Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

[*Supporting Information*]

Organocatalytic Difluorobenzylation of 1,2-Diketones via Mild Cleavage of Carbon-Carbon Bonds

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General information

Visualization on TLC was achieved by use of UV light (254 nm). NMR spectra were recorded on Bruker Avance-400 spectrometer (^{1}H 400 MHz, ^{13}C 101 MHz and ^{19}F 376 MHz) in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in per million (ppm, δ) and coupling constants *J* are given in Hertz (Hz). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR and ^{19}F NMR MHz are reported in terms of chemical shift (δ, ppm). High resolution mass spectroscopy (HRMS) analysis were performed at Waters G2-Xs QTof and Thermo Scientific LTQ-Orbitrap XL. Unless otherwise noted, all analytical grade solvents and commercially available reagents were used without further purification. *N*-protected isatins were prepared according to the literature procedures.[1-3]

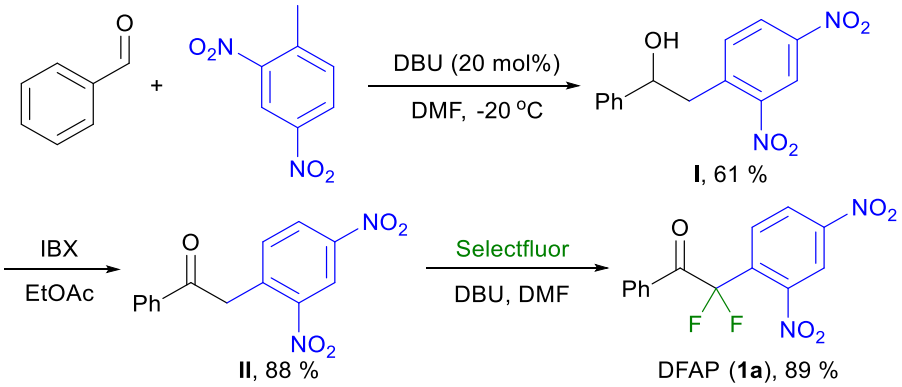
References

1. Y. C. Lee, S. S. Patil, C. Golz, C. Strohman, S. Ziegler, K. Kumar and H. Waldmann, A ligand-directed divergent catalytic approach to establish structural and functional scaffold diversity*, Nat. Commun.,* **2017**, *8*, 14043.

2. K. Dhara, T. Mandal, I. Das and J. Dash, Synthesis of Carbazole Alkaloids by Ring-Closing Metathesis and Ring Rearrangement–Aromatization, *Angew. Chem. Int. Ed.*, **2015**, 54, 15831.

3. H. H. Ji, Y. Z. Zhu, Y. Shao, J. Liu, Y. Yuan and X. D. Jia, Active sp3 C–H Bond Oxidation Initiated sp^3–sp^2 Consecutive C–H Functionalization of N-Arylglycine Amides: Construction of Isatins, *J. Org. Chem.*, **2017**, 82, 9859.

Synthesis of α-aryl-α,α-difluoroisoxazolacetophenone 1a



2,4-dinitrotoluene (1.82 g, 10.0 mmol), aldehyde (1.59 g, 15.0 mmol) and anhydrous DMF (10 mL) were mixed in a dry flask under N_2 atmosphere, and then

cooled to -20 °C, DBU (300 μL, 20 mol %) was injected and the mixture were stirred for 48 h under -20 °C. After the reaction was completed, the mixture was poured into water (40 mL) and extracted with ethyl acetate (20 mL x 5). The combined extracts were washed with water (40 mL) and brine (40 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude products were purified by silica gel column chromatography using PE/EA (v/v = 10/1) as eluents to afford 1.76 g of **I** (61 % yield).

To the solution of **I** (1.76 g, 6.1 mmol) in EtOAc (20 mL), *o*-iodoxybenzoic acid (IBX) (3.42 g, 12.2 mmol) was added and the mixture was refluxed at 80 °C (oil bath) for 10 h. After the reaction was completed (monitored by TLC), it was cooled to room temperature and filtered. The filtrate was concentrated and recrystallized from ethanol to give 1.55 g of **II** (88% yield).

To the mixture of **II** (1.55 g, 5.37 mmol), DBU (1.77 mL, 2.2 equiv) and 30 mL of anhydrous DMF, selectfluor (4.18 g，11.80 mmol) was added and the mixture was stirred at room temperature for 2 h. After the reaction was completed (monitored by TLC), it was filtered and washed several times with dichloromethane. The combined organic layers were washed with saturated aqueous ammonium chloride, dried over Na_2SO_4 and concentrated in vacuo. The crude products were purified by silica gel column chromatography using PE/EA (v/v = 30/1) as eluents to give ***α*-aryl-*α*,*α*-difluoroacetophenone 1a:** white solid; 1.54 g, 89% yield.

TGA-DSC analysis

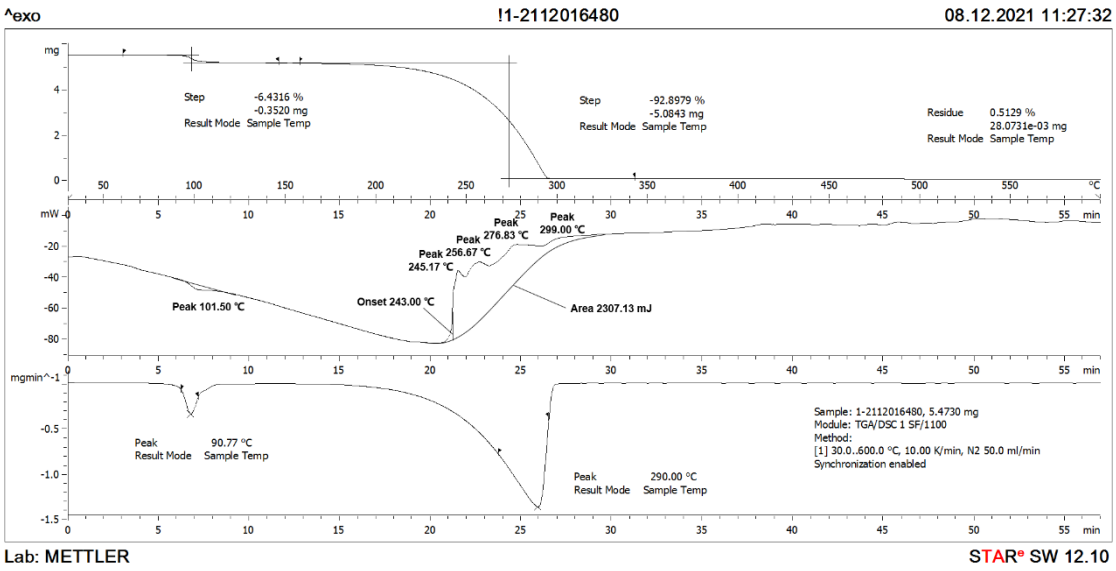
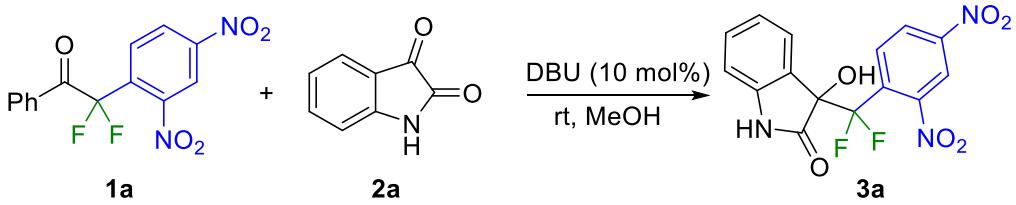


Figure S1 TGA-DSC analysis of DFAP (**1a**).

The thermal stability of DFAP (**1a**) was determined by thermogravimetric analysis-differential scanning calorimetric measurements (TGA-DSC) at a heating rate of 10 $K \cdot min^{-1}$. DFAP first losses organic solvents or impurities with 6.4136 % weight loss. Then there are four continuous exothermic peaks in the range of 245.1 ℃-299.0 ℃, which shows DFAP decompose gradually. Meanwhile, ΔH = -453.78 $J \cdot g^{-1}$ was

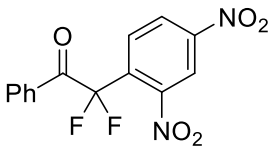
calculated by DSC analysis, which indicates an explosion risk with DFAP over 240 ℃. Therefore, we recommend using DFAP (**1a**) below 200 ℃.

Representative procedure for the difluorobenzylation reaction

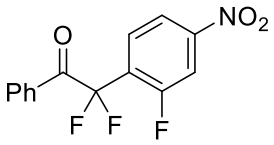


To the mixture of isatin **2a** (0.10 mmol), α-aryl-α,α-difluoroacetophenone **1a** (0.12 mmol) and 0.5 mL MeOH, DBU (10 mol%, 0.010 mmol) was added and the mixture was stirred at room temperature. After the reaction was completed (monitored by TLC), it was concentrated in vacuo, and the product **3a** was purified by silica gel chromatography (PE/acetone = 4/1, v/v) to give good yield.

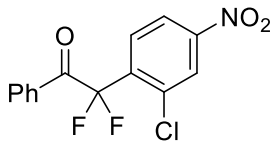
Characterization data of products



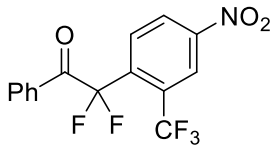
2-(2,4-Dinitrophenyl)-2,2-difluoro-1-phenylethan-1-one (1a): white solid; 1.54 g, 89% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.98 (d, J = 2.0 Hz, 1H), 8.63 (dd, J = 8.4, 2.0 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.16-8.14 (m, 2H), 7.73-7.68 (m, 1H), 7.57(t, J = 7.8 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 187.1 (t, $J_{C\text{-}F}$ = 29.9 Hz, 1C), 149.3, 147.3, 134.7, 134.5 (t, $J_{C\text{-}F}$ = 25.6 Hz, 1C), 131.6 (t, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 130.2 (t, $J_{C\text{-}F}$ = 10.2 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 3.0 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 3.0 Hz, 1C), 128.9, 128.9, 127.8, 121.0, 116.0 (t, $J_{C\text{-}F}$ = 261.3 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -94.7 (s, 2F).



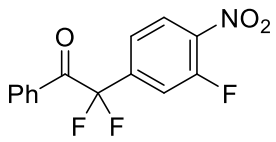
2,2-Difluoro-2-(2-fluoro-4-nitrophenyl)-1-phenylethan-1-one (1b): white solid; 82% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.14-8.12 (m, 3H), 7.97 (dd, J = 10.0, 0.8 Hz, 1H), 7.87 (dd, J = 8.0, 7.2 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 186.1 (t, $J_{C\text{-}F}$ = 31.6 Hz, 1C), 159.6 (dt, $J_{C\text{-}F}$ = 259.0, 4.3 Hz, 1C), 150.4 (d, $J_{C\text{-}F}$ = 8.6 Hz, 1C), 134.8, 131.0 (t, $J_{C\text{-}F}$ = 2.9 Hz, 1C), 130.1 (t, $J_{C\text{-}F}$ = 2.9 Hz, 1C), 128.8, 128.8, 128.3 (td, $J_{C\text{-}F}$ = 7.6, 2.7 Hz, 1C), 127.5 (td, $J_{C\text{-}F}$ = 25.6, 13.2 Hz, 1C), 119.1 (d, $J_{C\text{-}F}$ = 3.9 Hz, 1C), 115.4 (td, $J_{C\text{-}F}$ = 259.0, 2.0 Hz, 1C), 112.2, 111.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -97.5 (d, J = 9.4 Hz, 2F), -107.2 (t, J = 9.2 Hz, 1F).



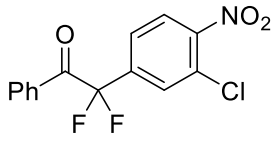
2-(2-Chloro-4-nitrophenyl)-2,2-difluoro-1-phenylethan-1-one (1c): pale yellow solid; 79% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.25-8.21 (m, 2H), 8.11 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 186.7 (t, $J_{C\text{-}F}$ = 31.0 Hz, 1C), 149.4, 137.8 (t, $J_{C\text{-}F}$ = 24.1 Hz, 1C), 134.6, 133.8 (t, $J_{C\text{-}F}$ = 3.9 Hz, 1C), 131.6 (t, $J_{C\text{-}F}$ = 2.7 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 2.8 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 2.8 Hz, 1C), 128.7, 128.7, 128.6 (t, $J_{C\text{-}F}$ = 8.9 Hz, 1C), 125.6, 121.6, 115.5 (t, $J_{C\text{-}F}$ = 259.4 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -97.6 (s, 2F).



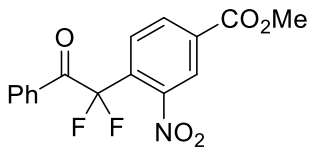
2,2-Difluoro-2-(4-nitro-2-(trifluoromethyl)phenyl)-1-phenylethan-1-one (1d): pale yellow oil; 72% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.66 (d, J = 1.6 Hz, 1H), 8.51 (dd, J = 8.4, 2.0 Hz, 1H), 8.16 (d, J = 7.2 Hz, 2H), 8.02 (d, J = 8.8 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 8.0 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 187.5 (t, $J_{C\text{-}F}$ = 32.0 Hz, 1C), 149.0, 137.4 (td, $J_{C\text{-}F}$ = 25.6, 4.0 Hz, 1C), 134.8, 131.1 (t, $J_{C\text{-}F}$ = 3.4 Hz, 1C), 130.3 (t, $J_{C\text{-}F}$ = 2.6 Hz, 1C), 130.1, 130.1 (dd, $J_{C\text{-}F}$ = 6.0, 2.9 Hz, 1C), 129.9, 128.8, 128.8, 126.3, 122.9 (q, $J_{C\text{-}F}$ = 5.9 Hz, 1C), 122.1 (q, $J_{C\text{-}F}$ = 275.5 Hz, 1C), 116.7 (t, $J_{C\text{-}F}$ = 261.1 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -58.5 (t, J = 11.7 Hz, 3F), -94.2 (q, J = 11.7 Hz, 2F). **HRMS (ESI)** Calcd for $[M - H]^-$ $C_{15}H_7F_2NO_3$, m/z: 344.0354, found: 344.0352.



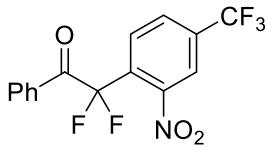
2-(3-Chloro-4-nitrophenyl)-2,2-difluoro-1-phenylethan-1-one (1e): orange solid; 76% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.13 (t, J = 8.0 Hz, 1H), 8.07 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.55-7.49 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 187.3 (t, $J_{C\text{-}F}$ = 31.4 Hz, 1C), 155.1 (d, $J_{C\text{-}F}$ = 276.9 Hz, 1C), 140.3 (td, $J_{C\text{-}F}$ = 26.1, 7.8 Hz, 1C), 138.6 (d, $J_{C\text{-}F}$ = 7.3 Hz, 1C), 134.9, 131.2 (t, $J_{C\text{-}F}$ = 2.4 Hz, 1C), 130.2 (t, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 130.2 (t, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 128.9, 128.9, 126.5 (d, $J_{C\text{-}F}$ = 2.6 Hz, 1C), 122.3 (dd, $J_{C\text{-}F}$ = 10.8, 6.1 Hz, 1C), 116.7 (dt, $J_{C\text{-}F}$ = 23.4, 6.4 Hz, 1C), 115.5 (td, $J_{C\text{-}F}$ = 258.4, 1.3 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -97.8 (s, 2F), -115.5 (s, 1F).



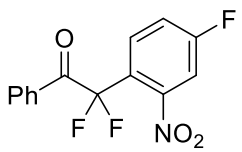
2-(3-Chloro-4-nitrophenyl)-2,2-difluoro-1-phenylethan-1-one (1f): yellow solid; 75% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.07 (dd, J = 8.4, 1.2 Hz, 2H), 7.93 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 1.6 Hz, 1H), 7.69-7.62 (m, 2H), 7.53-7.49 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 187.4 (t, $J_{C\text{-}F}$ = 31.5 Hz, 1C), 149.2, 138.0 (t, $J_{C\text{-}F}$ = 25.9 Hz, 1C), 134.9, 131.3 (t, $J_{C\text{-}F}$ = 2.3 Hz, 1C), 130.2 (t, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 130.2 (t, $J_{C\text{-}F}$ = 3.1 Hz, 1C), 129.6 (t, $J_{C\text{-}F}$ = 6.5 Hz, 1C), 128.9, 128.9, 127.5, 125.7, 125.5 (t, $J_{C\text{-}F}$ = 6.2 Hz, 1C), 115.6 (t, $J_{C\text{-}F}$ = 258.3 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -97.7 (s, 2F).



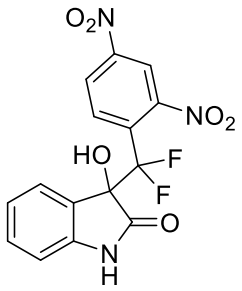
Methyl 4-(1,1-difluoro-2-oxo-2-phenylethyl)-3-nitrobenzoate (1g): white solid; 72% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.77 (s, 1H), 8.44 (d, J = 7.2 Hz, 1H), 8.14 (d, J = 6.4 Hz, 2H), 8.06 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 6.4 Hz, 1H), 7.54 (t, J = 6.8 Hz, 2H), 4.01 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 187.5 (t, $J_{C\text{-}F}$ = 30.4 Hz, 1C), 164.1, 146.9, 134.3, 134.2, 133.8, 132.7 (t, $J_{C\text{-}F}$ = 25.3 Hz, 1C), 132.0 (t, $J_{C\text{-}F}$ = 2.8 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 2.9 Hz, 1C), 128.9, 128.8, 128.7, 128.7, 126.5, 116.3 (t, $J_{C\text{-}F}$ = 259.7 Hz, 1C), 53.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -94.9 (s, 2F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{16}H_{11}F_2NO_5Na$, m/z: 358.0498, found: 358.0498.



2,2-Difluoro-2-(2-nitro-4-(trifluoromethyl)phenyl)-1-phenylethan-1-one (1h): white solid; 88% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.44 (s, 1H), 8.18-8.12 (m, 3H), 8.06 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 187.4 (t, $J_{C\text{-}F}$ = 30.2 Hz, 1C), 147.0, 134.4, 134.3 (dd, $J_{C\text{-}F}$ = 69.8, 35.7 Hz, 1C), 132.4 (t, $J_{C\text{-}F}$ = 25.6 Hz, 1C), 131.9 (t, $J_{C\text{-}F}$ = 3.2 Hz, 1C), 130.3 (q, $J_{C\text{-}F}$ = 3.2 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 3.0 Hz, 1C), 129.5 (t, $J_{C\text{-}F}$ = 10.2 Hz, 1C), 129.0, 128.8, 128.8, 122.9 (q, $J_{C\text{-}F}$ = 3.7 Hz, 1C), 122.3 (q, $J_{C\text{-}F}$ = 274.3 Hz, 1C), 116.2 (t, $J_{C\text{-}F}$ = 260.2 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -63.2 (s, 3F), -95.0 (s, 2F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{15}H_8F_5NO_3Na$, m/z: 368.0317, found: 368.0317.

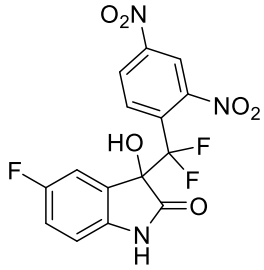


2,2-Difluoro-2-(4-fluoro-2-nitrophenyl)-1-phenylethan-1-one (1i): white solid; 53% yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.15 (dd, J = 8.0, 0.8 Hz, 2H), 7.99 (dd, J = 8.8, 5.2 Hz, 1H), 7.90 (dd, J = 8.4, 2.8 Hz, 1H), 7.70-7.65 (m, 1H), 7.57-7.50 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 187.7 (t, $J_{C\text{-}F}$ = 30.9 Hz, 1C), 163.4 (d, $J_{C\text{-}F}$ = 257.1 Hz, 1C), 147.8, 134.2, 132.2 (t, $J_{C\text{-}F}$ = 3.2, 1C), 130.4 (dt, $J_{C\text{-}F}$ = 10.4, 8.7 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 3.0 Hz, 1C), 129.9 (t, $J_{C\text{-}F}$ = 3.0 Hz, 1C), 128.7, 128.7, 125.1 (td, $J_{C\text{-}F}$ = 25.6, 4.1 Hz, 1C), 120.7 (d, $J_{C\text{-}F}$ = 21.3 Hz, 1C), 116.4 (t, $J_{C\text{-}F}$ = 258.9 Hz, 1C), 113.7 (d, $J_{C\text{-}F}$ = 27.3 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -94.1 (s, 2F), -105.1-(-105.2) (m, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{14}H_8F_2NO_3Na$, m/z: 318.0348, found: 318.0349.

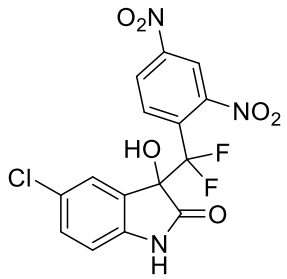


3-((2,4-Dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3a): pale yellow solid; 36.2 mg, 99% yield, **^{1}H NMR (400 MHz, DMSO-d_6)** δ (ppm) 10.73 (s, 1H), 8.81 (s, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H), 7.57 (s, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 6.8 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ (ppm) 173.2 (d, $J_{C\text{-}F}$ = 5.8 Hz, 1C), 149.1, 149.0, 142.9, 132.5 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 131.0, 129.2 (t, $J_{C\text{-}F}$ = 26.9 Hz, 1C), 126.3, 125.6, 125.2, 122.1,

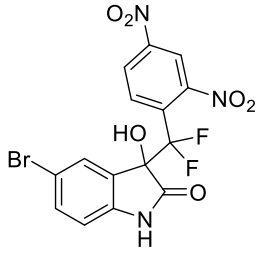
119.1, 119.0 (dd, $J_{C\text{-}F}$ = 255.0, 251.4 Hz, 1C), 110.2, 77.8 (dd, $J_{C\text{-}F}$ = 32.6, 27.4 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.9 (d, J = 177.1 Hz, 1F), -103.5 (d, J = 177.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{15}H_{10}F_2N_3O_6$, m/z: 366.0538, found: 366.0530.



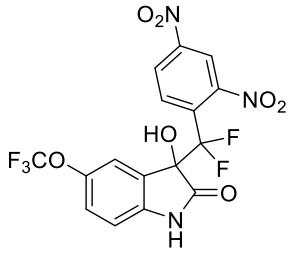
3-((2,4-Dinitrophenyl)difluoromethyl)-5-fluoro-3-hydroxyindolin-2-one (3b): pale yellow solid; 34.5 mg, 90% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.79 (s, 1H), 8.82 (s, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.8 Hz, 1H), 7.76 (s, 1H), 7.20 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 6.8 Hz, 1H), 6.89 (dd, J = 8.0, 4.0 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.2 (d, $J_{C\text{-}F}$ = 5.2 Hz, 1C), 158.0 (d, $J_{C\text{-}F}$ = 239.3 Hz, 1C), 149.2, 149.0, 139.2, 132.6 (t, $J_{C\text{-}F}$ = 6.0 Hz, 1C), 128.9 (t, $J_{C\text{-}F}$ = 26.8 Hz, 1C), 127.1 (d, $J_{C\text{-}F}$ = 7.8 Hz, 1C), 125.3, 119.2, 118.9 (dd, $J_{C\text{-}F}$ = 254.9, 252.3 Hz, 1C), 117.5 (d, $J_{C\text{-}F}$ = 23.7 Hz, 1C), 113.9 (d, $J_{C\text{-}F}$ = 24.9 Hz, 1C), 111.3 (d, $J_{C\text{-}F}$ = 7.9 Hz, 1C), 78.1 (dd, $J_{C\text{-}F}$ = 32.6, 28.4 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.8 (d, J = 177.5 Hz, 1F), -103.5 (d, J = 177.5 Hz, 1F), -120.8-(-120.9) (m, 1F). HRMS (ESI) Calcd for $[M + Na]^+$ $C_{15}H_9F_3N_3O_6Na$, m/z: 406.0257, found: 406.0281.



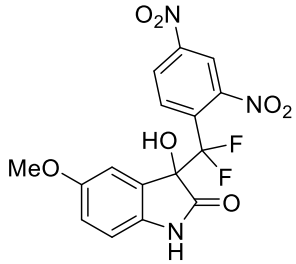
5-Chloro-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3c): pale yellow solid; 39.2 mg, 98% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.91 (s, 1H), 8.83 (s, 1H), 8.61 (d, J = 8.0, 1H), 8.18 (d, J = 8.4, 1H), 7.76 (s, 1H), 7.42 (d, J = 7.6, 1H), 7.16 (s, 1H), 6.91 (d, J = 8.0, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 172.7 (d, $J_{C\text{-}F}$ = 6.1 Hz, 1C), 149.1, 148.9, 141.8, 132.5 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 130.8, 128.7 (t, $J_{C\text{-}F}$ = 26.8 Hz, 1C), 127.4, 126.1 (d, $J_{C\text{-}F}$ = 1.4 Hz, 1C), 126.1, 125.2, 119.1, 118.8 (dd, $J_{C\text{-}F}$ = 256.6, 250.8 Hz, 1C), 111.8, 77.9 (dd, $J_{C\text{-}F}$ = 33.2, 26.9 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.0 (d, J = 266.2 Hz, 1F), -103.9 (d, J = 266.2 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{15}H_9ClF_2N_3O_6$, m/z: 400.0148, found: 400.0141.



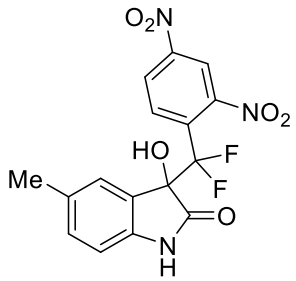
5-Bromo-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3d): pale yellow solid; 36.8 mg, 83% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.92 (s, 1H), 8.83 (d, J = 2.0 Hz, 1H), 8.61 (dd, J = 8.0, 2.0 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H), 7.55 (dd, J = 8.4, 2.0 Hz, 1H), 7.29 (s, 1H), 6.87 (d, J = 8.0 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 172.7 (d, $J_{C\text{-}F}$ = 6.2 Hz, 1C), 149.2, 149.0, 142.3, 133.8, 132.6 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 128.9, 128.9 (t, $J_{C\text{-}F}$ = 26.8 Hz, 1C), 127.9, 125.3, 119.2, 118.9 (dd, $J_{C\text{-}F}$ = 257.6, 250.8 Hz, 1C), 113.7, 112.4, 77.9 (dd, $J_{C\text{-}F}$ = 33.3, 26.3 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -98.7 (d, J = 176.0 Hz, 1F), -103.9 (d, J = 175.6 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{15}H_9BrF_2N_3O_6$, m/z: 443.9643, found: 443.9638.



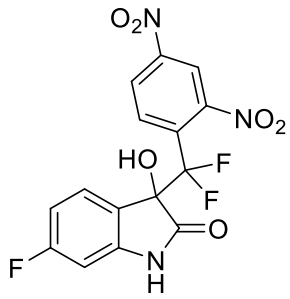
3-((2,4-Dinitrophenyl)difluoromethyl)-3-hydroxy-5-(trifluoromethoxy)indolin-2-one (3e): pale yellow solid; 42.7 mg, 95% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.94 (s, 1H), 8.81 (d, J = 2.4 Hz, 1H), 8.62 (dd, J = 8.8, 2.0 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H), 7.81 (s, 1H), 7.37 (dd, J = 8.4, 2.0 Hz, 1H), 7.00 (s, 1H), 6.99 (d, J = 8.4 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.1 (d, $J_{C\text{-}F}$ = 5.4 Hz, 1C), 149.2, 148.8, 143.2, 142.2, 132.5 (t, $J_{C\text{-}F}$ = 6.8 Hz, 1C), 128.6 (t, $J_{C\text{-}F}$ = 26.7 Hz, 1C), 127.1, 125.4, 124.5, 120.2 (q, $J_{C\text{-}F}$ = 256.5 Hz, 1C), 119.7, 119.2, 118.8 (dd, $J_{C\text{-}F}$ = 255.9, 252.2 Hz, 1C), 111.4, 77.9 (dd, $J_{C\text{-}F}$ = 32.0, 27.6 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -57.4 (s, 3F), -100.4 (d, J = 177.1 Hz, 1F), -103.4 (d, J = 177.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{16}H_9F_5N_3O_7$, m/z: 450.0361, found: 450.0357.



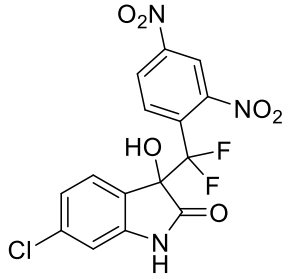
3-((2,4-Dinitrophenyl)difluoromethyl)-3-hydroxy-5-methoxyindolin-2-one (3f): pale yellow solid; 36.4 mg, 92 % yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.57 (s, 1H), 8.81 (s, 1H), 8.60 (s, 1H), 8.19 (s, 1H), 7.60 (s, 1H), 6.91−6.72 (m, 3H), 3.68 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.0 (d, $J_{C\text{-}F}$ = 5.5 Hz, 1C), 154.9, 149.1, 149.0, 136.1, 132.6 (t, $J_{C\text{-}F}$ = 6.5 Hz, 1C), 129.2 (t, $J_{C\text{-}F}$ = 26.5 Hz, 1C), 126.7, 125.2, 119.1, 119.0 (dd, $J_{C\text{-}F}$ = 254.8, 252.9 Hz, 1C), 115.8, 112.9, 110.7, 78.2 (dd, $J_{C\text{-}F}$ = 31.5, 25.6 Hz, 1C), 55.6. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.8 (d, J = 177.1 Hz, 1F), -103.6 (d, J = 177.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{16}H_{11}F_2N_3O_7Na$, m/z: 418.0457, found: 418.0451.



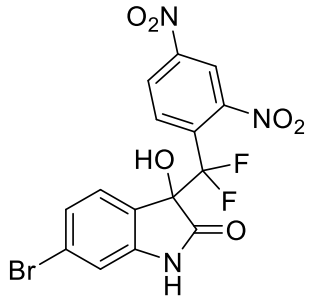
3-((2,4-Dinitrophenyl)difluoromethyl)-3-hydroxy-5-methylindolin-2-one (3g): pale yellow solid; 36.8 mg, 97% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.62 (s, 1H), 8.79 (s, 1H), 8.60 (s, 1H), 8.18 (s, 1H), 7.51 (s, 1H), 7.14 (s, 1H), 7.01 (s, 1H), 6.78 (s, 1H), 2.25 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.1 (d, $J_{C\text{-}F}$ = 6.2 Hz, 1C), 149.0, 149.0, 140.4, 132.5 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 131.0, 131.0, 129.3 (t, $J_{C\text{-}F}$ = 27.1 Hz, 1C), 126.8, 125.7, 125.0, 119.0, 118.9 (dd, $J_{C\text{-}F}$ = 258.0, 256.1 Hz, 1C), 109.8, 77.9 (dd, $J_{C\text{-}F}$ = 33.6, 27.0 Hz, 1C), 20.5. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.1 (d, J = 176.0 Hz, 1F), -103.7 (d, J = 175.6 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{16}H_{12}F_2N_3O_6$, m/z: 380.0694, found: 380.0685.



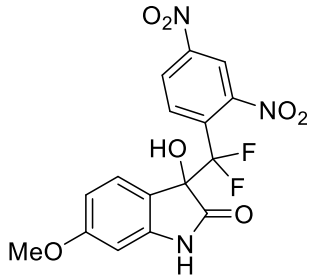
3-((2,4-Dinitrophenyl)difluoromethyl)-6-fluoro-3-hydroxyindolin-2-one (3h): pale yellow solid; 35.7 mg, 93% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm)** 10.89 (s, 1H), 8.80 (d, J = 2.4 Hz, 1H), 8.61 (dd, J = 8.8, 2.0 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.62 (s, 1H), 7.09 (dd, J = 8.0, 5.6 Hz, 1H), 6.82-6.77 (m, 1H), 6.72 (dd, J = 8.8, 2.0 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.4 (d, $J_{C\text{-}F}$ = 5.5 Hz, 1C), 163.7 (d, $J_{C\text{-}F}$ = 246.5 Hz, 1C), 149.1, 148.9, 144.8 (d, $J_{C\text{-}F}$ = 12.6 Hz, 1C), 132.4 (t, $J_{C\text{-}F}$ = 7.1 Hz, 1C), 128.9 (t, $J_{C\text{-}F}$ = 27.0 Hz, 1C), 128.0 (d, $J_{C\text{-}F}$ = 10.0 Hz, 1C), 125.2, 121.5 (d, $J_{C\text{-}F}$ = 2.6 Hz, 1C), 119.1, 118.8 (dd, $J_{C\text{-}F}$ = 255.3, 252.4 Hz, 1C), 108.4 (d, $J_{C\text{-}F}$ = 22.7 Hz, 1C), 98.5 (d, $J_{C\text{-}F}$ = 27.4 Hz, 1C), 77.4 (dd, $J_{C\text{-}F}$ = 32.4, 28.1 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.5 (d, J = 265.1 Hz, 1F), -103.3 (d, J = 265.1 Hz, 1F), -108.8 (s, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{15}H_8F_3N_3O_6Na$, m/z: 406.0257, found: 406.0281.



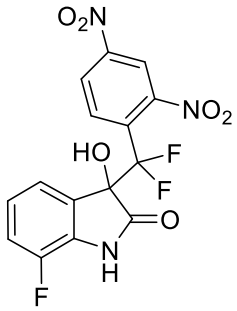
6-Chloro-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3i): pale yellow solid; 37.5 mg, 94% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.92 (s, 1H), 8.81 (s, 1H), 8.60 (d, J = 7.2 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.06 (d, J = 6.0 Hz, 2H), 6.92 (s, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.2 (d, $J_{C\text{-}F}$ = 5.5 Hz, 1C), 149.2, 148.9, 144.4, 135.3, 132.5 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 128.8 (t, $J_{C\text{-}F}$ = 26.8 Hz, 1C), 127.8, 125.3, 124.4, 122.0, 119.2, 118.8 (dd, $J_{C\text{-}F}$ = 254.3, 252.0 Hz, 1C), 110.3, 77.5 (dd, $J_{C\text{-}F}$ = 31.7, 28.5 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.3 (d, J = 180.5 Hz, 1F), -103.3 (d, J = 176.0 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{15}H_8ClF_2N_3O_6Na$, m/z: 421.9962, found: 421.9956.



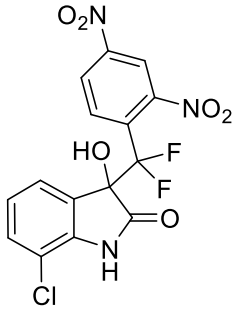
6-Bromo-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3j): pale yellow solid; 41.2 mg, 93% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.89 (s, 1H), 8.80 (d, J = 2.4 Hz, 1H), 8.60 (dd, J = 8.8, 2.0 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.68 (s, 1H), 7.19 (dd, J = 8.0, 2.0 Hz, 1H), 7.05 (d, J = 1.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.1 (d, $J_{C\text{-}F}$ = 5.5 Hz, 1C), 149.2, 149.0, 144.5, 132.5 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 128.9 (t, $J_{C\text{-}F}$ = 27.0 Hz, 1C), 128.1, 125.3, 124.9, 124.9, 123.8, 119.2, 118.8 (dd, $J_{C\text{-}F}$ = 255.4, 252.2 Hz, 1C), 113.1, 77.6 (dd, $J_{C\text{-}F}$ = 32.4, 28.1 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.1 (dd, J = 265.8, 158.3 Hz, 1F), -103.5 (dd, J = 265.5, 85.0 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{15}H_9BrF_2N_3O_6$, m/z: 443.9643, found: 443.9638.



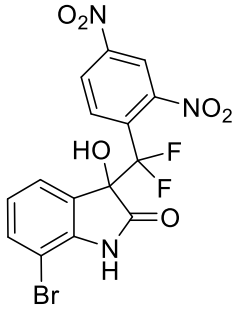
3-((2,4-Dinitrophenyl)difluoromethyl)-3-hydroxy-6-methoxyindolin-2-one (3k): pale yellow solid; 35.2 mg, 89% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.65 (s, 1H), 8.79 (d, J = 2.0 Hz, 1H), 8.59 (d, J = 8.8 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 7.42 (s, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.53 (dd, J = 8.4, 2.0 Hz, 1H), 6.41 (d, J = 2.0 Hz, 1H), 3.76 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.7 (d, $J_{C\text{-}F}$ = 5.8 Hz, 1C), 161.5, 149.0, 148.9, 144.3, 132.4 (t, $J_{C\text{-}F}$ = 6.9 Hz, 1C), 129.3 (t, $J_{C\text{-}F}$ = 27.0 Hz, 1C), 127.3, 125.1, 119.1, 118.9 (dd, $J_{C\text{-}F}$ = 254.8, 251.4 Hz, 1C), 117.2, 106.9, 96.8, 77.5 (dd, $J_{C\text{-}F}$ = 32.3, 27.8 Hz, 1C), 55.4. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.3 (d, J = 264.7 Hz, 1F), -103.1 (d, J = 264.7 Hz, 1F). **HRMS (ESI)** Calcd for $[M+H]^+$ $C_{16}H_{12}F_2N_3O_6$, m/z: 396.0646, found: 396.0634.



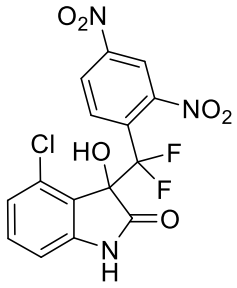
3-((2,4-Dinitrophenyl)difluoromethyl)-7-fluoro-3-hydroxyindolin-2-one (3l): white solid; 37.9 mg, 99% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 11.31 (s, 1H), 8.82 (s, 1H), 8.61 (d, J = 5.6 Hz, 1H), 8.18 (d, J = 4.8 Hz, 1H), 7.75 (s, 1H), 7.29 (s, 1H), 7.03 (s, 1H), 6.97 (s, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.0 (d, $J_{C\text{-}F}$ = 5.1 Hz, 1C), 149.1, 148.9, 146.4 (d, $J_{C\text{-}F}$ = 244.2 Hz, 1C), 132.4 (t, $J_{C\text{-}F}$ = 6.8 Hz, 1C), 130.0 (d, $J_{C\text{-}F}$ = 13.0 Hz, 1C), 128.8 (d, $J_{C\text{-}F}$ = 27.1 Hz, 1C), 128.4 (d, $J_{C\text{-}F}$ = 3.3 Hz, 1C), 125.2, 123.1 (d, $J_{C\text{-}F}$ = 5.8 Hz, 1C), 122.3, 119.1, 118.7 (dd, $J_{C\text{-}F}$ = 255.8, 252.0 Hz, 1C), 118.0 (d, $J_{C\text{-}F}$ = 17.2 Hz, 1C), 77.9 (dd, $J_{C\text{-}F}$ = 30.0, 28.4 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.9 (d, J = 176.0 Hz, 1F), -103.5 (d, J = 176.0 Hz, 1F), -132.5 (s, 1F). **HRMS (ESI)** Calcd for $[M+H]^+$ $C_{15}H_9F_3N_3O_6$, m/z: 384.0443, found: 384.0434.



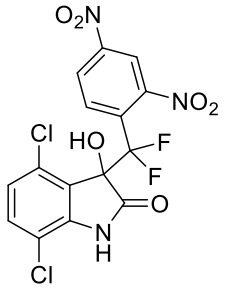
7-Chloro-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3m): pale yellow solid; 38.3 mg, 96% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 11.23 (s, 1H), 8.83 (d, J = 2.0 Hz, 1H), 8.62 (dd, J = 8.8, 2.0 Hz, 1H), 8.18 (d, J = 8.8 Hz, 1H), 7.76 (s, 1H), 7.43 (dd, J = 8.0, 0.8 Hz, 1H), 7.09-7.01 (m, 2H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.2 (d, $J_{C\text{-}F}$ = 5.8 Hz, 1C), 149.2, 149.0, 140.6, 132.5 (t, $J_{C\text{-}F}$ = 7.2 Hz, 1C), 130.9, 128.8 (t, $J_{C\text{-}F}$ = 26.8 Hz, 1C), 127.5, 125.3, 124.9, 123.6, 119.2, 118.8 (dd, $J_{C\text{-}F}$ = 256.3, 251.8 Hz, 1C), 114.4, 78.3 (dd, $J_{C\text{-}F}$ = 32.7, 27.7 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.8 (d, J = 177.5 Hz, 1F), -103.5 (d, J = 177.5 Hz, 1F). **HRMS (ESI)** Calcd for $[M+H]^+$ $C_{15}H_9F_2ClN_3O_6$, m/z: 400.0148, found: 400.0143.



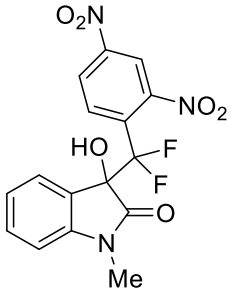
7-Bromo-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3n): pale yellow solid; 39.9 mg, 90% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.91(s, 1H), 8.81 (s, 1H), 8.61 (d, J = 8.8 Hz, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.69 (s, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.05 (s, 1H), 7.01 (d, J = 7.6 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.0 (d, $J_{C\text{-}F}$ = 5.1 Hz, 1C), 149.2, 148.9, 144.5, 132.4 (t, $J_{C\text{-}F}$ = 6.7 Hz, 1C), 128.8 (t, $J_{C\text{-}F}$ = 26.4 Hz, 1C), 128.0, 125.3, 124.9, 124.9, 123.8, 119.2, 118.8 (dd, $J_{C\text{-}F}$ = 256.1, 251.9 Hz, 1C), 113.1, 77.5 (dd, $J_{C\text{-}F}$ = 31.9, 27.9 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.0 (dd, J = 260.2, 156.8 Hz, 1F), -103.5 (dd, J = 265.5, 86.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{15}H_9BrF_2N_3O_6$, m/z: 443.9643, found: 443.9646



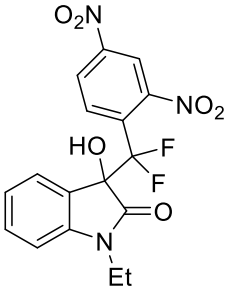
4-Chloro-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3o): pale yellow solid; 36.7 mg, 92% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 10.90 (s, 1H), 8.78 (s, 1H), 8.58 (s, 1H), 8.17 (s, 1H), 7.56 (s, 1H), 7.33 (s, 1H), 6.99 (s, 1H), 6.85 (s, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.2 (d, $J_{C\text{-}F}$ = 4.8 Hz, 1C), 149.1, 148.7, 145.1, 133.0 (t, $J_{C\text{-}F}$ = 6.8 Hz, 1C), 132.4, 132.2, 129.7 (t, $J_{C\text{-}F}$ = 26.2 Hz, 1C), 125.1, 123.7, 122.1, 119.1 (dd, $J_{C\text{-}F}$ = 254.6, 251.8 Hz, 1C), 119.0, 109.1, 79.6 (t, $J_{C\text{-}F}$ = 30.3 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -96.6 (d, J = 175.2 Hz, 1F), -101.7 (d, J = 175.2 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{15}H_8ClF_2N_3O_6Na$, m/z: 421.9962, found: 421.9956.



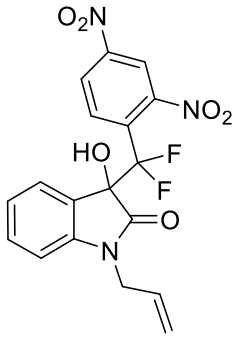
4,7-Dichloro-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3p): pale yellow solid; 41.6 mg, 96% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 11.37 (s, 1H), 8.80 (s, 1H), 8.59 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 173.2 (d, $J_{C\text{-}F}$ = 4.5 Hz, 1C), 149.3, 148.8, 142.6, 133.0 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 132.2, 130.8, 129.4 (t, $J_{C\text{-}F}$ = 26.7 Hz, 1C), 125.2, 124.9, 123.6, 119.2, 119.0 (dd, $J_{C\text{-}F}$ = 259.8, 254.6 Hz, 1C), 113.4, 80.4 (t, $J_{C\text{-}F}$ = 30.6 Hz, 1C); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -97.1 (d, J = 174.8 Hz, 1F), -101.5 (d, J = 175.2 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{15}H_7Cl_2F_2N_3O_6Na$, m/z: 455.9572, found: 455.9570.



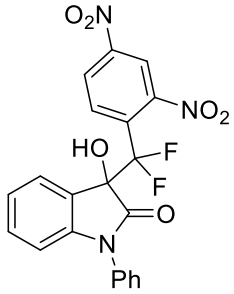
3-((2,4-Dinitrophenyl)difluoromethyl)-3-hydroxy-1-methylindolin-2-one (3q): pale yellow solid; 35.6 mg, 94% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.80 (s, 1H), 8.62 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.8, 1H), 7.63 (s, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 6.8, 1H), 7.10 (d, J = 7.2 Hz, 2H), 3.14 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.7 (d, $J_{C\text{-}F}$ = 5.7 Hz, 1C), 149.2, 149.0, 144.4, 132.6 (t, $J_{C\text{-}F}$ = 5.3 Hz, 1C), 131.2, 129.3 (t, $J_{C\text{-}F}$ = 27.0 Hz, 1C), 125.9, 125.3, 125.1, 122.9, 119.2, 119.1 (dd, $J_{C\text{-}F}$ = 257.7, 238.2 Hz, 1C), 109.2, 77.8 (dd, $J_{C\text{-}F}$ = 32.3, 28.8 Hz, 1C), 26.3. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.1 (d, J = 264.7 Hz, 1F), -103.2 (d, J = 264.7 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{16}H_{11}F_2N_3O_6$, m/z: 402.0508, found: 402.0493.



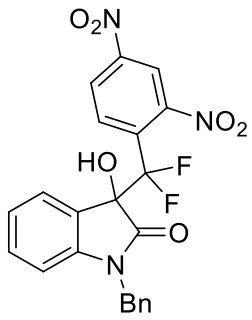
3-((2,4-Dinitrophenyl)difluoromethyl)-1-ethyl-3-hydroxyindolin-2-one (3r): pale yellow solid; 38.5 mg, 98% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.80 (d, J = 2.0 Hz, 1H), 8.61 (dd, J = 8.8, 2.0 Hz, 1H), 8.18 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.44 (td, J = 8.0, 1.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 3.78-3.60 (m, 2H), 1.15 (t, J = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.1 (d, $J_{C\text{-}F}$ = 6.7 Hz, 1C), 149.0, 148.8, 143.2, 132.5 (t, $J_{C\text{-}F}$ = 6.3 Hz, 1C), 131.0, 129.1 (t, $J_{C\text{-}F}$ = 26.0 Hz, 1C), 126.0, 125.1, 125.1, 122.6, 119.1, 118.9 (dd, $J_{C\text{-}F}$ = 257.4, 251.5 Hz, 1C), 109.1, 77.5 (dd, $J_{C\text{-}F}$ = 33.0, 27.8 Hz, 1C), 34.4, 12.1. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.5 (d, J = 265.1 Hz, 1F), -104.0 (d, J = 265.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{17}H_{13}F_2N_3O_6Na$, m/z: 416.0665, found: 416.0684.



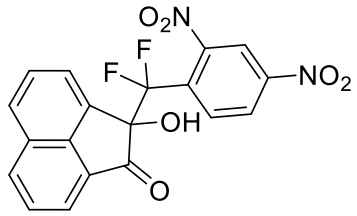
1-Allyl-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3s): pale yellow solid; 37.2 mg, 92% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.83 (s, 1H), 8.63 (s, 1H), 8.20 (s, 1H), 7.74 (s, 1H), 7.42 (s, 1H), 7.20-7.03 (m, 2H), 5.82 (s, 1H), 5.19 (d, J = 6.4 Hz, 2H), 4.36 (s, 1H), 4.26 (s, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.4 (d, $J_{C\text{-}F}$ = 5.9 Hz, 1C), 149.2, 149.0, 143.4, 132.5 (t, $J_{C\text{-}F}$ = 7.6 Hz, 1C), 131.2, 131.0, 129.1 (t, $J_{C\text{-}F}$ = 25.7 Hz, 1C), 126.0, 125.3, 125.0, 122.9, 119.2, 118.9 (dd, $J_{C\text{-}F}$ = 251.7, 250.0 Hz, 1C), 117.2, 109.7, 77.7 (dd, $J_{C\text{-}F}$ = 32.7, 27.4 Hz, 1C), 41.8. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.9 (d, J = 176.7 Hz, 1F), -103.2 (d, J = 177.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{18}H_{13}F_2N_3O_6Na$, m/z: 428.0665, found: 428.0667



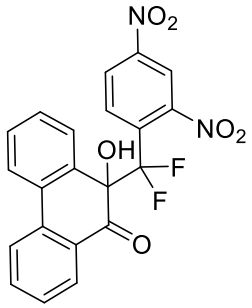
3-((2,4-Dinitrophenyl)difluoromethyl)-3-hydroxy-1-phenylindolin-2-one (3t): pale yellow solid; 42.8 mg, 97% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.84 (s, 1H), 8.64 (s, 1H), 8.24 (s, 1H), 7.89 (s, 1H), 7.61−7.19 (m, 8H), 6.82 (s, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.0 (d, $J_{C\text{-}F}$ = 5.8 Hz, 1C), 149.1, 148.8, 144.0, 133.5, 132.5 (t, $J_{C\text{-}F}$ = 5.8 Hz, 1C), 131.1, 129.8, 129.8, 129.0 (t, $J_{C\text{-}F}$ = 26.4 Hz, 1C), 128.4, 126.3, 126.3, 126.3, 125.3, 124.9, 123.4, 119.2, 118.9 (dd, $J_{C\text{-}F}$ = 257.8, 250.6 Hz, 1C), 109.5, 77.7 (dd, $J_{C\text{-}F}$ = 32.2, 27.5 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -98.9 (d, J = 176.3 Hz, 1F), -103.5 (d, J = 177.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{21}H_{13}F_2N_3O_6Na$, m/z: 464.0665, found :464.0664.



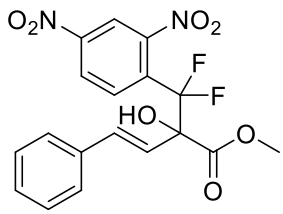
1-Benzyl-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (3u): pale yellow solid; 44.6 mg, 98% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.82 (s, 1H), 8.62 (d, J = 8.8 Hz, 1H), 8.23 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 7.38-7.32 (m, 5H), 7.30-7.25 (m, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 4.93 (dd, J = 36.0, 16.0 Hz, 2H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.8 (d, $J_{C\text{-}F}$ = 5.9 Hz, 1C), 149.1, 149.1, 143.3, 135.6, 132.5 (t, $J_{C\text{-}F}$ = 7.2 Hz, 1C), 131.0, 129.5, 129.1, 129.1 (t, $J_{C\text{-}F}$ = 27.0 Hz, 1C), 128.6, 127.6, 127.3, 126.1, 125.2, 125.0, 122.9, 119.2, 119.0 (dd, $J_{C\text{-}F}$ = 256.0, 252.6 Hz, 1C), 109.8, 77.8 (dd, $J_{C\text{-}F}$ = 32.4, 27.6 Hz, 1C), 43.0. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.7 (d, J = 265.5 Hz, 1F), -103.3 (d, J = 265.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{22}H_{16}F_2N_3O_6$, m/z: 456.1007, found: 456.1002.



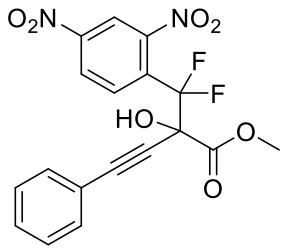
2-((2,4-Dinitrophenyl)difluoromethyl)-2-hydroxyacenaphthylen-1(2H)-one (4a): pale yellow solid; 35.2 mg, 88% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.84 (d, J = 2.0 Hz, 1H), 8.67 (dd, J = 8.8, 2.0 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.8 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 6.8 Hz, 1H), 7.89 (t, J = 7.6 Hz, 1H), 7.81 (s, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.48 (t, J = 6.8 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 196.5, 149.2, 148.5, 137.4, 135.9, 133.0 (d, $J_{C\text{-}F}$ = 1.7 Hz, 1C), 132.5 (t, $J_{C\text{-}F}$ = 6.5 Hz, 1C), 131.8, 130.3, 129.3, 128.8 (d, $J_{C\text{-}F}$ = 4.6 Hz, 1C), 128.2 (t, $J_{C\text{-}F}$ = 27.3 Hz, 1C), 127.2, 124.9, 124.6, 123.7, 119.8 (dd, $J_{C\text{-}F}$ = 254.7, 252.1 Hz, 1C), 118.8, 79.9 (dd, $J_{C\text{-}F}$ = 27.5, 26.4 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -96.1 (d, J = 253.8 Hz, 1F), -101.7 (d, J = 254.2 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{19}H_{10}F_2N_2O_6Na$, m/z: 423.0414, found: 423.0399.



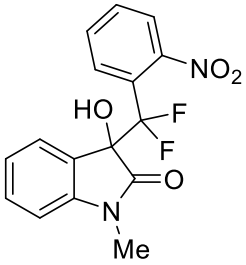
10-((2,4-Dinitrophenyl)difluoromethyl)-10-hydroxyphenanthren-9(10H)-one (4b): pale yellow solid; 35.1 mg, 82% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.70 (d, J = 2.0 Hz, 1H), 8.52 (dd, J = 8.8, 2.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H), 7.87 (dd, J = 7.6, 0.8 Hz, 1H), 7.83-7.78 (m, 2H), 7.56-7.50 (m, 2H), 7.36 (s, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 198.7 (d, $J_{C\text{-}F}$ = 3.8 Hz, 1C), 149.3, 148.7, 141.9, 134.6, 132.6, 132.6, 132.5 (t, $J_{C\text{-}F}$ = 7.9 Hz, 1C), 130.6, 130.2, 129.3 (t, $J_{C\text{-}F}$ = 27.8 Hz, 1C), 129.0, 129.0, 128.9, 126.7, 125.5, 123.1, 122.3, 119.4 (dd, $J_{C\text{-}F}$ = 251.4, 250.2 Hz, 1C), 119.3, 81.0 (dd, $J_{C\text{-}F}$ = 31.5, 27.1 Hz, 1C). **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -98.3 (d, J = 265.8 Hz, 1F), -101.3 (d, J = 265.8 Hz, 1F). **HRMS (ESI)** [M + Na]$^+$ Calcd for $C_{21}H_{12}F_2N_2O_6Na$, m/z: 449.0571, found: 449.0556.



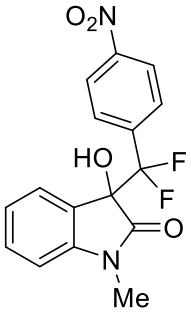
Methyl (E)-2-((2,4-dinitrophenyl)difluoromethyl)-2-hydroxy-4-phenylbut-3-enoate (4c): pale yellow oil; 20.8 mg, 51% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.80 (d, J = 2.4 Hz, 1H), 8.52 (dd, J = 8.8, 2.0 Hz, 1H), 8.04 (d, J = 9.2 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.43 (s, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.31-7.27 (m, 1H), 6.68 (d, J = 16.0 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 168.9, 149.1, 148.7, 135.2, 133.3, 132.4 (t, $J_{C\text{-}F}$ = 6.5 Hz, 1C), 129.1 (t, $J_{C\text{-}F}$ = 27.0 Hz, 1C), 128.7, 128.7, 128.5, 127.0, 127.0, 125.1, 122.8 (d, $J_{C\text{-}F}$ = 4.1 Hz, 1C), 119.4 (t, $J_{C\text{-}F}$ = 258.5 Hz, 1C), 119.0, 79.9 (t, $J_{C\text{-}F}$ = 27.7 Hz, 1C), 53.4. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -97.3 (d, J = 258.7 Hz, 1F), -101.4 (d, J = 258.3 Hz, 1F). **HRMS (ESI)** [M + H]$^+$ Calcd for $C_{18}H_{15}F_2N_2O_7$, m/z: 409.0832, found: 409.0842.



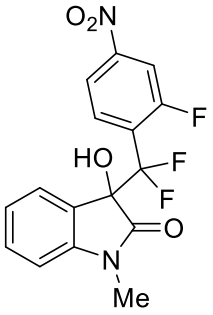
Methyl 2-((2,4-dinitrophenyl)difluoromethyl)-2-hydroxy-4-phenylbut-3-ynoate (4d): pale yellow solid; 26.9 mg, 66% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.87 (d, J = 2.4 Hz, 1H), 8.63 (dd, J = 8.8, 2.4 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.16 (s, 1H), 7.51-7.41 (m, 5H), 3.81 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 166.3, 149.3, 148.9, 132.2 (t, $J_{C\text{-}F}$ = 6.5 Hz, 1C), 131.7, 131.7, 129.8, 128.8, 128.8, 128.7 (t, $J_{C\text{-}F}$ = 26.8 Hz, 1C), 125.4, 120.3, 119.3, 117.9 (t, $J_{C\text{-}F}$ = 259.0 Hz, 1C), 87.4, 83.1 (d, $J_{C\text{-}F}$ = 5.3 Hz, 1C), 74.8 (dd, $J_{C\text{-}F}$ = 31.9, 29.5 Hz, 1C), 53.9. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -98.2 (d, J = 255.7 Hz, 1F), -101.0 (d, J = 255.7 Hz, 1F). **HRMS (ESI)** [M + H]$^+$ Calcd for $C_{18}H_{13}F_2N_2O_7$, m/z: 407.0691, found: 407.0685.



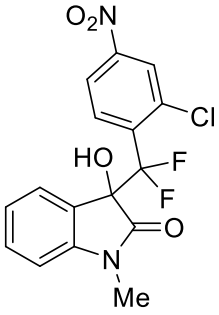
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5a): pale yellow oil; 6.8 mg, 20% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 7.88-7.84 (m, 1H), 7.79-7.76 (m, 3H), 7.43-7.39 (m, 2H), 7.06-7.03 (m, 3H), 3.11 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.9 (d, $J_{C\text{-}F}$ = 6.1 Hz, 1C), 148.8 (t, $J_{C\text{-}F}$ = 2.6 Hz, 1C), 144.2, 132.3, 130.7, 130.6, 130.2 (t, $J_{C\text{-}F}$ = 7.2 Hz, 1C), 125.6, 125.4, 123.5 (t, $J_{C\text{-}F}$ = 26.6 Hz, 1C), 123.5, 122.5, 119.3 (t, $J_{C\text{-}F}$ = 253.4 Hz, 1C) , 108.8, 77.7 (t, $J_{C\text{-}F}$ = 30.6 Hz, 1C), 26.1. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -99.9 (d, J = 263.2 Hz, 1F), -101.7 (d, J = 263.2 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{16}H_{13}F_2N_2O_4$, m/z: 335.0829, found: 335.0838.



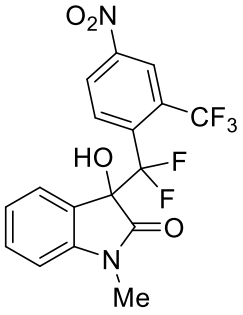
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5b): pale yellow solid; 33.0 mg, 99% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.27 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.37 (s, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.08 (td, J = 7.6, 0.8 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 3.05 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 172.0, 148.7, 144.0, 138.5 (t, $J_{C\text{-}F}$ = 26.0 Hz, 1C), 130.8, 128.7 (t, $J_{C\text{-}F}$ = 6.4 Hz, 1C), 128.7 (t, $J_{C\text{-}F}$ = 6.4 Hz, 1C), 125.8, 125.4, 122.7, 122.7, 122.6, 119.7 (d, $J_{C\text{-}F}$ = 253.3 Hz, 1C), 108.9, 77.3 (dd, $J_{C\text{-}F}$ = 30.2, 28.6 Hz, 1C), 26.0. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -105.6 (d, J = 250.0 Hz, 1F), -107.3 (d, J = 250.4 Hz, 1F). **HRMS (ESI)** Calcd for $[M - H]^-$ $C_{16}H_{11}F_2N_2O_4$, m/z: 333.0682, found: 333.0692.



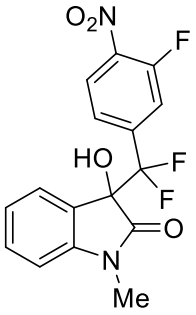
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5c): white solid; 30.8 mg, 87% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.16 (s, 2H), 7.74 (s, 1H), 7.41 (d, J = 22.8 Hz, 2H), 7.38 (s, 1H), 7.10 (d, J = 18.8 Hz, 2H), 3.13 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.8 (d, J = 5.4 Hz, 1C), 159.2 (d, $J_{C\text{-}F}$ = 259.6 Hz, 1C), 149.8 (d, $J_{C\text{-}F}$ = 9.1 Hz, 1C), 144.2, 131.9 (t, $J_{C\text{-}F}$ = 7.4 Hz, 1C), 130.8, 126.0, 125.3, 122.6, 119.6 (t, $J_{C\text{-}F}$ = 255.1 Hz, 1C), 118.4 (d, $J_{C\text{-}F}$ = 2.5 Hz, 1C), 112.2, 111.9, 108.9, 77.3 (dd, $J_{C\text{-}F}$ = 32.7, 27.7 Hz, 1C), 26.2. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -102.7 (dd, J = 259.8, 21.8 Hz, 1F), -105.6 (dd, J = 260.2, 29.3 Hz, 1F), -106.3 (dd, J = 29.0, 22.2 Hz, 1F). **HRMS (ESI)** Calcd for $[M - H]^-$ $C_{16}H_{10}F_3N_2O_4$, m/z: 351.0598, found: 351.0598.



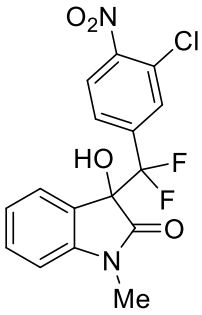
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5d): pale yellow solid; 29.2 mg, 79% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.28 (d, J = 12.4 Hz, 1H), 8.27 (s, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.35 (s, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.09 (dd, J = 14.0, 7.2 Hz, 2H), 3.13 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.9 (d, J = 5.6 Hz, 1C), 148.9, 144.2, 135.5 (t, $J_{C\text{-}F}$ = 24.7 Hz, 1C), 133.4, 132.8 (t, $J_{C\text{-}F}$ = 8.3 Hz, 1C), 130.8, 126.0, 125.6, 125.3, 122.6, 121.0, 119.9 (dd, $J_{C\text{-}F}$ = 255.8, 253.8 Hz, 1C), 108.9, 77.6 (dd, $J_{C\text{-}F}$ = 31.9, 28.1 Hz, 1C), 26.2. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.4 (d, J = 258.7 Hz, 1F), -102.5 (d, J = 258.7 Hz, 1F). **HRMS (ESI)** Calcd for $[M - H]^-$ $C_{16}H_{10}ClF_2N_2O_4$, m/z: 367.0300, found: 367.0303.



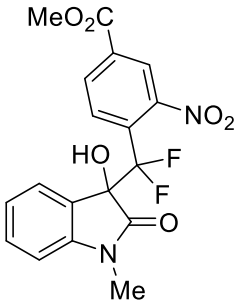
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5e): white solid; 30.2 mg, 75% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.72 (d, J = 8.8 Hz, 1H), 8.52 (d, J = 2.0 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 0.8 Hz, 1H), 7.45 (dt, J = 7.6, 0.8 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.12-7.07 (m, 2H), 3.12 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.8 (d, $J_{C\text{-}F}$ = 6.4 Hz, 1C), 148.5, 144.2, 136.5 (dd, $J_{C\text{-}F}$ = 28.0, 25.9 Hz, 1C), 133.7 (t, $J_{C\text{-}F}$ = 7.8 Hz, 1C), 130.9, 128.2 (d, $J_{C\text{-}F}$ = 33.5 Hz, 1C), 126.5, 125.6, 125.5, 122.6, 122.1 (d, $J_{C\text{-}F}$ = 275.8 Hz, 1C), 121.7 (q, $J_{C\text{-}F}$ = 7.2 Hz, 1C), 119.5 (dd, $J_{C\text{-}F}$ = 254.3, 252.3 Hz, 1C), 109.0, 77.6 (dd, $J_{C\text{-}F}$ = 32.9, 28.2 Hz, 1C), 26.1. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -57.0 (dd, J = 27.1, 15.8 Hz, 3F), -97.8 (dq, J = 263.8, 15.0 Hz, 1F), -102.1 (dq, J = 264.0, 27.1 Hz, 1F). **HRMS (ESI)** Calcd for $[M - H]^-$ $C_{17}H_{10}F_5N_2O_4$, m/z: 401.0564, found: 401.0566.



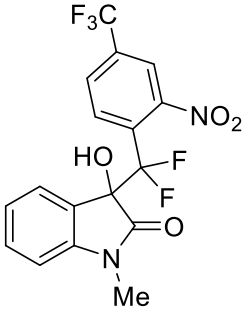
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5f): pale yellow solid; 30.4 mg, 86% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.24 (t, J = 8.2 Hz, 1H), 7.49 (dd, J = 12.0, 1.6 Hz, 1H), 7.45-7.41 (m, 3H), 7.24 (d, J = 7.2 Hz, 1H), 7.11 (dt, J = 7.2, 0.8 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 3.09 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.8 (d, $J_{C\text{-}F}$ = 4.0 Hz, 1C), 153.5 (d, $J_{C\text{-}F}$ = 262.7 Hz, 1C), 144.1, 139.8 (d, $J_{C\text{-}F}$ = 8.0 Hz, 1C), 138.0-137.9 (m, 1C), 130.9, 125.8, 125.7 (d, $J_{C\text{-}F}$ = 2.3 Hz, 1C), 125.2, 124.2-124.0 (m, 1C), 122.7, 119.0 (t, $J_{C\text{-}F}$ = 253.0 Hz, 1C), 117.5 (dt, $J_{C\text{-}F}$ = 23.3, 6.5 Hz, 1C), 109.0, 77.1 (dd, $J_{C\text{-}F}$ = 31.3, 28.2 Hz, 1C), 26.1. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -105.3 (d, J = 251.5 Hz, 1F), -107.4 (d, J = 251.9 Hz, 1F), -119.0 (s, 1F). **HRMS (ESI)** Calcd for $[M - H]^-$ $C_{16}H_{10}F_3N_2O_4$, m/z: 351.0595, found: 351.0598.



