Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Table of contents

1. General information S2

2. Optimization details S2

3. General procedure for the synthesis of C3-alkylated 3-thioxyindolin-2-one (4) S3

4. Mechanistic studies S3

5. Characterization data for C3-alkylated 3-thioxyindolin-2-one (4) S6

6. Spectroscopic data for C3-alkylated 3-thioxyindolin-2-one (4) S24

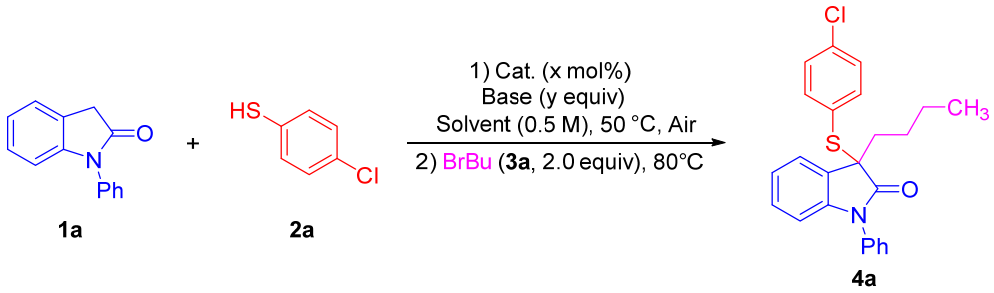
7. Spectroscopic data for compounds 5-8 ..... S58

1. General information

General information. Unless otherwise noted, all reagents including the starting materials (indolin-2-ones, thiols and alkyl halides) are commercially available (purchased from Sigma-Aldrich, Aladdin, and Alfa Aesar) and were used without further purification. Melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-*d*$_6$ or $CDCl_3$ as the solvent. Chemical shifts are reported relative to TMS as internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant in hertz, and number of protons. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource.

2. Optimization details

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



Entry	Cat. (10 mol%)	Base (equiv)	Solvent (0.5 M)	Time (h)	Yield (%)
1	CuTc	K_2CO_3(2.0)	DMF	1.5	72
2	---	K_2CO_3(2.0)	DMF	1.5	42
3	CuTc	---	DMF	1.5	0
4[b]	CuTc	K_2CO_3(2.0)	DMF	1.5	59
5	CuTc	K_2CO_3(1.0)	DMF	1.5	43
6	CuCl	K_2CO_3(2.0)	DMF	1.5	36
7	CuBr	K_2CO_3(2.0)	DMF	1.5	19
8	CuI	K_2CO_3(2.0)	DMF	1.5	52
9	$Cu(OAc)_2·H_2O$	K_2CO_3(2.0)	DMF	1.5	53
10	$FeCl_3$	K_2CO_3(2.0)	DMF	1.5	41
11	$Fe(NO_3)_3·9H_2O$	K_2CO_3(2.0)	DMF	1.5	60
12	$FeCl_2·4H_2O$	K_2CO_3(2.0)	DMF	1.5	35
13	CuTc	K_2CO_3(2.0)	DMF	1.5	72
14	CuTc	Na_2CO_3(2.0)	DMF	1.5	17

15	CuTc	Cs_2CO_3(2.0)	DMF	1.5	71
16	CuTc	tBuOK(2.0)	DMF	1.5	<5
17	CuTc	NaOH(2.0)	DMF	1.5	trace
18	CuTc	KOH(2.0)	DMF	1.5	<5
19	CuTc	piperidine(2.0)	DMF	2.5	<5
20	CuTc	TEA (2.0)	DMF	2.5	21
21	CuTc	K_2CO_3(2.0)	DMAc	1.5	59
22	CuTc	K_2CO_3(2.0)	DMSO	1.5	82
23	CuTc	K_2CO_3(2.0)	EtOH	1.5	5
24	CuTc	K_2CO_3(2.0)	H_2O	1.5	0
25	CuTc	K_2CO_3(2.0)	PhCl	1.5	11
26	CuTc	K_2CO_3(2.0)	DCE	1.5	0
27[c]	CuTc	K_2CO_3(2.0)	DMSO	2	64
28[d]	CuTc	K_2CO_3(2.0)	DMSO	2	62
29[e]	CuTc	K_2CO_3(2.0)	DMSO	1.5	75

[a] Reaction conditions: **1a** (1.0 mmol, 1.0 equiv), **2a** (1.0 mmol, 1.0 equiv), **3a** (2.0 mmol, 2.0 equiv), solvent (2.0 mL), under open air.

[b] CuTc 20 mol%.

[c] DMSO 0.25 M.

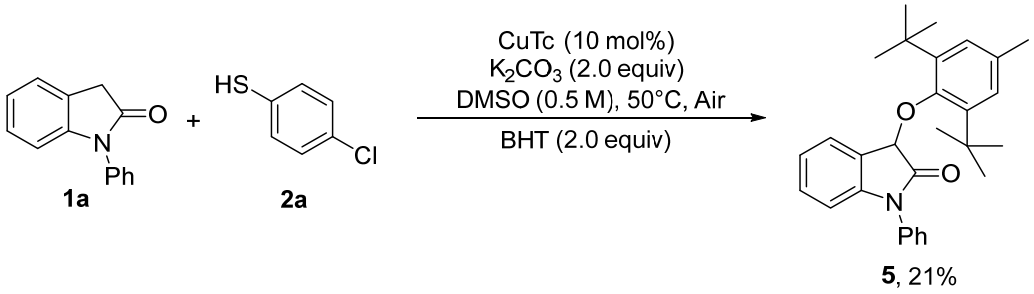
[d] DMSO 0.1 M.

[e] Under pure O_2.

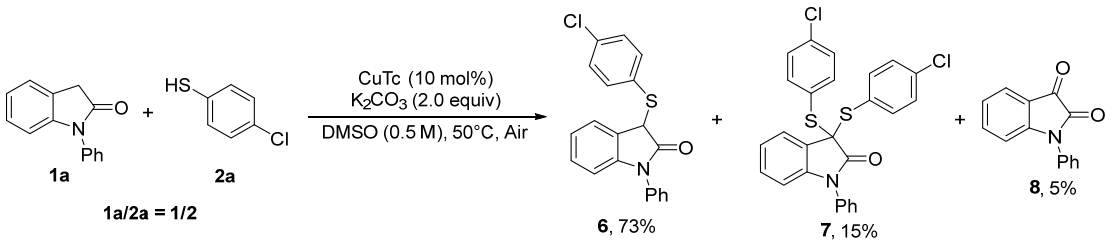
3. General procedure for the synthesis of C3-alkylated 3-thioxyindolin-2-one (4)

In a 10-mL reaction vial, equipped with a magnetic stirring bar, indolin-2-ones (1.0 mmol, 1.0 equiv), aryl thiols (1.0 mmol, 1.0 equiv), K_2CO_3 (2.0 mmol, 2.0 equiv, 276.4 mg) and CuTc (10 mol%, 16.2 mg) were added to DMSO (2.0 mL). Then the vial was placed in a pre-heated metal block at 50 ºC in the presence of ambient air. After stirring for 1 hour, alkyl halides (2.0 mmol, 2.0 equiv) was added to the mixture and heated up to 80 ºC. The reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with a saturated aqueous solution of NH_4Cl (15 mL) and extracted with ethyl acetate (2×20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (20/1−10/1) as eluent to afford the pure product.

