Electronic Supplementary Information

Synthesis of Oxyindole from Acetanilide via Ir(III)-Catalyzed C–H Carbenoid Functionalization

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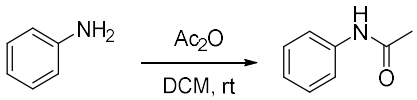
1. General Methods

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was carried out by using spectrochem silica gel (100–200, 230–400 mesh). IR spectra were recorded in Perkin Elmer, FTIR-system 2000. ^{1}H NMR spectra were recorded on Bruker AV 500 MHz spectrometers. TMS was used as an internal standard and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0.0 ppm) or $CDCl_3$ (7.27 ppm) or DMSO-*d*6 (2.50 ppm). In case of the peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J* are reported in Hertz (Hz). ^{13}C NMR spectra were obtained by Bruker AV (125 MHz) spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). For carbon appearing as doublet, its indicated as 'd'. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump and WATER's XEVO G2 XS9Tof instruments. Dichloro(η^5-pentamethylcyclopentadienyl)iridium(III) dimer (99%) was purchased from Alfa Aesar, and all the silver salts and metal catalyst were purchased from Aldrich Chemicals, TCI and Alfa Asear. $[Cp^*Co(CO)I_2]$[1] and $[IrCp^*(OAc)_2H_2O]$[2] were prepared according to reported literature procedure.

NOTE: *No further attempts were made for individual substrate to increase yield. For known compounds only melting point and NMR data are given with corresponding citation.*

2. General Procedure for the Preparation of Starting Materials

2.1. Preparation of Acetanilides (1)



In a 50 mL round bottom flask, Aniline (5.0 mmol, 1.0 equiv) was dissolved in 20 mL of dichloromethane under argon atmosphere. Then, acetic anhydride (6.0 mmol, 1.2 equiv) was added drop wise and the reaction was stirred at room temperature till complete consumption of anilines. After completion of the reaction, the mixture was washed with a saturated solution of

sodium carbonate, the organic layer dried with Na_2SO_4 and the solvent removed under reduced pressure to obtain the desider acetanilide in quantative yield. In most cases analytically pure acetanilides can be obtained after extraction however if necessary purification by flash chromatography with ethyl acetate/hexane was used.

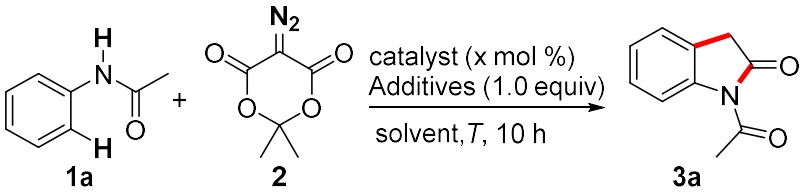
2.2. Preparation of Diazo substrate (2)

Meldrum's acid (2.6 g, 18.0 mmol) was treated with TsN_3 (3.91 g, 19.84 mmol) and K_2CO_3 (4.99 g, 36.08 mmol) in acetonitrile (50 mL) and the resulting mixture was stirred at room temperature for overnight. After complition of reaction, the mixture was filtered through a pad of celite and washed with EtOAc (20 mL x 3). The organic layers were combined, dried over Na_2SO_4 and the solvent was removed under reduce pressure. The crude residue was then purified by flash column chromatography using EtOAc/Hexane as elutent to furnish the pure diazo compound **2** (2.5 g, 81%) as white solid.

3. Optimization of Reaction Conditions

To a 3 mL screw capped vial with a spinvane triangular-shaped Teflon stirbar were added acetanilide (**1a**, 20.3 mg, 0.15 mmol), diazotized meldrum's acid (**2**, 30.6 mg, 0.18 mmol), catalyst, additive, and solvent (1.0 mL) under air. The reaction mixture was stirred in a pre-heated oil bath at the indicated temperature for 10 h. The reaction mixture was cooled to room temperature, filtered through a pad of celite and the pad was washed with CH_2Cl_2 (5 mL x 3). Combined solvents were removed under reduced pressure and the crude yield was measured by ^1H NMR spectrum using an internal standard (dibromomethane).

Table S1. Optimization of reaction parameters[a]



entry	catalyst (mol %)	additive	solvent	*T* (°C)	yield (%)[b]
1	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	-	1,2-DCE	25	0
2	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	-	1,2-DCE	70	20
3	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	1,2-DCE	70	93 (91)
4	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	AgOAc	1,2-DCE	70	15
5	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	CsOAc	1,2-DCE	70	10
6	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	KOAc	1,2-DCE	70	75
7[c]	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	1,2-DCE	70	65
8	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	Toluene	70	<5
9	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	1,2-Dioxane	70	<5
10	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	MeCN	70	<5
11	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	THF	70	<5
12	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	MeOH	70	<5
13	$[IrCp^*Cl_2]_2$ (2)/ $AgSbF_6$ (8)	NaOAc	1,2-DCE	70	82
14	$[IrCp^*Cl_2]_2$ (2)/ AgOAc (8)	NaOAc	1,2-DCE	70	15
15	$[IrCp^*Cl_2]_2$ (2)/ AgOTf (8)	NaOAc	1,2-DCE	70	30
16	$[IrCp^*Cl_2]_2$ (2)/ $AgBF_4$ (8)	NaOAc	1,2-DCE	70	45
17	$[IrCp^*Cl_2]_2$ (1)/ $AgNTf_2$ (4)	NaOAc	1,2-DCE	70	72
18	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	1,2-DCE	50	32
19	$[IrCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	1,2-DCE	100	85
20	$[IrCp^*Cl_2]_2$ (2)/ --	NaOAc	1,2-DCE	70	18
21	--/ $AgNTf_2$ (8)	NaOAc	1,2-DCE	70	n.r.
22	$[IrCp^*(OAc)_2]\cdot H_2O$ (4)	none	1,2-DCE	70	<5
23	$[IrCp^*(OAc)_2]\cdot H_2O$ (4)/ $AgNTf_2$ (4)	none	1,2-DCE	70	62
24[d]	$[IrCp^*Cl_2]_2$ (1)/ $AgNTf_2$ (4)	NaOAc	1,2-DCE	70	(79)[b]
25	$[RhCp^*Cl_2]_2$ (2)/ $AgNTf_2$ (8)	NaOAc	1,2-DCE	70	n.r.
26	[Ru(*p*-cymene)$Cl_2]_2$ (2)/$AgNTf_2$ (8)	NaOAc	1,2-DCE	70	n.r.
27	$[CoCp^*(CO)I_2]$ (4)/ $AgNTf_2$ (8)	NaOAc	1,2-DCE	70	n.r.

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2** (0.18 mmol, 1.2 equiv), catalyst and additive in solvent (1 mL) at 70 °C for 10 h. [b]^{1}H NMR yield (CH_2Br_2 as internal standard); isolated yield in parentheses. [c]0.5 equiv of NaOAc was used. [d]Reaction carried out with 1.0 g of **1a** for 20 h. n. r. = no reaction.

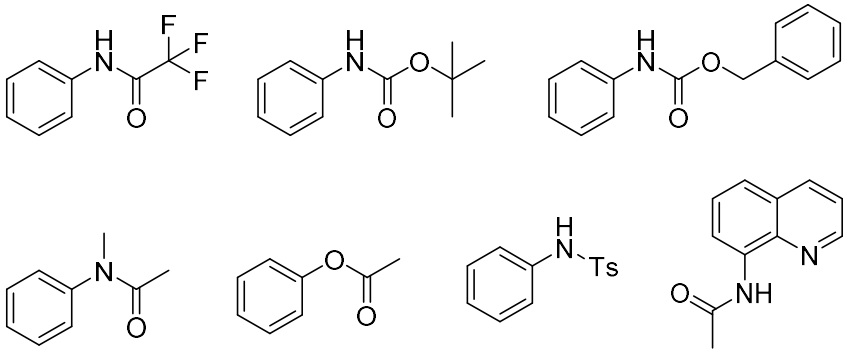
4. Experimental Procedure for Substrate Scope & Spectroscopic Data of Products

4.1. General procedure for Substrate Scope

To a 3 mL screw capped vial with a spinvane triangular-shaped Teflon stirbar were added acetanilide (0.20 mmol, 1.0 equiv), diazotized Meldrum's acid (0.24 mmol, 1.2 equiv), $[IrCp^*Cl_2]_2$ (2.0 mol %), $AgNTf_2$ (8.0 mol%), NaOAc (12.3 mg, 1.0 equiv) and 1,2-dichloroethane (1.0 mL) under air. The reaction mixture was stirred at 70 °C for 10 h. After the completion of reaction, the reaction mixture was filtered through a pad of celite followed by washing of the pad with CH_2Cl_2 (10 mL x 2). The combined solvents were removed under reduced pressure and the residue was purified by column chromatography (EtOAc/hexane) to obtain the pure product.

4.2. Unsuccessful substrates under standard conditions

a) Unsucessfull N-substituted arylamine

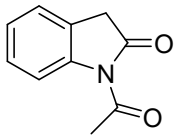


a) Unsucessfull diazo compounds

Figure S1. Some of the unsuccessful substrate (Scheme 2 and 3 in main text)

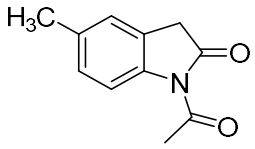
4.3. Spectroscopic data of synthesized compounds

1-Acetylindolin-2-one (3a)[3]



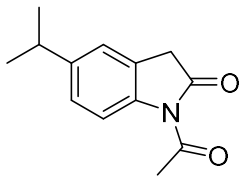
White crystalline solid, 91% yield; mp: 126-128 °C; FT-IR ($CHCl_3$, cm^{-1}): 2921, 2851, 1726, 1698, 1608, 1466, 1372, 1279, 1161, 1040, 759; ^1H NMR (500 MHz, $CDCl_3$) δ 2.68 (s, 3H), 3.73 (s, 2H), 7.20 (td, *J* = 7.48, 0.92 Hz, 1H), 7.26 - 7.30 (m, 1H), 7.30 - 7.36 (m, 1H), 8.22 (d, *J* = 8.24 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.8, 36.6, 116.6, 123.4, 124.0, 124.9, 128.2, 141.3, 171.0, 175.4 ppm. HRMS (ESI+): calcd. for $C_{10}H_{10}O_2N$ $[M+H]^+$: 176.0706, found: 176.0702.

1-Acetyl-5-methylindolin-2-one (3b)



White solid, 95% yield; mp: 146-149 °C; FT-IR ($CHCl_3$, cm^{-1}): 2955, 2922, 2852, 1732, 1698, 1595, 1479, 1466, 1342, 1280, 1161, 1098, 1014, 760; ^1H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.65 (s, 3H), 3.67 (s, 2H), 7.08 (s, 1H), 7.11 (d, *J* = 8.39 Hz, 1H), 8.08 (d, *J* = 8.24 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 26.8, 36.6, 116.2 (s), 123.3 (s), 124.5 (s), 128.5 (s), 134.6 (s), 138.8 (s), 170.8 (s), 175.5 (s) ppm. HRMS (ESI+): calcd. for $C_{11}H_{12}O_3N$ $[M+H]^+$: 190.0863, found: 190.0860.

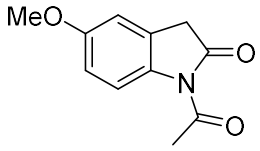
1-Acetyl-5-isopropylindolin-2-one (3c)



Off white solid, 89% yield; mp: 130-132 °C; FT-IR ($CHCl_3$, cm^{-1}): 3026, 2948, 2884, 1755, 1722, 1474, 1388, 1335, 1233, 1174, 742; ^1H NMR (500 MHz, $CDCl_3$): *δ* 1.25 (d, *J* = 7.0 Hz,

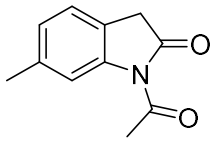
6H), 2.66 (s, 3H), 2.83 - 3.98 (m, 1H), 3.70 (s, 2H), 7.15 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.1, 26.7, 33.8, 36.7, 116.4, 121.9, 123.4, 126.1, 139.2, 145.8, 170.8, 175.6 ppm; HRMS (ESI+): calcd. for $C_{13}H_{16}O_2N$ $[M+H]^+$: 218.1176, found: 218.1172.

1-Acetyl-5-methoxyindolin-2-one (3d)



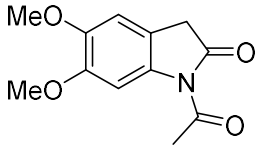
Brown solid, 92% yield; mp: 139-142 °C; FT-IR ($CHCl_3$, cm^{-1}): 3122, 2980, 2854, 1766, 1712, 1410, 1371, 1263, 1179, 1062, 835; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.66 (s, 3H), 3.71 (s, 2H), 3.82 (s, 3H), 6.76 - 6.91 (m, 2H), 8.06 - 8.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7, 36. 9, 55.5, 110.2, 112.5, 117.5, 124.8, 134.7, 156.9, 170.6, 175.3 ppm; HRMS (ESI+): calcd. for $C_{11}H_{12}O_3N$ $[M+H]^+$: 206.0812, found: 206.0808.

1-Acetyl-6-methylindolin-2-one (3e)



White solid, 74% yield; mp: 125-127 °C; FT-IR ($CHCl_3$, cm^{-1}): 3122, 2980, 2854, 1726, 1671, 1599, 1410, 1371, 1263, 1179, 1062, 835; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.67 (s, 3H), 3.68 (s, 2H), 7.01 (d, J = 7.5 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 8.07 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.9, 26.9, 36.4, 117.2, 120.2, 123.6, 125.5, 138.2, 141.2, 171.1, 175.9 ppm; HRMS (ESI+): calcd. for $C_{11}H_{12}O_2N$ $[M+H]^+$: 190.0863, found: 190.0860.

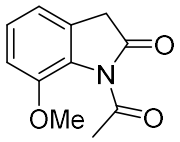
1-Acetyl-5,6-dimethoxyindolin-2-one (3f)



Off white solid, 62% yield; mp: 165-167 °C; FT-IR ($CHCl_3$, cm^{-1}): 2998, 2923, 1722, 1688, 1442, 1385, 1252, 682; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.66 (s, 3H), 3.67 (s, 2H), 3.88 (s, 3H),

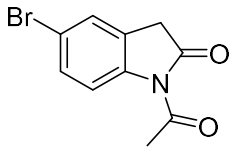
3.93 (s, 3H), 6.81 (s, 1H), 7.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7, 36.6, 56.1, 101.6, 106.9, 114.3, 134.7, 146.3, 148.2, 170.8, 175.8 ppm; HRMS (ESI+): calcd. for $C_{12}H_{14}O_4N$ $[M+H]^+$: 236.0917, found: 236.0915.

1-Acetyl-7-methoxylindolin-2-one (3g)



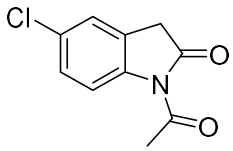
Off white solid, 55% yield; mp: 89-91 °C; FT-IR ($CHCl_3$, cm^{-1}): 2960, 2918, 2851, 1750, 1731, 1608, 1492, 1365, 1300, 1266, 1213, 1169, 1017, 772; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.65 (s, 3H), 3.70 (s, 2H), 3.88 (s, 3H), 6.89 (dd, J = 7.4, 1.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 7.14 - 7.19 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.6, 37.5, 56.0, 112.1, 116.4, 126.0, 126.1, 129.1, 147.3, 169.7, 175.1 ppm; HRMS (ESI+): calcd. for $C_{11}H_{12}O_3N$ $[M+H]^+$: 206.0812, found: 206.0810.

1-Acetyl-5-bromoindolin-2-one (3h)



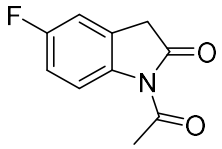
White solid, 82% yield; mp: 139-141 °C; FT-IR ($CHCl_3$, cm^{-1}): 2980, 2912, 2823, 1732, 1686, 1583, 1488, 1429, 1326, 1292, 1083, 1026, 785; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.67 (s, 3H), 3.72 (s, 2H), 7.40 - 7.42 (m, 1H), 7.44 (dt, J = 8.7, 1.0 Hz, 1H), 8.11 (d, J = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7, 36.2, 117.9, 118.1, 125.4, 127.0, 131.1, 140.2, 170.8, 174.4 ppm; HRMS (ESI+): calcd. for $C_{10}H_9O_2NBr$ $[M+H]^+$: 253.9811 and 255.9791, found: 253.9809 and 255.9788.

1-Acetyl-5-chloroindolin-2-one (3i)



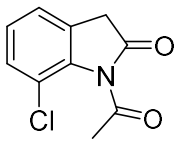
White solid, 78% yield; mp: 121-123 °C; FT-IR ($CHCl_3$, cm^{-1}): 2952, 2924, 2878, 1719, 1676, 1608, 1509, 1463, 1369, 1245, 1031, 828; ^1H NMR (500 MHz, $CDCl_3$): δ 2.68 (s, 3H), 3.74 (s, 2H), 7.28 (s, 1H), 7.31 (dt, J = 8.7, 1.0 Hz, 1H), 8.18 (d, J = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.8, 36.4, 117.8, 124.2, 125.1, 128.2, 130.3, 139.7, 170.8, 174.6 ppm; HRMS (ESI+): calcd. for $C_{10}H_9O_2NCl$ $[M+H]^+$: 210.0316, found: 210.0313.

1-Acetyl-5-fluoroindolin-2-one (3j)



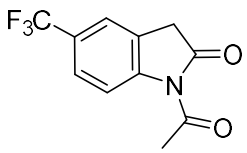
Off white solid, 80% yield; mp: 106-107 °C; FT-IR ($CHCl_3$, cm^{-1}): 3026, 2948, 1736, 1682, 1475, 1388, 1335, 1233, 1203, 1174, 1081, 742; ^1H NMR (500 MHz, $CDCl_3$): δ 2.67 (s, 3H), 3.72 (s, 2H), 6.89 - 7.12 (m, 2H), 8.21 (dd, J = 8.6, 4.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.5, 36.7, 112.3 (d, J = 24.5 Hz), 115.5 (d, J = 24.7 Hz), 118.1 (d, J = 8.2 Hz), 125.2 (d, J = 8.7 Hz), 137.4, 162.4 (d, J = 244.1 Hz), 170.7, 174.8 ppm; HRMS (ESI+): calcd. for $C_{10}H_9O_2NF$ $[M+H]^+$: 194.0612, found: 194.0610.

1-Acetyl-7-chloroindolin-2-one (3k)



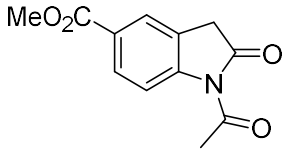
White solid, 47% yield; mp: 120-122 °C; FT-IR ($CHCl_3$, cm^{-1}): 2968, 2922, 2878, 1722, 1676, 1608, 1510, 1463, 1369, 1245, 1031, 828; ^1H NMR (500 MHz, $CDCl_3$): δ 2.71 (s, 3H), 3.75 (s, 2H), 7.11 - 7.16 (m, 1H), 7.17 - 7.21 (m, 1H), 7.31 - 7.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7, 37.3, 121.3, 122.4, 125.9, 127.1, 130.2, 138.2, 169.9, 174.7 ppm; HRMS (ESI+): calcd. for $C_{10}H_9O_2NCl$ $[M+H]^+$: 210.0316, found: 210.0314.

1-Acetyl-5-(trifluoromethyl)indolin-2-one (3l)



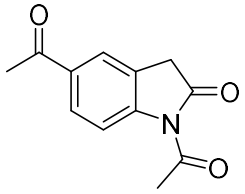
Off white solid, 64% yield; mp: 124-127 °C; FT-IR ($CHCl_3$, cm^{-1}): 3029, 2944, 2852, 1866, 1702, 1609, 1487, 1429, 1375, 1308, 1210, 1162, 1035, 967, 896,761; ^1H NMR (500 MHz, $CDCl_3$): δ 2.70 (s, 3H), 3.78 (s, 2H), 7.54 (s, 1H), 7.61 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.6, 36.3, 116.7, 121.1 (q, J = 3.6 Hz), 124.0 (q, J = 172.0 Hz), 124.1, 125.8 (q, J = 3.6 Hz), 127.2 q, J = 32.7 Hz, 144.0, 170.8, 174.4 ppm; HRMS (ESI-): calcd. for $C_{11}H_7O_2NF$ [M-H]: 242.0429, found: 242.0425.

Methyl 1-acetyl-2-oxoindoline-5-carboxylate (3m)



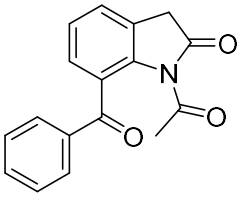
White solid, 72% yield; mp: 154-155 °C; FT-IR ($CHCl_3$, cm^{-1}): 3028, 2982, 2943, 1772, 1702, 1487, 1430, 1375, 1307, 1274, 1180, 1024, 834; ^1H NMR (500 MHz, $CDCl_3$): δ 2.70 (s, 3H), 3.78 (s, 2H), 3.93 (s, 3H), 7.96 (s, 1H), 8.02 - 8.06 (m, 1H), 8.25 - 8.30 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.8, 36.3, 52.3, 116.2, 123.5, 125.2, 126.6, 130.3, 144.9, 166.4, 170.9, 174.9 ppm; HRMS (ESI+): calcd. for $C_{12}H_{11}O_4NNa$ $[M+Na]^+$: 256.0580, found: 256.0577.

Methyl 1-acetyl-2-oxoindoline-5-carboxylate (3n)



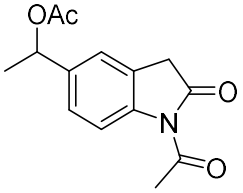
Off white solid, 83% yield; mp: 169-172 °C; FT-IR ($CHCl_3$, cm^{-1}): 2980, 2925, 2853, 1761, 1736, 1709, 1597, 1488, 1371, 1302, 1240, 1180, 772; ^1H NMR (500 MHz, $CDCl_3$): δ 2.61 (s, 3H), 2.70 (s, 3H), 3.77 (s, 2H), 7.90 (s, 1H), 7.94 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.5, 26.7, 36.3, 116.2, 123.8, 123.9, 129.5, 133.9, 145.1, 170.9, 174.8, 196.8 ppm; HRMS (ESI+): calcd. for $C_{12}H_{12}O_3N$ $[M+H]^+$: 218.0817, found: 218.0815.

Methyl 1-acetyl-2-oxoindoline-5-carboxylate (3o)



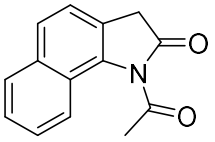
Off white solid, 52% yield; mp: 128-131 °C; FT-IR ($CHCl_3$, cm^{-1}): 3032, 2815, 2855, 1767, 1722, 1676, 1609, 1488, 1350, 1312, 1285, 1247, 1020, 841; ^1H NMR (500 MHz, $CDCl_3$): δ 2.51 (s, 3H), 3.82 (s, 2H), 7.22 - 7.27 (m, 1H), 7.29 - 7.34 (m, 1H), 7.42 (dd, J = 7.2, 1.1 Hz, 1H), 7.46 - 7.52 (m, 2H), 7.56 - 7.63 (m, 1H), 7.90 (dd, J = 8.3, 1.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.8, 37.1, 124.5, 125.3, 126.0, 127.8, 128.2, 128.4, 130.1, 133.0, 136.7, 137.7, 170.7, 174.6, 194.1 ppm; HRMS (ESI+): calcd. for $C_{17}H_{14}O_3N$ $[M+H]^+$: 280.0974, found: 280.0972.

Methyl 1-acetyl-2-oxoindoline-5-carboxylate (3p)



Off white solid, 80% yield; mp: 105-110 °C; FT-IR ($CHCl_3$, cm^{-1}): 2988, 2815, 2865, 1757, 1702, 1676, 1609, 1485, 1370, 1332, 1285, 1267, 1020, 841; ^1H NMR (500 MHz, $CDCl_3$): δ 1.53 (d, J = 6.6 Hz, 3H), 2.07 (s, 3H), 2.67 (s, 3H), 3.72 (s, 2H), 5.85 (q, J = 6.6 Hz, 1H), 7.28 (s, 1H), 7.31 (d, J = 8.9 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3, 22.2, 26.6, 36.6, 71.9, 116.6, 121.9, 123.7, 126.1, 138.6, 140.9, 170.3, 170.8, 175.2 ppm; HRMS (ESI+): calcd. for $C_{14}H_{16}O_4N$ $[M+H]^+$: 262.1079, found: 262.1078.

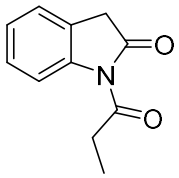
1-Acetyl-1,3-dihydro-2H-benzo[g]indol-2-one (3q)



Off white solid, 54% yield; mp: 112-115 °C; FT-IR ($CHCl_3$, cm^{-1}): 3020, 2956, 2836, 1765, 1697, 1595, 1481, 1370, 1300, 1172, 1015, 830; ^1H NMR (500 MHz, $CDCl_3$): δ 2.83 (s, 3H), 3.88 (s, 2H), 7.38 (d, J=8.2 Hz, 1H), 7.44 - 7.53 (m, 2H), 7.58 - 7.62 (m, 1H), 7.76 (d, J = 8.2

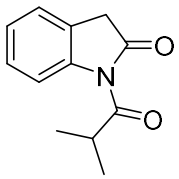
Hz, 1H), 7.84 - 7.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7, 38.1, 121.1, 121.9, 122.7, 124.4, 125.7, 125.7, 127.1, 128.9, 134.0, 136.2, 171.3, 176.5 ppm; HRMS (ESI+): calcd. for $C_{14}H_{12}O_2N$ $[M+H]^+$: 226.0863, found: 226.0862.

1-Propionylindolin-2-one (3r)



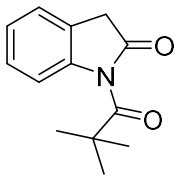
Off white solid, 88% yield; mp: 108-110 °C; FT-IR ($CHCl_3$, cm^{-1}): 3026, 2948, 2884, 1735, 1682, 1621, 1474, 1388, 1335, 1233, 1174, 742; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (t, J = 7.2 Hz, 3H), 3.08 (q, J = 7.2 Hz, 2H), 3.71 (s, 2H), 7.16 - 7.22 (m, 1H), 7.26 - 7.29 (m, 1H), 7.30 - 7.35 (m, 1H), 8.24 (d, J = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.3, 32.0, 36.7, 116.6, 123.5, 123.9, 124.8, 128.2, 128.2, 141.5, 175.0, 175.3 ppm; HRMS (ESI+): calcd. for $C_{11}H_{12}O_2N$ $[M+H]^+$: 190.0863, found: 190.0860.

1-Isobutyrylindolin-2-one (3s)



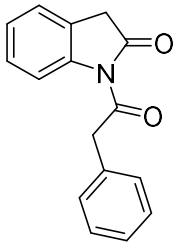
Yellow solid, 92% yield; mp: 88-90 °C; FT-IR ($CHCl_3$, cm^{-1}): 3022, 2985, 2855, 2802, 1736, 1680, 1620, 1475, 1305, 1232, 1203, 946; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (d, J = 6.9 Hz, 6 H), 3.72 (s, 2 H), 3.88 (hept, J = 6.9 Hz, 1 H), 7.14 - 7.21 (m, 1 H), 7.25 - 7.28 (m, 1 H), 7.31 (t, J = 7.9 Hz, 1 H), 8.19 (d, J = 8.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.9 (s), 18.5 - 19.3 (m), 35.0, 36.9, 116.8, 123.6, 123.9, 124.8, 128.2, 141.9, 174.9, 178.6 ppm; HRMS (ESI-): calcd. for $C_{12}H_{12}O_2N$ [M-H]: 202.0868, found: 202.0866.

1-Pivaloylindolin-2-one (3t)



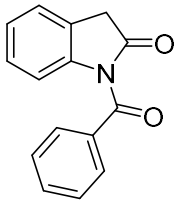
Brown solid, 91% yield; mp: 103-106 °C; FT-IR ($CHCl_3$, cm^{-1}): 3012, 2962, 1736, 1692, 1475, 1388, 1243, 1174, 1081, 742; ^1H NMR (500 MHz, $CDCl_3$): δ 1.43 (s, 9H), 3.67 (s, 2H), 7.09 - 7.16 (m, 1H), 7.21 - 7.32 (m, 2H), 7.45 (d, J = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.8, 36.6, 43.3, 114.2, 124.1, 124.3, 124.5, 128.0, 142.4, 174.0, 182.7 ppm; HRMS (ESI+): calcd. for $C_{13}H_{16}O_2N$ $[M+H]^+$: 218.1176, found: 218.1173.

