Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2022

Supporting Information

Practical, Scalable, and Transition Metal-Free Visible Light-Induced Heteroarylation Route to Substituted Oxindoles

Jadab Majhi, Albert Granados, Bianca Matsuo, Vittorio Ciccone, Roshan K. Dhungana, Mohammed Sharique, and Gary A. Molander*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States

*To whom correspondence should be addressed. E-mails: gmolandr@sas.upenn.edu

TABLE OF CONTENT

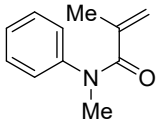
1. General Considerations

1.1 General: For irradiation, a Kessil PR160L-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm) was placed 1.5 inches away from the reaction vials. NMR spectra (^{1}H, ^{13}C {^{1}H decoupled}, ^{19}F {^{1}H decoupled}) were obtained at 298 K using 400, 500, and 600 MHz spectrometers. Chemical shifts are referenced to residual, nondeuterated $CHCl_3$ (δ 7.26 in the ^{1}H NMR and 77.2 in the ^{13}C NMR). The following conventions are used for multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublet of doublets; td, triplet of doublets; dt, doublet of triplets; br, broad. Reactions were monitored by GCMS, ^{1}H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using phosphomolybdic acid, ninhydrin, *p*-anisaldehyde, $KMNO_4$ stain, and/or UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (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 on an FT-IR using either neat oil or solid products. Melting points (°C) are uncorrected. UV/vis studies were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific.

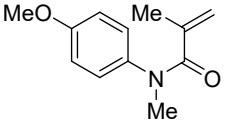
1.2 Chemicals: Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Dry DMSO was obtained from Acros Organics and used as received. THF and CH_2Cl_2 were purchased and dried *via* a solvent delivery system. Bulk solvents were purchased from Fisher Scientific. Photoredox-catalyzed reactions were performed using 8 mL Chemglass vials (2-dram, 17 x 60 mm, 15-425 Green Open Top Cap, TFE Septa).

2. List of Used Radical Acceptors

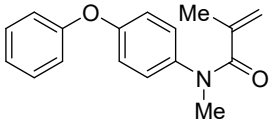
The acrylamides shown below have been prepared according to the reported procedures.[1] Full characterization data for compounds **1k** and **1l** is accessible in Section *4.1*.



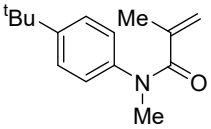
1a



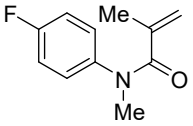
1b



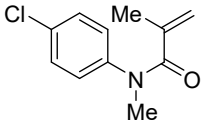
1c



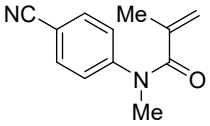
1d



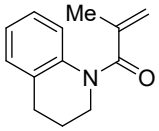
1e



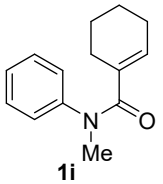
1f



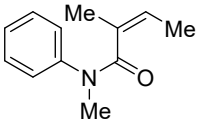
1g



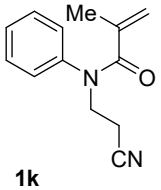
1h



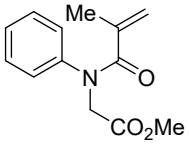
1i



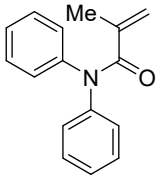
1j



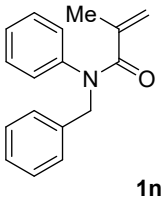
1k



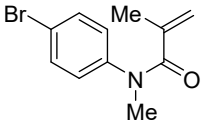
1l



1m



1n

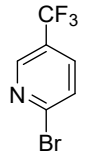


1o

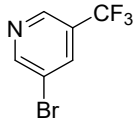
[1] (a) Cheng, H.; Lam, T.-L.; Liu, Y.; Tang, Z.; Che, C.-M. *Angew. Chem. Int. Ed.* **2021**, *60*, 1383-1389. (b) Li, Y.-L.; Wang, J.-B.; Wang, X.-L.; Cao, Y.; Deng, J. *Eur. J. Org. Chem.* **2017**, 6052-6059. (c) Oddy, M. J.; Kusza, D. A.; Petersen, W. F. *Org. Lett.* **2021**, *23*, 8963-8967. (d) Liu, Z.; Zhong, S.; Ji, X.; Deng, G.-J.; Huang, H. *Org. Lett.* **2022**, *24*, 349-353.

3. List of Used (Hetero)Aryl Bromides

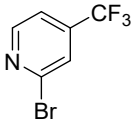
The (hetero)aryl halides shown below are commercially available, except **2p**, which was prepared according to reported procedures,[2] and **2q**, which was synthesized as indicated in Section *4.2.*



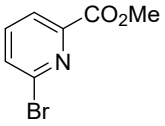
2a



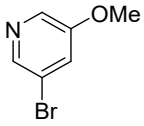
2b



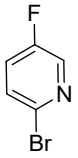
2c



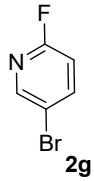
2d



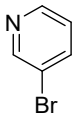
2e



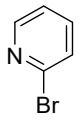
2f



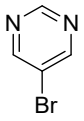
2g



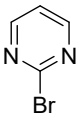
2h



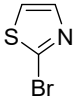
2i



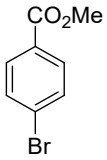
2j



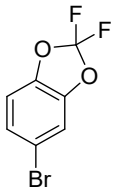
2k



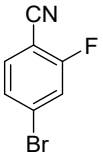
2l



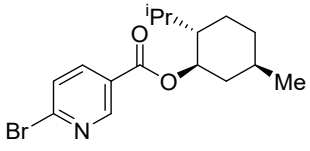
2m



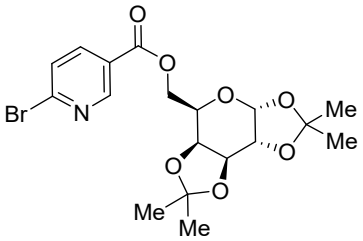
2n



2o



2p

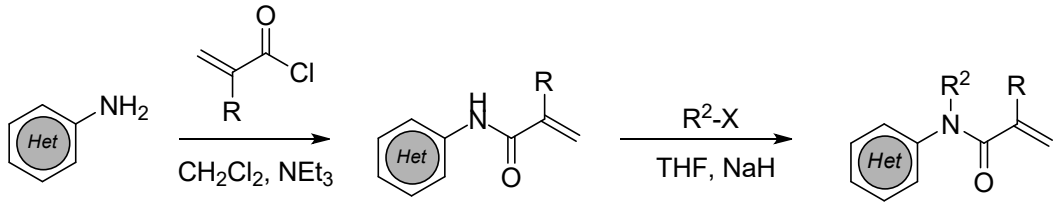


2q

[2] Alandini, N.; Buzzetti, L.; Favi, G.; Schulte, T.; Candish, L.; Collins, K. D.; Melchiorre, P. *Angew. Chem. Int. Ed.* **2020**, *59*, 5248–5253.

4. Preparation and Characterization of Starting Materials

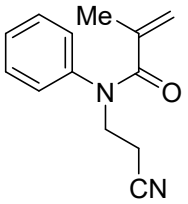
4.1. Synthesis of Acrylamides



Step 1: To a soln of the corresponding aniline (5.0 mmol) in CH_2Cl_2 (12.5 mL) was added Et_3N (1.39 mL, 10.0 mmol) at 0 ºC. Next, methacryloyl chloride (627 mg, 6 mmol, 1.2 equiv, 580 µL) was added dropwise, and the resulting soln was stirred overnight. The reaction mixture was poured into H_2O, and the aq layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by automated flash column chromatography using hexanes/EtOAc mixtures.

Step 2: To a soln of the corresponding amide (2.0 mmol, 1 equiv) in THF (6 mL) was added portionwise NaH (96 mg, 2.4 mmol, 1.2 equiv, 60% Wt) at 0 °C. After stirring for 15 min at the same temperature, the corresponding electrophile (MeI or R–X, 2.4 mmol, 1.2 equiv) was added. Then, the mixture was gradually warmed to rt and stirred for an additional 5 h. After reaction completion, the mixture was quenched by H_2O (10 mL), and extracted with EtOAc (3×10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by automated flash column chromatography using hexanes/EtOAc mixtures.

***N*-(2-Cyanoethyl)-*N*-phenylmethacrylamide (1k)**



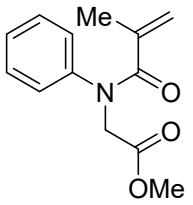
The title compound **1k** was obtained according to *Procedure in 4.1* (from 322 mg, 2.00 mmol 1.0 equiv) of aniline as a colorless oil (310 mg, 1.45 mmol, 73%) after purification by automated flash column chromatography (0-10% EtOAc in hexanes).

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 7.27 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 4.96 (s, 1H), 4.94 (s, 1H) 3.91 (t, *J* = 6.9 Hz, 2H), 2.61 (t, *J* = 7.0 Hz, 2H), 1.63 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 142.4, 140.0, 129.6, 127.7, 127.3, 120.4, 117.9, 45.9, 20.0, 16.2.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1650, 1625, 1595, 1493, 1389, 1370, 1285, 1230, 1191, 1064. **HRMS** (EI) calcd for $C_{13}H_{14}N_2O$ [M]: 214.1106, found 214.1098.

Methyl *N*-Methacryloyl-*N*-phenylglycinate (1l)



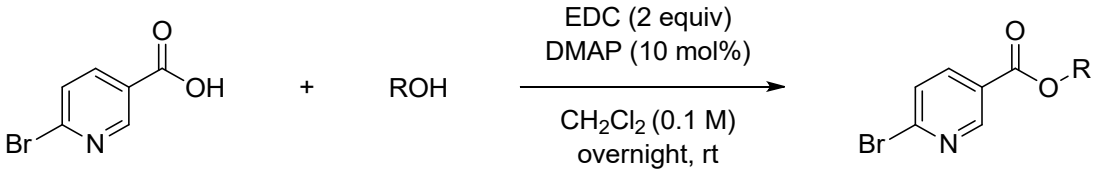
The title compound **1l** was obtained according to *Procedure in 4.1* (from 322 mg, 2.00 mmol 1.0 equiv) of aniline as a colorless oil (440 mg, 1.89 mmol, 94%) after purification by automated flash column chromatography (0-10% EtOAc in hexanes).

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.19 (m, 3H), 5.07 (s, 2H), 4.45 (s, 2H), 3.74 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 172.1, 169.5, 143.5, 139.9, 129.3, 127.4, 127.2, 120.3, 52.2, 51.5, 20.1.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1750, 1649, 1595, 1493, 1368, 1206, 1176, 1074. **HRMS** (EI) calcd for $C_{13}H_{15}NO_3$ [M]: 233.1052, found 233.1049.

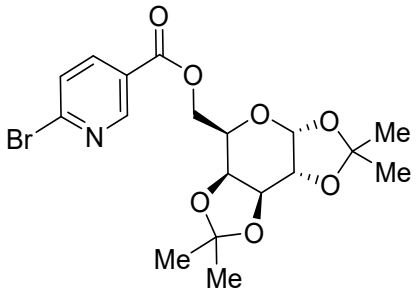
4.2. Synthesis of Heteroaryl Bromides



The brominated compounds were prepared according to the reported literature procedure:[3] In a 25 mL round-bottom flask, 6-bromonicotinic acid (606 mg, 3.0 mmol), DMAP (12 mg, 0.1 mmol), CH_2Cl_2 (10 mL), *N*,*N*'-diisopropylcarbodiimide (EDC, 383 mg, 2 mmol) and the desired alcohol (1 mmol) were successively added. The mixture was stirred at rt overnight. The reaction was quenched with H_2O and extracted with EtOAc (3 × 30 mL). The organics were combined and dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to automated flash column chromatography using hexanes/EtOAc mixtures.

[3] Huang, J.; Ouyang, L.; Li, J.; Zheng, J.; Yan, W.; Wu, W.; Jiang, H. *Org. Lett*. **2018**, *20*, 5090–5093.

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-*bis*([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 6-bromonicotinate (2q)



The title compound **2q** was obtained according to *Procedure in 4.2* as a white solid (868 mg, 1.95 mmol, 65%) from 288 mg of starting material (3.0 mmol, 1.0 equiv) after automated flash column chromatography (0-35% EtOAc in hexanes). **m.p.** 131.2-134.7 ºC.

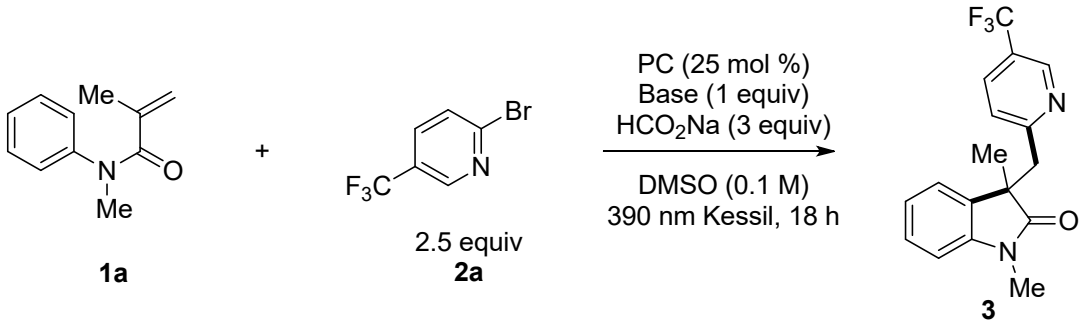
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 8.97 (d, *J* = 2.4 Hz, 1H), 8.12 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 5.55 (d, *J* = 4.9 Hz, 1H), 4.65 (dd, *J* = 7.8, 2.5 Hz, 1H), 4.57 – 4.45 (m, 2H), 4.35 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.29 (d, *J* = 1.9 Hz, 1H), 4.17 (td, *J* = 5.5, 2.8 Hz, 1H), 1.50 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$), δ (ppm) 164.6, 151.7, 147.0, 139.4, 128.2, 125.4, 110.0, 109.0, 96.4, 71.2, 70.9, 70.6, 66.2, 64.8, 26.2, 26.1, 25.1, 24.6.

FT-IR (cm^{-1}, neat, ATR), ṽ = 2988, 1934, 1727, 1580, 1453, 1371, 1288, 1264, 1111. **HRMS** (ESI) calcd for $C_{18}H_{23}BrNO_7$ $[M+H]^+$: 444.0658, found 444.0664.

5. Synthesis of (Hetero)aryl-containing Oxindoles: Reaction Optimization, Workflow, and Compound Characterization

HTE Screening:



		Na_2CO_3	K_2CO_3	Cs_2CO_3	$NaHCO_3$	$KHCO_3$	KH_2PO_4	K_2HPO_4	K_3PO_4	NaOAc	DIPEA	NEt_3	DIPA	No base	No formate No base
		1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***	***10***	***11***	***12***	***13***	***14***
4-methoxythiophenol	***A***	3,2	3,1	3,2	3,3	3,2	0,8	3,0	3,0	3,2	2,8	2,9	3,1	3,1	0,36
4-chlorothiophenol	***B***	2,3	2,8	2,8	2,5	0,8	2,8	2,7	3,2	2,7	2,6	2,7	2,6	2,2	0,36
4-methoxydisulfide	***C***	**3,95**	3,7	**3,9**	**3,9**	**4,3**	3,8	3,0	**3,9**	**3,9**	3,8	3,8	3,8	3,7	0,36
4-chlorodisulfide	***D***	3,3	3,5	2,8	2,95	3,45	3,3	3,3	3,3	2,7	2,7	3,1	3,1	3,4	0,36

Ratio: P/IS

P = Product
IS: 4,4'-di-*tert*-butyl-1,1'-biphenyl

A. Reaction Workflow

All photoredox reactions were performed with Kessil® PR160-390 nm lamps. The Kessil lamp was placed at a distance of 1.5 inches from the reaction vial within a ventilated fume hood. Additionally, two fans were used to ensure that the reaction mixture did not exceed 35 ºC. A typical reaction setup is shown below.

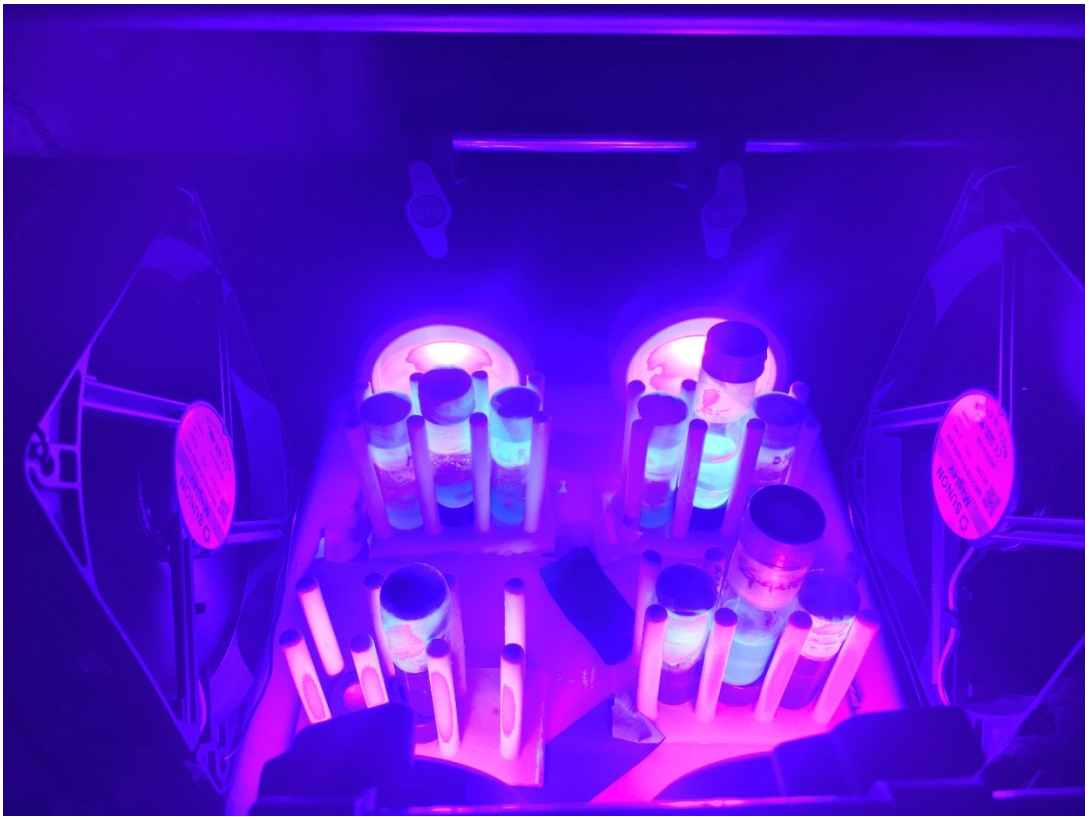
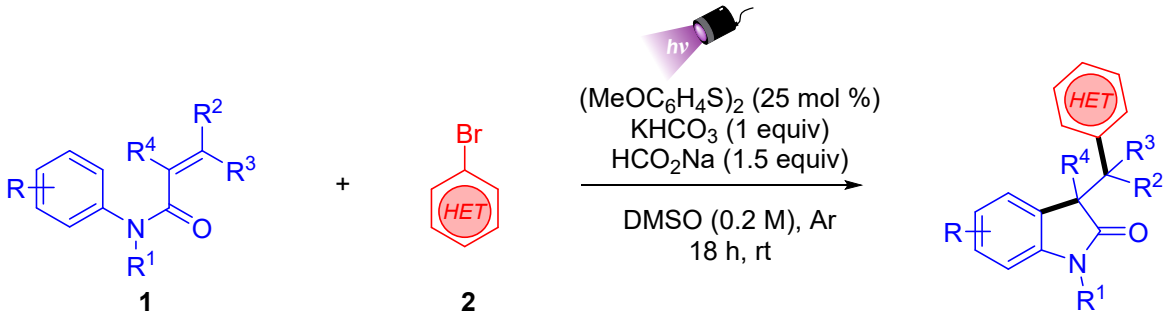


Figure S1. *Model Reaction Setup for the Photochemical Arylation on Acrylamides*

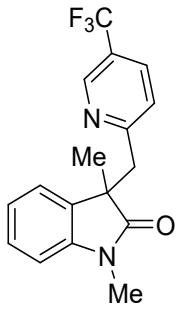
B. General Procedure



To a flame-dried 8 mL vial equipped with a magnetic stir bar were added acryl amide **1** (0.5 mmol, 1.0 equiv), (hetero)aryl bromide (1.25 mmol, 2.5 equiv), *bis*(4-methoxyphenyl) disulfide (35 mg, 0.125 mmol, 25 mol %), potassium bicarbonate (50 mg, 0.5 mmol, 1 equiv), and sodium formate (51 mg, 0.75 mmol, 1.5 equiv), and the vial was subjected to three cycles of vacuum/argon degassing. Subsequently, 2.5 mL of dry DMSO (0.2 M) were added under an inert atmosphere. The reaction was then irradiated with a Kessil® PR160-390 nm lamp at a distance of 1.5 inches as described in the "Workflow" section. The reaction was cooled with two compact fans, ensuring that the surface temperature of the vial did not exceed 35 °C. After 18 h, the reaction was quenched 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), and 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 by automated flash silica column chromatography eluting with hexanes/EtOAc mixtures to afford the desired product.

C. Characterization Data

1,3-Dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (3)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **3** was obtained as a yellow oil (110 mg, 0.35 mmol, 69%).

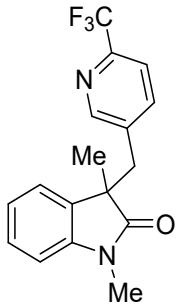
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 8.55 (s, 1H), 7.63 (dd, J = 8.3, 2.4 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 7.05 (d, J = 8.2 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.69 (d, J = 7.8 Hz, 1H), 3.49 (d, J = 13.5 Hz, 1H), 3.29 (d, J = 13.7 Hz, 1H), 3.13 (s, 3H), 1.50 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.8, 161.2, 145.6 (q, $J_{C\text{-}F}$ = 4.0 Hz), 143.0, 132.7 (q, $J_{C\text{-}F}$ = 3.5 Hz), 132.5, 128.0, 124.4 (q, $J_{C\text{-}F}$ = 33.0 Hz), 123.6 (q, $J_{C\text{-}F}$ = 272.5 Hz), 123.4, 123.2, 122.3, 107.9, 48.7, 45.7, 26.2, 23.9.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1708, 1611, 1573, 1493, 1471, 1378, 1251, 1162. **HRMS** (EI) calcd for $C_{17}H_{15}F_3N_2O$ [M]: 320.1136, found 320.1133.

1,3-Dimethyl-3-((6-(trifluoromethyl)pyridin-3-yl)methyl)indolin-2-one (4)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 5-bromo-2-(trifluoromethyl)pyridine **2b** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **4** was obtained as a yellow oil (96 mg, 0.30 mmol, 60%).

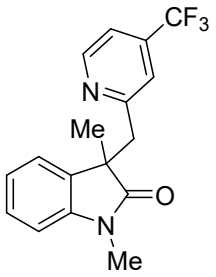
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.14 (d, J = 1.6 Hz, 1H), 7.36 (d, J = 1.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.07 (t, J = 7.5 Hz, 1H), 6.64 (d, J = 7.7 Hz, 1H), 3.23 (d, J = 13.2 Hz, 1H), 3.06 (d, J = 13.2 Hz, 1H), 2.97 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.0, 151.0, 146.6 (q, $J_{C\text{-}F}$ = 34.6 Hz), 143.0, 138.5, 135.3, 131.8, 128.7, 123.1, 122.9, 121.7 (q, $J_{C\text{-}F}$ = 274.1 Hz), 119.5 (q, $J_{C\text{-}F}$ = 2.7 Hz), 108.5, 49.9, 41.4, 26.1, 23.3.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -67.9.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1705, 1612, 1492, 1453, 1378, 1257, 1174. **HRMS** (ESI) calcd for $C_{17}H_{16}F_3O$ $[M+H]^+$: 321.1215, found 321.1205.

1,3-Dimethyl-3-((4-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (5)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv), and 2-bromo-4-(trifluoromethyl)pyridine **2c** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **5** was obtained as a yellow oil (124 mg, 0.38 mmol, 77%).

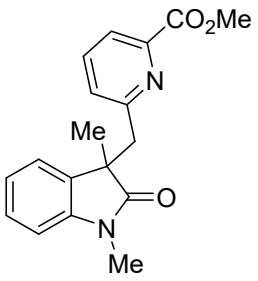
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.45 (d, J = 5.2 Hz, 1H), 7.12 – 7.05 (m, 3H), 7.09 (s, 1H), 6.98 (t, J = 7.0 Hz, 1H), 6.63 (dt, J = 7.7, 0.8 Hz, 1H), 3.50 (d, J = 13.5 Hz, 1H), 3.28 (d, J = 13.4 Hz, 1H), 3.09 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.2, 158.8, 149.8, 143.1, 138.1 (q, $J_{C\text{-}F}$ = 34.0 Hz), 132.5, 128.2, 123.5, 122.9 (q, $J_{C\text{-}F}$ = 273.1 Hz), 122.5, 119.4 (q, $J_{C\text{-}F}$ = 3.6 Hz), 117.2 (q, $J_{C\text{-}F}$ = 3.6 Hz), 108.0, 49.1, 46.2, 26.2, 23.6.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -64.9.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1704, 1611, 1492, 1453, 1378, 1256, 1175. **HRMS** (EI) calcd for $C_{17}H_{15}F_3O$ [M]: 320.1136, found 320.1150.

Methyl 6-((1,3-Dimethyl-2-oxoindolin-3-yl)methyl)picolinate (6)



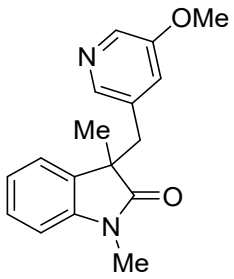
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and methyl 6-bromopicolinate **2d** (270 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **6** was obtained as a yellow oil (90 mg, 0.29 mmol, 58%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 7.79 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.18 – 7.14 (m, 3H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 3.90 (s, 3H), 3.52 (d, *J* = 14.0 Hz, 1H), 3.35 (d, *J* = 13.9 Hz, 1H), 3.14 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.1, 165.7, 157.6, 147.0, 143.1, 136.6, 132.8, 127.7, 126.9, 123.4, 122.9, 122.1, 107.7, 52.6, 48.6, 45.3, 26.1, 23.9.

FT-IR (cm^{-1}, neat, ATR), ṽ = 1808, 1455, 1316, 1267, 1193, 1114, 1078. **HRMS** (ESI) calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$: 311.1396, found 311.1396.

3-((5-Methoxypyridin-3-yl)methyl)-1,3-dimethylindolin-2-one (7)



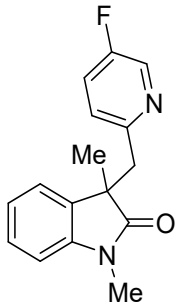
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 3-bromo-5-methoxypyridine **2e** (235 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **7** was obtained as a yellow oil (90 mg, 0.32 mmol, 64%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.02 (d, *J* = 2.8 Hz, 1H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.08 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.70 – 6.61 (m, 2H), 3.64 (s, 3H), 3.14 (d, *J* = 13.2 Hz, 1H), 3.00 (s, 3H), 2.98 (d, *J* = 13.2 Hz, 1H), 1.50 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.5, 154.9, 143.2, 143.2, 136.5, 132.5, 132.4, 128.3, 123.2, 122.5, 121.1, 108.2, 55.5, 49.9, 41.6, 26.1, 23.1.

FT-IR (cm^{-1}, neat, ATR), ṽ = 2967, 1777, 1708, 1590, 1470, 1378, 1182, 1123. **HRMS** (EI) calcd for $C_{17}H_{18}N_2O_2$ [M]: 282.1368, found 282.1355.

3-((5-Fluoropyridin-2-yl)methyl)-1,3-dimethylindolin-2-one (8)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-fluoropyridine **2f** (220 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **8** was obtained as a yellow oil (53 mg, 0.20 mmol, 40%).

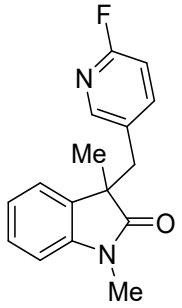
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.13 (d, J = 2.9 Hz, 1H), 7.16 (td, J = 7.7, 1.3 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.99 (t, J = 7.6 Hz, 1H), 6.90 (dd, J = 8.6, 4.4 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 3.38 (d, J = 13.4 Hz, 1H), 3.19 (d, J = 13.5 Hz, 1H), 3.10 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.0, 158.2 (d, $J_{C\text{-}F}$ = 254.5 Hz), 153.0 (d, $J_{C\text{-}F}$ = 4.2 Hz), 142.9, 136.7 (d, $J_{C\text{-}F}$ = 23.2 Hz), 132.7, 127.8, 124.5 (d, $J_{C\text{-}F}$ = 3.9 Hz), 123.3, 122.4 (d, $J_{C\text{-}F}$ = 18.1 Hz), 122.2, 107.8, 49.0, 45.2, 26.1, 23.5.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -130.5.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2966, 1709, 1612, 1483, 1471, 1377, 1249, 1123. **HRMS** (ESI) calcd for $C_{16}H_{16}FN_2O$ $[M+H]^+$: 271.1247, found 271.1249.

3-((6-Fluoropyridin-3-yl)methyl)-1,3-dimethylindolin-2-one (9)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 5-bromo-2-fluoropyridine **2g** (220 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column

chromatography (0-25% EtOAc in hexanes), the title compound **9** was obtained as a yellow oil (59 mg, 0.22 mmol, 44%).

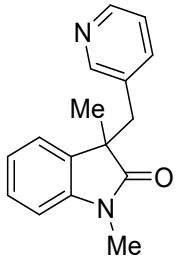
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.64 (d, J = 2.7 Hz, 1H), 7.33 – 7.25 (m, 1H), 7.22 (t, J = 7.2 Hz, 2H), 7.08 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 6.68 – 6.59 (m, 2H), 3.17 (d, J = 13.3 Hz, 1H), 3.00 – 2.97 (m, 4H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 179.2, 162.5 (d, $J_{C\text{-}F}$ = 238.0 Hz), 148.1 (d, $J_{C\text{-}F}$ = 14.5 Hz), 143.0, 142.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 132.0, 129.4 (d, $J_{C\text{-}F}$ = 4.5 Hz), 128.4, 122.9, 122.6, 108.2 (d, $J_{C\text{-}F}$ = 37.2 Hz), 108.2, 49.8, 40.6, 25.9, 22.9.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -130.5.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1704, 1611, 1594, 1470, 1395, 1375, 1245, 1123. **HRMS** (ESI) calcd for $C_{16}H_{16}FN_2O$ $[M+H]^+$: 271.1247, found 271.1261.

1,3-Dimethyl-3-(pyridin-3-ylmethyl)indolin-2-one (10)



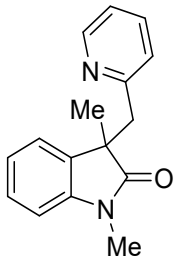
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 3-bromopyridine **2h** (197 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **10** was obtained as a yellow oil (63 mg, 0.25 mmol, 50%).

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 8.30 (dd, J = 4.8, 1.7 Hz, 1H), 8.04 (d, J = 2.3 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.06 (t, J = 7.6 Hz, 1H), 6.98 (dd, J = 7.9, 4.8 Hz, 1H), 6.62 (d, J = 7.7 Hz, 1H), 3.14 (d, J = 13.3 Hz, 1H), 3.00 – 2.98 (m, 4H), 1.50 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.5, 150.8, 148.0, 143.1, 137.2, 132.3, 131.8, 128.3, 123.2, 122.6, 122.6, 108.2, 49.9, 41.8, 26.0, 23.0.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1703, 1611, 1470, 1376, 1251, 1123. **HRMS** (EI) calcd for $C_{16}H_{16}N_2O$ [M]: 252.1263, found 252.1271.

1,3-Dimethyl-3-(pyridin-2-ylmethyl)indolin-2-one (11)



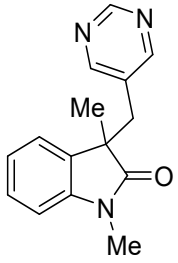
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 2-bromopyridine **2i** (197 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **11** was obtained as a yellow oil (50 mg, 0.20 mmol, 40%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.29 – 8.26 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 7.08 (dd, *J* = 7.4, 0.7 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.62 (s, 1H), 3.36 (d, *J* = 13.3 Hz, 1H), 3.19 (d, *J* = 13.3 Hz, 1H), 3.09 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.2, 157.1, 148.7, 143.0, 135.6, 133.0, 127.7, 123.9, 123.5, 122.2, 121.5, 107.7, 49.0, 46.1, 26.2, 23.5.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1704, 1611, 1590, 1469, 1376, 1248, 1122. **HRMS** (EI) calcd for $C_{16}H_{16}N_2O$ [M]: 252.1263, found 252.1273.

1,3-Dimethyl-3-(pyrimidin-5-ylmethyl)indolin-2-one (12)



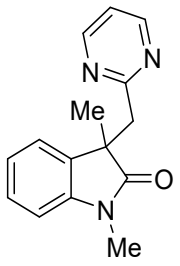
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 5-bromopyrimidine **2j** (198 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-100% EtOAc in hexanes), the title compound **12** was obtained as a yellow oil (58 mg, 0.23 mmol, 46%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.83 (s, 1H), 8.12 (s, 2H), 7.18 – 7.14 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 3.09 (d, *J* = 13.4 Hz, 1H), 3.10 – 2.88 (m, 4H), 1.45 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 178.7, 157.3, 157.2, 142.9, 131.4, 129.6, 128.7, 122.9, 122.8, 108.3, 49.5, 39.0, 26.0, 22.9.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1703, 1611, 1559, 1470, 1408, 1377, 1247, 1123. **HRMS** (EI) calcd for $C_{15}H_{15}N_3O$ [M]: 253.1215, found 253.1220.

1,3-Dimethyl-3-(pyrimidin-2-ylmethyl)indolin-2-one (13)



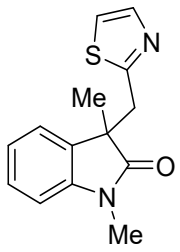
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 2-bromopyrimidine **2k** (198 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-100% EtOAc in hexanes), the title compound **13** was obtained as a yellow oil (56 mg, 0.22 mmol, 44%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.39 (d, *J* = 4.8 Hz, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.69 (d, *J* = 7.7 Hz, 1H), 3.68 (d, *J* = 14.8 Hz, 1H), 3.42 (d, *J* = 14.8 Hz, 1H), 3.21 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.7, 167.1, 156.5, 143.6, 133.1, 127.6, 122.7, 122.0, 118.6, 107.6, 47.6, 46.4, 26.3, 24.6.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1709, 1611, 1560, 1492, 1376, 1249, 1123. **HRMS** (EI) calcd for $C_{15}H_{15}N_3O$ [M]: 253.1215, found 253.1226.

1,3-Dimethyl-3-(thiazol-2-ylmethyl)indolin-2-one (14)



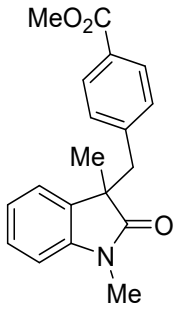
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 2-bromothiazole **2l** (205 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-80% EtOAc in hexanes), the title compound **14** was obtained as a yellow oil (47 mg, 0.18 mmol, 36%).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 7.53 (d, *J* = 3.3 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 6.0 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.73 (dd, *J* = 7.7, 0.9 Hz, 1H), 3.61 (d, *J* = 14.4 Hz, 1H), 3.51 (d, *J* = 14.4 Hz, 1H), 3.15 (s, 3H), 1.52 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.4, 165.0, 143.2, 141.8, 132.1, 128.2, 123.4, 122.6, 118.9, 108.0, 48.7, 40.7, 26.3, 23.6.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1703, 1612, 1470, 1451, 1377, 1249, 1123. **HRMS** (ESI) calcd for $C_{14}H_{15}N_2OS$ $[M+H]^+$: 259.0905, found 259.0916.

Methyl 4-((1,3-Dimethyl-2-oxoindolin-3-yl)methyl)benzoate (15)



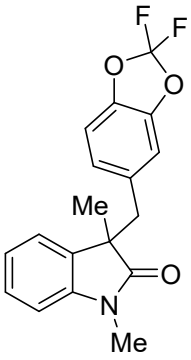
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and methyl 4-bromobenzoate **2m** (268 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-100% EtOAc in hexanes), the title compound **15** was obtained as a yellow oil (57 mg, 0.19 mmol, 37%).

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 7.71 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.13 (m, 2H), 7.07 – 7.01 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.60 (d, *J* = 7.8 Hz, 1H), 3.84 (s, 3H), 3.20 (d, *J* = 12.8 Hz, 1H), 3.06 (s, 1H), 2.97 (s, 3H), 1.49 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.5, 167.1, 143.1, 141.7, 132.5, 129.8, 128.8, 128.3, 128.0, 123.1, 122.2, 107.9, 52.0, 49.9, 44.4, 25.9, 23.0.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1708, 1610, 1469, 1376, 1275, 1180, 1105. **HRMS** (EI) calcd for $C_{19}H_{19}NO_3$ [M]: 309.1365, found 309.1379.

3-((2,2-Difluorobenzo[*d*][1,3]dioxol-5-yl)methyl)-1,3-dimethylindolin-2-one (16)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 5-bromo-2,2-difluorobenzo[*d*][1,3]dioxole **2n** (296 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-25% EtOAc in hexanes), the title compound **16** was obtained as a yellow oil (61 mg, 0.15 mmol, 30%).

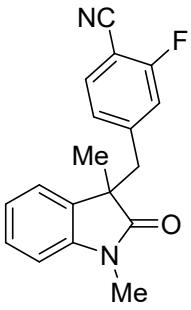
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 7.24 – 7.15 (m, 2H), 7.09 – 7.03 (m, 1H), 6.72 (d, J = 8.6 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 6.56 (d, J = 6.4 Hz, 2H), 3.14 (d, J = 13.3 Hz, 1H), 3.01 (s, 3H), 2.98 (d, J = 13.2 Hz, 1H), 1.46 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.5, 143.1, 143.0, 142.3, 131.8, 131.5 (t, $J_{C\text{-}F}$ = 254.3 Hz), 128.1, 125.1, 124.9, 123.0, 122.4, 110.8, 108.4, 108.1, 50.0, 44.1, 26.0, 23.1.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -50.0 (d, J = 97.8 Hz, 1F), -50.3 (d, J = 97.8 Hz, 1F).

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1708, 1611, 1573, 1470, 1380, 1249, 1220, 1163. **HRMS** (EI) calcd for $C_{18}H_{15}F_2NO_3$ [M]: 331.1020, found 331.1027.

4-((1,3-Dimethyl-2-oxoindolin-3-yl)methyl)-2-fluorobenzonitrile (17)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (88 mg, 0.50 mmol, 1.0 equiv) and 4-bromo-2-fluorobenzonitrile **2o** (250 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-100% EtOAc in hexanes), the title compound **17** was obtained as a yellow oil (73 mg, 0.25 mmol, 51%).

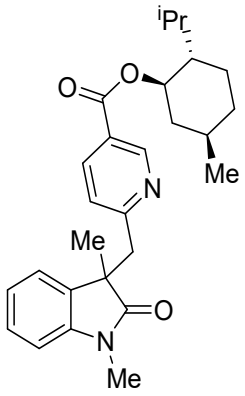
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 7.32 – 7.24 (m, 1H), 7.23 (d, J = 7.4 Hz, 2H), 7.10 (td, J = 7.4, 1.0 Hz, 1H), 6.76 (dd, J = 8.0, 1.6 Hz, 1H), 6.72 – 6.64 (m, 2H), 3.25 (d, J = 12.9 Hz, 1H), 3.04 (d, J = 12.9 Hz, 1H), 3.02 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 178.9, 162.4 (d, $J_{C\text{-}F}$ = 258.6 Hz), 145.3 (d, $J_{C\text{-}F}$ = 7.9 Hz), 143.0, 132.4, 131.8, 128.6, 126.3 (d, $J_{C\text{-}F}$ = 3.3 Hz), 122.9, 122.7, 117.5 (d, $J_{C\text{-}F}$ = 19.6 Hz), 114.1, 108.4, 99.5 (d, $J_{C\text{-}F}$ = 15.5 Hz), 49.9, 44.3 (d, $J_{C\text{-}F}$ = 1.7 Hz), 26.1, 23.4.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -107.3.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2951, 2221, 1704, 1612, 1568, 1470, 1377, 1115. **HRMS** (ESI) calcd for $C_{18}H_{16}FN_2O$ $[M+H]^+$: 295.1247, found 295.1237.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 6-(((*R/S*)-1,3-dimethyl-2-oxoindolin-3-yl)methyl)nicotinate (18)



Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (35 mg, 0.20 mmol, 1.0 equiv) and 2-isopropyl-5-methylcyclohexyl 6-bromonicotinate **2p** (136 mg, 0.40 mmol, 2.0 equiv). After purification by automated flash column chromatography (0-60% EtOAc in hexanes), the title compound **18** was obtained as a yellow oil (50 mg, 0.12 mmol, 58%). Compound **18** was formed as an inseparable mixture of diastereomers in a 1:1 ratio as determined in the crude reaction mixture by ^{1}H NMR (dia A = diastereoisomer A; dia B = diastereoisomer B).

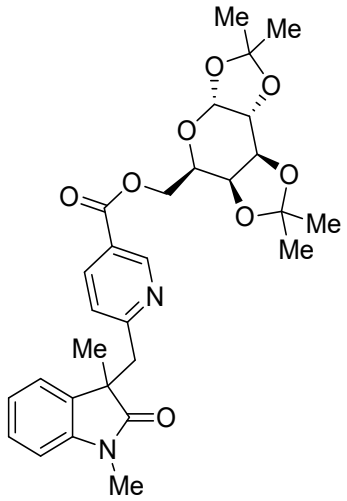
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.89 (bs, 1H), 8.01 (dd, J = 7.8, 2.1 Hz, 1H), 7.20 – 7.11 (m, 2H), 7.04 – 6.95 (m, 2H), 6.73 – 6.63 (m, 1H), 4.89 – 4.85 (m, 1H), 3.47 (dd, J = 13.5, 7.6 Hz, 1H), 3.36 – 3.26 (m, 1H), 3.15

(s, 3H, dia A), 3.12 (s, 3H, dia B), 2.08 – 2.05 (m, 1H), 1.86 (dd, *J* = 2.8, 1.1 Hz, 1H), 1.74 – 1.67 (m, 2H), 1.52 – 1.49 (m, 5H), 1.14 – 1.01 (m, 2H), 0.94 – 0.84 (m, 7H), 0.75 – 0.73 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.1, 180.0, 164.9, 161.4, 149.9, 143.2, 143.1, 137.1, 132.8, 132.7, 128.1, 128.0, 124.7, 123.6, 123.5, 123.4, 122.5, 122.4, 108.0, 75.6, 75.5, 49.0, 48.8, 47.3, 45.7, 41.0, 41.0, 34.4, 31.6, 26.7, 26.6, 26.4, 26.3, 24.1, 24.1, 23.8, 23.7, 22.2, 20.9, 20.8, 16.7, 16.6.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2955, 2927, 1709, 1613, 1596, 1469, 1376, , 1276, 1118. **HRMS** (ESI) calcd for $C_{27}H_{35}N_2O_3$ $[M+H]^+$: 435.2648, found 435.2642.

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 6-(((*R/S*)-1,3-Dimethyl-2-oxoindolin-3-yl)methyl)nicotinate (19)



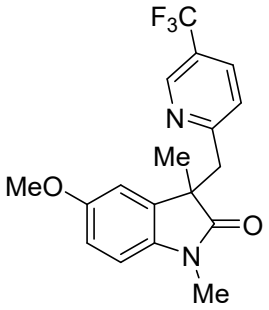
Prepared according to the *General Procedure* from the corresponding acrylamide **1a** (70 mg, 0.40 mmol, 1.0 equiv) and pyridine **2q** (343 mg, 0.8 mmol, 2.0 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **19** was obtained as a yellow oil (88 mg, 0.17 mmol, 42%). Compound **19** was formed as a mixture of inseparable diastereomers in a 1:1 ratio as determined in the crude reaction mixture by ^{1}H NMR (dia A = diastereoisomer A; dia B = diastereoisomer B).

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.89 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.03 – 6.92 (m, 2H), 6.65 (dd, *J* = 7.6, 1.0 Hz, 1H), 5.52 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.62 (ddd, *J* = 7.9, 2.5, 0.7 Hz, 1H), 4.46 – 4.39 (m, 2H), 4.32 (ddd, *J* = 5.0, 2.5, 1.6 Hz, 1H), 4.26 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.11 (ddd, *J* = 7.1, 4.9, 1.9 Hz, 1H), 3.47 (d, *J* = 13.4 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 3.12 (s, 3H, dia A), 3.11 (s, 3H, dia B), 1.49 – 1.47 (m, 6H), 1.44 (s, 3H), 1.31 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.9, 165.3, 161.8, 150.0, 143.1, 137.1, 132.6, 128.0, 128.0, 123.9, 123.5, 123.4, 122.4, 122.4, 109.8, 108.9, 108.0, 96.4, 71.2, 70.8, 70.6, 66.2, 66.1, 64.3, 48.9, 45.9, 26.3, 26.3, 26.2 26.1, 25.1, 24.6, 24.0, 24.0.

FT-IR (cm^{-1}, neat, ATR), ṽ = 2955, 2927, 1709, 1613, 1596, 1469, 1376, 1276, 1118. **HRMS** (ESI) calcd for $C_{29}H_{35}N_2O_8$ $[M+H]^+$: 539.2393, found 539.2402.

5-Methoxy-1,3-dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (20)



Prepared according to the *General Procedure* from the corresponding acrylamide **1b** (103 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **20** was obtained as a yellow oil (88 mg, 0.25 mmol, 49%).

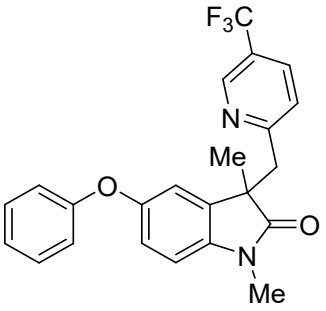
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.59 – 8.55 (m, 1H), 7.64 (dd, J = 8.2, 2.6 Hz, 1H), 7.06 (d, J = 8.2 Hz, 1H), 6.73 (d, J = 2.5 Hz, 1H), 6.70 (dd, J = 8.4, 2.5 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 3.75 (s, 3H), 3.47 (d, J = 13.7 Hz, 1H), 3.26 (d, J = 13.7 Hz, 1H), 3.11 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.6, 161.3, 155.9, 145.8 (q, $J_{C\text{-}F}$ = 4.4 Hz), 136.7, 134.1, 132.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.5 (q, $J_{C\text{-}F}$ = 32.7 Hz), 123.6 (q, $J_{C\text{-}F}$ = 273.1 Hz), 123.5, 112.1, 111.0, 108.2, 55.9, 49.1, 45.7, 26.4, 24.1.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), ṽ = 1703, 1605, 1470, 1375, 1289, 1225, 1163. **HRMS** (ESI) calcd for $C_{18}H_{18}F_3N_2O_2$ $[M+H]^+$: 351.1320, found 351.1321.

1,3-Dimethyl-5-phenoxy-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (21)



Prepared according to the *General Procedure* from the corresponding acrylamide **1c** (134 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **21** was obtained as a yellow oil (99 mg, 0.24 mmol, 48%).

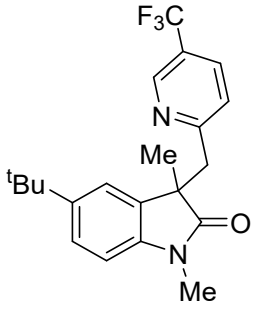
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 8.55 (s, 1H), 7.65 (dd, J = 8.4, 2.1 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.08 – 7.04 (m, 2H), 6.88 – 6.82 (m, 4H), 6.65 (d, J = 8.8 Hz, 1H), 3.50 (d, J = 13.6 Hz, 1H), 3.24 (d, J = 13.6 Hz, 1H), 3.15 (s, 3H), 1.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 179.9, 161.3, 158.8, 151.9, 145.8 (q, $J_{C\text{-}F}$ = 4.1 Hz), 139.4, 134.3, 133.0 (q, $J_{C\text{-}F}$ = 3.4 Hz), 129.8, 124.6 (q, $J_{C\text{-}F}$ = 33.0 Hz), 123.7 (q, $J_{C\text{-}F}$ = 272.2 Hz), 123.4, 122.8, 119.6, 117.6, 116.5, 108.7, 49.3, 45.7, 26.6, 24.1.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.3.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1703, 1603, 1470, 1434, 1355, 1289, 1160. **HRMS** (ESI) calcd for $C_{23}H_{20}F_3N_2O_2$ $[M+H]^+$: 413.1477, found 413.1492.

5-(*tert*-Butyl)-1,3-dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (22)



Prepared according to the *General Procedure* from the corresponding acrylamide **1d** (109 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **22** was obtained as a yellow oil (85 mg, 0.31 mmol, 62%).

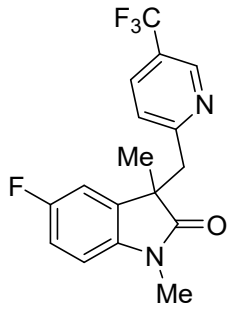
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 8.60 – 8.58 (m, 1H), 7.64 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.18 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.07 – 7.00 (m, 2H), 6.62 (d, *J* = 8.2 Hz, 1H), 3.41 (d, *J* = 13.3 Hz, 1H), 3.29 (d, *J* = 13.3 Hz, 1H), 3.14 (s, 3H), 1.51 (s, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 180.0, 161.4, 145.5 (q, $J_{C\text{-}F}$ = 4.0 Hz), 145.4, 140.5, 132.6 (q, $J_{C\text{-}F}$ = 3.6 Hz), 132.0, 124.9 (q, $J_{C\text{-}F}$ = 33.1 Hz), 124.4, 123.6, 122.9 (q, $J_{C\text{-}F}$ = 273.1 Hz), 120.9, 107.2, 48.8, 45.6, 34.5, 31.5, 26.2, 23.5.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), ṽ = 2955, 1706, 1620, 1604, 1466, 1375, 1163, 1127. **HRMS** (ESI) calcd for $C_{21}H_{24}F_3N_2O$ $[M+H]^+$: 377.1841, found 377.1842.

5-Fluoro-1,3-dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (23)



Prepared according to the *General Procedure* from the corresponding acrylamide **1e** (97 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (283 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **23** was obtained as a yellow oil (98 mg, 0.29 mmol, 58%).

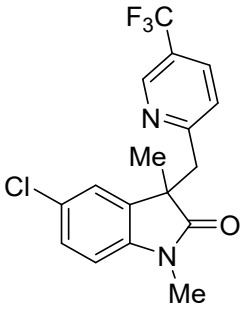
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.56 – 8.48 (m, 1H), 7.64 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.96 – 6.81 (m, 2H), 6.58 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.48 (d, *J* = 13.9 Hz, 1H), 3.25 (d, *J* = 13.9 Hz, 1H), 3.10 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.5, 160.8, 159.1 (d, $J_{C\text{-}F}$ = 240.3 Hz), 145.6 (q, $J_{C\text{-}F}$ = 4.2 Hz), 139.0 (d, $J_{C\text{-}F}$ = 1.8 Hz), 134.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 132.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 124.5 (q, $J_{C\text{-}F}$ = 33.2 Hz), 123.5 (q, $J_{C\text{-}F}$ = 272.2 Hz), 123.3, 114.1 (d, $J_{C\text{-}F}$ = 23.5 Hz), 111.3 (d, $J_{C\text{-}F}$ = 24.6 Hz), 108.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 49.0, 45.4, 26.3, 23.9.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4 (s, 3 F), -120.8 (s, 1F).

FT-IR (cm^{-1}, neat, ATR), ṽ = 1708, 1607, 1470, 1377, 1325, 1278, 1163. **HRMS** (EI) calcd for $C_{17}H_{14}F_4N_2O$ [M]: 338.1042, found 338.1042.

5-Chloro-1,3-dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (24)



Prepared according to the *General Procedure* from the corresponding acrylamide **1f** (103 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **24** was obtained as a yellow oil (109 mg, 0.31 mmol, 62%).

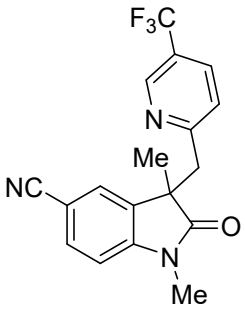
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 8.54 (s, 1H), 7.67 (dd, J = 8.6, 2.1 Hz, 1H), 7.20 – 7.09 (m, 3H), 6.61 (d, J = 8.2 Hz, 1H), 3.51 (d, J = 14.0 Hz, 1H), 3.28 (d, J = 14.0 Hz, 1H), 3.13 (s, 3H), 1.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 179.6, 160.8, 145.7 (q, $J_{C\text{-}F}$ = 4.2 Hz), 141.9, 134.6, 133.2 (q, $J_{C\text{-}F}$ = 3.5 Hz), 127.9, 127.8, 124.8 (q, $J_{C\text{-}F}$ = 11.3 Hz), 123.8, 123.4 (q, $J_{C\text{-}F}$ = 261.2 Hz), 123.5, 108.9, 48.8, 45.4, 26.4, 24.1.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1710, 1608, 1466, 1377, 1274, 1163, 1127. **HRMS** (ESI) calcd for $C_{17}H_{15}ClF_3N_2O$ $[M+H]^+$: 355.0825, found 355.0816.

1,3-Dimethyl-2-oxo-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indoline-5-carbonitrile (25)



Prepared according to the *General Procedure* from the corresponding acrylamide **1g** (100 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-100% EtOAc in hexanes), the title compound **25** was obtained as a white solid (73 mg, 0.21 mmol, 42%). mp = 165-168 °C.

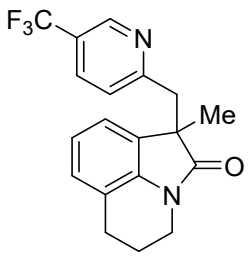
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.48 (dd, *J* = 1.5, 0.9 Hz, 1H), 7.69 (dd, *J* = 8.2, 3.1 Hz, 1H), 7.51 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.39 (dd, *J* = 1.6, 0.5 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 3.58 (d, *J* = 14.5 Hz, 1H), 3.32 (d, *J* = 14.5 Hz, 1H), 3.20 (s, 3H), 1.50 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.9, 160.4, 147.4, 145.9 (q, $J_{C\text{-}F}$ = 4.1 Hz), 134.0, 133.5, 133.3 (q, $J_{C\text{-}F}$ = 3.5 Hz), 126.4, 124.9 (q, $J_{C\text{-}F}$ = 33.0 Hz), 123.5 (q, $J_{C\text{-}F}$ = 268.4 Hz), 123.3, 119.4, 108.4, 105.4, 48.1, 45.1, 26.6, 24.3.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), ṽ = 2222, 1723, 1614, 1461, 1370, 1253, 1164. **HRMS** (ESI) calcd for $C_{18}H_{15}F_3N_3O$ $[M+H]^+$: 346.1167, found 346.1167.

1-Methyl-1-((5-(trifluoromethyl)pyridin-2-yl)methyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1*H*)-one (26)



Prepared according to the *General Procedure* from the corresponding acrylamide **1h** (101 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **26** was obtained as a yellow oil (83 mg, 0.24 mmol, 48%).

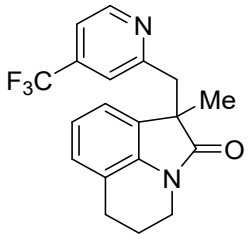
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 8.57 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.73 – 7.59 (m, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.98 – 6.83 (m, 3H), 3.68 – 3.56 (m, 2H), 3.45 (d, *J* = 13.4 Hz, 1H), 3.28 (d, *J* = 13.5 Hz, 1H), 2.74 – 2.55 (m, 2H), 1.99 – 1.90 (m, 1H), 1.78 – 1.69 (m, 1H), 1.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 178.7, 161.4, 145.5 (q, $J_{C\text{-}F}$ = 4.2 Hz), 138.8, 132.9 (q, $J_{C\text{-}F}$ = 3.5 Hz), 131.1, 126.9, 124.6 (q, $J_{C\text{-}F}$ = 33.1 Hz), 123.8, 123.7 (q, $J_{C\text{-}F}$ = 272.1 Hz), 121.9, 121.2, 120.1, 50.2, 45.7, 38.9, 24.6, 23.4, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), ṽ = 1701, 1626, 1603, 1573, 1481, 1373, 1296, 1241, 1162, 1123. **HRMS** (EI) calcd for $C_{19}H_{17}F_3N_2O$ [M]: 346.1293, found 346.1300.

1-Methyl-1-((4-(trifluoromethyl)pyridin-2-yl)methyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1*H*)-one (27)



Prepared according to the *General Procedure* from the corresponding acrylamide **1h** (101 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-4-(trifluoromethyl)pyridine **2c** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **27** was obtained as a yellow oil (97 mg, 0.28 mmol, 56%).

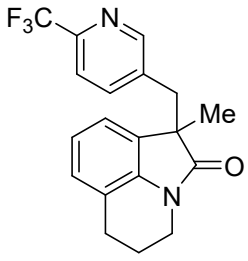
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 8.48 (d, J = 5.2 Hz, 1H), 7.18 (dd, J = 4.5, 0.8 Hz, 1H), 7.10 (d, J = 0.9 Hz, 1H), 6.94 (dd, J = 6.8, 1.8 Hz, 1H), 6.91 – 6.84 (m, 2H), 3.71 – 3.55 (m, 2H), 3.48 (d, J = 13.3 Hz, 1H), 3.29 (d, J = 13.3 Hz, 1H), 2.75 – 2.62 (m, 2H), 2.01 – 1.92 (m, 1H), 1.77 – 1.66 (m, 1H), 1.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 178.5, 158.8, 149.4, 138.6, 137.9 (q, $J_{C\text{-}F}$ = 33.9 Hz), 130.8, 126.7, 122.7 (q, $J_{C\text{-}F}$ = 273.2 Hz), 121.7, 121.1, 119.9, 119.2 (q, $J_{C\text{-}F}$ = 3.8 Hz), 116.9 (q, $J_{C\text{-}F}$ = 3.7 Hz), 50.1, 45.9, 38.8, 24.4, 23.0, 21.0.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -64.9.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1696, 1627, 1601, 1480, 1462, 1374, 1245, 1218, 1165. **HRMS** (ESI) calcd for $C_{19}H_{18}F_3N_2O$ $[M+H]^+$: 347.1371, found 347.1360.

1-Methyl-1-((6-(trifluoromethyl)pyridin-3-yl)methyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1*H*)-one (28)



Prepared according to the *General Procedure* from the corresponding acrylamide **1h** (108 mg, 0.50 mmol, 1.0 equiv) and 5-bromo-2-(trifluoromethyl)pyridine **2b** (282 mg, 1.25 mmol, 2.5 equiv). After purification by

automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **28** was obtained as a yellow oil (80 mg, 0.23 mmol, 46%).

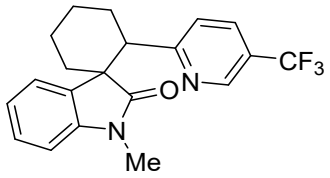
^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 8.14 (s, 1H), 7.37 (d, J = 1.5 Hz, 2H), 7.04 (dd, J = 5.2, 3.4 Hz, 1H), 6.95 (d, J = 5.2 Hz, 2H), 3.65 – 3.34 (m, 2H), 3.20 (d, J = 13.1 Hz, 1H), 3.04 (d, J = 13.1 Hz, 1H), 2.70 – 2.54 (m, 2H), 1.99 – 1.85 (m, 1H), 1.53 – 1.45 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm) 177.6, 150.8, 146.3 (q, $J_{C\text{-}F}$ = 34.6 Hz), 138.6, 138.4, 135.3, 130.2, 127.3, 122.2, 121.6 (q, $J_{C\text{-}F}$ = 273.9 Hz), 120.7, 120.4, 119.2 (q, $J_{C\text{-}F}$ = 2.8 Hz), 51.0, 41.5, 38.6, 24.4, 22.5, 21.0.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -67.8.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1699, 1627, 1600, 1462, 1409, 1374, 1250, 1218, 1165. **HRMS** (ESI) calcd for $C_{19}H_{18}F_3N_2O$ $[M+H]^+$: 347.1371, found 347.1376.

1'-Methyl-2-(5-(trifluoromethyl)pyridin-2-yl)spiro[cyclohexane-1,3'-indolin]-2'-one (29)



Prepared according to the *General Procedure* from the corresponding acrylamide **1i** (108 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-25% EtOAc in hexanes), the title compound **29** was obtained as a yellow oil (35 mg, 0.10 mmol, 20%). During isolation, the minor diastereomer eluted with the impurities, and the yield of the product was determined considering the mass of the major diastereomer only.

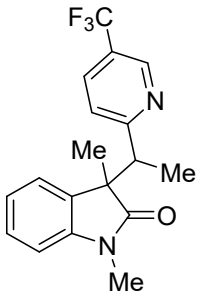
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.43 (s, 1H), 7.68 (d, J = 6.1 Hz, 1H), 7.53 (dd, J = 8.3, 2.5 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 7.7 Hz, 1H), 3.56 (dd, J = 13.3, 3.8 Hz, 1H), 3.00 (s, 3H), 2.43 (qd, J = 13.5, 3.8 Hz, 1H), 2.15 (ddt, J = 13.3, 8.8, 4.7 Hz, 2H), 2.02 – 1.85 (m, 3H), 1.72 (dt, J = 13.3, 4.1 Hz, 1H) 1.67 – 1.61 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.6, 164.6, 145.0 (q, $J_{C\text{-}F}$ = 4.0 Hz), 142.9, 132.3 (q, $J_{C\text{-}F}$ = 3.4 Hz), 131.3, 127.7, 125.6, 124.2 (q, $J_{C\text{-}F}$ = 33.0 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.9 Hz), 121.9, 121.7, 107.7, 52.9, 49.7, 34.2, 26.2, 26.1, 25.3, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2934, 1709, 1609, 1571, 1470, 1376, 1250, 1163, 1128. **HRMS** (ESI) calcd for $C_{20}H_{20}F_3N_2O$ $[M+H]^+$: 361.1528, found 361.1520.

