Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Electrochemical Fe-catalysed radical cyclization for the synthesis of oxindoles

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Table of contents

1. Material and methods

Unless stated otherwise, all reactions were performed in oven-dried two-neck glass tubes unless otherwise noted. The tubes were fitted with a rubber septum and a threaded Teflon cap with airtight electrical feed-throughs. The reactions were conducted under nitrogen atmosphere. Reactions required elevated temperature were performed in an oil bath. Acetonitrile (MeCN), Dimethyl sulfoxide (DMSO) and Methanol (MeOH) were purchased from commercial sources and used as received. Reagents obtained from commercial sources were used as supplied unless stated otherwise. All reactions were set up outside a glove box. Thin layer chromatography (TLC) was performed on pre-coated plates, silica gel 60 PF254 (0.25 mm). TLC were visualized with UV light (254 nm). Flash chromatography was performed on silica gel 60 (200-300 mesh). ^{1}H NMR spectra were recorded on a Bruker Avance (300, 400 or 500 MHz) spectrometer using $CDCl_3$ as solvent and referenced relative to deuterated chloroform (δ = 7.26 ppm). Chemical shifts are reported in ppm and coupling constants (*J*) in Hertz. ^{13}C NMR spectra were recorded on the same instruments (100 or 125 MHz) with total proton decoupling referenced relative to $CDCl_3$ (δ = 77.16 ppm). Infrared spectra were obtained on Thermo Fisher Nicolet 6700. High-resolution mass spectra were recorded on commercial instruments (APCI or ESI). Cyclic voltammetry spectra were recorded on Shanghai Chenhua CHI660E.

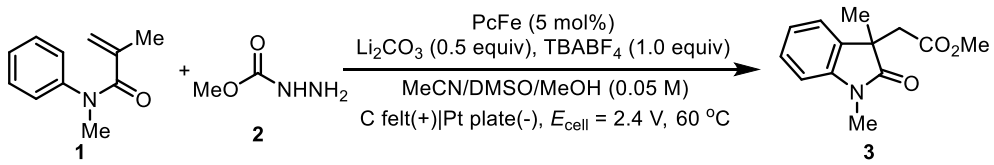
2. Experimental procedures

2.1 General procedure – Reaction optimization and substrate scope study:

An oven-dried, 10 mL two-neck glass tube was equipped with a magnetic stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feed throughs, a carbon felt anode (4*12*10 mm^3) (connected to the electrical feedthrough via a 9 cm in length, 2 mm in diameter graphite rod), and a platinum foil cathode (0.2*5*10 mm^3). To this reaction vessel was added *N*-aryl acrylamide **1** (35.1 mg, 0.2 mmol 1.0 equiv), carbazate **2** (36.0 mg, 0.4 mmol, 2.0 equiv), $TBABF_4$ (66.0 mg, 0.2 mmol, 1.0 equiv), Li_2CO_3 (7.4 mg, 0.1 mmol, 50 mol%), and PcFe (5.7 mg, 0.01 mmol, 5 mol %). The cell was sealed and flushed with nitrogen gas for 5 minutes, followed by adding MeOH (1 mL), DMSO (1 mL) and MeCN (2 mL) via syringe. The reaction mixture was then purged with nitrogen gas for another 5 minutes. A nitrogen-filled balloon was adapted through the septum to sustain a nitrogen atmosphere. Electrolysis was initiated with a cell potential of 2.4 V at 60 ℃. After the reaction, the tube cap was removed and electrodes were rinsed with EtOAc, which was combined with the crude mixture. The organic solution was further washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography.

Figure S1. Components of the reaction setup (left). Assembled reaction vessel (right)

Table S1. Reaction discovery and optimization[a]



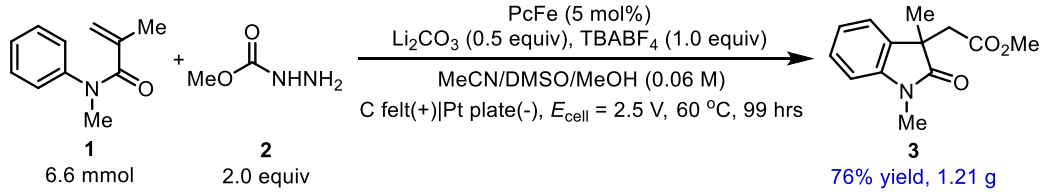
Entry	Variation	1 conv. (%)[b]	Yield (%)[b]
1	none	86	**74(70)**[c]
2	No PcFe	25	10
3	No Li_2CO_3	76	60
4	DIPEA instead of Li_2CO_3	77	60
5	$NaHCO_3$ instead of Li_2CO_3	60	38
6	MeCN (3 mL) as solvent	91	34
7	DMSO (3 mL) as solvent	64	40
8	MeOH (4 mL) as solvent	84	58
9	Ni foam as cathode	60	40
10	$TBAPF_6$ instead of $TBABF_4$	89	66
11	$LiClO_4$ instead of $TBABF_4$	84	70
12	H_2O (1 mL) instead of MeOH	91	52
13	TFE (1 mL) instead of MeOH	85	60
14	HFIP (1 mL) instead of MeOH	84	68
15	Constant current at 6.0 mA, 15 h	85	74
16	room temperature, 15 h	95	64(52)[c]
17	$FeCl_2$ instead of PcFe	59	26
18	Ferrocene instead of PcFe	17	10
19	$FeSO_4•6H_2O$ instead of PcFe	37	22

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol, 2.0 equiv), PcFe (5 mol%), Li_2CO_3 (50 mol%), $TBABF_4$ (1.0 equiv), MeCN/DMSO/MeOH (2:1:1, 4 mL), carbon felt anode (4*12*10 mm^3) , Pt cathode (0.2*5*10 mm^3), undivided cell, cell potential E_{cell} = 2.4 V, 60 °C, 15 hours. [b]Conversion and yield were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. [c]Isolated yield.

3. Reaction scale-up and product transformations

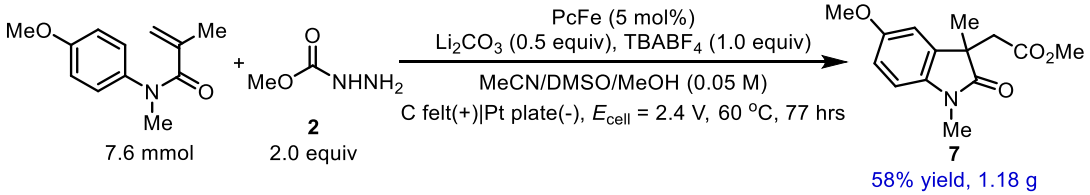
3.1 Scale-up reaction

a. Gram-scale synthesis of oxindole 3



An oven-dried two-neck flask (5.0 cm in diameter, 12.0 cm in length) was equipped with a stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feedthroughs, a carbon felt anode (4*20*40 mm^3), and a platinum plate cathode (0.2*20*40 mm^3). The distance between electrodes was ca. 10 mm. The electrodes were connected to the electrical feedthrough, each via a 9 cm in length, 2 mm in diameter graphite rod. To the flask were added *N*-methylphenyl acrylamide **1** (1.16 g, 6.6 mmol, 1.0 equiv), methyl carbazate **2** (1.19 g, 13.2 mmol, 2.0 equiv), $TBABF_4$ (2.17 g, 6.6 mmol, 1.0 equiv), Li_2CO_3 (243.8 mg, 3.3 mmol, 50 mol%), and PcFe (187.6 mg, 0.3 mmol, 5 mol%) under nitrogen atmosphere. Then MeCN/DMSO/MeOH (2:1:1, 104 mL) were added via syringe. The reaction mixture was then sparged with nitrogen gas for 10 minutes and maintained under nitrogen atmosphere with a balloon. Then electrolysis was initiated with a cell potential of 2.5 V. After 99 hours at 60 °C, the electrolysis was terminated, the tube cap was removed and electrodes were rinsed with EtOAc, which was combined with the crude mixture. The organic solution was further washed with brine. The two layers were separated, and the aqueous layer was extracted with EtOAc (2x). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:7) to furnish oxindole product **3** (1.21 g) as yellow oil in 76% yield.

b. Gram-scale synthesis of oxindole 7



An oven-dried two-neck flask (5.0 cm in diameter, 12.0 cm in length) was equipped with a stir bar, a rubber septum, a threaded Teflon cap fitted with electrical feedthroughs, a carbon felt anode (4*20*40 mm^3), and a platinum plate cathode

(0.2*20*40 mm^3). The distance between electrodes was ca. 10 mm. The electrodes were connected to the electrical feedthrough, each via a 9 cm in length, 2 mm in diameter graphite rod. To the flask were added *N*-arylacrylamide (1.56 g, 7.6 mmol, 1.0 equiv), methyl carbazate **2** (1.37 g, 15.2 mmol, 2.0 equiv) $TBABF_4$ (2.50 g, 7.6 mmol, 1.0 equiv), Li_2CO_3 (280.8 mg, 3.8 mmol, 50 mol%), and PcFe (216.0 mg, 0.38 mmol, 5 mol%) under nitrogen atmosphere. Then MeCN/DMSO/MeOH (2:1:1, 120 mL) were added. The reaction mixture was then sparged with nitrogen gas for 10 minutes and maintained under nitrogen atmosphere with a balloon. Then electrolysis was initiated with a cell potential of 2.4 V. After 77 hours at 60 °C, the electrolysis was terminated, the tube cap was removed and electrodes were rinsed with EtOAc, which was combined with the crude mixture. The organic solution was further washed with brine. The two layers were separated, and the aqueous layer was extracted with EtOAc (2x). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:7) to give oxindole product **7** (1.18 g) as pale-yellow oil in 58% yield.

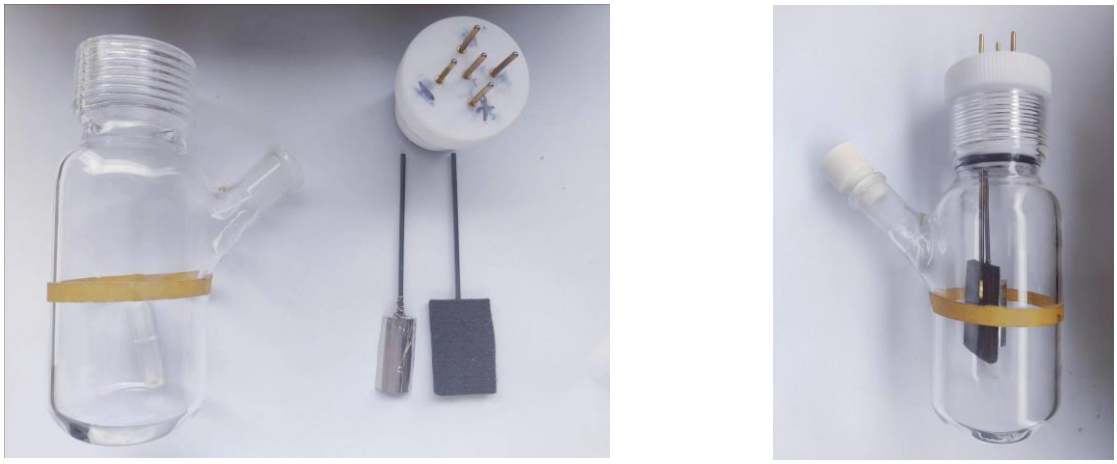
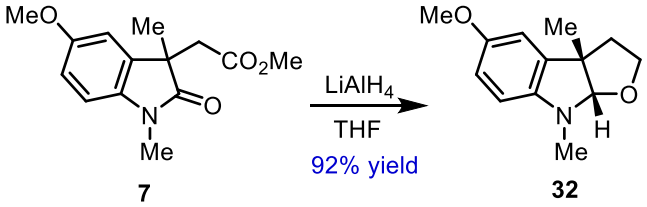
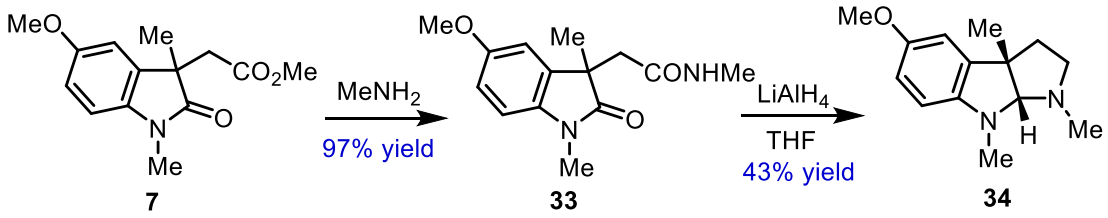


Figure S2. Components of the reaction setup (left). Assembled reaction vessel (right).

3.2 Product transformation



To a solution of **7** (131.7 mg, 0.5 mmol, 1.0 equiv) in THF (5 ml) was added $LiAlH_4$ (76 mg, 2 mmol, 4.0 equiv) at 0 ℃ under N_2 atmosphere. The reaction mixture was stirred at room temperature for 3 h. After full conversion, the reaction was quenched with EtOAc. After filtration, the filtrate was concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (EtOAc/petroleum ether, 1:5) to afford the product **32** as white solid (101 mg, 92% yield).



Step 1: Compound **7** (400 mg, 1.52 mmol) was dissolved in $MeNH_2$ (31 mL, 33% wt. in EtOH) at room temperature then heated to 60 ℃. The reaction was stirred at 60 ℃ for 48 hours and then cooled to room temperature. The solvent was removed *in vacuo* and the residue was purified by flash column chromatography (EtOAc/petroleum ether, 1:1) to afford the amide product **33** as a white solid (388 mg, 97% yield).

Step 2: To a solution of **33** (105 mg, 0.4 mmol, 1.0 equiv) in THF (6 mL) was added $LiAlH_4$ (76 mg, 2 mmol, 5.0 equiv) at 0 ℃ under N_2 atmosphere. The reaction mixture was stirred for 5 minutes at room temperature and then heated to 50 ℃ for 5 hours. After full conversion, the reaction was cooled to 0 ℃ and quenched with EtOAc. The solvent was removed *in vacuo* and the residue was purified by flash column chromatography (EtOAc/petroleum ether, 1:1) to afford the amide product **34** as yellow oil (40 mg, 43% yield).

4. Mechanistic studies

4.1 Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), an $Ag/AgNO_3$ reference electrode, and a platinum wire counter electrode. The solution was sparged with nitrogen gas for 3-5 minutes before data collection. Potentials were reported in V against the Fc^+/Fc redox couple.

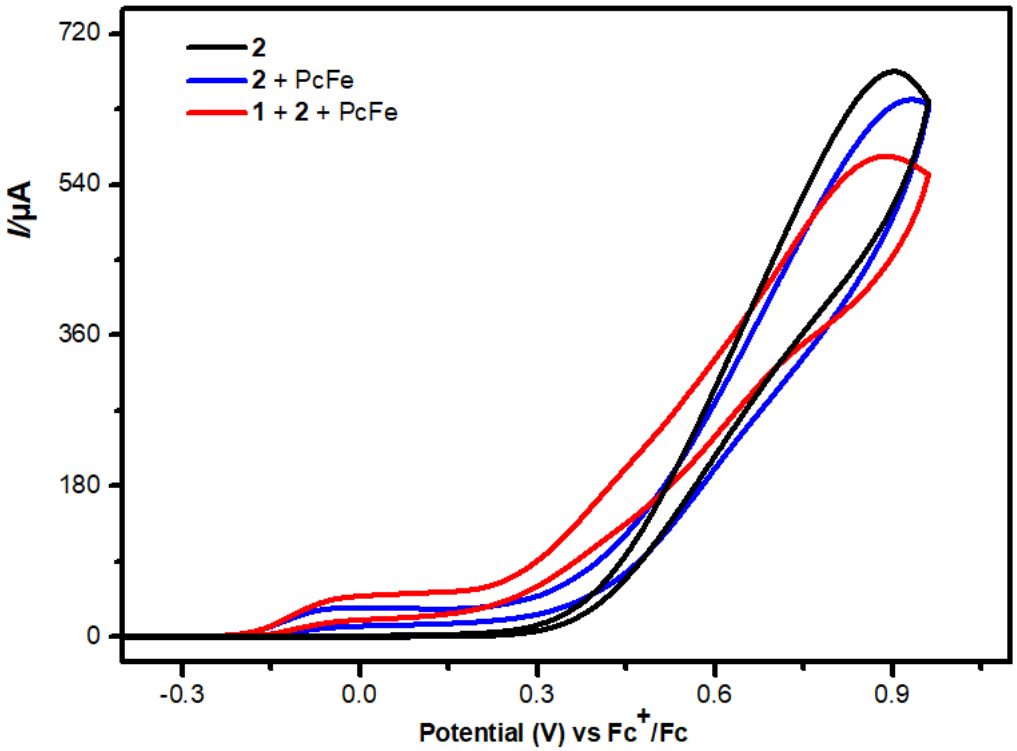
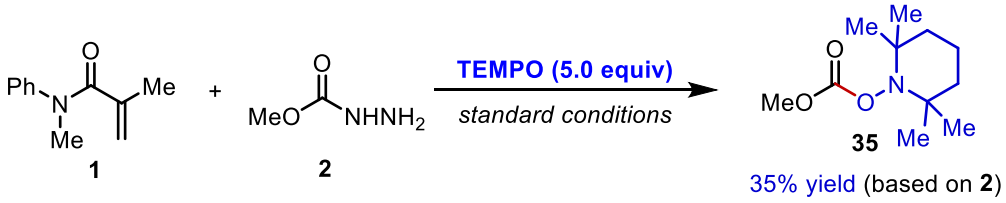


Figure S4. Cyclic voltammogram of *N*-methylphenyl acrylamide **1**, methyl carbazate **2**, PcFe and their mixture in MeCN/DMSO/MeOH. Conditions: $TBABF_4$ (0.05 M in MeCN/DMSO/MeOH), **1** (50 mM), **2** (0.1 M), (25 mM) PcFe(II) (2.5 mM). Scan rate: 50 mV/s.

4.2 Radical trapping experiment with TEMPO



The reaction shown above was set up following **general procedure** with addition of TEMPO (5.0 equiv). The residue was purified by silica gel flash column chromatography (EtOAc/petroleum ether, 1:5) to afford the product **35** as red oil (30.1

mg, 35% yield base on **2**).

4.3 Anode potential over the course of reaction

The reaction was set up following **general procedure** under standard conditions with an extra $Ag/AgNO_3$ electrode as the reference electrode. The anodic potential was monitored by Shanghai Chenhua CHI660E electrochemical workstation. The reaction was terminated and worked up after 15 hours, giving the desired product **3** in 67% isolated yield.

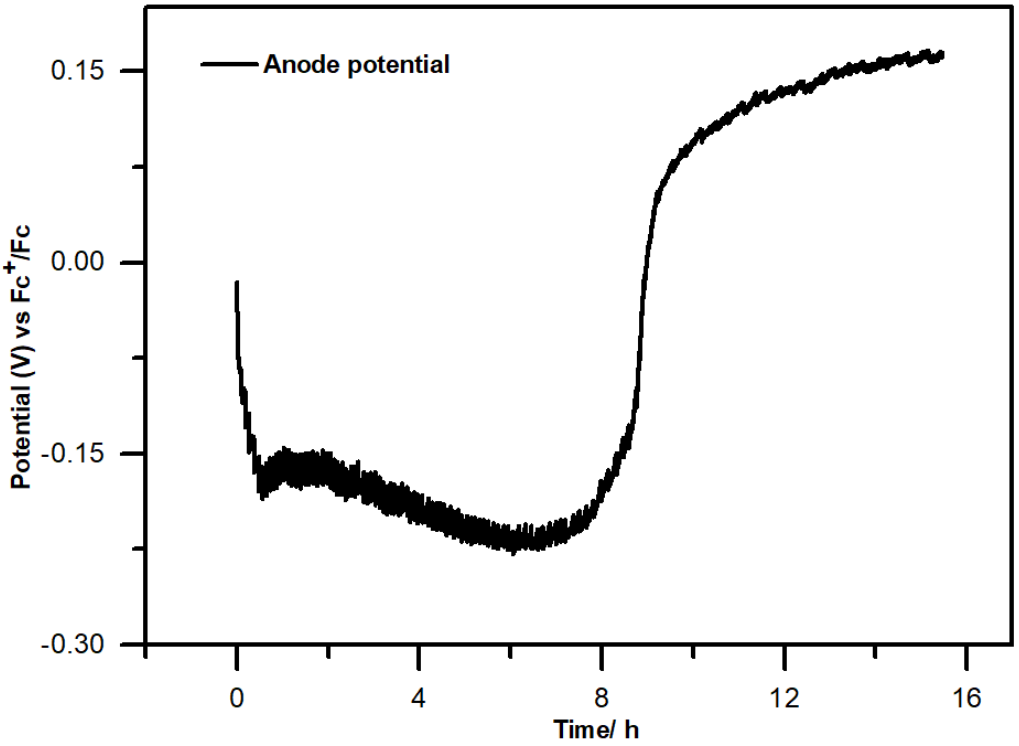
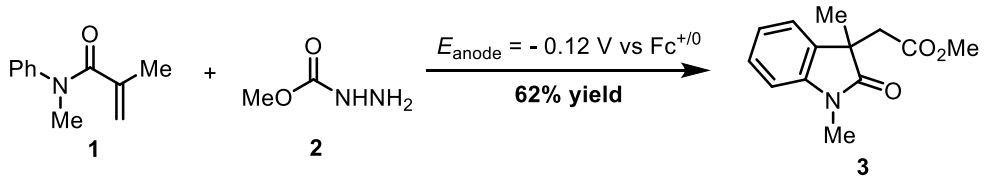


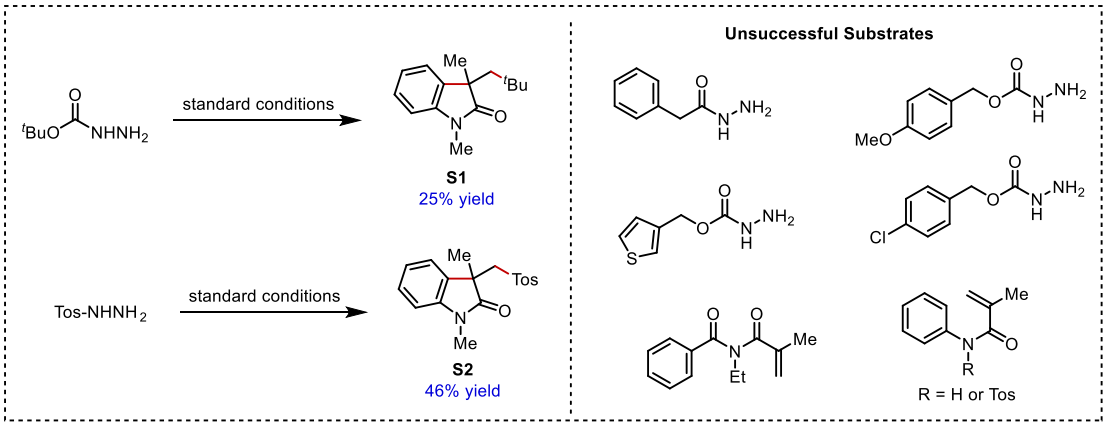
Figure S5. The anodic potential over the course of the model reaction.

4.4 Controlled anodic potential electrolysis experiment



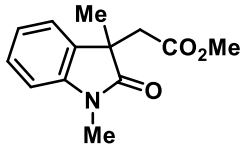
The controlled electrolysis reaction was set up following **general procedure** with an extra $Ag/AgNO_3$ electrode as the reference electrode. The anodic potential was maintained at −0.12 V (vs $Fc^{+/0}$) using Shanghai Chenhua CHI660E. The reaction was terminated and worked up after 15 hours. Followed **general procedure** and purified using silica gel chromatography to give the product **3**.

5. Suboptimal and unsuccessful substrates



6. Spectral data

Methyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (3)



Followed **general procedure** and purified using silica gel chromatography to give the product (32.7 mg, 70% yield) as yellow oil.

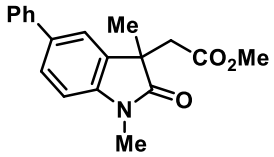
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (td, *J* = 7.7, 1.3 Hz, 1H), 7.18 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.02 (td, *J* = 7.5, 0.9 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.44 (s, 3H), 3.25 (s, 3H), 3.00 (d, *J* = 16.3 Hz, 1H), 2.84 (d, *J* = 16.3 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 170.4, 143.7, 133.0, 128.3, 122.5, 122.4, 108.2, 51.6, 45.6, 41.5, 26.5, 24.3.

Spectral data matched those previously reported.[1]

Methyl 2-(1,3-dimethyl-2-oxo-5-phenylindolin-3-yl)acetate (4)



Followed **general procedure** and purified using silica gel chromatography to give the product (45.8 mg, 74% yield) as light yellow solid.

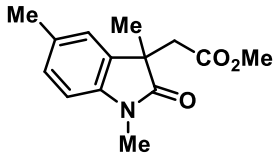
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.52 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.36 – 7.30 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 3.48 (s, 3H), 3.30 (s, 3H), 3.05 (d, *J* = 16.5 Hz, 1H), 2.92 (d, *J* = 16.5 Hz, 1H), 1.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0, 170.4, 143.2, 141.1, 135.9, 133.7, 128.9, 127.1, 127.0, 126.9, 121.3, 108.5, 51.7, 45.7, 41.5, 26.6, 24.4.

Spectral data matched those previously reported.[3]

Methyl 2-(1,3,5-trimethyl-2-oxoindolin-3-yl)acetate (5)



Followed **general procedure** and purified using silica gel chromatography to give the product (38.6 mg, 78% yield) as pale-yellow oil.

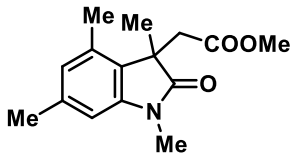
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 7.9 Hz 1H), 7.00 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 3.46 (s, 3H), 3.23 (s, 3H), 2.99 (d, *J* = 16.4 Hz, 1H), 2.82 (d, *J* = 16.4 Hz, 1H), 2.32 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.9, 170.4, 141.4, 133.1, 132.0, 128.5, 123.3, 107.9, 51.6, 45.7, 41.6, 26.5, 24.4, 21.2.

Spectral data matched those previously reported.[2]

Methyl 2-(1,3,4,6-tetramethyl-2-oxoindolin-3-yl)acetate (6)



Followed **general procedure** and purified using silica gel chromatography to give the product (45.0 mg, 86% yield) as light yellow green liquid.

R_f = 0.3 (EtOAc/petroleum ether, 1:3)

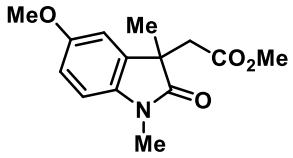
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (s, 1H), 6.52 (s, 1H), 3.38 (s, 3H), 3.22 (s, 3H), 3.11 (d, *J* = 16.0 Hz, 1H), 3.01 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 6H), 1.40 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.3, 170.4, 144.1, 138.1, 133.4, 126.7, 125.6, 107.0, 51.6, 46.3, 40.7, 26.5, 22.5, 21.7, 18.1.

IR (KBr, cm^{-1}): 2931, 2886, 1717, 1618, 1596, 1456, 1341, 1196, 1060, 835.

HRMS (ESI) calcd. for $C_{15}H_{19}NO_3H$ $[M+H]^+$ 262.1438; found 262.1434.

Methyl 2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (7)



Followed **general procedure** and purified using silica gel chromatography to give the product (31.6 mg, 60% yield) as pale-yellow oil.

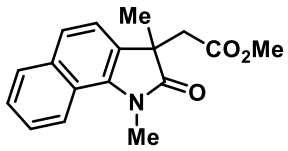
R_f = 0.4 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81-6.74 (m, 3H), 3.77 (s, 3H), 3.46 (s, 3H), 3.21 (s, 3H), 2.97 (d, *J* = 16.5 Hz, 1H), 2.81 (d, *J* = 16.5 Hz, 1H), 1.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.6, 170.3, 156.0, 137.3, 134.5, 112.2, 110.4, 108.4, 55.9, 51.6, 46.0, 41.4, 26.5, 24.3.

Spectral data matched those previously reported.[3]

Methyl 2-(1,3-dimethyl-2-oxo-2,3-dihydro-1H-benzo[g]indol-3-yl)acetate (8)



Followed **general procedure** and purified using silica gel chromatography to give the product (22.7 mg, 40% yield) as pale-yellow oil.

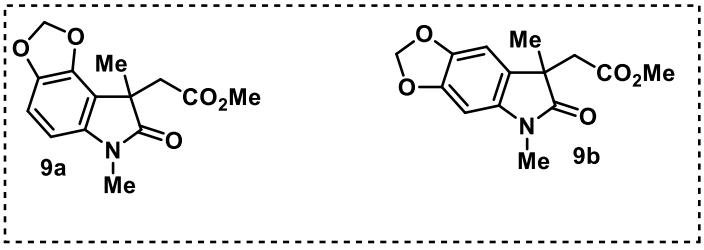
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.56 – 7.38 (m, 3H), 7.32 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.99 (dd, *J* = 7.6, 0.7 Hz, 1H), 3.76 (d, *J* = 16.8 Hz, 1H), 3.58 (s, 3H), 3.40 (s, 3H), 3.11 (d, *J* = 16.8 Hz, 1H), 1.58 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 171.4, 137.9, 137.1, 133.7, 126.9, 126.7, 126.4, 122.6, 121.5, 119.6, 108.7, 51.6, 45.4, 45.2, 32.6, 30.0.

Spectral data matched those previously reported.[2]

Methyl 2-(5,7-dimethyl-6-oxo-6,7-dihydro-5H-[1,3]dioxolo[4,5-f]indol-7-yl) acetate (9a) and Methyl 2-(6,8-dimethyl-7-oxo-7,8-dihydro-6H-[1,3]dioxolo[4,5-e]indol-8-yl)acetate (9b)



Followed **general procedure** and purified using silica gel chromatography to give the product (9a:9b = 2:3, 69% yield) as light green liquid.

R_f = 0.3 (EtOAc/petroleum ether, 1:3)

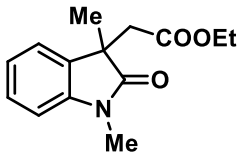
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (s, 1.5H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.46 (s, 1.5H), 6.25 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 5.91 (s, 3H), 3.48 (s, 4.5H), 3.47 (s, 3H), 3.19 (s, 7.5H), 3.00 – 2.88 (m, 3.5H), 2.76 (d, *J* = 16.3 Hz, 1.5H), 1.40 (s, 3H), 1.33 (s, 4.5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 178.9, 170.5, 170.4, 147.4, 144.4, 143.1, 142.9, 139.0, 138.0, 124.8, 113.5, 106.7, 104.4, 101.7, 101.2, 99.8, 92.3, 51.8, 51.7, 45.9, 44.9, 41.5, 40.4, 26.9, 26.7, 24.4, 22.8.