1-Pivaloylindolin-2-one (3u)



Yellow solid, 68% yield; mp: 109-112 °C; FT-IR ($CHCl_3$, cm^{-1}): 3022, 2985, 2855, 2802, 1736, 1680, 1620, 1475, 1305, 1232, 1203, 946; ^1H NMR (500 MHz, $CDCl_3$): δ 3.73 (s, 2H), 4.43 (s, 2H), 7.15 - 7.20 (m, 1 H), 7.24 - 7.30 (m, 3H), 7.31 - 7.37 (m, 4H), 8.21 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.8, 44.5, 116.8, 123.5, 124.0, 125.0, 127.1, 128.3, 128.5, 129.7, 133.8, 141.5, 171.9, 175.2 ppm; HRMS (ESI+): calcd. for $C_{16}H_{14}O_2N$ $[M+H]^+$: 252.1025, found: 252.1024.

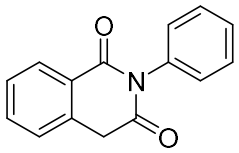
1-Benzoylindolin-2-one (3v-i)



Off white solid, 50% yield; mp: 134-136 °C; FT-IR ($CHCl_3$, cm^{-1}): 3022, 2978, 2836, 1765, 1720, 1559, 1476, 1370, 1300, 1172, 1015, 830; ^1H NMR (500 MHz, $CDCl_3$): δ 3.75 (s, 2H),

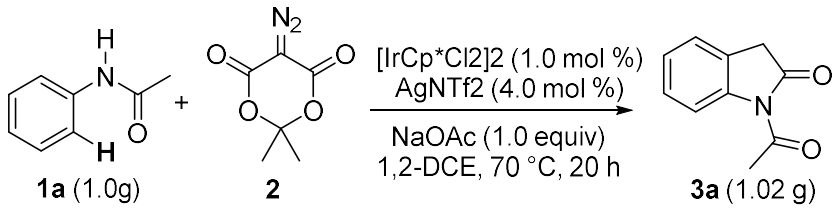
7.18 - 7.23 (m, 1H), 7.31 - 7.38 (m, 2H), 7.44 - 7.50 (m, 2H), 7.57 - 7.62 (m, 1H), 7.74 - 7.78 (m, 2H), 7.80 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.5, 115.0, 123.9, 124.4, 124.7, 128.2, 129.4, 132.9, 134.2, 141.5, 169.5, 174.2 ppm; HRMS (ESI+): calcd. for $C_{15}H_{12}O_2N$ $[M+H]^+$: 238.0863, found: 238.0861.

2-Phenylisoquinoline-1,3(2*H*,4*H*)-dione (3v-ii)[4]



Off white solid, 15% yield; mp: 184-188 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.23 (s, 2H), 7.19 - 7.23 (m, 2H), 7.35 (d, J = 7.6 Hz, 1H), 7.43 - 7.54 (m, 4H), 7.61 - 7.67 (m, 1H), 8.22 - 8.27 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.9, 125.4, 127.3, 127.9, 128.4, 128.7, 129.3, 129.5, 134.0, 134.2, 135.0, 165.0, 169.9 ppm.

5. Gram scale reaction for the synthesis of 3a

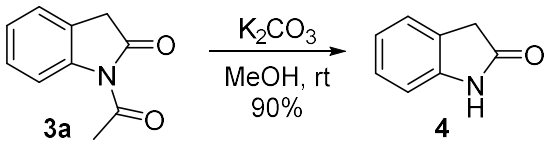


1a (1.0g) **2** **3a** (1.02 g)

N-acetylaniline (**1a**, 1.0g, 7.40 mmol) was added to a 15 mL shield tube along with diazo compound **2** (1.51 g, 8.88 mmol), $[IrCp^*Cl_2]_2$ (59.0 mg, 1.0 mol %), $AgNTf_2$ (115.0 mg, 4.0 mol %), NaOAc (607.0 mg, 7.40 mmol) and 1,2-dichloroethane (10 mL) under atmospheric conditions. The reaction mixture was stirred at 75 °C for 20 hour. Then it was cooled to room temperature and filtered through a pad of celite and the celite pad was washed with EtOAc (15 mL x 3). The solvent was removed under reduced pressure and the residue was purify by column chromatography (EtOAc/Hexane) to afford 1.02 g (78.7%) of the desired product **3a**.

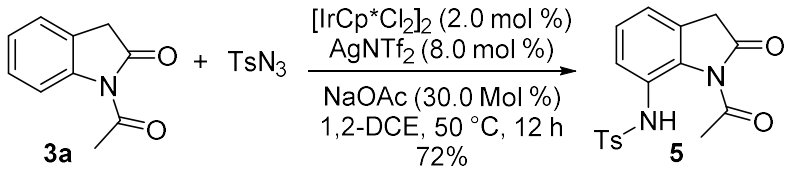
6. Synthetic utility of the synthesized products

6.1. Removal of *N*-acetyl group: Oxyindole (6)[CAS No: 59-48-3]



N-Acetyloxyindole (**3a**, 176.0 mg, 0.10 mmol) and K_2CO_3 (390.0 mg, 0.10 mmol) were placed in a round-bottomed flask and suspended in 5 mL methanol. The resulting mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with dichloromethane (10 mL) and filtered through celite to remove the solid precipitate. The celite pad was wash with dichloromethane (5 mL x 2) and the combined organic solvents were removed under reduced pressure to get the crude product, which upon silica gel column chromatography (n-hexane/ethyl acetate) afford the desired product **4** as off white solid. Yield 120.0 mg, 90 %. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.56 (s, 2H), 6.92 (d, J = 7.8 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 7.19 - 7.25 (m, 2H), 9.47 (br s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 36.3, 109.9, 122.3, 124.5, 125.2, 127.9, 142.5, 178.5 ppm.

6.2. Reaction on the aryl ring: Regioselective C7 amidation

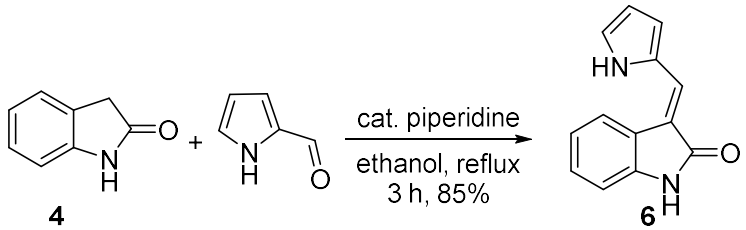


To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added *N*-acetylindolin-2-one (**3a**, 20 mg, 0.11 mmol), sulfonyl azide (27.0 mg, 0.14 mmol), $[IrCp^*Cl_2]_2$ (1.8 mg, 2.0 mol %), $AgNTf_2$ (3.5 mg, 8.0 mol %), NaOAc (2.8 mg, 30.0 mol %) and 1,2-dichloroethane (0.75 mL) under atmospheric conditions. The reaction mixture was stirred at 50 °C for 10 hours and after completion of reaction it was filtered through a pad of celite and then washed with ethylacetate (10 mL × 3). Solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford the desired product **5** (29.0 mg) as sticky brown solid in 72% yield. mp: 114-115 °C; FT-IR ($CHCl_3$,

cm^{-1}): 2954, 2923, 2823, 1757, 1681, 1609, 1479, 1465, 1346, 1285, 1199, 1070, 869, 754; ^1H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.42 (s, 3H), 3.62 (s, 2H), 7.16 (d, *J* = 8.5 Hz, 3H), 7.25 - 7.30 (m, 1H), 7.35 - 7.40 (m, 2 H), 7.46 (d, *J* = 8.2 Hz, 1H), 8.43 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 26.3, 36.4, 122.4, 125.1, 125.3, 126.8, 126.9, 128.1, 129.3, 134.2, 136.7, 143.9, 172.3, 174.5 ppm. ESI-MS (ESI^+) m/z calcd for $C_{17}H_{17}N_2O_4S$ $[M+H]^+$, 345.0904, found, 345.0902.

6.3. Functionalization on C3-carbon

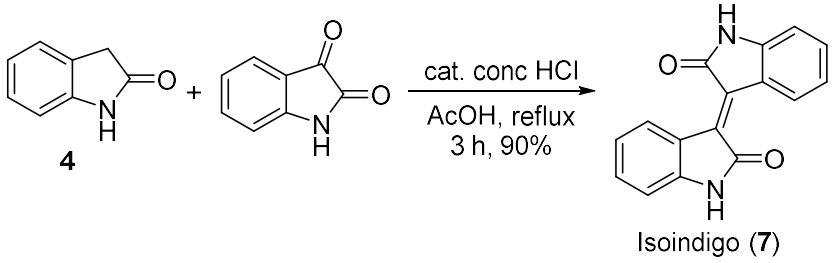
6.3.1. (E)-3-((1H-pyrrol-2-yl)methylene)indolin-2-one (6)[5]



4 6

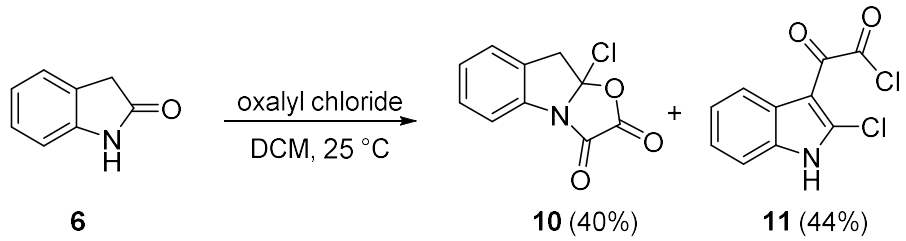
Oxyindole (**4**, 20.0 mg, 0.15 mmol) and 1*H*-pyrrole-2-carbaldehyde (14.3 mg, 0.15 mmol) were placed in a round-bottomed flask and suspended in 2 mL ethanol and two drops of piperidine. The resulting reaction mixture was refluxed for 3 hours. After cooling to room temperature, ethanol was removed and the residue was purified by column chromatography to afford the desired product **6**, as yellow solid. Yield 27.0 mg, 85 %; Mp: 148-152 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 6.34 - 6.41 (m, 1H), 6.75 - 6.82 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 7.02 - 7.09 (m, 1H), 7.15 - 7.20 (m, 2H), 7.45 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 8.06 (br s., 1H), 13.28 (br s., 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.5, 111.7, 116.2, 118.1, 120.6, 121.9, 125.5, 126.8, 129.9, 137.6, 169.5 ppm. ESI-MS (ES^+) m/z calcd for $C_{16}H_{10}N_2O_2$, 262.0742, found, 285.1973 $(M+Na)^+$.

6.3.2. Reaction with isatin: synthesis of Isoindigo (7)[6]



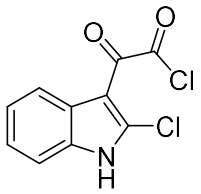
Indolin-2-one (**3a**, 20.0 mg, 0.15 mmol) and Isatin (22.1 mg, 0.15 mmol) were placed in a round-bottomed flask and suspended in 1 mL glacial acetic acid and two drops of concentrated hydrochloric acid. The resulting mixture was refluxed for 3 hours. The solution was allowed to cool to room temperature and the resulting solid product was filtered off and washed thoroughly with cold methanol, water, sodium bicarbonate solution and eventually pentane to afford the desired product **7** as dark reddish solid in analytically pure form. Yield 35.5 mg, 90 %; mp: 158 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.84 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 7.26 - 7.44 (m, 1H), 9.06 (d, *J* = 7.9 Hz, 1H), 10.90 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 109.5, 121.1, 121.7, 129.3, 132.6, 133.3, 144.1, 169.0 ppm.

6.4. Reaction on C3 and/or C2 carbon: Reaction with oxalyl chloride[7]



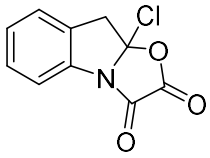
To a stirred solution of oxyindole (**6**, 200.0 mg, 1.50 mmol) in anhydrous dichloromethane was treated with oxalyl chloride (209.7 mg, 1.65 mmol) with drop wise addition at room temperature. After completion of addition, the reaction mixture was stirred until complete conversion as indicated by TLC. Compound **8** (140.0 mg, 40%) forms as precipitate which can be separate by filtration and the filtrate contains compound **9** (160.0 mg, 44%).

2-(2-Chloro-1H-indol-3-yl)-2-oxoacetyl chloride (8)[7]



Brown solid; 44 % yield; mp: 142-145 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.22 - 7.36 (m, 2H), 7.41 - 7.54 (m, 1H), 8.05 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 107.3 (s), 111.9, 120.2, 123.1, 124.1, 125.5, 132.6, 134.6, 167.0, 182.9 ppm.

9a-Chloro-9,9a-dihydrooxazolo[3,2-a]indole-2,3-dione (9)[7]

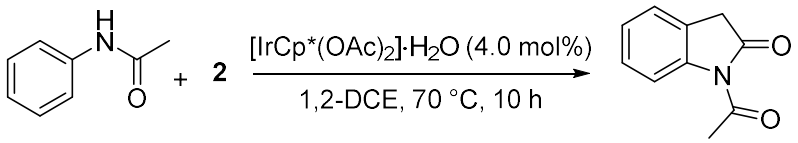


Sticky solid; 40% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 2H), 7.29 - 7.34 (m, 1H), 7.35 - 7.43 (m, 2H), 8.06 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.2, 115.7, 124.0, 124.8, 126.7, 128.8, 137.9, 155.9, 159.8, 174.4 ppm.

7. Experimental Procedures of the Mechanistic Studies

7.1. Control reaction on other Ir(III)-Catalyst

7.1.1. Reaction with [IrCp*(OAc)$_2$]·H$_2$O without any additive

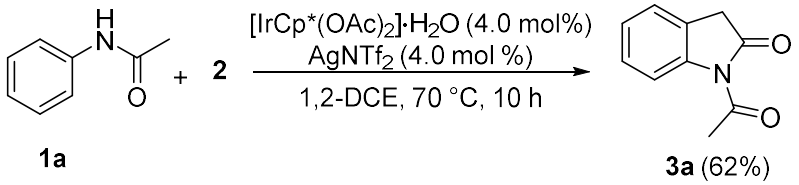


1a **3a** (<10%)

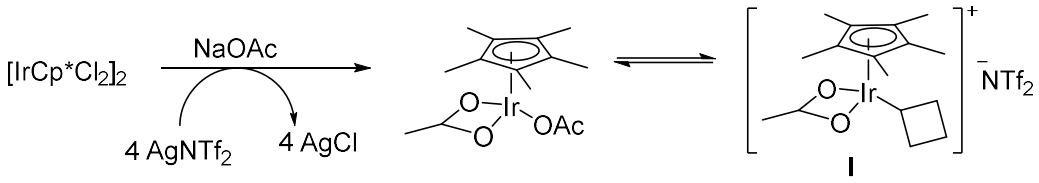
To a 3 mL screw capped vial with a spinvane triangular-shaped Teflon stirbar were added acetanilide (**1a**, 13.6 mg, 0.1 mmol), diazotized Meldrum's acid (**2**, 23.02 mg, 0.12 mmol), [IrCp*(OAc)$_2$]·H$_2$O (4.0 mol %) and 1,2-DCE (1.0 mL) under air. The reaction mixture was stirred in a pre-heated oil bath at the indicated temperature for 10 h. The reaction mixture was cooled to room temperature, filtered through a pad of celite and the pad was washed with CH_2Cl_2

(5 mL x 3). Combined solvents were removed under reduced pressure and the crude yield was measured by ^{1}H NMR spectrum using an internal standard (dibromomethane).

7.1.2. Reaction with $[IrCp^*(OAc)_2]\cdot H_2O$ and $AgNTf_2$

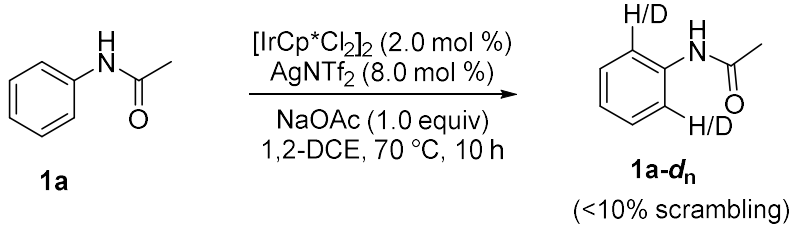


To a 3 mL screw capped vial with a spinvane triangular-shaped Teflon stirbar were added acetanilide (**1a**, 13.6 mg, 0.1 mmol), diazotized Meldrum's acid (**2**, 23.02 mg, 0.12 mmol), $[IrCp^*(OAc)_2]\cdot H_2O$ (4.0 mol %), AgNTf2 (4.0 mol %) and 1,2-DCE (1.0 mL) under air. The reaction mixture was stirred in a pre-heated oil bath at the indicated temperature for 10 h. The reaction mixture was cooled to room temperature, filtered through a pad of celite and the pad was washed with CH_2Cl_2 (5 mL x 3). Combined solvents were removed under reduced pressure and the crude yield was measured by ^{1}H NMR spectrum using an internal standard (dibromomethane), which shows 62% of **3a** was formed. This result indicates the putative involvement of **I** as active catalytic species.

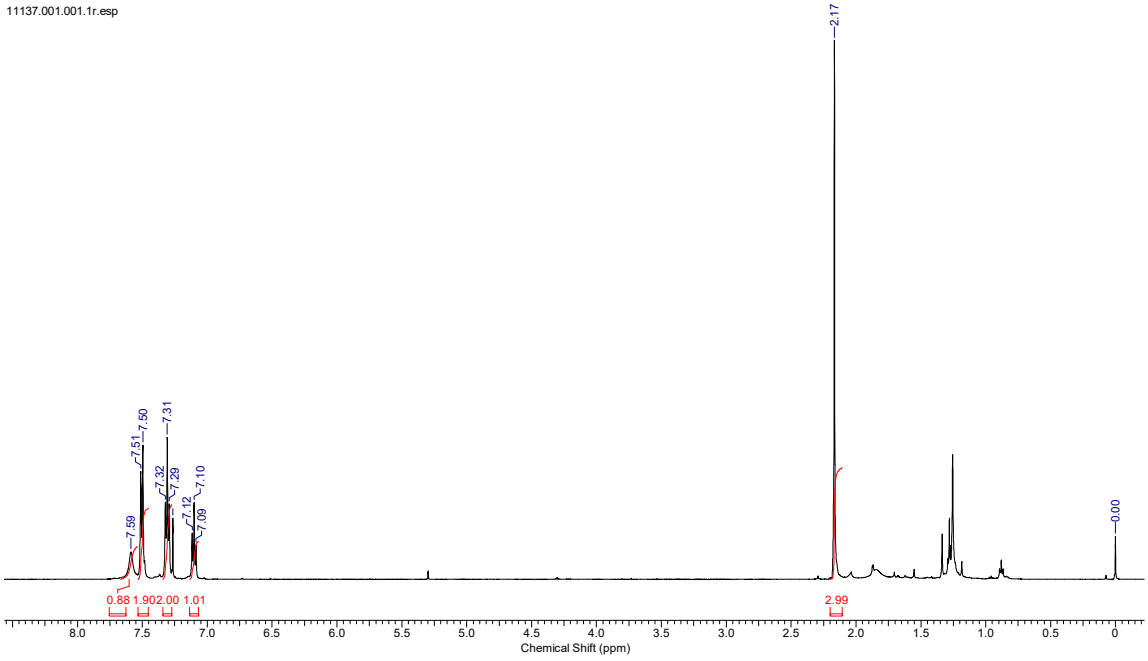


Scheme S1. Plausible formation of active catalytic species.

7.2. Deuterium Exchange Study in absence of Diazo compound



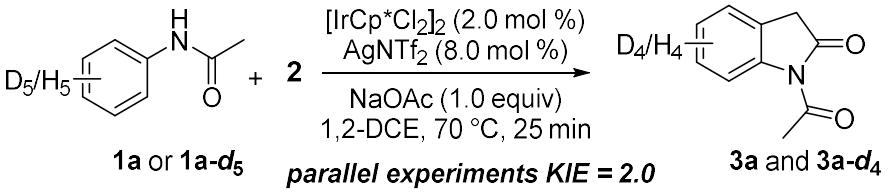
To a screw capped vial with a spinvane triangular-shaped Teflon stirbar were added *N*-acetylaniline (**1a**, 20.3 mg, 0.15 mmol), $[IrCp^*Cl_2]_2$ (2.4 mg, 2.0 mol %), $AgNTf_2$ (4.7 mg, 8.0 mol %), NaOAc (12.3 mg, 0.15 mmol), 1,2-dichloroethane (1.0 mL) and D_2O (100 µL) under air. The reaction mixture was stirred at 70 °C for 10 h. Next, the reaction mixture was cooled and filtered through a pad of celite and then the celite pad was washed with CH_2Cl_2 (5 mL x 3). Solvents were removed under reduced pressure and the compound was analyzed by ^{1}H NMR analysis which shows negligible (<10%) deuterium scrambling.



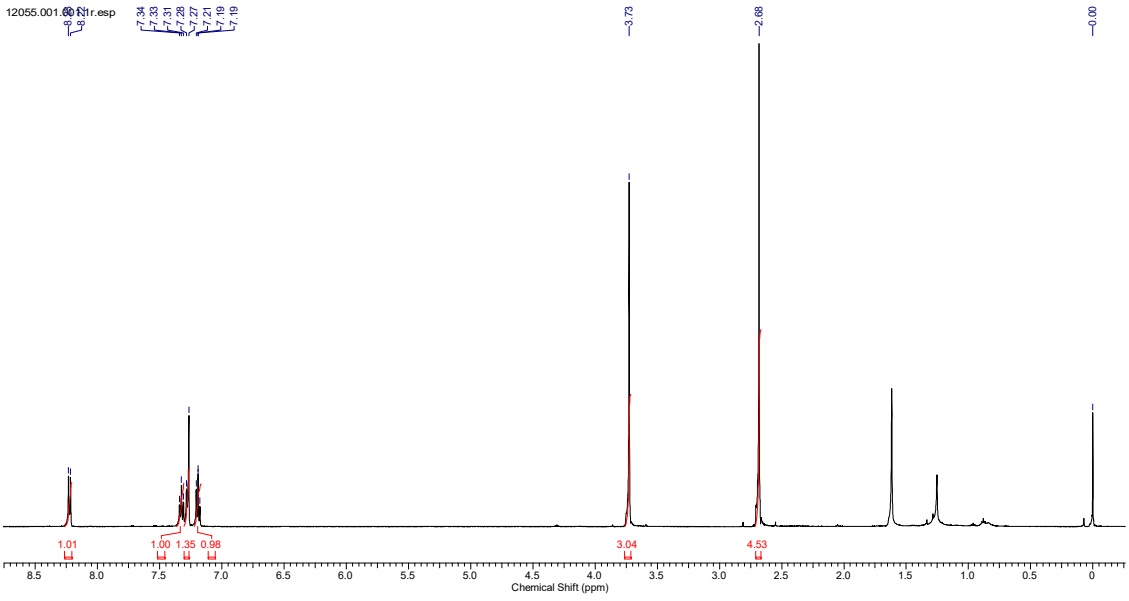
^{1}H NMR spectra of **1a-*d*$_n$** in $CDCl_3$

7.3. Study of Kinetic Isotop Effect

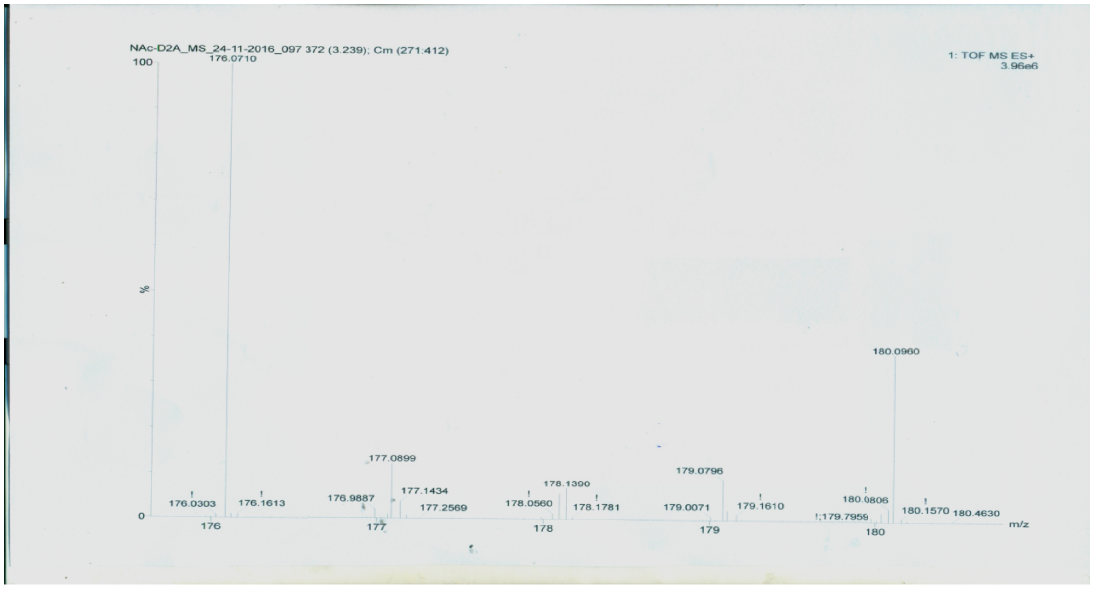
7.3.1. Parallel experiments



N-acetylaniline (**1a**, 13.6 mg, 0.1 mmol) or *N*-acetylaniline-d_5 (**1a-*d*$_5$**, 14.1 mg, 0.1 mmol) were added to two separate screw capped vials with spinvane triangular-shaped Teflon stirbar, along with diazo compound **2** (17.1 mg, 0.1 mmol), $[IrCp^*Cl_2]_2$ (1.6 mg, 2.0 mol %), $AgNTf_2$ (3.1 mg, 8.0 mol %), NaOAc (8.3 mg, 0.1 mmol) and 1,2-dichloroethane (0.75 mL) under atmospheric conditions. Each of the reaction mixture was stirred at 70 °C for 25 min. After cooling to room temperature, both the reaction mixture were combined and filtered through a pad of celite and the celite pad was washed with EtOAc (5 mL x 3). The solvent was removed under reduced pressure and the residue was purify by column chromatography (EtOAc/Hexane) to afford the mixture of **3a** and **3a-*d*$_4$**. From the ^{1}H NMR analysis the KIE was measure to be 2.0.

