Supporting Information

Base-Enabled Access to Diastereoselective Spirofuran Oxindoles and γ-Functionalized Allenoates

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CONTENT

1. General Methods

All the chemicals and solvents (anhydrous) were commercially purchased from Sigma-Aldrich used without further purification. Column chromatography was performed using silica gel (100-200 mesh), and a mixture of hexane-ethyl acetate was used for elution. NMR spectra were recorded at 500 (^{1}H) and 125 (^{13}C) MHz on Bruker ASCEND^{TM} spectrometer by using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) for ^{1}H NMR spectra are represented in parts per million (ppm) downfield from TMS (δ 0.0) and relative to the signal of $CDCl_3$ (δ 7.27, singlet). Coupling constants (*J*) are given in Hertz (Hz), and multiplicities were represented as s, d, t, q, m, and dd for singlet, doublet, triplet, quartet, multiplet, and doublet of a doublet, respectively. Chemical shifts (δ) for ^{13}C NMR are represented in parts per million (ppm) downfield from TMS (δ 0.0) and relative to the signal of $CDCl_3$ (δ 77.03, triplet). Infrared spectra were recorded with a Bruker Alpha-T FT-IR spectrometer. Mass spectra were recorded under HRMS (ESI) using Thermo Scientific Exactive mass spectrometer. Melting points were determined on a Buchi melting point apparatus and are uncorrected. All the substituted allenoates were synthesized using known procedures.[1] The *N*-protection of isatins was carried out using literature reports.[2]

References

(1) Lang, R. W.; Hansen, H.-J. *Org. Synth. vol.* **1990,** *7***,** 232 **1984**, *62*, 202.

(2) Shmidt, M. S.; Reverdito, A. M.; Kremenchuzky, L.; Perillo, I. A.; Blanco, M. M. **2008**, *13*, 831–840.

2. General experimental procedure

A. General experimental procedure for the synthesis of spirofuran oxindoles (3).

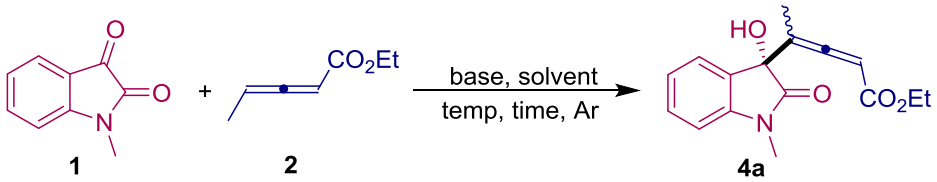
A solution of the isatin (50mg, 1.0 eq.) and the allenoate (0.6 eq.) in acetonitrile (3 mL) was taken in a 20mL reaction tube (Carousel 12 Plus Reaction station) under Argon atmosphere, stir for about 5 min at room temperature. To this solution, DBU (2.0 eq.) was added drop-wise through a glass syringe and continue stirring for 60 minutes by monitoring the TLC. After completion of the reaction, the product was extracted with ethyl acetate (3 x 10mL), evaporated in *vacuo*; the crude extract obtained was chromatographed on silica gel (100-200) by using hexane: ethyl acetate (75:25) as the eluent afforded spirofuran oxindoles.

B. General experimental procedure for the synthesis of γ-functionalized allenoate (4).

A solution of the isatin (30mg, 1.0 eq.) and the allenoate (1.5 eq.) in Dimethyl sulfoxide (1-2 mL) was taken in a 20mL reaction tube (Carousel 12 Plus Reaction station) under Argon atmosphere, stir for about 5 min at 0-5 ^{o}C. To this solution, DABCO (1.8 eq.) was added and stirred for 30 minutes by monitoring the TLC. After completion of the reaction, the product was extracted with ethyl acetate (3 x 10mL), evaporated in *vacuo*; the crude extract obtained was chromatographed on silica gel (100-200) by using hexane: ethyl acetate (80:20) as the eluent γ-functionalized allenoates.

(Carousel 12 Plus Reaction Station)

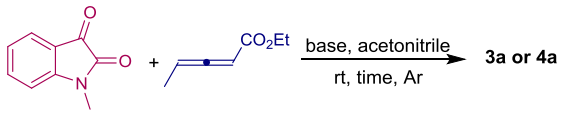
3. Table S1. Optimization of reaction conditions[a]



entry	1 (eq.)	2 (eq.)	base (eq.)	solvent	temp (°C)	time (min.)	yield[b] (%)	dr[c]
1	1	0.6	DABCO (2.0)	Acetonitrile	rt	60	36	1:0.76
2	1	1.0	DABCO (2.0)	Acetonitrile	rt	60	47	1:0.74
3	1	1.5	DABCO (2.0)	Acetonitrile	rt	60	56	1:0.77
4	1	2.0	DABCO (2.0)	Acetonitrile	rt	60	41	1:0.76
5	1	1.5	DABCO (2.0)	DMF	rt	60	60	1:0.79
6	1	1.5	DABCO (2.0)	Toluene	rt	60	NR	-
7	1	1.5	DABCO (2.0)	DCM	rt	60	28	1:0.70
8	1	1.5	DABCO (2.0)	1,4- Dioxane	rt	60	Trace	-
9	1	1.5	DABCO (2.0)	THF	rt	60	34	1:0.84
10	1	1.5	DABCO (2.0)	DMSO	rt	60	75	1:0.70
11	1	1.5	DABCO (1.0)	DMSO	rt	60	52	1:0.72
12	1	1.5	DABCO (1.5)	DMSO	rt	60	74	1:0.75
13	1	1.5	DABCO (2.5)	DMSO	rt	60	72	1:0.70
14	1	1.5	DABCO (3.0)	DMSO	rt	60	36	1:0.78
15	1	1.5	DABCO (1.8)	DMSO	rt	60	77	1:0.80
16	1	1.0	DABCO (1.8)	DMSO	rt	60	58	1:0.76
17	1	2.0	DABCO (1.8)	DMSO	rt	60	60	1:0.80
18	1	1.5	DABCO (1.8)	DMSO	0- 5	60	82	1:0.76
19	1	1.5	DABCO (1.8)	DMSO	50	60	65	1:0.68
20	1	1.5	DABCO (1.8)	DMSO	0- 5	15	73	1:0.70
21	1	1.5	DABCO (1.8)	DMSO	0- 5	30	87	1:0.68
22	1	1.5	DABCO (1.8)	DMSO	0- 5	120	72	1:0.71
23	1	1.5	DABCO (1.8)	DMSO	0- 5	180	60	1:0.68

[a]All the reactions were conducted with 1 equiv. of **1** (0.31 mmol). [b]Isolated yield. [c]Diastereomeric ratio was determined by ^{1}H NMR analysis.

4. Table S2. Control experiments[a] :

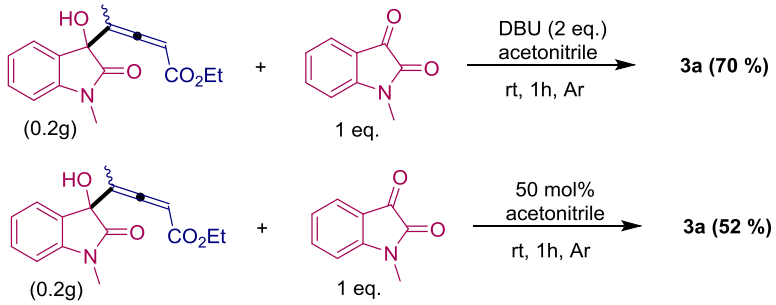


1 2

entry	2 (eq.)	base	time	3a (%)[b]	4a (%)[c]	byproducts
1	0.6	2 mol % (DBU)	1h	ND		
2	0.6	5 mol % (DBU)	1h	ND		
3	0.6	10 mol % (DBU)	1h	15	-	complex
4	0.6	20 mol % (DBU)	1h	17	-	complex
5	0.6	2 eq. (DBU)	24h	40	-	complex
6	0.6	2 eq. (DBU)	>1min	-	63	
7	1.5	5 mol % (DABCO)	0.5h	-	Trace	
8	1.5	10 mol % (DABCO)	0.5h	-	23	complex
9	1.5	20 mol % (DABCO)	0.5h	-	49	complex
10	1.5	1.8 eq. (DABCO)	24h	-	52	complex

[a]All the reactions were conducted with 1 equiv. of **1.** [b] Isolated yield of 3a.

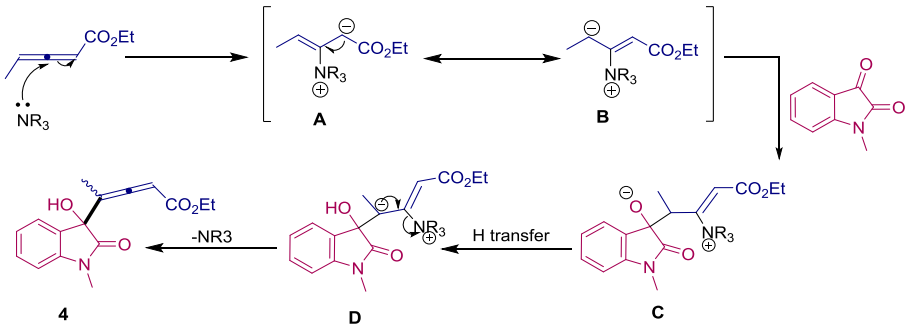
[c] Isolated yield of 4a.



Scheme S1: Catalytic amount v/s stoichiometric amount of base (DBU).

5. <u>Plausible mechanistic pathway for γ-functionalized allenoates (4)</u>

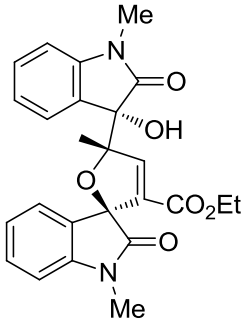
The mechanistic pathway for the formation of γ-functionalized allenoates can be invoked as follows; the initial event is the formation of zwitterion by nucleophilic addition of DABCO to allenoate. The zwitterionic form **B** attacks on the carbonyl carbon of isatin **2** results in an intermediate **C**, which upon proton transfer and DABCO elimination yields desired product **4 (Scheme S2).**



(Scheme S2)

6. Characterization data of Spirofuran Oxindoles

1. Ethyl 5-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1',5-dimethyl-2'-oxo-5H spiro[furan-2,3'-indoline]-3-carboxylate (3a)



3a

Yield**:** 52 mg, 75% yield as white solid; mp= 187- 188 ^{o}C.

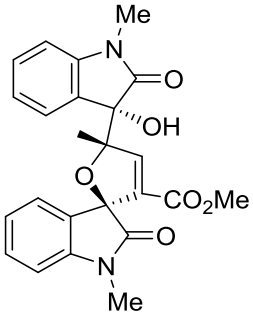
IR (neat, cm^{-1}): 3321, 2981, 2932, 1708, 1611, 1469, 1242, 1096, 1027, 972, 754.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.07 (t, 3H, *J*= 7 Hz), 1.18 (s, 3H), 3.16 (s, 3H), 3.27 (s, 3H), 3.95 (q, 2H, *J*= 7 Hz), 6.73 (d, 1H, *J*= 7.5 Hz), 6.86 (d, 1H, *J*= 8 Hz), 6.92 (t, 1H, *J*= 7.5 Hz), 7.01 (t, 1H, *J*= 7.5 Hz), 7.05 (bs, 1H), 7.06 (d, 1H, *J*= 8 Hz), 7.21 (d, 1H, *J*= 8 Hz), 7.32 (t, 2H, *J*= 7.5 Hz), 7.66 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 13.84, 22.95, 26.32, 26.93, 61.13, 79.75, 88.92, 95.84, 107.97, 108.97, 123.23, 123.68, 124.28, 126.32, 128.14, 129.32, 129.54, 130.81, 132.89, 143.86, 144.08, 144.57, 160.96, 175.07, 176.64.

HRMS (ESI): calcd for $[C_{25}H_{24}N_2O_6Na, M+Na]^+$: 471.1532; Found: 471.1541).

2. Methyl 5-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1',5-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3b)



3b

Yield**:** 58 mg, 86% yield as white solid; mp= 228- 230 ^{o}C.

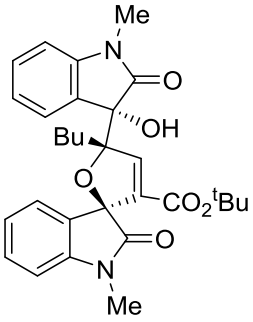
IR (neat, cm^{-1}): 3272, 3058, 2979, 2952, 1713, 1612, 1493, 1379, 1265, 1139, 847, 756.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.18 (s, 3H), 3.16 (s, 3H), 3.28 (s, 3H), 3.55 (s, 3H), 6.74 (d, 1H, *J*= 8 Hz), 6.87 (d, 1H, *J*= 8 Hz), 6.92 (t, 1H, *J*= 7.5 Hz), 7.01 (t, 1H, *J*= 7.5 Hz), 7.05 (s, 2H), 7.20 (d, 1H, 8 Hz), 7.32 (t, 2H, *J*= 7 Hz), 7.56 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 22.88, 26.30, 26.93, 51.97, 79.74, 88.93, 95.85, 107.95, 109.04, 123.21, 123.66, 124.23, 126.31, 128.04, 129.29, 129.54, 130.84, 132.54, 143.87, 144.08, 144.73, 161.43, 175.04, 176.56.

HRMS (ESI): calcd for $[C_{24}H_{22}N_2O_6Na, M+Na]^+$: 457.4310, Found: 457.1382).

3. tert-Butyl 5-butyl-5-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1'-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3c)



3c

Yield**:** 43 mg, 53% yield as white solid; mp= 228.-229 ^{o}C.

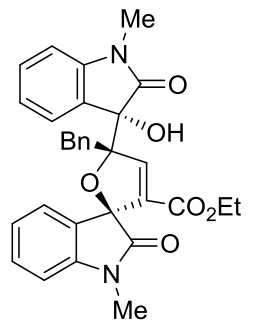
IR (neat, cm^{-1}): 3361, 2971, 2930, 1710, 1609, 1486, 1375, 1176, 1025, 974, 755.

^{1}H NMR (500MHz, CDCl$_3$): δ 0.83 (t, 3H, *J*= 7 Hz), 1.20 (s, 9H), 1.23-1.33 (m, 4H), 1.43-1.50 (m, 2H), 3.25 (s, 3H), 3.26 (s, 3H), 6.81 (d, 1H, *J*= 8.5 Hz), 6.94 (d, 1H, *J*= 8 Hz), 7.00 (t, 1H, *J*= 7.5 Hz), 7.11 (t, 1H, *J*= 7.5 Hz), 7.29 (t, 1H, *J*= 7.5 Hz), 7.36 (t, 2H, *J*= 7.5 Hz), 7.42 (t, 1H, *J*= 7.5 Hz), 7.62 (s, 1H), 7.79 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 13.90, 22.74, 26.26, 26.68, 26.88, 27.67, 33.53, 79.96, 81.82, 88.84, 99.23, 107.95, 108.87, 123.13, 123.64, 125.05, 126.27, 128.59, 130.15, 130.73, 135.06, 143.70, 144.15, 159.84, 175.48, 176.69.

HRMS (ESI): calcd for $[C_{30}H_{34}N_2O_6Na, M+Na]^+$: 541.2315; Found: 541.2359).

4. Ethyl 5-benzyl-5-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1'-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3d)



3d

Yield**:** 47 mg, 58% yield as white solid; mp= 196-197 ^{o}C.

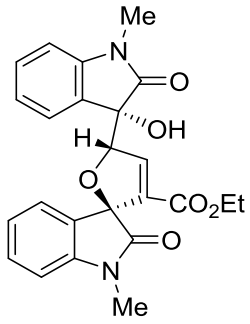
IR (neat, cm^{-1}): 3285, 2979, 2932, 2876, 1709, 1609, 1486, 1115, 1069, 971, 753.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.11 (t, 3H, *J*= 7 Hz), 2.47 (d, 1H, *J*= 13.5 Hz), 3.09 (d, 1H, *J*= 13.5 Hz), 3.28 (s, 3H), 3.30 (s, 3H), 3.95 - 4.0 (m, 2H), 4.75 (d, 1H, *J*= 7 Hz), 6.62 (t, 1H, *J*= 7.5 Hz), 6.80 (d, 1H, *J*= 8 Hz), 6.86 (d, 1H, *J*= 8 Hz), 6.99 (d, 2H, 8 Hz), 7.07 (t, 1H, 7.5 Hz), 7.20 - 7.25 (m, 3H), 7.31- 7.36 (m, 2H), 7.49 (d, 1H, *J*= 8 Hz), 7.85 (s, 1H), 7.89 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 13.77, 26.33, 26.85, 39.98, 60.99, 80.16, 89.10, 99.37, 108.10, 108.26, 123.35, 123.41, 125.23, 126.52, 126.86, 127.40, 128.42, 129.61, 129.76, 130.43, 131.71, 133.98, 134.99, 143.15, 143.55, 144.12, 160.62, 175.31, 176.51.

HRMS (ESI): calcd for $[C_{31}H_{28}N_2O_6Na, M+Na]^+$: 547.1845; Found: 547.1890).

5. Ethyl 5-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1'-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3e)



3e

Yield**:** 21 mg, 31% yield as white solid; mp= 191-192 ^{o}C.

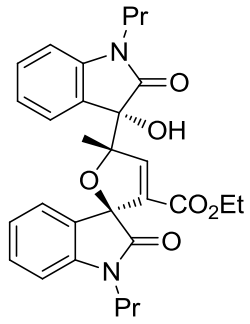
IR (neat, cm^{-1}): 3261, 2970, 2875, 1715, 1611, 1468, 1241, 1170, 1027, 932, 752, 698.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.38 (s, 3H), 3.25 (s, 3H), 3.28 (s, 3H), 4.42 (q, 2H, *J*= 7 Hz), 4.47 (s, 1H), 6.77 (t, 2H, *J*= 7.5 Hz), 6.91 (d, 1H, *J*= 8 Hz), 7.02 (d, 1H, *J*= 8 Hz), 7.08 (t, 1H, 7.5 Hz), 7.15 (t, 1H, 7.5 Hz), 7.34 (t, 1H, 7.5 Hz), 7.45 (d, 1H, *J*= 8 Hz), 7.62 (d, 2H, *J*= 8 Hz).

^{13}C NMR (125MHz, $CDCl_3$): δ 14.08, 26.03, 26.23, 62.51, 79.58, 86.10, 108.58, 109.91, 123.86, 124.58, 125.09, 125.34, 126.50, 126.67, 127.98, 128.13, 129.33, 131.07, 138.39, 143.47, 144.81, 165.55, 172.83, 174.62.

HRMS (ESI): calcd for $[C_{24}H_{22}N_2O_6Na, M+Na]^+$: 457.1376; Found: 457.1372).

6. Ethyl 5-(-3-hydroxy-2-oxo-1-propylindolin-3-yl)-5-methyl-2'-oxo-1'-propyl-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3f)



3f

Yield**:** 52 mg, 80% yield as white solid; mp= 175- 176 ^{o}C.

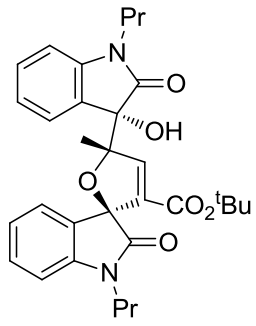
IR (neat, cm^{-1}): 3276, 2972, 2934, 1698, 1610, 1467, 1251, 1095, 1025, 971, 752, 693.

^{1}H NMR (500MHz, $CDCl_3$): δ 0.93 (t, 3H, *J*= 7 Hz), 0.98 (t, 3H, *J*= 7.5 Hz), 1.07 (t, 3H, *J*= 7 Hz), 1.19 (s, 3H), 1.64- 1.68 (m, 2H), 1.73- 1.77 (m, 2H), 3.48 (q, 1H, *J*= 7 Hz), 3.69 (q, 1H, *J*= 7.5 Hz), 3.72- 3.76 (m, 2H), 3.92- 4.01 (m, 2H), 6.75 (d, 1H, *J*= 7.5 Hz), 6.86- 6.91 (m, 2H), 6.99 (t, 1H, *J*= 7 Hz), 7.07 (d, 1H, *J*= 7.5 Hz), 7.12 (s,1H), 7.18 (d, 1H, *J*= 9 Hz), 7.29 (t, 2H, *J*= 8.5 Hz), 7.67 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 11.34, 11.52, 13.87, 20.63, 20.71, 22.99, 41.76, 42.35, 61.08, 79.60, 88.82, 95.74, 108.24, 109.29, 122.99, 123.43, 124.45, 126.44, 128.35, 129.42, 129.52, 130.70, 132.83, 143.41, 143.58, 144.72, 164.94, 175.08, 176.58.

HRMS (ESI): calcd for $[C_{29}H_{32}N_2O_6Na, M+Na]^+$: 527.2158; Found: 527.2166).

7. tert-Butyl 5-(3-hydroxy-2-oxo-1-propylindolin-3-yl)-5-methyl-2'-oxo-1'-propyl-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3g)



3g

Yield**:** 51 mg, 73% yield as white solid; mp= 231- 233 ^{o}C.

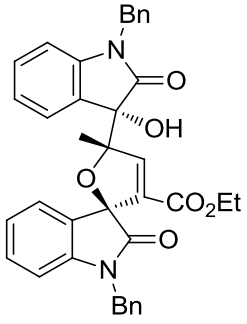
IR (neat, cm^{-1}): 3283, 2971, 2933, 2876, 1703, 1610, 1487, 1369, 1119, 971, 751.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.02 (t, 3H, *J*= 7.5 Hz), 1.07 (t, 3H, *J*= 7.5 Hz), 1.25 (s, 9H), 1.26 (s, 3H), 1.71- 1.78 (m, 2H), 1.80- 1.86 (m, 2H), 3.57- 3.68 (m, 2H), 3.80 (q, 1H, *J*= 7.5 Hz), 3.93 (q, 1H, *J*= 7.5 Hz), 6.83 (d, 1H, *J*= 8 Hz), 6.98 (t, 2H, *J*= 7.5 Hz), 7.09 (t, 1H, *J*= 7.5 Hz), 7.17 (d, 1H, *J*= 7 Hz) 7.26 (t, 2H, *J*= 7.5 Hz), 7.37 (t, 2H, *J*= 7.5 Hz), 7.67 (s, 1H).

^{13}C NMR (**125MHz**, $CDCl_3$): δ 11.30, 11.50, 20.59, 20.69, 23.06, 27.72, 41.73, 42.21, 79.57, 81.93, 88.71, 95.53, 108.20, 109.20, 122.93, 123.43, 124.44, 126.42, 129.35, 129.64, 130.53, 134.24, 143.43, 143.52,144.16, 159.92, 175.14, 176.74.

HRMS (ESI): calcd for $[C_{31}H_{36}N_2O_6Na, M+Na]^+$: 555.2471; Found: 555.2484).

8. Ethyl 1'-benzyl-5-(1-benzyl-3-hydroxy-2-oxoindolin-3-yl)-5-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3h)



3h

Yield**:** 41 mg, 65% yield as white solid; mp= 205- 206 ^{o}C.

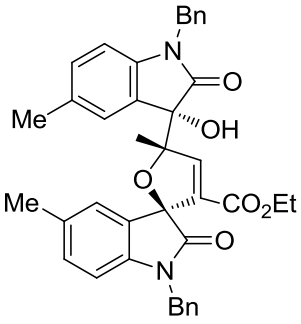
IR (neat, cm^{-1}): 3268, 2982, 2932, 1710, 1611, 1467, 1254, 1198, 1139, 1027, 972, 752.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.12 (t, 3H, *J*= 7 Hz), 1.32 (s, 3H), 4.01 (q, 1H, *J*= 7.5 Hz), 4.14 (q, 1H, *J*= 7.5 Hz), 4.84 (d, 1H, *J*= 15.5 Hz), 5.0 (d, 1H, *J*= 16 Hz), 5.07 (d, 1H, *J*= 15.5 Hz), 5.10 (d, 1H, *J*= 15.5 Hz), 6.77 (d, 1H, *J*= 7.5 Hz), 6.82 (d, 1H, *J*= 7.5 Hz), 6.99 (t, 1H, 7.5 Hz), 7.07 (t, 1H, 7.5 Hz), 7.18 (t, 2H, *J*= 7.5 Hz), 7.28- 741 (m, 11H), 7.47 (d, 2H, *J*= 7.5 Hz), 7.84 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 13.84, 14.14, 22.67, 23.15, 31.65, 44.05, 44.65, 61.17, 79.66, 88.93, 95.93, 109.05, 110.14, 123.26, 123.73, 124.39, 126.42, 127.46, 127.48, 127.76, 127.89, 128.26, 128.86, 128.88, 129.41, 129.48, 130.71, 132.82, 134.98, 135.60, 143.12, 143.27, 144.93, 160.94, 175.24, 176.91.

HRMS (ESI): calcd for $[C_{37}H_{32}N_2O_6Na, M+Na]^+$: 623.2158; Found: 623.2170).

9. Ethyl 1'-benzyl-5-(-1-benzyl-3-hydroxy-5-methyl-2-oxoindolin-3-yl)-5,5'-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3i)



3i

Yield**:** 44 mg, 70% yield as white solid; mp= 119- 120 ^{o}C.

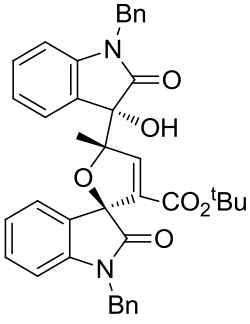
IR (neat, cm^{-1}): 3275, 3031, 2980, 2927, 1714, 1620, 1494, 1372, 1258, 1139, 1027, 810, 698.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.16 (t, 3H, *J*= 7 Hz), 1.33 (s, 3H), 2.25 (s, 3H), 2.28 (s, 3H), 4.04 (q, 1H, *J*= 7.5 Hz), 4.14 (q, 1H, *J*= 7 Hz), 4.83 (d, 1H, *J*= 15.5 Hz), 5.01 (d, 1H, *J*= 15.5 Hz), 5.07 (d, 1H, *J*= 16 Hz), 5.10 (d, 1H, *J*= 15.5 Hz), 6.64 (d, 1H, *J*= 8 Hz), 6.72 (d, 1H, *J*= 8 Hz), 6.99 (s, 2H), 7.07 (d, 1H, *J*= 8 Hz), 7.21-7.39 (m, 10H), 7.48 (d, 2H, *J*= 7.5 Hz), 7.83 (s, 1H).

^{13}C NMR (**125MHz, CDCl$_3$):** δ 13.87, 14.13, 21.03, 21.18, 22.66, 23.18, 31.60, 44.03, 44.56, 61.17, 79.82, 89.03, 95.92, 108.78, 109.90, 125.17, 127.21, 127.45, 127.46, 127.69, 127.84, 128.23, 128.81, 128.84, 129.40, 129.71, 131.01, 132.70, 132.76, 133.45, 135.12, 135.72, 140.71, 140.81, 144.99, 161.03, 175.25, 176.78.

HRMS (ESI): calcd for $[C_{39}H_{36}N_2O_6H, M+H]^+$: 629.2652; Found: 629.2667).

10. tert-Butyl 1'-benzyl-5-(1-benzyl-3-hydroxy-2-oxoindolin-3-yl)-5-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3j)



3j

Yield**:** 40 mg, 60% yield as white solid; mp= 191- 192 ^{o}C.

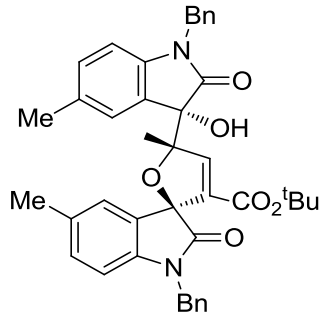
IR (neat, cm^{-1}): 3285, 3060, 2979, 2930, 1705, 1612, 1486, 1348, 1165, 1115, 972, 751, 697.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.28 (s, 9H), 1.30 (s, 3H), 4.84 (d, 1H, *J*= 15 Hz), 4.88 (d, 1H, *J*= 15 Hz), 5.06 (d, 1H *J*= 15.5 Hz), 5.20 (d, 1H, *J*= 15 Hz), 6.75 (d, 1H, *J*= 8 Hz), 6.84 (d, 1H, *J*= 8 Hz), 6.98 (t, 1H, *J*= 7.5 Hz), 7.07 (t, 1H, *J*= 7.5 Hz), 7.18 (d, 2H, *J*= 7.5 Hz), 7.28 (t, 3H, *J*= 7 Hz), 7.30- 7.40 (m, 8H), 7.47 (d, 2H, *J*= 7.5 Hz), 7.74 (s, 1H).

^{13}C NMR (**125MHz, CDCl$_3$):** δ 22.66, 23.24, 27.75, 44.02, 44.45, 79.64, 82.15, 88.82, 95.73, 109.03, 109.95, 123.23, 123.71, 124.37, 126.44, 127.46, 127.58, 127.74, 127.92, 128.44, 128.63, 128.85, 128.89, 129.42, 129.52, 130.55, 130.64, 134.23, 135.02, 135.60, 143.14, 143.22, 144.27, 159.98, 175.37, 177.04.

HRMS (ESI): calcd for $[C_{39}H_{36}N_2O_6Na, M+Na]^+$: 651.2471; Found: 651.2487).

11. tert-Butyl 1'-benzyl-5-(-1-benzyl-3-hydroxy-5-methyl-2-oxoindolin-3-yl)-5,5'-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3k)



3k

Yield**:** 41 mg, 63% yield as white solid; mp= 201- 202 ^{o}C.

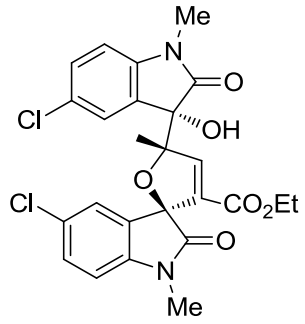
IR (neat, cm^{-1}): 3284, 2928, 2926, 2859, 1707, 1605, 1494, 1370, 1161, 1017, 810, 699.

^{1}H NMR (**500MHz**, $CDCl_3$): δ 1.20 (s, 9H), 1.22 (s, 3H), 2.14 (s, 3H), 2.19 (s, 3H), 4.65 (d, 1H, *J*= 15.5 Hz), 4.68 (d, 1H, *J*= 15.5 Hz), 4.93 (d, 1H, *J*= 15.5 Hz), 5.19 (d, 1H, *J*= 15.5 Hz), 6.53 (d, 1H, *J*= 8 Hz), 6.64 (d, 1H, *J*= 8 Hz), 6.87 (d, 2H, *J*= 8 Hz), 6.98 (d, 1H, *J*= 8 Hz), 7.09 (s, 1H), 7.18 (s, 1H), 7.20- 7.29 (m, 8H), 7.35 (d, 2H, *J*= 7.5 Hz), 7.6 (s, 1H).

^{13}C NMR (**125MHz**, $CDCl_3$): δ 20.99, 21.19, 23.25, 27.77, 44.00, 44.33, 79.79, 82.09, 88.92, 95.71, 108.77, 109.69, 125.13, 125.20 127.27, 127.43, 127.53, 127.66, 127.88, 127.95, 128.48, 128.59, 128.80, 128.84, 129.50, 129.64, 130.80, 132.62, 133.45, 134.20, 135.15, 135.71, 135.71, 140.71, 140.73, 144.36, 160.04, 175.34, 176.90.

HRMS (ESI): calcd for $[C_{41}H_{40}N_2O_6H, M+H]^+$: 657.2965; Found: 657.2970).

12. Ethyl 5'-chloro-5-(5-chloro-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1',5-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3l)



3l

Yield**:** 46 mg, 70% yield as white solid; mp= 223- 225 ^{o}C.

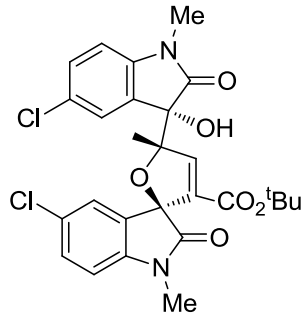
IR (neat, cm^{-1}): 3264, 3063, 2980, 2935, 1705, 1609, 1487, 1368, 1241, 1103, 1026, 876, 735.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.20 (t, 3H, *J*= 7 Hz), 1.28 (s, 3H), 3.25 (s, 3H), 3.37 (s, 3H), 4.08 (q, 2H, *J*= 7 Hz), 6.77 (d, 1H, *J*= 8 Hz), 6.90 (d, 1H, *J*= 7.5 Hz), 7.11 (s, 1H), 7.13 (s, 1H), 7.20 (d, 1H, *J*= 8 Hz), 7.39 (d, 2H, *J*= 8Hz), 7.72 (s, 1H)

^{13}C NMR (**125MHz, $CDCl_3$):** δ 13.86, 22.99, 26.48, 27.15, 61.39, 79.70, 88.78, 95.93, 109.09, 110.11, 124.79, 126.57, 128.59, 129.19, 129.58, 129.61, 130.76, 130.82, 142.47, 142.67, 144.41, 160.71, 174.49, 176.26.

HRMS (ESI): calcd for $C_{25}H_{22}Cl_2N_2O_6^+$ ($[M(^{35}Cl)+Na])^+$: 539.0753, **found:** 539.0767; ($[M(^{35}Cl\&^{37}Cl)+Na])^+$: 541.0753, **found** : 541.0738; ($[M(^{37}Cl)+Na])^+$: 543.0767, **found:** 543.0756).

13. tert-Butyl 5'-chloro-5-(5-chloro-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1',5-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3m)



3m

Yield**:** 49 mg, 71% yield as white solid; mp= 213- 215 ^{o}C.

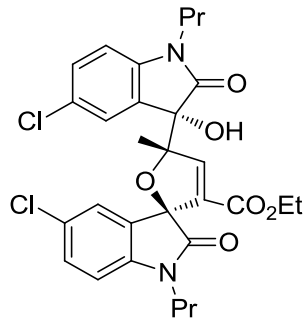
IR (neat, cm^{-1}): 3287, 3082, 2979, 1712, 1610, 1487, 1364, 1250, 1165, 1116, 957, 814.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.26 (s, 3H), 1.28 (s, 9H), 3.24 (s, 3H), 3.36 (s, 3H), 6.77 (d, 1H, *J*= 8 Hz), 6.89 (d, 1H, *J*= 8 Hz), 7.13 (s, 2H), 7.30 (s, 1H), 7.34 (s, 1H), 7.39 (d, 1H, *J*= 8 Hz), 7.65 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 23.05, 26.47, 27.11, 27.84, 79.66, 82.41, 88.62, 95.66, 109.05, 109.98, 124.75, 126.55, 128.54, 129.19, 129.55, 130.58, 130.94, 134.16, 142.50, 142.67, 144.04, 159.61, 174.56, 176.38.

HRMS (ESI): calcd for $C_{27}H_{26}Cl_2N_2O_6^+$ ([M(^{35}Cl)+Na])$^+$: 567.1066, **found** : 567.1067; ([M(^{35}Cl&^{37}Cl)+Na])$^+$: 569.1067, **found** : 569.1032; ([M(^{37}Cl)+Na])$^+$: 571.1067, **found:** 571.1004).

14. Ethyl 5'-chloro-5-(5-chloro-3-hydroxy-2-oxo-1-propylindolin-3-yl)-5-methyl-2'-oxo-1'-propyl-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3n)



3n

Yield**:** 47 mg, 73% yield as white solid; mp= 189 - 190 ^{o}C.

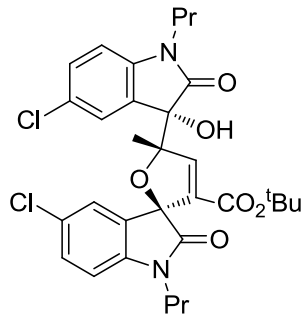
IR (neat, cm^{-1}): 3263, 2970, 2934, 1715, 1609, 1482, 1372, 1253, 1117, 1025, 977, 757.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.01 (t, 3H, *J*= 7.5 Hz), 1.06 (t, 3H, *J*= 7.5 Hz), 1.20 (t, 3H, *J*= 7.5 Hz), 1.30 (s, 3H), 1.73- 1.76 (m, 2H), 1.80- 1.83 (m, 2H), 3.59 (q, 1H, *J*= 7 Hz), 3.76 (q, 1H, *J*= 7 Hz), 3.79- 3.87 (m, 2H), 4.05- 4.12 (m, 2H), 6.78 (d, 1H, *J*= 8 Hz), 6.90 (d, 1H, *J*= 8 Hz), 7.11 (s, 1H), 7.21 (s, 1H), 7.28 (s,1H), 7.32 (s, 1H), 7.37 (d, 1H, *J*= 8 Hz), 7.72 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 11.28, 11.46, 13.88, 20.48, 20.62, 22.99, 41.91, 42.54, 61.34, 79.53, 88.66, 95.85, 109.32, 110.44, 124.94, 126.82, 128.32, 128.96, 129.45, 130.66, 131.02, 142.03, 142.14, 144.64, 160.70, 174.54, 176.27.

HRMS (ESI): calcd for $C_{29}H_{30}Cl_2N_2O_6^+$ ([M(^{35}Cl)+Na])$^+$: 595.1379, **found**: 595.1393; ([M(^{35}Cl&^{37}Cl)+Na])$^+$: 597.1349, **found**: 597.1365; ([M(^{37}Cl)+Na])$^+$: 599.1379, **found:** 599.1366).

15. tert-Butyl 5'-chloro-5-(5-chloro-3-hydroxy-2-oxo-1-propylindolin-3-yl)-5-methyl-2'-oxo-1'-propyl-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3o)



3o

Yield**:** 45 mg, 67% yield as white solid; mp= 190- 191 ^{o}C.

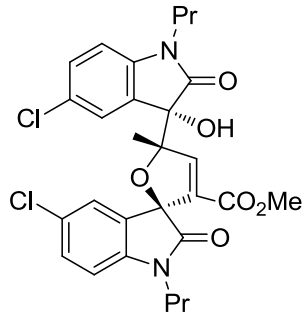
IR (neat, cm^{-1}): 3267, 3069, 2972, 2933, 1705, 1608, 1481, 1370, 1256, 1165, 984, 736.

^{1}H NMR (500MHz, CDCl$_3$): δ 0.92 (t, 3H, *J*= 7.5 Hz), 0.98 (t, 3H, *J*= 7.5 Hz), 1.19 (s, 3H), 1.21 (s, 9H), 1.62- 1.66 (m, 2H), 1.72- 1.76 (m, 2H), 3.47- 3.53 (m, 1H), 3.57- 3.62 (m, 1H), 3.67- 3.73 (m, 1H), 3.30- 3.86 (m, 1H), 6.67 (d, 1H, *J*= 7.5 Hz), 6.80 (d, 1H, *J*= 8 Hz), 7.04 (s, 1H), 7.17 (bs, 1H), 7.19 (d, 2H, *J*= 7 .5 Hz), 7.28 (d, 1H, *J*= 8 Hz), 7.54 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 11.25, 11.44, 20.42, 20.61, 23.07, 27.79, 41.89, 42.37, 79.51, 82.42, 88.56, 95.62, 109.29, 110.39, 124.87, 126.89, 128.28, 128.98, 129.38, 129.40, 130.49, 131.12, 142.03, 142.06, 144.10, 159.65, 174.62, 176.48.

HRMS (ESI): calcd for $C_{31}H_{34}Cl_2N_2O_6^+$ ([M(^{35}Cl)+Na])$^+$: 623.1692, **found** : 623.1700; ([M(^{35}Cl&^{37}Cl)+Na])$^+$: 625.1662, **found**: 625.1670; ([M(^{37}Cl)+Na])$^+$: 627.1692, **found:** 627.1626).

16. Methyl 5'-chloro-5-(-5-chloro-3-hydroxy-2-oxo-1-propylindolin-3-yl)-5-methyl-2'-oxo-1'-propyl-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3p)



3p

Yield**:** 50 mg, 80% yield as white solid; mp= 159- 160 ^{o}C.

IR (neat, cm^{-1}): 3281, 2968, 2928, 2875, 1719, 1609, 1482, 1374, 1257, 1116, 1020, 889, 738.

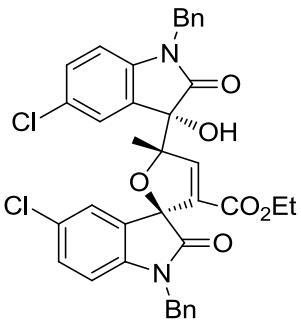
^{1}H NMR (500MHz, CDCl$_3$): δ 0.99 (t, 3H, *J*= 7.5 Hz), 1.04 (t, 3H, *J*= 7.5 Hz), 1.27 (s, 3H), 1.69- 1.75 (m, 2H), 1.78- 1.83 (m, 2H), 3.53- 3.59 (m, 1H), 3.64 (s, 3H), 3.74- 3.80 (m, 2H), 3.82- 3.88 (m, 1H), 6.75 (d, 1H, *J*= 8 Hz), 6.89 (d, 1H, *J*= 8 Hz), 7.08 (s, 1H), 7.12 (s, 1H), 7.24 (d, 1H, *J*= 8 Hz), 7.30 (s, 1H), 7.35 (d, 1H, *J*= 8 Hz), 7.70 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 11.28, 11.45, 20.49, 20.62, 22.93, 41.91, 42.56, 52.11, 79.53, 88.66, 95.87, 109.32, 110.49, 124.94, 126.80, 128.32, 128.98, 129.47, 129.73, 130.72, 130.98, 142.04, 142.13, 144.91, 161.14, 174.48, 176.20.

HRMS (ESI): calcd for $C_{28}H_{28}Cl_2N_2O_6^+$([M(^{35}Cl)+Na])$^+$: 581.1222,

found: 581.1241; ([M(^{35}Cl&^{37}Cl)+Na])$^{+}$: 583.1193, **found** : 583.1214; ([M(^{37}Cl)+Na])$^{+}$: 585.1223, **found:** 585.1219).

17. Ethyl 1'-benzyl-5-(1-benzyl-5-chloro-3-hydroxy-2-oxoindolin-3-yl)-5'-chloro-5-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3q).



3q

Yield**:** 37 mg, 60% yield as white solid; mp= 96- 97 ^{o}C.

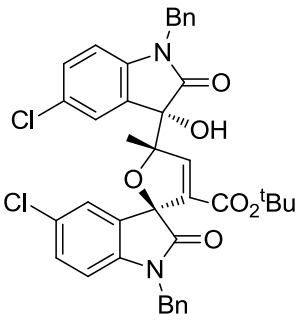
IR (neat, cm^{-1}): 3254, 2982, 2929, 2902, 1716, 1609, 1482, 1370, 1176, 1027, 813, 698.

^{1}H NMR (500MHz, CDCl$_3$): δ 0.99 (t, 3H, *J*= 7 Hz), 1.19 (s, 3H), 3.88 (q, 1H, *J*= 7 Hz), 4.0 (q, 1H, *J*= 7 Hz), 4.71 (d, 1H, *J*= 15.5 Hz), 4.86 (d, 1H, *J*= 15.5 Hz), 4.95 (d, 1H, *J*= 16 Hz), 4.98 (d, 1H, *J*= 15 Hz), 6.63 (d, 1H, *J*= 8 Hz), 6.69 (d, 1H, *J*= 7.5 Hz), 6.87 (s, 1H), 6.94 (s, 1H), 7.08 (s, 1H), 7.10- 7.33 (m, 10H), 7.35 (s, 2H), 7.71 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 13.47, 22.77, 43.68, 44.28, 60.79, 79.29, 88.56, 95.56, 108.67, 109.77, 122.89, 123.35, 124.01, 126.05, 127.09, 127.11, 127.39, 127.52, 127.89, 128.48, 128.51, 129.04, 129.11, 130.33, 132.45, 134.61, 135.23, 142.75, 142.90, 144.56, 160.57, 174.87, 176.54.

HRMS (ESI): calcd for $C_{37}H_{32}N_2O_6^{+}$([M(^{35}Cl)+Na])$^{+}$: 691.1379, **found**: 691.1369; ([M(^{35}Cl&^{37}Cl)+Na])$^{+}$: 693.1379, **found** : 693.1335; ([M(^{37}Cl)+Na])$^{+}$: 695.1379, **found** : 695.1356).

18. tert-Butyl 1'-benzyl-5-(1-benzyl-5-chloro-3-hydroxy-2-oxoindolin-3-yl)-5'-chloro-5-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3r)



3r

Yield**:** 33 mg, 51% yield as white solid; mp= 97- 98 ^{o}C.

IR (neat, cm^{-1}): 3257, 2977, 2927, 2854, 1711, 1609, 1482, 1367, 1166, 1079, 812, 738, 699.

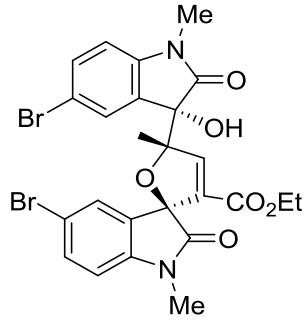
^{1}H NMR (500MHz, CDCl$_3$): δ 1.33 (s, 3H), 1.35 (s, 9H), 4,82 (d, 1H, *J*= 15.5 Hz), 4.87 (d, 1H, *J*= 15.5 Hz), 5.03 (d, 1H, *J*= 15.5 Hz), 5.26 (d, 1H *J*= 15.5 Hz), 6.63 (d, 1H, *J*= 8.5 Hz), 6.71 (d, 1H, *J*= 8 Hz), 7.25 (bs, 1H), 7.29 (s, 2H), 7.31- 7.46 (m, 11H), 7.50 (s, 1H, *J*= 7.5 Hz), 7.71 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 23.25, 27.85, 44.15, 44.58, 53.46, 79.59, 82.66, 88.65, 95.90, 110.69, 111.60, 116.07, 116.54,

127.35, 127.39, 127.58, 127.99, 128.15, 128.24, 128.99, 129.06, 129.17, 130.46, 131.40, 132.42, 133.45, 134.08, 134.34, 135.01, 142.18, 142.21, 144.20, 159.72, 174.67, 176.62.

HRMS (ESI): calcd for $C_{39}H_{34}Cl_2N_2O_6^+$([M(^{35}Cl)+H])$^+$: 697.1872, **found:** 697.1879; ([M(^{35}Cl&^{37}Cl)+2])$^+$: 699.1872, **found** : 699.1841; ([M(^{37}Cl)+4])$^+$: 701.1872, **found**: 701.1799).

19. Ethyl 5'-bromo-5-(5-bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1',5-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3s)



3s

Yield**:** 39 mg, 62% yield as white solid; mp= 192- 193 ^{o}C.

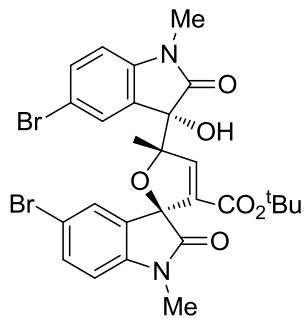
IR (neat, cm^{-1}): 3257, 3057, 2982, 2935, 1713, 1608, 1486, 1360, 1241, 1103, 1026, 812, 735.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.18 (t, 3H, *J*= 7 Hz), 1,26 (s, 3H), 3.22 (s, 3H), 3.34 (s, 3H), 4.05 (q, 2H, *J*= 7 Hz), 6.71 (d, 1H, *J*= 8 Hz), 6.83 (d, 1H, *J*= 8 Hz), 7.10 (bs, 1H), 7.21 (s, 1H), 7.44 (d, 2H, *J*= 8 Hz), 7.52 (d, 1H, *J*= 8Hz), 7.69 (s, 1H)

^{13}C NMR (125MHz, CDCl$_3$): δ 13.86, 23.01, 26.45, 27.13, 61.40, 79.67, 88.74, 95.94, 109.59, 110.58, 116.01, 116.40, 127.52, 129.18, 129.90, 131.18, 132.56, 132.77, 133.66, 142.98, 143.19, 144.38, 160.69, 174.39, 176.14.

HRMS (ESI): calcd for $C_{25}H_{22}Br_2N_2O_6^+$ ([M(^{79}Br)+H])$^+$: 604.9923, **found:** 604.9931; ([M(^{79}Br&^{81}Br)+2])$^+$: 606.9902, **found** : 606.9912; ([M(^{81}Br)+4])$^+$: 608.9923, **found** : 608.9989).

20. tert-Butyl 5'-bromo-5-(5-bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1',5-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3t)



3t

Yield**:** 37 mg, 56% yield as white solid; mp= 187- 188 ^{o}C.

IR (neat, cm^{-1}): 3270, 3075, 2978, 2929, 1710, 1608, 1364, 1247, 1105, 982, 737.

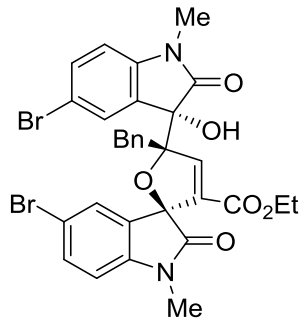
^{1}H NMR (500MHz, CDCl$_3$): δ 1.17 (s, 3H), 1.19 (s, 9H), 3.15 (s, 3H), 3.26 (s, 3H), 6.63 (d, 1H, *J*= 8 Hz), 6.76 (d, 1H, *J*= 8 Hz), 7.03 (bs, 1H), 7.18 (s, 1H), 7.36 (d, 2H, *J*= 8 Hz), 7.46 (d, 1H, 8 Hz), 7.56 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 23.07, 26.45, 27.09, 27.78, 79.64, 82.43, 88.58, 95.67, 109.57, 110.47, 115.97, 116.34, 127.50,

129.16, 131.30, 132.51, 133.50, 134.17, 143.0, 143.18, 144.03, 159.60, 174.46, 176.26.

HRMS (ESI): calcd for $[C_{27}H_{26}Br_2N_2O_6^+$ ([M(^{79}Br)+Na])$^+$: 655.0055, found: 655.0062; ([M(^{79}Br&^{81}Br)+Na])$^+$: 657.0062, found : 657.0049; ([M(^{81}Br)+Na])$^+$: 659.0055, found : 659.0021).

21. Ethyl 5-benzyl-5'-bromo-5-(5-bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1'-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3u)



3u

Yield**:** 32 mg, 45% yield as white solid; mp= 201-202 ^{o}C.

IR (neat, cm^{-1}): 3254, 2982, 2934, 2878, 1715, 1609, 1482, 1372, 1253, 1105, 1027, 814, 757.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.16 (t, 3H, *J*= 7 Hz), 2.46 (d, 1H, *J*= 14 Hz), 3.05 (d, 1H, *J*= 14 Hz), 3.27 (s, 3H), 3.30 (s, 3H), 3.99 - 4.03 (m, 2H), 4.85 (s, 1H), 6.71 (d, 1H, *J*= 8.5 Hz), 6.76 (d, 1H, *J*= 8.5 Hz), 7.01 (d, 2H, *J*= 8 Hz), 7.33 (t, 2H, 7.5 Hz), 7.39 (d, 1H, *J*= 8 Hz), 7.44 (t, 1H, 7.5 Hz), 7.50 (d, 1H, *J*= 8 Hz), 7.53 (s, 1H), 7.83 (s, 1H), 7.96 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 13.80, 26.47, 27.04, 39.83, 61.28, 80.17, 89.08, 99.60, 109.74, 109.90, 116.12, 116.62, 127.82, 128.36, 128.62, 129.09, 129.29, 129.31, 131.52, 131.62, 131.67, 133.83, 133.92, 142.70, 143.06, 143.25, 160.37, 174.73, 176.10.

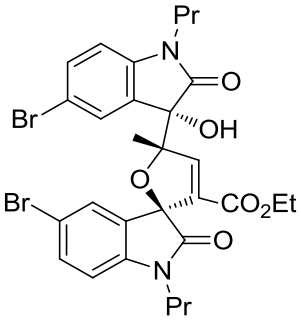
HRMS (ESI): calcd for $C_{31}H_{26}Br_2N_2O_6^+$ ([M(^{79}Br)+Na])$^+$: 703.0055, **found:** 703.0062; ([M(^{79}Br&^{81}Br)+2])$^+$: 705.0035, **found** : 705.0044; ([M(^{81}Br)+4])$^+$: 707.0055, **found:** 707.0025).

22. Ethyl 5'-bromo-5-(5-bromo-3-hydroxy-2-oxo-1-propylindolin-3-yl)-5-methyl-2'-oxo-1'-propyl-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3v)

Yield**:** 43 mg, 69% yield as white solid; mp= 209- 210 ^{o}C.

IR (neat, cm^{-1}): 3261, 2969, 2933, 2875, 1716, 1607, 1480, 1372, 1253, 1118, 1026, 886, 738.

^{1}H NMR (500MHz, CDCl$_3$): δ 0.99 (t, 3H, *J*= 7.5 Hz), 1.19 (t, 3H, *J*= 7 Hz), 1.20 (t, 3H, *J*= 7 Hz), 1.28 (s, 3H), 1.69- 1.73 (m, 2H), 1.78- 1.83 (m, 2H), 3.56 (q, 1H, *J*= 7 Hz), 3.77 (q, 1H, *J*= 7 Hz), 3.78- 3.83 (m, 2H), 3.84- 4.09 (m, 2H), 6.72 (d, 1H, *J*= 8 Hz), 6.84 (d, 1H, *J*= 8 Hz), 7.18 (s, 1H), 7.22 (s, 1H), 7.41 (d, 2H, 8 Hz), 7.50



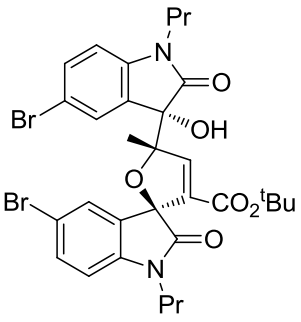
3v

(d, 1H, 8 Hz), 7.70 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 11.30, 11.45, 13.88, 20.45, 20.60, 23.01, 41.89, 42.50, 61.36, 79.50, 88.62, 95.86, 109.83, 110.94, 115.73, 116.20, 127.69, 129.50, 131.37, 132.39, 133.57, 142.53, 142.64, 144.63, 160.70, 174.44, 176.17.

HRMS (ESI): calcd for $C_{29}H_{30}Br_2N_2O_6^+$([M(^{79}Br)+H])$^+$: 661.0549, **found:** 661.0564; ([M(^{79}Br&^{81}Br)+2])$^+$: 663.0528, **found:** 663.0545; ([M(^{81}Br)+4])$^+$: 665.0549, **found**: 665.0519).

23. tert-Butyl 5'-bromo-5-(5-bromo-3-hydroxy-2-oxo-1-propylindolin-3-yl)-5-methyl-2'-oxo-1'-propyl-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3w)



3w

Yield**:** 40 mg, 62% yield as white solid; mp= 239- 241 ^{o}C.

IR (neat, cm^{-1}): 3270, 2970, 2932, 1708, 1607, 1480, 1369, 1165, 1119, 1004, 981, 737.

^{1}H NMR (500MHz, $CDCl_3$): δ 0.91 (t, 3H, *J*= 7.5 Hz), 0.98 (t, 3H, *J*= 7.5 Hz), 1.19 (s, 3H), 1.21 (s, 9H), 1.57- 1.64 (m, 2H), 1.66- 1.74 (m, 2H), 3.47- 3.53 (m, 1H), 3.56- 3.621 (m, 1H), 3.66- 3.72 (m, 1H), 3.81- 3.87 (m, 1H), 6.64 (d, 1H, *J*= 8 Hz), 6.76 (d, 1H, *J*= 8 Hz), 7.12 (bs, 1H), 7.17 (s, 1H), 7.32 (s, 2H), 7.43 (d, 1H, *J*= 8 Hz), 7.53 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 11.29, 11.44, 20.39, 20.60, 23.08, 27.80, 41.87, 42.32, 79.48, 82.44, 88.50, 95.64, 109.80, 110.89, 115.69, 116.17, 127.63, 129.58, 131.47, 132.31, 133.40, 142.53, 142.56, 144.11, 159.64, 174.52, 176.37.

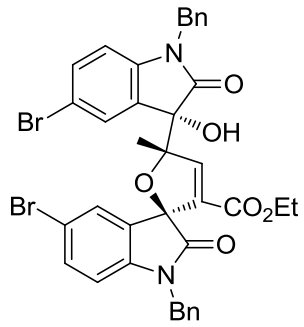
HRMS (ESI): calcd for $C_{31}H_{34}Br_2N_2O_6^+$ ([M(^{79}Br)+H])$^+$: 689.0862, **found:** 689.0868; ([M(^{79}Br&^{81}Br)+2])$^+$: 691.0841, **found** : 691.0855; ([M(^{81}Br)+4])$^+$: 693.0862, **found** : 693.0824).

24. Ethyl 1'-benzyl-5-(1-benzyl-5-bromo-3-hydroxy-2-oxoindolin-3-yl)-5'-bromo-5-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3x)

Yield**:** 29 mg, 48% yield as white solid; mp= 195- 196 ^{o}C.

IR (neat, cm^{-1}): 3258, 3033, 2978, 1716, 1607, 1479, 1370, 1251, 1128, 1027, 812, 698.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.10 (t, 3H, *J*= 7 Hz), 1.23 (s, 3H), 3.98 (q, 1H, *J*= 7.5 Hz), 4.04 (q, 1H, *J*= 7.5 Hz), 4.75 (d, 1H, *J*=



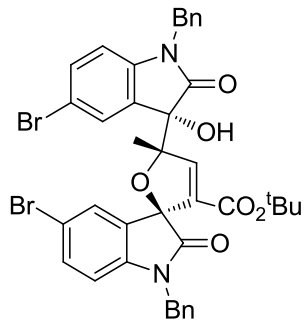
3x

15.5 Hz), 4.91 (d, 1H, *J*= 15.5 Hz), 4.95 (d, 1H, *J*= 15.5 Hz), 5.01 (d, 1H, *J*= 15.5 Hz), 6.54 (d, 1H, *J*= 8 Hz), 6.60 (d, 1H, *J*= 8 Hz), 7.11 (s, 1H), 7.16 (s, 1H), 7.19- 7.26 (m, 8H), 7.27 (s, 4H), 7.33 (s, 1H), 7.70 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 13.87, 23.15, 44.15, 44.77, 61.47, 79.59, 88.73, 96.09, 110.69, 111.80, 116.08, 116.58, 127.30, 127.40, 127.63, 127.99, 128.11, 128.88, 128.98, 129.11, 129.47, 130.08, 131.28, 132.44, 132.47, 132.65, 133.59, 134.33, 135.00, 142.18, 142.33, 144.80, 160.87, 174.56, 176.35.

HRMS (ESI): calcd for $C_{37}H_{30}Br_2N_2O_6^+$([M(^{79}Br)+H])$^+$: 757.0549, **found:** 757.0564; ([M(^{79}Br&^{81}Br)+2])$^+$: 759.0528, **found :** 759.0552; ([M(^{81}Br)+4])$^+$: 761.0549, **found** : 761.0576).

25. tert-Butyl 1'-benzyl-5-(1-benzyl-5-bromo-3-hydroxy-2-oxoindolin-3-yl)-5'-bromo-5-methyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3y)



3y

Yield**:** 25 mg, 40% yield as white solid; mp= 209- 211 ^{o}C.

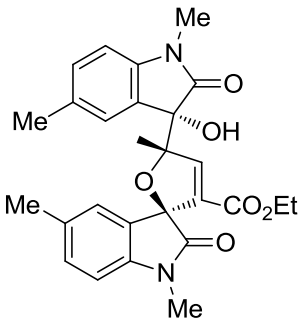
3283, 2978, 2928, 2854, 1709, 1608, 1479, 1344, 1172, 1014, 982, 735.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.32 (s, 3H), 1.33 (s, 9H), 4,80 (d, 1H, *J*= 15.5 Hz), 4.86 (d, 1H, *J*= 15.5 Hz), 5.01 (d, 1H, *J*= 15.5 Hz), 5.25 (d, 1H *J*= 15.5 Hz), 6.64 (d, 1H, *J*= 8.5 Hz), 6.70 (d, 1H, *J*= 8 Hz), 7.24 (bs, 1H), 7.28 (s, 2H), 7.30- 7.40 (m, 7H), 7.41 (s, 4H), 7.48 (s, 1H), 7.70 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 23.24, 27.83, 44.13, 44.57, 53.45, 79.58, 82.65, 88.63, 95.88, 110.67, 111.64, 116.05, 116.52, 127.34, 127.38, 127.57, 127.97, 128.13, 128.97, 129.15, 129.54, 130.44, 131.38, 132.40, 133.44, 134.07, 134.32, 135.00, 142.14, 142.19, 144.19, 159.70, 174.66, 176.60.

HRMS (ESI): calcd for $C_{39}H_{34}Br_2N_2O_6^+$([M(^{79}Br)+H])$^+$: 785.0862**, found:** 785.0882; ([M(^{79}Br&^{81}Br)+2])$^+$: 787.5130, **found:** 787.0866; ([M(^{81}Br)+4])$^+$: 789.0862, **found** : 789.0846).

26. Ethyl 5-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-1',5,5'-trimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3z)



3z

Yield**:** 55 mg, 81% yield as white solid; mp= 213- 214 ^{o}C.

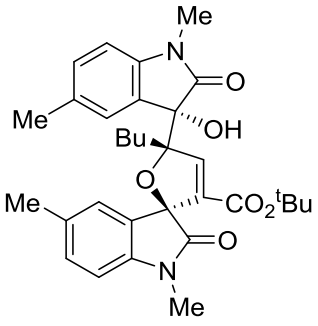
IR (neat, cm^{-1}): 3277, 2980, 2929, 1706, 1621, 1498, 1471, 1445, 1136, 1027, 811, 733.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.16 (t, 3H, *J*= 7 Hz), 1.27 (s, 3H), 2.25 (s, 3H), 2.31 (s, 3H), 3.21 (s, 3H), 3.33 (s, 3H), 4.03 (q, 2H, *J*= 6.5 Hz), 6.69 (d, 1H, *J*= 8 Hz), 6.83 (d, 1H, *J*= 8 Hz), 6.95 (s, 1H), 7.07 (d, 1H, *J*= 8Hz), 7.14 (bs, 1H), 7.18 (d, 2H, *J*= 9Hz), 7.74 (s, 1H)

^{13}C NMR (125MHz, CDCl$_3$): δ 13.84, 21.05, 21.14, 23.01, 26.33, 26.97, 61.01, 79.92, 89.04, 95.81, 107.69, 108.73, 125.06, 126.99, 129.31, 129.76, 131.05, 132.77, 132.85, 133.37, 141.47, 141.73, 144.60, 161.01, 175.07, 176.53

HRMS (ESI): calcd for [$C_{25}H_{28}N_2O_6Na$, M+Na]$^{+}$: 499.1845; Found: 499.1846).

