Supporting Information

Electrochemical C(sp^2)−H Deuterodifluoromethylation of Quinoxalinones and 2*H*-Indazoles with CF_2DSO_2Na

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Contents

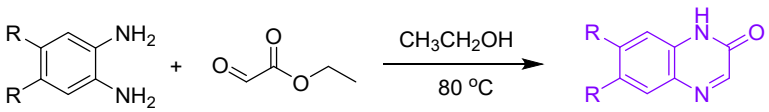
1. General information

Unless specifically emphasized, chemicals and materials used in the experiments were purchased from suppliers and used directly without further purification. Thin layer chromatography (TLC) was performed to monitor the reactions, which were carried out on commercially available GF254 plates (0.25 mm layer thickness) using 254 nm UV light as a visualizing agent. Column chromatography was performed with 200-300 mesh silica gels. NMR spectra were recorded on Bruker AVANCE NEO 400 MHz (resonance frequencies 400 MHz for ^{1}H, 101 MHz for ^{13}C and 377 MHz for ^{19}F) spectrometer with D_2O, $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard. In the ^{19}F NMR spectra, the signal that was marked but unassigned to the product corresponds to the difluoromethyl group (-CF_2H). High resolution mass spectra (HRMS) were measured with an Agilent 6230 TOF instrument. Deuterium incorporation was determined by ^{19}F NMR according to the equation below:

$$Deuterium\ incorporation\ (\%) = \frac{Area(CF_2D)}{Area(CF_2D) + Area(CF_2H)}$$

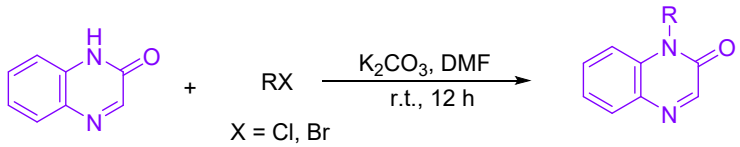
(equation S1)

2. General procedure for the synthesis of quinoxalinones (1)



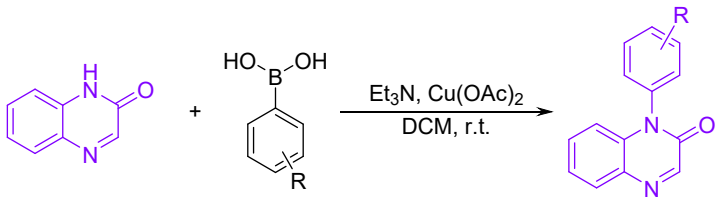
Quinoxalinones (**1a-1e**) were synthesized according to the procedure below.[1]

In a dry two-necked round-bottom flask, a mixture of benzene-1,2-diamine (1.0 equiv.) and ethyl 2-oxoacetate (1.2 equiv.) in ethanol (EtOH) was stirred and heated to 80 °C. The reaction was monitored by TLC until the complete consumption of benzene-1,2-diamine was observed. The mixture was then cooled to room temperature and subsequently to 0 °C, with stirring maintained for an additional 0.5 h. The solid product was collected by filtration, and the filter cake was thoroughly washed with EtOH at 0 °C. Finally, the filter cake was dried under reduced pressure at 70 °C to obtain quinoxalinones **1a-1e**.



Quinoxalinones (**1f-1s**) were synthesized according to the procedure below.[1]

A mixture of quinoxalin-2(1*H*)-one (1.0 equiv.), the appropriate alkyl halide (1.6 equiv.), and K_2CO_3 (1.2 equiv.) in DMF was stirred at 25 °C and monitored by TLC until complete consumption of the starting material. Upon completion, the reaction mixture was diluted with ethyl acetate (EA) and washed three times with saturated brine. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (eluent: petroleum ether (PE)/EA) to afford the N-alkylated products **1f-1s**.



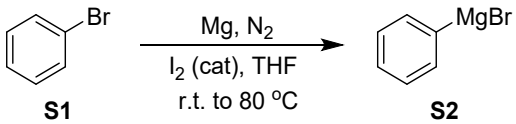
Quinoxalinones (**1t-1y**) were synthesized according to the procedure below.[1]

A dry round-bottom flask was charged with quinoxalin-2(1*H*)-one (1.0 equiv.), phenylboronic acid (2.0 equiv.), $Cu(OAc)_2$ (1.0 equiv.), and triethylamine (1.0 equiv.) in dichloromethane (DCM). The reaction mixture was stirred at 25 °C and monitored by TLC until complete consumption of the starting material. The mixture was then directly absorbed onto silica gel, and the solvent was removed under reduced pressure. The resulting powder was purified by silica gel column chromatography (eluent: PE/EA) to afford the products **1t-1y**.

3. Synthesis of sodium difluoromethylsulfinate (2)

Sodium difluoromethylsulfinate (**2**) was synthesized according to the literature.[2]

Step 1:

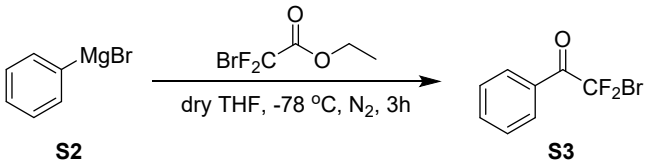


A dry three-necked flask, equipped with a magnetic stirrer, was charged with magnesium turnings (60.0 mmol, 1.44 g, 2.0 equiv.) and a catalytic amount of iodine (I_2). The flask was purged with N_2 (three times). Under an N_2 atmosphere, anhydrous tetrahydrofuran (THF, 20.0 mL) was added. A solution of bromobenzene (**S1**, 30.0 mmol, 4.71 g, 1.0 equiv.) in THF (10.0 mL) was added dropwise via a constant-pressure dropping funnel. (Note: to facilitate the formation of the Grignard reagent, a hairdryer should be used to heat the reaction until it initiates.) After the addition was complete,

the mixture was heated to reflux (approx. 80 °C) for 3–5 hours. Upon completion, the resulting Grignard reagent solution (**S2**, yield > 99.0% as determined by titration) was used directly in the next step without further purification.

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{180.0}{156.0 + 2} = 100\%$$

Step 2:

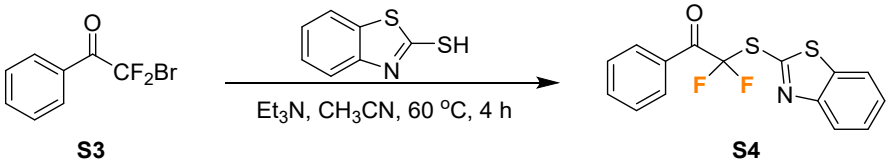


S2 **S3**

A reaction flask equipped with a mechanical stirrer was charged with ethyl 2,2-difluoro-3-bromopropanoate (25.0 mmol, 5.07 g, 1.0 equiv.) and THF (30.0 mL). The flask was evacuated and backfilled with N_2 (three times). Under an N_2 atmosphere, a freshly prepared solution of phenylmagnesium bromide in THF (**S2**, 1.0 M in THF, 30.0 mmol, 30.0 mL 1.2 equiv.) was added dropwise at –78 °C. After stirring at this temperature for 3 h, the reaction was carefully quenched with 3.0 M aqueous HCl. The mixture was extracted with EA, and the combined organic extracts were dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude residue, which was purified by silica gel column chromatography (eluent: PE) to yield the product **S3** (5.30 g, 22.8 mmol, 91% yield).

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{234.0}{180.0 + 2} = 61.3\%$$

Step 3:



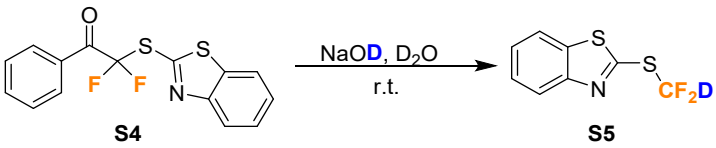
S3 **S4**

A mixture of 2-mercaptobenzothiazole (45.0 mmol, 7.54 g, 1.5 equiv.) and triethylamine (Et_3N, 6.0 mL, 2.0 equiv.) in acetonitrile (CH_3CN, 50.0 mL) was stirred at room temperature for 5 minutes. Compound **S3** (30.0 mmol, 7.06 g, 1.0 equiv.) was then added, and the resulting mixture was stirred at 60 °C until complete consumption of **S3** (monitored by TLC). The CH_3CN was removed under reduced pressure. The

residue was taken up in EA, and the resulting solution was washed sequentially with water and saturated sodium chloride solution, then dried over anhydrous Na_2SO_4. After filtration and concentration, the crude product was purified by silica gel column chromatography (eluent: PE/EA) to afford **S4** (9.16 g, 28.6 mmol, 95% yield).

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{321.0}{234.0 + 1} = 80.0\%$$

Step 4:

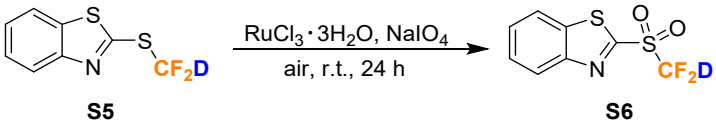


S4 **S5**

S4 (30.0 mmol, 9.64 g, 1.0 equiv.) was added to a dry reaction flask, which was purged with N_2 three times. Subsequently, under N_2 atmosphere, NaOD in D_2O (40 wt%, 45.0 mmol, 4.61 g, 1.5 equiv.) and D_2O (532.5 mmol, 10.65 g, 17.75 equiv.) were added. The mixture was stirred at 25 °C until the reaction was complete (monitored by TLC). Then, the reaction mixture was extracted with DCM, D_2O could be recovered via straightforward distillation. The DCM phase was dried over sodium sulfate (Na_2SO_4) and concentrated in vacuum. The product **S5** (29.4 mmol, 6.41 g, 98% yield, 98% D-inc) was isolated by purification of the residue by thin layer chromatography using petroleum ether (PE) and ethyl acetate (EA) as eluent.

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{218.0}{321.0 + 4} = 60.2\%$$

Step 5:



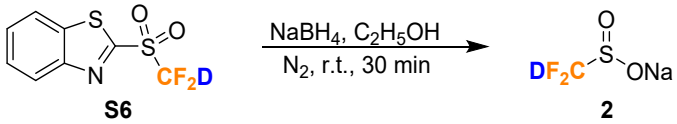
S5 **S6**

A reaction flask was charged with **S5** (20.0 mmol, 4.36 g, 1.0 equiv.), $RuCl_3 \cdot 3H_2O$ (0.20 mmol, 0.05 g, 0.01 equiv.), and a solvent mixture of CH_3CN/DCM/H_2O (1.0:1.0:2.0, 64.0 mL). Sodium periodate ($NaIO_4$, 40.0 mmol, 8.55 g, 2.0 equiv.) was then added in one portion with stirring. The resulting mixture was stirred at room temperature for 24 h (monitored by TLC). Upon completion, the mixture was carefully neutralized to pH = 7.0 with a saturated aqueous $NaHCO_3$ solution. The mixture was

filtered, and the solid residue was rinsed thoroughly with EA. The filtrate was extracted with EA, and the combined organic phases were dried over anhydrous Na_2SO_4. Concentration under reduced pressure afforded the crude residue, which was purified by silica gel column chromatography (eluent: PE/EA) to yield the product **S6** (19.2 mmol, 4.80 g, 96% yield, 98% D-inc).

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{250.0}{218.0 + 2} = 57.9\%$$

Step 6:

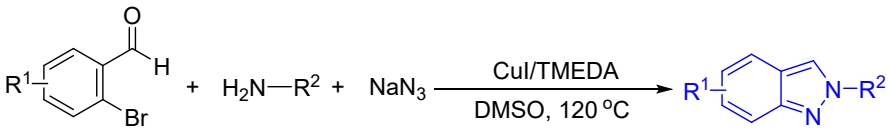


S6 **2**

A dry reaction flask equipped with a magnetic stirrer was charged with **S6** (20.0 mmol, 5.00 g, 1.0 equiv.) in anhydrous ethanol (EtOH, 26.0 mL) under a N_2 atmosphere. Sodium borohydride ($NaBH_4$, 22.0 mmol, 0.83 g, 1.1 equiv.) was then slowly added in portions. (Note: the addition of sodium borohydride generates a large amount of gas, so it must be added in batches slowly.) After the addition was complete, the reaction mixture was stirred for an additional 30 min. The solvent was removed under reduced pressure, and the residue was triturated with PE (16.0 mL) to induce precipitation. The resulting solid was collected by filtration. The crude product was then stirred in a mixture of EtOH (2.0 mL) and PE (30.0 mL) at room temperature for 30 min, filtered, and dried under vacuum at 60 °C for 30 min to afford **2** (18.0 mmol, 2.50 g, 90% yield, 95% D-inc). This decrease in deuterium incorporation might be due to the strong hygroscopicity of $NaBH_4$, which leads to the introduction of moisture into the reaction system.

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{139.0}{250.0 + 3} = 48.3\%$$

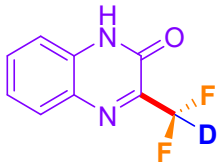
4. General procedure for the synthesis of 2*H*-indazoles (4)



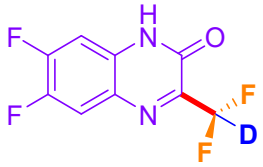
2*H*-Indazoles (**4**) were synthesized according to the literature.[3]

2-Bromobenzaldehydes (1.0 equiv.), primary amines (1.2 equiv.), sodium azide (NaN_3, 2.0 equiv.), copper(I) iodide (CuI, 0.1 equiv.) and N,N,N',N'-tetramethylethylenediamine (TMEDA, 0.1 equiv.) were added to a reaction flask containing a stir bar. Subsequently, dimethyl sulfoxide (DMSO) was added, and the reaction was carried out at 120 °C. After the reaction was completed, the solution was cooled to room temperature and EA was added. The mixture was washed with water and brine, respectively. The organic phase was collected and dried with anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography with PE/EA as eluent to afford compounds **4**.

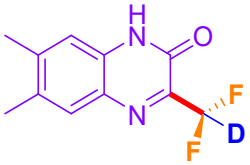
5. Characterization data of products 3



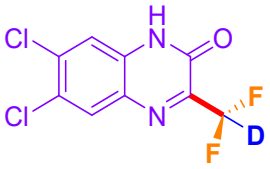
3-(difluoromethyl-d)quinoxalin-2(1H)-one (3a): Yield: 80%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.83 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.39 – 7.34 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 153.2, 149.7 (t, J = 21.3 Hz), 132.9, 132.3, 130.7, 129.5, 123.9, 115.8, 110.0 (tt, J = 31.5, 239.9 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.91 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_9H_6DF_2N_2O^+$ ([M+H$^+$]) 198.0584, found 198.0591.



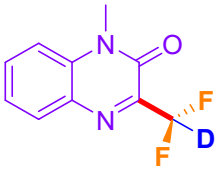
3-(difluoromethyl-d)-6,7-difluoroquinoxalin-2(1H)-one (3b): Yield: 71%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.93 (s, 1H), 7.97 (s, 1H), 7.20 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 152.9, 151.8 (dd, J = 14.8, 253.4 Hz), 150.2 (t, J = 20.6 Hz), 146.2 (dd, J = 14.4, 244.1 Hz), 130.7 (d, J = 10.8 Hz), 127.1 (d, J = 9.9 Hz), 117.2 (dd, J = 2.2, 18.3 Hz), 109.8 (tt, J = 28.0, 238.2 Hz), 103.6 (d, J = 22.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -125.29 (t, J = 7.5 Hz), -129.75 (d, J = 23.1 Hz), -142.20 (d, J = 23.2 Hz). HRMS m/z (ESI): calc. for $C_9H_4DF_4N_2O^+$ ([M+H$^+$]) 234.0395, found 234.0390.



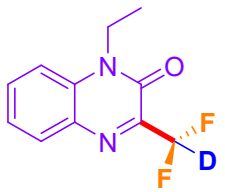
3-(difluoromethyl-d)-6,7-dimethylquinoxalin-2(1H)-one (3c): Yield: 75%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.70 (s, 1H), 7.61 (s, 1H), 7.09 (s, 1H), 2.32 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 153.3, 148.2 (t, J = 22.3 Hz), 142.4, 132.9, 130.9, 129.3, 129.1, 115.6, 110.2 (tt, J = 29.8, 239.9 Hz), 19.9, 18.8; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.38 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{11}H_{10}DF_2N_2O^+$ ([M+H$^+$]) 226.0897, found 226.0893.



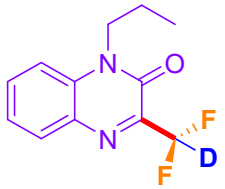
6,7-dichloro-3-(difluoromethyl-d)quinoxalin-2(1H)-one (3d): Yield: 66%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.96 (s, 1H), 8.20 (s, 1H), 7.50 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 152.8, 148.5 (t, J = 20.8 Hz), 134.4, 132.8, 130.5, 130.1, 125.7, 116.9, 111.2 (tt, J = 19.2, 265.6 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -125.5 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_9H_4DClF_2N_2O^+$ ([M+H$^+$]) 265,9804, found 265.9798.



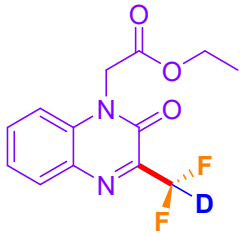
3-(difluoromethyl-d)-1-methylquinoxalin-2(1H)-one (3e): Yield: 85%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.46 – 7.35 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3, 148.7 (t, J = 22.6 Hz), 134.1, 132.8, 132.0, 131.5, 124.5, 114.1, 109.9 (tt, J = 29.3, 242.4 Hz), 29.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ -125.01 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{10}H_8DF_2N_2O^+$ ([M+H$^+$]) 212.0740, found 212.0745.



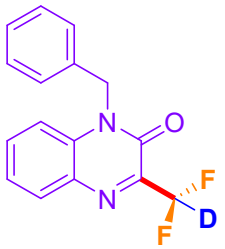
3-(difluoromethyl-d)-1-ethylquinoxalin-2(1H)-one (3f): Yield: 81%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 148.5 (t, *J* = 21.4 Hz), 133.1, 132.7, 132.3, 131.8, 124.3, 113.9, 109.6 (tt, *J* = 29.3, 232.5 Hz), 37.5, 12.5; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.96 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{11}H_{10}DF_2N_2O^+$ ([M+H$^+$]) 226.0897, found 226.0899.



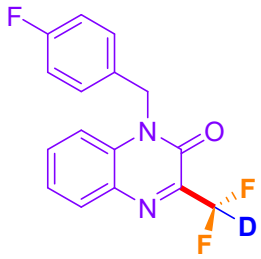
3-(difluoromethyl-d)-1-propylquinoxalin-2(1H)-one (3g) : Yield: 77%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.57 (m, 1H), 7.49 – 7.29 (m, 2H), 4.23 (t, *J* = 7.8 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 148.5 (t, *J* = 18.2 Hz), 133.4, 132.7, 132.3, 131.8, 124.3, 114.1, 106.0 (tt, *J* = 29.8, 230.4 Hz), 43.9, 20.7, 11.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -125.00 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{12}H_{12}DF_2N_2O^+$ ([M+H$^+$]) 240.1053, found 240.1056.



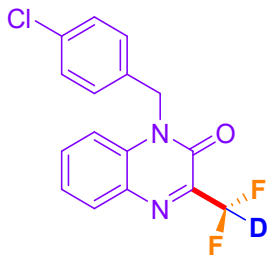
Ethyl 2-(3-(difluoromethyl-d)-2-oxoquinoxalin-1(2H)-yl)acetate (3h): Yield: 86%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 5.04 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 152.9, 148.6 (t, *J* = 22.7 Hz), 133.3, 133.0, 132.1, 131.9, 124.8, 113.6, 107.3 (tt, *J* = 29.4, 241.5 Hz), 62.5, 43.4, 14.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.92 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{13}H_{12}DF_2N_2O_3^+$ ([M+H$^+$]) 284.0952, found 284.0949.



1-benzyl-3-(difluoromethyl-d)quinoxalin-2(1H)-one (3i): Yield: 70%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.44 – 7.20 (m, 7H), 5.53 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 148.8, 134.7, 133.5, 132.7, 132.3, 131.6, 129.2, 128.1, 127.1, 124.5, 114.9, 109.8 (tt, *J* = 29.3， 243.4 Hz), 45.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.81 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{12}DF_2N_2O^+$ ([M+H$^+$]) 288.1053, found 288.1056.

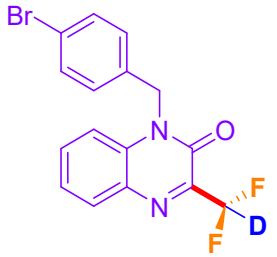


3-(difluoromethyl-d)-1-(4-fluorobenzyl)quinoxalin-2(1H)-one (3j): Yield: 63%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.48 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5 (d, *J* = 247.2 Hz), 153.4, 148.8 (t, *J* = 22.6 Hz), 133.4, 132.8, 132.3, 131.8, 130.5 (d, *J* = 3.5 Hz), 129.0 (d, *J* = 8.1 Hz), 124.7, 116.1 (d, *J* = 21.8 Hz), 114.6, 109.9 (tt, *J* = 31.4, 245.1 Hz), 45.3, 45.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ -113.73,-124.75 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{10}DF_3N_2ONa^+$ ([M+Na$^+$]) 328.0778, found 328.0783.

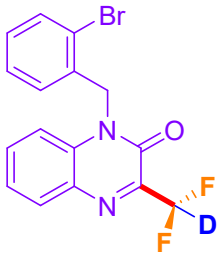


1-(4-chlorobenzyl)-3-(difluoromethyl-d)quinoxalin-2(1H)-one (3k): Yield: 55%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 6.5 Hz, 1H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 3H), 7.20 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 148.8 (t, *J* = 22.7 Hz), 134.1,

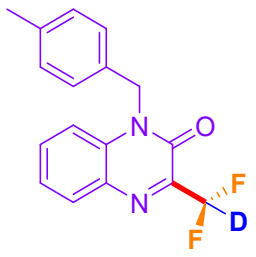
133.3, 133.2, 132.9, 132.3, 131.8, 129.4, 128.6, 124.7, 114.6, 109.9 (tt, J = 31.6, 241.0 Hz), 45.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.73 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{11}DClF_2N_2O^+$ ([M+H$^+$]) 322.0664, found 322.0666.



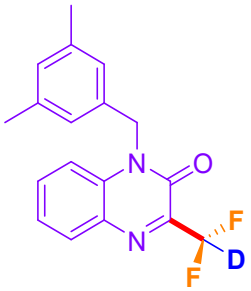
1-(4-bromobenzyl)-3-(difluoromethyl-d)quinoxalin-2(1H)-one (3l): Yield: 44%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.1 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.14 (d, J = 8.4 Hz, 2H), 5.45 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 148.9 (t, J = 22.8 Hz), 133.7, 133.3, 132.9, 132.4, 131.8, 128.9, 124.7, 122.1, 114.6, 109.9 (tt, J = 30.5, 238.2 Hz), 45.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.73 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{11}DBrF_2N_2O^+$ ([M+H$^+$]) 366.0158, found 366.0164.



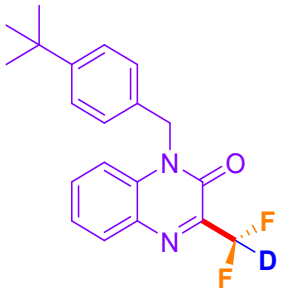
1-(2-bromobenzyl)-3-(difluoromethyl-d)quinoxalin-2(1H)-one (3m): Yield: 56%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 7.2 Hz, 1H), 7.75 – 7.62 (m, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.10 (d, J = 8.4 Hz, 1H), 6.75 – 6.69 (m, 1H), 5.57 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 148.9 (t, J = 22.6 Hz), 133.3, 133.3, 133.2, 133.0, 132.3, 131.7, 129.5, 128.2, 127.0, 124.8, 122.7, 114.9, 109.8 (tt, J = 29.0, 237.3 Hz), 46.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.78 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{11}DBrF_2N_2O^+$ ([M+H$^+$]) 366.0158, found 366.0168.



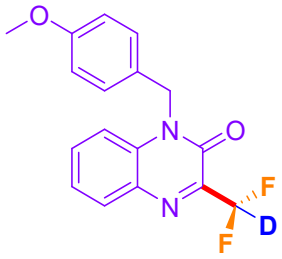
3-(difluoromethyl-d)-1-(4-methylbenzyl)quinoxalin-2(1H)-one (3n): Yield: 67%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.17 – 7.14 (m, 4H), 5.47 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 148.7 (t, *J* = 22.7 Hz), 137.9, 133.5, 132.7, 132.3, 131.6, 131.6, 129.8, 127.1, 124.5, 114.9, 109.8 (tt, *J* = 30.2, 241.8 Hz), 45.7, 21.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.77 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{17}H_{14}DF_2N_2O^+$ ([M+H$^+$]) 302.1210, found 302.1211.



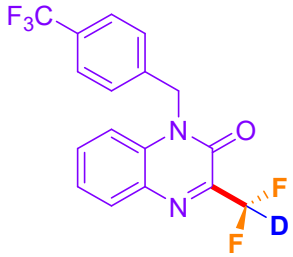
3-(difluoromethyl-d)-1-(3,5-dimethylbenzyl)quinoxalin-2(1H)-one (3o): Yield: 61%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.41 – 7.33 (m, 2H), 6.91 (s, 1H), 6.85 (s, 2H), 5.44 (s, 2H), 2.26 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 148.8 (t, *J* = 22.5 Hz), 138.8, 134.6, 133.6, 132.7, 132.3, 131.5, 129.8, 124.7, 124.5, 115.0, 109.8 (tt, *J* = 31.6, 245.3 Hz), 46.0, 21.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.76 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{18}H_{16}DF_2N_2O^+$ ([M+H$^+$]) 316.1366, found 316.1370.



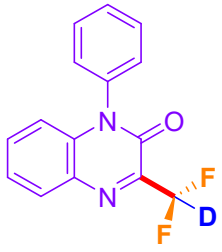
1-(4-(tert-butyl)benzyl)-3-(difluoromethyl-d)quinoxalin-2(1H)-one (3p): Yield: 50%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.43 – 7.30 (m, 4H), 7.20 (d, *J* = 8.2 Hz, 2H), 5.48 (s, 2H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 151.2, 148.9 (t, *J* = 22.5 Hz), 133.6, 132.7, 132.3, 131.6, 131.6, 126.9, 126.1, 124.5, 115.0, 109.8 (tt, *J* = 31.4, 241.6 Hz), 45.7, 34.6, 31.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.80 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{20}H_{20}DF_2N_2O^+$ ([M+H$^+$]) 344.1679, found 344.1683.



3-(difluoromethyl-d)-1-(4-methoxybenzyl)quinoxalin-2(1H)-one (3q): Yield: 61%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.47 – 7.37 (m, 3H), 7.27 (d, J = 8.1 Hz, 1H), 5.58 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 153.5, 148.8 (t, J = 22.6 Hz), 133.5, 132.7, 132.3, 131.7, 128.6, 126.7, 124.5, 114.9, 114.5, 109.9 (tt, J = 30.5, 241.7 Hz), 55.4, 45.5; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.82 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{17}H_{13}DF_2N_2O_2Na^+$ ([M+Na^+]) 340.0978, found 340.0976.

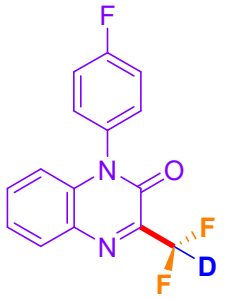


3-(difluoromethyl-d)-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1H)-one (3r): Yield: 50%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.48 – 7.30 (m, 3H), 7.25 (d, J = 8.1 Hz, 1H), 5.56 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 148.9 (t, J = 22.8 Hz), 138.7, 133.3, 133.0, 132.3, 131.9, 130.6 (q, J = 32.5 Hz), 127.4, 126.2 (q, J = 3.8 Hz), 124.9, 124.0 (q, J = 272.7 Hz), 114.5, 109.6 (tt, J = 31.5, 242.3 Hz), 45.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ -62.70, -124.74 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{17}H_{10}DF_5N_2ONa^+$ ([M+Na^+]) 378.0747, found 378.0737.

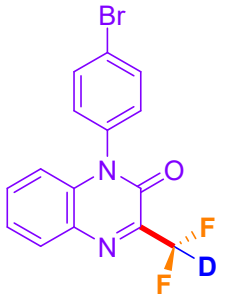


3-(difluoromethyl-d)-1-phenylquinoxalin-2(1H)-one (3s): Yield: 73%; D-inc: 94%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.8 Hz, 1H), 7.69 – 7.54 (m, 3H), 7.47 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 6.76 (d, J =

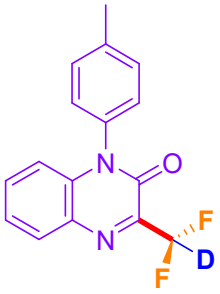
8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.1, 149.5 (t, *J* = 22.5 Hz), 135.0, 134.9, 132.4, 132.0, 131.1, 130.6, 130.0, 128.2, 124.7, 115.9, 109.5 (tt, *J* = 31.1, 240.3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.86 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_{10}DF_2N_2O^+$ ([M+H$^+$]) 274.0897, found 274.0900.



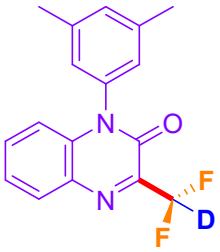
3-(difluoromethyl-d)-1-(4-fluorophenyl)quinoxalin-2(1H)-one (3t): Yield: 78%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.27 (m, 4H), 6.76 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.2 (d, *J* = 250.6 Hz), 153.1, 149.4 (t, *J* = 25.6 Hz), 135.0, 132.5, 132.0, 131.3, 130.7, 130.2 (d, *J* = 8.7 Hz), 124.8, 117.7 (d, *J* = 23.2 Hz), 115.7, 109.8 (tt, *J* = 32.8, 242.1 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -110.34, -124.84 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_9DF_3N_2O^+$ ([M+H$^+$]) 292.0803, found 292.0798.



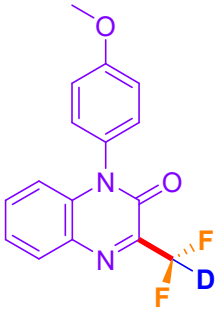
1-(4-bromophenyl)-3-(difluoromethyl-d)quinoxalin-2(1H)-one (3u): Yield: 71%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 149.5 (t, *J* = 23.0 Hz), 134.7, 133.9, 133.9, 132.6, 132.0, 131.4, 130.0, 124.9, 124.3, 115.6, 109.7 (tt, *J* = 30.6, 241.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.81 (t, *J* = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_9DBrF_2N_2O^+$ ([M+H$^+$]) 352.0002, found 351.9997.



3-(difluoromethyl-d)-1-(p-tolyl)quinoxalin-2(1H)-one (3v): Yield: 71%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (d, J = 7.8 Hz, 1H), 7.49 – 7.33 (m, 4H), 7.18 (d, J = 8.2 Hz, 2H), 6.80 (d, J = 8.3 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3, 149.5 (t, J = 22.4 Hz), 140.2, 135.2, 132.4, 132.2, 132.0, 131.2, 131.1, 127.9, 124.6, 116.0, 109.5 (tt, J = 31.0, 241.4 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.89 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{12}DF_2N_2O^+$ ([M+H$^+$]) 288.1053, found 288.1046.



3-(difluoromethyl-d)-1-(3,5-dimethylphenyl)quinoxalin-2(1H)-one (3w): Yield: 69%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.20 (s, 1H), 6.91 (s, 2H), 6.80 (d, J = 8.4 Hz, 1H), 2.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 149.5 (t, J = 22.4 Hz), 140.6, 135.1, 134.7, 132.3, 131.9, 131.7, 131.0, 125.5, 124.6, 116.2, 109.5 (tt, J = 31.5, 241.1 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.90 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{17}H_{14}DF_2N_2O^+$ ([M+H$^+$]) 302.1210, found 302.1207.

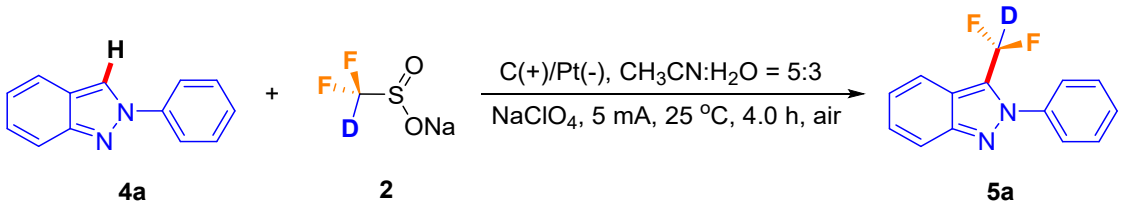


3-(difluoromethyl-d)-1-(4-methoxyphenyl)quinoxalin-2(1H)-one (3x): Yield: 72%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 6.8 Hz, 1H), 7.38 (d, J = 7.3 Hz, 1H), 7.21 (d, J = 8.9 Hz, 2H), 7.12 (d, J = 8.8

Hz, 2H), 6.82 (d, J = 8.8 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.5, 153.4, 149.5 (t, J = 22.4 Hz), 135.4, 132.4, 132.0, 131.1, 129.2, 127.2, 124.6, 116.0, 115.8, 109.2 (tt, J = 31.0, 241.4 Hz), 55.7; ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.87 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{12}DF_2N_2O_2^+$ ([M+H$^+$]) 304.1002, found 304.1004.

6. Optimization of reaction conditions for the difluorodeuteromethylation of 2-phenyl-2*H*-indazole (4a)

Table S1, Optimization of the reaction conditions for the difluorodeuteromethylation of 2-phenyl-2*H*-indazole (**4a**)[a]



4a **2** **5a**

Entry	Variation from standard conditions	Y[b,c] (%)
1	None	84
2	DMSO instead of CH_3CN	36
3	DMF instead of CH_3CN	83
4	DMA instead of CH_3CN	55
5	CH_3OH instead of CH_3CN	65
6	C_2H_5OH instead of CH_3CN	45
7	CH_3CN/H_2O = 6/2	78
8	without H_2O	49
9	CH_3CN/H_2O = 4/4	81
10	CH_3CN/H_2O = 3/5	20
11	C(+)/C(-) instead of C(+)/Pt(-)	18
12	Pt(+)/Pt(-) instead of C(+)/Pt(-)	37
13	C felt(+)/Pt(-) instead of C(+)/Pt(-)	45
14	C(+)/Cu foam(-) instead of C(+)/Pt(-)	82
15	C(+)/Ni foam(-) instead of C(+)/Pt(-)	72
16	$NaBF_4$ instead of $NaClO_4$	76
17	$LiClO_4$ instead of $NaClO_4$	71
18	$^nBu_4NBF_4$ instead of $NaClO_4$	56

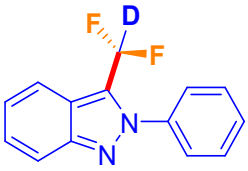
a) Standard conditions: **4a** (0.2 mmol), **2** (0.4 mmol, 95% **D**), $NaClO_4$ (0.1 M), CH_3CN/ H_2O (5.0/3.0, 8.0 mL), C(+)/Pt(-), 8 mA, 3 h, 25 °C, air. b) Isolated yield. c) The deuterium incorporation of product **5a** was 95% under all conditions, which was calculated based on the ^{19}F NMR.

Table S1, Optimization of the reaction conditions for the difluorodeuteromethylation of 2-phenyl-2*H*-indazole (**4a**) (continue)[a]

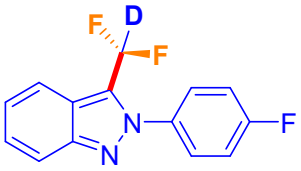
Entry	Variation from standard conditions	Y[b,c] (%)
19	$^{n}Bu_4NPF_6$ instead of $NaClO_4$	74
20	$^{n}Bu_4NClO_4$ instead of $NaClO_4$	70
21	TBAB instead of $NaClO_4$	78
22	Without $NaClO_4$	72
23	**2** (0.3 mmol) instead of **2** (0.4 mmol)	72
25	3 mA instead of 5 mA	70
26	4 mA instead of 5 mA	78
27	6 mA instead of 5 mA	76
28	7mA instead of 5 mA	70
29	15 °C instead of 25 °C	53
30	35 °C instead of 25 °C	77
31	N_2 instead of air	82
32	Without current	N.D.

a) Standard conditions: **4a** (0.2 mmol), **2** (0.4 mmol, 95% **D**), $NaClO_4$ (0.1 M), CH_3CN/ H_2O (5.0/3.0, 8.0 mL), C(+)/Pt(-), 8 mA, 3 h, 25 °C, air. b) Isolated yield. c) The deuterium incorporation of product **5a** was 95% under all conditions, which was calculated based on the ^{19}F NMR.

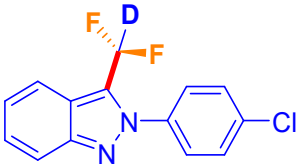
7. Characterization data of products 5



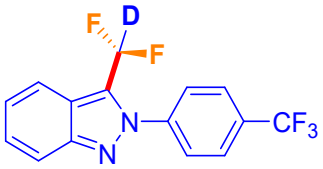
3-(difluoromethyl-d)-2-phenyl-2H-indazole (5a): Yield: 84%; D-inc: 95%; White solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.64 – 7.54 (m, 5H), 7.41 (t, J = 8.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.8, 139.1, 129.9, 129.7, 127.5 (t, J = 31.2 Hz), 127.4, 125.8, 124.2, 121.2, 112.0, 118.2, 109.6 (tt, J = 30.1, 236.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.76 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{14}H_{10}DF_2N_2^+$ ([M+H$^+$]) 246.0948, found 246.0940.



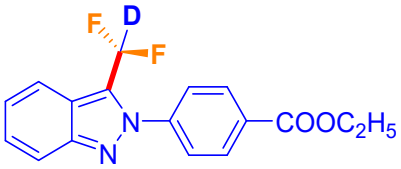
3-(difluoromethyl-d)-2-(4-fluorophenyl)-2H-indazole (5b): Yield: 80%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.43 – 7.39 (m, 1H), 7.29 – 7.24 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.23 (d, J = 250.8 Hz), 148.76, 135.29 (d, J = 3.1 Hz), 127.80 (d, J = 8.9 Hz), 127.6 (t, J = 3.4 Hz), 127.52, 124.42, 121.30, 119.81, 118.22, 116.73 (d, J = 23.2 Hz), 109.4 (tt, J = 29.3, 234.8 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.78 (t, J = 7.5 Hz), 110.31. HRMS m/z (ESI): calc. for $C_{14}H_9DF_3N_2^+$ ([M+H$^+$]) 264.0853, found 264.0846.



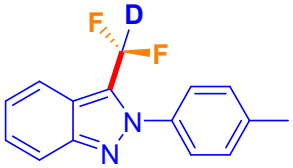
2-(4-chlorophenyl)-3-(difluoromethyl-d)-2H-indazole (5c): Yield: 72%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.59 – 7.53 (m, 4H), 7.42 – 7.38 (m, 1H), 7.26 – 7.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.9, 137.7, 136.0, 129.9, 127.6 (d, J = 114.7 Hz), 127.4 (t, J = 30.6 Hz), 127.0, 124.5, 121.5, 119.8, 118.2, 109.3 (tt, J = 29.5, 234.6 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.60 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{14}H_9DClF_2N_2^+$ ([M+H$^+$]) 280.0558, found 280.0551.



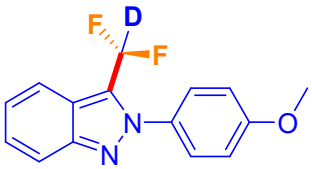
3-(difluoromethyl-d)-2-(4-(trifluoromethyl)phenyl)-2H-indazole (5d): Yield: 75%; D-inc: 94%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (d, J = 8.6 Hz, 1H), 7.87 – 7.79 (m, 5H), 7.42 (t, J = 6.8 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 142.1, 131.9 (q, J = 33.1 Hz), 127.9, 127.5 (t, J = 30.9 Hz), 126.9 (q, J = 3.7 Hz), 126.2, 124.8, 122.3, 121.8, 119.8, 118.4, 109.2 (tt, J = 29.7, 233.7 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -62.69, -109.47 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_9DF_5N_2^+$ ([M+H$^+$]) 314.0821, found 314.0818.



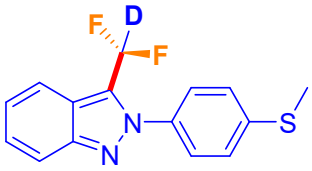
Ethyl 4-(3-(difluoromethyl-d)-2H-indazol-2-yl)benzoate (5e) : Yield: 77%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.6 Hz, 1H), 7.80 (s, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.39 (t, J = 7.1 Hz, 1H), 7.24 (t, J = 8.2 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.5, 149.0 (d, J = 2.1 Hz), 142.6, 131.7, 131.0, 127.7, 127.4 (t, J = 30.9 Hz), 125.5, 124.6, 121.7, 119.9, 118.3, 109.3 ((tt, J = 29.0, 231.9 Hz)), 61.6, 14.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.54 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{17}H_{14}DF_2N_2O_2^+$ ([M+H$^+$]) 318.1159, found 318.1157.



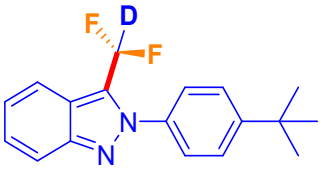
3-(difluoromethyl-d)-2-(p-tolyl)-2H-indazole (5f): Yield: 72%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.25 (t, J = 7.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.6, 140.1, 136.6, 130.2, 127.4 (t, J = 31.3 Hz), 127.2, 125.6, 124.1, 121.1, 119.9, 118.2, 109.7 (tt, J = 30.1, 230.4 Hz), 21.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.80 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_{12}DF_2N_2^+$ ([M+H$^+$]) 260.1104, found 260.1099.



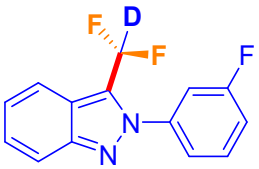
3-(difluoromethyl-d)-2-(4-methoxyphenyl)-2H-indazole (5g): Yield: 75%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.91 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 7.3 Hz, 1H), 7.24 (t, J = 6.5 Hz, 1H), 7.05 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.7, 148.5, 132.0, 127.5 (t, J = 26.6 Hz), 127.2, 127.1, 124.1, 121.0, 119.9, 118.1, 114.7, 110.40 (tt, J = 28.6, 231.6 Hz), 55.7; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.89 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_{12}DF_2N_2O^+$ ([M+H$^+$]) 276.1053, found 276.1048.



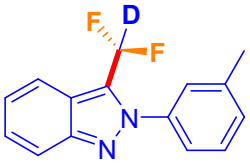
3-(difluoromethyl-d)-2-(4-(methylthio)phenyl)-2H-indazole (5h): Yield: 74%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.91 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.53 (d, J = 8.6 Hz, 2H), 7.41 – 7.38 (m, 3H), 7.25 (t, J = 7.8 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.7, 141.6, 135.9, 127.4 (t, J = 30.1 Hz), 127.4, 126.8, 126.0, 124.2, 121.3, 119.9, 118.2, 109.6 (tt, J = 30.7, 232.3 Hz), 15.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.73 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_{12}DF_2N_2S^+$ ([M+H$^+$]) 292.0825, found 292.0819.



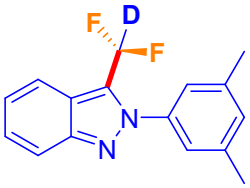
2-(4-(tert-butyl)phenyl)-3-(difluoromethyl-d)-2H-indazole (5i): Yield: 67%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.94 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.60 – 7.53 (m, 4H), 7.40 (t, J = 8.0 Hz, 1H), 7.26 (t, J = 8.7 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3, 148.7, 136.5, 127.4 (t, J = 31.5 Hz), 127.2, 126.6, 125.4, 124.1, 121.1, 120.0, 118.2, 109.7 (tt, J = 30.1, 233.6 Hz), 35.0, 31.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.76 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{18}H_{18}DF_2N_2^+$ ([M+H$^+$]) 302.1574, found 302.1564.



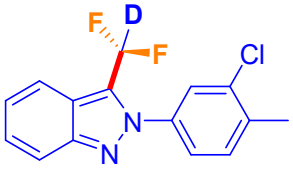
3-(difluoromethyl-d)-2-(3-fluorophenyl)-2H-indazole (5j): Yield: 77%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.47 – 7.40 (m, 3H), 7.29 (d, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8 (d, J = 249.8 Hz), 148.9, 140.4 (d, J = 9.8 Hz), 131.0 (d, J = 8.9 Hz), 127.6, 127.1 (t, J = 30.3 Hz), 124.5, 121.4 (d, J = 3.3 Hz), 119.1 (d, J = 160.6 Hz), 117.0 (d, J = 21.0 Hz), 113.6 (d, J = 24.9 Hz), 109.3 (tt, J = 29.1, 236.2 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.75 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{14}H_9DF_3N_2^+$ ([M+H$^+$]) 264.0853, found 264.0843.



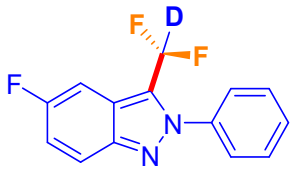
3-(difluoromethyl-d)-2-(m-tolyl)-2H-indazole (5k): Yield: 70%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.46 – 7.34 (m, 5H), 7.26 (t, J = 7.9 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.7, 140.1, 139.0, 130.7, 129.4, 127.5 (t, J = 31.3 Hz), 127.3, 126.4, 124.1, 122.8, 121.1, 120.0, 118.2, 109.6 (tt, J = 28.7, 234.5 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.79 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_{12}DF_2N_2^+$ ([M+H$^+$]) 260.1104, found 260.1097.



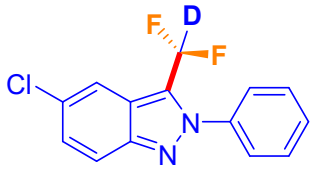
3-(difluoromethyl-d)-2-(3,5-dimethylphenyl)-2H-indazole (5l): Yield: 65%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.17 (s, 1H), 2.42 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.6, 139.7, 138.9, 131.6, 127.5 (t, J = 31.7 Hz), 127.2, 124.1, 123.5, 121.1, 120.0, 118.2, 109.7 (tt, J = 29.6, 232.9 Hz), 21.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.83 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{14}DF_2N_2^+$ ([M+H$^+$]) 274.1261, found 274.1252.



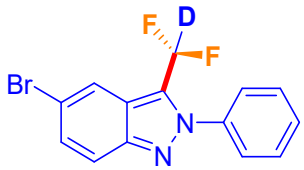
2-(3-chloro-4-methylphenyl)-3-(difluoromethyl-d)-2H-indazole (5m): Yield: 70%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.67 (s, 1H), 7.42 – 7.38 (m, 3H), 7.27 – 7.23 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.8, 138.4, 137.8, 135.4, 131.6, 127.5, 127.5 (t, J = 30.3 Hz), 126.4, 124.4, 123.8, 121.4, 119.9, 118.3, 109.4 (tt, J = 29.7, 234.9 Hz), 20.0; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.74 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_{11}DClF_2N_2^+$ ([M+H$^+$]) 294.0714, found 294.0709.



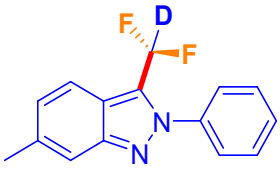
3-(difluoromethyl-d)-5-fluoro-2-phenyl-2H-indazole (5n): Yield: 77%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 – 7.77 (m, 1H), 7.62 – 7.56 (m, 5H), 7.51 – 7.48 (m, 1H), 7.23 – 7.17 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6 (d, J = 243.5 Hz), 146.2, 139.0, 130.1, 129.8, 128.2 (t, J = 36.5 Hz), 125.7, 120.8 (d, J = 12.4 Hz), 120.5 (d, J = 9.7 Hz), 119.2 (d, J = 29.1 Hz), 109.5 (tt, J = 29.3, 205.9 Hz), 102.8 (d, J = 25.3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -110.10 (t, J = 7.5 Hz), -116.04. HRMS m/z (ESI): calc. for $C_{14}H_9DF_3N_2^+$ ([M+H$^+$]) 264.0853, found 264.0854.



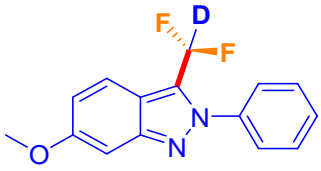
5-chloro-3-(difluoromethyl-d)-2-phenyl-2H-indazole (5o): Yield: 69%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.91 (s, 1H), 7.75 (d, J = 9.2 Hz, 1H), 7.61 – 7.57 (m, 5H), 7.35 – 7.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.1, 138.8, 130.2, 129.8, 128.9, 127.3 (t, J = 31.6 Hz), 125.7, 121.6, 121.1, 119.8, 118.8, 109.4 (tt, J = 29.7, 233.3 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.99 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{14}H_9DClF_2N_2^+$ ([M+H$^+$]) 280.0558, found 280.0552.



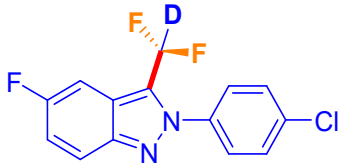
5-bromo-3-(difluoromethyl-d)-2-phenyl-2H-indazole (5p): Yield: 65%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.11 (s, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.61 – 7.57 (m, 5H), 7.47 – 7.44 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.2, 138.8, 131.2, 130.2, 129.8, 127.1 (t, J = 31.8 Hz), 125.8, 122.3, 122.2, 120.0, 118.1, 109.4 (tt, J = 28.3, 236.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.95 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{14}H_9DBrF_2N_2^+$ ([M+H$^+$]) 324.0053, found 324.0053.



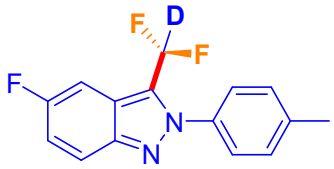
3-(difluoromethyl-d)-6-methyl-2-phenyl-2H-indazole (5q): Yield: 67%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (d, J = 8.7 Hz, 1H), 7.63 – 7.53 (m, 6H), 7.10 (d, J = 8.7 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 139.2, 137.4, 129.8, 129.7, 127.3 (t, J = 31.2 Hz), 127.2, 125.8, 119.7, 119.4, 116.4, 109.6 (tt, J = 28.8, 233.1 Hz), 22.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.76 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{15}H_{12}DF_2N_2^+$ ([M+H$^+$]) 260.1104, found 260.1097.



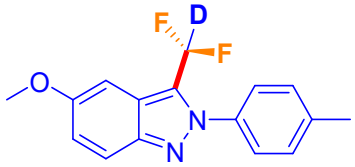
3-(difluoromethyl-d)-6-methoxy-2-phenyl-2H-indazole (5r): Yield: 73%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.71 – 7.68 (m, 1H), 7.62 – 7.52 (m, 5H), 7.11 – 7.08 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 145.7, 139.3, 129.7, 129.0, 126.4 (t, J = 29.2 Hz), 125.7, 122.7, 121.7, 119.7, 109.9 (tt, J = 28.8, 233.6 Hz), 95.8, 55.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.89 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{14}H_9DBrF_2N_2^+$ ([M+H$^+$]) 276.1053, found 276.1049.



2-(4-chlorophenyl)-3-(difluoromethyl-d)-5-fluoro-2H-indazole (5s): Yield: 73%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.79 – 7.76 (m, 1H), 7.58 – 7.53 (m, 4H), 7.48 – 7.45 (m, 1H), 7.23 – 7.18 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8 (d, J = 244.4 Hz), 146.3, 137.5, 136.2, 130.0, 127.8 (t, J = 31.0 Hz), 126.9, 121.1 (d, J = 12.2 Hz), 120.6 (d, J = 10.0 Hz), 119.5 (d, J = 29.4 Hz), 109.2 (tt, J = 29.6, 233.5 Hz), 102.7 (d, J = 25.4 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.89 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{14}H_8DClF_3N_2^+$ ([M+H$^+$]) 298.0464, found 298.0462.

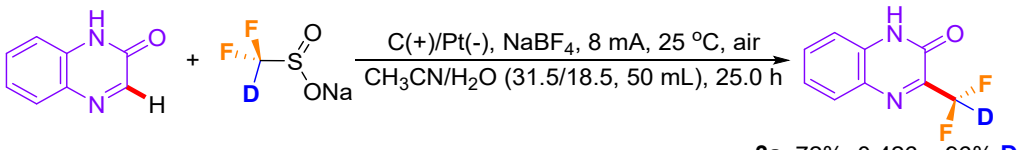


3-(difluoromethyl-d)-5-fluoro-2-(p-tolyl)-2H-indazole (5t): Yield: 75%; D-inc: 95%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.80 – 7.76 (m, 1H), 7.50 – 7.46 (m, 3H), 7.37 – 7.35 (m, 2H), 7.21 – 7.16 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6 (d, J = 243.5 Hz), 146.0, 140.4, 136.5, 130.3, 127.7 (t, J = 31.5 Hz), 125.5, 120.7 (d, J = 12.2 Hz), 120.5 (d, J = 9.9 Hz), 119.0 (d, J = 29.1 Hz), 109.6 (tt, J = 30.4, 232.0 Hz), 102.8 (d, J = 25.4 Hz), 21.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ -110.17 (t, J = 7.5 Hz), 116.3. HRMS m/z (ESI): calc. for $C_{15}H_{11}DF_3N_2^+$ ([M+H$^+$]) 278.1010, found 278.1002.



3-(difluoromethyl-d)-5-methoxy-2-(p-tolyl)-2H-indazole (5u): Yield: 70%; D-inc: 96%; White solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.77 (d, J = 9.2 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.01 (s, 1H), 6.94 (d, J = 9.2 Hz, 1H), 3.88 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 149.9, 139.9, 136.7, 130.2, 127.6 (t, J = 31.3 Hz), 125.5, 120.7, 119.4, 116.9, 109.9 (tt, J = 30.7, 233.6 Hz), 94.8, 55.4, 21.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ -110.00 (t, J = 7.5 Hz). HRMS m/z (ESI): calc. for $C_{16}H_{14}DF_2N_2^+$ ([M+H$^+$]) 290.1210, found 290.1215.

8. Gram-scale experiment for the synthesis of 3a

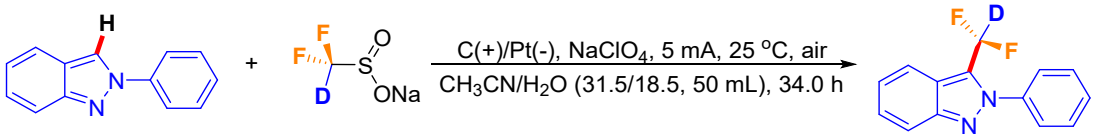


1a, 3.0 mmol **2**, 6.0 mmol **3a**, 72%, 0.426g, 96% **D**

1a (3.0 mmol, MW = 146.0, 0.438 g), **2** (6.0 mmol, MW = 139.0, 0.834g), $NaBF_4$ (5.0 mmol, MW = 109.8, 0.549g) and CH_3CN/H_2O (31.5/18.5, 50.0 mL) were added to a 100.0 mL undivided cell with a stir bar. The cell was equipped with a carbon plate anode (4.5 cm^2) and a platinum plate cathode (4.5 cm^2). The reaction mixture was

stirred at room temperature and electrolyzed at a constant current of 8 mA for 25 h. After the reaction was completed (monitored by TLC), the mixture was concentrated in vacuum, the obtained residue was purified by column chromatography using PE and EA as the eluent to afford the product **3a**.

9. Gram-scale experiment for the synthesis of 5a



4a, 3.0 mmol **2**, 6.0 mmol **5a**, 75%, 0.551 g, 95% **D**

4a (3.0 mmol, MW = 194.1, 0.582 g), **2** (6.0 mmol, MW = 139.0, 0.834g), $NaClO_4$ (5.0 mmol, MW = 122.4, 0.612g) and CH_3CN/H_2O (31.5/18.5, 50.0 mL) were added to a 100.0 mL undivided cell with a stir bar. The cell was equipped with a carbon plate anode (4.5 cm^2) and a platinum plate cathode (4.5 cm^2). The reaction mixture was stirred at room temperature and electrolyzed at a constant current of 5 mA for 34 h. After the reaction was completed, the mixture was directly purified by column chromatography using PE/THF as the eluent to afford the product **5a**.