4. Mechanistic studies



In a 10-mL reaction vial, equipped with a magnetic stirring bar, 1-phenylindolin-2-one (**1a**, 1.0 mmol, 209 mg), 4-chlorobenzenethiol (**2a**, 1.0 mmol, 144 mg), K_2CO_3 (2.0 mmol, 276.4 mg), CuTc (10 mol%, 16.2 mg) and BHT (2.0 mmol, 440.7 mg) were added to DMSO (2.0 mL). Then the vial was placed in a pre-heated metal block at 50 ºC in the presence of ambient air. The reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with a saturated aqueous solution of NH_4Cl (15 mL) and extracted with ethyl acetate (2×20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (20/1−10/1) as eluent. Compound **5** was isolated form the reaction mixture in 21% yield (89.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (t, J = 8.0 Hz, 2H, ArH), 7.47 (t, J = 7.6 Hz, 1H, ArH), 7.37 (d, J = 7.6 Hz, 2H, ArH), 7.17 (t, J = 8.0 Hz, 2H, ArH), 7.10 (d, J = 7.6 Hz, 1H, ArH), 6.92 (t, J = 7.6 Hz, 1H, ArH), 6.85 (d, J = 2.8 Hz, 1H, ArH), 6.68 (d, J = 7.6 Hz, 1H, ArH), 6.47 (d, J = 2.8 Hz, 1H, ArH), 3.99 (s, 1H, CH), 1.60 (s, 3H, CH_3), 1.24 (s, 9H, CH_3), 0.95 (s, 9H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 185.5, 174.3, 147.2, 146.1, 145.2, 144.1, 142.2, 134.6, 130.2, 128.8, 128.5, 126.9, 126.1, 125.8, 121.9, 108.7, 52.1, 43.6, 35.0, 34.6, 29.6, 29.3, 23.0. HRMS (ESI) m/z: calcd for $C_{29}H_{34}NO_2^+$ ($[M+H]^+$), 428.2584; found, 428.2580.



In a 10-mL reaction vial, equipped with a magnetic stirring bar, 1-phenylindolin-2-one (**1a**, 1.0 mmol, 209 mg), 4-chlorobenzenethiol (**2a**, 2.0 mmol, 288 mg), K_2CO_3 (2.0 mmol, 276.4 mg)

and CuTc (10 mol%, 16.2 mg) were added to DMSO (2.0 mL). Then the vial was placed in a pre-heated metal block at 50 ºC in the presence of ambient air. The reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with a saturated aqueous solution of NH_4Cl (15 mL) and extracted with ethyl acetate (2×20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (20/1−10/1) as eluent. Compound **6-8** were isolated form the reaction mixture.

3-((4-Chlorophenyl)thio)-1-phenylindolin-2-one (6):

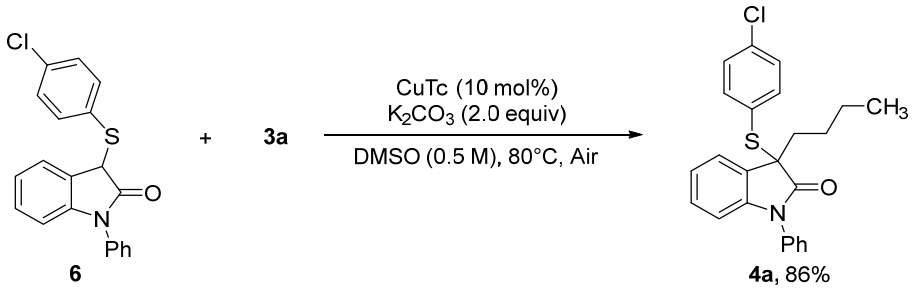
The title compound was isolated by column chromatography (eluent: petroleum ether /EtOAc = 6/1) as an orange solid in 73% yield (256.5 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (t, J = 7.6 Hz, 2H), 7.49 (d, J = 6.4 Hz, 1H), 7.45 (t, J = 7.2 Hz, 1H), 7.36-7.30 (m, 4H, ArH), 7.22 (t, J = 7.6 Hz, 1H, ArH), 7.15 (d, J = 8.0 Hz, 3H, ArH), 6.58 (d, J = 8.0 Hz, 1H, ArH), 5.31 (s, 1H, CH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.9, 144.7, 136.1, 135.1, 134.8, 130.9, 130.8, 130.3, 130.0, 129.4, 127.6, 126.9, 126.5, 124.3, 110.1, 49.3.

3,3-Bis((4-chlorophenyl)thio)-1-phenylindolin-2-one (7):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a white solid in 15% yield (74.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (t, J = 8.0 Hz, 2H, ArH), 7.45 (t, J = 7.6 Hz, 1H, ArH), 7.39 (d, J = 8.64 Hz, 4H, ArH), 7.31 (t, J = 8.8 Hz, 5H, ArH), 7.20 (t, J = 7.6 Hz, 1H, ArH), 7.12 (t, J = 7.6 Hz, 1H, ArH), 6.92 (d, J = 7.2 Hz, 2H, ArH), 6.46 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.7, 142.4, 138.3, 136.0, 133.7, 130.8, 130.3, 129.5, 129.1, 128.0, 126.9, 126.6, 126.0, 124.0, 109.7, 62.8.

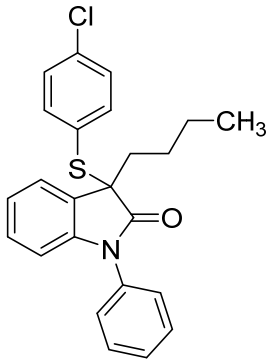
1-Phenylindoline-2,3-dione (8):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =2/1, v/v) as an orange solid in 5% yield (11.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (d, J = 7.2 Hz, 1H, ArH), 7.65 (t, J = 7.6 Hz, 3H, ArH), 7.53 (d, J = 7.6 Hz, 3H, ArH), 7.23 (t, J = 7.6 Hz, 1H, ArH), 6.86 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.2, 157.9, 151.7, 138.5, 133.8, 130.2, 128.9, 127.0, 125.2, 124.1, 118.1, 111.2.



In a 10-mL reaction vial, equipped with a magnetic stirring bar, 1-phenylindolin-2-one (**6**, 0.5 mmol, 176 mg), butyl bromide (**3a**, 1.0 mmol, 137 mg), K_2CO_3 (1.0 mmol, 138 mg) and CuTc (10 mol%, 8.1 mg) were added to DMSO (2.0 mL). Then the vial was placed in a pre-heated metal block at 80 ºC in the presence of ambient air. The reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with a saturated aqueous solution of NH_4Cl (15 mL) and extracted with ethyl acetate (2×20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (200–300 mesh) using petroleum/ethyl acetate (20/1−10/1) as eluent. Product **4a** was obtained in 86% yield (175.1 mg).

