

Supporting Information

Ag(I)-catalyzed Decarboxylation of Difluoroacetates with Activated Alkenes to Form Difluorooxindoles

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General Information

^1H -, ^{13}C - and ^{19}F -NMR spectra were recorded in CDCl_3 on a Bruker AV-500 spectrometer. Chemical shifts for ^1H NMR spectra are reported in ppm relative to residual CHCl_3 as internal reference (δ 7.26 ppm for ^1H) downfield from TMS, chemical shifts for ^{13}C NMR spectra are reported in ppm relative to internal CDCl_3 (δ 77.16 ppm for ^{13}C), and chemical shifts for ^{19}F NMR spectra are reported in ppm downfield from internal fluorotrichloromethane (CFCl_3). Coupling constants (J) are given in Hertz (Hz). The terms m, s, d, t, q refer to multiplet, singlet, doublet, triplet, quartlet respectively; br refers to a broad signal. Infrared spectra (IR) were recorded on AVATAR 370 FT-IR spectrometer, absorbance frequencies are given at maximum of intensity in cm^{-1} . Melting points were obtained on a X-4 digital melting point apparatus without correction. High resolution mass spectra (HRMS) and Mass spectra (MS) were recorded using an Electron impact (EI) or Electrospray ionization (ESI) techniques.

Preparation of Substrates:

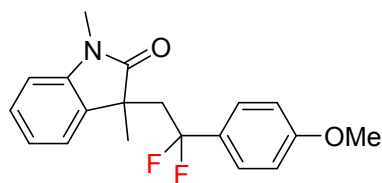
1. General Procedure for Preparation of Substrates

Difluoroacetates were synthesised through the known methods.^[S1, S2] All acrylamides **2** were prepared following the procedure reported.^[S3,S4]

2. General Procedure of Ag(I)-catalyzed Decarboxylation of Difluoroacetates with Activated Alkenes:

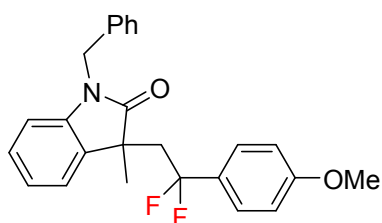
A 10 mL Schlenk tube was charged with Ag_2CO_3 (0.030 mmol), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.60 mmol), potassium 2,2-difluoro-2-phenylacetate **1a** (0.30 mmol), followed by N-methyl-N-phenylmethacrylamide **2a** (0.60 mmol). The tube was sealed with a septum, evacuated and backfilled with N_2 for three times. Anhydrous DMSO (3.0 mL) was added with syringe under N_2 . The mixture was stirred at 80 °C for 12 h. It was quenched by water and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The pure product was obtained by flash column chromatography on silica gel (Petroleum ether/ EtOAc = 10:1) to afford **3aa** in 82% yield.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (3aa):



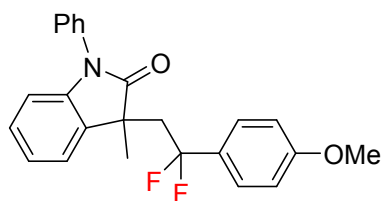
^1H NMR (500 MHz, CDCl_3) δ 7.24 (t, $J = 7.1$ Hz, 1H), 7.20 (d, $J = 7.4$ Hz, 1H), 7.02 (t, $J = 7.5$ Hz, 1H), 6.98 (d, $J = 8.7$ Hz, 2H), 6.74-6.71 (m, 3H), 3.76 (s, 3H), 3.01-2.91 (m, 4H), 2.75-2.66 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -85.03 (ddd, $J = 245.8, 18.8, 8.6$ Hz, 1F), -91.84 (dt, $J = 245.7, 18.0$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.1, 160.4, 142.8, 131.8, 128.2 (t, $J = 26.8$ Hz), 127.8, 126.5 (t, $J = 6.2$ Hz), 123.9, 122.1, 121.6 (t, $J = 246.9$ Hz), 113.1, 107.9, 55.2, 45.7 (t, $J = 29.4$ Hz), 45.1 (d, $J = 4.2$ Hz), 26.2, 26.0. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1714, 1612, 1463, 1251, 1175, 1032, 751$. HRMS (ESI-TOF): calcd. for $\text{C}_{19}\text{H}_{20}\text{F}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 332.1457; found 332.1453.

1-Benzyl-3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-3-methylindolin-2-one (3ab):



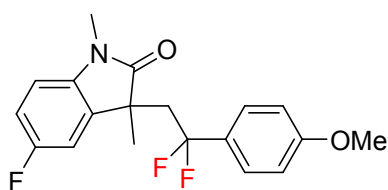
^1H NMR (500 MHz, CDCl_3) δ 7.33-7.24 (m, 5H), 7.20 (d, $J = 7.4$ Hz, 1H), 7.19-7.10 (m, 3H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 8.5$ Hz, 2H), 6.67 (d, $J = 7.8$ Hz, 1H), 4.75 (dd, $J = 110.6, 15.7$ Hz, 2H), 3.79 (s, 3H), 3.11 - 3.01 (m, 1H), 2.81-2.72 (m, 1H), 1.43 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -88.74 (ddd, $J = 245.6, 21.1, 10.8$ Hz, 1F), -90.10 (ddd, $J = 245.4, 20.3, 13.1$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.4, 160.4, 141.9, 135.9, 131.9, 128.8 (t, $J = 26.6$ Hz), 128.6, 127.7, 127.4, 127.1, 126.4 (t, $J = 6.3$ Hz), 123.8, 123.6, 121.7 (t, $J = 244.0$ Hz), 113.3, 109.0, 55.3, 45.7 (t, $J = 28.4$ Hz), 45.2, 43.7, 26.6. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1718, 1610, 1516, 1355, 1253, 1028, 834, 753, 697$. HRMS (ESI-TOF): calcd. for $\text{C}_{25}\text{H}_{24}\text{F}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 408.1770; found 408.17704.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-3-methyl-1-phenylindolin-2-one (3ac):



^1H NMR (500 MHz, CDCl_3) δ 7.49 (t, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 7.1$ Hz, 2H), 7.28 (d, $J = 7.4$ Hz, 1H), 7.19 (td, $J = 7.8, 1.3$ Hz, 1H), 7.15 (d, $J = 8.8$ Hz, 2H), 7.06 (t, $J = 7.0$ Hz, 1H), 6.82 (d, $J = 7.9$ Hz, 1H), 6.78 (d, $J = 8.8$ Hz, 2H), 3.72 (s, 3H), 3.20-3.10 (m, 1H), 2.88-2.79 (m, 1H), 1.50 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -87.54 (ddd, $J = 246.4, 20.5, 10.9$ Hz, 1F), -89.55 (ddd, $J = 246.1, 19.4, 13.9$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 178.4, 160.2, 142.5, 134.2, 131.4, 129.1, 128.4 (t, $J = 26.5$ Hz), 127.5, 127.4, 126.2 (t, $J = 5.9$ Hz), 126.1, 124.0, 122.3, 121.6 (t, $J = 245.0$ Hz), 113.2, 108.9, 54.8, 45.8 (t, $J = 28.2$ Hz), 45.0, 26.5. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1720, 1608, 1506, 1378, 1247, 1023, 748, 701$. HRMS (ESI-TOF): calcd. for $\text{C}_{24}\text{H}_{22}\text{F}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 394.1613; found 394.1611.

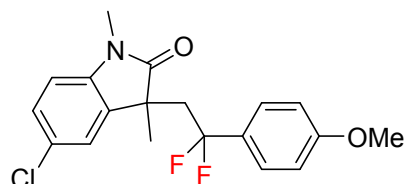
3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-5-fluoro-1,3-dimethylindolin-2-one (3ad):



^1H NMR (500 MHz, CDCl_3) δ 7.03 (d, 2H), 6.97-6.92 (m, 2H), 6.76 (d, $J = 8.8$ Hz, 2H), 6.65 (dd, $J = 8.3, 4.1$ Hz, 1H), 3.78 (s, 3H), 3.01-2.90 (m, 4H), 2.71-2.62 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -86.37 (ddd, $J = 246.1, 19.2, 9.4$ Hz, 1F), -91.54 (ddd, $J = 246.4, 19.4, 15.9$ Hz, 1F), -121.27 (td, $J = 8.6, 4.1$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 178.7, 160.5, 159.0 (d, $J = 239.9$ Hz), 138.8 (d, $J = 1.9$ Hz), 133.5 (d, $J = 8.1$ Hz), 128.1 (t, $J = 26.6$ Hz), 126.5 (t, $J = 6.3$ Hz), 121.5 (t, $J = 244.0$ Hz), 114.1 (d, $J = 23.5$ Hz), 113.2, 112.1 (d, $J = 24.9$ Hz), 108.2 (d, $J = 8.2$ Hz), 55.2, 45.6 (t, $J = 28.9$ Hz), 45.4, 26.2, 26.0. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1706, 1617, 1503,$

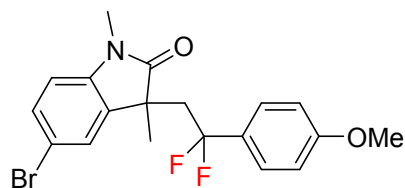
1337, 1255, 1180, 1110, 1034, 822, 735. HRMS (ESI-TOF): calcd. for $C_{19}H_{19}F_3NO_2$ $[M + H]^+$ 350.1362; found 350.1366.

5-Chloro-3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (3ae):



1H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, $J = 8.3, 2.1$ Hz, 1H), 7.07 (d, $J = 1.8$ Hz, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 8.8$ Hz, 2H), 6.66 (d, $J = 8.3$ Hz, 1H), 3.79 (s, 3H), 3.02-2.92 (m, 4H), 2.71-2.62 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -88.25 (ddd, $J = 247.1, 18.2, 11.6$ Hz, 1F), -89.90 (dt, $J = 246.8, 16.3$ Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 160.5, 141.5, 133.5, 128.2 (t, $J = 26.6$ Hz), 127.8, 127.6, 126.4 (t, $J = 6.3$ Hz), 124.5, 121.5 (t, $J = 243.4$ Hz), 113.3, 108.8, 55.3, 45.8 (t, $J = 28.9$ Hz), 45.3, 26.3, 26.1. IR (KBr, cm^{-1}): $\nu_{max} = 1709, 1612, 1488, 1337, 1248, 1034, 824$. HRMS (ESI-TOF): calcd. for $C_{19}H_{19}ClF_2NO_2$ $[M + H]^+$ 366.1067; found 366.1063.

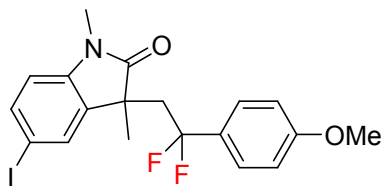
5-Bromo-3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (3af):



1H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.17 (d, $J = 1.9$ Hz, 1H), 7.00 (d, $J = 8.8$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.61 (d, $J = 8.2$ Hz, 1H), 3.79 (s, 3H), 3.02-2.92 (m, 4H), 2.71-2.62 (m, 1H), 1.32 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -88.71 (ddd, $J = 248.3, 16.1, 13.1$ Hz, 1F), -89.31 (dt, $J = 247.4, 16.4$ Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 160.5, 142.0, 133.8, 130.7, 128.2 (t, $J = 26.5$ Hz), 127.2, 126.4 (t, $J = 6.3$ Hz), 121.5 (t, $J = 244.0$ Hz), 114.9, 113.2, 109.3, 55.3, 45.8 (t,

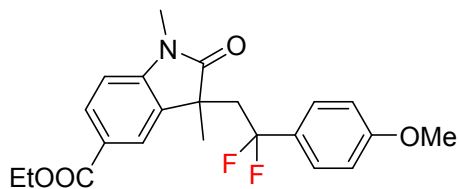
$J = 29.0$ Hz), 45.3 (t, $J = 2.8$ Hz), 26.2, 26.1. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1701, 1611, 1483, 1336, 1247, 1178, 1033, 821$. HRMS (ESI-TOF): calcd. for $\text{C}_{19}\text{H}_{19}\text{BrF}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 410.0562; found 410.0561.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-5-iodo-1,3-dimethylindolin-2-one (3ag):



^1H NMR (500 MHz, CDCl_3) δ 7.52 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.31 (s, 1H), 6.99 (d, $J = 8.7$ Hz, 2H), 6.74 (d, $J = 8.6$ Hz, 2H), 6.52 (d, $J = 8.1$ Hz, 1H), 3.80 (s, 3H), 3.01-2.92 (m, 4H), 2.70-2.61 (m, 1H), 1.32 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -88.15 (dt, $J = 247.5, 15.6$ Hz, 1F), -89.66 (ddd, $J = 247.7, 16.8, 13.2$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 178.4, 160.5, 142.6, 136.6, 134.1, 132.8, 128.2 (t, $J = 26.6$ Hz), 126.4 (t, $J = 6.4$ Hz), 121.4 (t, $J = 243.9$ Hz), 113.3, 109.9, 84.8, 55.3, 45.8 (t, $J = 29.1$ Hz), 45.1 (t, $J = 3.0$ Hz), 26.2, 26.1. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1713, 1602, 1482, 1250, 1173, 1010, 818, 607$. HRMS (ESI-TOF): calcd. for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{INO}_2$ $[\text{M} + \text{H}]^+$ 458.0423; found 458.0427.

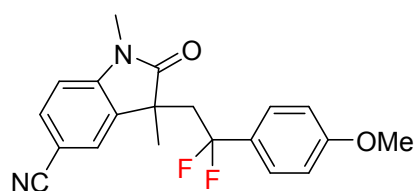
Ethyl 3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3ah):



^1H NMR (500 MHz, CDCl_3) δ 7.94 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.70 (s, 1H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.72 (d, $J = 8.2$ Hz, 1H), 6.66 (d, $J = 8.6$ Hz, 2H), 4.31 (q, $J = 7.1$ Hz, 2H), 3.69 (s, 3H), 3.00-2.91 (m, 4H), 2.71 (q, $J = 14.8$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.31 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -88.53 (t, $J = 15.7$ Hz), -89.06 (td, $J = 15.2, 8.0$ Hz), -89.59 (t, $J = 15.4$ Hz). ^{13}C NMR (126 MHz, CDCl_3) δ 179.2, 166.0,

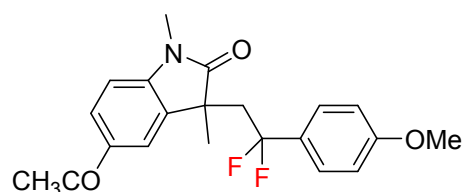
160.2, 146.7, 131.3, 130.2, 127.9 (t, $J = 26.5$ Hz), 126.1 (t, $J = 6.2$ Hz), 124.9, 124.2, 121.3 (t, $J = 243.9$ Hz), 113.0, 107.2, 60.5, 54.9, 45.6 (t, $J = 28.9$ Hz), 44.6, 26.1, 25.8, 14.1. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1730, 1703, 1616, 1499, 1465, 1286, 1248, 1108, 1034, 822, 775$. HRMS (ESI-TOF): calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_2\text{NO}_4$ $[\text{M} + \text{H}]^+$ 404.1668; found 404.1671.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3ai):



^1H NMR (500 MHz, CDCl_3) δ 7.53 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.33 (s, 1H), 6.98 (d, $J = 8.7$ Hz, 2H), 6.80 (d, $J = 8.2$ Hz, 1H), 6.73 (d, $J = 8.6$ Hz, 2H), 3.77 (s, 3H), 3.04 (s, 3H), 3.01-2.91 (m, 1H), 2.74-2.65 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -88.90 (ddd, $J = 247.2, 18.5, 12.2$ Hz, 1F), -89.82 (ddd, $J = 247.2, 17.9, 14.5$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 178.8, 160.5, 146.6, 133.0, 132.7, 127.9 (t, $J = 26.5$ Hz), 127.2, 126.2 (t, $J = 6.3$ Hz), 121.3 (t, $J = 244.0$ Hz), 119.1, 113.3, 108.3, 105.2, 55.2, 45.6 (t, $J = 28.8$ Hz), 44.8 (t, $J = 2.5$ Hz), 26.3, 25.7. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1714, 1613, 1506, 1337, 1251, 1175, 1032, 830$. HRMS (ESI-TOF): calcd. for $\text{C}_{20}\text{H}_{19}\text{F}_2\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 357.1409; found 357.1411.

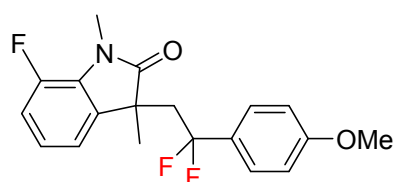
5-Acetyl-3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (3aj):



^1H NMR (500 MHz, CDCl_3) δ 7.83 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.63 (s, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.74 (d, $J = 8.1$ Hz, 1H), 6.65 (d, $J = 8.8$ Hz, 2H), 3.69 (s, 3H), 3.01-2.91 (m, 4H), 2.75-2.67 (m, 1H), 2.48 (s, 3H), 1.30 (s, 3H). ^{19}F NMR (471 MHz,

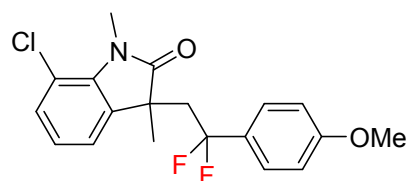
CDCl₃) δ ppm -88.52 (dq, J = 247.3, 15.9 Hz, 1F), -89.95 (ddd, J = 247.2, 17.6, 13.0 Hz, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 196.5, 179.3, 160.2, 147.0, 131.6, 131.5, 129.6, 128.0 (t, J = 26.6 Hz), 126.1 (t, J = 6.3 Hz), 123.6, 121.3 (t, J = 243.1 Hz), 113.0, 107.2, 55.0, 45.6 (t, J = 28.9 Hz), 44.6 (t, J = 2.9 Hz), 26.1, 26.0, 25.8. IR (KBr, cm⁻¹): ν_{max} = 1717, 1672, 1608, 1517, 1251, 1177, 1035, 831, 736. HRMS (ESI-TOF): calcd. for C₂₁H₂₂F₂NO₃ [M + H]⁺ 374.1562; found 374.1563.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-7-fluoro-1,3-dimethylindolin-2-one (3ak):



¹H NMR (500 MHz, CDCl₃) δ 7.01-6.94 (m, 5H), 6.77 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 3.16 (d, J = 2.8 Hz, 3H), 3.02-2.92 (m, 1H), 2.73-2.64 (m, 1H), 1.33 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -85.12 (ddd, J = 246.1, 19.1, 8.5 Hz, 1F), -91.89 (dt, J = 246.1, 17.9 Hz, 1F), -137.06 – -137.15 (m, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 178.7, 160.5, 147.6 (d, J = 242.9 Hz), 134.7 (d, J = 3.0 Hz), 129.6 (d, J = 8.2 Hz), 128.0 (t, J = 26.5 Hz), 126.6 (t, J = 6.3 Hz), 122.6 (d, J = 6.3 Hz), 121.5 (t, J = 244.6 Hz), 119.8, 115.7 (d, J = 19.1 Hz), 113.2, 55.3, 46.0 (t, J = 28.5 Hz), 45.4, 28.5 (d, J = 5.9 Hz), 26.4. IR (KBr, cm⁻¹): ν_{max} = 1720, 1615, 1517, 1483, 1256, 1178, 1034, 834, 733. HRMS (ESI-TOF): calcd. for C₁₉H₁₉F₃NO₂ [M + H]⁺ 350.1362; found 350.1366.

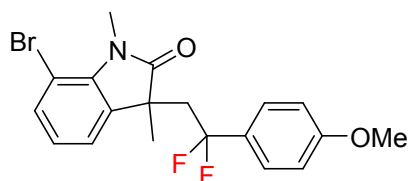
7-Chloro-3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (3al):



¹H NMR (500 MHz, CDCl₃) δ 7.12 (d, J = 8.1 Hz, 1H), 7.04 (d, J = 7.3 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.88 (t, J = 7.8 Hz, 1H), 6.73 (d, J = 8.7 Hz, 2H), 3.74 (s, 3H),

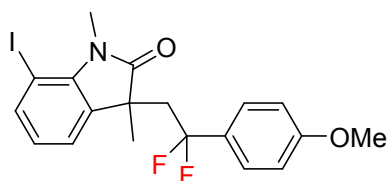
3.25 (s, 3H), 3.00-2.90 (m, 1H), 2.70-2.62 (m, 1H), 1.27 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -84.09 (ddd, $J = 246.3, 18.1, 8.4$ Hz, 1F), -91.38 (dq, $J = 246.6, 16.6, 15.2$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.1, 160.4, 138.7, 134.3, 129.9, 127.4 (t, $J = 26.4$ Hz), 126.5 (t, $J = 6.2$ Hz), 122.7, 122.4, 121.3 (t, $J = 245.0$ Hz), 115.0, 112.9, 55.0, 45.8 (t, $J = 29.2$ Hz), 44.6 (d, $J = 4.6$ Hz), 29.2, 26.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1719, 1609, 1517, 1465, 1255, 1178, 1033, 835, 737$. HRMS (ESI-TOF): calcd. for $\text{C}_{19}\text{H}_{19}\text{ClF}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 366.1067; found 366.1069.

7-Bromo-3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethylindolin-2-one (3am):



^1H NMR (500 MHz, CDCl_3) δ 7.32 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.09 (d, $J = 7.4$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.83 (dd, $J = 8.2, 7.3$ Hz, 1H), 6.74 (d, $J = 8.8$ Hz, 2H), 3.75 (s, 3H), 3.26 (s, 3H), 3.02-2.91 (m, 1H), 2.71-2.62 (m, 1H), 1.28 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -83.63 (ddd, $J = 246.3, 17.8, 8.3$ Hz, 1F), -91.33 (dt, $J = 246.3, 18.3$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.2, 160.4, 140.1, 134.6, 133.3, 127.3 (t, $J = 26.6$ Hz), 126.5 (t, $J = 6.3$ Hz), 123.1, 122.9, 121.3 (t, $J = 243.6$ Hz), 112.9, 102.0, 55.1, 45.8 (t, $J = 28.0, 28.1$ Hz), 44.6 (d, $J = 4.7$ Hz), 29.5, 26.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1720, 1612, 1516, 1461, 1250, 1175, 836, 780, 742$. HRMS (ESI-TOF): calcd. for $\text{C}_{19}\text{H}_{19}\text{BrF}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 410.0562; found 410.0563.

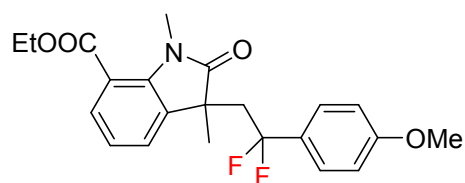
3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-7-iodo-1,3-dimethylindolin-2-one (3an):



^1H NMR (500 MHz, CDCl_3) δ 7.64 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.15 (d, $J = 7.4$ Hz, 1H),

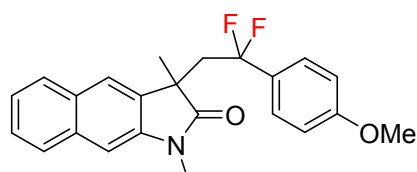
6.93 (d, $J = 8.8$ Hz, 2H), 6.77 (d, $J = 8.7$ Hz, 2H), 6.72 (t, $J = 7.5$ Hz, 1H), 3.80 (s, 3H), 3.27 (s, 3H), 3.04-2.94 (m, 1H), 2.77-2.65 (m, 1H), 1.30 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -83.00 (ddd, $J = 246.3, 17.2, 8.0$ Hz, 1F), -91.33 (dt, $J = 245.9, 18.4$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.6, 160.4, 143.0, 140.3, 134.5, 129.1, 127.3 (t, $J = 26.6$ Hz), 126.6 (t, $J = 6.3$ Hz), 123.7 (d, $J = 3.1$ Hz), 121.3 (t, $J = 245.0$ Hz), 113.0, 71.3, 55.2, 45.7 (t, $J = 28.4$ Hz), 44.4 (d, $J = 5.1$ Hz), 29.9, 26.4. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1715, 1613, 1454, 1255, 1061, 834, 738$. HRMS (ESI-TOF): calcd. for $\text{C}_{19}\text{H}_{19}\text{F}_2\text{INO}_2$ $[\text{M} + \text{H}]^+$ 458.0423; found 458.0425.

Ethyl 3-(2,2-difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethyl-2-oxoindoline-7-carboxylate (3ao):



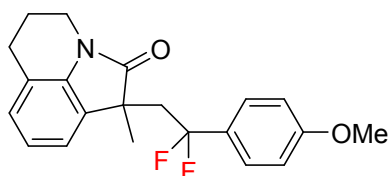
^1H NMR (500 MHz, CDCl_3) δ 7.47 (d, $J = 7.9$ Hz, 1H), 7.26 (d, $J = 7.2$ Hz, 1H), 6.99 (t, $J = 7.7$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.71 (d, $J = 8.3$ Hz, 2H), 4.35 (q, $J = 7.1$ Hz, 1H), 3.73 (s, 3H), 3.01-2.91 (m, 4H), 2.74-2.66 (m, 1H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.30 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -84.27 (ddd, $J = 246.6, 17.8, 8.8$ Hz, 1F), -91.29 (dt, $J = 246.6, 18.1$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.7, 166.6, 160.2, 141.3, 133.2, 128.7, 127.6 (t, $J = 26.7$ Hz), 126.4 (t, $J = 5.9$ Hz), 121.4 (t, $J = 244.6$ Hz), 121.2, 115.8, 113.0, 61.2, 55.0, 45.7 (t, $J = 29.0$ Hz), 43.7 (d, $J = 4.5$ Hz), 29.6, 26.2, 14.0. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1724, 1605, 1515, 1465, 1248, 836, 755$. HRMS (ESI-TOF): calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_2\text{NO}_4$ $[\text{M} + \text{H}]^+$ 404.1668; found 404.1665.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethyl-1H-benzo[f]indol-2(3H)-one (3ap):



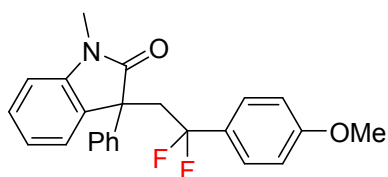
^1H NMR (500 MHz, CDCl_3) δ 7.69 (d, $J = 8.1$ Hz, 1H), 7.49 (dt, $J = 7.9, 3.6$ Hz, 2H), 7.42-7.38 (m, 2H), 6.90 (d, $J = 8.6$ Hz, 2H), 6.82 (d, $J = 7.8$ Hz, 1H), 6.59 (d, $J = 8.6$ Hz, 2H), 3.73 (s, 3H), 3.60-3.49 (m, 1H), 3.30 (s, 3H), 2.89-2.80 (m, 1H), 1.70 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -86.58 (ddd, $J = 247.0, 18.5, 10.2$ Hz, 1F), -88.66 (dt, $J = 247.1, 16.3$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 172.0, 160.1, 136.5, 135.9, 133.2, 128.6 (t, $J = 26.7$ Hz), 126.5 (t, $J = 6.3$ Hz), 126.1, 126.0, 124.0, 122.4, 122.1 (t, $J = 244.4$ Hz), 119.3, 112.9, 108.1, 55.2, 51.1 (t, $J = 27.4$ Hz), 44.1, 33.9, 29.6. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1662, 1614, 1516, 1253, 1178, 1027, 822, 770$. HRMS (ESI-TOF): calcd. for $\text{C}_{23}\text{H}_{22}\text{F}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 382.1613; found 382.1614.

2-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-1,2,6,7-tetrahydropyrido[3,2,1-ij]quinolin-3(5H)-one (3aq):



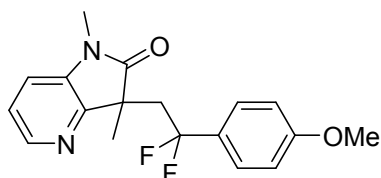
^1H NMR (500 MHz, CDCl_3) δ 7.07 (d, $J = 7.3$ Hz, 1H), 7.00 (t, $J = 6.5$ Hz, 3H), 6.92 (t, $J = 7.5$ Hz, 1H), 6.75 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 3.60-3.55 (m, 1H), 3.30-3.25 (m, 1H), 3.02-2.91 (m, 1H), 2.75-2.66 (m, 3H), 1.90-1.85 (m, 2H), 1.35 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -83.82 (ddd, $J = 245.7, 19.0, 8.2$ Hz, 1F), -92.26 (dt, $J = 245.6, 18.6$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 178.1, 160.4, 138.6, 130.5, 128.3 (t, $J = 26.4$ Hz), 126.7 (dd, $J = 7.2, 5.6$ Hz), 126.5, 121.9 (d, $J = 3.2$ Hz), 121.8 (dd, $J = 244.8, 242.1$ Hz), 121.6, 119.8, 113.1, 55.3, 46.4 (d, $J = 4.8$ Hz), 45.5 (dd, $J = 29.9, 27.8$ Hz), 38.7, 26.1, 24.5, 20.9. HRMS (ESI-TOF): calcd. for $\text{C}_{21}\text{H}_{22}\text{F}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 358.1613; found 358.16137.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-1-methyl-3-phenylindolin-2-one (3ar):



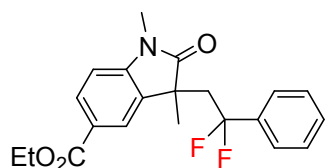
^1H NMR (500 MHz, CDCl_3) δ 7.39-7.35 (m, 4H), 7.31-7.24 (m, 3H), 7.16-7.13 (m, 1H), 7.07 (d, $J = 8.8$ Hz, 2H), 6.81 (t, $J = 8.7$ Hz, 3H), 3.82 (s, 3H), 3.64-3.52 (m, 1H), 3.19-3.10 (m, 1H), 2.97 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -83.74 (ddd, $J = 246.0$, 18.9, 8.5 Hz, F), -91.13 (dt, $J = 246.0$, 17.7 Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 177.2, 160.4, 143.9, 140.2, 129.5, 128.6, 128.4, 128.3 (t, $J = 26.8$ Hz), 127.5, 126.7 (t, $J = 6.6$ Hz), 126.4, 122.1, 121.6 (t, $J = 245.3$ Hz), 113.1, 108.2, 55.3, 52.8 (d, $J = 4.2$ Hz), 46.0 (dd, $J = 30.1$, 27.6 Hz), 26.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1717$, 1612, 1495, 1253, 1025, 835, 754. HRMS (ESI-TOF): calcd. for $\text{C}_{24}\text{H}_{22}\text{F}_2\text{NO}_2$ $[\text{M} + \text{H}]^+$ 394.1613; found 394.1610.

3-(2,2-Difluoro-2-(4-methoxyphenyl)ethyl)-1,3-dimethyl-1H-pyrrolo[3,2-b]pyridin 2(3H)-one (3as):



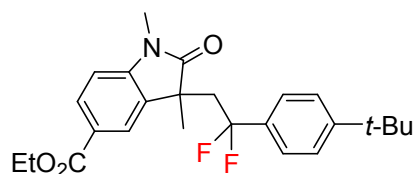
^1H NMR (500 MHz, CDCl_3) δ 8.17 (dd, $J = 5.2$, 1.6 Hz, 1H), 7.44 (d, $J = 7.3$, 1.6 Hz, 1H), 6.98 (d, $J = 8.6$ Hz, 2H), 6.92 (dd, $J = 7.3$, 5.2 Hz, 1H), 6.77 (d, $J = 8.7$ Hz, 2H), 3.77 (s, 3H), 3.04-2.94 (m, 4H), 2.75-2.67 (m, 1H), 1.36 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -84.87 (ddd, $J = 246.6$, 18.5, 8.7 Hz, 1F), -92.14 (dt, $J = 246.6$, 17.9 Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 178.8, 160.6, 156.2, 146.8, 131.4, 127.9 (t, $J = 26.5$ Hz), 126.5 (t, $J = 6.4$ Hz), 126.3, 121.6 (t, $J = 244.3$ Hz), 117.9, 113.4, 55.3, 45.4 (t, $J = 28.6$ Hz), 44.8 (d, $J = 4.3$ Hz), 25.6, 25.3. HRMS (ESI-TOF): calcd. for $\text{C}_{18}\text{H}_{19}\text{F}_2\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 333.1409; found 333.1406.

Ethyl 3-(2,2-difluoro-2-phenylethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3bh):



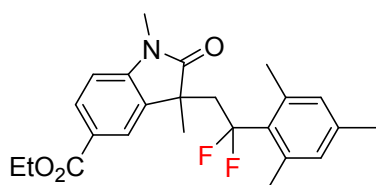
^1H NMR (500 MHz, CDCl_3) δ 7.97 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.78 (s, 1H), 7.27-7.24 (m, 1H), 7.20 (t, $J = 7.3$ Hz, 2H), 7.05 (d, $J = 7.7$ Hz, 2H), 6.75 (d, $J = 8.2$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.03-2.93 (m, 4H), 2.80-2.71 (m, 1H), 1.38 (t, $J = 7.1$ Hz, 3H), 1.34 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -89.71 (ddd, $J = 247.8, 18.8, 11.3$ Hz, 1F), -91.74 (ddd, $J = 247.8, 18.2, 15.0$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.3, 166.2, 146.9, 135.9 (t, $J = 26.1$ Hz), 131.5, 130.5, 129.5, 127.9, 125.0, 124.8 (t, $J = 6.3$ Hz), 124.4, 121.2 (t, $J = 244.0$ Hz), 107.4, 60.7, 45.6 (t, $J = 28.0$ Hz), 44.7, 26.2, 26.0, 14.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1713, 1611, 1498, 1454, 1234, 1112, 770, 694$. HRMS (ESI-TOF): calcd. for $\text{C}_{21}\text{H}_{22}\text{F}_2\text{NO}_3$ $[\text{M} + \text{H}]^+$ 374.1562; found 374.1558.