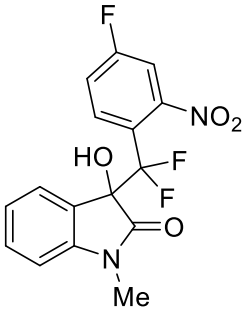
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5g): white solid; 36.2 mg, 98% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.16 (d, J = 8.4 Hz, 1H), 7.66 (s, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.46 (s, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 3.10 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.8 (d, J = 4.7 Hz, 1H), 148.6, 144.1, 137.5 (t, $J_{C\text{-}F}$ = 26.3 Hz, 1C), 130.9, 130.2 (t, $J_{C\text{-}F}$ = 6.6 Hz, 1C), 127.6 (t, $J_{C\text{-}F}$ = 6.4 Hz, 1C), 125.9, 125.3, 125.0, 124.3, 122.7, 119.1 (dd, $J_{C\text{-}F}$ = 255.7, 251.4 Hz, 1C), 109.0, 77.1 (dd, $J_{C\text{-}F}$ = 31.9, 28.0 Hz, 1C), 26.1. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -104.7 (d, J = 253.0 Hz, 1F), -107.7 (d, J = 252.7 Hz, 1F). **HRMS (ESI)** Calcd for $[M - H]^-$ $C_{16}H_{10}ClF_2N_2O_4$, m/z: 367.0300, found: 367.0303.



1- Benzyl-3-((2,4-dinitrophenyl)difluoromethyl)-3-hydroxyindolin-2-one (5h): white solid; 35.4 mg, 90% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.31 (d, J = 10.4 Hz, 1H), 8.30 (s, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.55 (s, 1H), 7.43 (td, J = 7.6, 1.2 Hz, 1H), 7.13-7.05 (m, 3H), 3.93 (s, 3H), 3.13 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.7 (d, $J_{C\text{-}F}$ = 5.5 Hz, 1C), 164.0, 149.0, 144.2, 133.2, 131.3 (t, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 130.9, 130.9, 127.6 (d, $J_{C\text{-}F}$ = 26.7 Hz, 1C), 125.7, 125.2, 124.0, 122.7, 119.1 (dd, $J_{C\text{-}F}$ = 255.1, 251.9 Hz, 1C), 109.0, 77.7 (dd, $J_{C\text{-}F}$ = 32.0, 28.3 Hz, 1C), 53.0, 26.2. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -100.0 (d, J = 264.0 Hz, 1F), -102.8 (d, J = 264.0 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{18}H_{15}F_2N_2O_6$, m/z: 393.0904, found: 393.0893.

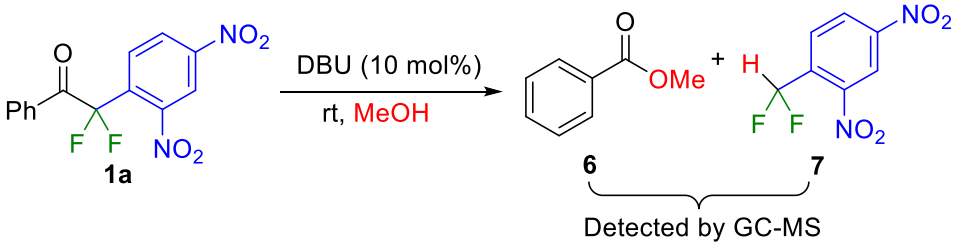


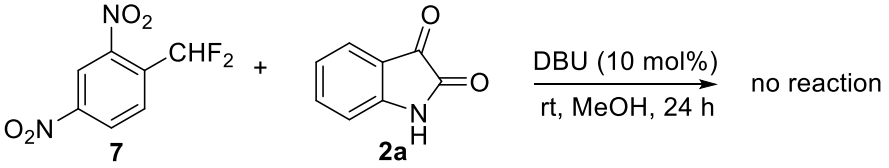
3-(Difluoro(2-nitro-4-(trifluoromethyl)phenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5i): pale yellow solid; 27.5 mg, 68% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.43 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 1.6 Hz, 1H), 7.44 (td, J = 7.6, 1.2 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.0 Hz, 2H), 3.13 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 171.6 (d, $J_{C\text{-}F}$ = 6.2 Hz, 1C), 149.0, 144.2, 132.5, 132.1, 132.0 (d, $J_{C\text{-}F}$ = 6.9 Hz, 1C), 131.0, 127.5 (dd, $J_{C\text{-}F}$ = 28.4, 25.6 Hz, 1C), 125.7, 125.1, 122.7, 122.6 (q, $J_{C\text{-}F}$ = 274.6 Hz, 1C), 121.0 (d, $J_{C\text{-}F}$ = 3.6 Hz, 1C), 118.9 (dd, $J_{C\text{-}F}$ = 256.0, 250.4 Hz, 1C), 109.0, 77.6 (dd, $J_{C\text{-}F}$ = 32.7, 27.6 Hz, 1C), 26.2. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -61.7 (s, 3F), -99.6 (d, J = 264.7 Hz, 1F), -103.5 (d, J = 264.7 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{17}H_{11}F_5N_2O_4Na$, m/z: 425.0532, found: 425.0531.



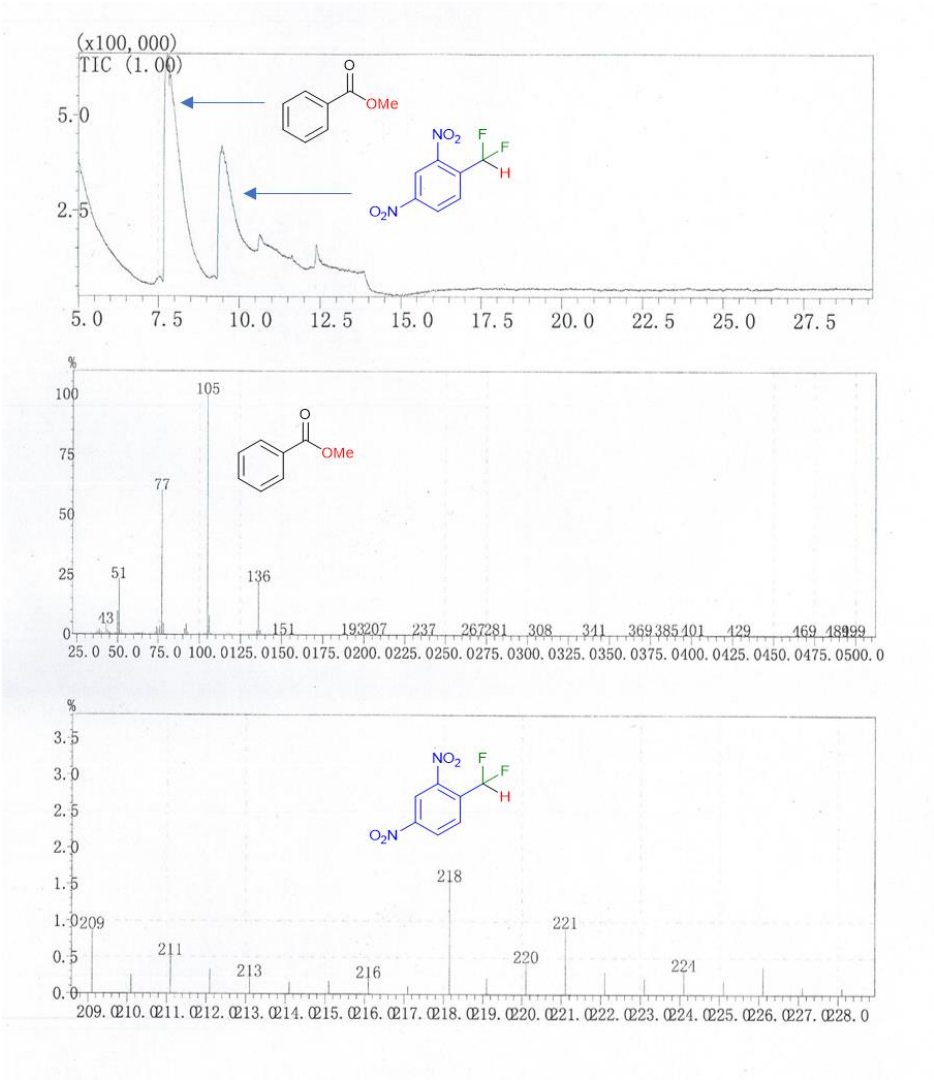
3-(Difluoro(4-fluoro-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (5j): white solid; 21.6 mg, 61% yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 8.02 (d, J = 7.6 Hz, 2H), 7.98 (d, J = 8.8 Hz, 1H), 7.80-7.76 (m, 2H), 7.64 (t, J = 7.8 Hz, 2H), 7.53 (dd, J = 8.8, 2.4 Hz, 1H), 3.95 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 187.3 (t, $J_{C\text{-}F}$ = 31.6 Hz, 1C), 161.7, 147.5, 134.6, 131.7 (t, $J_{C\text{-}F}$ = 2.5 Hz, 1C), 131.3 (d, $J_{C\text{-}F}$ = 295.5 Hz, 1C), 129.6 (t, $J_{C\text{-}F}$ = 9.6 Hz, 1C), 129.4 (t, $J_{C\text{-}F}$ = 2.5 Hz, 1C) , 129.1, 129.1, 128.4 (t, $J_{C\text{-}F}$ = 152.1 Hz, 1C), 119.5, 118.6 (t, $J_{C\text{-}F}$ = 25.5 Hz, 1C), 116.2 (t, $J_{C\text{-}F}$ = 256.0 Hz, 1C), 111.4, 56.5. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ (ppm) -59.1 (s, 1F), -93.0 (s, 2F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{16}H_{12}F_3N_2O_4$, m/z: 353.0746, found: 353.0744.

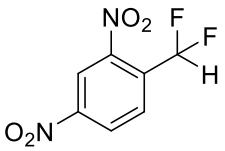
Control reactions





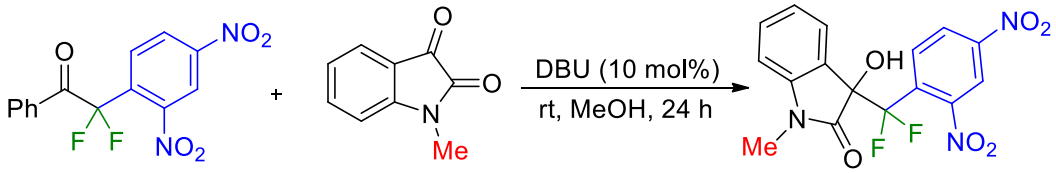
GC-MS Spectrum and the characterization data of 7





1-(Difluoromethyl)-2,4-dinitrobenzene (7): yellow oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.98 (t, J = 1.0 Hz, 1H), 8.62 (dd, J = 8.4, 2.0 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.45 (t, J = 54.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 149.2, 147.6, 134.6, 129.2 (t, $J_{C\text{-}F}$ = 8.0 Hz, 1C), 128.2, 120.7, 109.7 (t, $J_{C\text{-}F}$ = 243.7 Hz, 1C). **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -115.6 (s, 1F), -115.8 (s, 1F).

Gram-scale synthesis of 3q



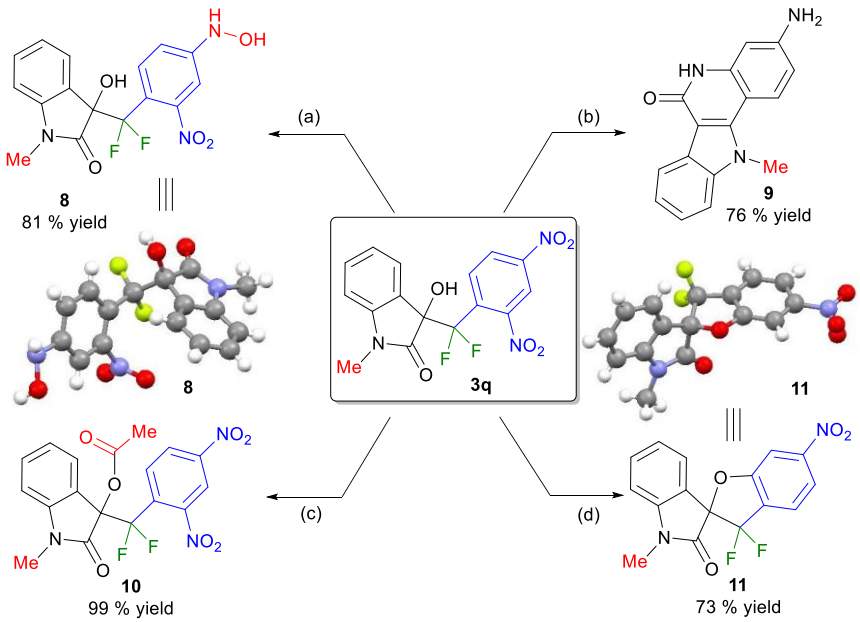
DFAP (**1a**)
1.40 g, 4.34 mmol

2q
0.58 g, 3.62 mmol

3q
1.24 g, 90 % yield

To a solution of **1a** (1.40 g, 4.34 mmol), **2q** (0.58 g, 3.62 mmol) and 18 mL MeOH, DBU (542 μL, 10 mol%) was added at room temperature and the mixture was stirred for 12 h at the same temperature. Subsequently, the reaction mixture was concentrated and purified by gel chromatography (PE/acetone = 4/1, v/v) to afford product **3q**.

Transformations of 3q

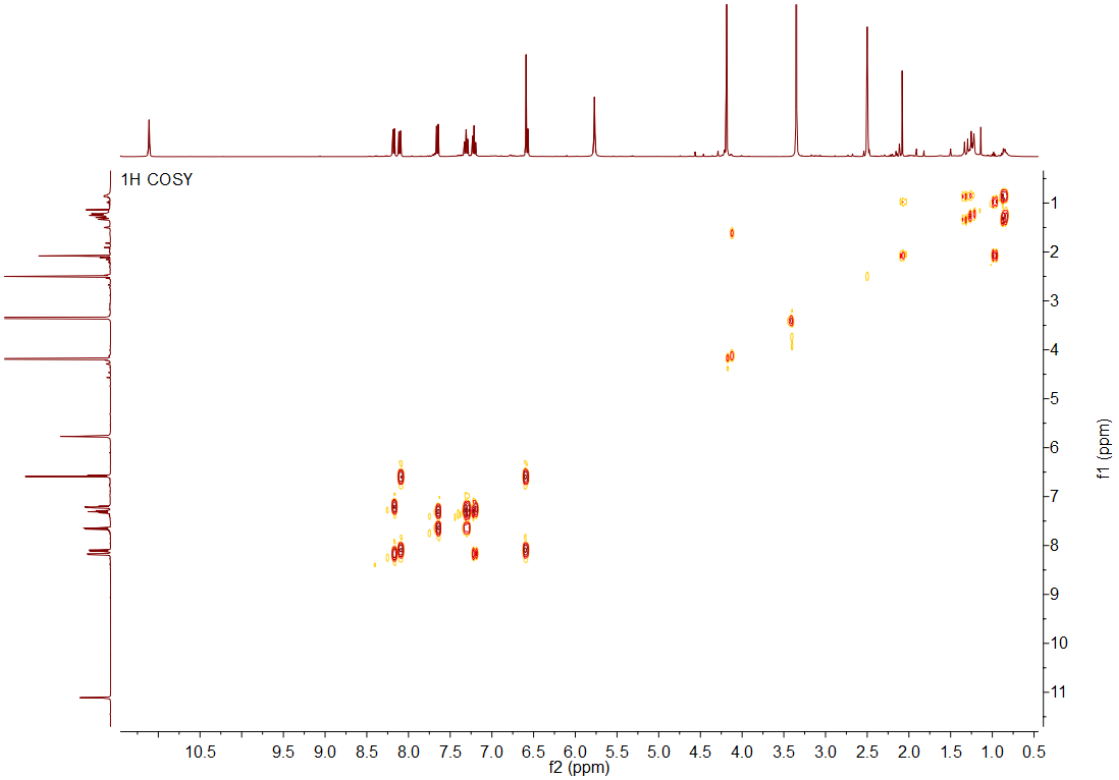


(a) To the solution of **3q** (76 mg, 0.20 mmol) in 2.0 mL ethanol, Pd/C (6 mg, 3 mol%, 10 wt% in charcoal) was added, the reaction was performed at 0 °C under 1 atm H_2 for 1 h. Then the mixture was filtered and concentrated in vacuum. The crude product was purified by flash chromatography (PE/Acetone = 2/1) to give a yellow solid. **3-(Difluoro(4-(hydroxyamino)-2-nitrophenyl)methyl)-3-hydroxy-1-methylindolin-2-one (8)**: yellow solid; 59.0 mg, 81 % yield, **^{1}H NMR (400 MHz, Acetone-d_6)** δ (ppm) 8.58 (s, 1H), 8.25 (s, 1H), 7.70 (d, J = 8.8, 1H), 7.39 (dt, J = 7.8,

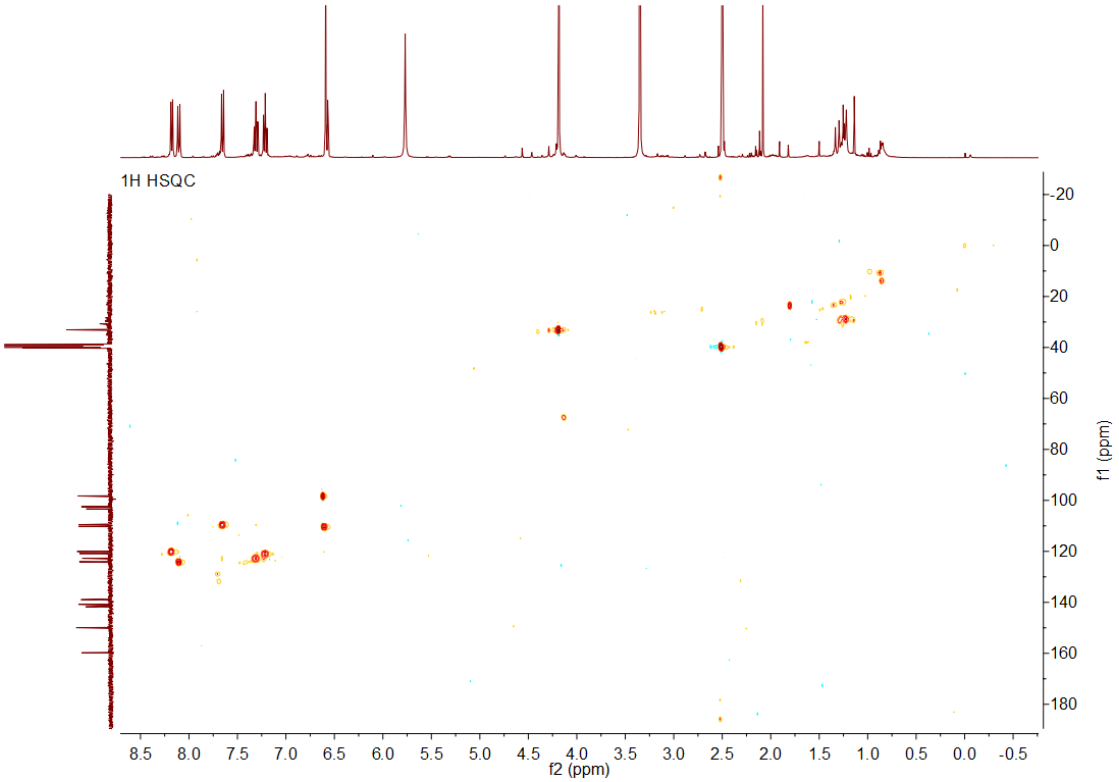
1.2 Hz, 1H), 7.16 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 7.03 (dt, J = 7.4, 0.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.11 (s, 1H), 3.16 (s, 3H); **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ (ppm) 172.5, 154.9, 150.6, 145.0, 131.1 (t, $J_{C\text{-}F}$ = 6.9 Hz, 1C), 131.0, 126.1, 125.8, 122.7, 125.1, 120.1, 114.4 (t, $J_{C\text{-}F}$ = 27.2 Hz, 1C), 113.7, 108.7, 106.8, 78.6 (t, $J_{C\text{-}F}$ = 31.4 Hz, 1C), 25.9. **^{19}F NMR (376 MHz, Acetone-*d*$_6$)** δ (ppm) -101.0 (s, 2F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{16}H_{13}F_2N_3O_5Na$, m/z: 388.0727, found: 388.0716.

(b) The mixture of **3q** (38 mg, 0.10 mmol), Pd/C (10 mg, 10 mol %, 10 wt % in charcoal) and ethanol (1.0 mL) was stirred at room temperature under 1 atm H_2 for 3 h. The mixture was filtered and concentrated in vacuum. The crude product was purified by flash chromatography (PE/Acetone = 1/1) to give a yellow solid. **3-Amino-11-methyl-5,11-dihydro-6H-indolo[3,2-c]quinolin-6-one (9):** yellow solid; 20.0 mg, 76 % yield, **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ (ppm) 11.11 (s, 1H), 8.18 (d, J = 7.2, 1H), 8.10 (d, J = 8.4, 1H), 7.65 (d, J = 8.4 Hz,1H), 7.33-7.29 (m, 1H), 7.23-7.19 (m, 1H), 6.59 (s, 1H), 6.58 (dd, J = 10.4, 2.0 Hz, 1H), 5.77 (s, 2H), 4.19 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ (ppm) 159.8, 149.9, 141.8, 140.8, 139.0, 124.1, 124.0, 122.7, 120.8, 120.1, 110.2, 109.5, 103.4, 102.5, 98.2, 33.1. **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{16}H_{13}N_3ONa$, m/z: 286.0955, found: 286.0951.

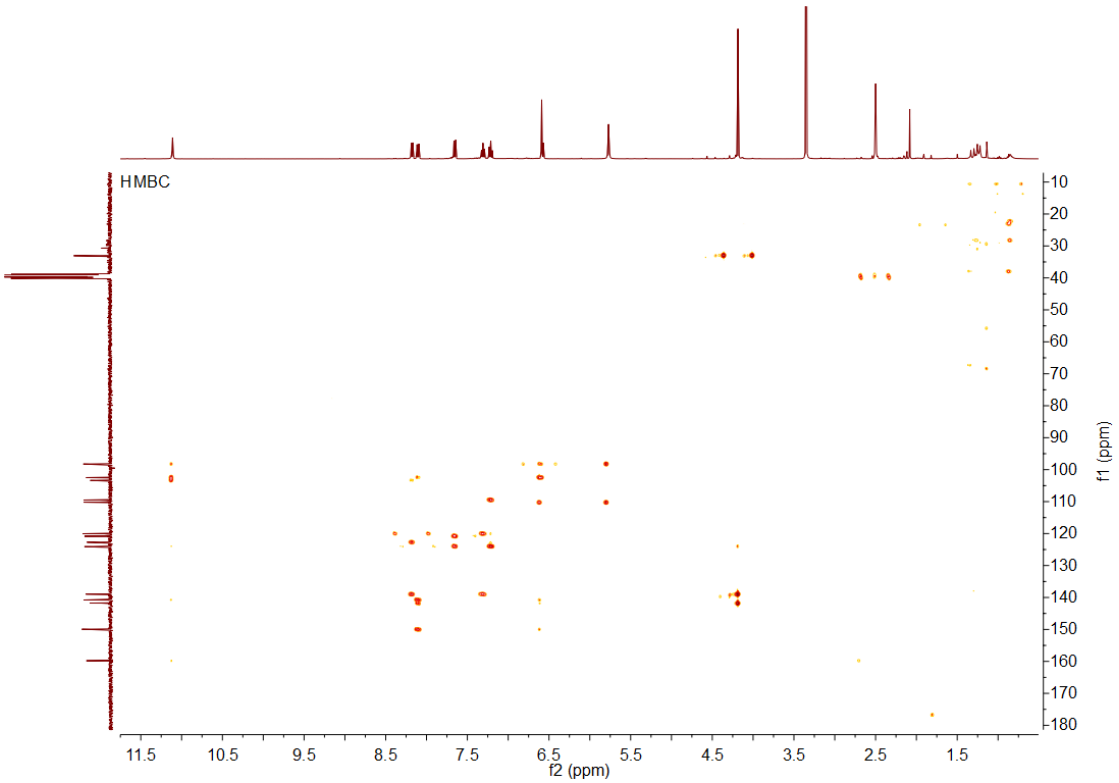
2D NMR spectrums of 9



H-H COSY of **9** in DMSO-*d*$_6$



HSQC of **9** in DMSO-d_6



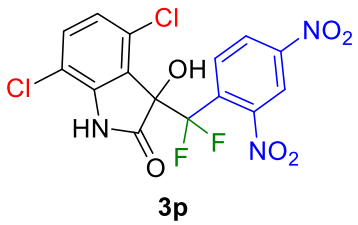
HMBC of **9** in DMSO-d_6

(c) To the mixture of **3q** (38 mg, 0.10 mmol), DMAP (2.4 mg, 20 mol%), TEA (21 μL, 1.5 equiv) and anhydrous DCM (0.5 mL), Ac_2O (12 μL, 1.2 equiv) was added and stirred at room temperature for 5 min. The mixture was washed with saturated aqueous ammonium chloride, dried over Na_2SO_4 and concentrated in vacuo. The crude product

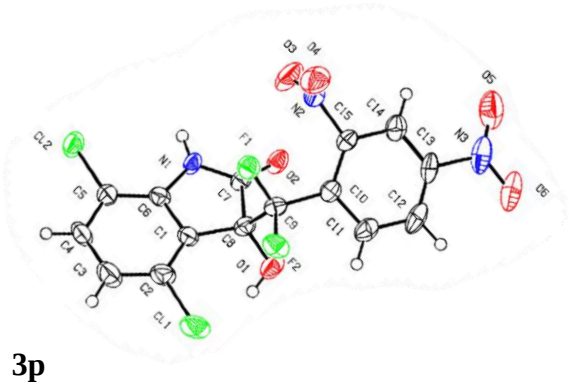
was purified by silica gel chromatography (PE/Acetone = 4/1) to give a colourless oil. **3-((2,4-dinitrophenyl)difluoromethyl)-1-methyl-2-oxoindolin-3-yl acetate (10):** colourless oil; 41.6 mg, 99 % yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.48-8.44 (m, 2H), 7.94 (d, J = 8.4 Hz, 1H), 7.45 (td, J = 8.0, 1.2 Hz, 1H), 7.38 (d, J = 7.2 Hz, 1H), 7.12 (td, J = 7.6, 0.4 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 3.26 (s, 3H), 2.10 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 168.6 (d, J = 6.3 Hz, 1C), 167.4, 149.8, 149.1, 145.2, 132.3 (dd, J = 8.9, 6.8 Hz, 1C), 131.7, 129.6 (t, J = 27.3 Hz, 1C), 125.3 (t, J = 2.9 Hz, 1C), 124.6, 123.2, 121.0, 119.4, 117.5 (dd, J = 260.1, 249.6 Hz, 1C), 108.9, 80.5 (dd, J = 38.9, 25.4 Hz, 1C), 26.8, 20.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -98.5 (d, J = 273.4 Hz, 1F), -103.2 (d, J = 273.0 Hz, 1F). **HRMS (ESI)** Calcd for $[M + Na]^+$ $C_{18}H_{13}F_2N_3O_7Na$, m/z: 444.0612, found: 444.0614.

(d) To the solution of **3q** (38 mg, 0.10 mmol) in 0.5 mL anhydrous DMF, DBU (30 μL, 2.0 equiv) was added, the reaction performed at room temperature for 5 min. Then the mixture was washed with saturated aqueous ammonium chloride, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel chromatography (PE/Acetone = 4/1) to give a pale yellow solid. **3,3-difluoro-1'-methyl-6-nitro-3H-spiro[benzofuran-2,3'-indolin]-2'-one (11):** pale yellow solid; 24.1 mg, 73 % yield, **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.03 (d, J = 6.4 Hz, 1H), 7.89 (s, 1H), 7.73 (d, J = 6.0 Hz, 1H), 7.51 (s, 1H), 7.42 (d, J = 3.6 Hz, 1H), 7.18 (s, 1H), 6.95 (d, J = 6.0 Hz, 1H), 3.23 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) 169.1 (dd, J = 7.9, 2.5 Hz, 1C), 161.1 (dd, J = 8.3, 6.9 Hz, 1C), 152.0 (d, J = 1.3 Hz, 1C), 145.3, 132.5, 127.8 (d, J = 3.4 Hz, 1C), 126.4 (t, J = 26.0 Hz, 1C), 125.2, 123.5, 123.3 (t, J = 255.2 Hz, 1C), 119.0 (d, J = 2.8 Hz, 1C), 118.0, 109.2, 107.9, 98.7 (dd, J = 29.0, 26.0 Hz, 1C), 26.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) -78.8 (d, J = 257.2 Hz, 1F), -109.6 (d, J = 256.5 Hz, 1F). **HRMS (ESI)** Calcd for $[M + H]^+$ $C_{16}H_{11}F_2N_2O_4$, m/z: 333.0686, found: 333.0681.

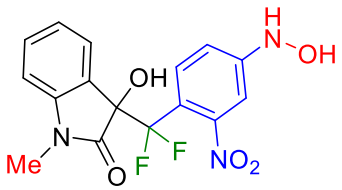
Sigle crystal data



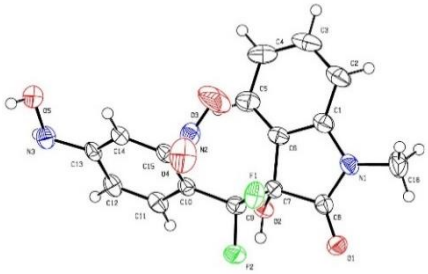
3p



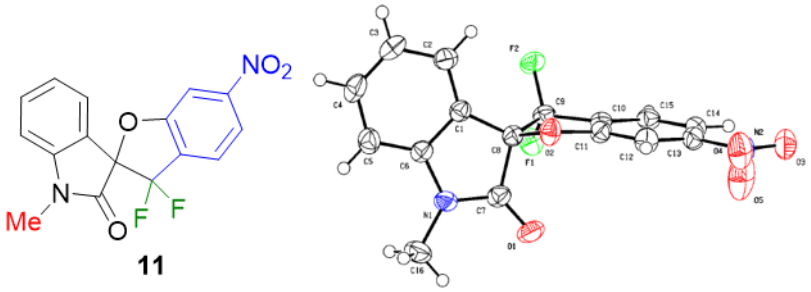
Identification code	**3p**	
Empirical formula	$C_{15}H_7Cl_2F_2N_3O_6$	
Formula weight	365.29	
Temperature	100.0(2) K	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4977(9) Å	α = 70.511(6) °
	b = 11.8470(8) Å	β = 80.465(6) °
	c = 12.9471(9) Å	γ = 79.851(6) °
Volume	1625.6(2) $Å^3$	
Z	4	
Density (calculated)	1.774 g/cm^3	
Absorption coefficient	4.225 mm^{-1}	
F (000)	872.0	
Crystal size	0.13 × 0.11 × 0.09 mm^3	
Radiation	Cu Kα (λ = 1.54184)	
Theta range for data collection	7.292 to 147.446°	
Index ranges	-10 ≤ h ≤ 13, -13 ≤ k ≤ 14, -14 ≤ l ≤ 15	
Reflections collected	11200	
Independent reflections	6351 [R_{int} = 0.0735, R_{sigma} = 0.0893]	
Completeness to theta = 73.723	96.6%	
Absorption correction	Multi-scan	
Data/restraints/parameters	6351/0/517	
Goodness-of-fit on F^2	1.033	
Final R indexes [I>=2σ (I)]	R_1 = 0.0770, wR_2 = 0.1972	
Final R indexes [all data]	R_1 = 0.1023, wR_2 = 0.2357	
Largest diff. peak/hole	0.68/-0.64 e $Å^{-3}$	



8

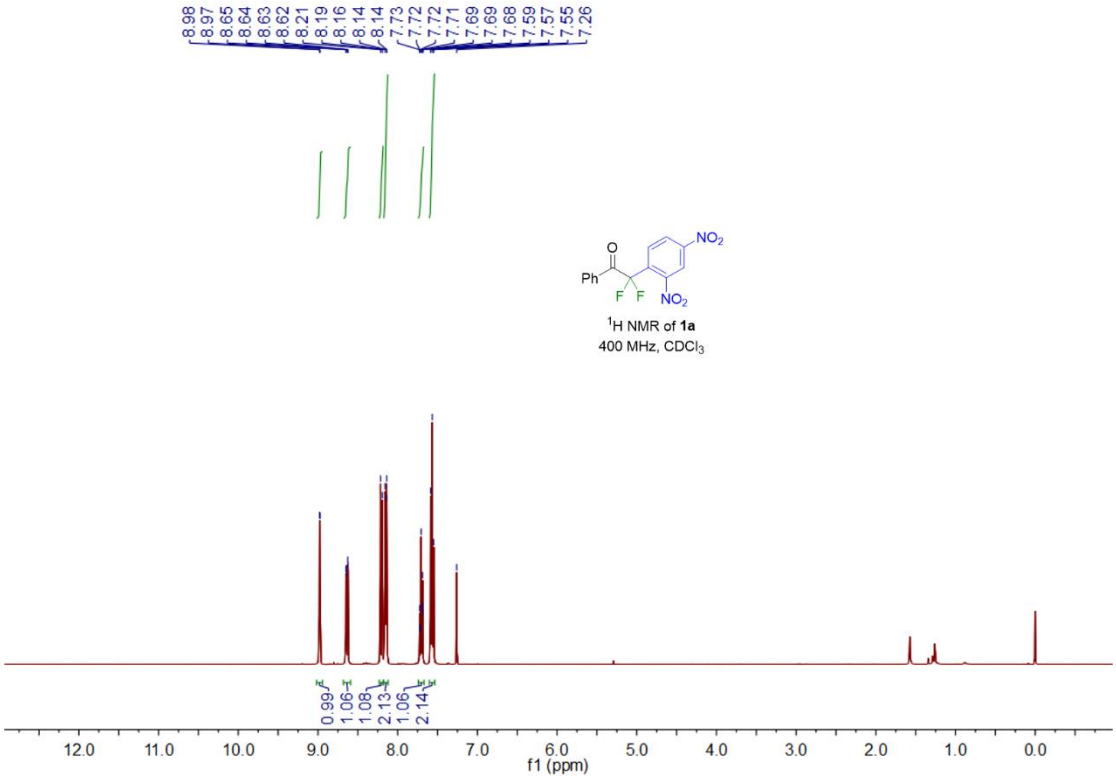


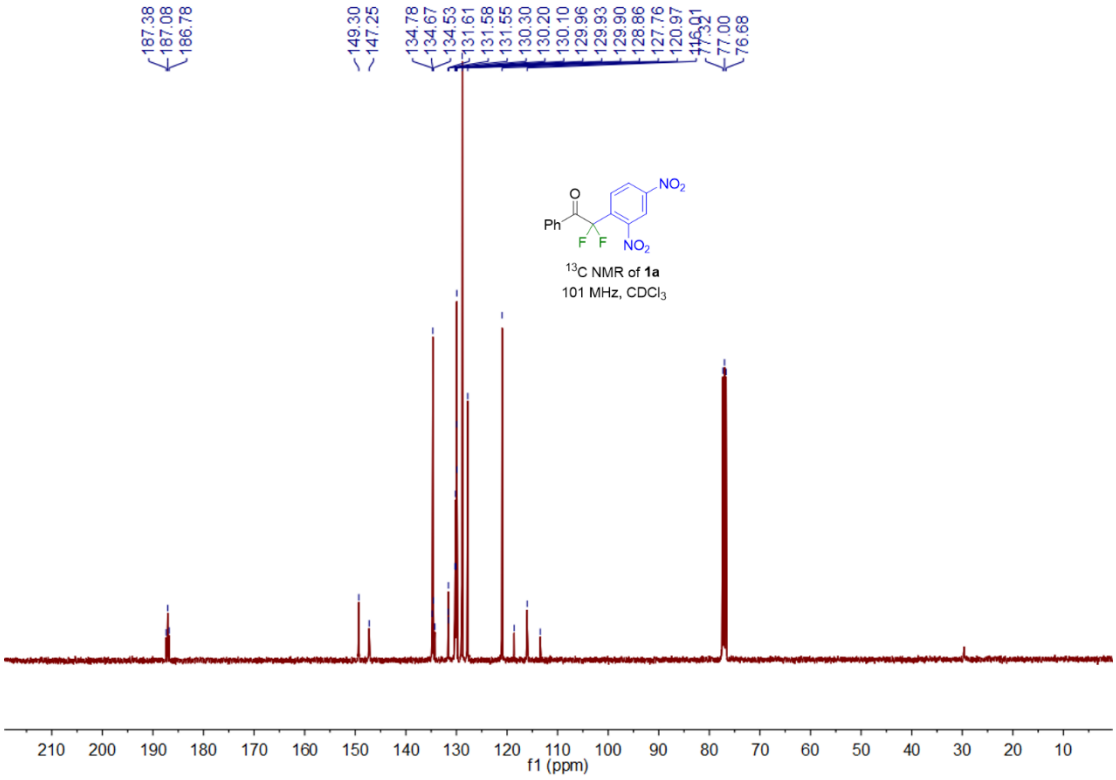
Identification code	**8**	
Empirical formula	$C_{16}H_{13}F_2N_3O_5$	
Formula weight	365.29	
Temperature	150.00(10) K	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.8331(6) Å	α = 88.789(7) °
	b = 9.3318(8) Å	β = 75.495(7) °
	c = 12.2430(11) Å	γ = 66.796(8) °
	88.789(7)	
	75.495(7)	
	66.796(8)	
Volume	793.29(13) $Å^3$	
Z	2	
Density (calculated)	1.529 g/cm^3	
Absorption coefficient	0.130 mm^{-1}	
F (000)	376.0	
Crystal size	0.15 × 0.13 × 0.12 mm^3	
Radiation	Mo Kα (λ = 0.71073)	
Theta range for data collection	4.768 to 49.99°	
Index ranges	-9 ≤ h ≤ 7, -10 ≤ k ≤ 11, -14 ≤ l ≤ 13	
Reflections collected	5179	
Independent reflections	2793 [R_{int} = 0.0206, R_{sigma} = 0.0388]	
Completeness to theta = 24.995	100%	
Absorption correction	Multi-scan	
Data/restraints/parameters	2793/0/242	
Goodness-of-fit on F^2	1.022	
Final R indexes [I>=2σ (I)]	R_1 = 0.0420, wR_2 = 0.0940	
Final R indexes [all data]	R_1 = 0.0547, wR_2 = 0.1024	
Largest diff. peak/hole	0.18/-0.19 e $Å^{-3}$	

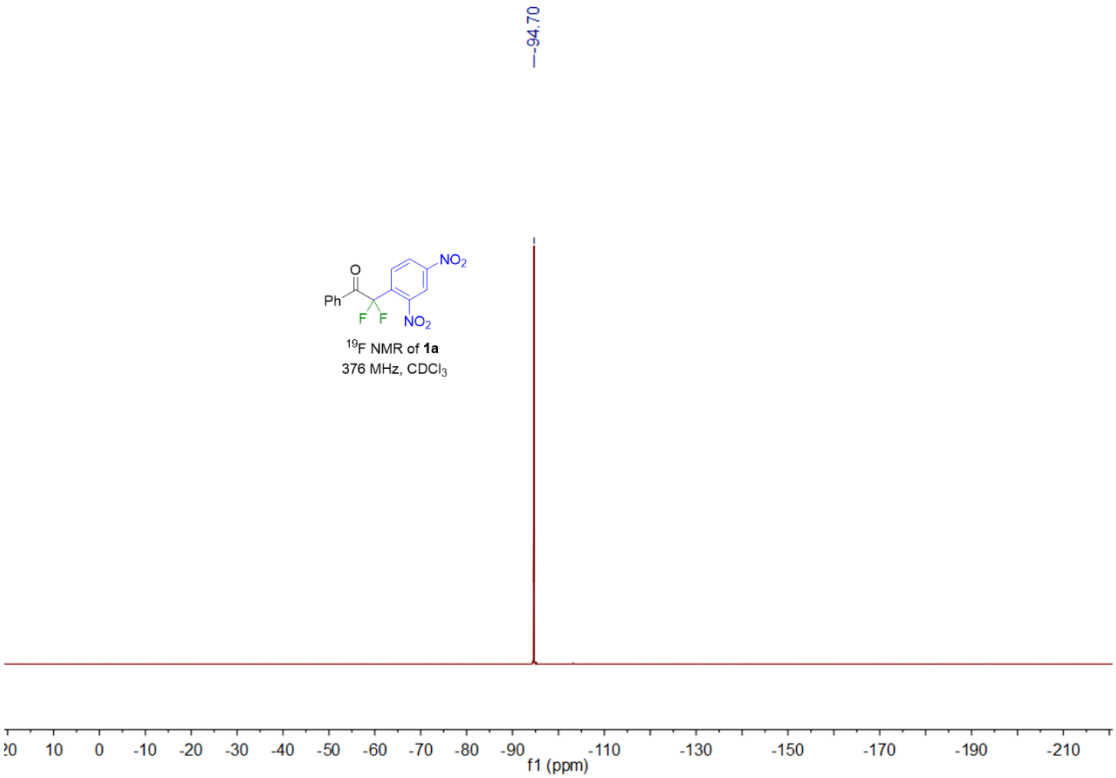


Identification code	**11**	
Empirical formula	$C_{16}H_{10}F_2N_2O_4$	
Formula weight	332.26	
Temperature	219.99(10) K	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.8185(5) Å	α = 92.612(6) °
	b = 8.7925(7) Å	β = 101.796(5) °
	c = 11.6820(7) Å	γ = 112.885(6) °
Volume	717.23(3) $Å^3$	
Z	2	
Density (calculated)	1.538 g/cm^3	
Absorption coefficient	0.129 mm^{-1}	
F (000)	340.0	
Crystal size	0.13 × 0.12 × 0.11 mm^3	
Radiation	Mo Kα (λ = 0.71073)	
Theta range for data collection	5.078 to 49.978°	
Index ranges	$-9 \le h \le 7$, $-6 \le k \le 10$, $-13 \le l \le 13$	
Reflections collected	4587	
Independent reflections	2531 [R_{int} = 0.0213, R_{sigma} = 0.0391]	
Completeness to theta = 24.986	100 %	
Absorption correction	Multi-scan	
Data/restraints/parameters	2531/0/228	
Goodness-of-fit on F^2	1.052	
Final R indexes [I>=2σ (I)]	R_1 = 0.0437, wR_2 = 0.1066	
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1170	
Largest diff. peak/hole	0.23/-0.22 e $Å^{-3}$	

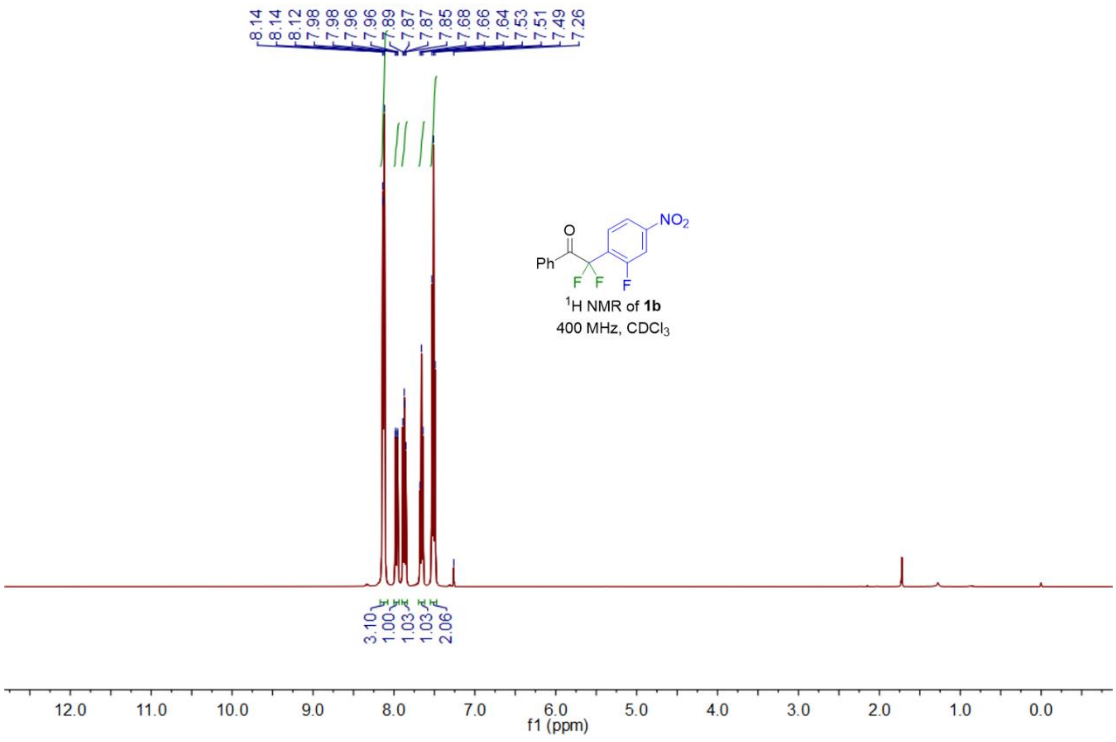
NMR spectrum



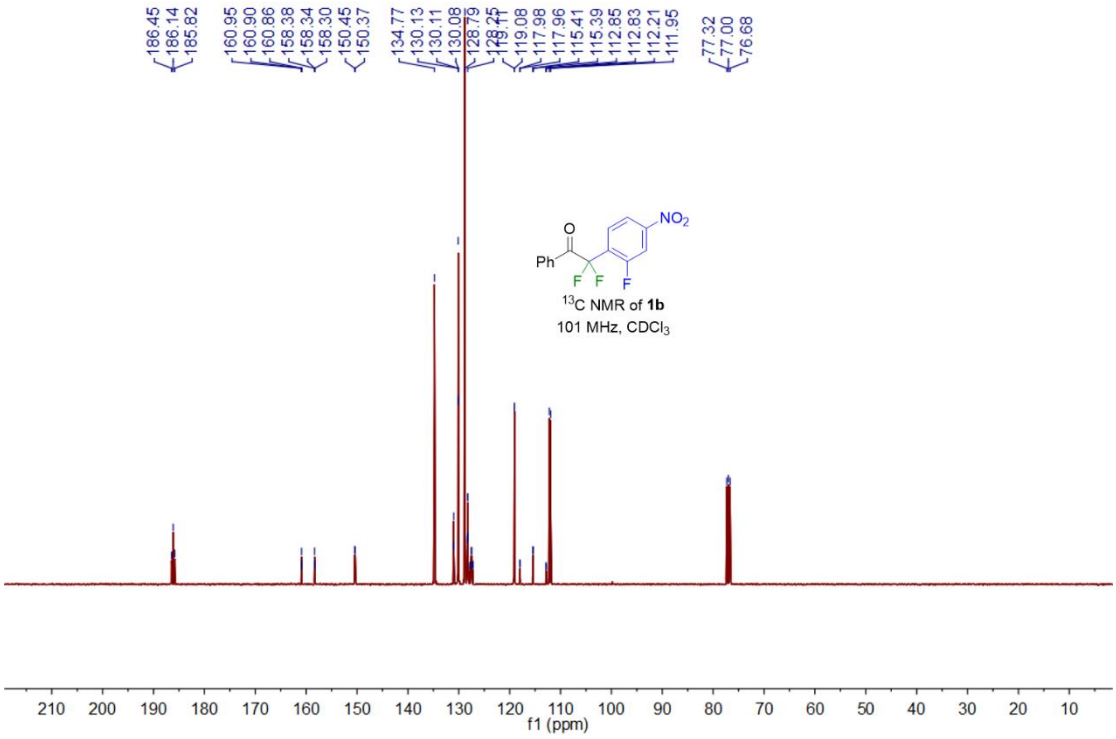




^{19}F NMR of **1a**
376 MHz, $CDCl_3$



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


186.45
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160.95
160.90
160.86
158.38
158.34
158.30
150.45
150.37
134.77
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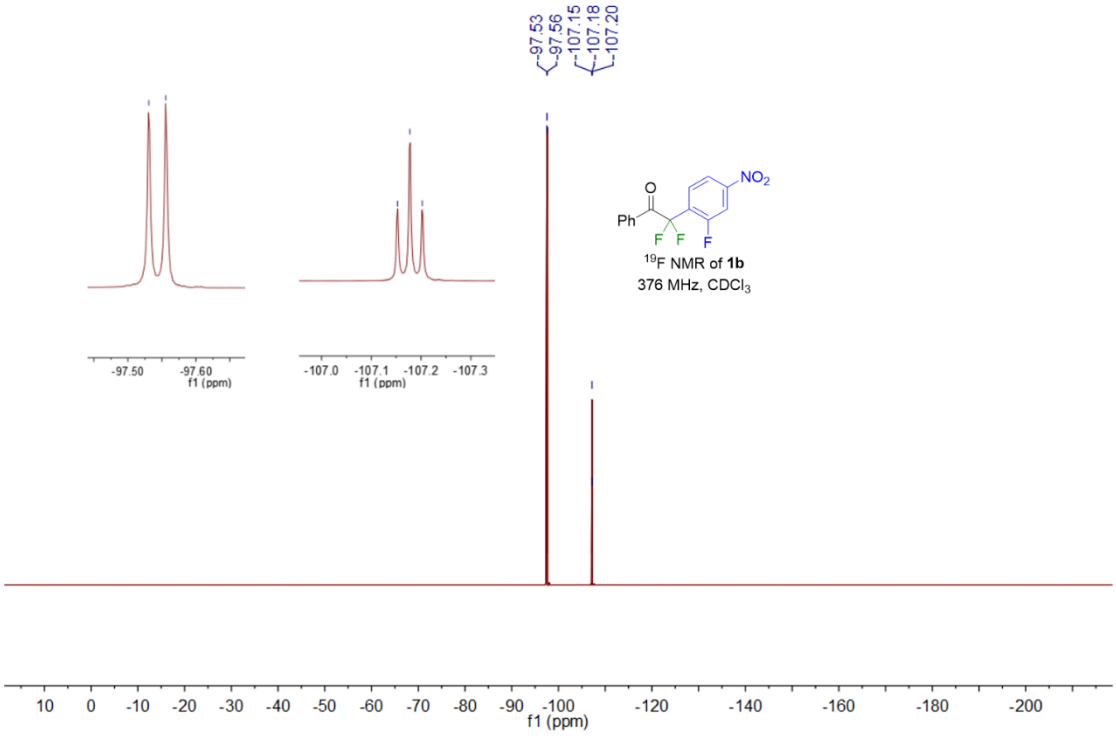
130.11
130.08
128.79
128.25
119.08
117.98
117.96
115.41
115.39
112.85
112.83
112.21
111.95
77.32
77.00
76.68
O
Ph
F F
F
NO2
13C NMR of 1b
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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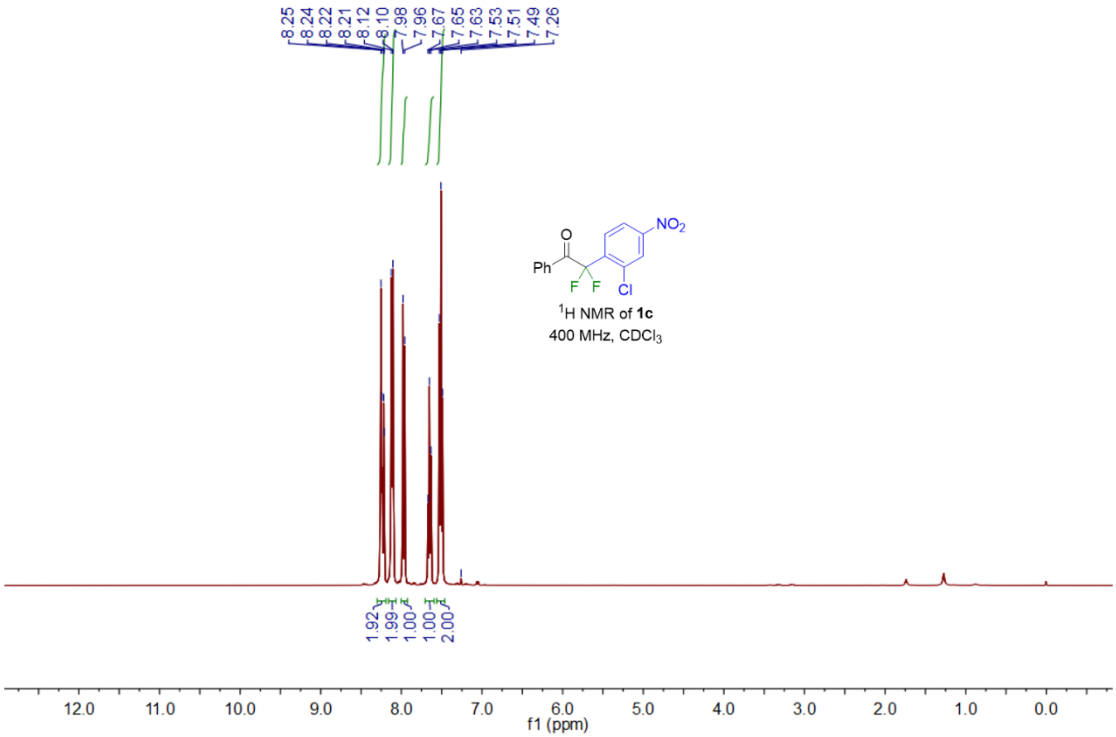
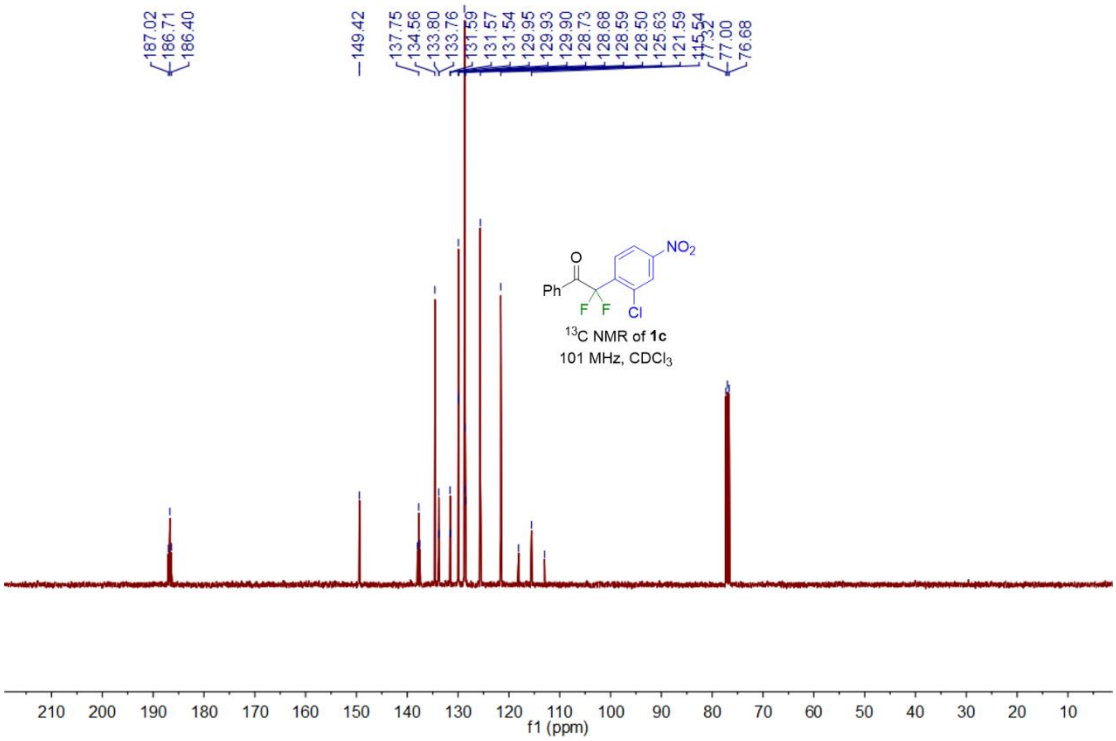
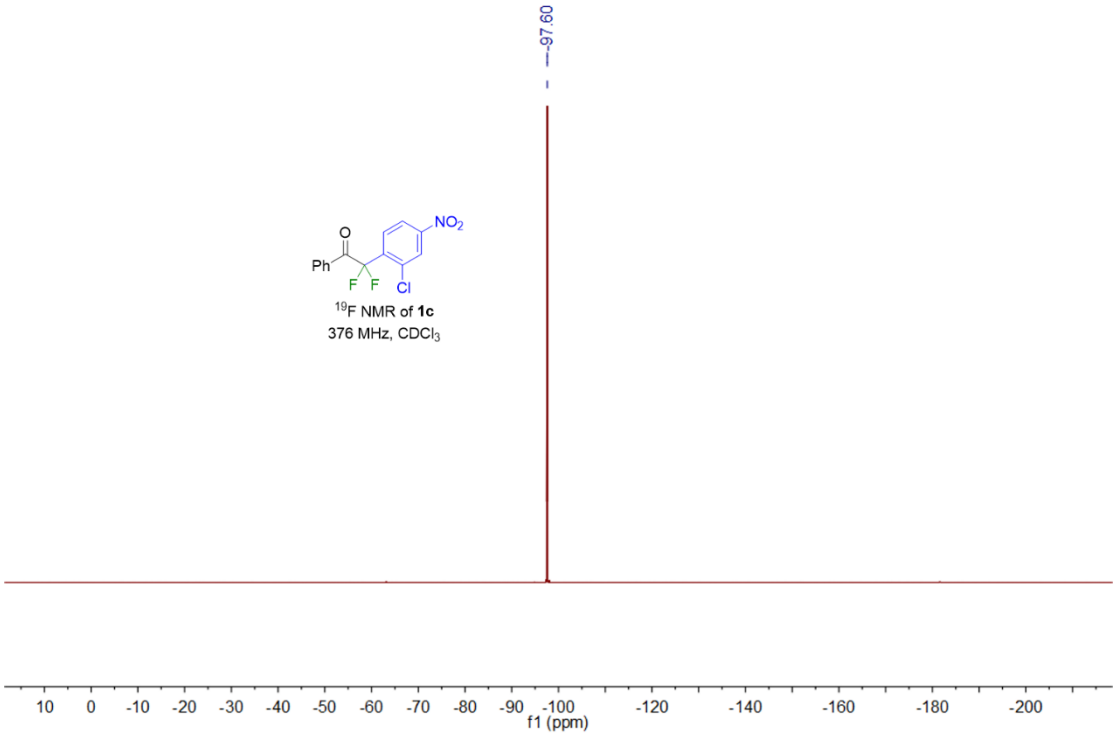
-97.60
f1 (ppm)
-107.0
-107.1
-107.2
-107.3
f1 (ppm)
O
Ph
F F
F
NO2
19F NMR of 1b
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



