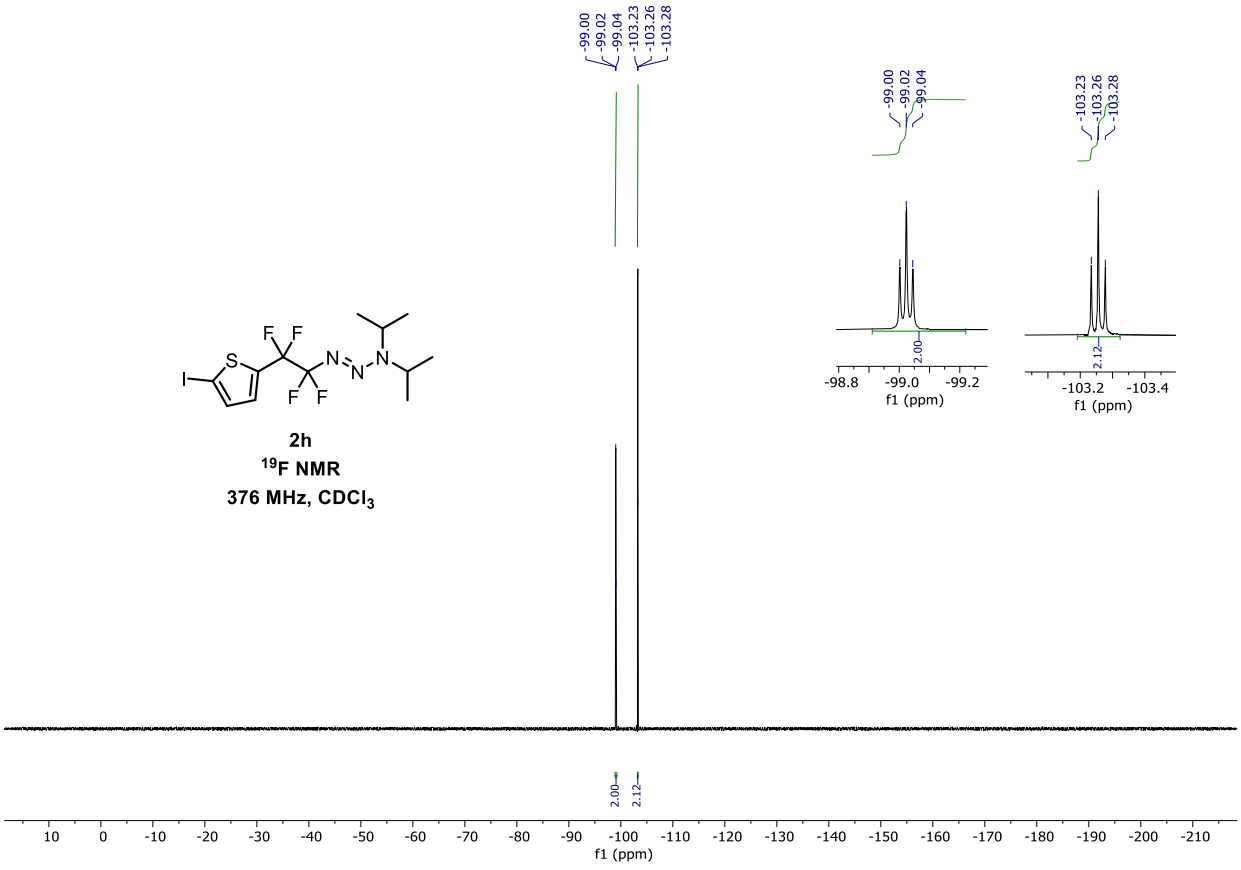


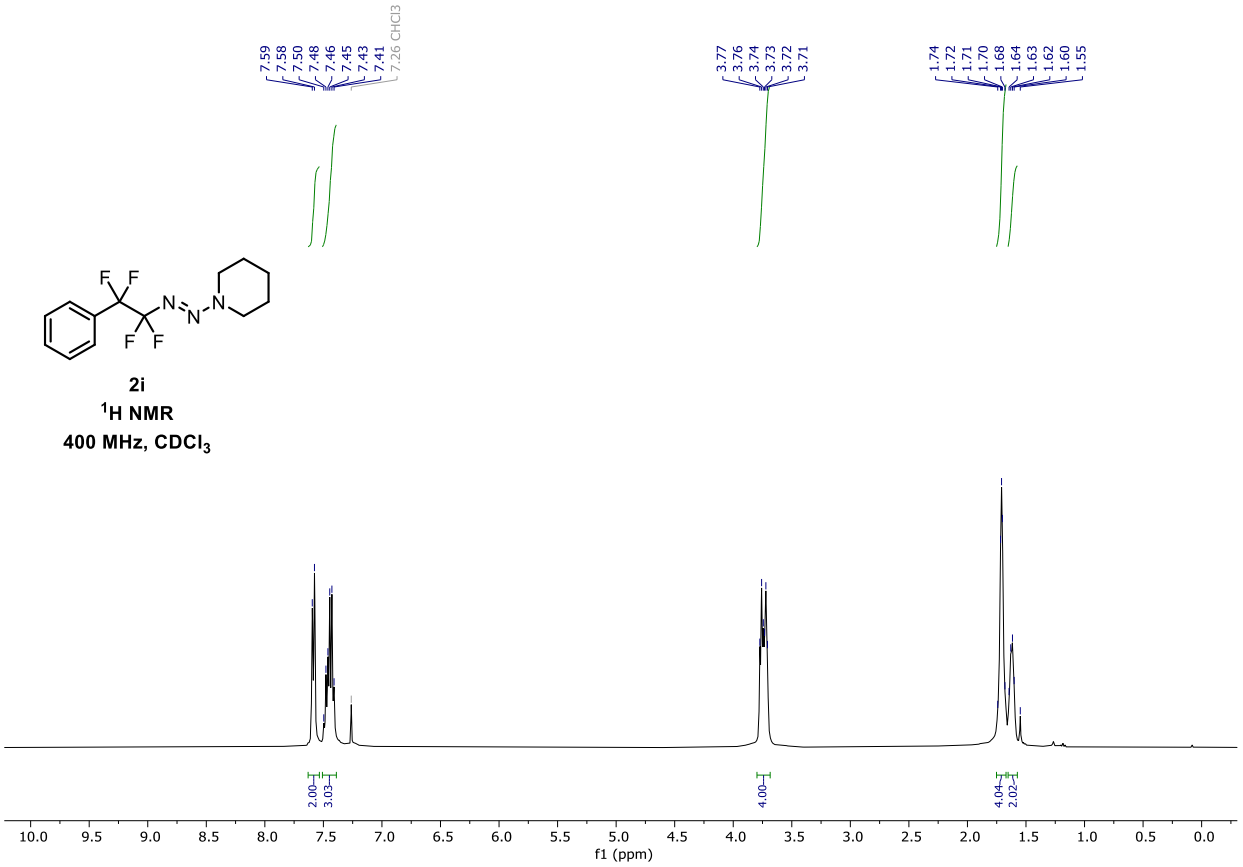
2g
^{19}F NMR
376 MHz, $CDCl_3$

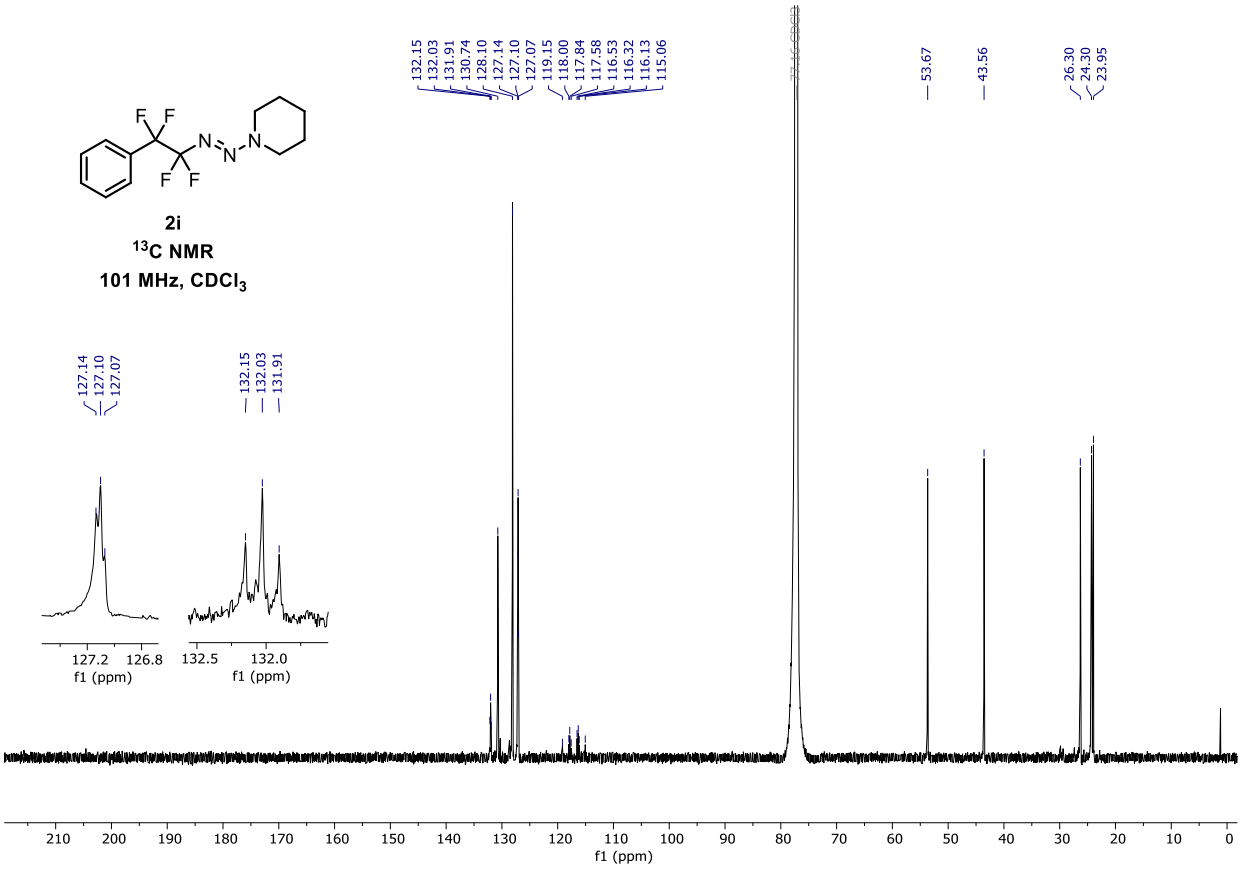


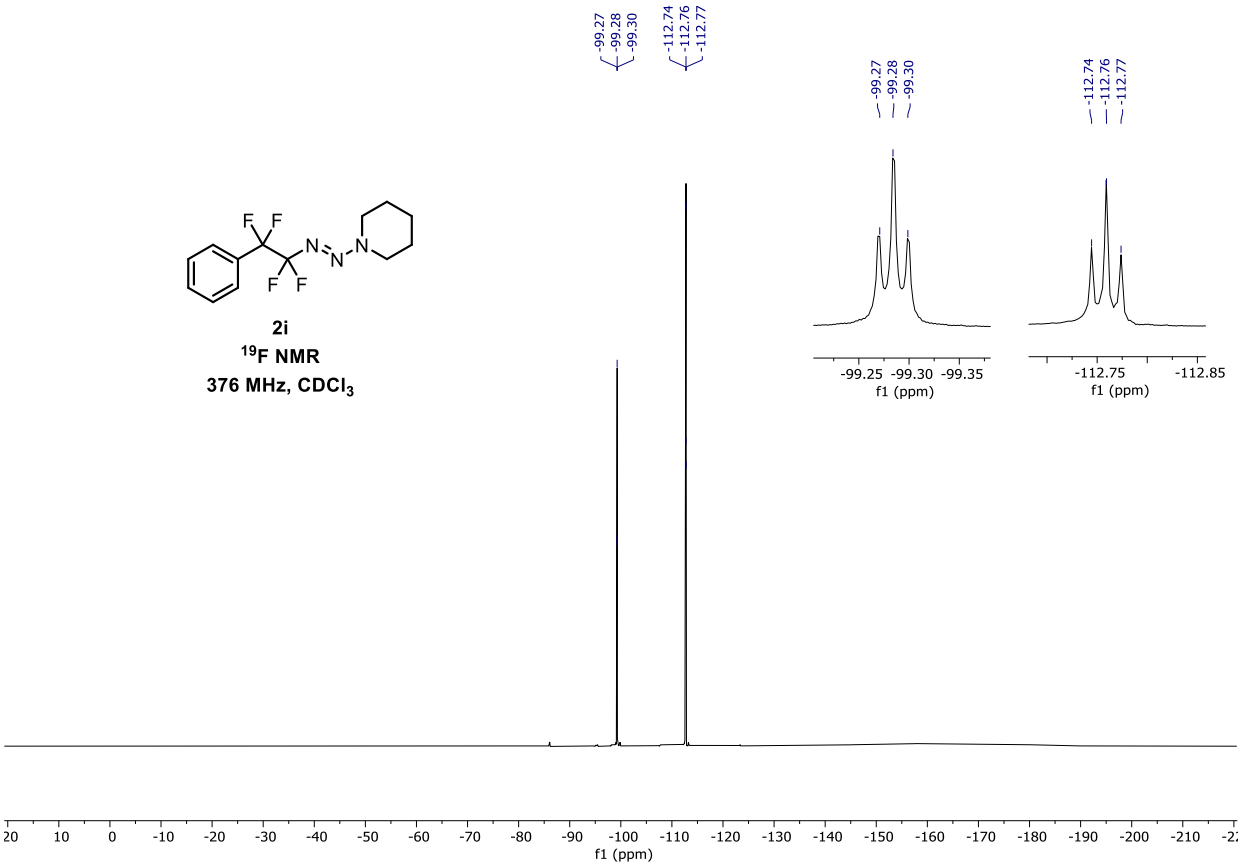
2h
^{1}H NMR
400 MHz, $CDCl_3$

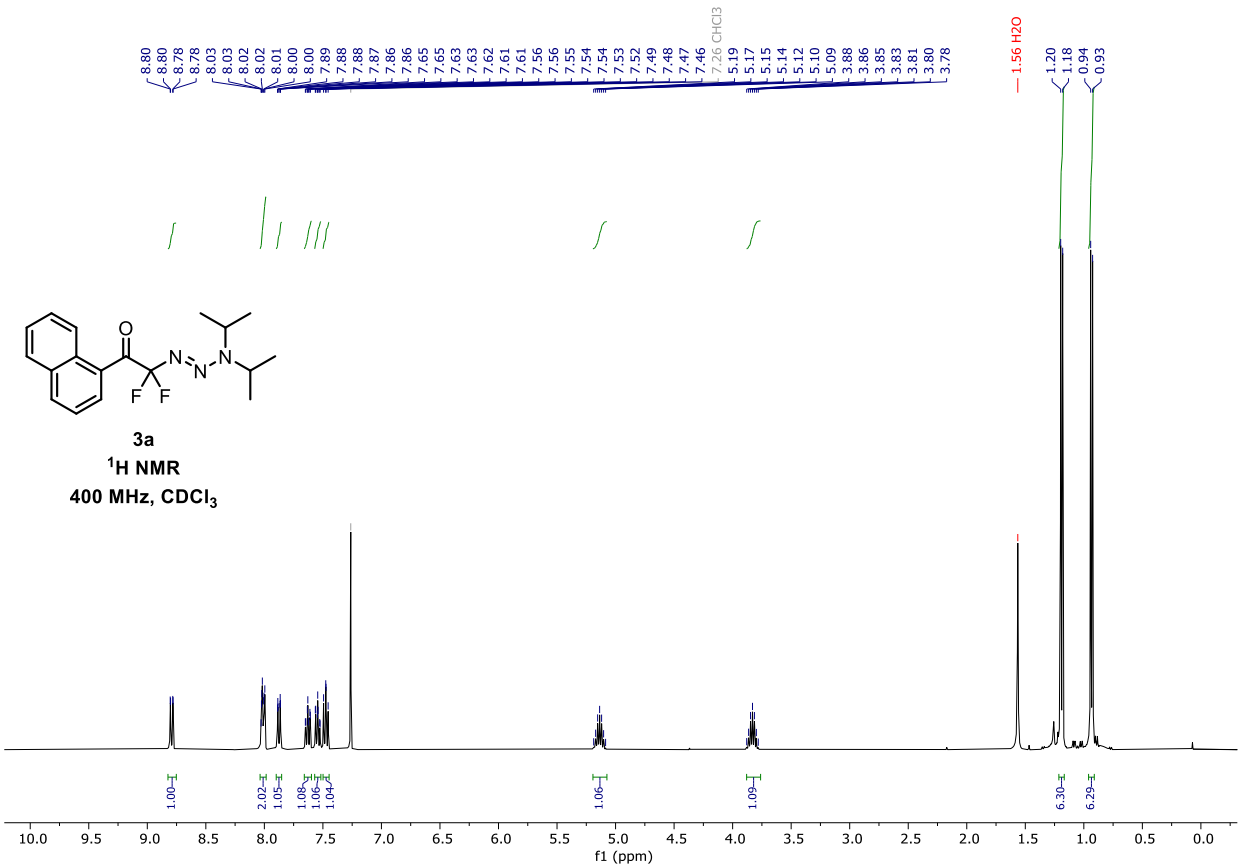

2h
13C NMR
101 MHz, CDCl3
f1 (ppm)

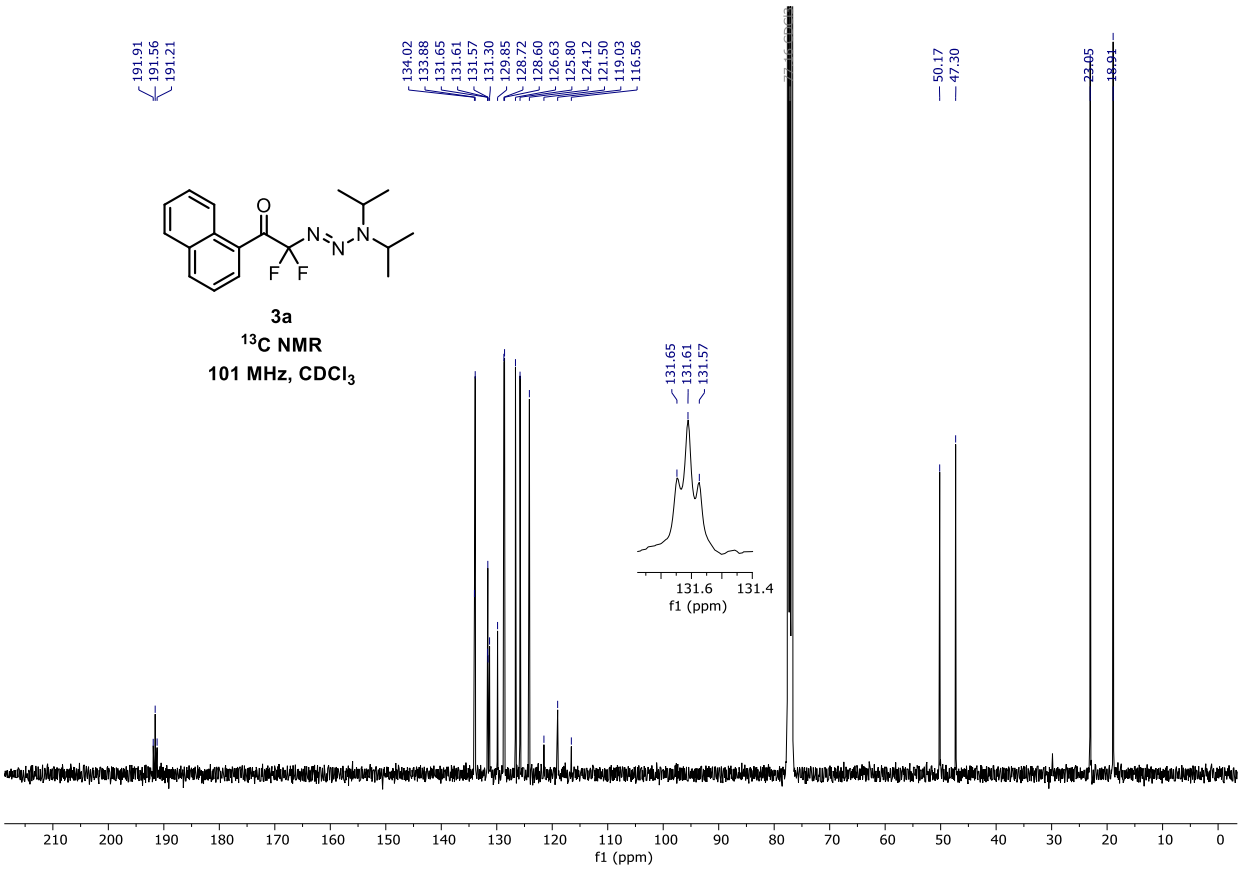

2h
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.59
7.58
7.50
7.48
7.46
7.45
7.43
7.41
7.26 CHCl3
3.77
3.76
3.74
3.73
3.72
3.71
1.74
1.72
1.71
1.70
1.68
1.64
1.63
1.62
1.60
1.55
F F
N
N
N
F F
2i
1H NMR
400 MHz, CDCl3
2.00
3.03
4.00
4.04
2.02
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)

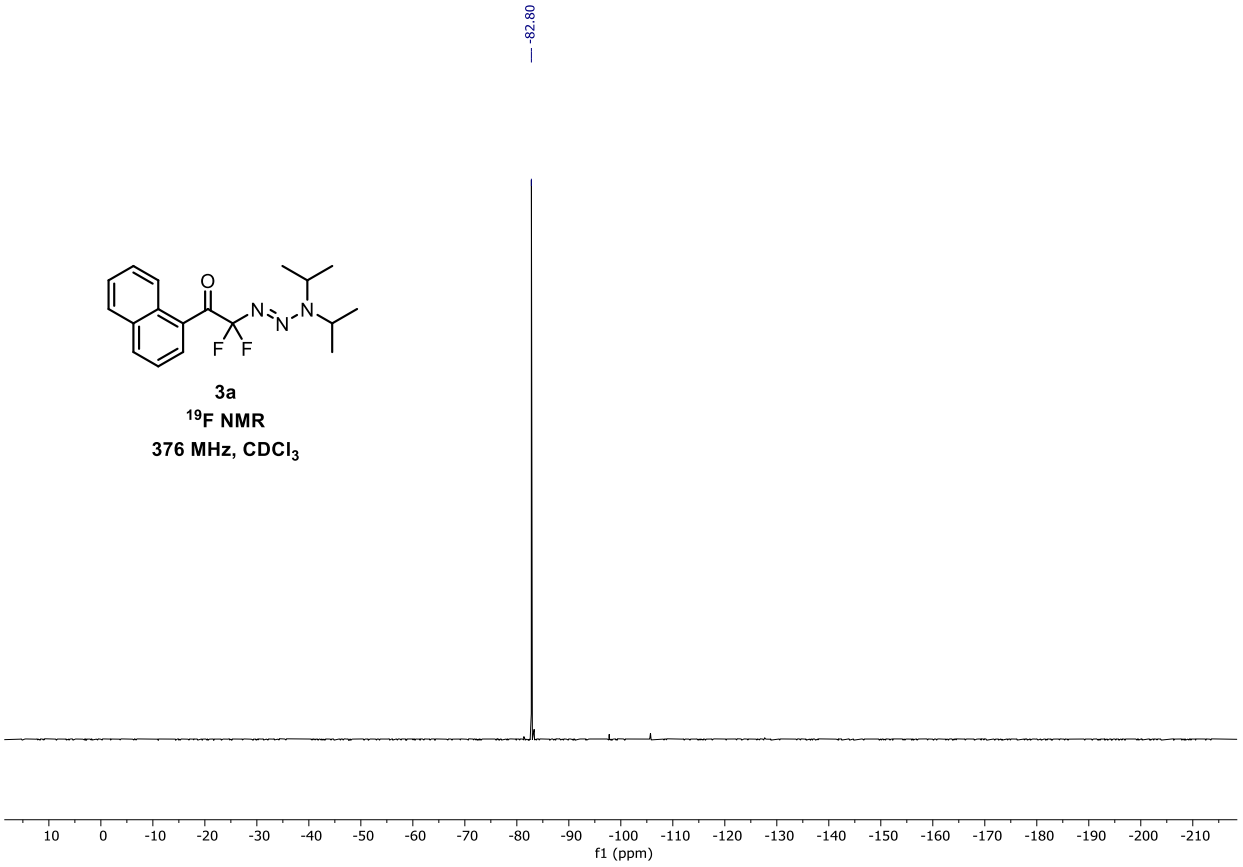

132.15
132.03
131.91
130.74
128.10
127.14
127.10
127.07
119.15
118.00
117.84
117.58
116.53
116.32
116.13
115.06
77.16 CDCl3
53.67
43.56
26.30
24.30
23.95
F F
N
N
N
F F
2i
13C NMR
101 MHz, CDCl3
127.14
127.10
127.07
132.15
132.03
131.91
127.2 126.8
f1 (ppm)
132.5 132.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-99.27
-99.28
-99.30
-112.74
-112.76
-112.77
F F
F F
N
N
N
2i
19F NMR
376 MHz, CDCl3
-99.25 -99.30 -99.35
f1 (ppm)
-112.75
-112.85
f1 (ppm)
f1 (ppm)

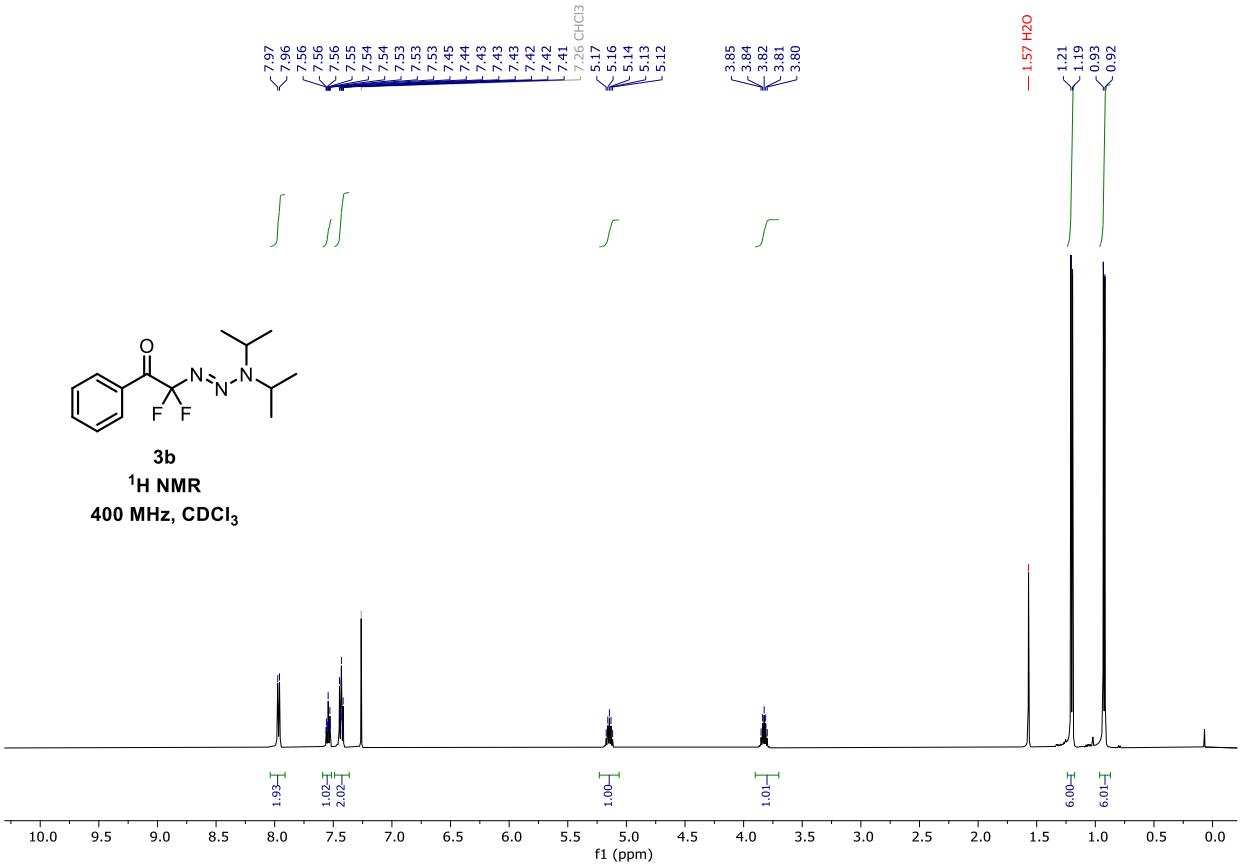

7.26 CHCl3
1.56 H2O
O
N
N
N
F F
3a
1H NMR
400 MHz, CDCl3
1.00
2.02
1.05
1.08
1.06
1.04
1.06
1.09
6.30
6.29
f1 (ppm)

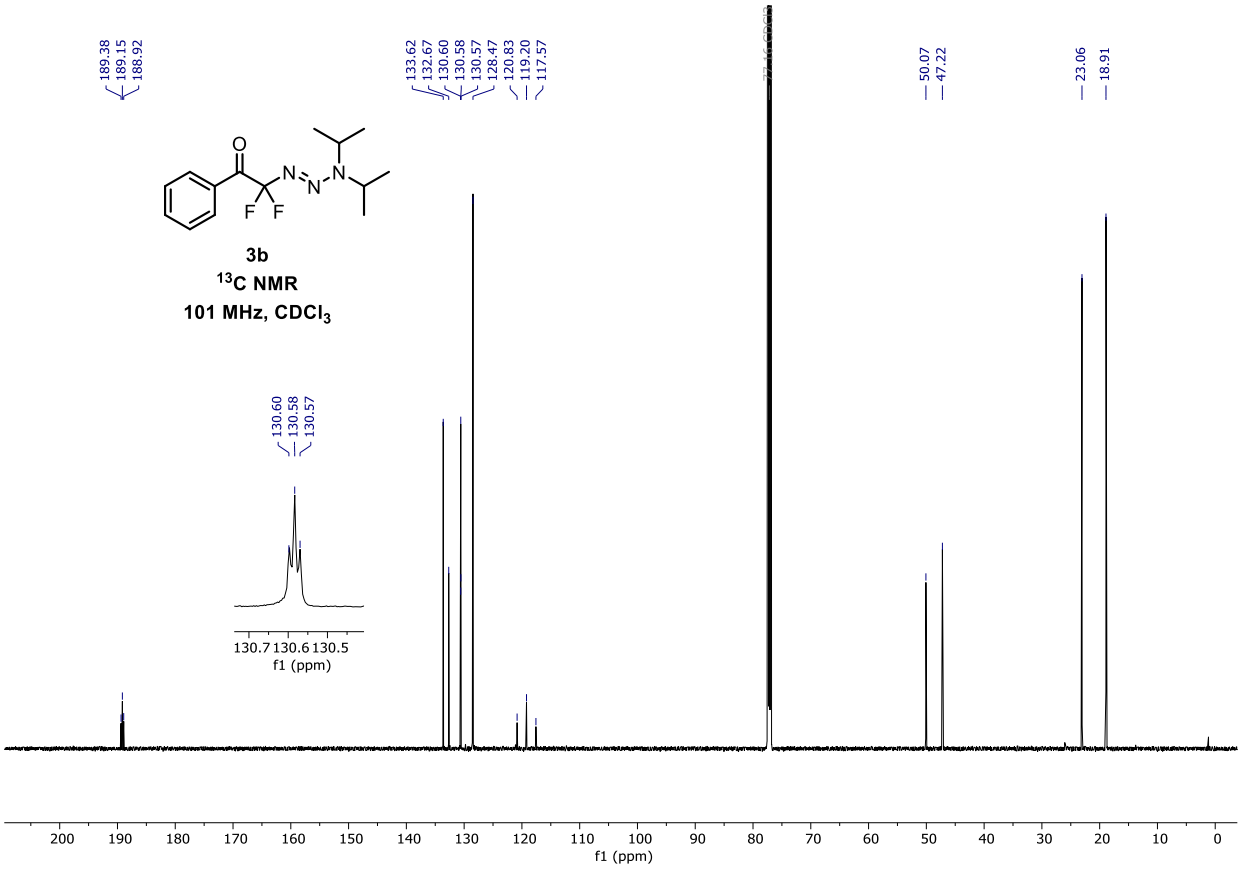


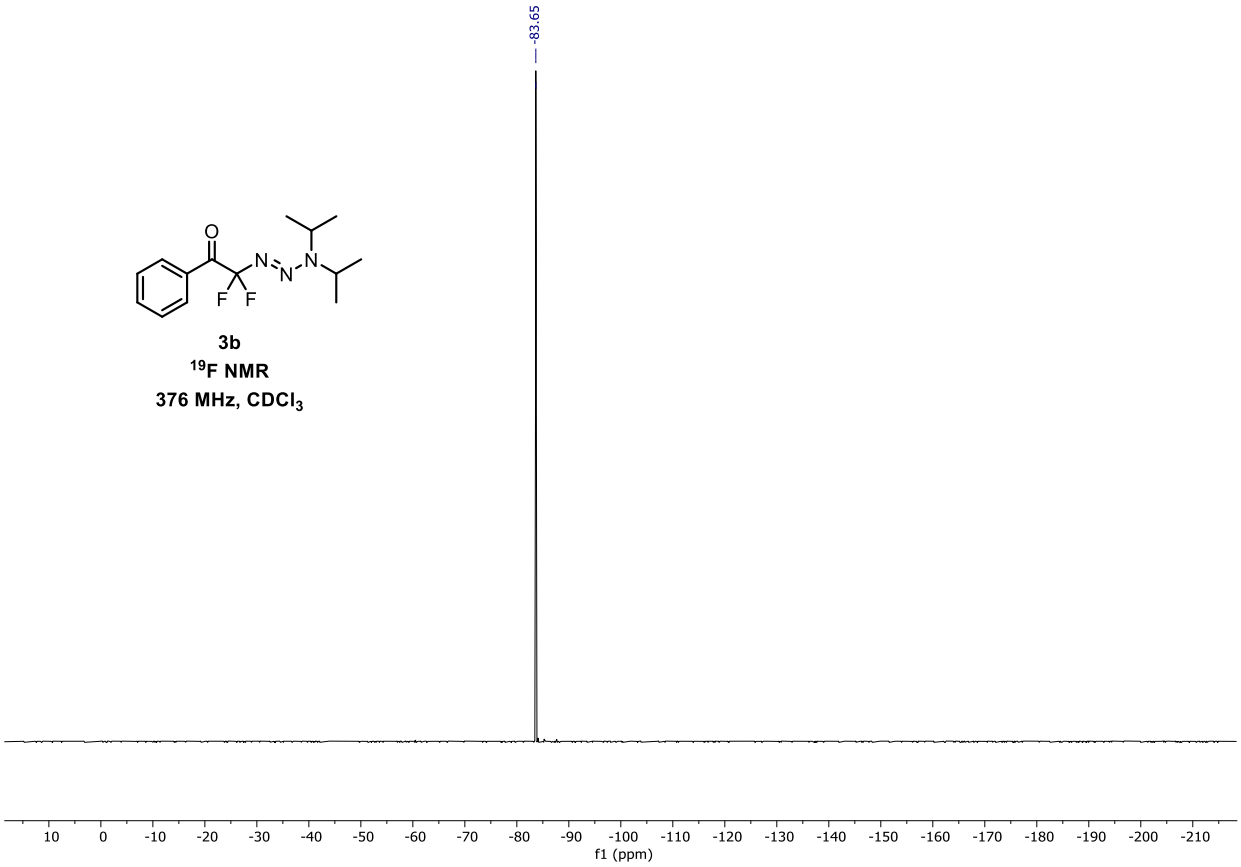
3a
^{13}C NMR
101 MHz, $CDCl_3$



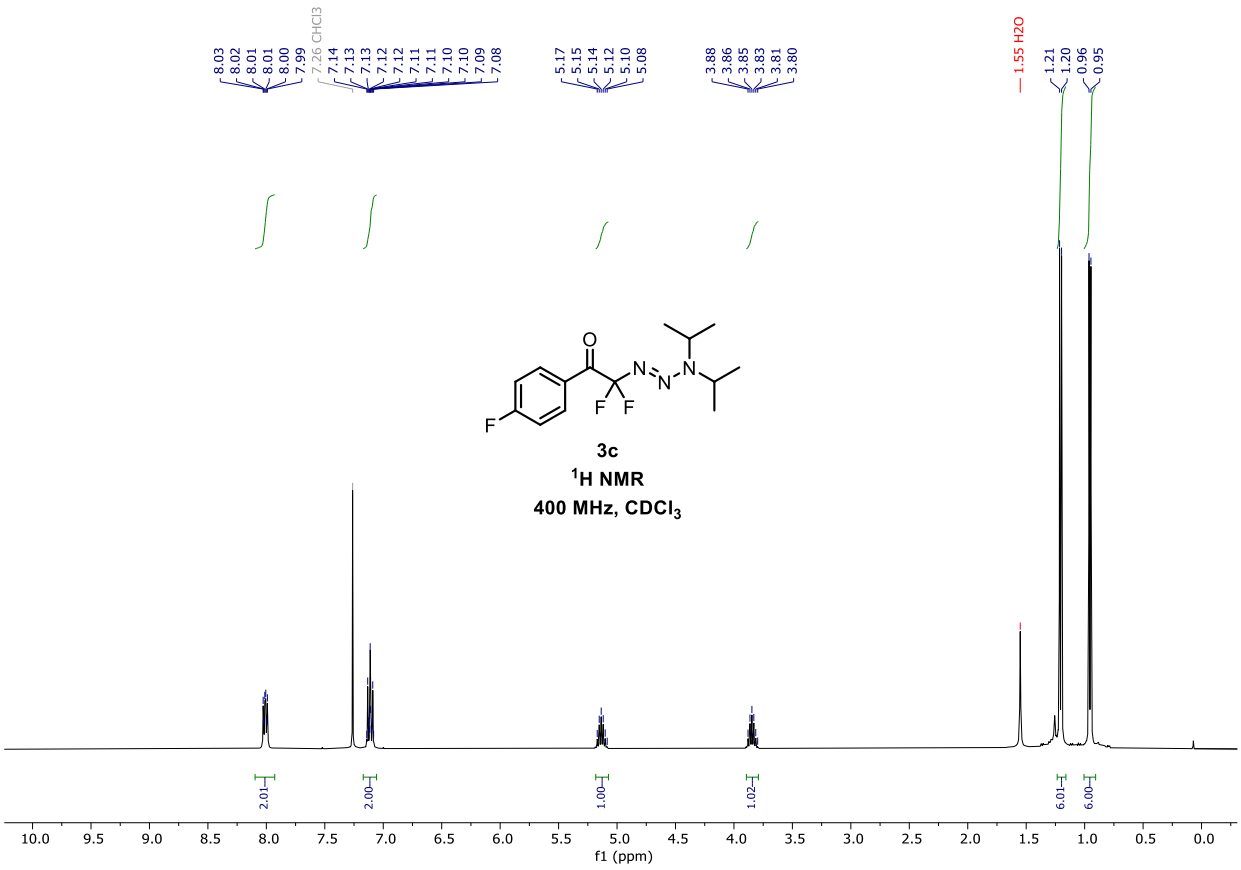
3a
^{19}F NMR
376 MHz, $CDCl_3$


7.97
7.96
7.56
7.56
7.56
7.55
7.54
7.54
7.53
7.53
7.53
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.26 CHCl3
5.17
5.16
5.14
5.13
5.12
3.85
3.84
3.82
3.81
3.80
1.57 H2O
1.21
1.19
0.93
0.92
O
N
N
N
F
F
3b
1H NMR
400 MHz, CDCl3
1.93
1.02
2.02
1.00
1.01
6.00
6.01
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 0.0
f1 (ppm)