10. The green chemistry metrics evaluation

The green chemistry metrics evaluation of the reaction between **1a** and **2** in our work:

$$E-factor = \frac{Total\ mass\ of\ wastes}{Mass\ of\ product} = \frac{0.438\ g + 0.834\ g + 0.549\ g - 0.4}{0.426\ g} = 3.27$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process}{Mass\ of\ product} = \frac{0.43}{} = 4.27$$

$$RME\ (\%) = \frac{Mass\ of\ product}{Total\ mass\ of\ input\ material\ in\ the\ whole\ process} \times 100\% = 23.4\%$$

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{197.1}{146.0 + 1} = 69.2\%$$

$$CE\ (\%) = \frac{Amount\ of\ carbon\ in\ product}{Total\ amount\ of\ carbon} \times 100\% = \frac{9 \times 2.2}{8 \times 3 + 1 \times 6} \times 1$$

The green chemistry metrics evaluation of the reaction between **4a** and **2** in our work:

$$E - factor = \frac{Total\ mass\ of\ wastes}{Mass\ of\ product} = \frac{0.582\ g + 0.834\ g + 0.612\ g - 0.5}{0.551\ g} = 2.68$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process}{Mass\ of\ product} = \frac{0.58}{} = 3.68$$

$$RME\ (\%) = \frac{Mass\ of\ product}{Total\ mass\ of\ input\ material\ in\ the\ whole\ process} \times 100\% \times 100\% = 27.2\%$$

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100\% = \frac{245.1}{194.1 + 1} = 73.6\%$$

$$CE\ (\%) = \frac{Amount\ of\ carbon\ in\ product}{Total\ amount\ of\ carbon} \times 100\% = \frac{14 \times 2.2}{13 \times 3 + 1 \times 6} \times 68.4\%$$

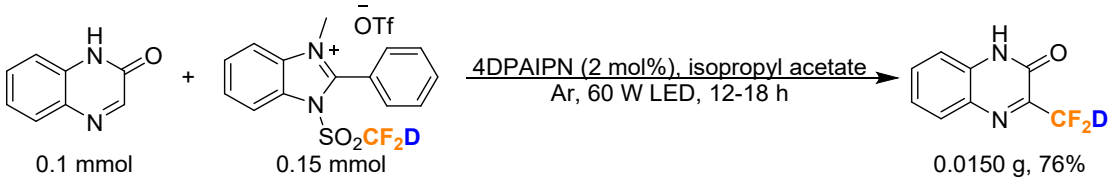
(Water and easily reusable solvents are generally excluded from the calculation.)

Our reaction utilizes a mixed solvent of CH_3CN and H_2O to achieve improved sustainability. The low boiling point and high reusability of CH_3CN are key to reducing waste, leading to well-performing sustainability indicators (E-factor, PMI and RME). Furthermore, the main by-products in the reaction are limited to sulfur dioxide (SO_2) and hydrogen gas (H_2), and the yields of the products are also satisfactory. Therefore,

in terms of atomic efficiency and carbon efficiency, the system maintains a good level in these aspects as well.

The green chemistry metrics of previous reactions:

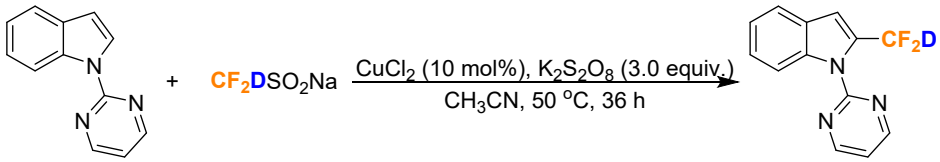
Chem. Sci. 2025, 16, 16039-16047:



0.1 mmol 0.15 mmol 0.0150 g, 76%

E-factor = 4.82 **PMI** = 5.82 **RME** = 17.2% **AE** = 31.8% **CE** = 21.4%

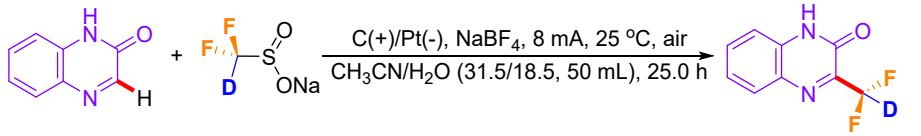
Org. Lett. 2021, 23, 5545-5548:



0.3 mmol 0.2 mmol 0.0404 g, 82%

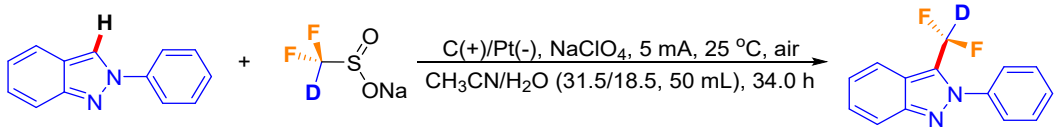
E-factor = 5.22 **PMI** = 6.22 **RME** = 19.2% **AE** = 40.7% **CE** = 56.1%

The green metrics of our work:



1a, 3.0 mmol **2**, 6.0 mmol **3a**, 72%, 0.426g, 96% **D**

E-factor = 3.27 **PMI** = 4.27 **RME** = 23.4% **AE** = 69.2% **CE** = 66.0%



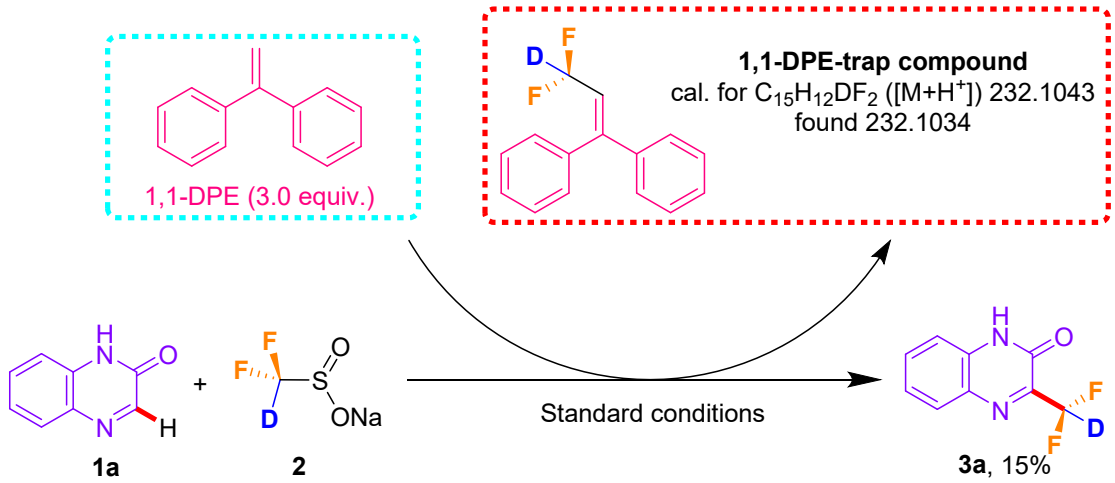
4a, 3.0 mmol **2**, 6.0 mmol **5a**, 75%, 0.551 g, 95% **D**

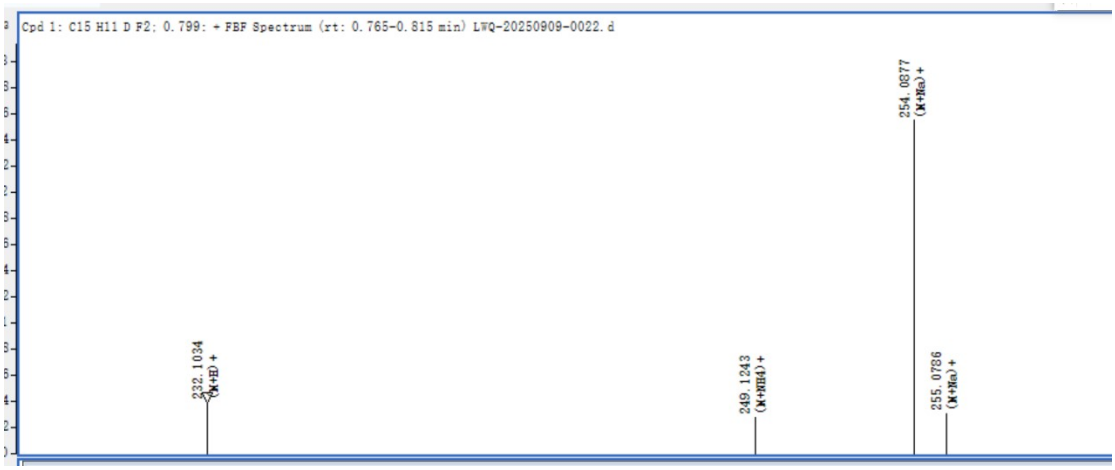
E-factor = 2.68 **PMI** = 3.68 **RME** = 27.2% **AE** = 73.6% **CE** = 68.4%

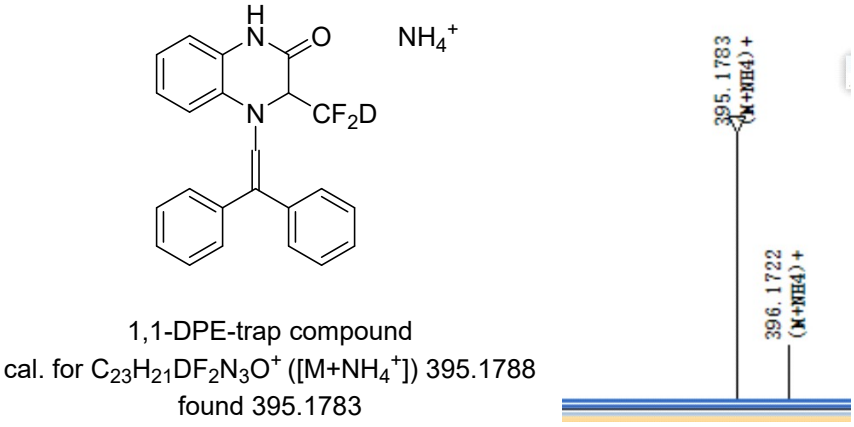
(Water and easily reusable solvents are generally excluded from the calculation.)

Compared to the previously reported deuterodifluoromethylation reactions, our strategy demonstrates superior performance in terms of green chemistry metrics.

11. HRMS of 1,1-DPE-trap compounds







1,1-DPE-trap compound
cal. for $C_{23}H_{21}DF_2N_3O^+$ ([M+NH_4^+]) 395.1788
found 395.1783

Figure S1, HRMS of 1,1-DPE-trap compounds

12. General procedure for cyclic voltammetry

Cyclic voltammetry experiments were carried out in a 10.0 mL undivided cell at room temperature on a CHI600e workstation. The total amount of solvent was 8.0 mL. The concentration of substrate was 0.01 M. The working electrode was an L-type glassy carbon (diameter, 3.0 mm) while the counter electrode was a platinum plate (2.25 cm^2). In addition, an Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN) was used as the reference electrode.

13. NMR spectra of prepared compounds

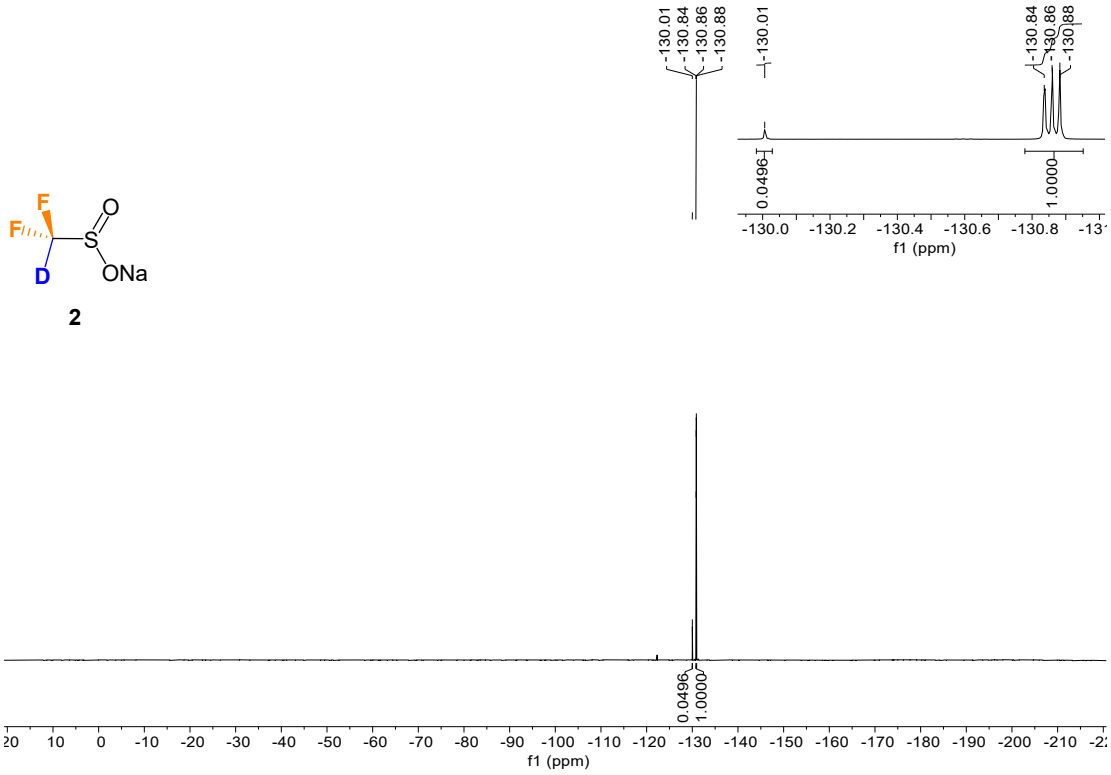


Figure S2, ^{19}F NMR spectrum of **2** (377 MHz, D_2O)

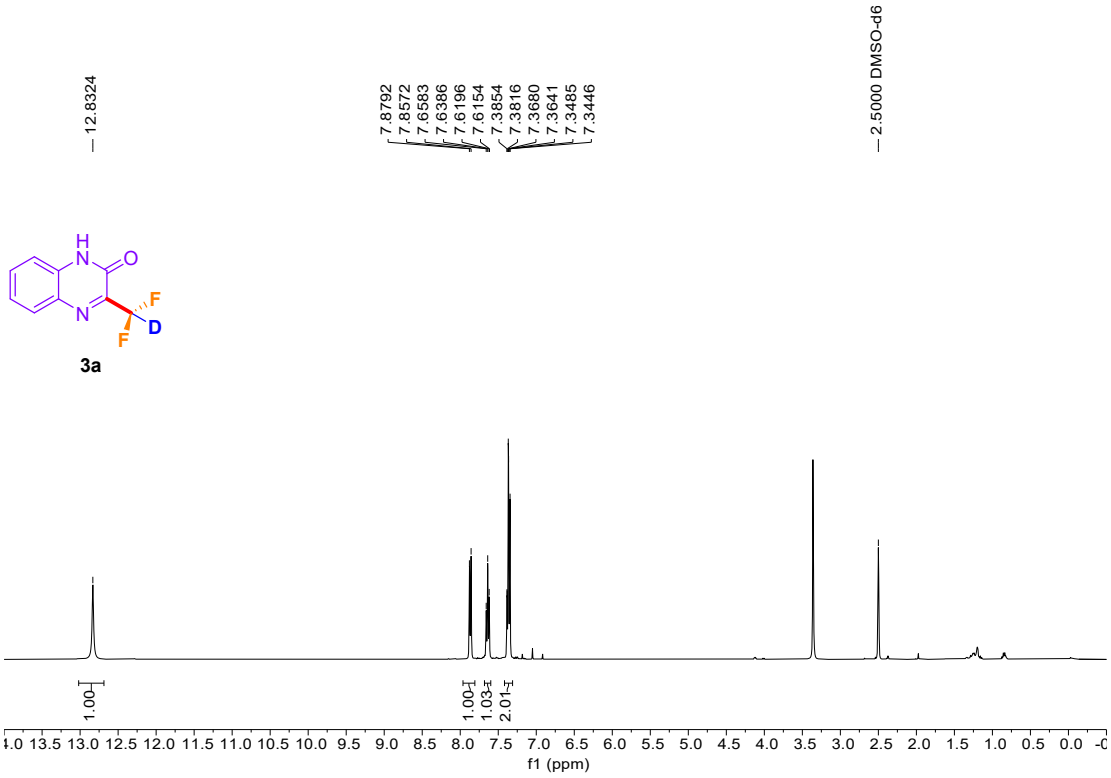


Figure S3, ^{1}H NMR spectrum of **3a** (400 MHz, DMSO-d_6)

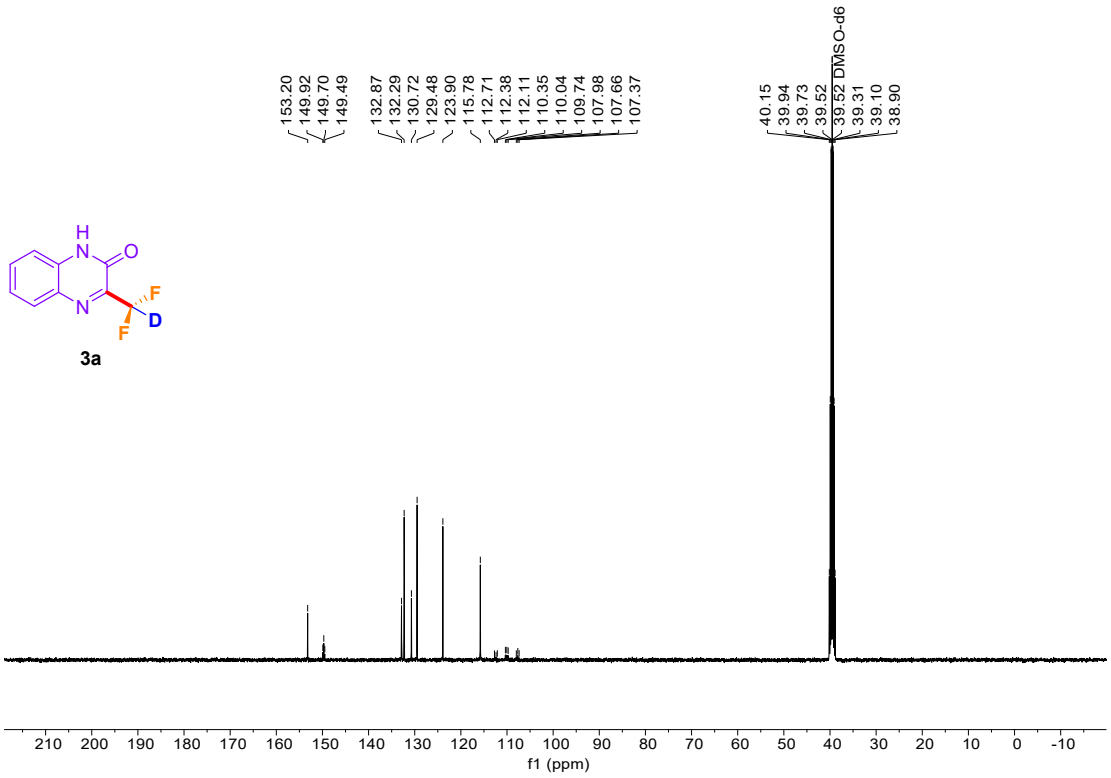


Figure S4, ^{13}C NMR spectrum of **3a** (101 MHz, DMSO-d_6)

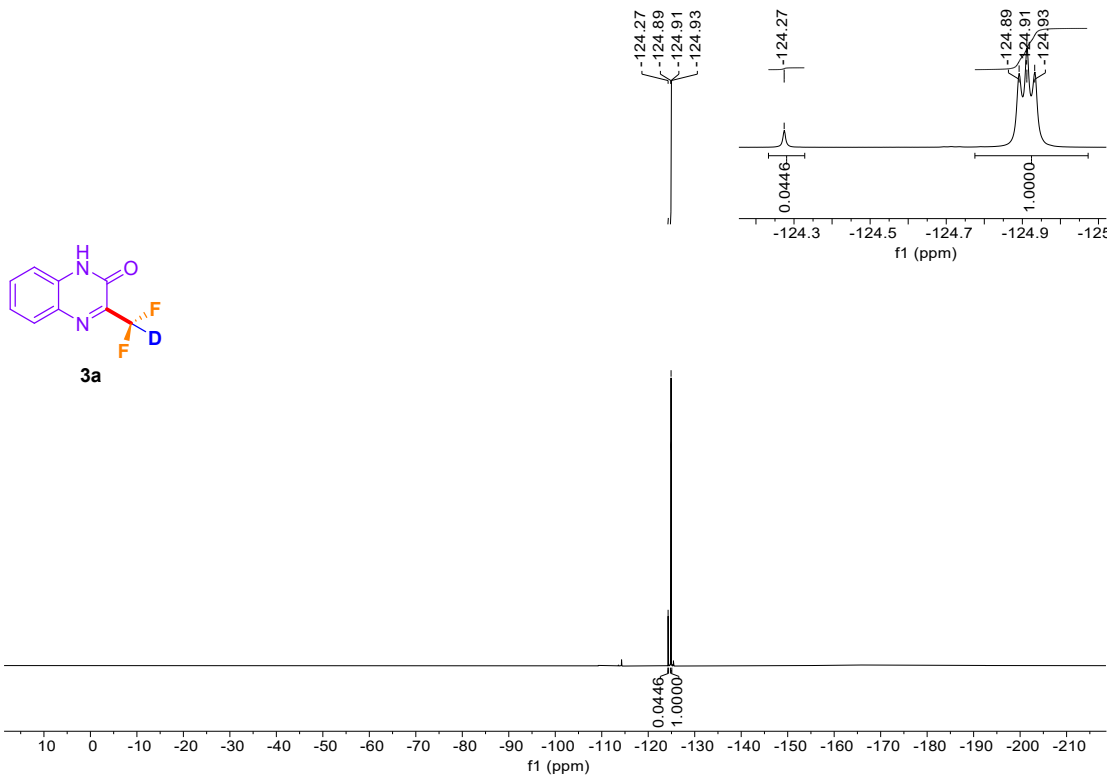


Figure S5, ^{19}F NMR spectrum of **3a** (377 MHz, DMSO-d_6)

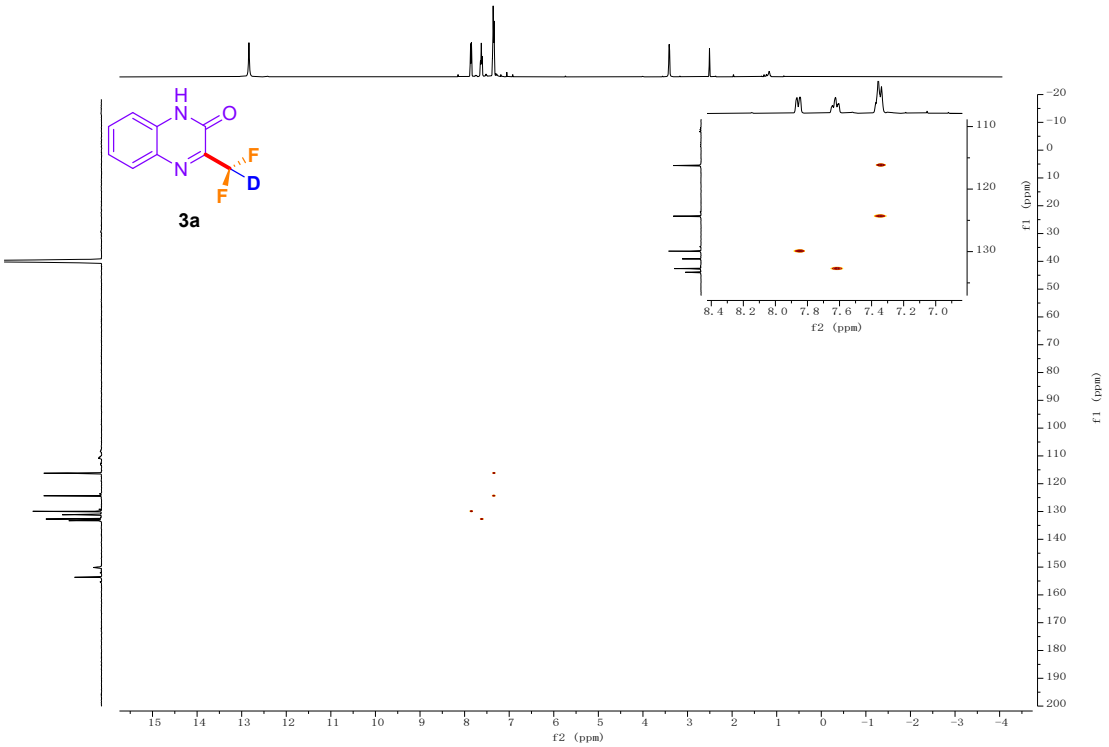


Figure S6, HSQC NMR spectrum of **3a** (400 MHz, DMSO-d_6)

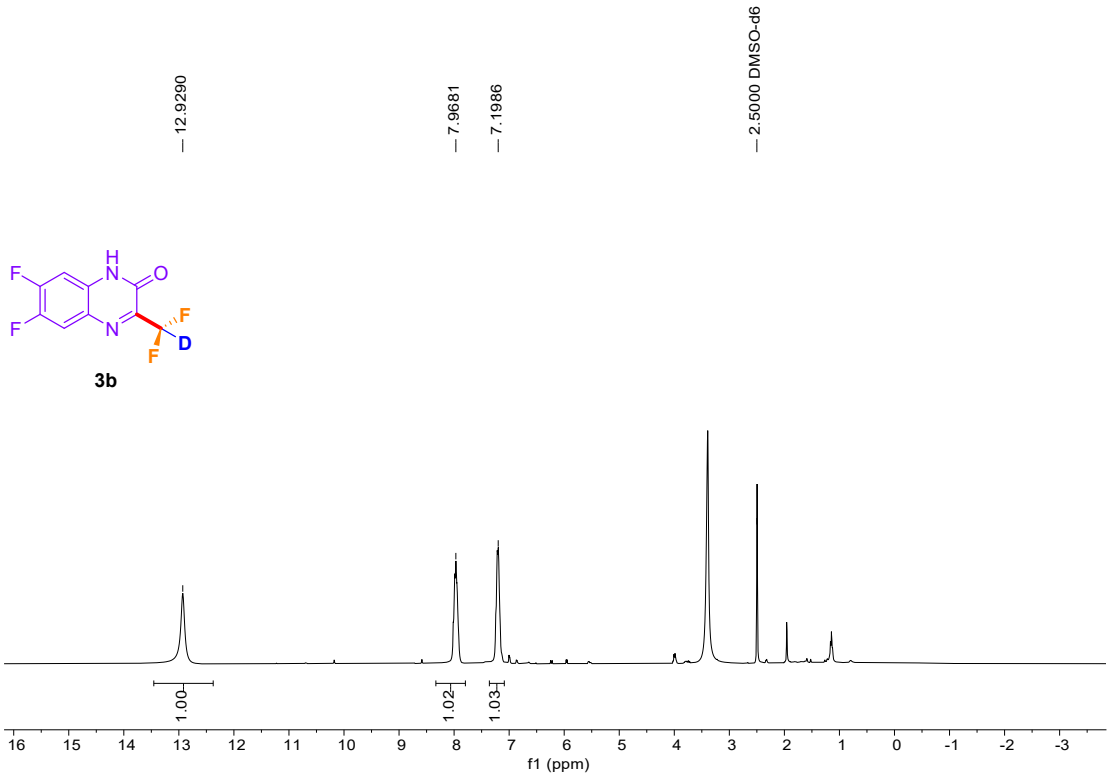


Figure S7, ^{1}H NMR spectrum of **3b** (400 MHz, DMSO-d_6)

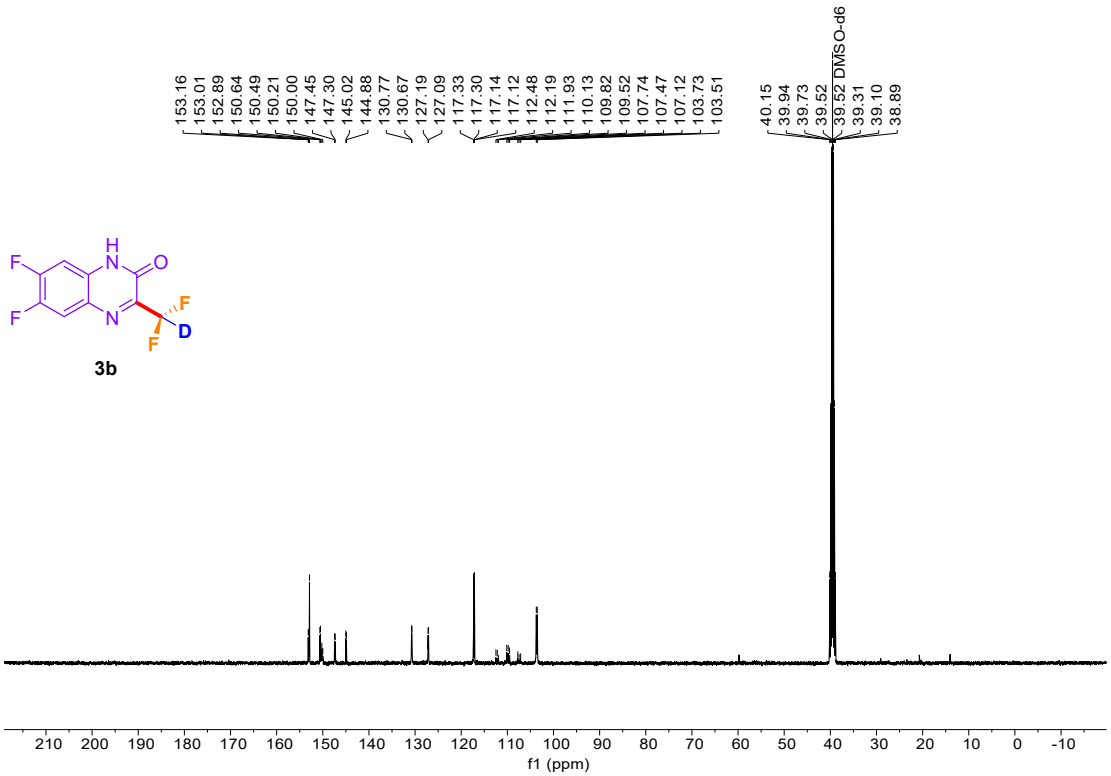


Figure S8, ^{13}C NMR spectrum of **3b** (101 MHz, DMSO-d_6)

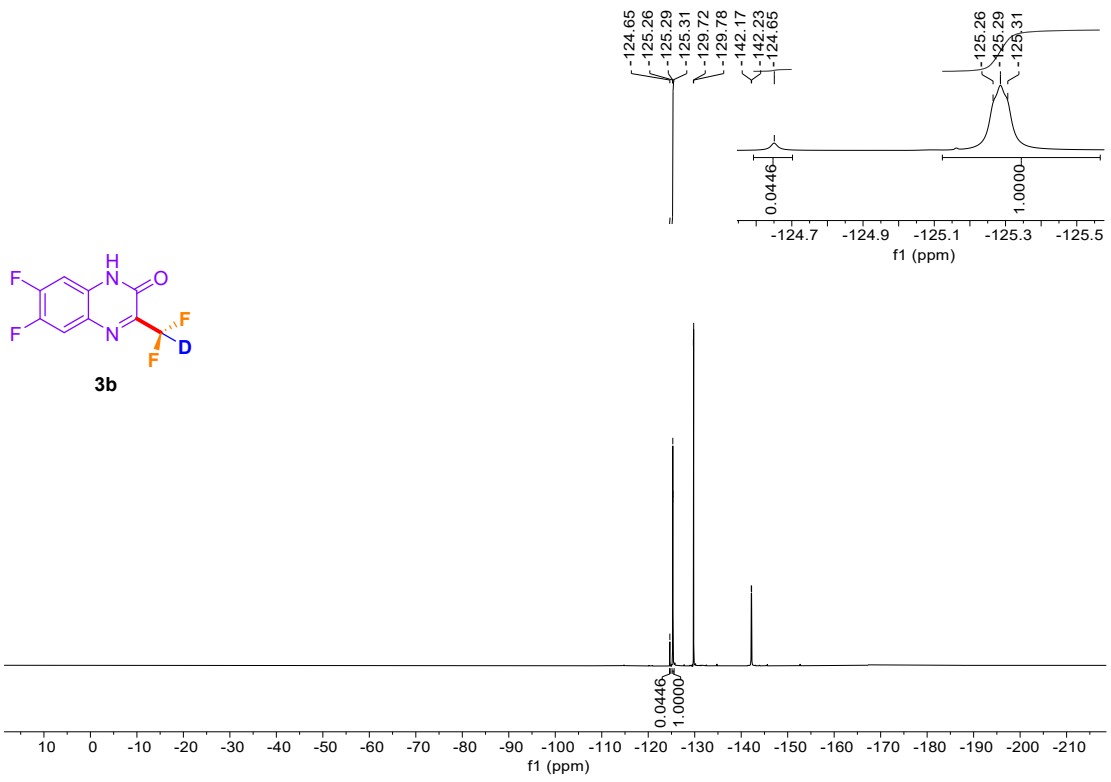


Figure S9, ^{19}F NMR spectrum of **3b** (377 MHz, DMSO-d_6)

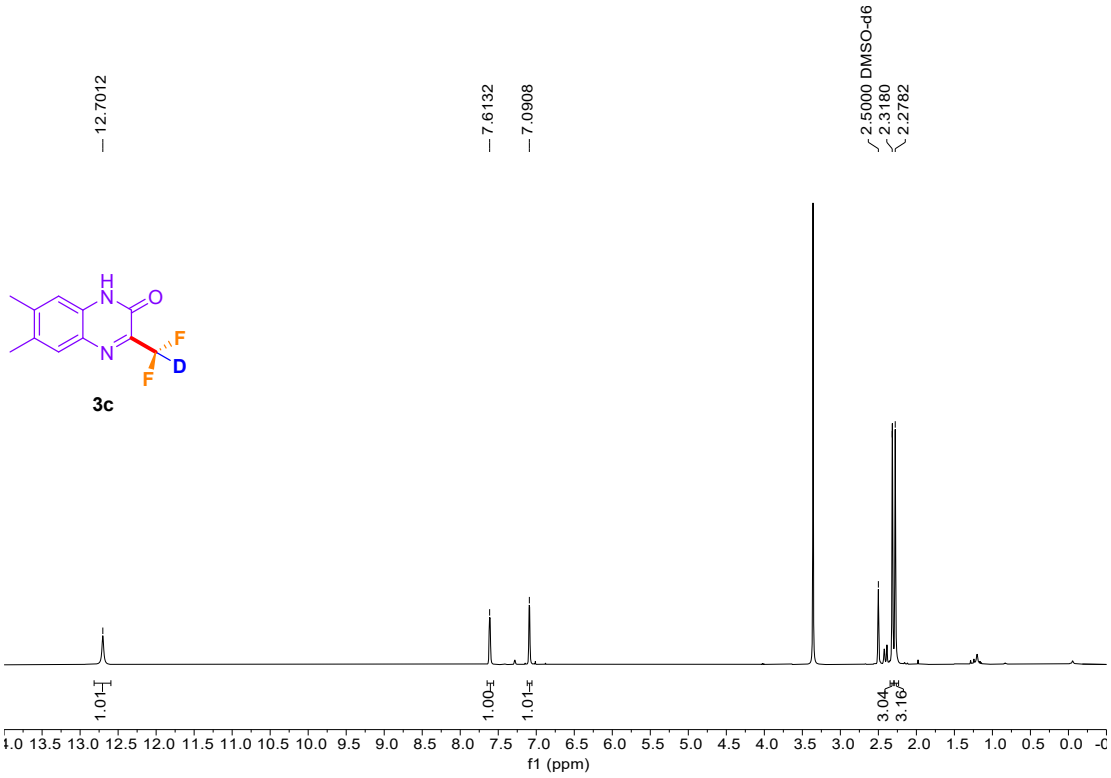


Figure S10, ^{1}H NMR spectrum of **3c** (400 MHz, DMSO-d_6)

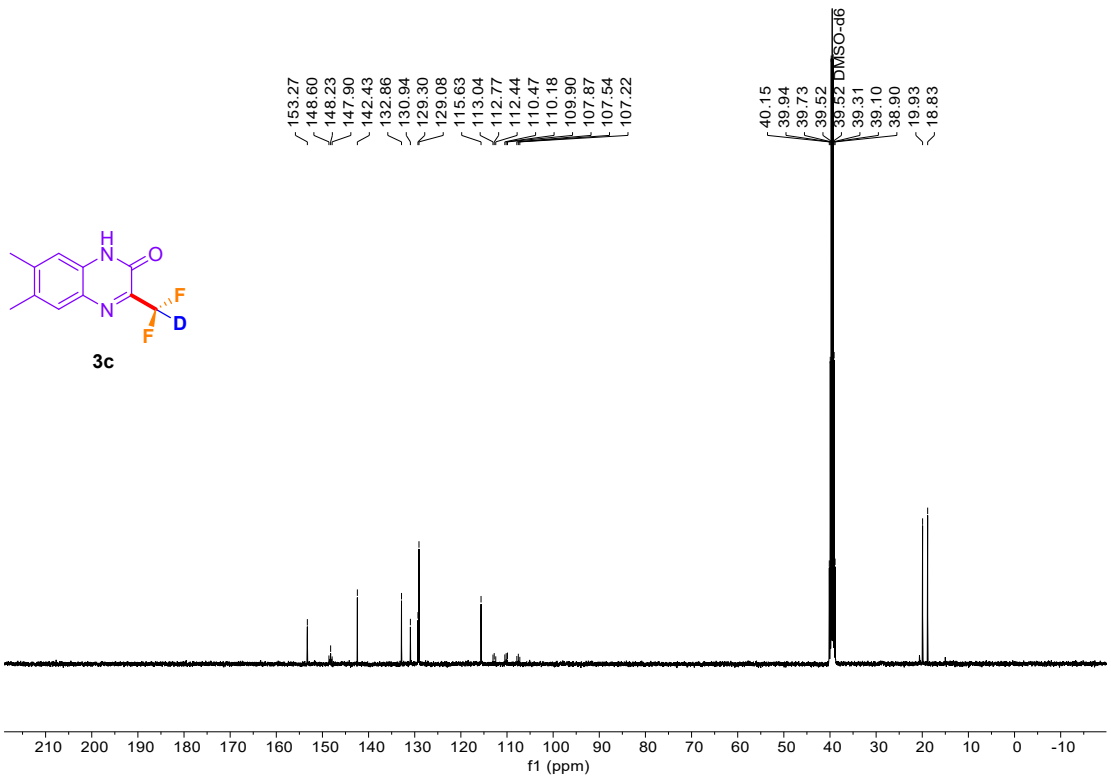


Figure S11, ^{13}C NMR spectrum of **3c** (101 MHz, DMSO-d_6)

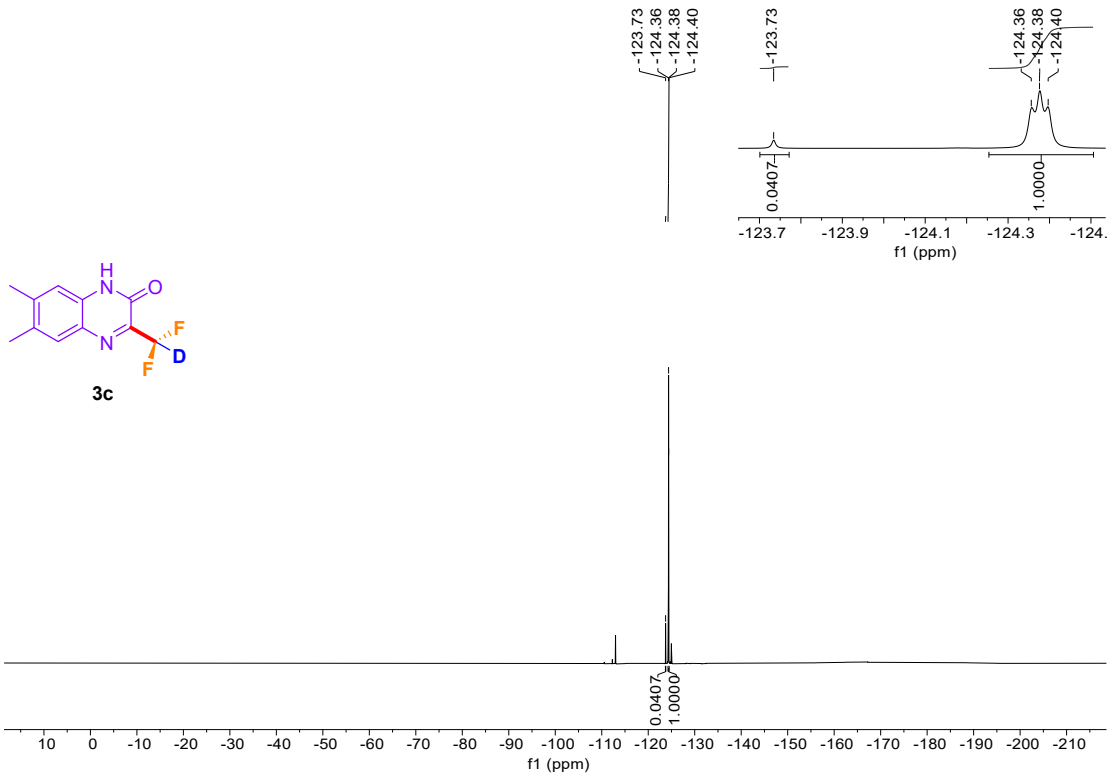


Figure S12, ^{19}F NMR spectrum of **3c** (377 MHz, DMSO-d_6)

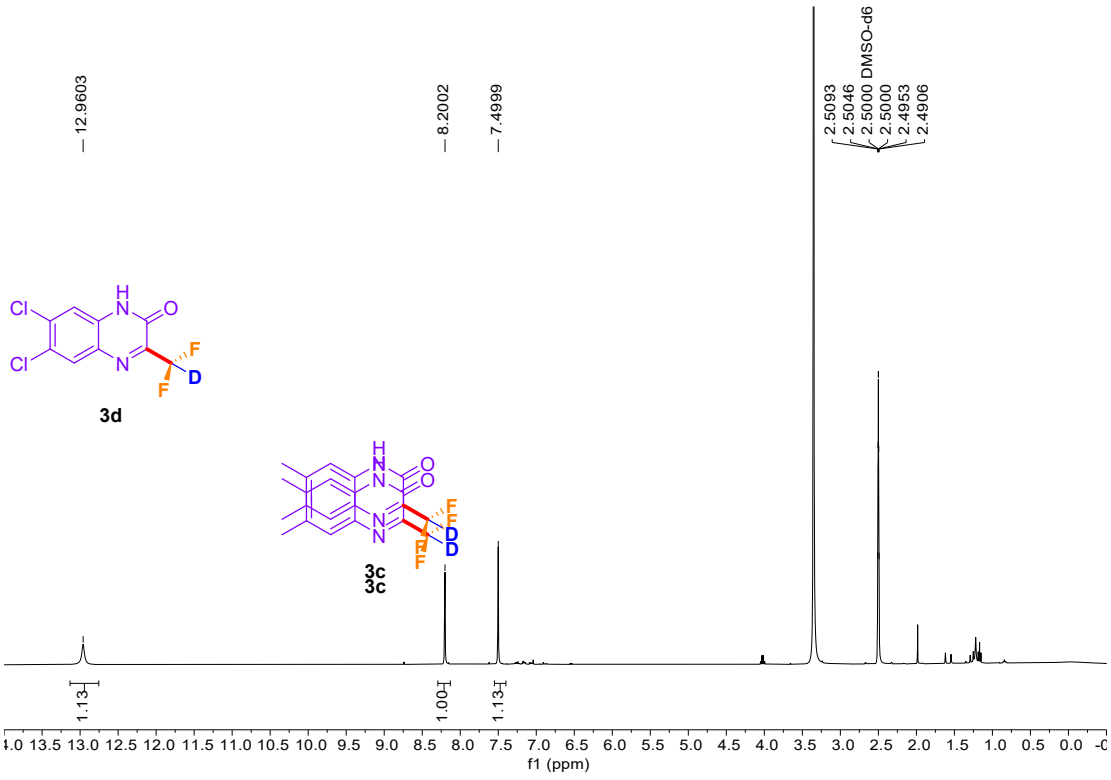


Figure S13, ^{1}H NMR spectrum of **3d** (400 MHz, DMSO-d_6)

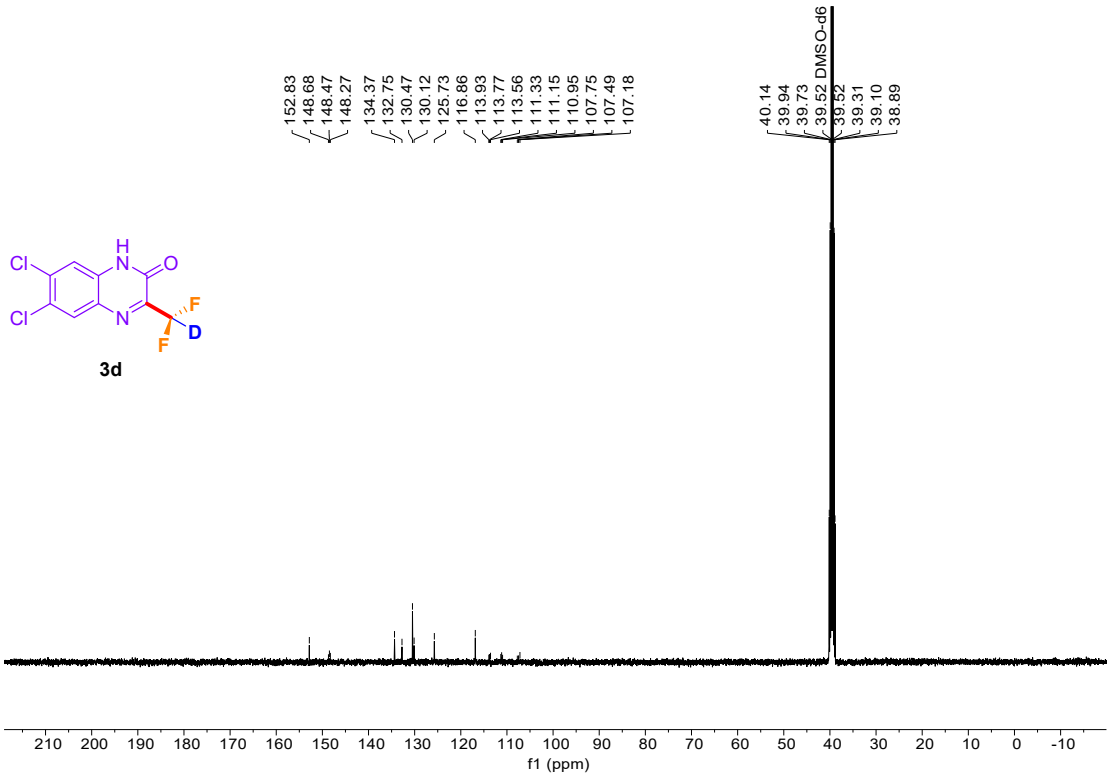


Figure S14, ^{13}C NMR spectrum of **3d** (101 MHz, DMSO-d_6)

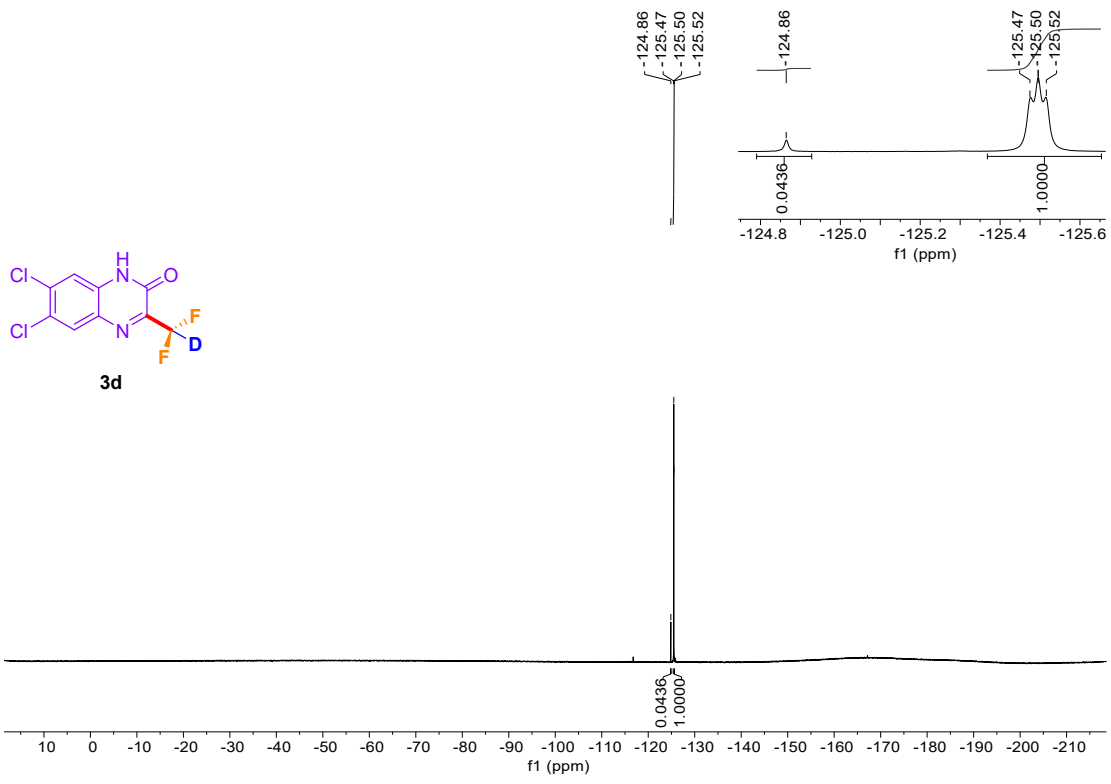


Figure S15, ^{19}F NMR spectrum of **3d** (377 MHz, DMSO-d_6)

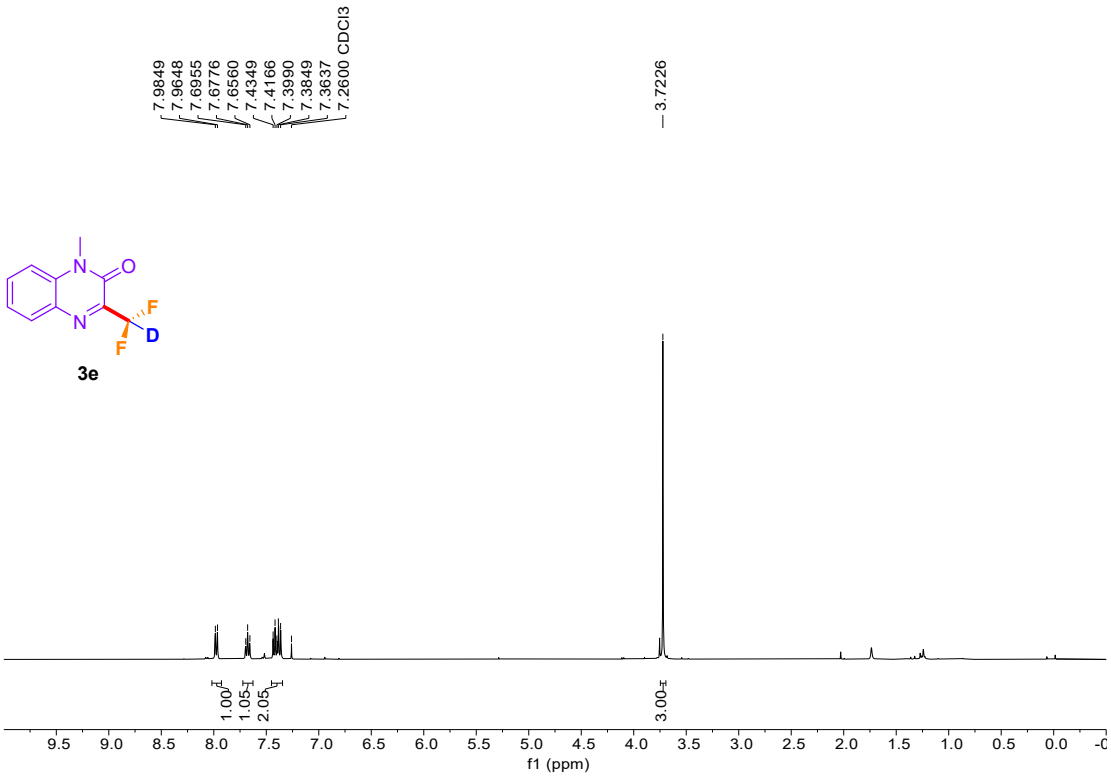


Figure S16, ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)

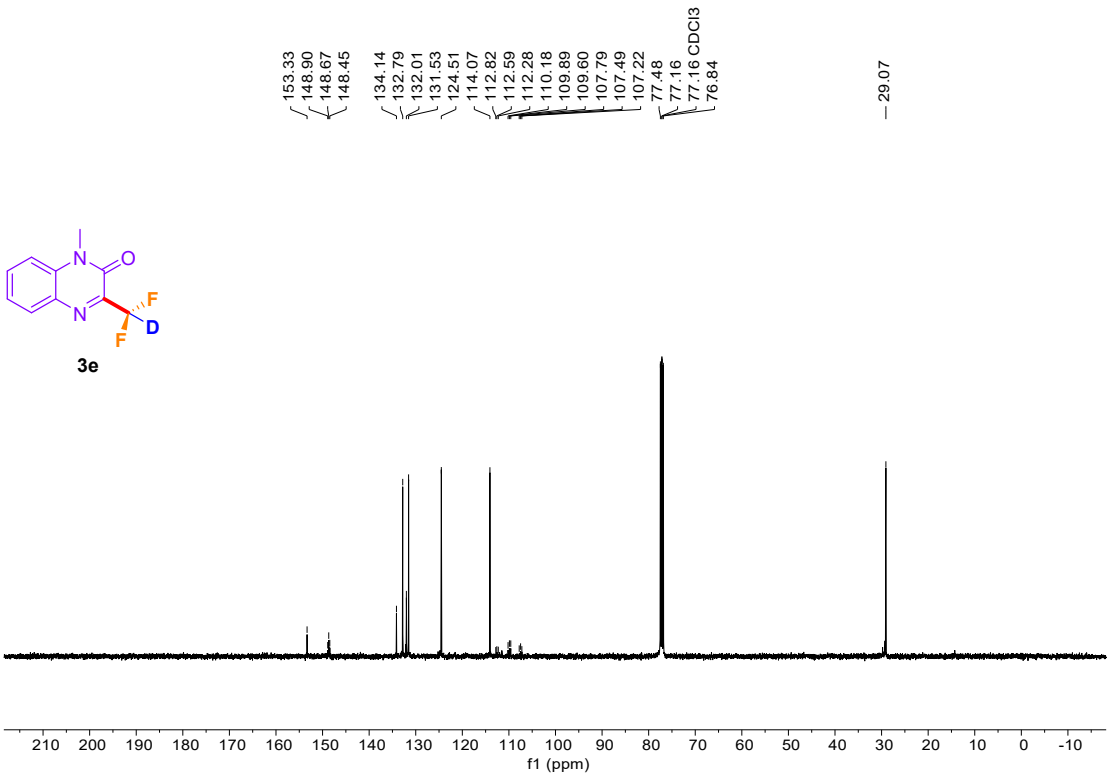


Figure S17, ^{13}C NMR spectrum of **3e** (101 MHz, $CDCl_3$)