Ethyl 3-(2-(4-(tert-butyl)phenyl)-2,2-difluoroethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3ch):



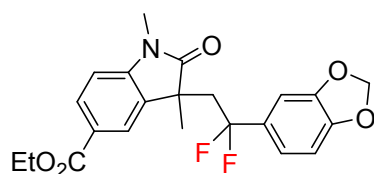
^1H NMR (500 MHz, CDCl_3) δ 7.94 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.79 (s, 1H), 7.18 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.71 (d, $J = 8.2$ Hz, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 3.02-2.92 (m, 4H), 2.78-2.70 (m, 1H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.31 (s, 3H), 1.21 (s, 9H). ^{19}F NMR (471 MHz, CDCl_3) δ -88.83 (ddd, $J = 247.9, 18.1, 11.9$ Hz, 1F), -90.40 (dt, $J = 247.9, 16.4$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.1, 166.1, 152.5, 146.8, 132.8 (t, $J = 26.1$ Hz), 131.5, 130.3, 125.0, 124.6, 124.5 (t, $J = 6.2$ Hz), 124.2, 121.3 (t, $J = 245.6$ Hz), 107.2, 60.6, 45.5 (t, $J = 28.4$ Hz), 44.6 (d, $J = 2.5$ Hz), 34.4, 30.9, 26.1, 25.9, 14.2. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1726, 1613, 1460, 1233, 1103, 1032, 835, 767$. HRMS (ESI-TOF): calcd. for $\text{C}_{25}\text{H}_{30}\text{F}_2\text{NO}_3$ $[\text{M} + \text{H}]^+$ 430.2188; found 430.2189.

Ethyl 3-(2,2-difluoro-2-mesitylethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3dh):



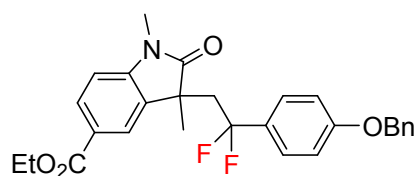
^1H NMR (500 MHz, CDCl_3) δ 8.04 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.98 (d, $J = 1.7$ Hz, 1H), 6.88 (d, $J = 8.2$ Hz, 1H), 6.77 (s, 2H), 4.38 (q, $J = 7.2$ Hz, 1H), 3.24 (s, 3H), 2.96-2.86 (m, 1H), 2.77-2.67 (m, 1H), 2.27 (t, $J = 4.4$ Hz, 6H), 2.21 (s, 3H), 1.41 (t, $J = 7.0$ Hz, 3H), 1.40 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -84.40 (dd, $J = 251.8, 31.3$ Hz, 1F), -88.06 (dd, $J = 255.6, 25.3$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.7, 166.4, 147.0, 138.7, 136.0 (t, $J = 3.0$ Hz), 132.5, 130.9, 130.5 (t, $J = 23.5$ Hz), 130.4, 124.8, 124.5, 124.3 (t, $J = 247.2$ Hz), 107.6, 60.7, 44.8 (t, $J = 25.7$ Hz), 26.4, 25.8, 21.8 (t, $J = 6.5$ Hz), 20.5, 14.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1712, 1613, 1457, 1247, 1173, 1106, 929, 762$. HRMS (ESI-TOF): calcd. for $\text{C}_{24}\text{H}_{28}\text{F}_2\text{NO}_3$ $[\text{M} + \text{H}]^+$ 416.2032; found 416.2035.

Ethyl 3-(2-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoroethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3eh):



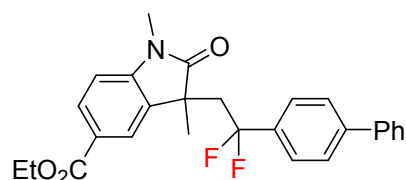
^1H NMR (500 MHz, CDCl_3) δ 7.99 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.70 (s, 1H), 6.81 (d, $J = 8.2$ Hz, 1H), 6.64- 6.58 (m, 2H), 6.48 (s, 1H), 5.92 (d, $J = 3.8$ Hz, 2H), 4.36 (q, $J = 7.1$ Hz, 2H), 3.13 (s, 3H), 3.02-2.93 (m, 1H), 2.76-2.67 (m, 1H), 1.40 (t, $J = 7.1$ Hz, 3H), 1.36 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -87.63 (dt, $J = 246.6, 14.8$ Hz, 1F), -91.45 (dt, $J = 246.6, 16.1$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.4, 166.2, 148.5, 147.3, 146.9, 131.5, 130.5, 130.1 (t, $J = 26.7$ Hz), 124.9, 124.4, 121.1 (t, $J = 244.9$ Hz), 118.9 (t, $J = 6.9$ Hz), 107.6, 107.4, 105.5 (t, $J = 6.6$ Hz), 101.3, 60.8, 46.0 (t, $J = 28.7$ Hz), 44.8, 26.3, 25.9, 14.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1715, 1614, 1502, 1449, 1363, 1249, 1106, 1034, 875, 768$. HRMS (ESI-TOF): calcd. for $\text{C}_{22}\text{H}_{22}\text{F}_2\text{NO}_5$ $[\text{M} + \text{H}]^+$ 418.1461; found 418.1463.

Ethyl 3-(2-(4-(benzyloxy)phenyl)-2,2-difluoroethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3fh):



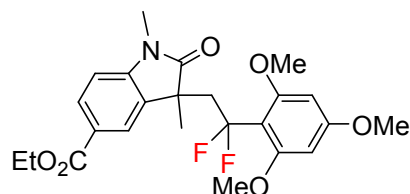
^1H NMR (500 MHz, CDCl_3) δ 7.99 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.79 (d, $J = 1.5$ Hz, 1H), 7.42-7.36 (m, 4H), 7.34 -7.31 (m, 1H), 6.96 (d, $J = 8.9$ Hz, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 6.71 (d, $J = 8.2$ Hz, 1H), 5.01 (q, $J = 2.8$ Hz, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 3.05-2.95 (m, 4H), 2.80-2.71 (m, 1H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.35 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -87.87 (ddd, $J = 247.2, 17.7, 11.4$ Hz, 1F), -89.80 (dt, $J = 247.1, 16.5$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.3, 166.2, 159.4, 146.8, 136.4, 131.4, 130.4, 128.4, 128.2 (t, $J = 26.7$ Hz), 127.9, 126.3 (t, $J = 6.3$ Hz), 125.0, 124.3, 121.3 (t, $J = 244.0$ Hz), 114.0, 107.3, 69.7, 60.7, 45.6 (t, $J = 28.8$ Hz), 44.7, 26.1, 25.9, 14.2. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1713, 1613, 1506, 1457, 1237, 1104, 1030, 833, 763, 742$. HRMS (ESI-TOF): calcd. for $\text{C}_{28}\text{H}_{28}\text{F}_2\text{NO}_4$ $[\text{M} + \text{H}]^+$ 480.1981; found 480.1979.

Ethyl 3-(2-([1,1'-biphenyl]-4-yl)-2,2-difluoroethyl)-1,3-dimethyl-2-oxoindoline- 5-carboxylate (3gh):



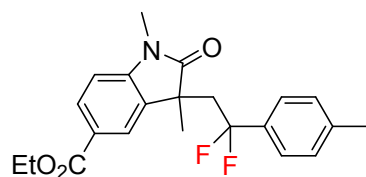
^1H NMR (500 MHz, CDCl_3) δ 7.99 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.76 (s, 1H), 7.52 (d, $J = 7.6$ Hz, 2H), 7.43 (t, $J = 8.6$ Hz, 4H), 7.35 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.76 (d, $J = 8.2$ Hz, 1H), 4.26 (dd, $J = 7.1, 3.1$ Hz, 2H), 3.13-3.03 (m, 4H), 2.86-2.77 (m, 1H), 1.38 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -89.55 (dt, $J = 248.6, 16.0$ Hz, 1F), -90.78 (ddd, $J = 248.7, 17.0, 13.6$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.3, 166.1, 146.9, 142.4, 139.9, 134.6 (t, $J = 26.2$ Hz), 131.3, 130.4, 128.8, 127.7, 127.0, 126.5, 125.3 (t, $J = 6.2$ Hz), 125.1, 124.5, 121.3 (t, $J = 244.5$ Hz), 107.4, 60.7, 45.7 (t, $J = 28.6$ Hz), 44.8, 26.2, 26.0, 14.2. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1731, 1700, 1613, 1497, 1286, 1247, 1106, 1033, 836, 767$. HRMS (ESI-TOF): calcd. for $\text{C}_{27}\text{H}_{26}\text{F}_2\text{NO}_3$ $[\text{M} + \text{H}]^+$ 450.1875; found 450.1877.

Ethyl 3-(2-(2,4-dimethoxyphenyl)-2,2-difluoroethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3hh):



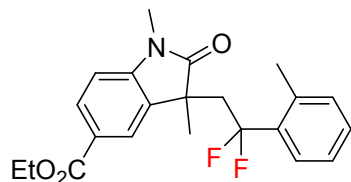
^1H NMR (500 MHz, CDCl_3) δ 7.87 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.65 (s, 1H), 6.64 (d, $J = 8.2$ Hz, 1H), 6.55 (d, $J = 8.6$ Hz, 1H), 6.27 (d, $J = 2.3$ Hz, 1H), 6.05 (dd, $J = 8.6, 2.4$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 3.16-3.07 (m, 1H), 3.02-2.94 (m, 4H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.32 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -85.25 (ddd, $J = 251.8, 17.9, 12.6$ Hz, 1F), -89.14 (ddd, $J = 251.7, 18.2, 12.2$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.2, 166.3, 162.0, 157.8 (t, $J = 4.3$ Hz), 146.8, 131.7, 130.3, 126.8 (t, $J = 9.0$ Hz), 124.7, 124.1, 120.6 (t, $J = 243.3$ Hz), 116.0 (t, $J = 25.5$ Hz), 107.1, 103.4, 98.6, 60.7, 55.5, 55.2, 44.8 (t, $J = 3.8$ Hz), 43.1 (t, $J = 28.1$ Hz), 26.2, 25.9, 14.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1713, 1613, 1463, 1287, 1241, 1030, 829, 768$. HRMS (ESI-TOF): calcd. for $\text{C}_{23}\text{H}_{26}\text{F}_2\text{NO}_5$ $[\text{M} + \text{H}]^+$ 434.1774; found 434.1776.

Ethyl 3-(2,2-difluoro-2-(p-tolyl)ethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3ih):



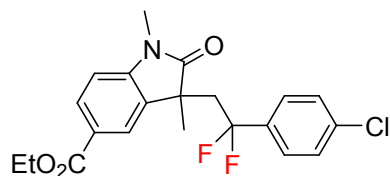
^1H NMR (500 MHz, CDCl_3) δ 7.97 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.75 (s, 1H), 7.00 (d, $J = 8.1$ Hz, 2H), 6.93 (d, $J = 8.1$ Hz, 2H), 6.75 (d, $J = 8.2$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.02-2.93 (m, 4H), 2.78-2.70 (m, 1H), 2.26 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.34 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -90.01 (ddd, $J = 247.9, 17.3, 13.8$ Hz, F), -90.70 (dt, $J = 247.2, 16.0$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.3, 166.2, 146.9, 139.5, 133.1 (t, $J = 26.3$ Hz), 131.5, 130.4, 128.5, 125.0, 124.7 (t, $J = 6.2$ Hz), 124.4, 121.4 (t, $J = 244.1$ Hz), 107.3, 60.7, 45.7 (t, $J = 28.4$ Hz), 44.8, 26.1, 26.0, 21.0, 14.3. RMS (ESI-TOF): calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_2\text{NO}_3$ $[\text{M} + \text{H}]^+$ 388.1719; found 388.1721.

Ethyl 3-(2,2-difluoro-2-(o-tolyl)ethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3jh):



^1H NMR (500 MHz, CDCl_3) δ 7.95 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.85 (s, 1H),), 7.09 (t, $J = 7.5$ Hz, 1H),), 7.03 (d, $J = 7.5$ Hz, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.68 (t, $J = 7.8$ Hz, 2H), 4.31 (q, $J = 7.1$ Hz, 2H), 3.06-2.96 (m, 1H), 2.88 (s, 3H), 2.76 -2.67 (m, 1H), 2.34 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.29 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ -86.53 (ddd, $J = 251.0, 18.8, 9.7$ Hz, 1F), -89.52 (dt, $J = 251.0, 17.9$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 178.8, 166.0, 146.8, 135.6, 133.4 (t, $J = 24.0$ Hz), 131.4, 131.4, 130.3, 129.4, 125.1 (t, $J = 9.2$ Hz), 124.8, 124.2, 121.7 (t, $J = 245.1$ Hz), 107.3, 60.5, 44.5 (d, $J = 3.7$ Hz), 43.9 (t, $J = 27.5$ Hz), 26.0, 25.9, 19.7, 14.1. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1713, 1611, 1445, 1286, 1238, 1023, 775$. HRMS (ESI-TOF): calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_2\text{NO}_3$ $[\text{M} + \text{H}]^+$ 388.1719; found 388.1715.

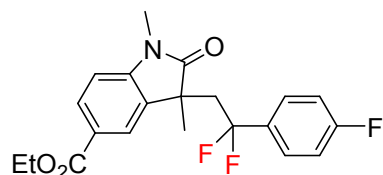
Ethyl 3-(2-(4-chlorophenyl)-2,2-difluoroethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3kh):



^1H NMR (500 MHz, CDCl_3) δ 7.98 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.71 (s, 1H), 7.17 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 8.2$ Hz, 2H), 6.77 (d, $J = 8.2$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 3.04-2.94 (m, 4H), 2.78-2.69 (m, 1H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.34 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ ppm -90.16 (dt, $J = 249.6, 16.0$ Hz, 1F), -90.88 (ddd, $J = 249.6, 16.8, 13.2$ Hz, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 179.1, 166.1, 146.8, 135.7, 134.4 (t, $J = 26.7$ Hz), 131.1, 130.5, 128.1, 126.3 (t, $J = 6.2$ Hz), 125.1, 124.5, 120.8 (t, $J = 250.0$ Hz), 107.4, 60.8, 45.5 (t, $J = 28.1$ Hz), 44.7 (t, $J = 3.0$ Hz), 26.2, 26.0, 14.3. IR (KBr, cm^{-1}): $\nu_{\text{max}} = 1700, 1611, 1501, 1452, 1380, 1248, 1100, 829, 755$. RMS

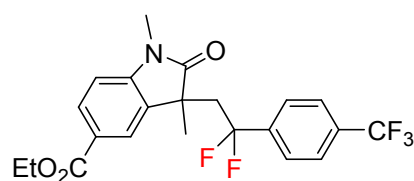
(ESI-TOF): calcd. for $C_{21}H_{21}ClF_2NO_3$ $[M + H]^+$ 408.1173; found 408.1174.

Ethyl 3-(2,2-difluoro-2-(4-fluorophenyl)ethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3lh):



1H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.75 (s, 1H), 7.03 (dd, $J = 8.6, 5.2$ Hz, 2H), 6.88 (t, $J = 8.5$ Hz, 2H), 6.77 (d, $J = 8.2$ Hz, 1H), 4.35 (q, $J = 7.2$ Hz, 2H), 3.03 -2.93 (m, 4H), 2.79- 2.70 (m, 1H), 1.38 (t, $J = 7.1$ Hz, 3H), 1.34 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -89.10 (ddd, $J = 249.0, 17.3, 11.9$ Hz, 1F), -90.24 (dt, $J = 248.9, 16.2$ Hz, 1F), -110.67 – -111.84 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.2, 166.2, 163.2 (d, $J = 249.3$ Hz), 146.8, 132.0 (t, $J = 27.0$ Hz), 131.3, 130.6, 127.1 (dt, $J = 8.9, 6.4$ Hz), 125.1, 124.6, 120.9 (t, $J = 244.5$ Hz), 114.9 (d, $J = 22.0$ Hz), 107.4, 60.8, 45.6 (t, $J = 28.2$ Hz), 44.8, 26.3, 26.0, 14.3. IR (KBr, cm^{-1}): $\nu_{max} = 1712, 1612, 1507, 1464, 1288, 1243, 1109, 1043, 832, 768$. HRMS (ESI-TOF): calcd. for $C_{21}H_{21}F_3NO_3$ $[M + H]^+$ 392.1468; found 392.1465.

Ethyl 3-(2,2-difluoro-2-(4-(trifluoromethyl)phenyl)ethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate



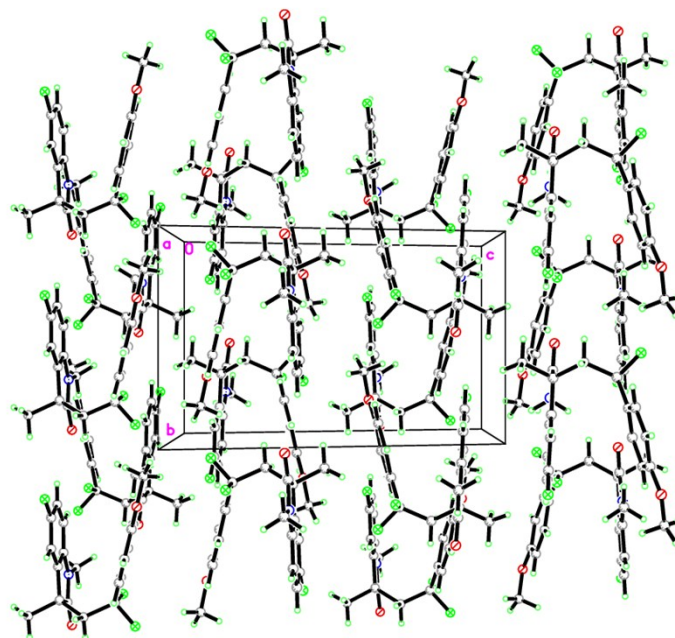
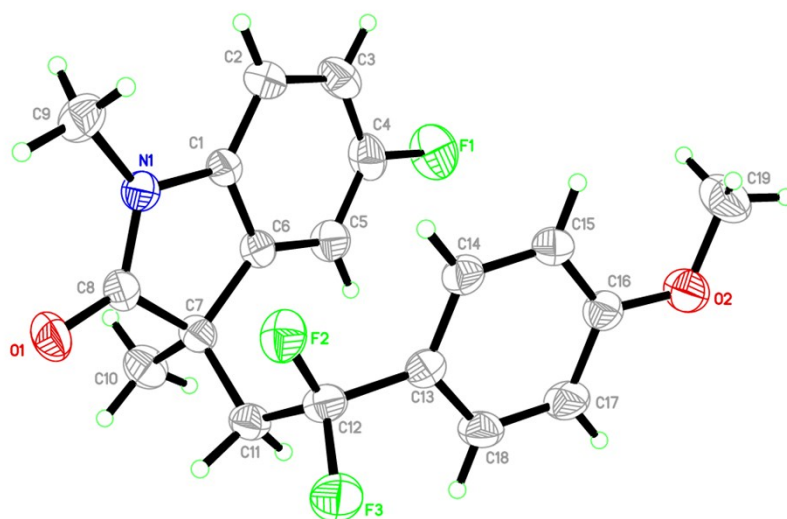
1H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, $J = 8.2, 1.7$ Hz, 1H), 7.72 (s, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 8.2$ Hz, 1H), 4.36 (q, $J = 7.0$ Hz, 2H), 3.10 – 2.96 (m, 4H), 2.86 – 2.71 (m, 1H), 1.40 (t, $J = 7.1$ Hz, 3H), 1.37 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.02 , -90.44 (t, $J = 16.0$ Hz), -90.97 (t, $J = 15.9$ Hz), -91.52 (dd, $J = 17.0, 13.5$ Hz), -92.05 (dd, $J = 17.2, 13.5$ Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1 , 166.1 , 146.8 , 139.5 (t, $J = 26.7$ Hz), 131.8 (q, $J = 33.5$ Hz), 131.1 , 130.7 , 125.5 (t, $J = 6.4$ Hz), 125.1 , 125.0 (q, $J = 3.8$ Hz), 124.7 , 123.5 (q, $J = 273.6$

Hz), 120.7 (t, J = 245.0 Hz), 107.5 , 60.9 , 45.5 (t, J = 27.6 Hz), 44.8 (t, J = 3.1 Hz), 26.3 , 26.1 , 14.3 . IR (KBr, cm⁻¹): ν_{max} = 1716, 1625, 1508, 1452, 1330, 1248, 1100, 1033, 922, 831, 560. HRMS (ESI-TOF): calcd. for C₂₂H₂₁F₅NO₃ [M + H]⁺ 442.1436; found 442.1439.

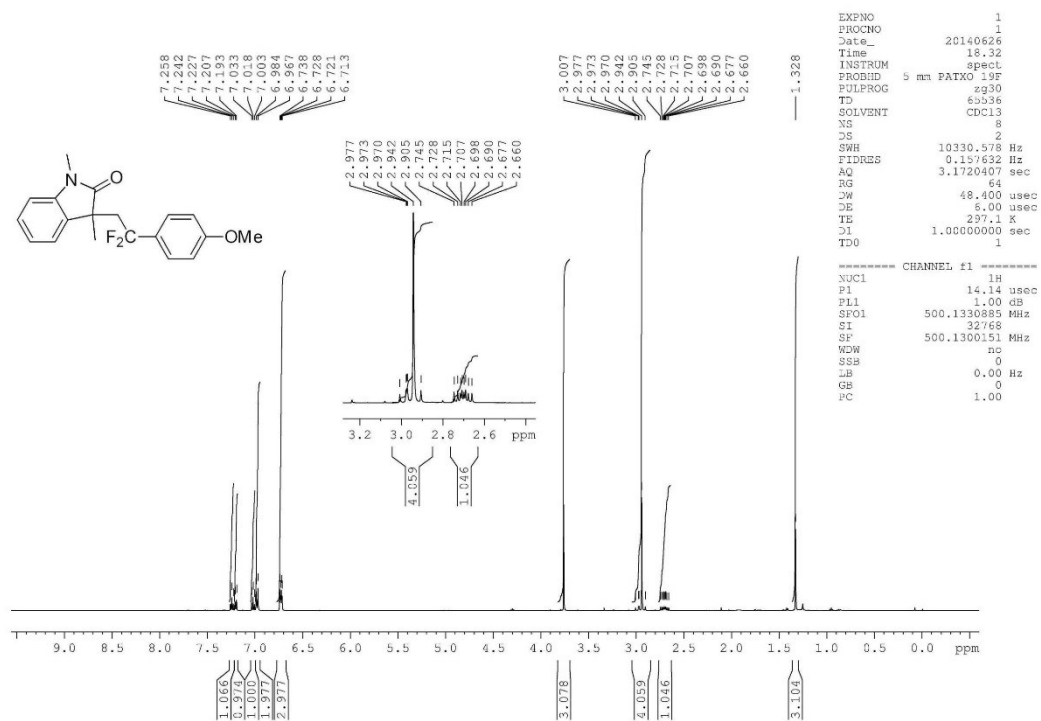
Reference

- [1] a) K. Sato, M. Omote, A. Ando, I. Kumadaki, *J. Fluorine Chem.* 2004, 125, 509; b) S. Mizuta, I. S. R. Stenhagen, M. O'Duill, J. Wolstenhulme, A. K. Kirjavainen, S. J. Forsback, M. Tredwell, G. Sandford, P. R. Moore, M. Huiban, S. K. Luthra, J. Passchier, O. Solin, V. Gouverneur, *Org. Lett.* 2013, 15, 2648; c) K. Fujikawa, Y. Fujioka, A. Kobayashi, H. Amii, *Org. Lett.* 2011, 13, 5560.
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- [3] a) A. Pinto, Y. Jia, L. Neuville, J.-P. Zhu, *Chem. Eur. J.* 2007, 13, 961-967. b) K. Jones, M. Thompson, C. Wright, *J. Chem. Soc., Chem. Commun.* 1986, 715-716. c) H. Wei, T. Piou, J. Dufour, L. Neuville, J.-P. Zhu, *Org. Lett.*, 2011, 13, 2244-2247.
- [4] X. Mu, T. Wu, H.-Y. Wang, Y.-L. Guo, G.-S. Liu, *J. Am. Chem. Soc.* 2012, 134, 878-881.