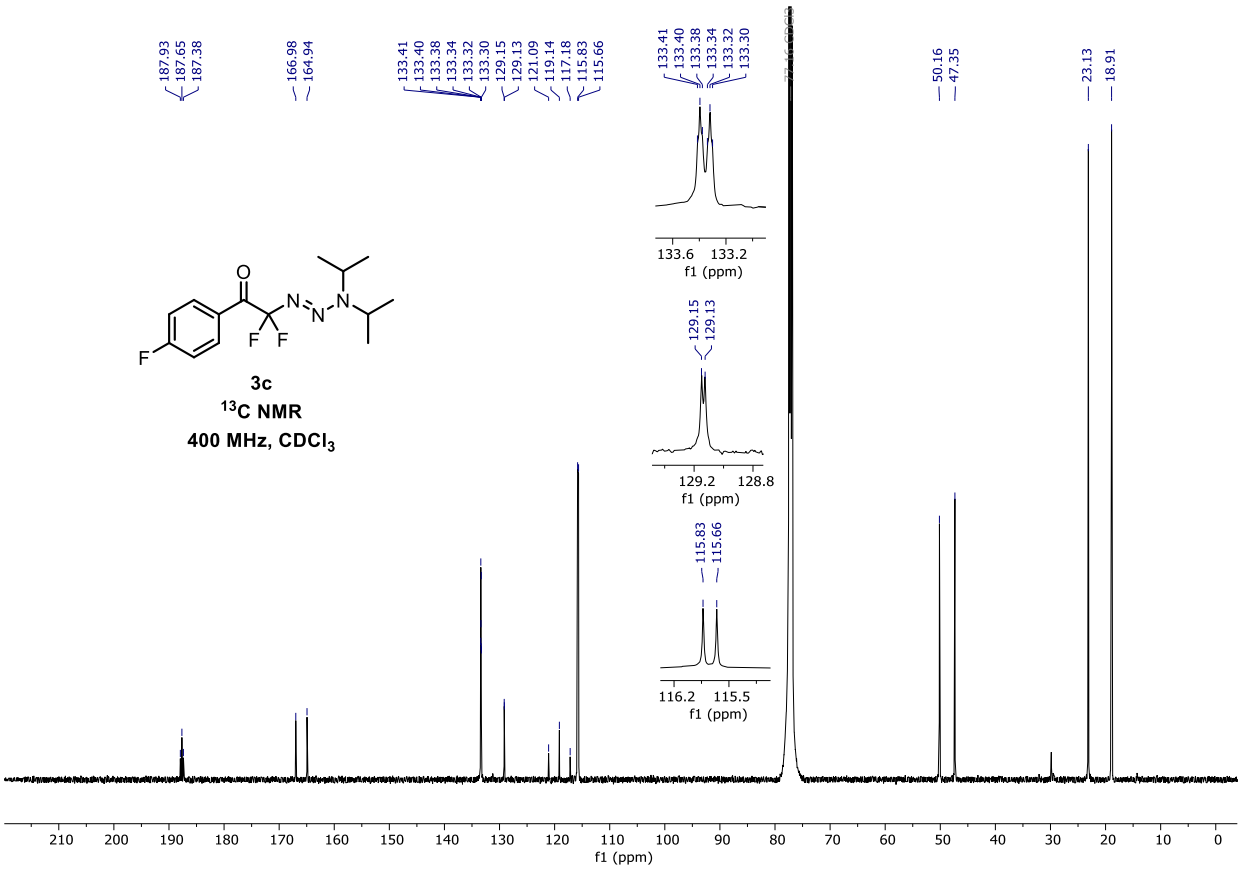

189.38
189.15
188.92
133.62
132.67
130.60
130.58
130.57
128.47
120.83
119.20
117.57
77.46
77.04
76.62
50.07
47.22
23.06
18.91
O
N
N
N
F
F
3b
13C NMR
101 MHz, CDCl3
130.60
130.58
130.57
130.7 130.6 130.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



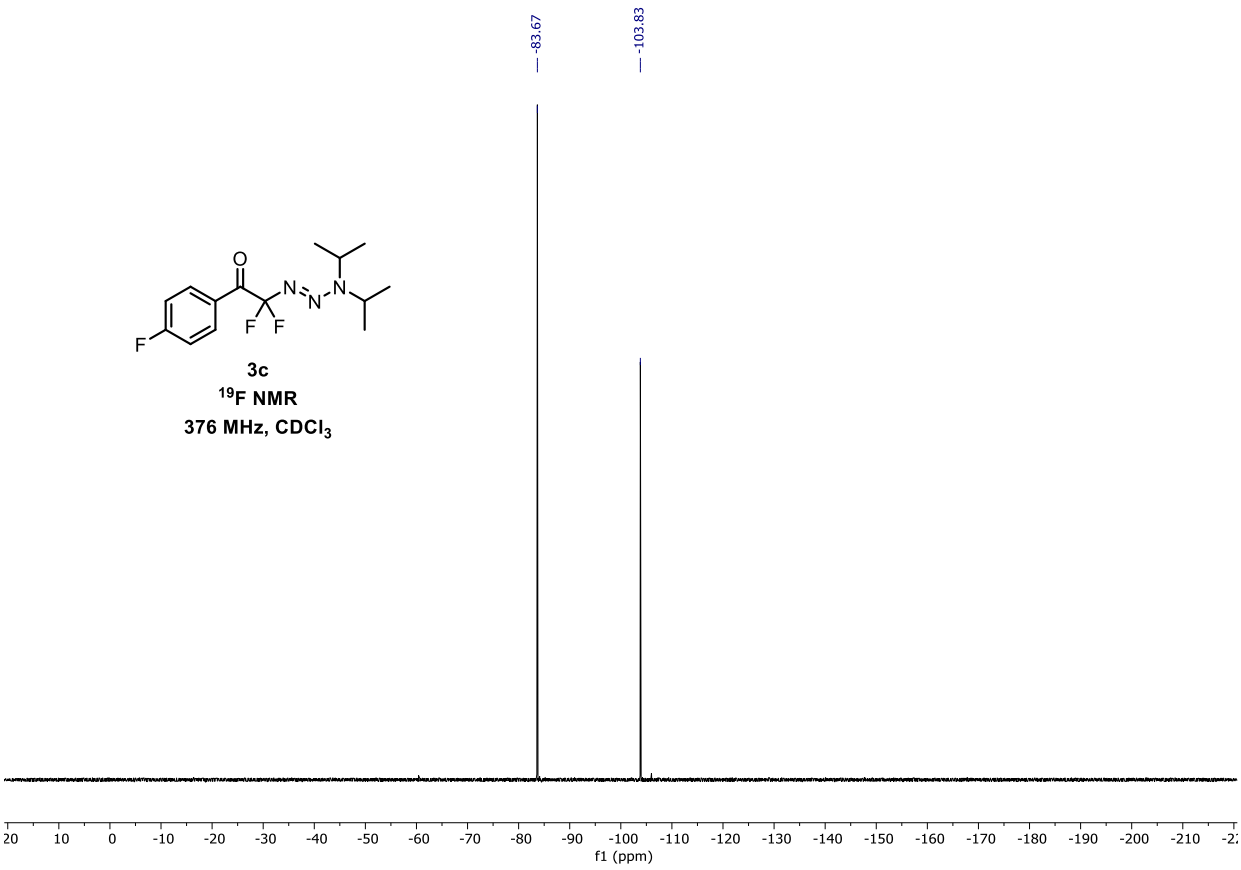
3b
^{19}F NMR
376 MHz, $CDCl_3$



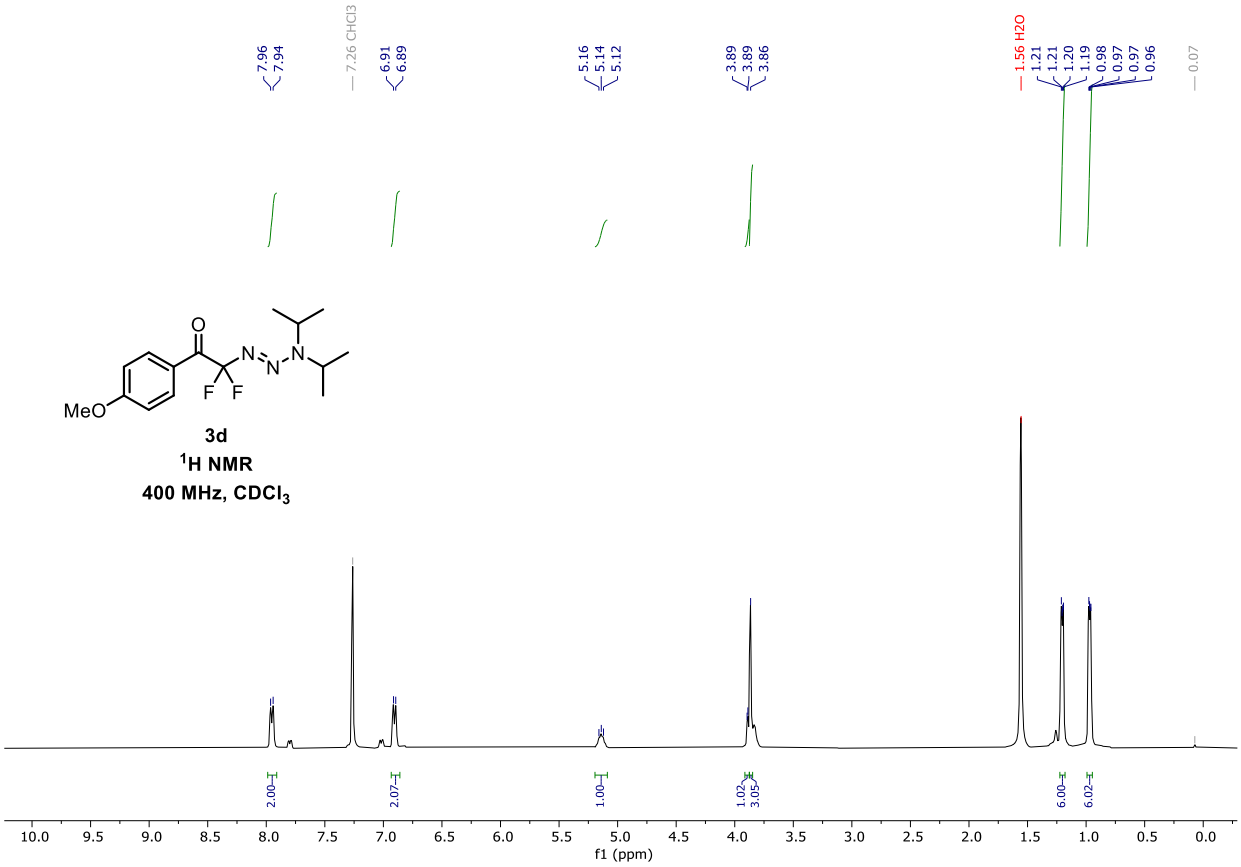
3c
^{1}H NMR
400 MHz, $CDCl_3$

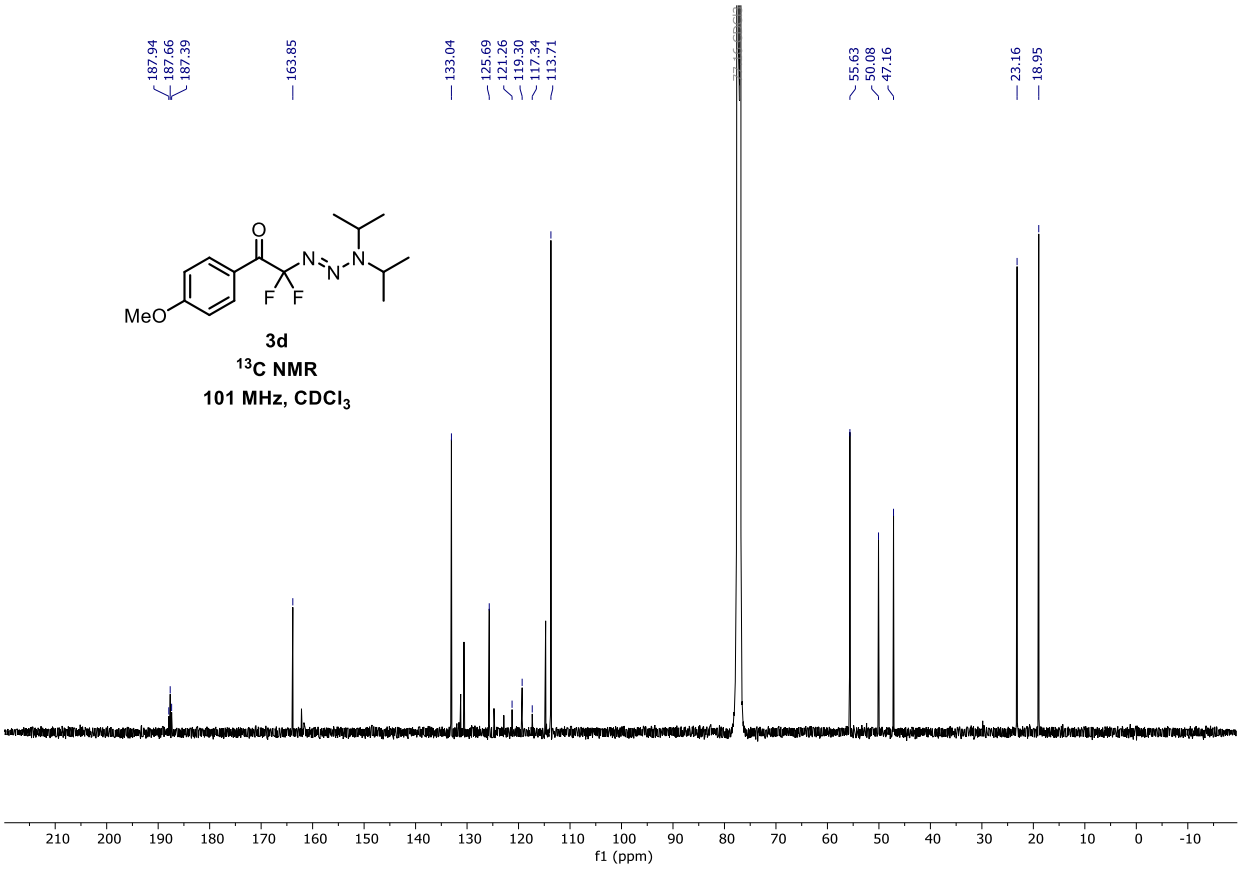


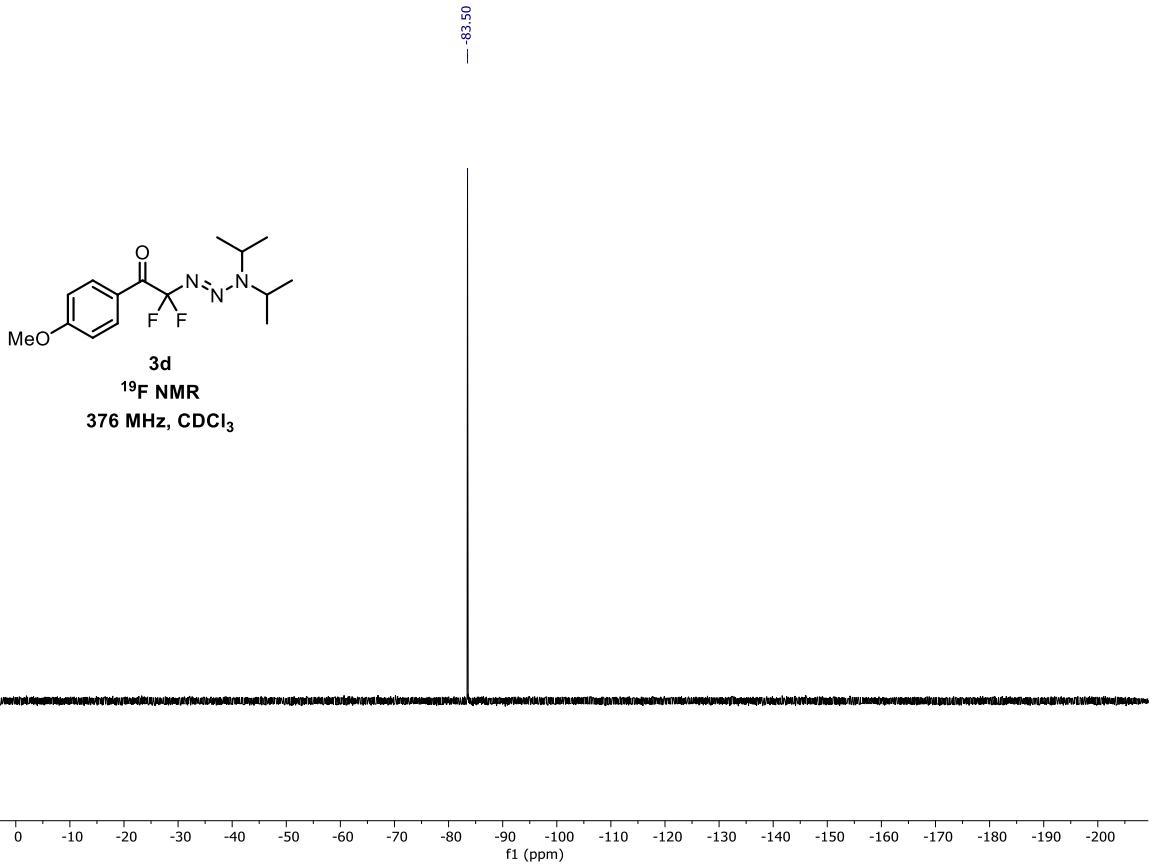
3c
^{13}C NMR
400 MHz, $CDCl_3$



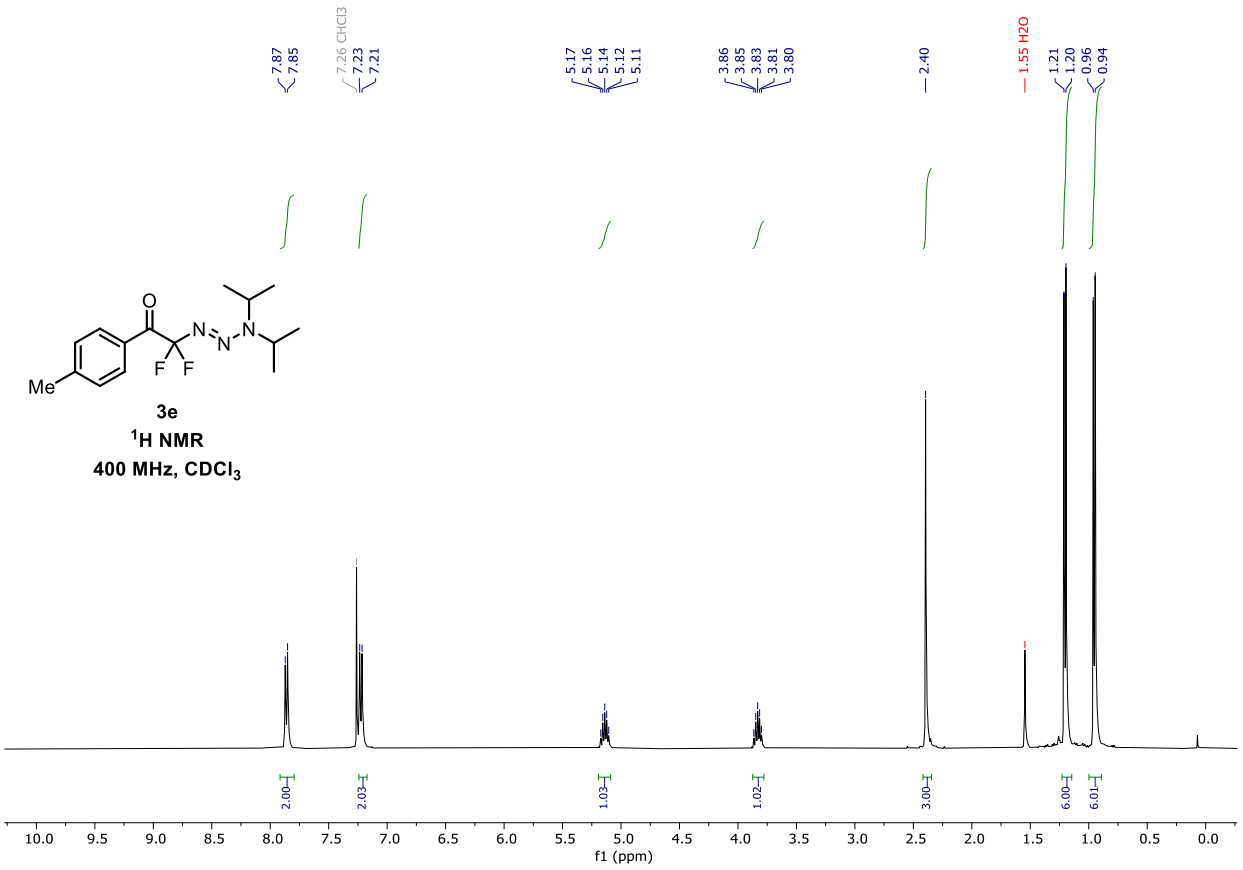
3c
^{19}F NMR
376 MHz, $CDCl_3$


7.96
7.94
7.26 CHCl3
6.91
6.89
5.16
5.14
5.12
3.89
3.89
3.86
1.56 H2O
1.21
1.21
1.20
1.19
0.98
0.97
0.97
0.96
0.07
MeO
3d
1H NMR
400 MHz, CDCl3
2.00
2.07
1.00
1.02
3.05
6.00
6.02
f1 (ppm)

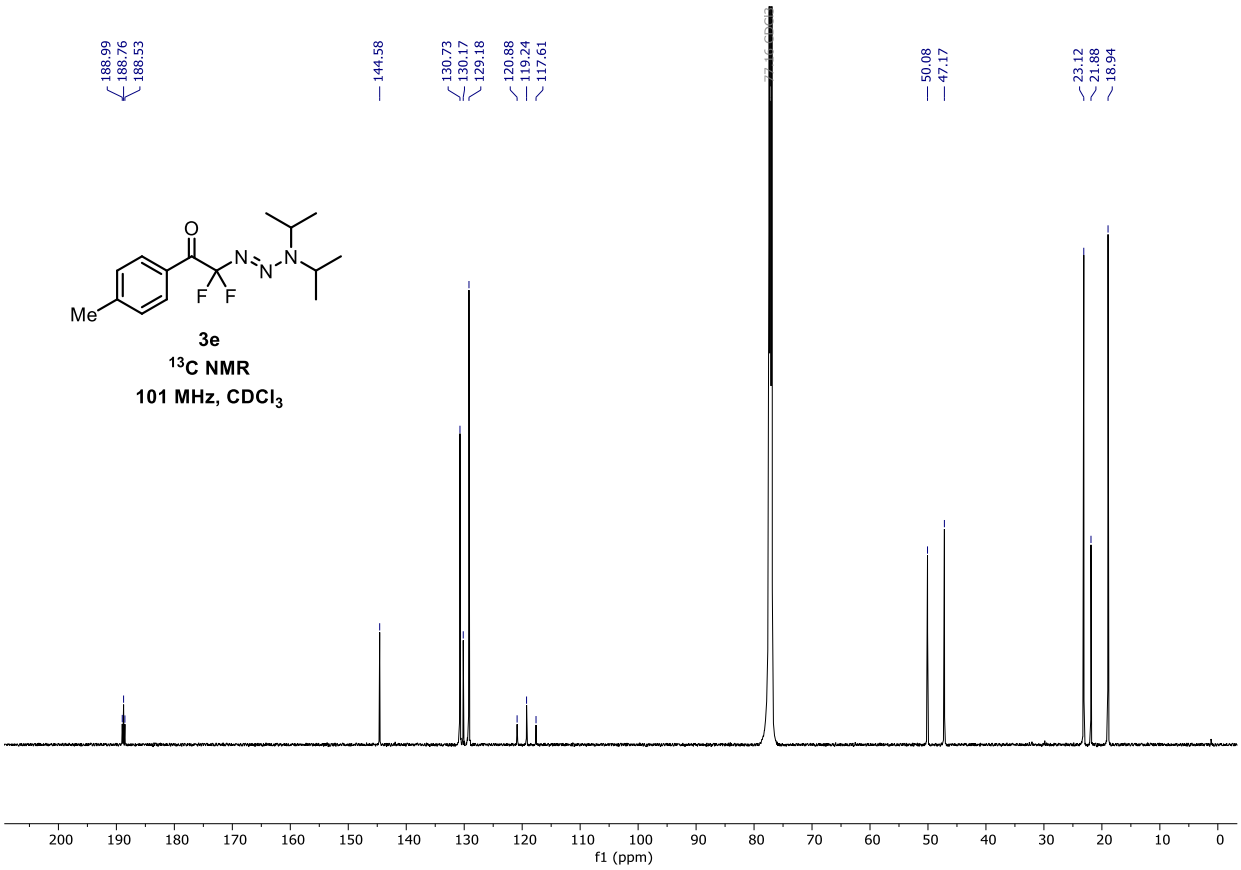

187.94
187.66
187.39
163.85
133.04
125.69
121.26
119.30
117.34
113.71
55.63
50.08
47.16
23.16
18.95
MeO
3d
13C NMR
101 MHz, CDCl3
f1 (ppm)