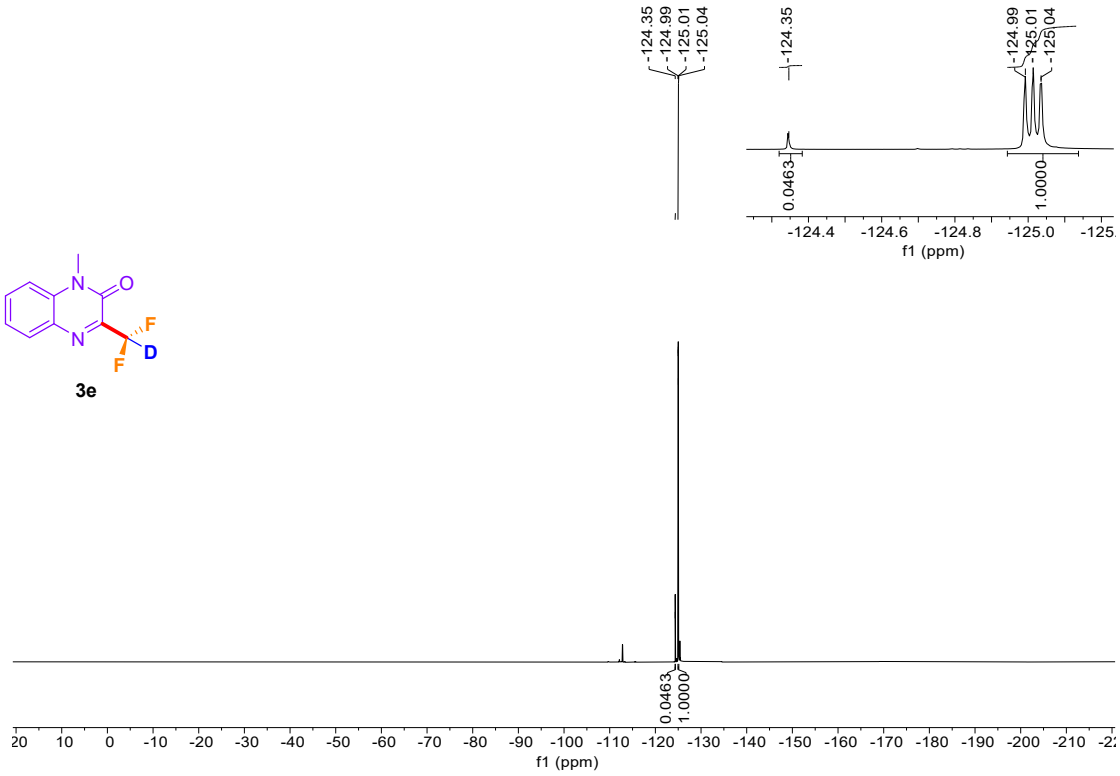


Figure S18, ^{19}F NMR spectrum of **3e** (377 MHz, $CDCl_3$)

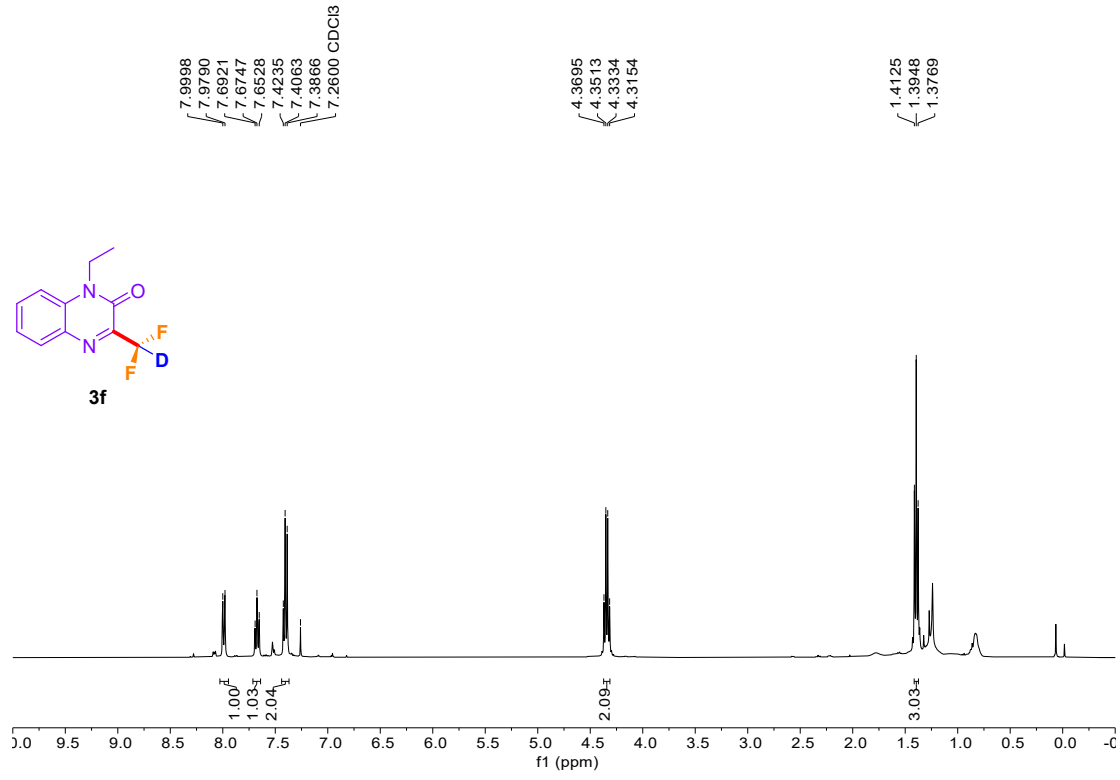


Figure S19, ^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)

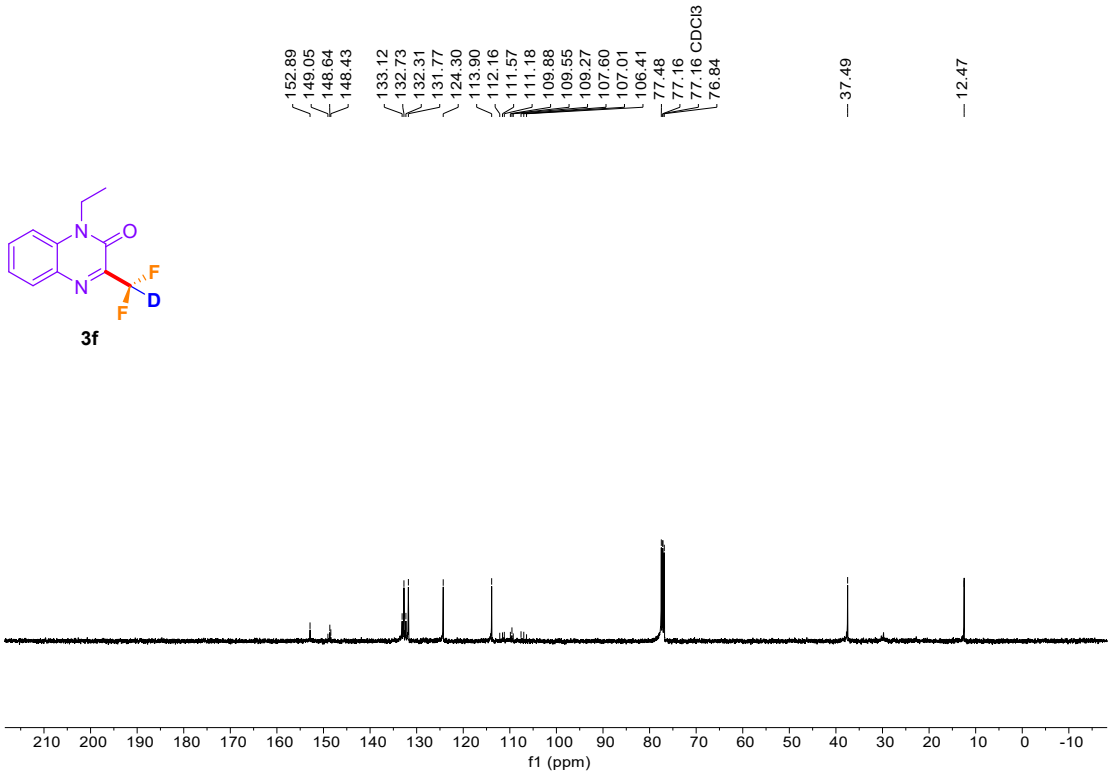


Figure S20 ^{13}C NMR spectrum of **3f** (101 MHz, $CDCl_3$)

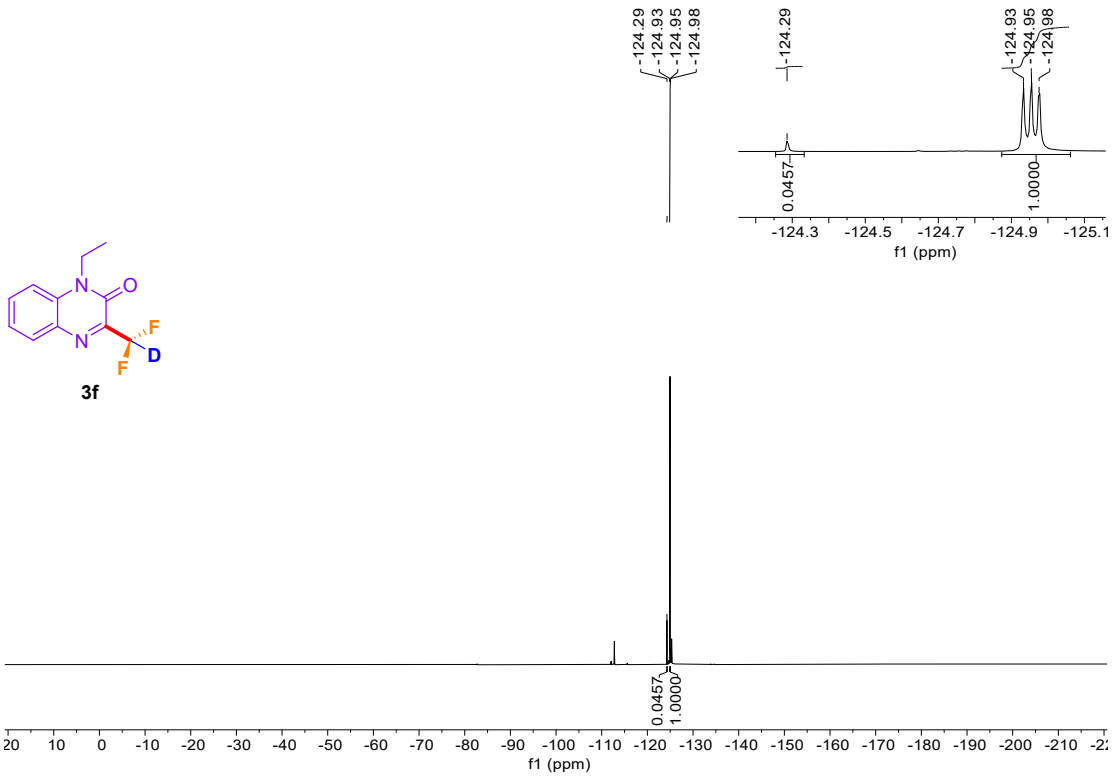


Figure S21, ^{19}F NMR spectrum of **3f** (377 MHz, $CDCl_3$)

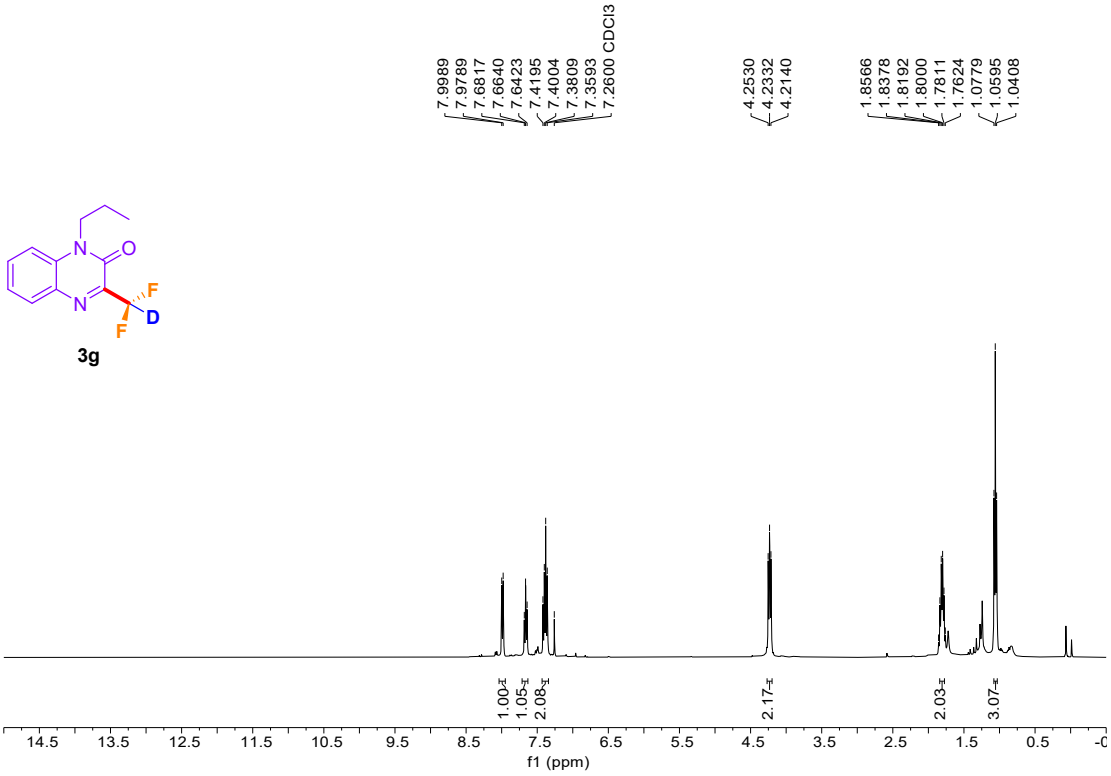


Figure S22, ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)

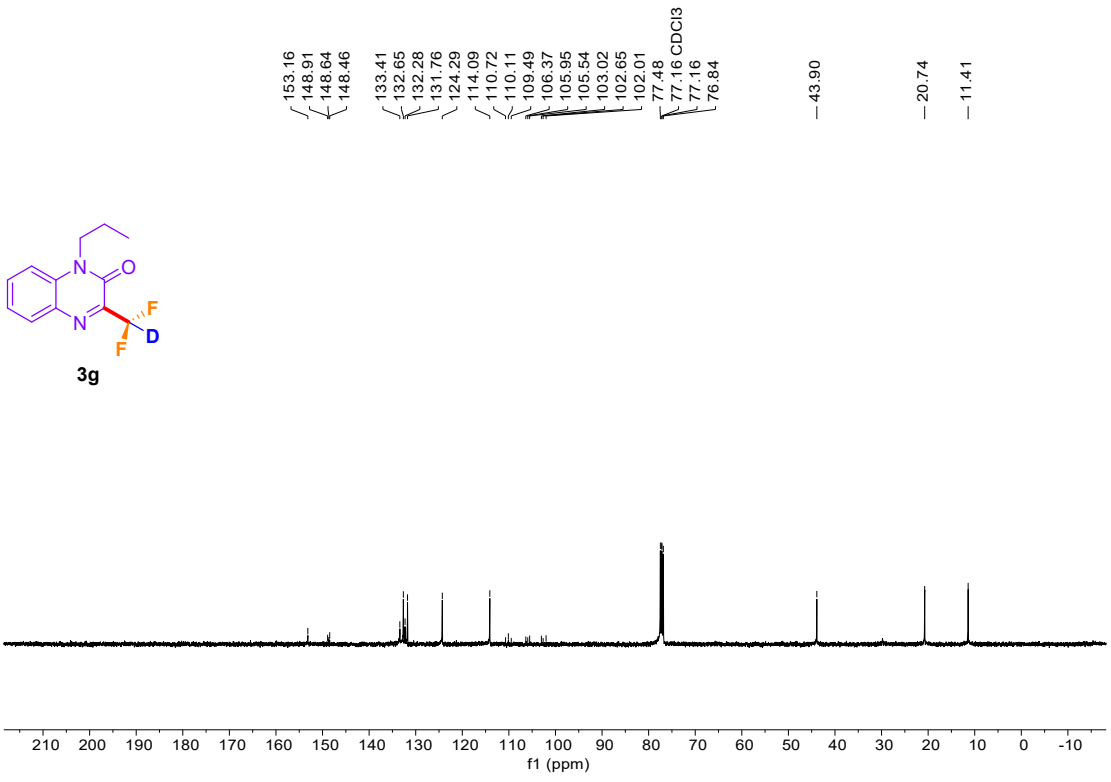


Figure S23, ^{13}C NMR spectrum of **3g** (101 MHz, $CDCl_3$)

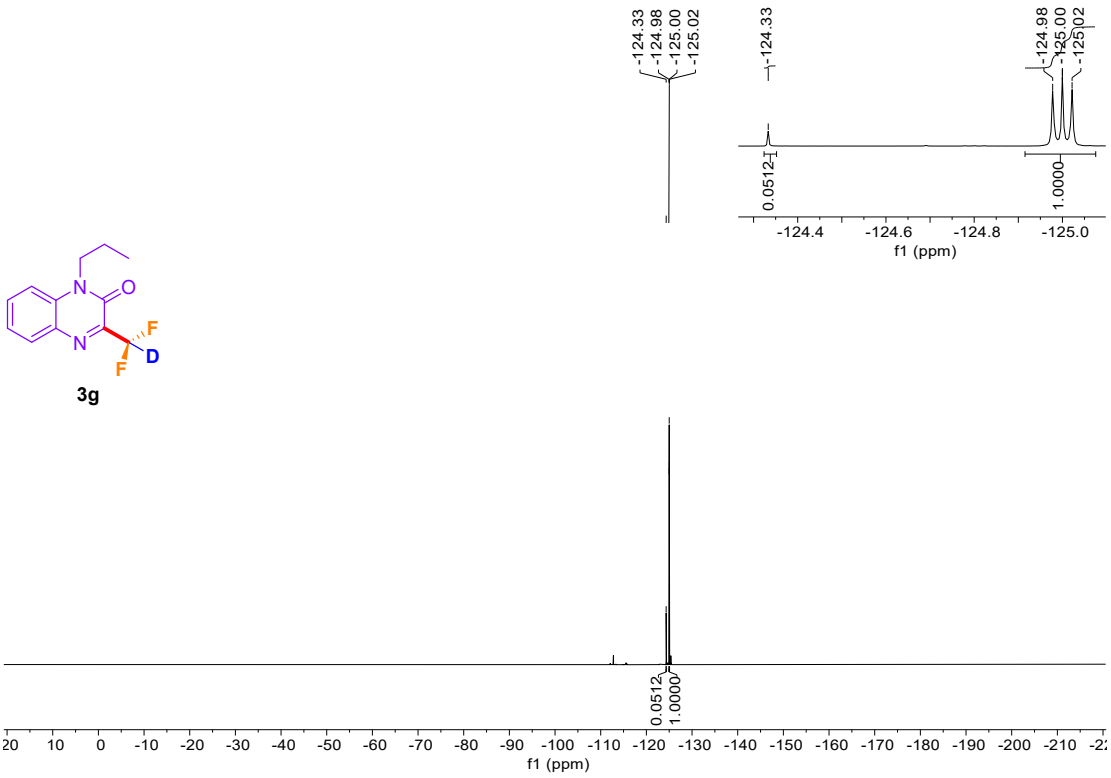


Figure S24, ^{19}F NMR spectrum of **3g** (377 MHz, $CDCl_3$)

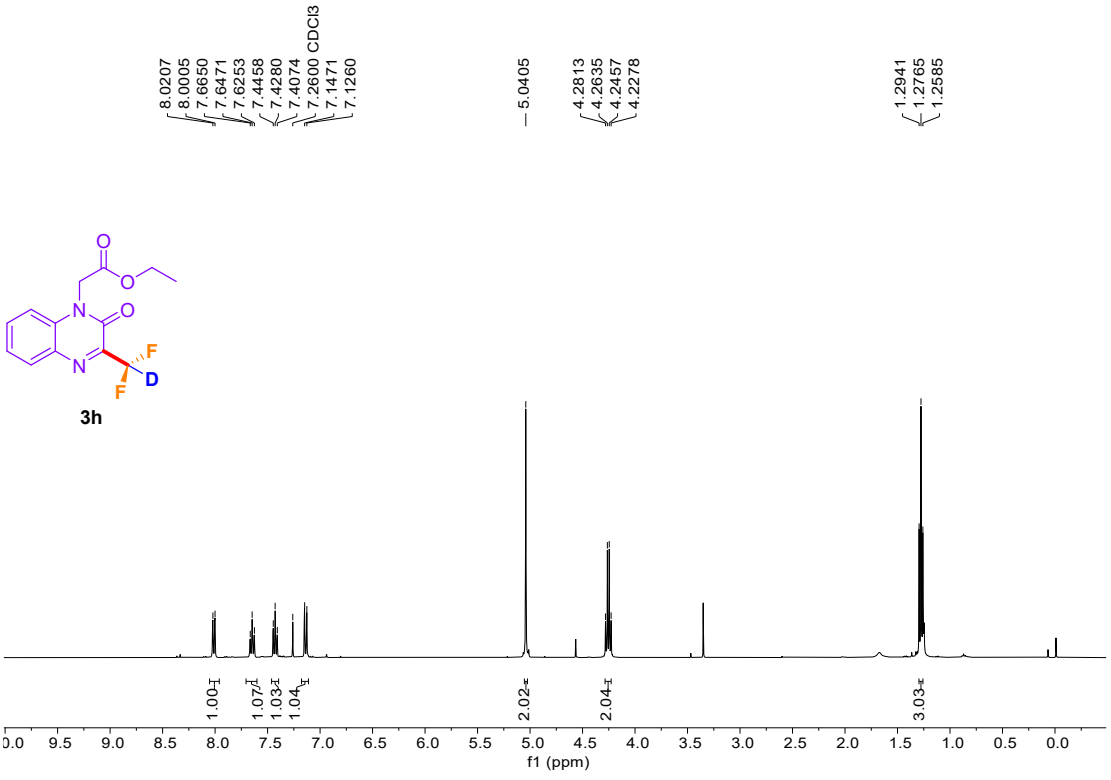


Figure S25, ^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)

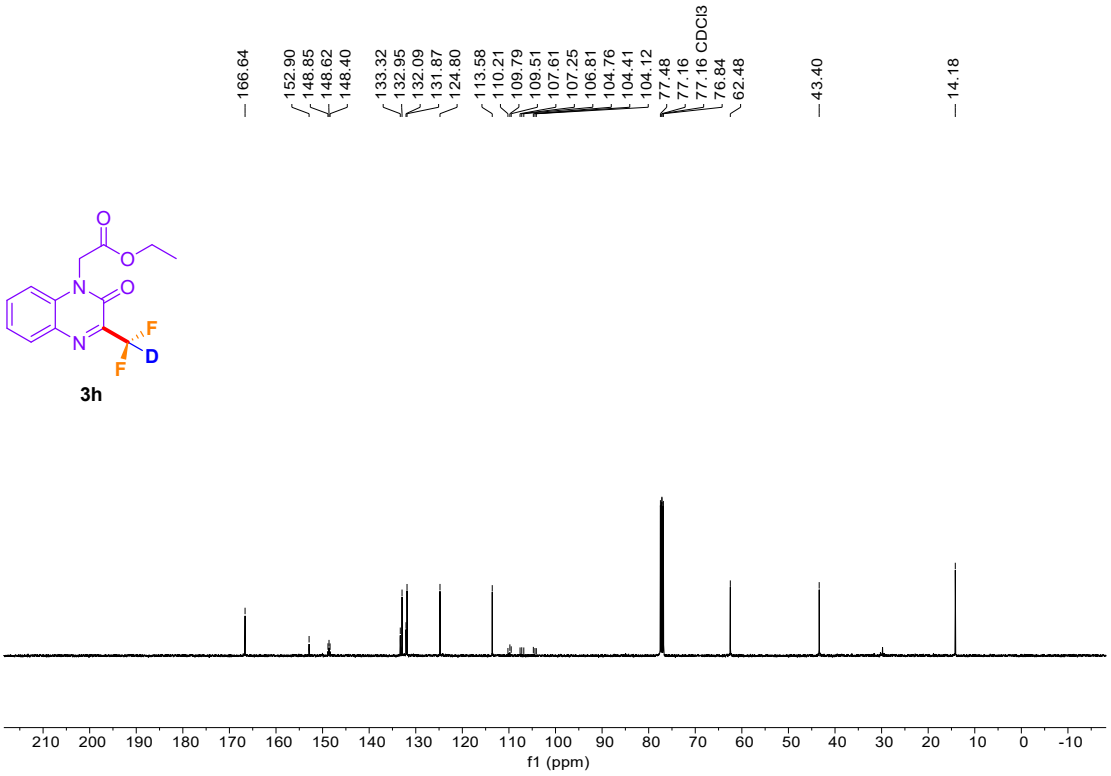


Figure S26, ^{13}C NMR spectrum of **3h** (101 MHz, $CDCl_3$)

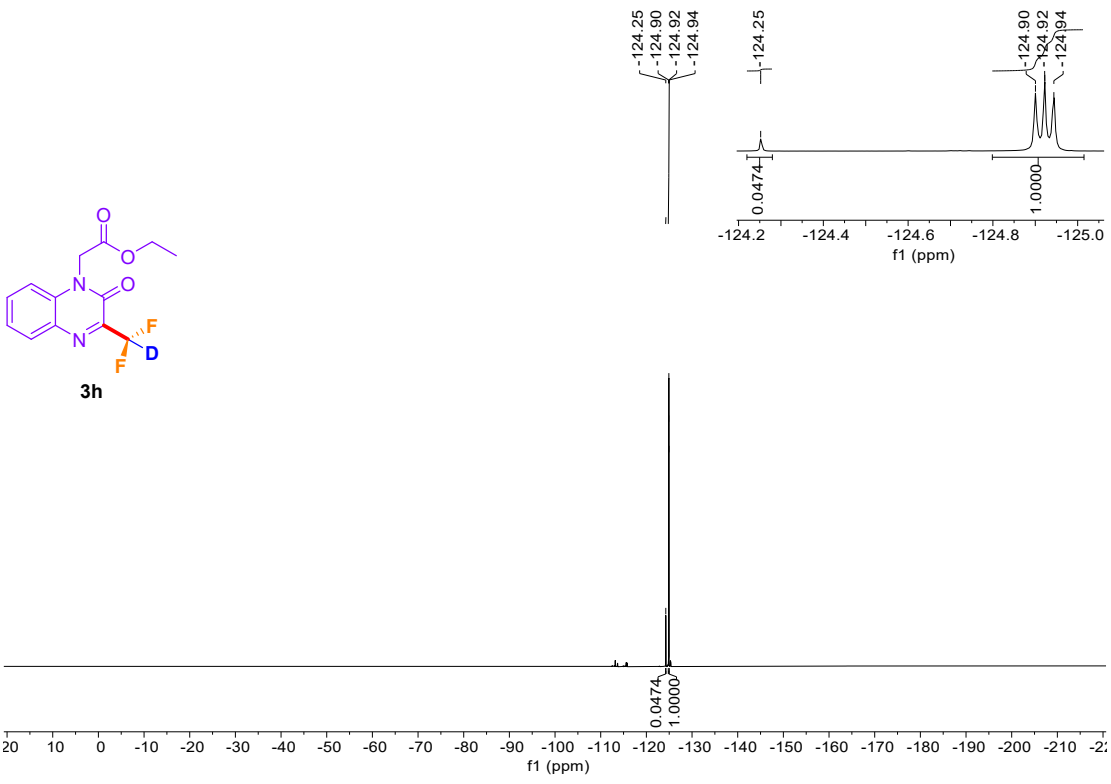


Figure S27, 19F NMR spectrum of **3h** (377 MHz, CDCl3)

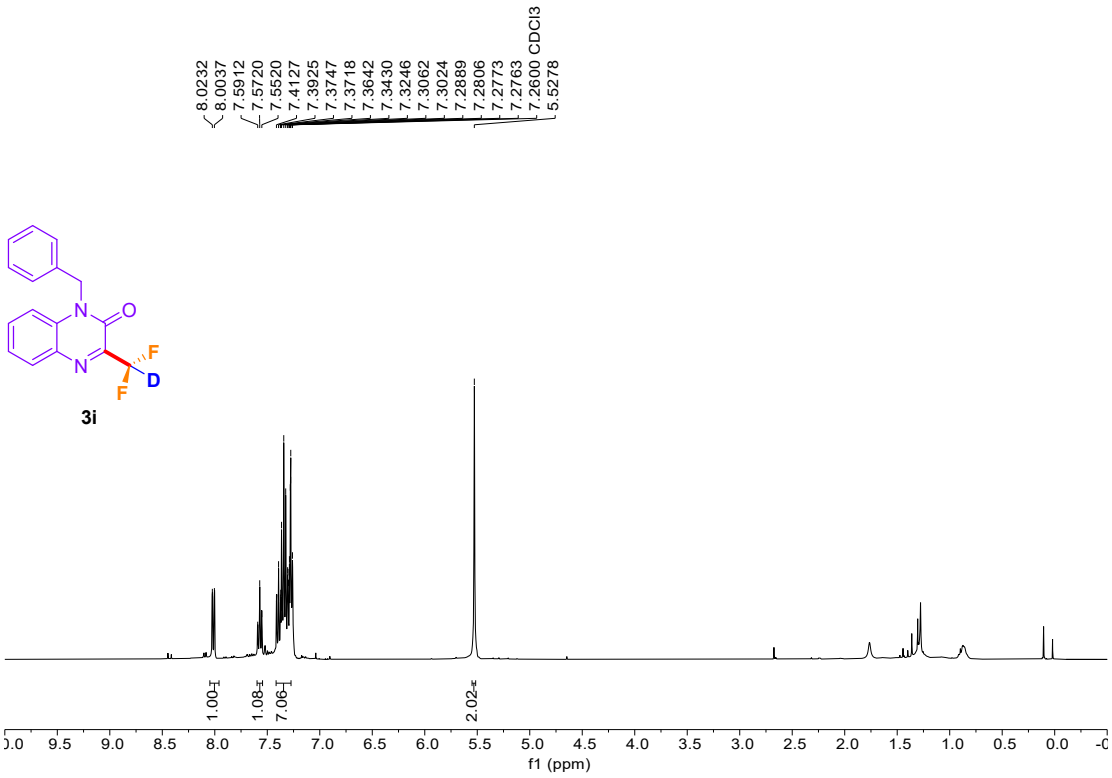


Figure S28, ^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)

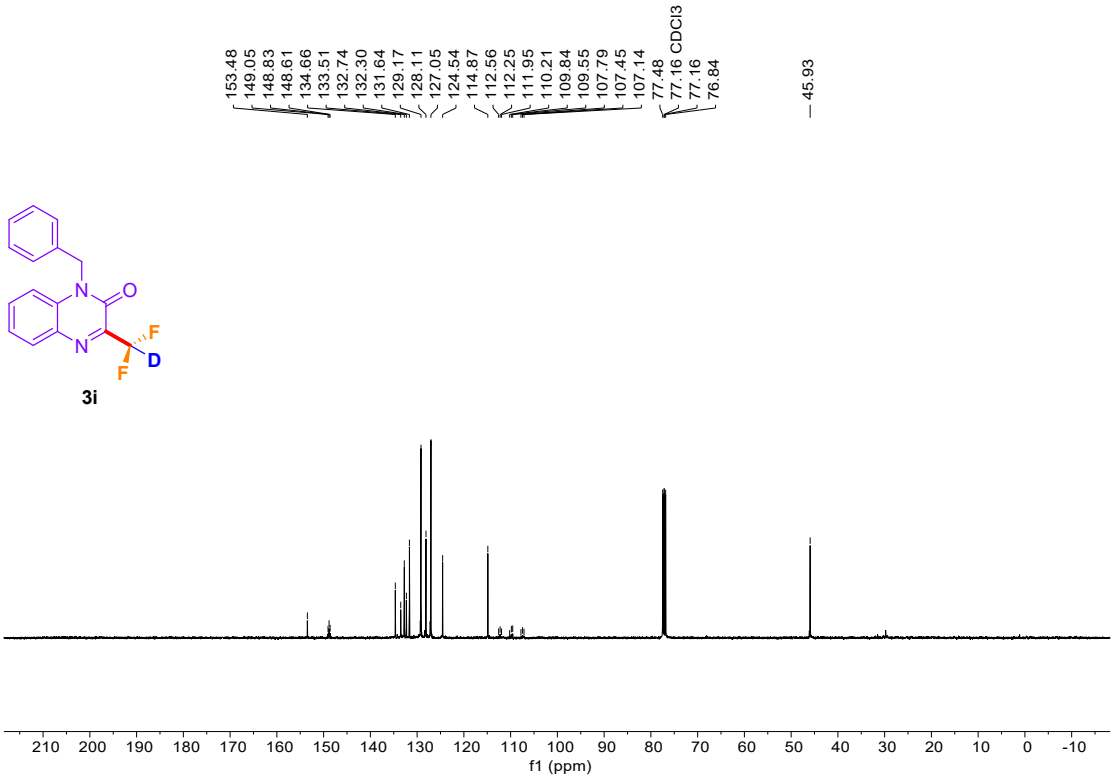


Figure S29, ^{13}C NMR spectrum of **3i** (101 MHz, $CDCl_3$)

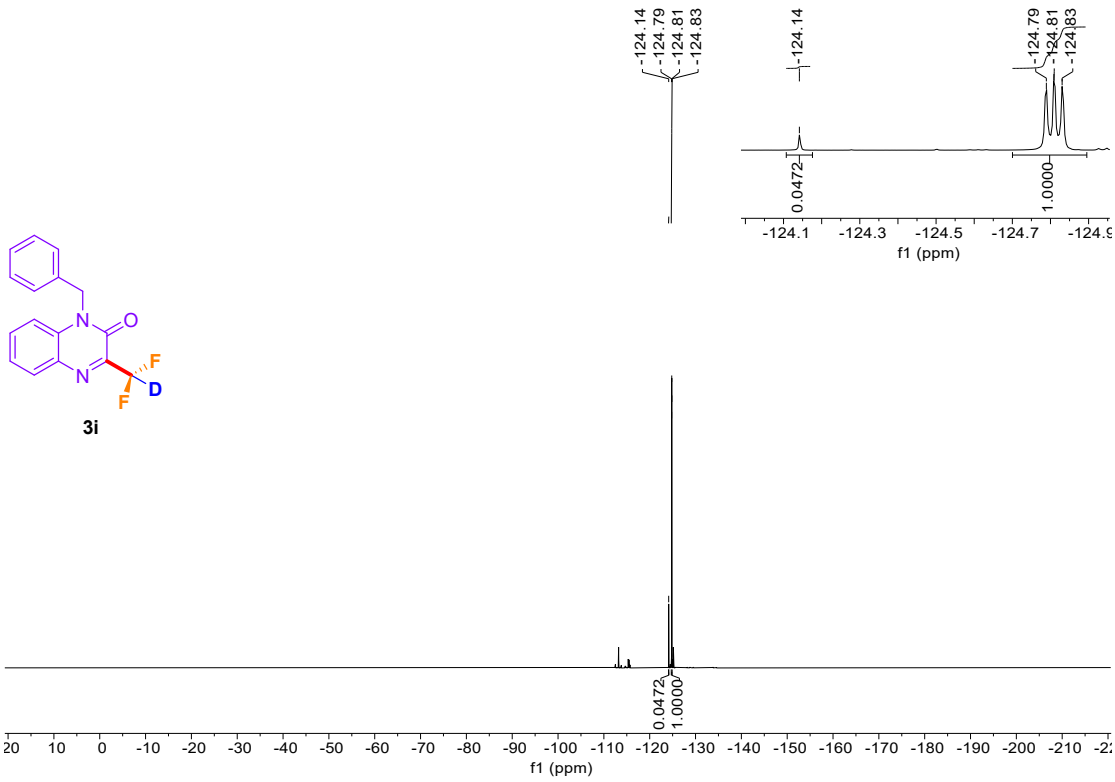


Figure S30, ^{19}F NMR spectrum of **3i** (377 MHz, $CDCl_3$)

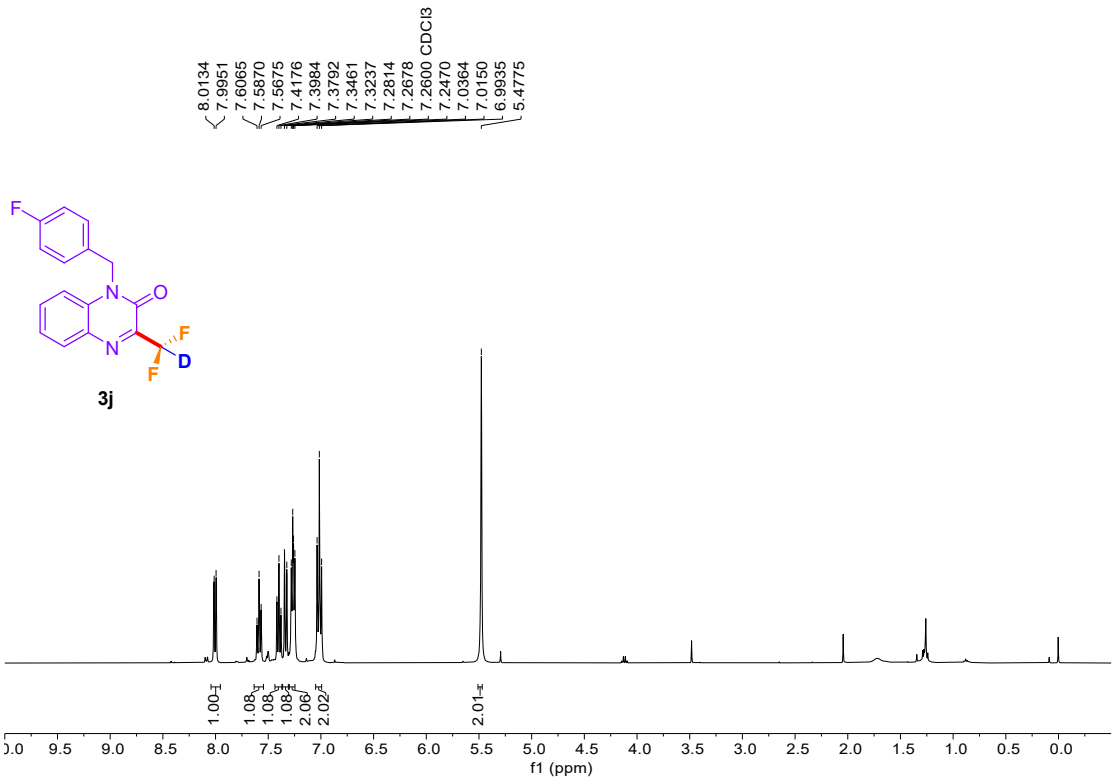


Figure S31, ^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)

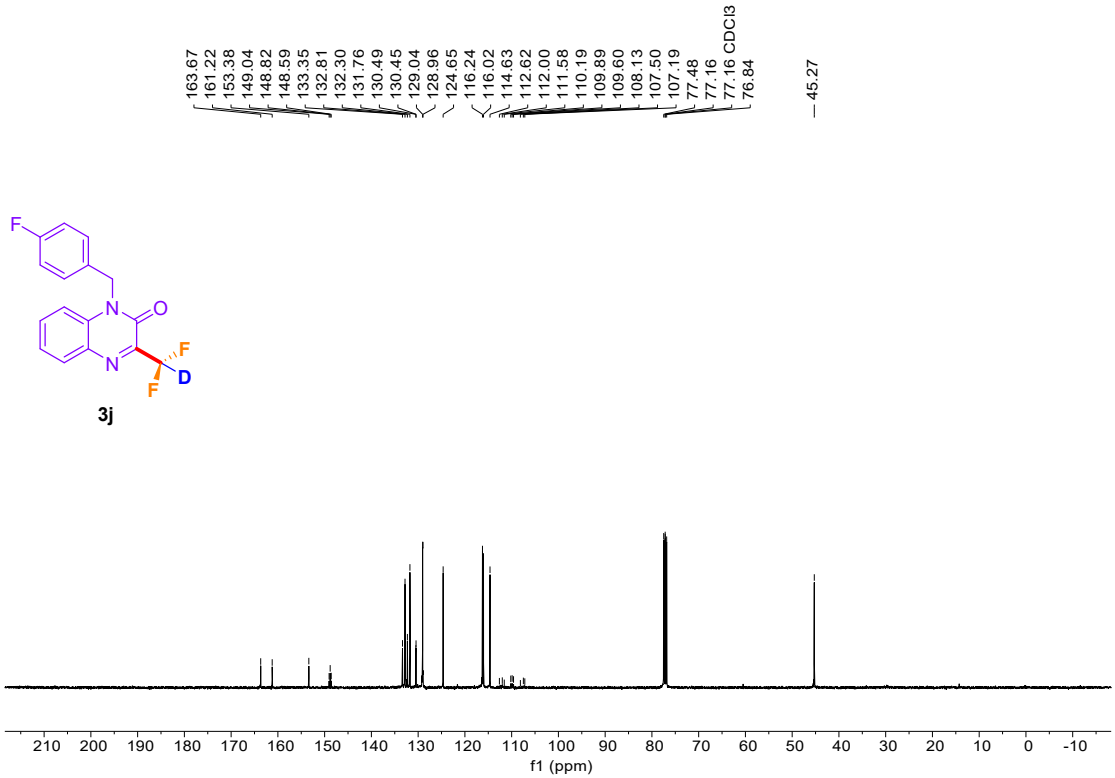


Figure S32, ^{13}C NMR spectrum of **3j** (101 MHz, $CDCl_3$)

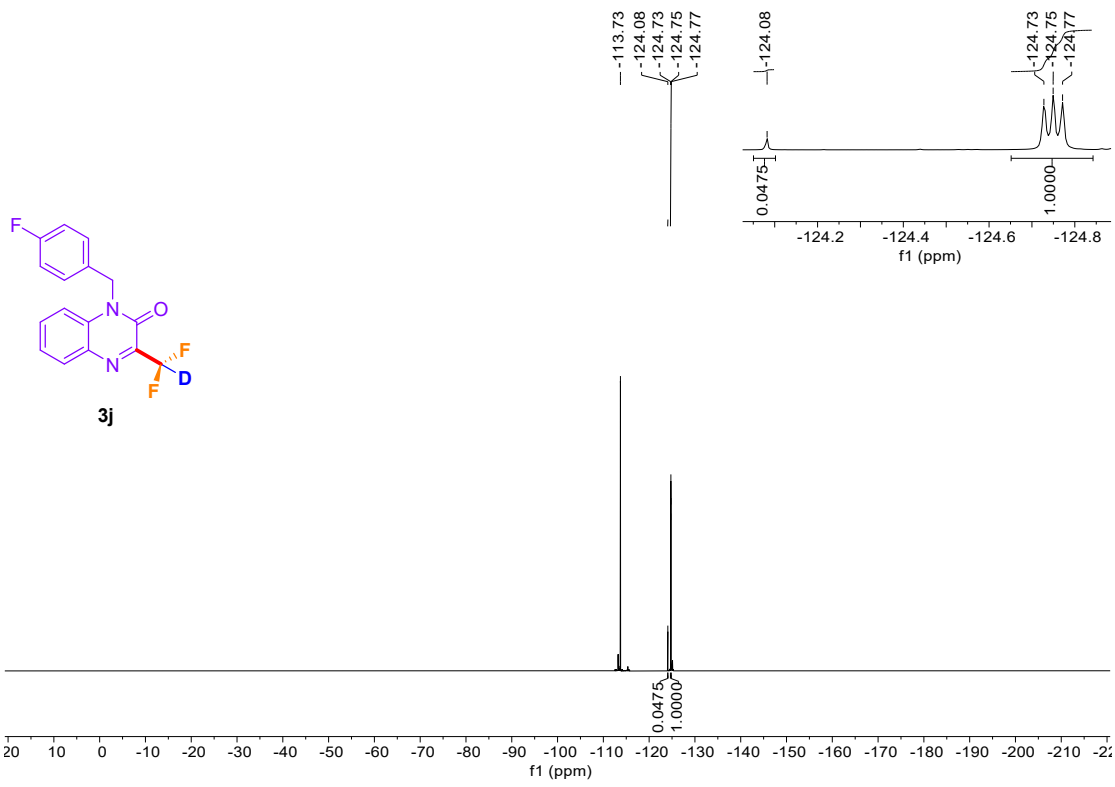


Figure S33, ^{19}F NMR spectrum of **3j** (377 MHz, $CDCl_3$)

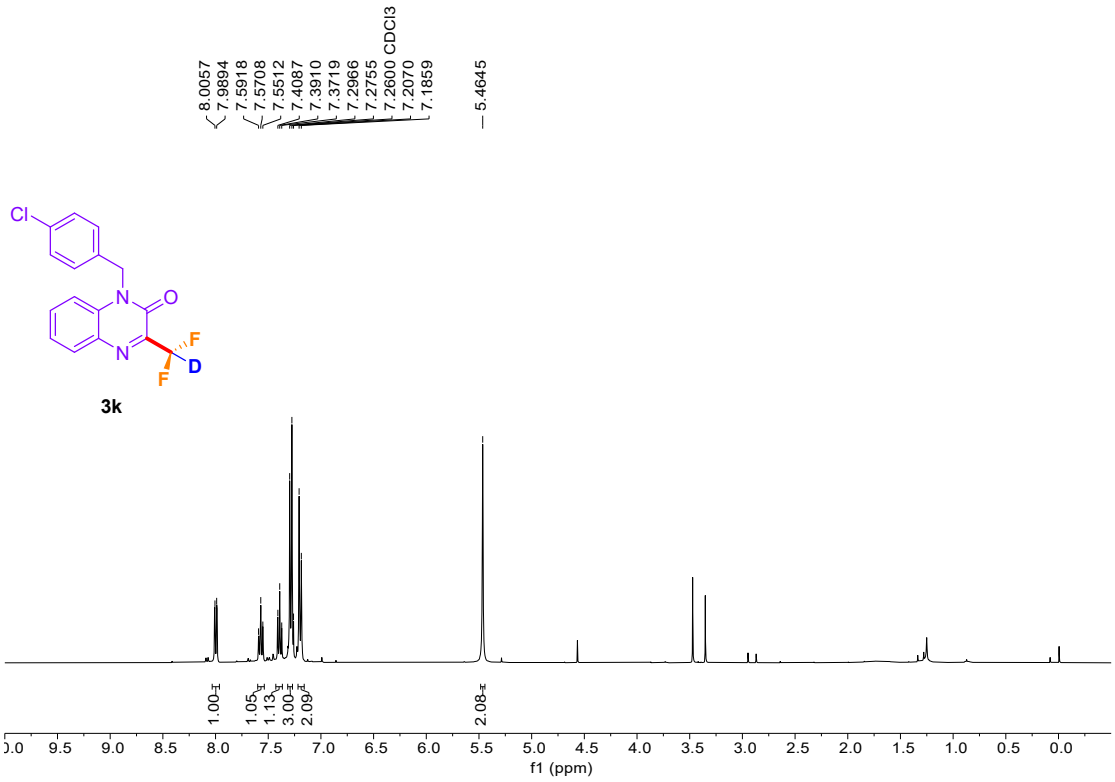


Figure S34, ^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)

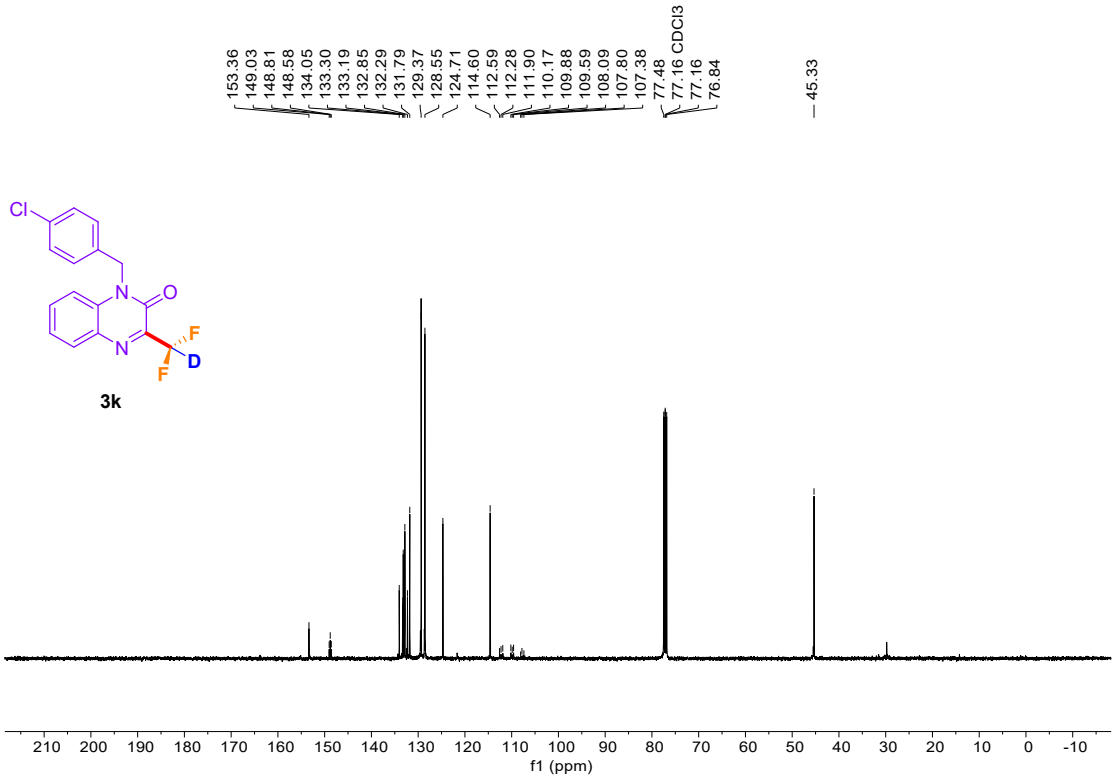


Figure S35, ^{13}C NMR spectrum of **3k** (101 MHz, $CDCl_3$)

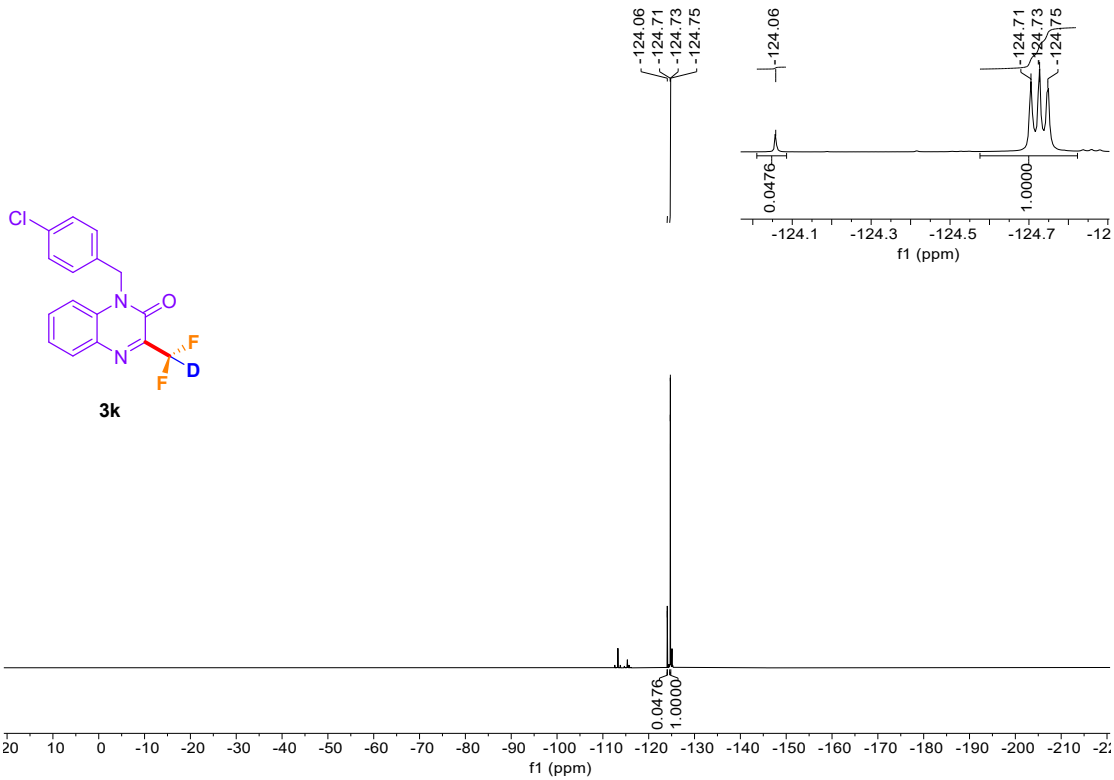


Figure S36, ^{19}F NMR spectrum of **3k** (377 MHz, $CDCl_3$)

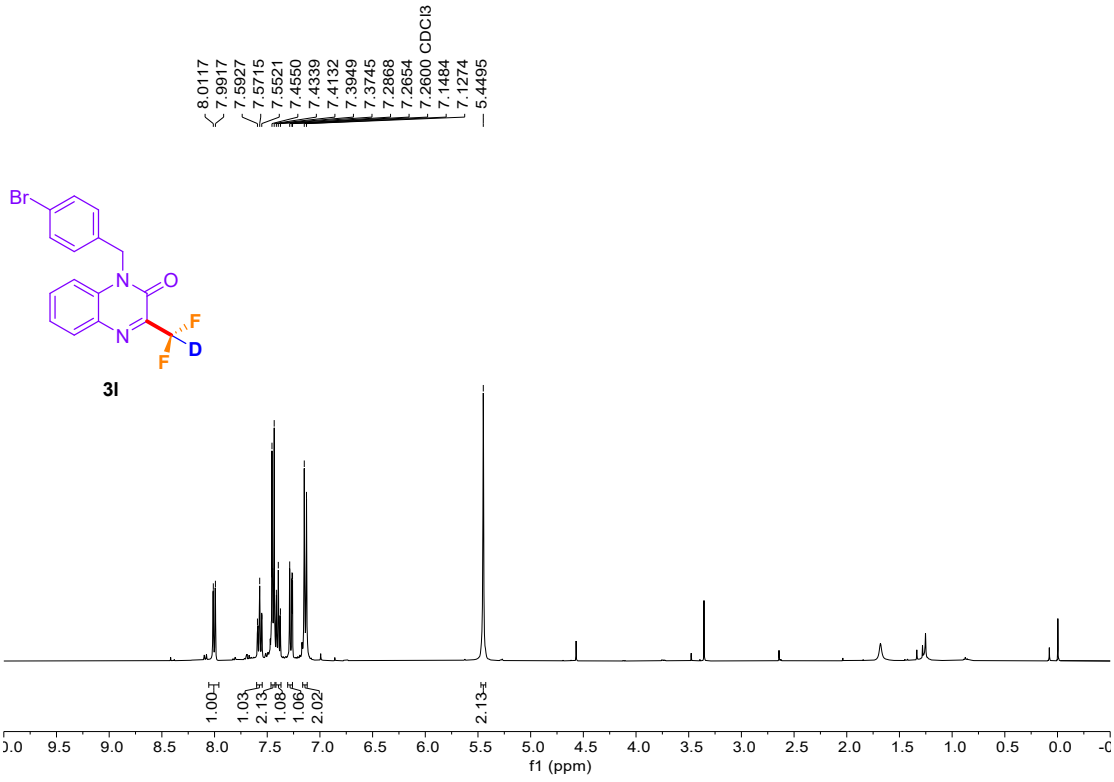


Figure S37, ^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)