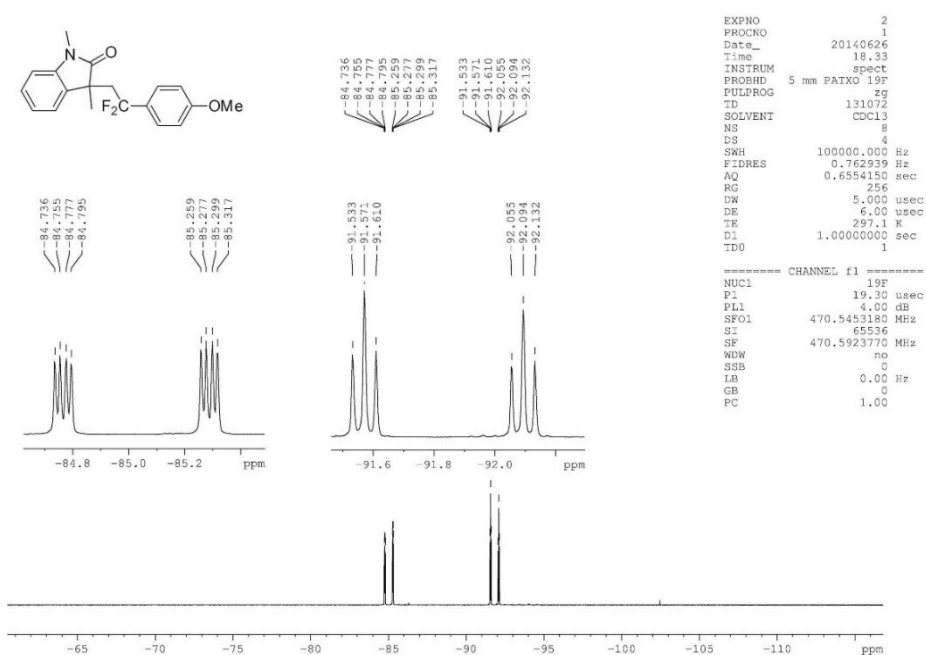
Single crystal X-ray analysis of 3ad



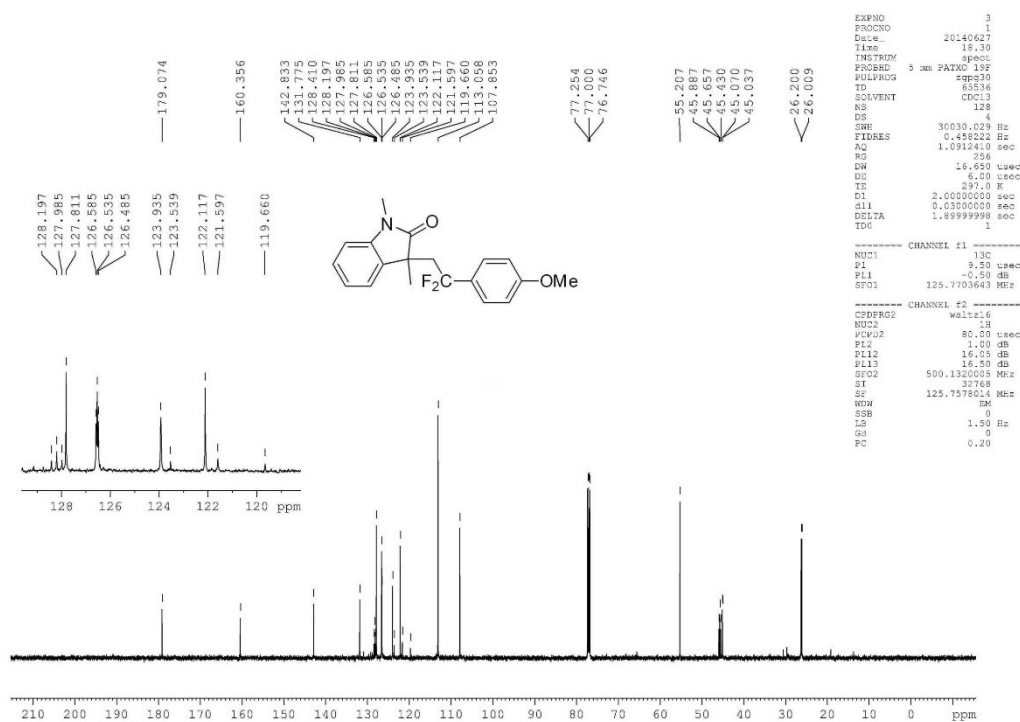
¹H NMR Spectra of 3aa



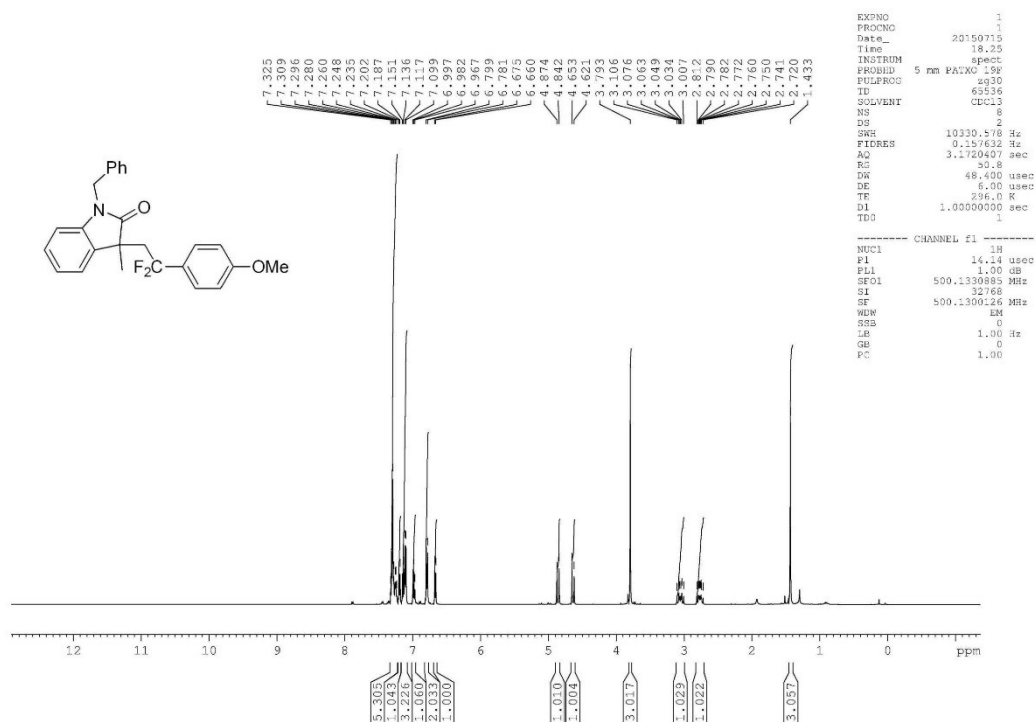
¹⁹F NMR Spectra of 3aa



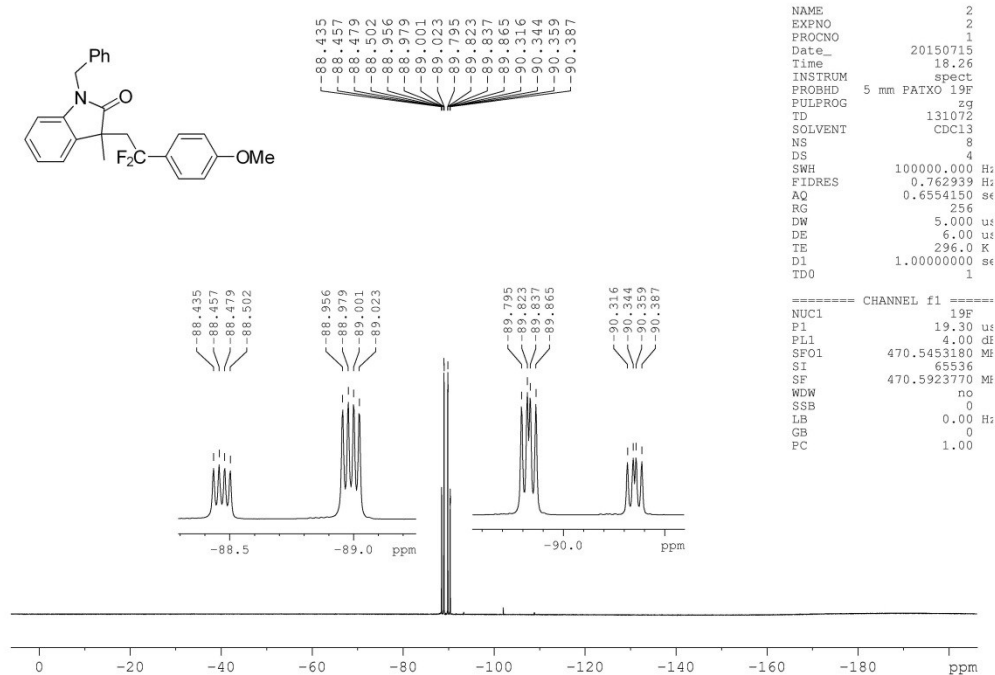
¹³C NMR Spectra of 3aa



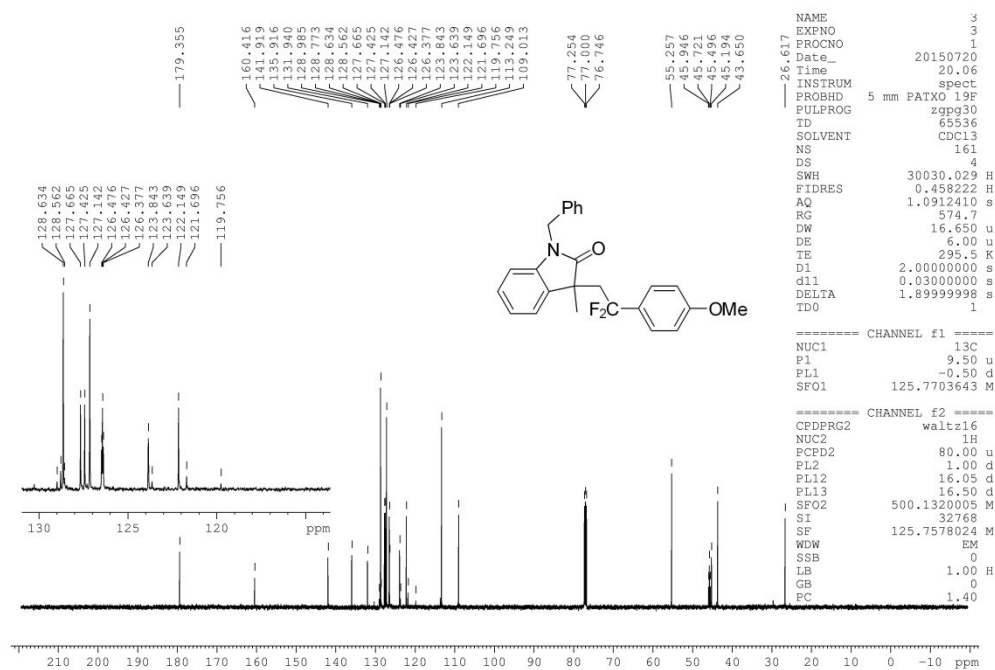
¹H NMR Spectra of 3ab



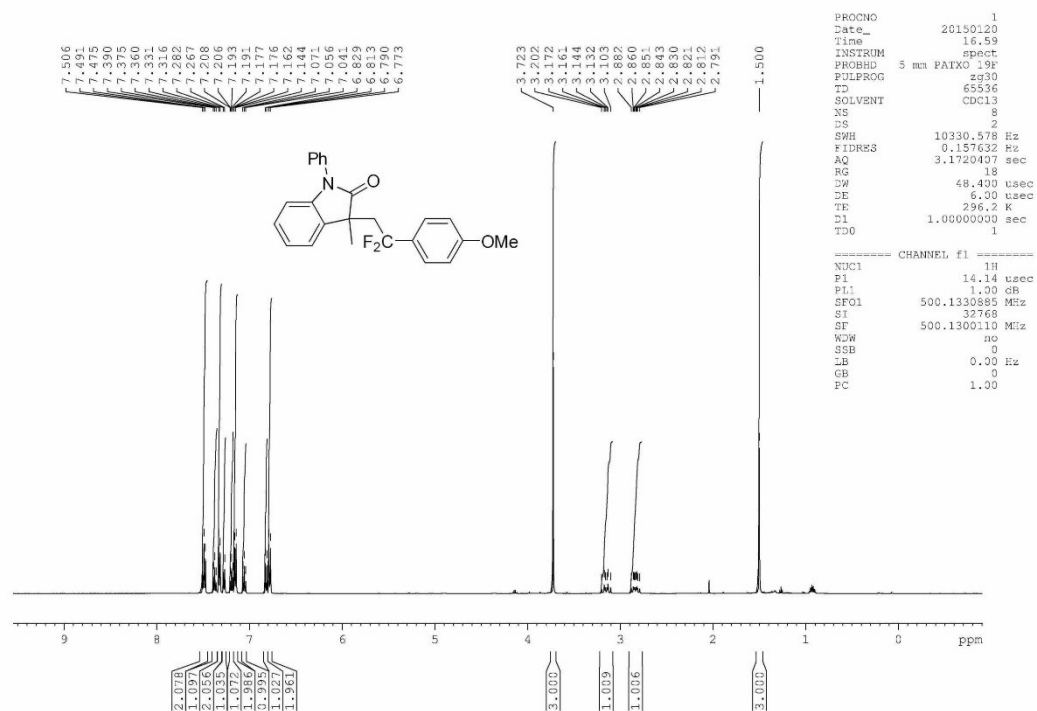
¹⁹F NMR Spectra of 3ab



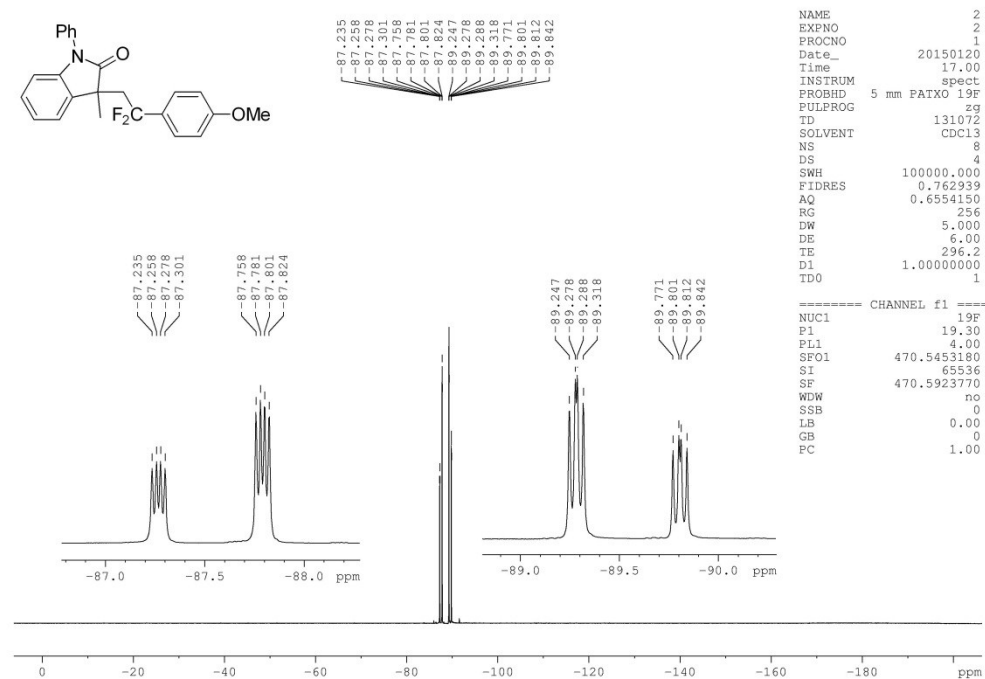
¹³C NMR Spectra of 3ab



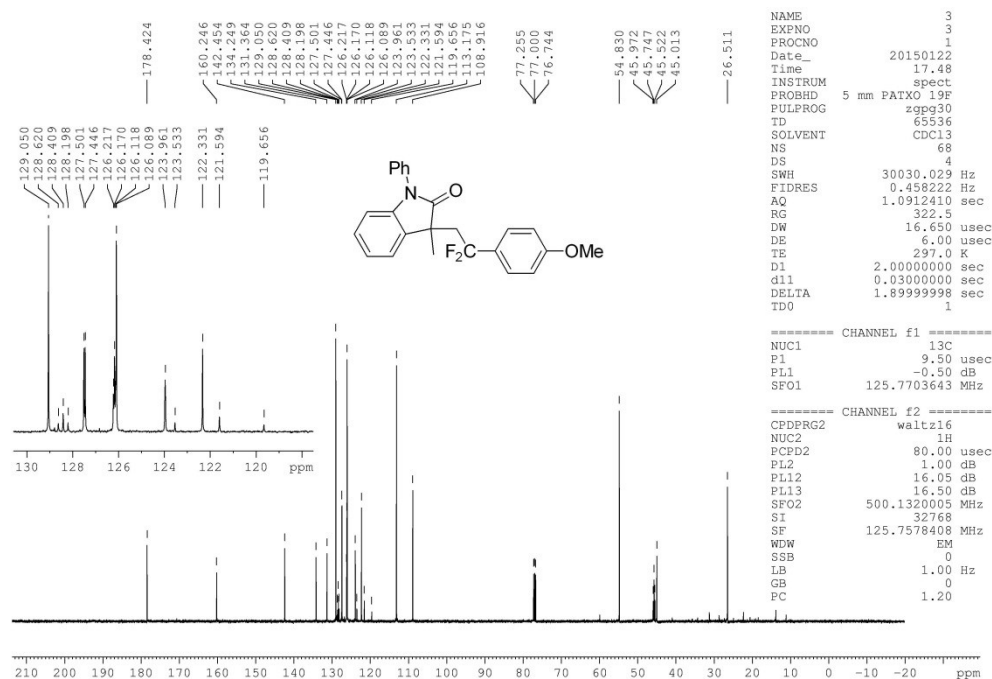
¹H NMR Spectra of 3ac



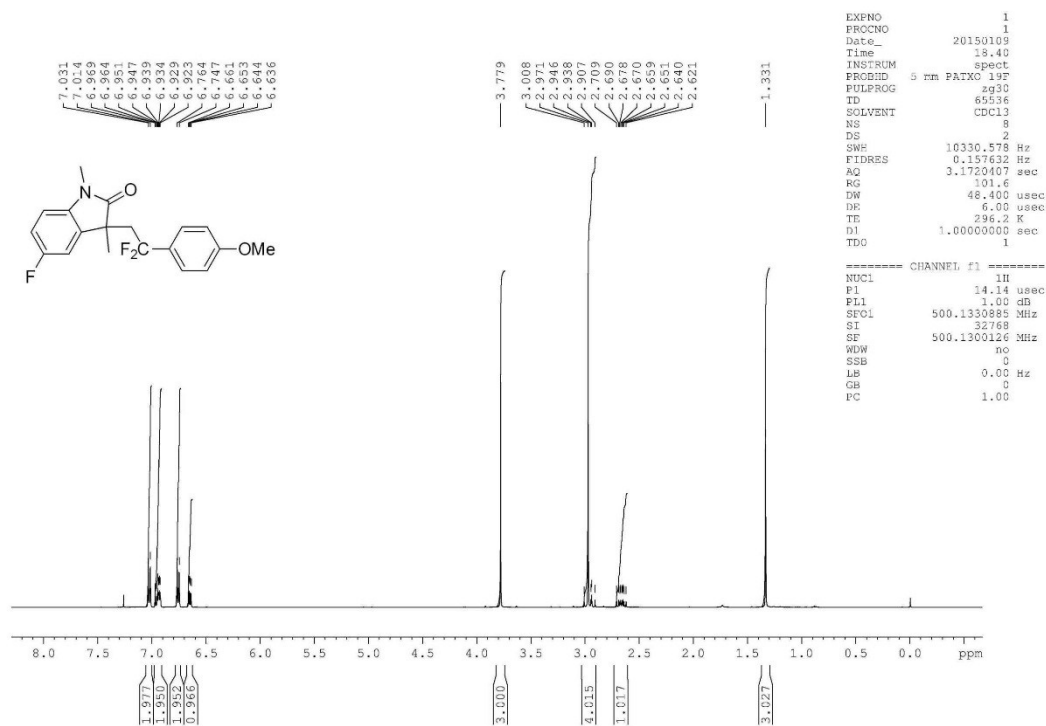
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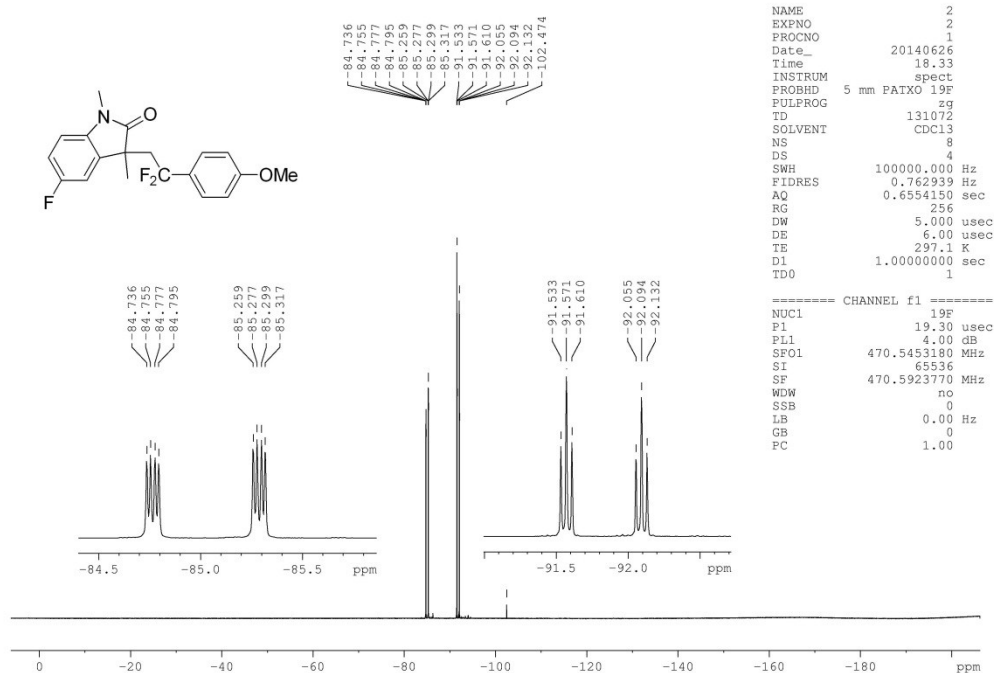
¹³C NMR Spectra of 3ac



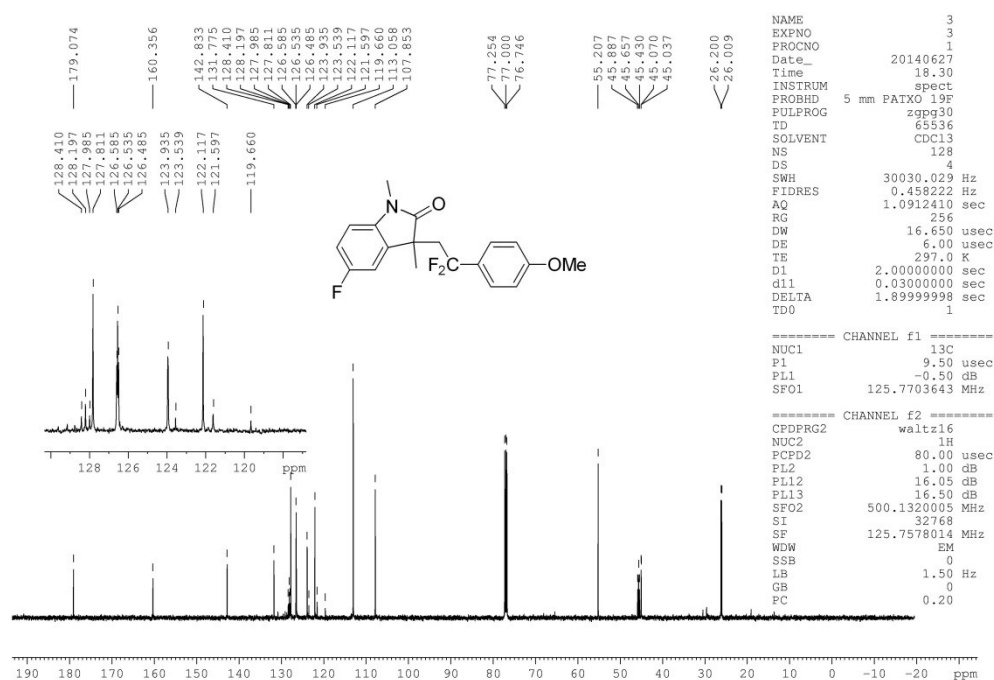
¹H NMR Spectra of 3ad



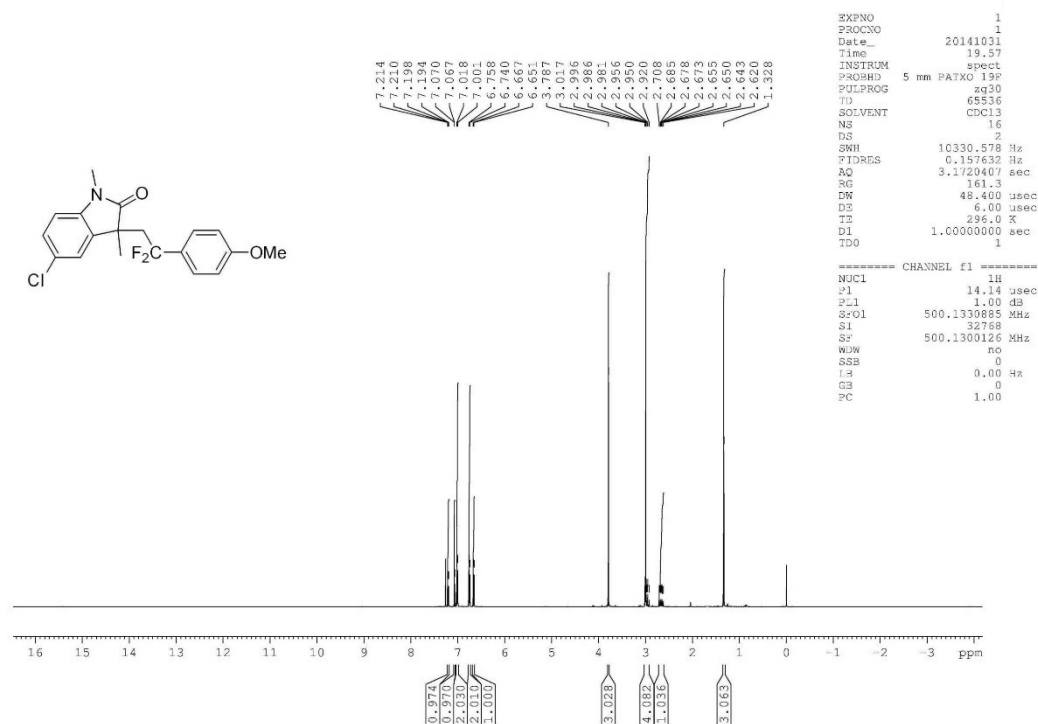
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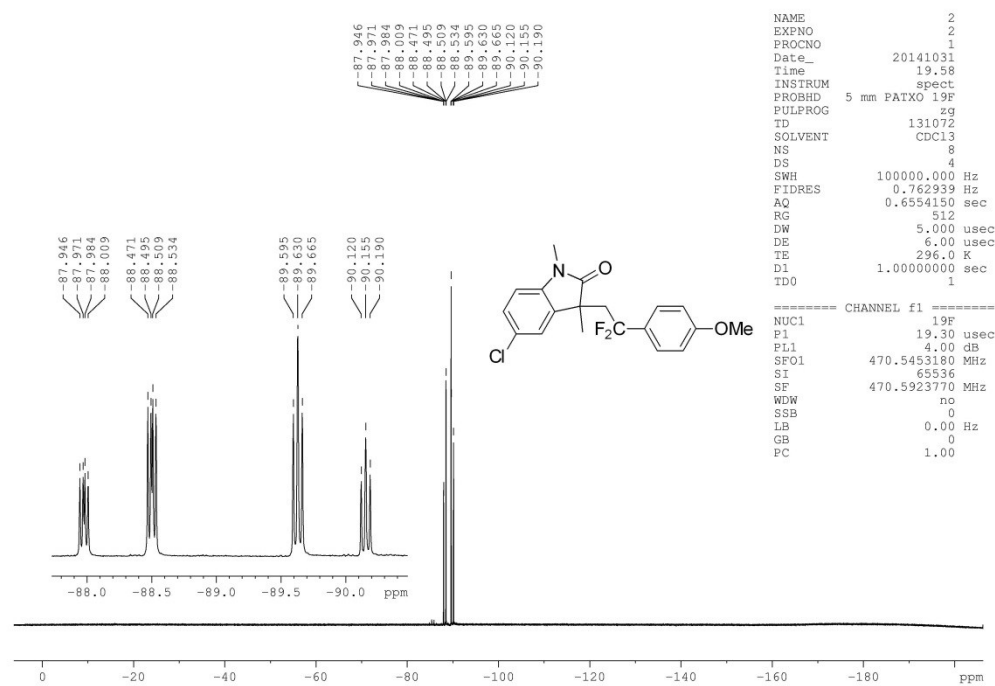
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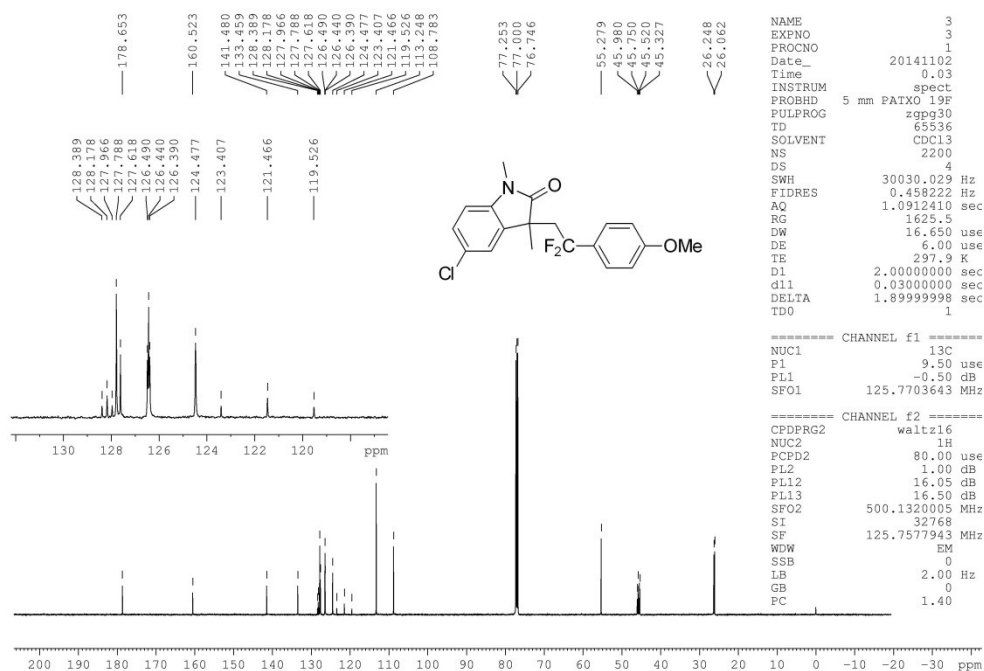
¹H NMR Spectra of 3ae