1,3-Dimethyl-3-(1-(5-(trifluoromethyl)pyridin-2-yl)ethyl)indolin-2-one (30)



Prepared according to the *General Procedure* from the corresponding acrylamide **1j** (95 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **30** was obtained as a yellow oil (62 mg, 0.19 mmol, 37%). Compound **30** was formed as a mixture of inseparable diastereomers in a 2:1 ratio as determined in the crude reaction mixture by ^{1}H NMR (dia A = diastereoisomer A; dia B = diastereoisomer B).

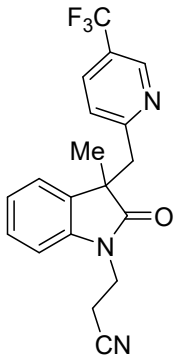
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.78 (s, 1H, dia A), 8.59 (s, 1H, dia B), 7.77 (dd, *J* = 8.2, 2.4 Hz, 1H, dia A), 7.69 (dd, *J* = 8.4, 2.4 Hz, 1H, dia B), 7.29 (dd, *J* = 7.4, 1.2 Hz, 1H, dia B), 7.26 – 7.19 (m, 2H), 7.13 – 7.02 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H, dia A), 6.74 (d, *J* = 7.7 Hz, 1H, dia A), 6.67 (d, *J* = 7.7 Hz, 1H, dia B), 3.59 – 3.52 (m, 1H), 3.20 (s, 3H, dia A), 3.00 (s, 3H, dia B), 1.41 (bs, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.0, 179.7, 166.2, 165.6, 145.8 (d, $J_{C\text{-}F}$ = 4.1 Hz), 145.1 (q, $J_{C\text{-}F}$ = 4.1 Hz), 143.4, 143.2, 132.9 (q, $J_{C\text{-}F}$ = 3.5 Hz), 132.6 (q, $J_{C\text{-}F}$ = 2.9 Hz), 132.1, 128.2, 128.1, 124.8, 124.6 (q, $J_{C\text{-}F}$ = 11.9 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272.3 Hz), 123.7, 123.6, 123.0, 122.5, 122.2, 107.9, 51.7, 51.4, 48.7, 48.5, 26.3, 26.0, 22.6, 21.6, 15.2, 14.7.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2971, 2934, 1709, 1606, 1572, 1471, 1395, 1257, 1126, 1082. **HRMS** (EI) calcd for $C_{18}H_{17}F_3N_2O$ [M]: 334.1293, found 334.1305.

3-(3-Methyl-2-oxo-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-1-yl)propanenitrile (31)



Prepared according to the *General Procedure* from the corresponding acrylamide **1k** (107 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **31** was obtained as a yellow oil (54 mg, 0.15 mmol, 30%).

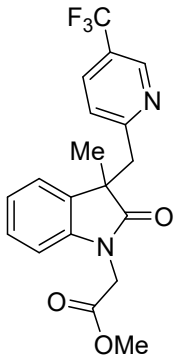
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.52 (s, 1H), 7.66 (dd, J = 8.3, 2.4 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 7.16 (dd, J = 7.7, 0.8 Hz, 1H), 7.06 (d, J = 8.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 4.07 (ddd, J = 13.8, 7.4, 6.2 Hz, 1H), 3.89 (dt, J = 14.2, 7.1 Hz, 1H), 3.58 (d, J = 14.3 Hz, 1H), 3.32 (d, J = 14.3 Hz, 1H), 2.74 – 2.64 (m, 2H), 1.51 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.2, 161.0, 145.7 (q, $J_{C\text{-}F}$ = 4.1 Hz), 141.3, 133.1 (q, $J_{C\text{-}F}$ = 3.5 Hz), 132.7, 128.3, 124.8 (q, $J_{C\text{-}F}$ = 33.1 Hz), 123.6 (q, $J_{C\text{-}F}$ = 272.1 Hz), 123.5, 123.4, 123.0, 117.4, 108.0, 48.2, 45.5, 36.1, 24.7, 16.2.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2927, 1712, 1609, 1573, 1452, 1376, 1248, 1168, 1125. **HRMS** (EI) calcd for $C_{19}H_{16}F_3N_3O$ [M]: 359.1245, found 359.1247.

Methyl 2-(3-Methyl-2-oxo-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-1-yl)acetate (32)



Prepared according to the *General Procedure* from the corresponding acrylamide **1l** (117 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **32** was obtained as a yellow oil (83 mg, 0.22 mmol, 44%).

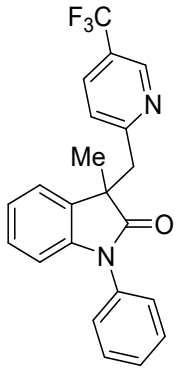
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 8.58 (s, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 6.5 Hz, 2H), 7.08 (d, J = 8.2 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.62 – 6.55 (m, 1H), 4.44 (d, J = 17.5 Hz, 1H), 4.39 (d, J = 17.6 Hz, 1H), 3.70 (s, 3H), 3.53 (d, J = 13.9 Hz, 1H), 3.34 (d, J = 13.8 Hz, 1H), 1.53 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.8, 168.0, 160.9, 145.7 (q, J_{C-F} = 4.3 Hz), 141.7, 133.1 (q, J_{C-F} = 3.6 Hz), 132.4, 128.1, 124.3 (q, J_{C-F} = 32.9 Hz), 123.7, 123.7 (q, J_{C-F} = 261.6 Hz), 123.5, 122.8, 108.2, 52.6, 48.8, 45.4, 41.2, 24.5.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ =1731, 1608, 1490, 1380, 1240, 1164, 1126, 1078. **HRMS** (ESI) calcd for $C_{19}H_{18}F_3N_2O_3$ $[M+H]^+$: 379.1220, found 379.1281.

3-Methyl-1-phenyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (33)



Prepared according to the *General Procedure* from the corresponding acrylamide **1m** (119 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by

automated flash column chromatography (0-50% EtOAc in hexanes), the title compound **33** was obtained as a yellow oil (101 mg, 0.26 mmol, 53%).

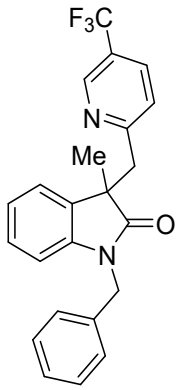
^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm) 8.57 (s, 1H), 7.66 (dd, J = 8.2, 2.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.27 – 7.23 (m, 3H), 7.14 – 7.02 (m, 3H), 6.66 (d, J = 7.8 Hz, 1H), 3.65 (d, J = 13.8 Hz, 1H), 3.38 (d, J = 13.9 Hz, 1H), 1.64 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.3, 161.2, 145.7 (q, $J_{C\text{-}F}$ = 4.1 Hz), 143.2, 134.7, 133.0 (q, $J_{C\text{-}F}$ = 3.5 Hz), 132.5, 129.7, 128.0, 128.0, 126.4, 124.9 (q, $J_{C\text{-}F}$ = 33.0 Hz), 123.7 (q, $J_{C\text{-}F}$ = 272.1 Hz), 123.6, 123.4, 122.9, 109.3, 48.8, 46.2, 24.5.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1716, 1606, 1596, 1481, 1466, 1376, 1299, 1202, 1161, 1123. **HRMS** (ESI) calcd for $C_{22}H_{18}F_3N_2O$ $[M+H]^+$: 383.1366, found 383.1371.

1-Benzyl-3-methyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (34)



Prepared according to the *General Procedure* from the corresponding acrylamide **1n** (127 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-30% EtOAc in hexanes), the title compound **33** was obtained as an oil (115 mg, 0.29 mmol, 58%).

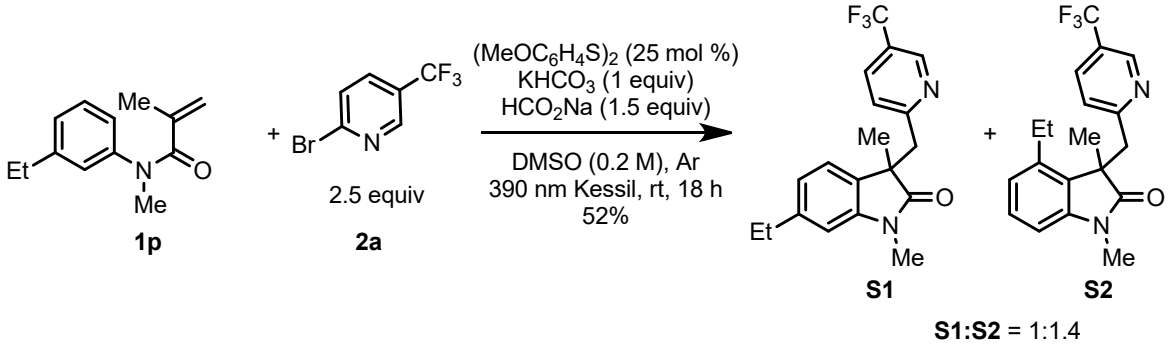
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.44 (s, 1H), 7.55 (dd, J = 8.2, 2.4 Hz, 1H), 7.25 – 7.23 (m, 3H), 7.21 (d, J = 7.4 Hz, 1H), 7.11 – 7.06 (m, 3H), 7.03 (d, J = 8.2 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 4.99 (d, J = 15.6 Hz, 1H), 4.68 (d, J = 15.6 Hz, 1H), 3.59 (d, J = 13.6 Hz, 1H), 3.35 (d, J = 13.7 Hz, 1H), 1.56 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.7, 160.9, 145.5 (q, $J_{C\text{-}F}$ = 4.6 Hz), 142.1, 135.8, 133.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 132.4, 128.6, 127.9, 127.6, 127.4, 124.5 (q, $J_{C\text{-}F}$ = 25.6 Hz), 123.5 (q, $J_{C\text{-}F}$ = 272.2 Hz), 123.6, 123.2, 122.4, 109.0, 48.8, 45.3, 43.8, 24.9.

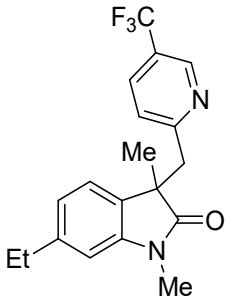
^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -64.8.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 1708, 1611, 1573, 1471, 1378, 1221, 1162. **HRMS** (EI) calcd for $C_{23}H_{19}F_3N_2O$ [M]: 396.1449, found 396.1461.

We examined the reaction with meta substituted acrylamide and standard aryl bromide. Gratifyingly, we observed the product formation with 52% yield, however, the regioselectivity was 1:1.4 (**S1**:**S2**) based on ^{1}H NMR analysis of crude reaction mixture.



6-Ethyl-1,3-dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (S1)



Prepared according to the *General Procedure* from the corresponding acrylamide **1p** (102 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-40% EtOAc in hexanes), the title compound **S1** was obtained as an oil (38 mg, 0.11 mmol, 22%).

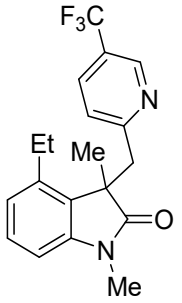
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.58 (dd, J = 2.4, 0.9 Hz, 1H), 7.64 (dd, J = 8.2, 2.6 Hz, 1H), 7.06 (d, J = 8.3 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.84 – 6.82 (m, 1H), 6.53 (s, 1H), 3.44 (d, J = 13.4 Hz, 1H), 3.27 (d, J = 13.4 Hz, 1H), 3.12 (s, 3H), 2.61 (q, J = 7.6 Hz, 2H), 1.48 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.2, 161.4, 145.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 144.7, 143.2, 132.8 (q, $J_{C\text{-}F}$ = 3.3 Hz), 129.8, 124.5 (q, $J_{C\text{-}F}$ = 32.7 Hz), 123.7 (q, $J_{C\text{-}F}$ = 272.3 Hz), 123.7, 123.2, 121.8, 107.8, 48.6, 45.9, 29.3, 26.3, 23.9, 15.7.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), ṽ = 1709, 1619, 1573, 1468, 1379, 1324, 1162. 1123. **MS** (ESI) calcd for $C_{19}H_{19}F_3N_2O$ $[M+H]^+$: 349.1528, found 349.1460.

4-Ethyl-1,3-dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (S2)



Prepared according to the *General Procedure* from the corresponding acrylamide **1p** (102 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (282 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (0-40% EtOAc in hexanes), the title compound **S2** was obtained as an oil (53 mg, 0.15 mmol, 30%).

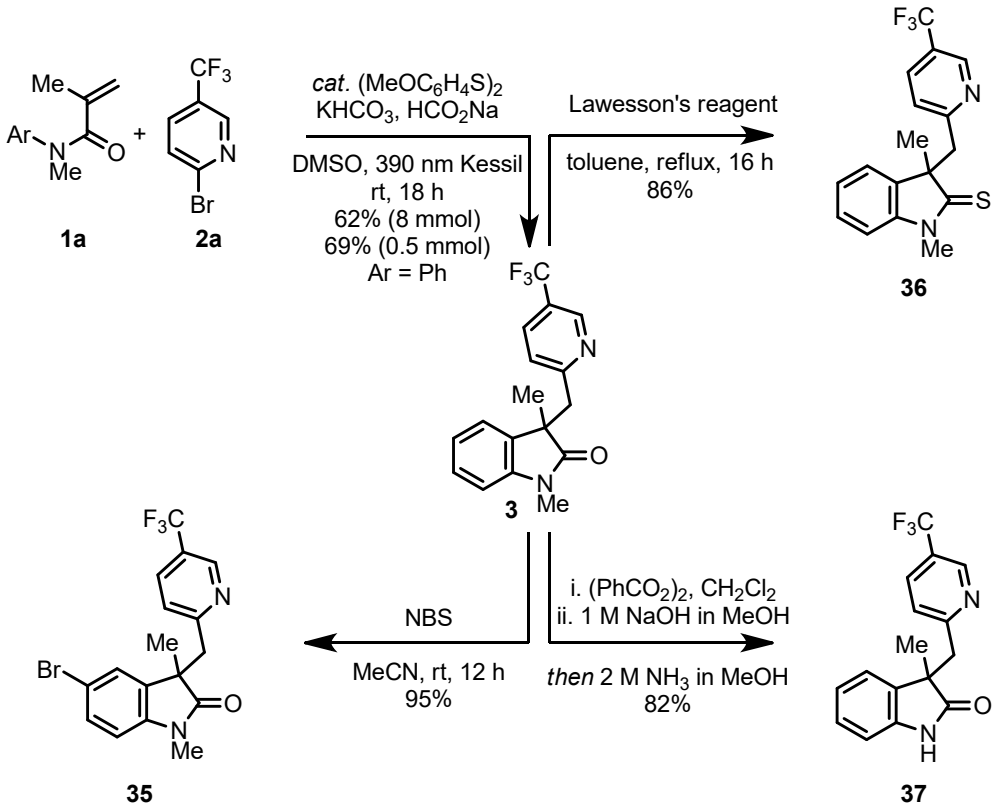
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.52 – 8.46 (m, 1H), 7.57 (dd, J = 8.2, 2.6 Hz, 1H), 7.11 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.83 (d, J = 7.9 Hz, 1H), 6.53 – 6.44 (m, 1H), 3.62 (d, J = 13.9 Hz, 1H), 3.47 (d, J = 13.9 Hz, 1H), 3.11 (s, 3H), 2.86 – 2.76 (m, 2H), 1.60 (s, 3H), 1.28 (t, J = 7.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 180.0, 161.5, 145.7 (q, J_{C-F} = 4.4 Hz), 143.3, 140.8, 132.7 (q, J_{C-F} = 3.3 Hz), 128.8, 128.1, 124.4 (q, J_{C-F} = 32.7 Hz), 123.7 (q, J_{C-F} = 272.3 Hz), 122.7, 122.7, 105.5, 49.8, 45.1, 26.4, 24.7, 23.5, 15.1.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

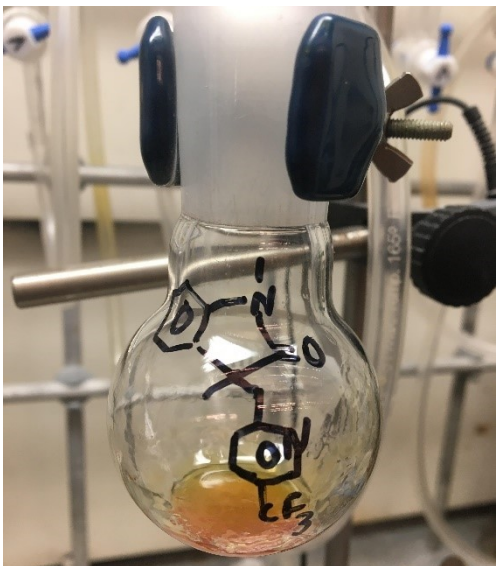
FT-IR (cm^{-1}, neat, ATR), ṽ = 1713, 1606, 1574, 1468, 1376, 1327, 1164. 1128. **MS** (ESI) calcd for $C_{19}H_{19}F_3N_2O$ $[M+H]^+$: 349.1528, found 349.0020.

6. Gram-scale reaction and synthetic application of the (hetero)aryl oxindole 3.

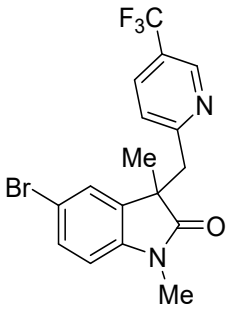


To a 200 mL round-bottomed flask charged with a magnetic stir bar were added acrylamide **1a** (1.41 g, 8.0 mmol, 1.0 equiv), 2-bromo-5-(trifluoromethyl)pyridine **2a** (4.50 g, 20.0 mmol, 2.5 equiv), *bis*(4-methoxyphenyl) disulfide (560 mg, 2.0 mmol, 25 mol %), $KHCO_3$ (800 mg, 8.0 mmol, 1 equiv), and HCO_2Na (816 mg, 12.0 mmol, 1.5 equiv), and the vial was subjected to three cycles of vacuum/argon degassing. Subsequently, 40 mL of dry DMSO (0.2 M) were added under an inert atmosphere. The reaction was then irradiated with four Kessil® PR160-390 nm lamps at a distance of 1.5 inches as shown below. The reaction was cooled with two compact fans, ensuring that the surface temperature of the vial did not exceed 35 °C. After the reaction time, the reaction was quenched with ice-cold H_2O (100 mL) and extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried (Na_2SO_4), and 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 by automated flash silica column chromatography eluting with hexanes/EtOAc mixtures to afford 1.60 g (5.0 mmol, 62% yield) of compound **3**.

Reaction setup



*Isolated compound **3***



To a Schlenk tube oxindole **3** (80 mg, 0.25 mmol, 1 equiv), *N*-bromosuccinimide (NBS) (53 mg, 0.30 mmol, 1.2 equiv) and 2.5 mL of MeCN were added. The reaction mixture was stirred at rt for 12 h. The mixture was quenched with brine and extracted with EtOAc (3 × 5 mL). The organics were combined, dried (anhyd Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by automated flash column chromatography (0-50% EtOAc) to afford compound **35** (95 mg, 0.24 mmol, 95%) as a yellow oil.

The isolated compound **35** was also prepared according to the *General Procedure* from the corresponding acrylamide **1o** (127 mg, 0.50 mmol, 1.0 equiv) and 2-bromo-5-(trifluoromethyl)pyridine **2a** (283 mg, 1.25 mmol, 2.5 equiv). After purification by automated flash column chromatography (from hexanes to 50% EtOAc in hexanes), the title compound **35** was obtained as a yellow oil (105 mg, 0.27 mmol, 54%).

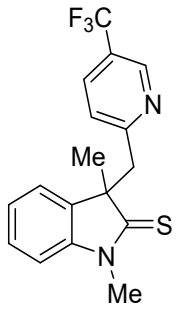
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.53 (d, *J* = 1.0 Hz, 1H), 7.66 (dd, *J* = 8.4, 2.7 Hz, 1H), 7.29 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 3.50 (d, *J* = 14.1 Hz, 1H), 3.26 (d, *J* = 14.1 Hz, 1H), 3.12 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 179.3, 160.7, 145.7 (q, $J_{C\text{-}F}$ = 4.4 Hz), 142.2, 134.8, 132.9 (q, $J_{C\text{-}F}$ = 3.3 Hz), 130.8, 126.3, 124.5 (q, $J_{C\text{-}F}$ = 33.0 Hz), 123.5 (q, $J_{C\text{-}F}$ = 272.5 Hz), 123.3, 114.9, 109.3, 48.6, 45.3, 26.3, 24.0.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), ṽ = 1711, 1605, 1573, 1467, 1418, 1376, 1363, 1273, 1241, 1162, 1122. **HRMS** (EI) calcd for $C_{17}H_{15}BrF_3N_2O$ $[M+H]^+$: 399.0320, found 399.0323.

1,3-Dimethyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indoline-2-thione (36)



Oxindole **3** (80 mg, 0.25 mmol, 1 equiv) and Lawesson's reagent (81 mg, 0.20 mmol, 0.80 equiv) were added to a Schlenk tube under argon. Dry toluene (1 mL) of was added by syringe, and the reaction mixture was heated at reflux for 16 h. After cooling to rt, the mixture was quenched with brine and extracted with EtOAc (3 × 5 mL). The organics were combined, dried (anhyd Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by automated flash column chromatography (0-10% EtOAc) to afford compound **36** (72 mg, 0.21 mmol, 86%) as a light-yellow oil.

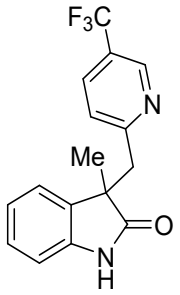
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.45 (s, 1H), 7.60 (dd, J = 8.2, 2.4 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.15 – 7.10 (m, 2H), 6.87 (d, J = 8.4 Hz, 1H), 3.60 (d, J = 13.4 Hz, 1H), 3.54 (s, 3H), 3.48 (d, J = 13.4 Hz, 1H), 1.58 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 209.3, 161.1, 145.4 (q, $J_{C\text{-}F}$ = 4.4 Hz), 144.4, 137.2, 132.7 (q, $J_{C\text{-}F}$ = 3.5 Hz), 128.1, 124.5 (q, $J_{C\text{-}F}$ = 33.0 Hz), 124.1, 124.0, 123.7 (q, $J_{C\text{-}F}$ = 272.5 Hz), 123.6, 109.4, 59.3, 48.7, 31.5, 27.8.

^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.3.

FT-IR (cm^{-1}, neat, ATR), ṽ = 1605, 1466, 1369, 1324, 1159, 1121, 1077, 1016. **HRMS** (ESI) calcd for $C_{17}H_{16}F_3N_2S$ $[M+H]^+$: 337.0986, found 337.0999.

3-Methyl-3-((5-(trifluoromethyl)pyridin-2-yl)methyl)indolin-2-one (37)



Prepared according to a modified reported procedure: To a Schlenk tube oxindole **3** (80 mg, 0.25 mmol, 1 equiv), and benzoyl peroxide (121 mg, 0.50 mmol, 2 equiv) in CH_2Cl_2 (1 mL) were heated at 80 ºC for 18 h. Afterward, the reaction mixture was cooled to rt, and the solvent was removed under a high vacuum. The residue was dissolved in MeOH (1 mL) and NaOH (40 mg, 1 mmol, 4 equiv) and stirred for an additional 18 h at rt. The resulting slurry was then poured onto 10 mL of satd NH_4Cl soln and extracted with CH_2Cl_2 (3 × 15 mL). The organics were combined, dried ($NaSO_4$), and concentrated in a vacuo. The residue was redissolved in 5 mL of methanolic NH_3 solution (2 M) and stirred for 3 h at rt. The solvent was removed under a high vacuum, and the residue was purified by automated flash column chromatography (0-40% EtOAc) to afford compound **37** (63 mg, 0.21 mmol, 82%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) 8.51 – 8.44 (m, 2H), 7.56 (ddd, J = 8.2, 2.4, 0.7 Hz, 1H), 7.07 – 6.99 (m, 3H), 6.90 (td, J = 7.6, 1.1 Hz, 1H), 6.71 (dd, J = 8.0, 1.1 Hz, 1H), 3.44 (d, J = 13.7 Hz, 1H), 3.25 (d, J = 13.7 Hz, 1H), 1.46 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$), δ (ppm) 182.2, 161.0, 145.7 (d, $J_{C\text{-}F}$ = 3.8 Hz), 140.1, 133.0, 132.9 (q, $J_{C\text{-}F}$ = 3.5 Hz), 127.9, 124.5 (q, $J_{C\text{-}F}$ = 32.7 Hz), 123.6 (q, $J_{C\text{-}F}$ = 272.2 Hz), 123.5, 123.4, 122.3, 109.8, 49.2, 45.4, 24.2.

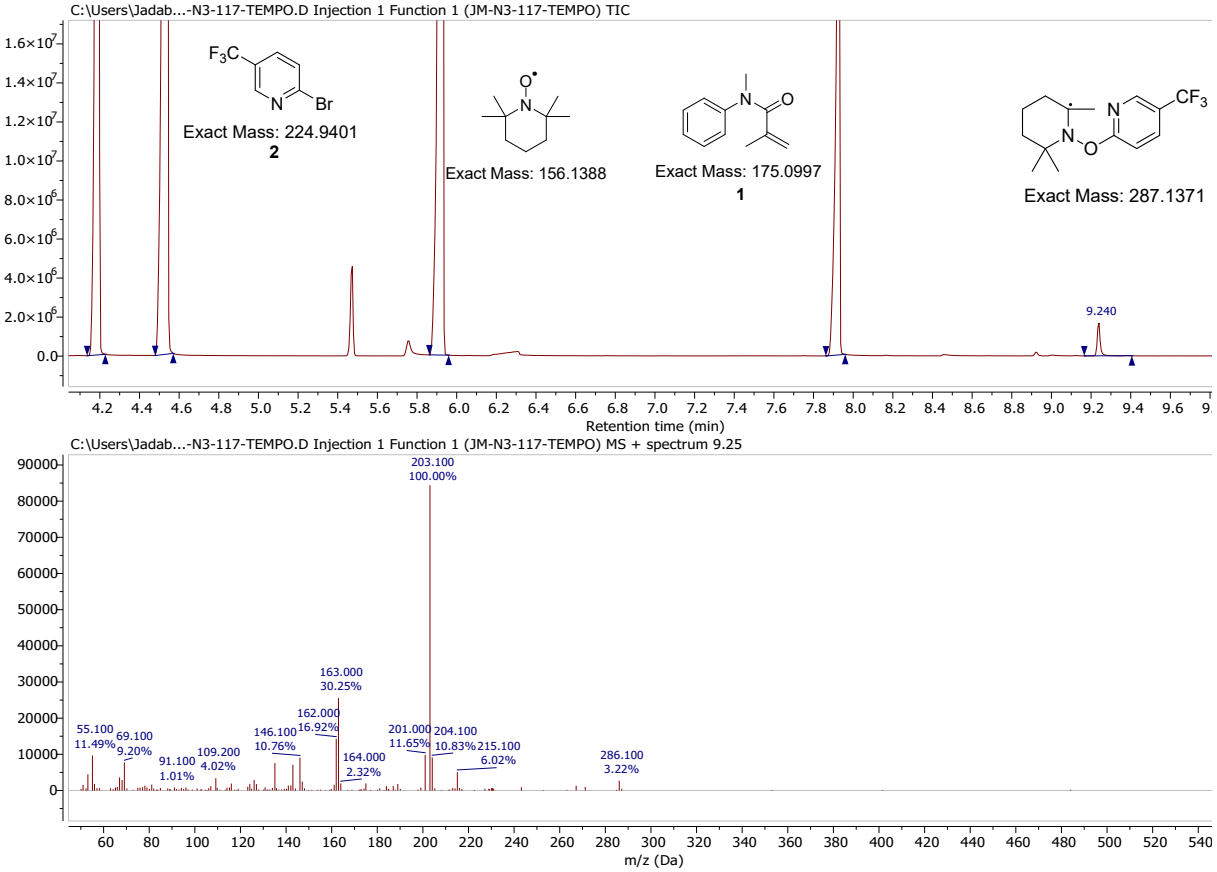
^{19}F NMR (376 MHz, $CDCl_3$), δ (ppm) -62.4.

FT-IR (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3210, 1707, 1619, 1574, 1472, 1324, 1163, 1123, 1078. **HRMS** (ESI) calcd for $C_{16}H_{14}F_3N_2O$ $[M+H]^+$: 307.1058, found 307.1062.

7. Mechanistic Investigations

A. TEMPO experiment

Radical trapping studies were performed following the *General Procedure*. Addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 5 equiv) inhibited the product formation. Specifically, the heteroaryl-TEMPO adduct was detected along with starting materials **1**, **2** and TEMPO by GC/MS.



B. Quantum yield

The quantum yield of the reaction was determined using the procedure reported previously:[4]

The quantum yield of the reaction is defined as:

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

[4] El Khatib, M.; Serafim, R. A. M.; Molander, G. A. *Angew. Chem. Int. Ed.*, **2016**, *55*, 254.

where Φ is the quantum yield of the reaction, t is the time of the reaction(s), and f is the incident light absorbed by all the reaction components at 390 nm. The photon flux is calculated by standard ferrioxalate actinometry[4] (see Section *B.3*).

B.1. Incident light absorbed by the reaction mixture

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 at 438 nm. The wavelength of 438 nm was chosen based on the known absolute $\Phi(Fe^{+2})$[5] value and its close proximity to our wavelength irradiation. The absorbance of the reaction mixture was measured (0.25 M **1a**, 0.625 M **2a**, 0.062 M *bis*(4-methoxyphenyl) disulfide, 0.25 M $KHCO_3$, and 0.37 M HCO_2Na) in DMSO (0.5 mL) to a cuvette equipped with a Teflon-coated magnetic stir bar and stirred for 30 s. The solution was filtered, and the absorbance was recorded. The absorbance (A) at 390 nm was determined to be 2.83 (*Figure S1*), thus indicating the fraction of light absorbed is ~1 according to equation 2.

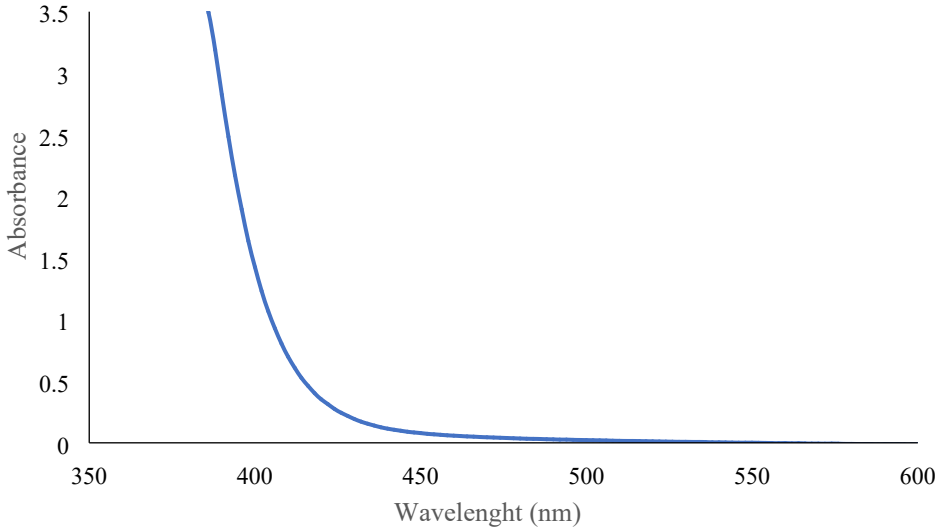


Figure S1. UV-Vis spectra of all reaction components in DMSO

B.2. The photoredox reaction

[5] Demas, J. N.; Bowman, W. D.; Zalewski, E. F.; Velapoidl, R. *J. Phys. Chem.*, **1981**, *85*, 2766.

The photoredox transformation was developed using the general procedure for 45 min (2700 s). Afterwards, 1,3,5-trimethoxybenzene was added as internal standard, and the reaction was worked up. The yield of the reaction was determined by ^{1}H NMR (Figure S2), where 0.025 mmols (25%) of the desired compound were obtained.

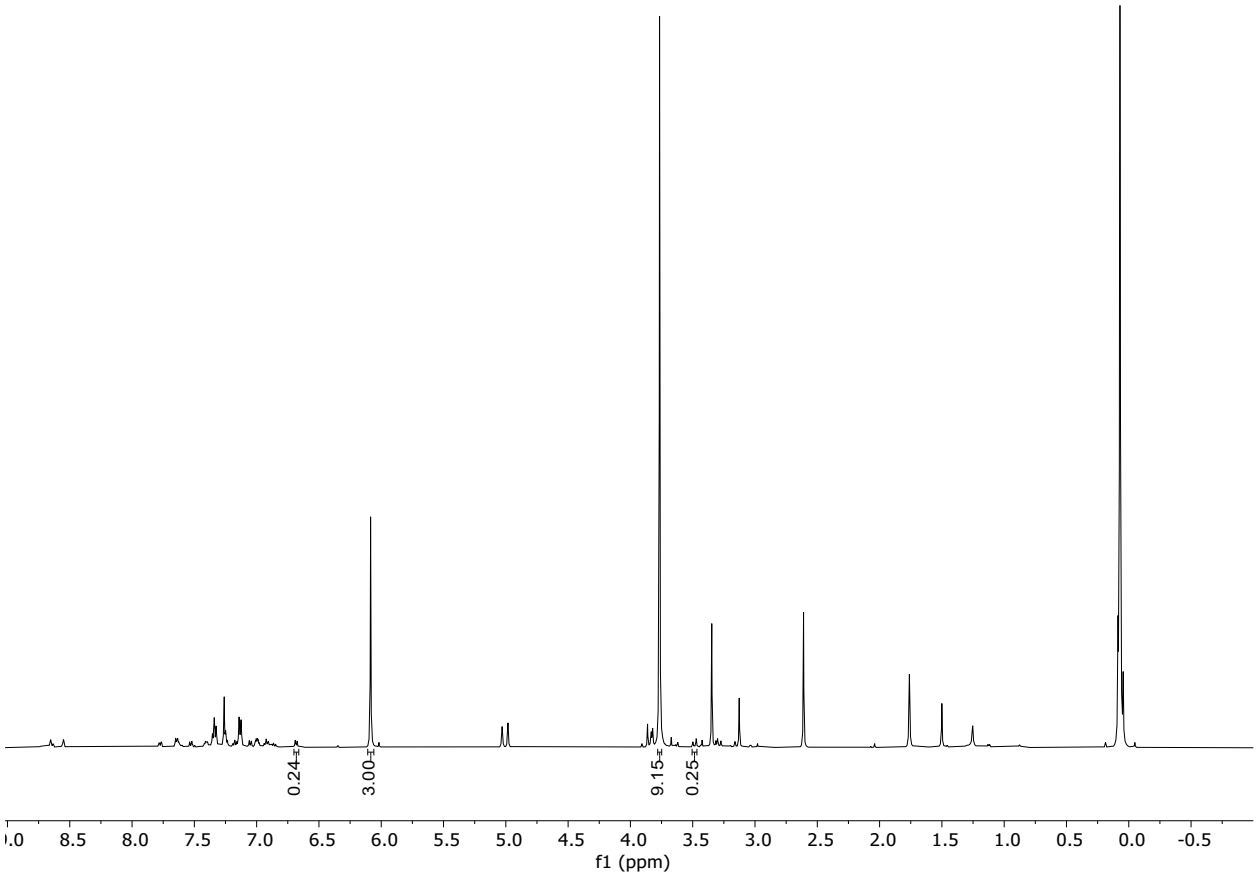


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) of the standard reaction after 45 min in the presence of 1,3,5-trimethoxybenzene as internal standard

B.3. Photon flux at 438 nm

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 through the following reactions:[3]

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

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

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).[2] The photon flux is defined as shown in equation 3:

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

where Φ is the quantum yield for the ferrioxalate actinometer (1.01 at λ = 438 nm),[2] 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), and ε is the molar absorptivity at 510 nm (11110 L mol^{-1} cm^{-1}).[2]

B.4. Experimental

The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

– Ferrioxalate solution (0.15 M): Potassium ferrioxalate hydrate (1.312 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (20 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 (50 mg) and NaOAc (11.25 g) was added to a flask containing H_2SO_4 (50 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 a 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 solution was measured at 510 nm to be 0.13 (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. 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 2.90 (average of two determinations).

Photon flux sample calculation. Sample calculation:

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

$$mol\left(Fe^{+2}\right) = \frac{0.00235\ L \cdot 2.77}{1.0\ cm \cdot 11100\ L \cdot mol^{-1} cm^{-1}} = 5.8x10^{-7} mol$$

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

$$Photon\ flux = \frac{5.8x10^{-7}mol}{1.1 \cdot 30\ s \cdot 1} = 1.78x10^{-8}\ einstein\ s^{-1}$$

B.5. Quantum yield of the photoinduced transformation

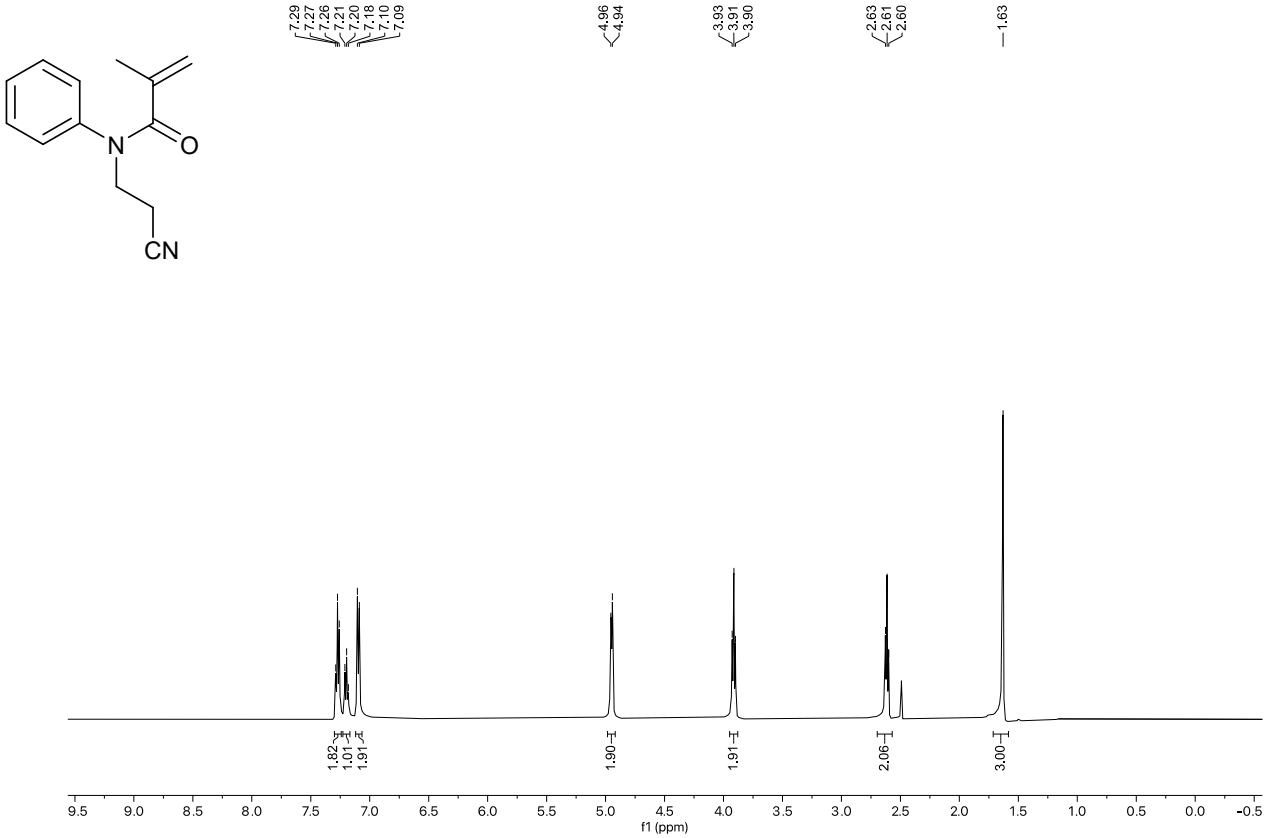
Therefore, the quantum yield of the reaction was determined to be:

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

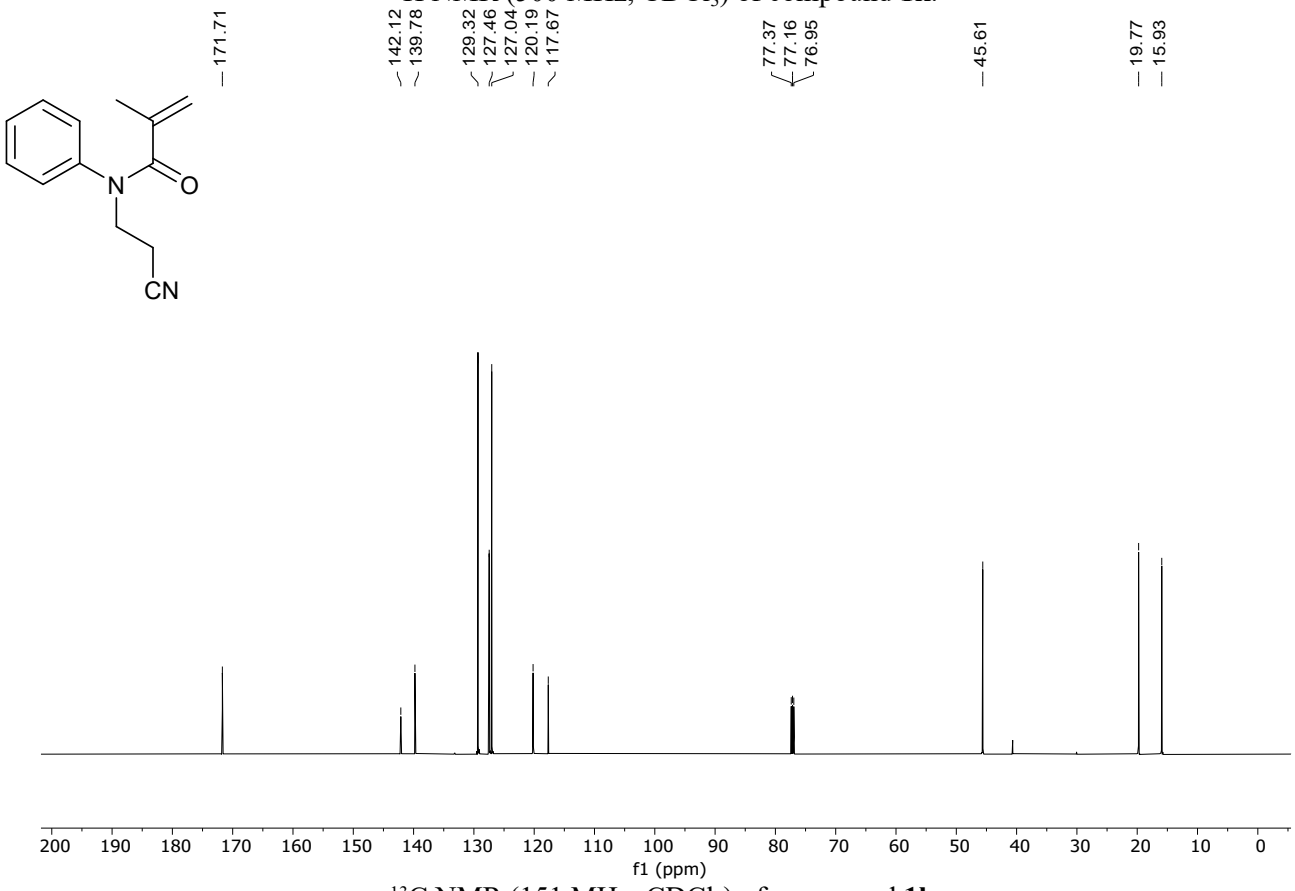
$$\Phi = \frac{2.5x10^{-5}\ mol}{1.78x10^{-8}\ einstein\ s^{-1} \cdot 2700\ s \cdot 1} = 0.53$$

The photochemical quantum yield study indicates that the mechanism is more likely proceeding through a closed catalytic cycle.

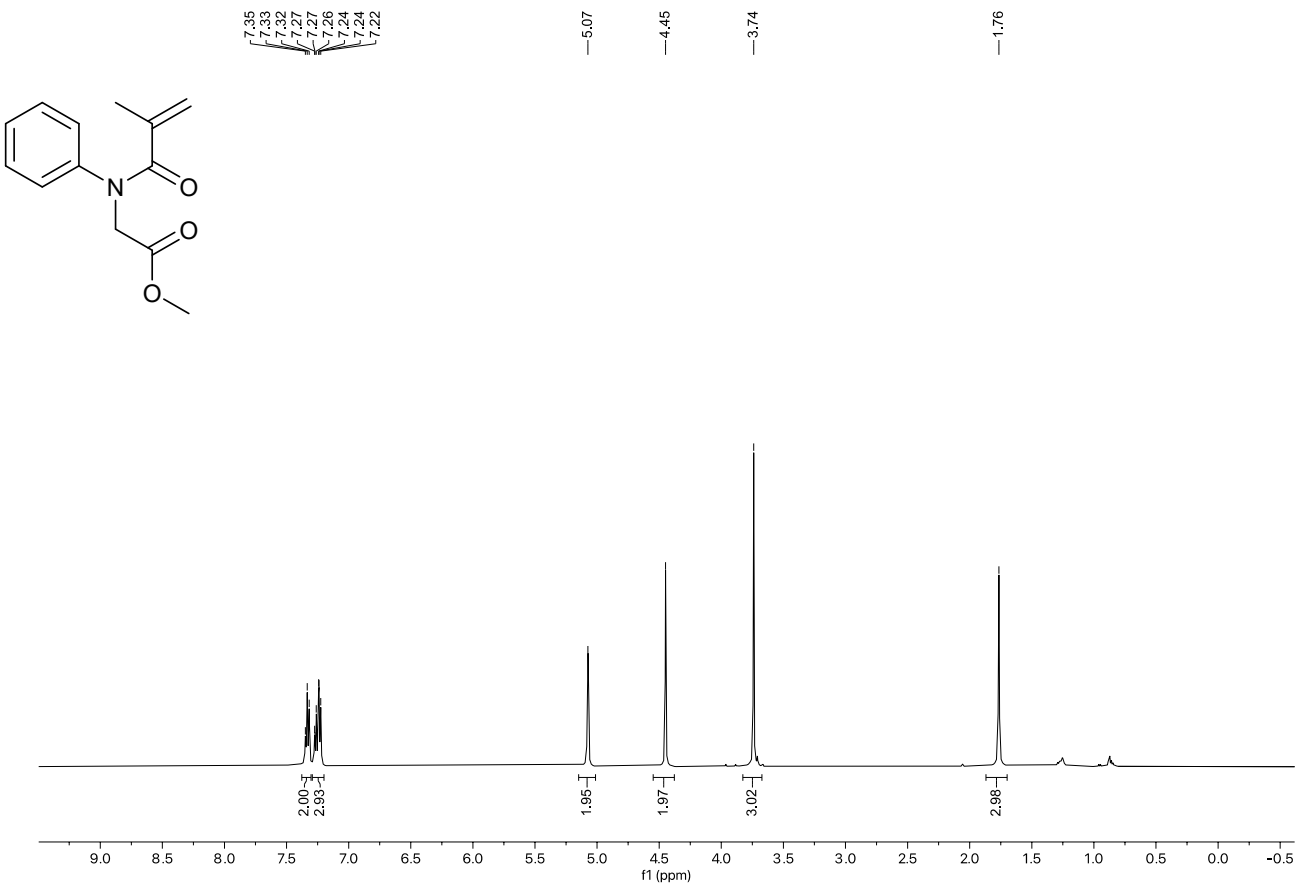
8. NMR spectra



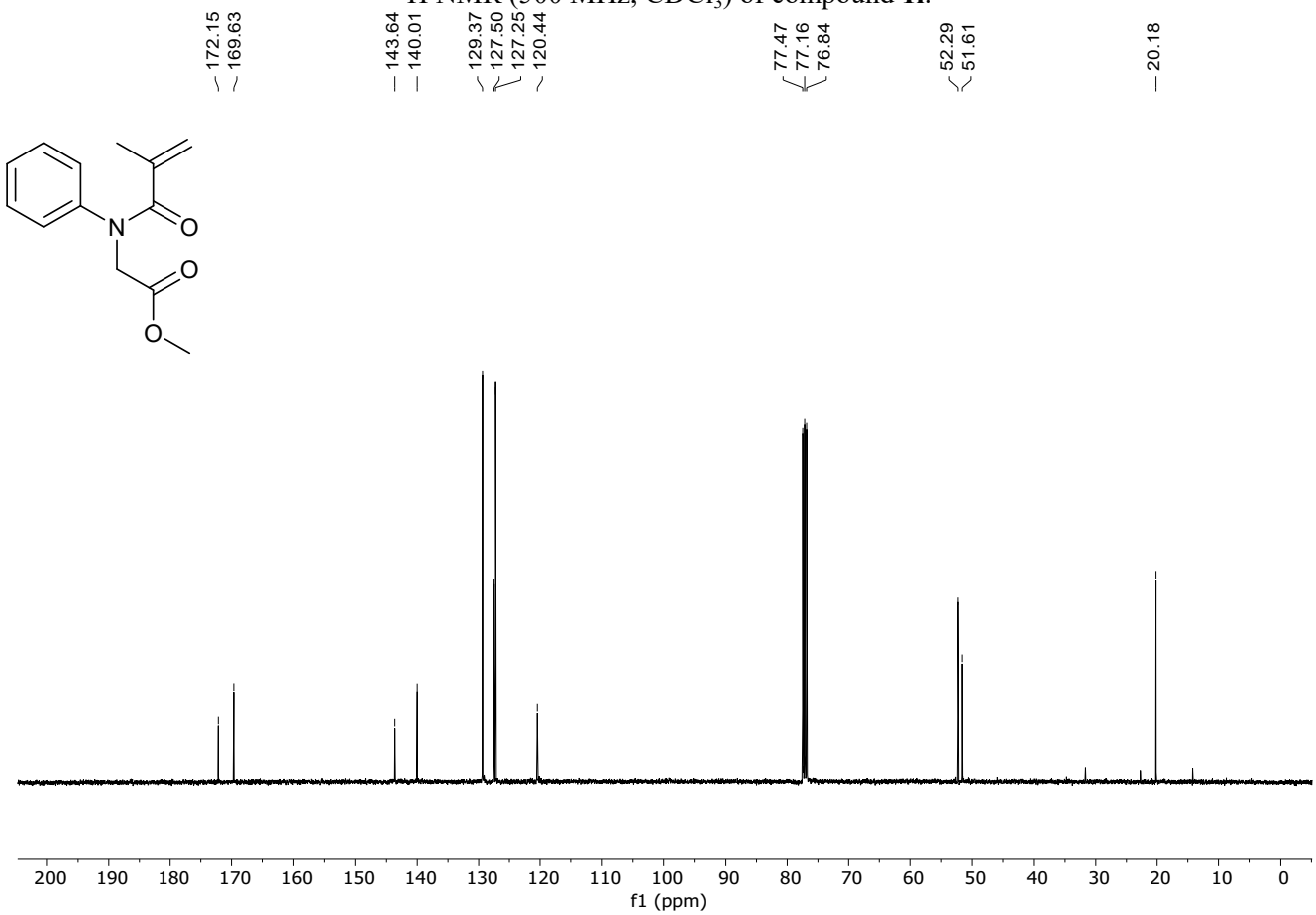
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1k**.



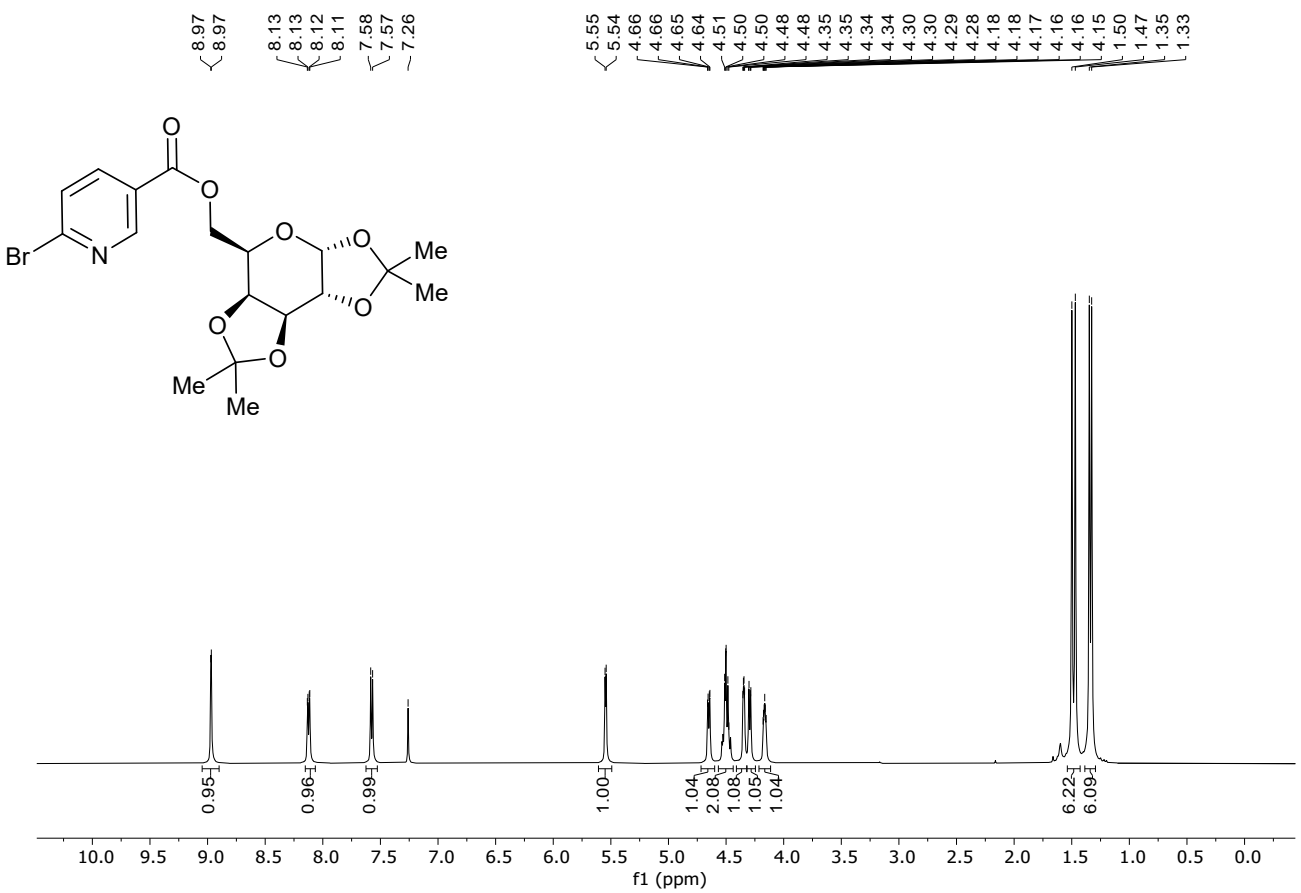
^{13}C NMR (151 MHz, $CDCl_3$) of compound **1k**.



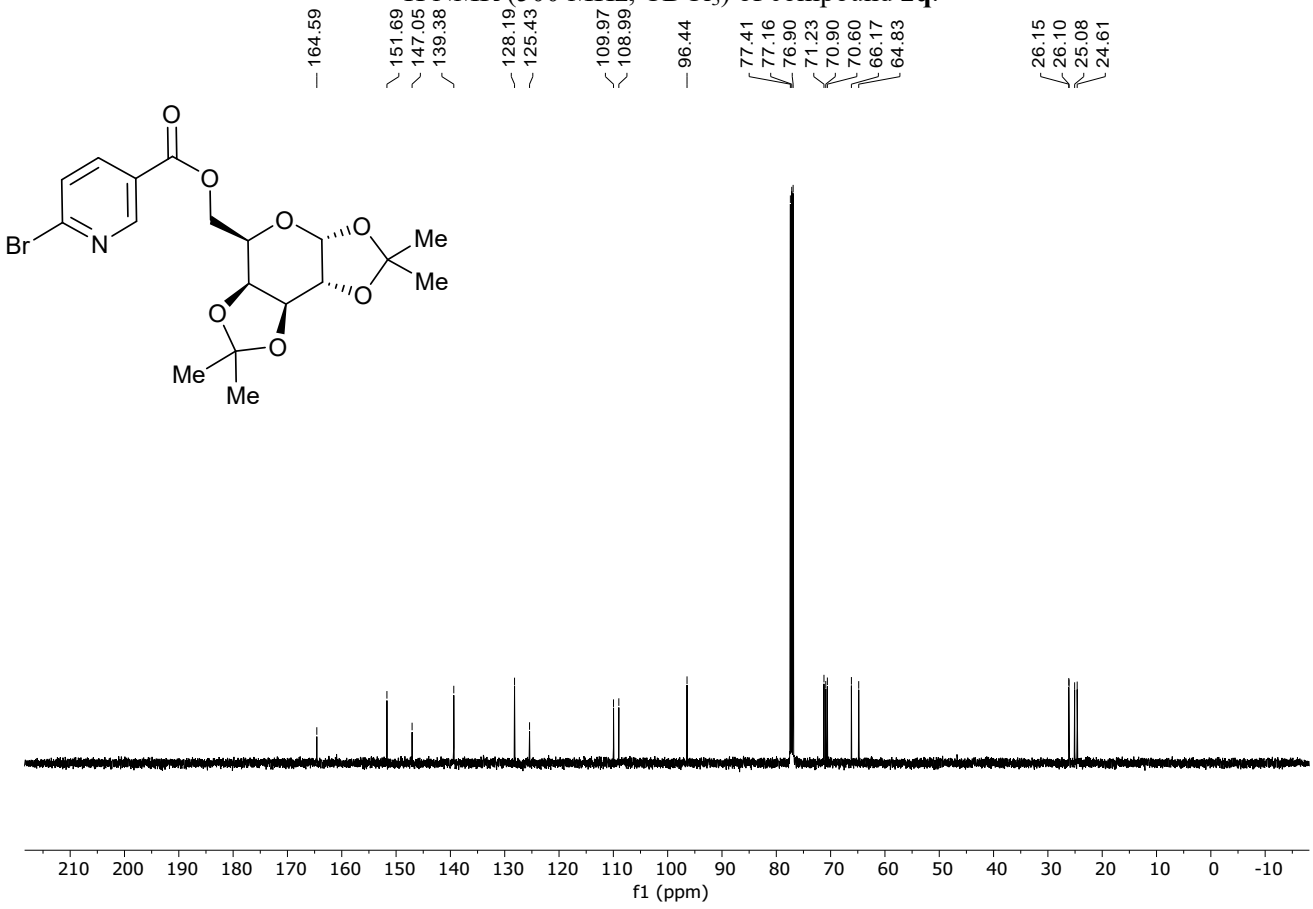
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1l**.



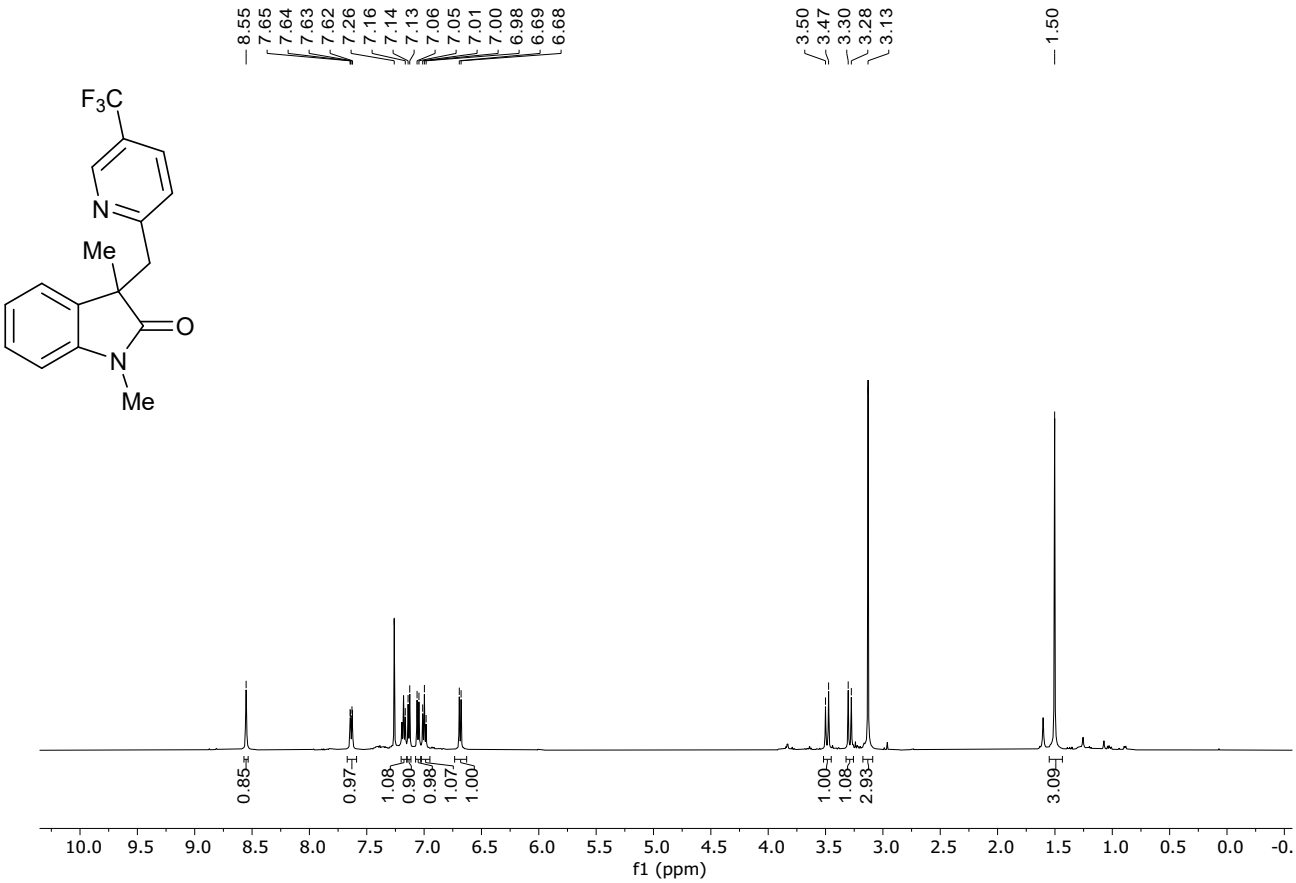
^{13}C NMR (101 MHz, $CDCl_3$) of compound **1l**.