IR (KBr, cm^{-1}): 3458, 2089, 1719, 1633, 1467, 1375, 1351, 1235, 1100, 1063, 923.

HRMS (ESI) calcd. for $C_{14}H_{15}NO_5Na$ $[M+Na]^+$ 300.0842; found 300.0844

Ethyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (10)



Followed **general procedure** and purified using silica gel chromatography to give the product (23.7 mg, 48% yield) as pale-yellow oil.

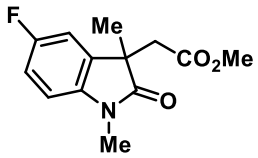
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 - 7.24 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.09 – 6.96 (m, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.97 – 3.73 (m, 2H), 3.24 (s, 3H), 3.01 (d, *J* = 16.1 Hz, 1H), 2.82 (d, *J* = 16.1 Hz, 1H), 1.37 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0, 169.8, 143.8, 133.2, 128.3, 122.5, 122.5, 108.2, 60.5, 45.7, 42.0, 26.5, 24.5, 14.0.

Spectral data matched those previously reported.[4]

Methyl 2-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetate (11)



Followed **general procedure** and purified using silica gel chromatography to give the product (25.1 mg, 50% yield) as colorless oil.

R_f = 0.3 (EtOAc/petroleum ether, 1:3)

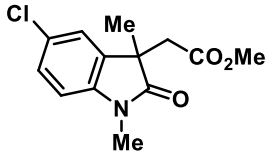
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 – 6.89 (m, 2H), 6.78 – 6.74 (m, 1H), 3.48 (s, 3H), 3.23 (s, 3H), 2.99 (d, *J* = 16.6 Hz, 1H), 2.82 (d, *J* = 16.6 Hz, 1H), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.6, 170.2, 160.2, 158.4, 139.7 (d, *J* = 2 Hz), 134.8, (d, *J* = 8.0 Hz), 114.4, 114.3, 110.9, 110.7, 108.6 (d, *J* = 8.0 Hz), 51.7, 46.0 (d, *J* = 1.8 Hz), 41.3, 26.6, 24.2.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -120.81.

Spectral data matched those previously reported.[1]

Methyl 2-(5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)acetate (12)



Followed **general procedure** and purified using silica gel chromatography to give the product (39.1 mg, 73% yield) as colorless oil.

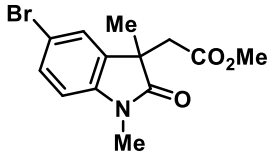
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.49 (s, 3H), 3.24 (s, 3H), 3.01 (d, *J* = 16.8 Hz, 1H), 2.83 (d, *J* = 16.8 Hz, 1H), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.5, 170.2, 142.4, 134.9, 128.2, 127.8, 123.0, 109.1, 51.8, 45.8, 41.3, 26.6, 24.2.

Spectral data matched those previously reported.[2]

Methyl 2-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (13)



Followed **general procedure** and purified using silica gel chromatography to give the product (53.1 mg, 85% yield) as pale-yellow oil.

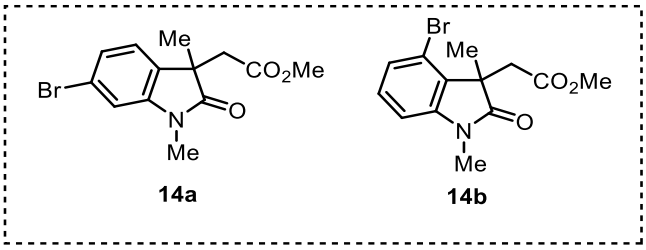
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.29 (d, *J* = 2.0 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 3.48 (s, 3H), 3.22 (s, 3H), 3.00 (d, *J* = 16.8 Hz, 1H), 2.82 (d, *J* = 16.8 Hz, 1H), 1.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 170.1, 142.9, 135.3, 131.1, 125.7, 115.1, 109.7, 51.8, 45.7, 41.3, 26.6, 24.3.

Spectral data matched those previously reported.[2]

Methyl 2-(6-bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (14a) and Methyl 2-(4-bromo-1,3-dimethyl-2-oxoindolin-3-yl)acetate (14b)



Followed **general procedure** and purified using silica gel chromatography to give the product (14a:14b = 2:5, 71% yield) as pale-yellow oil.

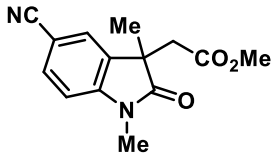
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 2.34H), 7.05 (d, *J* = 5.8 Hz 0.37H), 6.99(d, *J* = 3 Hz 0.37H), 6.80 (dd, *J* = 5.8, 2.8 Hz, 1H), 3.56 (s, 0.44 H), 3.50 (s, 0.55H), 3.47 (s, 1H), 3.45 (s, 3H), 3.24 (s, 3H), 3.22 (s, 1H), 3.04 (d, *J* = 5.8 Hz 0.37H), 2.99 (d, *J* = 5.8 Hz 0.37H), 1.47 (s, 3H), 1.35 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 170.5, 170.3, 146.0, 145.1, 132.0, 130.8, 129.7, 126.5, 125.2, 123.6, 121.8, 118.1, 111.8, 107.3, 51.8, 47.6, 45.3, 41.3, 39.2, 26.7, 24.2, 21.5.

Spectral data matched those previously reported.[2]

Methyl 2-(5-cyano-1,3-dimethyl-2-oxoindolin-3-yl)acetate (15)



Followed **general procedure** and purified using silica gel chromatography to give the Product (36.2 mg, 70% yield) as white solid.

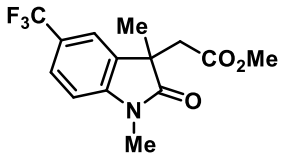
R_f = 0.4 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 3.48 (s, 3H), 3.27 (s, 3H), 3.04 (d, *J* = 17.0 Hz, 1H), 2.88 (d, *J* = 17.0 Hz, 1H), 1.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.7, 170.1, 147.8, 134.3, 133.7, 125.7, 119.3, 108.6, 105.6, 51.9, 45.3, 41.2, 26.7, 24.1.

Spectral data matched those previously reported.[2]

Methyl 2-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetate (16)



Followed **general procedure** and purified using silica gel chromatography to give the product (41.6 mg, 69% yield) as white solid.

R_f = 0.4 (EtOAc/petroleum ether, 1:3)

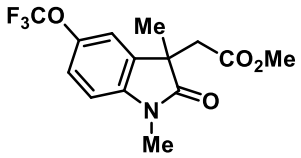
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* =8.2 Hz, 1H), 7.46 – 7.34 (m, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 3.48 (s, 3H), 3.28 (s, 3H), 3.04 (d, *J* = 16.8 Hz, 1H), 2.89 (d, *J* = 16.8 Hz, 1H), 1.39 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.9, 170.2, 146.9, 133.8, 126.2 (q, *J* = 4.0 Hz), 124.7 (q, *J* = 32.6 Hz), 124.6 (q, *J* = 271.6 Hz), 119.4 (q, *J* = 3.7 Hz), 108.0, 51.8, 45.5, 41.4, 26.7, 24.2.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -61.34.

Spectral data matched those previously reported.[2,3]

Methyl 2-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)acetate (17)



Followed **general procedure** and purified using silica gel chromatography to give the product (53.9 mg, 85% yield) as white solid.

R_f = 0.3 (EtOAc/petroleum ether, 1:3)

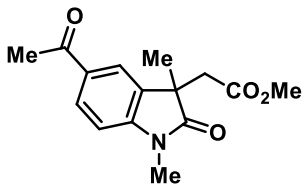
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 3.47 (s, 3H), 3.25 (s, 3H), 3.00 (d, *J* = 16.6 Hz, 1H), 2.84 (d, *J* = 16.6 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.7, 170.2, 144.8, 142.5, 134.7, 121.7, 120.7, 116.6, 108.6, 51.7, 46.0, 41.4, 26.7, 24.1.

^{19}F NMR (377 MHz, Chloroform-*d*) δ -58.39.

Spectral data matched those previously reported.[2]

Methyl 2-(5-acetyl-1,3-dimethyl-2-oxoindolin-3-yl)acetate (18)



Followed **general procedure** and purified using silica gel chromatography to give the product (28.6 mg, 52% yield) as pale-yellow oil.

R_f = 0.3 (EtOAc/petroleum ether, 1:3)

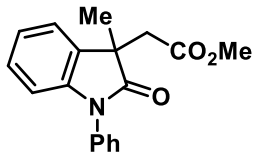
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.45 (s, 3H), 3.29 (s, 3H), 3.06 (d, *J* = 17.0 Hz, 1H), 2.92 (d, *J* = 17.0 Hz, 1H), 2.56 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 180.4, 170.3, 148.3, 133.6, 132.0, 130.6, 121.9, 107.6, 51.8, 45.3, 41.3, 26.8, 26.5, 24.4.

IR (KBr, cm^{-1}): 3650, 2961, 1723, 1673, 1610, 1500, 1445, 1352, 1290, 1255, 1120, 1050, 825.

HRMS (ESI) calcd. for $C_{15}H_{17}NO_4Na$ $[M+Na]^+$ 298.1050; found 298.1049.

Methyl 2-(3-methyl-2-oxo-1-phenylindolin-3-yl)acetate (19)



Followed **general procedure** and purified using silica gel chromatography to give the product (48.4 mg, 82% yield) as light yellow liquid.

R_f = 0.3 (EtOAc/petroleum ether, 1:3)

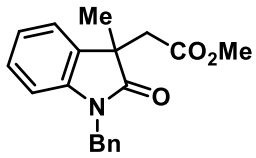
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.50 – 7.44 (m, 2H), 7.41 (ddt, *J* = 7.2, 5.1, 1.5 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.19 (td, *J* = 7.8, 1.3 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 3.49 (s, 3H), 3.16 (d, *J* = 16.4 Hz, 1H), 2.95 (d, *J* = 16.4 Hz, 1H), 1.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 170.4, 143.9, 135.0, 132.8, 129.7, 128.2, 128.1, 126.8, 122.9, 122.5, 109.5, 51.8, 45.7, 42.1, 24.8.

IR (KBr, cm^{-1}): 3462, 3062, 2986, 1728, 1611, 1499, 1456, 1376, 1303, 1278, 1206, 1174, 1083, 981.

HRMS (ESI) calcd. for $C_{18}H_{17}NO_3Na$ $[M+Na]^+$ 318.1101; found 318.1098.

Methyl 2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetate (20)



Followed **general procedure** and purified using silica gel chromatography to give the product (51.4 mg, 83% yield) as light yellow liquid.

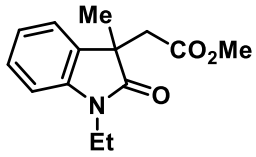
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.09 (m, 7H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 5.02 – 4.91 (m, 2H), 3.42 (s, 3H), 3.10 (d, *J* = 16.3 Hz, 1H), 2.91 (d, *J* = 16.3 Hz, 1H), 1.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0, 170.3, 142.8, 136.3, 133.1, 128.8, 128.2, 127.6, 127.5, 122.6, 122.5, 109.3, 51.6, 45.7, 44.1, 41.5, 25.0.

Spectral data matched those previously reported.[1]

Methyl 2-(1-ethyl-3-methyl-2-oxoindolin-3-yl)acetate (21)



Followed **general procedure** and purified using silica gel chromatography to give the product (38.1 mg, 77% yield) as pale-yellow liquid.

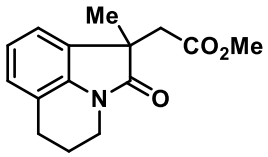
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.22 – 7.16 (m, 1H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.79 – 3.69 (m, 1H), 3.44 (s, 3H), 3.02 (d, *J* = 16.2 Hz, 1H), 2.84 (d, *J* = 16.2 Hz, 1H), 1.37 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 170.3, 142.7, 133.2, 128.2, 122.5, 122.2, 108.4, 51.6, 45.5, 41.5, 34.8, 24.5, 12.5.

Spectral data matched those previously reported.[4]

Methyl 2-(1-methyl-2-oxo-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl) Acetate (24)



Followed **general procedure** and purified using silica gel chromatography to gi ve the product (34.2 mg, 66% yield) as colorless oil.

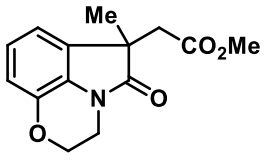
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 – 6.96 (m, 2H), 6.96 – 6.82 (m, 1H), 3.87 – 3.64 (m, 2H), 3.48 (s, 3H), 2.96 (d, *J* = 16.2 Hz, 1H), 2.84 – 2.75 (m, 3H), 2.07 – 1.98 (m, 2H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 170.5, 139.4, 131.5, 127.0, 121.9, 120.3, 120.2, 51.6, 46.8, 41.3, 39.0, 24.7, 23.9, 21.3.

Spectral data matched those previously reported.[2]

Methyl 2-(6-methyl-5-oxo-2,3,5,6-tetrahydro-[1,4]oxazino[2,3,4-hi]indol-6-yl) Acetate (25)



Followed **general procedure** and purified using silica gel chromatography to gi ve the product (29.3 mg, 56% yield) as pale-yellow liquid.

R_f = 0.2 (EtOAc/petroleum ether, 1:3)

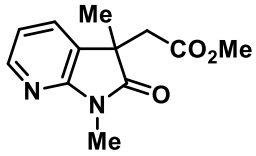
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 – 6.87 (m, 1H), 6.85 – 6.76 (m, 2H), 4.29 (t, J = 4.8 Hz, 2H), 3.89 (t, J = 4.8 Hz, 2H), 3.48 (s, 3H), 3.00 (d, J = 16.5 Hz, 1H), 2.85 (d, J = 16.5 Hz, 1H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 170.4, 141.4, 132.5, 128.4, 122.9, 115.7, 115.1, 65.0, 51.8, 47.8, 41.4, 39.4, 23.9.

IR (KBr, cm^{-1}): 3679, 2926, 2536, 1712, 1637, 1601, 1493, 1449, 1350, 1244, 1198, 1041, 909, 784.

HRMS (ESI) calcd. for $C_{14}H_{15}NO_4Na$ $[M+Na]^+$ 284.0893; found 284.0892.

Methyl 2-(1,3-dimethyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (26)



Followed **general procedure** and purified using silica gel chromatography to give the product (35.1 mg, 75% yield) as light yellow liquid.

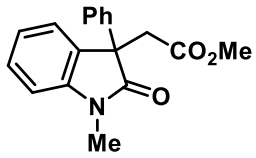
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.44 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.91 (dd, *J* = 7.2, 5.3 Hz, 1H), 3.48 (s, 3H), 3.32 (s, 3H), 2.98 (d, *J* = 16.6 Hz, 1H), 2.85 (d, *J* = 16.6 Hz, 1H), 1.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.6, 170.2, 157.2, 147.1, 130.0, 127.5, 118.1, 51.8, 45.2, 41.0, 25.6, 23.6.

Spectral data matched those previously reported.[3]

Methyl 2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (27)



Followed **general procedure** and purified using silica gel chromatography to give the product (38.4 mg, 65% yield) as pale-yellow oil.

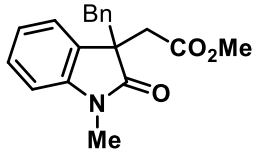
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 7H), 7.08 (t, *J* = 7.6, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.53 (d, *J* = 16.4 Hz, 1H), 3.42 (s, 3H), 3.27 -3.22 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 170.2, 144.7, 139.2, 131.2, 128.81, 127.8, 126.7, 124.6, 122.6, 108.5, 53.3, 51.8, 41.9, 26.8.

Spectral data matched those previously reported.[1]

Methyl 2-(3-benzyl-1-methyl-2-oxoindolin-3-yl)acetate (28)



Followed **general procedure** and purified using silica gel chromatography to give the product (30.9 mg, 50% yield) as pale-yellow oil.

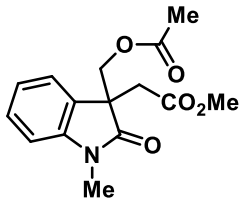
R_f = 0.3 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (td, *J* = 7.7, 1.4 Hz, 1H), 7.12 – 6.97 (m, 5H), 6.83 – 6.77 (m, 2H), 6.60 (dt, *J* = 7.8, 0.8 Hz, 1H), 3.44 (s, 3H), 3.16 (d, *J* = 16.3 Hz, 1H), 3.04 (s, 2H), 2.99 (s, 3H), 2.96 (d, *J* = 16.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 170.4, 144.2, 134.9, 130.3, 130.2, 128.4, 127.6, 126.9, 123.3, 122.0, 108.0, 51.8, 51.3, 44.0, 40.3, 26.1.

Spectral data matched those previously reported.[3]

Methyl 2-(3-(acetoxymethyl)-1-methyl-2-oxoindolin-3-yl)acetate (29)



Followed **general procedure** and purified using silica gel chromatography to give the product (30.9 mg, 53% yield) as pale-yellow oil.

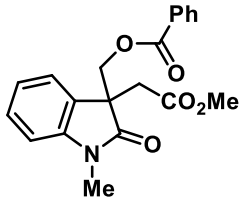
R_f = 0.2 (EtOAc/petroleum ether, 1:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.8, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.11 (d, *J* = 10.8 Hz, 1H), 3.47 (s, 3H), 3.26 (s, 3H), 3.12 – 2.91 (m, 2H), 1.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 170.3, 169.8, 144.5, 129.1, 128.7, 123.4, 122.6, 108.4, 67.0, 51.9, 49.4, 37.5, 26.6, 20.7.

Spectral data matched those previously reported.[6]

(3-(2-methoxy-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)methyl benzoate (30)



Followed **general procedure** and purified using silica gel chromatography to give the product (41.7 mg, 59% yield) as pale-yellow oil.

R_f = 0.2 (EtOAc/petroleum ether, 1:3)

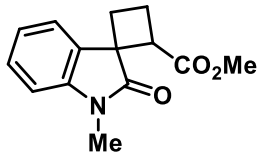
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.74 (m, 2H), 7.57 – 7.49 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.03 (td, *J* = 7.6, 1.0 Hz, 1H), 6.89 (d, *J* = 6 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 3.49 (s, 3H), 3.30 (s, 3H), 3.21 – 3.03 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 169.9, 165.8, 144.5, 133.3, 129.6, 129.1, 128.8, 128.6, 123.4, 122.7, 108.4, 67.7, 52.0, 49.7, 37.5, 26.7.

IR (KBr, cm^{-1}): 3089, 2956, 1723, 1612, 1499, 1466, 1353, 1268, 1204, 1116, 1002, 898, 735, 712.

HRMS (ESI) calcd. for $C_{20}H_{19}NO_5Na$ $[M+Na]^+$ 376.1155; found 376.1150.

Methyl 1'-methyl-2'-oxospiro[cyclobutane-1,3'-indoline]-2-carboxylate (31)



Followed **general procedure** and purified using silica gel chromatography to give the product (26.5 mg, 54% yield) as pale-yellow oil.

R_f = 0.3 (EtOAc/petroleum ether, 1:3)

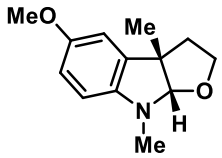
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.32 – 7.24 (m, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 3.59 (s, 3H), 3.65 – 3.52 (m, 1H), 3.20 (s, 3H), 2.98 – 2.79 (m, 1H), 2.56 – 2.17 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.7, 172.1, 143.8, 131.9, 128.6, 122.6, 122.5, 107.9, 51.8, 51.4, 46.3, 28.5, 26.2, 20.3.

IR (KBr, cm^{-1}): 2925, 2850, 1734, 1707, 1610, 1466, 1374, 1347, 1210, 1000.

HRMS (ESI) calcd. for $C_{14}H_{15}NO_3Na$ $[M+Na]^+$ 268.0944; found 268.0945.

5-methoxy-3a,8-dimethyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (32)



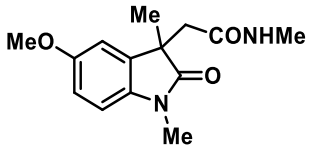
R_f = 0.7 (EtOAc/petroleum ether, 1:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 – 6.60 (m, 2H), 6.29 (d, *J* = 8.2 Hz, 1H), 5.03 (s, 1H), 3.97 (d, *J* = 1.9 Hz, 1H), 3.75 (s, 3H), 3.54 – 3.40 (m, 1H), 2.88 (s, 3H), 2.18 – 1.96 (m, 2H), 1.45 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 145.1, 136.2, 112.3, 110.6, 105.7, 105.4, 67.5, 56.2, 52.6, 41.6, 31.8, 24.6.

Spectral data matched those previously reported.[7]

2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-N-methylacetamide (33)



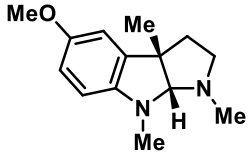
R_f = 0.4 (EtOAc/petroleum ether, 1:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (d, *J* = 2.3 Hz, 1H), 6.84 – 6.69 (m, 2H), 6.49 (s, 1H), 3.78 (s, 3H), 3.21 (s, 3H), 2.79 – 2.67 (m, 4H), 2.63 (d, *J* = 15.0 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 169.7, 156.3, 136.2, 135.0, 112.4, 110.2, 108.6, 55.8, 46.4, 43.7, 26.5, 26.2, 23.4.

Spectral data matched those previously reported.[7]

6-methoxy-1,3a,8-trimethyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole (34)



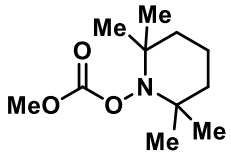
R_f = 0.3 (petroleum ether/EtOAc 1:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 – 6.59 (m, 2H), 6.35 (dd, *J* = 7.9, 1.0 Hz, 1H), 4.04 (s, 1H), 3.75 (s, 3H), 2.89 (s, 3H), 2.77 – 2.69 (m, 1H), 2.64 (dt, *J* = 9.1, 7.4 Hz, 1H), 2.53 (s, 3H), 1.98 – 1.91 (m, 2H), 1.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 146.7, 138.4, 112.3, 110.0, 107.6, 98.5, 56.2, 53.3, 52.9, 41.0, 38.3, 38.1, 27.6.

Spectral data matched those previously reported.[7]

Methyl (2,2,6,6-tetramethylpiperidin-1-yl) carbonate (35)



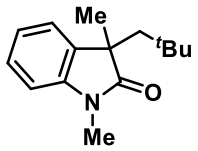
R_f = 0.8 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H), 1.80 – 1.56 (m, 5H), 1.48-1.40 (m, 1H), 1.24 (s, 6H), 1.20 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 55.0, 49.9, 33.8, 26.1, 15.0, 11.5.

Spectral data for this compound were consistent with those in the literature.[8]

Methyl (2,2,6,6-tetramethylpiperidin-1-yl) carbonate (S1)



Followed **general procedure** and purified using silica gel chromatography to gi ve the product (11.6 mg, 25% yield) as pale-yellow oil.

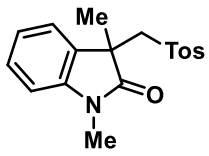
R_f = 0.4 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.8 Hz 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.6 Hz 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 2.15 (d, J = 14.4 Hz, 1H), 1.85 (d, J = 14.4 Hz, 1H), 1.29 (s, 3H), 0.61 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 143.0, 134.4, 127.7, 124.0, 122.1, 108.2, 51.0, 47.6, 31.9, 31.0, 28.4, 26.4.

Spectral data matched those previously reported.[9]

Methyl (2,2,6,6-tetramethylpiperidin-1-yl) carbonate (S2)



Followed **general procedure** and purified using silica gel chromatography to gi ve the product (30.0 mg, 46% yield) as colorless oil.

R_f = 0.1 (EtOAc/petroleum ether, 1:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.30 - 7.26 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.85 (d, *J* = 14.5 Hz, 1H), 3.65 (d, *J* = 14.5 Hz, 1H), 3.15 (s, 3H), 2.40 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 144.5, 143.4, 137.2, 129.8, 129.6, 128.7, 128.0, 124.3, 122.6, 108.5, 77.2, 62.0, 45.8, 26.6, 25.6, 21.7.

Spectral data matched those previously reported.[10]

7. References

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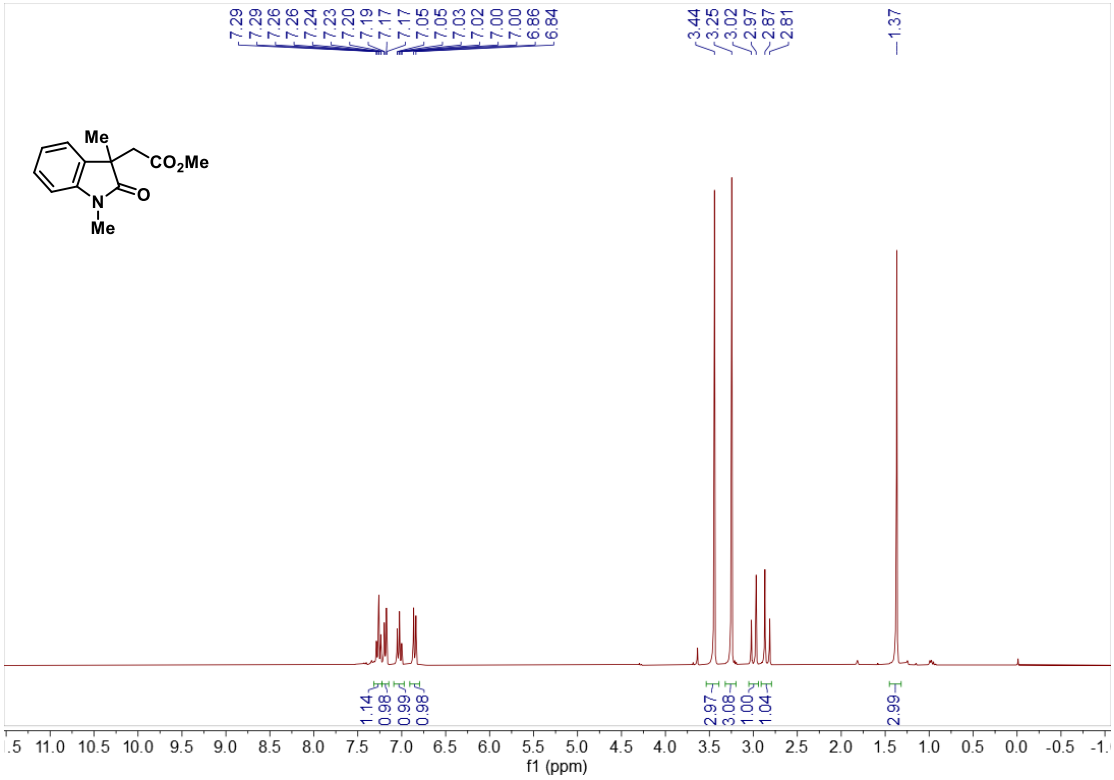
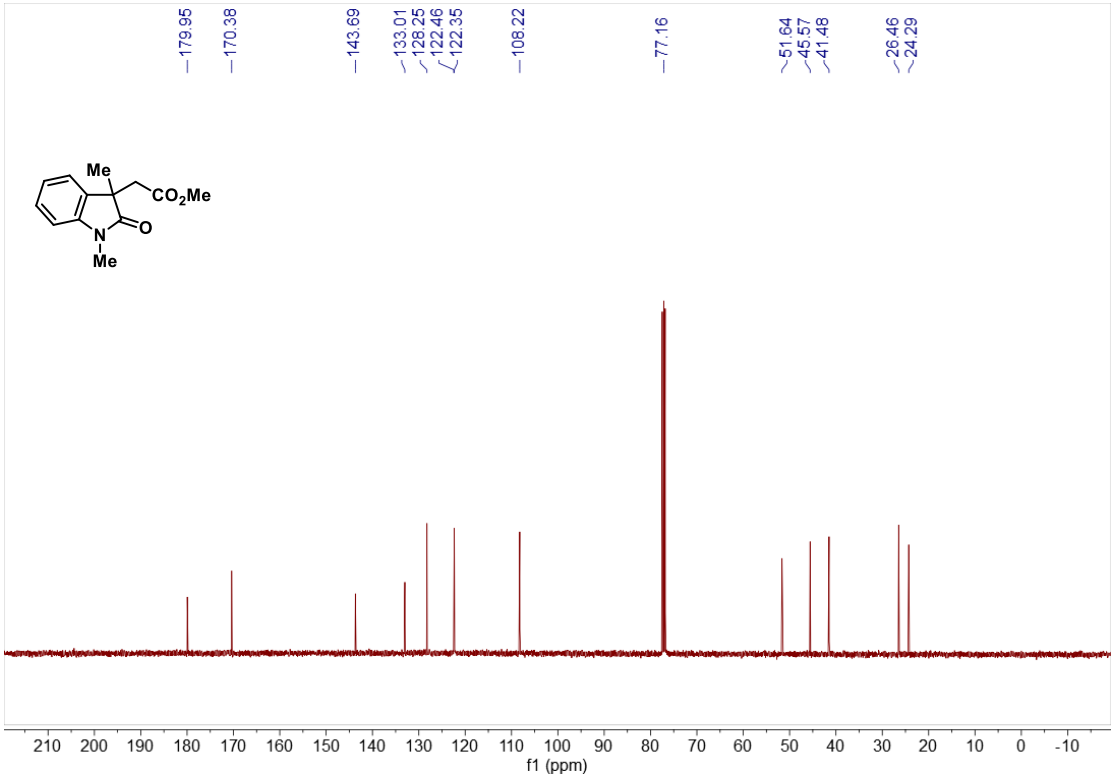
8. NMR Spectra

