Supporting Information

Transition Metal-Free Photochemical C–F Activation for the Preparation of Difluorinated-Oxindole Derivatives

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1. General Considerations

All reagents were purchased and used as received from their respective suppliers unless otherwise noted. For purple light irradiation, a Kessil PR160L-purple LED lamp (52 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) was placed 2 cm away from the reaction vials. The reaction was cooled with two compact fans, ensuring that the surface temperature of the vial did not exceed 35 °C. Reactions were monitored by ^{1}H NMR, ^{19}F NMR, or TLC using silica gel F254 plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using EtOAc/hexanes and visualized using permanganate stain, ceric ammonium molybdate (Hanessian's) stain, and/or UV light. Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm in conjunction with an evaporative light scattering detector) with silica cartridges (60 Å porosity, 20-40 μm). Accurate mass measurement analyses were conducted using electron ionization (EI) or electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GCMS, and leucine enkephalin for ESI-LCMS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded using either neat oil or solid products. Data are presented as follows: wavenumber (cm^{-1}) peak shape/intensity (w = weak, m = medium, s = strong, vs = very strong, br = broad). Melting points (°C) are uncorrected. NMR spectra [^{1}H, ^{13}C (^{1}H decoupled), ^{11}B, ^{19}F (^{1}H coupled and decoupled)] were obtained at 298 K. ^{1}H NMR (600.4 and 400 MHz) chemical shifts are referenced to residual, non-deuterated $CHCl_3$ (δ 7.26). ^{13}C (^{1}H decoupled) NMR (151 and 101 MHz) chemical shifts are reported relative to $CDCl_3$ (δ 77.16). ^{19}F NMR (376 MHz) spectra are ^{1}H decoupled unless otherwise noted. ^{19}F NMR spectra were referenced to hexafluorobenzene (δ –164.9). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublet, td = triplet of doublet, dt = doublet of triplet), coupling constant *J* (Hz) and integration.

2. Preparation of Non-Commercial Starting Materials

The following compounds were prepared according to the established procedures, and all spectral data matched that which was reported in the literature.

List of prepared *N*-arylmethacrylamides[1]

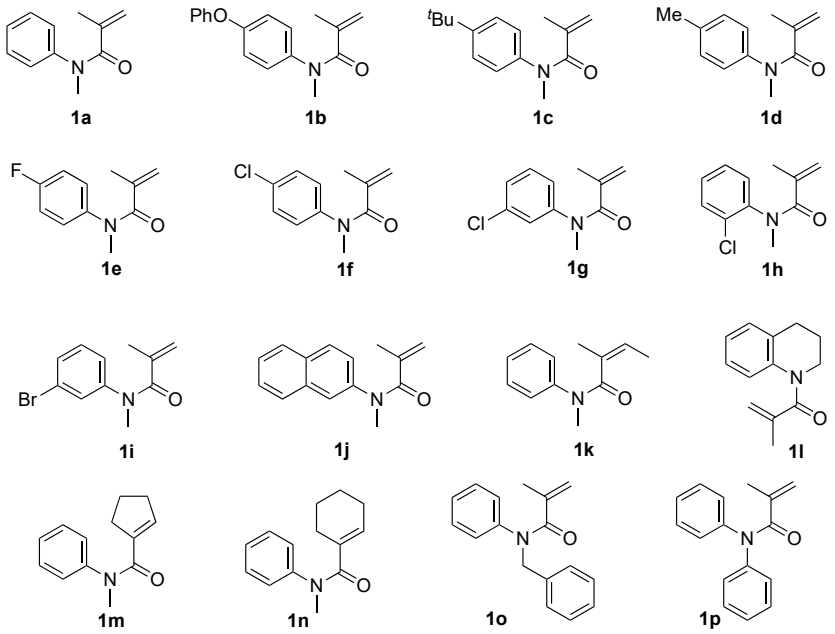


Figure S1. *N-Arylmethacrylamides used in the scope of the transformation.*

List of prepared trifluoromethyl carbonyl compounds[2]

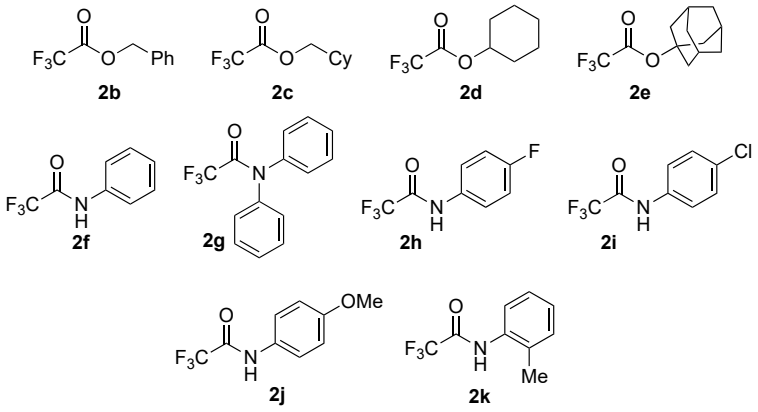
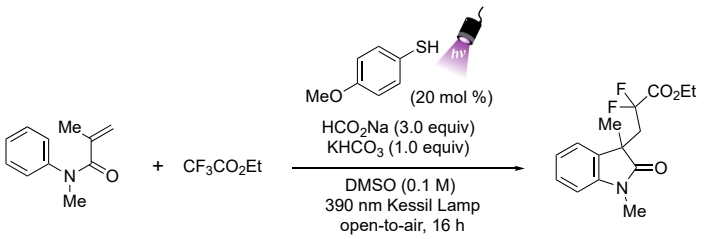


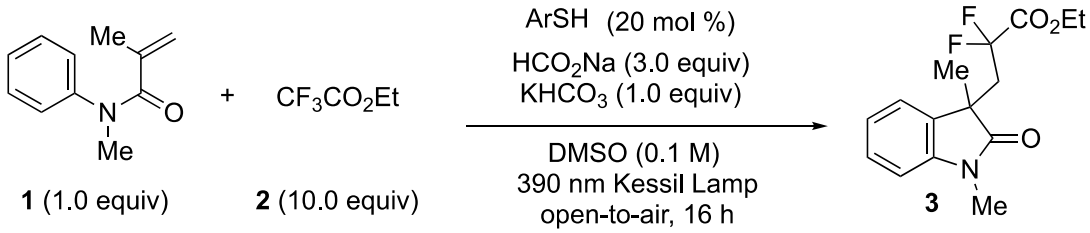
Figure S2. *Trifluoromethylated compounds used in the scope of the transformation.*

3. Optimization of the Reaction Conditions



To a 4 mL vial equipped with a magnetic stir bar was added HCO_2Na (20.4 mg, 0.3 mmol, 3.0 equiv), $KHCO_3$ (10 mg, 0.1 mmol, 1.0 equiv) and acrylamide (17.5 mg, 0.1 mmol, 1.0 equiv). The vial was capped and then charged with dry solvent (1.0 mL, c = 0.1 M) and closed with a cap. Ethyl trifluoroacetate (120 µL, 1.0 mmol, 10.0 equiv), followed by 4-methoxythiophenol (2.8 mg, 2.5 µL, 0.02 mmol, 0.20 equiv) were added by syringe, and the vial was sealed with Parafilm. The reaction was then irradiated with a Kessil® PR160-390 nm lamp at 2 cm (as mentioned in the general considerations section). The reaction was stirred for 16 h of irradiation without the use of cooling fan (temperature of the vial at ~ 50 °C). After 16 h of irradiation, the reaction was quenched slowly with ice-cold H_2O (5 mL) and extracted with EtOAc (3 x 5 mL). The combined organic extracts were washed with brine (10 mL), dried (Na_2SO_4), then decanted, and the solvent was removed via rotary evaporation. The crude material was then redissolved in CH_2Cl_2 and evaporated onto 2-3 g of silica to be purified via automated flash silica column chromatography eluting with 15-30% EtOAc/hexane to afford the desired product. The crude reaction material was analyzed by ^{19}F NMR in $CDCl_3$ using 4-bromo-2-fluoro-1-iodobenzene as an internal standard.

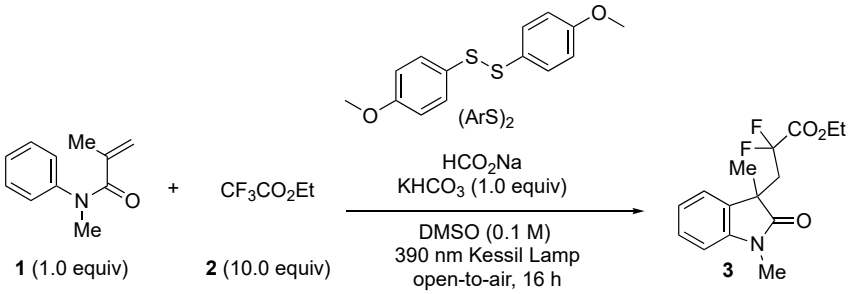
Table S1: Optimization of the Reaction Conditions



entry	deviation from std condition	yield (%)
1	none	95
2	0.10 equiv of ArSH	50
3	7.0 equiv of 2	64
4	5.0 equiv of 2	50
5	0.10 equiv of Ar^1SH	22
6	DMF	traces
7	DMA	0
8	MeOH	traces
9	HFIP	traces
10	tetramethylene sulfoxide	30
11	sulfolane	traces
12	violet LED 427 nm	10
13	rt, fan on	53
14	1.0 equiv of HCO_2Na	10
15	1,4-cyclohexadiene (1.0 equiv) instead HCO_2Na	11
16	0.5 equiv base	95
17	0.2 equiv base	82
18	without base	56
19	under Ar	76
20	in the presence of TEMPO	0
21	in the dark (at 60 ^oC)	0

ArSH = 4-methoxybenzenethiol. Ar^1SH = 4-chlorobenzenethiol.

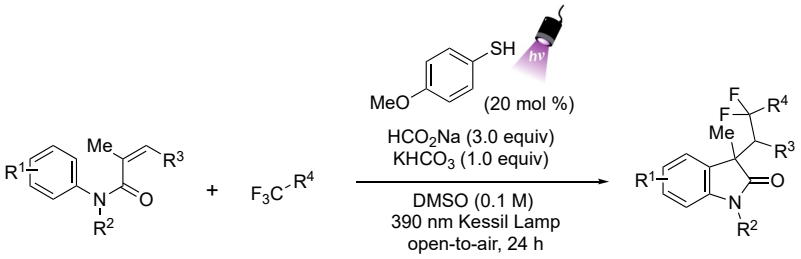
Table S2: Optimization of Reaction Condition: Catalyst



entry	$(ArS)_2$ (equiv)	HCO_2Na (equiv)	yield (%)
1	1.0	3	95
2	1.0	-	66
3[a]	1.0	3	0
4	0.2	3	95
5	0.2	1	18
6	0.1	3	73
7[b]	0.2	3	0

[a] absence of base. [b] in the dark, at 80 °C.

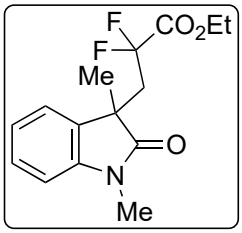
4. General Procedure: Photoinduced Preparation of Difluorinated Oxindole Derivatives via C-F Activation



To an 8 mL vial equipped with a magnetic stir bar was added HCO_2Na (102 mg, 1.50 mmol, 3.0 equiv), $KHCO_3$ (50 mg, 0.50 mmol, 1.0 equiv) and the desired acrylamide (0.5 mmol, 1.0 equiv). The vial was capped, and then charged with dry DMSO (5.0 mL, c = 0.1 M) and closed with a cap. Then, ethyl trifluoroacetate (600 µL, 5.0 mmol, 10.0 equiv), 4-methoxythiophenol (14 mg, 12 µL, 0.10 mmol, 0.20 equiv) were added by syringe, and the vial was sealed with Parafilm. The reaction was then irradiated with a Kessil® PR160-390 nm lamp at 2 cm. The reaction was stirred for 24 h of irradiation without the use of cooling fan. After 24 h of irradiation, the reaction was quenched

slowly with ice-cold H_2O (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine (10 mL), dried (Na_2SO_4), then decanted, and the solvent was removed via rotary evaporation. The crude material was then redissolved in CH_2Cl_2 and evaporated onto 2-3 g of silica to be purified via automated flash silica column chromatography eluting with 15-30% EtOAc/hexane to afford the desired product.

5. Characterization Data for Oxindole Products



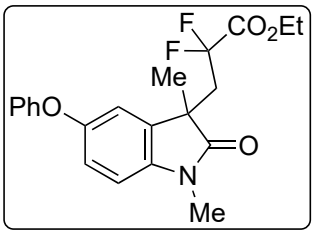
Ethyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 3 (0.130 g, 90%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (td, J = 7.7, 1.3 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.04 (td, J = 7.5, 1.0 Hz, 1H), 6.8 – 6.84 (m, 1H), 4.06 – 4.00 (m, 1H), 3.97 – 3.91 (m, 1H), 3.23 (s, 3H), 2.86 – 2.72 (m, 2H), 1.39 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.0, 163.7 (t, J_{CF} = 32.2 Hz), 143.5, 131.0, 128.7, 123.9, 122.3, 114.7 (dd, J_{CF} = 255.3, 248.8 Hz), 108.5, 63.0, 44.5 (d, J_{CF} = 6.0 Hz), 41.3 (dd, J_{CF} = 24.5, 22.3 Hz), 26.5, 25.6, 13.8.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -102.0 (d, J = 267.6 Hz, 1F), -109.2 (d, J = 267.6 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2970 (w), 1761 (m), 1715 (s), 1099 (s), 754 (s). **HRMS** (ESI) calcd for $C_{15}H_{18}F_2NO_3$ $[M + H]^+$: 298.1255, found: 298.1253.



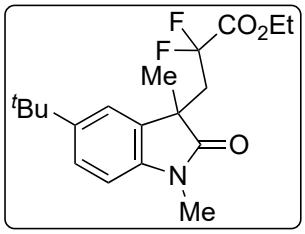
Ethyl 3-(1,3-Dimethyl-2-oxo-5-phenoxyindolin-3-yl)-2,2-difluoropropanoate, 4 (0.136 g, 70%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.06 (tt, J = 7.4, 1.1 Hz, 1H), 6.97 (dq, J = 4.6, 2.4 Hz, 2H), 6.96 – 6.94 (m, 2H), 6.81 (d, J = 9.1 Hz, 1H), 4.16 – 4.07 (m, 2H), 3.22 (s, 3H), 2.83 (ddd, J = 17.3, 15.1, 12.5 Hz, 1H), 2.68 (dt, J = 19.2, 15.1 Hz, 1H), 1.39 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 178.9, 163.6 (t, J_{CF} = 32.2 Hz), 158.4, 152.5, 139.4, 133.0, 130.0, 123.1, 119.8, 118.0, 116.6, 114.8 (dd, J_{CF} = 254.1, 250.2 Hz), 109.3, 63.3, 45.1 (d, J_{CF} = 4.8 Hz), 41.3 (t, J_{CF} = 22.9 Hz), 26.8, 25.8, 14.1.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -103.7 (d, J = 266.9 Hz, 1F), -107.6 (d, J = 267.0 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2970 (w), 1761 (m), 1715 (s), 1099 (s), 754 (s). **HRMS** (ESI) calcd for $C_{21}H_{22}F_2NO_4$ $[M + H]^+$: 390.1511, found: 390.1512.



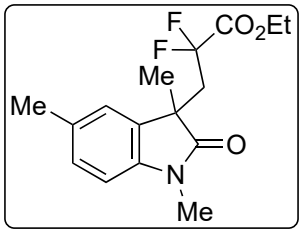
Ethyl 3-(5-(*tert*-Butyl)-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 5 (0.132 g, 75%) was prepared according to the General Procedure. The compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, J = 8.2, 1.9 Hz, 1H), 7.18 (d, J = 1.9 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 3.98 (dq, J = 10.7, 7.2 Hz, 1H), 3.84 (dq, J = 10.7, 7.2 Hz, 1H), 3.13 (s, 3H), 2.77 – 2.64 (m, 2H), 1.32 (s, 3H), 1.24 (s, 9H), 1.10 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 179.3, 163.9 (t, J_{CF} = 32.1 Hz), 145.7, 141.1, 130.8, 125.3, 121.4, 115.0 (dd, J_{CF} = 255.7, 249.0 Hz), 107.9, 63.0, 45.0 (d, J_{CF} = 5.5 Hz), 41.3 (dd, J_{CF} = 24.1, 22.2 Hz), 34.8, 31.9, 26.6, 25.9, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -102.4 (d, J = 267.2 Hz, 1F), -108.3 (d, J = 267.0 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2965 (w), 1760 (m), 1713 (s), 1051 (s), 751 (s). **HRMS** (ESI) calcd for $C_{19}H_{26}F_2NO_3$ $[M + H]^+$: 354.1875, found: 354.1886.



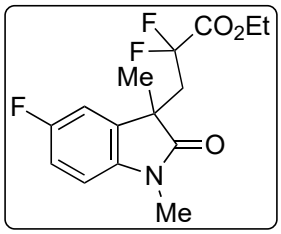
Ethyl 2,2-Difluoro-3-(1,3,5-trimethyl-2-oxoindolin-3-yl)propanoate, 6 (0.105 g, 68%) was prepared according to the General Procedure. The compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 – 7.07 (m, 1H), 6.99 (s, 1H), 6.74 (d, J = 7.9 Hz, 1H), 4.01 (dq, J = 10.8, 7.2 Hz, 1H), 3.94 (dq, J = 10.7, 7.2 Hz, 1H), 3.20 (s, 3H), 2.85 – 2.70 (m, 2H), 2.32 (s, 3H), 1.37 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 179.1, 163.9 (t, J_{CF} = 32.2 Hz), 141.3, 131.9, 131.2, 129.1, 124.9, 114.9 (dd, J_{CF} = 255.3, 248.8 Hz), 108.4, 63.1, 44.8 (d, J_{CF} = 6.1 Hz), 41.5 (dd, J_{CF} = 24.6, 22.2 Hz), 26.7, 25.8, 21.3, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.6 (d, J = 267.1 Hz, 1F), -109.4 (d, J = 267.3 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2950 (w), 1760 (m), 1710 (s), 1050 (s), 784 (s). **HRMS** (ESI) calcd for $C_{16}H_{20}F_2NO_3$ $[M + H]^+$: 312.1406, found: 312.1412.



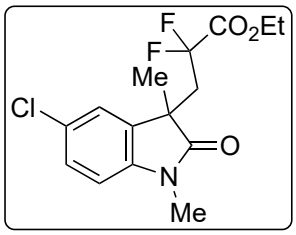
Ethyl 3-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 7 (0.115 g, 73%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 – 6.93 (m, 2H), 6.78 (dd, J = 8.5, 4.1 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.21 (s, 3H), 2.88 – 2.66 (m, 2H), 1.39 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 178.5, 163.4 (t, J_{C-F} = 32.2 Hz), 159.0 (d, J = 240.4 Hz), 139.2 (d, J_{C-F} = 2.0 Hz), 132.6, 114.8 (d, J_{C-F} = 23.5 Hz), 114.5 (dd, J_{C-F} = 254.5, 249.6), 111.9 (d, J_{C-F} = 24.7 Hz), 108.8, 63.0, 44.9 (d, J_{C-F} = 5.3 Hz), 41.0 (dd, J_{C-F} = 24.2, 22.2 Hz), 26.6, 25.4, 13.7.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -103.0 (d, J = 267.7 Hz, 1F), -108.4 (d, J = 267.7 Hz, 1F), -124.1 (s, 1F).

FT-IR (cm^{-1}, neat, ATR) 2963 (w), 1725 (m), 1142 (vs), 1075, 726 (m). **HRMS** (EI) calcd for $C_{15}H_{16}F_3NO_3$ [M]: 315.1082, found: 315.1091.



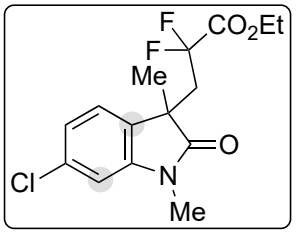
Ethyl 3-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 8 (0.035 g, 51%, 0.2 mmol scale) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.18 (d, J = 2.1 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.24 (s, 3H), 2.90 – 2.71 (m, 2H), 1.41 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 178.4, 163.3 (t, J_{C-F} = 32.1 Hz), 141.9, 132.6, 128.5, 127.7, 124.3, 114.4 (dd, J_{C-F} = 254.5, 249.6 Hz), 109.4, 63.1, 44.7 (d, J_{C-F} = 5.9 Hz), 41.1 (dd, J_{C-F} = 24.7, 22.3 Hz), 26.6, 25.4, 13.7.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -99.1 (d, J = 268.6 Hz, 1F), -106.0 (d, J = 268.6 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2963 (w), 1725 (m), 1142 (vs), 1075, 726 (m). **HRMS** (ESI) calcd for $C_{15}H_{17}ClF_2NO_3$ $[M+H]^+$: 332.0865, found: 332.0857.



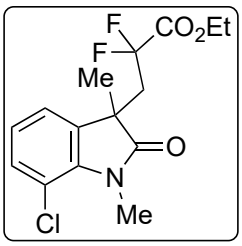
Ethyl 3-(6-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 9 (0.082 g, 52%, 2:1 mixture of regioisomers) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.13 (d, J = 7.9 Hz, 0.6H), 7.04 (dd, J = 7.9, 1.9 Hz, 0.6H), 7.01 – 6.98 (m, 1H), 6.88 (d, J = 1.9 Hz, 0.55H), 6.80 – 6.79 (m, 1H), 6.90 – 6.77 (m, 1H), 4.12 (q, J = 7.1 Hz, 2H), 4.02 (dd, J = 10.8, 7.2 Hz, 0.5H), 3.24 (s, 3H), 3.23 (s, 1.8H), 2.91 – 2.73 (m, 2.5H), 1.55 (s, 3H), 1.40 (s, 1.6H), 1.29 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 1.6H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 178.8, 178.1, 163.3 (t, $J_{C\text{-}F}$ = 32.3 Hz), 145.0, 144.5, 134.4, 131.2, 129.7, 129.3, 127.6, 124.8, 123.4, 122.0, 116.1 – 112.6 (m), 109.1, 106.9, 63.1, 62.9, 45.5 (d, $J_{C\text{-}F}$ = 4.6 Hz), 44.2 (d, $J_{C\text{-}F}$ = 5.4 Hz), 41.1 (dd, $J_{C\text{-}F}$ = 24.3, 22.3 Hz), 40.1 – 38.8 (m), 26.6, 26.5, 25.4, 22.4, 13.8, 13.7.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -102.8 (d, J = 267.6 Hz, 0.5F), -105.9 (d, J = 264.3 Hz, 1F), -108.5 (d, J = 264.4 Hz, 1F), -108.7 (d, J = 267.6 Hz, 0.5F).

FT-IR (cm^{-1}, neat, ATR) 2963 (w), 1725 (m), 1142 (vs), 1075, 726 (m). **HRMS** (EI) calcd for $C_{15}H_{17}ClF_2NO_3$ $[M+H]^+$: 332.0865, found: 332.0822.



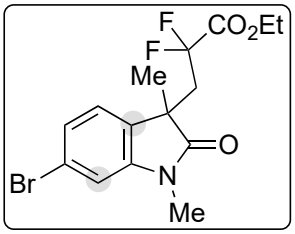
Ethyl 3-(7-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 10 (0.083 g, 50%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, J = 8.2, 1.2 Hz, 1H), 7.07 (dd, J = 7.4, 1.2 Hz, 1H), 6.95 (dd, J = 8.2, 7.3 Hz, 1H), 4.08 (dq, J = 10.7, 7.1 Hz, 1H), 3.99 (dq, J = 10.8, 7.2 Hz, 1H), 3.60 (s, 3H), 2.84 (ddd, J = 15.9, 15.1, 12.7 Hz, 1H), 2.72 (ddd, J = 20.5, 15.0, 13.7 Hz, 1H), 1.38 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.4, 163.8 (t, J_{CF} = 31.9 Hz), 139.6, 134.1, 131.1, 123.3, 122.6, 116.5 – 113.0 (m), 116.1, 63.4, 44.5 (d, J_{CF} = 5.5 Hz), 41.7 (dd, J_{CF} = 24.4, 22.3 Hz), 30.1, 26.2, 14.0.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -102.7 (d, J = 267.5 Hz, 1F), -108.3 (d, J = 267.5 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2970 (w), 1762 (m), 1608 (s), 1466 (s), 1089 (s), 778 (m). **HRMS** (EI) calcd for $C_{15}H_{17}ClF_2NO_3$ $[M+H]^+$: 332.0860, found: 332.0825.



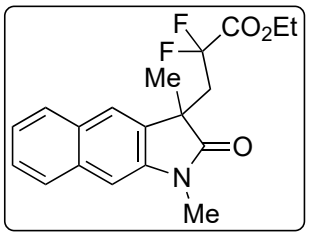
Ethyl 3-(6-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 11 (0.084 g, 45%, obtained as a 2:1 mixture of regioisomers) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 2.5H), 7.05 (d, J = 7.9 Hz, 0.6H), 7.01 (d, J = 1.7 Hz, 0.6H), 6.81 (dd, J = 5.6, 3.1 Hz, 1H), 4.14 – 4.05 (m, 2.7H), 4.03 – 3.97 (m, 0.7H), 3.33 – 3.23 (m, 1.8H), 3.22 (s, 3H), 3.20 (s, 1.9H), 2.85 – 2.69 (m, 2.5H), 1.54 (s, 3H), 1.37 (s, 1.9H), 1.27 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 178.7, 178.3, 163.6 (t, J = 32.1 Hz), 163.3 (t, J = 32.3 Hz), 145.4, 144.8, 130.0, 129.9, 129.4, 126.7, 125.3, 125.1, 122.2, 119.7, 116.4 – 112.8 (m), 112.0, 107.6, 63.2, 63.1, 46.4 (d, J = 4.5 Hz), 44.4 (d, J = 5.4 Hz), 41.1 (dd, J = 24.4, 22.1 Hz), 38.9 (t, J = 22.9 Hz), 26.7, 26.6, 25.5, 22.4, 13.9, 13.8.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -102.8 (d, J = 267.6 Hz, 0.6F), -105.9 (d, J = 264.3 Hz, 1F), -108.1 (d, J = 264.2 Hz, 1F), -108.7 (d, J = 267.6 Hz, 06F).

FT-IR (cm^{-1}, neat, ATR) 2970 (w), 1763 (s), 1694 (m), 1424 (s), 1306 (s), 1098 (s), 755 (m). **HRMS** (EI) calcd for $C_{15}H_{17}BrF_2NO_3$ $[M+H]^+$: 376.0354, found: 376.0368.



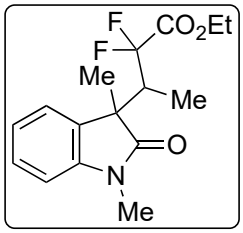
Ethyl 3-(1,3-Dimethyl-2-oxo-2,3-dihydro-1*H*-benzo[*f*]indol-3-yl)-2,2-difluoropropanoate, 12 (0.026 g, 20%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.39 – 7.33 (m, 1H), 7.22 (d, J = 8.6 Hz, 1H), 3.44 (dq, J = 10.6, 7.1 Hz, 1H), 3.35 (s, 3H), 3.29 – 3.01 (m, 3H), 1.64 (s, 3H), 0.96 (t, J = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 180.2, 162.9 (t, J_{CF} = 33.8 Hz), 141.5, 130.5, 130.2, 129.8, 129.7, 127.2, 123.6, 122.4, 122.2, 114.5 (dd, J_{CF} = 254.9, 248.7 Hz), 110.0, 62.5, 45.8 (d, J_{CF} = 6.9 Hz), 42.1 (dd, J_{CF} = 24.9, 22.3 Hz), 26.8, 24.8, 13.5.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -101.6 (d, J = 266.5 Hz, 1F), -110.6 (d, J = 266.5 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2930 (w), 1765 (m), 1713 (s), 1175 (m), 1062 (m), 747 (m). **HRMS** (ESI) calcd for $C_{19}H_{20}F_2NO_3$ $[M + H]^+$: 348.1411, found: 348.1401.



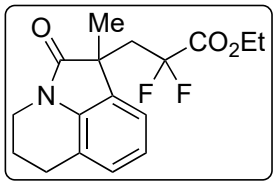
Ethyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluorobutanoate, 13 (0.124 g, 80%, *dr* = 1:1, based on ^{1}H NMR of the crude mixture) was prepared according to the General Procedure. The compound was obtained as a colorless oil. Data reported for one diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.6, 1.7 Hz, 1H), 7.29 (td, J = 7.7, 1.3 Hz, 1H), 7.07 (td, J = 7.6, 1.1 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.22 (s, 3H), 3.11 – 2.93 (m, 1H), 1.46 (d, J = 2.6 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 0.87 (d, J = 7.1, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 164.3 (t, J_{CF} = 33.2 Hz), 143.7, 131.3, 128.6, 125.6, 122.9, 118.0 (t, J_{CF} = 253.2 Hz), 108.4, 63.3, 50.0 (d, J_{CF} = 2.0 Hz), 43.3 (t, J_{CF} = 21.3 Hz), 26.6, 23.3, 14.2, 10.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -105.1 (d, J = 258.4 Hz, 1F), -107.6 (d, J = 258.4 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2950 (w), 1762 (m), 1709 (s), 1482 (m), 1452 (m), 1080 (s), 751 (s). **HRMS** (ESI) calcd for $C_{16}H_{20}F_2NO_3$ [M + H]:$^+$ 312.1406, found: 312.1391.



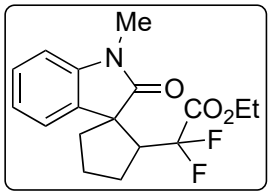
Ethyl 2,2-Difluoro-3-(1-methyl-2-oxo-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-yl)propanoate, 14 (0.081 g, 50%) was prepared according to the General Procedure. The compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 – 7.00 (m, 2H), 6.92 (t, J = 7.5 Hz, 1H), 4.03 (dq, J = 10.7, 7.2 Hz, 1H), 3.95 (dq, J = 10.7, 7.2 Hz, 1H), 3.77 – 3.67 (m, 2H), 2.84 – 2.70 (m, 4H), 2.01 (ttd, J = 6.7, 5.1, 2.9 Hz, 2H), 1.40 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 178.0, 163.9 (t, J_{CF} = 32.2 Hz), 139.5, 129.7, 127.5, 122.0, 122.0, 121.9, 115.0 (dd, J_{CF} = 255.2, 248.9 Hz), 63.2, 46.0 (d, J_{CF} = 5.9 Hz), 41.4 (dd, J_{CF} = 24.4, 22.2 Hz), 39.3, 25.4, 25.0, 21.4, 14.0.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -102.0 (d, J = 267.0 Hz, 1F), -108.9 (d, J = 267.0 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2950 (w), 1762 (m), 1709 (s), 1482 (m), 1452 (m), 1080 (s), 751 (s). **HRMS** (ESI) calcd for $C_{17}H_{20}F_2NO_3$ [M + H]$^+$: 324.1406, found: 324.1431.



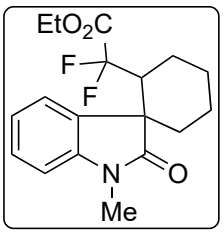
Ethyl 2,2-Difluoro-2-(1'-methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-yl)acetate, 15 (0.145 g, 90%, *dr* = 2:1, based on ^{1}H NMR of the crude mixture) was prepared according to the General Procedure. The compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.18 (m, 1H), 7.07 (d, *J* = 8.9 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 3.74 – 3.62 (m, 2H), 3.12 (s, 3H), 3.00 (dtd, *J* = 19.5, 11.3, 7.9 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.29 – 2.20 (m, 1H), 2.15 – 2.07 (m, 2H), 2.00 – 1.93 (m, 1H), 1.91 (ddd, *J* = 14.0, 8.6, 4.1 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 178.1, 163.8 (t, J_{CF} = 32.2 Hz), 144.2, 131.3, 128.6, 122.5, 122.5, 115.4 (dd, J_{CF} = 256.2, 250.4 Hz), 108.2, 62.9, 53.9 (d, J_{CF} = 5.2 Hz), 53.5 (dd, J_{CF} = 25.4, 22.9 Hz), 39.2, 26.4, 24.8, 22.2, 14.0.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -105.8 (d, *J* = 258.5 Hz, 1F), -114.6 (d, *J* = 258.5 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2956 (w), 1763 (m), 1710 (s), 1482 (m), 1420 (m), 1078 (s), 751 (s).
HRMS (ESI) calcd for $C_{17}H_{20}F_2NO_3$ $[M + H]^+$: 324.1406, found: 324.1410.



Ethyl 2,2-Difluoro-2-(1'-methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-yl)acetate, 16 (0.115 g, 68%, *dr* = 2:1, based on ^{1}H NMR of the crude mixture) was prepared according to the General Procedure. The compound was obtained as a dense, colorless oil.

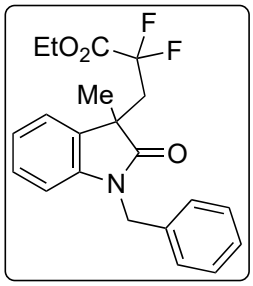
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.10 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 3.82 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.74 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.19 (s, 3H), 2.81 (dddd, *J* = 20.2, 12.7, 9.0, 3.4 Hz, 1H), 2.47 (qd, *J* = 13.2, 3.8 Hz, 1H),

2.23 (qt, J = 13.4, 3.9 Hz, 1H), 2.08 – 2.04 (m, 1H), 1.90 – 1.85 (m, 1H), 1.75 (td, J = 13.7, 3.9 Hz, 1H), 1.68 – 1.62 (m, 1H), 1.60 – 1.54 (m, 1H), 1.45 (dtd, J = 17.2, 13.2, 3.8 Hz, 1H), 1.16 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 164.3 (t, J_{CF} = 32.7 Hz), 143.6, 132.3, 128.5, 123.3, 122.0, 116.1 (dd, J_{CF} = 258.3, 251.8 Hz), 108.2, 62.9, 48.0 (t, J_{CF} = 21.7 Hz), 46.5 (d, J_{CF} = 4.4 Hz), 37.9, 26.4, 25.4, 20.1, 19.8, 14.0.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -107.7 (d, J = 259.2 Hz, 1F), -112.9 (d, J = 259.2 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2934 (m), 1763 (m), 1708 (s), 1482 (m), 1494 (m), 1066 (m), 756 (s).
HRMS (ESI) calcd for $C_{18}H_{22}F_2NO_3$ $[M + H]^+$: 338.1562, found: 338.1564.



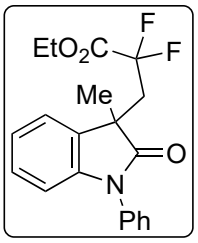
Ethyl 3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 17 (0.091g, 68%) was prepared according to the General Procedure. The compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 4H), 7.20 – 7.16 (m, 1H), 7.11 (d, J = 6.4 Hz, 1H), 7.07 (td, J = 7.8, 1.2 Hz, 1H), 6.92 (t, J = 7.1 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 4.91 (d, J = 15.8 Hz, 1H), 4.82 (d, J = 15.8 Hz, 1H), 3.92 (dq, J = 10.7, 7.1 Hz, 1H), 3.77 (dq, J = 10.7, 7.1 Hz, 1H), 2.87 – 2.71 (m, 2H), 1.38 (s, 3H), 1.05 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 179.2, 163.9 (t, J_{CF} = 32.0 Hz), 142.8, 136.0, 131.1, 129.0, 128.7, 127.9, 127.5, 124.2, 122.5, 115.0 (dd, J_{CF} = 256.2, 248.2 Hz), 109.8, 63.2, 44.8 (d, J_{CF} = 6.5 Hz), 44.3, 41.3 (dd, J_{CF} = 24.8, 22.1 Hz), 26.5, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.2 (d, J = 266.8 Hz), -109.1 (d, J = 266.9 Hz).

FT-IR (cm^{-1}, neat, ATR) 2950 (w), 1758 (s), 1611 (s), 1467 (s), 1327 (s), 1082 (s), 754 (m).
HRMS (ESI) calcd for $C_{21}H_{22}F_2NO_3$ $[M + H]^+$: 374.1562, found: 374.1550.



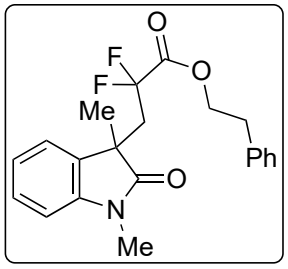
Ethyl 2,2-difluoro-3-(3-methyl-2-oxo-1-phenylindolin-3-yl)propanoate, 18 (0.072 g, 40%) was prepared according to the General Procedure. The compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.45 – 7.38 (m, 3H), 7.25 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.21 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (dt, *J* = 7.9, 0.8 Hz, 1H), 4.02 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.92 (dq, *J* = 10.8, 7.2 Hz, 1H), 2.98 – 2.82 (m, 2H), 1.52 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 163.6 (t, *J* = 32.1 Hz), 143.6, 134.6, 130.6, 129.7, 128.6, 128.3, 126.9, 124.2, 122.6, 114.8 (dd, *J* = 255.6, 248.9 Hz), 109.8, 63.0, 44.6 (d, *J* = 6.2 Hz), 41.8 (dd, *J* = 24.6, 22.1 Hz), 25.9, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.5 (d, *J* = 267.9 Hz), -109.0 (d, *J* = 267.9 Hz).

FT-IR (cm^{-1}, neat, ATR) 2970 (w), 1758 (m), 1712 (s), 1612 (m), 1482 (m), 1453 (m), 1278 (s), 1028 (s), 754 (s). **HRMS** (ESI) calcd for $C_{20}H_{20}F_2NO_3$ $[M + H]^+$: 360.1411, found: 360.1411.



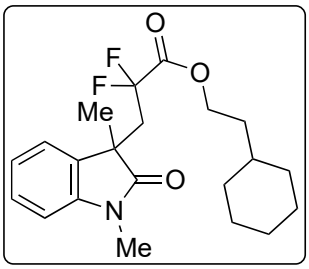
Phenethyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 19 (0.093 g, 76%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 – 7.18 (m, 2H), 6.97 (td, J = 7.5, 1.0 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.82 – 6.80 (m, 1H), 4.14 – 4.10 (m, 1H), 4.09 – 4.04 (m, 1H), 3.21 (s, 3H), 2.90 – 2.83 (m, 2H), 2.82 – 2.67 (m, 2H), 1.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 178.8, 163.3 (t, J_{CF} = 32.2 Hz), 143.5, 137.1, 130.7, 129.1, 128.7, 128.7, 127.0, 123.8, 122.2, 114.6 (dd, J_{CF} = 255.3, 248.8 Hz), 108.5, 67.2, 44.4 (d, J_{CF} = 6.5 Hz), 41.4 (dd, J_{CF} = 24.8, 22.1 Hz), 34.6, 26.5, 25.5.

^{19}F NMR ($CDCl_3$, 376 MHz) -101.2 (d, J = 268.2 Hz, 1F), -109.9 (d, J = 268.2 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2935 (w), 1768 (m), 1712 (s), 1063 (m), 752 (s). **HRMS** (ESI) calcd for $C_{21}H_{22}F_2NO_3$ $[M + H]^+$ 374.1568, found: 374.1573.



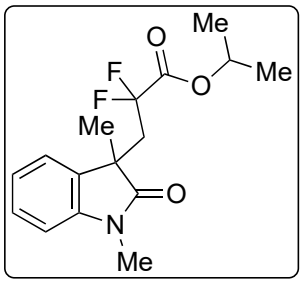
2-Cyclohexylethyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 20 (0.087 g, 46%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (td, J = 7.7, 1.3 Hz, 1H), 7.18 (dd, J = 7.5, 1.2 Hz, 1H), 7.04 (td, J = 7.6, 1.0 Hz, 1H), 6.85 (dt, J = 7.9, 0.7 Hz, 1H), 4.01 (dt, J = 10.8, 7.1 Hz, 1H), 3.90 (dt, J = 10.8, 7.1 Hz, 1H), 3.23 (s, 3H), 2.88 – 2.69 (m, 2H), 1.73 – 1.62 (m, 4H), 1.44 (qd, J = 7.0, 1.2 Hz, 2H), 1.39 (s, 3H), 1.33 – 1.10 (m, 5H), 0.97 – 0.83 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.2, 163.9 (t, J_{CF} = 32.1 Hz), 143.7, 131.2, 128.9, 124.1, 122.5, 115.0 (dd, J_{CF} = 255.5, 249.0 Hz), 108.7, 65.6, 44.8 (d, J_{CF} = 6.0 Hz), 41.5 (dd, J_{CF} = 24.5, 22.2 Hz), 35.7, 34.7, 33.4, 33.4, 26.7, 26.7, 26.4, 25.8.

^{19}F NMR ($CDCl_3$, 376 MHz) -98.7 (d, J = 267.8 Hz, 1F), -106.1 (d, J = 267.3 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2935 (w), 1768 (m), 1712 (s), 1063 (m), 752 (s). **HRMS** (ESI) calcd for $C_{21}H_{28}F_2NO_3$ $[M + H]^+$ 380.2032, found: 380.2008.



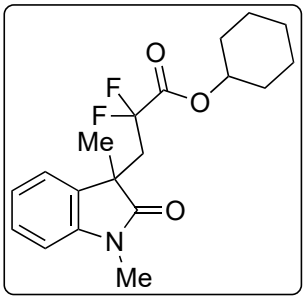
Isopropyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 21 (0.084 g, 54%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (td, J = 7.7, 1.2 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.85 – 4.79 (m, 1H), 3.22 (s, 3H), 2.84 – 2.71 (m, 2H), 1.39 (s, 3H), 1.24 (d, J = 6.3 Hz, 3H), 1.14 (d, J = 6.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 163.3 (t, J_{CF} = 31.9 Hz), 143.6, 131.4, 128.8, 124.2, 122.5, 115.0 (dd, J_{CF} = 255.1, 249.7 Hz), 108.6, 71.6, 44.8 (d, J_{CF} = 4.9 Hz), 41.2 (dd, J_{CF} = 24.1, 22.0 Hz), 26.7, 25.8, 21.7, 21.6.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -103.1 (d, J = 268.1 Hz, 1F), -108.5 (d, J = 267.9 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2970 (w), 1709 (s), 1611 (s), 1231 (m), 741 (s). **HRMS** (ESI) calcd for $C_{16}H_{19}F_2NNaO_3$ $[M + Na]^+$: 334.1231, found: 334.1234.



Cyclohexyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 22 (0.070 g, 57%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

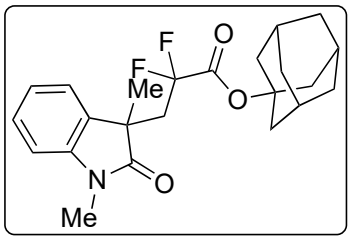
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (td, J = 7.7, 1.3 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.86 – 6.84 (m, 1H), 4.60 (tt, J = 9.1, 3.8 Hz, 1H), 3.22 (s, 3H), 2.88 – 2.64 (m,

2H), 1.85 – 1.78 (m, 1H), 1.75 – 1.61 (m, 3H), 1.64 – 1.41 (m, 2H), 1.39 (s, 3H), 1.38 – 1.21 (m, 4H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.1, 163.0 (t, J_{CF} = 31.9 Hz), 143.4, 131.3, 128.6, 124.0, 122.3, 114.8 (dd, J_{CF} = 254.8, 249.9 Hz), 108.4, 76.0, 44.6 (d, J_{CF} = 4.9 Hz), 41.0 (dd, J_{CF} = 24.0, 21.8 Hz), 31.1, 31.0, 26.5, 25.6, 25.2, 23.5, 23.5.

^{19}F NMR ($CDCl_3$, 376 MHz) -103.2 (d, J = 268.2 Hz, 1F), -108.2 (d, J = 268.2 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2937 (w), 1756 (m), 1715 (s), 1062 (w), 754 (m). **HRMS** (ESI) calcd for $C_{19}H_{24}F_2NO_3$ $[M + H]^+$: 352.1724, found: 352.1727.



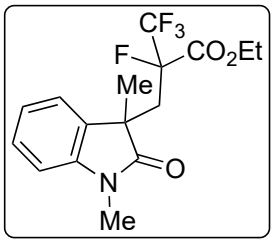
Adamantan-1-yl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanoate, 23 (0.101 g, 50%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (td, J = 7.7, 1.3 Hz, 1H), 7.26 – 7.25 (m, 1H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 3.22 (s, 3H), 2.88 – 2.57 (m, 2H), 2.17 (s, 3H), 2.04 (s, 6H), 1.64 (s, 6H), 1.39 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 162.1 (t, J_{CF} = 31.6 Hz), 143.2, 131.8, 128.4, 124.1, 122.6, 114.7 (dd, J_{CF} = 254.5, 251.2 Hz), 108.4, 84.7, 44.7 (t, J_{CF} = 4.4 Hz), 41.0, 40.7 (d, J_{CF} = 22.3 Hz), 36.0, 31.0, 26.5, 25.6.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -104.6 (d, J = 265.9 Hz, 1F), -106.6 (d, J = 265.9 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2919 (s), 2852 (m), 1717 (s), 1046 (m), 753 (m). **HRMS** (ESI) calcd for $C_{23}H_{27}F_2NNaO_3$ $[M + Na]^+$ 426.1857, found: 426.1835.



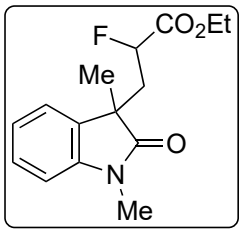
Ethyl 2-((1,3-Dimethyl-2-oxoindolin-3-yl)methyl)-2,3,3,3-tetrafluoropropanoate, 24 (0.135 g, 78%, *dr* = 2:1, based on ^{1}H NMR of the crude mixture) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil and the major compound's data is reported.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.11 – 7.08 (m, 1H), 7.02 – 6.99 (m, 1H), 6.87 – 6.84 (m, 1H), 3.91 – 3.85 (m, 1H), 3.67 – 3.60 (m, 1H), 3.22 (s, 3H), 2.93 – 2.76 (m, 2H), 1.38 (s, 3H), 1.05 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.0, 164.3 (d, J_{CF} = 23.4 Hz), 144.2, 129.7, 128.9, 124.5, 121.9, 121.4 (dd, J_{CF} = 286.4, 28.1 Hz), 108.5, 92.3 (dq, J_{CF} = 208.2, 31.1 Hz), 63.2, 44.7 (d, J_{CF} = 2.7 Hz), 37.5 (d, J_{CF} = 18.5 Hz), 26.5, 25.8, 13.5.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -82.4 (d, J = 6.8 Hz, 3F), -184.1 (q, J = 6.8 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2930 (w), 1713 (s), 1199 (s), 1051 (m), 754 (m). **HRMS** (ESI) calcd for $C_{16}H_{18}F_4NO_3$ $[M + H]^+$: 348.1223, found: 348.1229.



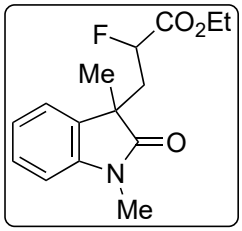
Ethyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2-fluoropropanoate, 25 (0.056 g, 40%, *dr* = 1:1, based on ^{1}H NMR of the crude mixture) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil (data for diastereomer A).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 1H), 7.24 – 7.21 (m, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.7 Hz, 1H), 4.71 – 4.59 (m, 1H), 4.20 – 4.10 (m, 2H), 3.21 (s, 3H), 2.60 – 2.52 (m, 1H), 2.36 – 2.25 (m, 1H), 1.43 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.7, 169.4 (d, J_{CF} = 22.9 Hz), 143.7, 132.0, 128.6, 123.0, 122.7, 108.5, 86.7 (d, J_{CF} = 185.8 Hz), 61.8, 45.9, 40.1 (d, J_{CF} = 20.2 Hz), 26.5, 24.3, 14.2.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -194.1 (s, 1F).

FT-IR (cm^{-1}, neat, ATR) 2974 (w), 1758 (m), 1711 (s), 1612 (m), 1105 (m), 1062 (m), 754 (m).
HRMS (ESI) calcd for $C_{15}H_{18}FNNaO_3$ $[M + Na]^+$: 302.1168, found: 302.1171.



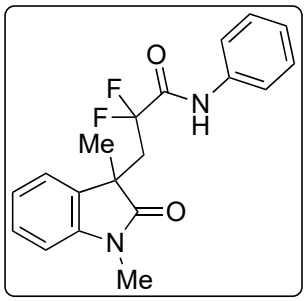
Ethyl 3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2-fluoropropanoate, 25 (0.056 g, 40%, *dr* = 1:1, based on ^{1}H NMR of the crude mixture) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil (data for diastereomer B).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.22 – 7.19 (m, 1H), 7.08 – 7.04 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 4.85 – 4.73 (m, 1H), 4.14 – 3.98 (m, 2H), 3.23 (s, 3H), 2.65 – 2.39 (m, 2H), 1.42 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.6, 169.3 (d, J_{CF} = 23.4 Hz), 143.3, 132.3, 128.4, 123.6, 122.6, 108.4, 87.0 (d, J_{CF} = 186.9 Hz), 61.8, 46.2, 39.4 (d, J_{CF} = 19.6 Hz), 26.5, 24.9, 14.1.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -193.5 (s, 1F).

FT-IR (cm^{-1}, neat, ATR) 2972 (w), 1757 (m), 1709 (s), 1612 (m), 1110 (m), 1026 (w), 753 (m).
HRMS (ESI) calcd for $C_{15}H_{18}FNNaO_3$ $[M + Na]^+$: 302.1168, found: 302.1171.



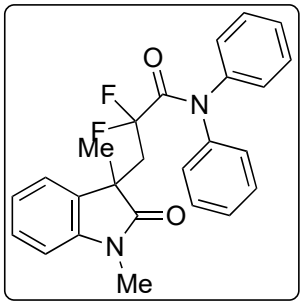
3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-phenylpropanamide, 26 (0.103 g, 60%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (br s, 1H), 7.33 – 7.30 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.23 (m, 1H), 7.16 – 7.12 (m, 2H), 6.92 – 6.89 (m, 1H), 6.80 (d, J = 7.7 Hz, 1H), 3.21 (s, 3H), 3.05 – 2.85 (m, 2H), 1.40 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 161.5 (t, J_{CF} = 27.8 Hz), 143.0, 135.9, 130.9, 129.0, 128.5, 125.5, 124.4, 122.7, 120.2, 116.7 (dd, J_{CF} = 257.2, 254.0 Hz), 108.2, 44.6 (d, J_{CF} = 5.4 Hz), 40.4 (dd, J_{CF} = 24.5, 22.3 Hz), 26.6, 25.9.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -101.0 (d, J = 260.2 Hz, 1F), -110.3 (d, J = 260.2 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 3290 (w, br.), 1693 (s), 1612 (m), 909 (m), 729 (s). **HRMS** (ESI) calcd for $C_{19}H_{19}F_2N_2O_2$ $[M + H]^+$: 345.1415, found: 345.1400.



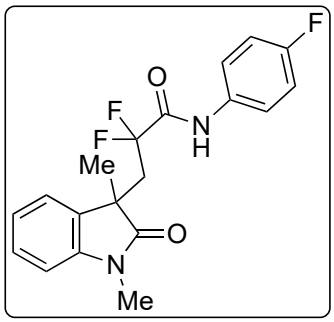
3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*,*N*-diphenylpropanamide, 27 (0.110 g, 52%) was prepared according to the General Procedure. The desired compound was obtained as a white solid (mp = 130 – 132 °C).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (td, J = 7.7, 1.3 Hz, 1H), 7.31 – 7.25 (m, 5H), 7.24 – 7.19 (m, 2H), 7.11 (td, J = 7.5, 1.0 Hz, 1H), 7.07 – 7.02 (m, 4H), 6.88 – 6.86 (m, 1H), 3.18 – 3.09 (m, 1H), 3.12 (s, 3H), 2.86 – 2.77 (m, 1H), 1.37 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.5, 163.1 (d, J_{CF} = 28.9 Hz), 143.5, 131.8, 129.1 (2C), 128.3, 127.6 (br), 124.7, 122.5, 118.1 (dd, J_{CF} = 262.1, 253.4 Hz), 108.2, 44.8 (dd, J_{CF} = 4.9, 2.2 Hz), 41.5 (dd, J_{CF} = 24.5, 21.8 Hz), 26.4, 26.1.

^{19}F NMR ($CDCl_3$, 376 MHz) -92.4 (d, J = 280.1 Hz, 1F), -100.1 (d, J = 280.1 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2925 (w), 1715 (s), 1686 (s), 1046 (m), 758 (s). **HRMS** (ESI) calcd for $C_{25}H_{23}F_2N_2O_2$ $[M + H]^+$ 421.1728, found: 421.1741.



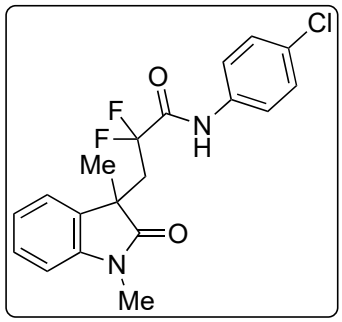
3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-(4-fluorophenyl)propenamide, 28 (0.097 g, 54%) was prepared according to the General Procedure. The desired compound was obtained as a white solid (mp = 120 – 122 °C).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (br s, 1H), 7.34 – 7.25 (m, 2H), 7.25 – 7.20 (m, 1H), 7.15 (td, J = 7.7, 1.3 Hz, 1H), 6.99 – 6.95 (m, 2H), 6.91 (td, J = 7.5, 1.0 Hz, 1H), 6.81 (dt, J = 7.8, 0.7 Hz, 1H), 3.20 (s, 3H), 3.03 – 2.94 (m, 1H), 2.92 – 2.83 (m, 1H), 1.39 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 161.5 (t, J_{CF} = 28.1 Hz), 160.1 (d, J_{CF} = 245.2 Hz), 143.0, 132.0 (d, J_{CF} = 2.7 Hz), 130.9, 128.6, 124.4, 122.7, 122.1 (d, J_{CF} = 7.6 Hz), 116.7 (d, J_{CF} = 25.7, 253.4 Hz), 115.7 (d, J_{CF} = 22.3 Hz), 108.2, 44.6 (d, J_{CF} = 5.4 Hz), 40.4 (dd, J = 24.8, 22.1 Hz), 26.6, 25.8.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -100.8 (d, J = 260.2 Hz, 1F), -110.3 (d, J = 260.2 Hz, 1F), -119.4 (s, 1F).

FT-IR (cm^{-1}, neat, ATR) 3280 (w, br.), 1693 (s), 1614 (m), 1552 (m), 1060 (w), 755 (w). **HRMS** (ESI) calcd for $C_{19}H_{18}F_3N_2O_2$ $[M + H]^+$: 363.1320, found: 363.1306.



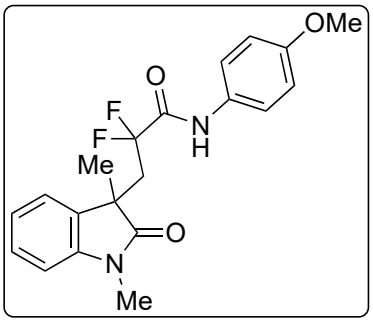
***N*-(4-Chlorophenyl)-3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-difluoropropanamide, 29** (0.133 g, 41%) was prepared according to the General Procedure. The desired compound was obtained as a white solid (mp = 160 – 161 °C).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (br. s, 1H), 7.30 – 7.24 (m, 4H), 7.22 (d, J = 7.2 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 3.22 (s, 3H), 3.05 – 2.94 (m, 1H), 2.94 – 2.85 (m, 1H), 1.40 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 161.5 (t, J_{CF} = 28.1 Hz), 143.1, 134.5, 130.9, 130.7, 129.1, 128.6, 124.5, 122.7, 121.4, 116.7 (dd, J_{CF} = 258.2, 259.7 Hz), 108.2, 44.6 (d, J_{CF} = 5.4 Hz), 40.4 (dd, J_{CF} = 24.8, 22.1 Hz), 26.6, 25.8.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -100.5 (d, J = 260.8 Hz, 1F), -110.6 (d, J = 260.8 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 3260 (w, br.), 1693 (s), 1060 (m), 756 (m). **HRMS** (ESI) calcd for $C_{19}H_{18}ClF_2N_2O_2$ $[M + H]^+$: 379.1025, found: 379.1020.



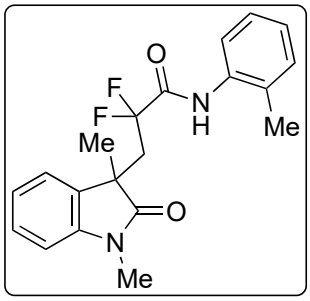
3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-(4-methoxyphenyl)propenamide, 30 (0.037 g, 20%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (br s, 1H), 7.26 – 7.22 (m, 1H), 7.24 – 7.18 (m, 2H), 7.17 (td, J = 7.7, 1.3 Hz, 1H), 6.93 (td, J = 7.5, 1.0 Hz, 1H), 6.86 – 6.79 (m, 3H), 3.79 (s, 3H), 3.22 (s, 3H), 3.07 – 2.85 (m, 2H), 1.40 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 161.2 (t, J_{CF} = 27.8 Hz), 157.3, 143.1, 131.0, 128.9, 128.5, 124.5, 122.7, 122.0, 116.9 (dd, J_{CF} = 257.5, 253.7 Hz), 114.2, 108.2, 55.6, 40.4 (dd, J_{CF} = 24.8, 22.1 Hz), 26.6, 25.9.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -100.8 (d, J = 260.2 Hz, 1F), -110.5 (d, J = 260.2 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 3280 (w, br.) 2935 (w), 1693 (s), 1511 (s), 1242 (s), 1057 (m), 826 (m), 751 (m). **HRMS** (ESI) calcd for $C_{20}H_{21}F_2N_2O_3$ $[M + H]^+$: 375.1520, found: 375.1530.