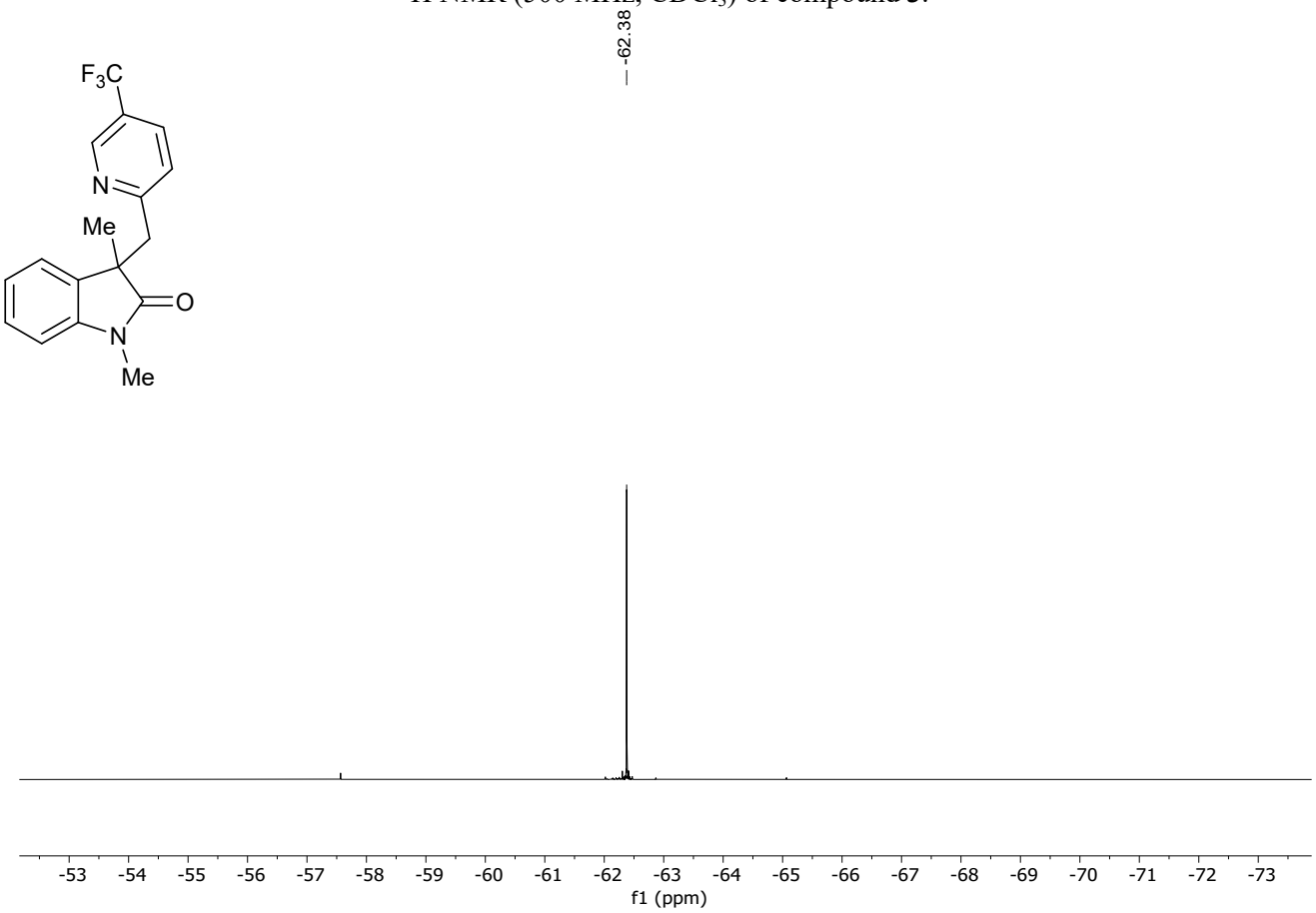
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2q**.



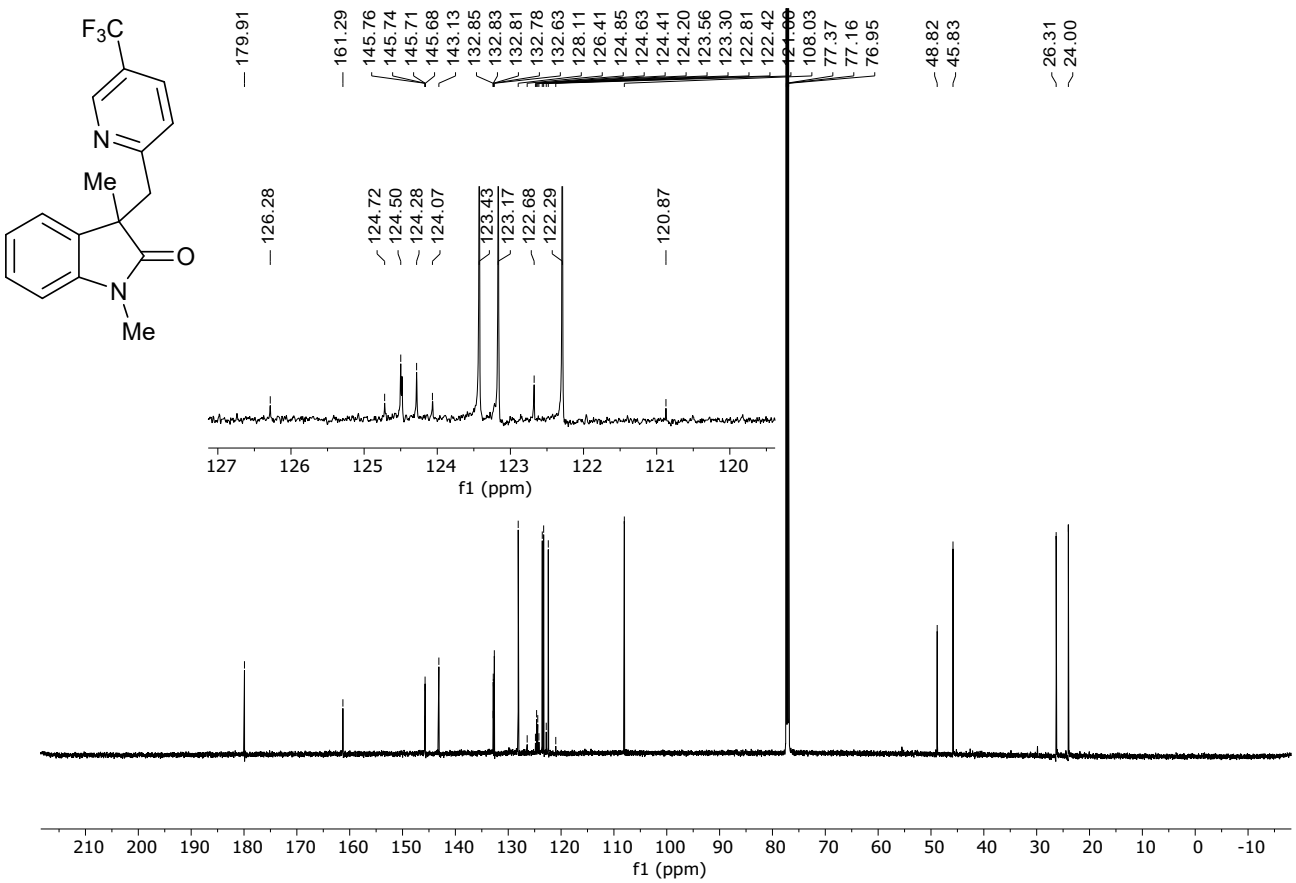
^{13}C NMR (126 MHz, $CDCl_3$) of compound **2q**.



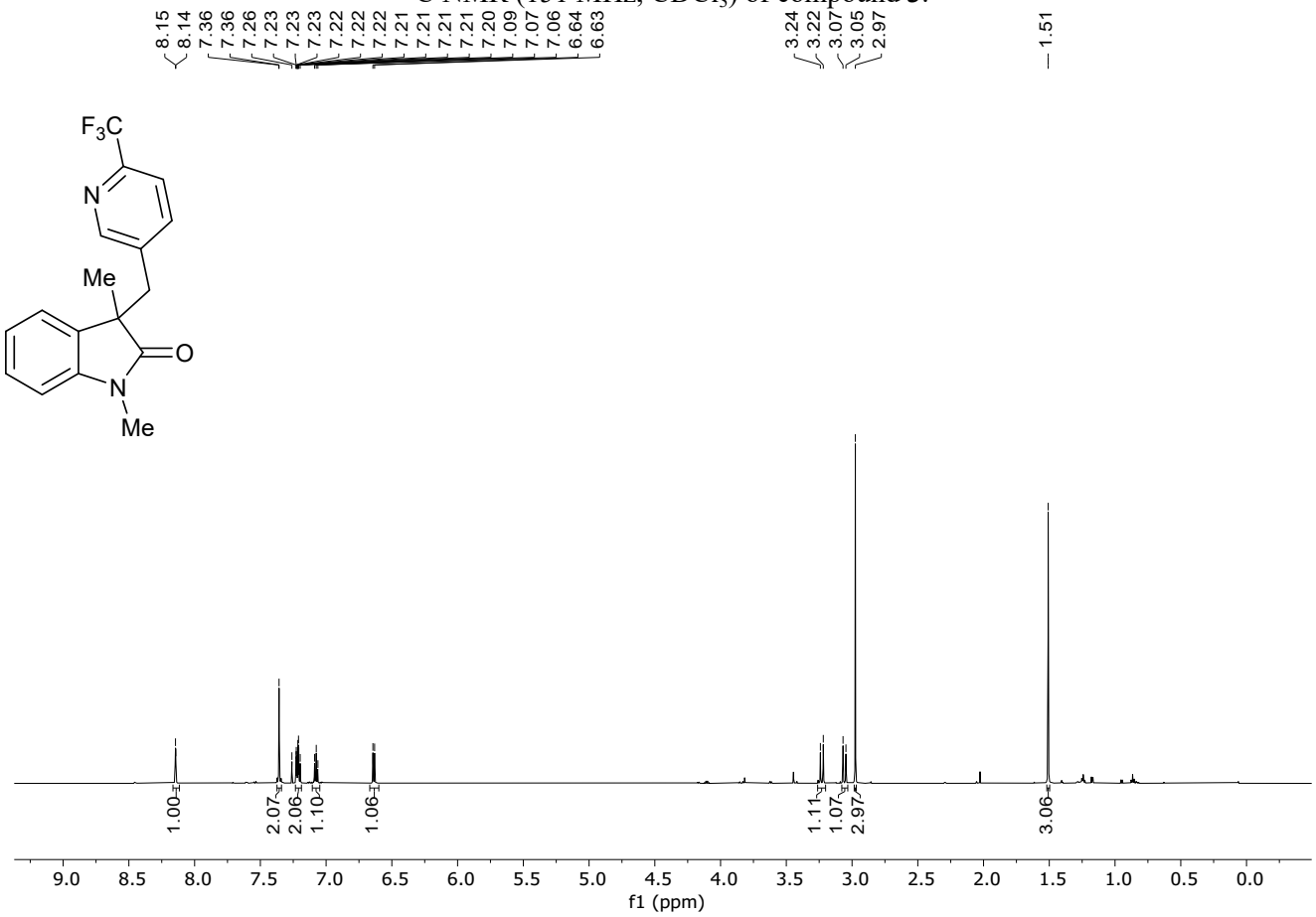
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3**.



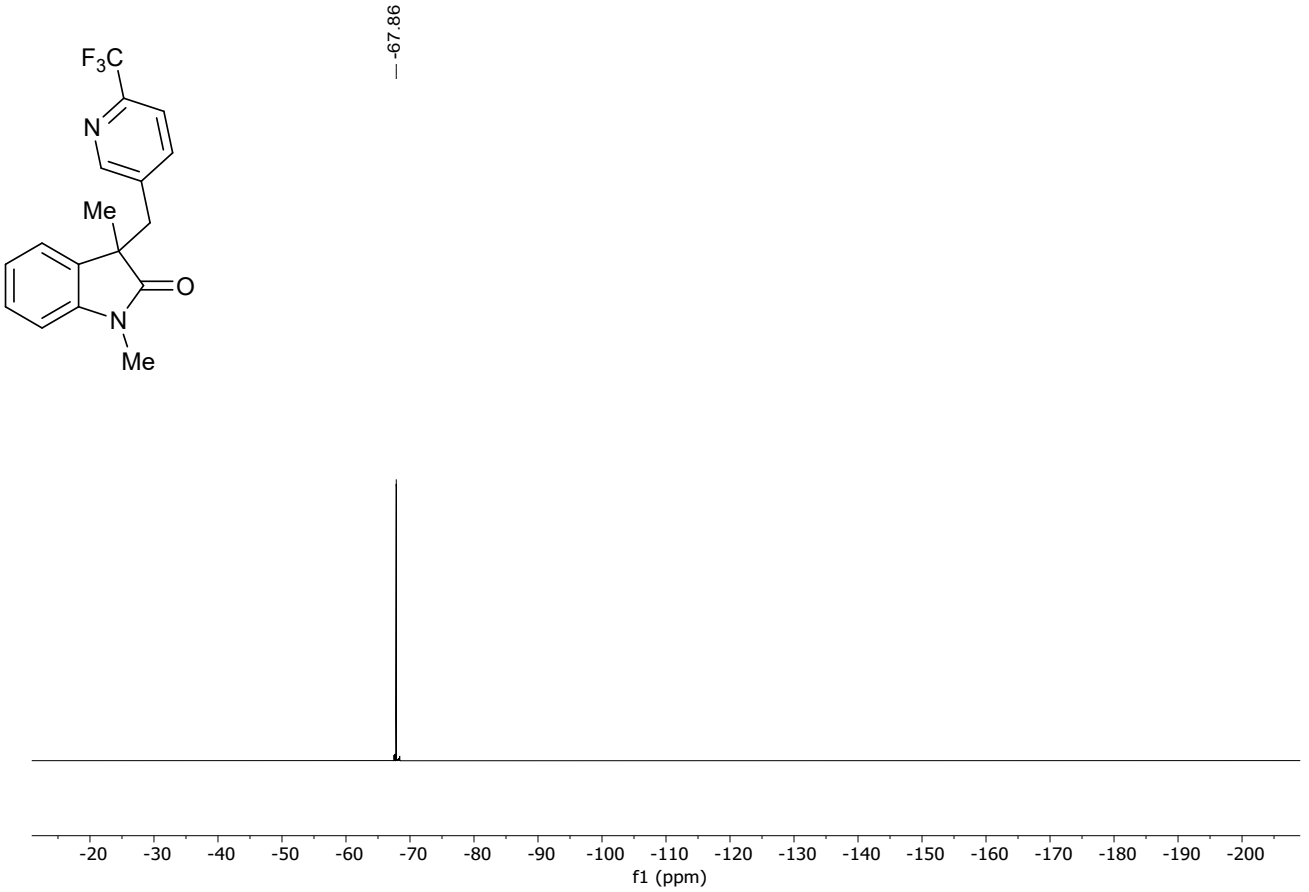
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3**.



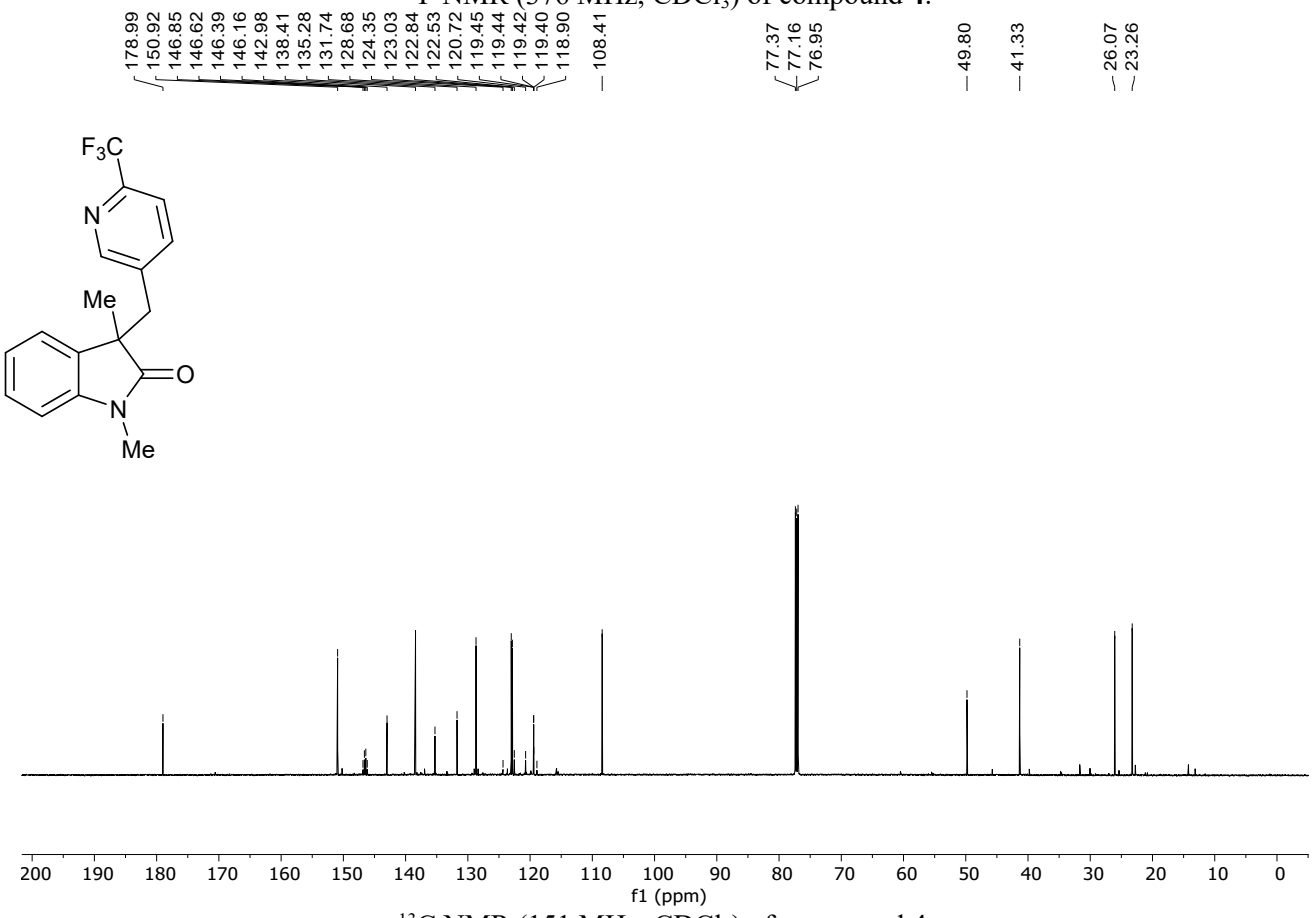
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3**.



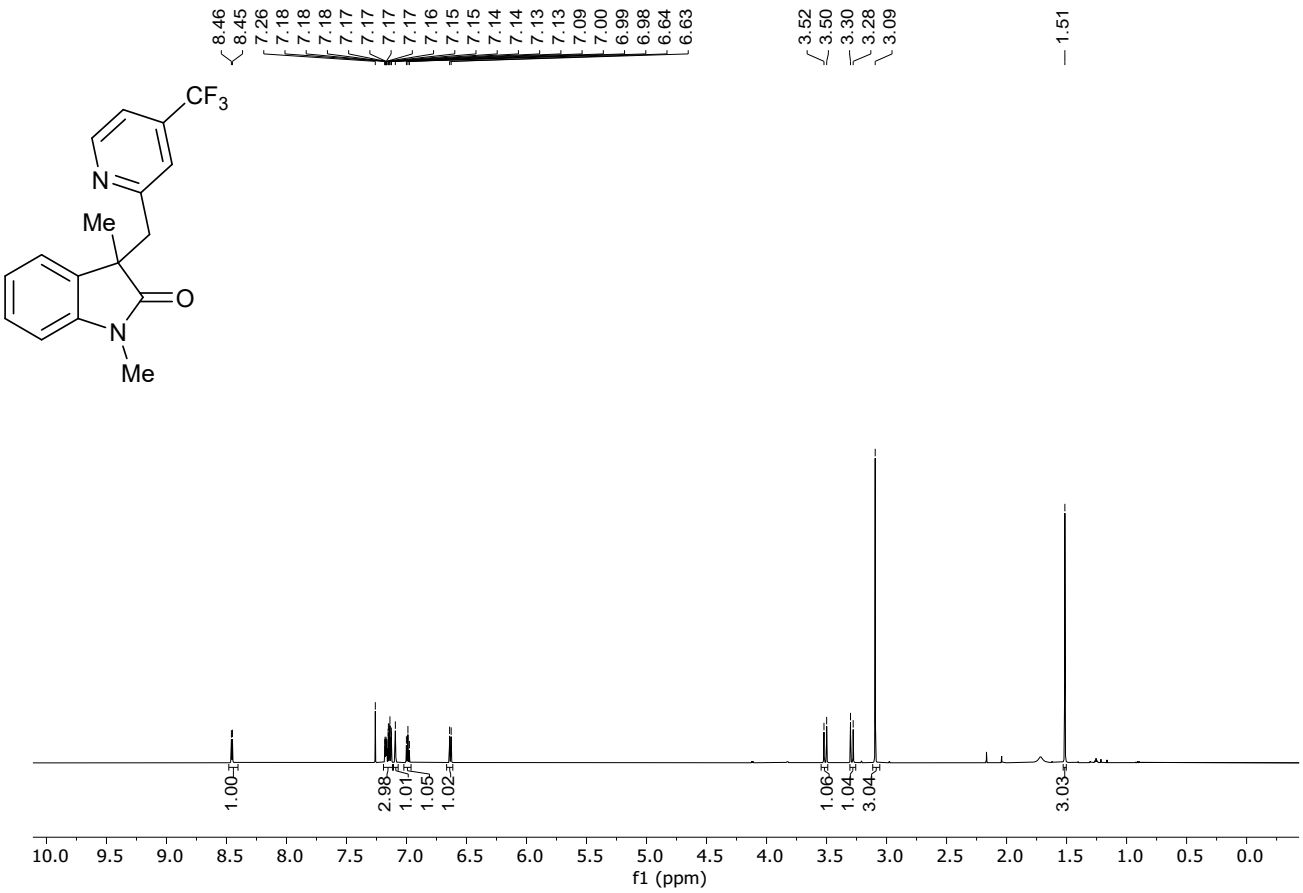
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4**.



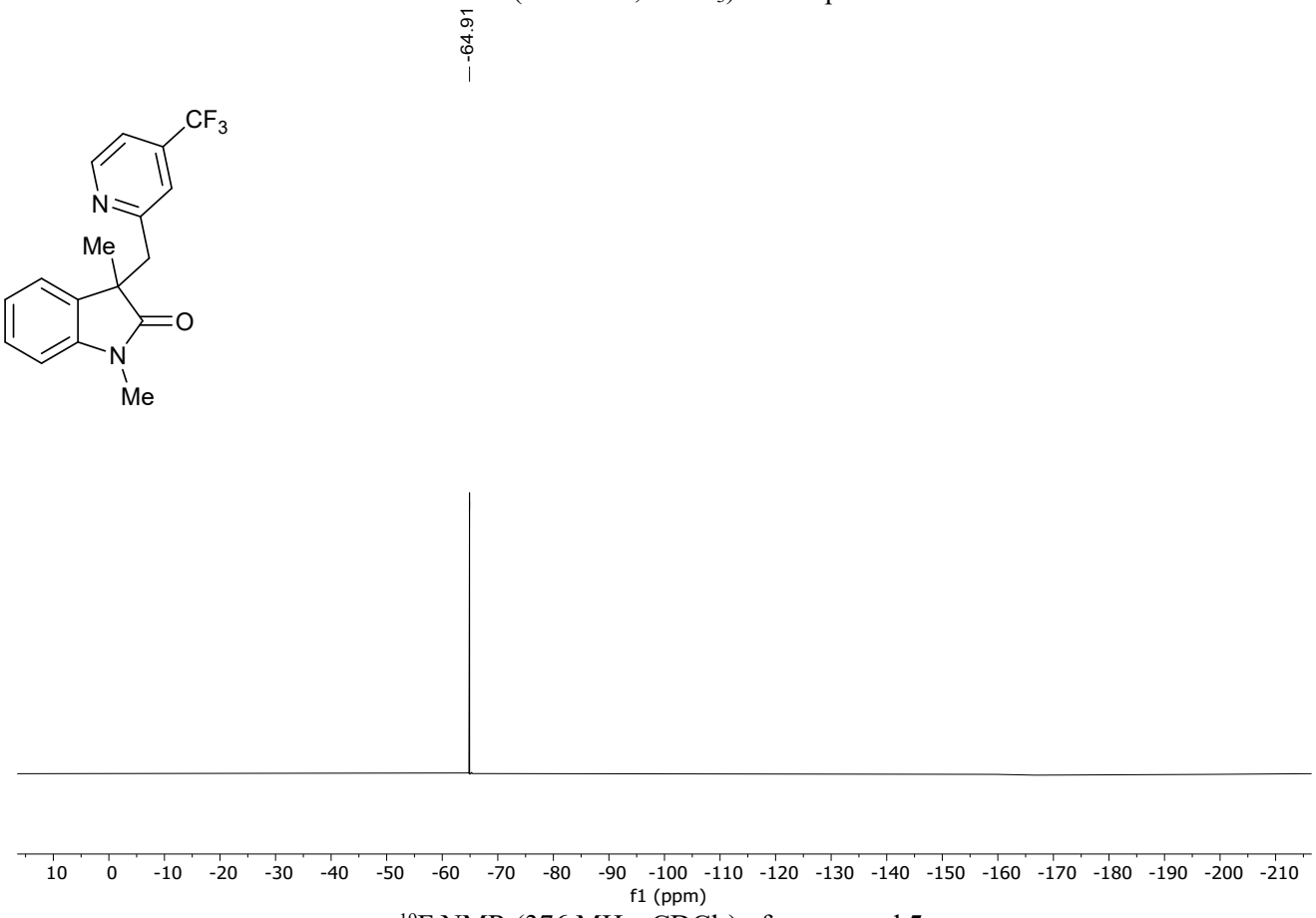
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4**.



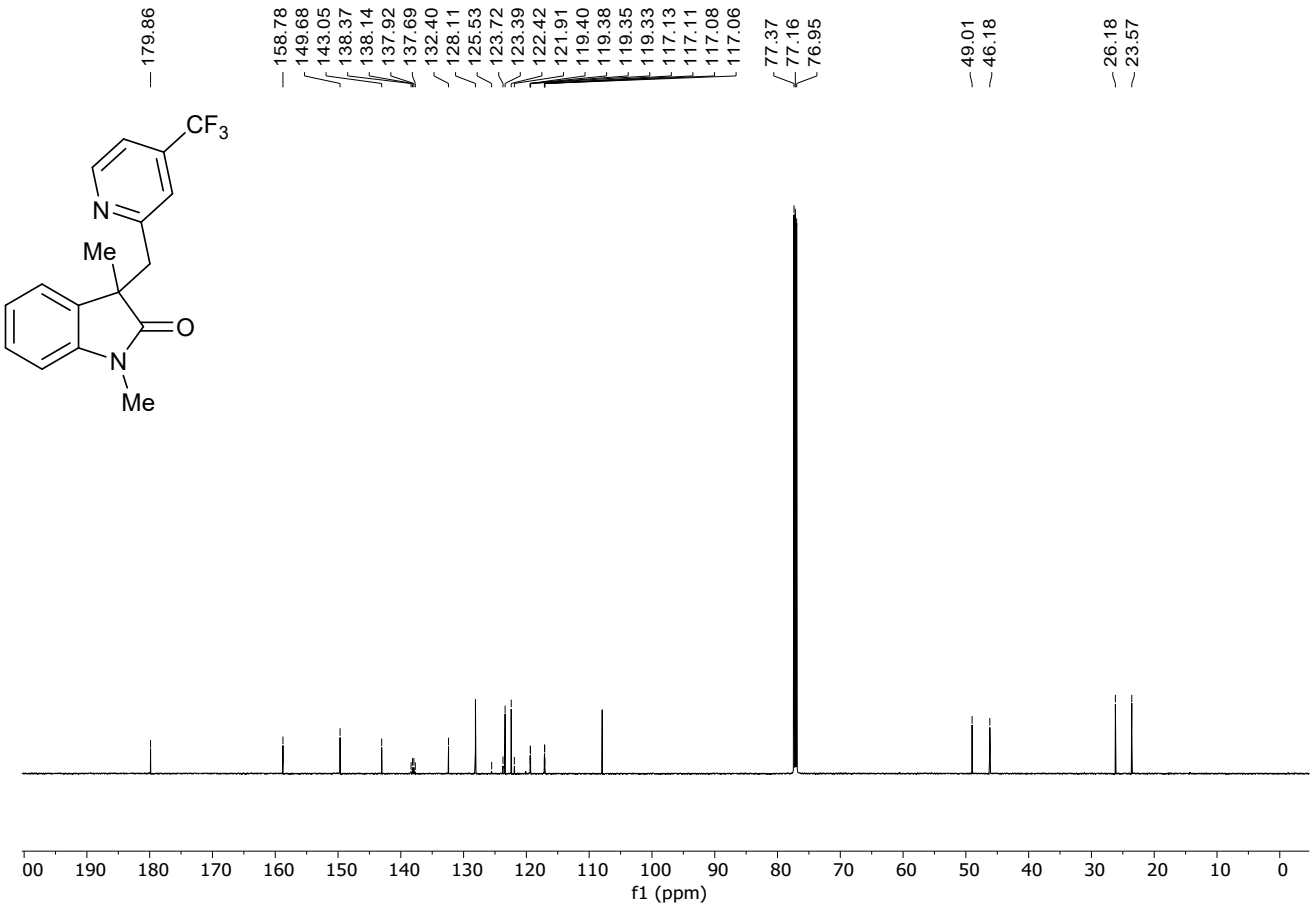
^{13}C NMR (151 MHz, $CDCl_3$) of compound **4**.



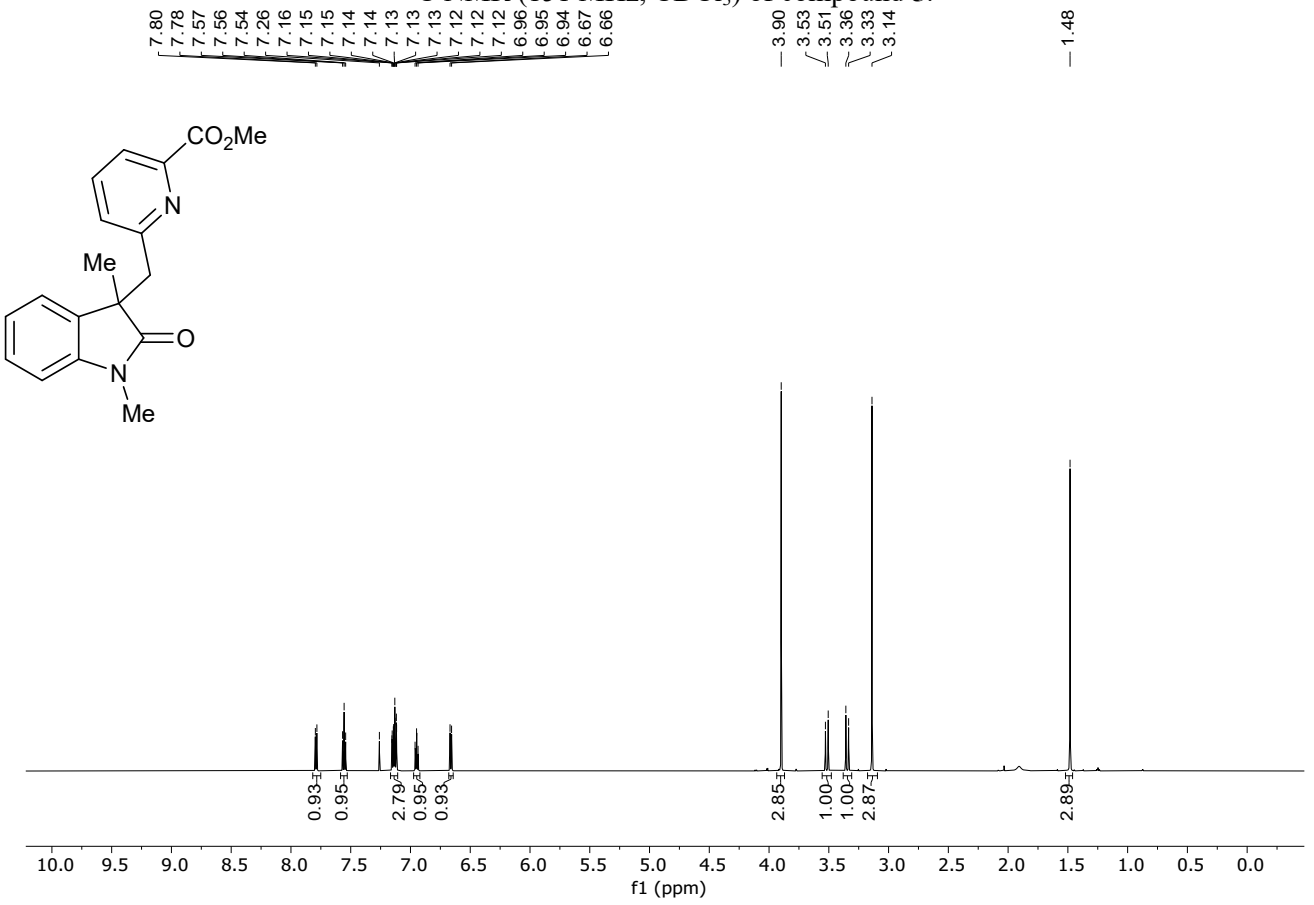
^{1}H NMR (600 MHz, $CDCl_3$) of compound **5**.



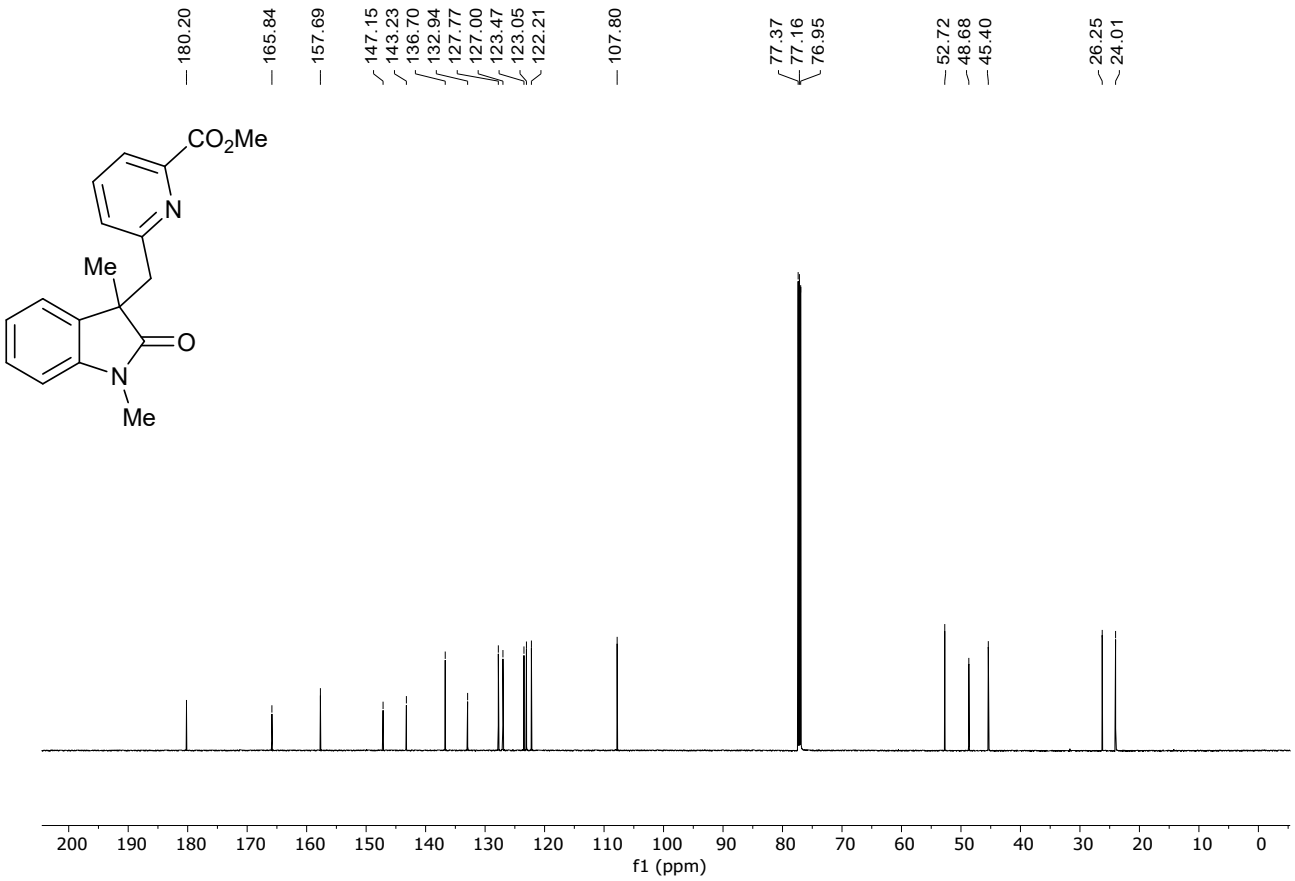
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5**.



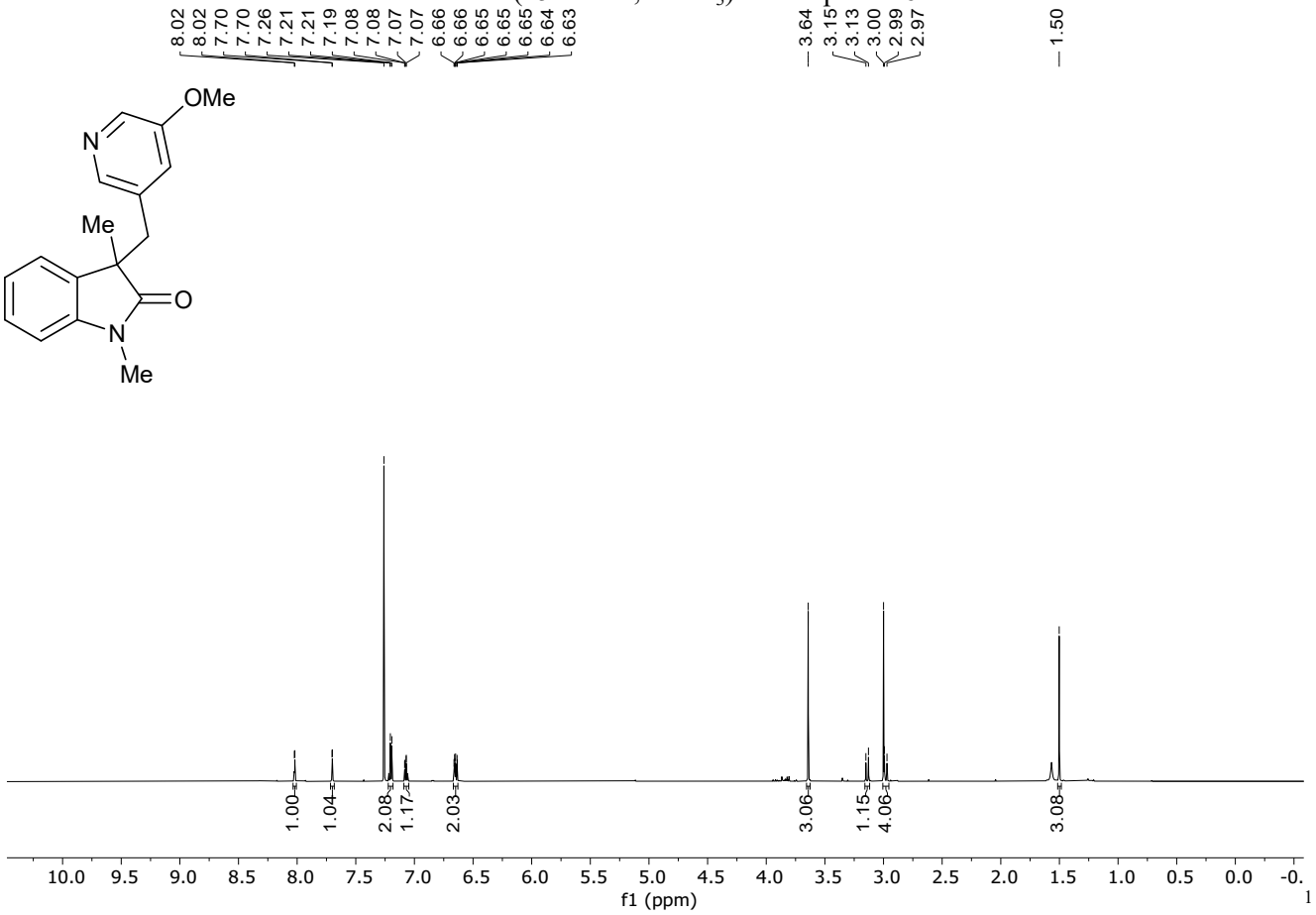
^{13}C NMR (151 MHz, $CDCl_3$) of compound **5**.



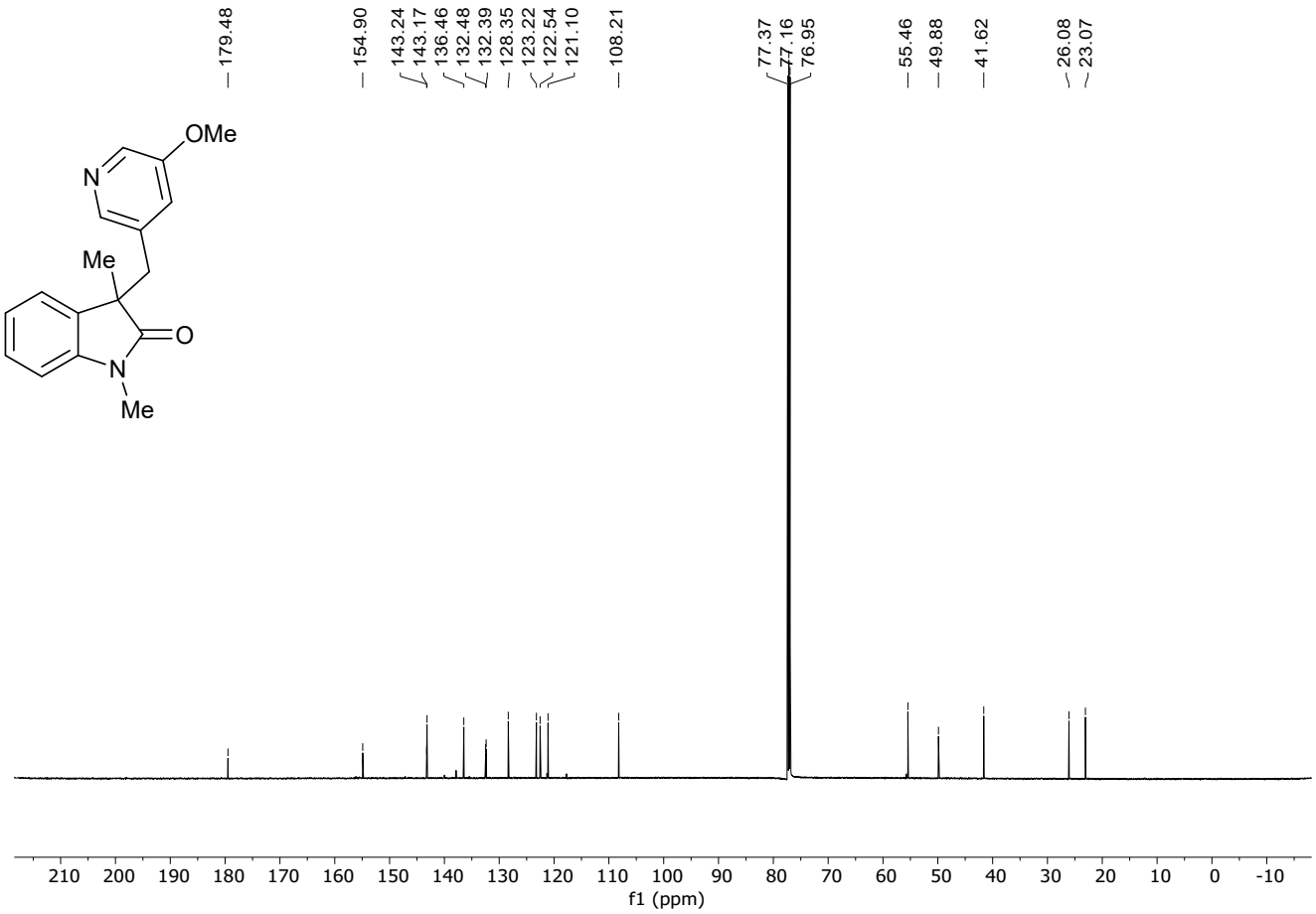
^{1}H NMR (600 MHz, $CDCl_3$) of compound **6**.



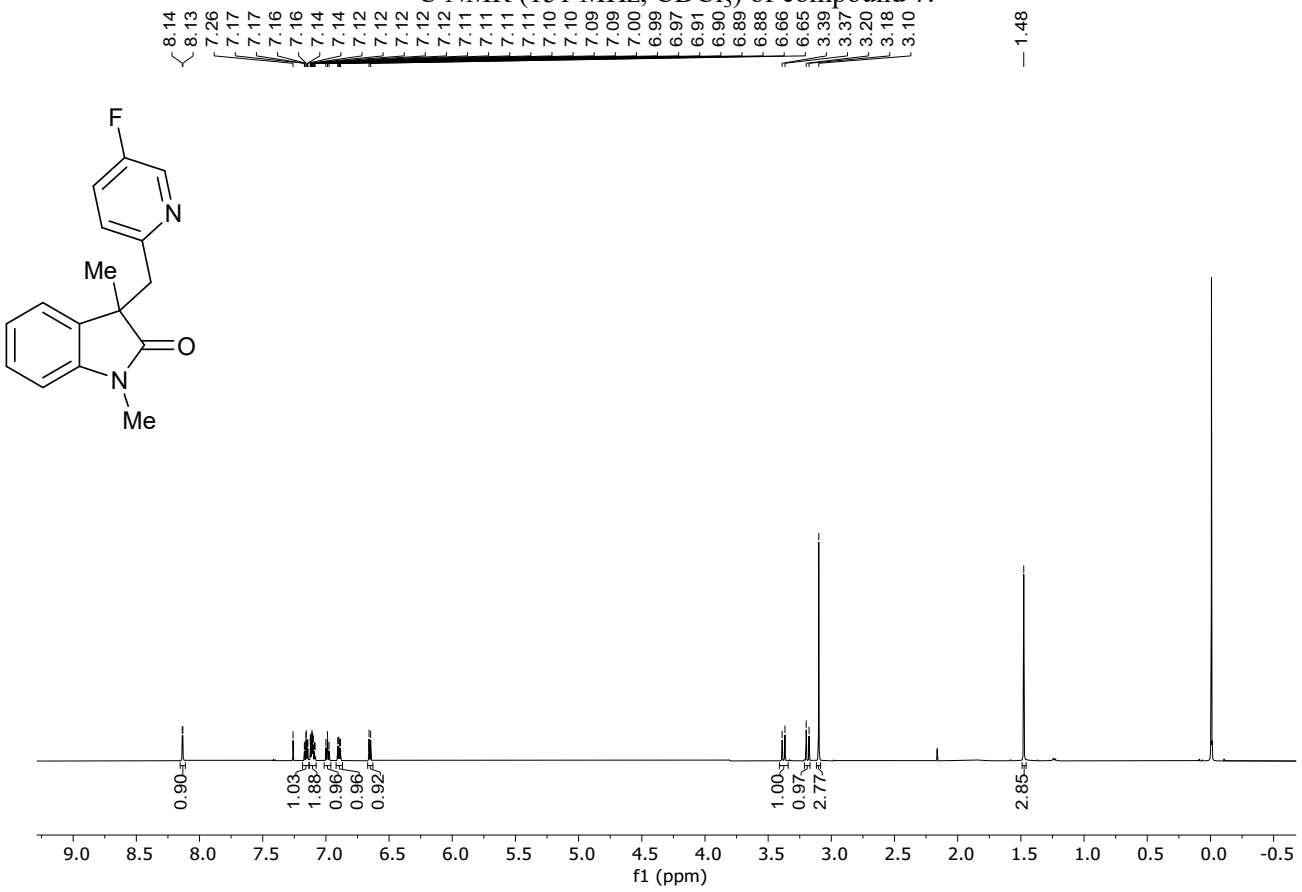
^{13}C NMR (151 MHz, $CDCl_3$) of compound **6**.



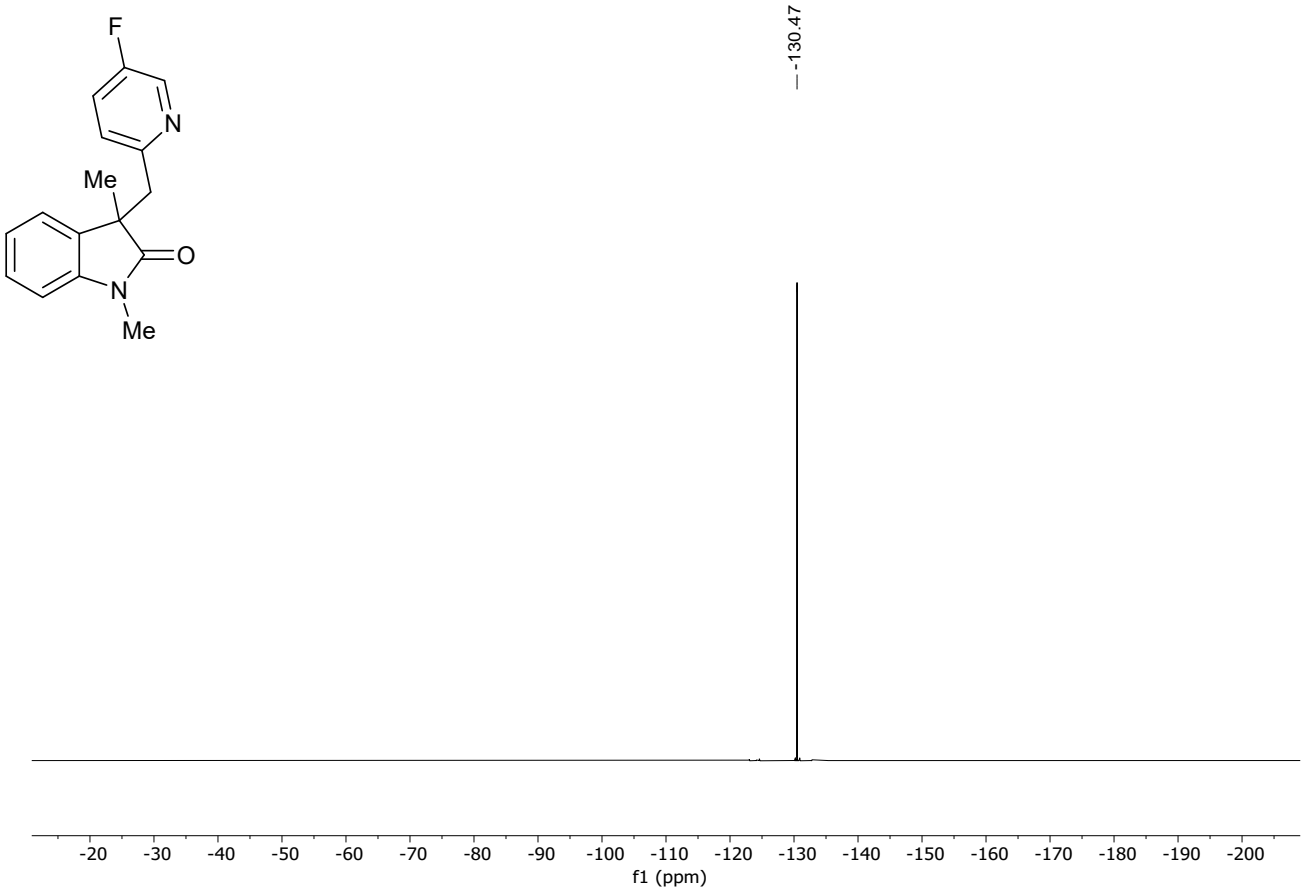
H NMR (600 MHz, $CDCl_3$) of compound **7**.



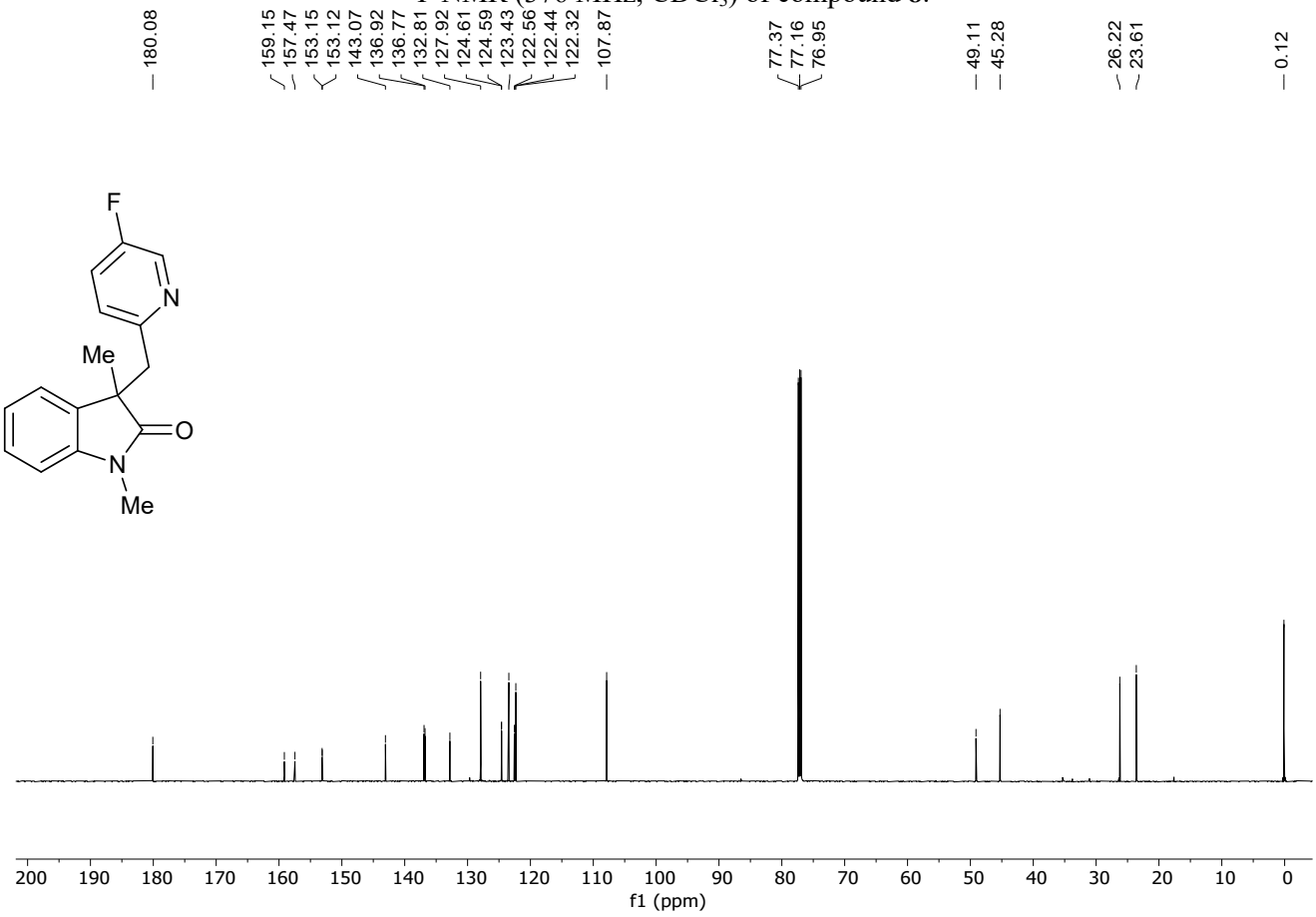
^{13}C NMR (151 MHz, $CDCl_3$) of compound **7**.



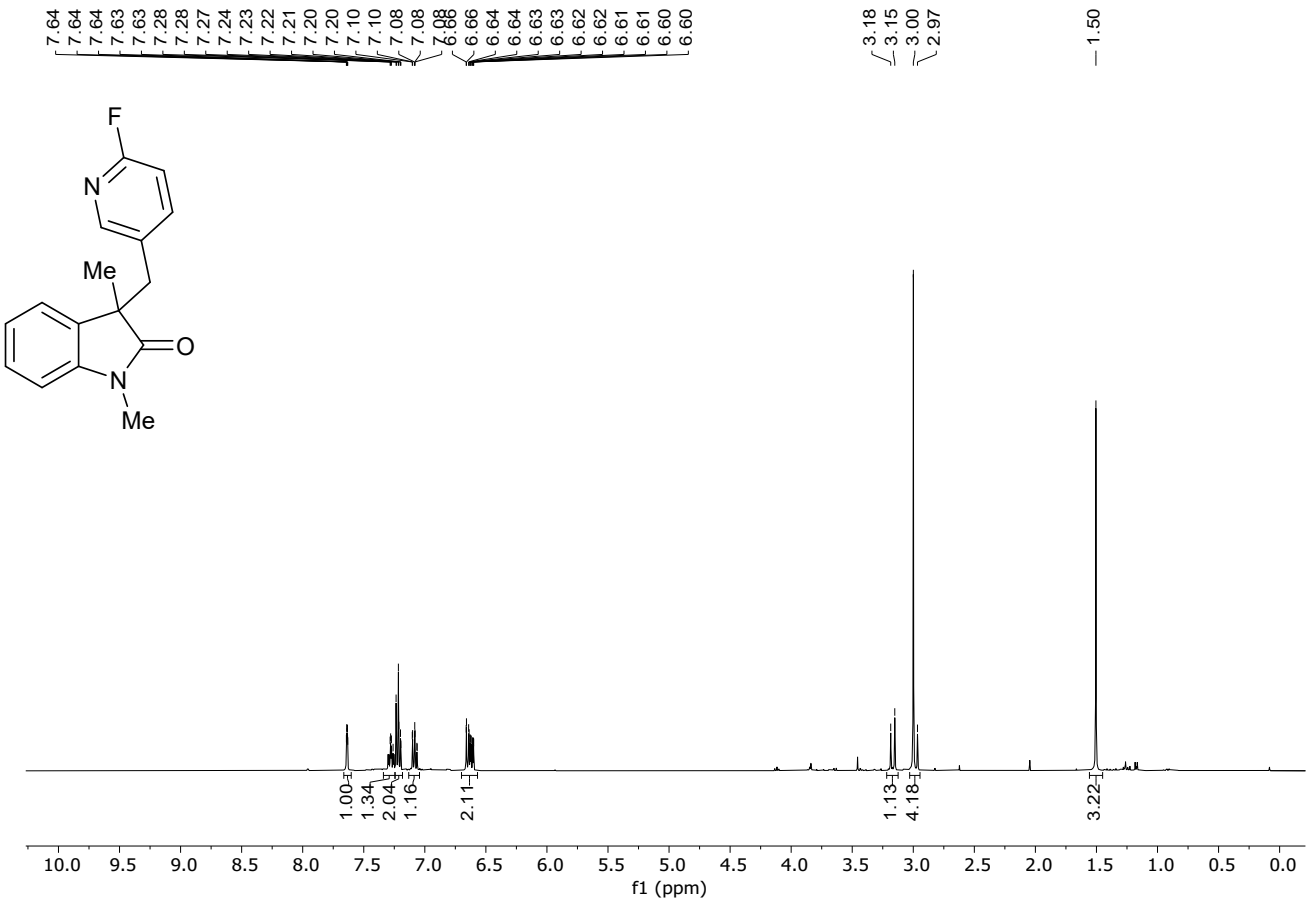
^{1}H NMR (600 MHz, $CDCl_3$) of compound **8**.



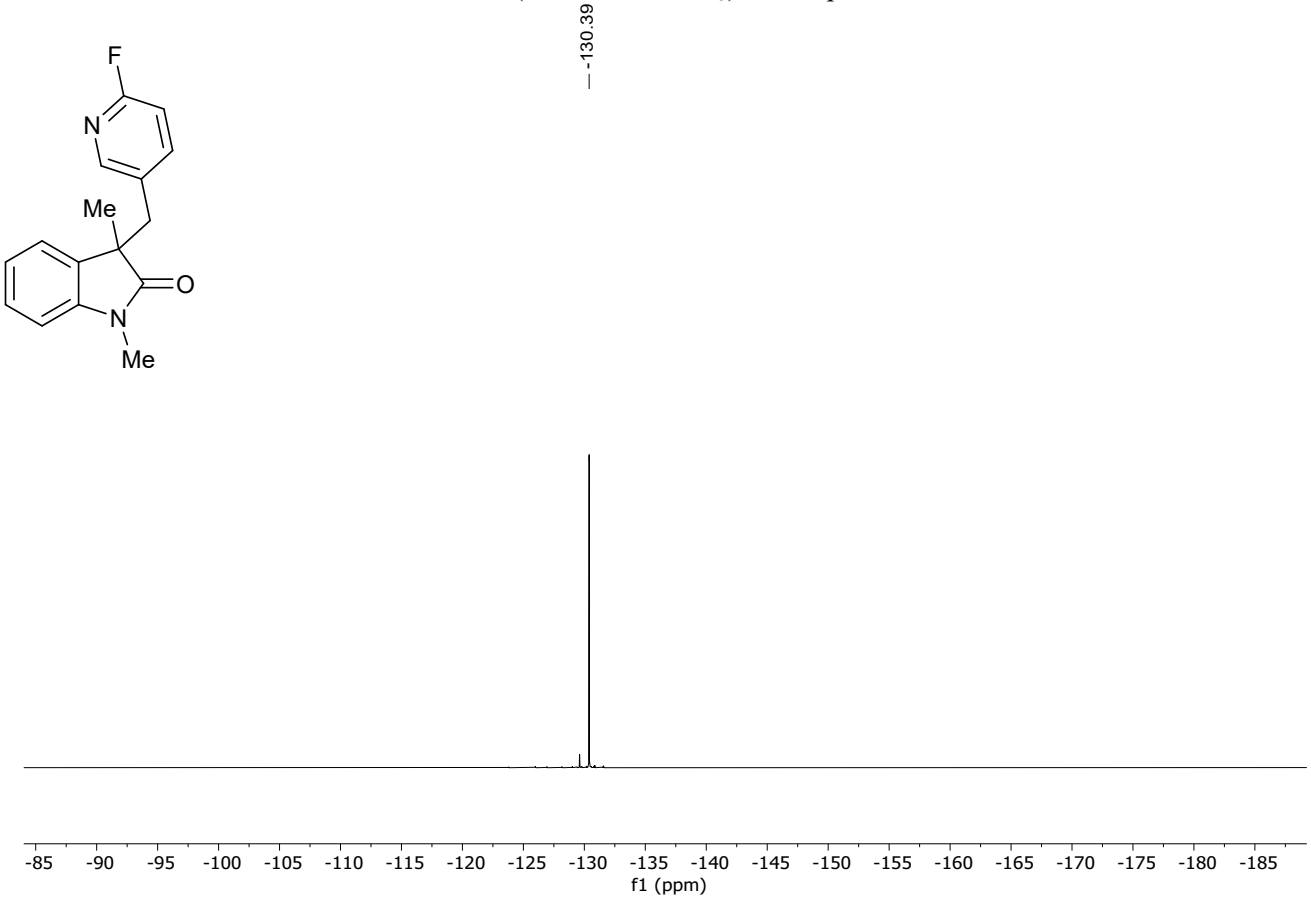
^{19}F NMR (376 MHz, $CDCl_3$) of compound **8**.