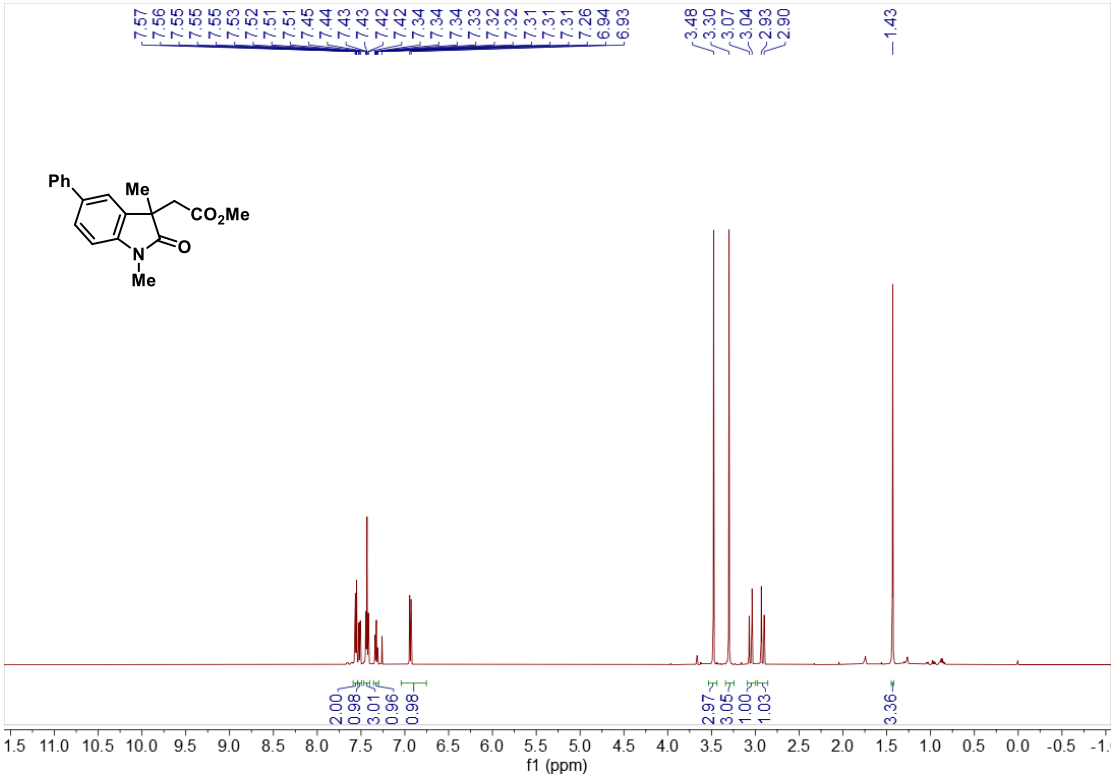
^{1}H NMR of compound 3 ($CDCl_3$, 300 MHz)



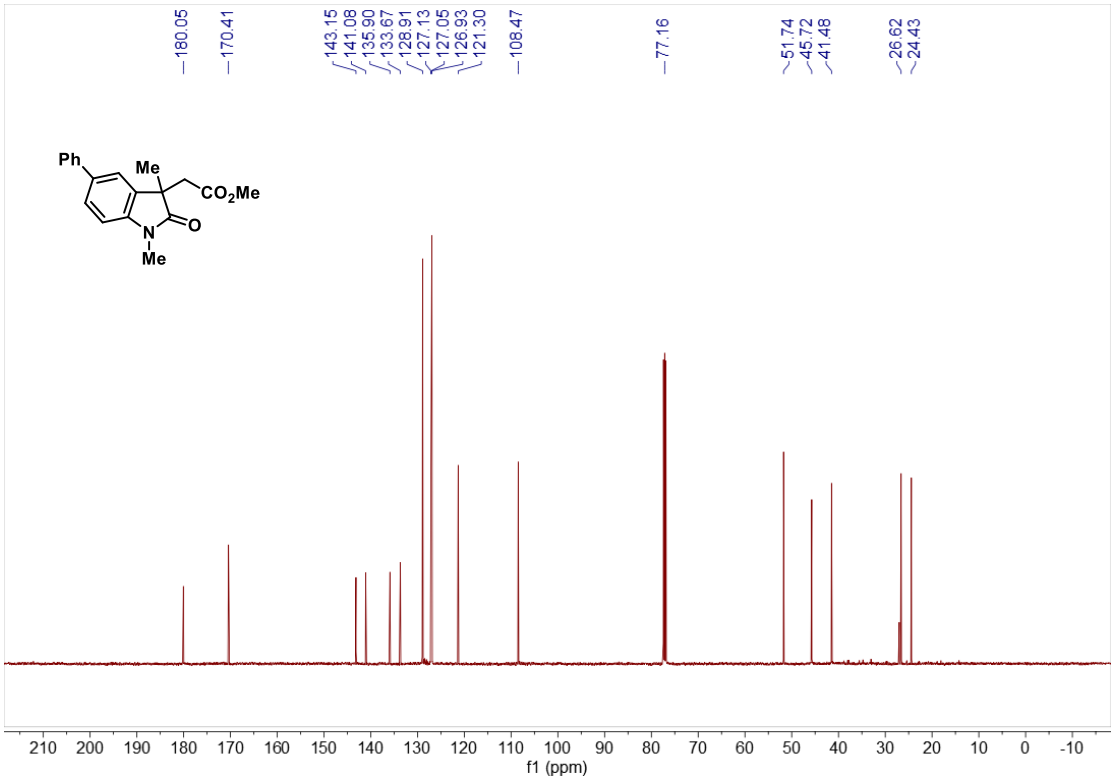
^{13}C NMR of compound 3 ($CDCl_3$, 100 MHz)



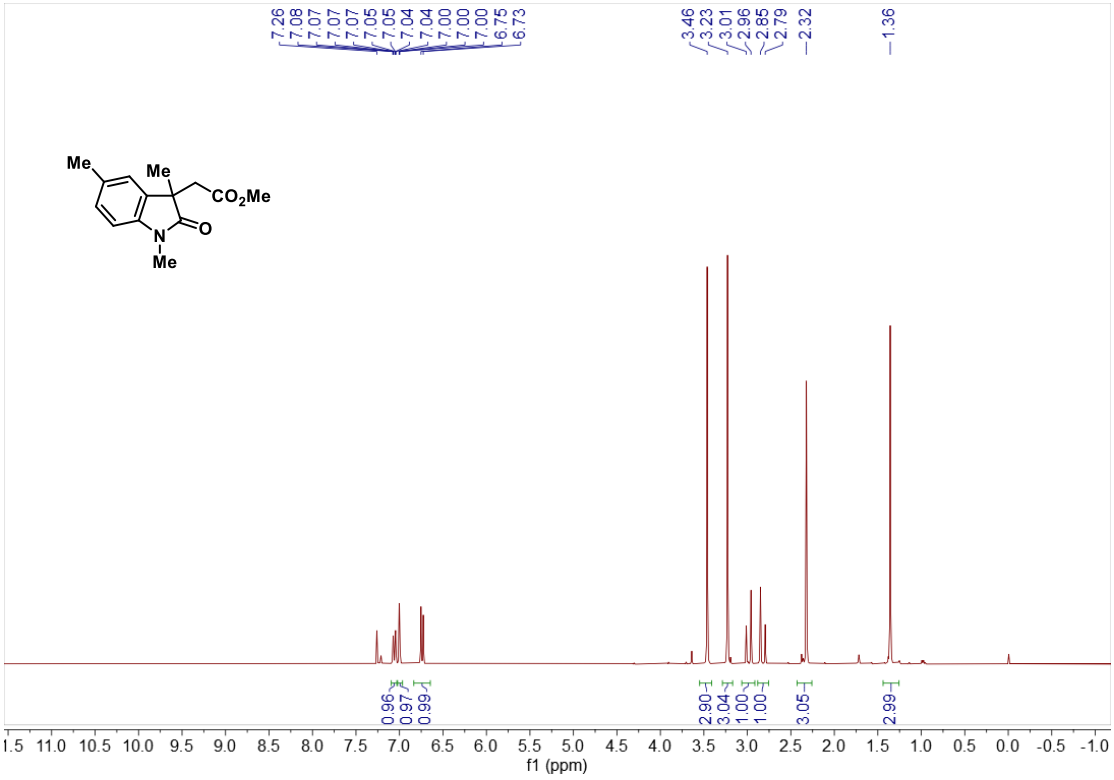
^{1}H NMR of compound 4 ($CDCl_3$, 500 MHz)



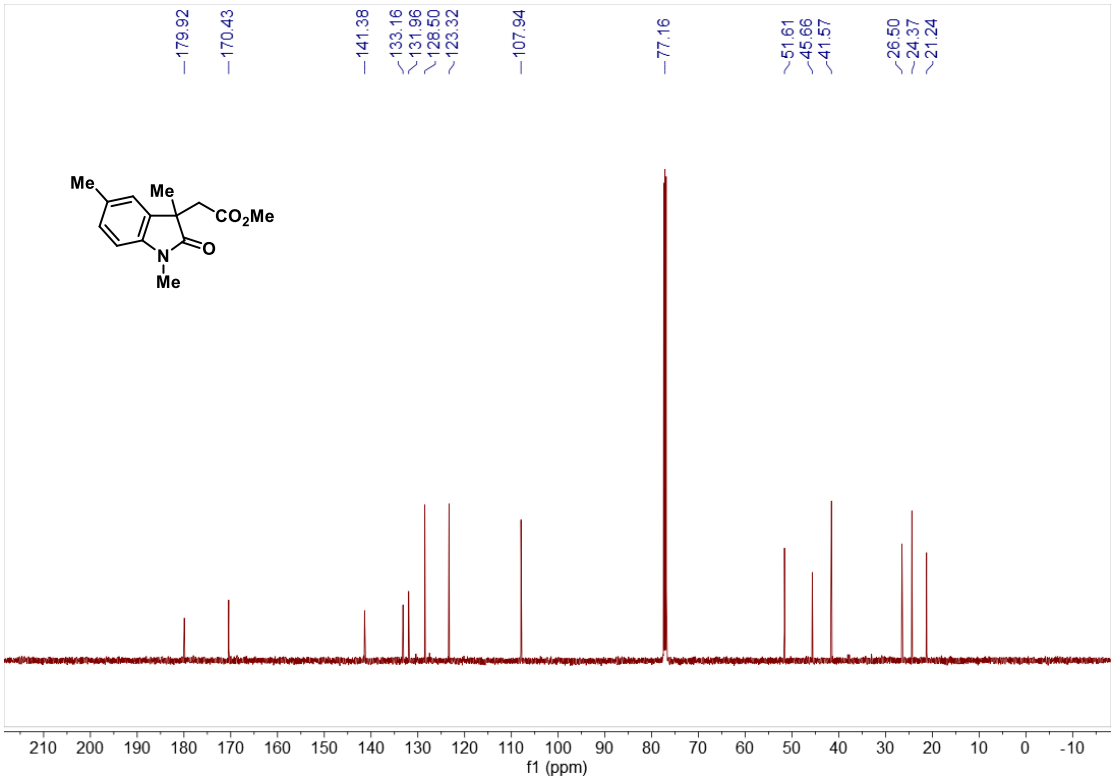
^{13}C NMR of compound 4 ($CDCl_3$, 125 MHz)



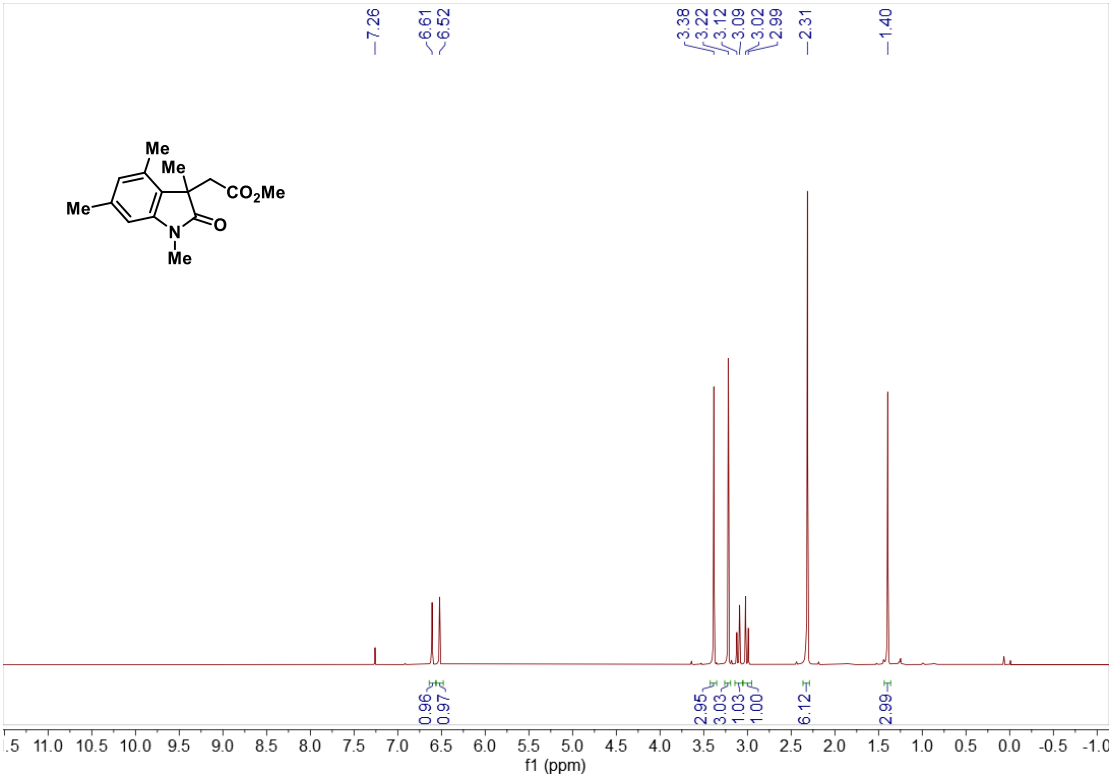
^{1}H NMR of compound 5 ($CDCl_3$, 300 MHz)



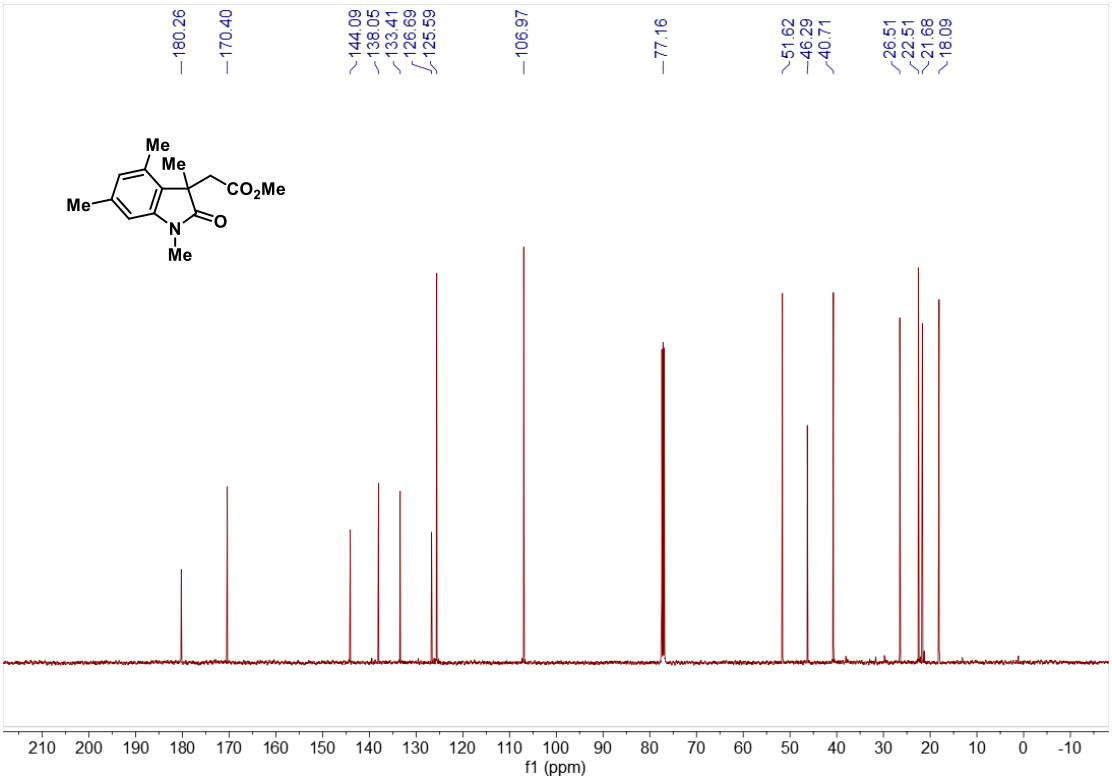
^{13}C NMR of compound 5 ($CDCl_3$, 125 MHz)



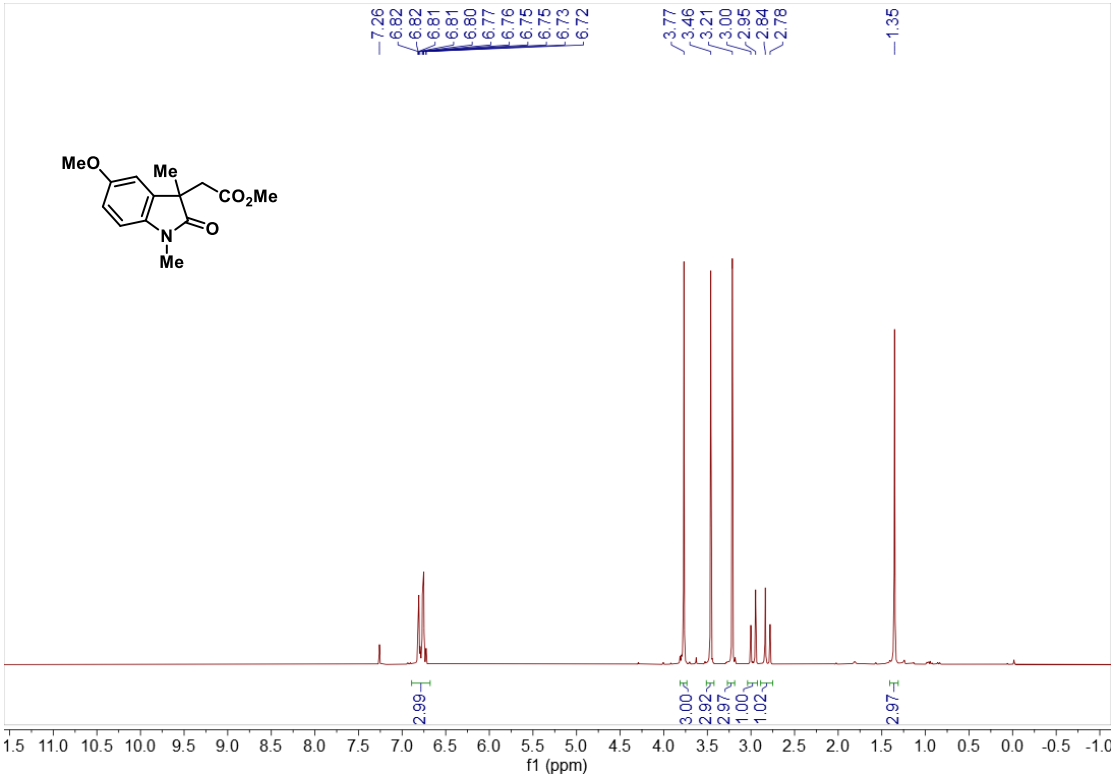
^{1}H NMR of compound 6 ($CDCl_3$, 500 MHz)



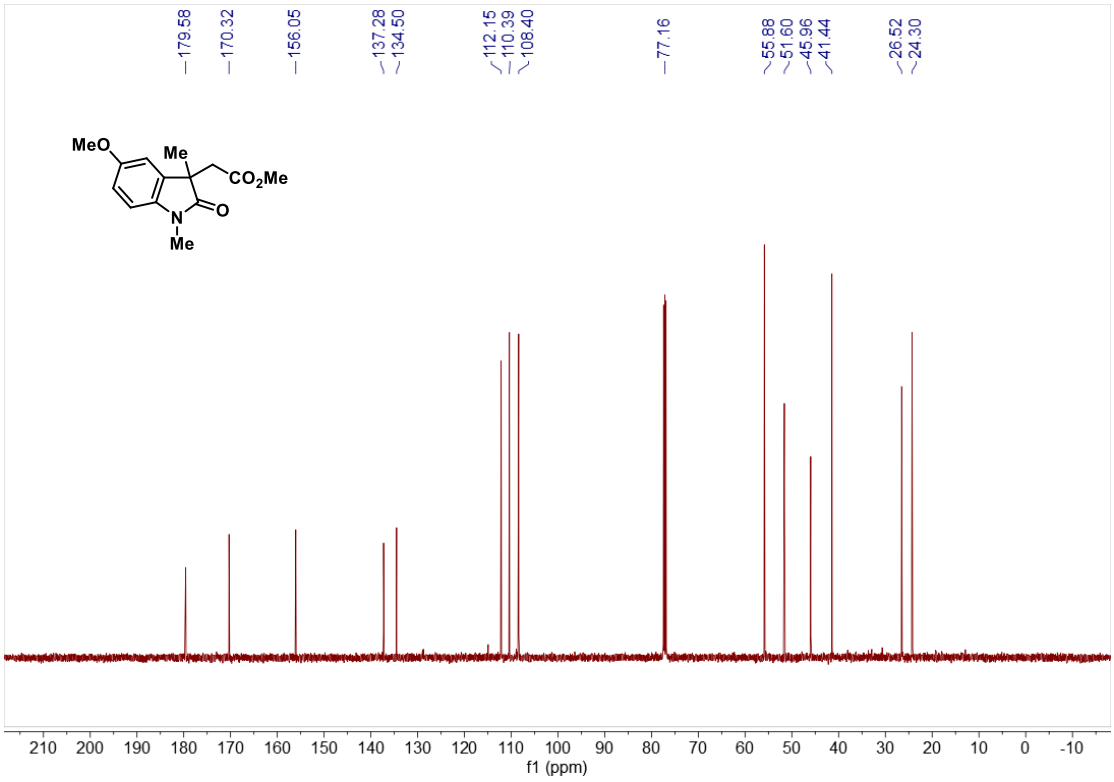
^{13}C NMR of compound 6 ($CDCl_3$, 125 MHz)



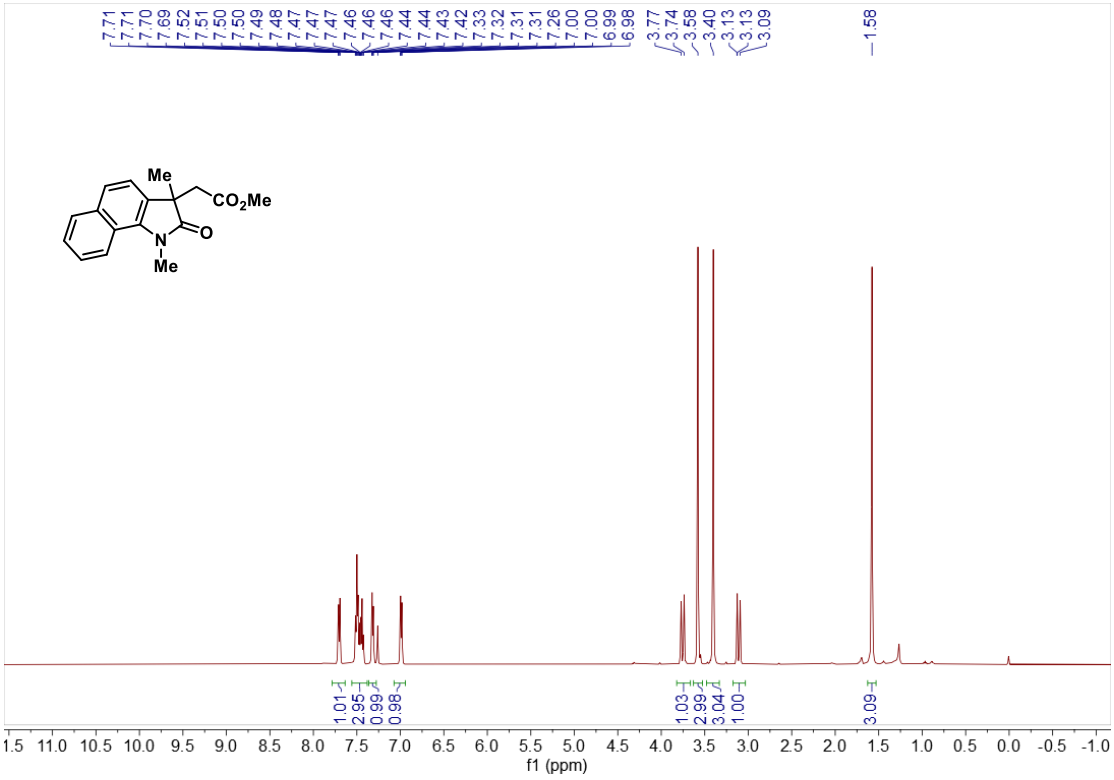
^{1}H NMR of compound 7 ($CDCl_3$, 300 MHz)



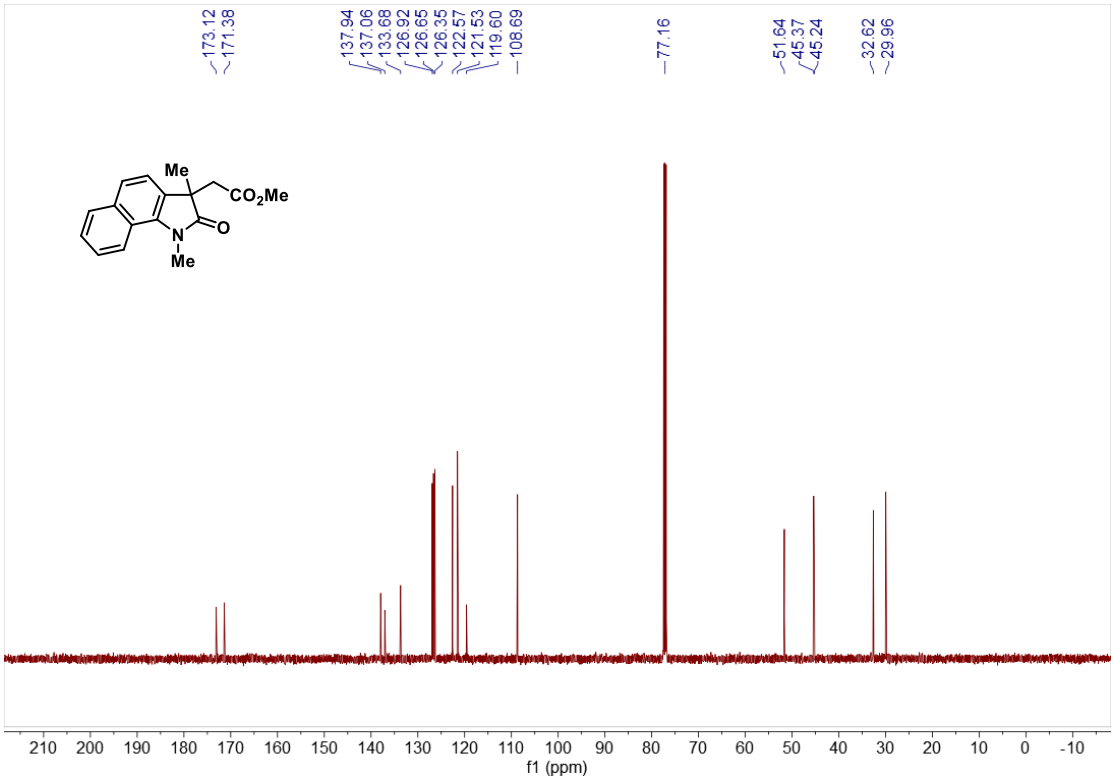
^{13}C NMR of compound 7 ($CDCl_3$, 125 MHz)



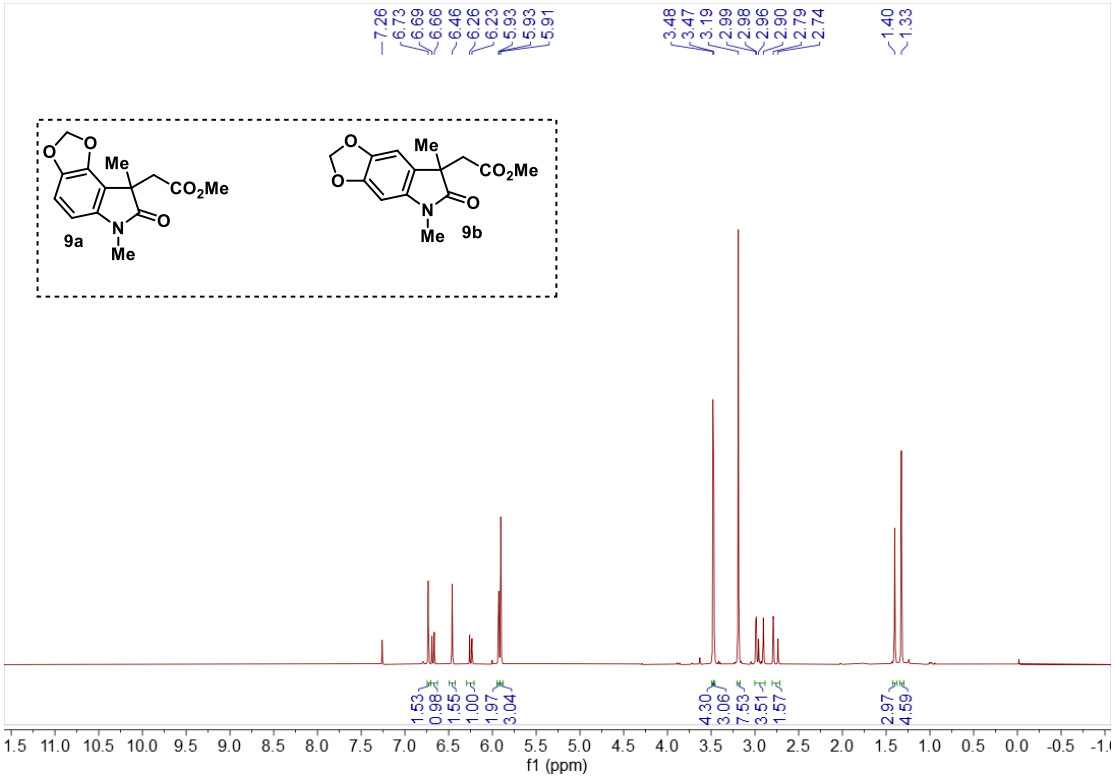
^{1}H NMR of compound 8 ($CDCl_3$, 500 MHz)