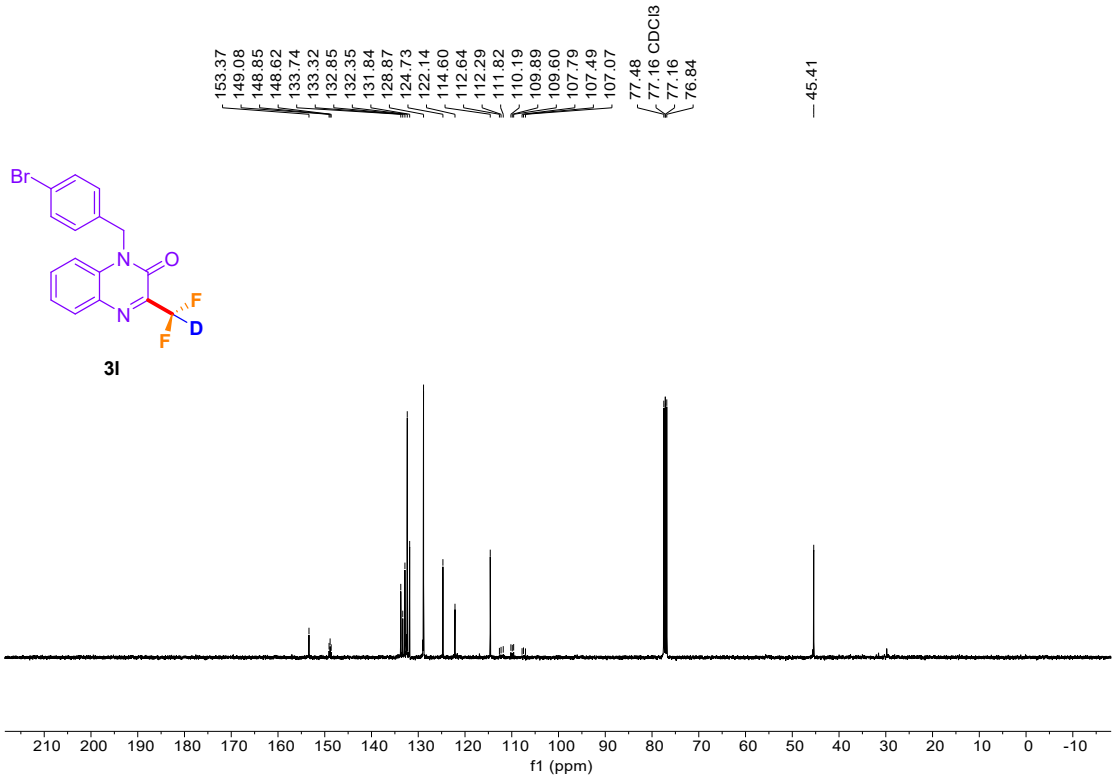


Figure S38, ^{13}C NMR spectrum of **3l** (101 MHz, $CDCl_3$)

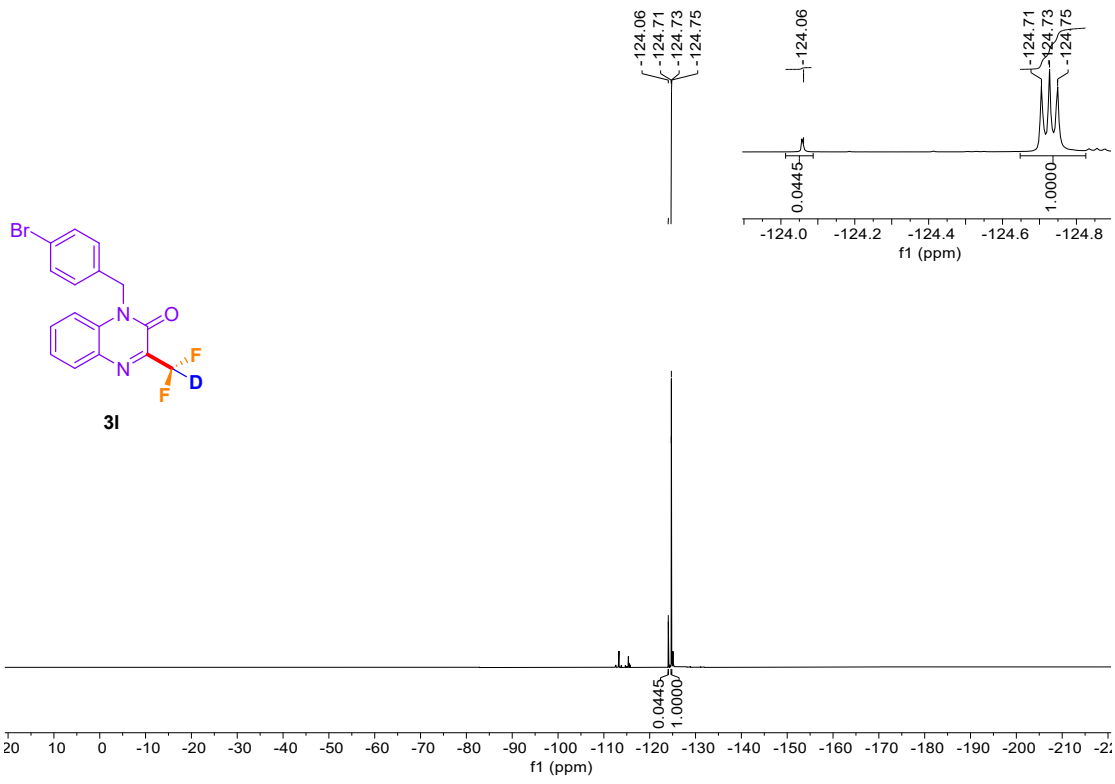


Figure S39, ^{19}F NMR spectrum of **3l** (377 MHz, $CDCl_3$)

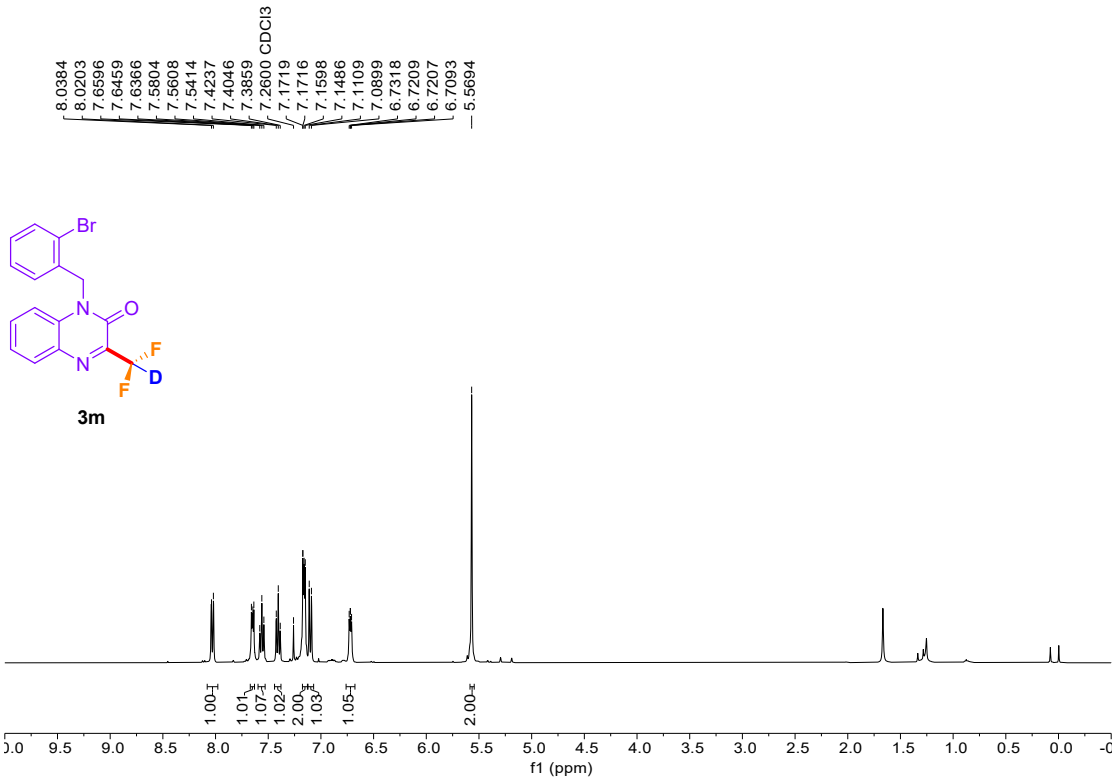


Figure S40, ^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)

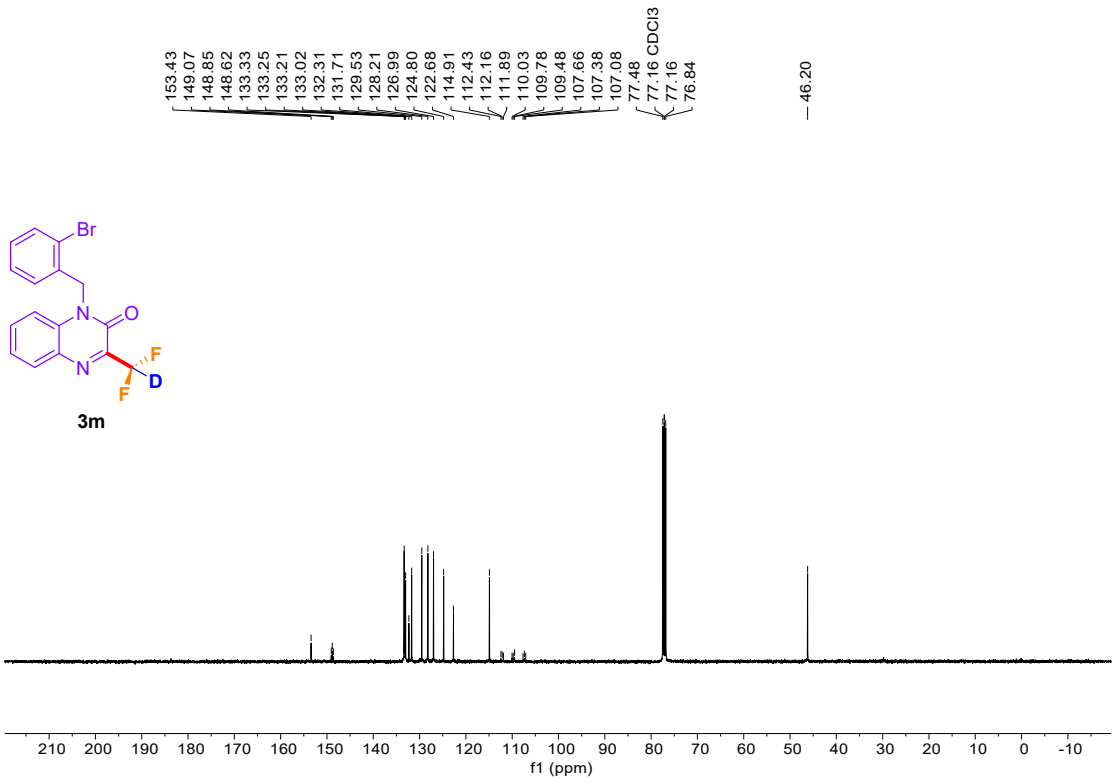


Figure S41, ^{13}C NMR spectrum of **3m** (101 MHz, $CDCl_3$)

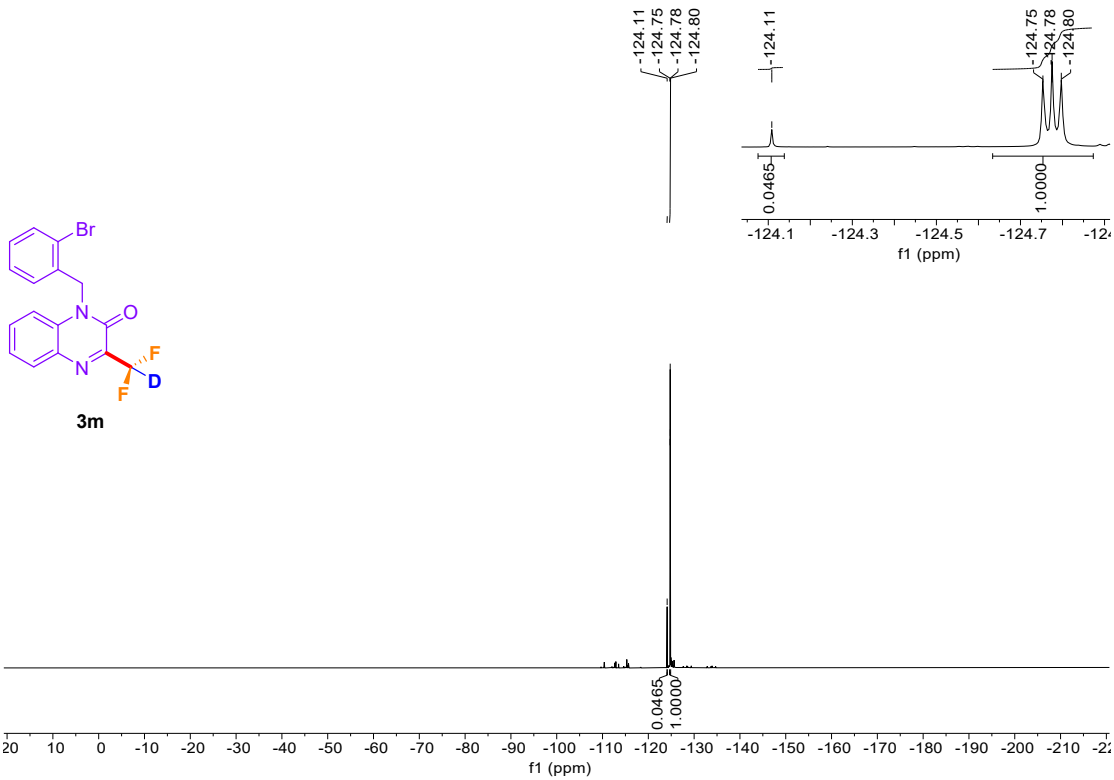


Figure S42, ^{19}F NMR spectrum of **3m** (377 MHz, $CDCl_3$)

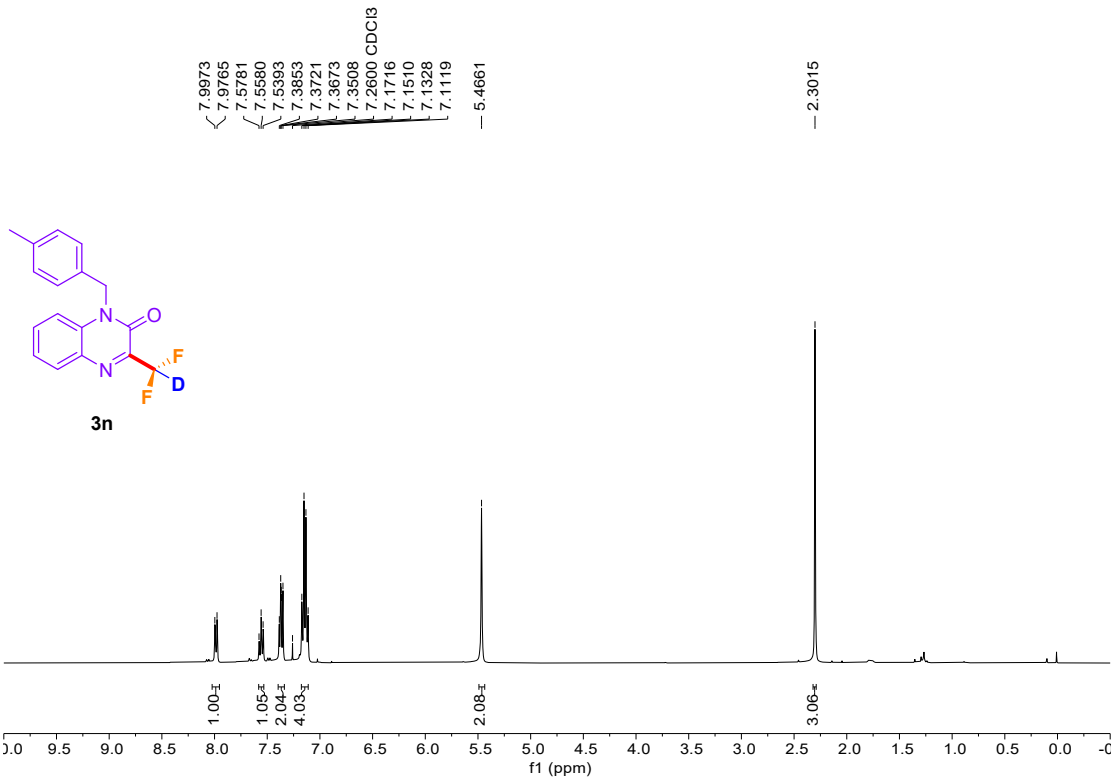


Figure S43, ^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)

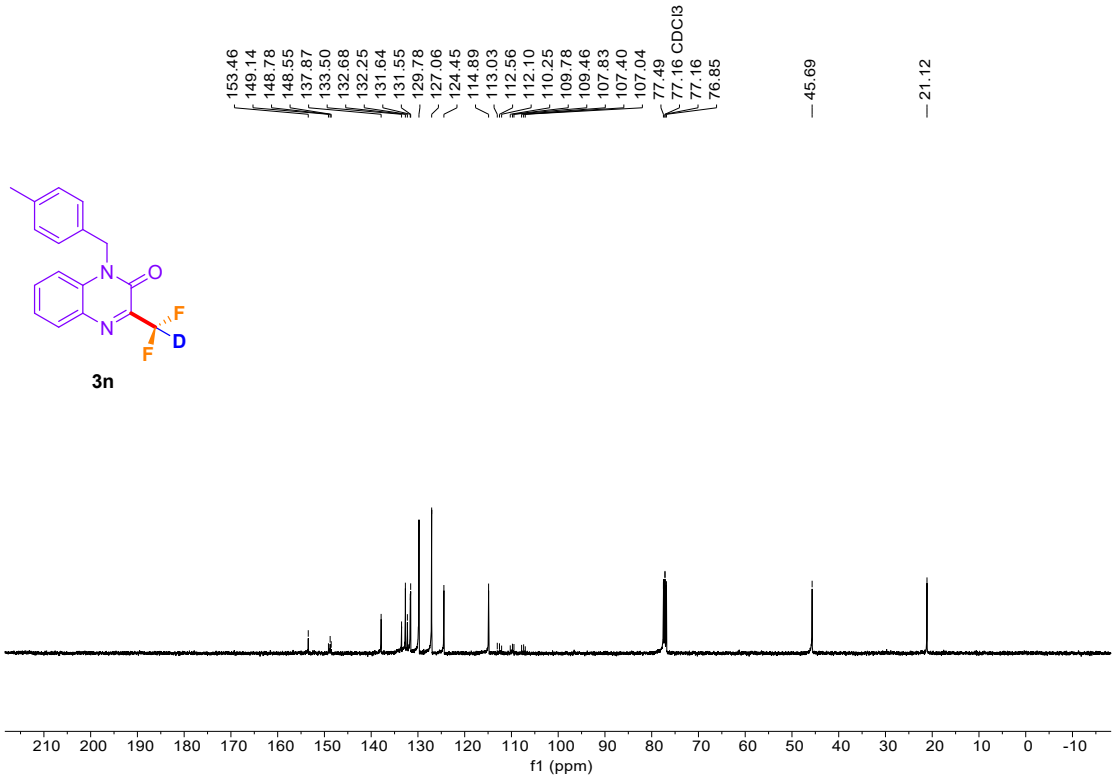


Figure S44, ^{13}C NMR spectrum of **3n** (101 MHz, $CDCl_3$)

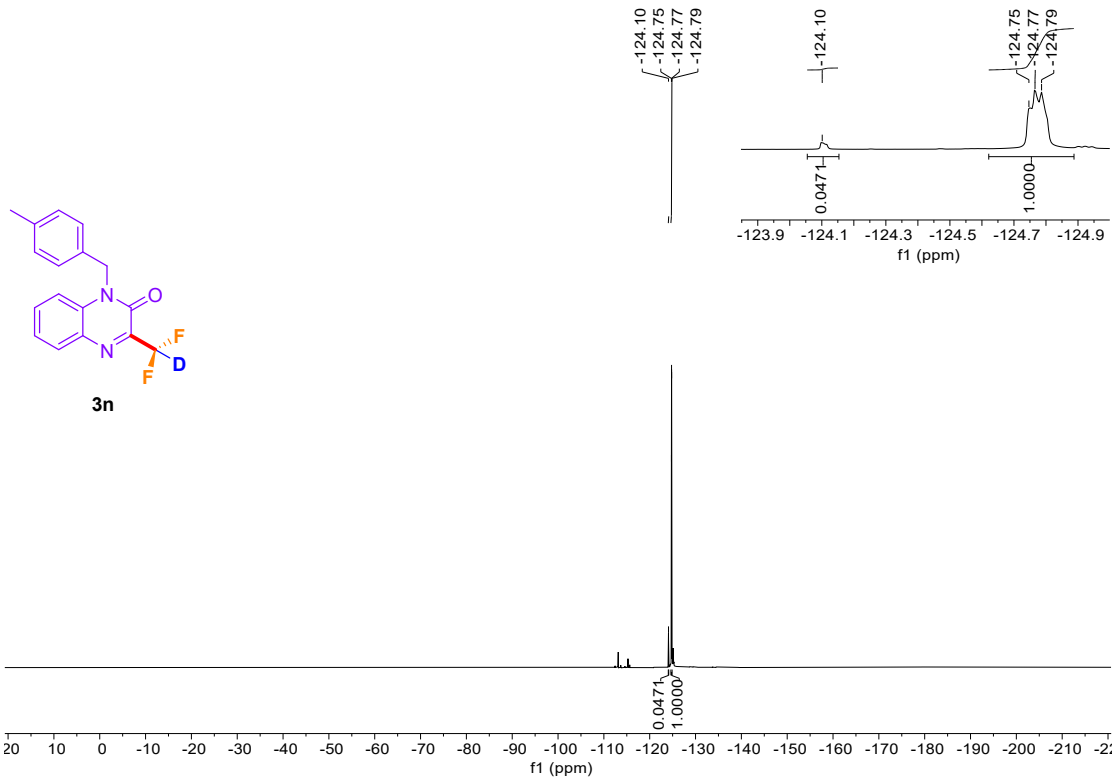


Figure S45, ^{19}F NMR spectrum of **3n** (377 MHz, $CDCl_3$)

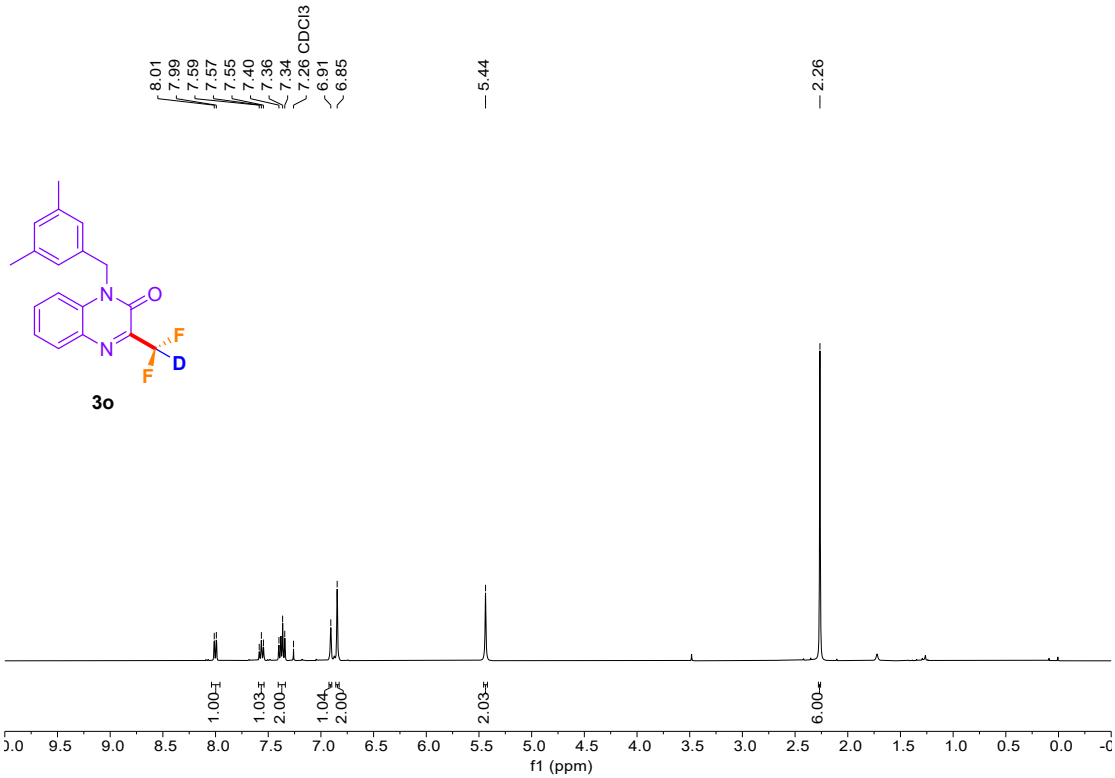


Figure S46, ^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)

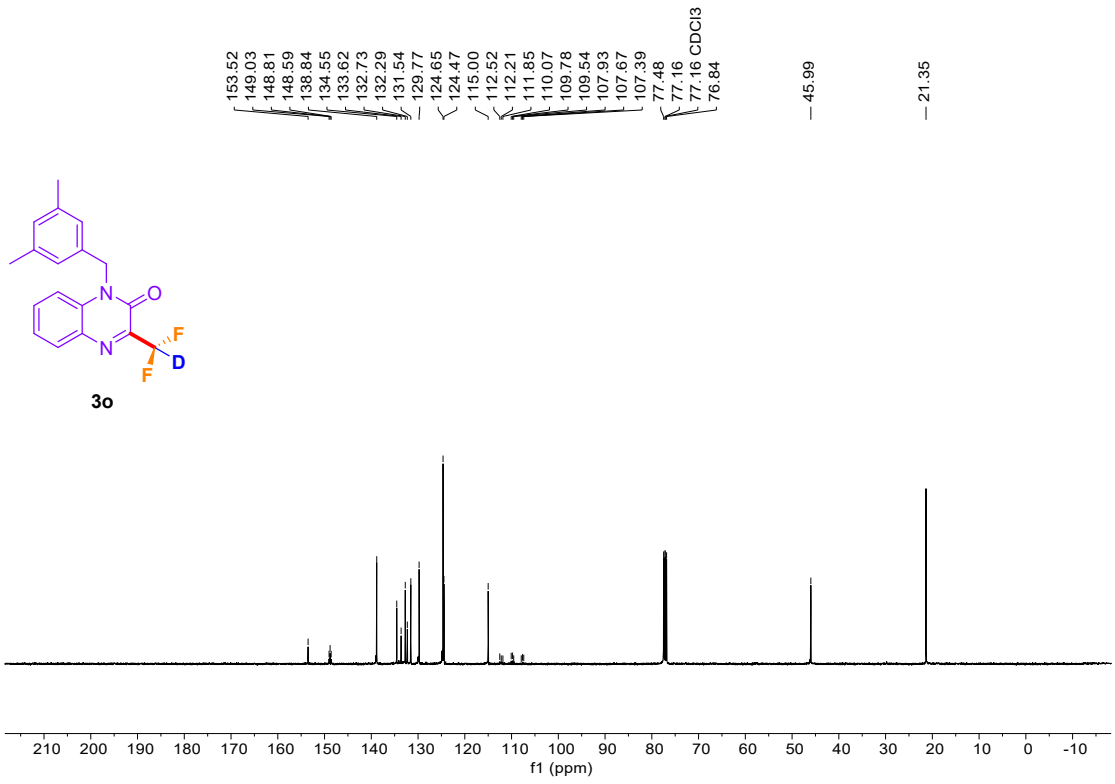


Figure S47, ^{13}C NMR spectrum of **3o** (101 MHz, $CDCl_3$)

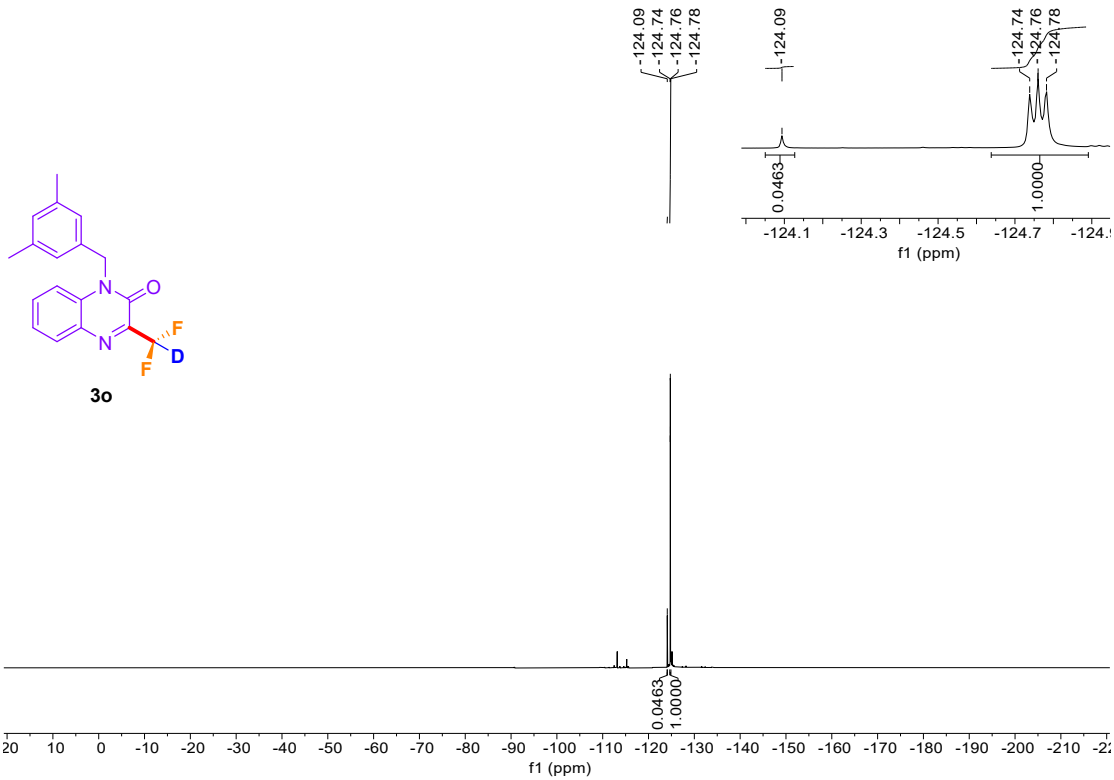


Figure S48, ^{19}F NMR spectrum of **3o** (377 MHz, $CDCl_3$)

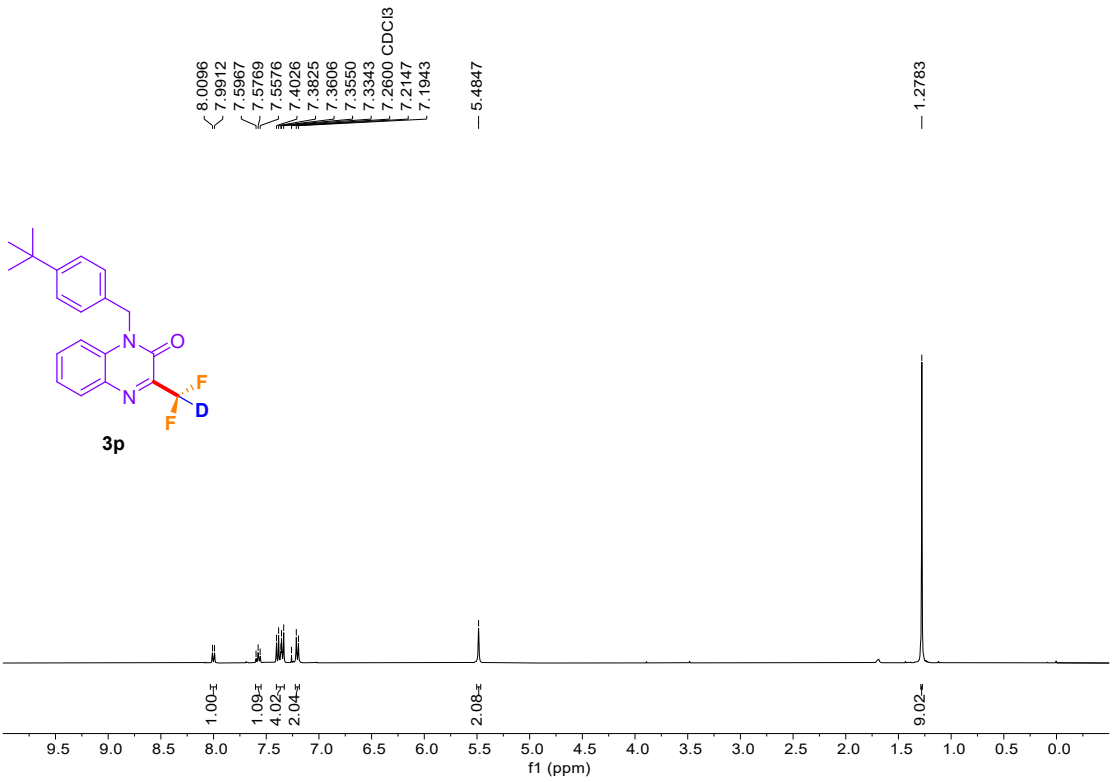


Figure S49, ^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)

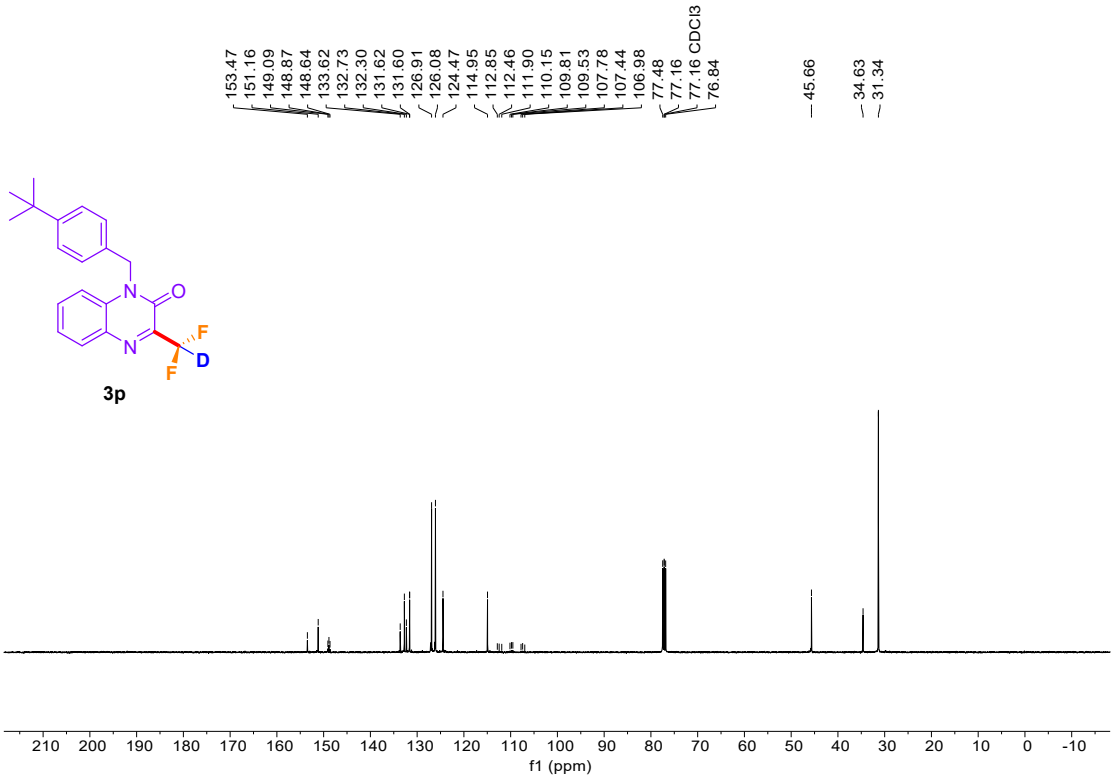


Figure S50, ^{13}C NMR spectrum of **3p** (101 MHz, $CDCl_3$)

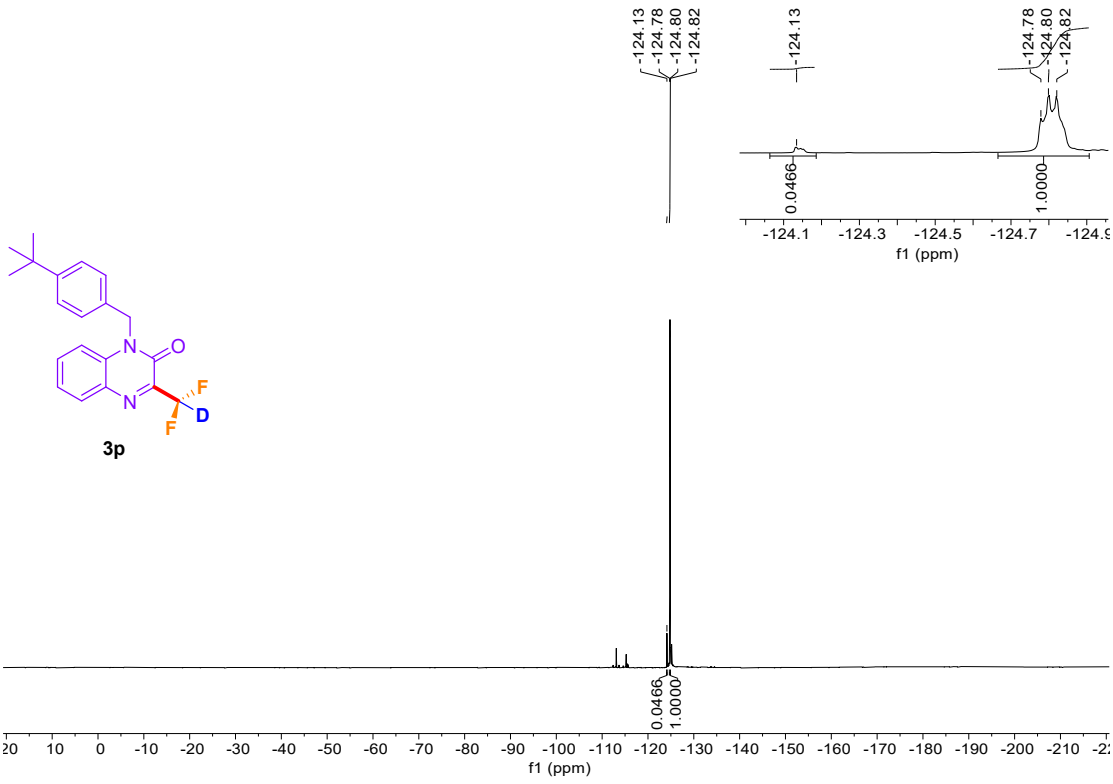


Figure S51, ^{19}F NMR spectrum of **3p** (377 MHz, $CDCl_3$)

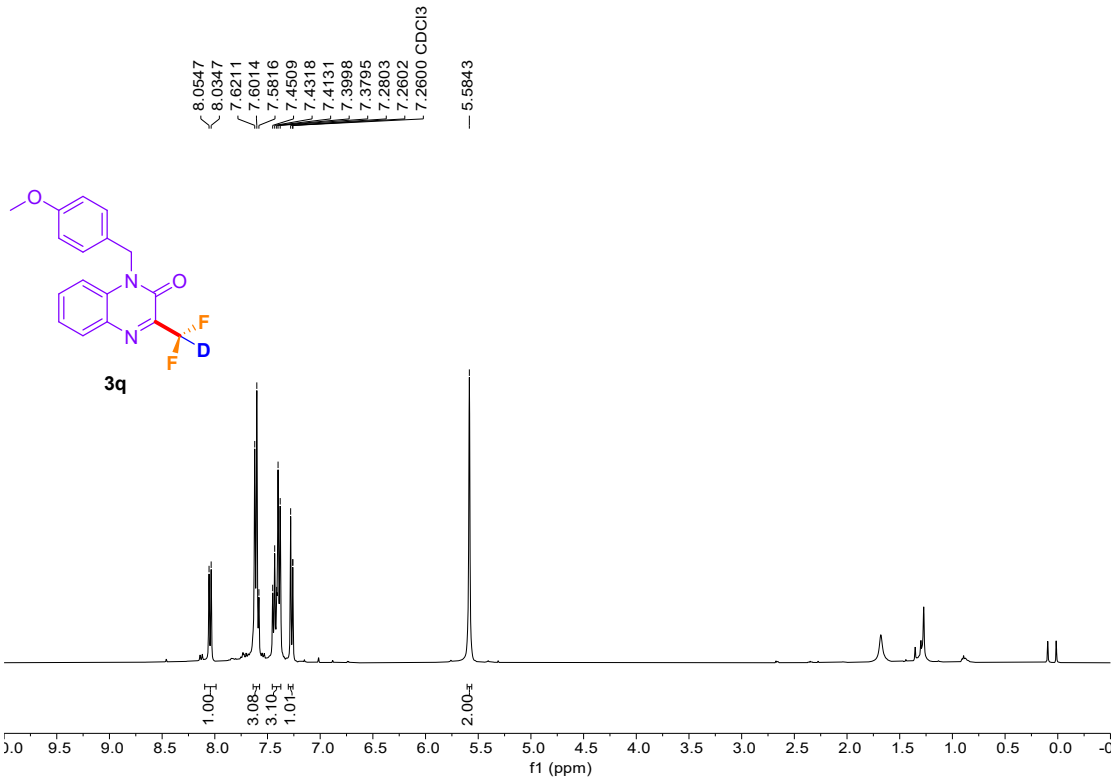


Figure S52, ^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)

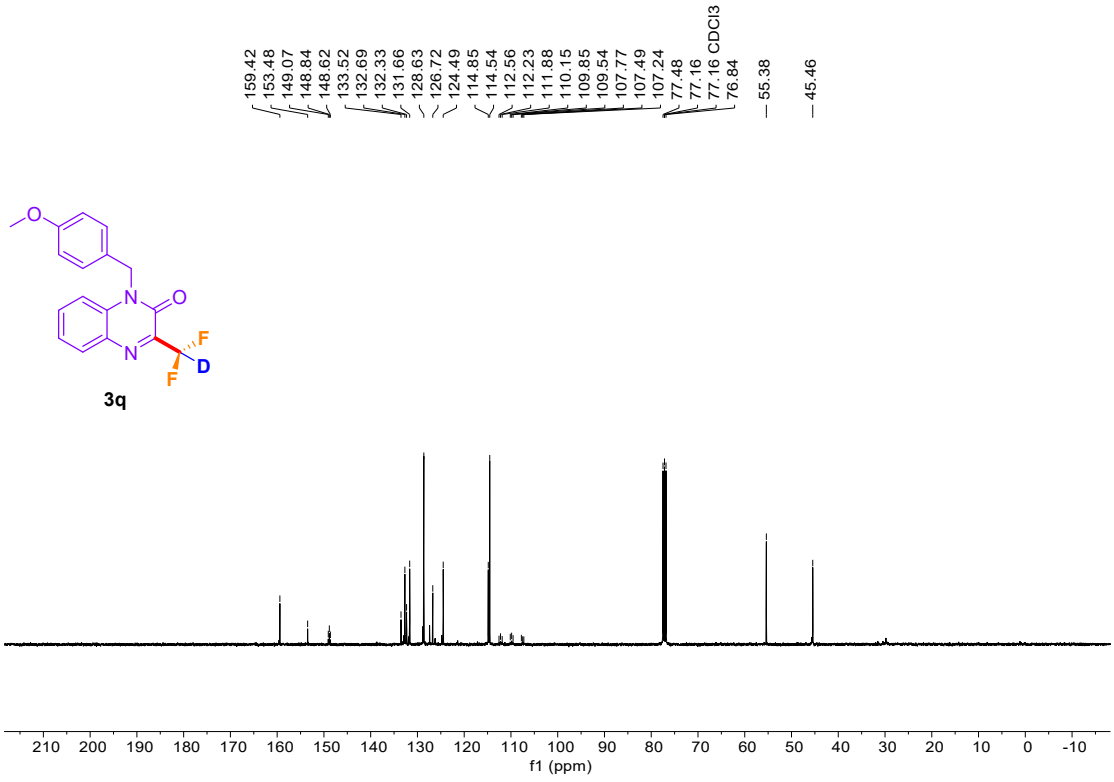


Figure S53, ^{13}C NMR spectrum of **3q** (101 MHz, $CDCl_3$)

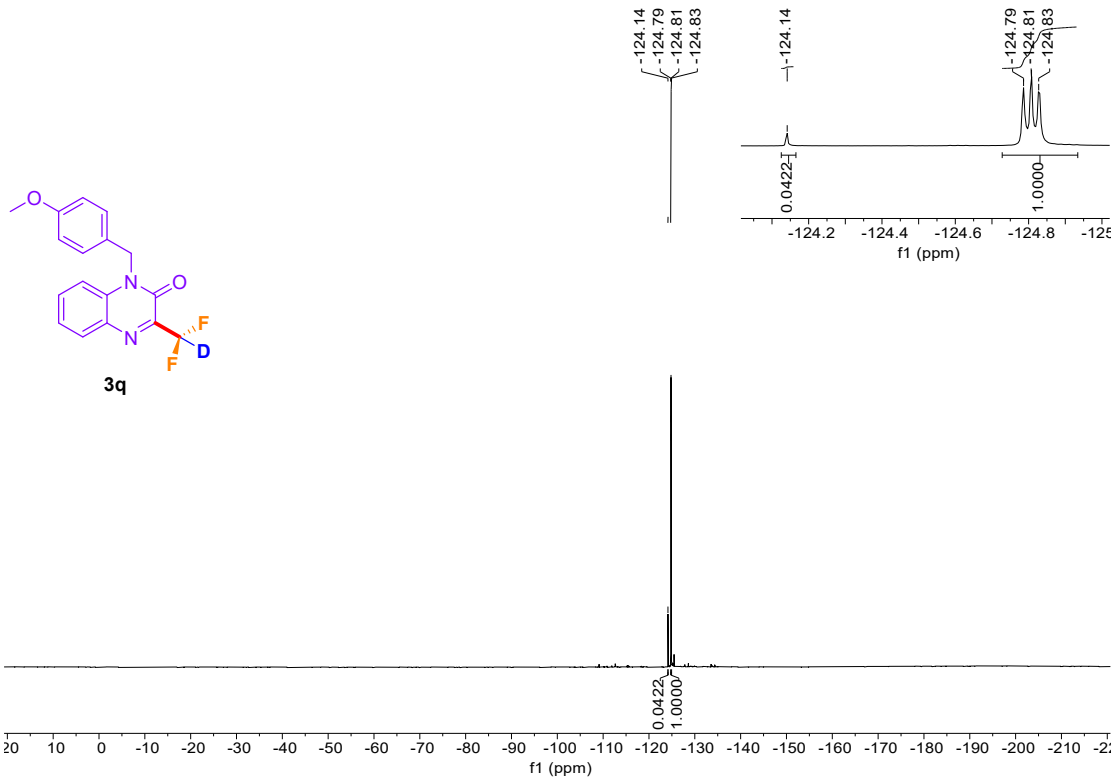


Figure S54, ^{19}F NMR spectrum of **3q** (377 MHz, $CDCl_3$)

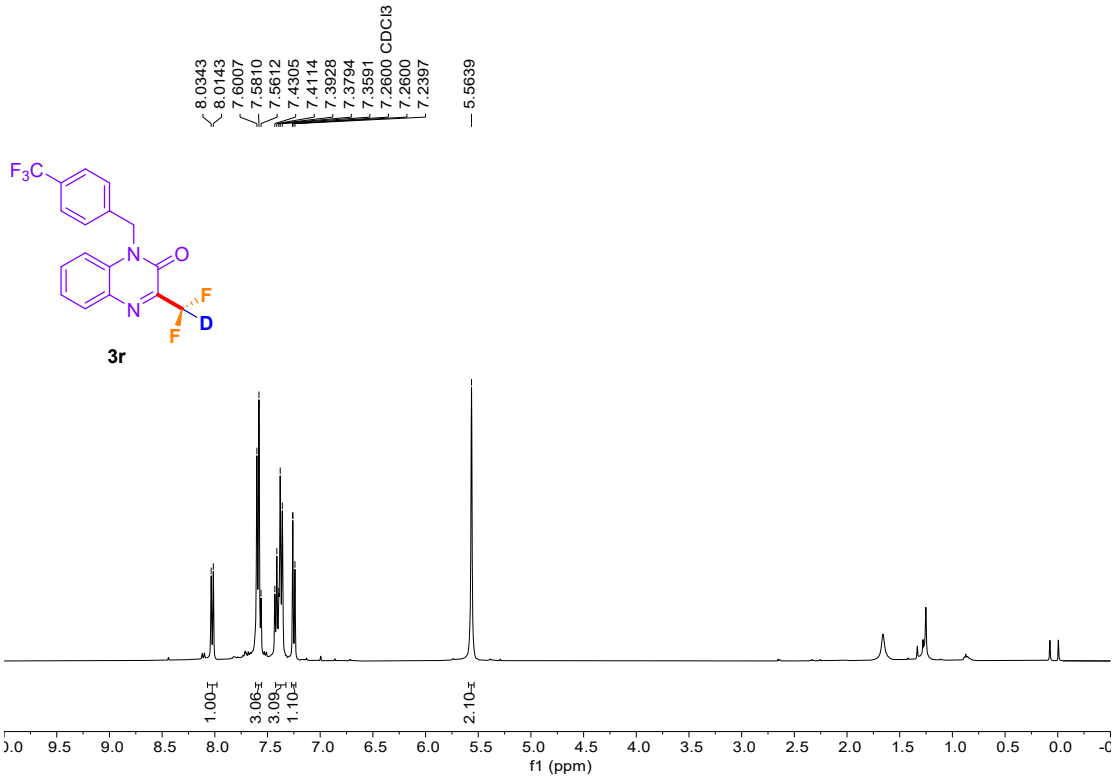


Figure S55, ^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)

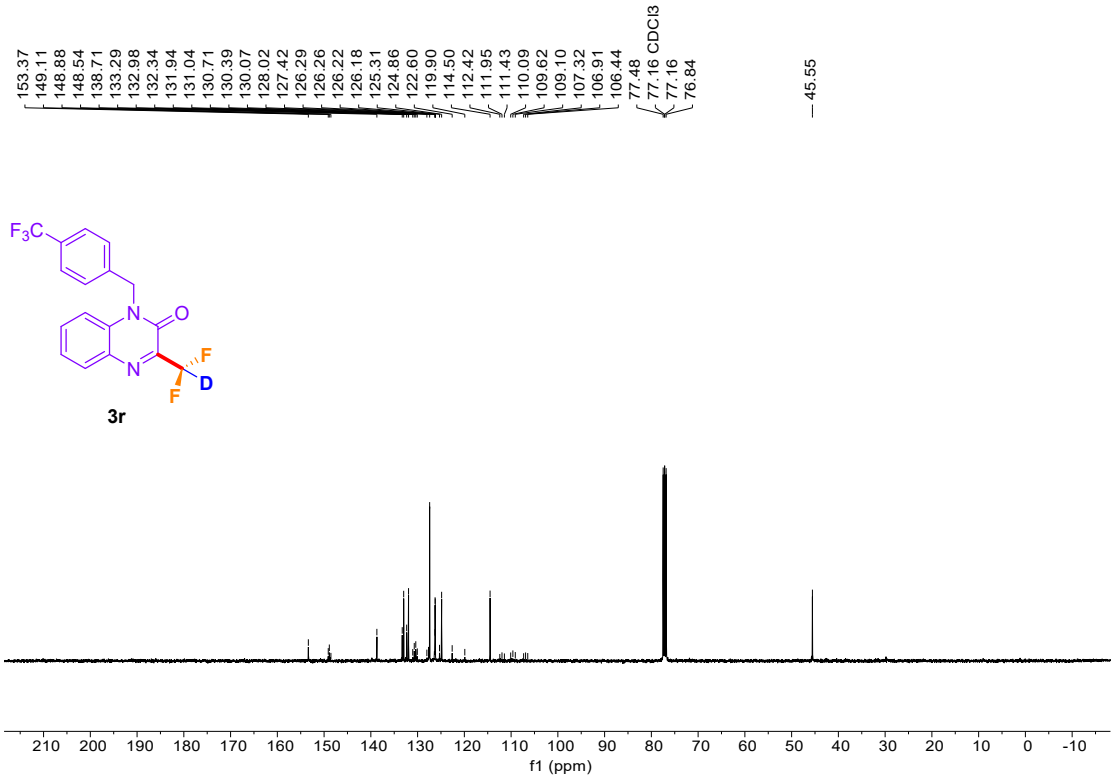


Figure S56, ^{13}C NMR spectrum of **3r** (101 MHz, $CDCl_3$)

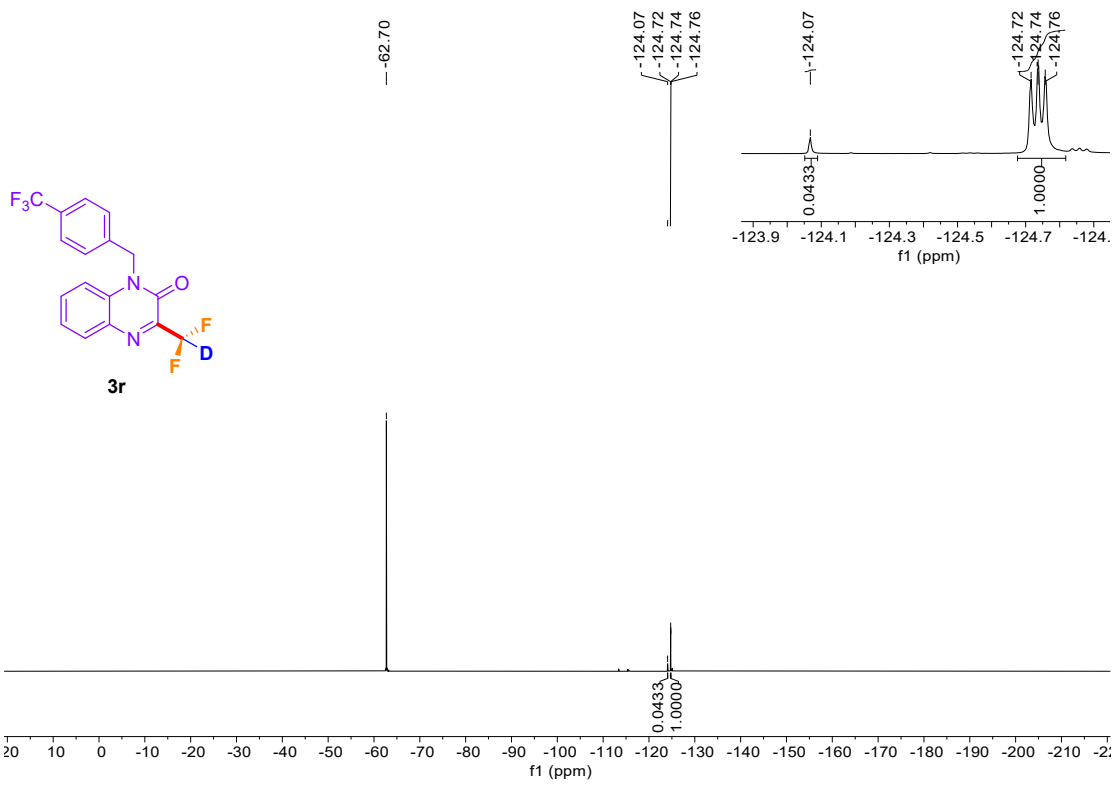


Figure S57, ^{19}F NMR spectrum of **3r** (377 MHz, $CDCl_3$)

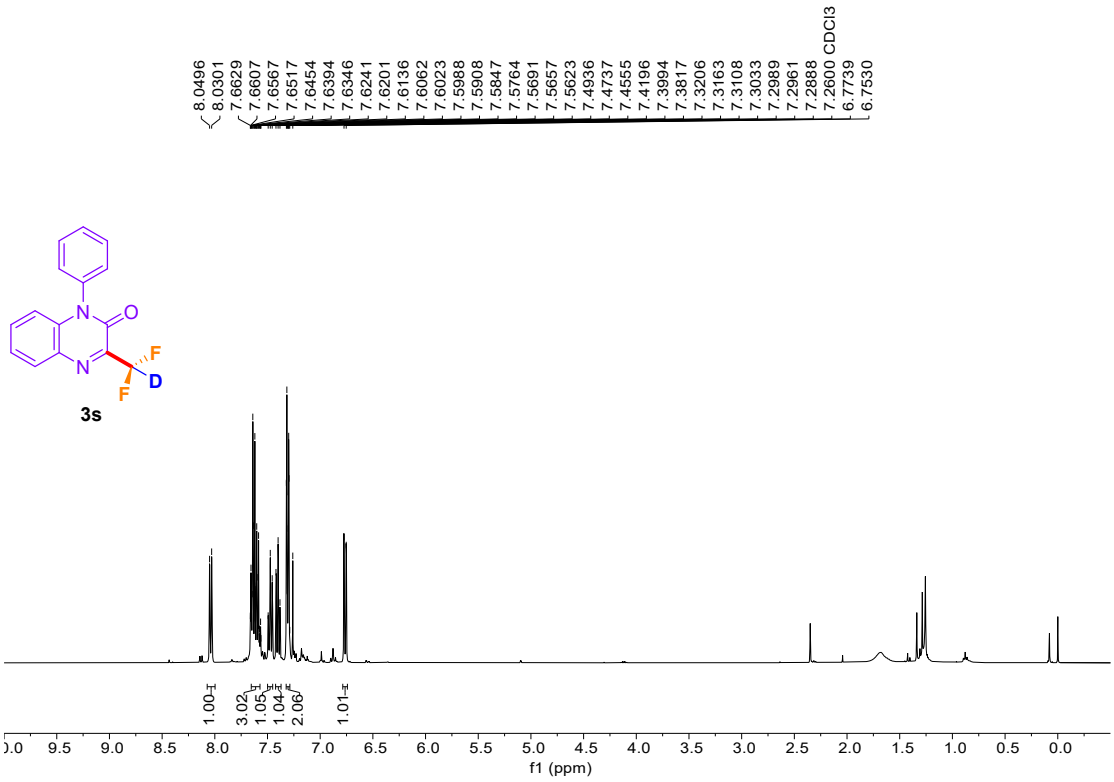


Figure S58, ^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)