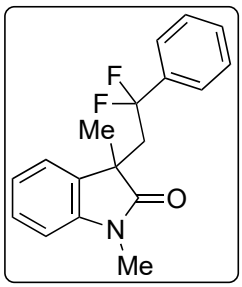
3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-difluoro-*N*-(*o*-tolyl)propenamide, 31 (0.054 g, 30%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 1H), 7.39 (br. s, 1H), 7.27 – 7.24 (m, 1H), 7.20 – 7.15 (m, 2H), 7.14 - 7.11 (m, 1H), 7.10 – 7.06 (m, 1H), 6.96 – 6.91 (m, 1H), 6.81 (d, J = 7.7 Hz, 1H), 3.23 (s, 3H), 3.09 – 2.99 (m, 1H), 2.97 – 2.88 (m, 1H), 2.05 (s, 3H), 1.41 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 161.4 (t, J = 27.5 Hz), 143.1, 133.9, 131.1, 130.6, 128.7, 128.4, 126.9, 126.0, 124.5, 122.7, 122.2, 117.0 (dd, J = 257.2, 253.9 Hz), 108.1, 44.6 (d, J = 5.4 Hz), 40.2 (dd, J = 24.5, 21.8 Hz), 26.6, 26.0, 17.3.

^{19}F NMR ($CDCl_3$, 376 MHz) -100.8 (d, J = 261.3 Hz, 1F), -110.2 (d, J = 261.3 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 3290 (w, br), 2924 (w), 1697 (s), 1612 (m), 1048 (m), 750 (s). **HRMS** (ESI) calcd for $C_{20}H_{21}F_2N_2O_2$ $[M + H]^+$: 359.1571, found: 359.1565.



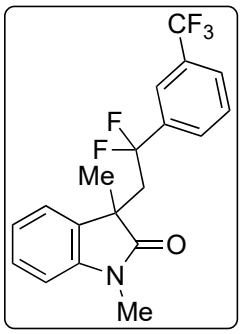
3-(2,2-difluoro-2-phenylethyl)-1,3-dimethylindolin-2-one, 32 (0.080 g, 53%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32– 7.30 (m, 1H), 7.28 – 7.21 (m, 4H), 7.09 – 7.07 (m, 2H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.74 (d, J = 7.7 Hz, 1H), 3.02 – 2.93 (m, 1H), 2.96 (s, 3H), 2.73 (ddd, J = 19.5, 15.2, 9.1 Hz, 1H), 1.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 143.2, 136.3 (t, J_{CF} = 26.1 Hz), 132.0, 129.9 (2C), 128.2 (2C), 128.1, 125.3 (t, J_{CF} = 6.4 Hz), 124.2, 122.5, 121.8 (dd, J_{CF} = 243.3, 242.8 Hz), 108.2, 45.9 (t, J_{CF} = 27.7 Hz), 45.4 (d, J_{CF} = 4.2 Hz), 26.5, 26.3.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -87.2 (d, J = 246.7 Hz, 1F), -93.30(d, J = 247.0 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2990 (w), 1720 (s), 1650 (m), 1124 (s), 730 (s). **HRMS** (ESI) calcd for $C_{18}H_{18}F_2NO$ $[M + H]^+$: 302.1351, found: 302.1358



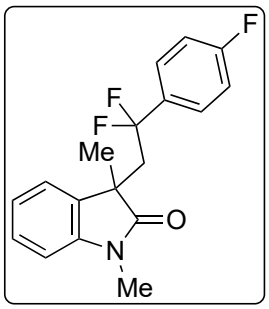
3-(2,2-Difluoro-2-(3-(trifluoromethyl)phenyl)ethyl)-1,3-dimethylindolin-2-one, 33 (0.089 g, 53%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.28 – 7.21 (m, 1H), 7.18 – 7.13 (m, 2H), 7.02 – 6.98 (m, 1H), 6.72 (d, J = 7.8 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.92 (s, 3H), 2.81 – 2.71 (m, 1H), 1.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 178.9, 142.8, 137.0 (t, J_{CF} = 27.0 Hz), 131.3, 130.5 (q, J_{CF} = 32.7 Hz), 129.1 (t, J_{CF} = 6.0 Hz), 128.8, 128.4, 126.7 (m), 123.6 (q, J_{CF} = 272.5 Hz), 124.1 (d, J_{CF} = 2.7 Hz), 122.5, 122.0 (m), 121.0 (t, J_{CF} = 243.1 Hz), 108.3, 45.5 (t, J_{CF} = 27.8 Hz), 45.1 (dd, J_{CF} = 3.0, 1.5 Hz), 26.6, 26.1.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -65.7 (s, 3F), -90.3 (d, J = 250.5 Hz, 1F), -95.2 (d, J = 250.5 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR) 2920 (w), 1712 (s), 1600 (m), 1123 (s), 701 (m). **HRMS** (ESI) calcd for $C_{19}H_{17}F_5NO$ $[M + H]^+$ 370.1230, found: 370.1228.



3-(2,2-Difluoro-2-(4-fluorophenyl)ethyl)-1,3-dimethylindolin-2-one, 34 (0.070 g, 44%) was prepared according to the General Procedure. The desired compound was obtained as a dense, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.17 (m, 1H), 7.12 (d, J = 7.4 Hz, 1H), 6.98 – 6.94 (m, 3H), 6.84 (t, J = 8.7 Hz, 2H), 6.66 (d, J = 7.8 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.89 (s, 3H), 2.65 (ddd, J = 18.4, 15.2, 9.4 Hz, 1H), 1.27 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz) δ 179.3, 163.6 (d, J_{CF} = 249.0 Hz), 143.2, 132.3 (td, J_{CF} = 26.7, 3.2 Hz), 131.9, 128.4, 127.7 (dt, J_{CF} = 8.6, 6.2 Hz), 124.4, 124.3, 122.6, 121.5 (dd, J_{CF} = 245.6, 243.3 Hz), 115.2, 115.1, 108.3, 46.2 – 45.7 (m), 45.4 (d, J_{CF} = 4.3 Hz), 26.7, 26.4.

^{19}F NMR ($CDCl_3$, 376 MHz) δ -88.9 (dd, J = 248.3, 2.9 Hz, 1F), -95.0 (dd, J = 248.5, 2.4 Hz, 1F), -114.54 (s, 1F).

FT-IR (cm^{-1}, neat, ATR) 2970 (w), 1709 (s), 1611 (m), 1162 (s), 741 (s). **HRMS** (ESI) calcd for $C_{18}H_{16}F_3NNaO$ [M + Na^+]: 342.1082, found: 342.1079.

6. Procedure for the Photoinduced Large Scale Preparation of Difluorinated-Oxindole Derivatives via C-F Activation

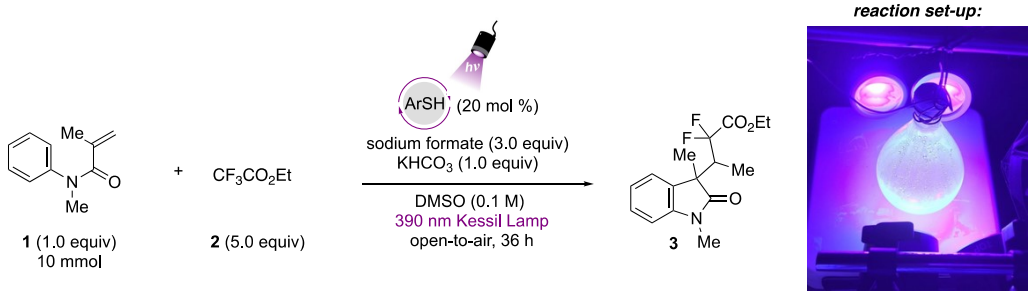
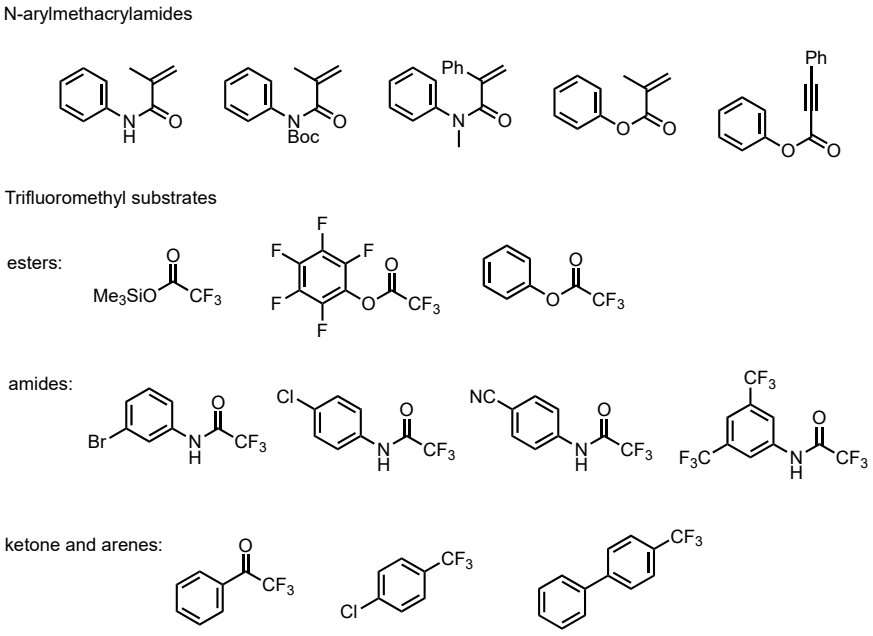


Figure S3*. Reaction conditions and set-up.*

To a 200 mL round bottom flask equipped with a magnetic stir bar was added HCO_2Na (2.0 g, 30 mmol, 3.0 equiv), $KHCO_3$ (1.0 g, 10 mmol, 1.0 equiv) and acrylamide (10 mmol, 1.0 equiv). The vial was capped and then the flask was charged with dry DMSO (100.0 mL, c = 0.1 M) and closed with a septum. Ethyl trifluoroacetate (6.0 mL, 50.0 mmol, 10.0 equiv), 4-methoxythiophenol (0.280 g, 240 µL, 0.002 mmol, 0.20 equiv) were added by syringe, and the flask was sealed with Parafilm. The reaction was then irradiated with four Kessil® PR160-390 nm lamp at 4 cm distance. The reaction was stirred for 36 h of irradiation without the use of cooling fan. After 36 h of irradiation, the reaction was quenched slowly with ice-cold H_2O (100 mL) and extracted with EtOAc (3 X 60 mL). The combined organic extracts were washed with brine (50 mL), dried (Na_2SO_4) then decanted, and the solvent was removed via rotary evaporation. The crude material was then redissolved in CH_2Cl_2 and evaporated onto silica to be purified via automated flash silica

column chromatography. Eluting with 15-30% EtOAc/hexane provided the desired product in 64% yield (1.9 g, 6.4 mmol).

7. Unsuccessful Substrates



8. Mechanistic Studies

Quantum Yield Experiment

Determination of light intensity for 370 nm PR160 Lamp

The photon flux of the light source was determined by standard potassium ferrioxalate actinometry as previously reported.[3] The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at rt. Ferrioxalate solution (0.15 M): Potassium ferrioxalate hydrate (1.312 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (25 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light. Developer solution: 1,10-Phenanthroline (25 mg) and NaOAc (5.63 g) was added to a flask containing H_2SO_4 (25 mL, 0.5 M) and sonicated until completely solvated.

The absorbance of the non-irradiated sample: The buffered solution of phen (350 μL) was added to the ferrioxalate solution (2.0 mL) in a vial that had been covered with aluminum foil and with the lights of the laboratory switched off. The vial was capped and allowed to rest for 1 h and then

transferred to a cuvette. The absorbance of the non-irradiated was measured at 510 nm to be 0.056 (average of two determinations).

The absorbance of the irradiated sample: In a cuvette equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 30 s at λ = 390 nm with an excitation slit width = 10.0 nm. After irradiation, the buffered phen solution (350 μL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance was measured at 510 nm to be 2.358 (average of two determinations).

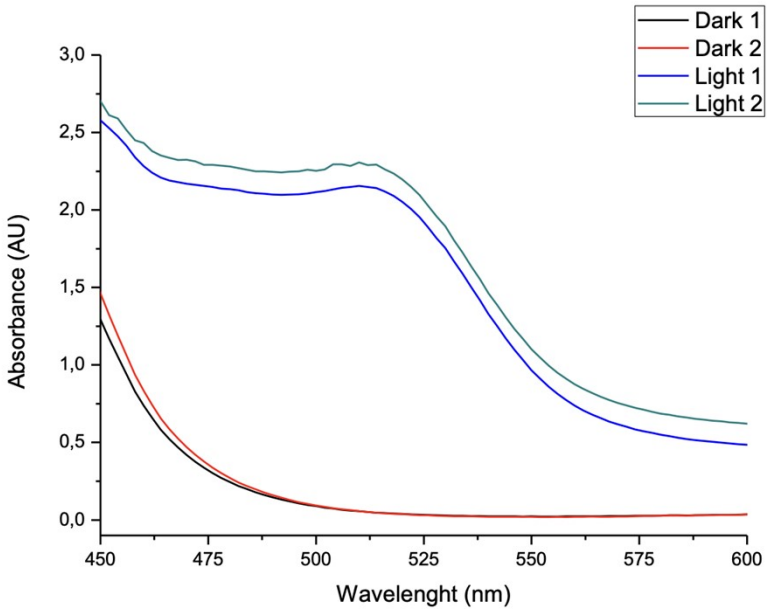


Figure S4. *Absorbance of the non-irradiated sample (Dark 1 and Dark 2) and the irradiated sample (Light 1 and Light 2).*

The quantum yield of the reaction was determined using the equation (1) and the experimental procedure previously reported:

$$\Phi(reaction\ at\ 370\ nm) = \frac{mol\ of\ formed\ product}{mol\ of\ photon\ flux \cdot t \cdot f} \qquad (1)$$

where Φ is the quantum yield of the reaction, t is the time of the reaction (s), f is the incident light absorbed by the reaction mixture at 370 nm and the photon flux is calculated by standard ferrioxalate actinometry.

The fraction of light, f, absorbed was determined according to equation 2:

$$F = 1 - 10^{-A} \qquad (2)$$

where A is the absorbance of the reaction mixture in DMSO at 370 nm. The absorbance (A) at 370 nm was determined to be 1.034, thus indicating the fraction of light absorbed is 0.91 according to equation 2.

The standard ferrioxalate actinometry was used to determine the photon flux of the spectrophotometer using equations 3 and 4. For the ferrioxalate actinometer the production of Iron (II) ions proceeds by the following reactions:

$$[Fe(C_2O_4)n]^{+(3-2n)} \xrightarrow{\text{light}} Fe^{+2} + (n-1)(C_2O_4)^{-2} + C_2O_4^{-}$$

$$[Fe(C_2O_4)n]^{+(3-2n)} + C_2O_4^{-} \longrightarrow Fe^{+2} + n(C_2O_4)^{-2} + 2\,CO_2$$

The moles of Fe^{+2} formed are determined spectrophotometrically by development with 1,10-phenanthroline (phen) to form the red $[Fe(phen)3]^{+2}$ moiety (λ = 510 nm). The photon flux is defined as shown in equation 3:

$$Photon\ flux = \frac{mol\ Fe^{+2}}{\Phi\left(Fe^{+2}\right)\cdot t\cdot f} \qquad (3)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.1 at λ = 370 nm and 0.15 M), t is the time (s), f ~1, and the mol of Fe^{+2} is calculated according to equation 4.

$$mol\left(Fe^{+2}\right) = \frac{V\cdot\Delta A}{l\cdot\epsilon} \qquad (4)$$

Where V is the total volume of the solution, ΔA is the difference in absorbance between irradiated and nonirradiated solutions, l is the path length (1.0 cm), ε is the molar absorptivity at 510 nm (11110 L mol^{-1} cm^{-1}).

$$mol\left(Fe^{+2}\right) = \frac{V\cdot\Delta A}{l\cdot\epsilon} \qquad (4)$$

$$mol\left(Fe^{+2}\right) = \frac{0.00235\ L \cdot 2.301}{1.0\ cm \cdot 11100\ L \cdot mol^{-1} cm^{-1}} = 4.87x10^{-7} mol$$

$$Photon\ flux = \frac{mol\ Fe^{+2}}{\Phi\left(Fe^{+2}\right) \cdot t \cdot f} \qquad (3)$$

$$Photon\ flux = \frac{4.87x10^{-7} mol}{1.1 \cdot 30\ s \cdot 1} = 1.48x10^{-8}\ einstein\ s^{-1}$$

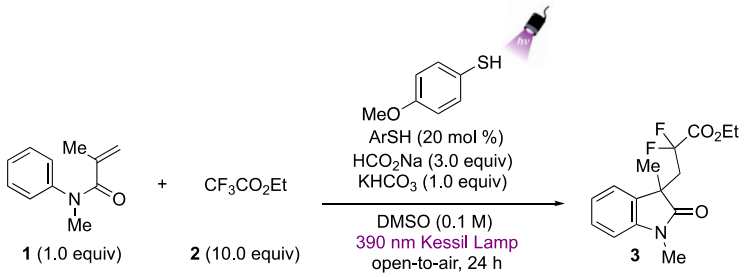
Therefore, the quantum yield of the reaction is determined to be:

$$\Phi(reaction\ at\ 370\ nm) = \frac{mol\ of\ formed\ product}{mol\ of\ photon\ flux \cdot t \cdot f} \qquad (1)$$

The mol of formed product was determined based on the reaction yield after 1h reaction ($1.7x10^{-5}\ mol$, 17% yield).

$$\Phi(reaction\ at\ 370\ nm) = \frac{1.7x10^{-5}\ mol}{1.48x10^{-8}\ einstein\ s^{-1} \cdot 3600\ s \cdot 0.91} = 0.35$$

UV-VIS



The UV-Vis spectra of the solutions of the components 2, the thiol catalyst ArSH, and the thiol catalyst in the presence of base were collected (Figure S5). The data was also acquired for the solution containing the mixture of all the reaction components, following the same stoichiometry of the reaction at 0.1M. All solutions were prepared in DMSO and in the presence of air.

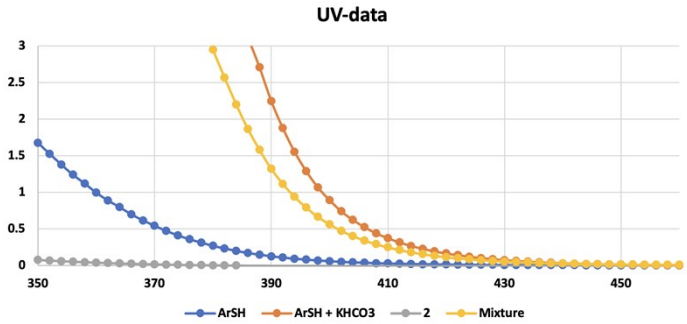


Figure S5. *Results of UV-Spectral studies. ArSH = 4-methoxybenzenethiol.*

Fluorescence Quenching Experiment

For the Stern-Volmer quenching experiment, the fluorescence measurements were acquired at room temperature using a Photon Technologies International (PTI) QuantaMaster40 fluorometer with excitation slits open at 3.0 nm and emission slit open at 3.0 nm. The emission quenching was performed using quartz cuvettes. The sample was prepared in dry DMSO (1 mL) with 4-methoxybenzenethiol (1.0 mM) and $KHCO_3$ (10 equiv) to ensure the formation of the corresponding thiolate. The excitation wavelength was fixed at 390 nm, the emission light was acquired from 405 nm to 650 nm.

The emission profile of continuously irradiated solution of 4-methoxybenzenethiol and $KHCO_3$ was recorded initially in absence of quencher, with maximum emission at λ = 435 nm. Then, aliquots of the quencher ethyl trifluoroacetate were successively added, leading to the concentrations indicated in Figure S6, and the corresponding emissions were recorded. As observed from the ratio of Io/I *vs* λ (nm) (Figure S7) an obvious radiative deactivation of the excited states occurred as the quencher concentration was increased. When the same experiment was performed using *N*-arylmethacrylamide 1, no quenching was observed.

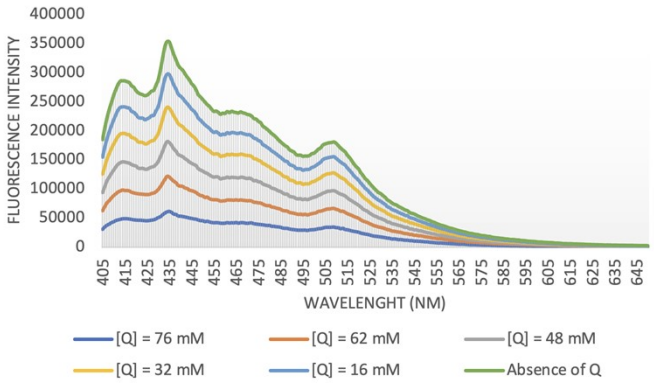


Figure S6. *Emission profile of the 4-methoxybenzenethiolate (1mM in DMSO) recorded in presence of increasing amounts of ethyl trifluoroacetate as quencher.*

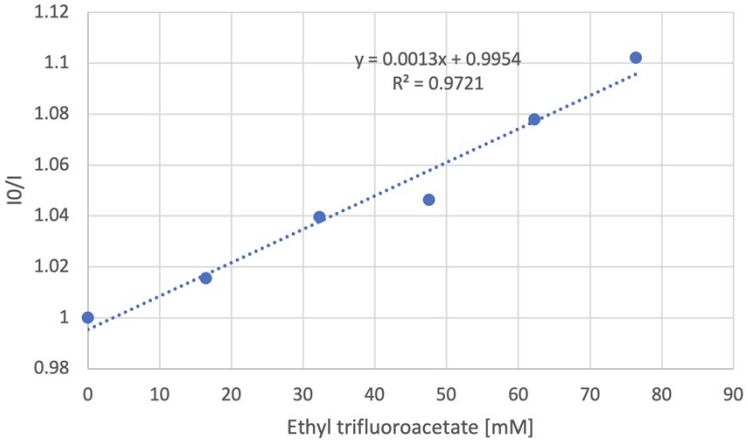
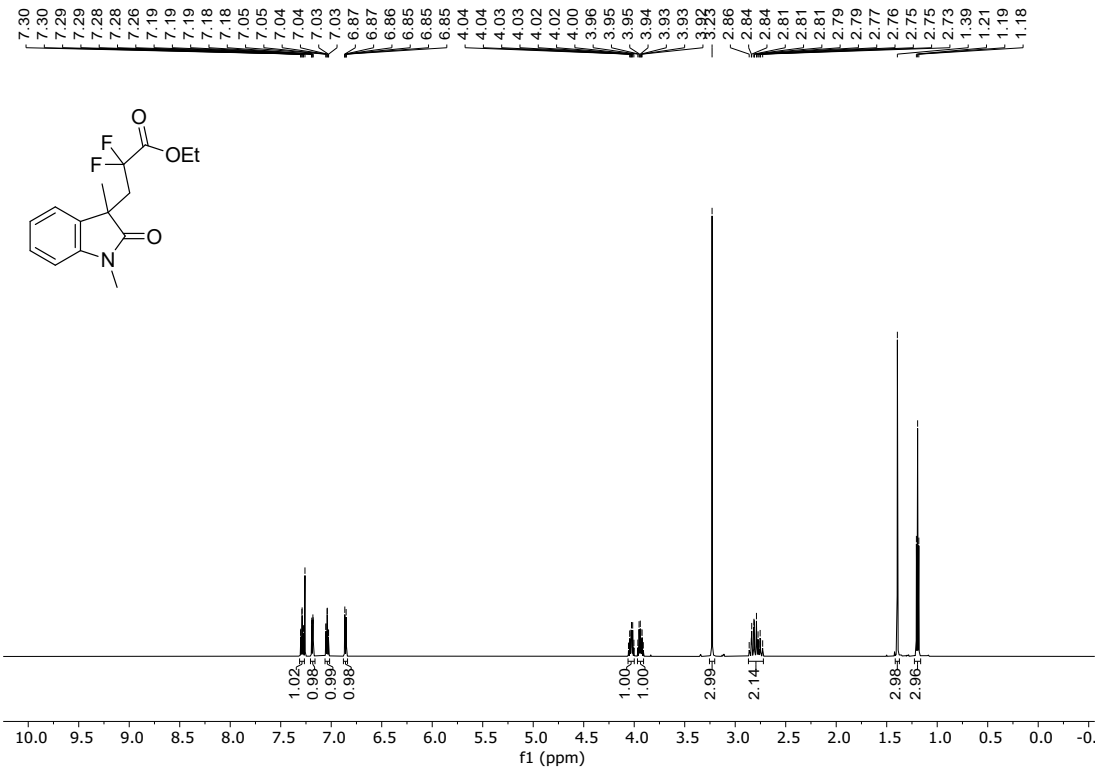
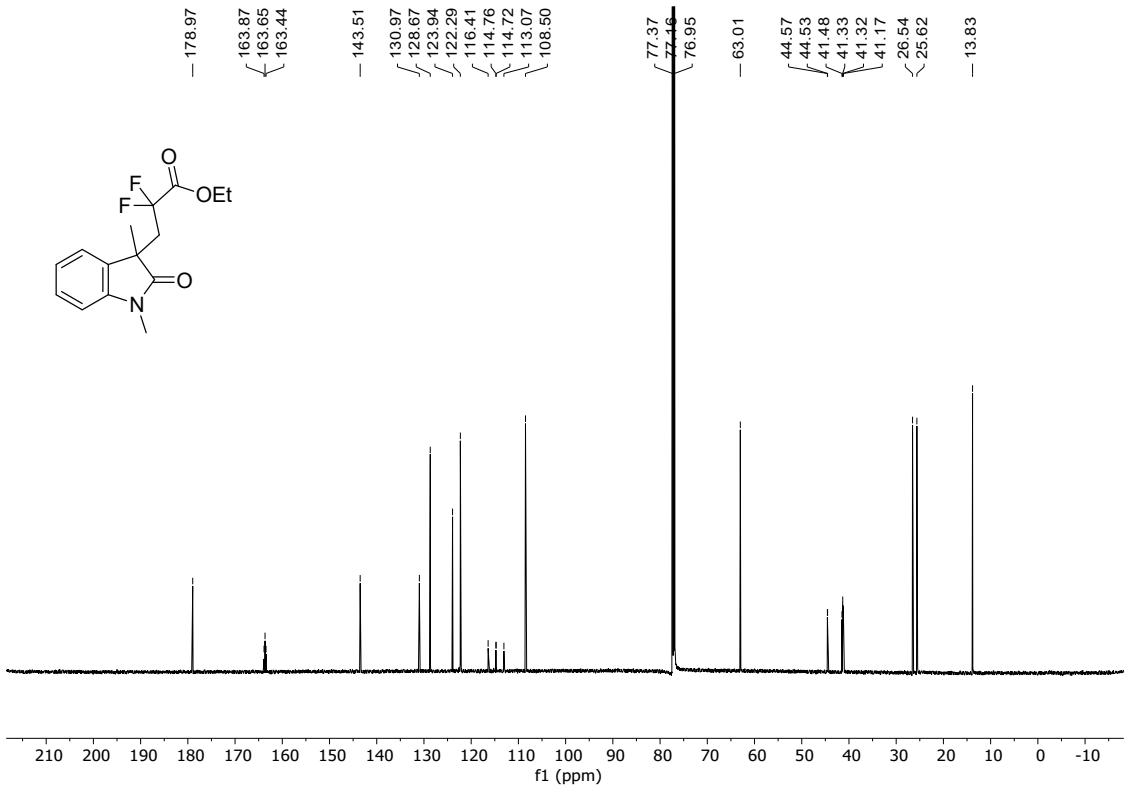


Figure S7. *Stern-Volmer plot analysis.*

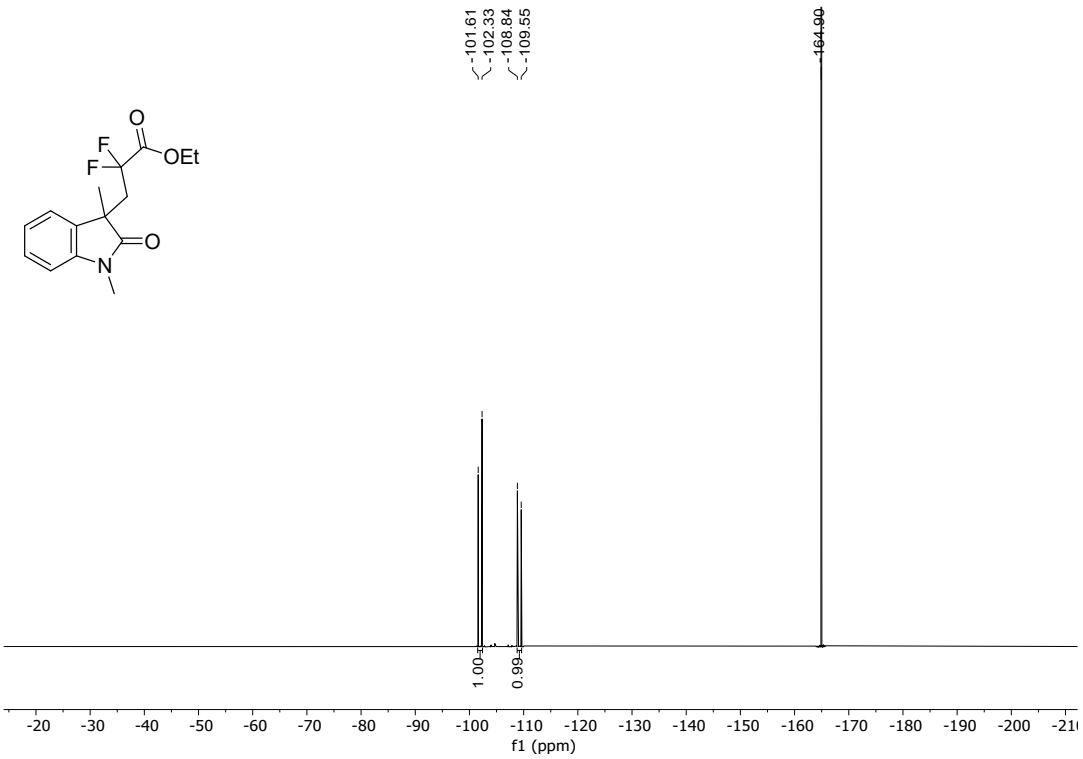
9. NMR Spectra of Synthesized Compounds



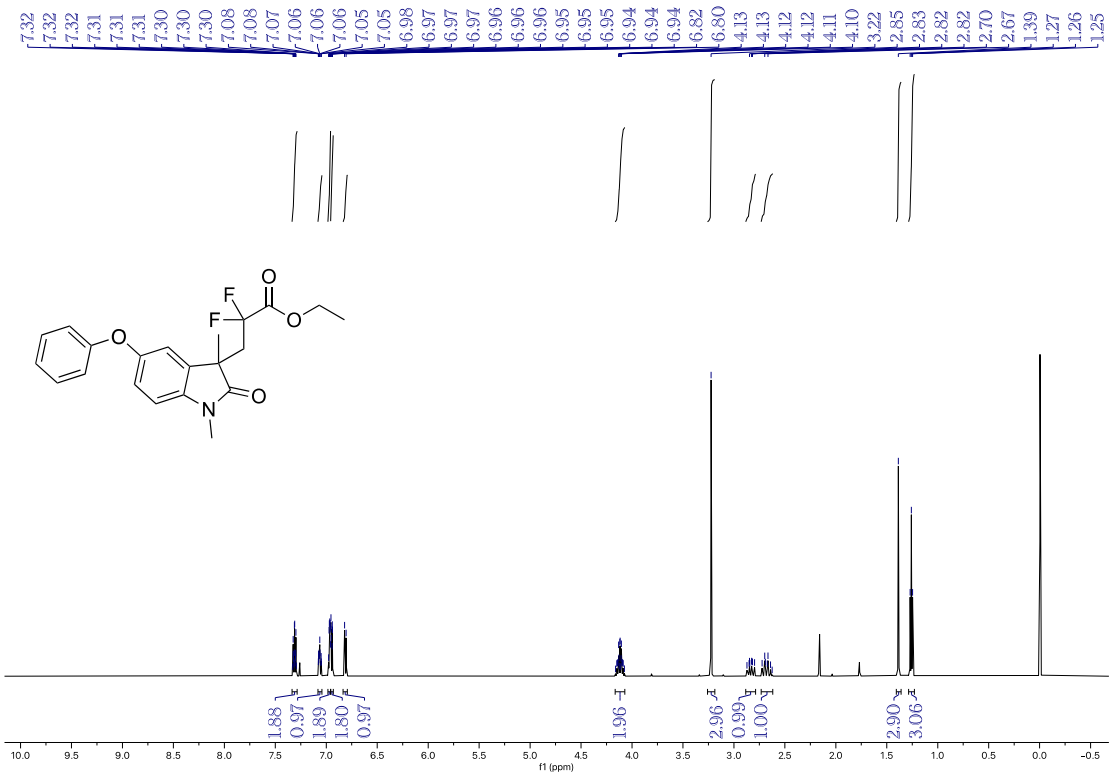
^{1}H NMR (600 MHz, $CDCl_3$) of compound **3**.



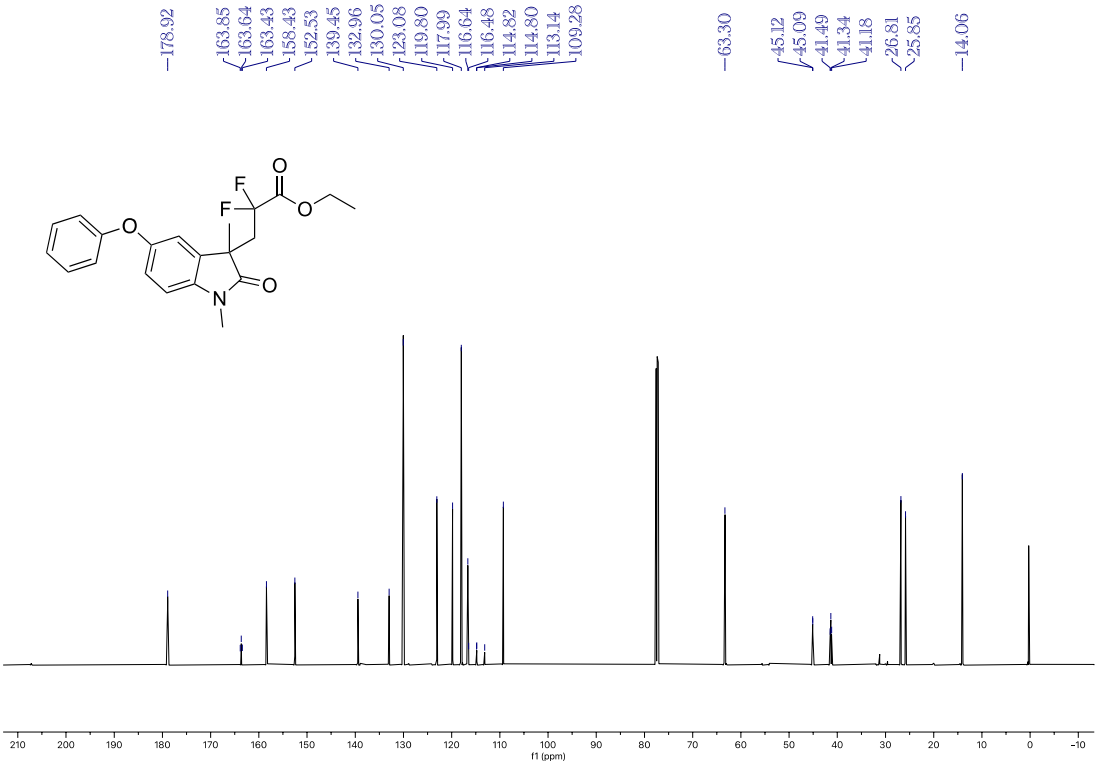
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3**.



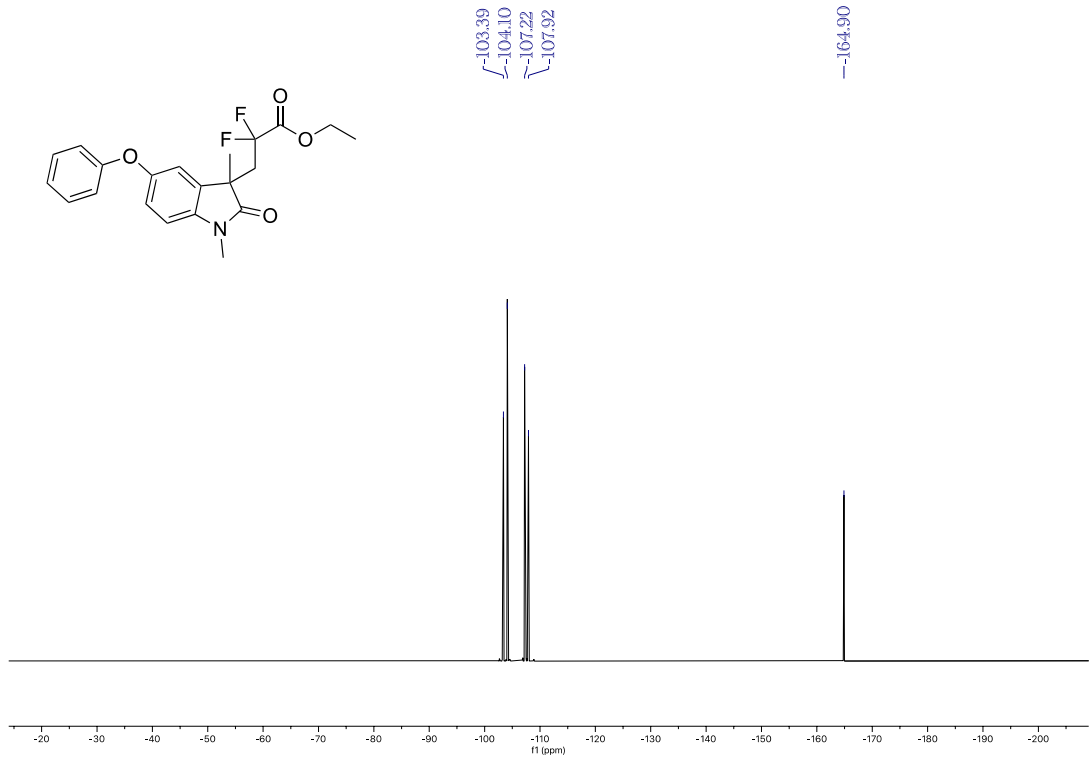
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



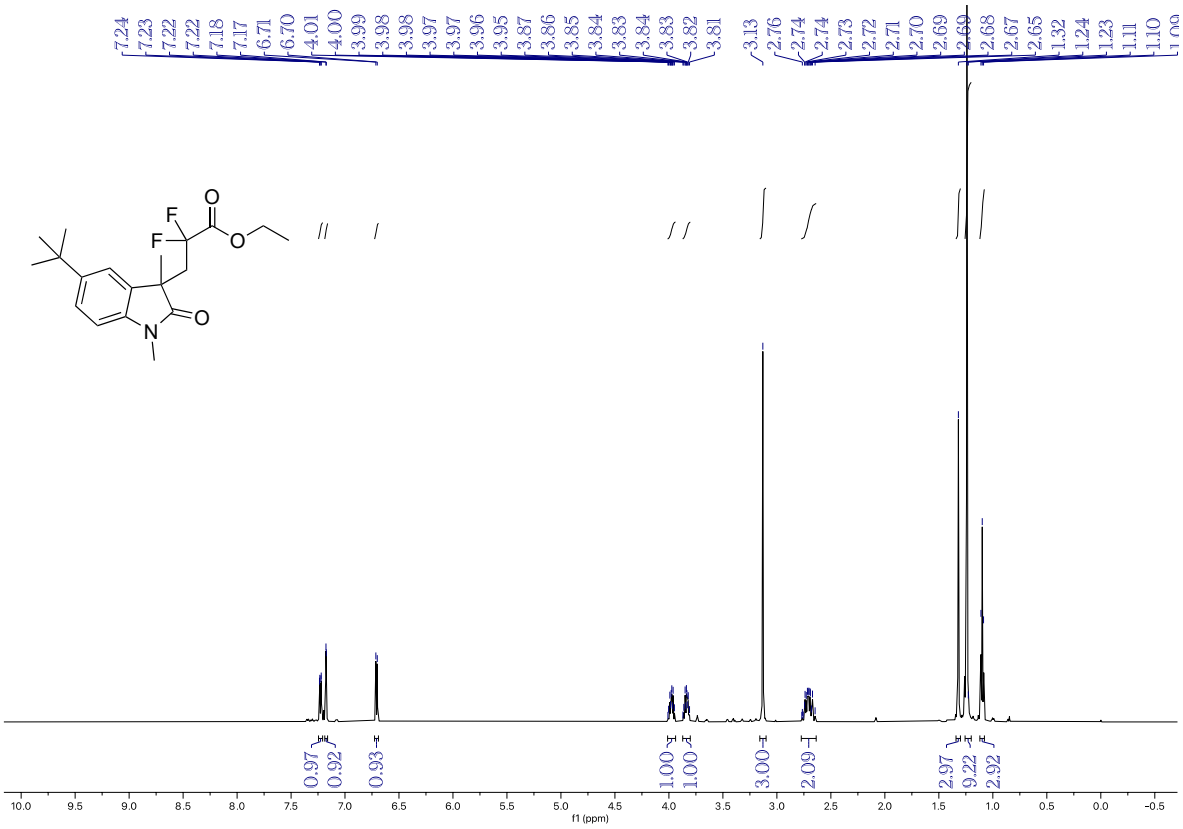
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4**.



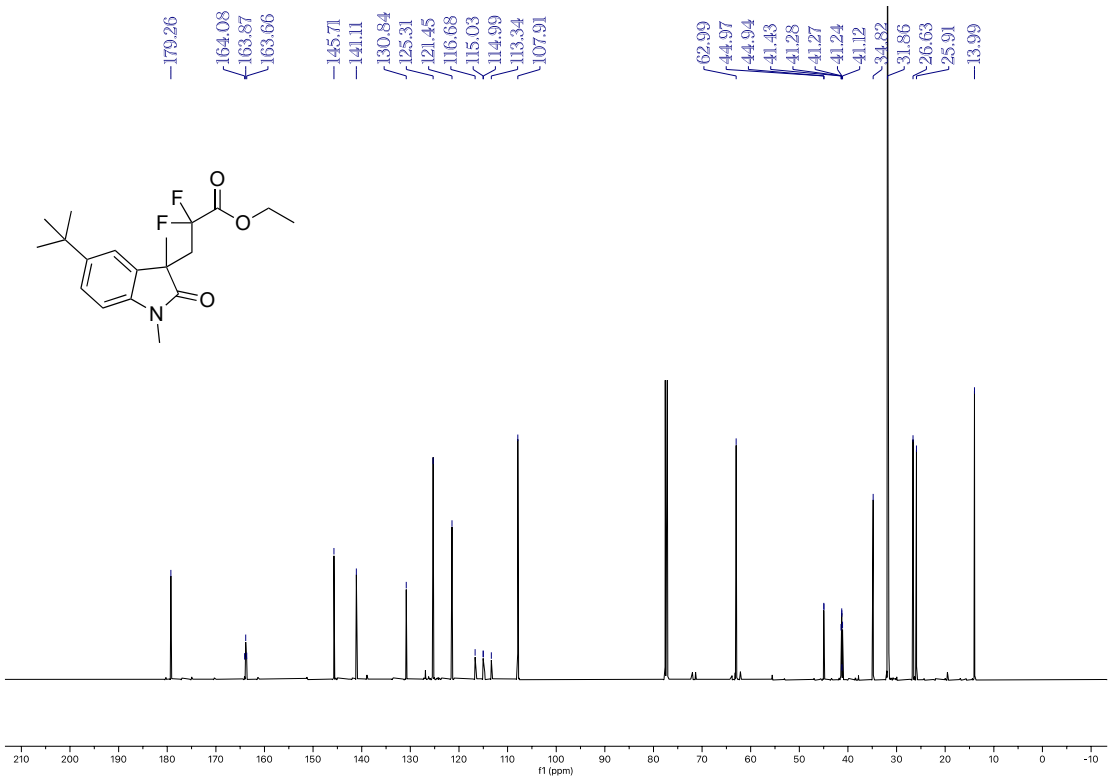
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4**.



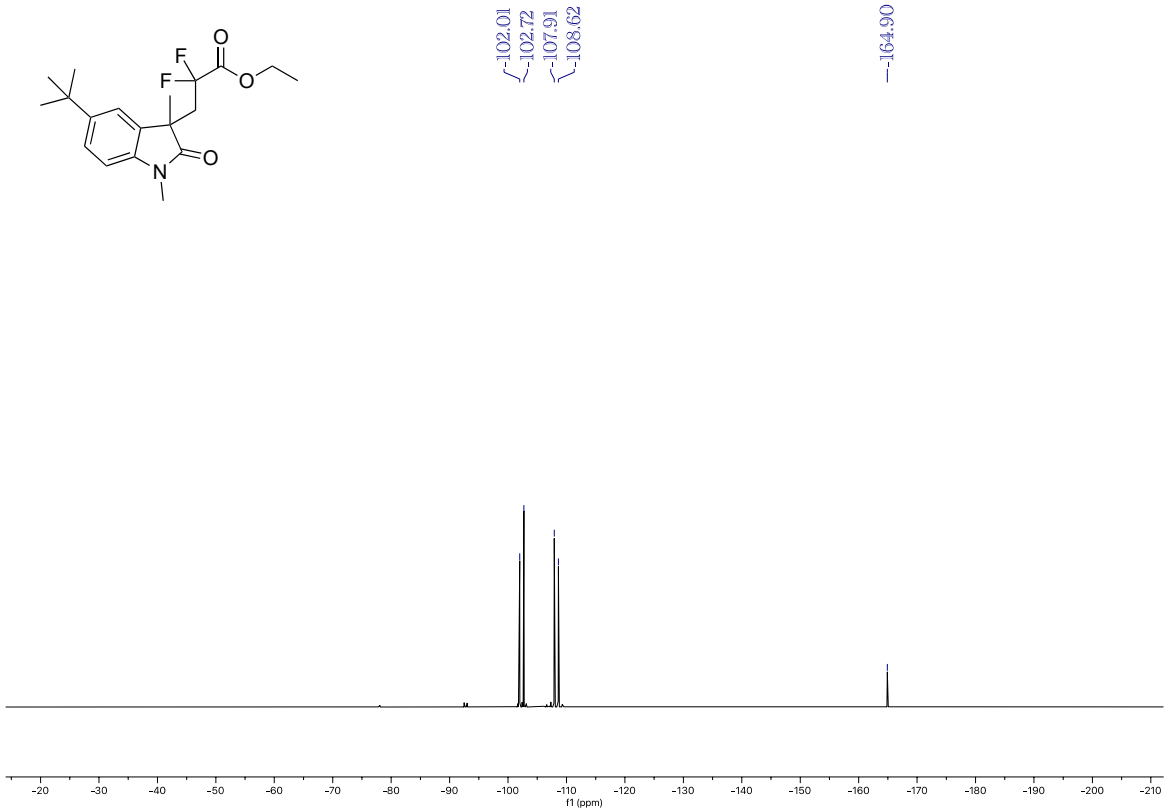
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



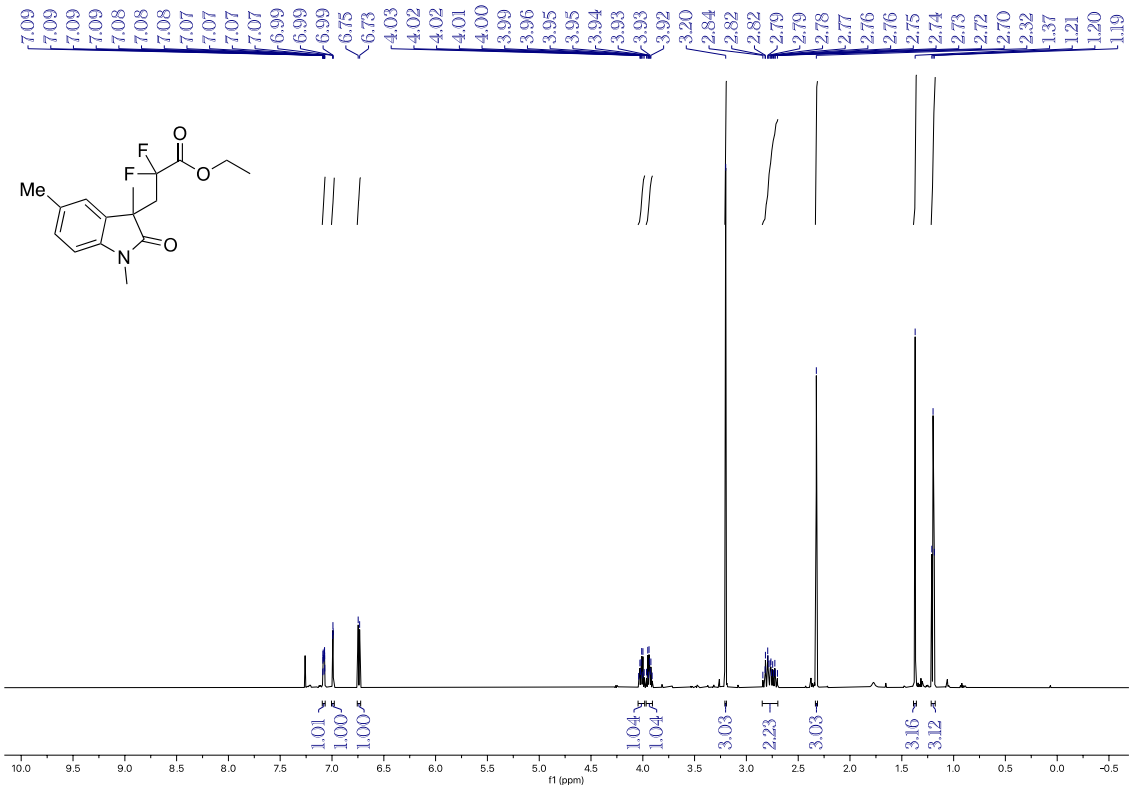
^{1}H NMR (600 MHz, $CDCl_3$) of compound **5**.



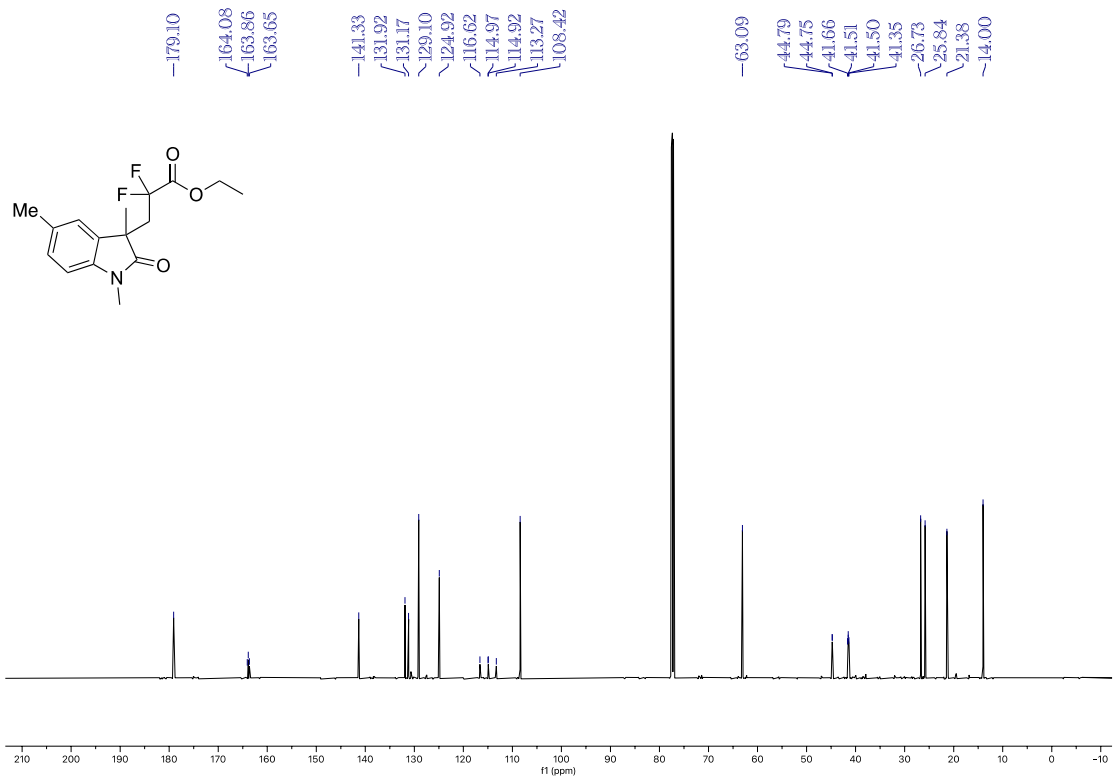
^{13}C NMR (151 MHz, $CDCl_3$) of compound **5**.



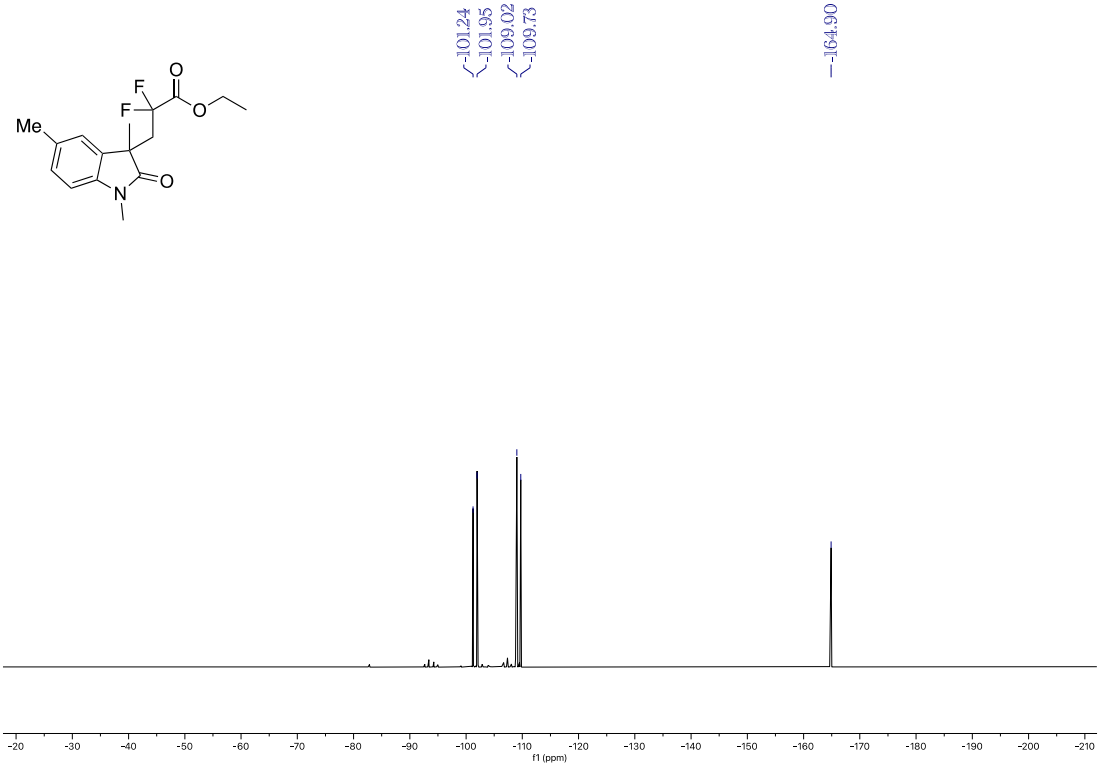
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



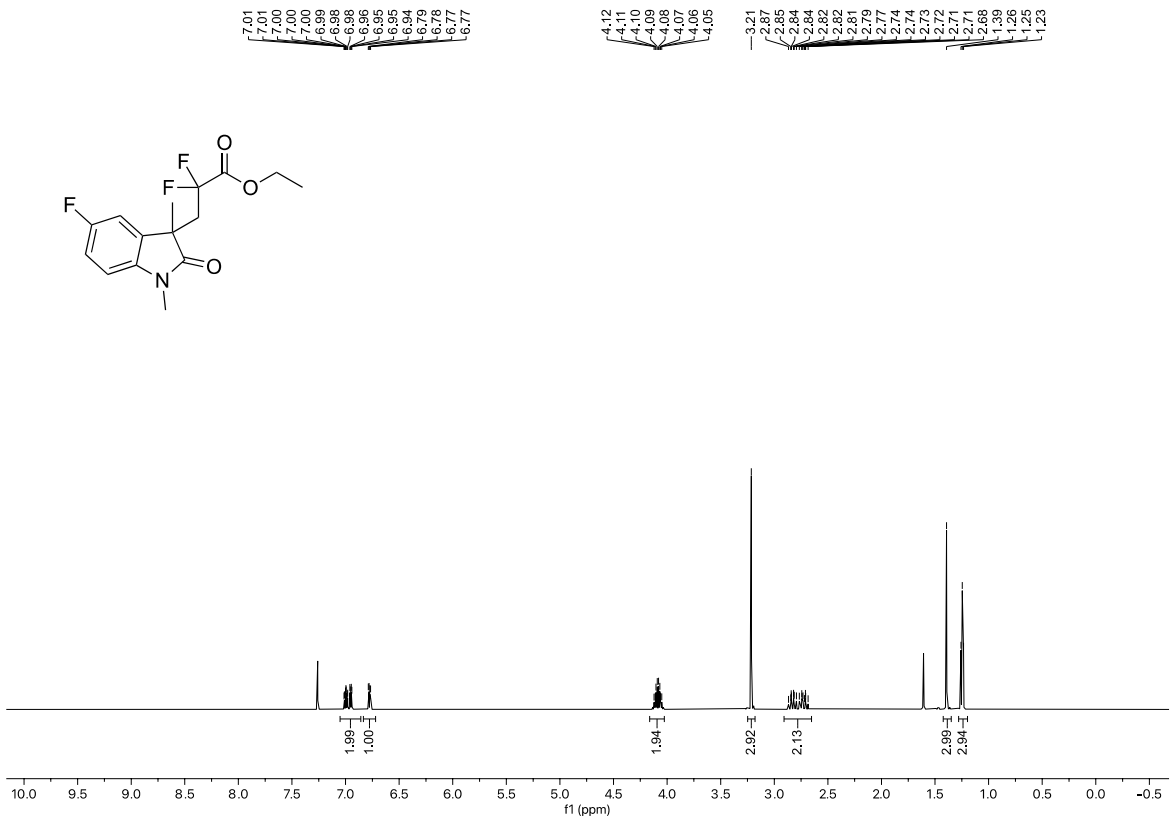
^{1}H NMR (600 MHz, $CDCl_3$) of compound **6**.