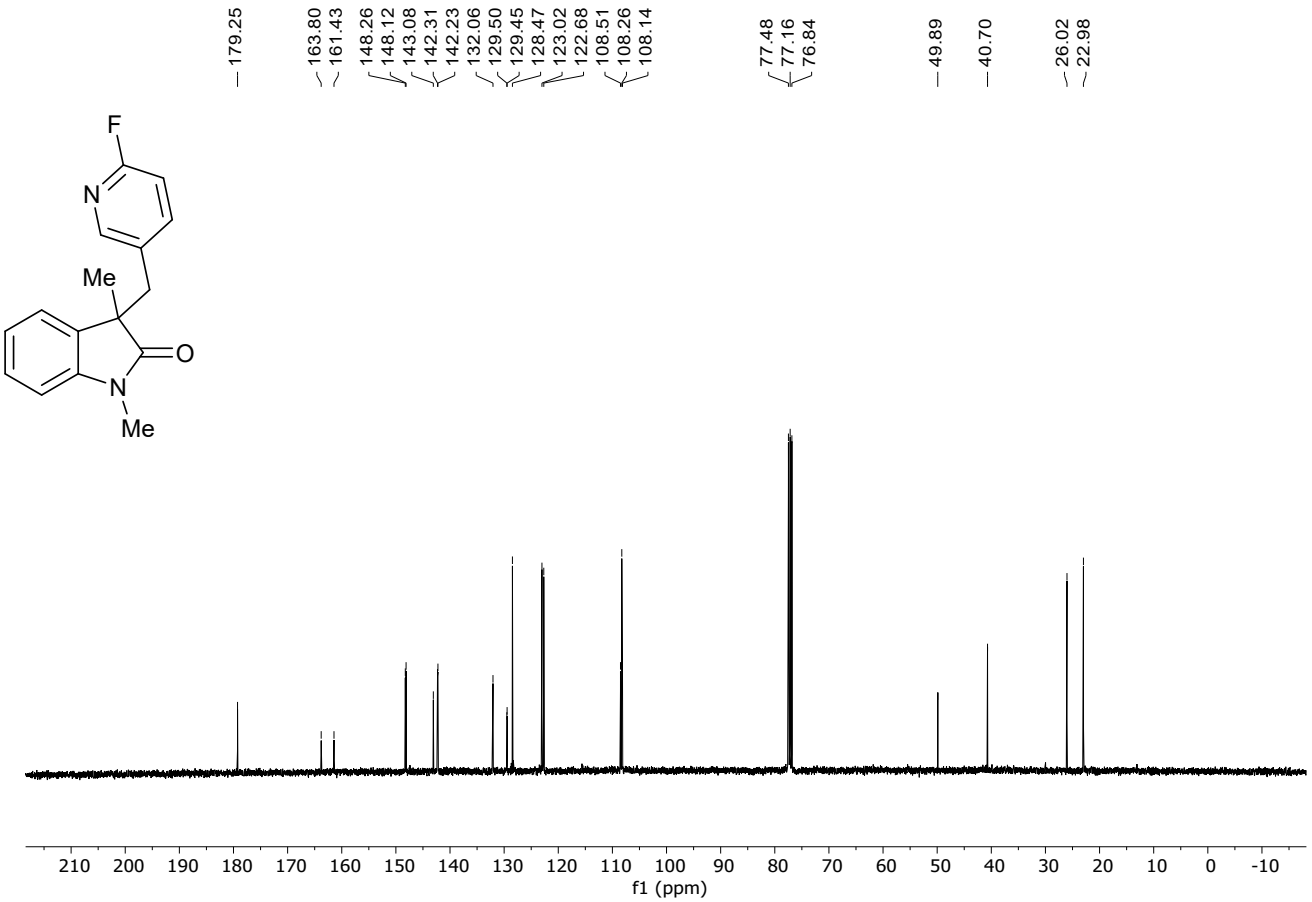
^{13}C NMR (151 MHz, $CDCl_3$) of compound **8**.



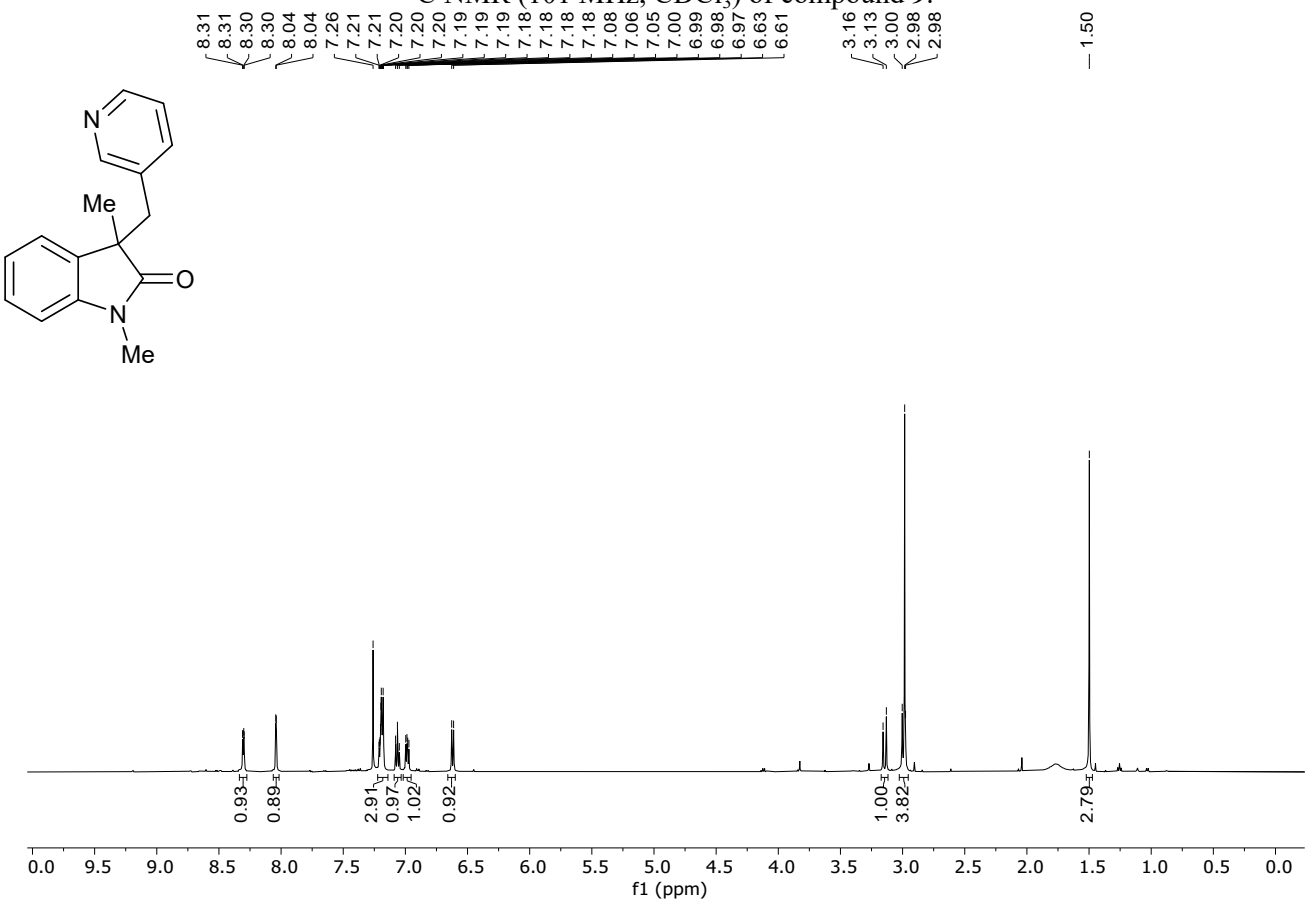
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**.



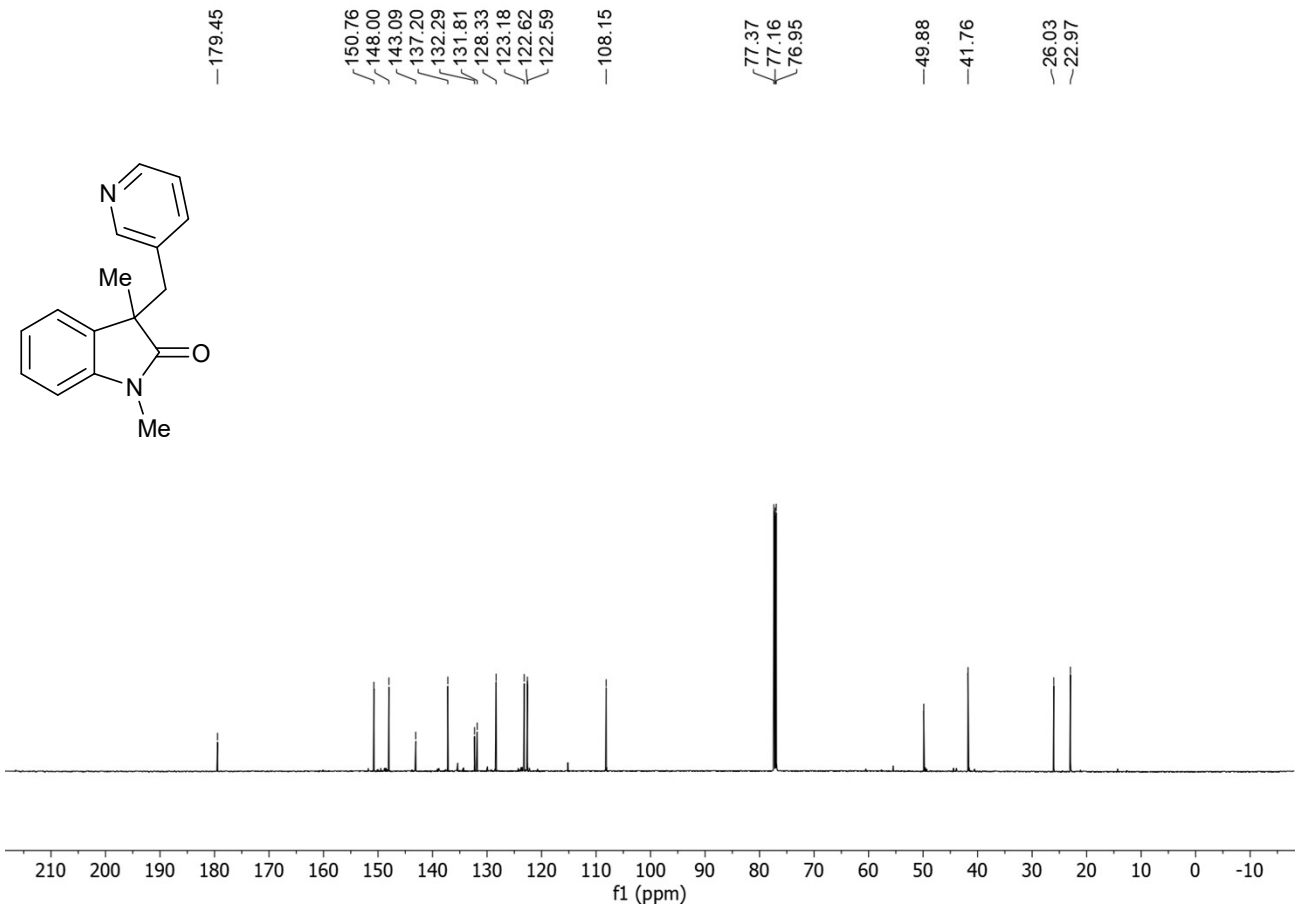
^{19}F NMR (376 MHz, $CDCl_3$) of compound **9**.



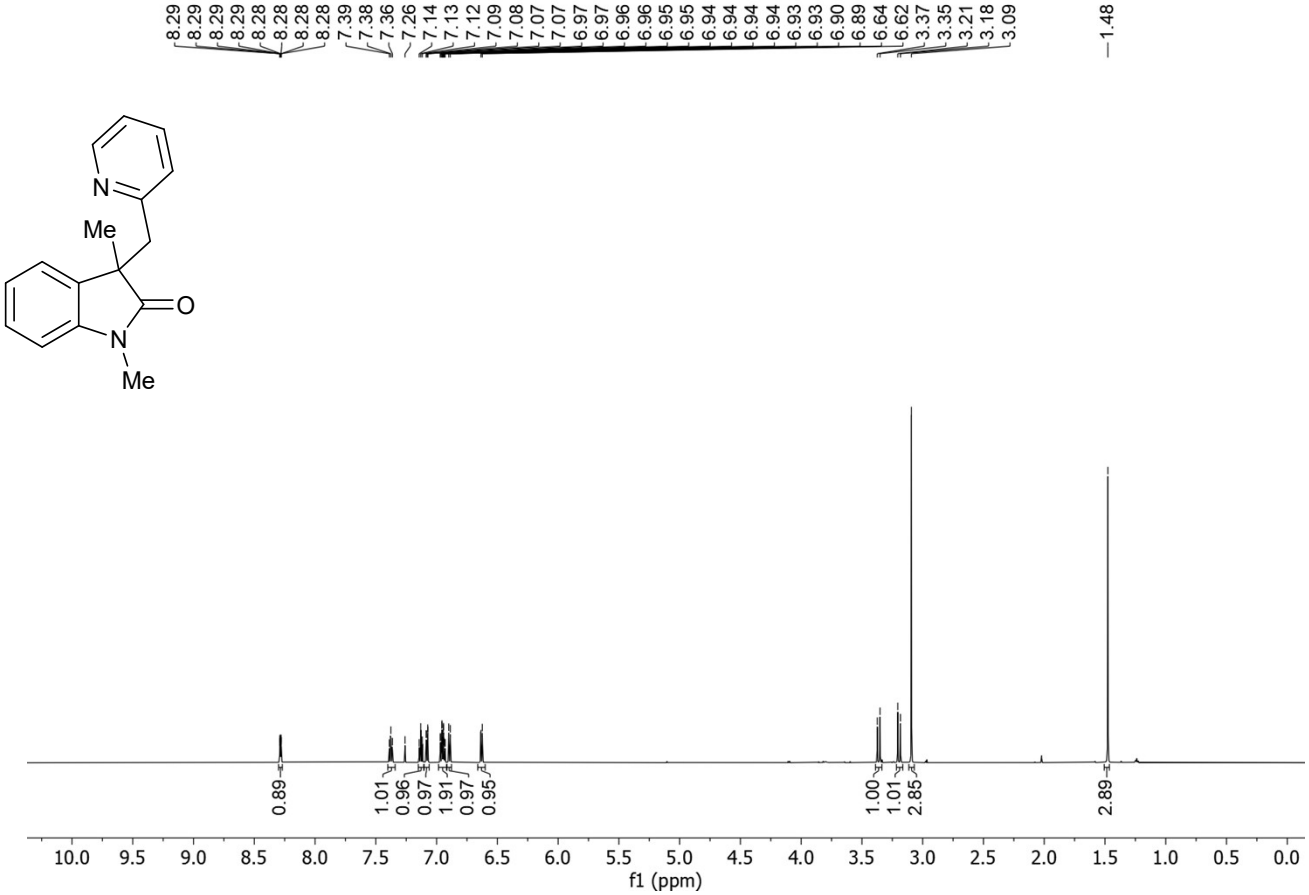
^{13}C NMR (101 MHz, $CDCl_3$) of compound **9**.



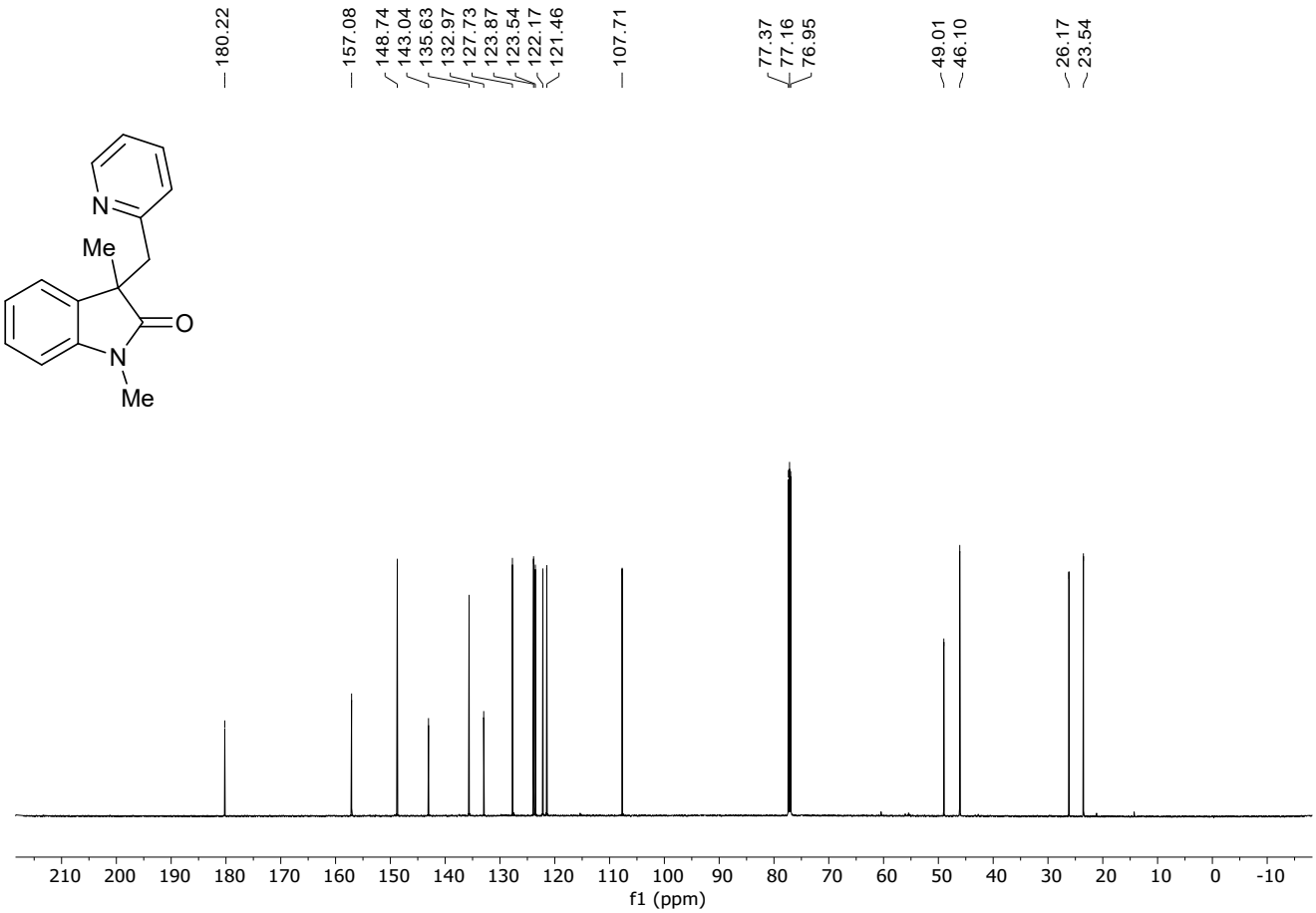
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**.



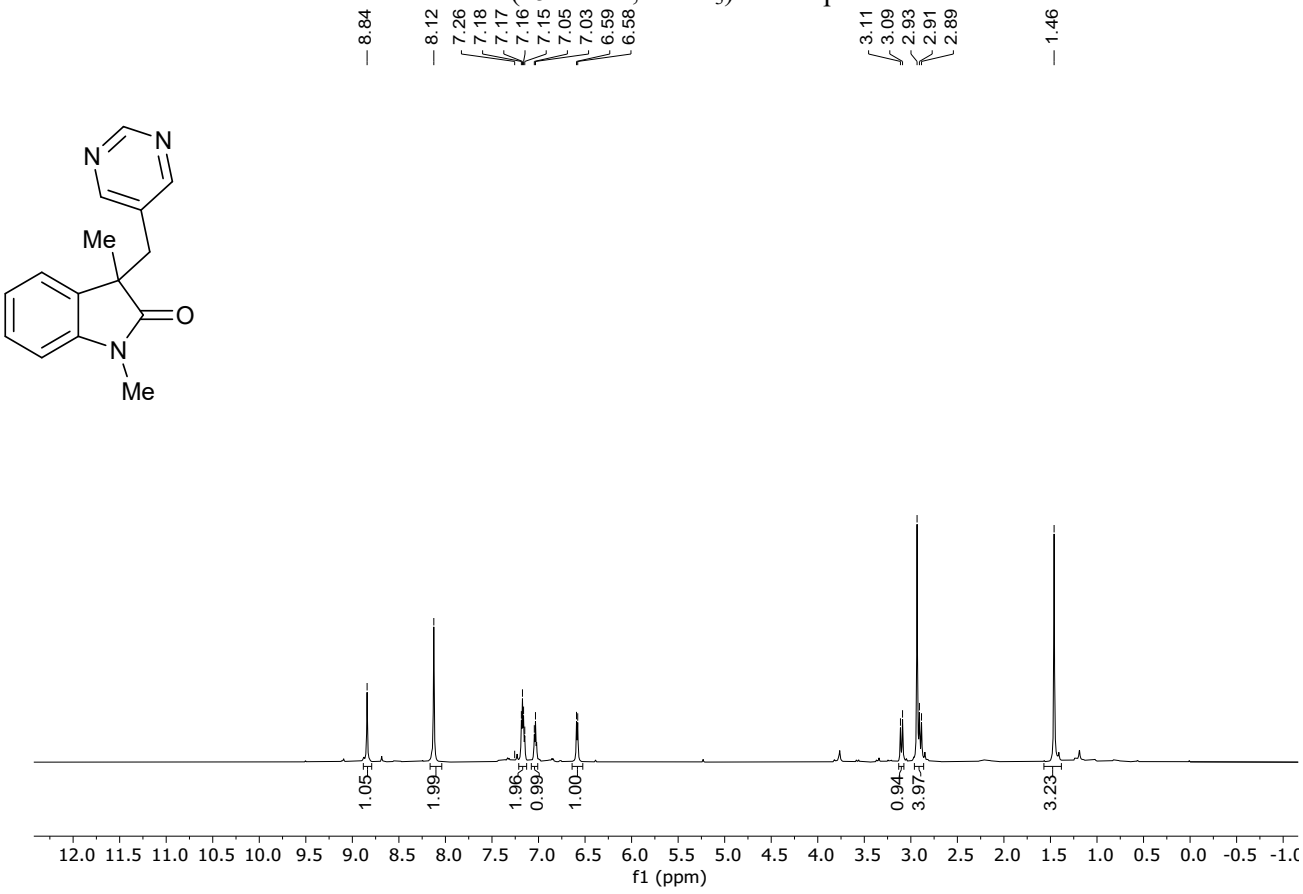
^{13}C NMR (151 MHz, $CDCl_3$) of compound **10**.



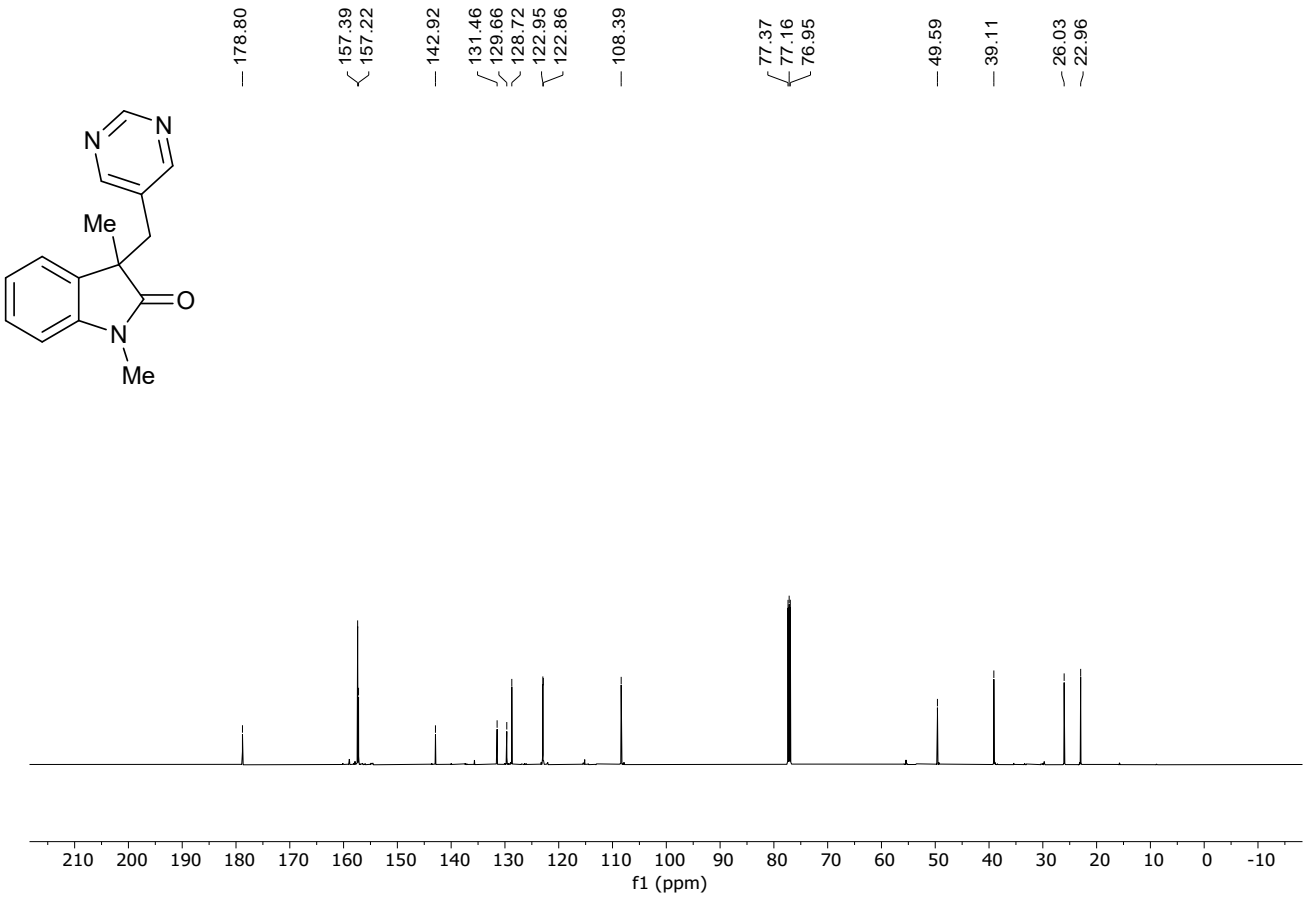
^{1}H NMR (600 MHz, $CDCl_3$) of compound **11**.



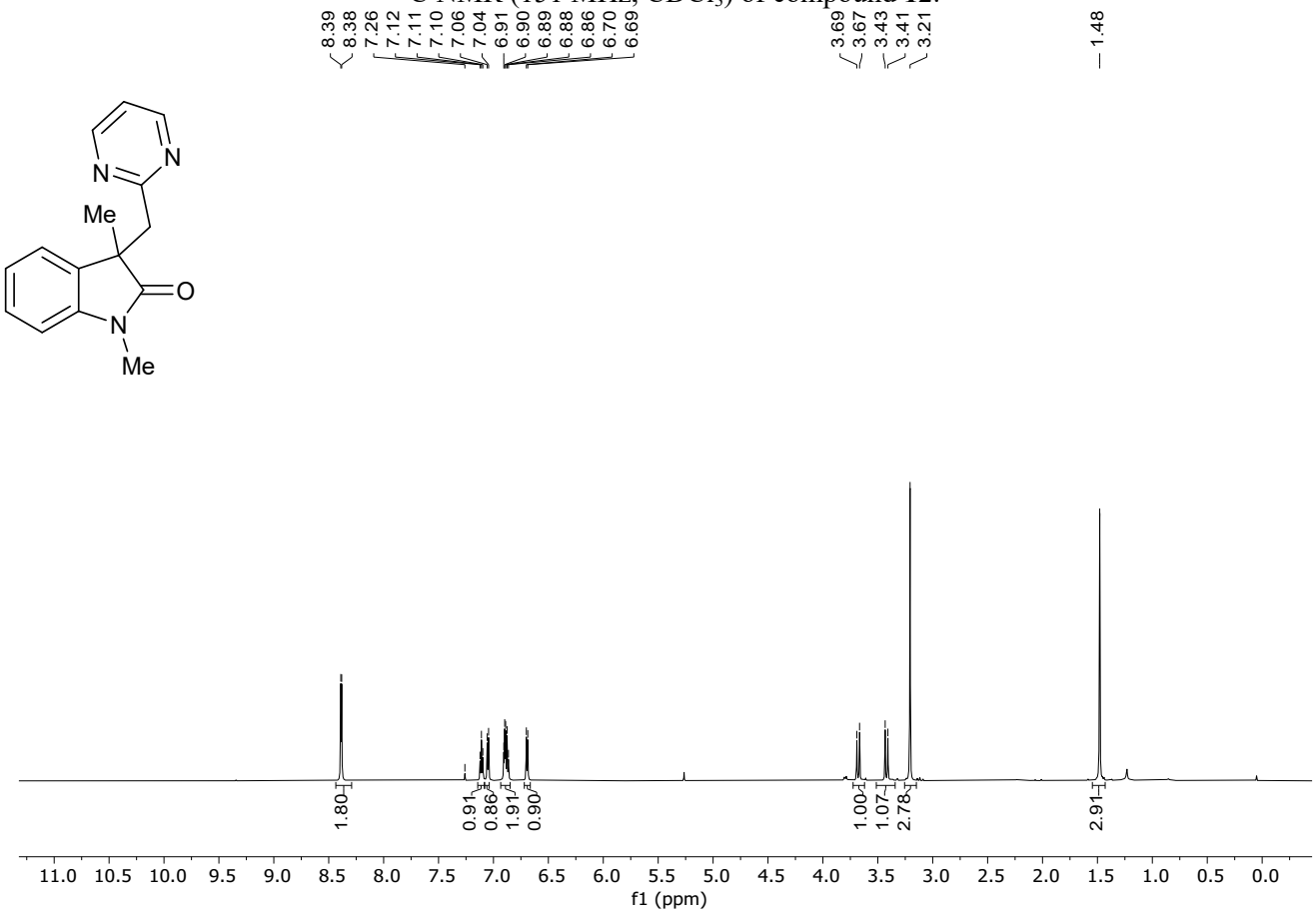
^{13}C NMR (151 MHz, $CDCl_3$) of compound **11**.



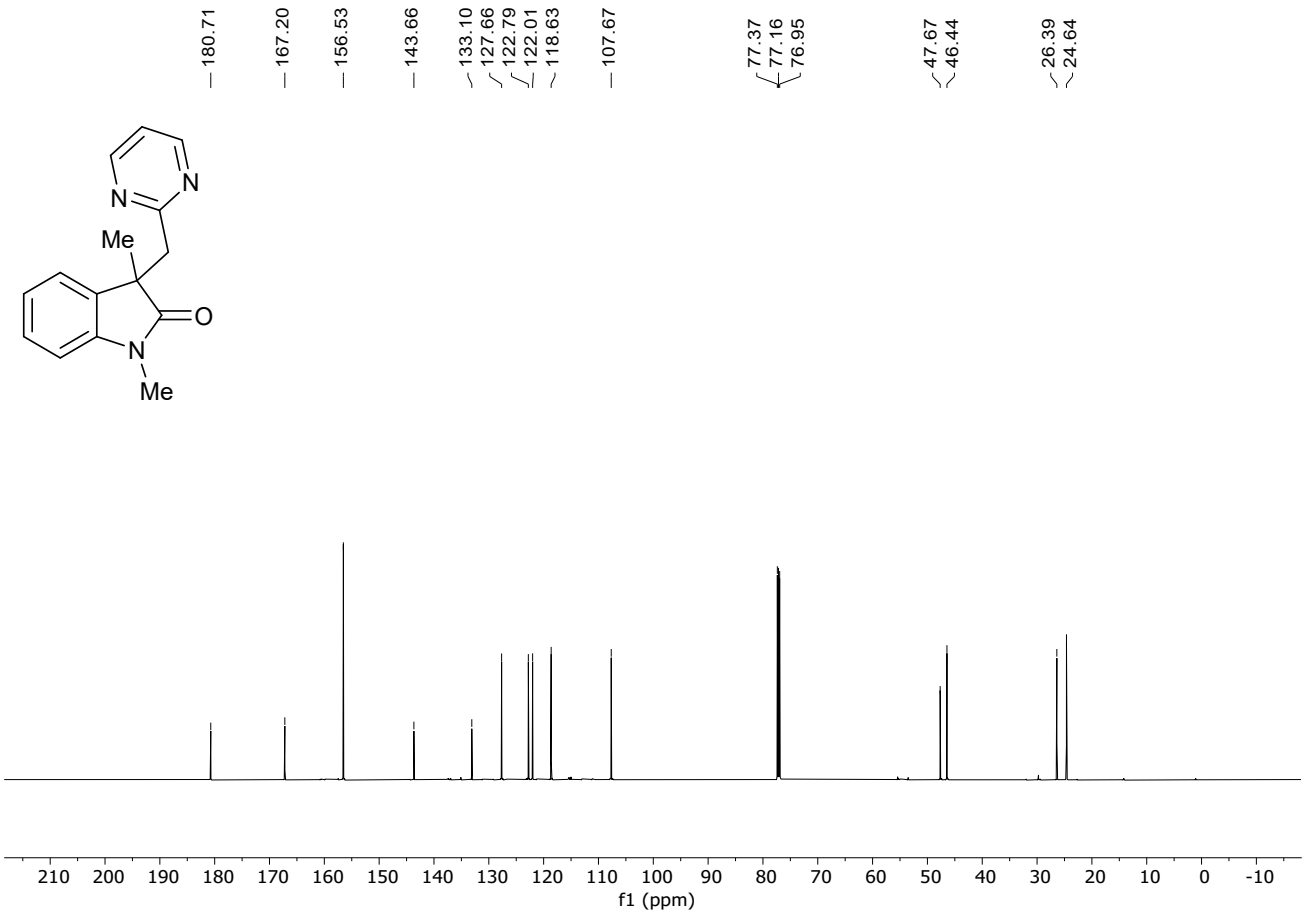
^{1}H NMR (600 MHz, $CDCl_3$) of compound **12**.



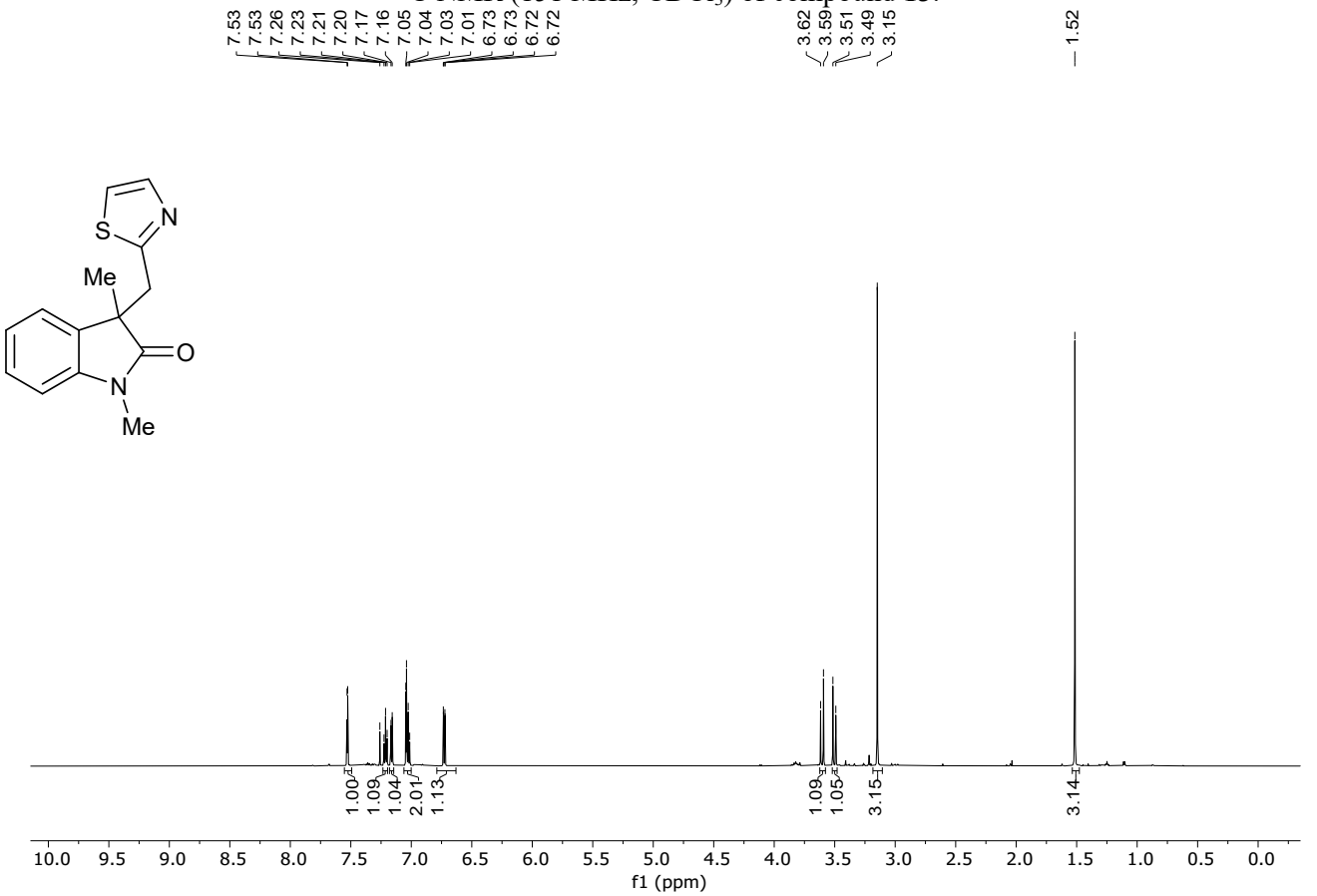
^{13}C NMR (151 MHz, $CDCl_3$) of compound **12**.



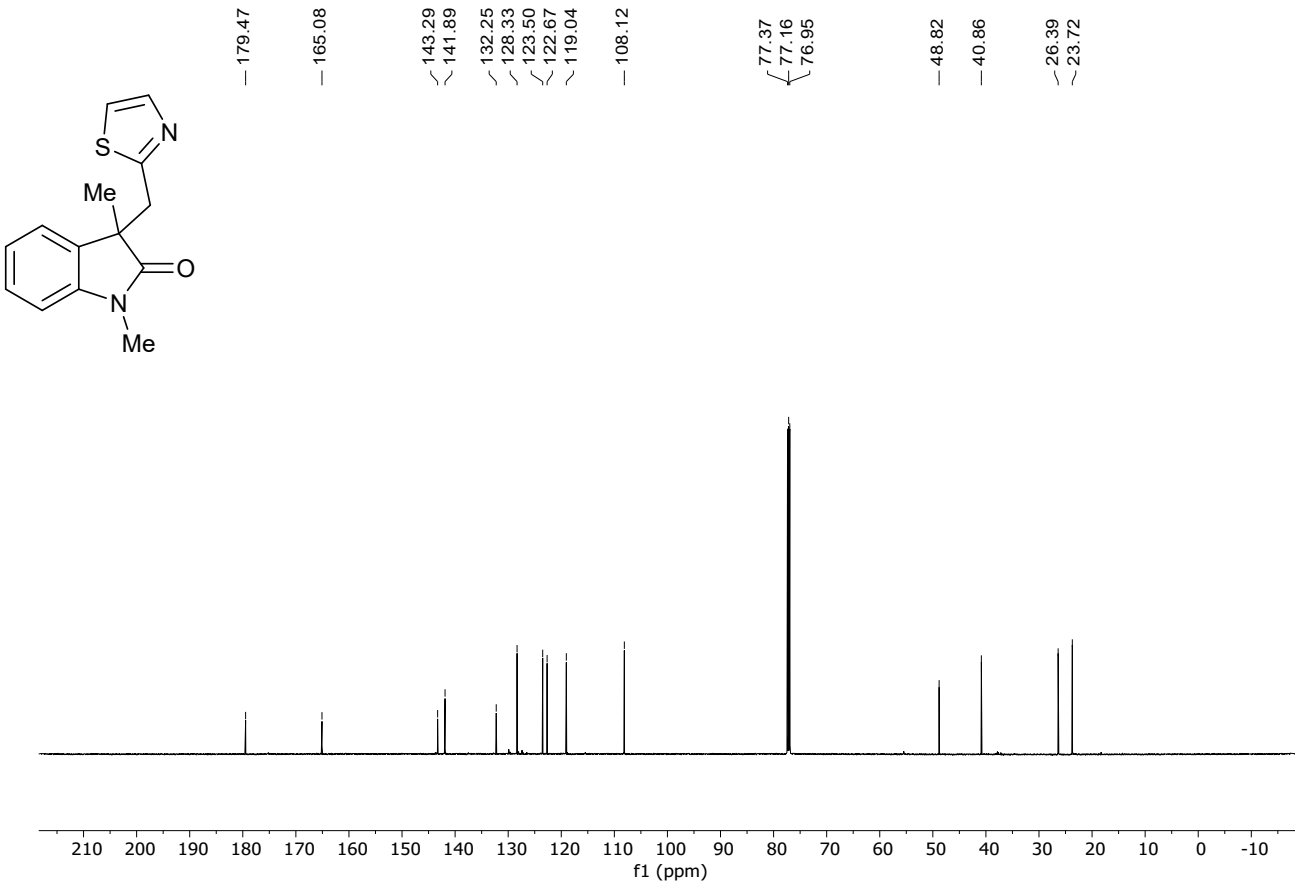
^{1}H NMR (600 MHz, $CDCl_3$) of compound **13**.



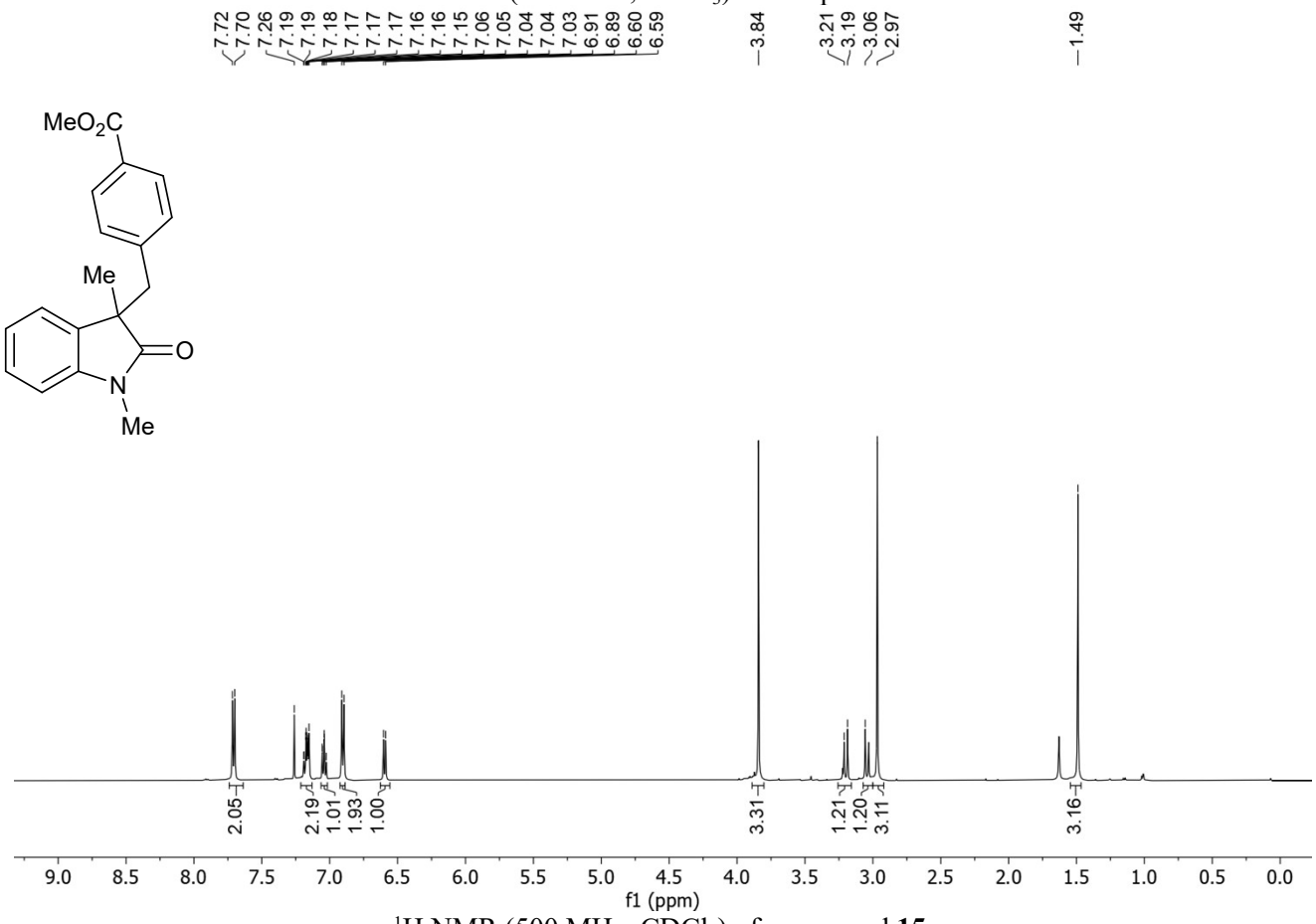
^{13}C NMR (151 MHz, $CDCl_3$) of compound **13**.



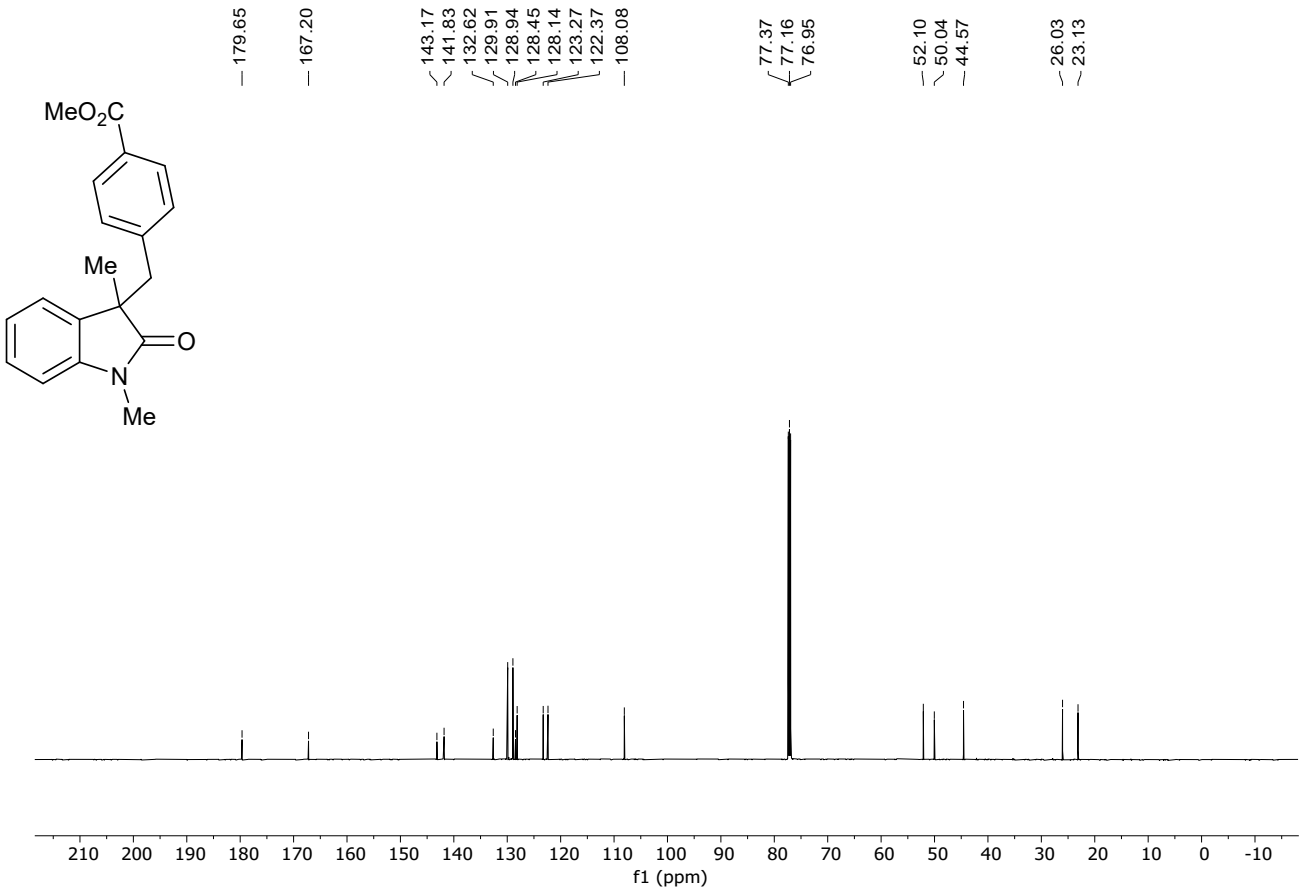
^{1}H NMR (600 MHz, $CDCl_3$) of compound **14**.



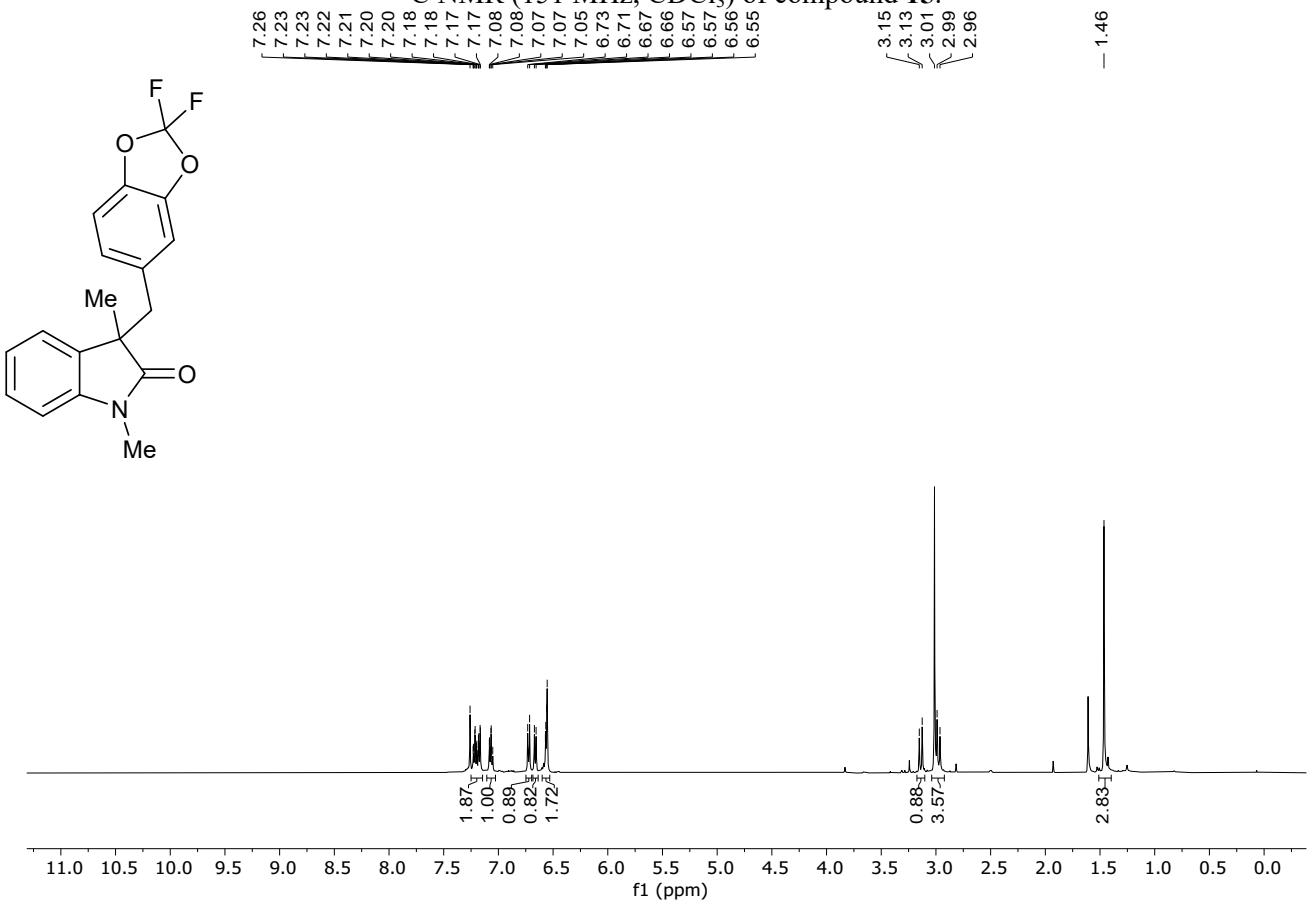
^{13}C NMR (151 MHz, $CDCl_3$) of compound **14**.



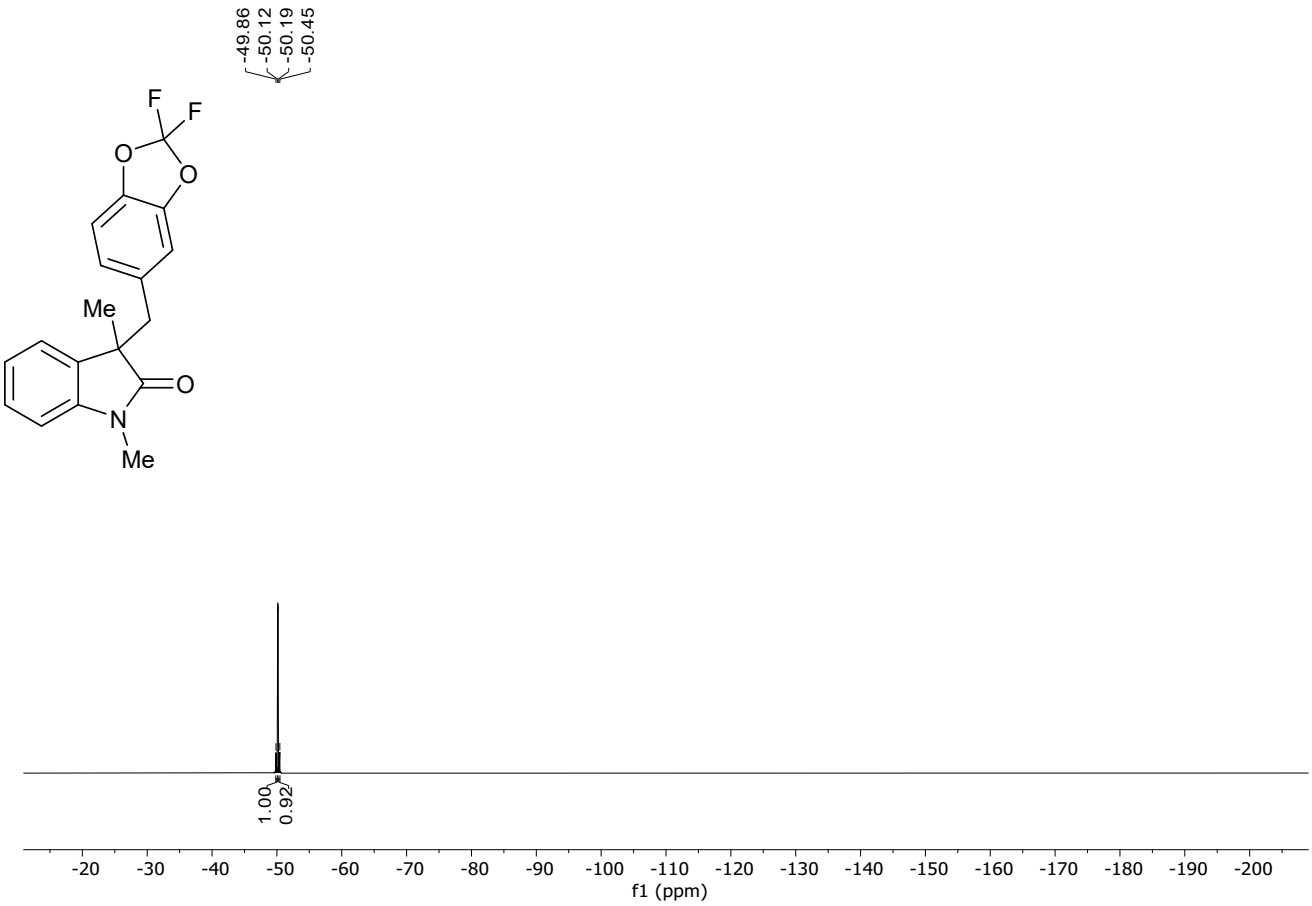
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15**.



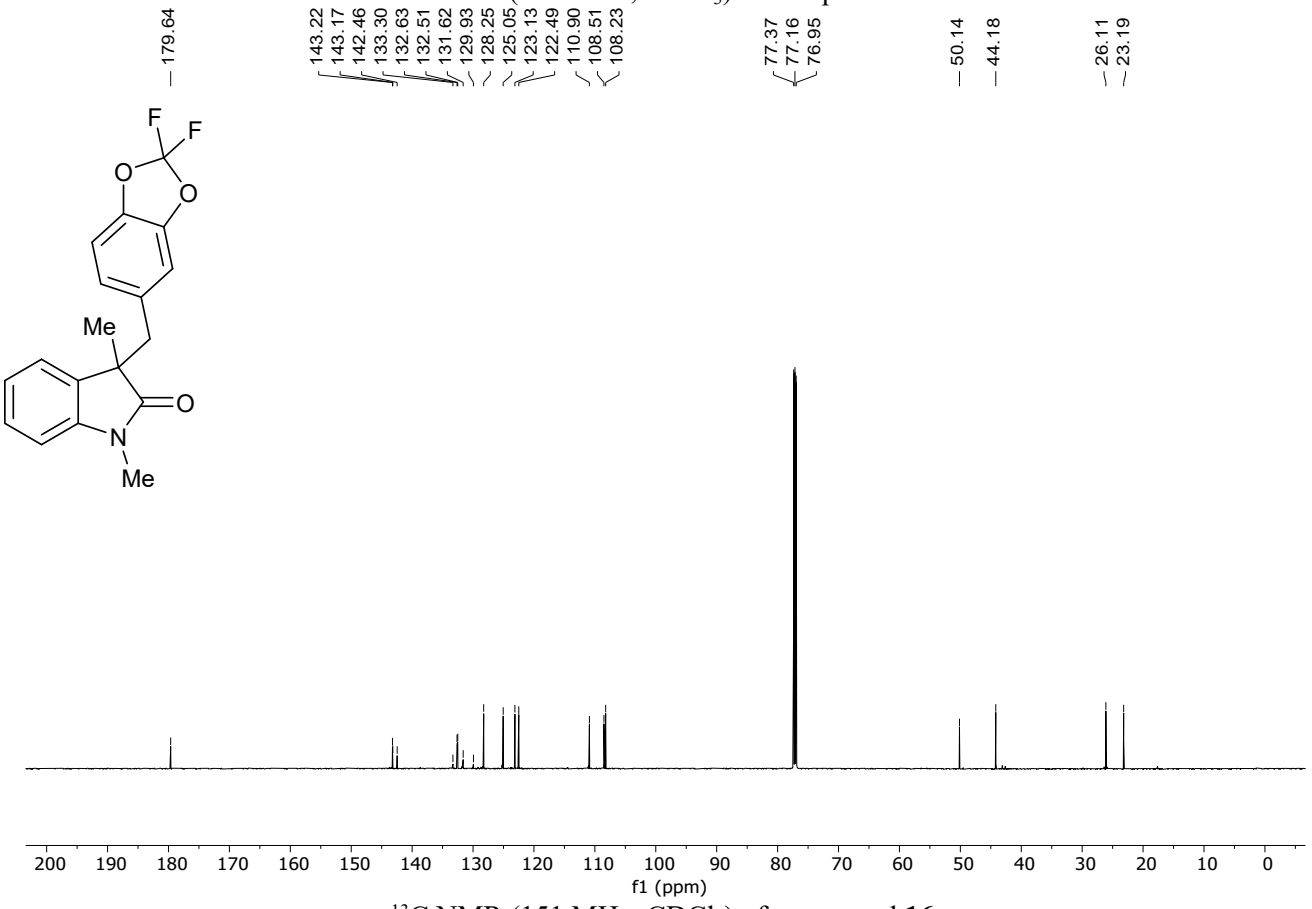
^{13}C NMR (151 MHz, $CDCl_3$) of compound **15**.