27. tert-Butyl 5-butyl-5-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-1',5'-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3aa)



3aa

Yield**:** 41 mg, 52% yield as white solid; mp= 215-216 ^{o}C.

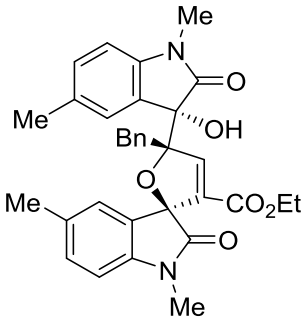
IR (neat, cm^{-1}): 3257, 2982, 2930, 1713, 1608, 1484, 1372, 1175, 1027, 813, 698.

^{1}H NMR (500MHz, CDCl$_3$): δ 0.77 (t, 3H, *J*= 7 Hz), 1.12 (s, 9H), 1.18-1.22 (m, 4H), 1.33-1.41 (m, 2H), 2.18 (s, 3H), 2.22 (s, 3H), 3.13 (s, 3H), 3.25 (s, 3H), 6.61 (d, 1H, *J*= 8.5 Hz), 6.75 (d, 1H, *J*= 8 Hz), 6.98 (d, 1H, *J*= 8 Hz), 7.06 (s, 1H), 7.13, (d, 2H, 8.5 Hz), 7.54 (s, 1H), 7.70 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 14.03, 21.04, 21.20, 22.82, 26.28, 26.91, 27.06, 27.69, 33.59, 80.14, 81.77, 88.94, 99.23, 107.67, 108.61, 125.97, 126.94, 128.58, 129.56, 130.13, 130.85, 132.61, 133.29, 135.05, 141.65, 141.81, 143.72, 159.92, 175.45, 176.60.

HRMS (ESI): calcd for [$C_{32}H_{38}N_2O_6Na$, M+Na]$^{+}$: 569.2628, **found :** 569.2625).

28. Ethyl 5-benzyl-5-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-1',5'-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3ab)



3ab

Yield**:** 49 mg, 62% yield as white solid; mp= 193-194 ^{o}C.

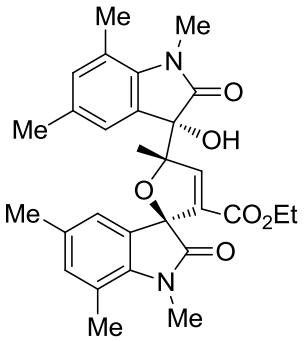
IR (neat, cm^{-1}): 3253, 2971, 2875, 1705, 1608, 1482, 1375, 1251, 1119, 1027, 957, 757.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.12 (t, 3H, *J*= 7.5 Hz), 2.03 (s, 3H), 2.33 (s, 3H), 2.50 (d, 1H, *J*= 13.5 Hz), 3.09 (d, 1H, *J*= 13.5 Hz), 3.25 (s, 3H), 3.28 (s, 3H), 3.97-4.01 (q, 2H, *J*= 7 Hz), 4.64 (s, 1H), 6.70 (d, 1H, *J*= 8 Hz), 6.75 (d, 1H, *J*= 8 Hz), 7.03 (t, 3H, *J*= 7.5 Hz), 7.13 (d, 1H, 8 Hz), 7.27 - 7.33 (m, 3H), 7.35 (d, 1H, 8 Hz), 7.88 (s, 1H), 8.0 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 13.78, 20.06, 21.25, 26.34, 26.83, 39.93, 60.96, 80.41, 89.26, 99.43, 107.83, 108.03, 125.61, 127.12, 127.28, 127.40, 128.21, 129.79, 129.87, 130.76, 131.82, 132.90, 133.08, 134.00, 135.14, 141.22, 141.74, 143.03, 143.20, 160.68, 175.37, 176.45.

HRMS (ESI): calcd for [$C_{33}H_{32}N_2O_6Na$, M+Na]$^{+}$: 575.2158; Found: 575.2135).

29. Ethyl 5-(3-hydroxy-1,5,7-trimethyl-2-oxoindolin-3-yl)-1',5,5',7'-tetramethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3ac)



3ac

Yield**:** 43 mg, 64% yield as white solid; mp= 186- 187 ^{o}C.

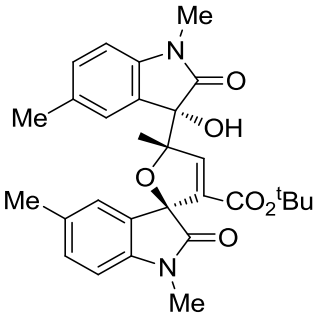
IR (neat, cm^{-1}): 3251, 2981, 2987, 2870, 1713, 1698, 1478, 1368, 1104, 1026, 859, 735.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.18 (t, 3H, *J*= 7 Hz), 1.25 (s, 3H), 2.19 (s, 3H), 2.24 (s, 3H), 2.50 (s, 3H), 2.56 (s, 3H), 3.48 (s, 3H), 3.58 (s, 3H), 4.05 (q, 2H, *J*= 7 Hz), 6.76 (s, 1H), 6.79 (s, 1H), 6.90 (s, 1H), 7.03 (s, 1H), 7.18 (bs, 1H), 7.73 (s, 1H)

^{13}C NMR (125MHz, CDCl$_3$): δ 13.86, 18.78, 18.94, 20.72, 20.83, 23.06, 29.71, 30.40, 61.05, 79.22, 88.56, 95.65, 119.03, 120.37, 122.99, 124.91, 128.91, 130.09, 132.53, 132.89, 132.91, 133.17, 135.0, 139.01, 139.27, 144.61, 161.11, 175.88, 177.24.

HRMS (ESI): calcd for [$C_{29}H_{32}N_2O_6Na$, M+Na]$^{+}$: 527.2158; Found: 527.2165).

30. tert-Butyl 5-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-1',5,5'-trimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3ad)



3ad

Yield**:** 55 mg, 76% yield as white solid; mp= 195- 196 ^{o}C.

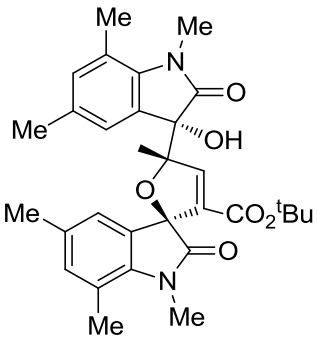
IR (neat, cm^{-1}): 3290, 2977, 2929, 2873, 1706, 1606, 1498, 1368, 1166, 1107, 1019, 957, 798.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.24 (s, 9H), 1.26 (s, 3H), 2.27 (s, 3H), 2.32 (s, 3H), 3.22 (s, 3H), 3.33 (s, 3H), 6.70 (d, 1H, *J*= 8 Hz), 6.83 (d, 1H, *J*= 8 Hz), 6.99 (bs, 1H), 7.07 (d, 1H, *J*= 8 Hz), 7.19 (t, 3H, *J*= 7 Hz), 7.69 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 20.99, 21.44, 23.06, 26.32, 26.91, 27.72, 79.87, 81.88, 88.89, 95.57, 107.65, 108.60, 125.05, 129.47, 126.97, 129.70, 130.84, 132.71, 133.41, 134.31, 141.49, 141.73, 144.17, 159.99, 175.13, 176.63.

HRMS (ESI): calcd for $[C_{29}H_{32}N_2O_6Na, M+Na]^+$: 527.2158; Found: 527.2162).

31. tert-Butyl 5-(3-hydroxy-1,5,7-trimethyl-2-oxoindolin-3-yl)-1',5,5',7'-tetramethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3ae)



3ae

Yield**:** 40 mg, 57% yield as white solid; mp= 151- 153 ^{o}C.

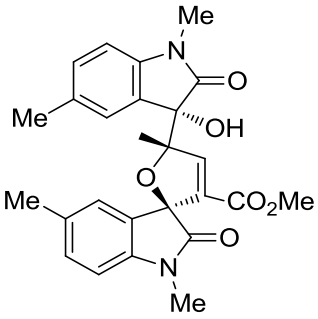
IR (neat, cm^{-1}): 3274, 2955, 2921, 2852, 1710, 1605, 1464, 1369, 1285, 1168, 1107, 856, 739.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.26 (s, 9H), 1.27 (s, 3H), 2.21 (s, 3H), 2.26 (s, 3H), 2.51 (s, 3H), 2.57 (s, 3H), 3.49 (s, 3H), 3.59 (s, 3H), 6.80 (s, 2H), 6.92 (s, 1H), 7.04 (s, 1H), 7.23 (s, 1H), 7.68 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 18.78, 18.95, 20.66, 20.84, 23.13, 27.72, 29.71, 30.31, 79.16, 81.72, 88.39, 95.42, 119.0, 120.13, 123.02, 124.88, 129.29, 130.21, 132.46, 133.23, 134.38, 134.75, 139.03, 139.22, 144.23, 160.04, 175.94, 177.30.

HRMS (ESI): calcd for $[C_{31}H_{36}N_2O_6Na, M+Na]^+$: 555.2471; Found: 555.2494).

32. Methyl 5-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-1',5,5'-trimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3af)



3af

Yield**:** 58 mg, 88% yield as white solid; mp= 224- 226 ^{o}C.

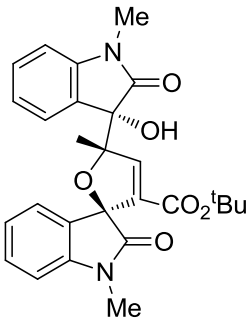
IR (neat, cm^{-1}): 3279, 3025, 2976, 2926, 1708, 1614, 1497, 1348, 1272, 1106, 1025, 953, 733.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.20 (s, 3H), 2.18 (s, 3H), 2.23 (s, 3H), 3.14 (s, 3H), 3.27 (s, 3H), 3.56 (s, 3H), 6.62 (d, 1H, *J*= 8 Hz), 6.67 (d, 1H, *J*= 8 Hz), 6.87 (s, 1H), 6.99 (d, 2H, *J*= 8 Hz), 7.06 (s, 1H), 7.11 (s, 1H), 7.66 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 21.03, 21.11, 22.94, 26.32, 26.98, 51.96, 79.92, 89.06, 95.83, 107.67, 108.79, 125.03, 126.98, 128.02,129.29, 129.75, 131.10, 132.51, 132.75, 133.35, 141.49, 141.74, 144.72, 161.46, 175.03, 176.47.

HRMS (ESI): calcd for [$C_{26}H_{26}N_2O_6Na$, M+Na]$^{+}$: 485.1689, Found: 485.1687).

33. tert-Butyl 5-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-1',5-dimethyl-2'-oxo-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3ag)



3ag

Yield**:** 53 mg, 71% yield as white solid; mp= 239- 241 ^{o}C.

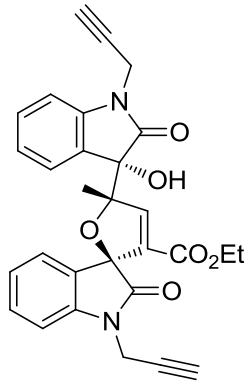
IR (neat, cm^{-1}): 3280, 3057, 2978, 2934, 1706, 1611, 1470, 1369, 1247, 1128, 1093, 1020, 971, 752.

^{1}H NMR (500MHz, CDCl$_3$): δ 1.14 (s, 9H), 1.16 (s, 3H), 3.16 (s, 3H), 3.25 (s, 3H), 6.73 (d, 1H, *J*= 7,5 Hz), 6.84 (d, 1H, *J*= 8 Hz), 6.91 (t, 1H, *J*= 7.5 Hz), 7.02 (t, 1H, *J*= 7.5 Hz), 7.08 (d, 2H, *J*= 7 Hz), 7.28 (t, 1H, *J*= 7.5 Hz), 7.31 (t, 2H, *J*= 7 Hz), 7.57 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): δ 23.01, 26.31, 26.86, 27.69, 79.70, 81.94, 88.75, 95.60, 107.93, 108.83, 123.17, 123.68, 124.31, 126.29, 128.48, 129.43, 129.48, 130.66, 134.33, 143.88, 144.07, 144.14, 159.51, 175.13, 176.72.

HRMS (ESI): calcd for [$C_{27}H_{28}N_2O_6Na$, M+Na]$^{+}$: 499.1845; Found: 499.1850).

34. Ethyl 5-(3-hydroxy-2-oxo-1-(prop-2-yn-1-yl)indolin-3-yl)-5-methyl-2'-oxo-1'-(prop-2-yn-1-yl)-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3ah)



3ah

Yield**:** 48 mg, 72% yield as white solid; mp = 140- 141 ^{o}C.

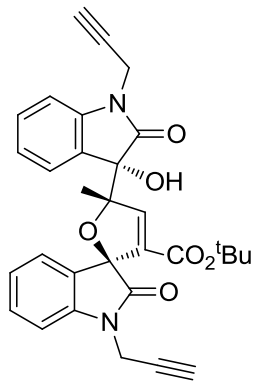
IR (neat, cm^{-1}): 3291, 2981, 2927, 1712, 1612, 1487, 1369, 1183, 1025, 932, 755.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.13 (t, 3H, *J*= 7 Hz), 1.29 (s, 3H), 2.26 (s, 1H), 2.36 (s, 1H), 4.01- 4.10 (m, 2H), 4.30 (dd, 1H, J_1= 17.5 Hz, J_2= 1.5 Hz), 4.65 (dq, 2H, J_1= 16 Hz, J_2= 2 Hz), 4.8 (d, 1H, *J*= 15 Hz), 6.96 (s, 1H), 7.04 (t, 2H, 8 Hz), 7.14 (t, 1H, 7.5 Hz), 7.18 (d, 2H, *J*= 8 Hz), 7.33 (t, 1H, *J*= 7Hz), 7.42 (t, 2H, *J*= 5Hz), 7.74 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 13.86, 22.82, 29.34, 30.11, 61.21, 72.40, 73.16, 76.06, 76.46, 79.71, 88.88, 96.11, 108.92, 110.10, 123.63, 124.05, 124.44, 126.37, 127.92, 129.03, 129.59, 130.80, 132.94, 141.85, 142.22, 144.57, 160.77, 174.04, 175.84.

HRMS (ESI): calcd for $[C_{29}H_{24}N_2O_6Na, M+Na]^+$: 519.1532; Found: 519.1534).

35. tert-Butyl 5-(3-hydroxy-2-oxo-1-(prop-2-yn-1-yl)indolin-3-yl)-5-methyl-2'-oxo-1'-(prop-2-yn-1-yl)-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3ai)



3ai

Yield**:** 43 mg, 61% yield as white solid; mp= 194- 195 ^{o}C.

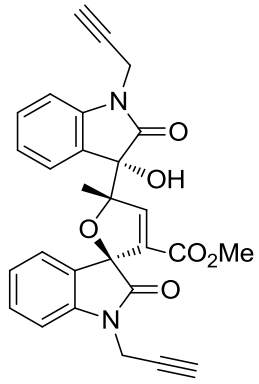
IR (neat, cm^{-1}): 3288, 3060, 2979, 2930, 1710, 1613, 1467, 1260, 1164, 1069, 982, 753.

^{1}H NMR (500MHz, $CDCl_3$): δ 1.24 (s, 9H), 1.26 (s, 3H), 2.26 (s, 1H), 2.36 (s, 1H), 4.28 (d, 1H, *J*= 17.5 Hz), 4.47 (d, 1H, *J*= 18 Hz), 4.79 (d, 2H, *J*= 17.5 Hz), 6.99 (bs, 1H), 7.04 (t, 2H, 7.5 Hz), 7.13- 7.20 (m, 3H), 7.32 (t, 1H, *J*= 7.5 Hz), 7.42 (t, 2H, *J*= 7,5 Hz), 7.68 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 22.90, 27.77, 29.33, 30.17, 72.38, 73.33, 76.11, 76.48, 79.67, 82.24, 88.70, 95.83, 108.89, 110.07, 123.61, 124.06, 124.42, 126.36, 128.33, 129.14, 129.53, 130.66, 134.23, 141.87, 142.28, 144.26, 159.79, 174.11, 176.01.

HRMS (ESI): calcd for $[C_{31}H_{28}N_2O_6Na, M+Na]^+$: 547.1845; Found: 547.1861).

36. Methyl 5-(3-hydroxy-2-oxo-1-(prop-2-yn-1-yl)indolin-3-yl)-5-methyl-2'-oxo-1'-(prop-2-yn-1-yl)-5H-spiro[furan-2,3'-indoline]-3-carboxylate (3aj)



3aj

Yield**:** 52 mg, 81% yield as white solid; mp= 96- 97 ^{o}C.

IR (neat, cm^{-1}): 3272, 2975, 2929, 1710, 1612, 1482, 1365, 1164, 1009, 934, 698.

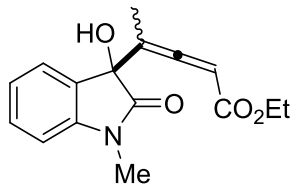
^{1}H NMR (500MHz, $CDCl_3$): δ 1.20 (s, 3H), 2.17 (s, 1H), 2.28 (s, 1H), 3.35 (s, 3H), 4.20 (dd, 1H, J_1= 17.5 Hz, J_2= 3 Hz), 4.55 (s, 2H), 4.70 (dd, 1H, J_1= 17.5 Hz, J_2= 3 Hz), 6.86 (s, 1H), 6.96 (t, 2H, 7.5 Hz), 7.03- 7.10 (m, 3H), 7.24 (t, 1H, *J*= 7.5 Hz), 7.34 (t, 2H, *J*= 7,5 Hz), 7.65 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): δ 14.13, 22.66, 22.75, 29.34, 30.08, 31.59, 52.10, 72.41, 73.09, 76.09, 76.45, 79.92, 88.91, 96.15, 108.94, 110.15, 123.63, 124.06, 124.43, 126.36, 129.60, 130.86, 141.86, 142.15, 144.68, 161.26, 174.0, 175.78.

HRMS (ESI): calcd for $[C_{28}H_{22}N_2O_6Na, M+Na]^+$: 505.1376; Found: 547.505.1395).

7. Characterization data γ-functionalized allenoates

1. Ethyl-4-(-3-hydroxy-1-methyl-2-oxoindolin-3-yl)penta-2,3-dienoate (4a)



4a

Yield**:** 47 mg, 87% yield as a colorless oil.

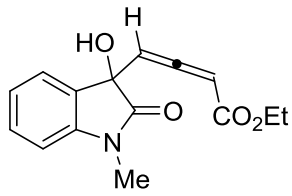
IR (neat, cm^{-1}): 3376, 2984, 2933, 1963, 1705, 1610, 1488, 1360, 1242, 1151, 1099, 812, 733.

^{1}H NMR (500MHz, $CDCl_3$): 1.26 (t, 3H, *J*= 7 Hz), 1.31 (t, 3H, *J*= 7 Hz), 1.62 (s, 3H), 1.84 (s, 3H), 3.19 (s, 3H), 3.21 (s, 3H), 4.13- 4.26 (m, 4H), 5.62 (s, 1H), 5.82 (s, 1H), 6.84 (t, 2H, *J*= 7 Hz), 7.08 (t, 1H, *J*= 7.5 Hz), 7.13 (t, 1H, *J*= 7 Hz), 7.32- 7.37 (m, 2H), 7.40 (d, 1H, *J*= 8 Hz), 7.51 (d, 1H, *J*= 7.5 Hz).

^{13}C NMR (125MHz, $CDCl_3$): 13.01, 13.39, 14.19, 14.22, 26.36, 26.44, 61.05, 61.08, 90.08, 92.09, 106.69, 106.83, 108.15, 108.51, 108.54, 123.23, 123.59, 124.64, 124.95, 128.48, 128.87, 130.19, 130.35, 143.29, 143.64, 165.80, 165.92, 175.79, 175.84, 209.81, 209.93.

HRMS (ESI): calcd for $[C_{16}H_{17}NO_4Na, M+Na]^+$: 310.1055; Found: 310.1053).

2. Ethyl 4-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)buta-2,3-dienoate (4b)



4b

Yield**:** 43 mg, 85% yield as a colorless oil.

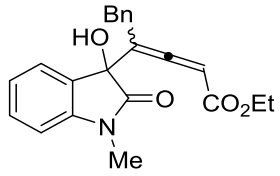
IR (neat, cm^{-1}): 3382, 2983, 2935, 1964, 1706, 1612, 1487, 1359, 1245, 1112, 1095, 812, 757.

^{1}H NMR (500MHz, $CDCl_3$): 1.22 (t, 3H, *J*= 7 Hz), 1.26 (t, 3H, *J*= 7 Hz), 3.18 (s, 6H), 4.10 - 4.21 (m, 4H), 4.51 (s, 1H), 4.63 (s, 1H), 5.62 (d, 1H, *J*= 6 Hz), 5.82 (d, 1H, *J*= 6 Hz), 5.89 (d, 1H, *J*= 6 Hz), 6.05 (d, 1H, *J*= 6 Hz), 6.83 (d, 2H, *J*= 8 Hz), 7.07 (t, 1H, *J*= 7 Hz), 7.10 (t, 1H, *J*= 7 Hz), 7.31- 7.34 (m, 2H), 7.41 (d, 1H, *J*= 8 Hz), 7.44 (d, 1H, *J*= 7.5 Hz).

^{13}C NMR (125MHz, $CDCl_3$): 14.11, 14.18, 26.43, 26.48, 61.19, 61.28, 74.45, 74.70, 91.91, 92.62, 97.74, 97.78, 108.66, 108.69, 123.30, 123.49, 124.85, 124.90, 128.46, 128.71, 130.23, 130.28, 142.94, 165.01, 165.21, 175.70, 175.77, 211.77, 211.98.

HRMS (ESI): calcd for $[C_{15}H_{15}NO_4Na, M+Na]^+$: 296.0899; Found: 296.0902).

3. Ethyl 4-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-5-phenylpenta-2,3-dienoate (4c)



4c

Yield**:** 48 mg, 70% yield as a colorless oil.

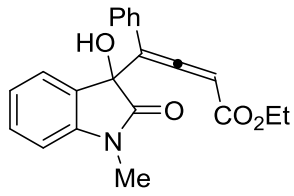
IR (neat, cm^{-1}): 3379, 2985, 2930, 2859, 1963, 1705, 1611, 1489, 1361, 1245, 1152, 1026, 813, 736.

^{1}H NMR (500MHz, $CDCl_3$): 1.29 (t, 3H, *J*= 7 Hz), 1.32 (t, 3H, *J*= 7 Hz), 3.09 (s, 3H), 3.14 (s, 3H), 3.17 (dd, 1H, J_1= 2 Hz, J_2= 15.5 Hz), 3.30 (dd, 1H, J_1= 2 Hz, J_2= 15.5 Hz), 3.45 (dd, 1H, J_1= 2 Hz, J_2= 15.5 Hz), 3.52 (dd, 1H, J_1= 2.5 Hz, J_2= 15.5 Hz), 3.73 (bs, 1H), 4.13 (bs, 1H), 4.15 - 4.23 (m, 4H), 5.59 (s, 1H), 5.79 (s, 1H), 6.78 (d, 1H, *J*= 8.5 Hz), 6.80 (d, 1H, *J*= 8.5 Hz), 6.99 (d, 2H, *J*= 8 Hz), 7.09 – 7.21 (m, 10H), 7.31 - 7.39 (m, 3H), 7.49 (d, 1H, *J*= 8 Hz).

^{13}C NMR (125MHz, $CDCl_3$): 14.21, 14.24, 26.29, 26.37, 33.99, 34.53, 61.01, 61.06, 76.41, 76.47, 92.80, 93.82, 108.55, 111.95, 123.25, 123.29, 123.52, 123.59, 124.80, 125.15, 126.63, 126.66, 127.93, 127.96, 128.08, 128.42, 128.46, 128.51, 129.01, 129.11, 130.31, 130.41, 165.38, 165.56, 175.54, 175.63, 210.89, 211.01.

HRMS (ESI): calcd for $[C_{22}H_{21}NO_4Na, M+Na]^+$: 386.1368; Found: 386.1363).

4. Ethyl 4-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4d)



4d

Yield**:** 45 mg, 68% yield as colorless solid.

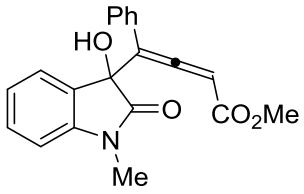
IR (neat, cm^{-1}): 3378, 2984, 2937, 1965, 1707, 1609, 1487, 1365, 1244, 1157, 1098, 812, 753.

^{1}H NMR (500MHz, CDCl$_3$): 1.17 (t, 3H, *J*= 7 Hz), 3.25 (s, 3H), 4.01 (bs, 1H), 4.07 - 4.19 (m, 2H), 6.85 (s, 1H), 6.86 (s, 1H) 7.11 (t, 1H, *J*= 7 Hz), 7.33 - 7.42 (m, 7H).

^{13}C NMR (125MHz, CDCl$_3$): 14.00, 26.46, 61.59, 75.12, 102.82, 106.28, 108.60, 123.08, 124.11, 126.31, 127.70, 128.56, 128.81, 129.01, 129.27, 130.30, 131.06, 144.33, 164.64, 175.75, 211.19

HRMS (ESI): calcd for [$C_{21}H_{19}NO_4Na$, M+Na]$^+$: 372.1212; Found: 372.1208).

5. Methyl 4-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4e)



4e

Yield**:** 14 mg, 23% yield as colorless solid.

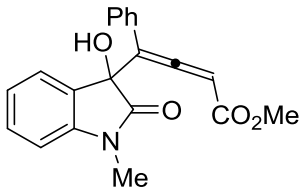
IR (neat, cm^{-1}): 3379, 2980, 2934, 1964, 1709, 1610, 1451, 1360, 1257, 1183, 1027, 856, 735.

^{1}H NMR (500MHz, CDCl$_3$): 3.24 (s, 3H), 3.69 (s, 3H), 4.08 (bs, 1H), 6.84 (s, 1H), 6.87 (d, *J*= 8 Hz, 1H), 7.05 (t, 1H, *J*= 7.5 Hz), 7.30 - 7.40 (m, 7H).

^{13}C NMR (125MHz, CDCl$_3$): 26.42, 52.60, 75.40, 102.58, 105.91, 108.57, 123.05, 124.21, 127.71, 128.64, 129.06, 130.32, 130.34, 130.65, 130.67, 144.23, 165.11, 175.52, 211.04.

HRMS (ESI): calcd for [$C_{20}H_{17}NO_4Na$, M+Na]$^+$: 358.1055; Found: 358.1047).

6. Methyl 4-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4e')



4e'

Yield**:** 34 mg, 54% yield as colorless solid.

IR (neat, cm^{-1}): 3381, 2984, 2933, 1963, 1706, 1608, 1457, 1364, 1249, 1189, 1057, 857, 734.

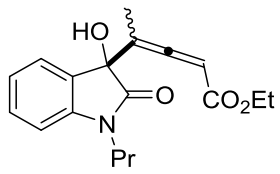
^{1}H NMR (500MHz, CDCl$_3$): 3.26 (s, 3H), 3.68 (s, 3H), 4.05 (bs, 1H), 6.86 (s, 1H), 6.87 (d, *J*= 8 Hz, 1H), 7.11 (t, 1H, *J*= 7.5 Hz), 7.32 - 7.43 (m, 7H).

^{13}C NMR (125MHz, CDCl$_3$): 26.47, 52.55, 75.11, 102.85, 106.03,

108.65, 123.08, 124.13, 127.72, 128.64, 129.04, 130.32, 130.36, 130.93, 130.94, 144.37, 165.16, 175.67, 211.28.

HRMS (ESI): calcd for $[C_{20}H_{17}NO_4Na, M+Na]^+$: 358.1055; Found: 358.1086).

7. Ethyl-4-(-3-hydroxy-2-oxo-1-propylindolin-3-yl)penta-2,3-dienoate (4f)



4f

Yield**:** 41 mg, 81% yield as a colorless oil.

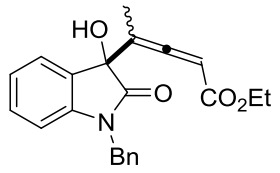
IR (neat, cm^{-1}): 3386, 2968, 2934, 2876, 1963, 1704, 1611, 1488, 1366, 1250, 1153, 1110, 1032, 831, 754.

^{1}H NMR (500MHz, $CDCl_3$): 0.96 (t, 3H, *J*= 7.5 Hz), 0.99 (t, 3H, *J*= 7.5 Hz), 1.26 (t, 3H, *J*= 7 Hz), 1.33 (t, 3H, *J*= 7 Hz), 1.63 (s, 3H), 1.69- 1.75 (m, 4H), 1.82 (s, 3H), 3.56- 3.62 (m, 2H), 3.71- 3.77 (m, 2H), 4.17- 4.26 (m, 4H), 5.68 (s, 1H), 5.85 (s, 1H), 6.87 (t, 2H, *J*= 7.5 Hz), 7.08 (t, 1H, *J*= 7.5 Hz), 7.12 (t, 1H, *J*= 7 Hz), 7.32 (t, 1H, *J*= 7.5 Hz), 7.36 (t, 1H, *J*= 7.5 Hz), 7.41 (d, 1H, *J*= 8 Hz), 7.52 (d, 1H, *J*= 8 Hz).

^{13}C NMR (125MHz, $CDCl_3$): 11.31, 11.35, 13.11, 13.43, 14.16. 14.22, 20.69, 20.71, 41.82, 41.89, 61.05, 76.47, 76.63, 91.01, 92.16, 106.75, 106.91, 108.81, 123.03, 123.34, 124.74, 125.11, 128.05, 128.90, 130.14, 130.29, 142.92, 143.23, 165.71, 165.81, 175.68, 209.69, 209.77

HRMS (ESI): calcd for $[C_{18}H_{21}NO_4Na, M+Na]^+$: 338.1368; Found: 338.1334).

8. Ethyl-4-(1-benzyl-3-hydroxy-2-oxoindolin-3-yl)penta-2,3-dienoate (4g)



4g

Yield**:** 35 mg, 76% yield as a colorless oil.

IR (neat, cm^{-1}): 3389, 2983, 2928, 2859, 1964, 1712, 1607, 1479, 1367, 1253, 1165, 1034, 815, 736.

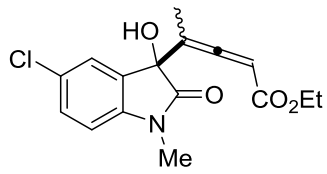
^{1}H NMR (500MHz, $CDCl_3$): 1.23 (t, 3H, *J*= 7 Hz), 1.34 (t, 3H, *J*= 7 Hz), 1.69 (s, 3H), 1.85 (s, 3H), 4.15- 4.26 (m, 4H), 4.77 (dd, 2H, J_1= 3 Hz, J_2= 16 Hz), 5.05 (d, 2H, J_1= 3 Hz, J_2= 16 Hz), 5.70 (s, 1H), 5.85 (s, 1H), 6.74 (d, 1H, *J*= 8 Hz), 6.76 (d, 1H, *J*= 8 Hz), 7.06 (t, 1H, *J*= 7.5 Hz), 7.09 (t, 1H, *J*= 7.5 Hz), 7.23- 7.34 (m, 12H), 7.42 (d, 1H, *J*= 8 Hz), 7.53 (d, 1H, *J*= 8 Hz).

^{13}C NMR (125MHz, $CDCl_3$): 13.23, 13.53, 14.12, 14.23, 44.04, 44.12, 61.09, 76.53, 76.72, 91.12, 92.22, 106.70, 106.86, 109.61, 123.29, 123.57, 124.67, 125.03, 127.03, 127.24, 127.31, 127.79,

127.84, 128.41, 128.70, 128.75, 128.83, 128.87, 130.15, 130.29, 165.68, 165.77, 175.86, 176.02, 209.69, 209.80.

HRMS (ESI): calcd for $[C_{22}H_{21}NO_4Na, M+Na]^+$: 386.1368; Found: 386.1310).

9. Ethyl-4-(5-chloro-3-hydroxy-1-methyl-2-oxoindolin-3-yl)penta-2,3-dienoate (4h)



4h

Yield**:** 39 mg, 79% yield as a colorless oil.

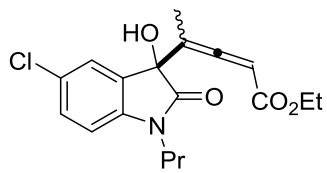
IR (neat, cm^{-1}): 3379, 3027, 2984, 2933, 1964, 1708, 1611, 1489, 1360, 1246, 1101, 1035, 814, 734.

^{1}H NMR (500MHz, $CDCl_3$): 1.29 (t, 3H, *J*= 7.5 Hz), 1.35 (t, 3H, *J*= 7.5 Hz), 1.63 (s, 3H), 1.87 (s, 3H), 3.19 (s, 3H), 3.21 (s, 3H), 4.18-4.27 (m, 4H), 5.62 (s, 1H), 5.84 (s, 1H), 6.77 (d, 1H, *J*= 8 Hz), 6.79 (d, 1H, *J*= 8 Hz), 7.32 (d, 1H, *J*= 8 Hz), 7.34 (d, 1H, *J*= 8 Hz), 7.39 (s, 1H), 7.49 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): 12.83, 13.36, 14.20, 14.26, 26.48, 26.57, 61.22, 61.27, 76.40, 76.63, 91.01, 92.45, 106.19, 106.40, 109.47, 109.55, 125.31, 125.46, 128.64, 129.06, 130.04, 130.14, 130.27, 130.52, 141.81, 142.21, 165.26, 165.71, 175.35, 209.53, 209.81.

HRMS (ESI): calcd for $C_{16}H_{16}NO_4^+$ $[M(^{35}Cl)+Na]^+$: 344.0666, Found: 344.06918, $[M(^{37}Cl)+Na]^+$: 346.0636, Found : 346.0662).

10. Ethyl-4-(-5-chloro-3-hydroxy-2-oxo-1-propylindolin-3-yl)penta-2,3-dienoate (4i)



4i

Yield**:** 33 mg, 72% yield as a colorless oil.

IR (neat, cm^{-1}): 3378, 2972, 2934, 2877, 1965, 1707, 1609, 1482, 1346, 1254, 1152, 1152, 1036, 822, 693.

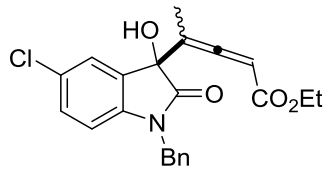
^{1}H NMR (500MHz, $CDCl_3$): 0.87 (t, 3H, *J*= 7.5 Hz), 0.89 (t, 3H, *J*= 7.5 Hz), 1.20 (t, 3H, *J*= 7 Hz)), 1.27 (t, 3H, *J*= 7 Hz)), 1.55 (s, 3H), 1.59- 1.63 (m, 4H), 1.76 (s, 3H), 3.47- 3.63 (m, 2H), 3.64- 3.66 (m, 2H), 4.08- 4.19 (m, 4H), 5.58 (s, 1H), 5.76 (s, 1H), 6.70 (d, 1H, *J*= 8 Hz), 6.72 (d, 1H, *J*= 8 Hz), 7.20 (d, 1H, *J*= 8 Hz), 7.23 (d, 1H, *J*= 8 Hz), 7.31 (s, 1H), 7.41 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): 11.25, 11.31, 12.96, 13.41, 14.18, 14.26, 20.60, 20.64, 41.93, 42.03, 61.22, 61.25, 76.34, 76.53, 91.14, 92.48, 106.23, 106.51, 109.77, 109.83, 125.38, 125.59, 128.45, 128.82, 129.99, 130.20, 130.23, 130.63, 141.39, 141.77,

165.54, 165.68, 175.32, 175.44, 209.49, 209.69.

HRMS (ESI): calcd for $C_{18}H_{20}ClNO_4^+$[M(^{35}Cl)+Na]$^+$: 372.0979, Found: 372.0985; [M(^{37}Cl)+Na]$^+$: 374.0979, Found : 374.0956).

11. Ethyl-4-(1-benzyl-5-chloro-3-hydroxy-2-oxoindolin-3-yl)penta-2,3-dienoate (4j)



4j

Yield**:** 29 mg, 65% yield as a colorless oil.

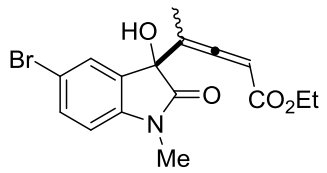
IR (neat, cm^{-1}): 3389, 3033, 2983, 1964, 1712, 1607, 1479, 1367, 1165, 1034, 815, 736, 699.

^{1}H NMR (500MHz, CDCl$_3$): 1.28 (t, 3H, *J*= 7 Hz), 1.36 (t, 3H, *J*= 7 Hz), 1.69 (s, 3H), 1.88 (s, 3H), 4.18- 4.29 (m, 4H), 4.76 (d, 2H, *J*= 15.5 Hz), 5,03 (dd, 2H, J_1= 3 Hz, J_2= 15.5 Hz), 5.70 (s, 1H), 5.87 (s, 1H), 6.60 (d, 1H, *J*= 8 Hz), 6.62 (d, 1H, *J*= 8 Hz), 7.25- 7.36 (m, 12H), 7.54 (s, 1H), 7.63 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): 13.09, 13.53, 14.18, 14.31, 44.11, 44.22, 61.28, 61.32, 76.32, 76.57, 91.35, 92.57, 106.17, 106.51, 111.10, 115.15, 116.01, 116.33, 127.17, 127.25, 127.31, 127.39, 127.98, 128.03, 128.07, 128.23, 128.80, 128.85, 128.88, 128.98, 129.10, 132.94, 133.14, 134.78, 165.47, 165.66, 175.33, 175.45, 209.44, 209.73.

HRMS (ESI): calcd for $C_{22}H_{20}ClNO_4^+$[M(^{35}Cl)+Na]$^+$: 420.0949, Found: 420.0978, [M(^{37}Cl)+Na]$^+$: 422.0949, 422.0950).

12. Ethyl-4-(-5-bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)penta-2,3-dienoate (4k)



4k

Yield**:** 33 mg, 72% yield as a colorless oil.

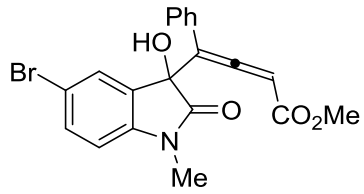
IR (neat, cm^{-1}): 3379, 2982, 2930, 2859, 1964, 1708, 1608, 1483, 1354, 1245, 1152, 1110, 1034, 816, 690.

^{1}H NMR (500MHz, CDCl$_3$): 1.22 (t, 3H, *J*= 7 Hz), 1.27 (t, 3H, *J*= 7 Hz), 1.55 (s, 3H), 1.77 (s, 3H), 3.10 (s, 3H), 3.13 (s, 3H), 4.10-4.21 (m, 4H), 5.55 (s, 1H), 5.76 (s, 1H), 6.64 (d, 1H, *J*= 8 Hz), 6.67 (d, 1H, *J*= 8 Hz), 7.38 (d, 1H, *J*= 8 Hz), 7.41 (d, 1H, *J*= 8 Hz), 7.44 (s, 1H), 7.53 (s, 1H).

^{13}C NMR (125MHz, CDCl$_3$): 12.86, 13.38, 14.23, 14.31, 26.46, 26.55, 61.23, 61.32, 76.35, 76.56, 91.13, 92.52, 106.17, 106.43, 109.97, 110.04, 115.88, 116.28, 128.07, 128.19, 130.39, 130.75, 132.99, 133.21, 142.34, 142.75, 165.51, 165.71, 175.20, 175.23, 209.47, 209.82.

HRMS (ESI): calcd for $C_{16}H_{16}BrNO_4^+$ [M(^{79}Br)+Na]$^+$: 388.0160, Found: 388.0166; [M(^{81}Br)+Na]$^+$: 390.0140, Found: 390.0140).

13. Methyl 4-(5-bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4l)



4l

Yield**:** 10 mg, 19% yield as colorless solid.

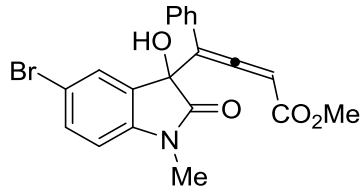
IR (neat, cm^{-1}): 3380, 2984, 2933, 1967, 1707, 1610, 1484, 1360, 1154, 1057, 816, 734.

^{1}H NMR (500MHz, $CDCl_3$): 3.21 (s, 3H), 3.70 (s, 3H), 4.01 (bs, 1H), 6.75 (d, 1H, *J*= 8 Hz), 6.89 (s, 1H), 7.33 (t, 1H, *J*= 7.5 Hz), 7.38 (d, 4H, *J*= 8 Hz), 7.47 (d, 1H, *J*= 8.5 Hz), 7.50 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): 26.52, 52.68, 75.14, 103.12, 105.74, 110.04, 115.60, 127.55, 127.76, 128.83, 129.14, 130.35, 131.10, 133.06, 143.38, 164.88, 175.08, 211.11.

HRMS (ESI): calcd for $C_{20}H_{16}BrNO_4^+$ ([M(^{79}Br)+Na])$^+$: 436.0160, **found:** 436.0153; ([M(^{81}Br)+Na])$^+$: 438.0140, **found :** 438.0153).

14. Methyl 4-(5-bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4l')



4l'

Yield**:** 18 mg, 35% yield as colorless solid.

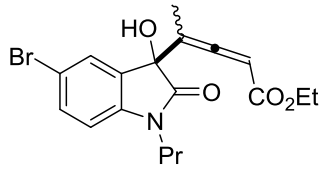
IR (neat, cm^{-1}): 3379, 2982, 2930, 1963, 1705, 1609, 1487, 1365, 1150, 1051, 819, 737.

^{1}H NMR (500MHz, $CDCl_3$): 3.23 (s, 3H), 3.70 (s, 3H), 4.12 (bs, 1H), 6.74 (d, 1H, *J*= 8 Hz), 6.89 (s, 1H), 7.34 – 7.43 (m, 5H), 7.49 (d, 1H, *J*= 8.5 Hz), 7.51 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): 26.57, 52.68, 74.98, 103.23, 105.64, 110.12, 115.61, 127.50, 127.76, 128.85, 129.12, 130.62, 131.15, 133.10, 143.43, 165.08, 175.15, 211.28.

HRMS (ESI): calcd for $C_{20}H_{16}BrNO_4^+$ ([M(^{79}Br)+Na])$^+$: 436.0160, **found:** 436.01565; ([M(^{81}Br)+Na])$^+$: 438.0140, **found :** 438.0145).

15. Ethyl-4-(5-bromo-3-hydroxy-2-oxo-1-propylindolin-3-yl)penta-2,3-dienoate (4m)



4m

Yield**:** 30 mg, 67% yield as a colorless oil.

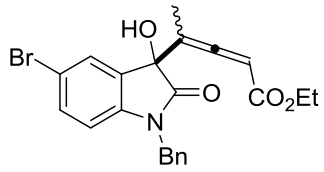
IR (neat, cm^{-1}): 3385, 2969, 2934, 2876, 1964, 1709, 1607, 1480, 1343, 1254, 1150, 1115, 1036, 812, 691.

^{1}H NMR (500MHz, $CDCl_3$): 0.96 (t, 3H, *J*= 7.5 Hz), 0.98 (t, 3H, *J*= 7.5 Hz), 1.30 (t, 3H, *J*= 7 Hz)), 1.37 (t, 3H, *J*= 7 Hz), 1.64 (s, 3H), 1.69- 1.72 (m, 4H), 1.84 (s, 3H), 3.55- 3.59 (m, 2H), 3.70- 3.74 (m, 2H), 4.19- 4.29 (m, 4H), 5.68 (s, 1H), 5.86 (s, 1H), 6.74 (d, 1H, *J*= 9 Hz), 6.76 (d, 1H, *J*= 8.5 Hz), 7.44 (d, 1H, *J*= 8 Hz), 7.80 (d, 1H, *J*= 8 Hz), 7.52 (s, 1H), 7.62 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): 11.26, 11.31, 12.98, 13.43, 14.21, 14.32, 20.60, 20.62, 41.92, 42.01, 61.23, 61.29, 76.29, 76.47, 91.22, 92.52, 106.20, 106.54, 110.27, 110.32, 115.67, 116.02, 128.15, 128.32, 130.52, 130.90, 132.92, 133.13, 141.92, 142.30, 165.51, 165.70, 175.19, 175.12, 209.44, 209.70.

HRMS (ESI): calcd for $C_{18}H_{20}BrNO_4^+$[M(^{79}Br)+Na]$^+$: 416.0473, Found: 416.0492; [M(^{81}Br)+Na]$^+$: Found : 418.0453, 418.0471).

16. Ethyl-4-(1-benzyl-5-bromo-3-hydroxy-2-oxoindolin-3-yl)penta-2,3-dienoate (4n)



4n

Yield**:** 25 mg, 59% yield as a colorless oil.

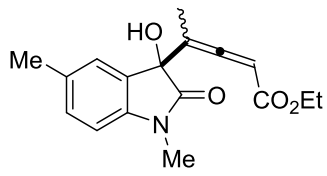
IR (neat, cm^{-1}): 3392, 3034, 2983, 2929, 1964, 1964, 1705, 1613, 1455, 1366, 1170, 1032, 831, 753, 692.

^{1}H NMR (500MHz, $CDCl_3$): 1.17 (t, 3H, *J*= 7 Hz), 1.26 (t, 3H, *J*= 7 Hz), 1.60 (s, 3H), 1.80 (s, 3H), 4.07- 4.19 (m, 4H), 4.66 (dd, 2H, J_1= 2.5 Hz, J_2= 15.5 Hz), 4.89 (dd, 2H, J_1= 2.5 Hz, J_2= 15.5 Hz), 5.59 (s, 1H), 5.77 (s, 1H), 6.54 (d, 1H, *J*= 8 Hz), 6.58 (d, 1H, *J*= 8 Hz), 7.09- 7.24 (m, 12H), 7.31 (s, 1H), 7.41 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): 13.07, 13.51, 14.15, 14.26, 44.12, 44.24, 61.27, 76.43, 76.64, 91.26, 92.53, 106.20, 106.48, 110.61, 110.67, 125.30, 125.50, 127.17, 127.22, 127.25, 127.32, 127.46, 127.96, 128.01, 128.44, 128.76, 128.79, 128.96, 128.98, 129.07, 129.10, 130.01, 130.21, 134.82, 165.05, 165.64, 175.47, 175.57.

HRMS (ESI): calcd for $C_{22}H_{20}BrNO_4^+$[M(^{79}Br)+Na]$^+$: 464.0473, Found: 464.0434; [M(^{81}Br)+Na]$^+$: 466.0473, Found: 466.0446).

17. Ethyl-4-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)penta-2,3-dienoate (4o)



4o

Yield**:** 41 mg, 79% yield as a colorless oil.

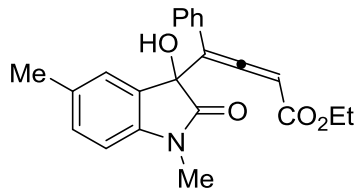
IR (neat, cm^{-1}): 3374, 2982, 2925, 2871, 1963, 1709, 1605, 1482, 1352, 1249, 1153, 1035, 834, 735.

^{1}H NMR (500MHz, $CDCl_3$): 1.29 (t, 3H, *J*= 7 Hz), 1.34 (t, 3H, *J*= 7 Hz), 1.61 (s, 3H), 1.81 (s, 3H), 2.32 (s, 3H), 2.36 (s, 3H), 3.18 (s, 3H), 3.20 (s, 3H), 4.16- 4.28 (m, 4H), 5.67 (s, 1H), 5.84 (s, 1H), 6.74 (d, 1H, *J*= 8 Hz), 6.74 (d, 1H, *J*= 8 Hz), 7.15 (t, 2H, *J*= 8.5 Hz), 7.22 (s, 1H), 7.32 (s, 1H).

^{13}C NMR (125MHz, $CDCl_3$): 13.06, 13.46, 14.22, 14.26, 21.0, 21.05, 26.38, 26.46, 61.01, 61.08, 76.65, 76.82, 90.77, 92.20, 106.75, 106.97, 108.26, 108.30, 125.42, 125.61, 128.34, 128.65, 130.42, 130.42, 130.61, 133.03, 140.97, 141.33, 165.73, 165.88, 175.70, 175.80, 209.61, 209.89.

HRMS (ESI): calcd for $[C_{17}H_{19}NO_4Na, M+Na]^+$: 324..1212; Found: 324.1291).

18. Ethyl 4-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4p)



4p

Yield**:** 12 mg, 19% yield as colorless solid.

IR (neat, cm^{-1}): 3377, 2989, 2933, 1962, 1706, 1608, 1487, 1368, 1152, 1027, 812, 757.

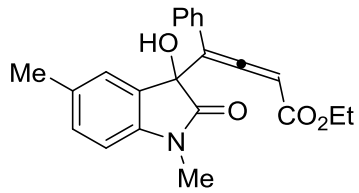
^{1}H NMR (500MHz, $CDCl_3$): 1.17 (t, 3H, *J*= 7.5 Hz), 2.23 (s, 3H), 3.21 (s, 3H), 4.12 (bs, 1H), 4.14 (q, 2H, *J*= 6.5 Hz), 6.73 (d, 1H, *J*= 8 Hz), 6.80 (s, 1H), 7.11 (d, 1H, *J*= 8 Hz), 7.19 (s, 1H), 7.30 – 7.38 (m, 5H).

^{13}C NMR (125MHz, $CDCl_3$): 13.98, 20.93, 26.43, 61.63, 75.57, 102.43, 106.20, 108.23, 125.13, 127.68, 128.52, 129.00, 129.15, 130.44, 130.85, 132.65, 141.75, 164.66, 175.60, 211.04.

HRMS (ESI): calcd for $C_{22}H_{21}NO_4^+$ $([M+Na])^+$: 386.1368, **found:** 386.1387.

19. Ethyl 4-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4p')

Yield**:** 27 mg, 44% yield as colorless solid.



4p'

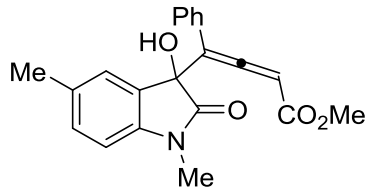
IR (neat, cm^{-1}): 3381, 2985, 2931, 1965, 1705, 1610, 1456, 1357, 1245, 1157, 1089, 812, 754.

^{1}H NMR (500MHz, CDCl$_3$): 1.16 (t, 3H, *J*= 7.5 Hz), 2.34 (s, 3H), 3.21 (s, 3H), 3.97 (bs, 1H), 4.06 – 4.18 (m, 2H), 6.73 (d, 1H, *J*= 8 Hz), 6.84 (s, 1H), 7.14 (d, 1H, *J*= 8 Hz), 7.21 (s, 1H), 7.30 – 7.39 (m, 5H).

^{13}C NMR (125MHz, CDCl$_3$): 14.00, 21.13, 26.48, 61.57, 75.25, 102.71, 106.37, 108.34, 124.93, 127.73, 128.54, 128.98, 130.49, 131.14, 132.63, 144.91, 164.67, 175.63, 211.22.

HRMS (ESI): calcd for $C_{22}H_{21}NO_4^+$ ([M+Na])$^+$: 386.1368, **found:** 386.1396.

20. Methyl 4-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4q)



4q

Yield**:** 12 mg, 21% yield as colorless solid.

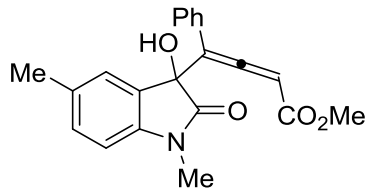
IR (neat, cm^{-1}): 3377, 2980, 2932, 1965, 1707, 1609, 1488, 1361, 1240, 1157, 1089, 854, 757.

^{1}H NMR (500MHz, CDCl$_3$): 2.23 (s, 3H), 3.19 (s, 3H), 3.67 (s, 3H), 4.10 (bs, 1H), 6.71 (d, 1H, *J*= 8 Hz), 6.79 (s, 1H), 7.10 (d, 1H, *J*= 8 Hz), 7.17 (s, 1H), 7.29 - 7.32 (m, 1H), 7.35 (d, 4H, *J*= 8 Hz).

^{13}C NMR (125MHz, CDCl$_3$): 20.94, 26.44, 52.60, 75.53, 102.45, 105.96, 108.29, 125.10, 127.71, 128.60, 129.03, 130.51, 130.70, 132.65, 141.78, 165.13, 175.52, 211.19

HRMS (ESI): calcd for [$C_{21}H_{19}NO_4Na$, M+Na]$^+$: 372.1212; Found: 372.1207).

21. Methyl 4-(3-hydroxy-1,5-dimethyl-2-oxoindolin-3-yl)-4-phenylbuta-2,3-dienoate (4q')



4q'

Yield**:** 30 mg, 50% yield as colorless solid.

IR (neat, cm^{-1}): 3380, 2983, 2933, 1963, 1706, 1610, 1486, 1363, 1247, 1150, 1089, 812, 733.

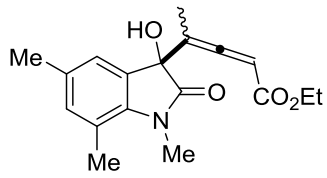
^{1}H NMR (500MHz, CDCl$_3$): 2.33 (s, 3H), 3.21 (s, 3H), 3.66 (s, 3H), 4.00 (bs, 1H), 6.73 (d, 1H, *J*= 8 Hz), 6.84 (s, 1H), 7.13 (d, 1H, *J*= 8 Hz), 7.20 (s, 1H), 7.30 - 7.32 (m, 1H), 7.37 (d, 4H, *J*=

8 Hz).

^{13}C NMR (125MHz, $CDCl_3$): 21.15, 26.50, 52.55, 75.23, 102.77, 106.14, 108.40, 124.94, 127.75, 128.62, 129.01, 129.12, 130.57, 131.01, 132.65, 141.94, 165.16, 175.62, 211.35.

HRMS (ESI): calcd for $[C_{21}H_{19}NO_4Na, M+Na]^+$: 372.1212; Found: 372.1210).

22. Ethyl-4-(3-hydroxy-1,5,7-trimethyl-2-oxoindolin-3-yl)penta-2,3-dienoate (4r)



4r

Yield**:** 34 mg, 68% yield as a colorless oil.

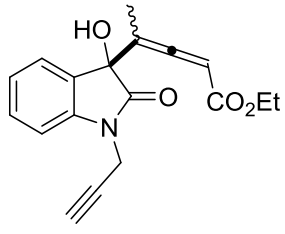
IR (neat, cm^{-1}): 3392, 2983, 2927, 2871, 1964, 1697, 1605, 1501, 1360, 1240, 1149, 1093, 1034, 810, 699.

^{1}H NMR (500MHz, $CDCl_3$): 1.30 (t, 3H, *J*= 7 Hz), 1.34 (t, 3H, *J*= 7 Hz), 1.58 (s, 3H), 1.77 (s, 3H), 2.27 (s, 3H), 2.30 (s, 3H), 2.52 (s, 3H), 2.53 (s, 3H), 3.46 (s, 3H), 3.47 (s, 3H), 4.18- 4.29 (m, 4H), 5.70 (s, 1H), 5.86 (s, 1H), 6.88 (s, 1H), 6.90 (s, 1H), 7.05 (s, 1H), 7.17 (s, 1H),

^{13}C NMR (125MHz, $CDCl_3$): 13.17, 13.53, 14.23, 14.28, 18.71, 18.74, 20.73, 29.74, 29.82, 66.09, 61.09, 76.01, 76.21, 91.08, 92.29, 107.10, 107.28, 119.83, 119.90, 123.29, 123.46, 128.95, 129.26, 132.82, 133.20, 134.40, 134.57, 138.60, 138.95, 165.73, 165.91, 176.38, 176.52, 209.51, 209.88.

HRMS (ESI): calcd for $[C_{18}H_{21}NO_4Na, M+Na]^+$: 338.1363; Found: 338.1317).

23. Ethyl-4-(3-hydroxy-2-oxo-1-(prop-2-yn-1-yl)indolin-3-yl)penta-2,3-dienoate (4s)



4s

Yield**:** 27 mg, 54% yield as a colorless oil.

IR (neat, cm^{-1}): 3288, 2982, 2854, 2196, 1705, 1613, 1488, 1360, 1250, 1155, 1033, 835, 754.

^{1}H NMR (500MHz, $CDCl_3$): 1.26 (t, 3H, *J*= 7 Hz), 1.33 (t, 3H, *J*= 7 Hz), 1.63 (s, 3H), 1.82 (s, 3H), 2.27 (s, 2H), 4.16- 4.25 (m, 4H), 4.38 (d, 2H, *J*= 17.5 Hz), 4.60 (td, 2H, J_1= 2 Hz, J_2= 15.5 Hz), 5.68 (s, 1H), 5.85 (s, 1H), 7.07 (t, 2H, *J*= 7.5 Hz), 7.13 (t, 1H, *J*= 7.5 Hz), 7.18 (t, 1H, *J*= 7.5 Hz), 7.38 (t, 2H, *J*= 8 Hz), 7.43 (d, 1H, *J*= 8 Hz), 7.53 (d, 1H, *J*= 8 Hz).

^{13}C NMR (125MHz, $CDCl_3$): 13.00, 13.31, 14.00, 14.15, 14.23,

29.48, 29.54, 61.10, 72.67, 72.71, 76.32, 76.51, 76.70, 91.23, 92.35, 106.71, 106.80, 109.41, 109.53, 109.57, 123.60, 123.94, 124.70, 125.05, 128.26, 128.65, 130.21, 130.66, 141.47, 141.75, 165.66, 174.47, 174.91, 209.74.

HRMS (ESI): calcd for $[C_{18}H_{17}NO_4Na, M+Na]^+$: 334.1055; Found: 334.0907).