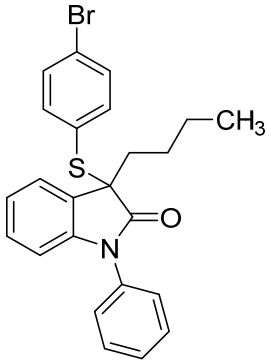
5. Characterization data for C3-alkylated 3-thioxyindolin-2-one (4)



3-Butyl-3-((4-chlorophenyl)thio)-1-phenylindolin-2-one (4a):

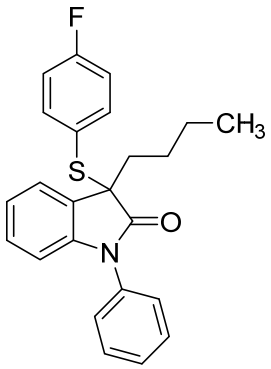
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 82% yield (334.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59-7.54 (m, 1H, ArH), 7.51 (t, J = 8.0 Hz, 2H, ArH), 7.43 (t, J = 7.6 Hz, 1H, ArH), 7.29 (d, J = 8.4 Hz, 2H, ArH), 7.22-7.18 (m, 2H, ArH), 7.10 (d, J = 8.4 Hz, 1H, ArH), 6.97 (d, J = 7.6 Hz, 2H, ArH), 6.53-6.48 (m, 1H, ArH), 2.24-2.09 (m, 2H, CH_2), 1.29-1.20 (m, 2H, CH_2), 1.15-1.02 (m, 2H, CH_2), 0.79 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-

*d*6) δ 174.8, 143.2, 138.1, 135.5, 134.1, 130.1, 129.6, 129.1, 129.1, 128.7, 128.4, 126.6, 125.0, 123.8, 109.3, 59.3, 34.8, 27.1, 22.5, 14.1. HRMS (ESI) m/z: calcd for $C_{24}H_{23}ClNOS^+$ ($[M+H]^+$), 408.1183; found, 408.1189.



3-((4-Bromophenyl)thio)-3-butyl-1-phenylindolin-2-one (4b):

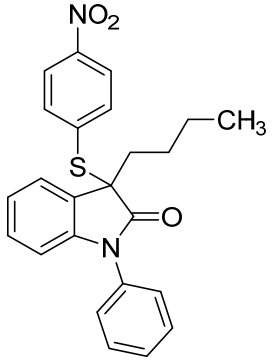
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 83% yield (376.1 mg). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 7.58-7.54 (m, 1H, ArH), 7.51 (t, *J* = 7.6 Hz, 2H, ArH), 7.43 (t, *J* = 8.4 Hz, 3H, ArH), 7.23-7.17 (m, 2H, ArH), 7.03 (d, *J* = 8.4 Hz, 2H, ArH), 6.97 (d, *J* = 7.2 Hz, 2H, ArH), 6.53-6.48 (m, 1H, ArH), 2.24-2.09 (m, 2H, CH_2), 1.29-1.20 (m, 2H, CH_2), 1.16-1.00 (m, 2H, CH_2), 0.79 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-*d*6) δ 174.8, 143.2, 138.3, 134.1, 132.1, 130.1, 129.6, 129.1, 128.9, 128.7, 126.6, 125.0, 124.3, 123.8, 109.3, 59.3, 34.8, 27.1, 22.5, 14.1. HRMS (ESI) m/z: calcd for $C_{24}H_{22}BrNNaOS^+$ ($[M+Na]^+$), 474.0498; found, 474.0494.



3-Butyl-3-((4-fluorophenyl)thio)-1-phenylindolin-2-one (4c):

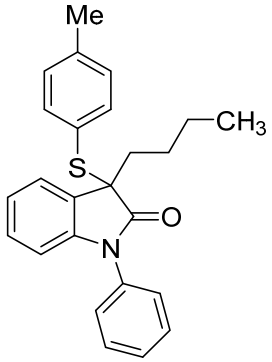
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 73% yield (285.2 mg). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 7.58-7.55 (m, 1H, ArH), 7.51 (t, *J* = 7.6 Hz, 2H, ArH), 7.42 (t, *J* = 7.2 Hz, 1H,

ArH), 7.22-7.16 (m, 2H, ArH, 7.15-7.12 (m, 2H, ArH), 7.07 (t, J = 8.8 Hz, 2H, ArH), 6.98 (d, J = 7.6 Hz, 2H, ArH), 6.51-6.47 (m, 1H, ArH), 2.24-2.09 (m, 2H, CH_2), 1.27-1.20 (m, 2H, CH_2), 1.14-1.01 (m, 2H, CH_2), 0.79 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 163.6 (d, J_{C-F} = 248.2 Hz), 143.2, 138.9 (d, J_{C-F} = 9.0 Hz), 134.2, 130.1, 129.4, 129.2, 128.6, 126.6, 125.2 (d, J_{C-F} = 3.0 Hz), 125.0, 123.7, 116.2 (d, J_{C-F} = 19.1 Hz), 109.2, 59.4, 34.7, 27.1, 22.5, 14.1. ^{19}F NMR (376 MHz, DMSO-d_6) δ -111.0. HRMS (ESI) m/z: calcd for $C_{24}H_{23}FNOS^+$ ($[M+H]^+$), 392.1479; found, 392.1485.



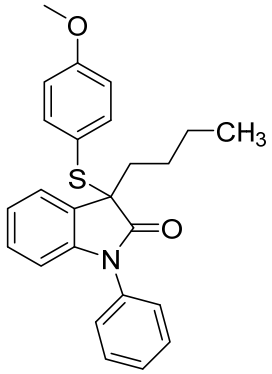
3-Butyl-3-((4-nitrophenyl)thio)-1-phenylindolin-2-one (4d):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 74% yield (309.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 9.2 Hz, 2H, ArH), 7.66 (d, J = 8.8 Hz, 2H, ArH), 7.53 (t, J = 7.6 Hz, 2H, ArH), 7.43 (t, J = 7.2 Hz, 1H, ArH), 7.40-7.37 (m, 2H, ArH), 7.33-7.28 (m, 2H, ArH), 7.22-7.18 (m, 1H, ArH), 6.93 (d, J = 8.0 Hz, 1H, ArH), 2.54-2.47 (m, 1H, CH_2), 2.31-2.23 (m, 1H, CH_2), 1.38-1.24 (m, 3H, CH_2), 1.03-0.95 (m, 1H, CH_2), 0.85 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 147.7, 147.1, 136.5, 134.2, 130.8, 129.7, 128.7, 128.4, 128.1, 126.6, 125.0, 123.7, 123.5, 110.1, 56.9, 38.5, 26.6, 22.8, 13.8. HRMS (ESI) m/z: calcd for $C_{24}H_{23}N_2O_3S^+$ ($[M+H]^+$), 419.1424; found, 419.1419.