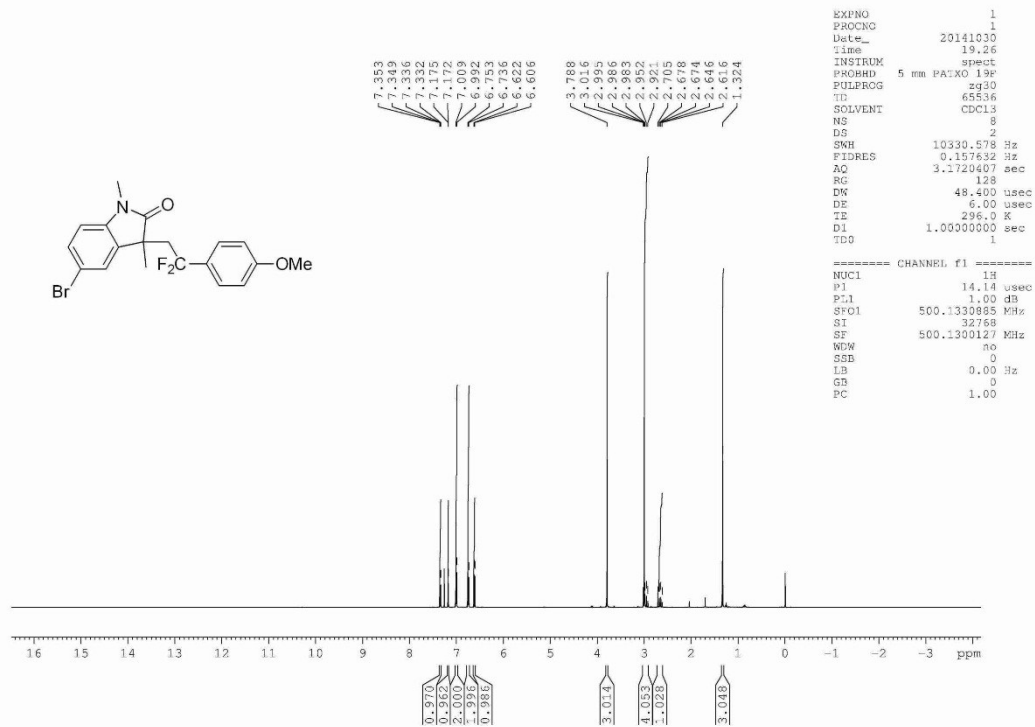
¹⁹F NMR Spectra of 3ae



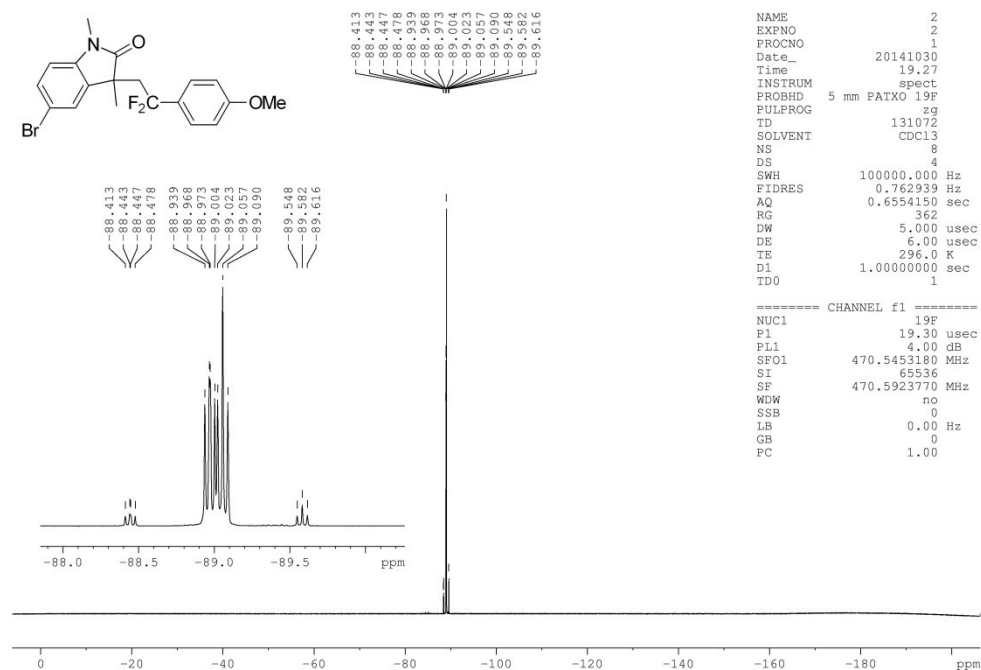
¹³C NMR Spectra of 3ae



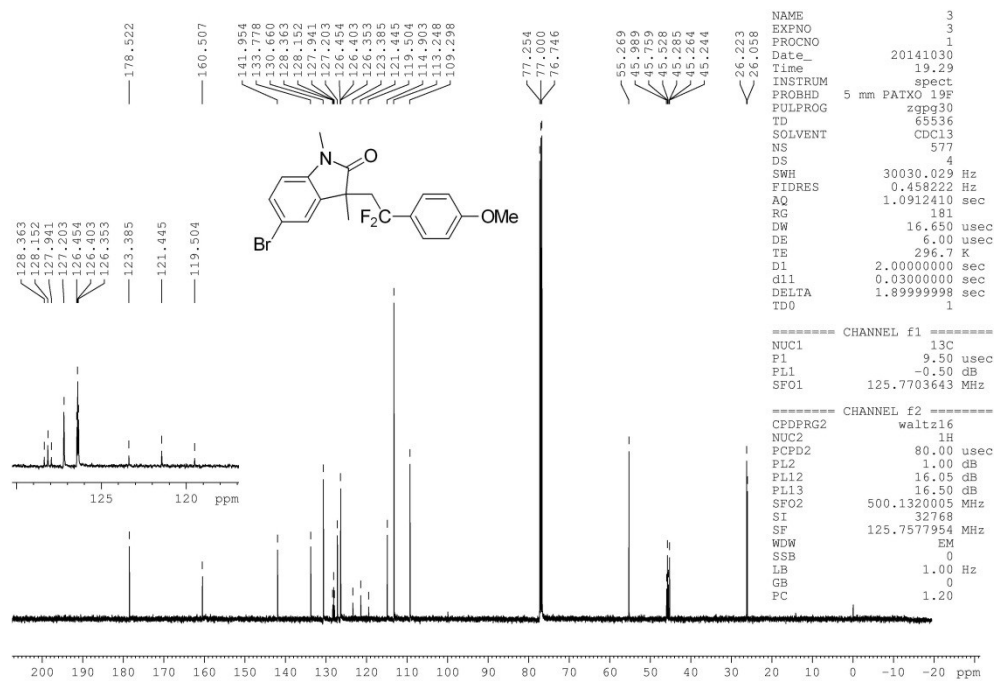
¹H NMR Spectra of 3af



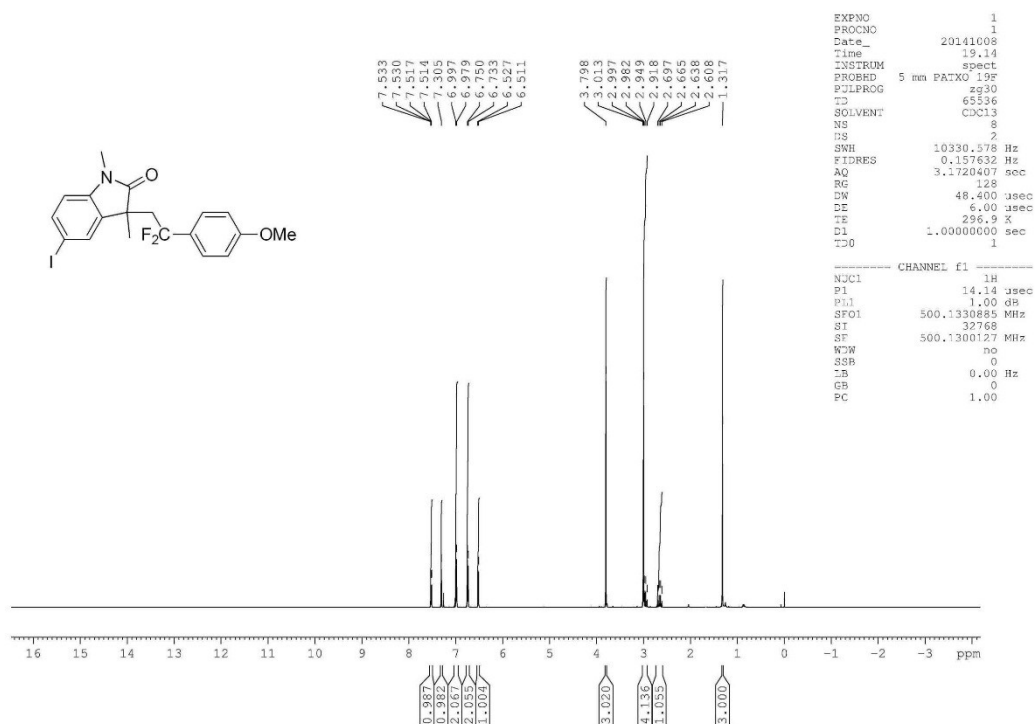
¹⁹F NMR Spectra of 3af



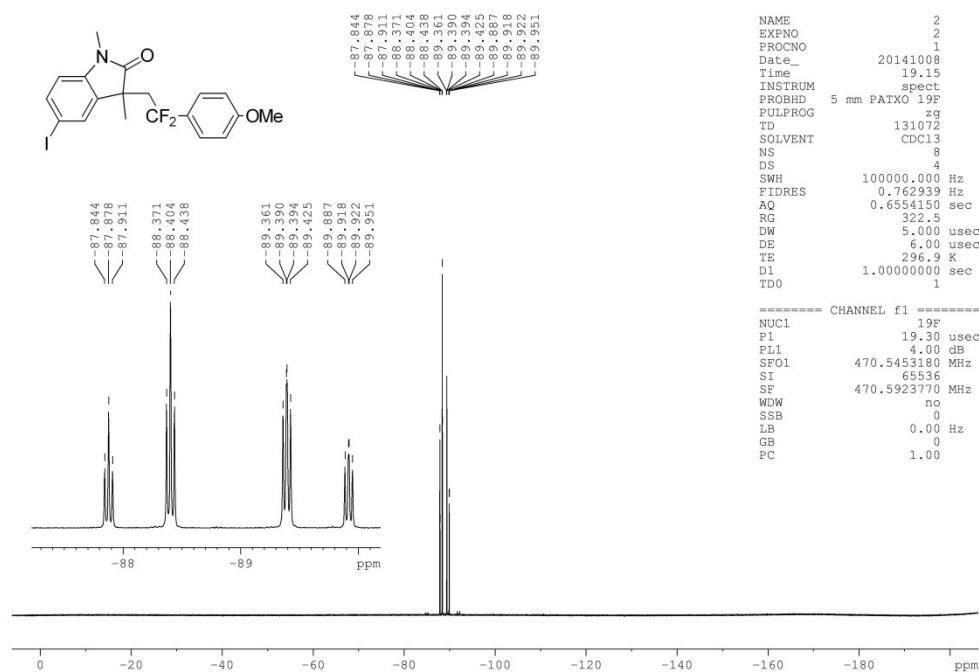
¹³C NMR Spectra of 3af



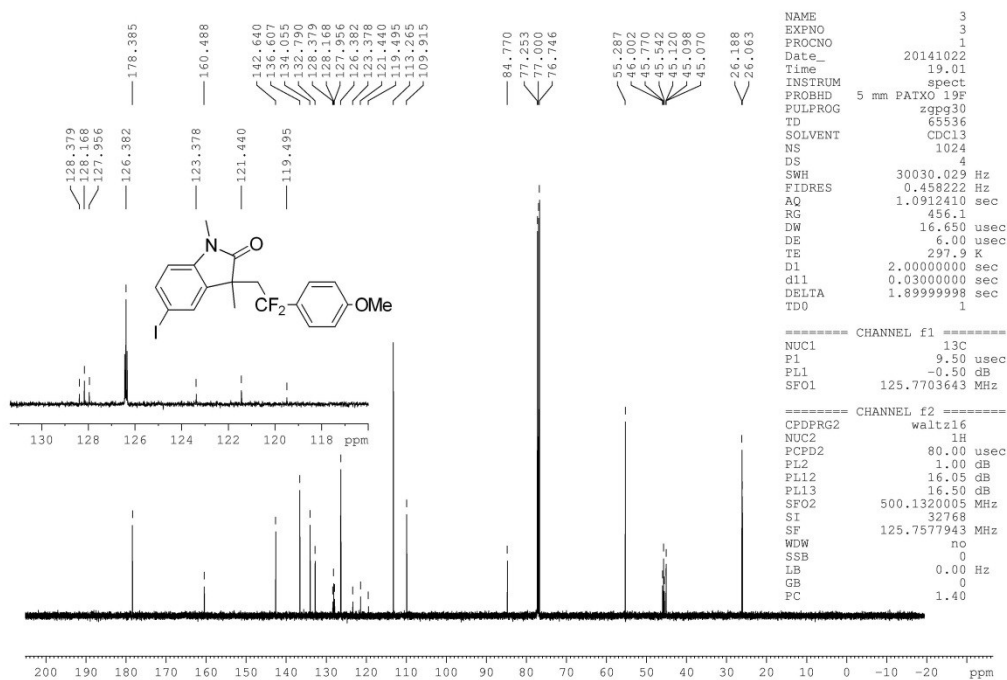
¹H NMR Spectra of 3ag



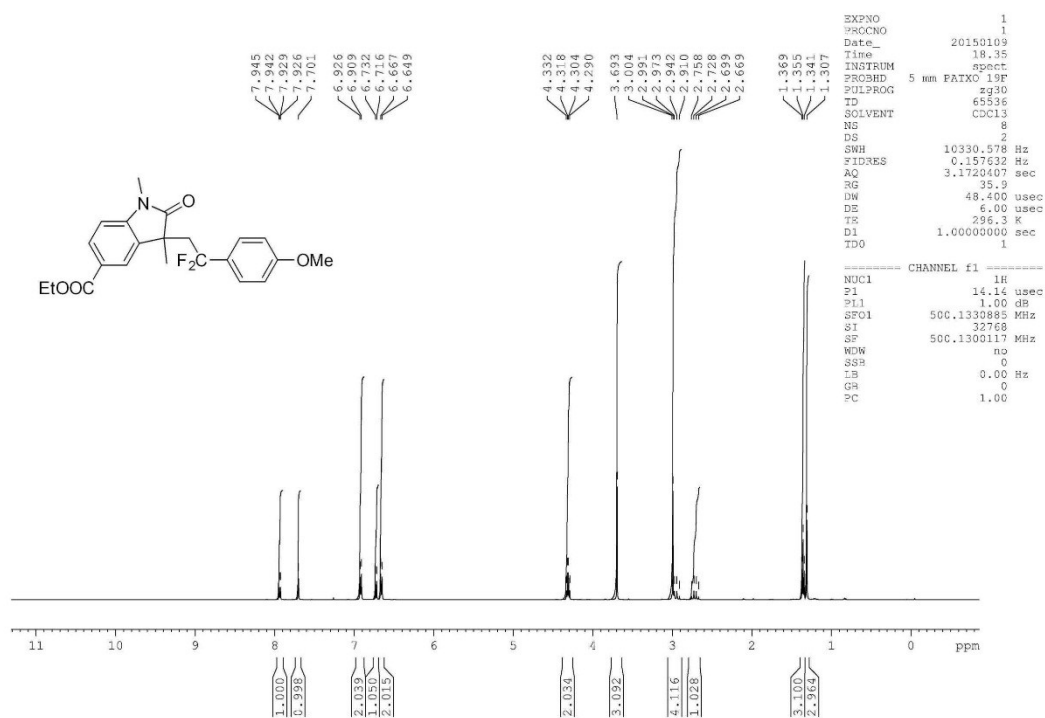
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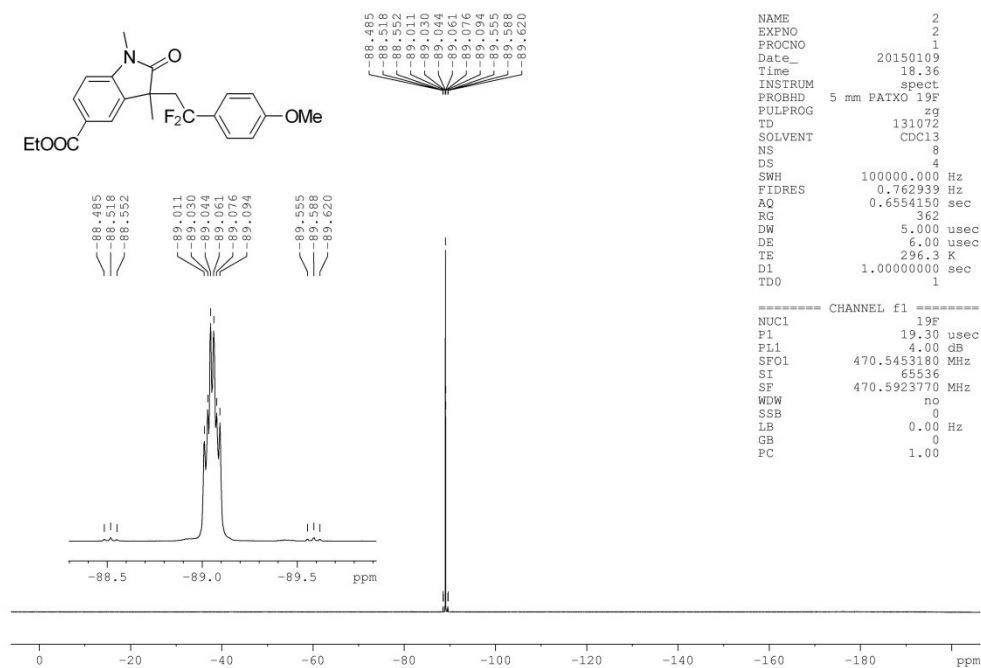
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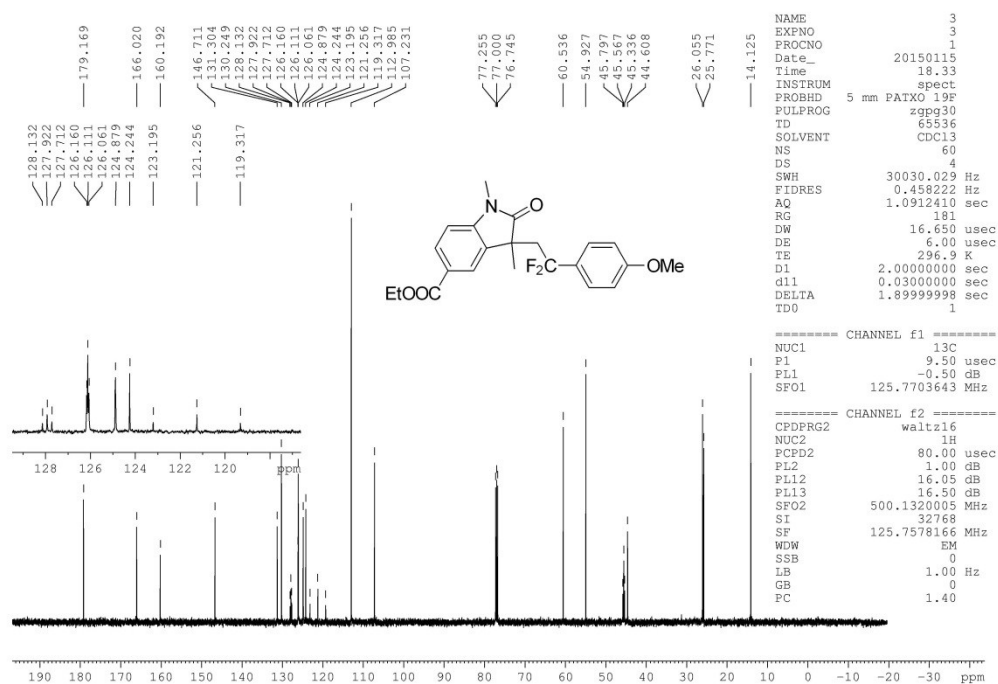
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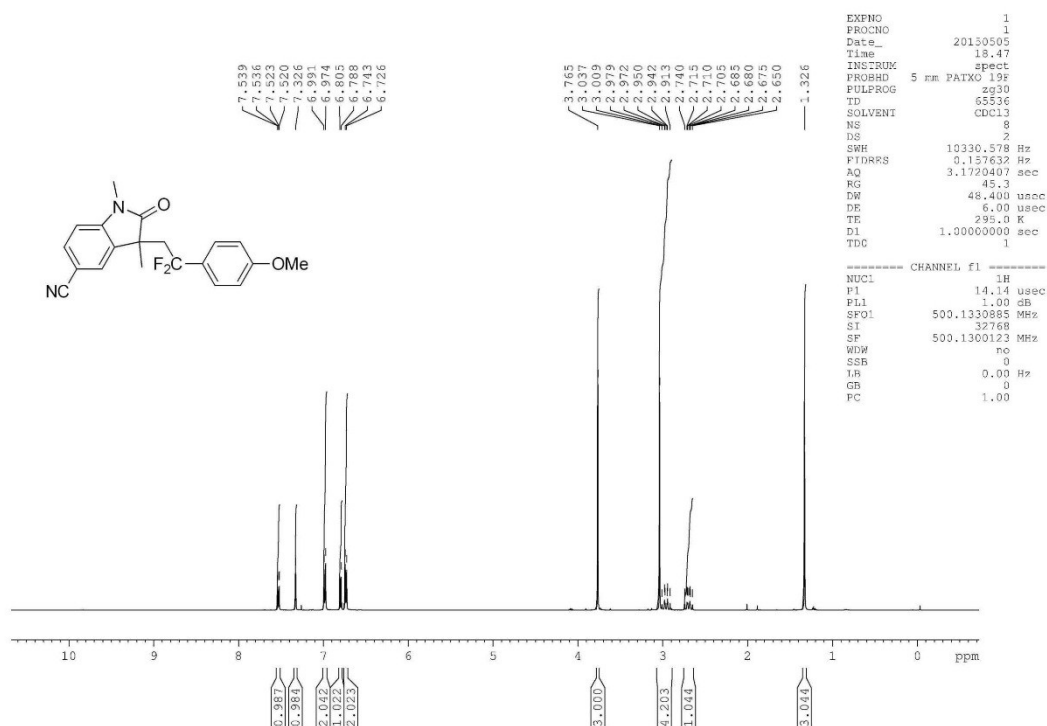
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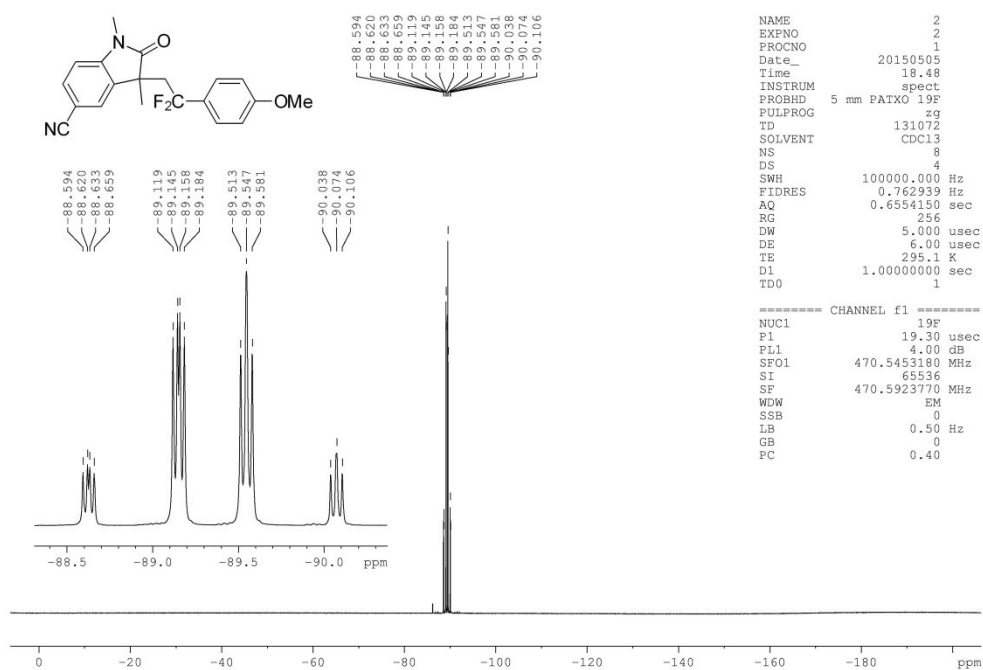
¹³C NMR Spectra of 3ah



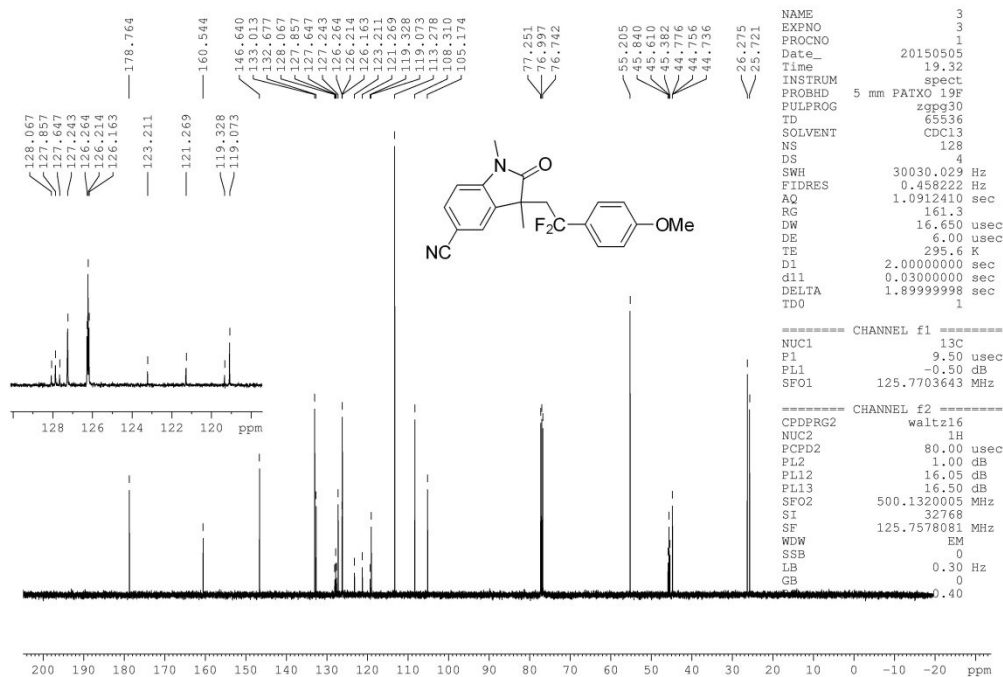
¹H NMR Spectra of 3ai



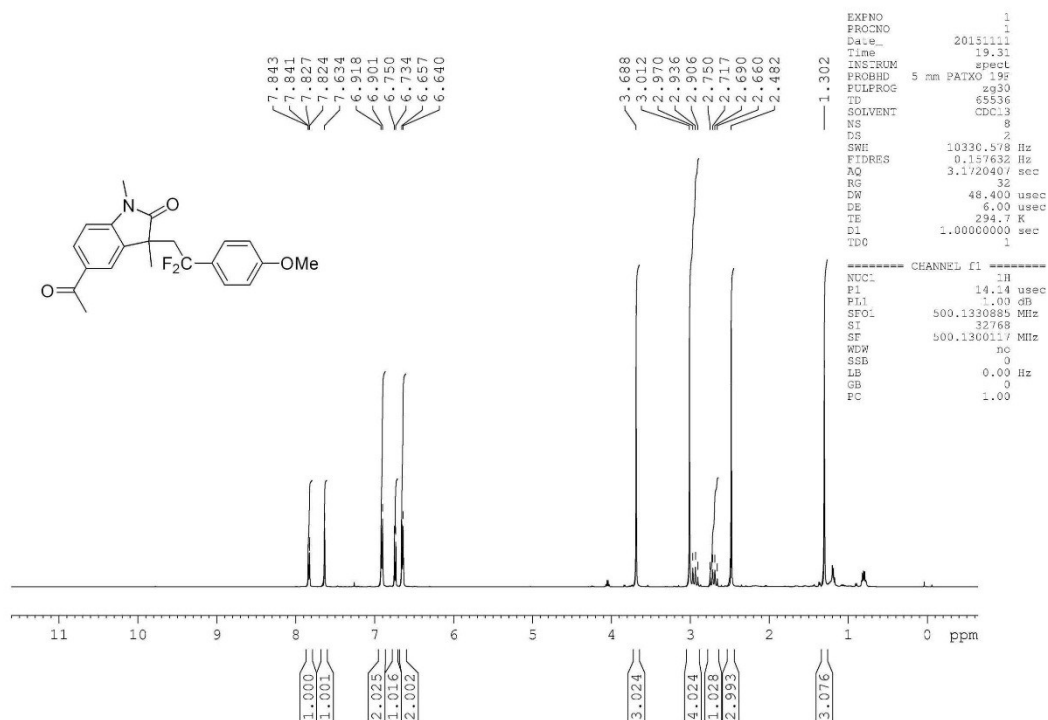
¹⁹F NMR Spectra of 3ai



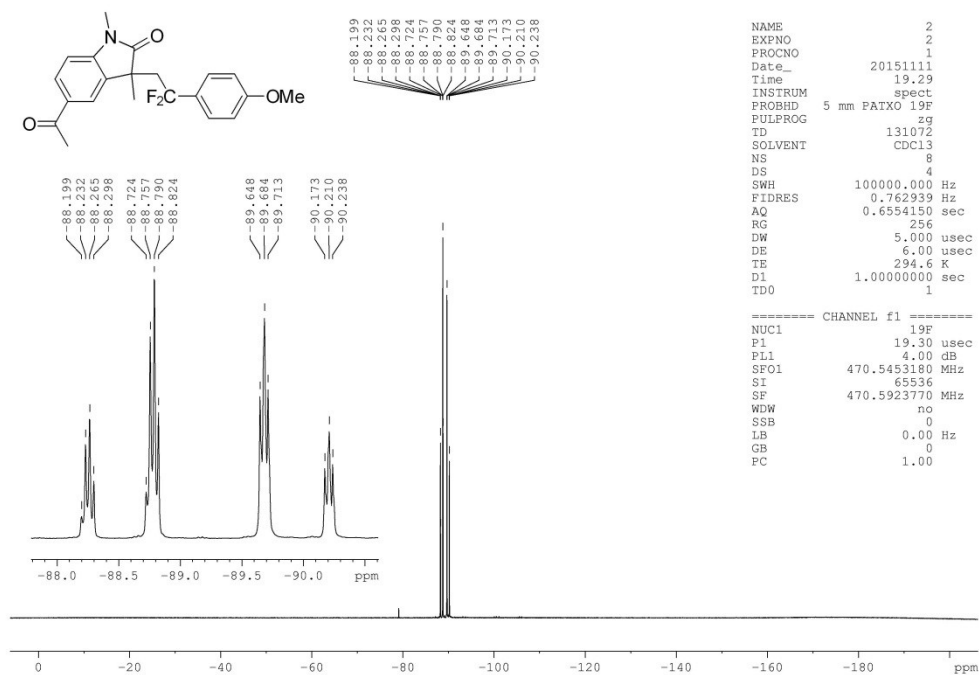
¹³C NMR Spectra of 3ai



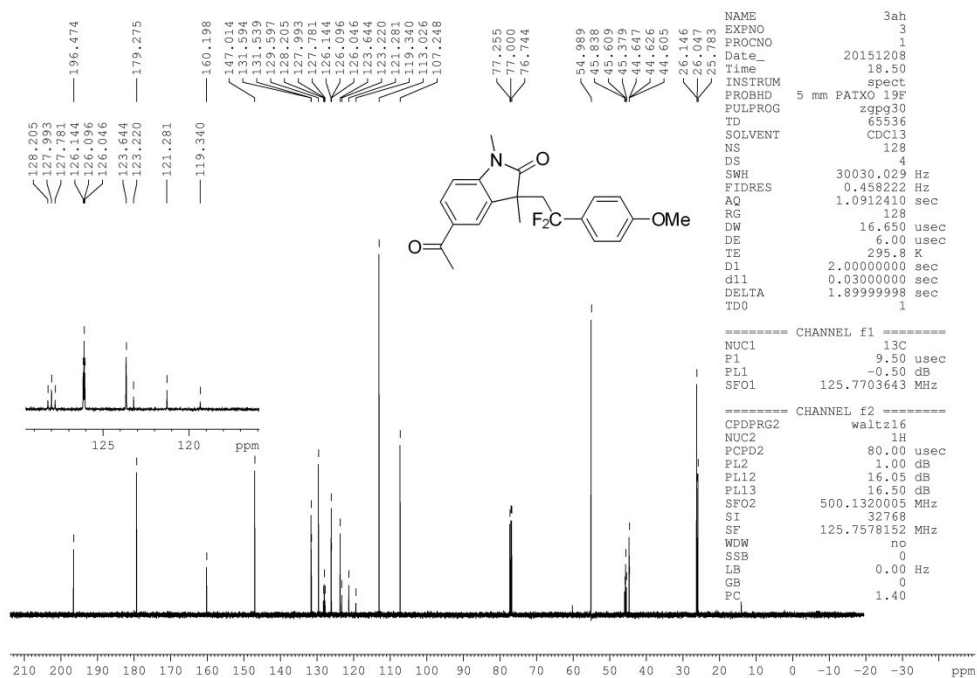
¹H NMR Spectra of 3aj



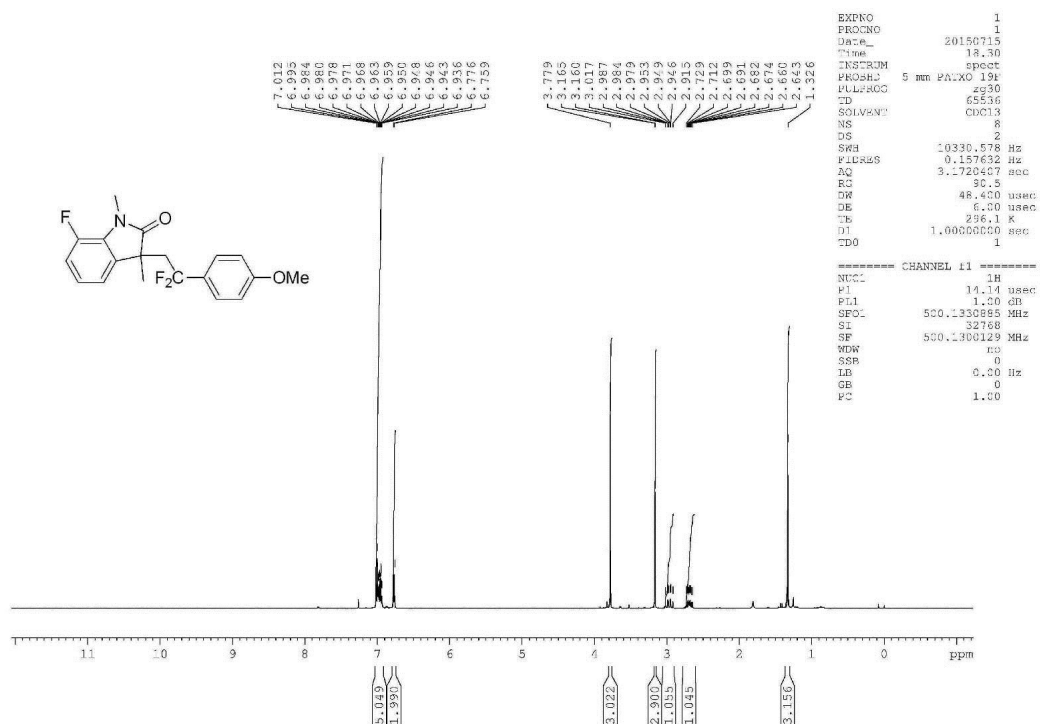
¹⁹F NMR Spectra of 3aj



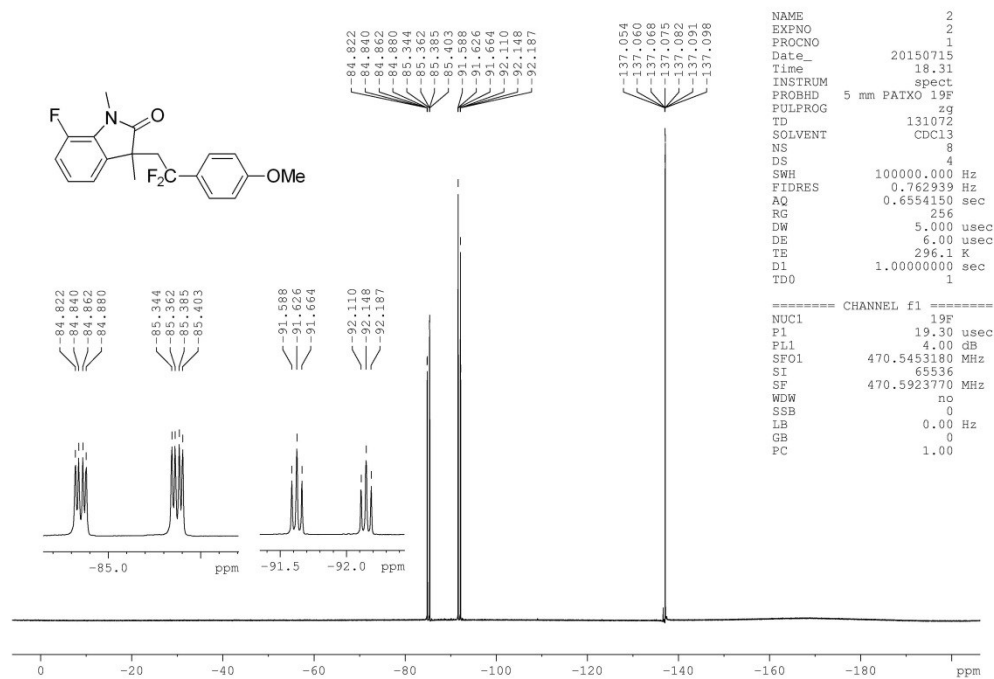
¹³C NMR Spectra of 3aj



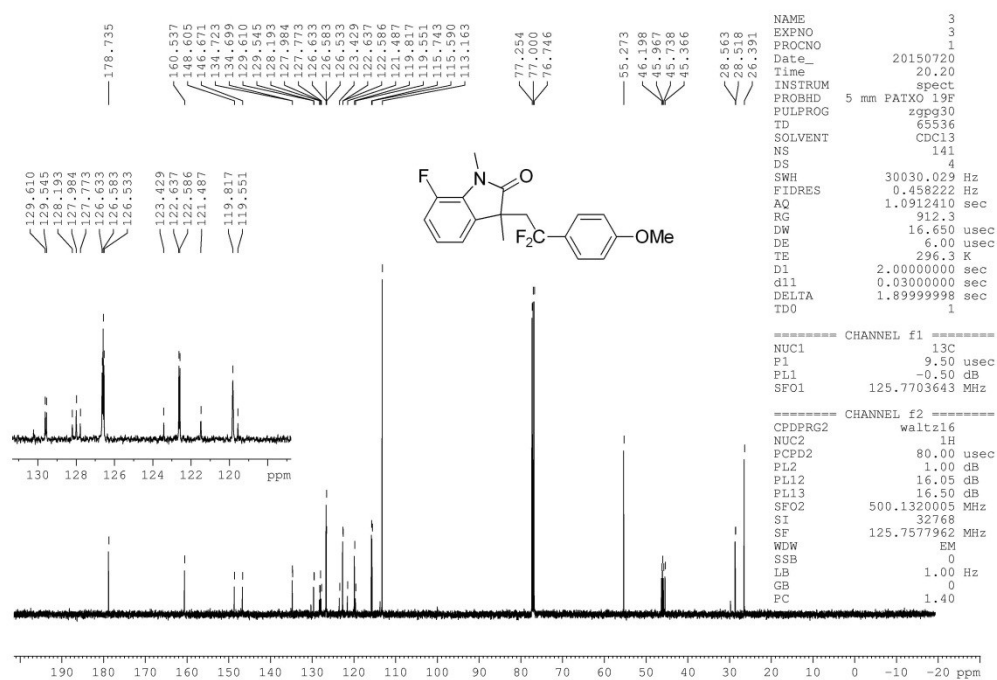
¹H NMR Spectra of 3ak



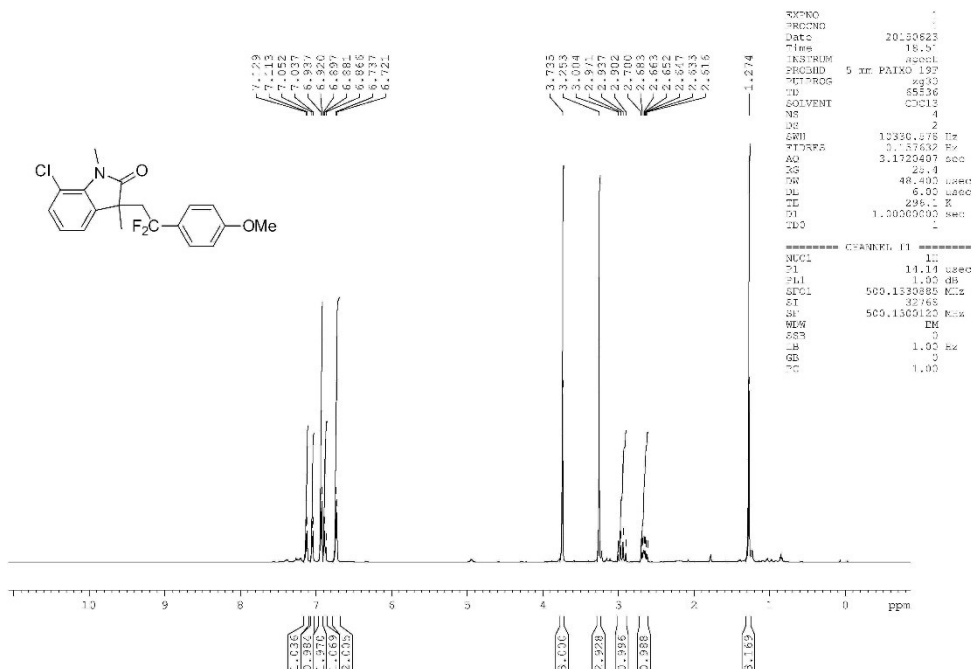
¹⁹F NMR Spectra of 3ak



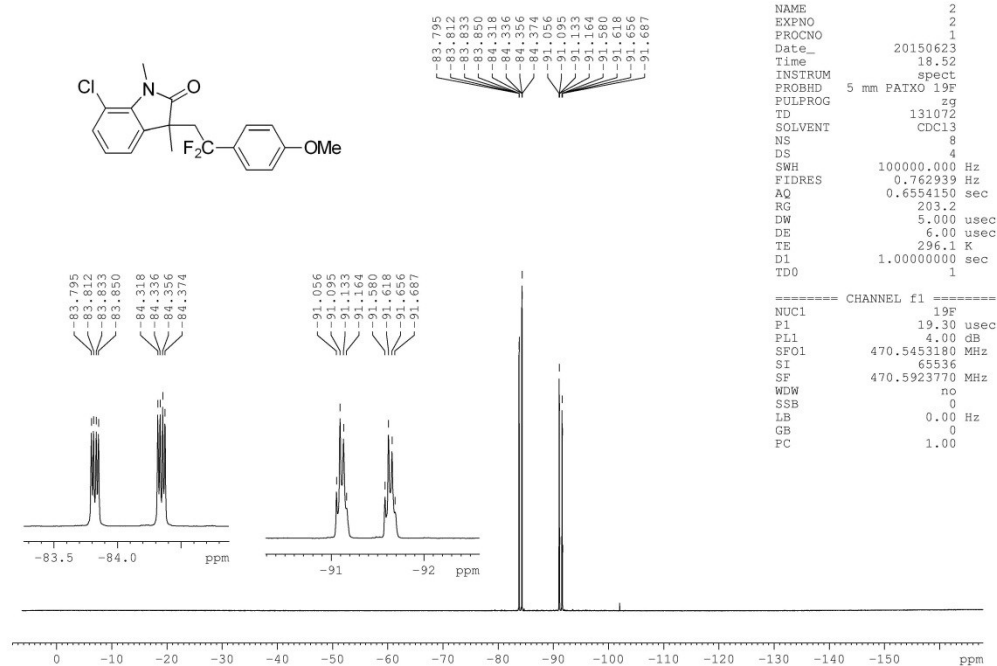
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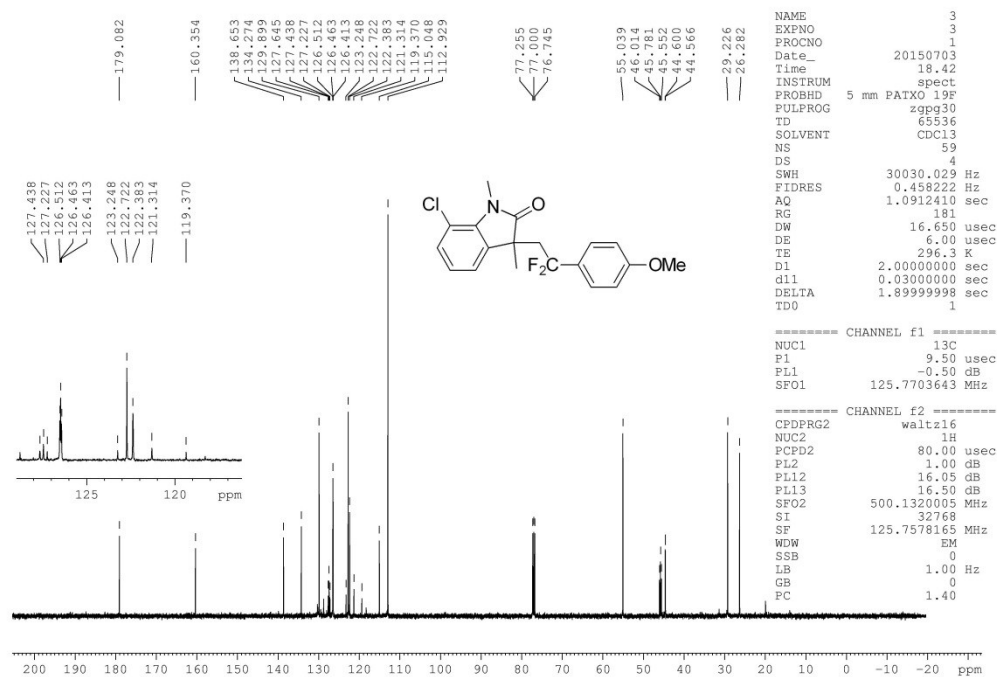
¹H NMR Spectra of 3al