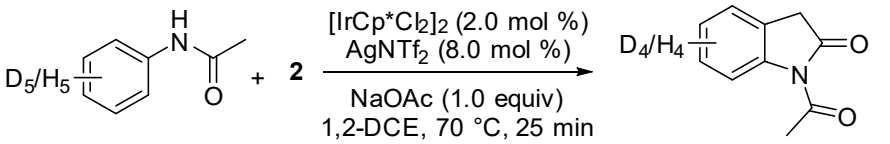


^{1}H NMR spectra of **3a** and **3a-*d*$_4$** in $CDCl_3$



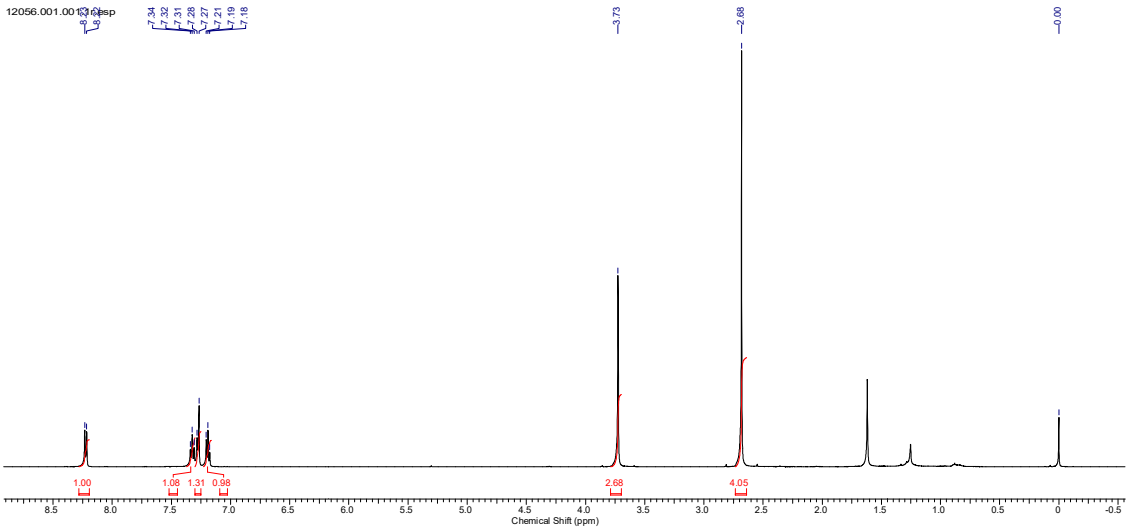
HRMS spectra of **3a** and **3a-*d*$_4$**

7.3.2. Competitive experiments

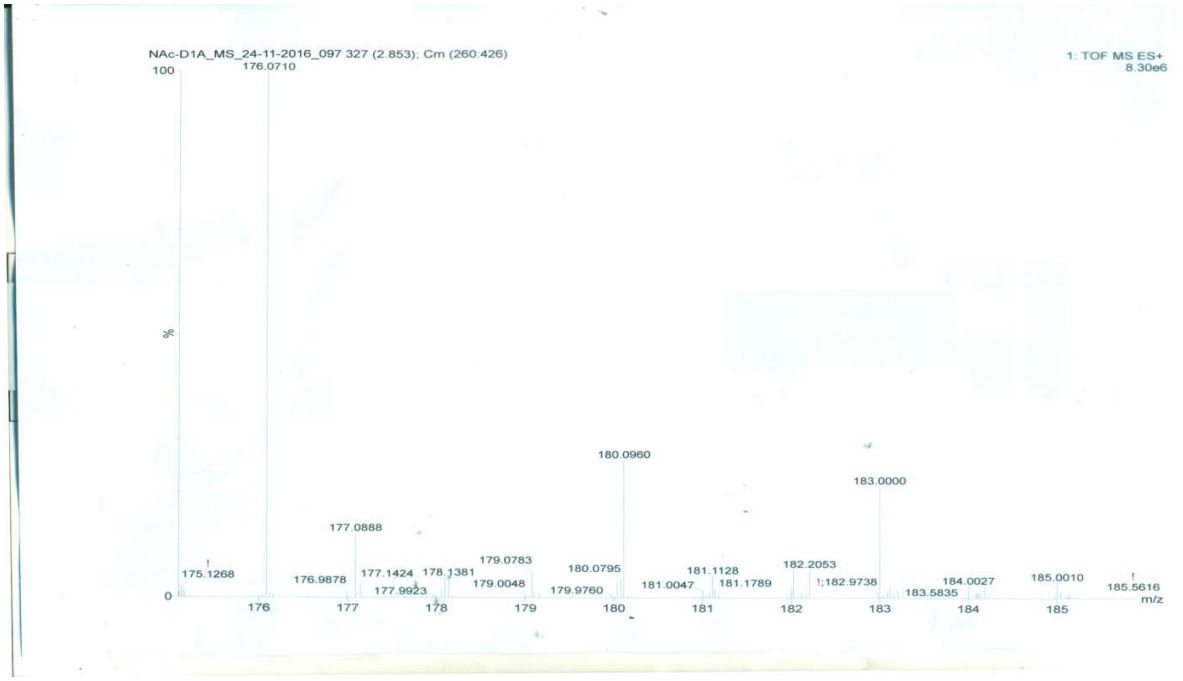


1a + **1a-*d*$_5$** ***Competitive experiments KIE = 2.9*** **3a** and **3a-*d*$_4$**

N-acetylaniline (**1a**, 13.6 mg, 0.1 mmol) and *N*-acetylaniline-d_5 (**1a-*d*$_5$**, 14.1 mg, 0.1 mmol) were added to a screw capped vials with spinvane triangular-shaped Teflon stirbar, along with diazo compound **2** (17.1 mg, 0.10 mmol), [IrCp*Cl_2]$_2$ (1.6 mg, 2.0 mol %), $AgNTf_2$ (3.1 mg, 8.0 mol %), NaOAc (8.3 mg, 0.1 mmol) and 1,2-dichloroethane (0.75 mL) under atmospheric conditions. The reaction mixture was stirred at 70 °C for 25 min. After cooling, the reaction mixture was filtered through a pad of celite and the celite pad was washed with EtOAc (5 mL x 3). The solvent was removed under reduced pressure and the residue was purify by column chromatography (EtOAc/Hexane) to afford the mixture of **3a** and **3a-*d*$_4$**. From the ^{1}H NMR analysis the KIE was measure to be 2.9.



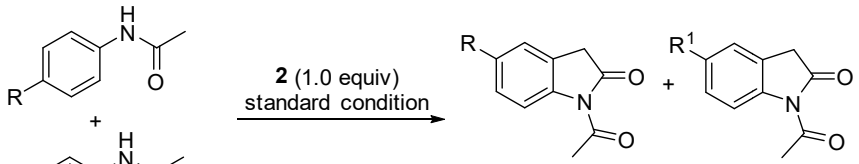
^{1}H NMR spectra of **3a** and **3a-*d*$_4$** in $CDCl_3$.



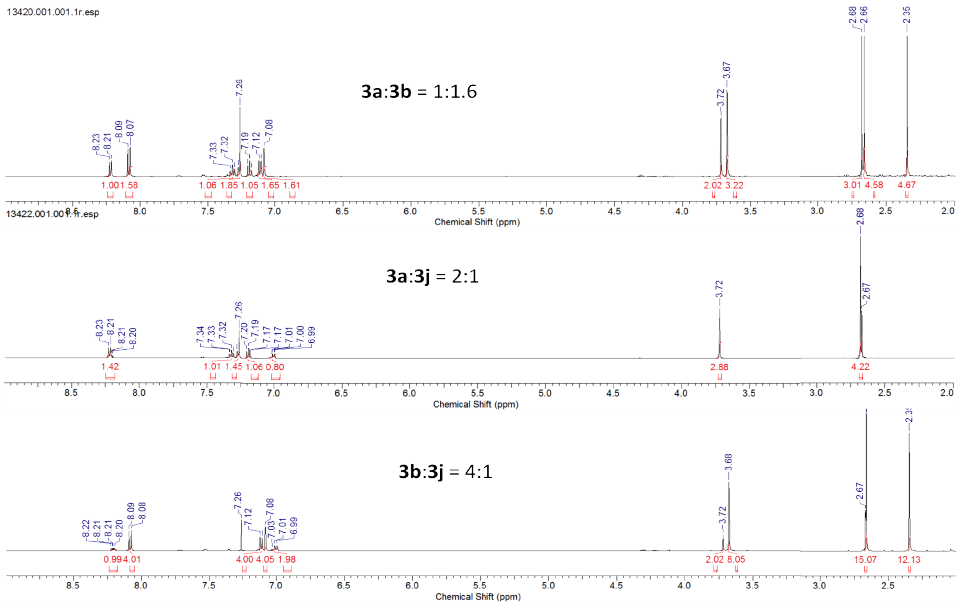
HRMS spectra of **3a** and **3a-*d*$_4$**

7.4. Competitive experiments

Acetanilide (**1a**, 13.6 mg, 0.1 mmol) and 4-methylacetanilide (**1b**, 14.9 mg, 0.1 mmol) were added to a screw capped vials with spinvane triangular-shaped Teflon stirbar, along with diazo compound **2** (17.1 mg, 0.10 mmol), $[IrCp^*Cl_2]_2$ (1.6 mg, 2.0 mol %), $AgNTf_2$ (3.1 mg, 8.0 mol %), NaOAc (8.3 mg, 0.10 mmol) and 1,2-dichloroethane (1 mL) under atmospheric conditions. The reaction mixture was stirred at 70 °C for 2 hours. After cooling, the reaction mixture was filtered through a pad of celite and the celite pad was washed with EtOAc (5 mL x 3). The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc/Hexane) to afford the mixture of **3a** and **3b** and the ratio were calculated from ^{1}H NMR. Same procedure was followed for other experiments and the results were shown in the scheme below.



entry	R	R^1	ratio
1	H	Me	1:1.6
2	H	F	2:1
3	Me	F	4:1



7. References

(S1) S. A. Frith and J. Spencer, *Inorg. Synth.*, 1990, **28**, 273.

(S2) P. M. Boyer, C. P. Roy, J. M. Bielski and J. S. Merola, *Inorg. Chim. Acta*, 1996, **245**, 7.

(S3) W. Lin, M.-H. Hu, X. Feng, L. Fu, C.-P. Cao, Z.-B.uang and D.-Q. Shi, *Tetrahedron Lett.*, 2014, **55**, 2238.

(S4) A. Nakagawa, S. Uno, M. Makishima, H. Miyachi, and Y. Hashimoto, *Bioorg. Med. Chem.*, 2008, **16**, 7046.

(S5) Ngai, M. H.; So, C. L.; Sullivan, M. B.; Ho, H. K.; Chai, C. L. L. *ChemMedChem* **2016**, *11*, 72–80.

(S6) W. Zhang and M.-L. Go, *Bioorg. Med. Chem.*, 2009, **17**, 2077.

(S7) J. Bergman, R. Carlsson and B. Sjöberg, *J. Heterocyclic Chem.*, 1977, **14**, 1123.

8. X-Ray Crystallographic Information for compound 3a

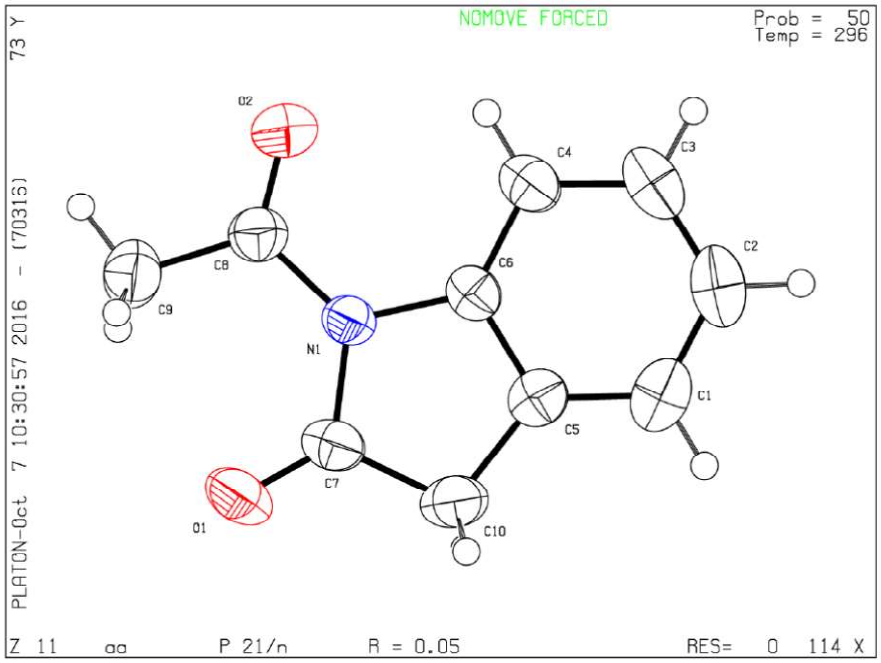


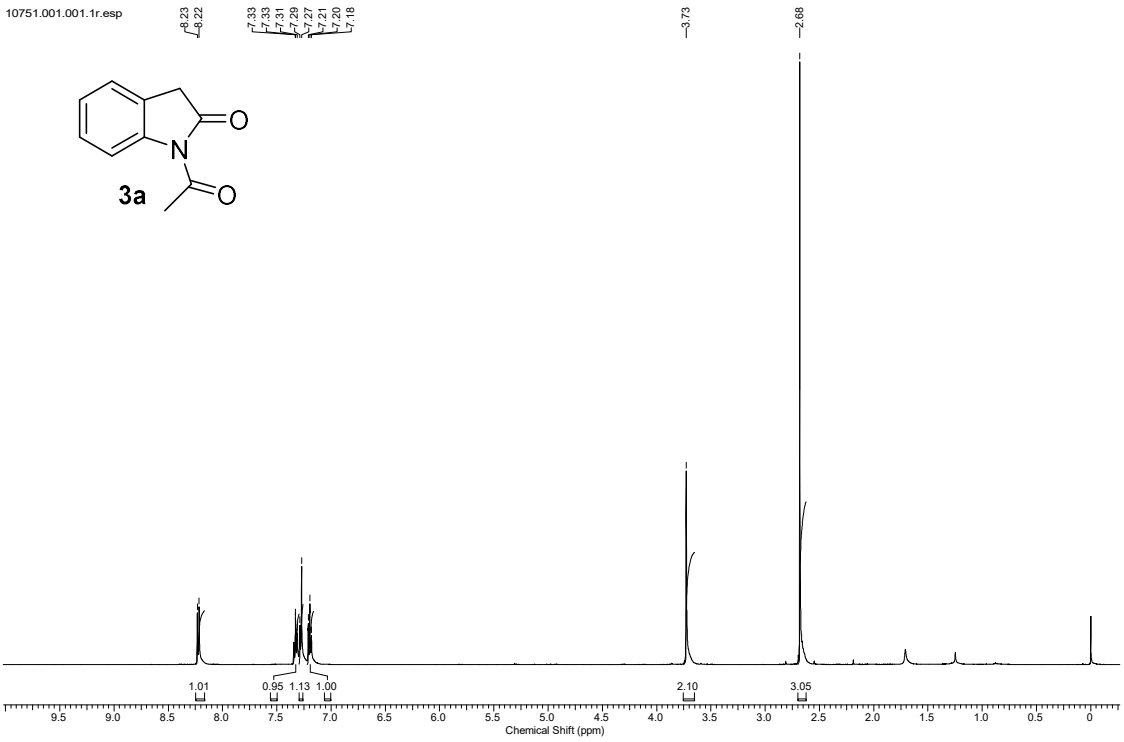
Figure S1. ORTEP diagram of compound **3a**

Table S2. X-ray crystallographic data for compound 3a

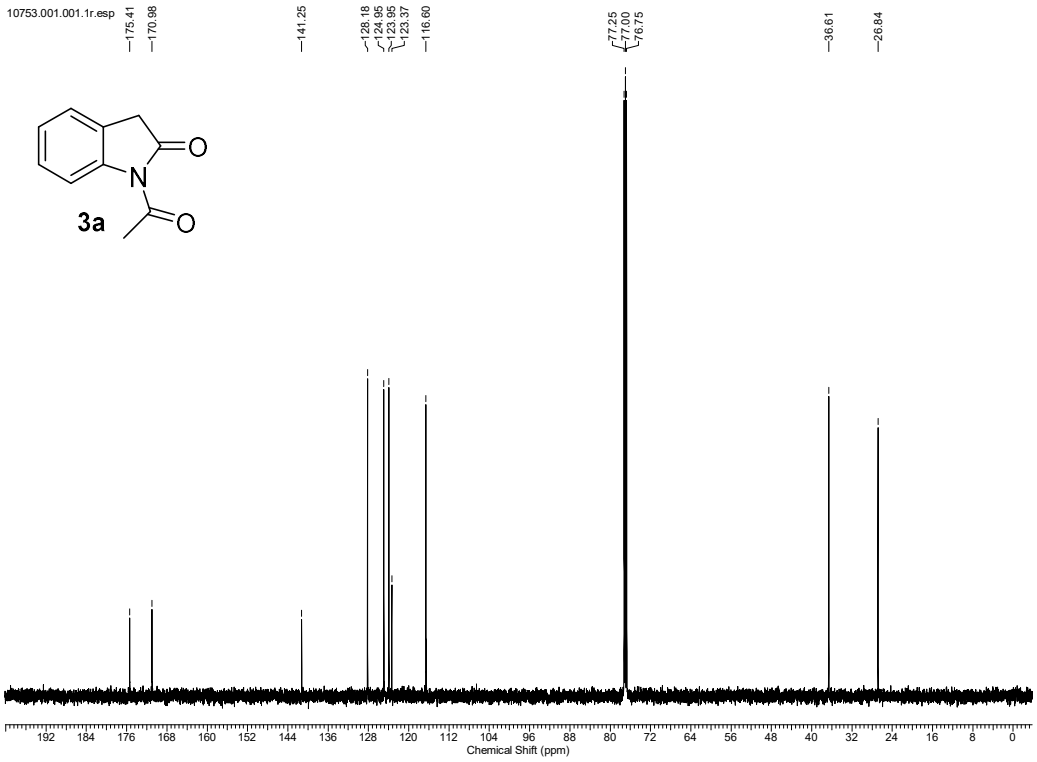
Crystal Data	**Compound 3a**
Formula	$C_{10}H_9NO_2$
Mass	175.18
Temp. (K)	296(2) K
Crystal Syst.	Monoclinic
Space Group	*P-21/n*
a/Å	7.444(8)
b/Å	8.2789(9)
c/Å	13.8475 (15)
$\alpha/^0$	90
$\beta/^0$	93.494(4)
$\gamma/^0$	90
V/Å3	851.86(16)
Z	4
μ/mm^{-1}	0.096
F(000)	368
Ab. Correct.	multi-scan
Tmin/ Tmax	0.8307/0.9200
Total reflns.	21338
h, k, l (min, max)	(-8, 8) (-9, 9) (-16, 16)
No. of para	119
*R*_factor_gt	0.0453
*wR*_factor_ref	0.1399
*R*_factor_all	0.0515
*wR*_factor_gt	0.1298
goodness-offit	1.143
CCDC no.	**1508522**