8. ^{1}H NMR and ^{13}C NMR spectra of products

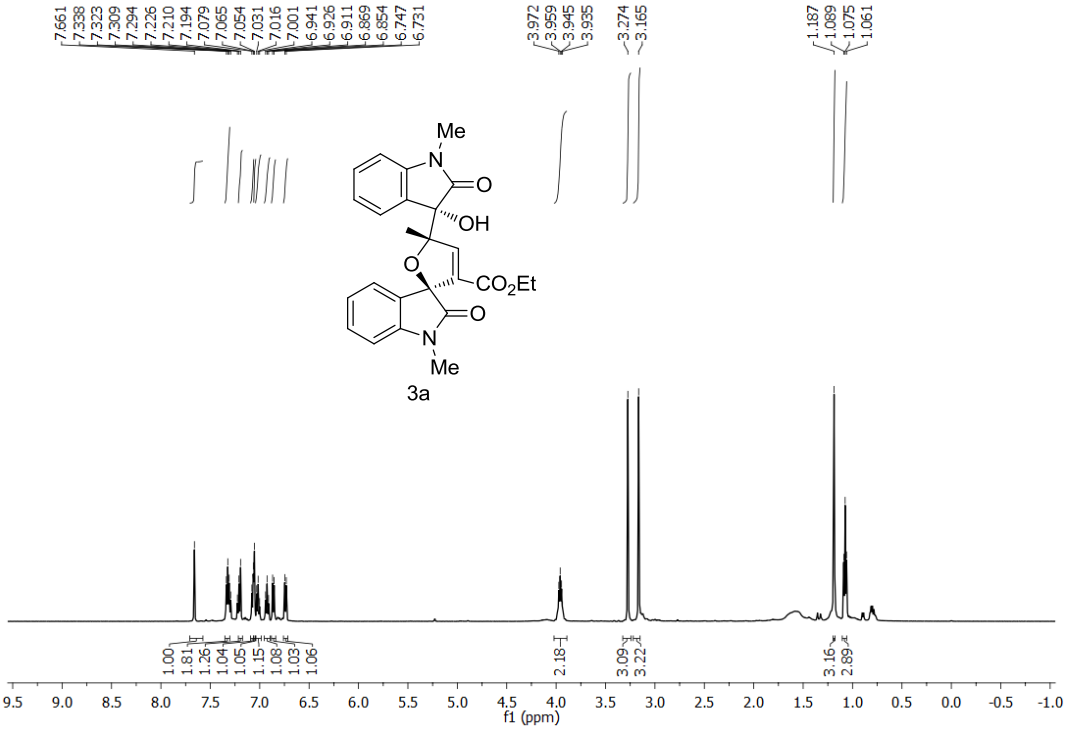


Fig S1. ^{1}H NMR of 3a

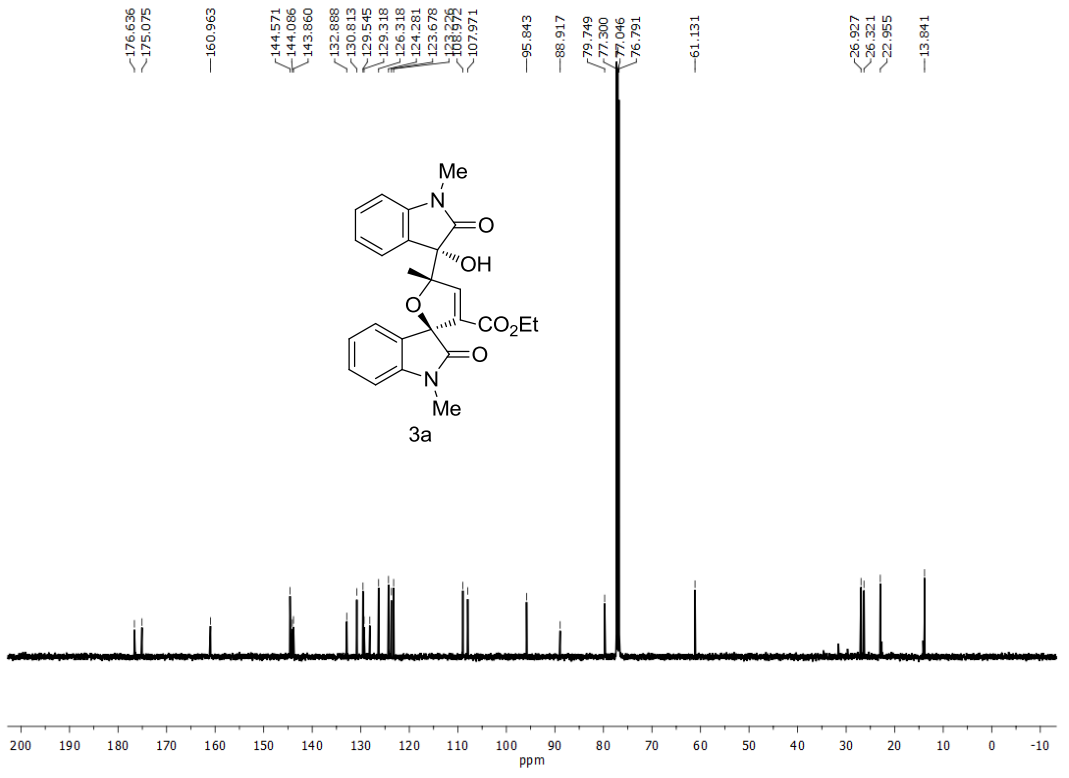


Fig S2. ^{13}C NMR of 3a

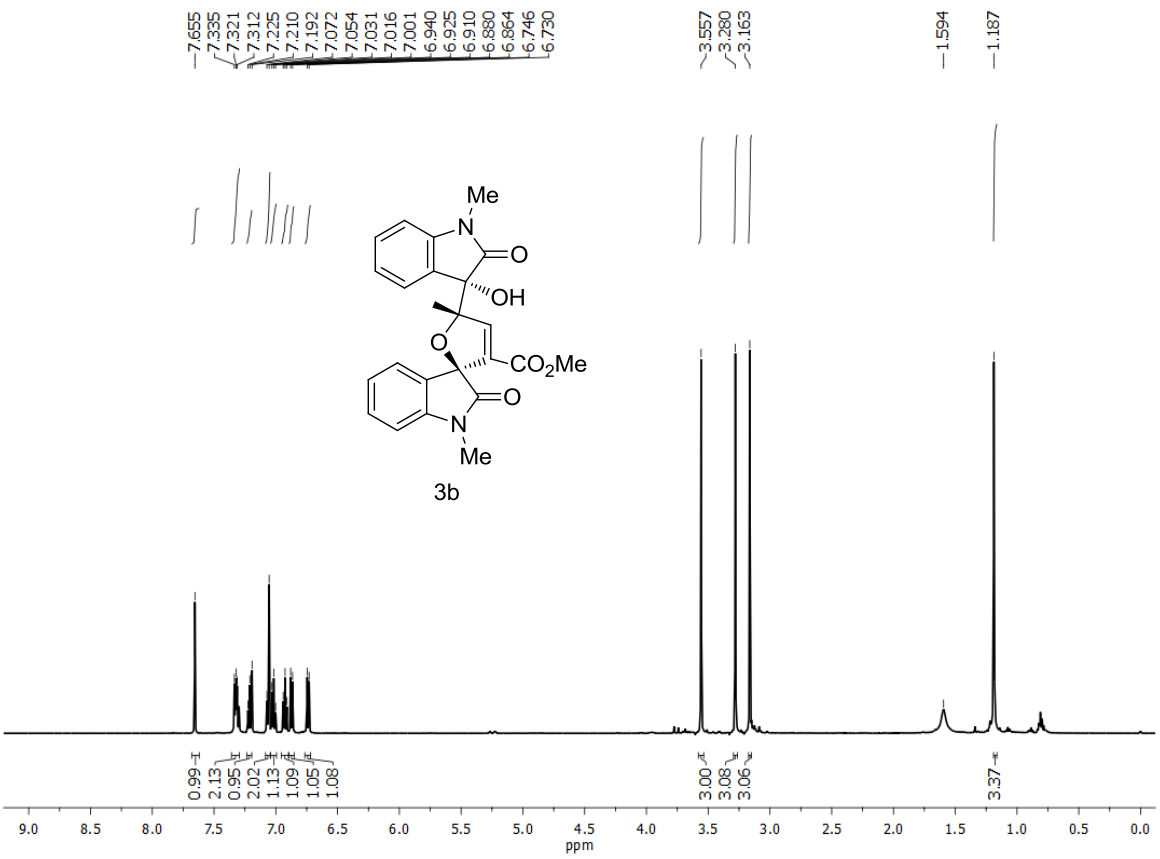


Fig S3. ^{1}H NMR of 3b

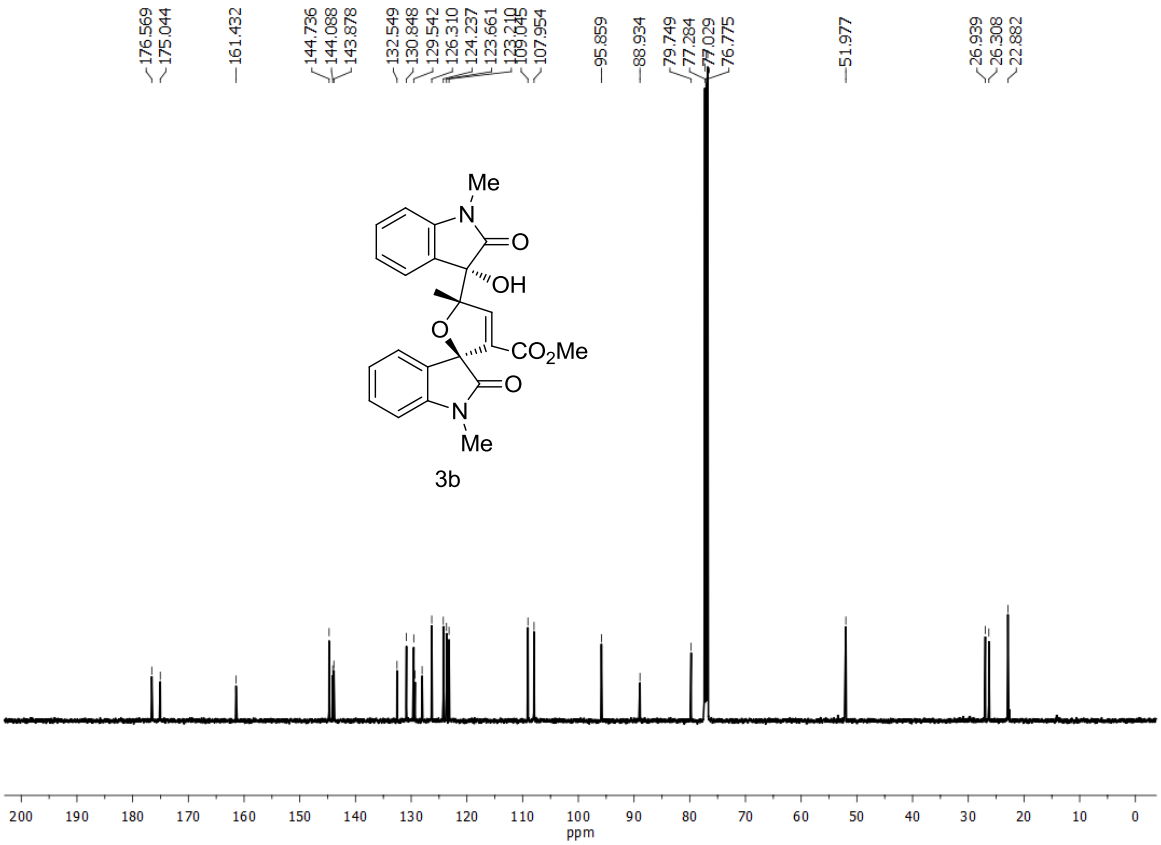


Fig S4. ^{13}C NMR of 3b

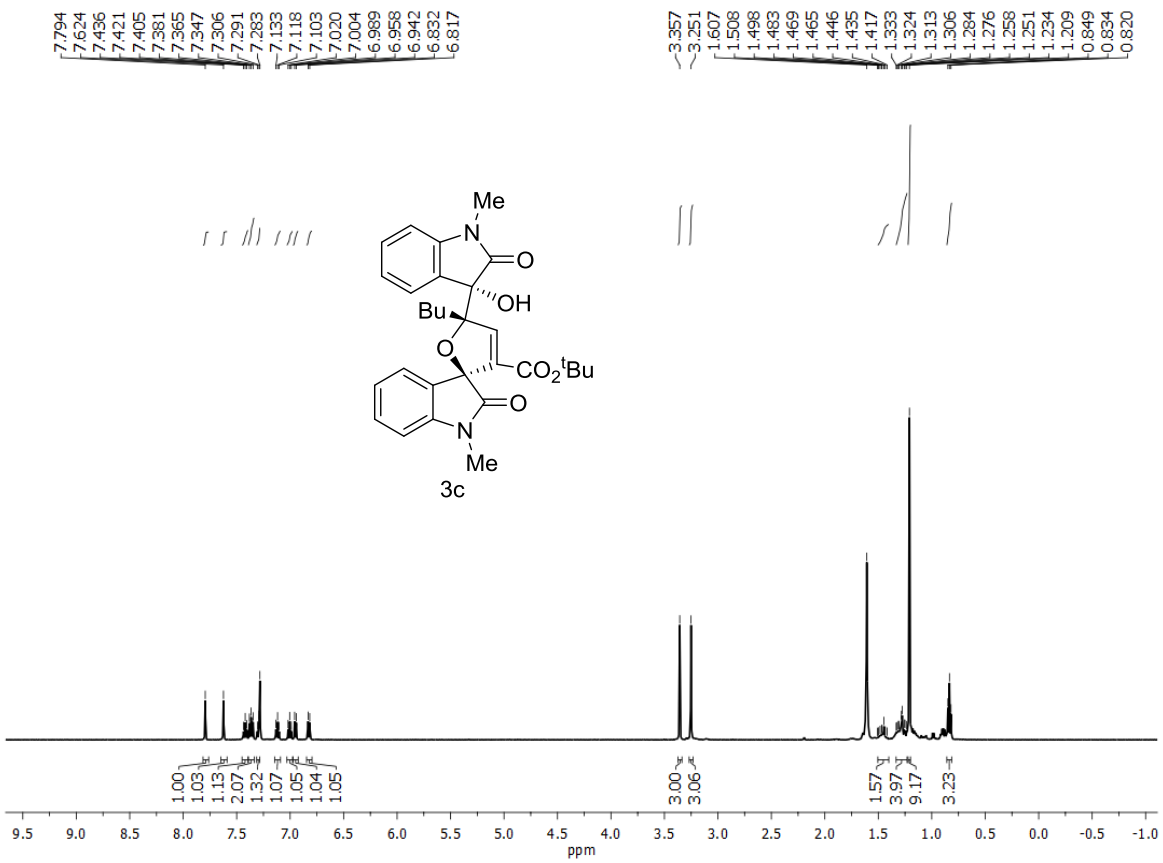


Fig S5. ^{1}H NMR of 3c

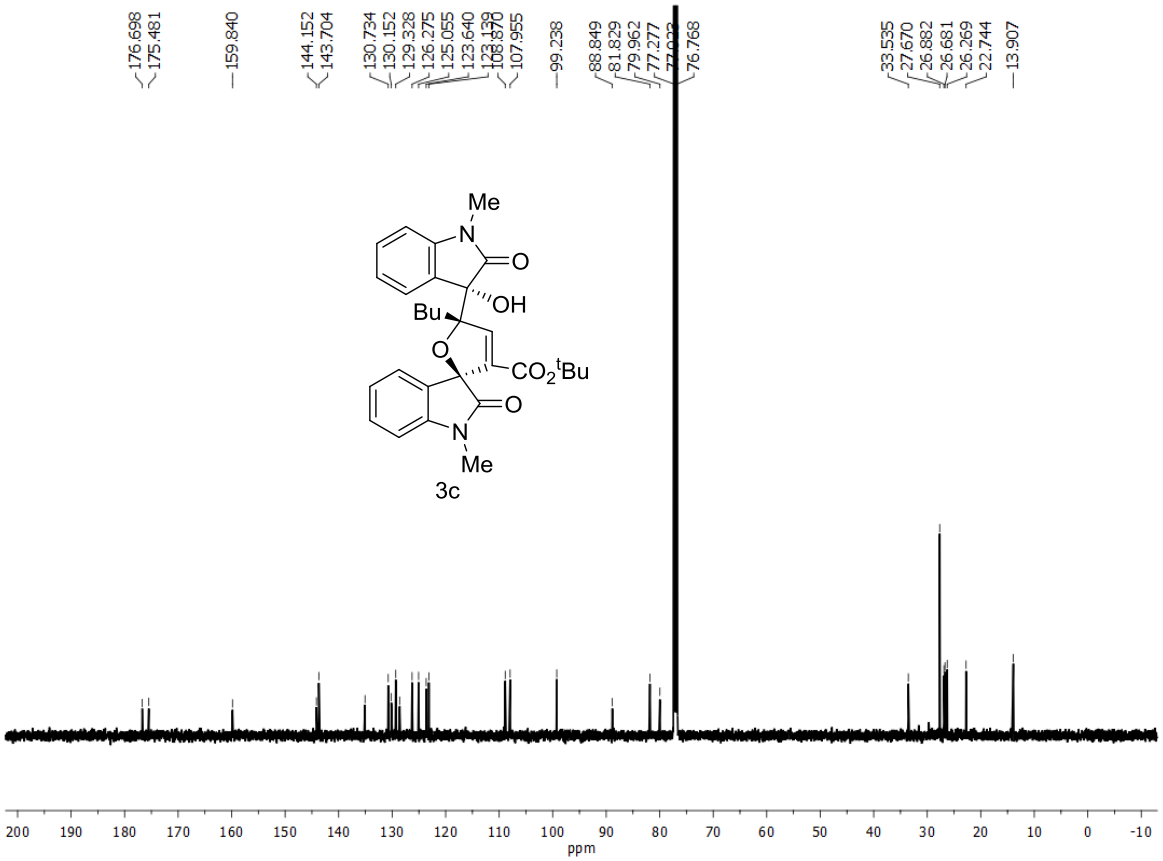


Fig S6. ^{13}C NMR of 3c

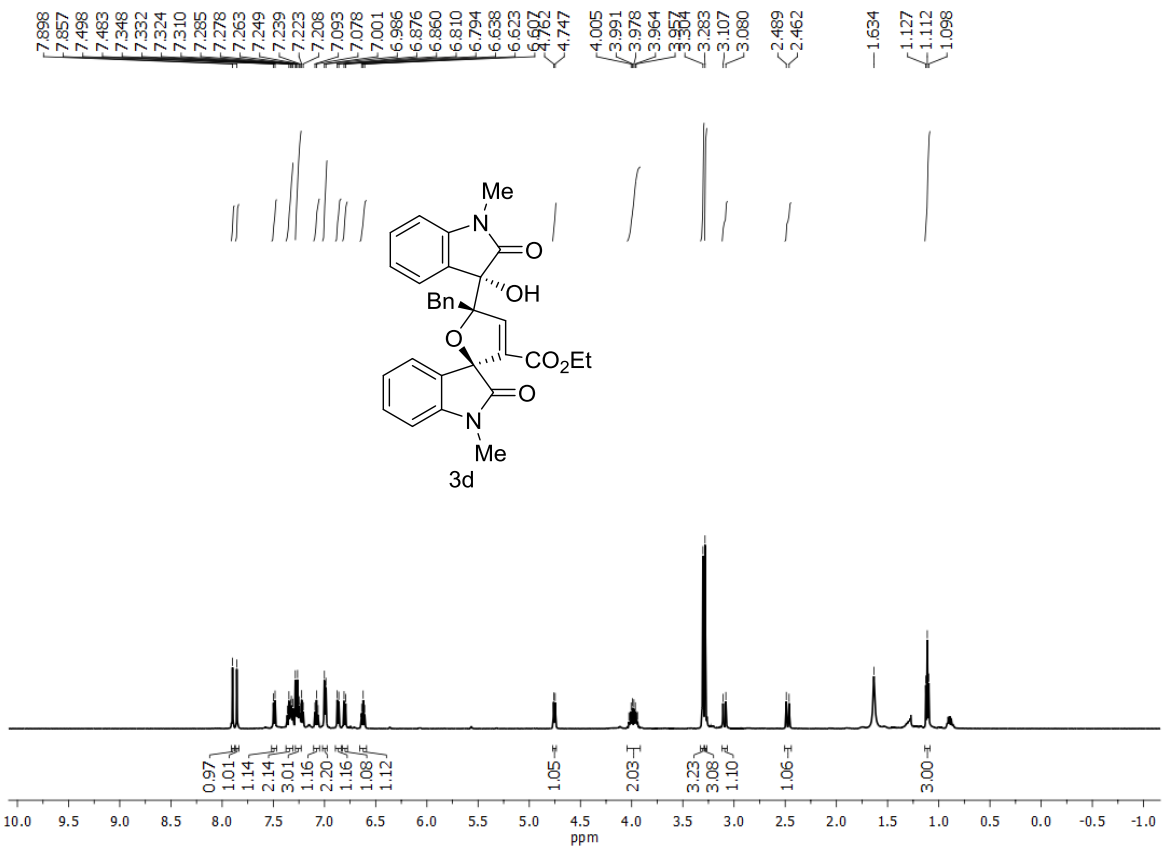


Fig S7. ^{1}H NMR of 3d

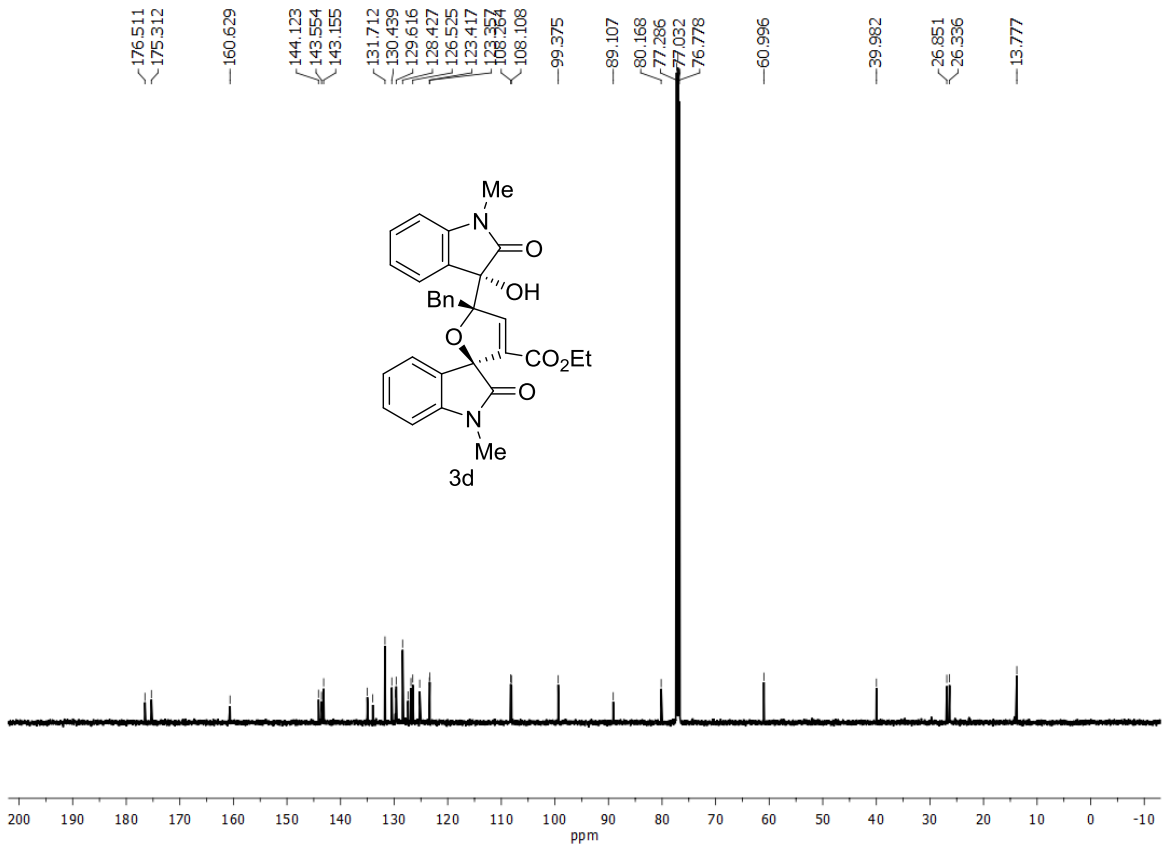


Fig S8. ^{13}C NMR of 3d

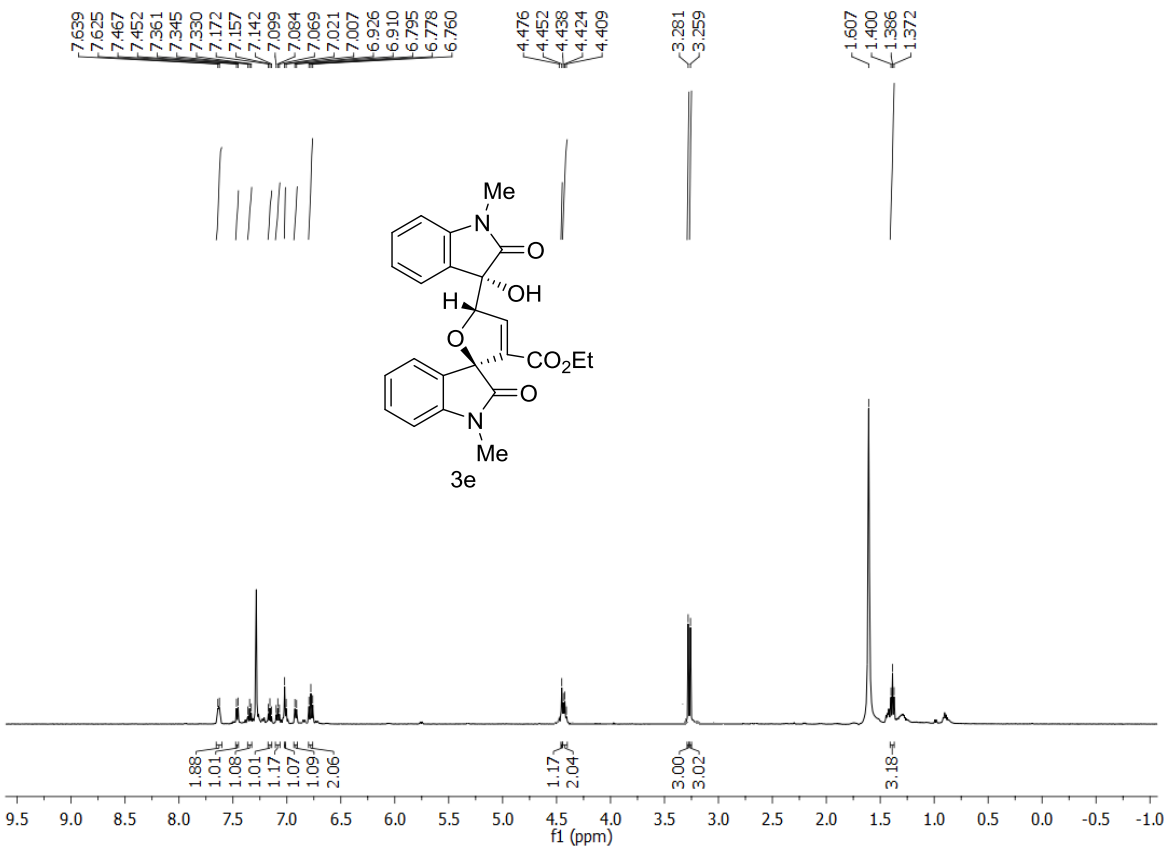


Fig S9. ^{1}H NMR of 3e

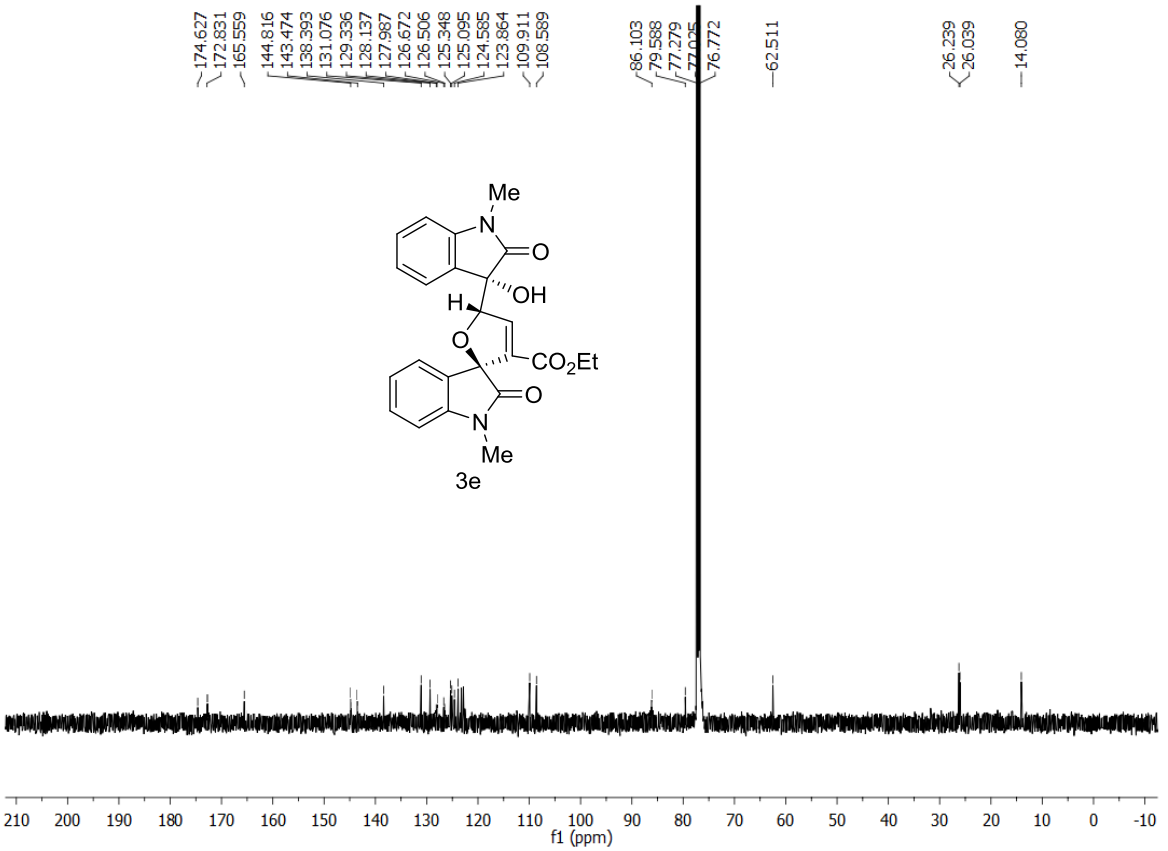


Fig S10. ^{13}C NMR of 3e

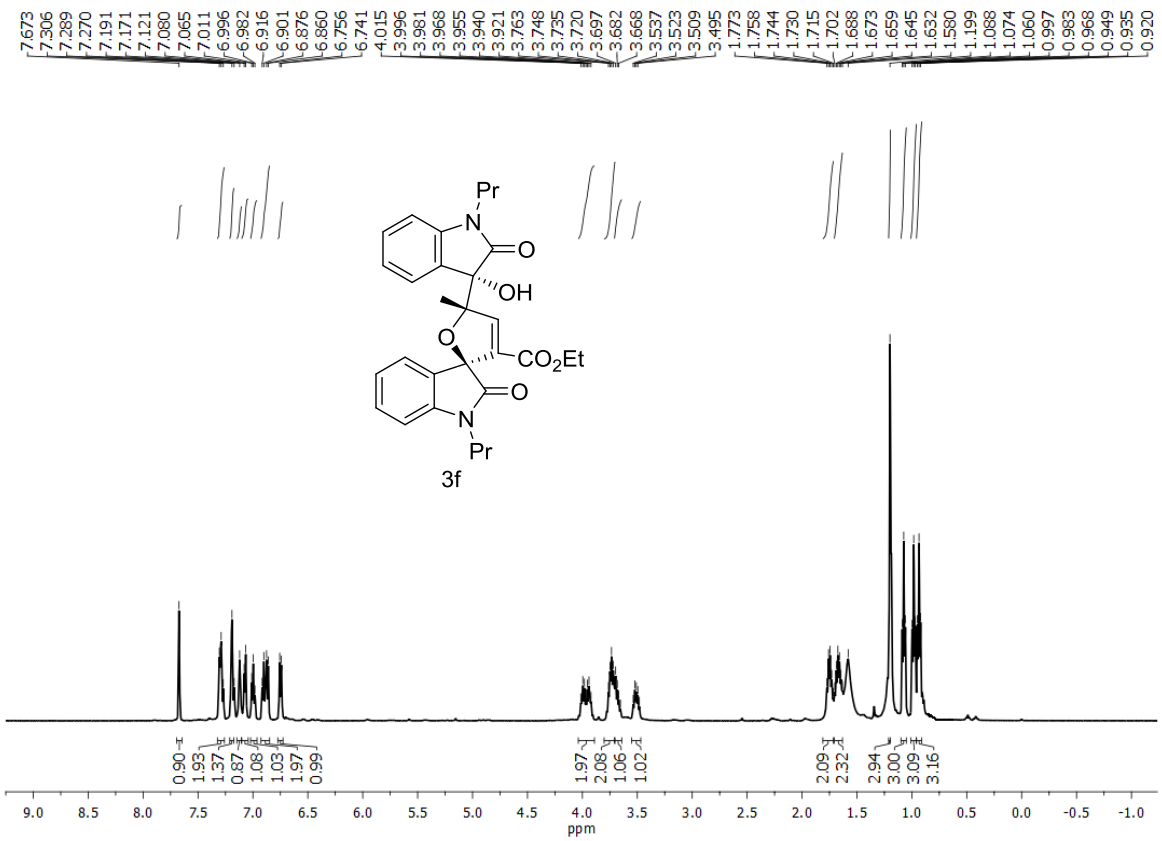


Fig S11. ^{1}H NMR of 3f

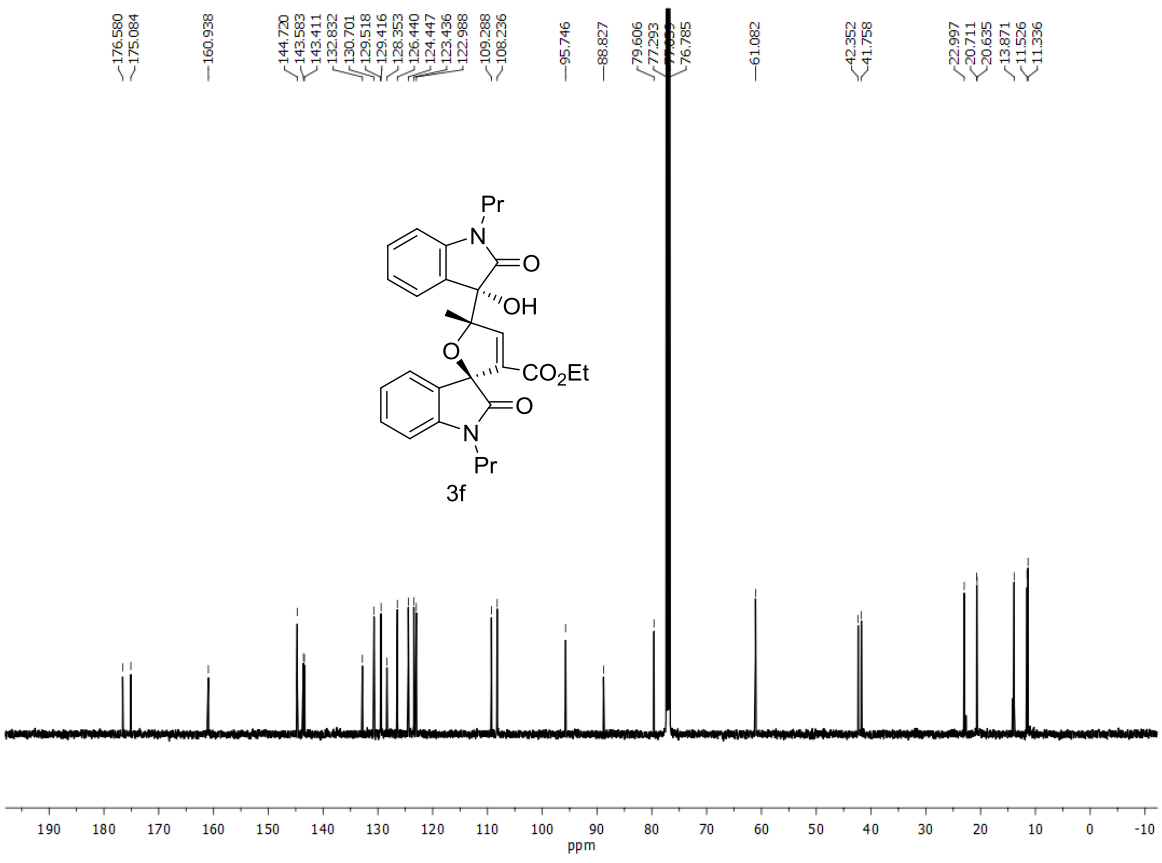


Fig S12. ^{13}C NMR of 3f

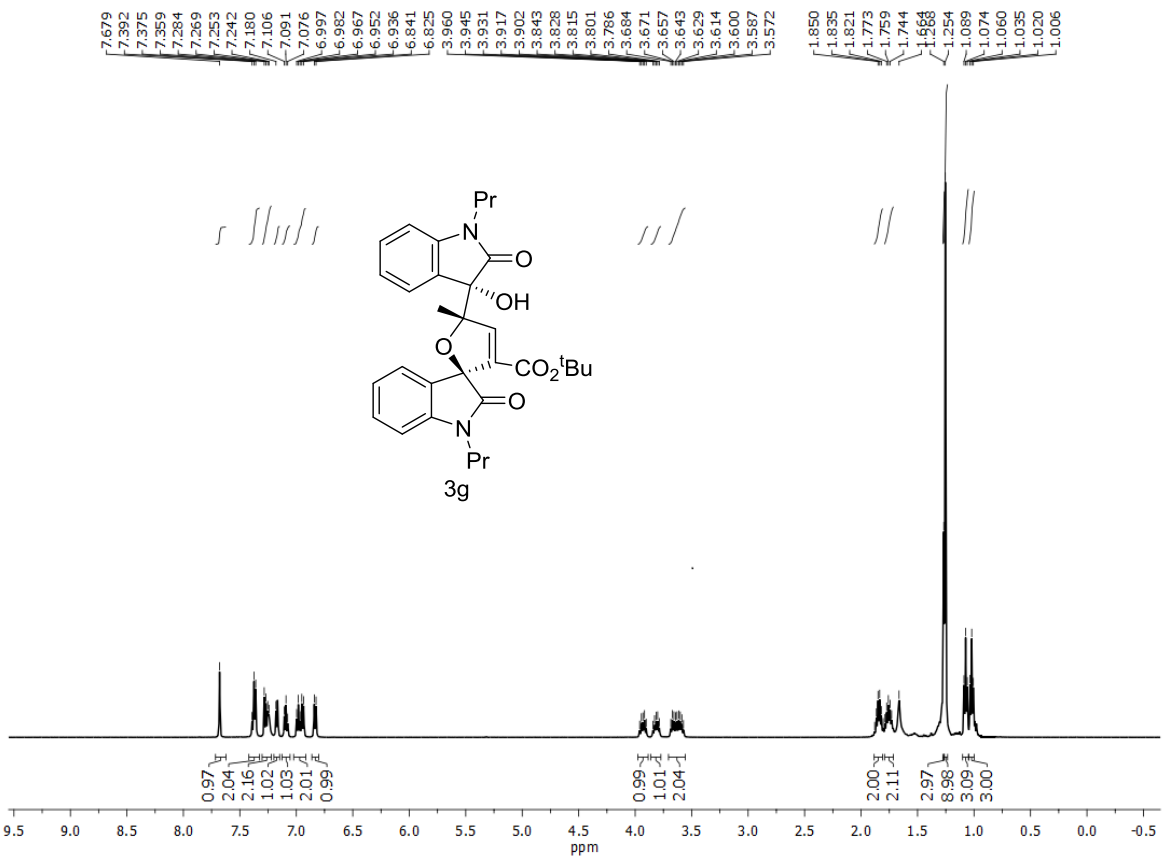


Fig S13. ^{1}H NMR of 3g

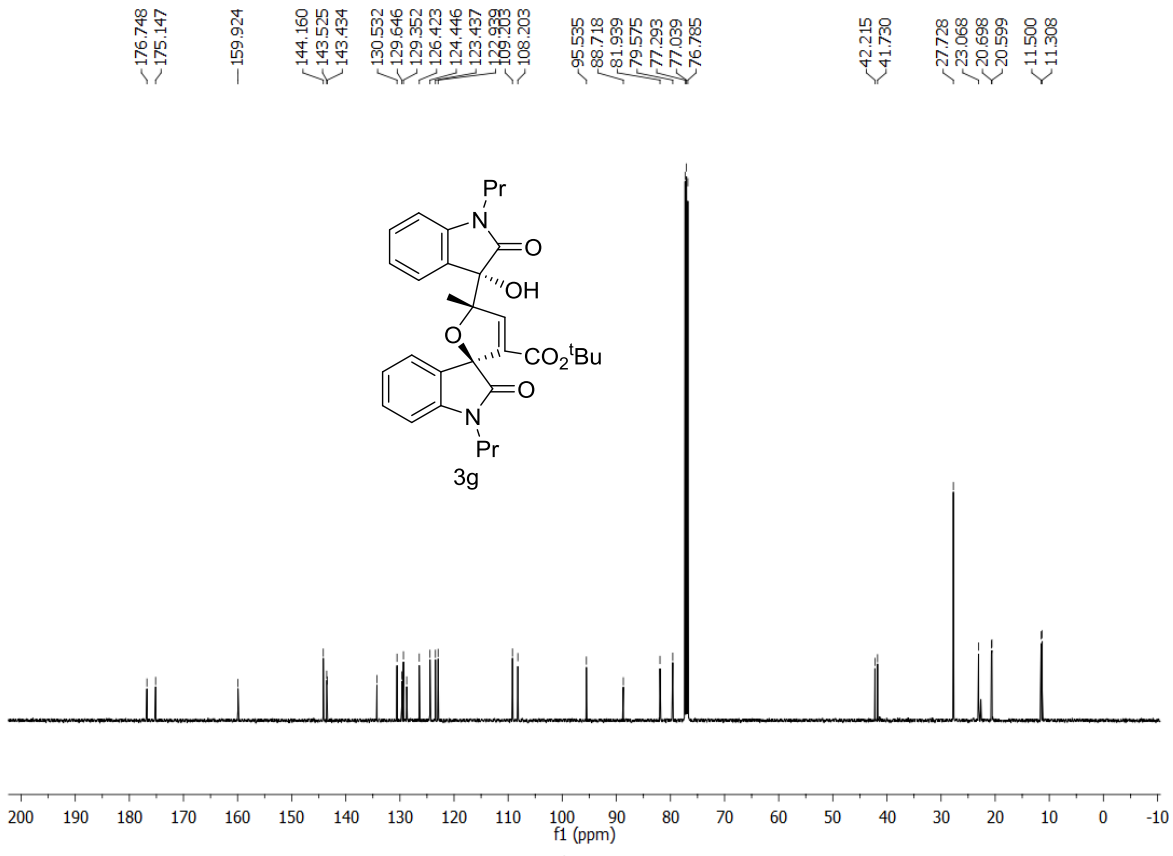


Fig S14. ^{13}C NMR of 3g

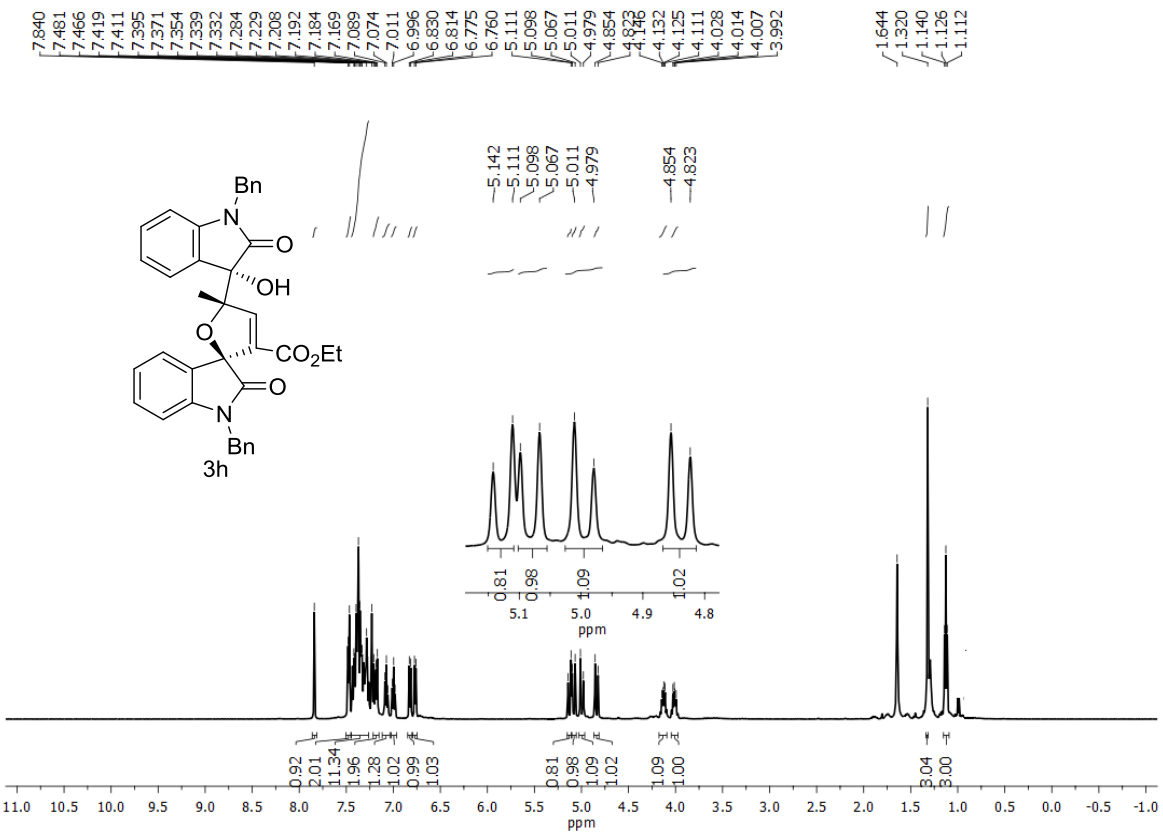


Fig S15. ^{1}H NMR of 3h

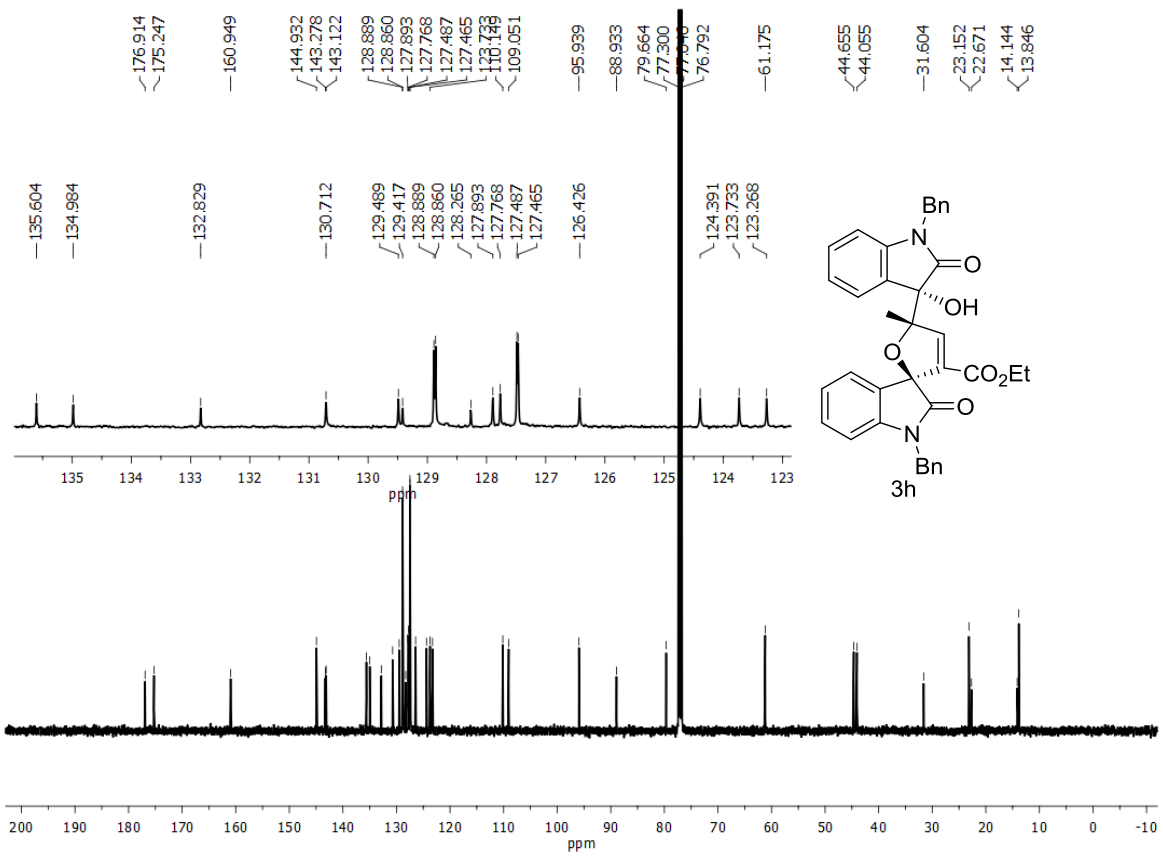


Fig S16. ^{13}C NMR of 3h

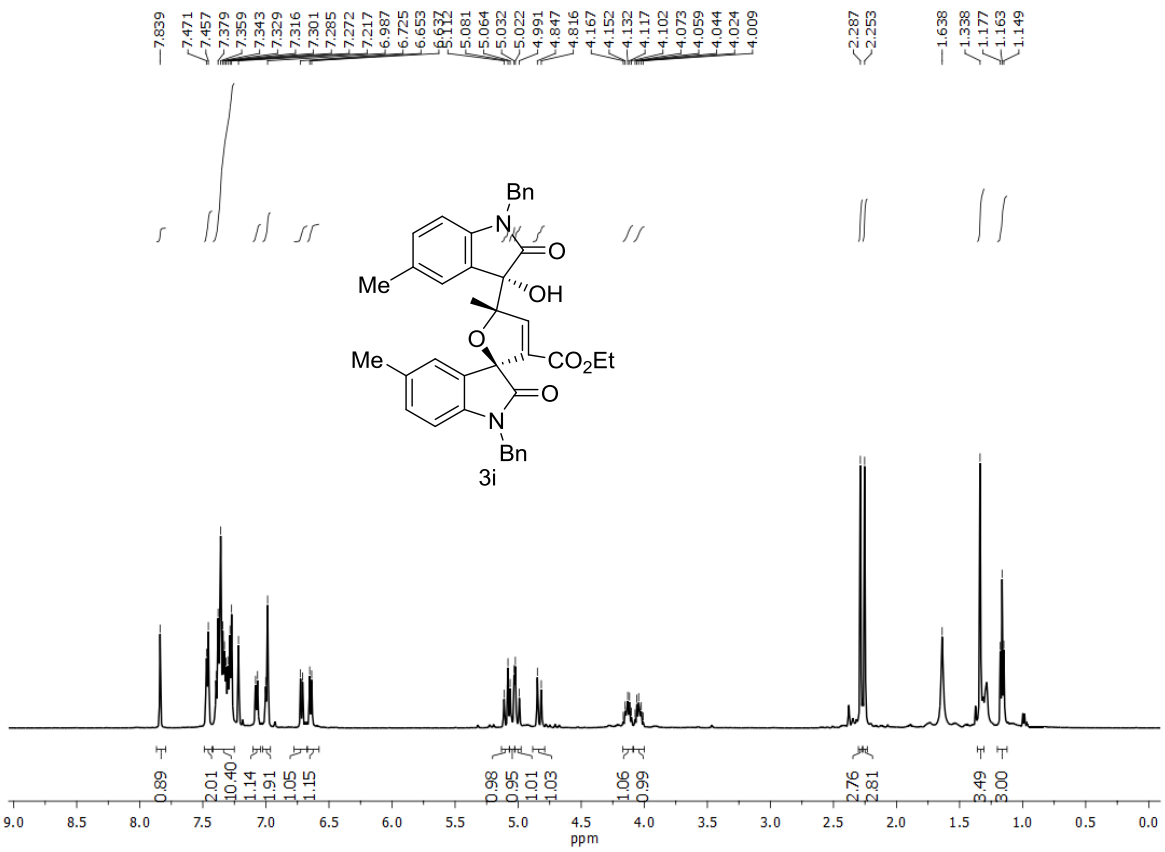


Fig S17. ^{1}H NMR of 3i

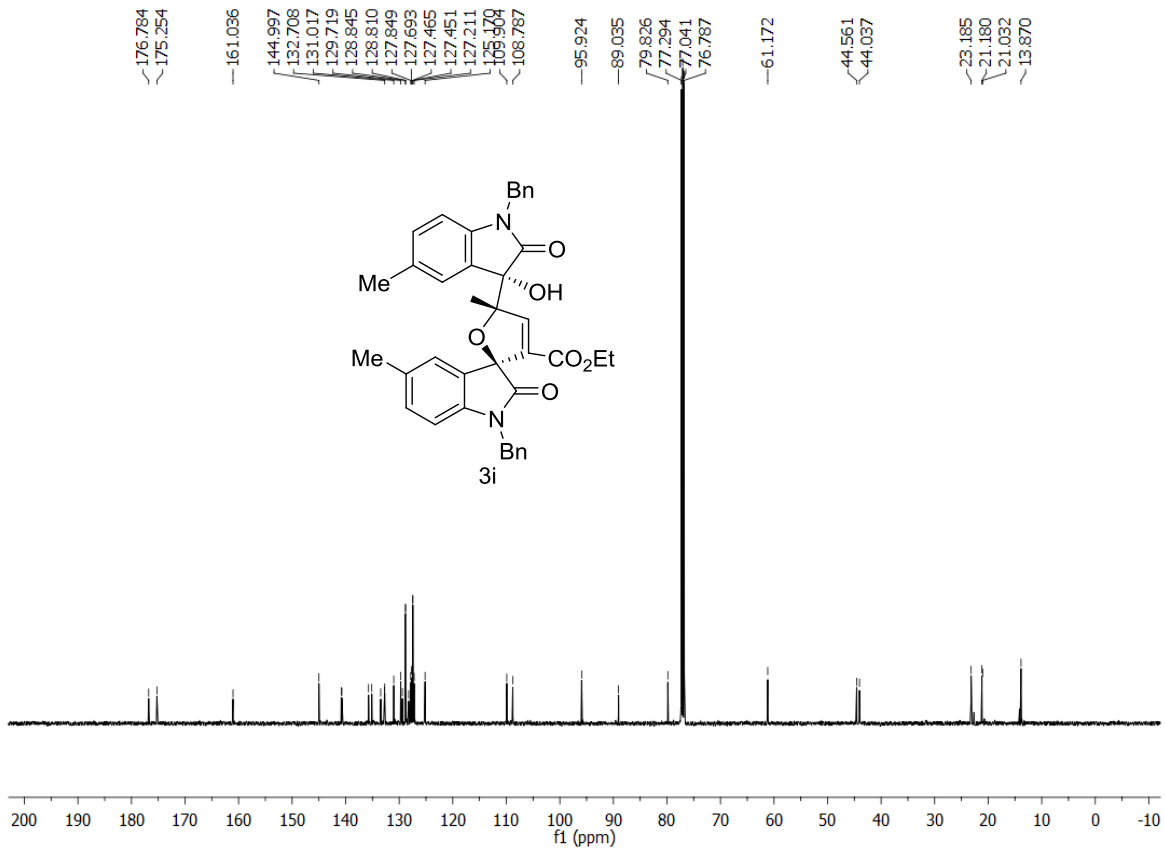


Fig S18. ^{13}C NMR of 3i

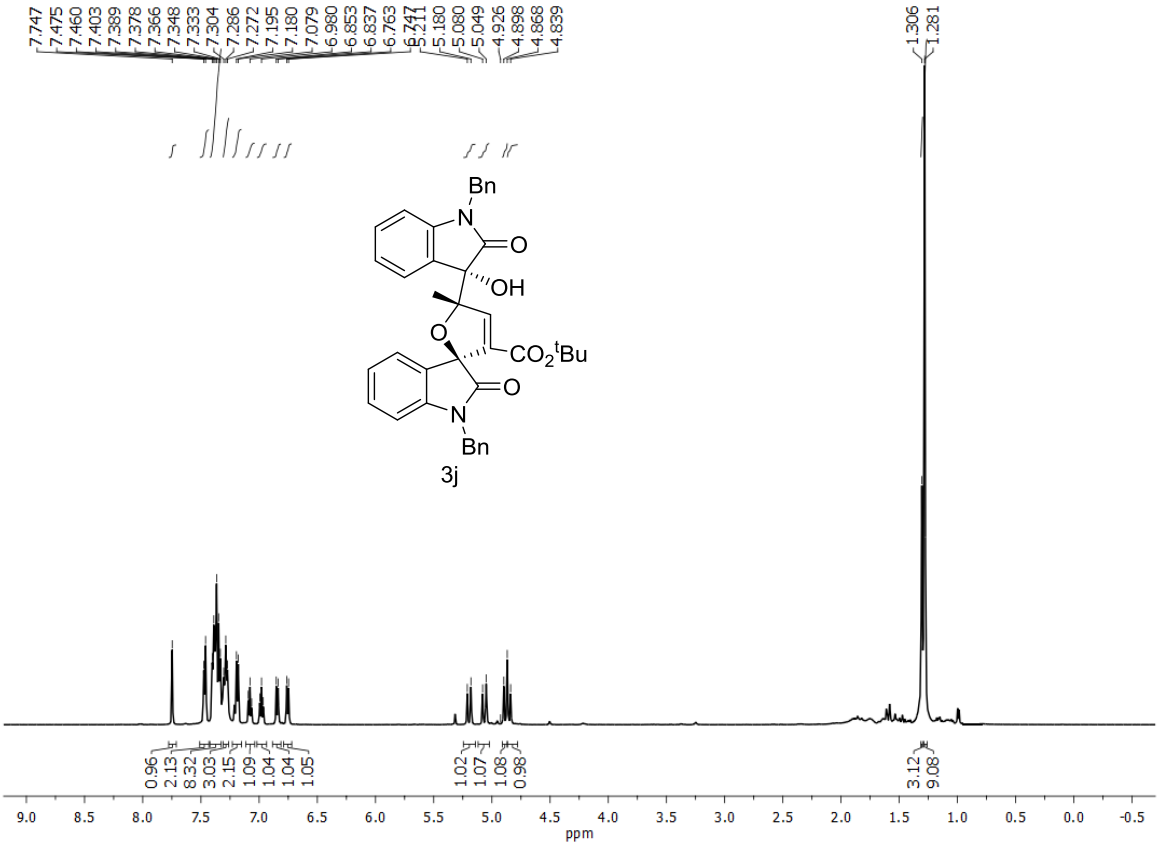


Fig S19. ^{1}H NMR of 3j

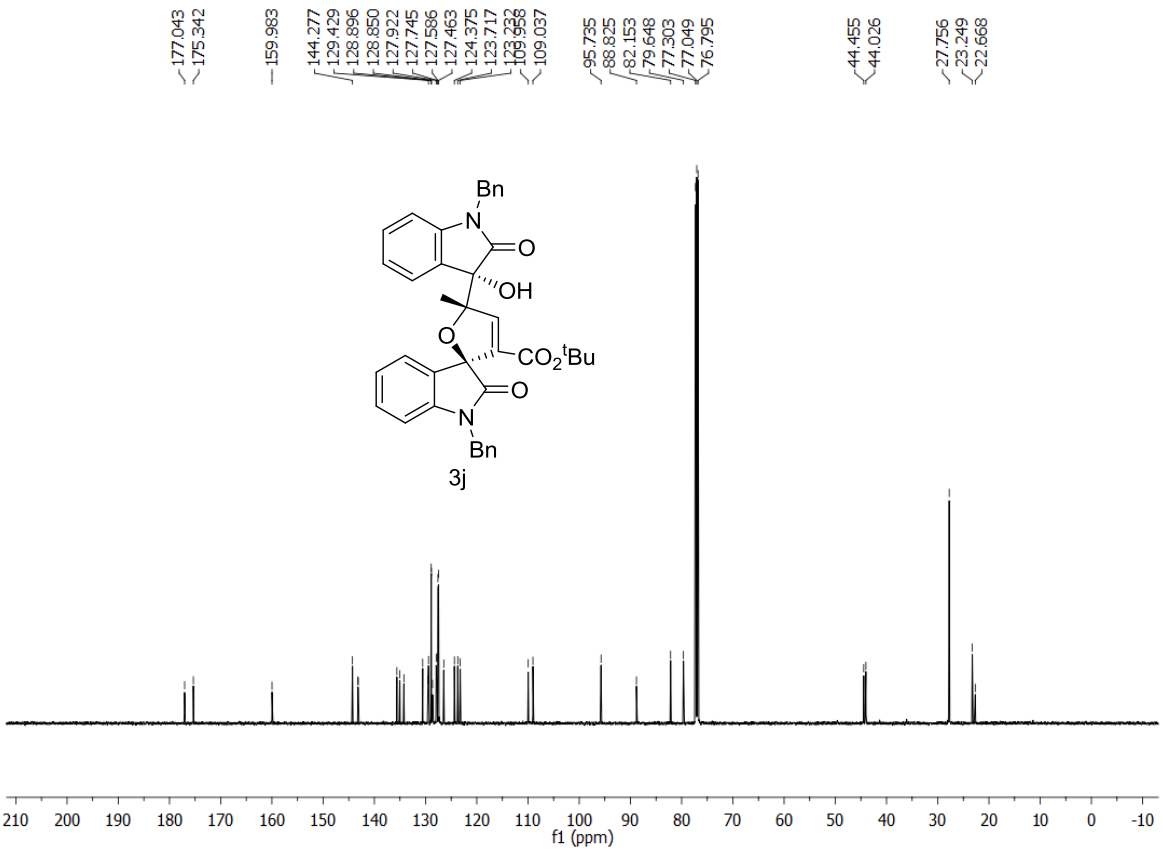


Fig S20. ^{13}C NMR of 3j

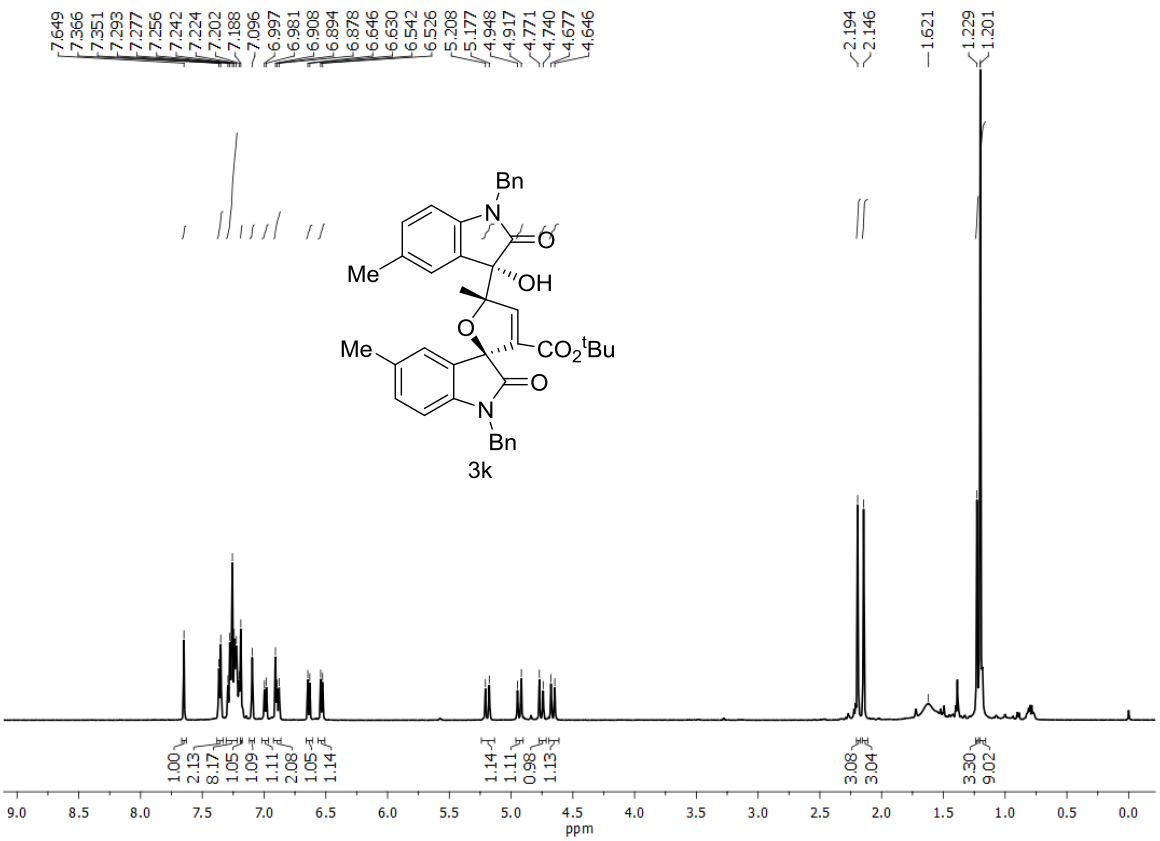