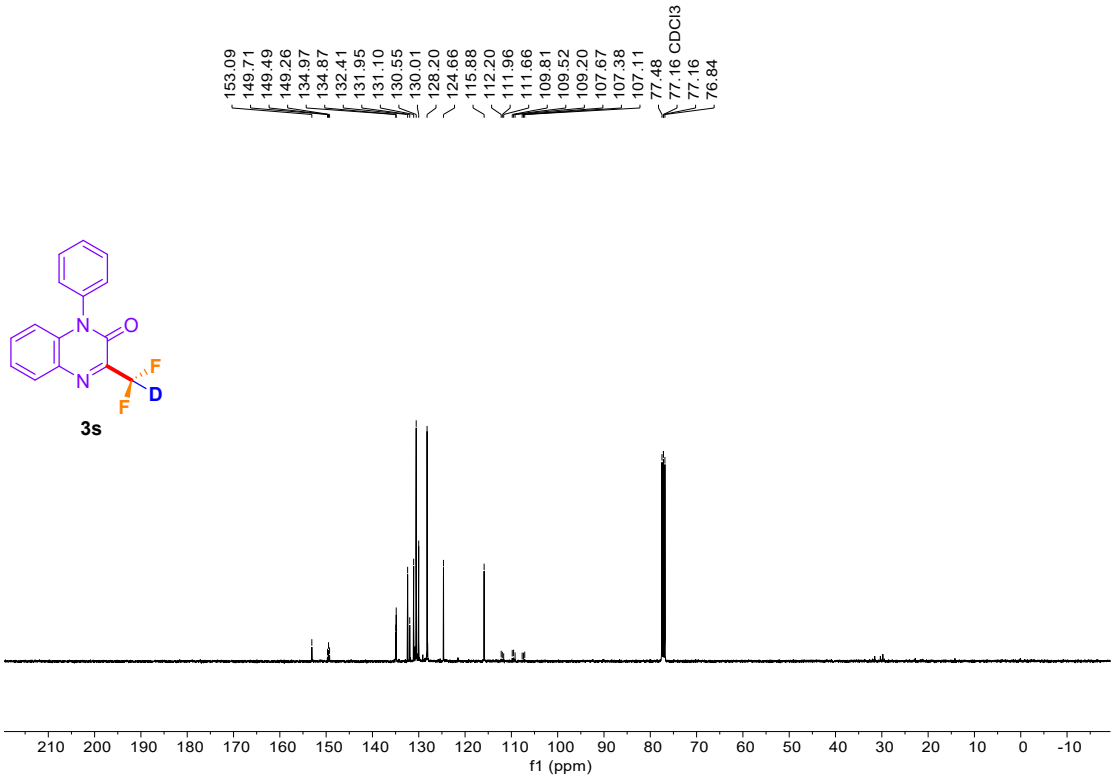


Figure S59, ^{13}C NMR spectrum of **3s** (101 MHz, $CDCl_3$)

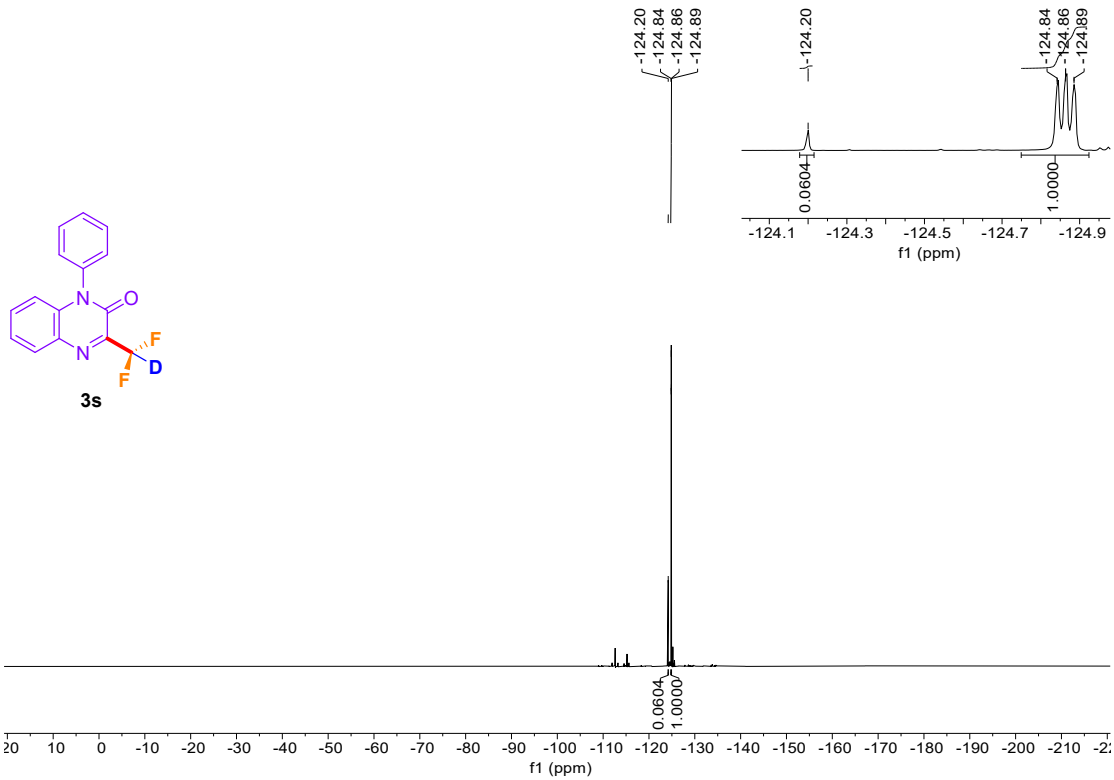


Figure S60, ^{19}F NMR spectrum of **3s** (377 MHz, $CDCl_3$)

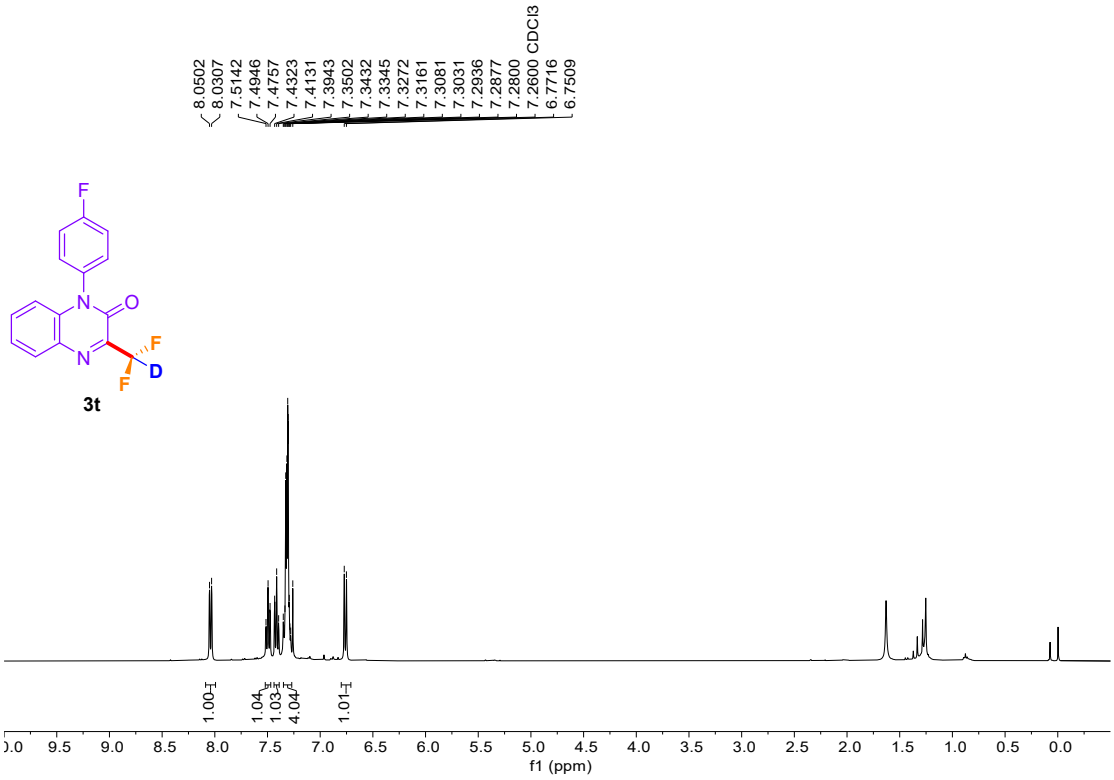


Figure S61, ^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)

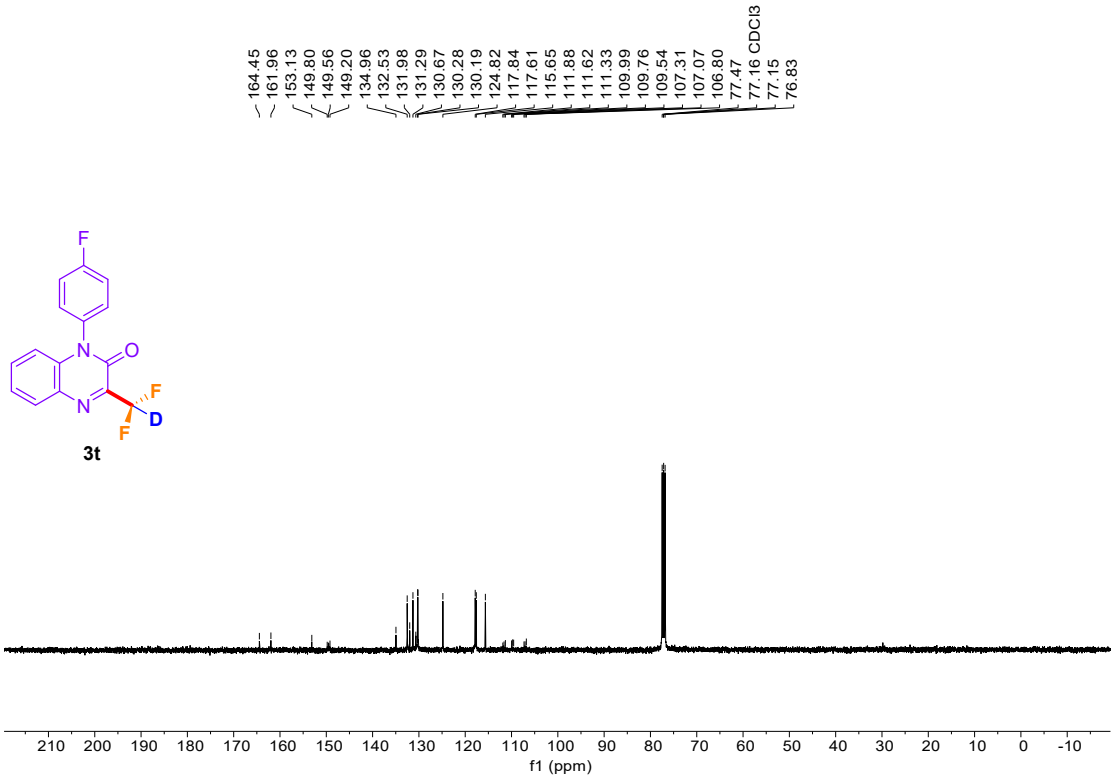


Figure S62, ^{13}C NMR spectrum of **3t** (101 MHz, $CDCl_3$)

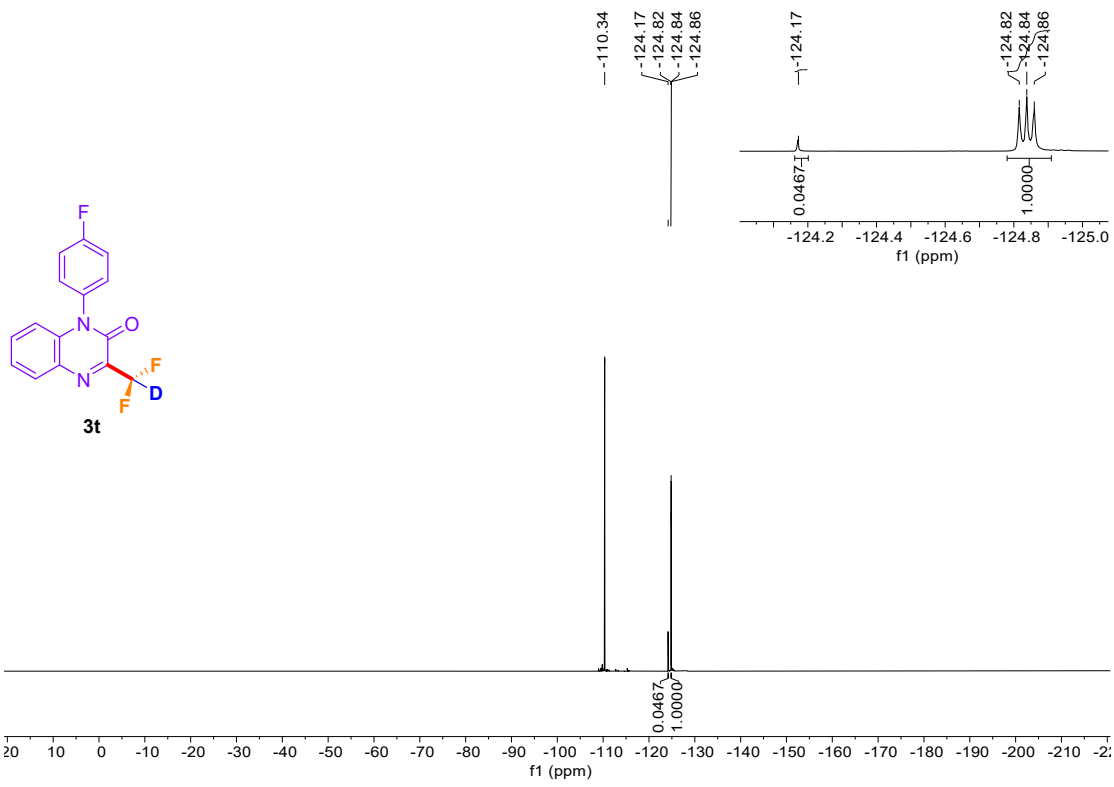


Figure S63, ^{19}F NMR spectrum of **3t** (377 MHz, $CDCl_3$)

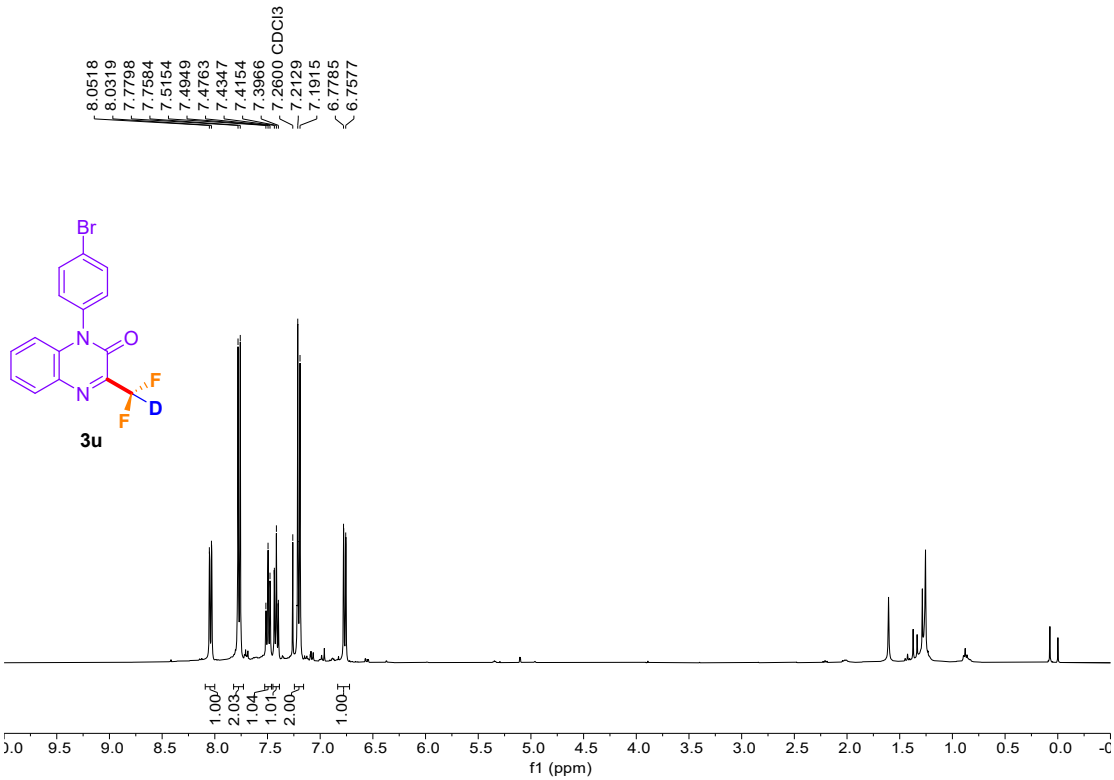


Figure S64, ^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)

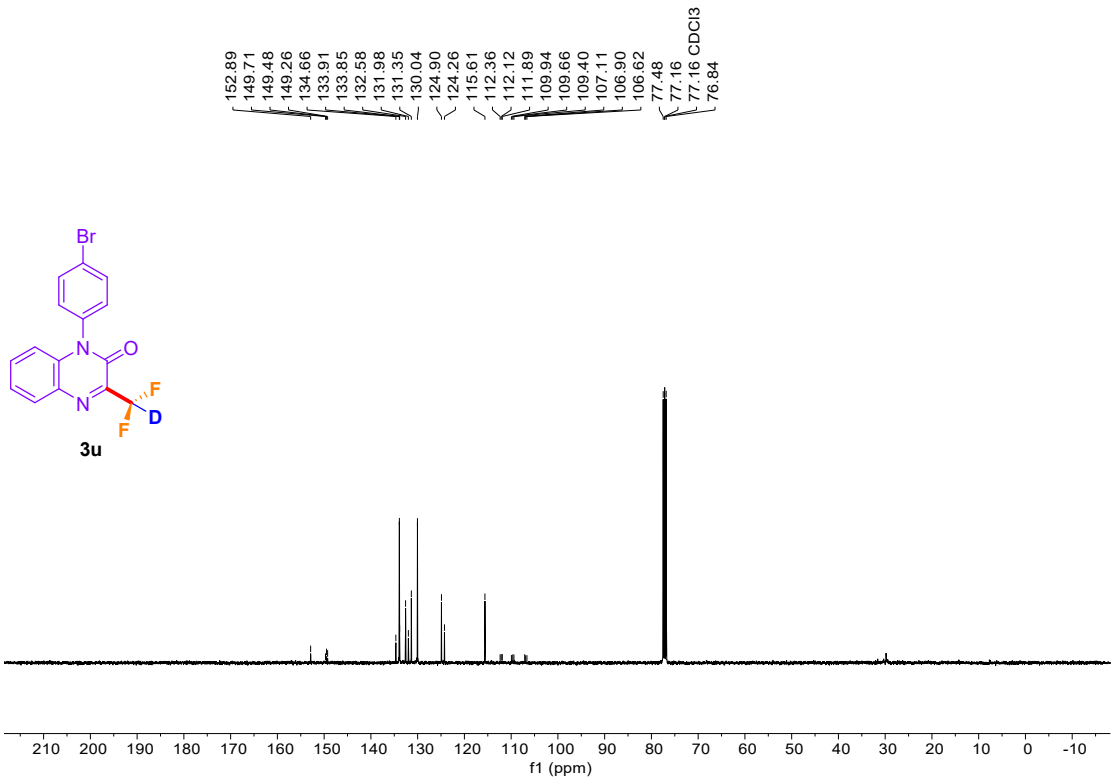


Figure S65, ^{13}C NMR spectrum of **3u** (101 MHz, $CDCl_3$)

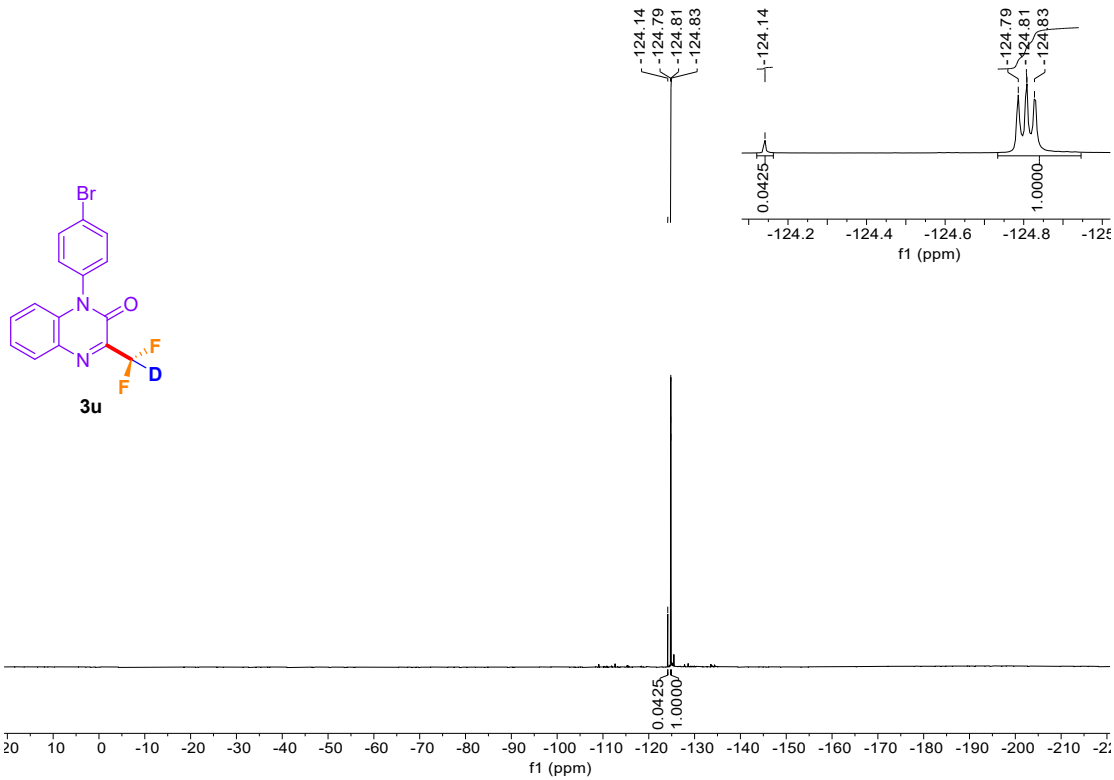


Figure S66, ^{19}F NMR spectrum of **3u** (377 MHz, $CDCl_3$)

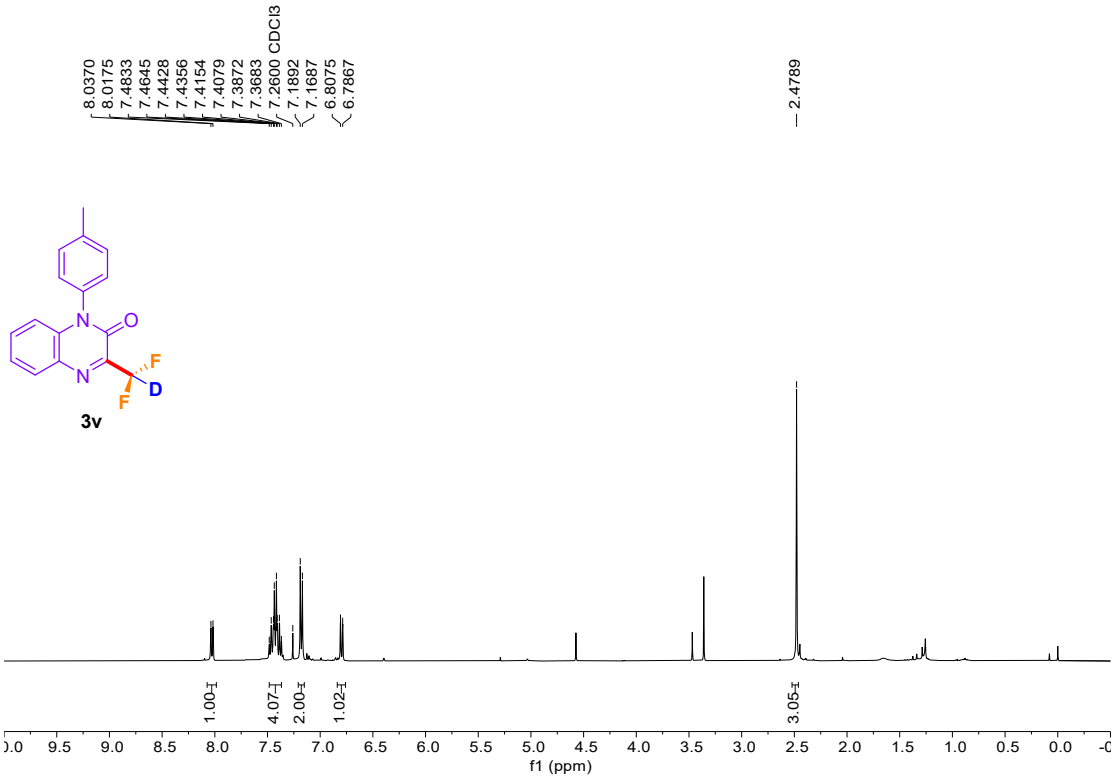


Figure S67, ^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$)

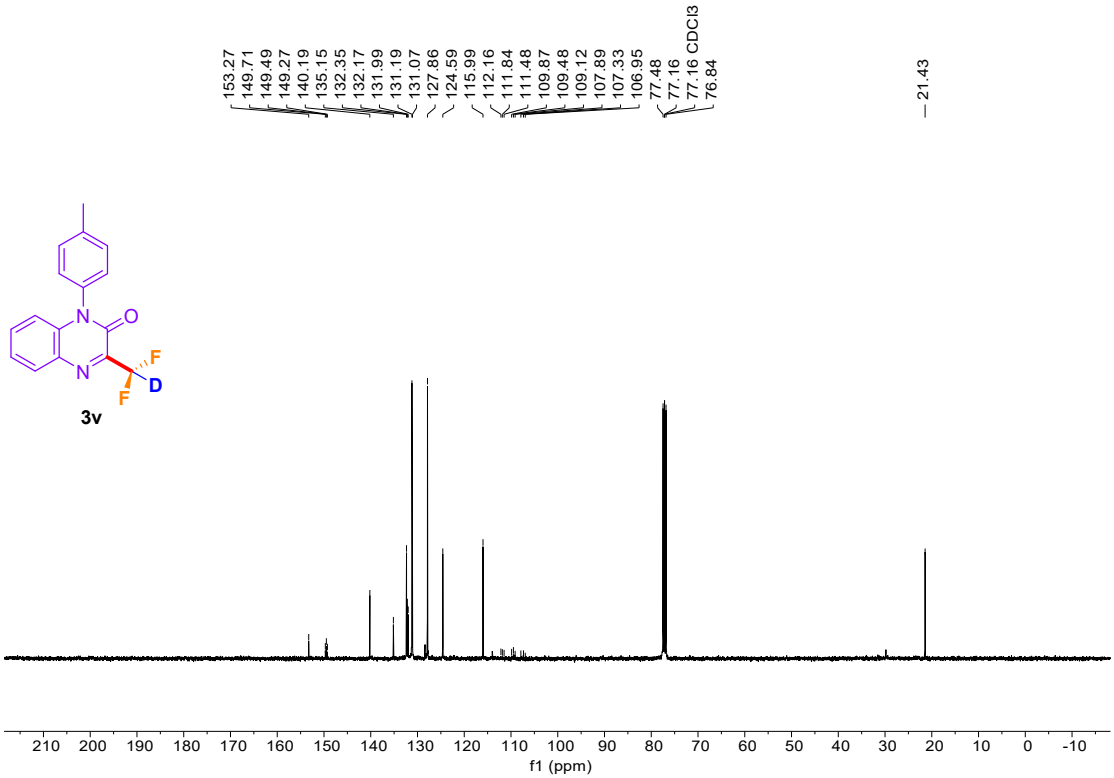


Figure S68, ^{13}C NMR spectrum of **3v** (101 MHz, $CDCl_3$)

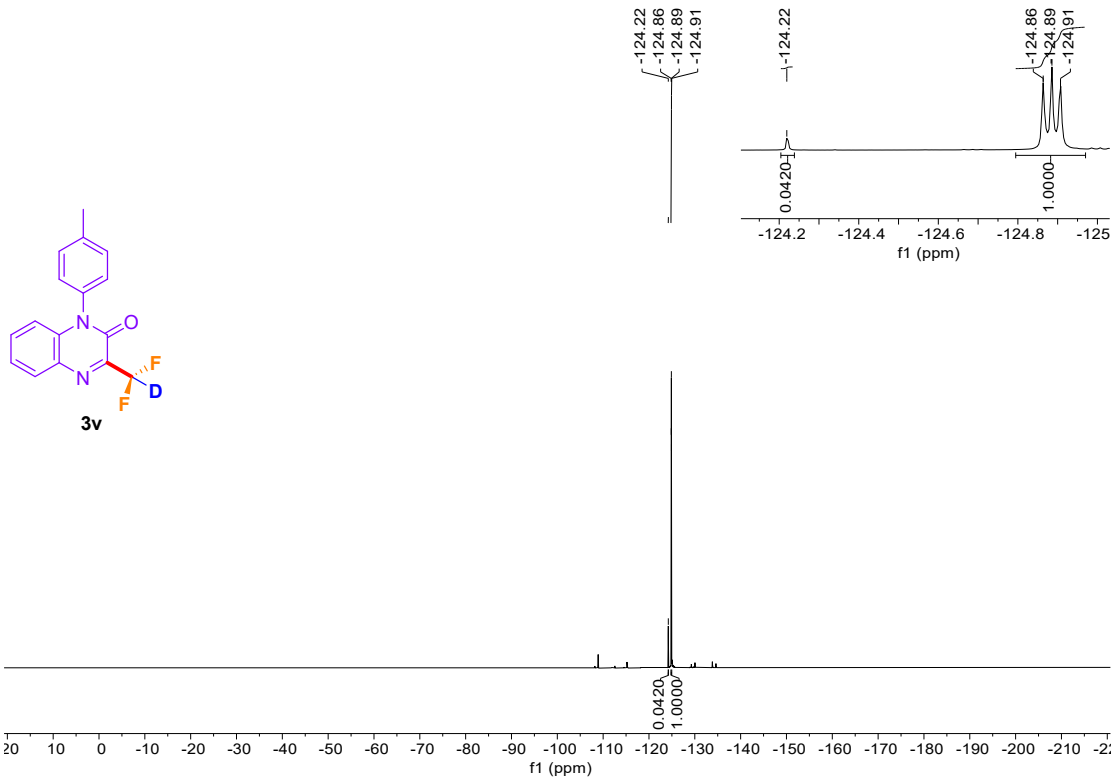


Figure S69, ^{19}F NMR spectrum of **3v** (377 MHz, $CDCl_3$)

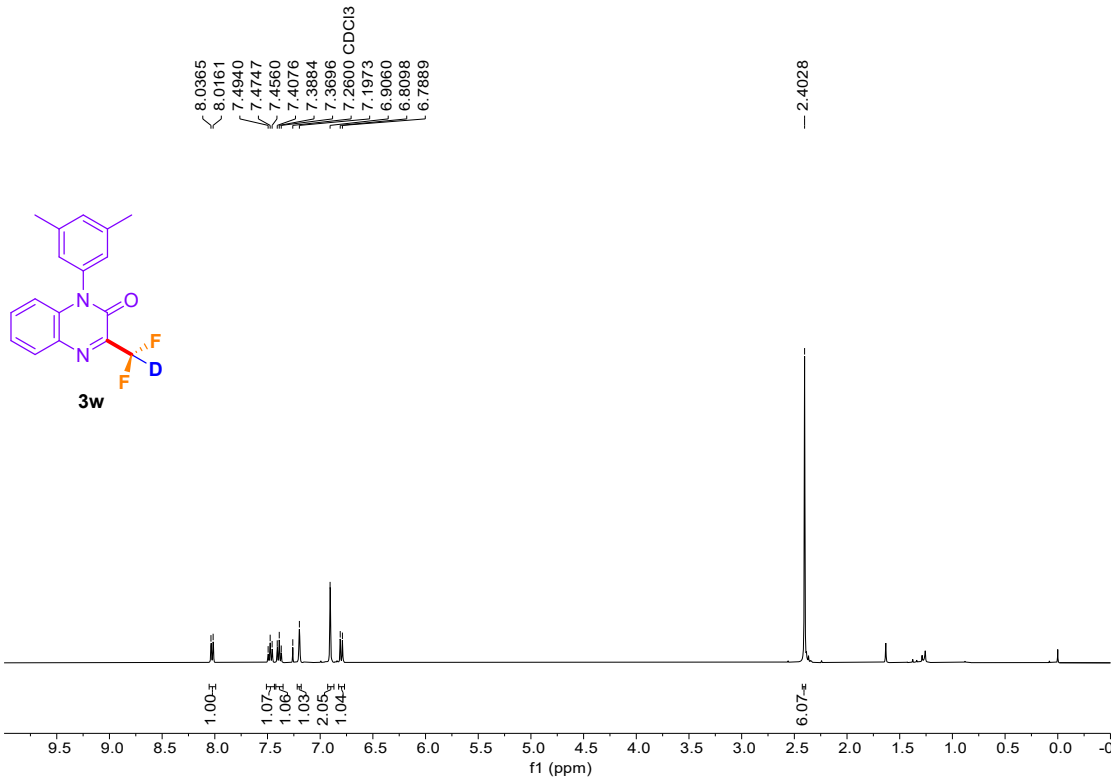


Figure S70, ^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$)

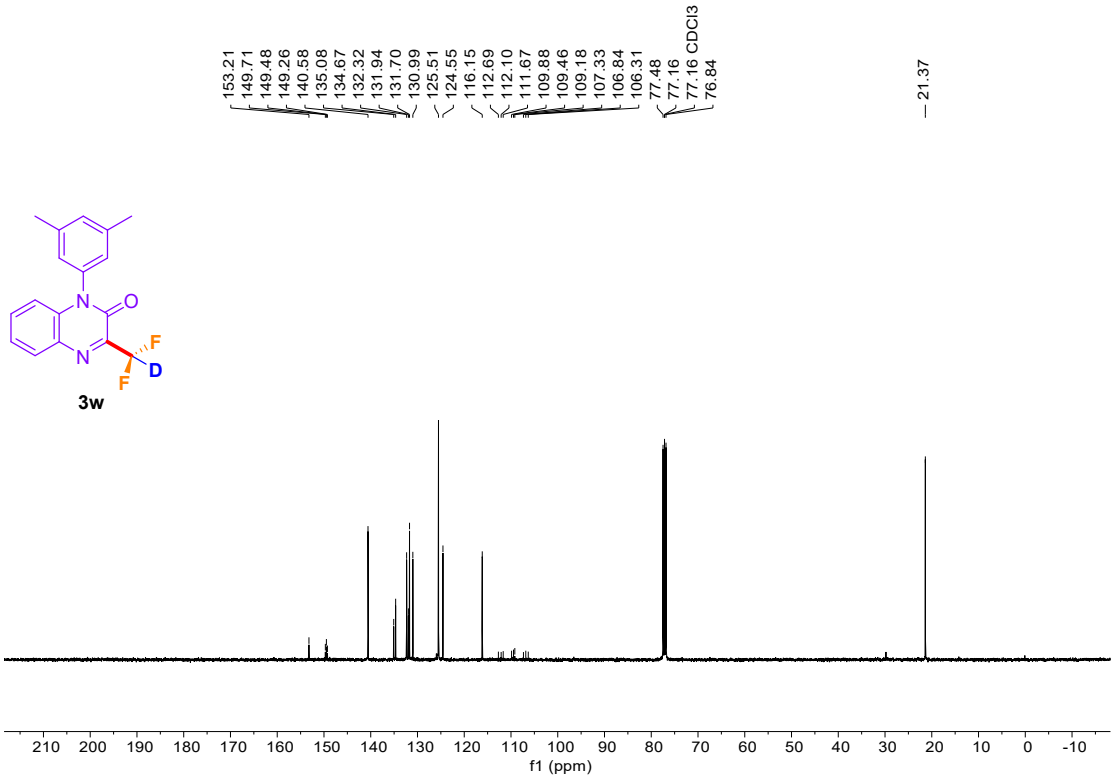


Figure S71, ^{13}C NMR spectrum of **3w** (101 MHz, $CDCl_3$)

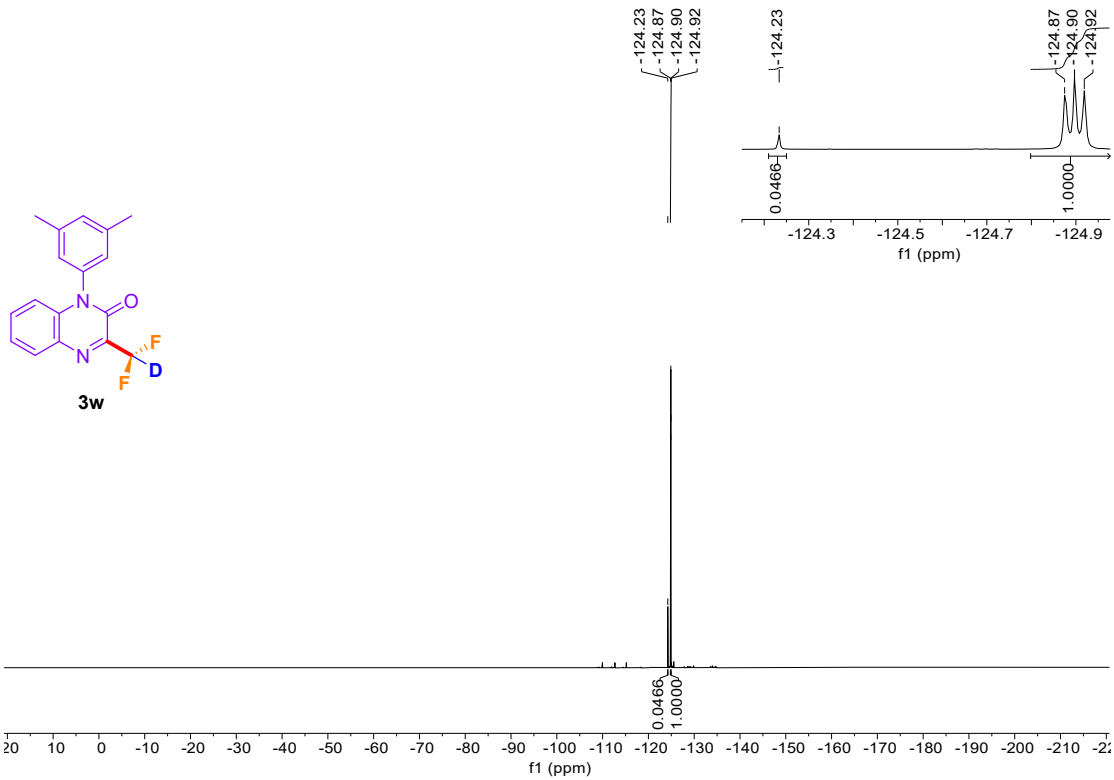


Figure S72, ^{19}F NMR spectrum of **3w** (377 MHz, $CDCl_3$)

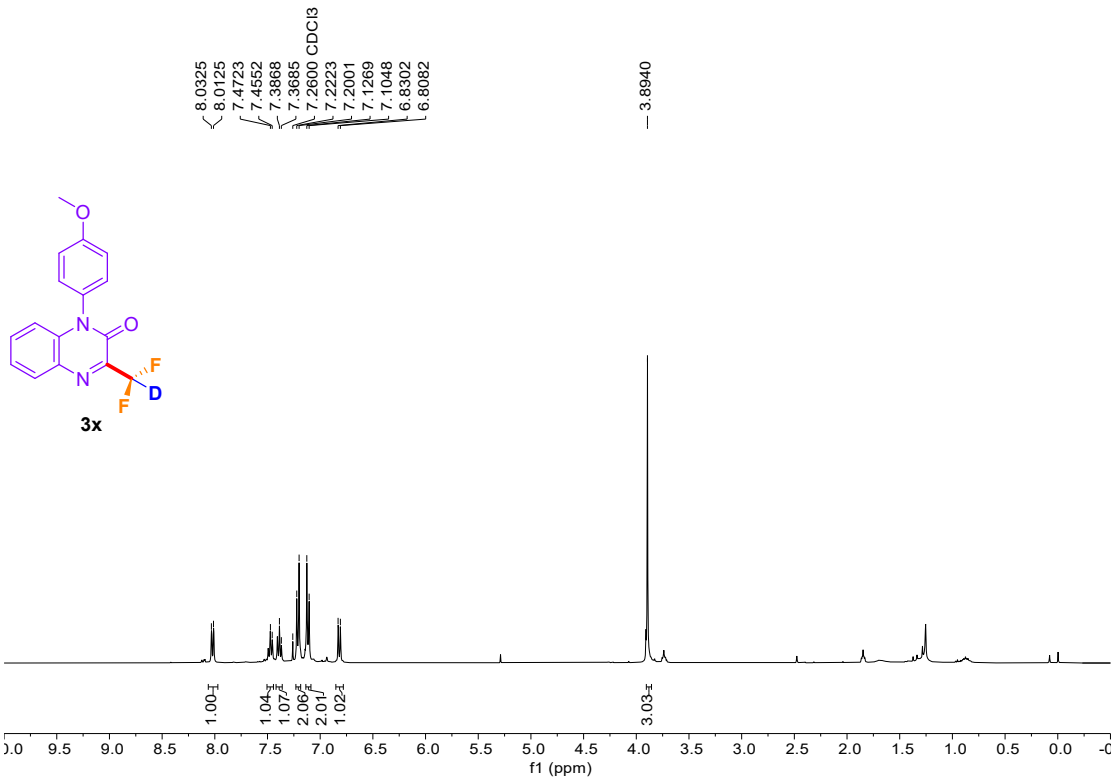


Figure S73, ^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$)

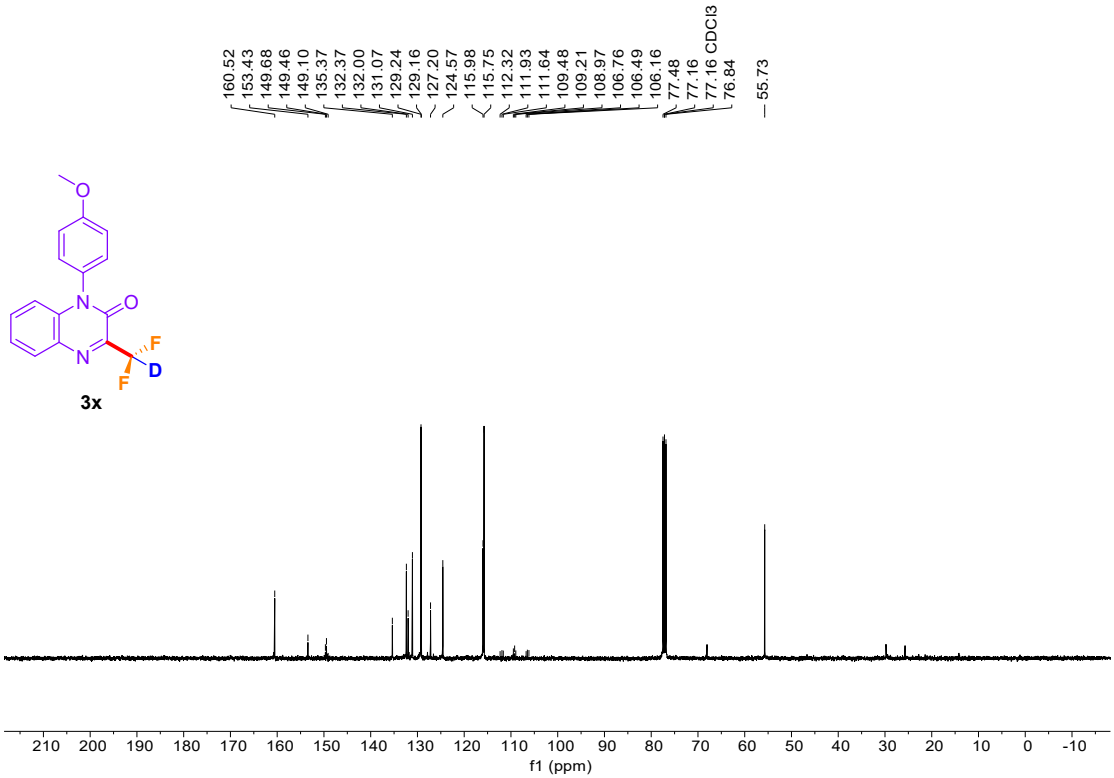


Figure S74, ^{13}C NMR spectrum of **3x** (101 MHz, $CDCl_3$)

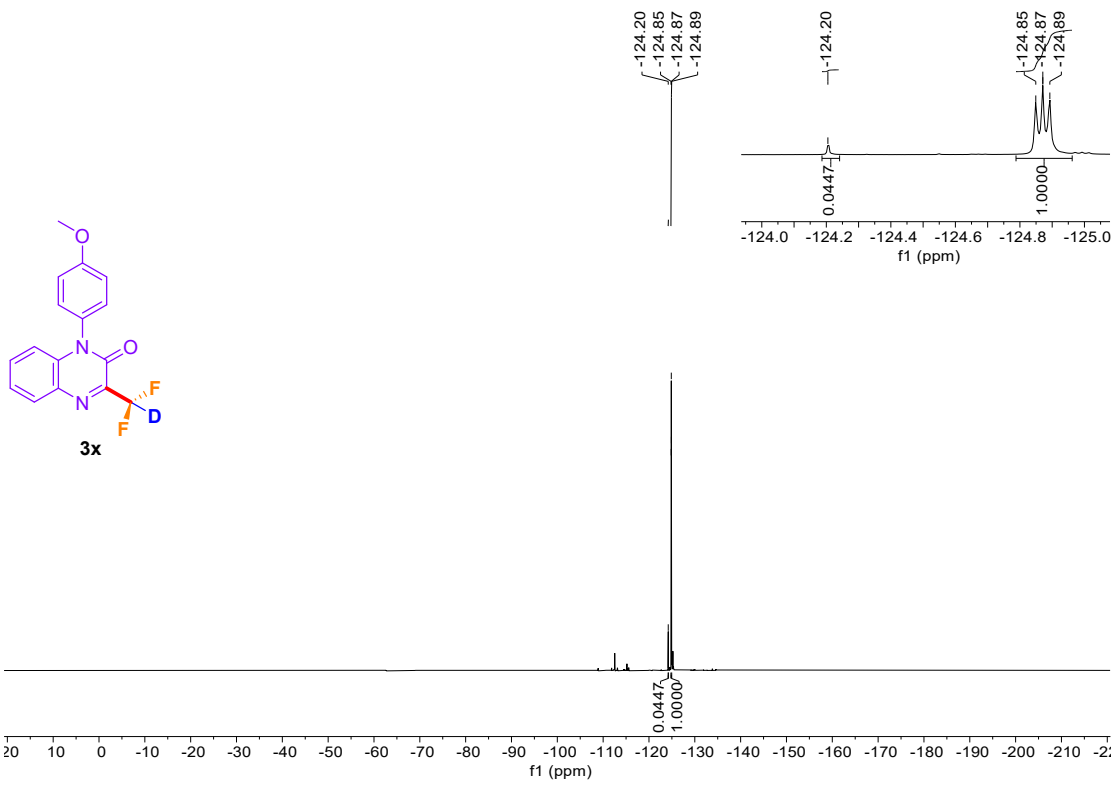


Figure S75, ^{19}F NMR spectrum of **3x** (377 MHz, $CDCl_3$)

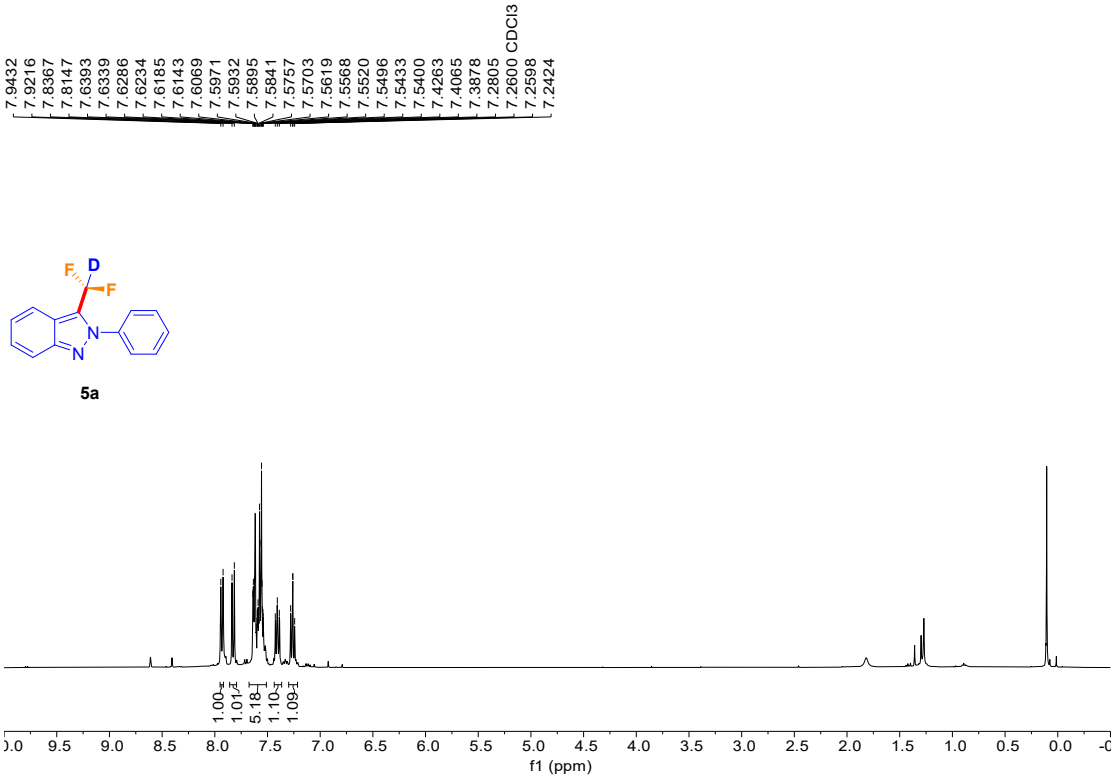


Figure S76, ^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)

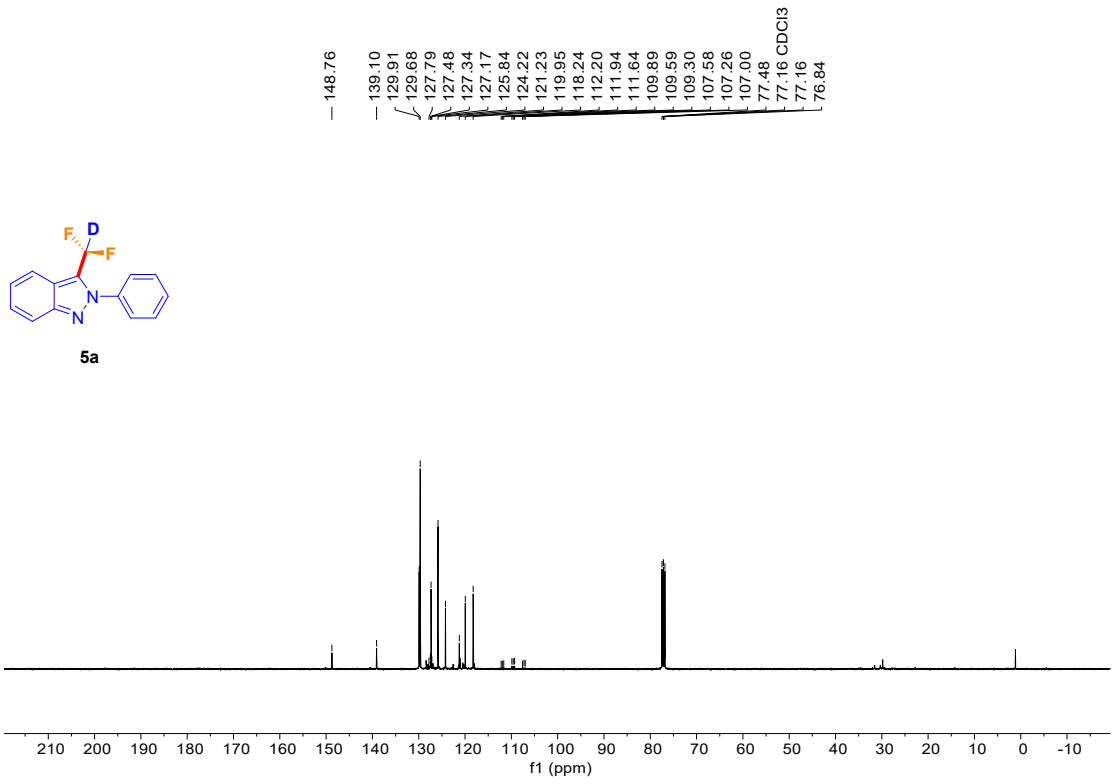


Figure S77, ^{13}C NMR spectrum of **5a** (101 MHz, $CDCl_3$)

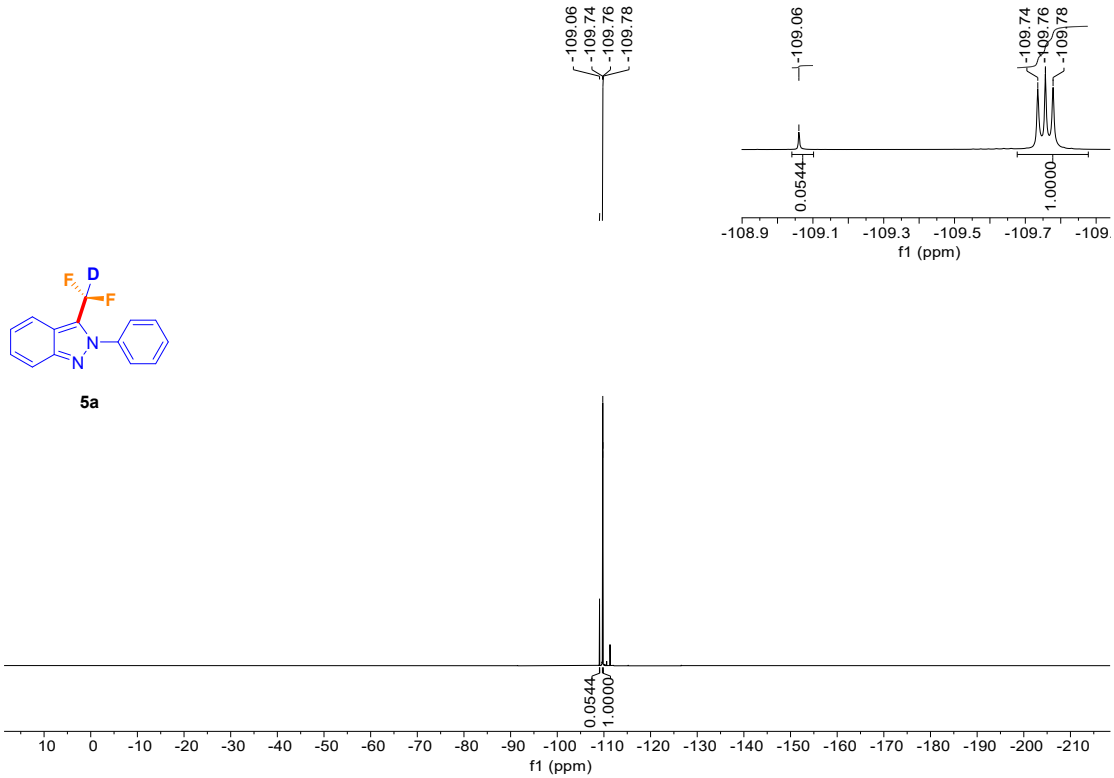


Figure S78, ^{19}F NMR spectrum of **5a** (377 MHz, $CDCl_3$)