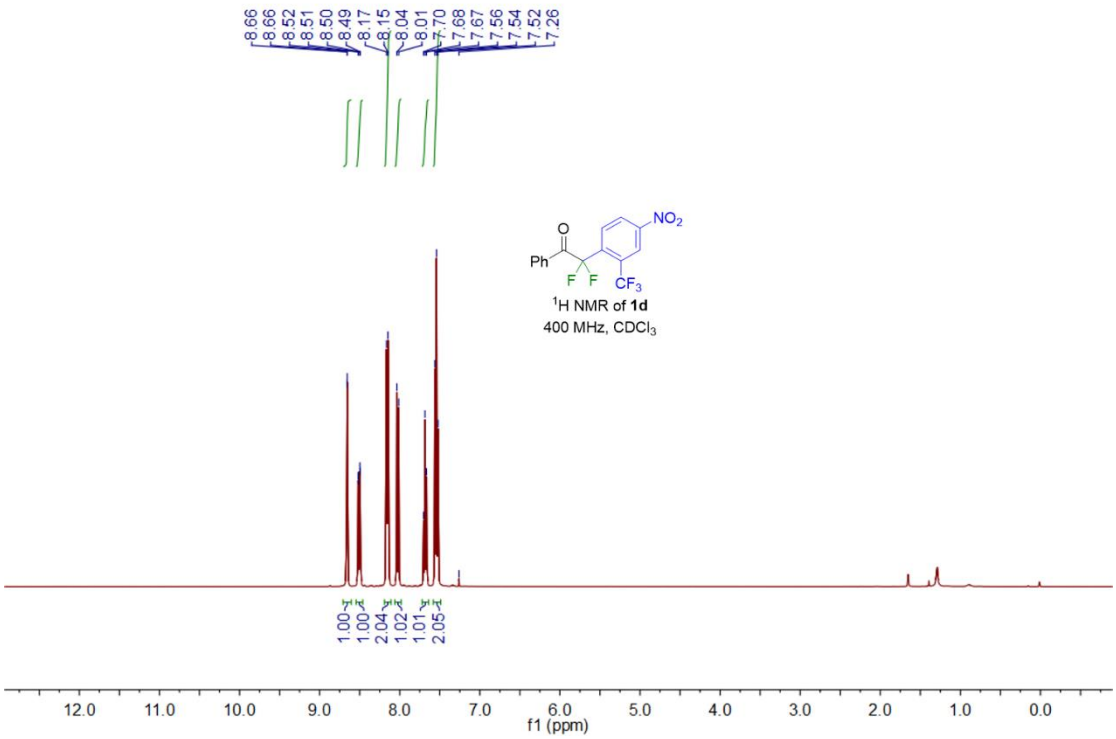
^{1}H NMR of **1c**
400 MHz, $CDCl_3$



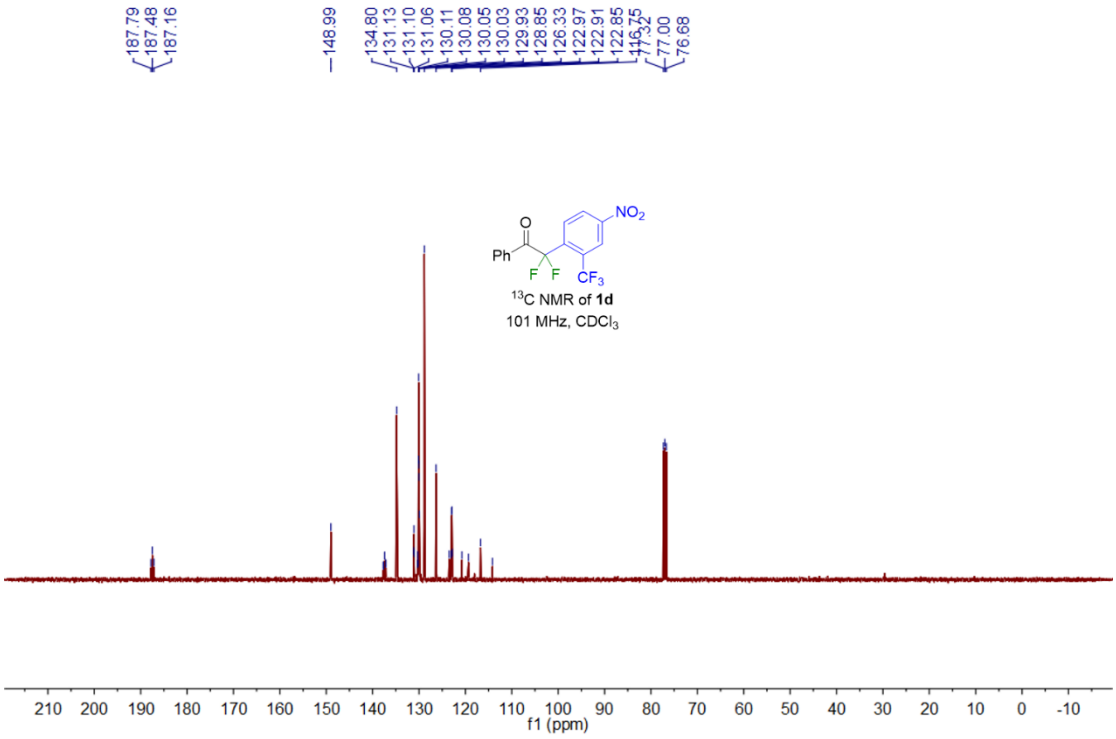
^{13}C NMR of **1c**
101 MHz, $CDCl_3$



^{19}F NMR of **1c**
376 MHz, $CDCl_3$



^{1}H NMR of **1d**
400 MHz, $CDCl_3$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131.06
130.11
130.08
130.05
130.03
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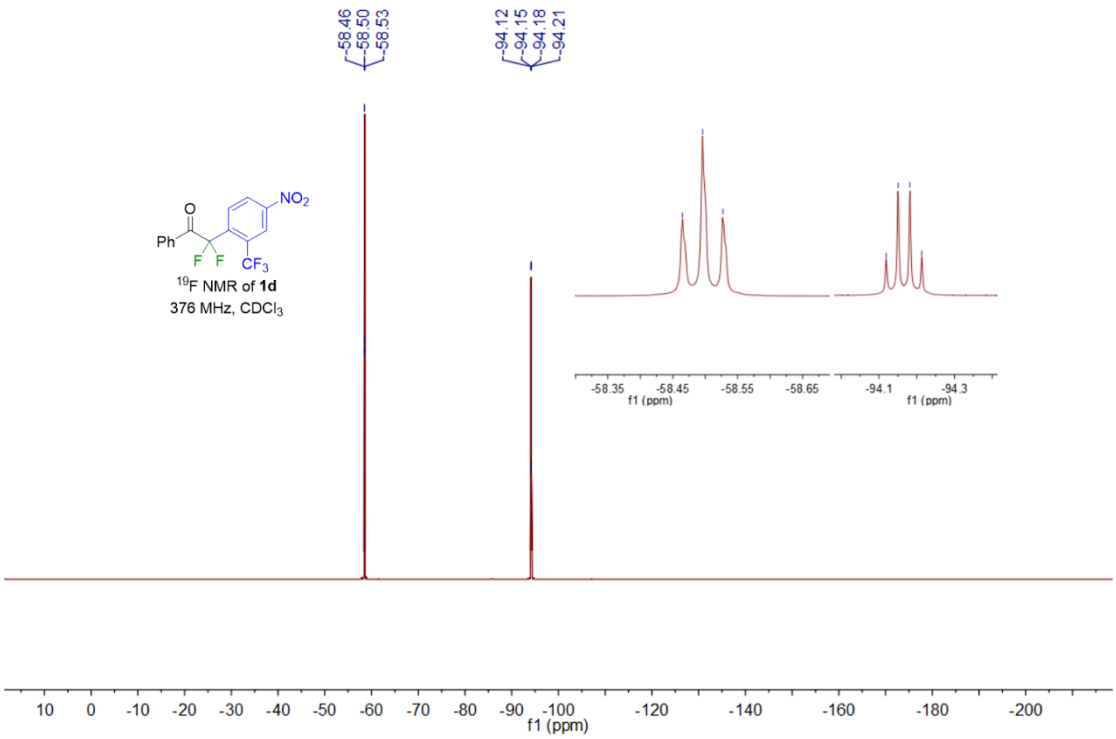
128.85
126.33
122.97
122.91
122.85
77.32
77.00
76.68
NO2
Ph
O
F F
CF3
13C NMR of 1d
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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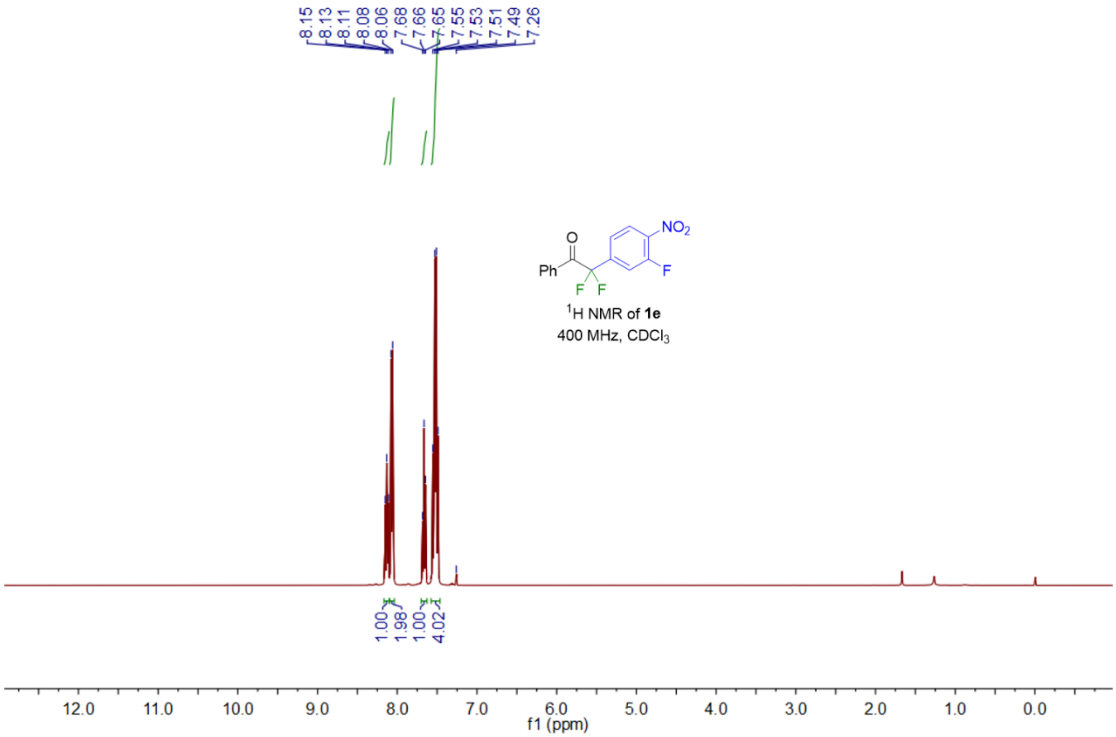
94.12
94.15
94.18
94.21
NO2
Ph
O
F F
CF3
19F NMR of 1d
376 MHz, CDCl3
-58.35 -58.45 -58.55 -58.65
f1 (ppm)
-94.1 -94.3
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)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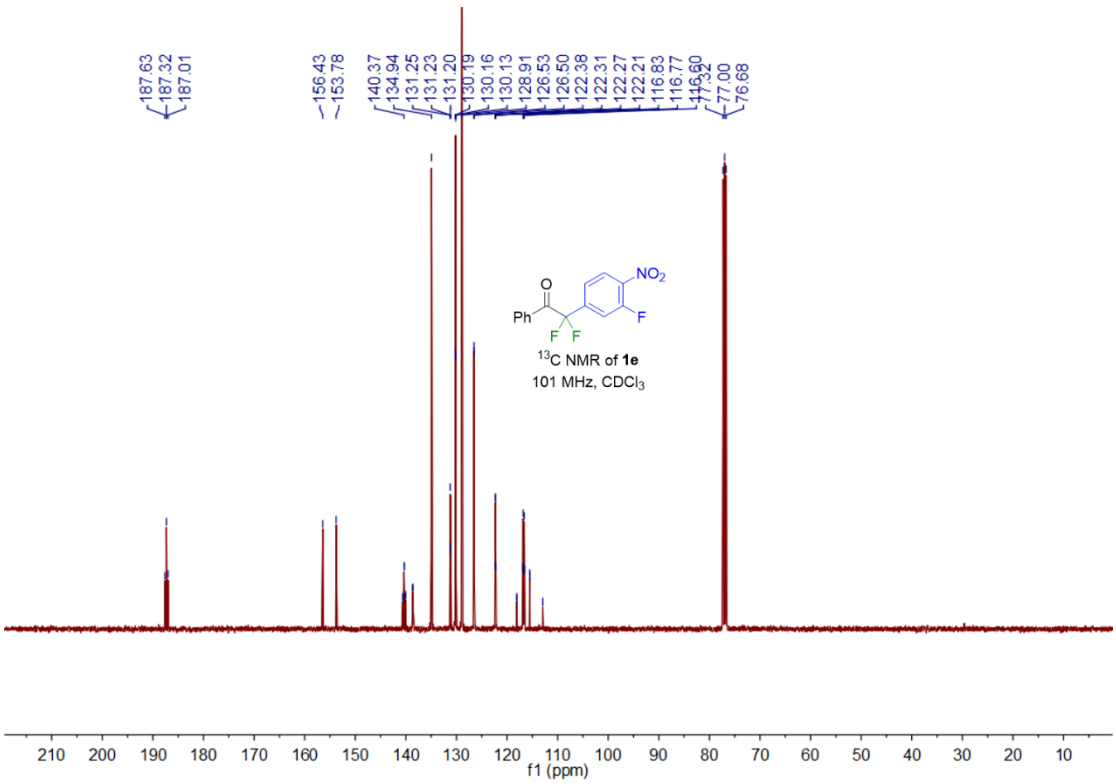
8.13
8.11
8.08
8.06
7.68
7.66
7.65
7.55
7.53
7.51
7.49
7.26
O
Ph
F F
NO2
F
1H NMR of 1e
400 MHz, CDCl3
1.00
1.98
1.00
4.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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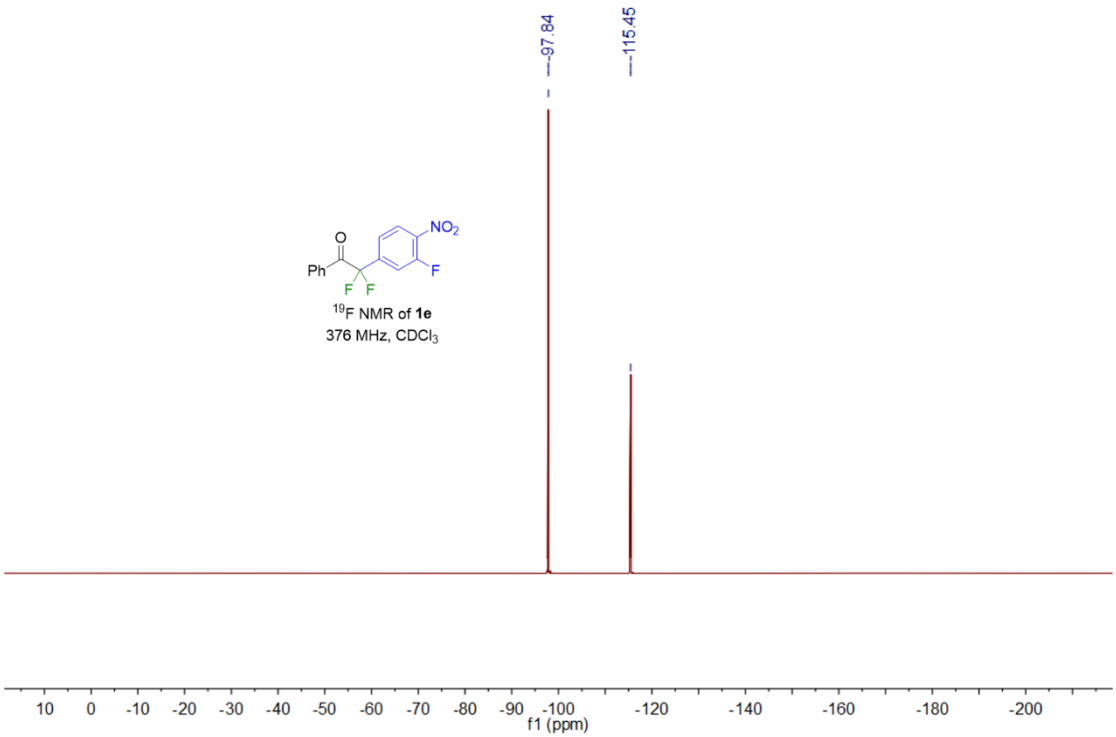
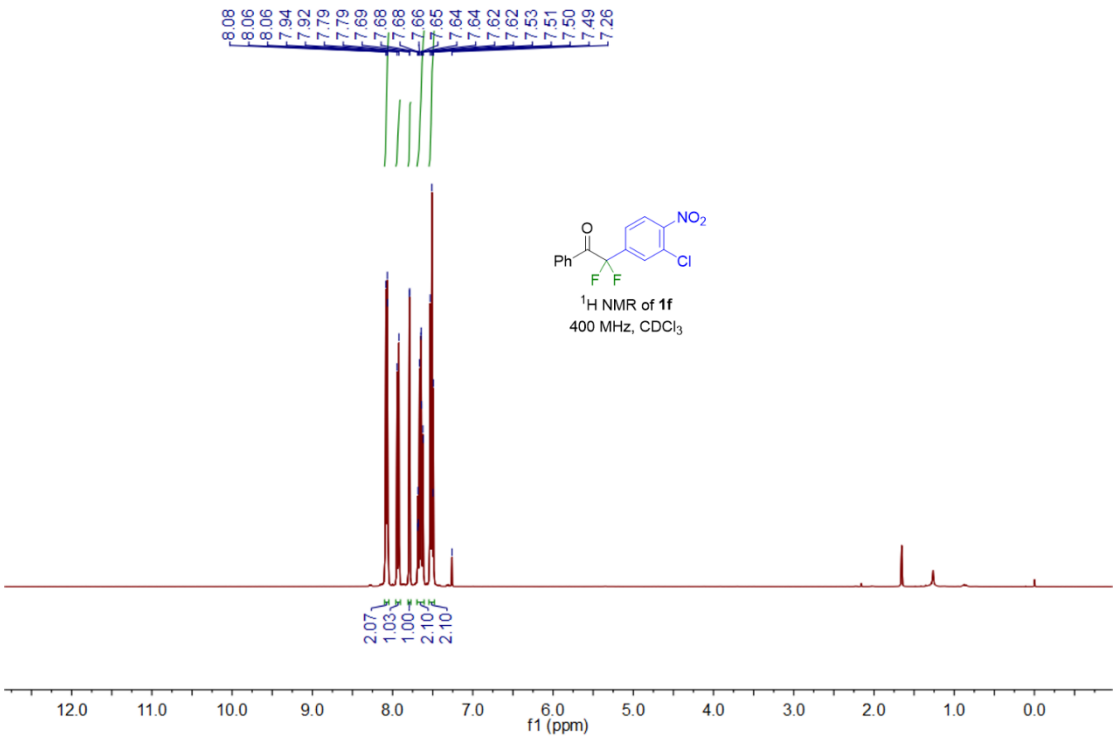
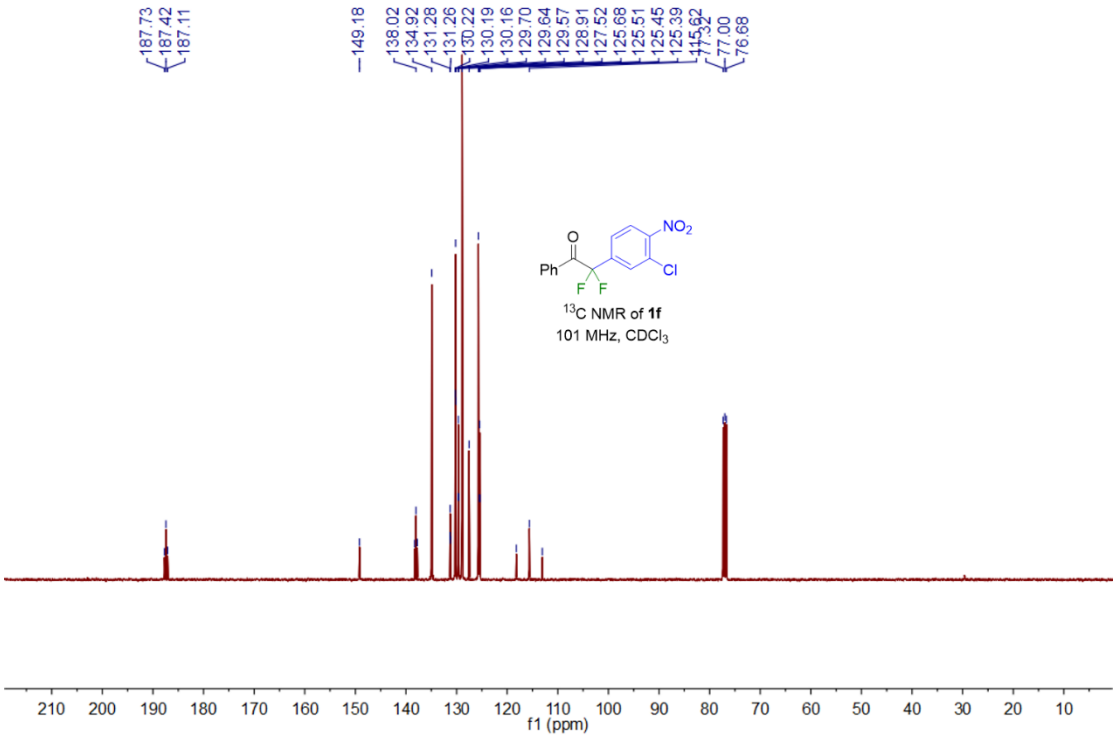
128.91
126.53
126.50
122.38
122.31
122.27
122.21
116.83
116.77
77.32
77.00
76.68
O
Ph
F F
NO2
F
13C NMR of 1e
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



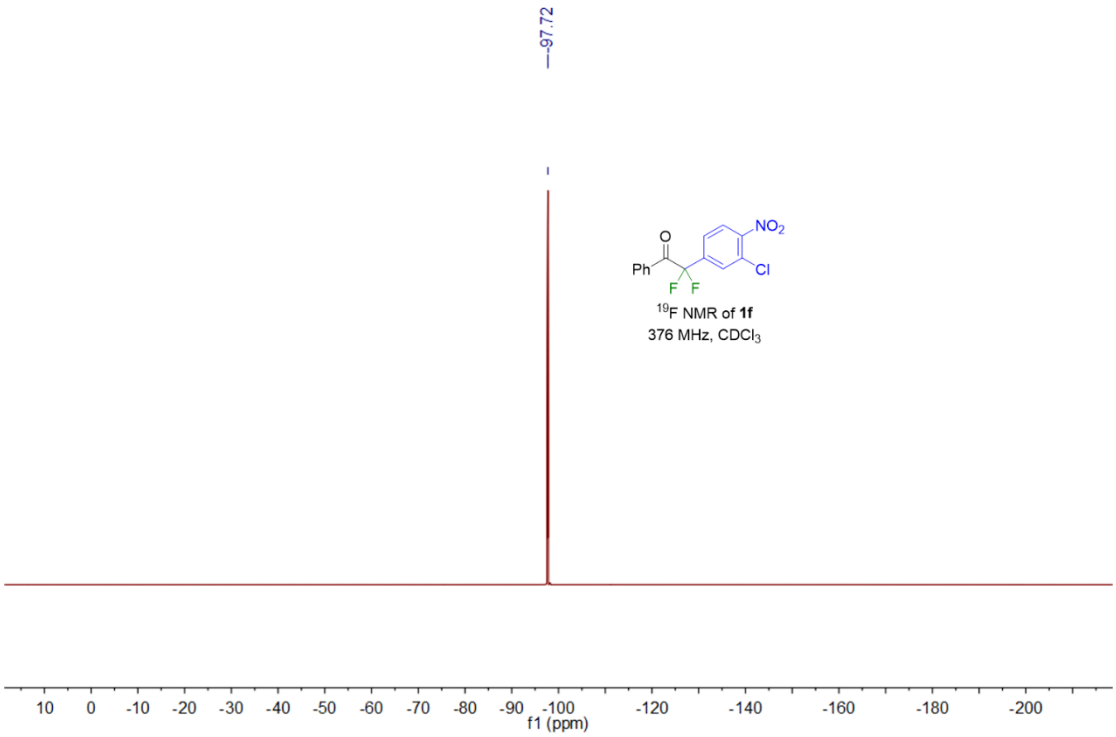
^{19}F NMR of **1e**
376 MHz, $CDCl_3$



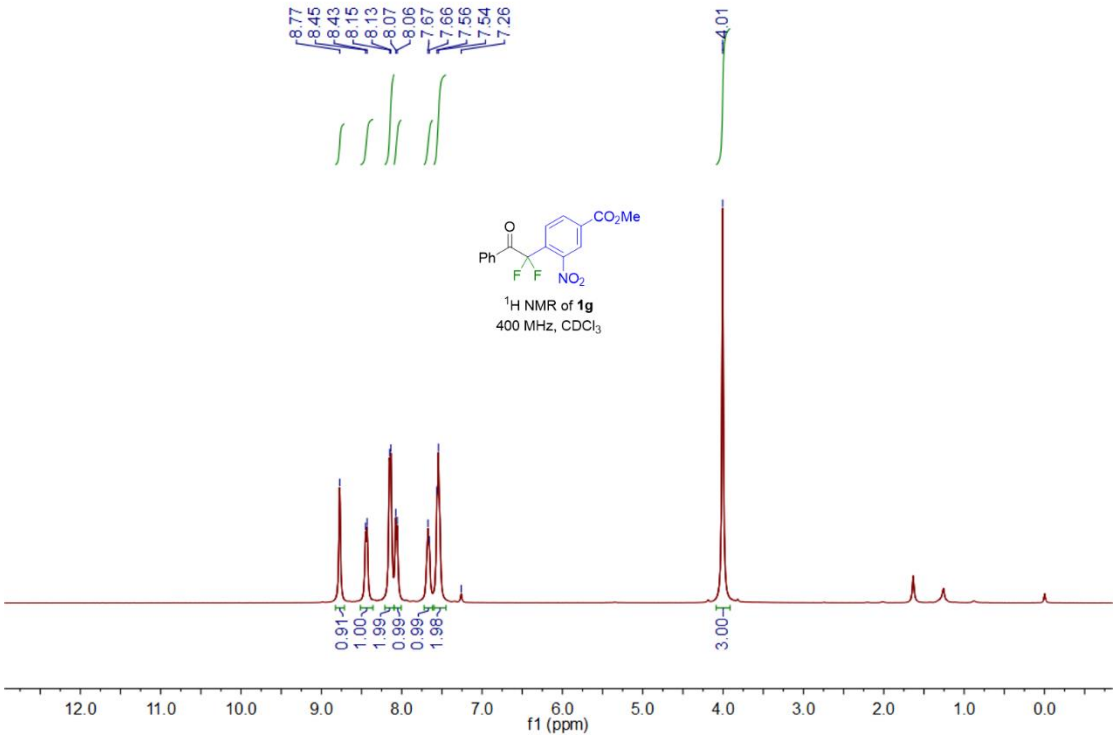
^{1}H NMR of **1f**
400 MHz, $CDCl_3$

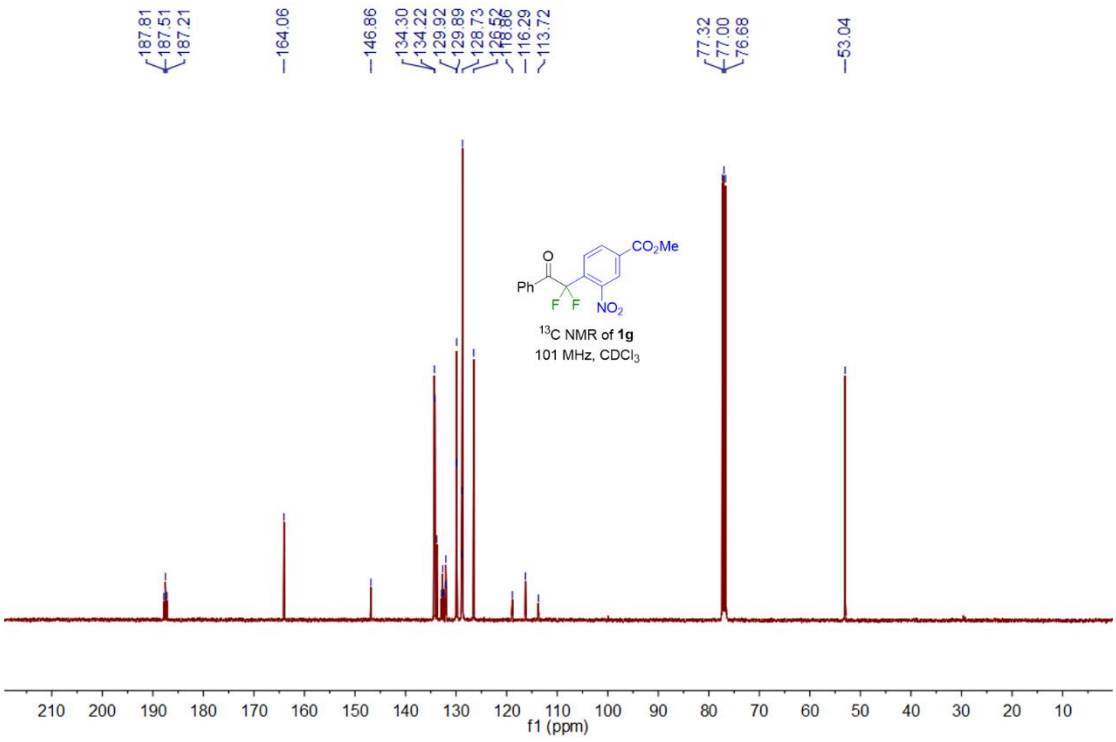


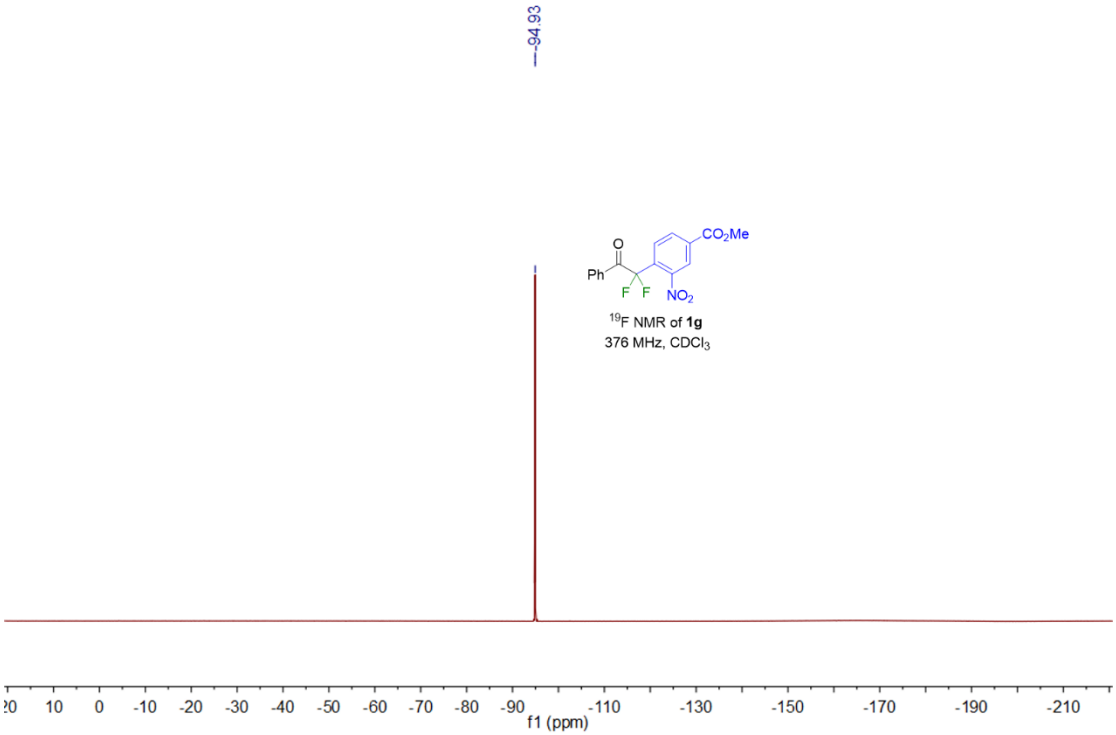
^{13}C NMR of **1f**
101 MHz, $CDCl_3$

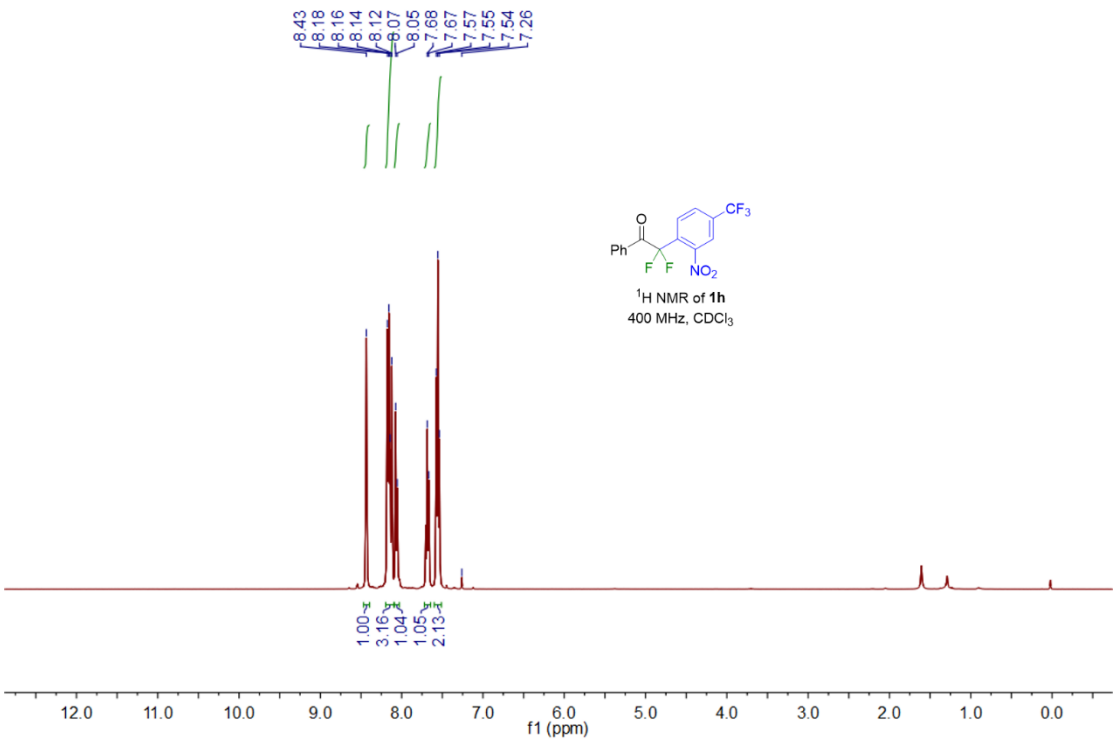


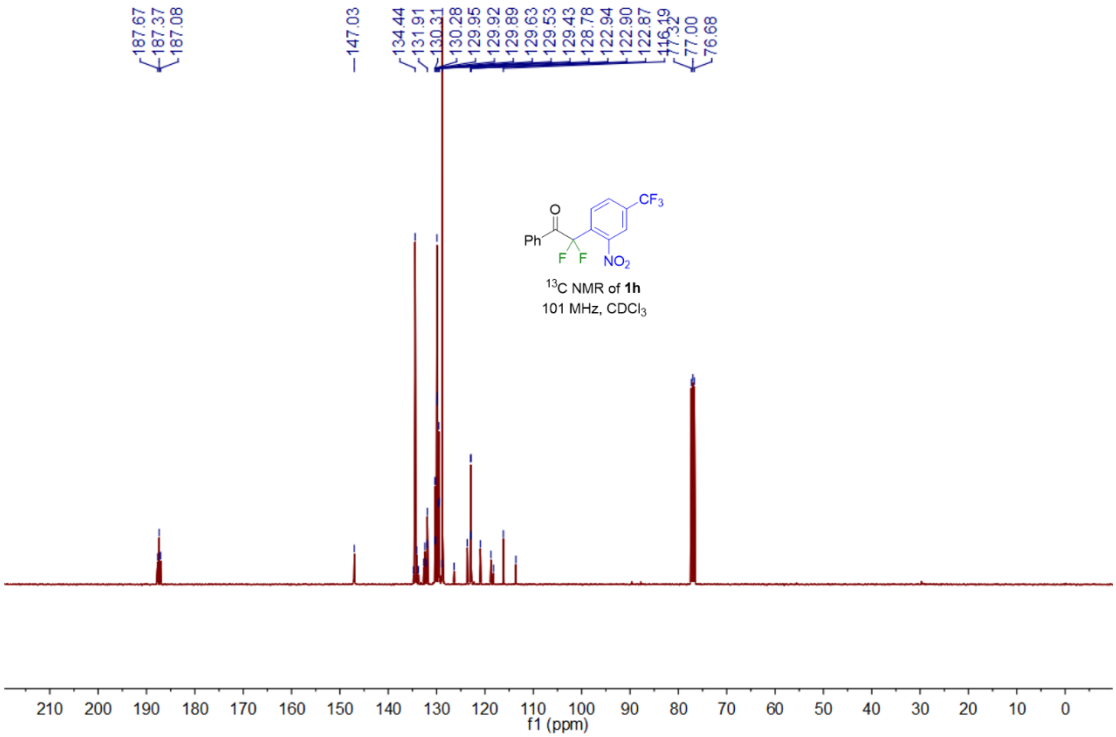
^{19}F NMR of **1f**
376 MHz, $CDCl_3$


8.77
8.45
8.43
8.15
8.13
8.07
8.06
7.67
7.66
7.56
7.54
7.26
4.01
CO2Me
Ph
O
F F
NO2
1H NMR of 1g
400 MHz, CDCl3
0.91
1.00
1.99
0.99
0.99
1.98
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

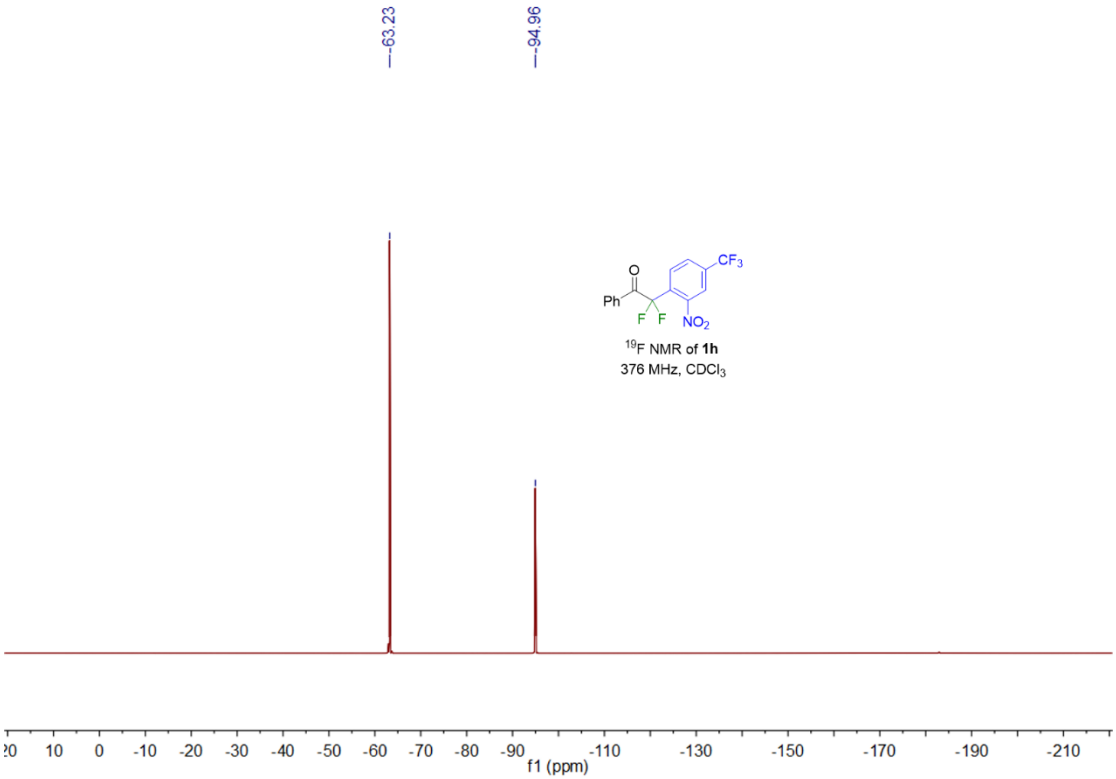

187.81
187.51
187.21
164.06
146.86
134.30
134.22
129.92
129.89
128.73
116.29
113.72
77.32
77.00
76.68
53.04
CO2Me
Ph
O
F F
NO2
13C NMR of 1g
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-94.93
CO2Me
O
Ph
F F
NO2
19F NMR of 1g
376 MHz, CDCl3
f1 (ppm)

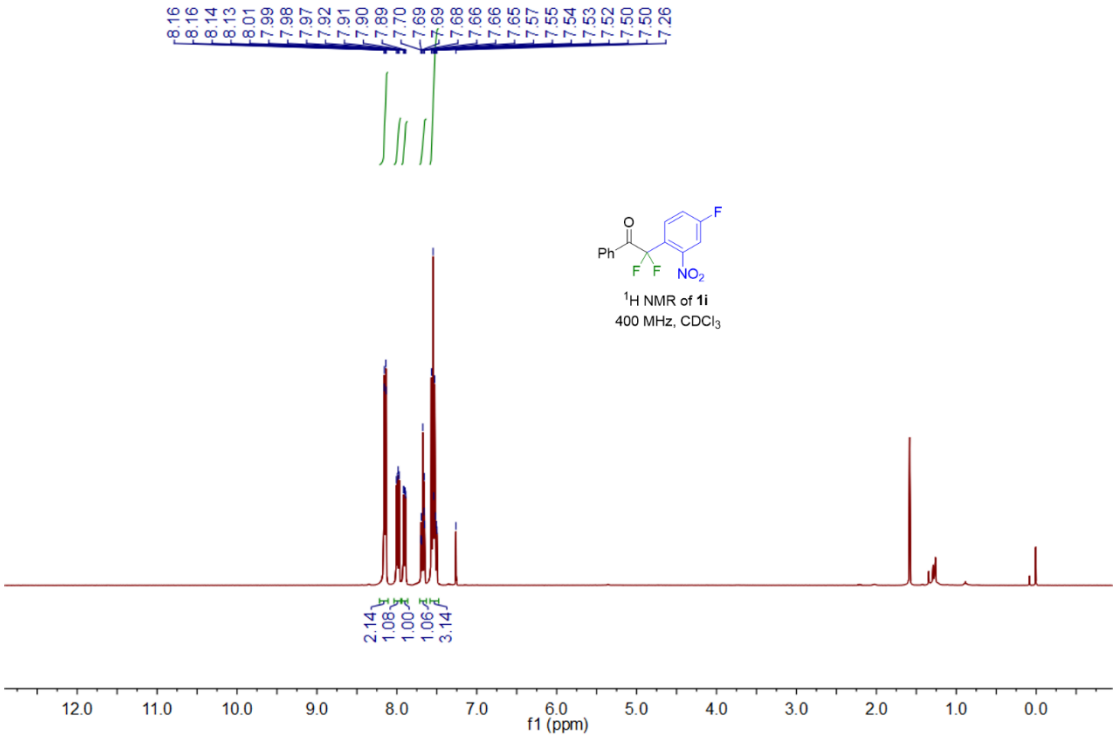

8.43
8.18
8.16
8.14
8.12
8.07
8.05
7.68
7.67
7.57
7.55
7.54
7.26
CF3
O
Ph
F F
NO2
1H NMR of 1h
400 MHz, CDCl3
1.00
3.16
1.04
1.05
2.13
f1 (ppm)

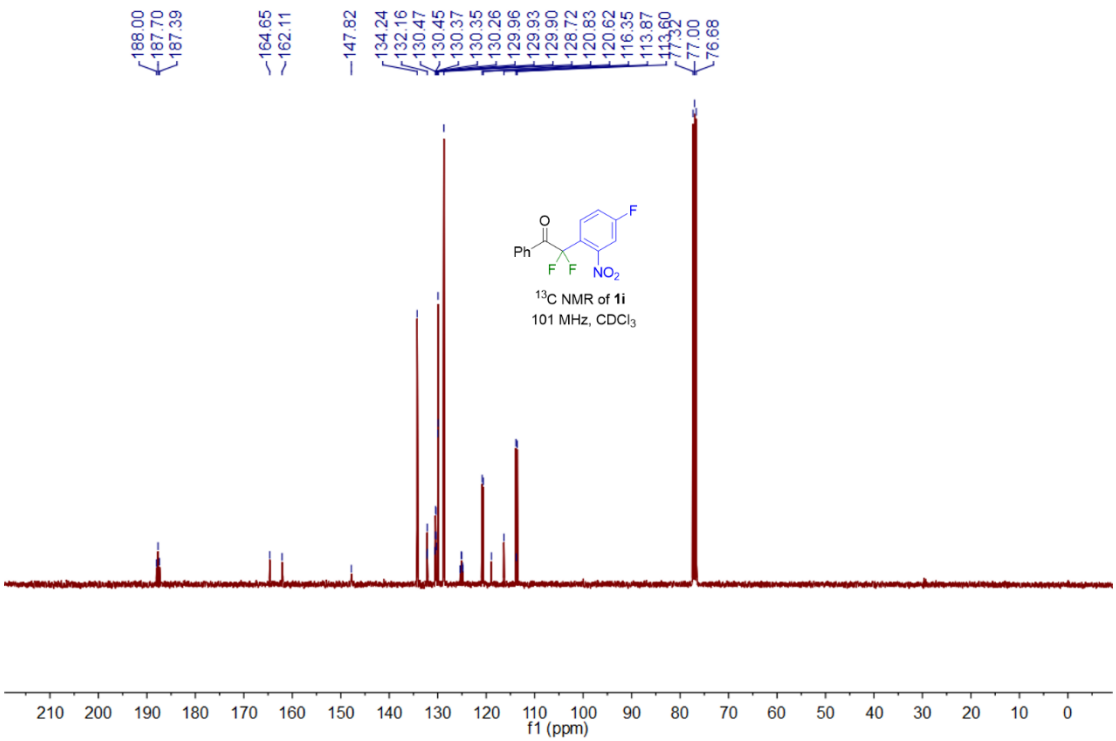


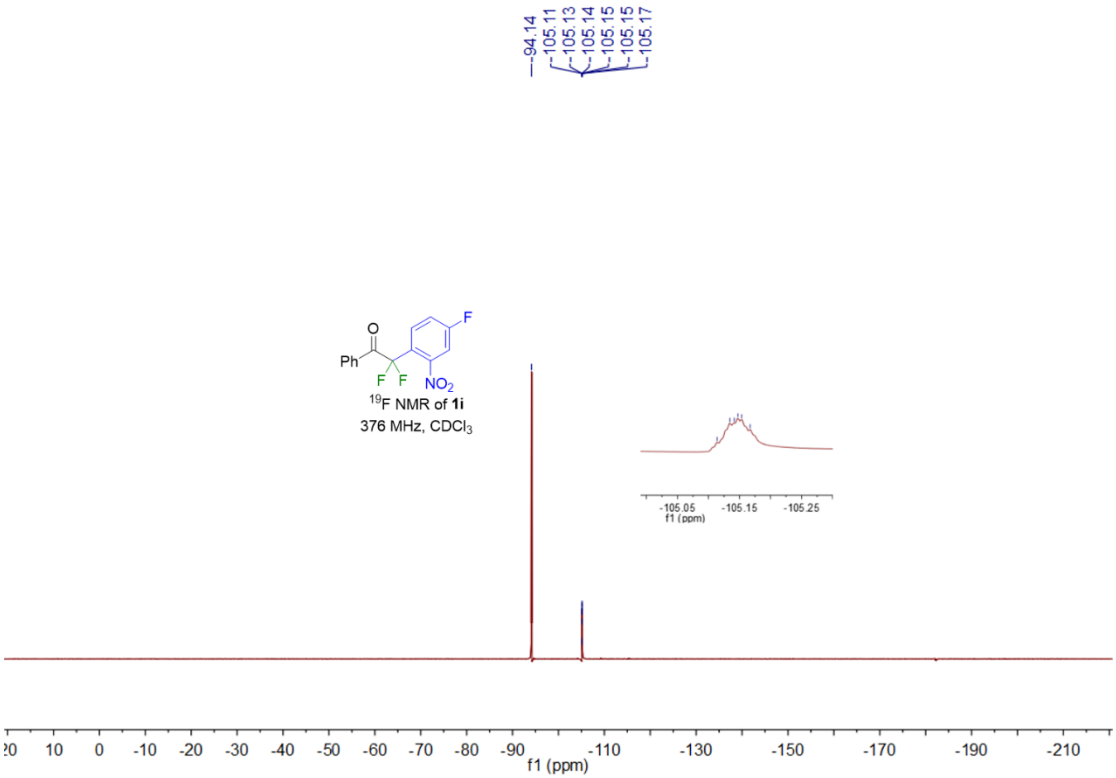
^{13}C NMR of **1h**
101 MHz, $CDCl_3$

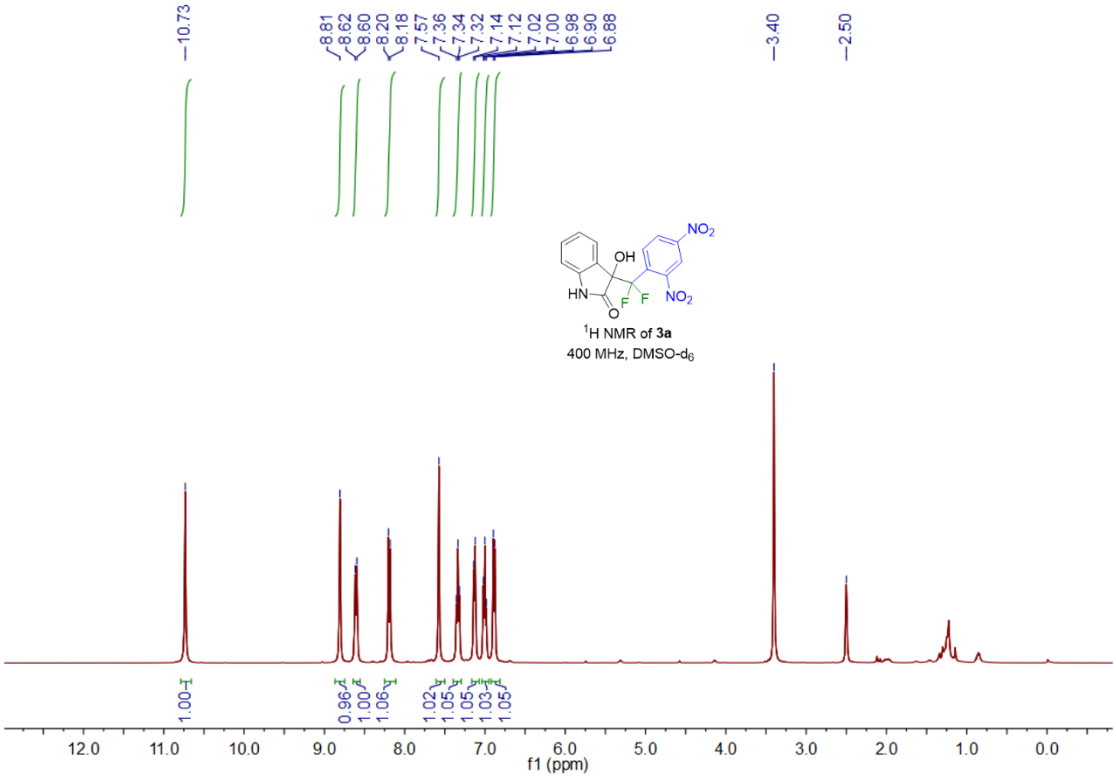


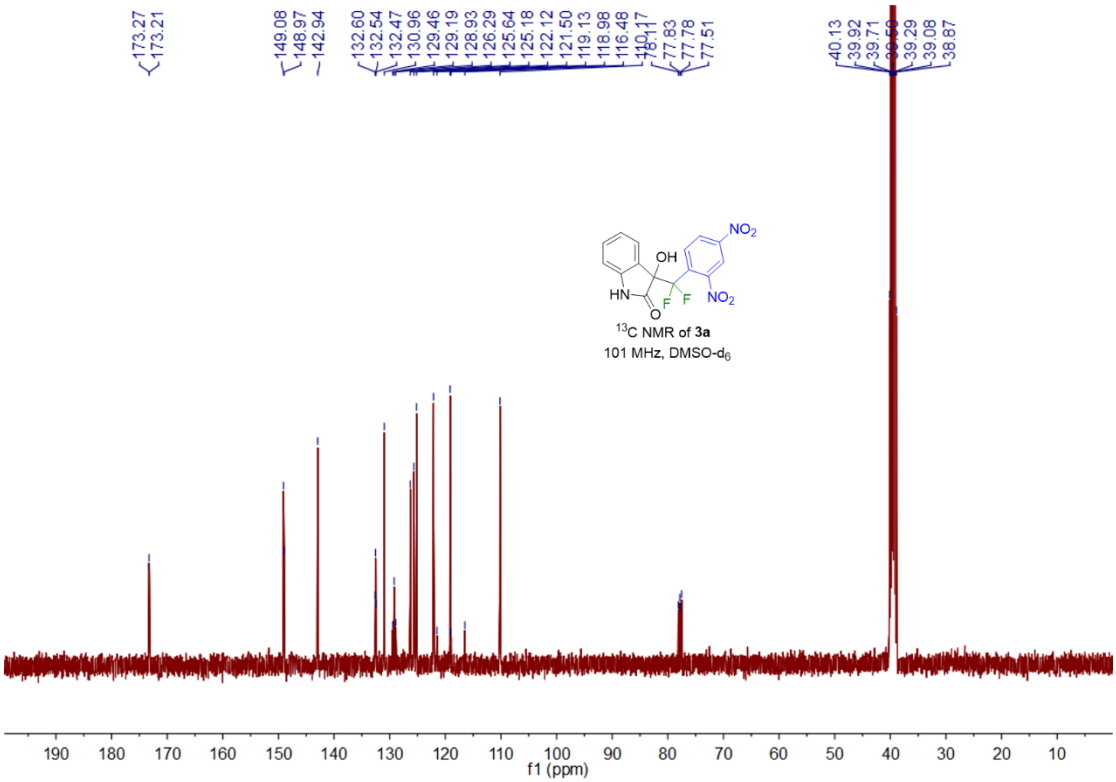
^{19}F NMR of **1h**
376 MHz, $CDCl_3$

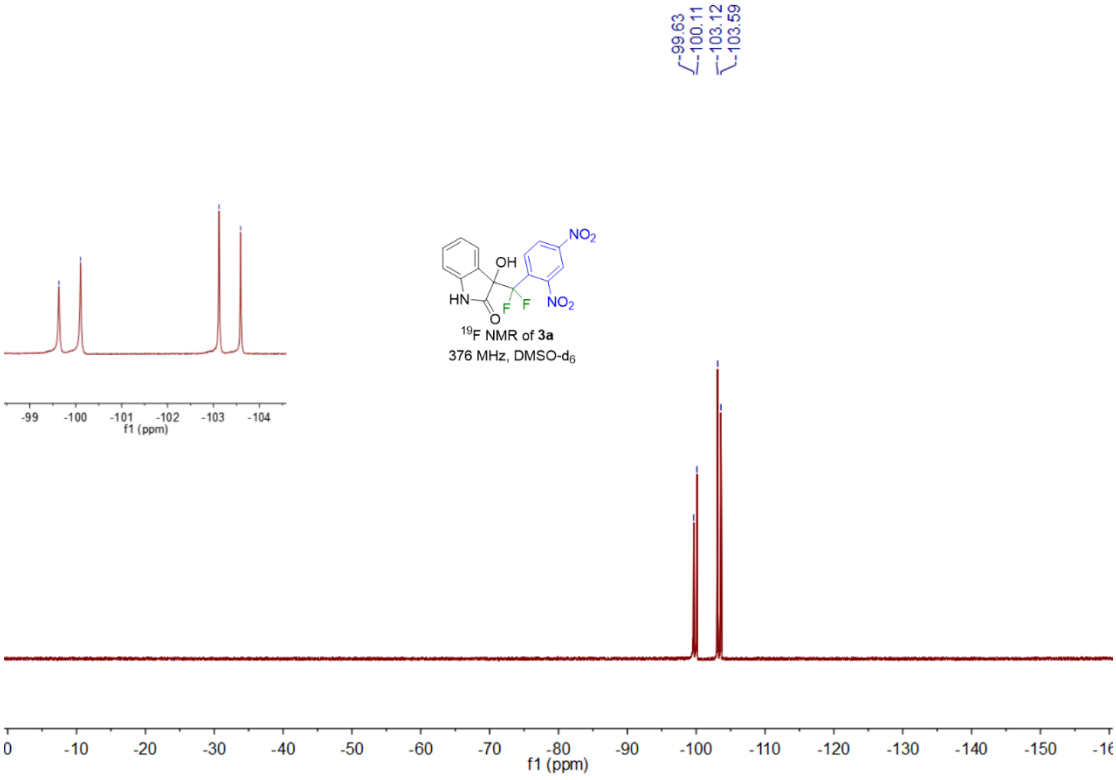

8.16
8.16
8.14
8.13
8.01
7.99
7.98
7.97
7.92
7.91
7.90
7.89
7.70
7.69
7.69
7.68
7.66
7.66
7.65
7.57
7.55
7.54
7.53
7.52
7.50
7.50
7.26
Ph
O
F
F F
NO2
1H NMR of 1i
400 MHz, CDCl3
2.14
1.08
1.00
1.06
3.14
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

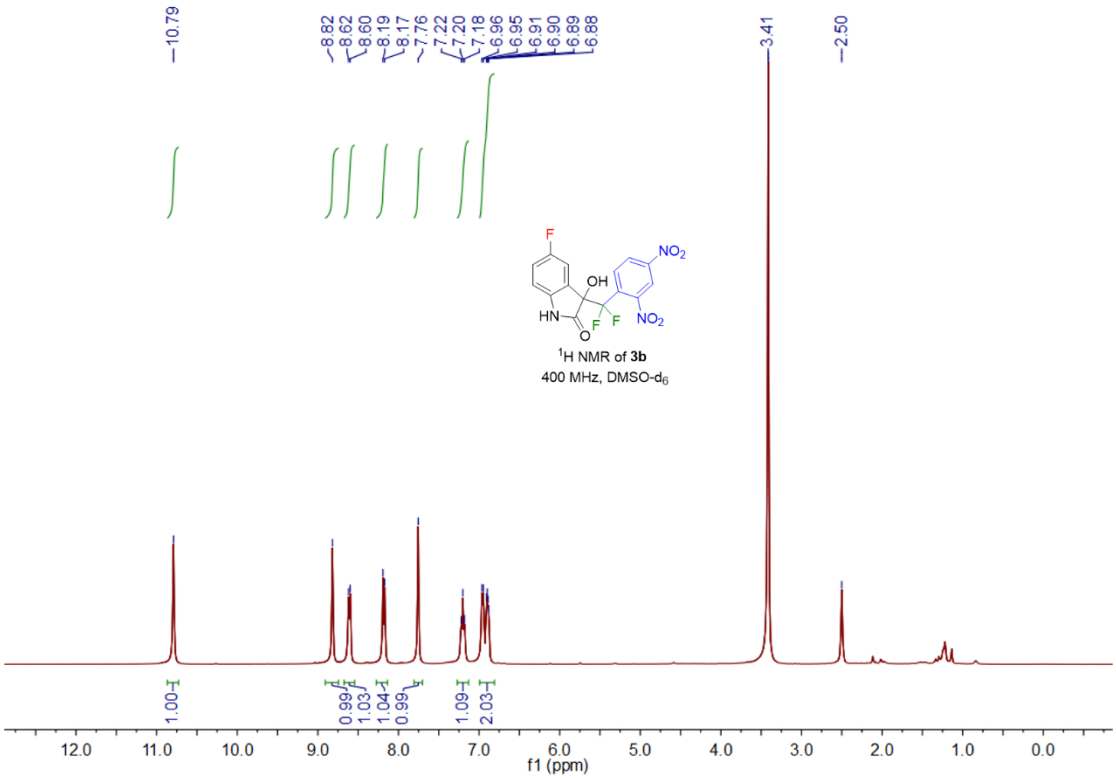

188.00
187.70
187.39
164.65
162.11
147.82
134.24
132.16
130.47
130.45
130.37
130.35
130.26
129.96
129.93
129.90
128.72
120.83
120.62
116.35
113.87
113.60
77.32
77.00
76.68
Ph
O
F
F F
NO2
13C NMR of 1i
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

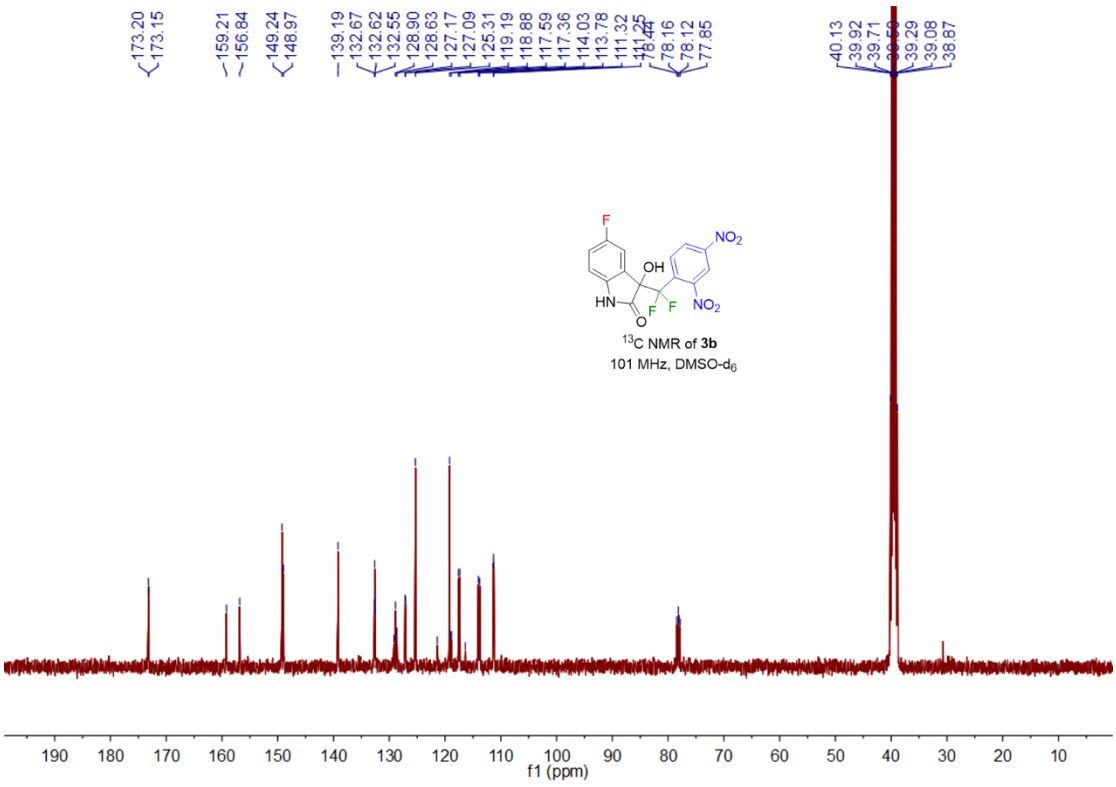

-94.14
-105.11
-105.13
-105.14
-105.15
-105.15
-105.17
O
Ph
F
F F
NO2
19F NMR of 1i
376 MHz, CDCl3
-105.05
-105.15
-105.25
f1 (ppm)
f1 (ppm)

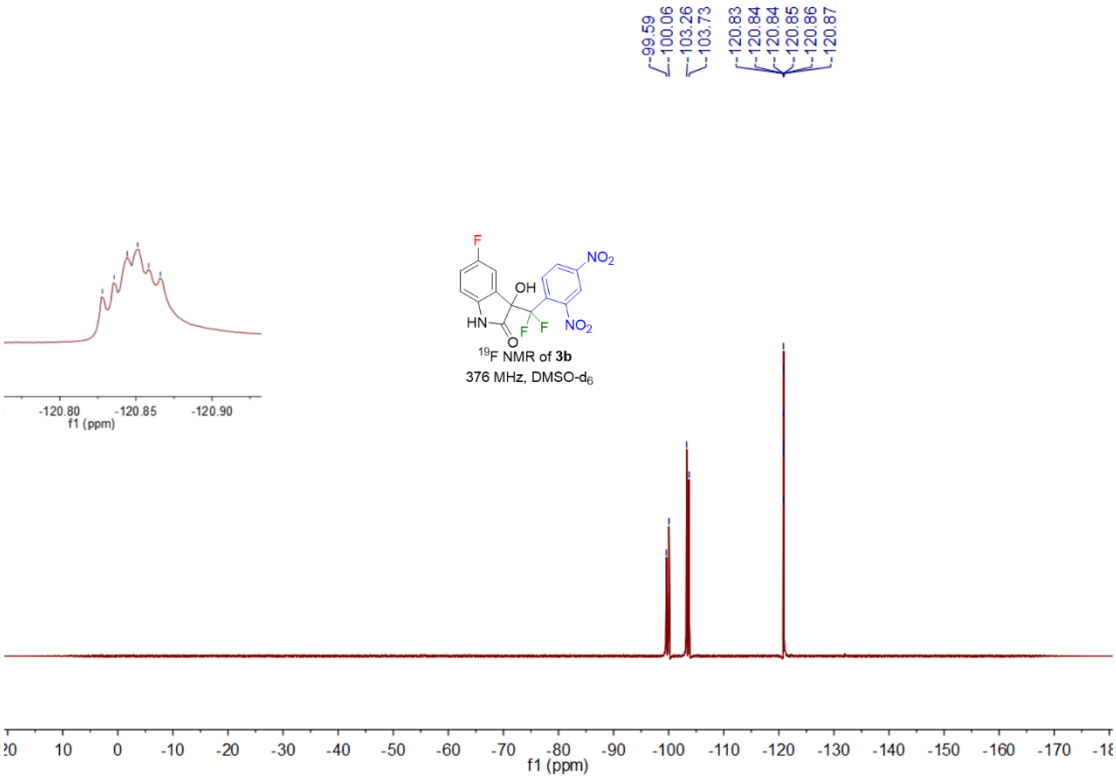

10.73
8.81
8.62
8.60
8.20
8.18
7.57
7.36
7.34
7.32
7.14
7.12
7.02
7.00
6.98
6.90
6.88
3.40
2.50
NO2
OH
HN
O
F F
NO2
1H NMR of 3a
400 MHz, DMSO-d6
1.00
0.96
1.00
1.06
1.02
1.05
1.05
1.03
1.05
f1 (ppm)

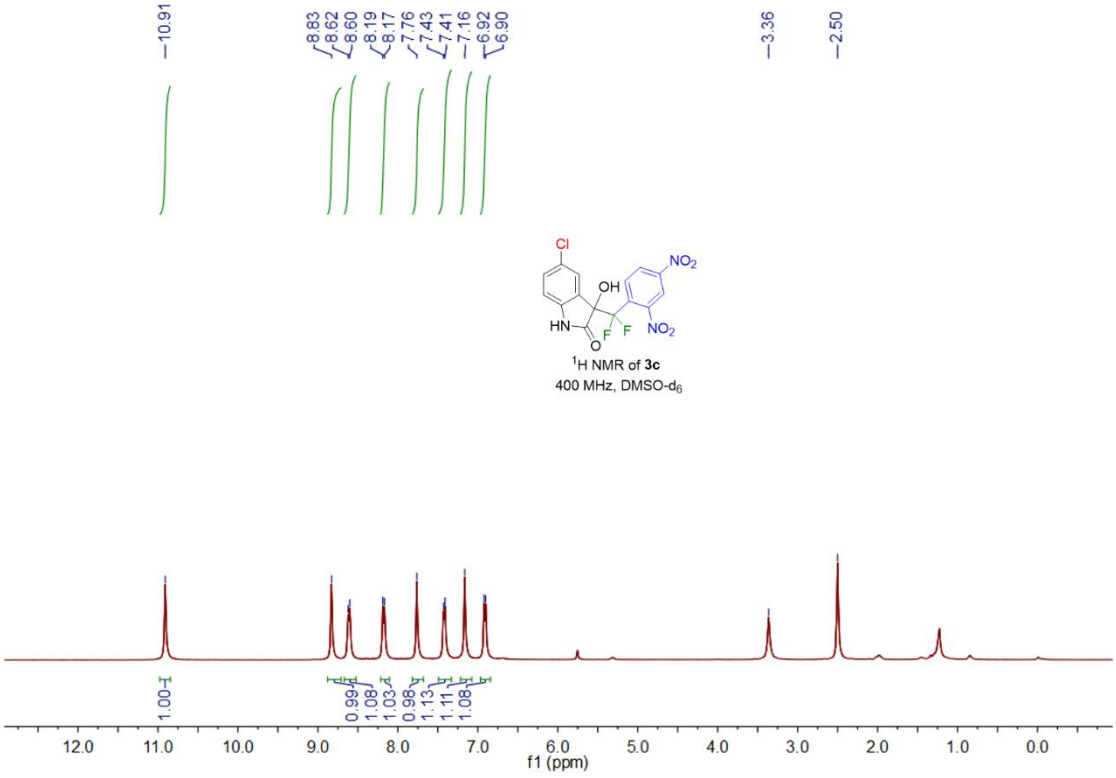

173.27
173.21
149.08
148.97
142.94
132.60
132.54
132.47
130.96
129.46
129.19
128.93
126.29
125.64
125.18
122.12
121.50
119.13
118.98
116.48
110.17
78.11
77.83
77.78
77.51
40.13
39.92
39.71
39.50
39.29
39.08
38.87
OH
HN
O
F
F
NO2
NO2
13C NMR of 3a
101 MHz, DMSO-d6
f1 (ppm)

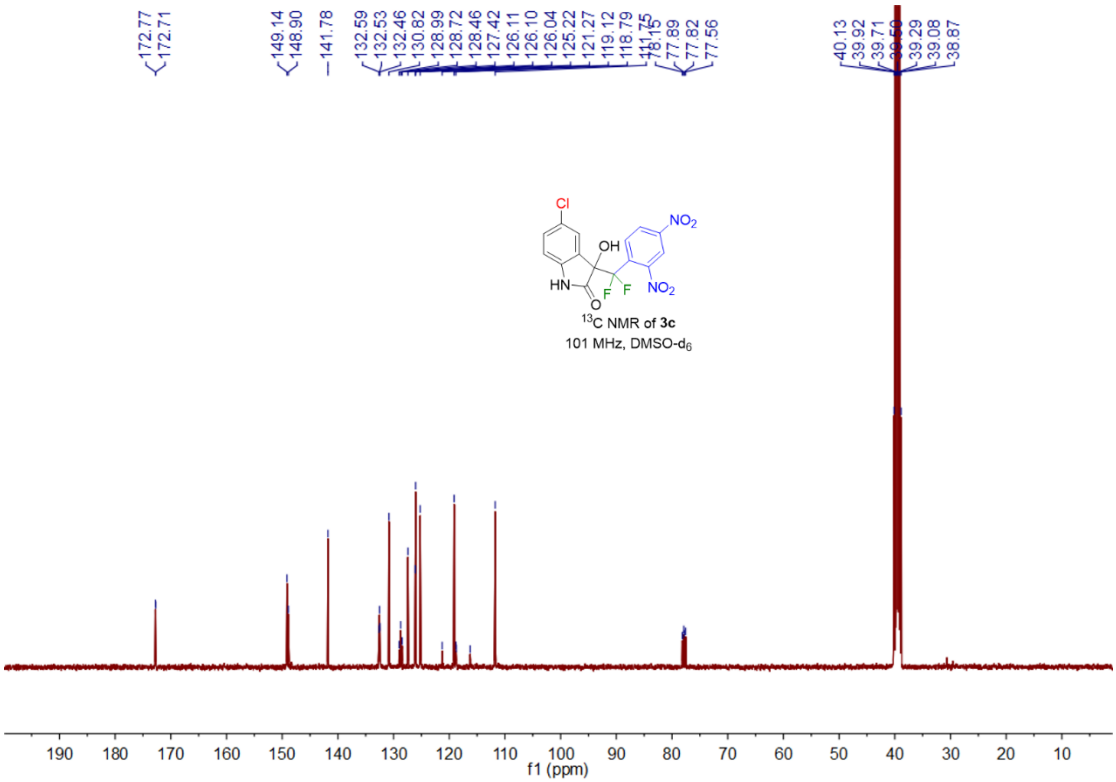

-99.63
-100.11
-103.12
-103.59
OH
HN
O
F
F
NO2
NO2
19F NMR of 3a
376 MHz, DMSO-d6
f1 (ppm)