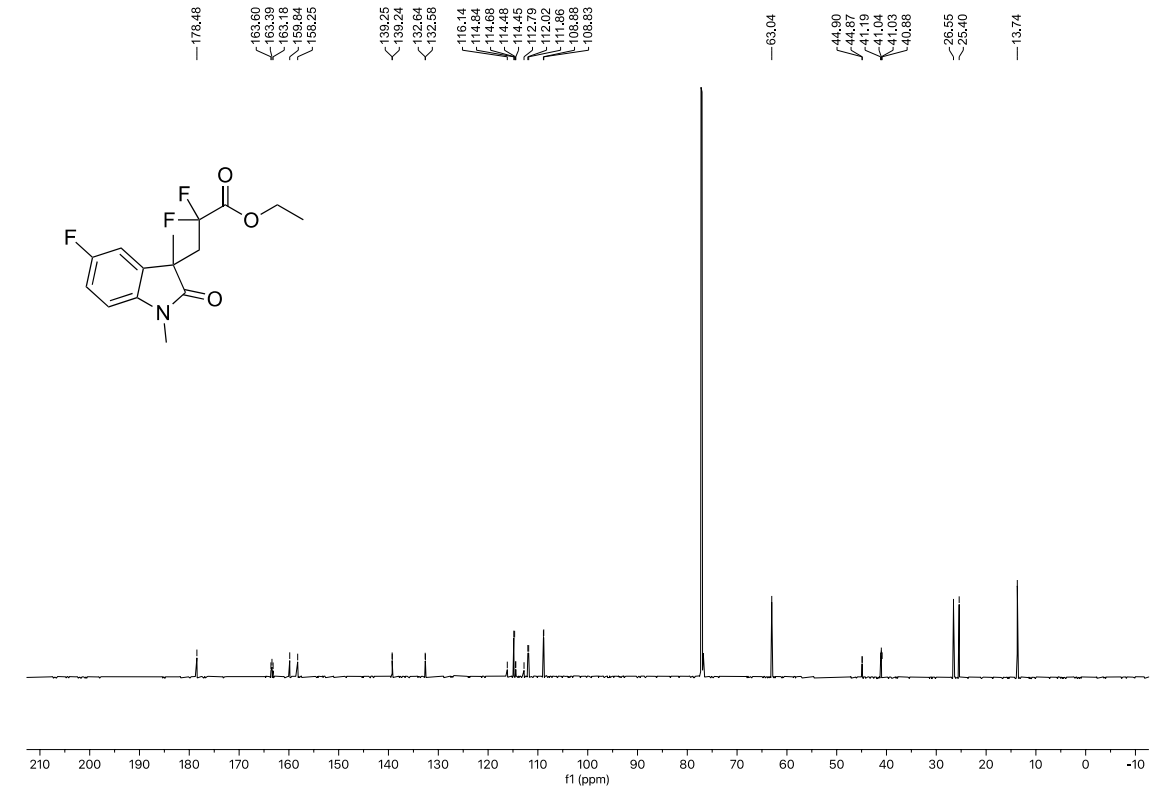
^{13}C NMR (151 MHz, $CDCl_3$) of compound **6**.



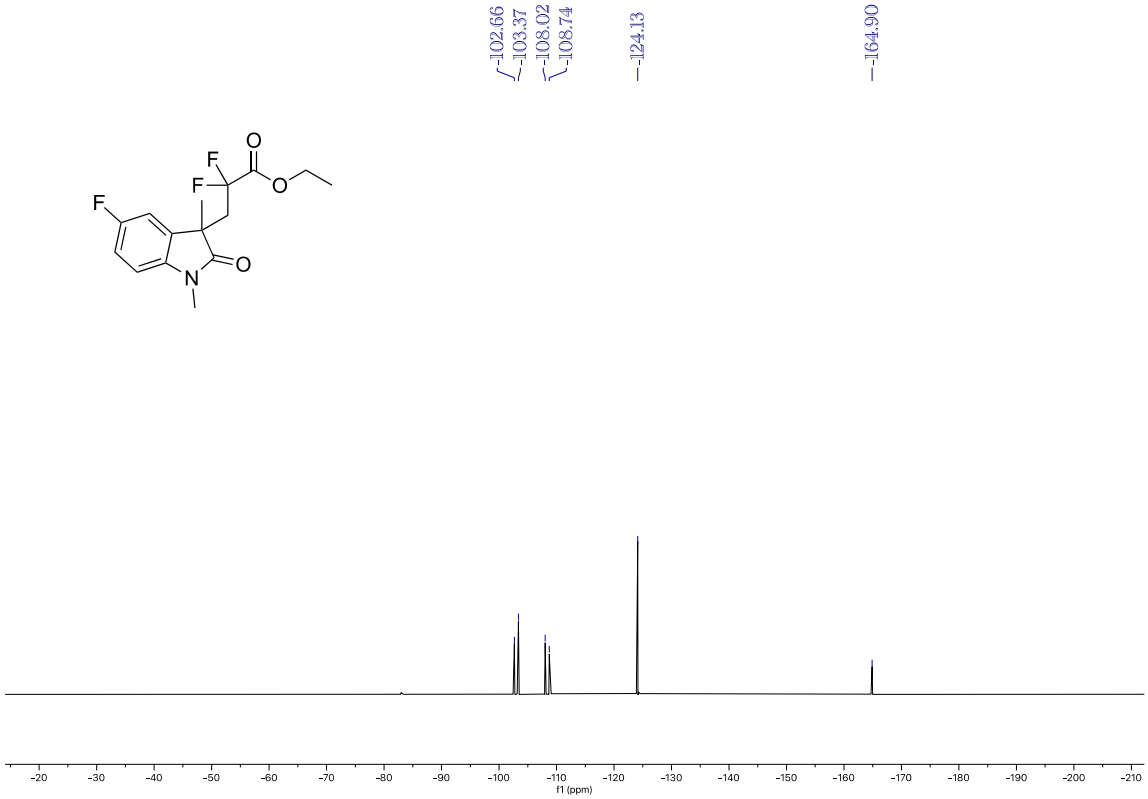
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



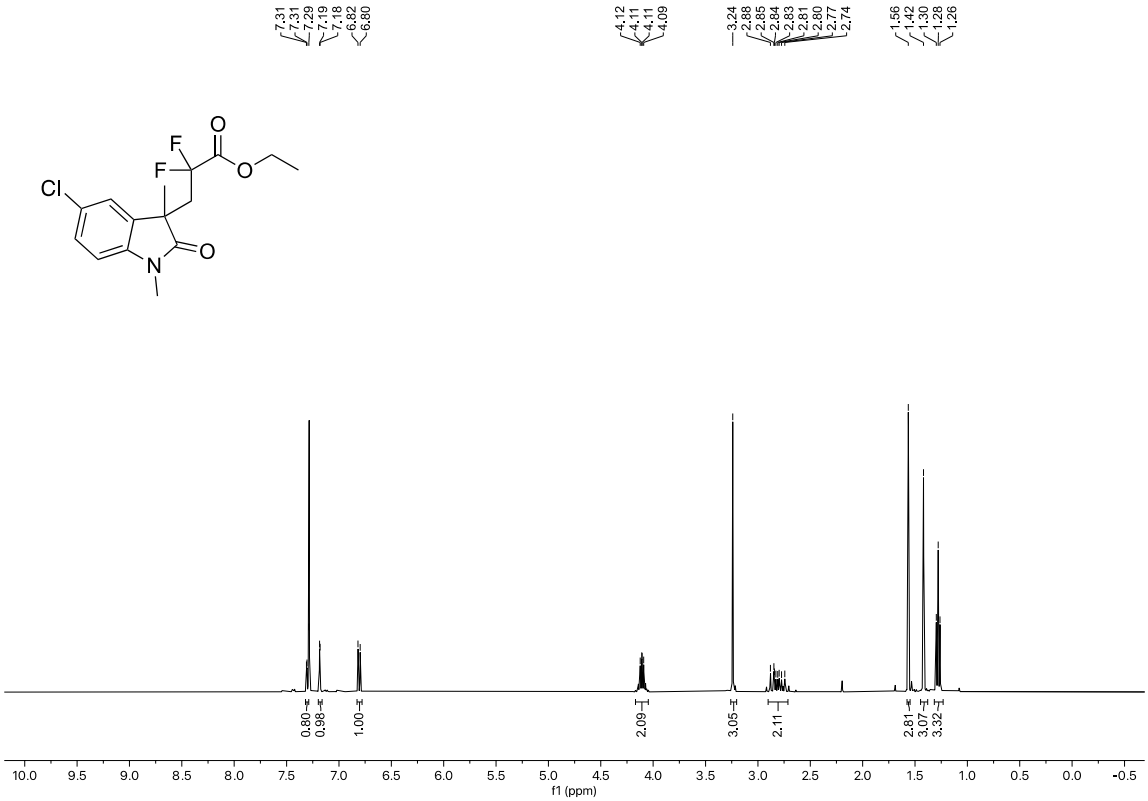
^{1}H NMR (600 MHz, $CDCl_3$) of compound **7**.



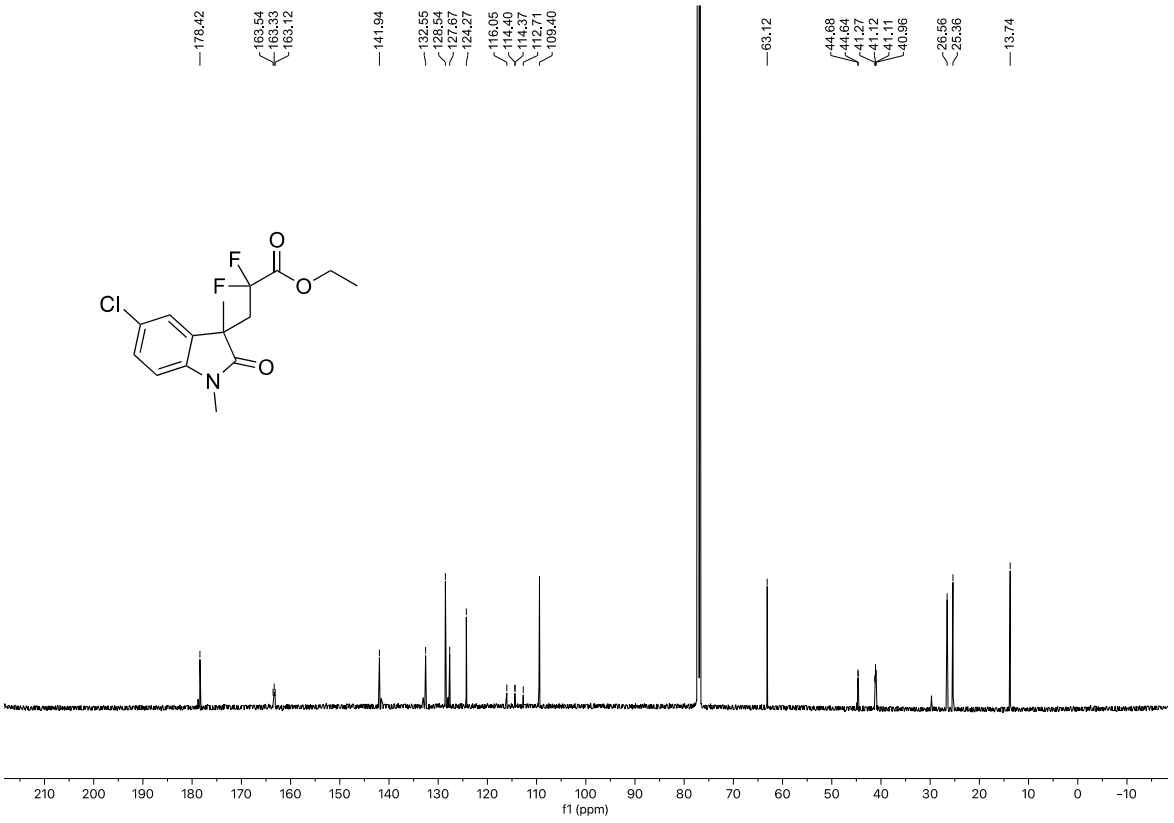
^{13}C NMR (151 MHz, $CDCl_3$) of compound **7**.



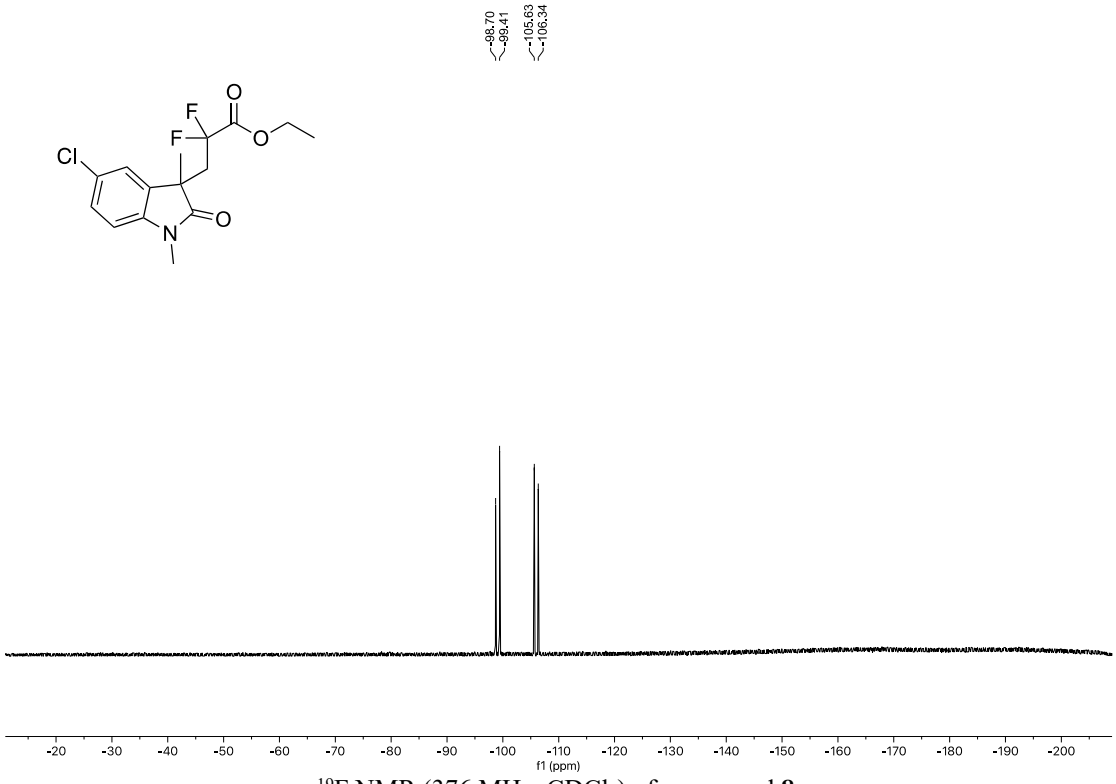
^{19}F NMR (376 MHz, $CDCl_3$) of compound **7**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



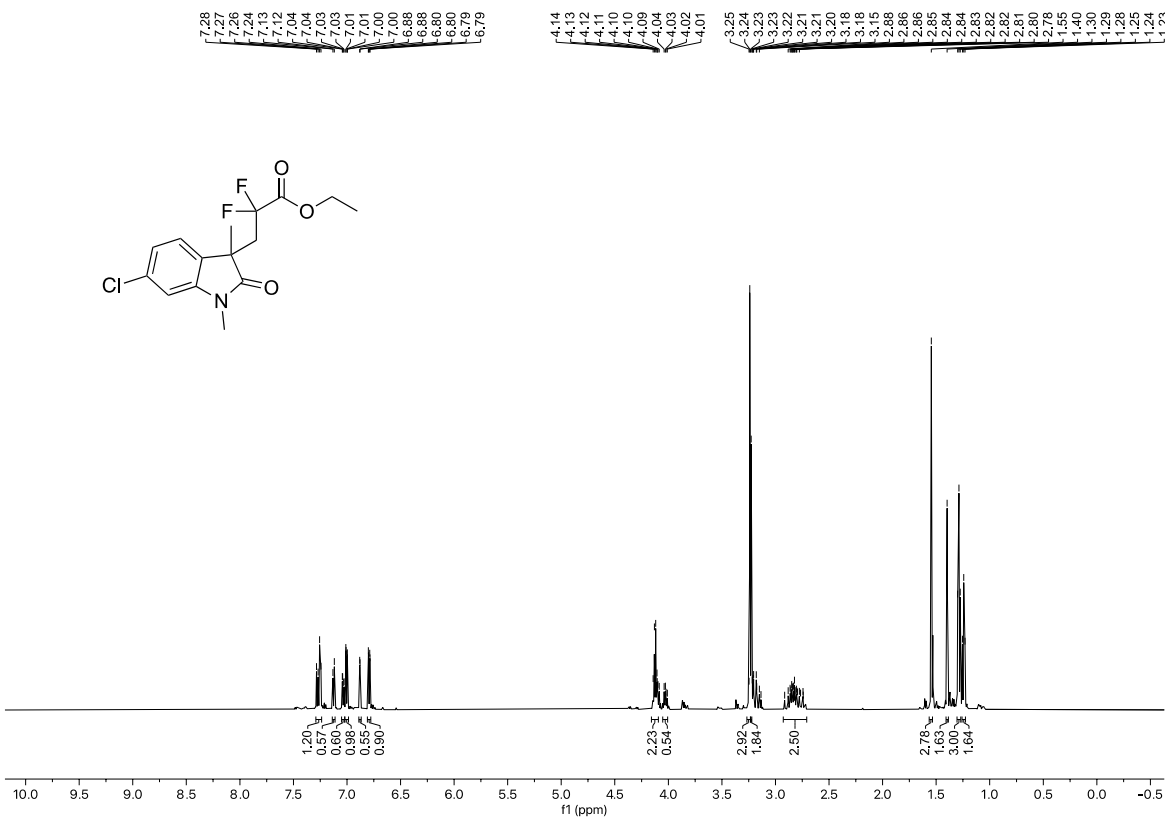
^{1}H NMR (600 MHz, $CDCl_3$) of compound **8**.



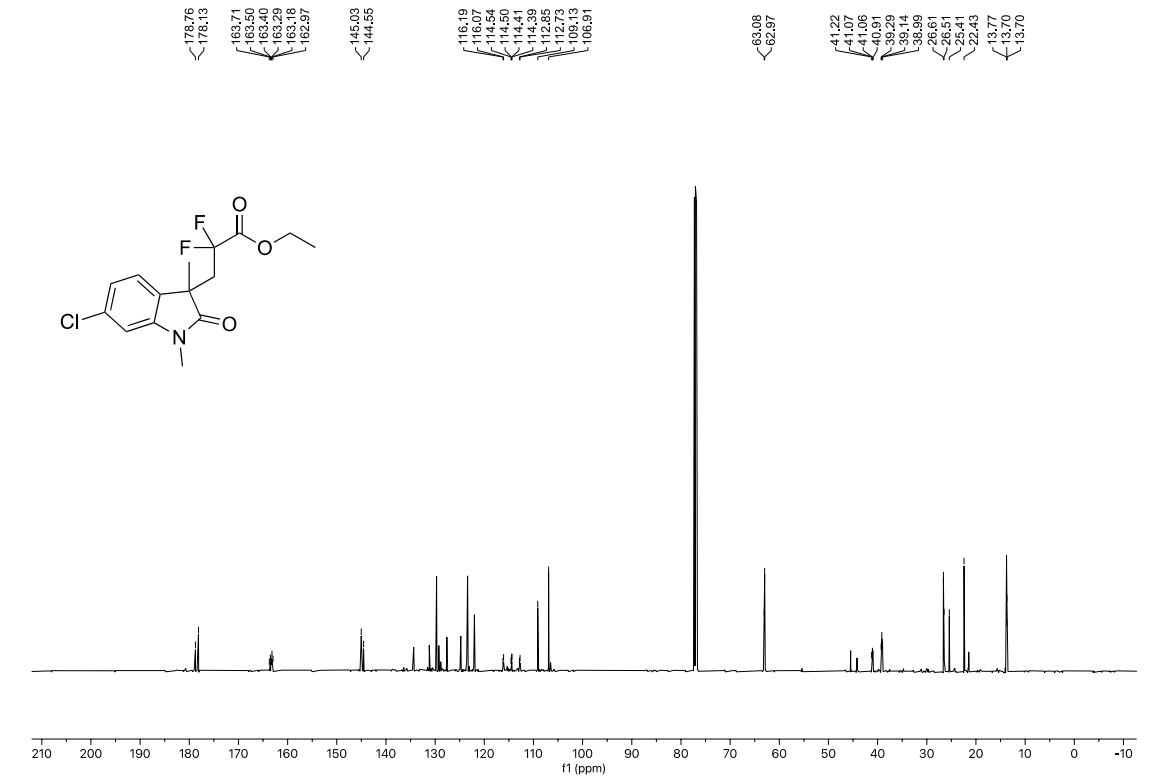
^{13}C NMR (151 MHz, $CDCl_3$) of compound **8**.



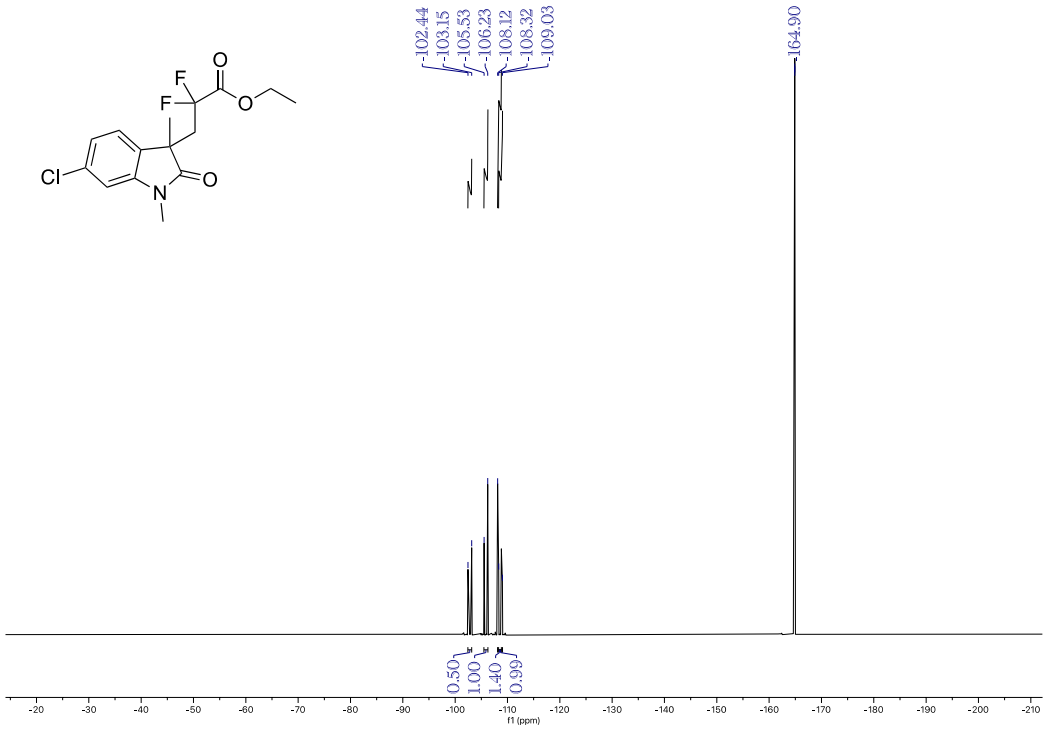
^{19}F NMR (376 MHz, $CDCl_3$) of compound **8**.



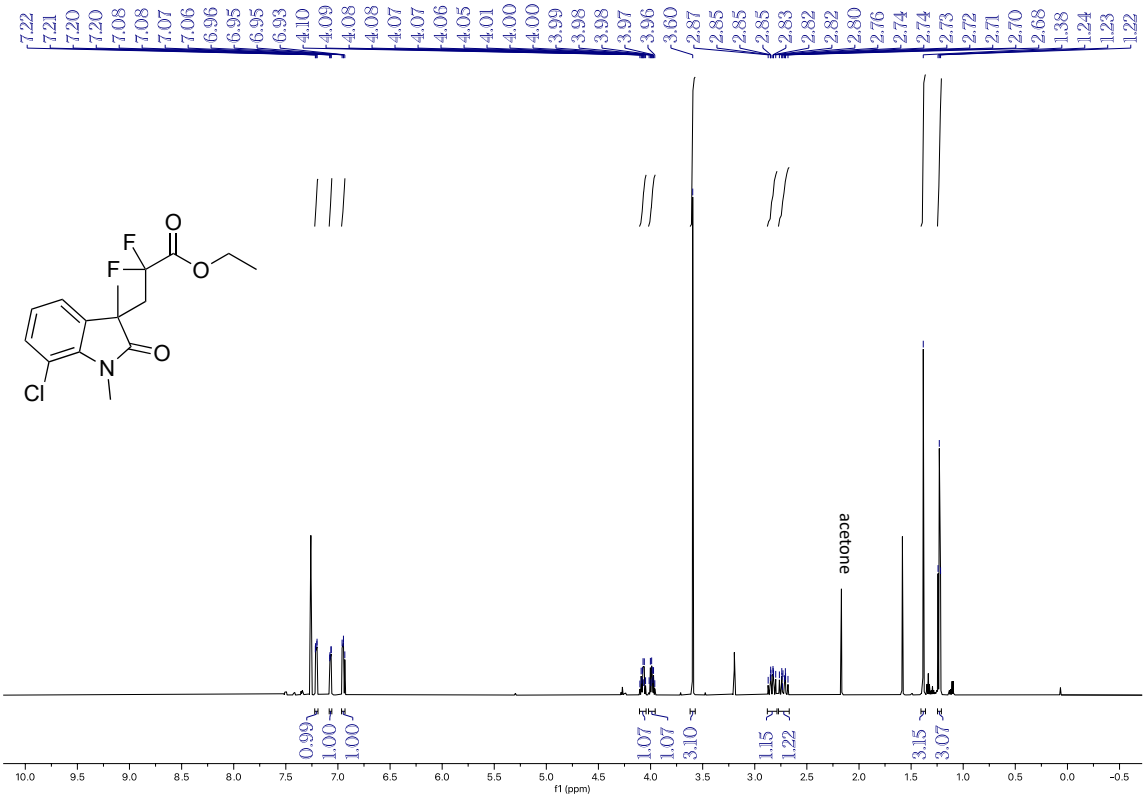
^{1}H NMR (600 MHz, $CDCl_3$) of compound **9**.



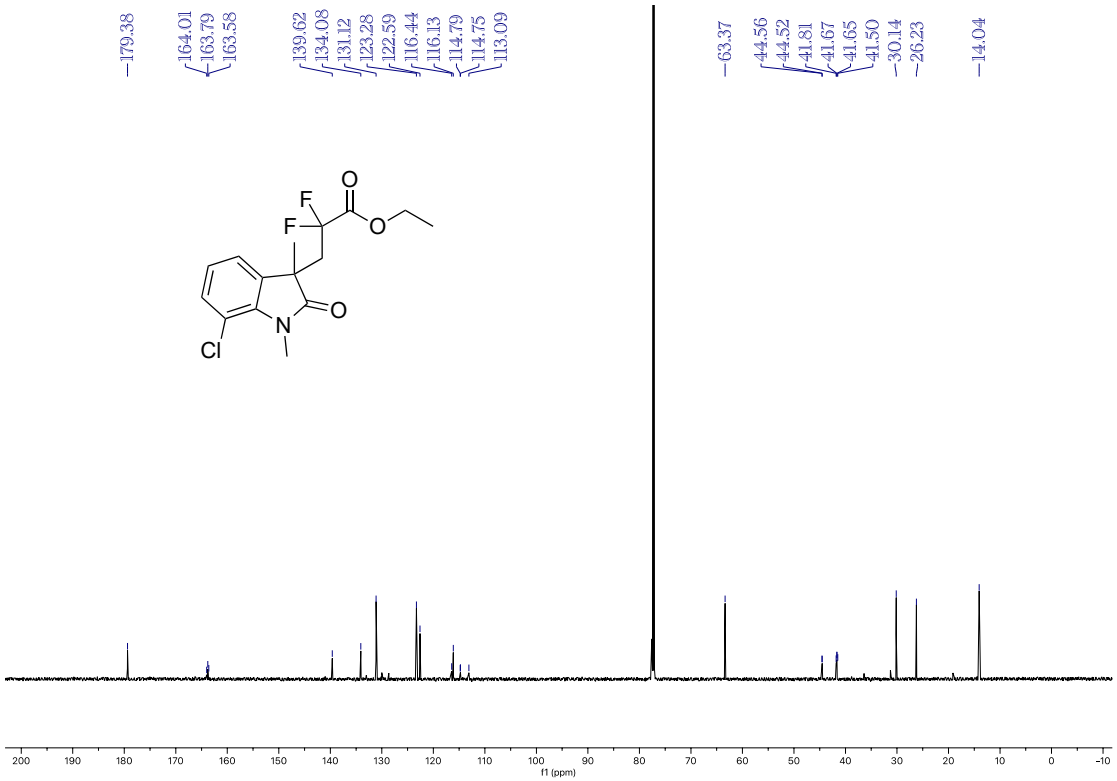
^{13}C NMR (151 MHz, $CDCl_3$) of compound **9**.



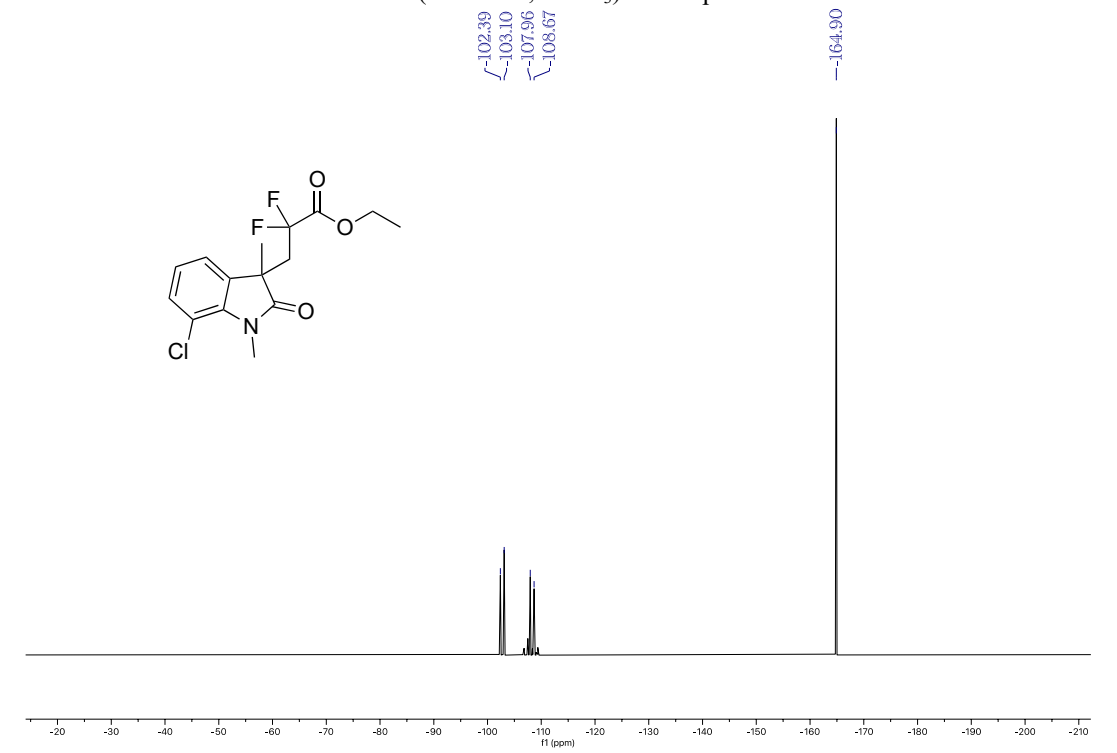
^{19}F NMR (376 MHz, $CDCl_3$) of compound **9**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



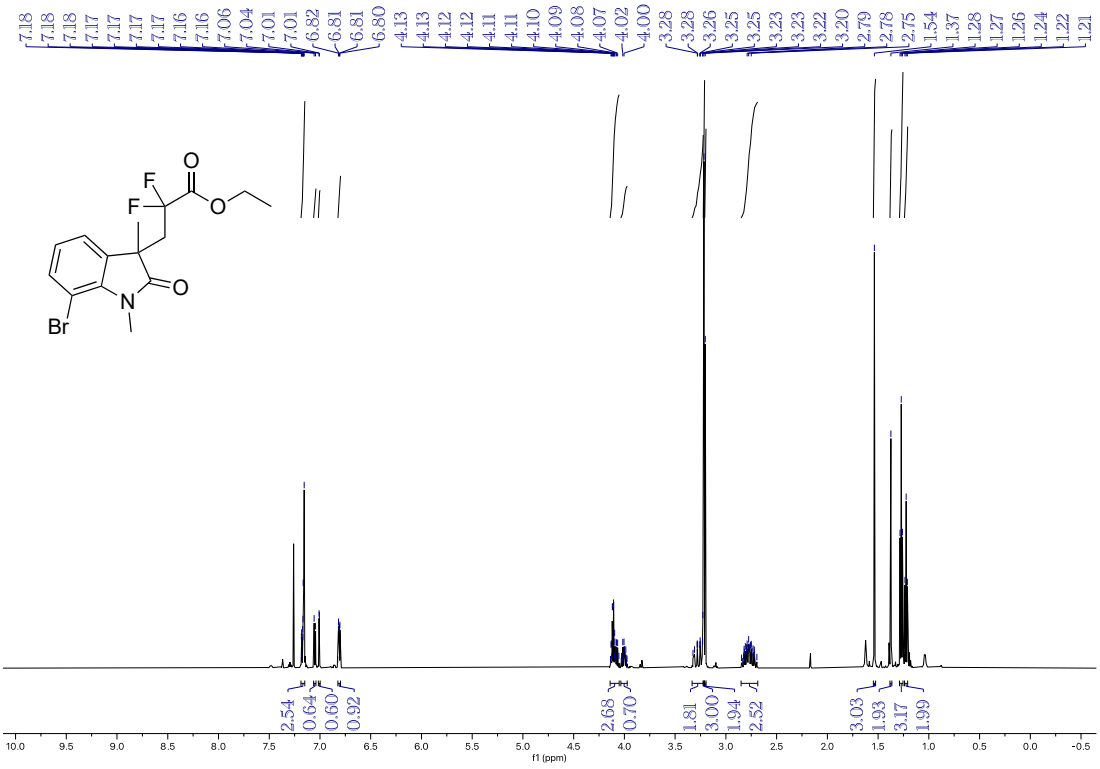
^{1}H NMR (600 MHz, $CDCl_3$) of compound **10**.



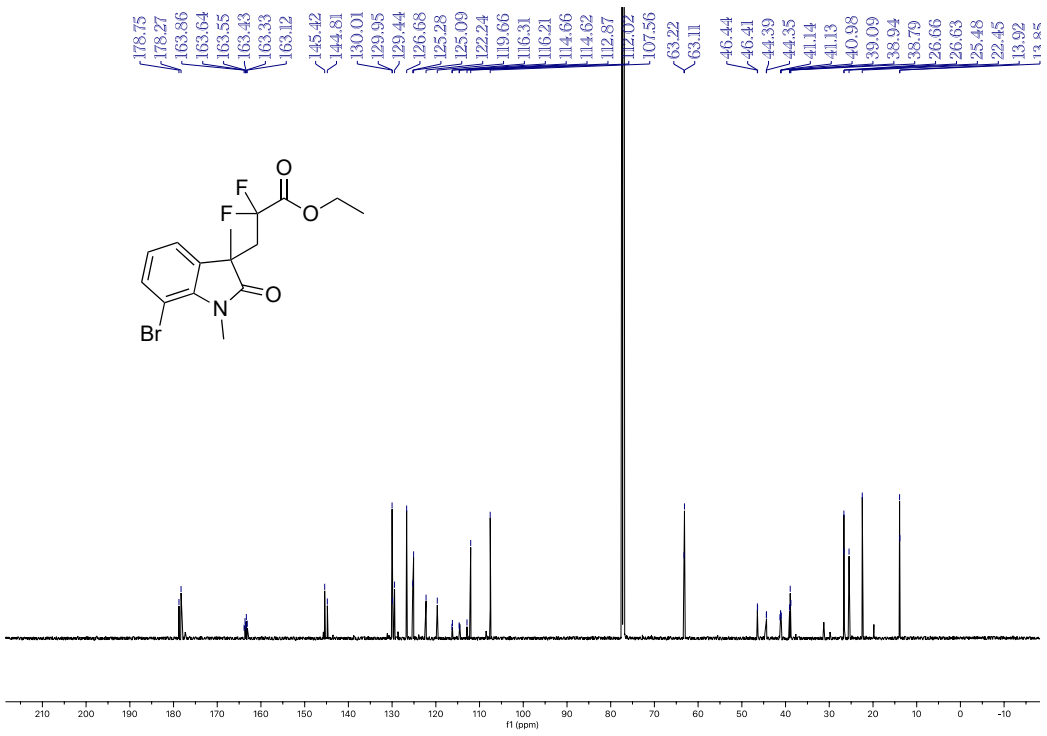
^{13}C NMR (151 MHz, $CDCl_3$) of compound **10**.



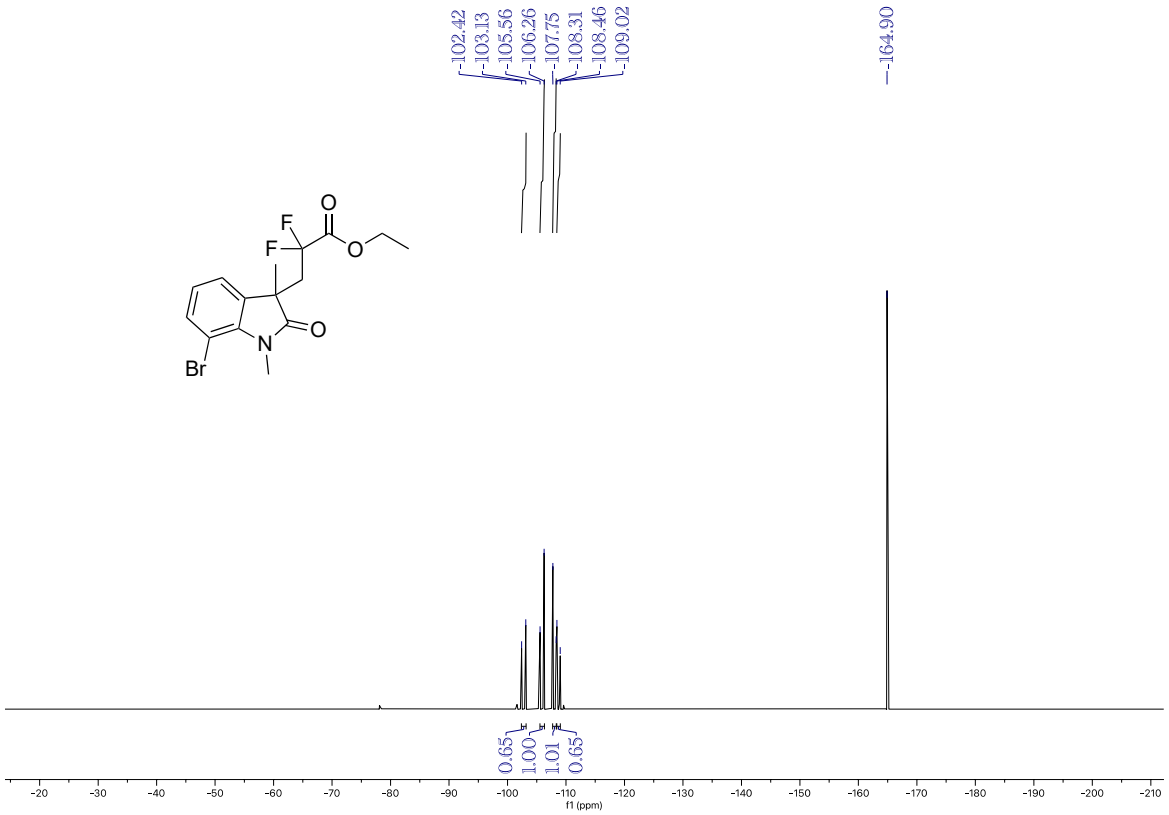
^{19}F NMR (376 MHz, $CDCl_3$) of compound **10**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



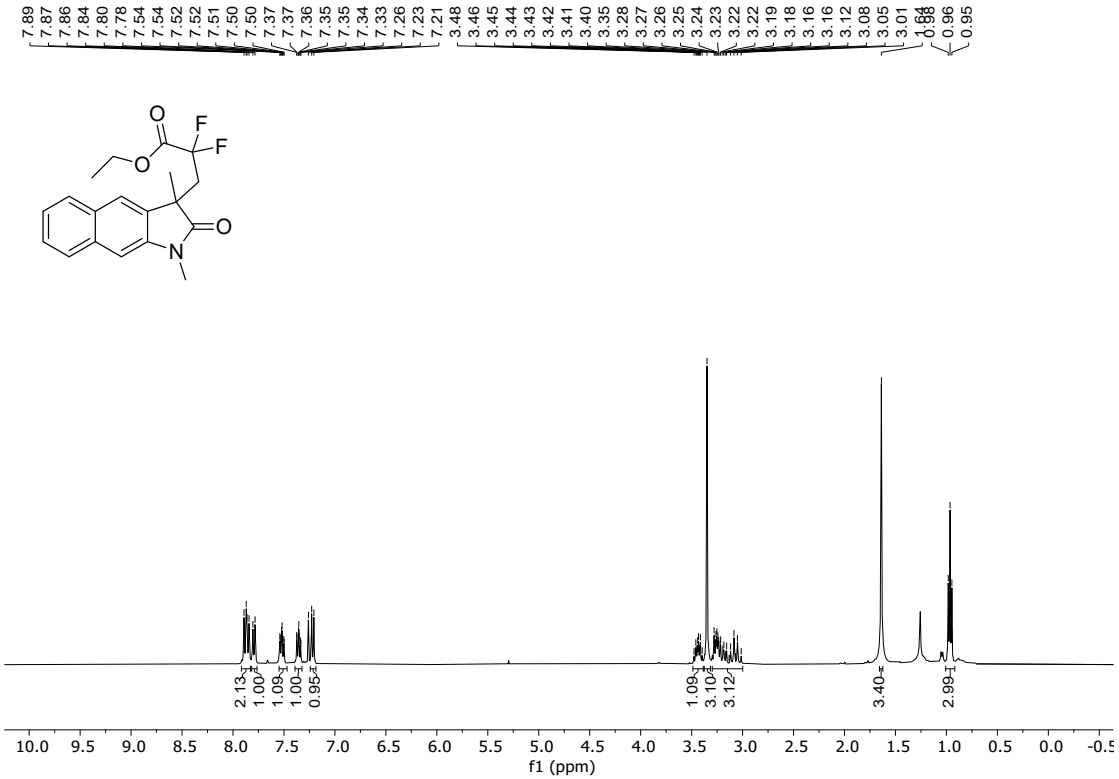
^{1}H NMR (400 MHz, $CDCl_3$) of compound **11**.



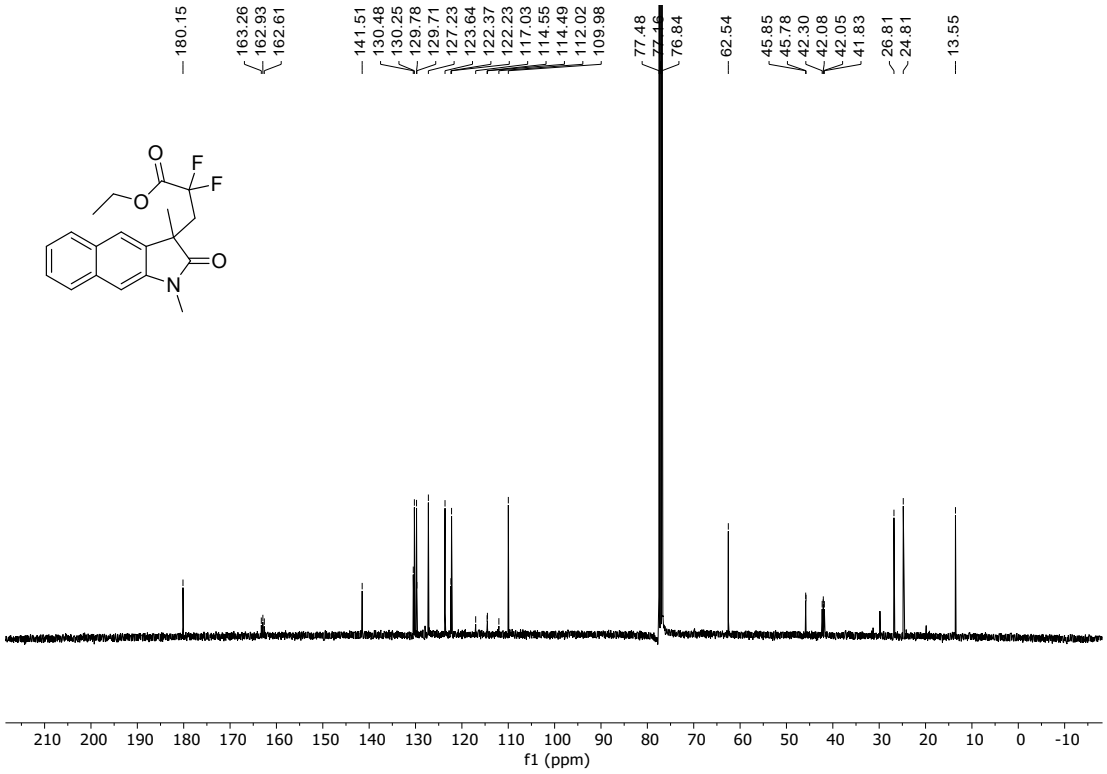
^{13}C NMR (151 MHz, $CDCl_3$) of compound **11**.



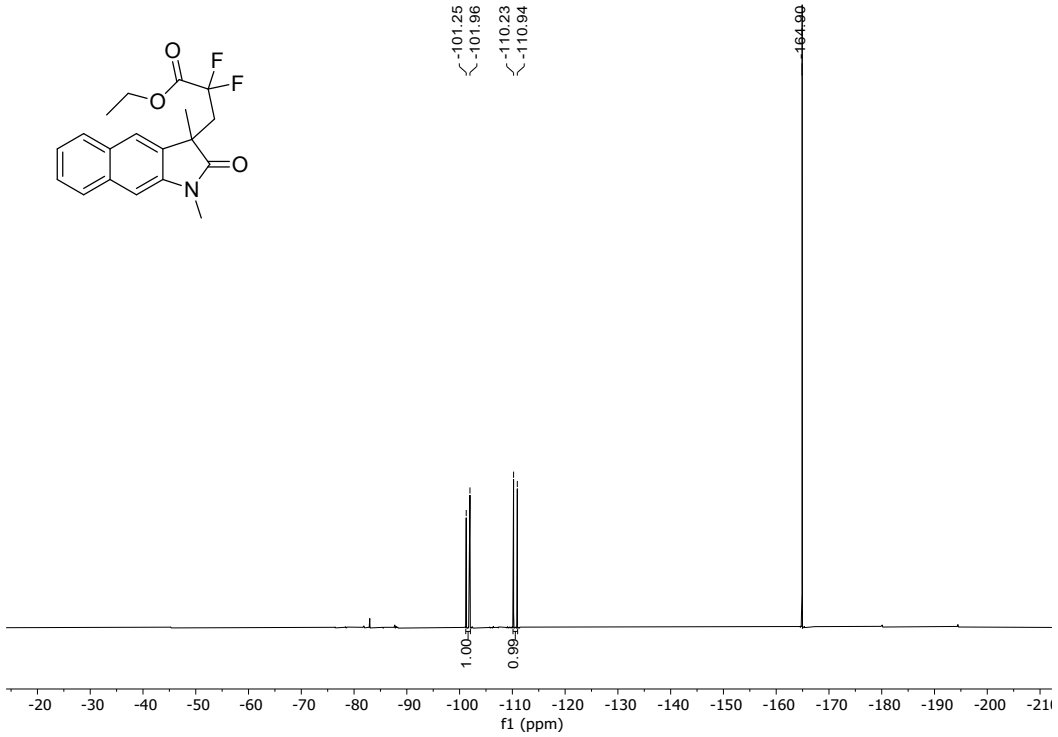
^{19}F NMR (376 MHz, $CDCl_3$) of compound **11**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



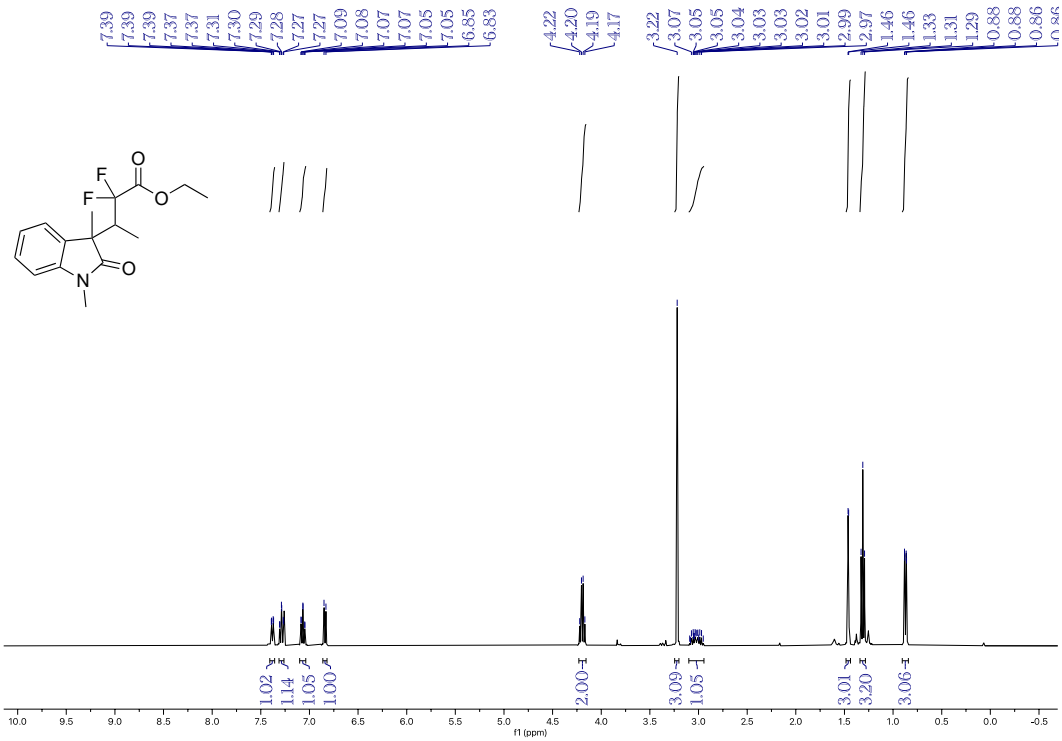
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**.



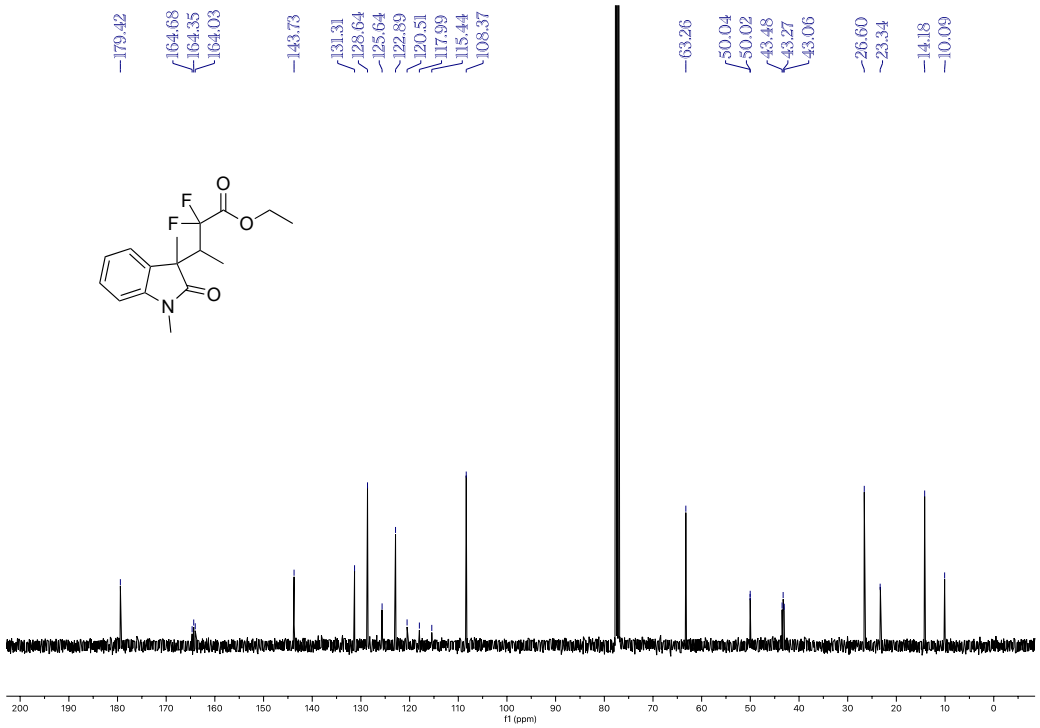
^{13}C NMR (101 MHz, $CDCl_3$) of compound **12**.