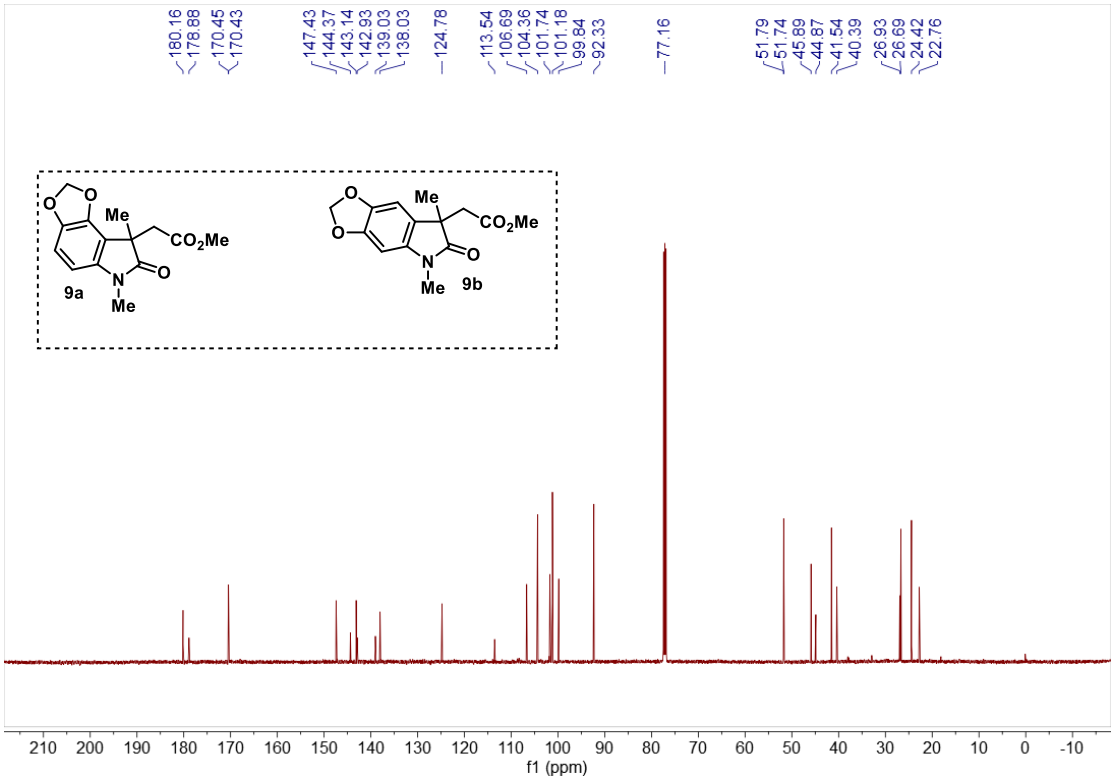
^{13}C NMR of compound 8 ($CDCl_3$, 125 MHz)



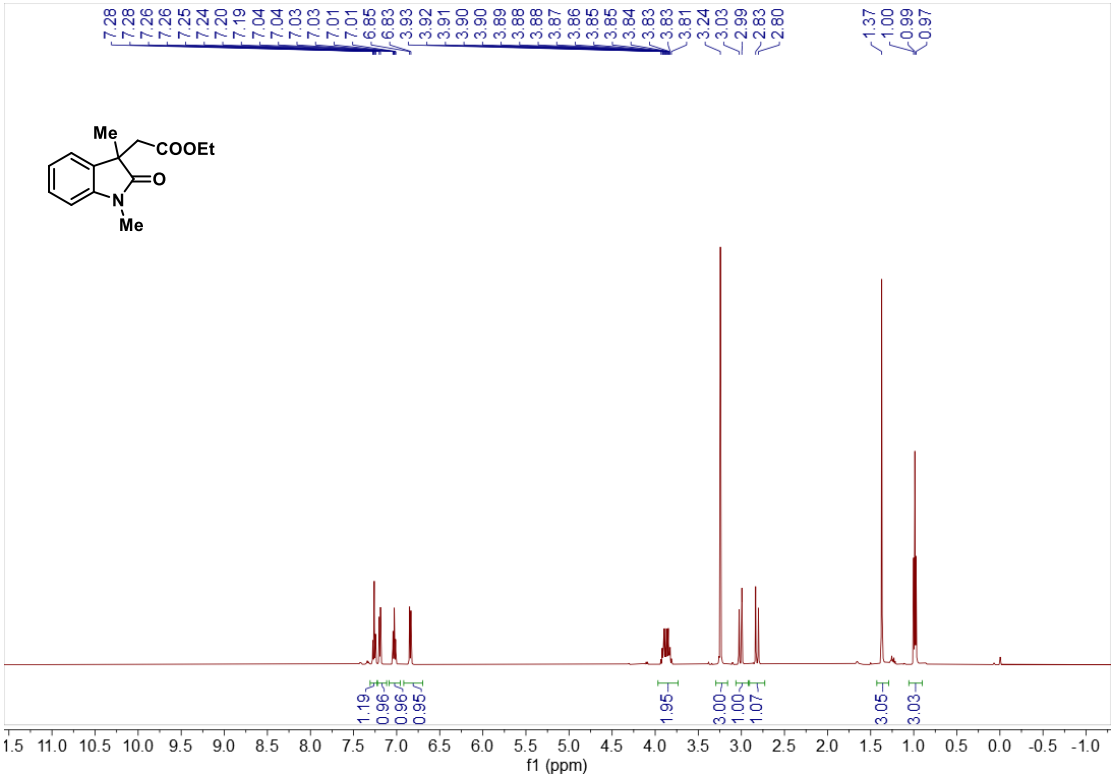
^{1}H NMR of compound 9a and 9b ($CDCl_3$, 300 MHz)



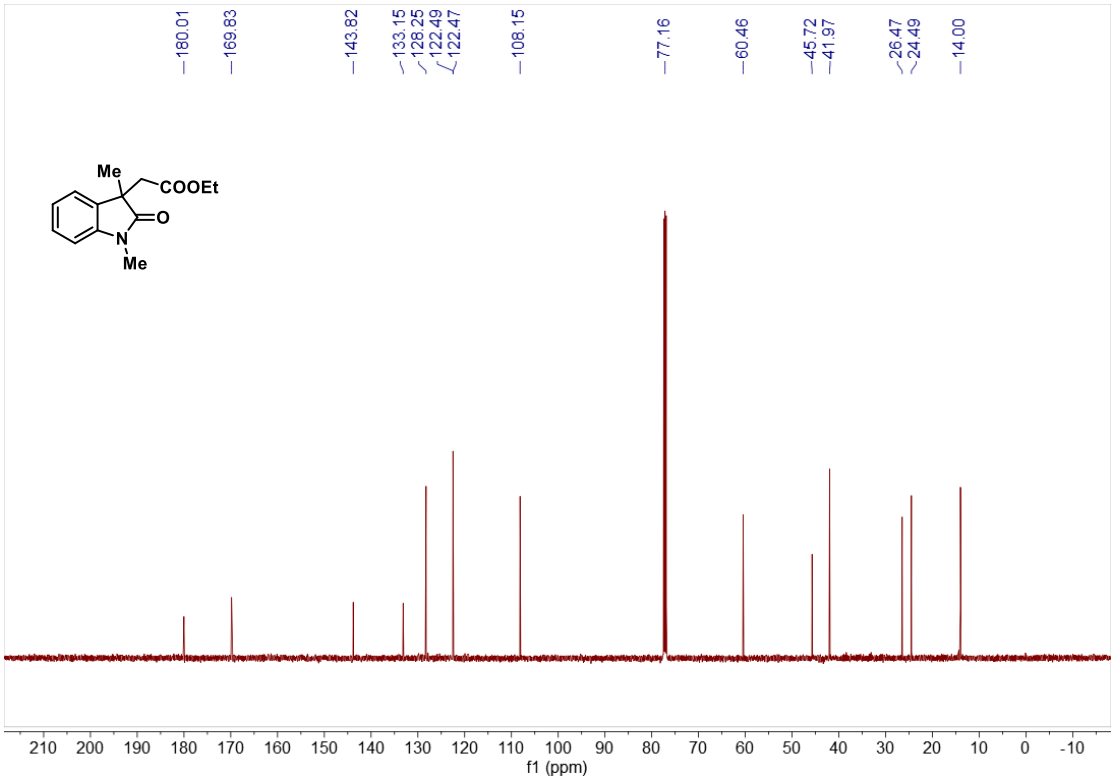
^{13}C NMR of compound 9a and 9b ($CDCl_3$, 125 MHz)



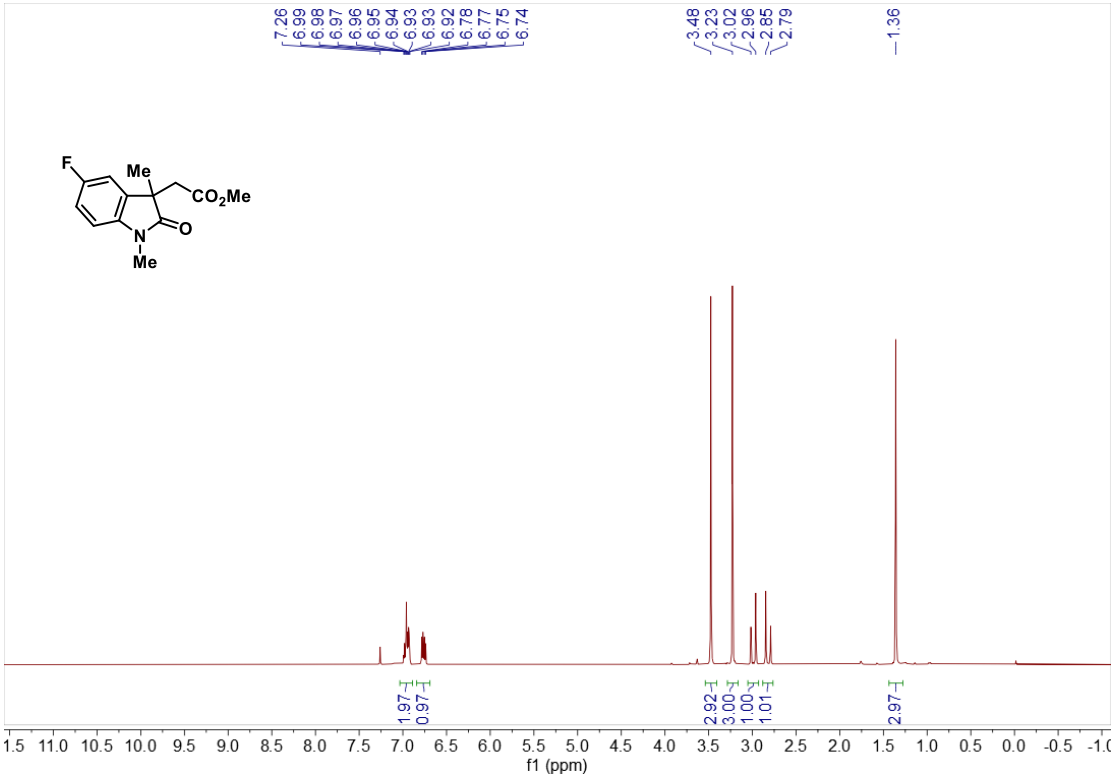
^{1}H NMR of compound 10 ($CDCl_3$, 500 MHz)



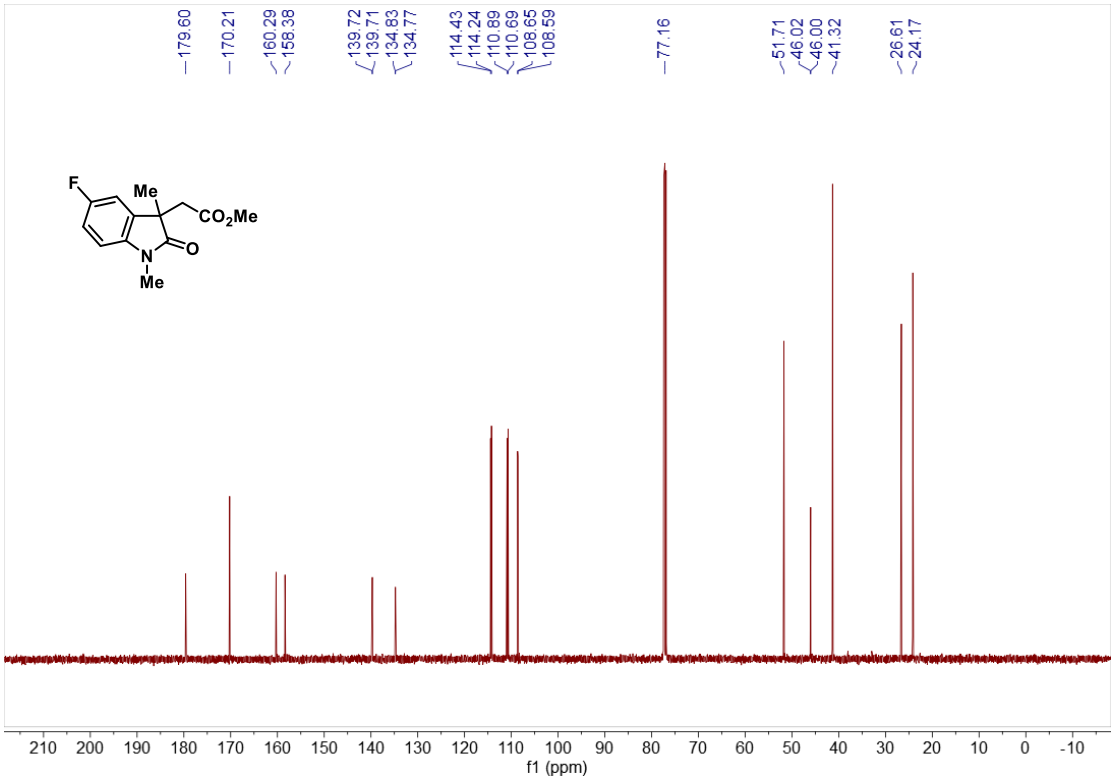
^{13}C NMR of compound 10 ($CDCl_3$, 125 MHz)



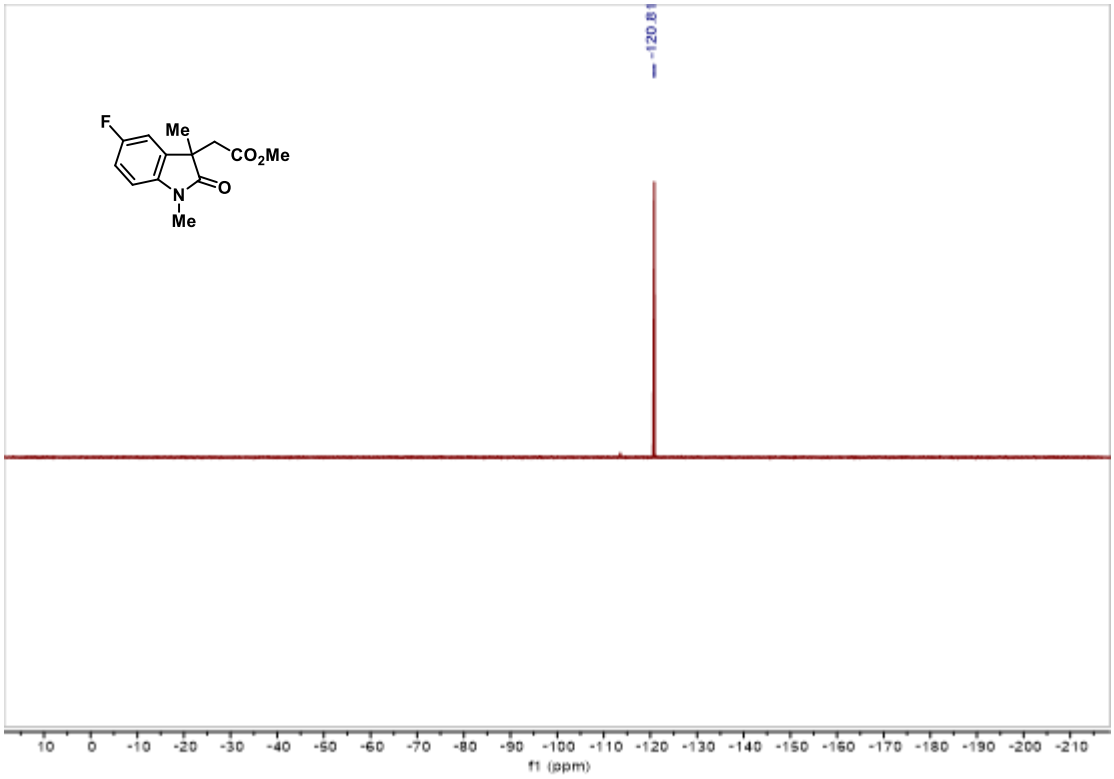
^{1}H NMR of compound 11 ($CDCl_3$, 300 MHz)



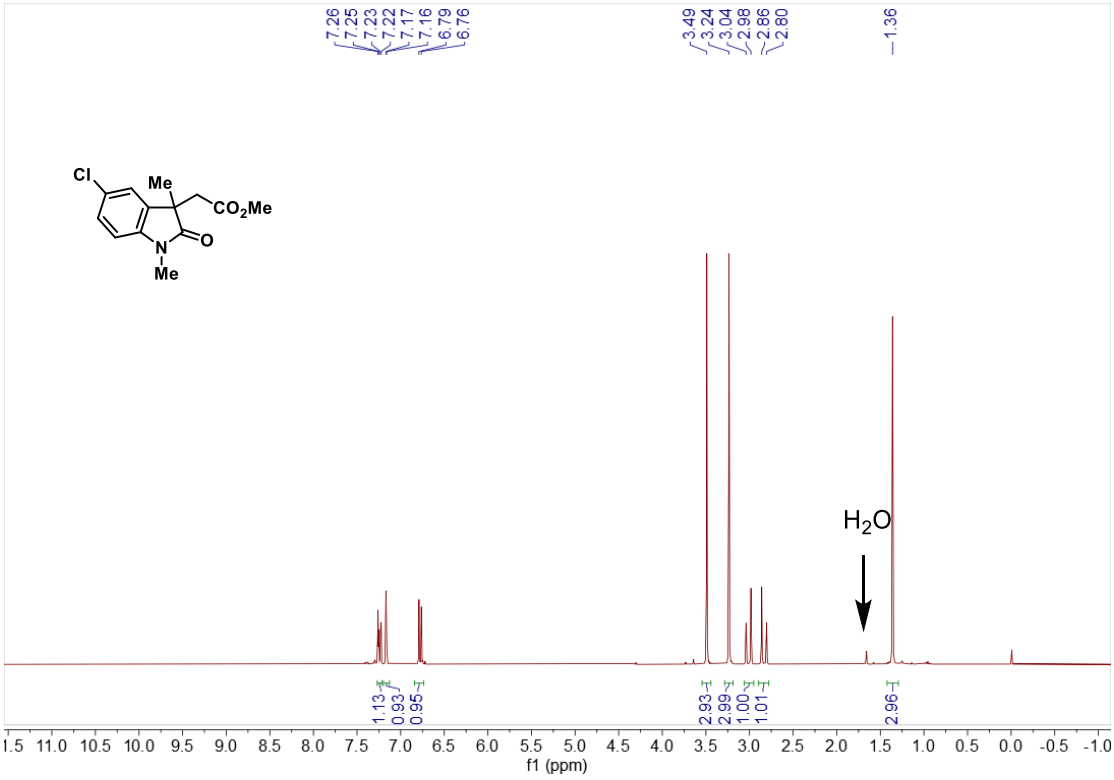
^{13}C NMR of compound 11 ($CDCl_3$, 125 MHz)



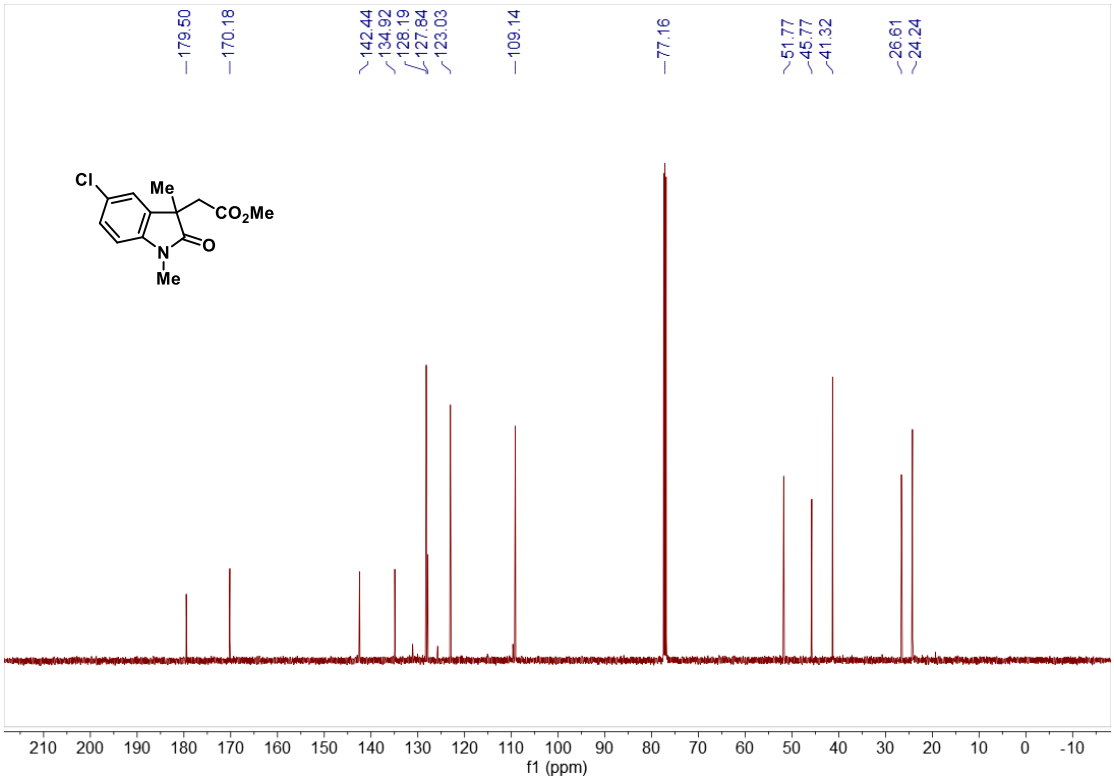
^{19}F NMR of compound 11 (377 MHz, Chloroform-*d*)



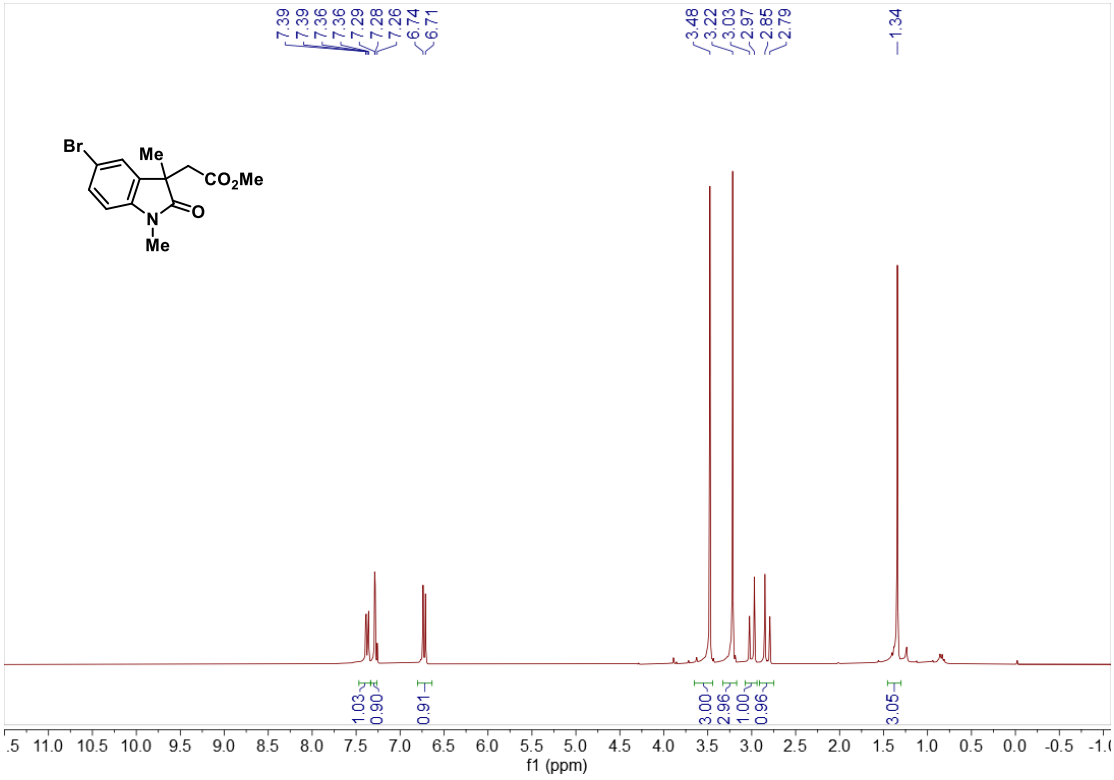
^{1}H NMR of compound 12 ($CDCl_3$, 300 MHz)



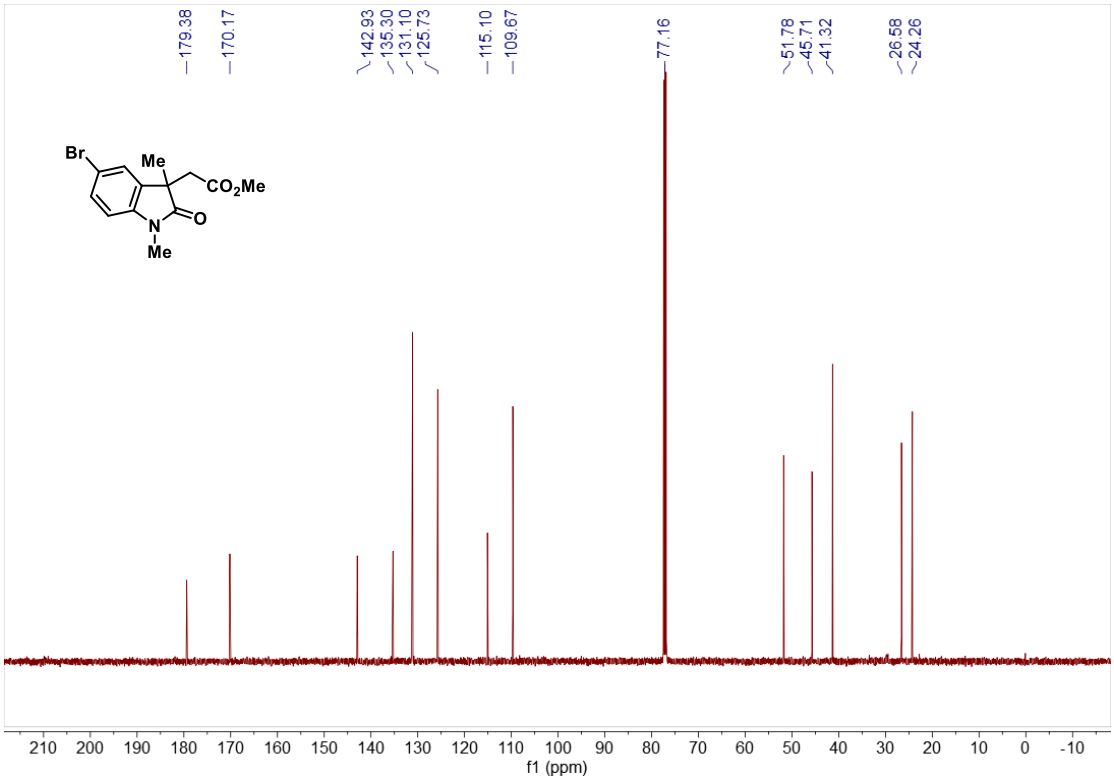
^{13}C NMR of compound 12 ($CDCl_3$, 125 MHz)



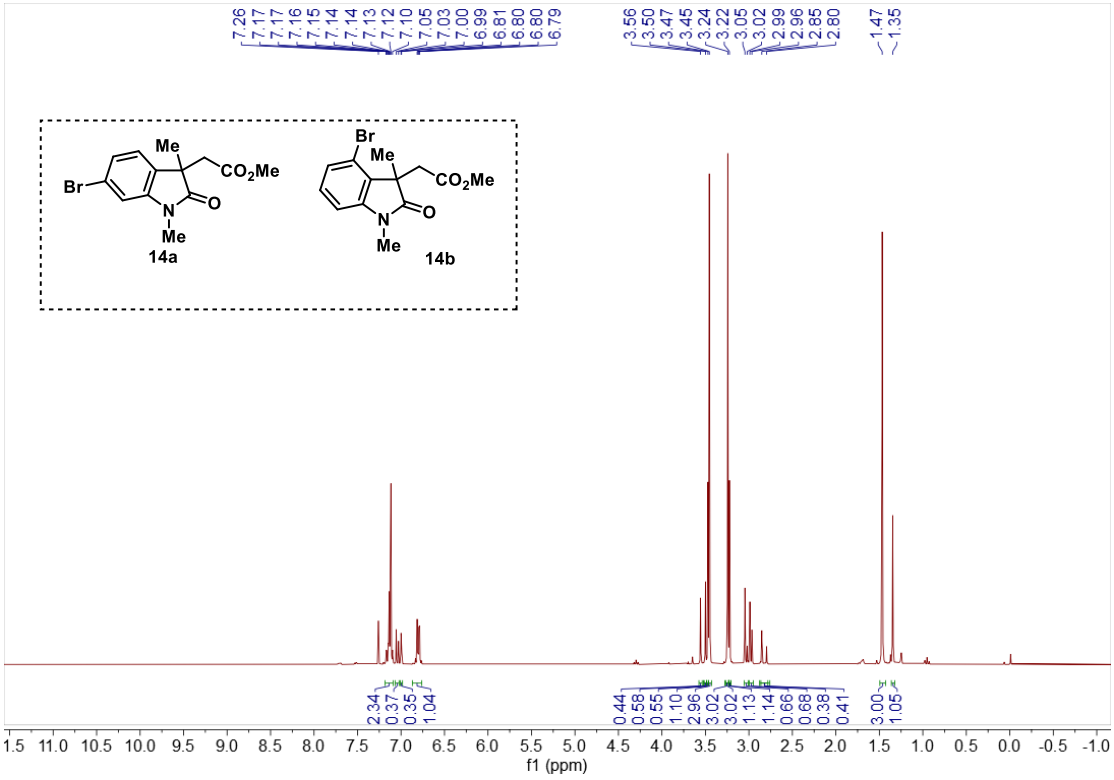
^{1}H NMR of compound 13 ($CDCl_3$, 300 MHz)