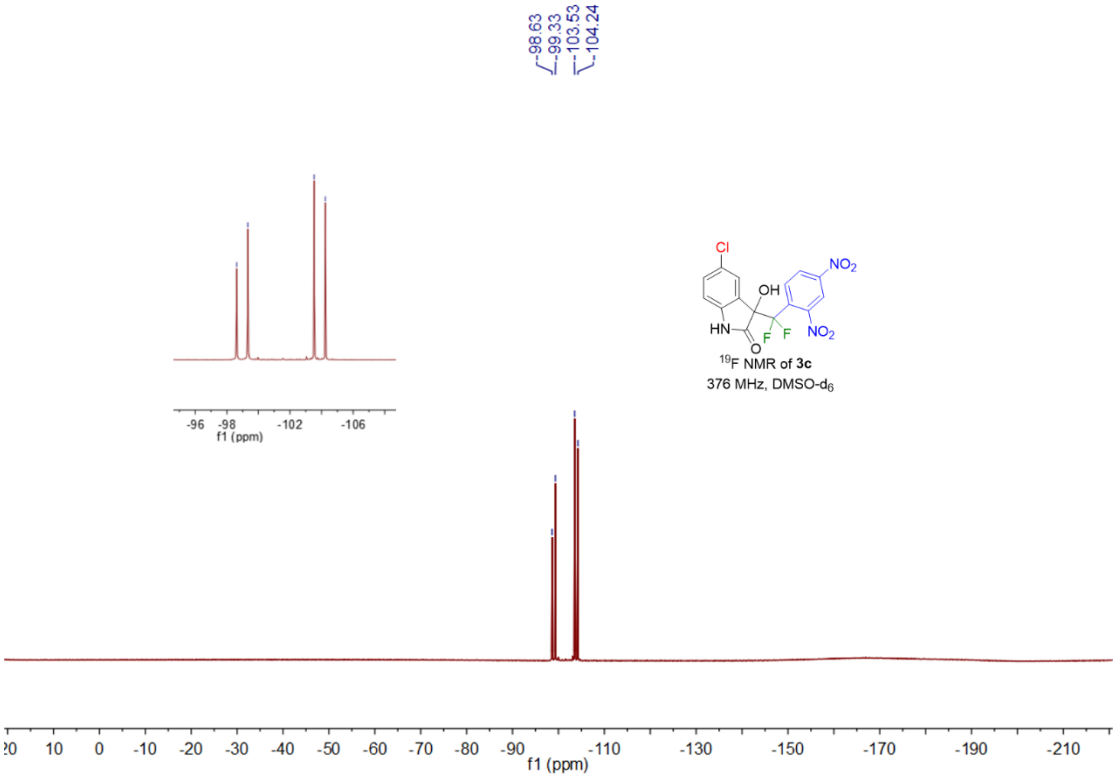

10.79
8.82
8.62
8.60
8.19
8.17
7.76
7.22
7.20
7.18
6.96
6.95
6.91
6.90
6.89
6.88
3.41
2.50
F
NO2
OH
HN
O
F
F
NO2
1H NMR of 3b
400 MHz, DMSO-d6
1.00
0.99
1.03
1.04
0.99
1.09
2.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

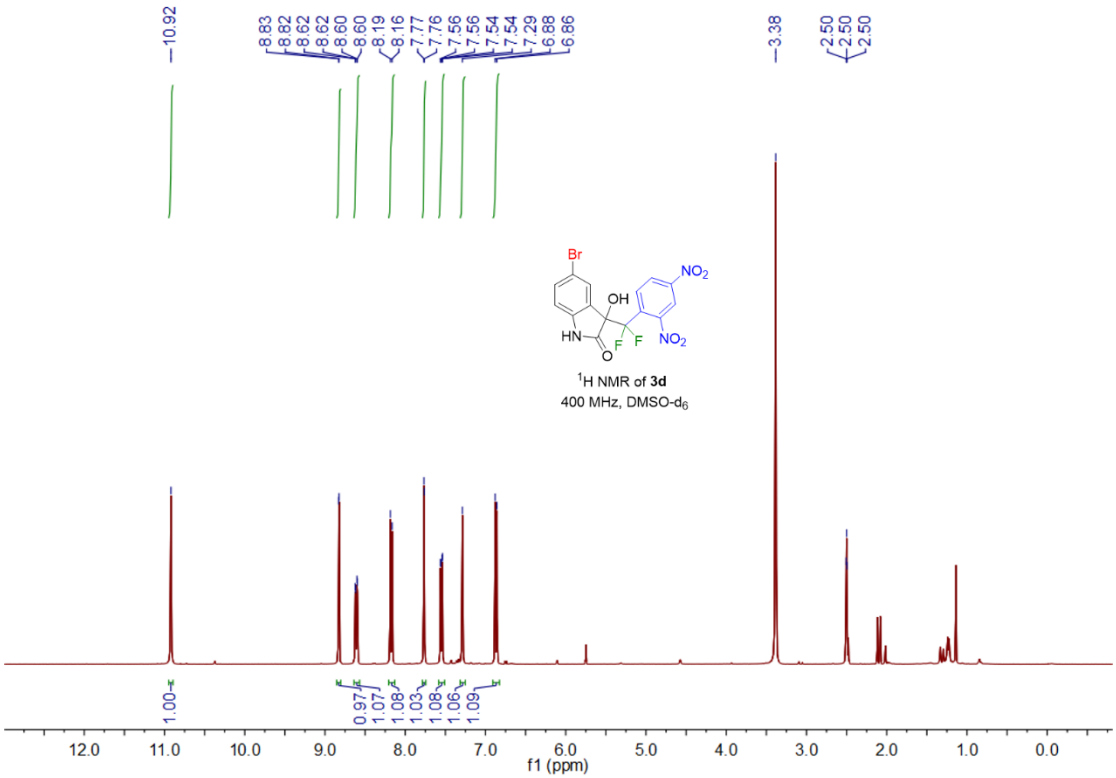

173.20
173.15
159.21
156.84
149.24
148.97
139.19
132.67
132.62
132.55
128.90
128.63
127.17
127.09
125.31
119.19
118.88
117.59
117.36
114.03
113.78
111.32
111.25
78.44
78.16
78.12
77.85
40.13
39.92
39.71
39.50
39.29
39.08
38.87
F
NO2
OH
HN
O
F
F
NO2
13C NMR of 3b
101 MHz, DMSO-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

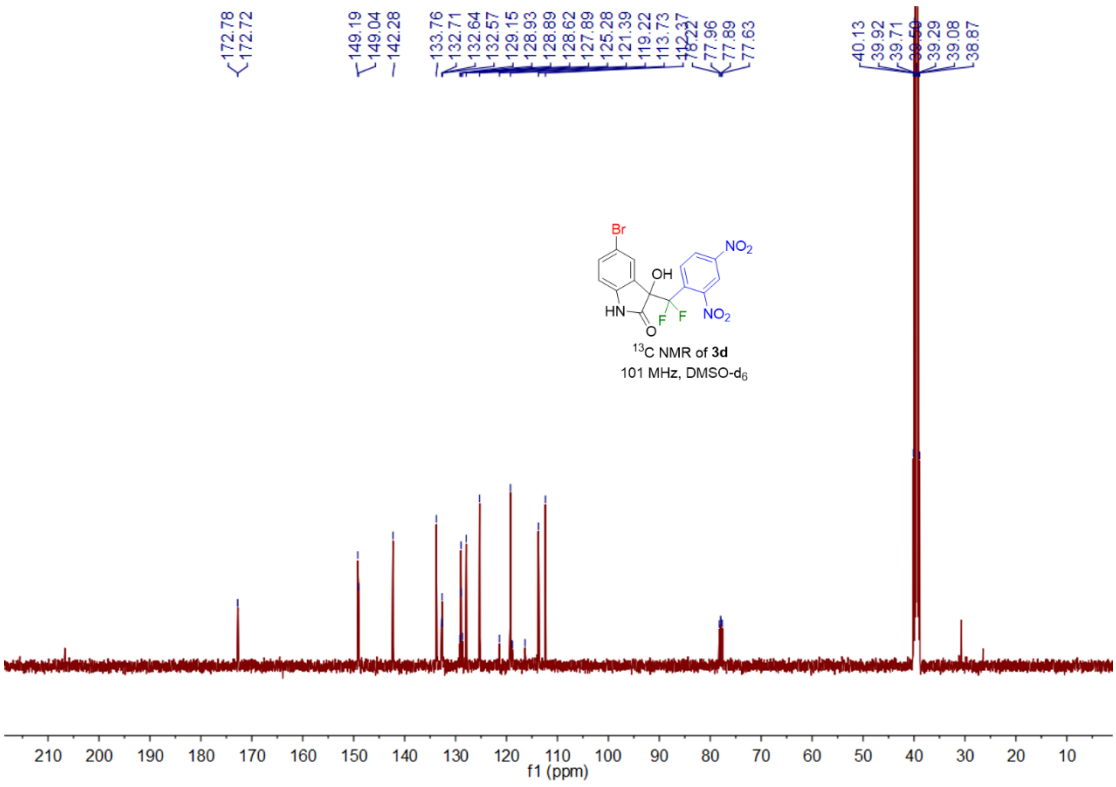

-99.59
-100.06
-103.26
-103.73
-120.83
-120.84
-120.84
-120.85
-120.86
-120.87
F
NO2
OH
HN
O
F
F
NO2
19F NMR of 3b
376 MHz, DMSO-d6
-120.80
-120.85
-120.90
f1 (ppm)
f1 (ppm)

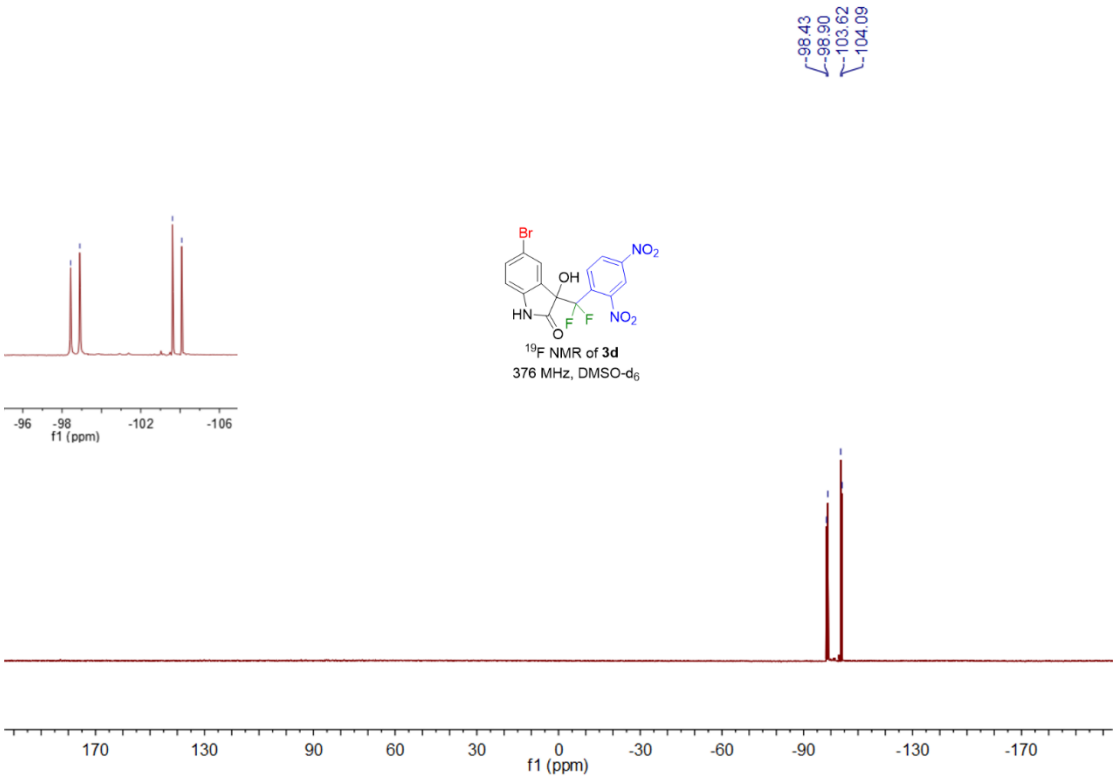

10.91
8.83
8.62
8.60
8.19
8.17
7.76
7.43
7.41
7.16
6.92
6.90
3.36
2.50
Cl
NO2
OH
HN
O
F
F
NO2
1H NMR of 3c
400 MHz, DMSO-d6
1.00
0.99
1.08
1.03
0.98
1.13
1.11
1.08
f1 (ppm)

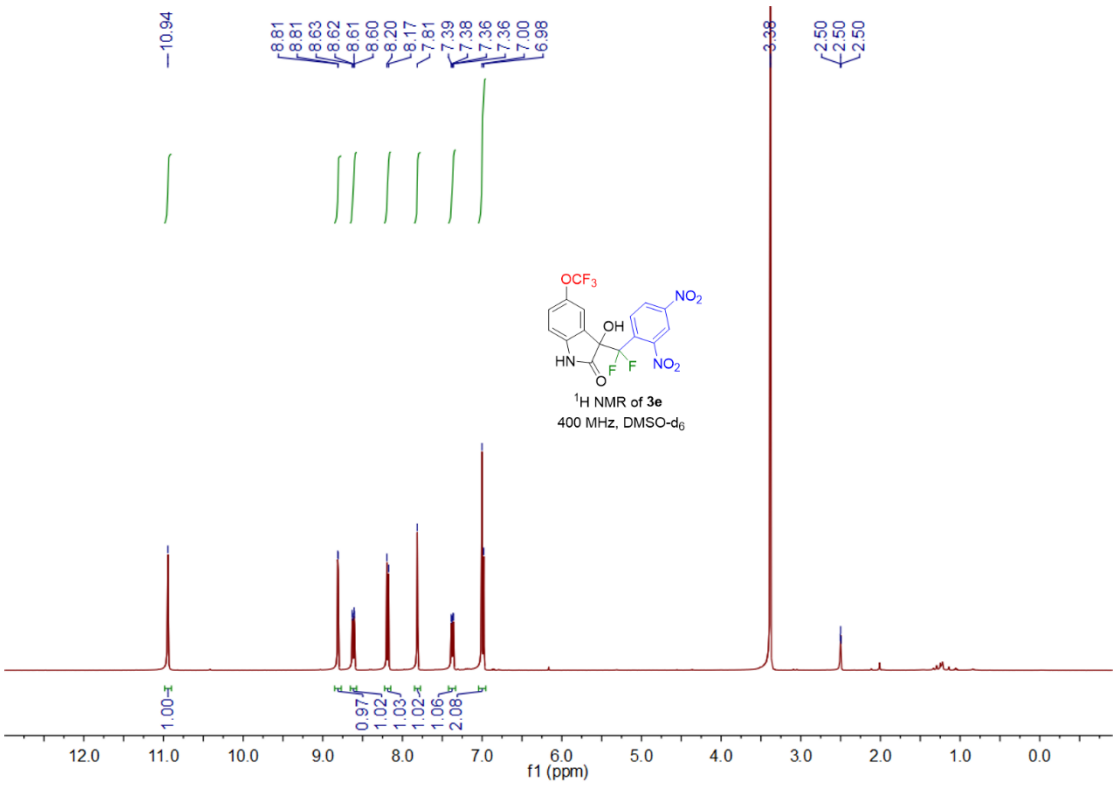

172.77
172.71
149.14
148.90
141.78
132.59
132.53
132.46
130.82
128.99
128.72
128.46
127.42
126.11
126.10
126.04
125.22
121.27
119.12
118.79
111.75
78.15
77.89
77.82
77.56
40.13
39.92
39.71
39.50
39.29
39.08
38.87
Cl
OH
HN
O
F
F
NO2
NO2
13C NMR of 3c
101 MHz, DMSO-d6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

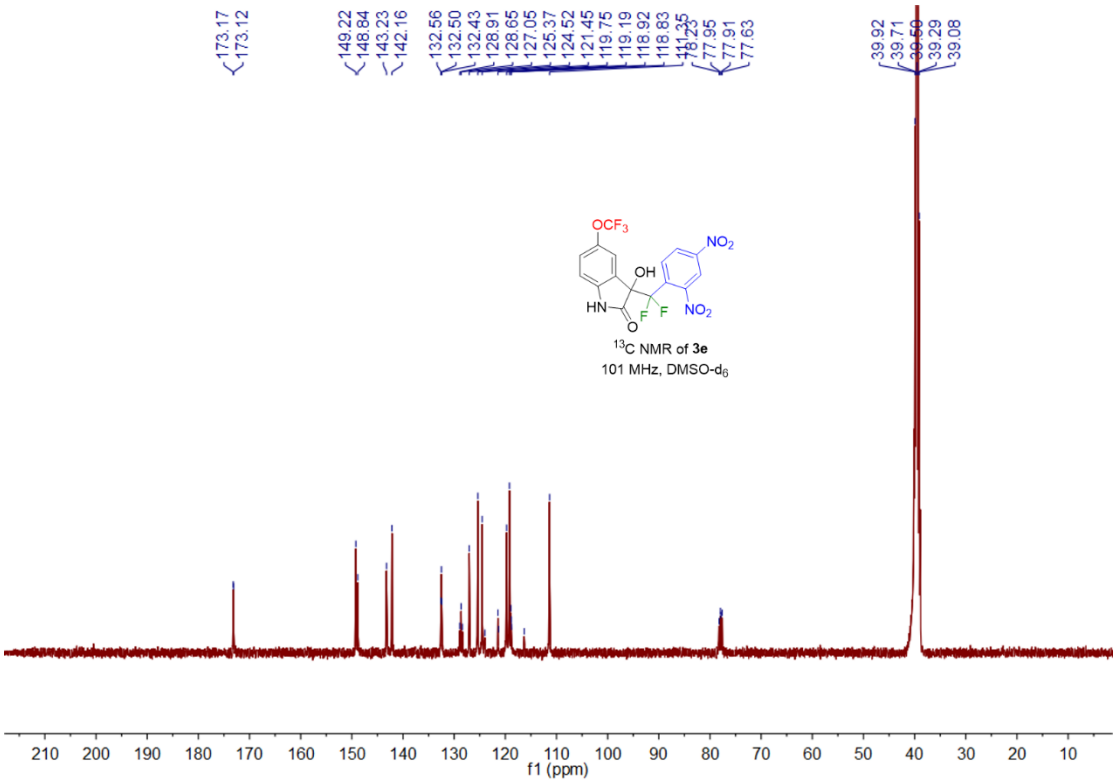

-98.63
-99.33
-103.53
-104.24
-96 -98 -102 -106
f1 (ppm)
Cl
OH
HN
O
F
F
NO2
NO2
19F NMR of 3c
376 MHz, DMSO-d6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

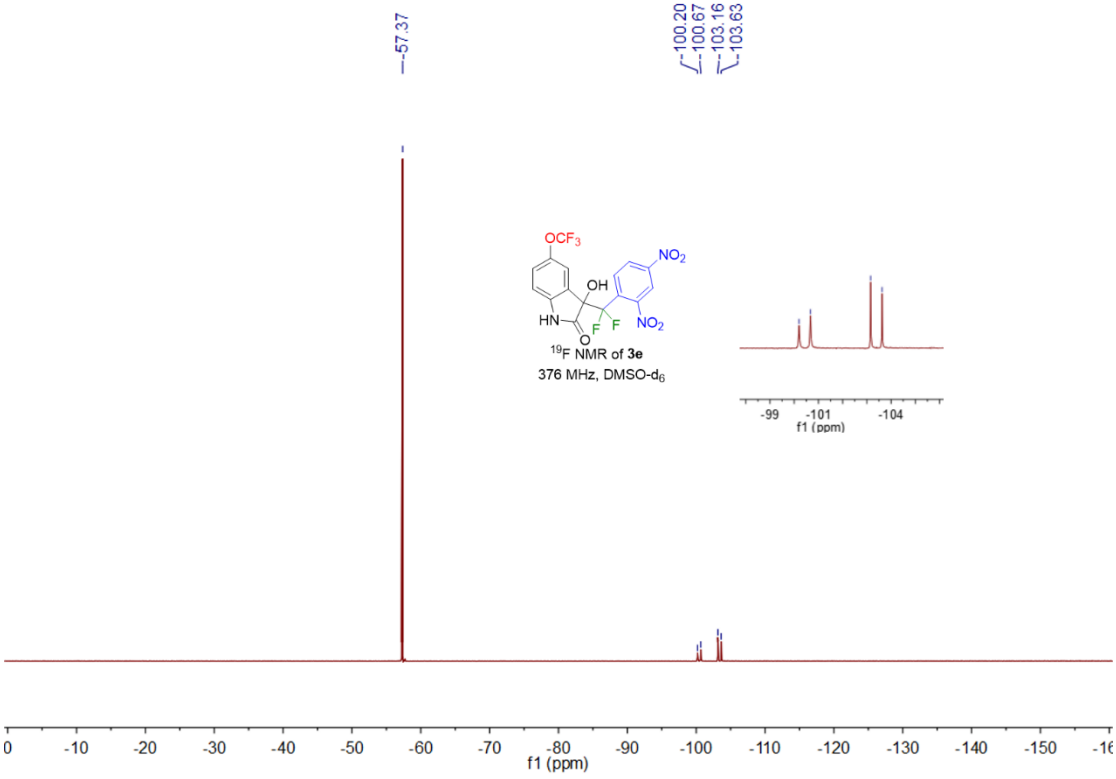

10.92
8.83
8.82
8.62
8.62
8.60
8.60
8.19
8.16
7.77
7.76
7.56
7.56
7.54
7.54
7.29
6.88
6.86
3.38
2.50
2.50
2.50
Br
NO2
OH
HN
O
F
F
NO2
1H NMR of 3d
400 MHz, DMSO-d6
1.00
0.97
1.07
1.08
1.03
1.08
1.06
1.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

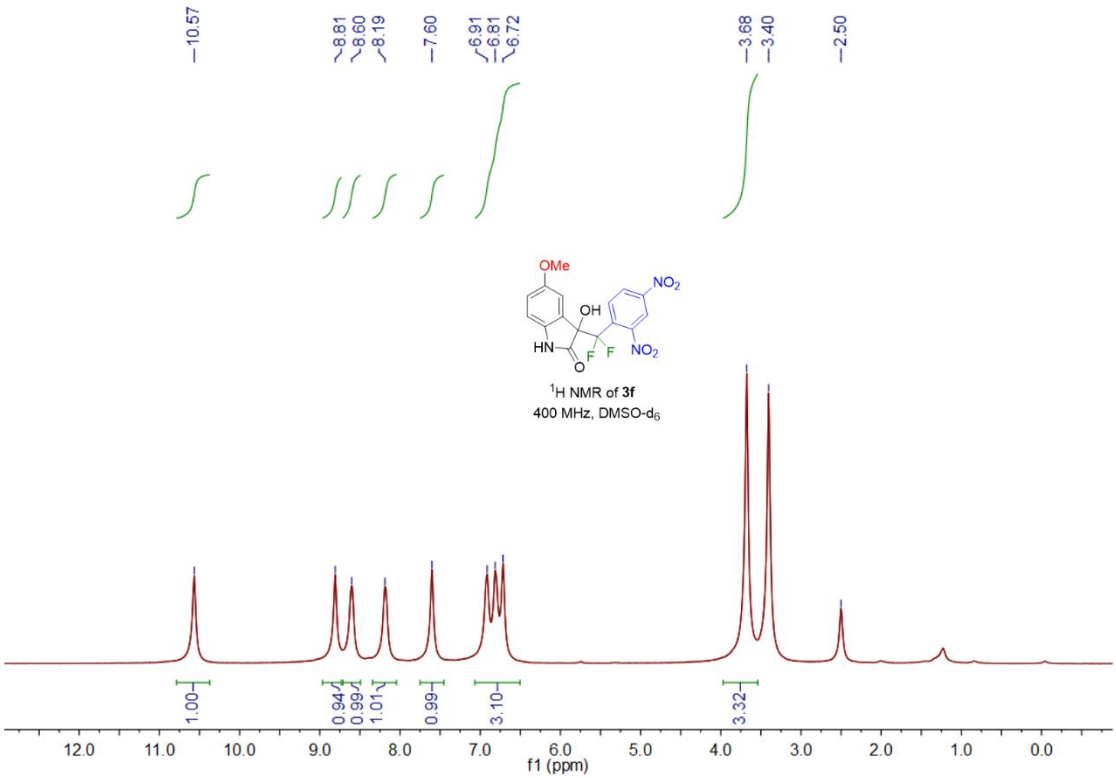

172.78
172.72
149.19
149.04
142.28
133.76
132.71
132.64
132.57
129.15
128.93
128.89
128.62
127.89
125.28
121.39
119.22
113.73
112.37
78.22
77.96
77.89
77.63
40.13
39.92
39.71
39.50
39.29
39.08
38.87
Br
NO2
OH
HN
O
F
F
NO2
13C NMR of 3d
101 MHz, DMSO-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

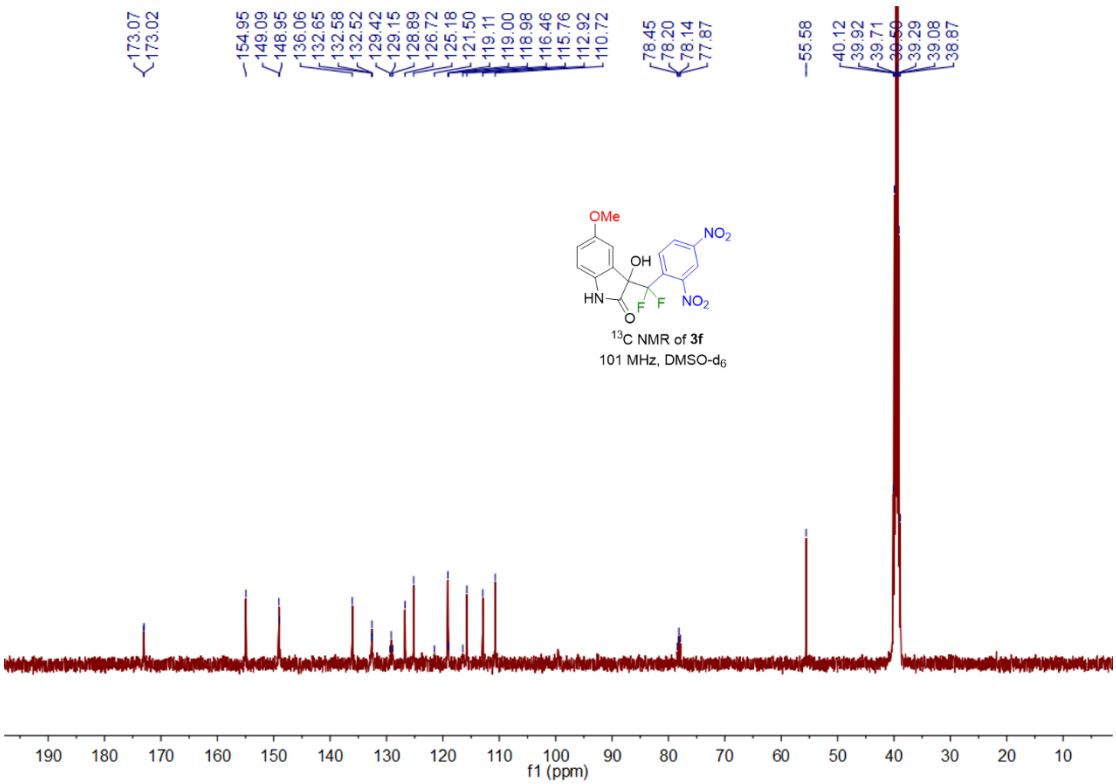

-98.43
-98.90
-103.62
-104.09
Br
OH
HN
O
F
F
NO2
NO2
19F NMR of 3d
376 MHz, DMSO-d6
-96
-98
-102
-106
f1 (ppm)
170
130
90
60
30
0
-30
-60
-90
-130
-170
f1 (ppm)

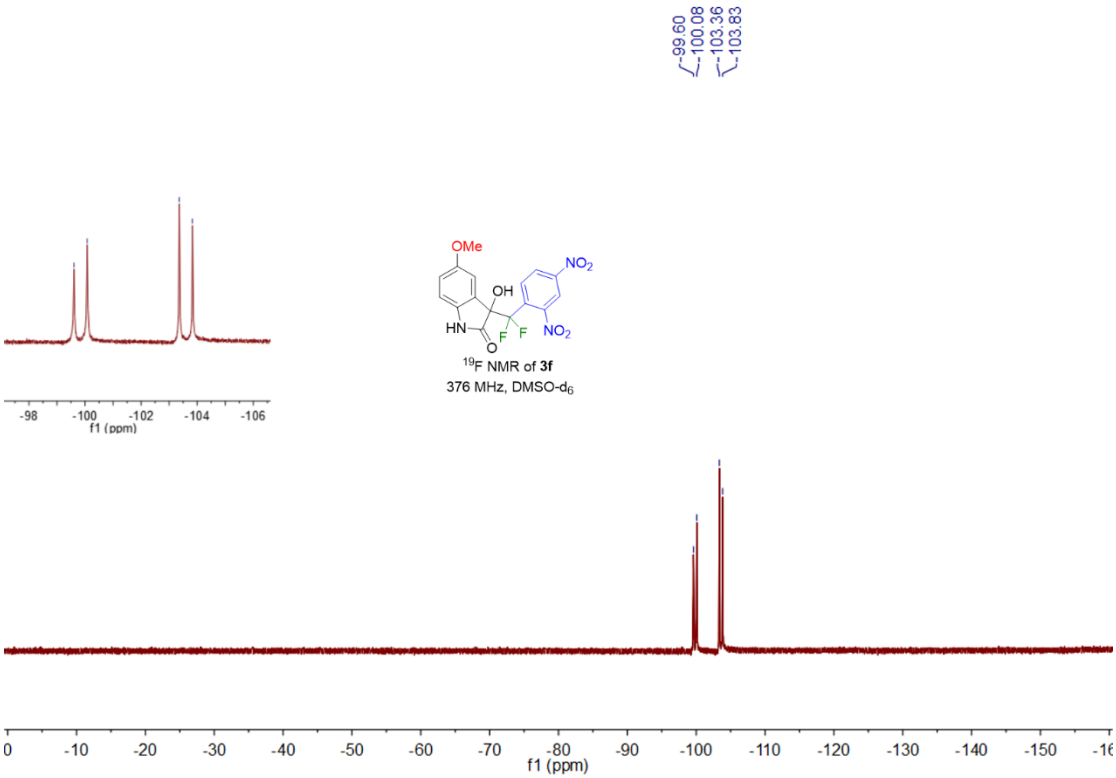

10.94
8.81
8.81
8.63
8.62
8.61
8.60
8.20
8.17
7.81
7.39
7.38
7.36
7.36
7.00
6.98
3.38
2.50
2.50
2.50
OCF3
OH
HN
O
F
F
NO2
NO2
1H NMR of 3e
400 MHz, DMSO-d6
1.00
0.97
1.02
1.03
1.02
1.06
2.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

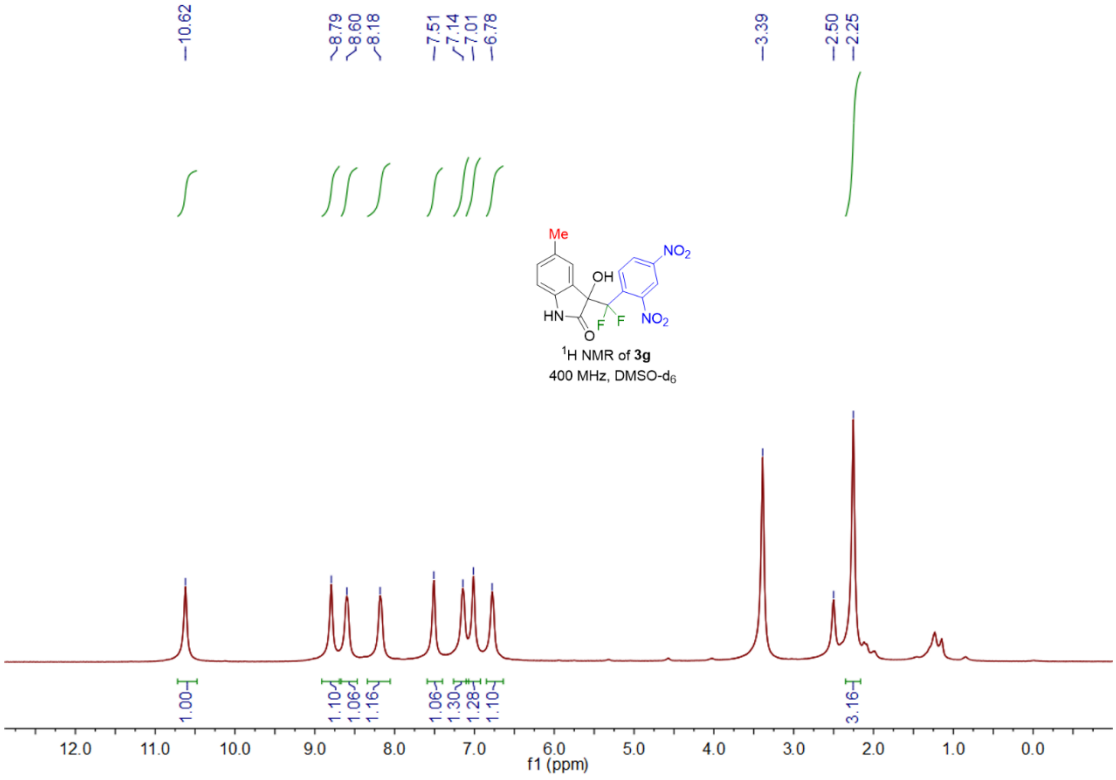

173.17
173.12
149.22
148.84
143.23
142.16
132.56
132.50
132.43
128.91
128.65
127.05
125.37
124.52
121.45
119.75
119.19
118.92
118.83
111.35
78.23
77.95
77.91
77.63
39.92
39.71
39.50
39.29
39.08
OCF3
NO2
OH
HN
O
F
F
NO2
13C NMR of 3e
101 MHz, DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

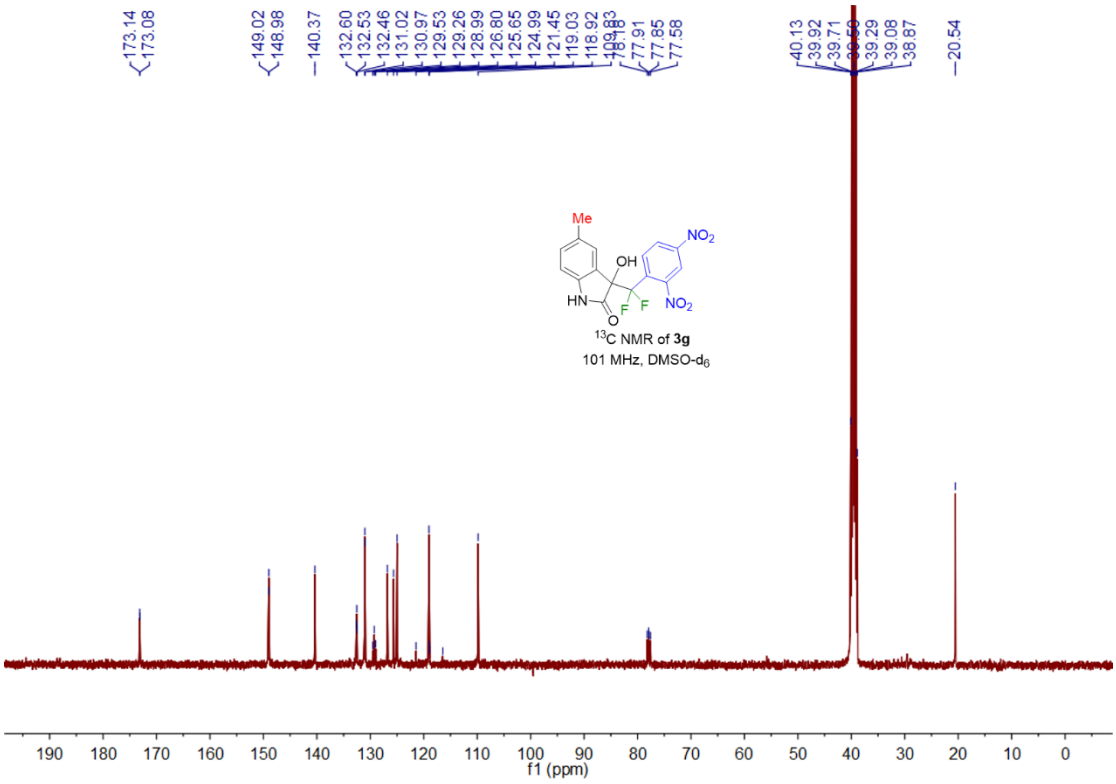

-57.37
-100.20
-100.67
-103.16
-103.63
OCF3
NO2
OH
HN
O
F
F
NO2
19F NMR of 3e
376 MHz, DMSO-d6
-99
-101
-104
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

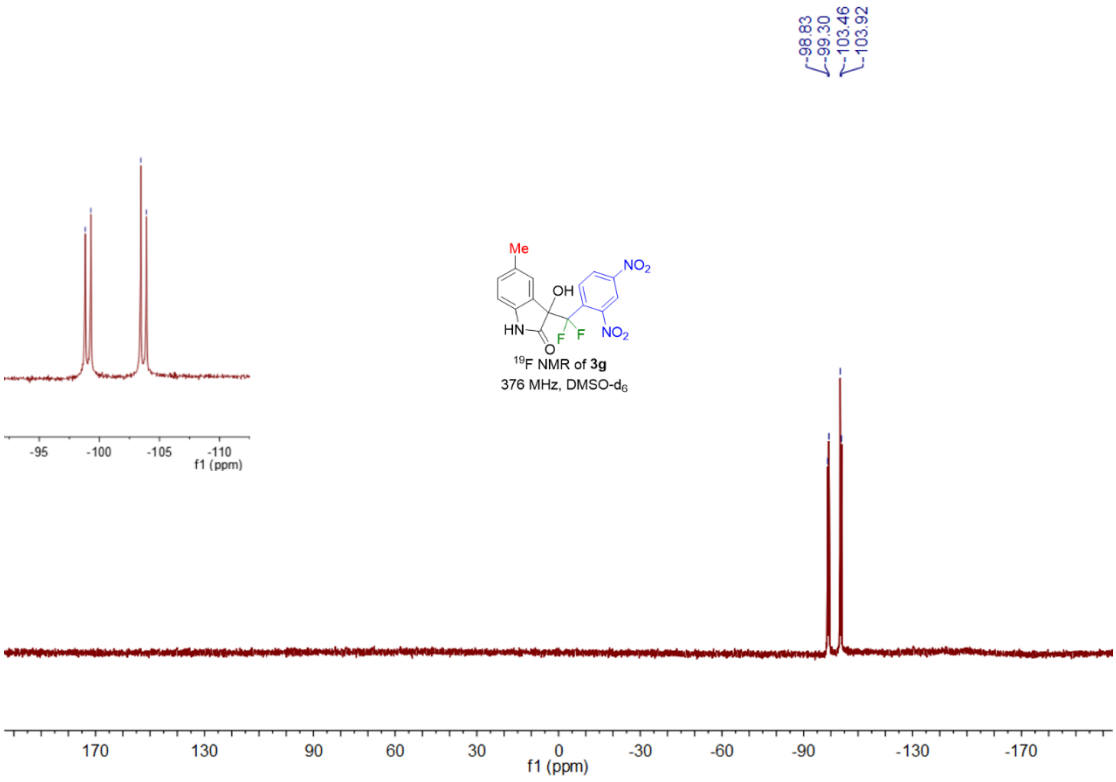

10.57
8.81
8.60
8.19
7.60
6.91
6.81
6.72
3.68
3.40
2.50
OMe
NO2
OH
HN
F
F
NO2
O
1H NMR of 3f
400 MHz, DMSO-d6
1.00
0.94
0.99
1.01
0.99
3.10
3.32
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

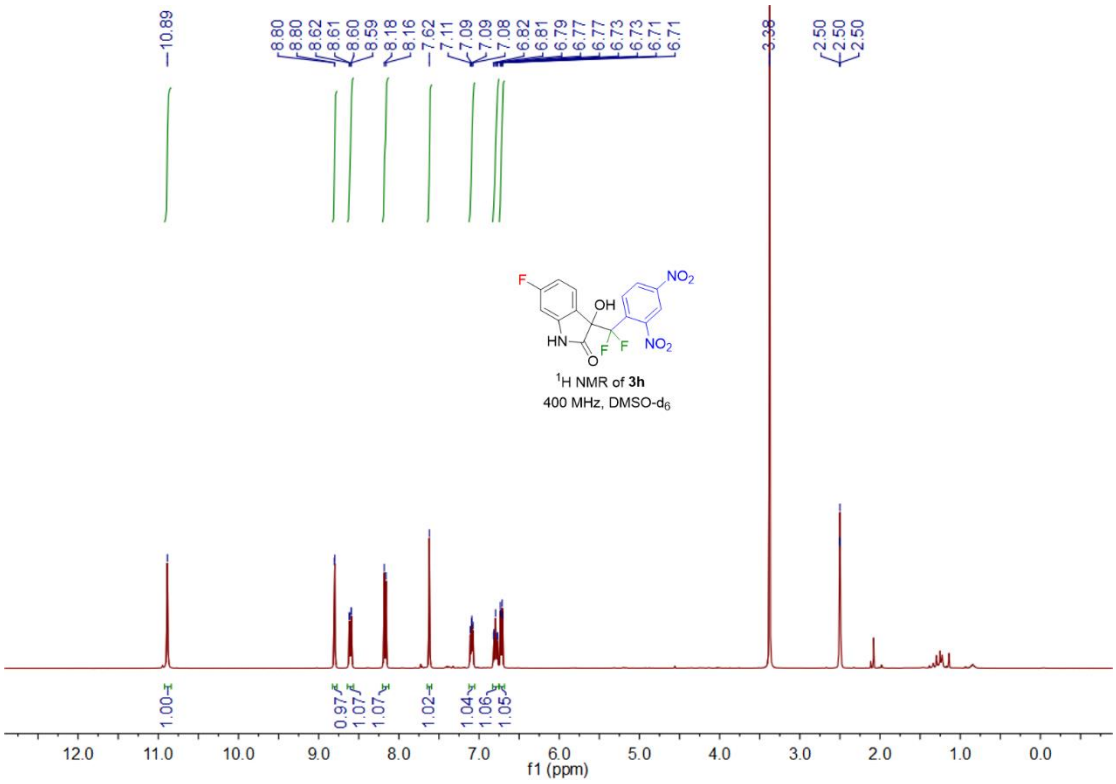

173.07
173.02
154.95
149.09
148.95
136.06
132.65
132.58
132.52
129.42
129.15
128.89
126.72
125.18
121.50
119.11
119.00
118.98
116.46
115.76
112.92
110.72
78.45
78.20
78.14
77.87
55.58
40.12
39.92
39.71
39.50
39.29
39.08
38.87
OMe
NO2
OH
HN
F
F
NO2
O
13C NMR of 3f
101 MHz, DMSO-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-99.60
-100.08
-103.36
-103.83
OMe
NO2
OH
HN
O
F
F
NO2
19F NMR of 3f
376 MHz, DMSO-d6
-98
-100
-102
-104
-106
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

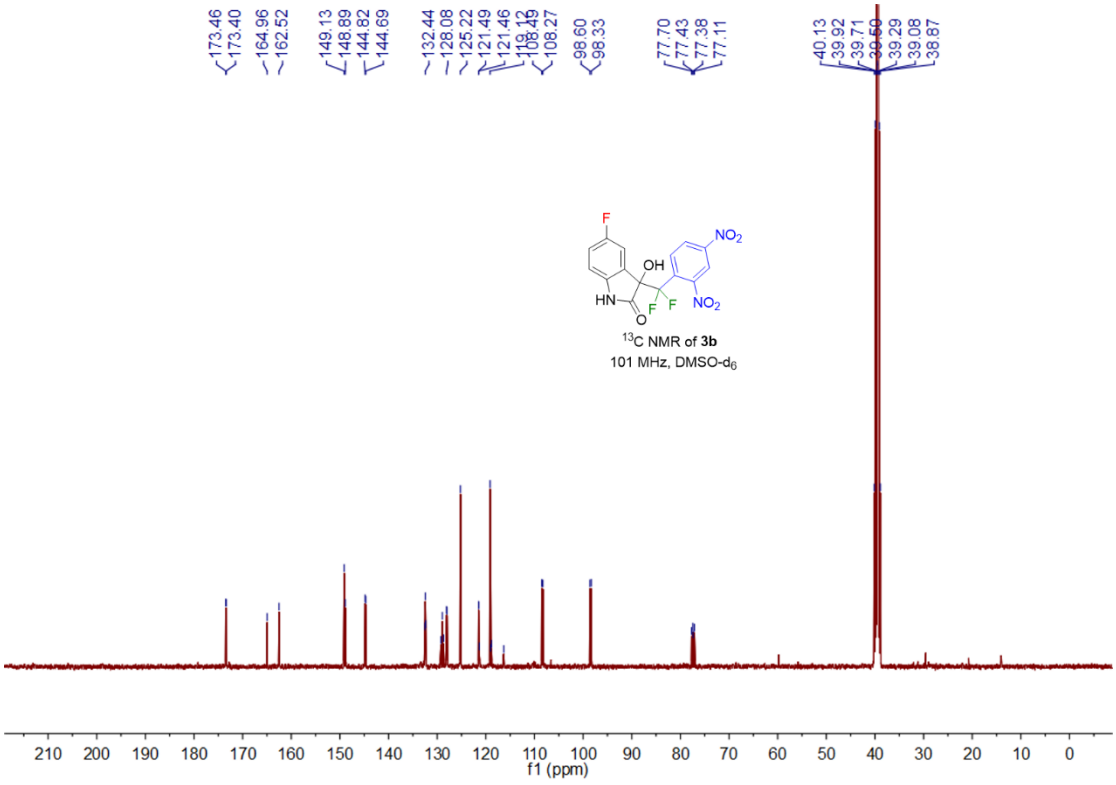

10.62
8.79
8.60
8.18
7.51
7.14
7.01
6.78
3.39
2.50
2.25
Me
NO2
OH
HN
O
F
F
NO2
1H NMR of 3g
400 MHz, DMSO-d6
1.00
1.10
1.06
1.16
1.06
1.30
1.28
1.10
3.16
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


173.14
173.08
149.02
148.98
140.37
132.60
132.53
132.46
131.02
130.97
129.53
129.26
128.99
126.80
125.65
124.99
121.45
119.03
118.92
77.91
77.85
77.58
40.13
39.92
39.71
39.29
39.08
38.87
20.54
Me
OH
HN
O
F
F
NO2
NO2
13C NMR of 3g
101 MHz, DMSO-d6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

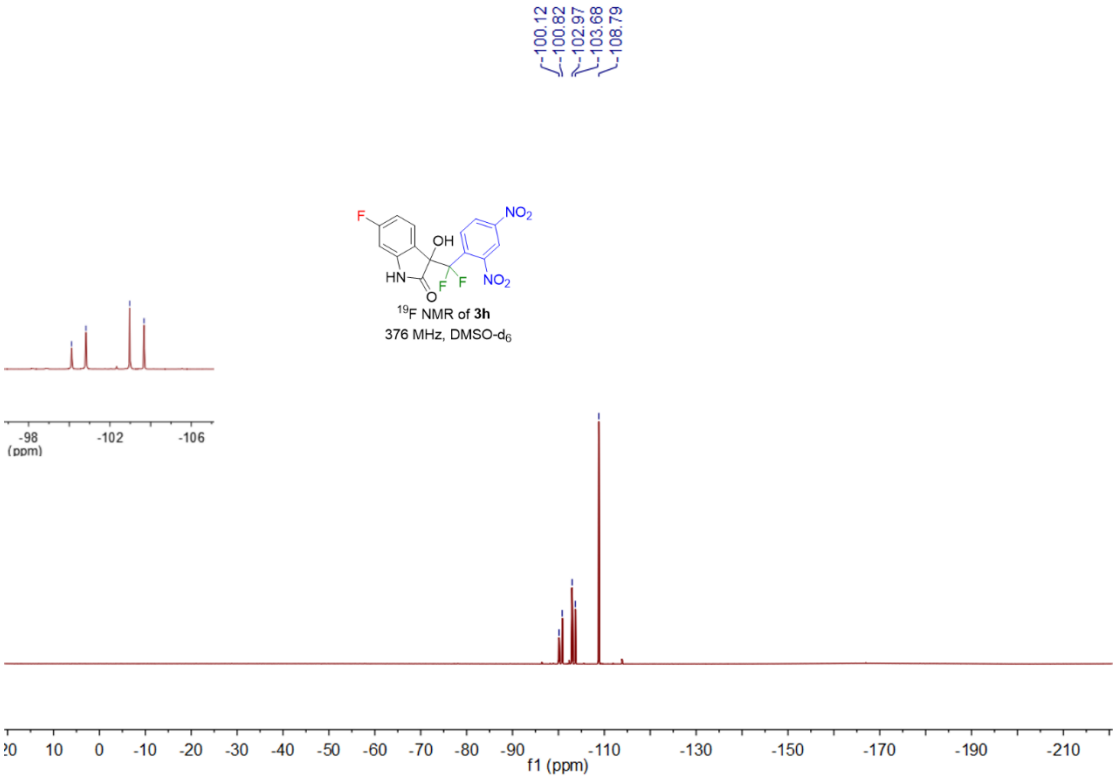

-98.83
-99.30
-103.46
-103.92
Me
OH
HN
O
F
F
NO2
NO2
19F NMR of 3g
376 MHz, DMSO-d6
-95 -100 -105 -110
f1 (ppm)
170 130 90 60 30 0 -30 -60 -90 -130 -170
f1 (ppm)

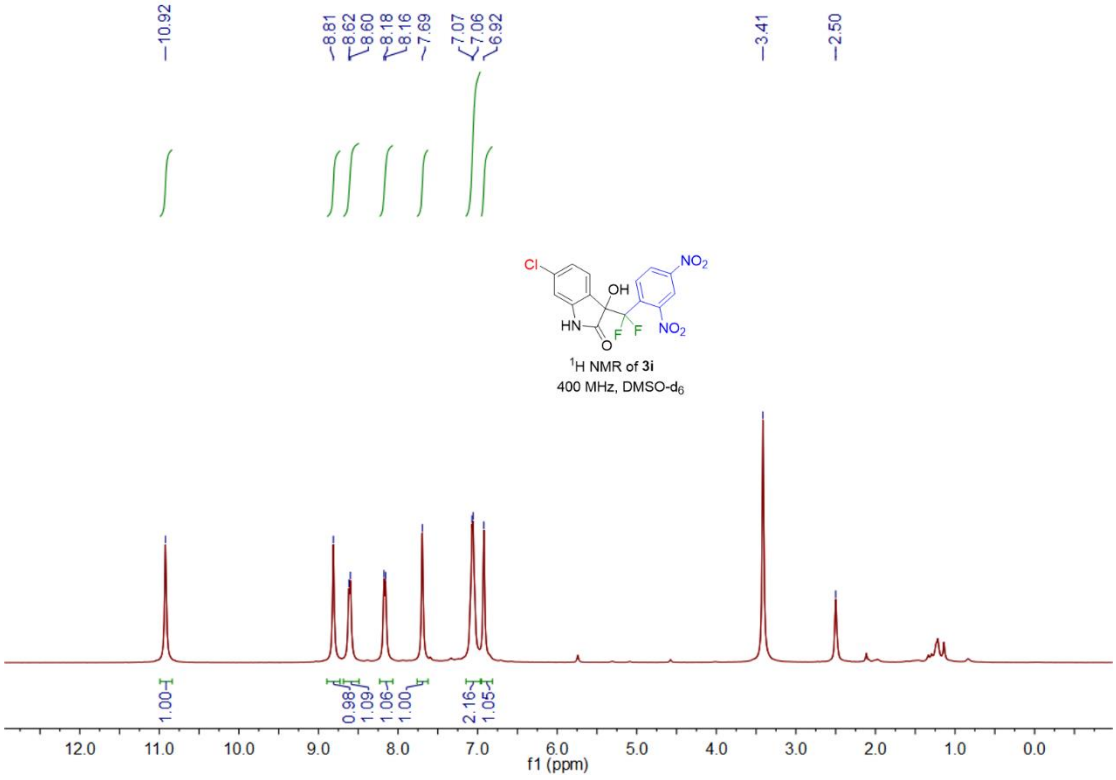


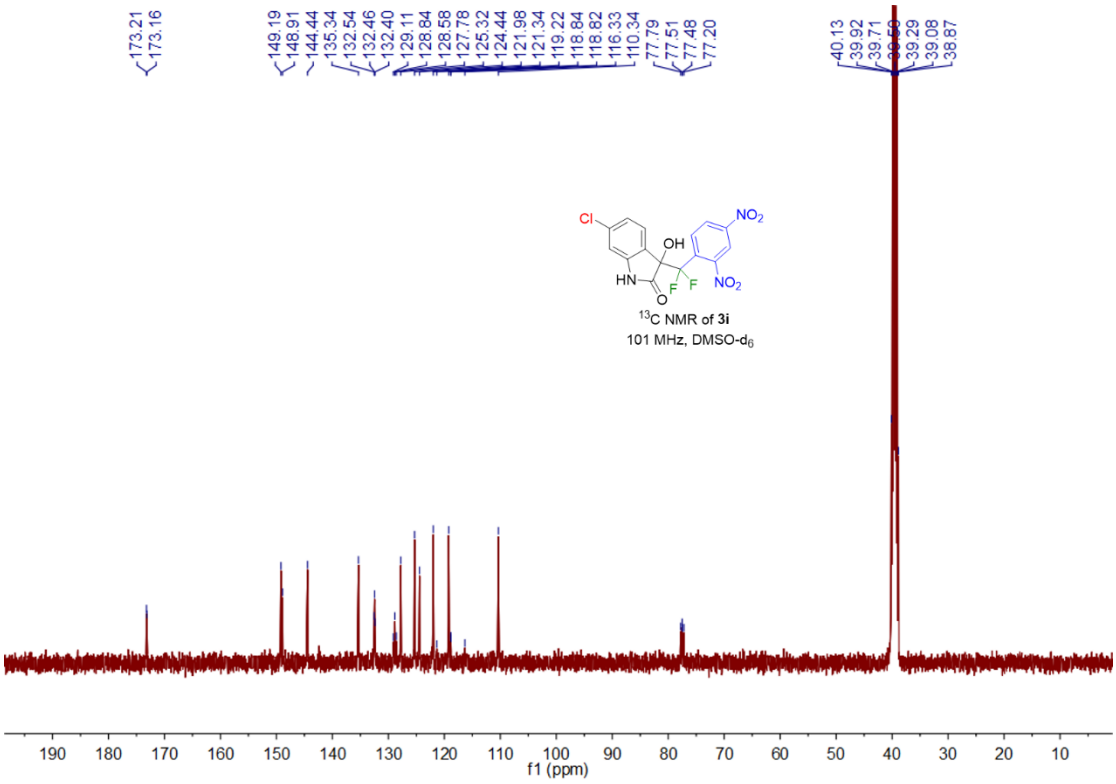
^{1}H NMR of **3h**
400 MHz, DMSO-d_6



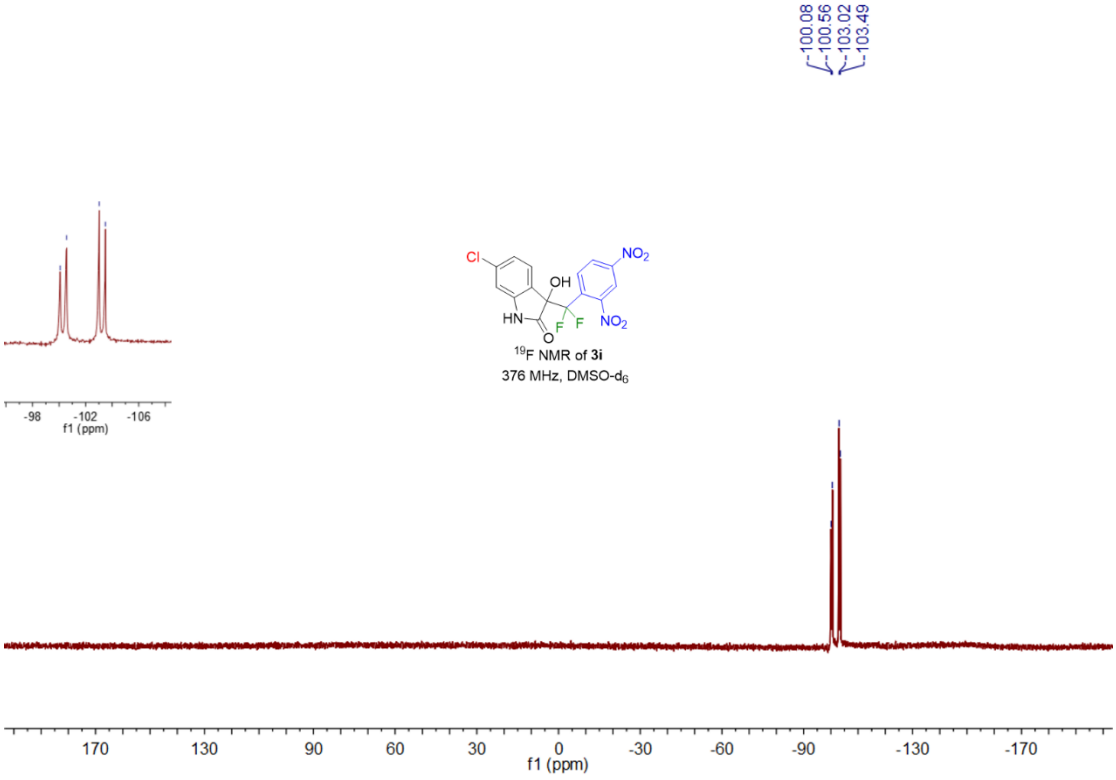
^{13}C NMR of **3b**
101 MHz, DMSO-d_6


-100.12
-100.82
-102.97
-103.68
-108.79
F
OH
HN
O
F
F
NO2
NO2
19F NMR of 3h
376 MHz, DMSO-d6
-98
-102
-106
(ppm)
f1 (ppm)

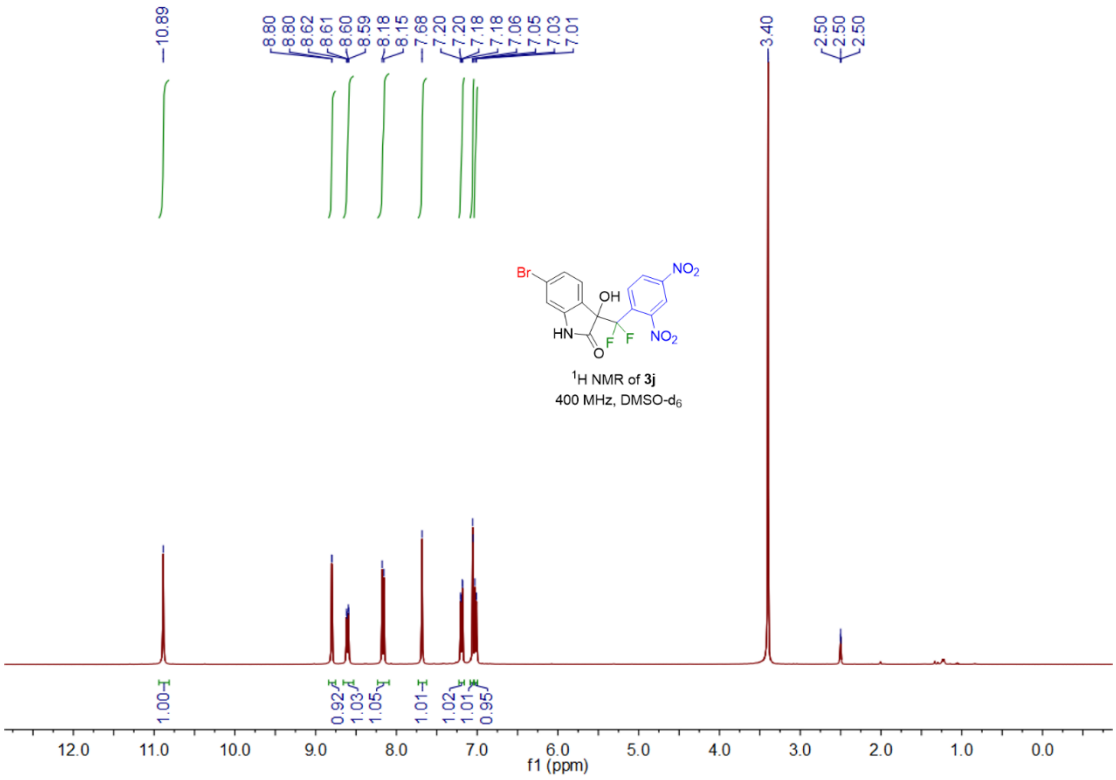

10.92
8.81
8.62
8.60
8.18
8.16
7.69
7.07
7.06
6.92
3.41
2.50
Cl
OH
HN
O
F
F
NO2
NO2
1H NMR of 3i
400 MHz, DMSO-d6
1.00
0.98
1.09
1.06
1.00
2.16
1.05
f1 (ppm)