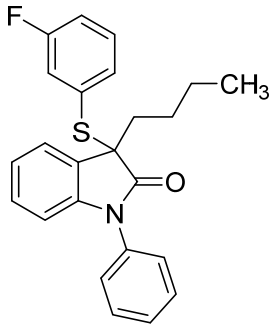
3-Butyl-1-phenyl-3-(p-tolylthio)indolin-2-one (4e):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellow oily liquid in 67% yield (258.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56-7.52 (m, 1H, ArH), 7.48 (t, J = 8.0 Hz, 2H, ArH), 7.41 (t, J = 7.2 Hz, 1H, ArH), 7.20-7.15 (m, 2H, ArH), 6.98 (q, J = 9.6 Hz, 4H, ArH), 6.89 (d, J = 7.2 Hz, 2H, ArH), 6.47-6.43 (m, 1H, ArH), 2.24 (s, 3H, CH_3), 2.18-2.07 (m, 2H, CH_2), 1.23 (t, J = 7.2 Hz, 2H, CH_2), 1.14-1.01 (m, 2H, CH_2), 0.79 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 143.4, 139.7, 136.5, 134.2, 130.1, 129.4, 129.1, 128.3, 128.0, 126.5, 124.4, 123.1, 109.1, 59.5, 35.0, 27.1, 22.8, 21.2, 13.8. HRMS (ESI) m/z: calcd for $C_{25}H_{26}NOS^+$ ($[M+H]^+$), 388.1730; found, 388.1746.



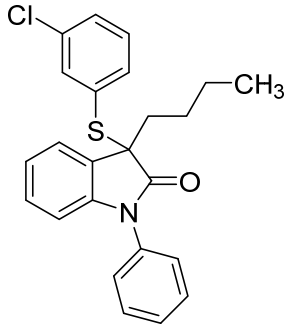
3-Butyl-3-((4-methoxyphenyl)thio)-1-phenylindolin-2-one (4f):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =10/1, v/v) as a colorless oil in 65% yield (261.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, 1H, ArH, J = 7.2 Hz), 7.39 (t, 2H, ArH, J = 7.6 Hz), 7.31 (t, 1H, ArH, J = 7.2 Hz), 7.15-7.19 (m, 4H, ArH), 7.93 (d, 2H, ArH, J = 8.0 Hz), 6.63 (d, 2H, ArH, J = 8.8 Hz), 6.48 (d, 1H, ArH, J = 7.6 Hz), 3.71 (s, 3H, CH_3), 2.34-2.27 (m, 1H, CH_2), 2.18-2.11 (m, 1H, CH_2), 1.32-1.25 (m, 2H, CH_2), 1.24-1.09 (m, 2H, CH_2), 0.84 (t, 3H, CH_3, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 160.8, 143.3, 138.1, 134.2, 130.1, 129.4, 128.3, 127.9, 126.4, 124.4, 123.1, 120.5, 113.9, 109.1, 59.7, 55.3, 34.9, 27.2, 22.8, 13.9. HRMS (ESI) m/z: calcd for $C_{25}H_{26}NO_2S^+$ ($[M+H]^+$), 404.1679; found, 404.1681.



3-Butyl-3-((3-fluorophenyl)thio)-1-phenylindolin-2-one (4g):

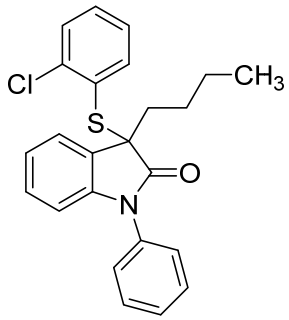
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 75% yield (293.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60-7.56 (m, 1H, ArH), 7.52 (t, J = 7.6 Hz, 2H, ArH), 7.43 (t, J = 7.6 Hz, 1H, ArH), 7.31-7.18 (m, 4H, ArH), 6.99 (t, J = 7.2 Hz, 3H, ArH), 6.83 (dt, J = 8.8, 2.0 Hz, 1H, ArH), 6.52-6.48 (m, 1H, ArH), 2.26-2.12 (m, 2H, CH_2), 1.28-1.21 (m, 2H, CH_2), 1.18-1.05 (m, 2H, CH_2), 0.79 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.8, 161.7 (d, J_{C-F} = 246.2 Hz), 143.2, 134.1, 132.5 (d, J_{C-F} = 2.0 Hz), 131.6 (d, J_{C-F} = 8.0 Hz), 130.8 (d, J_{C-F} = 8.0 Hz), 130.1, 129.5, 129.1, 128.7, 126.6, 125.1, 123.8, 122.5 (d, J_{C-F} = 21.1 Hz), 117.2 (d, J_{C-F} = 20.1 Hz), 109.2, 59.5, 34.9, 27.1, 22.5, 14.1. ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.5. HRMS (ESI) m/z: calcd for $C_{24}H_{23}FNOS^+$ ([M+H]$^+$), 392.1479; found, 392.1488.



3-Butyl-3-((3-chlorophenyl)thio)-1-phenylindolin-2-one (4h):

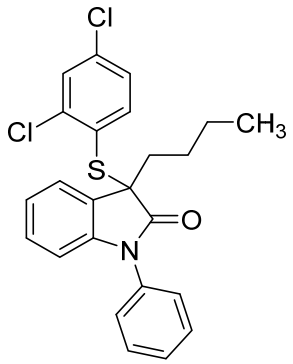
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 79% yield (322.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.2 Hz, 1H, ArH), 7.43 (t, J = 8.0 Hz, 2H, ArH), 7.34 (t, J = 7.2 Hz, 1H, ArH), 7.24-7.22 (m, 1H, ArH), 7.18-7.06 (m, 4H, ArH), 7.03 (t, J = 8.0 Hz, 1H, ArH), 6.96 (d, J = 7.2 Hz, 2H, ArH), 6.51 (d, J = 7.2 Hz, 1H, ArH), 2.35-2.28 (m, 1H, CH_2), 2.20-2.12 (m, 1H, CH_2), 1.38-1.21 (m, 3H, CH_2), 1.20-1.11 (m, 1H, CH_2), 0.84 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 143.3, 135.9, 134.7, 134.0, 133.8, 131.5, 129.6, 129.4, 129.4, 128.7,

128.1, 126.4, 124.4, 123.3, 109.3, 109.1, 59.7, 35.1, 27.1, 22.7, 13.9. HRMS (ESI) m/z: calcd for $C_{24}H_{23}ClNOS^+$ ([M+H]$^+$), 408.1183; found, 408.1199.