Fig S21. ^{1}H NMR of 3k

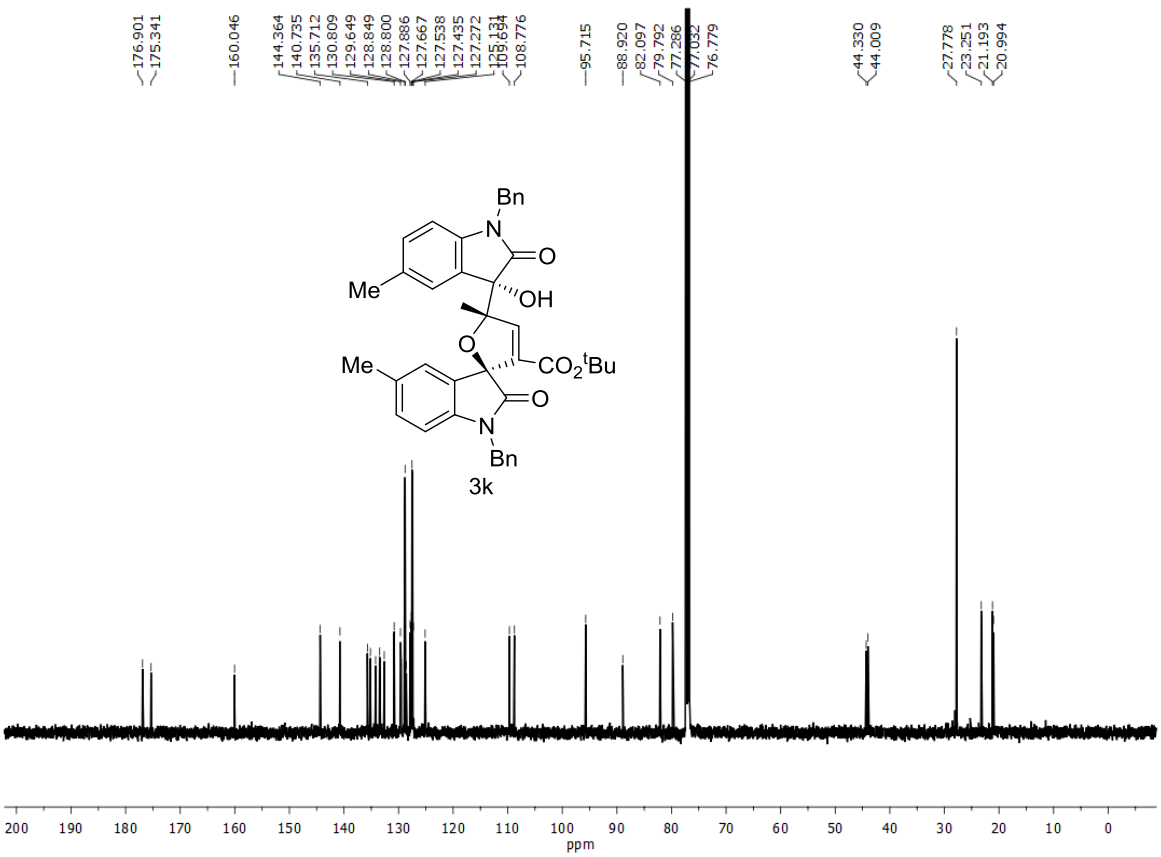


Fig S22. ^{13}C NMR of 3k

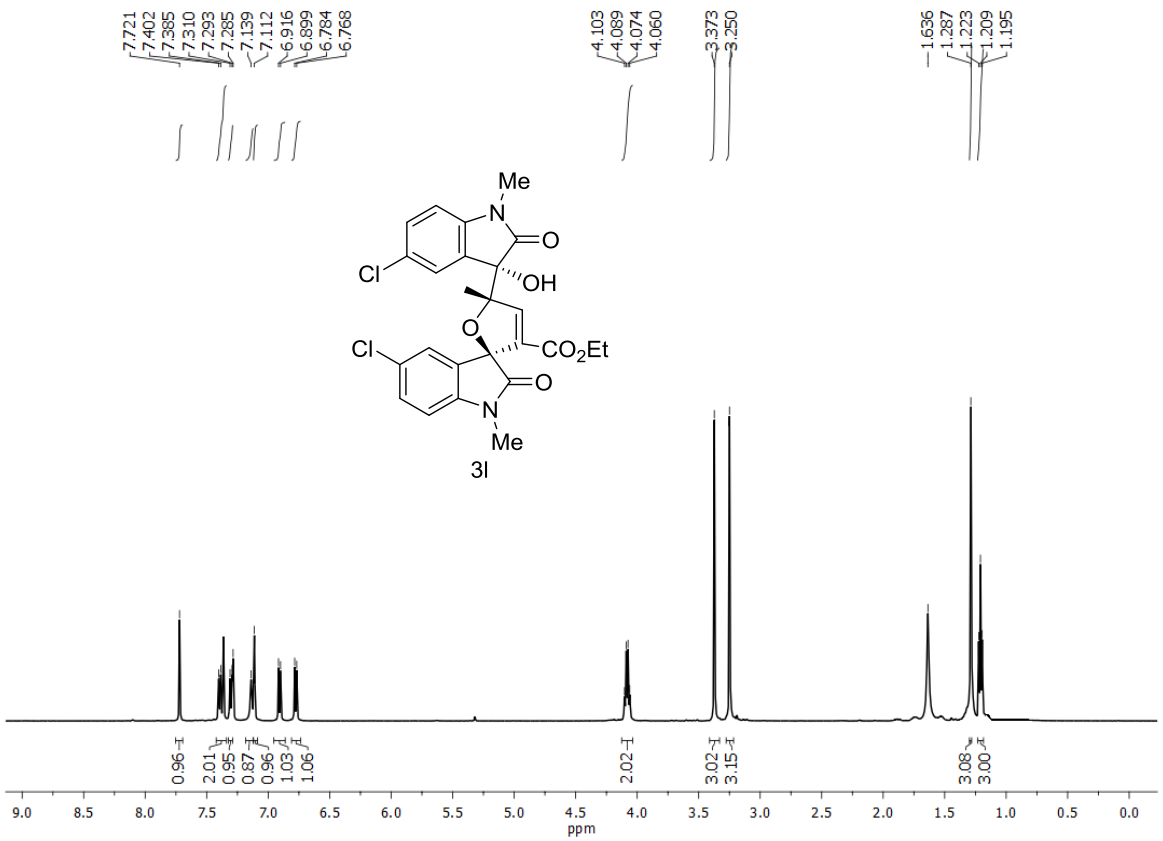


Fig S23. ^{1}H NMR of 3l

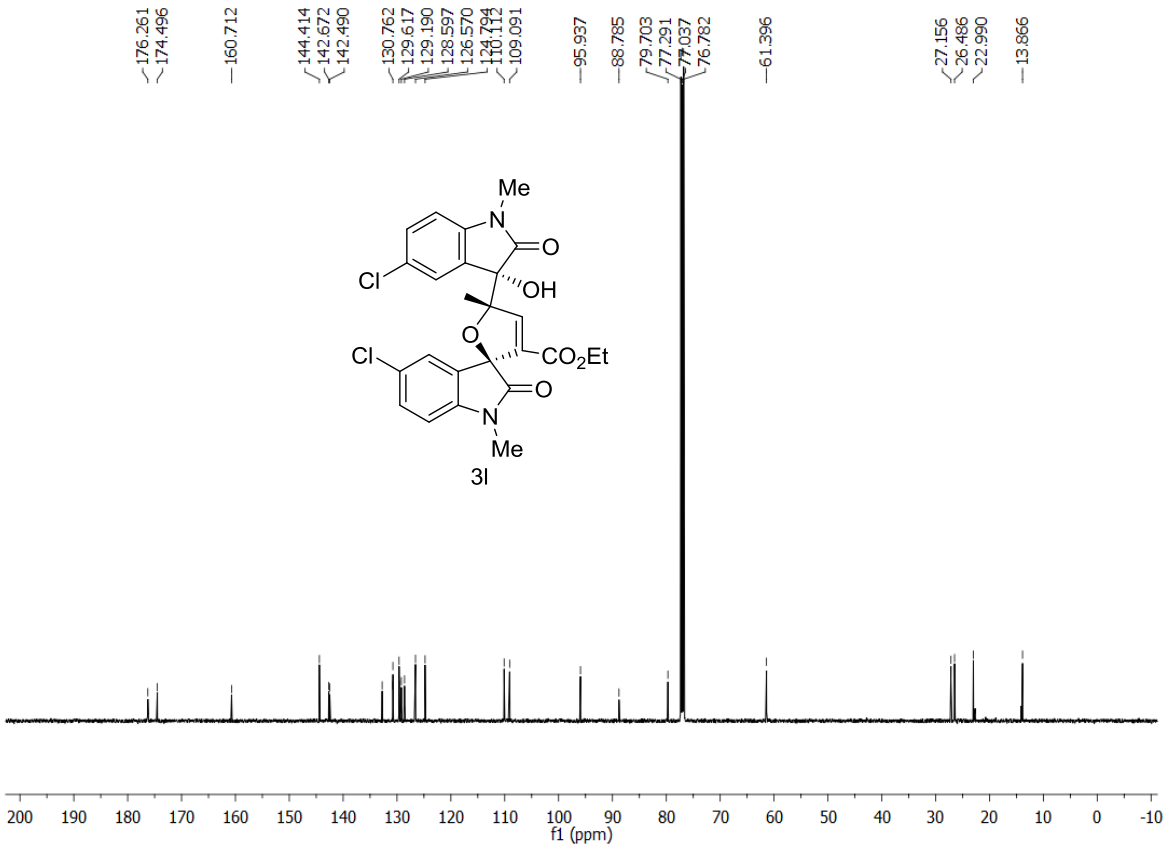


Fig S24. ^{13}C NMR of 3l

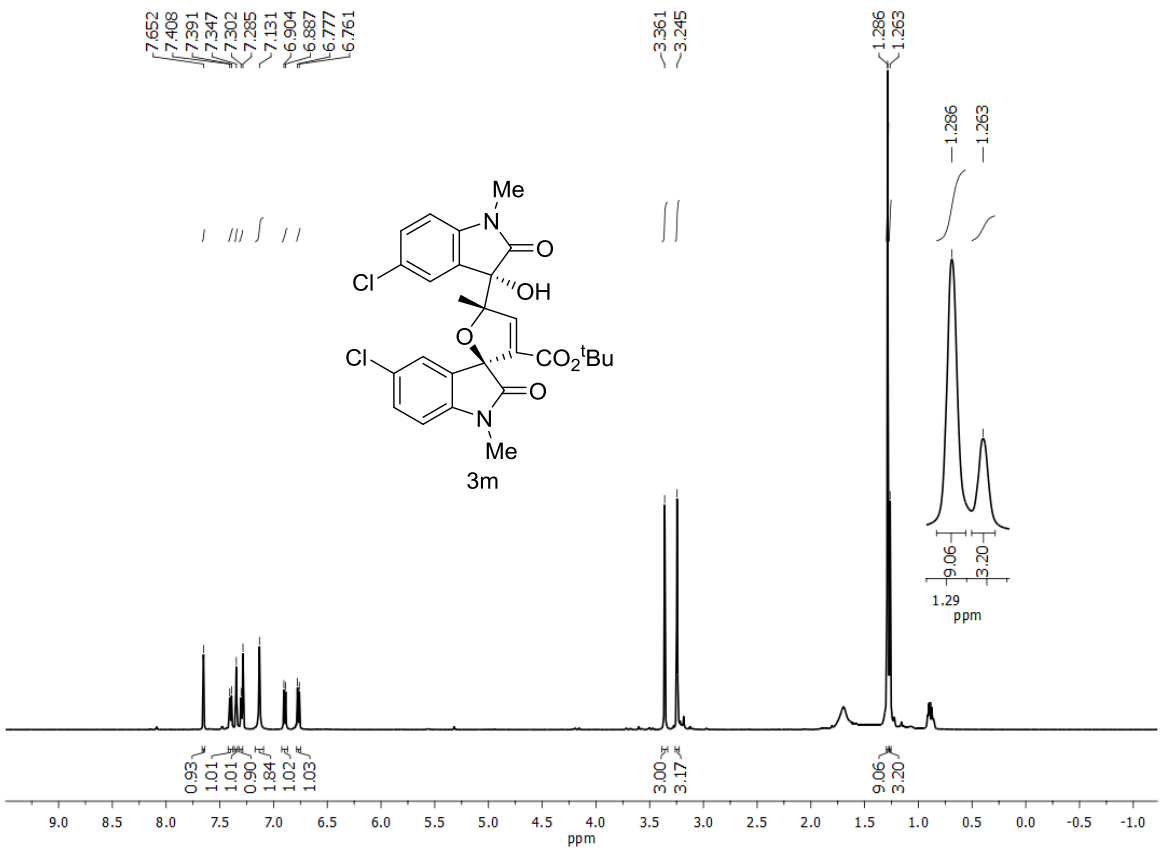


Fig S25. ^{1}H NMR of 3m

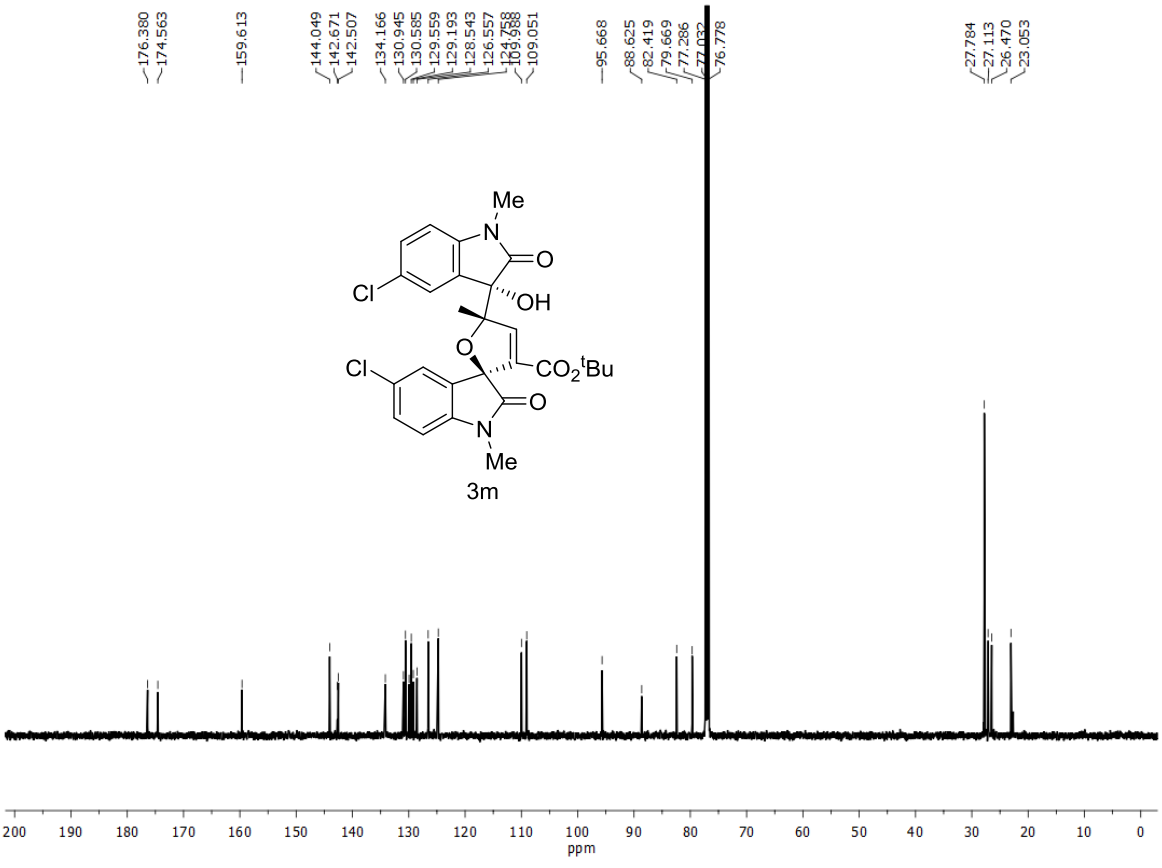


Fig S26. ^{13}C NMR of 3m

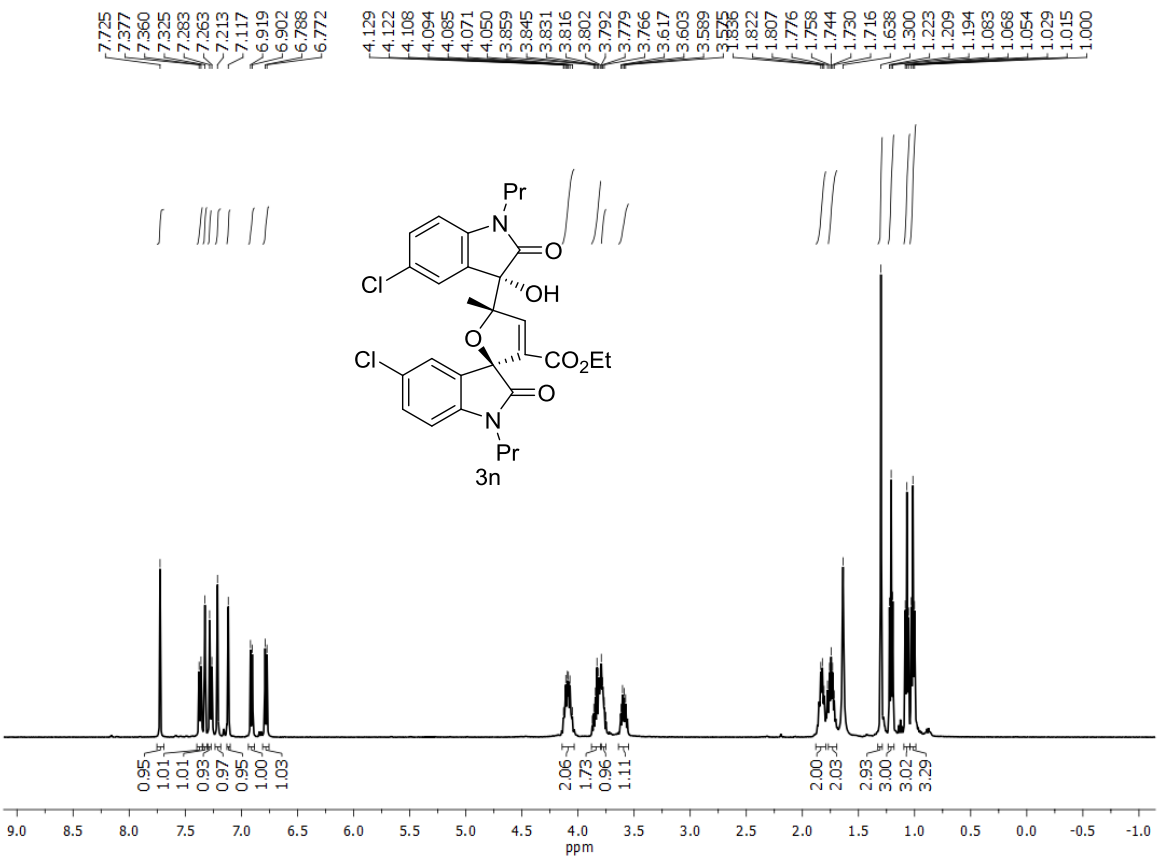


Fig S27. ^{1}H NMR of 3n

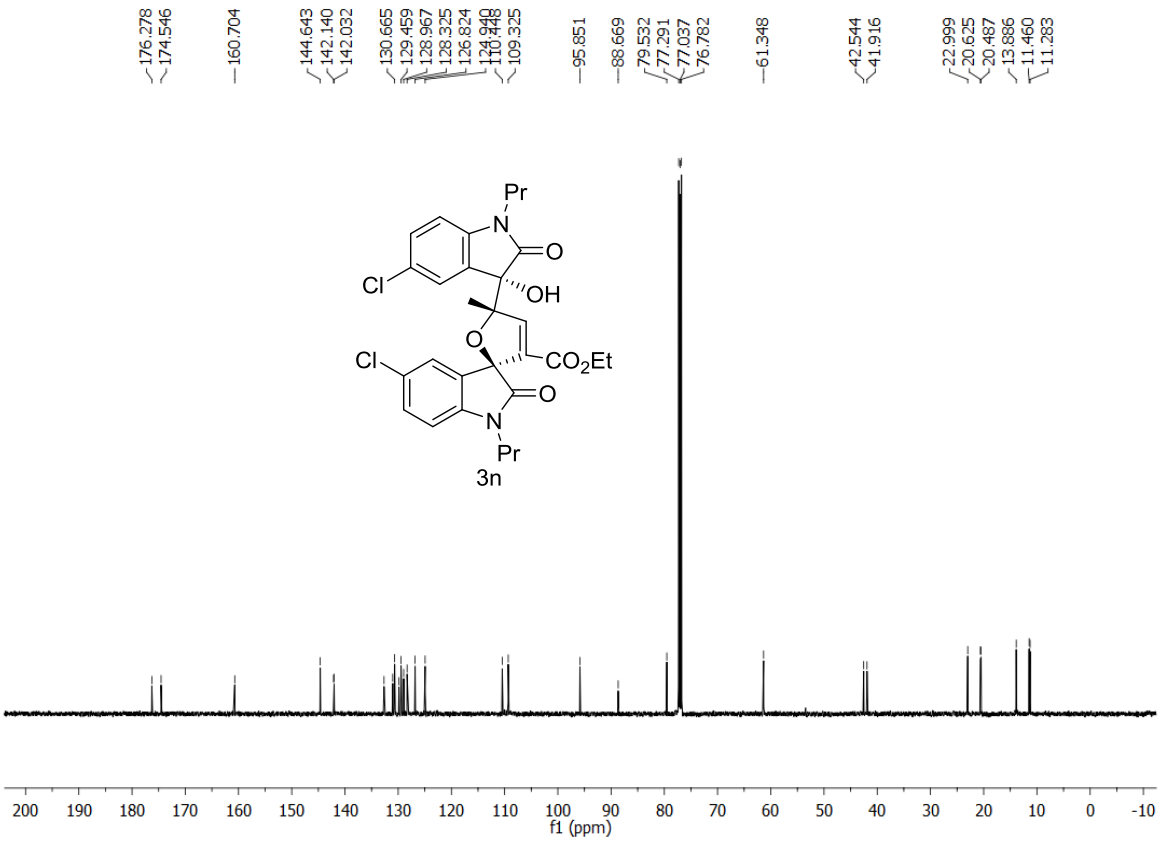


Fig S28. ^{13}C NMR of 3n

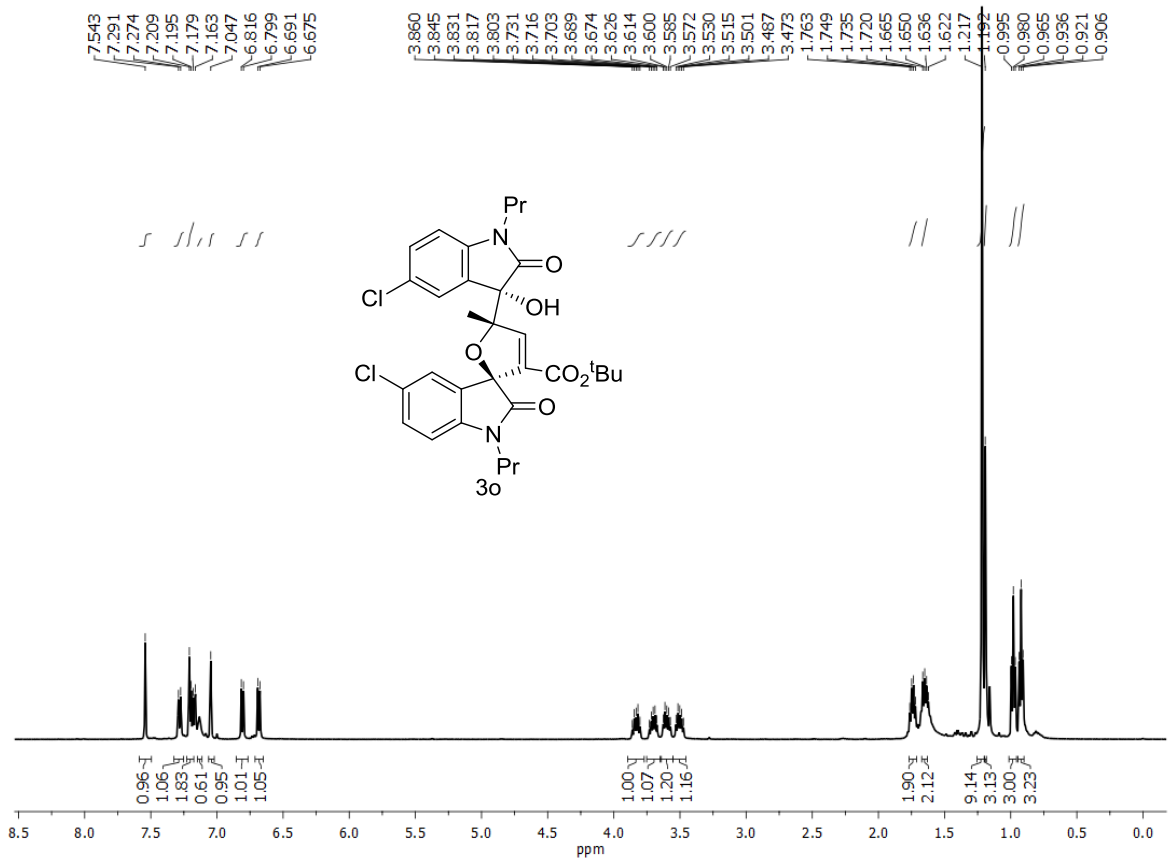


Fig S29. ^{1}H NMR of 3o

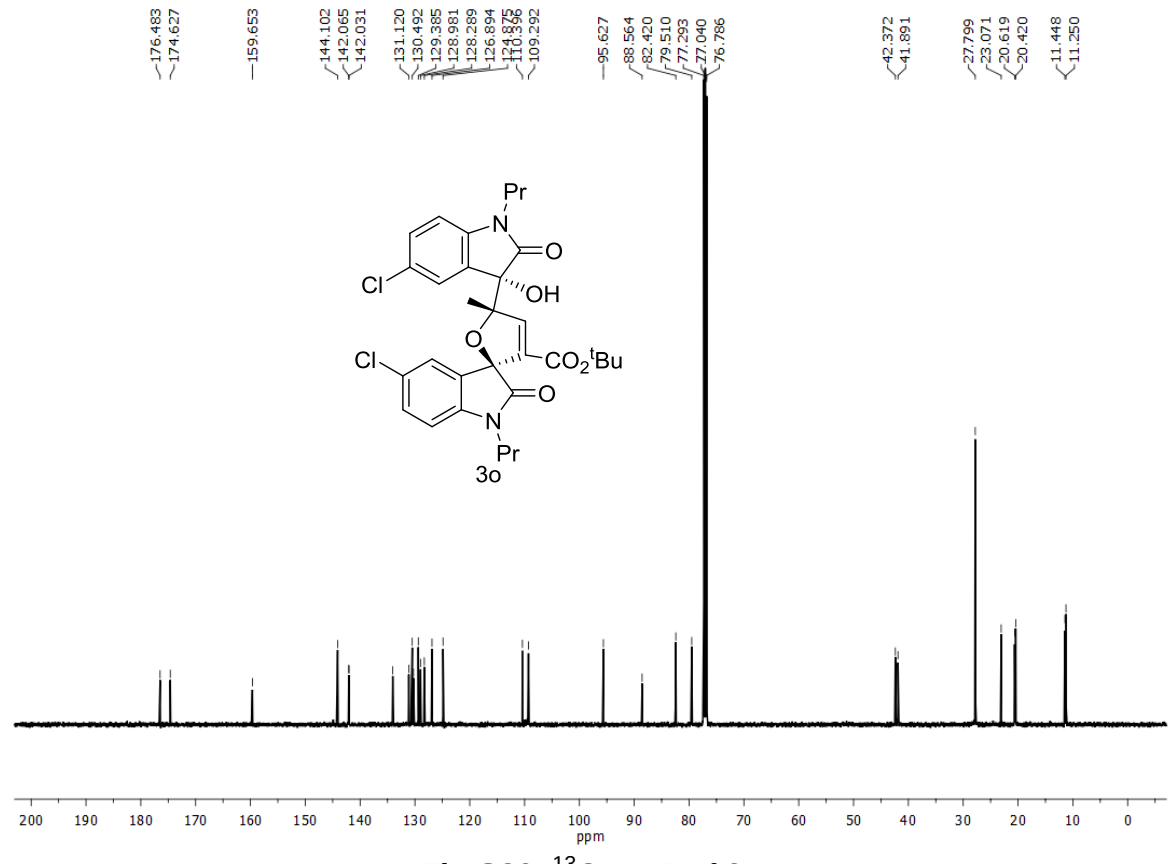


Fig S30. ^{13}C NMR of 3o

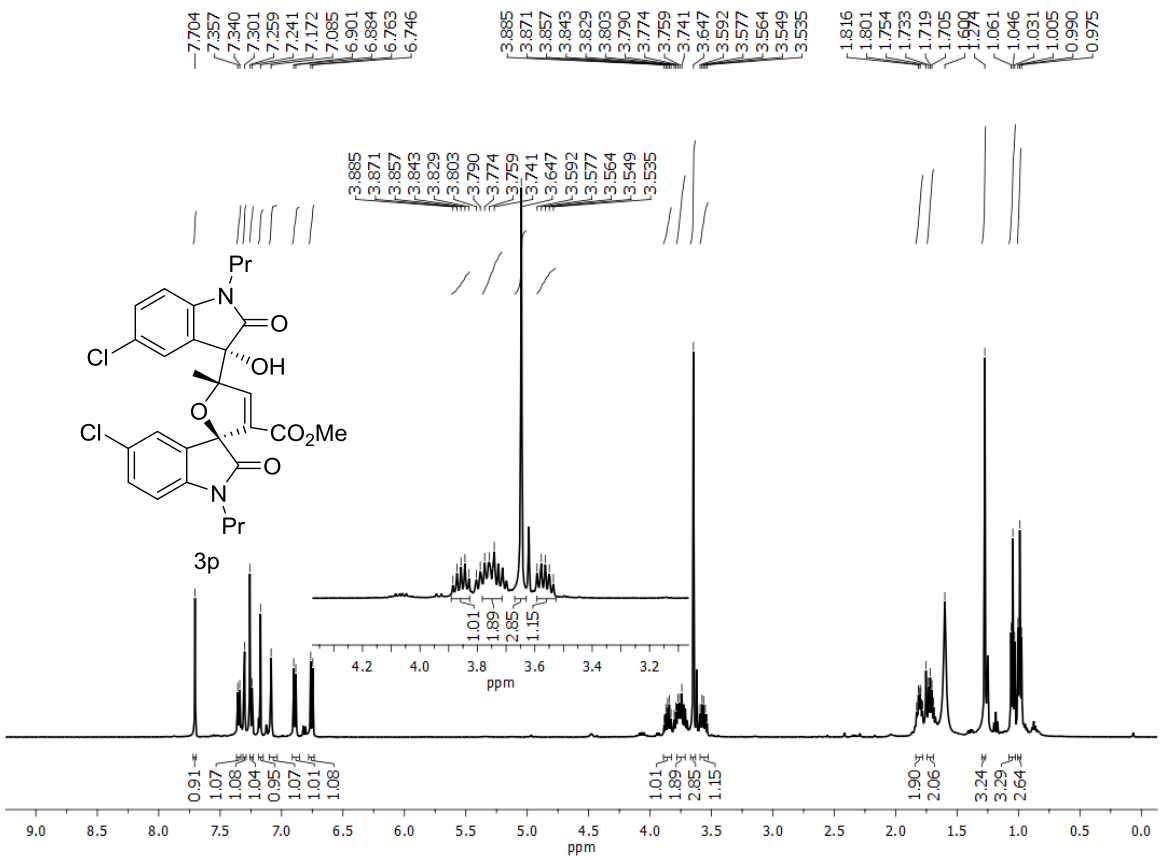


Fig S31. ^{1}H NMR of 3p

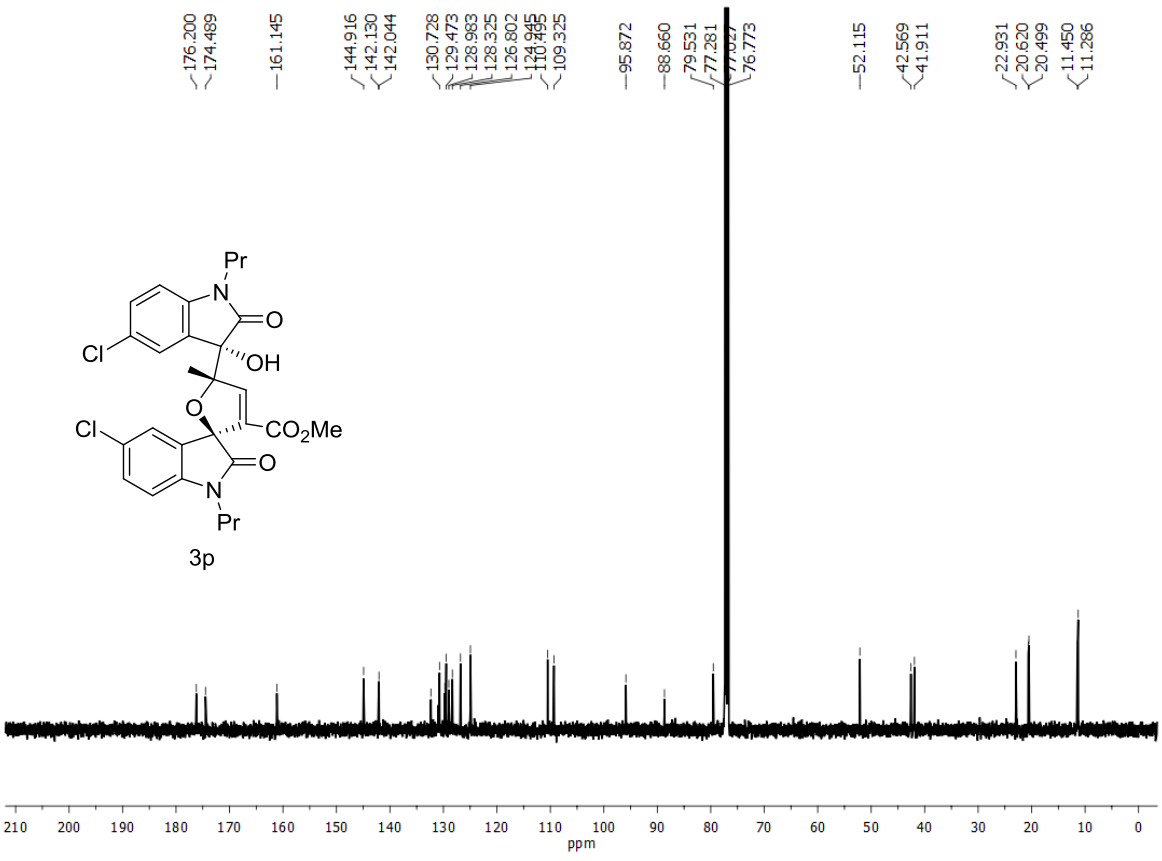


Fig S32. ^{13}C NMR of 3p

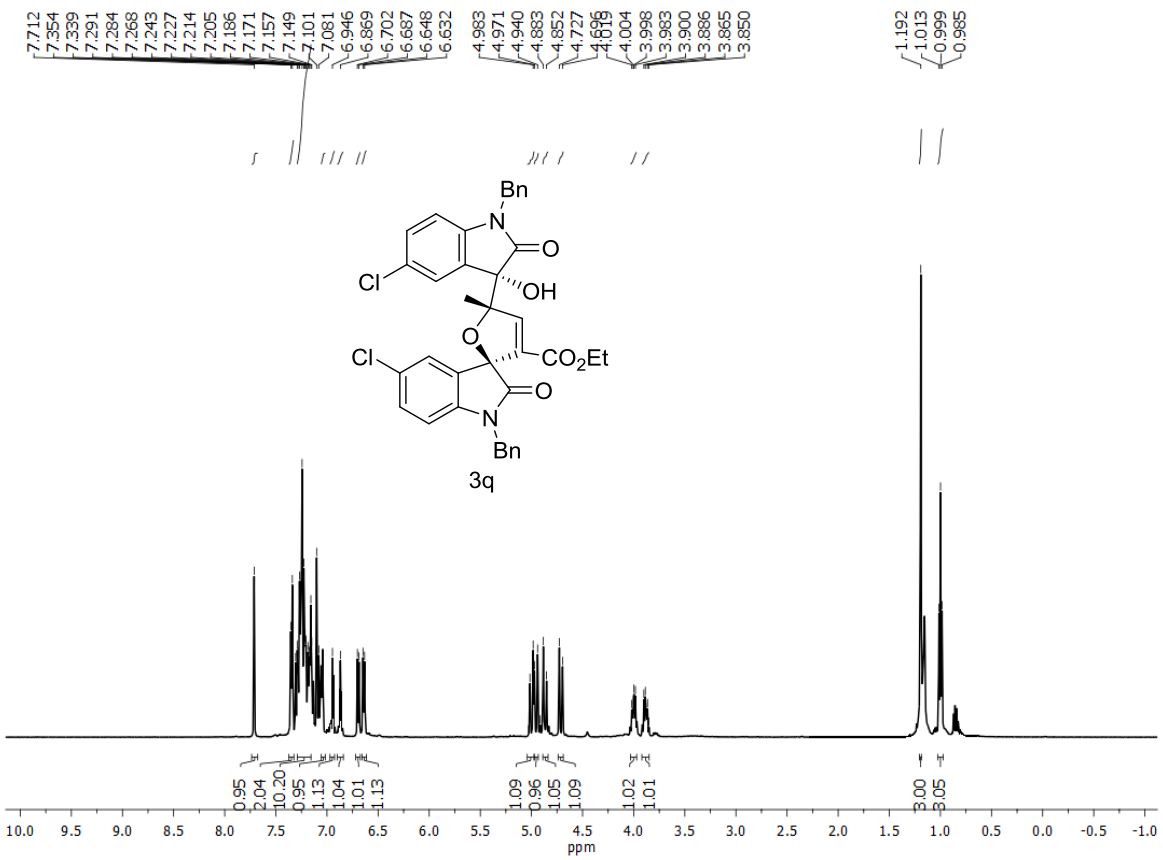


Fig S33. ^{1}H NMR of 3q

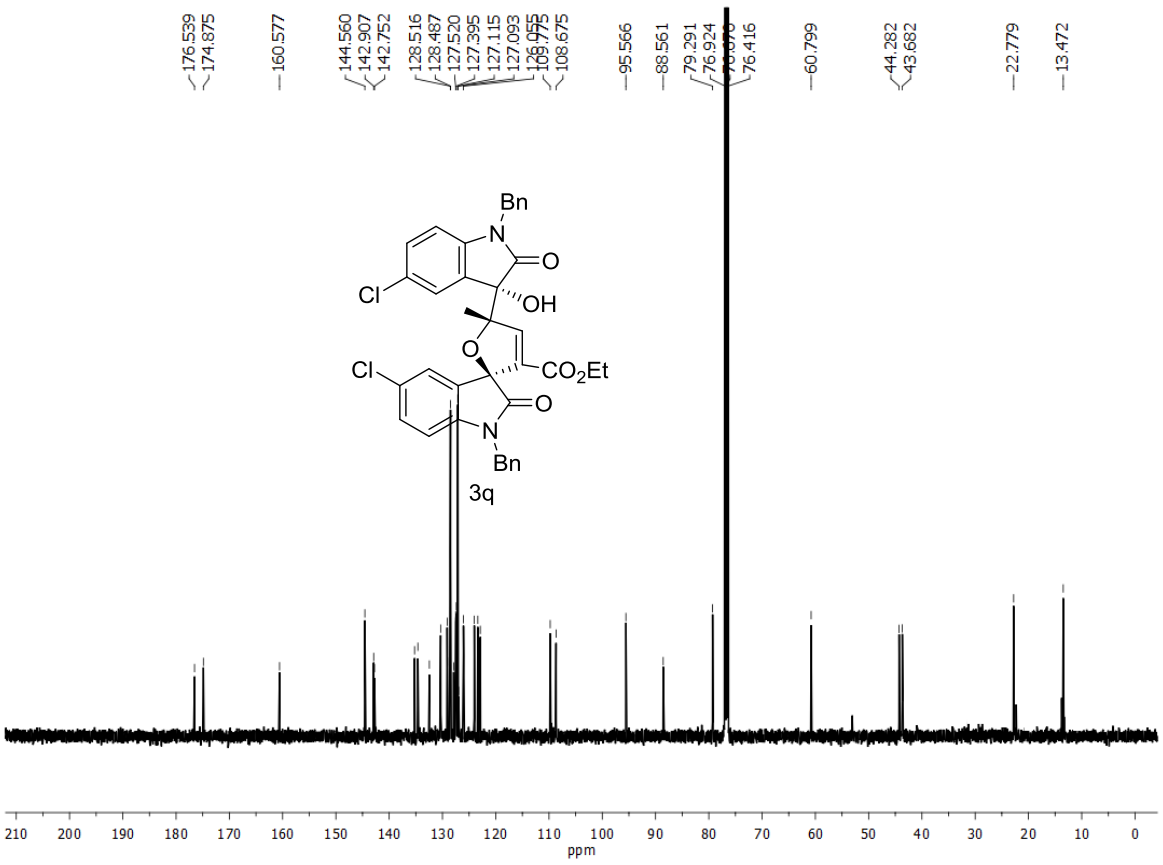


Fig S34. ^{13}C NMR of 3q

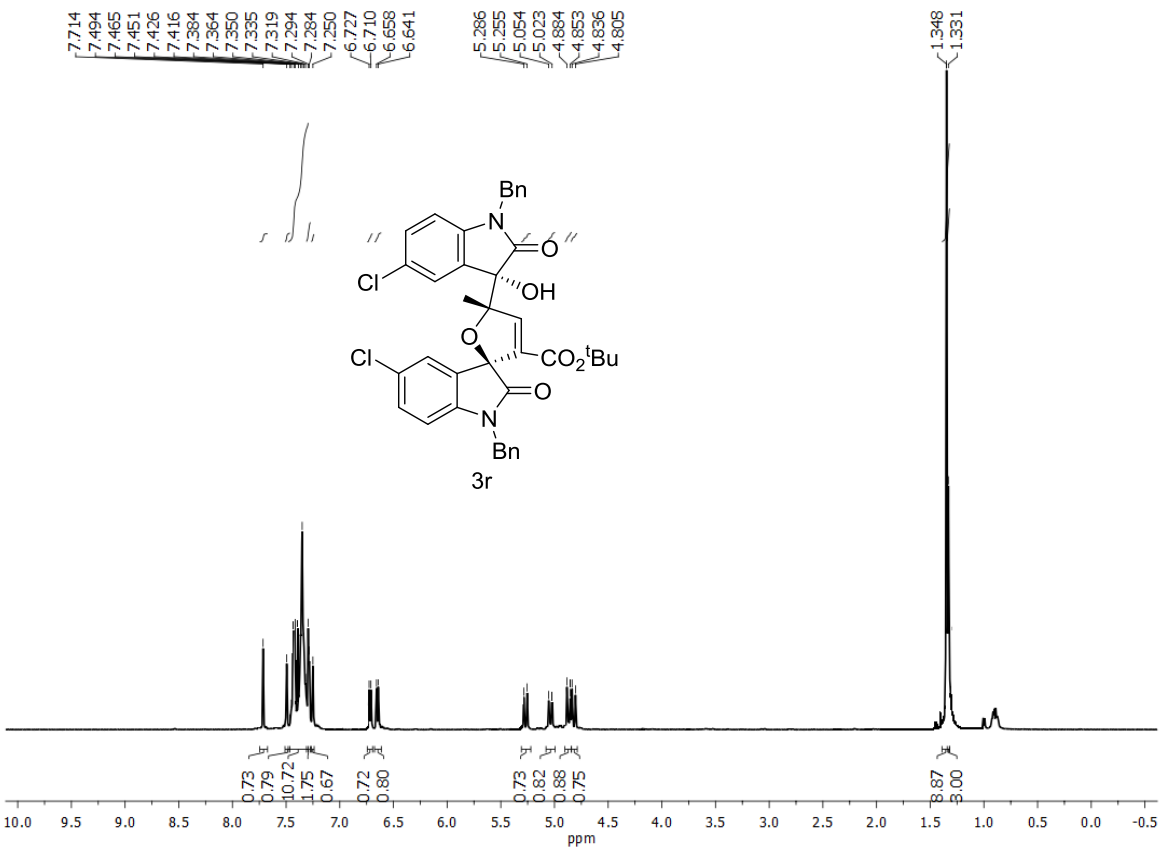


Fig S35. ^{1}H NMR of 3r

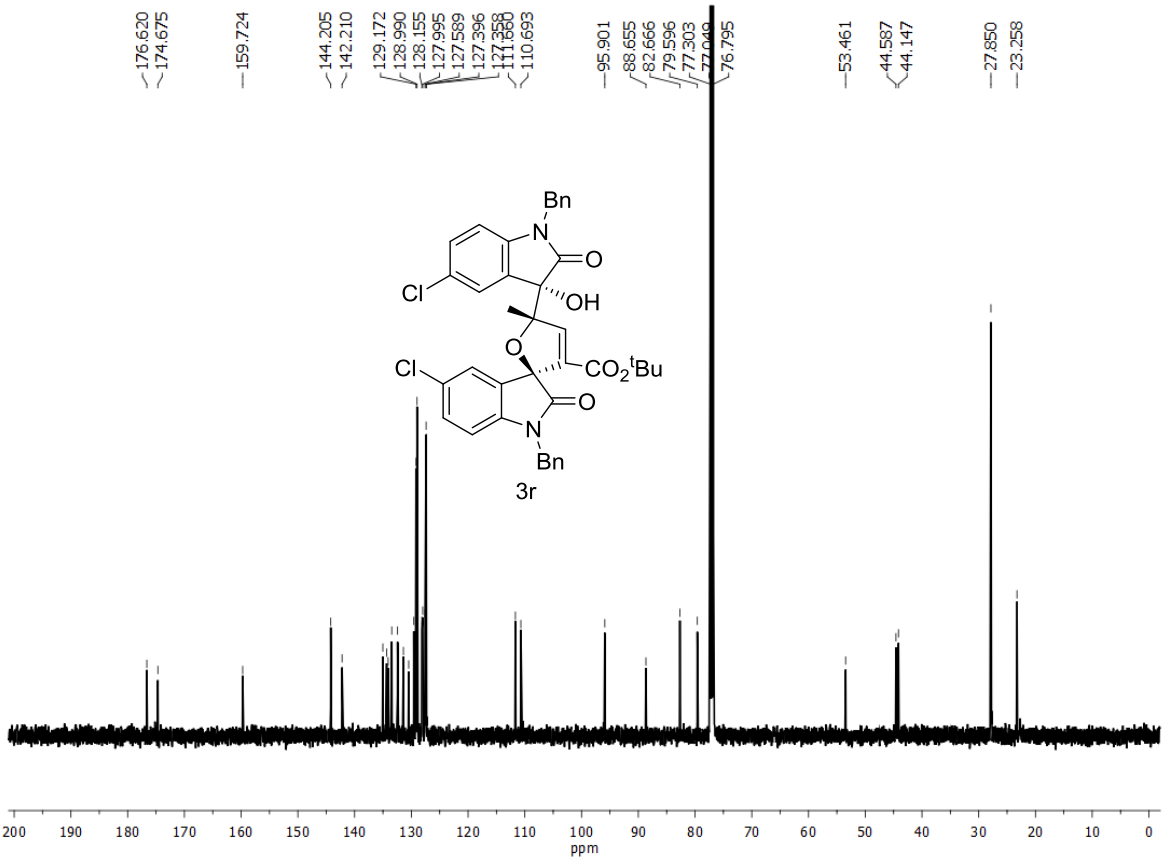


Fig S36. ^{13}C NMR of 3r

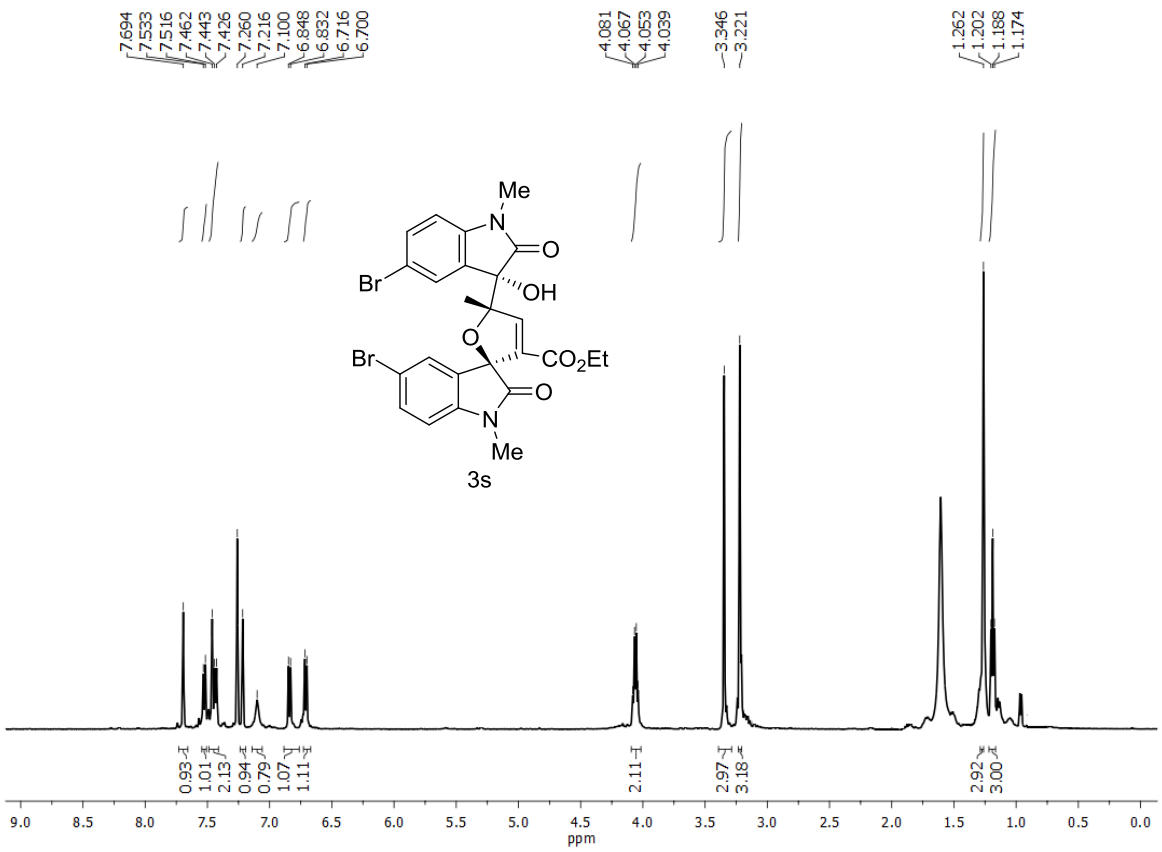


Fig S37. ^{1}H NMR of 3s

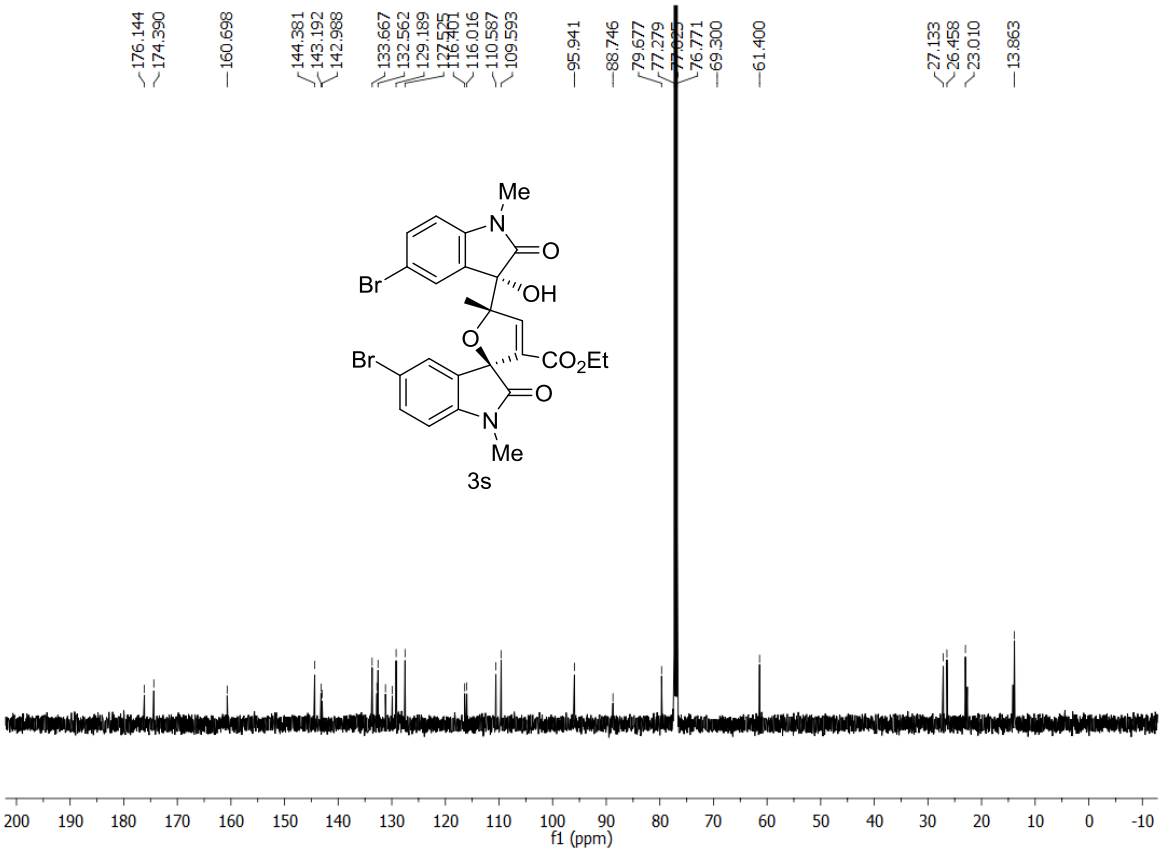


Fig S38. ^{13}C NMR of 3s

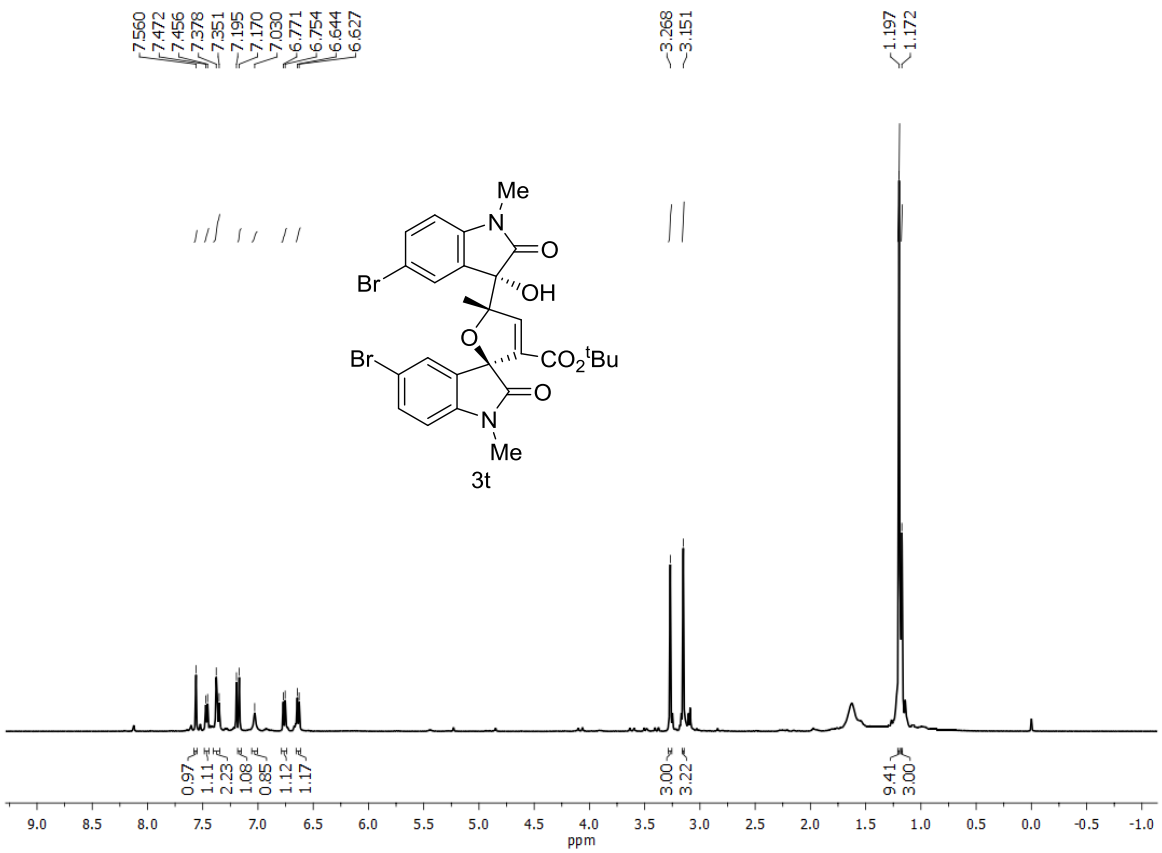


Fig S39. ^{1}H NMR of 3t

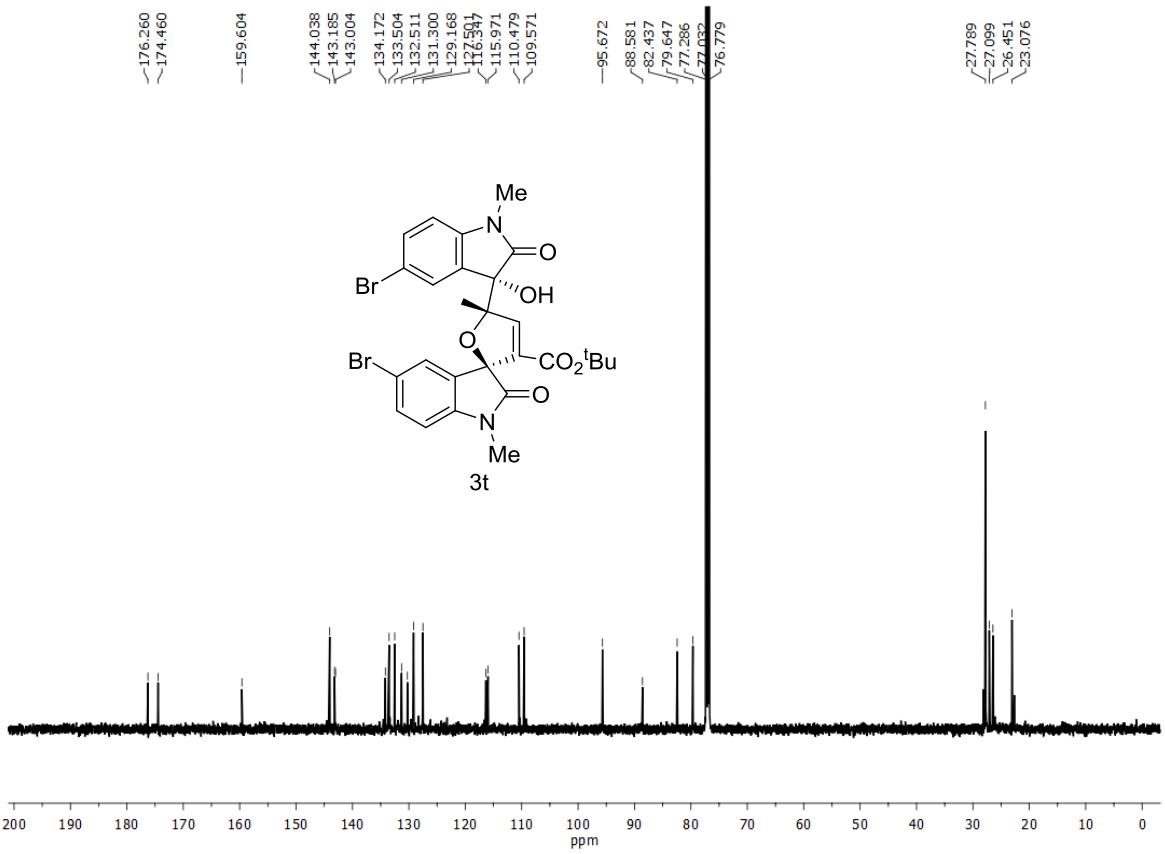


Fig S40. ^{13}C NMR of 3t

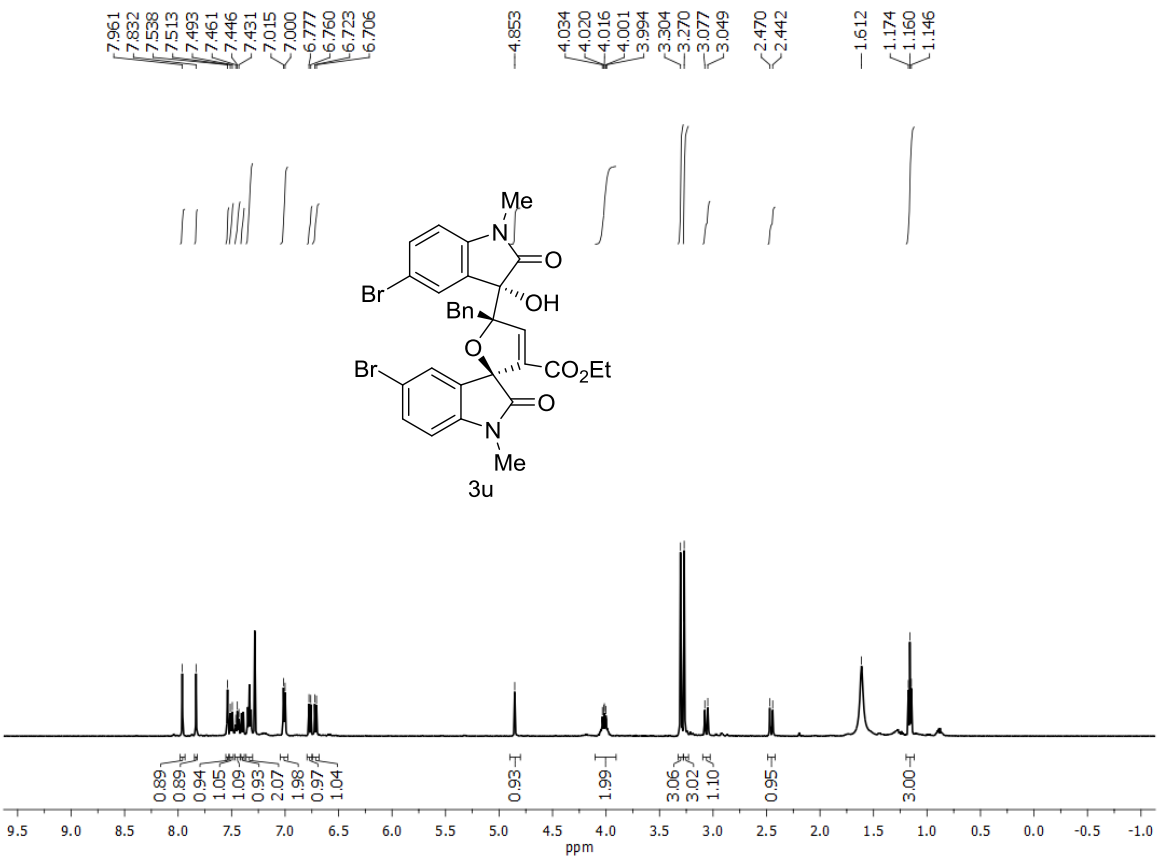


Fig S41. ^{1}H NMR of 3u