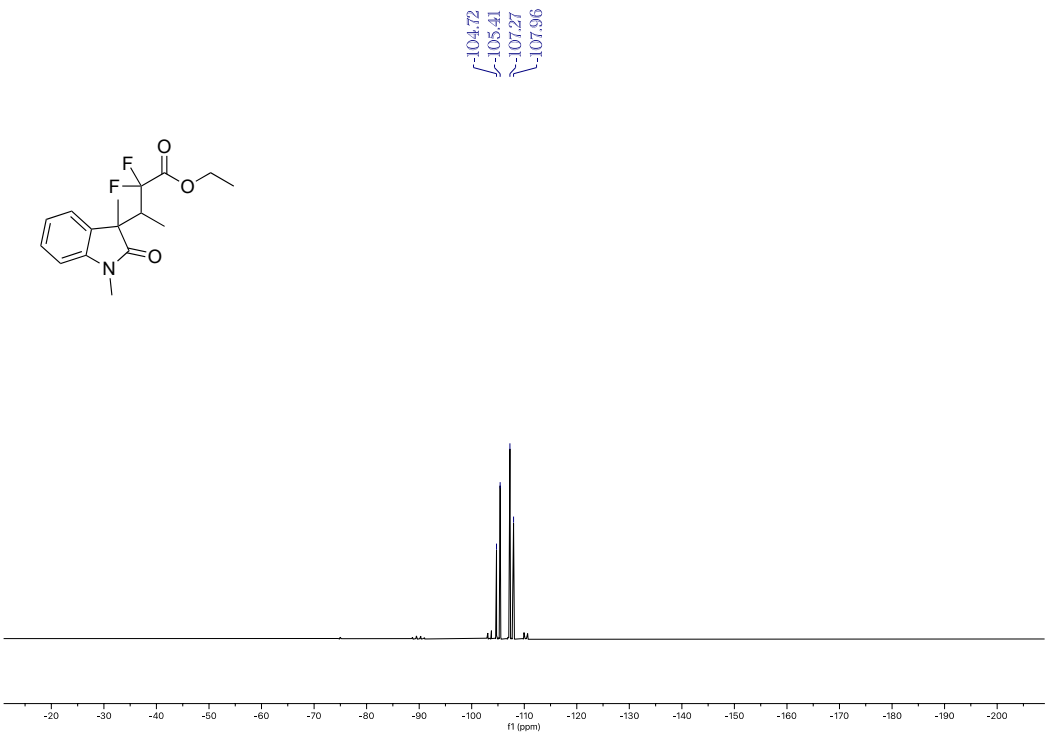
^{19}F NMR (376 MHz, $CDCl_3$) of compound **12**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



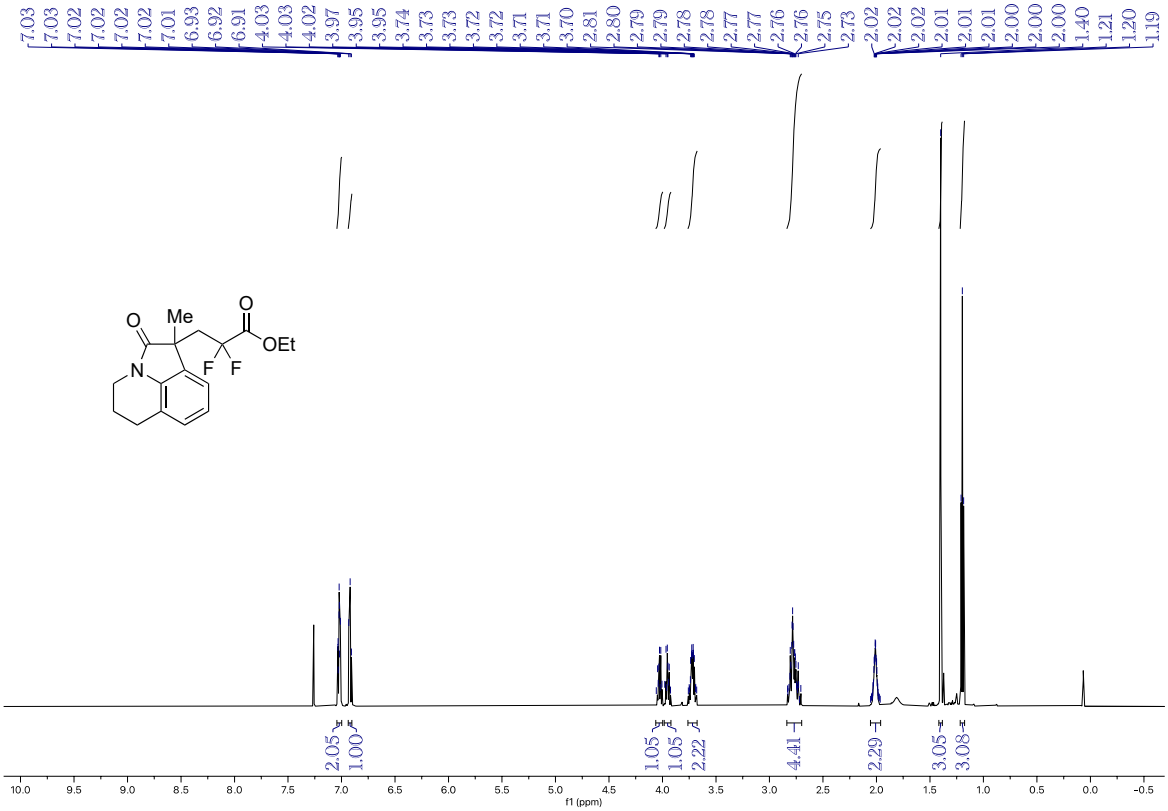
^{1}H NMR (400 MHz, $CDCl_3$) of compound **13**.



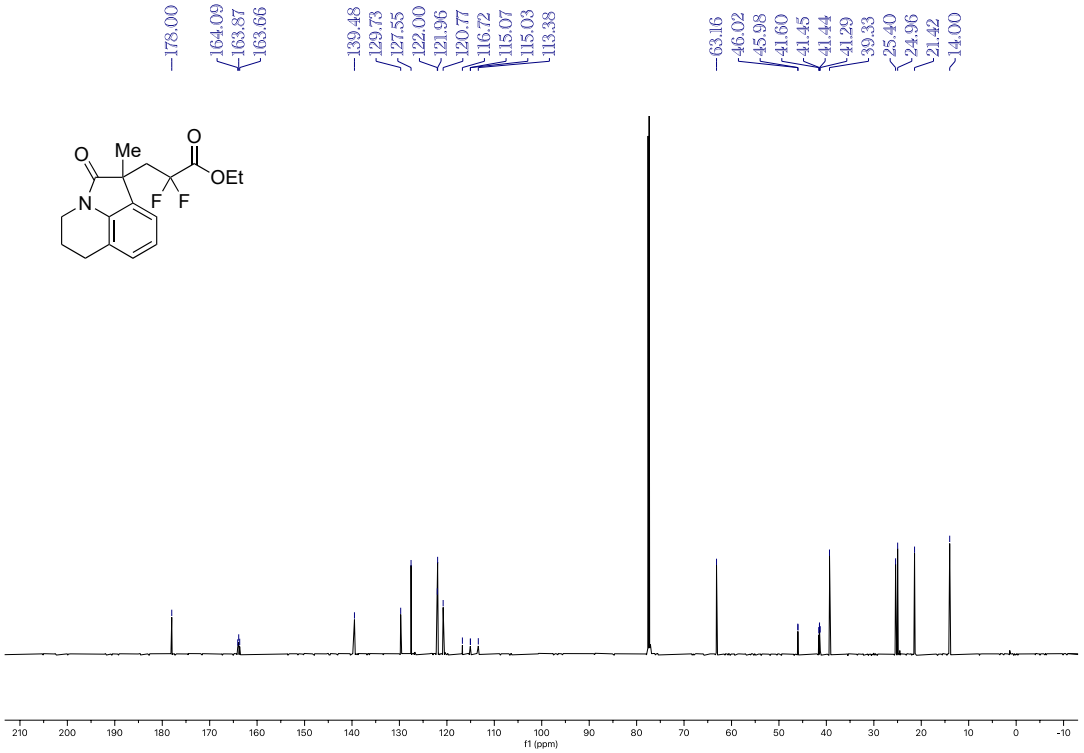
^{13}C NMR (101 MHz, $CDCl_3$) of compound **13**.



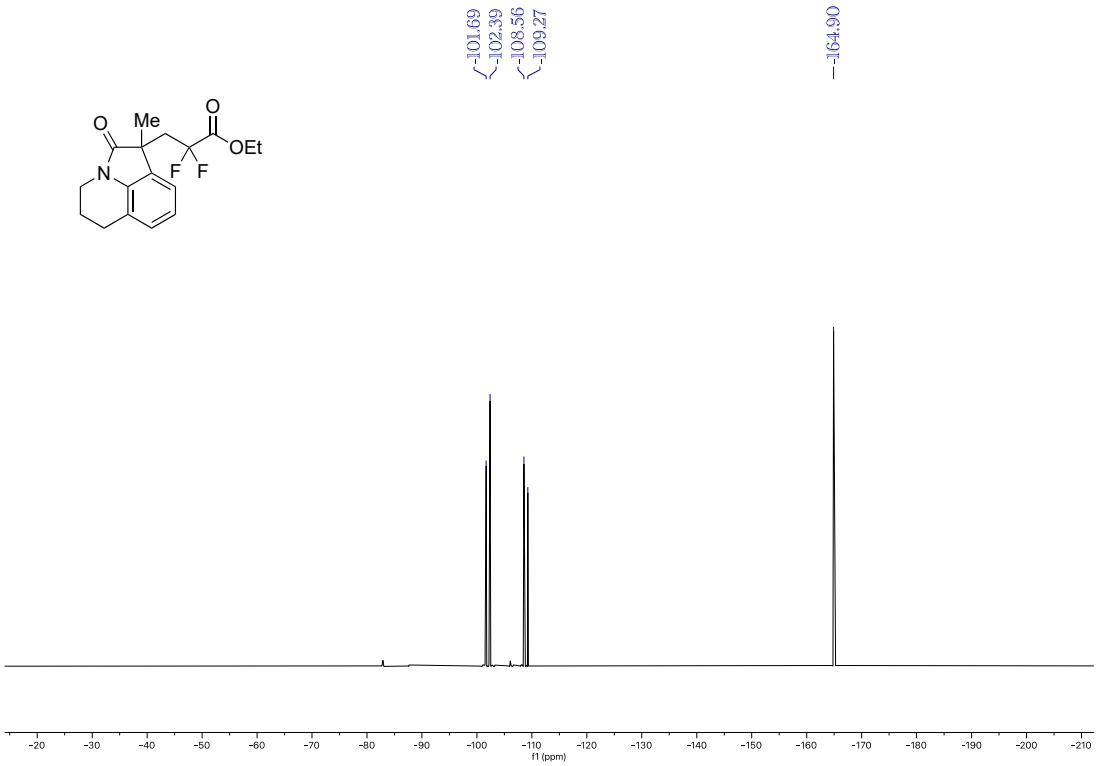
^{19}F NMR (376 MHz, $CDCl_3$) of compound **13**.



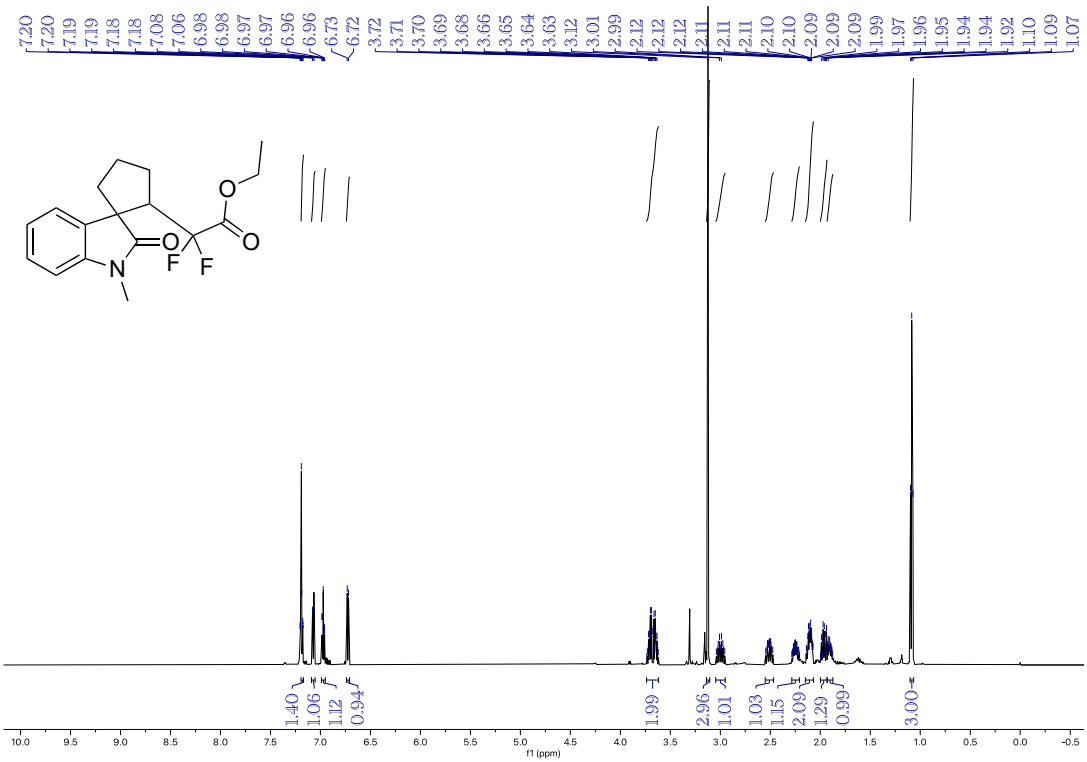
^{1}H NMR (600 MHz, $CDCl_3$) of compound **14**.



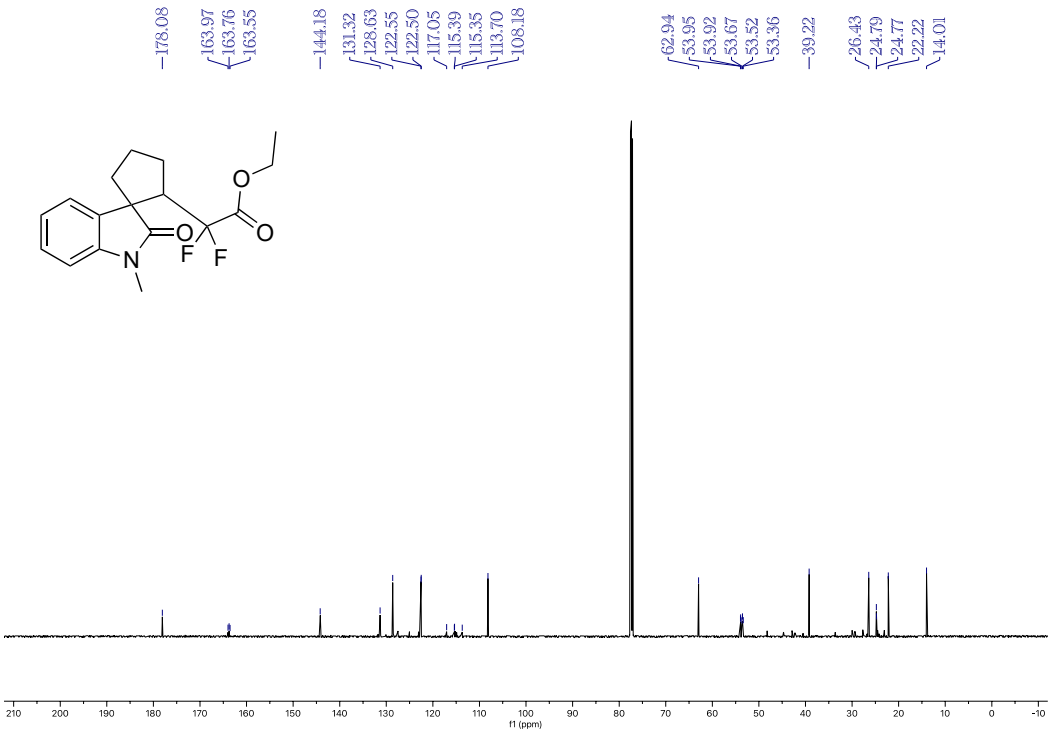
^{13}C NMR (151 MHz, $CDCl_3$) of compound **14**.



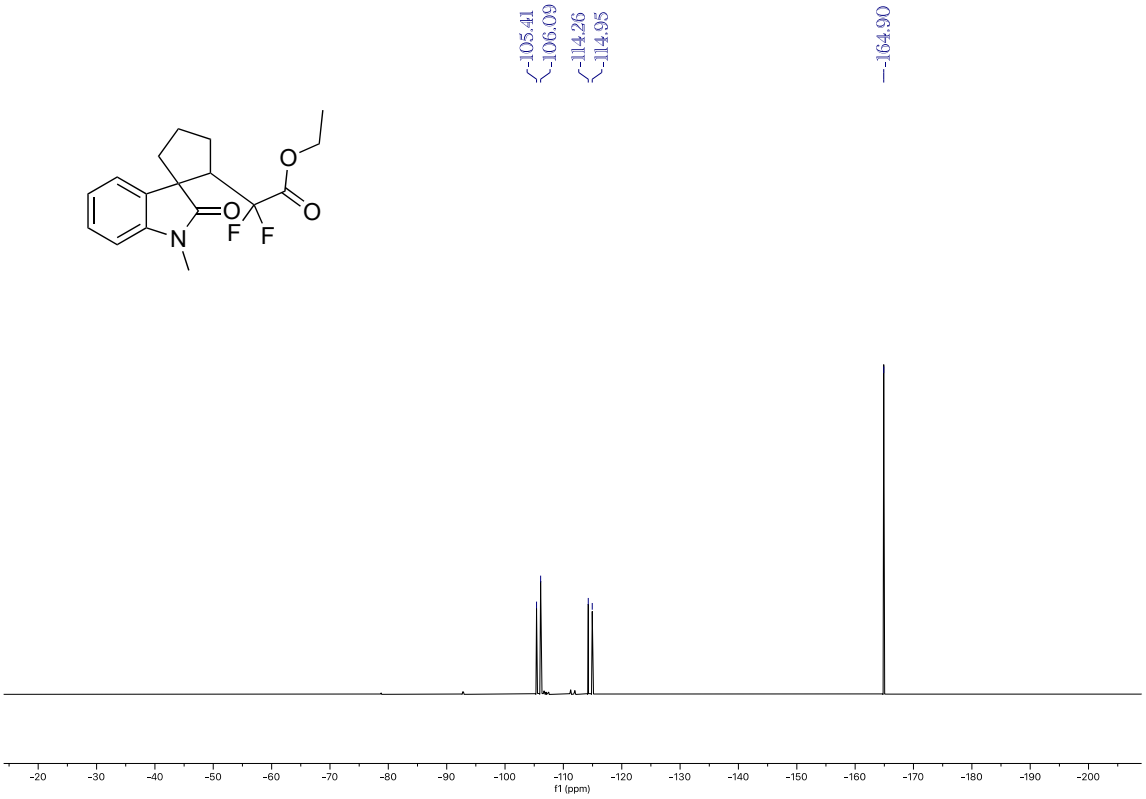
^{19}F NMR (376 MHz, $CDCl_3$) of compound **14**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



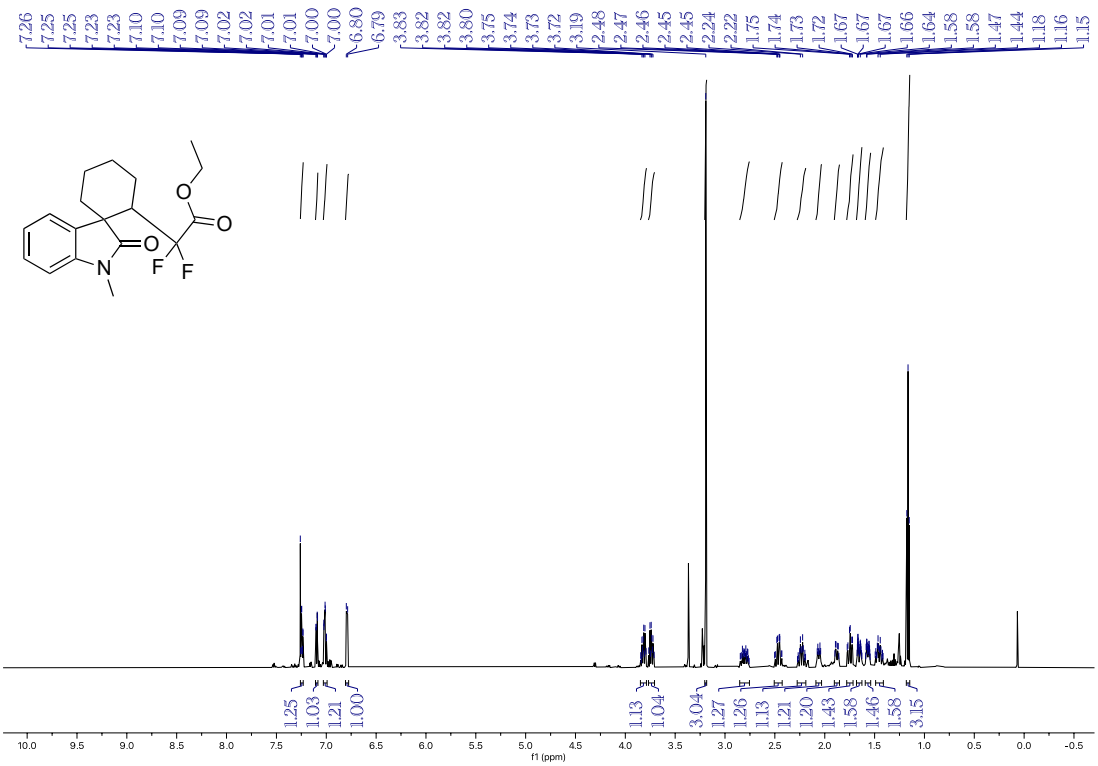
^{1}H NMR (600 MHz, $CDCl_3$) of compound **15.**



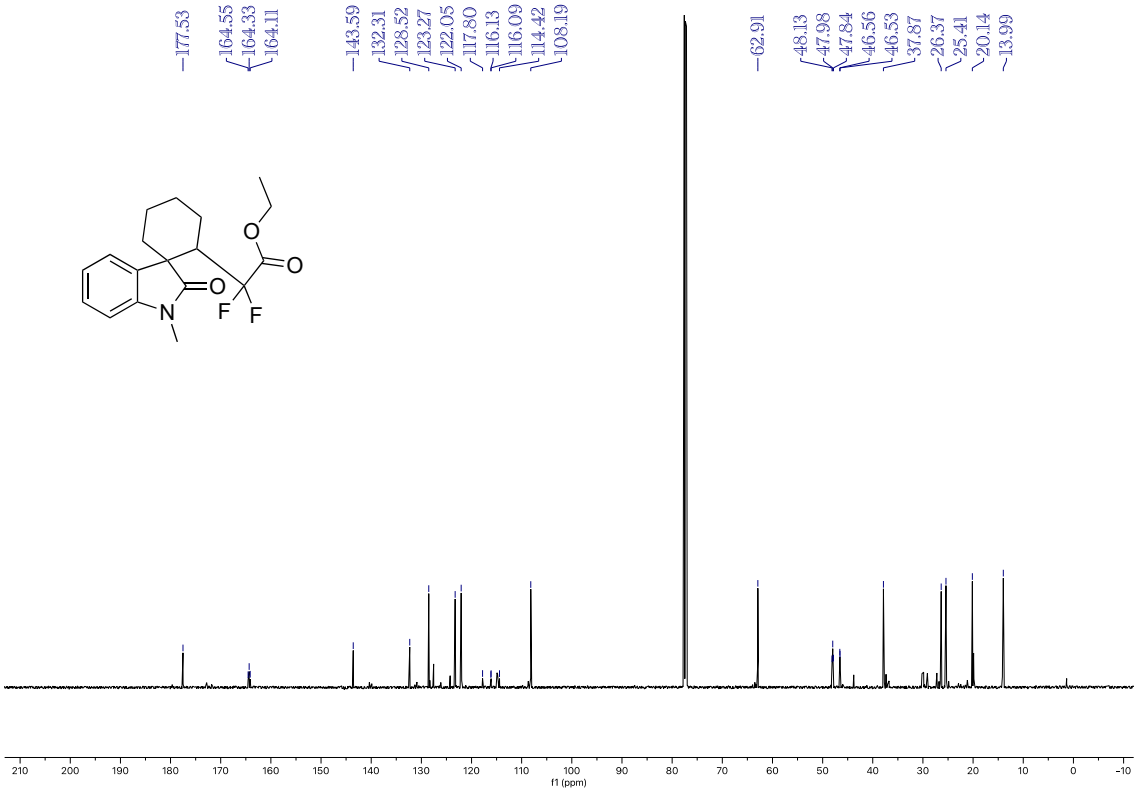
^{13}C NMR (151 MHz, $CDCl_3$) of compound **15**.



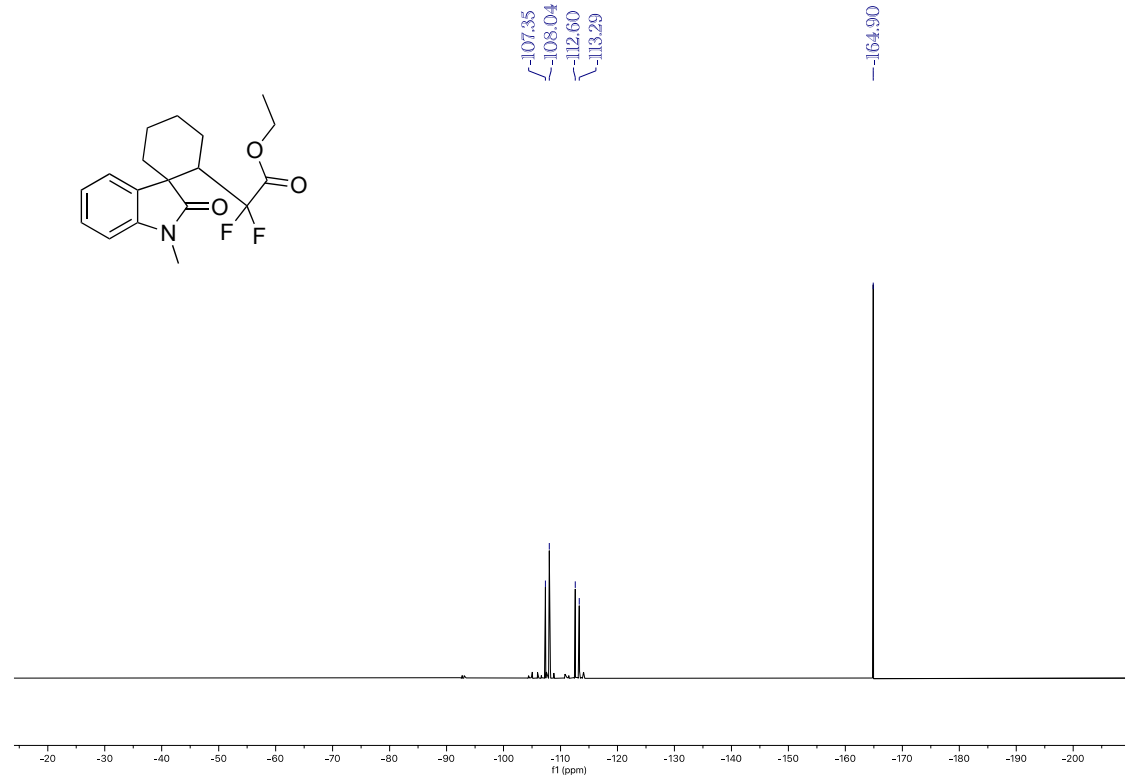
^{19}F NMR (376 MHz, $CDCl_3$) of compound **15**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



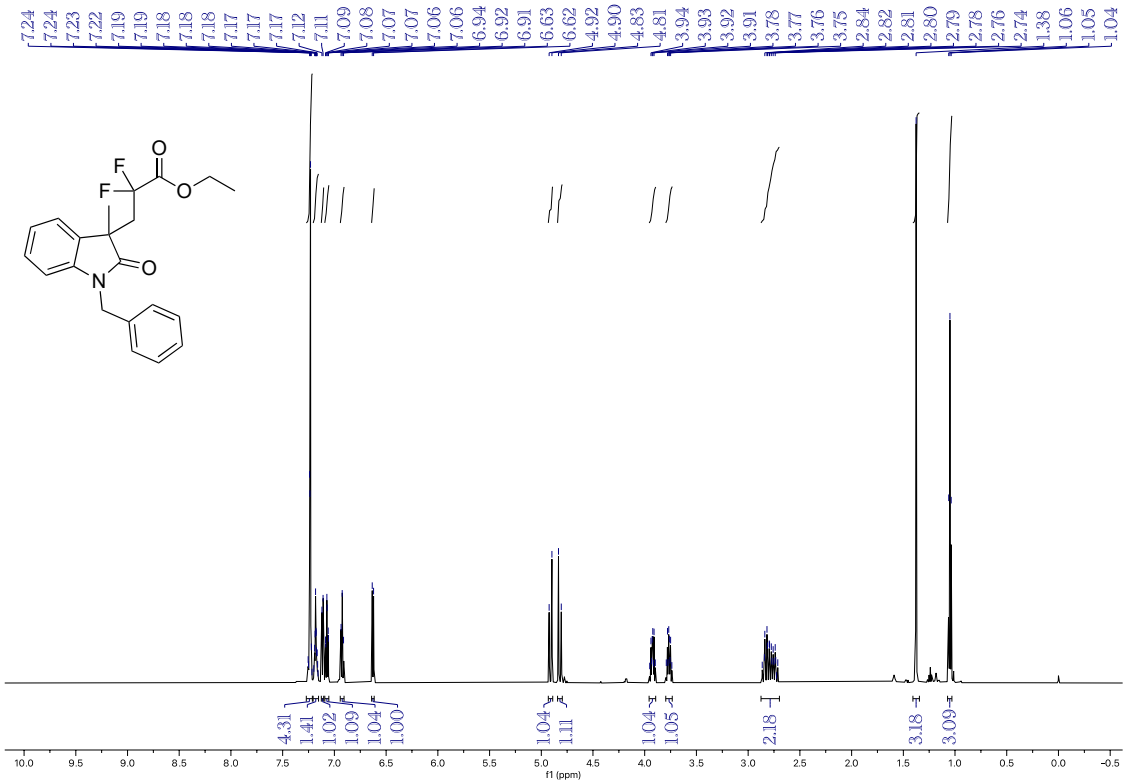
^{1}H NMR (600 MHz, $CDCl_3$) of compound **16**.



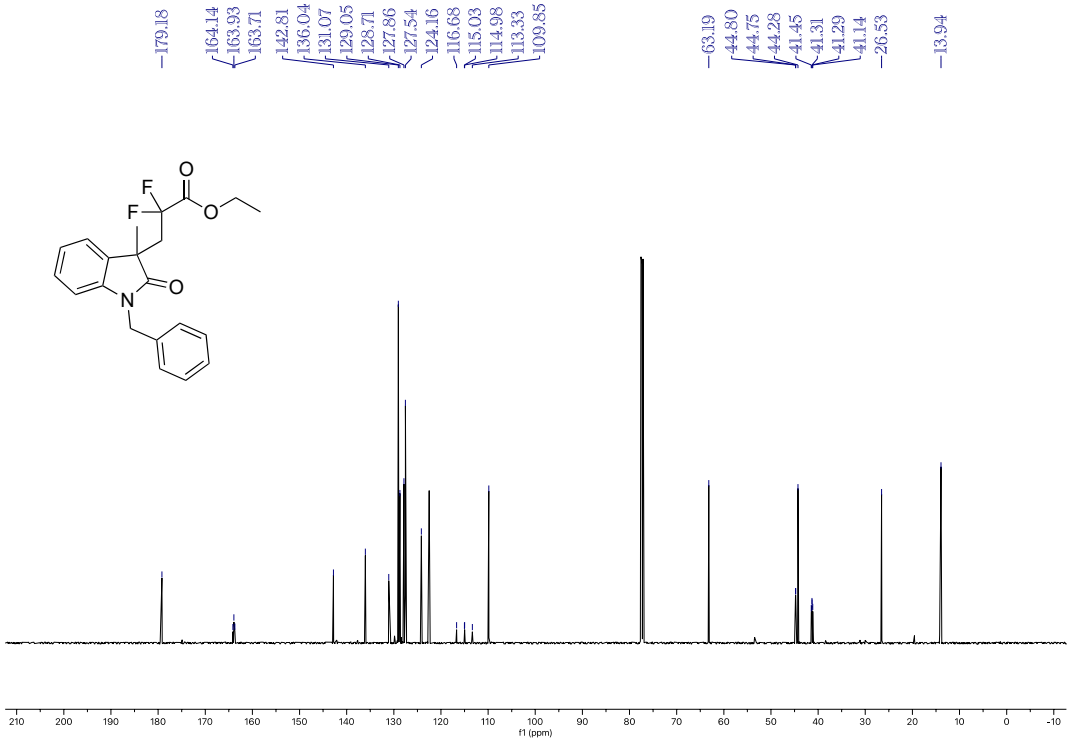
^{13}C NMR (151 MHz, $CDCl_3$) of compound **16**.



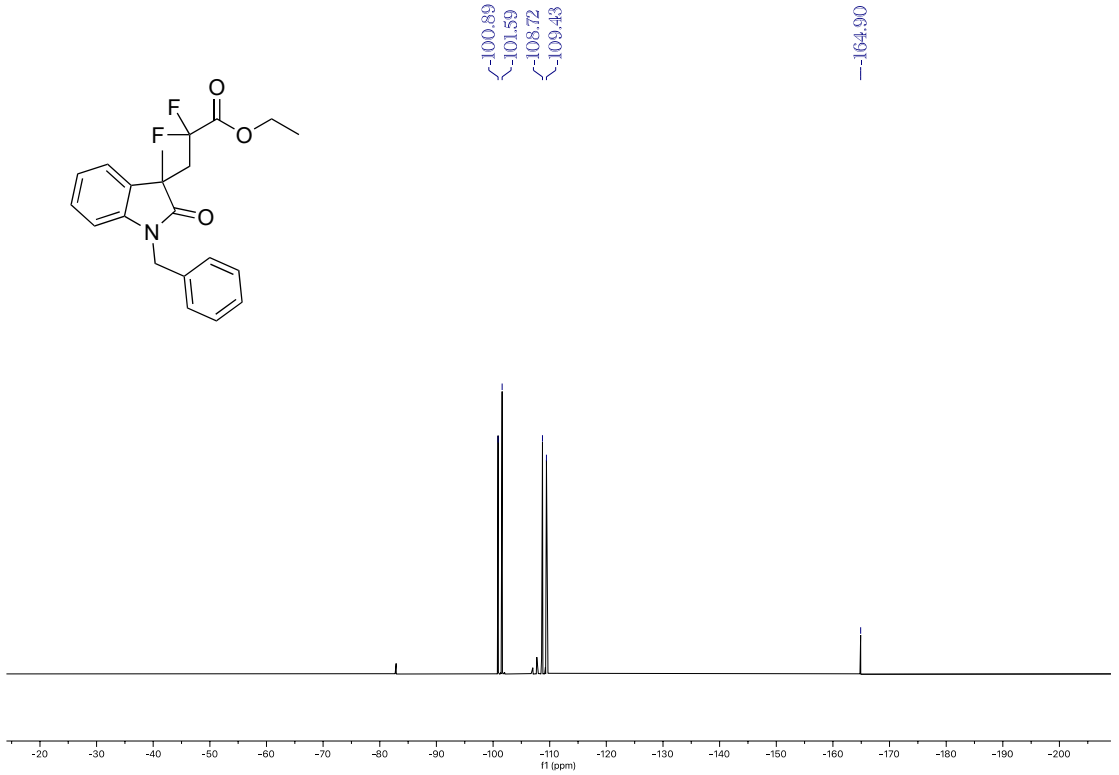
^{19}F NMR (376 MHz, $CDCl_3$) of compound **16**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



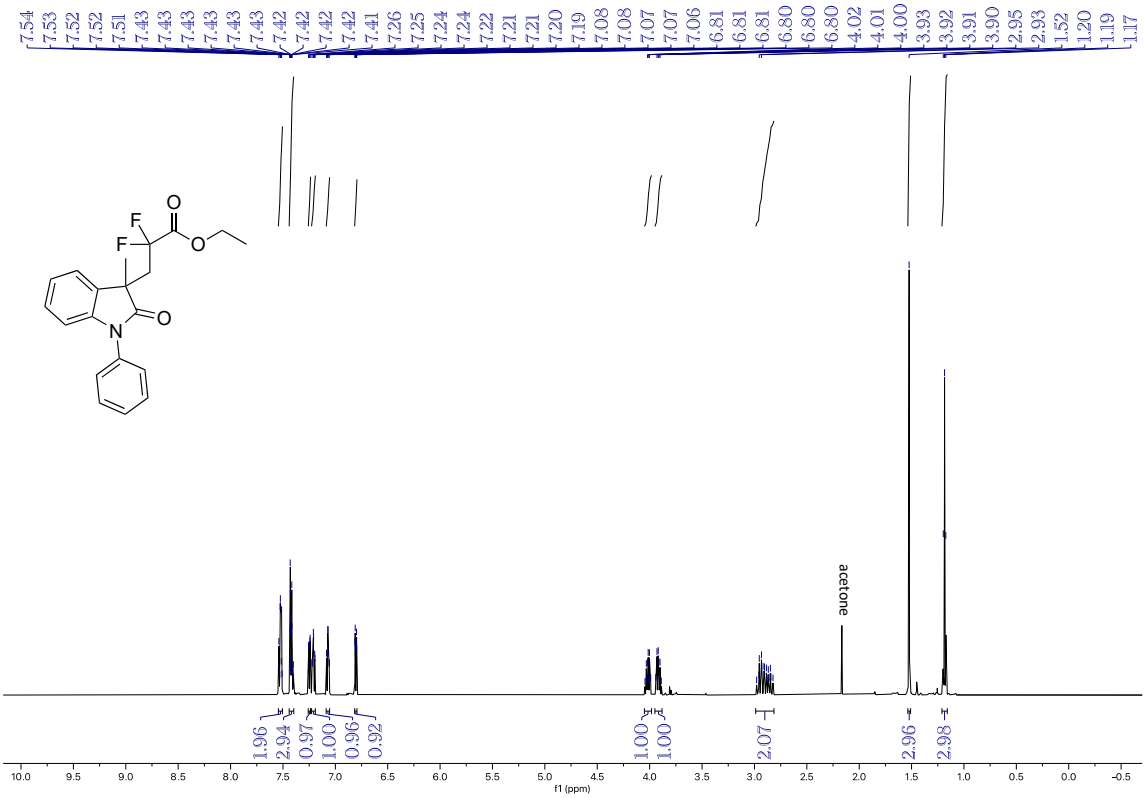
^{1}H NMR (600 MHz, $CDCl_3$) of compound **17**.



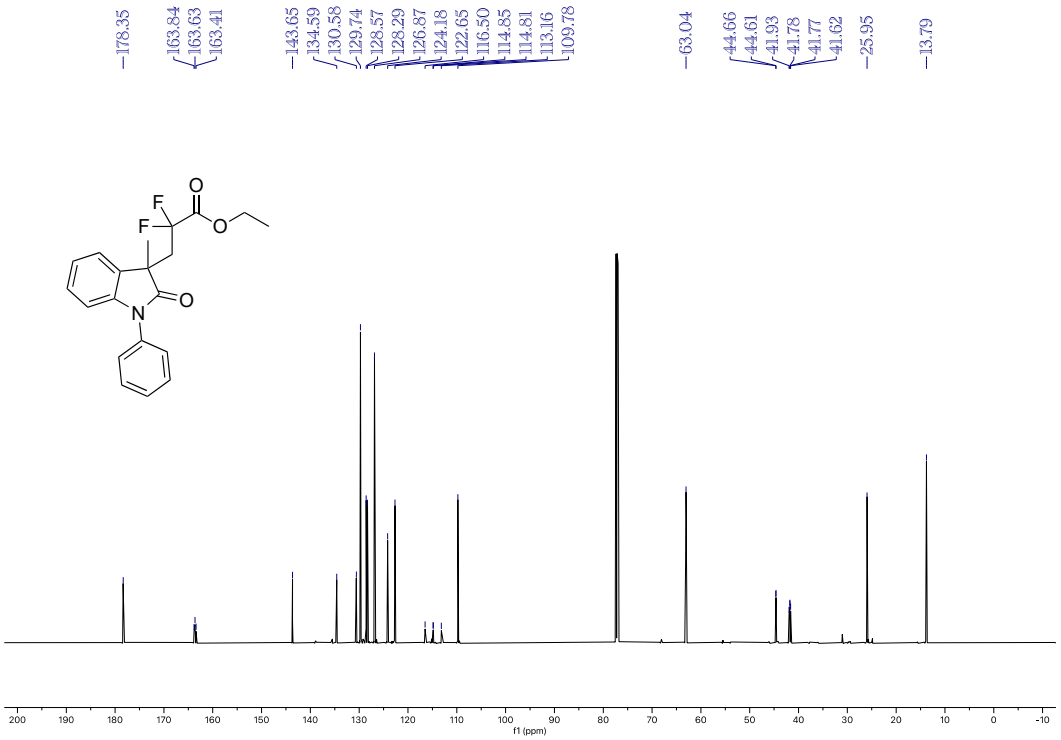
^{13}C NMR (151 MHz, $CDCl_3$) of compound **17**.



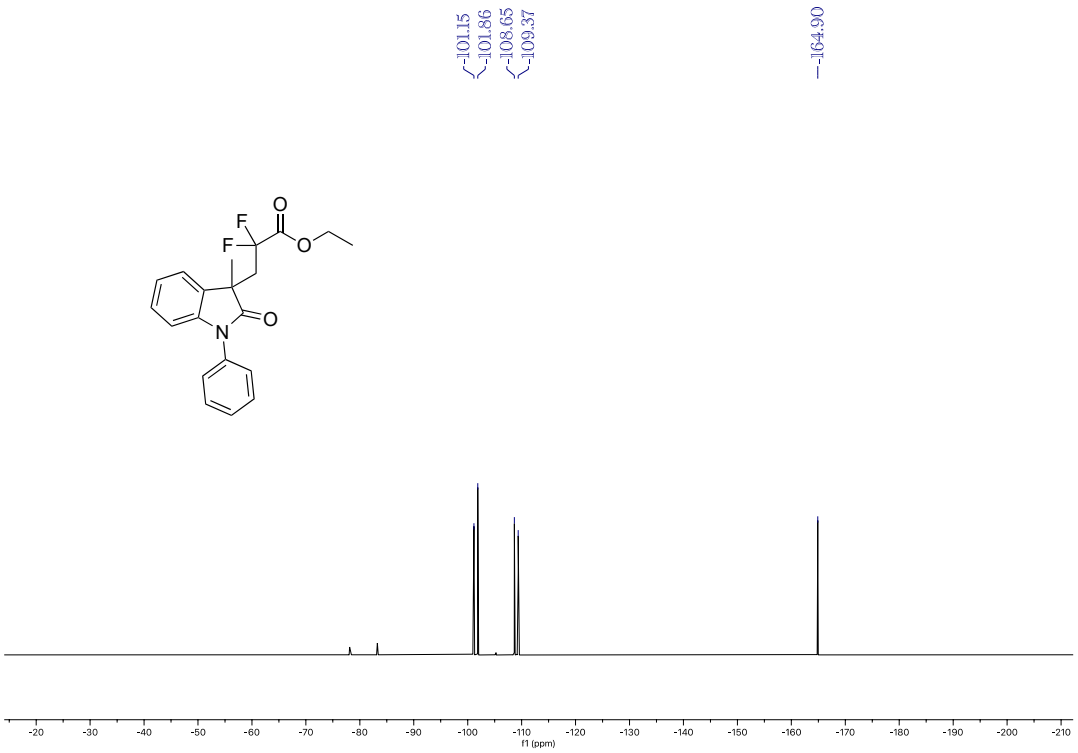
^{19}F NMR (376 MHz, $CDCl_3$) of compound **17**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



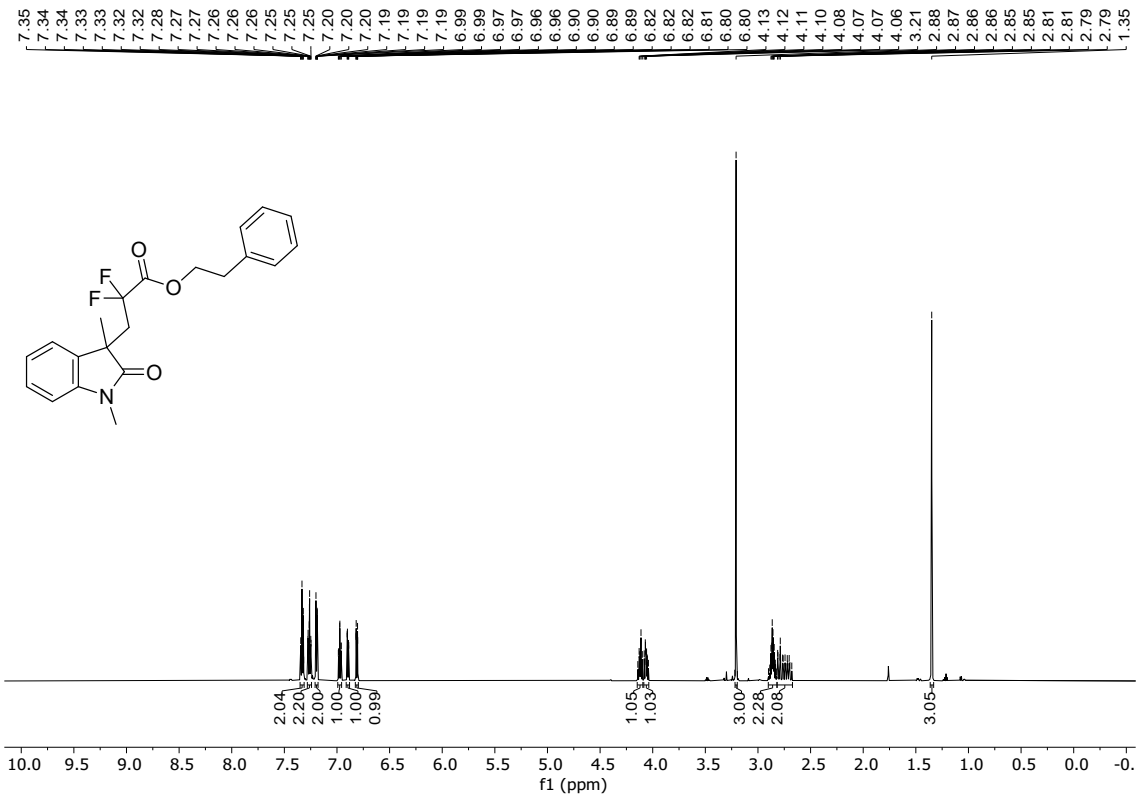
^{1}H NMR (600 MHz, $CDCl_3$) of compound **18**.



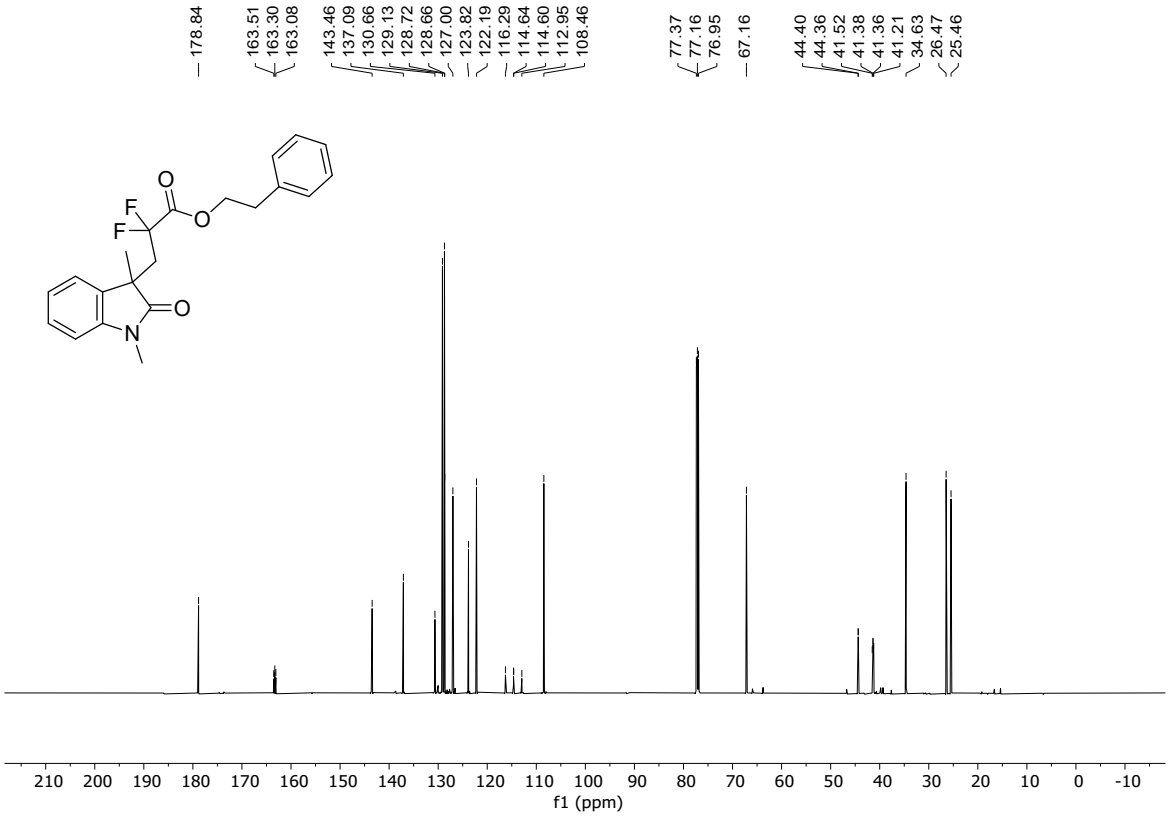
^{13}C NMR (151 MHz, $CDCl_3$) of compound **18.**



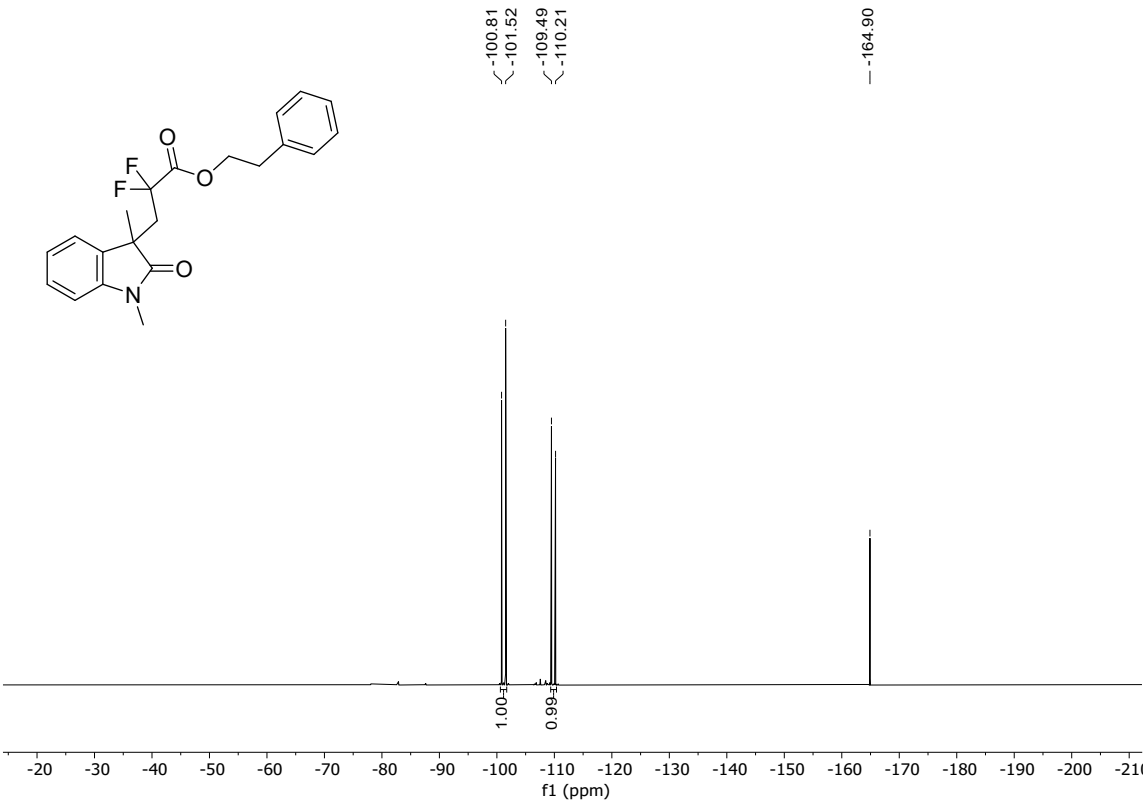
^{19}F NMR (376 MHz, $CDCl_3$) of compound **18**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



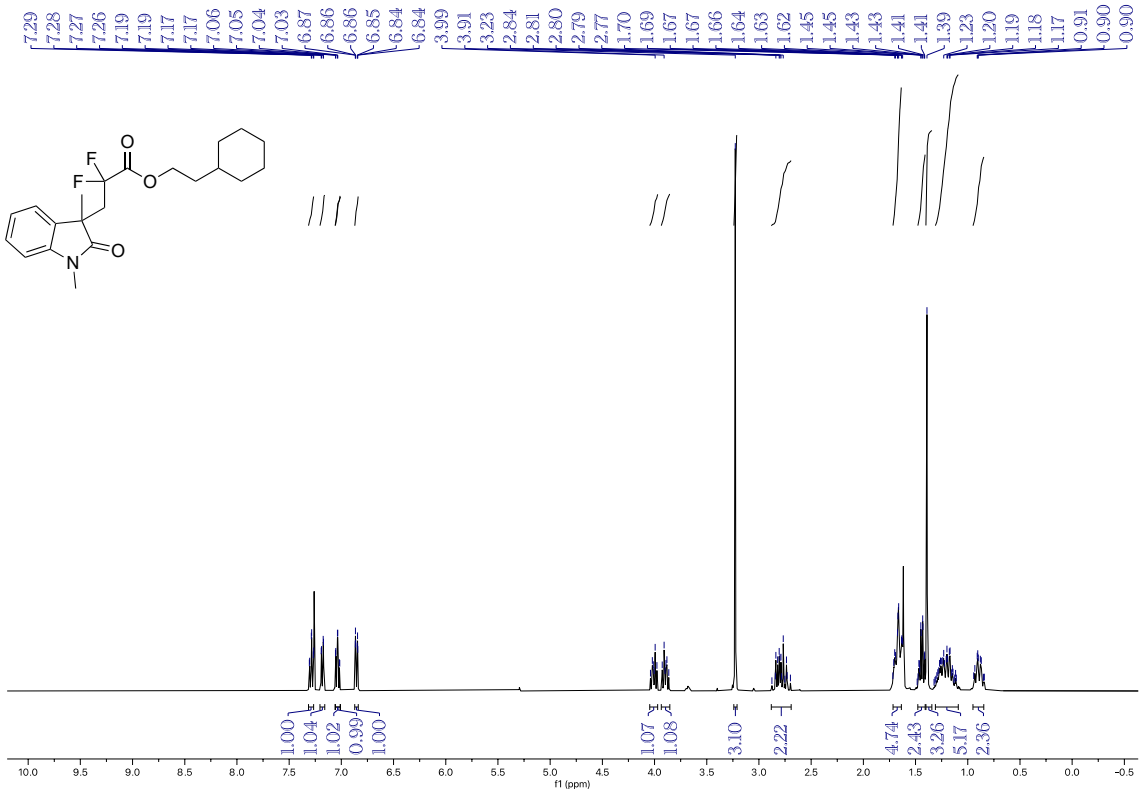
^{1}H NMR (600 MHz, $CDCl_3$) of compound **19**.