3-Butyl-3-((2-chlorophenyl)thio)-1-phenylindolin-2-one (4i):

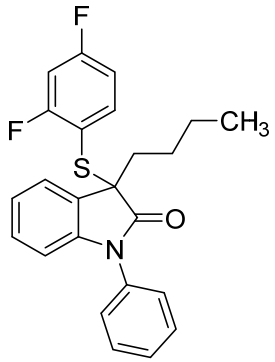
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 78% yield (317.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 4H, ArH), 7.37 (t, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.0 Hz, 1H, ArH), 7.20-7.13 (m, 3H, ArH), 7.12-7.01 (m, 3H, ArH), 6.57 (d, J = 7.2 Hz, 1H, ArH), 2.36-2.20 (m, 2H, CH_2), 1.33-1.25 (m, 2H, CH_2), 1.22-1.13 (m, 1H, CH_2), 1.12-1.03 (m, 1H, CH_2), 0.83 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 143.2, 140.3, 138.7, 134.3, 130.7, 129.8, 129.6, 129.3, 128.7, 128.0, 126.5, 126.3, 125.0, 123.0, 109.1, 109.0, 59.3, 35.6, 27.0, 22.7, 13.8. HRMS (ESI) m/z: calcd for $C_{24}H_{23}ClNOS^+$ ([M+H]$^+$), 408.1183; found, 408.1195.



3-Butyl-3-((2,4-dichlorophenyl)thio)-1-phenylindolin-2-one (4j):

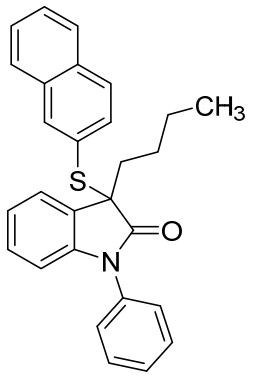
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 85% yield (375.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, J = 8.0 Hz, 2H, ArH), 7.43 (d, J = 6.4 Hz, 1H, ArH), 7.40-7.32 (m, 3H, ArH), 7.18-7.07 (m, 4H, ArH), 7.02 (dd, J_1 = 8.4, J_2 = 2.4 Hz, 1H, ArH), 6.63 (d, J = 7.6 Hz, 1H, ArH), 2.33-2.18 (m, 2H, CH_2), 1.32-1.24 (m, 2H, CH_2), 1.22-1.14 (m, 1H, CH_2), 1.13-1.04 (m, 1H, CH_2), 0.82 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 143.2, 141.2, 139.4,

136.2, 134.2, 129.7, 129.6, 129.0, 128.4, 128.1, 128.0, 126.9, 126.2, 124.9, 123.2, 109.3, 59.3, 35.5, 27.0, 22.7, 13.8. HRMS (ESI) m/z: calcd for $C_{24}H_{22}Cl_2NOS^+$ ($[M+H]^+$), 442.0794; found, 442.0808.



3-Butyl-3-((2,4-difluorophenyl)thio)-1-phenylindolin-2-one (4k):

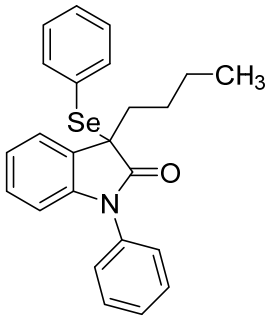
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 72% yield (294.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (q, J = 8.0, 7.6 Hz, 3H, ArH), 7.39-7.31 (m, 2H, ArH), 7.15-7.08 (m, 4H, ArH), 6.73-6.66 (m, 2H, ArH), 6.63-6.56 (m, 1H, ArH), 2.31-2.16 (m, 2H, CH_2), 1.34-1.26 (m, 2H, CH_2), 1.20-1.03 (m, 2H, CH_2), 0.83 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 165.5 (dd, $J_{1\ C\text{-}F}$ = 11.1 Hz, $J_{2\ C\text{-}F}$ = 6.0 Hz) 163.0 (dd, $J_{1\ C\text{-}F}$ = 11.1 Hz, $J_{2\ C\text{-}F}$ = 4.0 Hz), 143.1, 140.4 (d, $J_{C\text{-}F}$ = 10.0 Hz), 134.2, 129.6, 128.8, 128.7, 128.1, 126.2, 124.7, 123.2, 112.6 (dd, $J_{1\ C\text{-}F}$ = 19.1 Hz, $J_{2\ C\text{-}F}$ = 5.0 Hz), 111.4 (dd, $J_{1\ C\text{-}F}$ = 21.1 Hz, $J_{2\ C\text{-}F}$ = 4.0 Hz), 109.1, 104.1 (dd, $J_{1\ C\text{-}F}$ = 28.1 Hz, $J_{2\ C\text{-}F}$ = 26.1 Hz), 58.9, 35.2, 27.1, 22.7, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.9, -105.6. HRMS (ESI) m/z: calcd for $C_{24}H_{22}F_2NOS^+$ ($[M+H]^+$), 410.1385; found, 410.1402.



3-Butyl-3-(naphthalen-2-ylthio)-1-phenylindolin-2-one (4l):

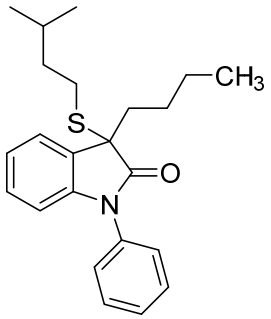
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether

/EtOAc =40/1, v/v) as a yellowish oily liquid in 56% yield (236.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H, ArH), 7.59 (d, J = 8.0 Hz, 1H, ArH), 7.55-7.52 (m, 2H, ArH), 7.47-7.38 (m, 2H, ArH), 7.23-7.13 (m, 5H, ArH), 7.06 (td, J_1 = 7.6, J_2 = 1.2 Hz, 1H, ArH), 6.65-6.62 (m, 2H, ArH), 6.33 (d, J = 7.6 Hz, 1H, ArH), 2.41-2.34 (m, 1H, CH_2), 2.25-2.18 (m, 1H, CH_2), 1.39-1.25 (m, 3H, CH_2), 1.20-1.12 (m, 1H, CH_2), 0.85 (t, J = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 143.4, 136.6, 134.0, 133.3, 133.1, 132.8, 130.0, 129.3, 128.5, 128.1, 127.9, 127.9, 127.7, 127.5, 127.0, 126.3, 126.2, 124.5, 123.1, 109.1, 59.8, 35.1, 27.2, 22.8, 13.9. HRMS (ESI) m/z: calcd for $C_{28}H_{26}NOS^+$ ($[M+H]^+$), 424.1730; found, 424.1729.



3-Butyl-1-phenyl-3-(phenylselanyl)indolin-2-one (4m):

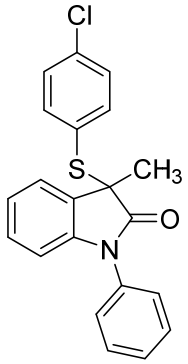
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 81% yield (339.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 3H, ArH), 7.28 (m, 4H, ArH), 7.12-7.05 (m, 4H, ArH), 6.90 (d, J = 7.2 Hz, 2H, ArH), 6.47 (dd, J_1 = 6.8, J_2 = 2.0 Hz, 1H, ArH), 2.42-2.21 (m, 2H, CH_2), 1.35-1.13 (m, 4H, CH_2), 0.83 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 143.0, 137.6, 134.3, 130.2, 129.3, 129.3, 128.5, 128.1, 127.9, 126.4, 126.0, 124.4, 123.0, 109.1, 53.8, 34.5, 27.8, 22.7, 13.9. HRMS (ESI) m/z: calcd for $C_{24}H_{24}NOSe^+$ ($[M+H]^+$), 422.1018; found, 422.1030.