3d
^{19}F NMR
376 MHz, $CDCl_3$



3e
^{1}H NMR
400 MHz, $CDCl_3$



3e

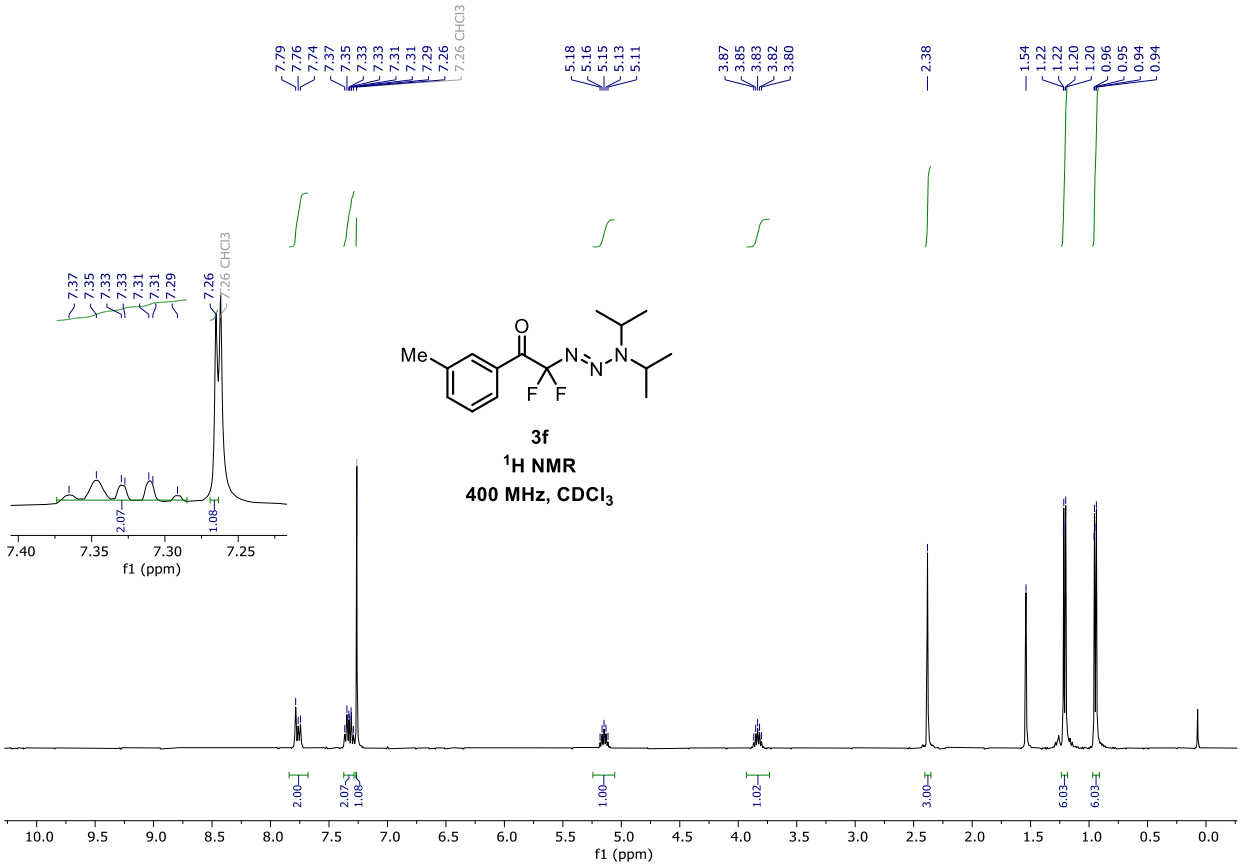
^{13}C NMR

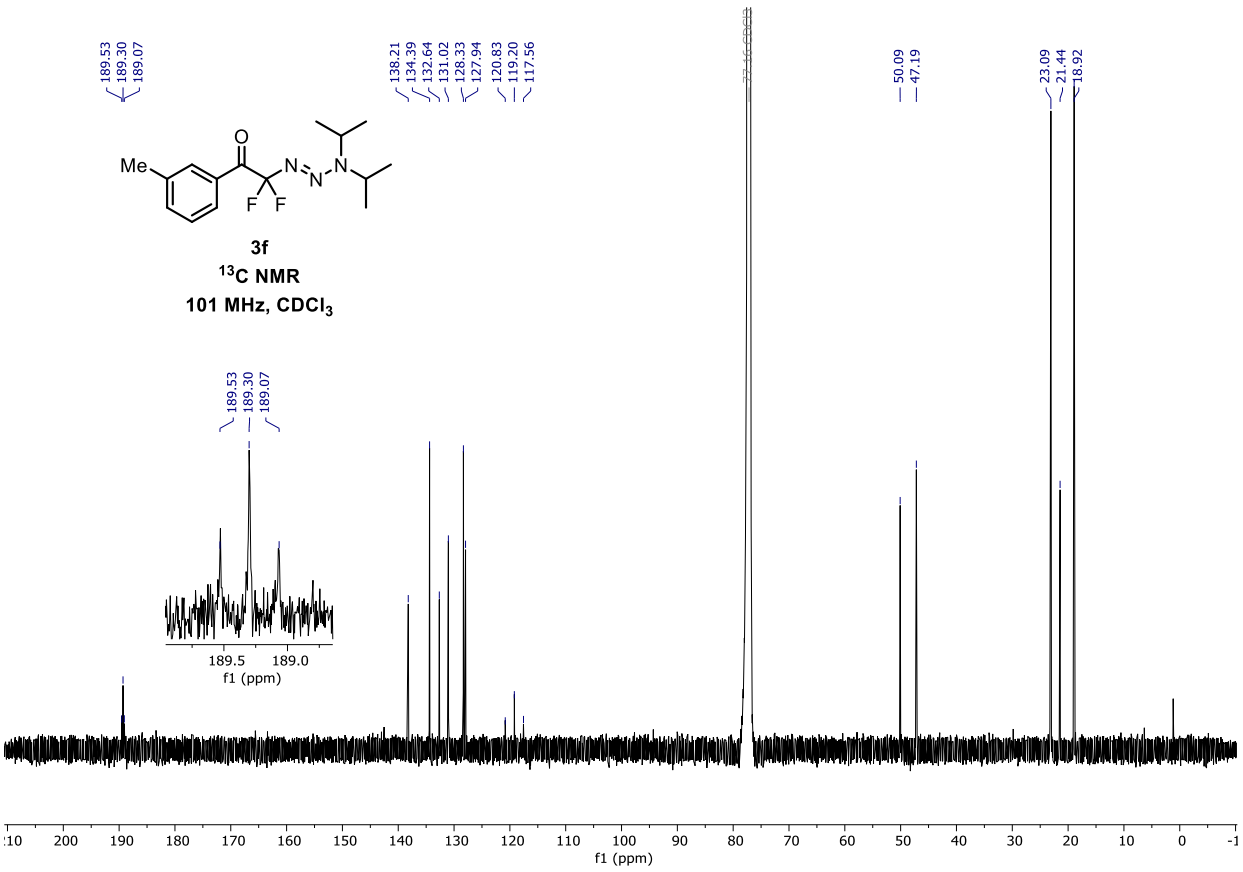
101 MHz, $CDCl_3$

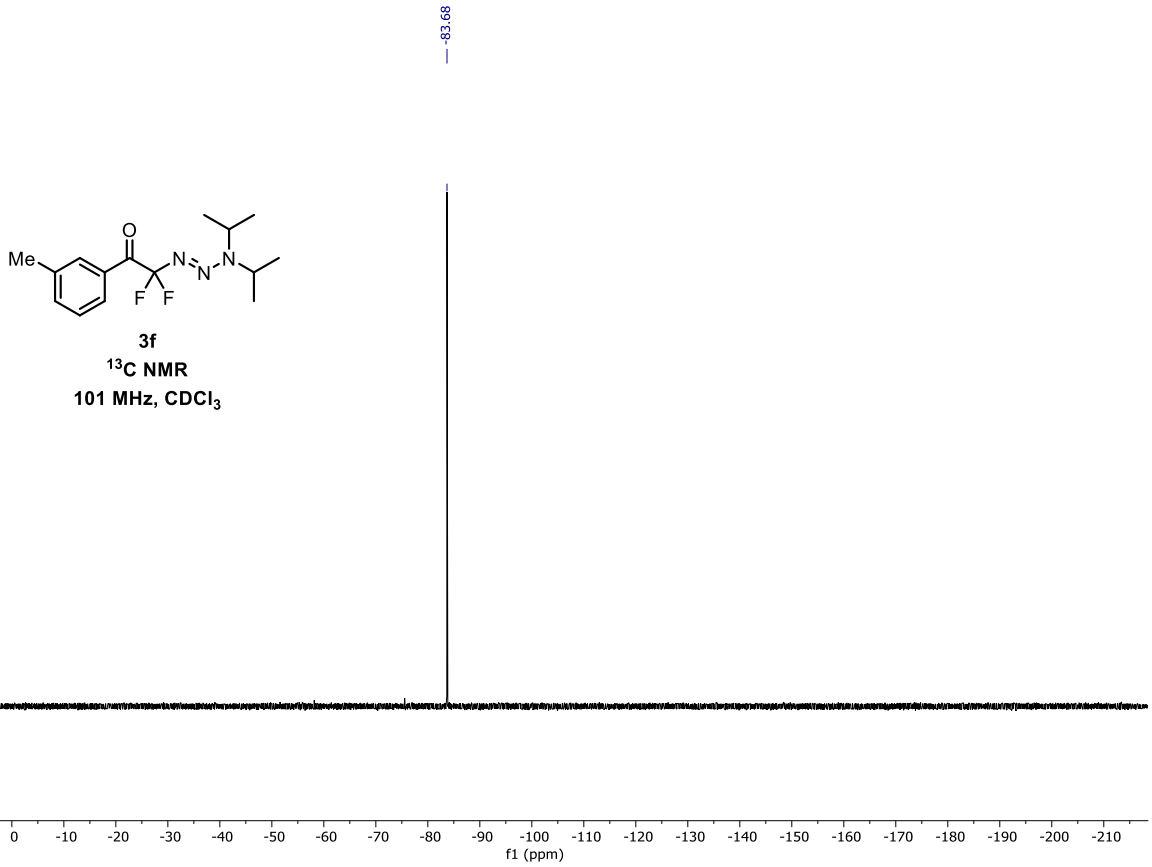
3e

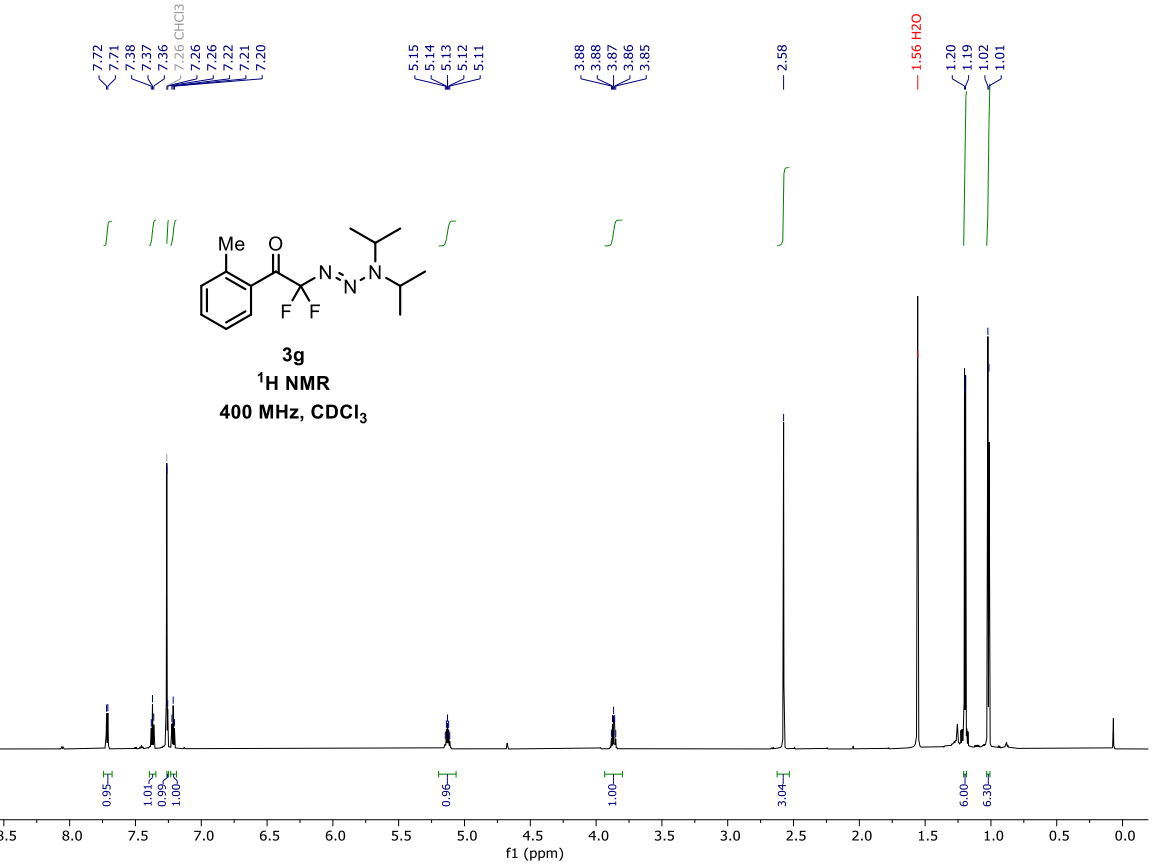
^{19}F NMR

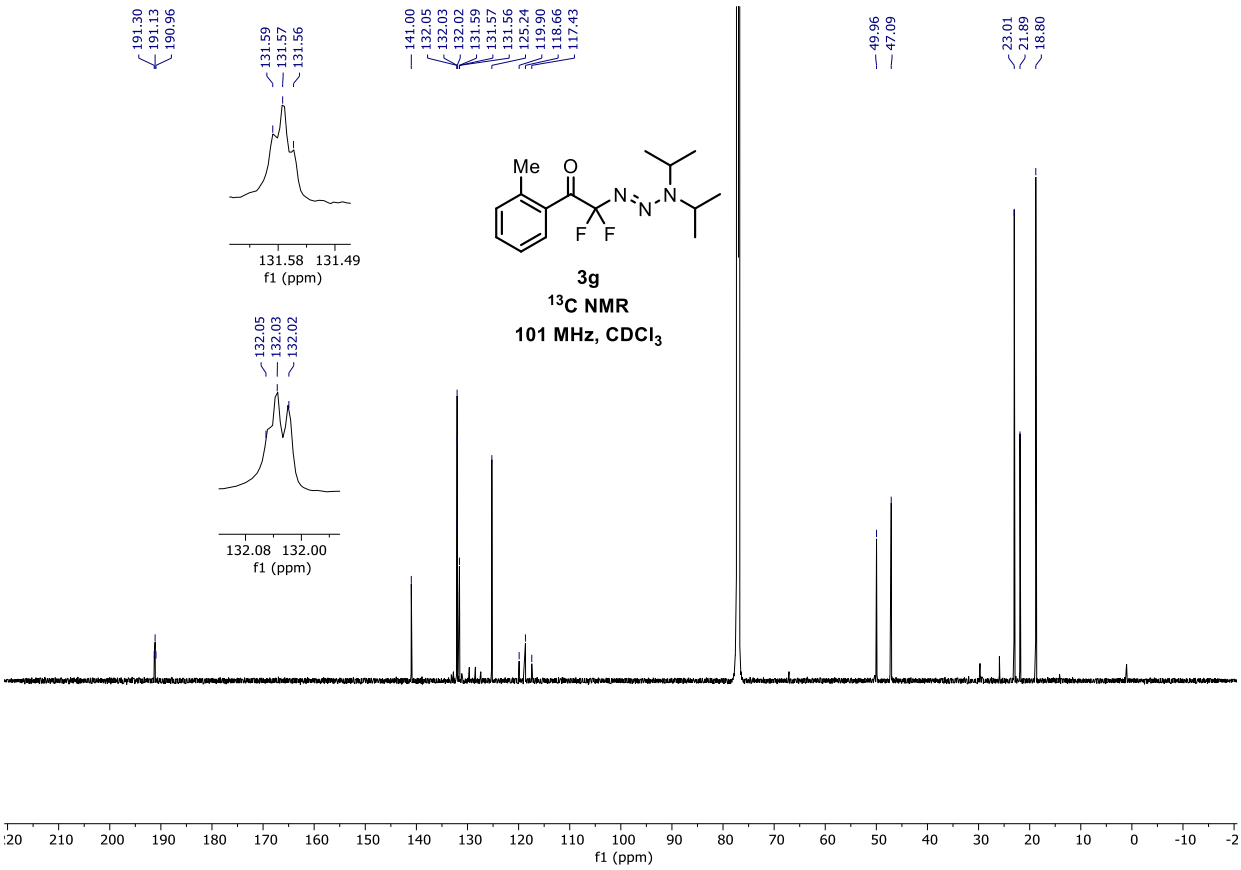
376 MHz, $CDCl_3$

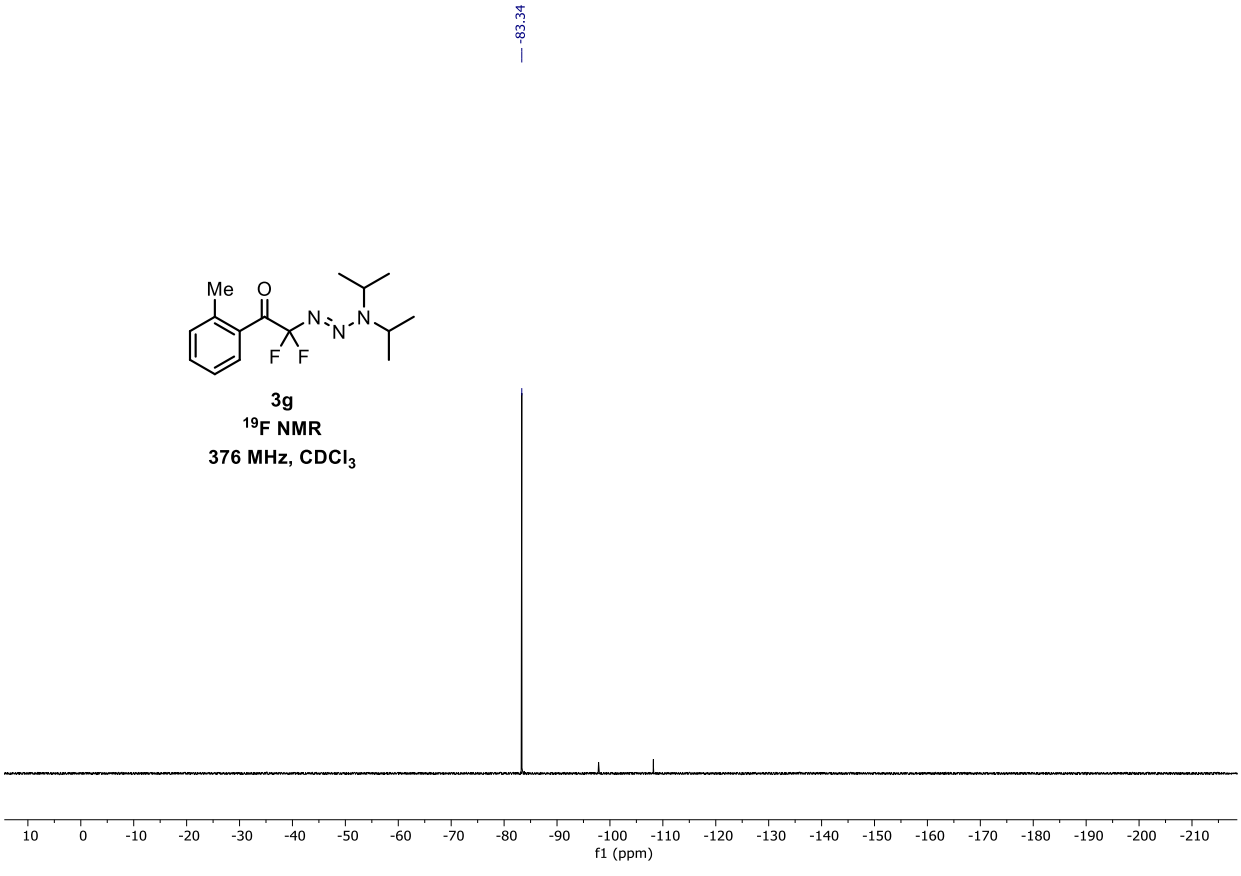

7.79
7.76
7.74
7.37
7.35
7.33
7.33
7.31
7.31
7.29
7.26
7.26 CHCl3
5.18
5.16
5.15
5.13
5.11
3.87
3.85
3.83
3.82
3.80
2.38
1.54
1.22
1.22
1.20
1.20
0.96
0.95
0.94
0.94
Me
O
N
N
N
F F
3f
1H NMR
400 MHz, CDCl3
2.00
2.07
1.08
1.00
1.02
3.00
6.03
6.03
f1 (ppm)

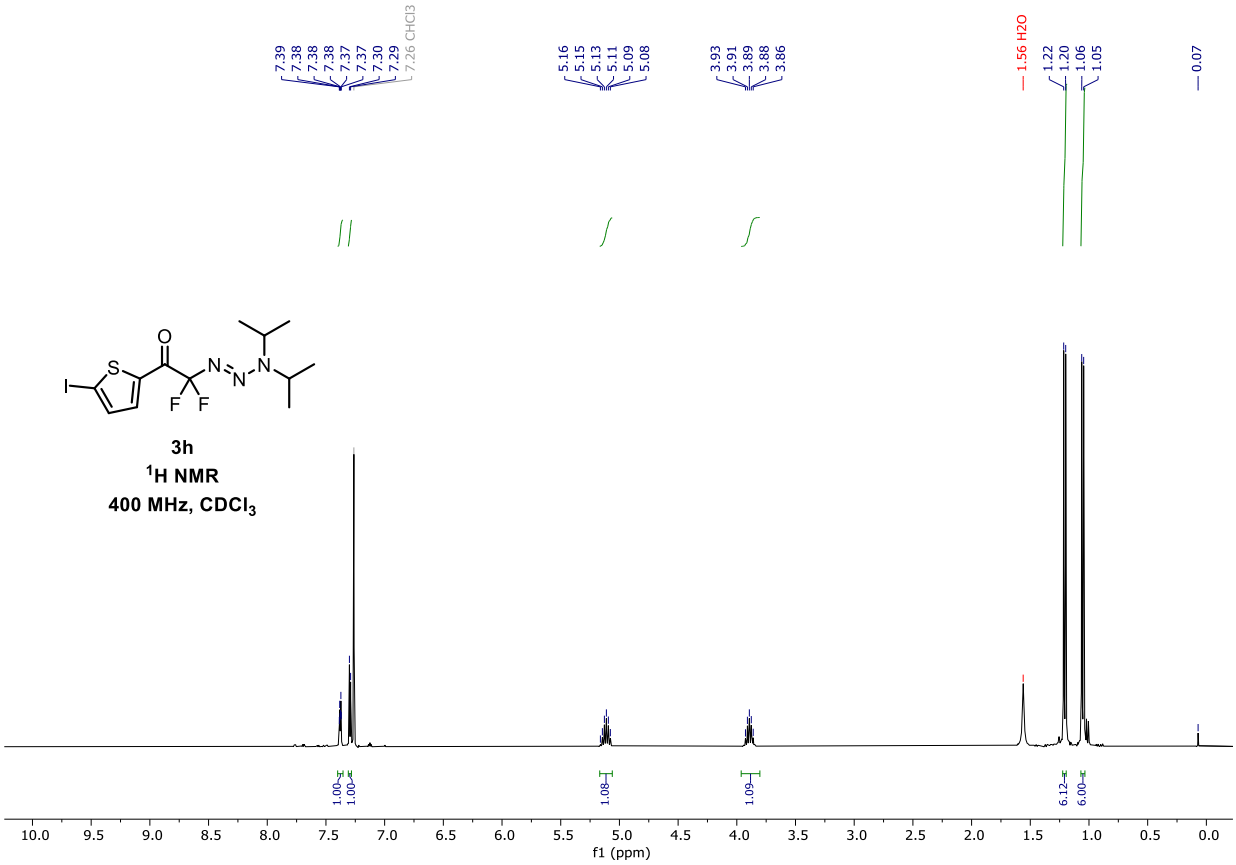

189.53
189.30
189.07
138.21
134.39
132.64
131.02
128.33
127.94
120.83
119.20
117.56
77.16 CDCl3
50.09
47.19
23.09
21.44
18.92
Me
O
N
N
N
F F
3f
13C NMR
101 MHz, CDCl3
f1 (ppm)


-83.68
Me
O
N
N
N
F
F
3f
13C NMR
101 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

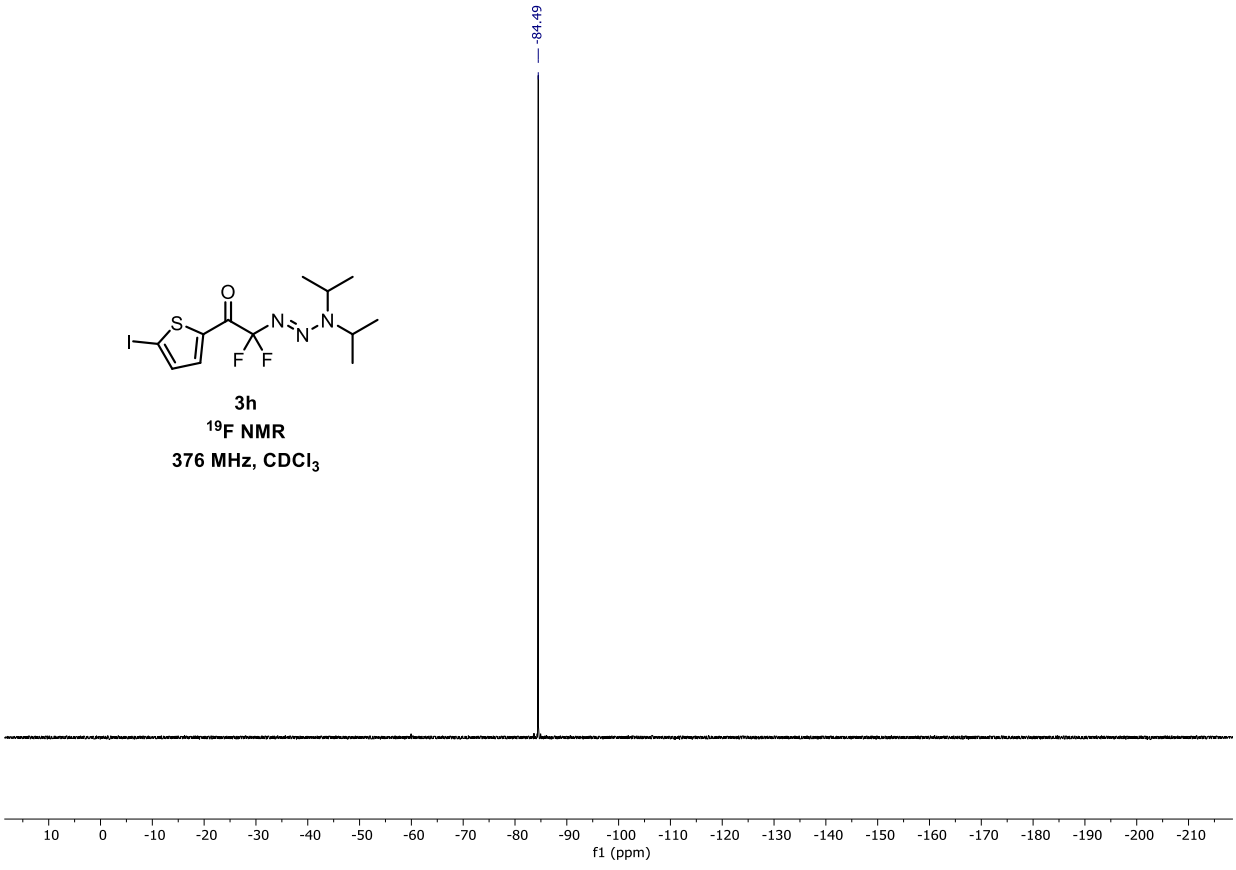

7.72
7.71
7.38
7.37
7.36
7.26 CHCl3
7.26
7.26
7.22
7.21
7.20
5.15
5.14
5.13
5.12
5.11
3.88
3.88
3.87
3.86
3.85
2.58
1.56 H2O
1.20
1.19
1.02
1.01
Me
O
N
N
N
F
F
3g
1H NMR
400 MHz, CDCl3
0.95
1.01
0.99
1.00
0.96
1.00
3.04
6.00
6.30
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


191.30
191.13
190.96
131.59
131.57
131.56
141.00
132.05
132.03
132.02
131.59
131.57
131.56
125.24
119.90
118.66
117.43
49.96
47.09
23.01
21.89
18.80
131.58 131.49
f1 (ppm)
132.05
132.03
132.02
132.08 132.00
f1 (ppm)
Me
O
N
N
N
F F
3g
13C NMR
101 MHz, CDCl3
f1 (ppm)

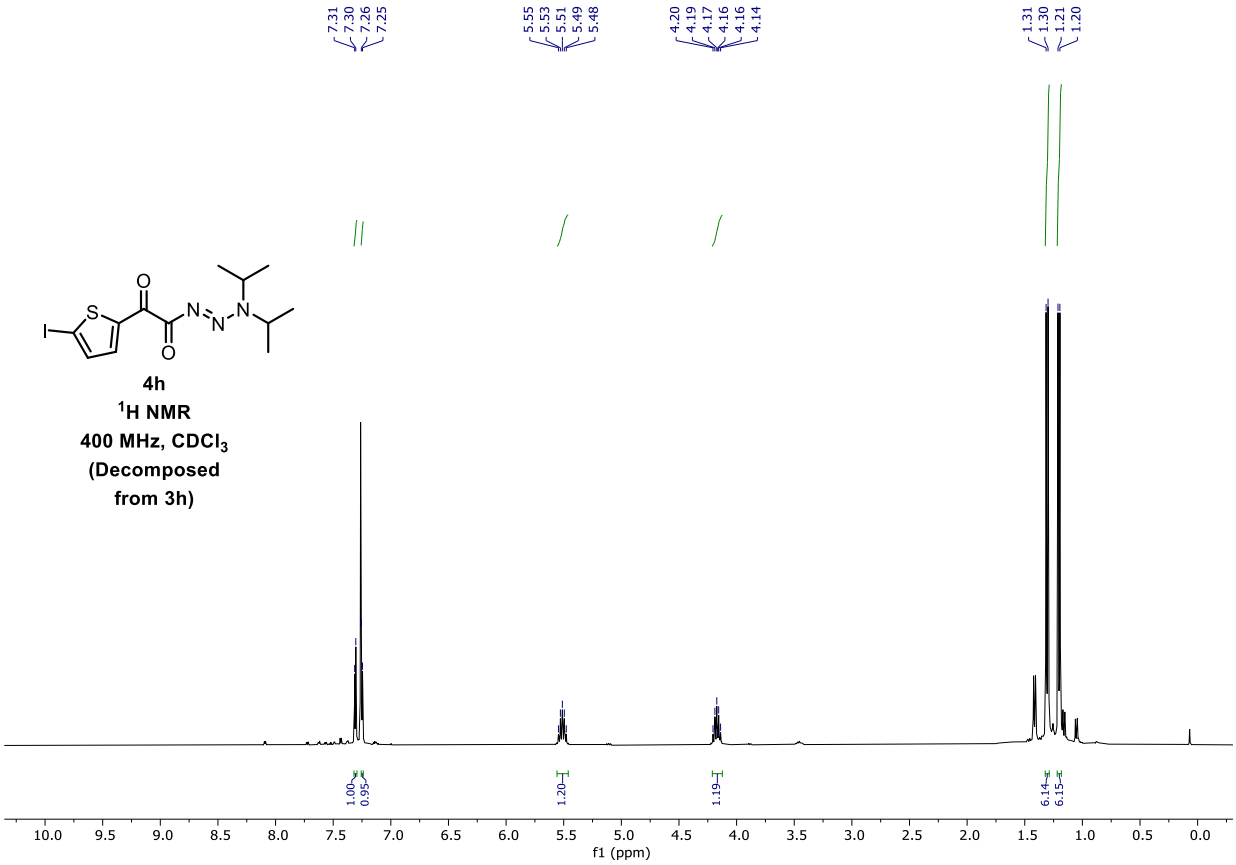

-83.34
Me
O
N
N
N
F F
3g
19F NMR
376 MHz, CDCl3
f1 (ppm)



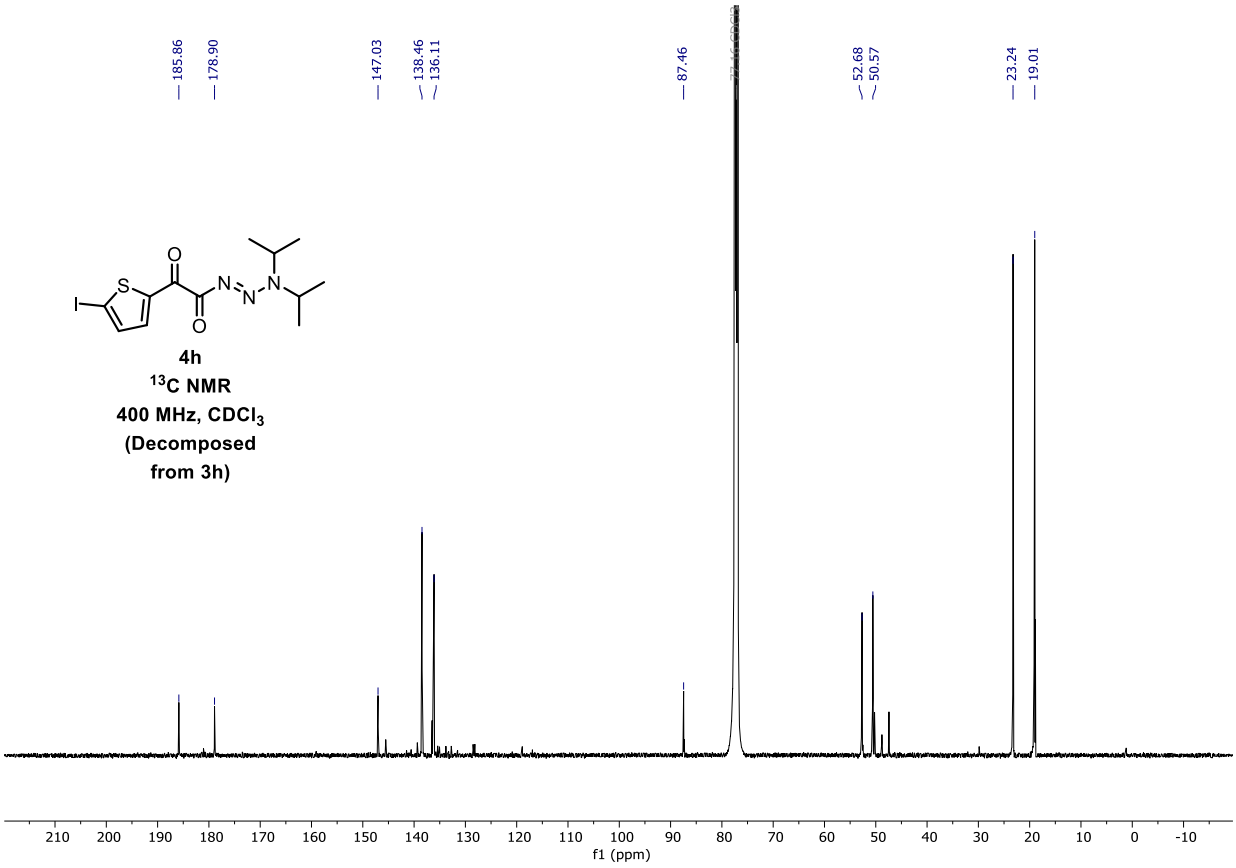
3h
^{1}H NMR
400 MHz, $CDCl_3$



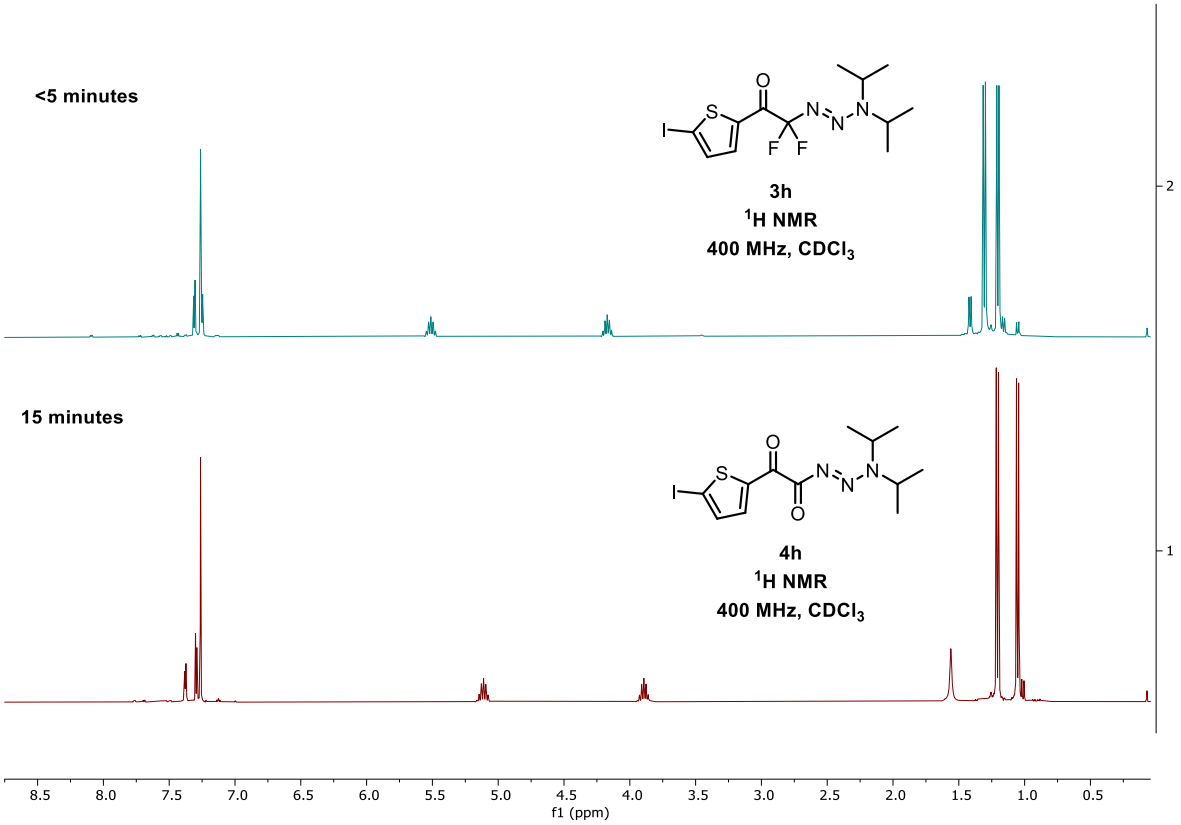
3h
^{19}F NMR
376 MHz, $CDCl_3$

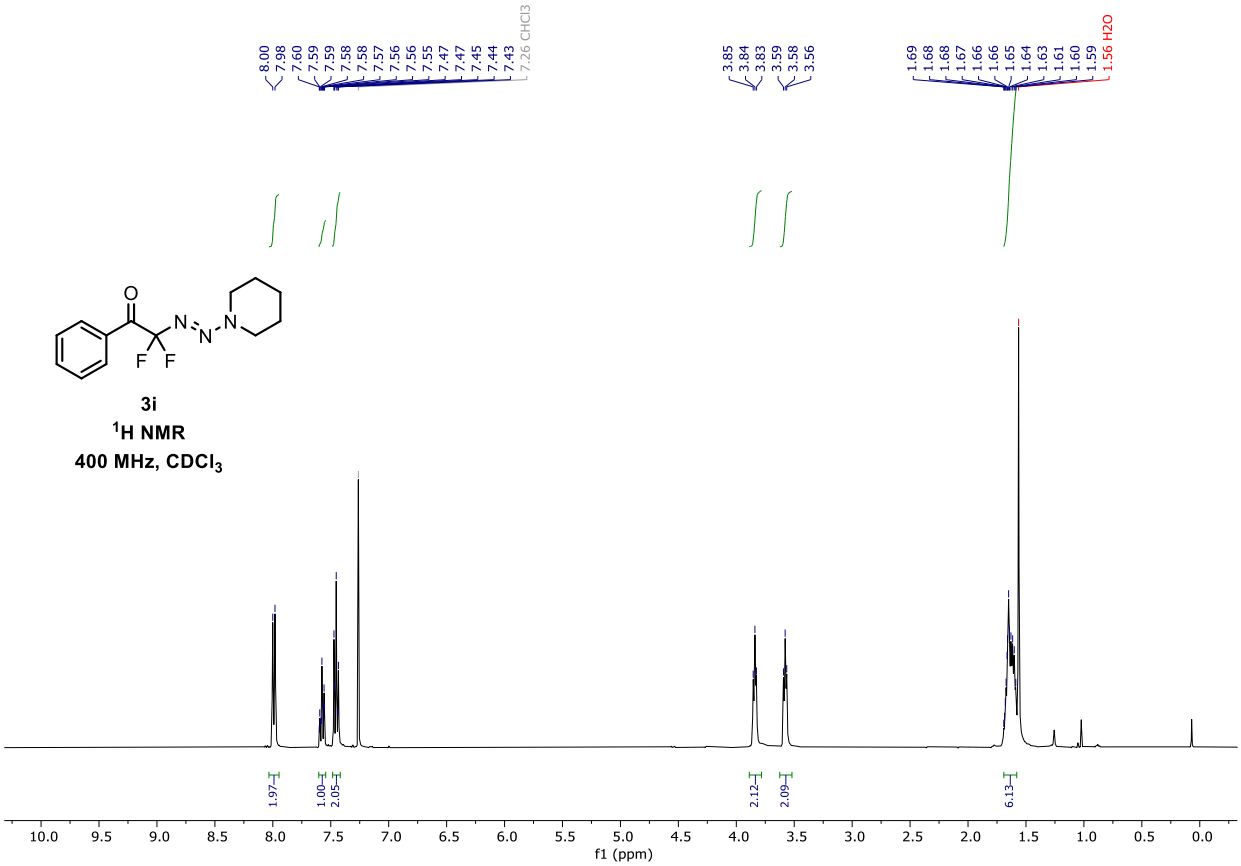


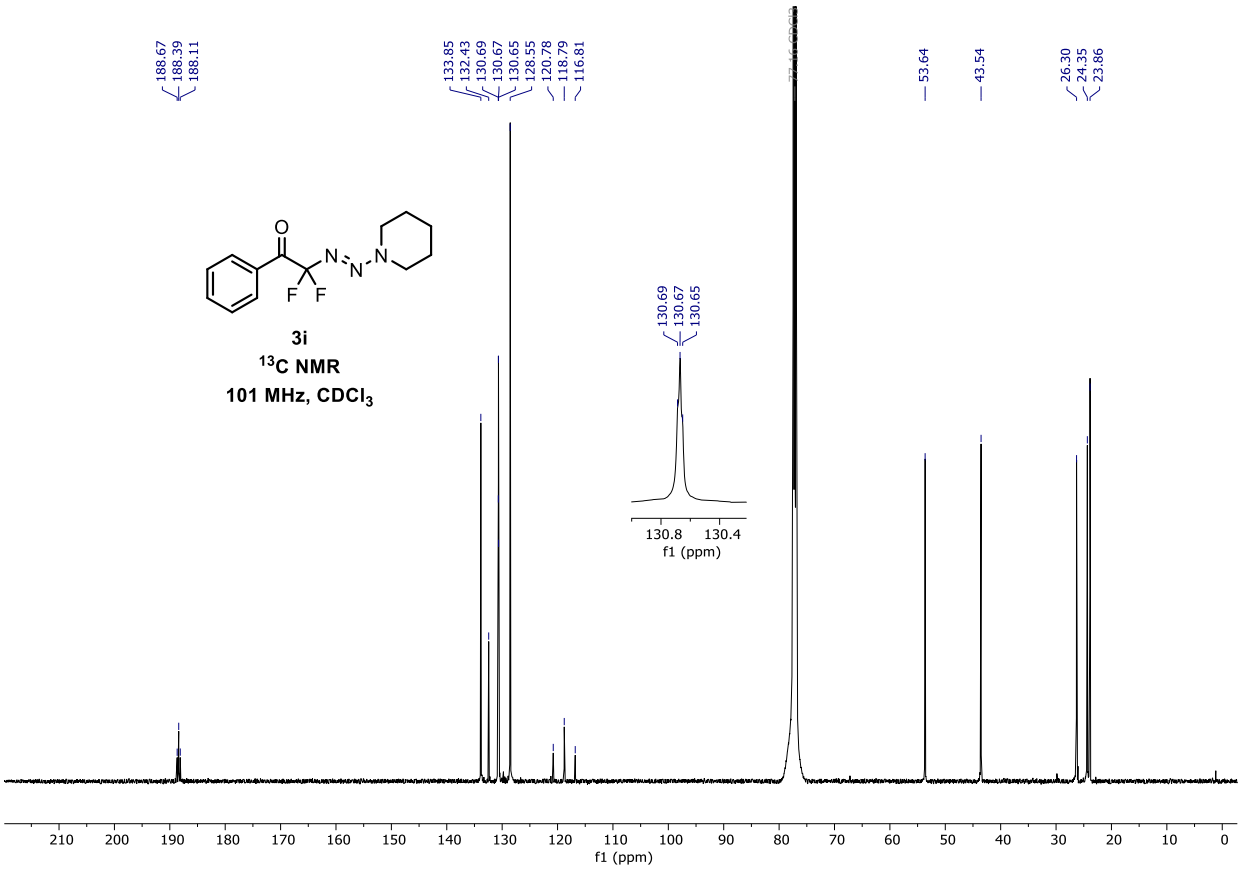
4h
^{1}H NMR
400 MHz, $CDCl_3$
(Decomposed from 3h)