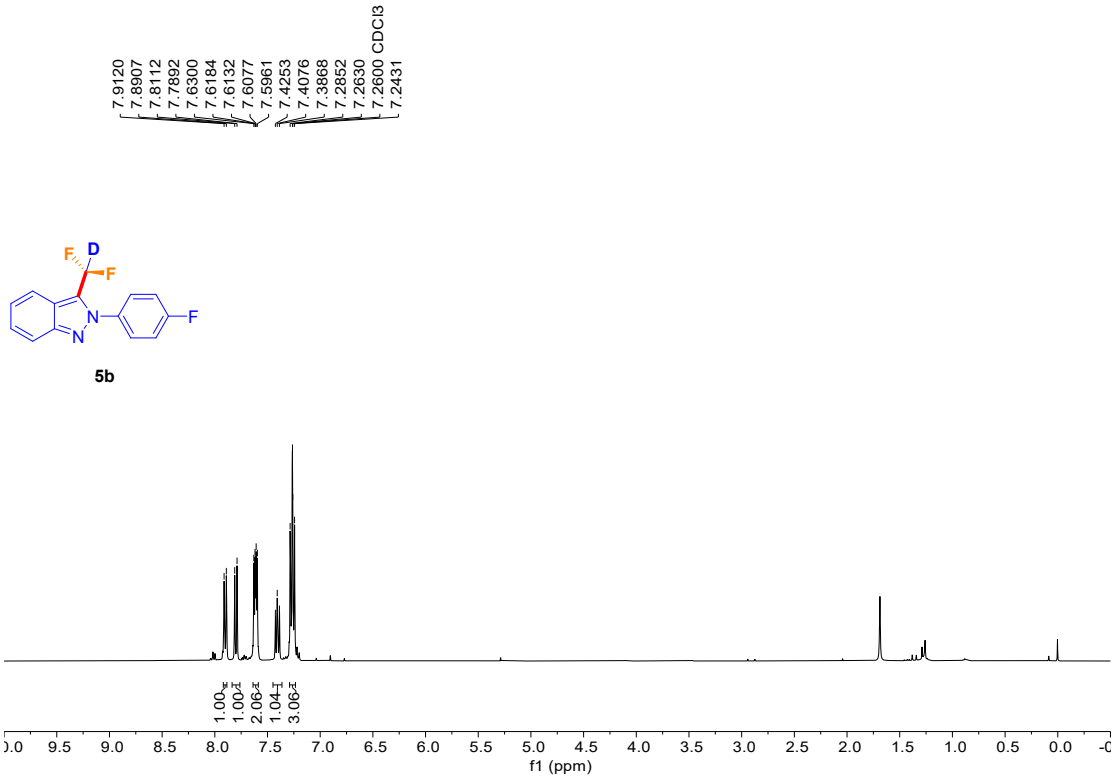


Figure S79, ^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)

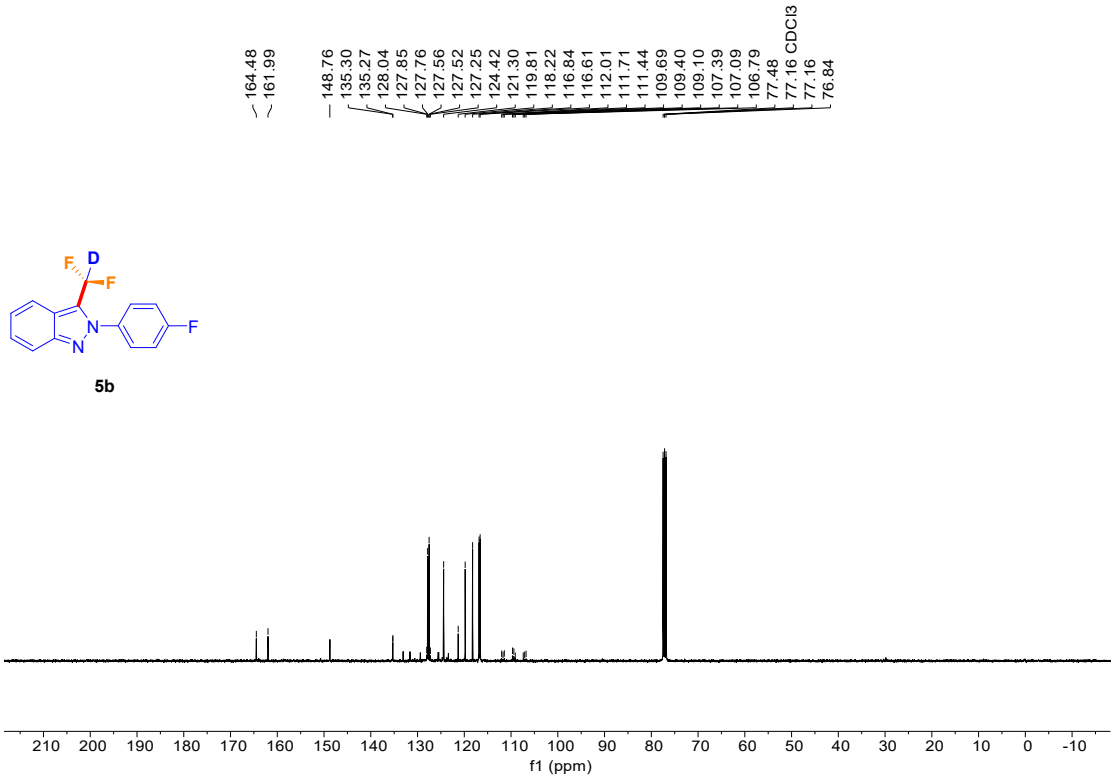


Figure S80, ^{13}C NMR spectrum of **5b** (101 MHz, $CDCl_3$)

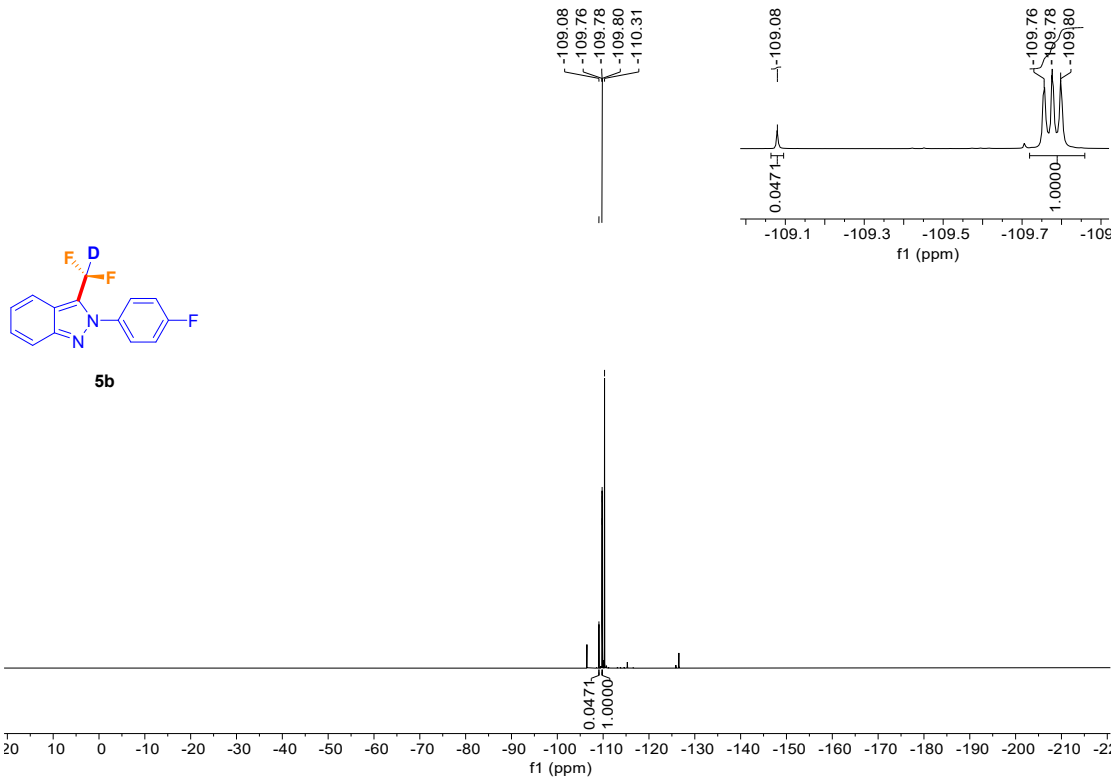


Figure S81, ^{19}F NMR spectrum of **5b** (377 MHz, $CDCl_3$)

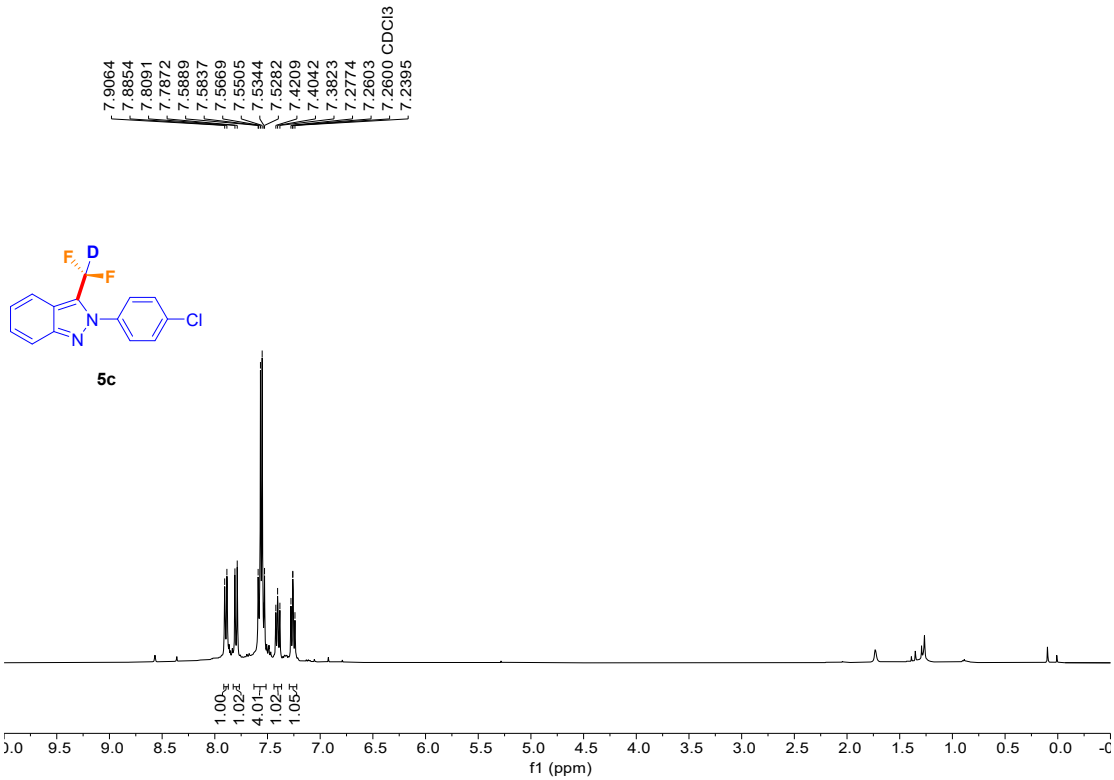


Figure S82, ^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)

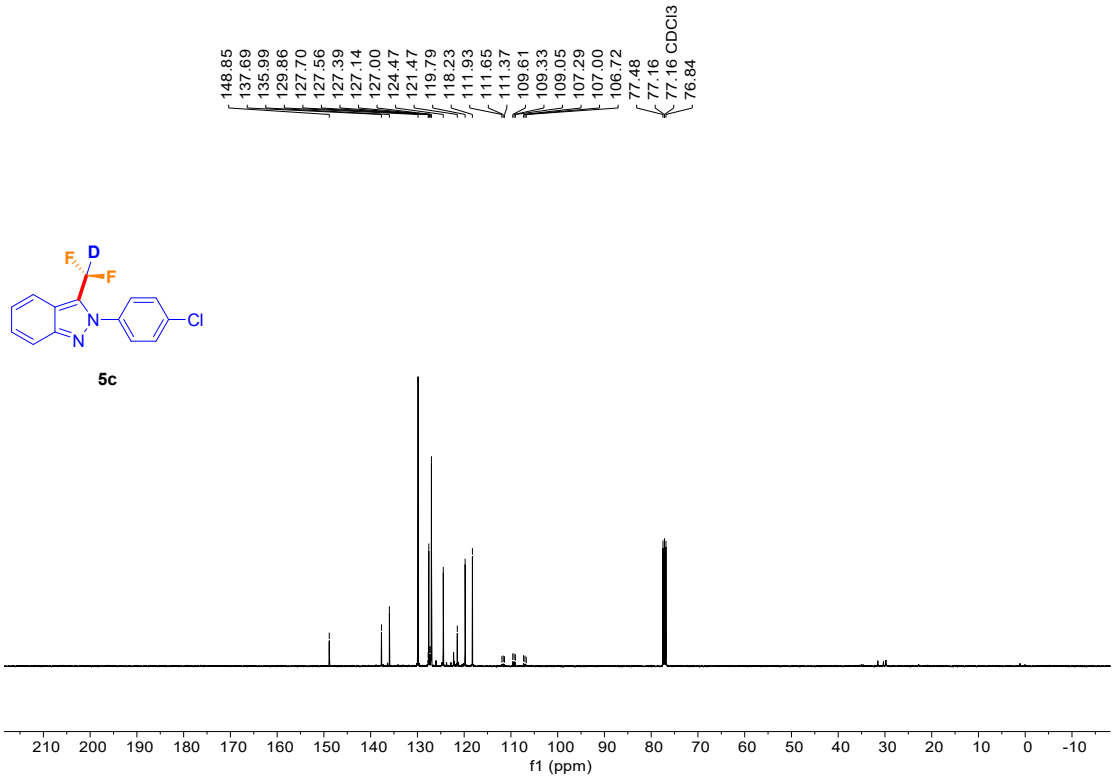


Figure S83, ^{13}C NMR spectrum of **5c** (101 MHz, $CDCl_3$)

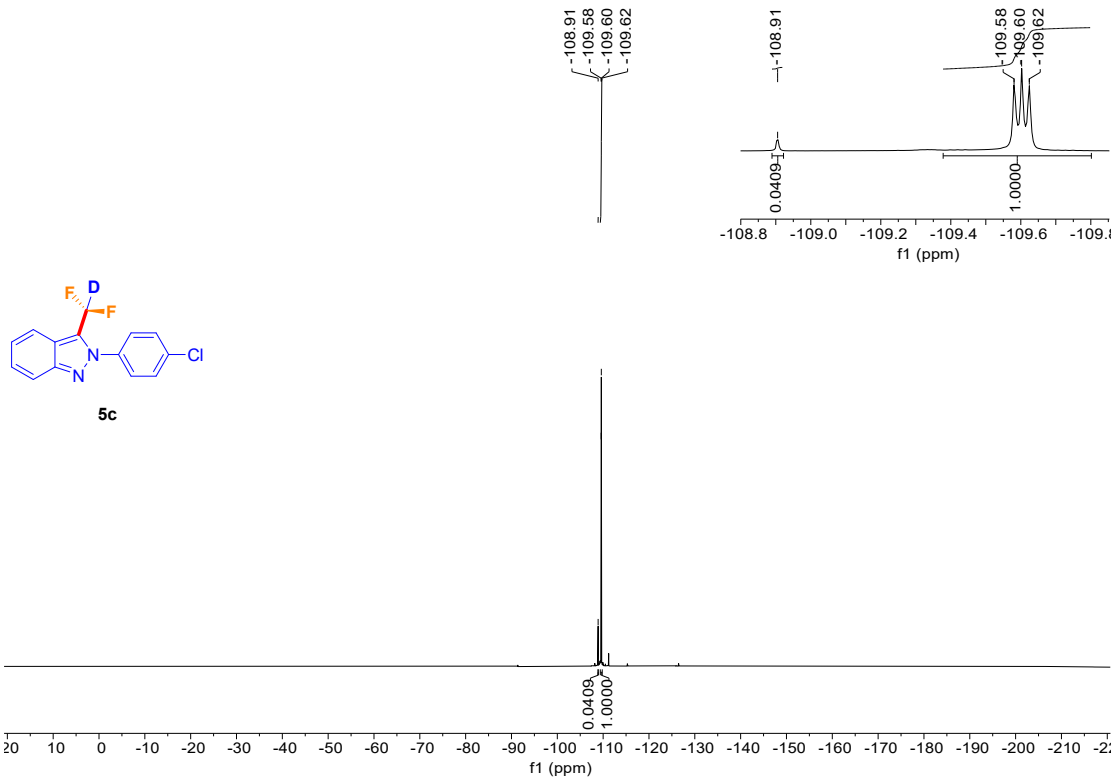


Figure S84, ^{19}F NMR spectrum of **5c** (377 MHz, $CDCl_3$)

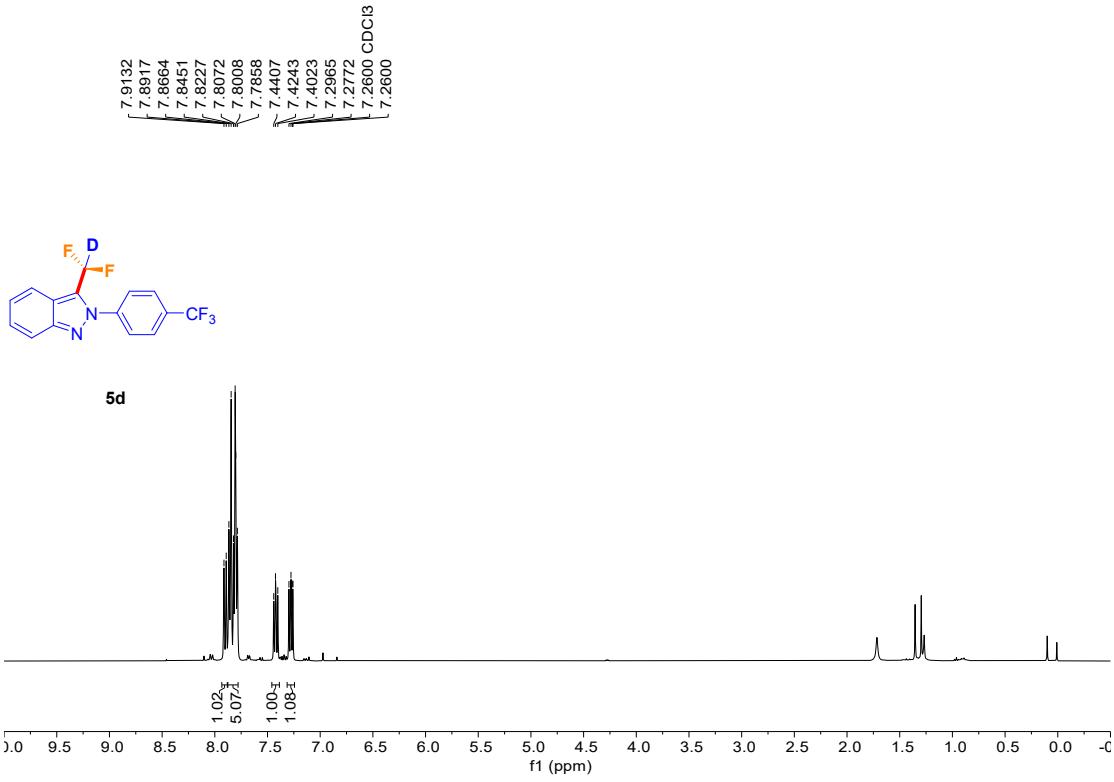


Figure S85, ^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)

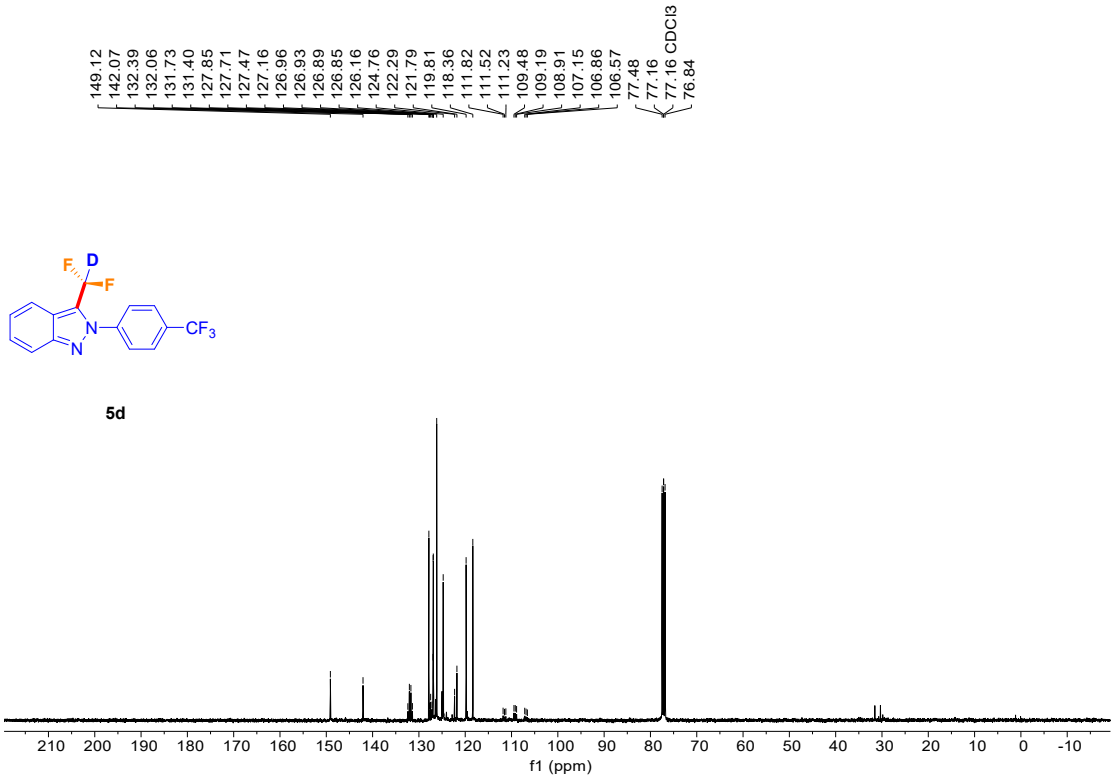


Figure S86, ^{13}C NMR spectrum of **5d** (101 MHz, $CDCl_3$)

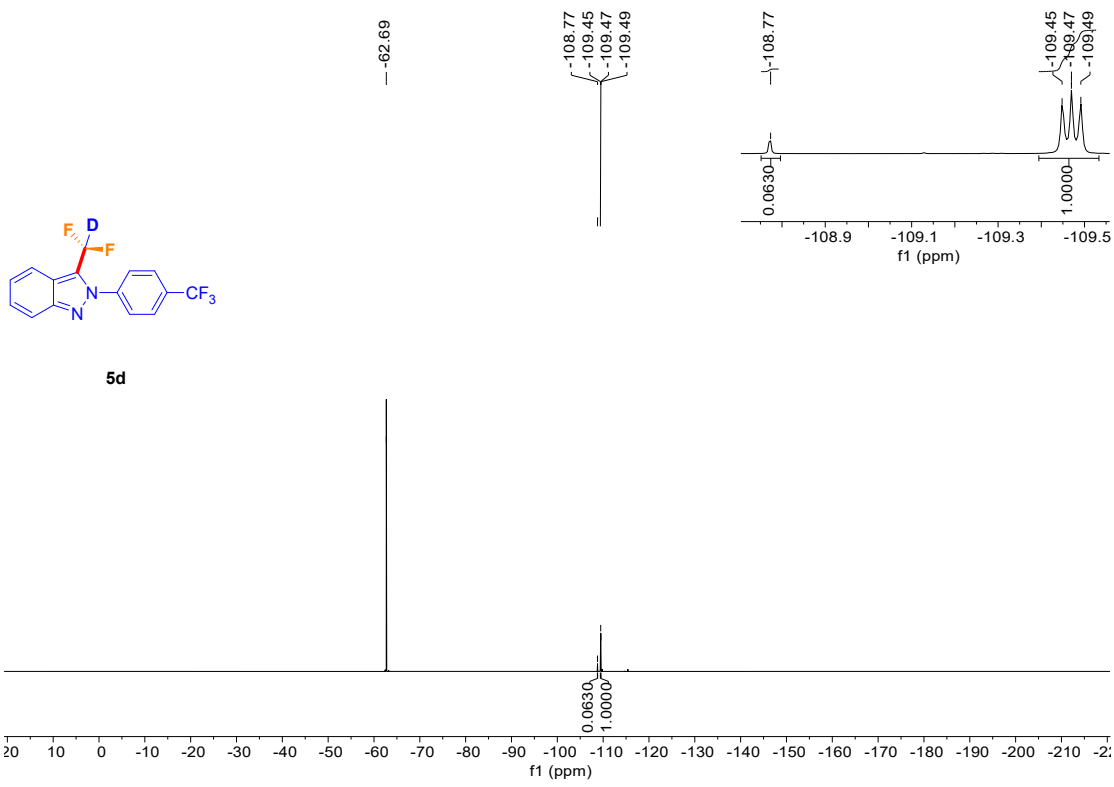


Figure S87, ^{19}F NMR spectrum of **5d** (377 MHz, $CDCl_3$)

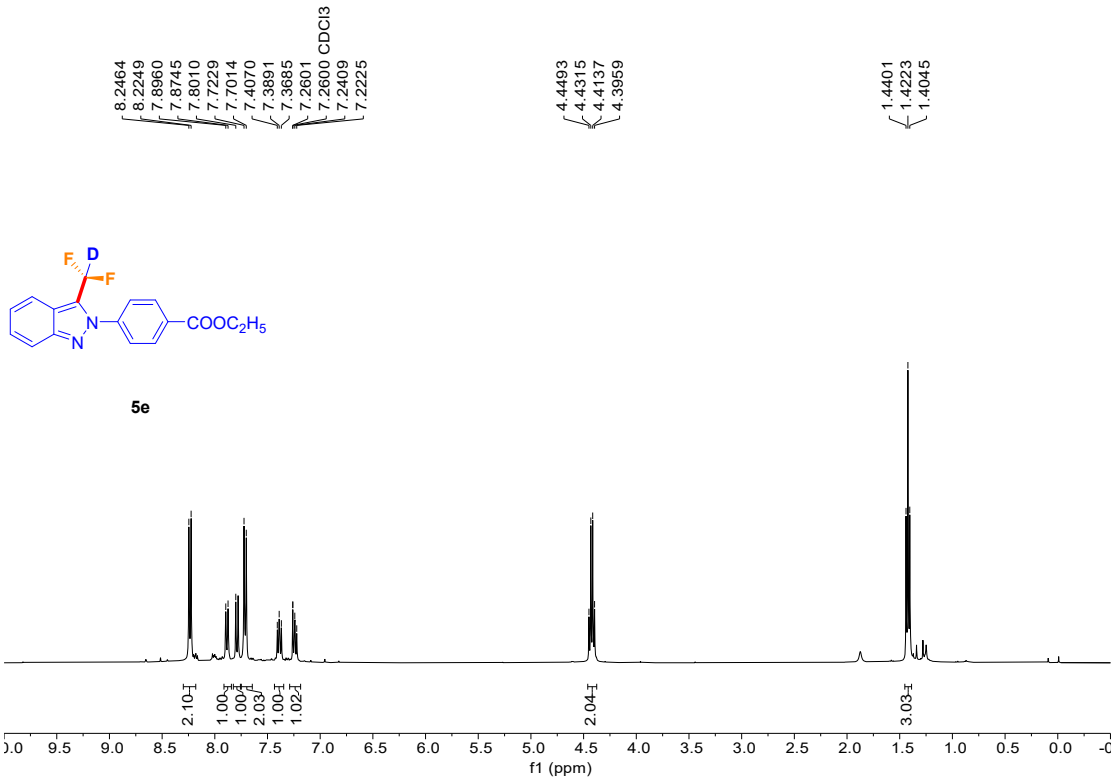


Figure S88, ^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$)

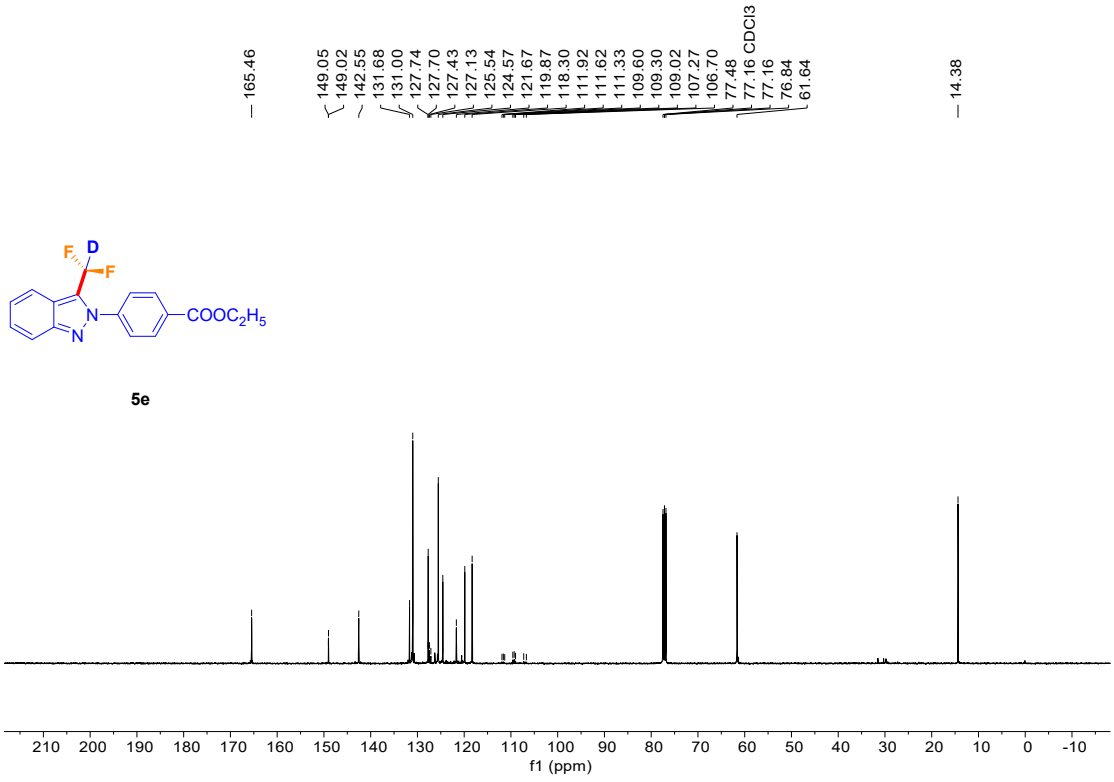


Figure S89, ^{13}C NMR spectrum of **5e** (101 MHz, $CDCl_3$)

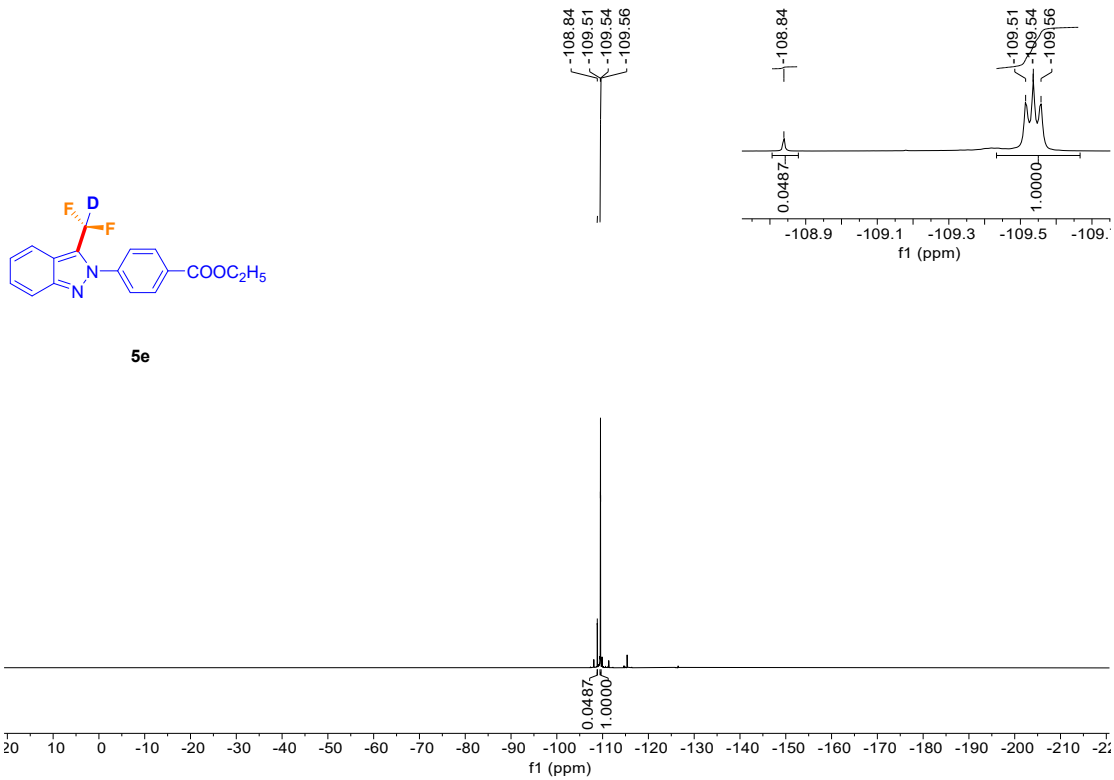


Figure S90, ^{19}F NMR spectrum of **5e** (377 MHz, $CDCl_3$)

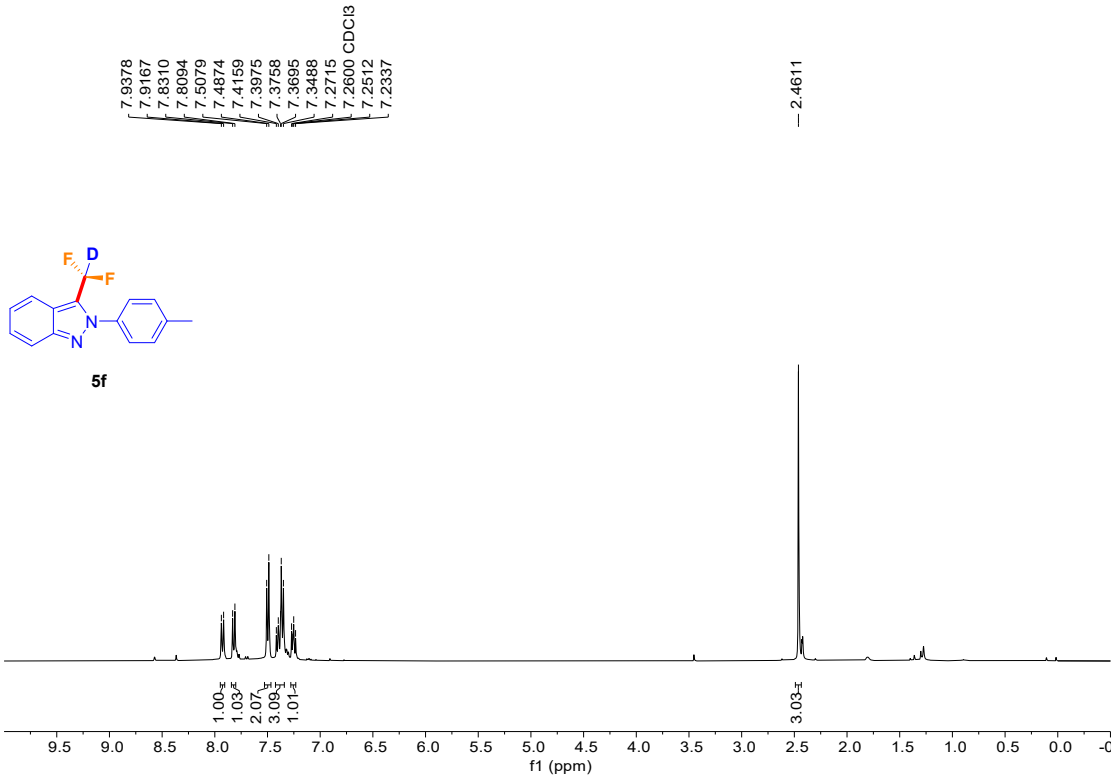


Figure S91, ^{1}H NMR spectrum of **5f** (400 MHz, $CDCl_3$)

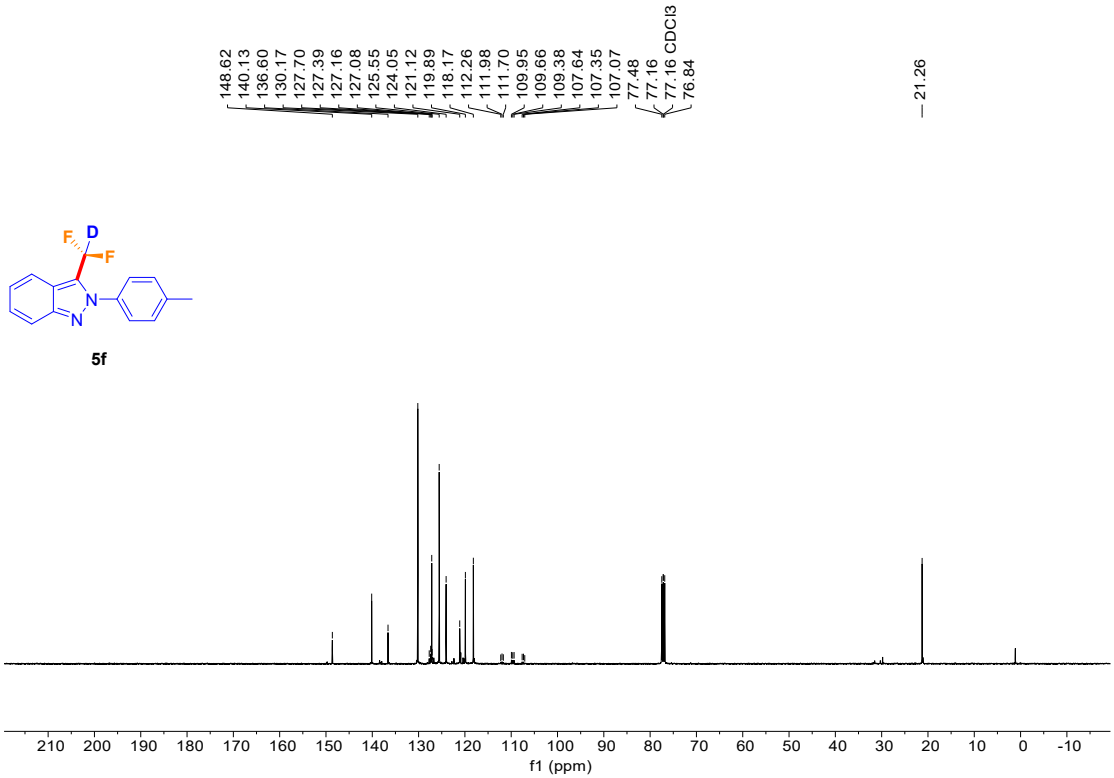


Figure S92, ^{13}C NMR spectrum of **5f** (101 MHz, $CDCl_3$)

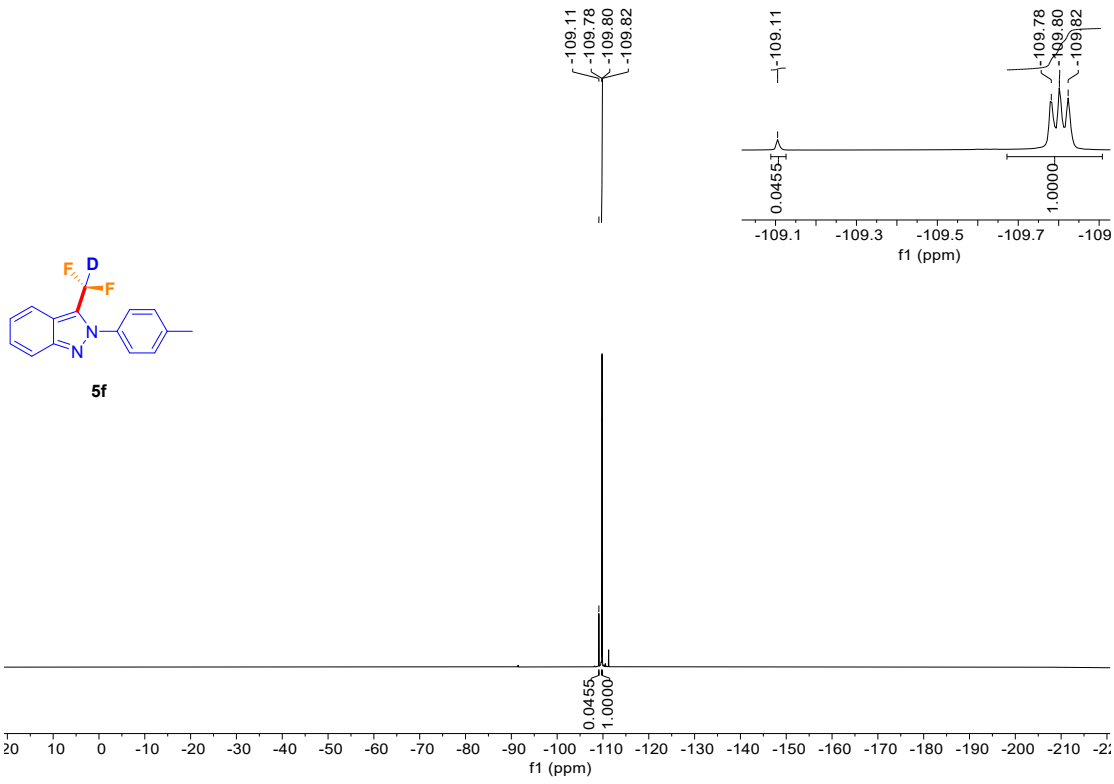


Figure S93, ^{19}F NMR spectrum of **5f** (377 MHz, $CDCl_3$)

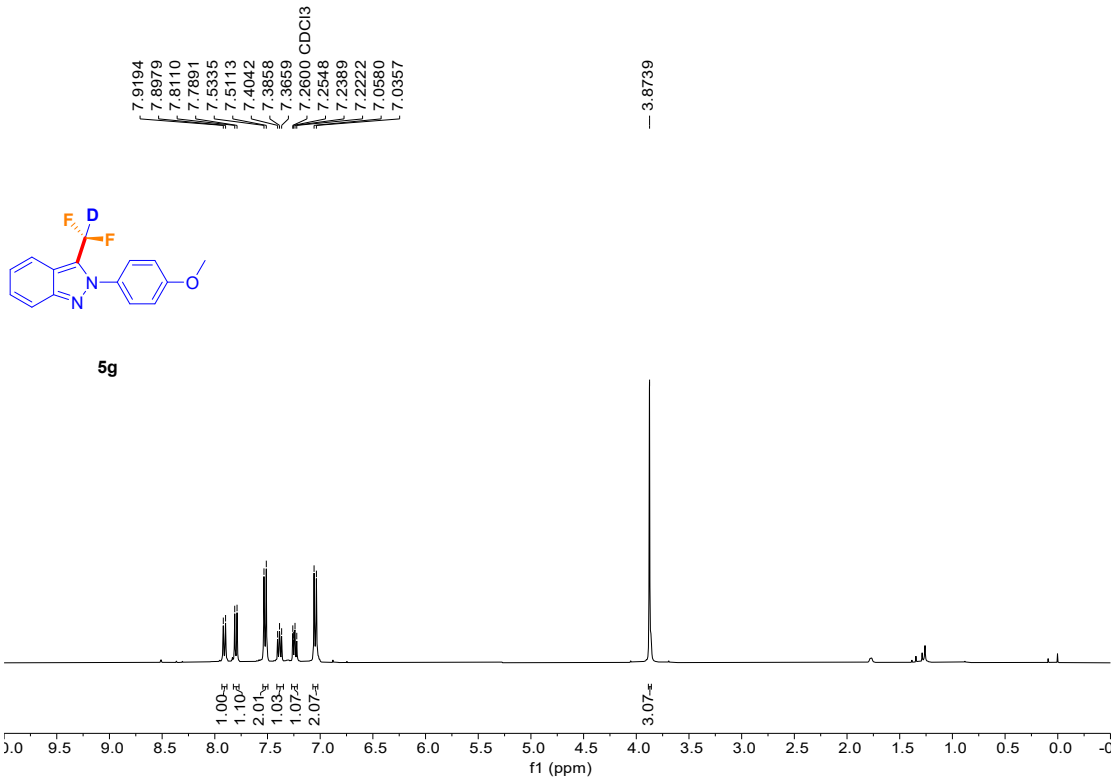


Figure S94, ^{1}H NMR spectrum of **5g** (400 MHz, $CDCl_3$)

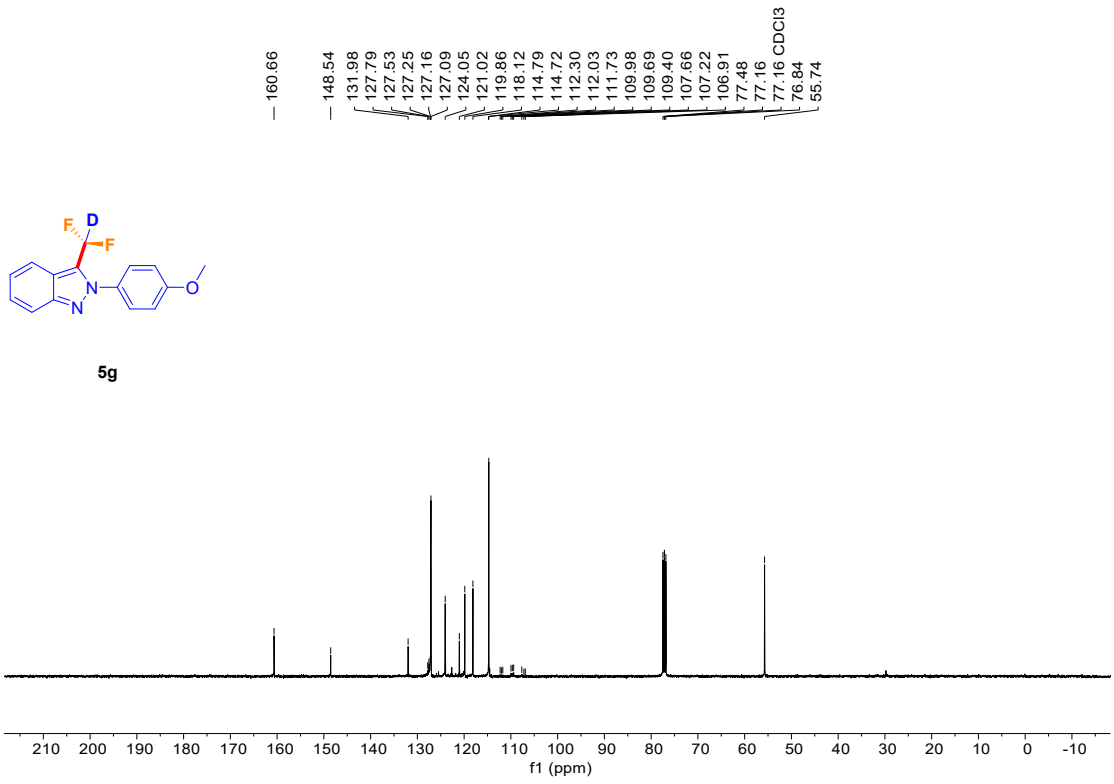


Figure S95, ^{13}C NMR spectrum of **5g** (101 MHz, $CDCl_3$)

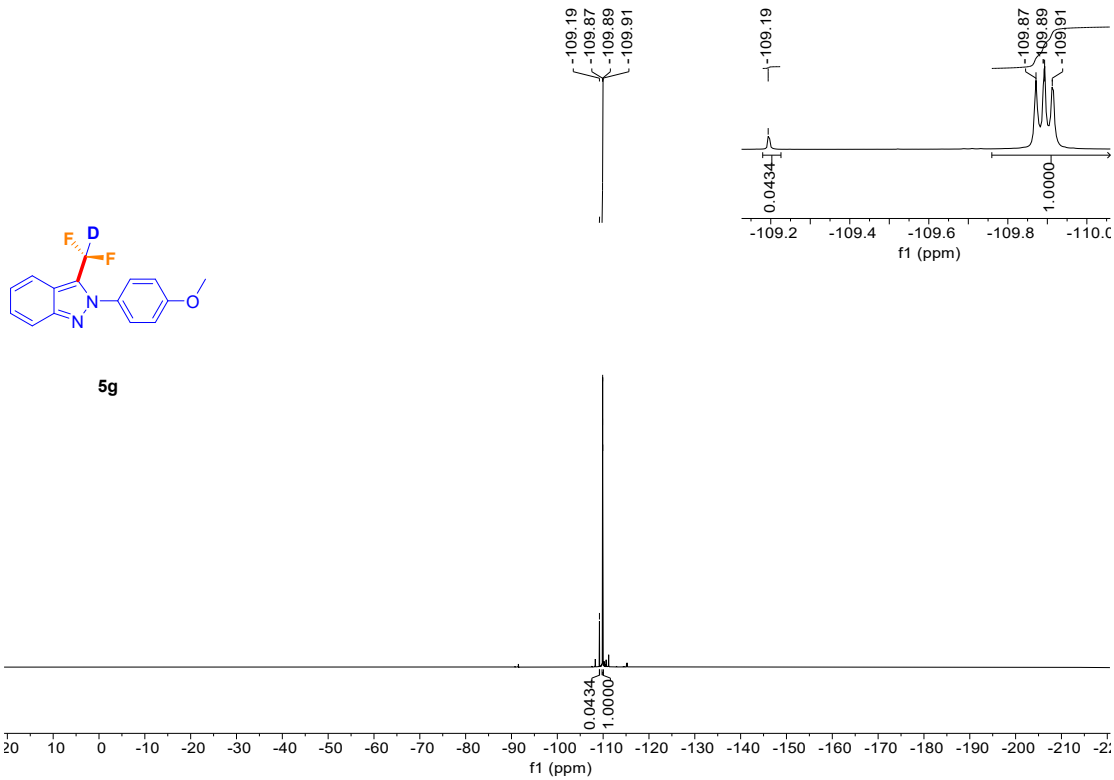


Figure S96, ^{19}F NMR spectrum of **5g** (377 MHz, $CDCl_3$)

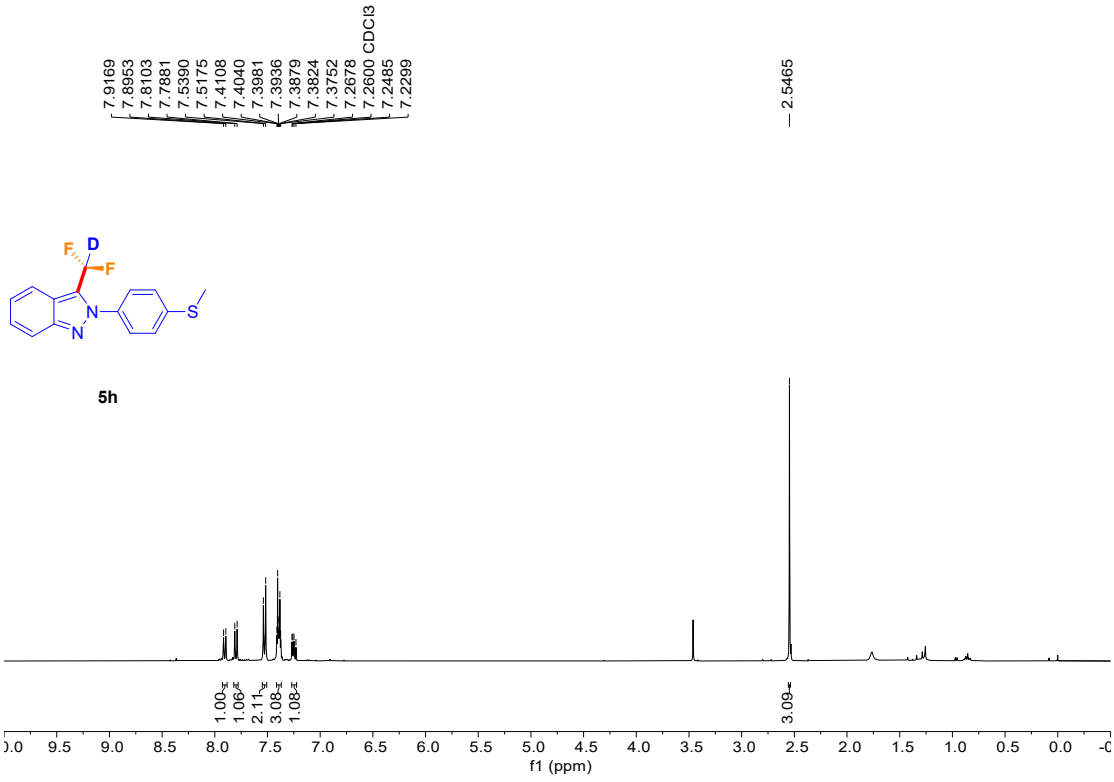


Figure S97, ^{1}H NMR spectrum of **5h** (400 MHz, $CDCl_3$)

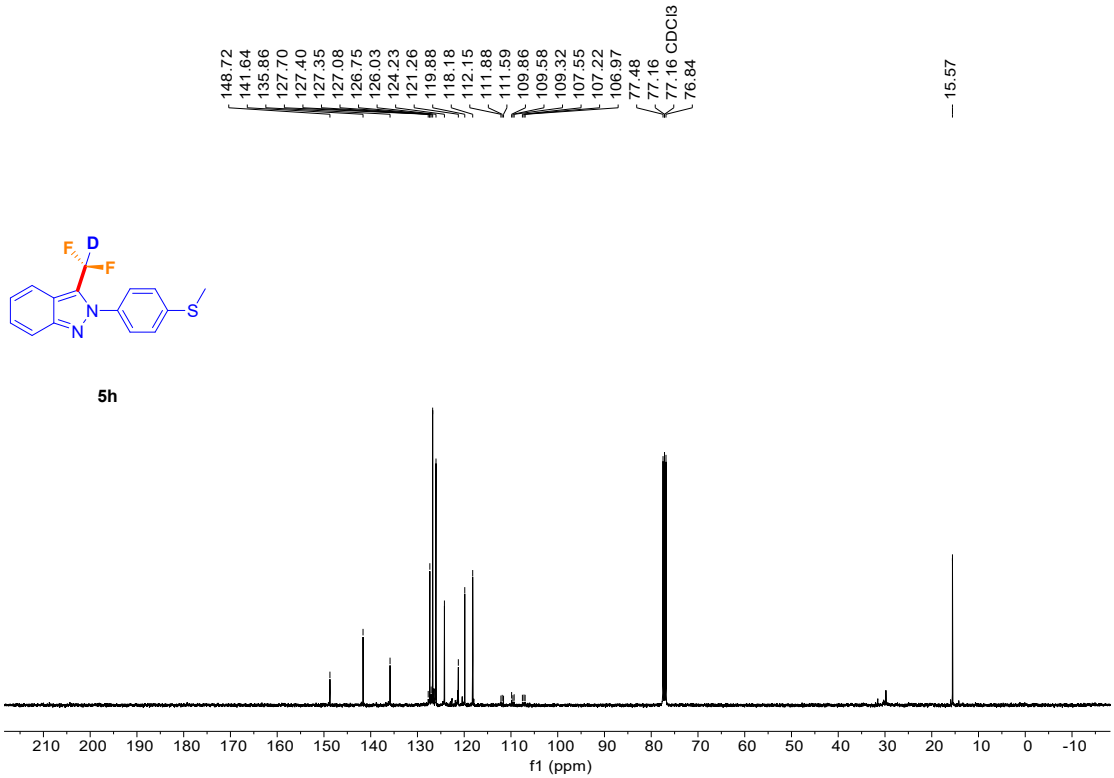


Figure S98, ^{13}C NMR spectrum of **5h** (101 MHz, $CDCl_3$)