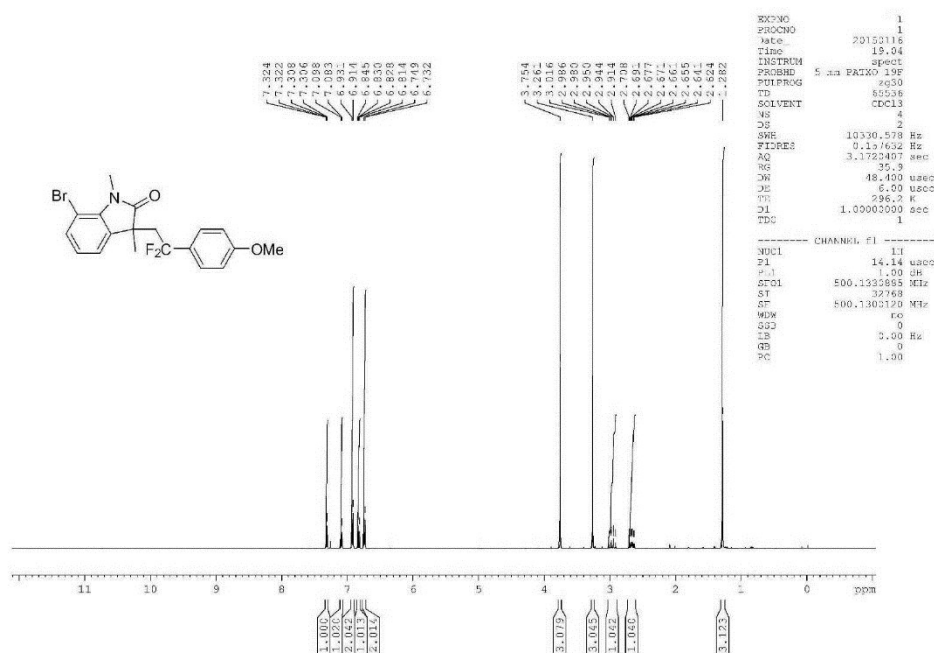
¹⁹F NMR Spectra of 3al



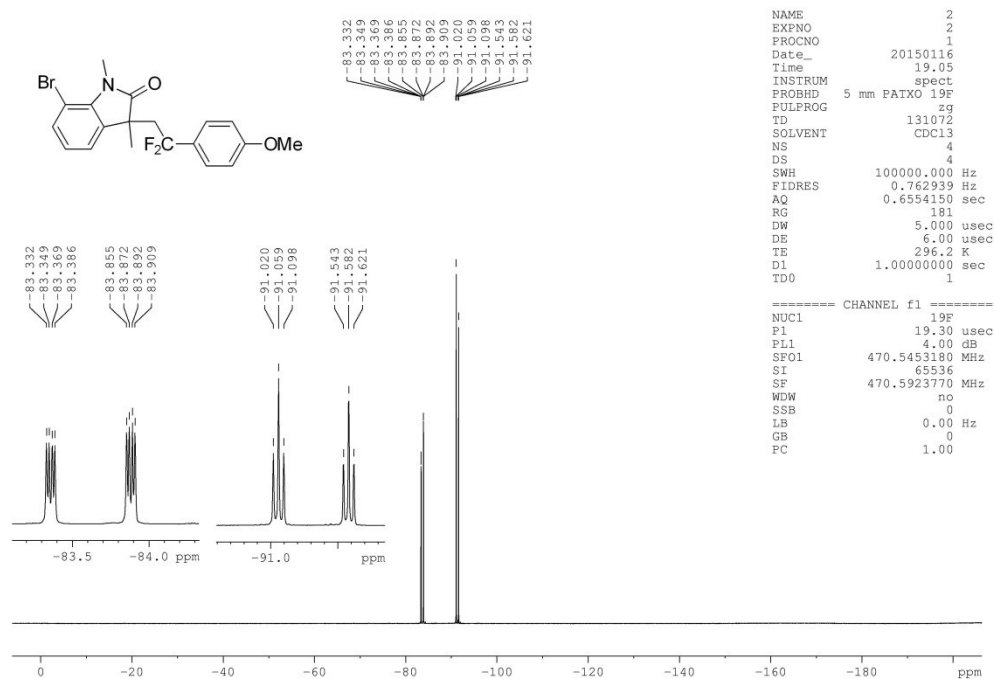
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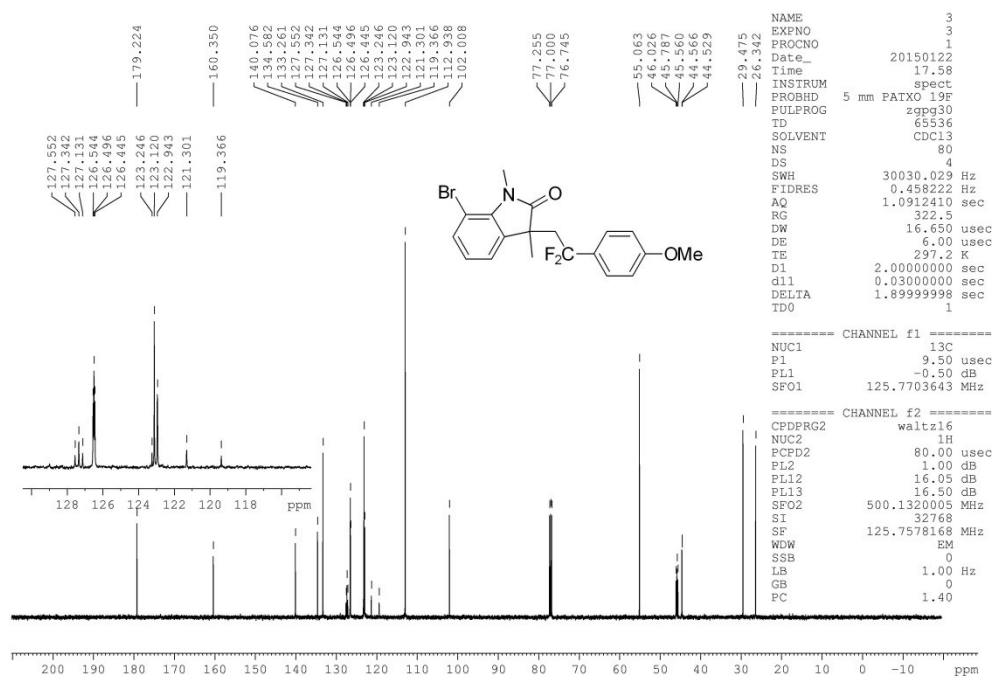
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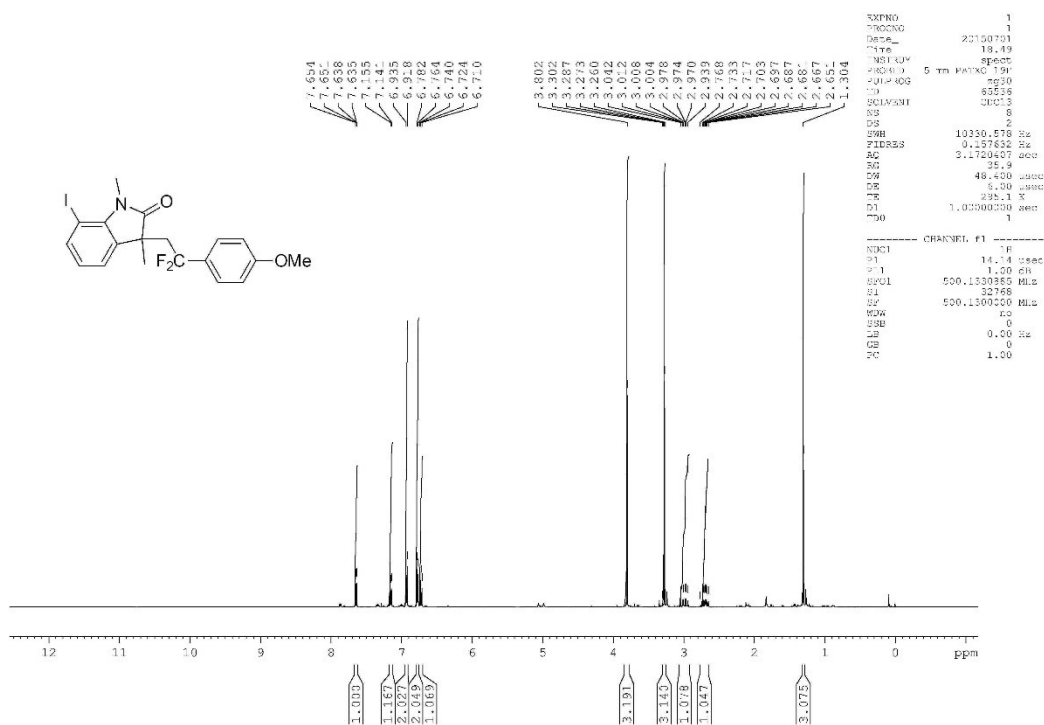
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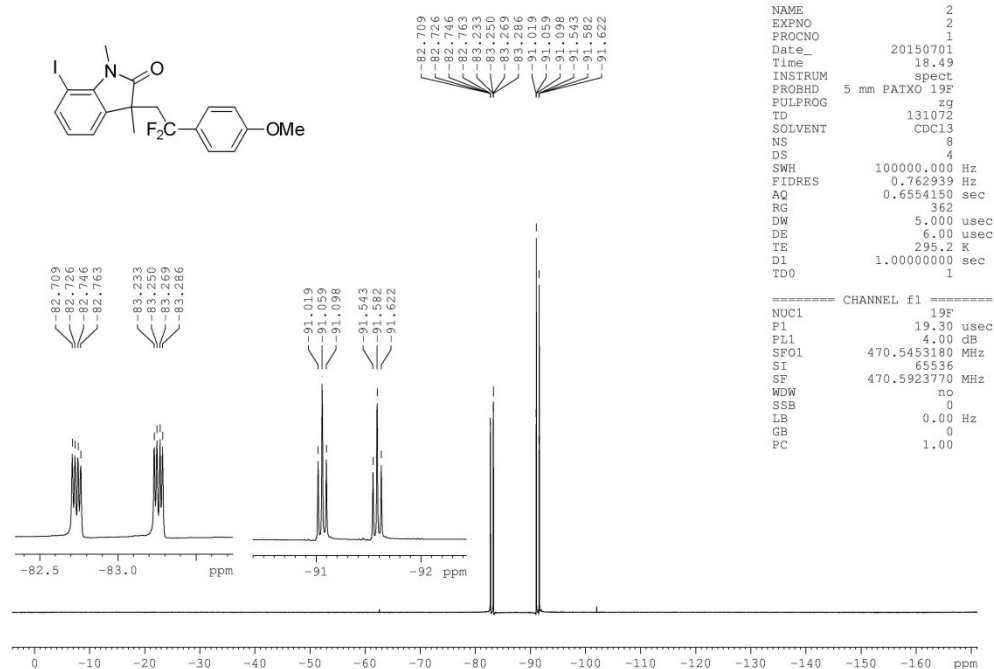
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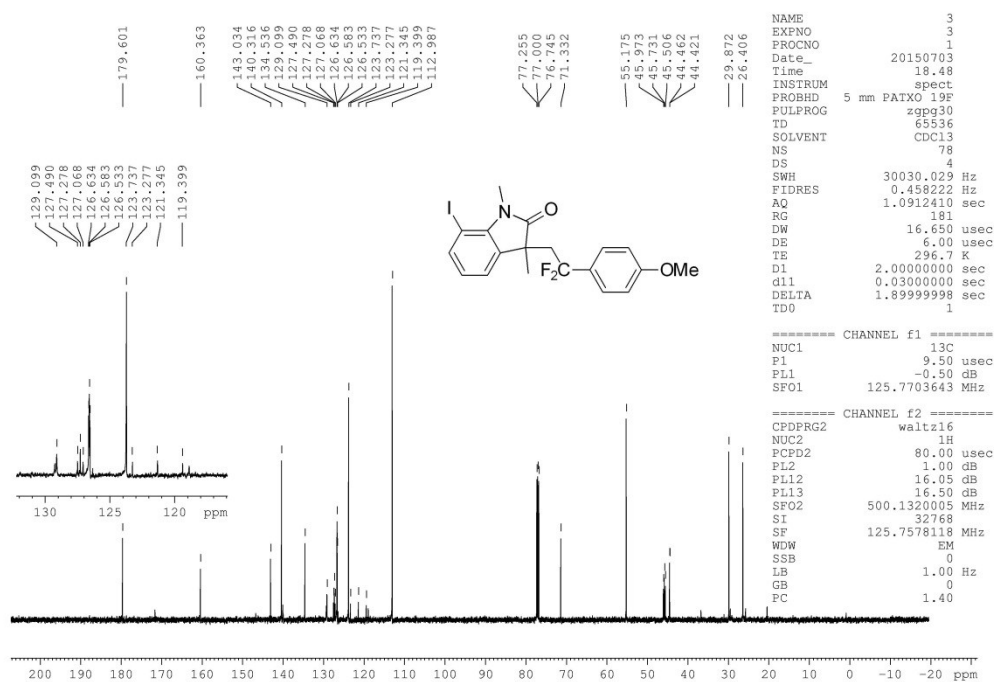
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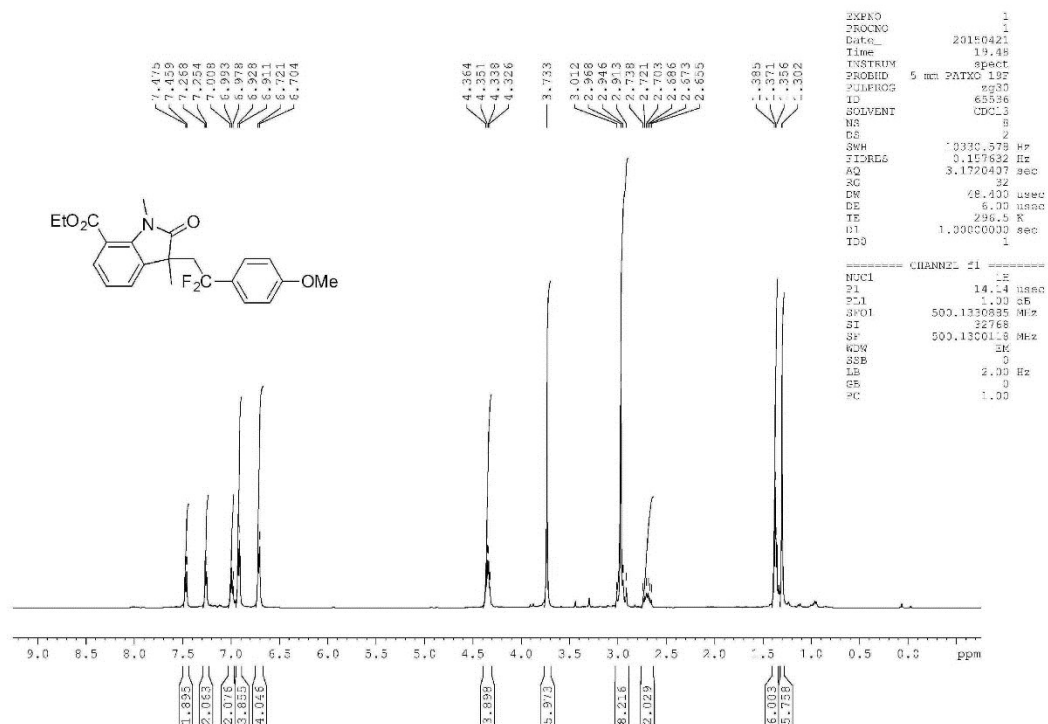
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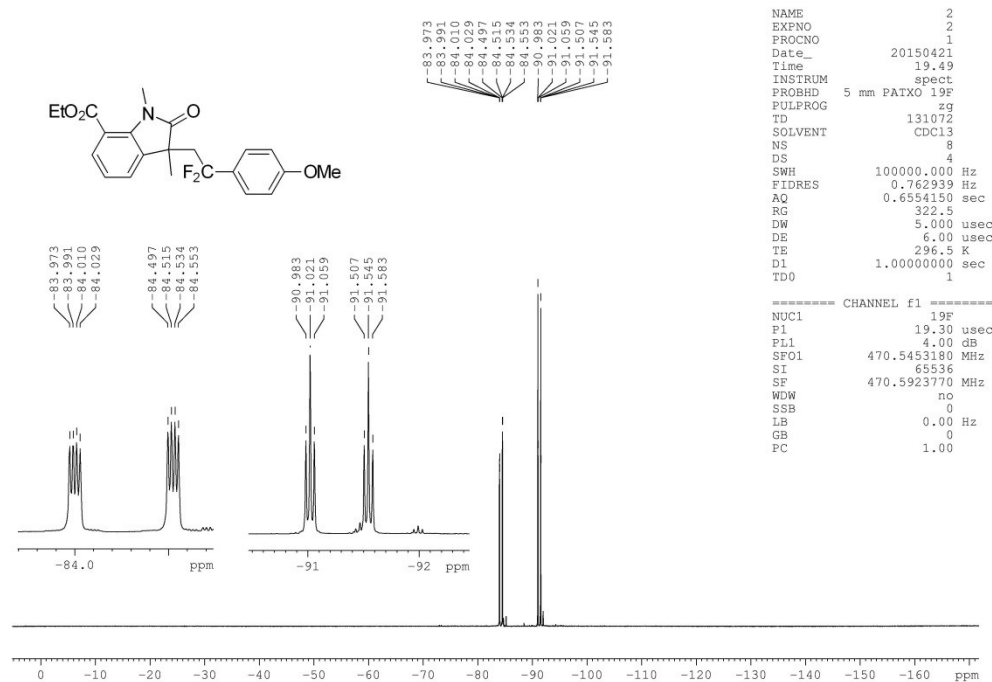
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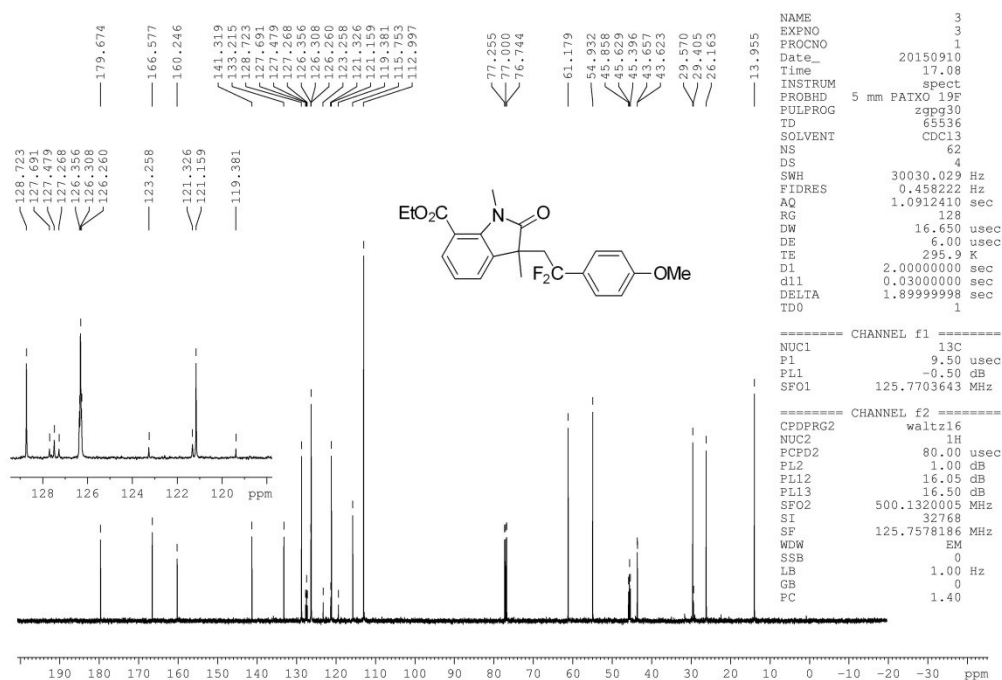
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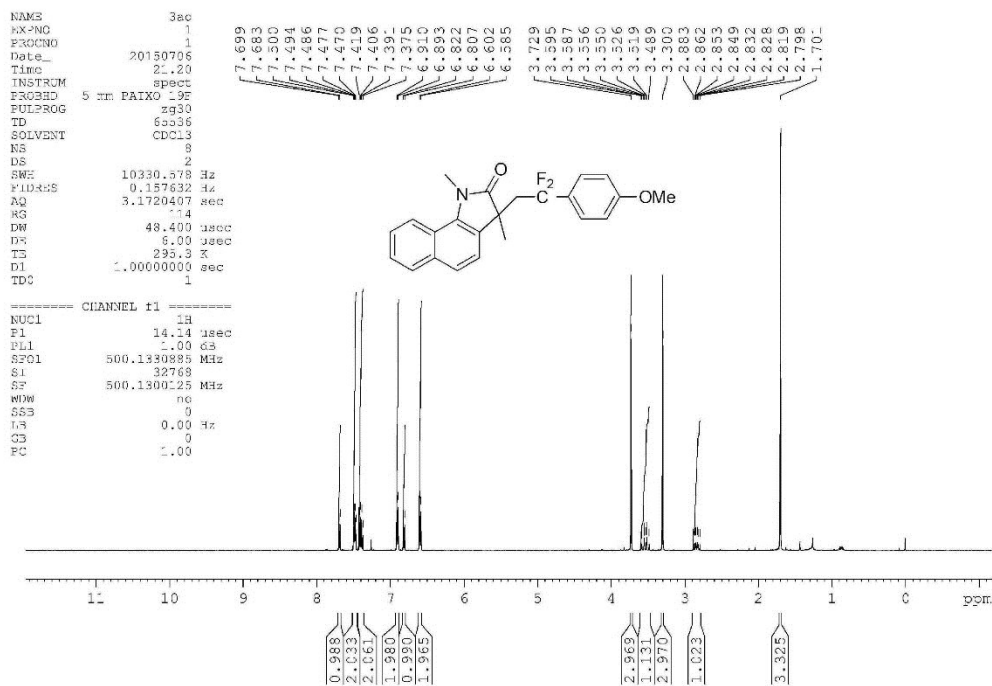
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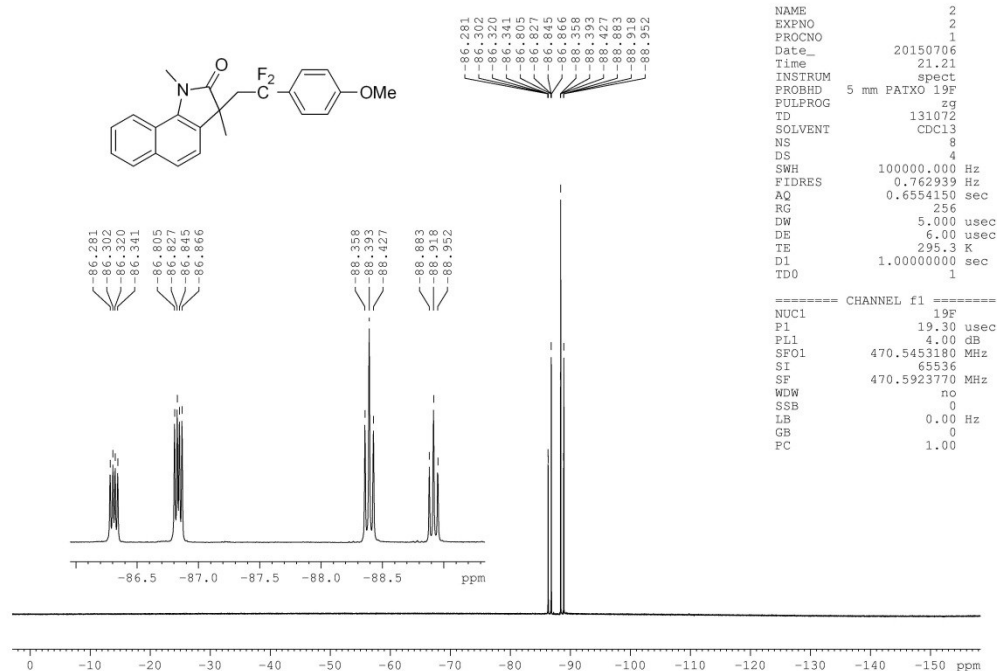
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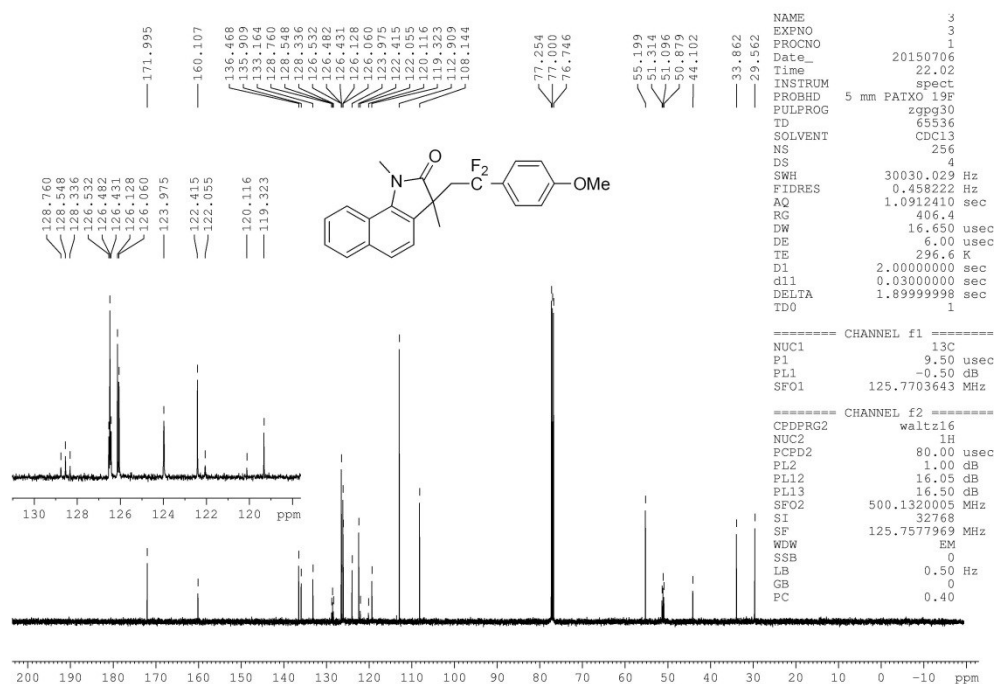
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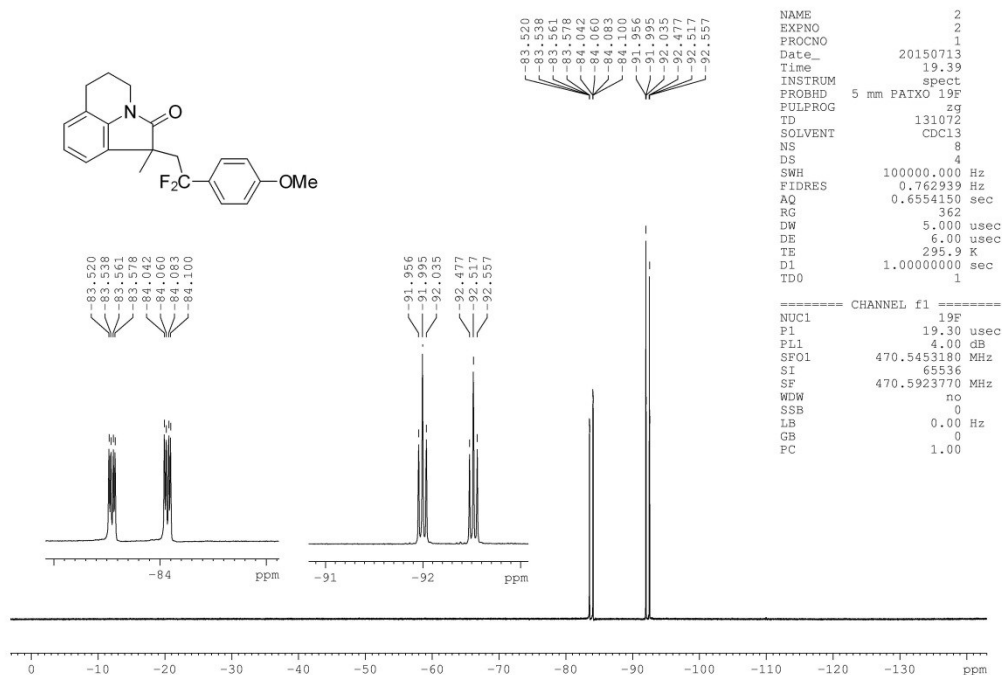
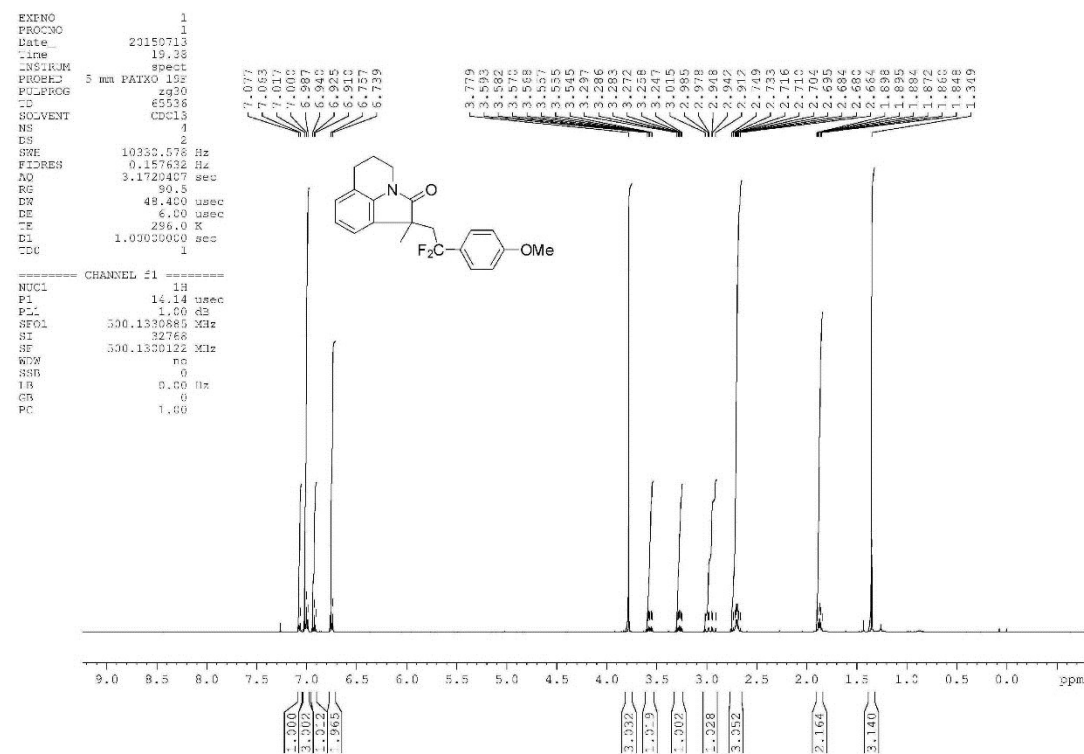