3-Butyl-3-(isopentylthio)-1-phenylindolin-2-one (4n):

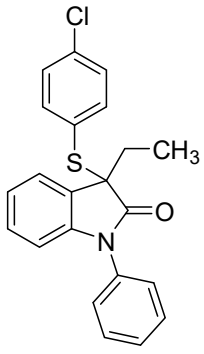
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether

/EtOAc =40/1, v/v) as a colorless oil in 43% yield (157.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, 2H, ArH, *J* = 7.6 Hz), 7.32-7.28 (m, 4H, ArH), 7.12 (t, 1H, ArH, *J* = 7.6 Hz), 7.04 (t, 1H, ArH, *J* = 7.6 Hz), 6.73 (d, 1H, ArH, *J* = 7.6 Hz), 2.49-2.43 (m, 1H, CH_2), 2.38-2.31 (m, 1H, CH_2), 2.20-2.13 (m, 1H, CH_2), 2.03-1.95 (m, 1H, CH_2), 1.51-1.44 (m, 1H, CH), 1.26-1.16 (m, 4H, CH_2), 1.14-1.01 (m, 2H, CH_2), 0.75-0.67 (m, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 143.2, 134.5, 129.9, 129.6, 128.6, 128.1, 126.5, 124.2, 123.4, 109.3, 54.5, 37.9, 36.2, 27.4, 26.8, 26.7, 22.7, 22.3, 22.1, 13.8. HRMS (ESI) m/z: calcd for $C_{23}H_{30}NOS^{+}$ ($[M+H]^{+}$), 368.2043; found, 368.2045.



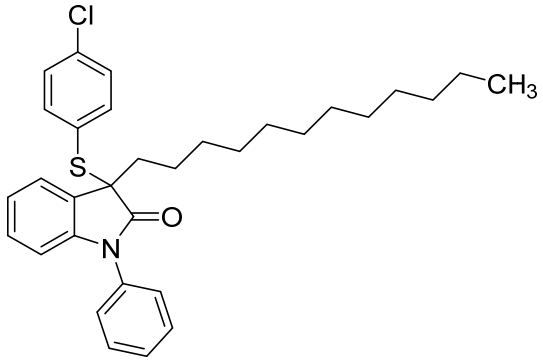
3-((4-Chlorophenyl)thio)-3-methyl-1-phenylindolin-2-one (4o):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish solid in 81% yield (295.6 mg). Mp 100-102ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 1H, ArH), 7.43 (t, *J* = 8.0 Hz, 2H, ArH), 7.34 (t, *J* = 7.2 Hz, 1H, ArH), 7.17-7.13 (m, 2H, ArH), 7.10 (s, 4H, ArH), 6.91 (d, *J* = 8.0 Hz, 2H, ArH), 6.55-6.51 (m, 1H, ArH), 1.82 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 142.6, 137.7, 136.2, 133.9, 131.3, 129.5, 128.8, 128.7, 128.5, 128.1, 126.2, 124.1, 123.4, 109.4, 55.2, 21.5. HRMS (ESI) m/z: calcd for $C_{21}H_{17}ClNOS^{+}$ ($[M+H]^{+}$), 366.0714; found, 366.0726.



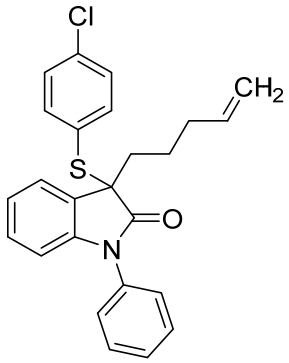
3-((4-Chlorophenyl)thio)-3-ethyl-1-phenylindolin-2-one (4p):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 84% yield (318.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.41 (m, 3H, ArH), 7.34 (t, *J* = 7.6 Hz, 1H, ArH), 7.17-7.07 (m, 6H, ArH), 6.92 (d, *J* = 7.6 Hz, 2H, ArH), 6.52 (d, *J* = 8.4 Hz, 1H, ArH), 2.39-2.30 (m, 1H, CH_2), 2.24-2.15 (m, 1H, CH_2), 0.85 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 143.5, 137.9, 136.1, 134.0, 129.5, 129.2, 128.7, 128.6, 128.2, 128.1, 126.3, 124.4, 123.3, 109.3, 60.3, 28.7, 9.4. HRMS (ESI) m/z: calcd for $C_{22}H_{19}ClNOS^+$ ([M+H]$^+$), 380.0870; found, 380.0865.



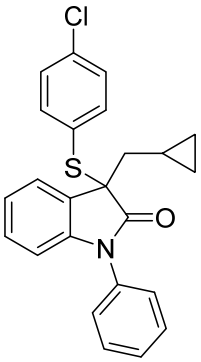
3-((4-Chlorophenyl)thio)-3-dodecyl-1-phenylindolin-2-one (4q):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 64% yield (331.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 1H, ArH), 7.42 (t, *J* = 8.0 Hz, 2H, ArH), 7.33 (t, *J* = 7.2 Hz, 1H, ArH), 7.17-7.06 (m, 6H, ArH), 6.90 (d, *J* = 7.2 Hz, 2H, ArH), 6.54-6,48 (m, 1H, ArH), 2.33-2.26 (m, 1H, CH_2), 2.18-2.11 (m, 1H, CH_2), 1.30-1.16 (m, 20H, CH_2), 0.87 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 143.3, 137.8, 136.1, 134.0, 129.7, 129.5, 128.6, 128.6, 128.2, 128.1, 126.2, 124.4, 123.2, 109.2, 59.6, 35.3, 31.9, 29.6(2), 29.5, 29.4, 29.3, 25.0, 22.7, 14.2. HRMS (ESI) m/z: calcd for $C_{32}H_{39}ClNOS^+$ ([M+H]$^+$), 520.2435; found, 520.2430.



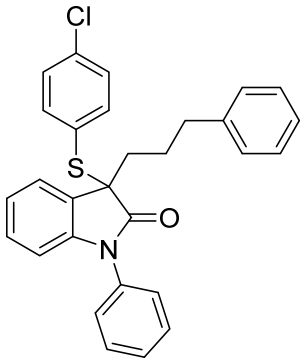
3-((4-Chlorophenyl)thio)-3-(pent-4-en-1-yl)-1-phenylindolin-2-one (4r):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 83% yield (347.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 1H, ArH), 7.42 (t, *J* = 8.0 Hz, 2H, ArH), 7.33 (t, *J* = 7.2 Hz, 1H, ArH), 7.15-7.06 (m, 6H, ArH), 6.90 (d, *J* = 7.2 Hz, 2H, ArH), 6.53-6.49 (m, 1H, ArH), 5.75-5.64 (m, 1H, CH), 5.00-4.92 (m, 2H, CH_2), 2.34-2.27 (m, 1H, CH_2), 2.20-2.13 (m, 1H, CH_2), 2.07-1.19 (m, 2H, CH_2), 1.40-1.20 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 143.3, 138.2, 137.9, 137.7, 136.1, 134.0, 129.5, 128.9, 128.7, 128.6, 128.1, 126.2, 124.4, 123.3, 115.3, 109.3, 59.5, 34.8, 33.6, 24.2. HRMS (ESI) m/z: calcd for $C_{25}H_{22}ClNNaOS^+$ ($[M+Na]^+$), 442.1003; found, 442.0999.