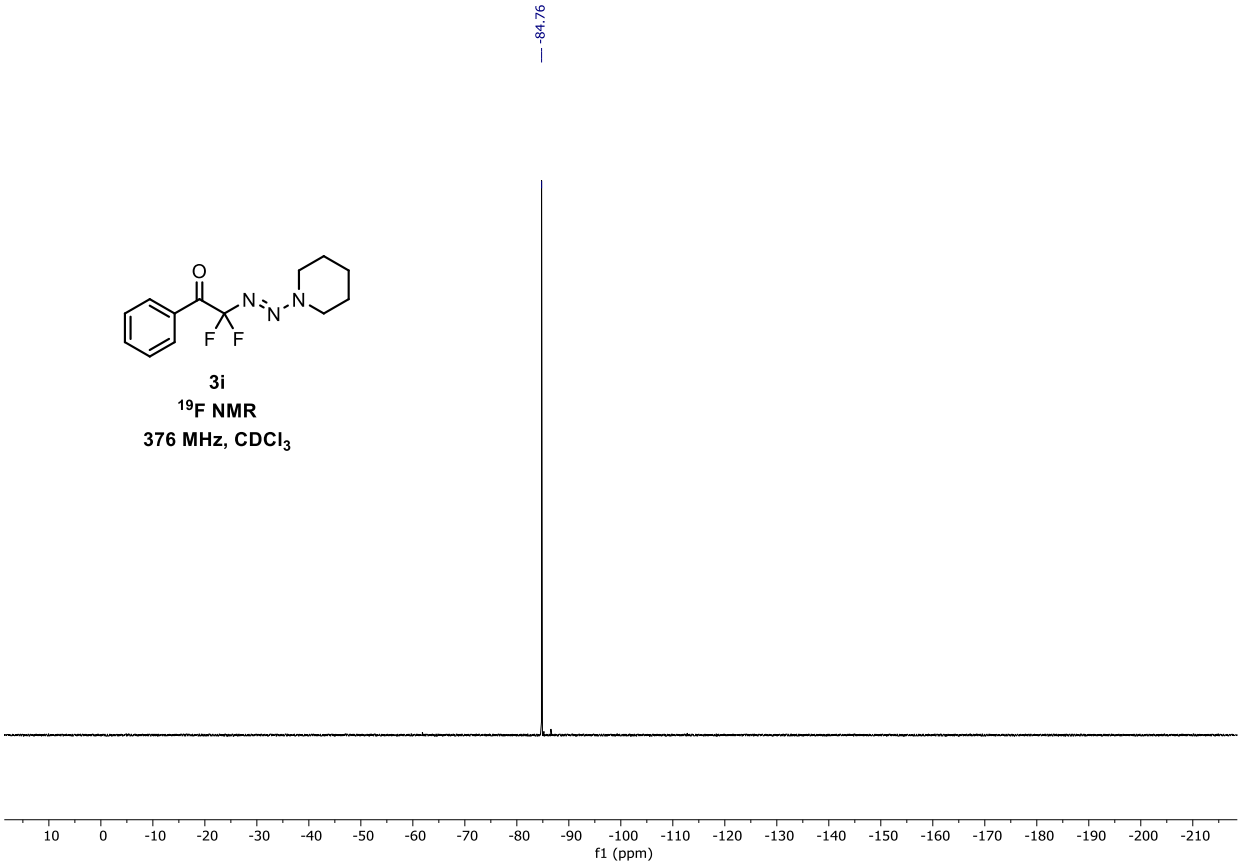
4h
^{13}C NMR
400 MHz, $CDCl_3$
(Decomposed from 3h)


<5 minutes
3h
1H NMR
400 MHz, CDCl3
15 minutes
4h
1H NMR
400 MHz, CDCl3
f1 (ppm)

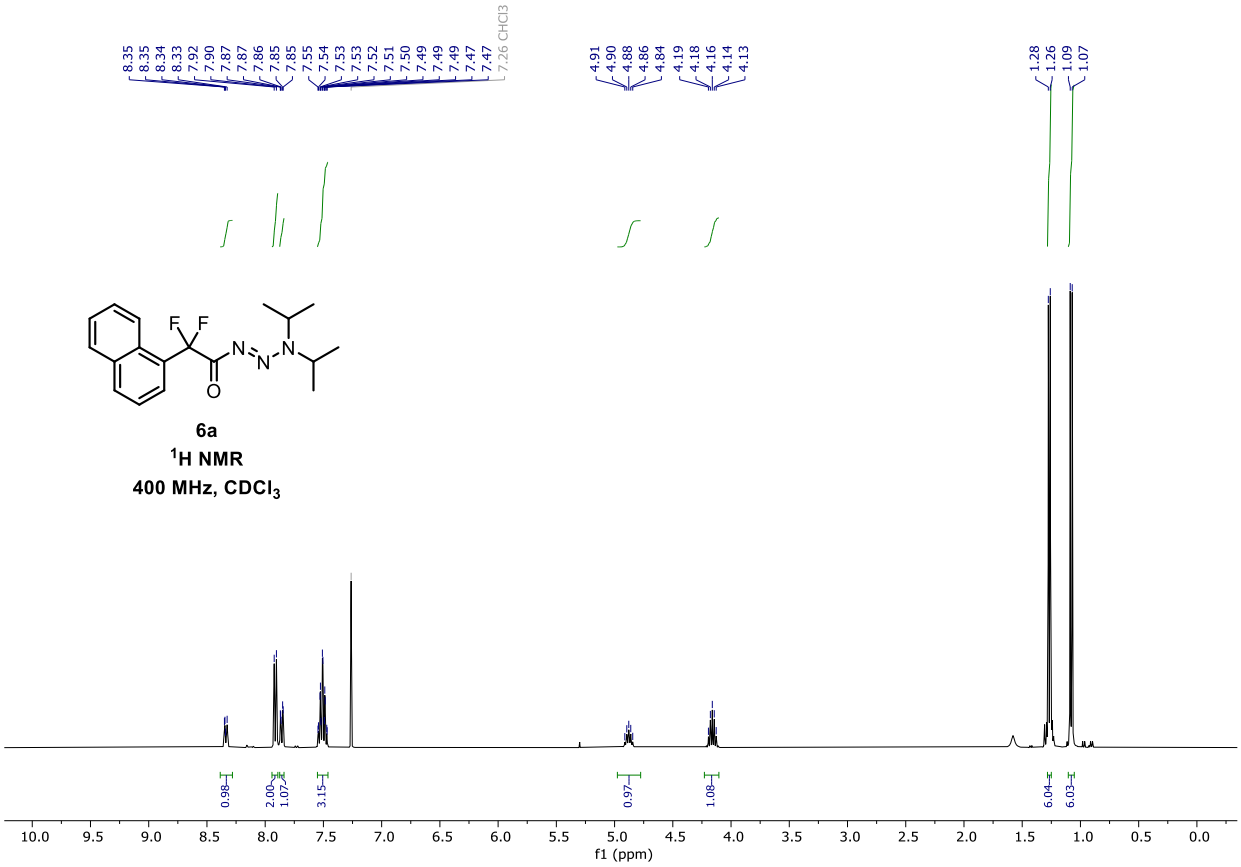

3i
1H NMR
400 MHz, CDCl3
f1 (ppm)

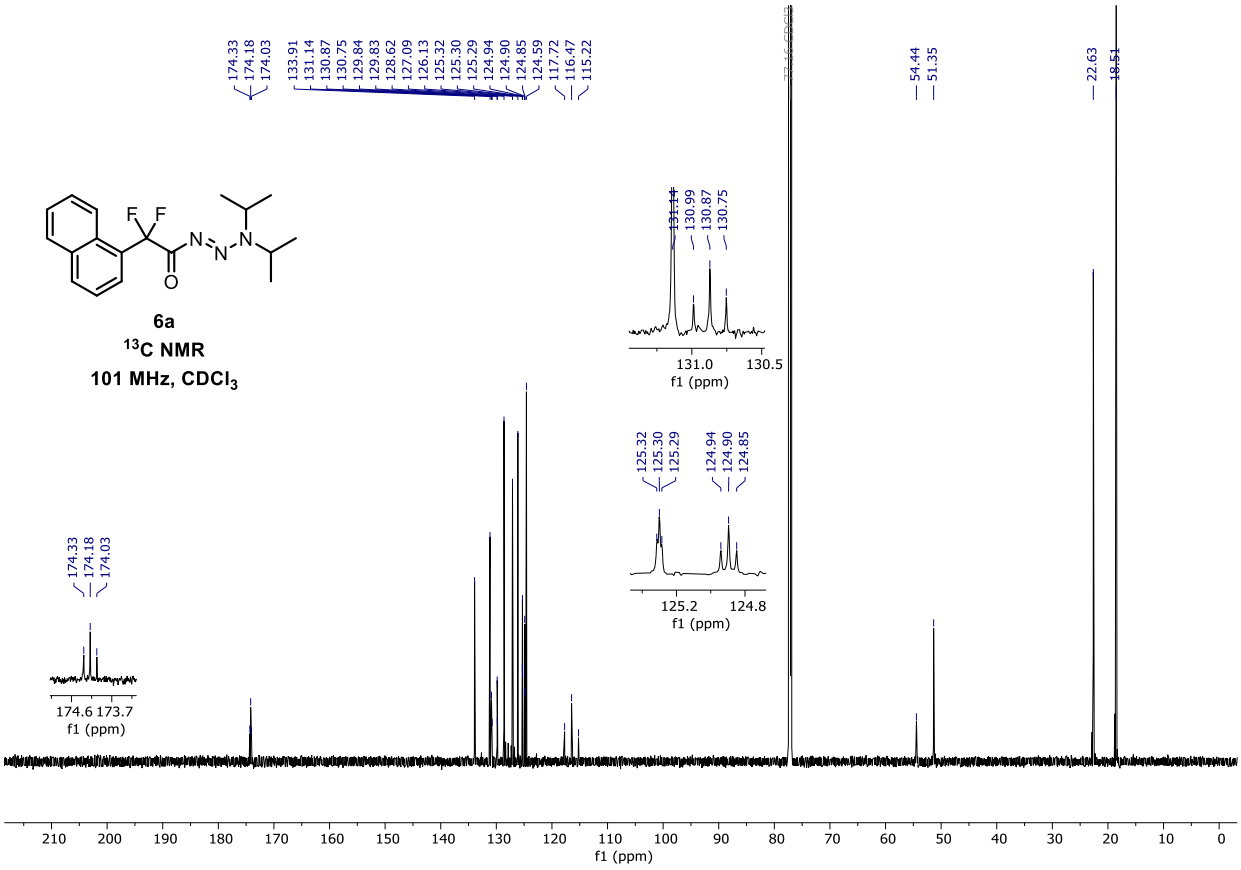


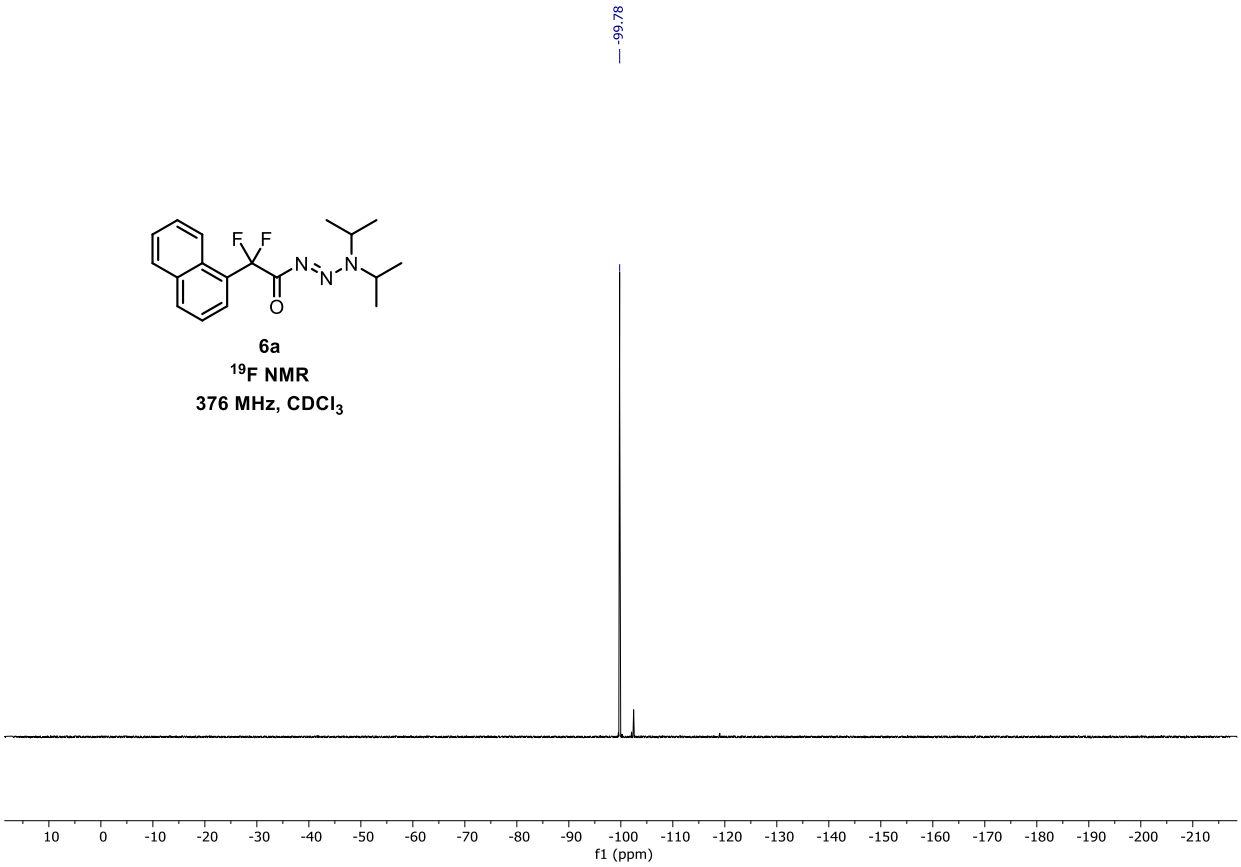
3i
^{13}C NMR
101 MHz, $CDCl_3$



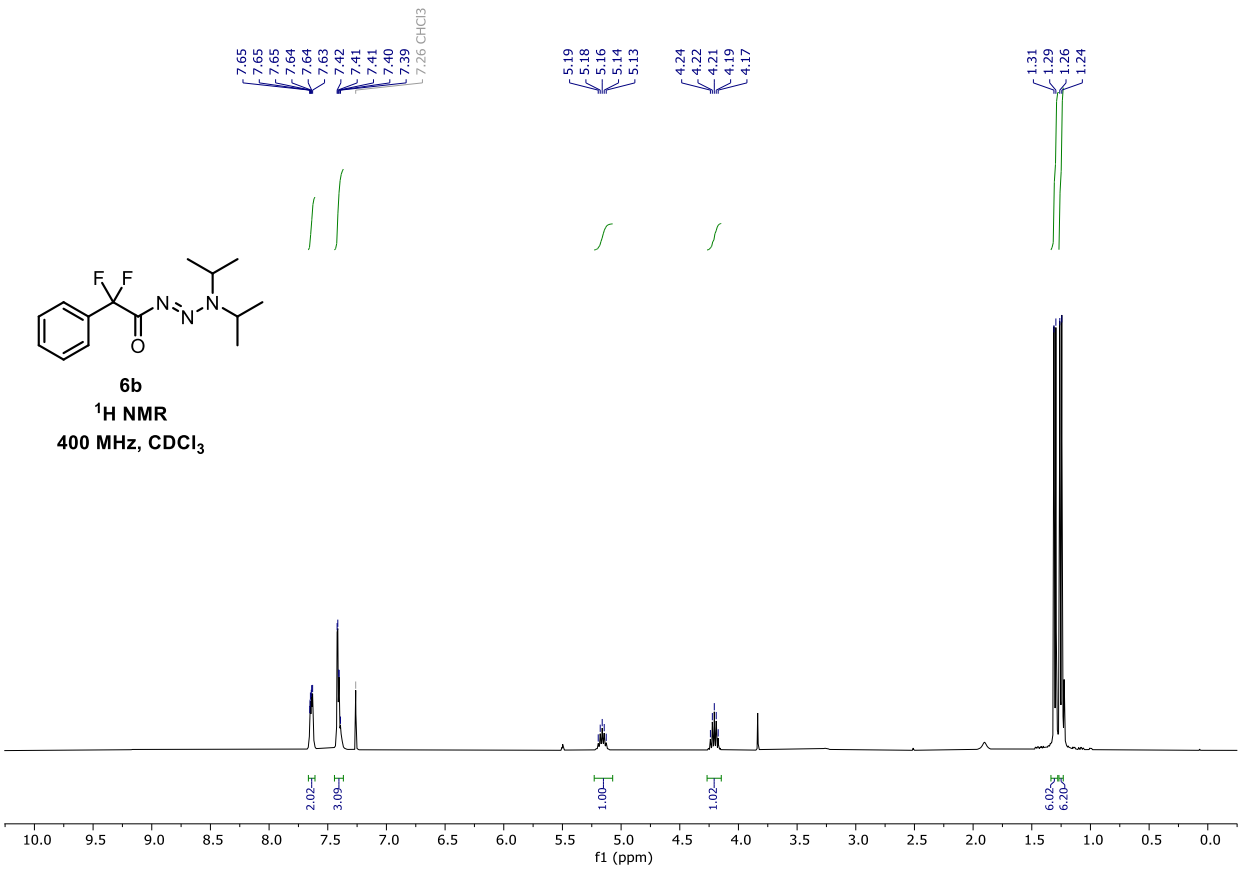
3i
^{19}F NMR
376 MHz, $CDCl_3$


8.35
8.35
8.34
8.33
7.92
7.90
7.87
7.87
7.86
7.85
7.85
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.49
7.49
7.47
7.47
7.26 CHCl3
4.91
4.90
4.88
4.86
4.84
4.19
4.18
4.16
4.14
4.13
1.28
1.26
1.09
1.07
F
F
N
N
N
O
6a
1H NMR
400 MHz, CDCl3
0.98
2.00
1.07
3.15
0.97
1.08
6.04
6.03
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)

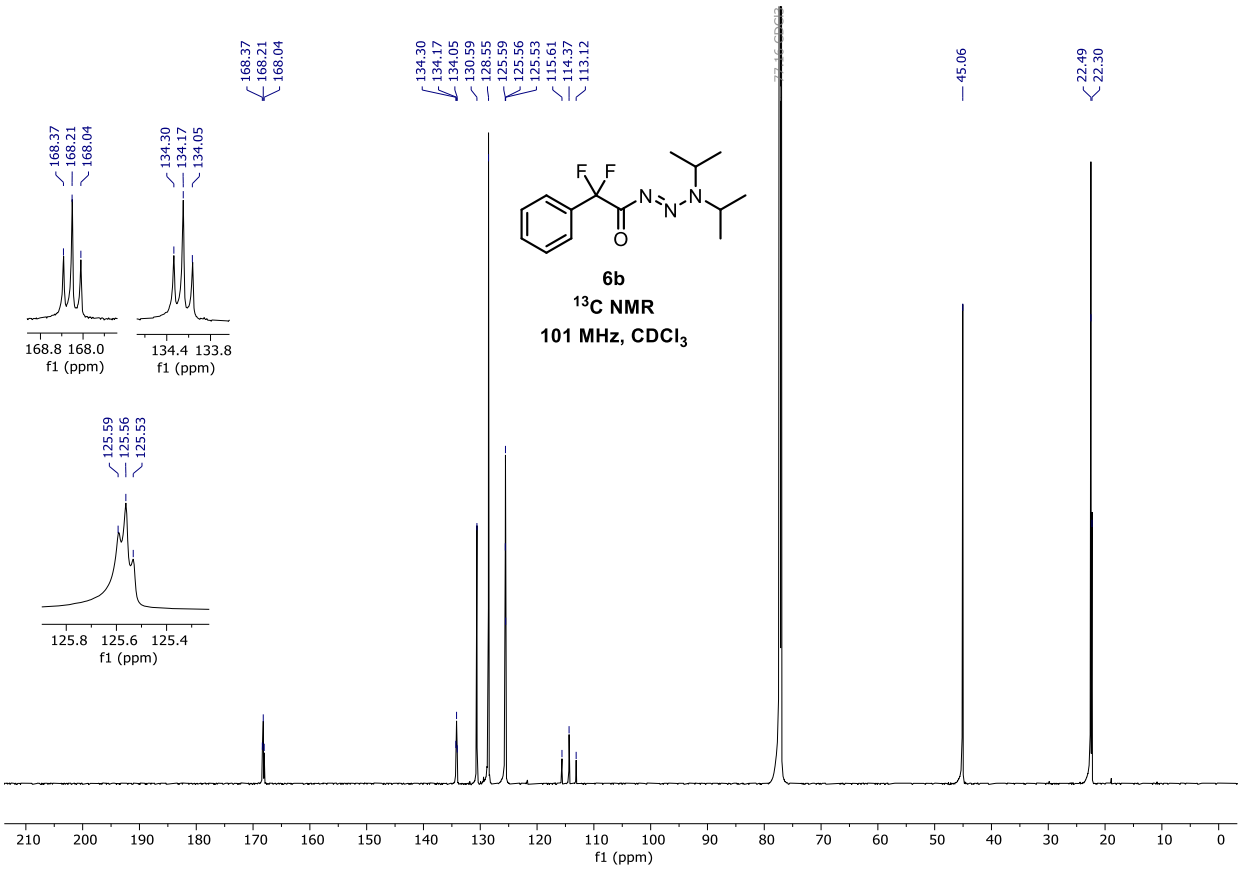

174.33
174.18
174.03
133.91
131.14
130.87
130.75
129.84
129.83
128.62
127.09
126.13
125.32
125.30
125.29
124.94
124.90
124.85
124.59
117.72
116.47
115.22
77.16 CDCl3
54.44
51.35
22.63
19.51
F
F
N
N
N
O
6a
13C NMR
101 MHz, CDCl3
131.14
130.99
130.87
130.75
131.0 130.5
f1 (ppm)
125.32
125.30
125.29
124.94
124.90
124.85
125.2 124.8
f1 (ppm)
174.33
174.18
174.03
174.6 173.7
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

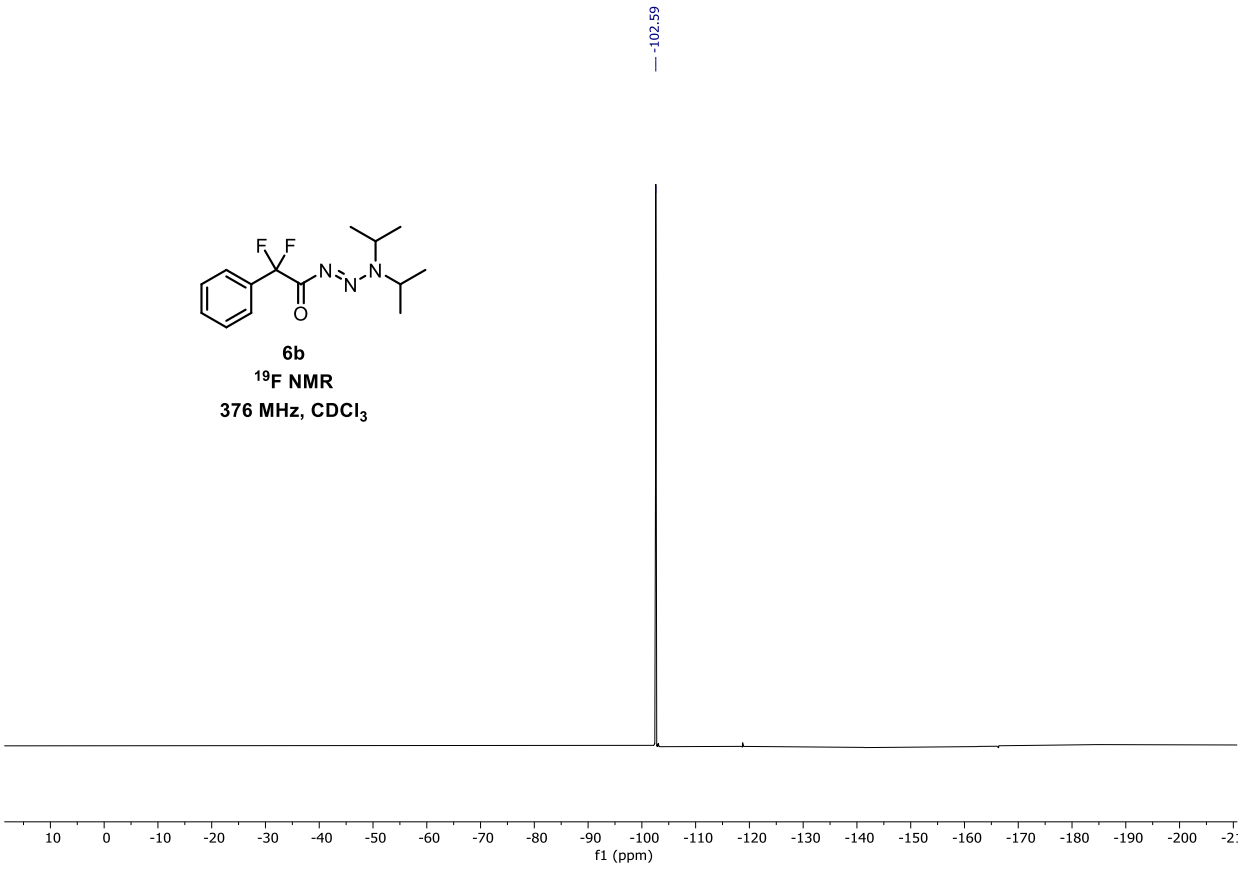


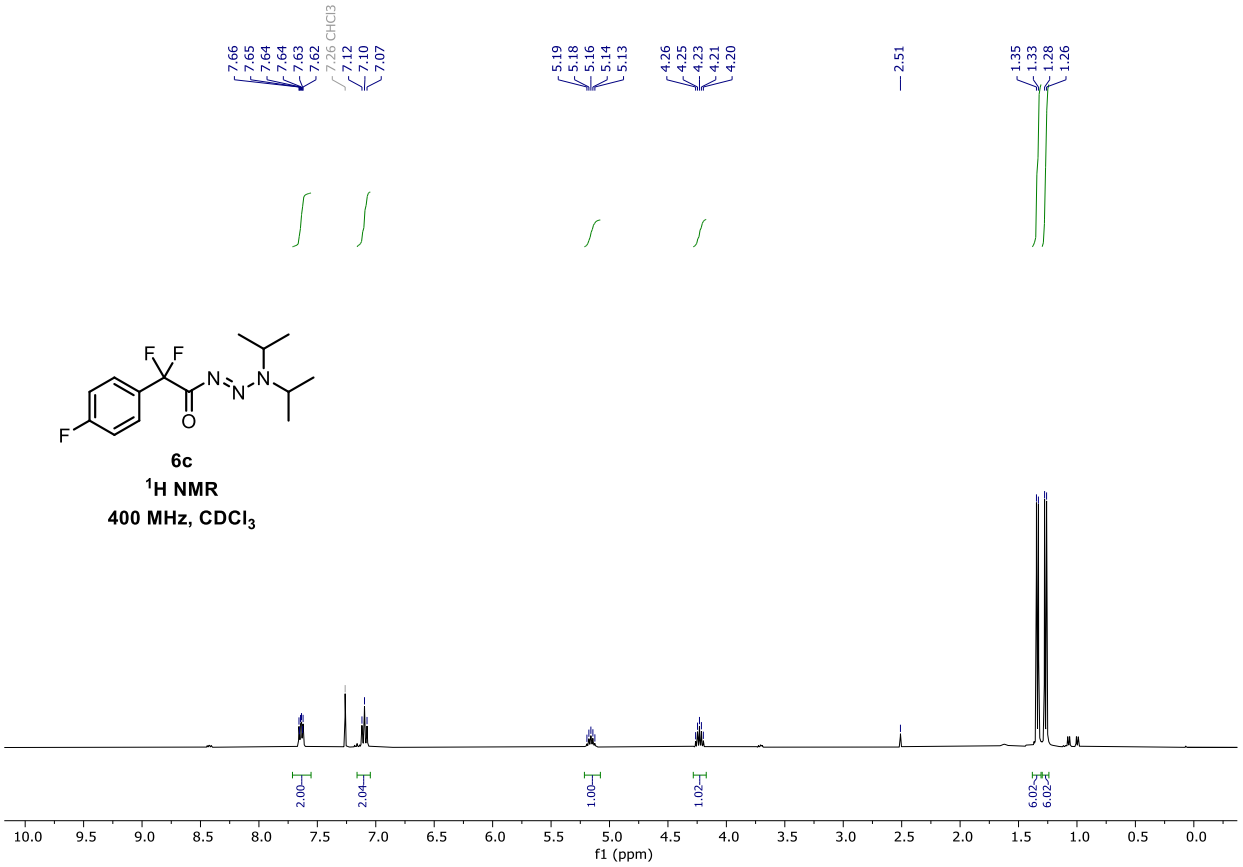
6a
^{19}F NMR
376 MHz, $CDCl_3$

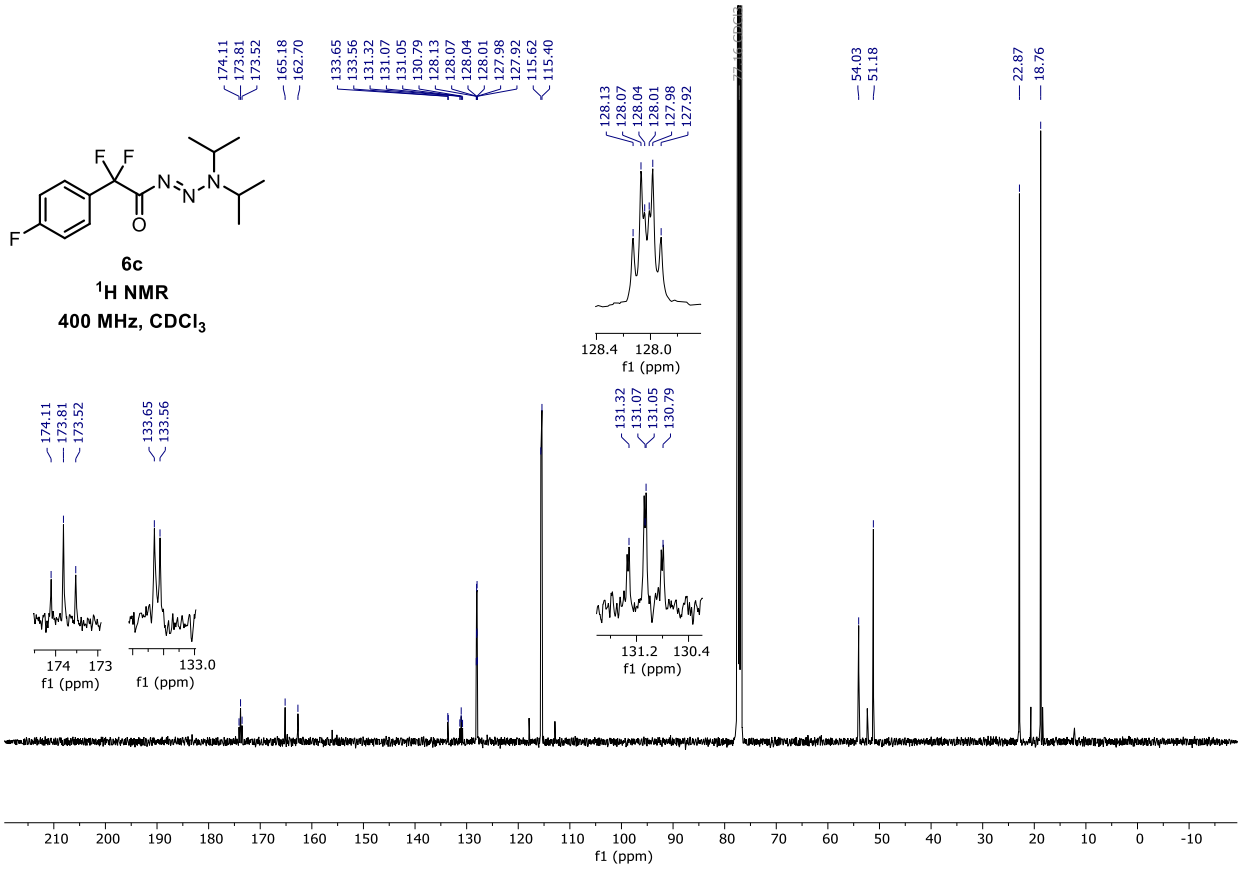


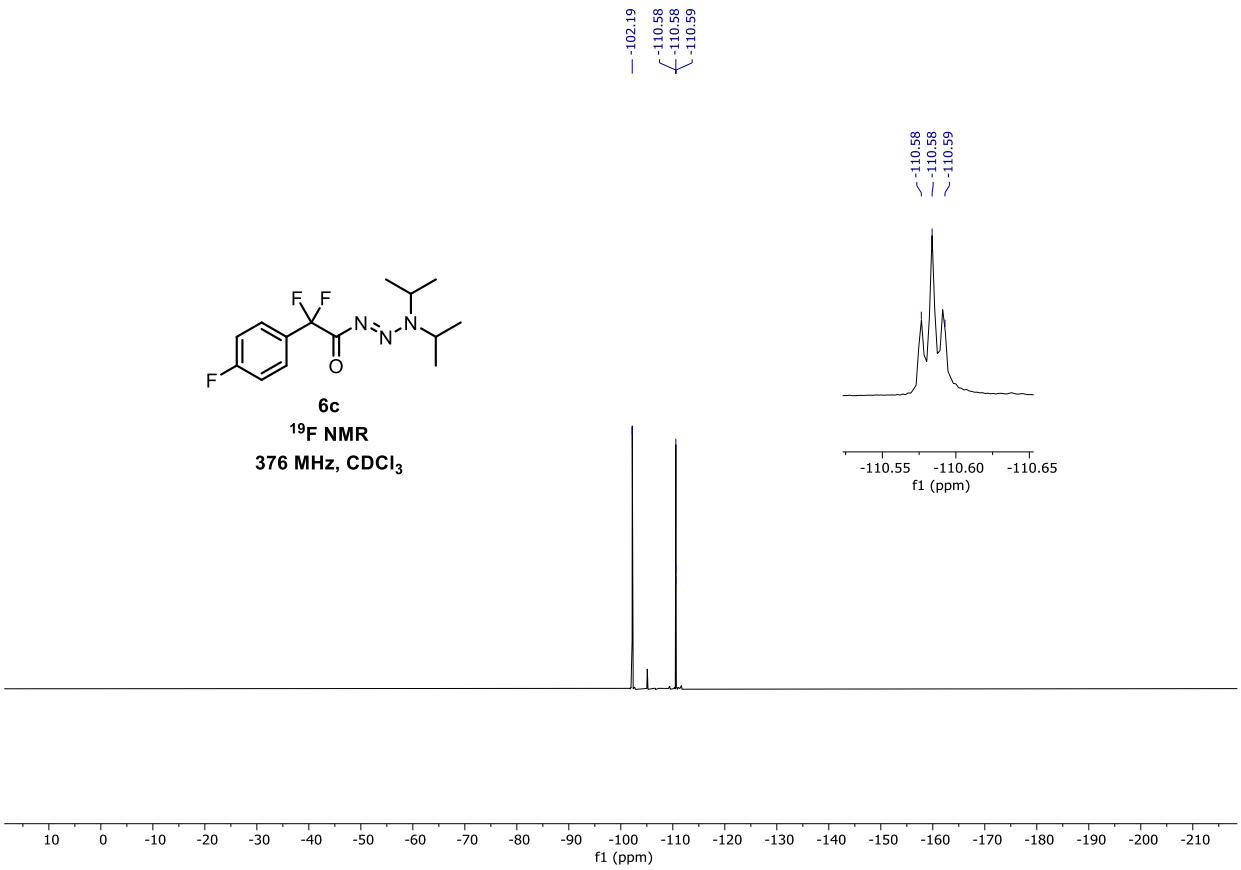
6b
^{1}H NMR
400 MHz, $CDCl_3$


168.37
168.21
168.04
134.30
134.17
134.05
130.59
128.55
125.59
125.56
125.53
115.61
114.37
113.12
77.46 CDCl3
45.06
22.49
22.30
F F
N
N
N
O
6b
13C NMR
101 MHz, CDCl3
168.8 168.0
f1 (ppm)
134.4 133.8
f1 (ppm)
125.8 125.6 125.4
f1 (ppm)
f1 (ppm)