¹⁹F NMR Spectra of 3ap

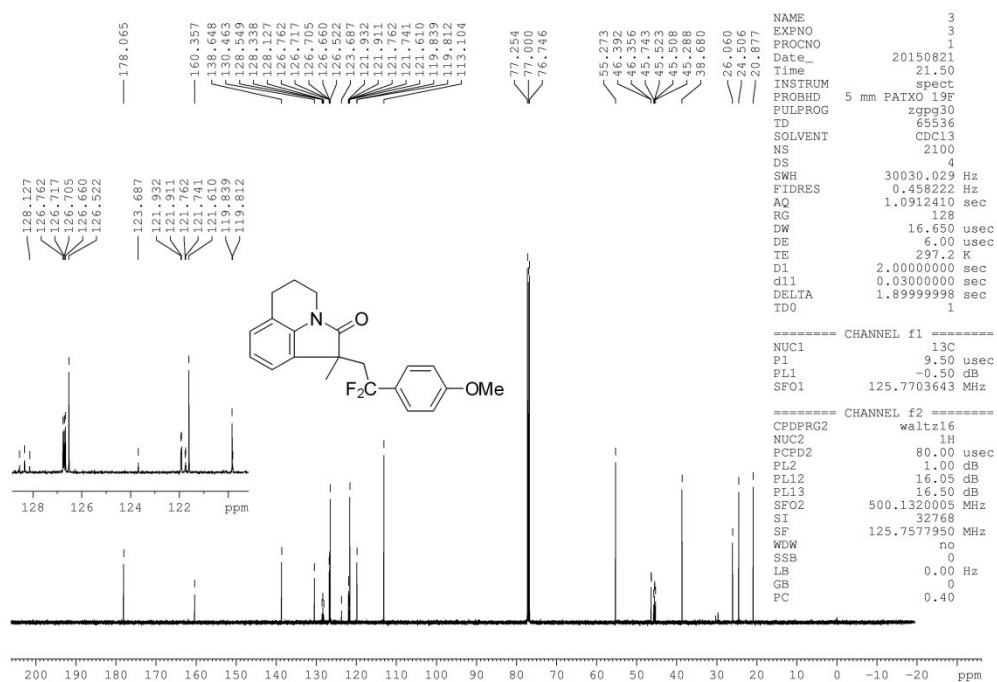


¹³C NMR Spectra of 3ap

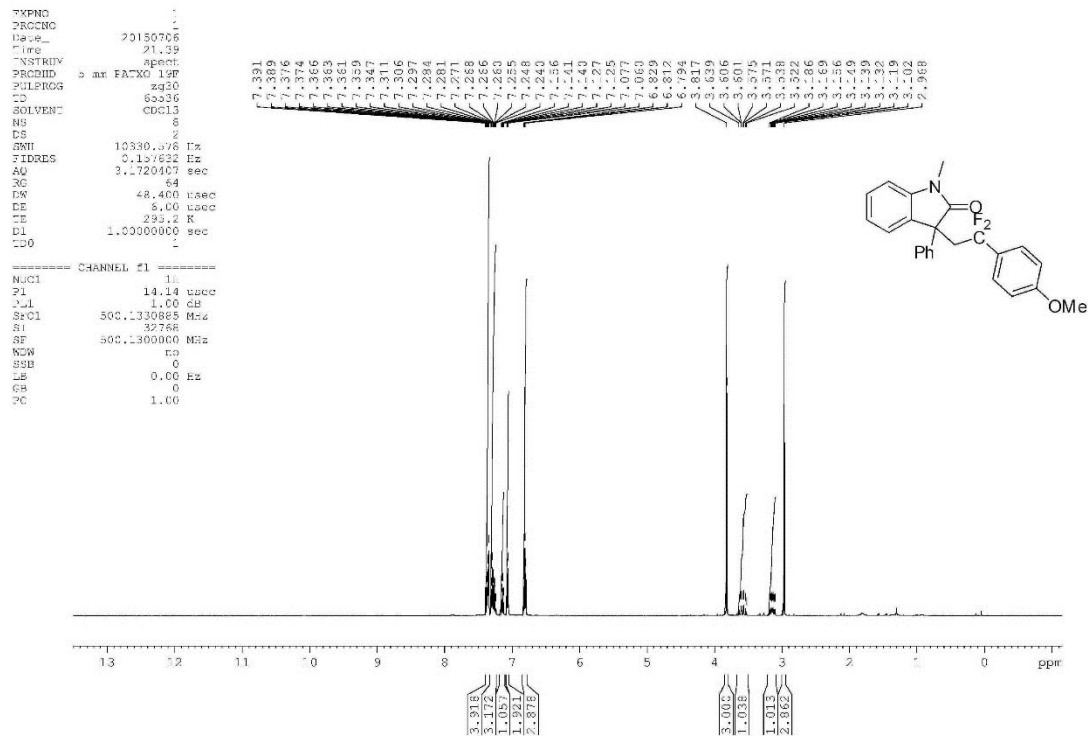




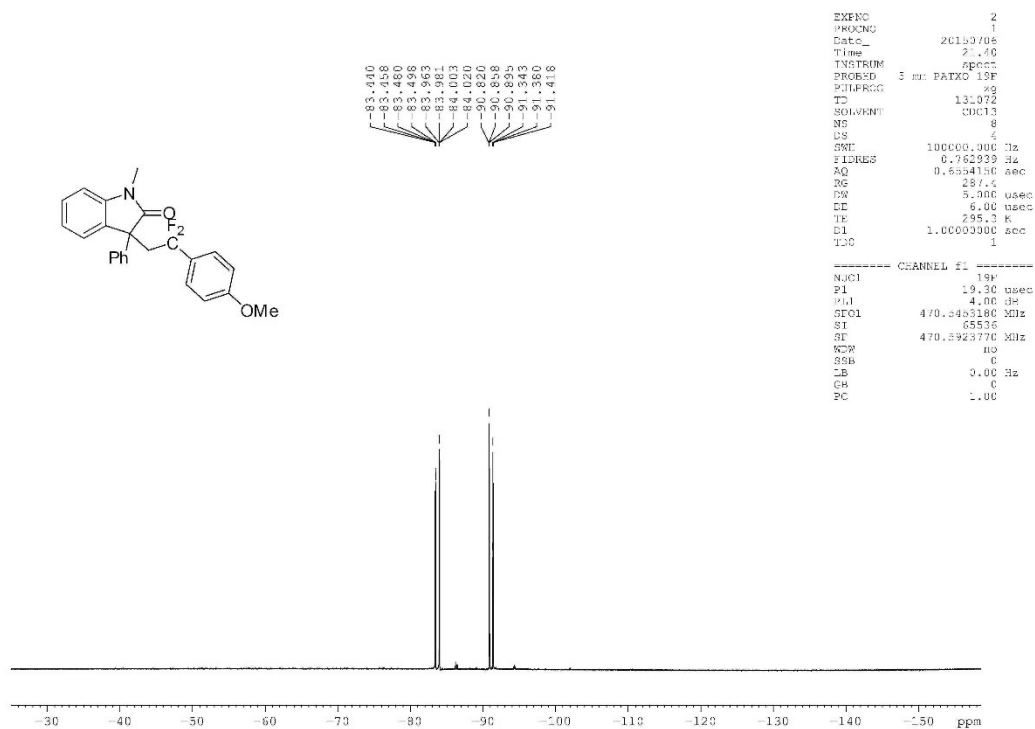
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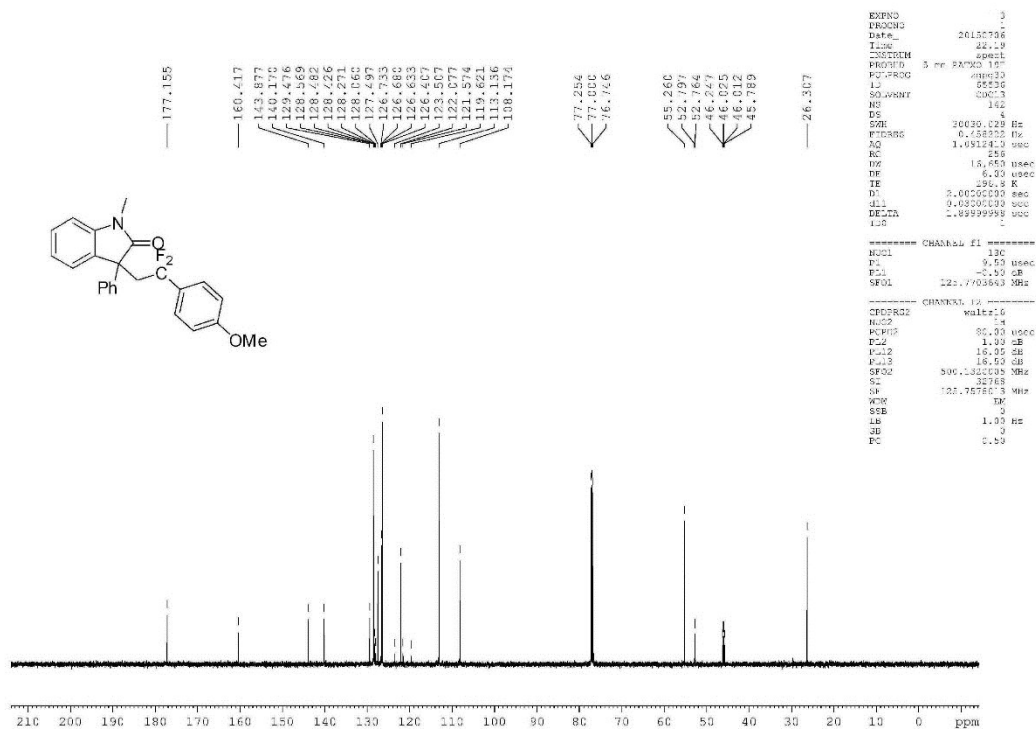
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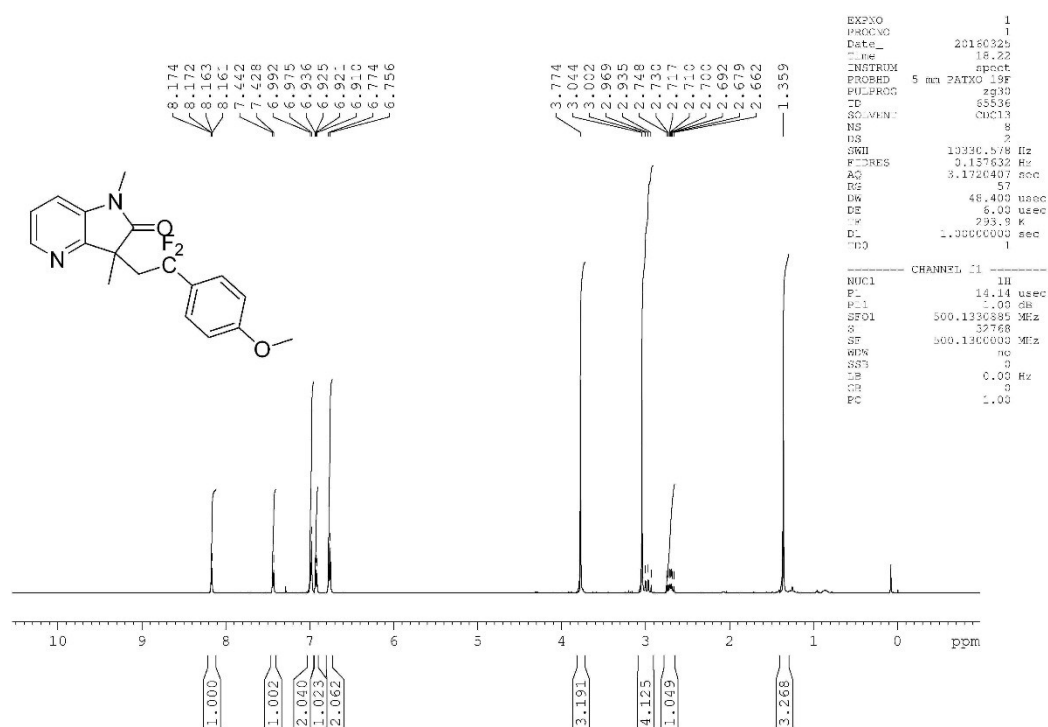
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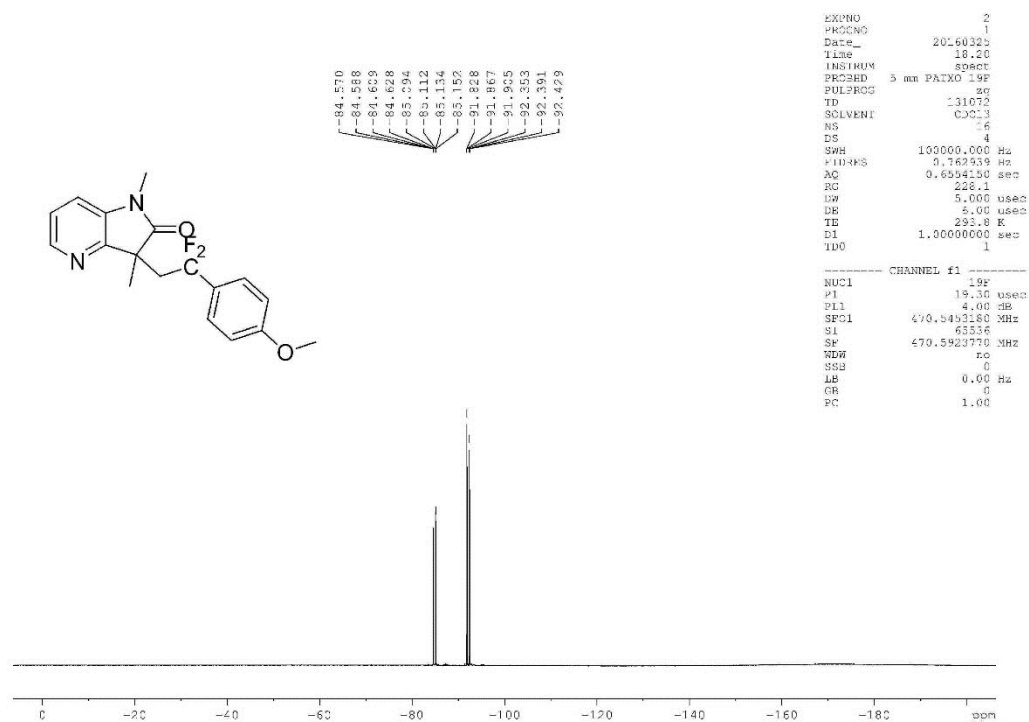
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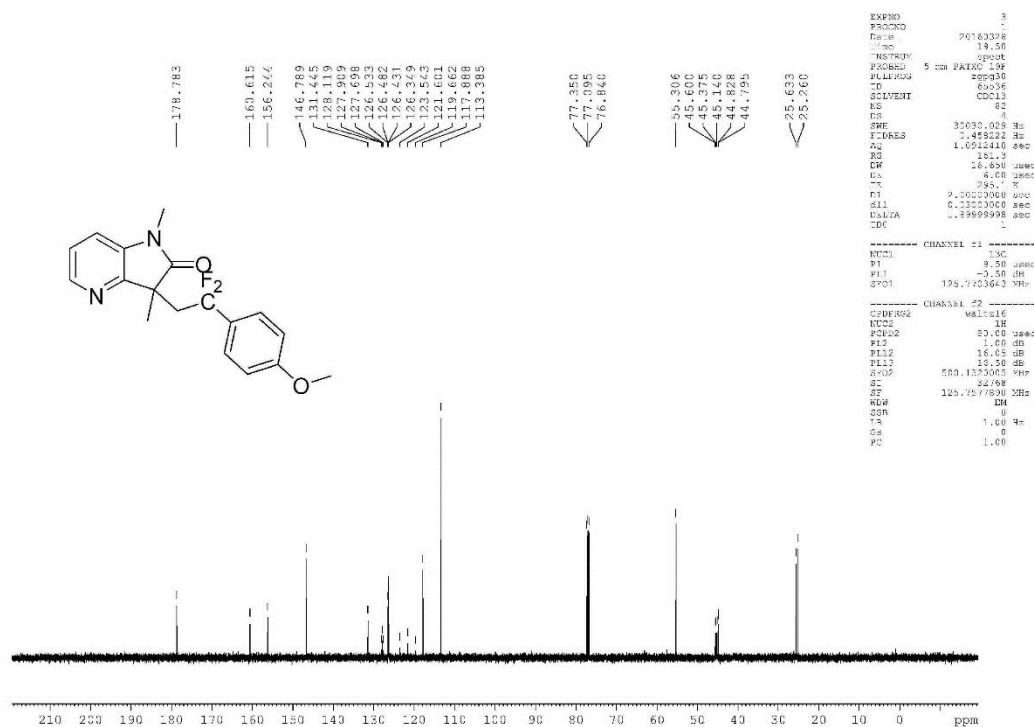
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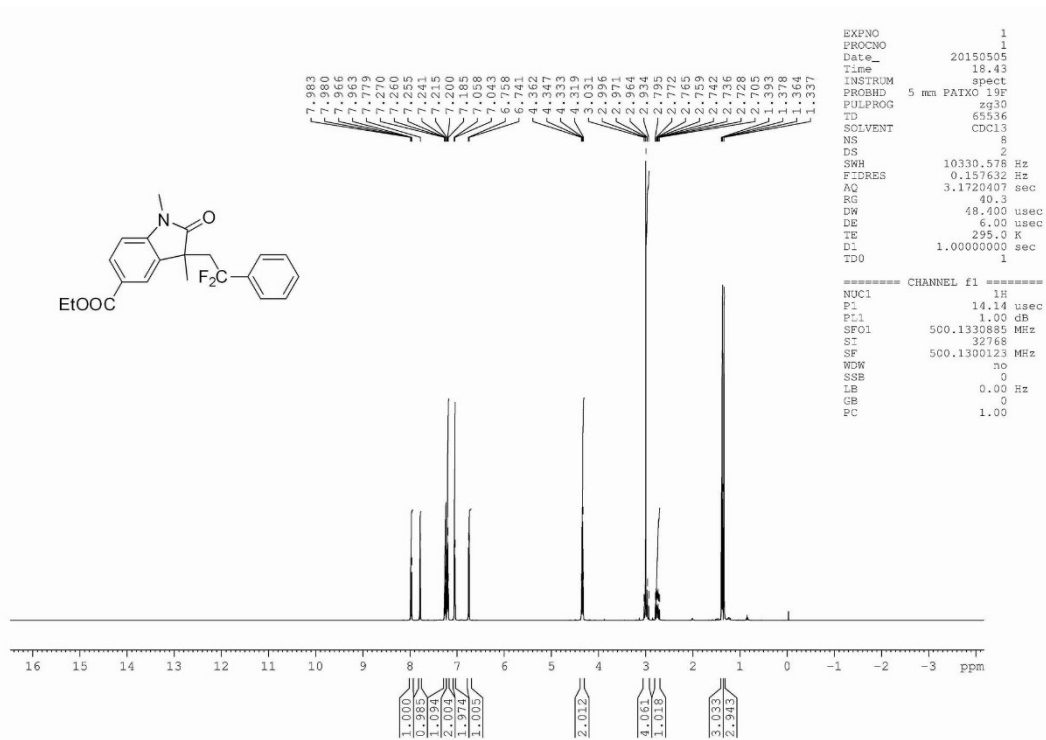
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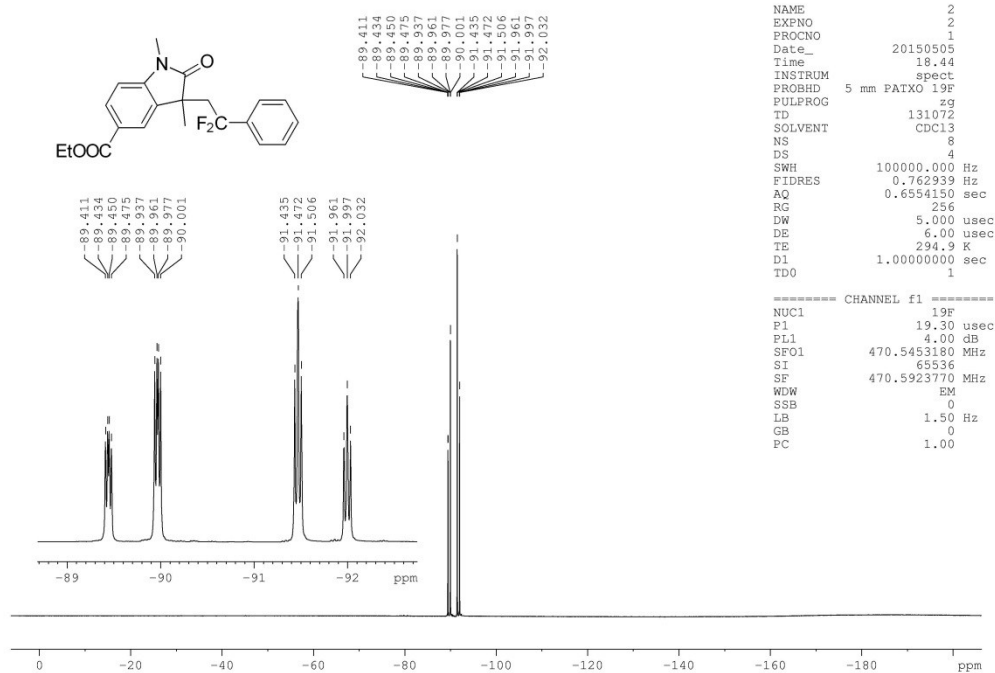
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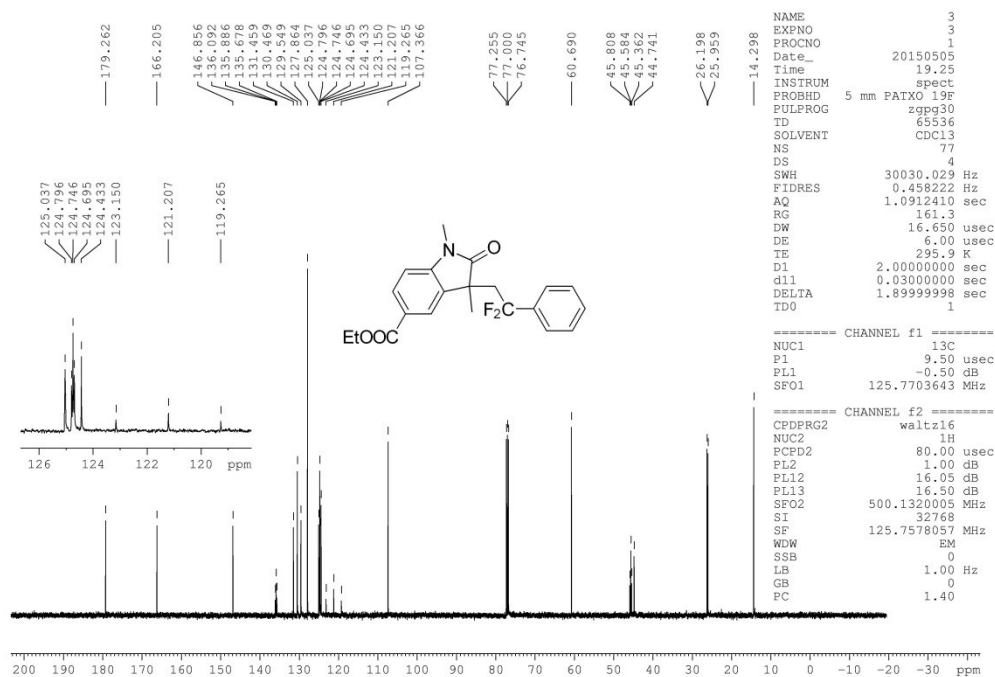
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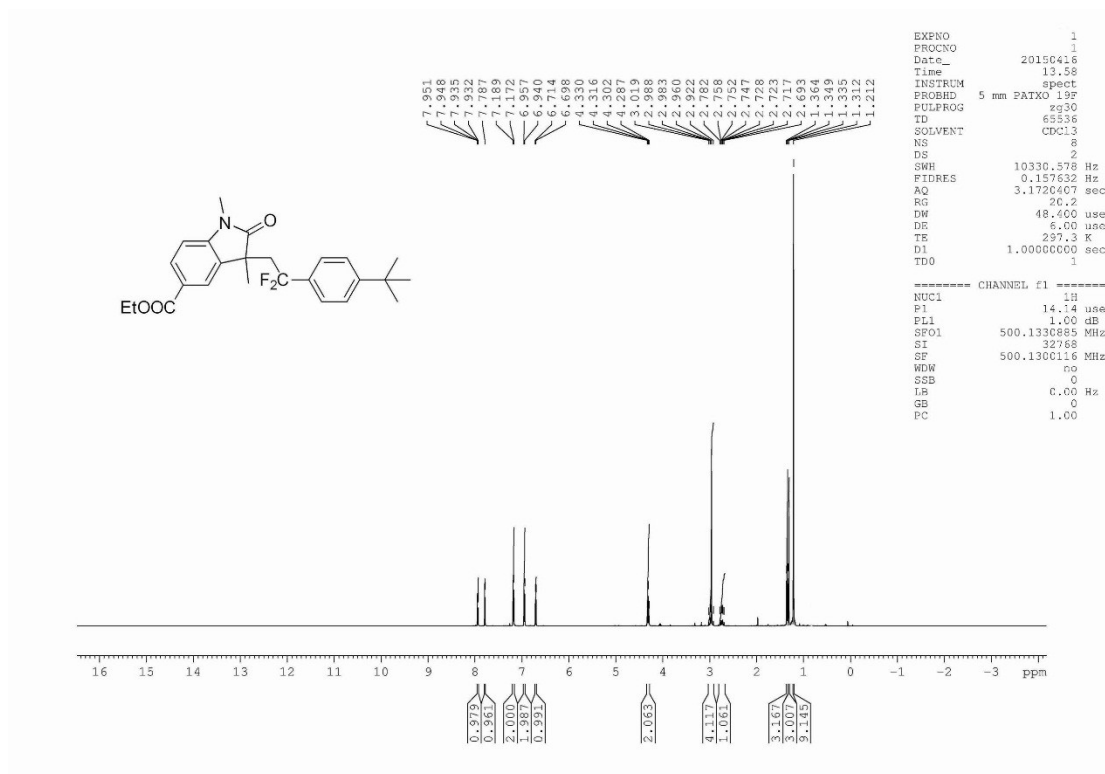
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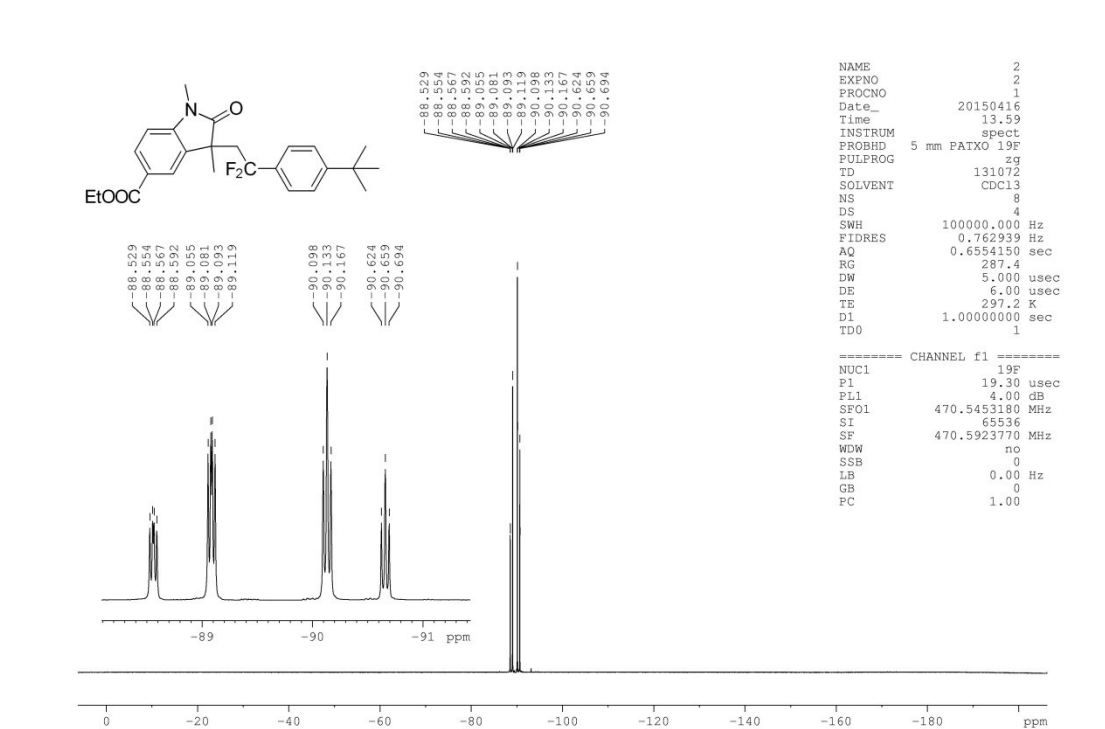
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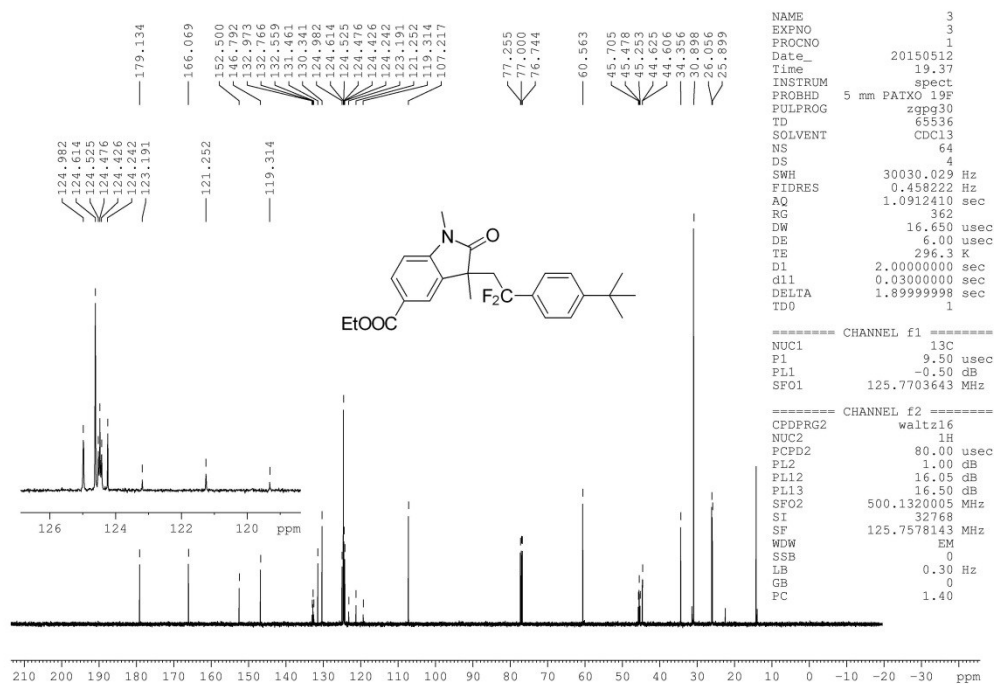
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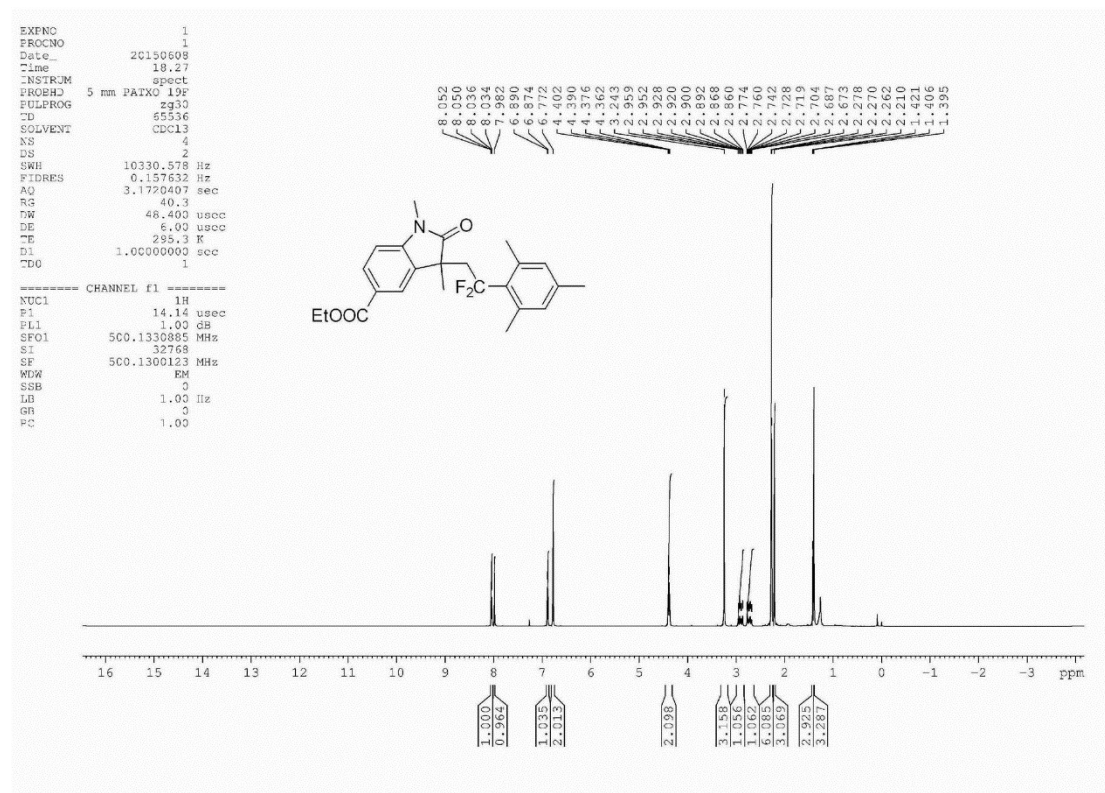
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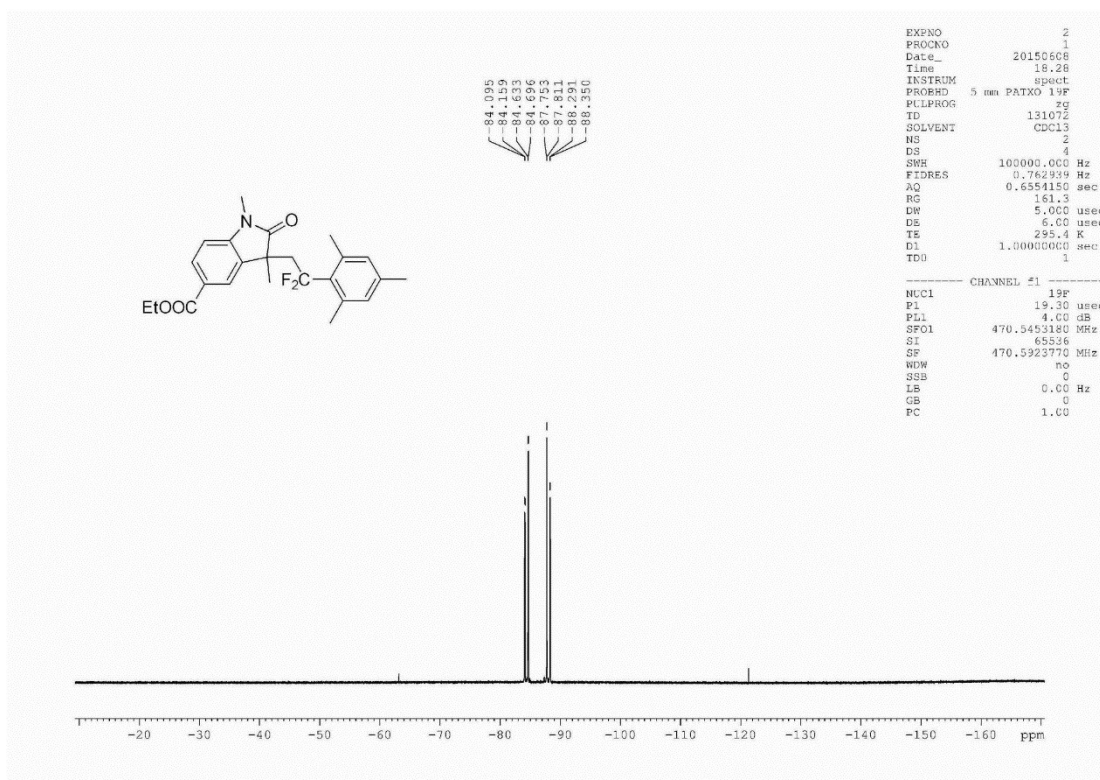
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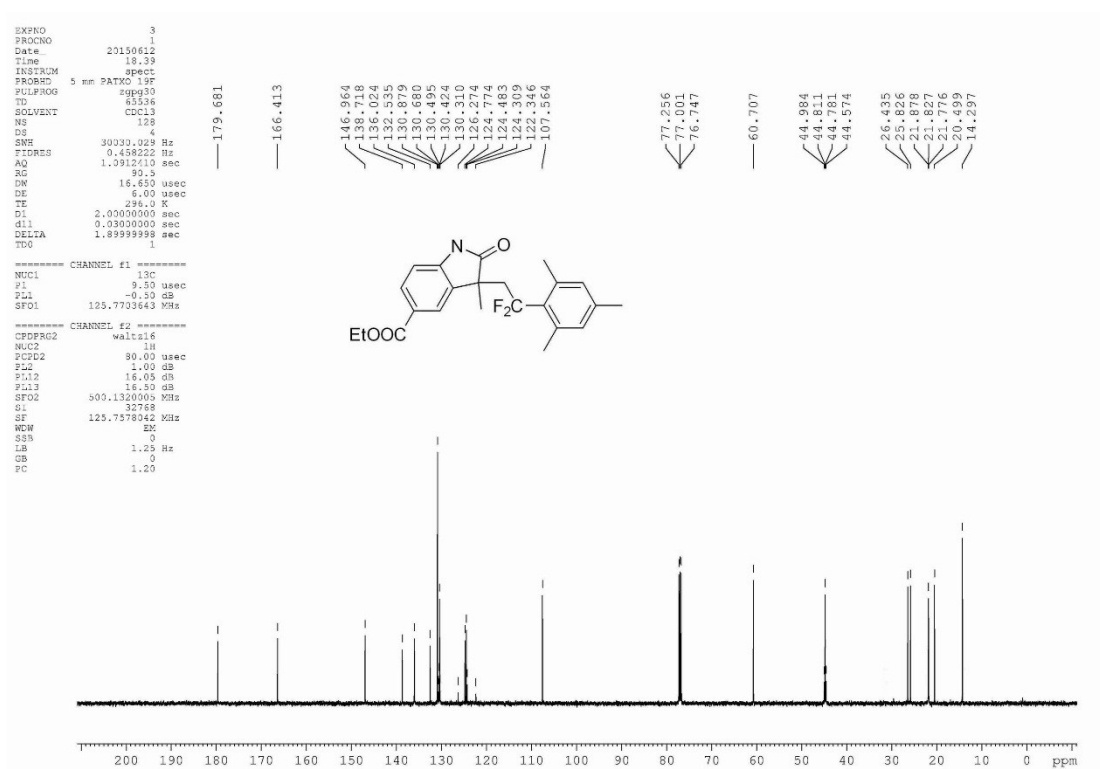
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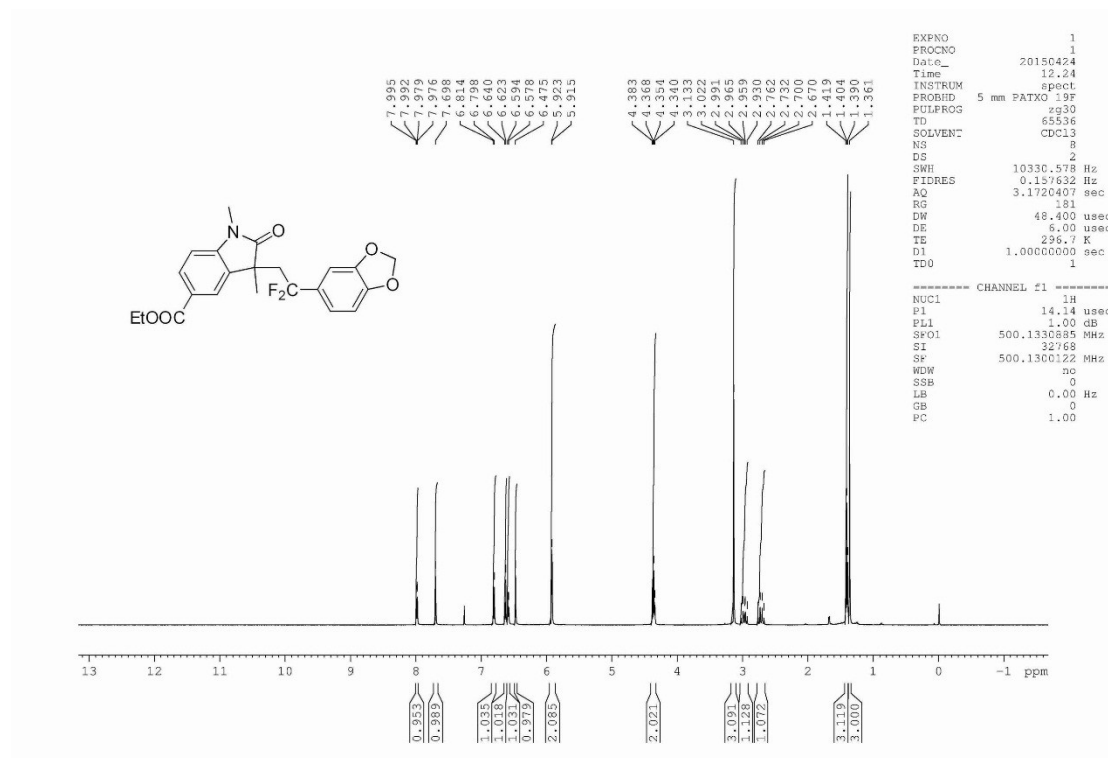