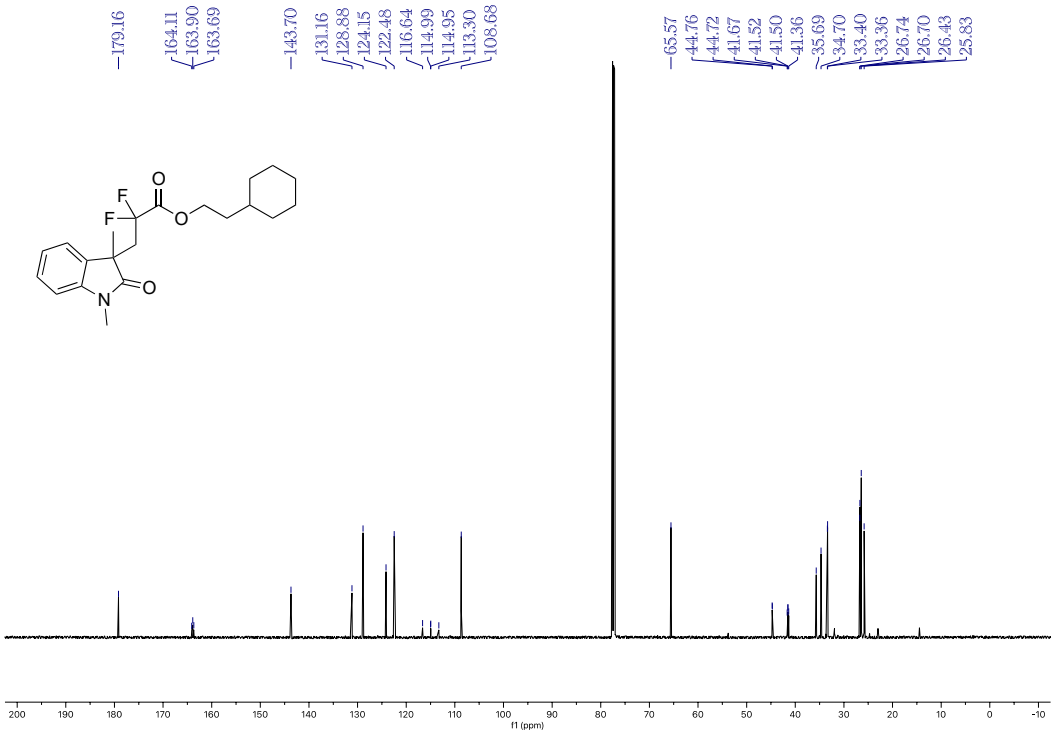
^{13}C NMR (151 MHz, $CDCl_3$) of compound **19.**



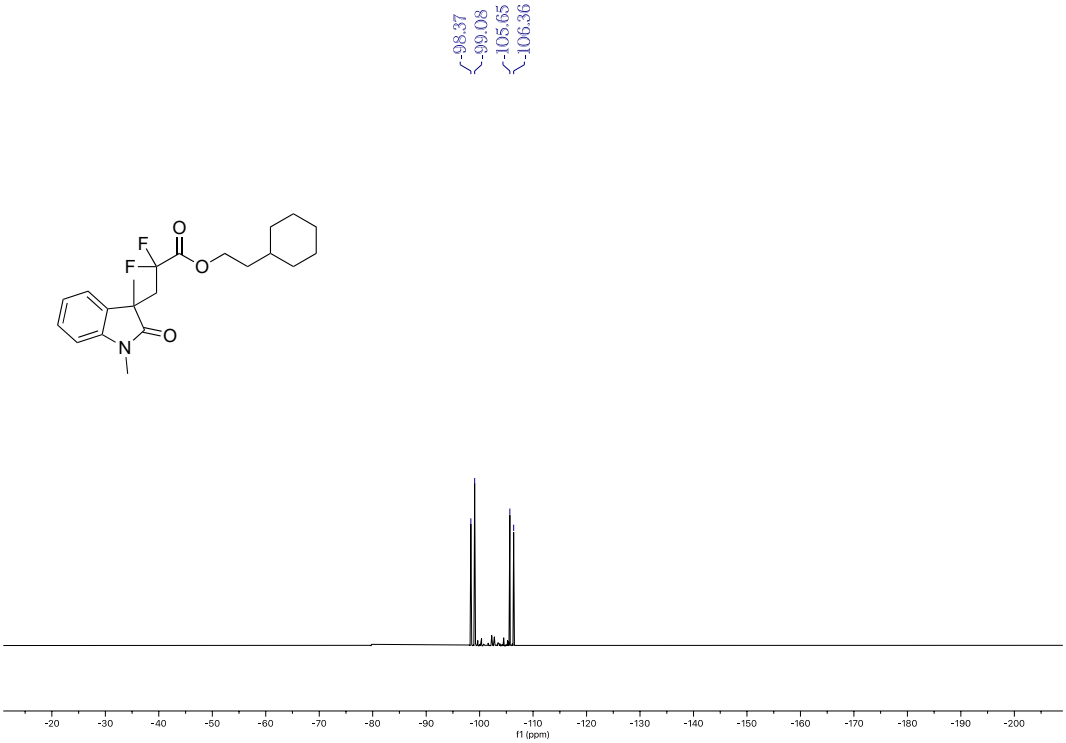
^{19}F NMR (376 MHz, $CDCl_3$) of compound **19**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



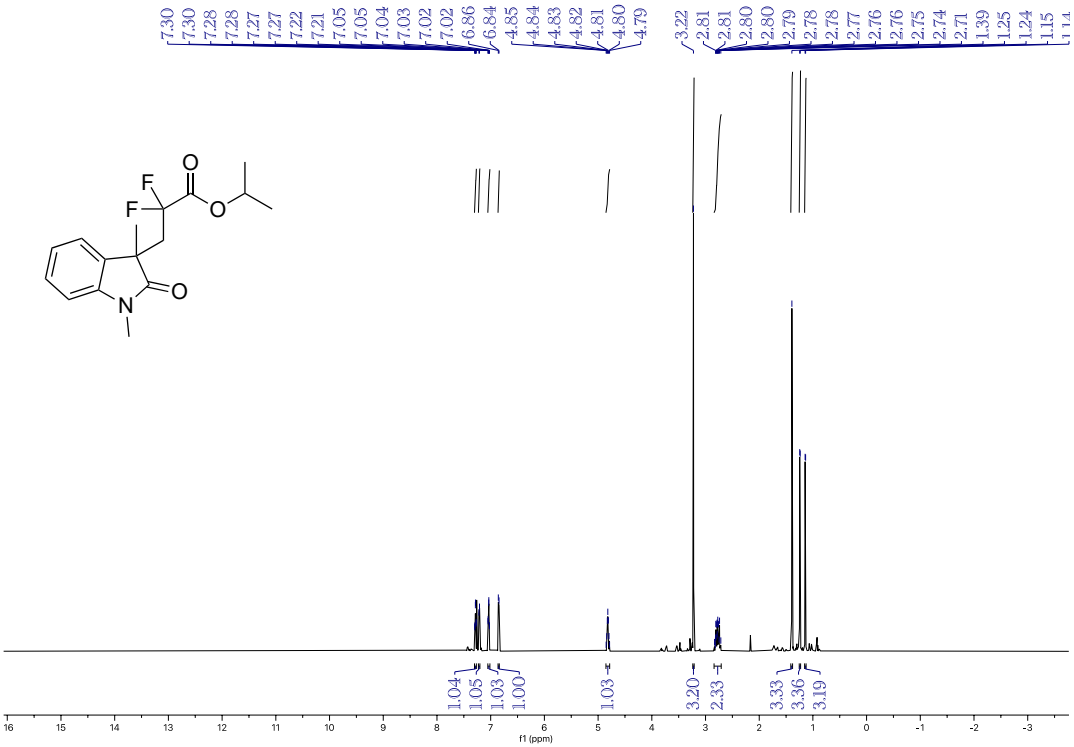
^{1}H NMR (600 MHz, $CDCl_3$) of compound **20**.



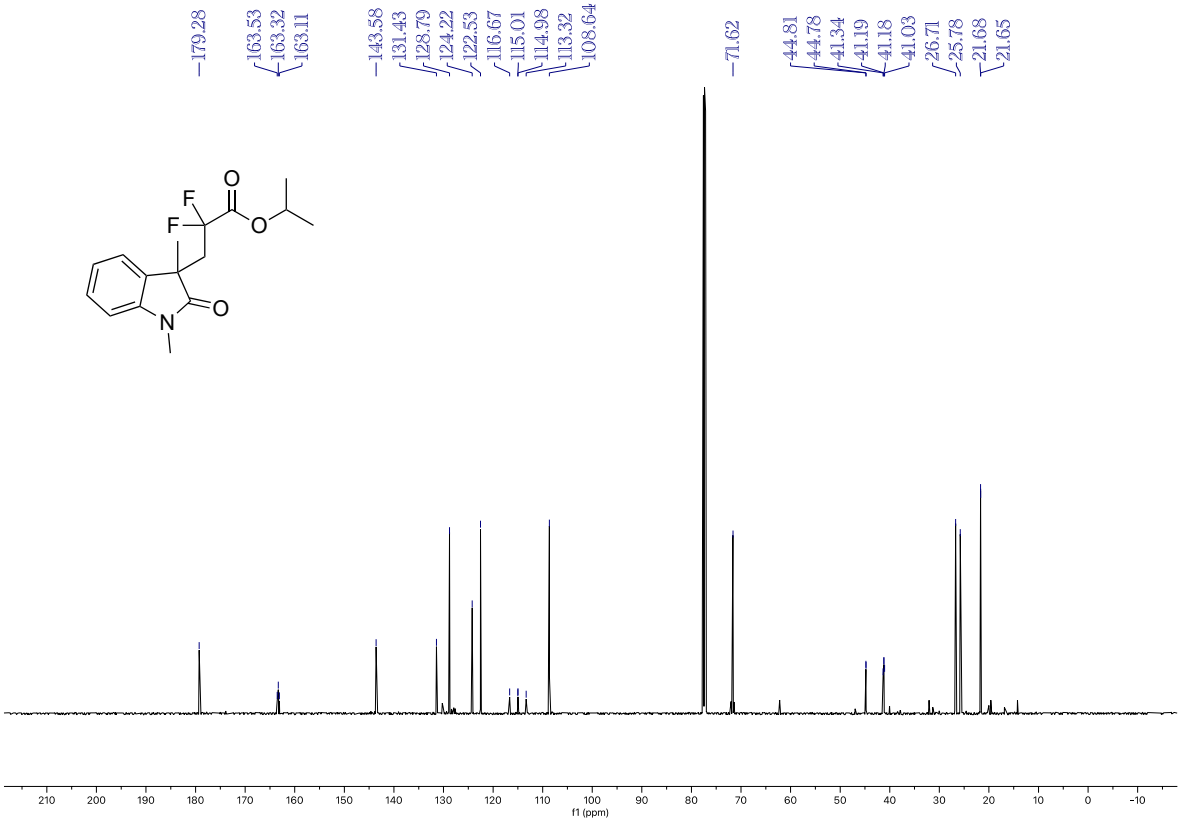
^{13}C NMR (151 MHz, $CDCl_3$) of compound **20**.



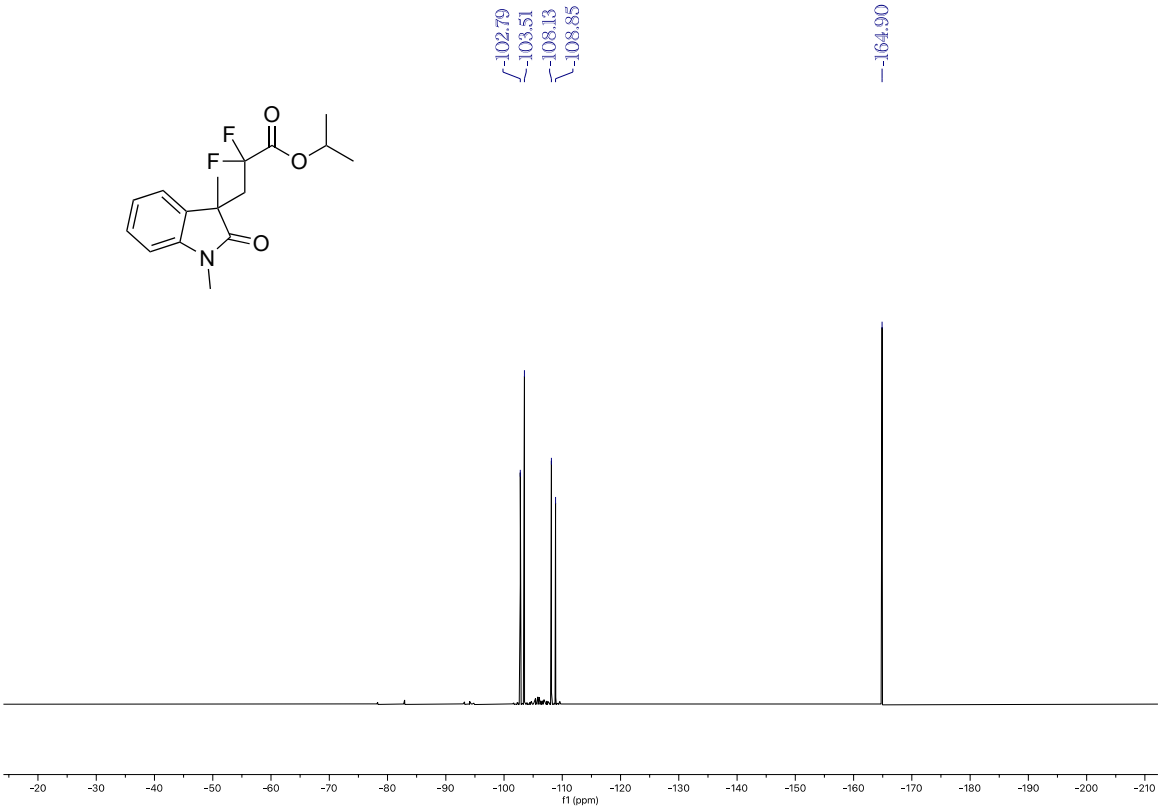
^{19}F NMR (376 MHz, $CDCl_3$) of compound **20**.



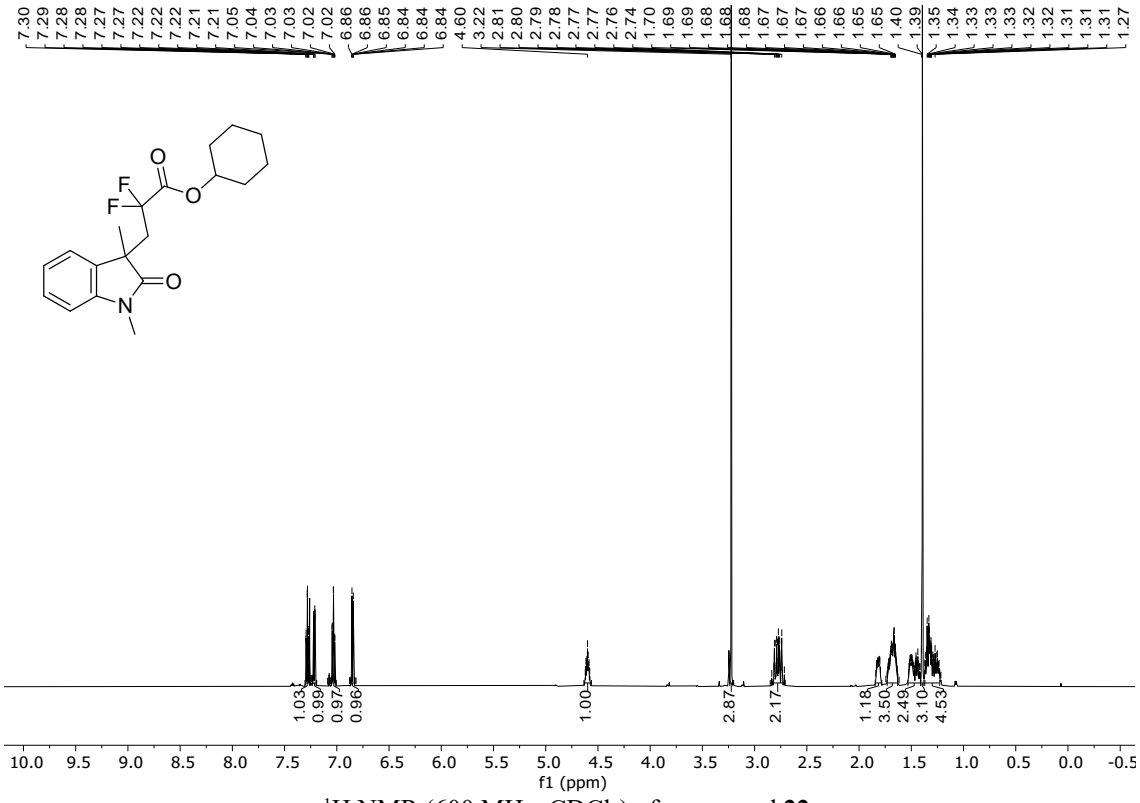
^{1}H NMR (600 MHz, $CDCl_3$) of compound **21**.



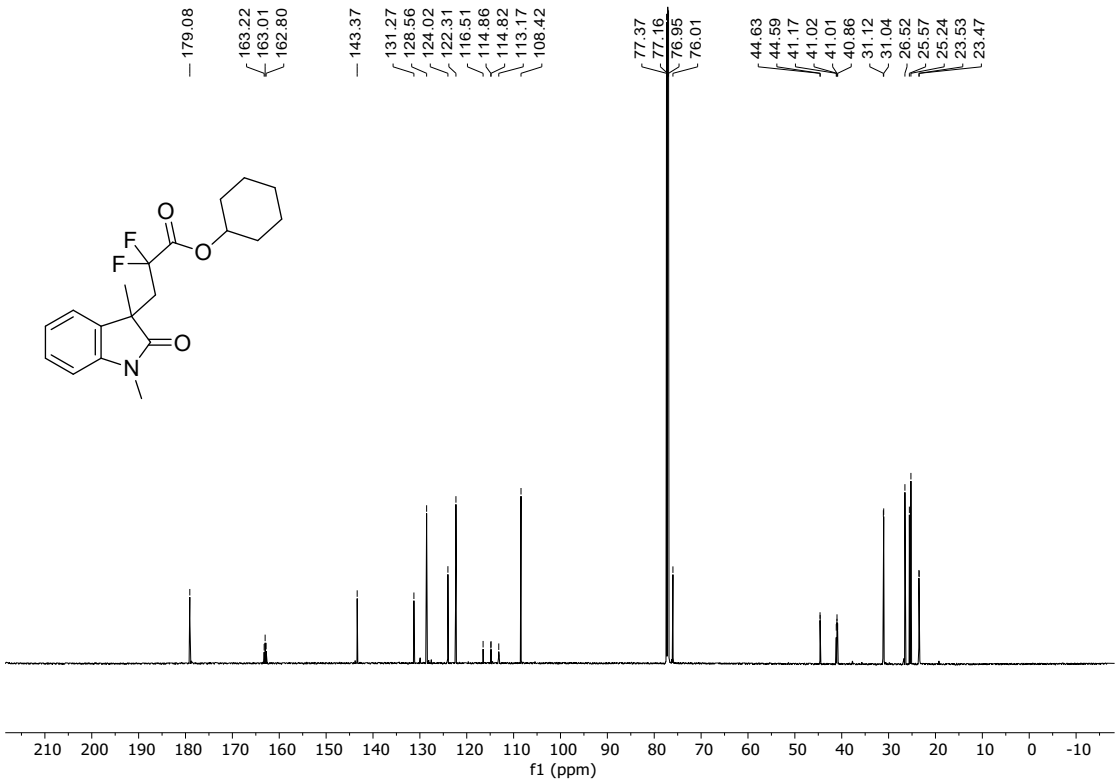
^{13}C NMR (151 MHz, $CDCl_3$) of compound **21**.



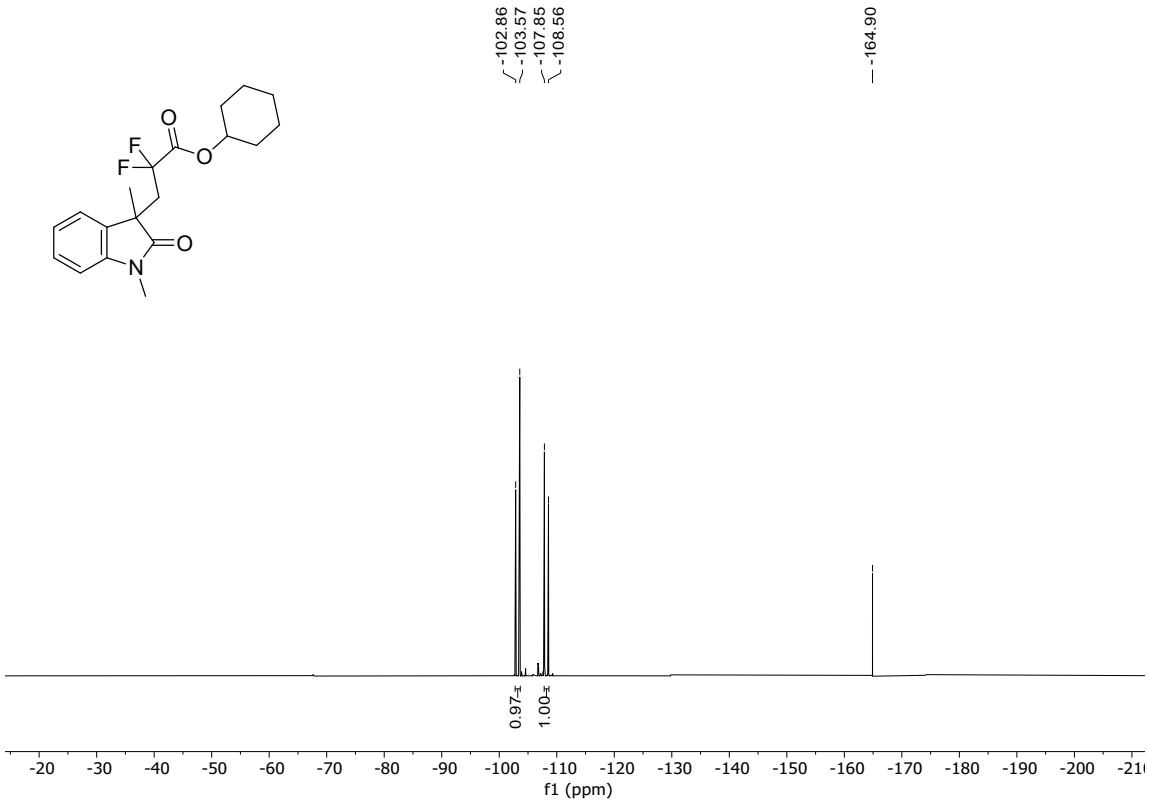
^{19}F NMR (376 MHz, $CDCl_3$) of compound **21**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



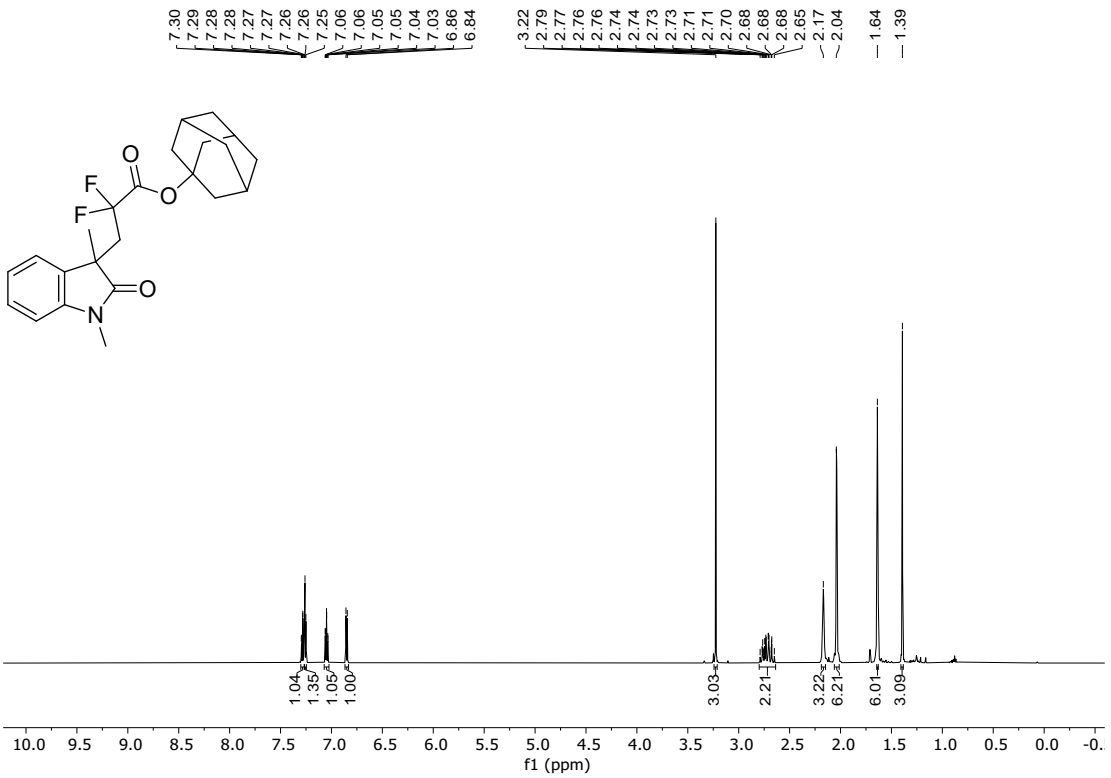
^{1}H NMR (600 MHz, $CDCl_3$) of compound **22**.



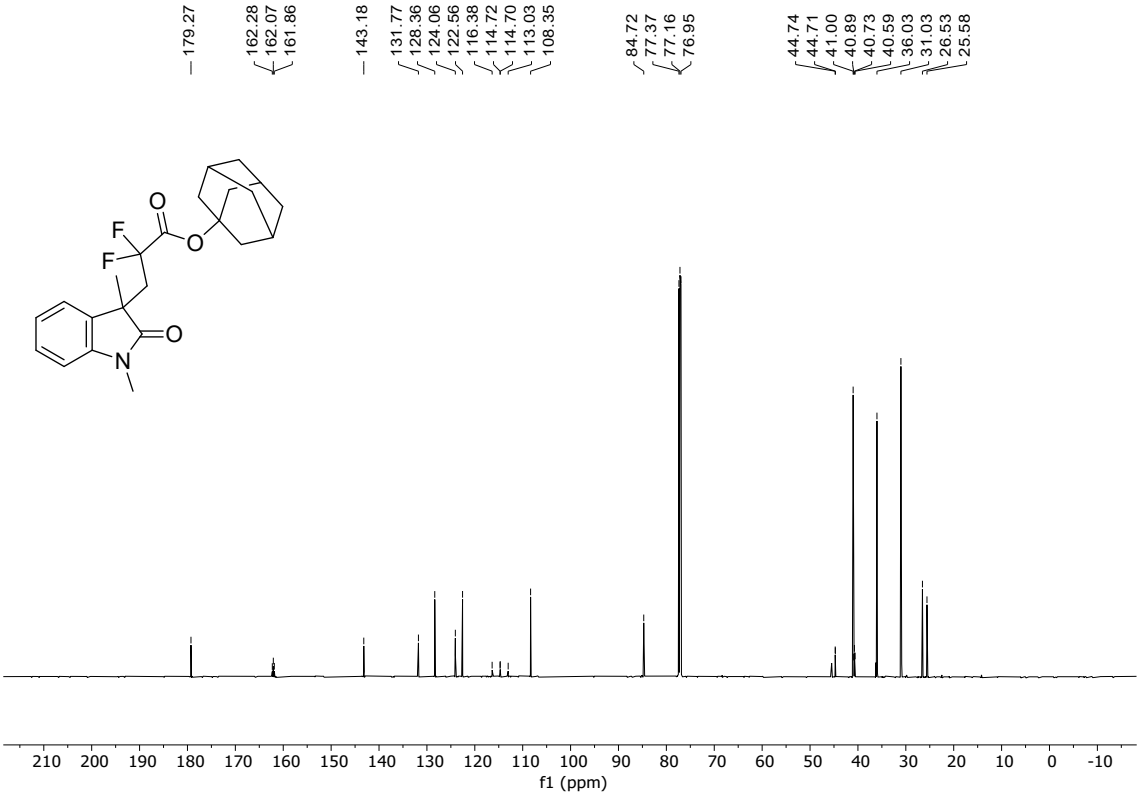
^{13}C NMR (151 MHz, $CDCl_3$) of compound **22**.



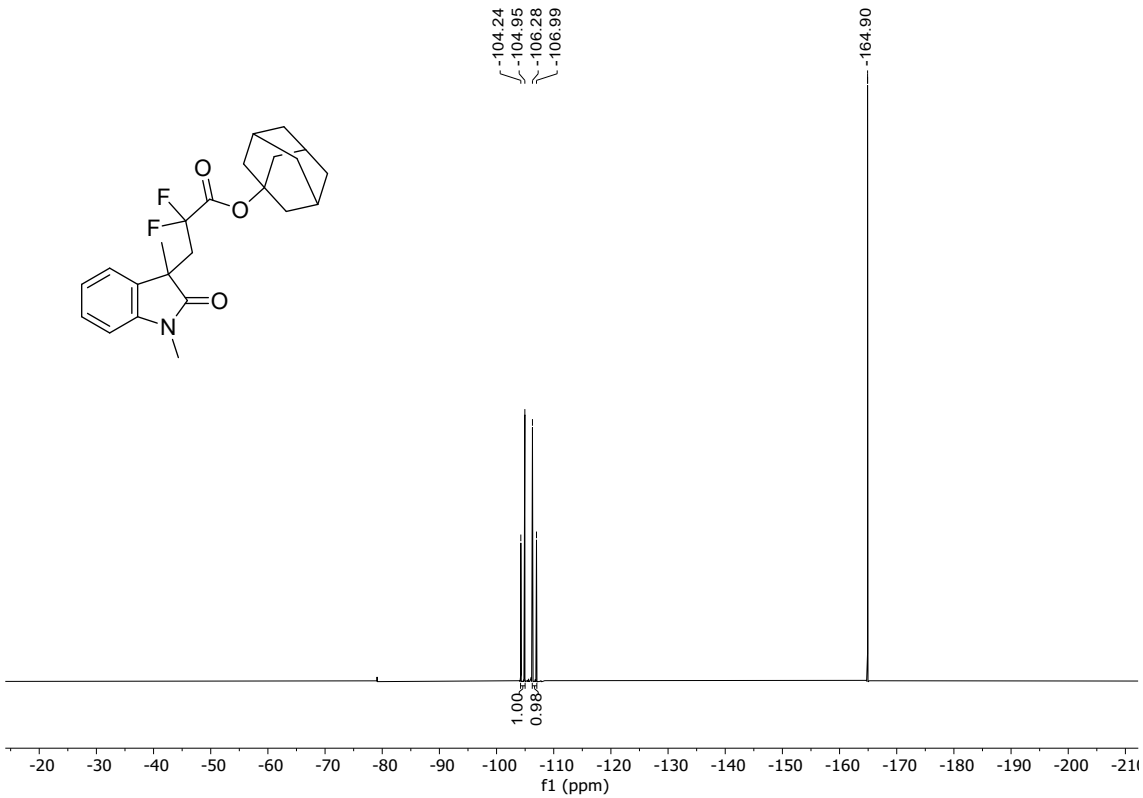
^{19}F NMR (376 MHz, $CDCl_3$) of compound **22**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



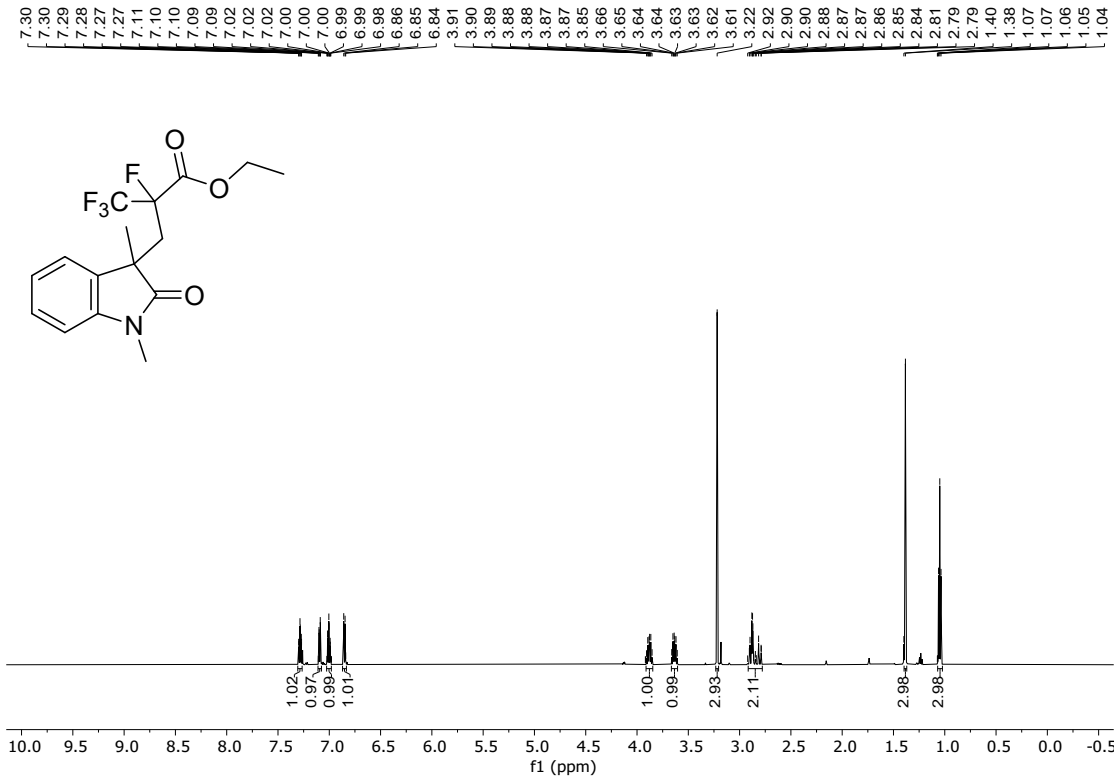
^{1}H NMR (600 MHz, $CDCl_3$) of compound **23**.



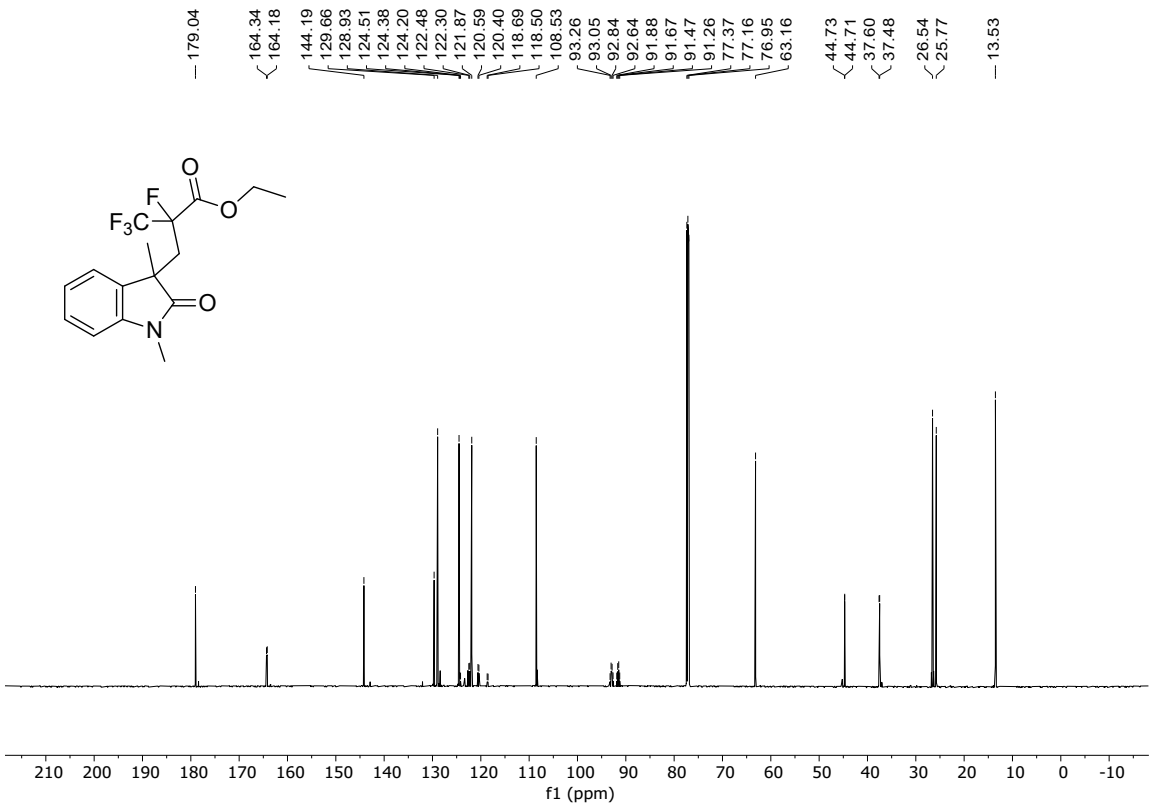
^{13}C NMR (151 MHz, CDCl3) of compound **23**.



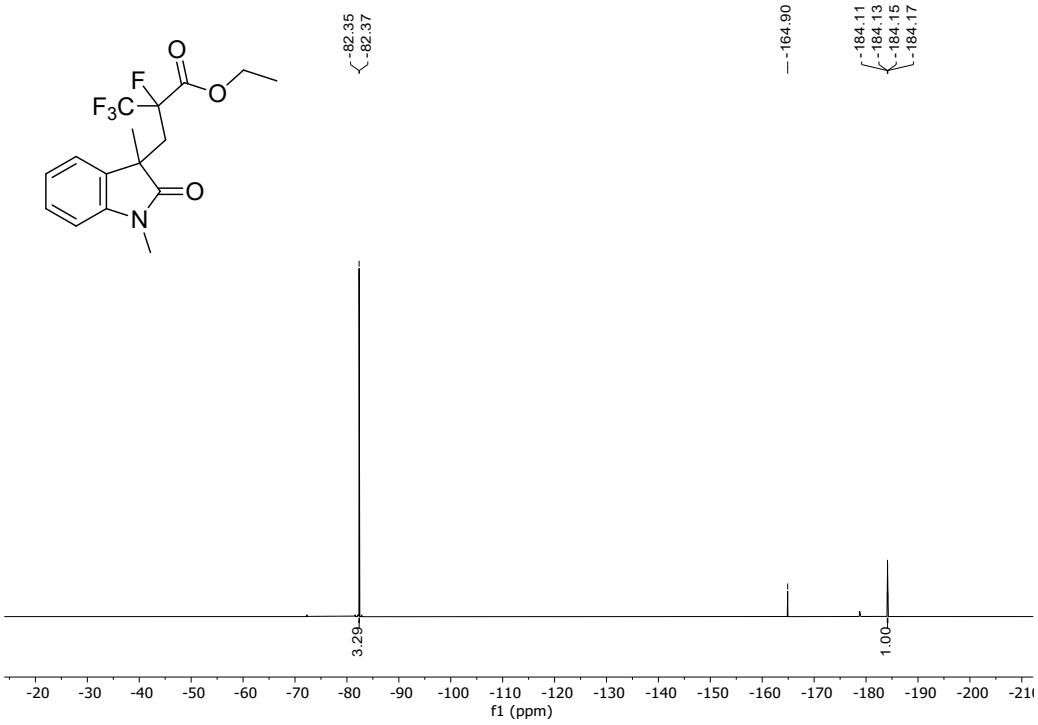
^{19}F NMR (376 MHz, $CDCl_3$) of compound **23**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



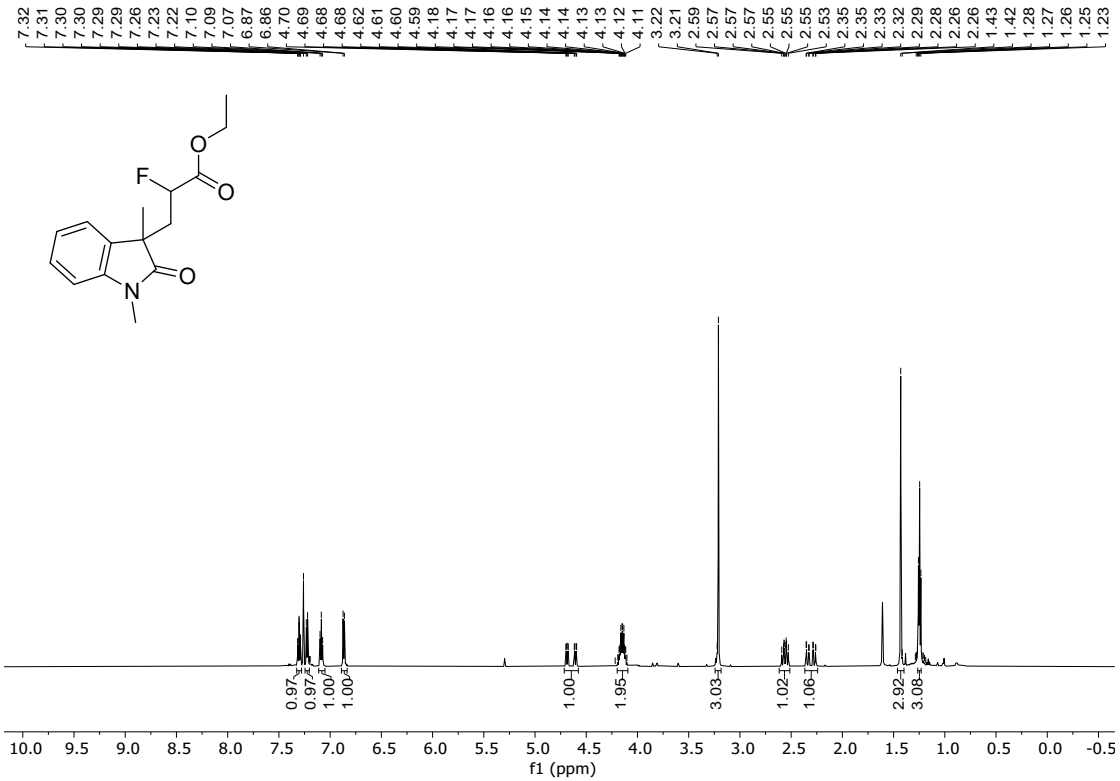
^{1}H NMR (600 MHz, $CDCl_3$) of compound **24.**



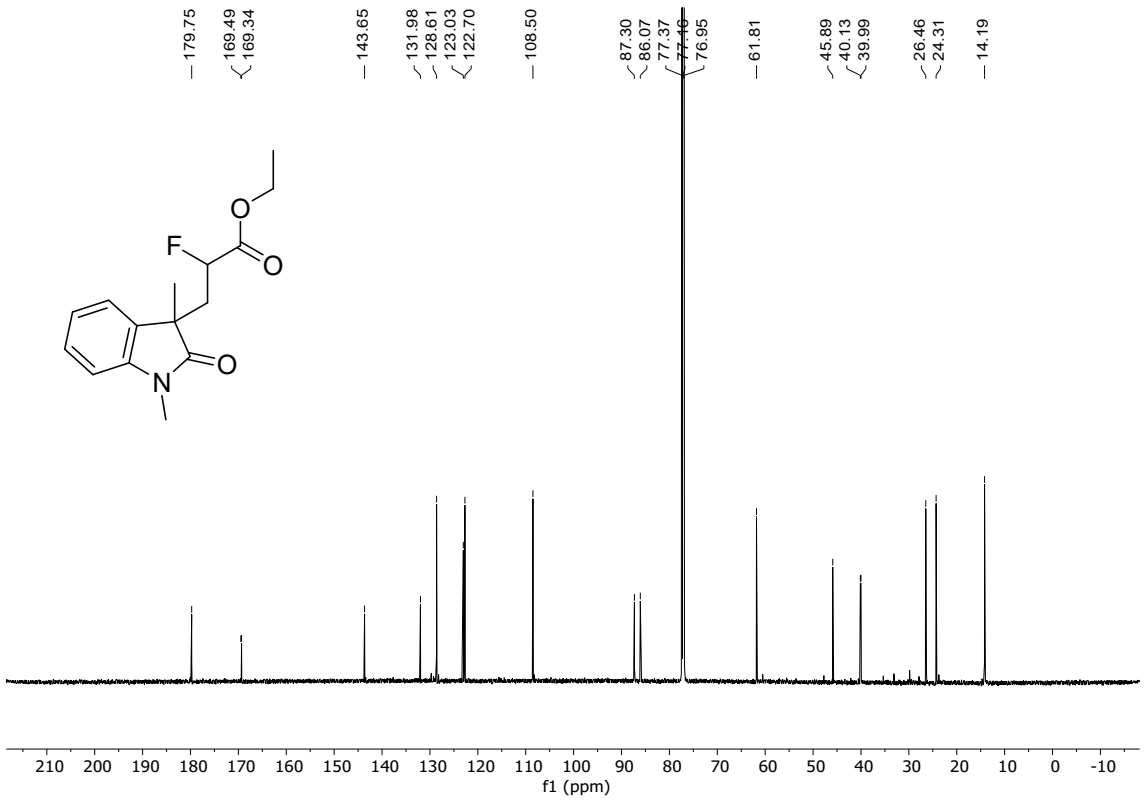
^{13}C NMR (151 MHz, CDCl3) of compound **24**.



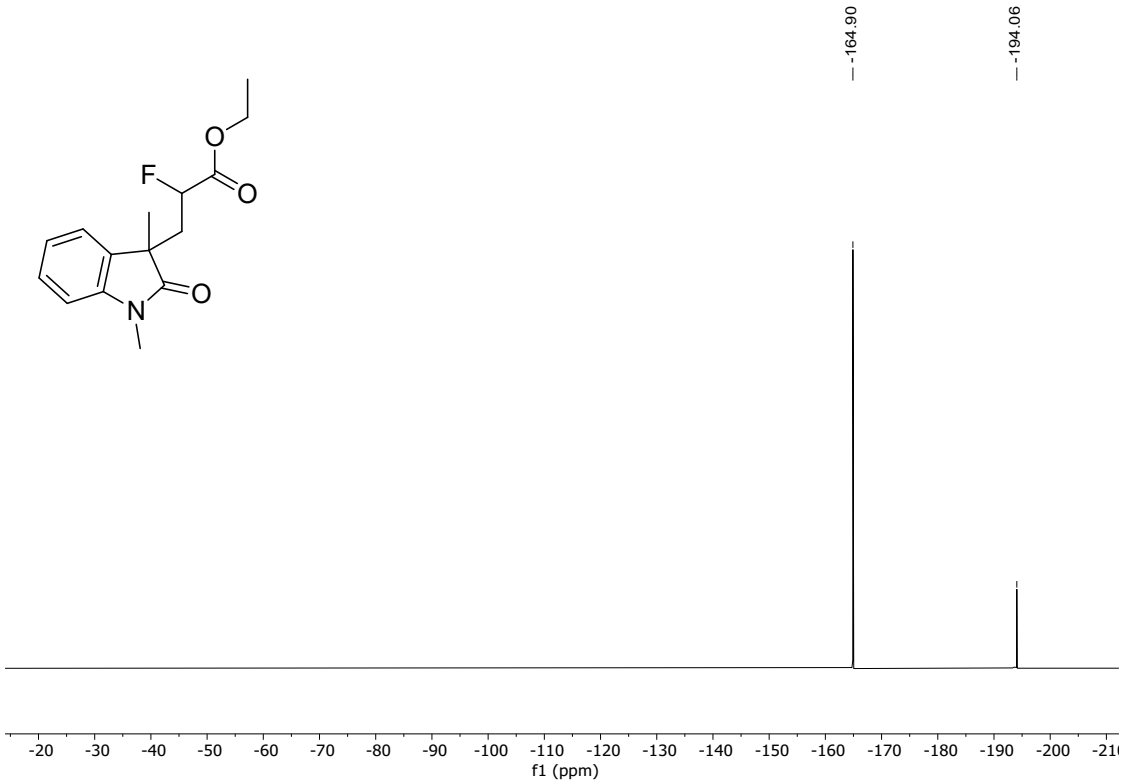
^{19}F NMR (376 MHz, $CDCl_3$) of compound **24**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



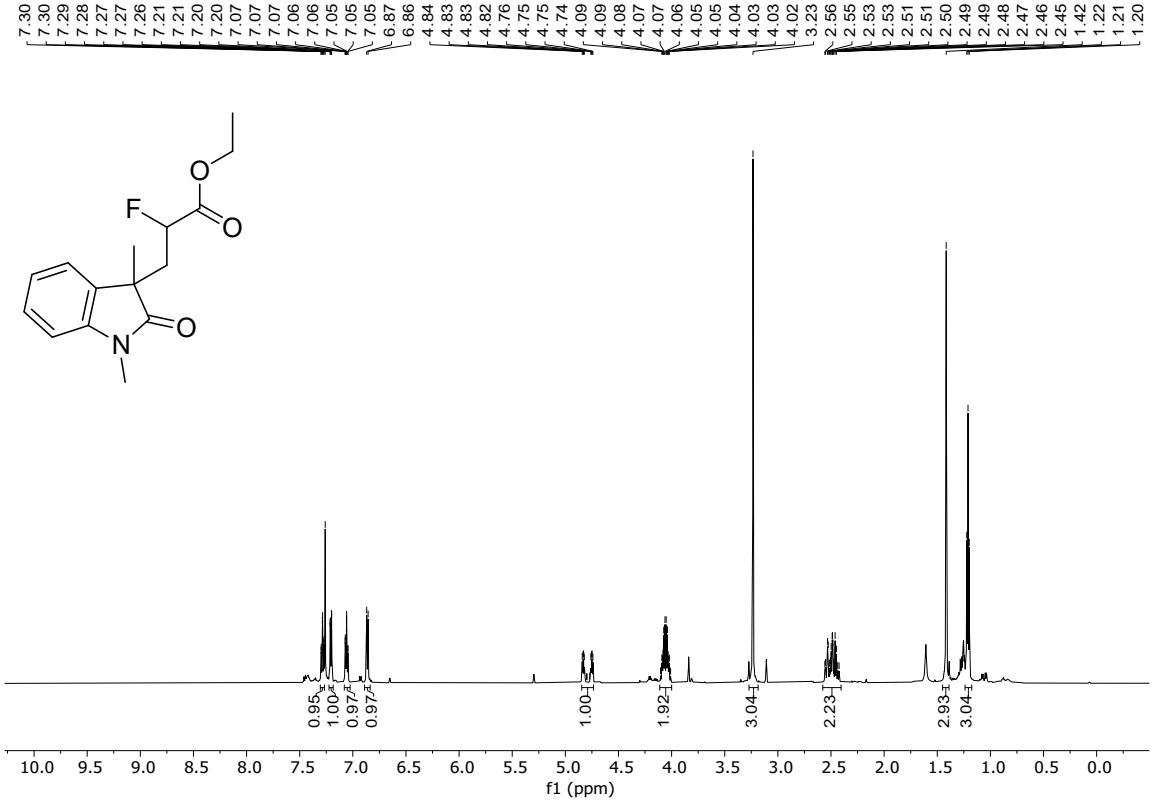
^{1}H NMR (600 MHz, $CDCl_3$) of compound **25**.



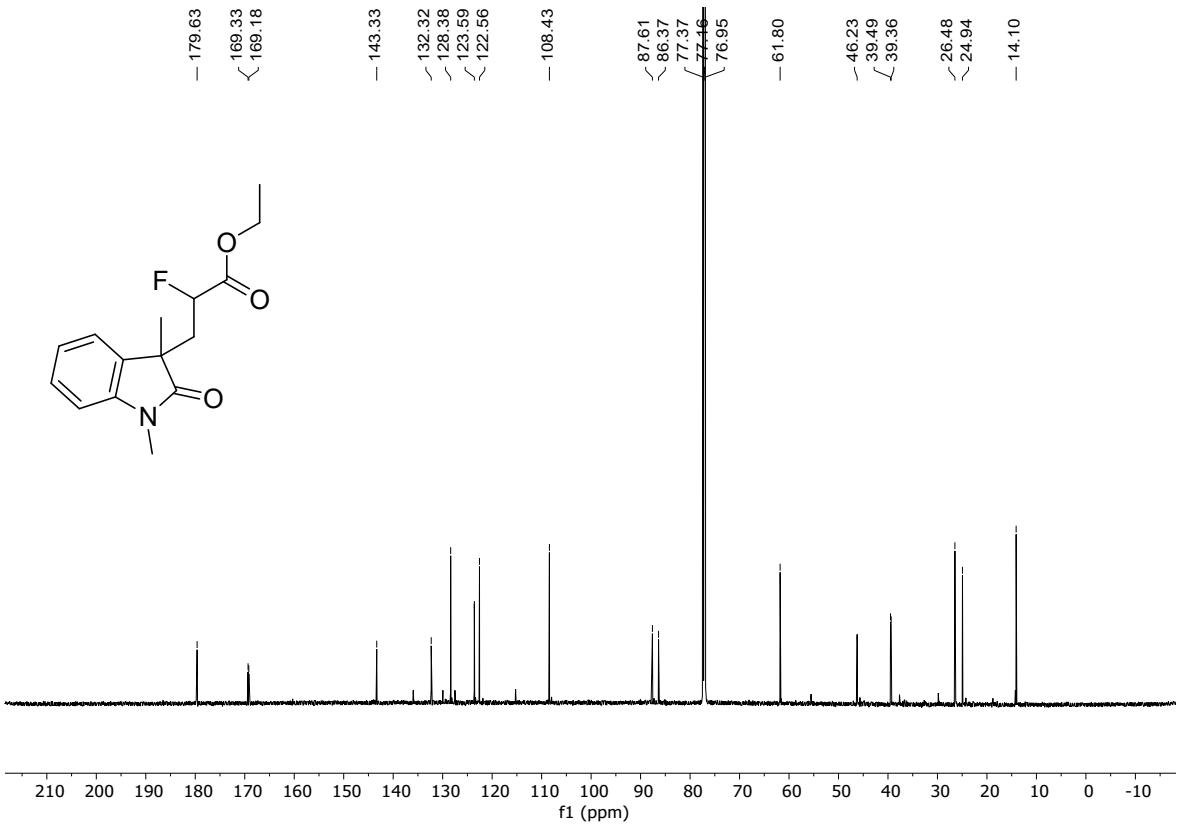
^{13}C NMR (151 MHz, CDCl3) of compound **25**.



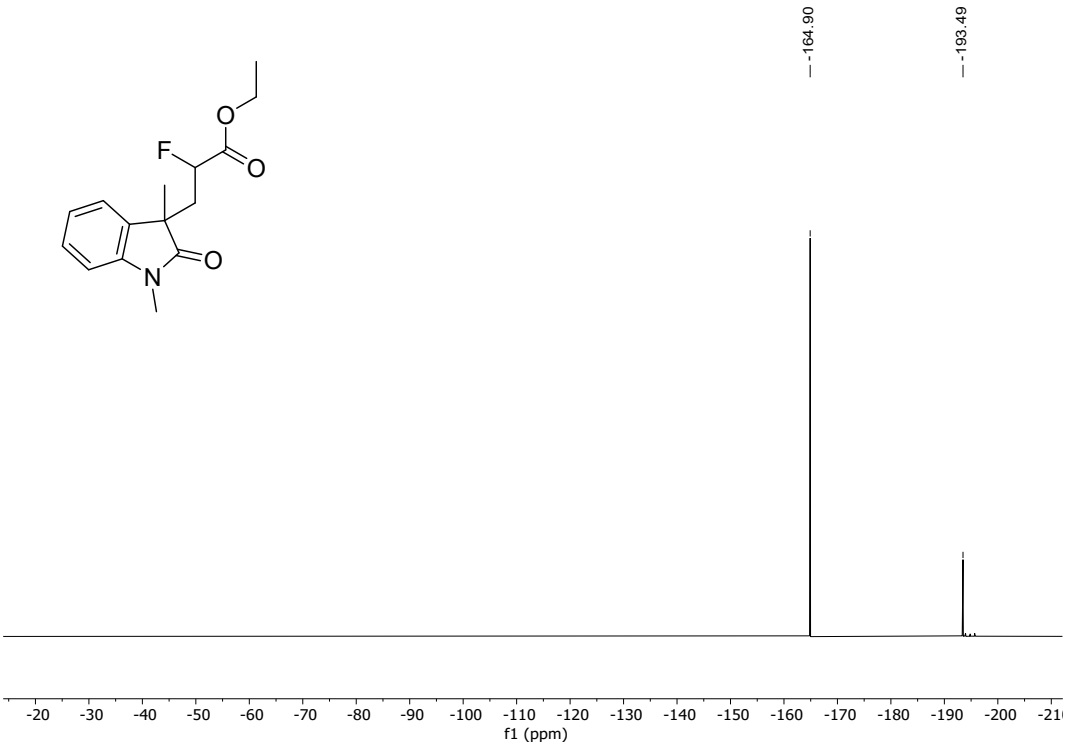
^{19}F NMR (376 MHz, $CDCl_3$) of compound **25**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



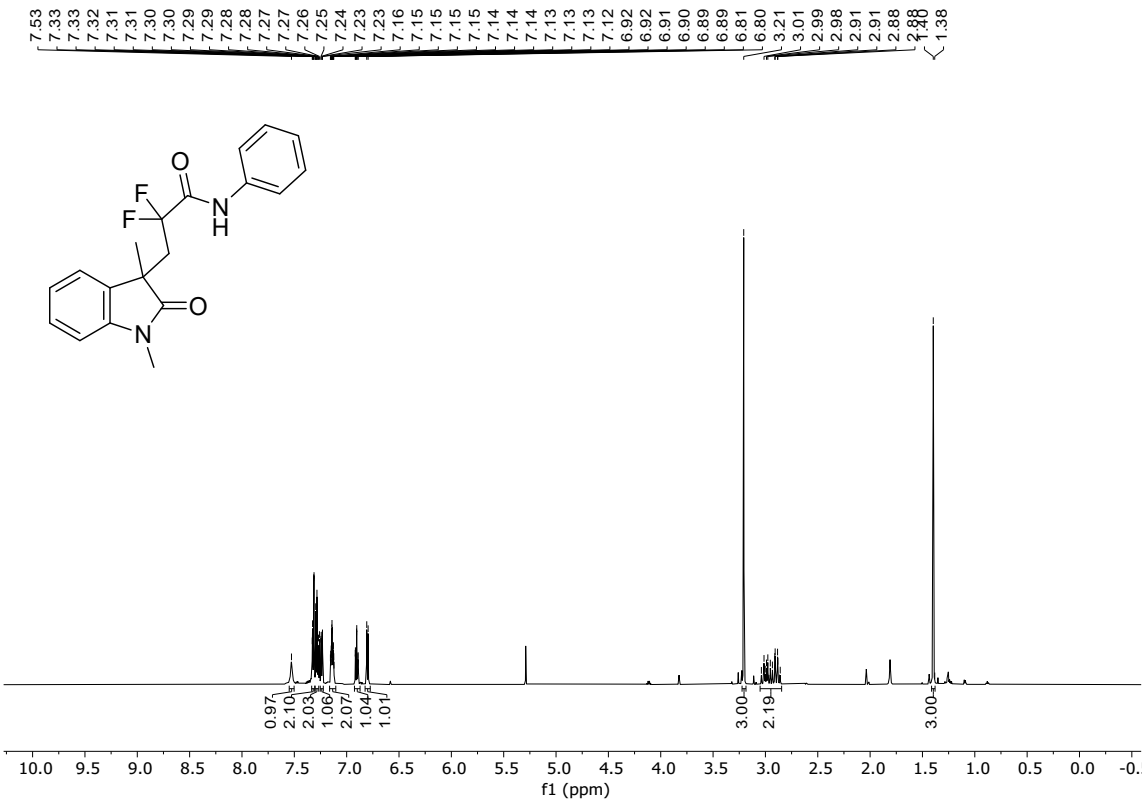
^{1}H NMR (600 MHz, $CDCl_3$) of compound **25**.