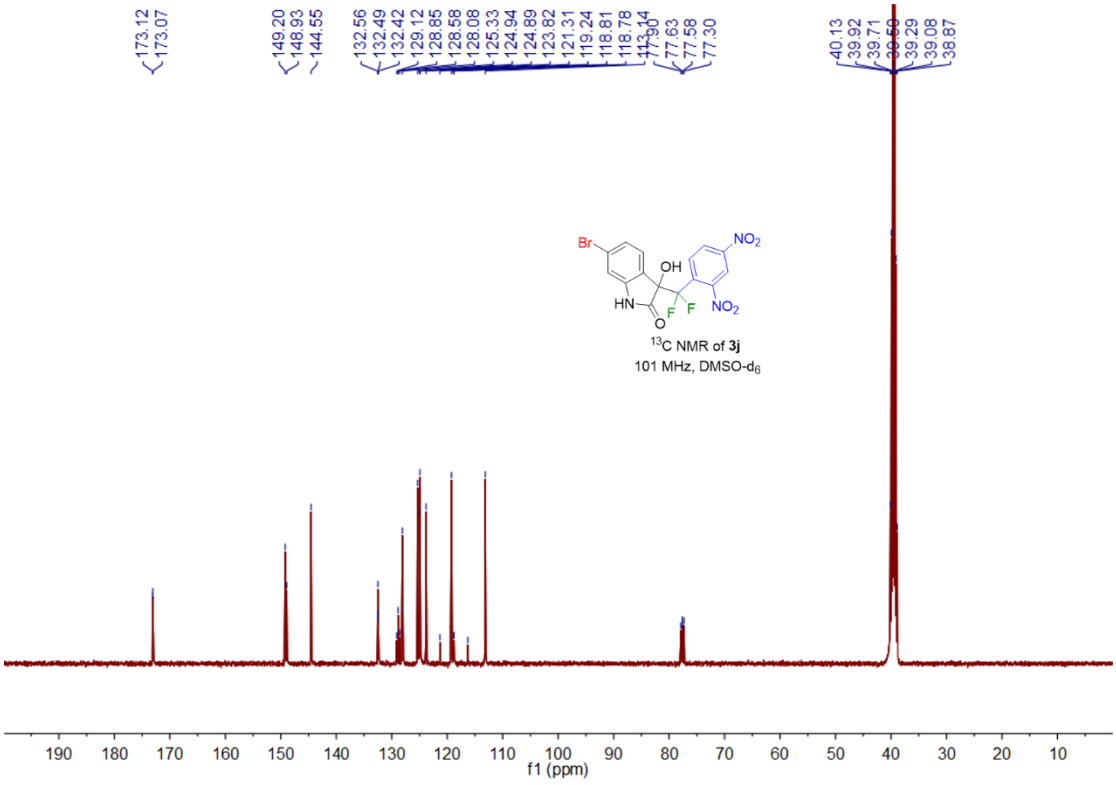


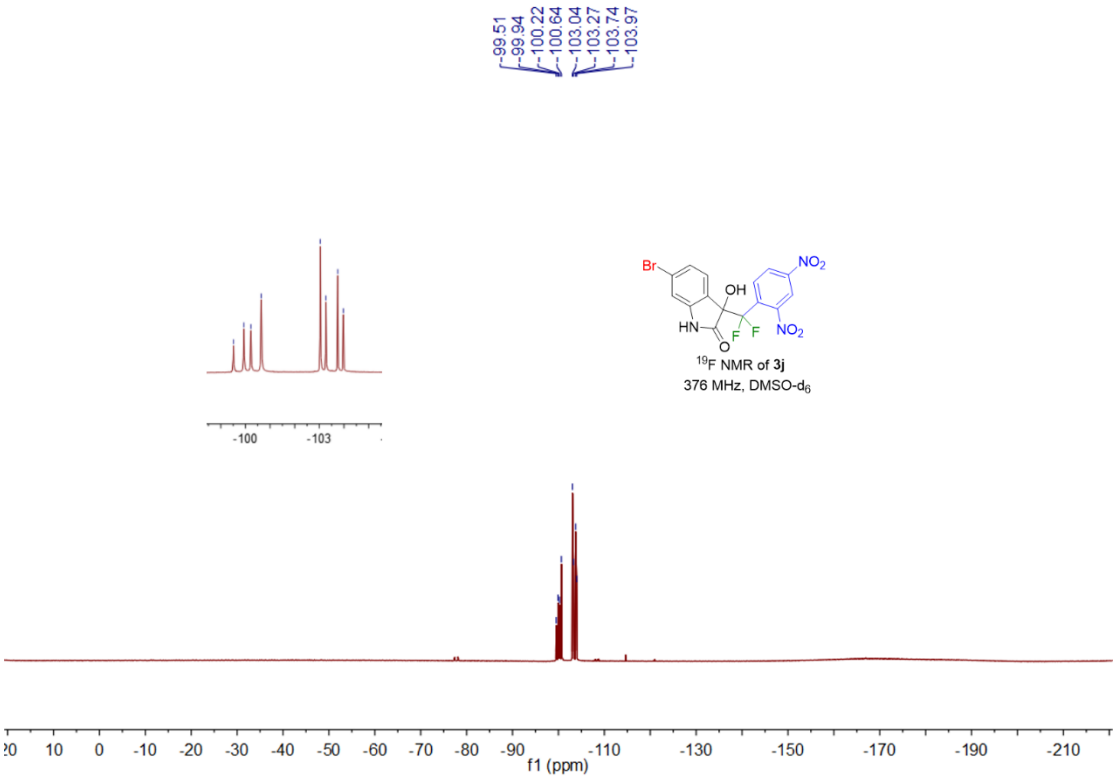
^{13}C NMR of **3i**
101 MHz, DMSO-d_6



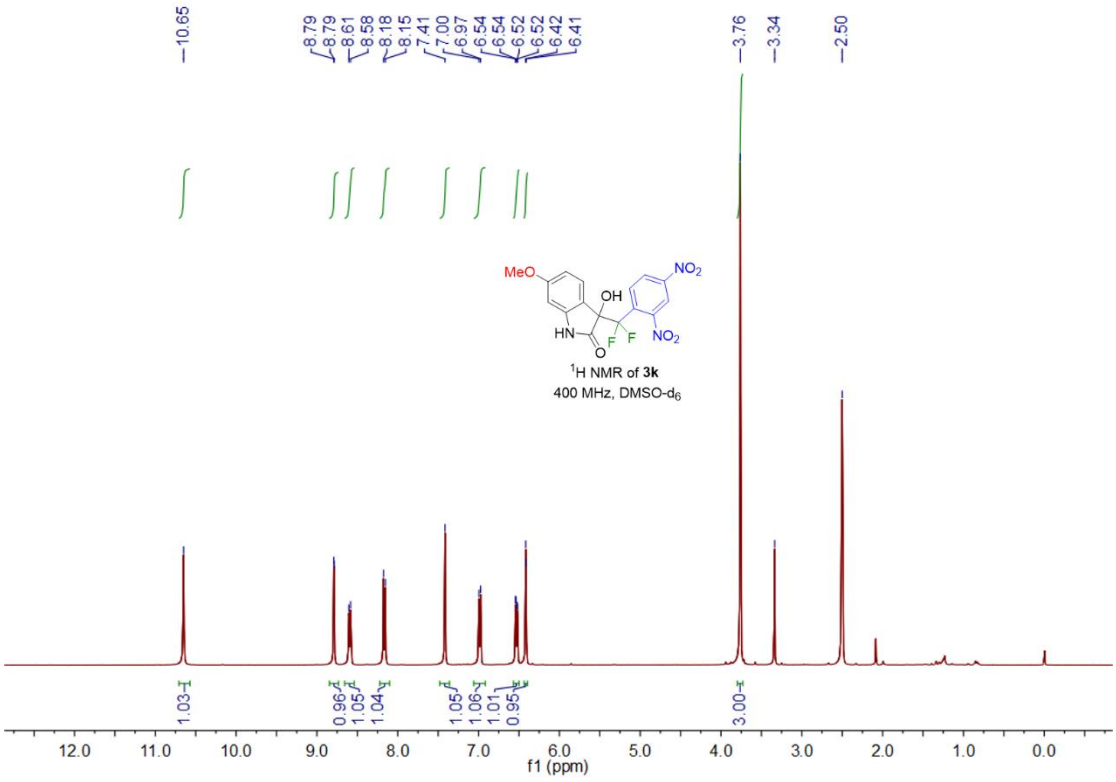
^{19}F NMR of **3i**
376 MHz, DMSO-d_6


10.89
8.80
8.80
8.62
8.61
8.60
8.59
8.18
8.15
7.68
7.20
7.20
7.18
7.18
7.06
7.05
7.03
7.01
3.40
2.50
2.50
2.50
Br
OH
HN
O
F
F
NO2
NO2
1H NMR of 3j
400 MHz, DMSO-d6
1.00
0.92
1.03
1.05
1.01
1.02
1.01
0.95
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

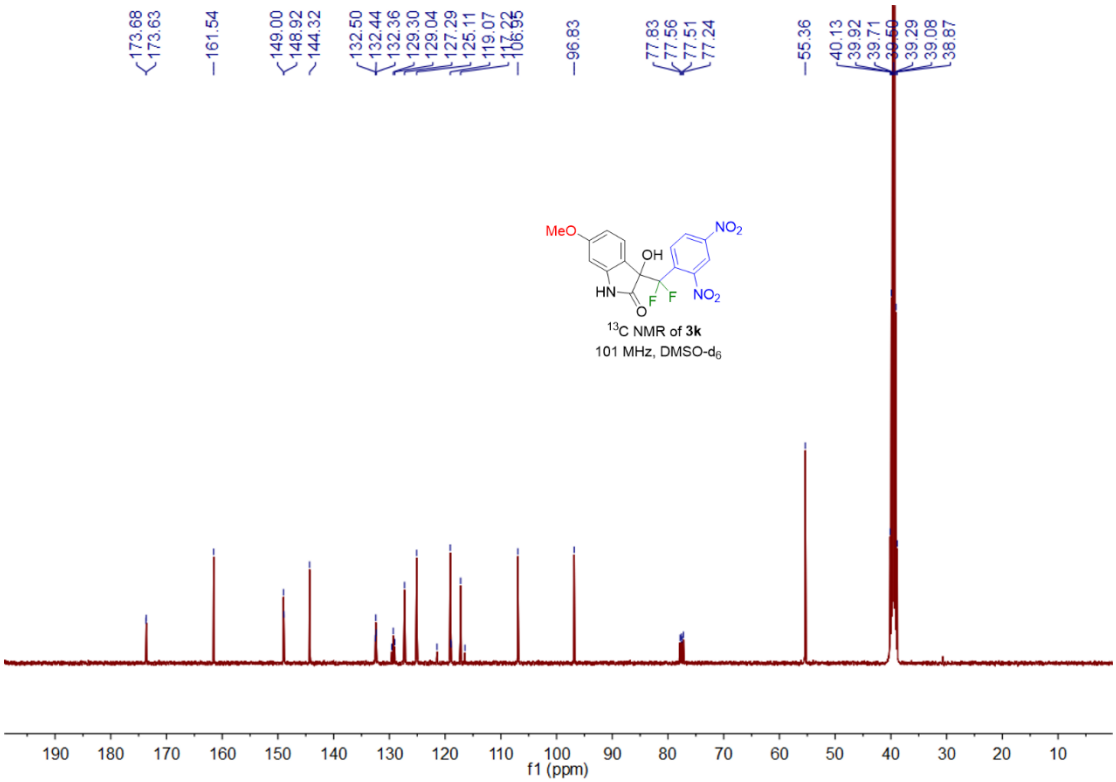

173.12
173.07
149.20
148.93
144.55
132.56
132.49
132.42
129.12
128.85
128.58
128.08
125.33
124.94
124.89
123.82
121.31
119.24
118.81
118.78
113.14
77.90
77.63
77.58
77.30
40.13
39.92
39.71
39.50
39.29
39.08
38.87
Br
OH
HN
O
F
F
NO2
NO2
13C NMR of 3j
101 MHz, DMSO-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



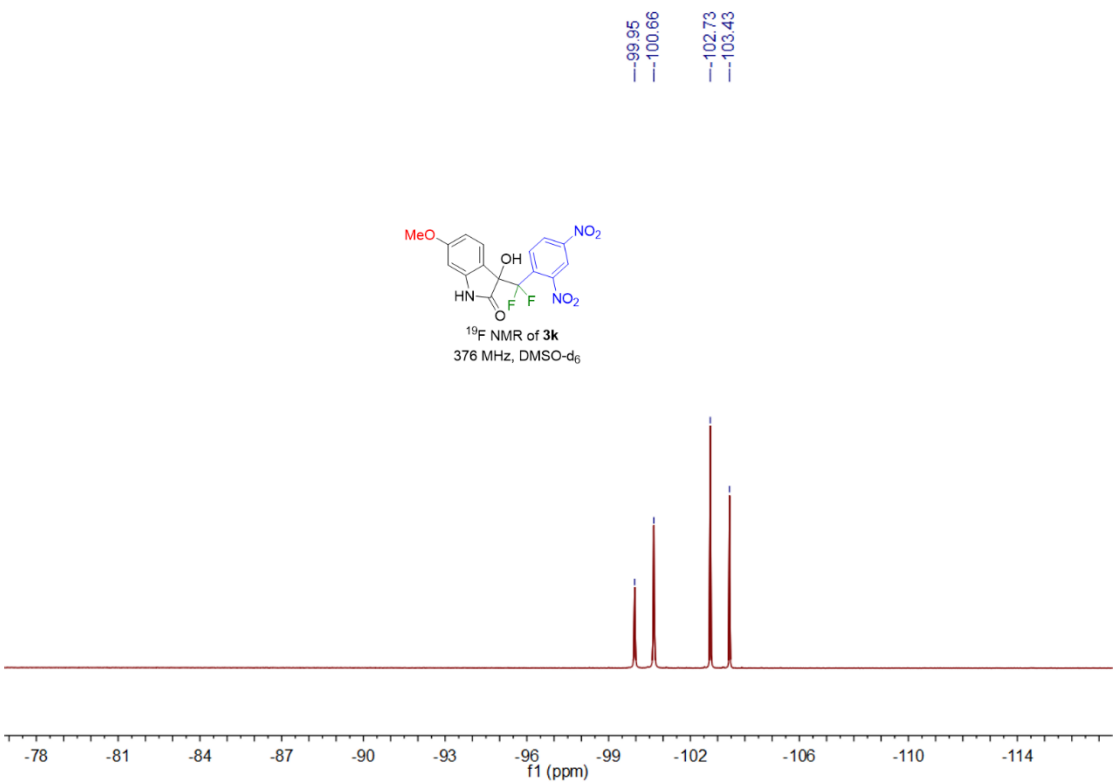
^{19}F NMR of **3j**
376 MHz, DMSO-d_6



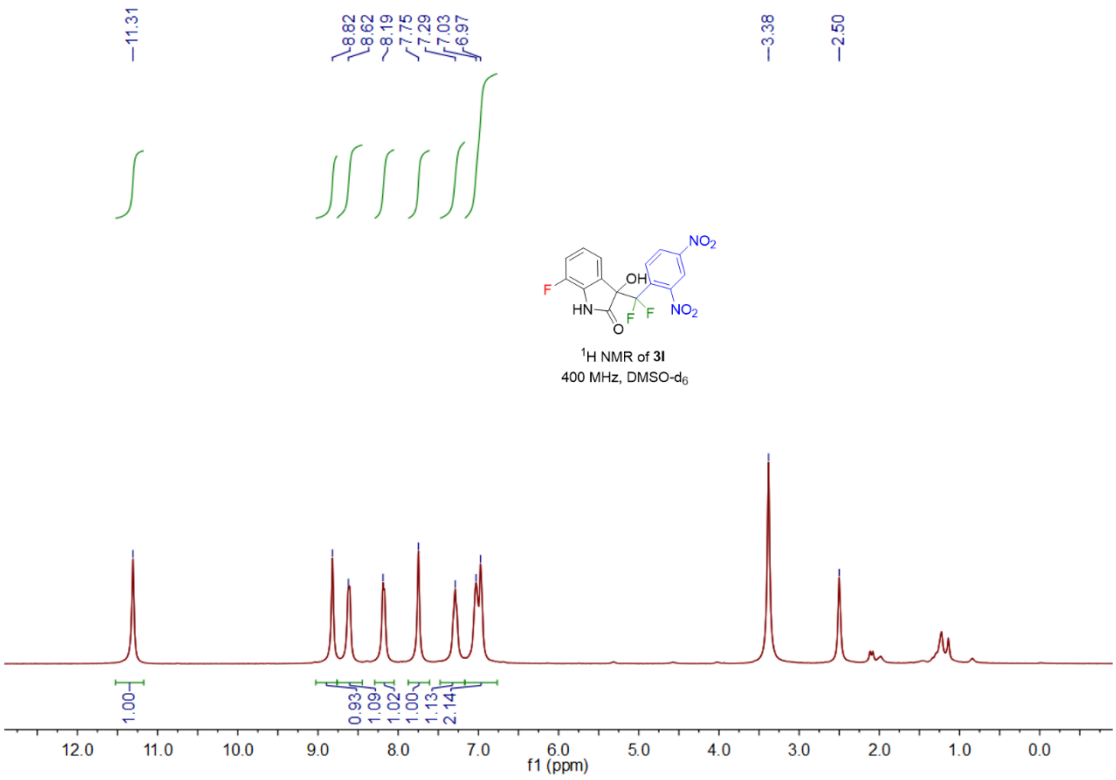
^{1}H NMR of **3k**
400 MHz, DMSO-d_6

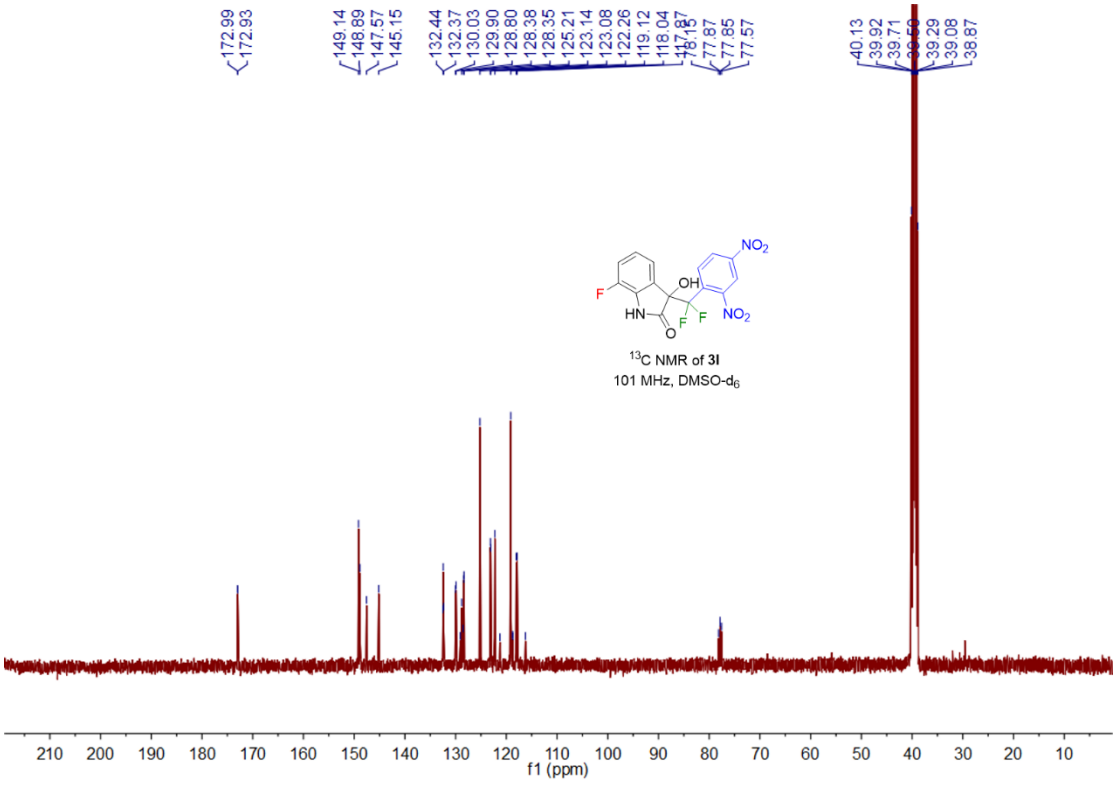


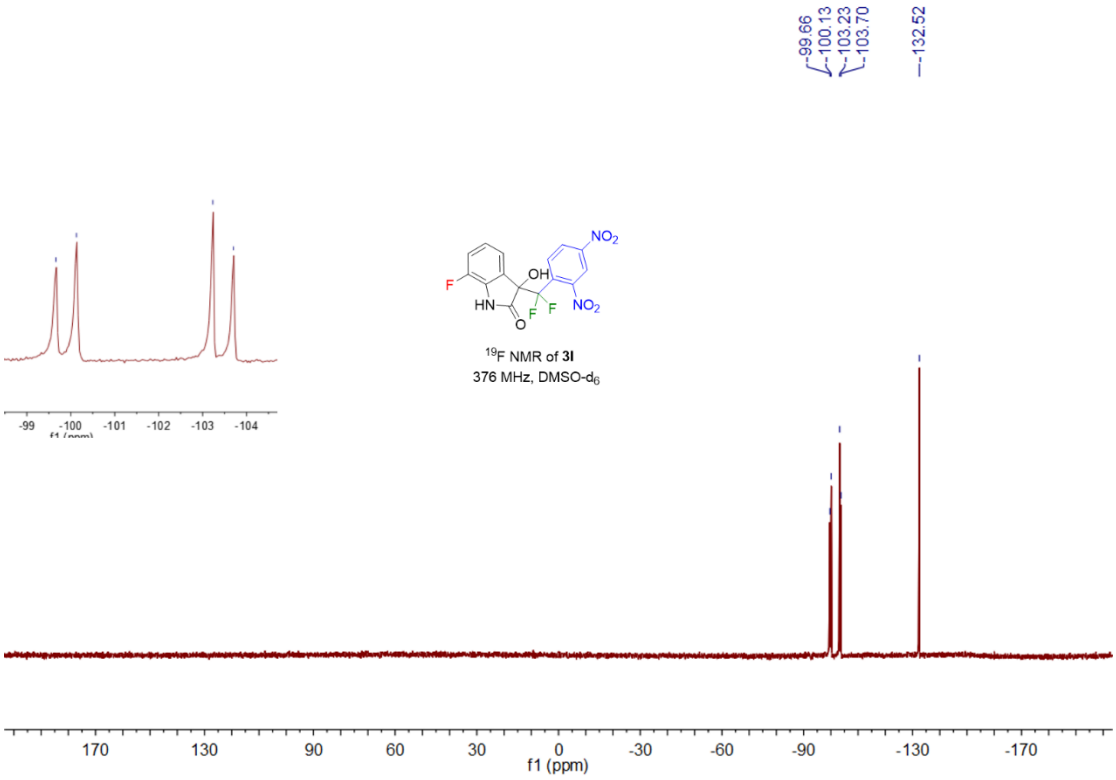
^{13}C NMR of **3k**
101 MHz, DMSO-d_6

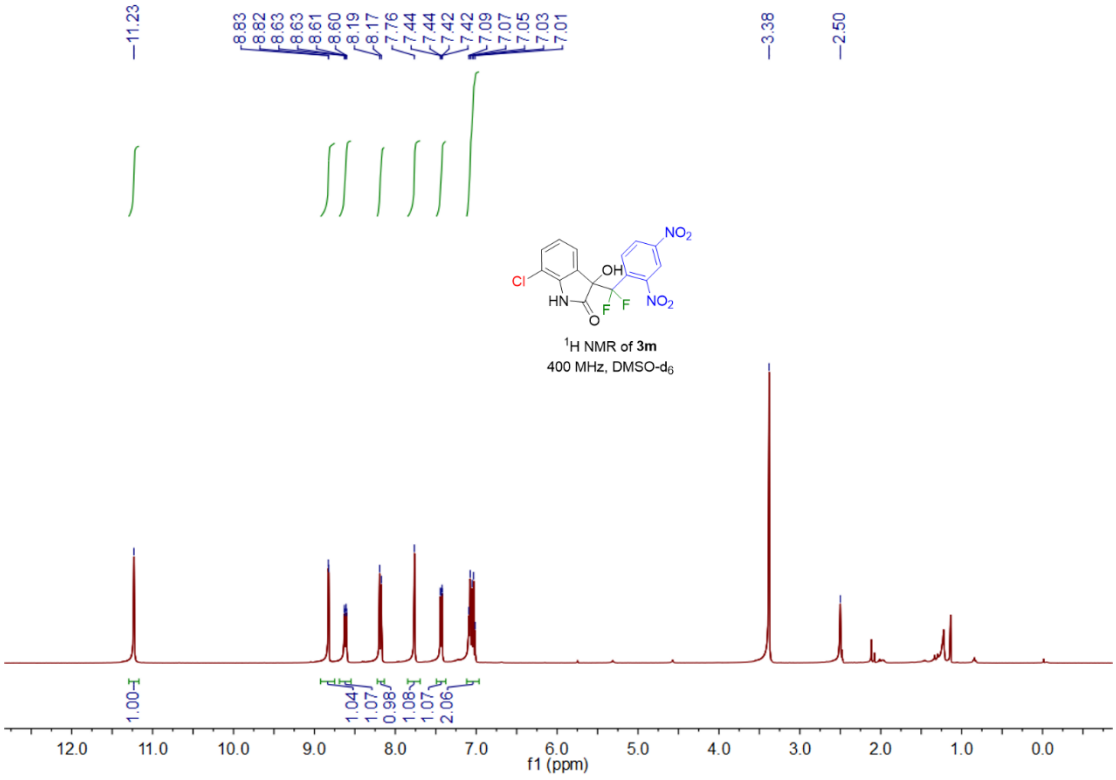


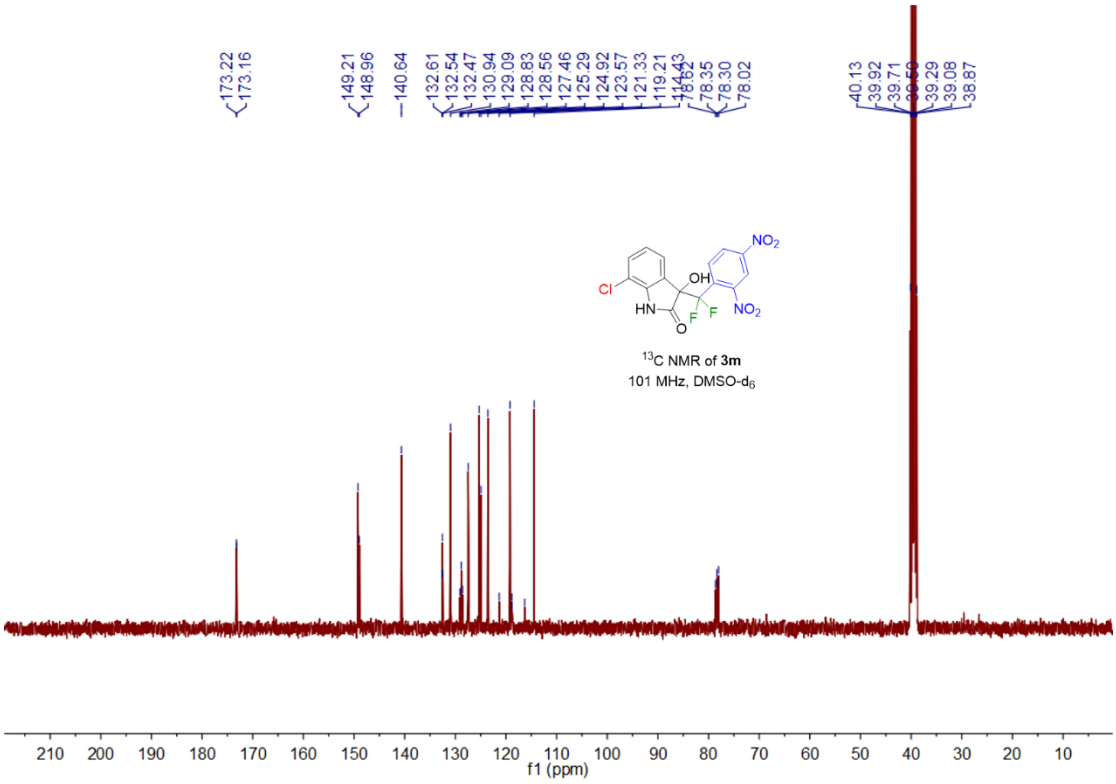
^{19}F NMR of **3k**
376 MHz, DMSO-d_6


11.31
8.82
8.62
8.19
7.75
7.29
7.03
6.97
3.38
2.50
NO2
OH
F
HN
O
F
F
NO2
1H NMR of 3l
400 MHz, DMSO-d6
1.00
0.93
1.09
1.02
1.00
1.13
2.14
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

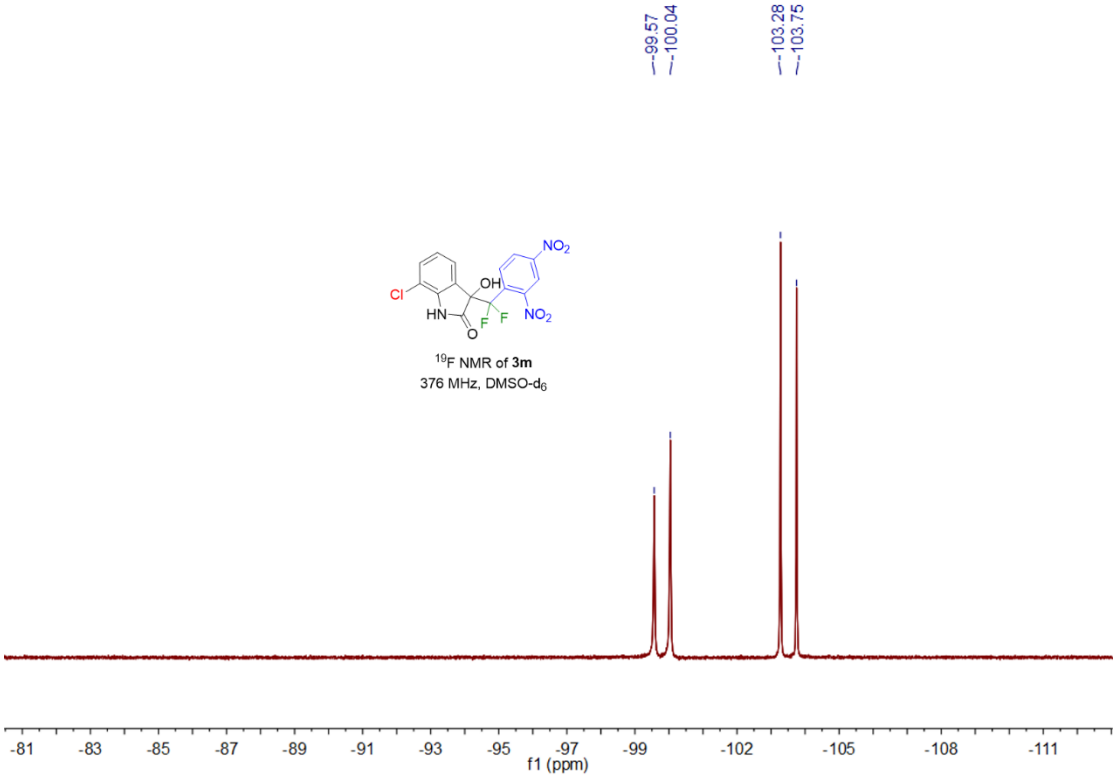

172.99
172.93
149.14
148.89
147.57
145.15
132.44
132.37
130.03
129.90
128.80
128.38
128.35
125.21
123.14
123.08
122.26
119.12
118.04
117.87
78.15
77.87
77.85
77.57
40.13
39.92
39.71
39.50
39.29
39.08
38.87
NO2
OH
F
HN
O
F
F
NO2
13C NMR of 3l
101 MHz, DMSO-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-99.66
-100.13
-103.23
-103.70
-132.52
F
OH
HN
O
F
F
NO2
NO2
19F NMR of 3l
376 MHz, DMSO-d6
-99
-100
-101
-102
-103
-104
170
130
90
60
30
0
-30
-60
-90
-130
-170
f1 (ppm)

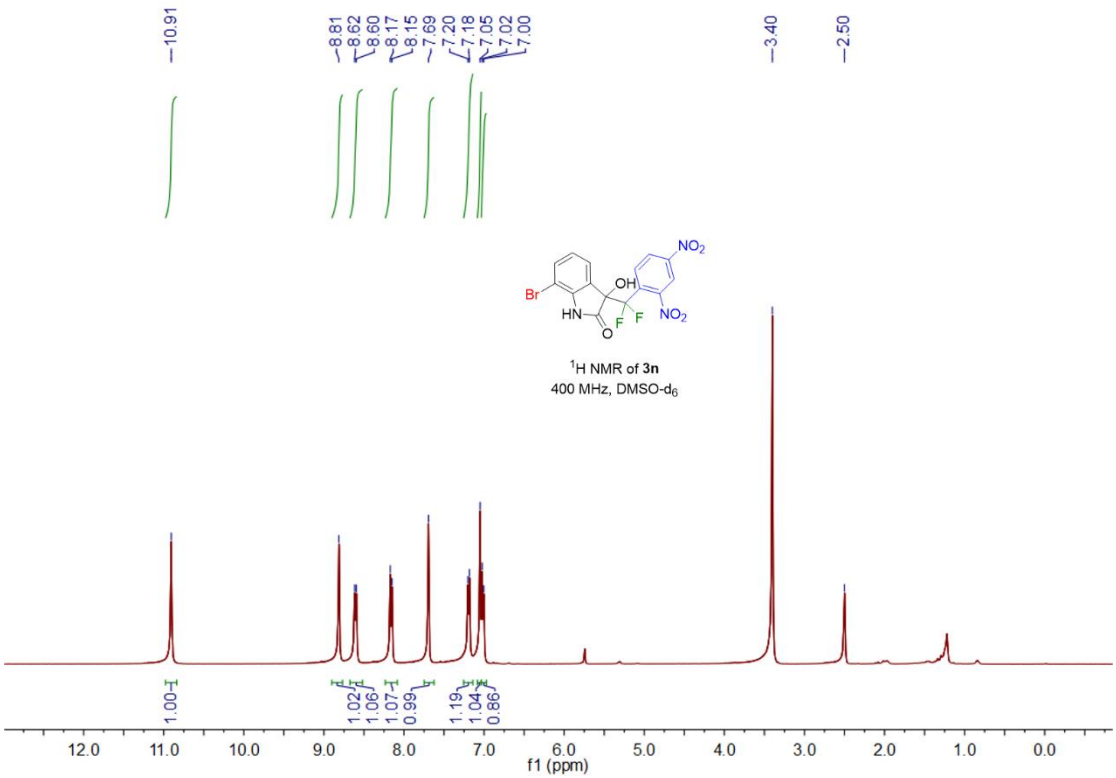

11.23
8.83
8.82
8.63
8.63
8.61
8.60
8.19
8.17
7.76
7.44
7.44
7.42
7.42
7.09
7.07
7.05
7.03
7.01
3.38
2.50
Cl
OH
HN
O
F
F
NO2
NO2
1H NMR of 3m
400 MHz, DMSO-d6
1.00
1.04
1.07
0.98
1.08
1.07
2.06
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



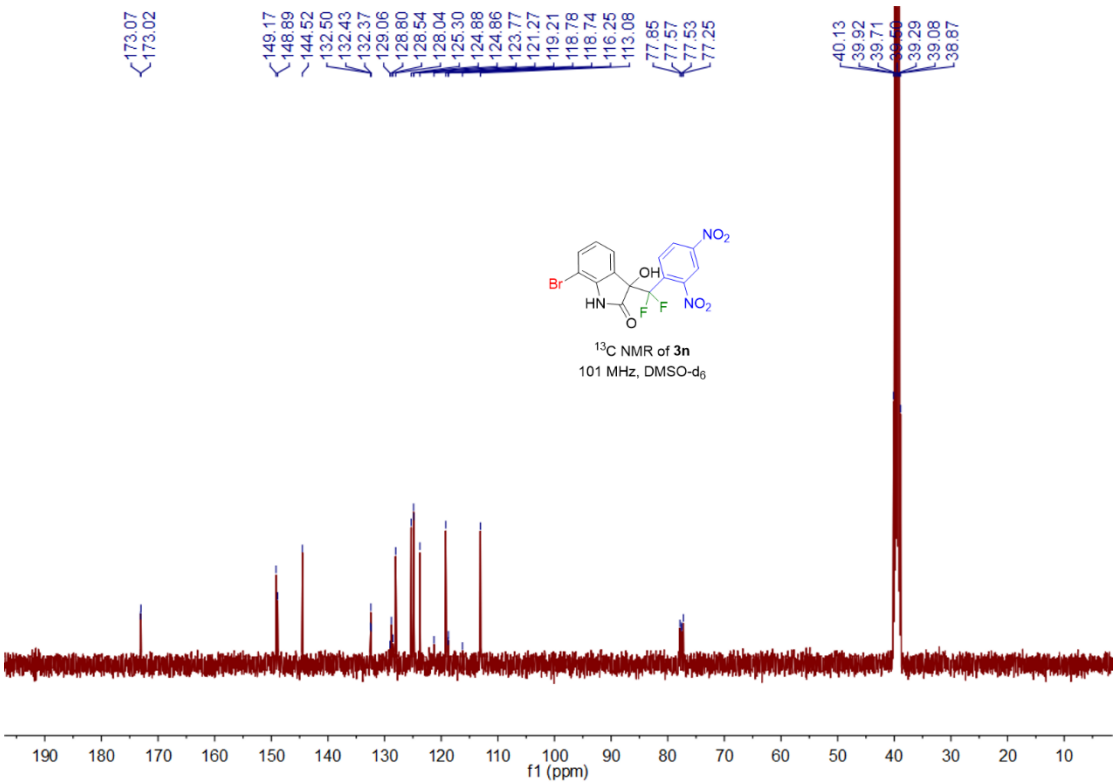
^{13}C NMR of **3m**
101 MHz, DMSO-d_6



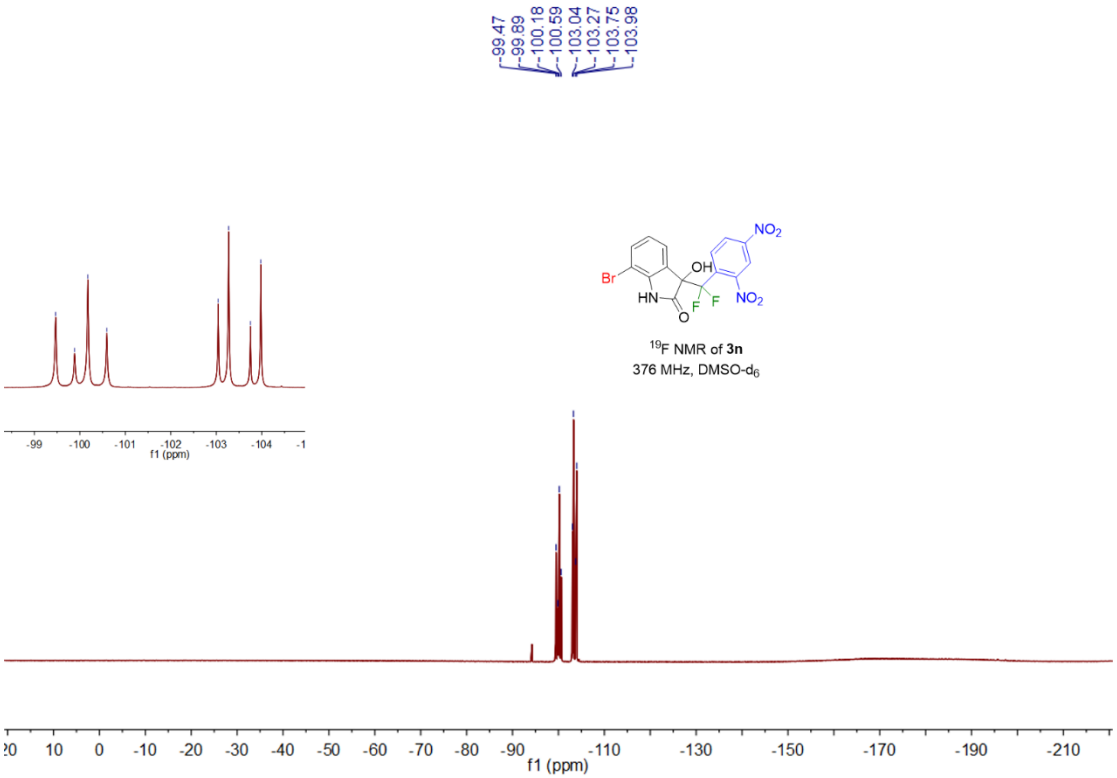
^{19}F NMR of **3m**
376 MHz, DMSO-d_6



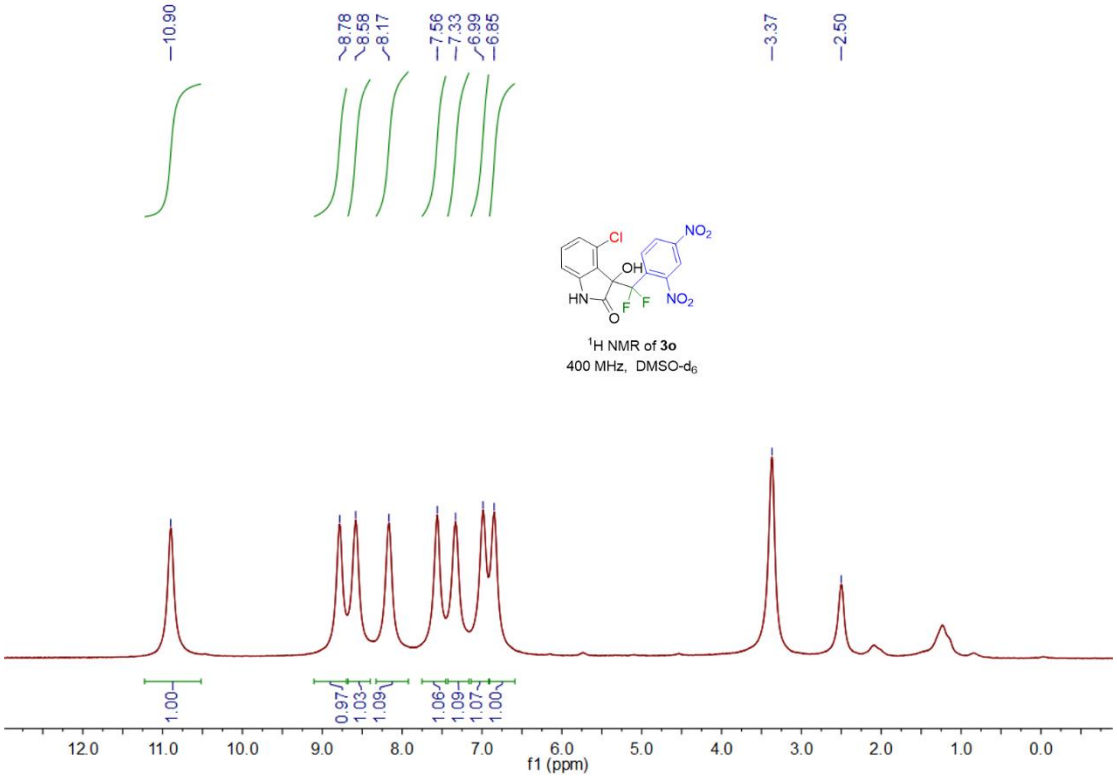
^{1}H NMR of **3n**
400 MHz, DMSO-d_6



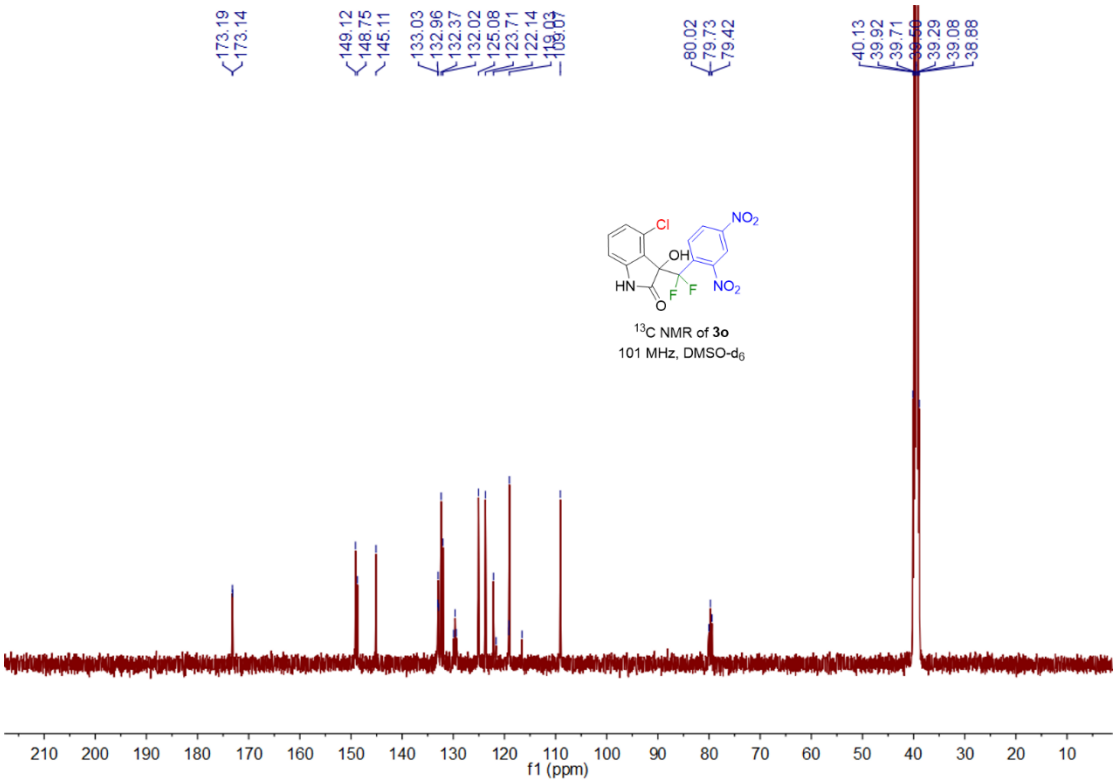
^{13}C NMR of **3n**
101 MHz, DMSO-d_6



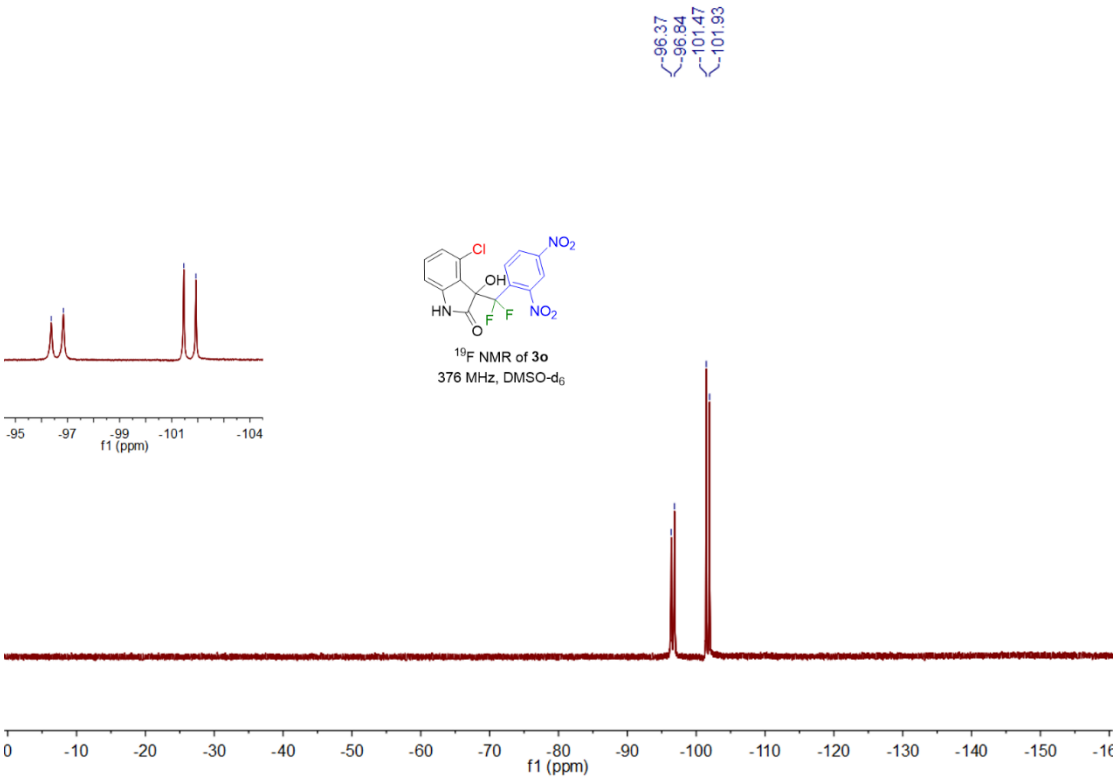
^{19}F NMR of **3n**
376 MHz, DMSO-d_6



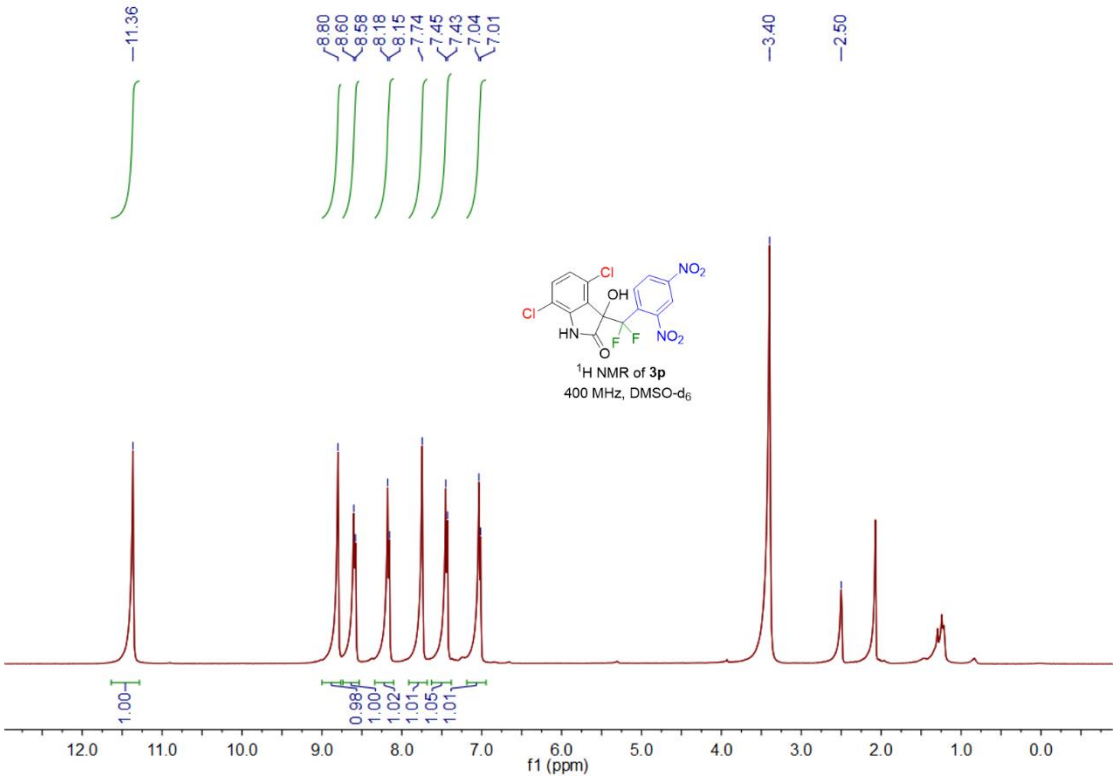
^{1}H NMR of **3o**
400 MHz, DMSO-d_6

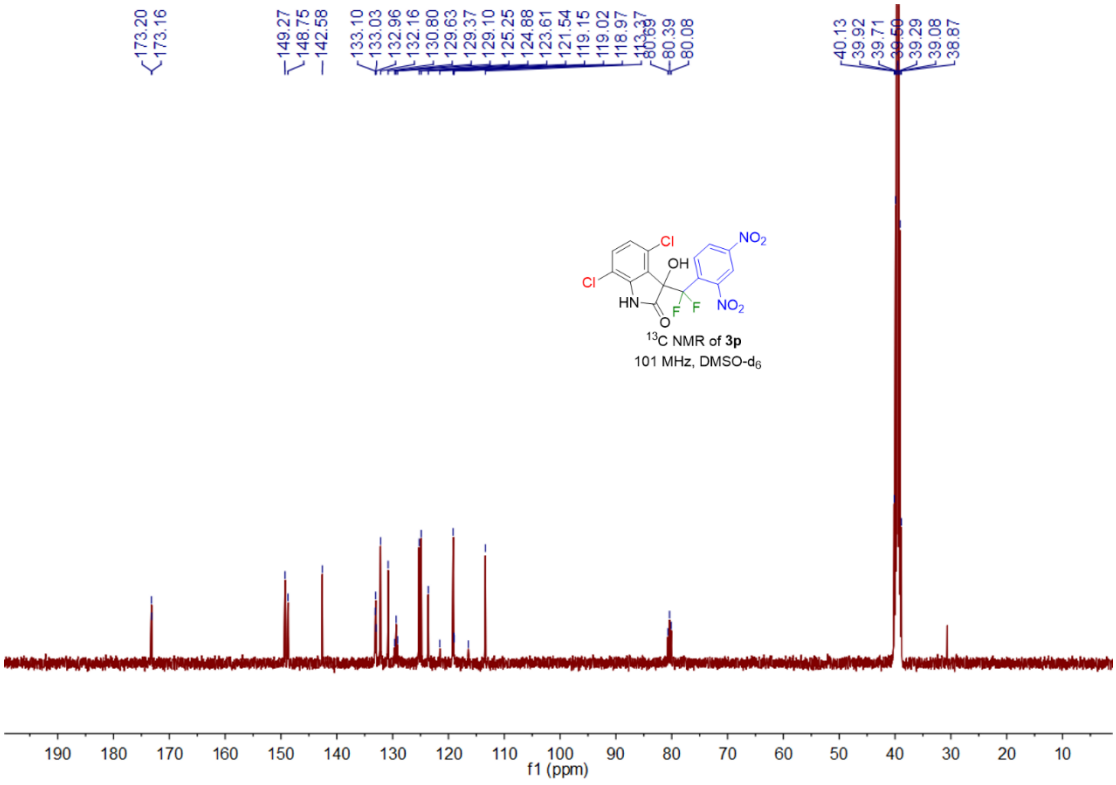


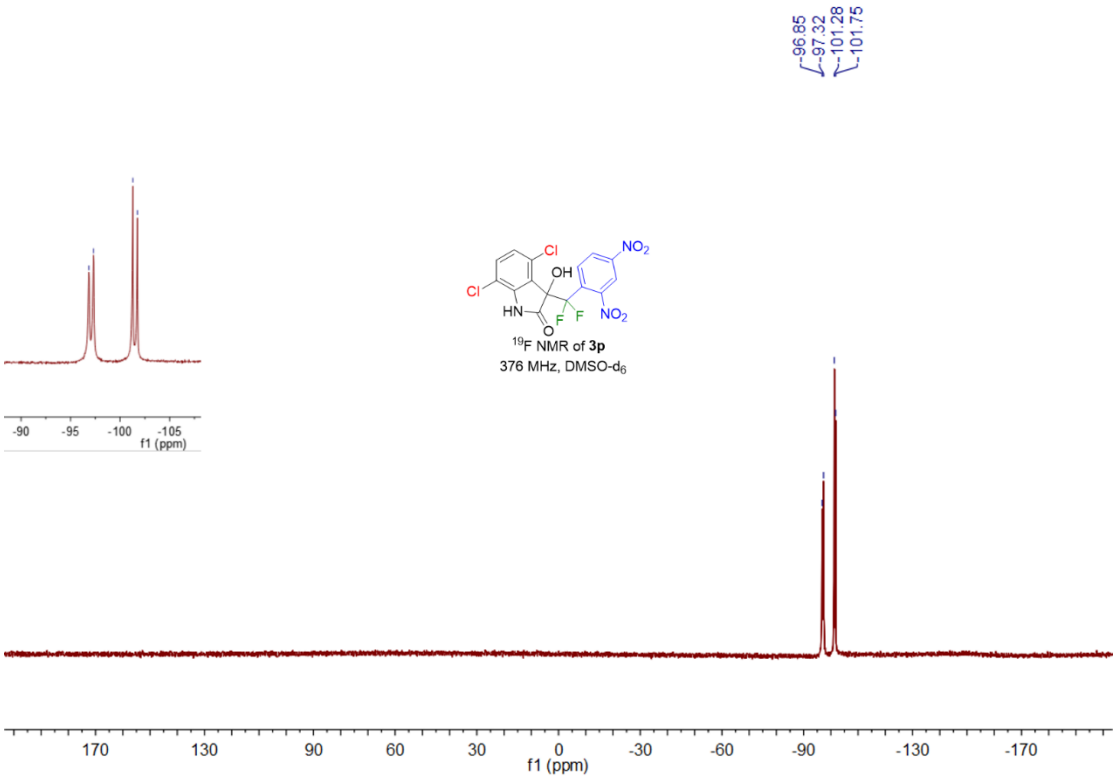
^{13}C NMR of **3o**
101 MHz, DMSO-d_6

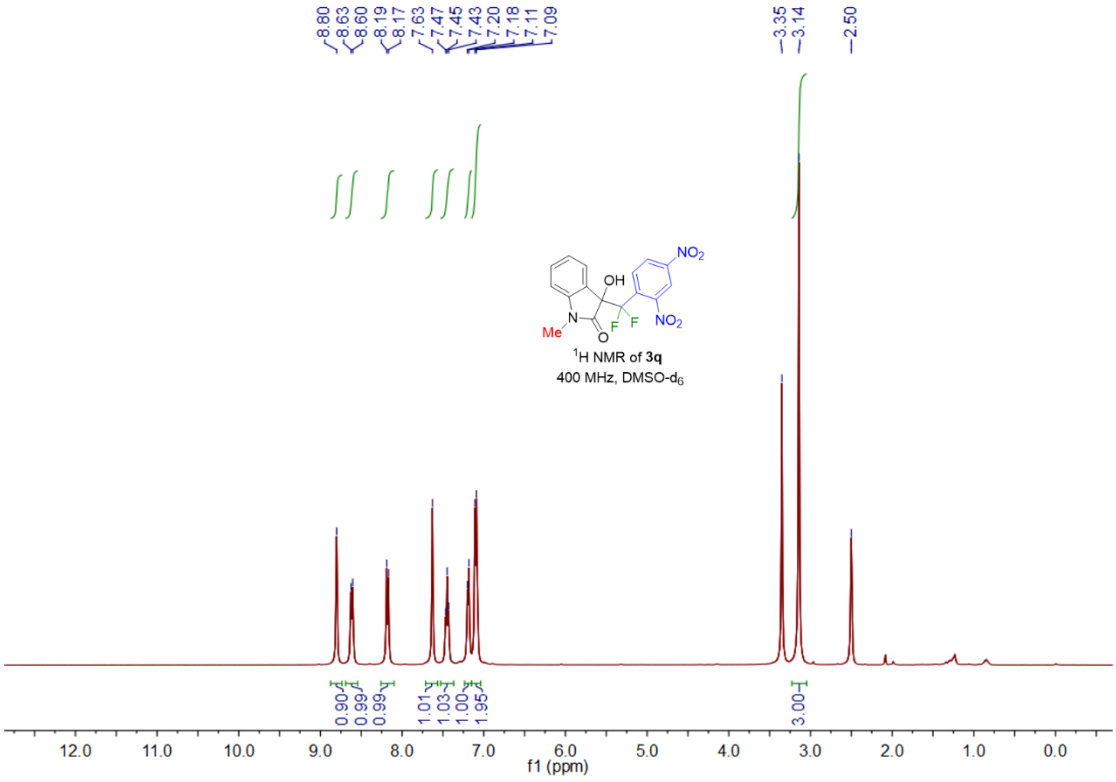


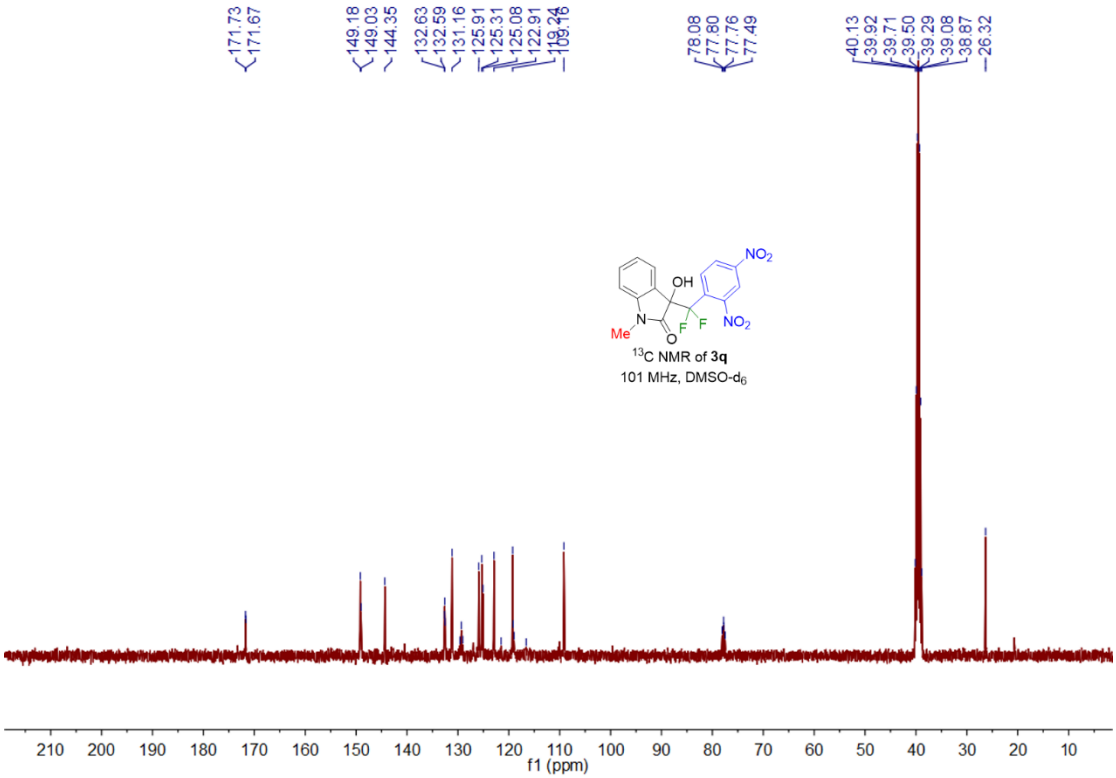
^{19}F NMR of **3o**
376 MHz, DMSO-d_6

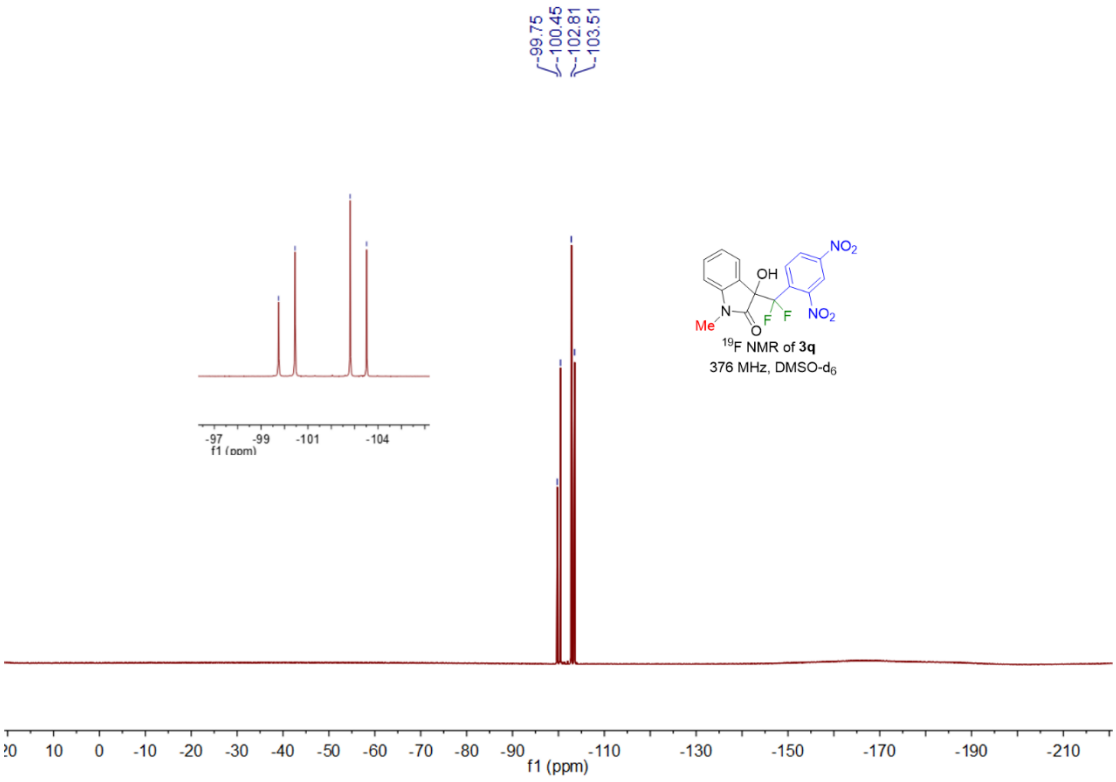

11.36
8.80
8.60
8.58
8.18
8.15
7.74
7.45
7.43
7.04
7.01
3.40
2.50
Cl
NO2
OH
Cl
HN
F
F
NO2
O
1H NMR of 3p
400 MHz, DMSO-d6
1.00
0.98
1.00
1.02
1.01
1.05
1.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

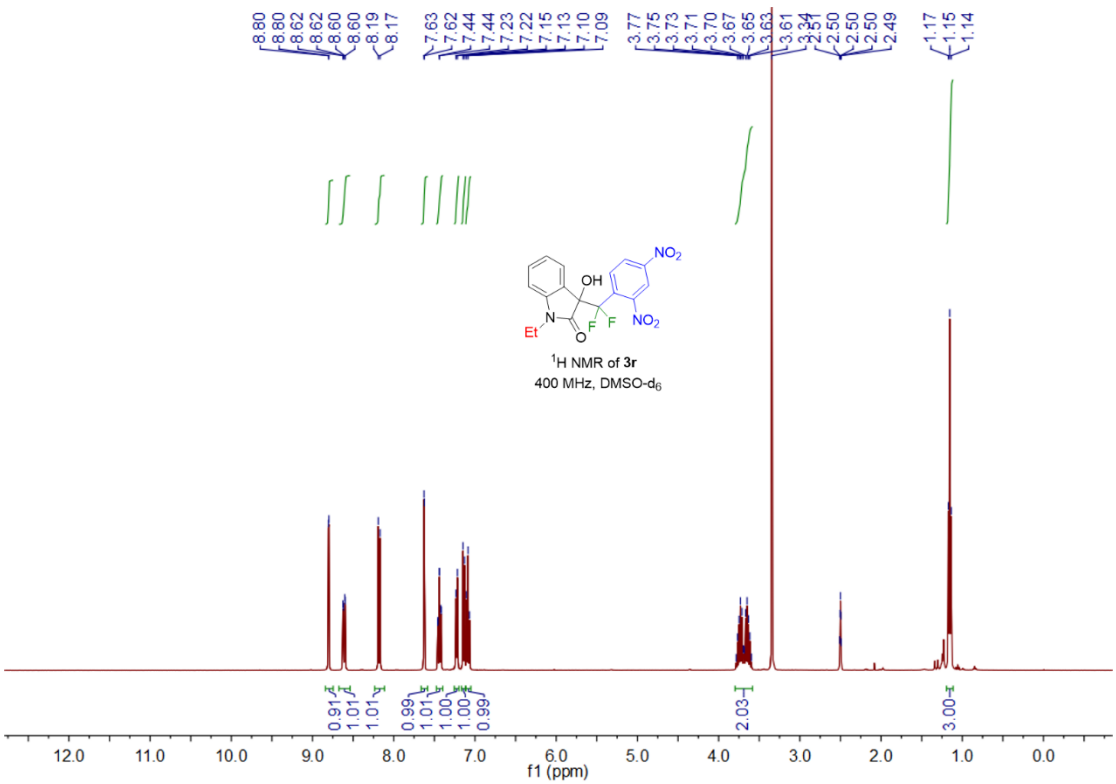

173.20
173.16
149.27
148.75
142.58
133.10
133.03
132.96
132.16
130.80
129.63
129.37
129.10
125.25
124.88
123.61
121.54
119.15
119.02
118.97
113.37
80.69
80.39
80.08
40.13
39.92
39.71
39.50
39.29
39.08
38.87
Cl
NO2
OH
Cl
HN
F
F
NO2
O
13C NMR of 3p
101 MHz, DMSO-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-96.85
-97.32
-101.28
-101.75
Cl
OH
NO2
Cl
HN
F
F
NO2
O
19F NMR of 3p
376 MHz, DMSO-d6
-90
-95
-100
-105
f1 (ppm)
170
130
90
60
30
0
-30
-60
-90
-130
-170
f1 (ppm)