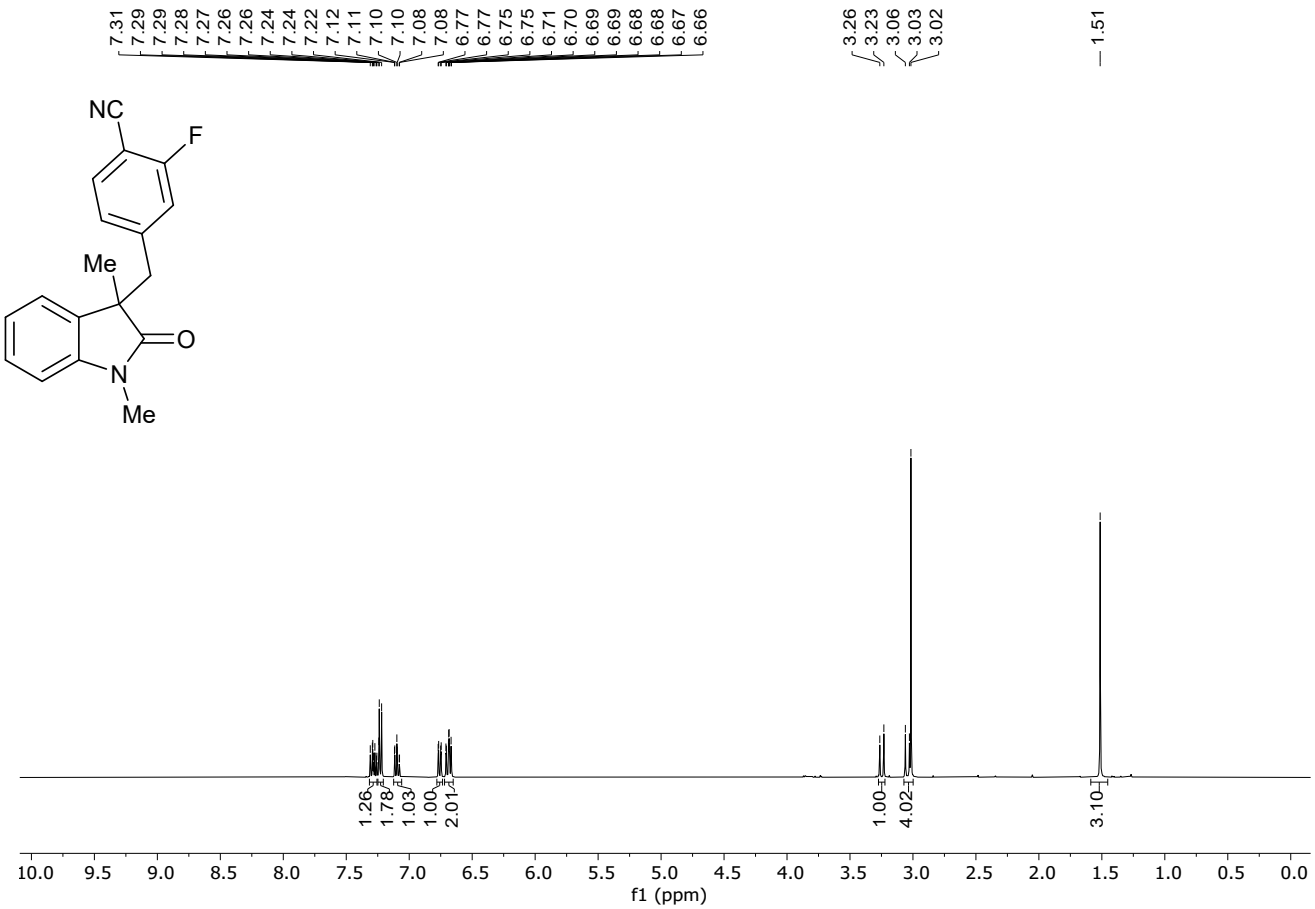
^{1}H NMR (500 MHz, $CDCl_3$) of compound **16**.



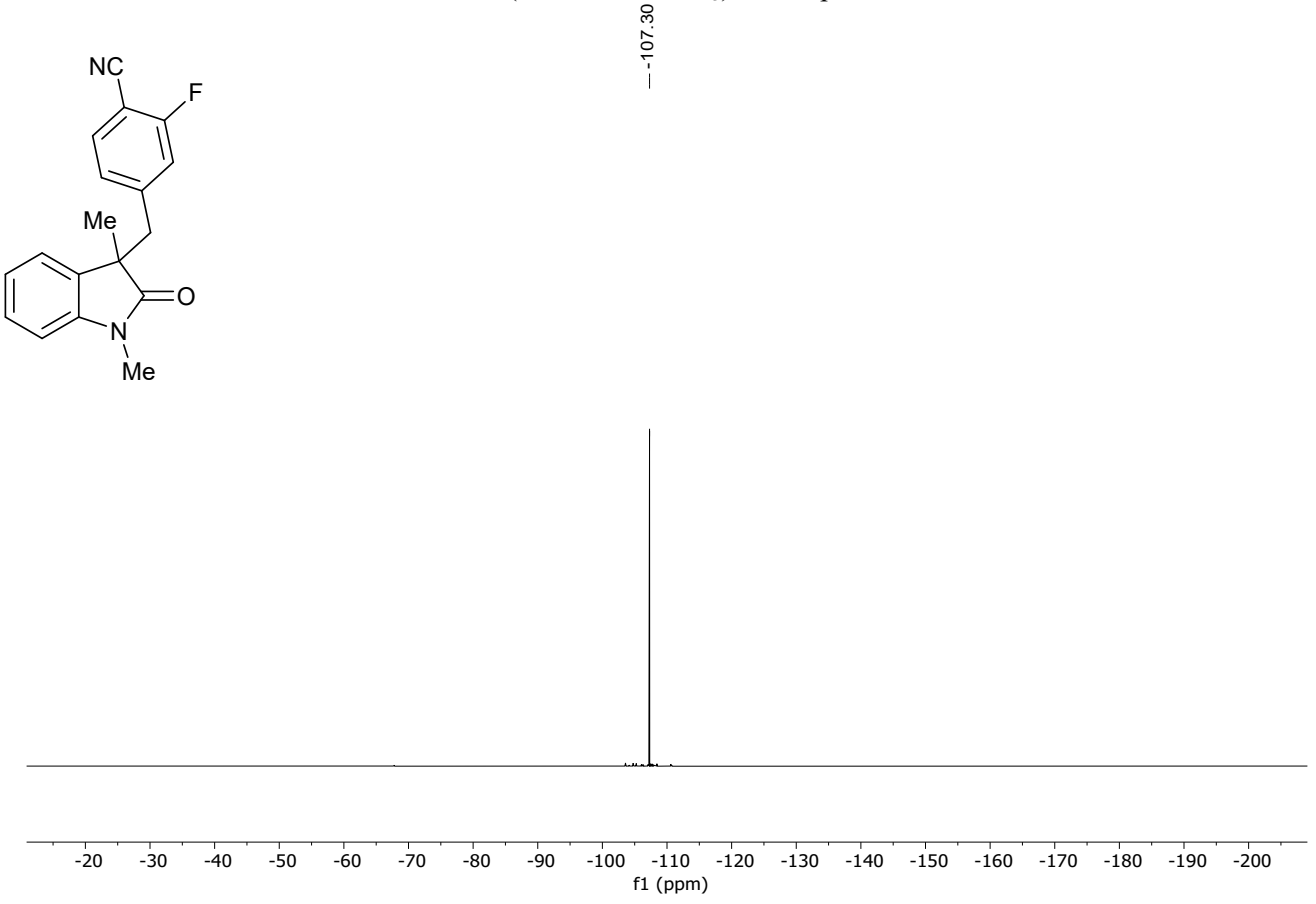
^{19}F NMR (376 MHz, $CDCl_3$) of compound **16**.



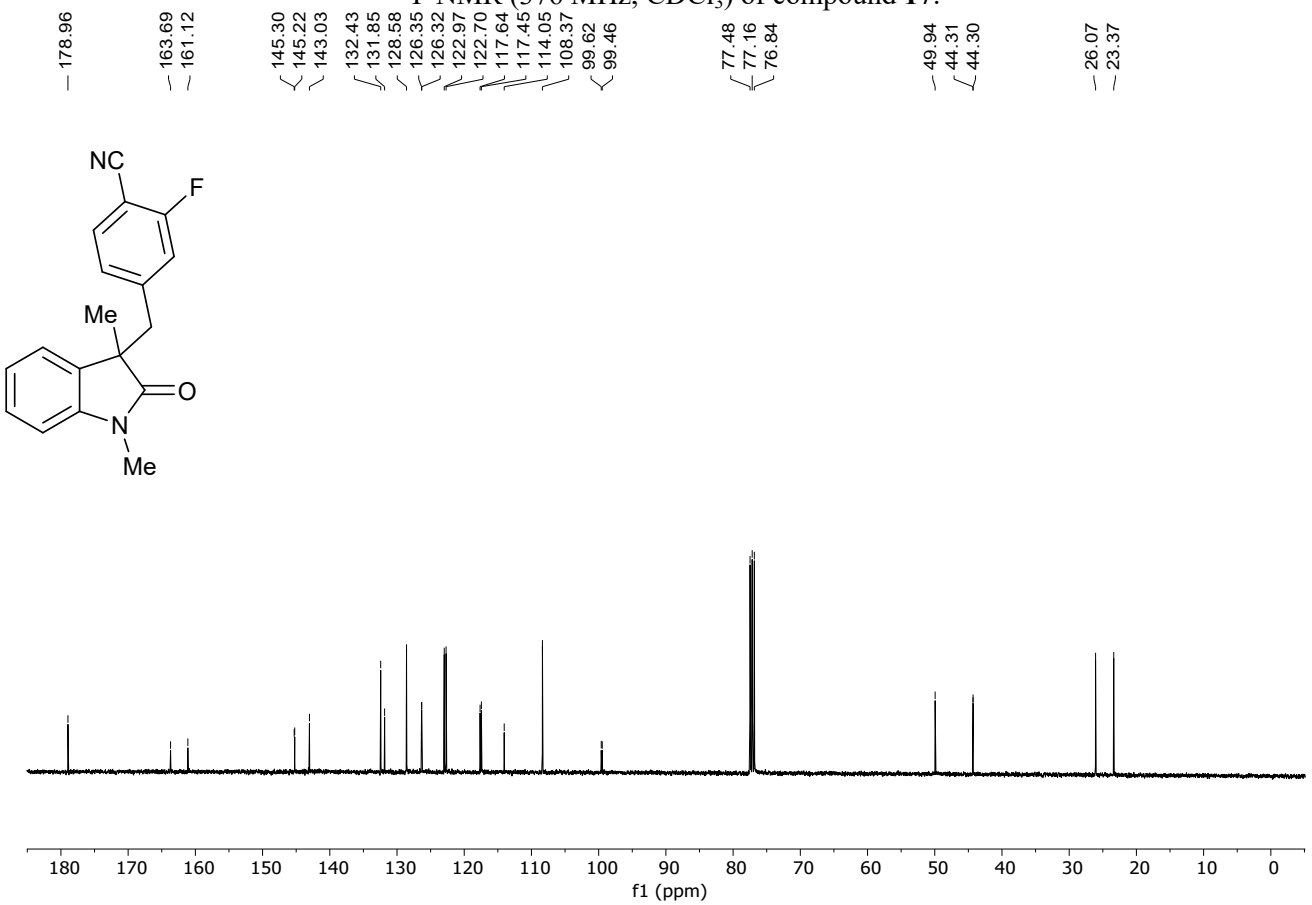
^{13}C NMR (151 MHz, $CDCl_3$) of compound **16**.



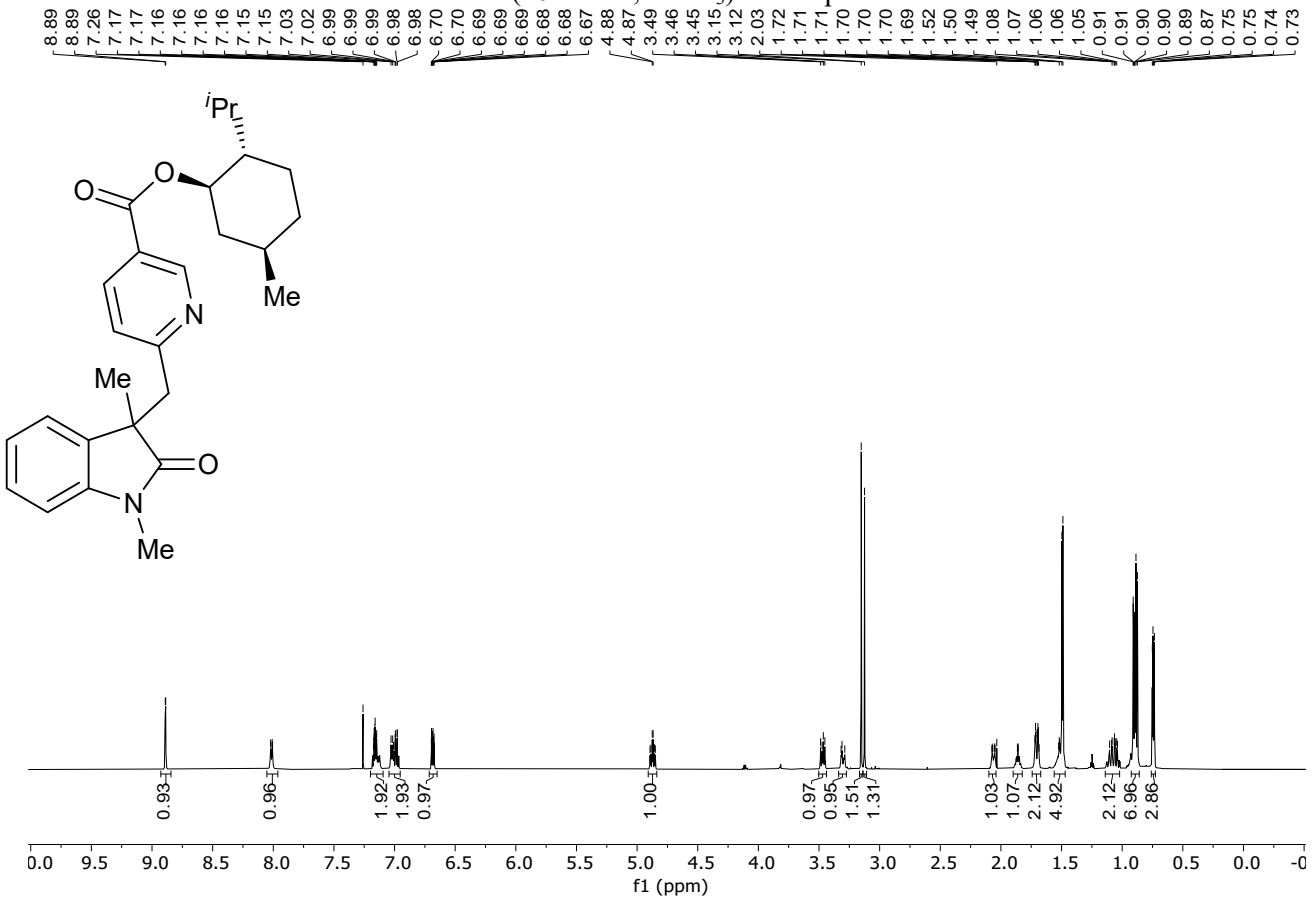
^{1}H NMR (400 MHz, $CDCl_3$) of compound **17**.



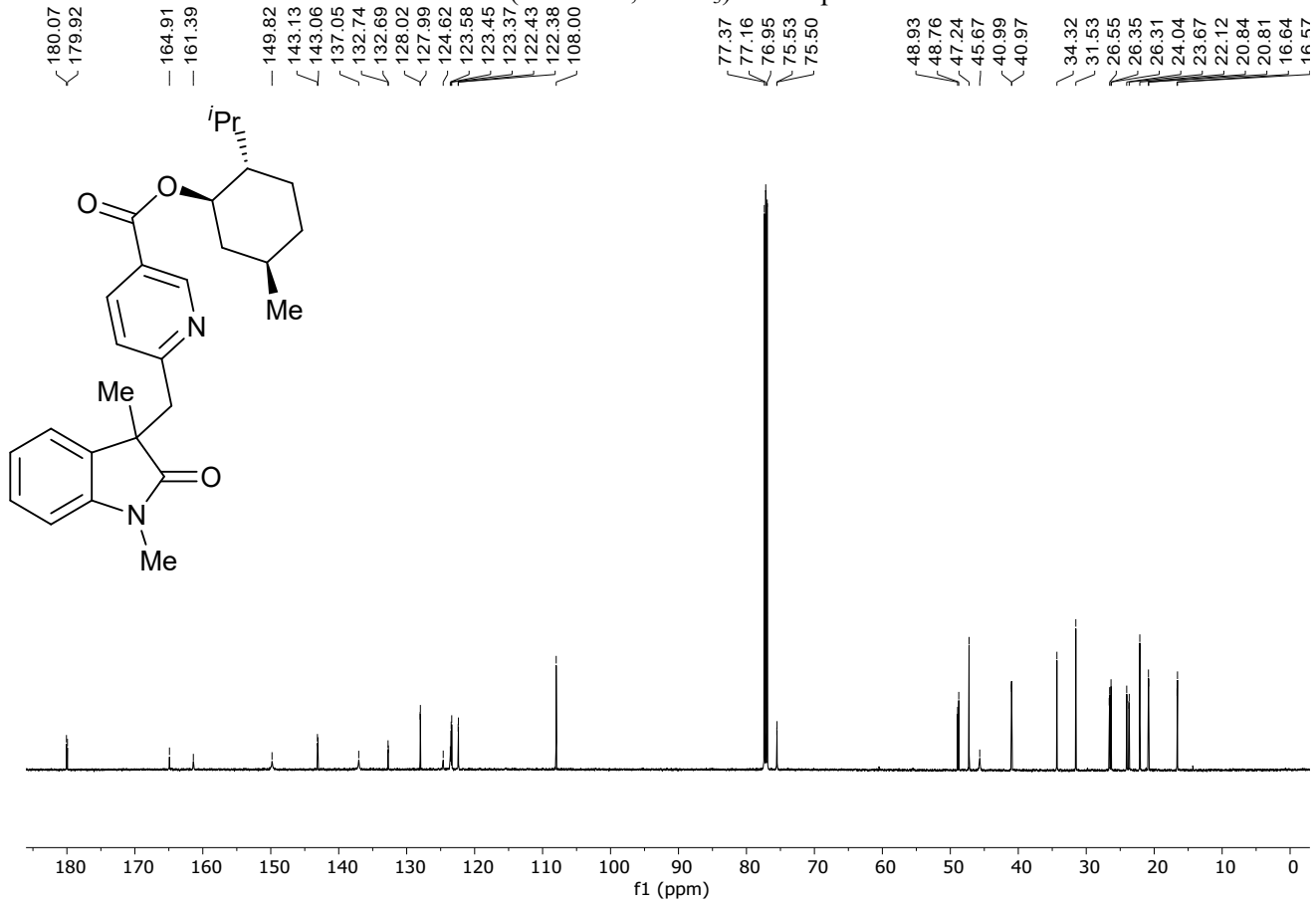
^{19}F NMR (376 MHz, $CDCl_3$) of compound **17**.



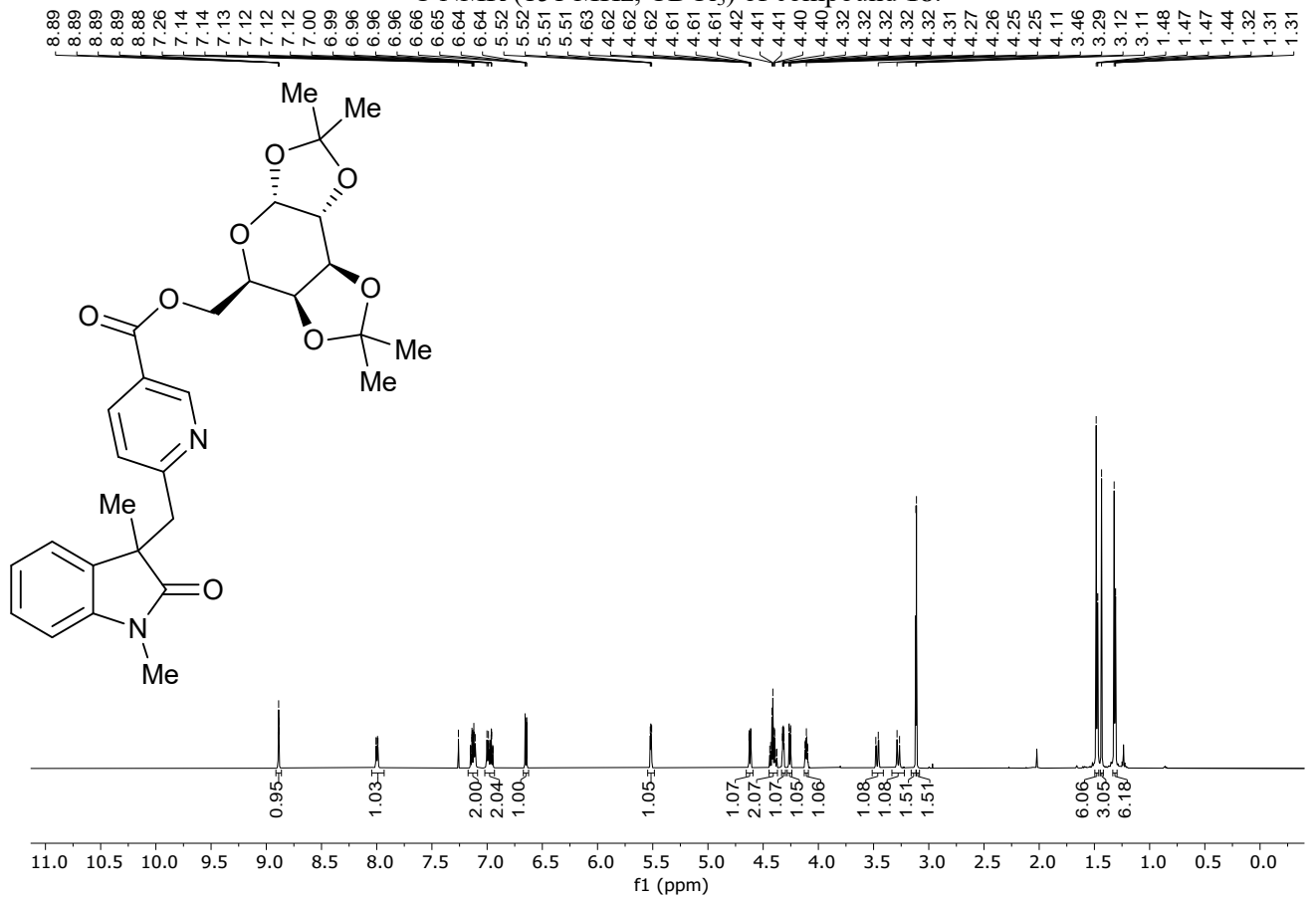
^{13}C NMR (101 MHz, $CDCl_3$) of compound **17**.



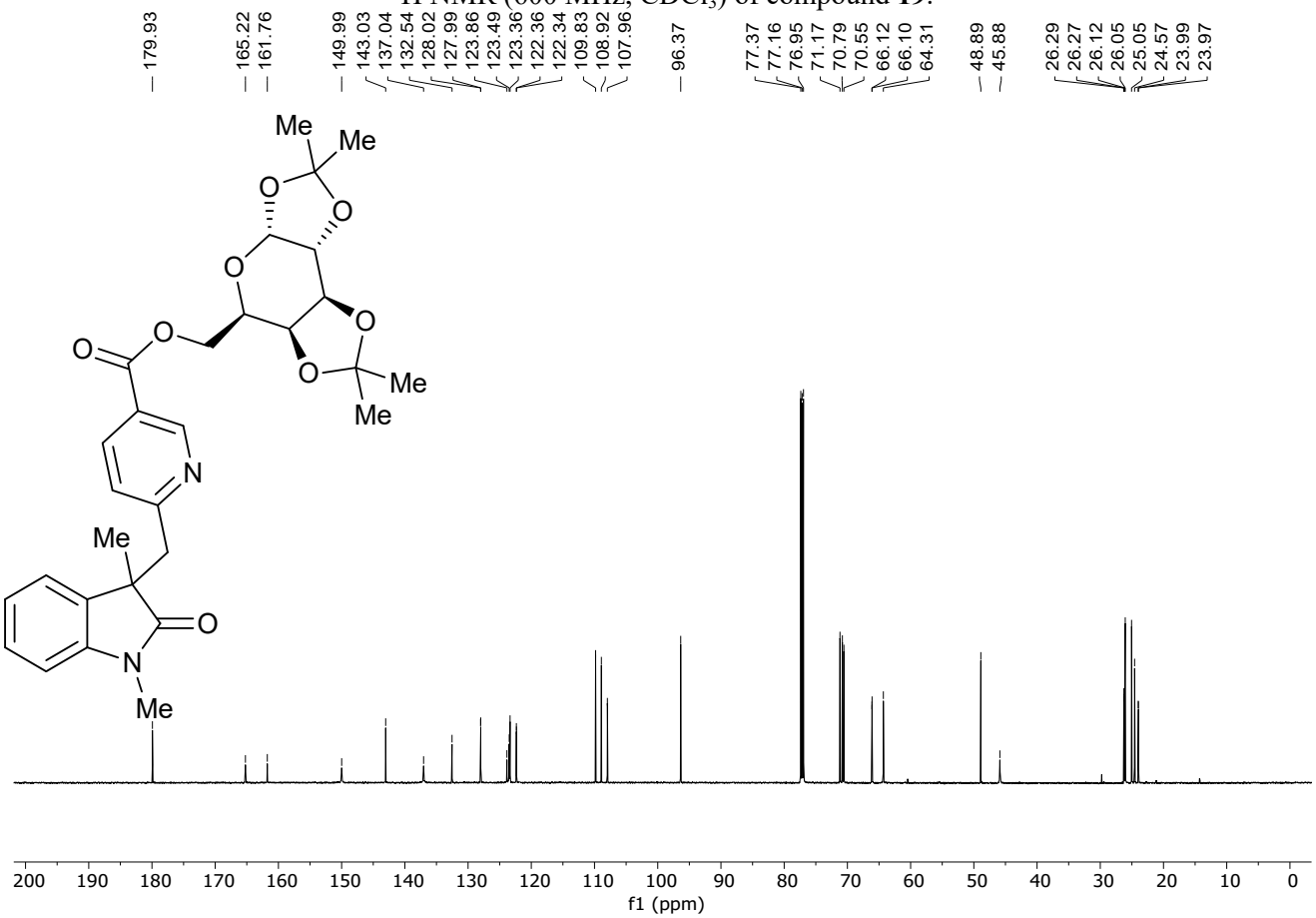
^{1}H NMR (600 MHz, $CDCl_3$) of compound **18**.



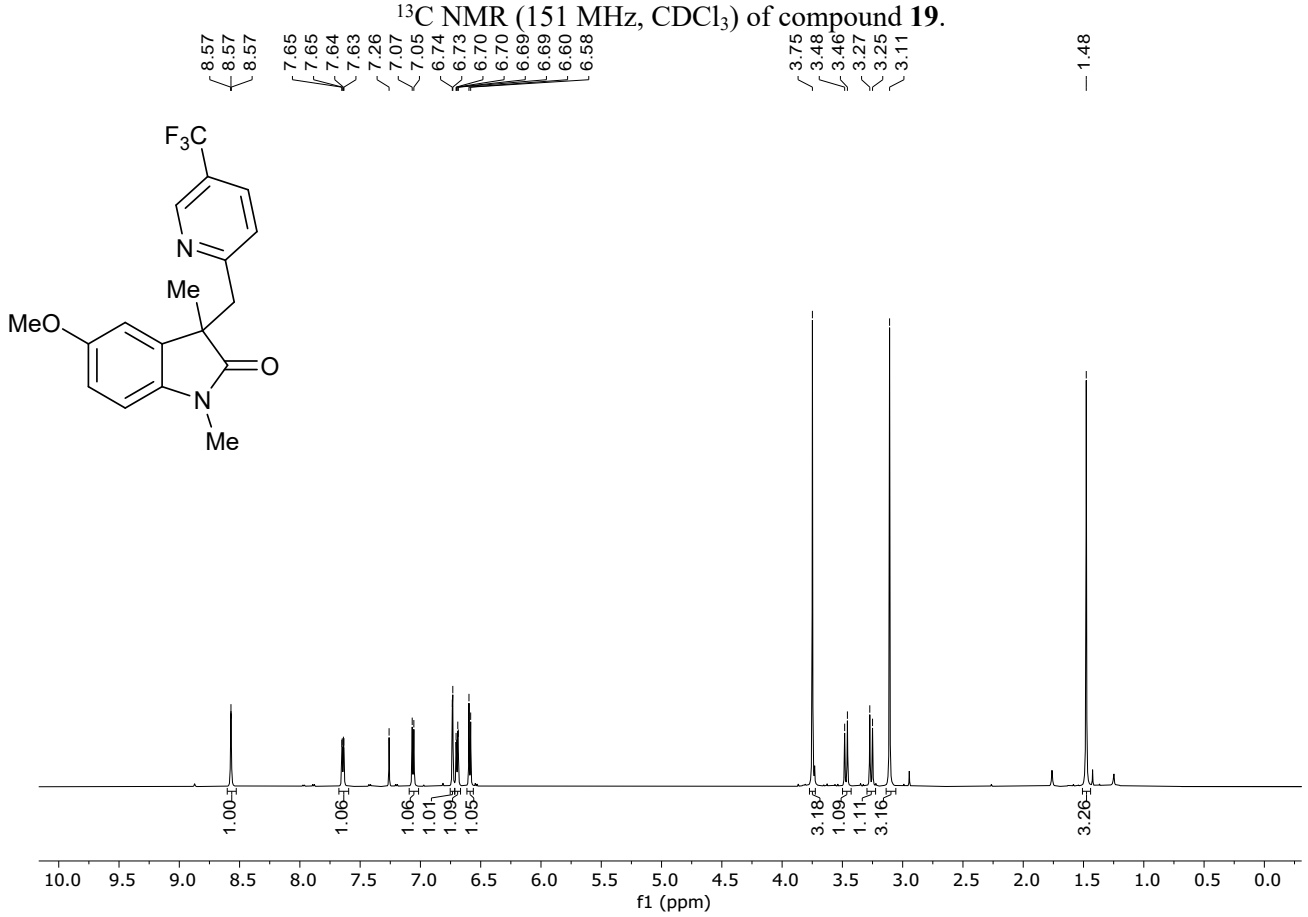
^{13}C NMR (151 MHz, $CDCl_3$) of compound **18**.



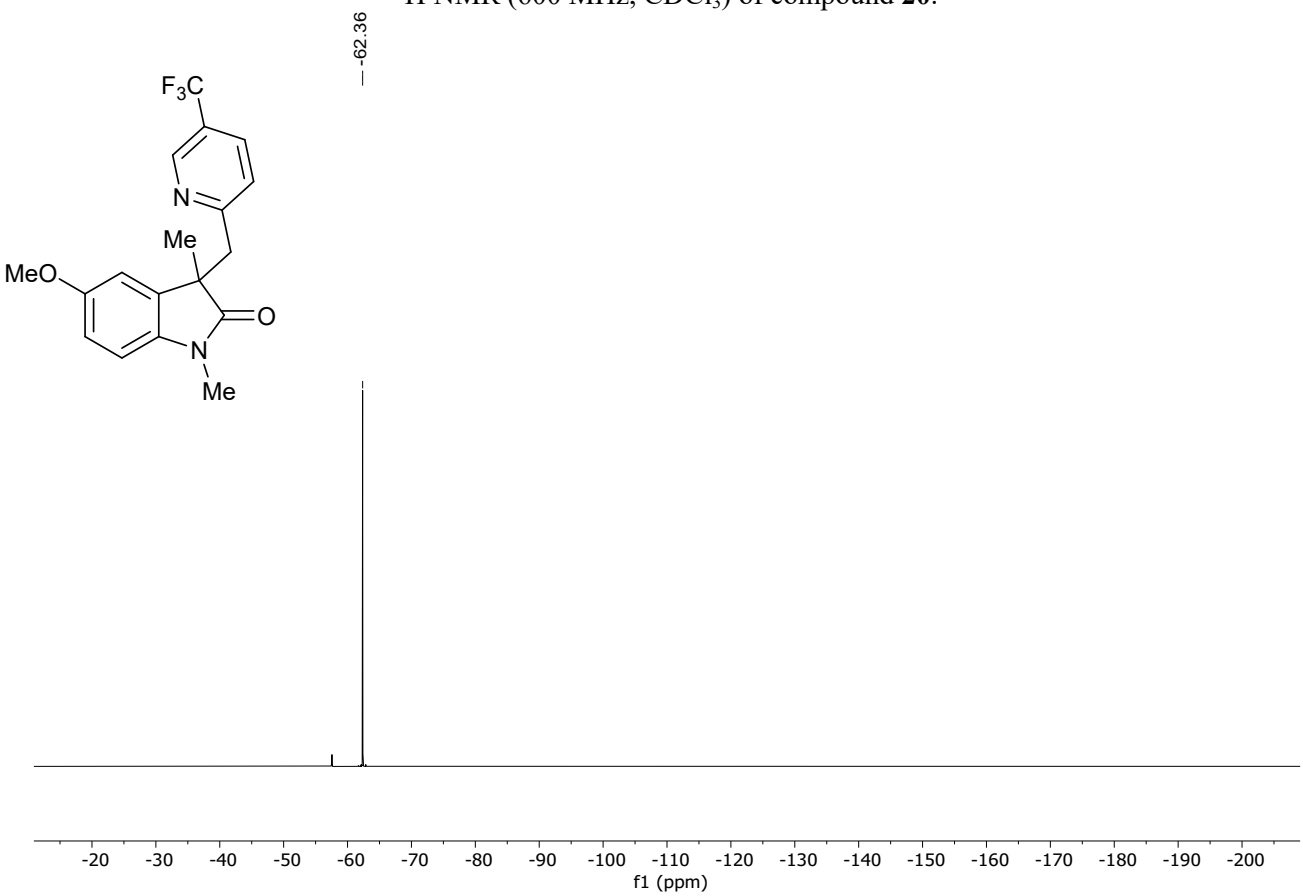
^{1}H NMR (600 MHz, $CDCl_3$) of compound **19**.



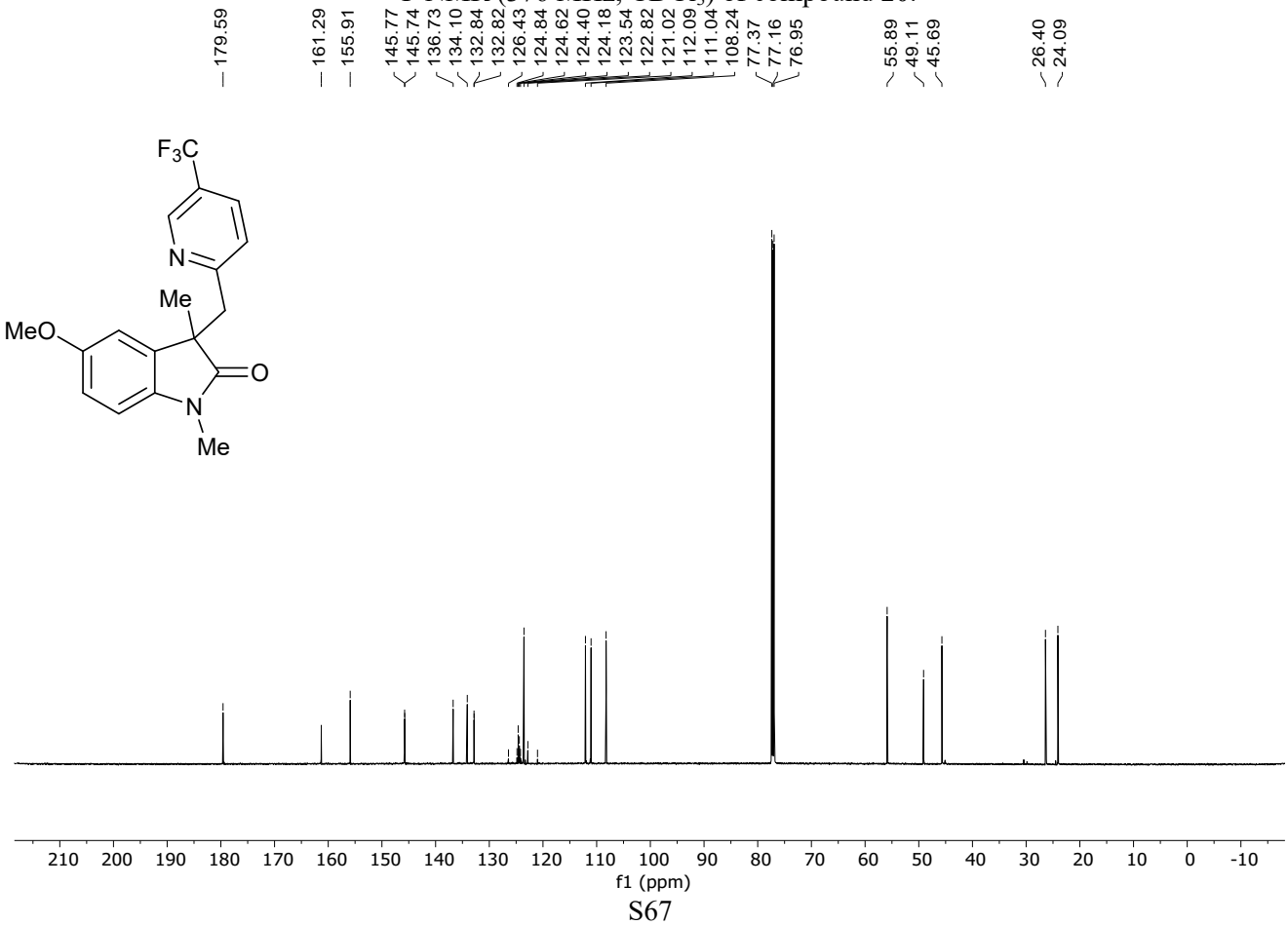
^{13}C NMR (151 MHz, $CDCl_3$) of compound **19**.



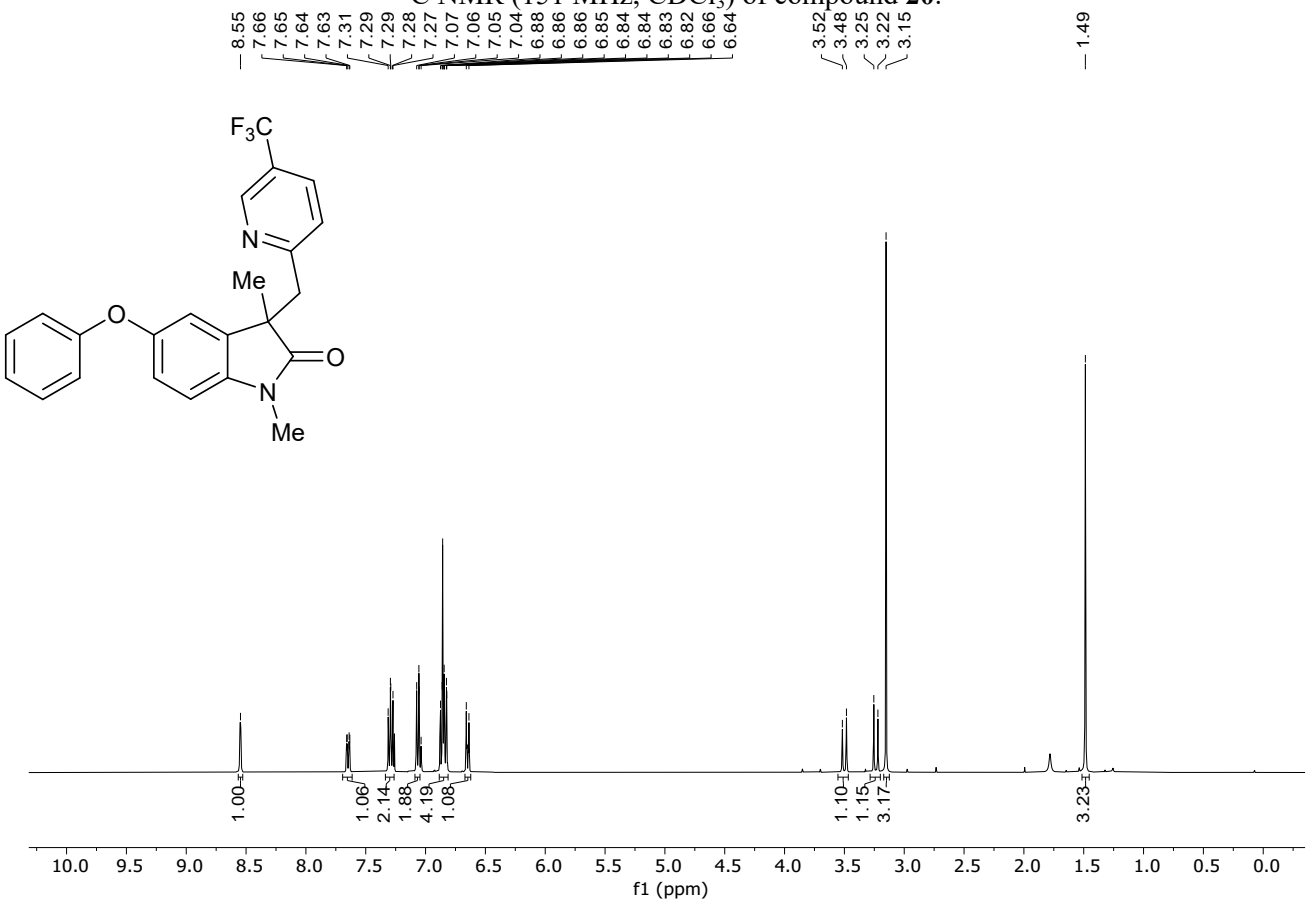
^{1}H NMR (600 MHz, $CDCl_3$) of compound **20**.



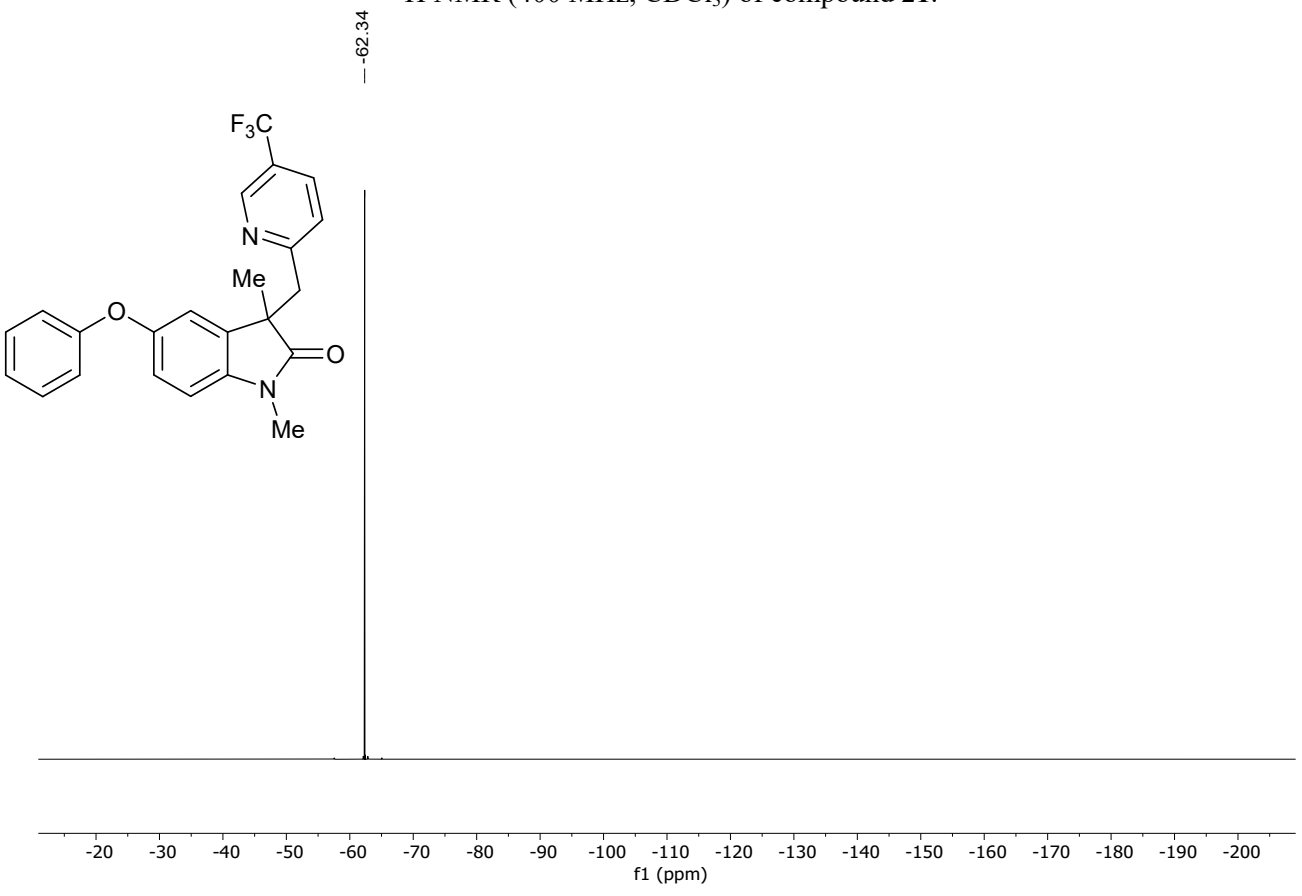
^{19}F NMR (376 MHz, $CDCl_3$) of compound **20**.



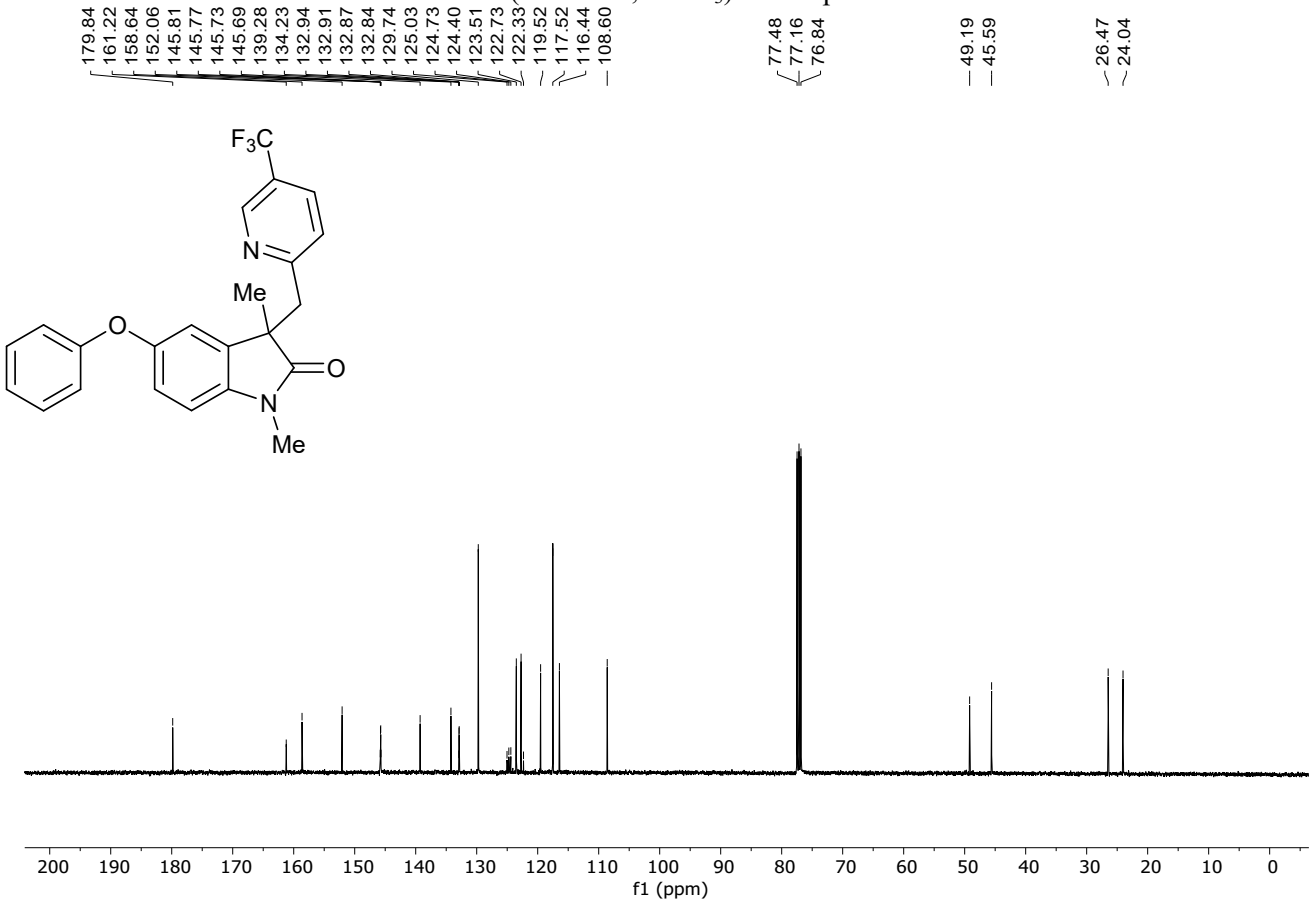
^{13}C NMR (151 MHz, $CDCl_3$) of compound **20**.



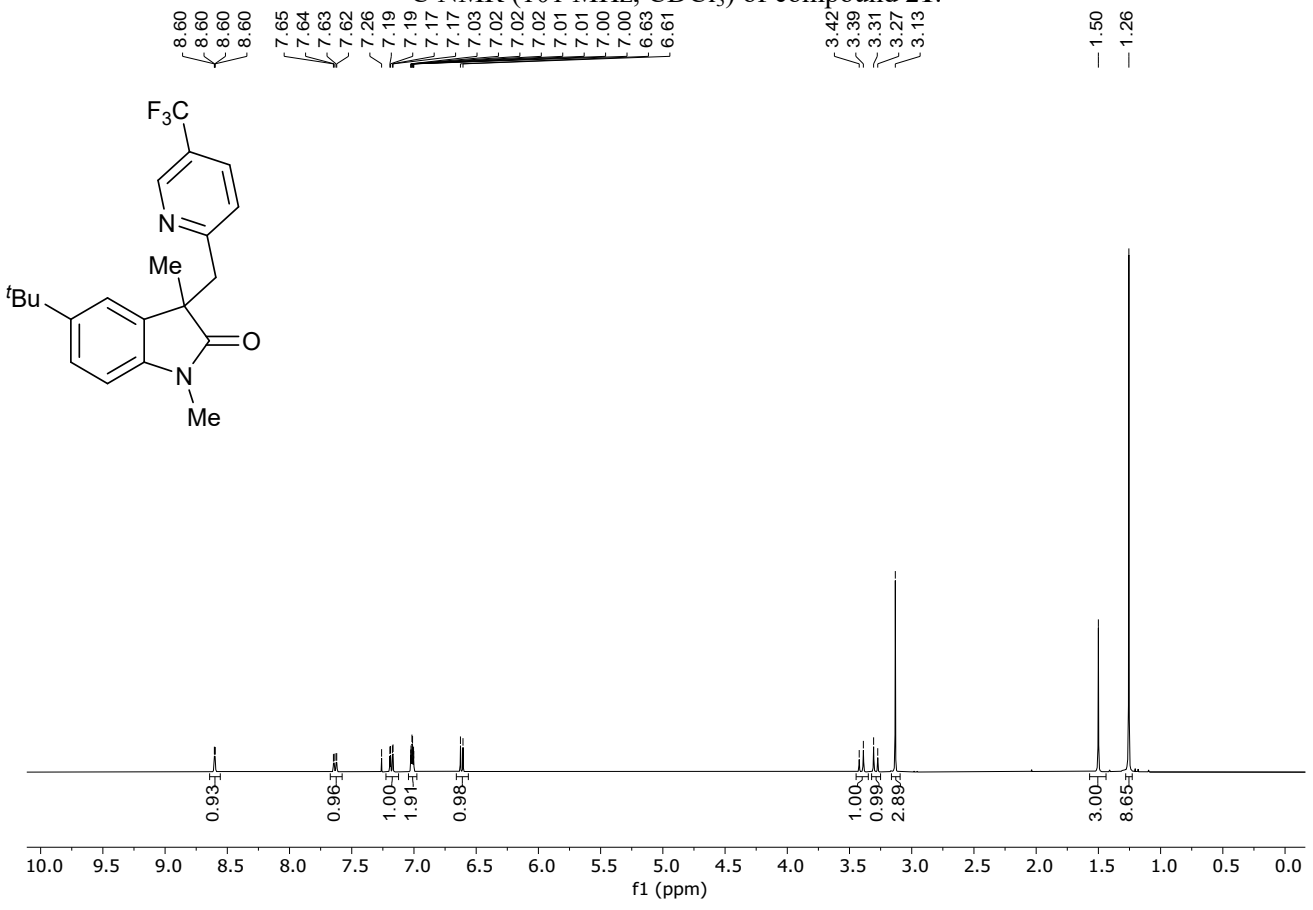
^{1}H NMR (400 MHz, $CDCl_3$) of compound **21**.



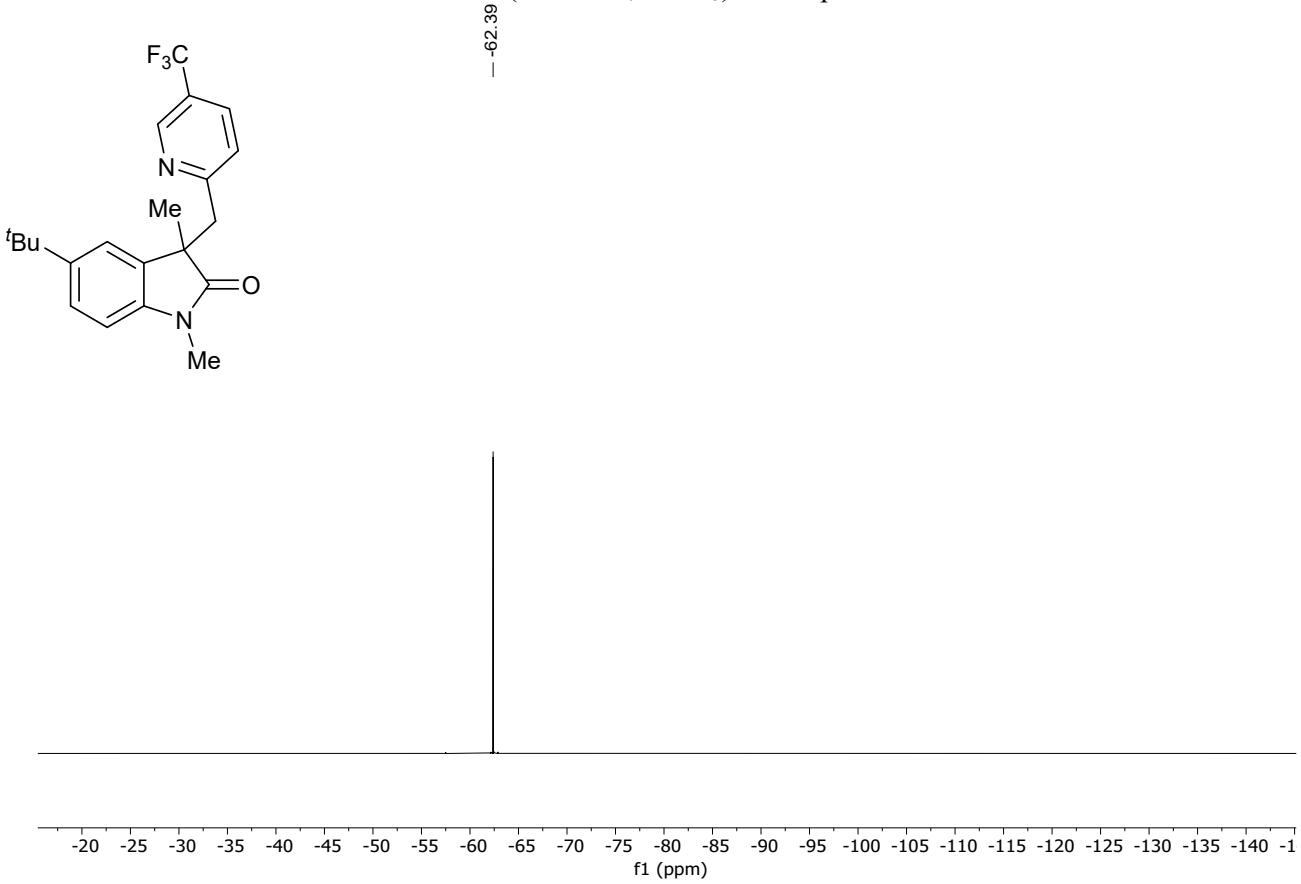
^{19}F NMR (376 MHz, $CDCl_3$) of compound **21**.



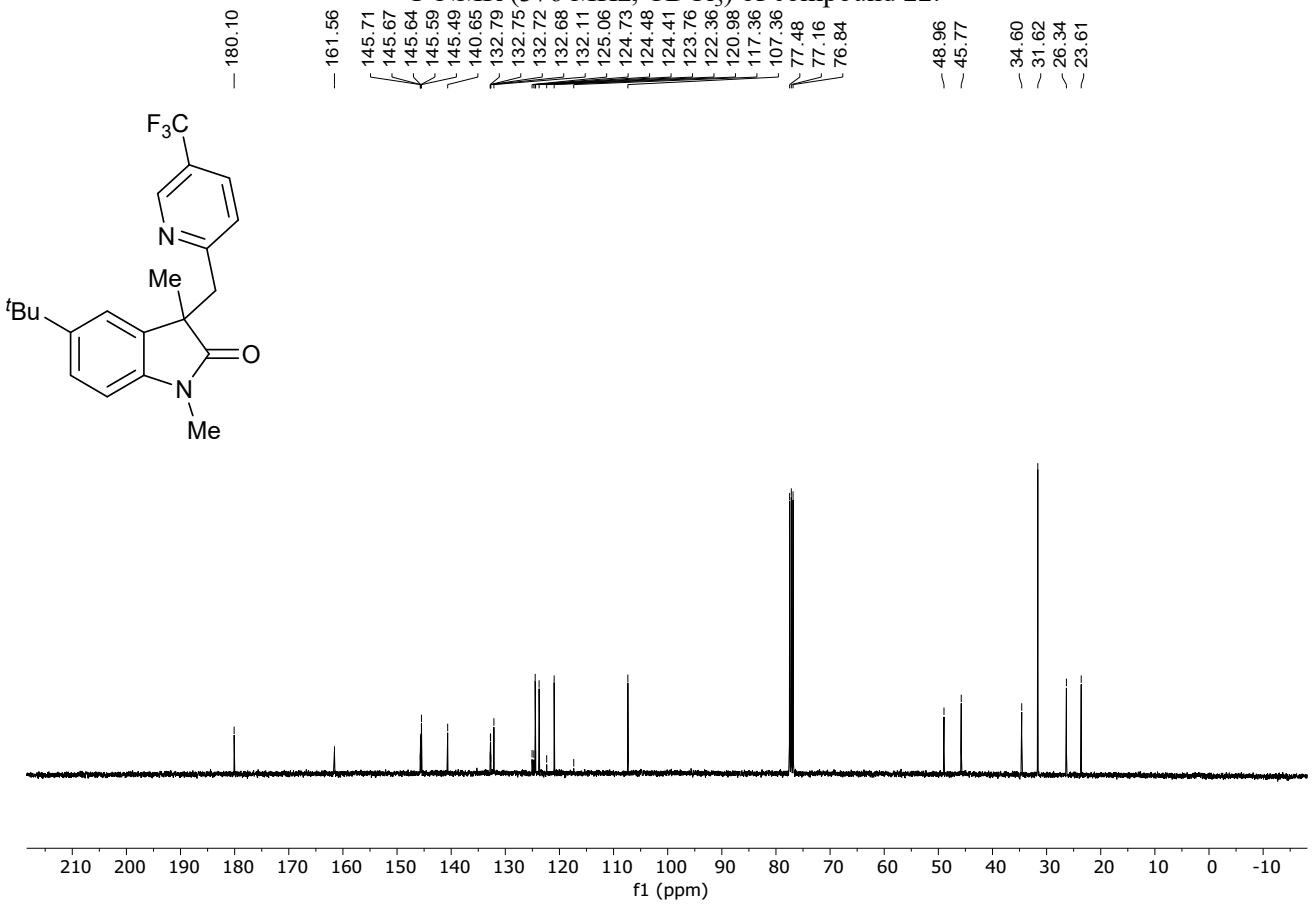
^{13}C NMR (101 MHz, $CDCl_3$) of compound **21**.



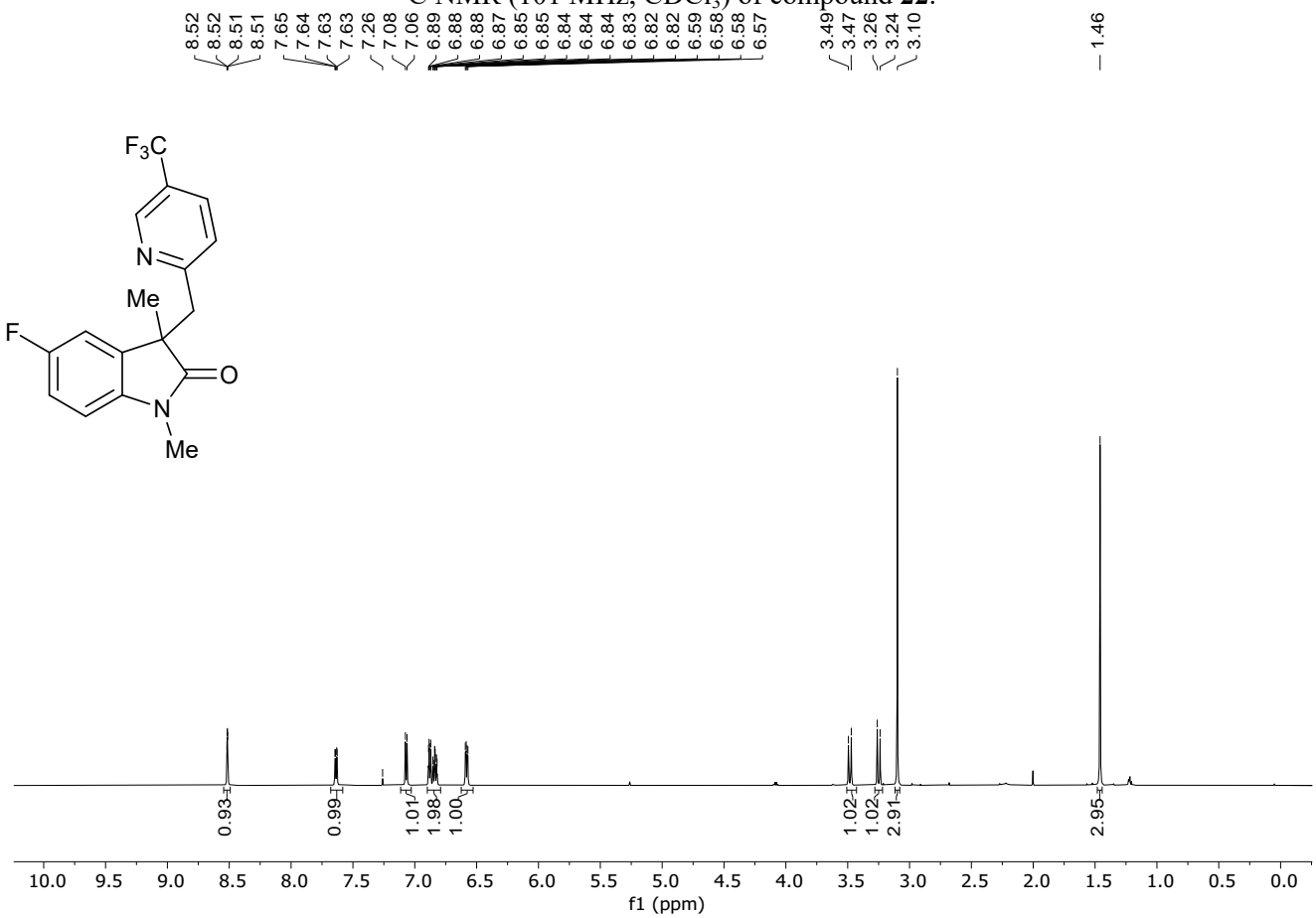
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22**.