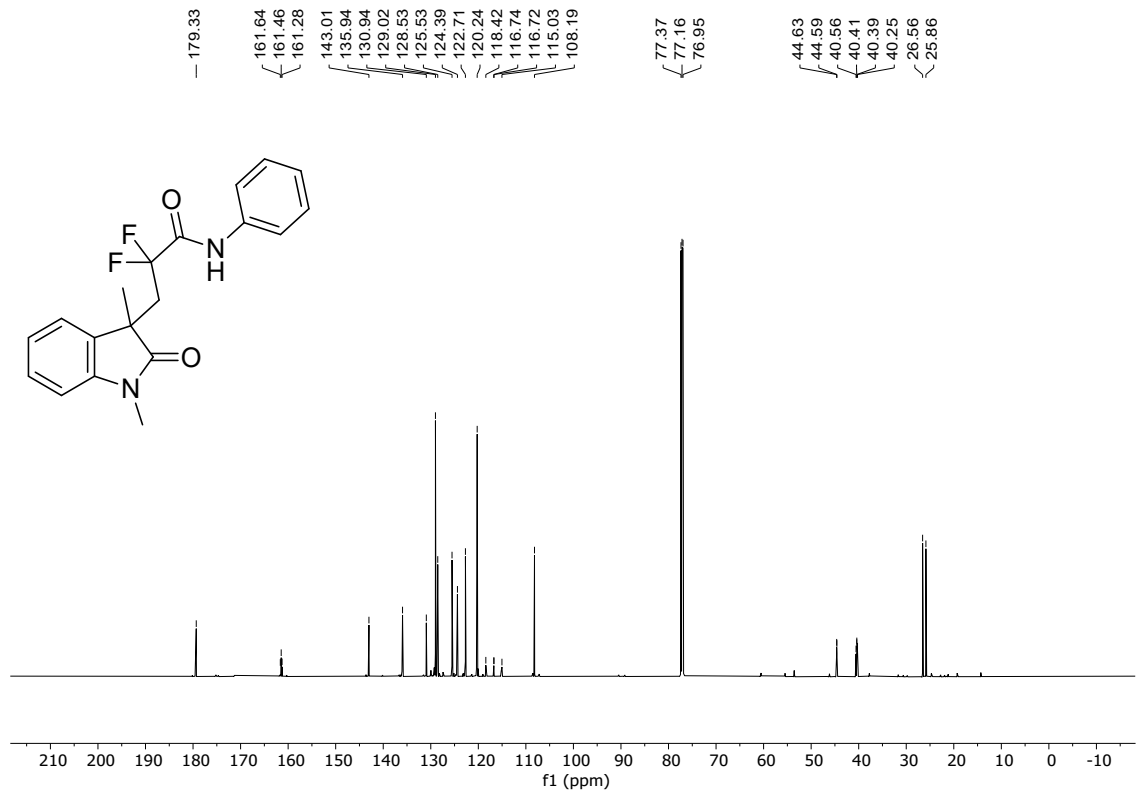
^{13}C NMR (151 MHz, $CDCl_3$) of compound **25**.



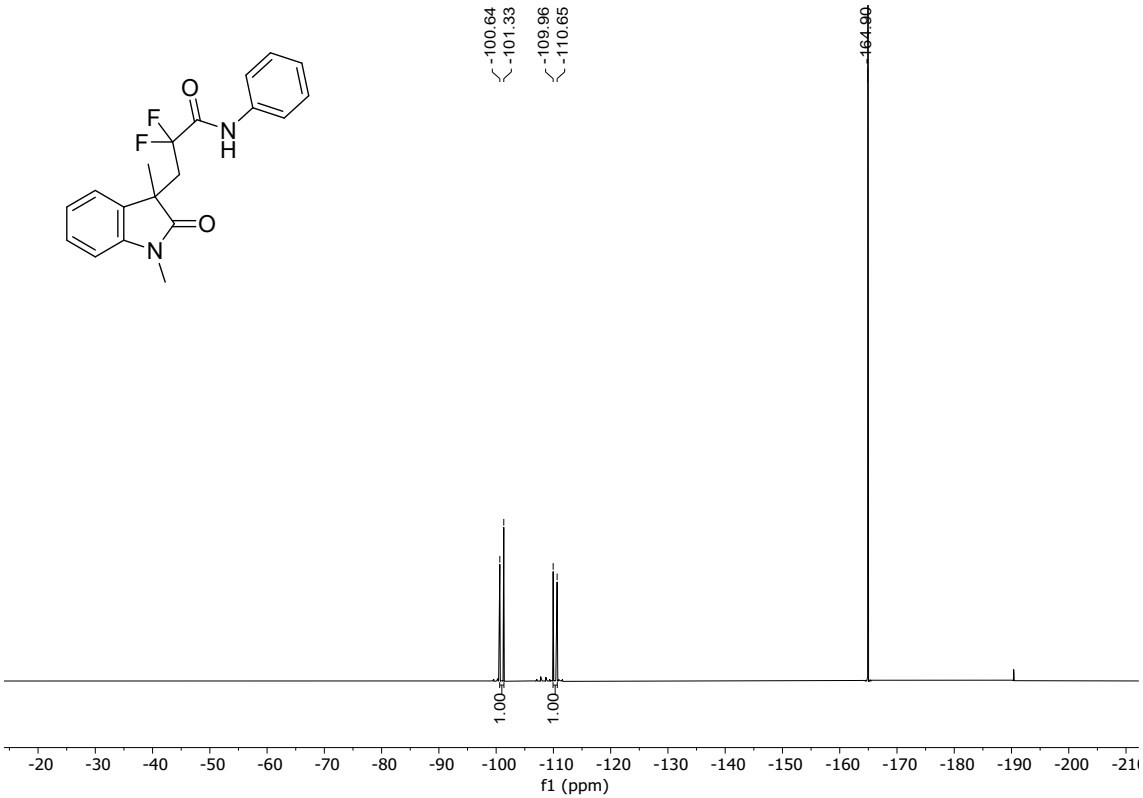
^{19}F NMR (376 MHz, $CDCl_3$) of compound **25**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



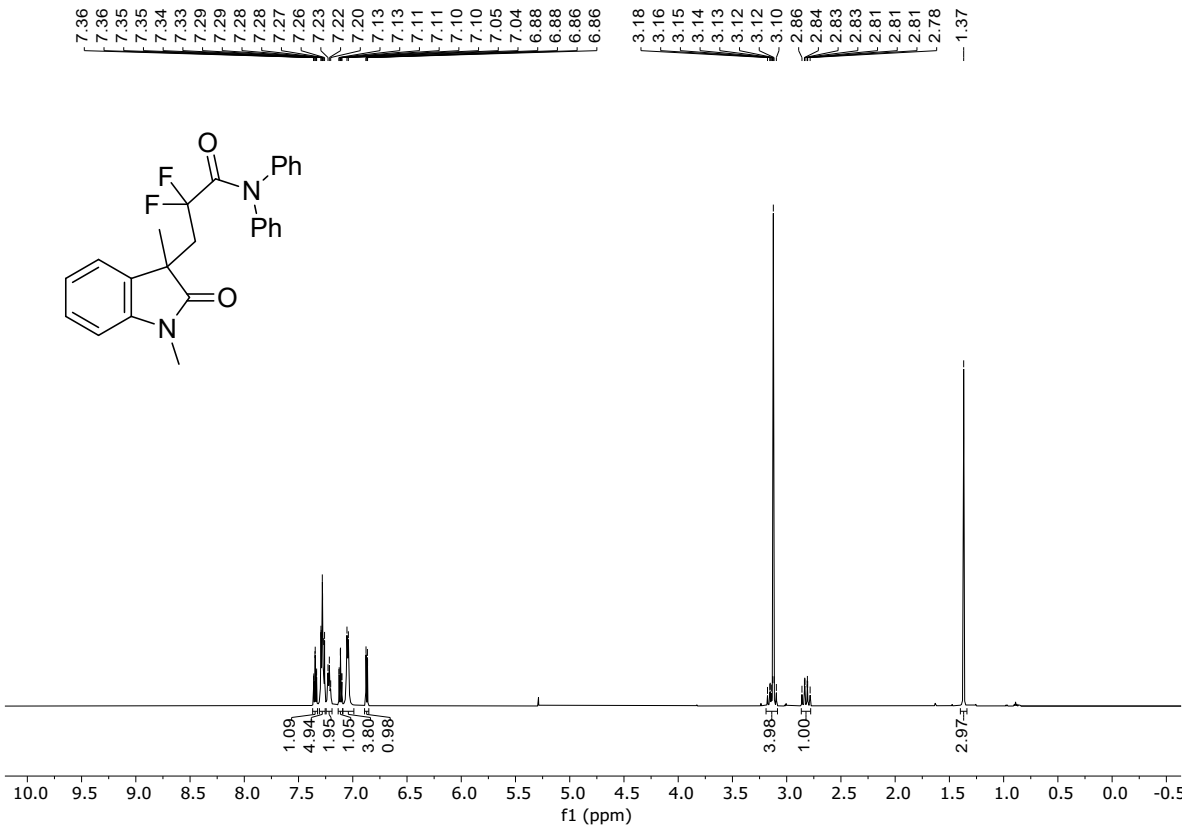
^{1}H NMR (600 MHz, $CDCl_3$) of compound **26**.



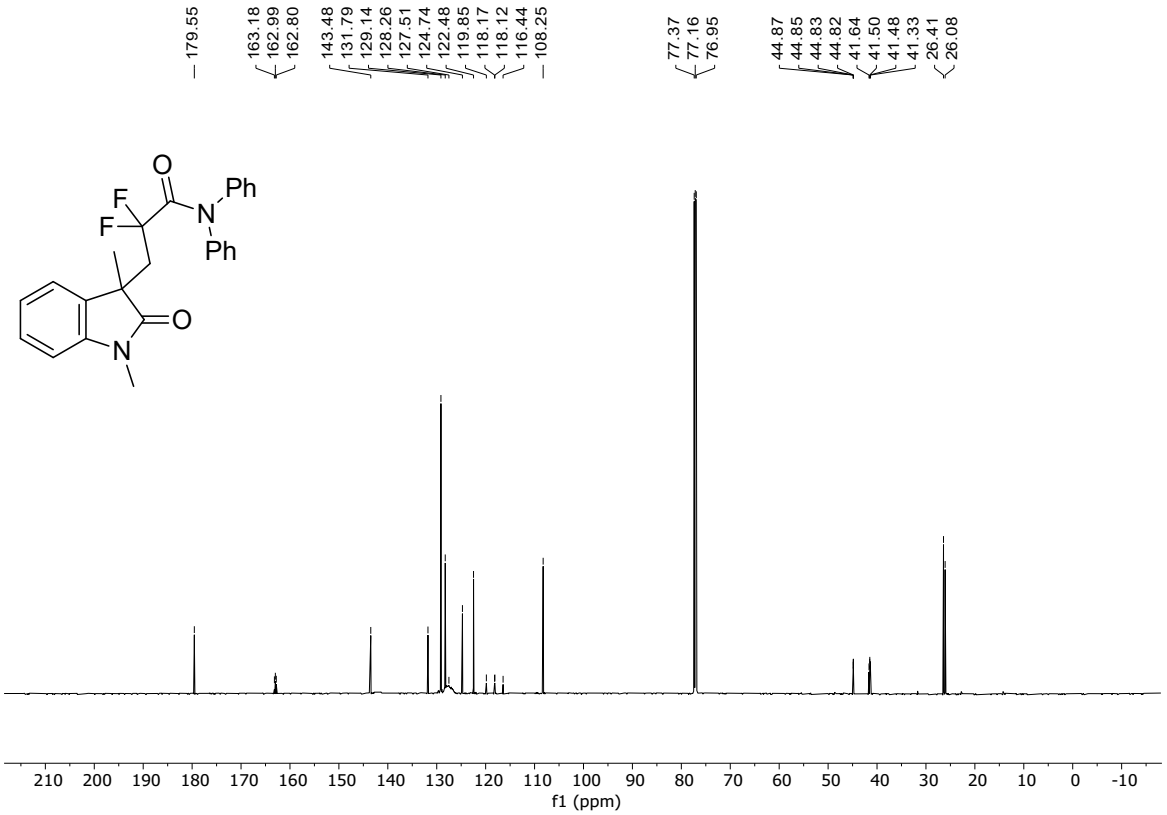
^{13}C NMR (151 MHz, $CDCl_3$) of compound **26**.



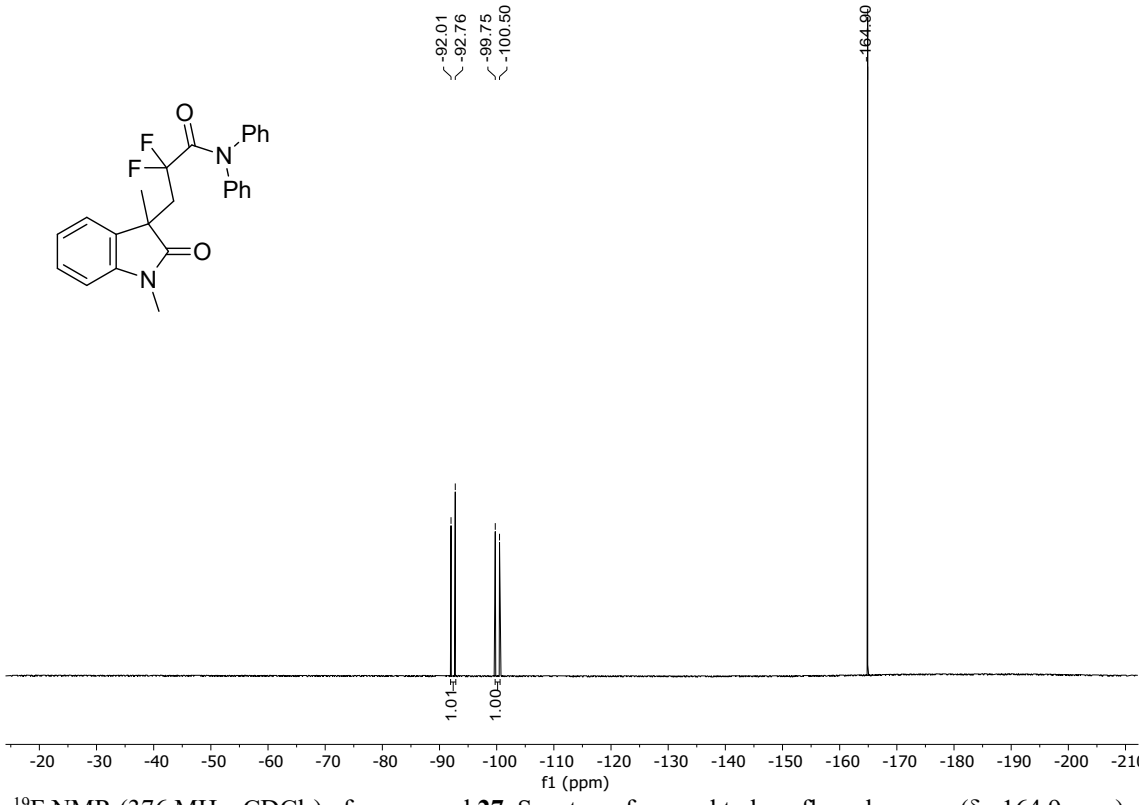
^{19}F NMR (376 MHz, $CDCl_3$) of compound **26**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



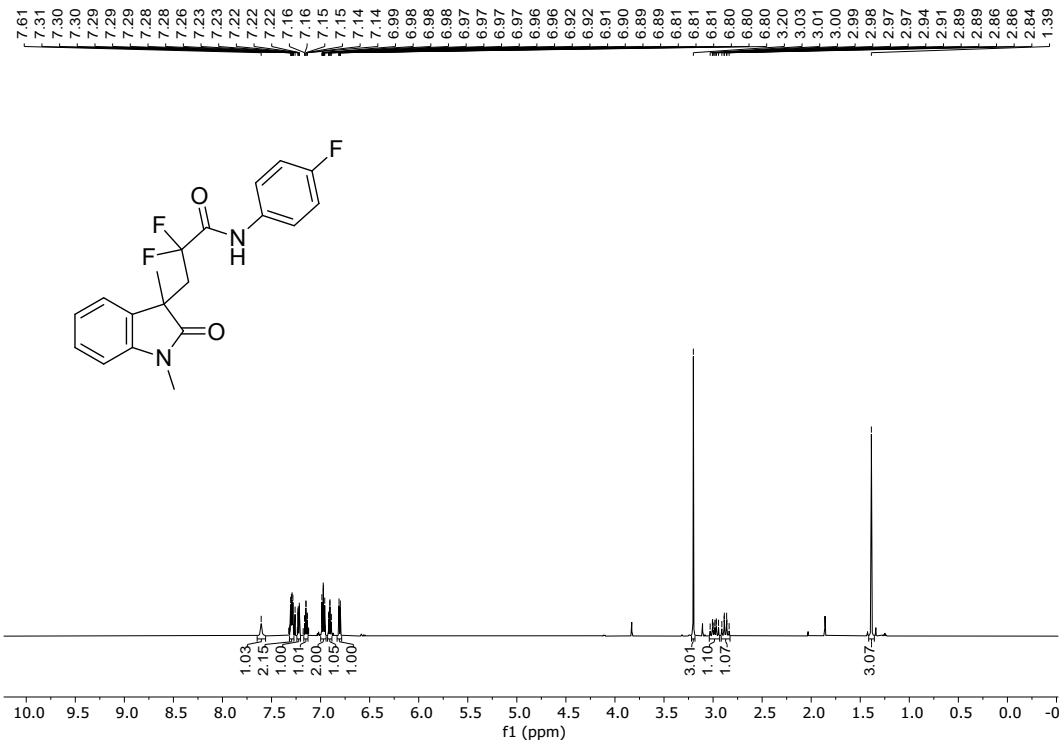
^{1}H NMR (600 MHz, $CDCl_3$) of compound **27**.



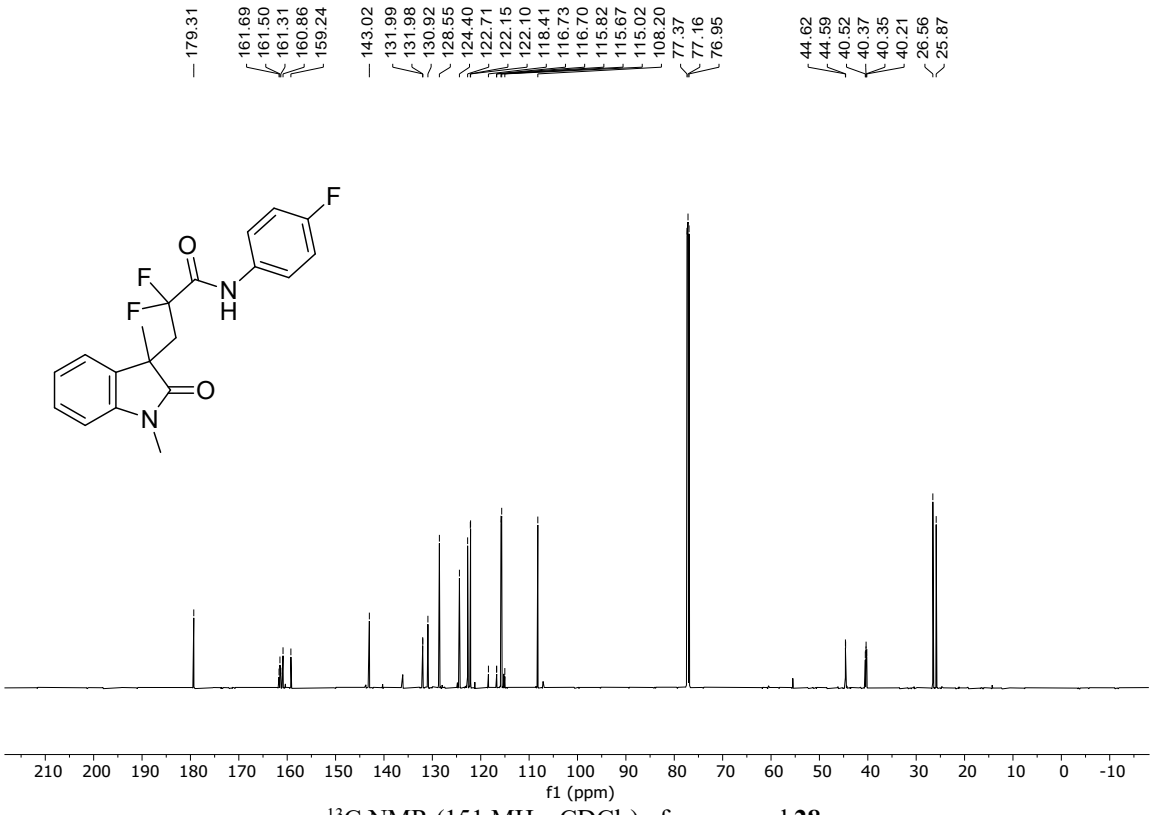
^{13}C NMR (151 MHz, $CDCl_3$) of compound **27**.



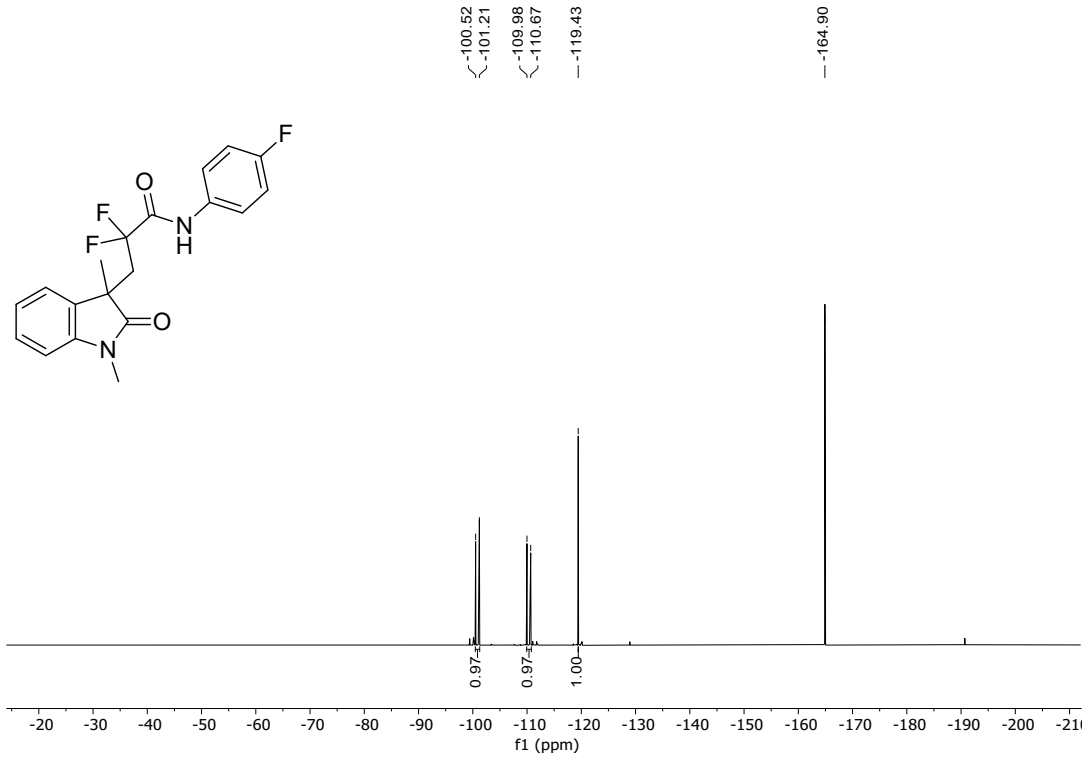
^{19}F NMR (376 MHz, $CDCl_3$) of compound **27**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



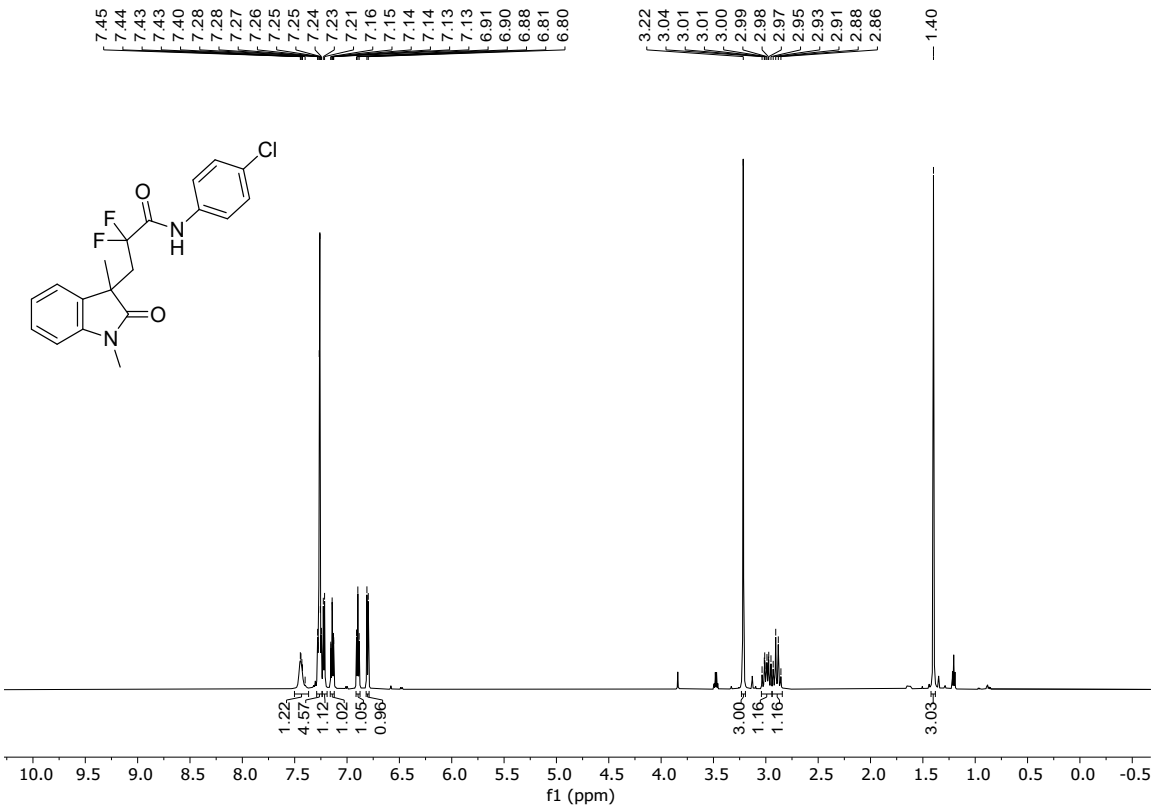
^{1}H NMR (600 MHz, $CDCl_3$) of compound **28**.



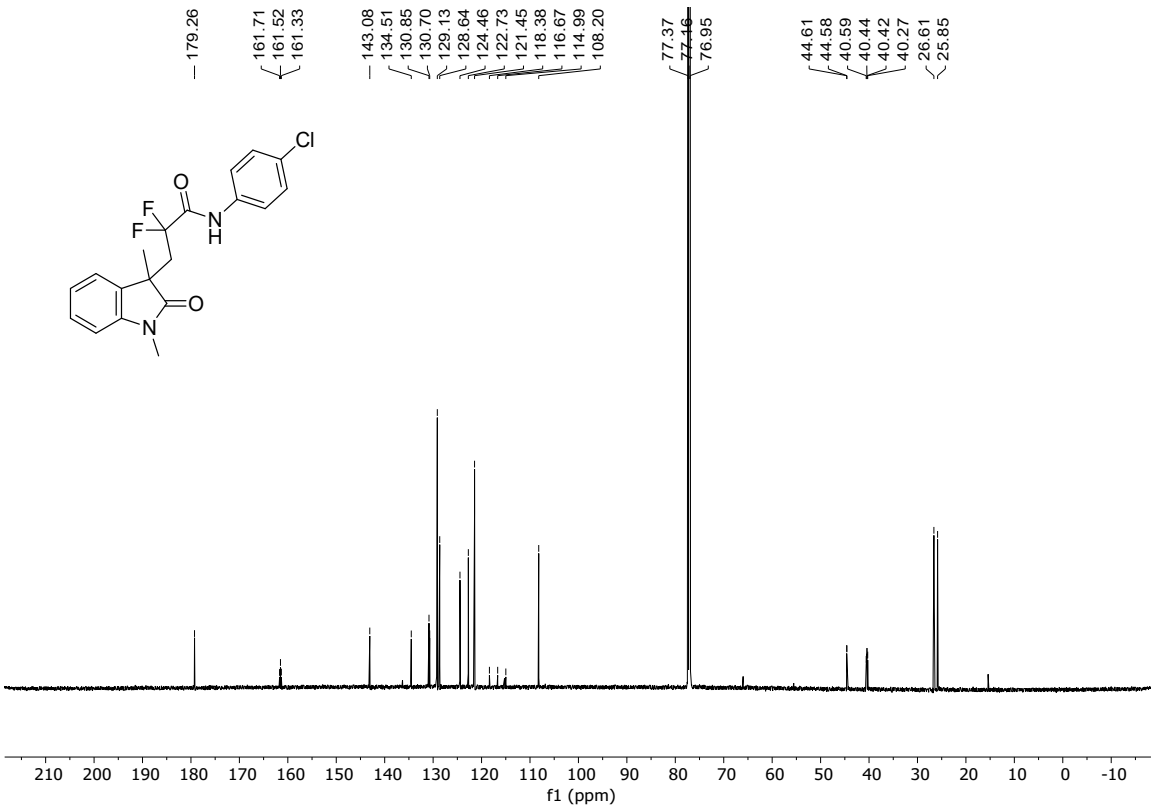
^{13}C NMR (151 MHz, $CDCl_3$) of compound **28**.



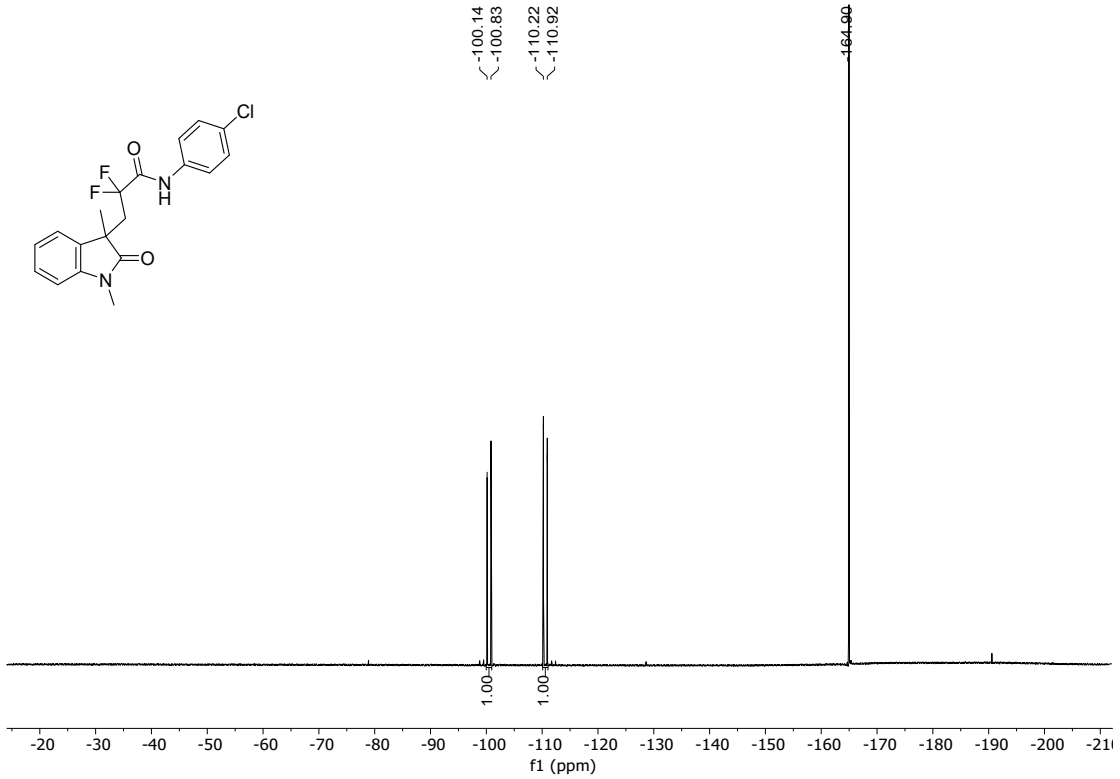
^{19}F NMR (376 MHz, $CDCl_3$) of compound **28**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



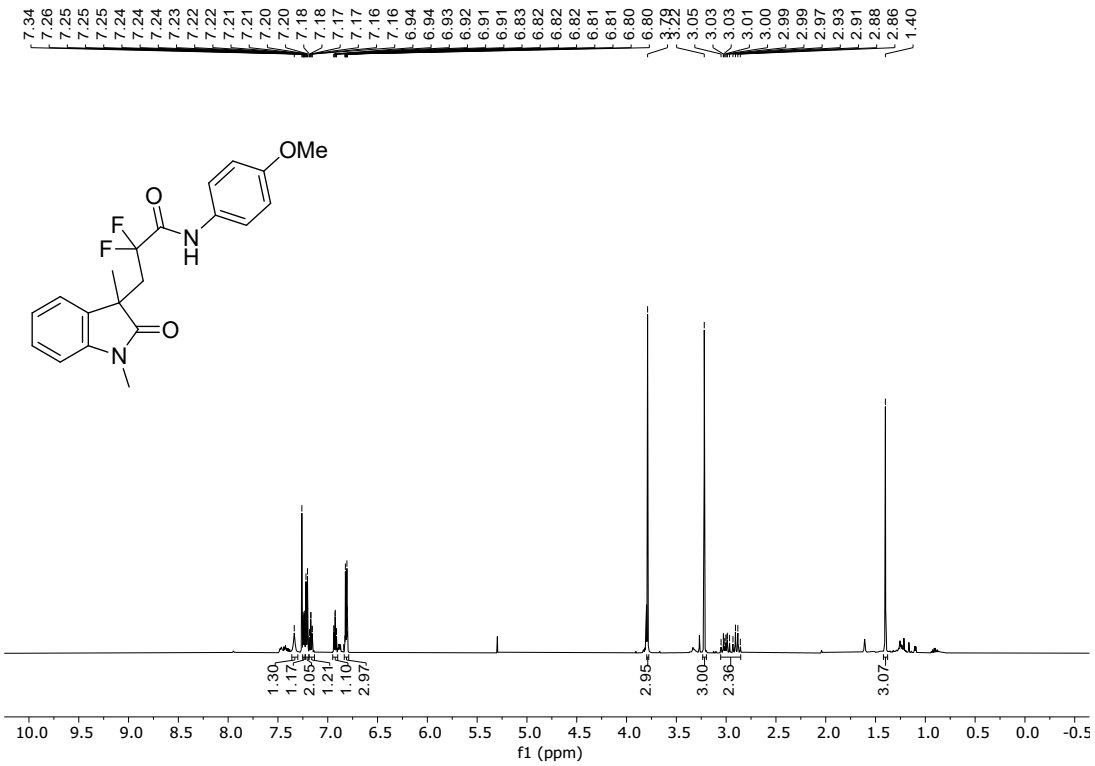
^{1}H NMR (600 MHz, $CDCl_3$) of compound **29**.



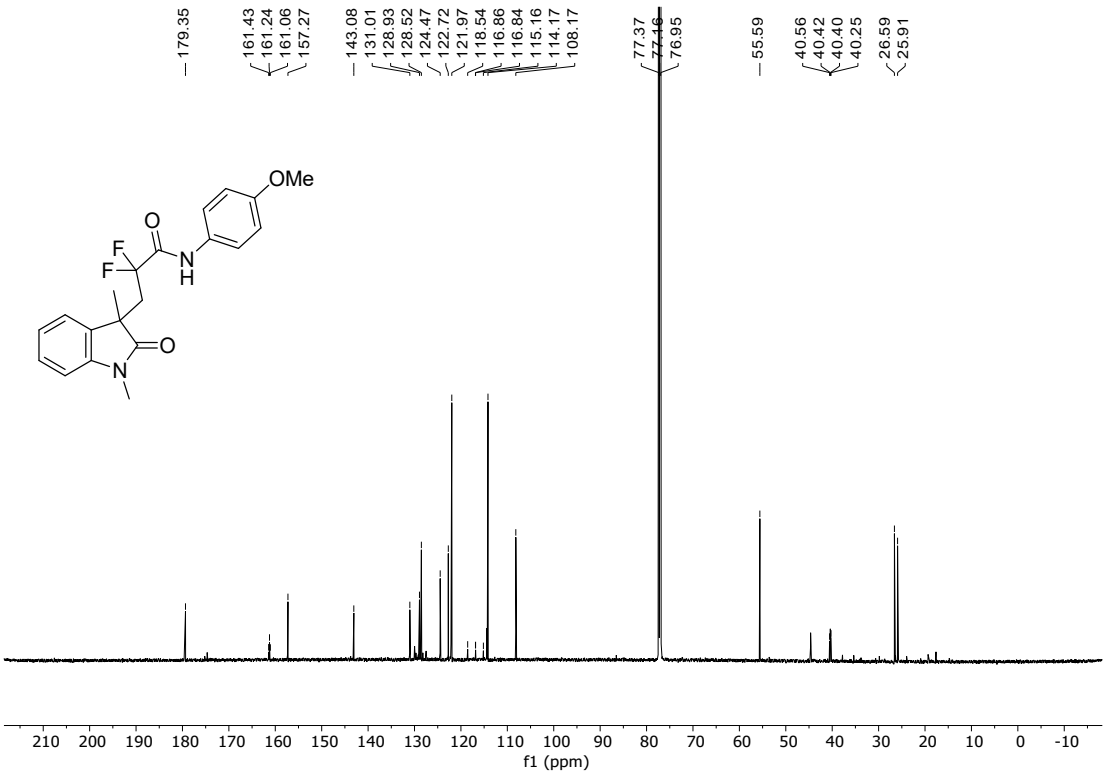
^{13}C NMR (151 MHz, $CDCl_3$) of compound **29**.



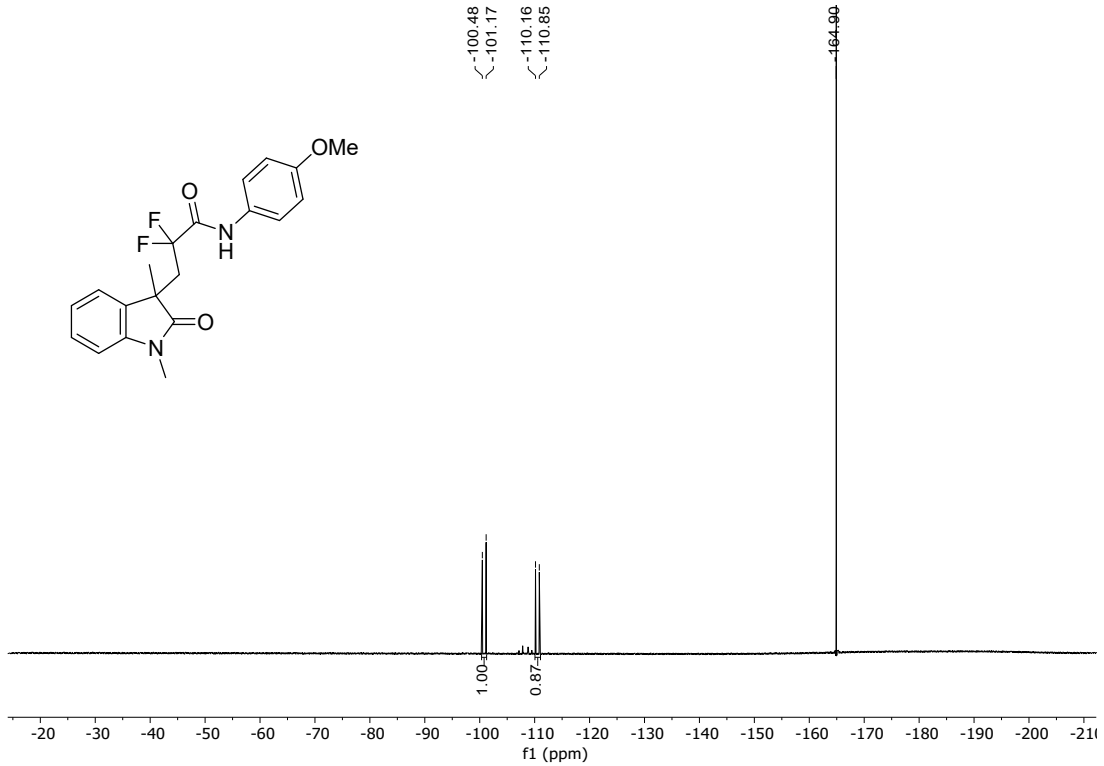
^{19}F NMR (376 MHz, $CDCl_3$) of compound **29**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



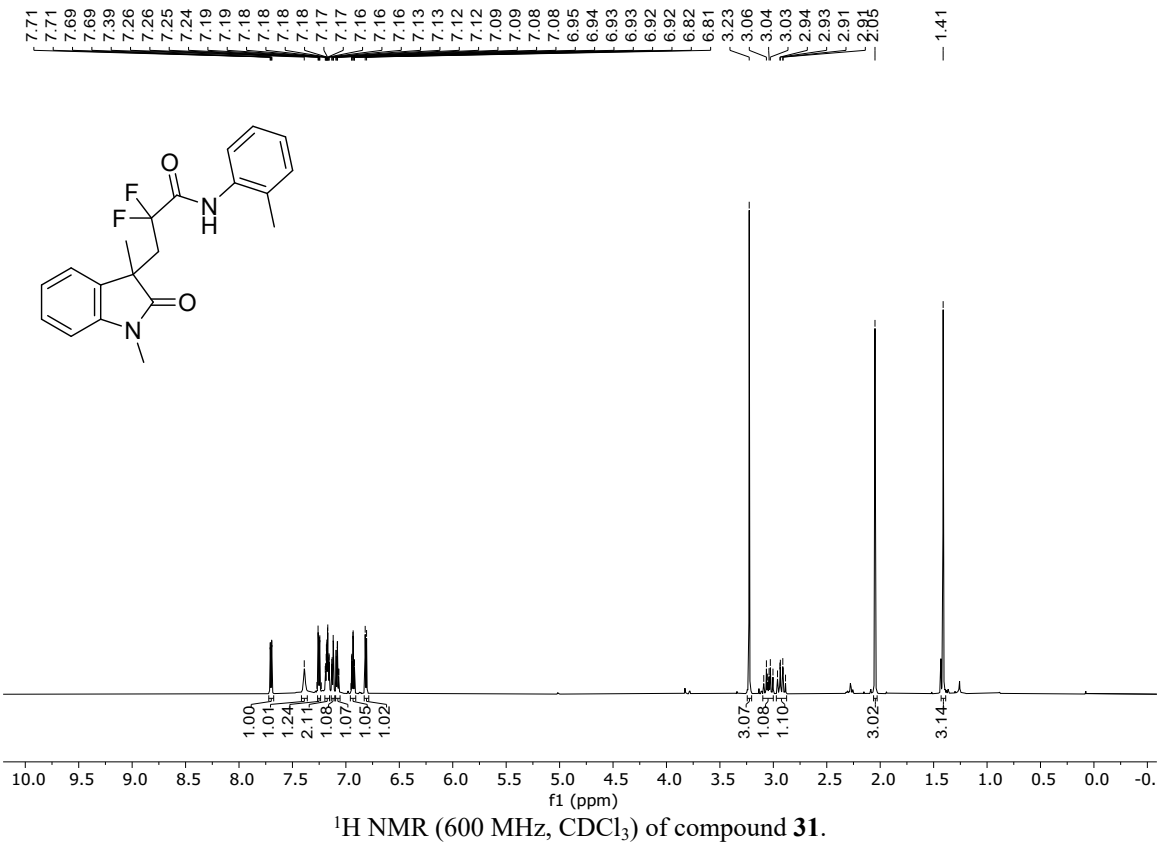
^{1}H NMR (600 MHz, $CDCl_3$) of compound **30**.



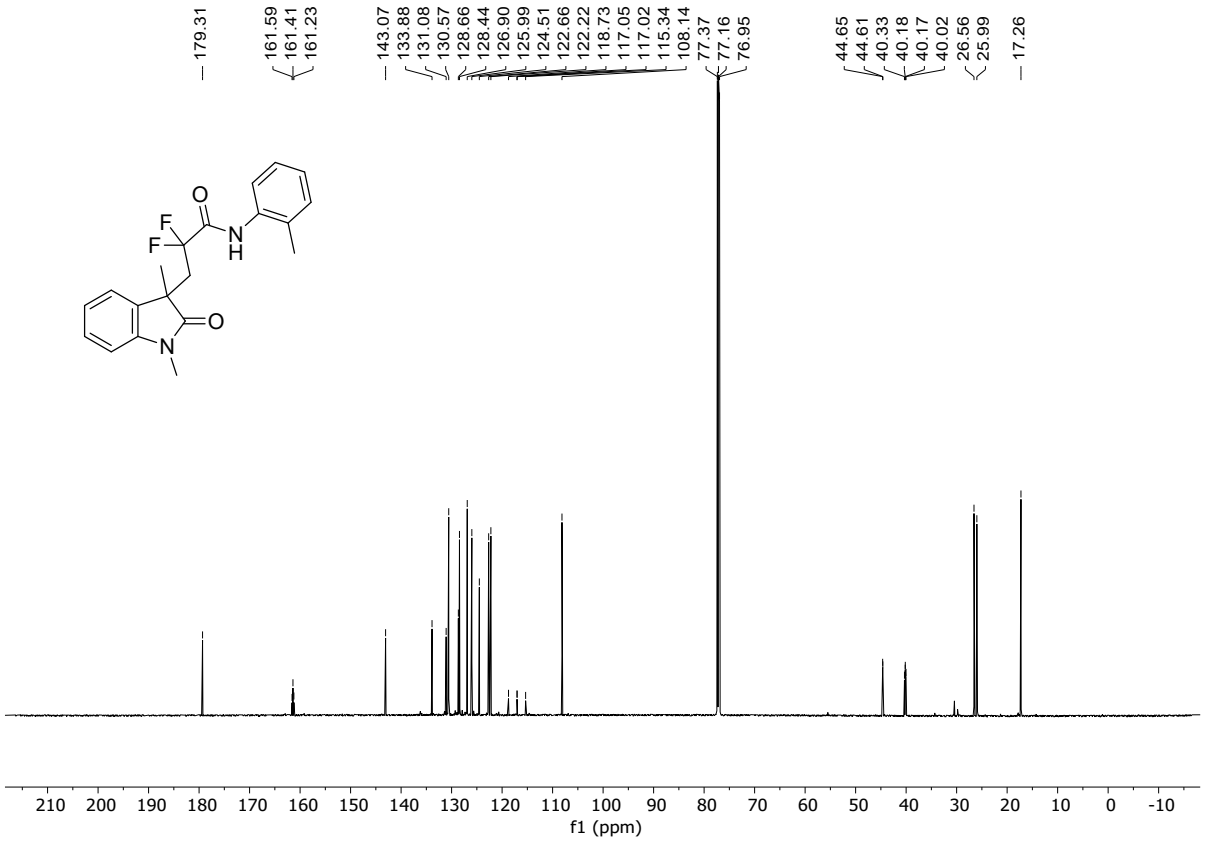
^{13}C NMR (151 MHz, $CDCl_3$) of compound **30**.



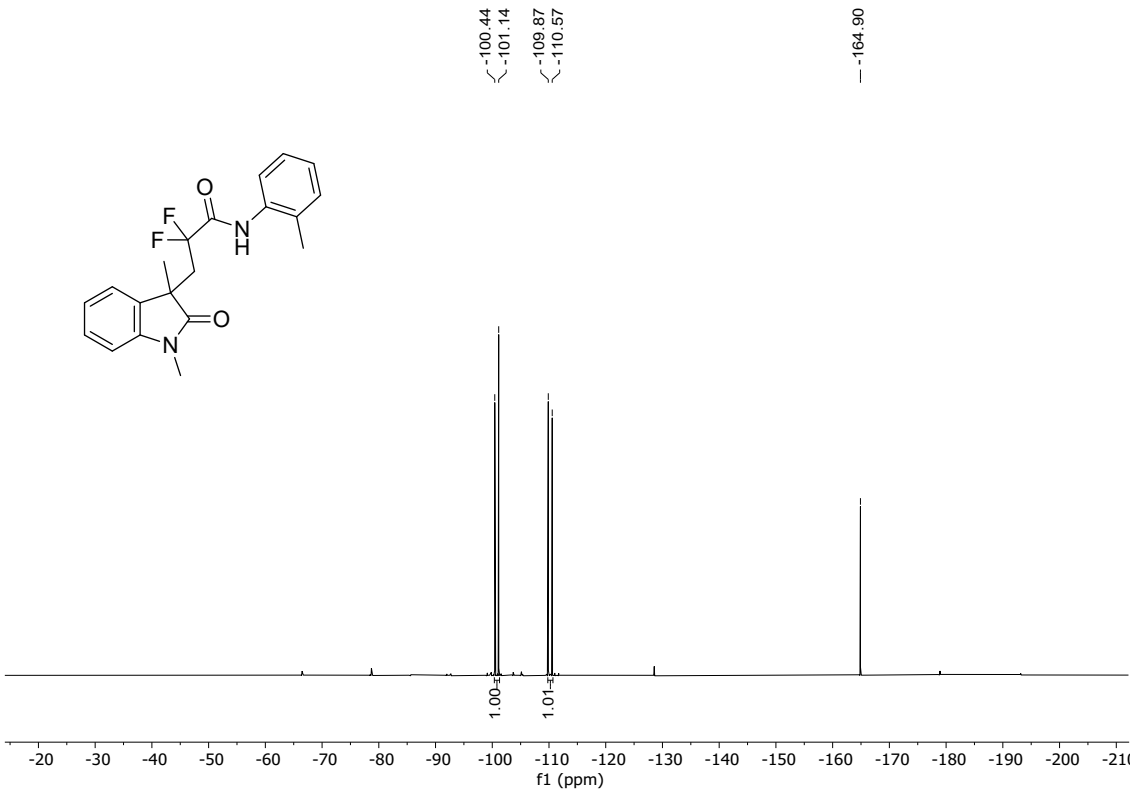
^{19}F NMR (376 MHz, $CDCl_3$) of compound **30**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



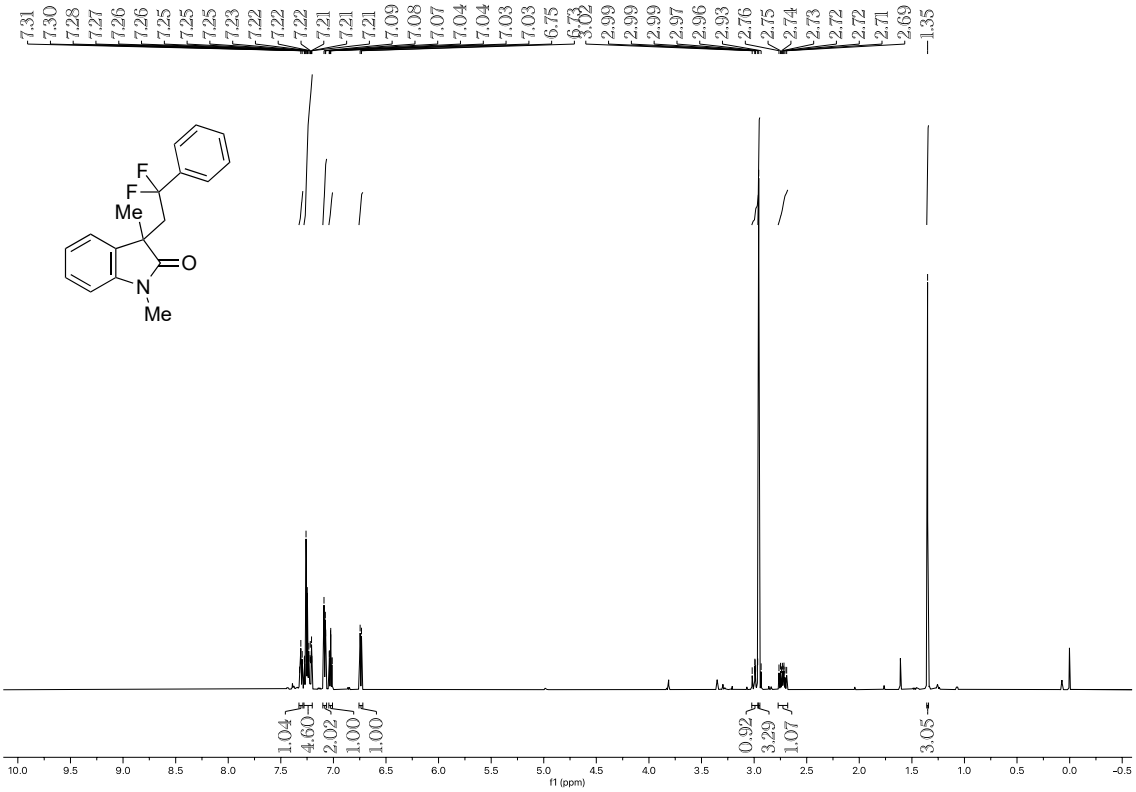
^{1}H NMR (600 MHz, $CDCl_3$) of compound **31**.



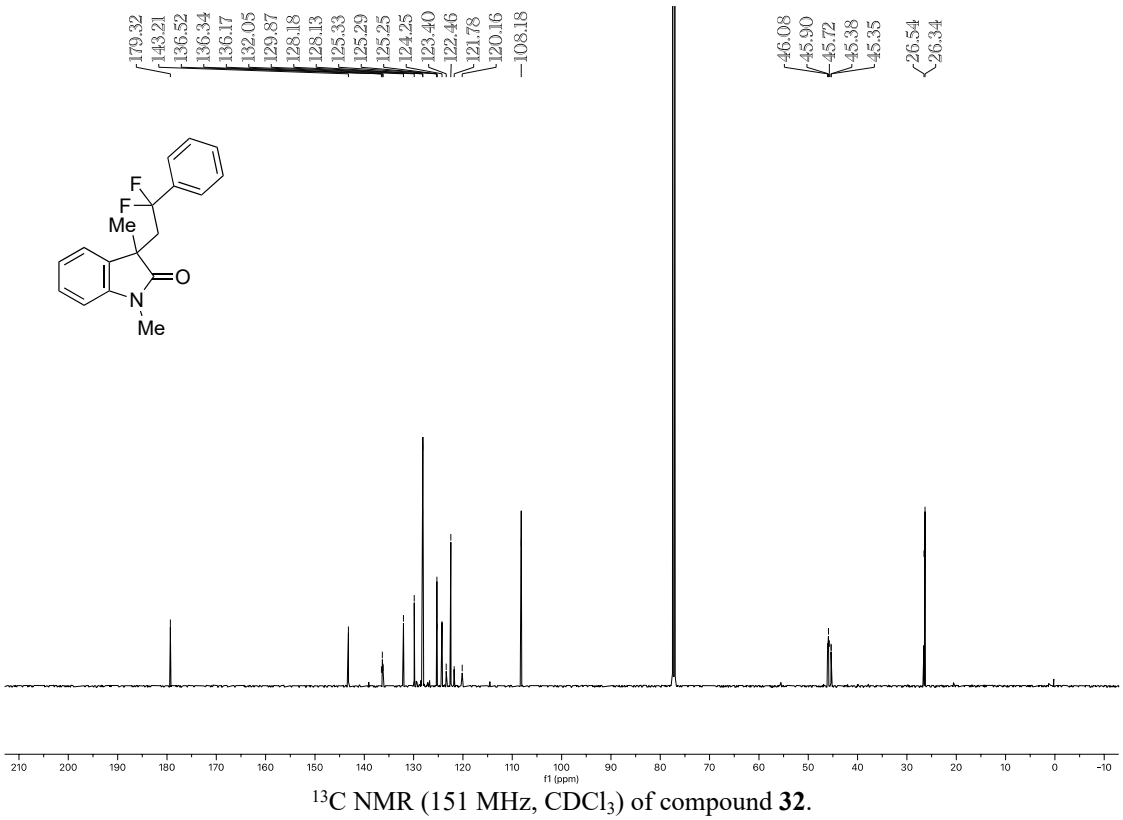
^{13}C NMR (151 MHz, $CDCl_3$) of compound **31**.



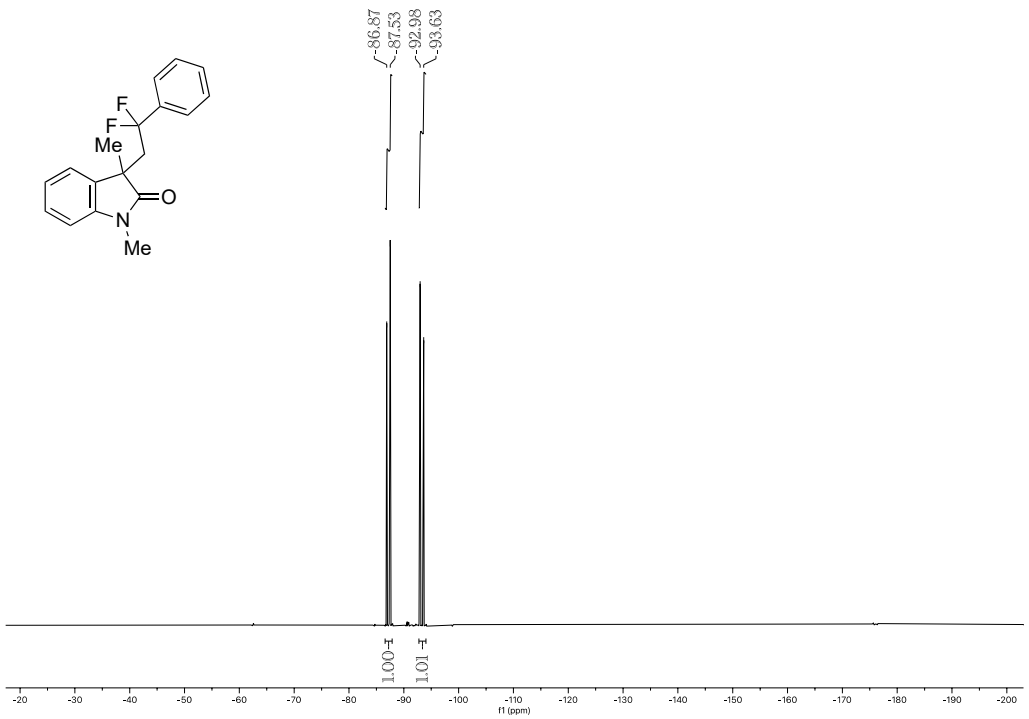
^{19}F NMR (376 MHz, $CDCl_3$) of compound **31**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



^{1}H NMR (600 MHz, $CDCl_3$) of compound **32**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **32**.