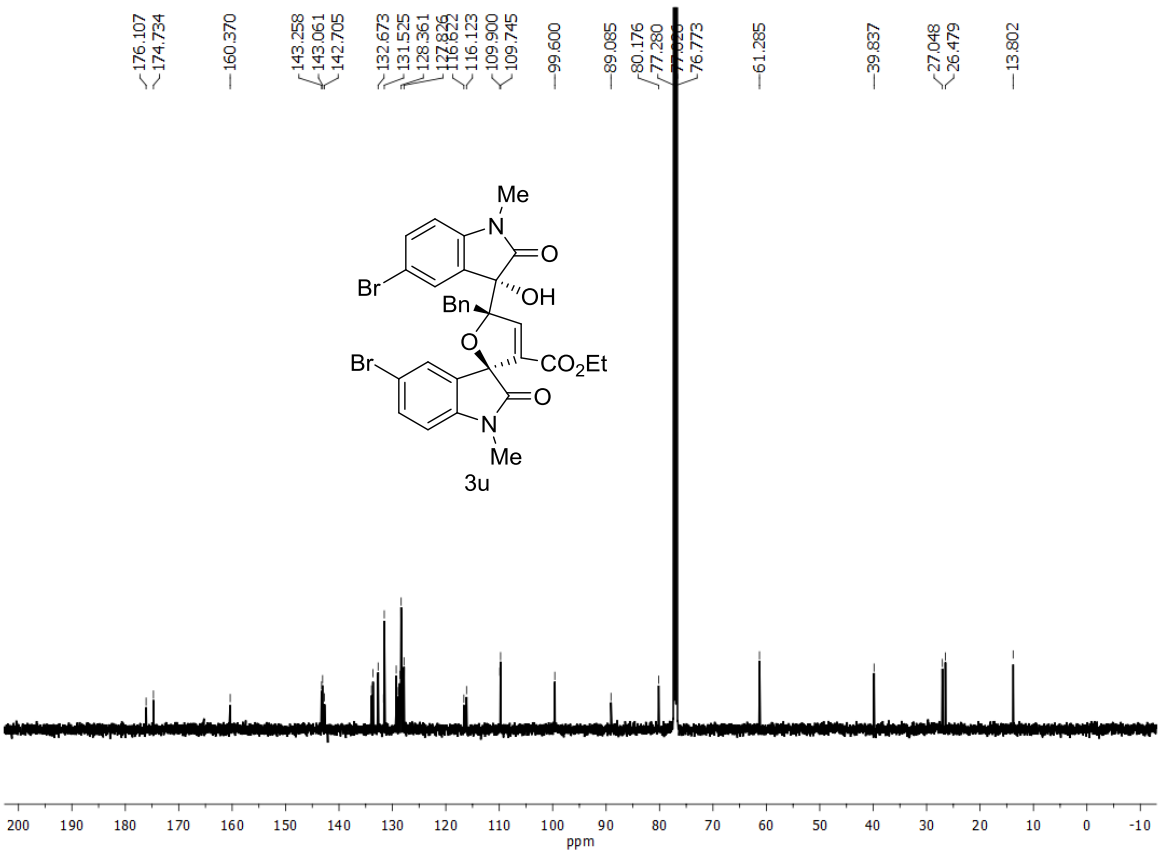


Fig S42. ^{13}C NMR of 3u

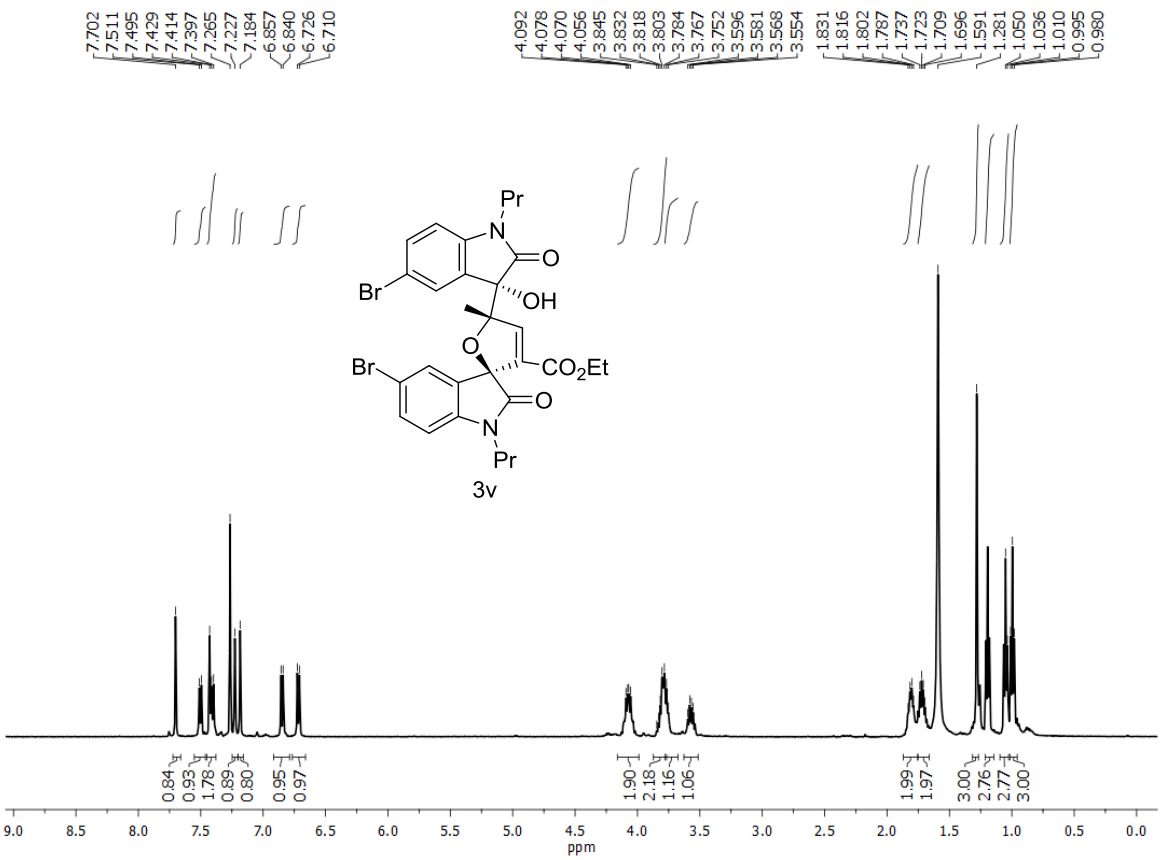


Fig S43. ^{1}H NMR of 3v

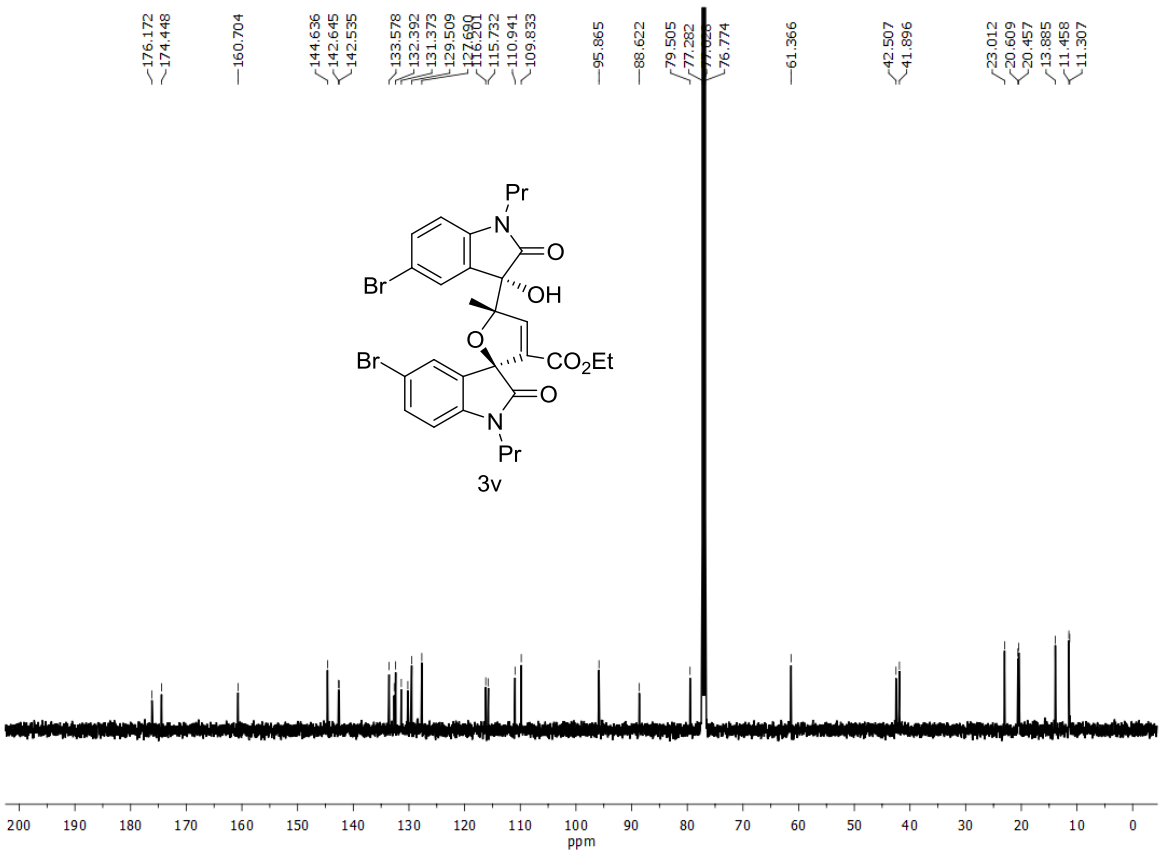


Fig S44. ^{13}C NMR of 3v

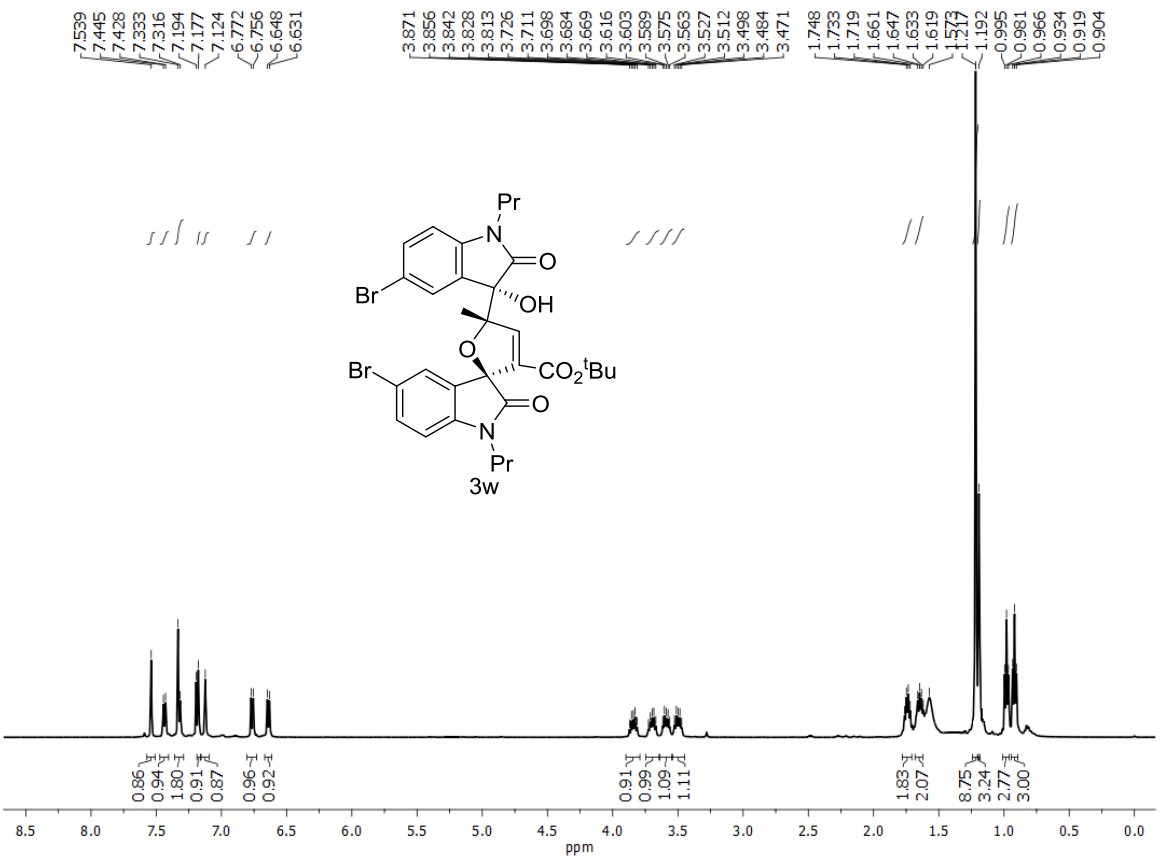


Fig S45. ^{1}H NMR of 3w

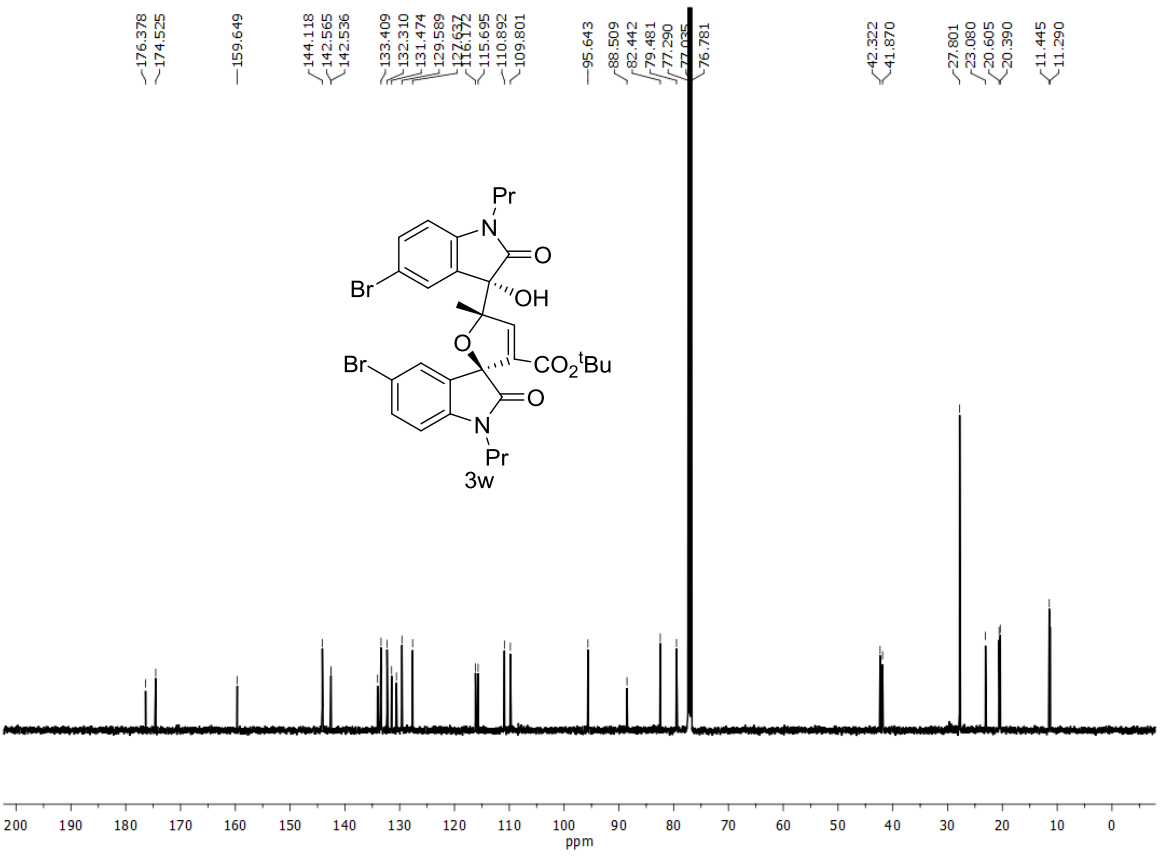


Fig S46. ^{13}C NMR of 3w

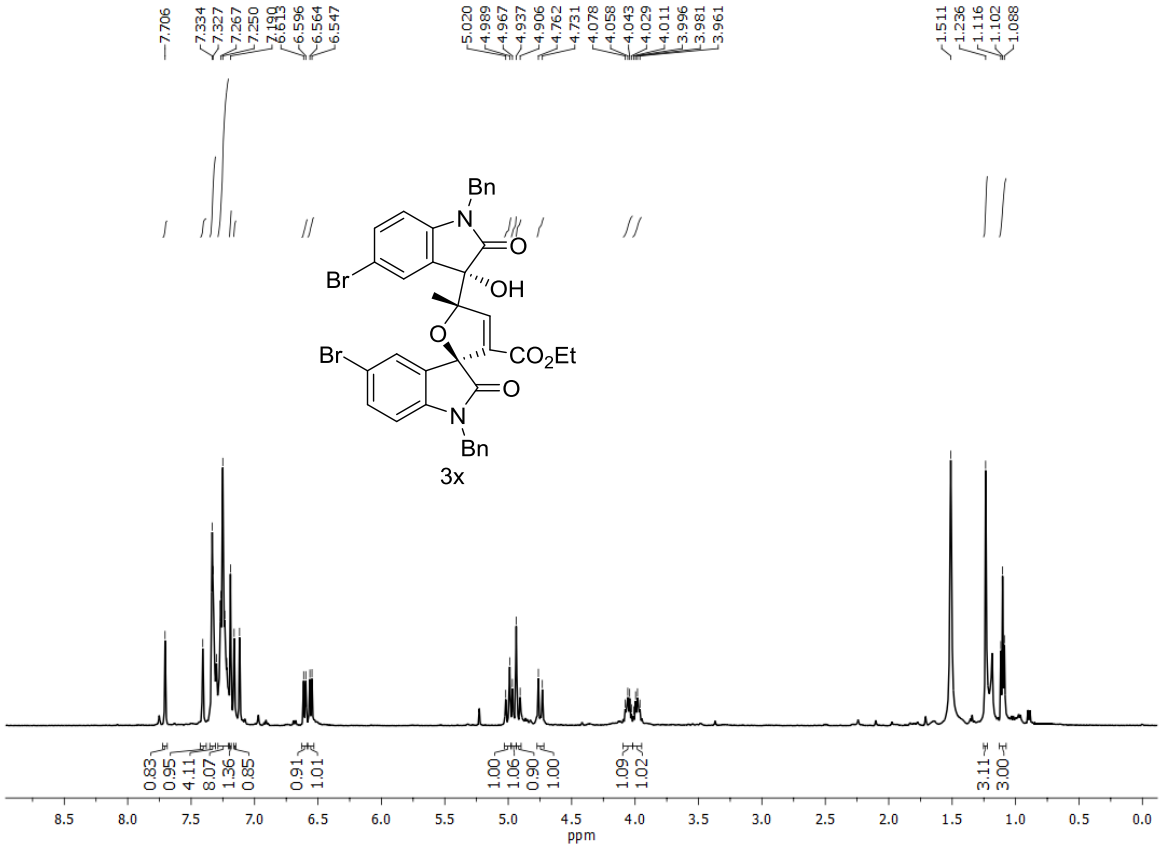


Fig S47. ^{1}H NMR of 3x

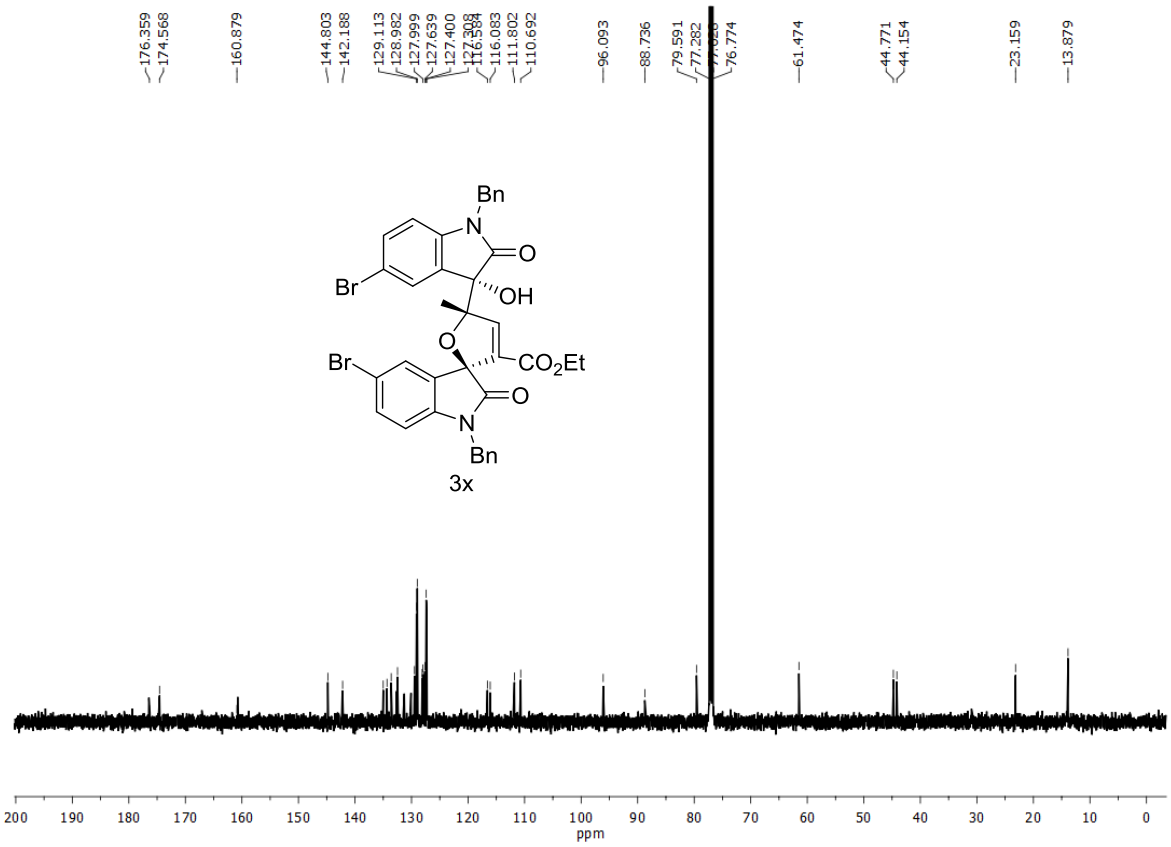


Fig S48. ^{13}C NMR of 3x

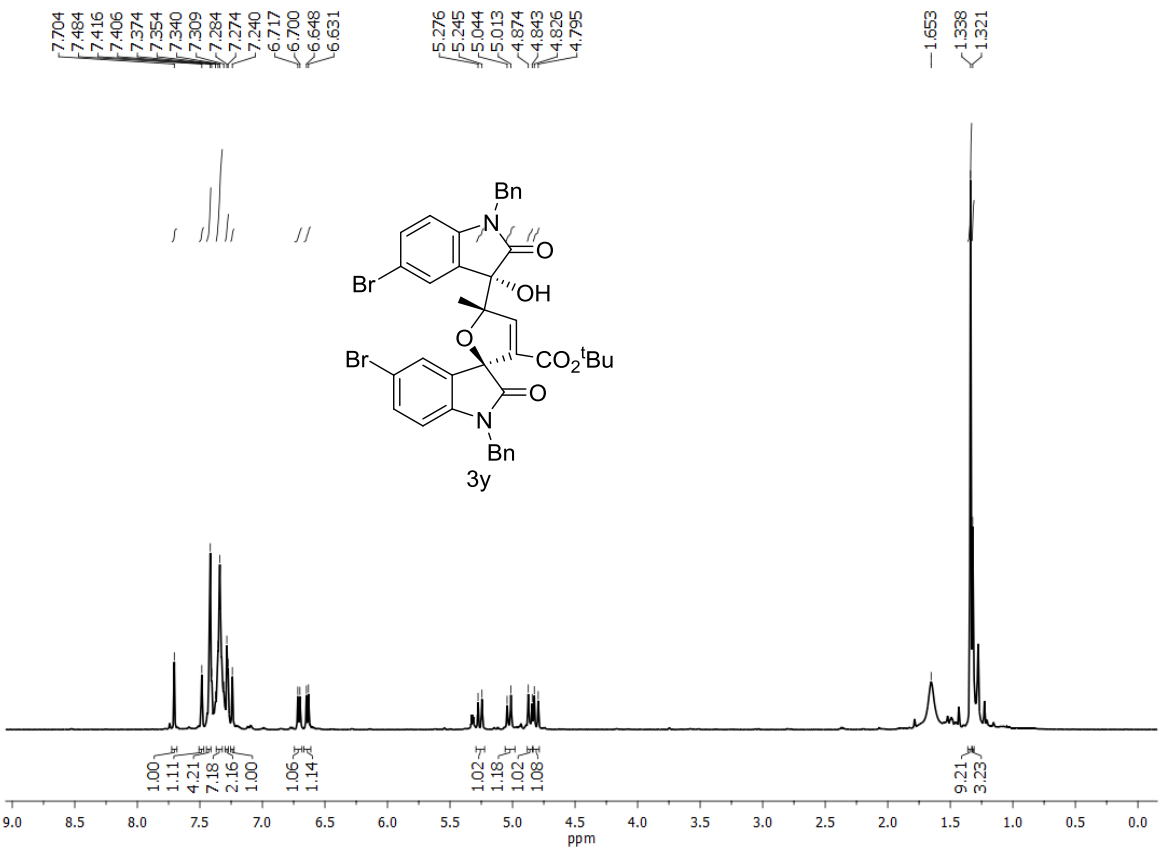


Fig S49. ^{1}H NMR of 3y

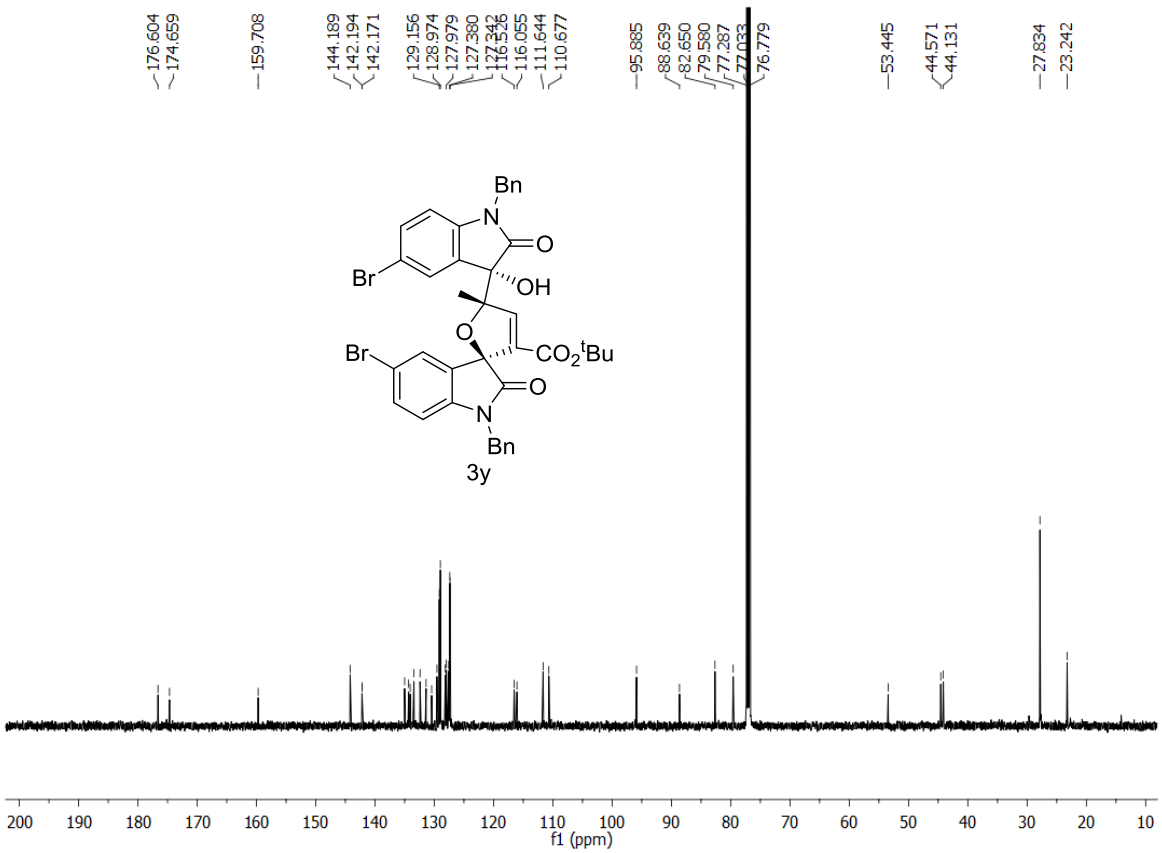


Fig 50. ^{13}C NMR of 3y

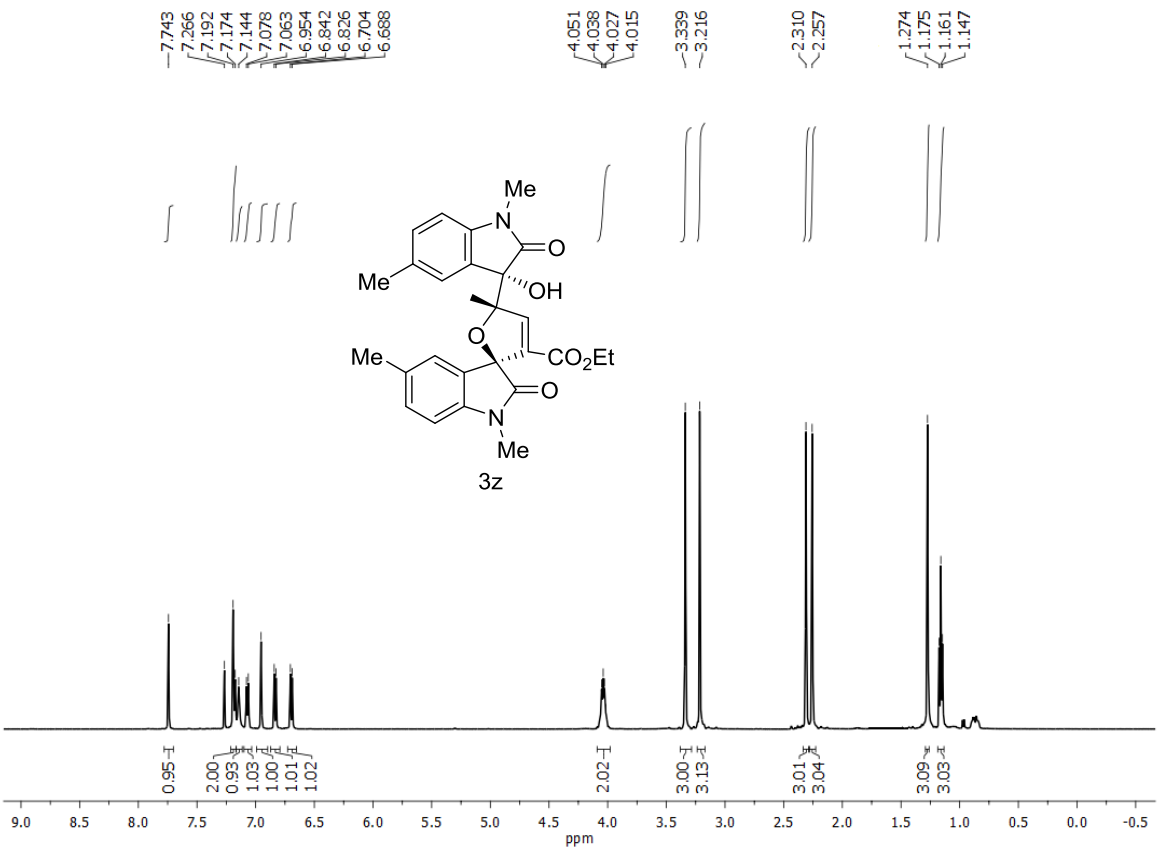


Fig S51. ^{1}H NMR of 3z

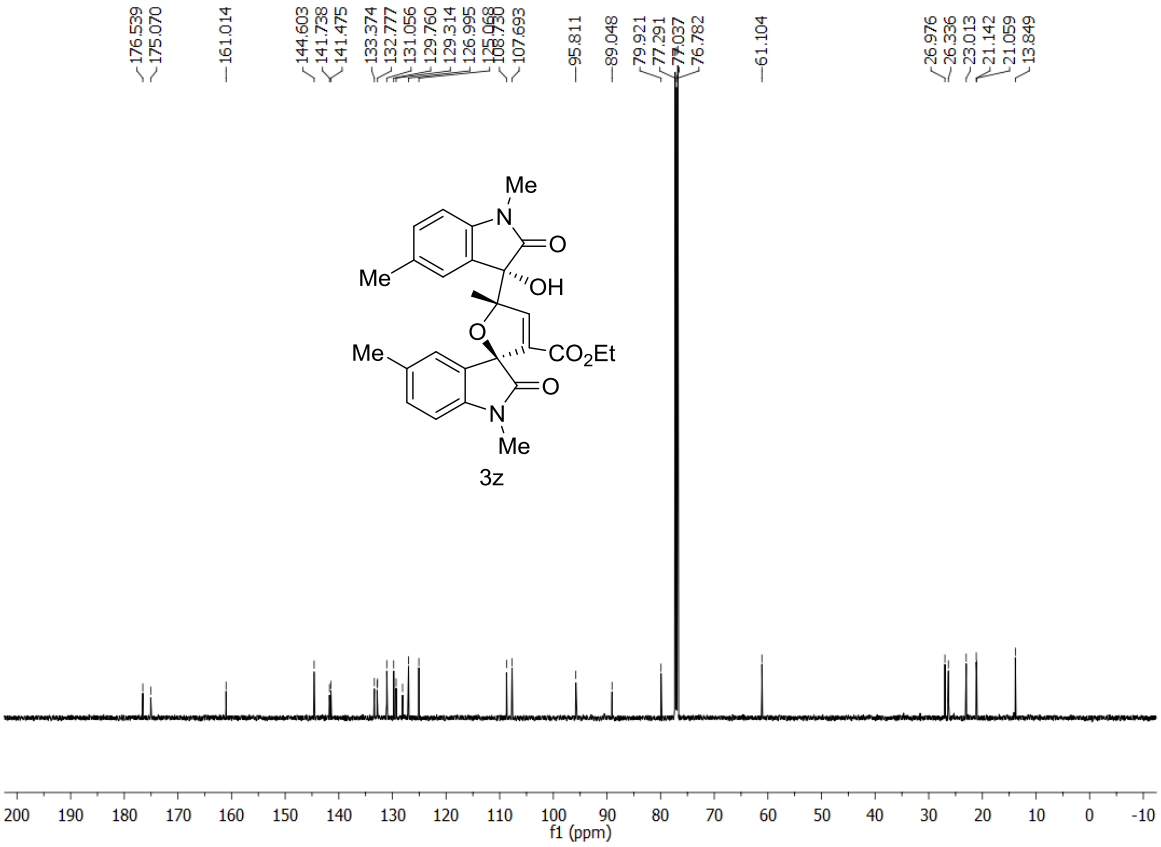


Fig S52. ^{13}C NMR of 3z

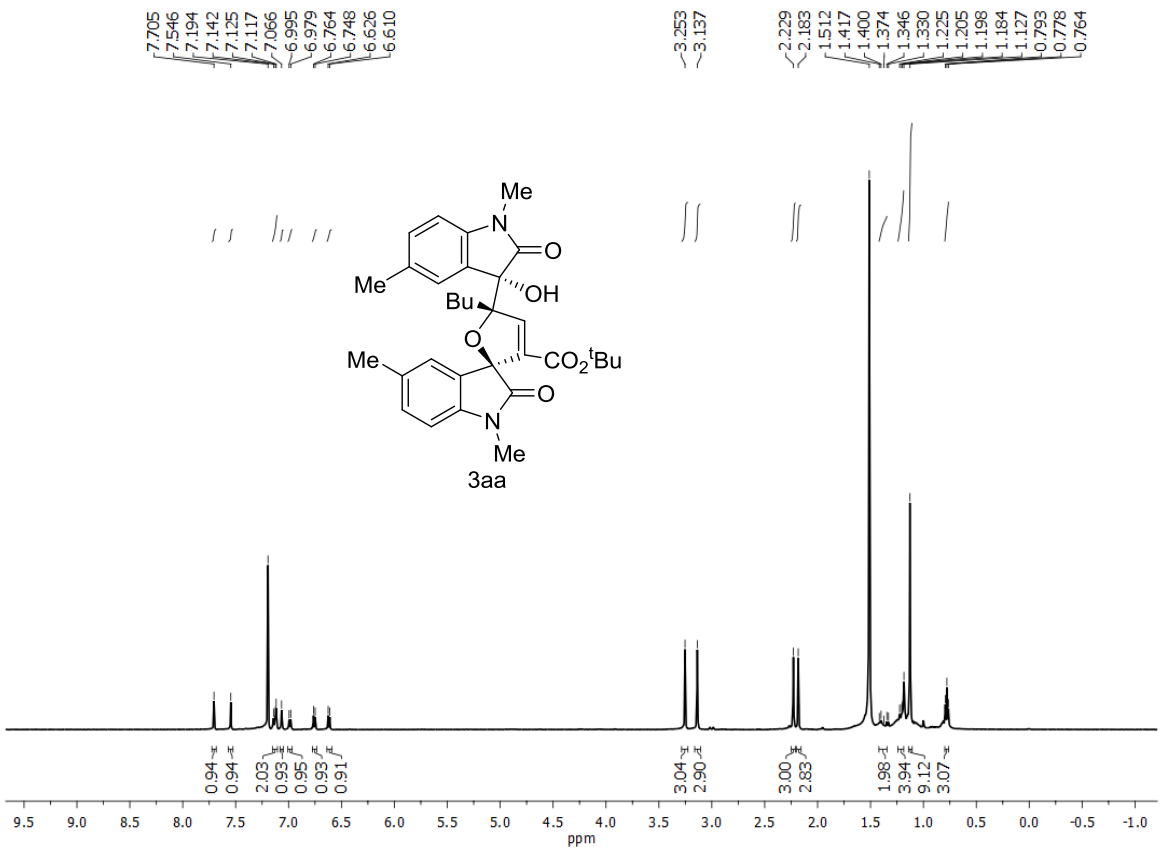


Fig S53. ^{1}H NMR of 3aa

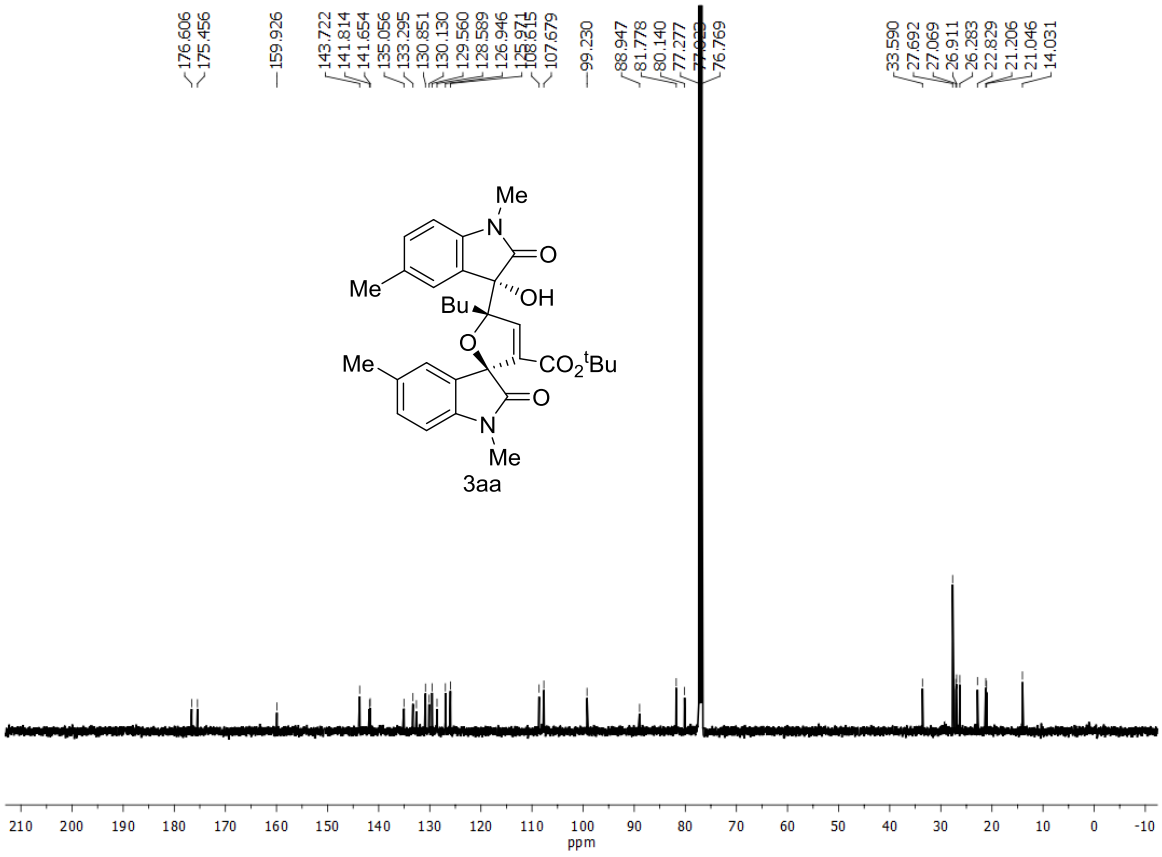


Fig S54. ^{13}C NMR of 3aa

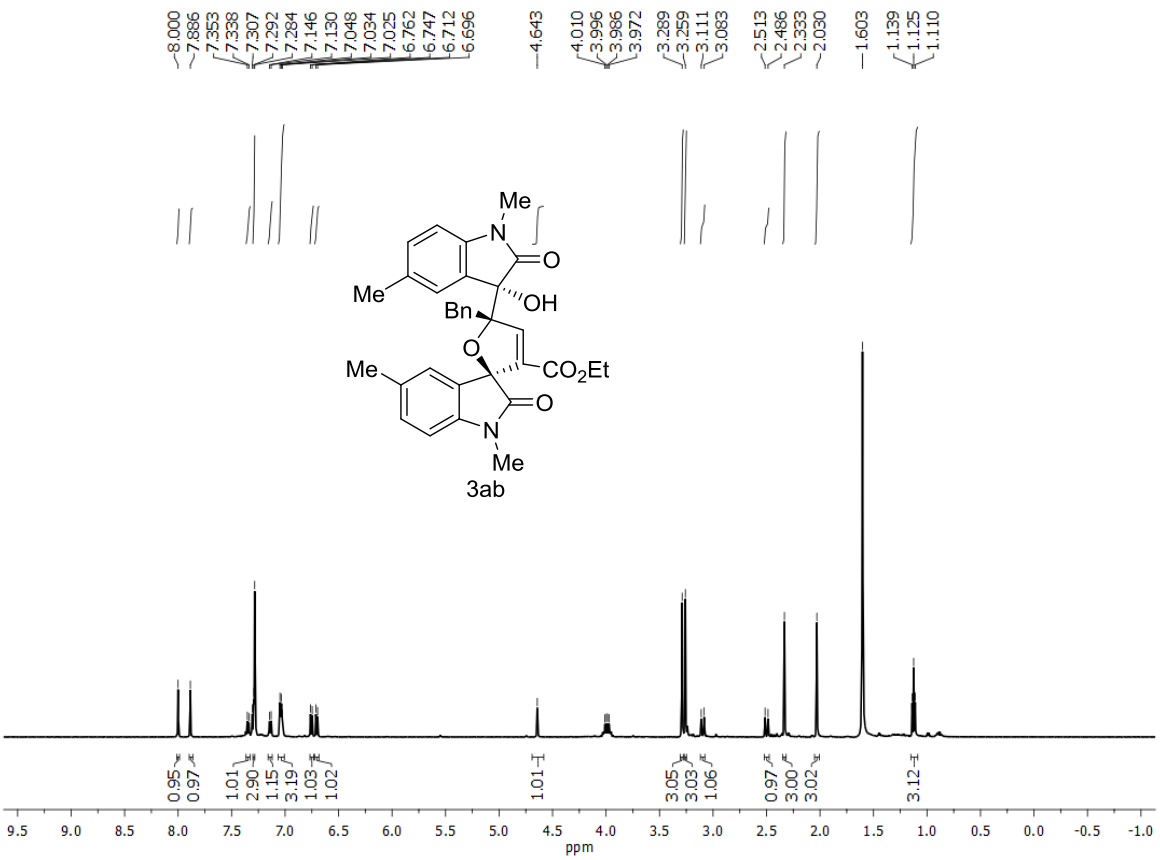


Fig S55. ^{1}H NMR of 3ab

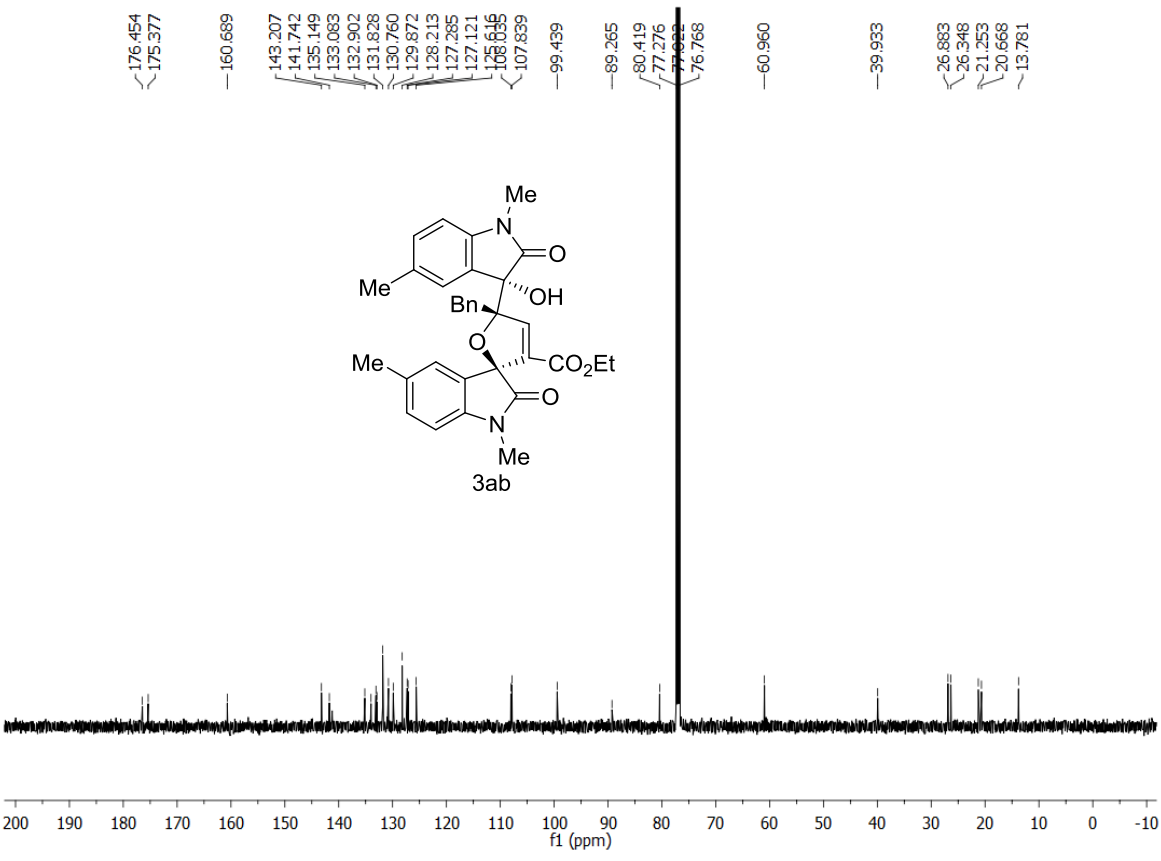


Fig S56. ^{13}C NMR of 3ab

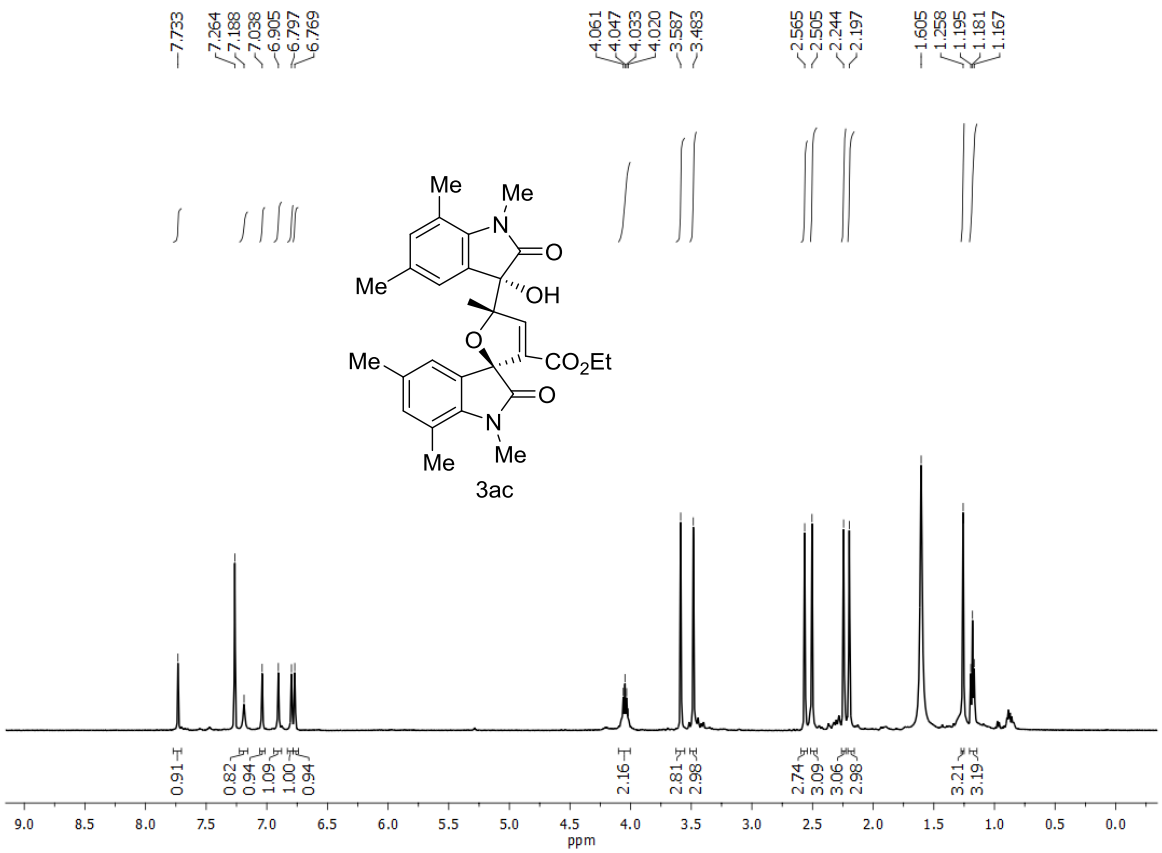


Fig S57. ^{1}H NMR of 3ac

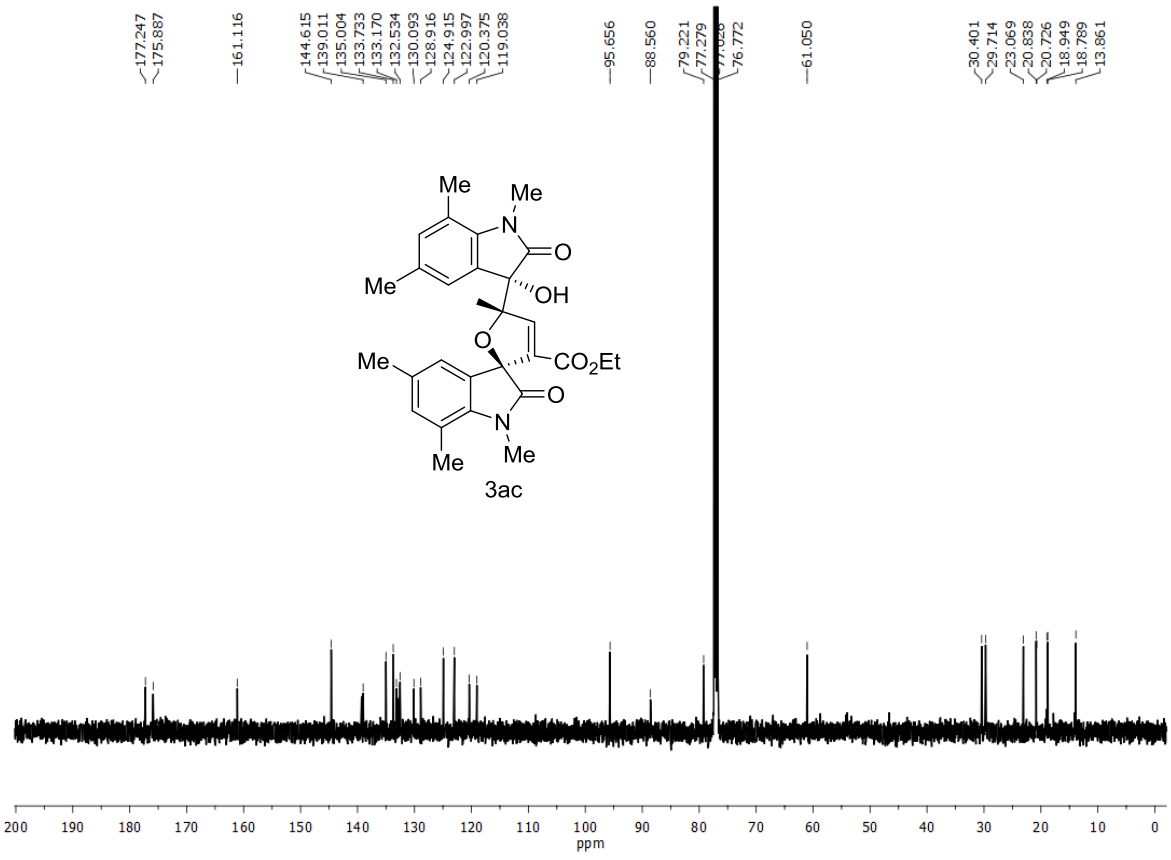


Fig S58. ^{1}C NMR of 3ac

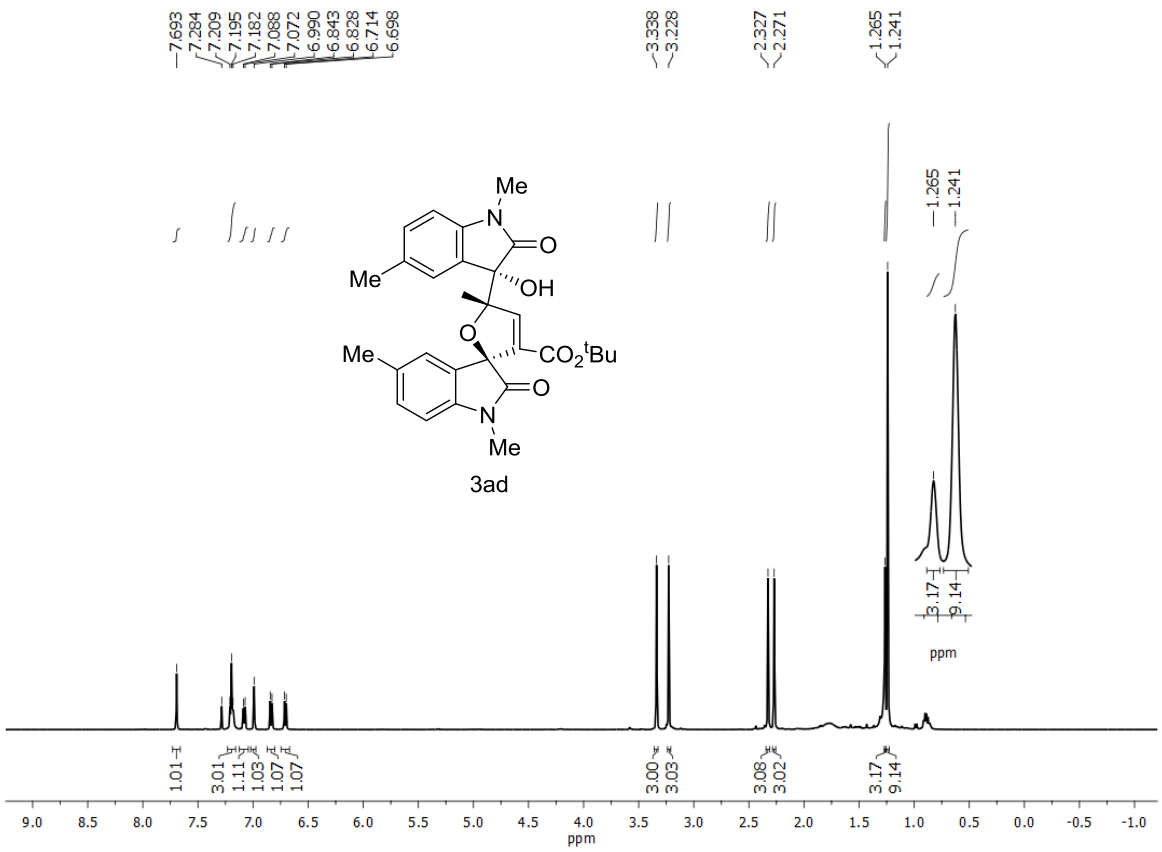


Fig S59. ^{1}H NMR of 3ad

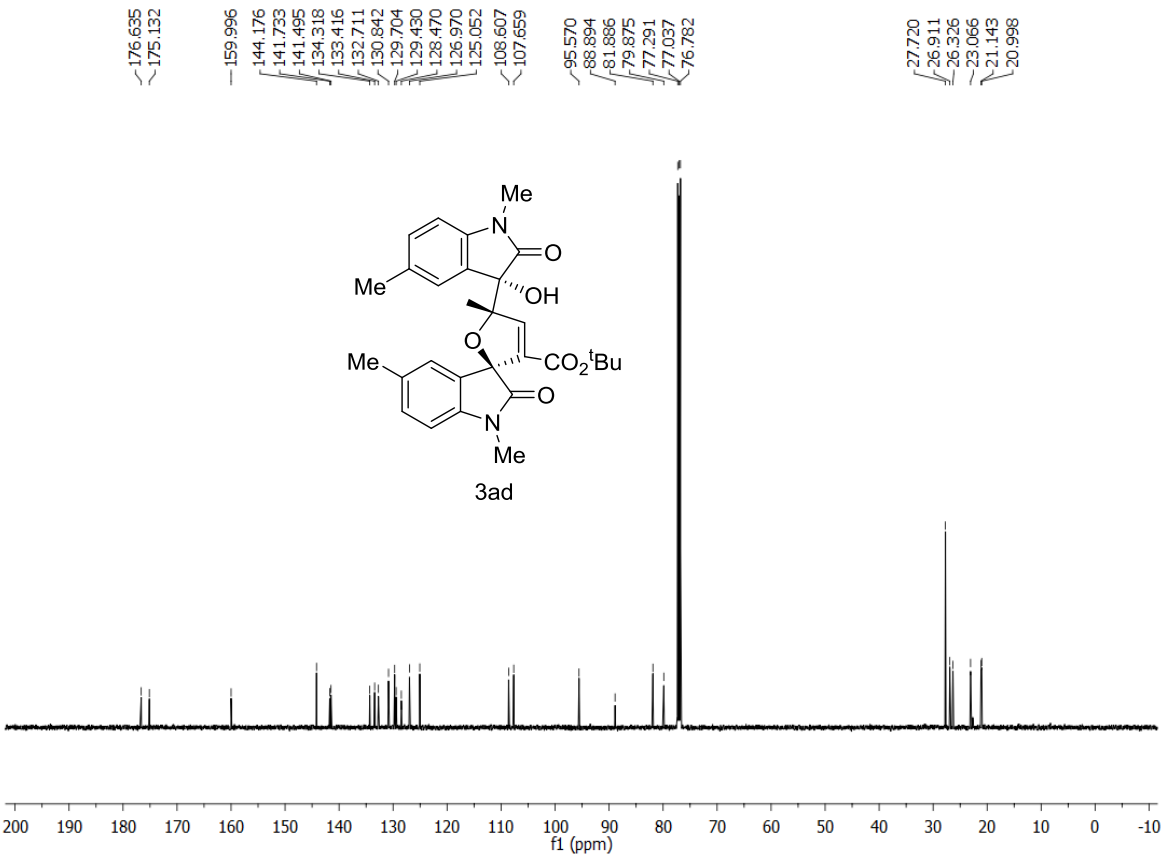


Fig S60. ^{13}C NMR of 3ad

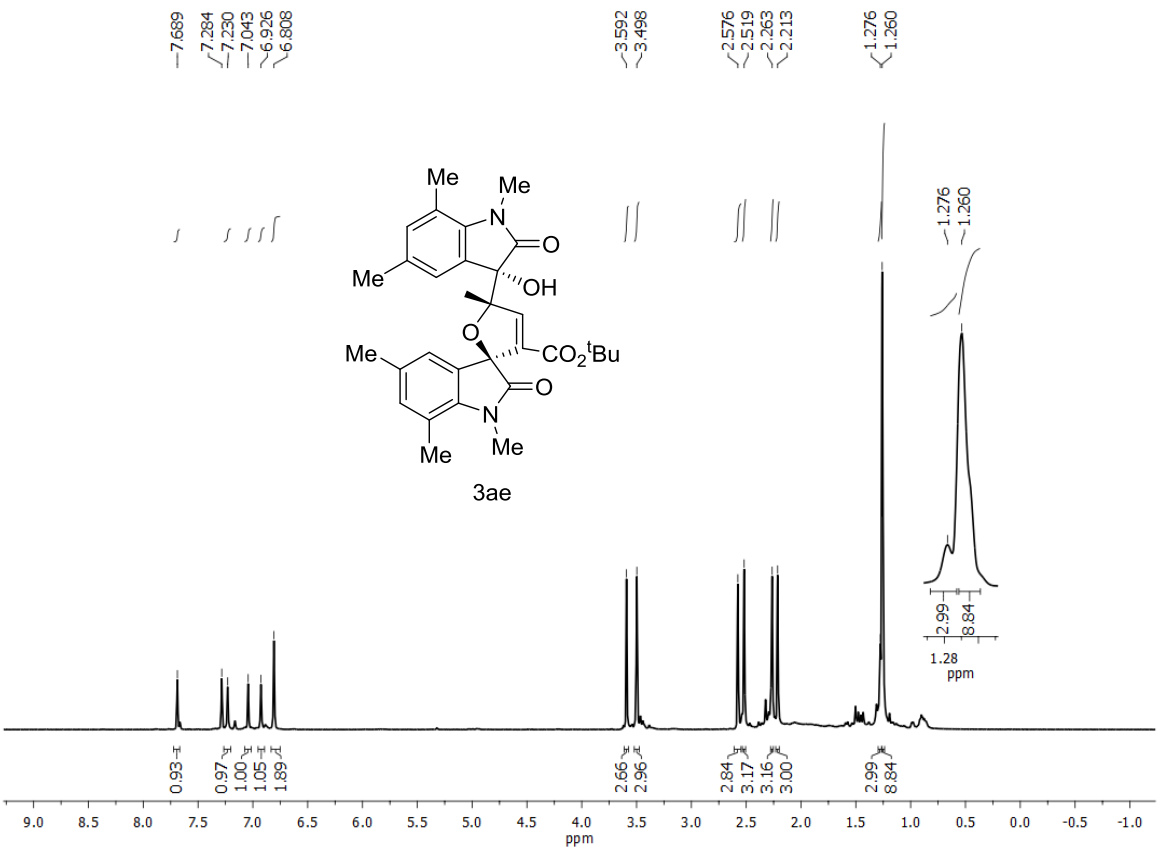


Fig S61. ^{1}H NMR of 3ae

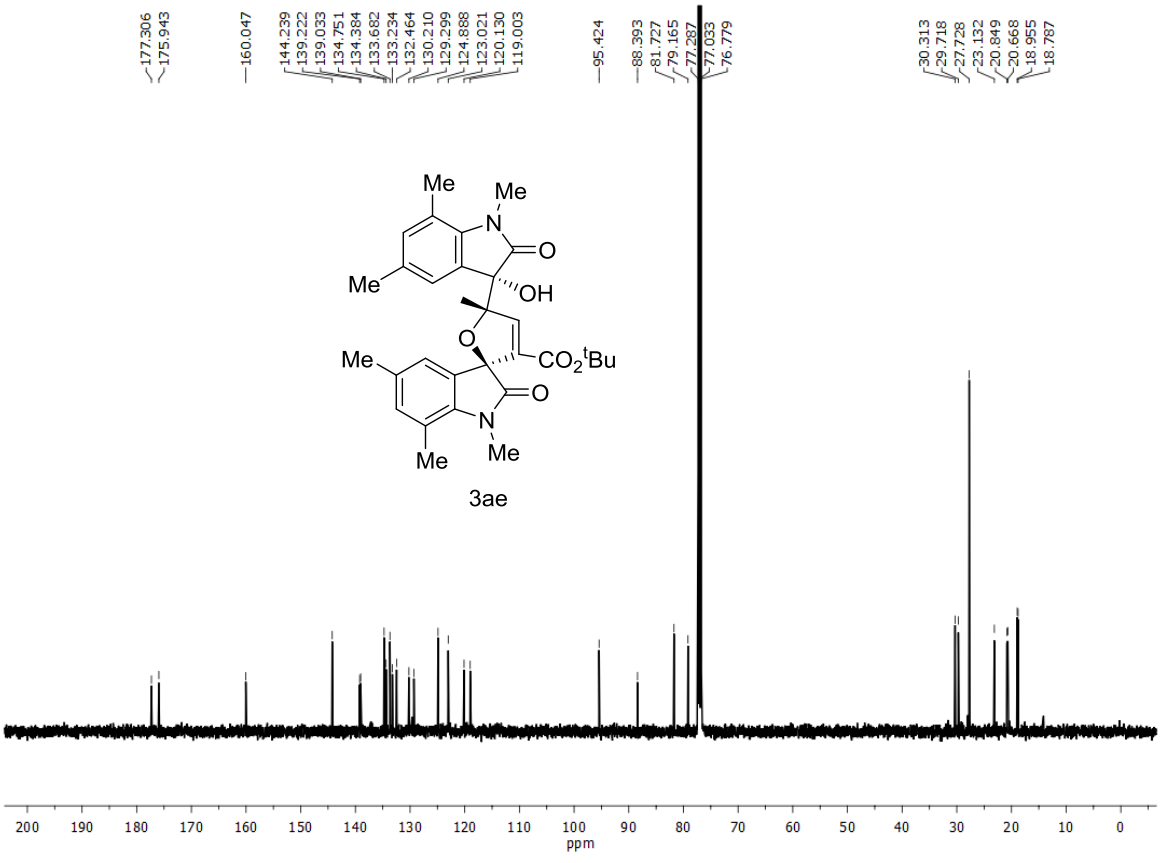


Fig S62. ^{13}C NMR of 3ae