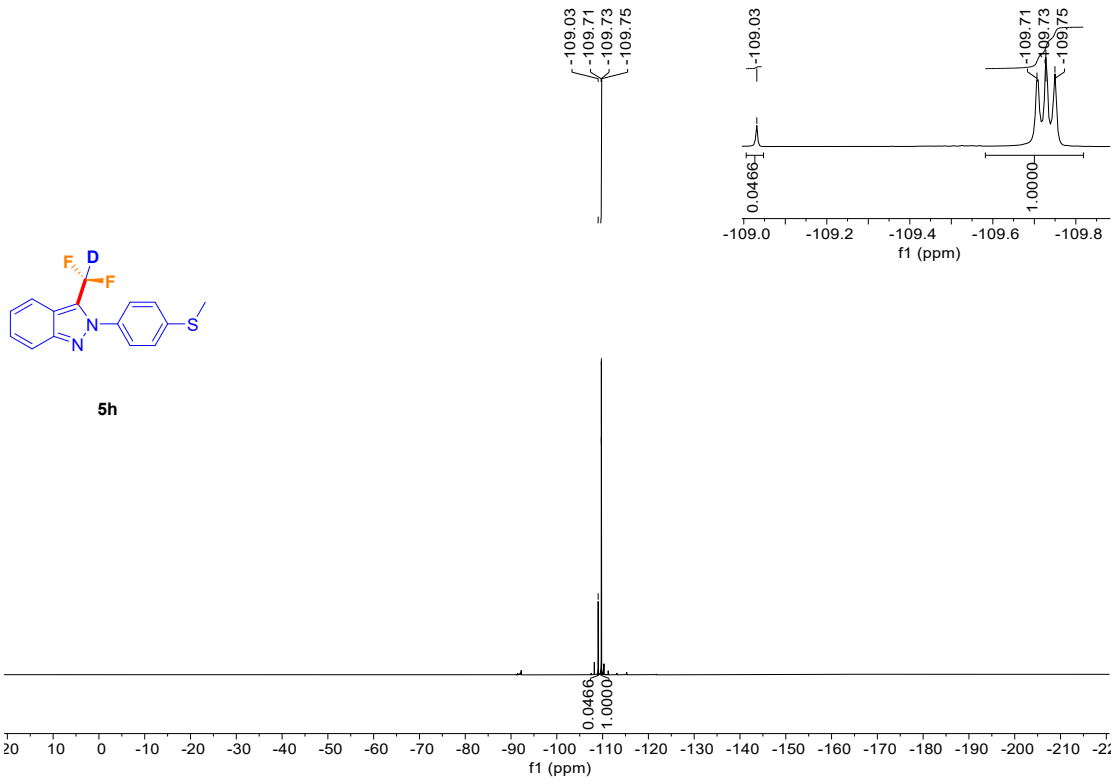


Figure S99, ^{19}F NMR spectrum of **5h** (377 MHz, $CDCl_3$)

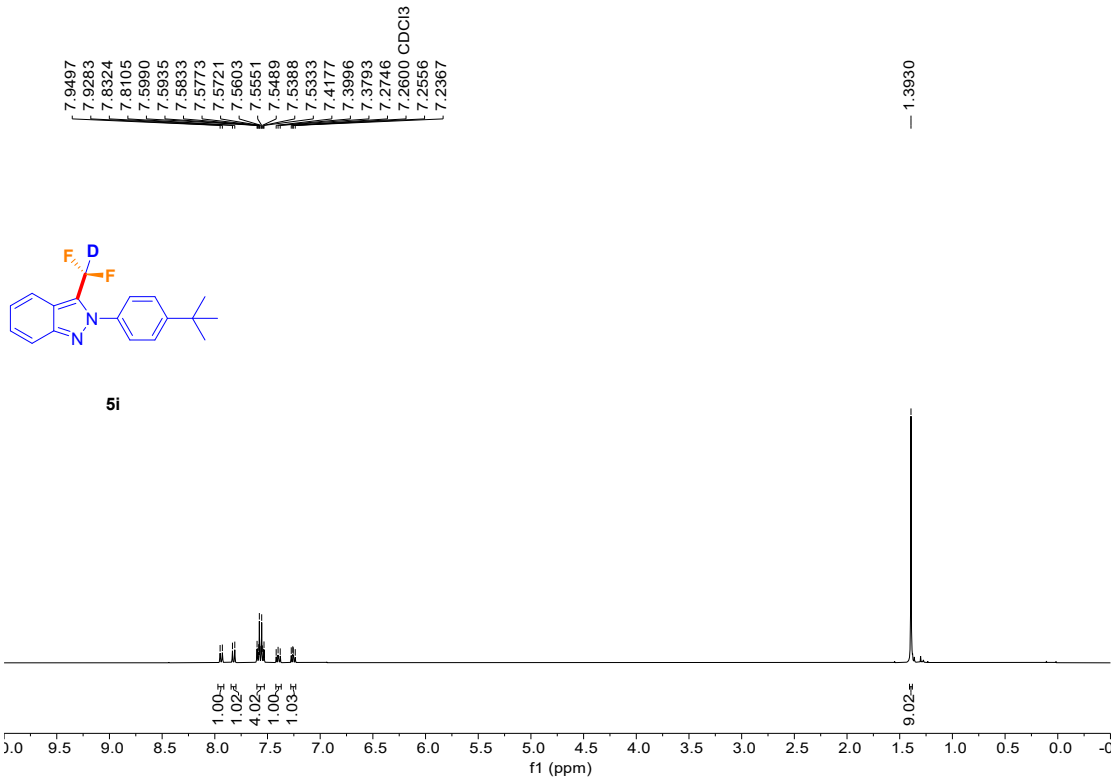


Figure S100, ^{1}H NMR spectrum of **5i** (400 MHz, $CDCl_3$)

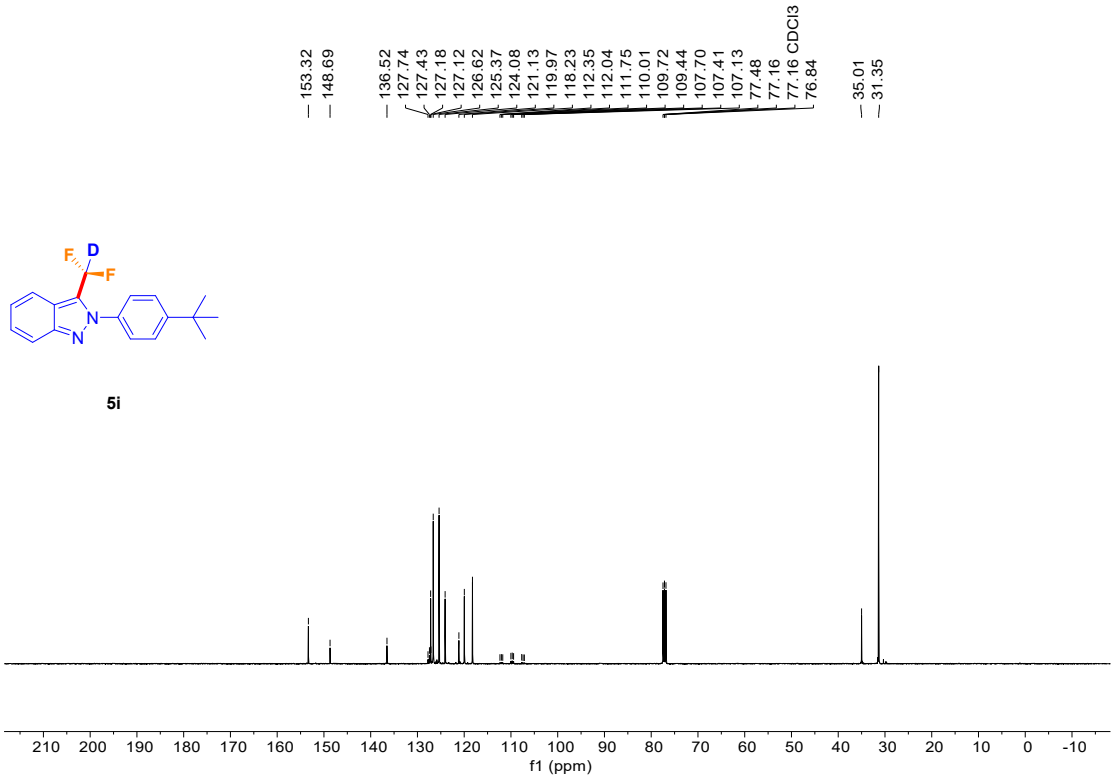


Figure S101, ^{13}C NMR spectrum of **5i** (101 MHz, $CDCl_3$)

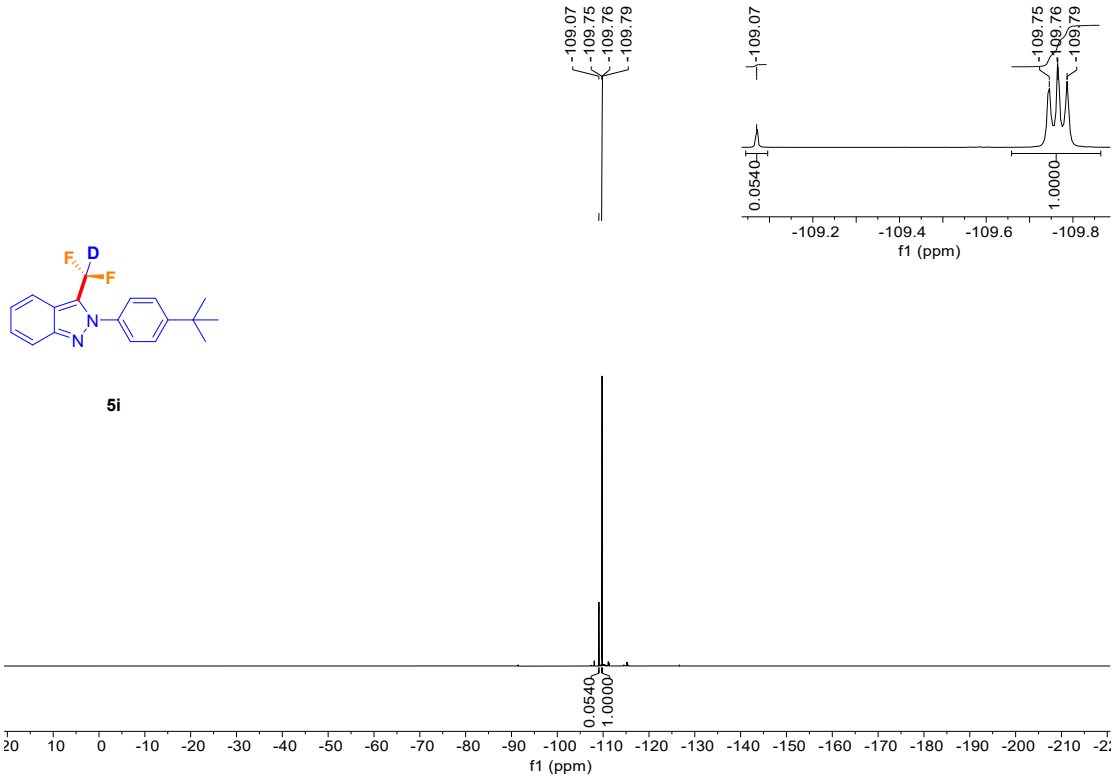


Figure S102, ^{19}F NMR spectrum of **5i** (377 MHz, $CDCl_3$)

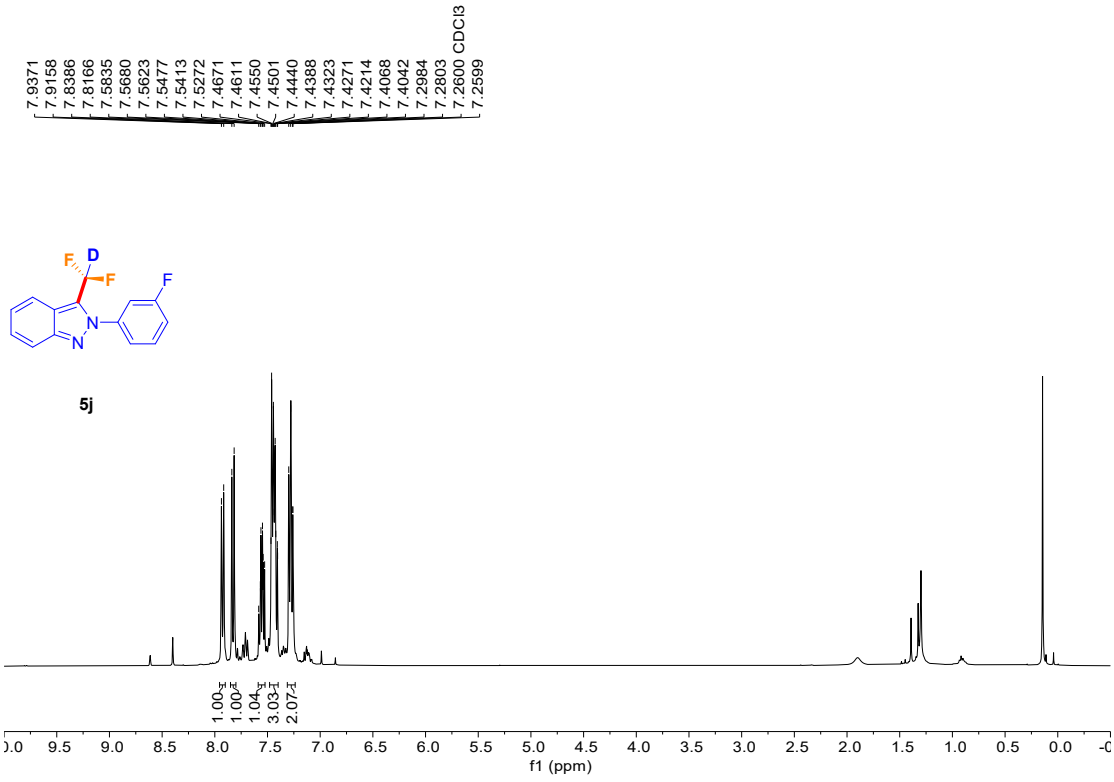


Figure S103, ^{1}H NMR spectrum of **5j** (400 MHz, $CDCl_3$)

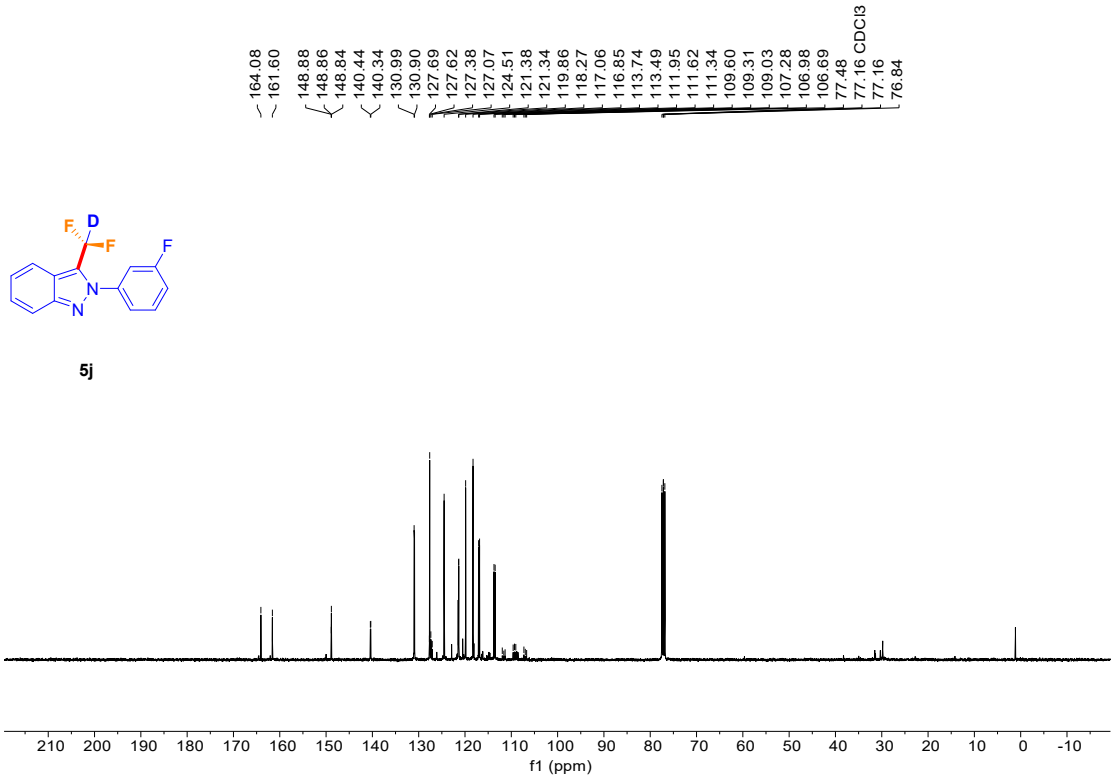


Figure S104, ^{13}C NMR spectrum of **5j** (101 MHz, $CDCl_3$)

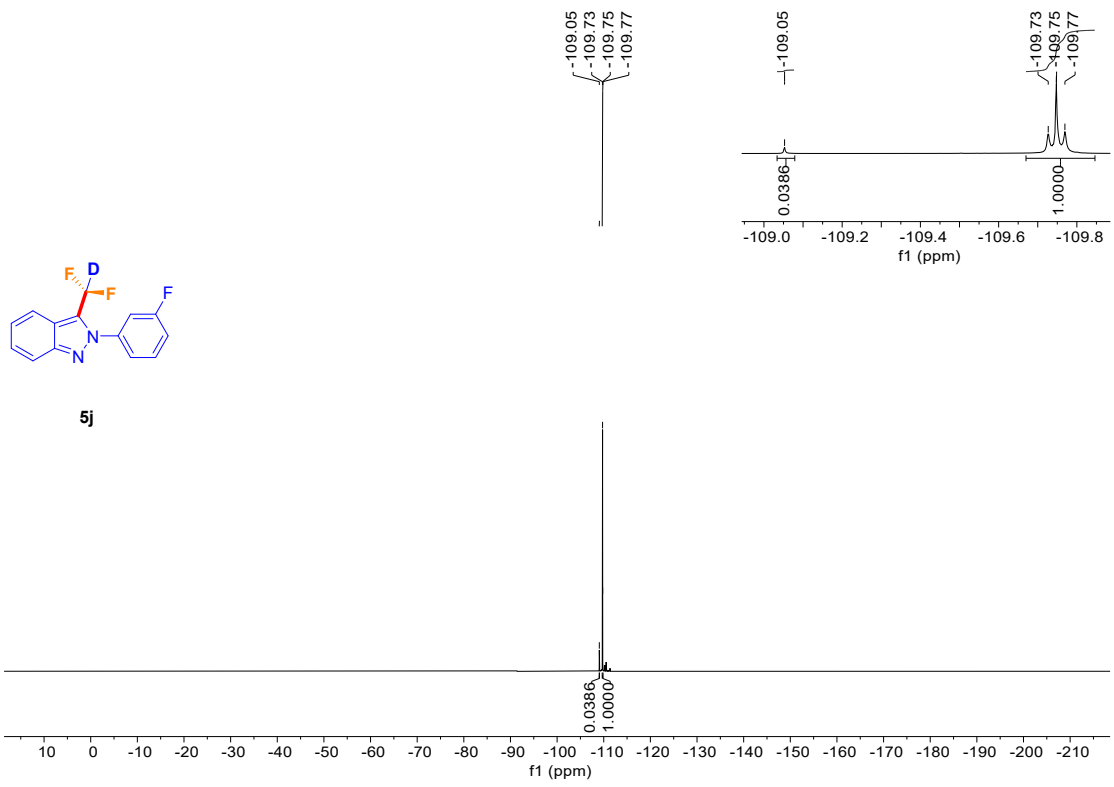


Figure S105, ^{19}F NMR spectrum of **5j** (377 MHz, $CDCl_3$)

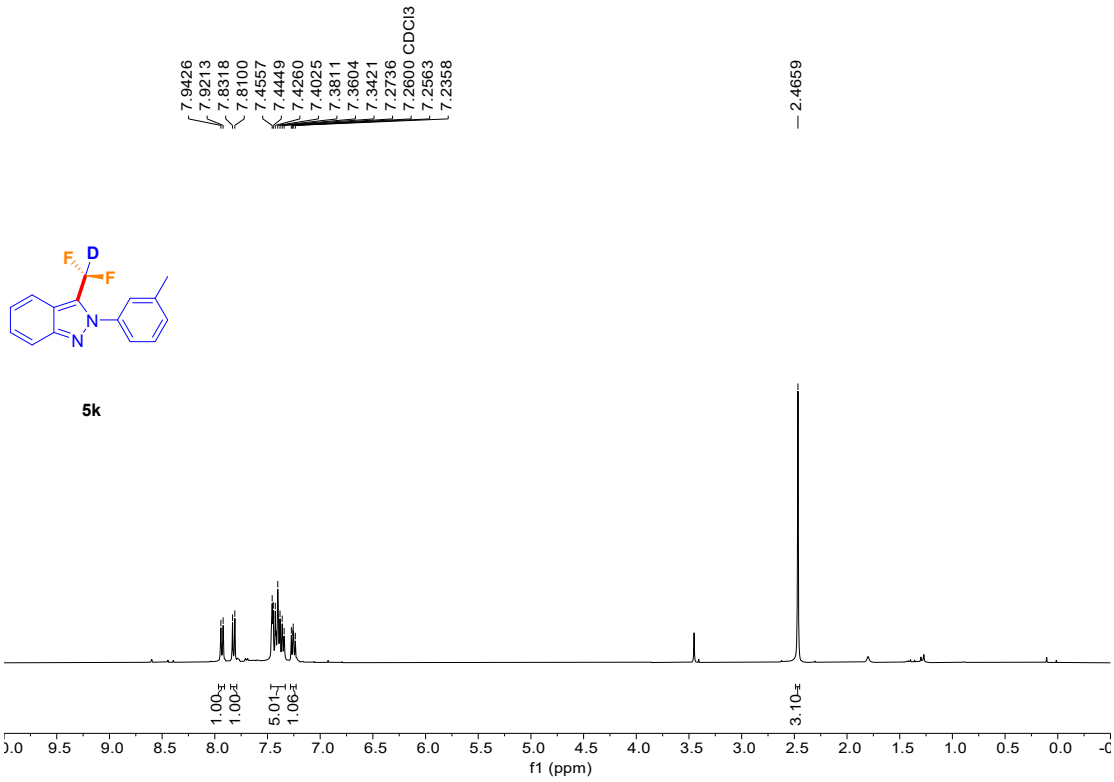


Figure S106, ^{1}H NMR spectrum of **5k** (400 MHz, $CDCl_3$)

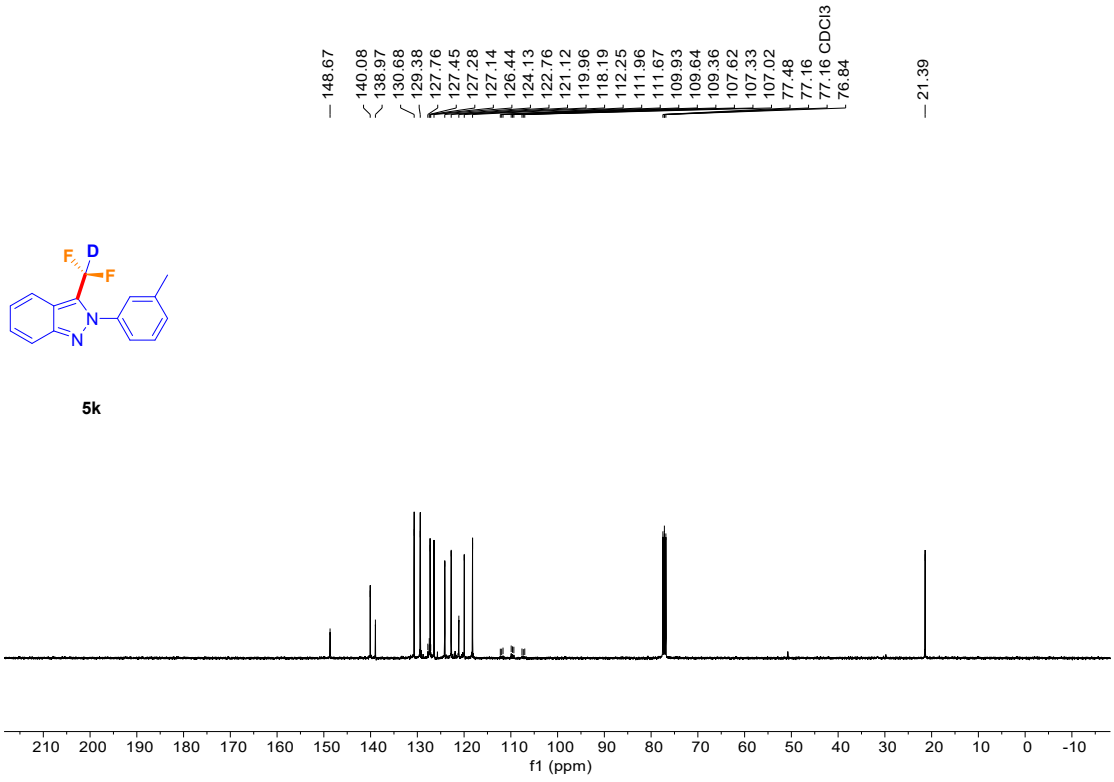


Figure S107, ^{13}C NMR spectrum of **5k** (101 MHz, $CDCl_3$)

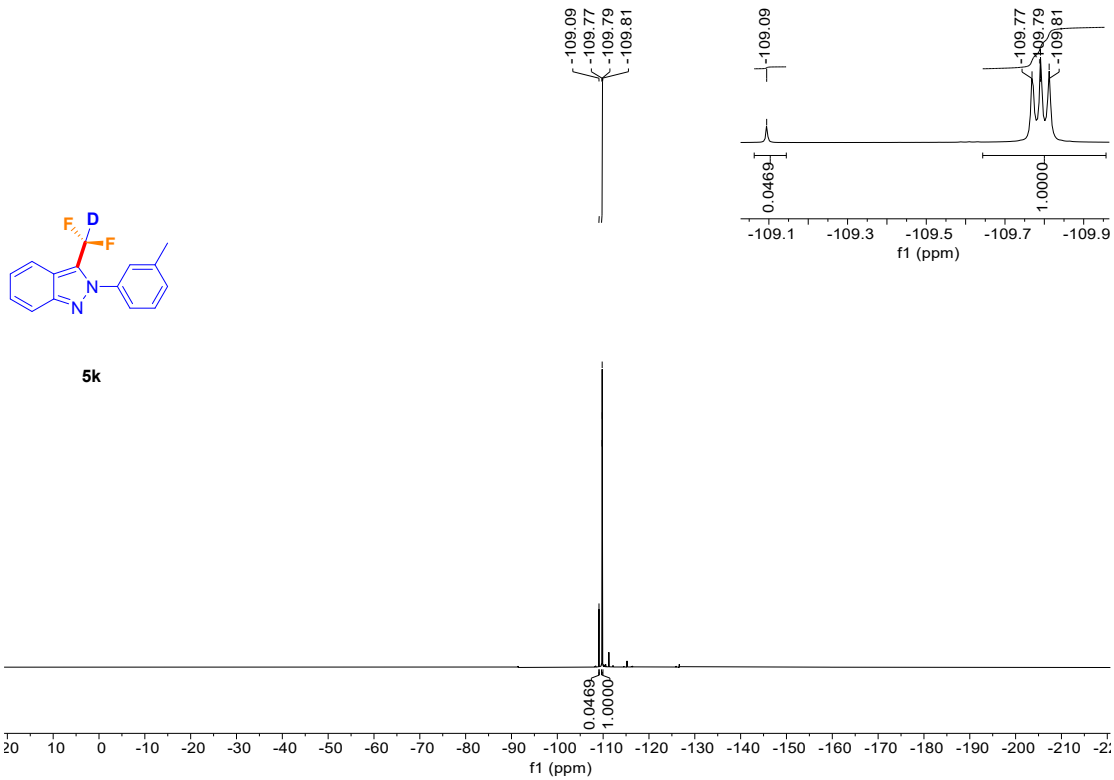


Figure S108, ^{19}F NMR spectrum of **5k** (377 MHz, $CDCl_3$)

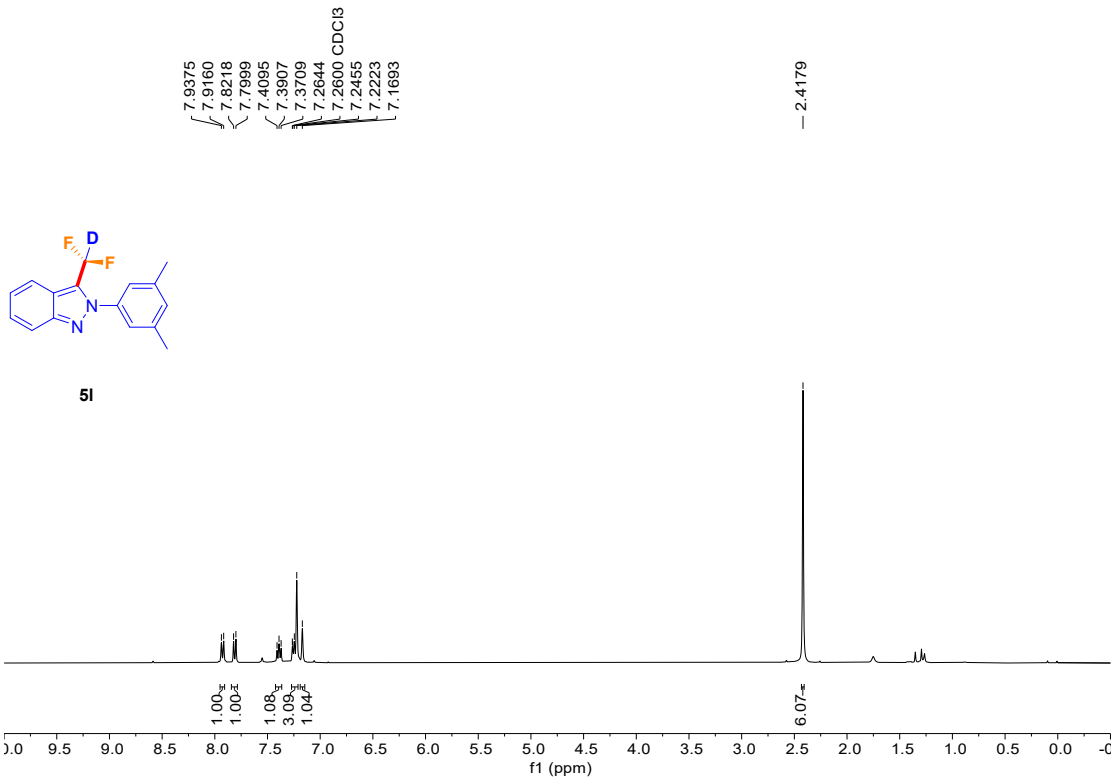


Figure S109, ^{1}H NMR spectrum of **5l** (400 MHz, $CDCl_3$)

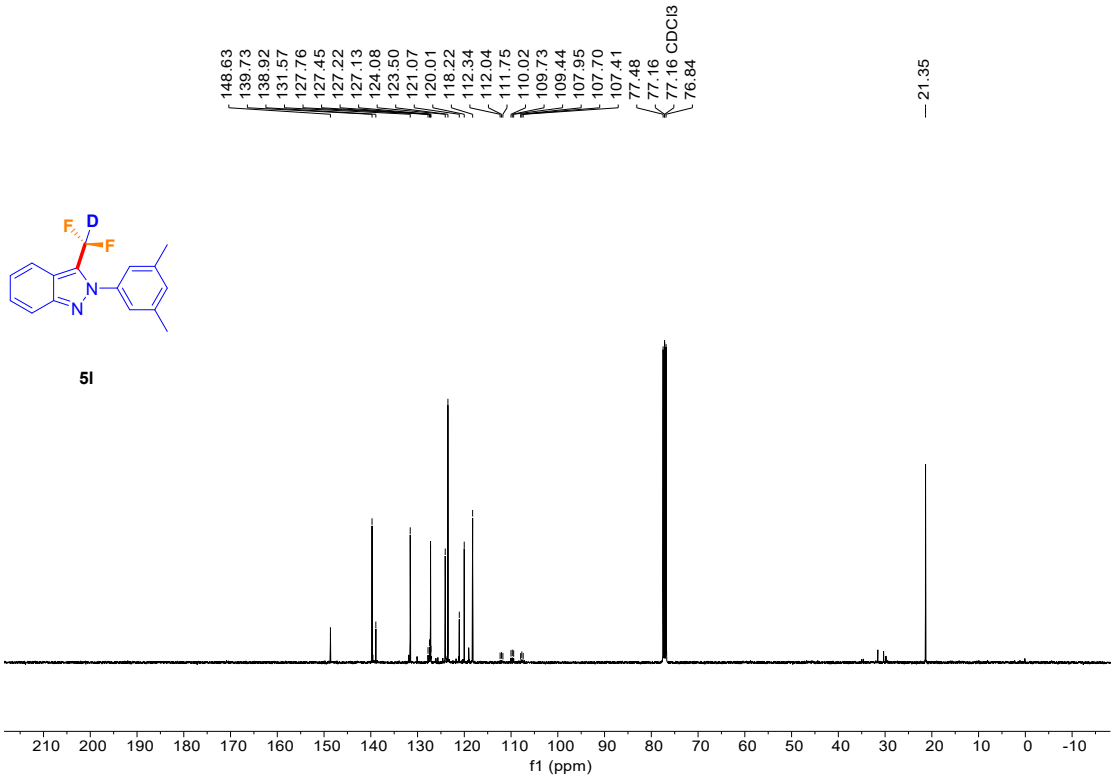


Figure S110, ^{13}C NMR spectrum of **5l** (101 MHz, $CDCl_3$)

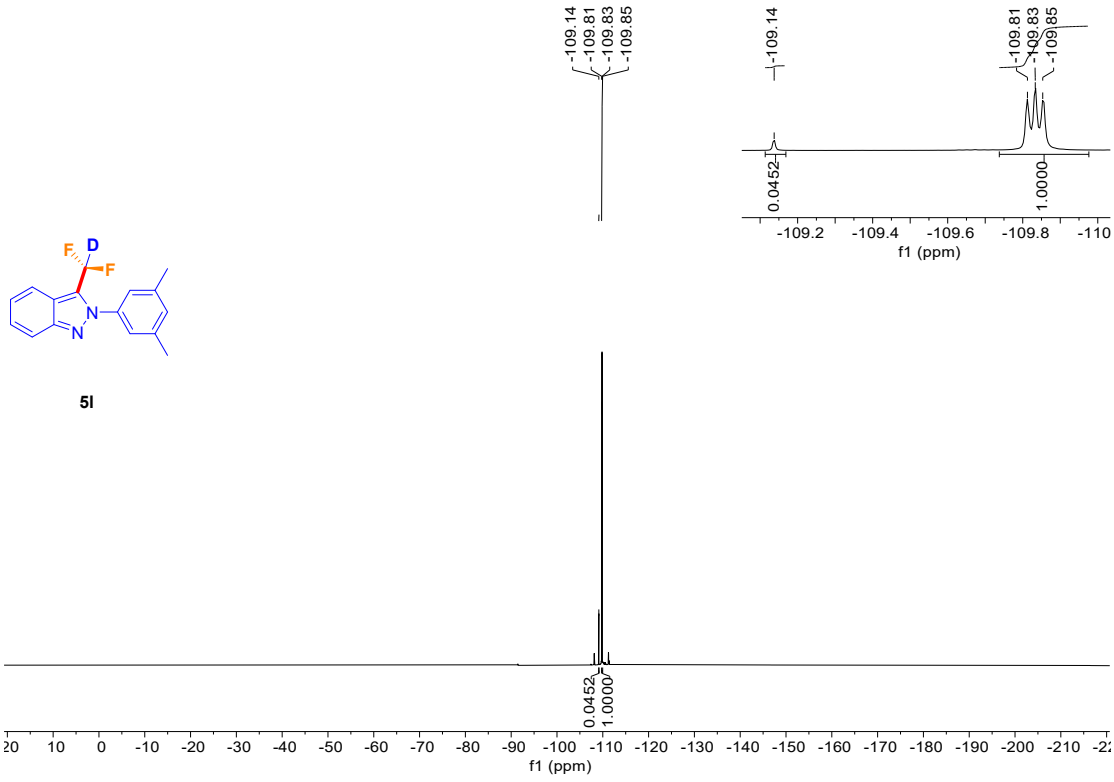


Figure S111, ^{19}F NMR spectrum of **5l** (377 MHz, $CDCl_3$)

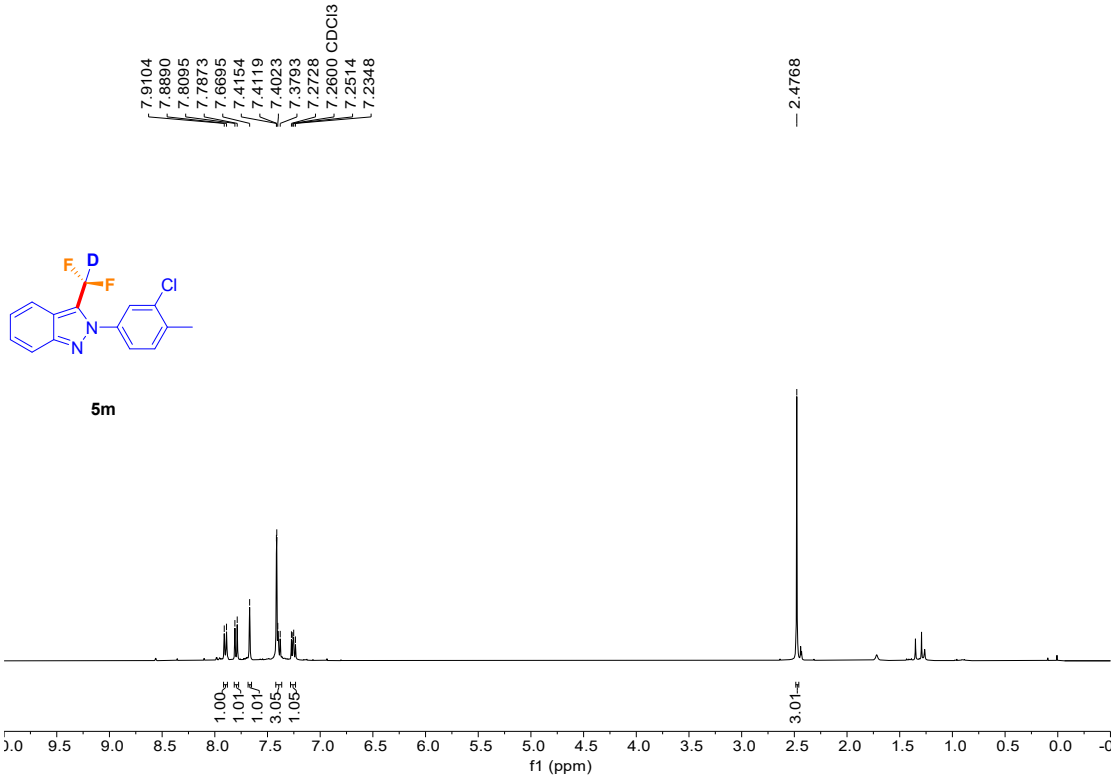


Figure S112, ^{1}H NMR spectrum of **5m** (400 MHz, $CDCl_3$)

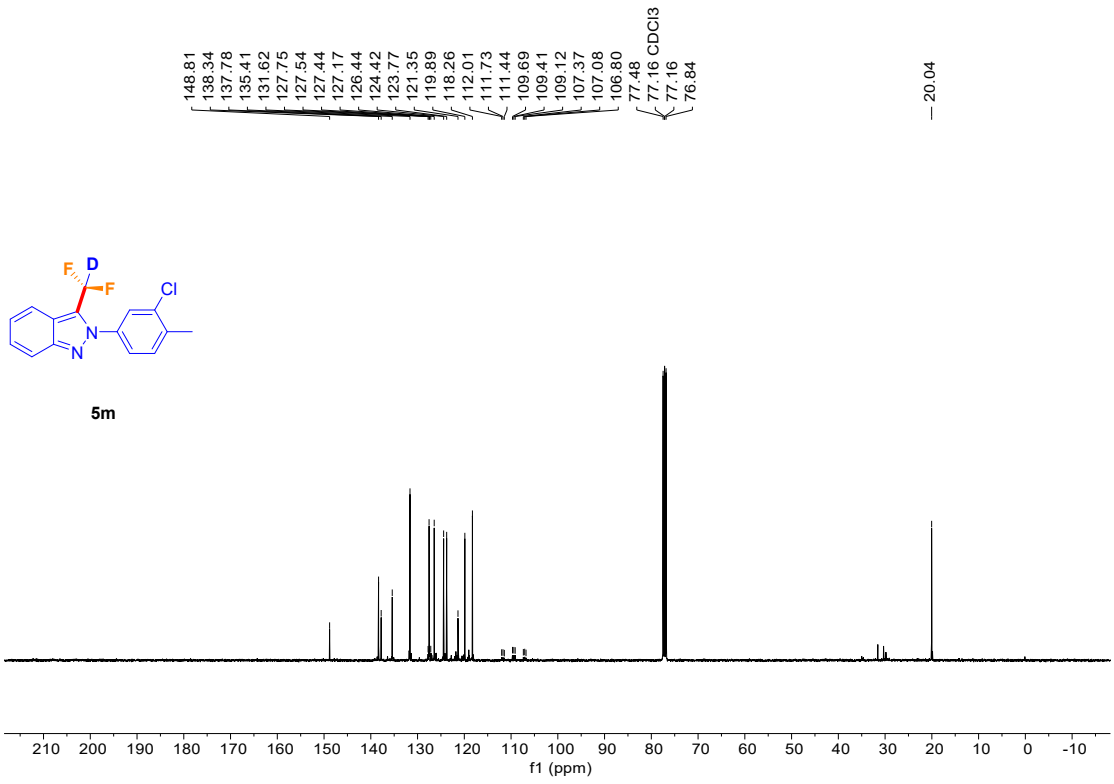


Figure S113, ^{13}C NMR spectrum of **5m** (101 MHz, $CDCl_3$)

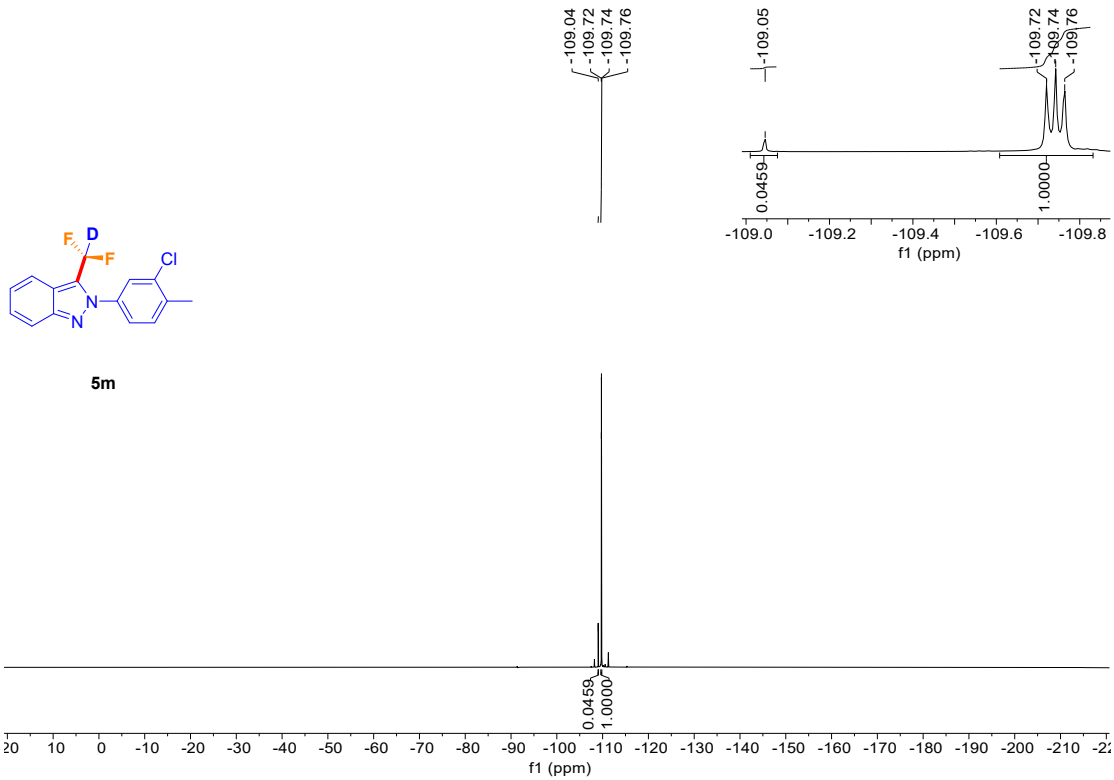


Figure S114, ^{19}F NMR spectrum of **5m** (377 MHz, $CDCl_3$)

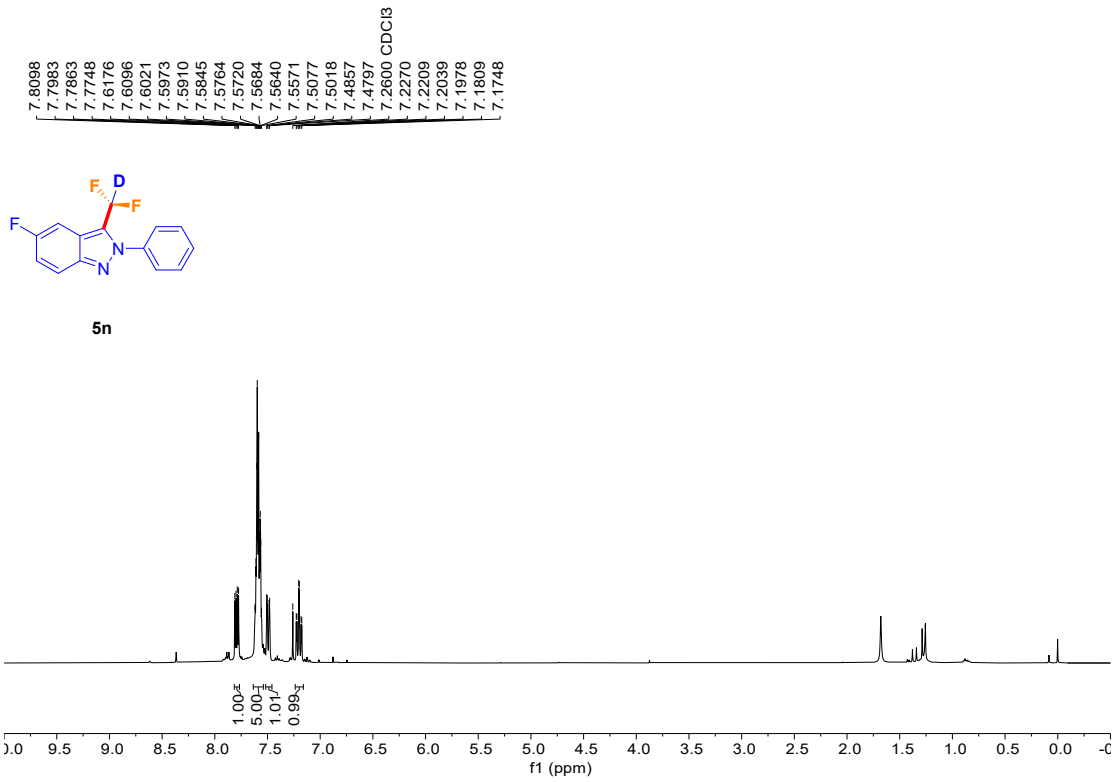


Figure S115, ^{1}H NMR spectrum of **5n** (400 MHz, $CDCl_3$)

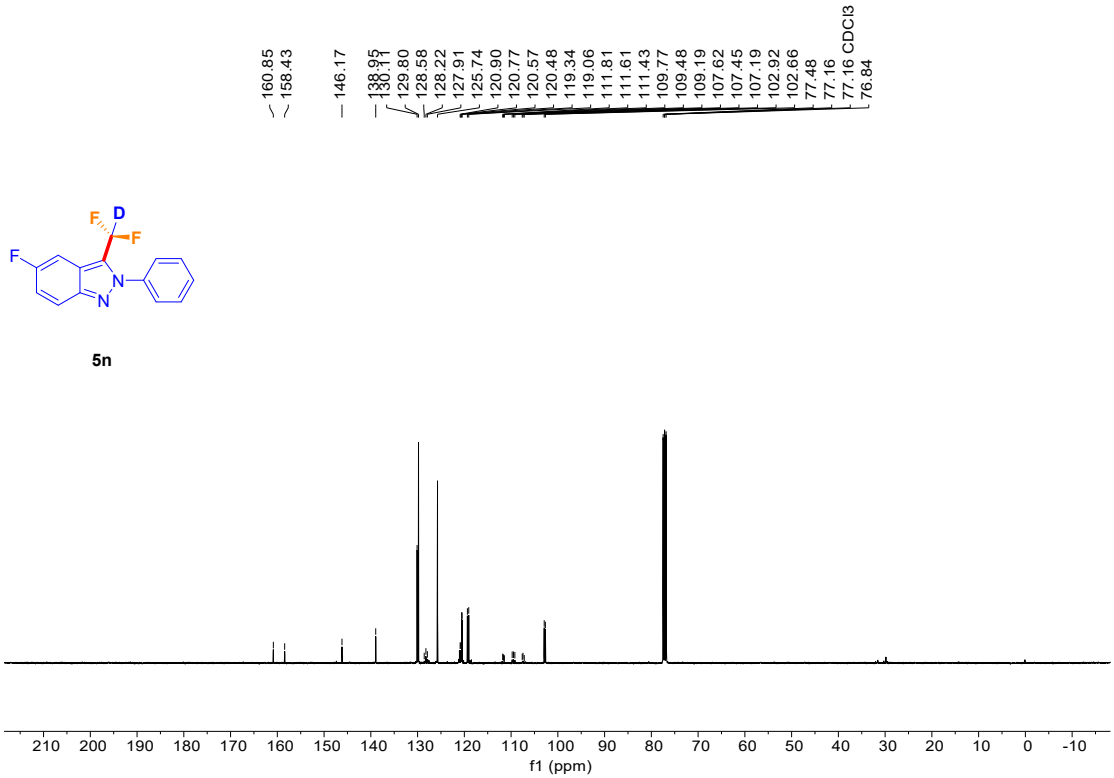


Figure S116, ^{13}C NMR spectrum of **5n** (101 MHz, $CDCl_3$)

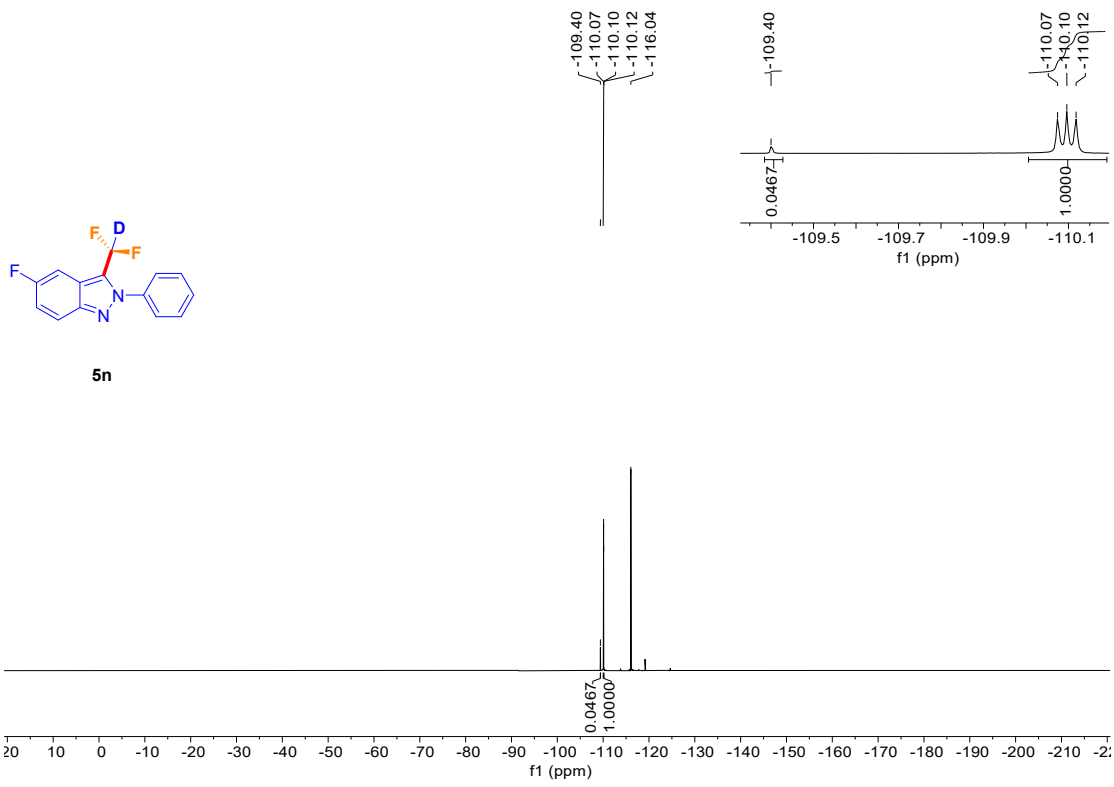


Figure S117, ^{19}F NMR spectrum of **5n** (377 MHz, $CDCl_3$)

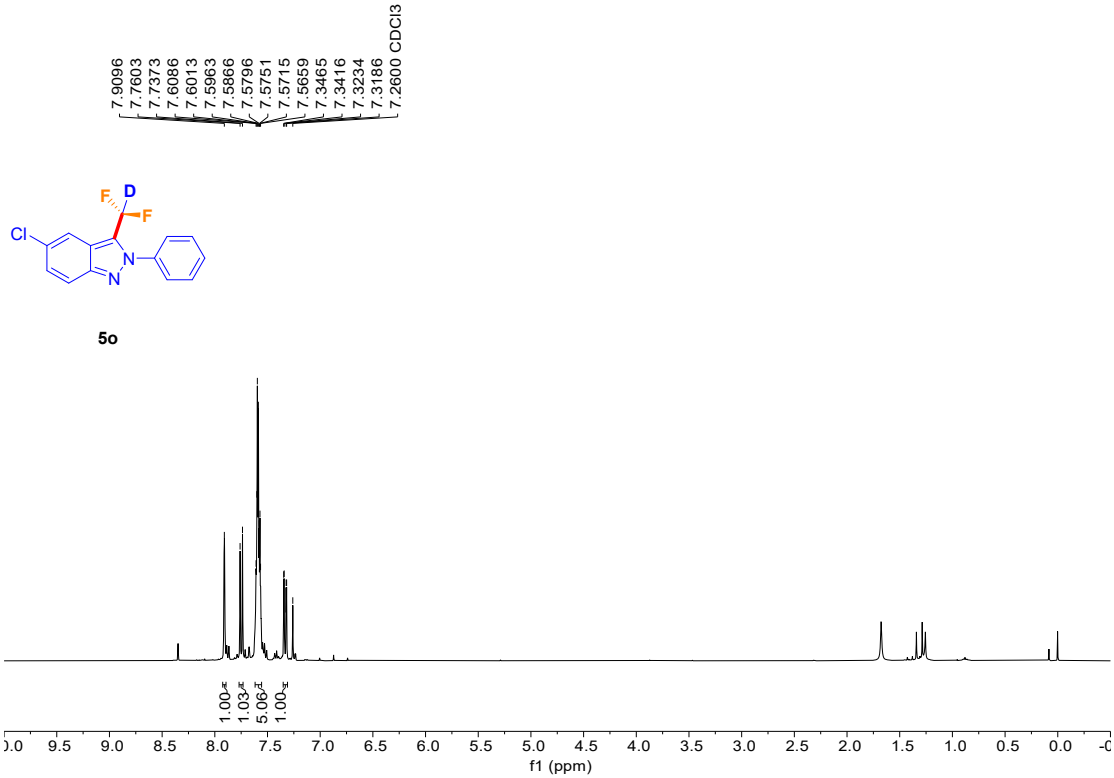


Figure S118, ^{1}H NMR spectrum of **5o** (400 MHz, $CDCl_3$)