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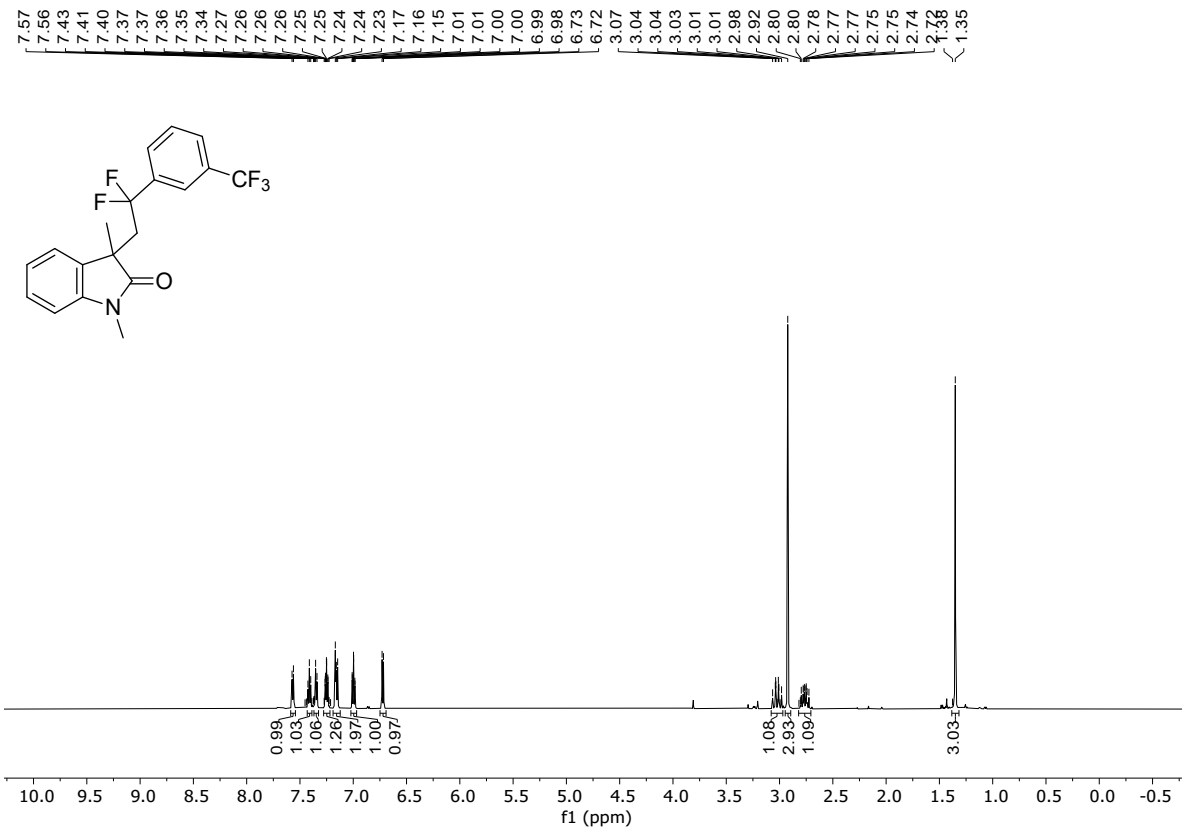
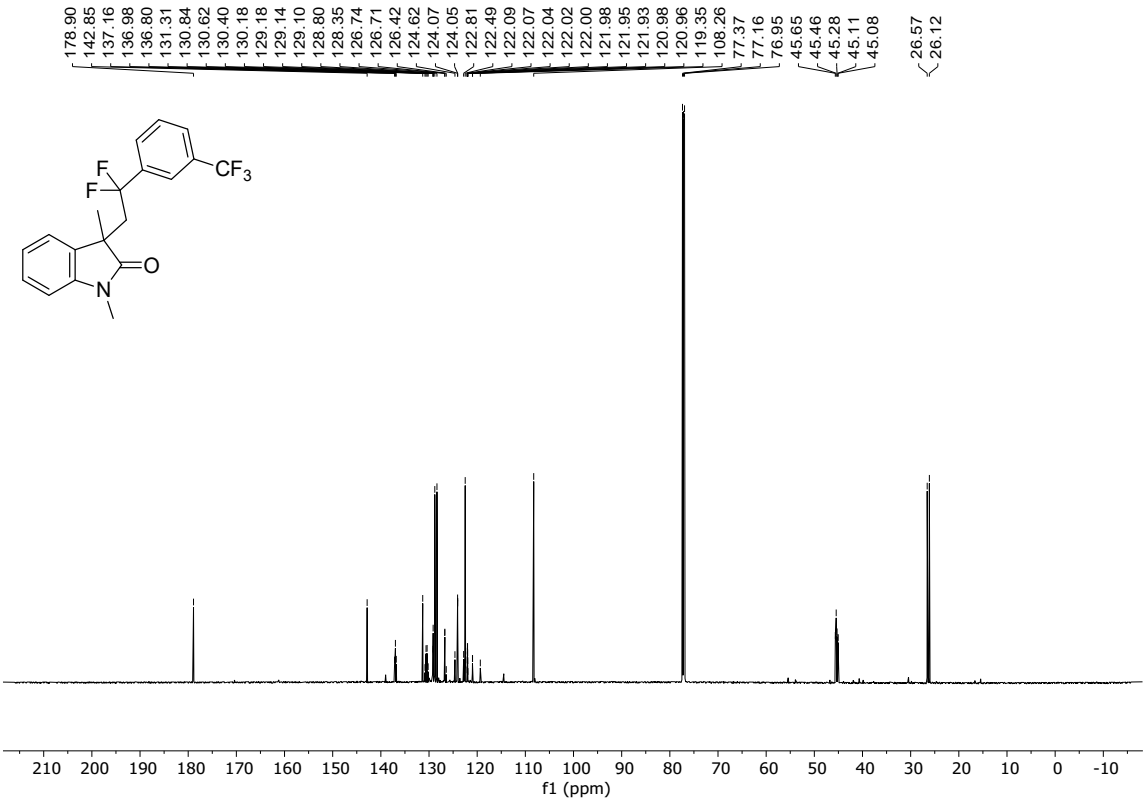
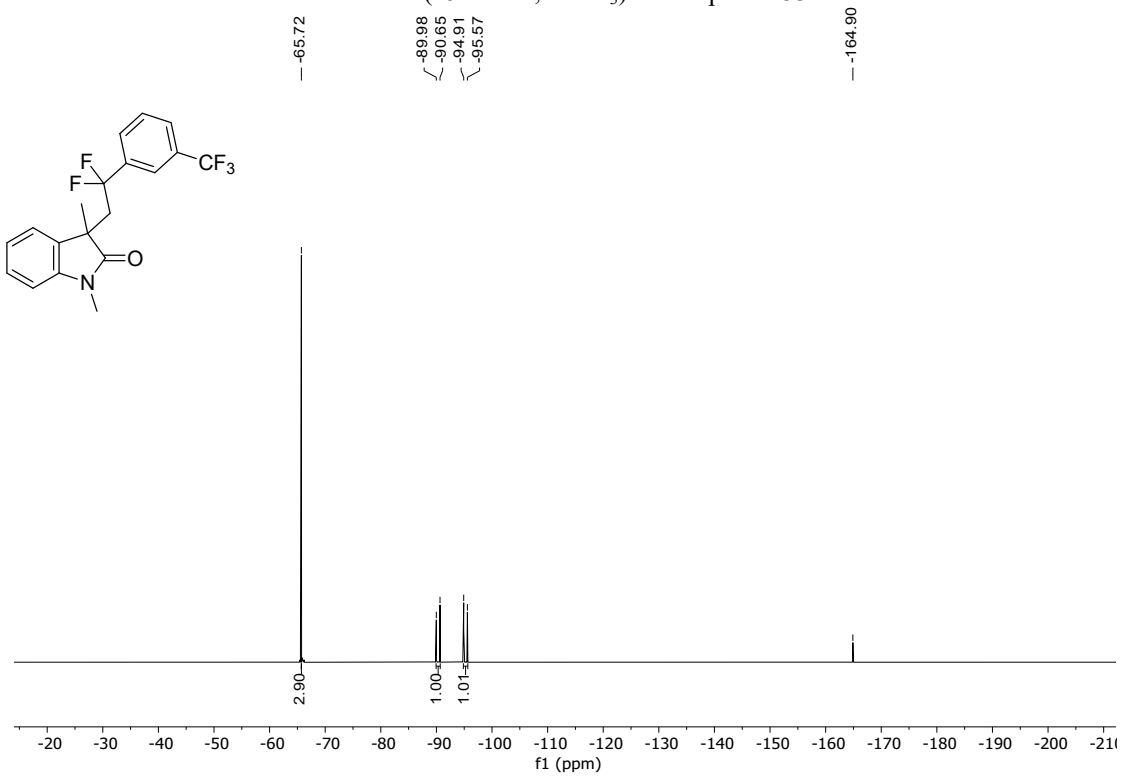


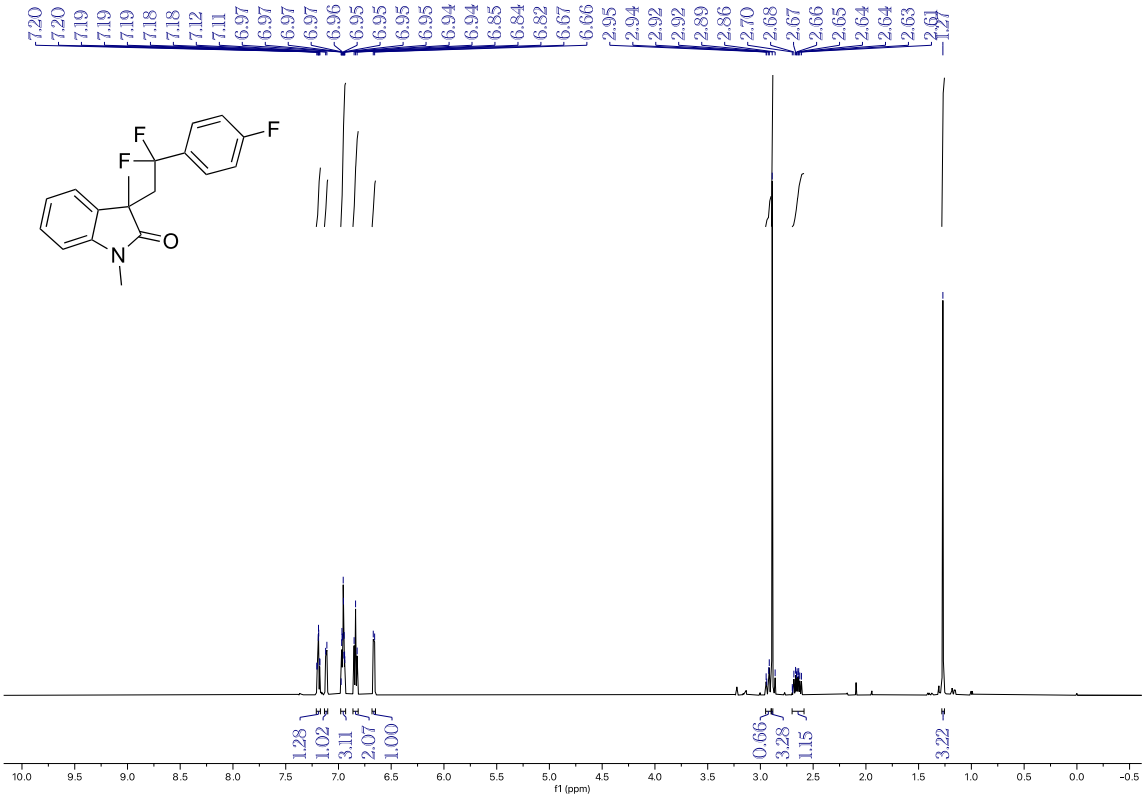
^{1}H NMR (600 MHz, $CDCl_3$) of compound **33.**



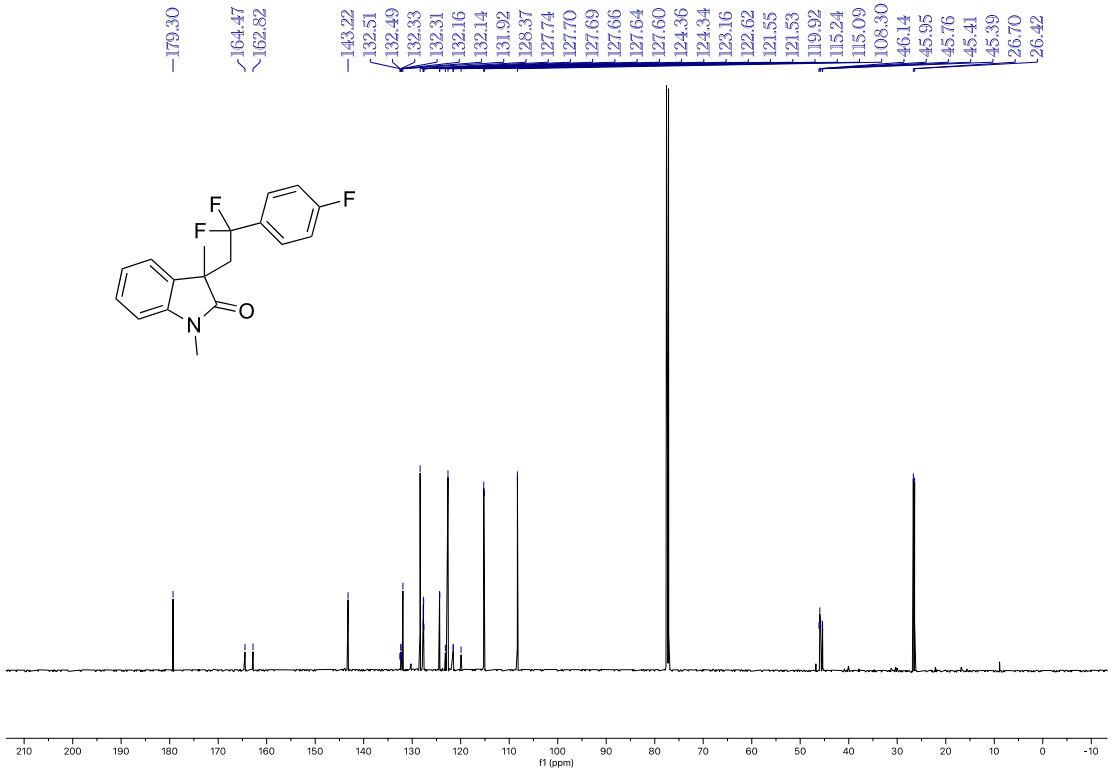
^{13}C NMR (151 MHz, $CDCl_3$) of compound **33**.



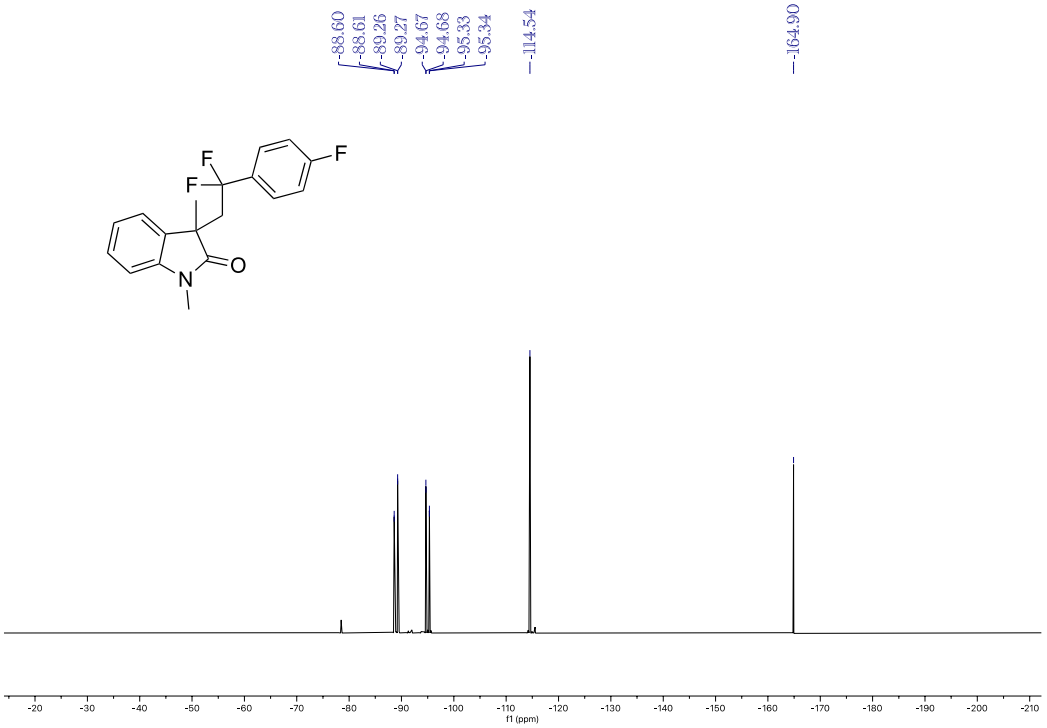
^{19}F NMR (376 MHz, $CDCl_3$) of compound **33**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).



^{1}H NMR (600 MHz, $CDCl_3$) of compound **34**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **34**.



^{19}F NMR (376 MHz, $CDCl_3$) of compound **34**. Spectra referenced to hexafluorobenzene (δ –164.9 ppm).

10. Density Functional Theory (DFT) Calculations

General Remarks

All optimizations of intermediates and transition states were calculated using unrestricted UB3LYP-D3/def2-SVP[4,5] level of theory, with the "guess=mix," "nosymm," and "empiricaldispersion=gd3"[6] keywords as implemented in Gaussian16 Revision C.01. These optimizations were performed using the CPCM implicit solvation model[7] with dimethyl sulfoxide (DMSO) as the solvent by using the "SCRF=(CPCM,solvent=DMSO) keyword. Frequency calculations (at the same level of theory) were used to obtain thermal corrections (at 298K) and to characterize all optimized structures as either transition states (containing only one imaginary frequency) or intermediates (containing no imaginary frequencies). In order to determine the excitation energy for the thiolate anion, Time-Dependent DFT (TD-DFT)[8] computations were employed. To this end, single point energies of the singlet state structure were calculated using the "td=(nstates=6)" keyword. To refine energetics and for method comparison, single point energy calculations were performed in implicit solvent (CPCM(DMSO), as above) using UωB97XD/def2-SVP[9] and UB3LYP-D3/def2-TZVPP[4,5] levels of theory. All 3-D structures were

generated using CYLview[10]. Exhaustive conformational searches were performed for all structures to elucidate the lowest energy profiles for each potential reaction pathway.

Minimum energy crossing point (MECP)[11] calculations were performed using the ORCA software[12]. Optimizations were performed in the gas phase with a triplet spin state at the UB3LYP-D3/def2-SVP level of theory using the "SurfCrossOpt," "SlowConv," "UNO," "UCO," and "D3" keywords to obtain the geometries of the MECPs. In the "%mecp" block, the keyword "Mult 1" was used to identify the crossing point between the triplet and singlet states. Frequency calculations were then performed using these optimized geometries at the UB3LYP-D3/def2-SVP level of theory with implicit solvent (CPCM(DMSO)) in order to obtain thermal corrections (at 298K). Energetics of the MECPs were then confirmed using single-point calculations using UωB97XD/def2-SVP[5] and UB3LYP-D3/def2-TZVPP[1,2] levels of theory with implicit solvent (CPCM(DMSO)) in Gaussian16.

Full Reference of Gaussian16 software:

Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Computational Analysis

We proposed that the mechanism for the benzenethiol promoted C-F activation discussed in the manuscript would initiate from defluorination of ethyl 2,2,2-trifluoroacetate (**2**). In order to accomplish this defluorination, we proposed the catalytic cycle shown in ***Figure S8*** below. In this reaction, the thiophenol (**I**) is deprotonated by the base ($KHCO_3$) to form a thiophenolate anion (**II**). This anion can then be excited (by purple-light irradiation) to an excited singlet state (**II***) before relaxation to the triplet anion **III**. The triplet state anion III can then undergo single-electron

transfer (SET) with ethyl 2,2,2-trifluoroacetate (**2**) to concurrently form **A•-** and the thiolate radical (**IV**). This SET process is exergonic (ΔG = -5.6 kcal/mol at UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO) level of theory) and will result in the formation of the radical anion species **A•-** which can undergo a spin-center shift to allow for defluorination (see *Figure S9* below). The thiolate radical **IV** is then able to undergo hydrogen atom transfer (HAT) with the sodium formate to reform **I**, which can then proceed through the catalytic cycle again, while a CO_2•- radical anion is also formed. The thiolate radical is also prone to undergo dimerization to form **V**, as this process is highly exergonic. From this dimer, SET with the CO_2•- radical anion species formed during the HAT process is highly exergonic and creates both **II**, which can continue the catalytic cycle, and **IV**, which can undergo HAT again and form **I**.

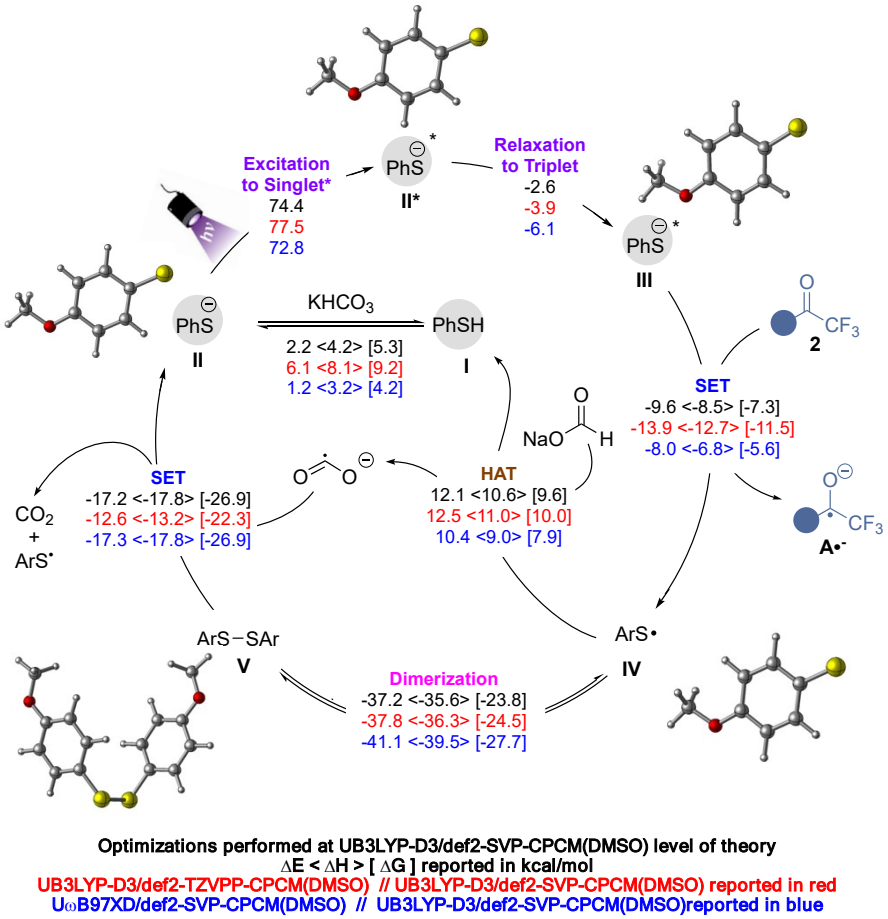


Figure S8. *Energetics of thiolate catalytic cycle. Optimizations performed at UB3LYP-D3/def2-SVP-CPCM(DMSO) level of theory, ΔE <ΔH in angle brackets> [ΔG in square brackets] for each relevant step reported in kcal/mol. Single point energies are also shown.*

The thiophenol-based catalytic cycle described herein can be exploited to form **A•⁻** via SET between **2** and **III** as described above. Once **A•⁻** is formed, it can undergo the mechanistic pathway outlined in ***Figure S9*** below. **A•⁻** can undergo a spin-center shift (SCS) to form the carbon centered radical **B•⁻**. Scans of the C-F bond suggest that this spin-center shift proceeds via a 1,2-F migration pathway where the fluorine is transferred to the carbonyl carbon to form **B•⁻** before being released as a fluoride anion. This migration pathway via **TS-A-B** is energetically feasible and reversible ($\Delta G^{\ddagger}$ = 13.3 kcal/mol). Even though the process to form the carbon-centered radical **C•** is endergonic (ΔG = 6.1 kcal/mol), following Giese addition step (**TS-C-D**) is highly exergonic (ΔG = -23.0 kcal/mol) with a relatively low energy barrier ($\Delta G^{\ddagger}$ = 10.5 kcal/mol), so the SCS process is reasonable. Following radical addition of **C•** to the alkene (*N*-arylmethacrylamide, **1**) to form **D•**, ring closure can proceed via **TS-D-E** to form the closed ring radical species **E•**. Subsequently, numerous radical species in solution, including intermediates **A•⁻**, **C•**, and the radical anion $CO_2^{\bullet-}$, can be used to perform HAT with **E•** to yield the oxindole product **3**. A comparison of the energetics for these pathways can be seen in ***Figure S9*** below. This HAT will proceed through a MECP (**MECP-E-3**) to form the product **3** irreversibly. This process is extremely exergonic (ΔG = -67.9 kcal/mol) with a very low energy barrier ($\Delta G^{\ddagger}$ = 5.6 kcal/mol).

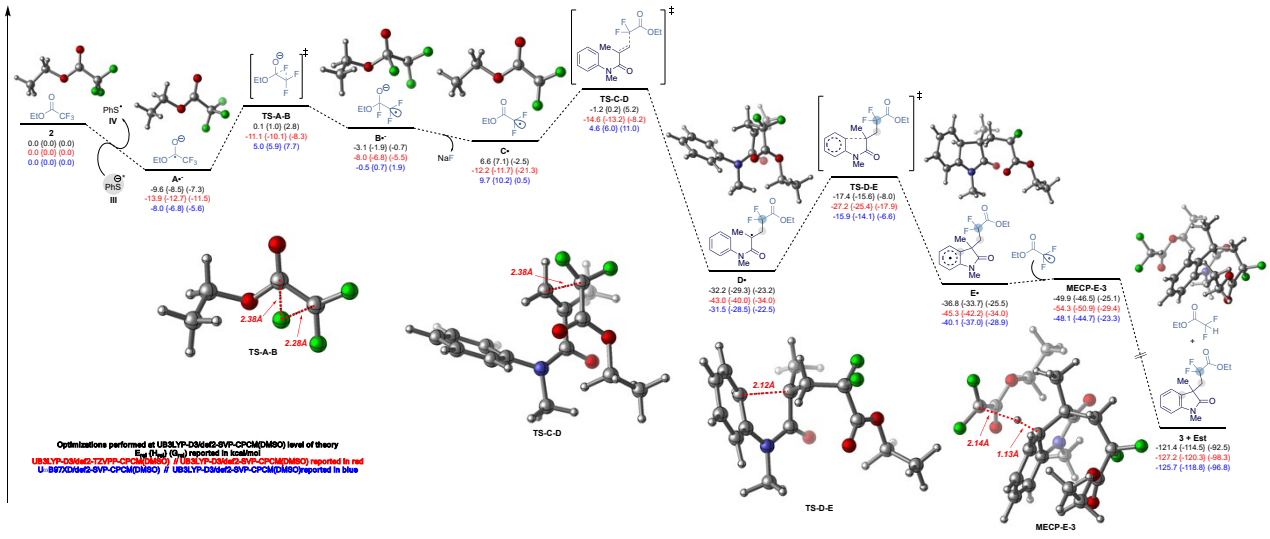


Figure S9. *Potential energy surface for C-F activation to form difluorinated-oxindole derivatives. Optimizations performed at UB3LYP-D3/def2-SVP-CPCM(DMSO) level of theory, E_{rel} {H_{rel} in braces} (G_{rel} in parenthesis) for each relevant step reported in kcal/mol. Single point energies are also shown.*

Each of these potential HAT pathways can proceed either in the triplet state (via **TS-E-3***) before relaxation to the singlet, or via a MECP to cross between the triplet and singlet states during the

HAT process. These MECPs are significantly lower in energy than the corresponding triplet state transition states, suggesting that the pathways through the MECPs are more feasible. We propose that HAT with intermediate **C•** is the most likely pathway. The products of this MECP (**3** + **Est**) are significantly lower in energy than the alternatives for intermediate **A•**$^{-}$ and CO_2•$^{-}$. Experimental evidence also suggests that ethyl 2,2-difluoroacetate, which is formed concurrently with product **3,** is observed over the course of the reaction, further supporting HAT with intermediate **C•** as a major pathway for HAT.

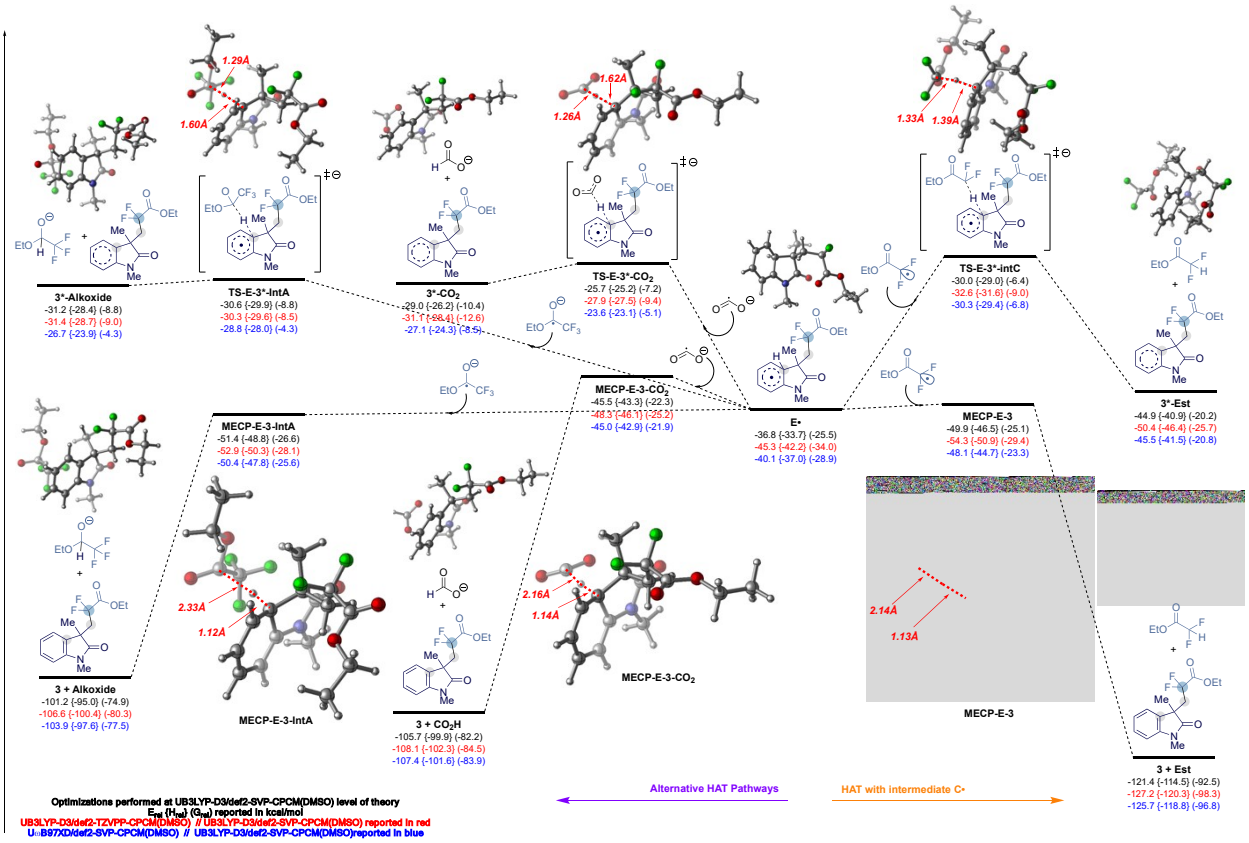


Figure S10. *Comparison of energetics for potential radical HAT pathways. Optimizations performed at UB3LYP-D3/def2-SVP-CPCM(DMSO) level of theory,* E_{rel} *{*H_{rel} *in braces} (*G_{rel} *in parenthesis) for each relevant step reported in kcal/mol. Single point energies are also shown.*

It is also possible that the HAT could proceed via a carbocation pathway. In this case, the thiol radical **IV** could undergo SET to form the thiolate anion **II** and the carbocation **F**. From here, deprotonation with base can rapidly yield the desired product. The energetics of such pathways are shown in ***Figure S11*** below. While this pathway is slightly less energetically favorable than the radical HAT pathways described above, the reaction is still energetically feasible and the rearomatization process is irreversible.

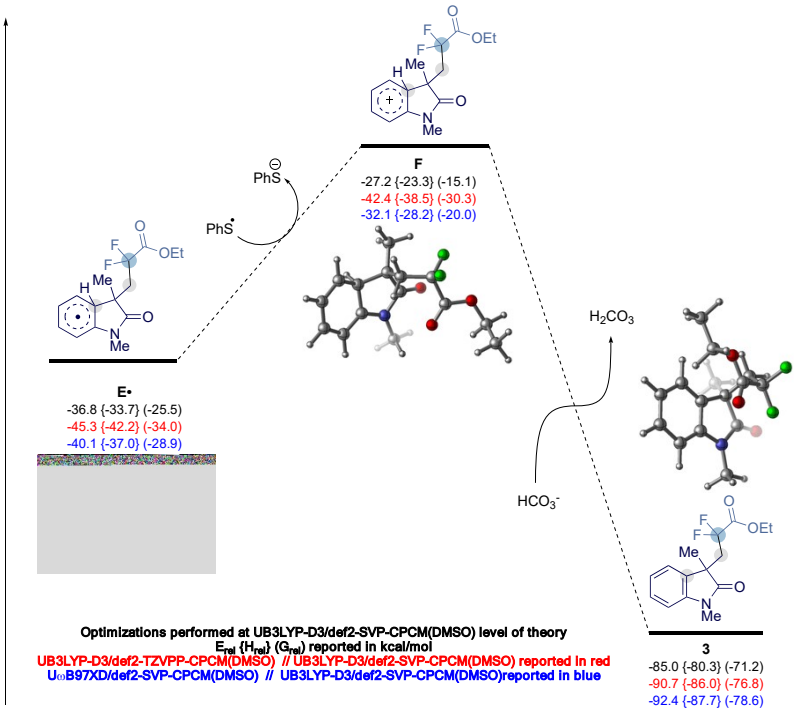
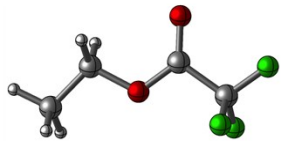


Figure S11. *Energetics for polar HAT pathway. Optimizations performed at UB3LYP-D3/def2-SVP-CPCM(DMSO) level of theory, E_{rel} {H_{rel} in braces} (G_{rel} in parenthesis) for each relevant step reported in kcal/mol. Single point energies are also shown.*

11. Coordinates and Energies

2



Zero-point correction= 0.095012 (Hartree/Particle)

Thermal correction to Energy= 0.104217

Thermal correction to Enthalpy= 0.105161

Thermal correction to Gibbs Free Energy= 0.058725

Sum of electronic and zero-point Energies= -604.882779

Sum of electronic and thermal Energies= -604.873574

Sum of electronic and thermal Enthalpies= -604.872629

Sum of electronic and thermal Free Energies= -604.919065

C	-1.06225900	0.49809000	0.00181400	C	-1.95999800	-3.01666100	0.00236700
O	0.13254300	0.63209200	0.00762100	H	-1.40954300	-3.96953300	0.00393800
O	-1.74224200	-0.63147200	-0.00179800	H	-2.60057800	-2.98339200	0.89662100
C	-2.04483300	1.69556700	-0.00374100	H	-2.60004600	-2.98605100	-0.89236100
C	-0.97738200	-1.86902400	0.00100700	F	-1.37478400	2.84597300	0.00601200
H	-0.33009800	-1.86847100	0.89162100	F	-2.81980700	1.66349900	-1.09637900
H	-0.32904200	-1.87155400	-0.88887100	F	-2.84112300	1.65741800	1.07312300

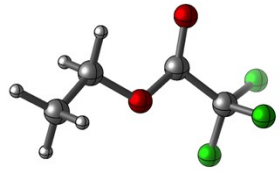
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -605.7000313

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -604.7964875

A•-



Zero-point correction= 0.091431 (Hartree/Particle)

Thermal correction to Energy= 0.100856

Thermal correction to Enthalpy= 0.101800

Thermal correction to Gibbs Free Energy= 0.054908

Sum of electronic and zero-point Energies= -604.944204

Sum of electronic and thermal Energies= -604.934779

Sum of electronic and thermal Enthalpies= -604.933835

Sum of electronic and thermal Free Energies= -604.980727

C	-0.98763700	0.54110500	0.05531800	C	-1.00775000	-1.84717100	0.09913700
O	0.06970000	0.62083600	-0.65341900	H	-0.41770700	-1.89846500	1.04214500
O	-1.77088500	-0.66664300	0.06060800	H	-0.26869100	-1.85777300	-0.72408800
C	-1.95651200	1.67575500	0.05965400	C	-1.94412200	-3.03947000	-0.00191900

H	-1.38014600	-3.98569800	0.02787300	F	-1.32892800	2.85700400	0.27989900
H	-2.66729000	-3.04011000	0.82994500	F	-2.65313400	1.87684900	-1.12890600
H	-2.51348800	-3.00323800	-0.94499300	F	-2.92991800	1.56350000	0.99972000

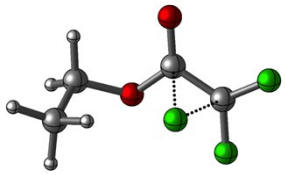
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -605.7739675

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -604.8526834

TS-A-B



Zero-point correction= 0.090957 (Hartree/Particle)

Thermal correction to Energy= 0.100424

Thermal correction to Enthalpy= 0.101368

Thermal correction to Gibbs Free Energy= 0.055444

Sum of electronic and zero-point Energies= -604.929217

Sum of electronic and thermal Energies= -604.919750

Sum of electronic and thermal Enthalpies= -604.918806

Sum of electronic and thermal Free Energies= -604.964730

C	-0.97637300	0.49528700	0.09732300	C	-1.96377000	-2.51224200	-0.30838200
O	-0.07927500	0.64238700	-0.72192700	H	-1.67571900	-3.41053700	-0.87928600
O	-1.11933700	-0.59917200	0.89801700	H	-2.68976700	-2.81239400	0.46546500
C	-1.92833200	1.50305600	0.43998200	H	-2.44752500	-1.76299800	-0.95687100
C	-0.74274200	-1.86184200	0.32838000	F	-1.97599400	2.65440300	-0.20461700
H	-0.33038800	-2.46331300	1.15402300	F	-2.95983700	0.28334300	-1.19162000
H	0.05822900	-1.70115600	-0.40960500	F	-2.92567600	1.34165900	1.29009100

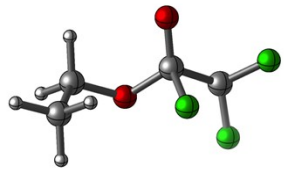
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -605.7694438

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -604.8320015

B•$^-$



Zero-point correction= 0.091330 (Hartree/Particle)

Thermal correction to Energy= 0.100878

Thermal correction to Enthalpy= 0.101822

Thermal correction to Gibbs Free Energy= 0.054967

Sum of electronic and zero-point Energies= -604.933886

Sum of electronic and thermal Energies= -604.924338

Sum of electronic and thermal Enthalpies= -604.923394

Sum of electronic and thermal Free Energies= -604.970249

C	-1.35342400	0.45587800	-0.14363300	C	-1.87596500	-2.64419300	-0.39722700
O	-0.44887200	0.55205600	-0.99094800	H	-1.46536000	-3.61914000	-0.70923100
O	-1.32433500	-0.58854300	0.81677200	H	-2.75119400	-2.82456000	0.24835400
C	-1.72091500	1.70888600	0.65015500	H	-2.22134100	-2.09062500	-1.28086400
C	-0.82211400	-1.82842700	0.34606900	F	-1.80383100	2.82555600	-0.08302100
H	-0.47194100	-2.37471200	1.23847300	F	-2.76853400	0.21229800	-0.84692100
H	0.04962400	-1.64893200	-0.30681200	F	-2.77200600	1.64833800	1.47870700

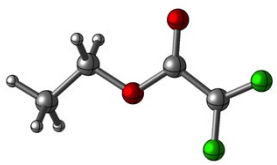
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -605.7645067

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -604.8407847

C•



Zero-point correction= 0.089757 (Hartree/Particle)

Thermal correction to Energy= 0.098566

Thermal correction to Enthalpy= 0.099510

Thermal correction to Gibbs Free Energy= 0.054431

Sum of electronic and zero-point Energies= -505.056123

Sum of electronic and thermal Energies= -505.047314

Sum of electronic and thermal Enthalpies= -505.046370

Sum of electronic and thermal Free Energies= -505.091448

C	-1.12302600	0.51266400	0.01505800	C	-1.94731600	-3.02961900	-0.00041200
O	0.08811500	0.63907600	0.00551400	H	-1.37308100	-3.96843900	-0.00934700
O	-1.79332300	-0.64590000	0.00816200	H	-2.58199500	-3.01839800	0.89888500
C	-2.03070700	1.64470200	0.08805600	H	-2.59708100	-3.01076300	-0.88875000
C	-0.99767200	-1.85215800	-0.00357900	F	-1.57994200	2.86701800	-0.03115900
H	-0.33834500	-1.84792100	0.87959200	F	-3.32769400	1.54289100	-0.06346600
H	-0.35342500	-1.84151700	-0.89758000				

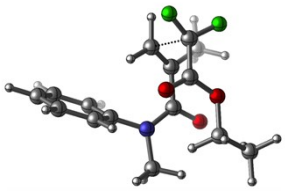
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -505.7471489

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -504.9872887

TS-C-D



Zero-point correction= 0.307244 (Hartree/Particle)

Thermal correction to Energy= 0.329110

Thermal correction to Enthalpy= 0.330055

Thermal correction to Gibbs Free Energy= 0.254285

Sum of electronic and zero-point Energies= -1061.443596

Sum of electronic and thermal Energies= -1061.421730

Sum of electronic and thermal Enthalpies= -1061.420785

Sum of electronic and thermal Free Energies= -1061.496555

C	0.85305500	0.51257900	0.55367800	H	0.55508600	-0.39858000	-2.24084700
C	1.84639700	0.50824100	-0.43415600	H	-0.57529000	-1.83197700	-2.55196100
C	1.95801400	1.58783500	-1.32202900	C	0.76820000	-3.73500300	-1.18469000
C	1.06732300	2.66011700	-1.22731800	H	1.52891800	-4.35602800	-1.68545900
C	0.06290400	2.65829400	-0.25166500	H	0.77230600	-4.03599400	-0.12473600
C	-0.04278600	1.58253000	0.63679800	H	-0.21532100	-3.96100000	-1.61914700
H	0.78232500	-0.32965900	1.24532800	C	2.53807000	-1.09357400	-4.17696600
H	2.71620100	1.55683500	-2.10703900	O	2.70143100	0.10345500	-4.30932500
H	1.15002100	3.49507900	-1.92739400	O	3.45192300	-1.96932300	-3.75985600
H	-0.63644900	3.49512100	-0.18410600	C	1.22708600	-1.74259500	-4.33490900
H	-0.82211900	1.57767800	1.40281200	C	4.76287500	-1.44725500	-3.43716100
N	2.77511900	-0.57908100	-0.52057300	H	4.64003300	-0.62957500	-2.71163700
C	4.10786400	-0.30718300	0.02561000	H	5.20211500	-1.01914600	-4.35225000
H	4.42135200	0.70005300	-0.27803500	C	5.58326700	-2.58841300	-2.87914300
H	4.10269800	-0.35833200	1.12851200	H	6.58507600	-2.22302200	-2.60631200
H	4.82469400	-1.04518700	-0.35064900	H	5.09798900	-2.99927900	-1.98193000
C	2.42377600	-1.90103200	-0.70463400	H	5.69709900	-3.39014100	-3.62486100
O	3.20895100	-2.79990000	-0.39740100	F	0.30535000	-1.09433200	-5.02007400
C	1.11084200	-2.27872300	-1.33746200	F	1.15080700	-3.04924800	-4.50319000
C	0.36873800	-1.46546800	-2.14003300				

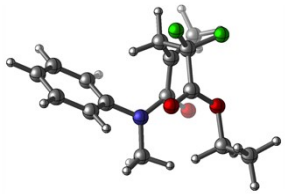
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1062.9623091

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1061.3881983

D•



Zero-point correction= 0.310329 (Hartree/Particle)

Thermal correction to Energy= 0.331637

Thermal correction to Enthalpy= 0.332581

Thermal correction to Gibbs Free Energy= 0.258477

Sum of electronic and zero-point Energies= -1061.490013

Sum of electronic and thermal Energies= -1061.468705

Sum of electronic and thermal Enthalpies= -1061.467761

Sum of electronic and thermal Free Energies= -1061.541865

C	0.76321300	0.40463500	0.41071700	H	0.51173400	-0.35873100	-2.23818600
C	1.81916700	0.53335500	-0.50399200	H	-0.50958800	-1.76488900	-2.58048800
C	1.92461500	1.69242400	-1.28885400	C	0.77758700	-3.66571300	-1.23771900
C	0.97180300	2.70565000	-1.16615600	H	1.03150900	-4.24418400	-2.14674200
C	-0.09498100	2.56825400	-0.26875100	H	1.26028400	-4.15034100	-0.38031600
C	-0.19758800	1.41511600	0.51591700	H	-0.31933600	-3.72448700	-1.13348000
H	0.69654300	-0.49085300	1.03221400	C	2.60777200	-1.02770000	-3.90304900
H	2.73254800	1.77077000	-2.01840100	O	2.86307800	0.13152700	-4.11638000
H	1.05383500	3.60155600	-1.78641200	O	3.47402600	-1.98368200	-3.61483000
H	-0.84360900	3.35928400	-0.18192000	C	1.15961500	-1.56177400	-3.84926000
H	-1.02328200	1.30343800	1.22289200	C	4.87333100	-1.61602600	-3.49509200
N	2.79765400	-0.50025200	-0.62954400	H	4.93772300	-0.70253200	-2.88568300
C	4.13453900	-0.18556900	-0.12104700	H	5.25064100	-1.37672900	-4.50162100
H	4.40480800	0.83411200	-0.42304000	C	5.59443200	-2.78528000	-2.86353100
H	4.16899300	-0.25153700	0.98048500	H	6.65735500	-2.53418600	-2.72806800
H	4.86571800	-0.89306200	-0.52815700	H	5.15249900	-3.01716400	-1.88310700
C	2.45983500	-1.84610800	-0.71045300	H	5.52688800	-3.67872300	-3.50282500
O	3.23680000	-2.70707400	-0.28189200	F	0.41573300	-0.83907500	-4.72964100
C	1.21576000	-2.24860300	-1.39566100	F	1.12547900	-2.85975800	-4.26876200
C	0.53330700	-1.43232500	-2.45737600				

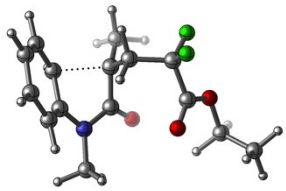
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1063.007626

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1061.4457544

TS-D-E



Zero-point correction= 0.309343 (Hartree/Particle)

Thermal correction to Energy= 0.329795

Thermal correction to Enthalpy= 0.330739

Thermal correction to Gibbs Free Energy= 0.258981

Sum of electronic and zero-point Energies= -1061.467282

Sum of electronic and thermal Energies= -1061.446829

Sum of electronic and thermal Enthalpies= -1061.445885

Sum of electronic and thermal Free Energies= -1061.517644

C	0.93782000	-1.14096400	1.18979800	N	2.92200300	-0.55095800	0.04993400
C	1.76489200	-0.07519100	0.68682100	C	4.11110100	0.25595900	-0.15796300
C	1.31525900	1.23639000	0.63504900	H	4.93657000	-0.41103800	-0.43527300
C	0.00308600	1.53053900	1.05815300	H	3.95761300	0.98517600	-0.97138000
C	-0.85223300	0.49936400	1.48474600	H	4.36519700	0.79400900	0.76565500
C	-0.39455200	-0.81354100	1.57691100	C	2.74832500	-1.76065800	-0.59562800
H	1.42563800	-1.97856700	1.69848700	O	3.65784900	-2.37904400	-1.13412300
H	1.95264400	2.02116300	0.22304900	C	1.30867400	-2.22709800	-0.58761100
H	-0.35689000	2.56107900	1.02176600	C	0.38724900	-1.53194200	-1.56961200
H	-1.87356700	0.73896900	1.79184500	H	0.52456000	-0.44133800	-1.53523600
H	-1.03742100	-1.59425000	1.99041300	H	-0.66314700	-1.74809800	-1.31641900

C	1.11579700	-3.70256900	-0.38533700	H	4.39585400	-3.56461900	-4.34934500
H	1.48427400	-4.26688000	-1.25930300	H	4.49718700	-1.94804000	-3.59420500
H	1.66889100	-4.06160900	0.49687700	C	4.17021800	-1.91683900	-5.75512800
H	0.04950200	-3.94433700	-0.25692700	H	5.23827600	-1.89557300	-6.02224500
C	1.98992300	-1.61864700	-3.54353600	H	3.63452400	-2.50356600	-6.51706900
O	2.44024700	-0.50018300	-3.45323900	H	3.78941500	-0.88546200	-5.76532400
O	2.60669100	-2.68162700	-4.02099400	F	-0.30468400	-1.20223200	-3.79637400
C	0.56723000	-1.92917600	-3.02936500	F	0.25069800	-3.23967700	-3.21996900
C	4.00739600	-2.53826300	-4.38127600				

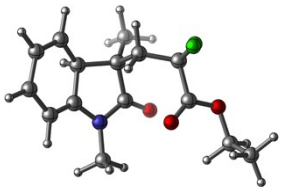
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1062.9825259

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1061.4209749

E•



Zero-point correction= 0.311631 (Hartree/Particle)

Thermal correction to Energy= 0.331880

Thermal correction to Enthalpy= 0.332824

Thermal correction to Gibbs Free Energy= 0.261991

Sum of electronic and zero-point Energies= -1061.495942

Sum of electronic and thermal Energies= -1061.475692

Sum of electronic and thermal Enthalpies= -1061.474748

Sum of electronic and thermal Free Energies= -1061.545582

C	0.79232500	-1.15342800	0.83947800	H	0.37373900	-0.72065700	-1.69313000
C	1.79459900	-0.06185500	0.57551800	H	-0.68945100	-2.11719400	-1.45644600
C	1.56083700	1.26442100	0.82980300	C	0.88774300	-3.64846400	0.14251900
C	0.25472200	1.65672000	1.23364200	H	1.27646300	-4.33668600	-0.61821500
C	-0.80700900	0.70722600	1.26031000	H	1.39156700	-3.86694400	1.09643800
C	-0.59969800	-0.62728900	1.01289100	H	-0.18920100	-3.83871300	0.26902100
H	1.09524100	-1.64502400	1.79411100	C	2.17113900	-1.79828500	-3.39522100
H	2.33955500	2.01310200	0.66976700	O	2.46220500	-0.64218800	-3.19225300
H	0.04946600	2.70727100	1.44836700	O	2.87428700	-2.67461300	-4.08619800
H	-1.81975700	1.06106900	1.47425600	C	0.83375200	-2.38740800	-2.88726100
H	-1.42798800	-1.33987800	1.03968100	C	4.16177000	-2.24382400	-4.60155800
N	2.90995200	-0.65137300	-0.00477200	H	4.71791700	-3.17856200	-4.75098900
C	4.15053900	0.04273700	-0.28581300	H	4.66200600	-1.64886600	-3.82350000
H	4.87107500	-0.68710400	-0.67415300	C	4.00913200	-1.46583800	-5.89482200
H	3.98512300	0.82542000	-1.04321300	H	5.00505400	-1.22037500	-6.29514700
H	4.54618800	0.50388800	0.63092000	H	3.46959100	-2.06105100	-6.64727800
C	2.63428200	-1.91846100	-0.47343600	H	3.46311500	-0.52697200	-5.72301100
O	3.43334400	-2.66023700	-1.02040500	F	-0.09470400	-2.05112800	-3.84625100
C	1.13005900	-2.19789200	-0.27073600	F	0.88040500	-3.74697500	-2.86633600
C	0.36192900	-1.81230900	-1.56435400				

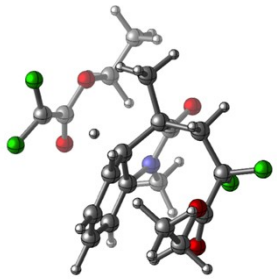
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1063.0112537

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1061.4594913

MECP-E-3



Zero-point correction= 0.401729 (Hartree/Particle)

Thermal correction to Energy= 0.431867

Thermal correction to Enthalpy= 0.432812

Thermal correction to Gibbs Free Energy= 0.338146

Sum of electronic and zero-point Energies= -1566.572703

Sum of electronic and thermal Energies= -1566.542564

Sum of electronic and thermal Enthalpies= -1566.541620

Sum of electronic and thermal Free Energies= -1566.636286

C	4.803973000	-0.844278000	-0.371083000	O	5.463672000	2.049424000	-2.009894000
C	3.881033000	0.998278000	1.035403000	O	3.747461000	3.228763000	-1.137499000
C	5.175434000	1.308325000	1.370678000	C	4.647505000	4.178917000	-0.513679000
C	6.277810000	0.537887000	0.905121000	H	5.063300000	4.817631000	-1.308167000
C	6.089167000	-0.519570000	-0.016394000	H	5.473881000	3.619027000	-0.055848000
H	3.043274000	1.597824000	1.396810000	C	3.857703000	4.968889000	0.502119000
H	5.375034000	2.182677000	1.995569000	H	4.513534000	5.715855000	0.974510000
H	7.290420000	0.815395000	1.202943000	H	3.016918000	5.496584000	0.026855000
H	6.945498000	-1.017051000	-0.473331000	H	3.459844000	4.309699000	1.288489000
N	4.359376000	-1.724441000	-1.338349000	F	3.789268000	0.418461000	-3.223185000
C	5.235469000	-2.568840000	-2.125205000	F	2.539750000	2.211340000	-3.356481000
H	5.742734000	-3.291326000	-1.470585000	C	3.605519000	-0.276373000	0.319469000
H	4.623041000	-3.101494000	-2.861956000	H	3.375355000	-1.033069000	1.124665000
H	5.982406000	-1.951866000	-2.648041000	C	3.840375000	-3.741212000	1.216081000
C	3.004078000	-1.593371000	-1.586700000	O	4.945833000	-4.066889000	0.816400000
O	2.372832000	-2.253910000	-2.390752000	O	2.672129000	-4.110044000	0.677212000
C	2.447422000	-0.461429000	-0.696899000	C	3.638148000	-2.799581000	2.303380000
C	1.145815000	-0.914439000	-0.024744000	C	2.719285000	-5.022128000	-0.445041000
H	0.769571000	-0.125793000	0.644165000	H	3.127832000	-5.981488000	-0.090309000
H	0.378533000	-1.127628000	-0.782342000	H	3.407136000	-4.617270000	-1.199664000
H	1.310235000	-1.826940000	0.564617000	C	1.315504000	-5.161286000	-0.985307000
C	2.115932000	0.772171000	-1.569389000	H	1.316209000	-5.881534000	-1.817812000
H	1.729544000	1.577980000	-0.930110000	H	0.627943000	-5.528029000	-0.207832000
H	1.304642000	0.482741000	-2.254261000	H	0.953718000	-4.194465000	-1.363273000
C	3.179649000	1.376580000	-2.470801000	F	4.662622000	-2.444088000	3.046894000
C	4.288212000	2.238013000	-1.828072000	F	2.485168000	-2.706144000	2.937733000

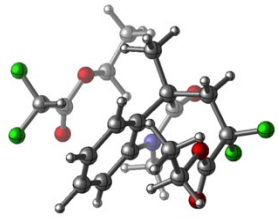
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1568.7728033

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1566.4595704

3 + Est



Zero-point correction= 0.407353 (Hartree/Particle)