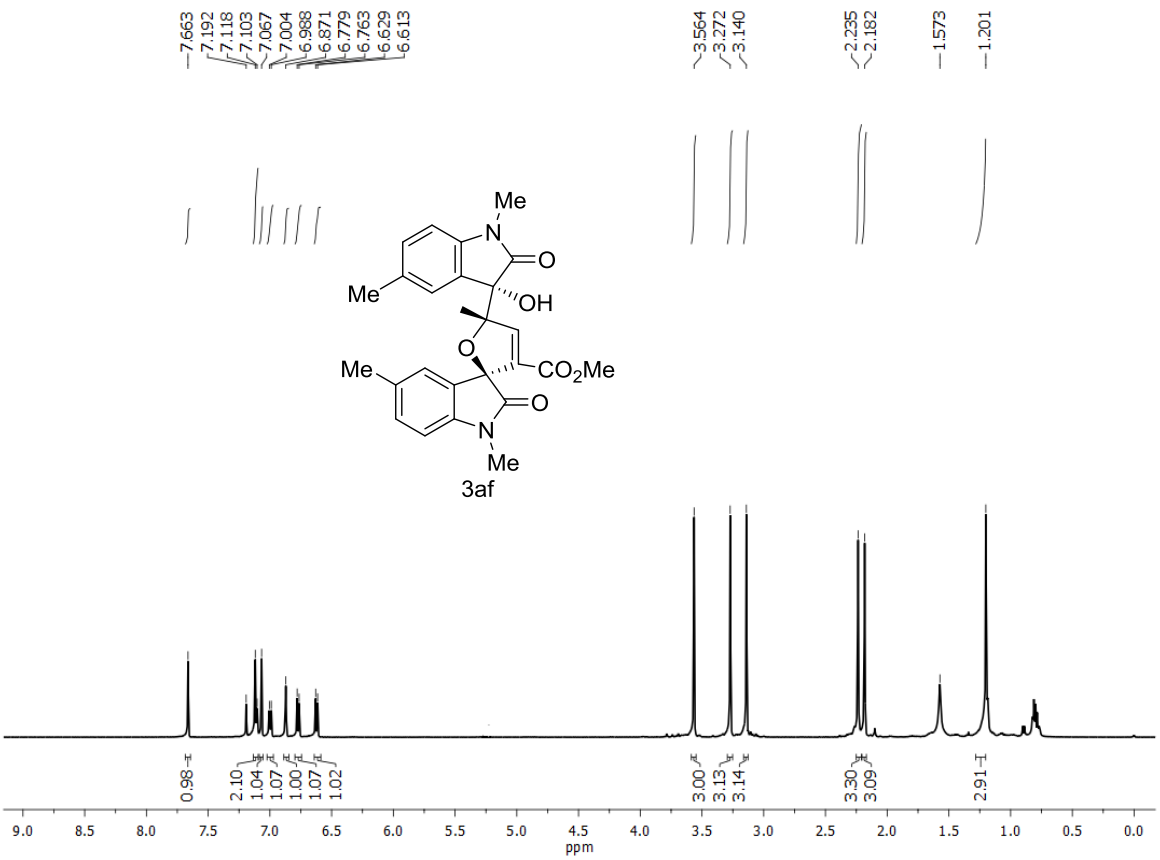


Fig S63. ^{1}H NMR of 3af

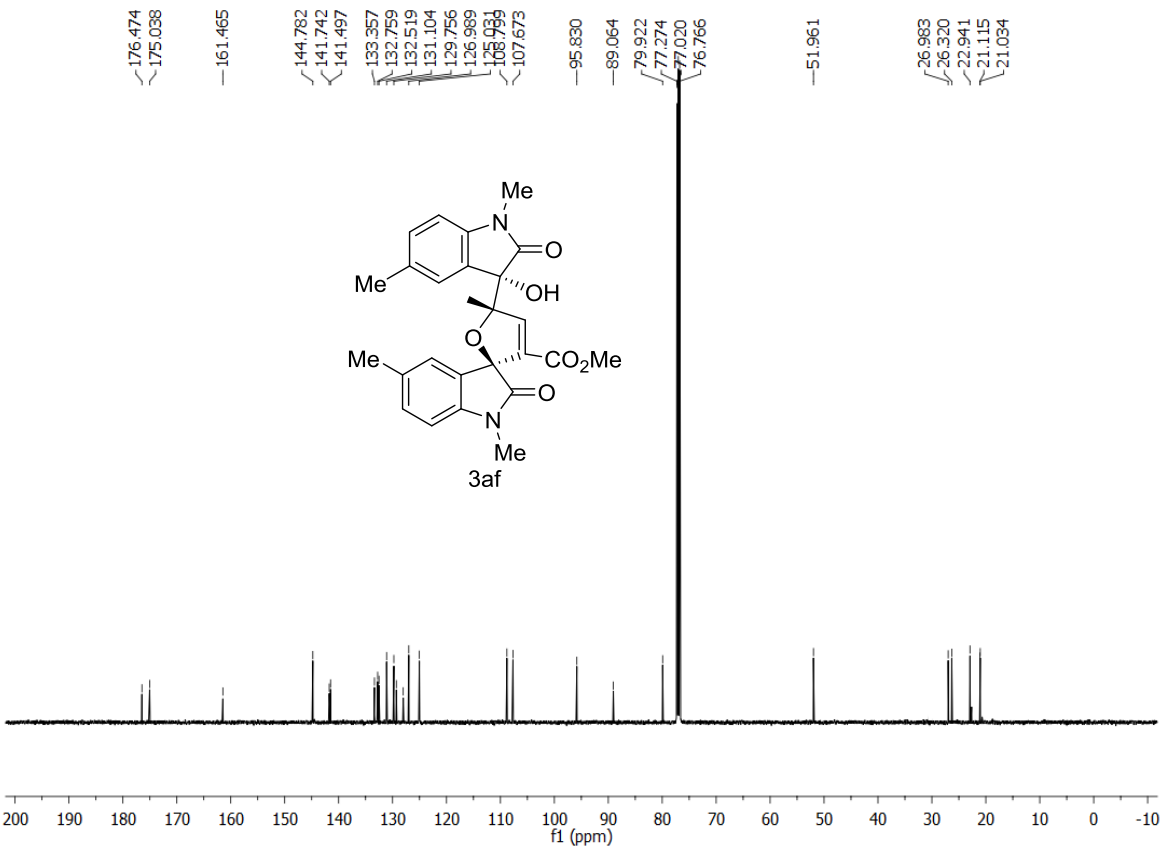


Fig S64. ^{13}C NMR of 3af

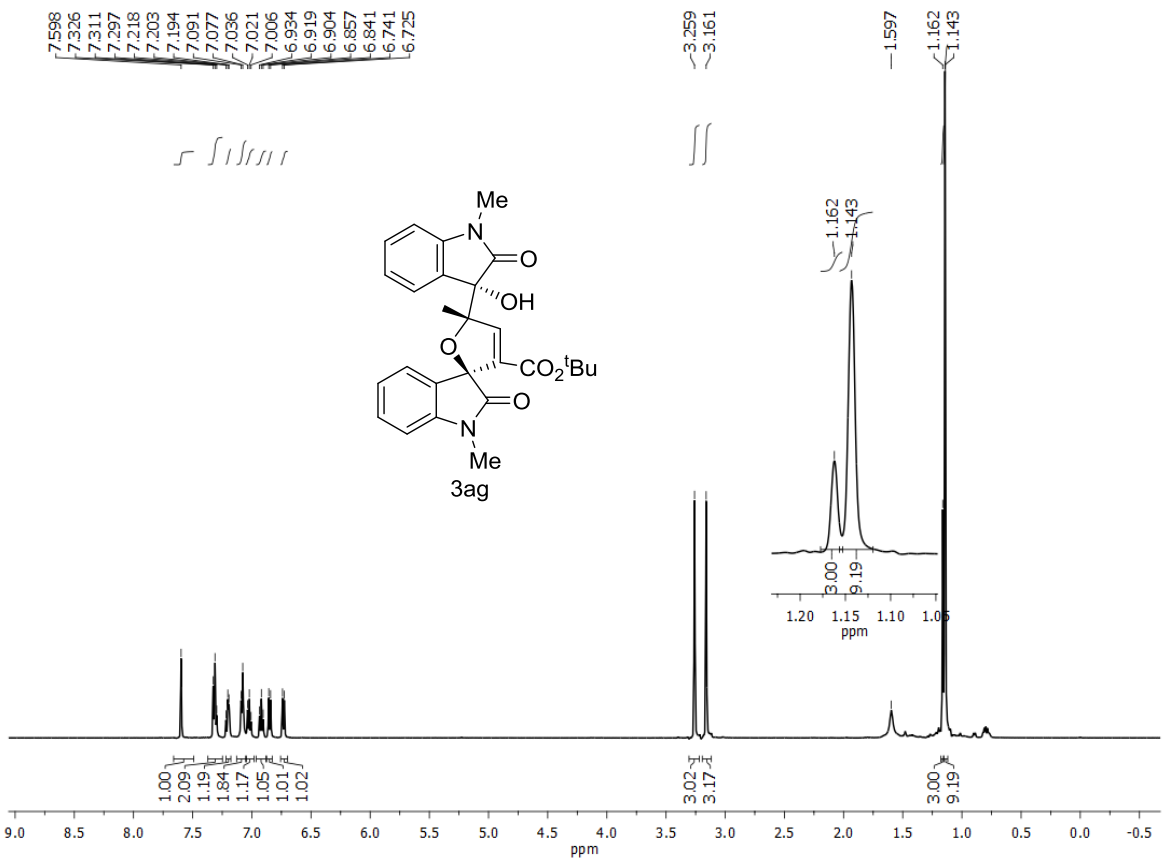


Fig S65. ^{1}H NMR of 3ag

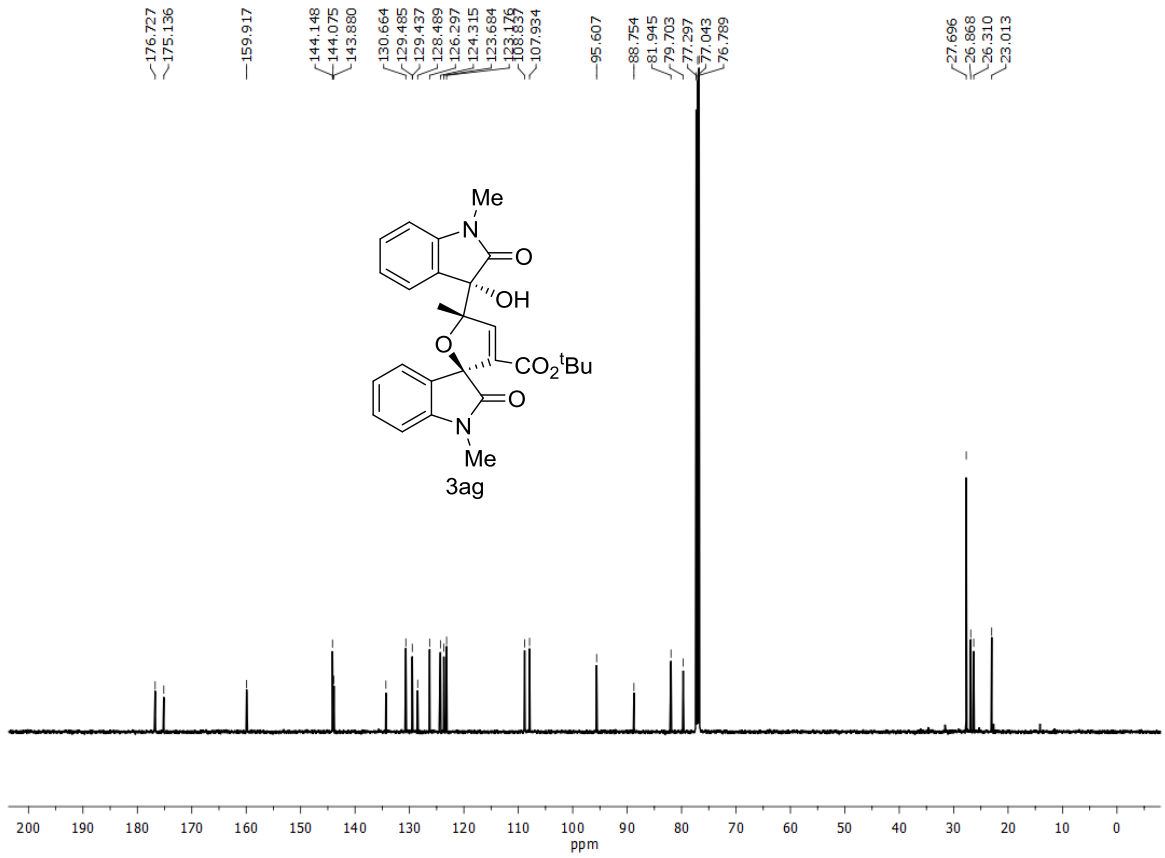


Fig S66. ^{13}C NMR of 3ag

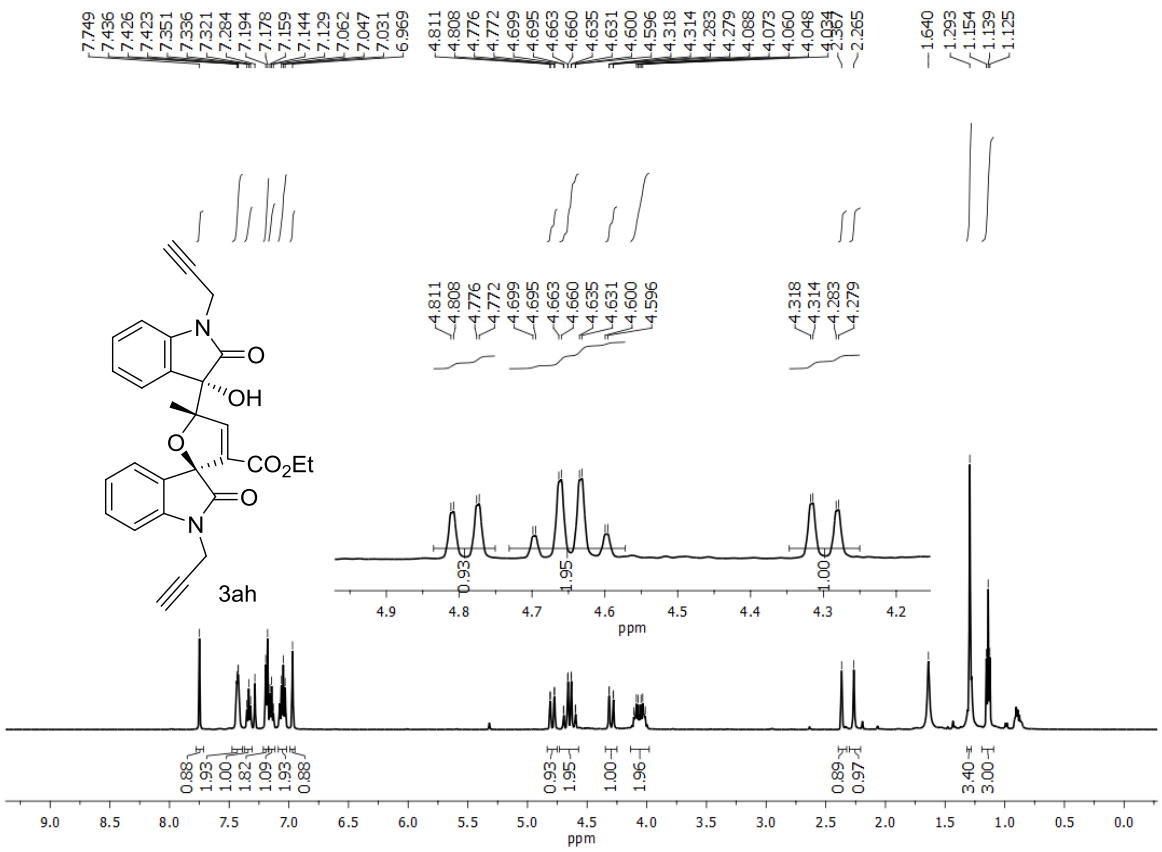


Fig S67. ^{1}H NMR of 3ah

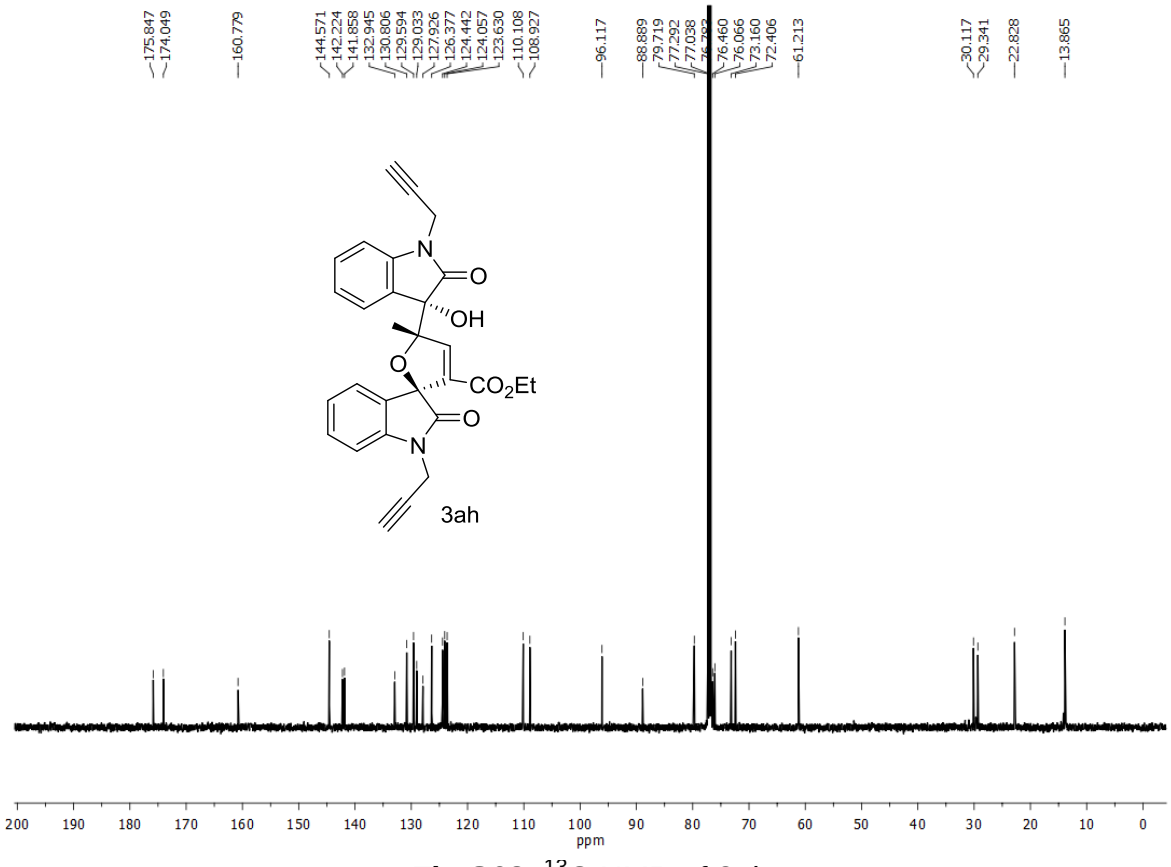


Fig S68. ^{13}C NMR of 3ah

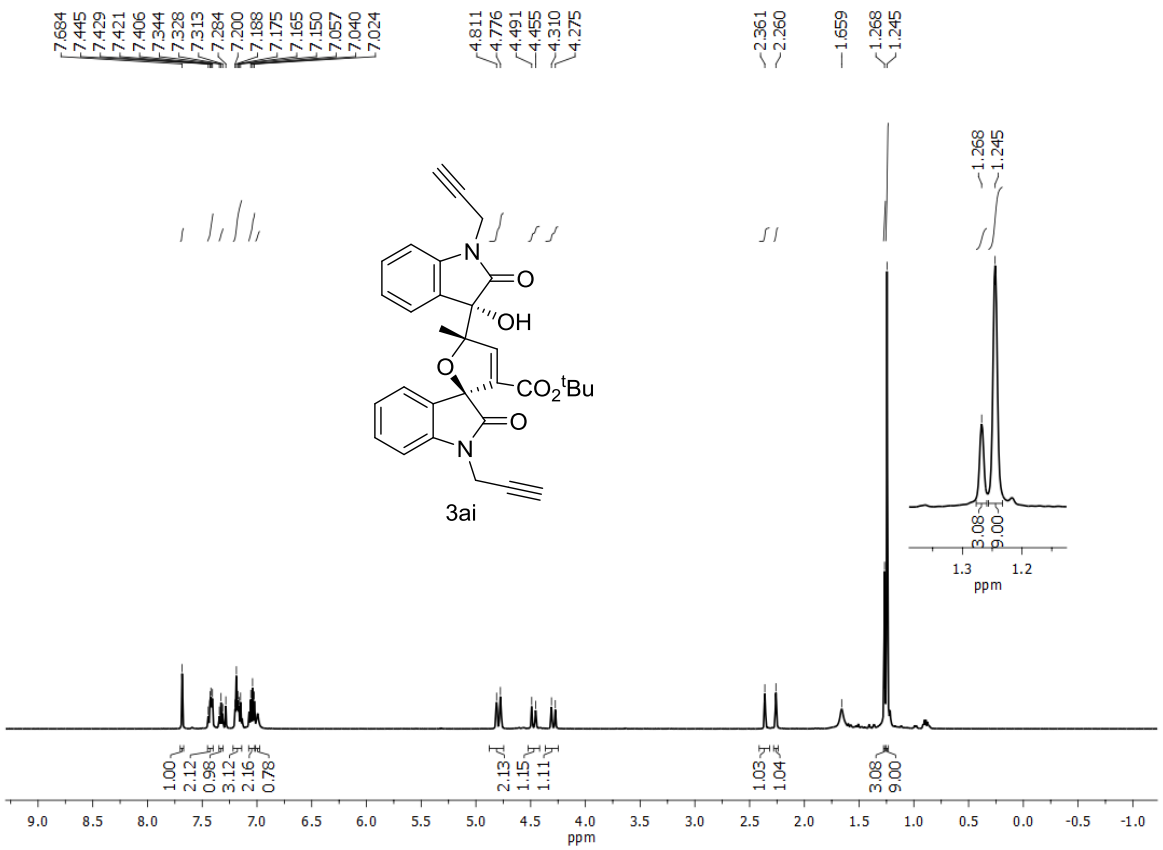


Fig S69. ^{1}H NMR of 3ai

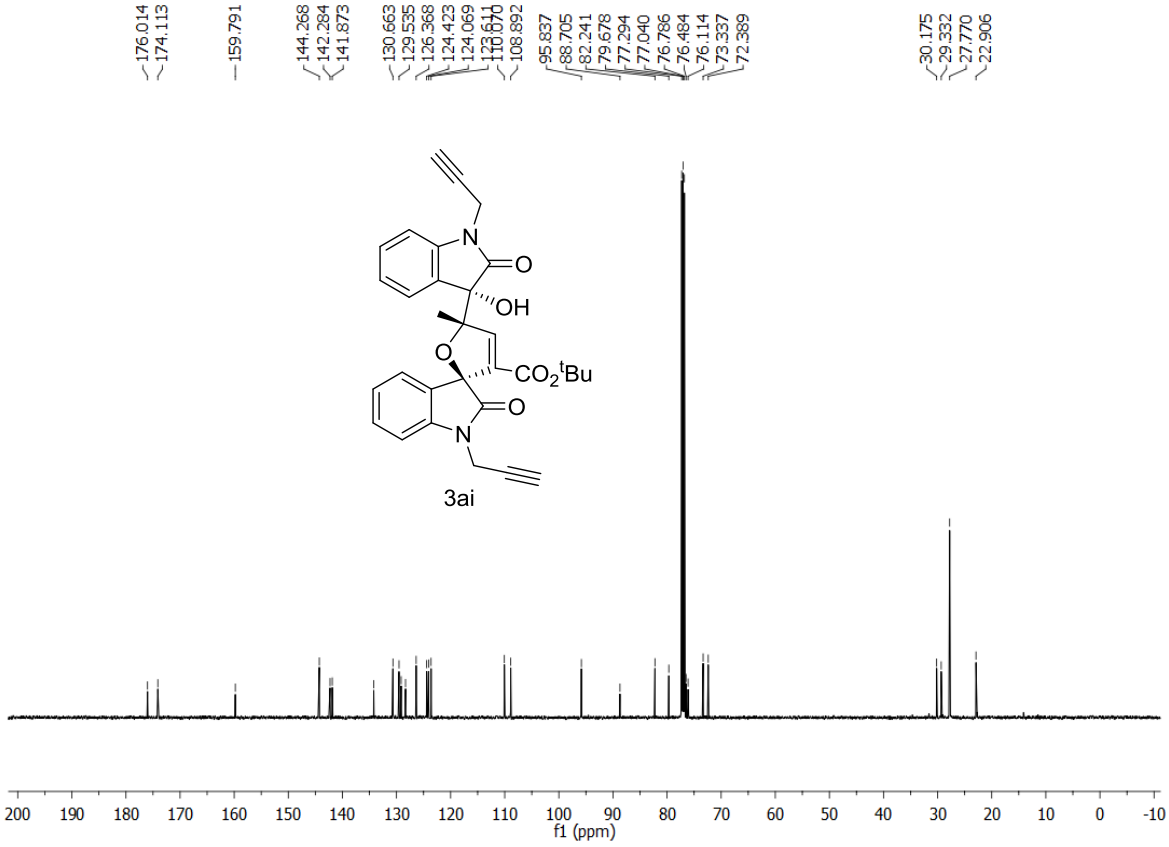


Fig S70. ^{13}C NMR of 3ai

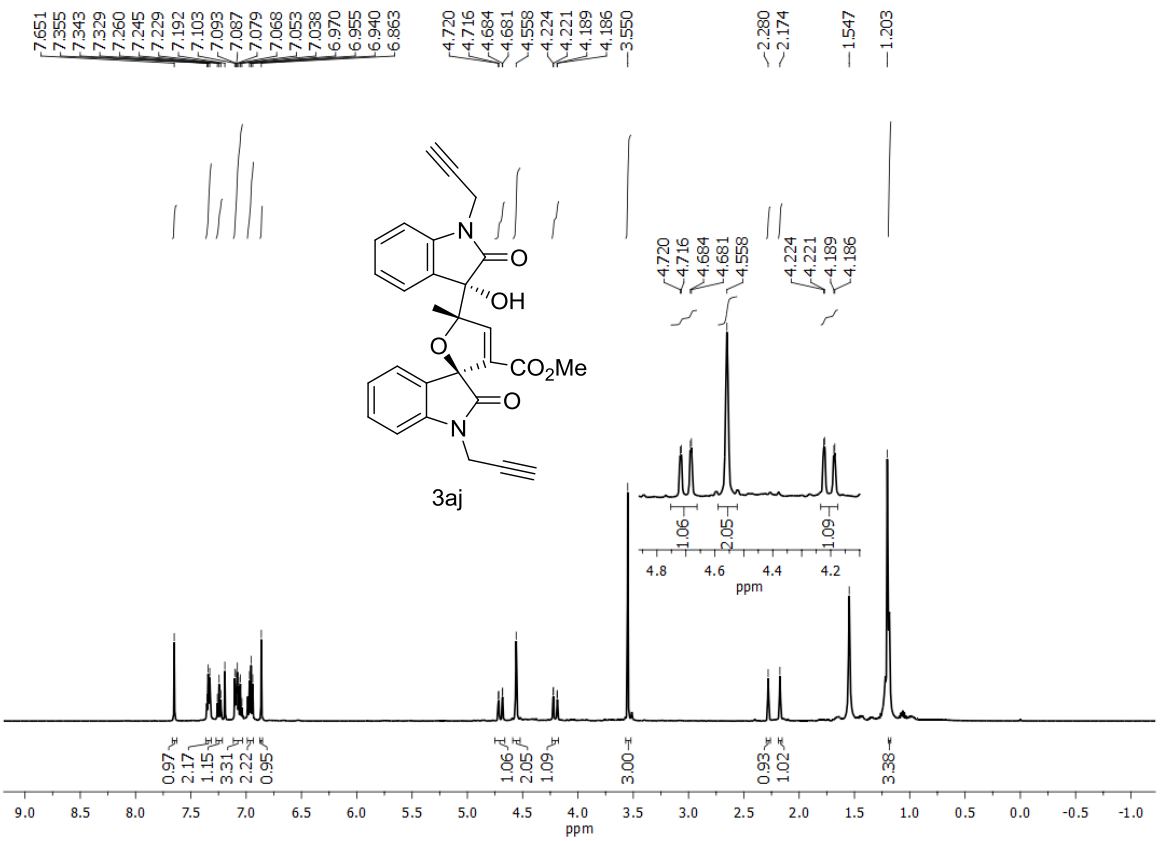


Fig S71. ^{1}H NMR of 3aj

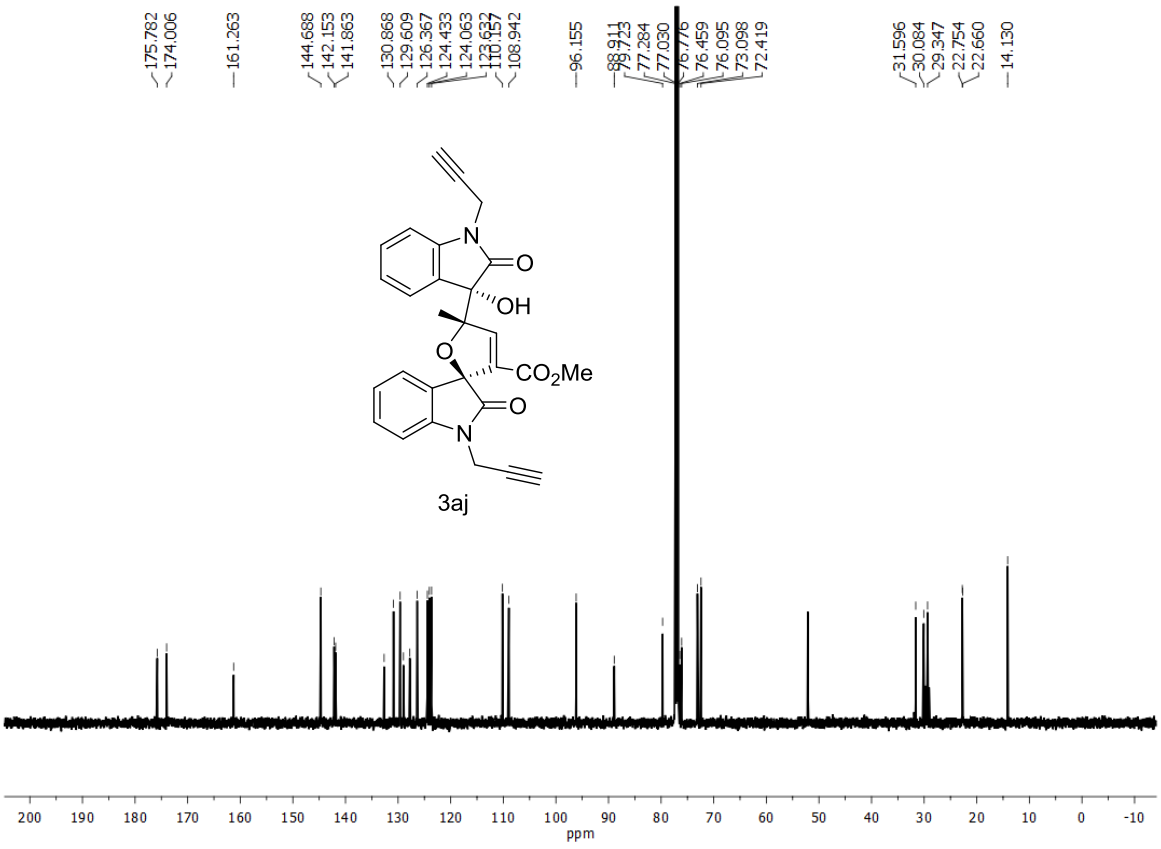


Fig S72. ^{13}C NMR of 3aj

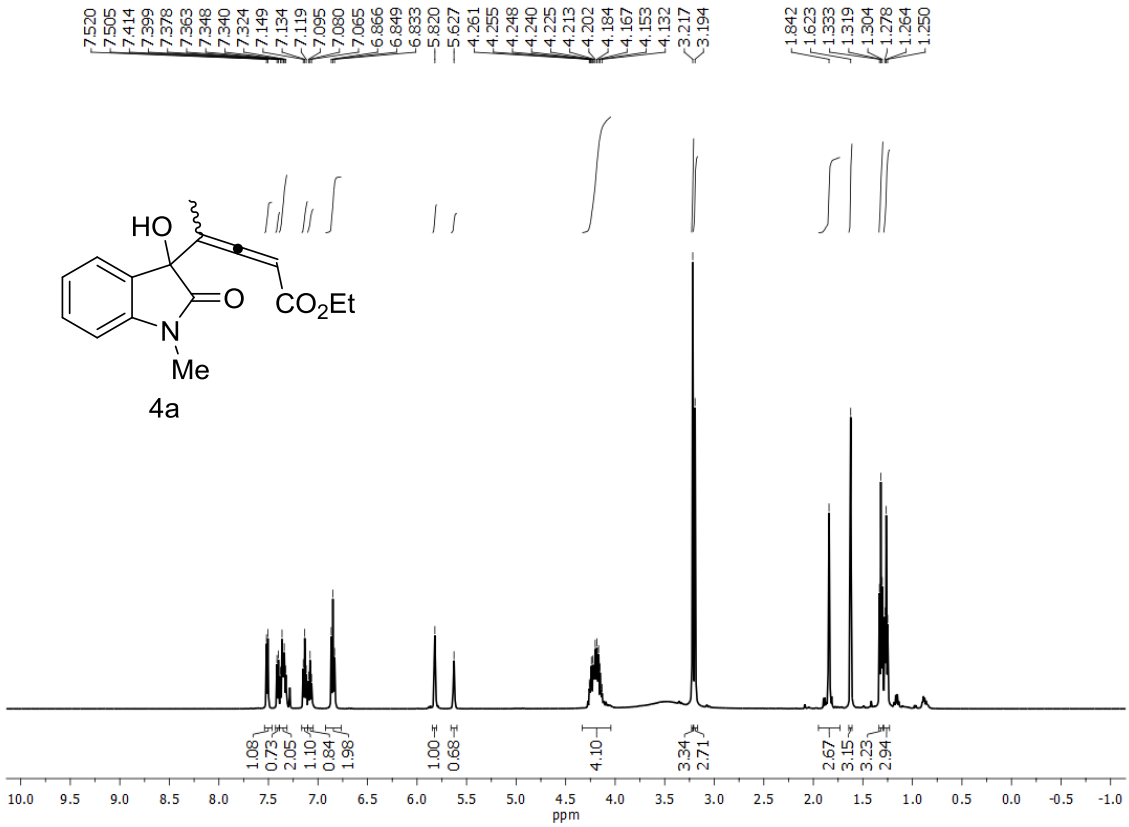


Fig 73. ^{1}H NMR of 4a

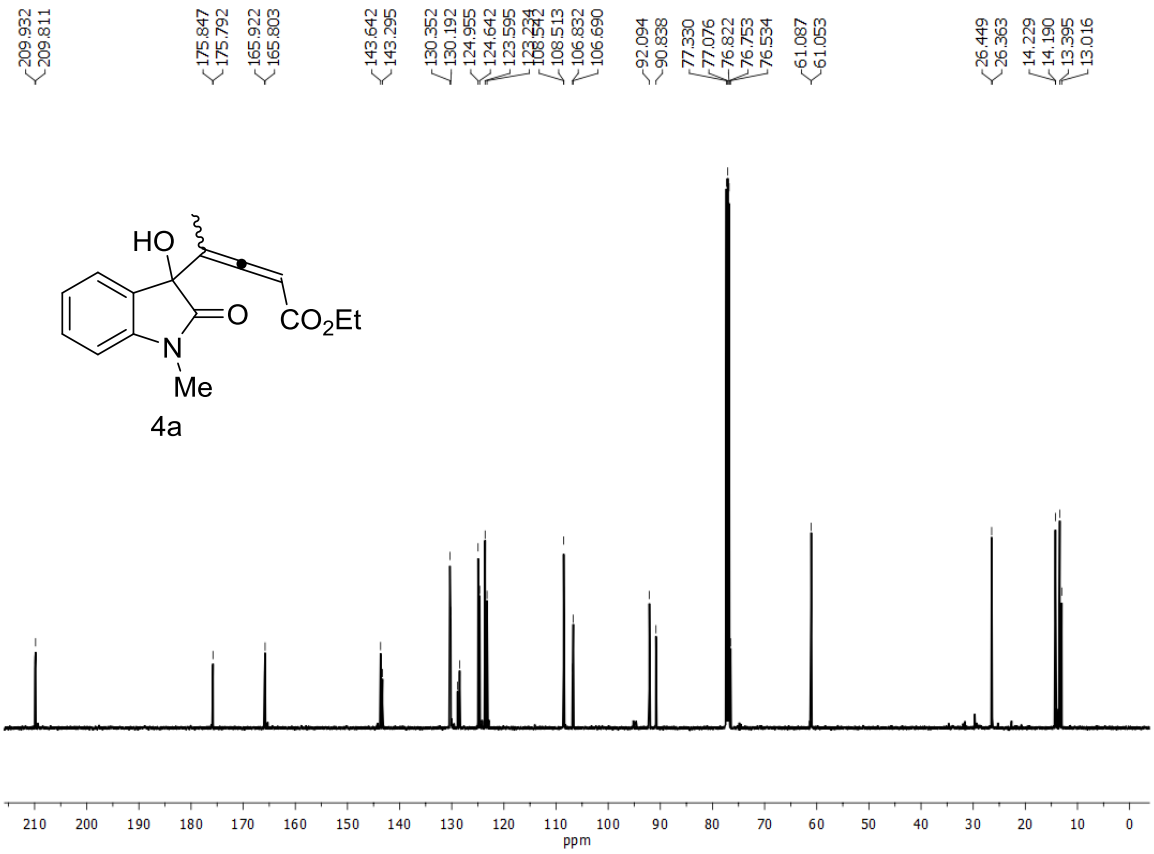


Fig 74. ^{13}C NMR of 4a

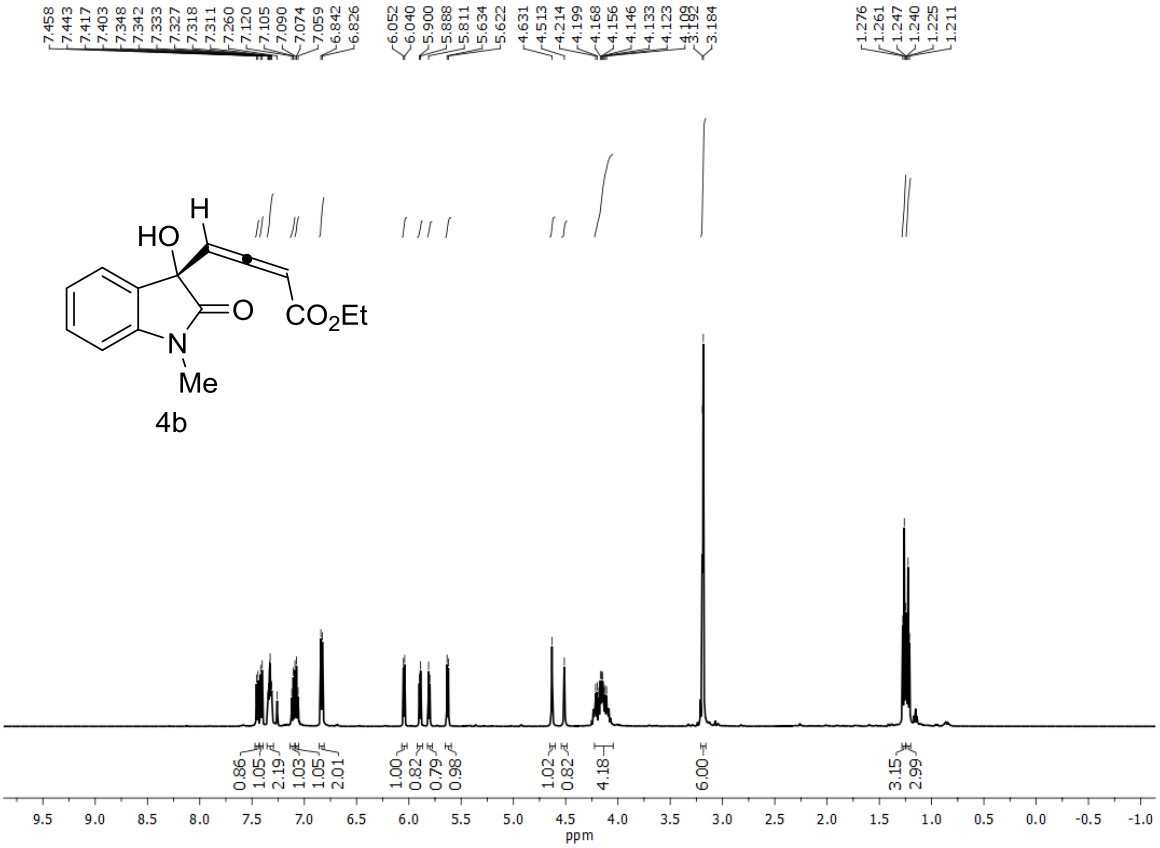


Fig 75. ^{1}H NMR of 4b

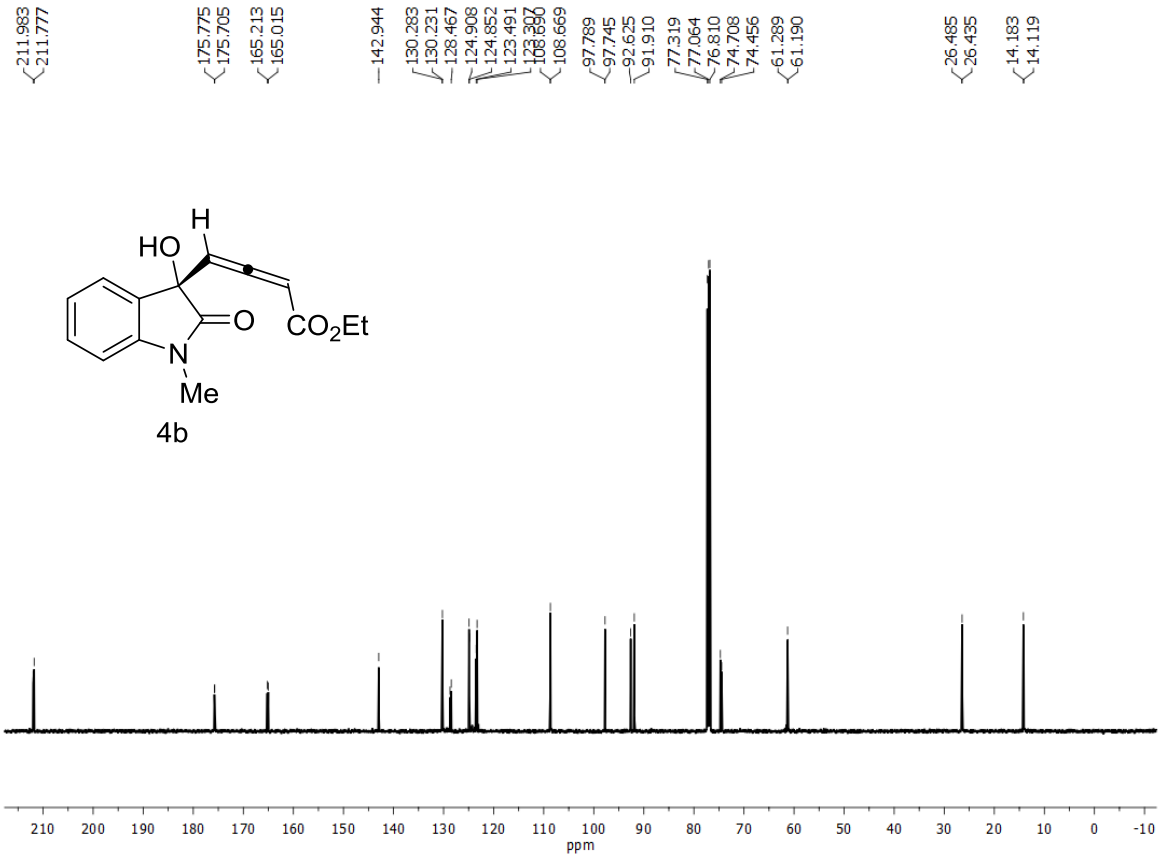


Fig 76. ^{13}C NMR of 4b

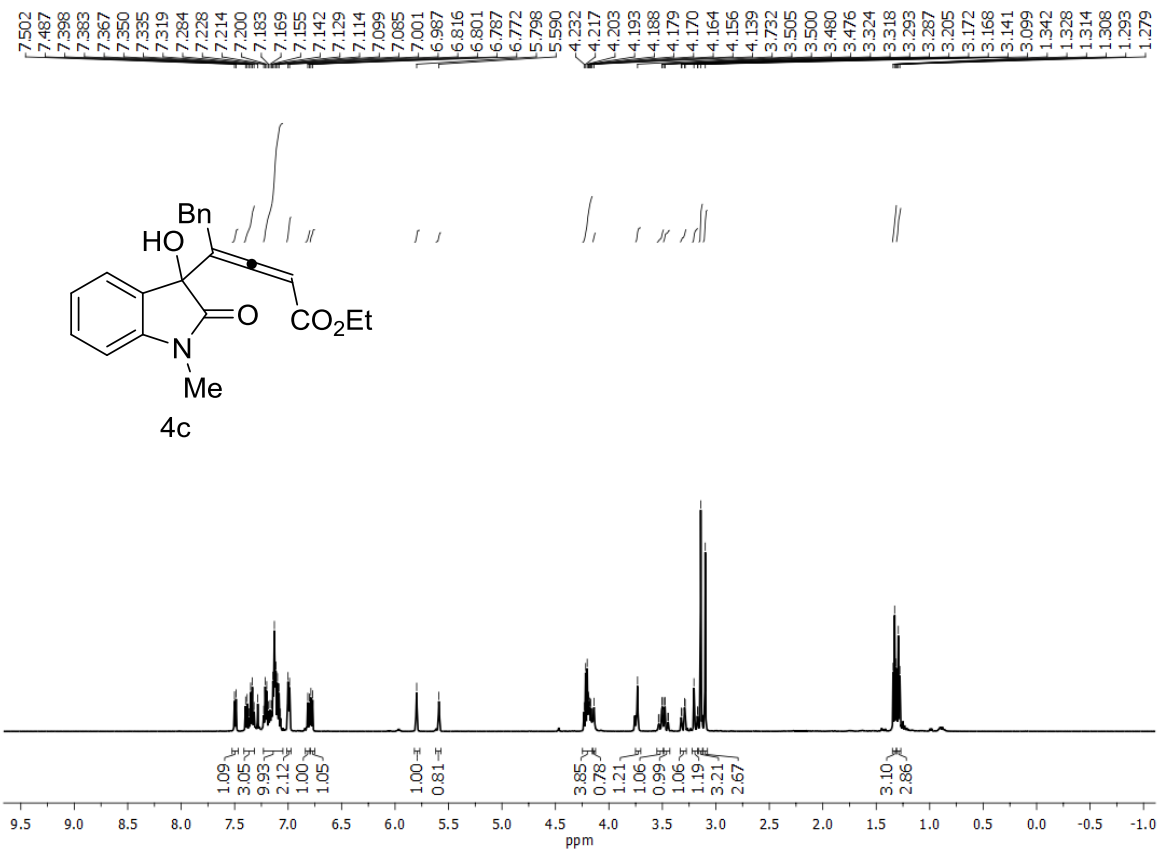


Fig 77. ^{1}H NMR of 4c

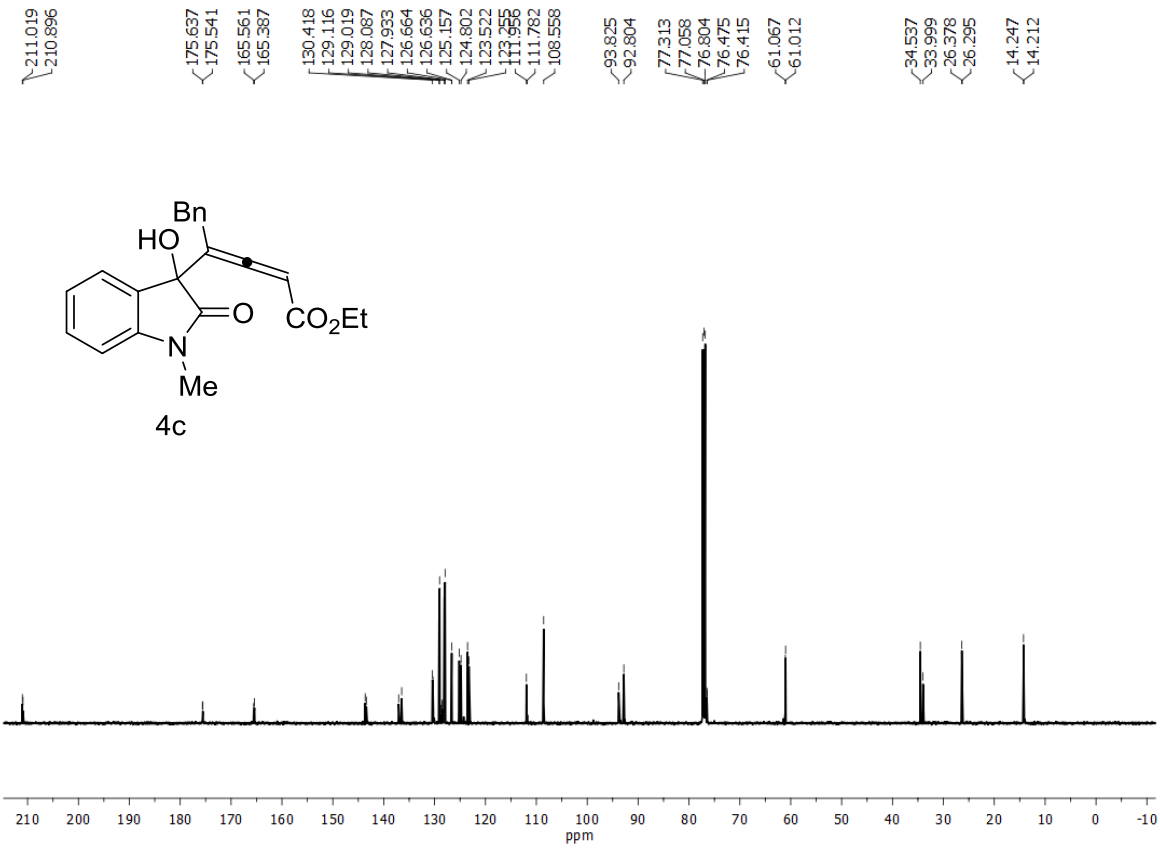


Fig 78. ^{13}C NMR of 4c

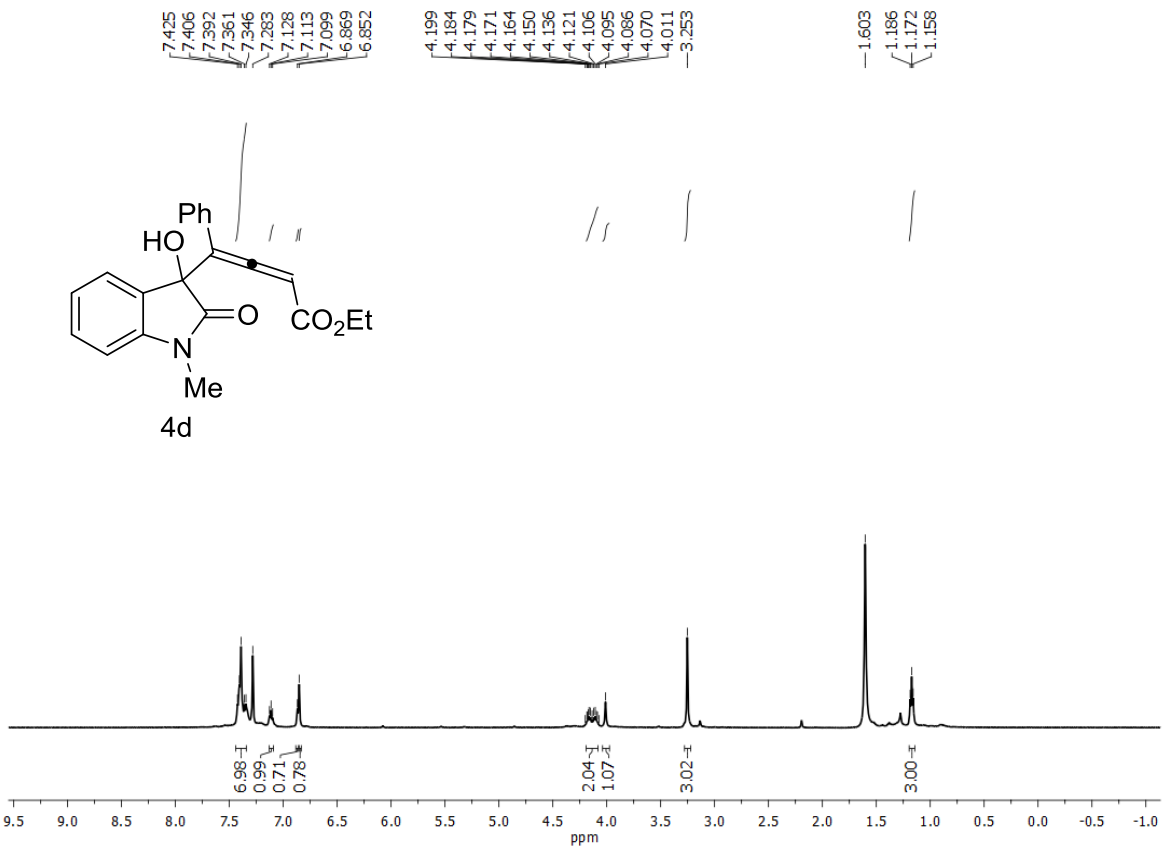


Fig 79. ^{1}H NMR of 4d

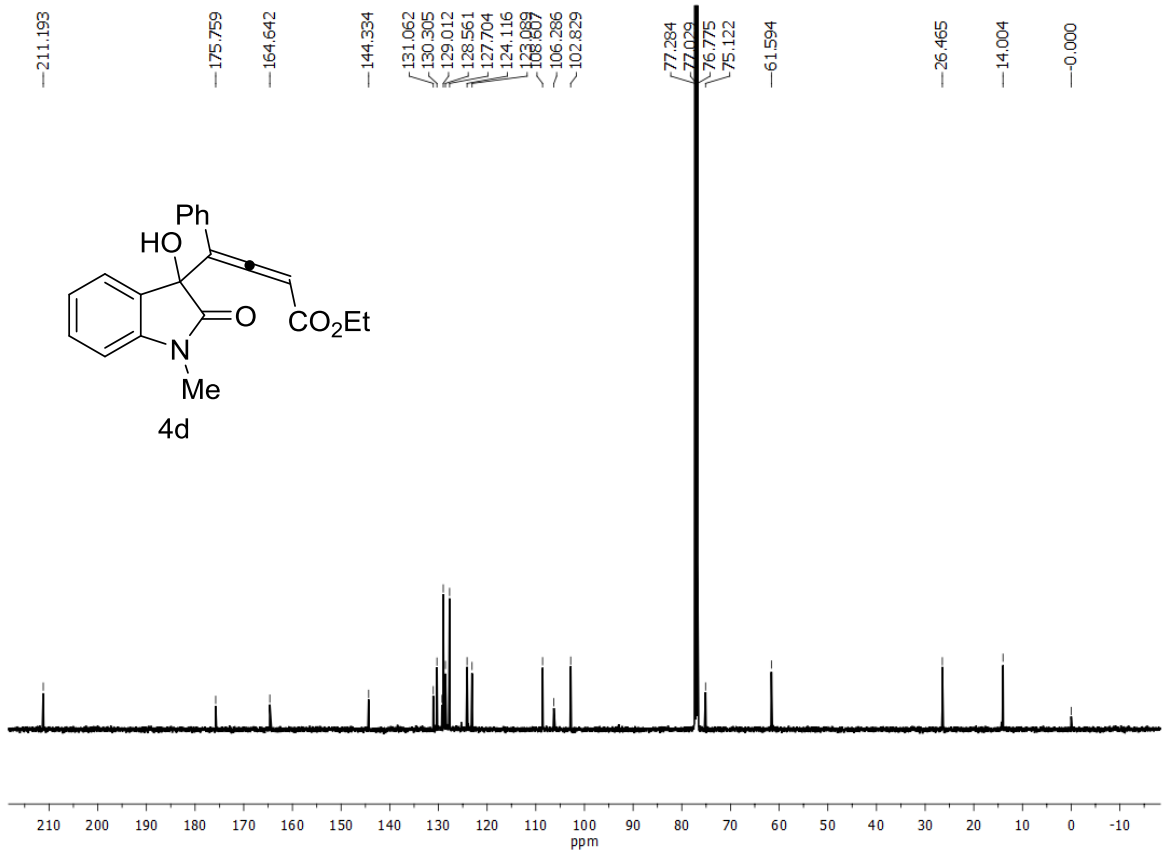


Fig 80. ^{13}C NMR of 4d

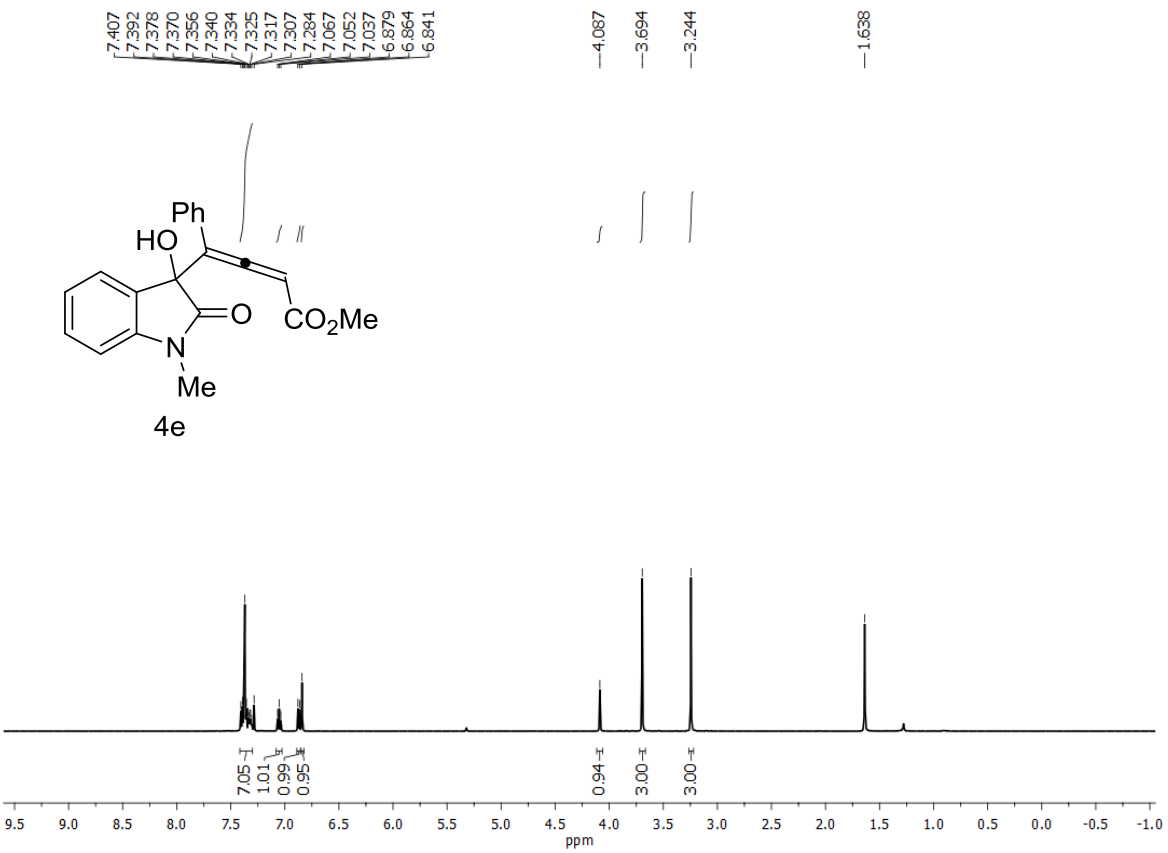


Fig 81. ^{1}H NMR of 4e

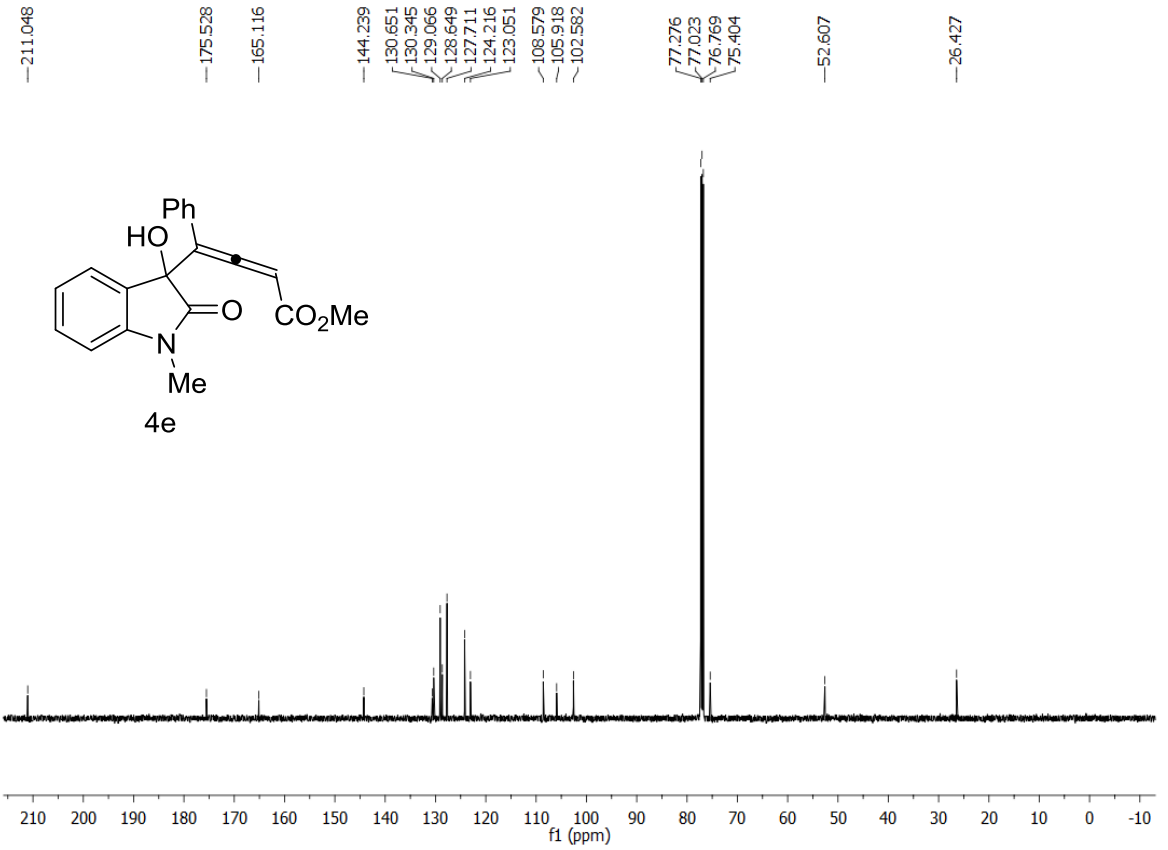


Fig 82. ^{13}C NMR of 4e

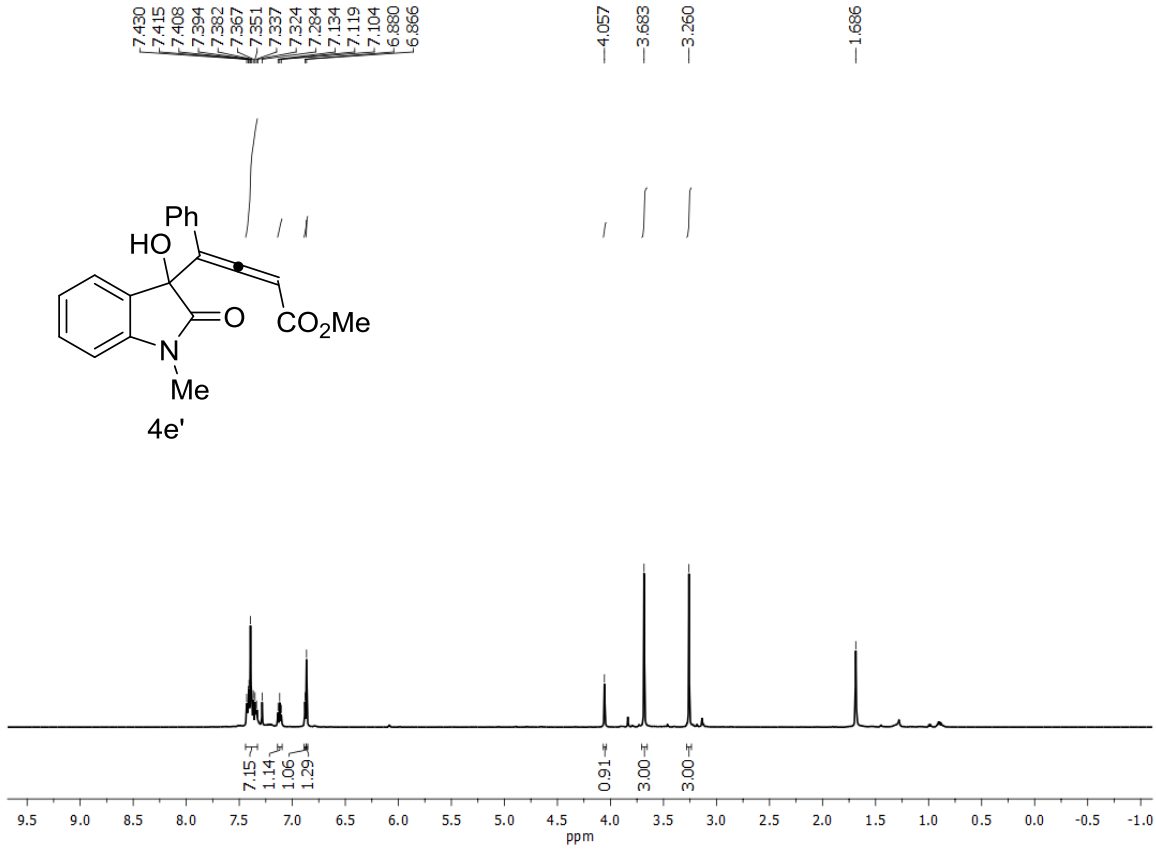


Fig 83. ^{1}H NMR of 4e'