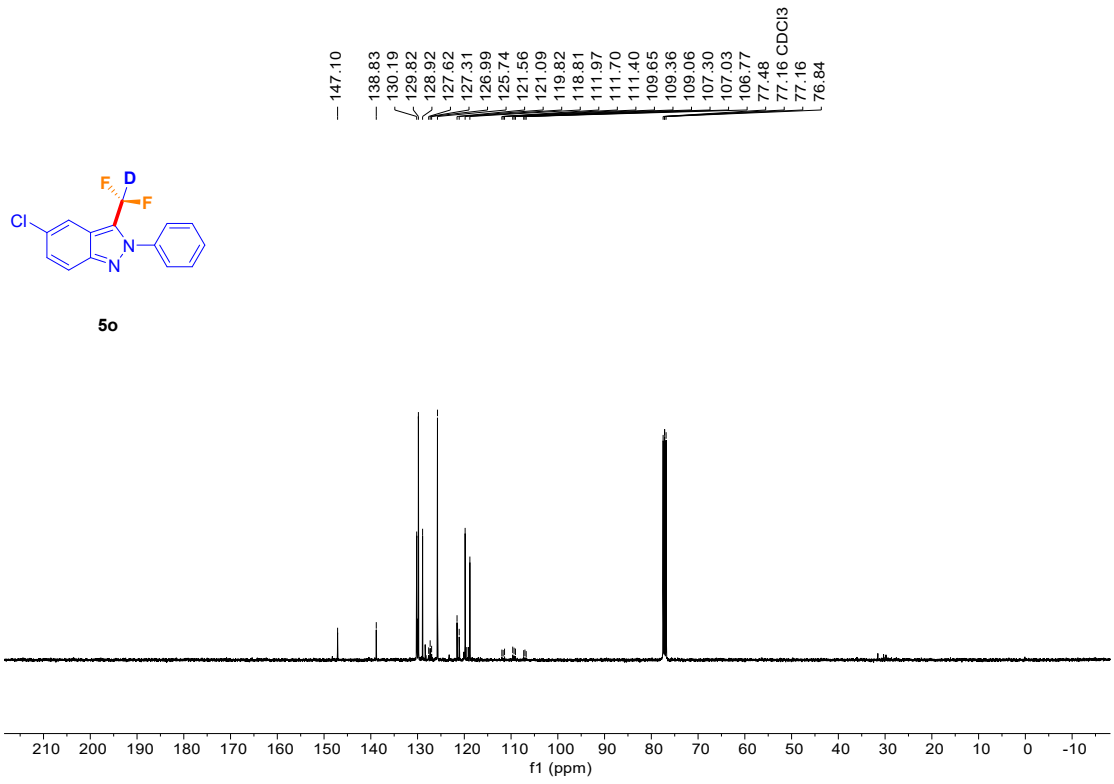


Figure S119, ^{13}C NMR spectrum of **5o** (101 MHz, $CDCl_3$)

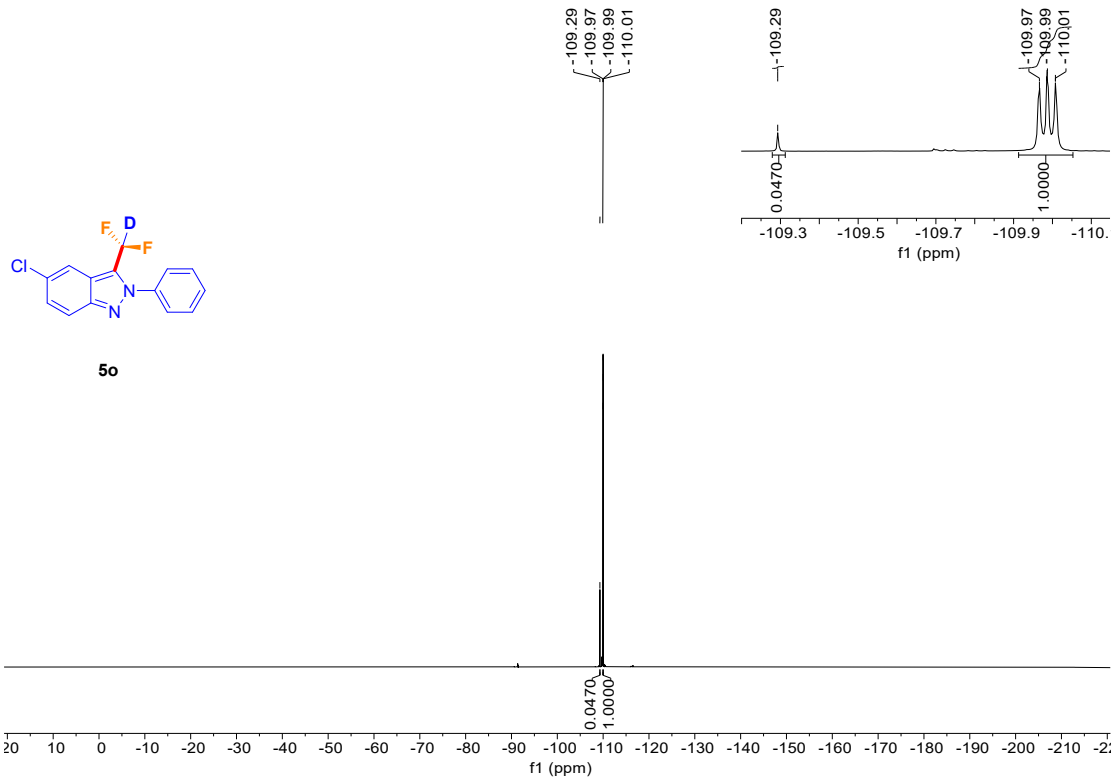


Figure S120, ^{19}F NMR spectrum of **5o** (377 MHz, $CDCl_3$)

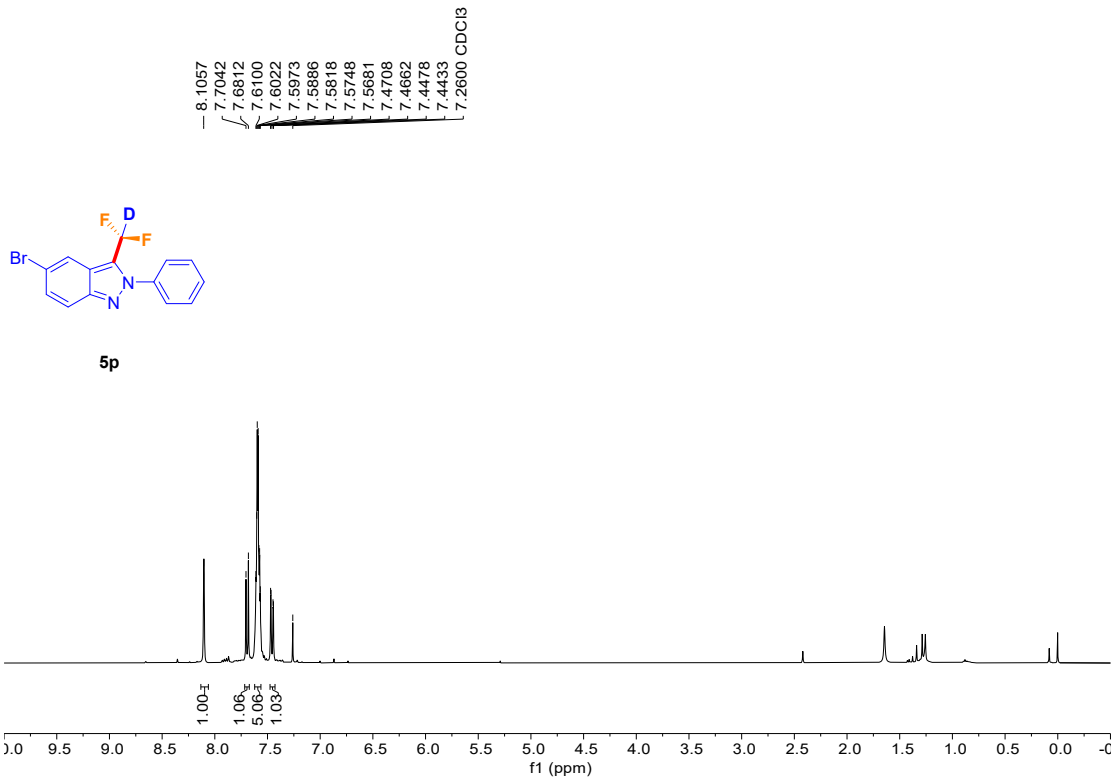


Figure S121, ^{1}H NMR spectrum of **5p** (400 MHz, $CDCl_3$)

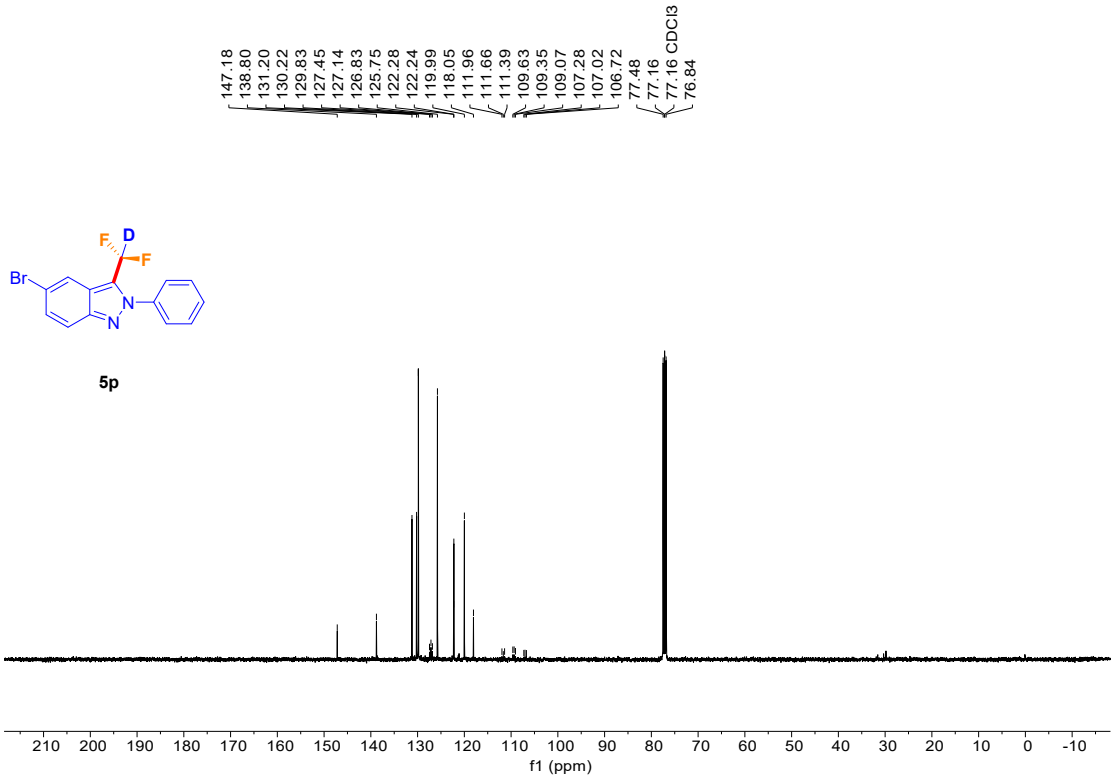


Figure S122, ^{13}C NMR spectrum of **5p** (101 MHz, $CDCl_3$)

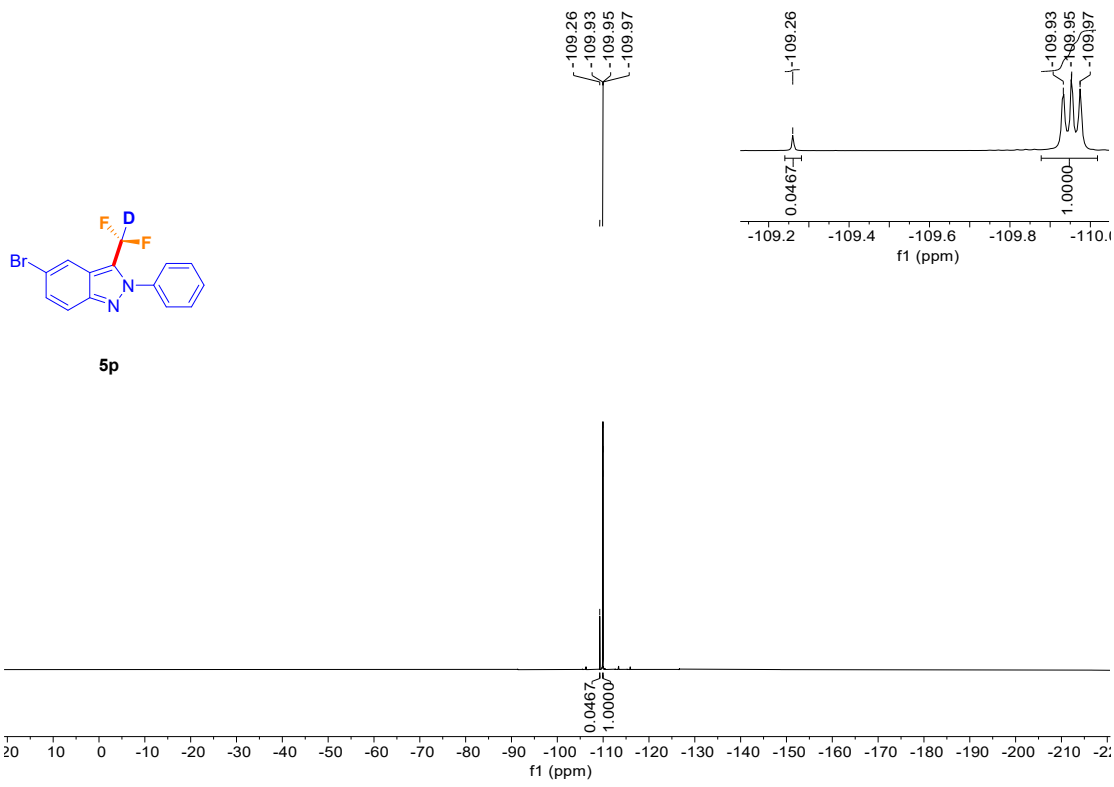


Figure S123, ^{19}F NMR spectrum of **5p** (377 MHz, $CDCl_3$)

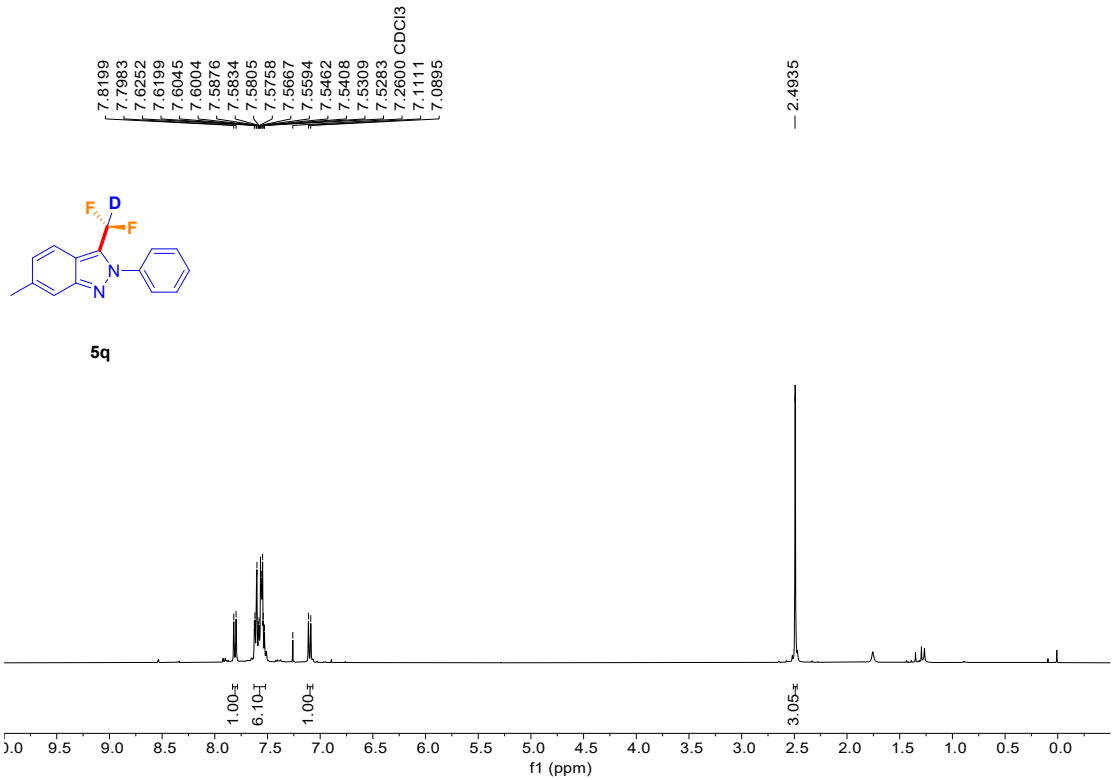


Figure S124, ^{1}H NMR spectrum of **5q** (400 MHz, $CDCl_3$)

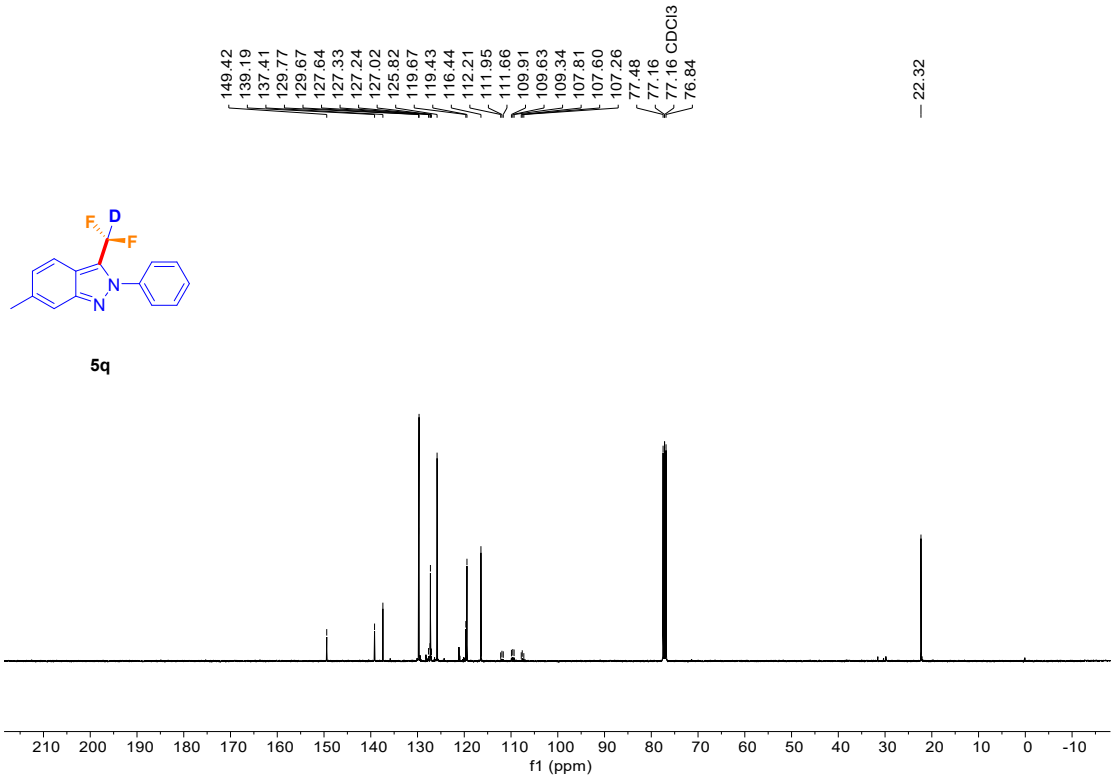


Figure S125, ^{13}C NMR spectrum of **5q** (101 MHz, $CDCl_3$)

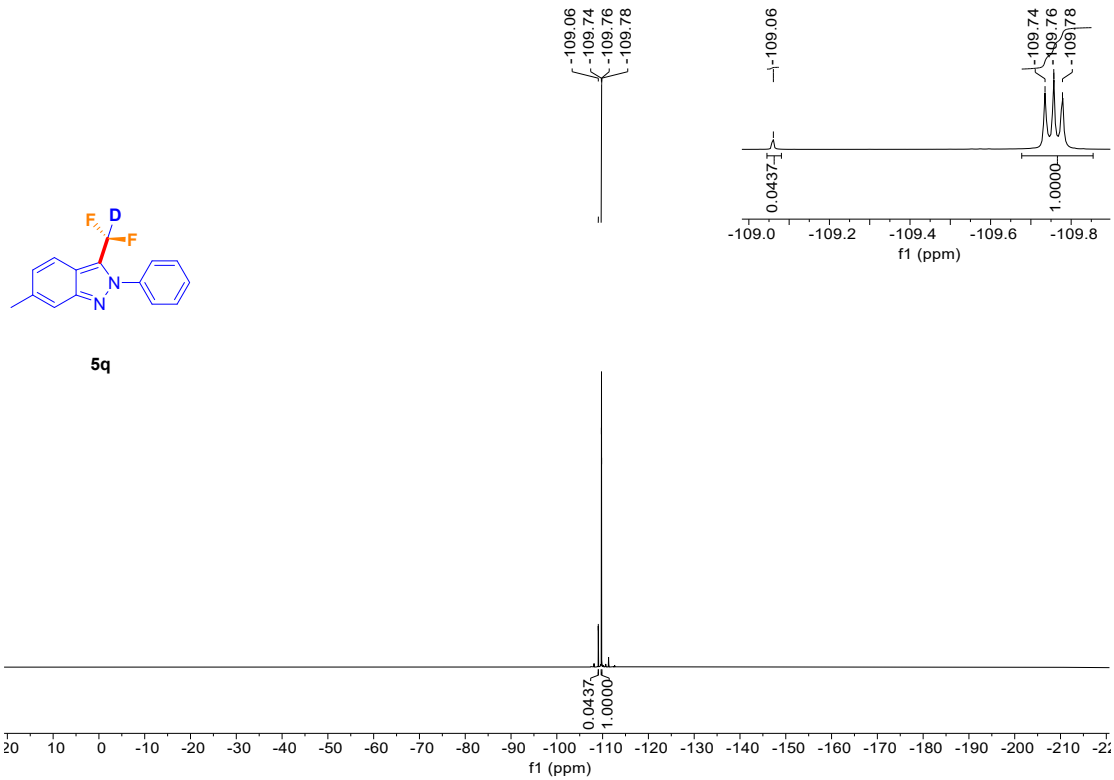


Figure S126 ^{19}F NMR spectrum of **5q** (377 MHz, $CDCl_3$)

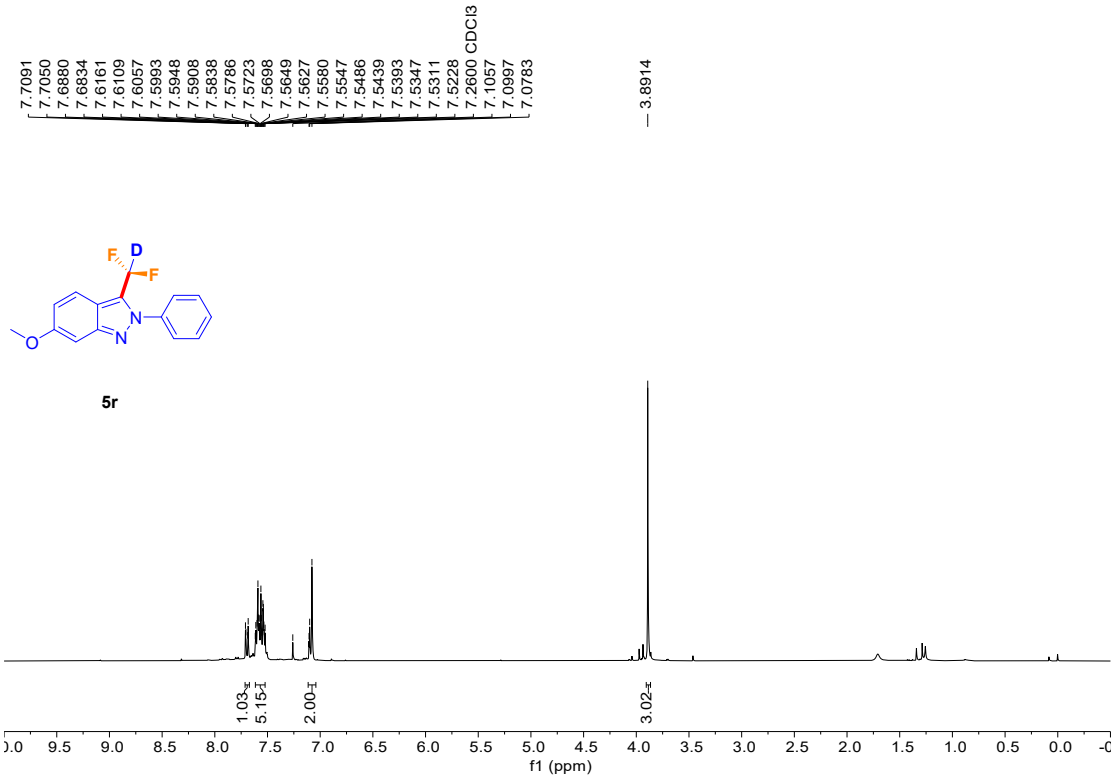


Figure S127 ^{1}H NMR spectrum of **5r** (400 MHz, $CDCl_3$)

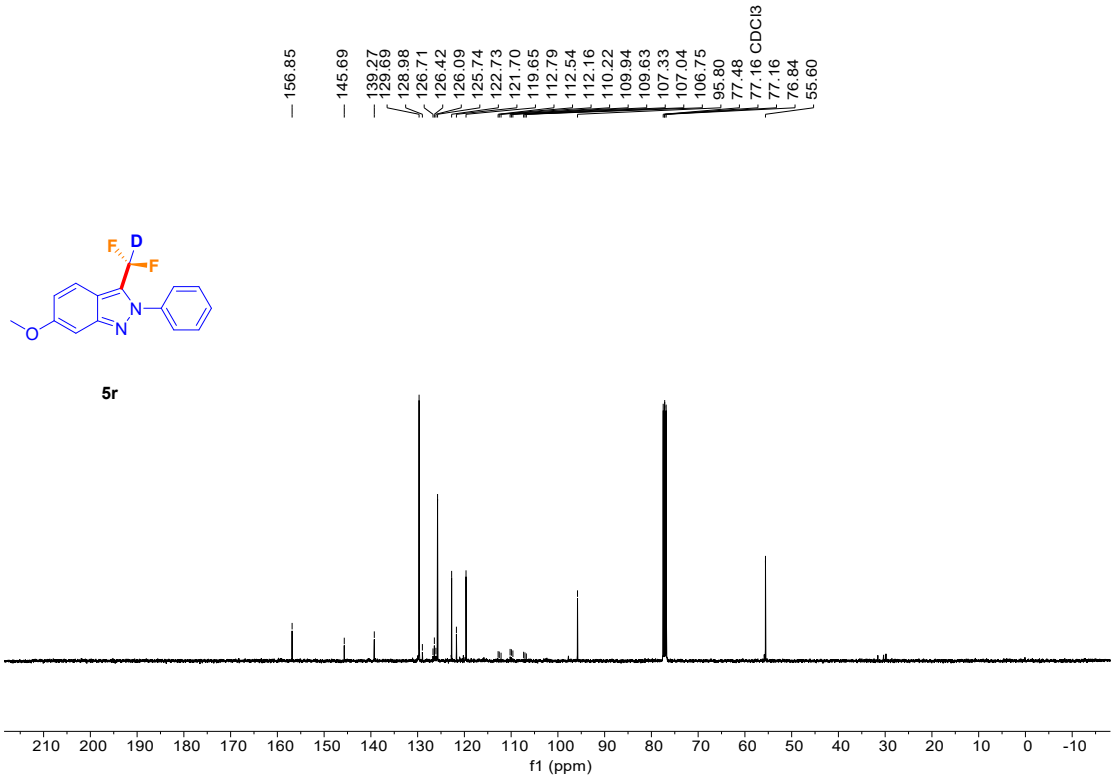


Figure S128 ^{13}C NMR spectrum of **5r** (101 MHz, $CDCl_3$)

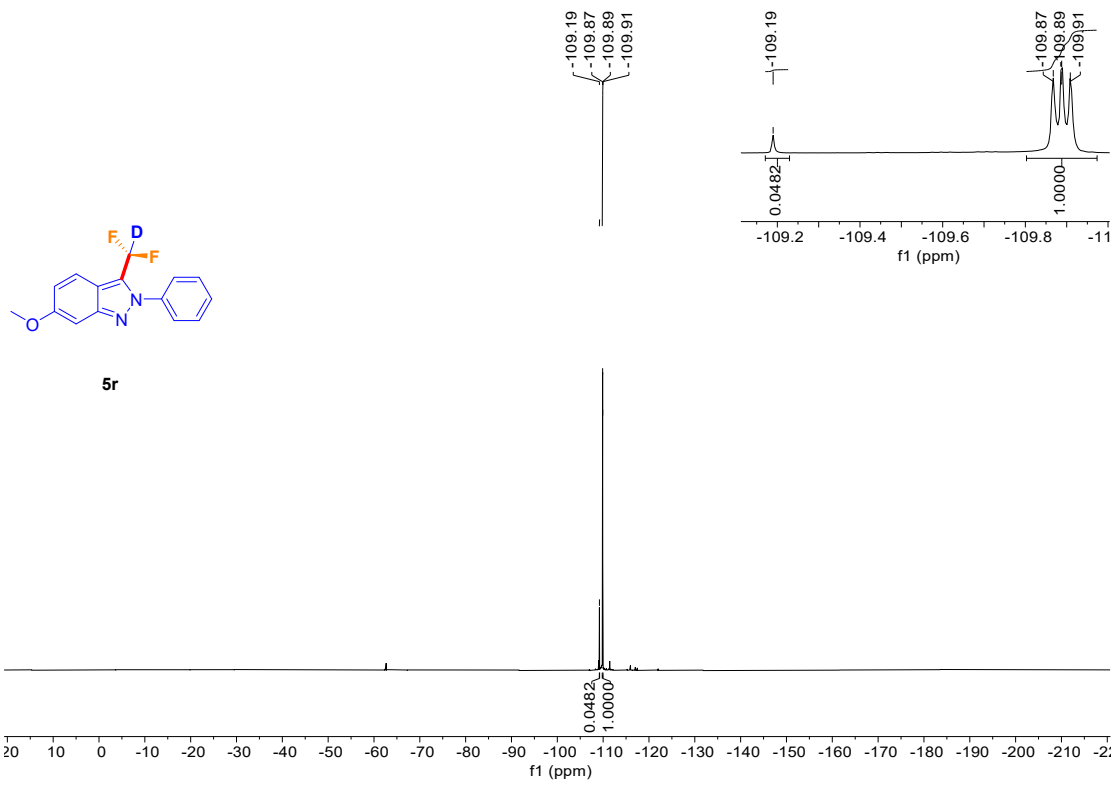


Figure S129 ^{9}F NMR spectrum of **5r** (377 MHz, $CDCl_3$)

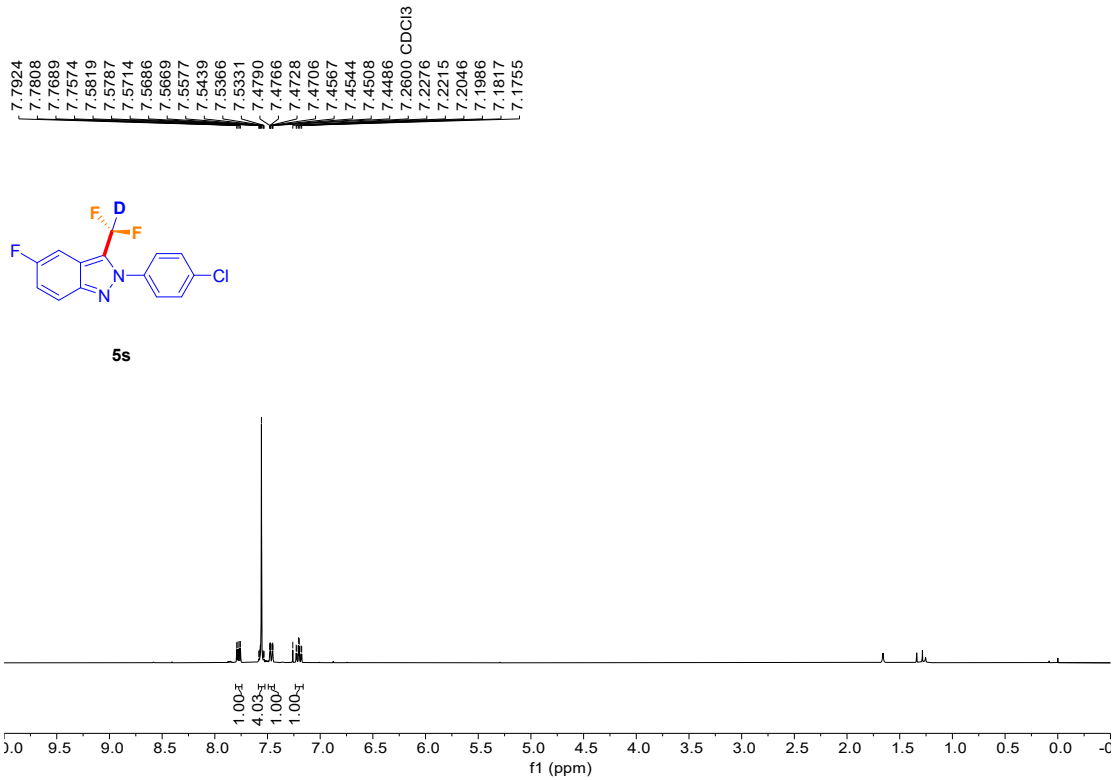


Figure S130 ^{1}H NMR spectrum of **5s** (400 MHz, $CDCl_3$)

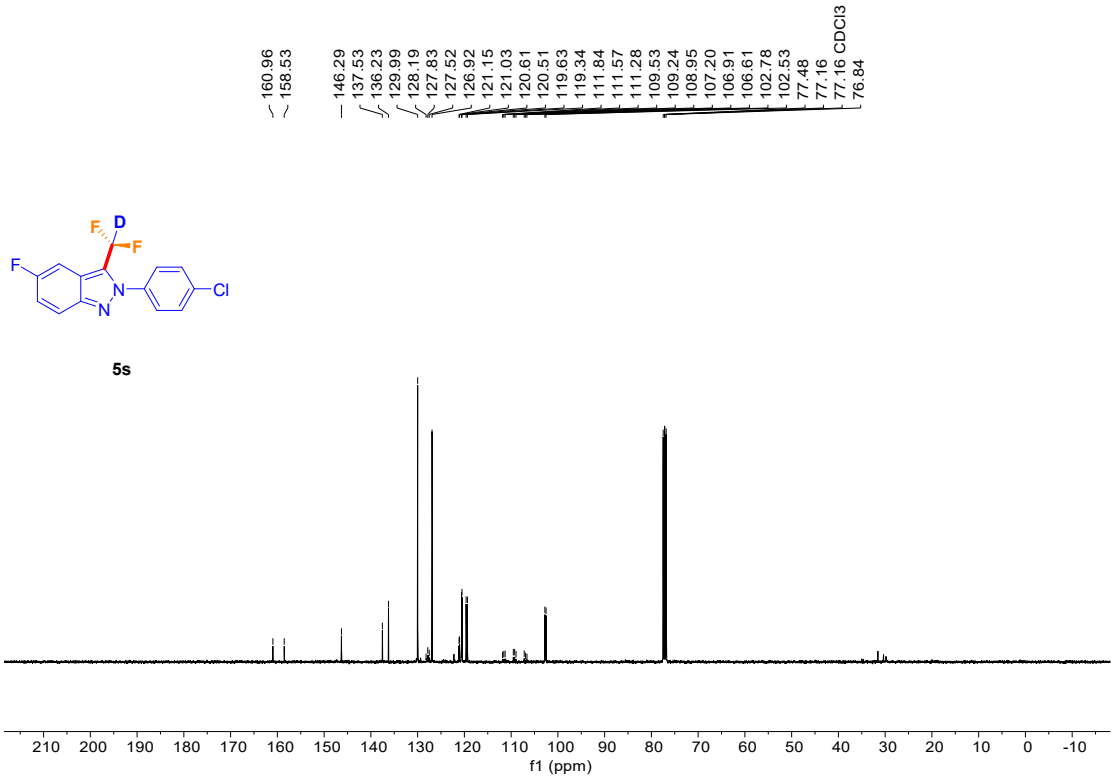


Figure S131 ^{13}C NMR spectrum of **5s** (101 MHz, $CDCl_3$)

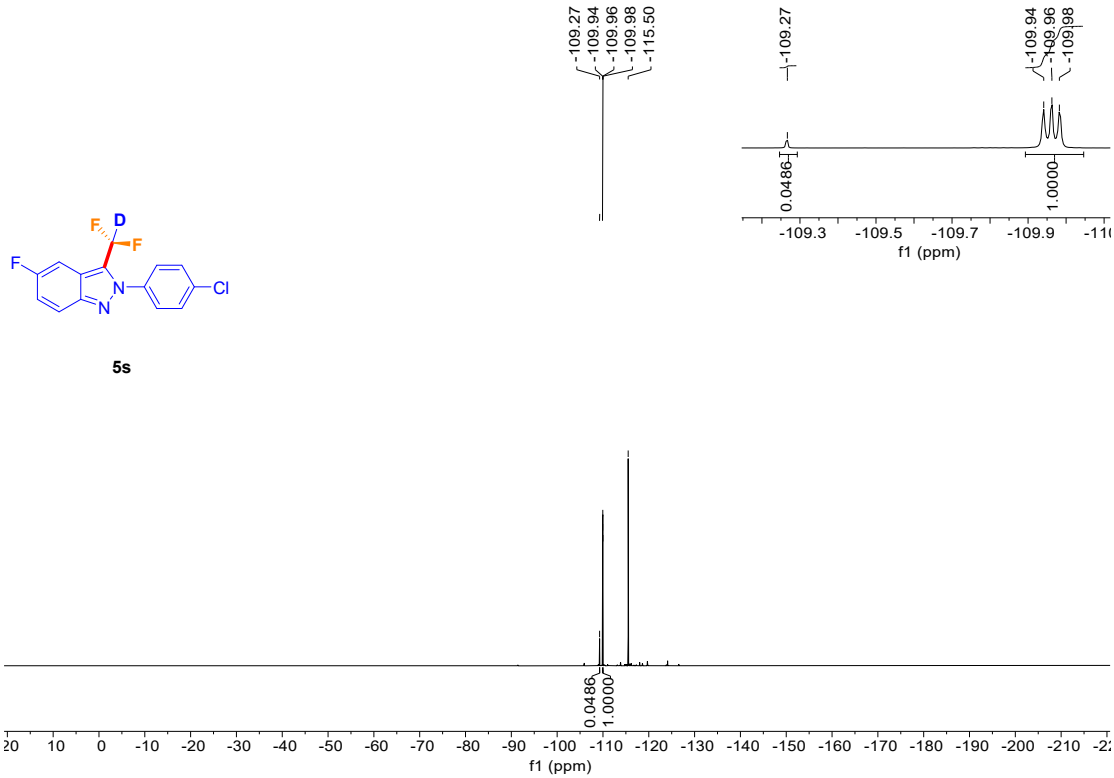


Figure S132 ^{19}F NMR spectrum of **5s** (377 MHz, $CDCl_3$)

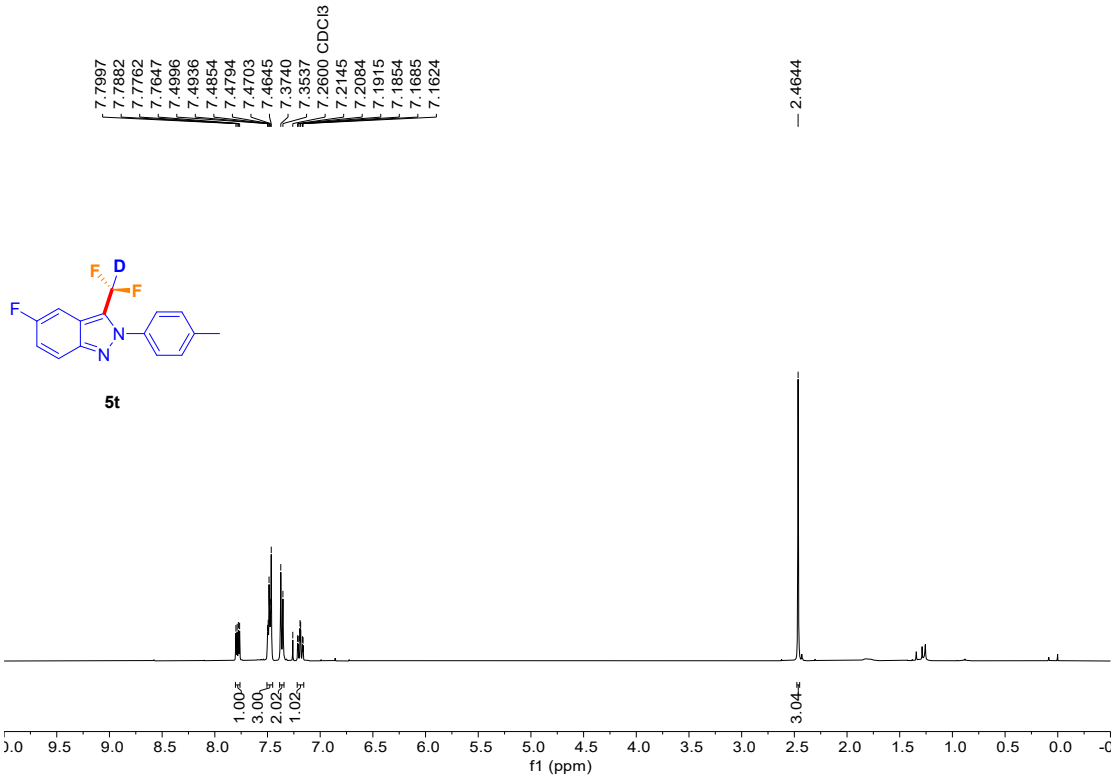


Figure S133 ^{1}H NMR spectrum of **5t** (400 MHz, $CDCl_3$)

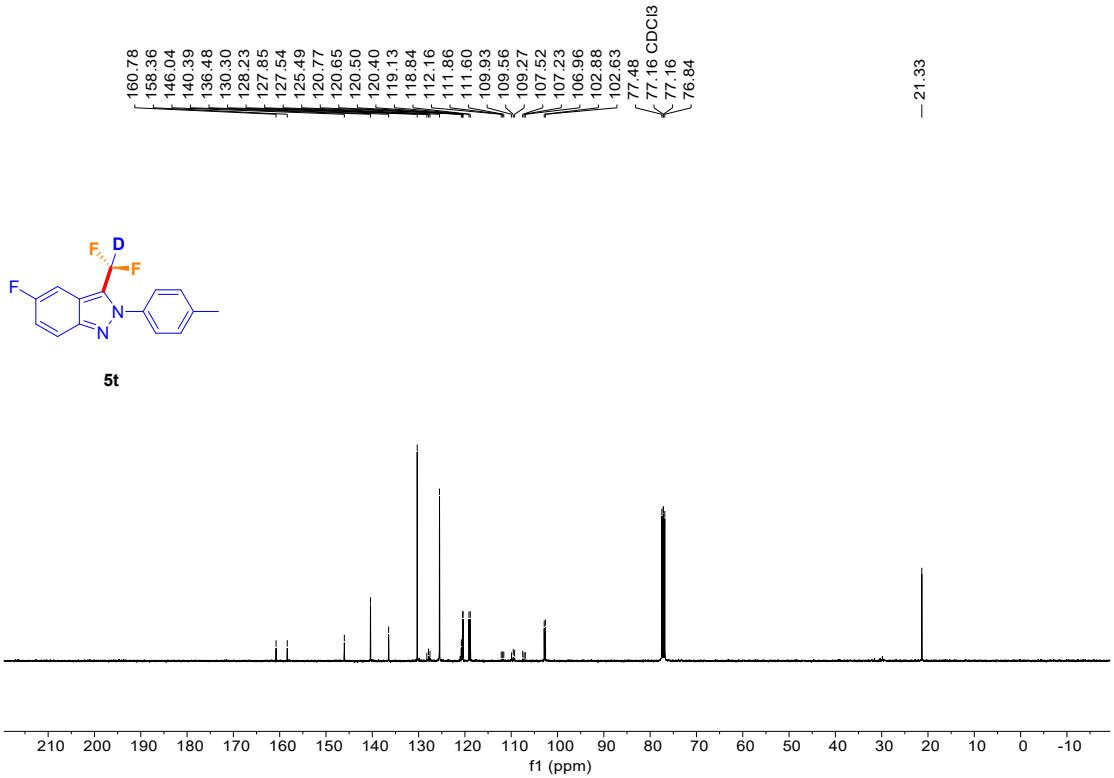


Figure S134 ^{13}C NMR spectrum of **5t** (101 MHz, $CDCl_3$)

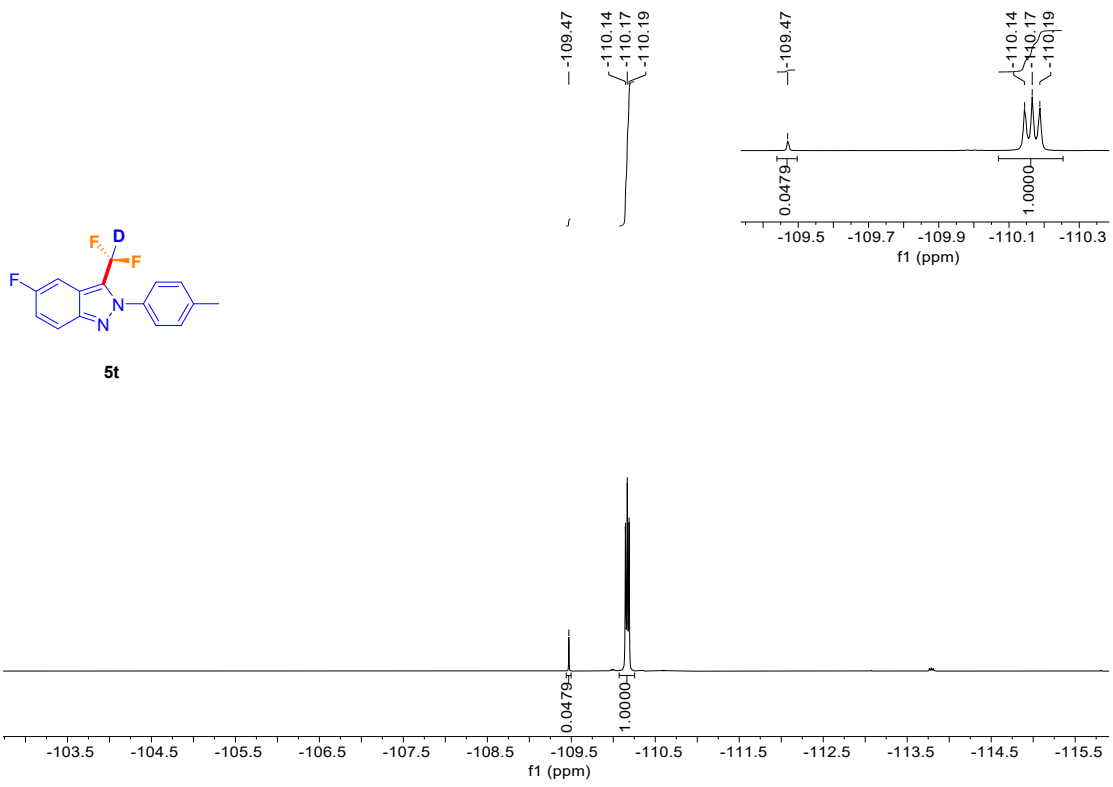


Figure S135 ^{19}F NMR spectrum of **5t** (377 MHz, $CDCl_3$)

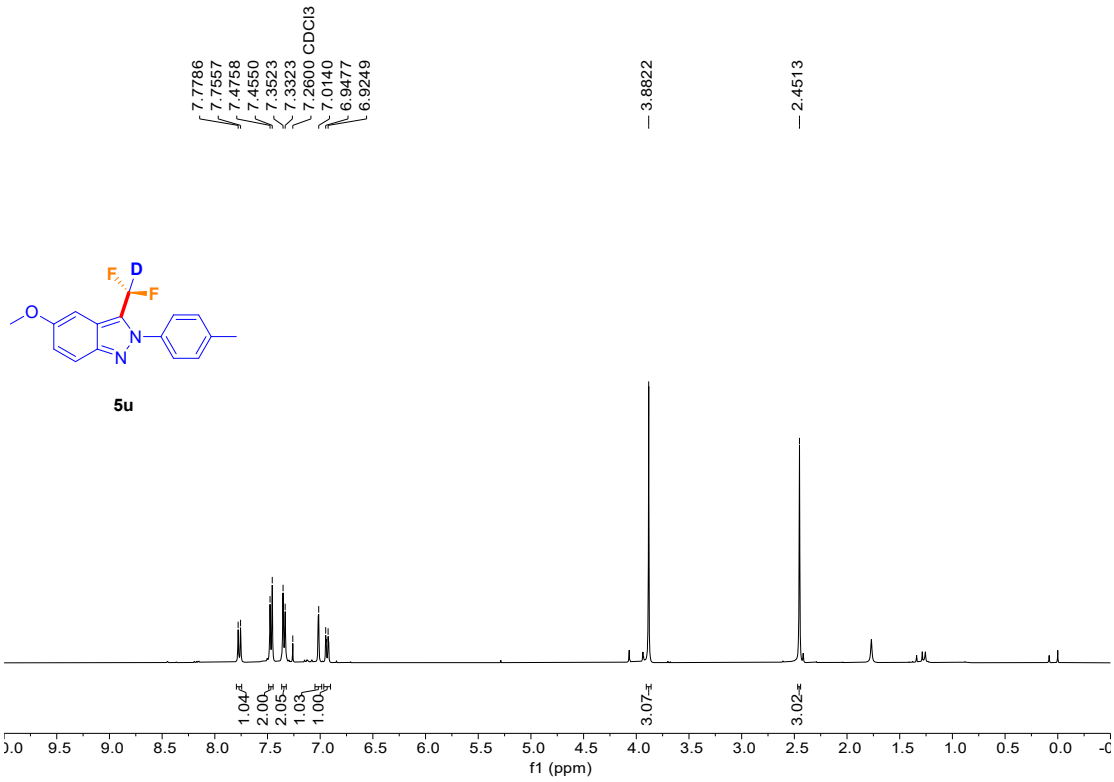


Figure S136 ^{1}H NMR spectrum of **5u** (400 MHz, $CDCl_3$)

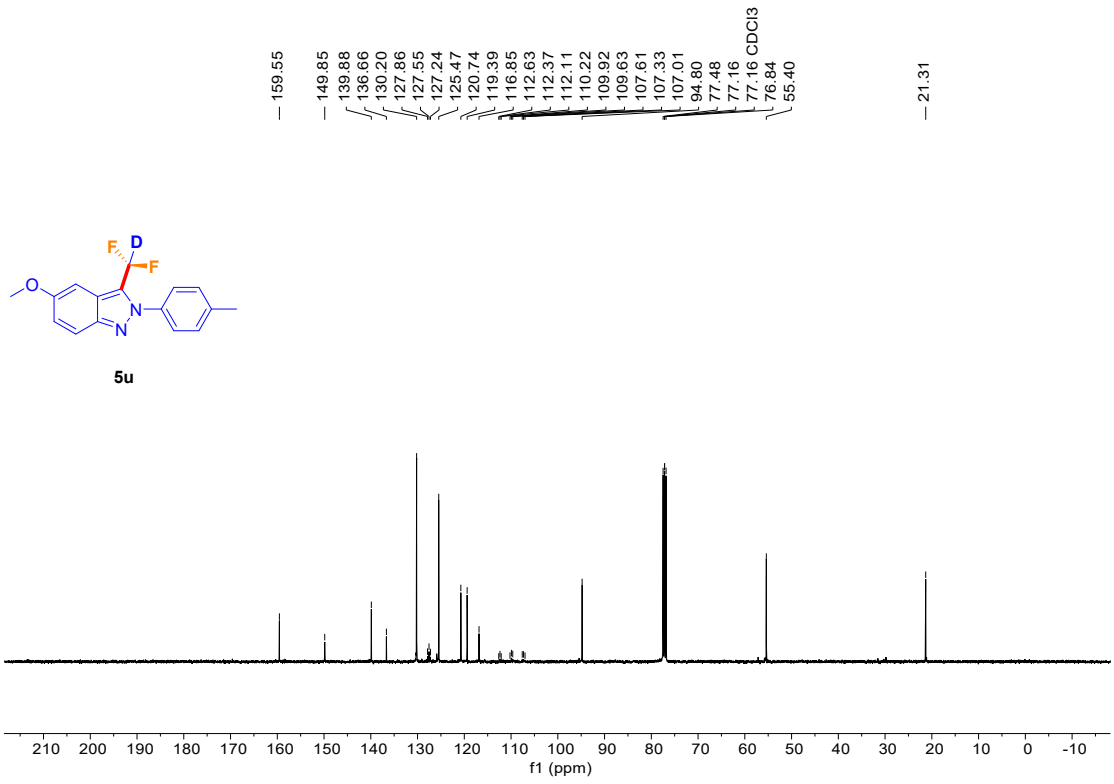


Figure S137 ^{13}C NMR spectrum of **5u** (101 MHz, $CDCl_3$)

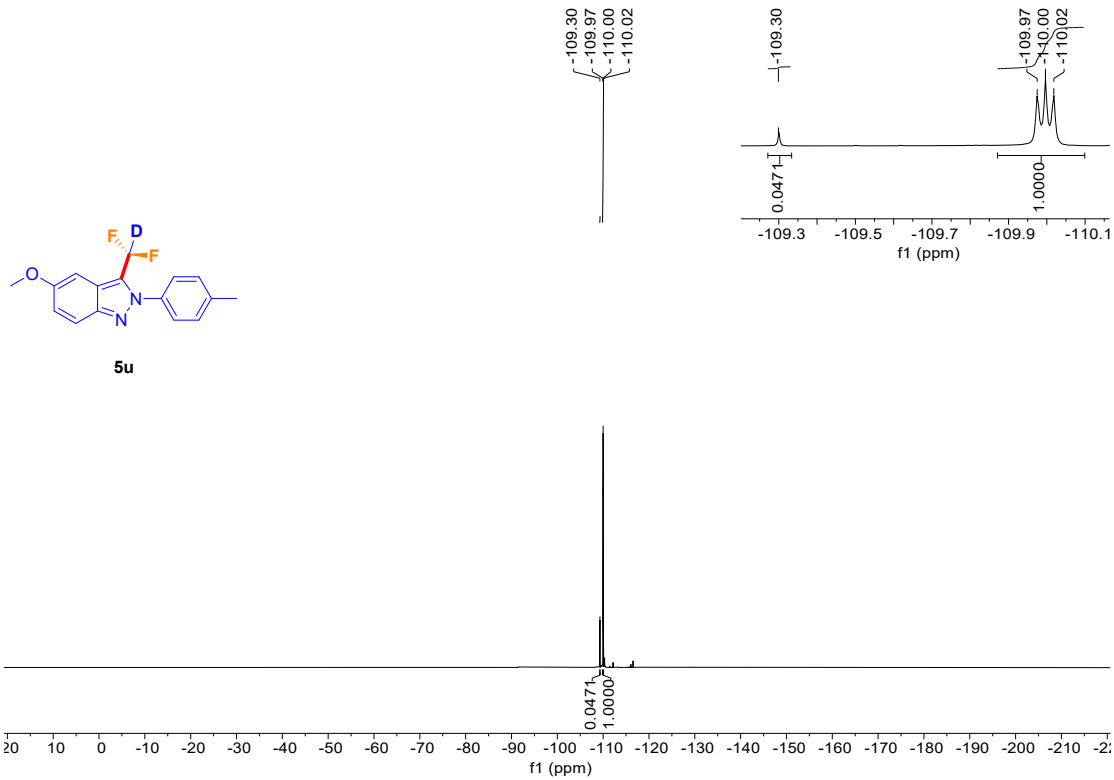


Figure S138 ^{19}F NMR spectrum of **5u** (377 MHz, $CDCl_3$)

14. References

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