Spectral Copies of ^{1}H and ^{13}C NMR of Compounds Obtained in this Study

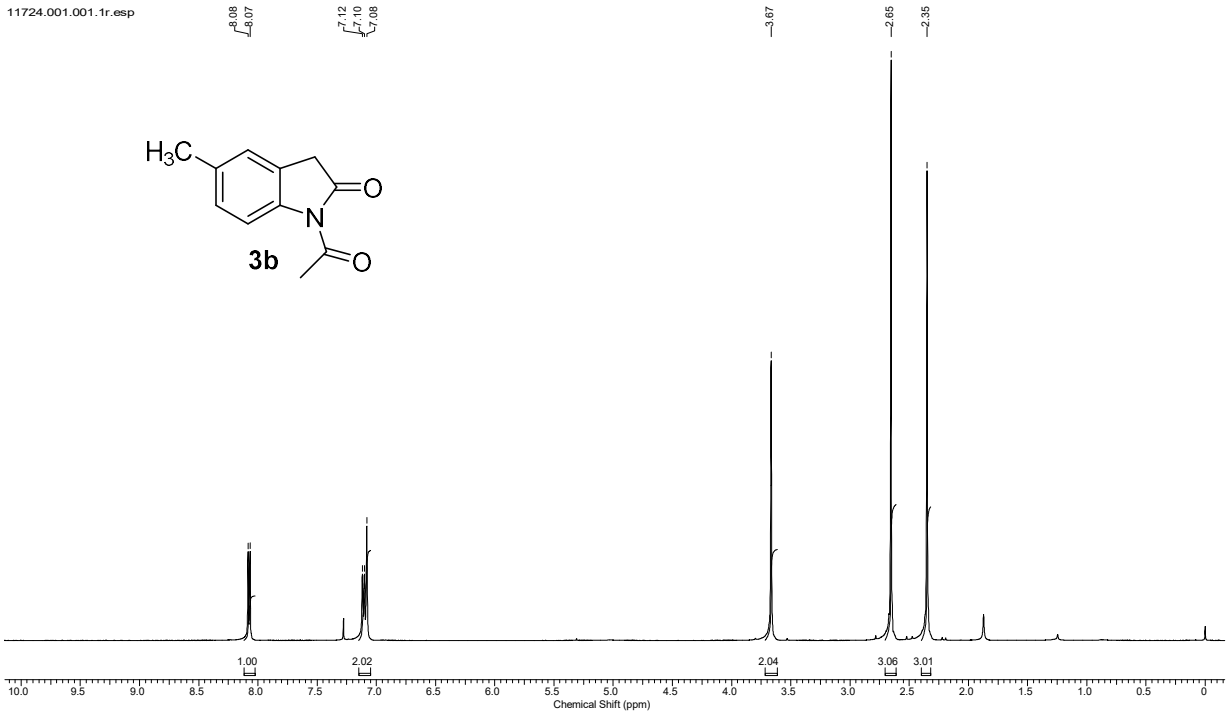
^{1}H NMR of Compound 3a in $CDCl_3$



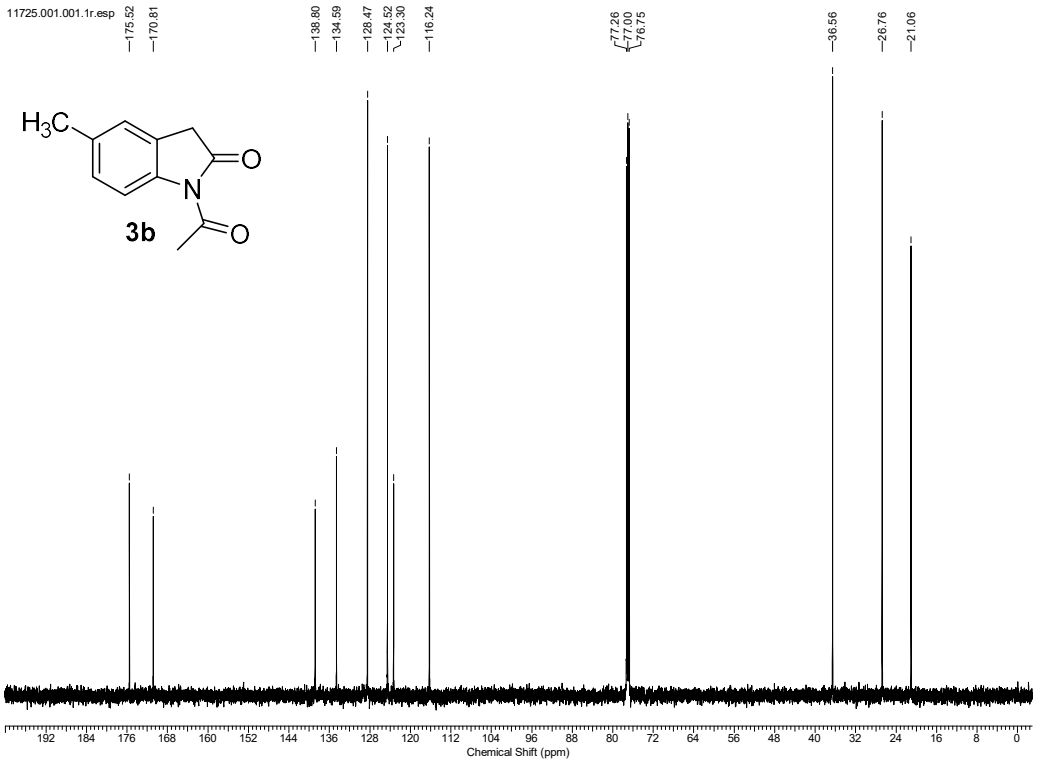
^{13}C NMR of Compound 3a in $CDCl_3$



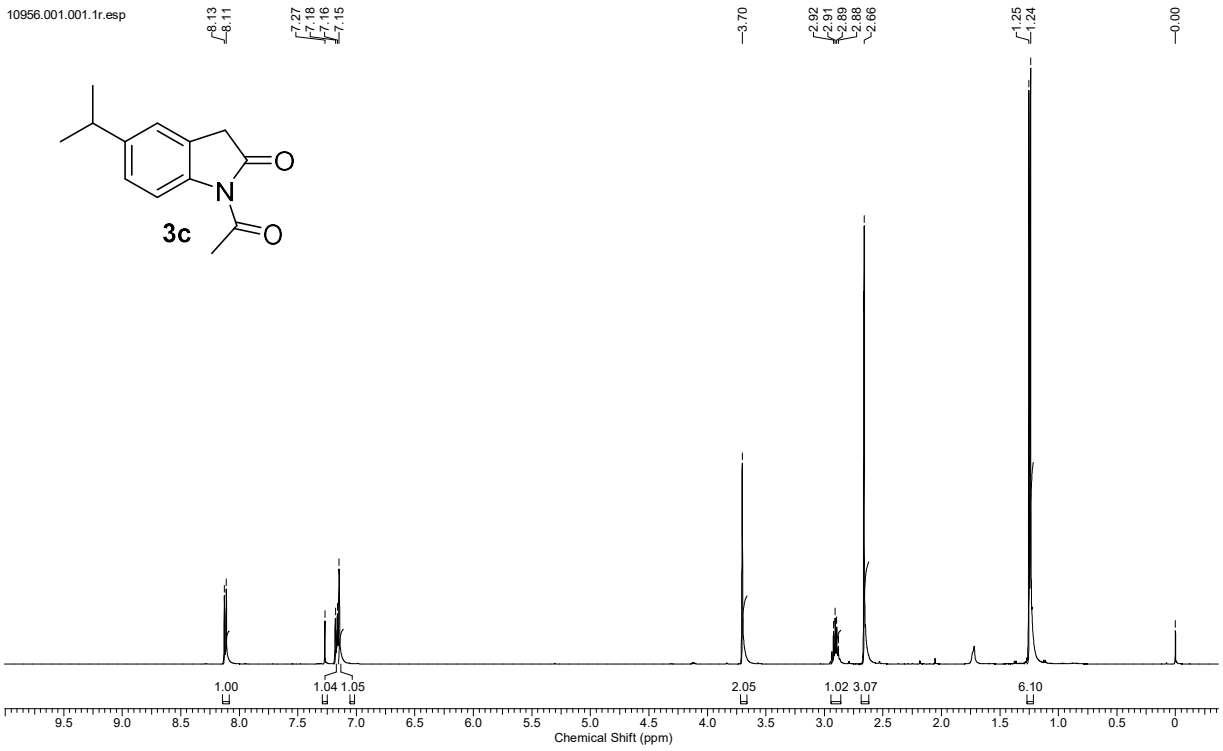
^{1}H NMR of Compound 3b in $CDCl_3$



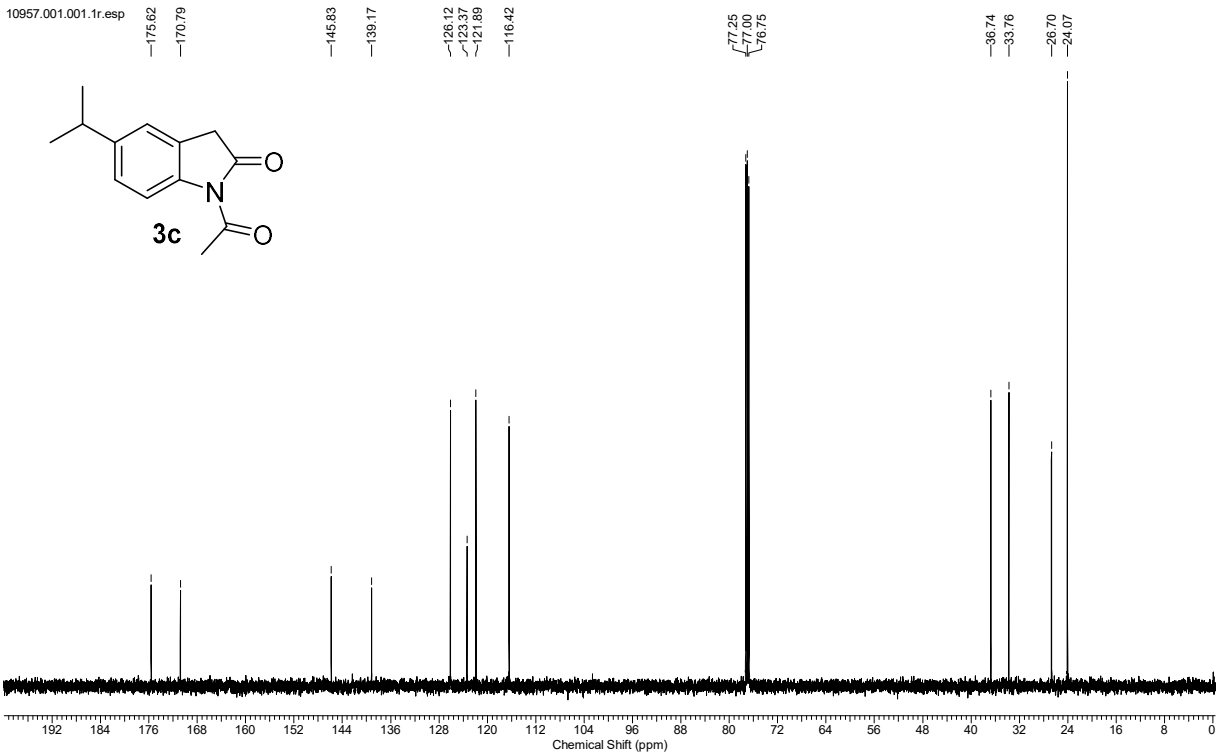
^{13}C NMR of Compound 3b in $CDCl_3$



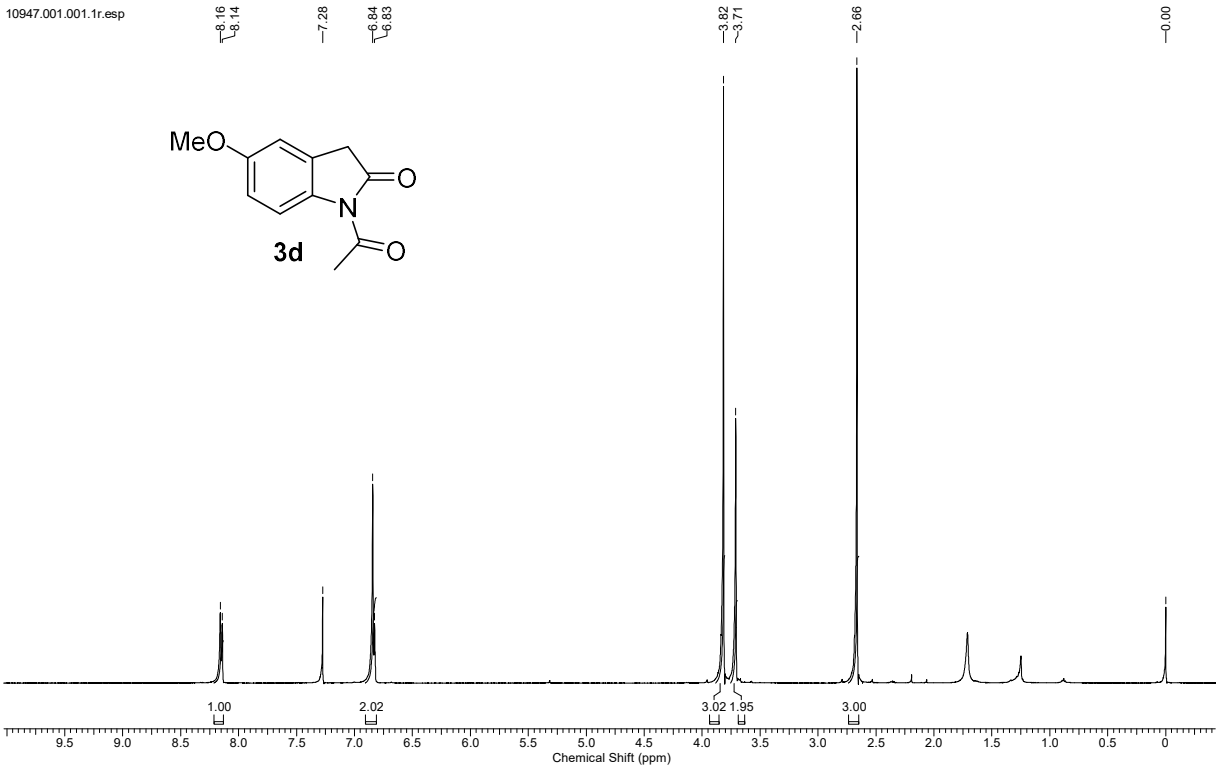
^{1}H NMR of Compound 3c in $CDCl_3$



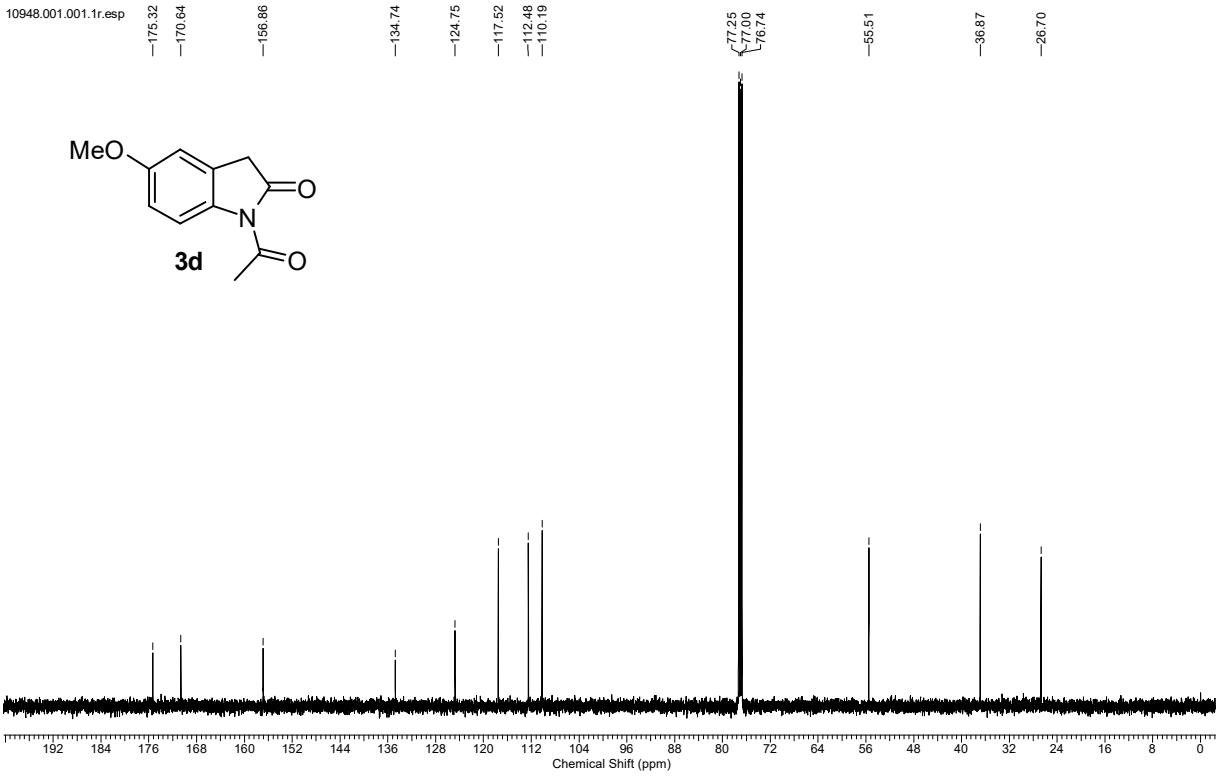
^{13}C NMR of Compound 3c in $CDCl_3$



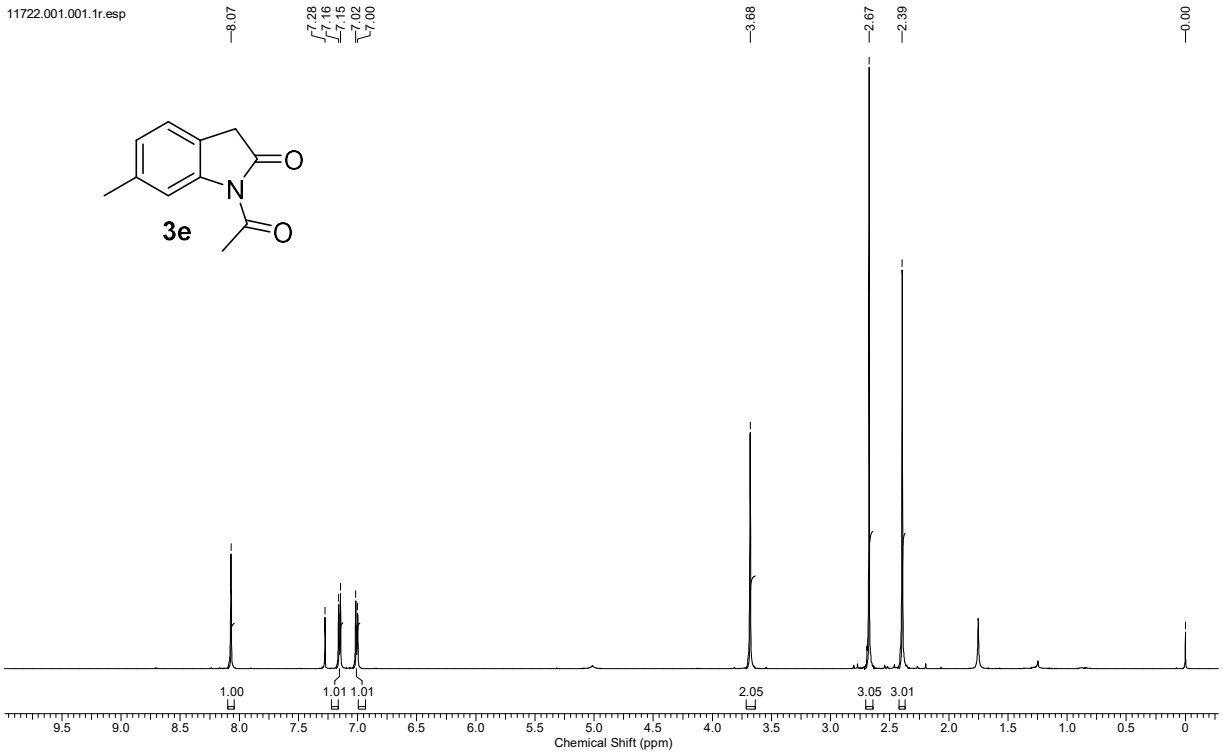
^{1}H NMR of Compound 3d in $CDCl_3$



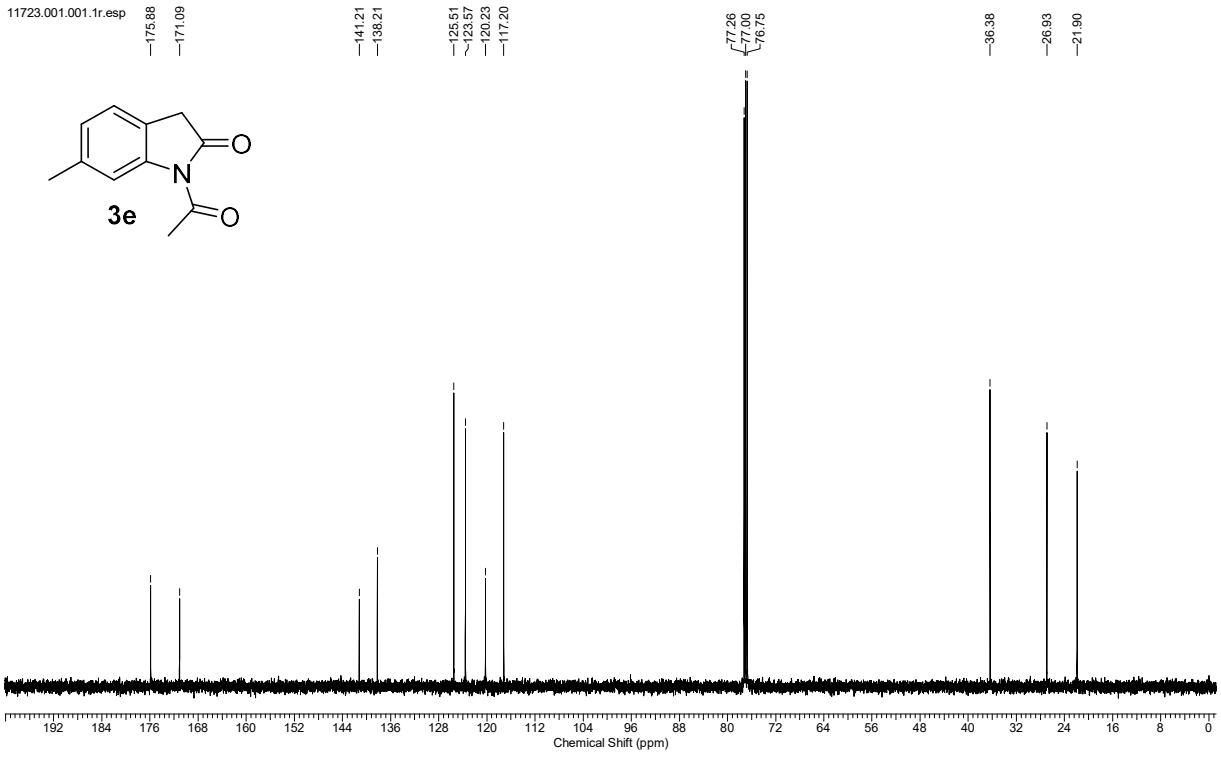
^{13}C NMR of Compound 3d in $CDCl_3$



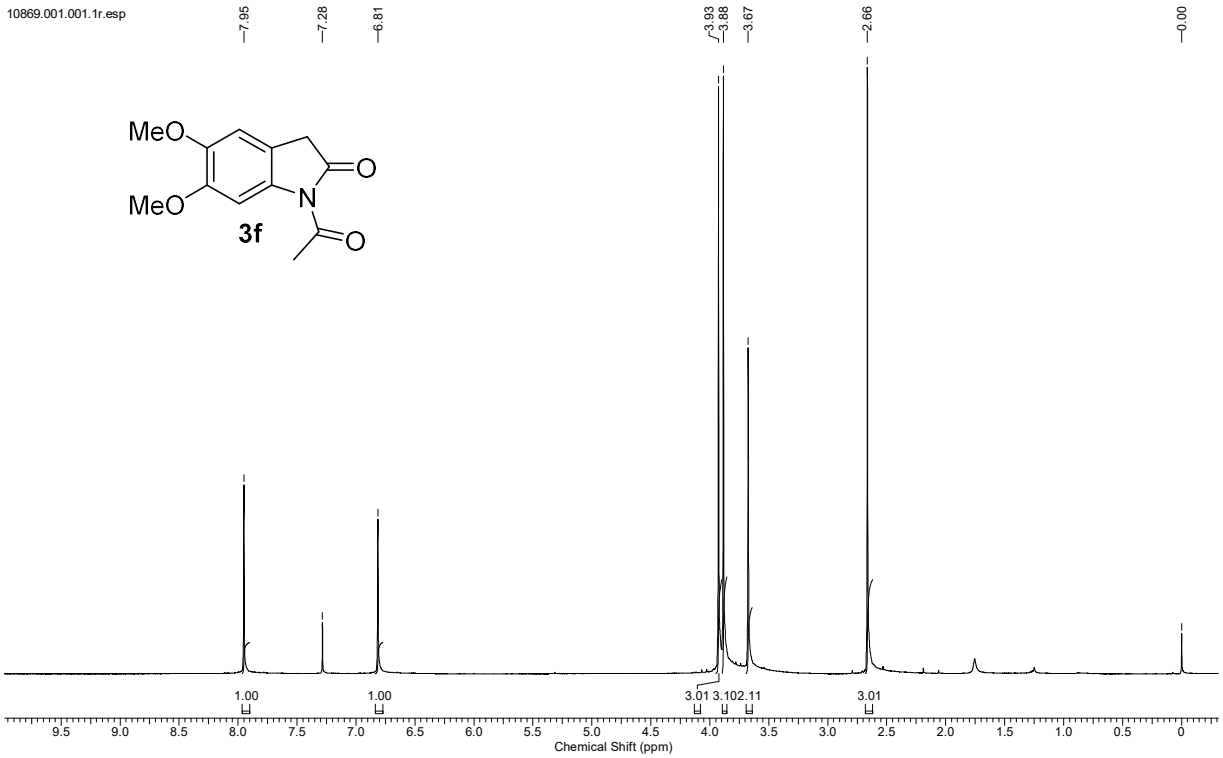
^{1}H NMR of Compound 3e in $CDCl_3$



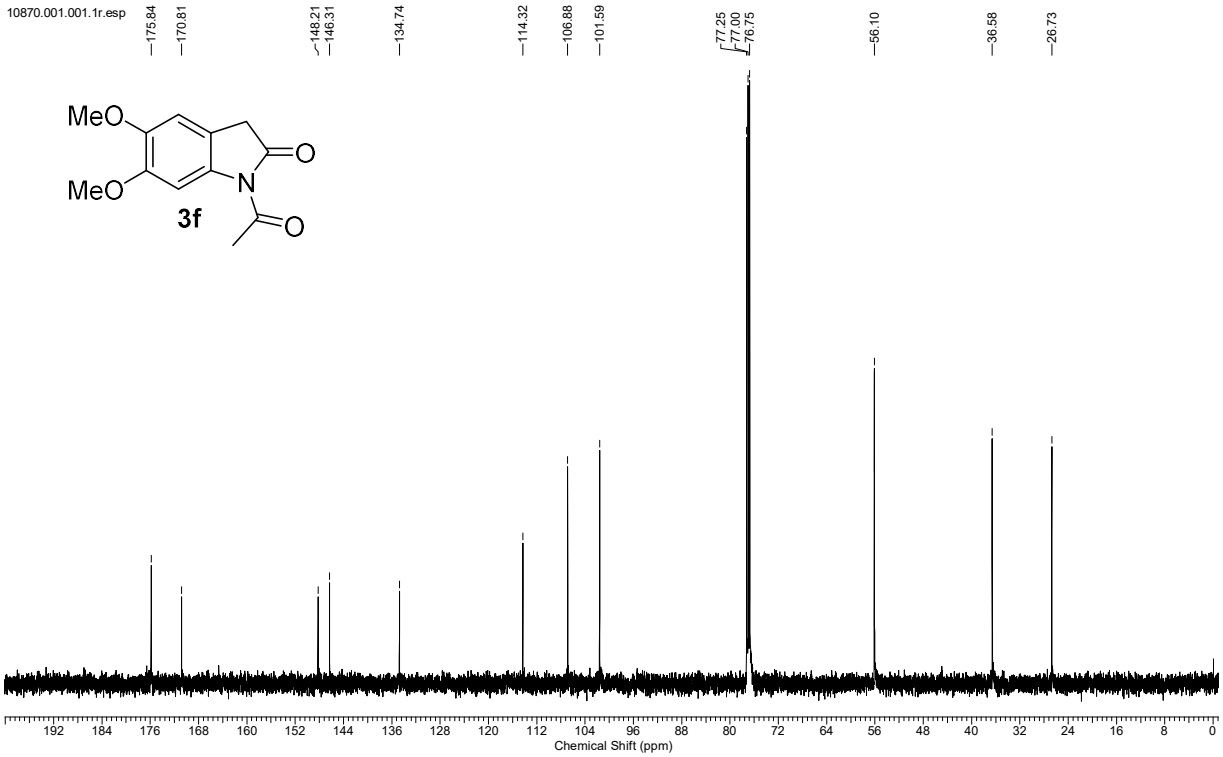
^{13}C NMR of Compound 3e in $CDCl_3$



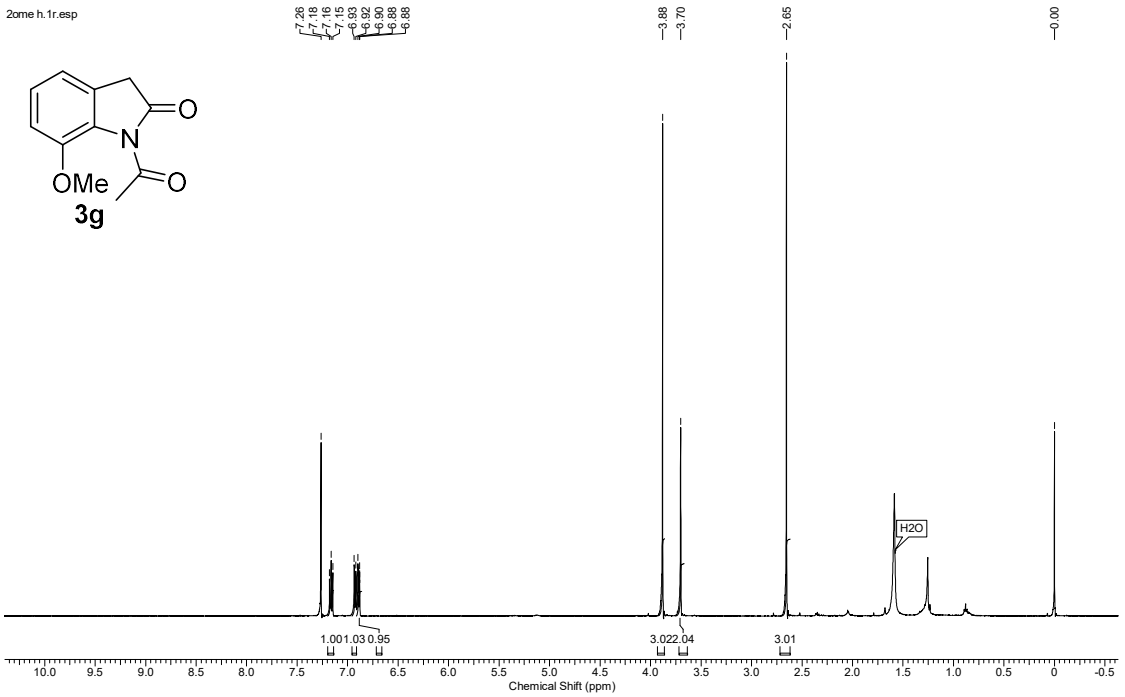
^{1}H NMR of Compound 3f in $CDCl_3$