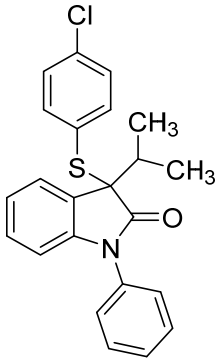
3-((4-Chlorophenyl)thio)-3-(cyclopropylmethyl)-1-phenylindolin-2-one (4s):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 82% yield (332.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.49 (m, 1H, ArH), 7.43 (t, *J* = 8.0 Hz, 2H, ArH), 7.34 (t, *J* = 7.6 Hz, 1H, ArH), 7.17-7.07 (m, 6H, ArH), 6.93 (d, *J* = 7.2 Hz, 2H, ArH), 6.55-6.49 (m, 1H, ArH), 2.42 (dd, J_1 = 13.6 Hz, J_2 = 4.8 Hz, 1H, CH_2), 1.95 (dd, J_1 = 14.0 Hz, J_2 = 9.2 Hz, 1H, CH_2), 0.59-0.49 (m, 1H, CH), 0.32-0.25 (m, 3H, CH_2), 0.10-0.03 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 143.5, 137.8, 136.0, 134.2, 129.9, 129.6, 129.6, 128.7, 128.6, 128.1, 126.3, 124.7, 123.1, 109.2, 59.9, 40.1, 7.1, 4.5, 4.2. HRMS (ESI) m/z: calcd for $C_{24}H_{21}ClNOS^+$ ($[M+H]^+$), 406.1027; found, 406.1024.



3-((4-Chlorophenyl)thio)-1-phenyl-3-(3-phenylpropyl)indolin-2-one (4t):

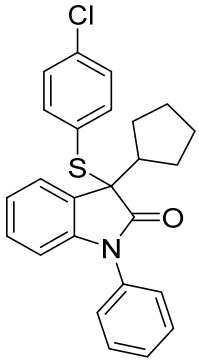
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish solid in 90% yield (422.6 mg). Mp 128-129ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H, ArH), 7.33 (t, *J* = 7.2 Hz, 1H, ArH), 7.24 (t, *J* = 7.6 Hz, 2H, ArH), 7.18-7.06 (m, 9H, ArH), 6.88 (d, *J* = 7.2 Hz, 2H, ArH), 6.53-6.47 (m, 1H, ArH), 2.68-2.52 (m, 2H, CH_2), 2.40-2.32 (m, 1H, CH_2), 2.23-2.15 (m, 1H, CH_2), 1.63-1.43 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 143.3, 141.4, 137.9, 136.2, 133.9, 129.5, 129.4, 128.8, 128.6, 128.4, 128.1, 128.0, 126.2, 126.0, 124.4, 123.3, 109.3, 59.4, 35.8, 34.9, 26.8. HRMS (ESI) m/z: calcd for $C_{29}H_{24}ClNNaOS^+$ ($[M+Na]^+$), 492.1159; found, 492.1153.



3-((4-Chlorophenyl)thio)-3-isopropyl-1-phenylindolin-2-one (4u):

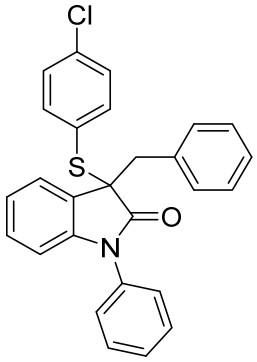
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 45% yield (176.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.54 (m, 1H, ArH), 7.42 (t, *J* = 8.0 Hz, 2H, ArH), 7.34 (t, *J* = 7.6 Hz, 1H, ArH), 7.17-7.12 (m, 2H, ArH), 7.11-7.05 (m, 4H, ArH), 6.86 (d, *J* = 7.2 Hz, 2H, ArH), 6.51-6.46 (m, 1H, ArH), 2.70-2.59 (m, 1H, CH), 1.32 (d, *J* = 6.8 Hz, 3H, CH_3), 0.96 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 143.5, 137.9, 135.9, 134.0, 129.5, 128.7, 128.6, 128.5, 128.4, 128.1, 126.3, 125.4, 123.0, 109.1, 64.2, 34.6, 18.3, 17.8. HRMS (ESI) m/z: calcd for

$C_{23}H_{21}ClNOS^+$ ([M+H]$^+$), 394.1027; found, 394.1043.



3-((4-Chlorophenyl)thio)-3-cyclopentyl-1-phenylindolin-2-one (4v):

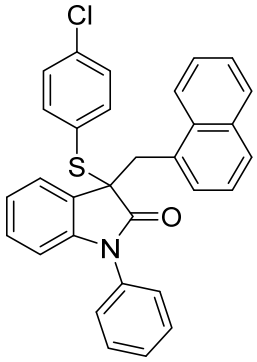
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 48% yield (200.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 1H, ArH), 7.42 (t, *J* = 7.6 Hz, 2H, ArH), 7.34 (t, *J* = 7.2 Hz, 1H, ArH), 7.14-7.09 (m, 4H, ArH), 7.08-7.05 (m, 2H, ArH), 6.88 (d, *J* = 7.2 Hz, 2H, ArH), 6.50-6.46 (m, 1H, ArH), 2.81-2.72 (m, 1H, CH), 2.02-1.94 (m, 1H, CH_2), 1.84-1.74 (m, 2H, CH_2), 1.66-1.54 (m, 4H, CH_2), 1.40-1.33 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 143.4, 137.7, 135.8, 134.0, 129.5, 129.3, 128.5, 128.1, 126.4, 125.3, 123.0, 109.1, 62.4, 45.8, 28.1, 27.8, 25.3, 25.1. HRMS (ESI) m/z: calcd for $C_{25}H_{23}ClNOS^+$ ([M+H]$^+$), 420.1183; found, 420.1190.



3-Benzyl-3-((4-chlorophenyl)thio)-1-phenylindolin-2-one (4w):

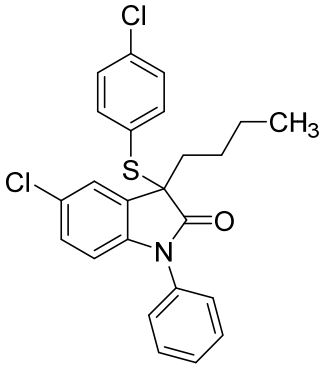
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a White solid in 52% yield (228.9 mg). Mp 105-107ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H, ArH), 7.36-7.27 (m, 3H, ArH), 7.22-7.18 (m, 2H, ArH), 7.13-7.06 (m, 6H, ArH), 7.04-6.99 (m, 3H, ArH), 6.62-6.59 (m, 2H, ArH), 6.24 (d, *J* = 8.0 Hz, 1H, ArH), 3.59 (d, *J* = 12.8 Hz, 1H, CH_2), 3.40 (d, *J* = 13.2 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 143.3, 137.9, 136.1, 134.7, 133.8, 130.3(2), 129.5, 128.8,

128.7, 128.1, 127.9, 127.0, 126.3, 125.1, 122.9, 109.2, 109.0, 60.8, 41.6. HRMS (ESI) m/z: calcd for $C_{27}H_{21}ClNOS^+$ ([M+H]$^+$), 442.1027; found, 442.1038.