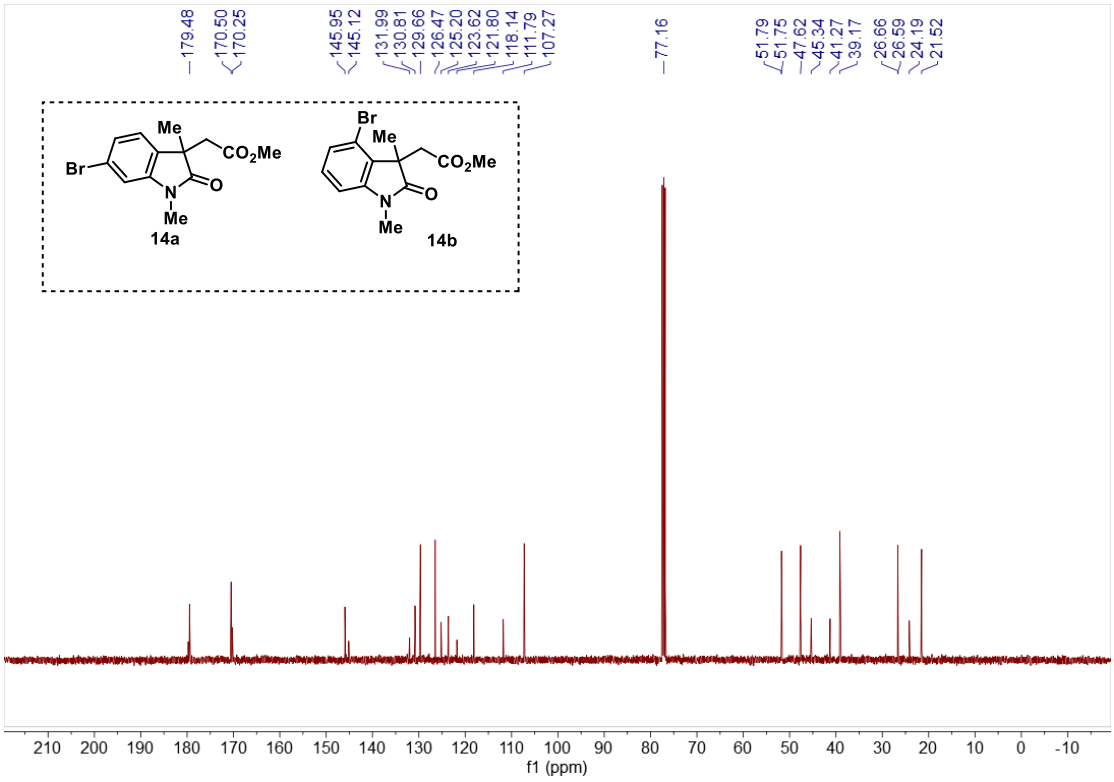
^{13}C NMR of compound 13 ($CDCl_3$, 125 MHz)



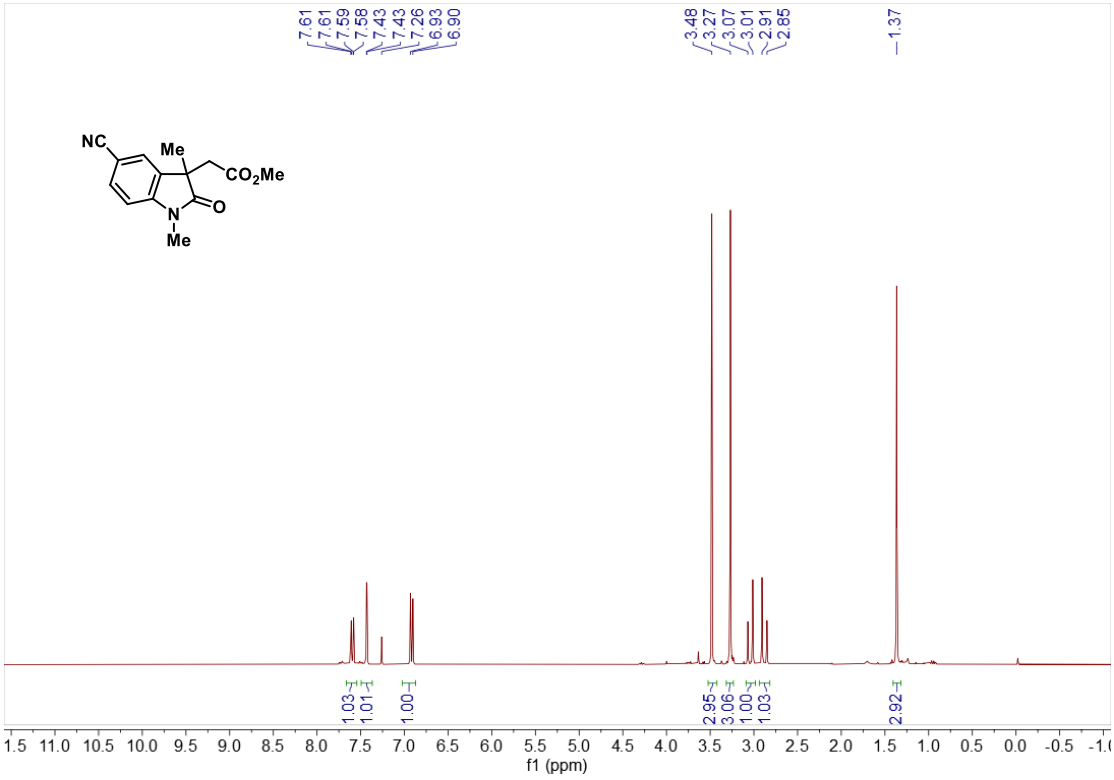
^{1}H NMR of compound 14a and 14b ($CDCl_3$, 300 MHz)



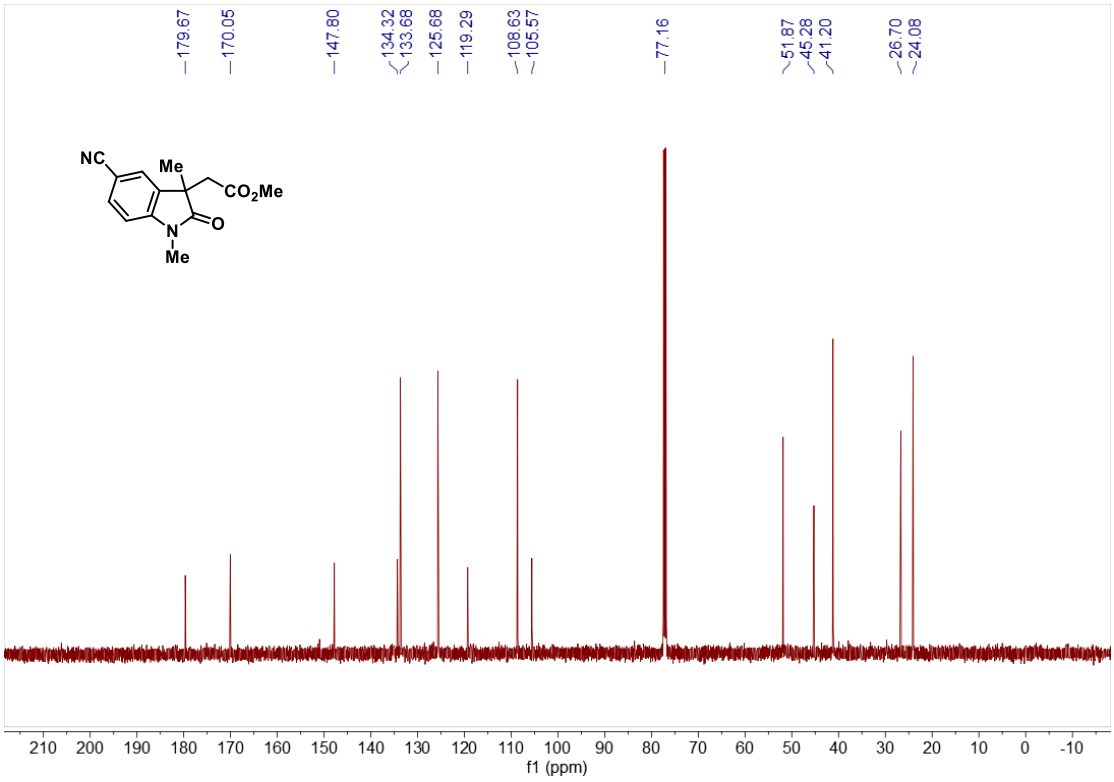
^{13}C NMR of compound 14a and 14b ($CDCl_3$, 100 MHz)



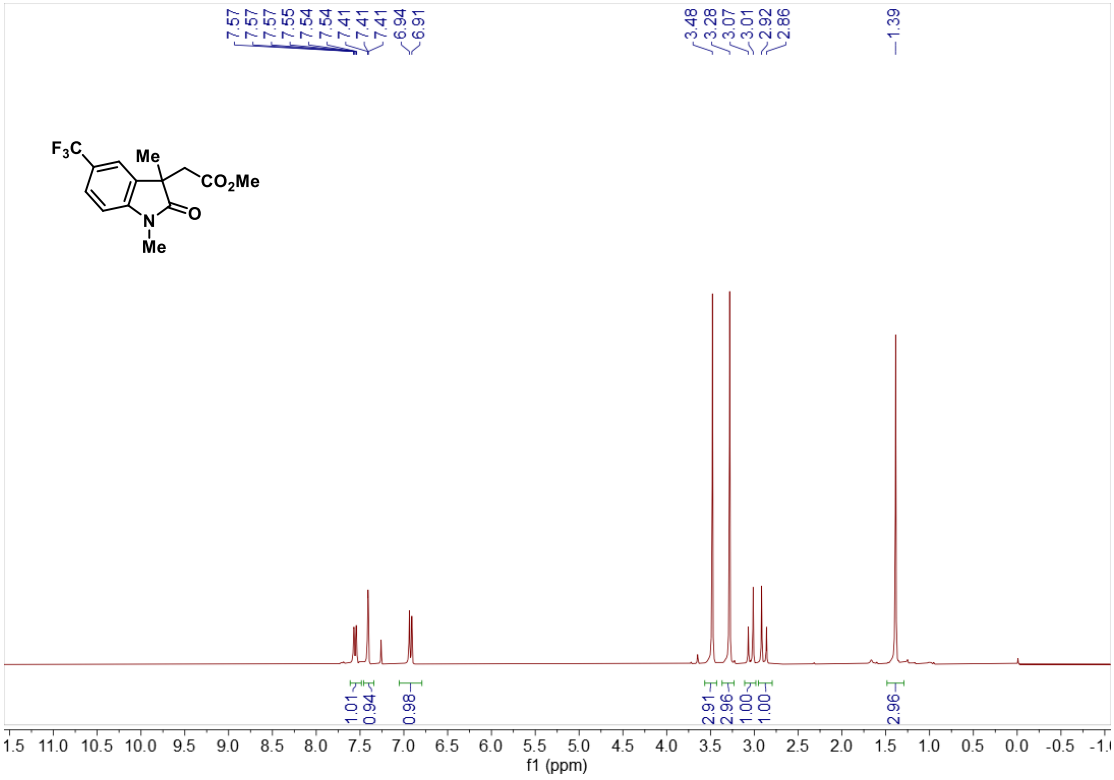
^{1}H NMR of compound 15 ($CDCl_3$, 300 MHz)



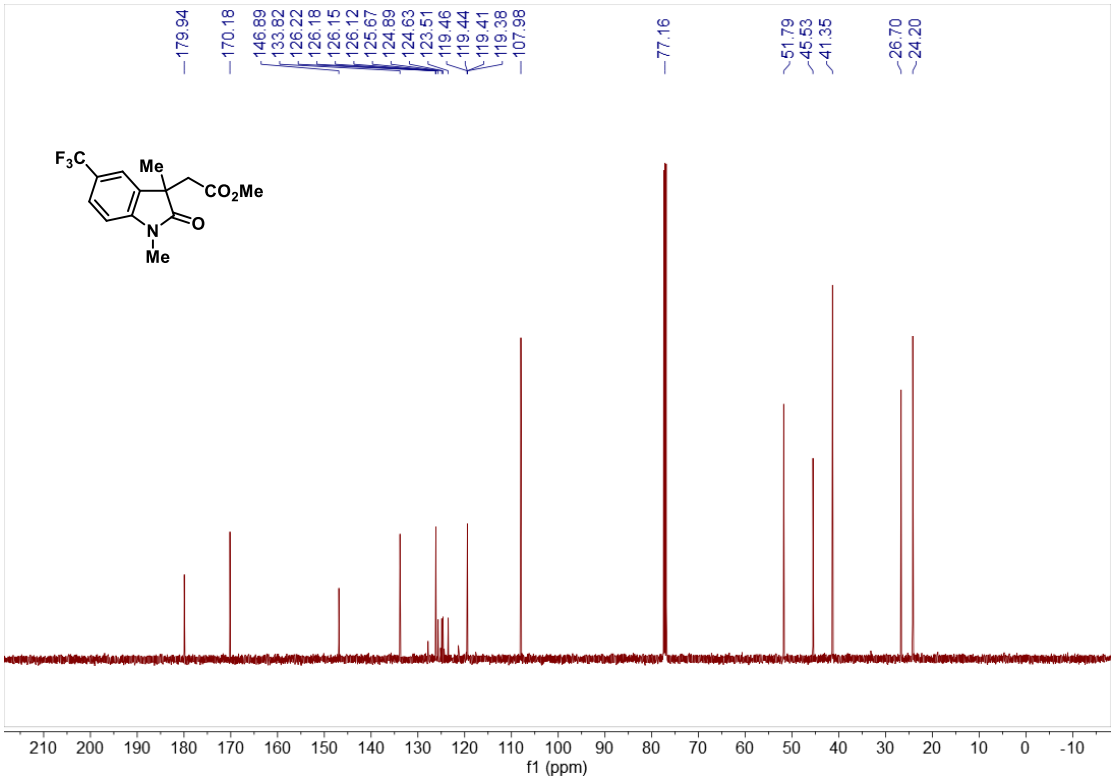
^{13}C NMR of compound 15 ($CDCl_3$, 125 MHz)



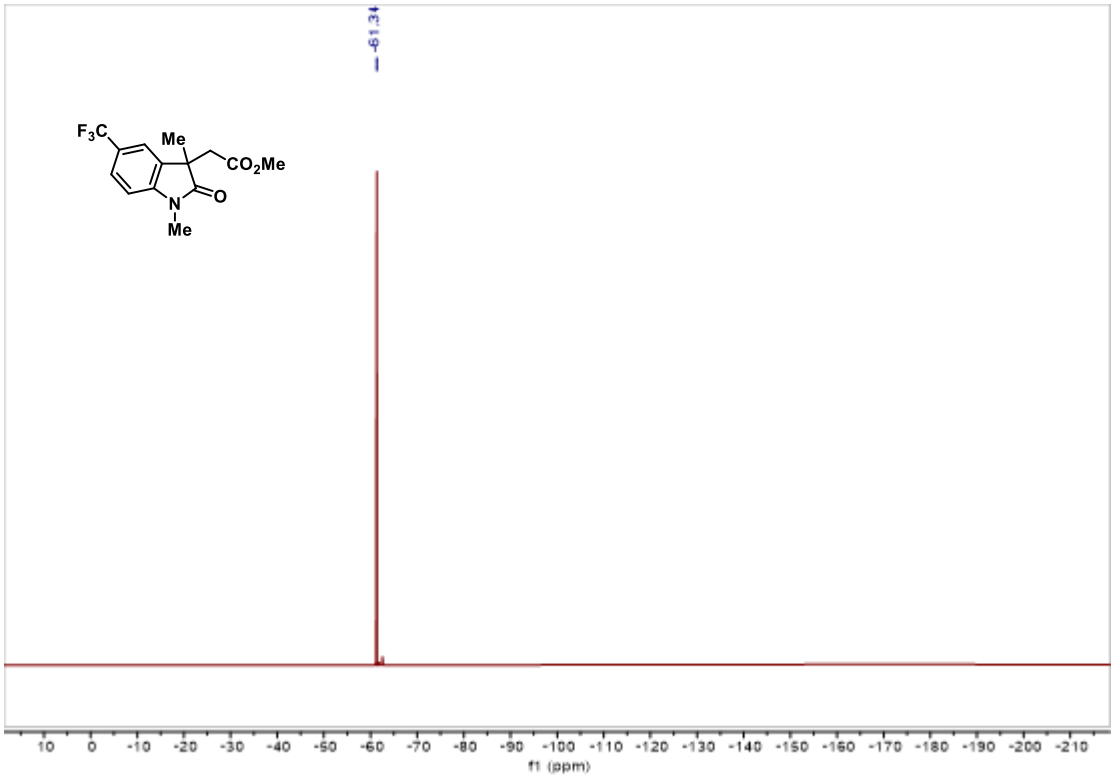
^{1}H NMR of compound 16 ($CDCl_3$, 300 MHz)



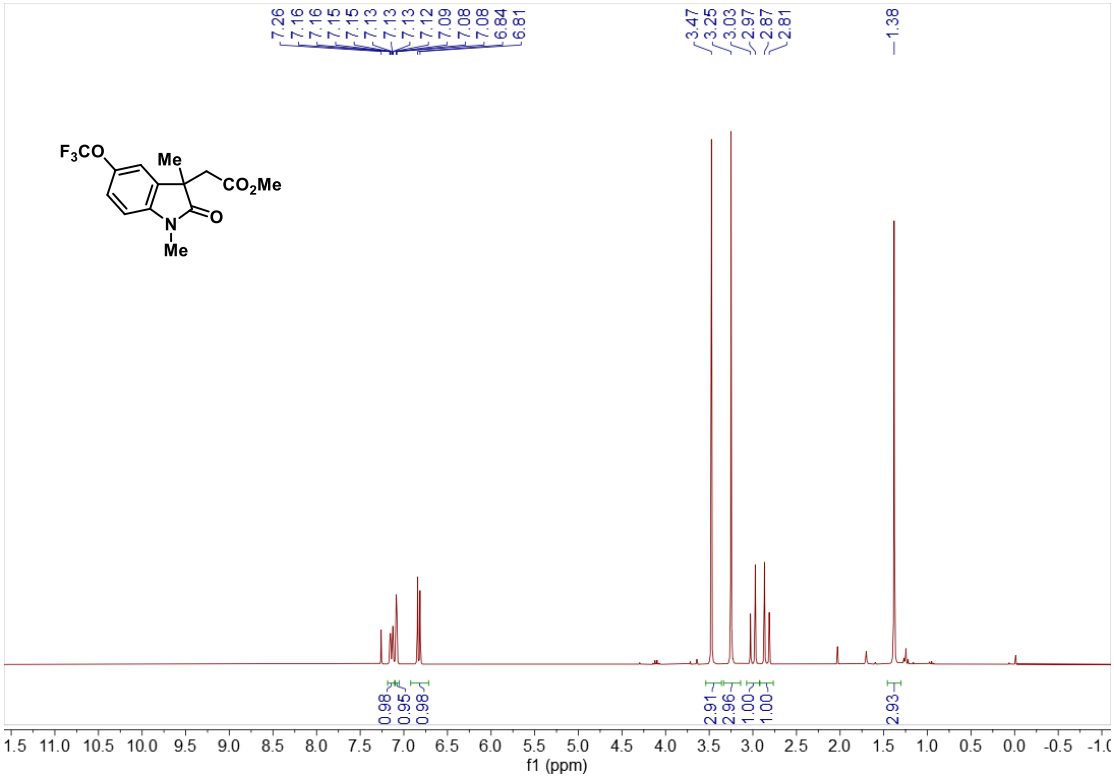
^{13}C NMR of compound 16 ($CDCl_3$, 125 MHz)



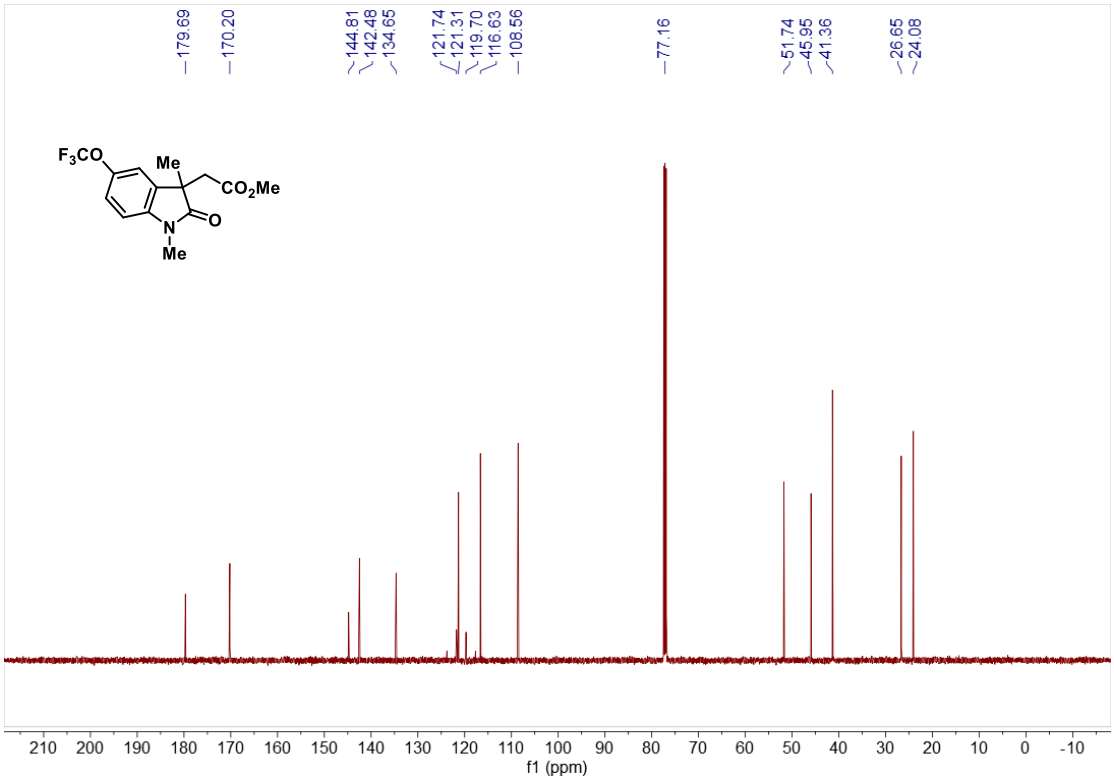
^{19}F NMR of compound 16 (377 MHz, Chloroform-*d*)



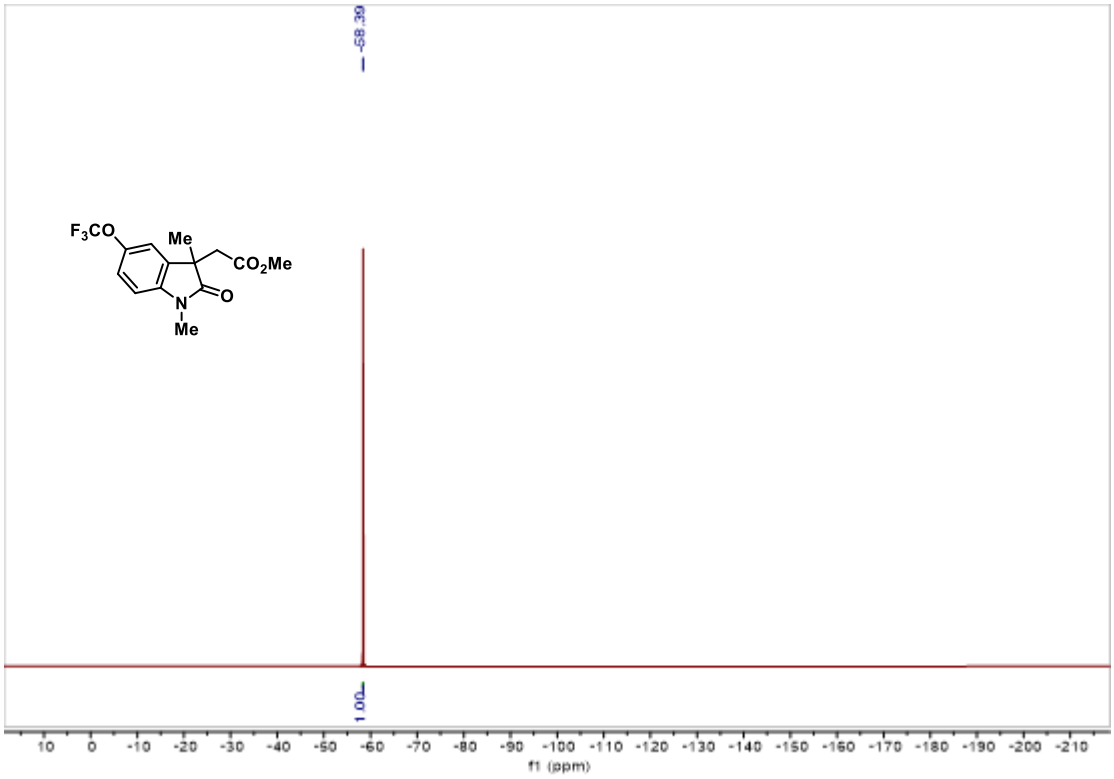
^{1}H NMR of compound 17 ($CDCl_3$, 300 MHz)



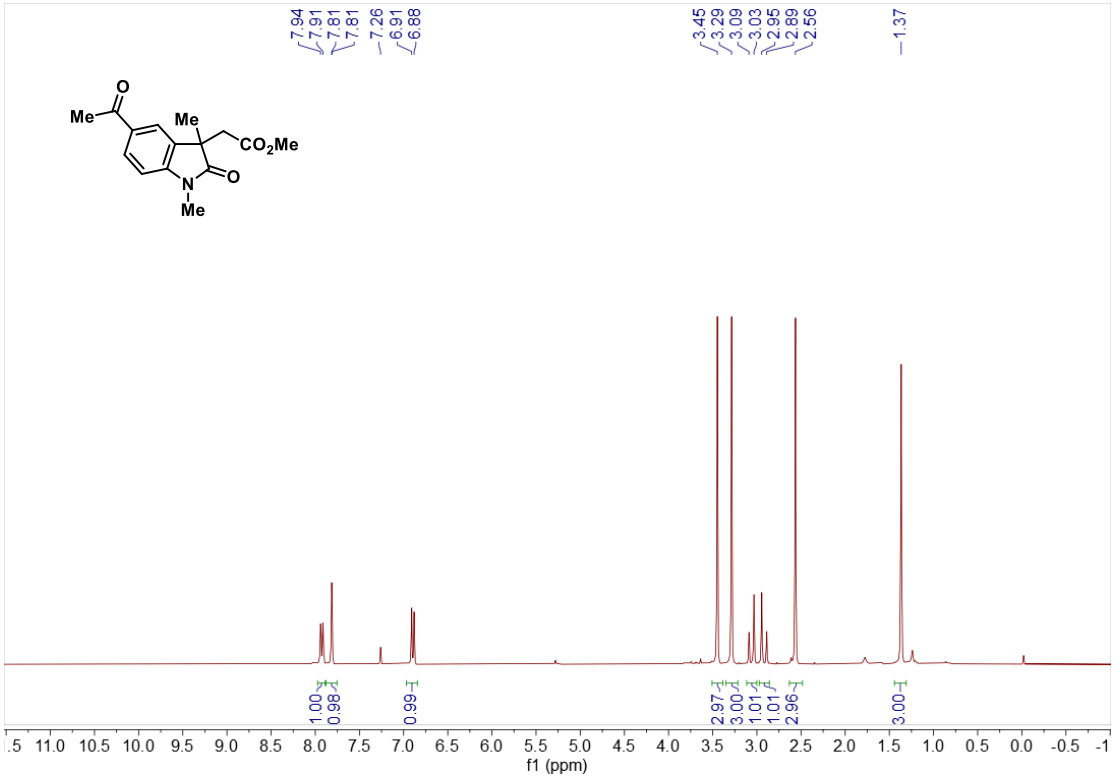
^{13}C NMR of compound 17 ($CDCl_3$, 125 MHz)



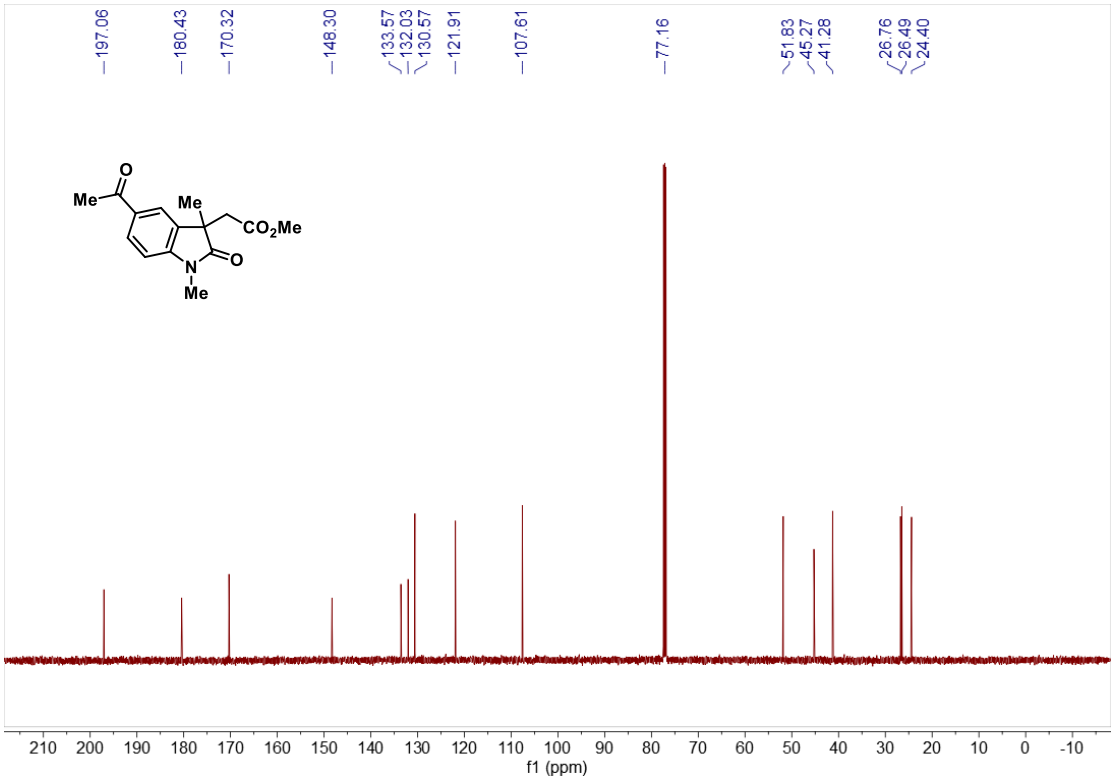
^{19}F NMR of compound 17 (377 MHz, Chloroform-*d*)