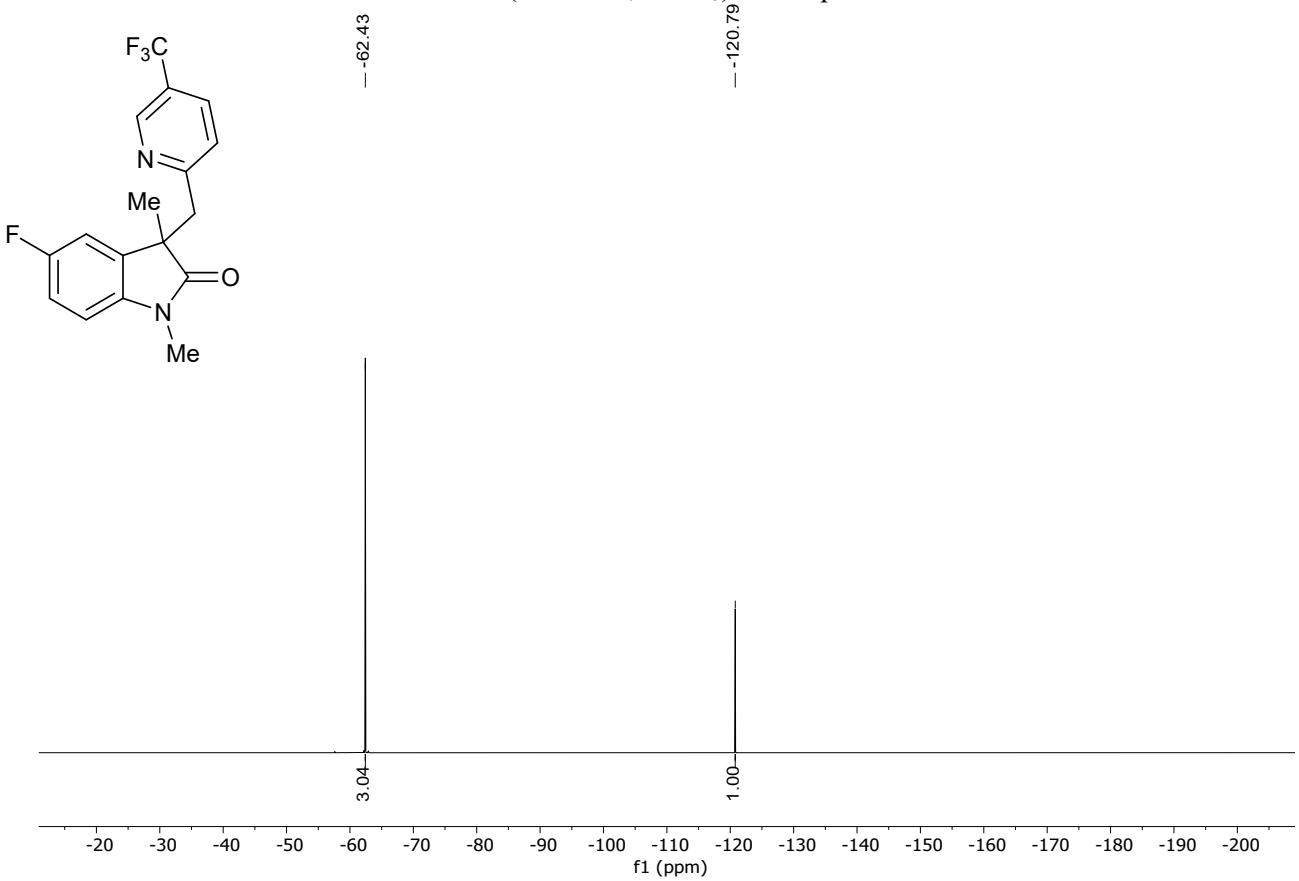
^{19}F NMR (376 MHz, $CDCl_3$) of compound **22**.



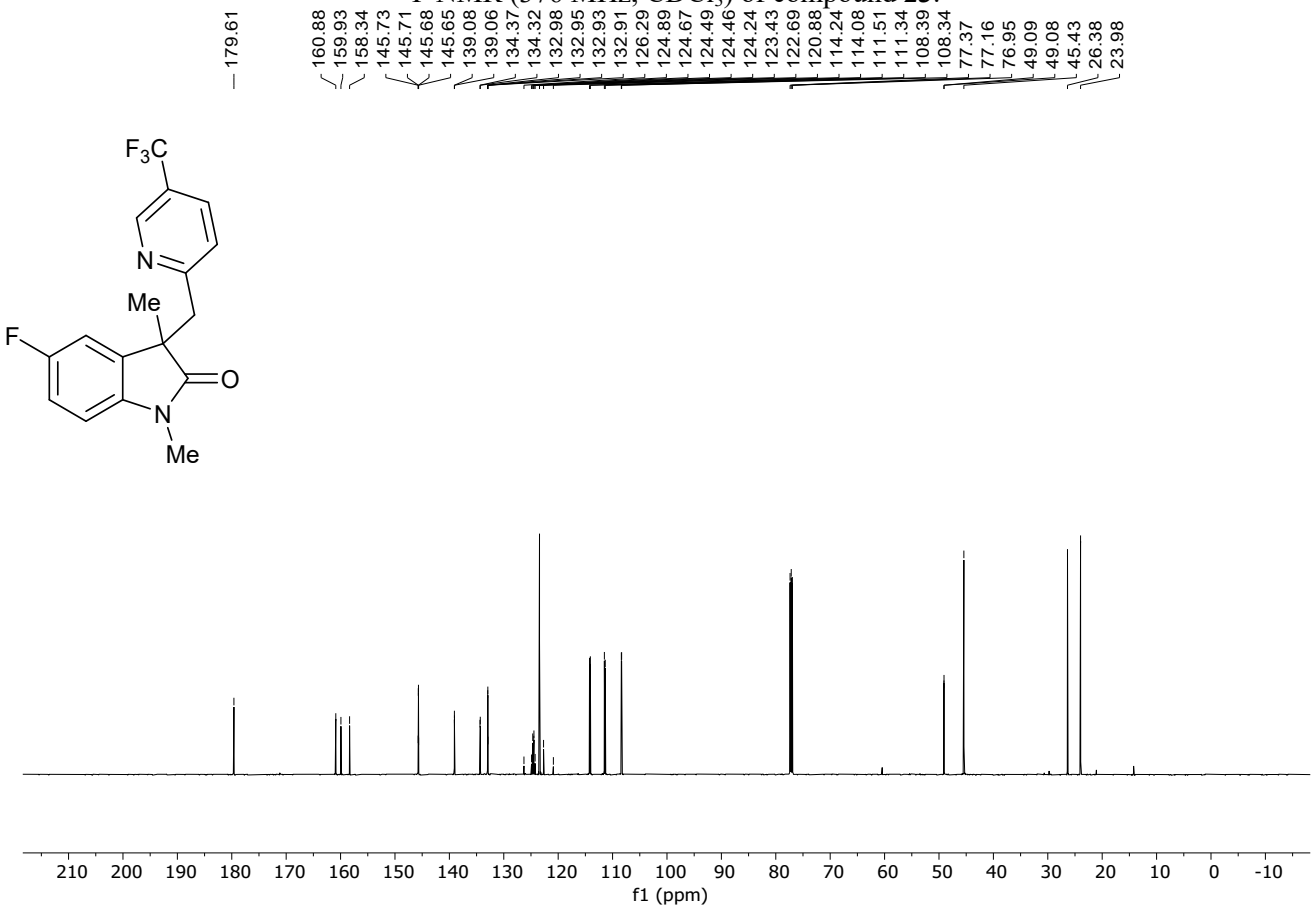
^{13}C NMR (101 MHz, $CDCl_3$) of compound **22**.



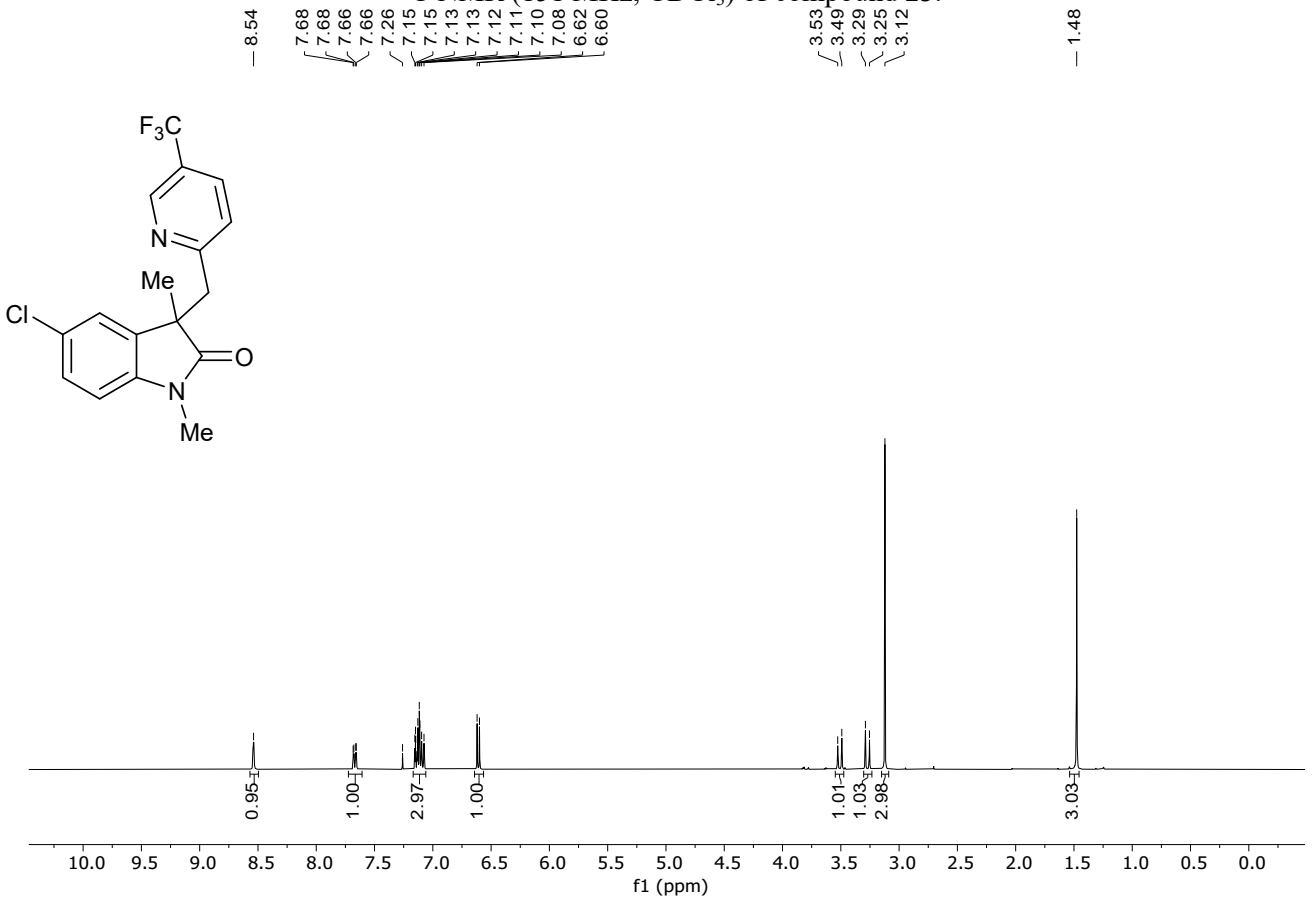
^{1}H NMR (600 MHz, $CDCl_3$) of compound **23**.



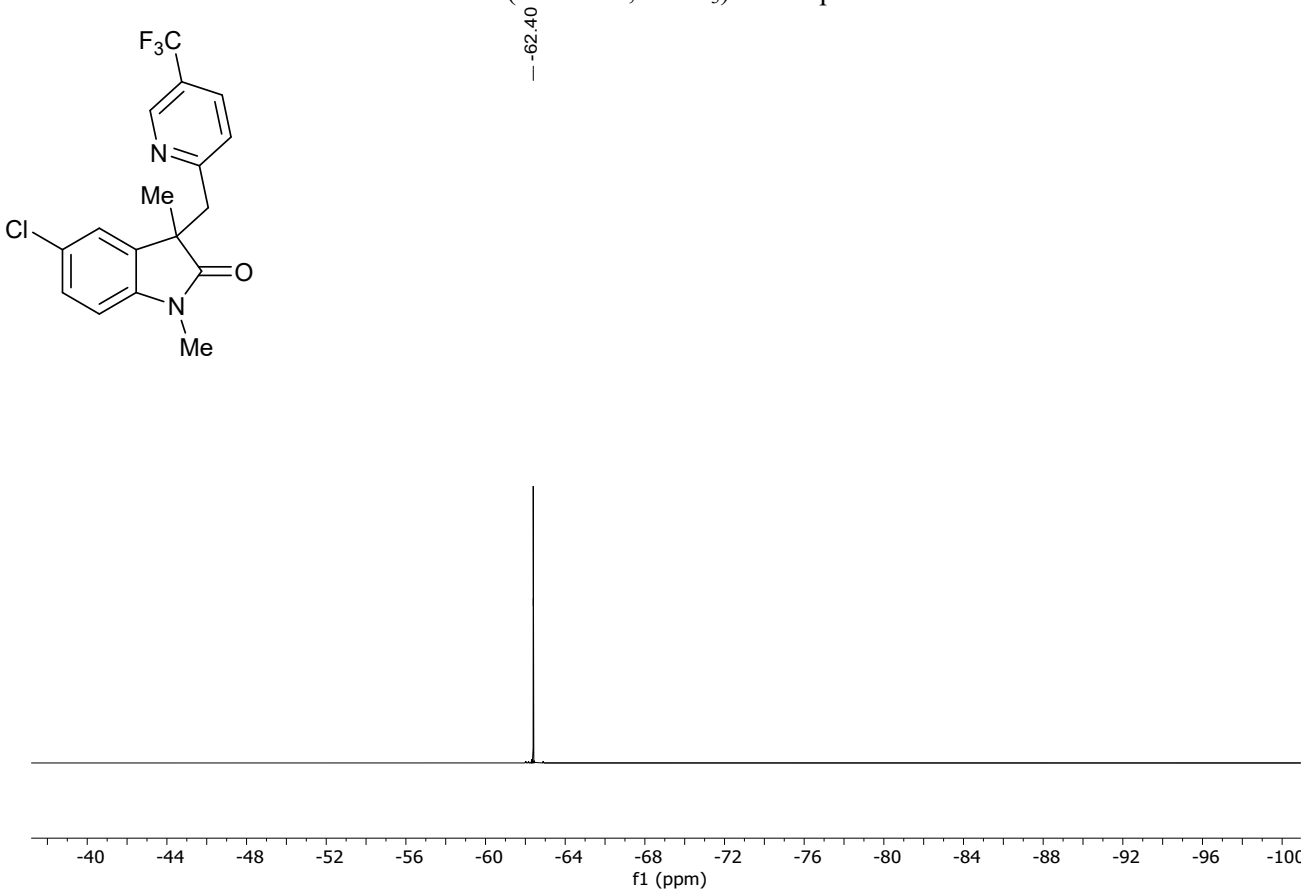
^{19}F NMR (376 MHz, $CDCl_3$) of compound **23**.



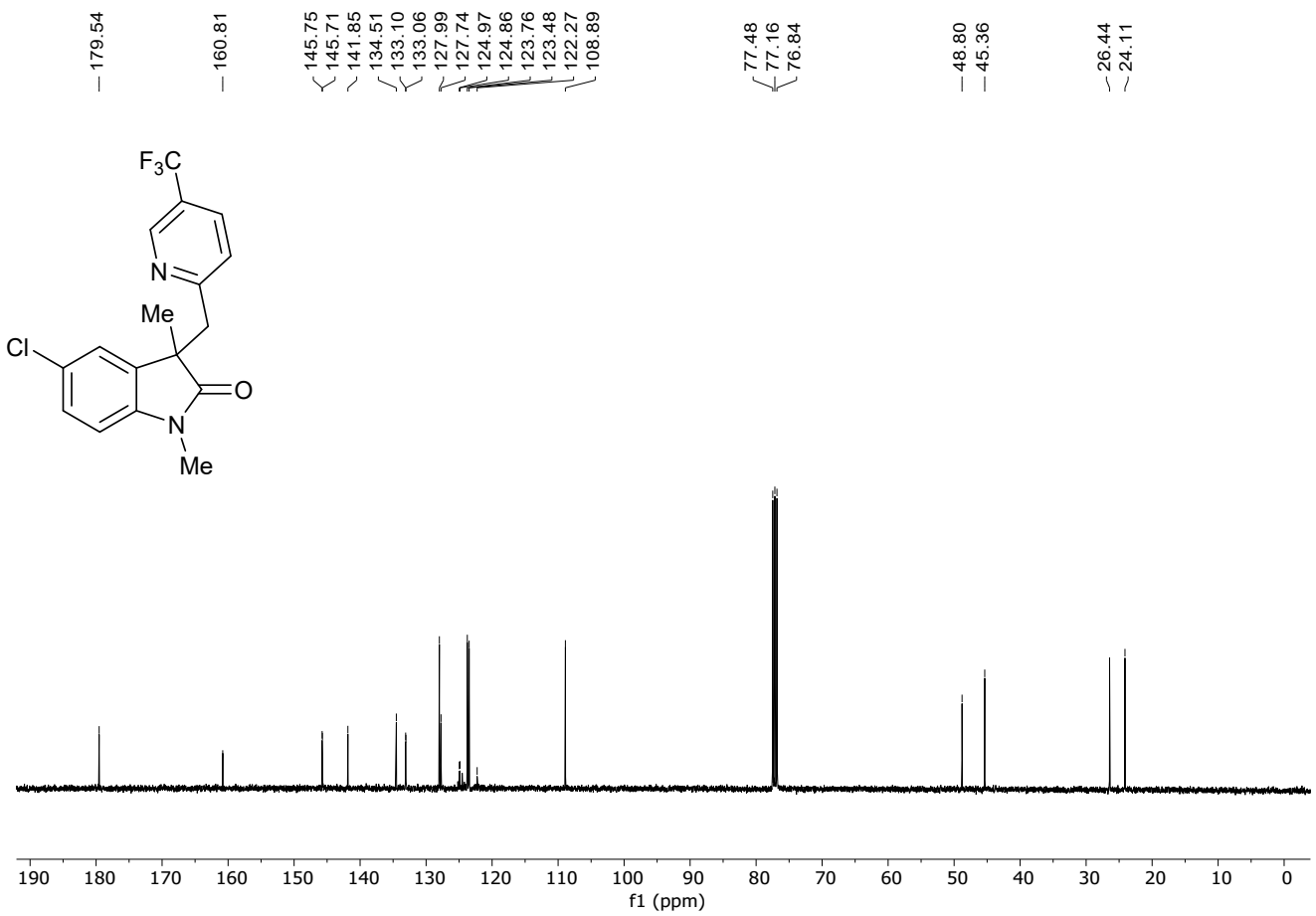
^{13}C NMR (151 MHz, $CDCl_3$) of compound **23**.



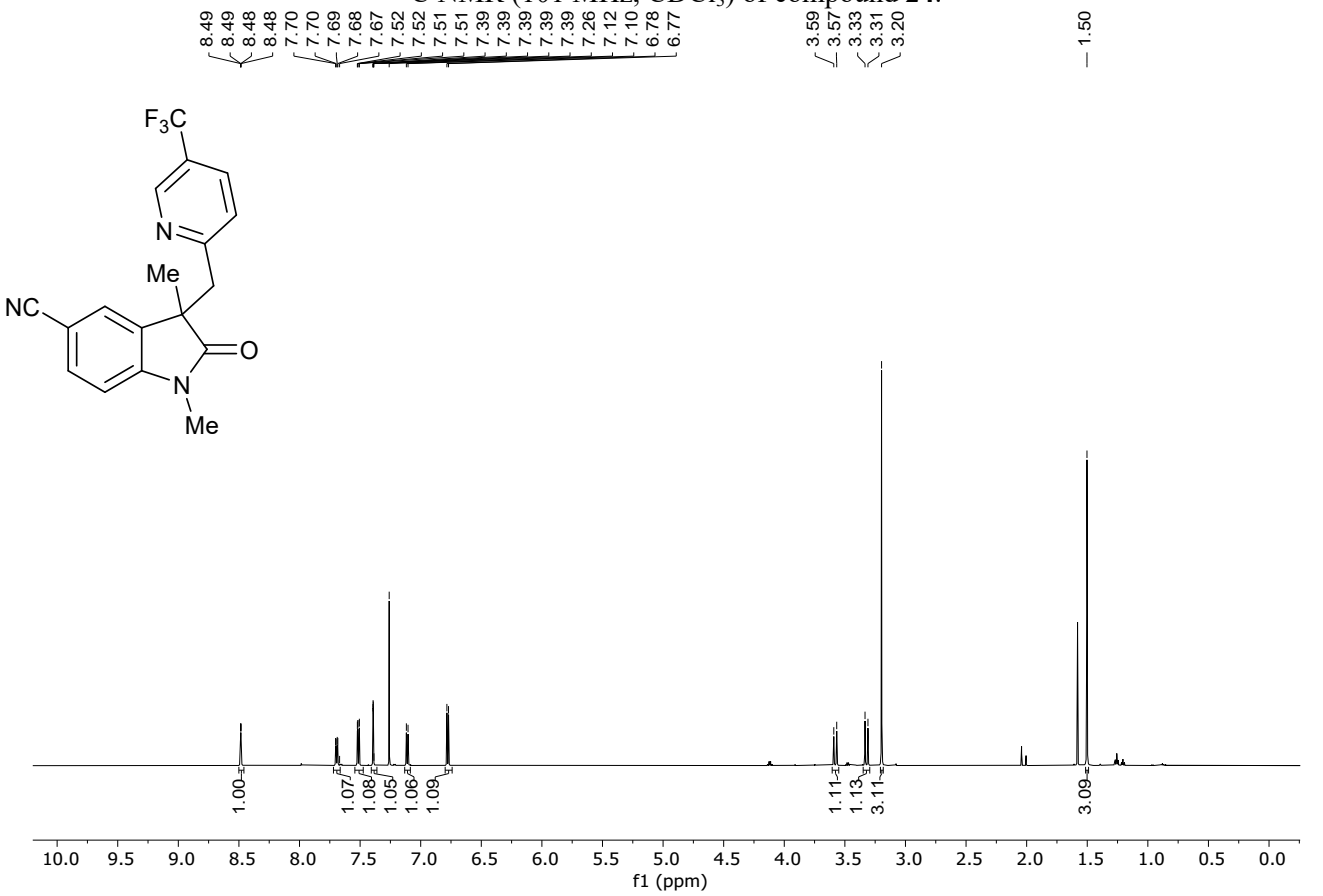
^{1}H NMR (400 MHz, $CDCl_3$) of compound **24**.



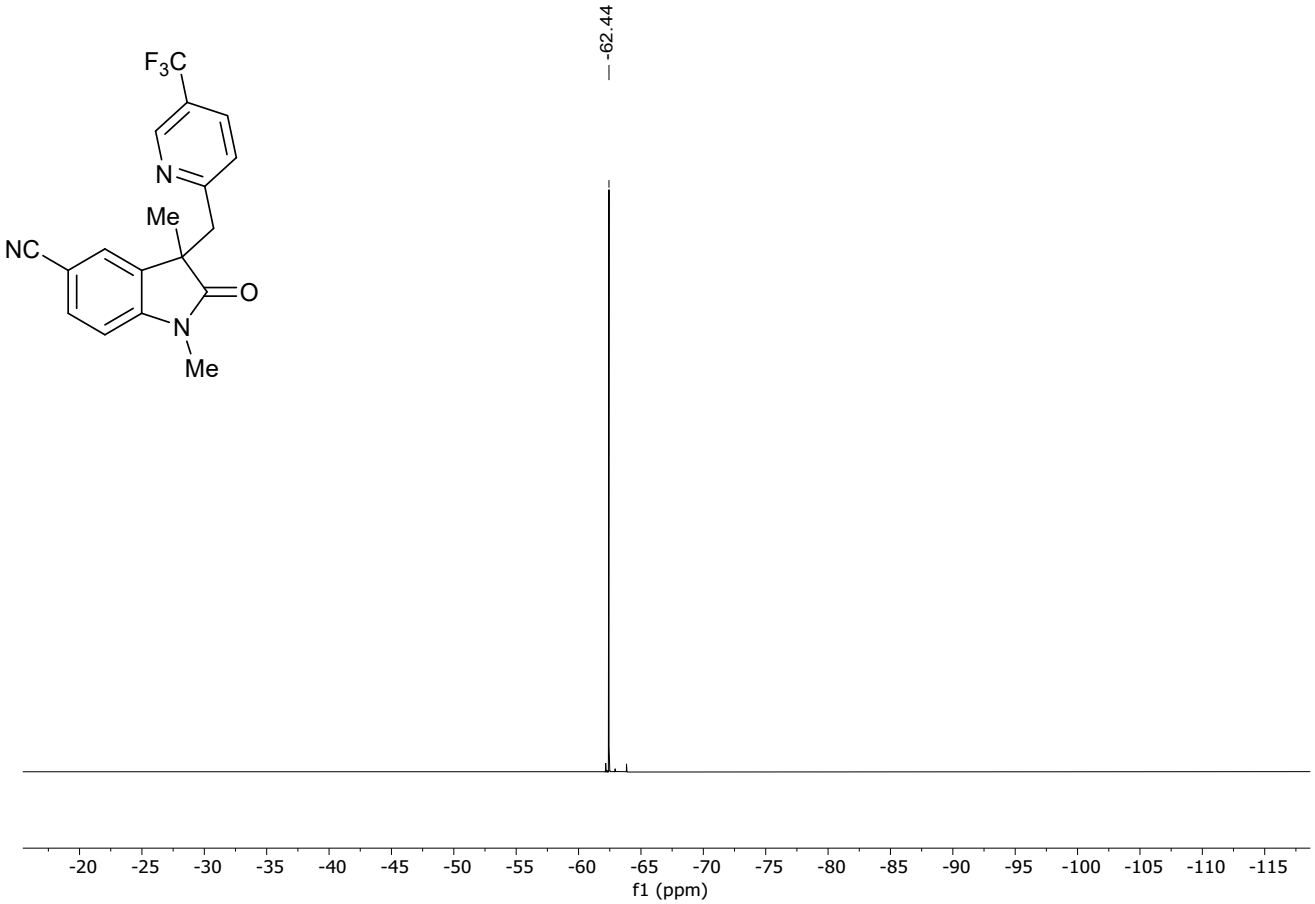
^{19}F NMR (376 MHz, $CDCl_3$) of compound **24**.



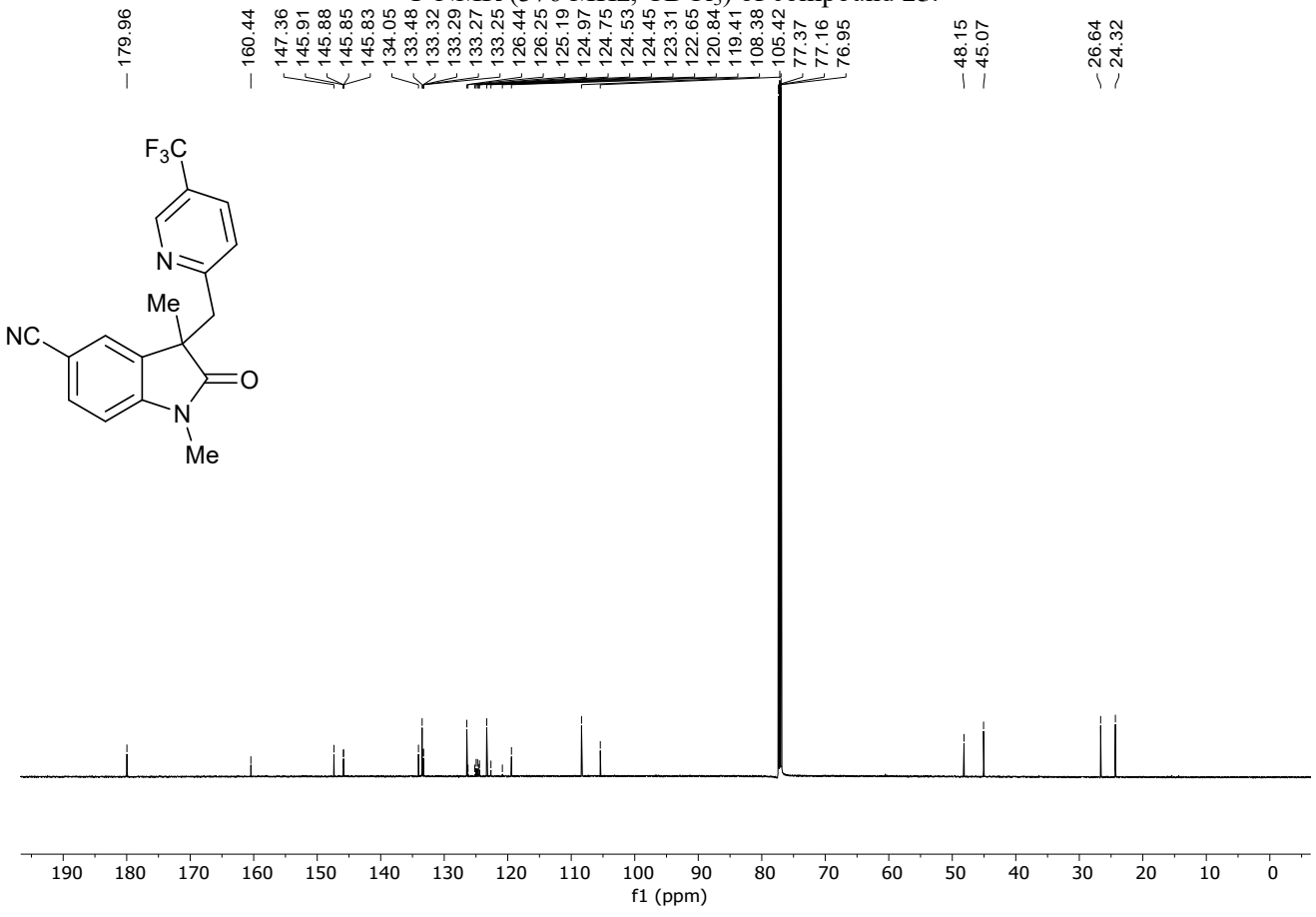
^{13}C NMR (101 MHz, $CDCl_3$) of compound **24**.



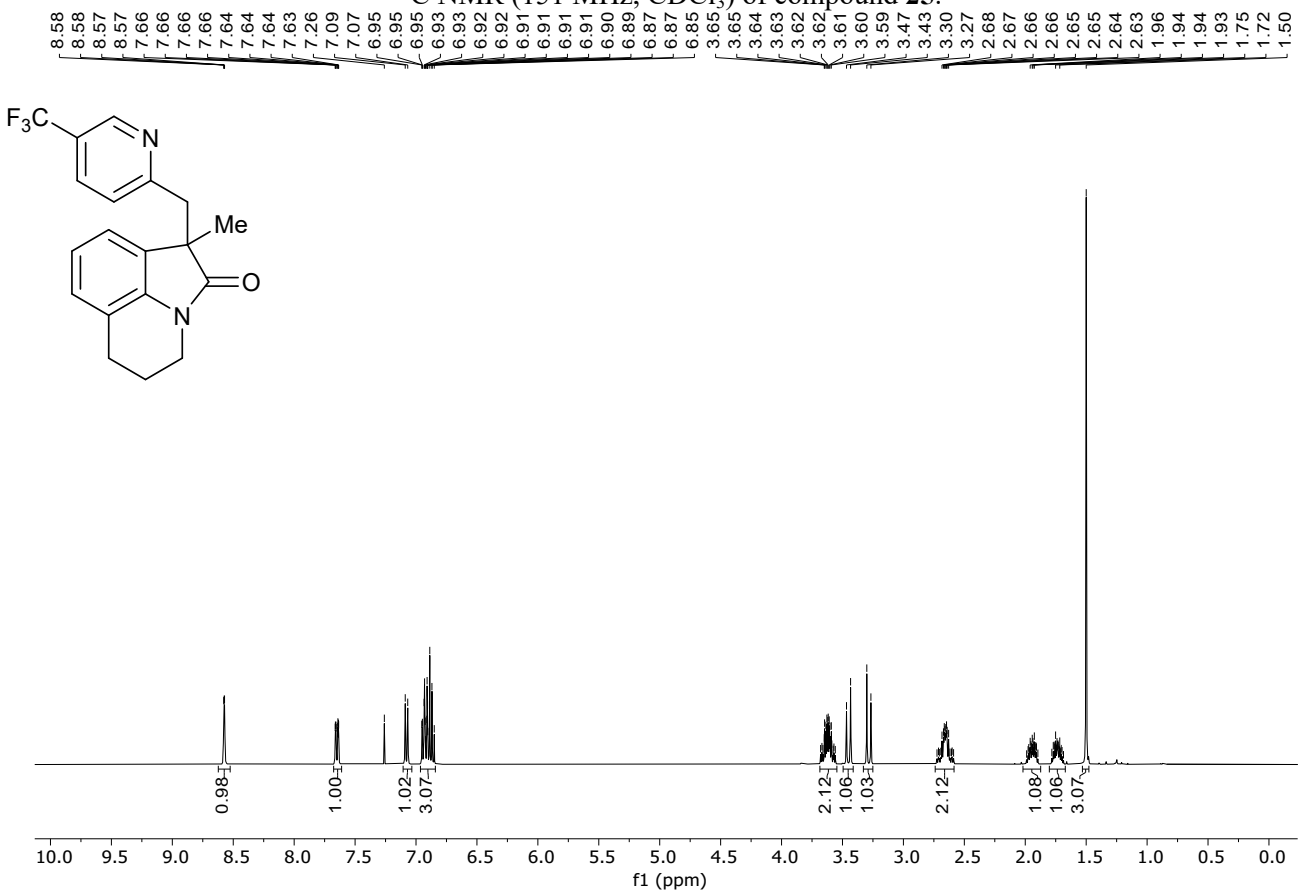
^{1}H NMR (600 MHz, $CDCl_3$) of compound **25**.



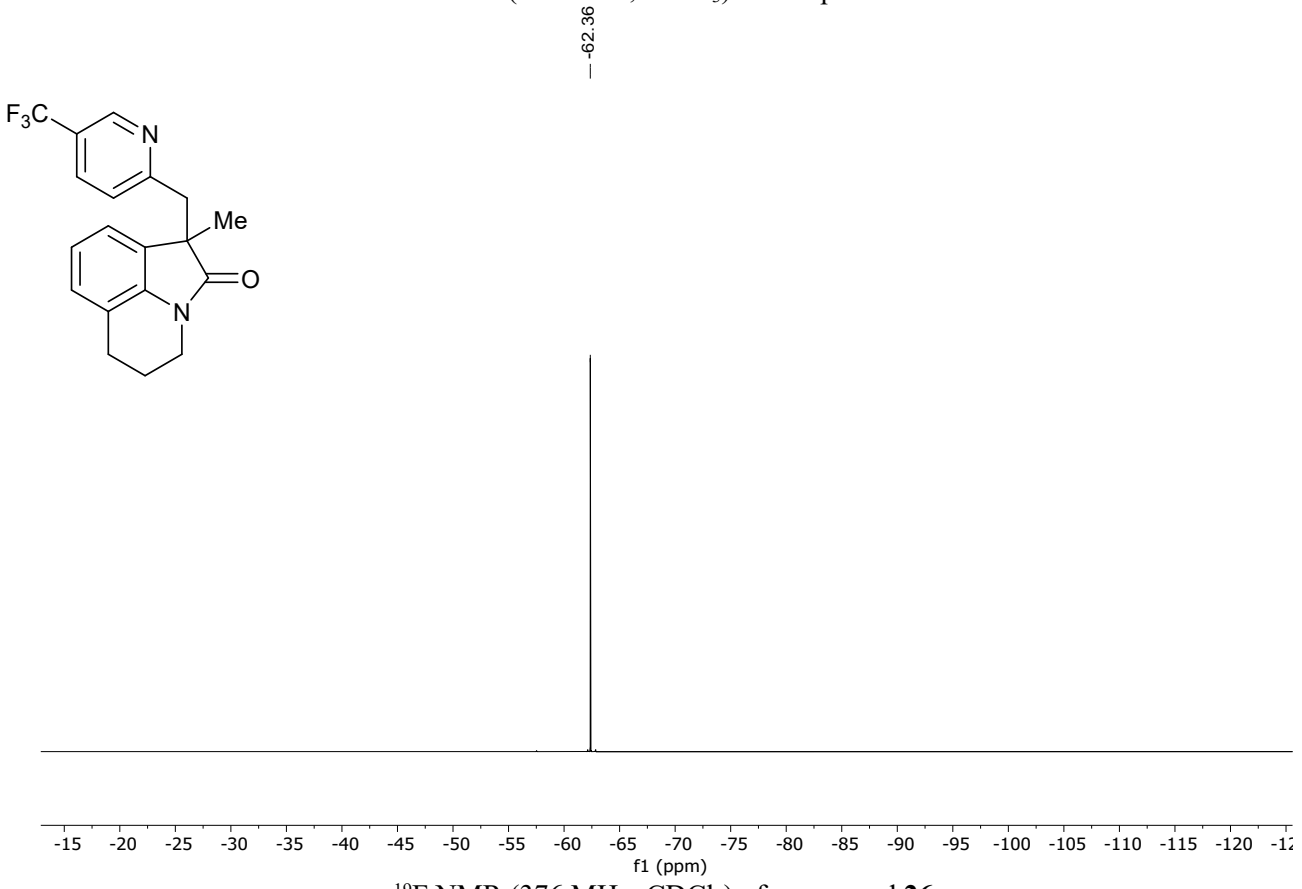
^{19}F NMR (376 MHz, $CDCl_3$) of compound **25**.



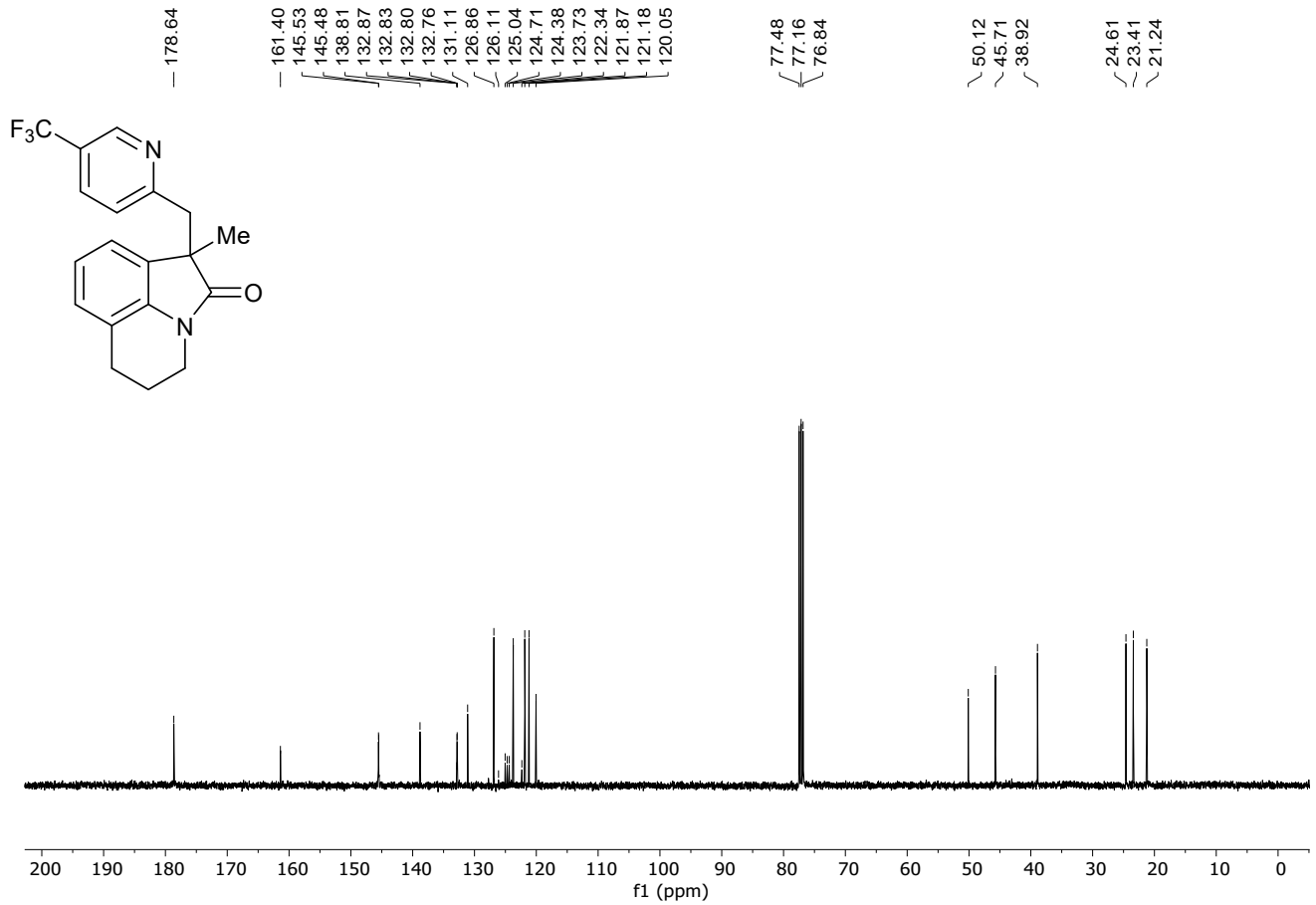
^{13}C NMR (151 MHz, $CDCl_3$) of compound **25**.



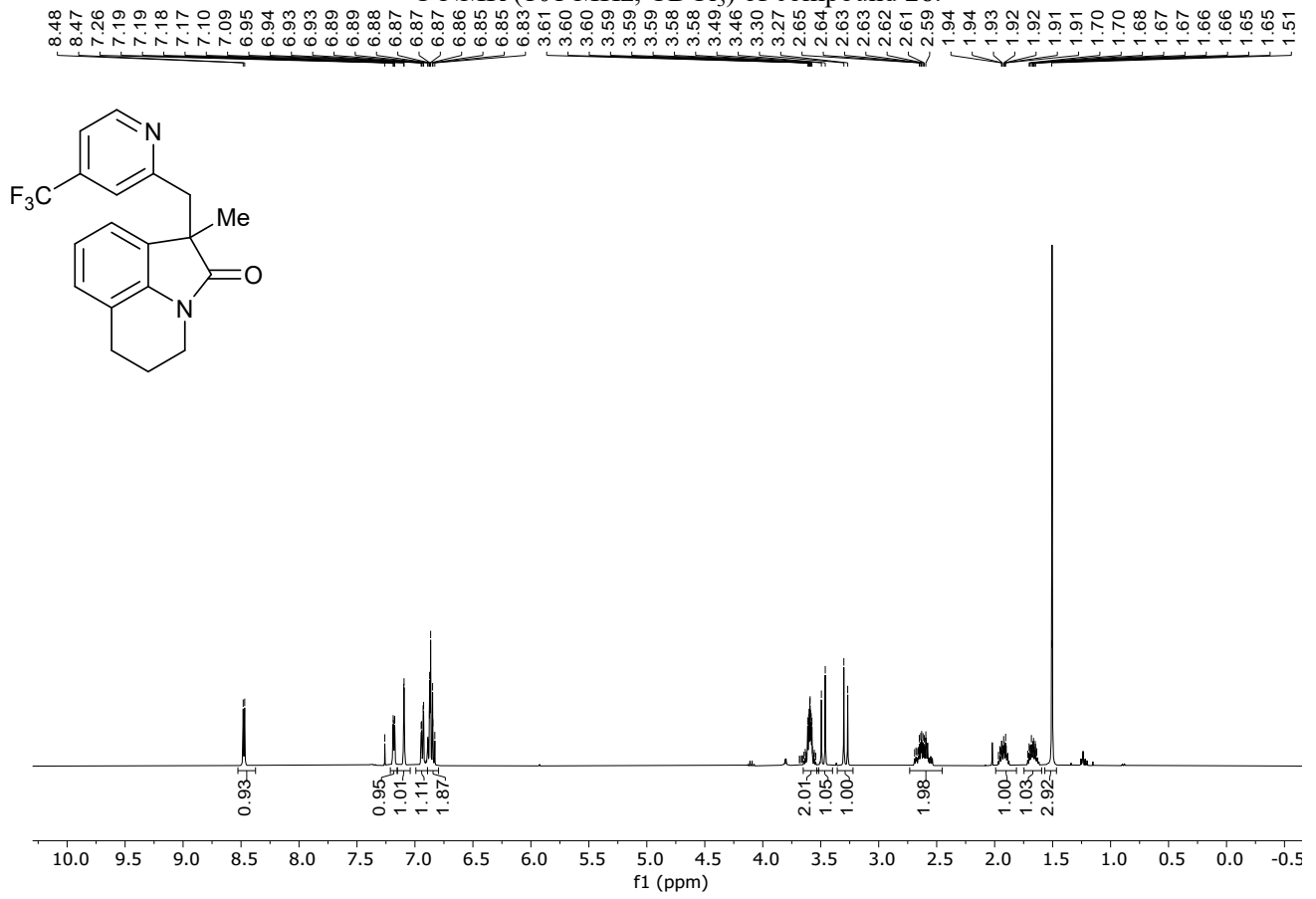
^{1}H NMR (400 MHz, $CDCl_3$) of compound **26**.



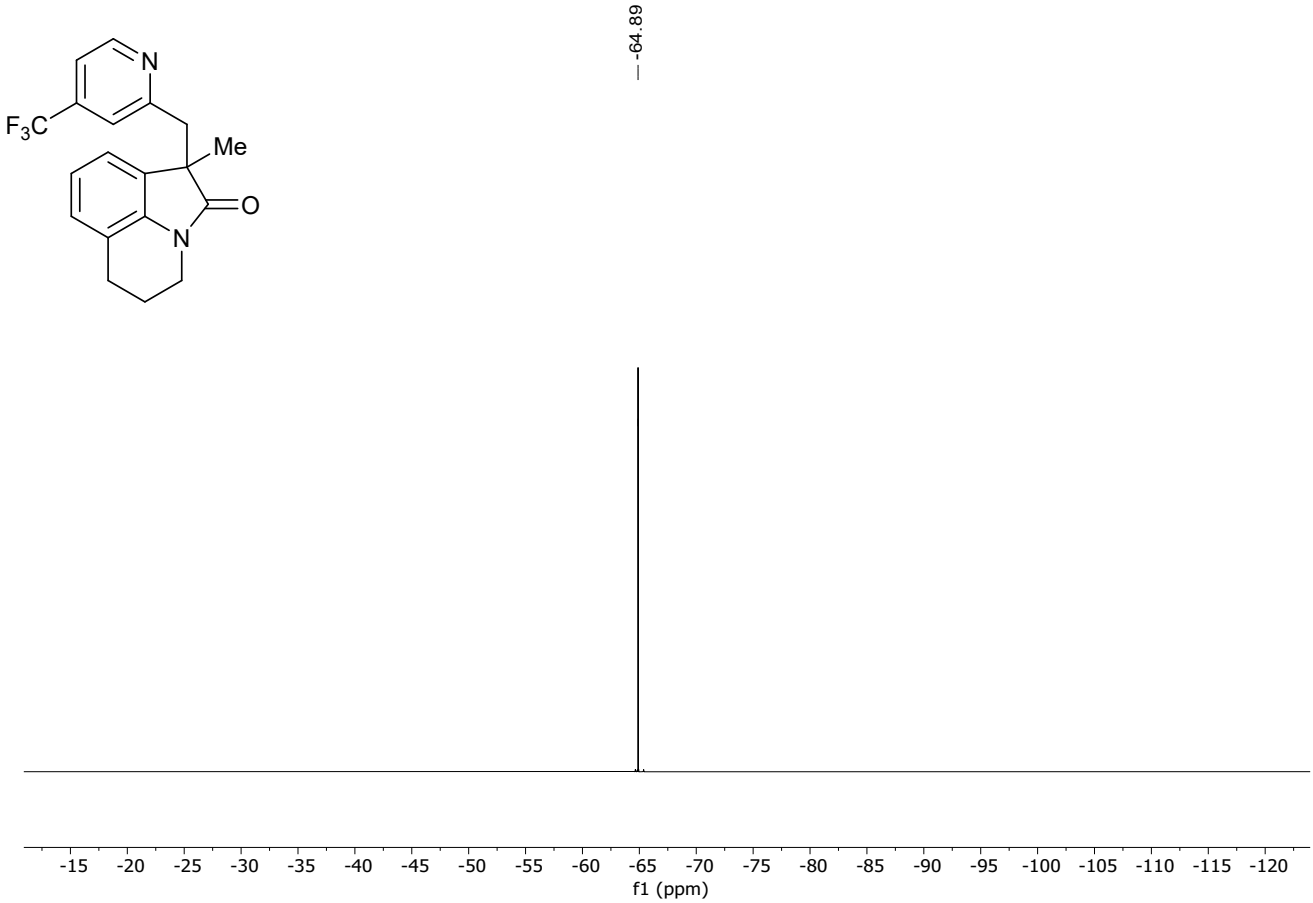
^{19}F NMR (376 MHz, $CDCl_3$) of compound **26**.



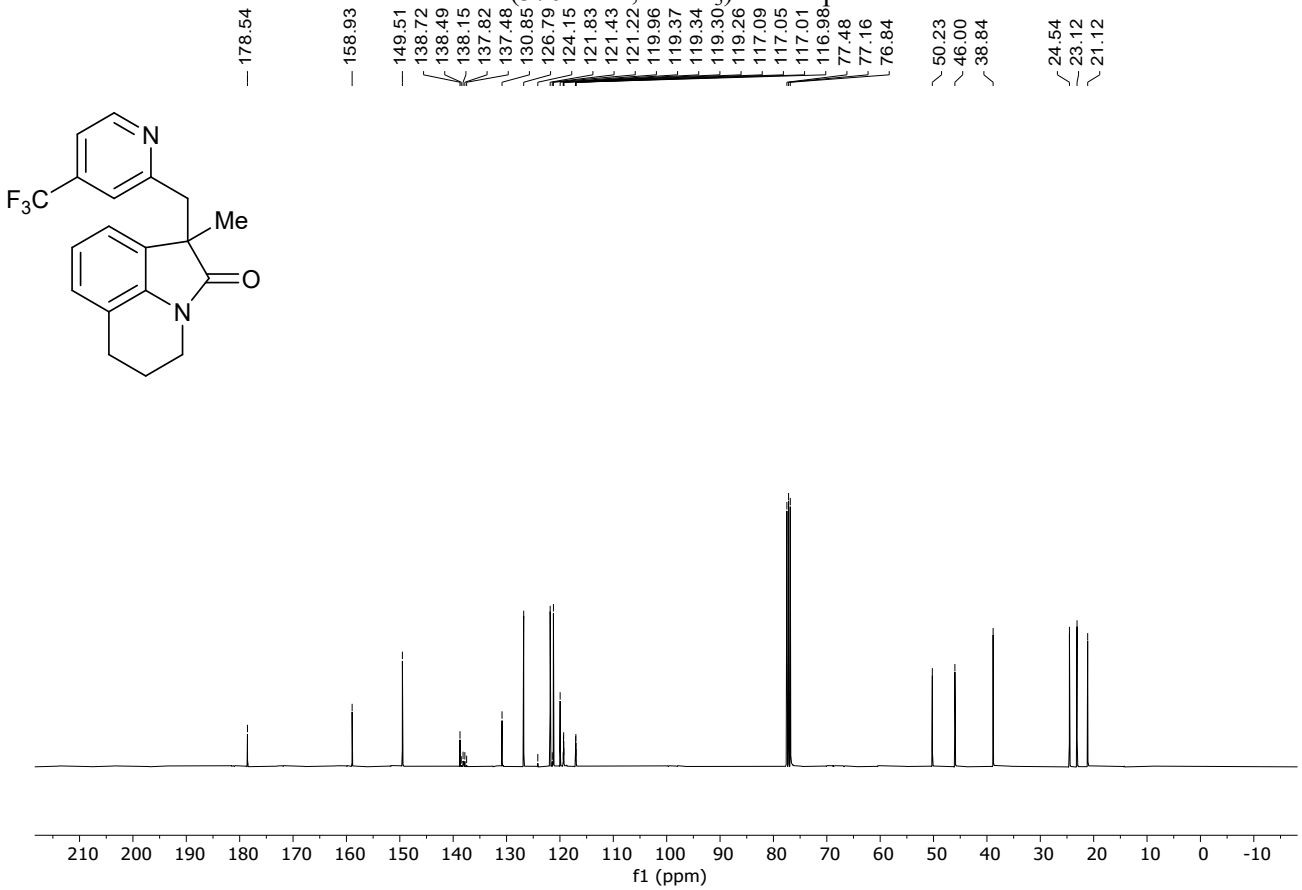
^{13}C NMR (101 MHz, $CDCl_3$) of compound **26**.



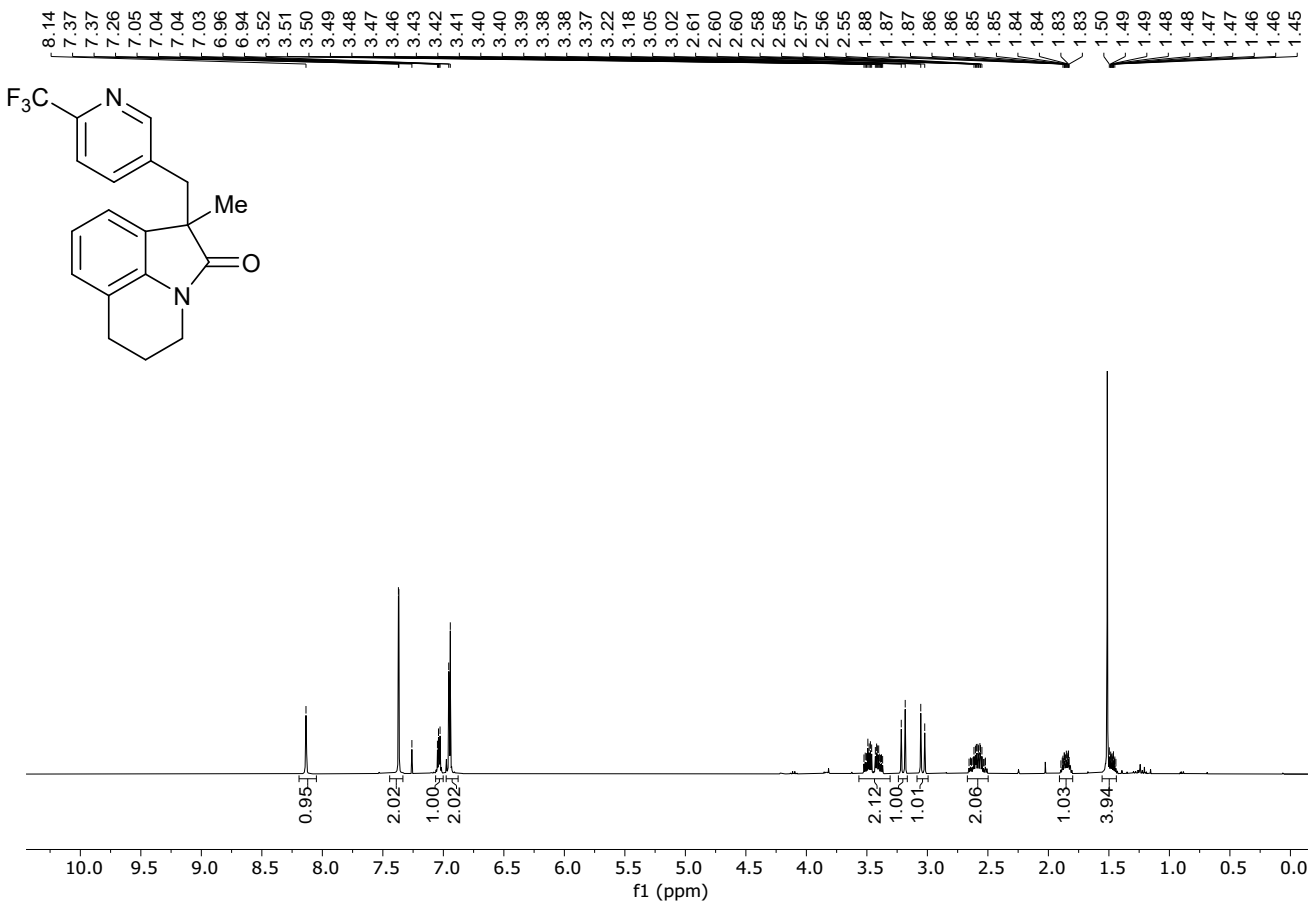
^{1}H NMR (400 MHz, $CDCl_3$) of compound **27**.



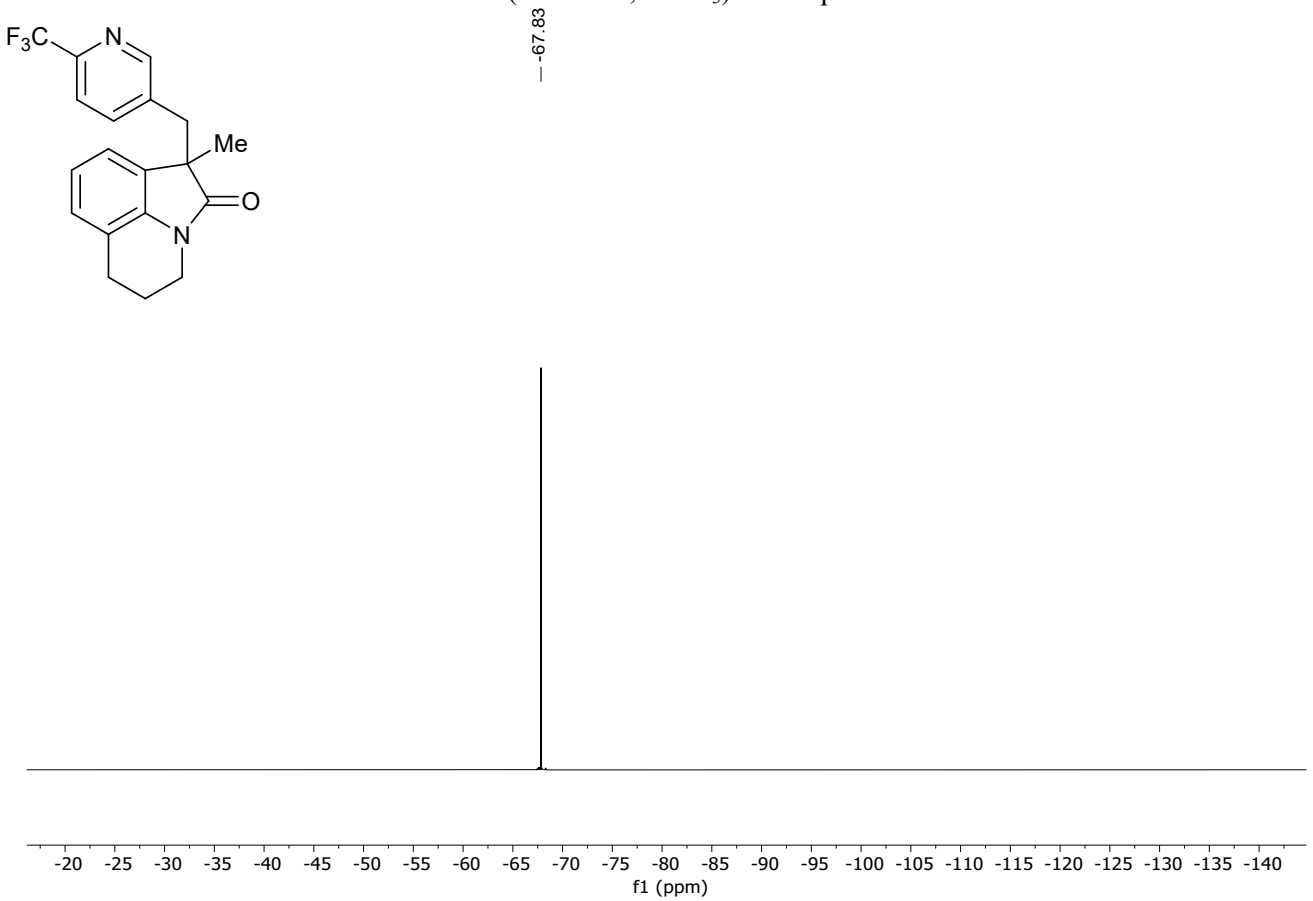
^{19}F NMR (376 MHz, $CDCl_3$) of compound **27**.