Thermal correction to Energy= 0.437476

Thermal correction to Enthalpy= 0.438420

Thermal correction to Gibbs Free Energy= 0.344607

Sum of electronic and zero-point Energies= -1566.681024

Sum of electronic and thermal Energies= -1566.650901

Sum of electronic and thermal Enthalpies= -1566.649957

Sum of electronic and thermal Free Energies= -1566.743770

C	4.72371400	-0.83164400	-0.49735600		O	5.36209700	2.06908600	-2.13477900
C	3.78148500	0.86832200	0.94786900		O	3.63000500	3.18152400	-1.20921700
C	5.02275400	0.95620700	1.60314900		C	4.52399500	4.01877900	-0.43092000
C	6.09466300	0.15361800	1.19592900		H	5.10672100	4.63958000	-1.12947600
C	5.96124400	-0.75864000	0.13772300		H	5.22350700	3.36246500	0.10800100
H	2.94405900	1.49553900	1.26101400		C	3.67690400	4.84745200	0.50684900
H	5.14796200	1.65155800	2.43569300		H	4.32526100	5.50796600	1.10214000
H	7.05165300	0.22558300	1.71763800		H	2.96456400	5.47174300	-0.05362600
H	6.79099400	-1.40025000	-0.16019100		H	3.11215100	4.20226300	1.19705600
N	4.33194700	-1.68670400	-1.53647900		F	3.70661400	0.56292900	-3.53576400
C	5.22296500	-2.59032400	-2.23543900		F	2.47402800	2.37602400	-3.58690200
H	5.64025400	-3.33573700	-1.54283200		C	3.64128600	-0.02153400	-0.10943900
H	4.64321400	-3.09959300	-3.01546900		H	3.87146900	-1.61132800	2.08997100
H	6.04558400	-2.02671600	-2.70354100		C	4.16748600	-3.60026500	1.19478300
C	3.00457600	-1.50211000	-1.85930300		O	5.15327100	-4.13417700	0.75242300
O	2.37597700	-2.14395000	-2.68032300		O	2.93091300	-3.74238800	0.73825700
C	2.45149600	-0.34665600	-0.98769200		C	4.18146900	-2.62617700	2.38750300
C	1.23599200	-0.84141100	-0.18344700		C	2.71995500	-4.69340000	-0.34318300
H	0.85350200	-0.03436100	0.45910300		H	3.07659700	-5.67674800	-0.00042400
H	0.43423700	-1.15775700	-0.86727300		H	3.33487600	-4.38584300	-1.20009500
H	1.51163500	-1.69532300	0.44989000		C	1.24833900	-4.69721600	-0.68472900
C	2.00689900	0.82065100	-1.89963600		H	1.05974100	-5.45786900	-1.45751800
H	1.54362900	1.61015700	-1.29135200		H	0.63930800	-4.94068600	0.19895500
H	1.25028100	0.44857300	-2.60789900		H	0.93914000	-3.72113900	-1.08341900
C	3.08309100	1.48118000	-2.74606500		F	5.42804300	-2.58005100	2.90464000
C	4.18301200	2.26484700	-1.99011800		F	3.33188700	-3.08396400	3.34632800

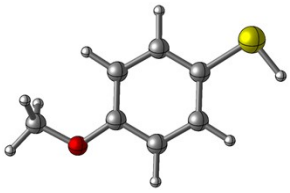
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1568.8889485

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1566.5832335

I



Zero-point correction= 0.131695 (Hartree/Particle)

Thermal correction to Energy= 0.140573

Thermal correction to Enthalpy= 0.141517

Thermal correction to Gibbs Free Energy= 0.097239

Sum of electronic and zero-point Energies= -744.487926

Sum of electronic and thermal Energies= -744.479049

Sum of electronic and thermal Enthalpies= -744.478104

Sum of electronic and thermal Free Energies= -744.522382

C	-2.56670100	-0.03507900	0.28963600		H	-4.12366000	1.26799600	-0.42784300
C	-1.18960600	-0.16892700	0.52709900		S	0.37266200	3.39273700	-0.65574600
C	-0.32182200	0.88882700	0.23177800		H	-0.51582400	4.30889300	-1.10014000
C	-0.80247300	2.09222000	-0.30291900		O	-3.49231200	-0.99648500	0.53981700
C	-2.18370900	2.22021900	-0.53923900		C	-3.07024000	-2.23682700	1.07762400
C	-3.05104300	1.17145800	-0.24598100		H	-2.58996200	-2.11268300	2.06448400
H	-0.77527900	-1.08778300	0.94171900		H	-3.97297500	-2.85063900	1.19498100
H	0.74665500	0.76233900	0.42619900		H	-2.36756300	-2.75740200	0.40288900
H	-2.58883200	3.14567000	-0.95584400					

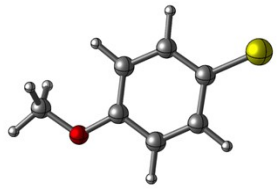
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -745.1455532

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -744.4747876

II



Zero-point correction= 0.122424 (Hartree/Particle)

Thermal correction to Energy= 0.130459

Thermal correction to Enthalpy= 0.131403

Thermal correction to Gibbs Free Energy= 0.089120

Sum of electronic and zero-point Energies= -744.015707

Sum of electronic and thermal Energies= -744.007672

Sum of electronic and thermal Enthalpies= -744.006728

Sum of electronic and thermal Free Energies= -744.049012

C	-1.95155400	-0.41564300	0.31955500		H	-2.84781400	2.87753300	0.36340200
C	-0.64410600	-0.25818500	-0.17144800		H	-3.75720700	0.65806600	0.88573600
C	-0.13910400	1.00664900	-0.46511700		S	-0.25665800	3.78904300	-0.66274100
C	-0.90192700	2.19594800	-0.28876100		O	-2.35908700	-1.69974000	0.57939700
C	-2.21507800	1.99851700	0.20797100		C	-3.66382300	-1.90710400	1.07240600
C	-2.73627800	0.73185000	0.50694900		H	-4.43662400	-1.55158900	0.36530200
H	-0.03281900	-1.15359400	-0.31715300		H	-3.78393800	-2.99066100	1.21126800
H	0.88214400	1.09812500	-0.84673900		H	-3.82583400	-1.40430700	2.04427100

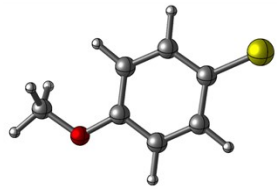
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -744.6745878

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -743.994557

II*



UB3LYP-D3/def2-SVP-CPCM(DMSO)

Excitation energies and oscillator strengths:

Excited State 1: 3.000-?Sym 2.8303 eV 438.06 nm f=0.0000 <S**2>=2.000

37A -> 38A 0.69116

37B -> 38B -0.69116

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -744.034119982

UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

Excited State 1: 3.000-?Sym 2.9628 eV 418.47 nm f=0.0000 <S**2>=2.000

35A -> 38A 0.11311

37A -> 38A 0.66766

37A -> 39A -0.18869

35B -> 38B -0.11311

37B -> 38B -0.66766

37B -> 39B 0.18869

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -744.565707516

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

Excited State 1: 3.000-?Sym 3.1032 eV 399.54 nm f=0.0000 <S**2>=2.000

34A -> 38A 0.15400

35A -> 38A 0.16864

35A -> 39A -0.11936

37A -> 38A -0.45560

37A -> 39A 0.46933

34B -> 38B -0.15400

35B -> 38B -0.16864

35B -> 39B 0.11936

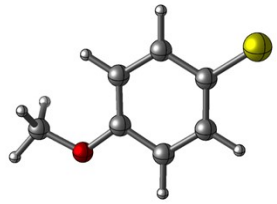
37B -> 38B 0.45560

37B -> 39B -0.46933

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -743.880518206

III



Zero-point correction= 0.117055 (Hartree/Particle)

Thermal correction to Energy= 0.126131

Thermal correction to Enthalpy= 0.127075

Thermal correction to Gibbs Free Energy= 0.081874

Sum of electronic and zero-point Energies= -743.921281

Sum of electronic and thermal Energies= -743.912205

Sum of electronic and thermal Enthalpies= -743.911261

Sum of electronic and thermal Free Energies= -743.956462

C	-1.97948400	-0.38539600	0.32329100	H	-2.83236800	2.94041400	0.39894800
C	-0.61439800	-0.28825200	-0.18637400	H	-3.78332200	0.64063600	0.91152000
C	-0.09962000	1.00154500	-0.47789800	S	-0.25796700	3.74632800	-0.63568400
C	-0.85555700	2.16763500	-0.28460500	O	-2.37634400	-1.66447300	0.56084800
C	-2.23574300	2.04106600	0.24325600	C	-3.67851000	-1.90514900	1.05511000
C	-2.76481600	0.73345800	0.53105700	H	-4.45267100	-1.54194100	0.35521900
H	-0.03947800	-1.20386600	-0.32914000	H	-3.77941900	-2.99282400	1.17208000
H	0.91835300	1.10425700	-0.86759300	H	-3.83836300	-1.41853000	2.03426300

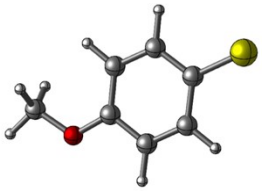
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -744.5718713

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -743.8903174

IV



Zero-point correction= 0.123354 (Hartree/Particle)

Thermal correction to Energy= 0.131388

Thermal correction to Enthalpy= 0.132332

Thermal correction to Gibbs Free Energy= 0.089507

Sum of electronic and zero-point Energies= -743.872507

Sum of electronic and thermal Energies= -743.864473

Sum of electronic and thermal Enthalpies= -743.863529

Sum of electronic and thermal Free Energies= -743.906355

C	-2.59188700	-0.03291000	0.30740100	C	-0.88928000	2.16689100	-0.25622200
C	-1.20011600	-0.14165100	0.52926800	C	-2.30075600	2.24751800	-0.47014700
C	-0.37511900	0.93811500	0.25116500	C	-3.12837900	1.17833200	-0.19619500

H	-0.76504100	-1.06267100	0.91628000	O	-3.47528900	-1.01105700	0.54078500
H	0.70021700	0.85410600	0.42250700	C	-3.03648900	-2.26899000	1.04540600
H	-2.71915300	3.17855600	-0.85832500	H	-2.55495300	-2.15757700	2.03078800
H	-4.20653900	1.23584000	-0.35844000	H	-3.93612900	-2.88778900	1.14866100
S	0.14525900	3.49480200	-0.59617400	H	-2.33605200	-2.75660600	0.34754000

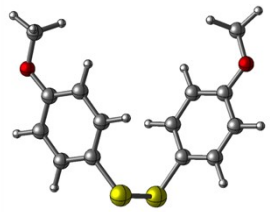
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -744.520087

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -743.84685

V



Zero-point correction= 0.248805 (Hartree/Particle)

Thermal correction to Energy= 0.266251

Thermal correction to Enthalpy= 0.267196

Thermal correction to Gibbs Free Energy= 0.200236

Sum of electronic and zero-point Energies= -1487.802139

Sum of electronic and thermal Energies= -1487.784693

Sum of electronic and thermal Enthalpies= -1487.783749

Sum of electronic and thermal Free Energies= -1487.850708

C	-1.66568100	1.34433200	-0.37426000	S	3.18542200	2.58230900	-2.50084100
C	-0.92024100	0.32767300	-1.00769700	C	2.56126200	4.22083600	-2.18577800
C	0.46456900	0.40615200	-1.06942800	C	1.22238000	4.52325000	-2.47289400
C	1.14277500	1.50212600	-0.50012500	C	3.38302200	5.22020100	-1.62788500
C	0.39809500	2.51145800	0.12709000	C	0.70066300	5.79551900	-2.21946500
C	-0.99649100	2.43981300	0.19753400	H	0.57528000	3.75196700	-2.89536400
H	-1.45936700	-0.51601900	-1.44358900	C	2.87316900	6.48520500	-1.36843800
H	1.03413300	-0.38220200	-1.56666000	H	4.42551600	4.99341700	-1.39353900
H	0.91424400	3.36970500	0.56191100	C	1.52608700	6.78615700	-1.66078000
H	-1.54507500	3.24130000	0.69127000	H	-0.34409500	5.99728900	-2.45387200
O	-3.00594600	1.17765400	-0.36739000	H	3.49818600	7.26978000	-0.93684200
C	-3.82928600	2.15897500	0.24359600	O	1.12497400	8.04288100	-1.37124800
H	-3.71874700	3.14255900	-0.24494000	C	-0.21734000	8.42490300	-1.62886100
H	-4.86423900	1.81343900	0.12496800	H	-0.30781600	9.47250800	-1.31433800
H	-3.60500300	2.26447000	1.31916400	H	-0.46210000	8.34790000	-2.70235800
S	2.91670700	1.63791800	-0.59118500	H	-0.93139700	7.81178600	-1.05221500

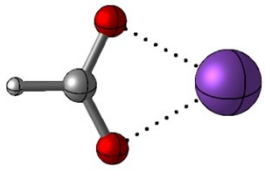
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1489.1004792

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1487.759139

HCOONa



Zero-point correction= 0.021982 (Hartree/Particle)

Thermal correction to Energy= 0.026698

Thermal correction to Enthalpy= 0.027642

Thermal correction to Gibbs Free Energy= -0.005742

Sum of electronic and zero-point Energies= -351.352880

Sum of electronic and thermal Energies= -351.348164

Sum of electronic and thermal Enthalpies= -351.347220

Sum of electronic and thermal Free Energies= -351.380604

O	-0.84574300	0.97696500	1.56679500	O	1.27667900	0.24658500	1.48578100
C	0.39777800	1.14315500	1.50722400	Na	-0.46116800	-1.33521400	1.57766300
H	0.76362200	2.21135800	1.46834900				

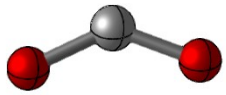
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -351.6648884

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -351.2948563

CO_2•⁻ Radical Anion



Zero-point correction= 0.008776 (Hartree/Particle)

Thermal correction to Energy= 0.011715

Thermal correction to Enthalpy= 0.012659

Thermal correction to Gibbs Free Energy= -0.015228

Sum of electronic and zero-point Energies= -188.492593

Sum of electronic and thermal Energies= -188.489655

Sum of electronic and thermal Enthalpies= -188.488711

Sum of electronic and thermal Free Energies= -188.516598

O	-0.85384600	1.30246100	1.49916800	O	1.09492900	0.11004500	1.54080800
C	0.37252100	1.11745100	1.50562800				

UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -188.7465999

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -188.4380354

CO_2

Zero-point correction= 0.011678 (Hartree/Particle)

Thermal correction to Energy= 0.014316

Thermal correction to Enthalpy= 0.015260

Thermal correction to Gibbs Free Energy= -0.009027

Sum of electronic and zero-point Energies= -188.434130

Sum of electronic and thermal Energies= -188.431491

Sum of electronic and thermal Enthalpies= -188.430547

Sum of electronic and thermal Free Energies= -188.454835

C	0.38648600	1.25634400	1.50077800	O	-0.77678600	1.25634400	1.50077800
O	1.54975800	1.25634400	1.50077800				

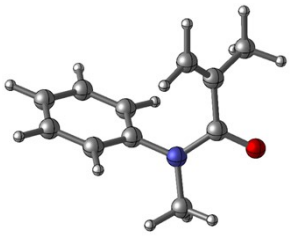
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -188.6725431

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -188.3832588

AlkSM



Zero-point correction= 0.215412 (Hartree/Particle)

Thermal correction to Energy= 0.228232

Thermal correction to Enthalpy= 0.229176

Thermal correction to Gibbs Free Energy= 0.175093

Sum of electronic and zero-point Energies= -556.377104

Sum of electronic and thermal Energies= -556.364284

Sum of electronic and thermal Enthalpies= -556.363340

Sum of electronic and thermal Free Energies= -556.417423

C	0.59432200	0.28276100	0.61169600	C	3.71938800	-1.25601700	0.86251400
C	1.85768300	0.13621500	0.02136300	H	3.45721000	-1.43427200	1.91993100
C	2.48671900	1.24881600	-0.55528400	H	4.32537600	-2.09911100	0.50910100
C	1.85079800	2.49275700	-0.55130800	H	4.30542000	-0.33052900	0.79787100
C	0.58071500	2.63406700	0.02047800	C	1.92799300	-2.29461800	-0.40556900
C	-0.04558900	1.52525900	0.59978900	O	2.34479500	-3.39820400	-0.06141000
H	0.11558000	-0.58259500	1.07529900	C	0.78312300	-2.20626400	-1.38684000
H	3.46848200	1.13028200	-1.01931800	C	0.86682000	-1.43087600	-2.47706700
H	2.34588700	3.35365900	-1.00734300	H	1.71637200	-0.76470400	-2.64473700
H	0.08232800	3.60641500	0.01668000	H	0.08213000	-1.44329700	-3.23954200
H	-1.03396800	1.62800800	1.05456800	C	-0.35202300	-3.15515600	-1.11516000
N	2.51840100	-1.13276500	0.03414500	H	0.03299400	-4.18063500	-1.00163700

H -0.85638300 -2.89811800 -0.16733200 H -1.09747700 -3.13560800 -1.92276200

UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -557.211362

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -556.3928833

NaF

Zero-point correction= 0.001090 (Hartree/Particle)

Thermal correction to Energy= 0.003691

Thermal correction to Enthalpy= 0.004635

Thermal correction to Gibbs Free Energy= -0.020146

Sum of electronic and zero-point Energies= -262.093149

Sum of electronic and thermal Energies= -262.090548

Sum of electronic and thermal Enthalpies= -262.089604

Sum of electronic and thermal Free Energies= -262.114384

F -1.05199600 -0.09864300 -0.92600600 Na -3.01608400 -0.09864300 -0.92600600

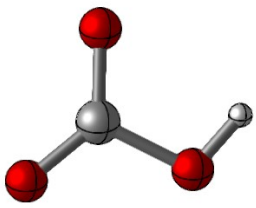
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -262.2970078

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -262.0494951

HCO_3-



Zero-point correction= 0.026496 (Hartree/Particle)

Thermal correction to Energy= 0.029997

Thermal correction to Enthalpy= 0.030941

Thermal correction to Gibbs Free Energy= 0.000748

Sum of electronic and zero-point Energies= -264.314546

Sum of electronic and thermal Energies= -264.311045

Sum of electronic and thermal Enthalpies= -264.310101

Sum of electronic and thermal Free Energies= -264.340294

O -0.74100800 1.07561400 1.73888100 C 0.46452000 1.34907700 1.56081300

O	1.00852800	2.39337800	1.16683600	H	0.81315100	-0.43591800	2.14436000
O	1.37093600	0.30029300	1.85433200				

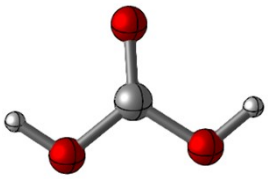
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -264.6796935

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -264.2593954

H_2CO_3



Zero-point correction= 0.039606 (Hartree/Particle)

Thermal correction to Energy= 0.043314

Thermal correction to Enthalpy= 0.044258

Thermal correction to Gibbs Free Energy= 0.013718

Sum of electronic and zero-point Energies= -264.779367

Sum of electronic and thermal Energies= -264.775658

Sum of electronic and thermal Enthalpies= -264.774714

Sum of electronic and thermal Free Energies= -264.805254

O	-0.86203900	1.35089400	1.11022600	H	-0.02811300	-0.60184900	2.08604800
C	0.27719000	1.13620900	1.44946700	O	1.29777300	1.98783700	1.33005400
O	0.72330700	0.00808600	2.00557800	H	0.95966400	2.80294800	0.92462200

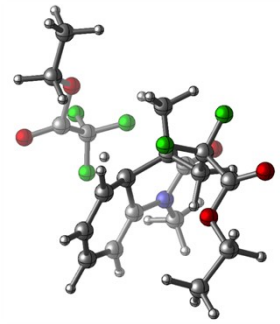
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -265.1409055

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -264.7377114

MECP-E-3-IntA



Zero-point correction= 0.402426 (Hartree/Particle)

Thermal correction to Energy= 0.432861

Thermal correction to Enthalpy= 0.433805

Thermal correction to Gibbs Free Energy= 0.338480

Sum of electronic and zero-point Energies= -1666.464082

Sum of electronic and thermal Energies= -1666.433647

Sum of electronic and thermal Enthalpies= -1666.432703

Sum of electronic and thermal Free Energies= -1666.528029

C	5.093120000	-1.672665000	-1.427395000	C	0.841165000	-1.169680000	-4.695903000
C	3.798790000	0.436379000	-1.706848000	O	-0.050507000	-1.699709000	-5.311245000
C	4.952522000	1.009252000	-2.183697000	O	1.821310000	-0.445445000	-5.206876000
C	6.186620000	0.302667000	-2.236571000	C	1.844838000	-0.259777000	-6.645133000
C	6.233668000	-1.078180000	-1.896926000	H	1.845960000	-1.252257000	-7.119921000
H	2.867566000	1.001277000	-1.672857000	H	0.919004000	0.257953000	-6.938836000
H	4.925135000	2.040793000	-2.546697000	C	3.081095000	0.539685000	-6.983560000
H	7.083796000	0.798032000	-2.612907000	H	3.991300000	0.004546000	-6.672270000
H	7.144472000	-1.657954000	-2.061471000	H	3.126300000	0.702102000	-8.070919000
N	4.852424000	-3.020667000	-1.201167000	H	3.062507000	1.520501000	-6.485644000
C	5.880637000	-4.037015000	-1.147454000	F	-0.127325000	-1.853673000	-2.671816000
H	6.596866000	-3.800877000	-0.347232000	F	1.012367000	0.010148000	-2.671427000
H	5.396798000	-4.998568000	-0.938442000	C	4.458630000	-0.746284000	2.282144000
H	6.417224000	-4.100395000	-2.107335000	O	5.220182000	0.206541000	2.643157000
C	3.510228000	-3.294612000	-1.077166000	O	3.076789000	-0.749527000	2.646404000
O	3.031427000	-4.402344000	-0.896749000	C	4.956294000	-2.148958000	2.350699000
C	2.714911000	-1.985371000	-1.293030000	C	2.433702000	0.490742000	2.432351000
C	2.235683000	-2.062660000	-2.770123000	H	2.478605000	0.758094000	1.356481000
H	1.986950000	-3.104780000	-3.023822000	H	2.967411000	1.289862000	2.976419000
H	3.057613000	-1.753730000	-3.431338000	C	0.993996000	0.387207000	2.897563000
C	1.585008000	-1.895509000	-0.265779000	H	0.477325000	1.352302000	2.771685000
H	1.021672000	-0.960236000	-0.381255000	H	0.445997000	-0.375234000	2.321663000
H	2.007300000	-1.916936000	0.747626000	H	0.951732000	0.109000000	3.963045000
C	3.837874000	-0.923845000	-1.085619000	F	6.140315000	-2.279773000	1.699881000
H	3.889124000	-0.783710000	0.025268000	F	5.216313000	-2.626147000	3.627118000
H	0.887848000	-2.737237000	-0.382998000	F	4.108450000	-3.063612000	1.816045000
C	1.001265000	-1.270635000	-3.162479000				

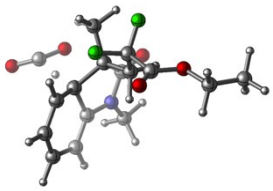
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1668.7973434

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1666.3285172

MECP-E-3-CO_2



Zero-point correction= 0.319728 (Hartree/Particle)

Thermal correction to Energy= 0.343039

Thermal correction to Enthalpy= 0.343983

Thermal correction to Gibbs Free Energy= 0.265705

Sum of electronic and zero-point Energies= -1250.003058

Sum of electronic and thermal Energies= -1249.979747

Sum of electronic and thermal Enthalpies= -1249.978803

Sum of electronic and thermal Free Energies= -1250.057082

C	4.957717000	-1.447284000	-1.131096000	C	5.174688000	1.324998000	-1.278731000
C	3.904271000	0.797056000	-1.226852000	C	6.338920000	0.514527000	-1.197110000

C	6.214113000	-0.902922000	-1.179759000
H	3.031335000	1.446470000	-1.294348000
H	5.297318000	2.405788000	-1.403944000
H	7.329507000	0.972415000	-1.233725000
H	7.099169000	-1.538574000	-1.257285000
N	4.588891000	-2.780178000	-1.256689000
C	5.510941000	-3.891742000	-1.196103000
H	6.018096000	-3.913061000	-0.219220000
H	4.938165000	-4.816795000	-1.332522000
H	6.270564000	-3.811850000	-1.990207000
C	3.237949000	-2.928593000	-1.456600000
O	2.658742000	-3.992840000	-1.607292000
C	2.600544000	-1.523734000	-1.571909000
C	2.477357000	-1.283610000	-3.103775000
H	2.228153000	-2.228448000	-3.608148000
H	3.453480000	-0.956556000	-3.494927000
C	1.262499000	-1.504382000	-0.831564000
H	0.813934000	-0.501864000	-0.845986000
H	1.424471000	-1.810091000	0.210358000
C	3.709620000	-0.647372000	-0.914068000
H	3.505325000	-0.752475000	0.202319000
C	3.572494000	-1.879008000	2.046231000
O	3.178022000	-2.973716000	1.645369000
O	4.104268000	-1.429449000	3.057994000
H	0.557043000	-2.205994000	-1.297983000
C	1.426644000	-0.301130000	-3.590463000
C	1.636088000	0.075290000	-5.072821000
O	1.924329000	1.185437000	-5.445228000
O	1.479516000	-0.989277000	-5.841520000
C	1.672574000	-0.816184000	-7.269792000
H	0.958054000	-0.057162000	-7.622018000
H	2.689889000	-0.429384000	-7.432414000
C	1.456289000	-2.156608000	-7.931029000
H	0.436563000	-2.526943000	-7.743671000
H	1.594249000	-2.052928000	-9.018153000
H	2.177241000	-2.900147000	-7.558404000
F	0.168388000	-0.837108000	-3.474078000
F	1.413558000	0.857326000	-2.877495000

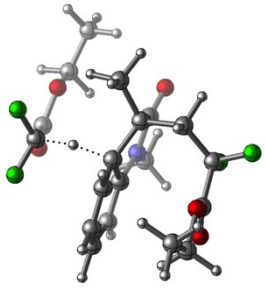
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1251.7626414

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1249.9054008

TS-E-3*-IntC



Zero-point correction= 0.398021 (Hartree/Particle)

Thermal correction to Energy= 0.427977

Thermal correction to Enthalpy= 0.428921

Thermal correction to Gibbs Free Energy= 0.336031

Sum of electronic and zero-point Energies= -1566.544569

Sum of electronic and thermal Energies= -1566.514612

Sum of electronic and thermal Enthalpies= -1566.513668

Sum of electronic and thermal Free Energies= -1566.606559

C	4.79057000	-0.88511600	-0.45221900
C	3.88593400	0.91184200	1.06520300
C	5.17651900	1.14333200	1.43637000
C	6.28563500	0.34729100	0.94624900
C	6.07900000	-0.64263300	-0.04183400
H	3.06424500	1.52696600	1.43571100
H	5.39858200	1.97100500	2.11559100
H	7.29501300	0.56491800	1.29768600
H	6.92157400	-1.17573500	-0.48527600
N	4.30988700	-1.73575100	-1.42146800
C	5.14549400	-2.61750300	-2.21337400
H	5.68858900	-3.30860400	-1.55241500
H	4.49765900	-3.18254800	-2.89412900
H	5.86763500	-2.02707600	-2.79844500
C	2.94592500	-1.57477500	-1.64739100
O	2.29566900	-2.21599000	-2.44902300
C	2.42248400	-0.43472900	-0.74323700
C	1.11563400	-0.86221000	-0.05026900
H	0.76873200	-0.06924700	0.62919500
H	0.33356600	-1.04890900	-0.80035300
H	1.25920100	-1.78303000	0.52916100
C	2.09019200	0.81153600	-1.61687400
H	1.70998200	1.61581700	-0.97184700
H	1.28203100	0.53167500	-2.30991700
C	3.17037300	1.41658300	-2.50133700
C	4.28177700	2.24608800	-1.81635900

O	5.45794600	2.04819600	-1.97820800	C	3.88472800	-3.54087200	1.19046400
O	3.73656600	3.21334400	-1.09336300	O	4.97361700	-4.04020000	1.01884500
C	4.63129800	4.12539400	-0.40891300	O	2.75031000	-3.91083000	0.59856100
H	5.10929500	4.76557600	-1.16741600	C	3.64294400	-2.29546100	2.00563400
H	5.41774800	3.53386200	0.08150200	C	2.80459700	-5.03292800	-0.31915500
C	3.80977800	4.91989300	0.58002500	H	3.09459500	-5.92914000	0.25147600
H	4.45714400	5.63915500	1.10405100	H	3.59279700	-4.83650600	-1.06126500
H	3.01027100	5.47835400	0.06989700	C	1.44199500	-5.16750700	-0.95944200
H	3.35225300	4.25449300	1.32804900	H	1.44395400	-6.02699500	-1.64703100
F	3.77576900	0.45969000	-3.25876200	H	0.66584200	-5.33463300	-0.19709200
F	2.55283100	2.27449100	-3.37764300	H	1.19924200	-4.26069300	-1.53180500
C	3.59511000	-0.26206700	0.21686100	F	4.67732600	-1.97019500	2.78638400
H	3.46820200	-1.29597600	1.14428200	F	2.50868400	-2.31515600	2.73077600

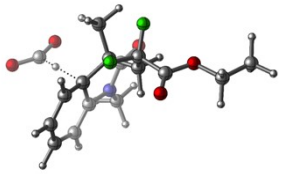
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1568.7381923

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1566.4312041

TS-E-3*-CO_2



Zero-point correction= 0.315925 (Hartree/Particle)

Thermal correction to Energy= 0.340316

Thermal correction to Enthalpy= 0.341260

Thermal correction to Gibbs Free Energy= 0.258340

Sum of electronic and zero-point Energies= -1249.975290

Sum of electronic and thermal Energies= -1249.950900

Sum of electronic and thermal Enthalpies= -1249.949955

Sum of electronic and thermal Free Energies= -1250.032875

C	5.01383500	-1.47033800	-1.07476100	H	0.87854300	-0.55959800	-0.98283600
C	3.89554500	0.76172100	-1.03423000	H	1.45616800	-1.90045400	0.05280500
C	5.13065600	1.31543600	-0.83388900	C	3.74670000	-0.69675300	-1.04756600
C	6.32611000	0.50720700	-0.70679300	H	3.63107600	-1.01366400	0.53724200
C	6.24889900	-0.90570900	-0.85598500	C	3.70232900	-1.53125500	1.68474600
H	3.01060100	1.39219100	-1.12876400	O	3.30327700	-2.70414200	1.66085300
H	5.22857600	2.40350300	-0.76795100	O	4.13310600	-0.77162600	2.55645200
H	7.29115500	0.98679700	-0.53235000	H	0.62246800	-2.24756600	-1.48893000
H	7.14970400	-1.52247000	-0.81545900	C	1.54940700	-0.27281600	-3.72033800
N	4.68586300	-2.79323300	-1.30021100	C	1.72605900	0.04741500	-5.22106600
C	5.60170500	-3.90299300	-1.15270900	O	2.17823300	1.08447700	-5.63738600
H	5.95032400	-3.97370100	-0.10978400	O	1.35490400	-0.99270700	-5.95710200
H	5.07095700	-4.82417900	-1.42327800	C	1.50301000	-0.87711100	-7.39428200
H	6.47454000	-3.77492200	-1.81147100	H	0.90103200	-0.02088800	-7.73730900
C	3.34149400	-2.95403700	-1.58503300	H	2.55848000	-0.65503100	-7.61758500
O	2.79214200	-4.02651700	-1.78624600	C	1.04779800	-2.18096000	-8.00948900
C	2.68200100	-1.55768700	-1.69968000	H	-0.00579300	-2.38312600	-7.76334700
C	2.52876800	-1.33322200	-3.25099700	H	1.14495100	-2.12693800	-9.10439400
H	2.19253600	-2.26836400	-3.72311100	H	1.66090100	-3.02014000	-7.64689600
H	3.51786100	-1.09034900	-3.67018200	F	0.25507200	-0.68469300	-3.52721600
C	1.32143600	-1.56528100	-0.98424700	F	1.68854800	0.89562100	-3.03388300

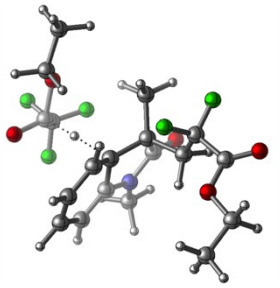
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1251.73021

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1249.8711735

TS-E-3*-IntA



Zero-point correction= 0.398821 (Hartree/Particle)

Thermal correction to Energy= 0.429924

Thermal correction to Enthalpy= 0.430869

Thermal correction to Gibbs Free Energy= 0.333801

Sum of electronic and zero-point Energies= -1666.434562

Sum of electronic and thermal Energies= -1666.403458

Sum of electronic and thermal Enthalpies= -1666.402514

Sum of electronic and thermal Free Energies= -1666.499582

C	5.11461000	-1.76977200	-1.33071900		C	0.77263200	-1.14265100	-4.64648100
C	3.82221800	0.34880900	-1.45166800		O	-0.14041800	-1.63796200	-5.26017300
C	5.01123400	1.00024300	-1.66389800		O	1.76092400	-0.42253200	-5.16663100
C	6.27052600	0.30921700	-1.66113200		C	1.74835400	-0.20692200	-6.59842800
C	6.30150100	-1.11556500	-1.54218100		H	1.73980300	-1.18834300	-7.09850800
H	2.87674900	0.89107900	-1.46901500		H	0.81359800	0.31189100	-6.86400900
H	5.00744900	2.07938900	-1.84919300		C	2.97407400	0.60573800	-6.94993700
H	7.19814200	0.86289100	-1.82112200		H	3.89321800	0.06829600	-6.67062900
H	7.24176700	-1.66478000	-1.62746600		H	2.99623600	0.79322200	-8.03416100
N	4.87879400	-3.13430800	-1.24493800		H	2.96272900	1.57530900	-6.42900700
C	5.91281900	-4.14366800	-1.18049700		F	-0.16083400	-1.84688100	-2.61240500
H	6.53563600	-3.99019900	-0.28588100		F	1.05930400	-0.02863300	-2.59178500
H	5.42841600	-5.12671100	-1.12740600		C	4.41503000	-0.68935400	1.70656700
H	6.55415900	-4.10001600	-2.07495100		O	5.23346200	0.28058800	1.85306200
C	3.53023000	-3.41947500	-1.16256900		O	3.10667600	-0.59564800	2.29751300
O	3.05518600	-4.54176600	-1.06233700		C	4.93285300	-2.06849900	2.16266000
C	2.73100400	-2.10194500	-1.30495100		C	2.45661300	0.63855300	2.05805300
C	2.18876000	-2.14153200	-2.78637500		H	2.43657600	0.85042900	0.97095100
H	1.89448600	-3.17291500	-3.03668000		H	3.02223300	1.46401900	2.52798000
H	3.00350400	-1.85195600	-3.46510900		C	1.04713700	0.55782300	2.61412600
C	1.59008700	-2.06718800	-0.27622100		H	0.52191400	1.51663500	2.47925700
H	1.03356200	-1.12310200	-0.35017000		H	0.47165600	-0.22940400	2.10210700
H	1.99973200	-2.13857600	0.73837700		H	1.06952900	0.32249600	3.69035100
C	3.83313200	-1.07672200	-1.09638400		F	6.12750000	-2.33936600	1.60034100
H	4.13947200	-0.89508200	0.46734900		F	5.10879800	-2.14275700	3.50041500
H	0.88895000	-2.89658100	-0.44963400		F	4.10343200	-3.08208300	1.82392700
C	0.97513600	-1.29464900	-3.12374200					

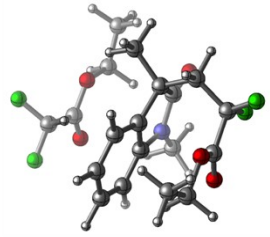
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1668.7613853

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1666.2940773

3*-Est



Zero-point correction= 0.401927 (Hartree/Particle)

Thermal correction to Energy= 0.432775

Thermal correction to Enthalpy= 0.433719

Thermal correction to Gibbs Free Energy= 0.337892

Sum of electronic and zero-point Energies= -1566.564481

Sum of electronic and thermal Energies= -1566.533633

Sum of electronic and thermal Enthalpies= -1566.532689

Sum of electronic and thermal Free Energies= -1566.628516

C	4.66784300	-0.67468300	-0.38998600	O	5.15985200	1.59312800	-2.30905700
C	3.45972900	0.94142400	1.08441900	O	3.76025300	3.04833200	-1.29111600
C	4.64442200	1.10137000	1.76964600	C	4.86519800	3.68803400	-0.60323700
C	5.89073200	0.39248700	1.36291700	H	5.49232800	4.18955700	-1.35765200
C	5.86656500	-0.50180200	0.29164700	H	5.47355700	2.90716200	-0.12249200
H	2.56301700	1.48176000	1.39630500	C	4.28461000	4.65997600	0.39761400
H	4.68697600	1.76766600	2.63397900	H	5.10041100	5.17867100	0.92358100
H	6.79999400	0.54604100	1.94360800	H	3.65818200	5.41409200	-0.10275600
H	6.75608600	-1.06612700	0.00700100	H	3.67293400	4.12947400	1.14276500
N	4.35007300	-1.49204100	-1.43310400	F	3.17345800	0.59995700	-3.72408000
C	5.30142600	-2.33525200	-2.13489800	F	2.16395400	2.51962100	-3.41212800
H	5.74475300	-3.06351200	-1.44099700	C	3.42482000	0.08680800	-0.04003600
H	4.76747300	-2.86015700	-2.93563300	H	3.71141300	-1.62116000	2.09931600
H	6.09478300	-1.70655800	-2.56606600	C	4.21443900	-3.54871200	1.15930200
C	2.99471300	-1.41513600	-1.79407800	O	5.24064500	-4.04195500	0.76293800
O	2.47153900	-2.13528800	-2.62401100	O	3.00783600	-3.73085300	0.63943100
C	2.30182300	-0.32701100	-0.94700000	C	4.12031300	-2.60693800	2.37328300
C	1.09735900	-0.94071300	-0.19181700	C	2.87897700	-4.69042200	-0.44729100
H	0.62377200	-0.17769700	0.44379600	H	3.28786800	-5.65098700	-0.09856800
H	0.34889900	-1.31428100	-0.90672800	H	3.49102500	-4.34321900	-1.29109600
H	1.42406300	-1.77648100	0.44126800	C	1.41773700	-4.78141400	-0.81941600
C	1.76275800	0.82616200	-1.83976000	H	1.29139800	-5.54492300	-1.60201000
H	1.35389300	1.61450500	-1.19100200	H	0.80751400	-5.06952000	0.04990300
H	0.94945000	0.46046200	-2.48586700	H	1.05862000	-3.82147300	-1.21550400
C	2.77574000	1.48135900	-2.76229600	F	5.34778900	-2.45253900	2.91191100
C	4.05554000	2.03048000	-2.09004500	F	3.30789200	-3.17558800	3.30610400

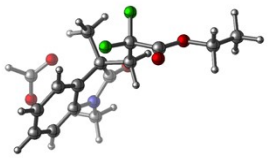
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1568.7665357

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1566.4553869

3*-CO_2



Zero-point correction= 0.318405 (Hartree/Particle)

Thermal correction to Energy= 0.343952

Thermal correction to Enthalpy= 0.344896

Thermal correction to Gibbs Free Energy= 0.258477

Sum of electronic and zero-point Energies= -1249.978089

Sum of electronic and thermal Energies= -1249.952543

Sum of electronic and thermal Enthalpies= -1249.951599

Sum of electronic and thermal Free Energies= -1250.038017

C	5.05740400	-1.29722600	-0.99927100	H	1.09719100	-0.25376700	-1.23895500
C	4.00733900	0.94211400	-1.28203300	H	1.75823900	-1.51959800	-0.14657600
C	5.12966800	1.47619700	-0.67449100	C	3.91961500	-0.44654200	-1.49203600
C	6.25705200	0.61592400	-0.20478000	H	3.79648800	-1.62437700	2.89966300
C	6.18176500	-0.76435300	-0.37145300	C	4.05670800	-2.43264200	2.13429800
H	3.19529000	1.59637700	-1.60165100	O	3.17075500	-2.68688600	1.28940500
H	5.20018900	2.55570700	-0.51933300	O	5.19416400	-2.94152200	2.26345900
H	7.11381700	1.07961200	0.28545000	H	0.77969200	-1.97421500	-1.57961700
H	6.96952000	-1.42302800	-0.00172000	C	1.60507800	-0.12404600	-4.02043800
N	4.73259200	-2.59136700	-1.25049800	C	1.63684700	0.06415500	-5.55485800
C	5.52012400	-3.73224300	-0.82282800	O	2.01389500	1.06891300	-6.10246100
H	5.53189700	-3.74389200	0.28159200	O	1.21656800	-1.04177700	-6.15446300
H	5.04582500	-4.63913400	-1.21614000	C	1.20462700	-1.05113200	-7.60439800
H	6.54390300	-3.64566200	-1.21728300	H	0.53271800	-0.24964800	-7.94979100
C	3.46640100	-2.72967700	-1.81723600	H	2.21949500	-0.81484400	-7.96070200
O	2.95918000	-3.80073100	-2.11408400	C	0.74253200	-2.41931000	-8.05142700
C	2.82901400	-1.33715900	-2.02388000	H	-0.26861300	-2.63403200	-7.67335800
C	2.55050200	-1.21627400	-3.55653400	H	0.71861900	-2.45990200	-9.15094100
H	2.11293500	-2.16074000	-3.91149000	H	1.42711300	-3.20144500	-7.68925700
H	3.50682600	-1.08130100	-4.08450600	F	0.31042400	-0.41187000	-3.66964600
C	1.52521500	-1.26471500	-1.18962900	F	1.89886600	1.07975700	-3.45426300

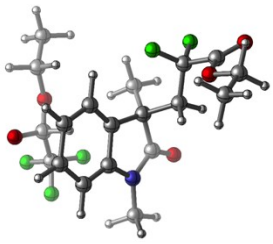
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1251.7353466

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1249.8767345

3*-Alkoxide



Zero-point correction= 0.401351 (Hartree/Particle)

Thermal correction to Energy= 0.433094

Thermal correction to Enthalpy= 0.434038

Thermal correction to Gibbs Free Energy= 0.334639

Sum of electronic and zero-point Energies= -1666.432915

Sum of electronic and thermal Energies= -1666.401172

Sum of electronic and thermal Enthalpies= -1666.400228

Sum of electronic and thermal Free Energies= -1666.499627

C	5.13022700	-1.67973200	-1.29189500		C	0.67954400	-1.05861700	-4.73975500
C	3.83998600	0.44652100	-1.32731900		O	-0.31135500	-1.51496900	-5.25830500
C	5.03811400	1.11354600	-1.25930700		O	1.68876900	-0.47001400	-5.37715400
C	6.30484000	0.41041800	-1.19319700		C	1.59503600	-0.37091500	-6.81787400
C	6.33081200	-1.00874900	-1.24190700		H	1.46989400	-1.38483700	-7.23013200
H	2.89913100	0.99382300	-1.38938800		H	0.69041800	0.20503900	-7.07007800
H	5.04681100	2.20773800	-1.26497000		C	2.85617900	0.29830100	-7.31618000
H	7.23695100	0.97428400	-1.12503800		H	3.74508300	-0.29403700	-7.05021400
H	7.27620900	-1.55453600	-1.20824600		H	2.81706100	0.39384700	-8.41190600
N	4.88556500	-3.04035300	-1.29963200		H	2.96250100	1.30455200	-6.88283200
C	5.90616500	-4.05911000	-1.17992400		F	-0.17621100	-1.52854500	-2.61054800
H	6.43204400	-3.96027400	-0.21822500		F	1.21369300	0.15778400	-2.78863700
H	5.41714200	-5.03978600	-1.23212900		C	4.49602600	-0.77075400	1.76034400
H	6.63800400	-3.96947800	-1.99788300		O	5.33268900	0.19543300	1.95221300
C	3.53025900	-3.32409700	-1.31577000		O	3.19959400	-0.67834900	2.38634700
O	3.05094500	-4.45256200	-1.28592200		C	5.00802400	-2.16074200	2.21120700
C	2.73169500	-2.00653500	-1.44303300		C	2.52542600	0.54036700	2.12987100
C	2.12259800	-2.05456300	-2.90347400		H	2.45833100	0.71344900	1.03887900
H	1.74665900	-3.07258300	-3.09109000		H	3.09827100	1.38723100	2.55038800
H	2.92729900	-1.85597400	-3.62487400		C	1.14009500	0.46252000	2.74378200
C	1.61835900	-1.96459500	-0.37616400		H	0.59770100	1.41007500	2.59767700
H	1.07054900	-1.01353300	-0.42941700		H	0.55478300	-0.34795300	2.28107800
H	2.05856200	-2.04732000	0.62615300		H	1.20717300	0.26358700	3.82550600
C	3.82739500	-0.99423100	-1.25697700		F	6.22467200	-2.41533100	1.69241900
H	4.27025300	-0.91745400	0.62823800		F	5.12506000	-2.25854300	3.54929600
H	0.90130800	-2.78479400	-0.53086100		F	4.19518400	-3.16390000	1.80919800
C	0.97036700	-1.12486800	-3.22769400					

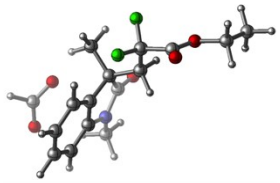
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1668.7631322

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1666.2907636

3 + CO_2H



Zero-point correction= 0.324080 (Hartree/Particle)

Thermal correction to Energy= 0.348794

Thermal correction to Enthalpy= 0.349739

Thermal correction to Gibbs Free Energy= 0.266390

Sum of electronic and zero-point Energies= -1250.094714

Sum of electronic and thermal Energies= -1250.069999

Sum of electronic and thermal Enthalpies= -1250.069055

Sum of electronic and thermal Free Energies= -1250.152403

C	4.97948800	-1.29187600	-1.04079700	H	1.10010200	-0.26807100	-1.20288400
C	4.01139800	0.91032300	-1.28292400	H	1.79216900	-1.52543100	-0.11804000
C	5.16393600	1.45107900	-0.68434500	C	3.92305700	-0.46465300	-1.46818000
C	6.20520500	0.61394700	-0.26945000	H	3.80413400	-1.51734100	2.85898900
C	6.12596500	-0.77675100	-0.43910600	C	4.05951400	-2.37073000	2.14054600
H	3.19717400	1.56323100	-1.59715500	O	3.15929900	-2.68231800	1.32984000
H	5.24195500	2.53122300	-0.53846900	O	5.20279700	-2.86038200	2.28127700
H	7.09309200	1.04487000	0.20091700	H	0.79364000	-1.99521200	-1.52963300
H	6.92321800	-1.43388200	-0.09132000	C	1.59779300	-0.11791300	-3.98963200
N	4.68338300	-2.63238900	-1.30442000	C	1.61874500	0.08314600	-5.52366300
C	5.49347700	-3.74629200	-0.85554400	O	1.93231300	1.11332900	-6.06290200
H	5.55553200	-3.72386200	0.24539400	O	1.25781600	-1.03903800	-6.13010600
H	5.00522600	-4.67106100	-1.18845600	C	1.23259000	-1.03664600	-7.58043700
H	6.50110800	-3.69032400	-1.29828600	H	0.52040000	-0.26475400	-7.91200400
C	3.42850700	-2.76464400	-1.83288900	H	2.23200600	-0.74976300	-7.94310100
O	2.88211900	-3.81360700	-2.13443900	C	0.83133900	-2.42131200	-8.03512900
C	2.81601000	-1.34937400	-2.01588800	H	-0.16525500	-2.68631200	-7.65042600
C	2.55453900	-1.20577500	-3.53607700	H	0.79967300	-2.45377900	-9.13470300
H	2.12603300	-2.14795900	-3.90851600	H	1.55511300	-3.17332000	-7.68564000
H	3.51189500	-1.05599900	-4.05905000	F	0.30782000	-0.42596300	-3.63839800
C	1.53730600	-1.27495000	-1.15760300	F	1.87584600	1.08423500	-3.41551200

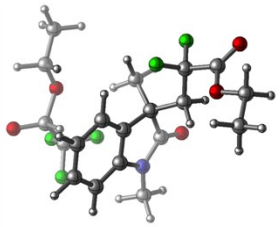
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1251.8579692

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1250.0047732

3 + Alkoxide



Zero-point correction= 0.407302 (Hartree/Particle)

Thermal correction to Energy= 0.438687

Thermal correction to Enthalpy= 0.439631

Thermal correction to Gibbs Free Energy= 0.340993

Sum of electronic and zero-point Energies= -1666.538602

Sum of electronic and thermal Energies= -1666.507218

Sum of electronic and thermal Enthalpies= -1666.506274

Sum of electronic and thermal Free Energies= -1666.604912

C	1.86049500	-0.27368400	-0.24075300	H	3.37936400	-2.66224000	-0.68285100
C	0.70474100	1.83338100	-0.47627400	C	0.25533600	-1.89929100	-0.34826100
C	1.93556100	2.49193600	-0.30659400	O	-0.27189700	-2.99861100	-0.33967500
C	3.11060500	1.76046000	-0.10693400	C	-0.48188500	-0.54537800	-0.53084400
C	3.08990900	0.35813800	-0.06898600	C	-1.16583400	-0.63102200	-1.91982800
H	-0.21047300	2.40660300	-0.62119000	H	-1.60217600	-1.63633000	-2.03128400
H	1.97105900	3.58379800	-0.32494100	H	-0.40960300	-0.51005200	-2.70767900
H	4.06008100	2.28453900	0.02936900	C	-1.46974500	-0.38198600	0.64144700
H	4.00071200	-0.21464300	0.10991400	H	-1.99951800	0.57684200	0.56511200
N	1.59614700	-1.64883200	-0.20717000	H	-0.93145000	-0.39918500	1.59916000
C	2.58567100	-2.66375400	0.08092500	C	0.66873700	0.44434600	-0.45183200
H	3.03414900	-2.48465300	1.06952200	H	1.41399900	0.90095200	2.30563000
H	2.08194200	-3.63838000	0.07907000	H	-2.21187900	-1.19364100	0.62312800

C	-2.29767800	0.33904600	-2.20684600
C	-2.71464900	0.35229200	-3.69886700
O	-3.80920800	0.03863500	-4.09074600
O	-1.69858300	0.74989700	-4.45116000
C	-1.91605300	0.82628400	-5.88339400
H	-2.24013700	-0.16495600	-6.23705700
H	-2.73805700	1.53509000	-6.06996300
C	-0.61921400	1.26930100	-6.52129600
H	0.18527500	0.54664600	-6.31603200
H	-0.75051500	1.34293100	-7.61144500
H	-0.31247600	2.25532400	-6.14040200
F	-3.40401700	0.02774600	-1.47979300
F	-1.96388300	1.62823200	-1.87124600
C	1.34083400	0.63886900	3.40618400
O	1.99108600	1.37385900	4.23788700
O	-0.14466900	0.53888100	3.63209500
C	1.73639000	-0.86147000	3.45759700
C	-0.77246900	1.78381400	3.48434600
H	-0.67693200	2.14953100	2.43627300
H	-0.27212400	2.53843700	4.12324800
C	-2.24157500	1.65836700	3.85388200
H	-2.75409800	2.63129000	3.77655100
H	-2.75256800	0.94528900	3.18645800
H	-2.34665000	1.29027800	4.88759600
F	3.02644600	-1.01745600	3.05743200
F	1.65436200	-1.38835900	4.69549700
F	1.00458500	-1.67070300	2.64553900

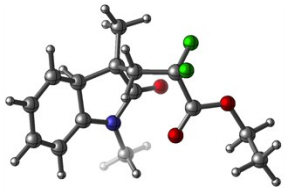
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1668.8830096

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1666.4138105

F



Zero-point correction= 0.313725 (Hartree/Particle)

Thermal correction to Energy= 0.334122

Thermal correction to Enthalpy= 0.335067

Thermal correction to Gibbs Free Energy= 0.263823

Sum of electronic and zero-point Energies= -1061.336352

Sum of electronic and thermal Energies= -1061.315955

Sum of electronic and thermal Enthalpies= -1061.315011

Sum of electronic and thermal Free Energies= -1061.386254

C	0.73733500	-1.09837100	0.76771200
C	1.82334900	-0.09622200	0.55747100
C	1.63310600	1.26831600	0.83179700
C	0.33650200	1.68362600	1.07435900
C	-0.79981400	0.79963400	1.06551600
C	-0.63259100	-0.53511800	0.87889700
H	0.93047000	-1.48506000	1.79591600
H	2.45280700	1.98320300	0.76495900
H	0.15622800	2.74861600	1.24239000
H	-1.79362400	1.22205600	1.21955700
H	-1.47792400	-1.22609900	0.90655200
N	2.90602600	-0.69061900	0.05111400
C	4.20052900	-0.06955700	-0.20392300
H	4.92260100	-0.87312800	-0.38922800
H	4.12911800	0.56809800	-1.09652900
H	4.51227600	0.51932000	0.66767400
C	2.61210800	-2.02285400	-0.36421000
O	3.43764700	-2.79133400	-0.77510700
C	1.09853600	-2.24392600	-0.22331200
C	0.38610400	-1.94691800	-1.57696700
H	0.35299300	-0.86474400	-1.76273100
H	-0.65122100	-2.30307800	-1.50338600
C	0.80189200	-3.65120000	0.29781900
H	1.15543900	-4.40032400	-0.42038700
H	1.30105800	-3.82634000	1.26187100
H	-0.28110100	-3.78326500	0.43513700
C	2.27091700	-1.88720100	-3.32929100
O	2.58528600	-0.77588400	-2.96687900
O	2.92098200	-2.65044200	-4.17988600
C	0.96530500	-2.56454100	-2.84010300
C	4.14684800	-2.12520900	-4.76649000
H	4.69425000	-3.02098800	-5.08606000
H	4.71599000	-1.61587600	-3.97538000
C	3.84182500	-1.20023400	-5.92864500
H	4.78520900	-0.87918400	-6.39654500
H	3.23426600	-1.71487500	-6.68833400
H	3.30329900	-0.30467200	-5.58593900
F	0.05421900	-2.38858000	-3.84643400
F	1.15306600	-3.90476900	-2.71075100

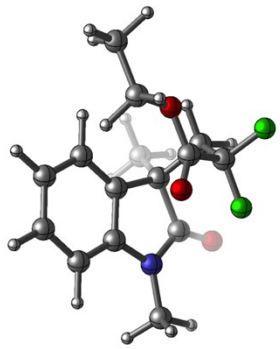
UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1062.8522237

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1061.2990665

3



Zero-point correction= 0.302016 (Hartree/Particle)

Thermal correction to Energy= 0.322039

Thermal correction to Enthalpy= 0.322983

Thermal correction to Gibbs Free Energy= 0.253523

Sum of electronic and zero-point Energies= -1060.962266

Sum of electronic and thermal Energies= -1060.942244

Sum of electronic and thermal Enthalpies= -1060.941299

Sum of electronic and thermal Free Energies= -1061.010760

C	4.73006600	-0.86752900	-0.50154800	H	0.47794600	-1.20402900	-0.90355600
C	3.82191800	0.87771400	0.91111800	H	1.56562600	-1.72068000	0.41625000
C	5.06619100	0.95970900	1.56065100	C	2.01399700	0.84146100	-1.89519800
C	6.12346900	0.13157700	1.16690200	H	1.54673800	1.61586500	-1.27048800
C	5.97085000	-0.80197100	0.12911500	H	1.25781700	0.47785800	-2.60841000
H	2.99769700	1.52943000	1.20972900	C	3.08213900	1.52516300	-2.73333500
H	5.20694700	1.67376400	2.37509700	C	4.17137000	2.31709200	-1.97080500
H	7.08718600	0.20674900	1.67672000	O	5.35308400	2.14043800	-2.11844000
H	6.79537000	-1.45128500	-0.16902600	O	3.60636200	3.22224500	-1.18455800
N	4.32898500	-1.71689900	-1.54130500	C	4.49016300	4.06813000	-0.40472300
C	5.18120700	-2.69806000	-2.17624800	H	5.07107300	4.69219100	-1.10194900
H	5.54783800	-3.43236000	-1.44154000	H	5.19271700	3.41855100	0.13847200
H	4.59040800	-3.21518100	-2.94269400	C	3.63268700	4.89229400	0.52767800
H	6.04731300	-2.20998400	-2.65141900	H	4.27317900	5.55932500	1.12422900
C	3.02005100	-1.48430300	-1.90082100	H	2.91780000	5.50965900	-0.03725800
O	2.39534400	-2.08418500	-2.75550300	H	3.06993900	4.24437000	1.21701400
C	2.47399400	-0.33887600	-1.01199800	F	3.71889000	0.62382700	-3.53156200
C	1.26812900	-0.86989000	-0.21453200	F	2.46238500	2.42094500	-3.56639900
H	0.86281000	-0.08076300	0.43643000	C	3.66426600	-0.02902700	-0.12857400

UB3LYP-D3/def2-TZVPP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1062.4678667

UωB97XD/def2-SVP-CPCM(DMSO) // UB3LYP-D3/def2-SVP-CPCM(DMSO)

HF = -1060.916768

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