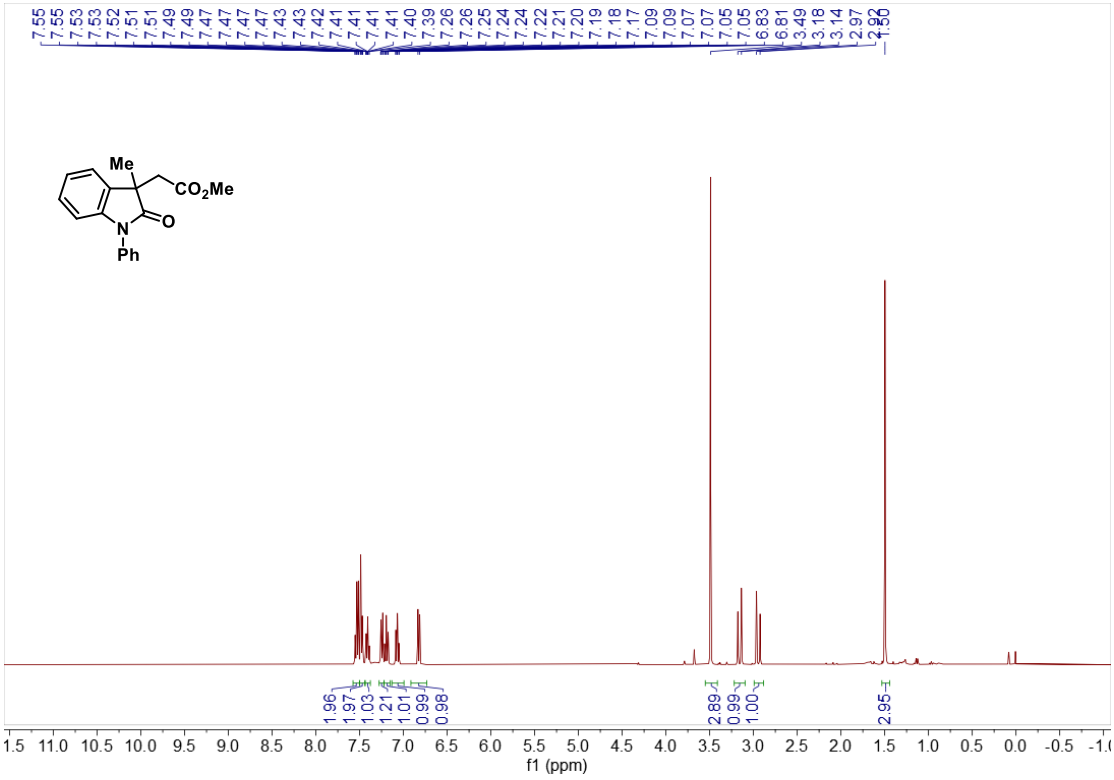
^{1}H NMR of compound 18 ($CDCl_3$, 300 MHz)



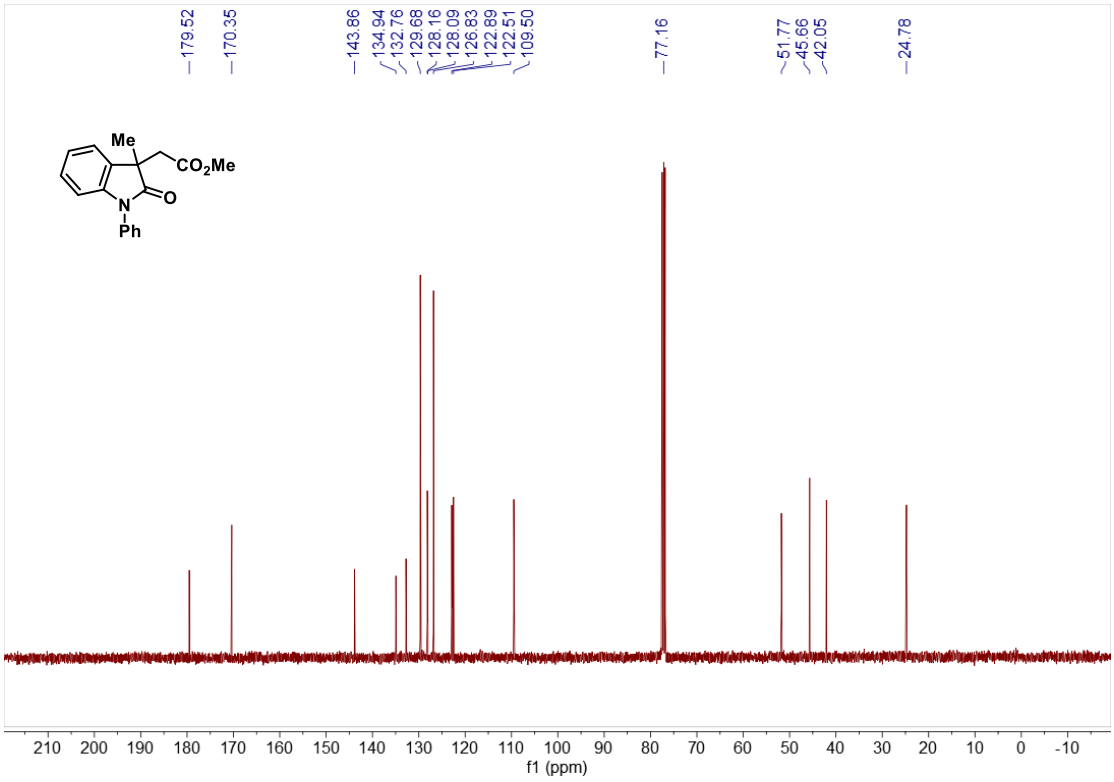
^{13}C NMR of compound 18 ($CDCl_3$, 125 MHz)



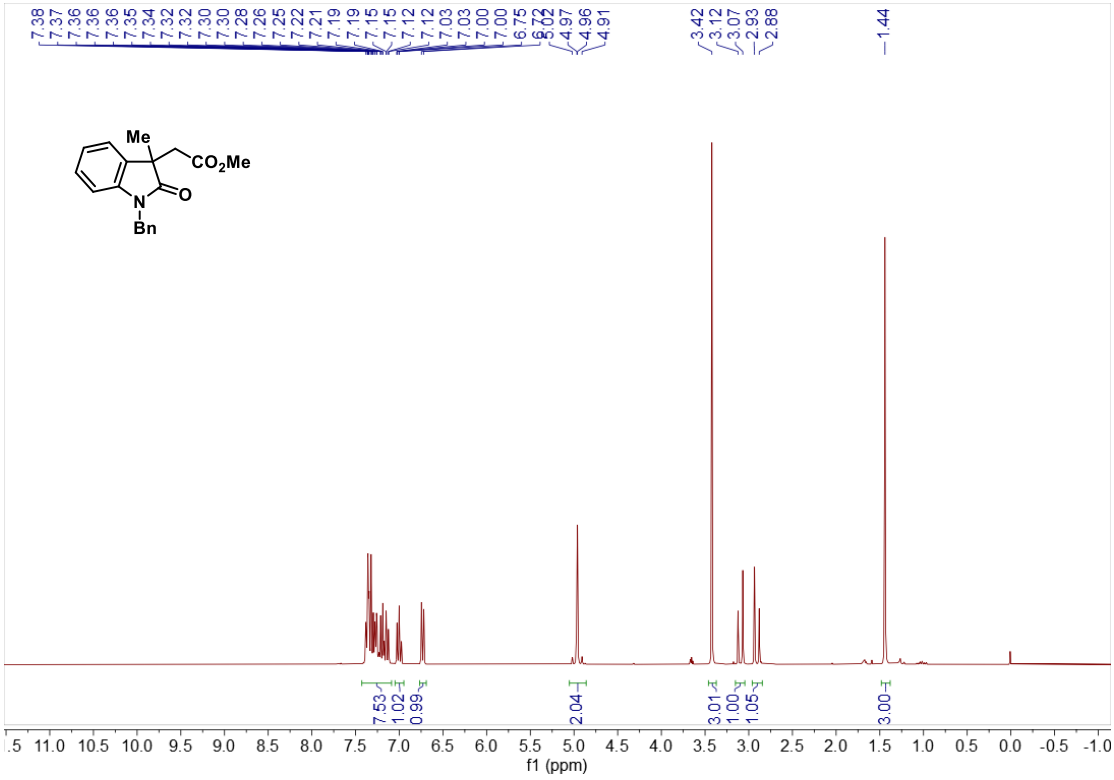
^{1}H NMR of compound 19 ($CDCl_3$, 400 MHz)



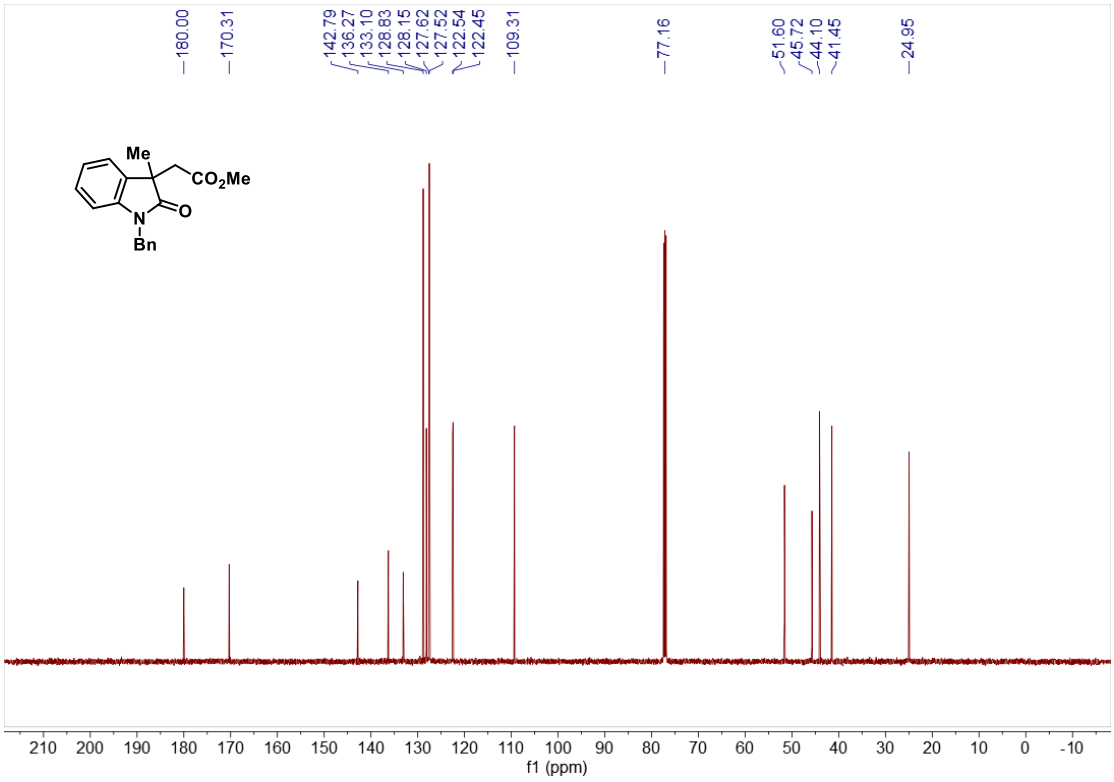
^{13}C NMR of compound 19 ($CDCl_3$, 100 MHz)



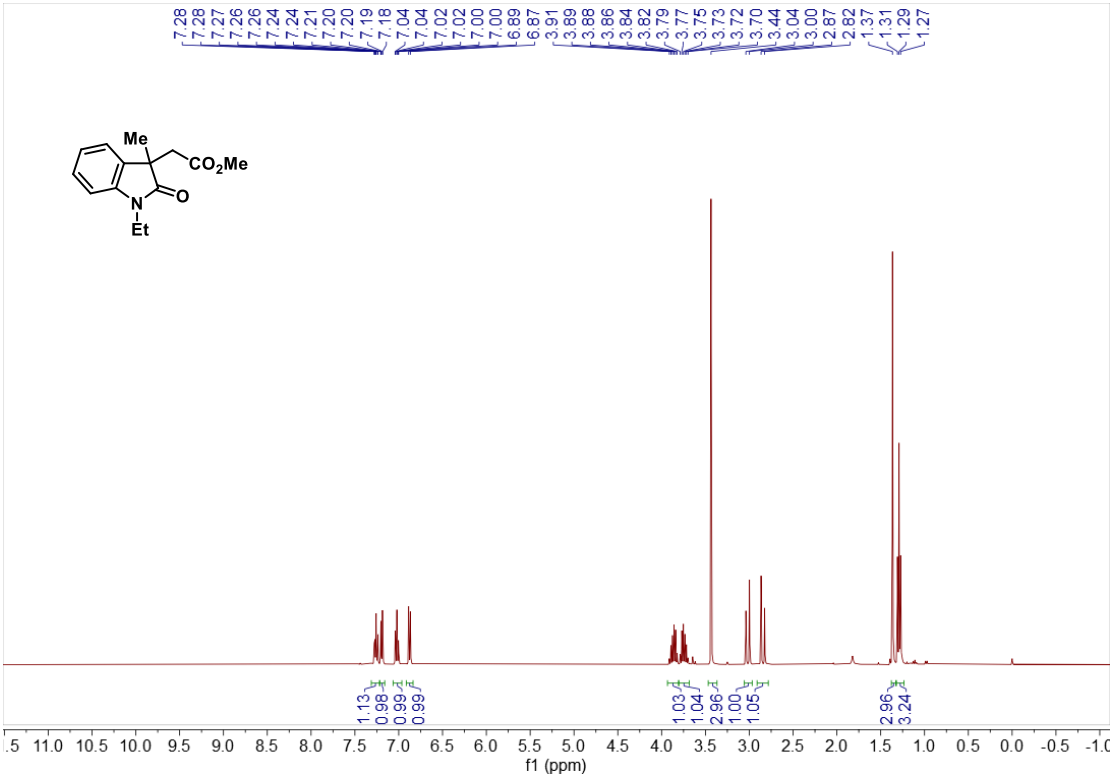
^{1}H NMR of compound 20 ($CDCl_3$, 300 MHz)



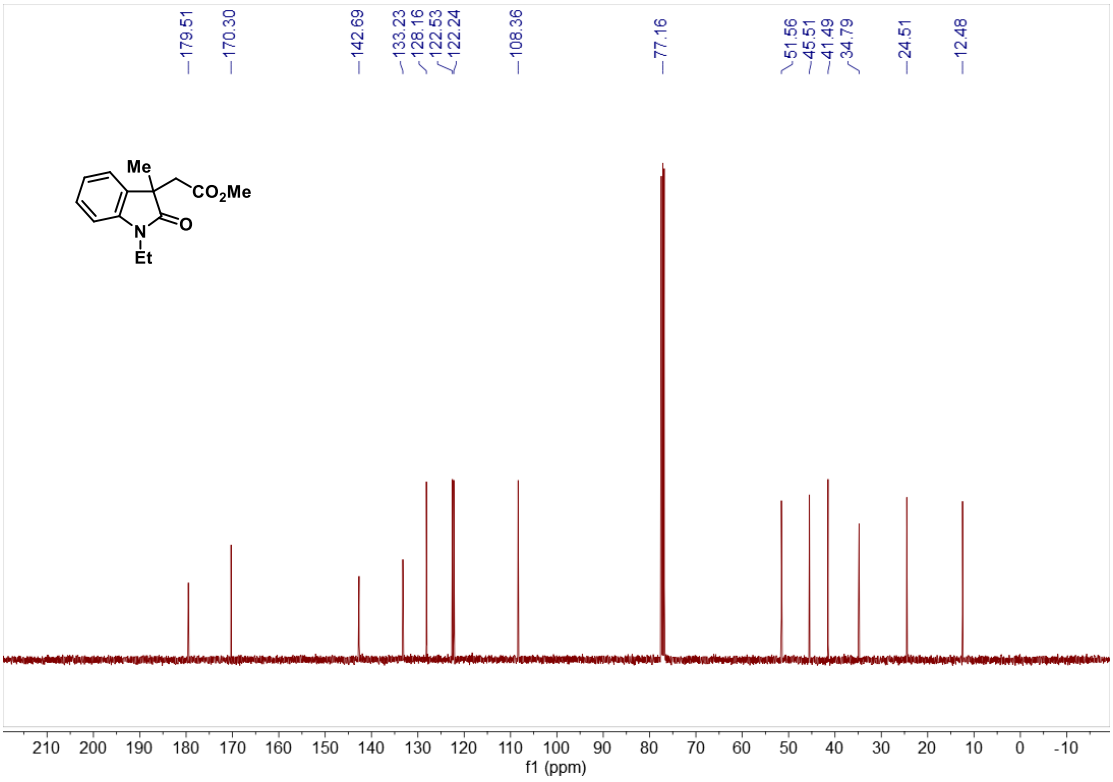
^{13}C NMR of compound 20 ($CDCl_3$, 125 MHz)



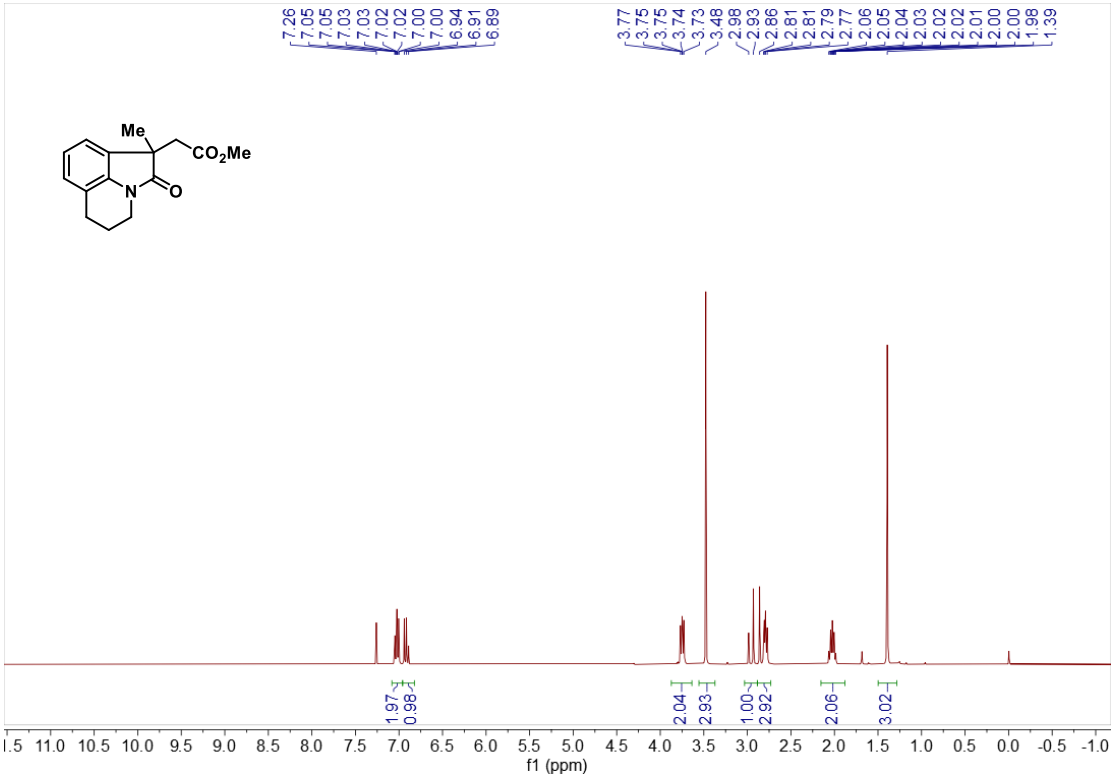
^{1}H NMR of compound 21 ($CDCl_3$, 400 MHz)



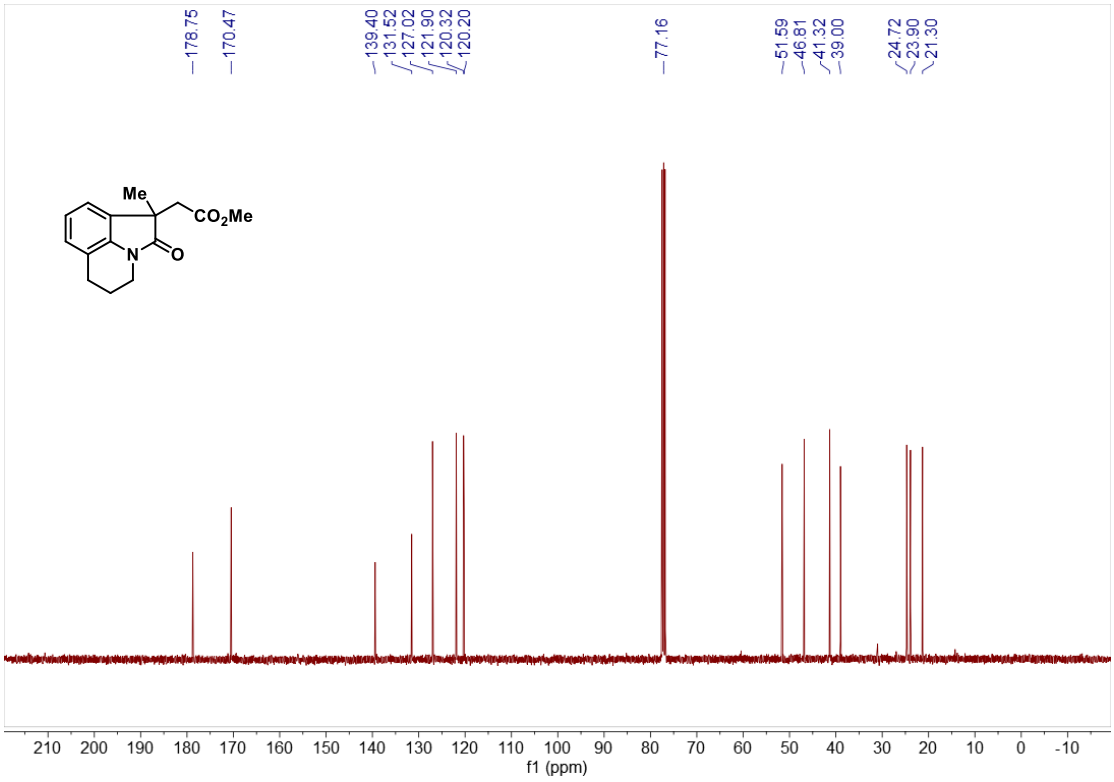
^{13}C NMR of compound 21 ($CDCl_3$, 100 MHz)



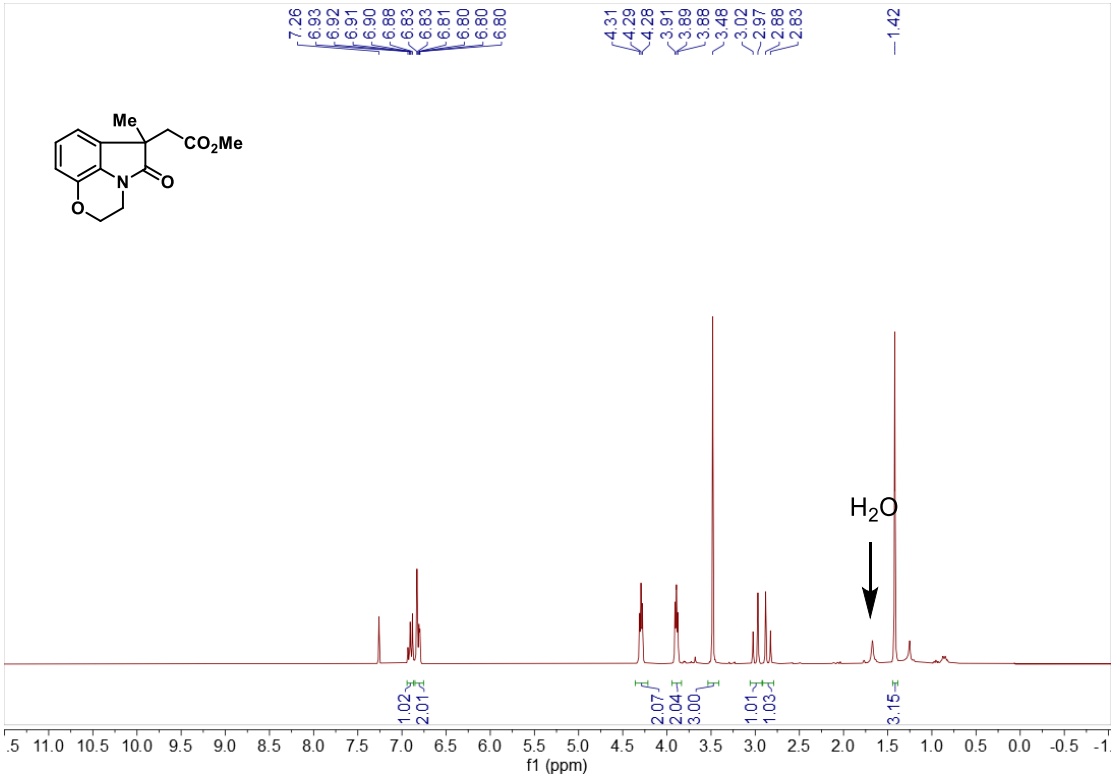
^{1}H NMR of compound 24 ($CDCl_3$, 300 MHz)



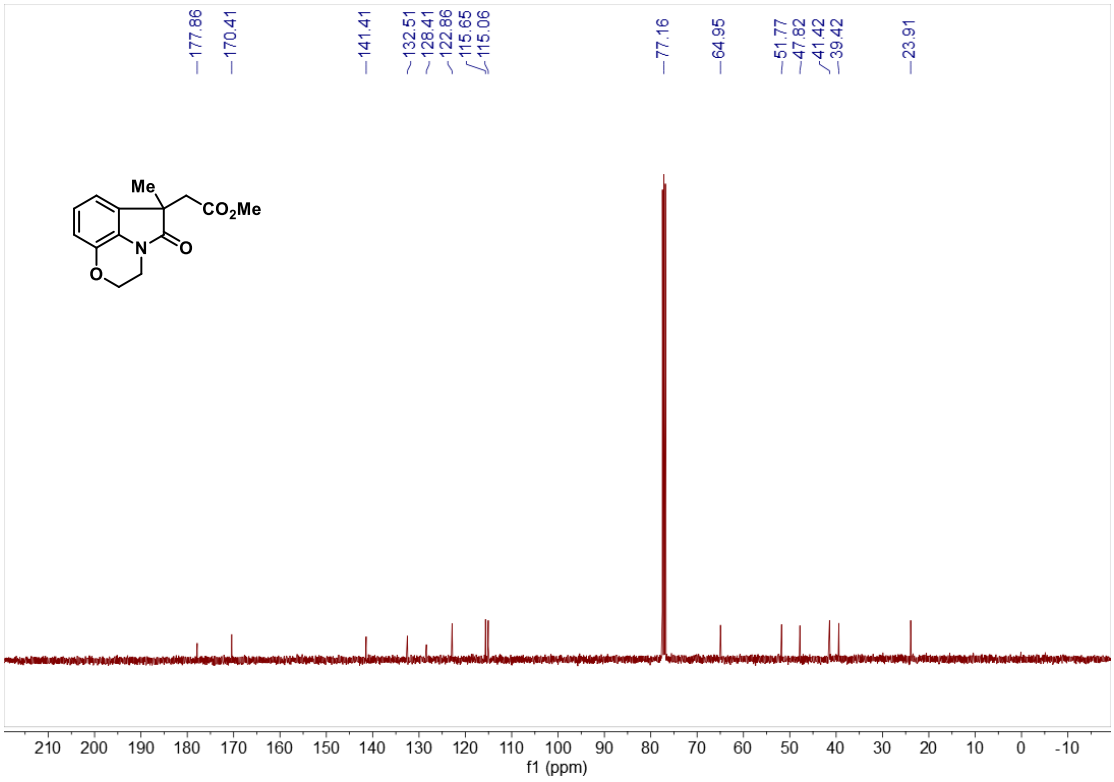
^{13}C NMR of compound 24 ($CDCl_3$, 100 MHz)



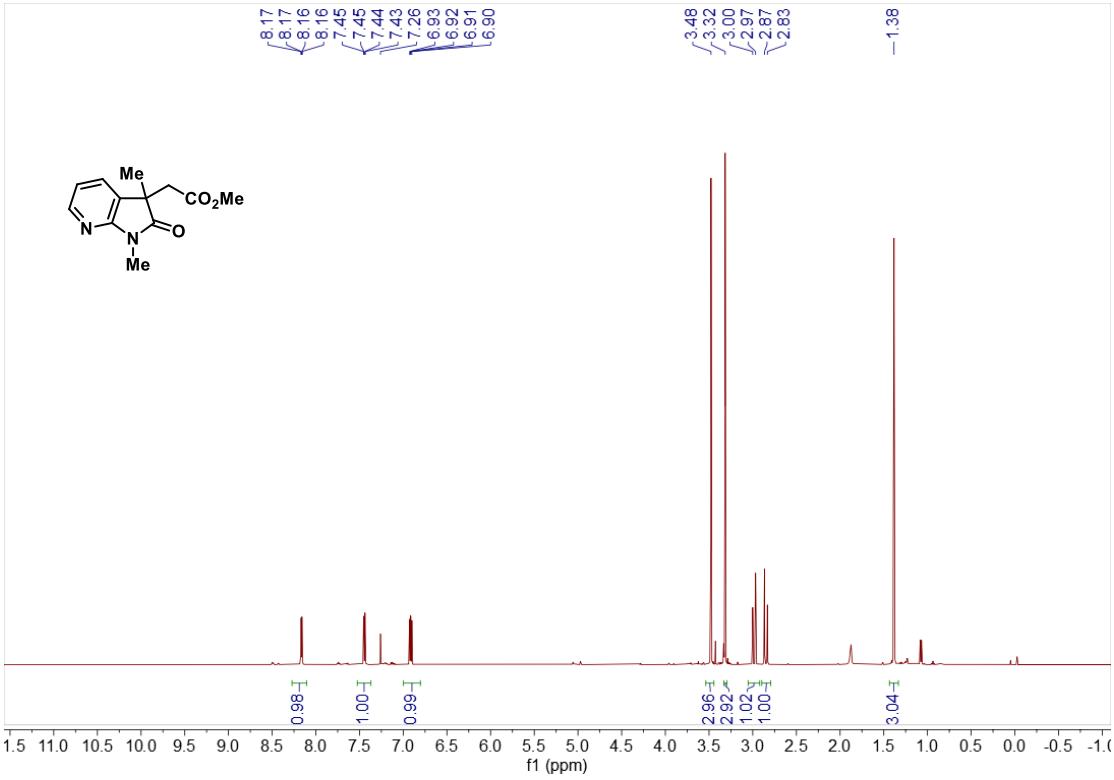
^{1}H NMR of compound 25 ($CDCl_3$, 300 MHz)