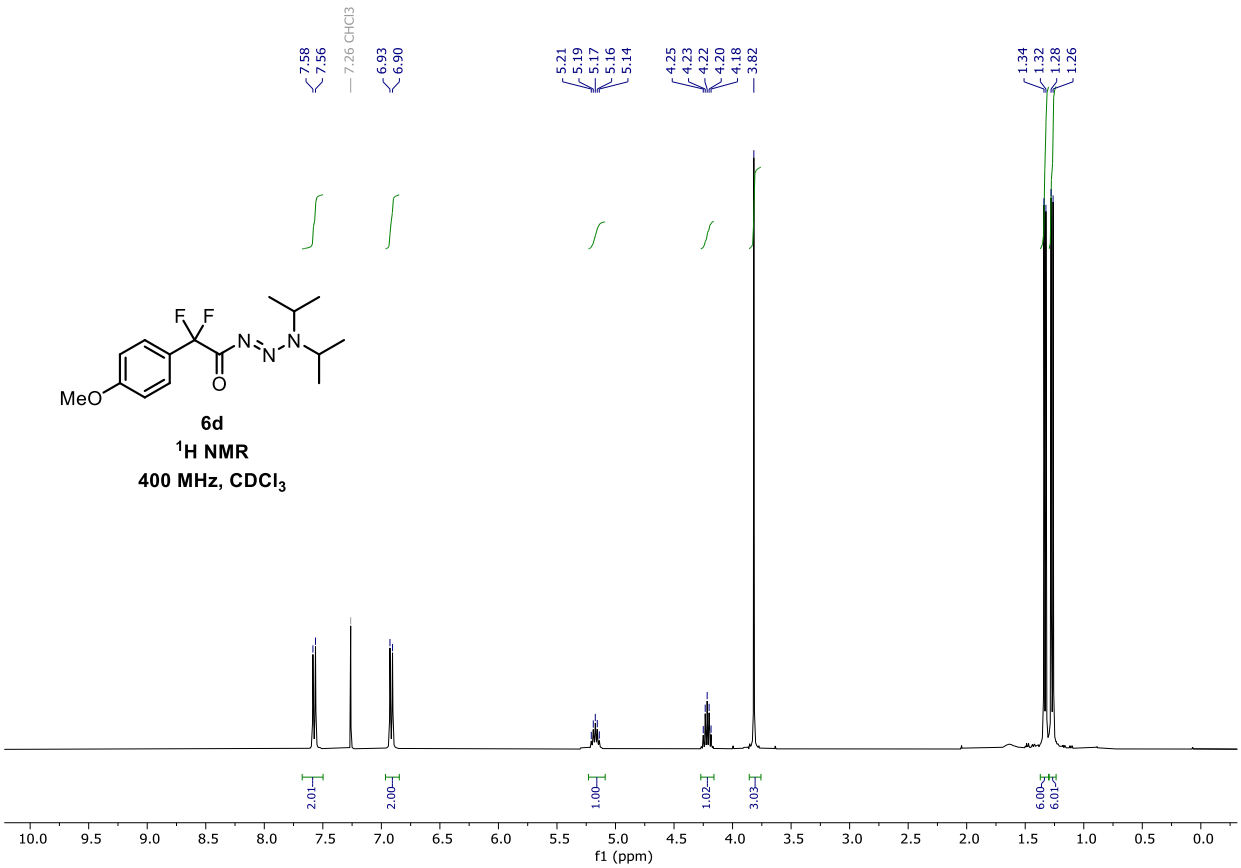

-102.59
F F
N
N
N
O
6b
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.66
7.65
7.64
7.64
7.63
7.62
7.26 CHCl3
7.12
7.10
7.07
5.19
5.18
5.16
5.14
5.13
4.26
4.25
4.23
4.21
4.20
2.51
1.35
1.33
1.28
1.26
F F
N
N
N
O
F
6c
1H NMR
400 MHz, CDCl3
2.00
2.04
1.00
1.02
6.02
6.02
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)

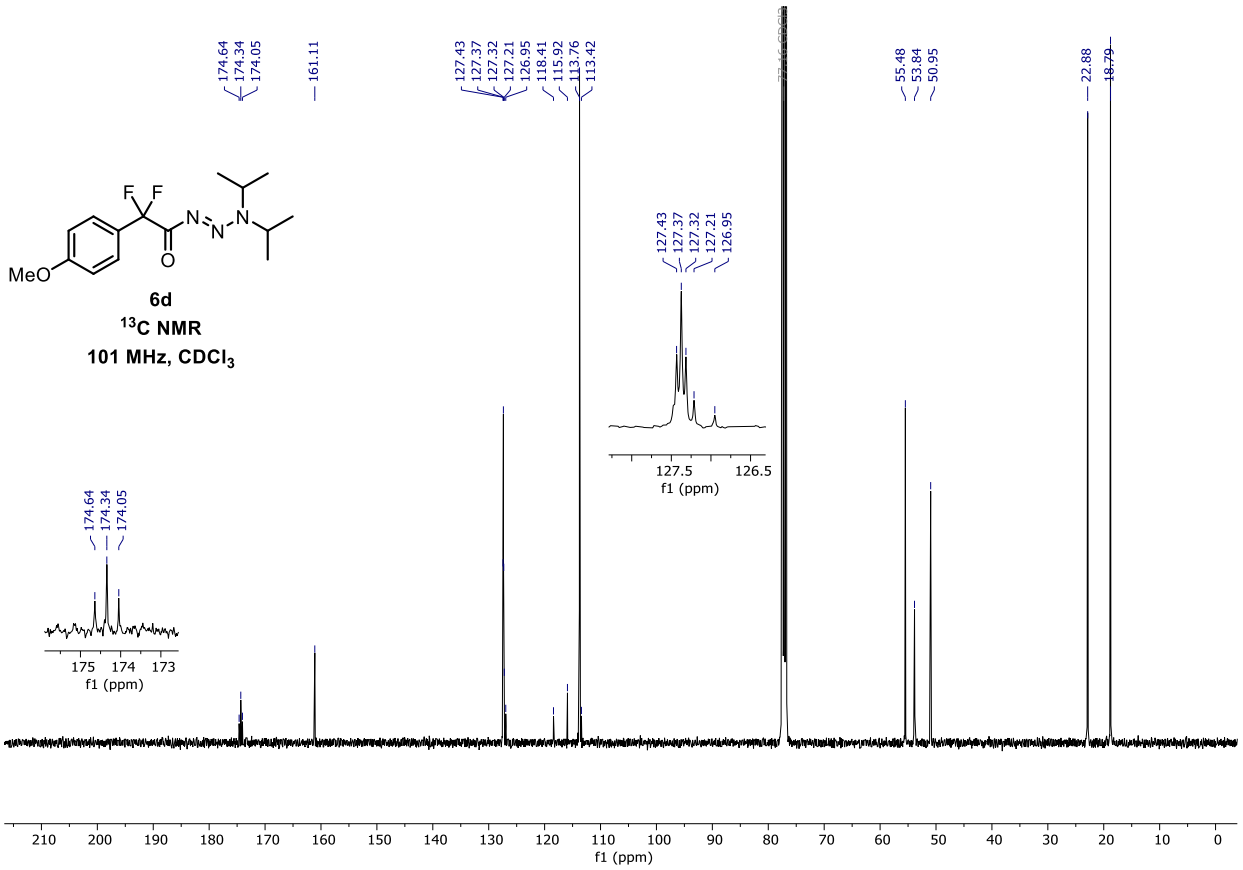

174.11
173.81
173.52
165.18
162.70
133.65
133.56
131.32
131.07
131.05
130.79
128.13
128.07
128.04
128.01
128.04
128.01
127.98
127.92
115.62
115.40
77.16
54.03
51.18
22.87
18.76
F F
N
N
N
O
F
6c
1H NMR
400 MHz, CDCl3
128.13
128.07
128.04
128.01
127.98
127.92
128.4 128.0
f1 (ppm)
174.11
173.81
173.52
174 173
f1 (ppm)
133.65
133.56
133.0
f1 (ppm)
131.32
131.07
131.05
130.79
131.2 130.4
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)



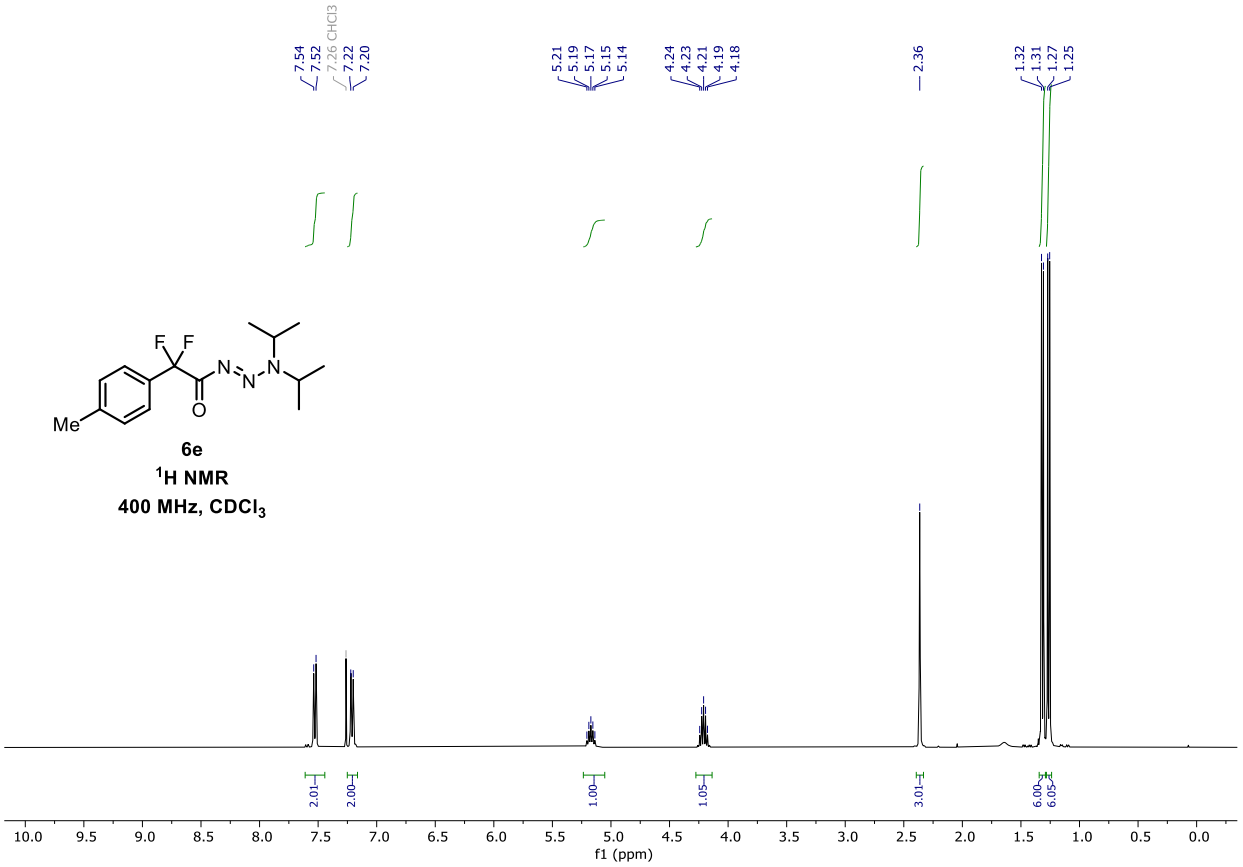
6c
^{19}F NMR
376 MHz, $CDCl_3$



6d
^{1}H NMR
400 MHz, $CDCl_3$


174.64
174.34
174.05
161.11
127.43
127.37
127.32
127.21
126.95
118.41
115.92
113.76
113.42
55.48
53.84
50.95
22.88
18.79
MeO
F F
N
N
N
O
6d
13C NMR
101 MHz, CDCl3
f1 (ppm)

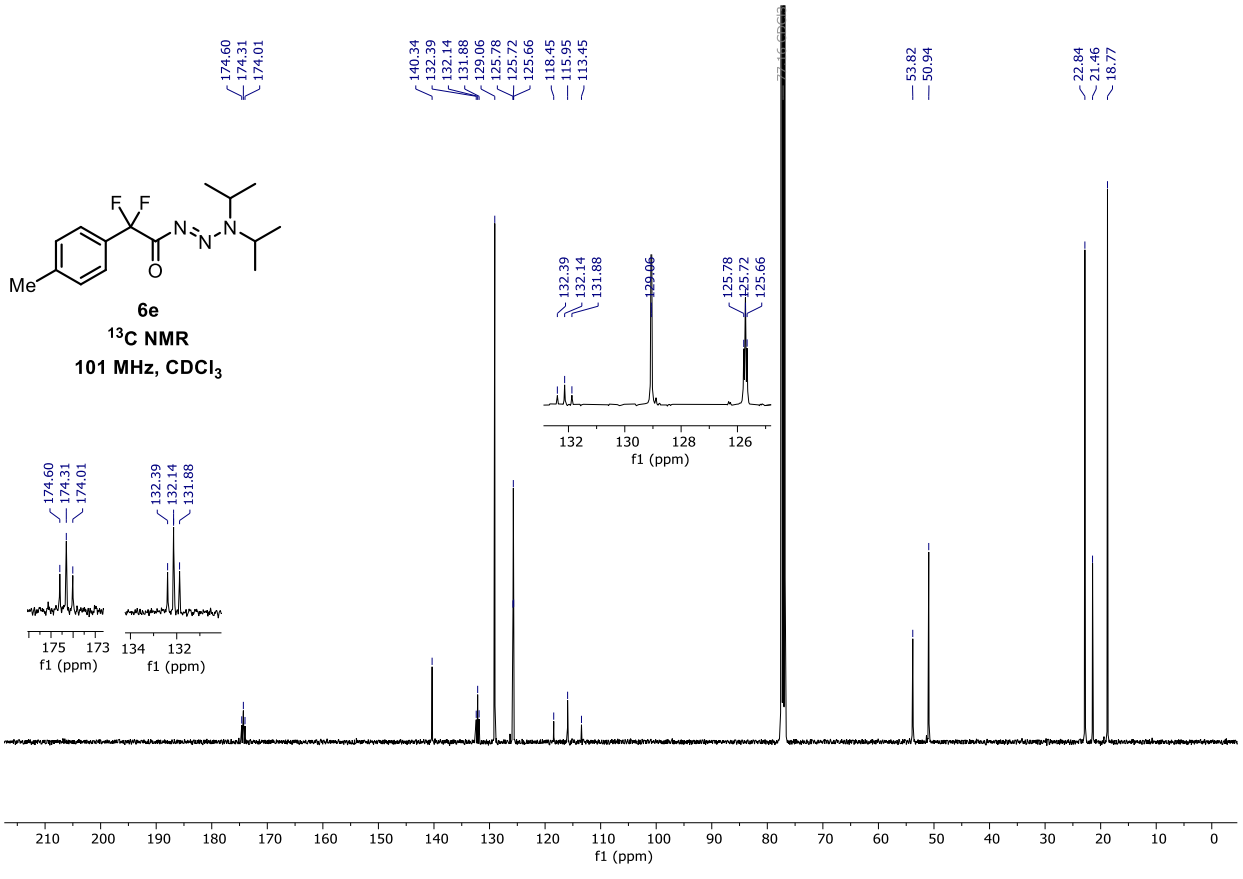

-101.59
MeO
F F
N
N
N
O
6d
19F NMR
376 MHz, CDCl3
f1 (ppm)