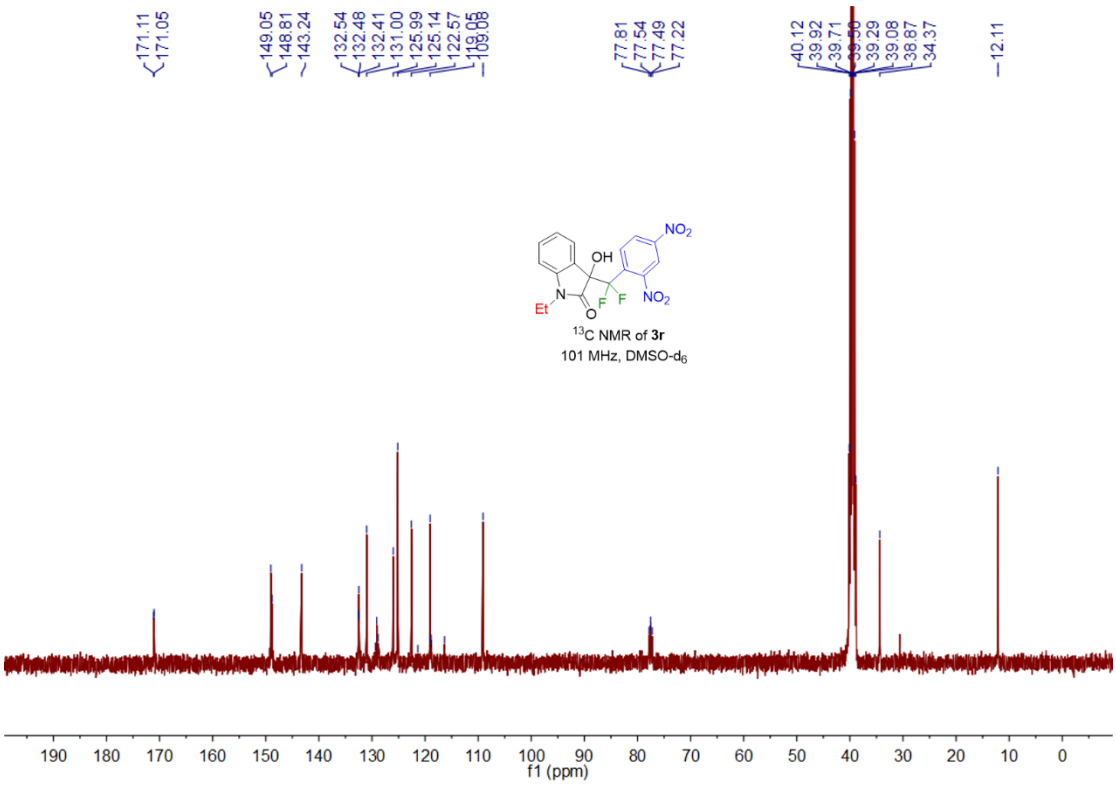

8.80
8.63
8.60
8.19
8.17
7.63
7.47
7.45
7.43
7.20
7.18
7.11
7.09
3.35
3.14
2.50
NO2
OH
N
Me
F
F
NO2
O
1H NMR of 3q
400 MHz, DMSO-d6
0.90
0.99
0.99
1.01
1.03
1.00
1.95
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.73
171.67
149.18
149.03
144.35
132.63
132.59
131.16
125.91
125.31
125.08
122.91
78.08
77.80
77.76
77.49
40.13
39.92
39.71
39.50
39.29
39.08
38.87
26.32
OH
NO2
NO2
Me
N
O
F
F
13C NMR of 3q
101 MHz, DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

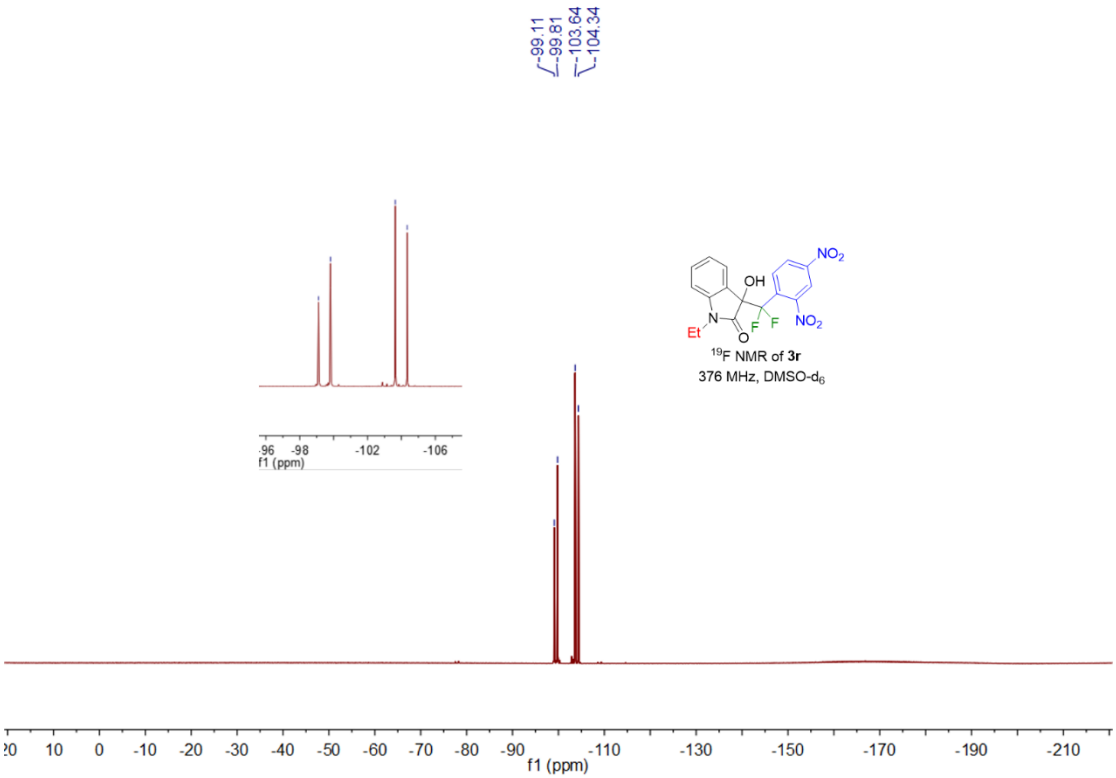

99.75
100.45
102.81
103.51
-97 -99 -101 -104
f1 (ppm)
OH
NO2
NO2
Me
N
O
F
F
19F NMR of 3q
376 MHz, DMSO-d6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

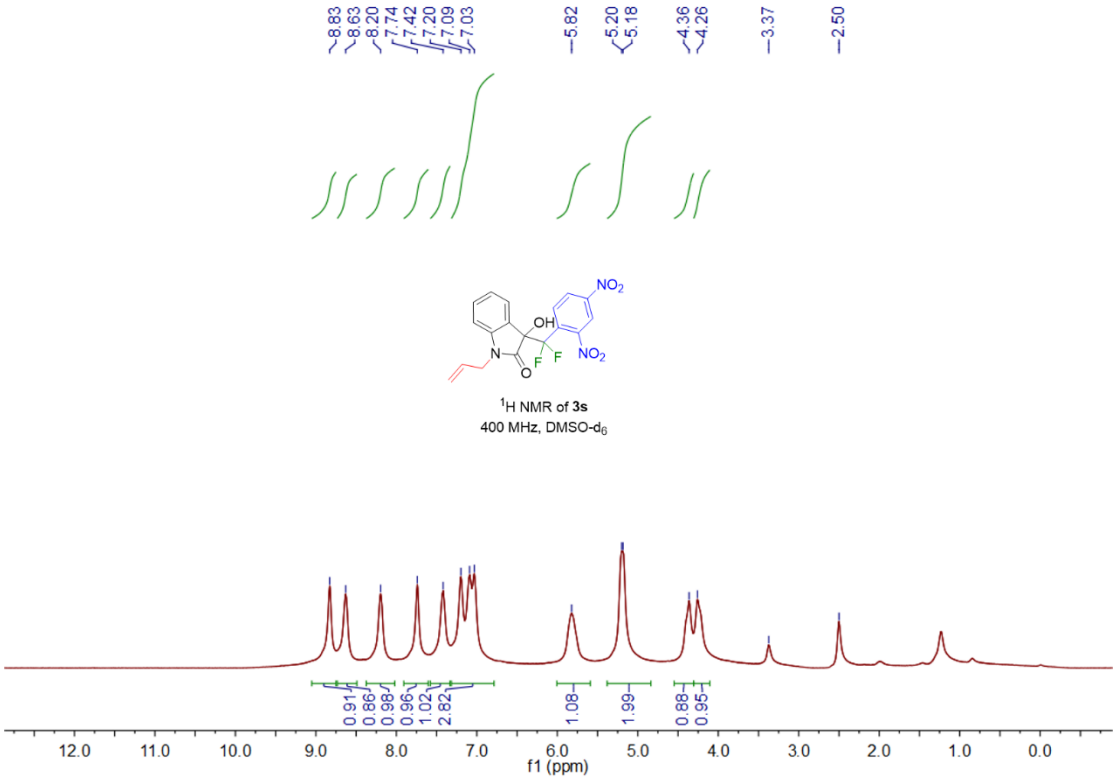


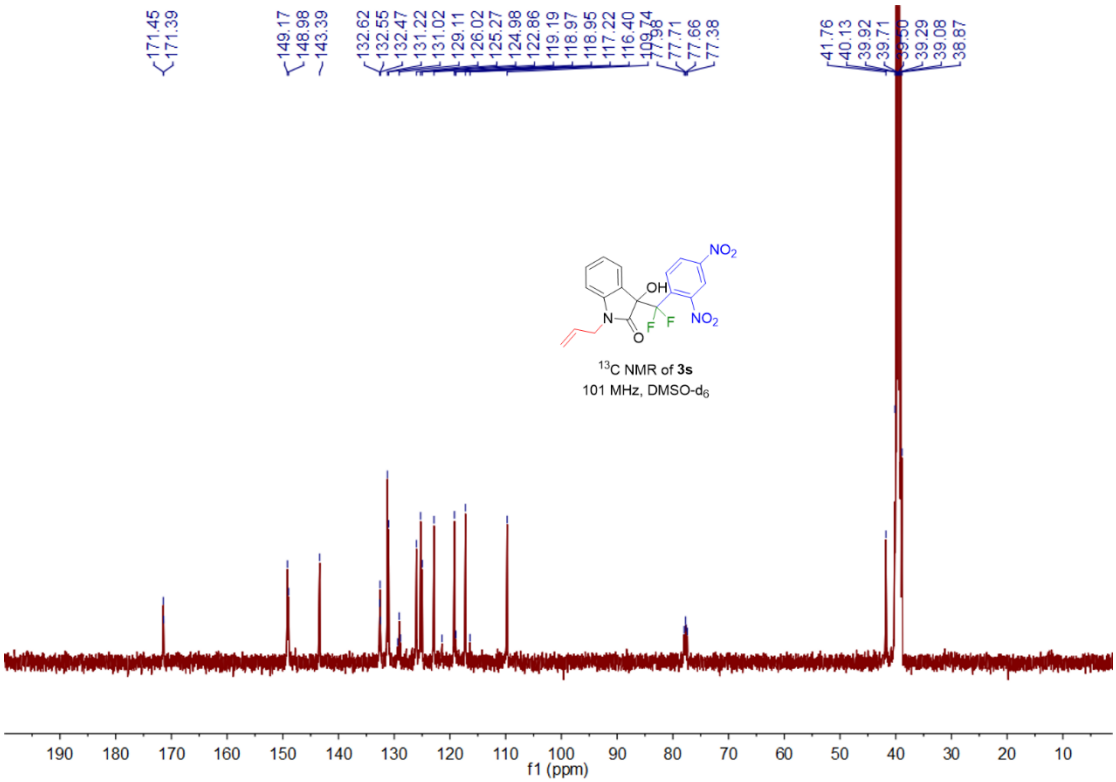
^{1}H NMR of **3r**
400 MHz, DMSO-d_6



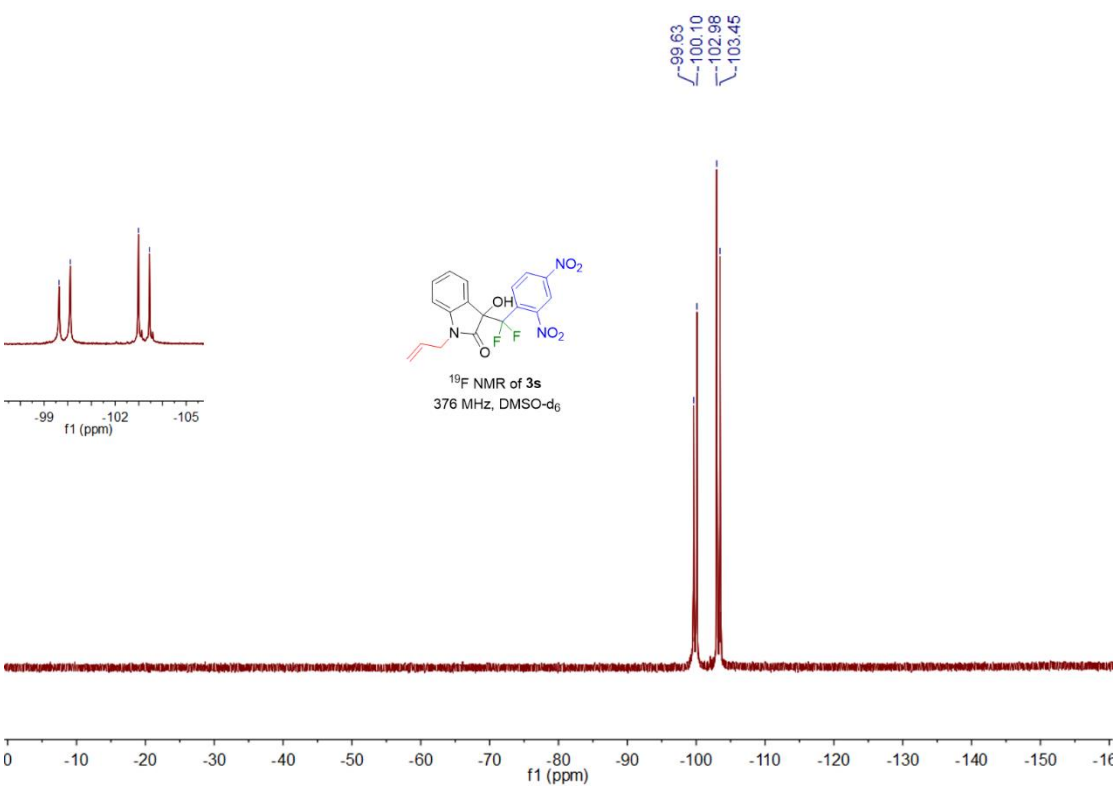
^{13}C NMR of **3r**
101 MHz, DMSO-d_6


-99.11
-99.81
-103.64
-104.34
OH
NO2
NO2
Et
N
O
F
F
19F NMR of 3r
376 MHz, DMSO-d6
f1 (ppm)

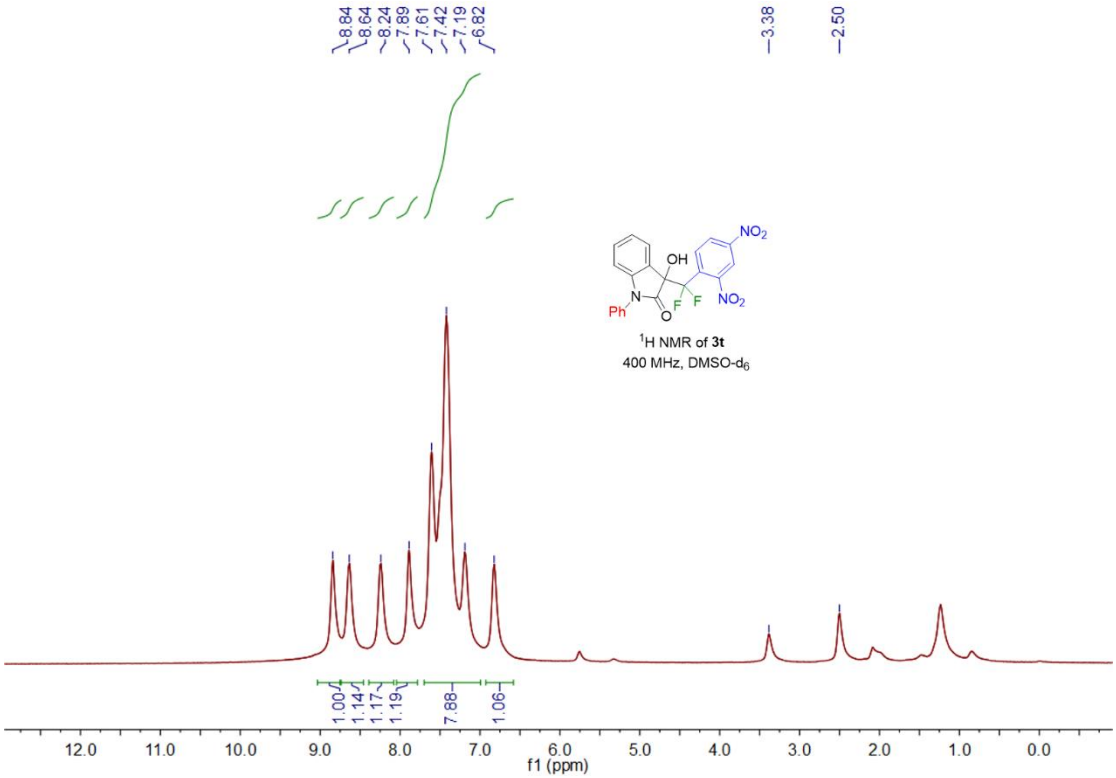

8.83
8.63
8.20
7.74
7.42
7.20
7.09
7.03
5.82
5.20
5.18
4.36
4.26
3.37
2.50
OH
NO2
NO2
N
O
F
F
1H NMR of 3s
400 MHz, DMSO-d6
0.91
0.86
0.98
0.96
1.02
2.82
1.08
1.99
0.88
0.95
f1 (ppm)

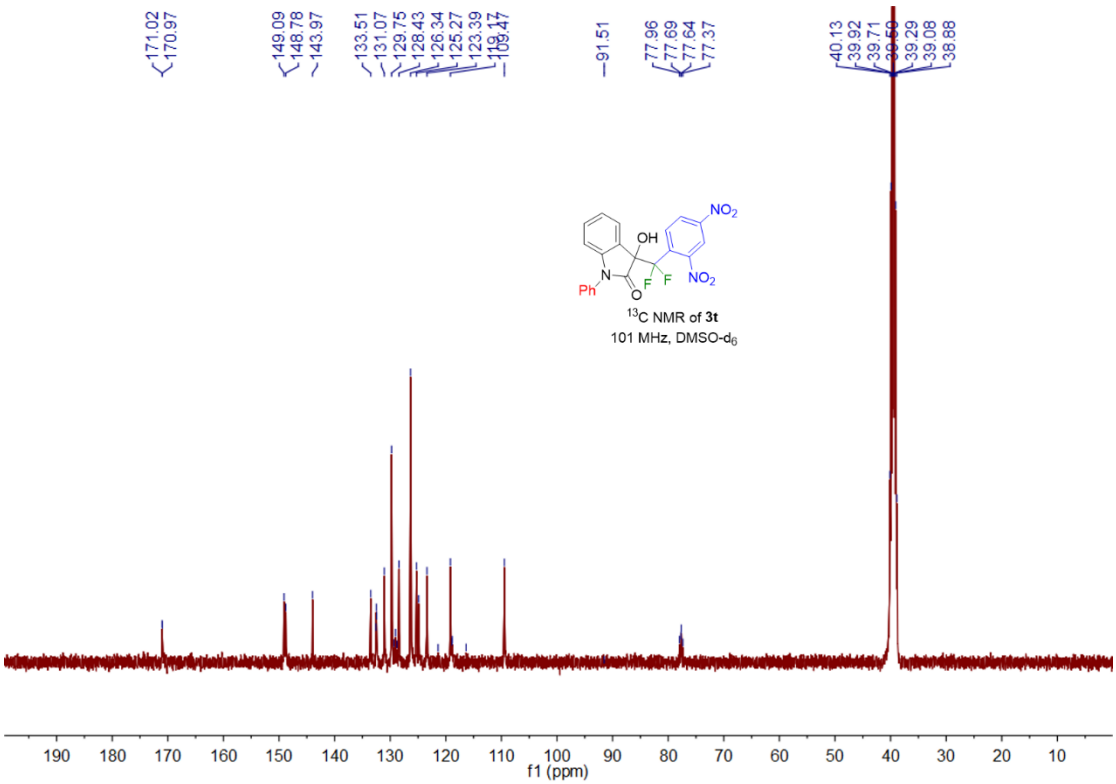


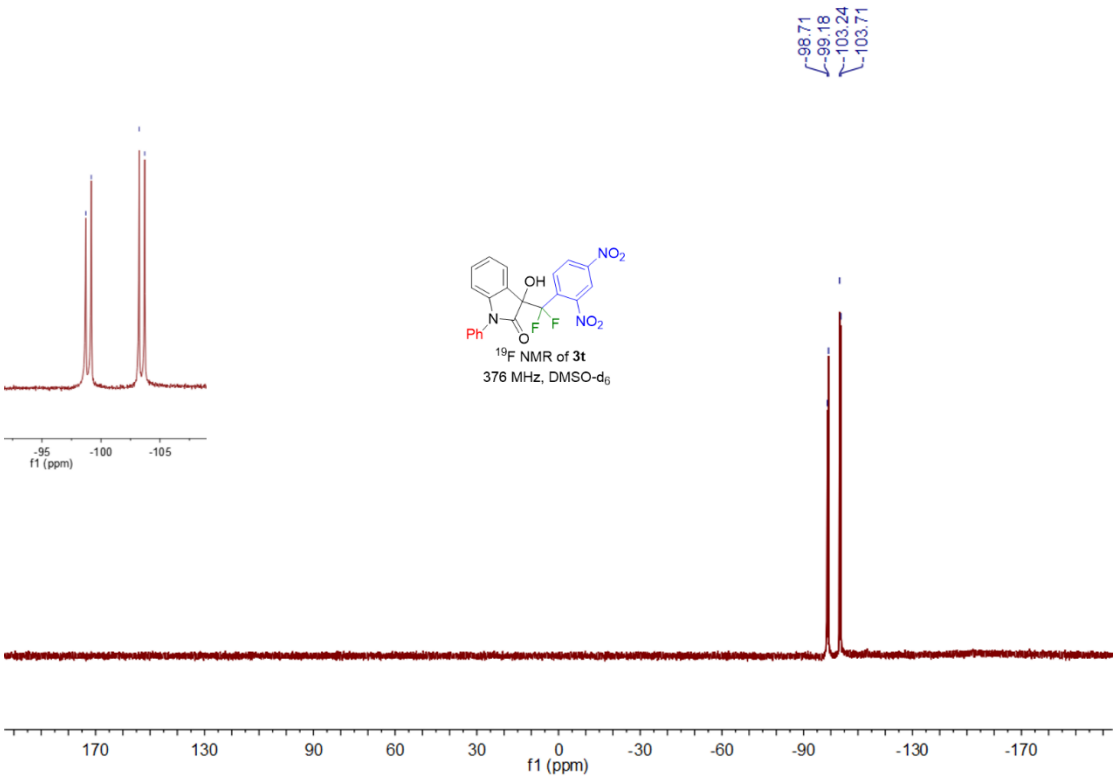
^{13}C NMR of **3s**
101 MHz, DMSO-d_6

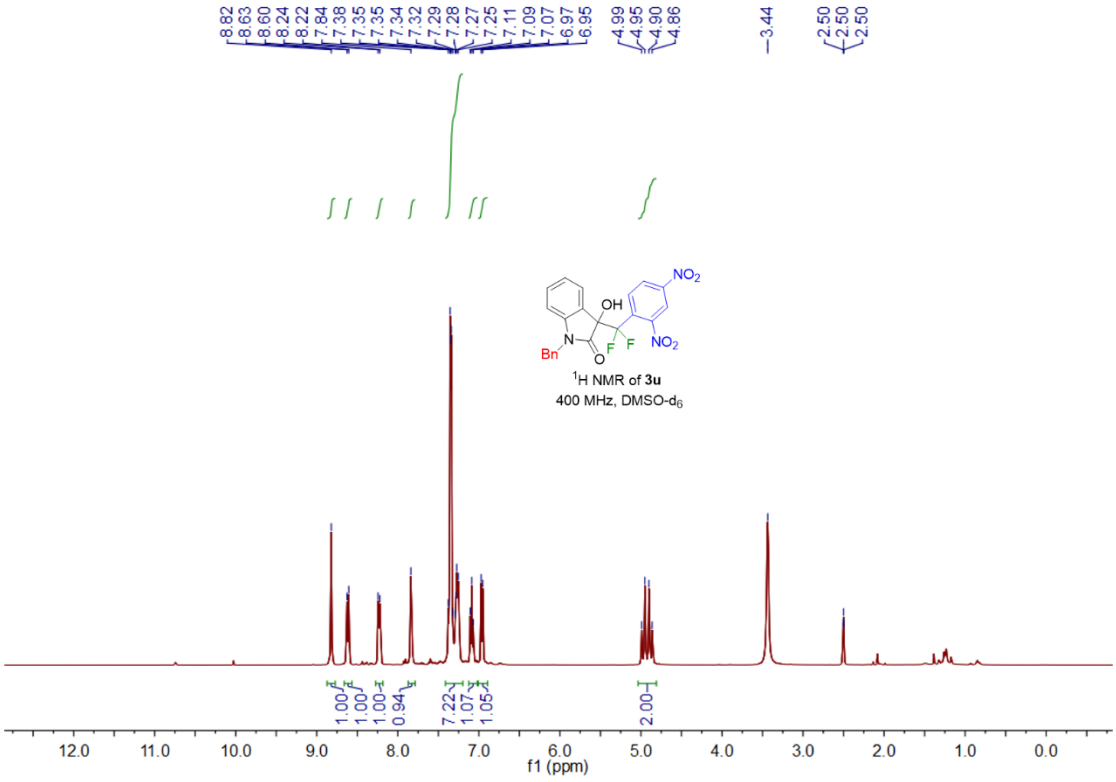


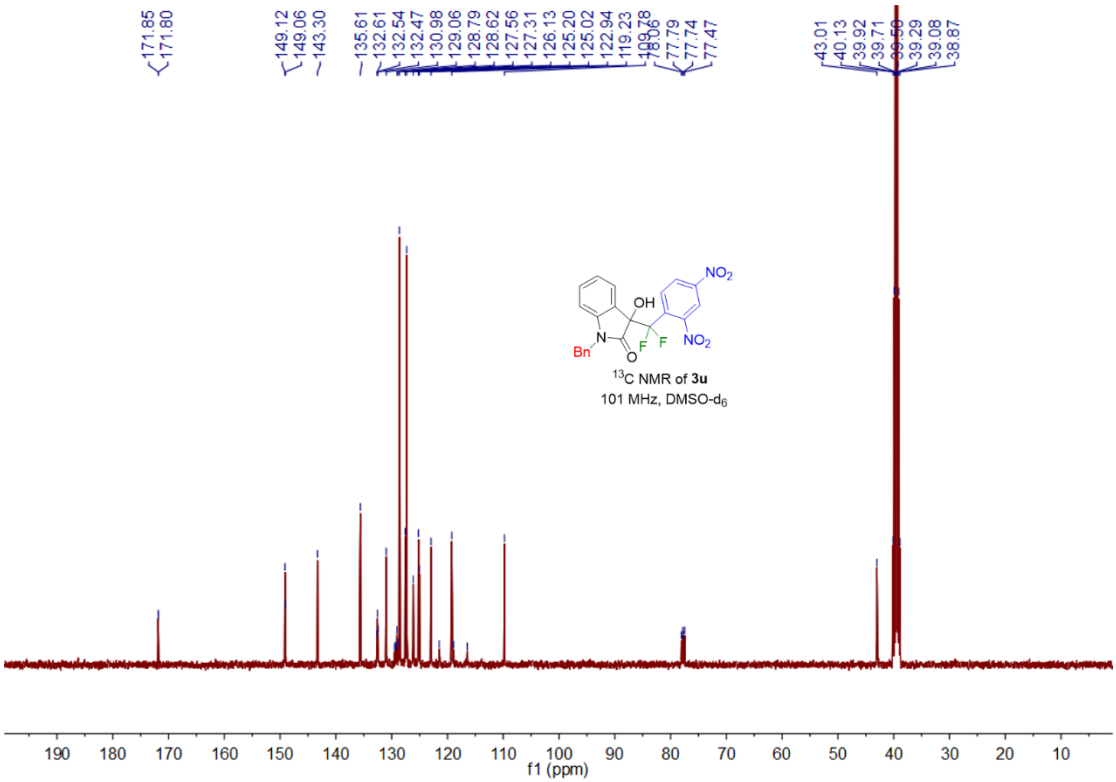
^{19}F NMR of **3s**
376 MHz, DMSO-d_6

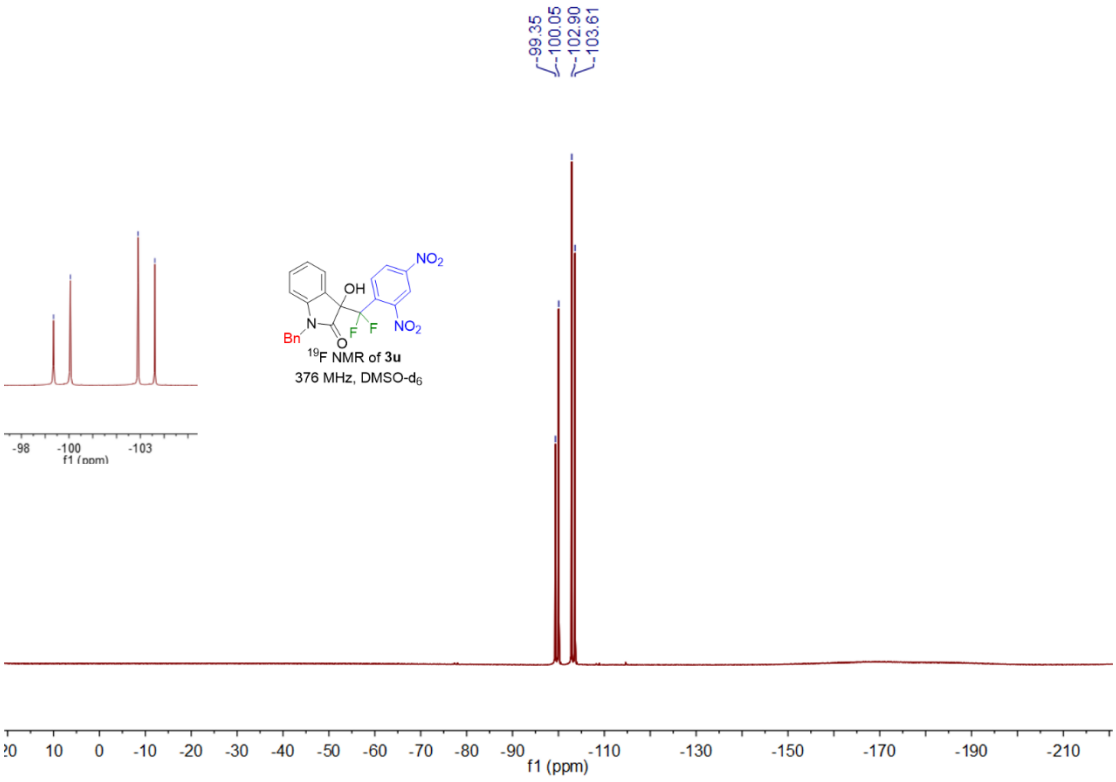

8.84
8.64
8.24
7.89
7.61
7.42
7.19
6.82
3.38
2.50
NO2
OH
N
Ph
O
F
F
NO2
1H NMR of 3t
400 MHz, DMSO-d6
1.00
1.14
1.17
1.19
7.88
1.06
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

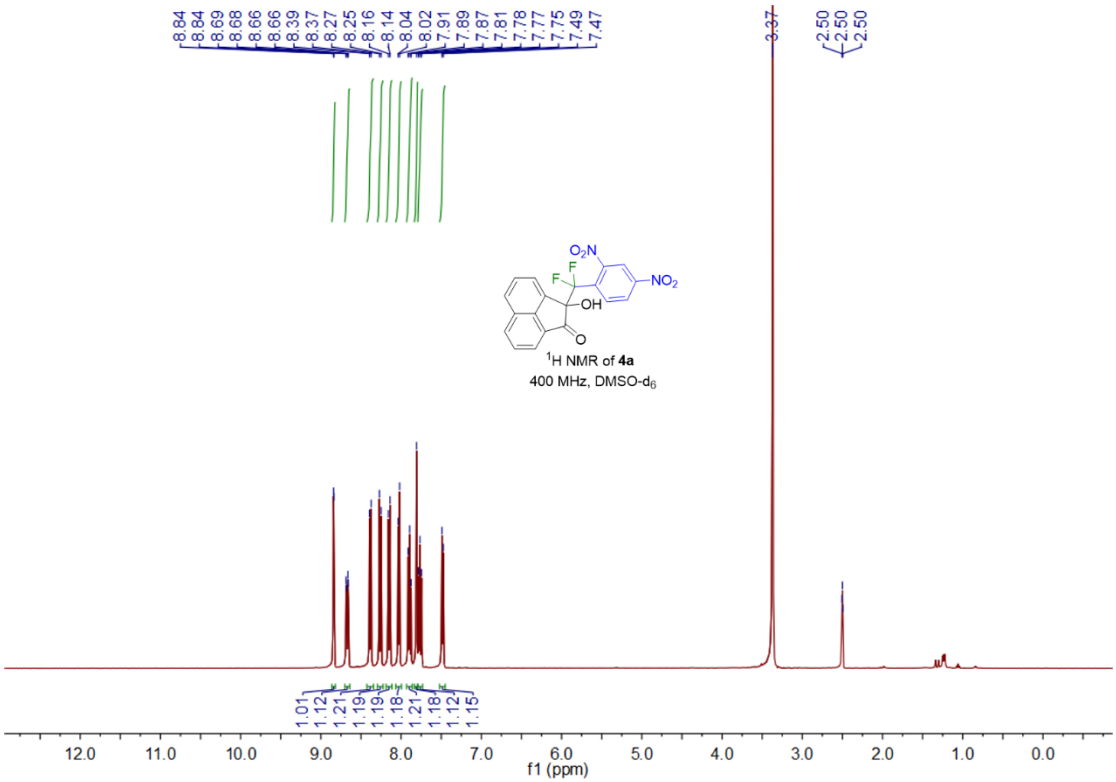

171.02
170.97
149.09
148.78
143.97
133.51
131.07
129.75
128.43
126.34
125.27
123.39
91.51
77.96
77.69
77.64
77.37
40.13
39.92
39.71
39.50
39.29
39.08
38.88
NO2
OH
N
Ph
O
F
F
NO2
13C NMR of 3t
101 MHz, DMSO-d6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

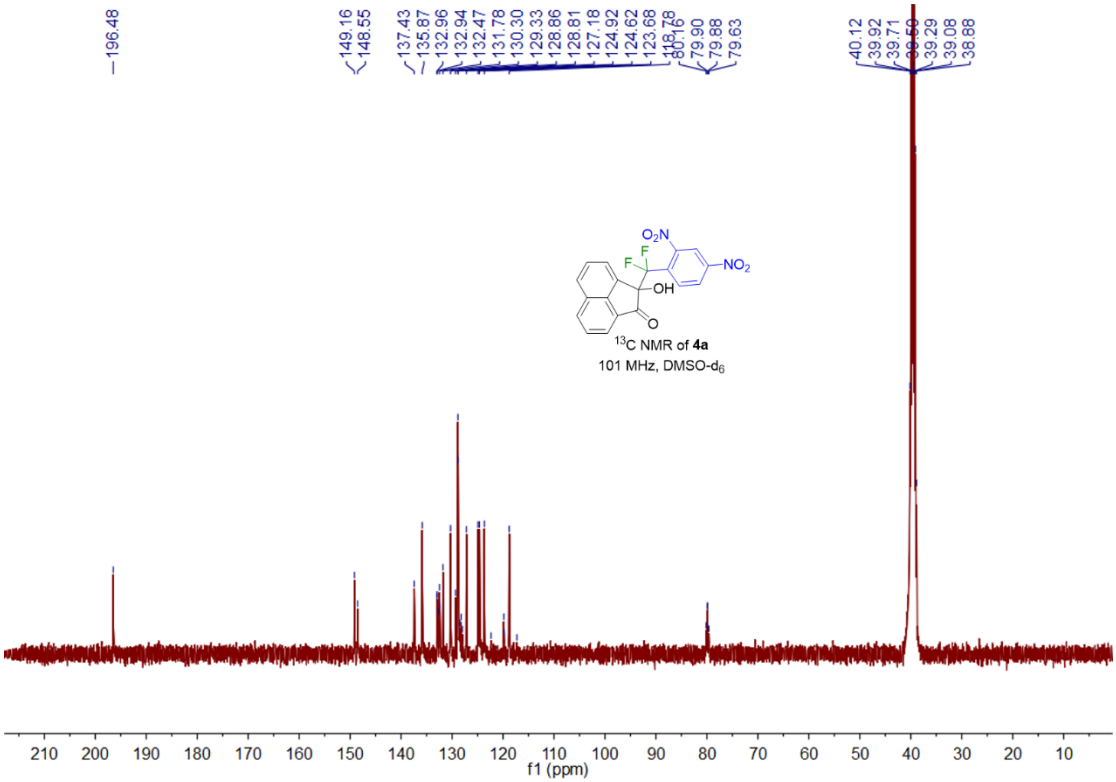

-98.71
-99.18
-103.24
-103.71
NO2
OH
N
Ph
O
F
F
NO2
19F NMR of 3t
376 MHz, DMSO-d6
-95
-100
-105
f1 (ppm)
170
130
90
60
30
0
-30
-60
-90
-130
-170
f1 (ppm)

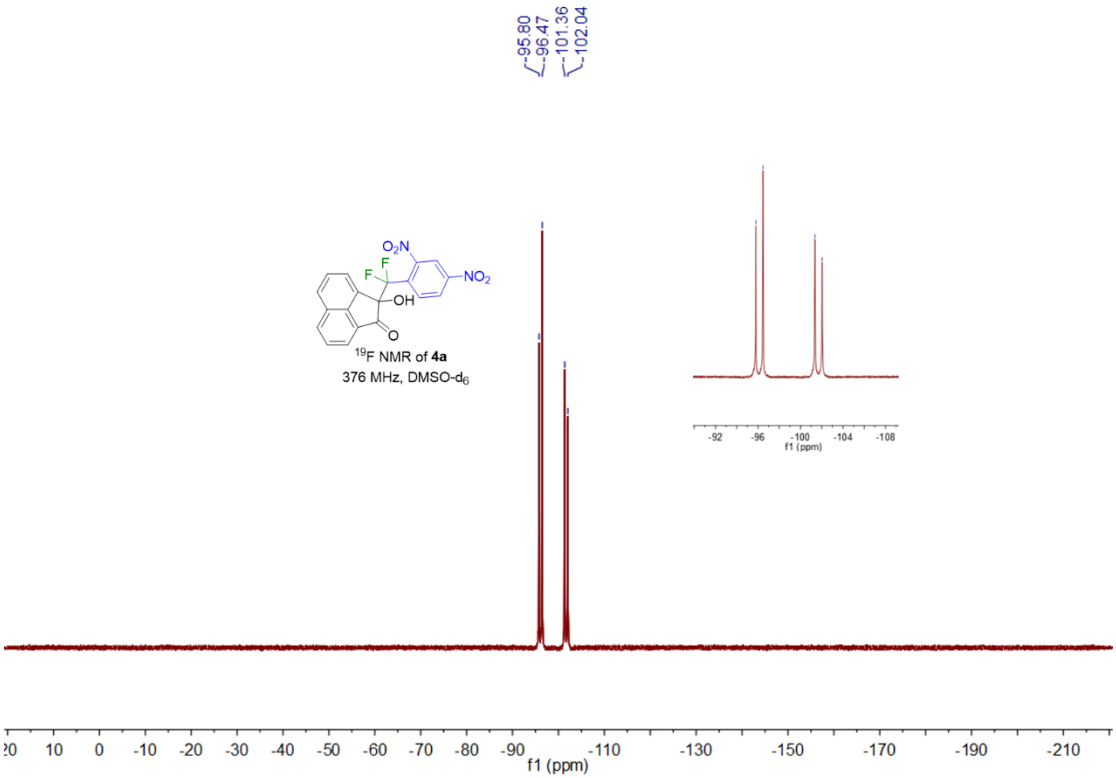

8.82
8.63
8.60
8.24
8.22
7.84
7.38
7.35
7.35
7.34
7.32
7.29
7.28
7.27
7.25
7.11
7.09
7.07
6.97
6.95
4.99
4.95
4.90
4.86
3.44
2.50
2.50
2.50
NO2
OH
N
Bn
O
F
F
NO2
1H NMR of 3u
400 MHz, DMSO-d6
1.00
1.00
1.00
0.94
7.22
1.07
1.05
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

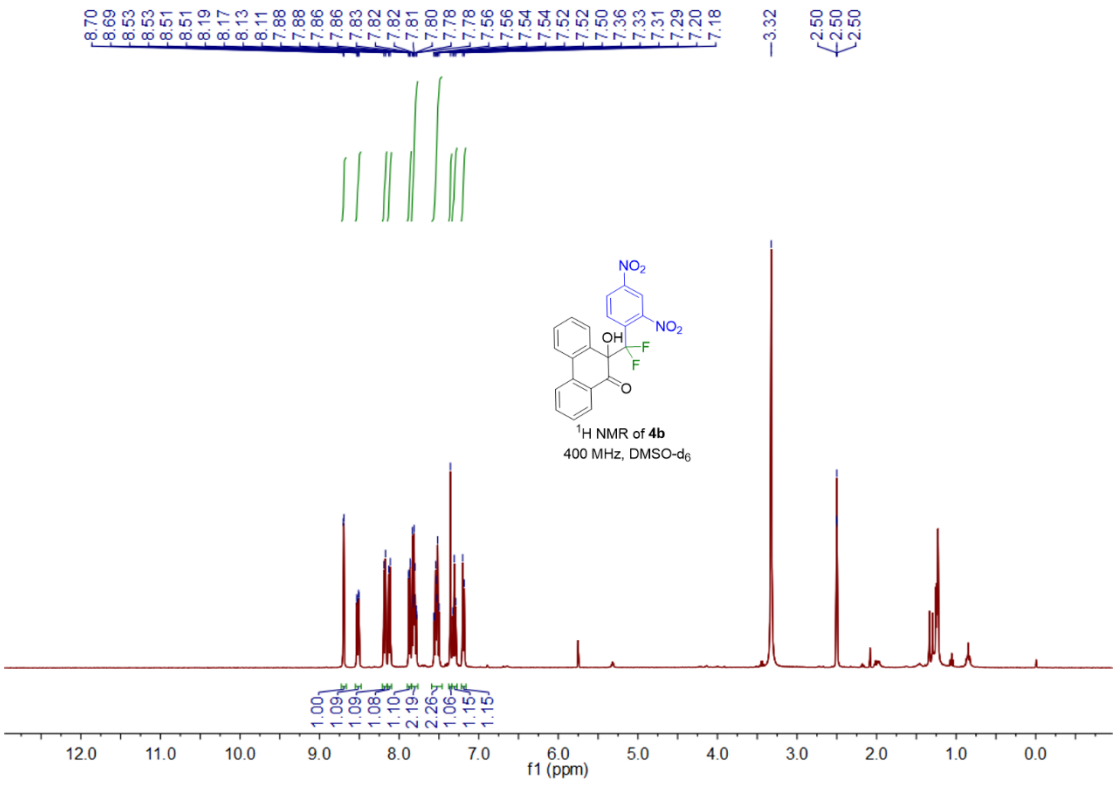

171.85
171.80
149.12
149.06
143.30
135.61
132.61
132.54
132.47
130.98
129.06
128.79
128.62
127.56
127.31
126.13
125.20
125.02
122.94
119.23
109.78
109.06
77.79
77.74
77.47
43.01
40.13
39.92
39.71
39.50
39.29
39.08
38.87
NO2
OH
N
Bn
O
F
F
NO2
13C NMR of 3u
101 MHz, DMSO-d6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

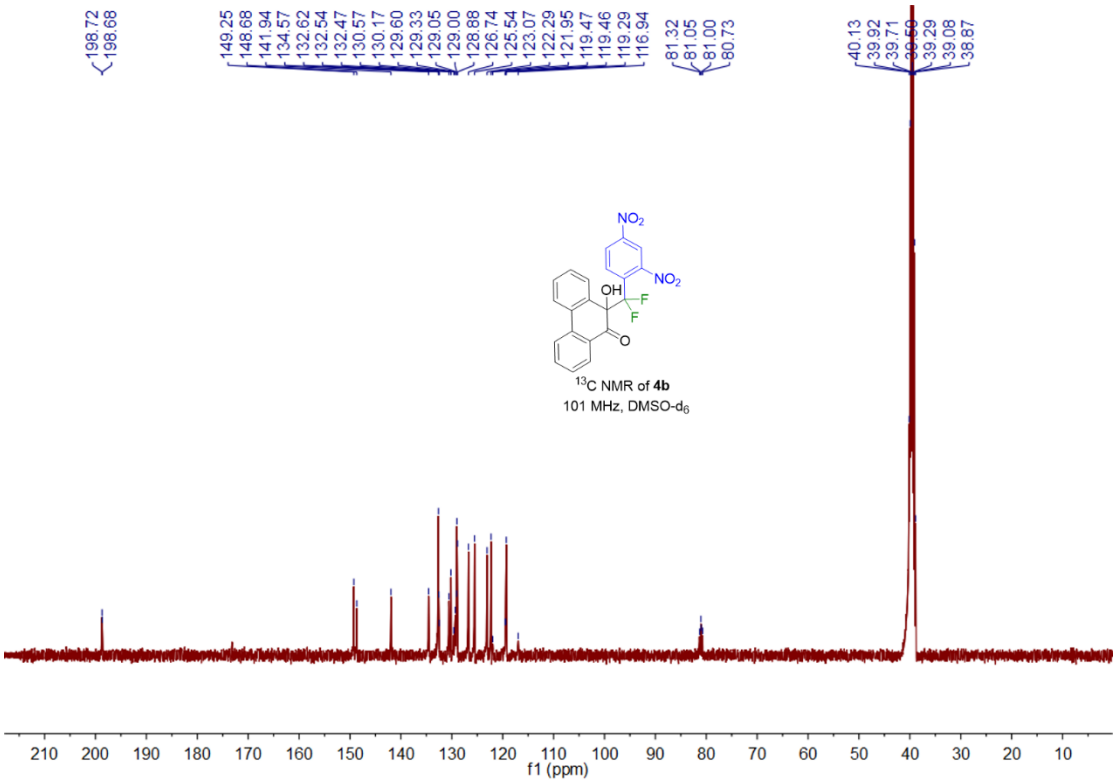

-99.35
-100.05
-102.90
-103.61
NO2
OH
N
Bn
O
F
F
NO2
19F NMR of 3u
376 MHz, DMSO-d6
-98 -100 -103
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

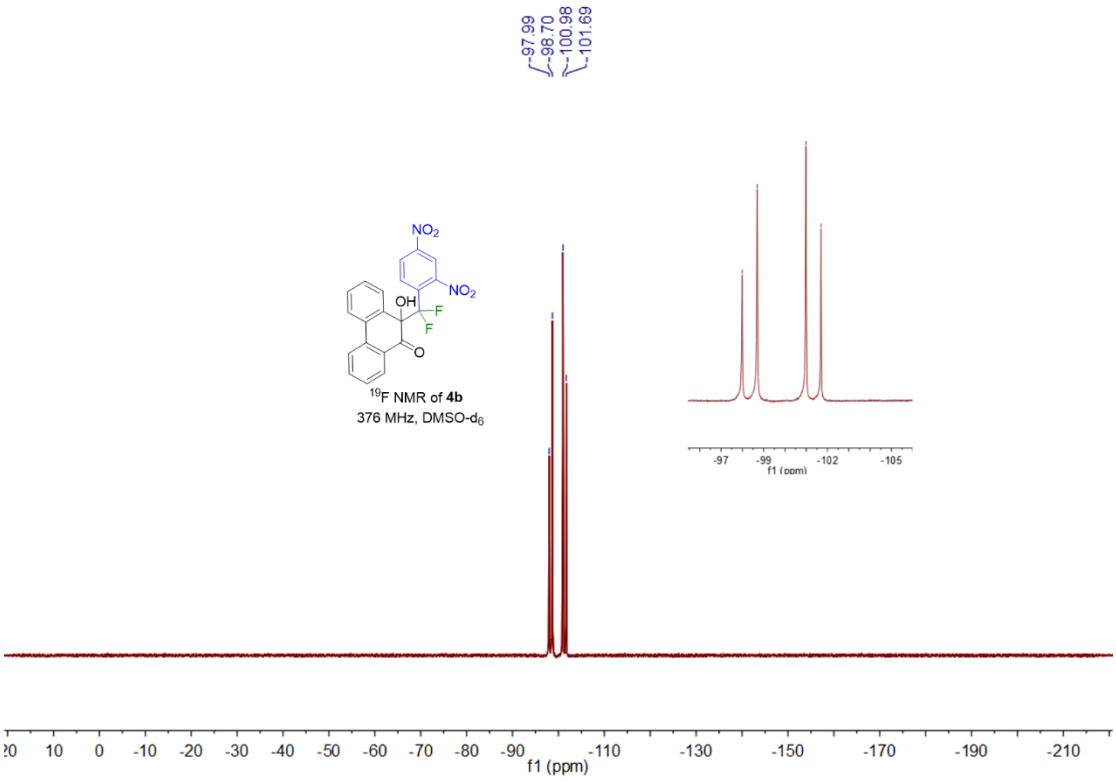

8.84
8.84
8.69
8.68
8.66
8.66
8.39
8.37
8.27
8.25
8.16
8.14
8.04
8.02
7.91
7.89
7.87
7.81
7.78
7.77
7.75
7.49
7.47
3.37
2.50
2.50
2.50
O2N
F
F
NO2
OH
O
1H NMR of 4a
400 MHz, DMSO-d6
1.01
1.12
1.21
1.19
1.19
1.18
1.21
1.18
1.12
1.15
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

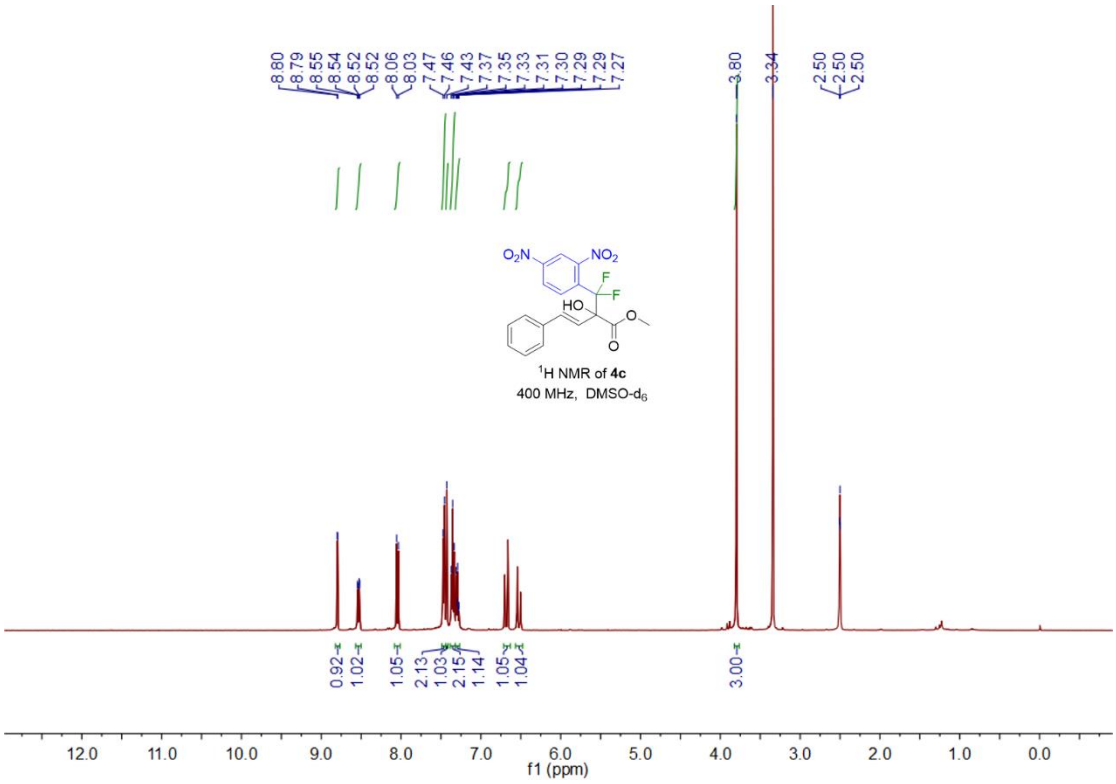

196.48
149.16
148.55
137.43
135.87
132.96
132.94
132.47
131.78
130.30
129.33
128.86
128.81
127.18
124.92
124.62
123.68
118.78
80.16
79.90
79.88
79.63
40.12
39.92
39.71
39.50
39.29
39.08
38.88
O2N
F
F
NO2
OH
O
13C NMR of 4a
101 MHz, DMSO-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-95.80
-96.47
-101.36
-102.04
^{19}F NMR of **4a**
376 MHz, DMSO-d$_6$
f1 (ppm)

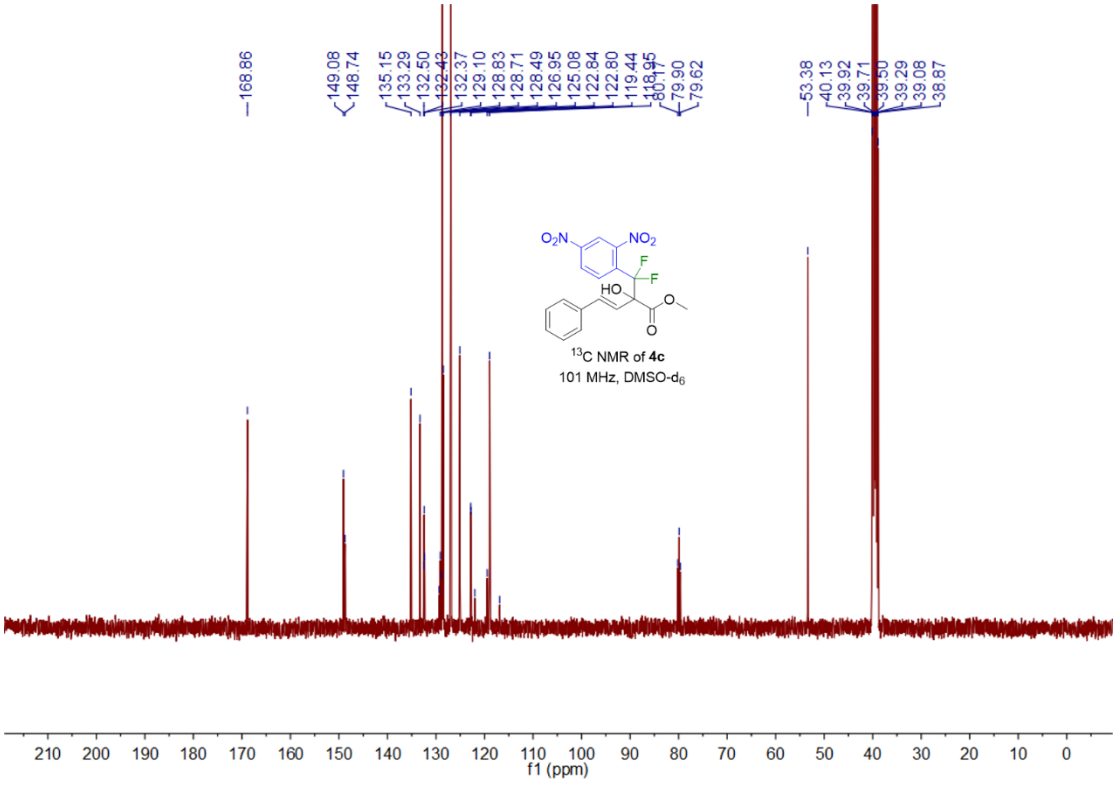

^{1}H NMR of **4b**
400 MHz, DMSO-d$_6$
f1 (ppm)


198.72
198.68
149.25
148.68
141.94
134.57
132.62
132.54
132.47
130.57
130.17
129.60
129.33
129.05
129.00
128.88
126.74
125.54
123.07
122.29
121.95
119.47
119.46
119.29
116.94
81.32
81.05
81.00
80.73
40.13
39.92
39.71
39.50
39.29
39.08
38.87
NO2
NO2
OH
F
F
O
13C NMR of 4b
101 MHz, DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

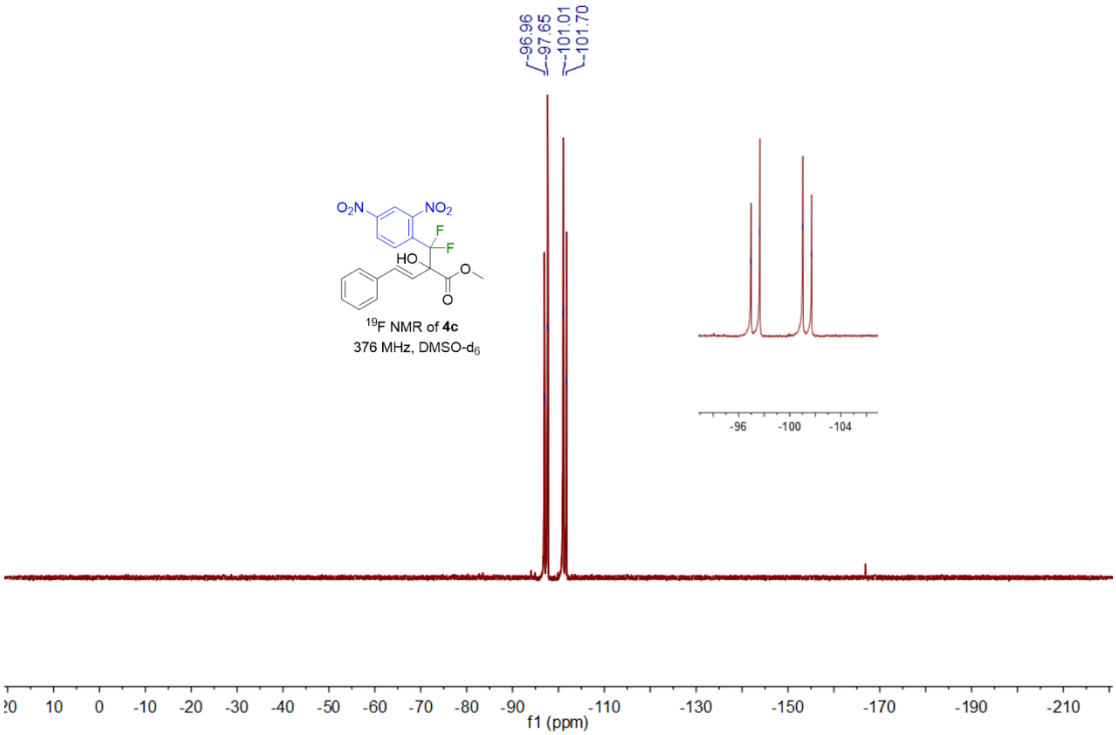

97.99
98.70
100.98
101.69
NO2
NO2
OH
F
F
O
19F NMR of 4b
376 MHz, DMSO-d6
-97
-99
-102
-105
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

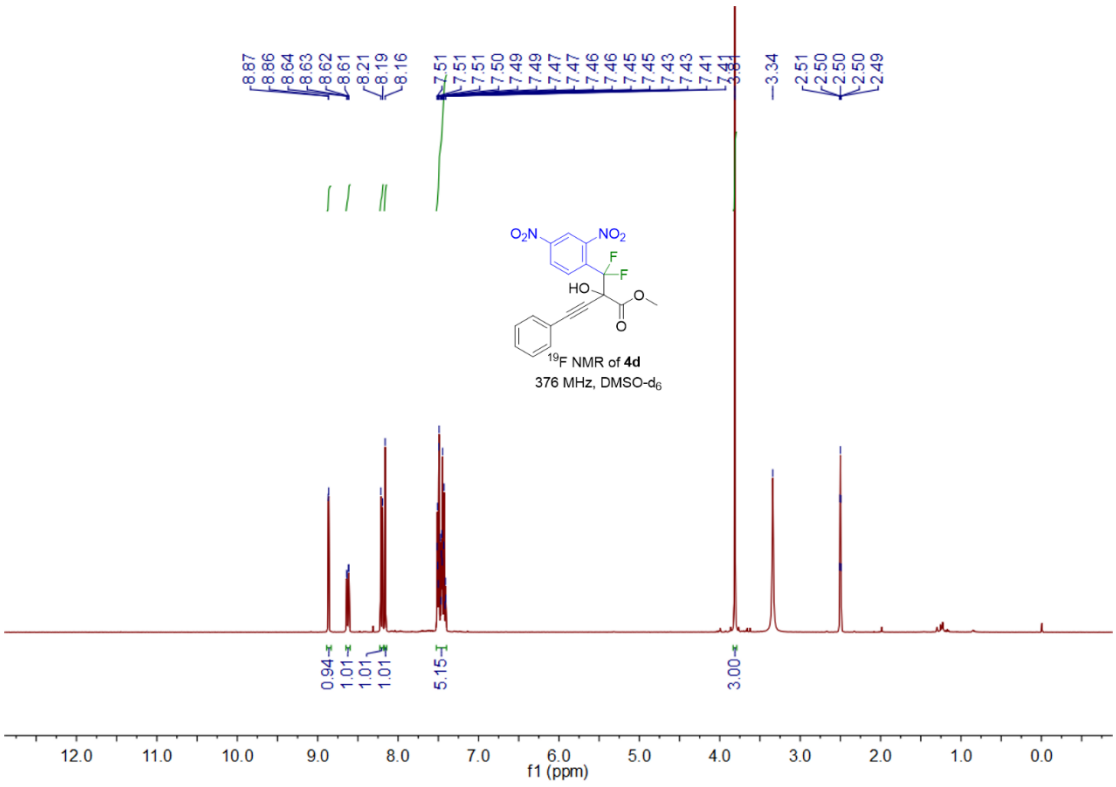


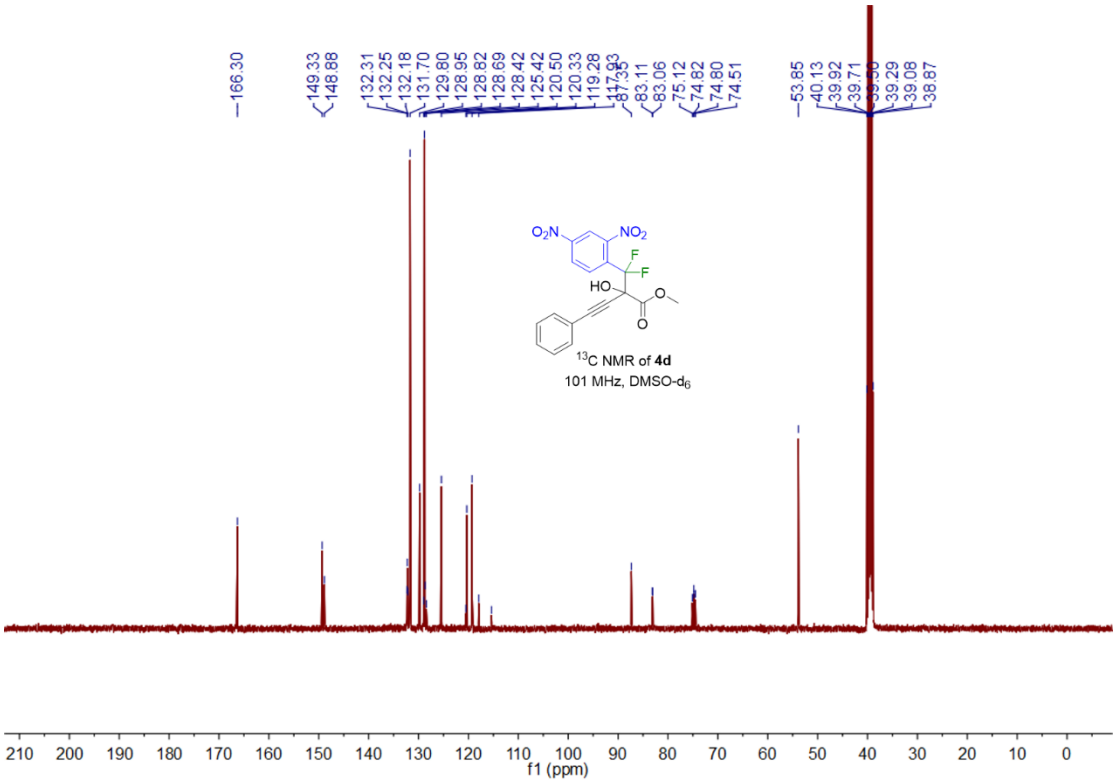
^{1}H NMR of **4c**
400 MHz, DMSO-d_6

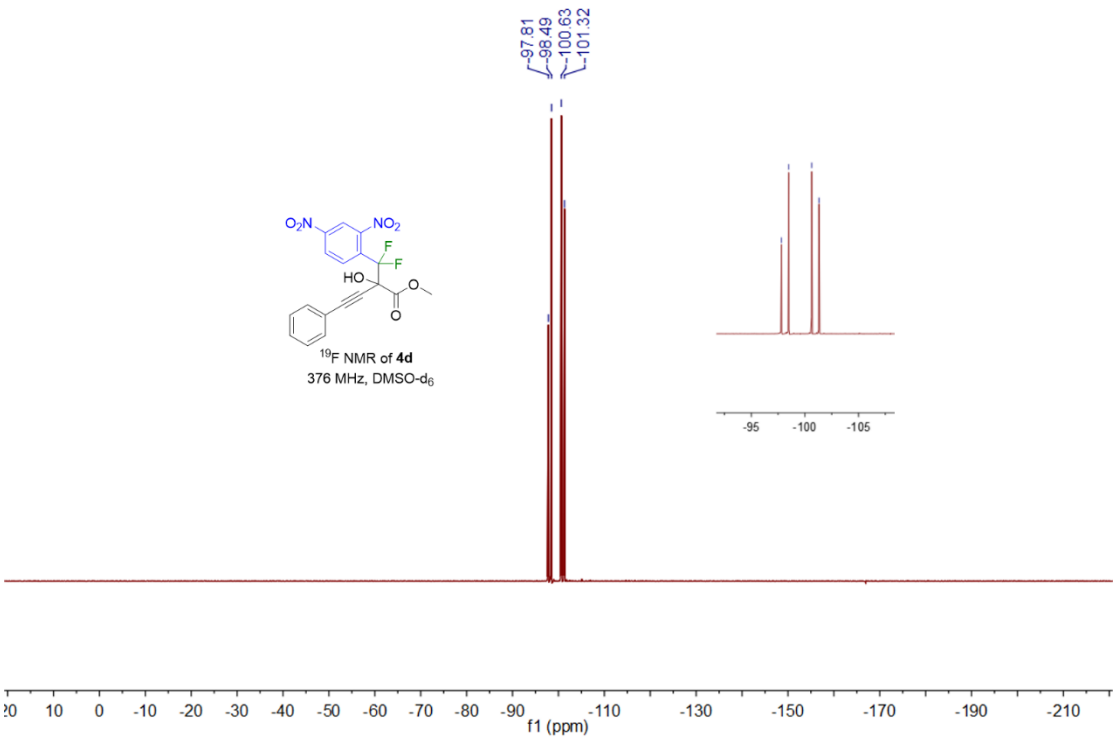


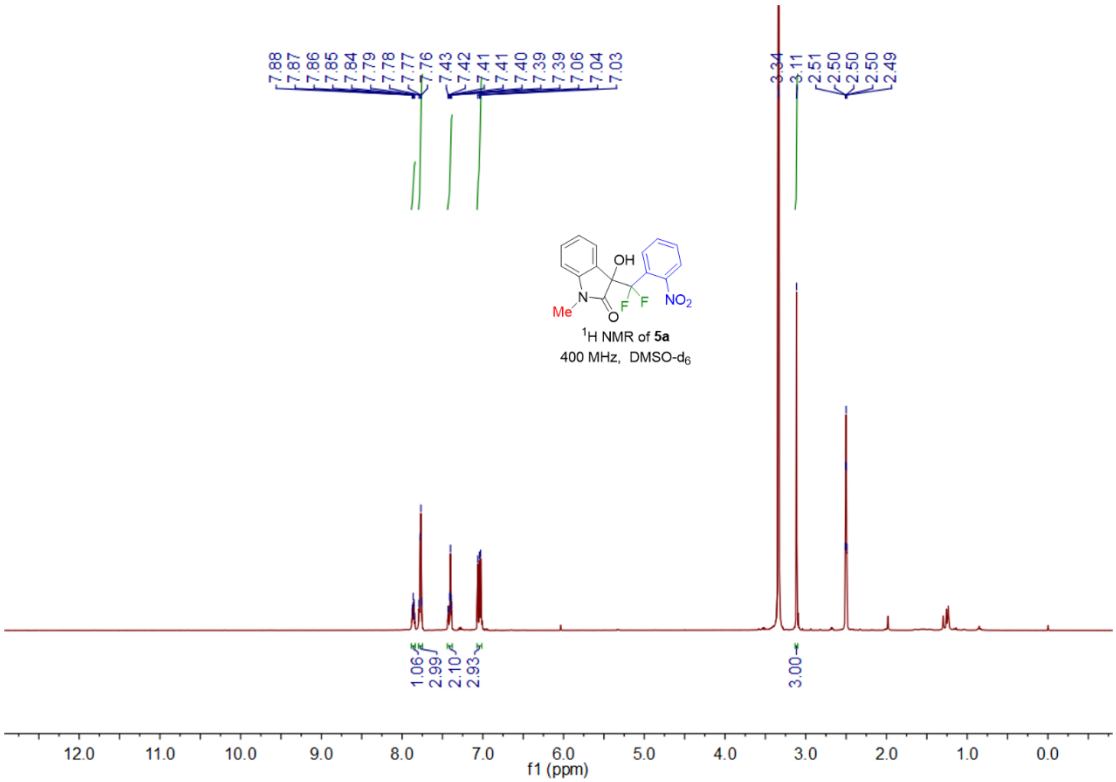
^{13}C NMR of **4c**
101 MHz, DMSO-d_6


-96.96
-97.65
-101.01
-101.70
^{19}F NMR of **4c**
376 MHz, DMSO-d$_6$
f1 (ppm)