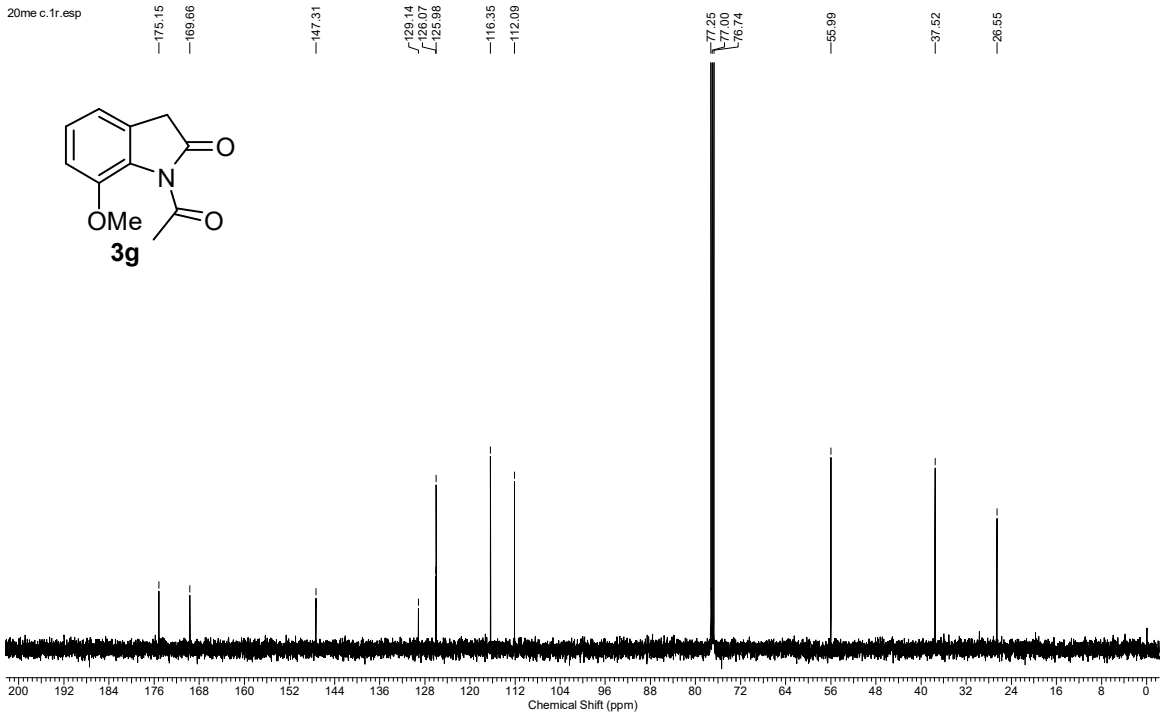
^{13}C NMR of Compound 3f in $CDCl_3$



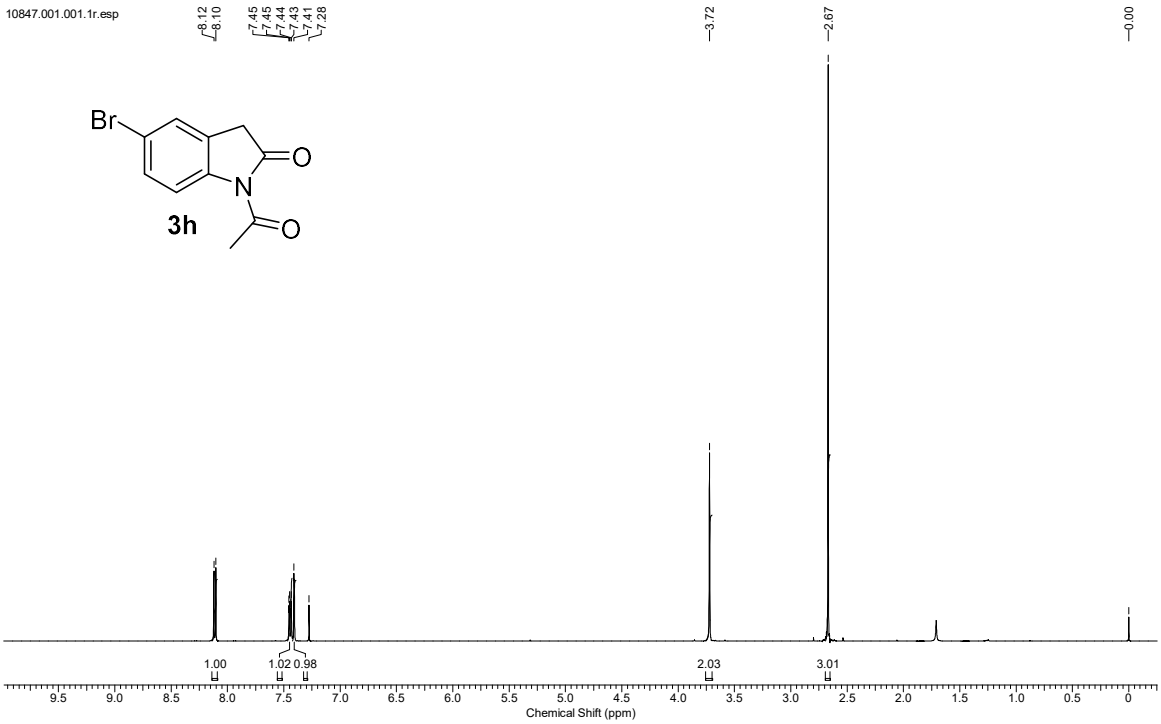
^{1}H NMR of Compound 3g in $CDCl_3$



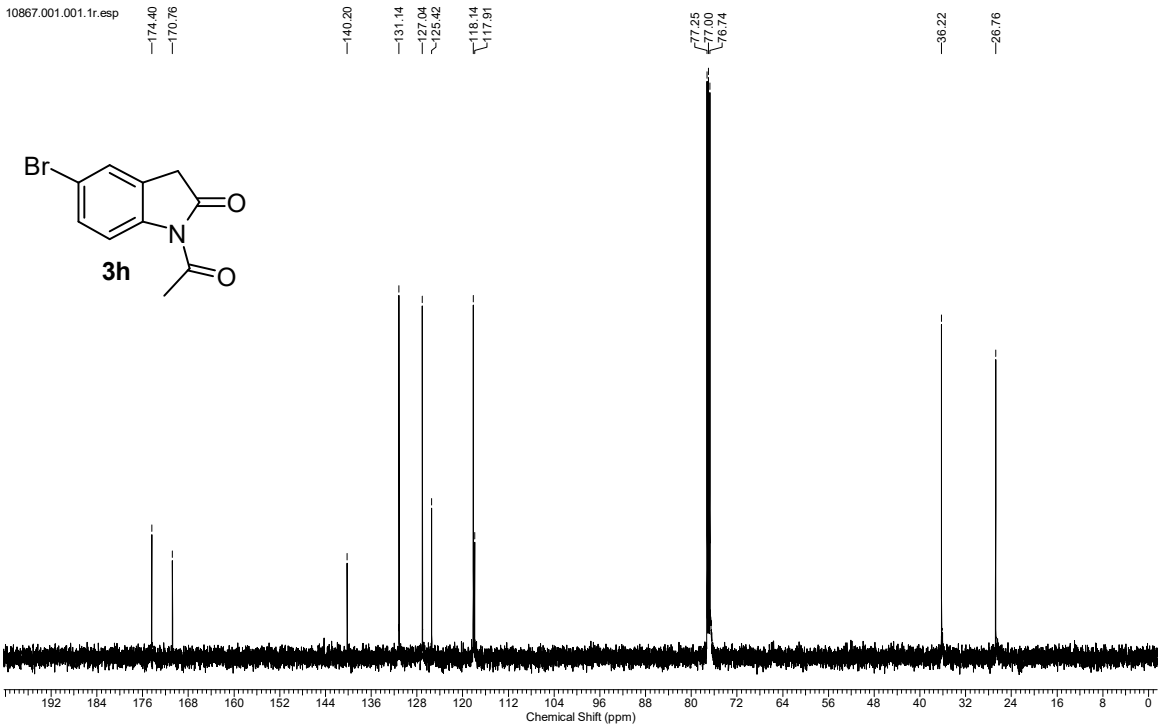
^{13}C NMR of Compound 3g in $CDCl_3$



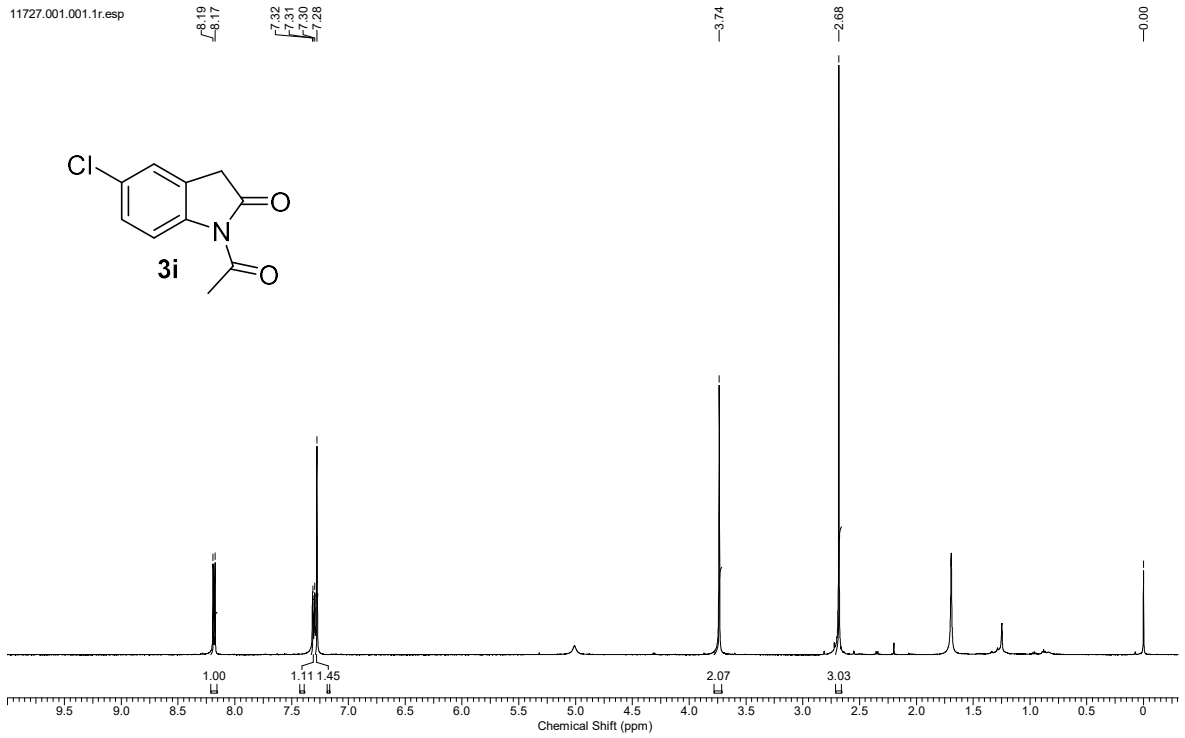
^{1}H NMR of Compound 3h in $CDCl_3$



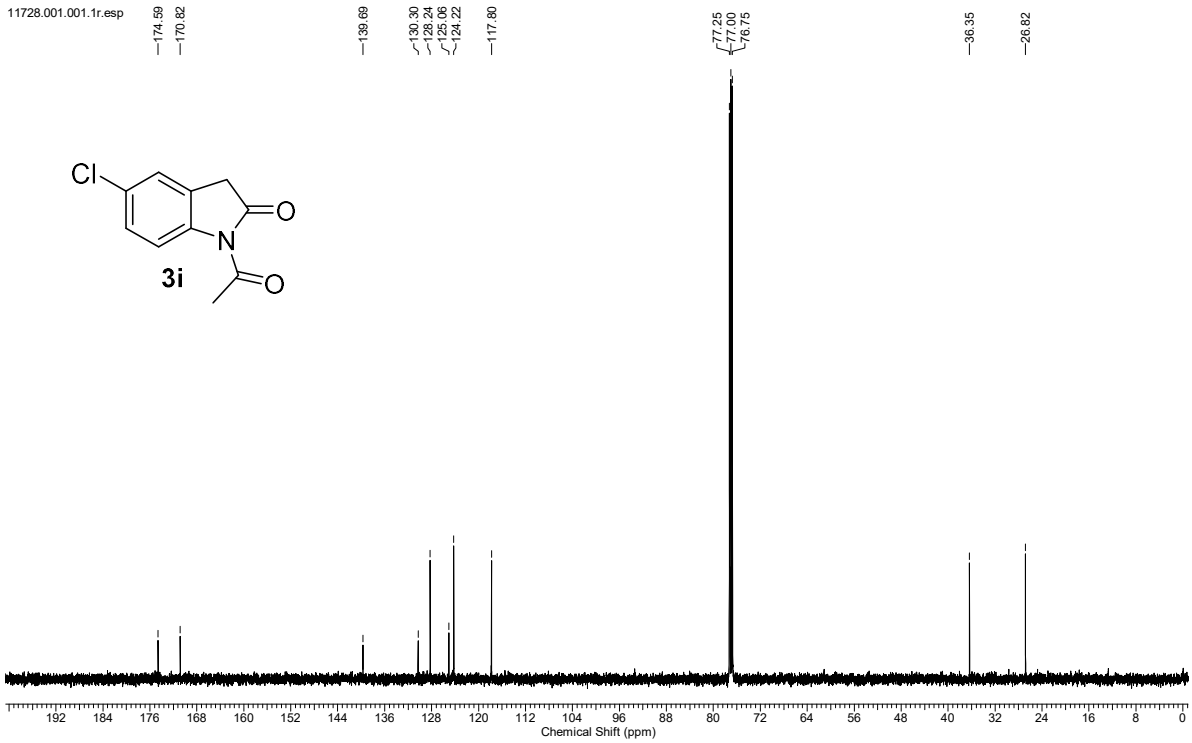
^{13}C NMR of Compound 3h in $CDCl_3$



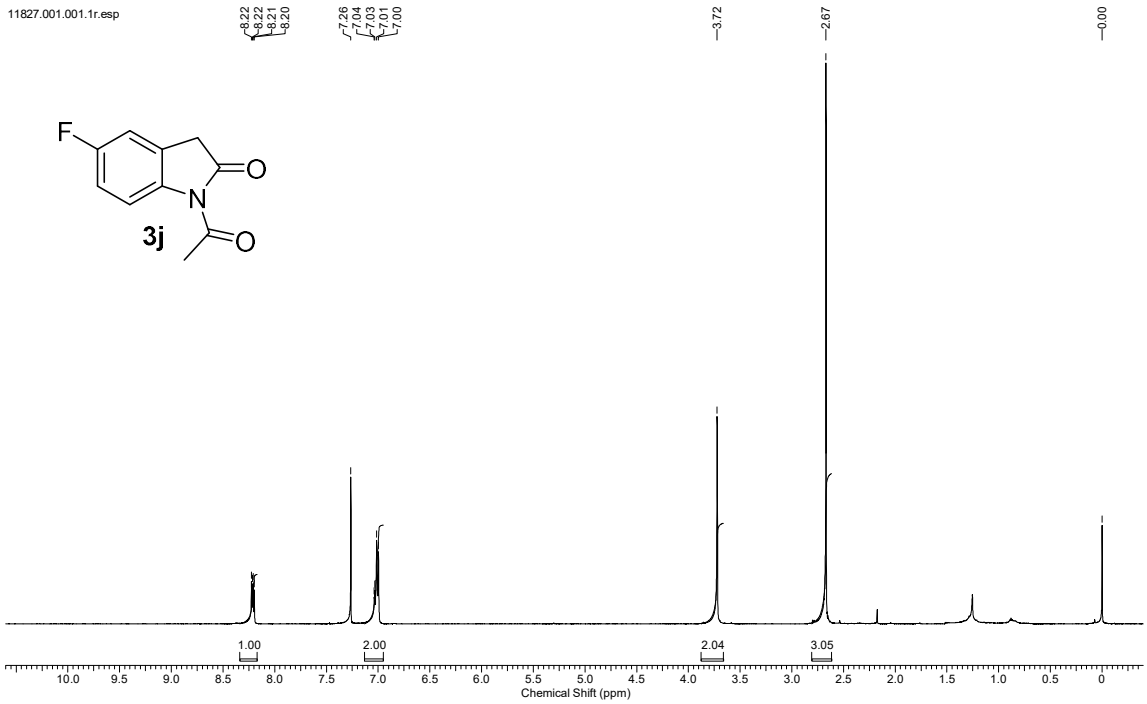
^{1}H NMR of Compound 3i in $CDCl_3$



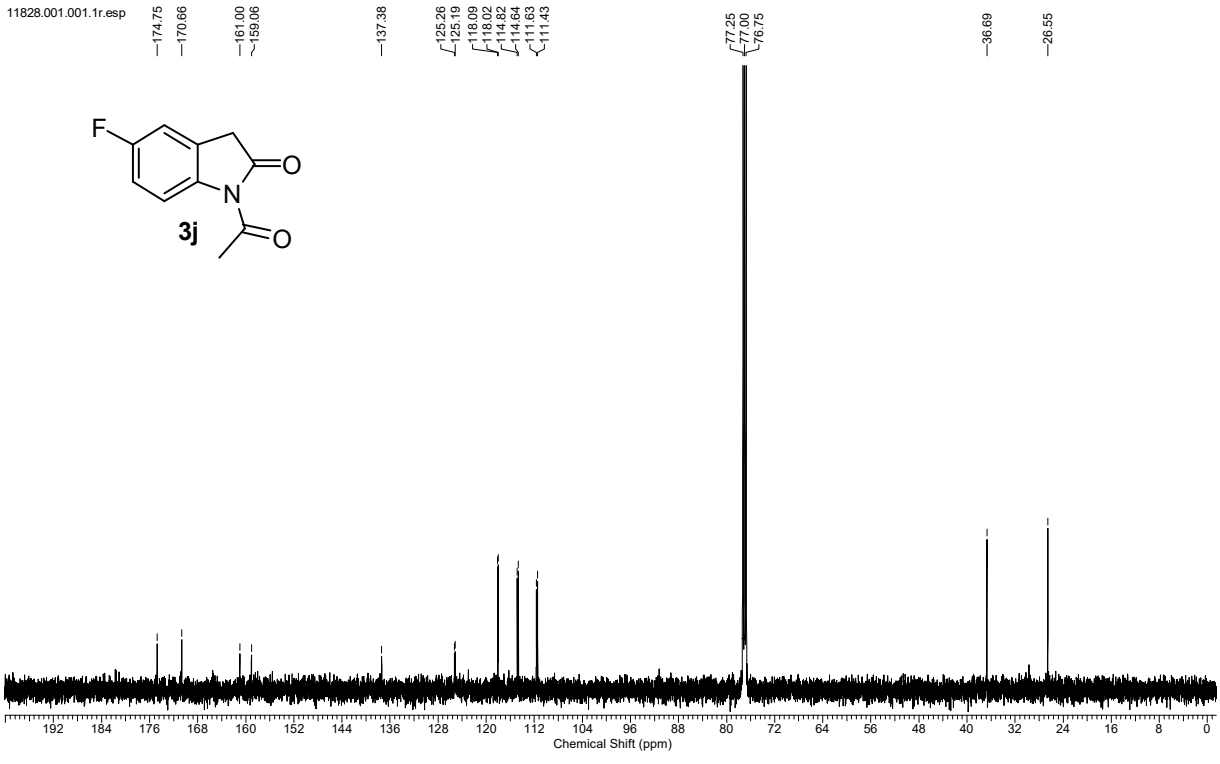
^{13}C NMR of Compound 3i in $CDCl_3$



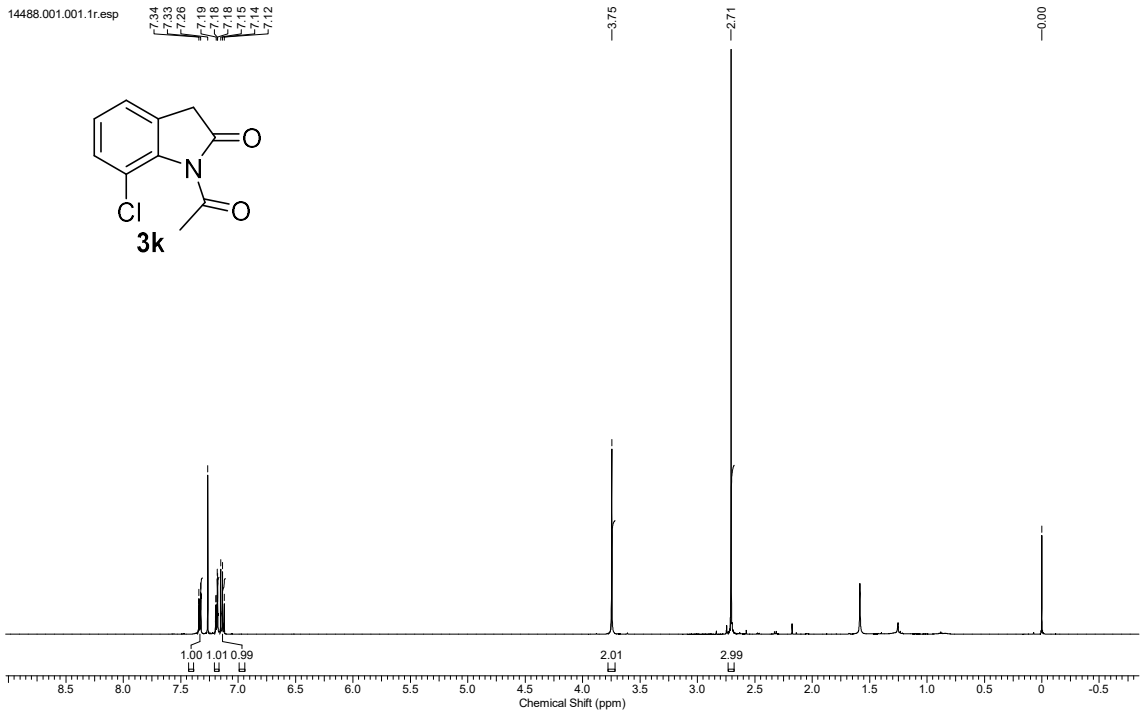
^{1}H NMR of Compound 3j in $CDCl_3$



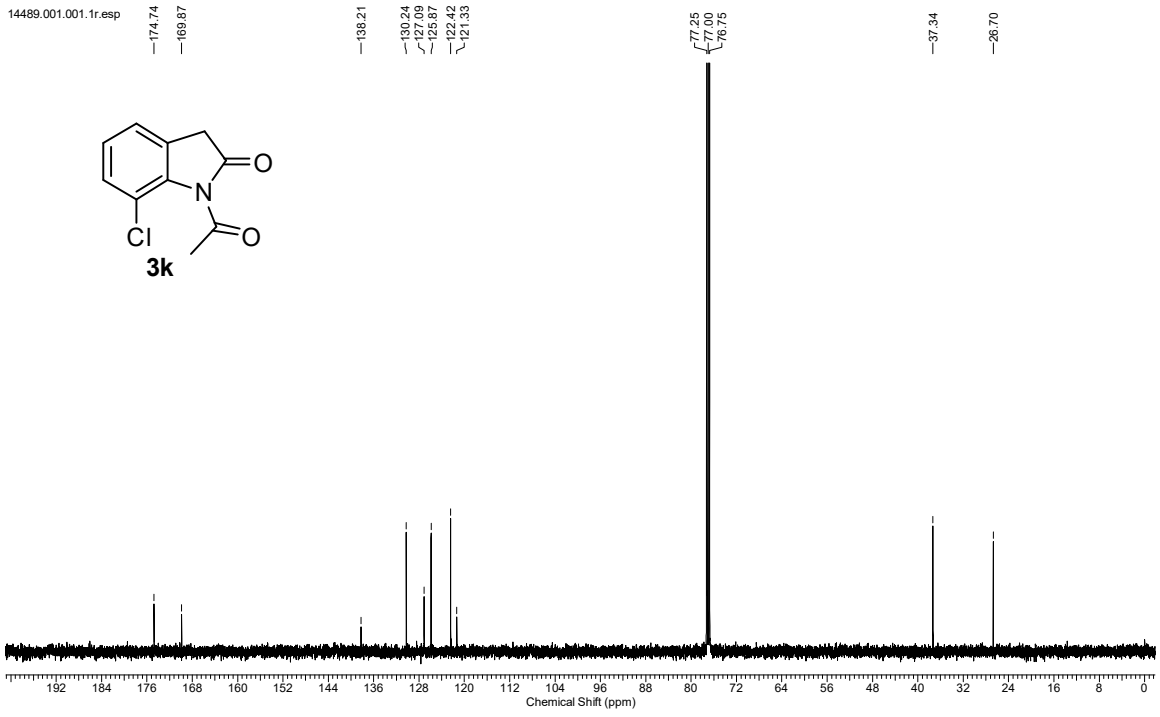
^{13}C NMR of Compound 3j in $CDCl_3$



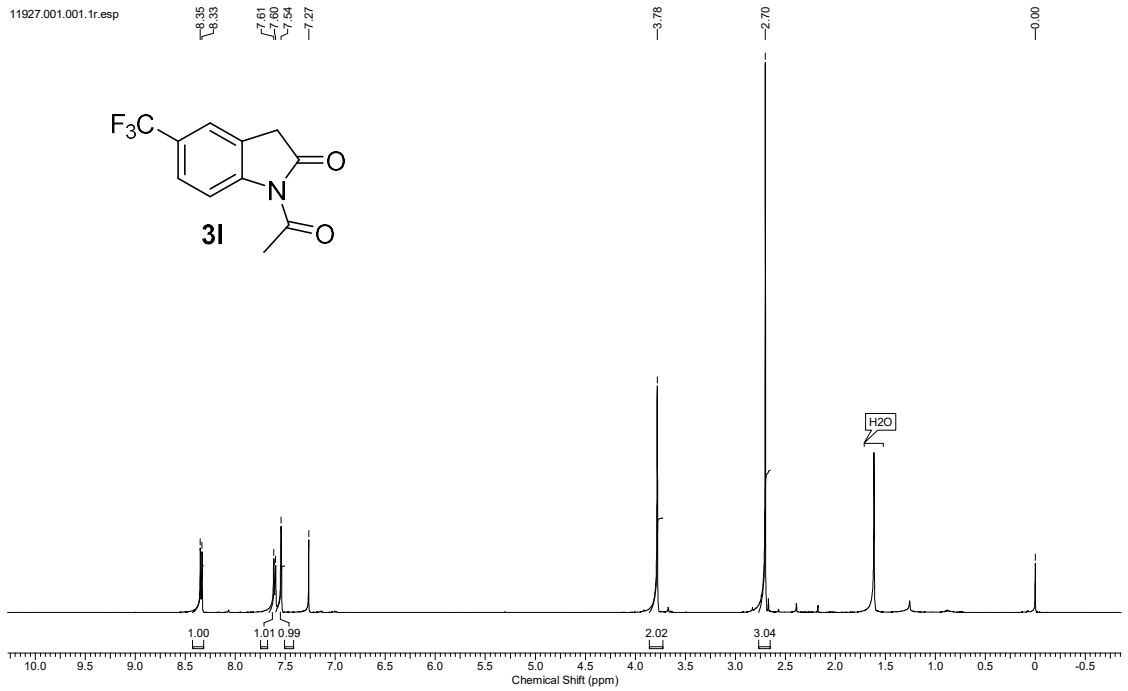
^{1}H NMR of Compound 3k in $CDCl_3$



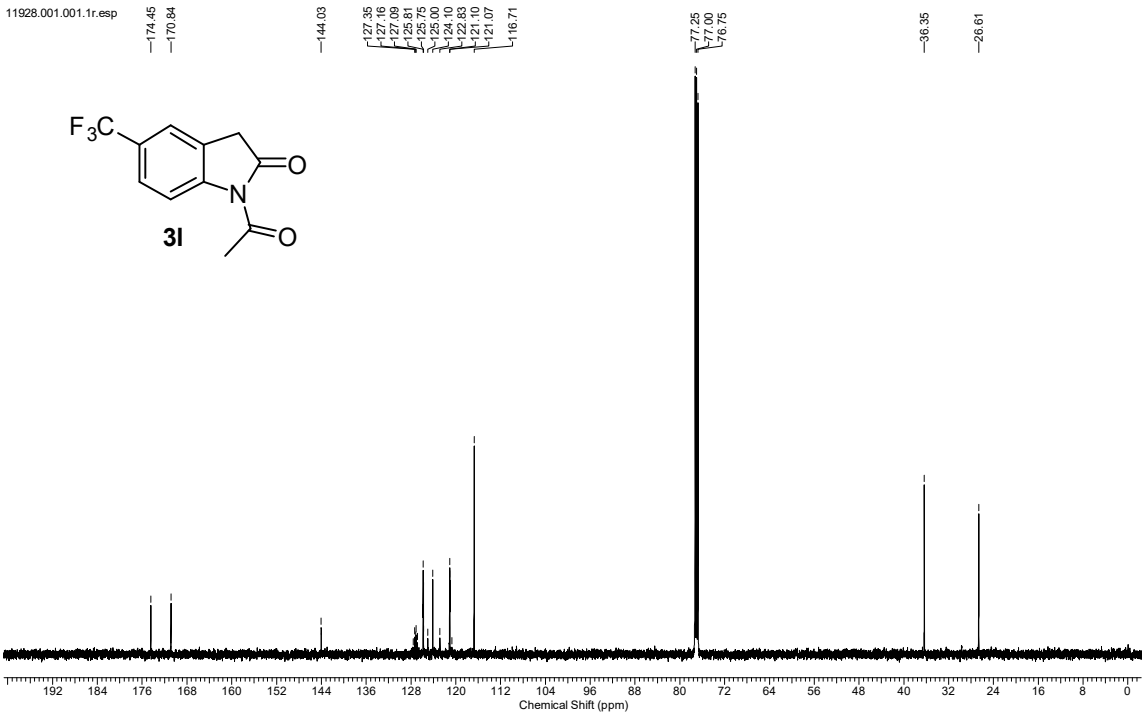
^{13}C NMR of Compound 3k in $CDCl_3$



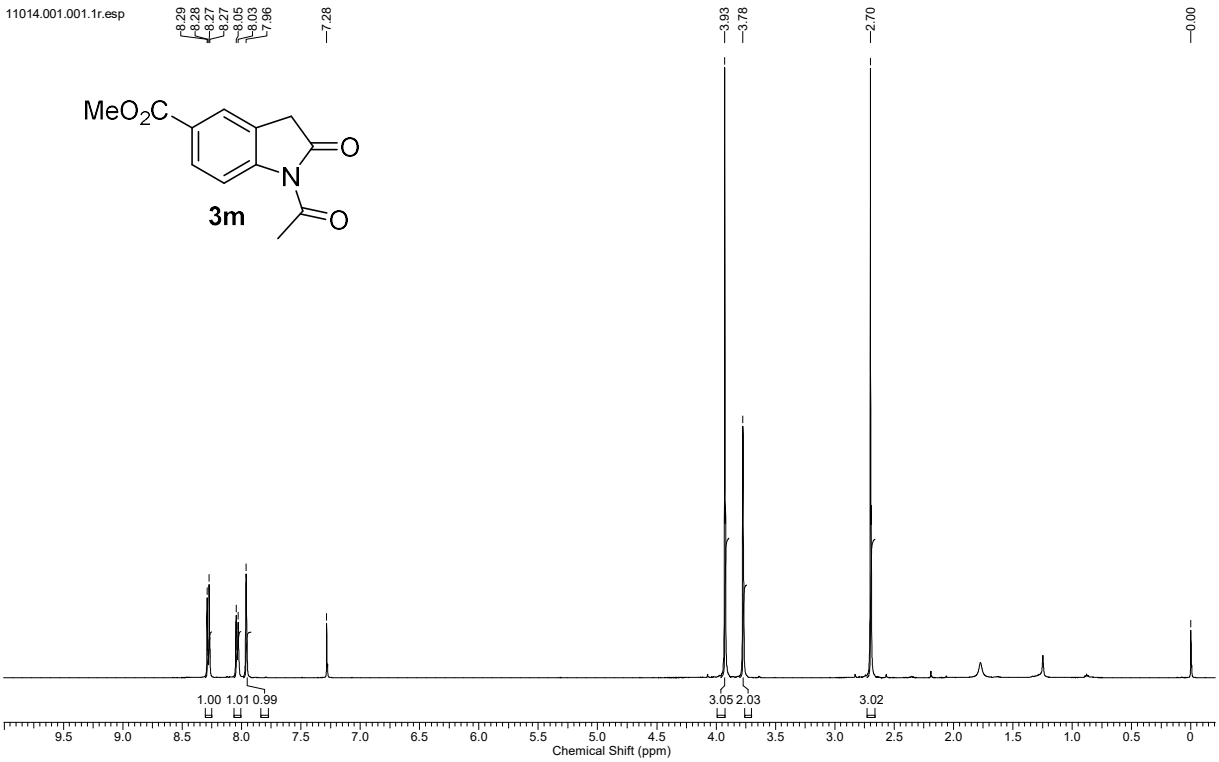