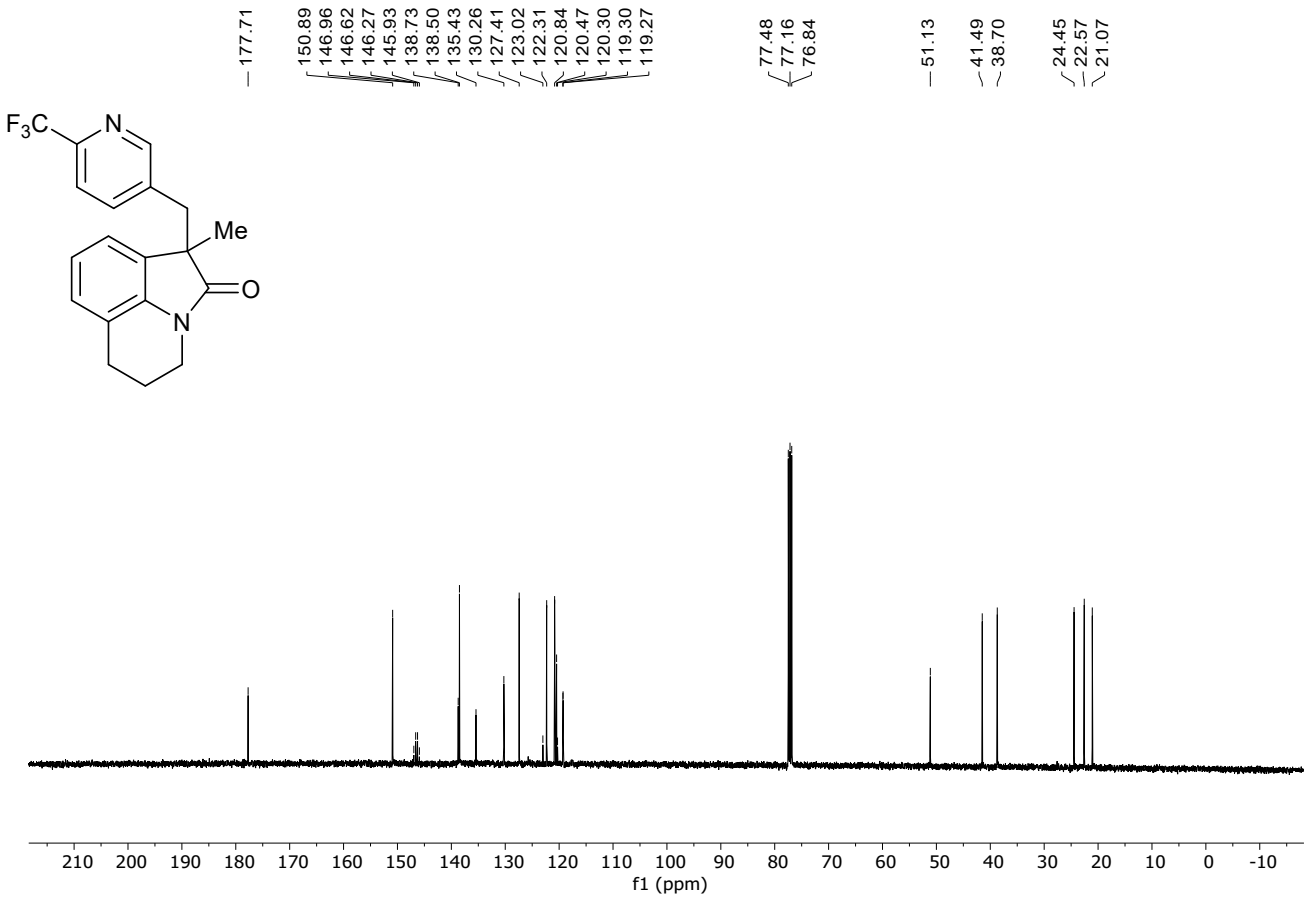
^{13}C NMR (101 MHz, $CDCl_3$) of compound **27**.



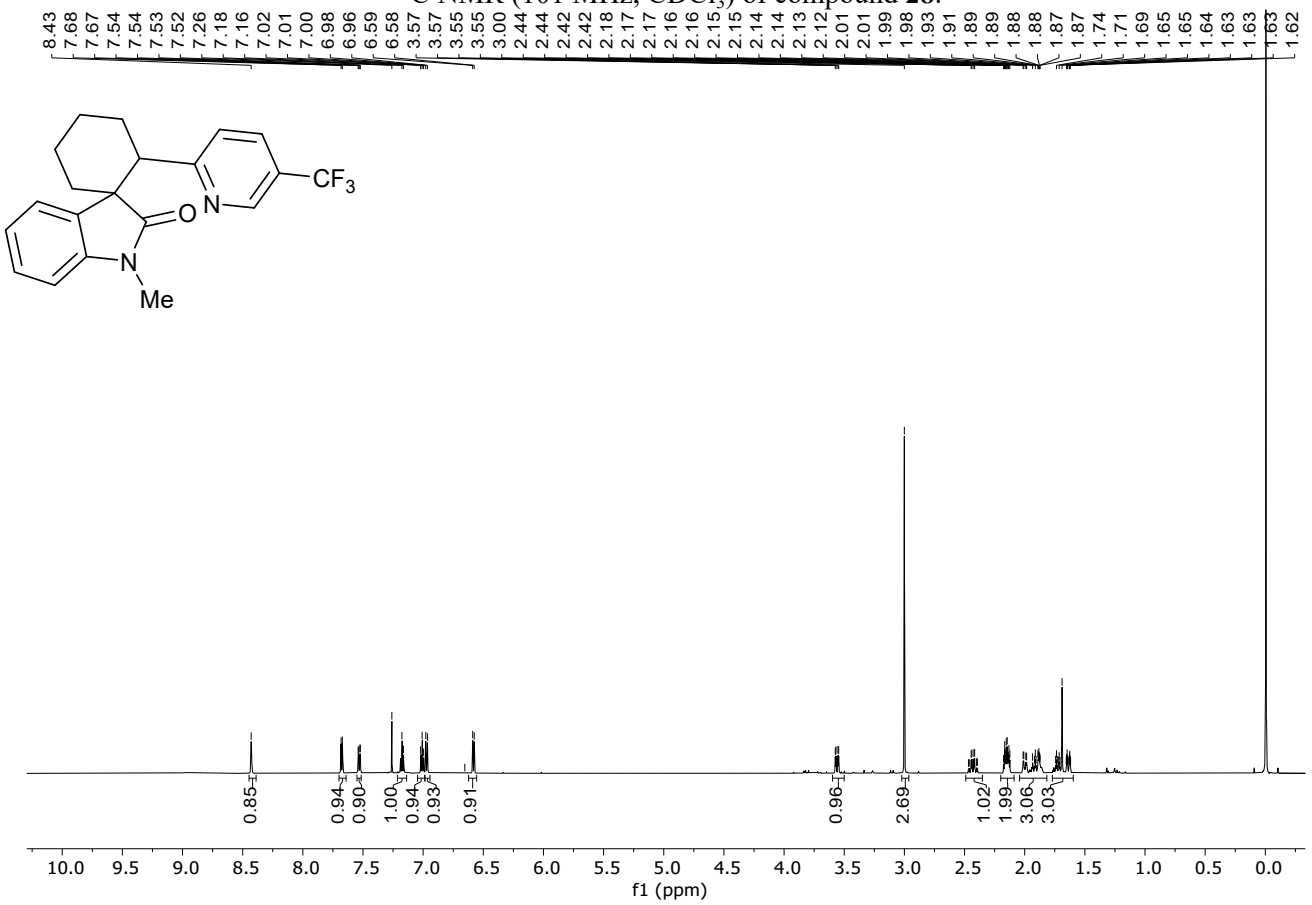
^{1}H NMR (400 MHz, $CDCl_3$) of compound **28**.



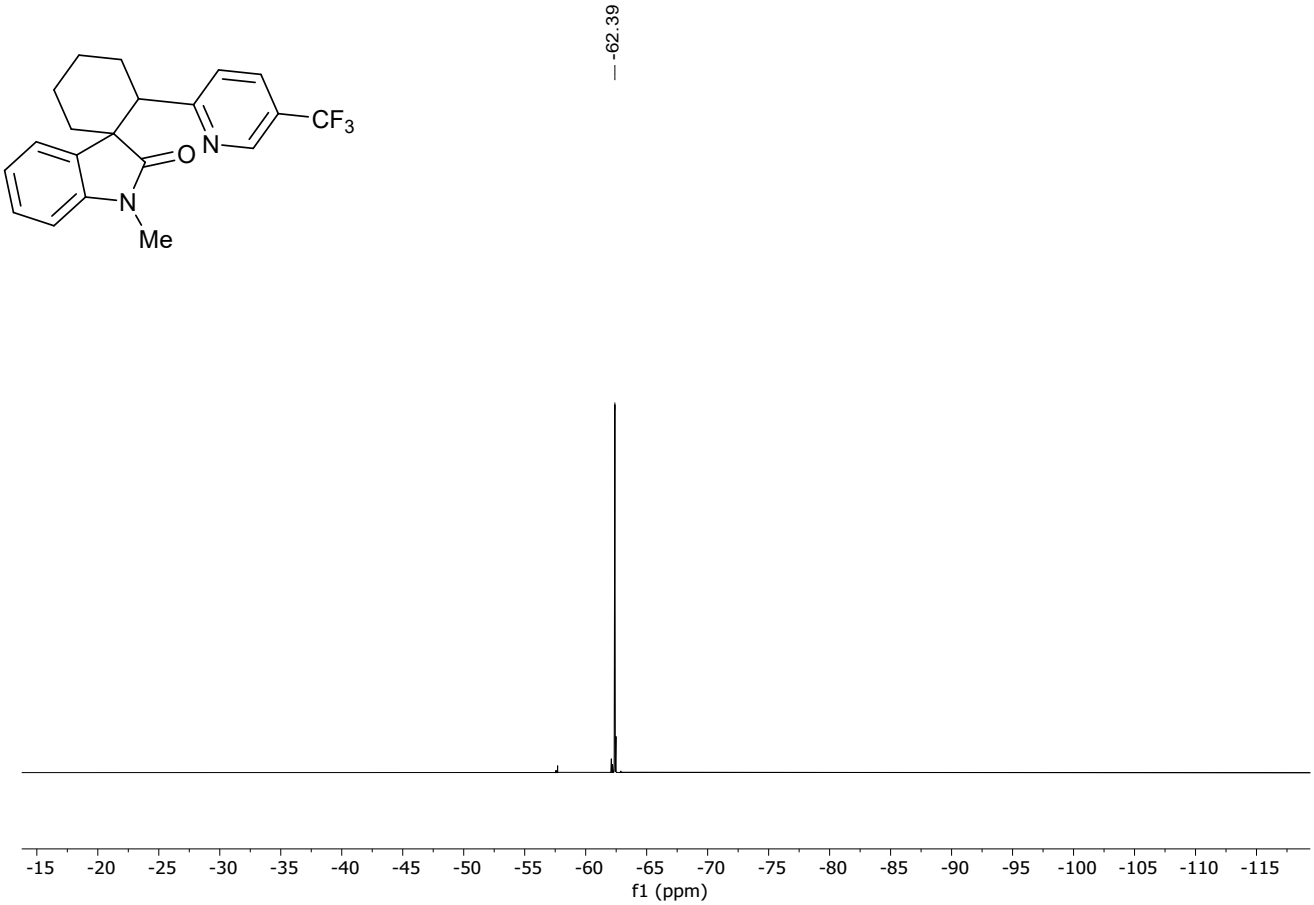
^{19}F NMR (376 MHz, $CDCl_3$) of compound **28**.



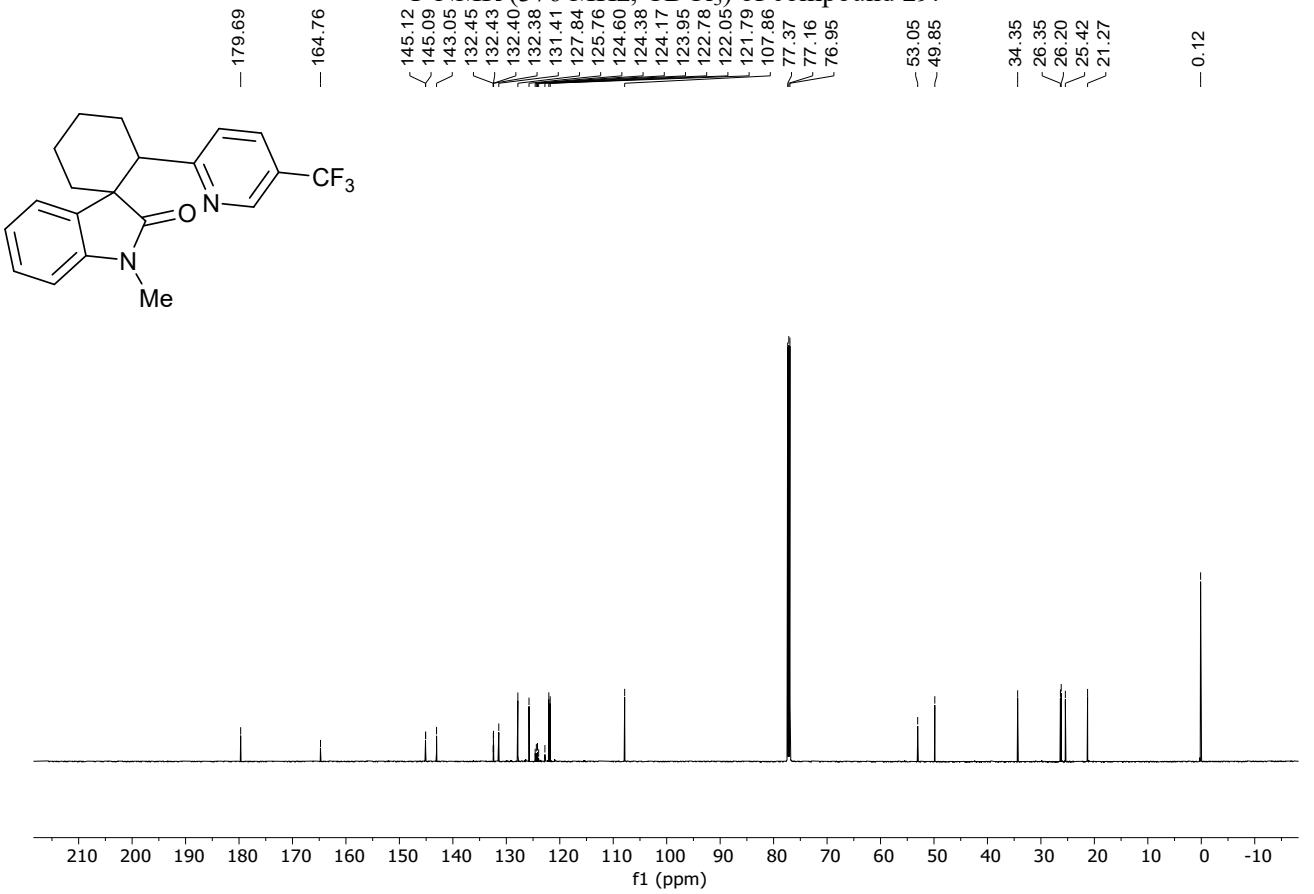
^{13}C NMR (101 MHz, $CDCl_3$) of compound **28**.



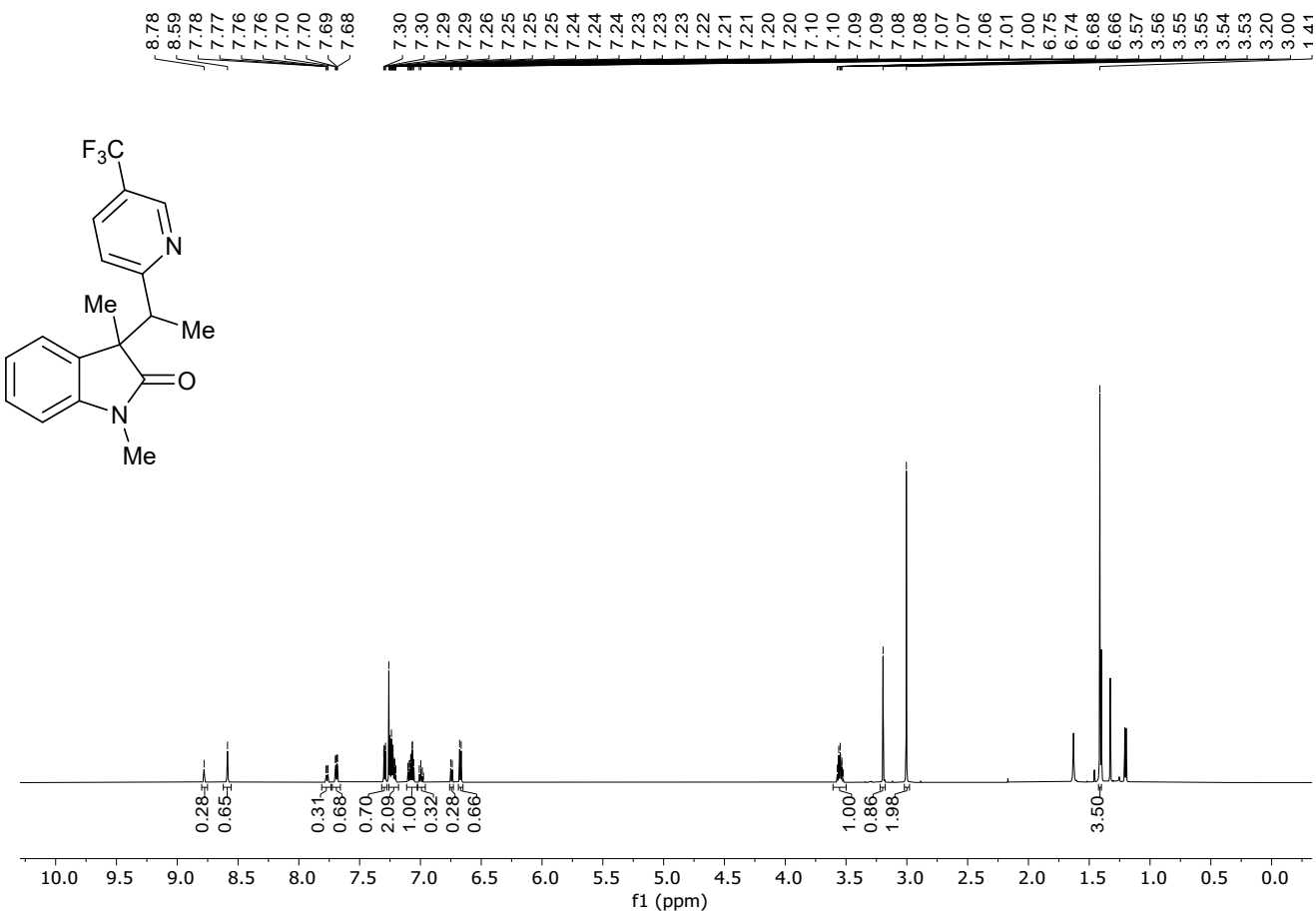
^{1}H NMR (600 MHz, $CDCl_3$) of compound **29**.



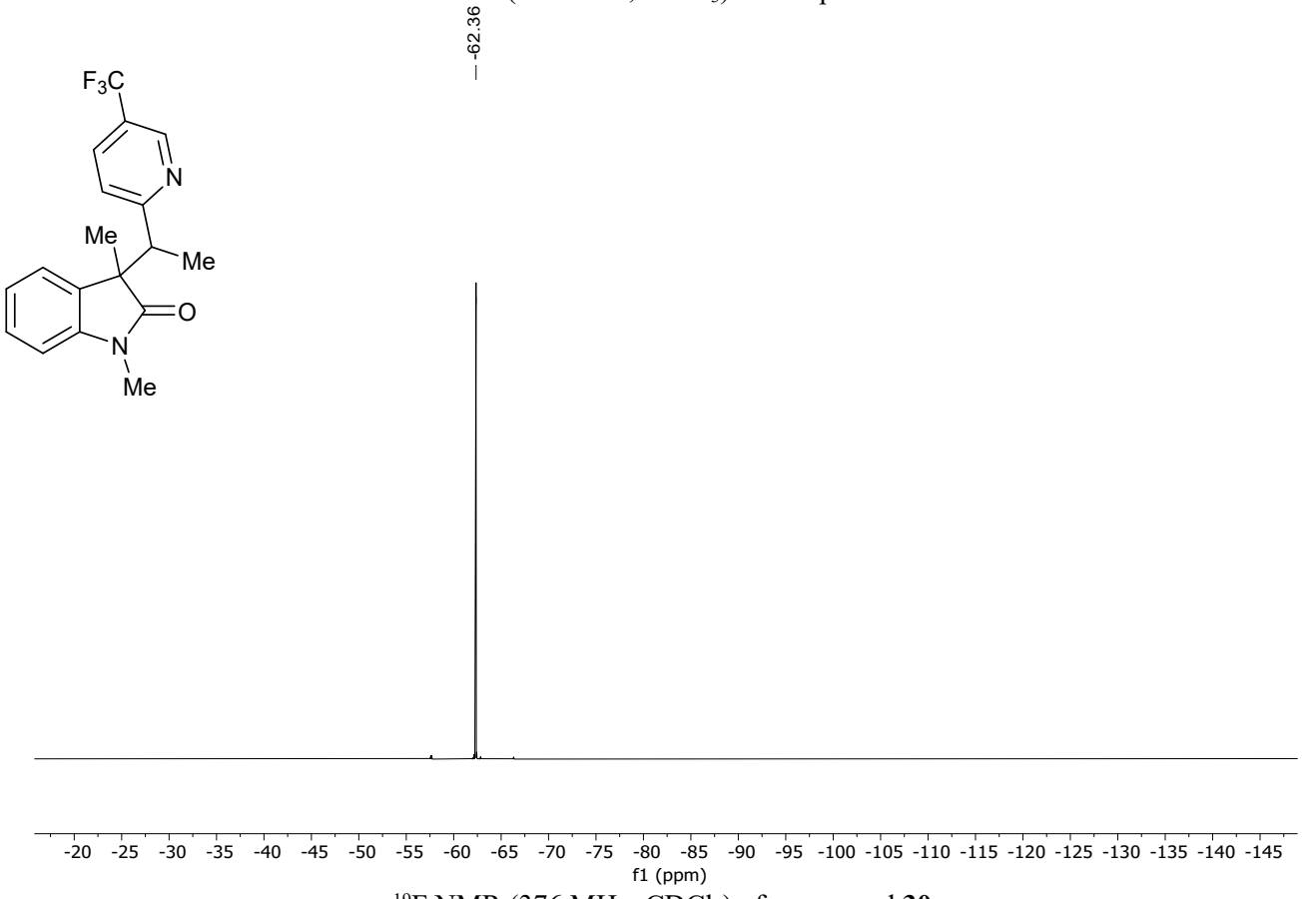
^{19}F NMR (376 MHz, $CDCl_3$) of compound **29**.



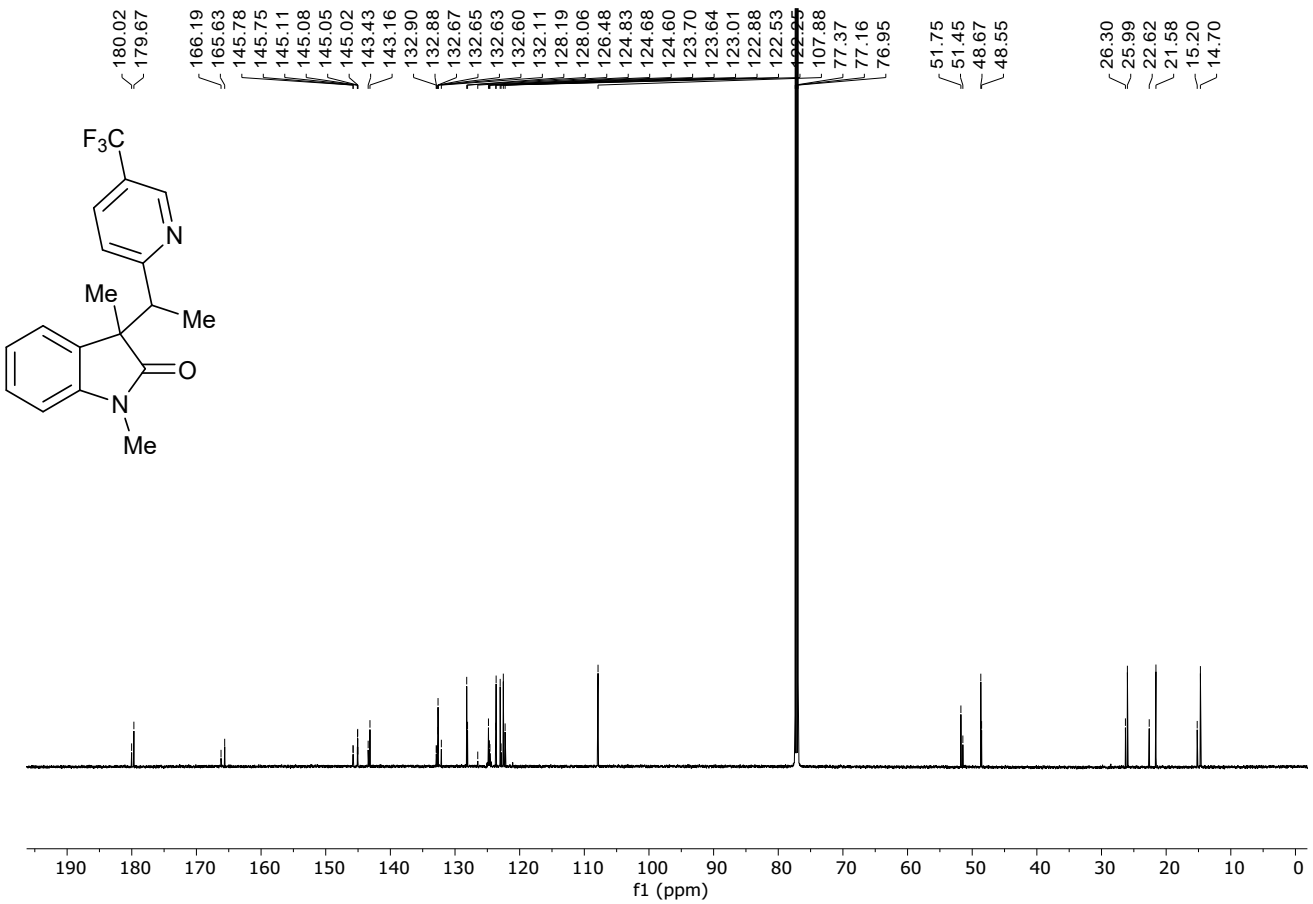
^{13}C NMR (151 MHz, $CDCl_3$) of compound **29**.



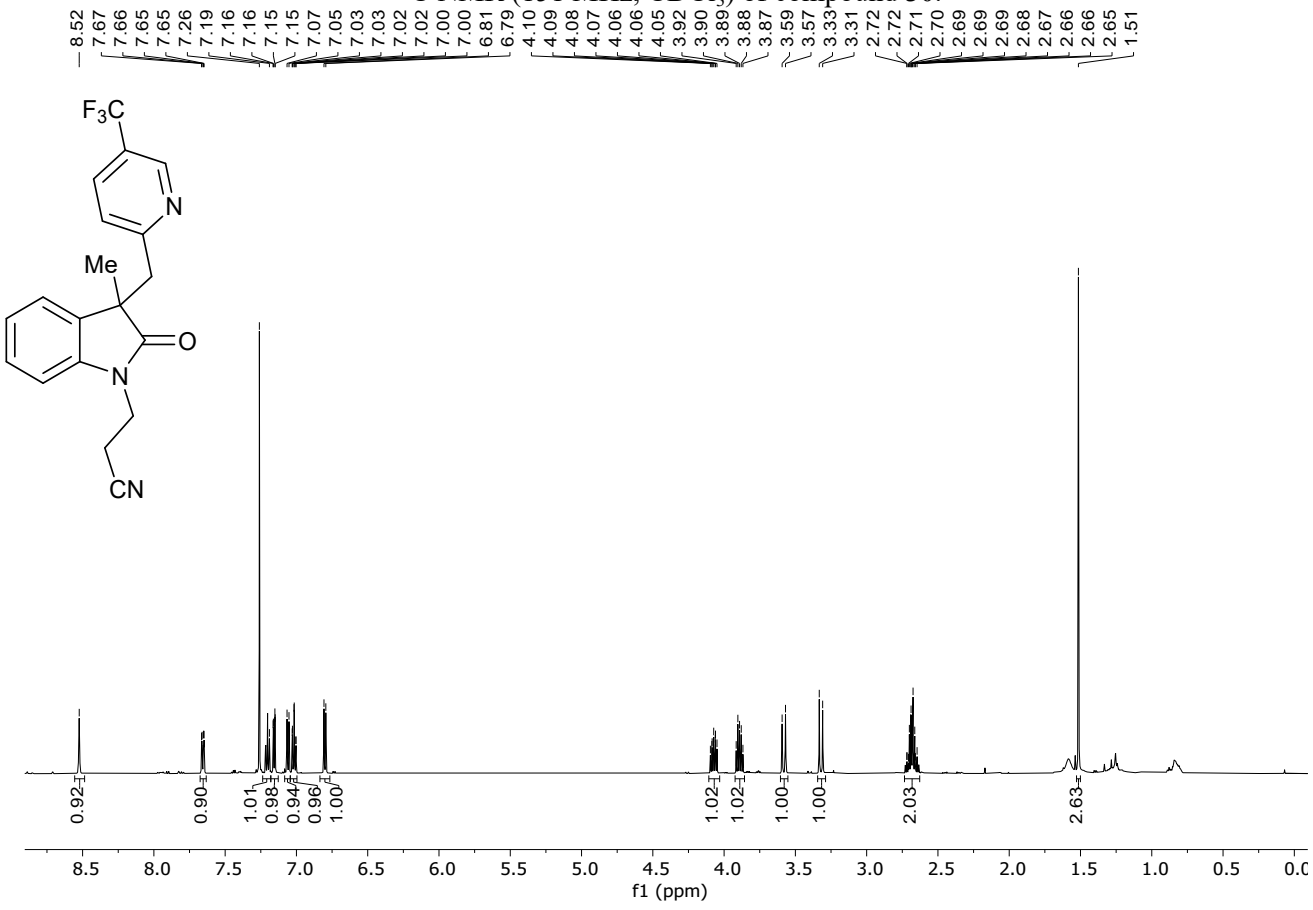
^{1}H NMR (600 MHz, $CDCl_3$) of compound **30**.



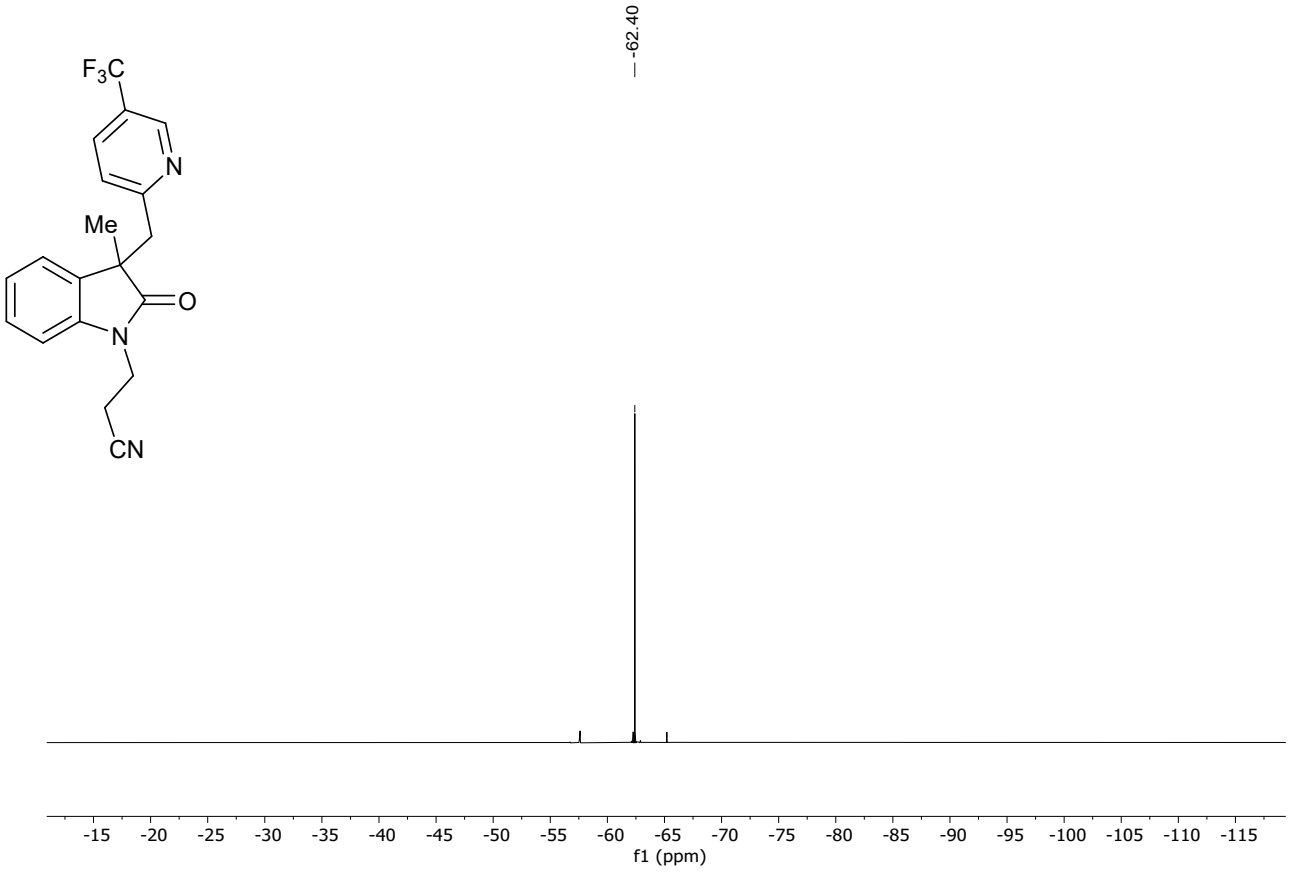
^{19}F NMR (376 MHz, $CDCl_3$) of compound **30**.



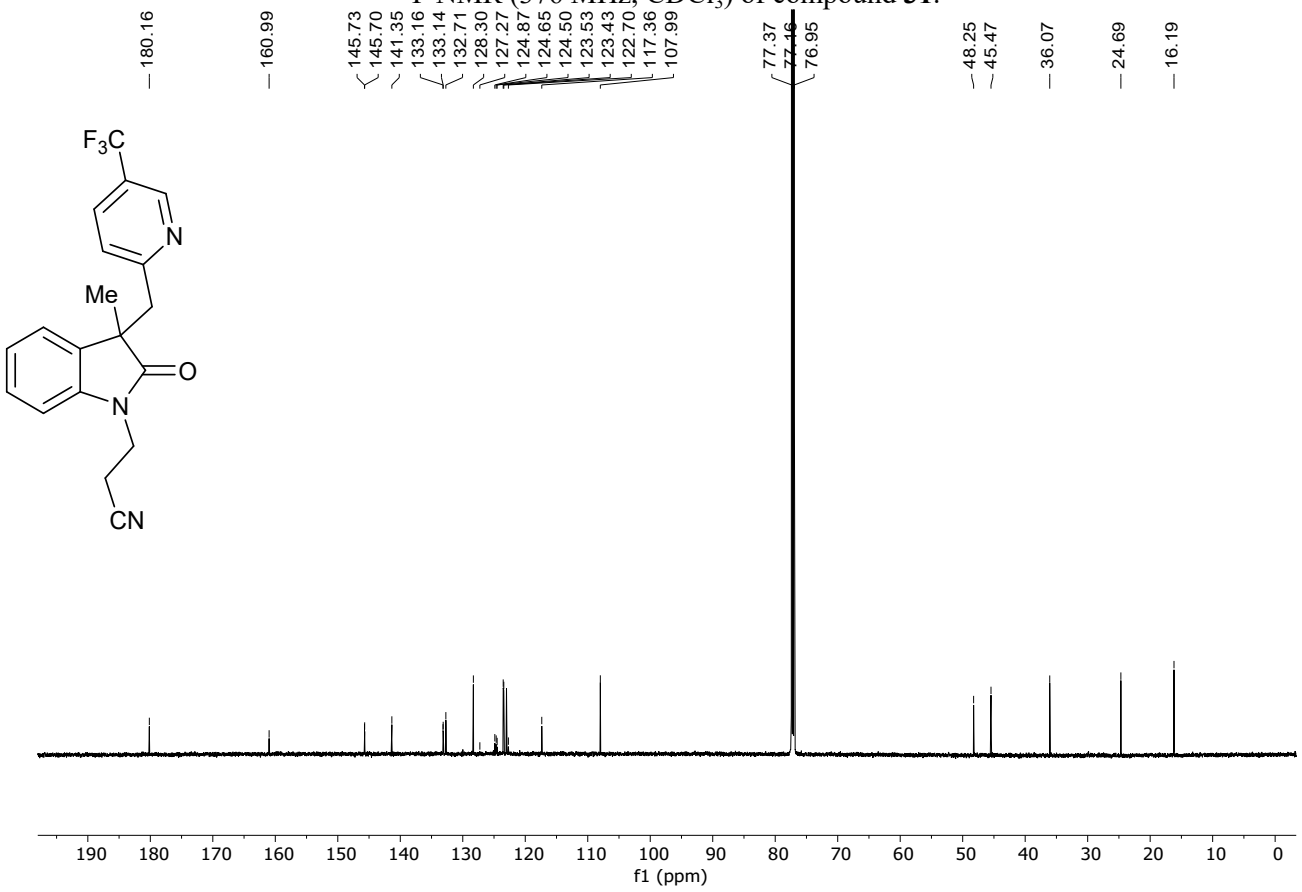
^{13}C NMR (151 MHz, $CDCl_3$) of compound **30**.



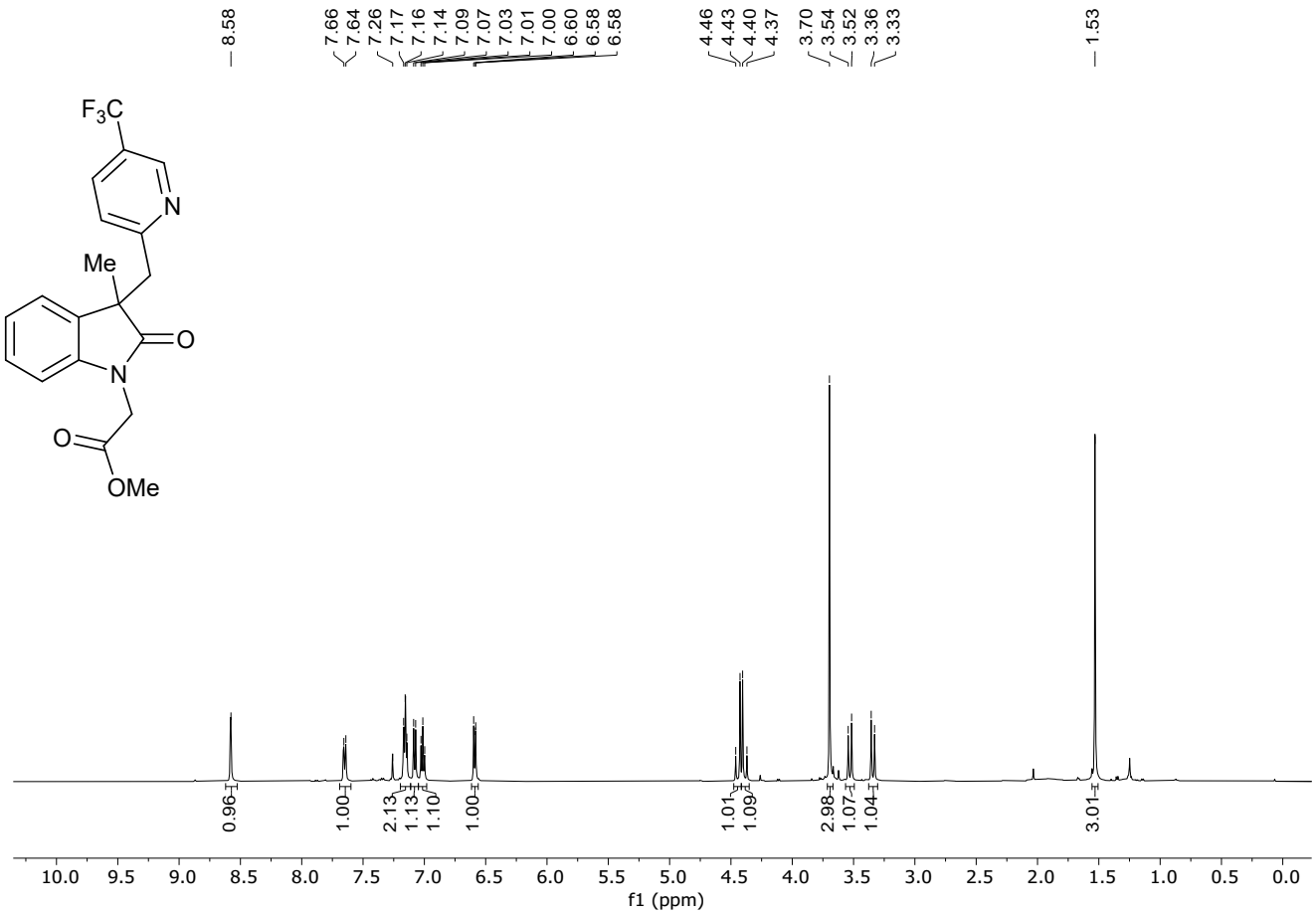
^{1}H NMR (600 MHz, $CDCl_3$) of compound **31**.



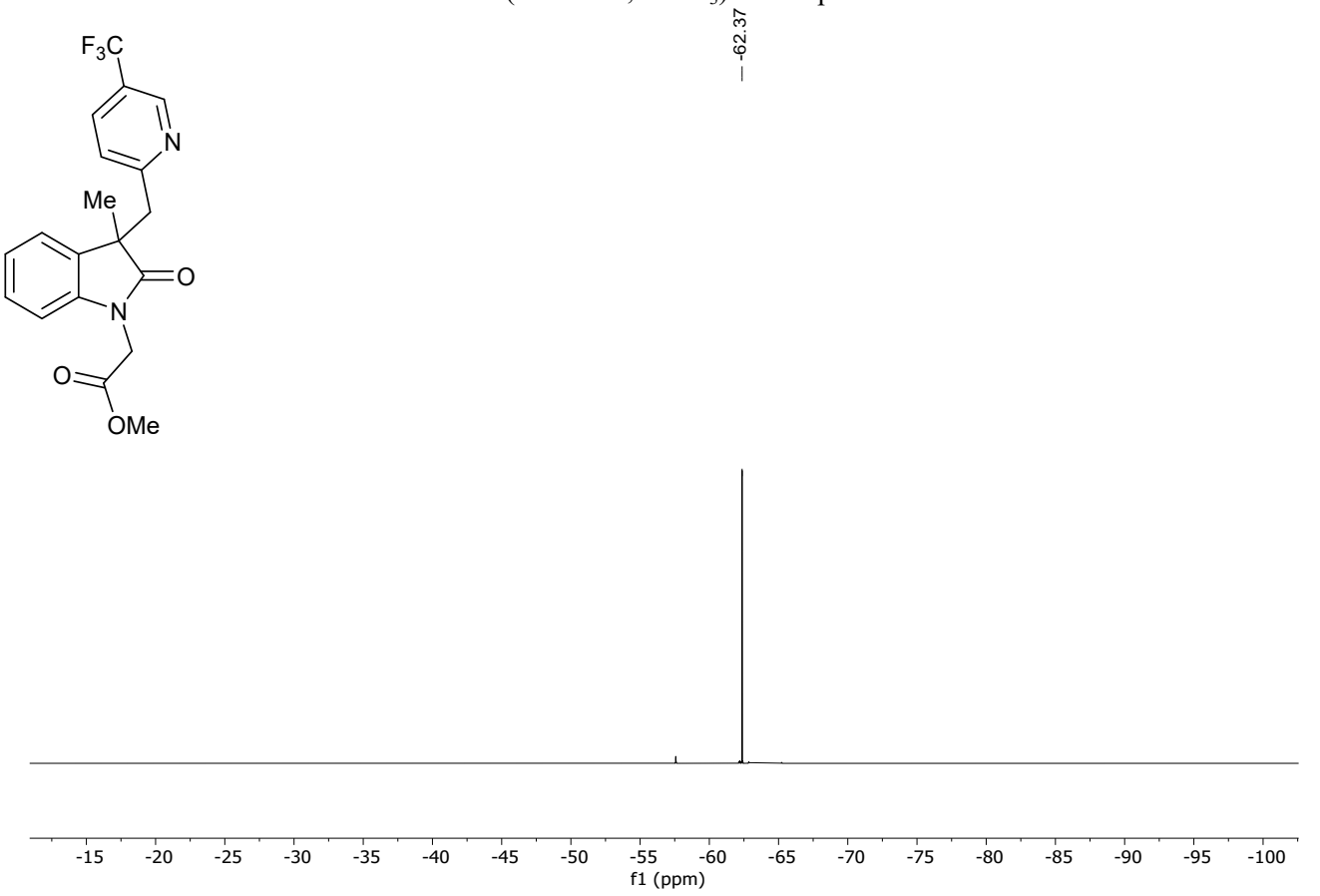
^{19}F NMR (376 MHz, $CDCl_3$) of compound **31**.



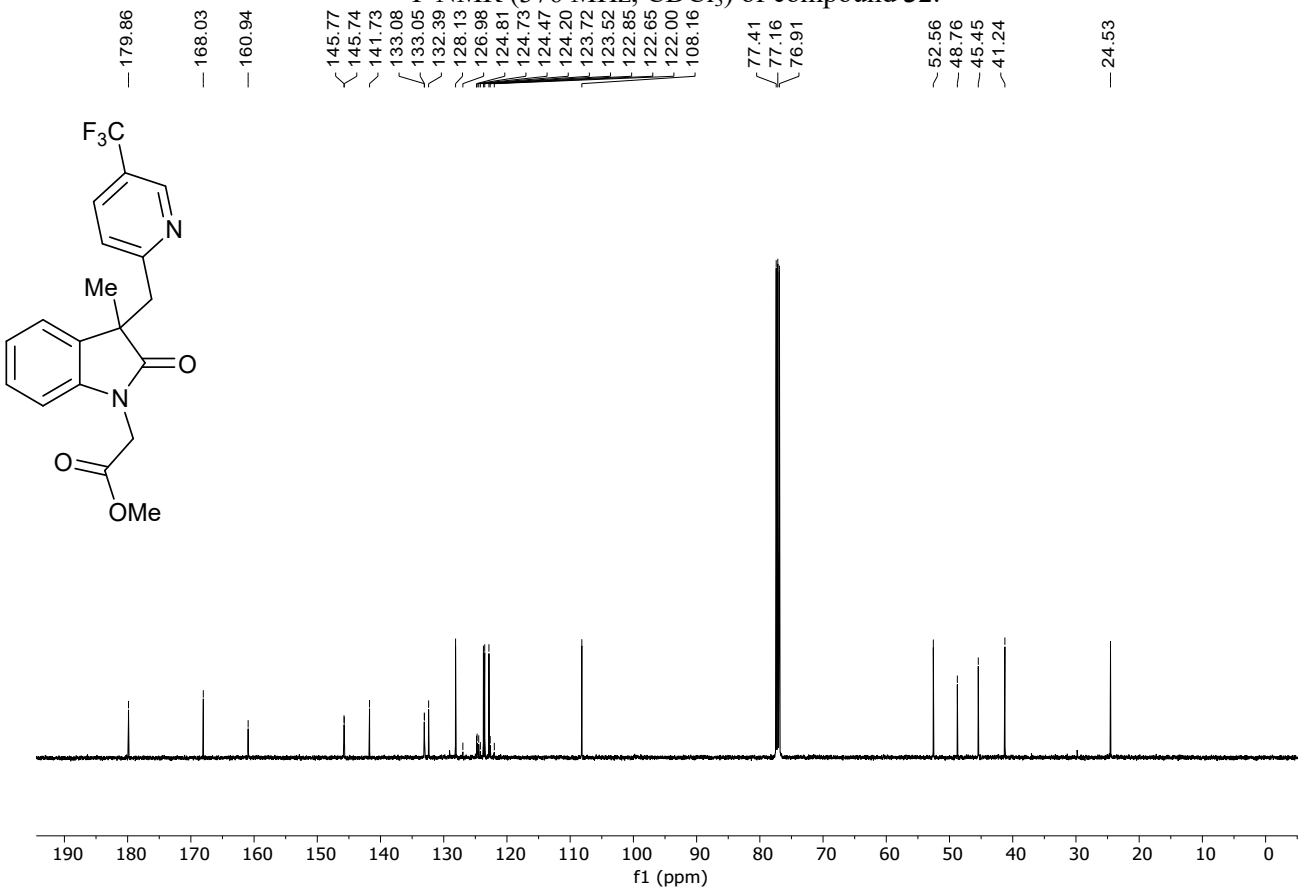
^{13}C NMR (151 MHz, $CDCl_3$) of compound **31**.



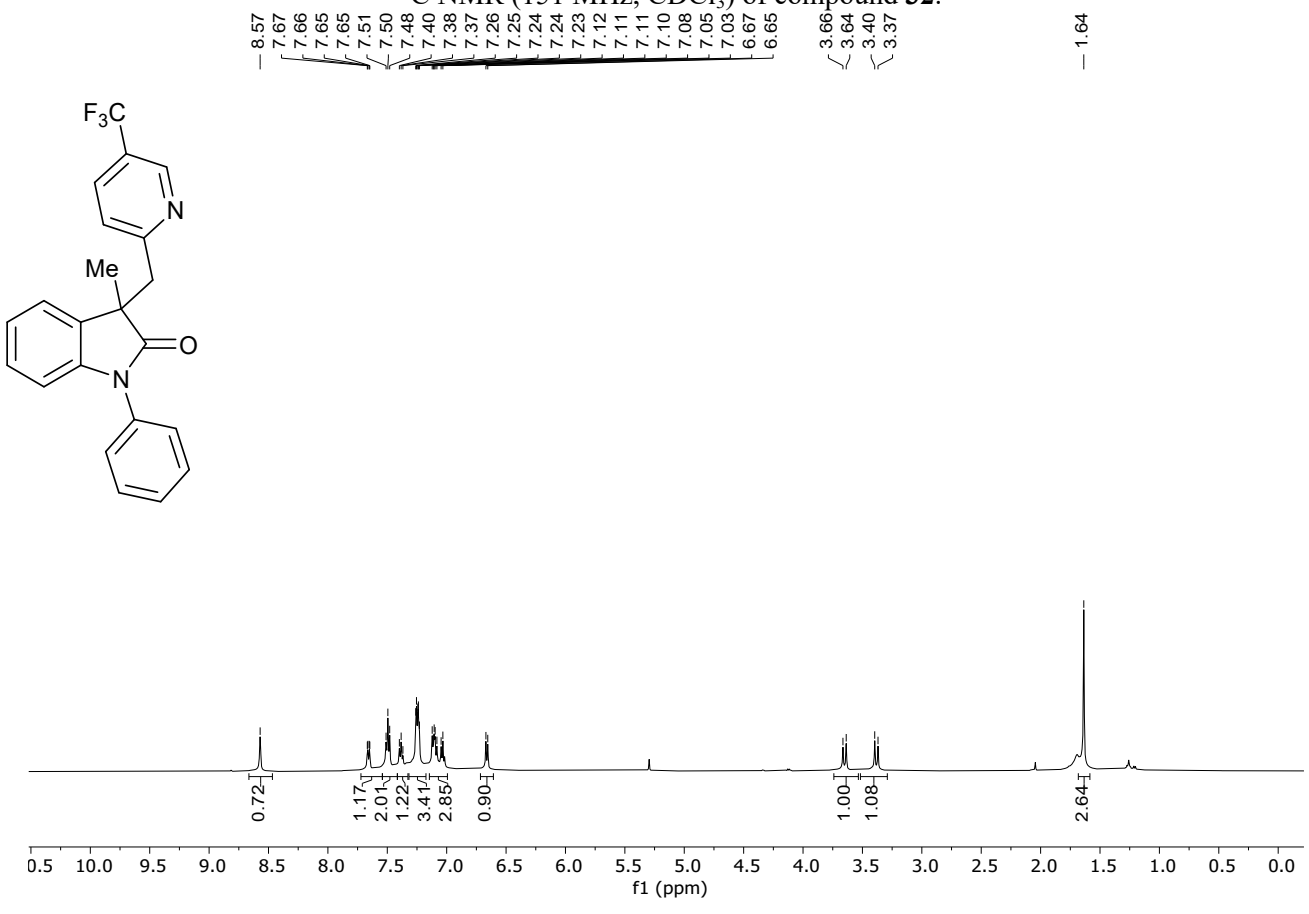
^{1}H NMR (500 MHz, $CDCl_3$) of compound **32**.



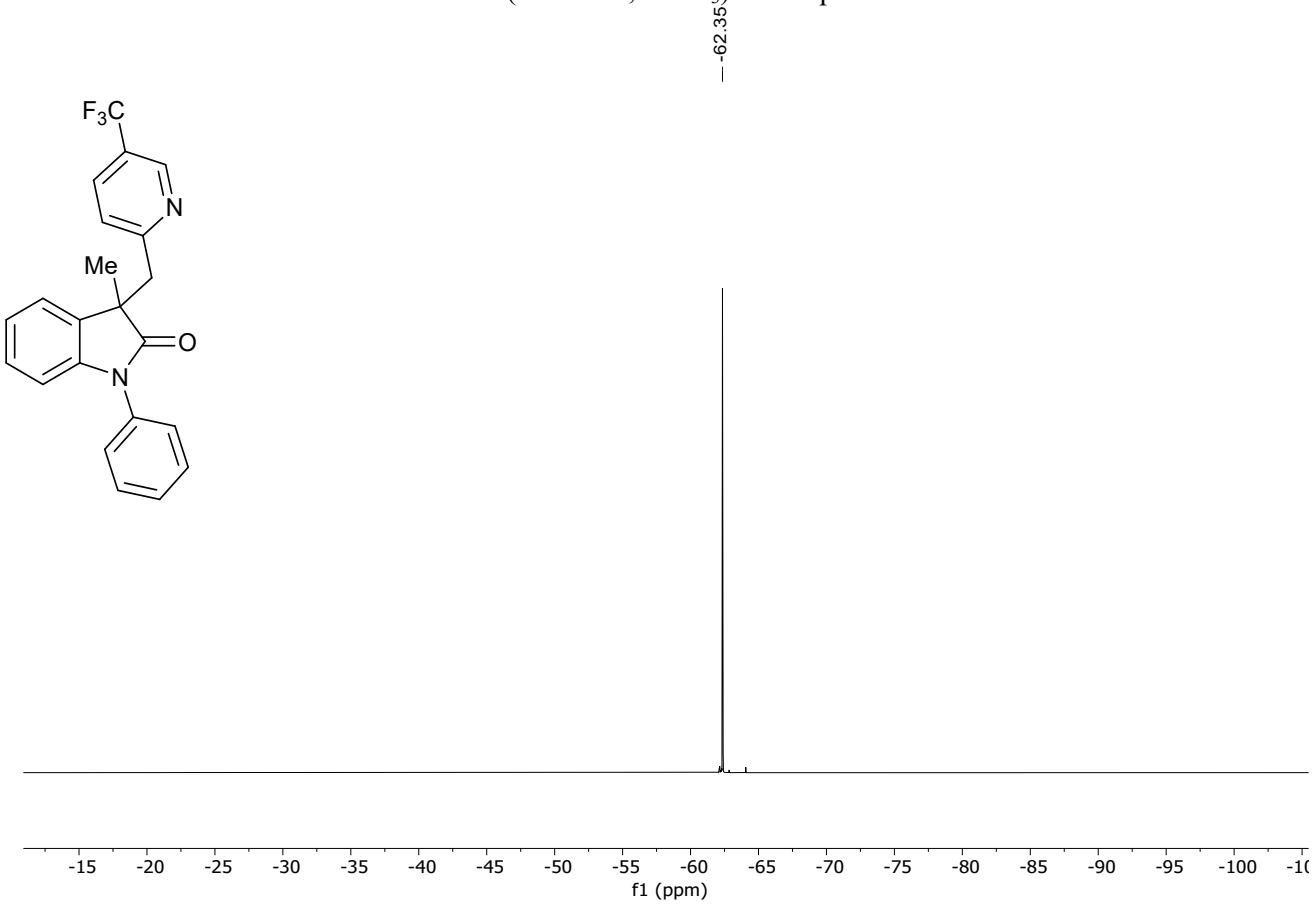
^{19}F NMR (376 MHz, $CDCl_3$) of compound **32**.



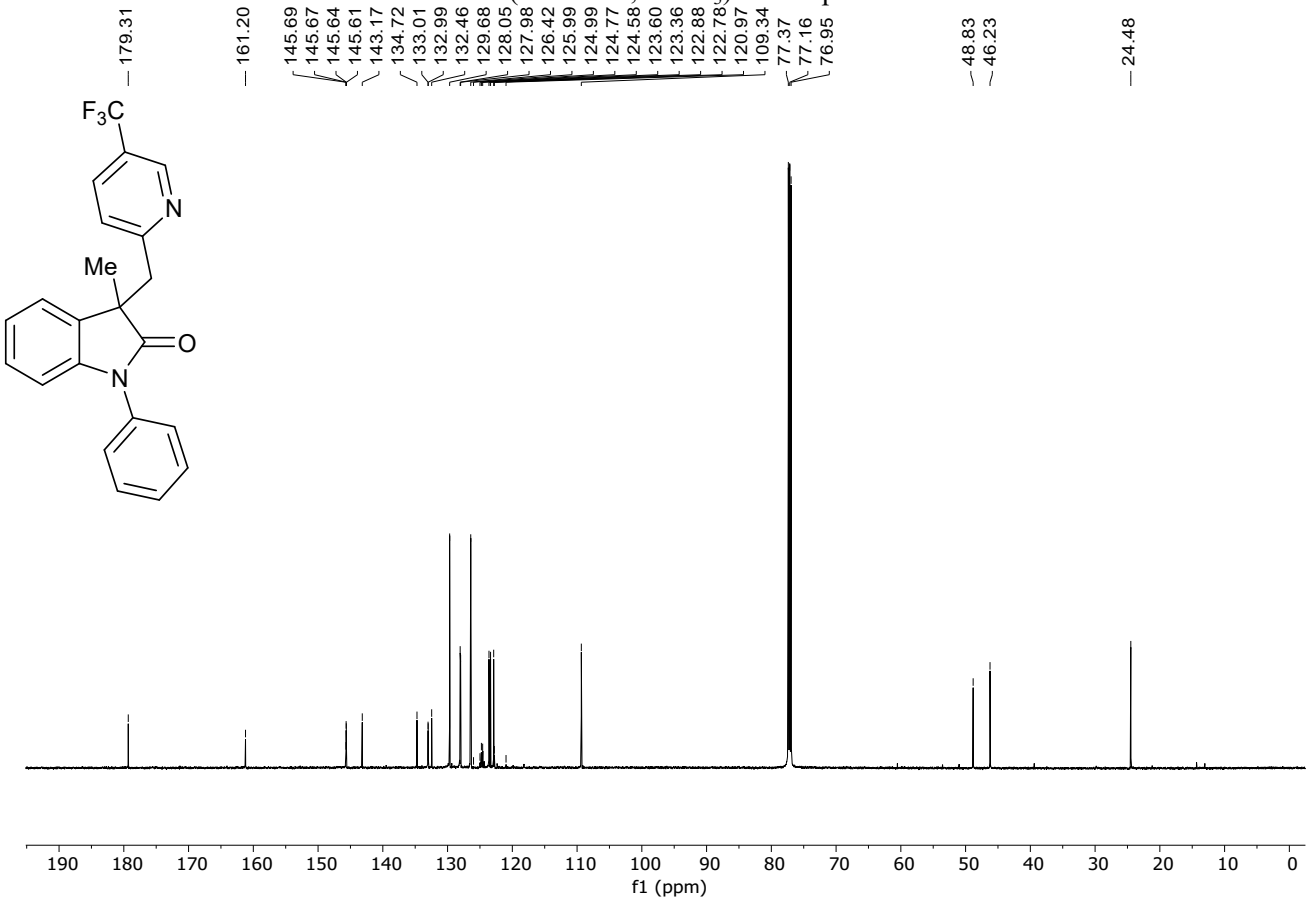
^{13}C NMR (151 MHz, $CDCl_3$) of compound **32**.



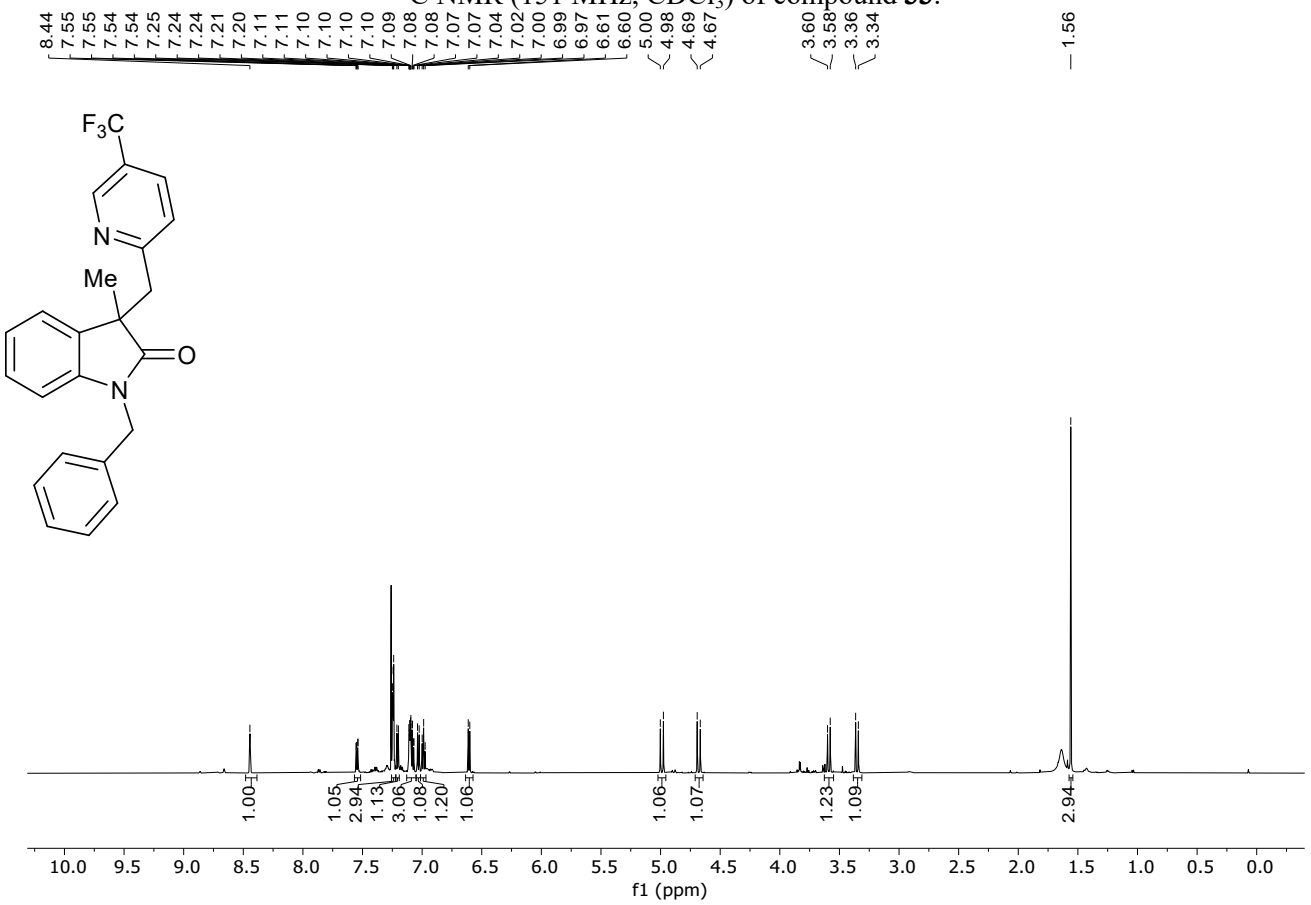
^{1}H NMR (500 MHz, $CDCl_3$) of compound **33**.