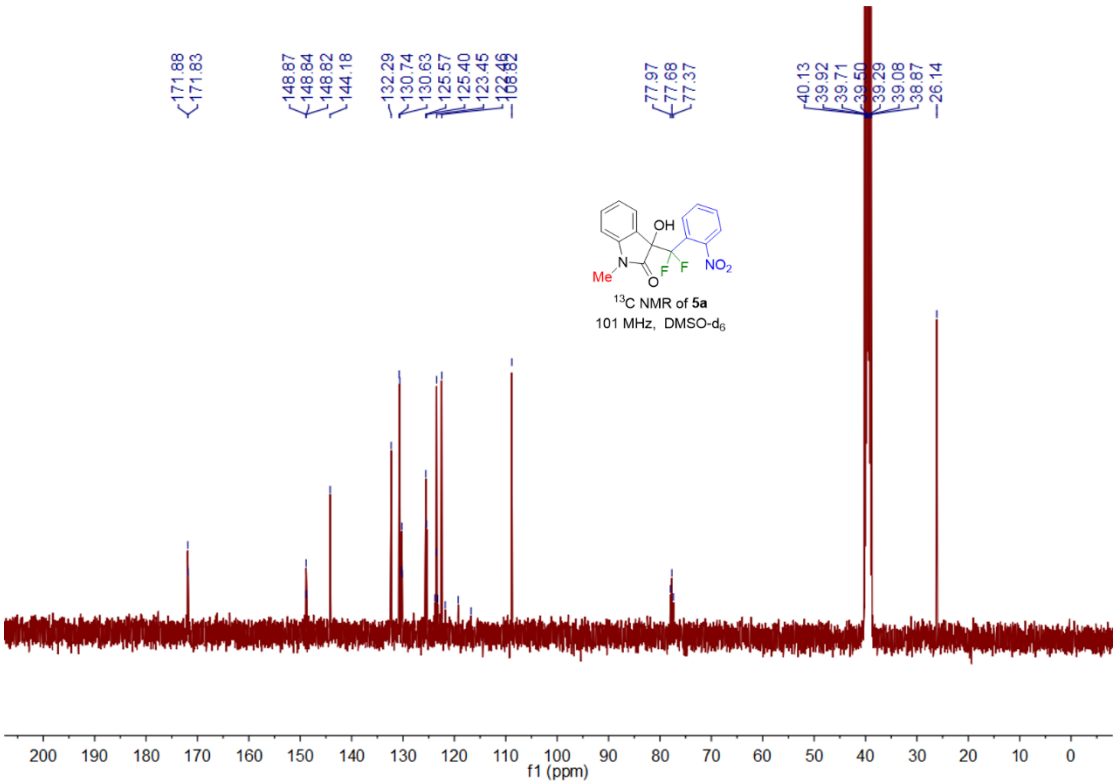

^{19}F NMR of **4d**
376 MHz, DMSO-d$_6$
f1 (ppm)


166.30
149.33
148.88
132.31
132.25
132.18
131.70
129.80
128.95
128.82
128.69
128.42
125.42
120.50
120.33
119.28
117.93
87.35
83.11
83.06
75.12
74.82
74.80
74.51
53.85
40.13
39.92
39.71
39.50
39.29
39.08
38.87
O2N
NO2
F
F
HO
O
O
13C NMR of 4d
101 MHz, DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

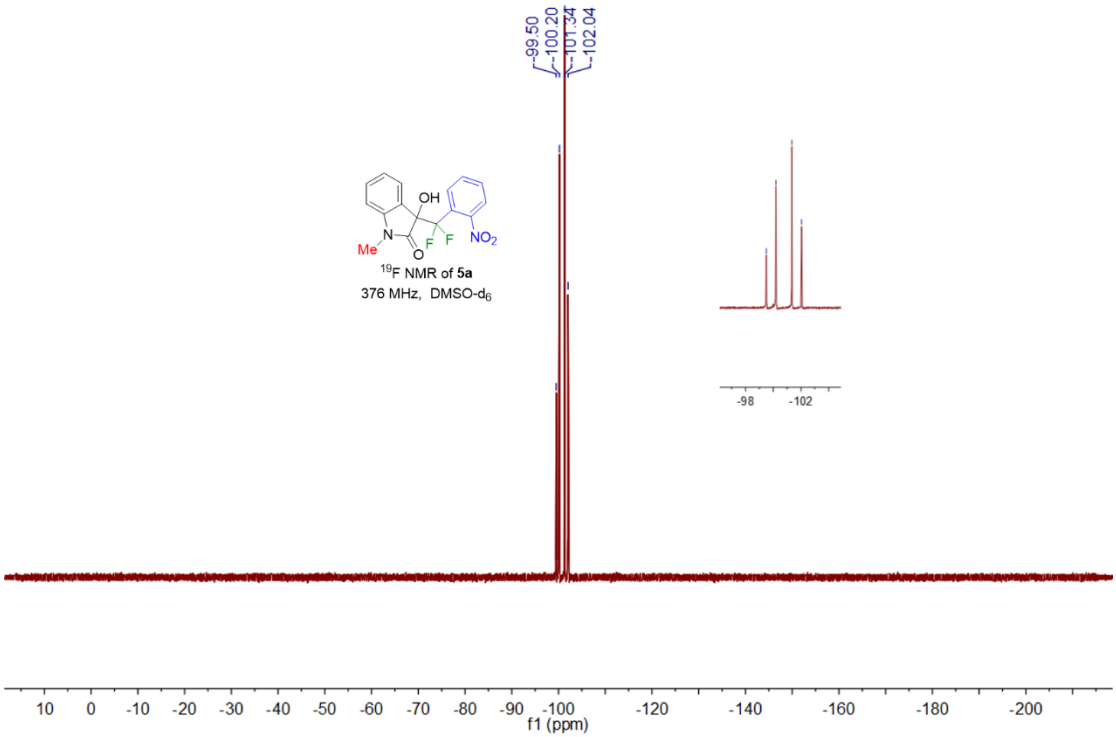

97.81
98.49
100.63
101.32
O2N
NO2
F
F
HO
O
O
19F NMR of 4d
376 MHz, DMSO-d6
-95
-100
-105
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)



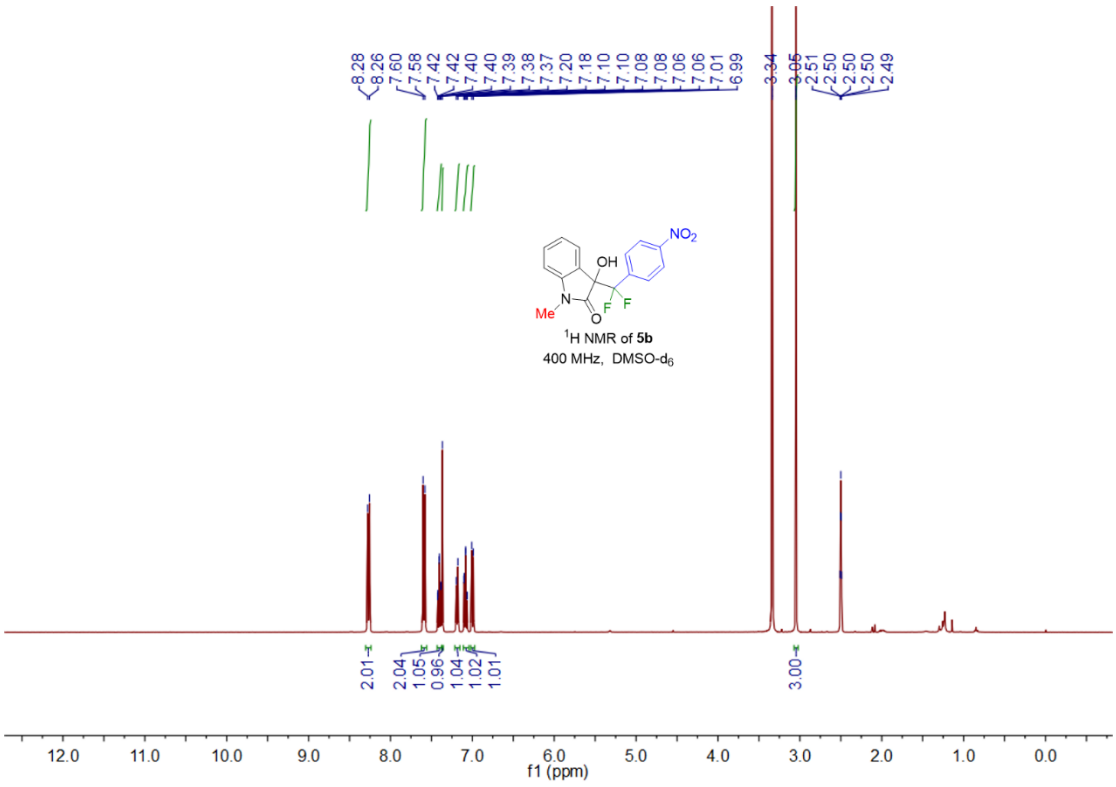
^{1}H NMR of **5a**
400 MHz, DMSO-d_6



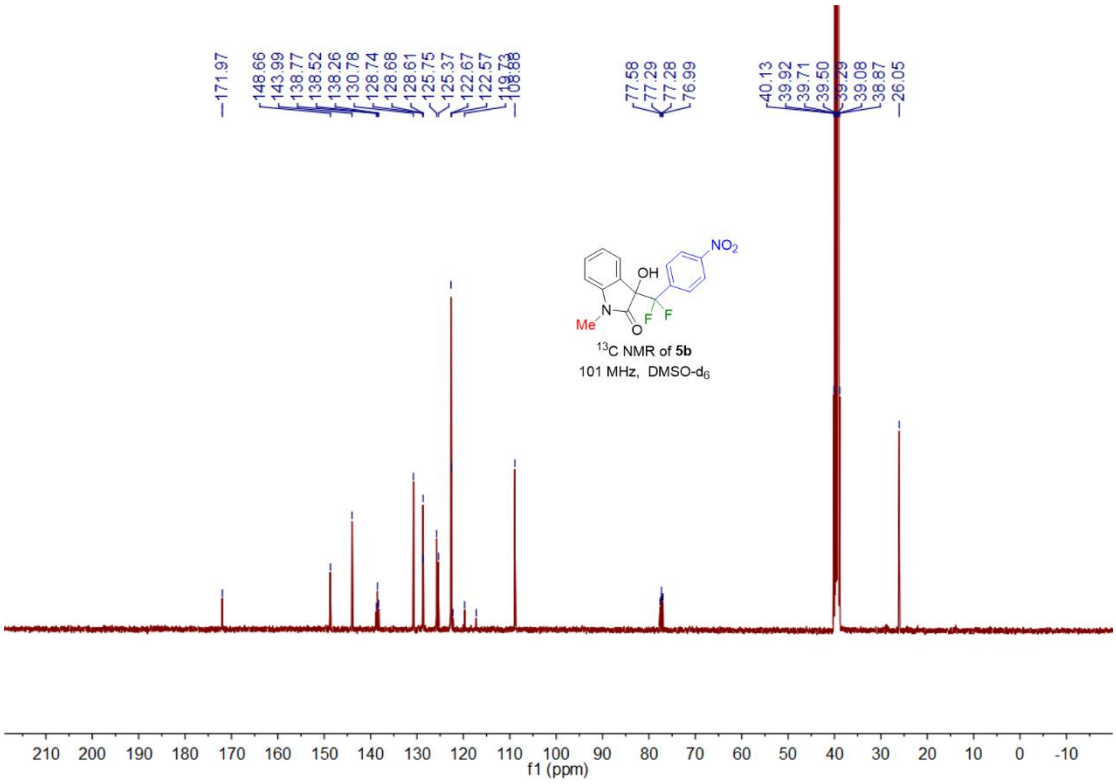
^{13}C NMR of **5a**
101 MHz, DMSO-d_6

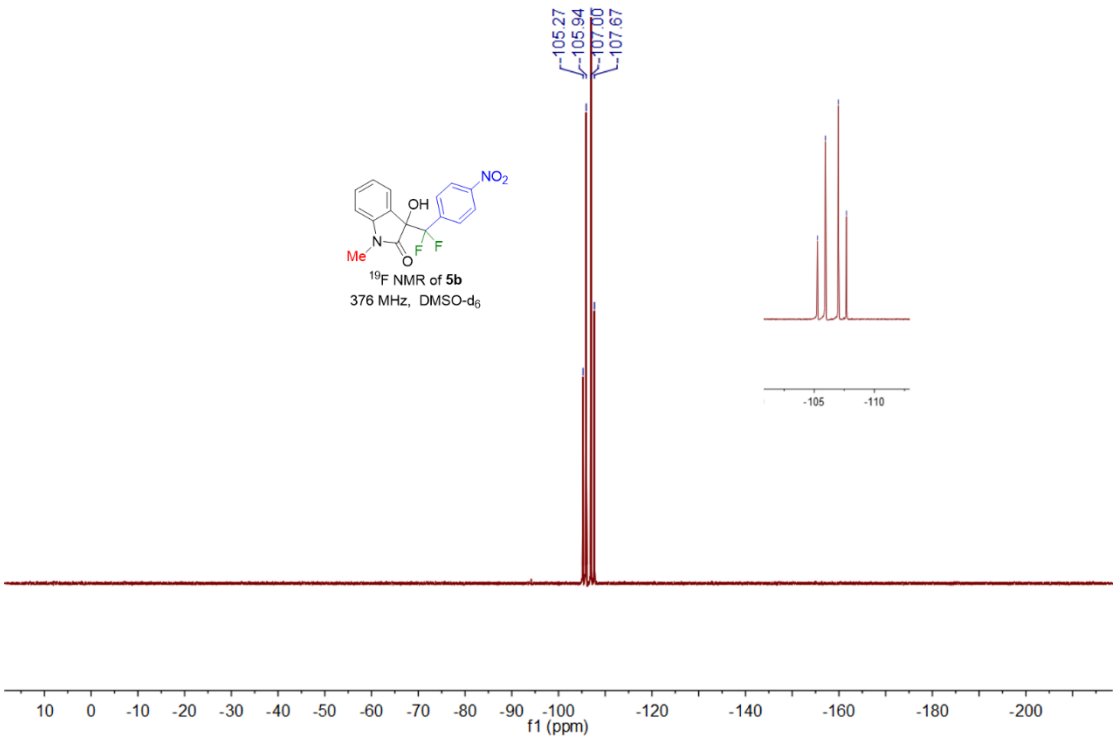


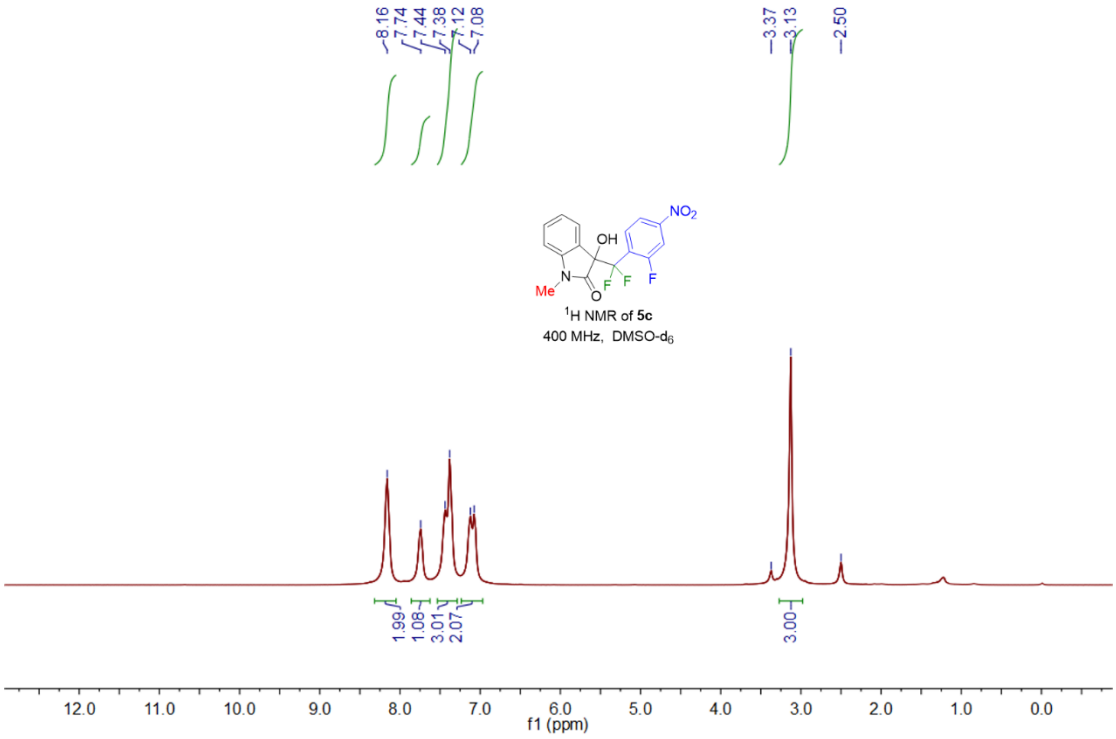
^{19}F NMR of **5a**
376 MHz, DMSO-d_6

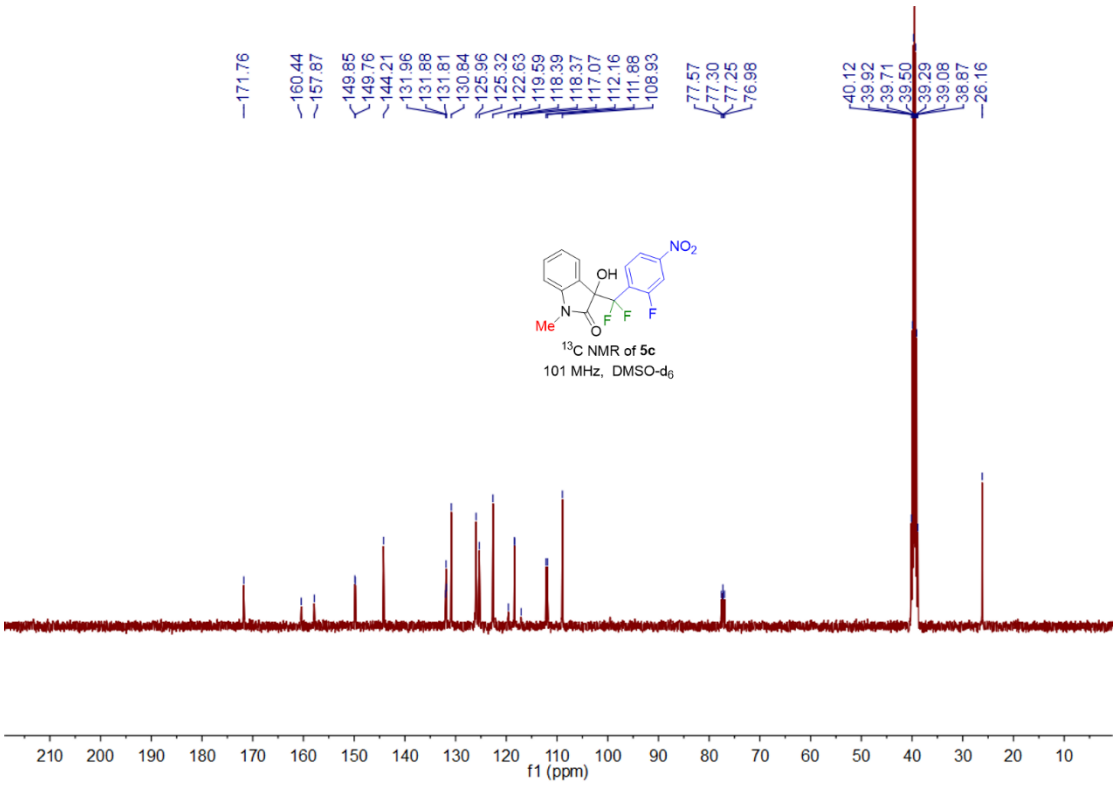


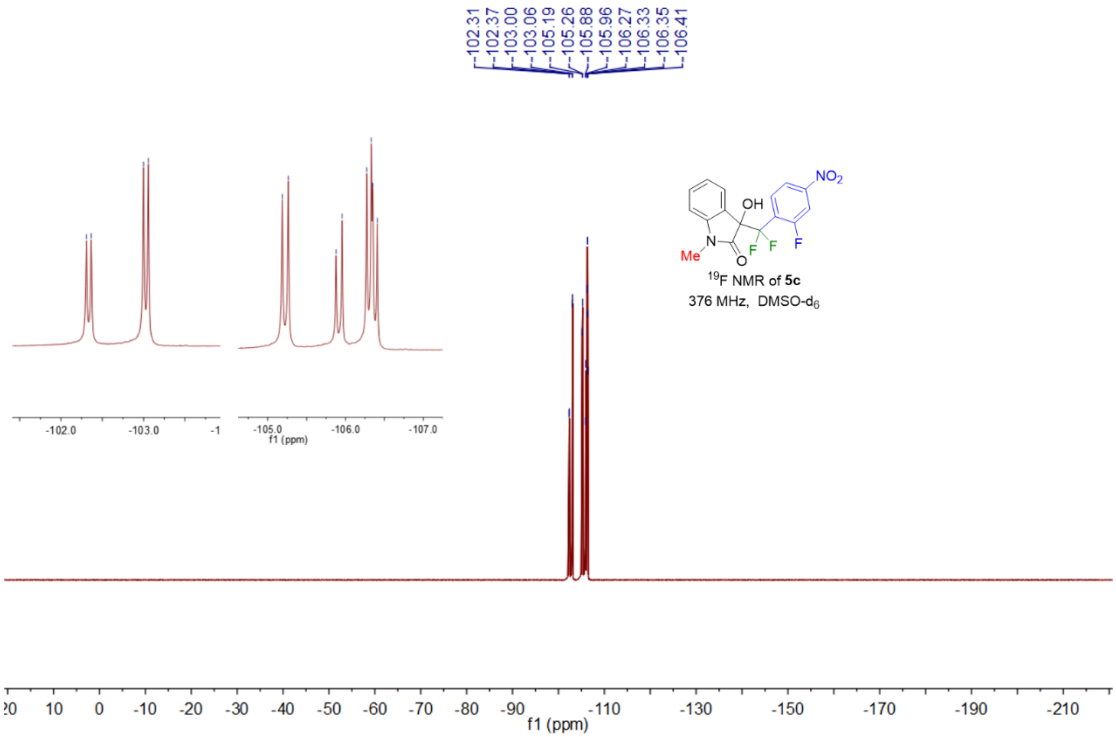
^{1}H NMR of **5b**
400 MHz, DMSO-d_6

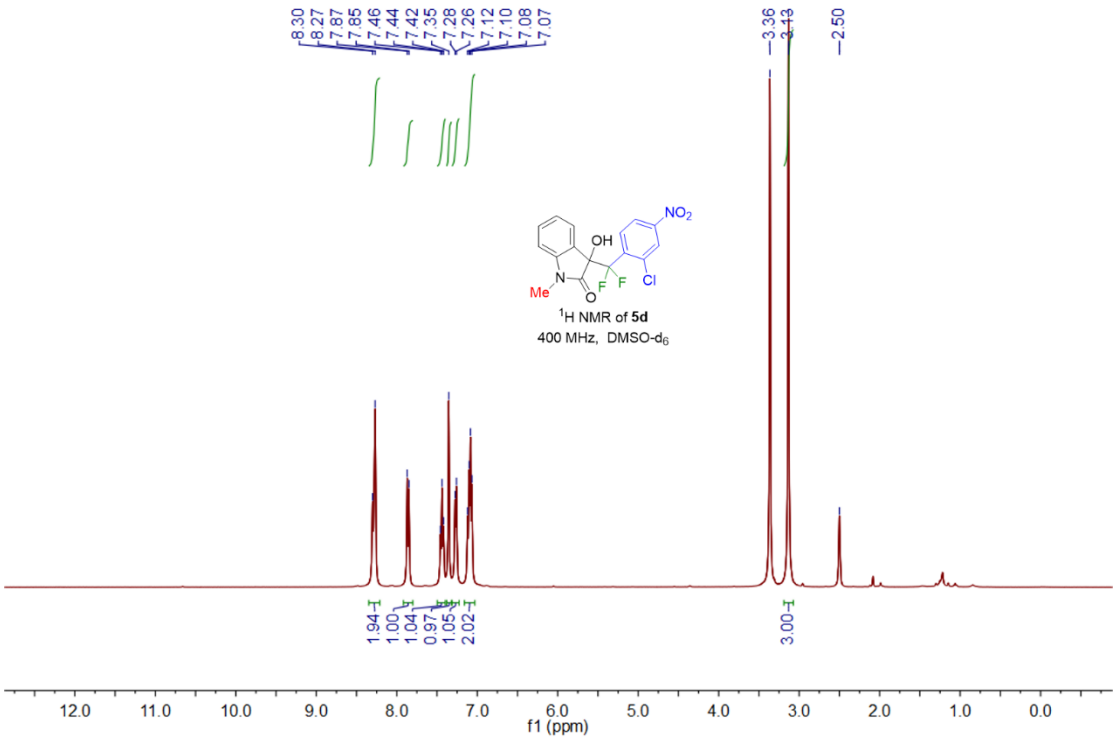

171.97
148.66
143.99
138.77
138.52
138.26
130.78
128.74
128.68
128.61
125.75
125.37
122.67
122.57
119.73
108.88
77.58
77.29
77.28
76.99
40.13
39.92
39.71
39.50
39.29
39.08
38.87
26.05
NO2
OH
N
Me
O
F
F
13C NMR of 5b
101 MHz, DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

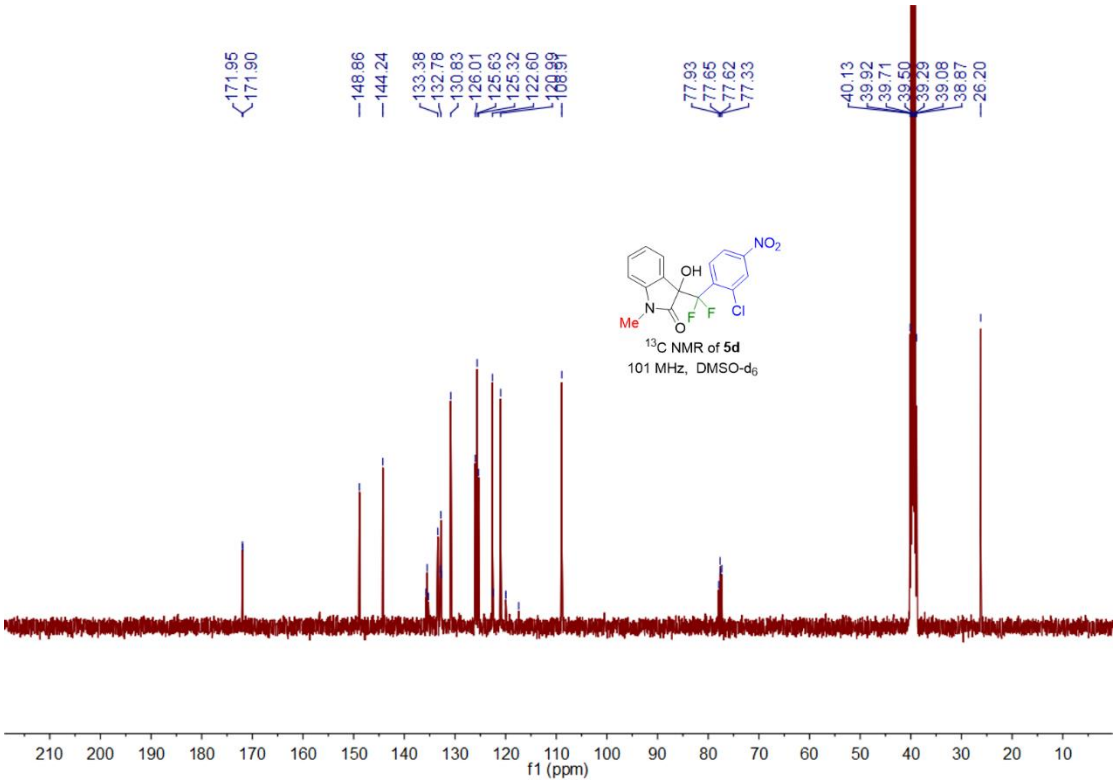

105.27
105.94
107.00
107.67
NO2
OH
N
Me
O
F
F
19F NMR of 5b
376 MHz, DMSO-d6
-105
-110
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

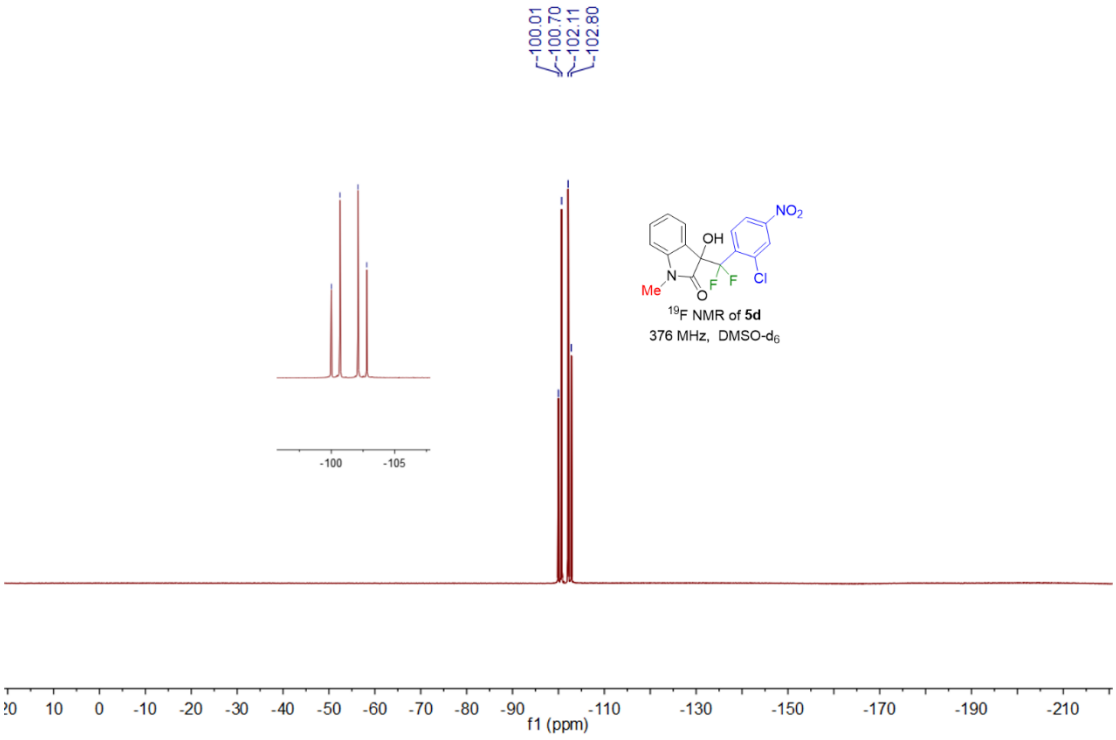

8.16
7.74
7.44
7.38
7.12
7.08
3.37
3.13
2.50
NO2
OH
N
Me
O
F
F
F
1H NMR of 5c
400 MHz, DMSO-d6
1.99
1.08
3.01
2.07
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

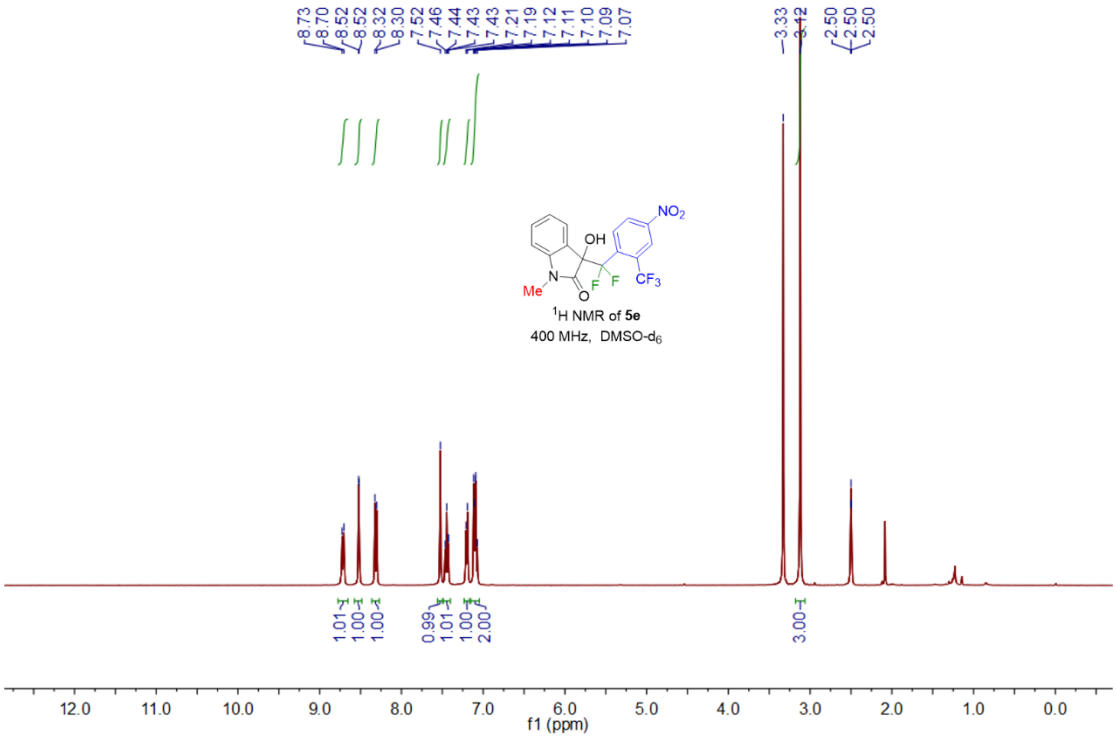

171.76
160.44
157.87
149.85
149.76
144.21
131.96
131.88
131.81
130.84
125.96
125.32
122.63
119.59
118.39
118.37
117.07
112.16
111.88
108.93
77.57
77.30
77.25
76.98
40.12
39.92
39.71
39.50
39.29
39.08
38.87
26.16
NO2
OH
N
Me
O
F
F
F
13C NMR of 5c
101 MHz, DMSO-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-102.31
-102.37
-103.00
-103.06
-105.19
-105.26
-105.88
-105.96
-106.27
-106.33
-106.35
-106.41
NO2
OH
N
Me
O
F
F
F
-102.0
-103.0
-105.0
-106.0
-107.0
f1 (ppm)
19F NMR of 5c
376 MHz, DMSO-d6
f1 (ppm)

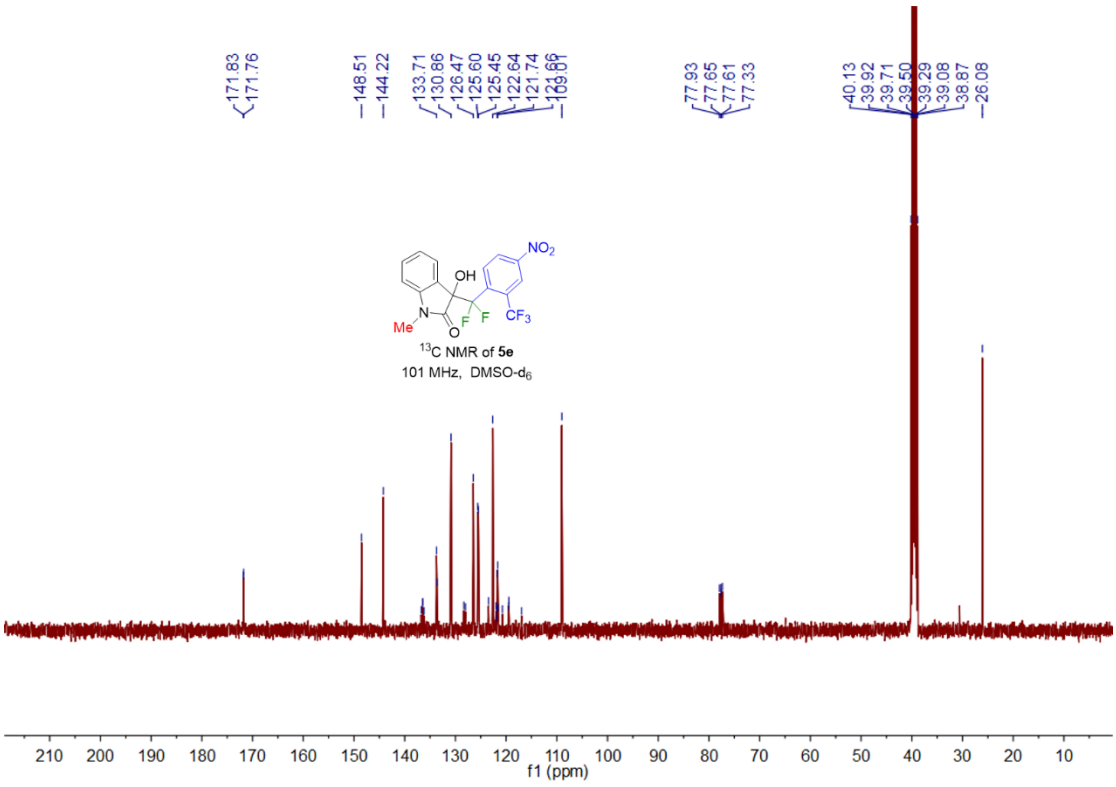

8.30
8.27
7.87
7.85
7.46
7.44
7.42
7.35
7.28
7.26
7.12
7.10
7.08
7.07
3.36
3.43
2.50
NO2
OH
N
Me
O
F
F
Cl
1H NMR of 5d
400 MHz, DMSO-d6
1.94
1.00
1.04
0.97
1.05
2.02
3.00
f1 (ppm)


171.95
171.90
148.86
144.24
133.38
132.78
130.83
126.01
125.63
125.32
122.60
77.93
77.65
77.62
77.33
40.13
39.92
39.71
39.50
39.29
39.08
38.87
26.20
NO2
OH
N
Me
O
F
F
Cl
13C NMR of 5d
101 MHz, DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

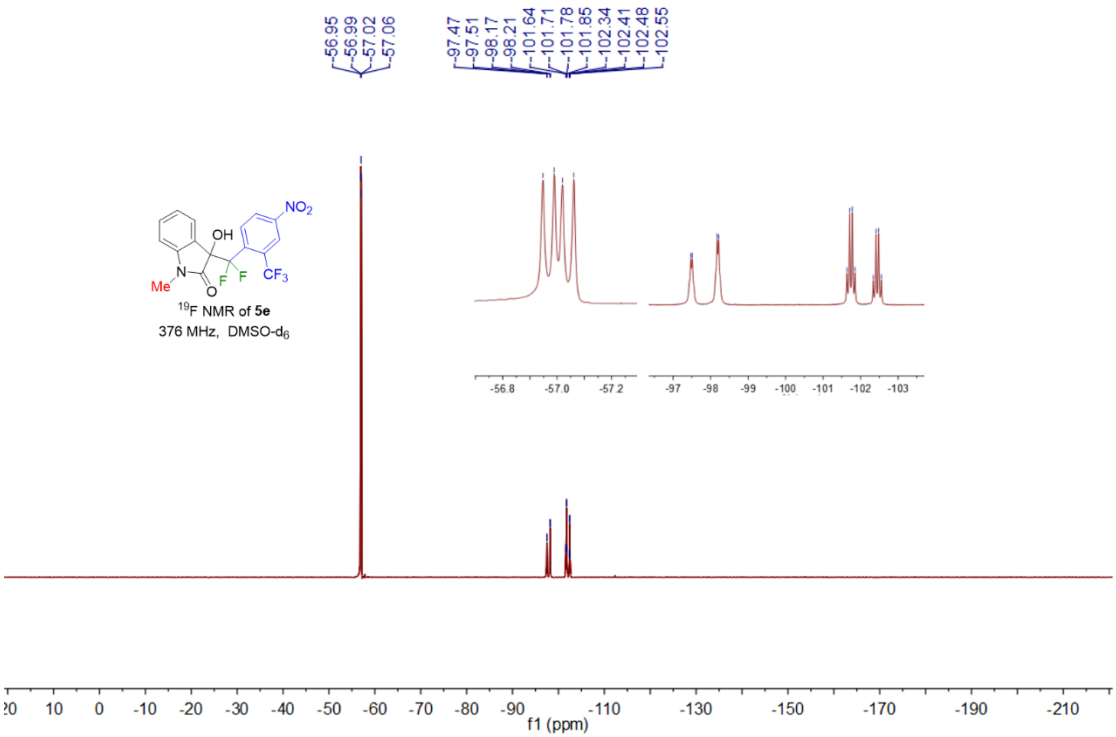

100.01
100.70
102.11
102.80
-100
-105
NO2
OH
N
Me
O
F
F
Cl
19F NMR of 5d
376 MHz, DMSO-d6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

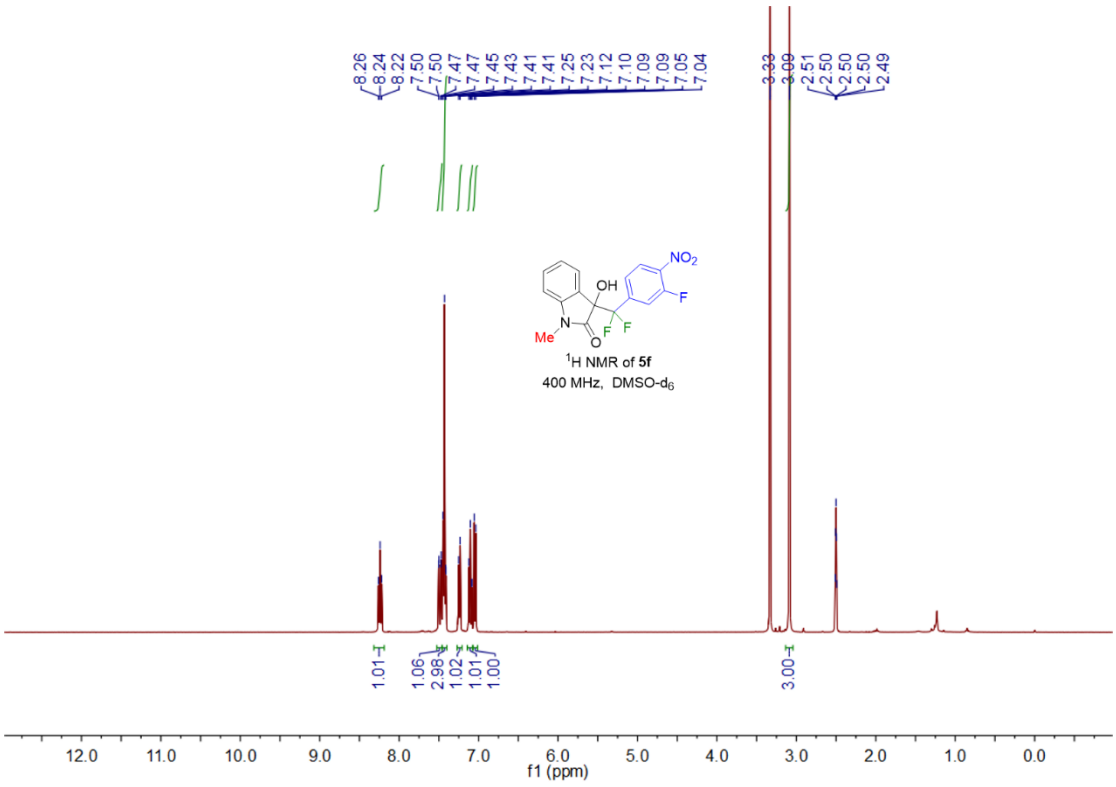


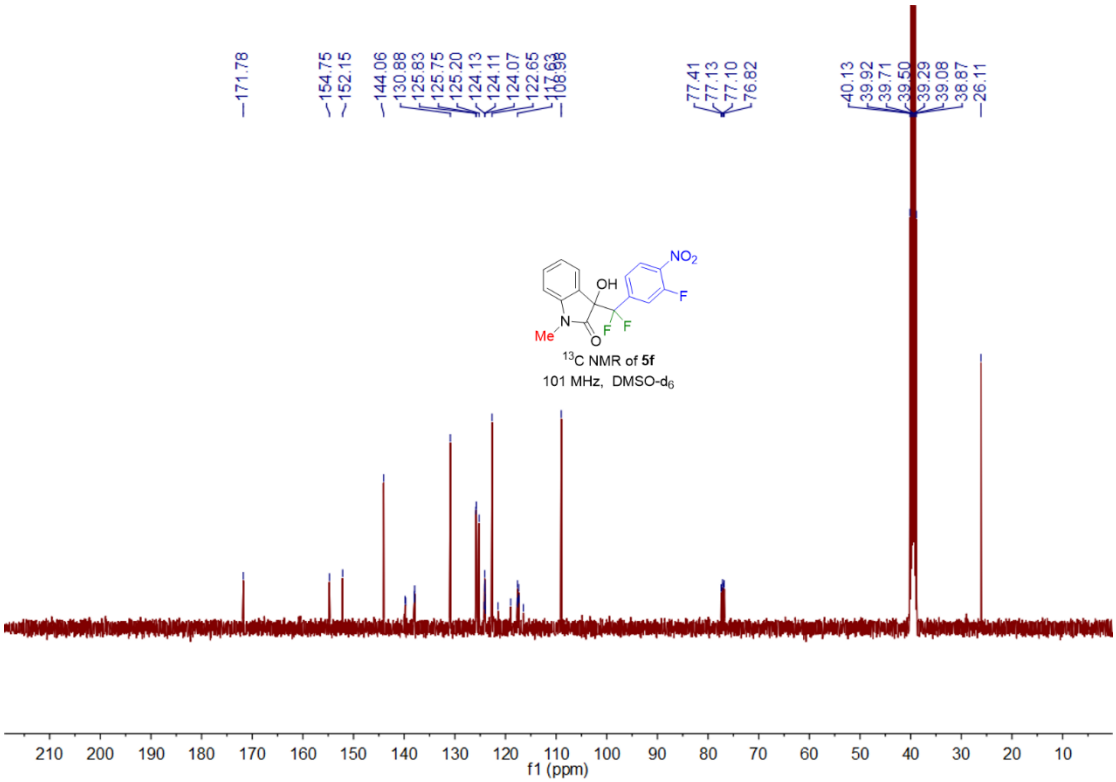
^{1}H NMR of **5e**
400 MHz, DMSO-d_6

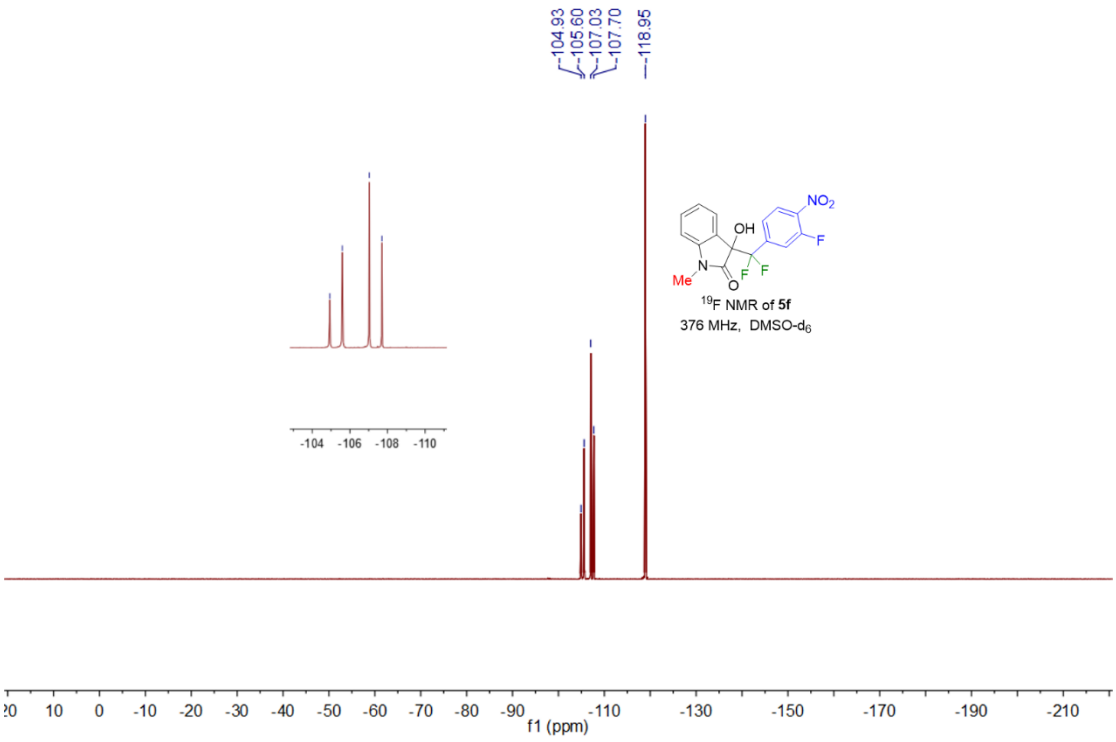


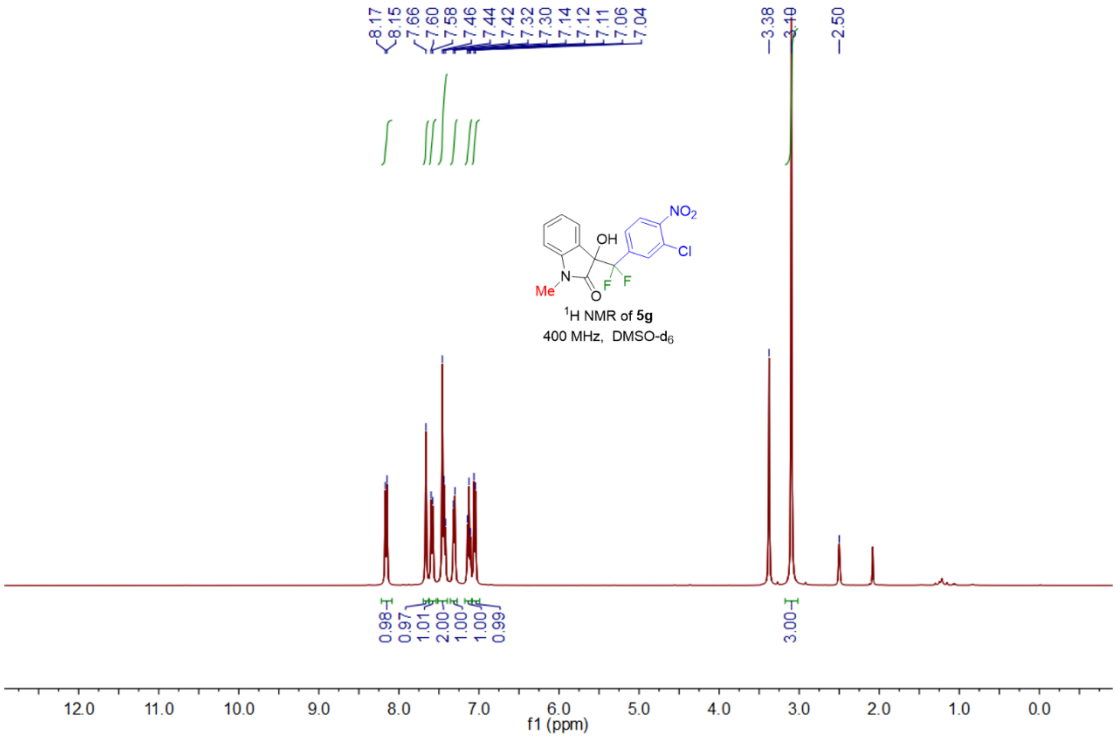
^{13}C NMR of **5e**
101 MHz, DMSO-d_6

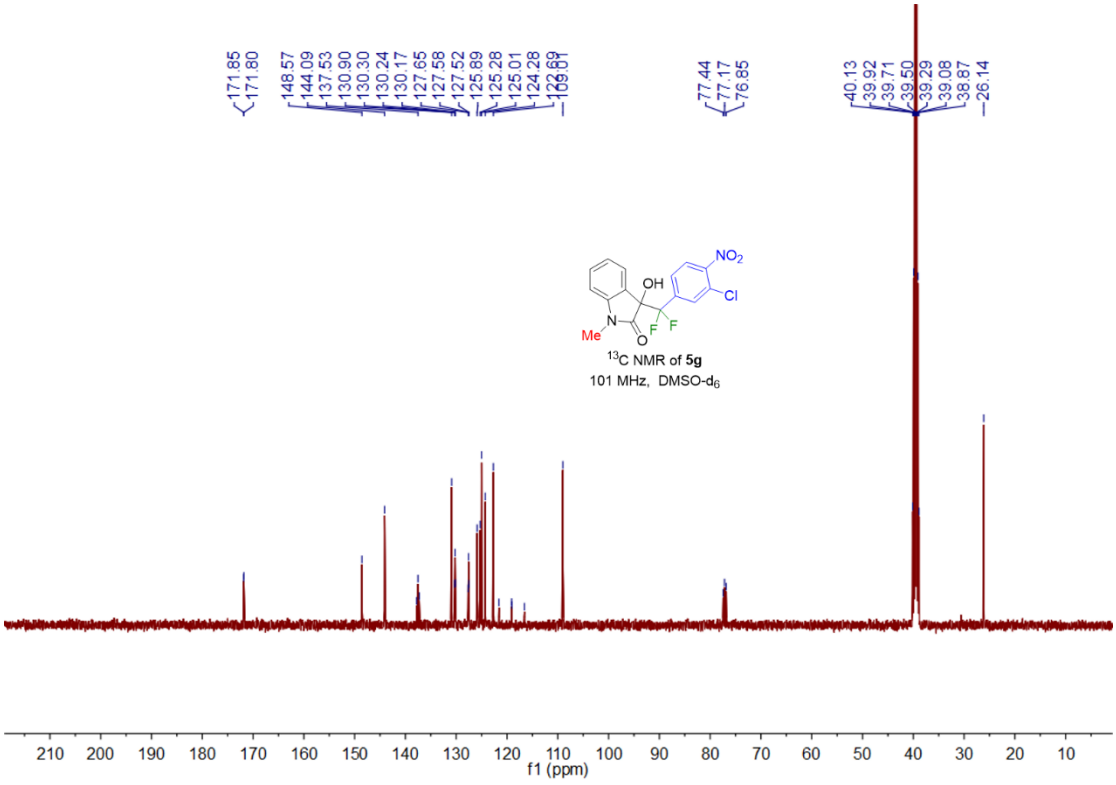

-56.95
-56.99
-57.02
-57.06
-97.47
-97.51
-98.17
-98.21
-101.64
-101.71
-101.78
-101.85
-102.34
-102.41
-102.48
-102.55
NO2
OH
Me
N
O
F
F
CF3
19F NMR of 5e
376 MHz, DMSO-d6
-56.8
-57.0
-57.2
-97
-98
-99
-100
-101
-102
-103
f1 (ppm)

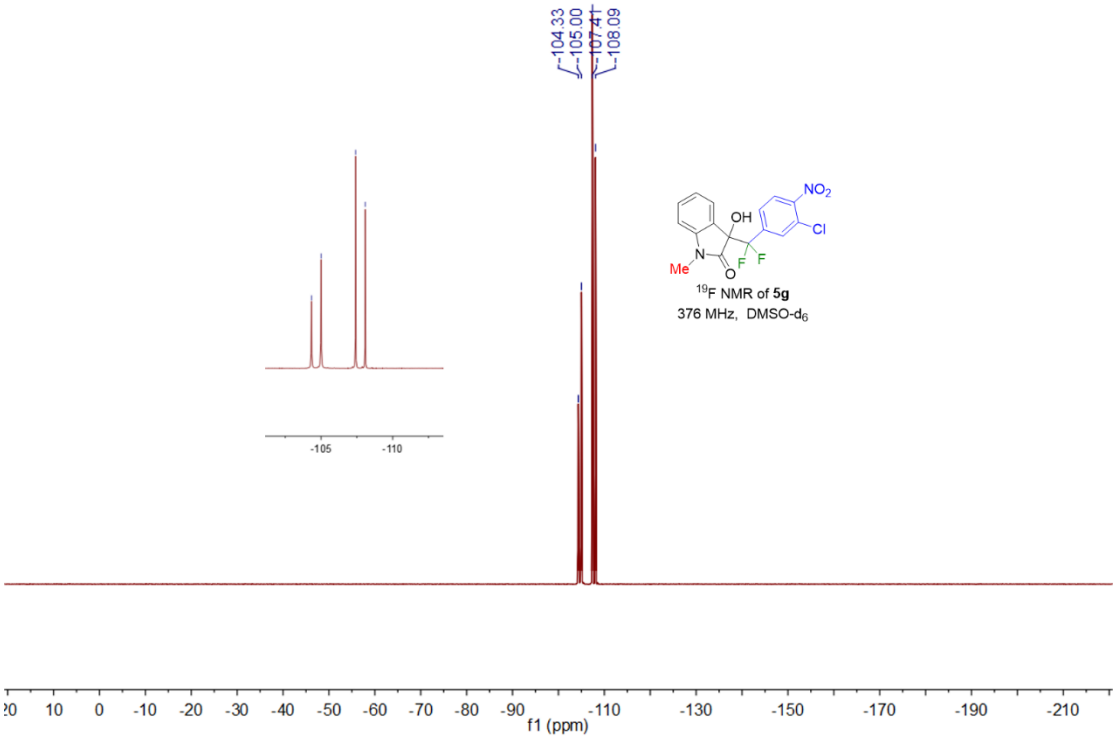

8.26
8.24
8.22
7.50
7.50
7.47
7.47
7.45
7.43
7.41
7.41
7.25
7.23
7.12
7.10
7.09
7.09
7.05
7.04
3.33
3.09
2.51
2.50
2.50
2.50
2.49
NO2
OH
Me
N
O
F
F
F
1H NMR of 5f
400 MHz, DMSO-d6
1.01
1.06
2.98
1.02
1.01
1.00
3.00
f1 (ppm)


171.78
154.75
152.15
144.06
130.88
125.83
125.75
125.20
124.13
124.11
124.07
122.65
108.98
77.41
77.13
77.10
76.82
40.13
39.92
39.71
39.50
39.29
39.08
38.87
26.11
NO2
OH
F
N
Me
O
F
F
13C NMR of 5f
101 MHz, DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

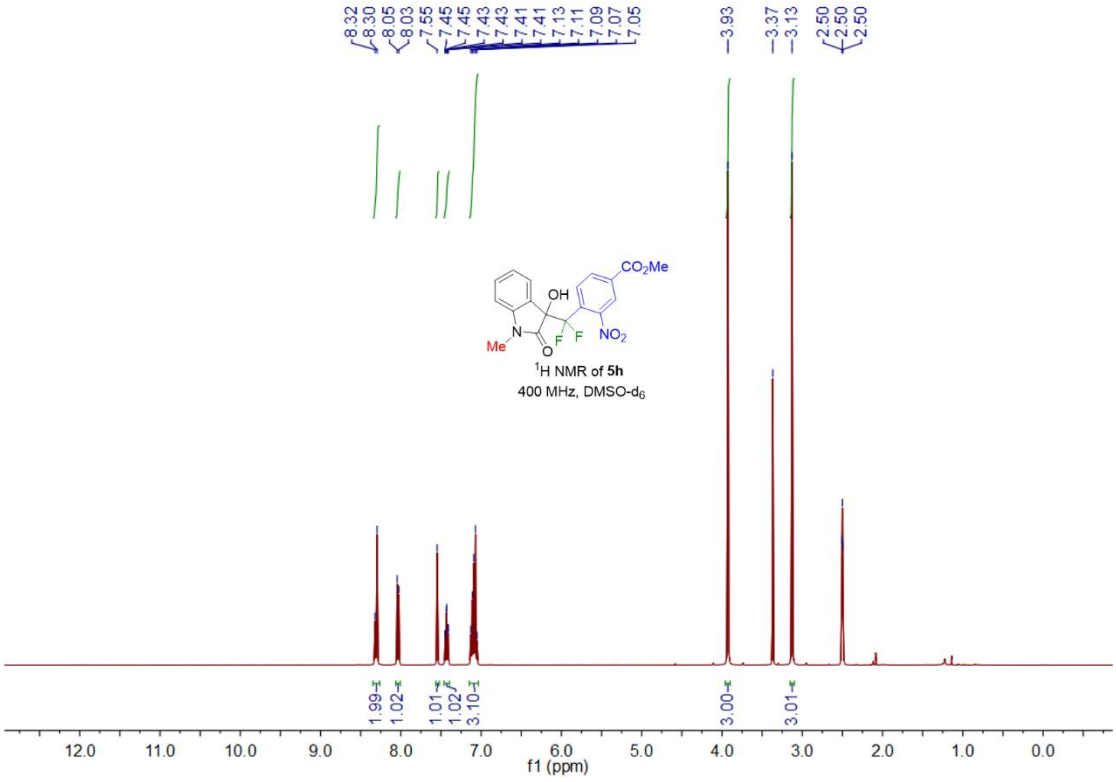

104.93
105.60
107.03
107.70
118.95
-104 -106 -108 -110
NO2
OH
F
N
Me
O
F
F
19F NMR of 5f
376 MHz, DMSO-d6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