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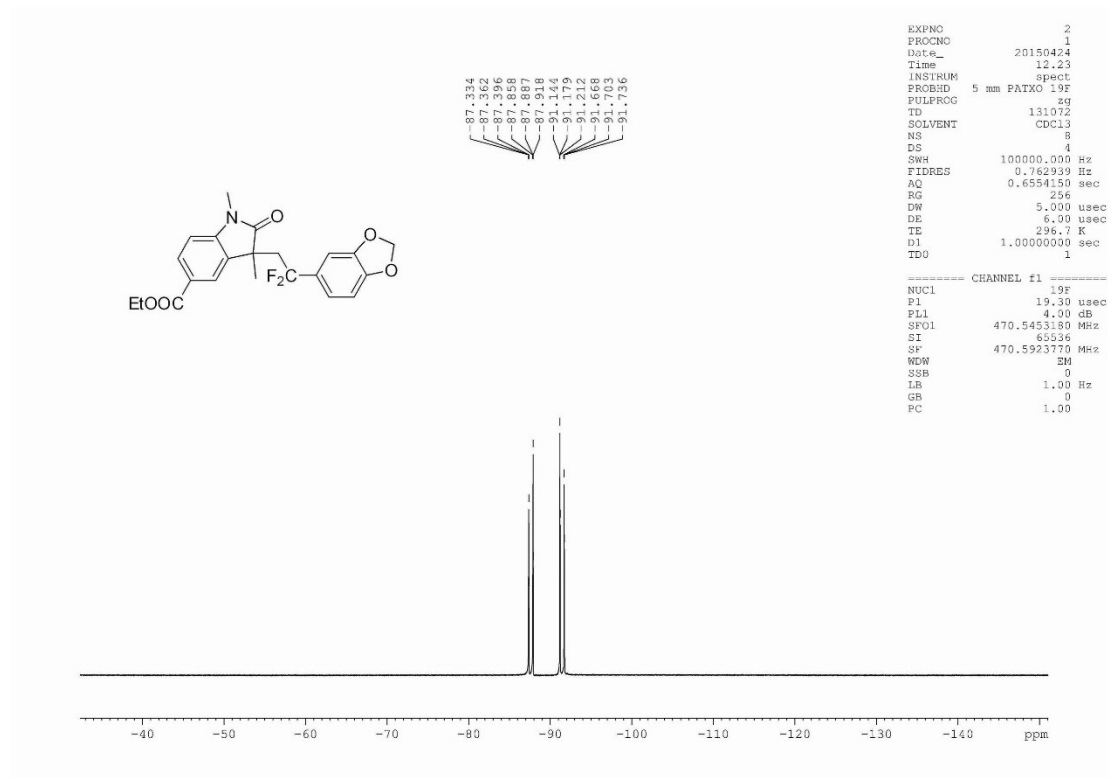
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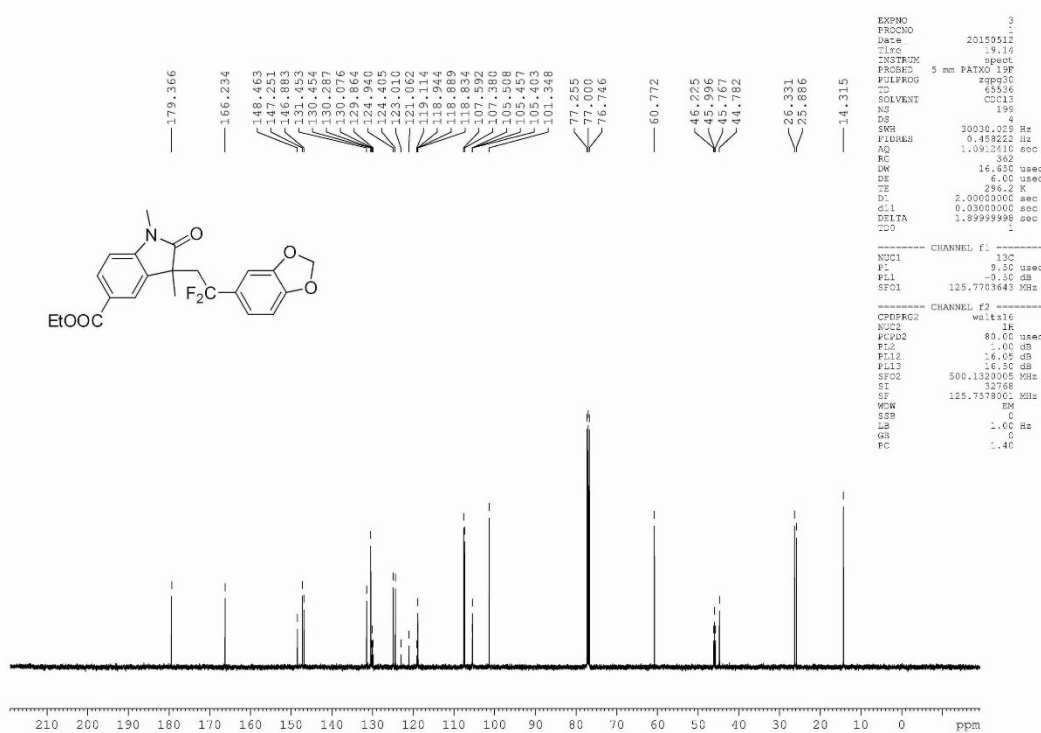
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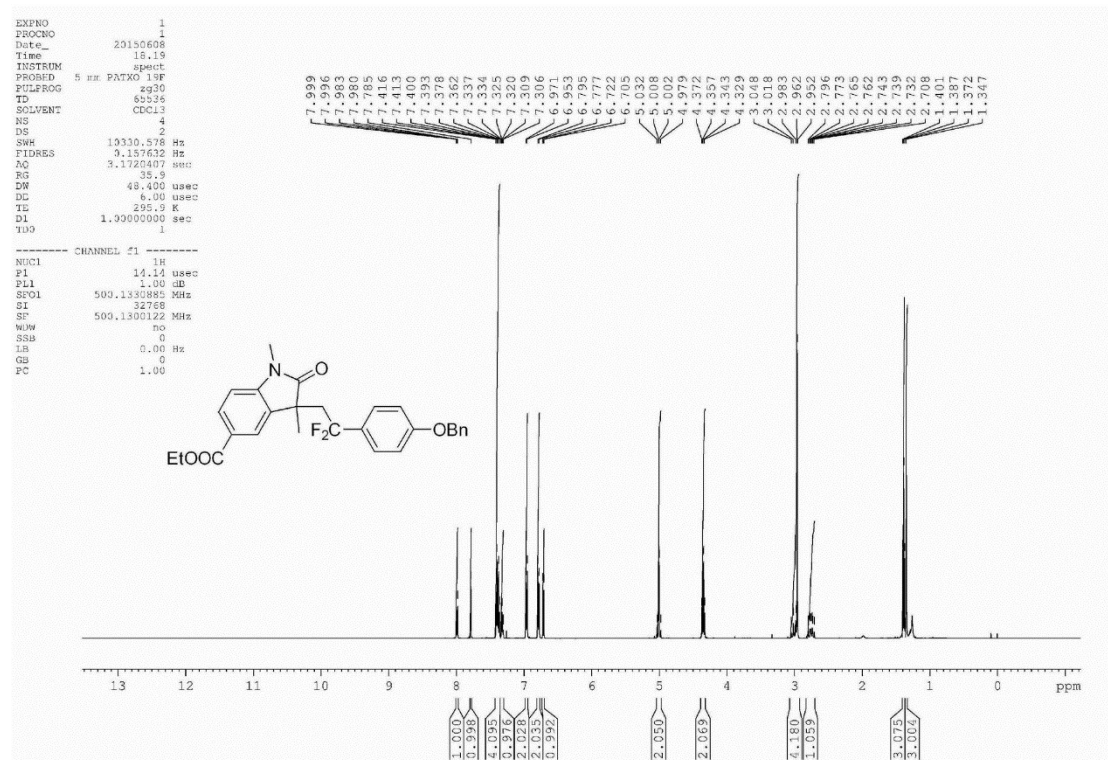
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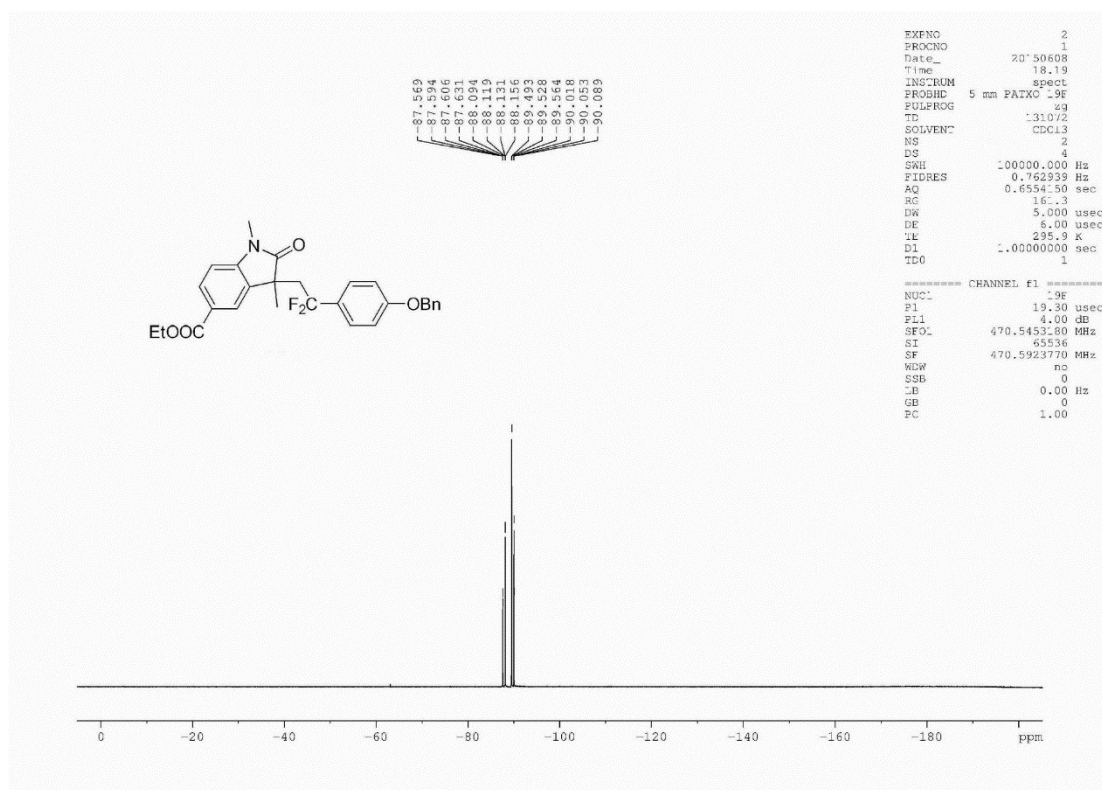
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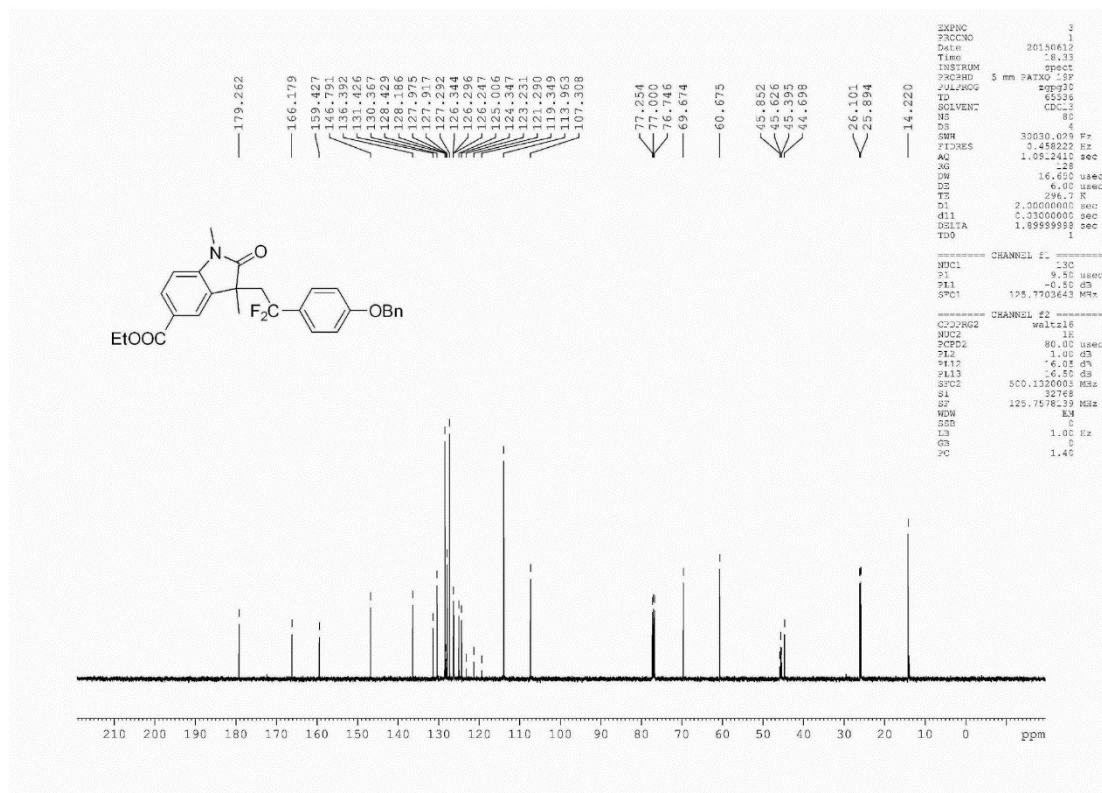
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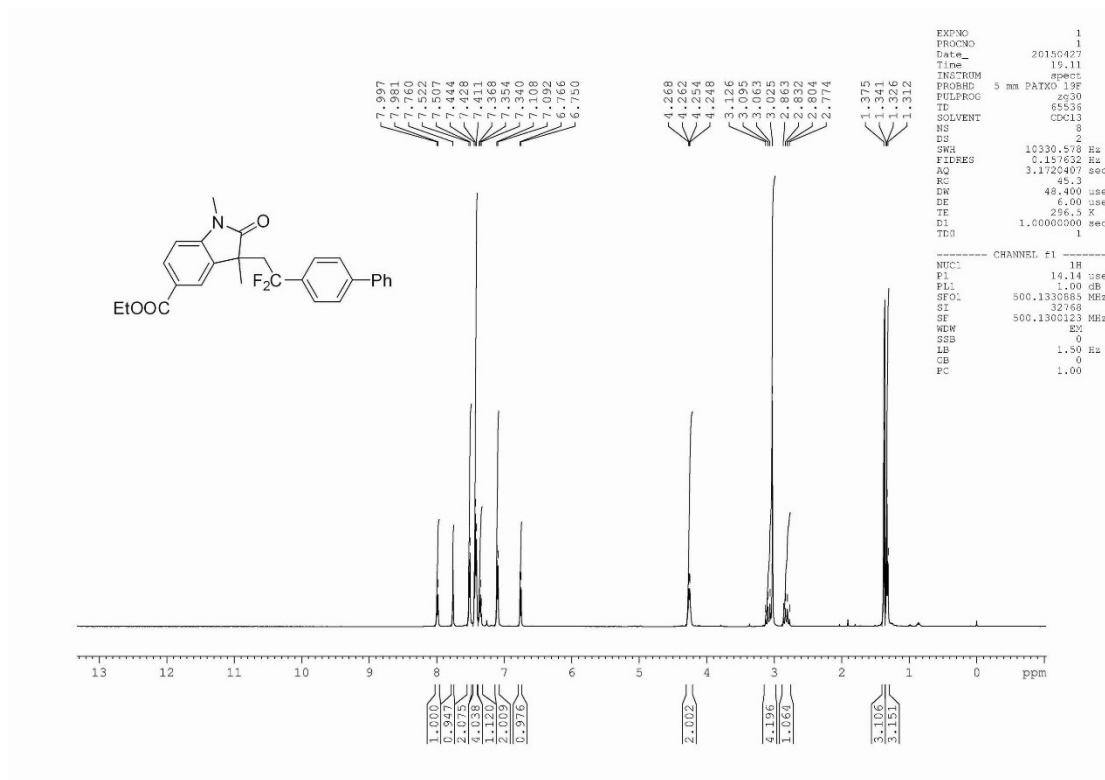
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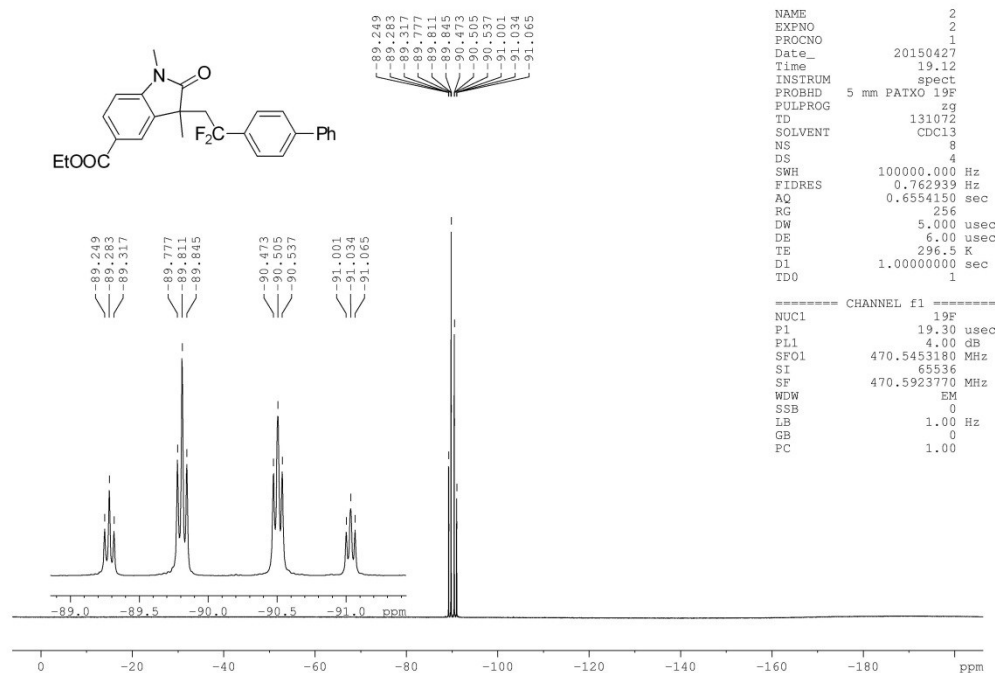
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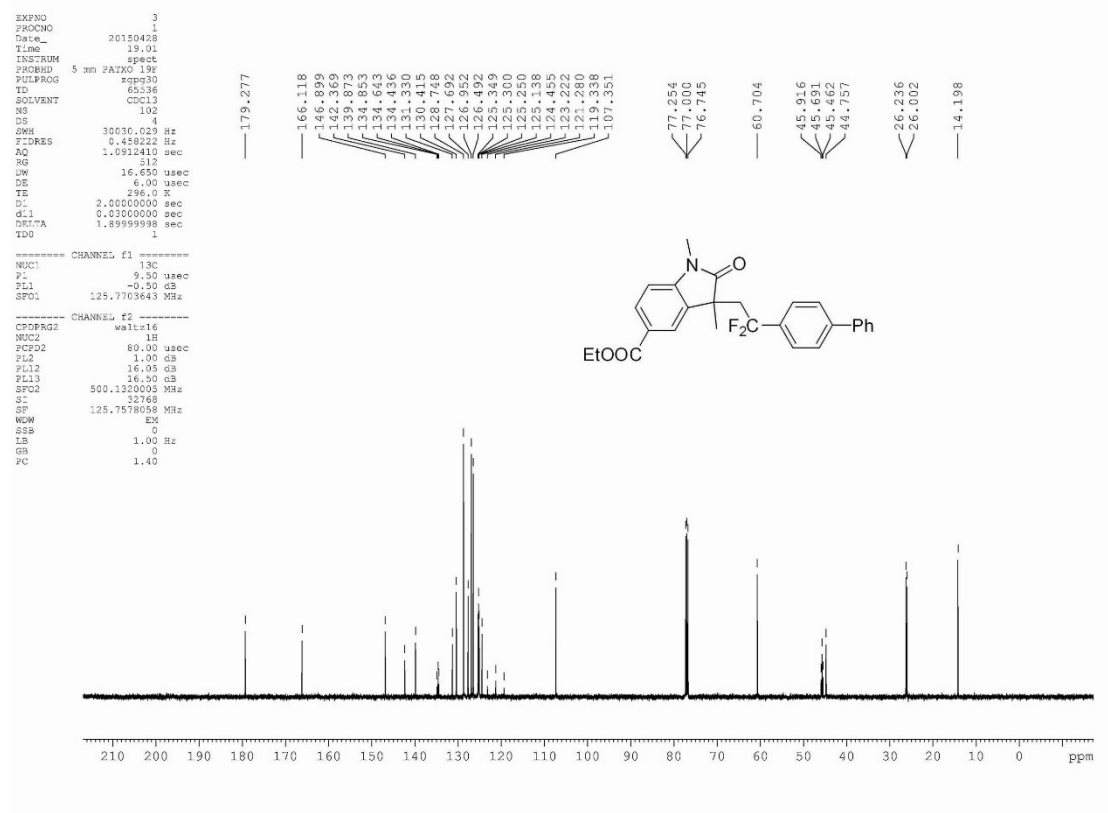
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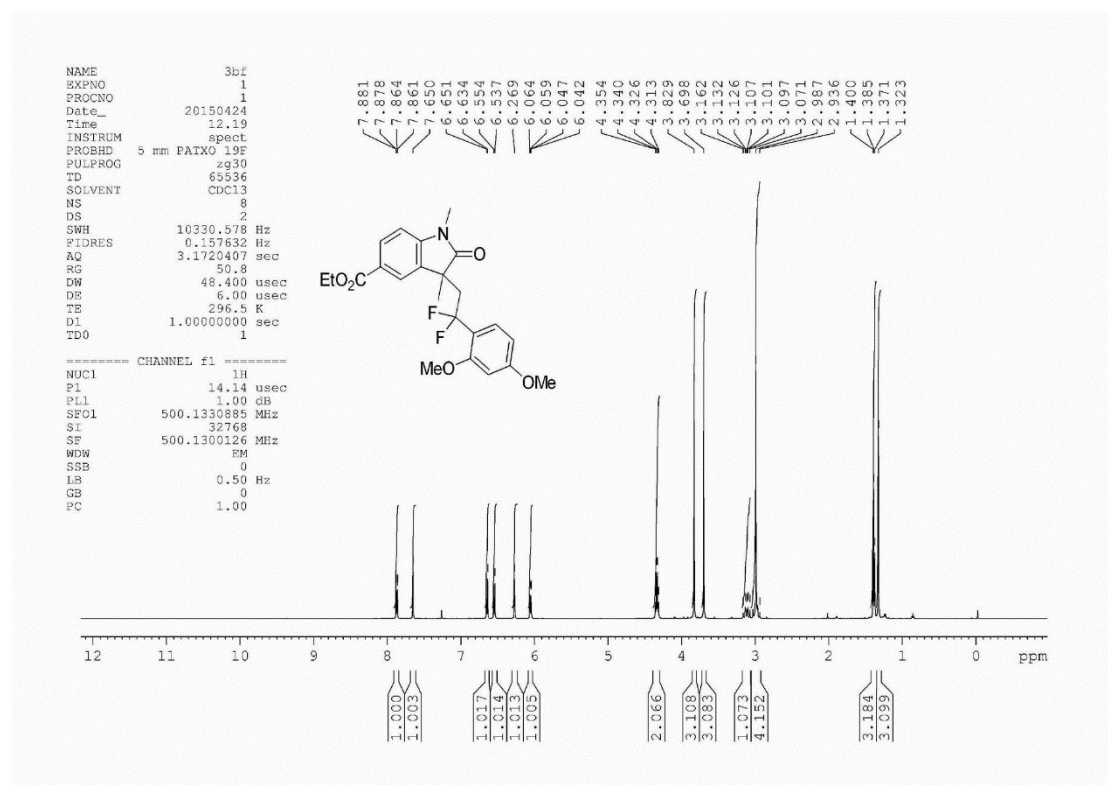
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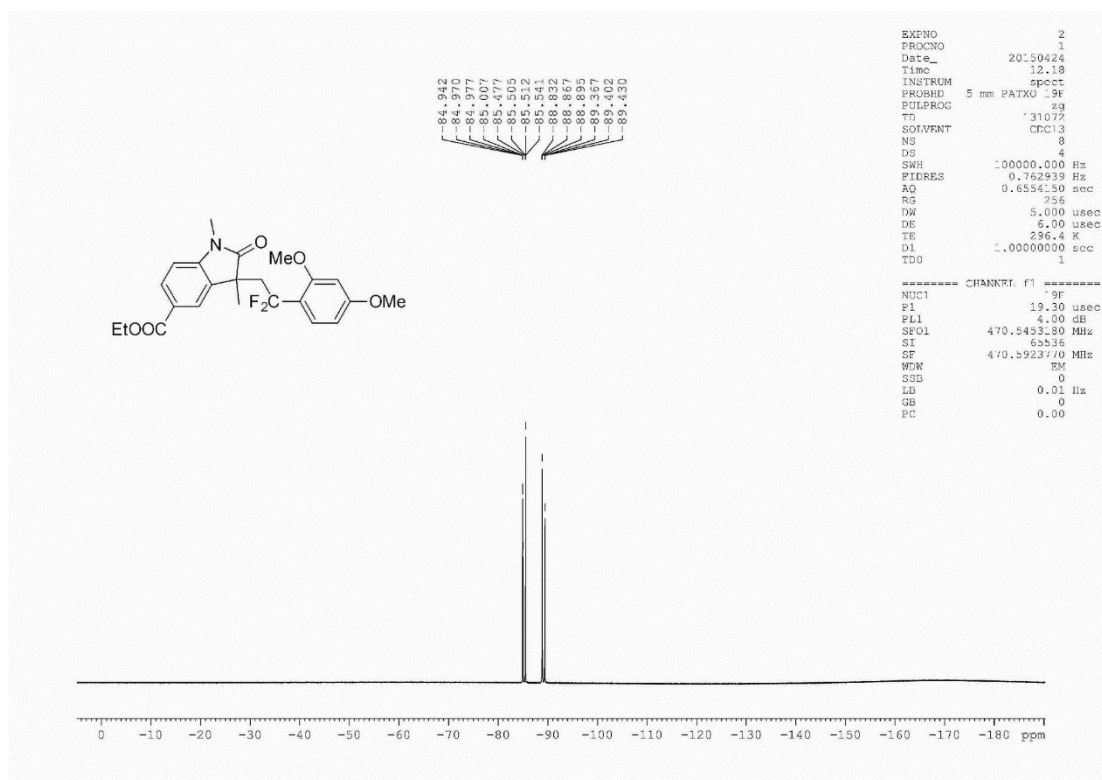
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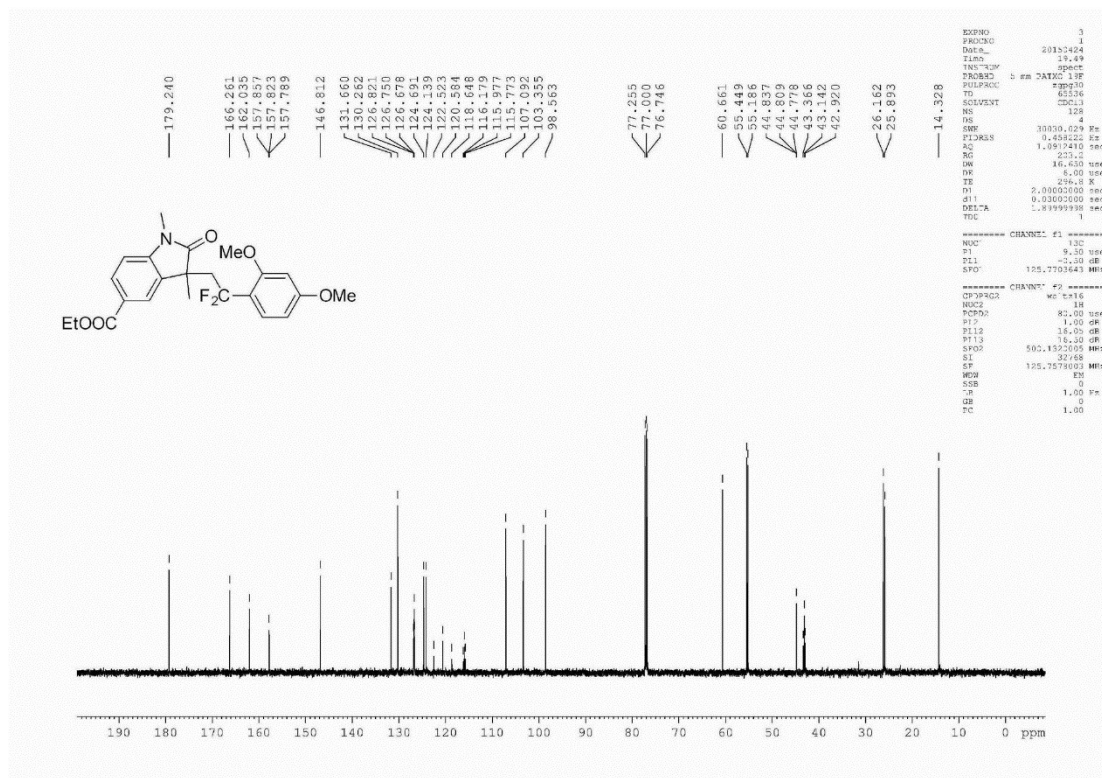
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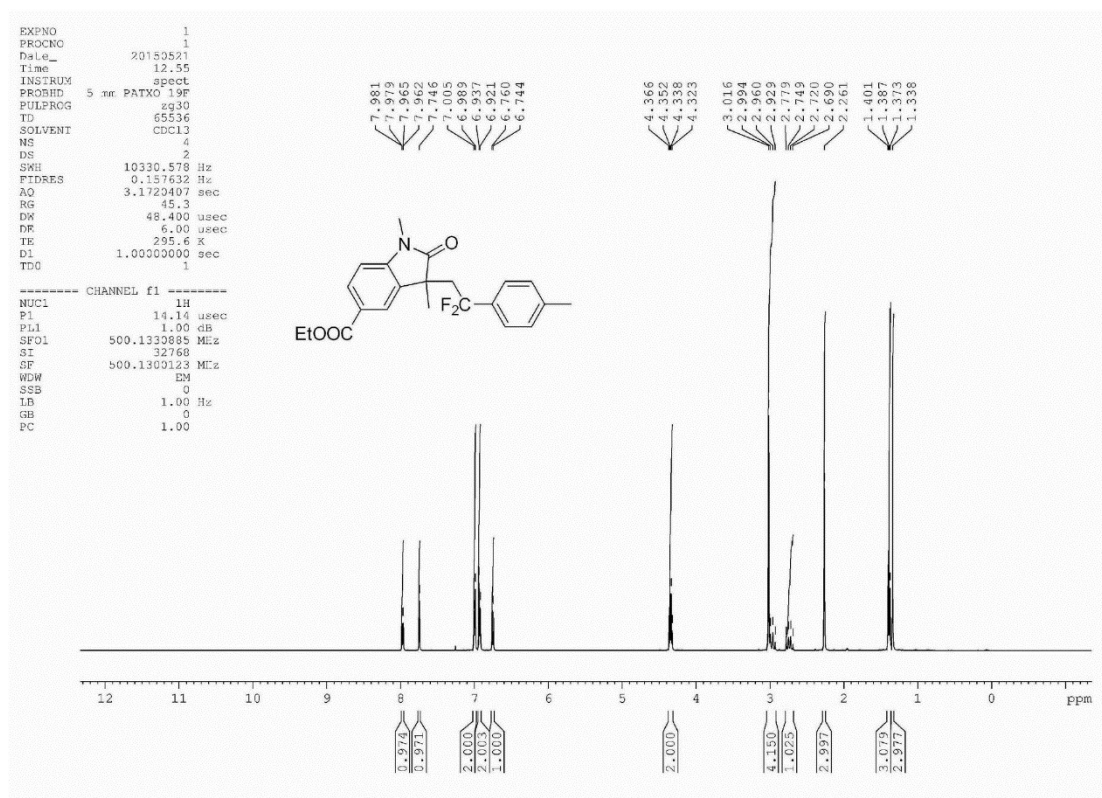
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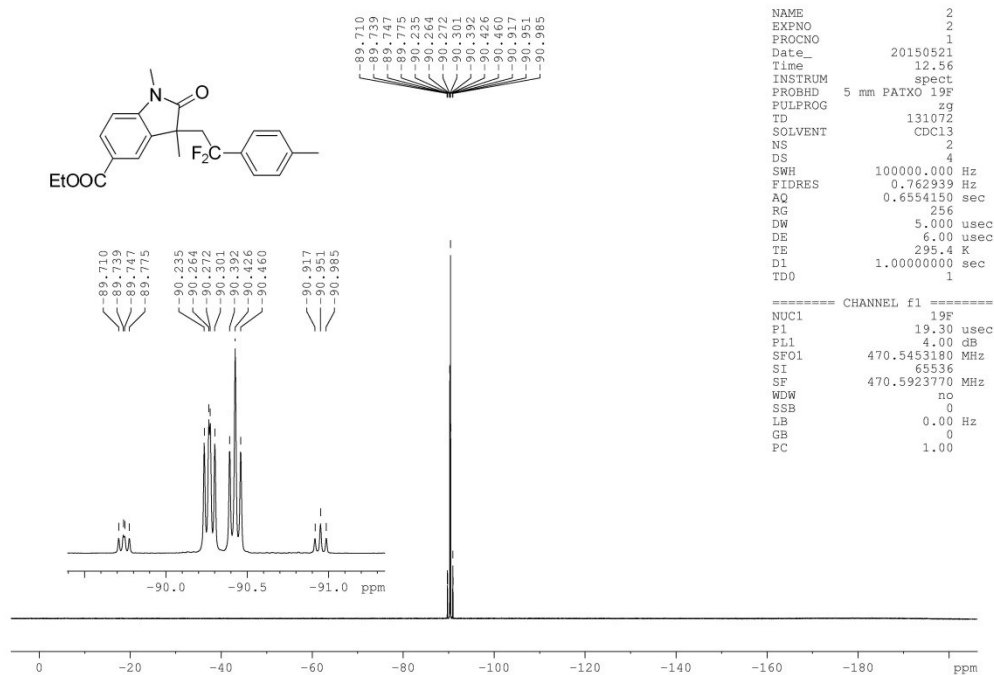
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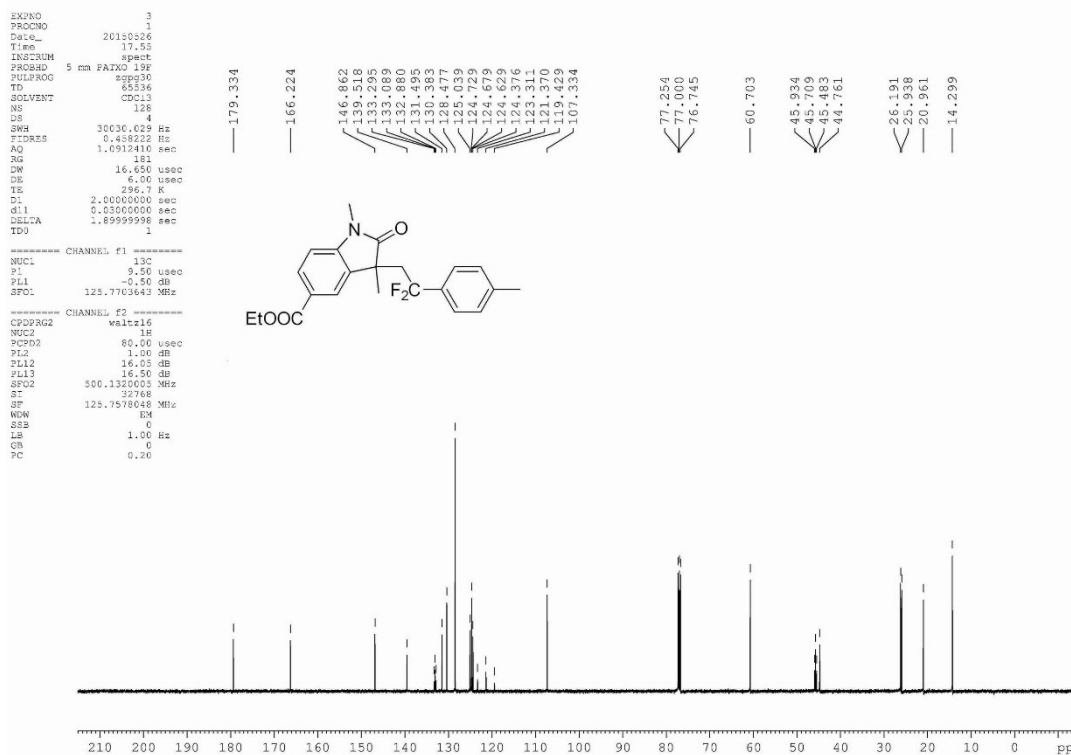
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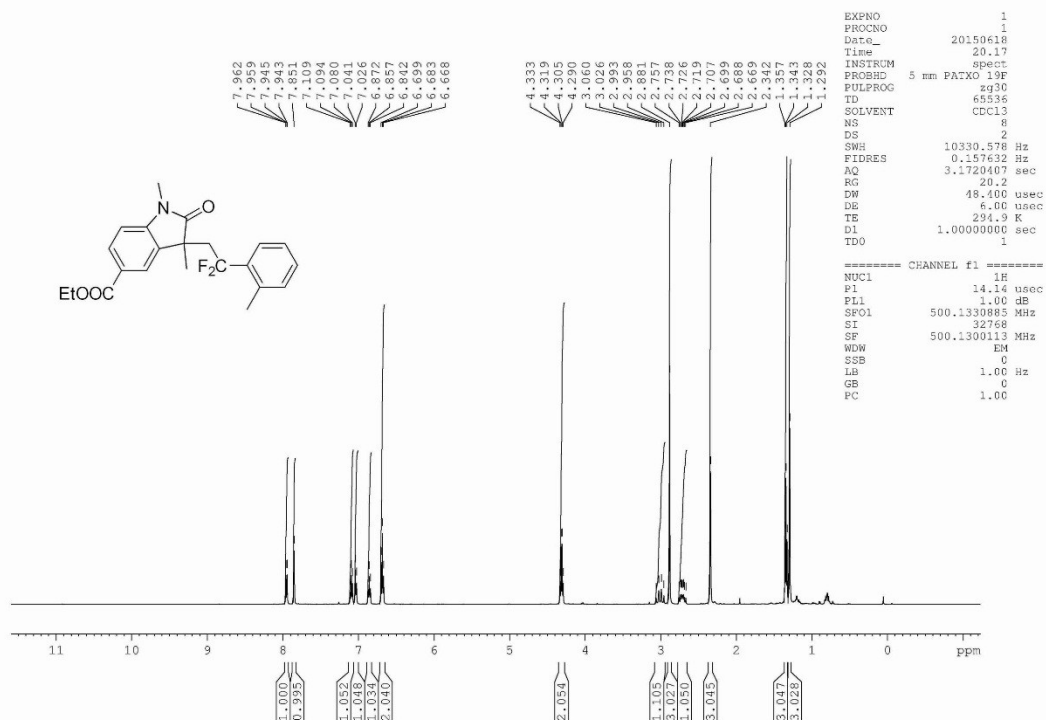
¹⁹F NMR Spectra of 3ih