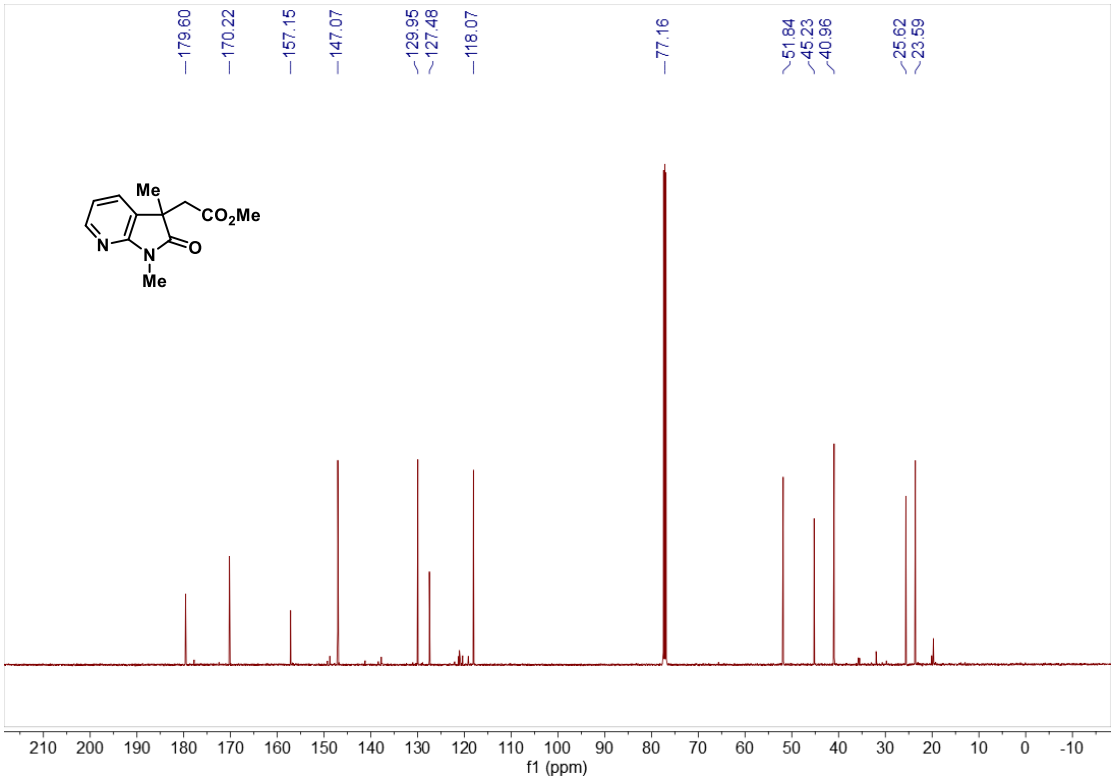
^{13}C NMR of compound 25 ($CDCl_3$, 100 MHz)



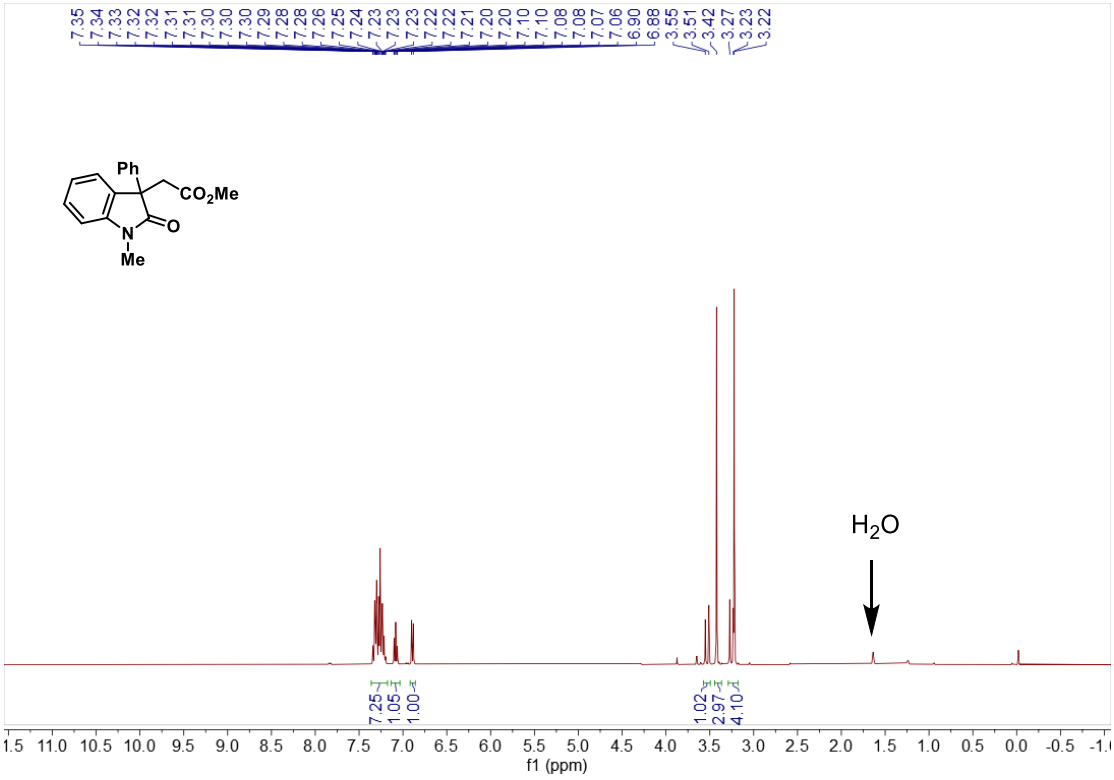
^{1}H NMR of compound 26 ($CDCl_3$, 500 MHz)



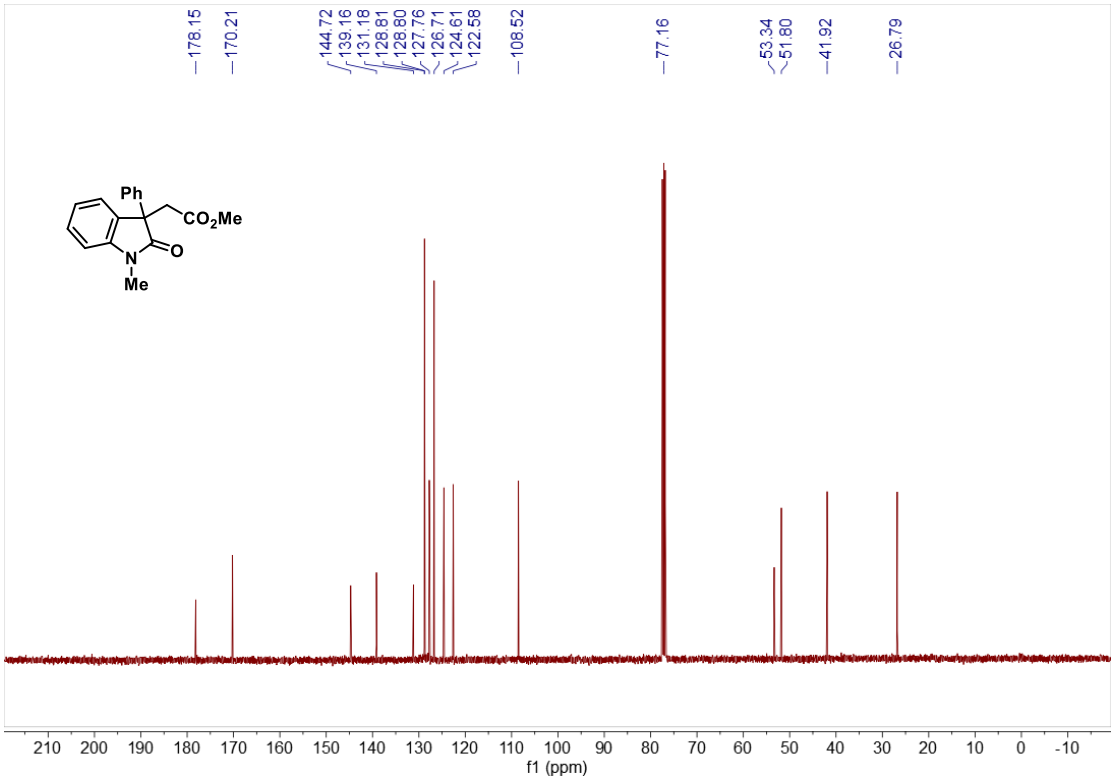
^{13}C NMR of compound 26 ($CDCl_3$, 125 MHz)



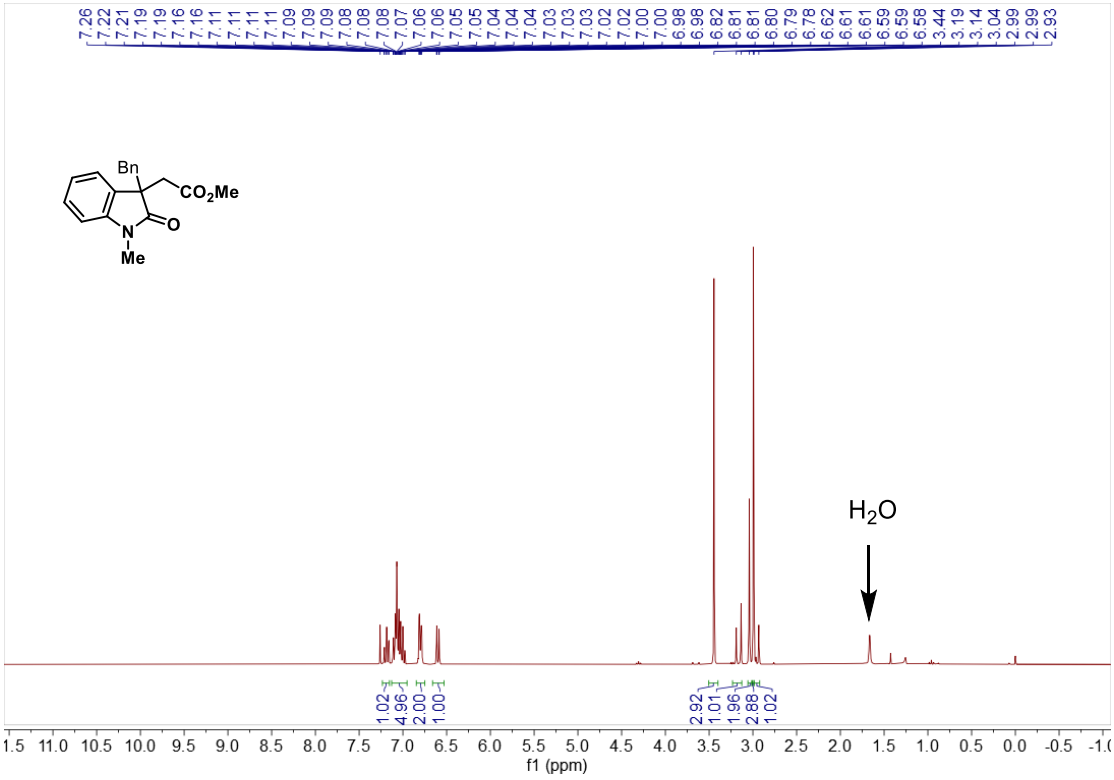
^{1}H NMR of compound 27 ($CDCl_3$, 400 MHz)



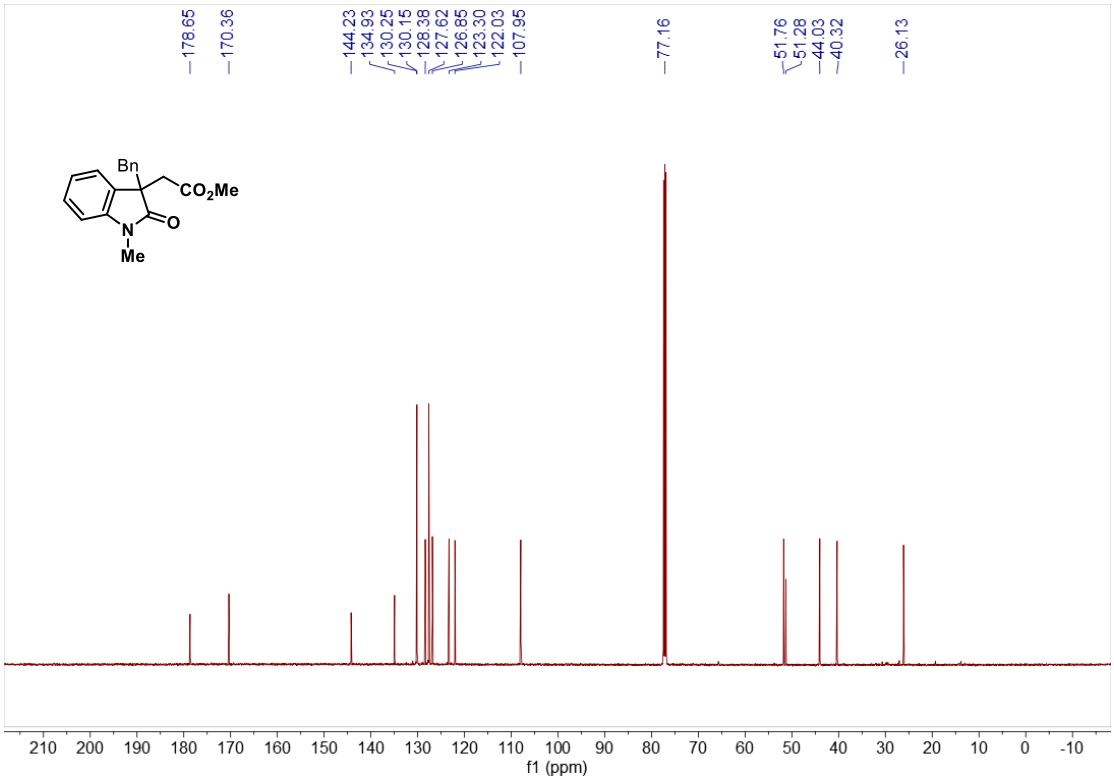
^{13}C NMR of compound 27 ($CDCl_3$, 100 MHz)



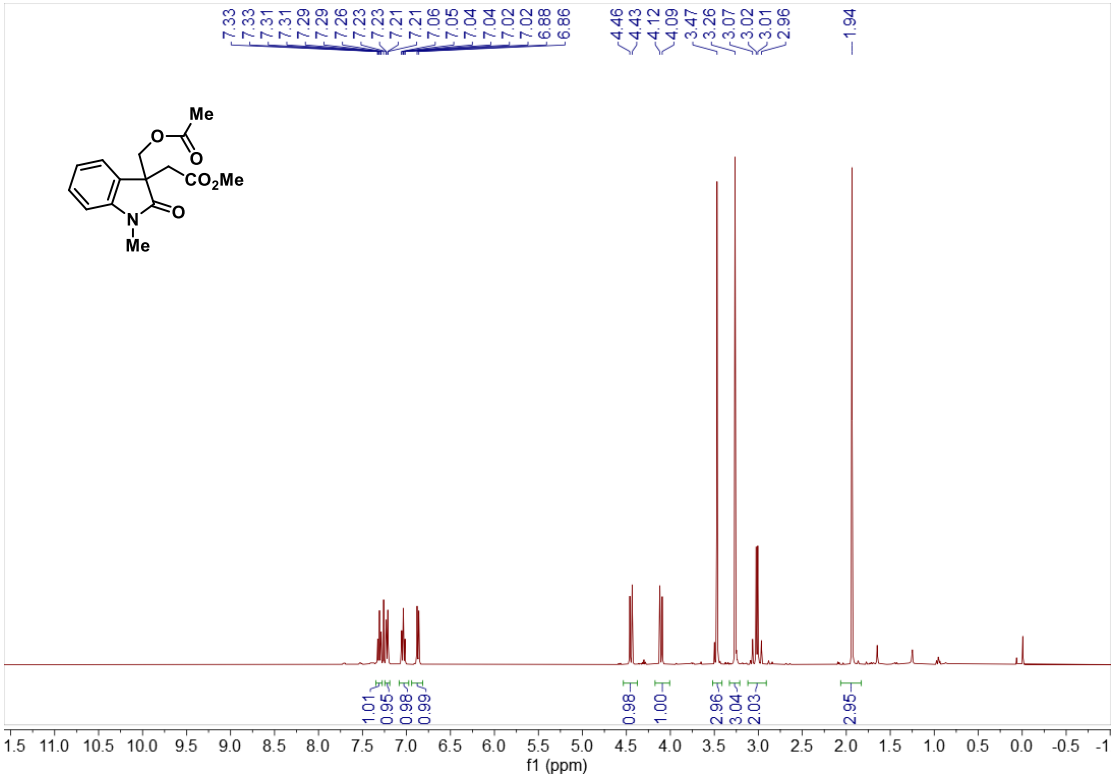
^{1}H NMR of compound 28 ($CDCl_3$, 300 MHz)



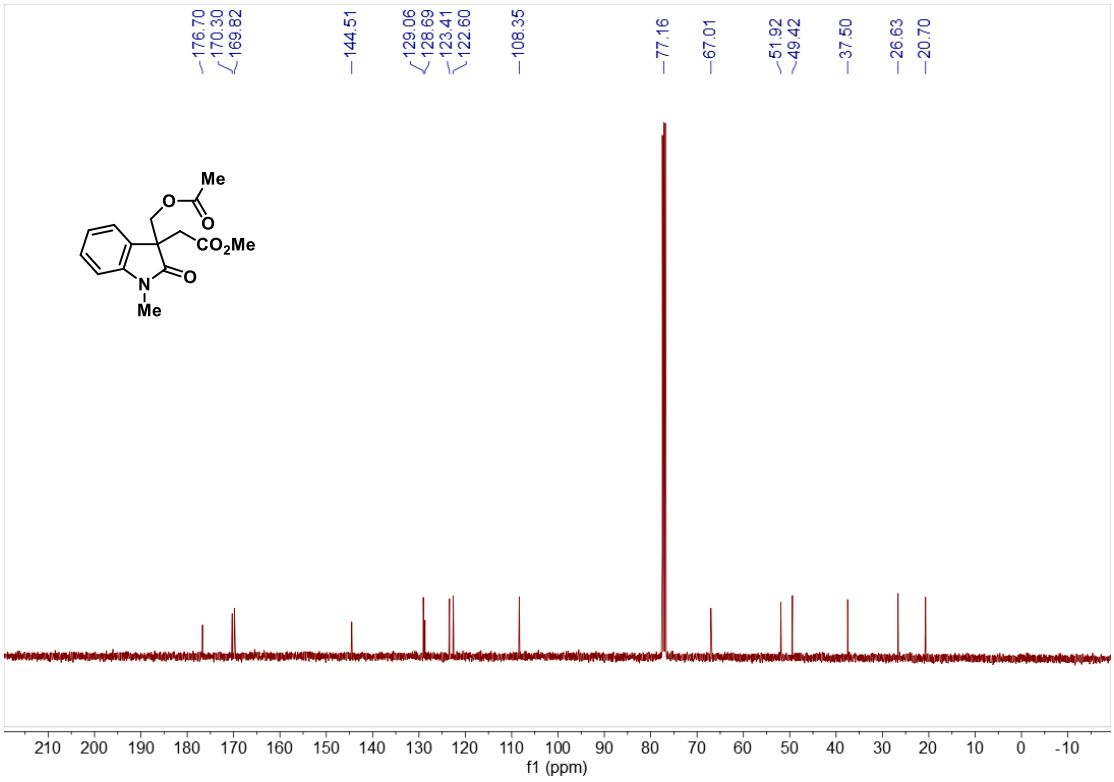
^{13}C NMR of compound 28 ($CDCl_3$, 125 MHz)



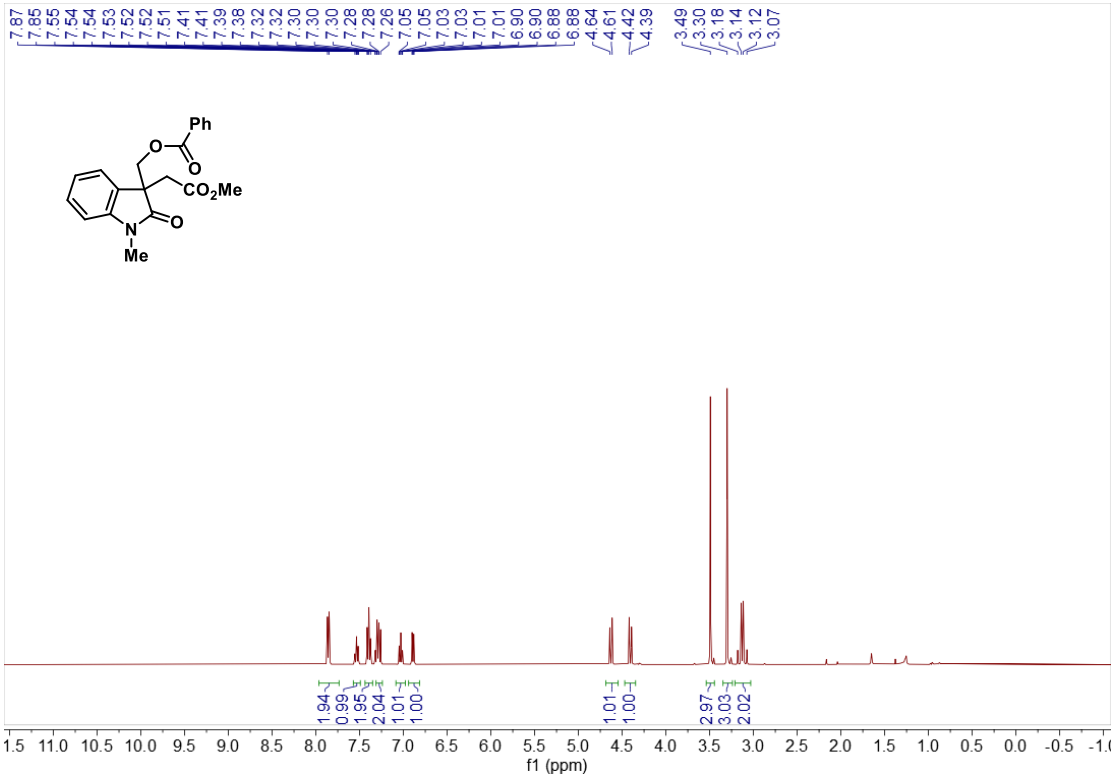
^{1}H NMR of compound 29 ($CDCl_3$, 400 MHz)



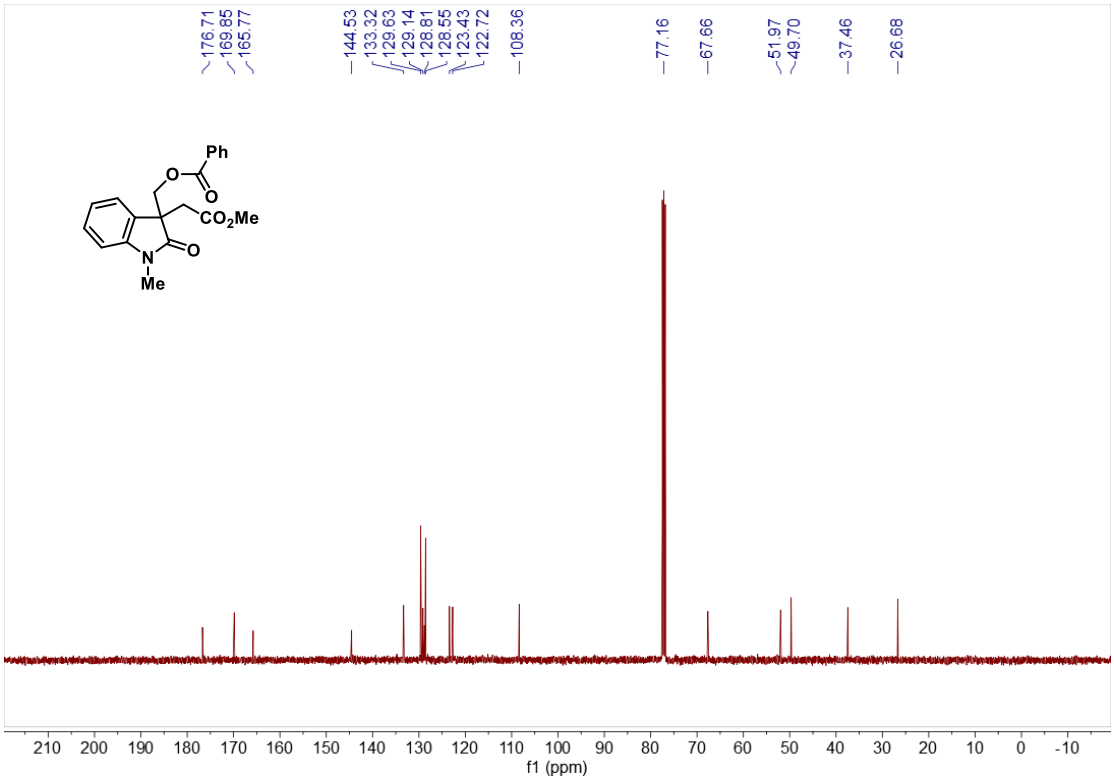
^{13}C NMR of compound 29 ($CDCl_3$, 100 MHz)



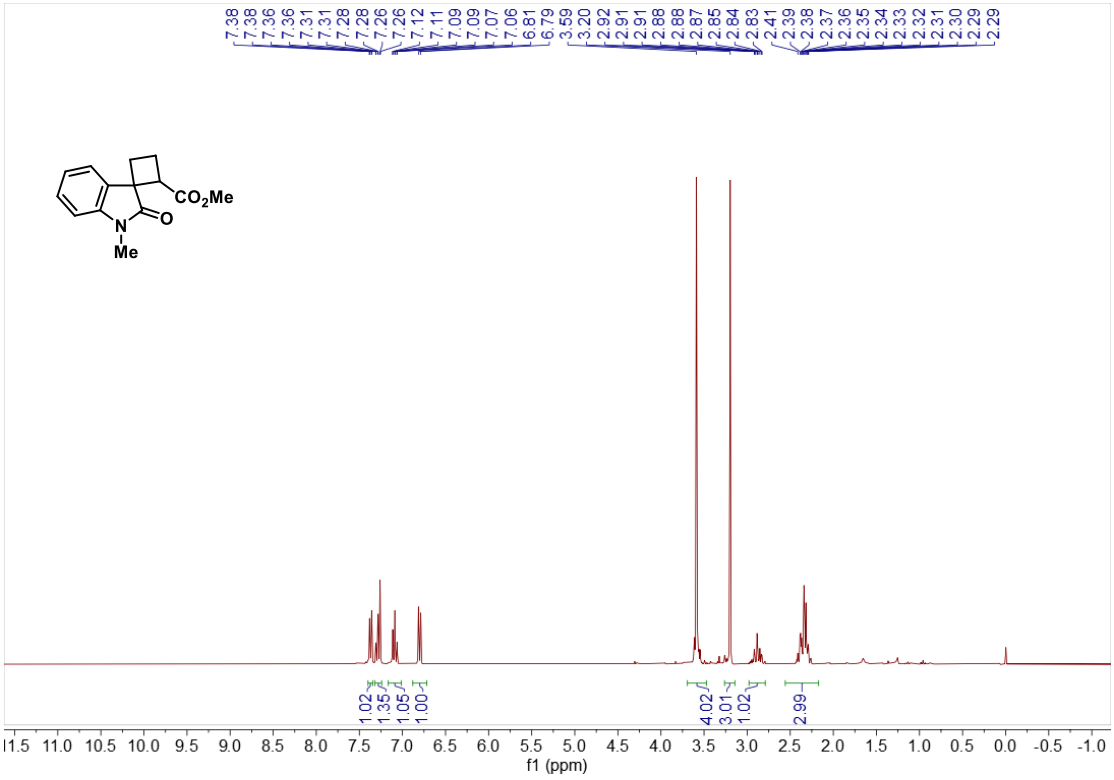
^{1}H NMR of compound 30 ($CDCl_3$, 400 MHz)



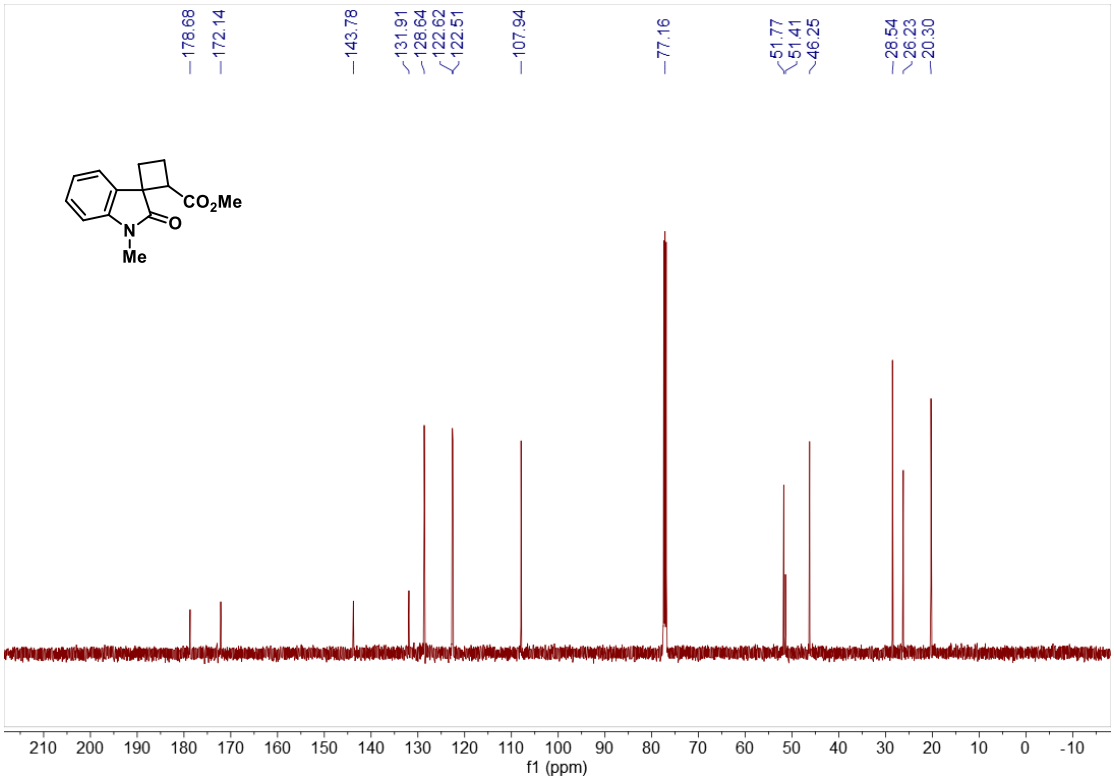
^{13}C NMR of compound 30 ($CDCl_3$, 100 MHz)