6e

^{1}H NMR

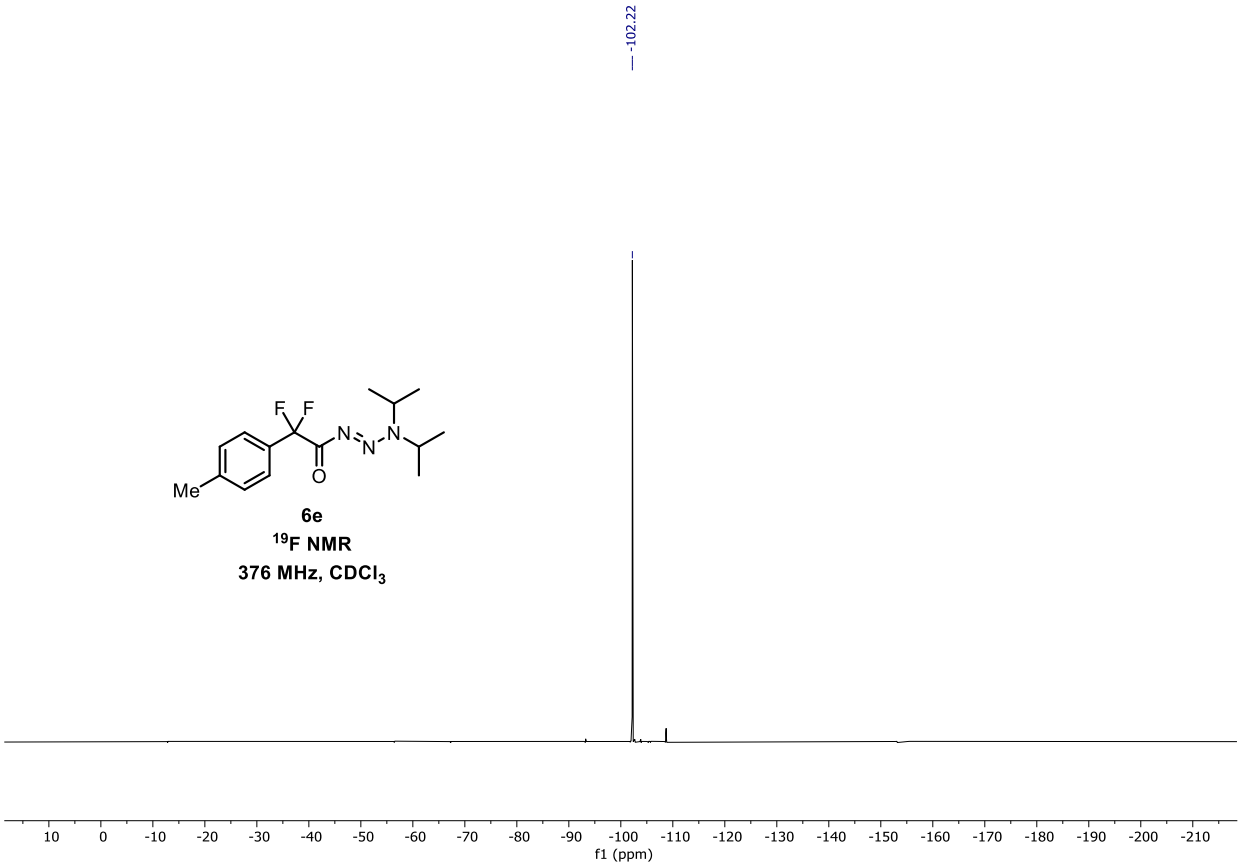
400 MHz, $CDCl_3$



6e

^{13}C NMR

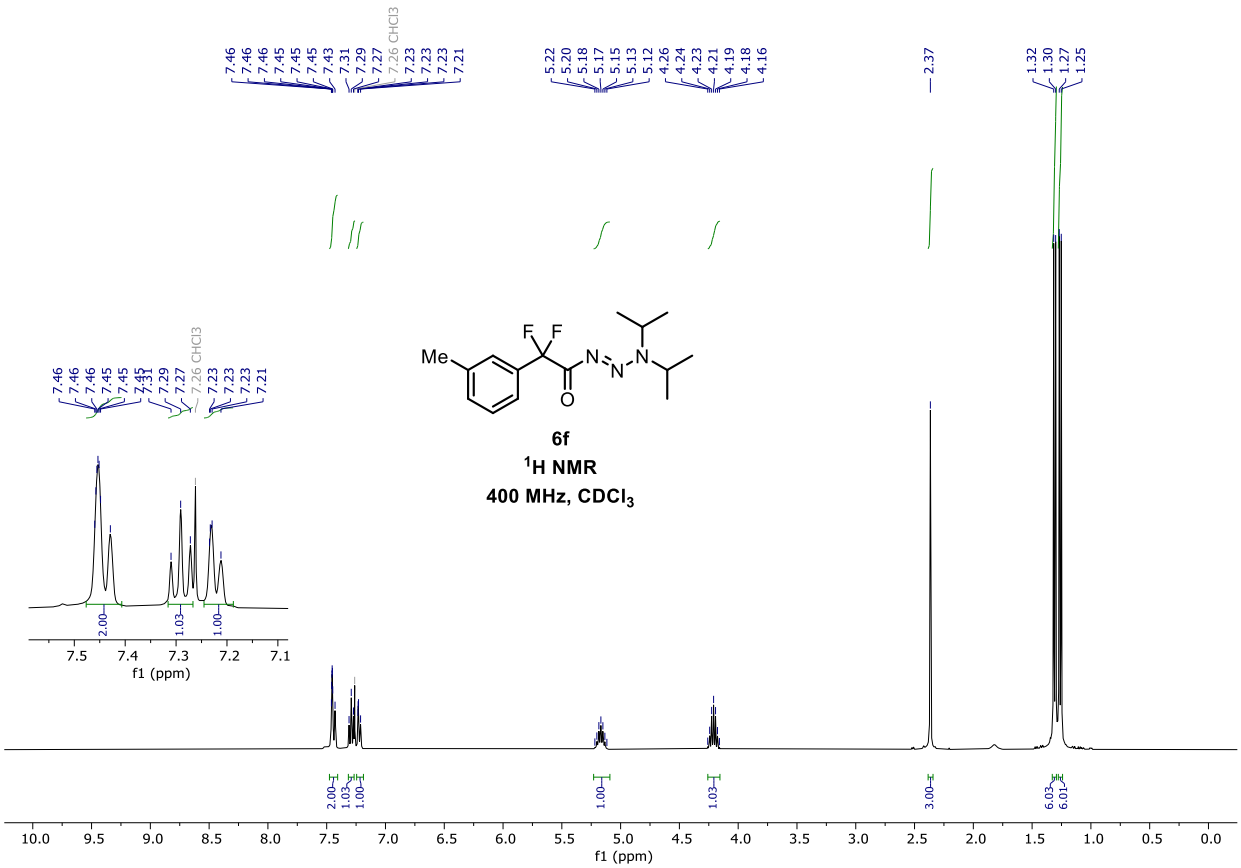
101 MHz, $CDCl_3$



6e

^{19}F NMR

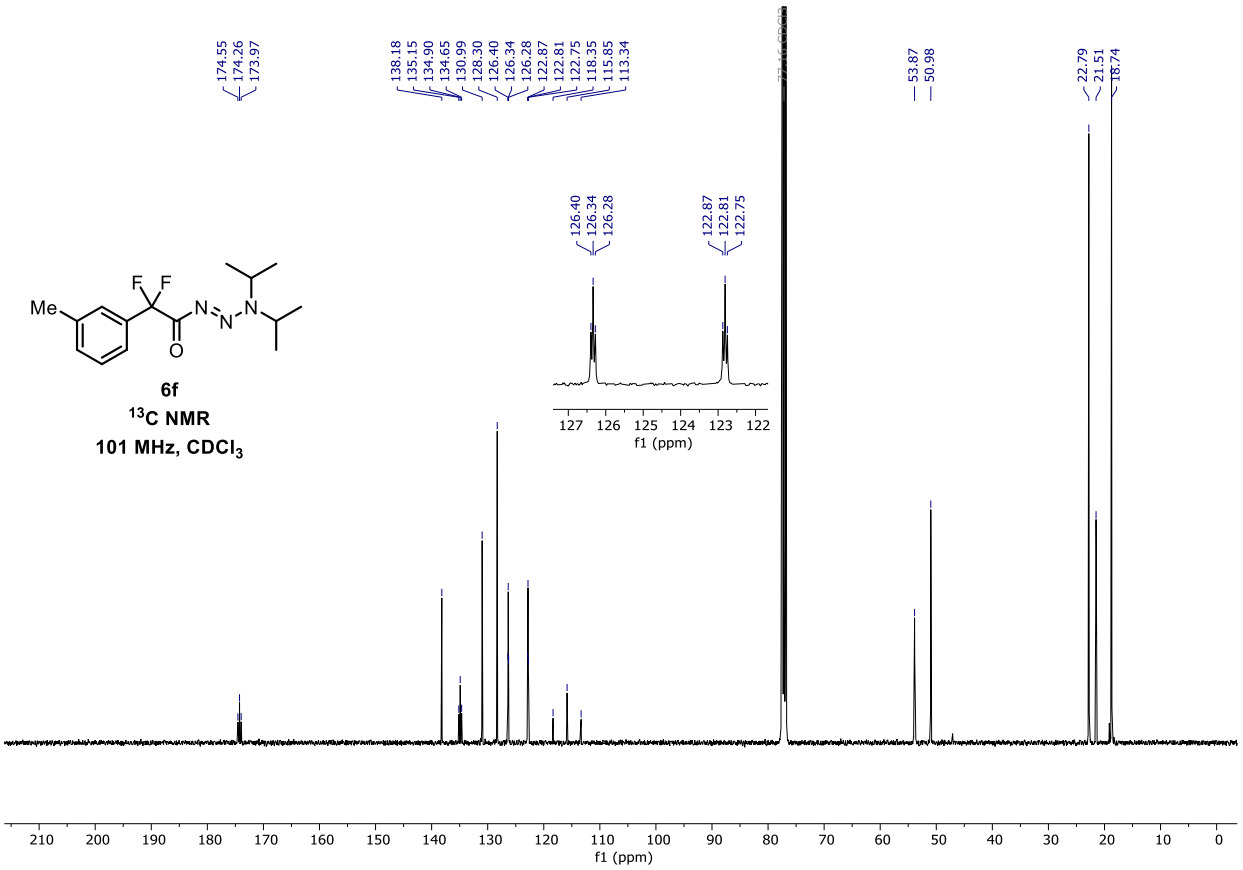
376 MHz, $CDCl_3$



6f

^{1}H NMR

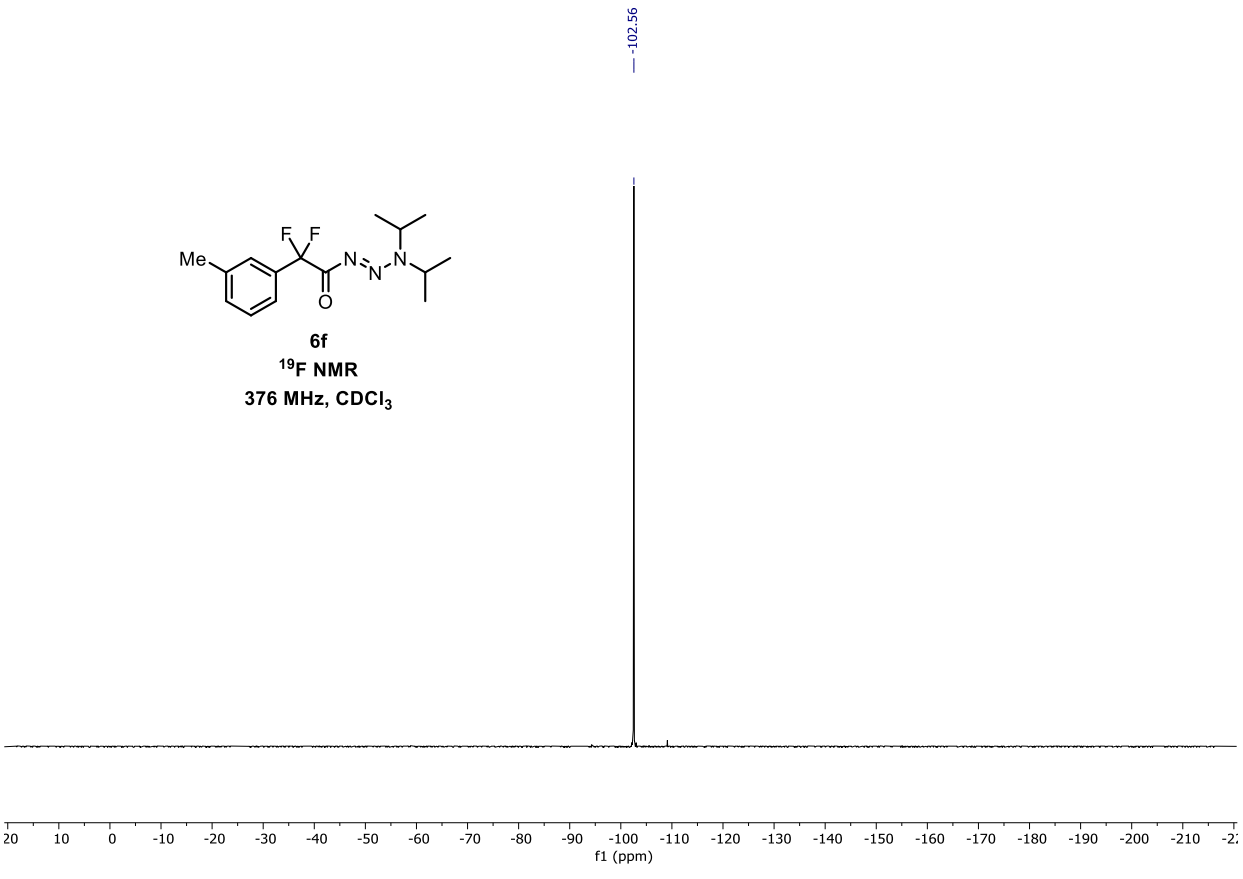
400 MHz, $CDCl_3$



6f

^{13}C NMR

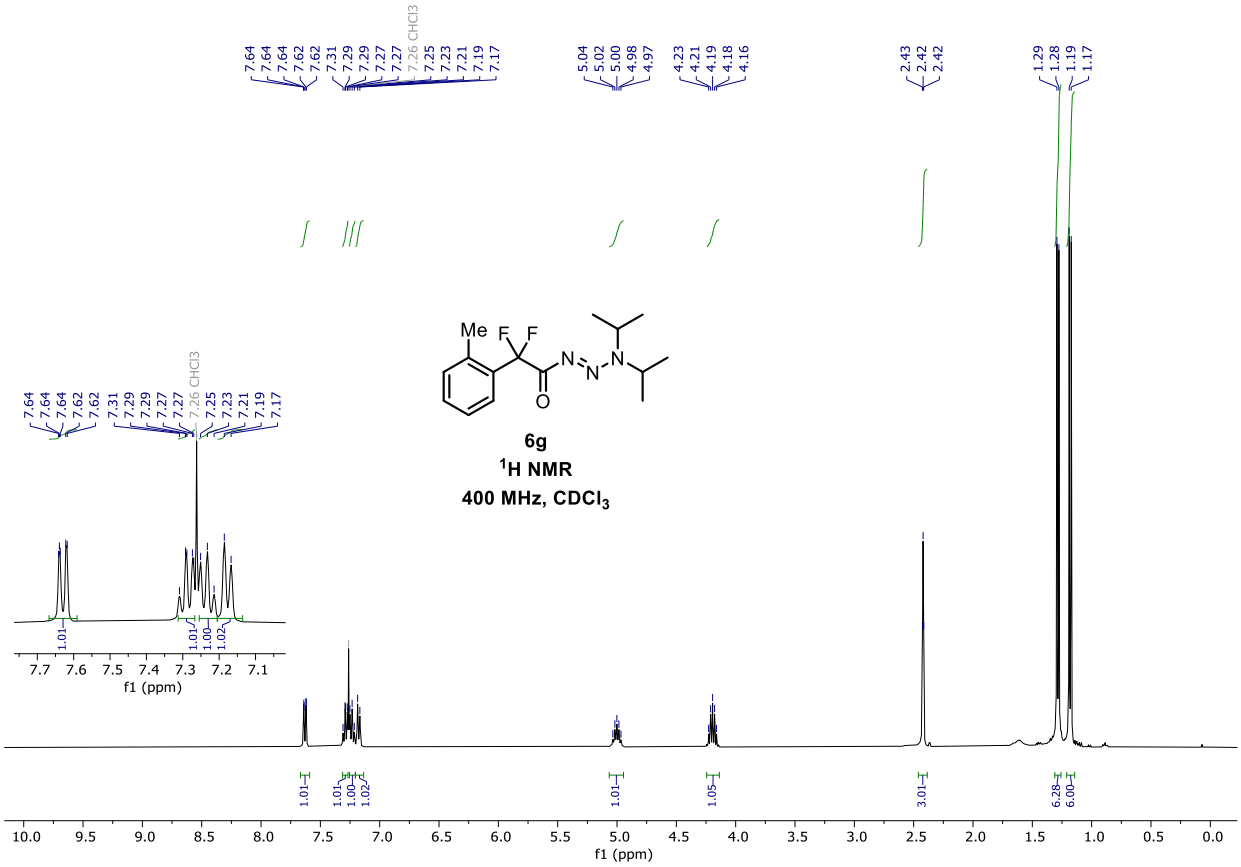
101 MHz, $CDCl_3$

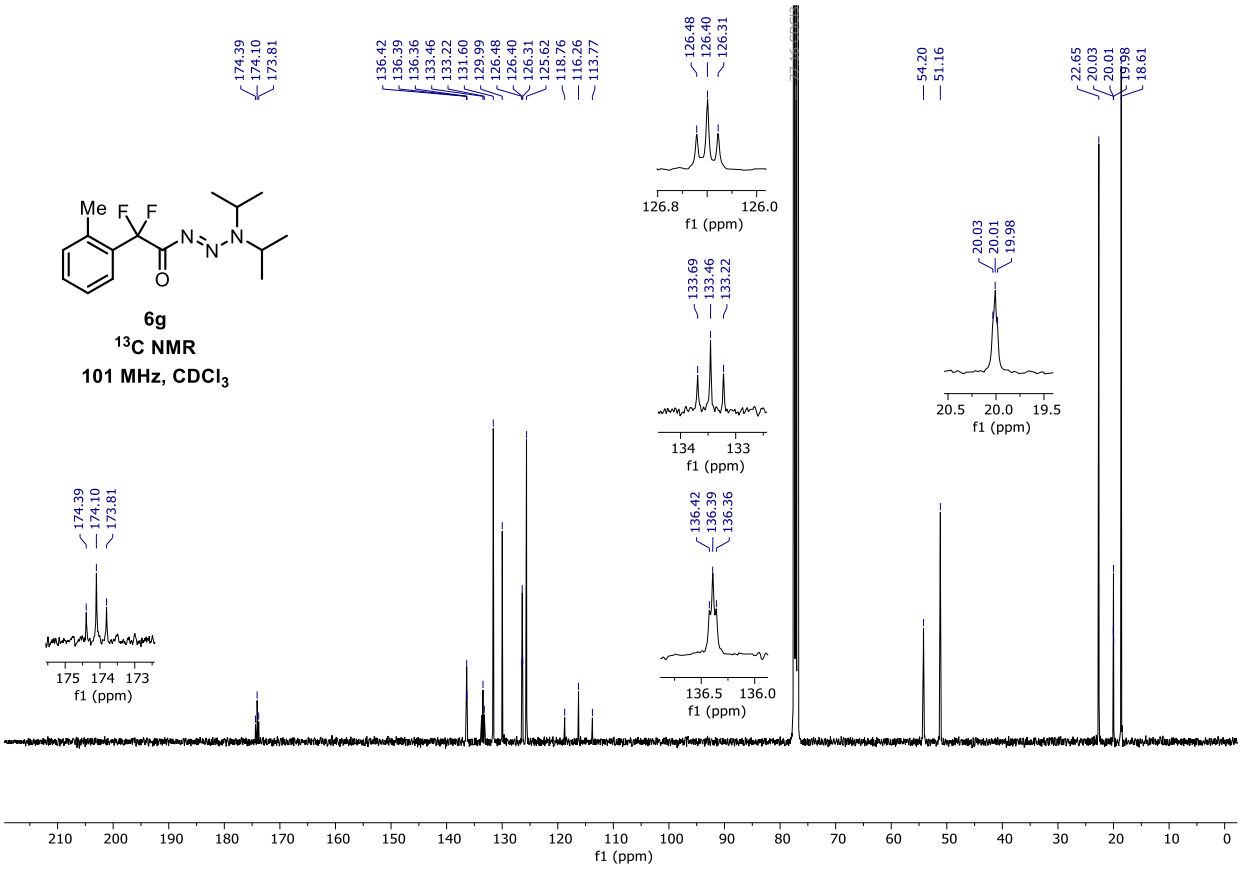


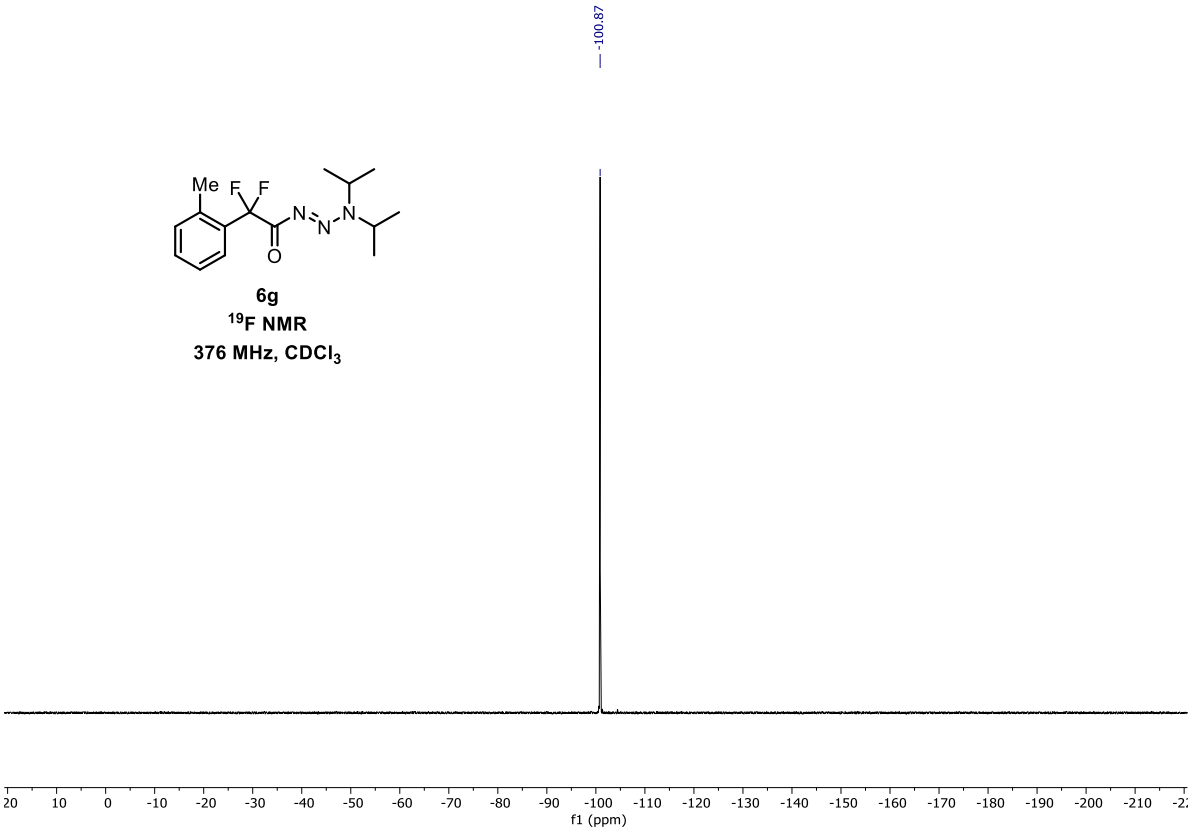
6f

^{19}F NMR

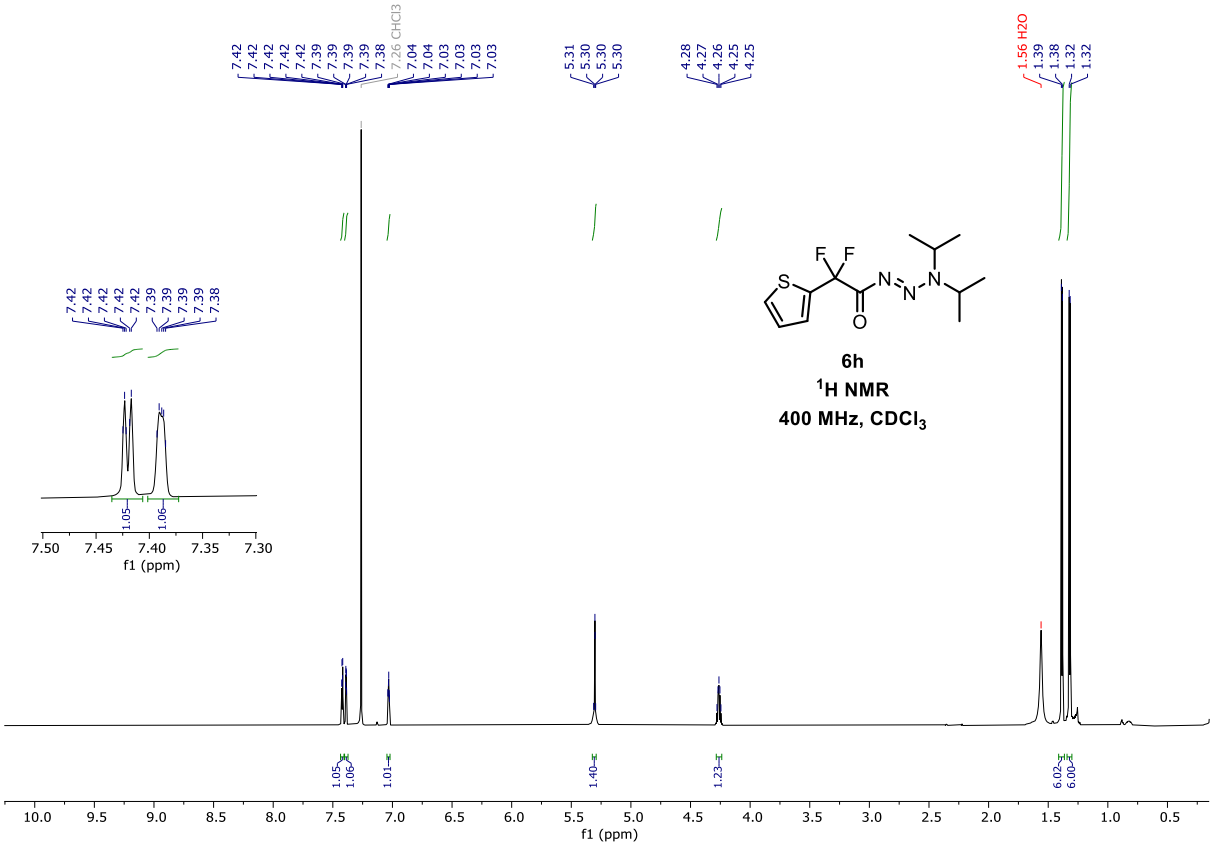
376 MHz, $CDCl_3$


7.64 7.64 7.64 7.62 7.62 7.31 7.29 7.29 7.27 7.27 7.26 CHCl3 7.25 7.23 7.21 7.19 7.17
5.04 5.02 5.00 4.98 4.97 4.23 4.21 4.19 4.18 4.16
2.43 2.42 2.42
1.29 1.28 1.19 1.17
Me F F N N N O
6g
1H NMR
400 MHz, CDCl3
1.01 1.01 1.00 1.02 1.01 1.05 3.01 6.28 6.00
f1 (ppm)

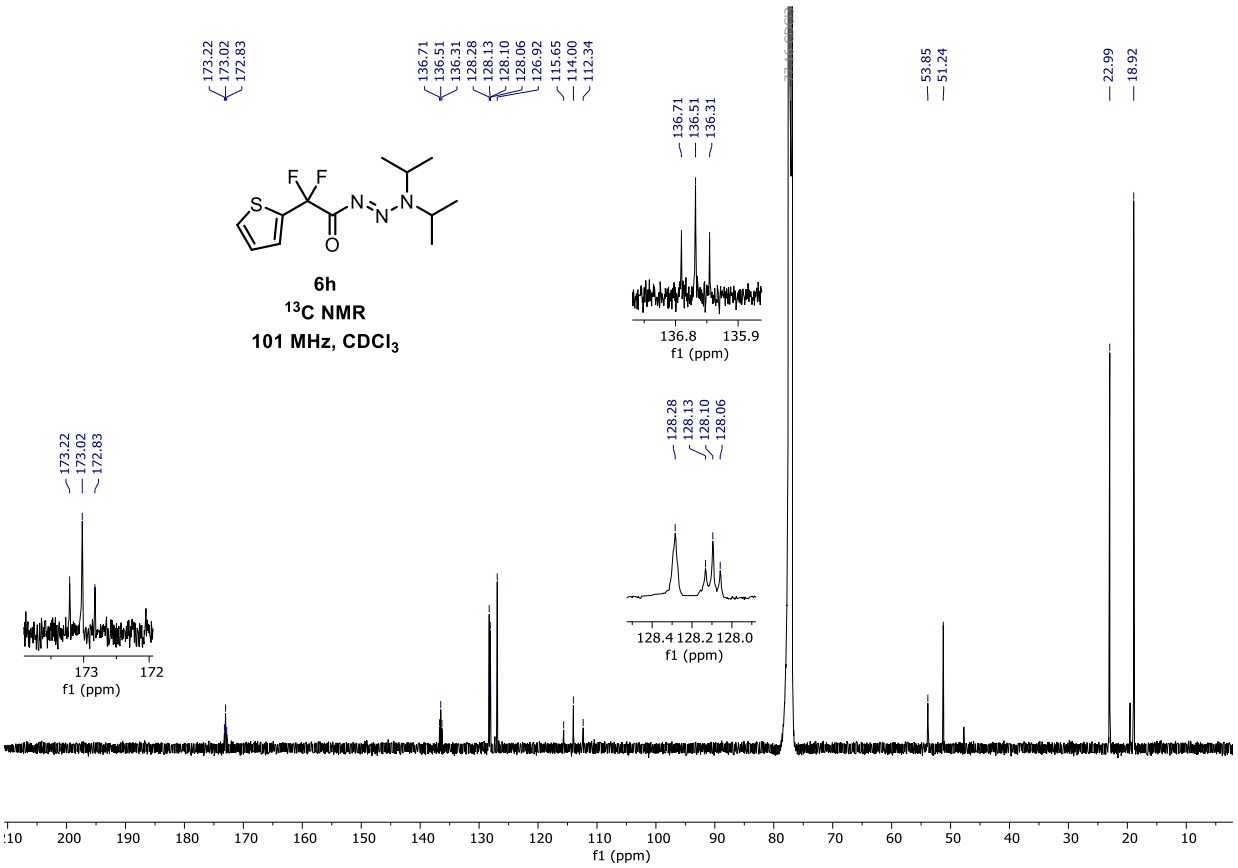

174.39 174.10 173.81
136.42 136.39 136.36 133.46 133.22 131.60 129.99 126.48 126.40 126.31 125.62 118.76 116.26 113.77
126.48 126.40 126.31
77.16 76.99 76.73
54.20 51.16
22.65 20.03 20.01 19.98 18.61
Me F F N N N O
6g
13C NMR
101 MHz, CDCl3
f1 (ppm)

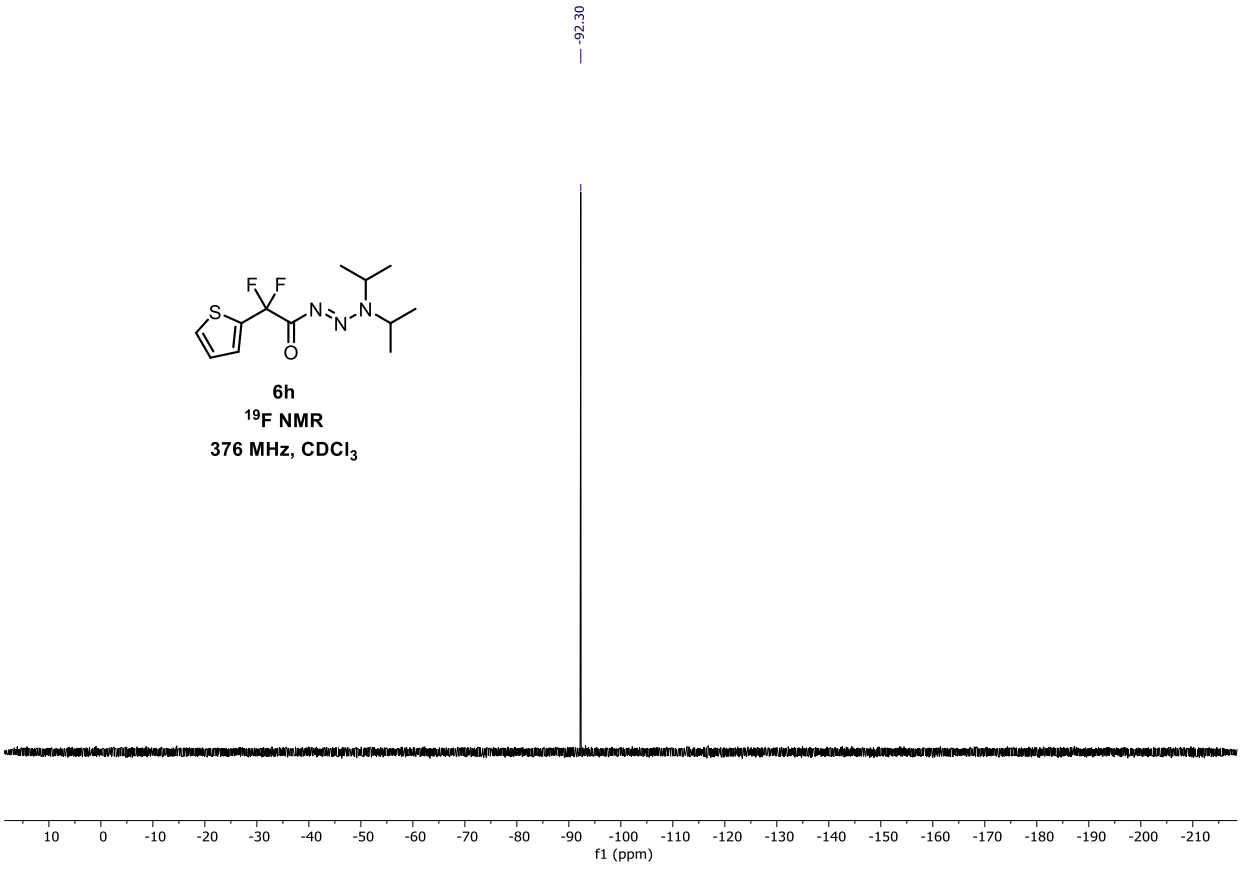


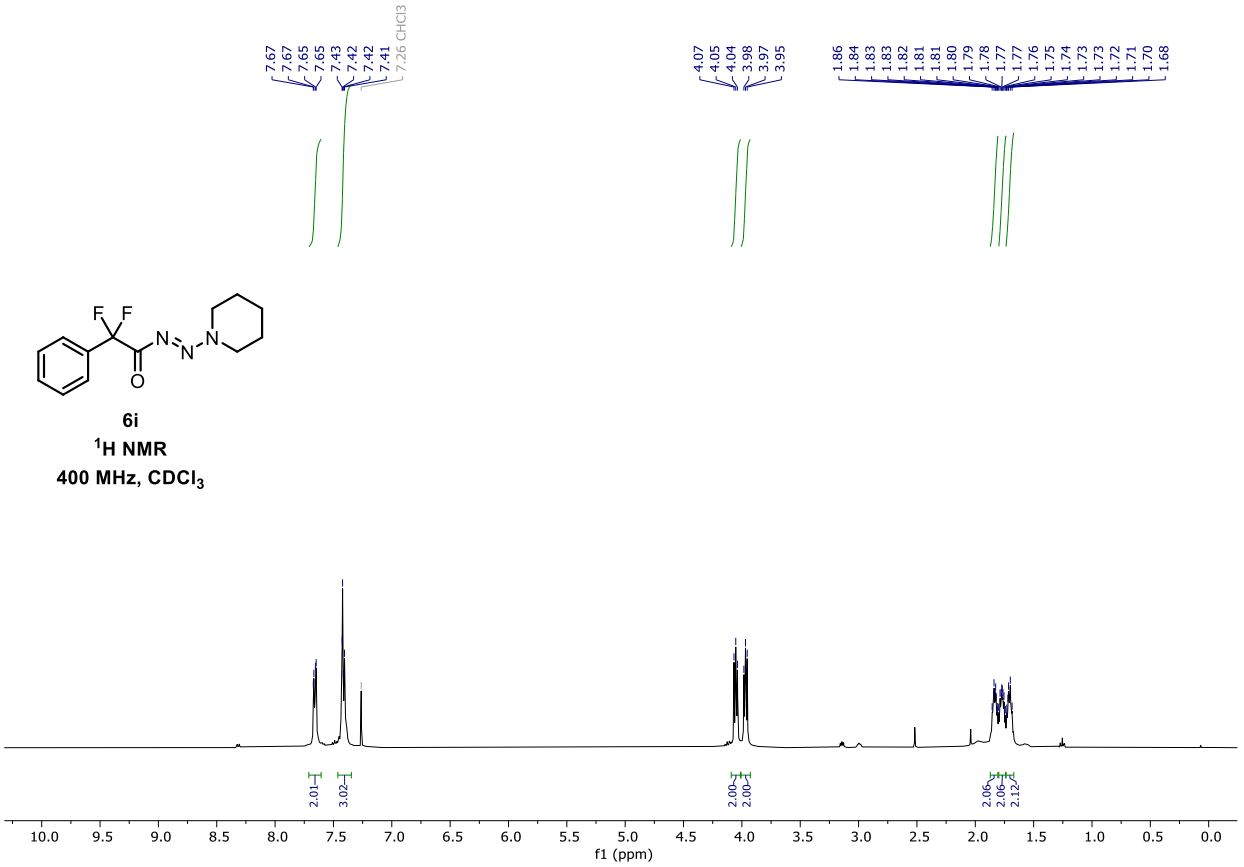
6g
^{19}F NMR
376 MHz, $CDCl_3$

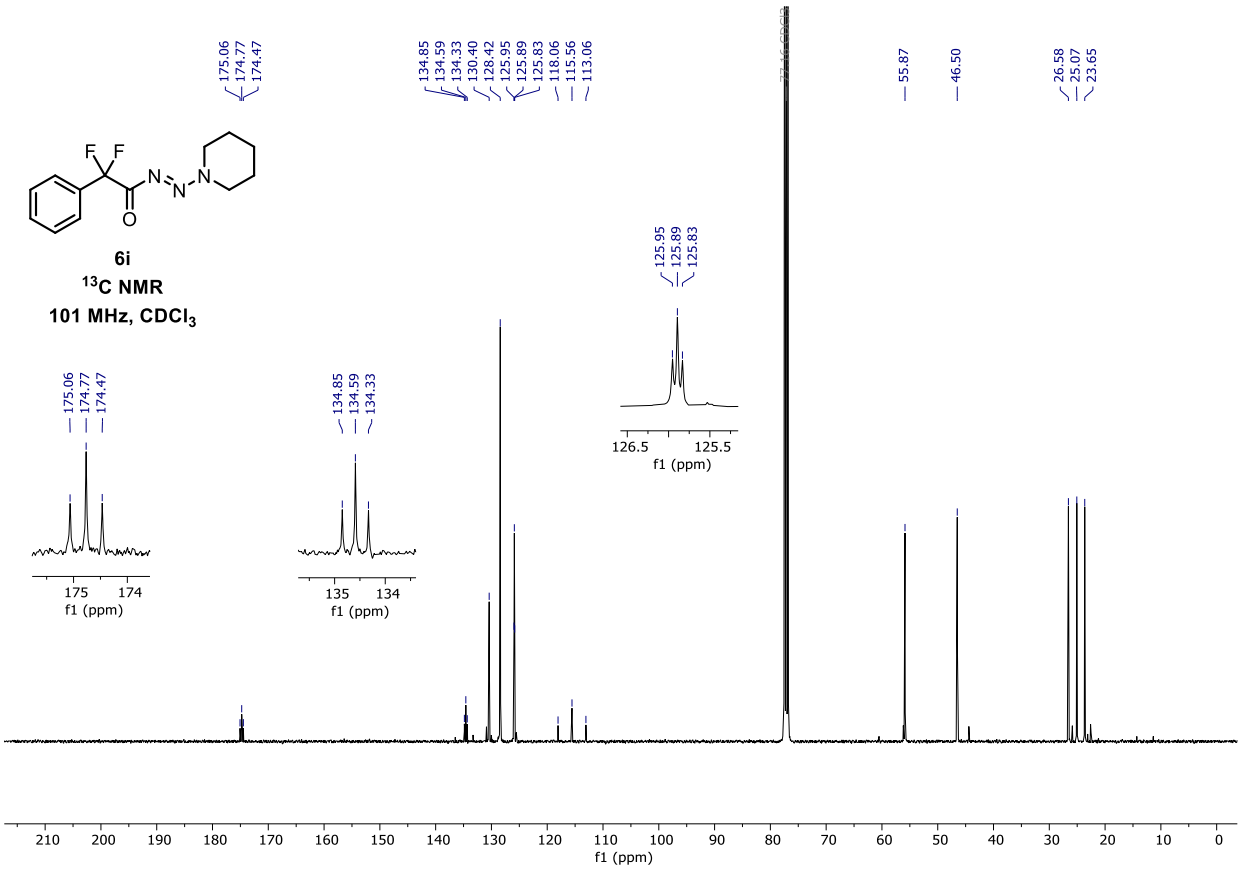


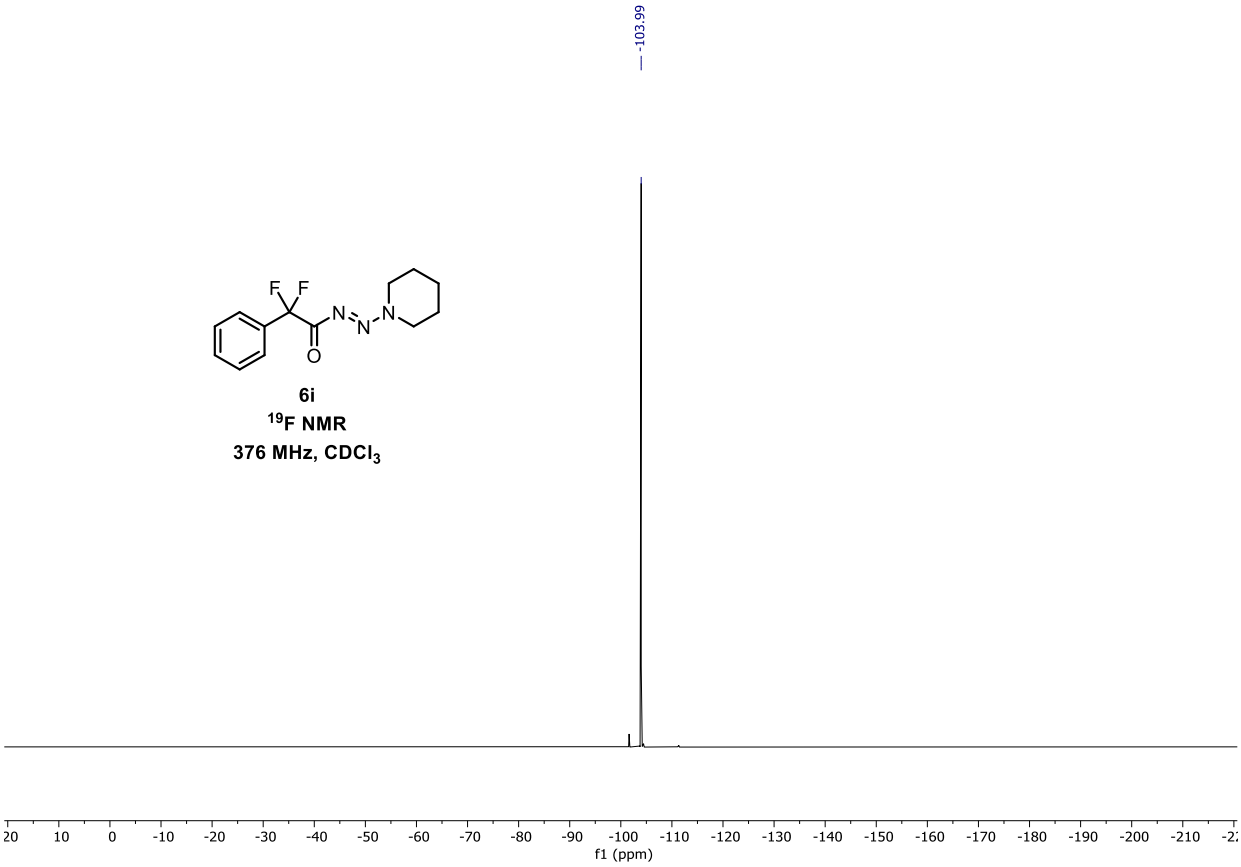
6h
^{1}H NMR
400 MHz, $CDCl_3$


173.22
173.02
172.83
136.71
136.51
136.31
128.28
128.13
128.10
128.06
126.92
115.65
114.00
112.34
53.85
51.24
22.99
18.92
F F
S
N
N
N
O
6h
13C NMR
101 MHz, CDCl3
f1 (ppm)

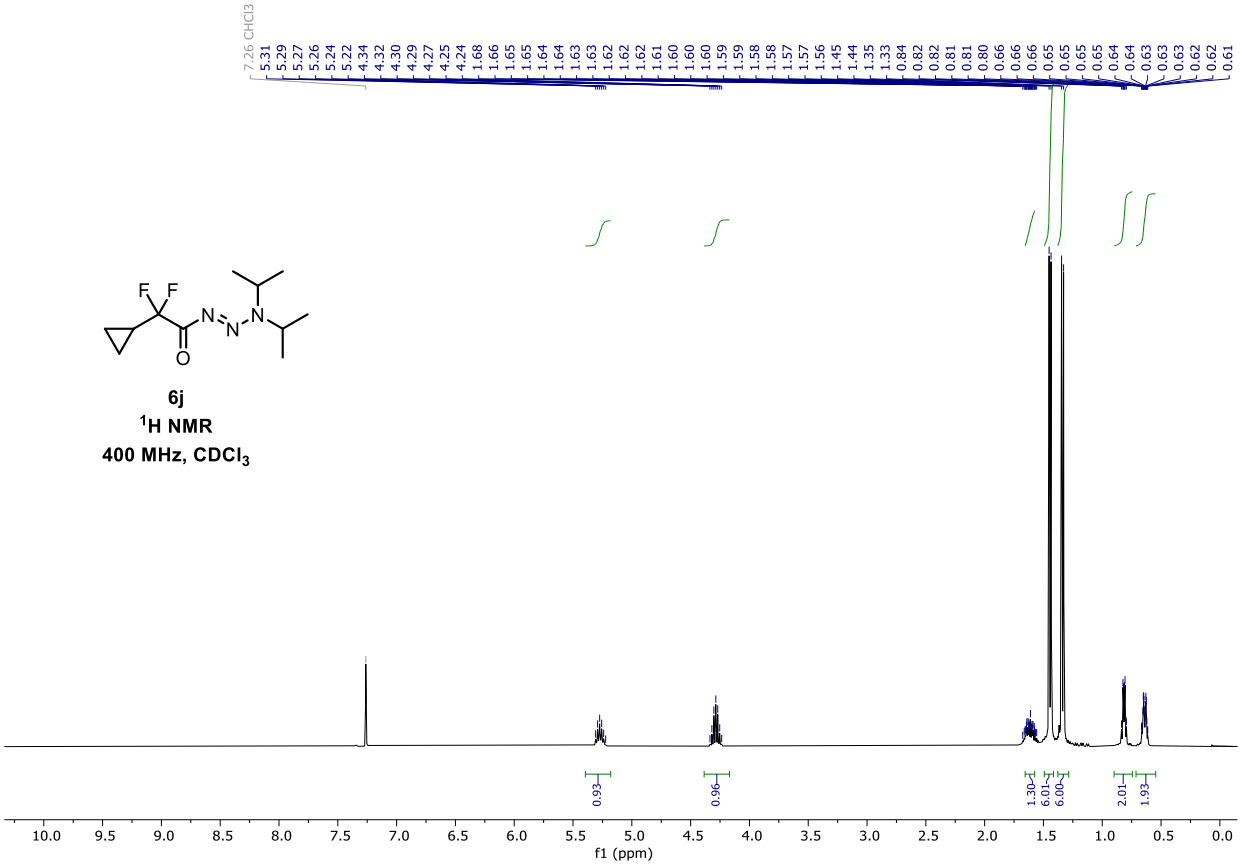

-92.30
F F
S
N
N
N
O
6h
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.67
7.67
7.65
7.65
7.43
7.42
7.42
7.41
7.26 CHCl3
4.07
4.05
4.04
3.98
3.97
3.95
1.86
1.84
1.83
1.83
1.82
1.81
1.81
1.80
1.79
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.73
1.72
1.71
1.70
1.68
F F
N
N
N
O
6i
1H NMR
400 MHz, CDCl3
2.01
3.02
2.00
2.00
2.06
2.06
2.12
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)

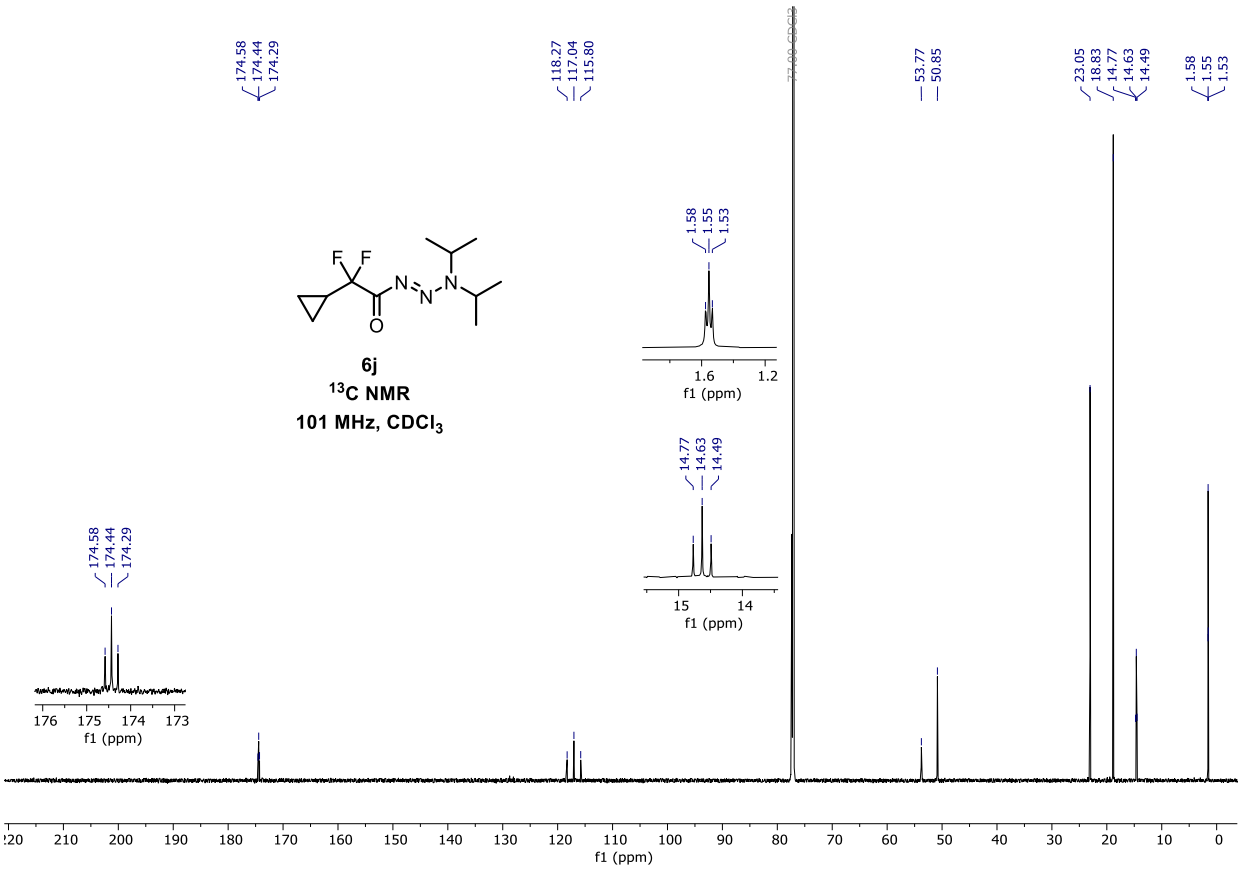

175.06
174.77
174.47
134.85
134.59
134.33
130.40
128.42
125.95
125.89
125.83
118.06
115.56
113.06
77.46
77.00
76.53
55.87
46.50
26.58
25.07
23.65
F F
N
N
N
O
6i
13C NMR
101 MHz, CDCl3
175.06
174.77
174.47
175 174
f1 (ppm)
134.85
134.59
134.33
135 134
f1 (ppm)
125.95
125.89
125.83
126.5 125.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