^{1}H NMR of Compound 3l in $CDCl_3$



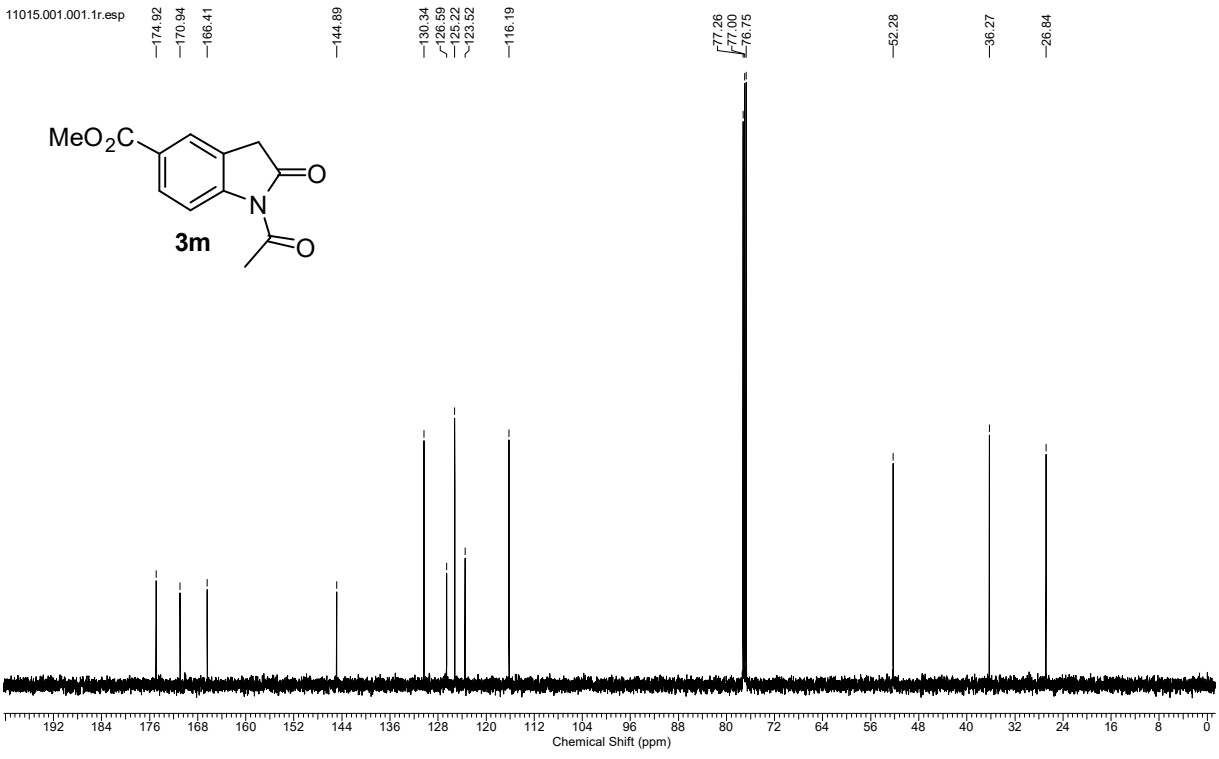
^{13}C NMR of Compound 3l in $CDCl_3$



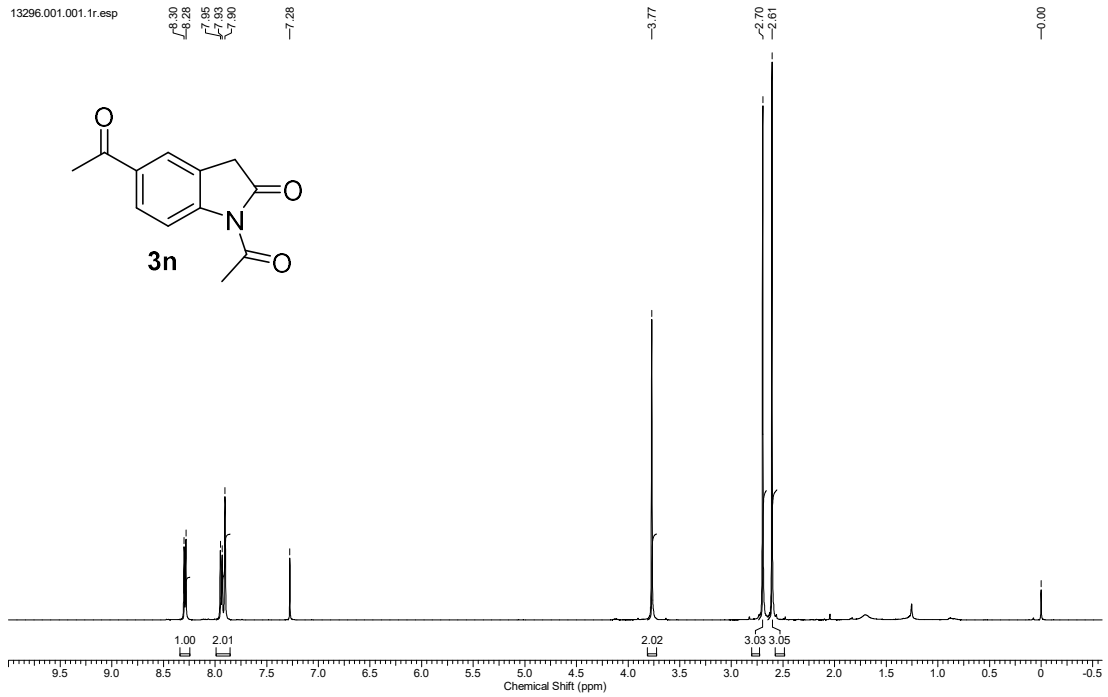
^{1}H NMR of Compound 3m in $CDCl_3$



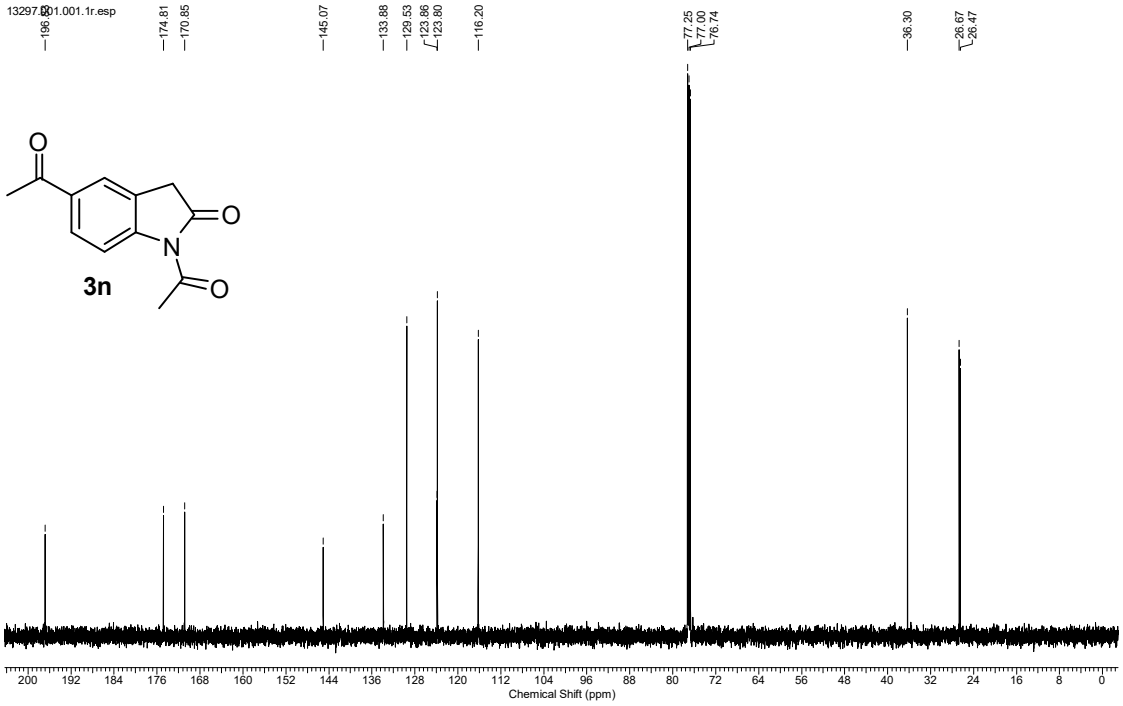
^{13}C NMR of Compound 3m in $CDCl_3$



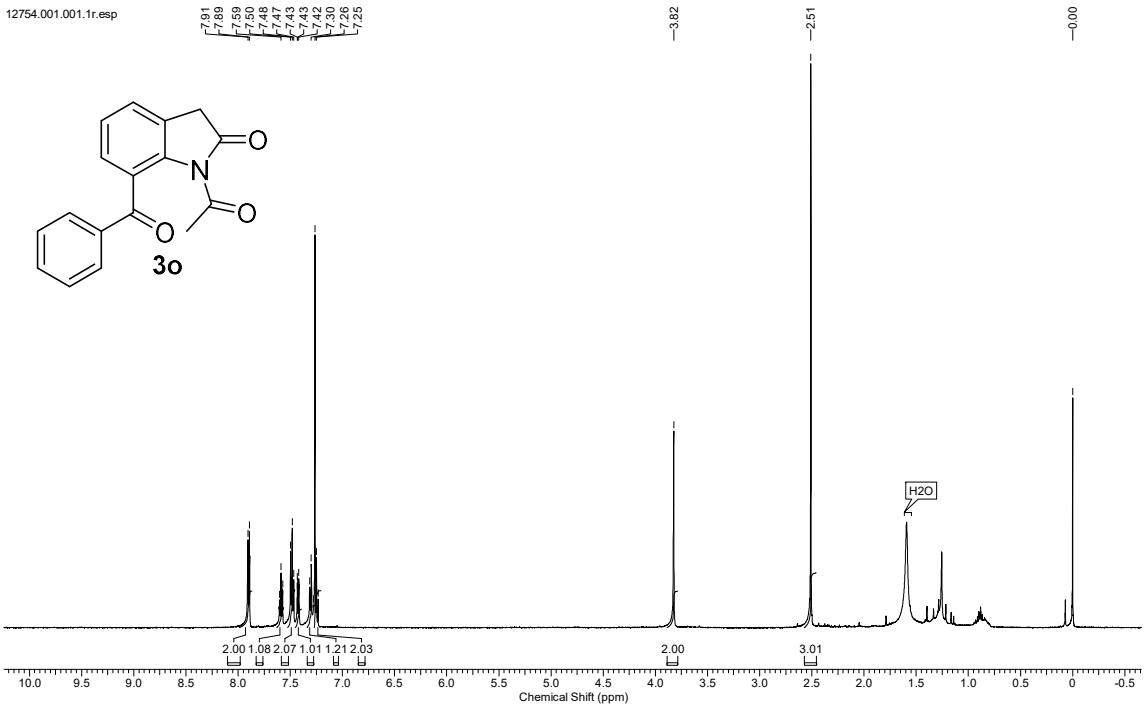
^{1}H NMR of Compound 3n in $CDCl_3$



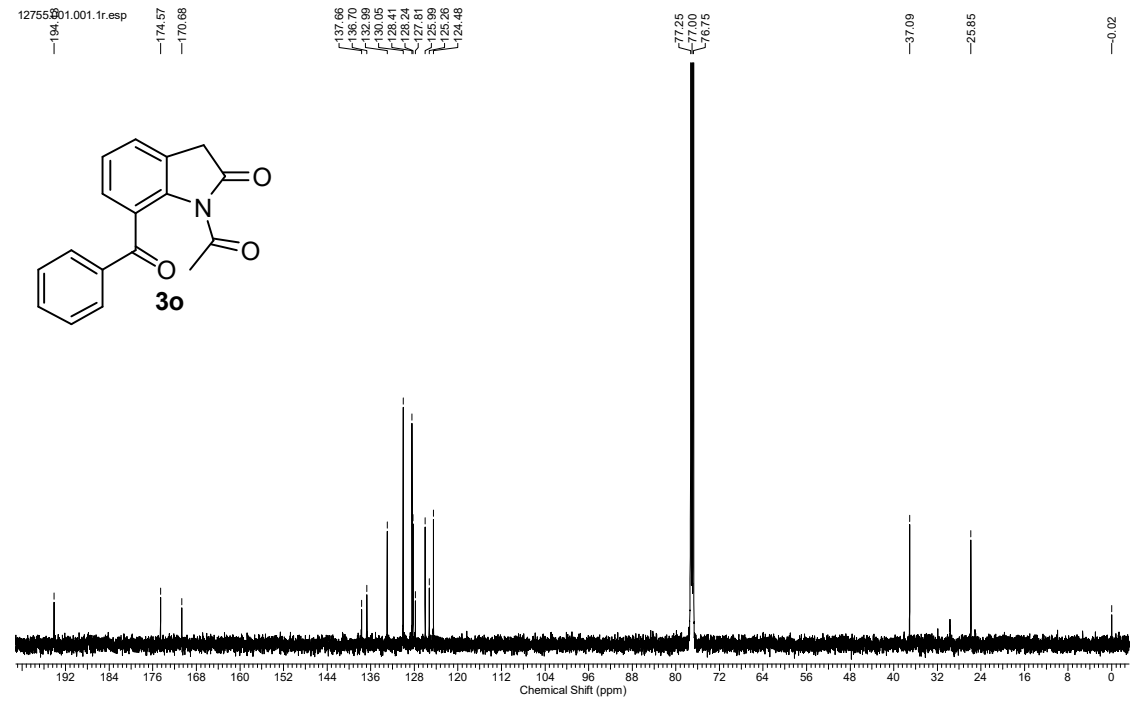
^{13}C NMR of Compound 3n in $CDCl_3$



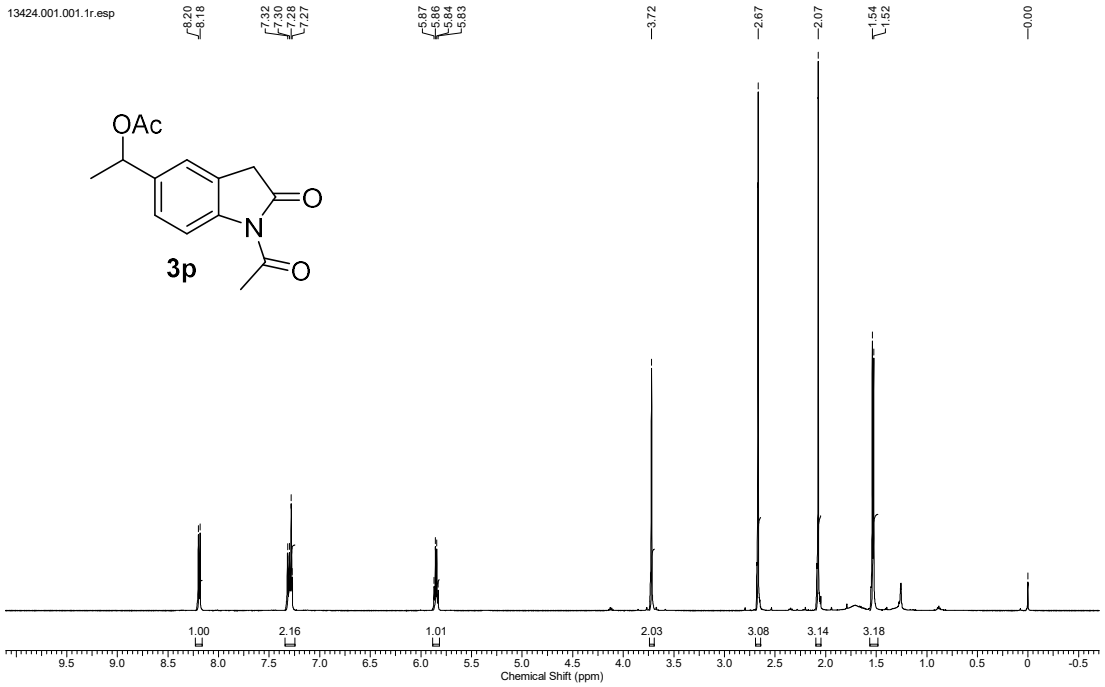
^{1}H NMR of Compound 3o in $CDCl_3$



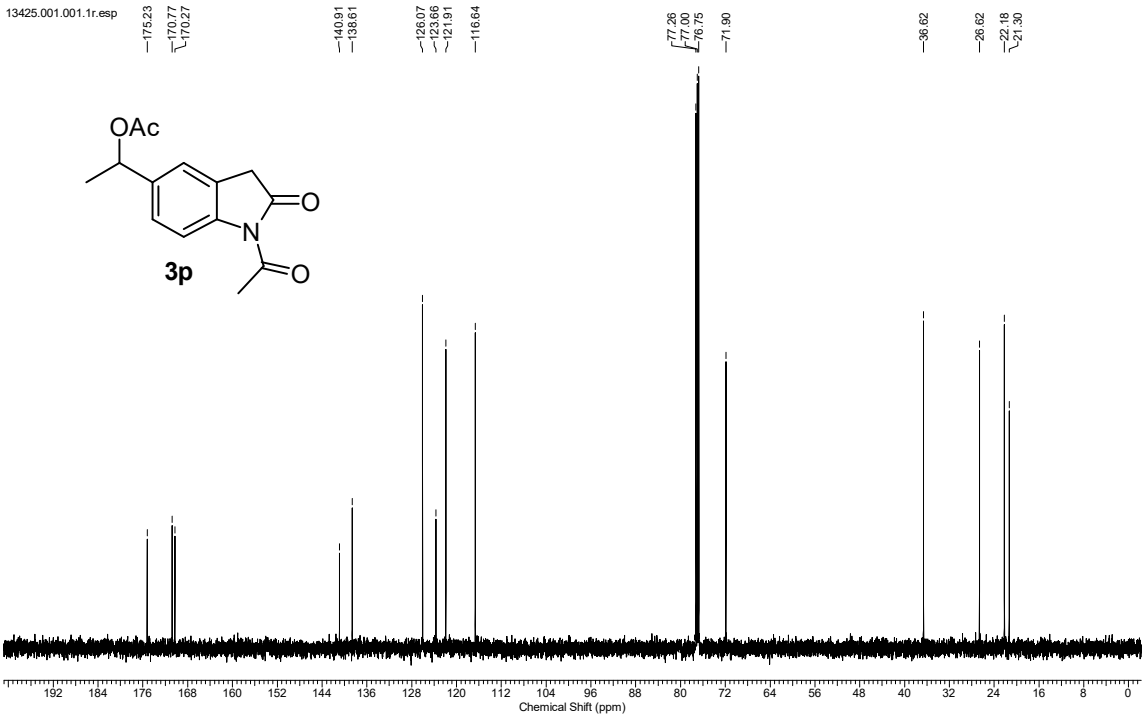
^{13}C NMR of Compound 3o in $CDCl_3$



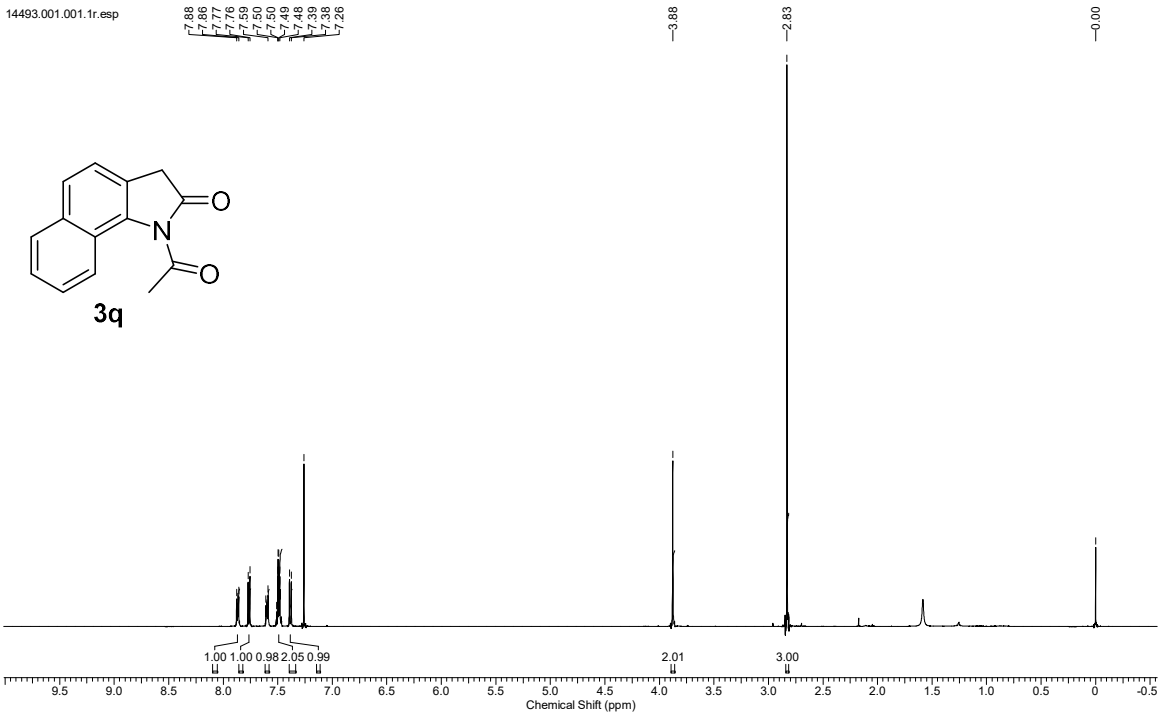
^{1}H NMR of Compound 3p in $CDCl_3$



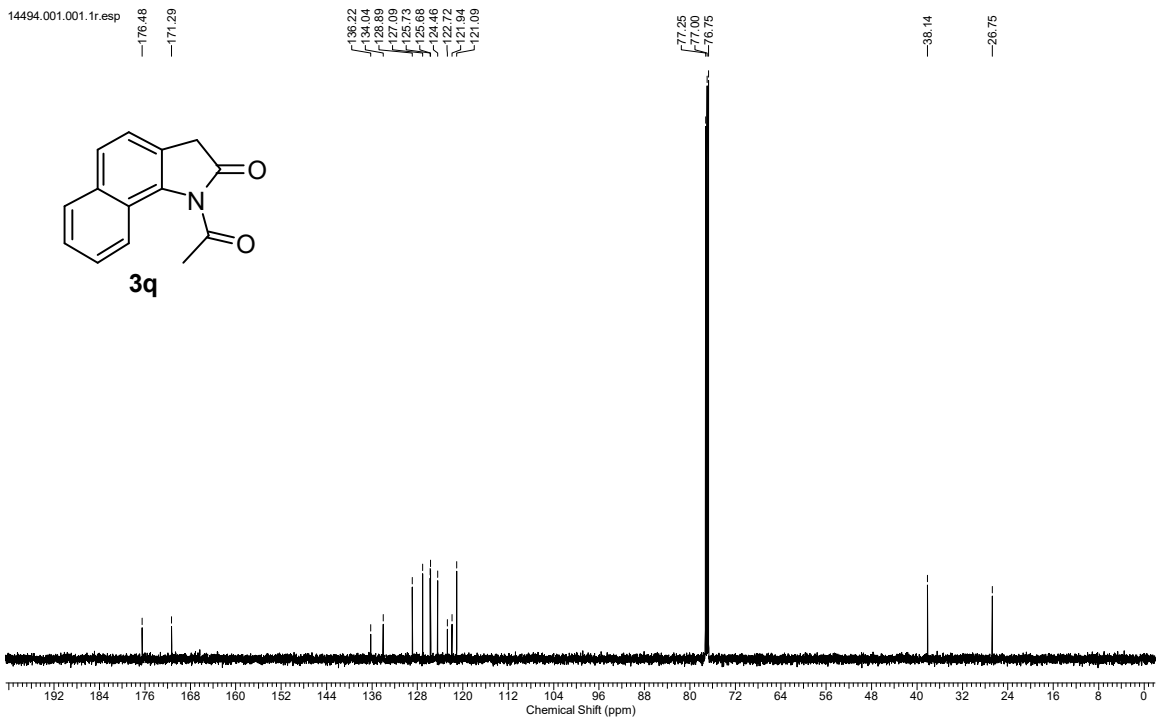
^{13}C NMR of Compound 3p in $CDCl_3$



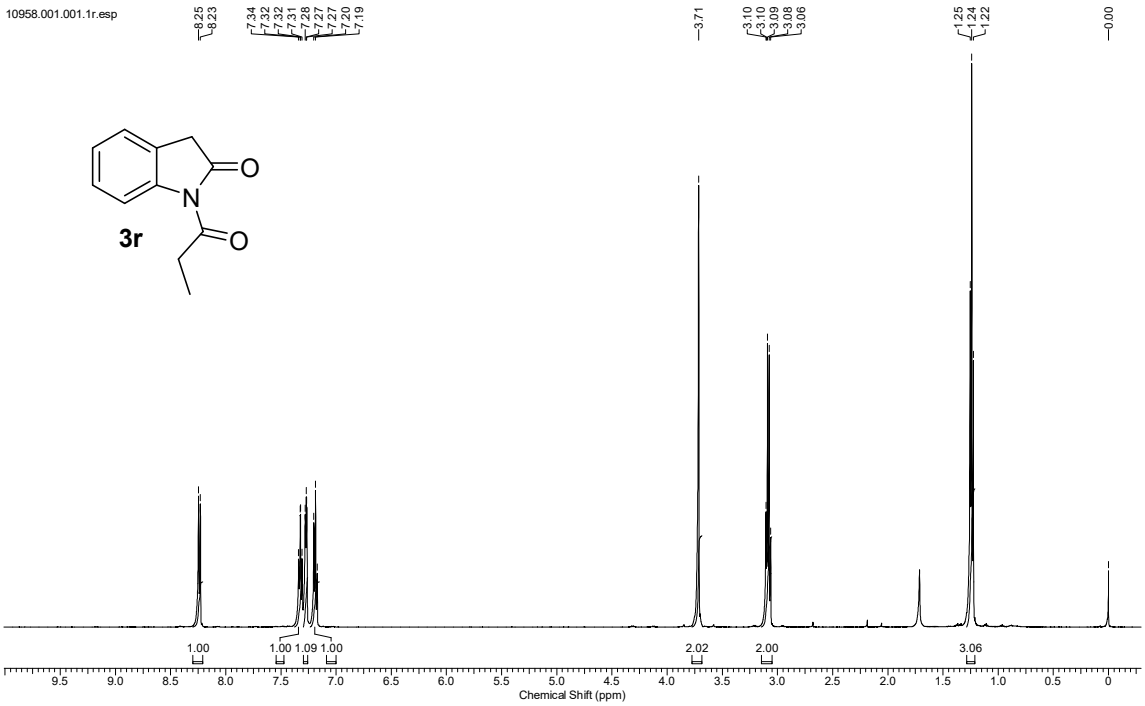
^{1}H NMR of Compound 3q in $CDCl_3$



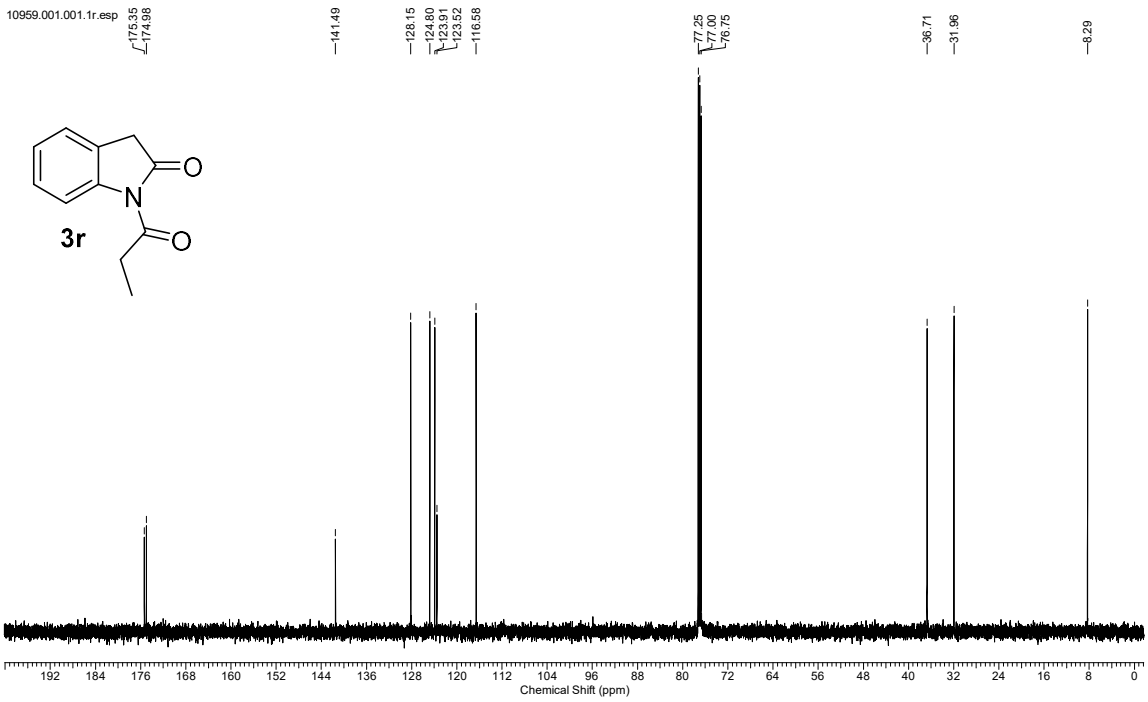
^{13}C NMR of Compound 3q in $CDCl_3$



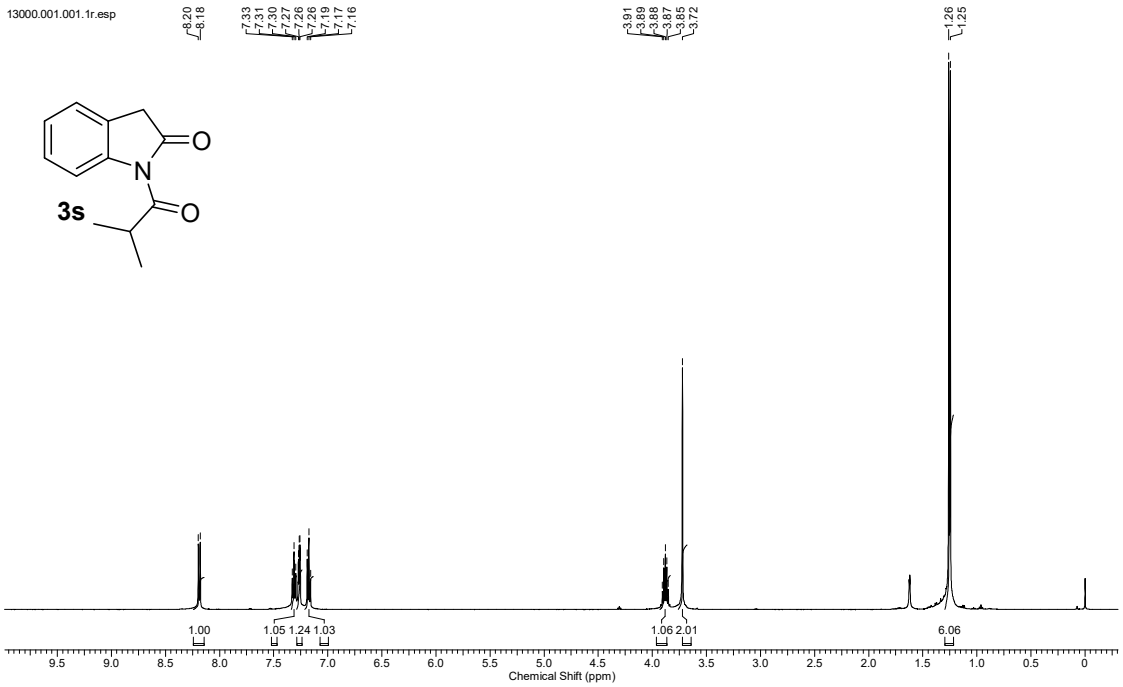