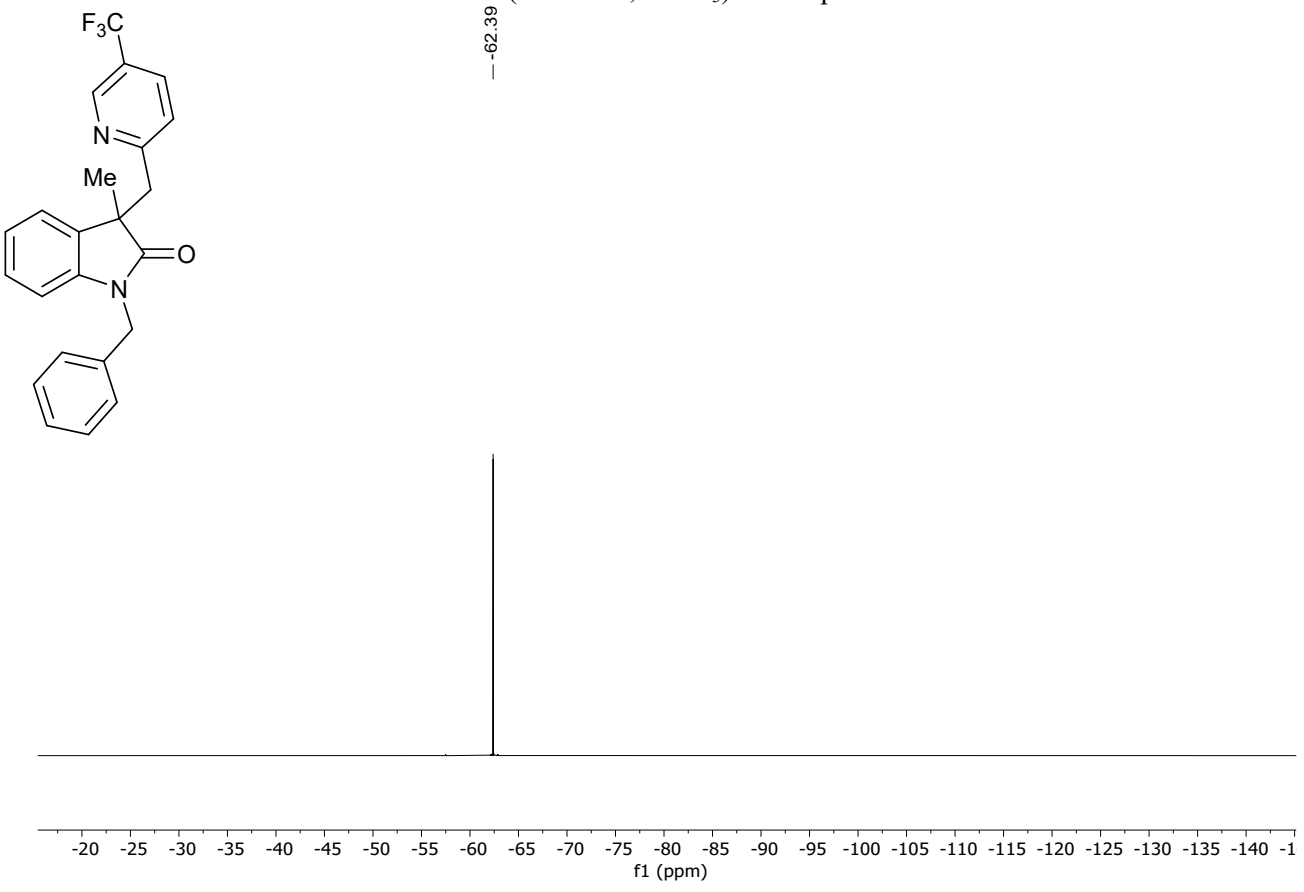
^{19}F NMR (376 MHz, $CDCl_3$) of compound **33**.



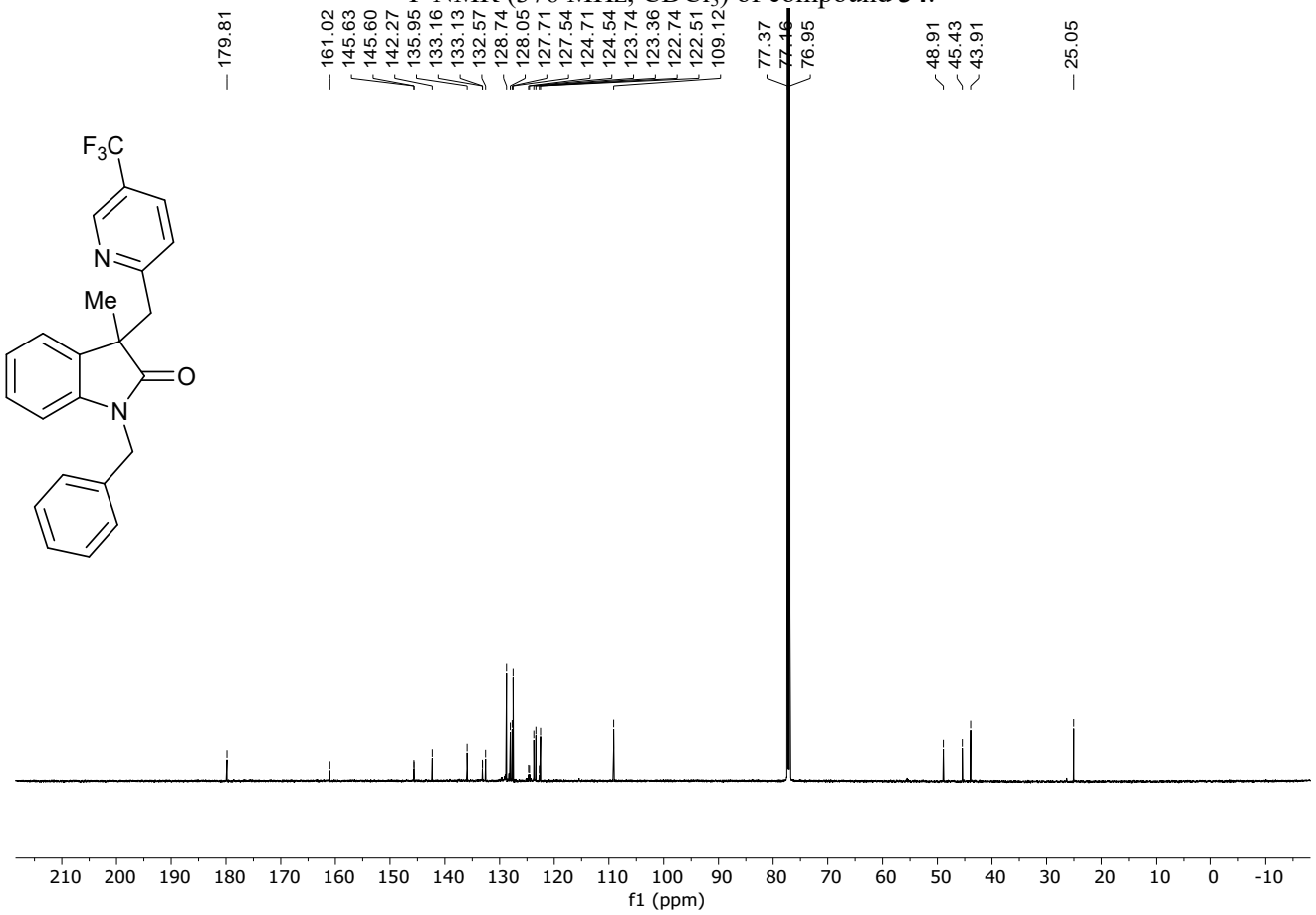
^{13}C NMR (151 MHz, $CDCl_3$) of compound **33**.



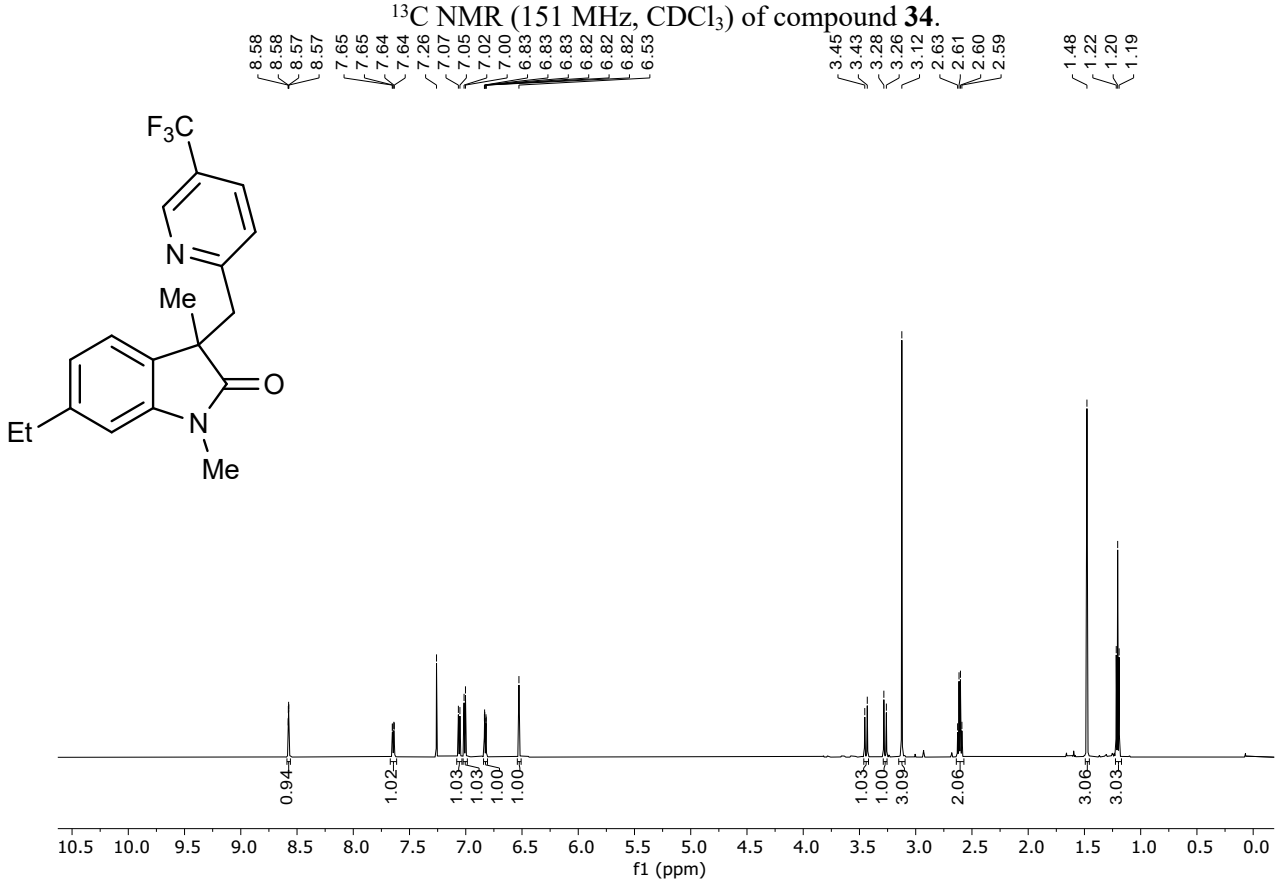
^{1}H NMR (600 MHz, $CDCl_3$) of compound **34**.



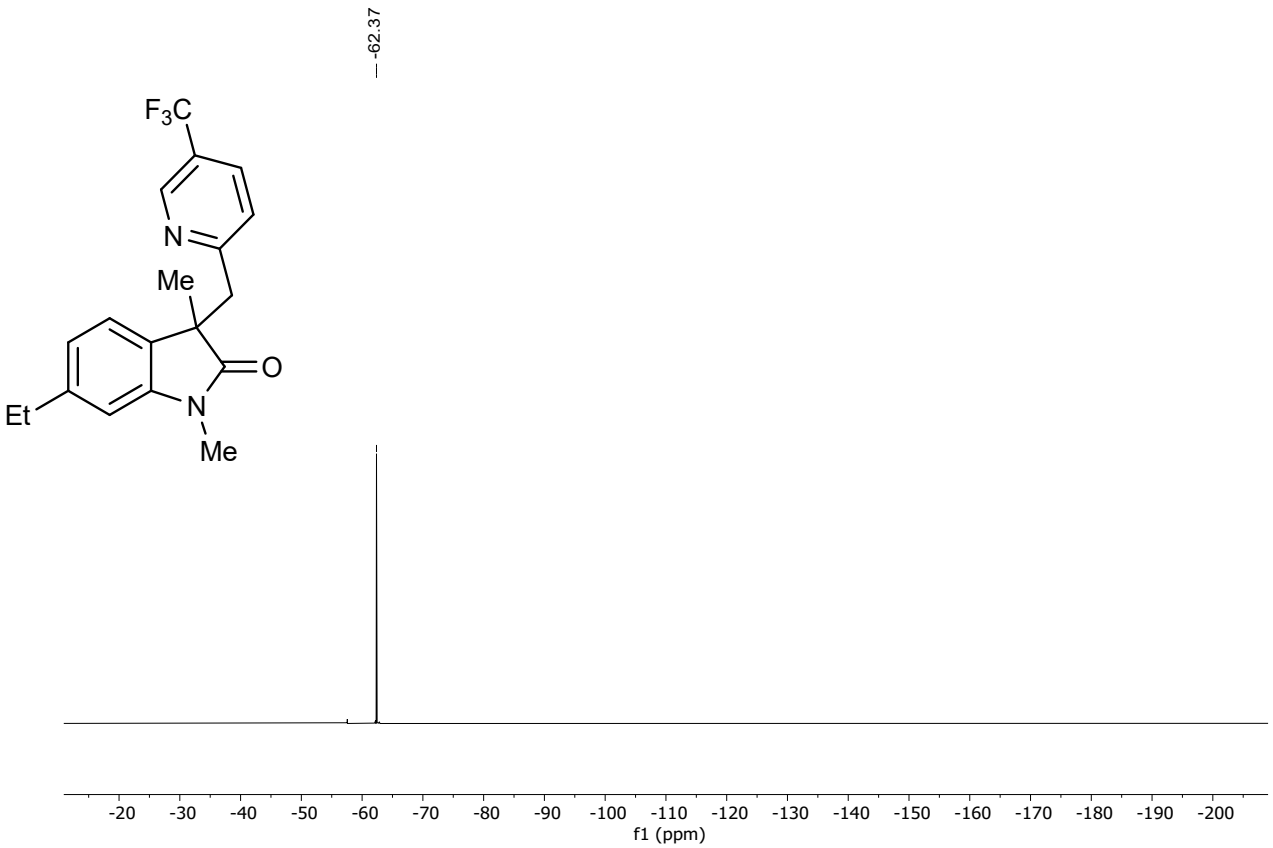
^{19}F NMR (376 MHz, $CDCl_3$) of compound **34**.



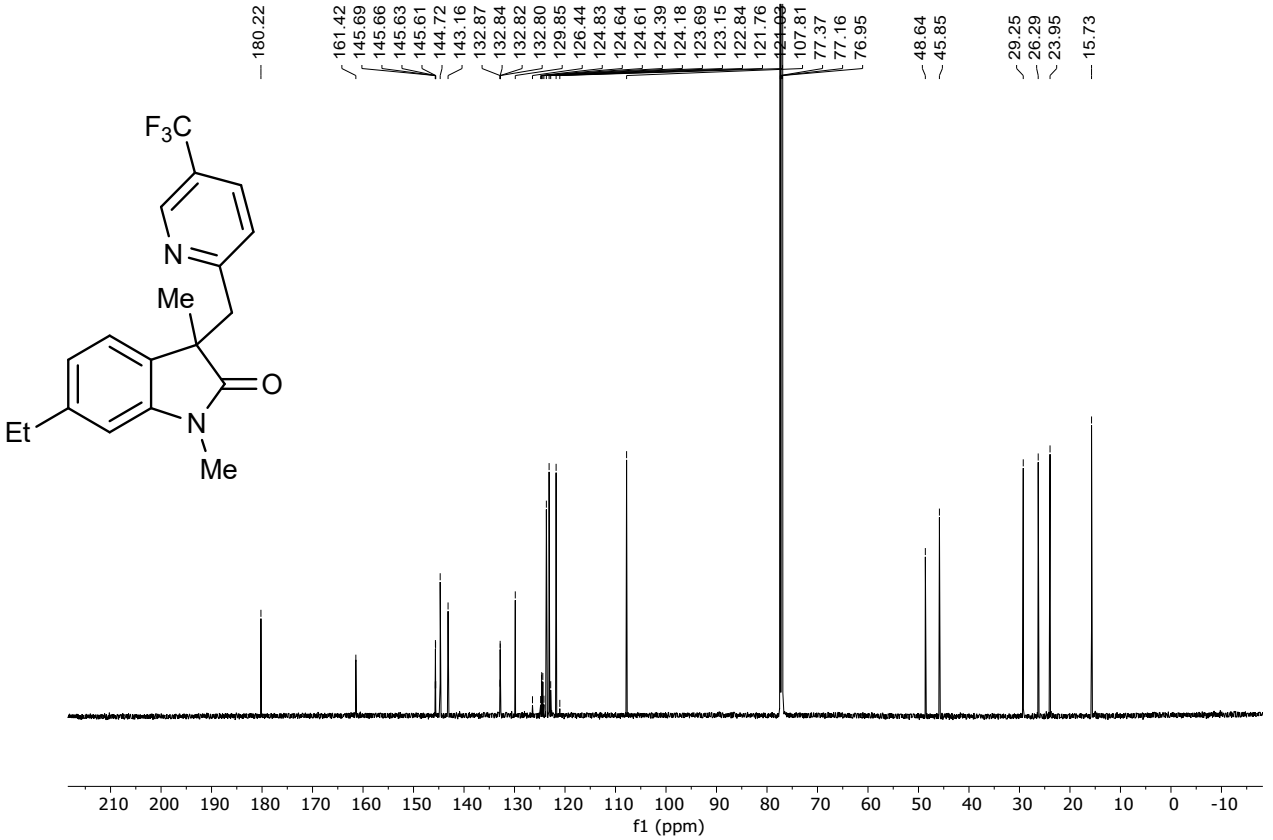
^{13}C NMR (151 MHz, $CDCl_3$) of compound **34**.



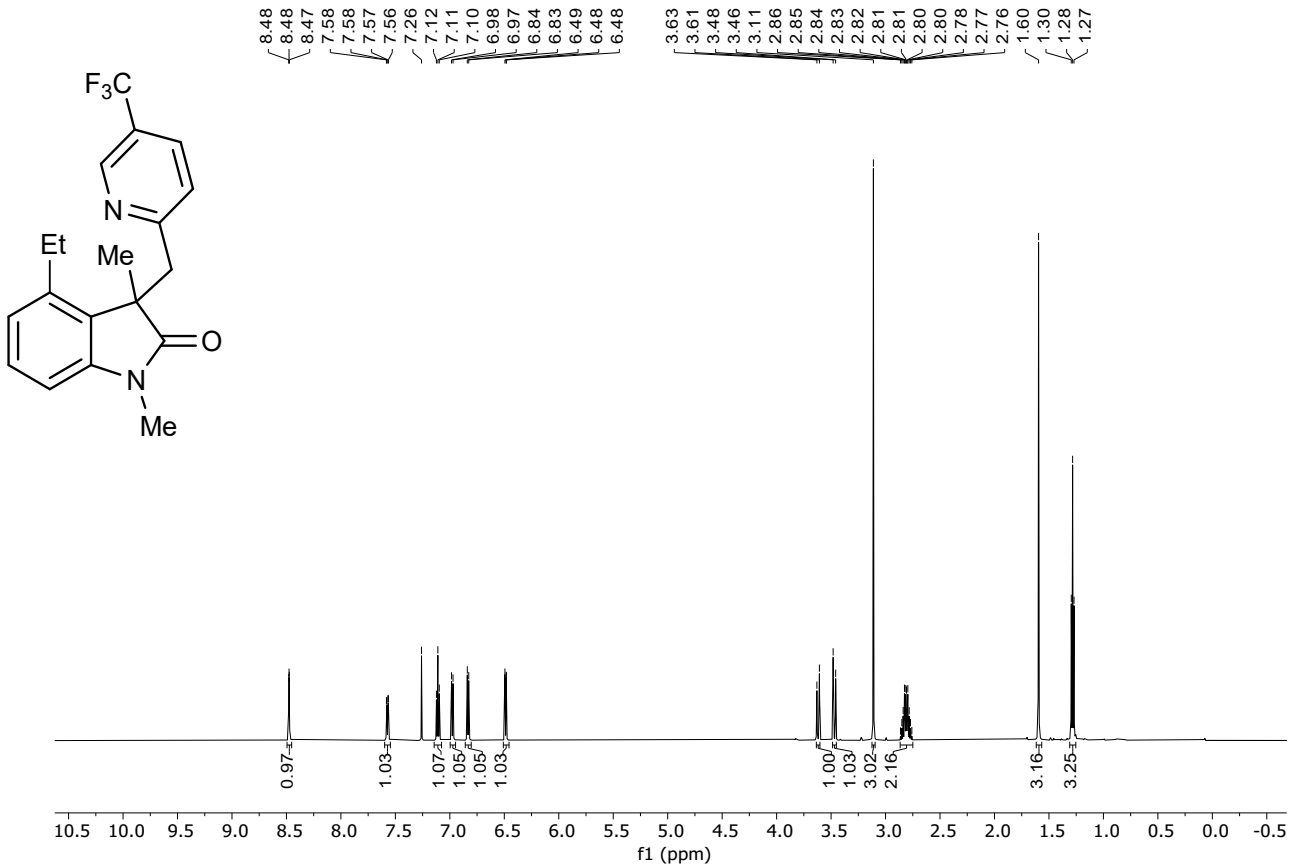
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S1**.



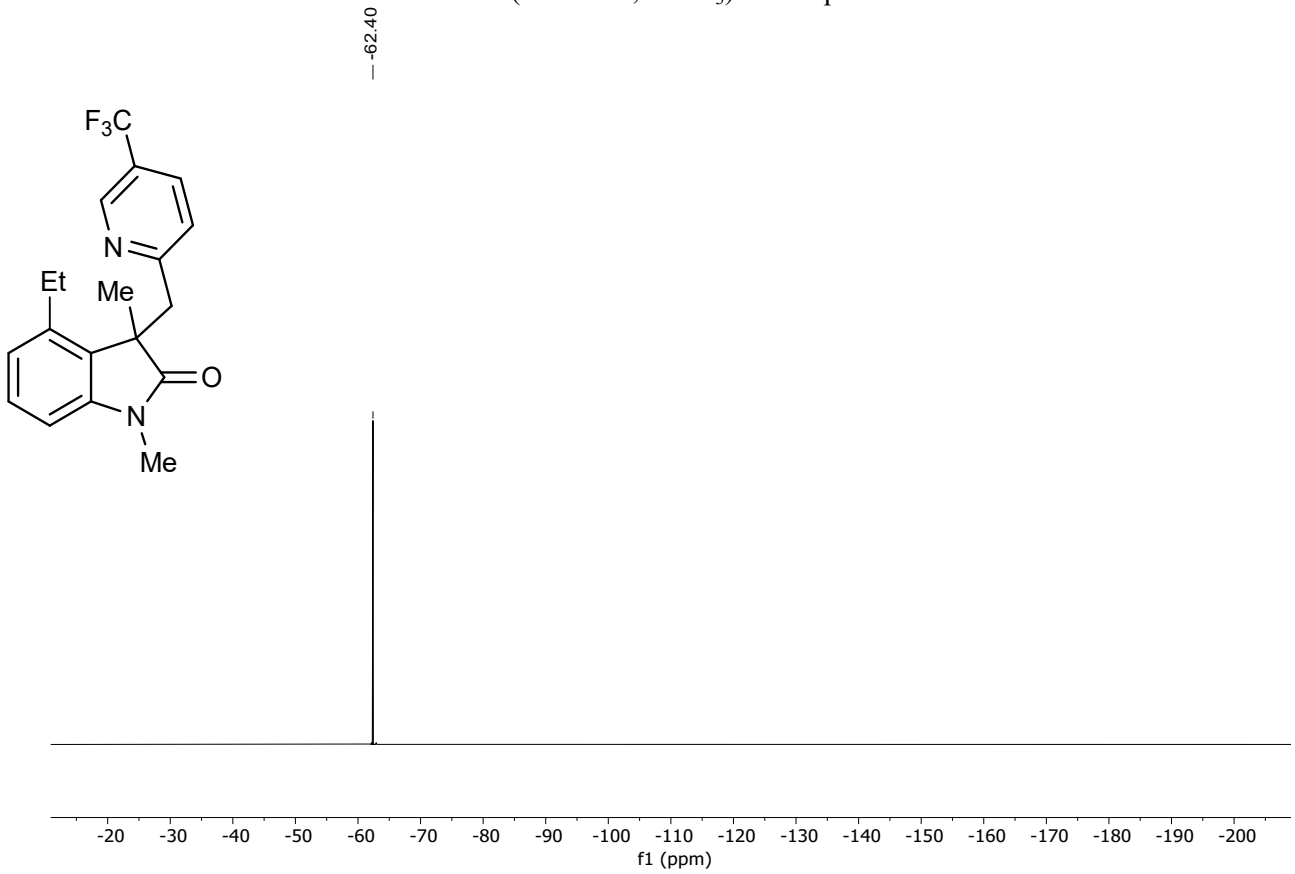
^{19}F NMR (376 MHz, $CDCl_3$) of compound **S1**.



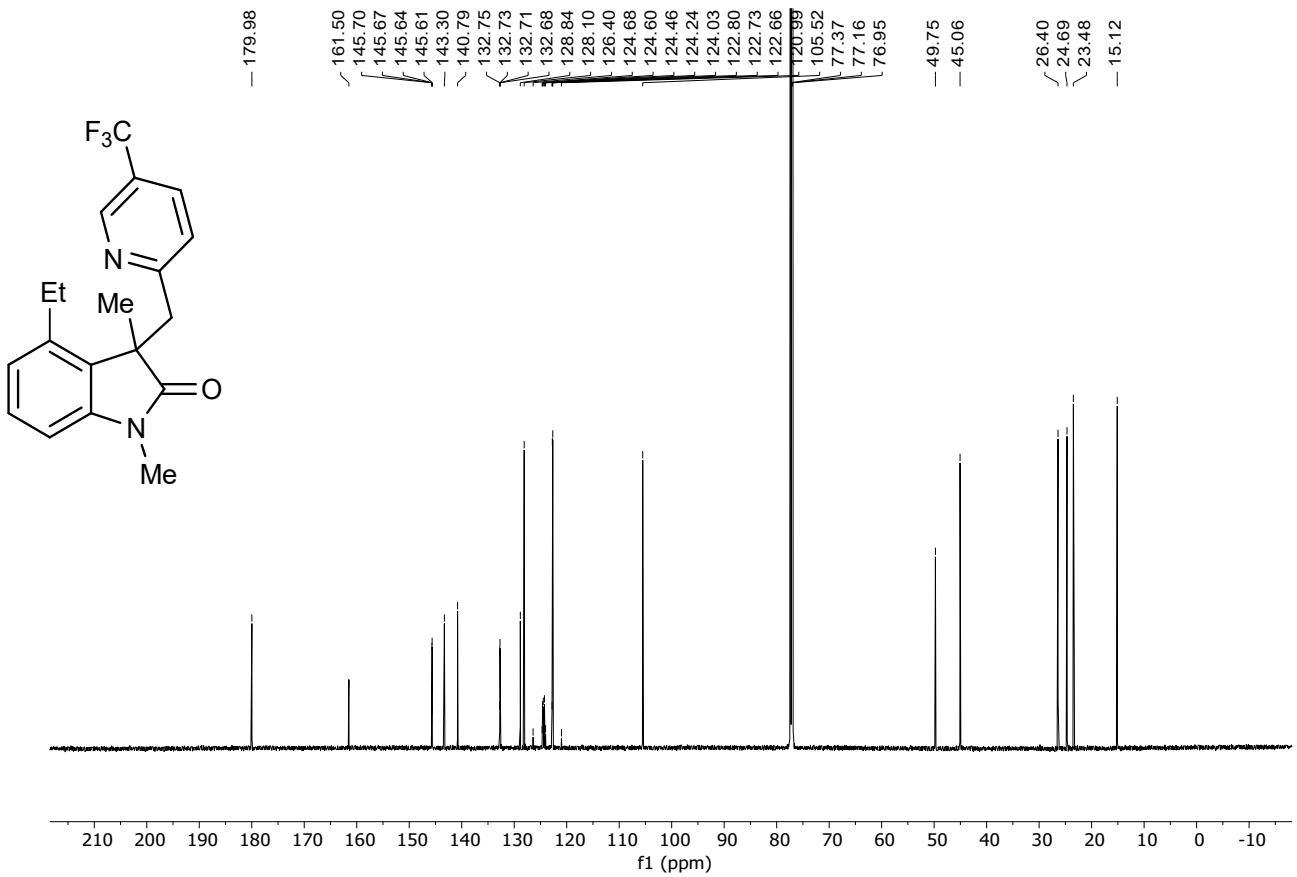
^{13}C NMR (151 MHz, $CDCl_3$) of compound **S1**.



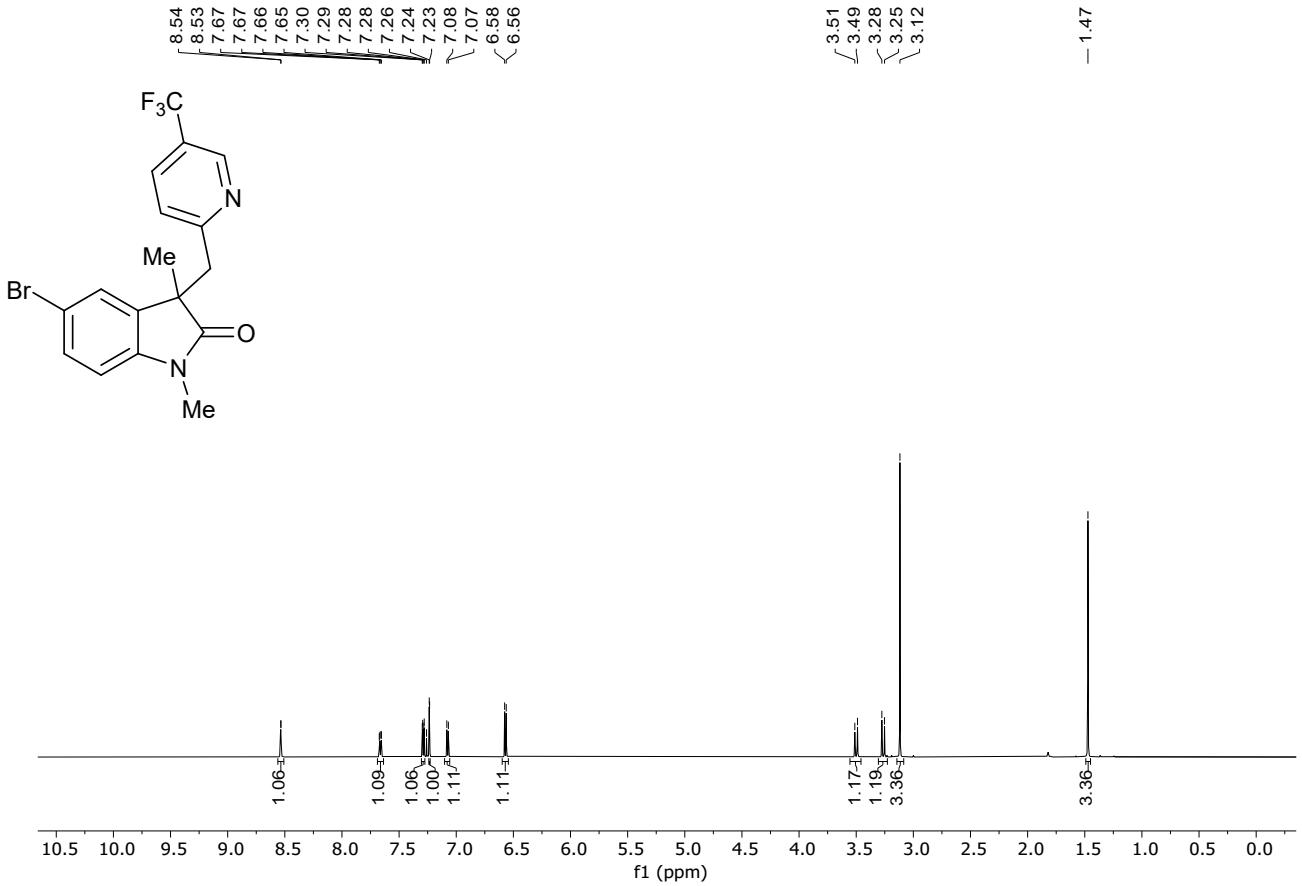
^{1}H NMR (600 MHz, $CDCl_3$) of compound **S2**.



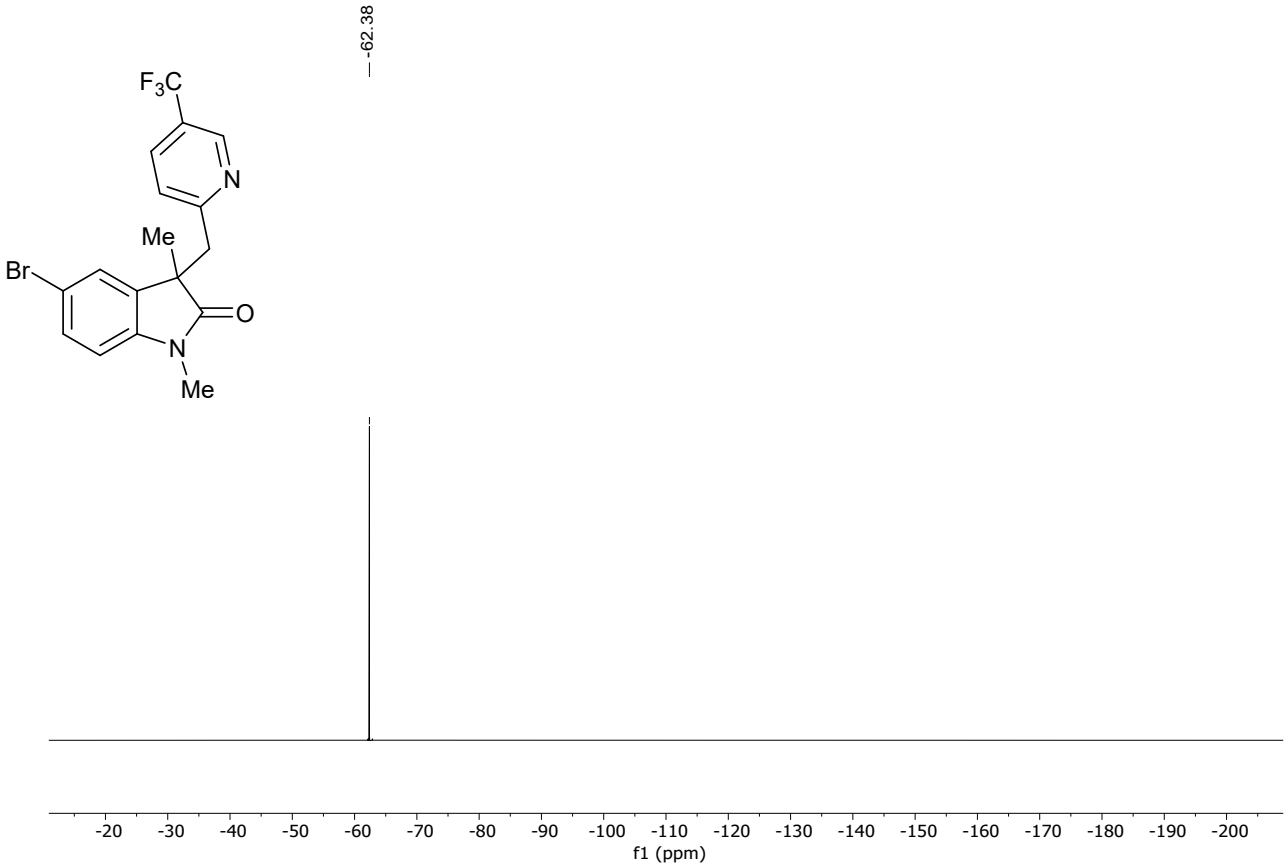
^{19}F NMR (376 MHz, $CDCl_3$) of compound **S2**.



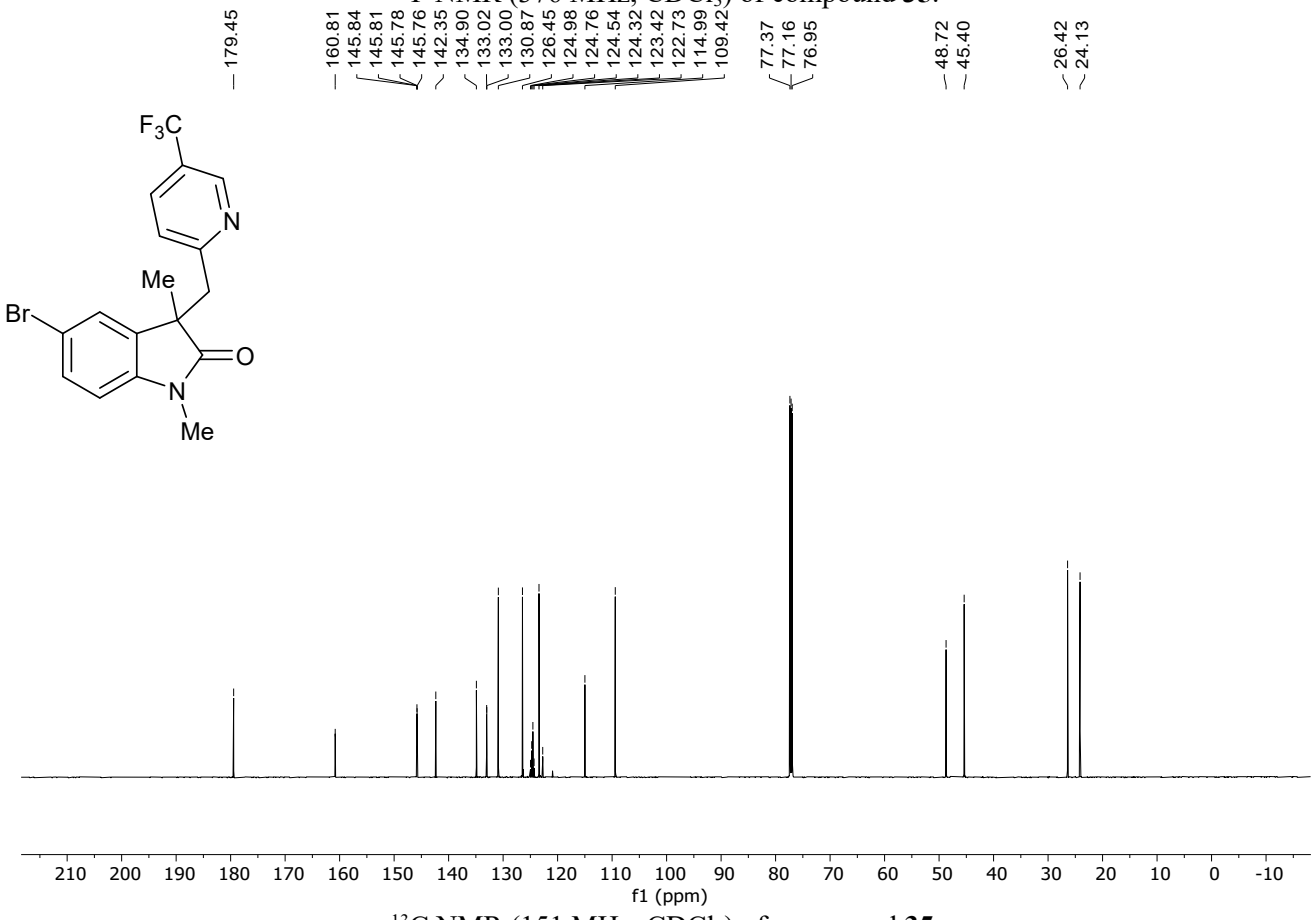
^{13}C NMR (151 MHz, $CDCl_3$) of compound **S2**.



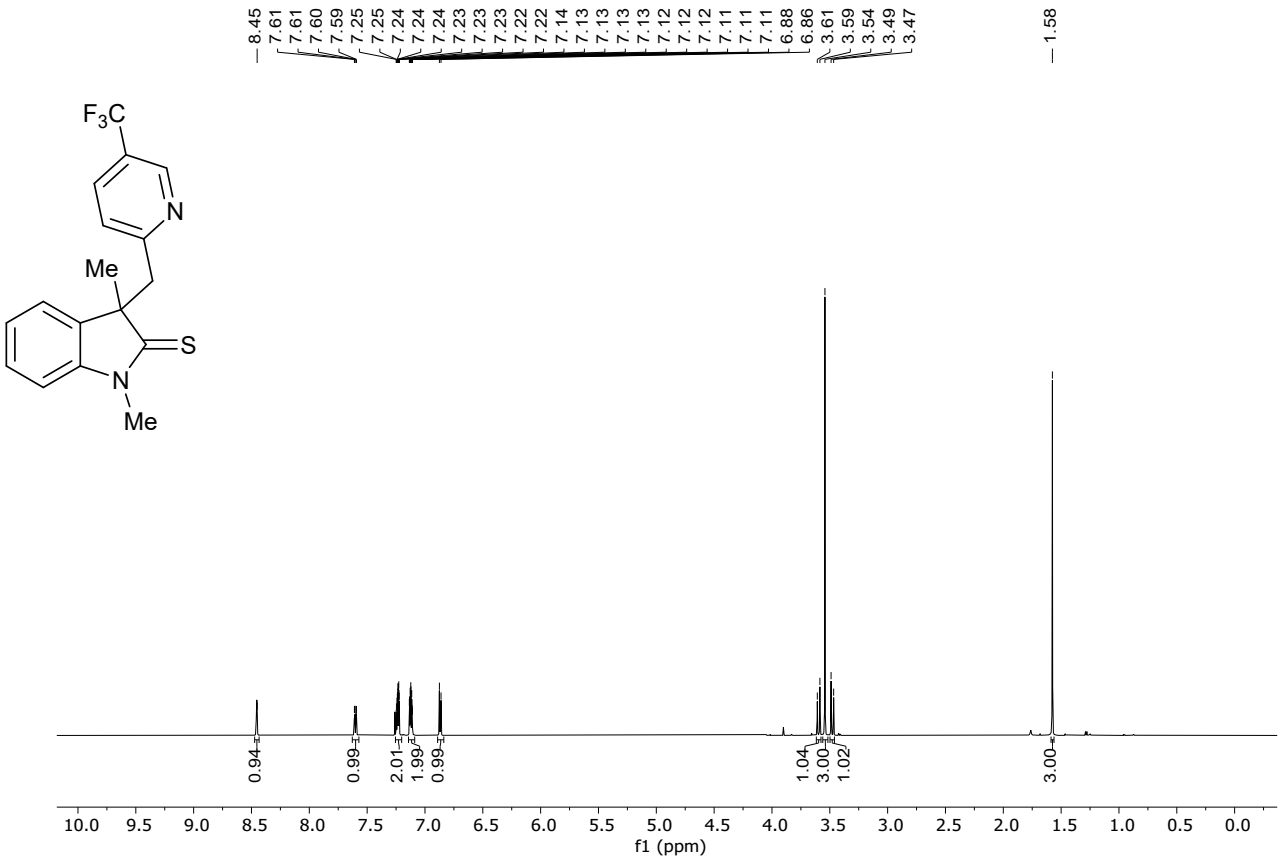
^{1}H NMR (600 MHz, $CDCl_3$) of compound **35**.



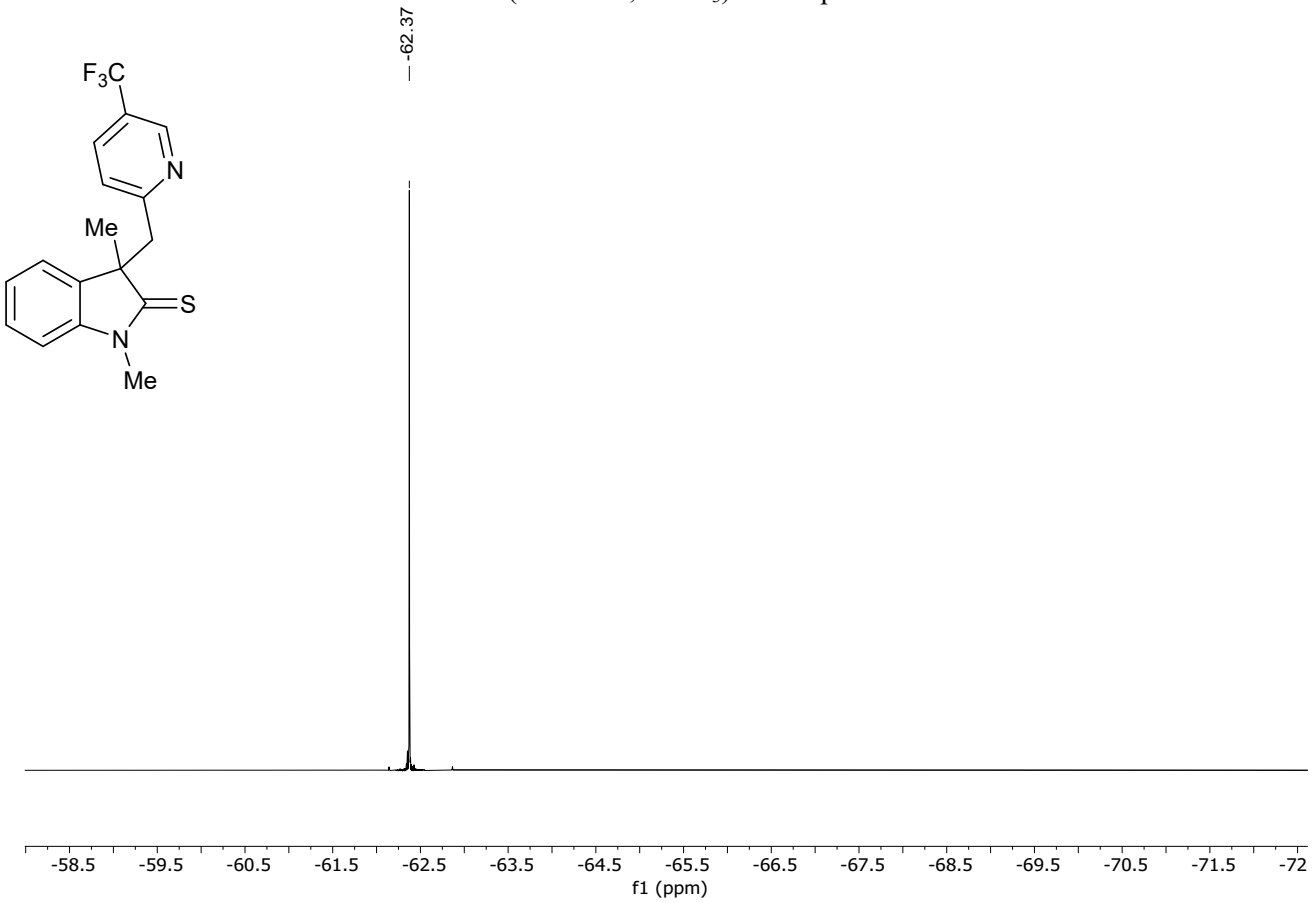
^{19}F NMR (376 MHz, $CDCl_3$) of compound **35**.



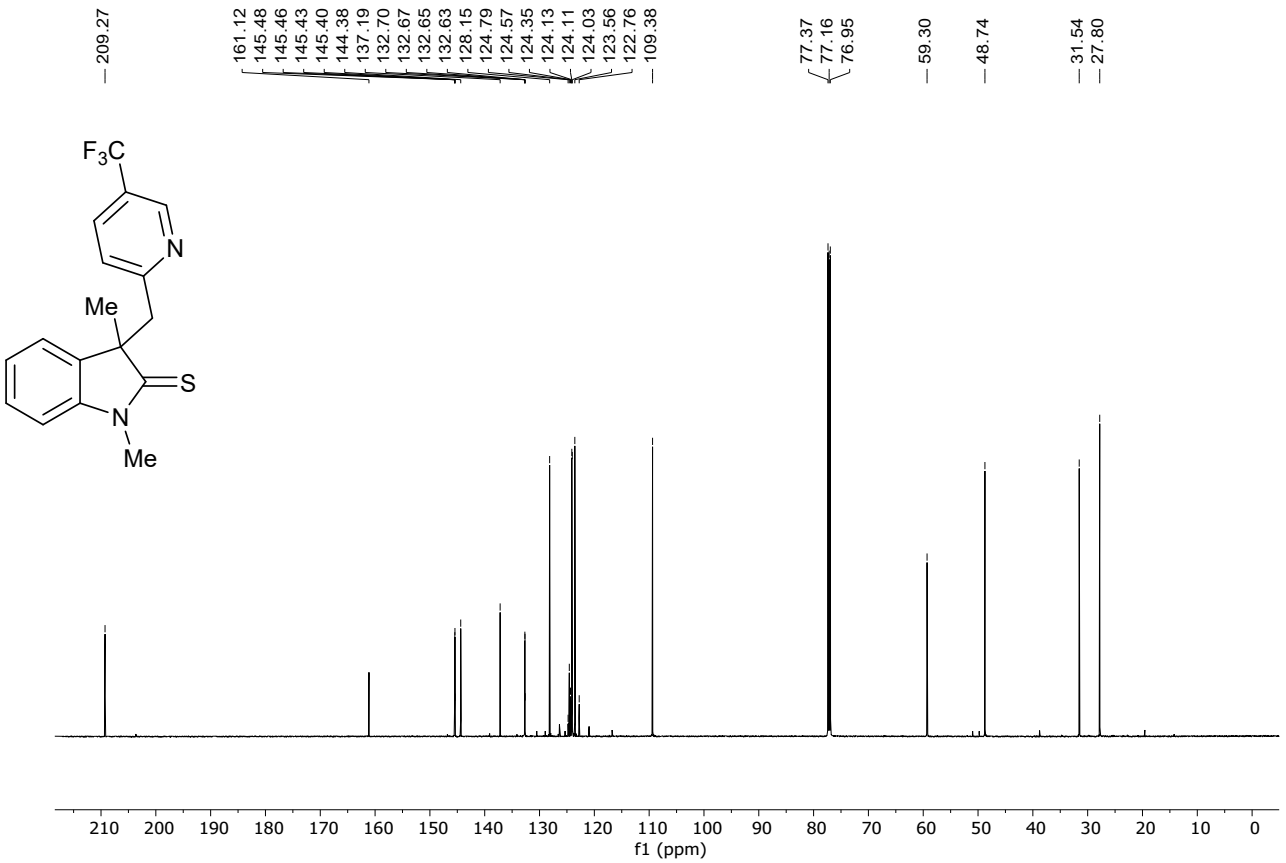
^{13}C NMR (151 MHz, $CDCl_3$) of compound **35**.



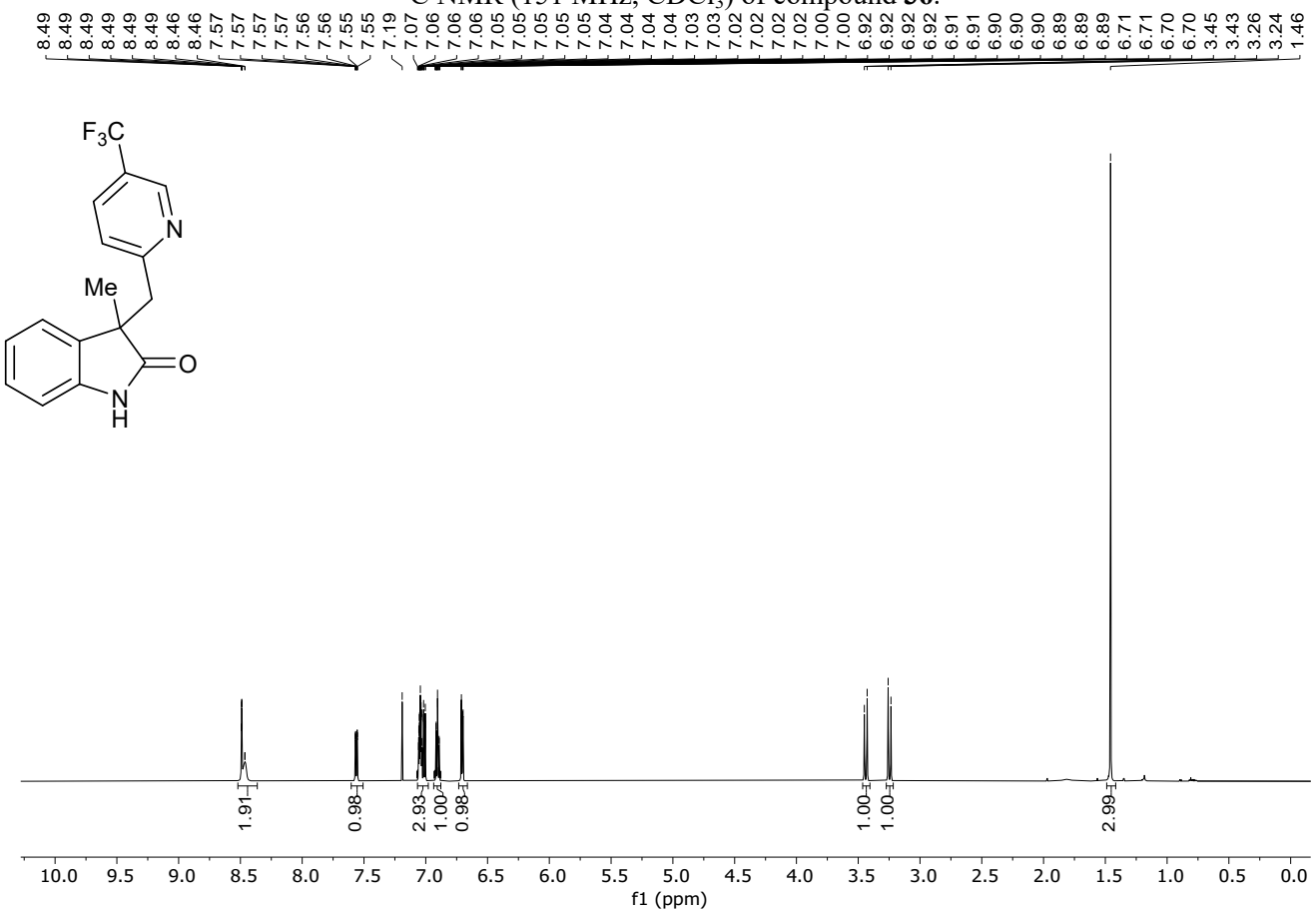
^{1}H NMR (600 MHz, $CDCl_3$) of compound **36**.



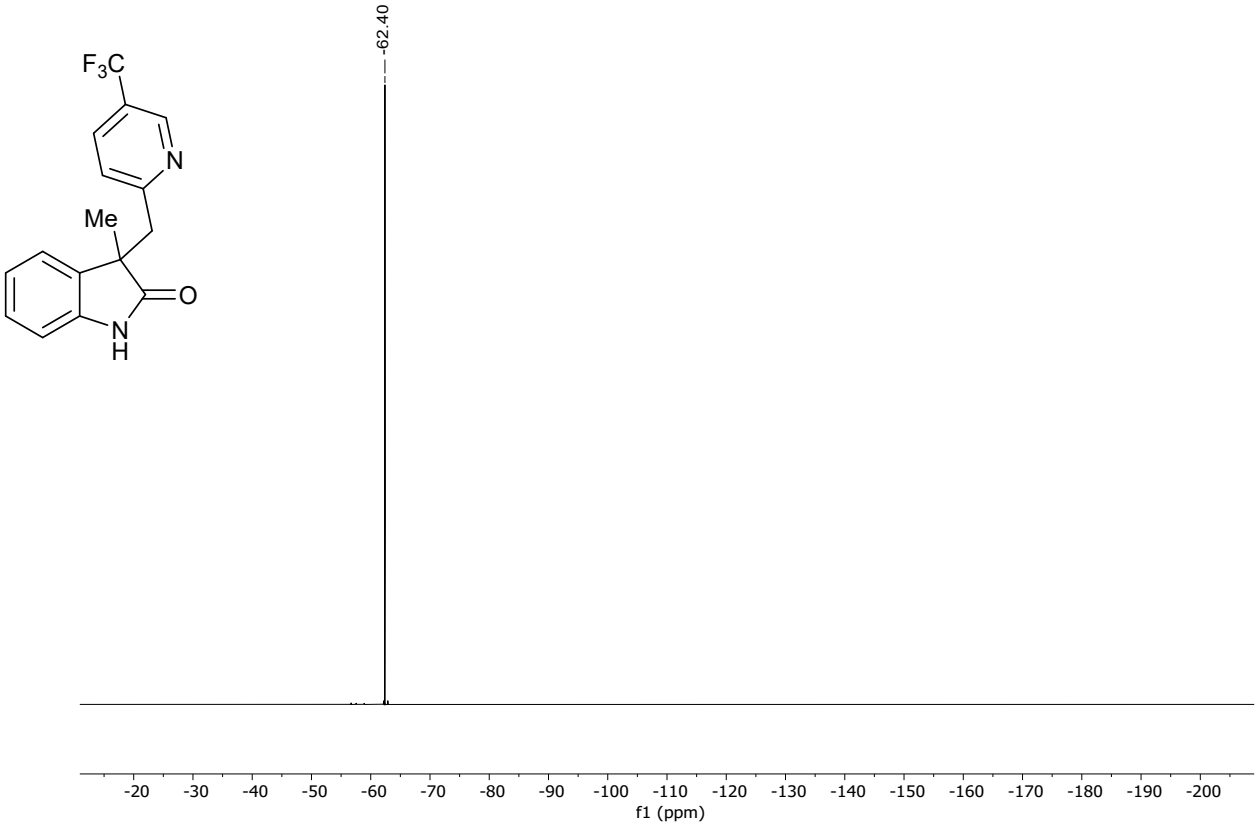
^{19}F NMR (376 MHz, $CDCl_3$) of compound **36**.



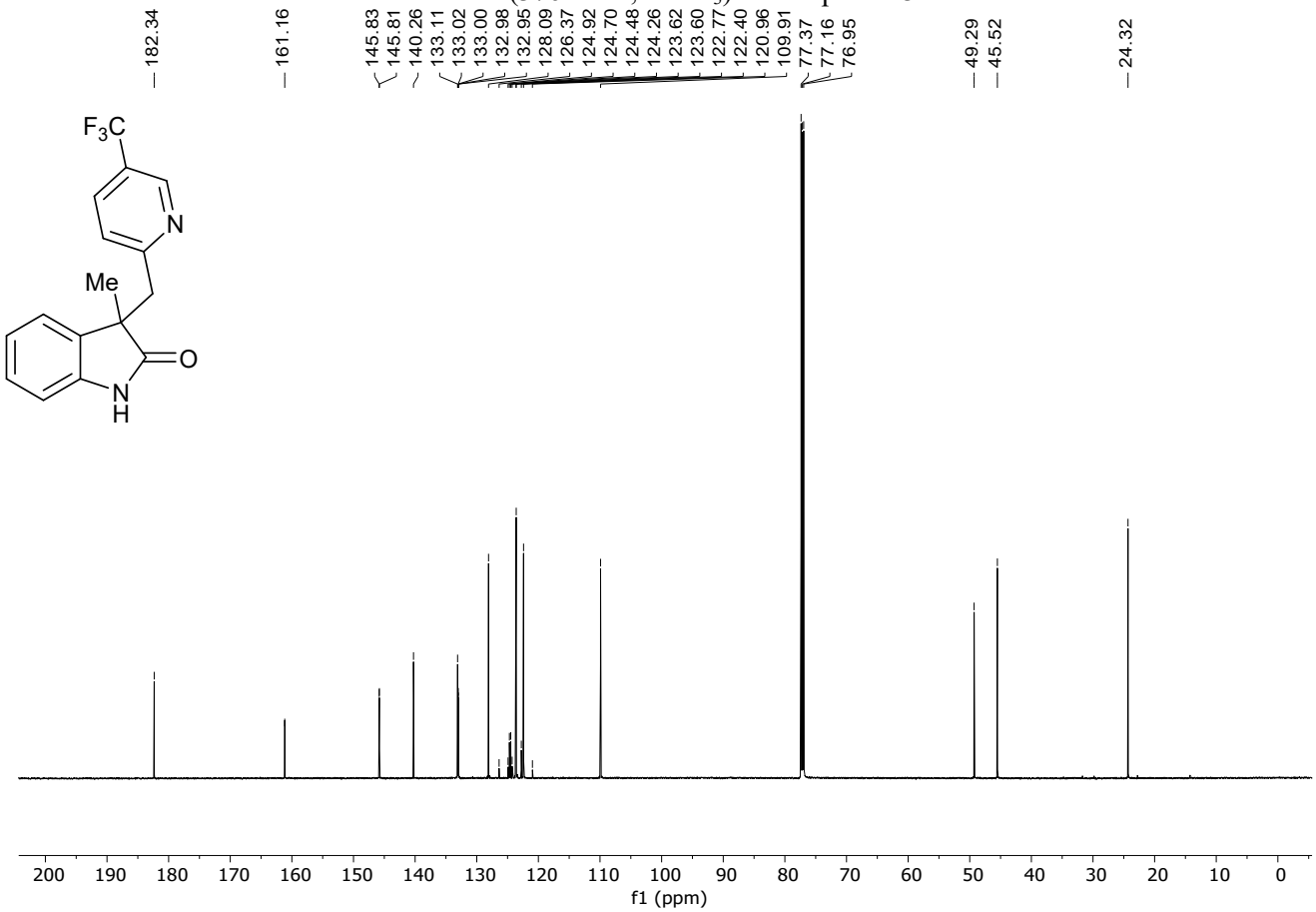
^{13}C NMR (151 MHz, $CDCl_3$) of compound **36**.



^{1}H NMR (600 MHz, $CDCl_3$) of compound **37**.



^{19}F NMR (376 MHz, $CDCl_3$) of compound **37**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **37**.