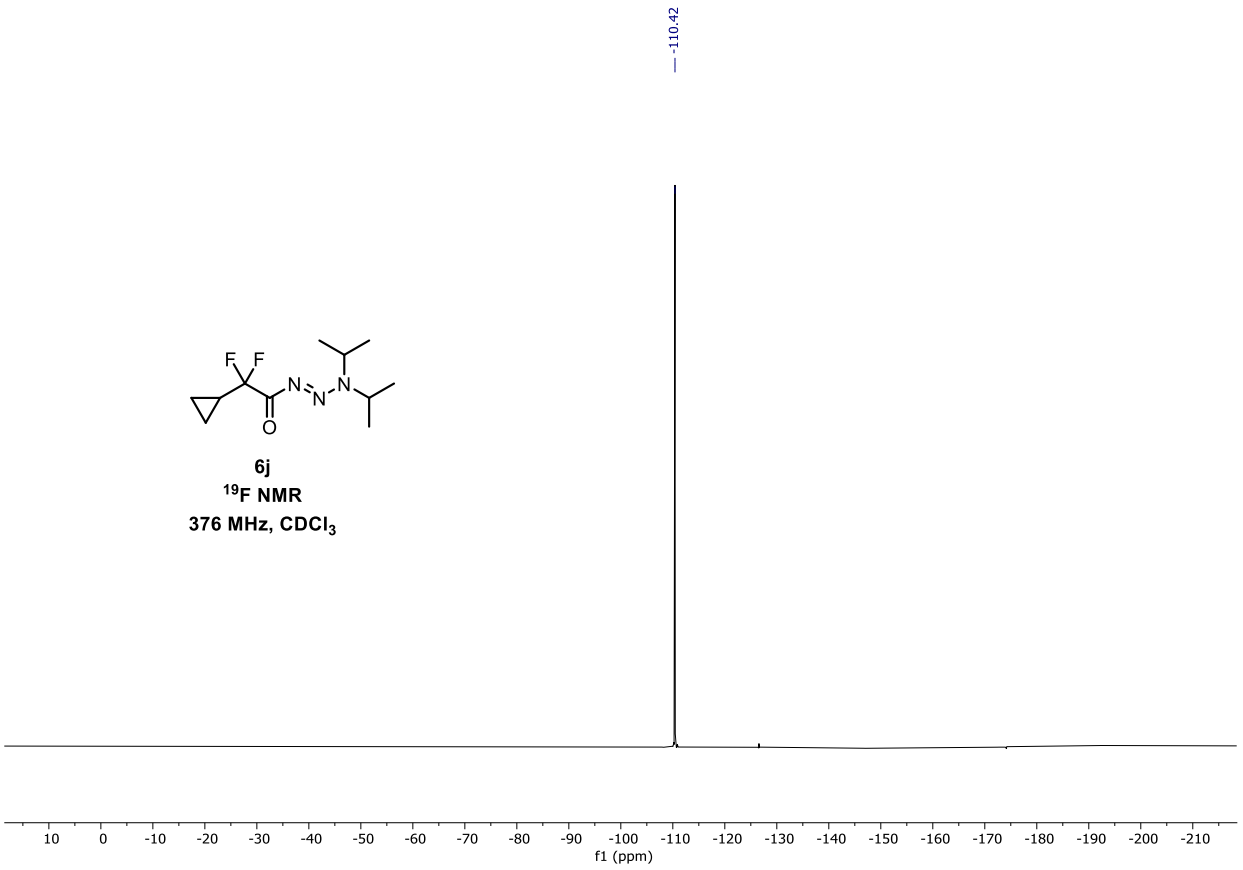


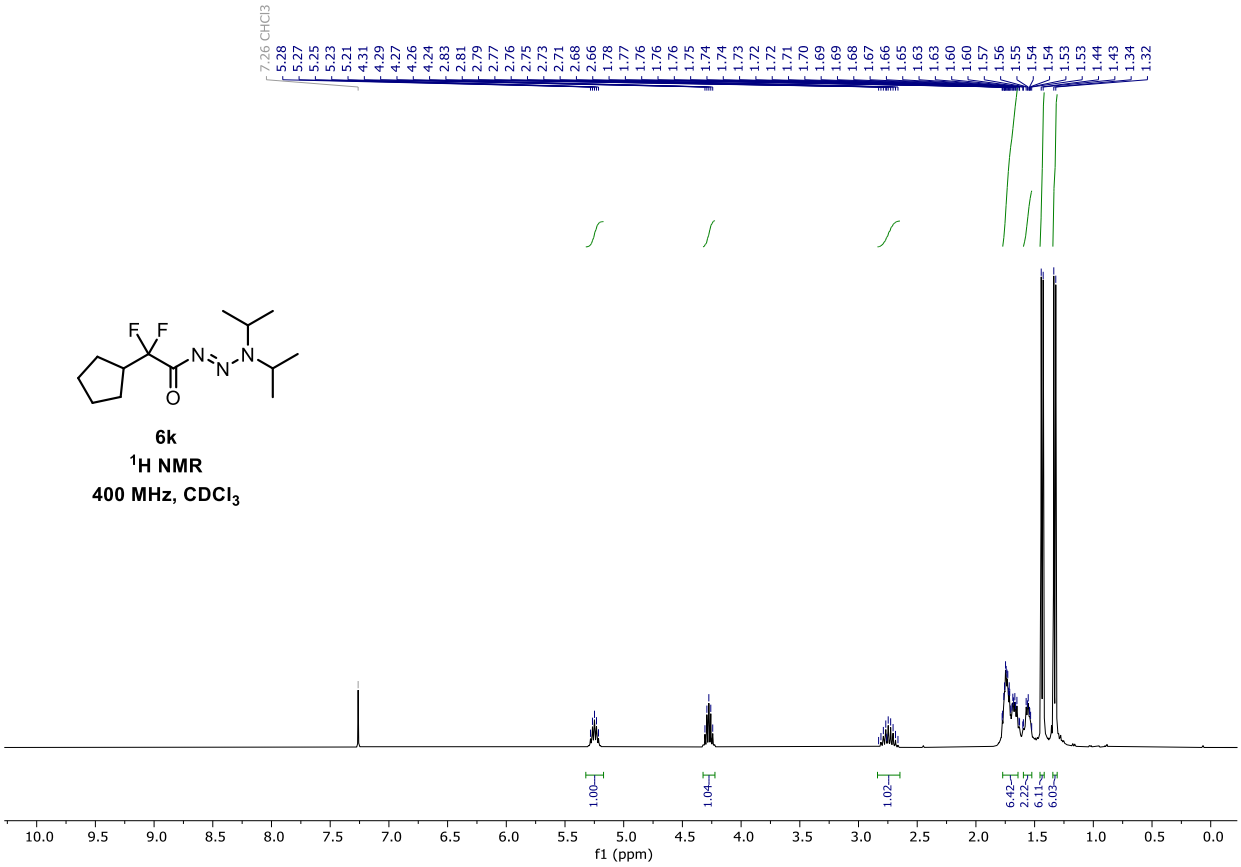
6i
^{19}F NMR
376 MHz, $CDCl_3$

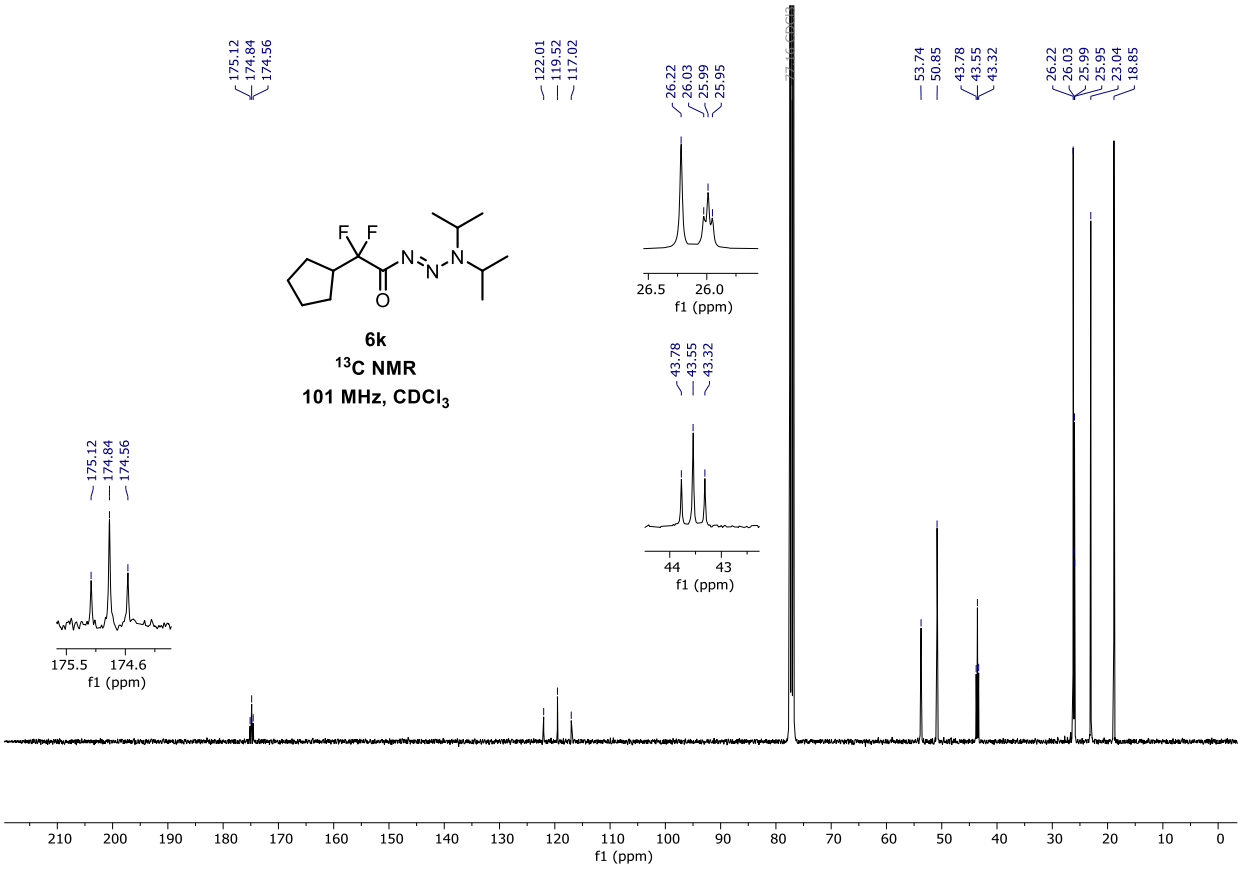


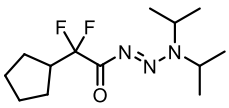
6j
^{1}H NMR
400 MHz, $CDCl_3$


174.58
174.44
174.29
118.27
117.04
115.80
77.00 CDCl3
53.77
50.85
23.05
18.83
14.77
14.63
14.49
1.58
1.55
1.53
F F
N N N
O
6j
13C NMR
101 MHz, CDCl3
f1 (ppm)

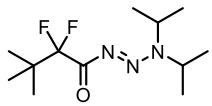

-110.42
F F
N N N
O
6j
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.26 CHCl3
5.28 5.27 5.25 5.23 5.21 4.31 4.29 4.27 4.26 4.24 2.83 2.81 2.79 2.77 2.76 2.75 2.73 2.71 2.68 2.66 1.78 1.77 1.76 1.76 1.76 1.75 1.74 1.74 1.73 1.72 1.72 1.71 1.70 1.69 1.69 1.68 1.67 1.66 1.65 1.63 1.63 1.60 1.60 1.57 1.56 1.55 1.54 1.54 1.53 1.53 1.44 1.43 1.34 1.32
F F N N N O
6k
1H NMR
400 MHz, CDCl3
1.00 1.04 1.02 6.42 2.22 6.11 6.03
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)

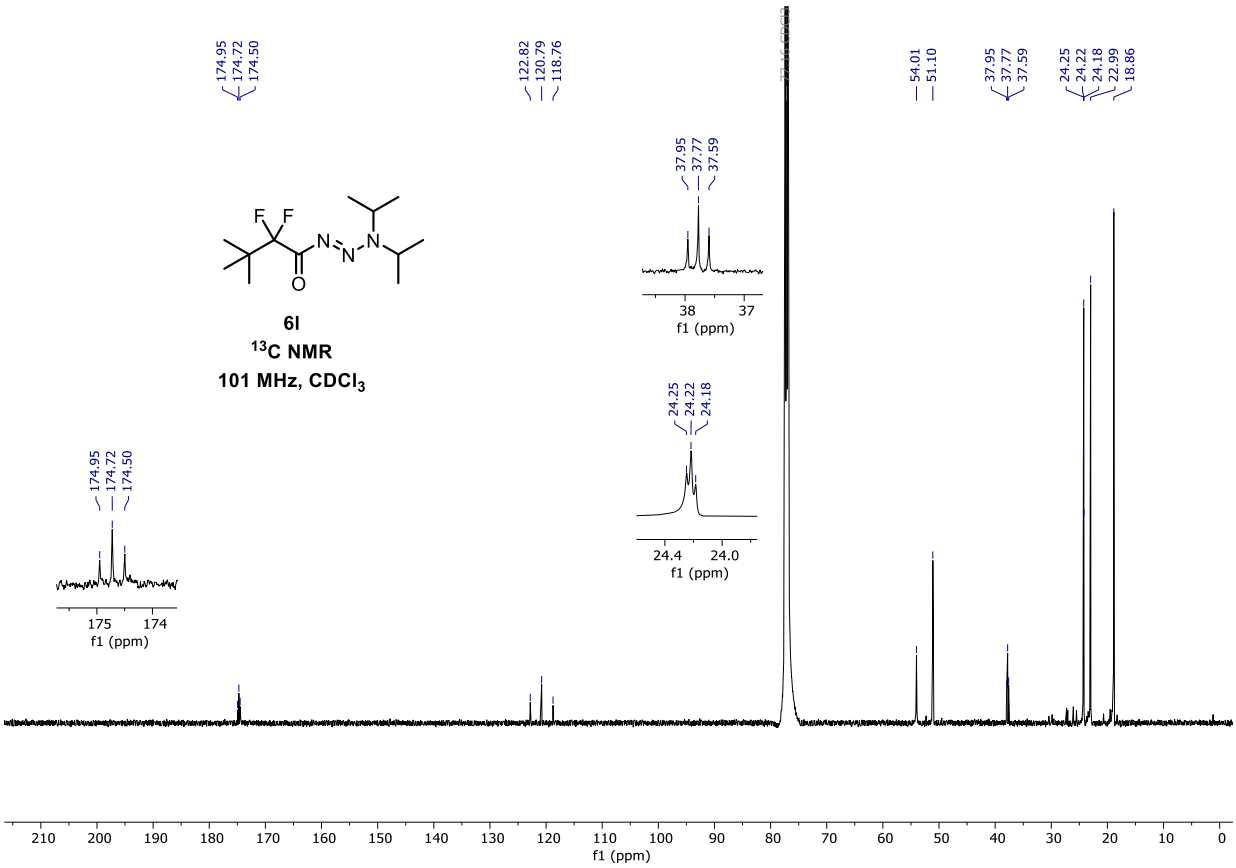

175.12 174.84 174.56
122.01 119.52 117.02
26.22 26.03 25.99 25.95
77.16 77.00 76.84
53.74 50.85 43.78 43.55 43.32
26.22 26.03 25.99 25.95 23.04 18.85
F F N N N O
6k
13C NMR
101 MHz, CDCl3
26.5 26.0
f1 (ppm)
43.78 43.55 43.32
44 43
f1 (ppm)
175.12 174.84 174.56
175.5 174.6
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

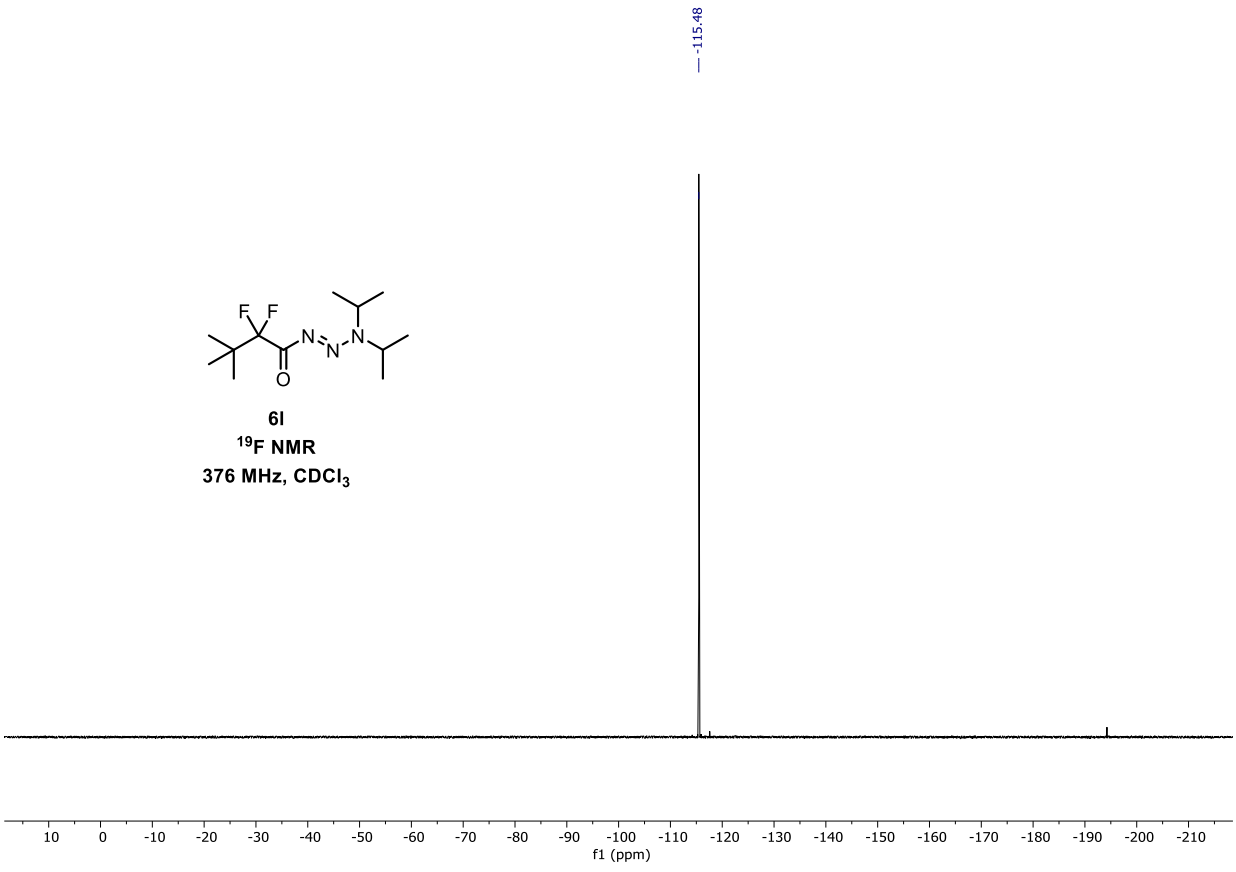


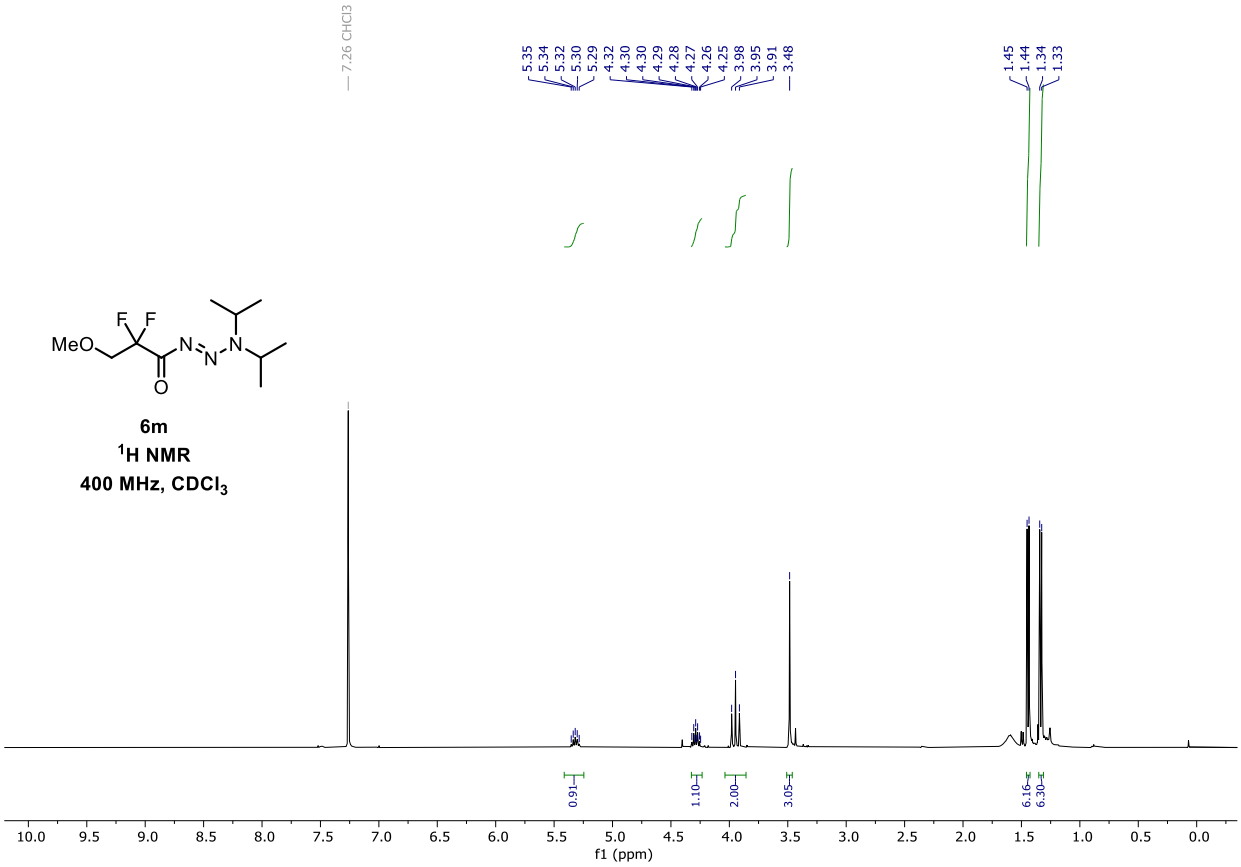
6k
^{19}F NMR
376 MHz, $CDCl_3$

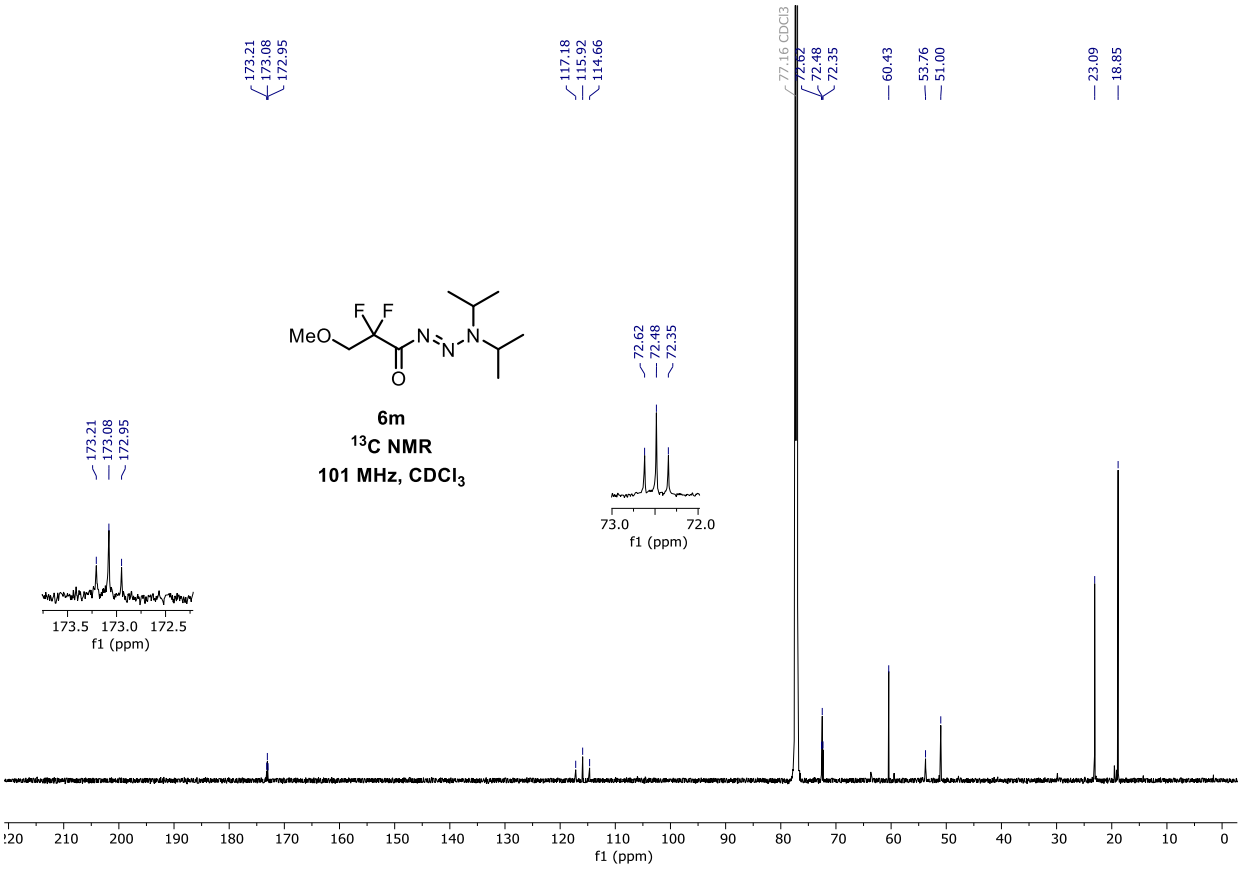


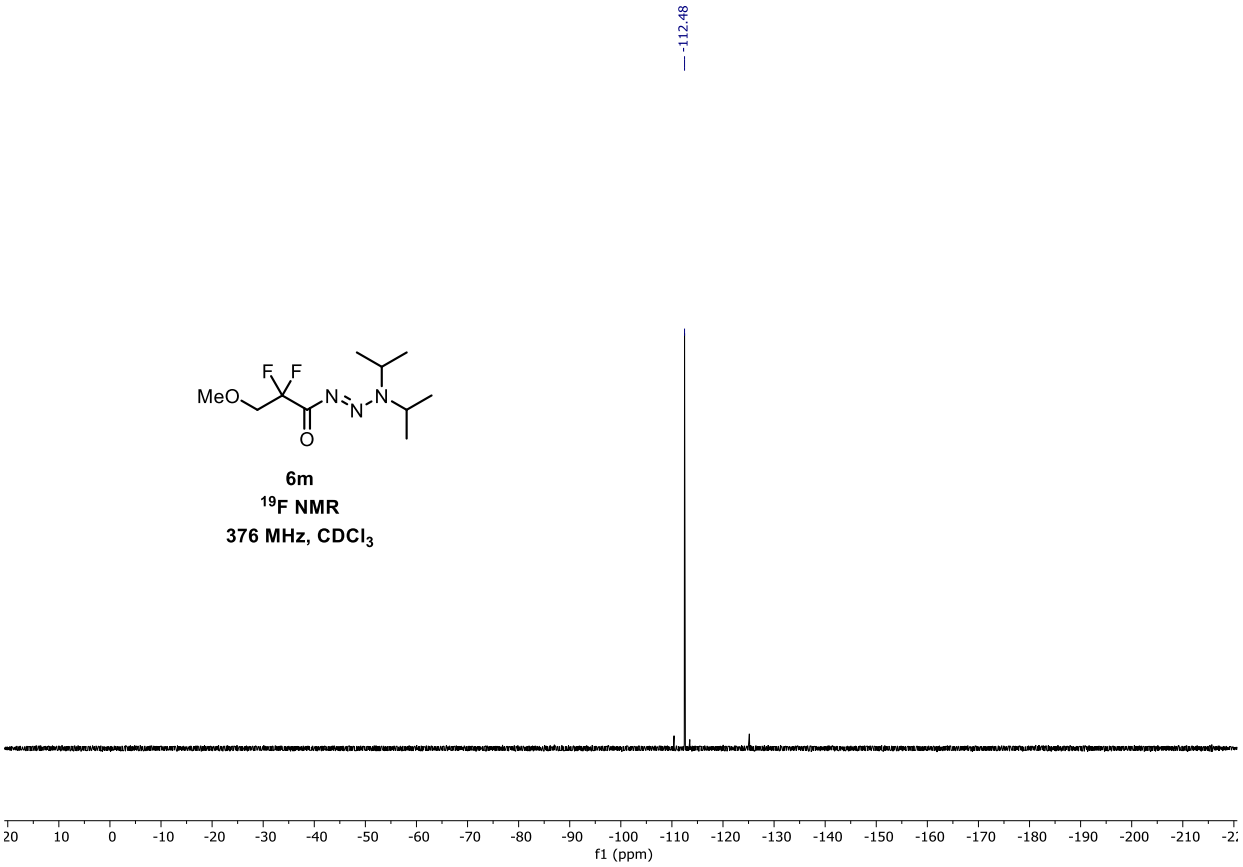
6l
^{1}H NMR
400 MHz, $CDCl_3$


174.95
174.72
174.50
122.82
120.79
118.76
54.01
51.10
37.95
37.77
37.59
24.25
24.22
24.18
22.99
18.86
F F
N
N
N
O
6l
13C NMR
101 MHz, CDCl3
f1 (ppm)

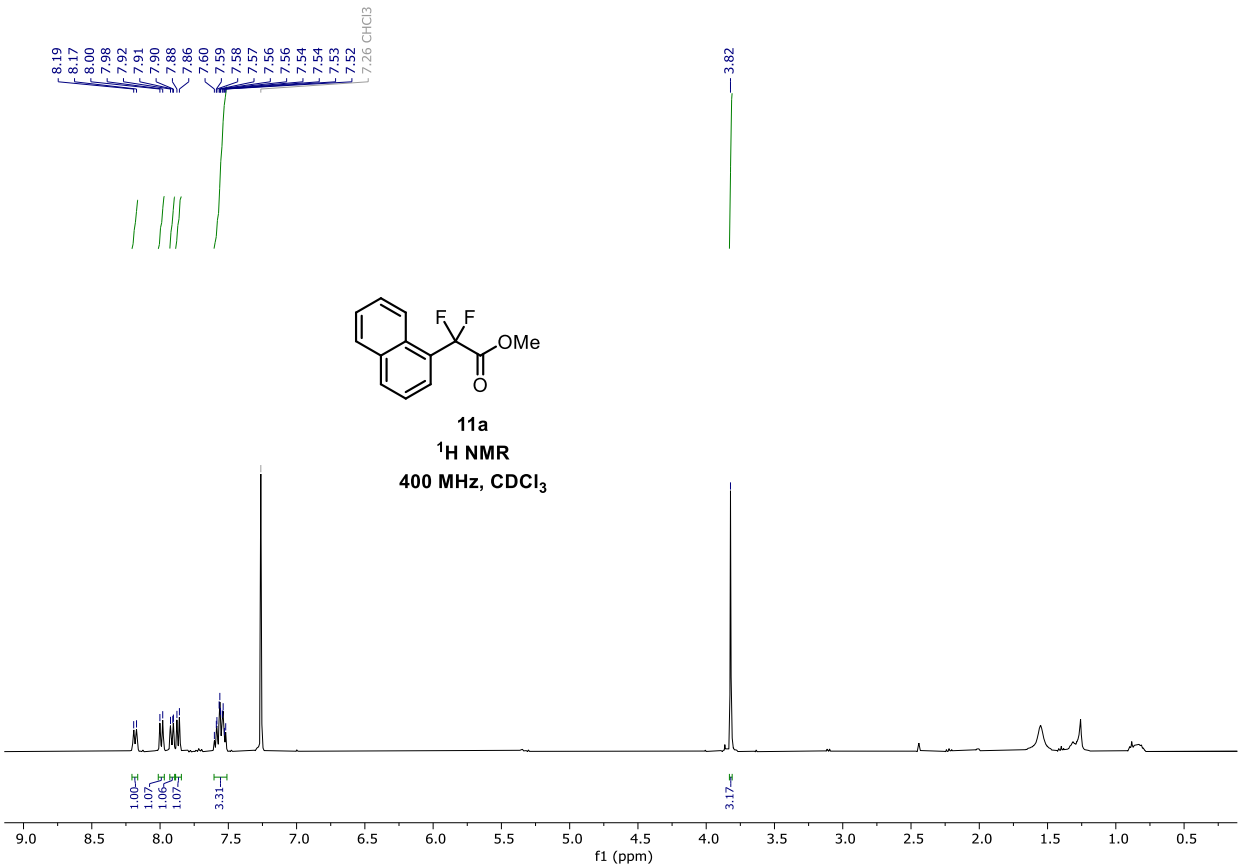

-115.48
F F
N
N
N
O
6l
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.26 CHCl3
5.35
5.34
5.32
5.30
5.29
4.32
4.30
4.30
4.29
4.28
4.27
4.26
4.25
3.98
3.95
3.91
3.48
1.45
1.44
1.34
1.33
F F
MeO
N
N
N
O
6m
1H NMR
400 MHz, CDCl3
0.91
1.10
2.00
3.05
6.16
6.30
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)