^{1}H NMR of Compound 3r in $CDCl_3$



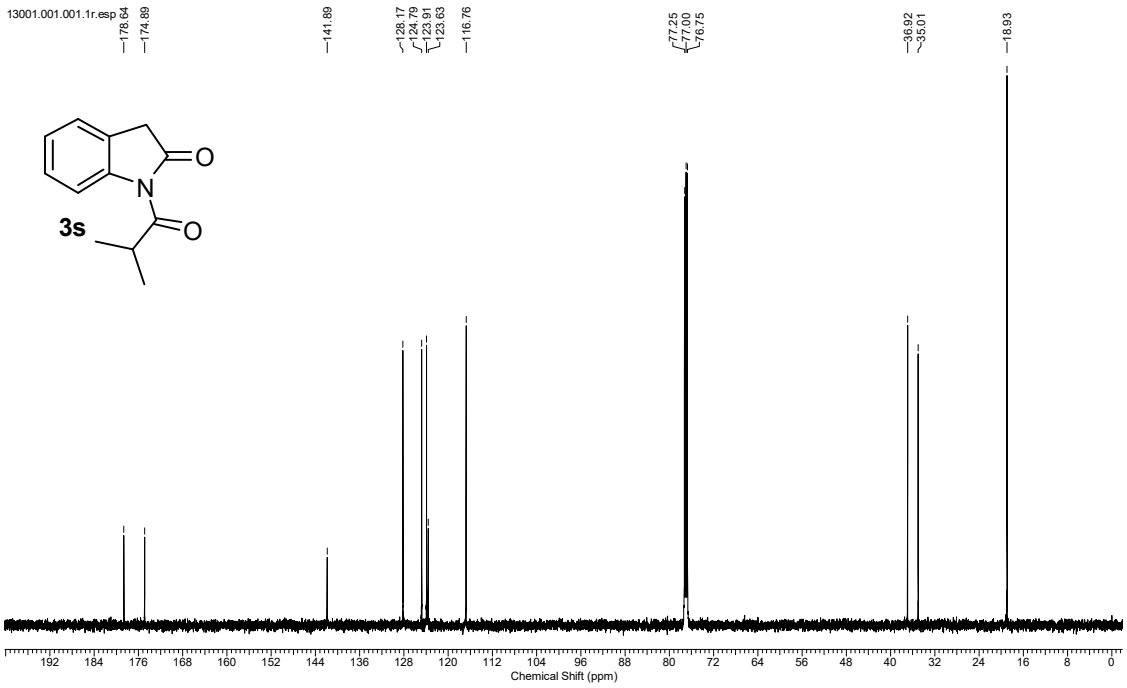
^{13}C NMR of Compound 3r in $CDCl_3$



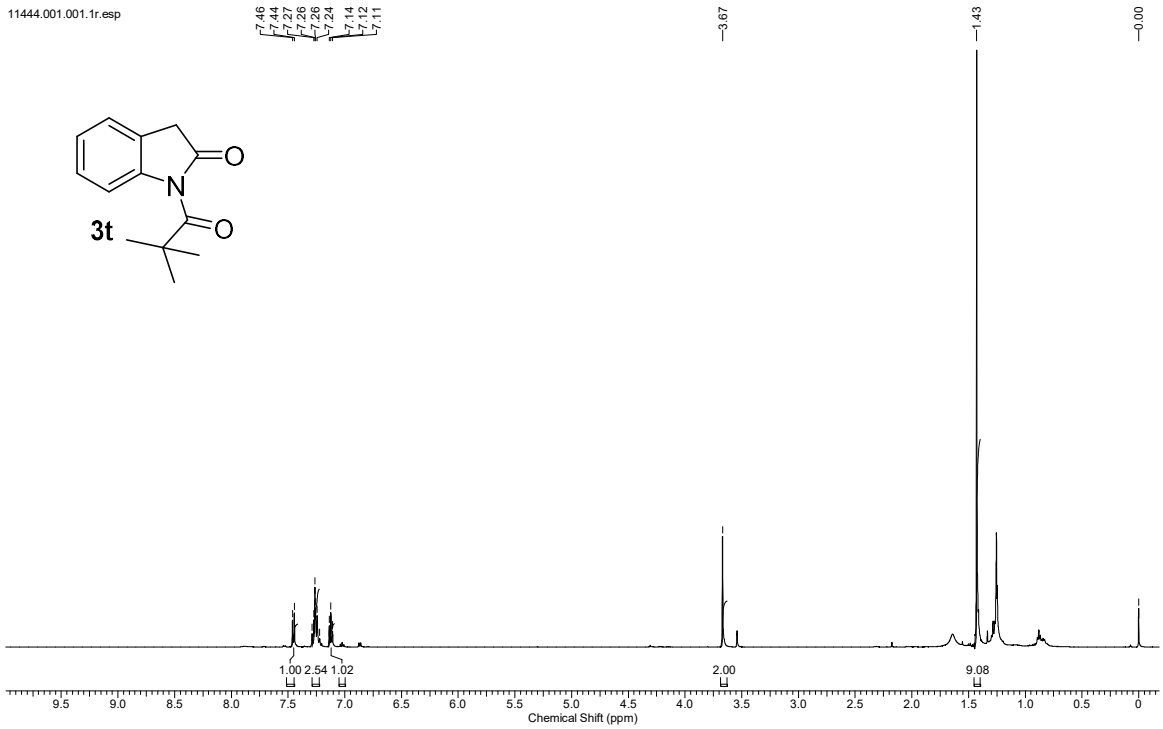
^{1}H NMR of Compound 3s in $CDCl_3$



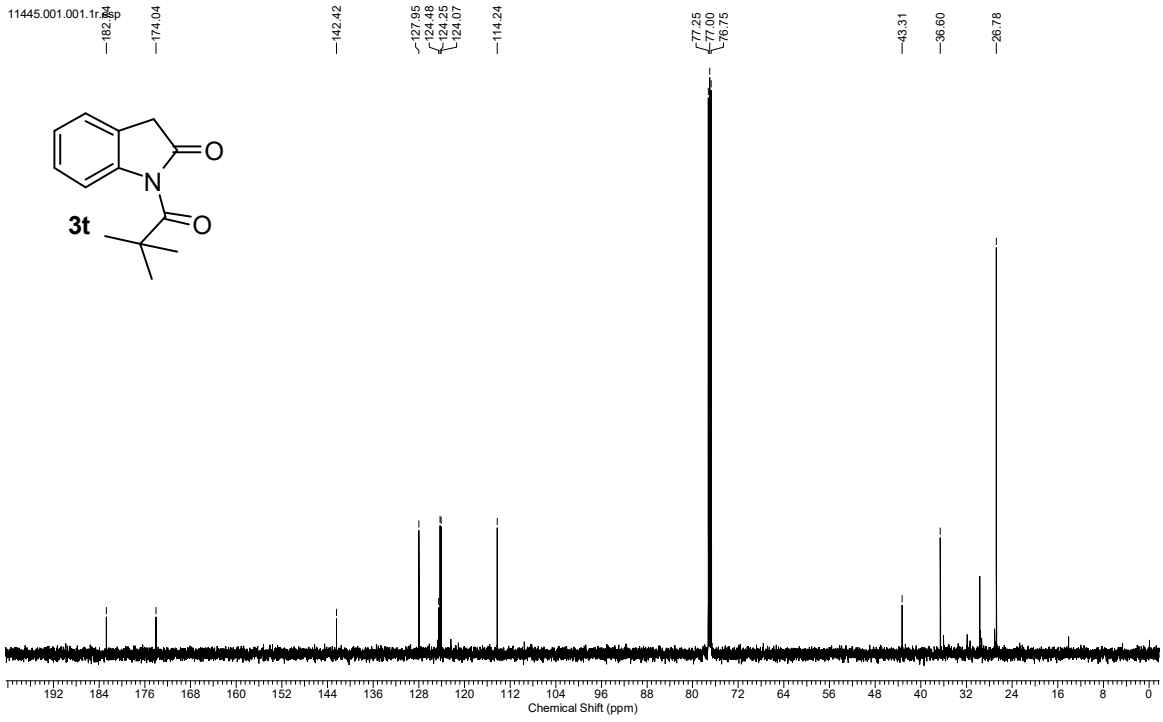
^{13}C NMR of Compound 3s in $CDCl_3$



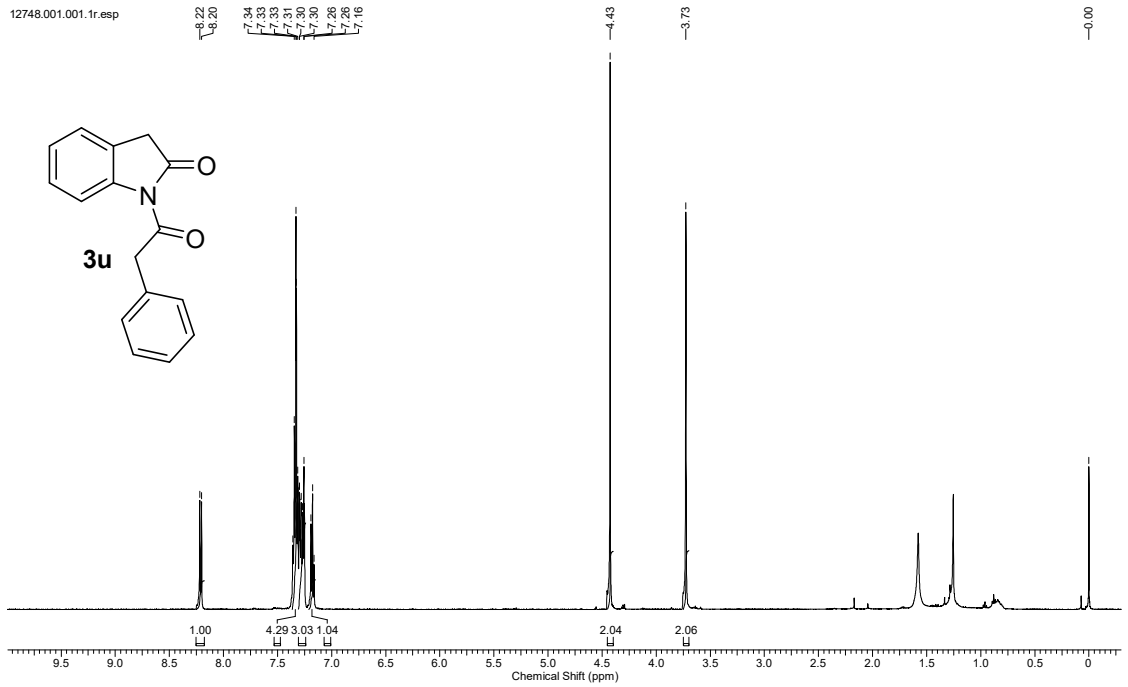
^{1}H NMR of Compound 3t in $CDCl_3$



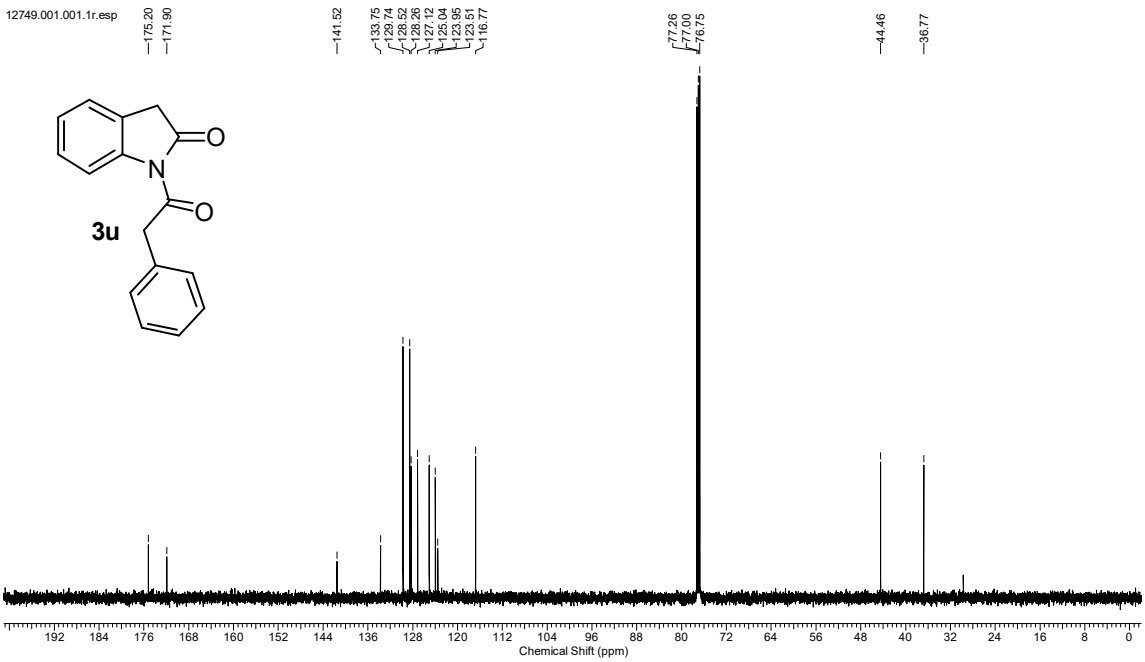
^{13}C NMR of Compound 3t in $CDCl_3$



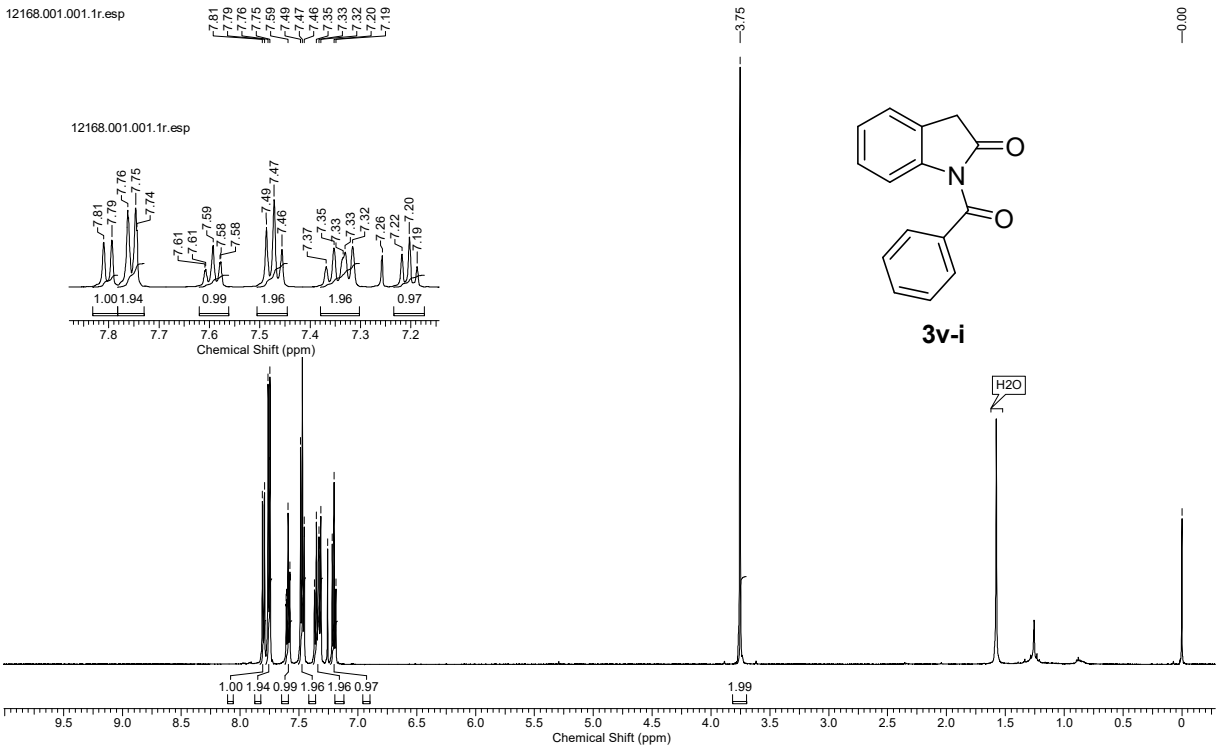
^{1}H NMR of Compound 3u in $CDCl_3$



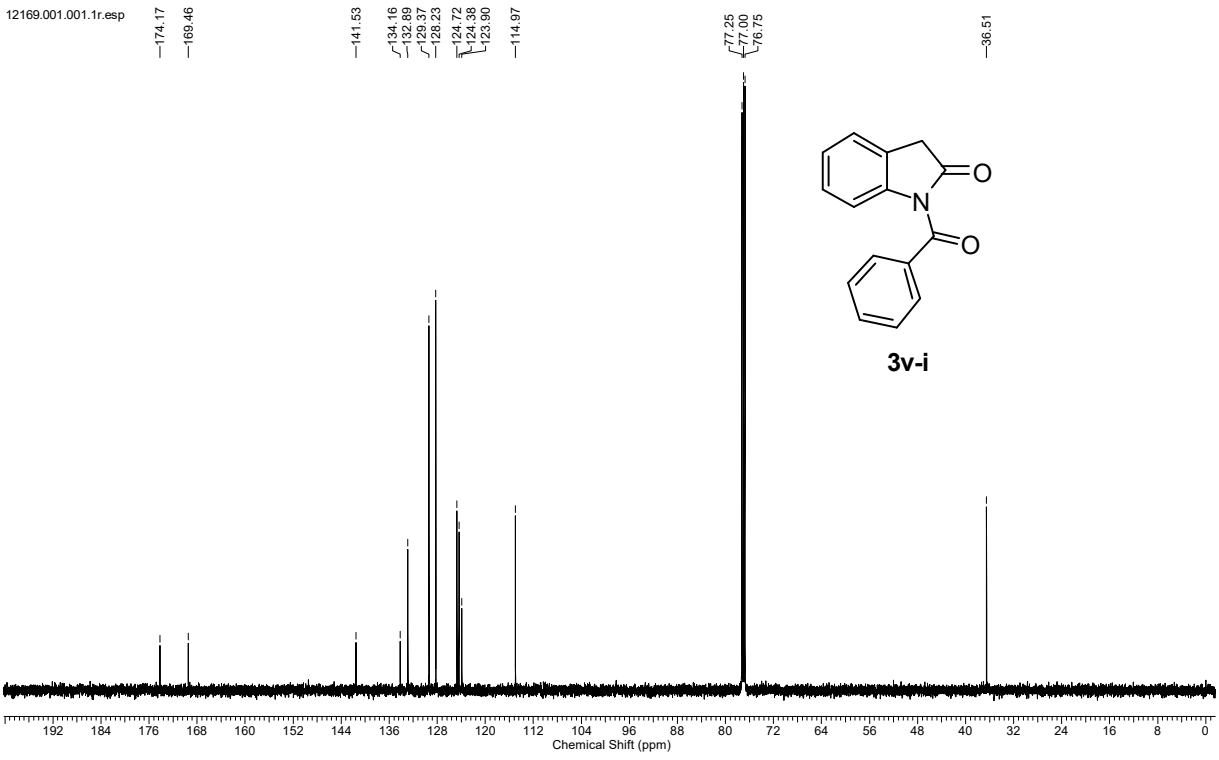
^{13}C NMR of Compound 3u in $CDCl_3$



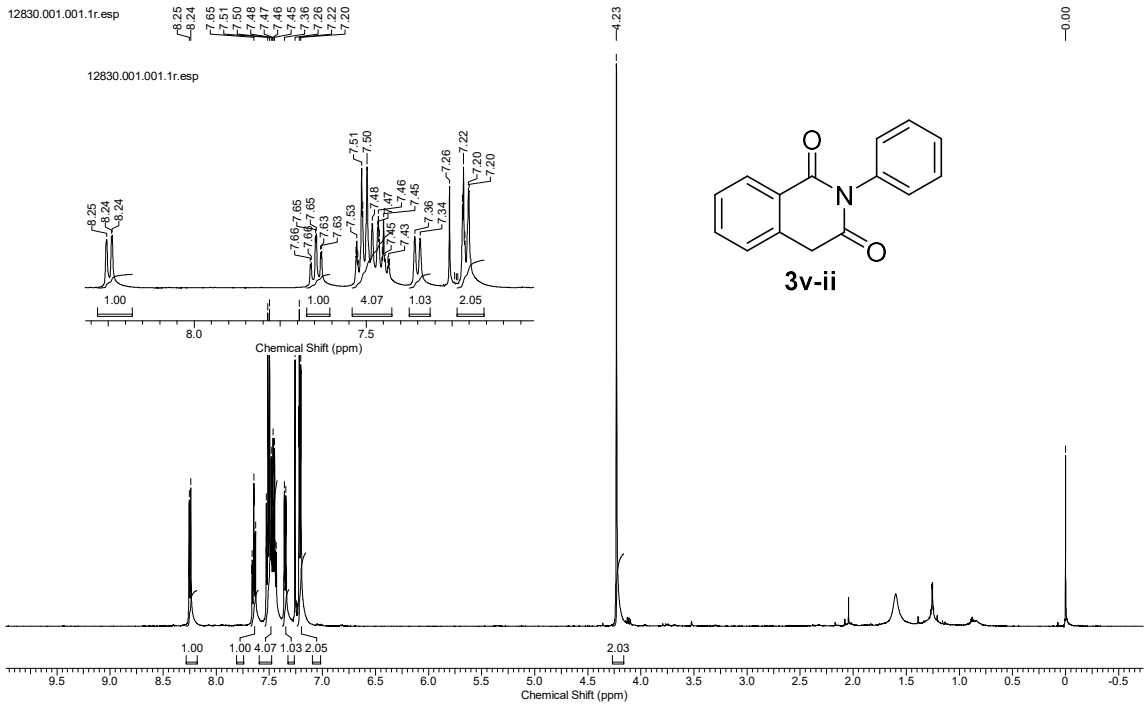
^{1}H NMR of Compound 3v-i in $CDCl_3$



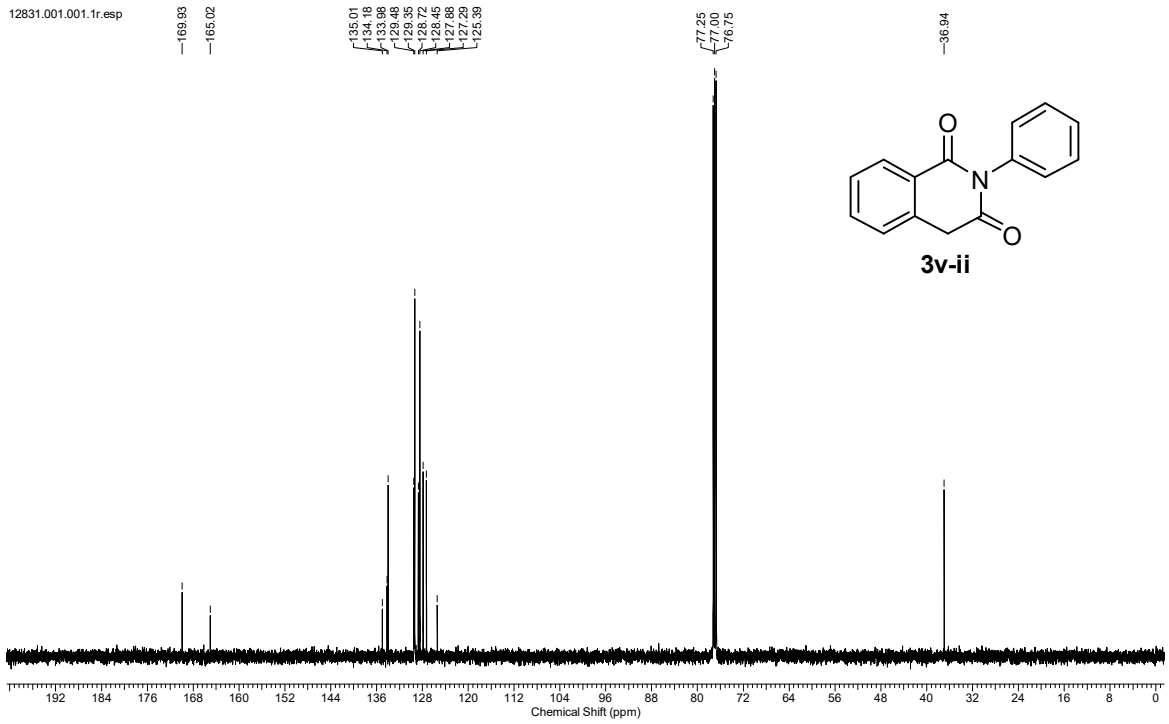
^{13}C NMR of Compound 3v-i in $CDCl_3$



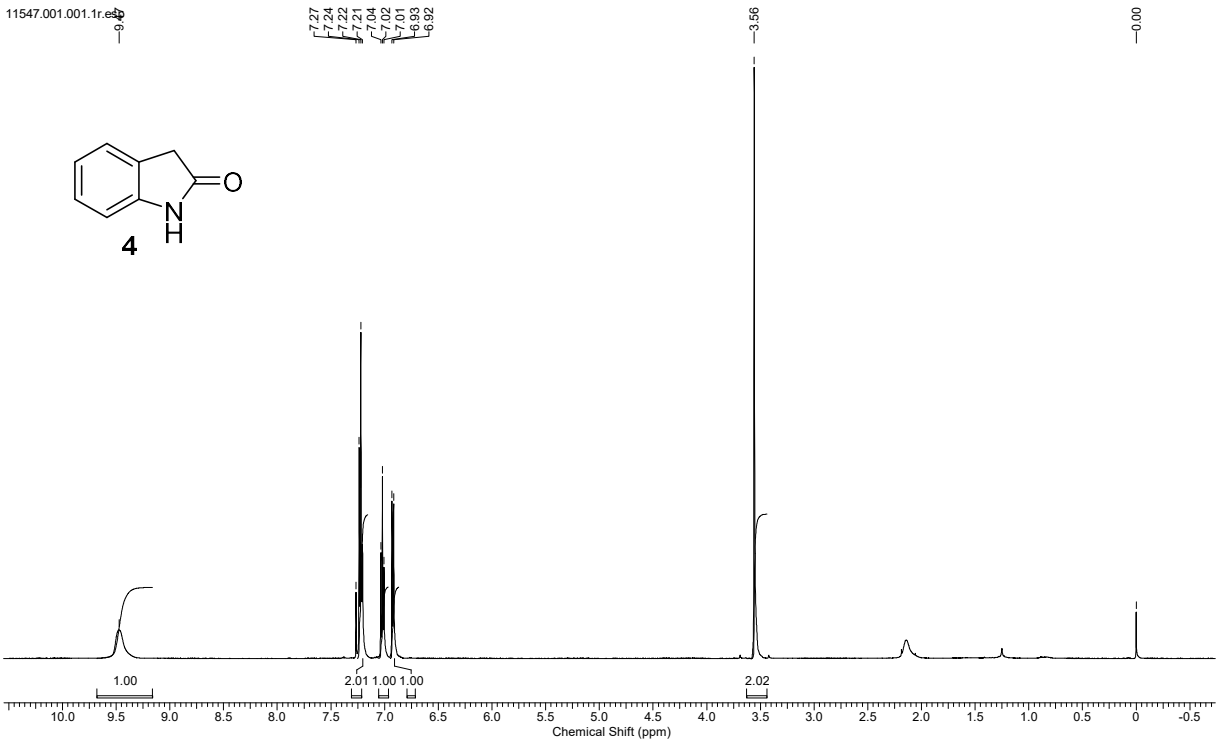
^{1}H NMR of Compound 3v-ii in $CDCl_3$



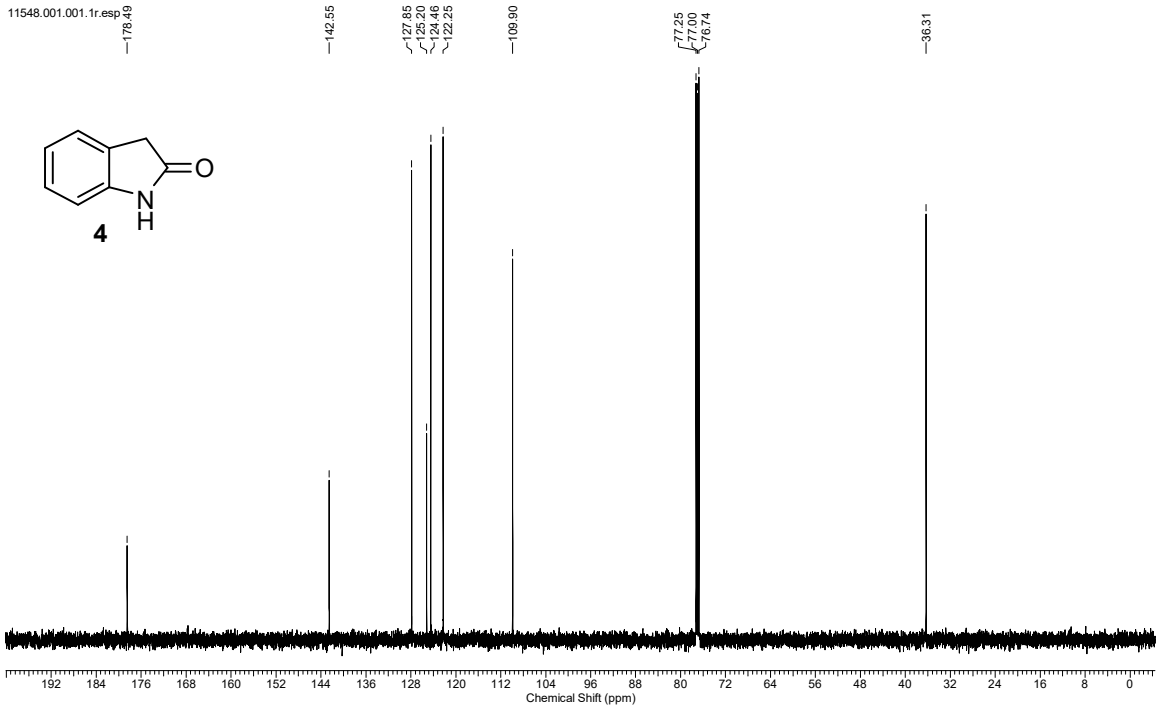
^{13}C NMR of Compound 3v-ii in $CDCl_3$