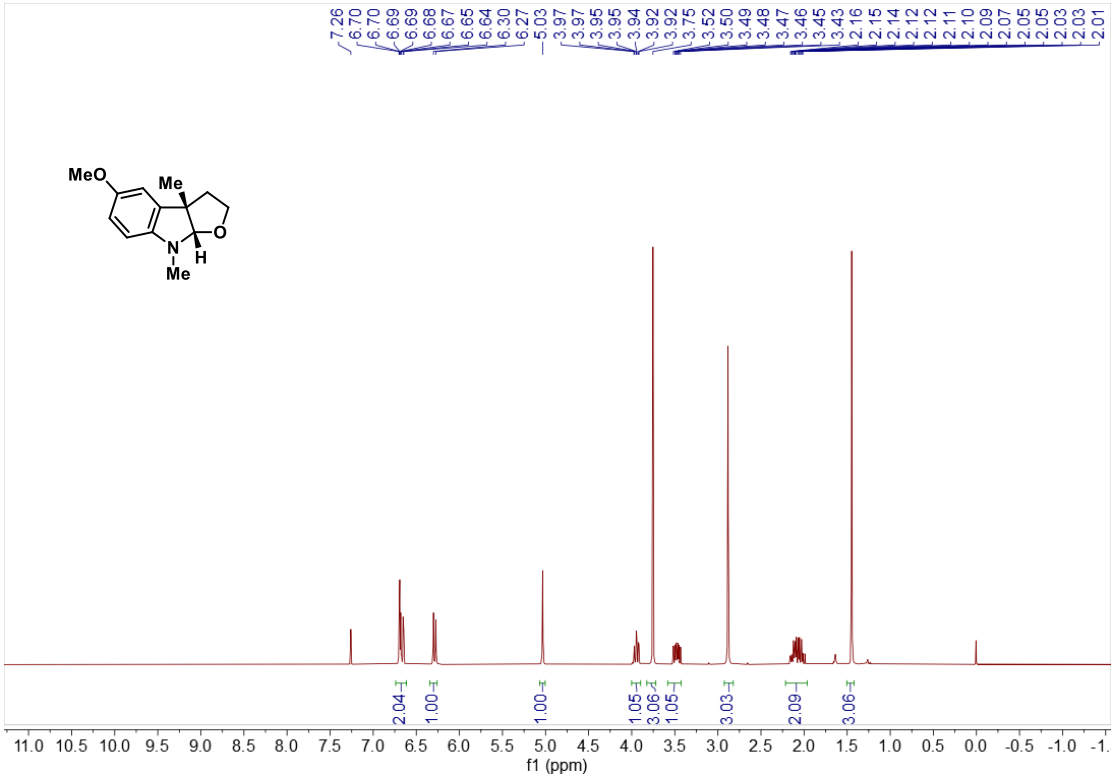
^{1}H NMR of compound 31 ($CDCl_3$, 300 MHz)



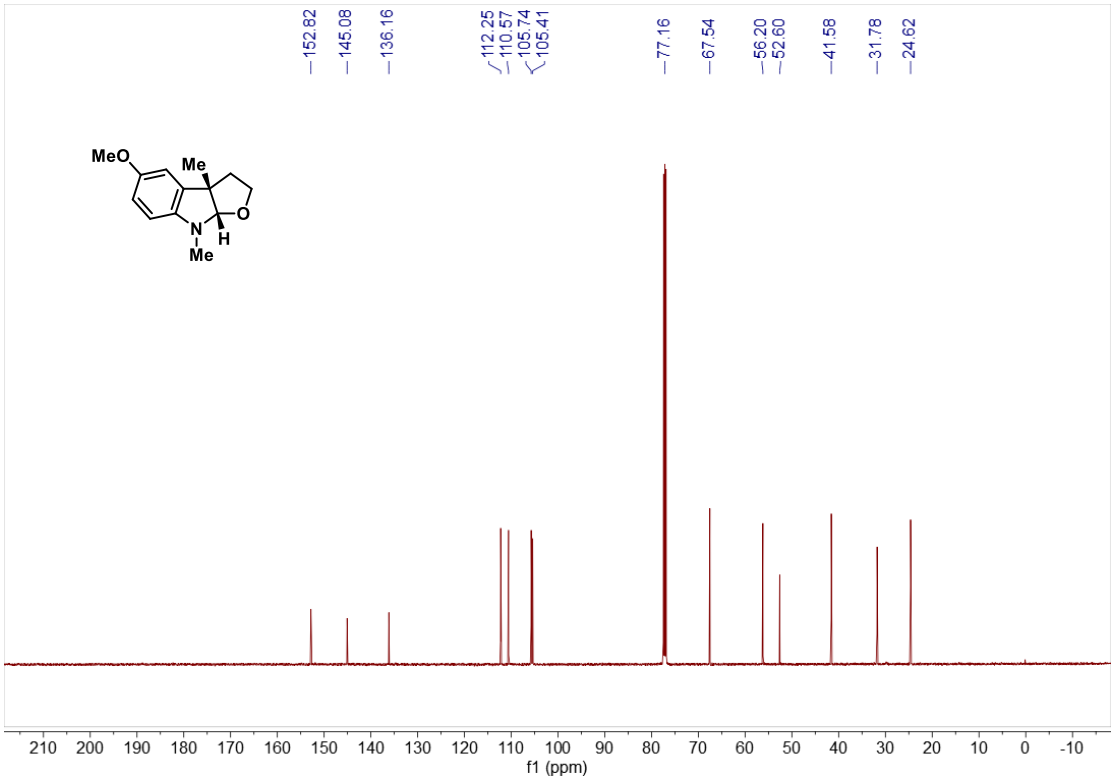
^{13}C NMR of compound 31 ($CDCl_3$, 125 MHz)



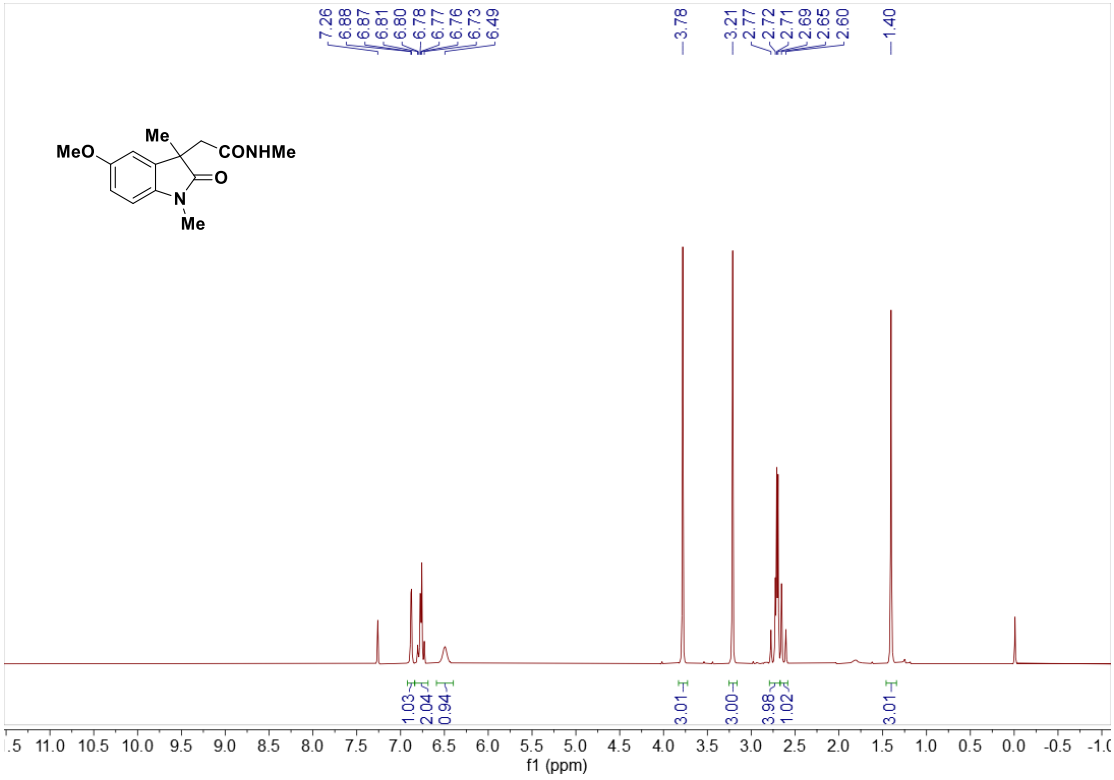
^{1}H NMR of compound 32 ($CDCl_3$, 300 MHz)



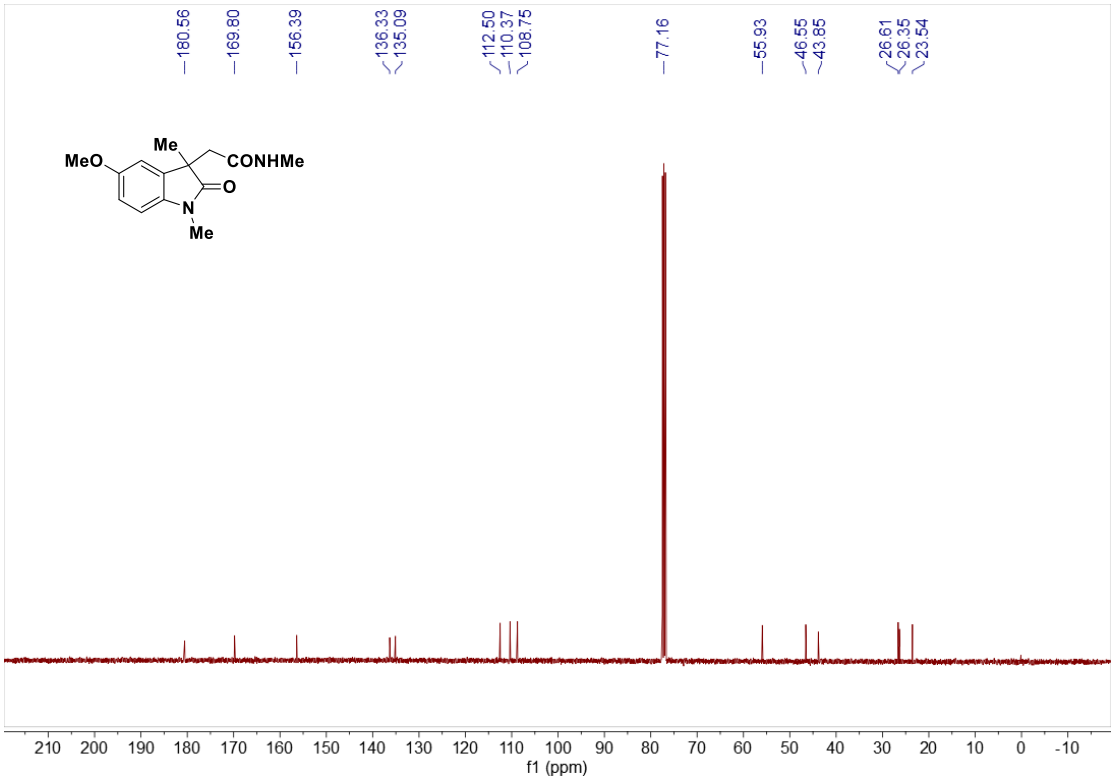
^{13}C NMR of compound 32 ($CDCl_3$, 125 MHz)



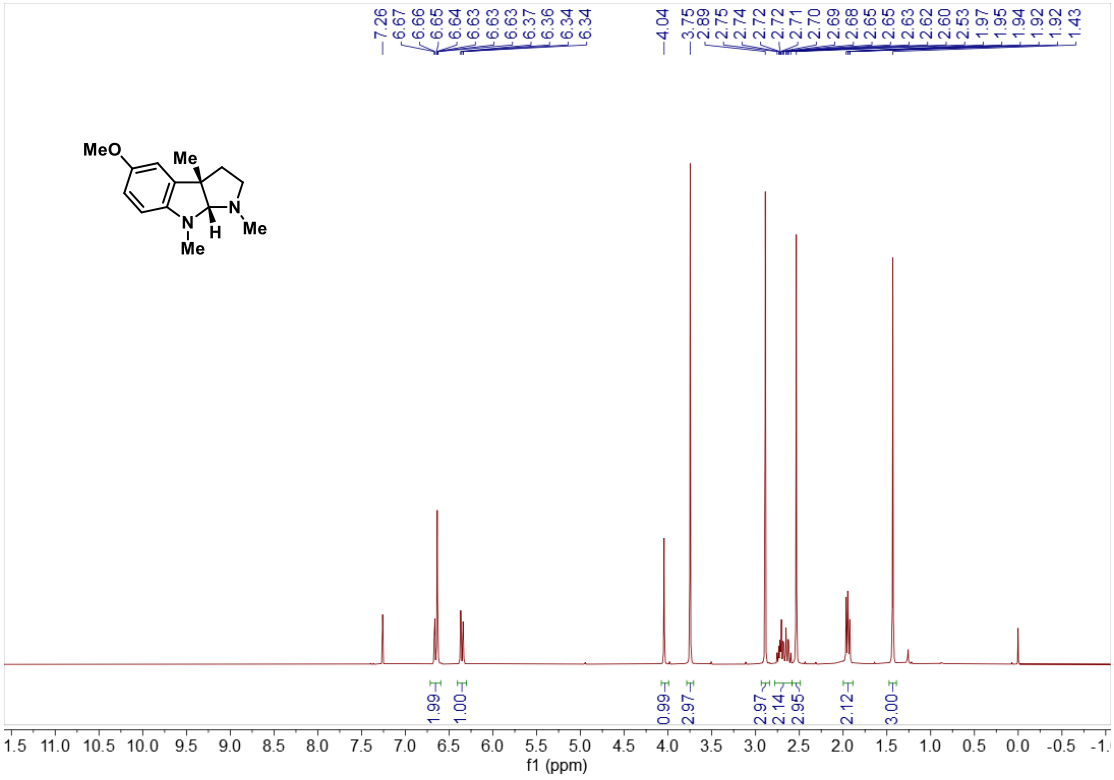
^{1}H NMR of compound 33 ($CDCl_3$, 300 MHz)



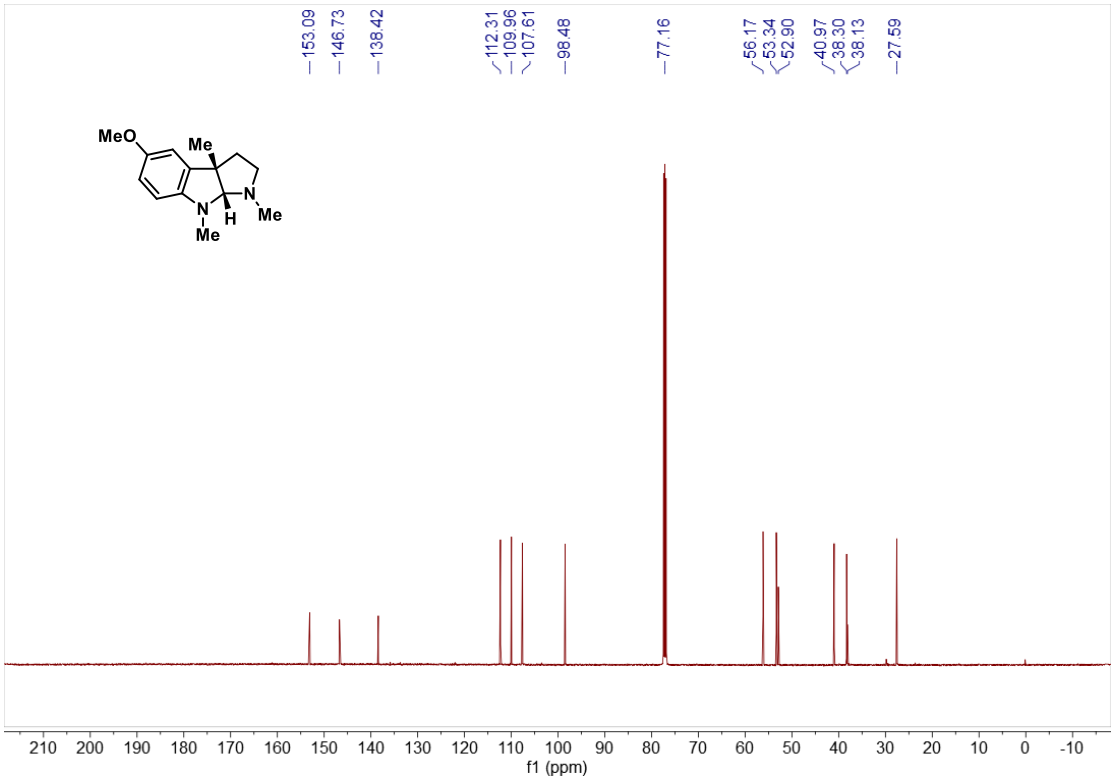
^{13}C NMR of compound 33 ($CDCl_3$, 100 MHz)



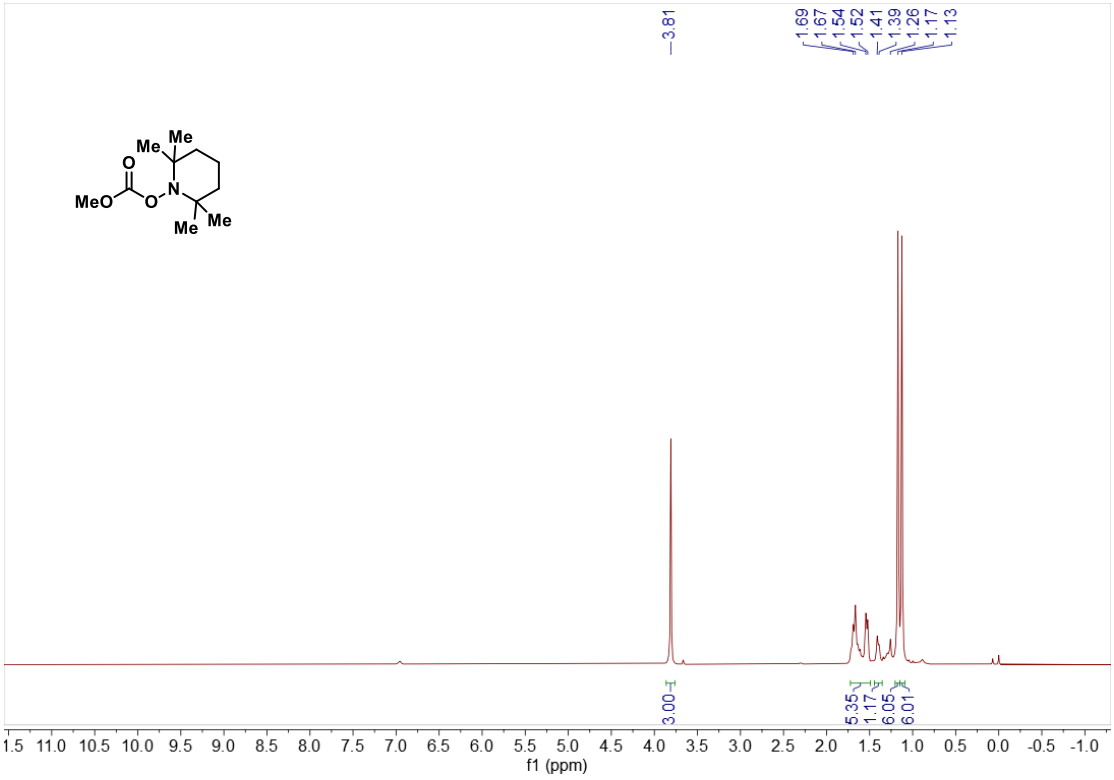
^{1}H NMR of compound 34 ($CDCl_3$, 300 MHz)



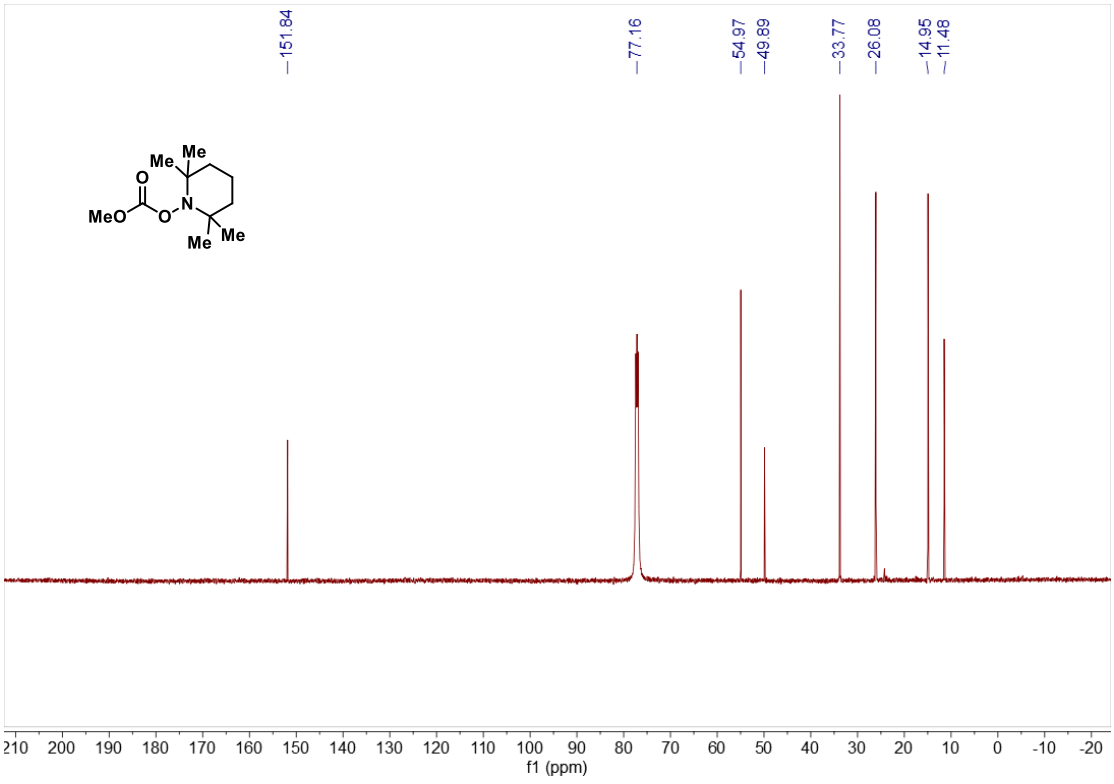
^{13}C NMR of compound 34 ($CDCl_3$, 125 MHz)



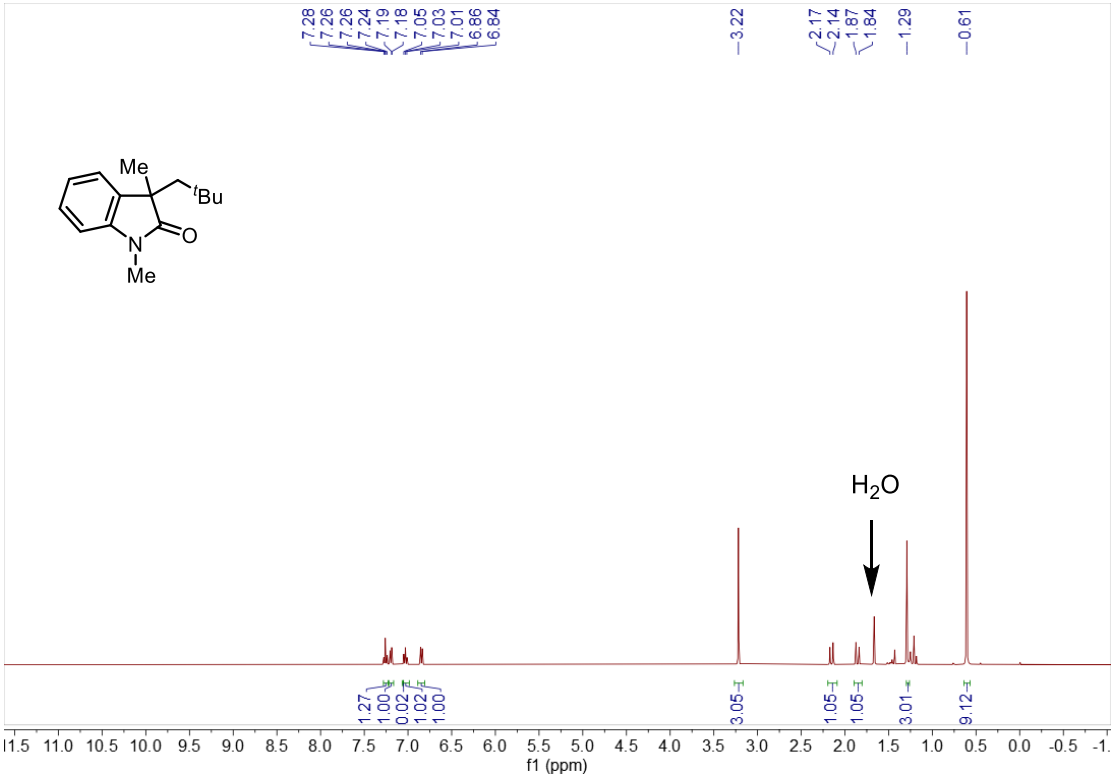
^{1}H NMR of compound 35 ($CDCl_3$, 500 MHz)



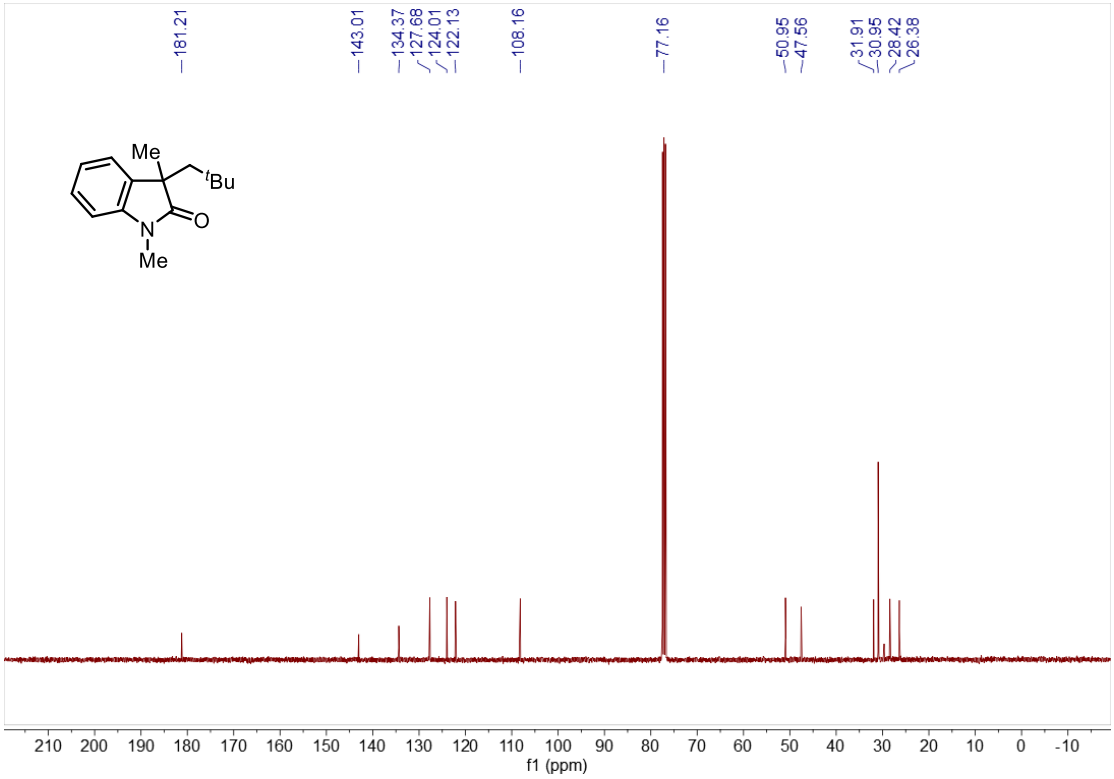
^{13}C NMR of compound 35 ($CDCl_3$, 125 MHz)



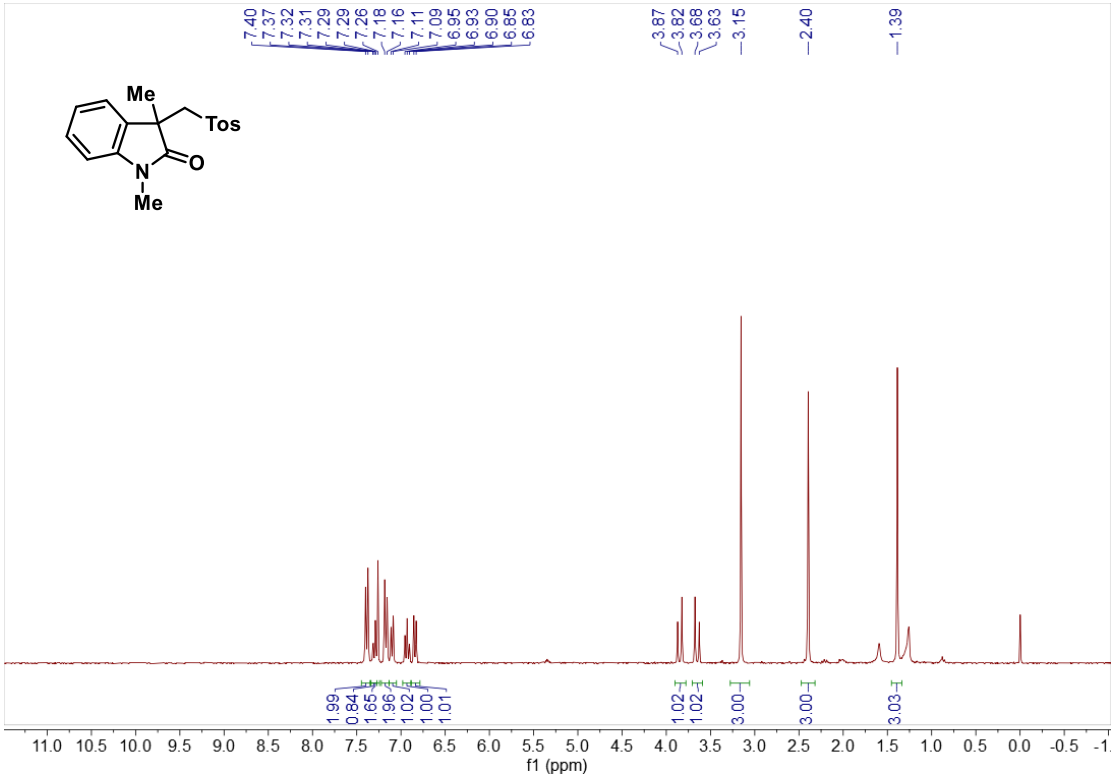
^{1}H NMR of compound S1 ($CDCl_3$, 400 MHz)



^{13}C NMR of compound S1 ($CDCl_3$, 100 MHz)



^{1}H NMR of compound S2 ($CDCl_3$, 300 MHz)



^{13}C NMR of compound S2 ($CDCl_3$, 100 MHz)