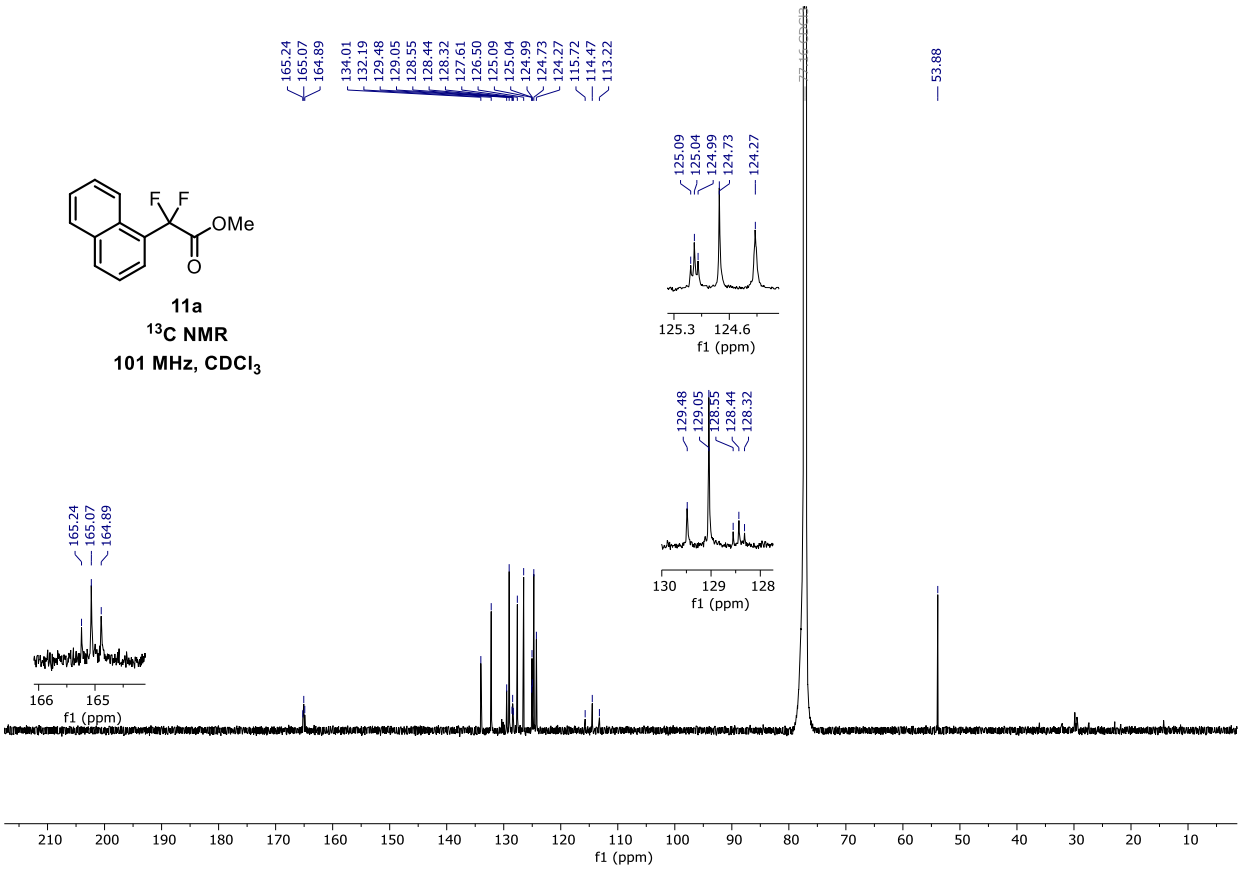

173.21
173.08
172.95
117.18
115.92
114.66
77.16 CDCl3
72.62
72.48
72.35
60.43
53.76
51.00
23.09
18.85
F F
MeO
N
N
N
O
6m
13C NMR
101 MHz, CDCl3
72.62
72.48
72.35
73.0
72.0
f1 (ppm)
173.21
173.08
172.95
173.5 173.0 172.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

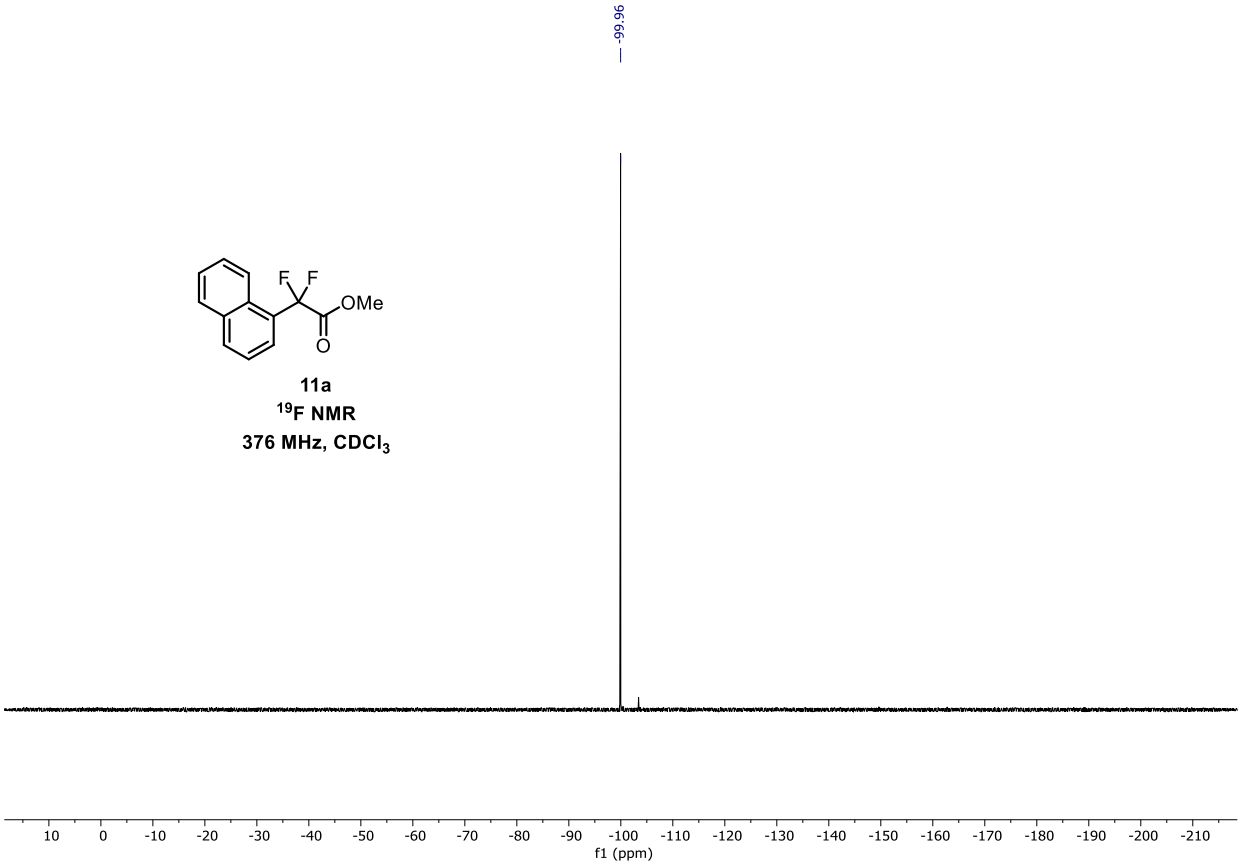


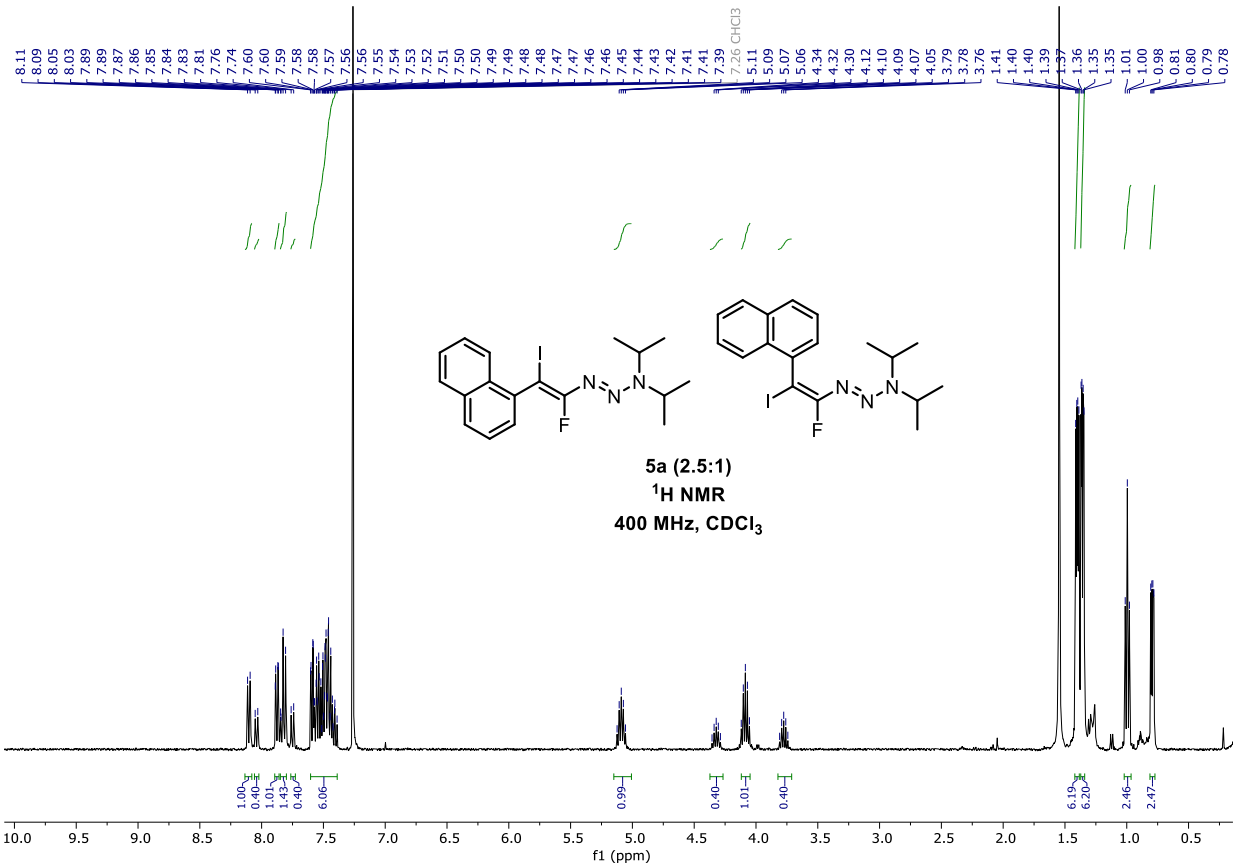
6m
^{19}F NMR
376 MHz, $CDCl_3$

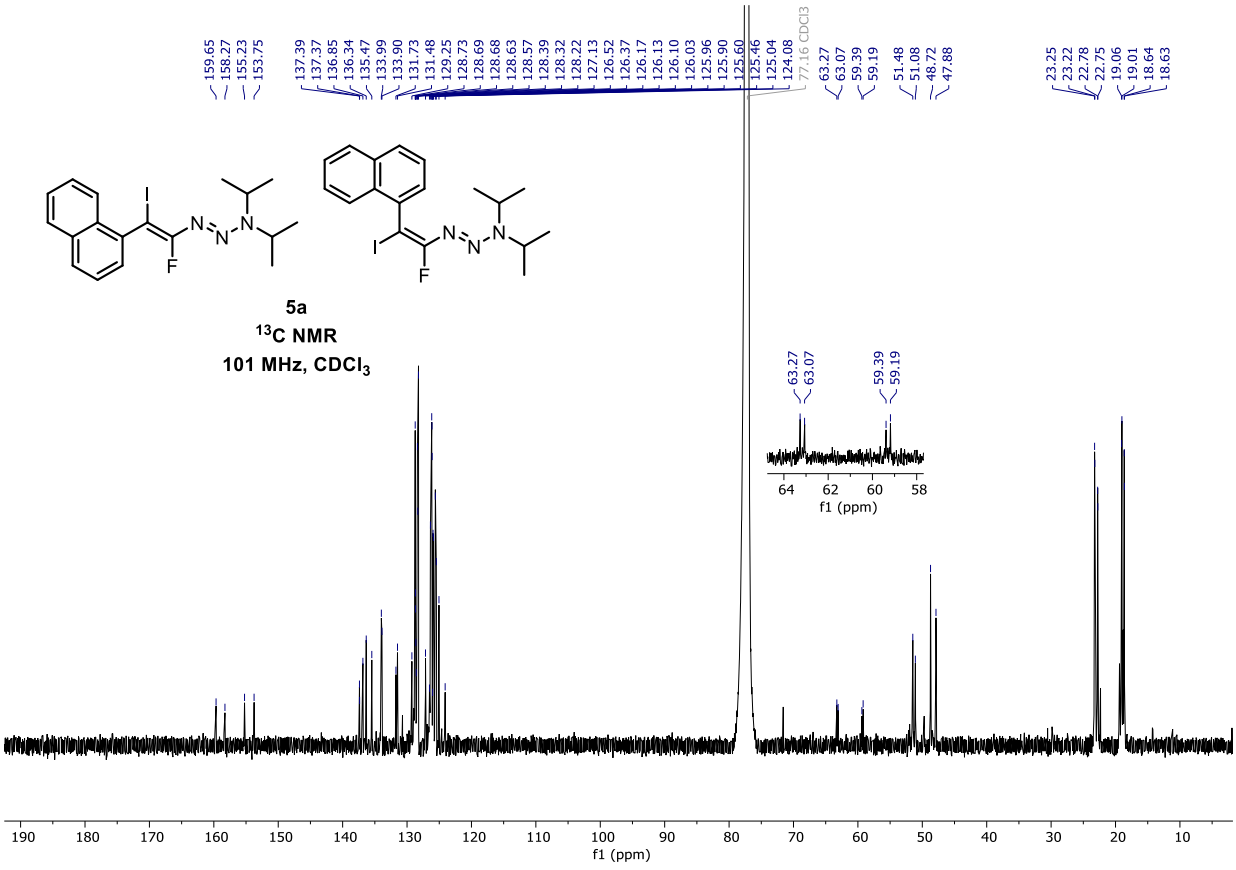


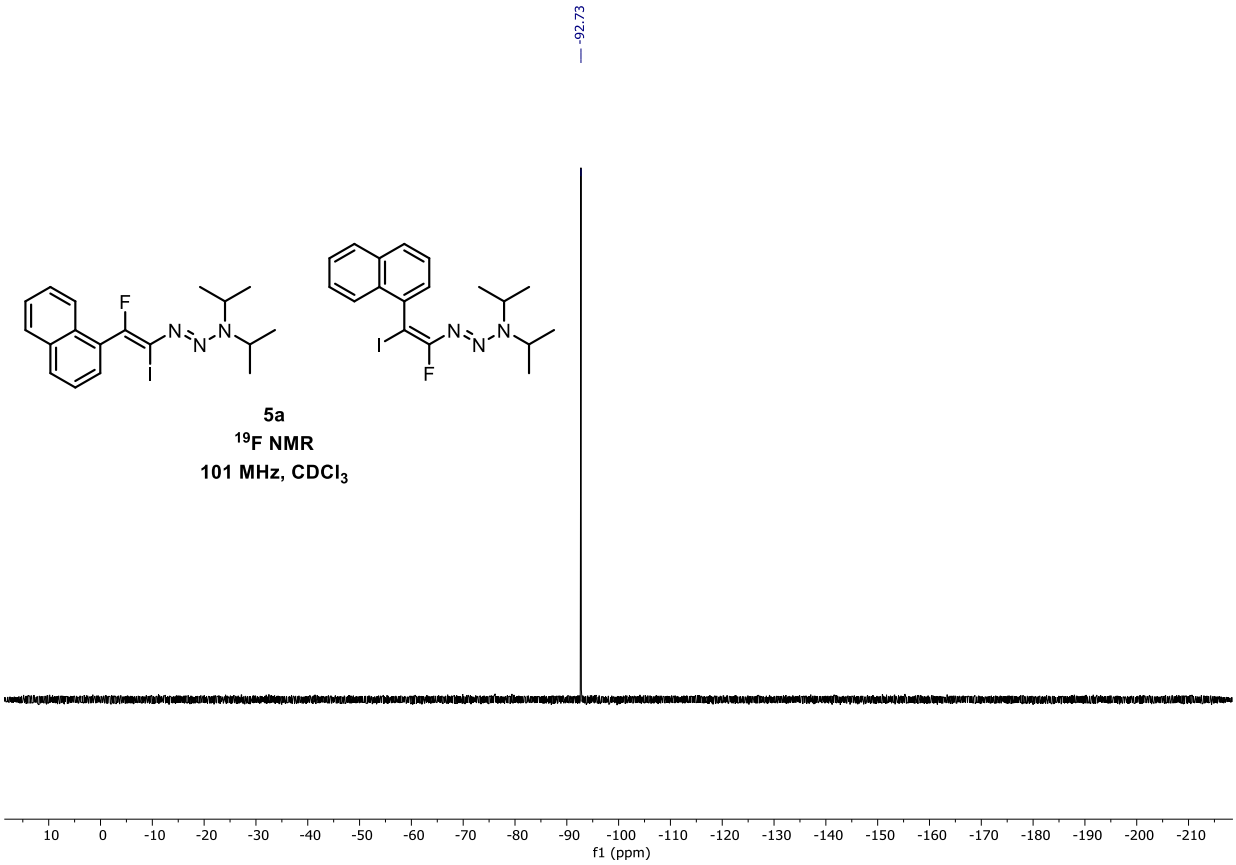
11a
^{1}H NMR
400 MHz, $CDCl_3$


165.24
165.07
164.89
134.01
132.19
129.48
129.05
128.55
128.44
128.32
127.61
126.50
125.09
125.04
124.99
124.73
124.27
115.72
114.47
113.22
77.16 CDCl3
53.88
F F
OMe
O
11a
13C NMR
101 MHz, CDCl3
125.09
125.04
124.99
124.73
124.27
125.3
124.6
f1 (ppm)
129.48
129.05
128.55
128.44
128.32
130
129
128
f1 (ppm)
165.24
165.07
164.89
166
165
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

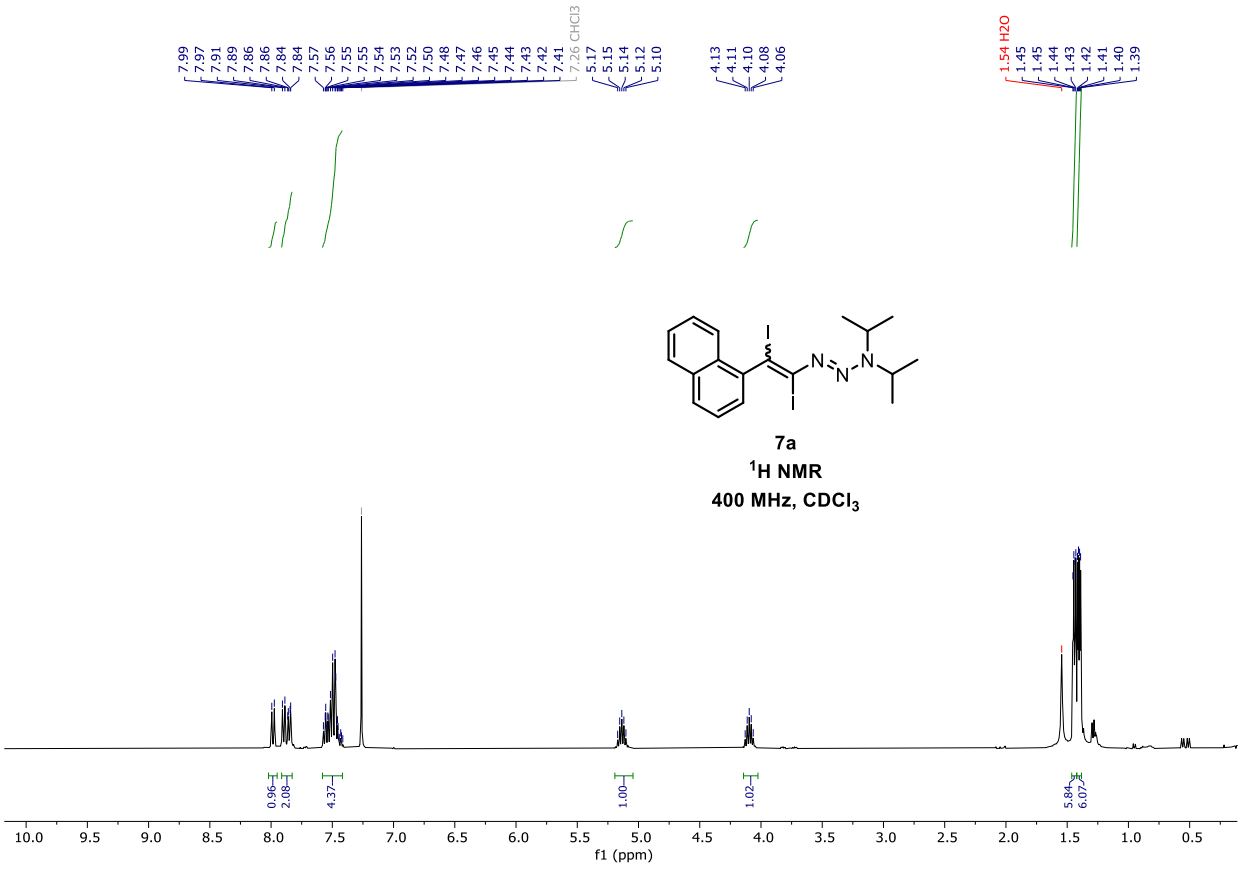

-99.96
F F
OMe
O
11a
19F NMR
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


5a (2.5:1)
1H NMR
400 MHz, CDCl3
f1 (ppm)

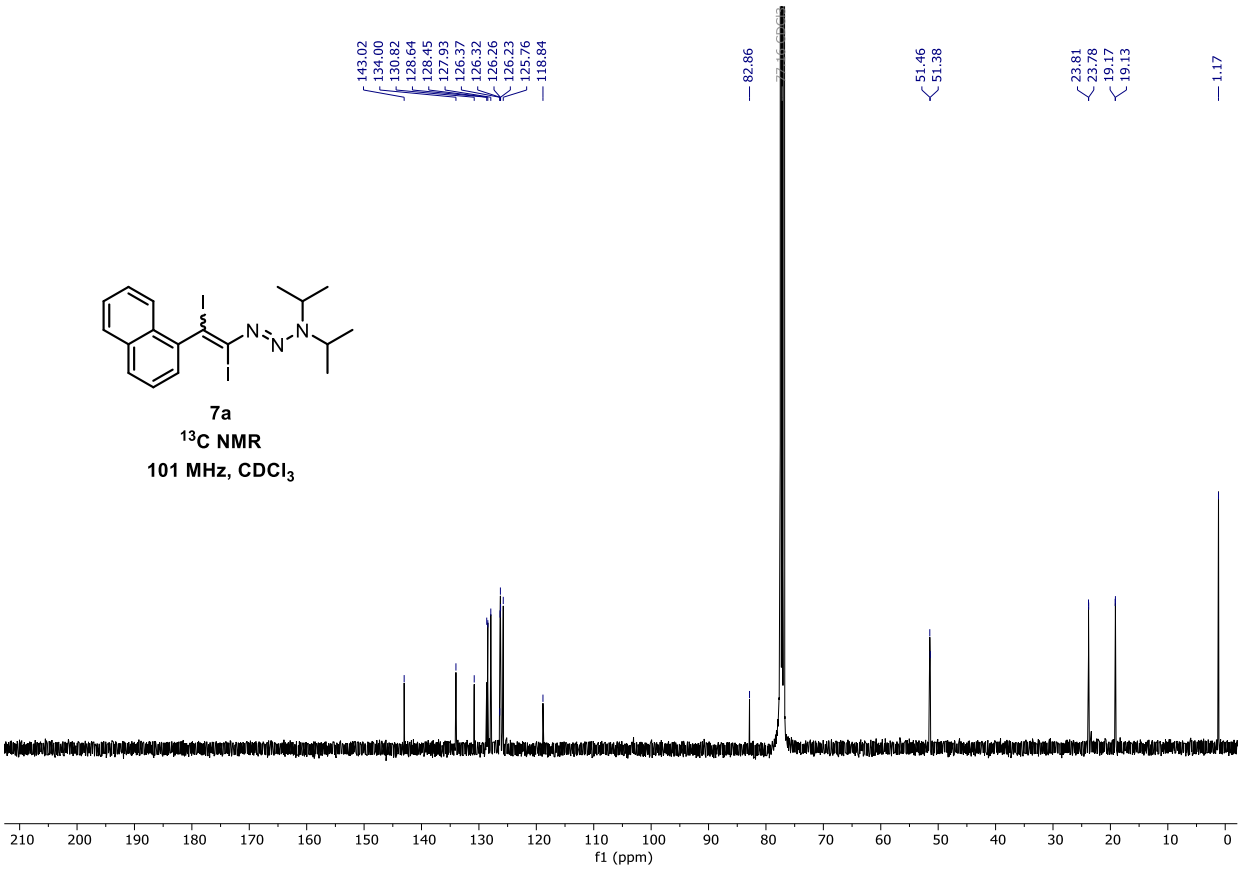

5a
13C NMR
101 MHz, CDCl3
f1 (ppm)

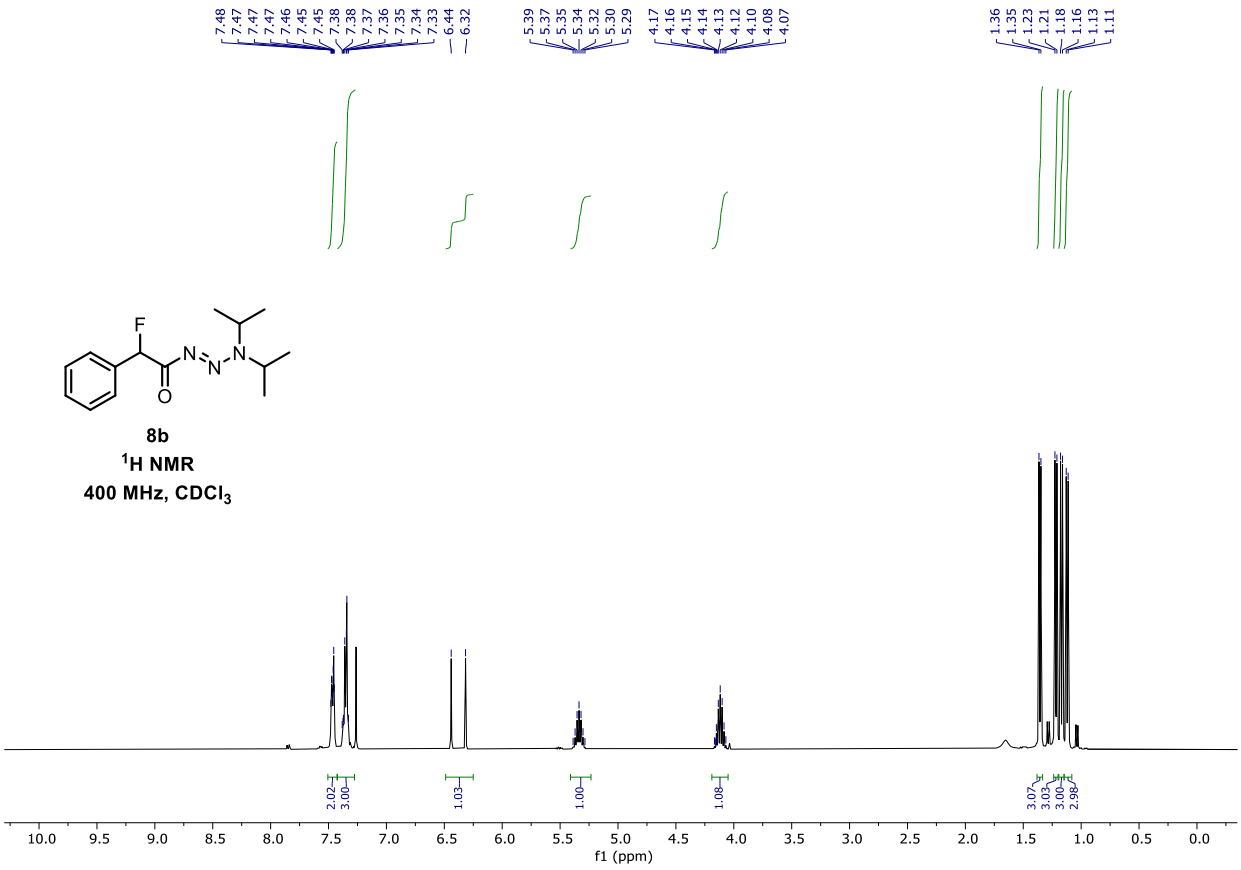


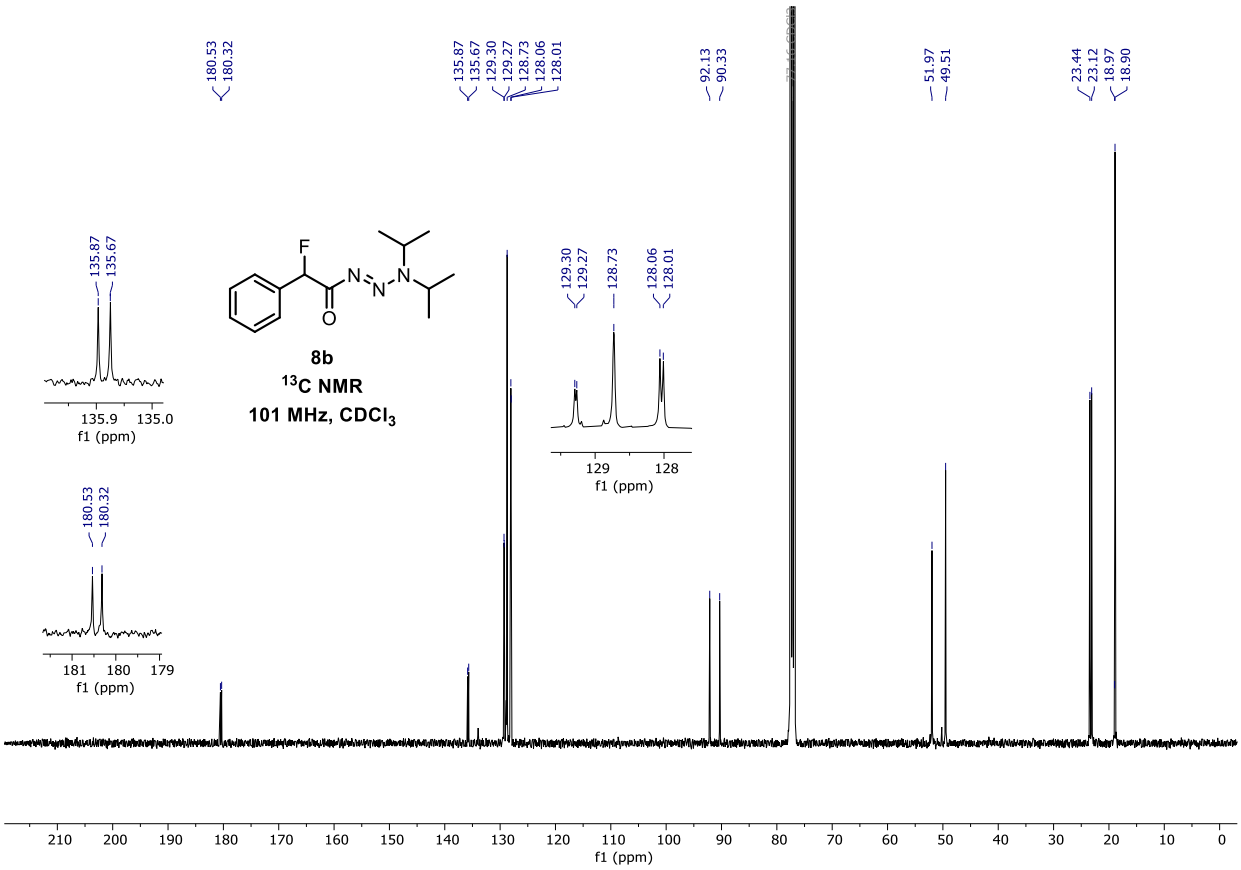
5a
^{19}F NMR
101 MHz, $CDCl_3$

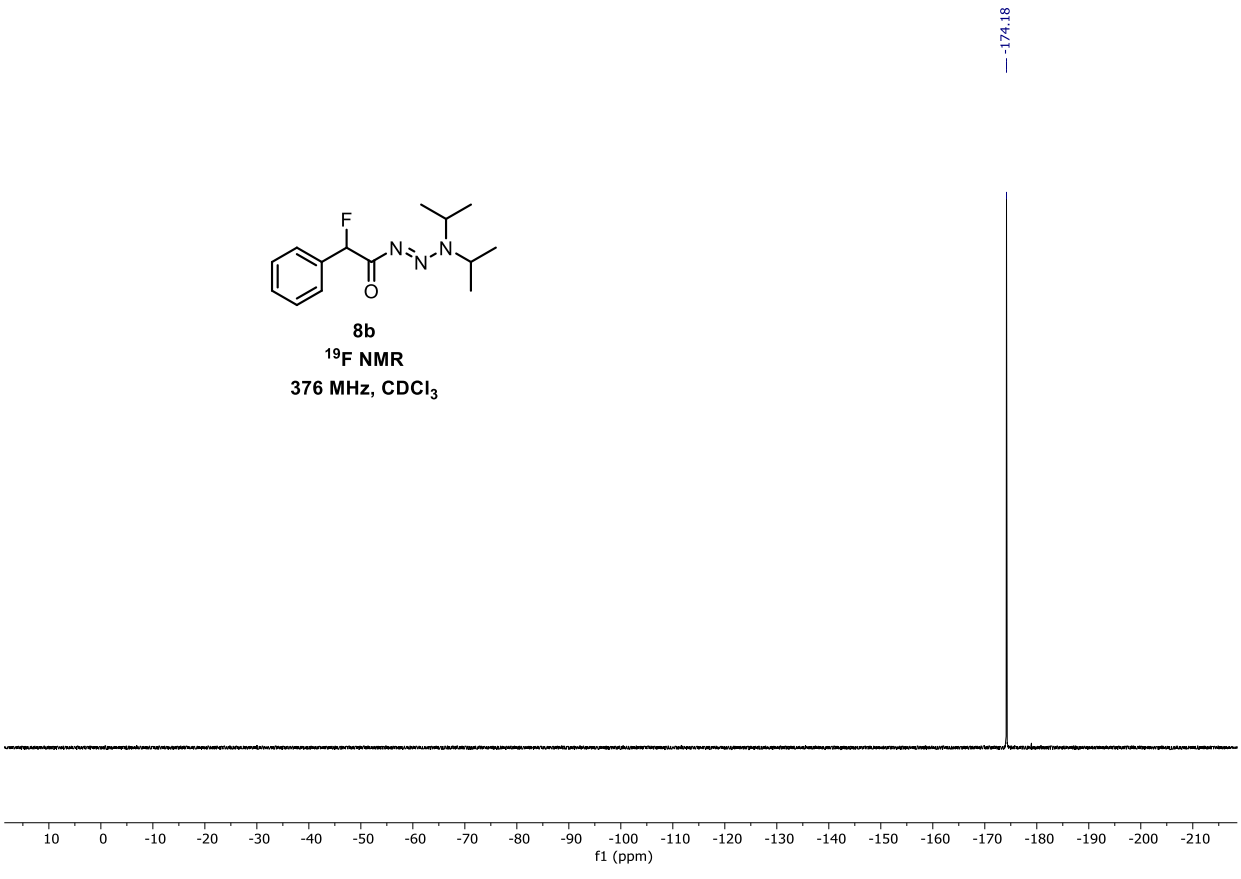


7a
^{1}H NMR
400 MHz, $CDCl_3$


143.02
134.00
130.82
128.64
128.45
127.93
126.37
126.32
126.26
126.23
125.76
118.84
82.86
77.16
51.46
51.38
23.81
23.78
19.17
19.13
1.17
I
I
N
N
N
7a
13C NMR
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.48
7.47
7.47
7.47
7.46
7.45
7.45
7.38
7.38
7.37
7.36
7.35
7.34
7.33
6.44
6.32
5.39
5.37
5.35
5.34
5.32
5.30
5.29
4.17
4.16
4.15
4.14
4.13
4.12
4.10
4.08
4.07
1.36
1.35
1.23
1.21
1.18
1.16
1.13
1.11
F
N
N
N
O
8b
1H NMR
400 MHz, CDCl3
2.02
3.00
1.03
1.00
1.08
3.07
3.03
3.00
2.98
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)


180.53
180.32
135.87
135.67
129.30
129.27
128.73
128.06
128.01
92.13
90.33
51.97
49.51
23.44
23.12
18.97
18.90
135.87
135.67
135.9
135.0
f1 (ppm)
129.30
129.27
128.73
128.06
128.01
129
128
f1 (ppm)
180.53
180.32
181
180
179
f1 (ppm)
F
N
N
N
O
8b
13C NMR
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-174.18
F
N
N
N
O
8b
19F NMR
376 MHz, CDCl3
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)

10. References:

(1) G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti and K. Severin, *Angew. Chem. Int. Ed.*, 2015, **54**, 302−305; *Angew. Chem.*, 2015, **127**, 306–310.

(2) J.-F. Tan, C. T. Bormann, F. G. Perrin, F. M. Chadwick, K. Severin and N. Cramer, *J. Am. Chem. Soc.*, 2019, **141**, 10372–10383.

(3) W. J. Middleton and E. M. Bingham, *J. Org. Chem.*, 1980, **45**, 2883–2887.

(4) S. Ge, W. Chaładaj and J. F. Hartwig, J. Am. Chem. Soc., 2014, **136**, 4149–4152.