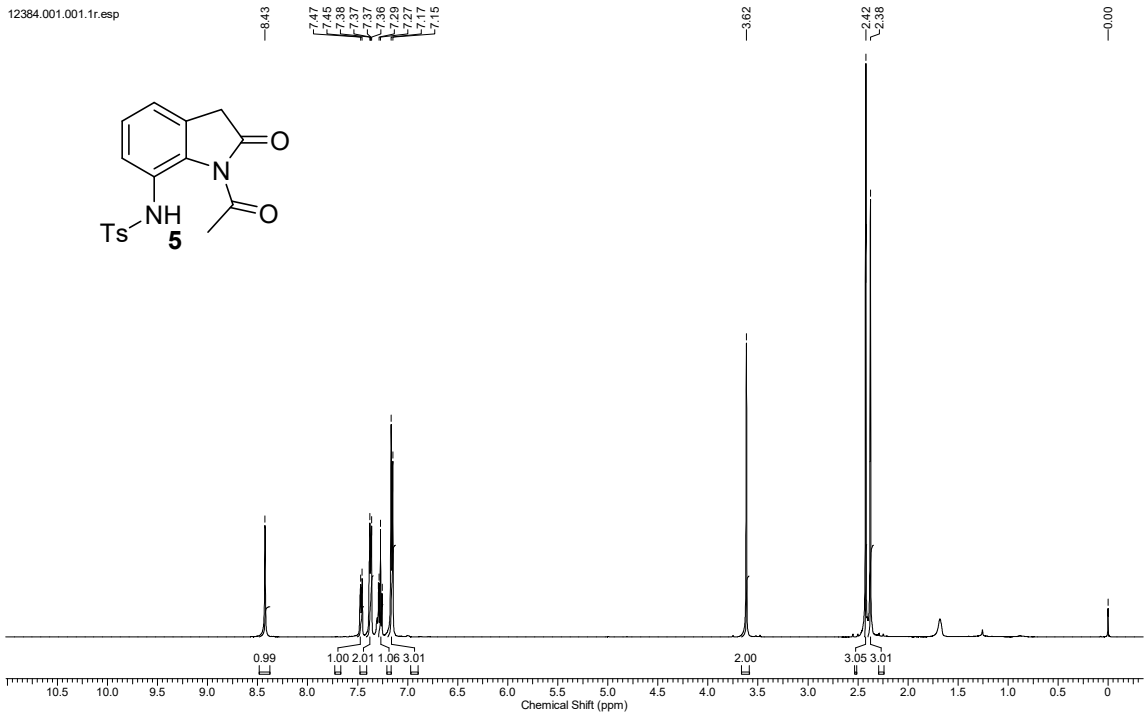
^{1}H NMR of Compound 4 in $CDCl_3$



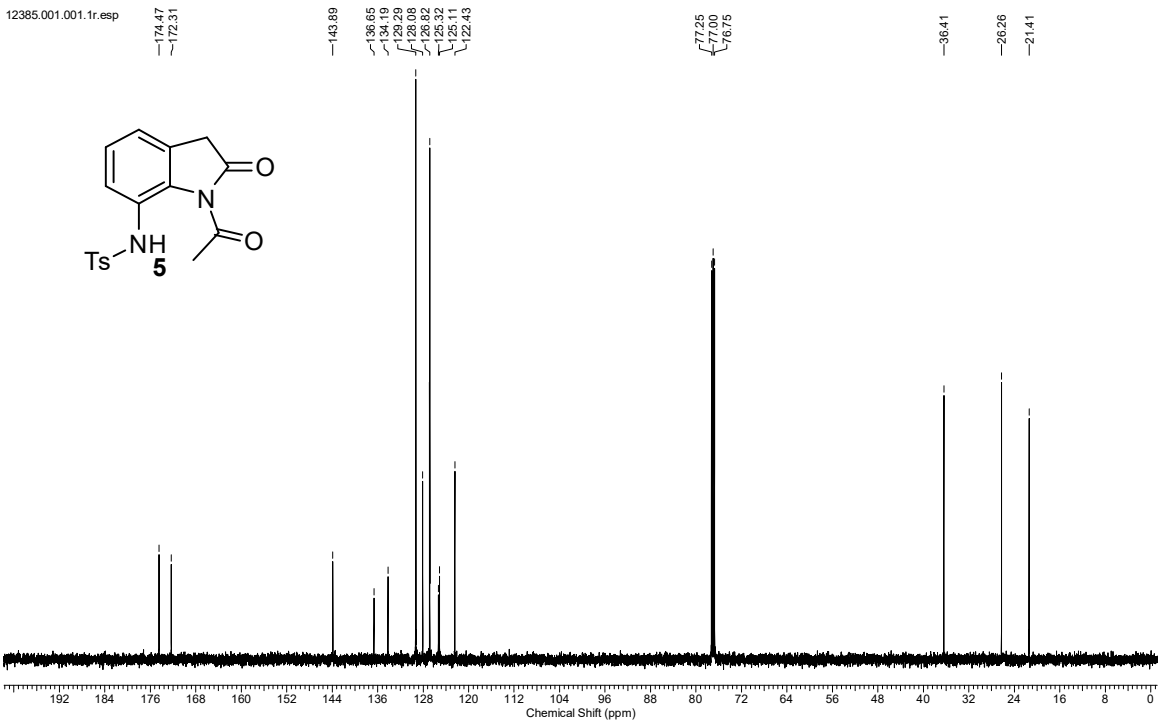
^{13}C NMR of Compound 4 in $CDCl_3$



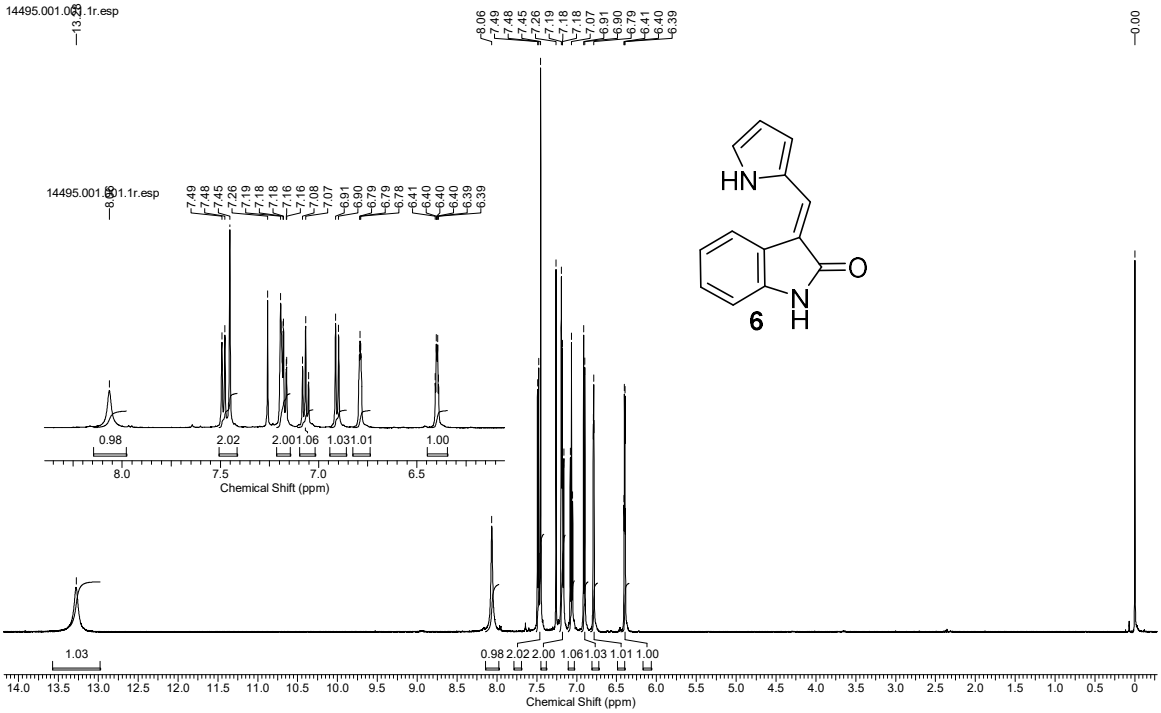
^{1}H NMR of Compound 5 in $CDCl_3$



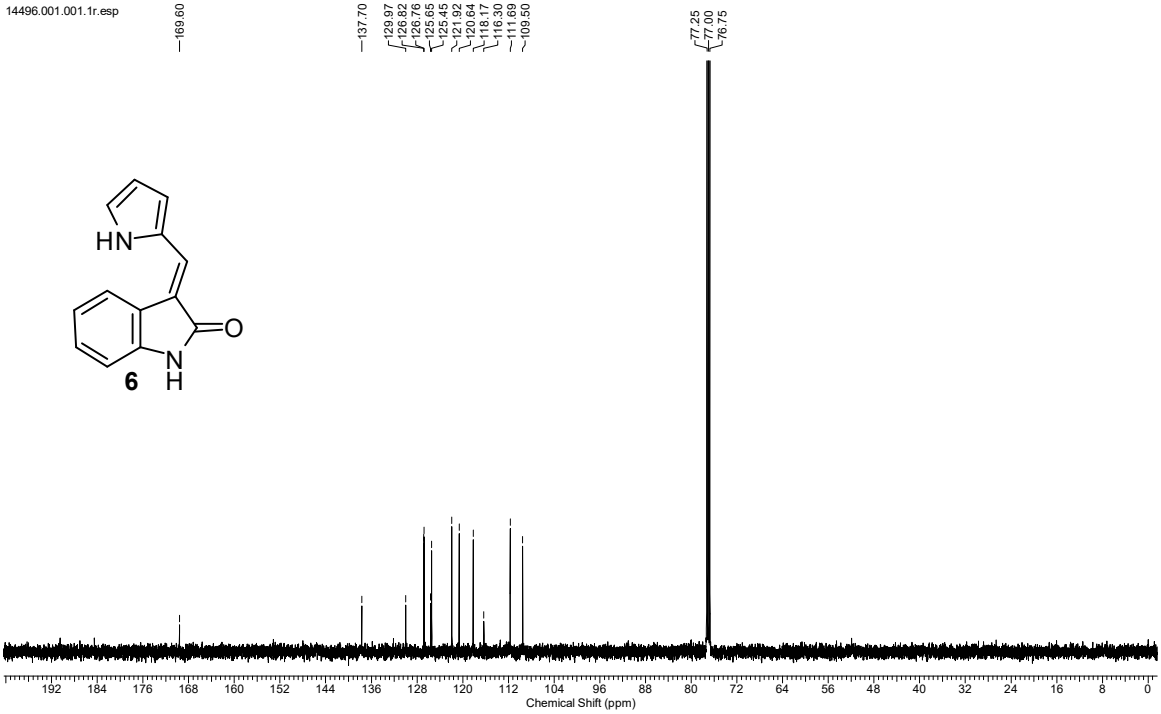
^{13}C NMR of Compound 5 in $CDCl_3$



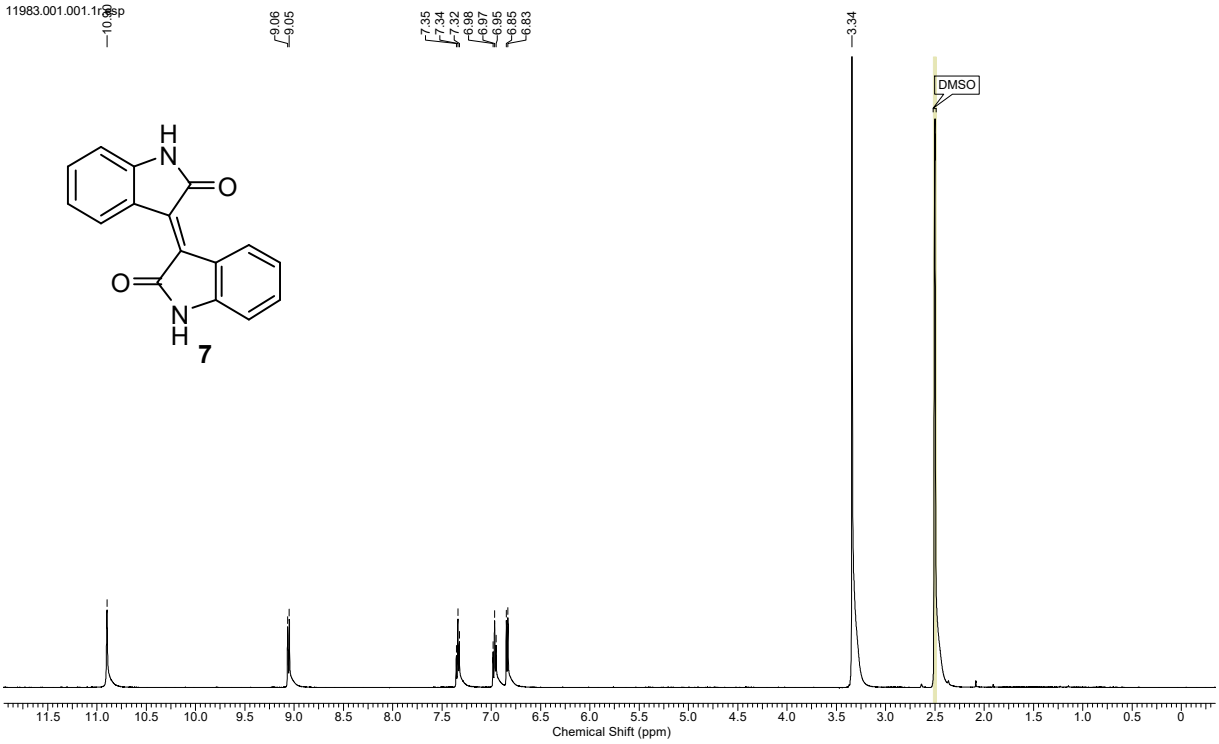
^{1}H NMR of Compound 6 in $CDCl_3$



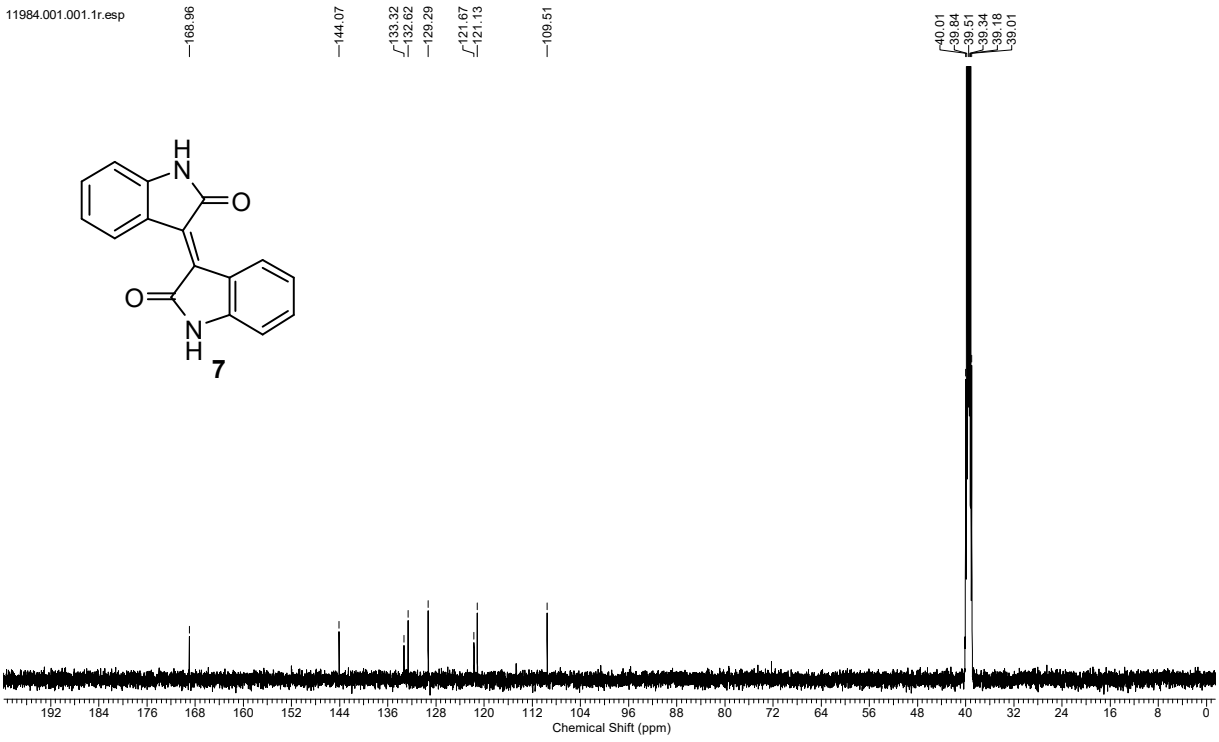
^{13}C NMR of Compound 6 in $CDCl_3$



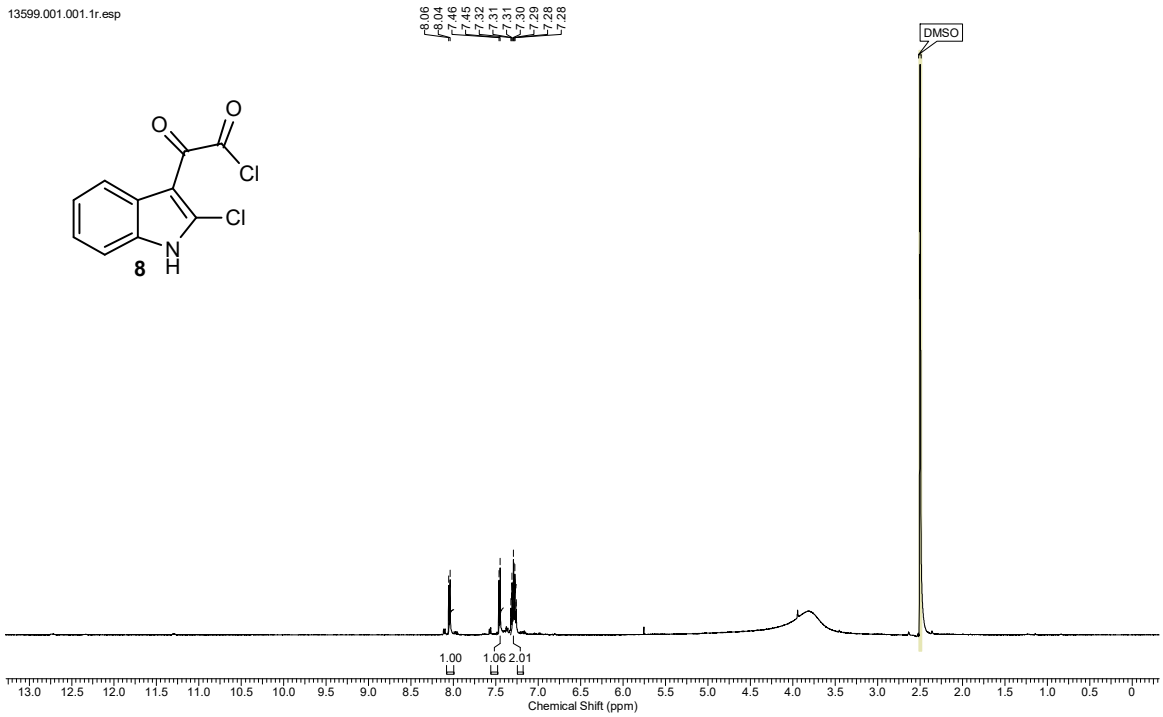
^{1}H NMR of Compound 7 in DMSO-*d*6



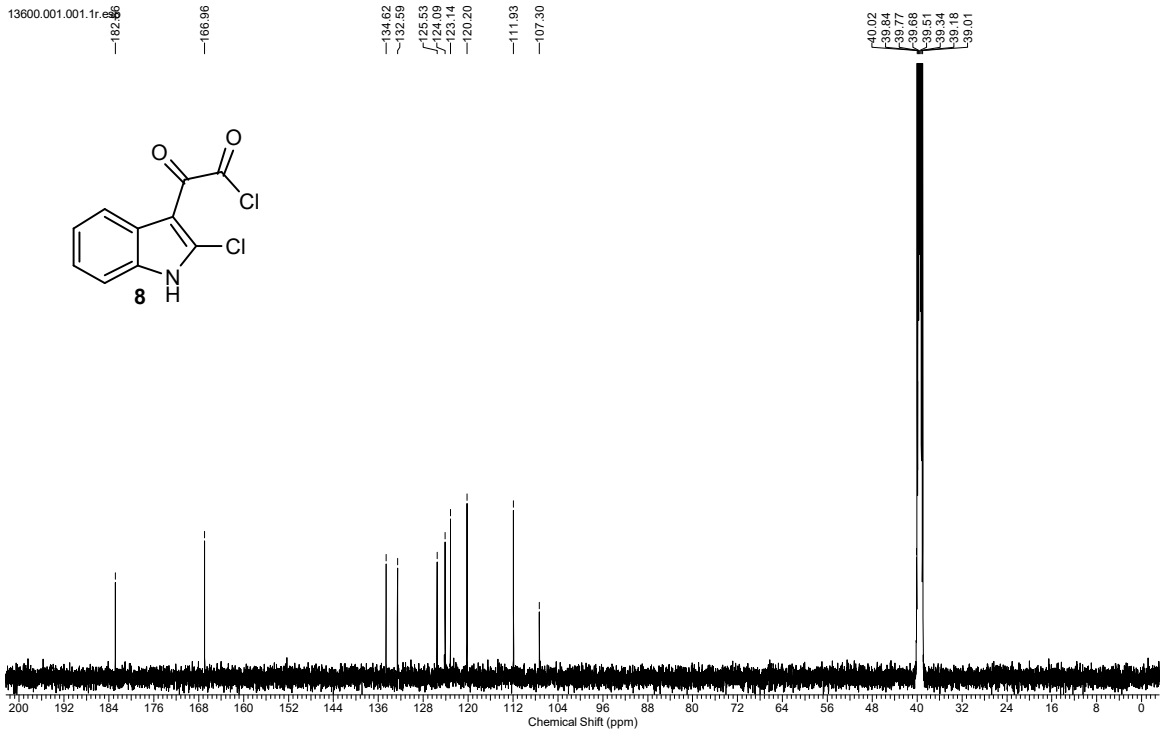
^{13}C NMR of Compound 7 in DMSO-*d*6



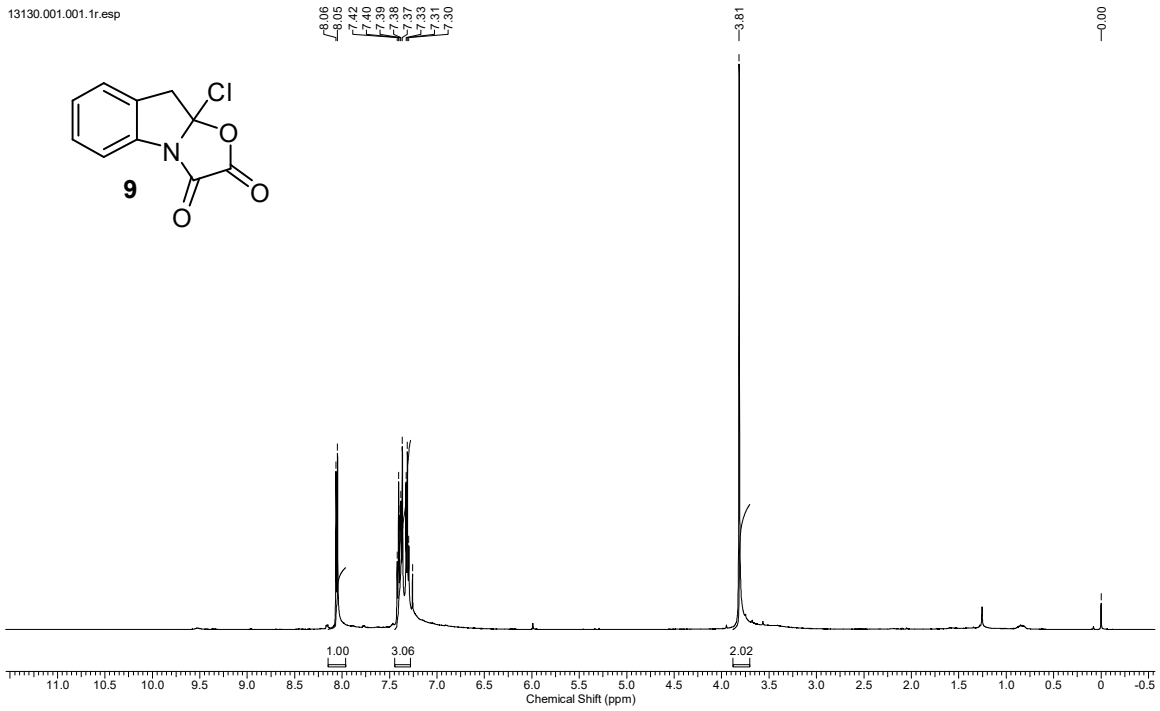
^{1}H NMR of Compound 8 in DMSO-*d*6



^{13}C NMR of Compound 8 in DMSO-*d*6



^{1}H NMR of Compound 9 in $CDCl_3$



^{13}C NMR of Compound 9 in $CDCl_3$