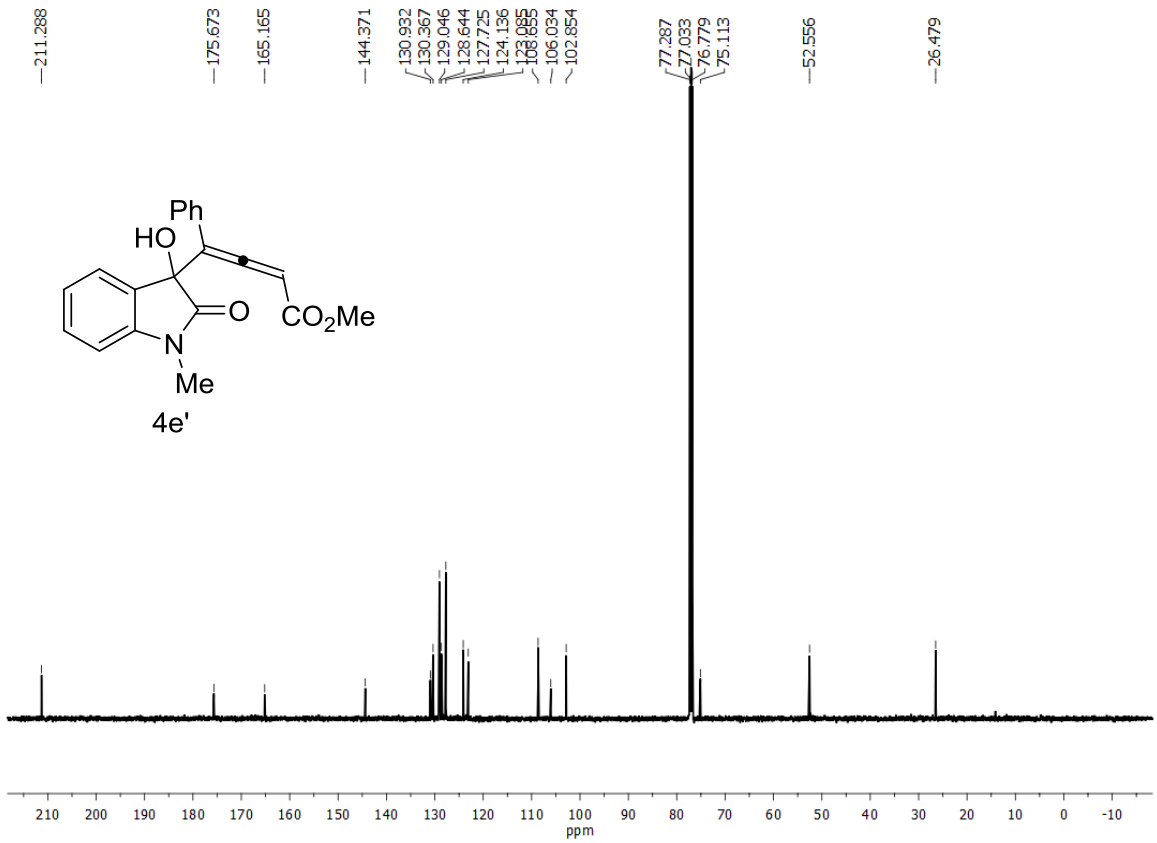


Fig 84. ^{13}C NMR of 4e'

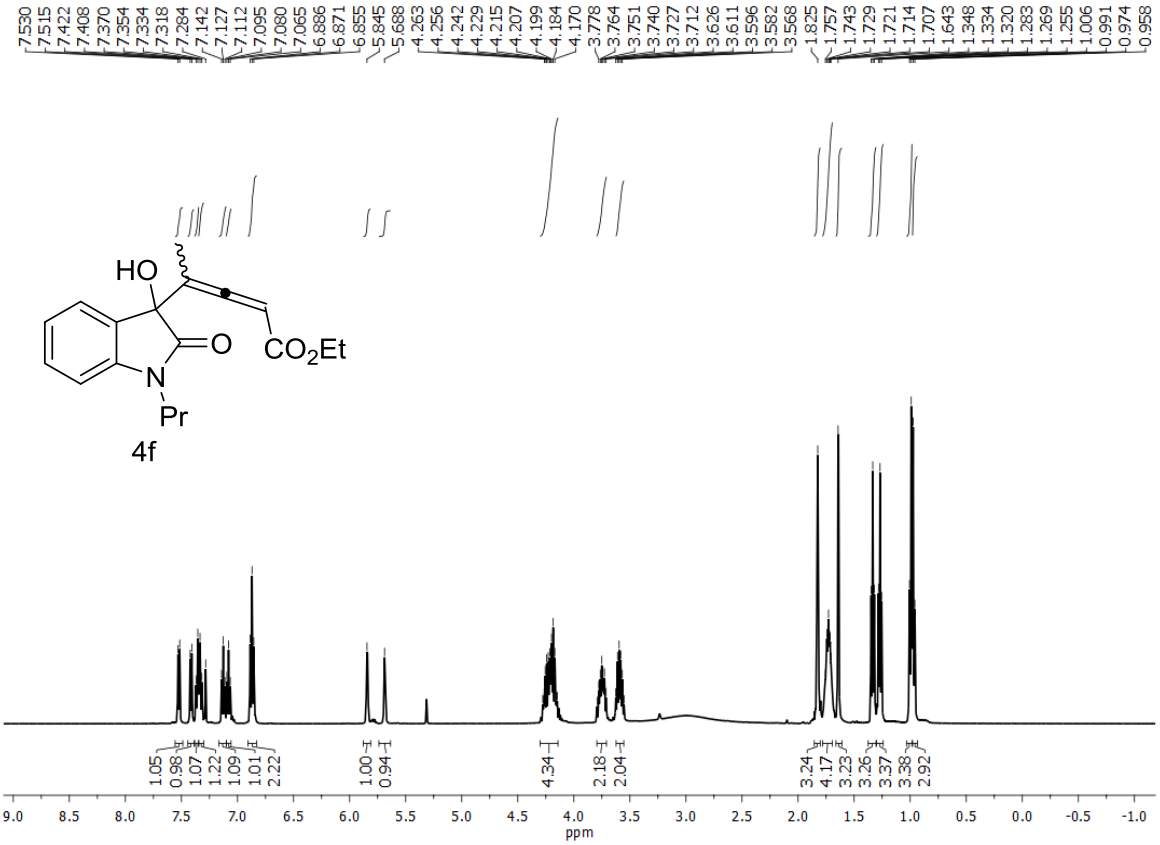


Fig 85. ^{1}H NMR of 4f

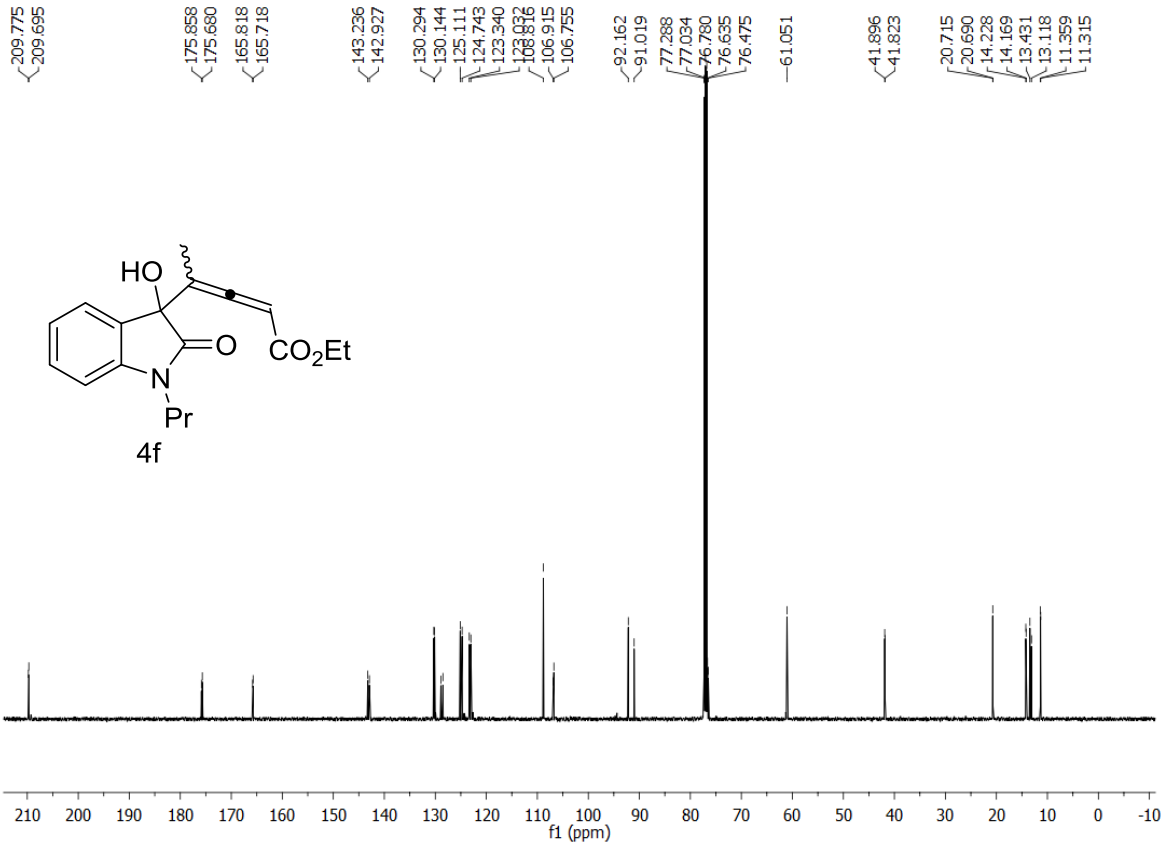


Fig 86. ^{13}C NMR of 4f

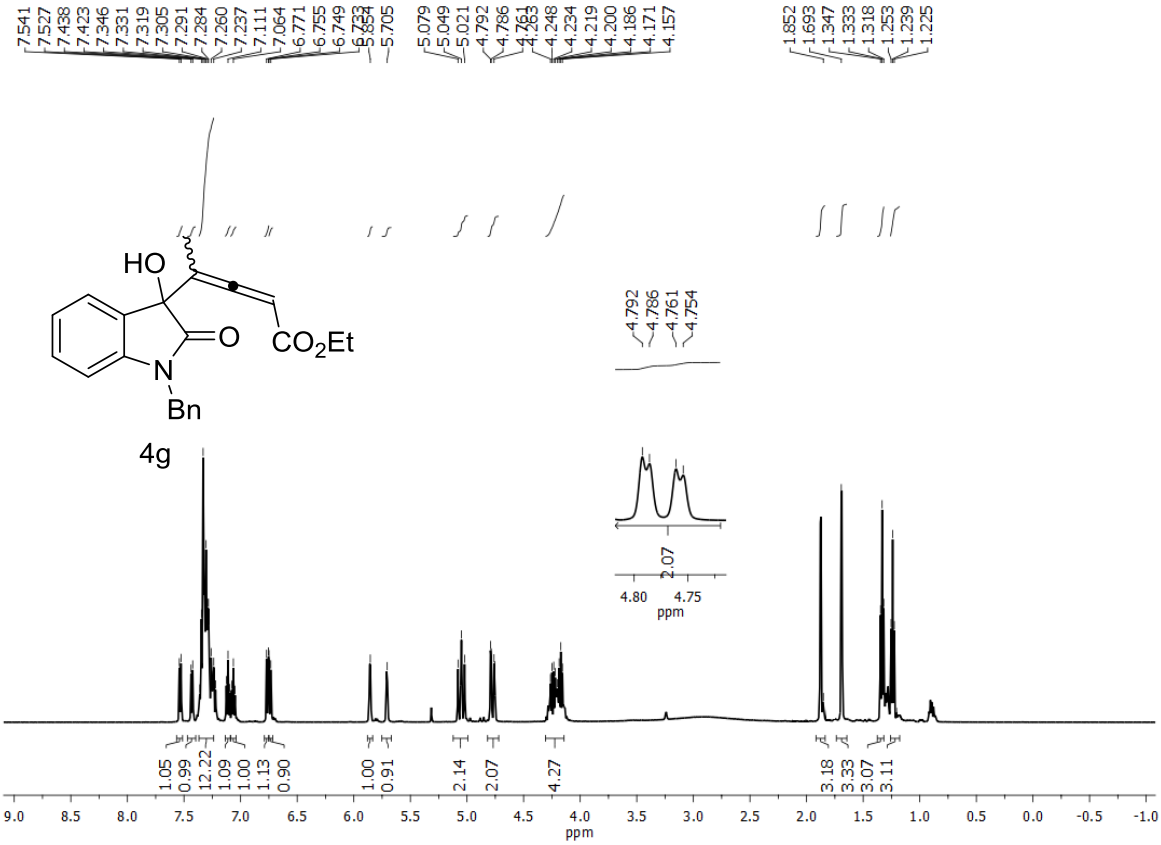


Fig 87. ^{1}H NMR of 4g

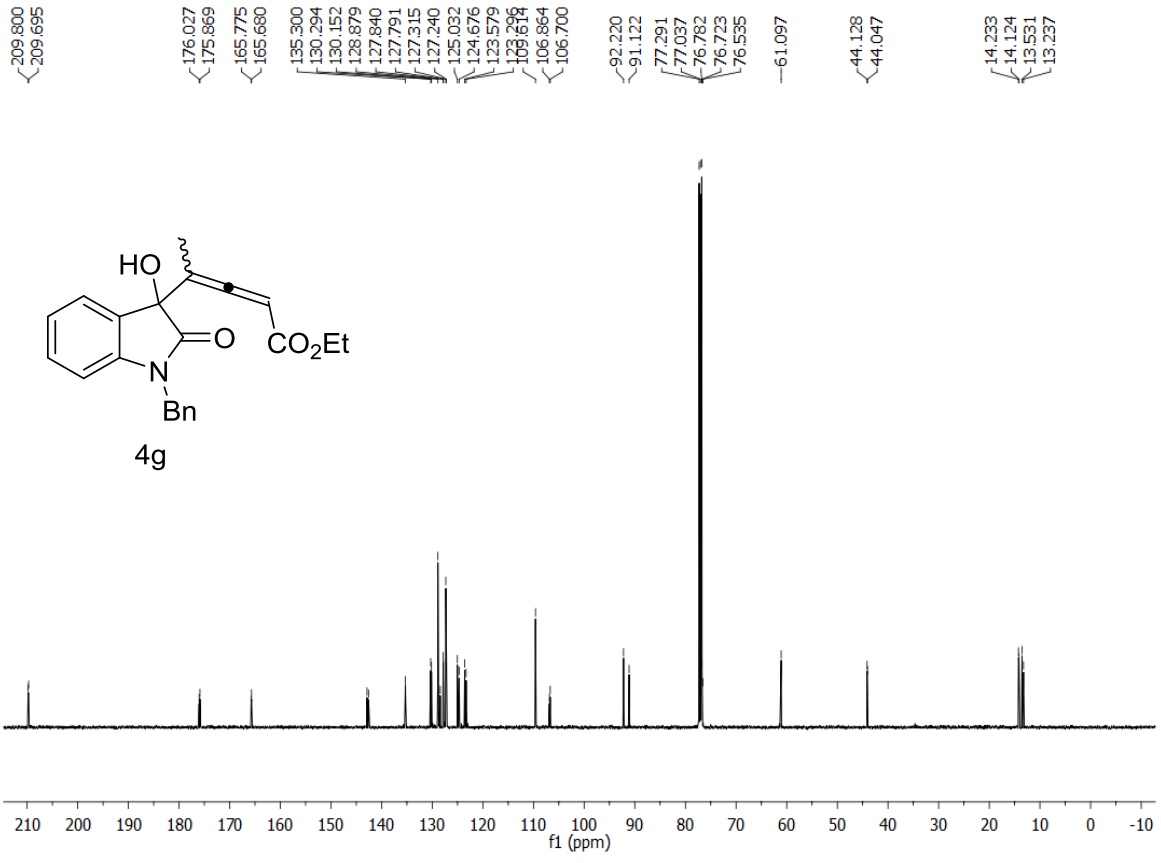


Fig 88. ^{13}C NMR of 4g

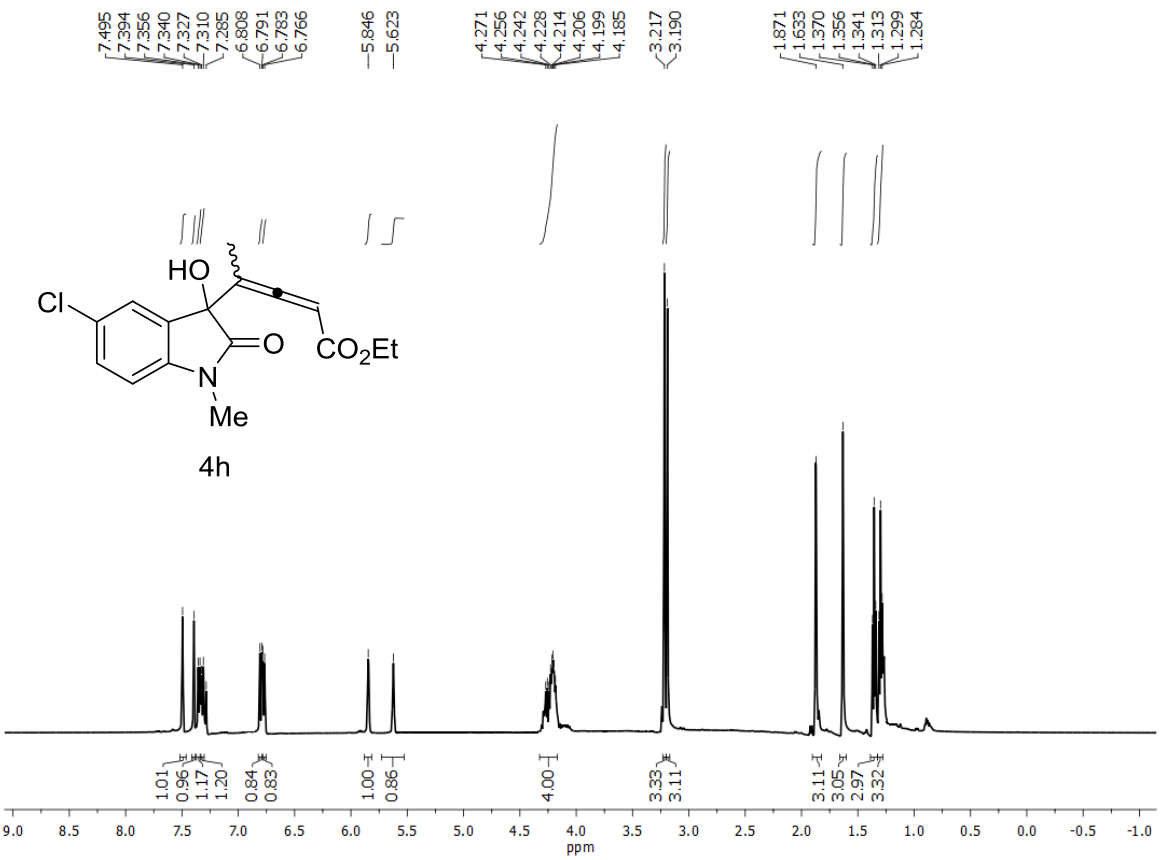


Fig 89. ^{1}H NMR of 4h

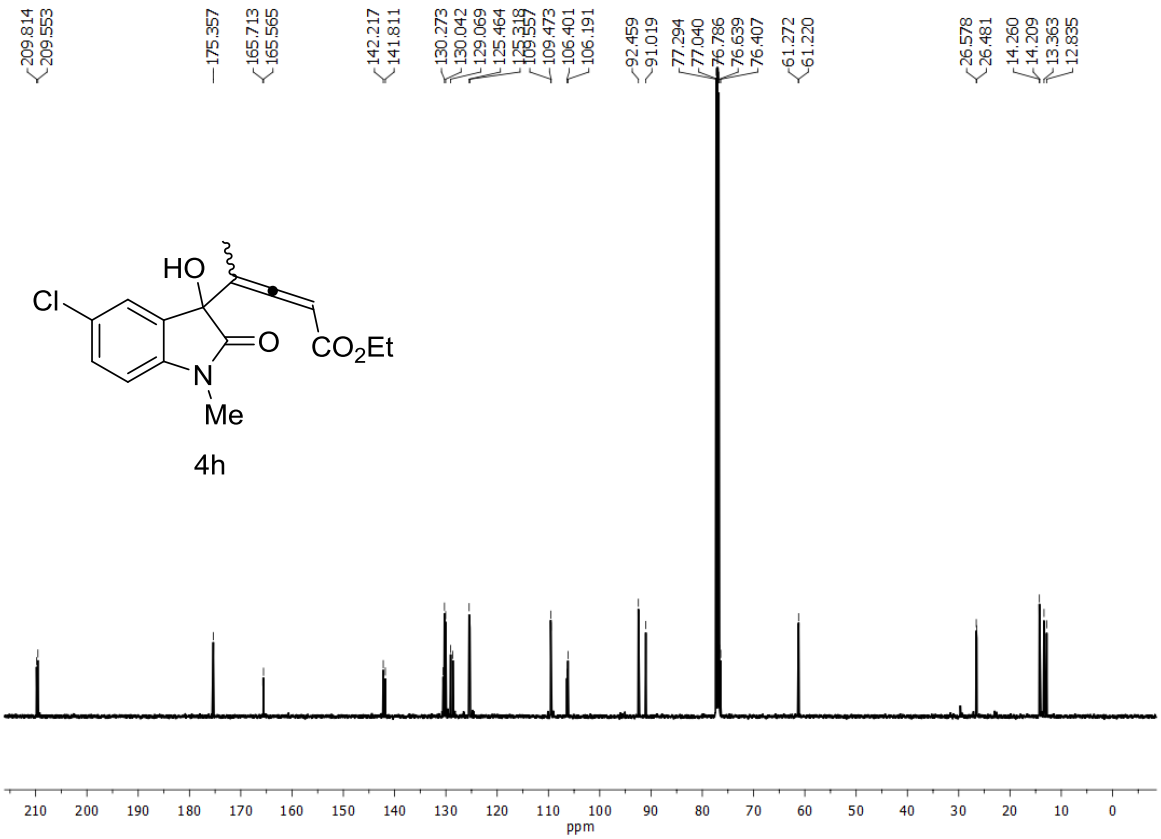


Fig 90. ^{13}C NMR of 4h

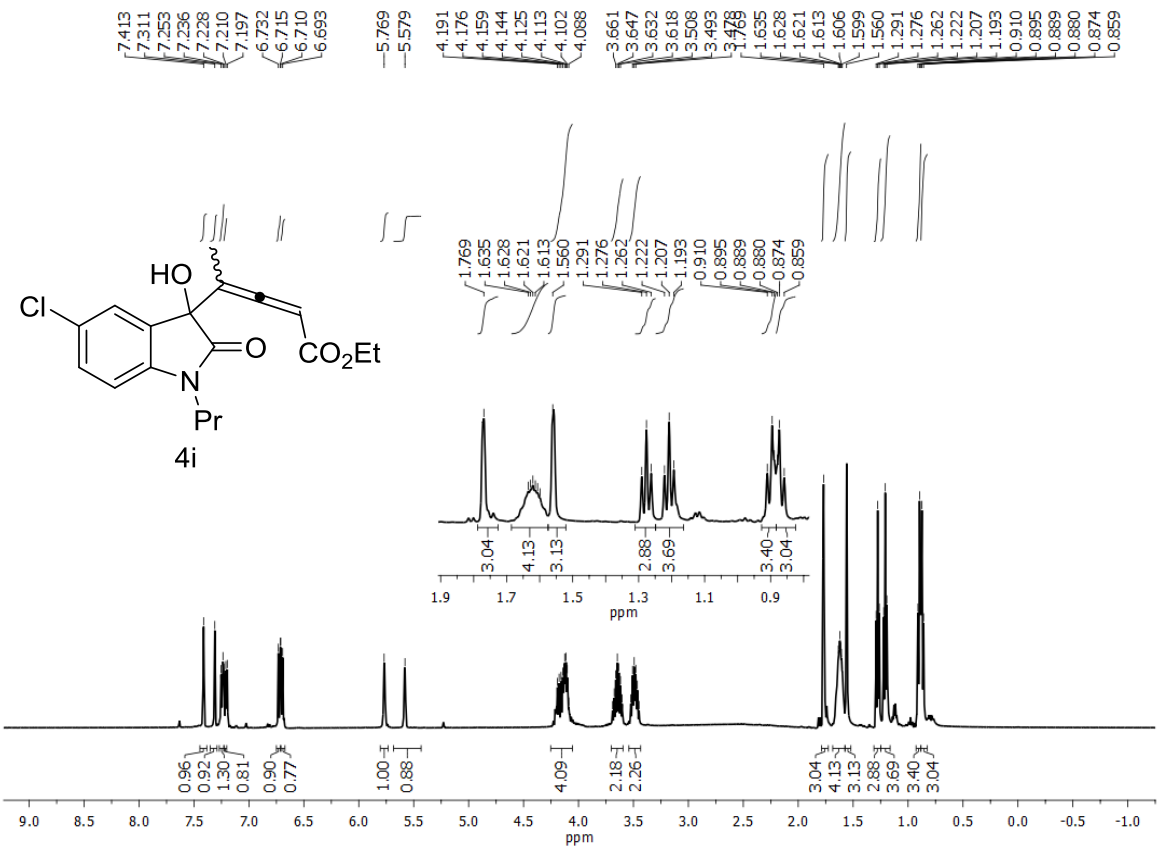


Fig 91. ^{1}H NMR of 4i

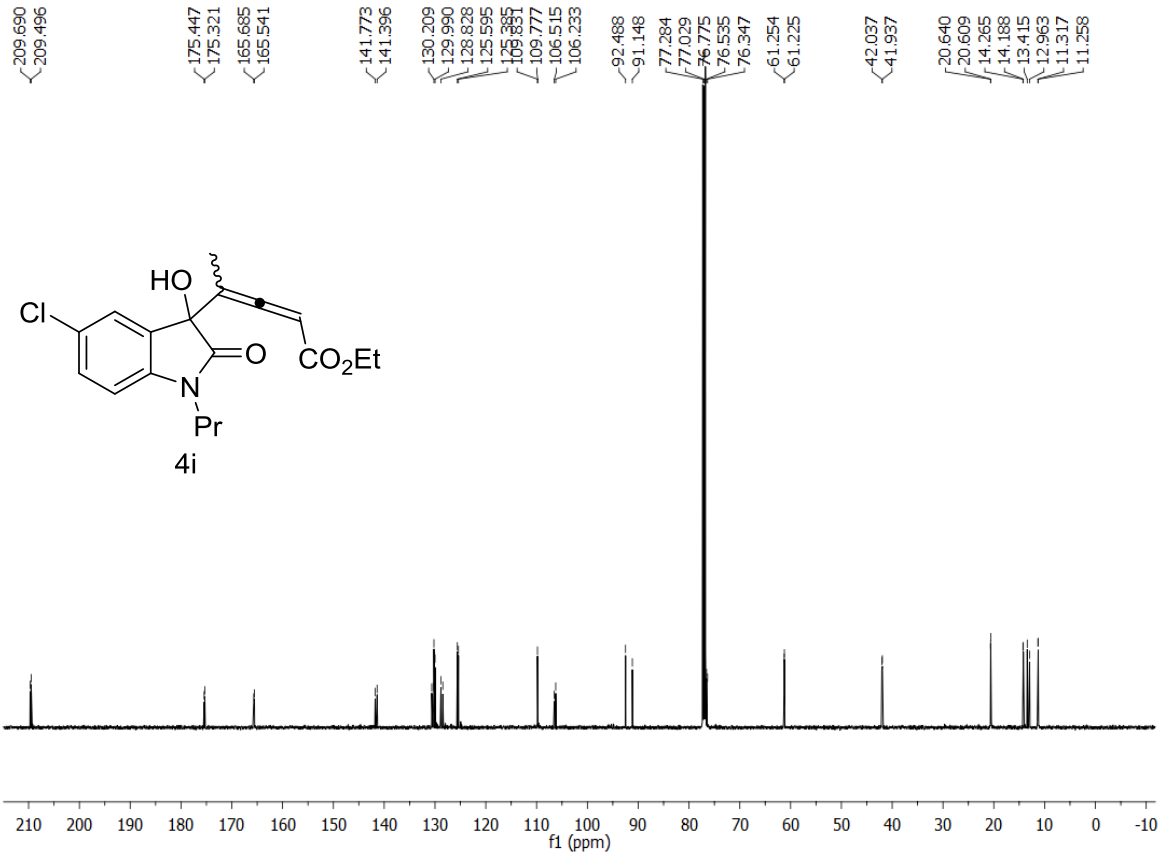


Fig 92. ^{13}C NMR of 4i

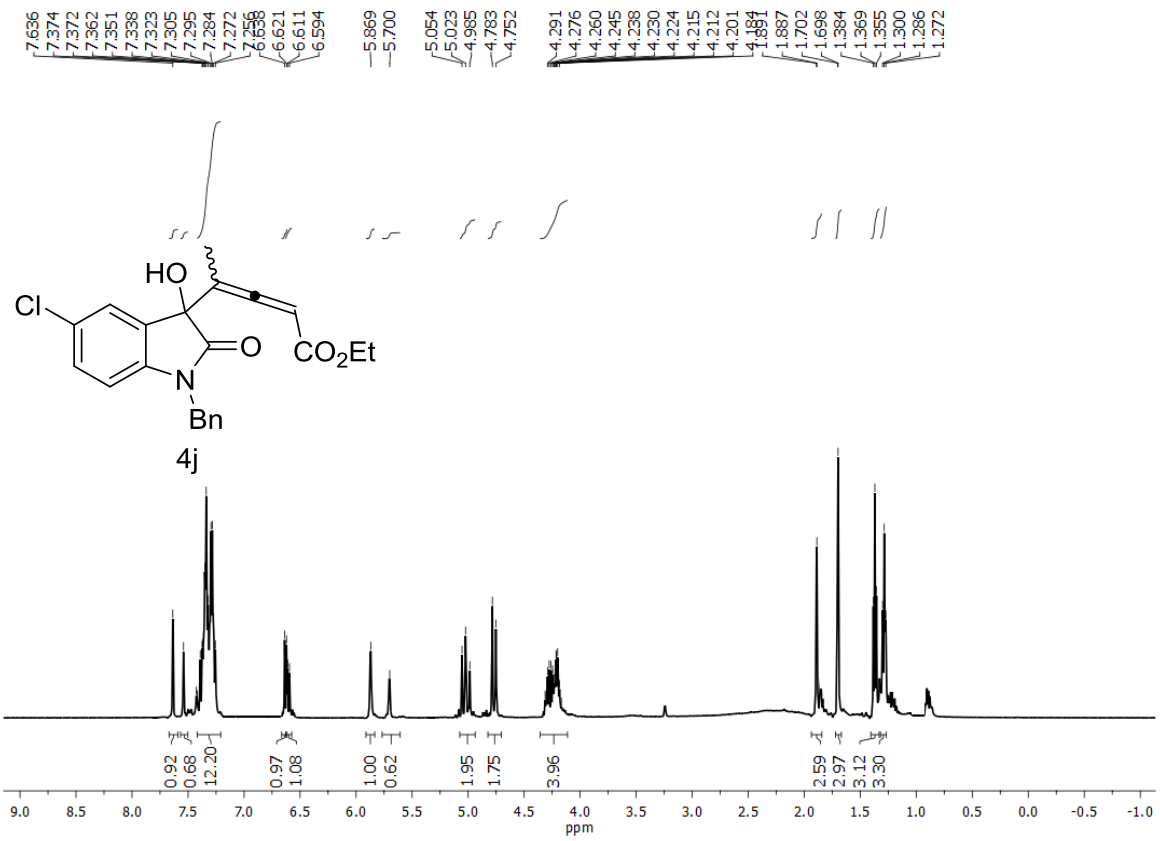


Fig 93. ^{1}H NMR of 4j

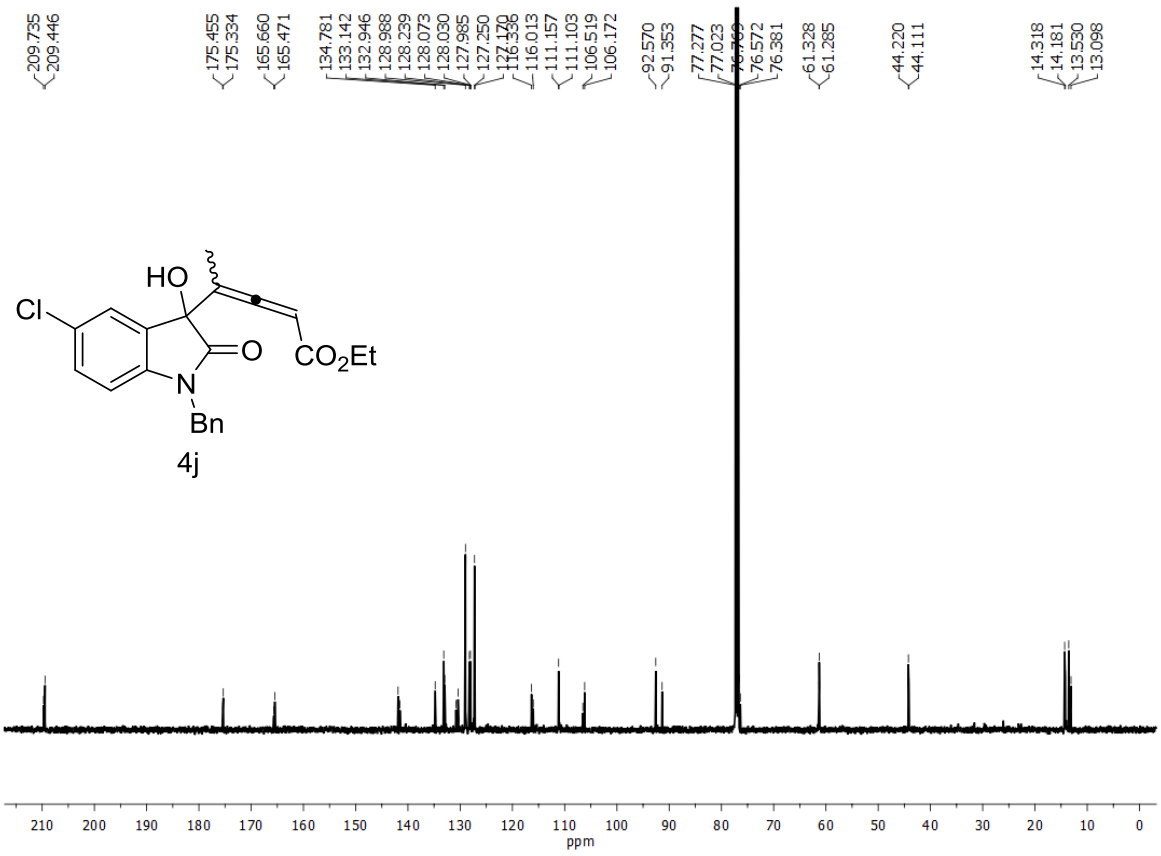


Fig 94. ^{13}C NMR of 4j

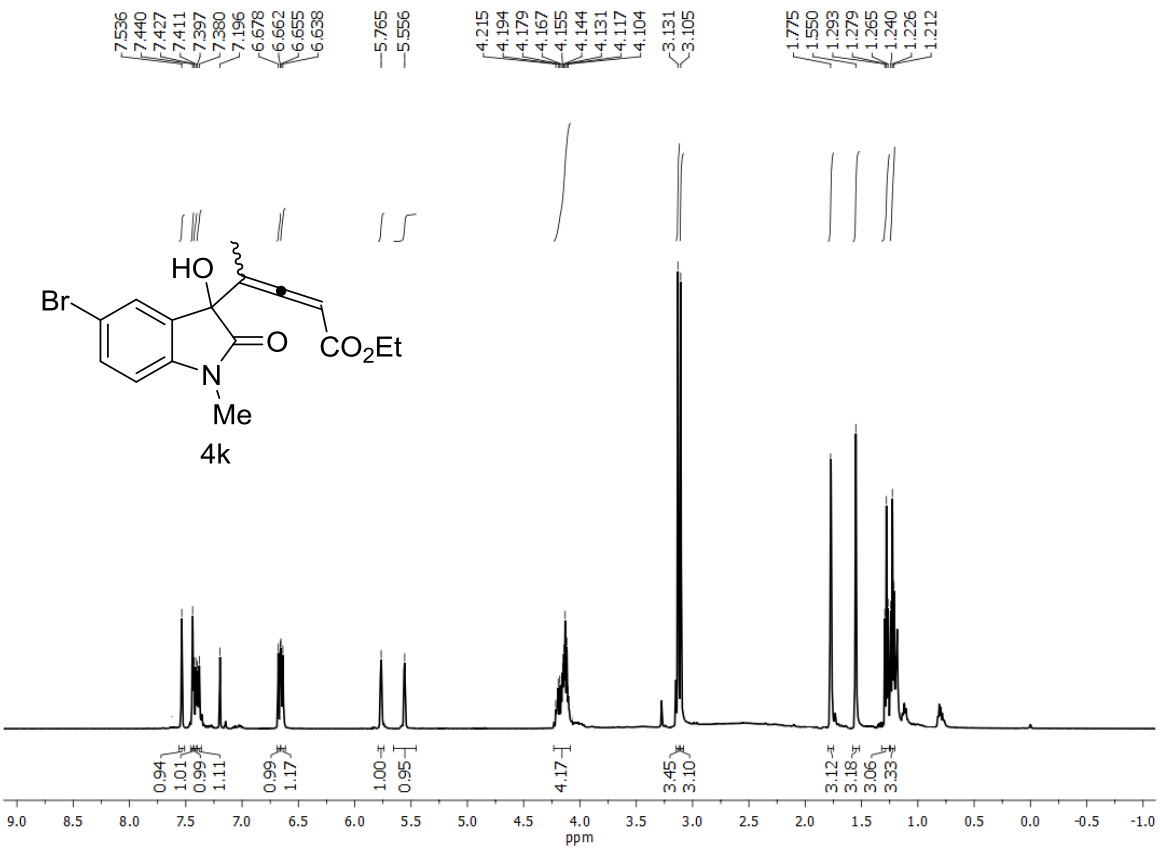


Fig 95. ^{1}H NMR of 4k

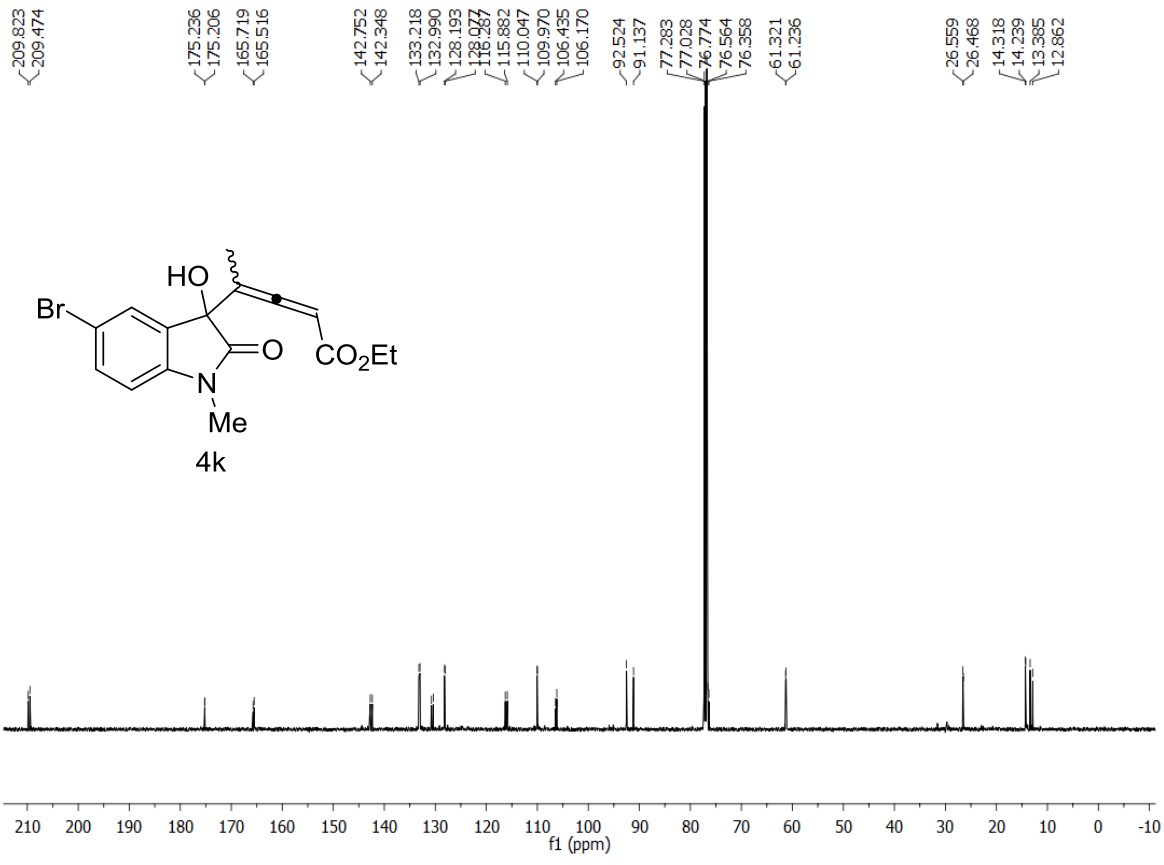


Fig 96. ^{13}C NMR of 4k

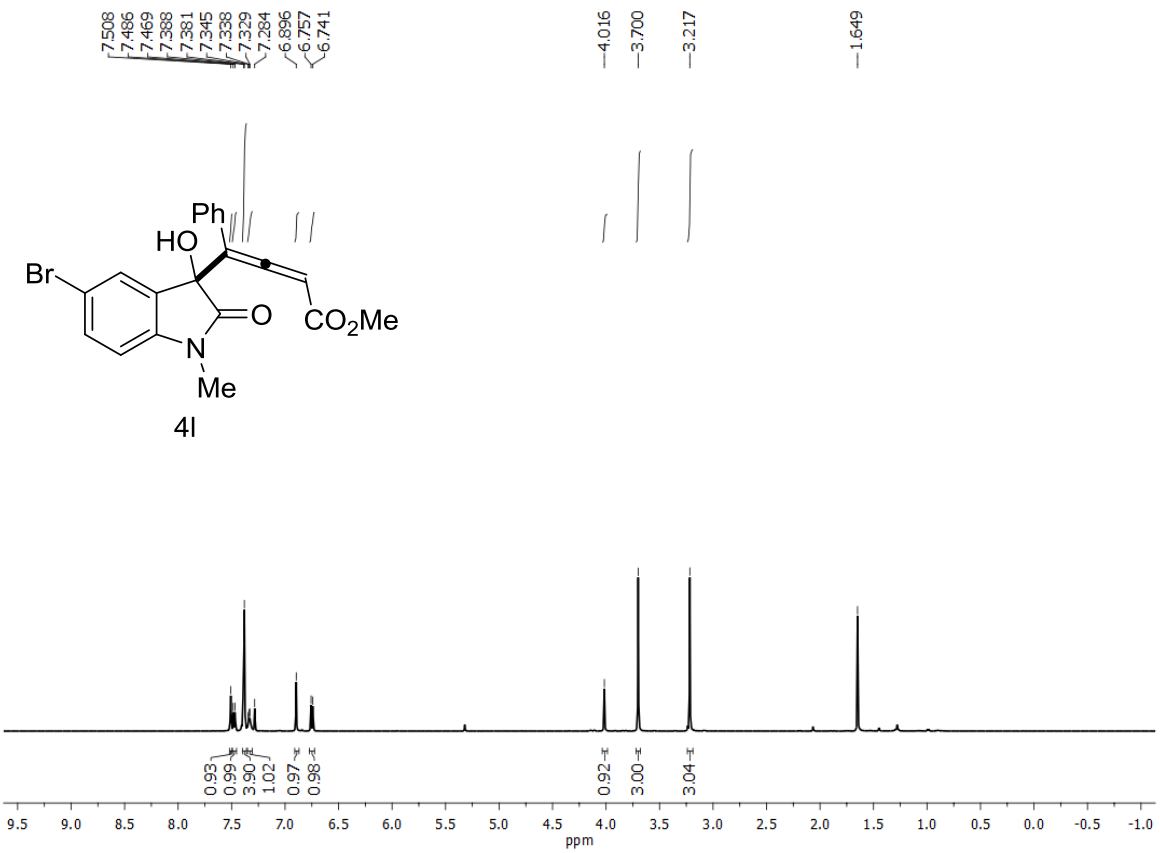


Fig 97. ^{1}HNMR of 4l

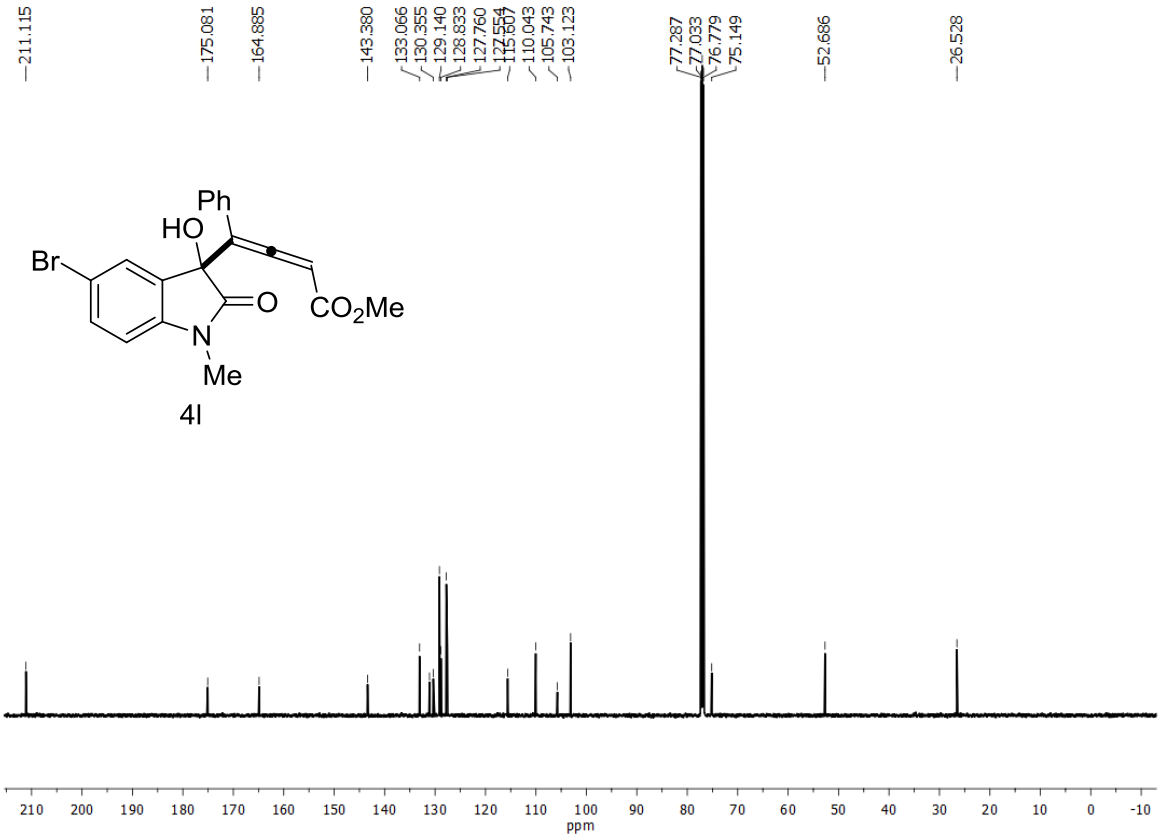


Fig 98. ^{13}CNMR of 4l

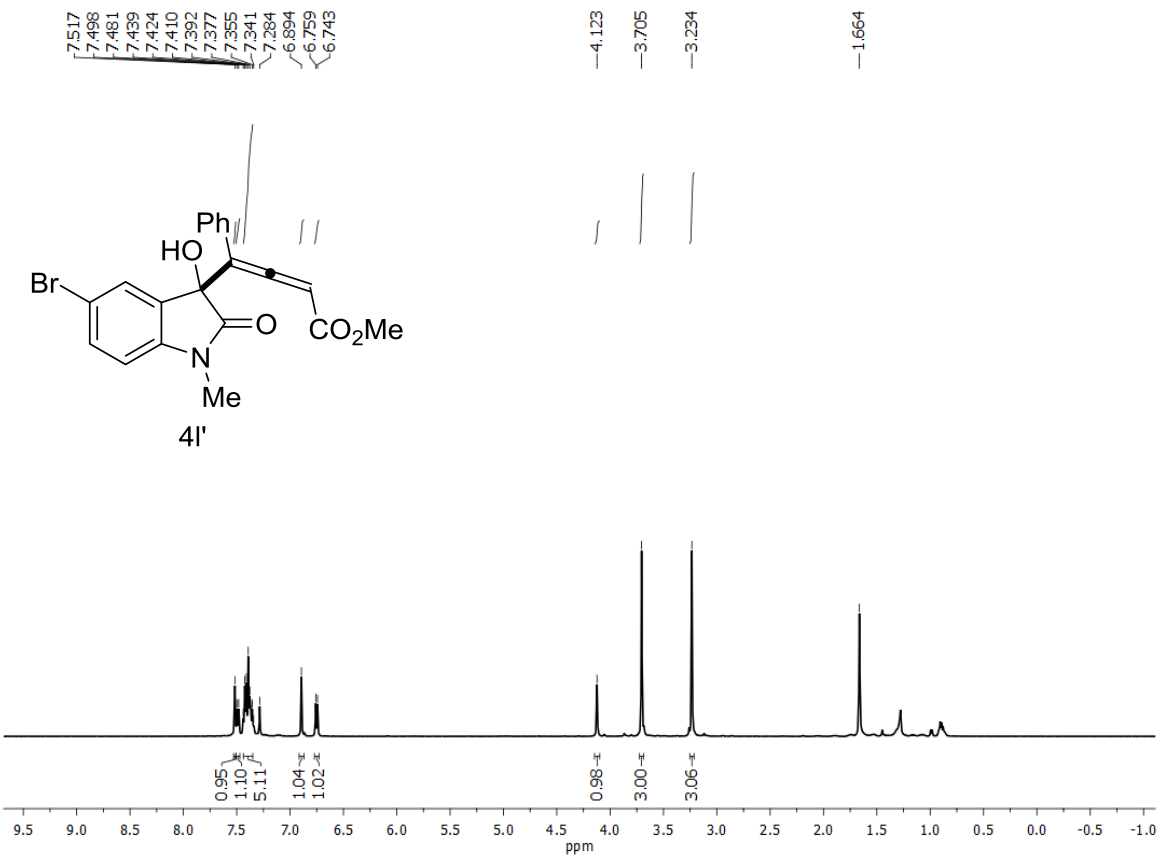


Fig 99. ^{1}HNMR of 4l'

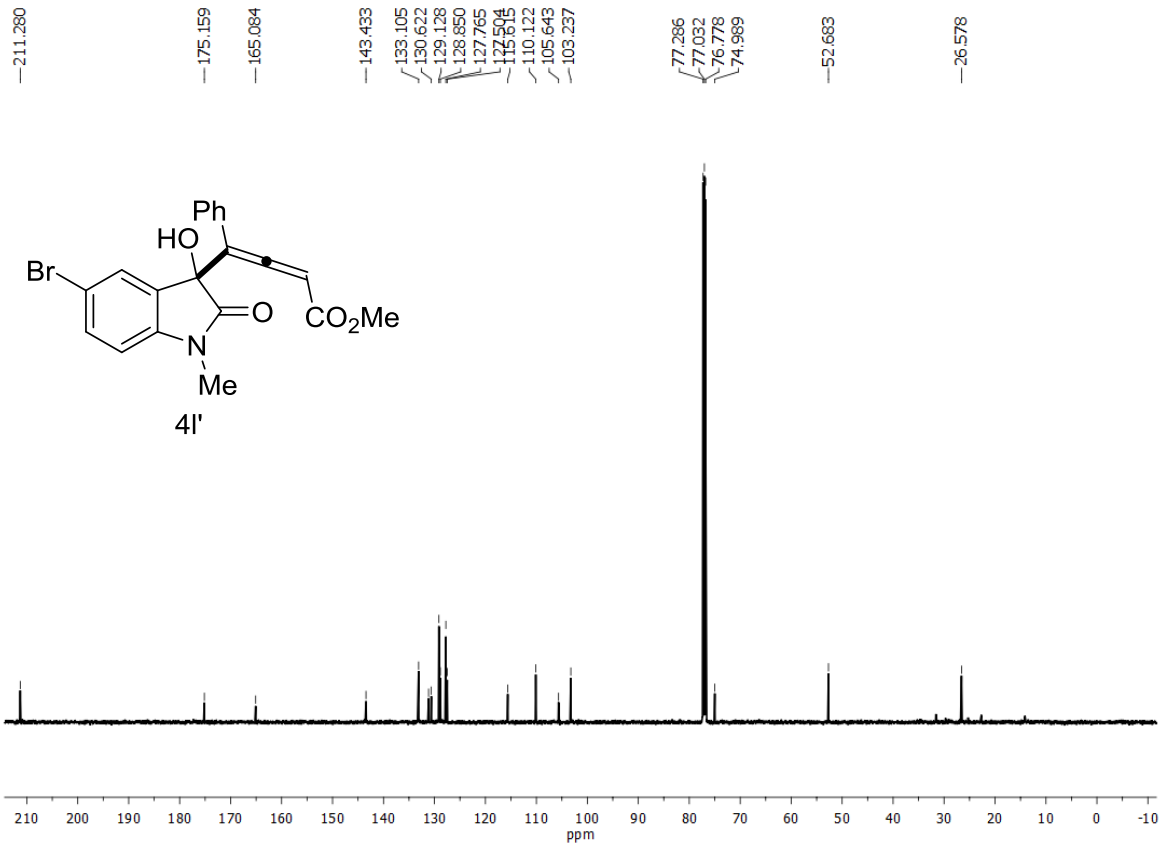


Fig 100. ^{13}CNMR of 4l'