¹³C NMR Spectra of 3ih



¹H NMR Spectra of 3jh



Chemical Structure:

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Acquisition Parameters:

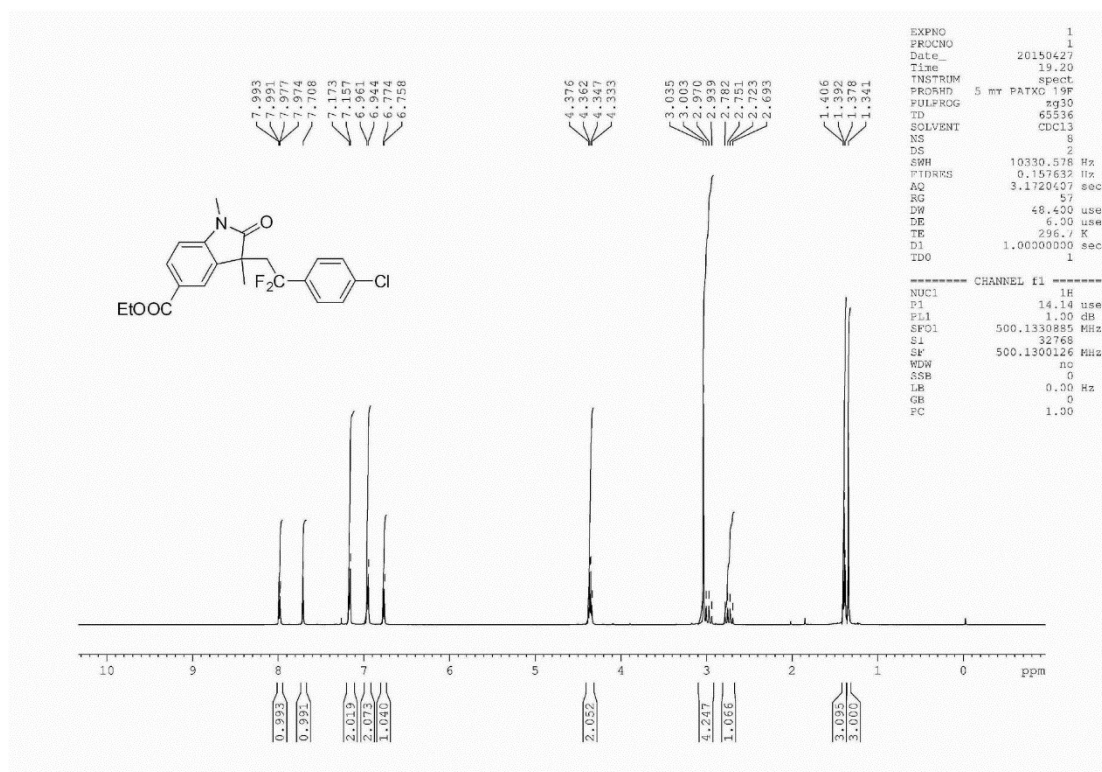
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PULPROG	zg
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SOLVENT	CDCl3
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DS	4
SWH	100000.000 Hz
FIDRES	0.762939 Hz
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DE	6.00 usec
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DL	1.00000000 sec
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Channel f1:

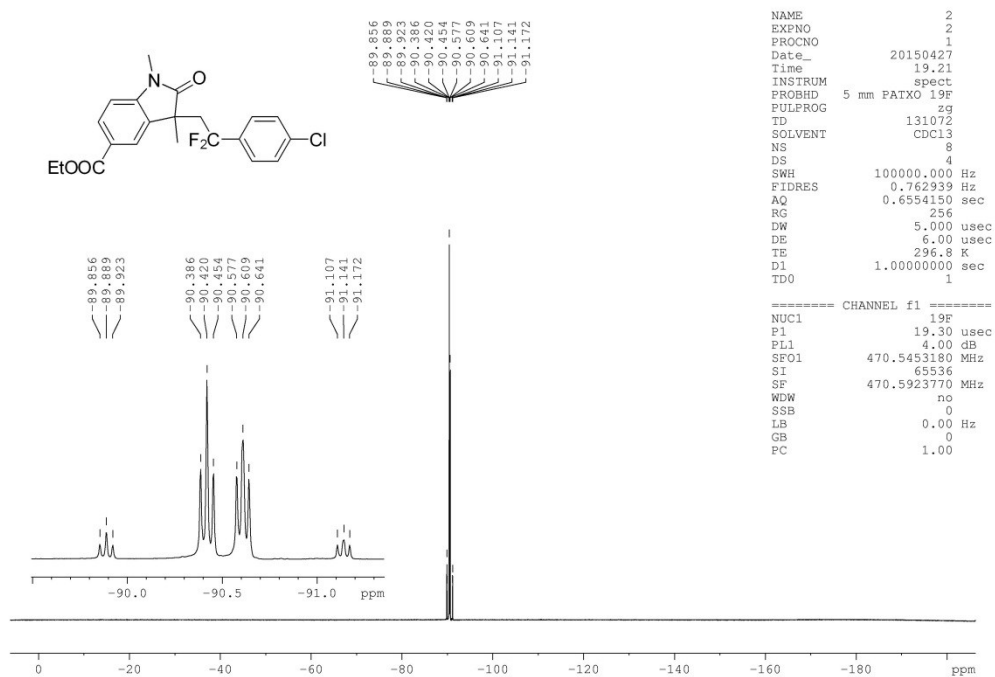
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[illegible]

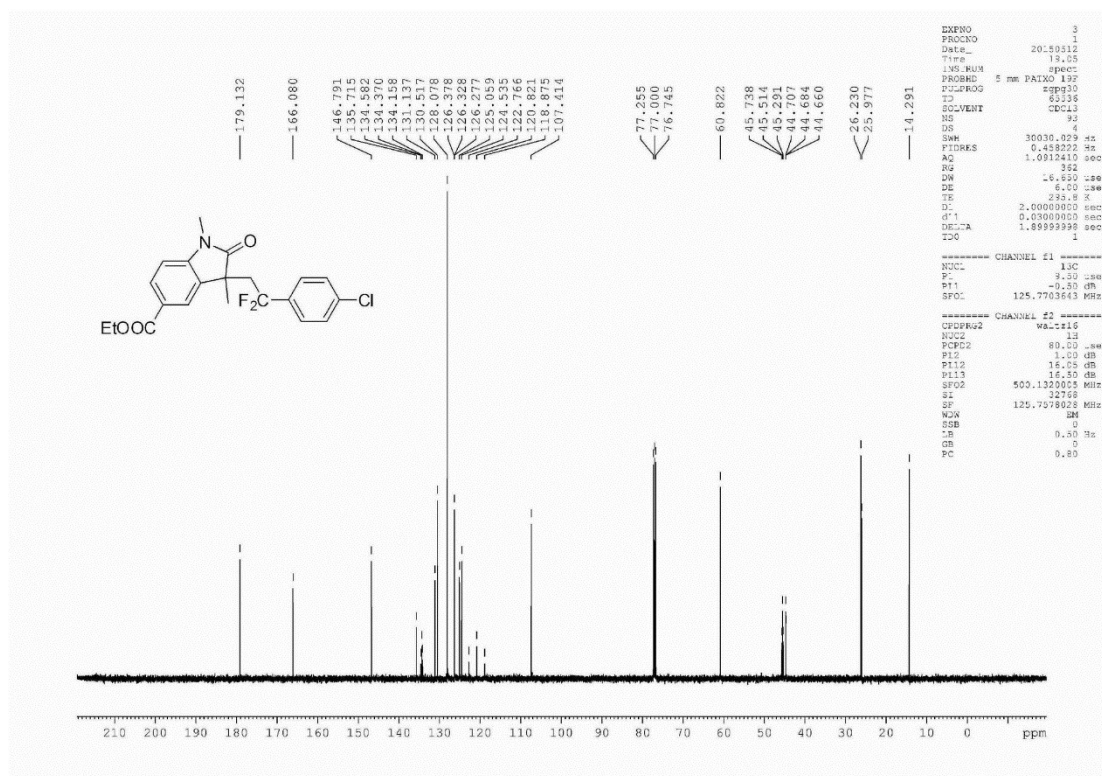
¹H NMR Spectra of 3kh



¹⁹F NMR Spectra of 3kh



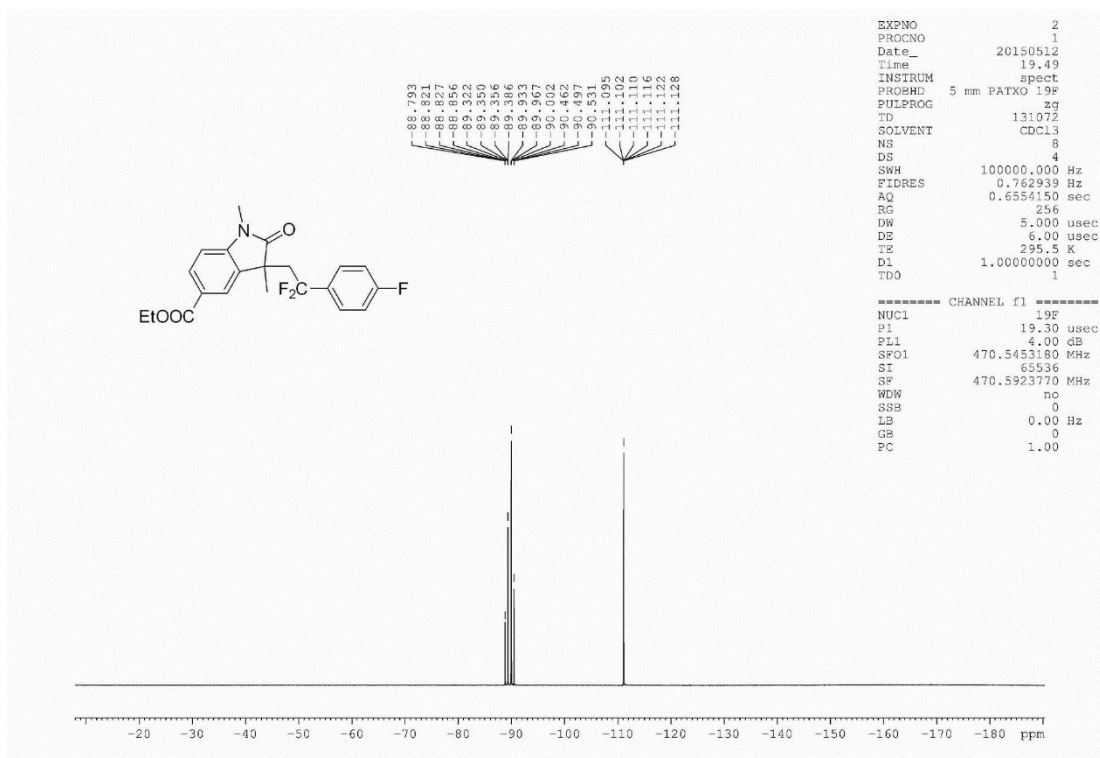
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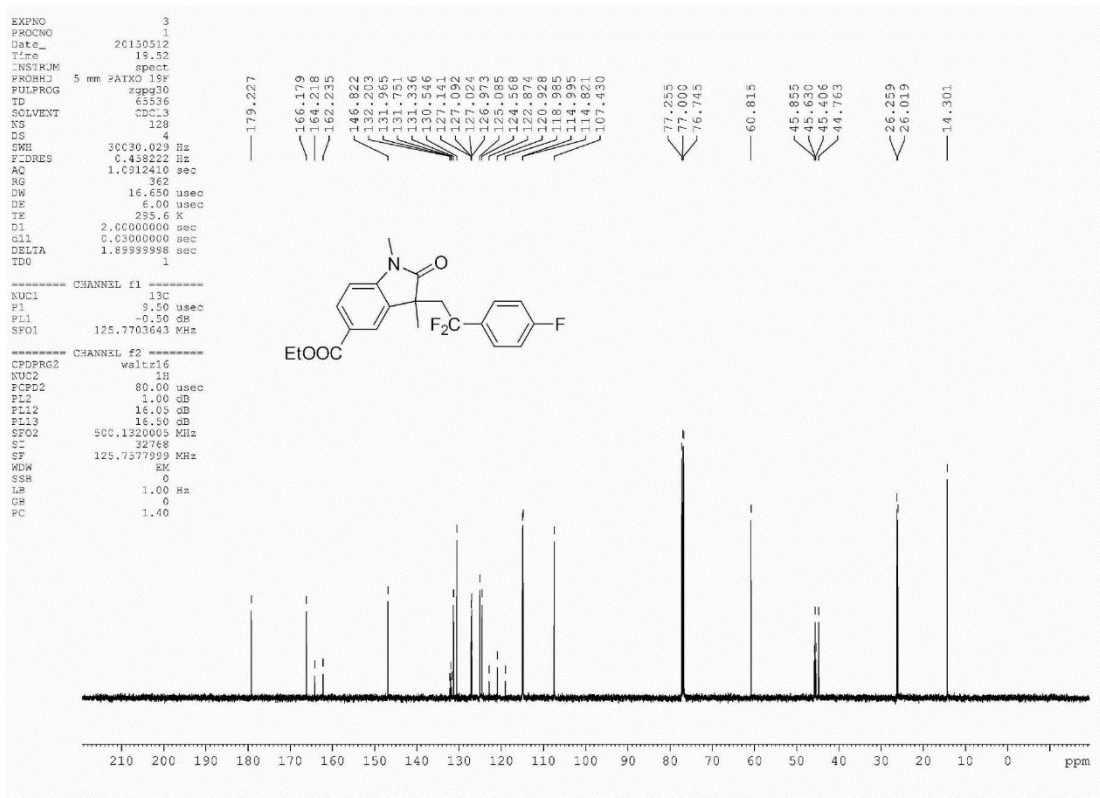
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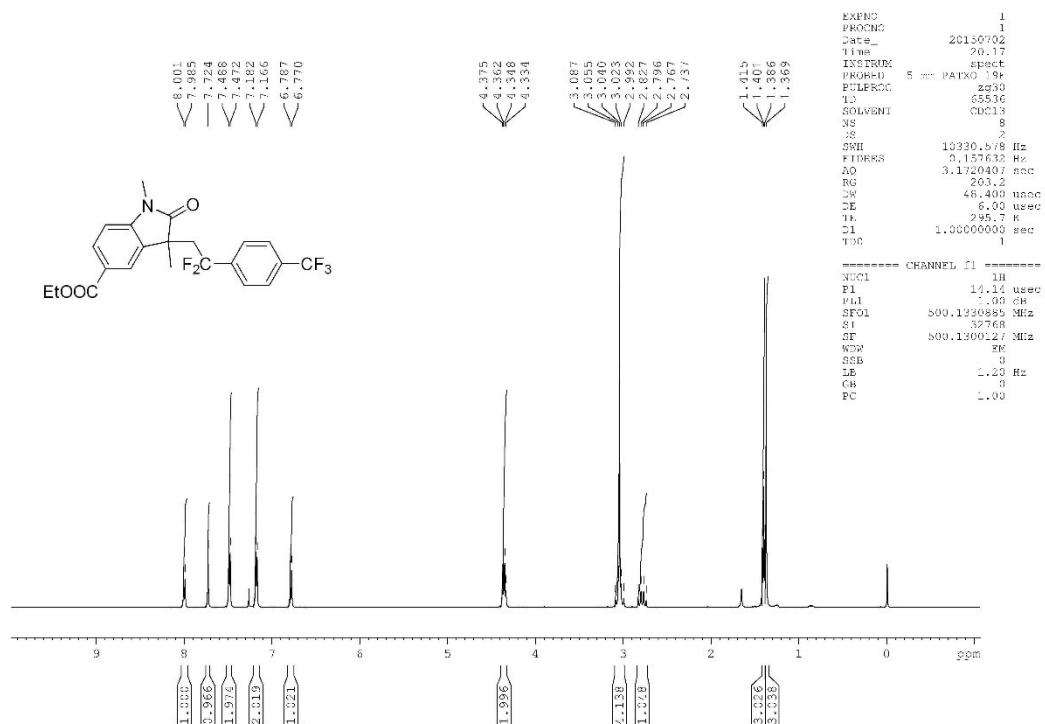
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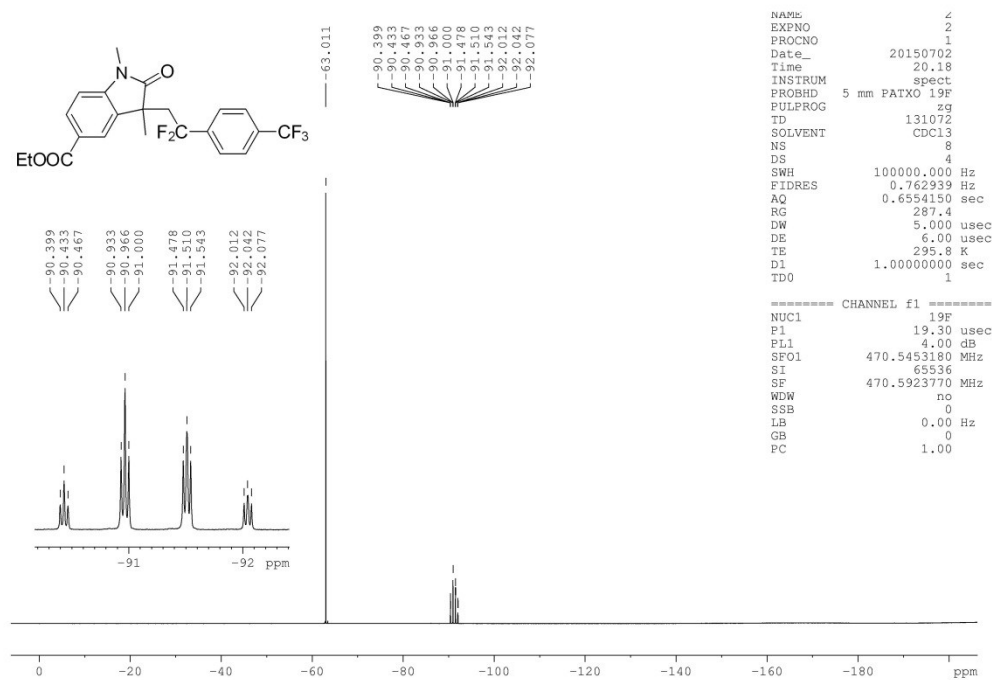
¹³C NMR Spectra of 3lh



¹H NMR Spectra of 3mh



¹⁹F NMR Spectra of 3mh



¹³C NMR Spectra of 3mh