8.17
8.15
7.66
7.60
7.58
7.46
7.44
7.42
7.32
7.30
7.14
7.12
7.11
7.06
7.04
3.38
3.40
2.50
NO2
Cl
OH
N
Me
O
F
F
1H NMR of 5g
400 MHz, DMSO-d6
0.98
0.97
1.01
2.00
1.00
1.00
0.99
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

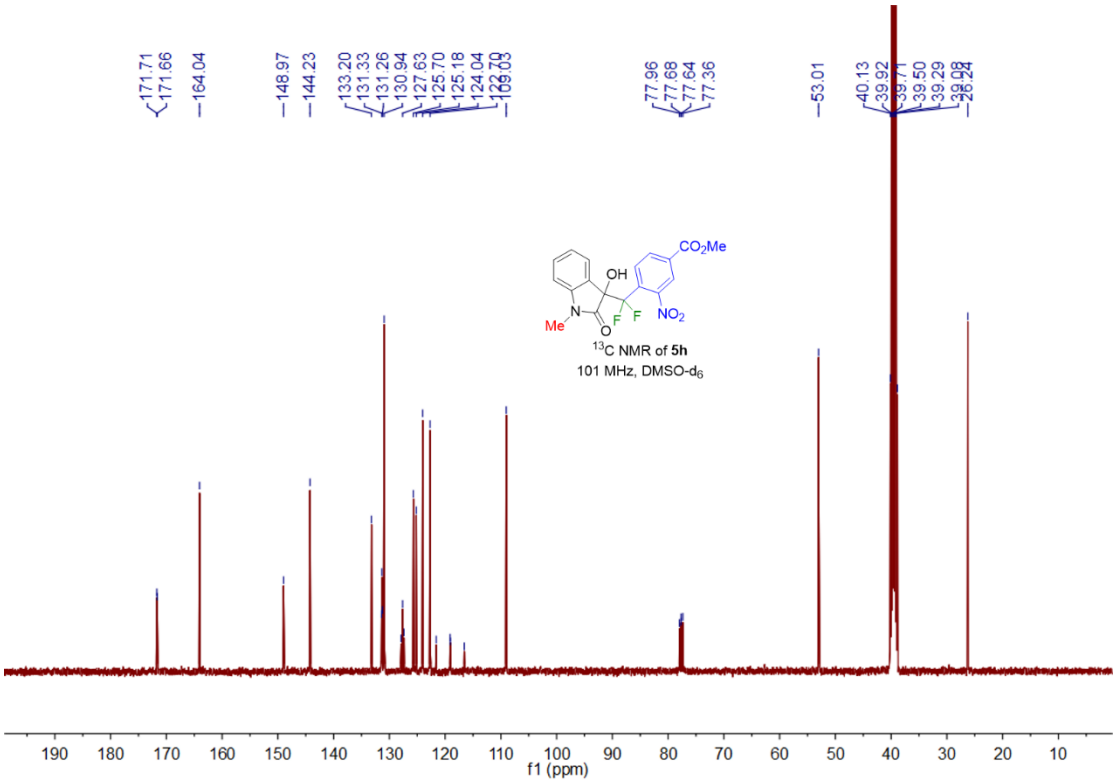

171.85
171.80
148.57
144.09
137.53
130.90
130.30
130.24
130.17
127.65
127.58
127.52
125.89
125.28
125.01
124.28
77.44
77.17
76.85
40.13
39.92
39.71
39.50
39.29
39.08
38.87
26.14
NO2
Cl
OH
N
Me
O
F
F
13C NMR of 5g
101 MHz, DMSO-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

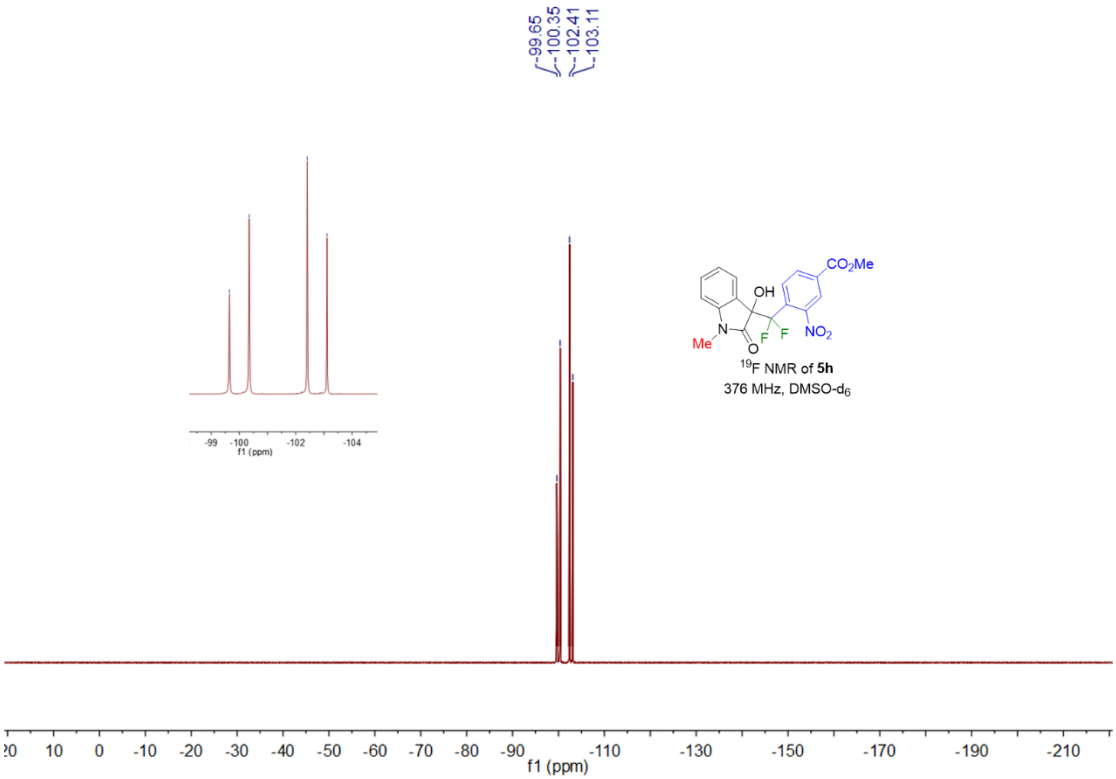


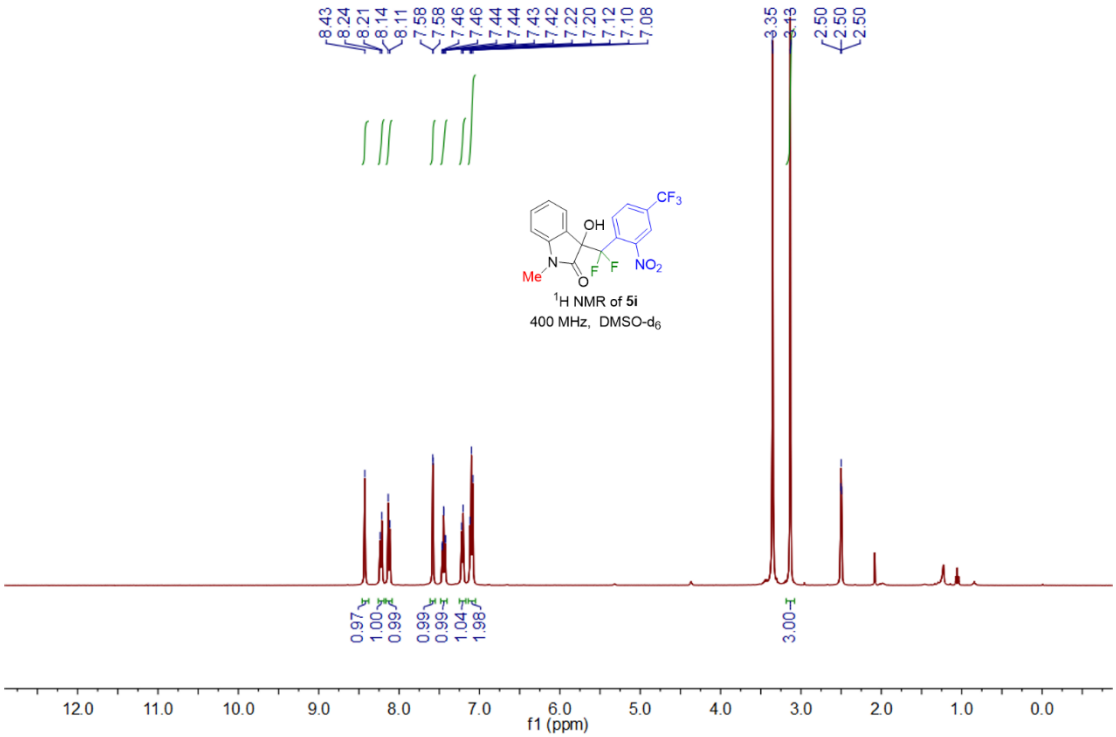
^{19}F NMR of **5g**
376 MHz, DMSO-d_6



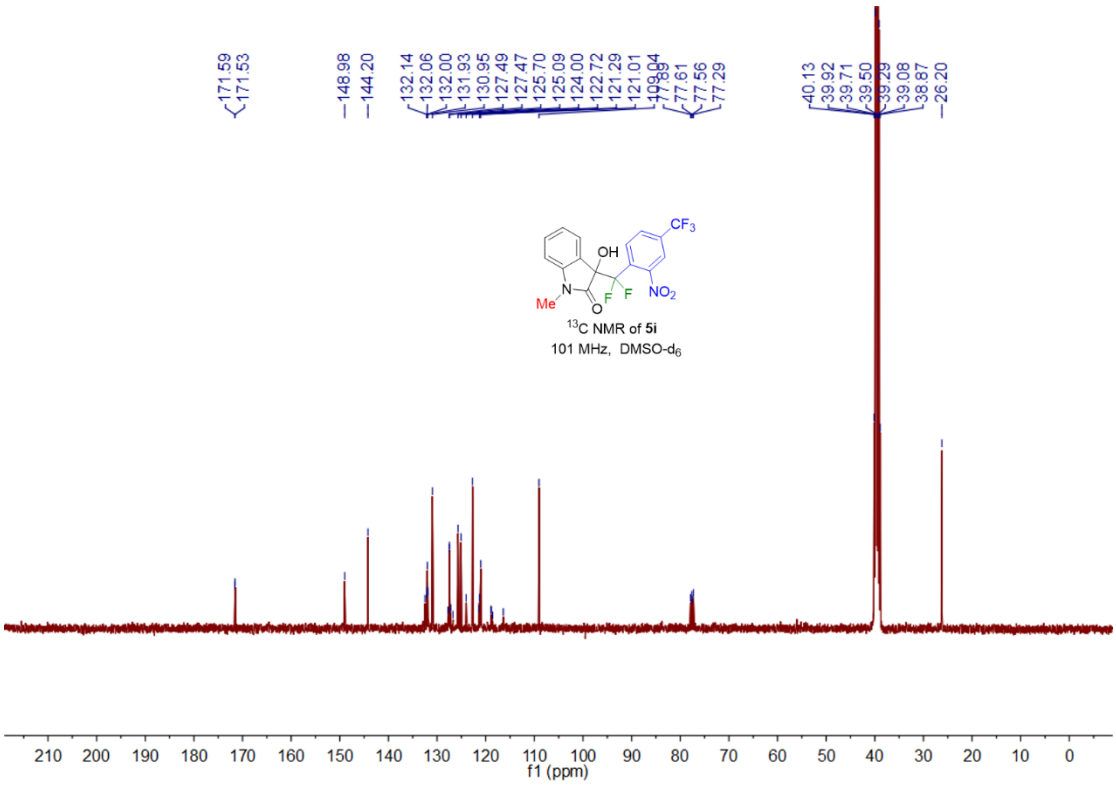
^{1}H NMR of **5h**
400 MHz, DMSO-d_6


171.71
171.66
164.04
148.97
144.23
133.20
131.33
131.26
130.94
127.63
125.70
125.18
124.04
77.96
77.68
77.64
77.36
53.01
40.13
39.92
39.71
39.50
39.29
26.24
CO2Me
OH
Me
N
O
F
F
NO2
13C NMR of 5h
101 MHz, DMSO-d6
f1 (ppm)

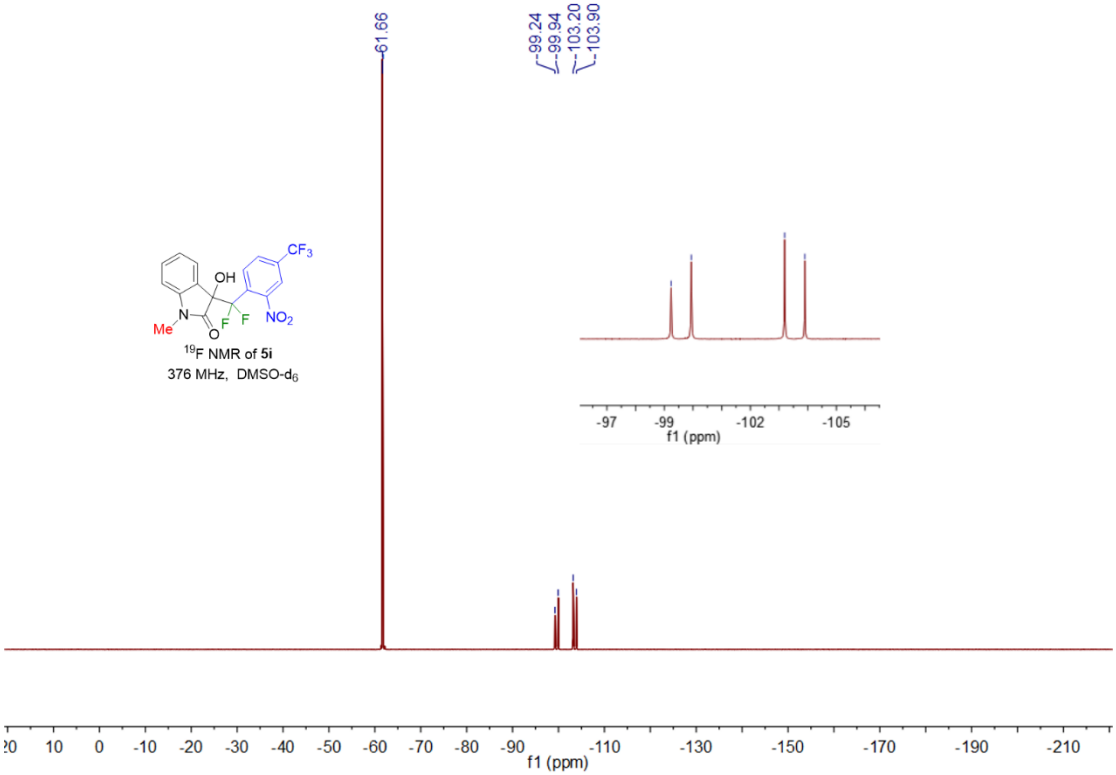

99.65
100.35
102.41
103.11
CO2Me
OH
Me
N
O
F
F
NO2
19F NMR of 5h
376 MHz, DMSO-d6
f1 (ppm)

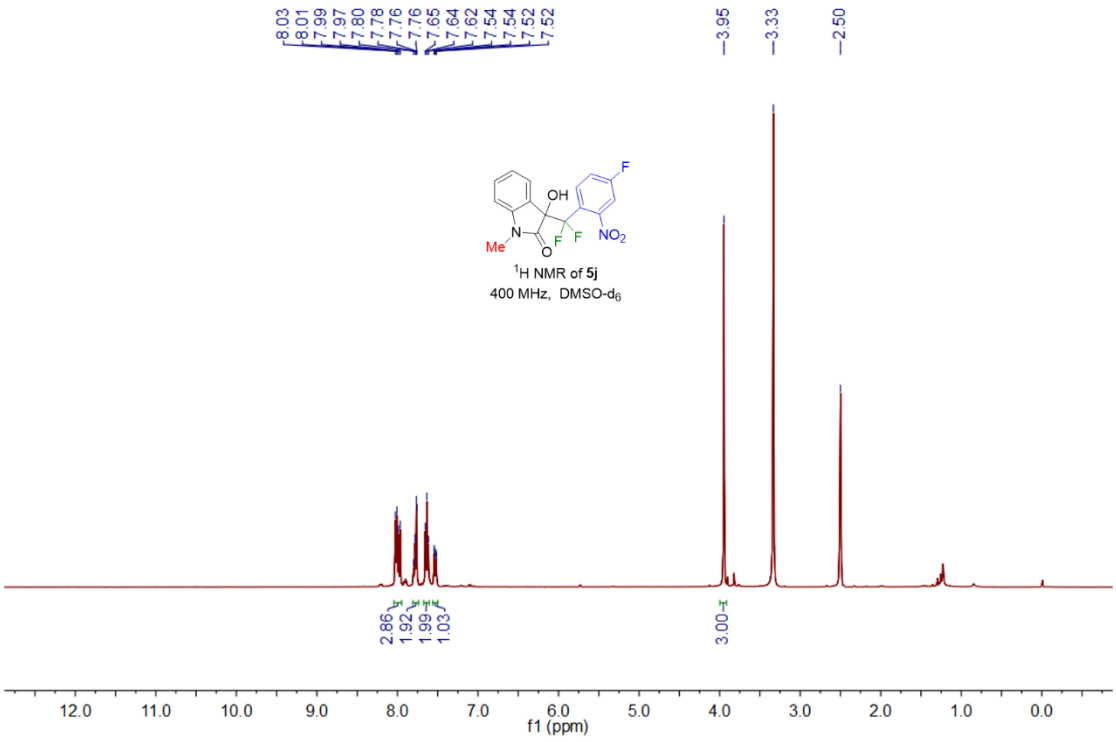


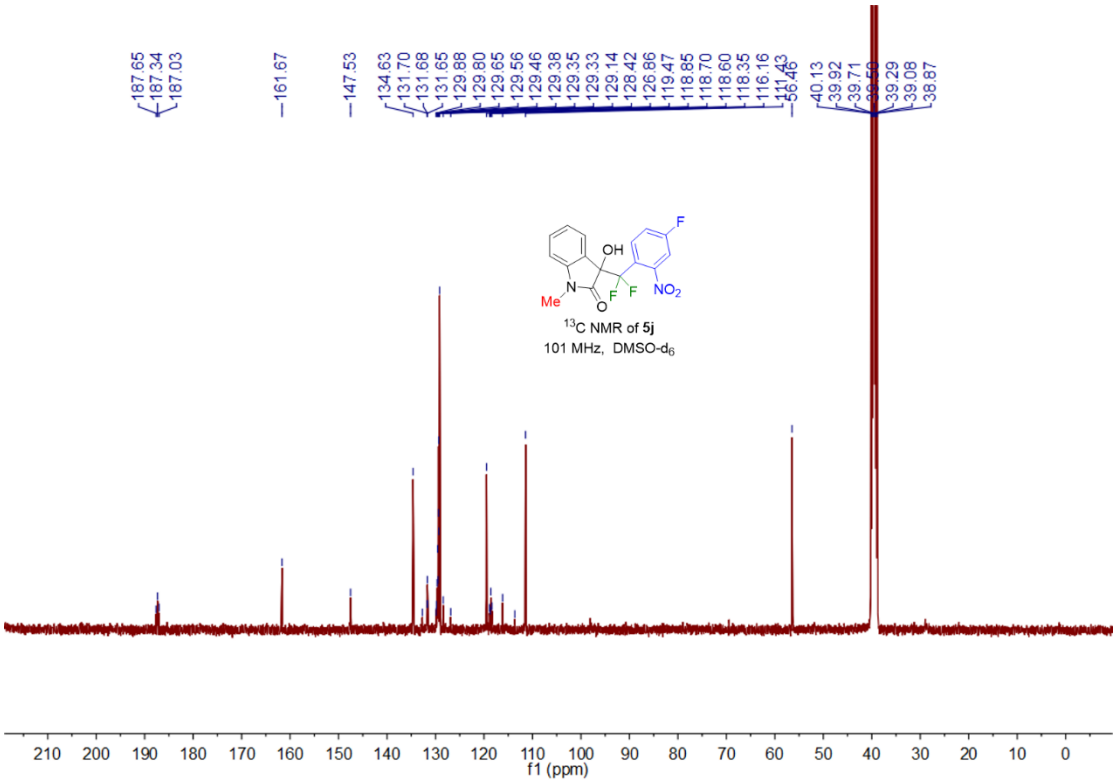
^{1}H NMR of **5i**
400 MHz, DMSO-d_6



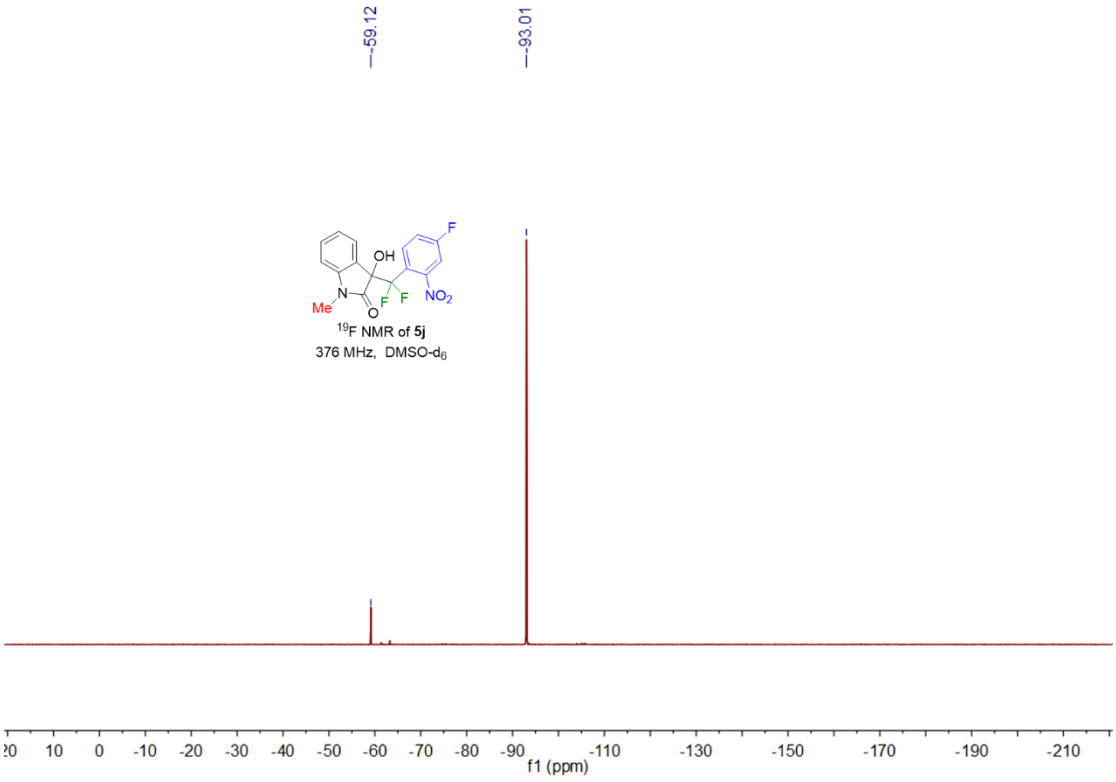
^{13}C NMR of **5i**
101 MHz, DMSO-d_6


61.66
-99.24
-99.94
-103.20
-103.90
CF3
OH
N
Me
O
F
F
NO2
19F NMR of 5i
376 MHz, DMSO-d6
-97
-99
-102
-105
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

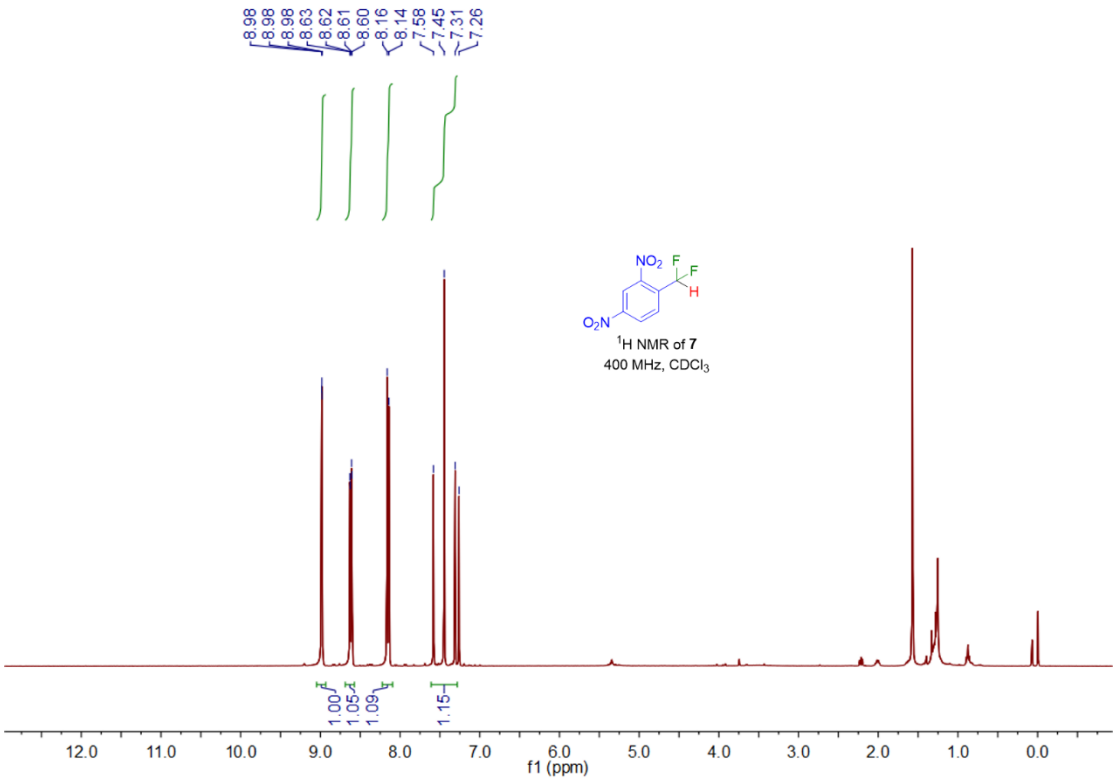

8.03
8.01
7.99
7.97
7.80
7.78
7.76
7.76
7.65
7.64
7.62
7.54
7.54
7.52
7.52
3.95
3.33
2.50
F
OH
N
Me
O
F
F
NO2
1H NMR of 5j
400 MHz, DMSO-d6
2.86
1.92
1.99
1.03
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

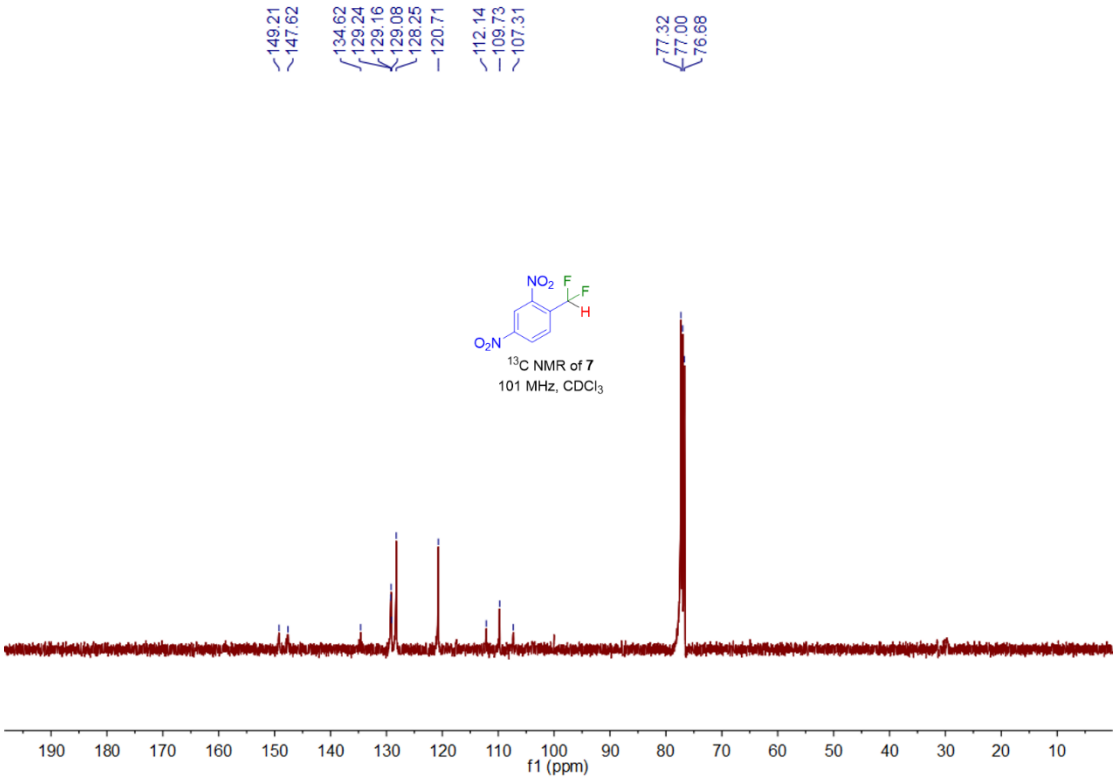


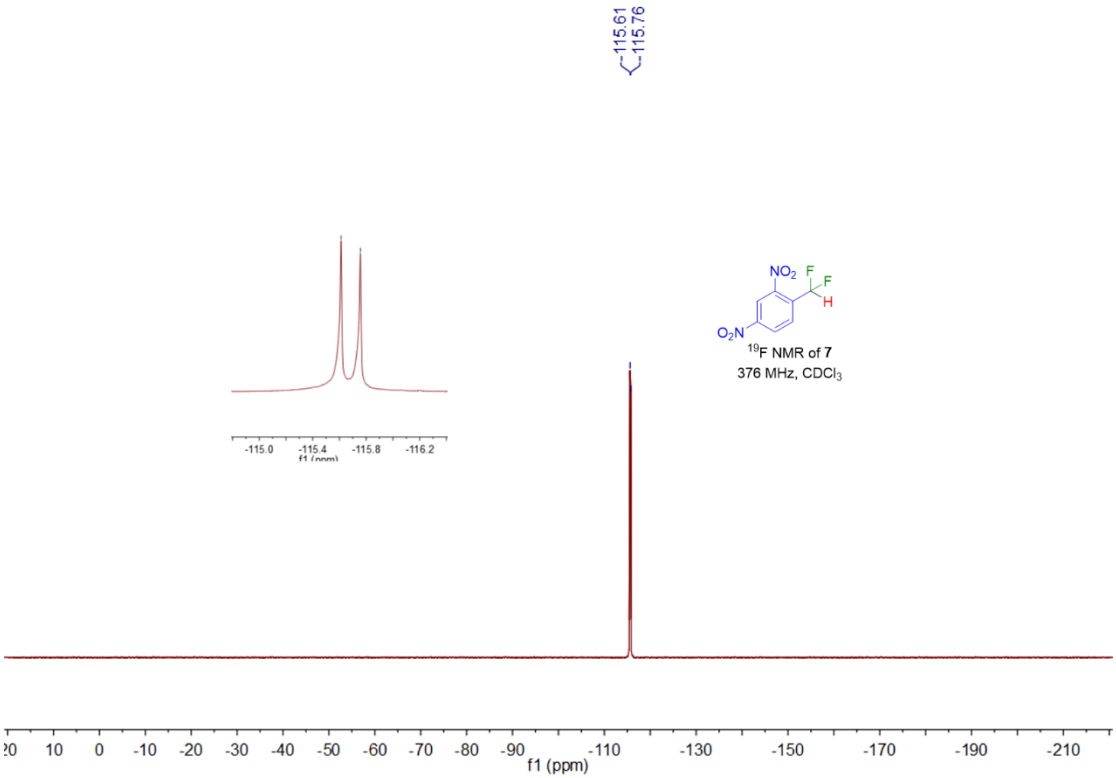
^{13}C NMR of **5j**
101 MHz, DMSO-d_6

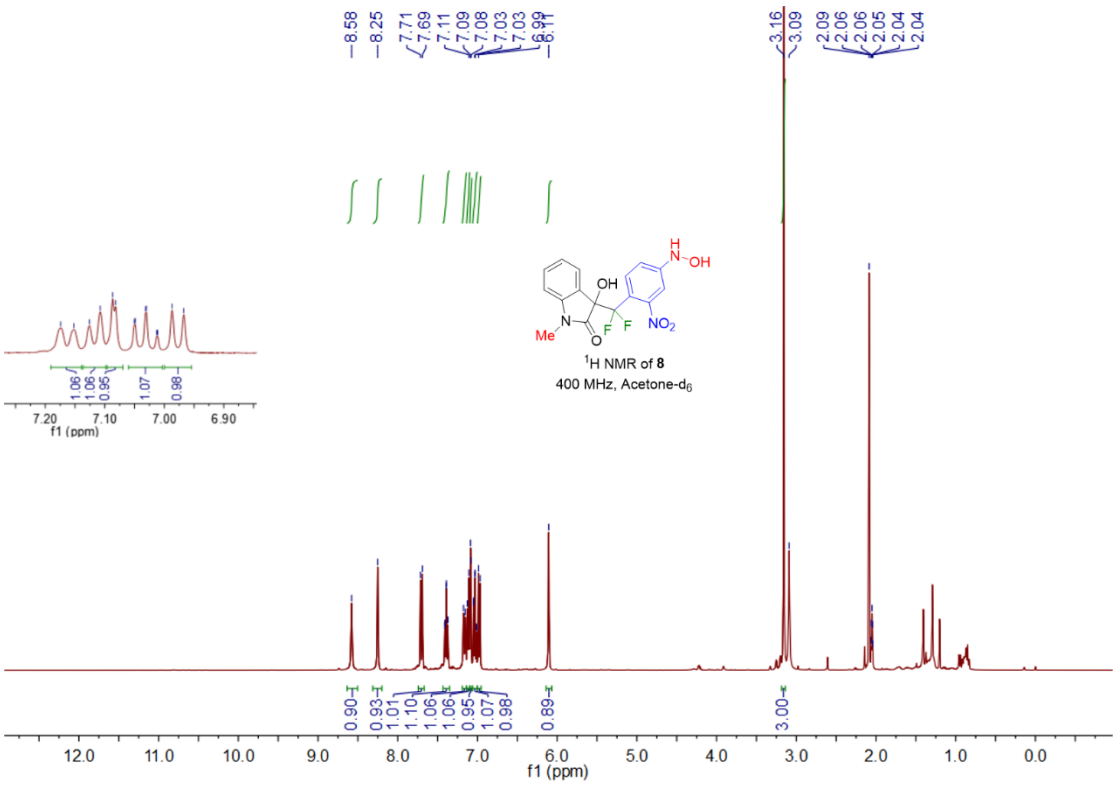


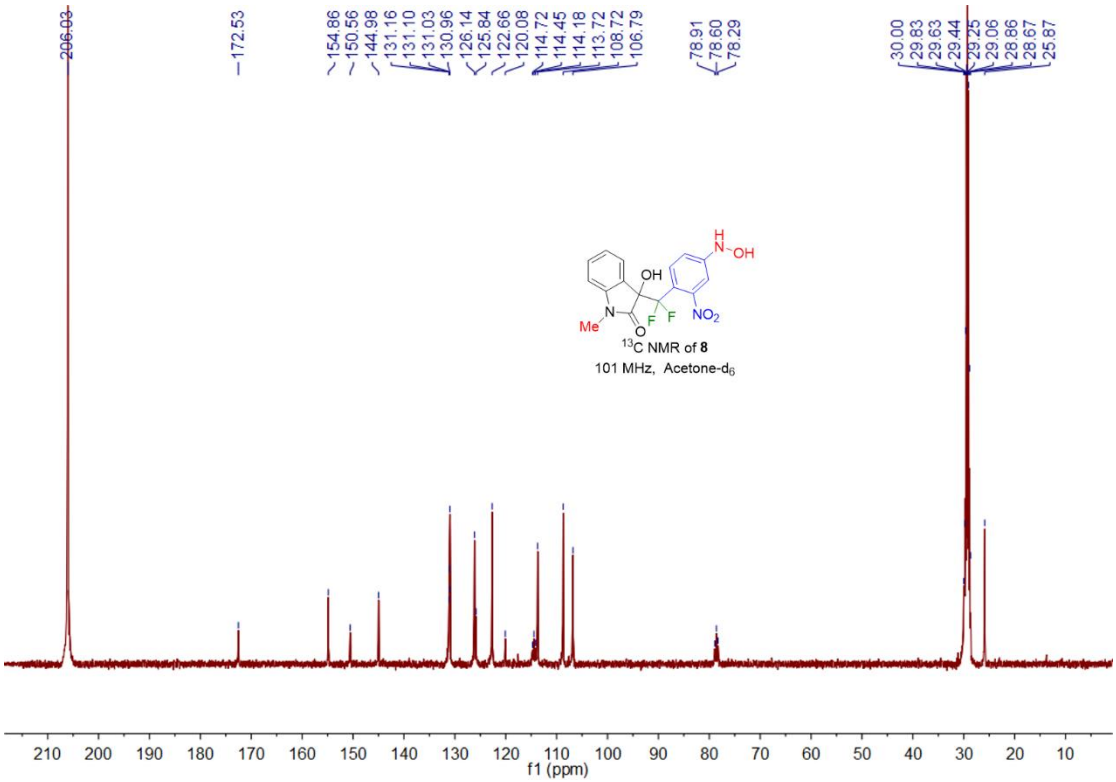
^{19}F NMR of **5j**
376 MHz, DMSO-d_6

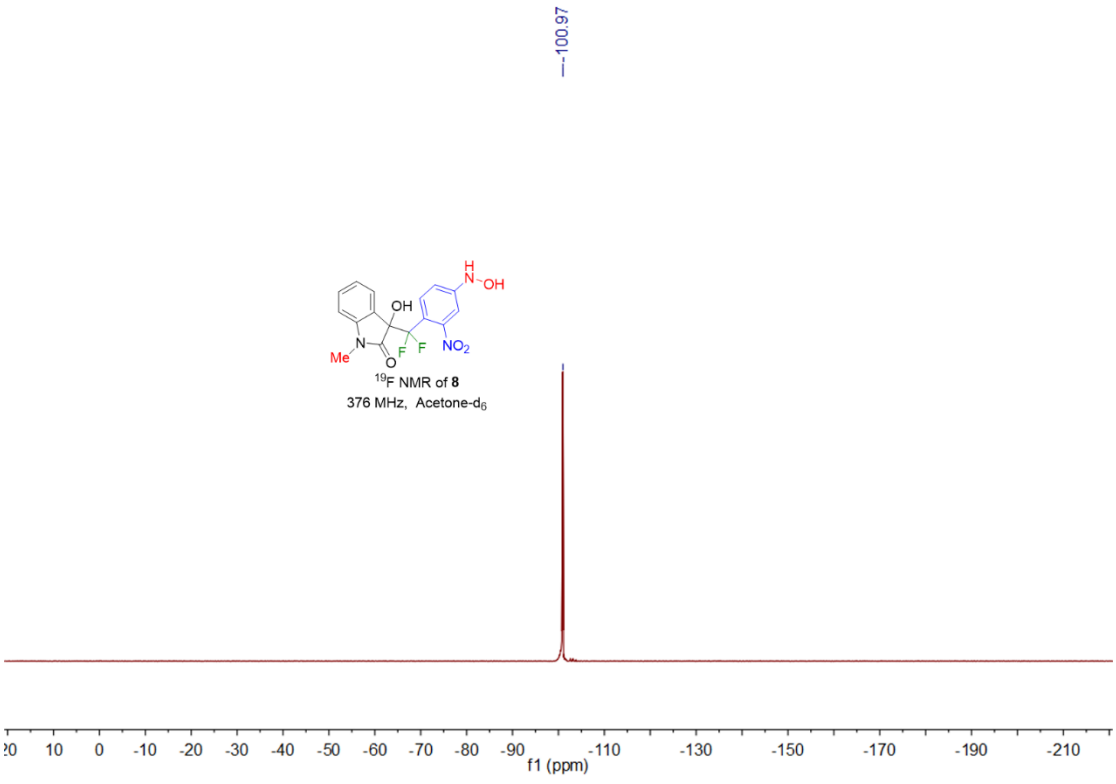

8.98
8.98
8.98
8.63
8.62
8.61
8.60
8.16
8.14
7.58
7.45
7.31
7.26
NO2
F
F
H
O2N
1H NMR of 7
400 MHz, CDCl3
1.00
1.05
1.09
1.15
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

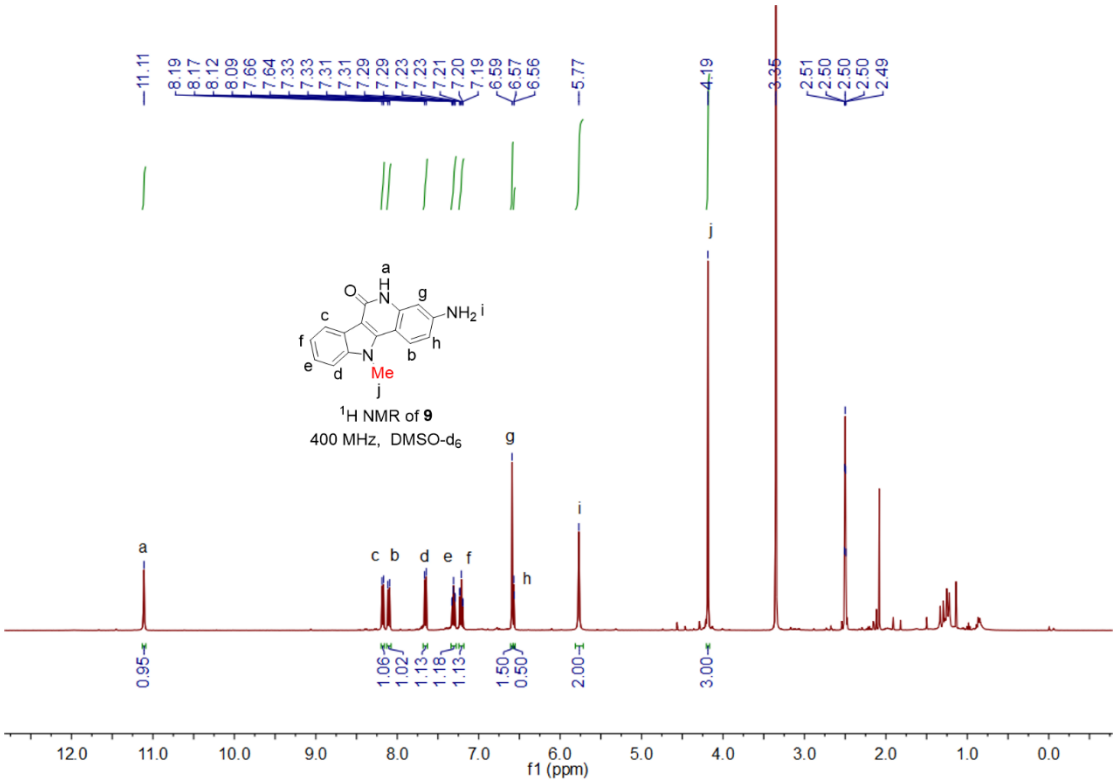

149.21
147.62
134.62
129.24
129.16
129.08
128.25
120.71
112.14
109.73
107.31
77.32
77.00
76.68
NO2
F
F
H
O2N
13C NMR of 7
101 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

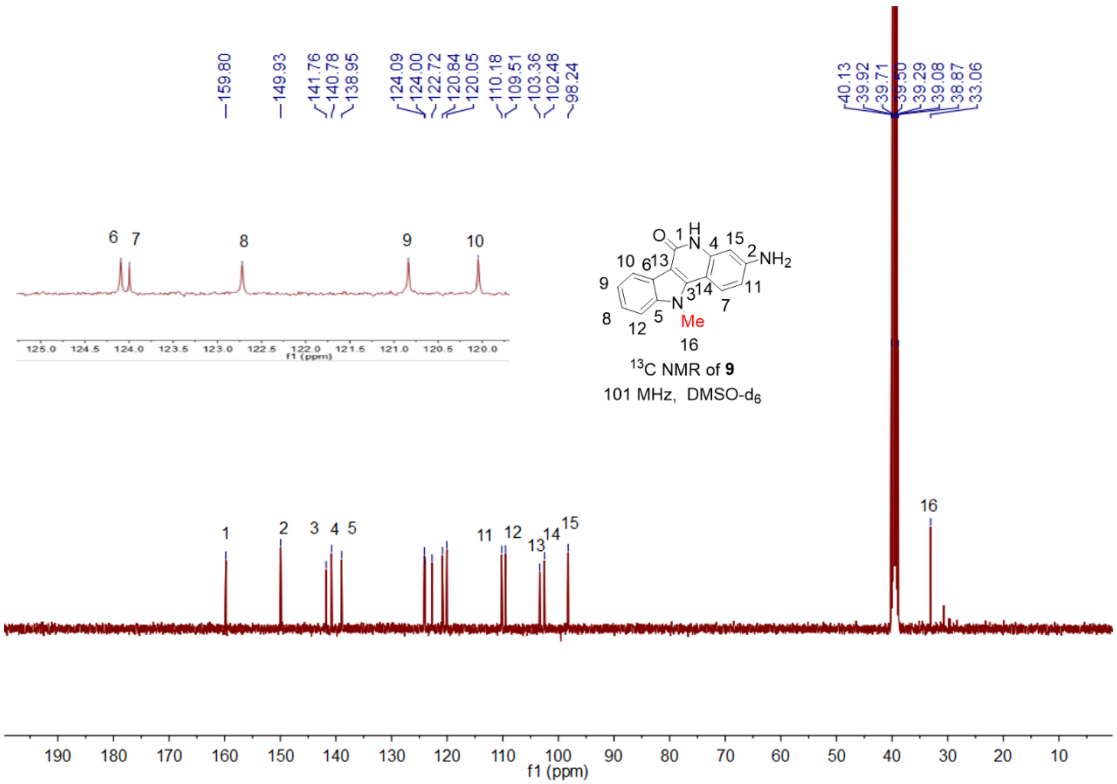

115.61
115.76
-115.0
-115.4
-115.8
-116.2
f1 (ppm)
^{19}F NMR of **7**
376 MHz, $CDCl_3$
f1 (ppm)

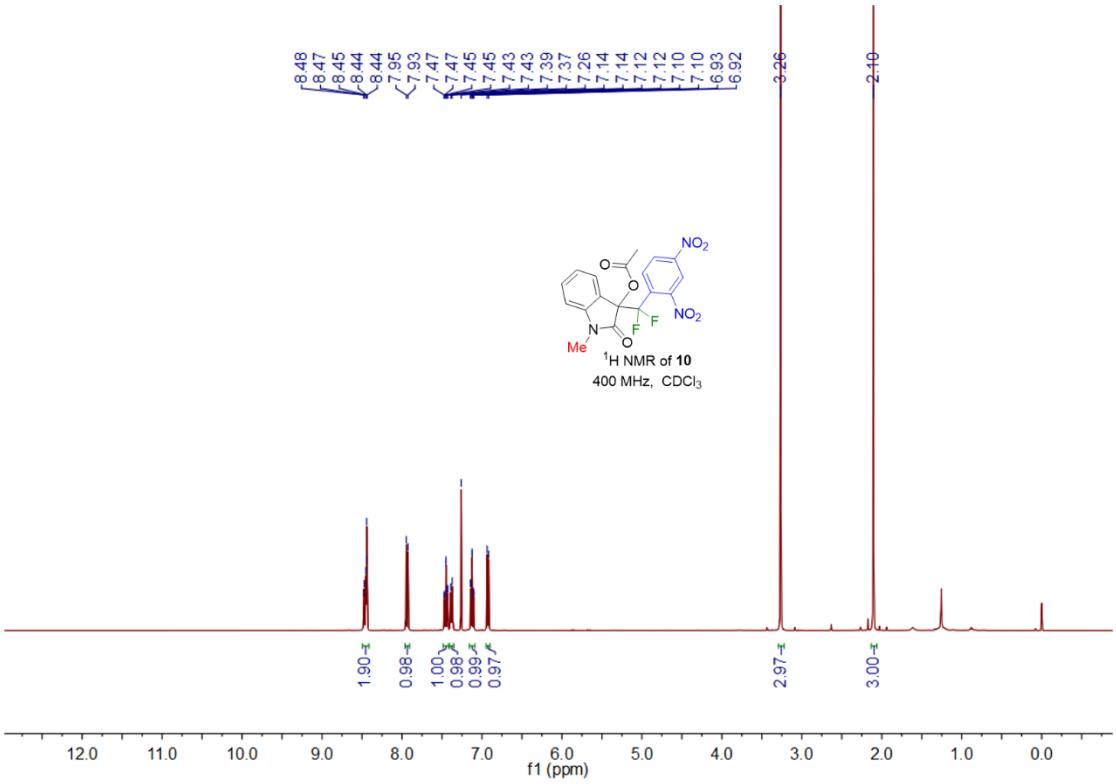

8.58
8.25
7.71
7.69
7.11
7.09
7.08
7.03
7.03
6.99
6.91
3.16
3.09
2.09
2.06
2.06
2.05
2.04
2.04
1.06
1.06
0.95
1.07
0.98
7.20
7.10
7.00
6.90
f1 (ppm)
^{1}H NMR of **8**
400 MHz, Acetone-d_6
0.90
0.93
1.01
1.10
1.06
1.06
0.95
1.07
0.98
0.89
3.00
f1 (ppm)

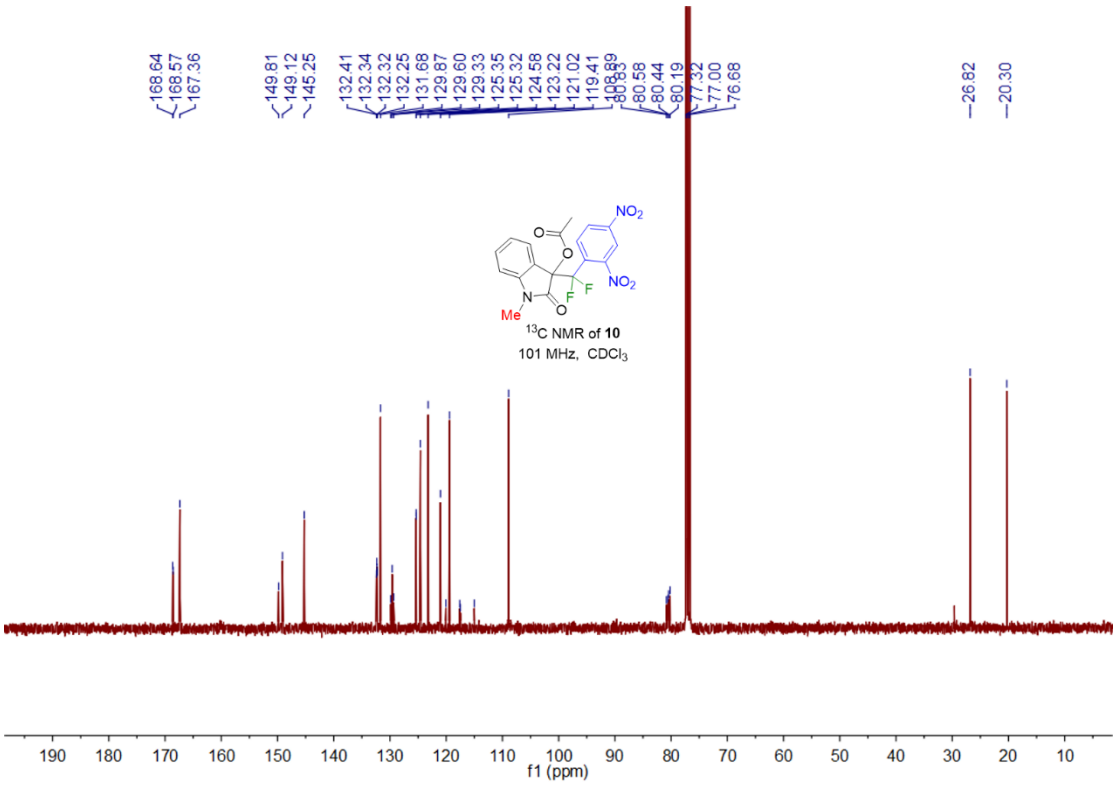

206.03
172.53
154.86
150.56
144.98
131.16
131.10
131.03
130.96
126.14
125.84
122.66
120.08
114.72
114.45
114.18
113.72
108.72
106.79
78.91
78.60
78.29
30.00
29.83
29.63
29.44
29.25
29.06
28.86
28.67
25.87
OH
N
Me
O
F
F
NO2
H
N
OH
13C NMR of 8
101 MHz, Acetone-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

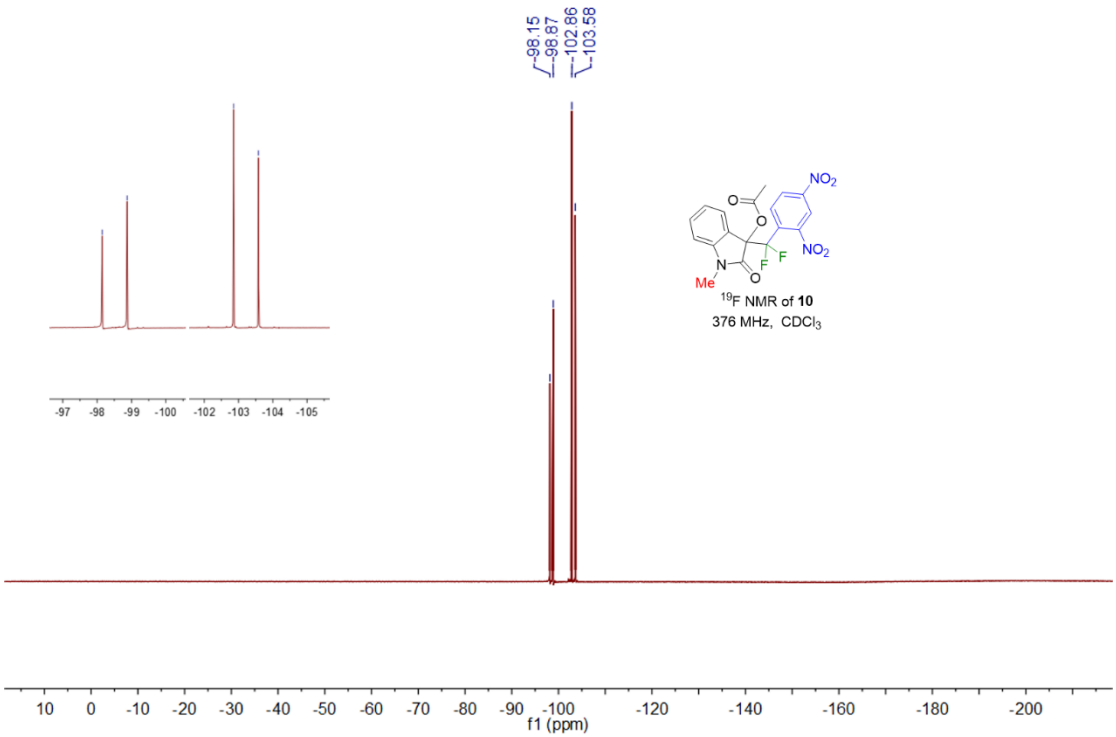

-100.97
OH
N
Me
O
F
F
NO2
H
N
OH
19F NMR of 8
376 MHz, Acetone-d6
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)


11.11
8.19
8.17
8.12
8.09
7.66
7.64
7.33
7.33
7.31
7.31
7.29
7.29
7.23
7.23
7.21
7.20
7.19
6.59
6.57
6.56
5.77
4.19
3.35
2.51
2.50
2.50
2.50
2.49
a
b
c
d
e
f
g
h
i
j
0.95
1.06
1.02
1.13
1.18
1.13
1.50
0.50
2.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
Me
NH2
1H NMR of 9
400 MHz, DMSO-d6

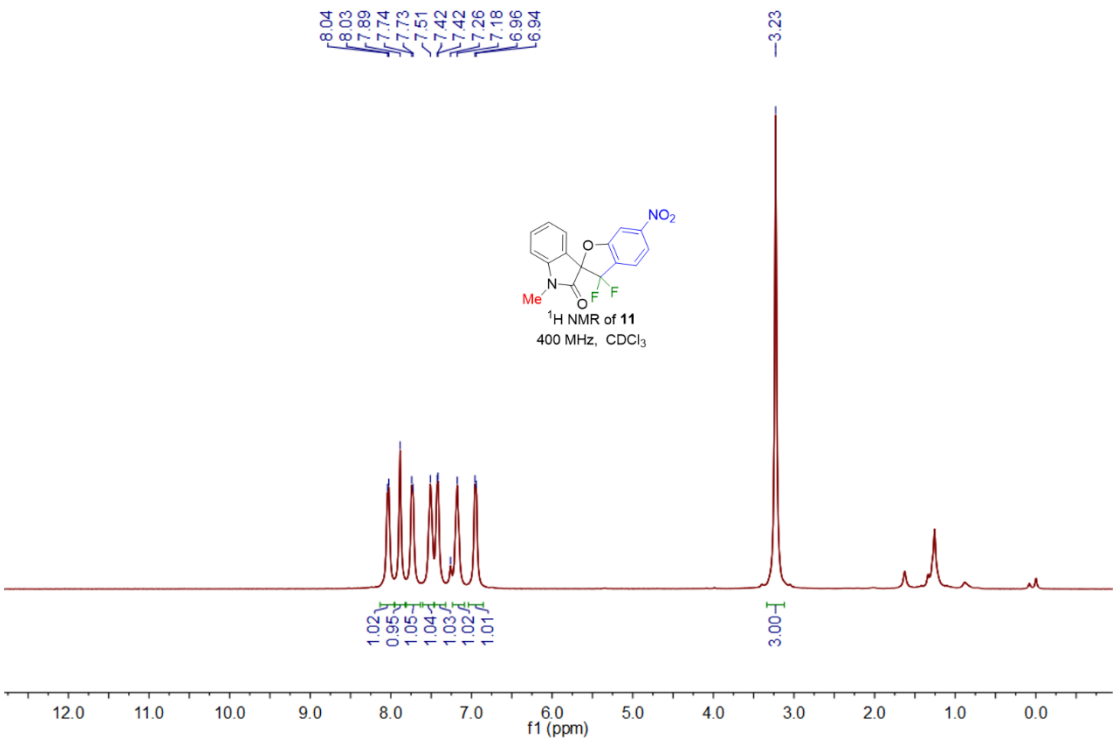

159.80
149.93
141.76
140.78
138.95
124.09
124.00
122.72
120.84
120.05
110.18
109.51
103.36
102.48
98.24
40.13
39.92
39.71
39.50
39.29
39.08
38.87
33.06
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
Me
NH2
13C NMR of 9
101 MHz, DMSO-d6


8.48
8.47
8.45
8.44
8.44
7.95
7.93
7.47
7.47
7.45
7.45
7.43
7.43
7.39
7.37
7.26
7.14
7.14
7.12
7.12
7.10
7.10
6.93
6.92
3.26
2.10
NO2
NO2
O
O
F
F
N
Me
O
1H NMR of 10
400 MHz, CDCl3
1.90
0.98
1.00
0.98
0.99
0.97
2.97
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

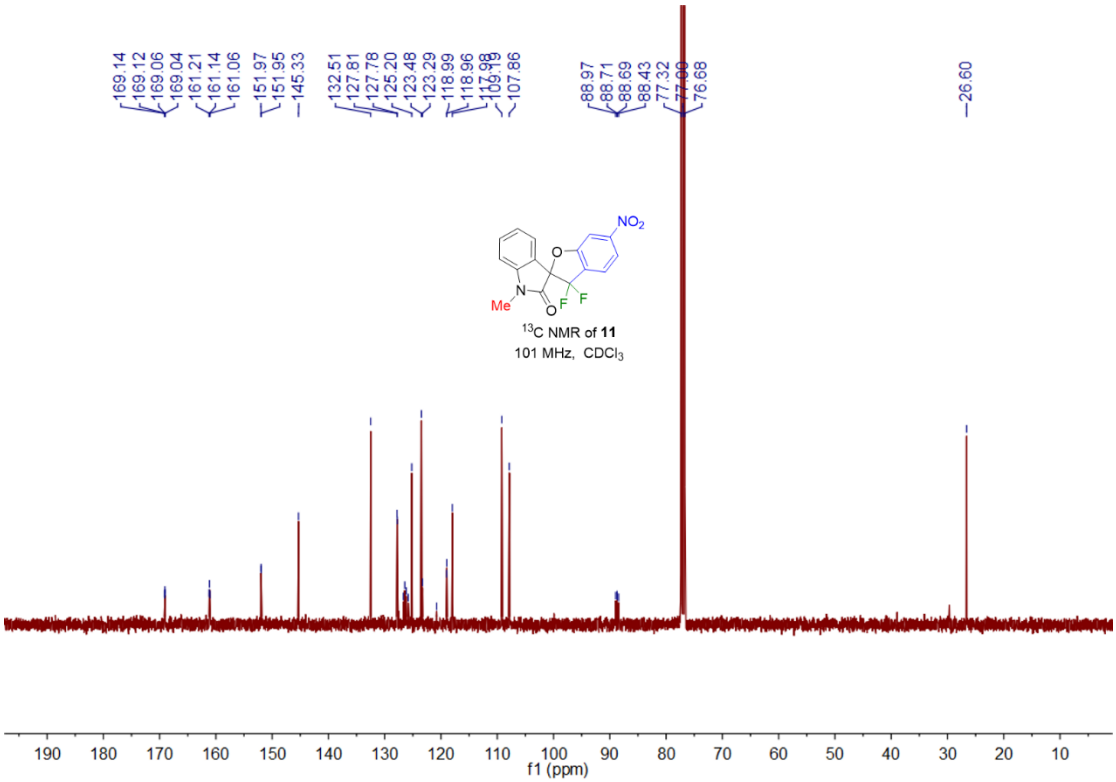

168.64
168.57
167.36
149.81
149.12
145.25
132.41
132.34
132.32
132.25
131.68
129.87
129.60
129.33
125.35
125.32
124.58
123.22
121.02
119.41
80.58
80.44
80.19
77.32
77.00
76.68
26.82
20.30
NO2
NO2
O
O
F
F
N
Me
O
13C NMR of 10
101 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



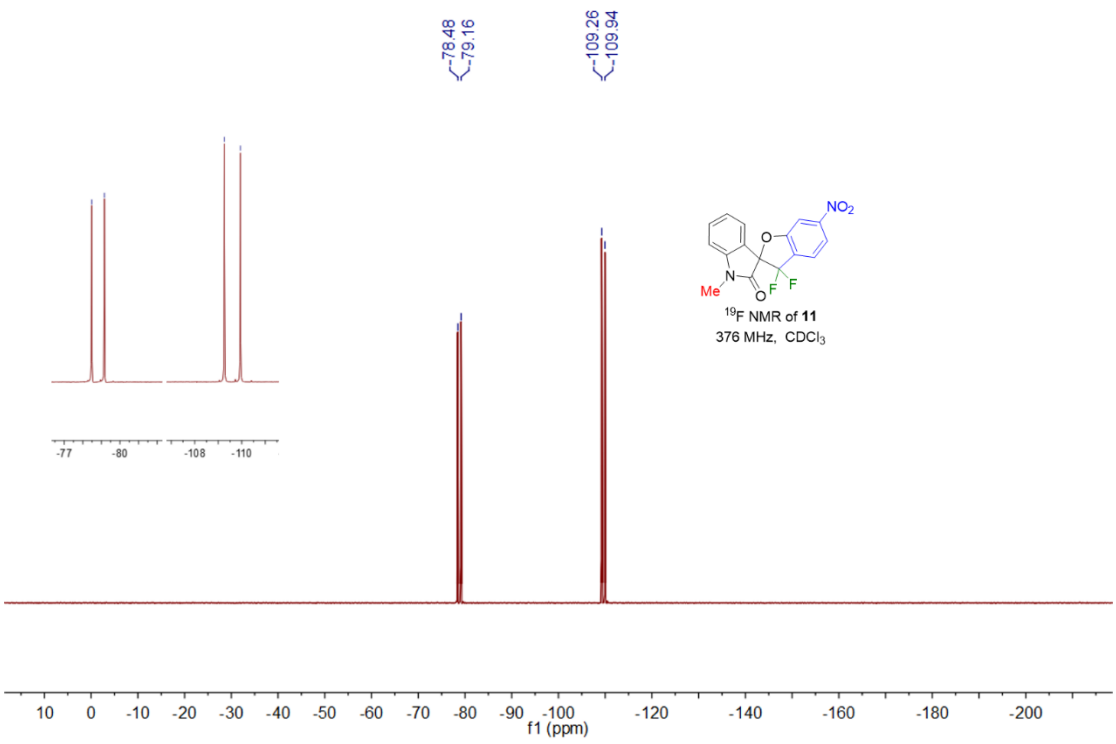
^{19}F NMR of **10**
376 MHz, $CDCl_3$



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



^{13}C NMR of **11**
101 MHz, $CDCl_3$



^{19}F NMR of **11**
376 MHz, $CDCl_3$