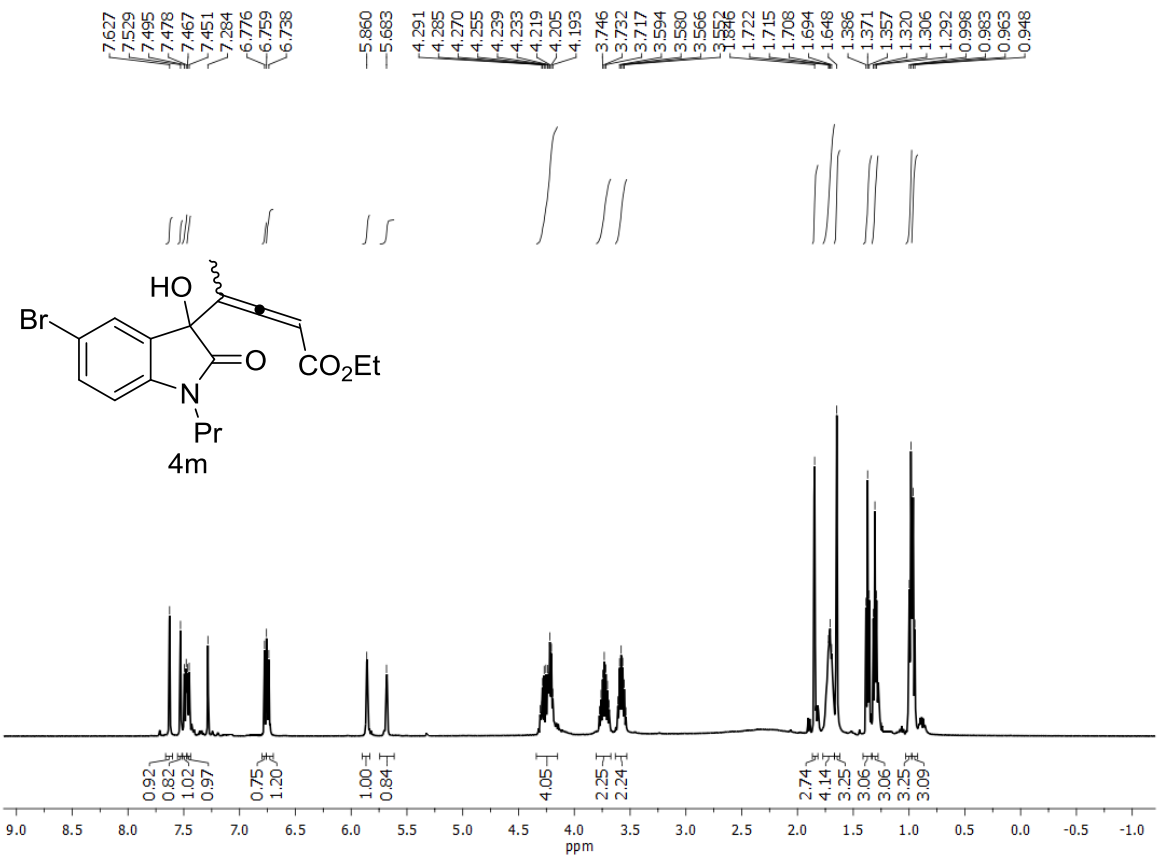


Fig 101. ^{1}H NMR of 4m

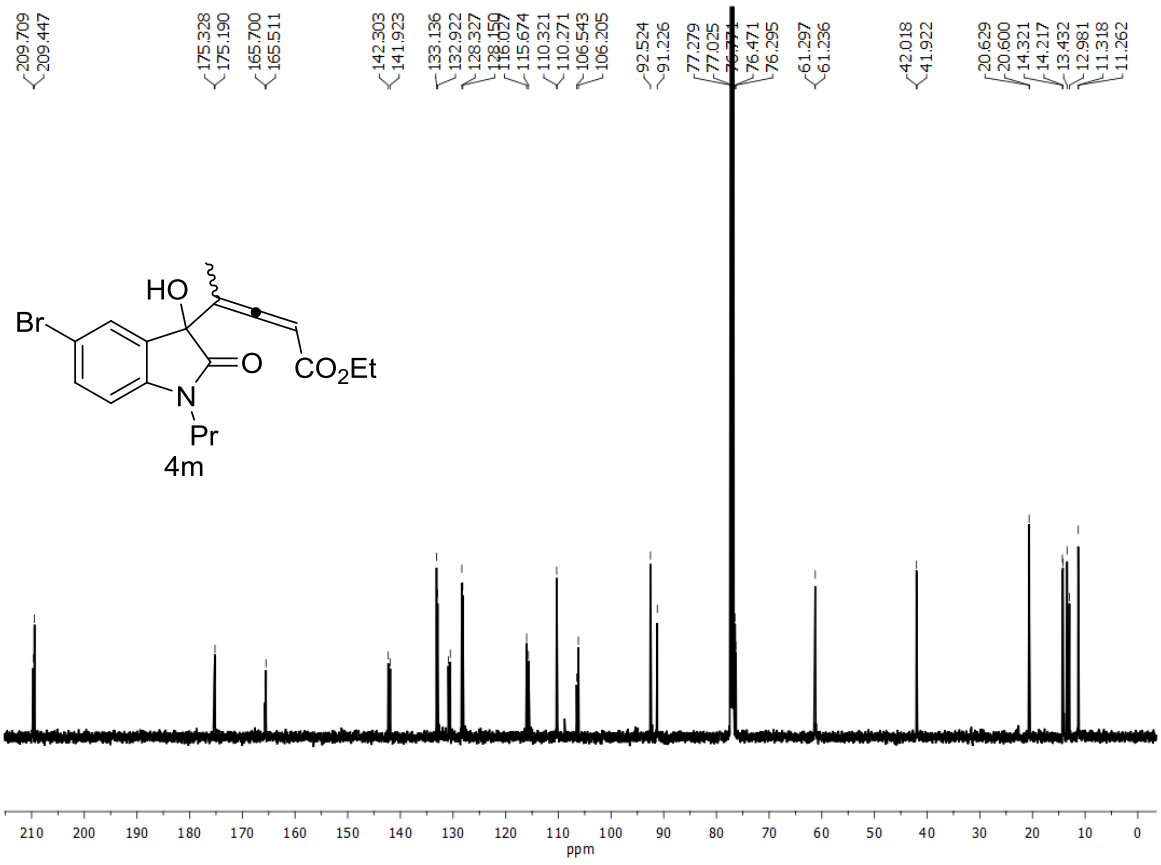


Fig 102. ^{13}C NMR of 4m

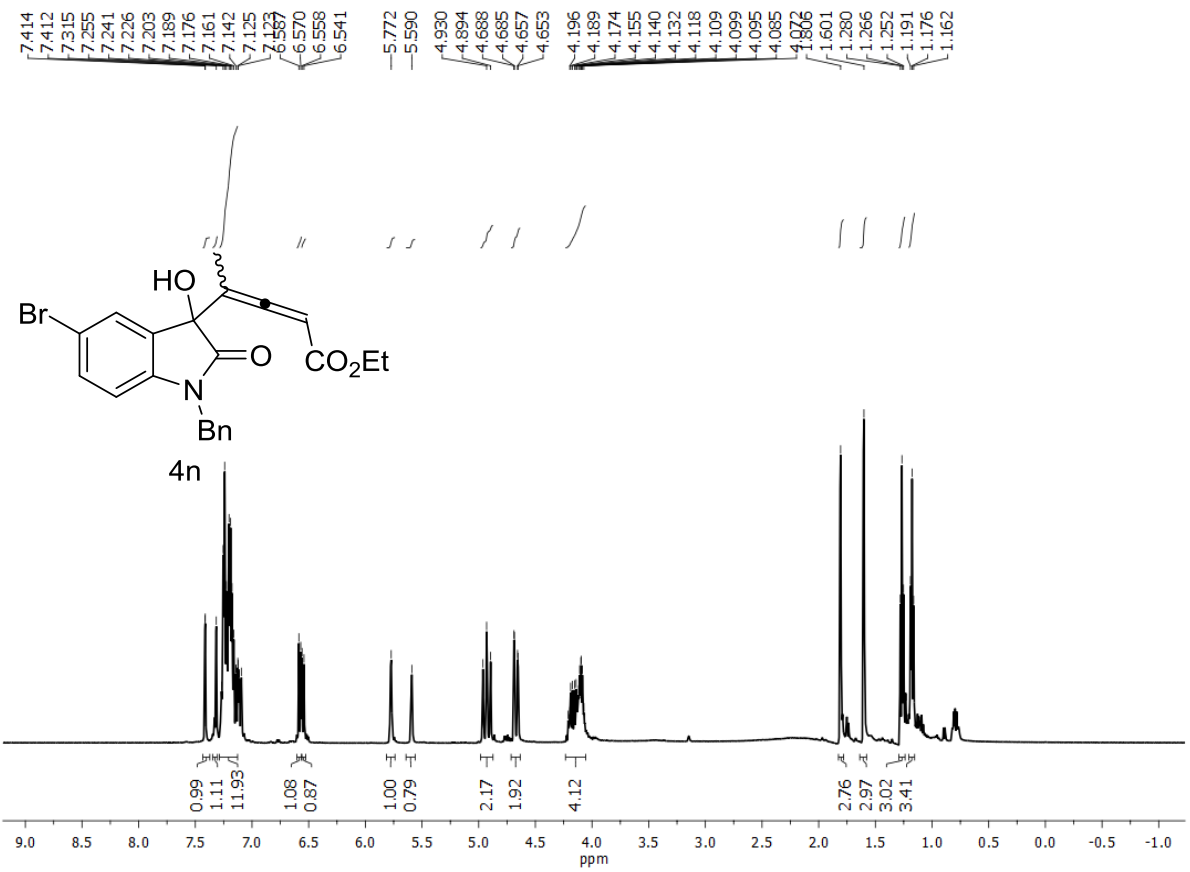


Fig 103. ^{1}H NMR of 4n

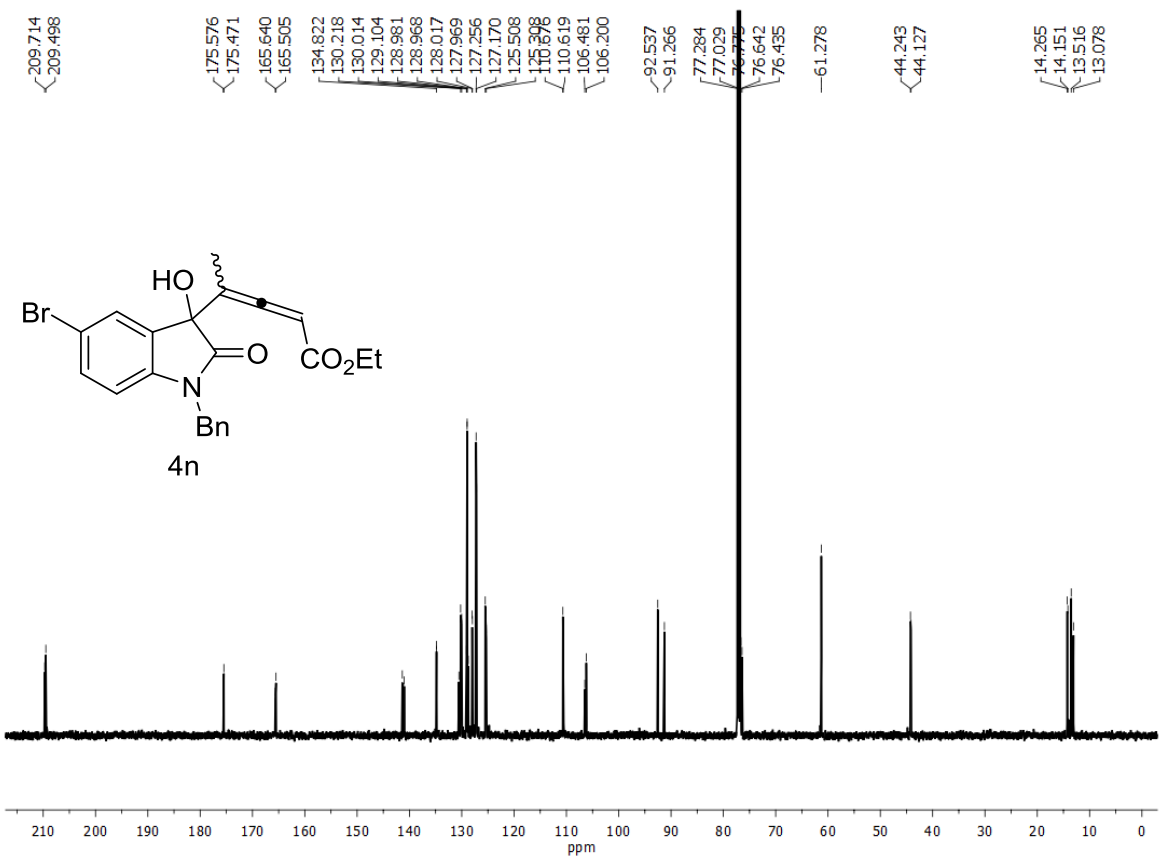


Fig 104. ^{13}C NMR of 4n

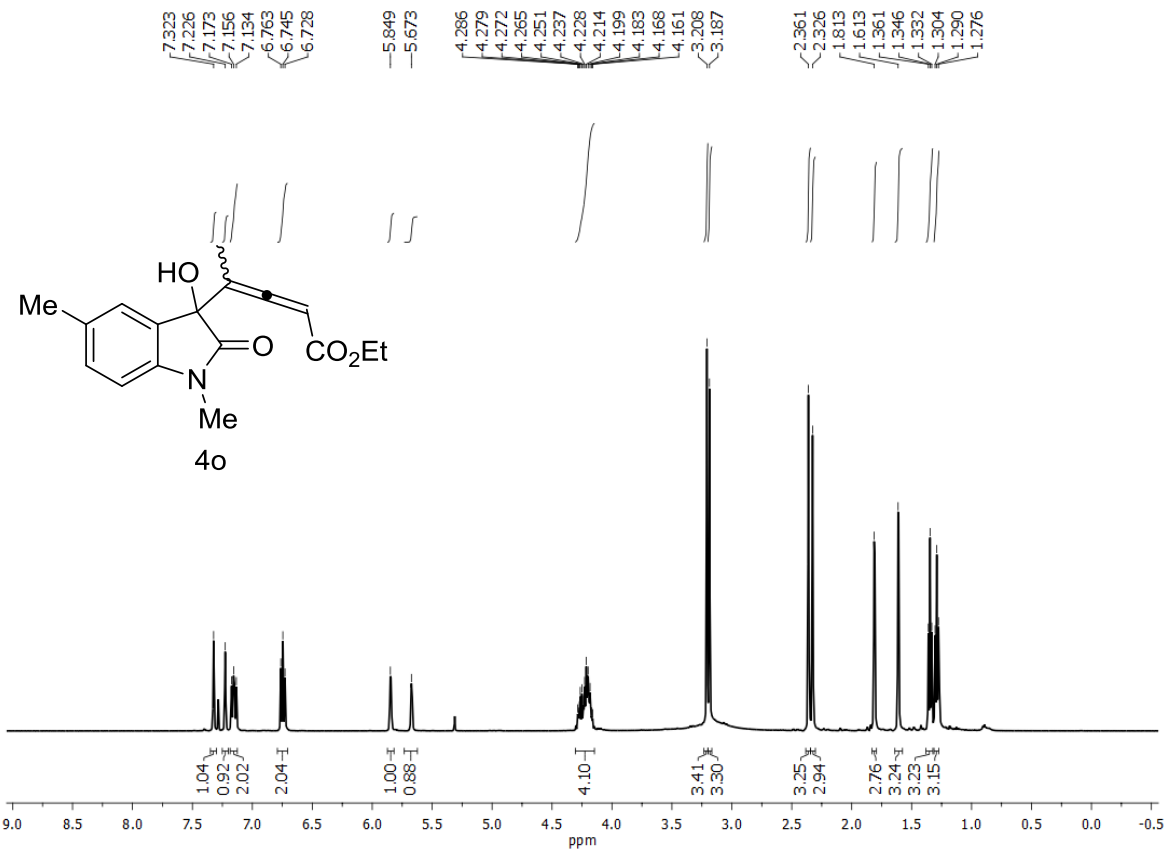


Fig 105. ^{1}H NMR of 4o

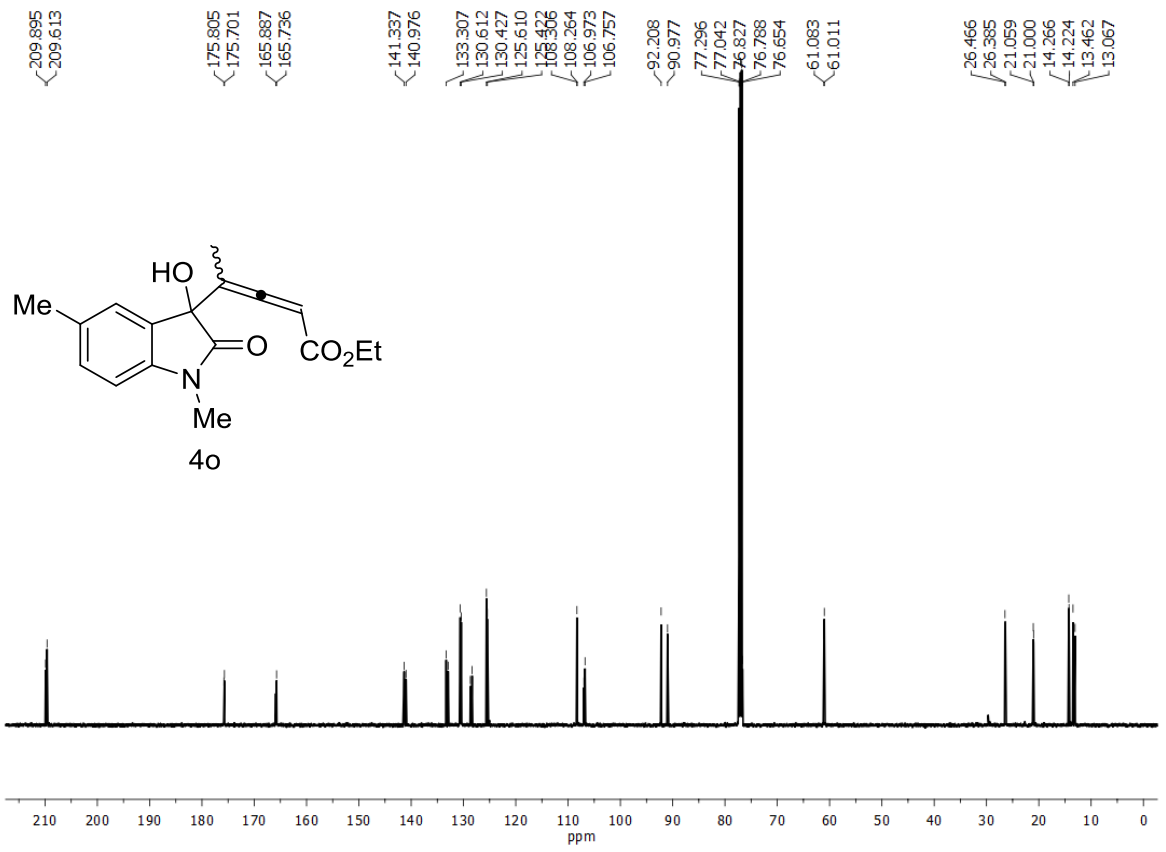


Fig 106. ^{13}C NMR of 4o

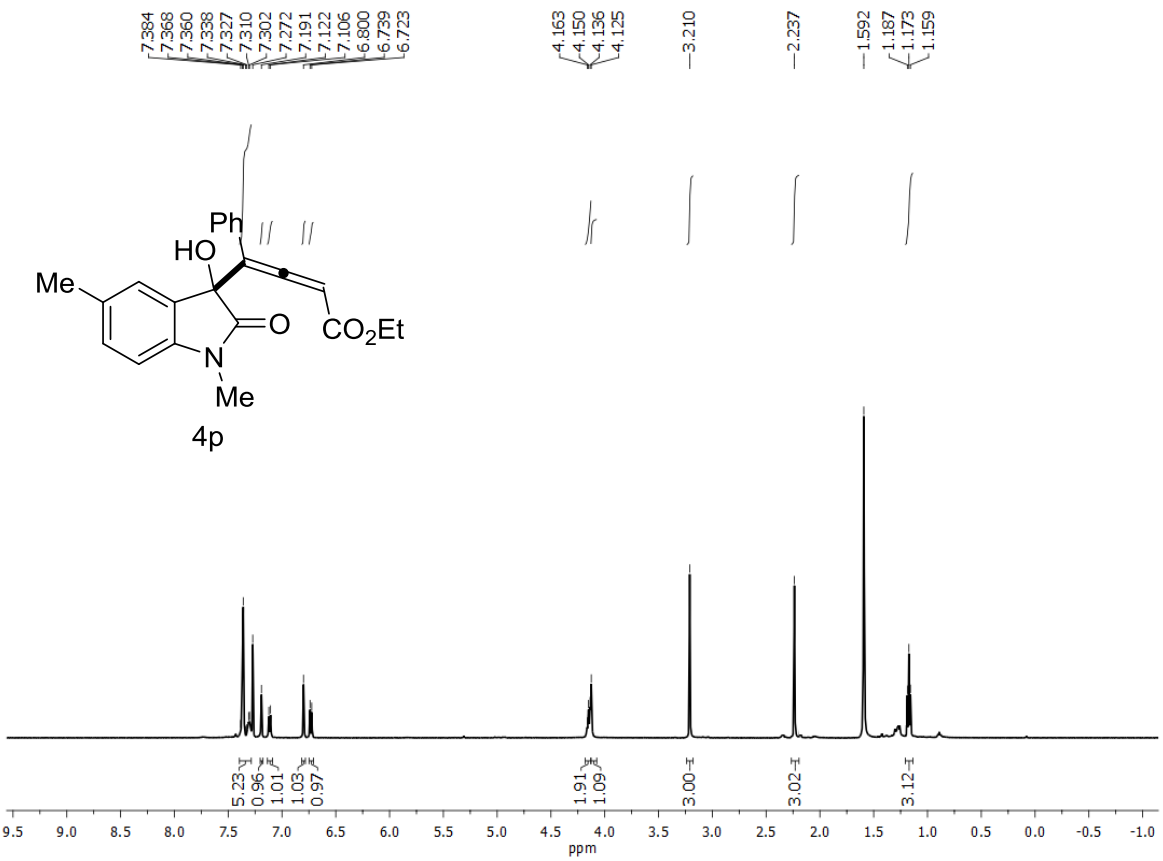


Fig 107. ^{1}H NMR of 4p

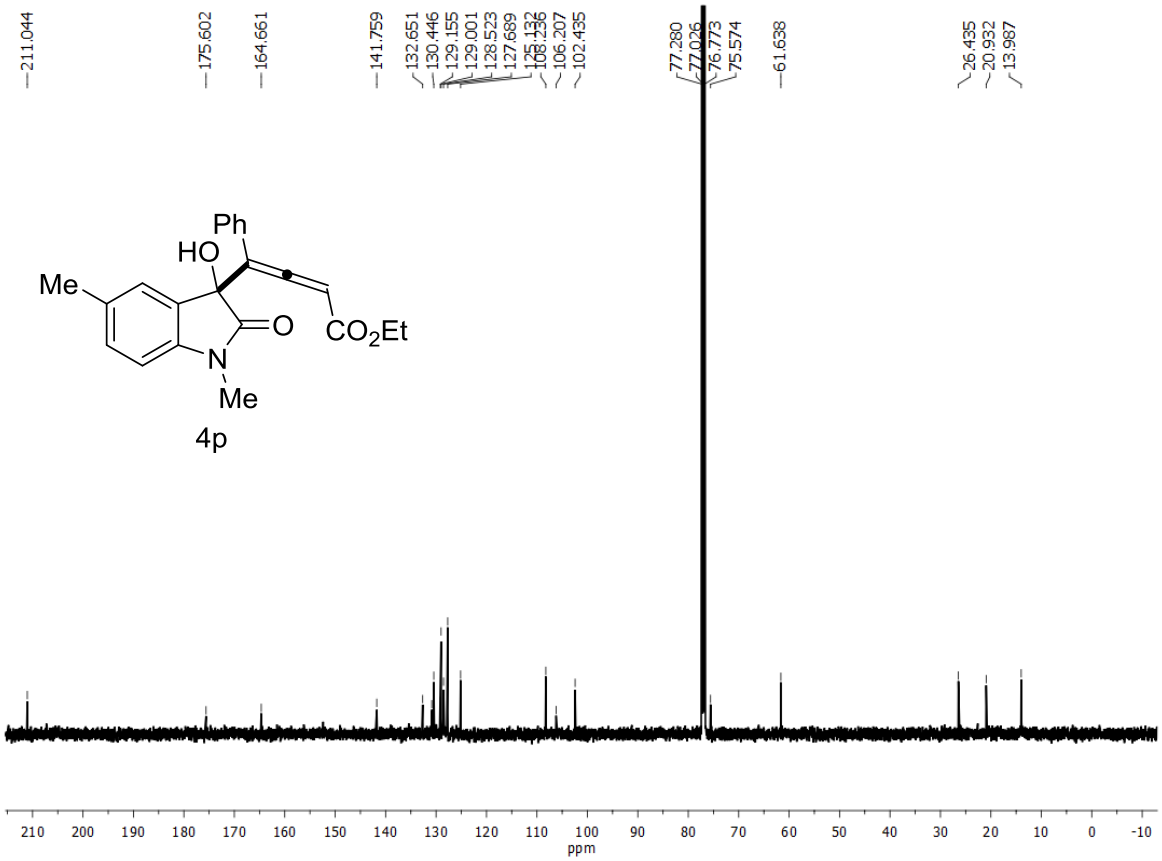


Fig 108. ^{13}C NMR of 4p

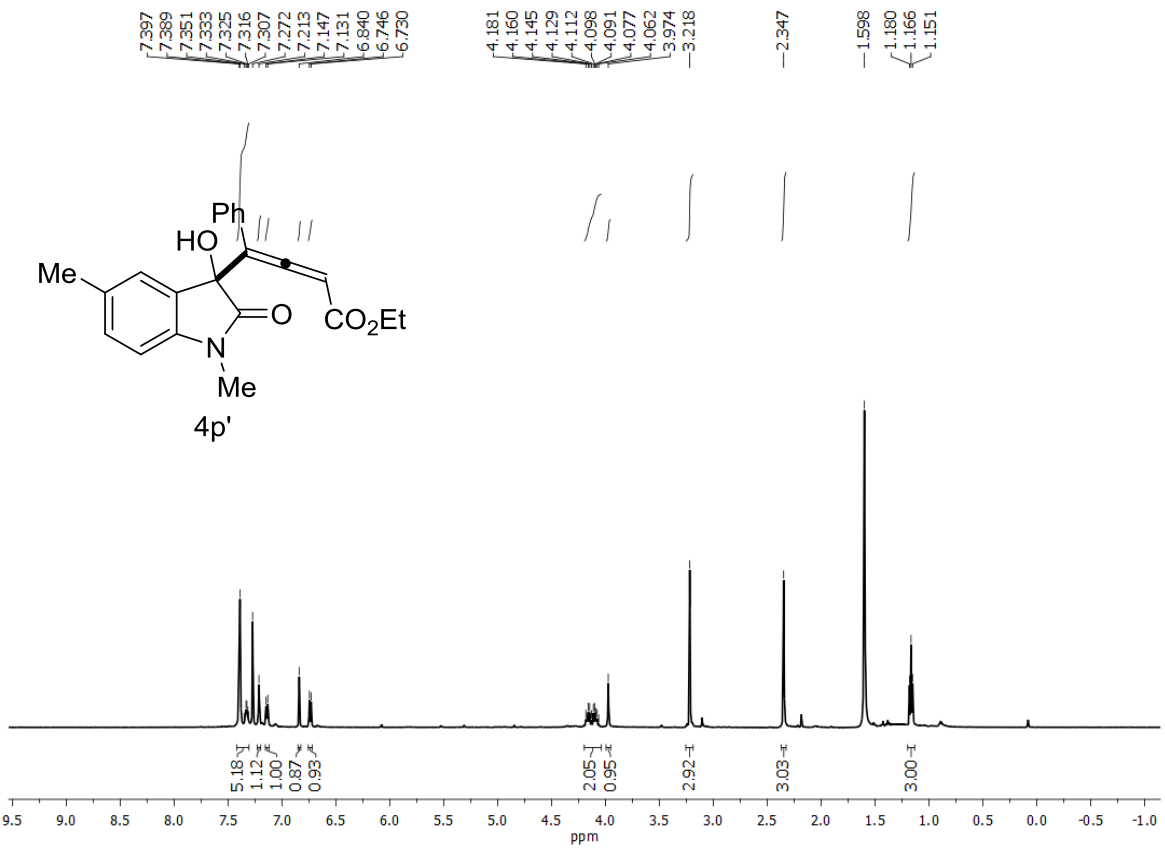


Fig 109. ^{1}H NMR of 4p'

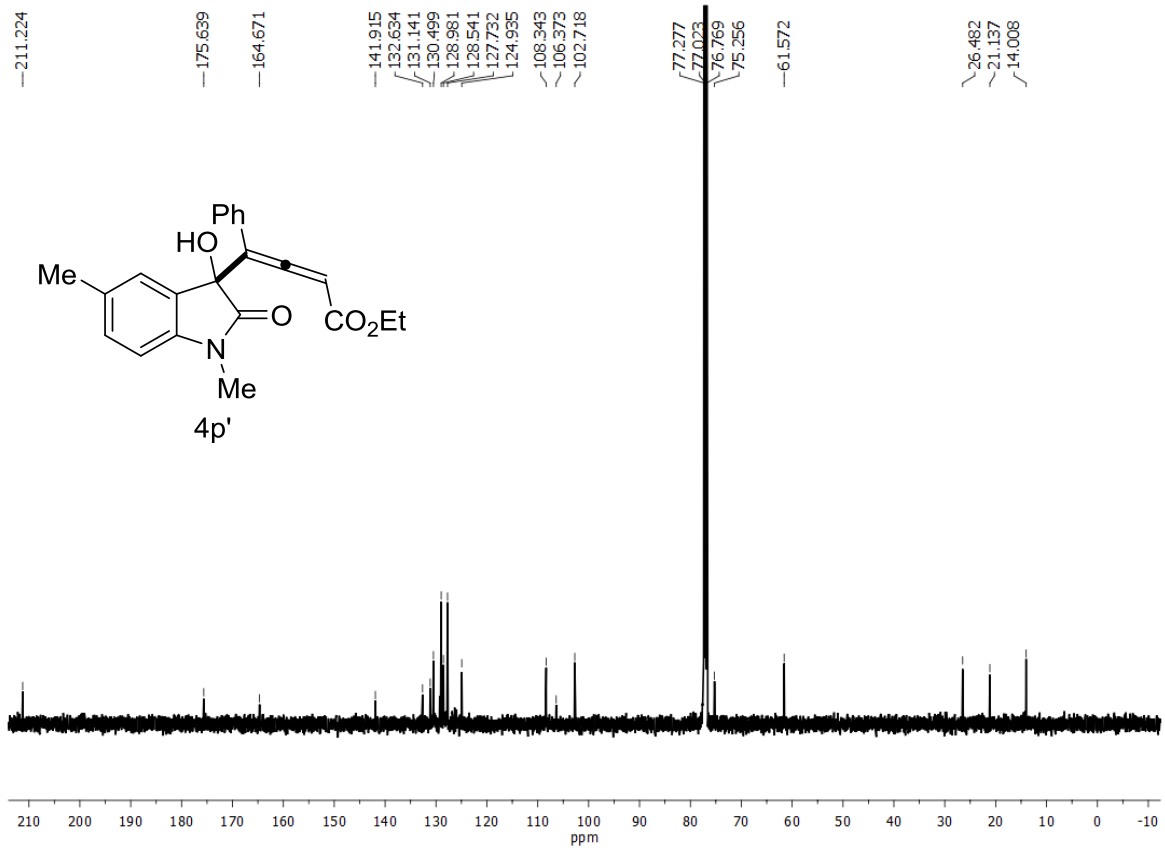


Fig 110. ^{13}C NMR of 4p'

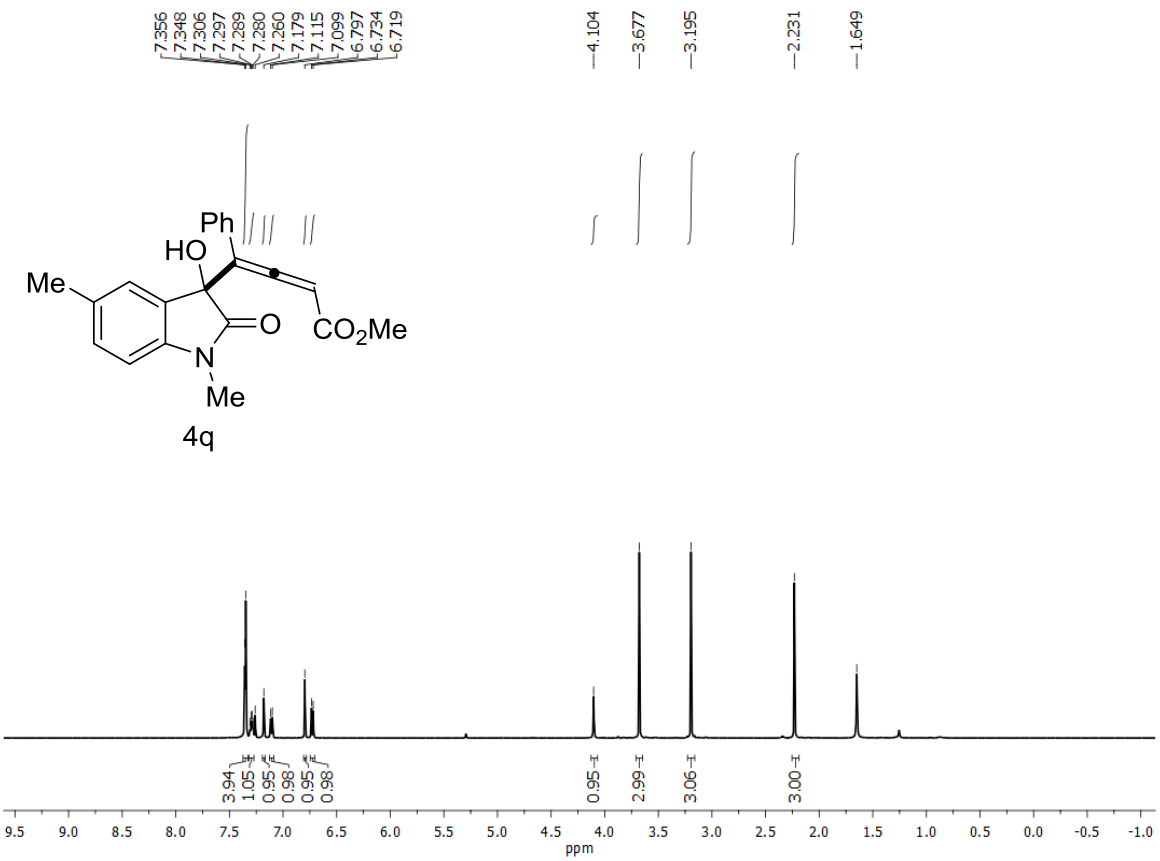


Fig 111. ^{1}H NMR of 4q

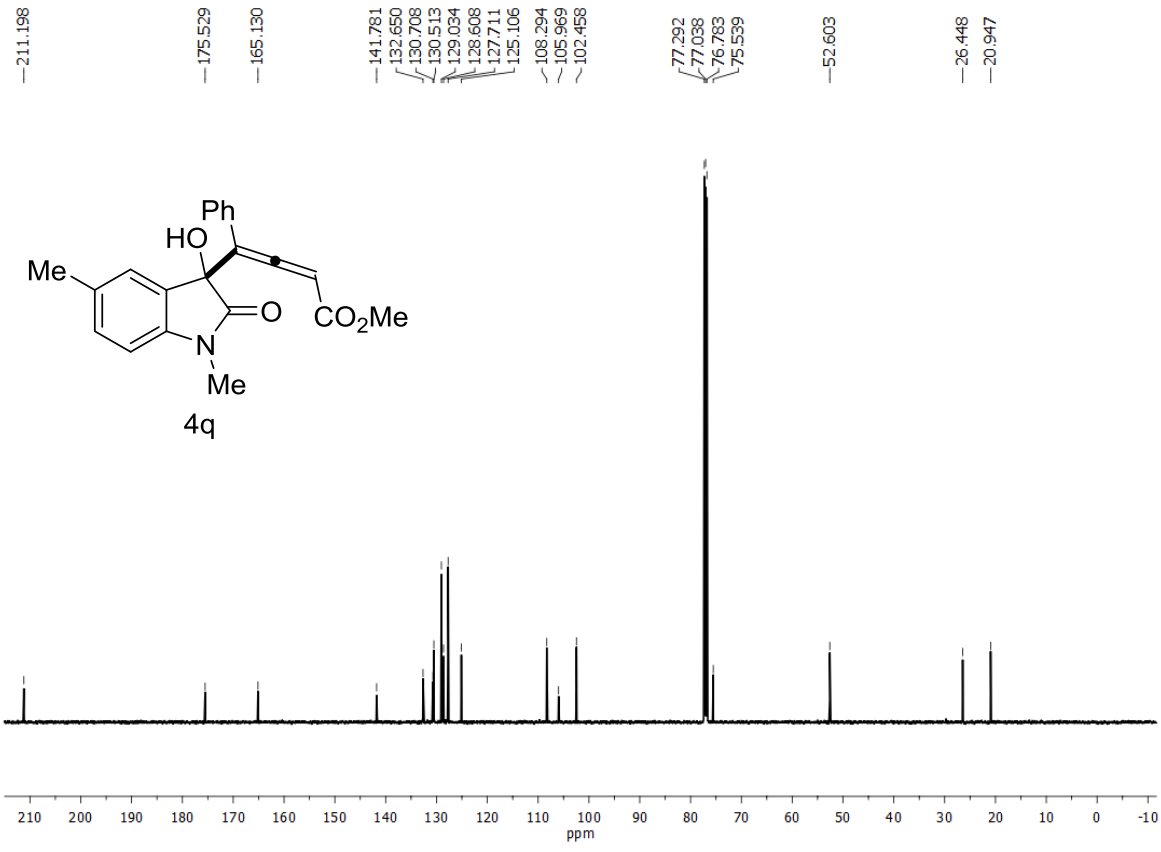


Fig 112. ^{13}C NMR of 4q

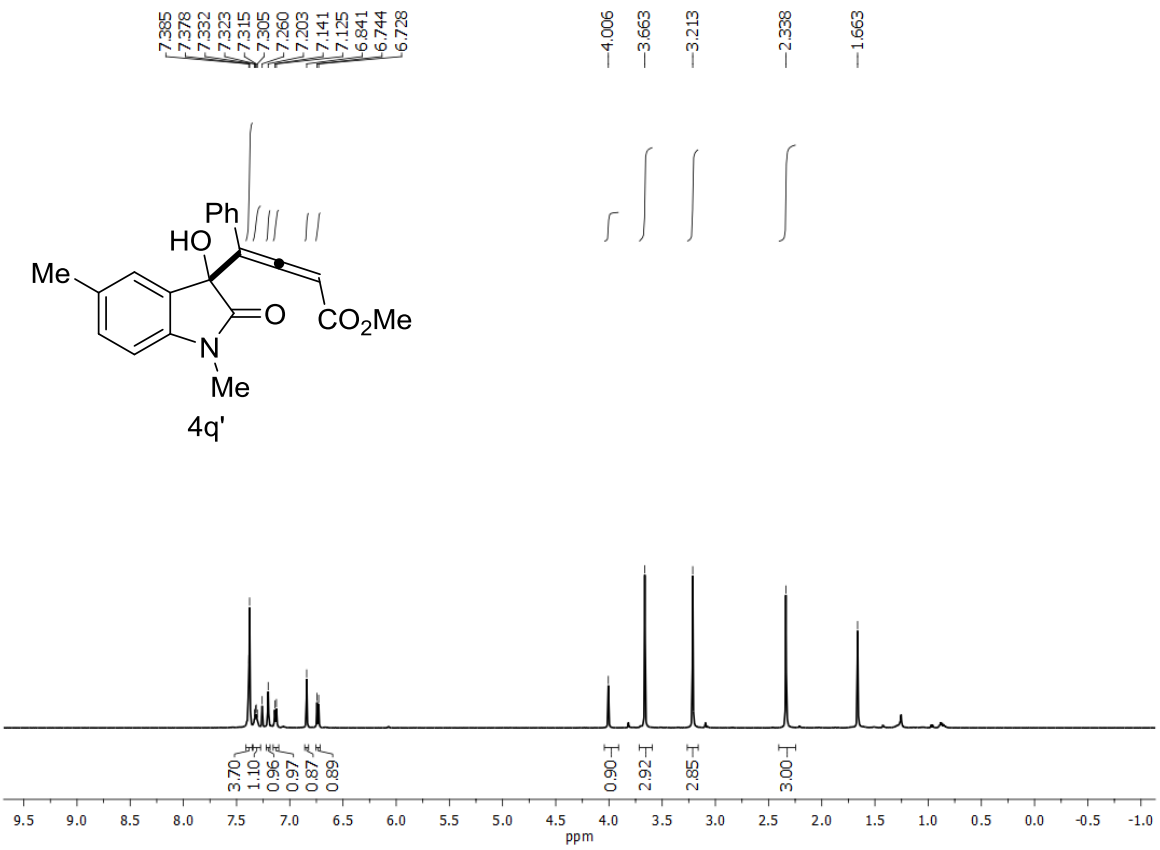


Fig 113. ^{1}H NMR of 4q'

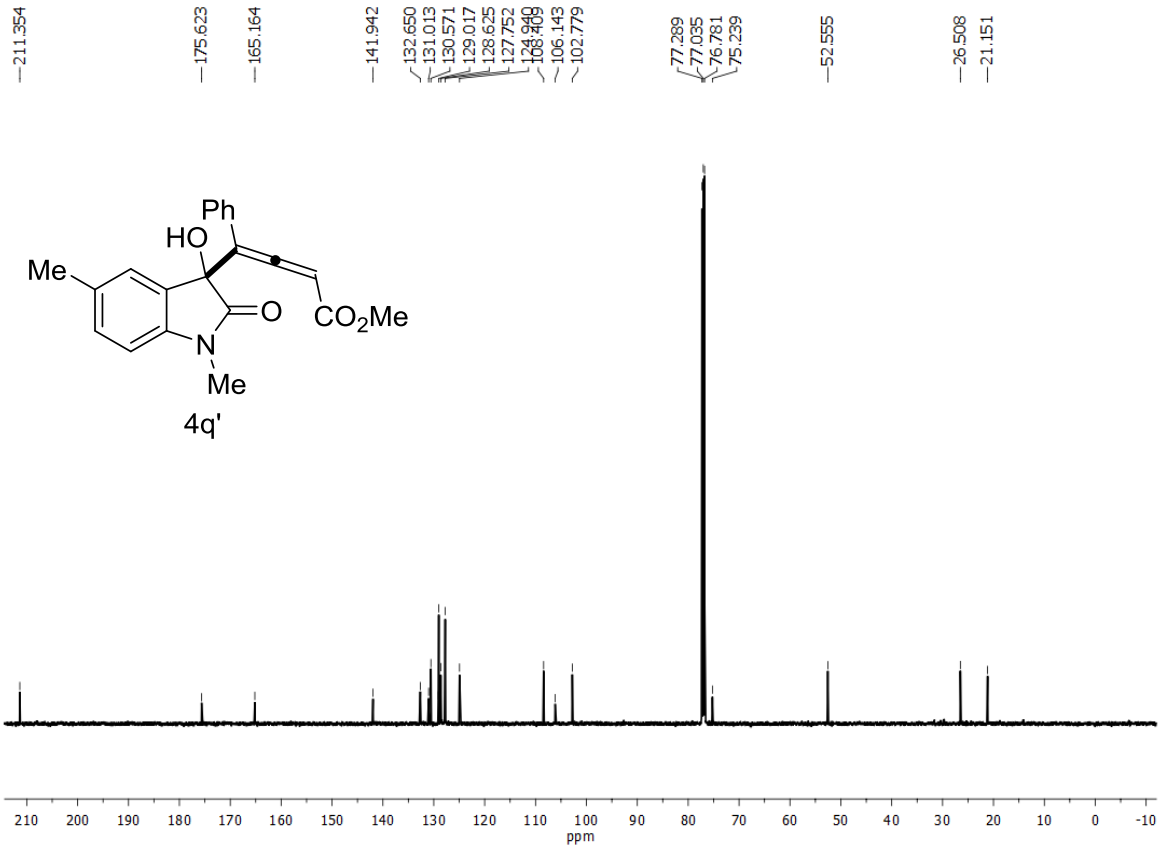


Fig 114. ^{13}C NMR of 4q'

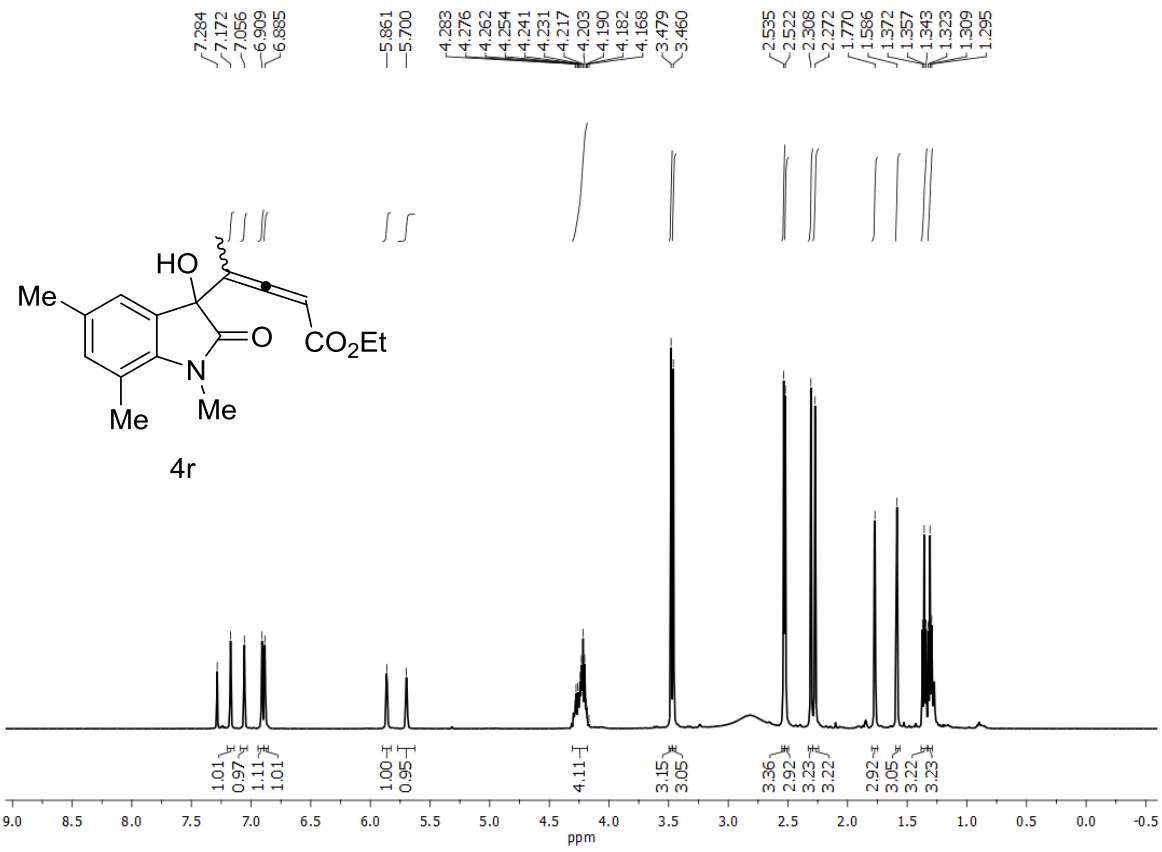


Fig 115. ^{1}H NMR of 4r

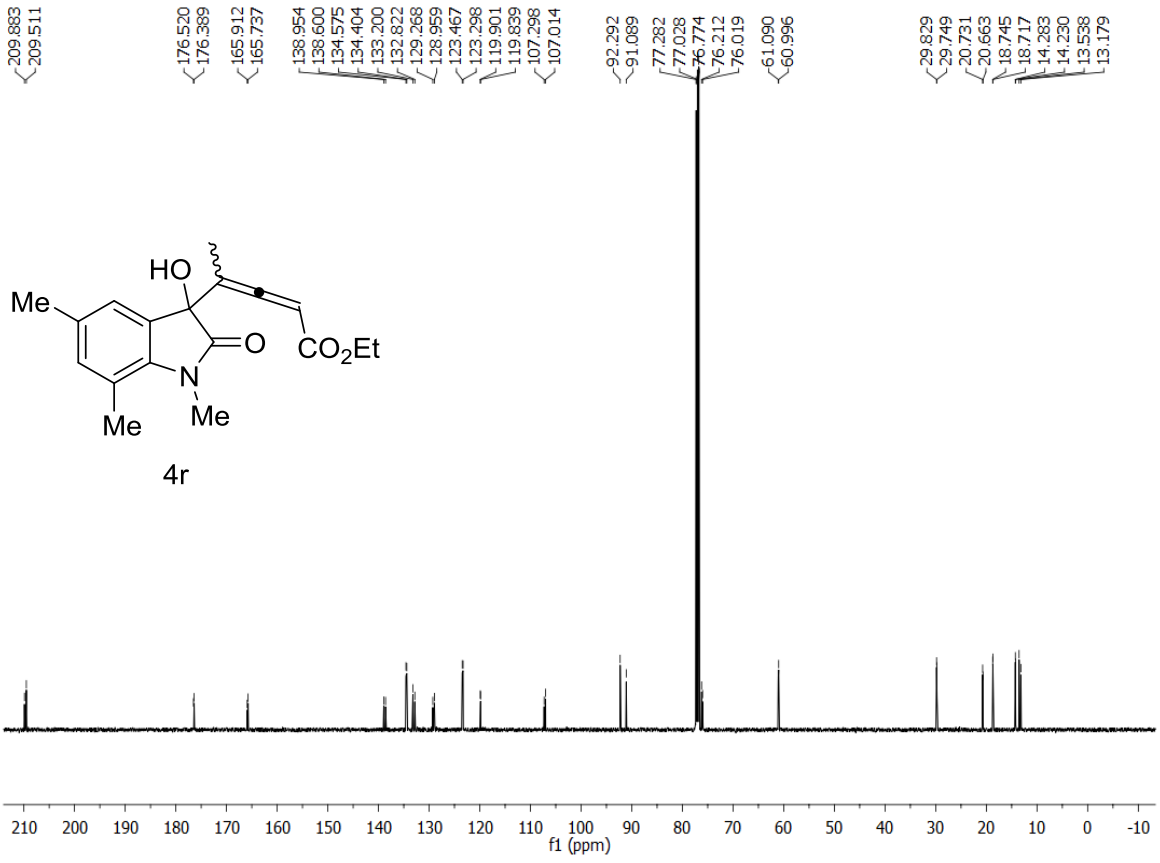


Fig 116. ^{13}C NMR of 4r

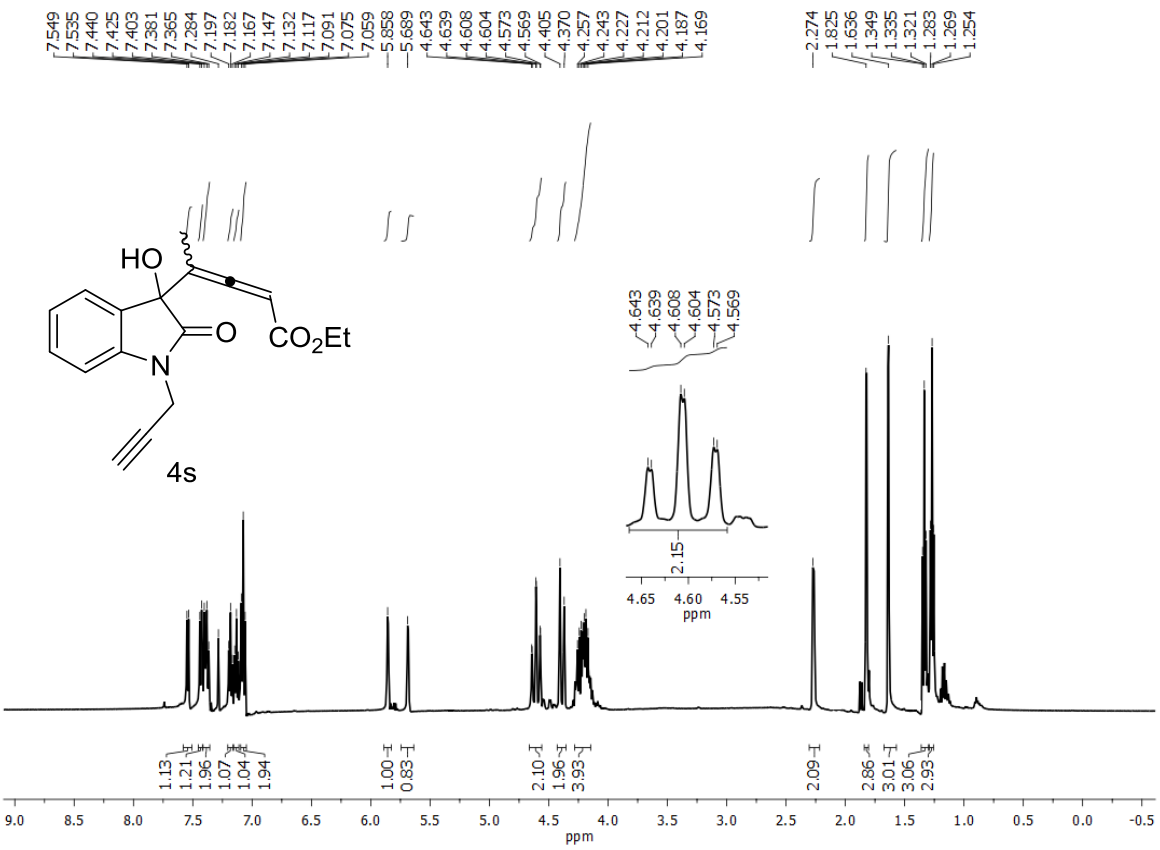


Fig 117. ^{1}H NMR of 4s

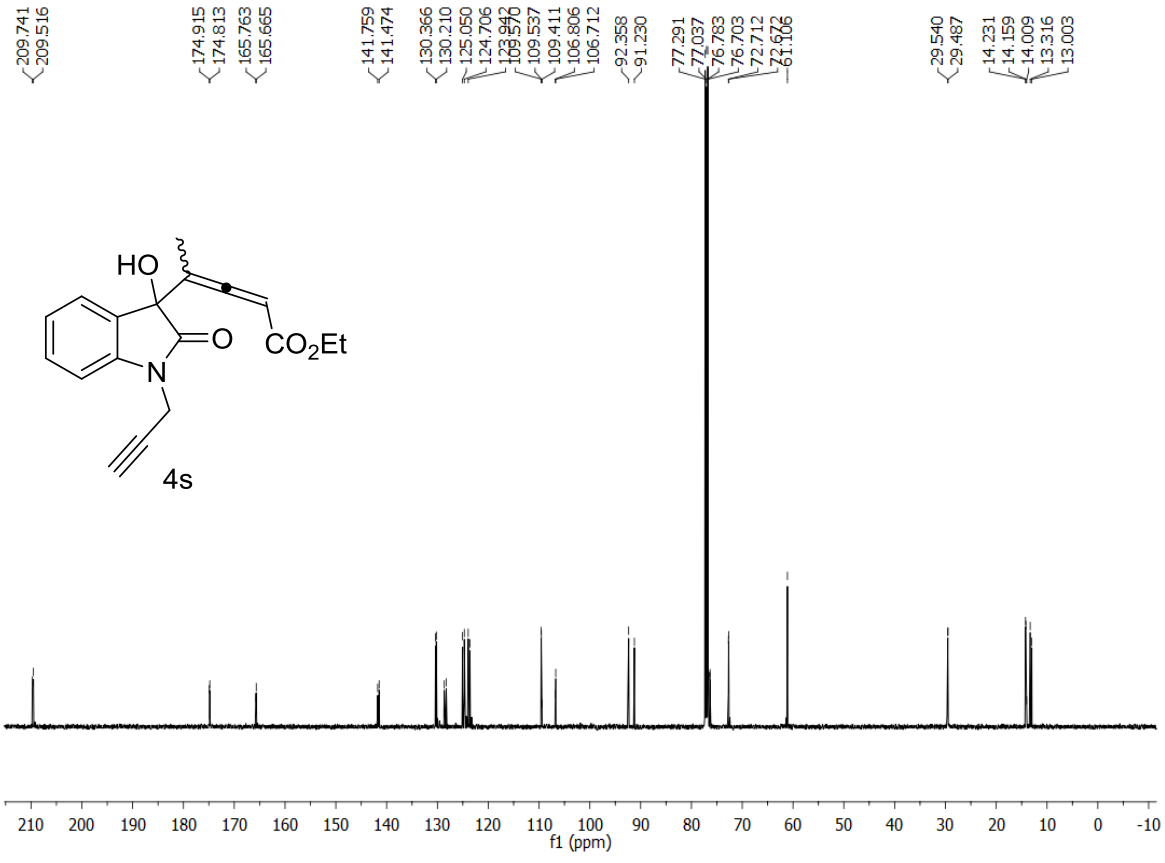


Fig 118. ^{13}C NMR of 4s

9. ORTEP diagram of compound 3ag and compound 4h

CCDC 1979517

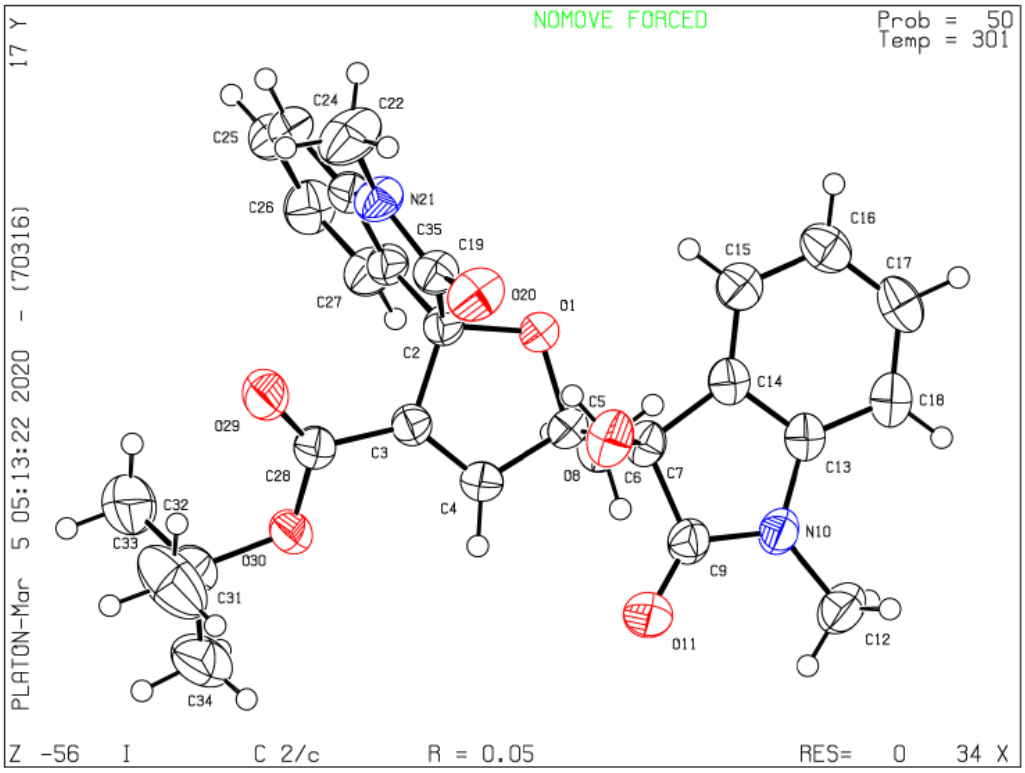


Fig 85. ORTEP drawing of compound 3ag

CCDC 1979628

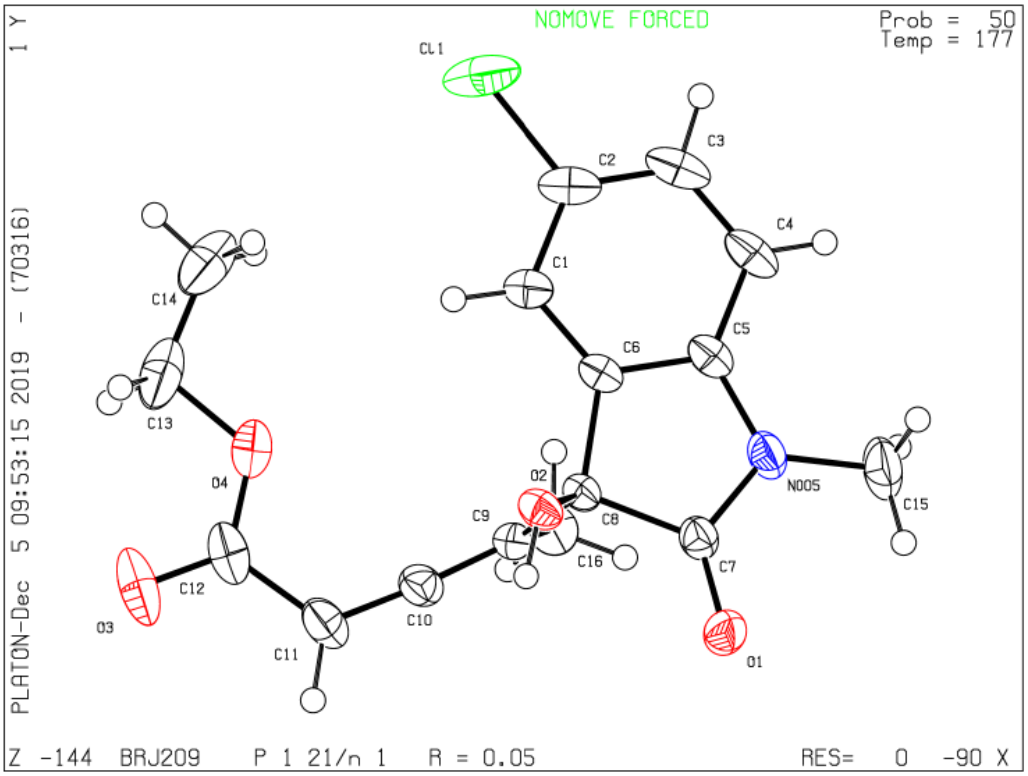


Fig 86. ORTEP drawing for compound 4h