3-((4-Chlorophenyl)thio)-3-(naphthalen-1-ylmethyl)-1-phenylindolin-2-one (4x):

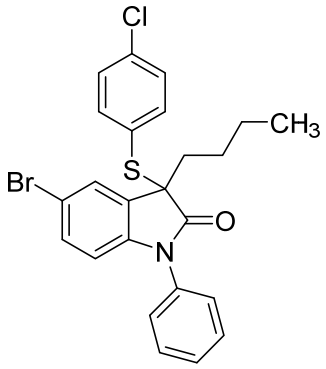
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a white solid in 56% yield (275.1 mg). Mp 119-120ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H, ArH), 7.73 (d, *J* = 8.0 Hz, 1H, ArH), 7.64 (d, *J* = 7.6 Hz, 1H, ArH), 7.46-7.37 (m, 3H, ArH), 7.33-7.23 (m, 5H, ArH), 7.17 (d, *J* = 8.4 Hz, 2H, ArH), 7.08 (d, *J* = 8.8 Hz, 2H, ArH), 6.94-6.88 (m, 2H, ArH), 6.53 (d, *J* = 7.2 Hz, 2H, ArH), 6.18 (d, *J* = 8.8 Hz, 1H, ArH), 4.10 (d, *J* = 14.0 Hz, 1H, CH_2), 3.96 (d, *J* = 14.0 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 143.1, 137.9, 136.1, 133.8, 133.7, 132.1, 131.4, 129.5, 128.7(3), 128.5, 128.4, 128.2, 128.1, 126.2, 125.9, 125.5, 124.8, 124.7, 124.6, 122.6, 109.0, 108.9, 60.9, 37.1. HRMS (ESI) m/z: calcd for $C_{31}H_{23}ClNOS^+$ ([M+H]$^+$), 492.1183; found, 492.1182.



3-Butyl-5-chloro-3-((4-chlorophenyl)thio)-1-phenylindolin-2-one (4y):

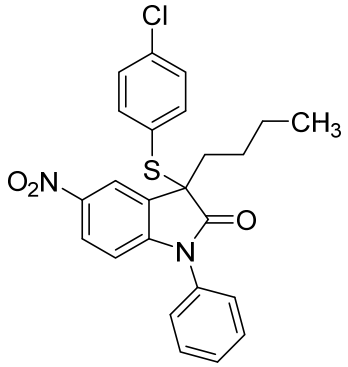
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 79% yield (348.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 3H, ArH), 7.36 (t, *J* = 7.6 Hz, 1H, ArH), 7.13-7.10 (m, 5H, ArH), 6.86 (d, *J* = 7.6 Hz, 2H, ArH), 6.44 (d, *J* = 8.4 Hz, 1H, ArH), 2.34-2.27 (m, 1H, CH_2), 2.15-2.07 (m,

1H, CH_2), 1.35-1.26 (m, 2H, CH_2), 1.24-1.09 (m, 2H, CH_2), 0.85 (t, *J* = 7.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 141.8, 137.9, 136.4, 133.6, 131.6, 129.6, 128.8, 128.6, 128.6, 128.3, 127.7, 126.1, 124.6, 110.3, 59.6, 35.0, 27.0, 22.7, 13.8. HRMS (ESI) m/z: calcd for $C_{24}H_{22}Cl_2NOS^+$ ($[M+H]^+$), 442.0794; found, 442.0794.



5-Bromo-3-butyl-3-((4-chlorophenyl)thio)-1-phenylindolin-2-one (4z):

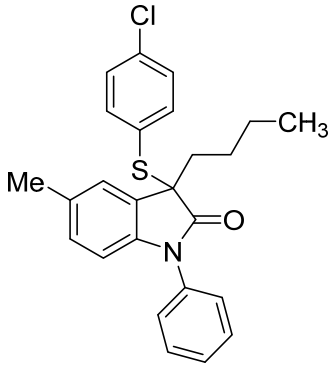
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 84% yield (407.3 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.6 Hz, 1H, ArH), 7.46-7.41 (m, 3H, ArH), 7.36 (t, *J* = 7.6 Hz, 1H, ArH), 7.13 (s, 4H, ArH), 6.84 (d, J = 7.2 Hz, 2H, ArH), 6.30 (d, *J* = 8.4 Hz, 1H, ArH), 2.33-2.25 (m, 1H, CH_2), 2.13-2.05 (m, 1H, CH_2), 1.34-1.25 (m, 2H, CH_2), 1.21-1.09 (m, 2H, CH_2), 0.86 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 141.9, 136.8, 136.4, 135.3, 132.5, 132.0, 131.2, 128.6, 127.7, 127.3, 126.6, 126.3, 125.0, 110.2, 58.2, 34.0, 26.0, 21.7, 12.8. HRMS (ESI) m/z: calcd for $C_{24}H_{22}BrClNOS^+$ ($[M+H]^+$), 486.0289; found, 486.0274.



3-Butyl-3-((4-chlorophenyl)thio)-5-nitro-1-phenylindolin-2-one (4aa):

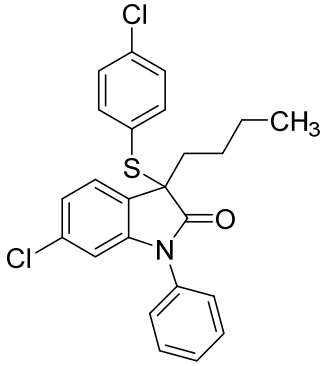
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 71% yield (321.2 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H, ArH), 8.11 (d, *J* = 8.8 Hz, 1H, ArH), 7.50-7.43 (m, 3H, ArH), 7.13 (s, 4H,

ArH), 6.87 (d, J = 6.4 Hz, 2H, ArH),6.60 (d, J = 8.8 Hz, 1H, ArH), 2.39-2.33 (m, 1H, CH_2), 2.24-2.17 (m, 1H, CH_2), 1.34-1.30 (m, 2H, CH_2), 1.22-1.09 (m, 2H, CH_2), 0.86 (t, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 147.5, 142.8, 136.9, 135.7, 131.9, 129.9, 128.9, 128.0(2), 126.2, 125.1, 124.6, 119.2, 108.0, 58.1, 33.9, 26.0, 21.6, 12.7. HRMS (ESI) m/z: calcd for $C_{24}H_{22}ClN_2O_3S^+$ ($[M+H]^+$), 453.1034; found, 453.1038.



3-Butyl-3-((4-chlorophenyl)thio)-5-methyl-1-phenylindolin-2-one (4ab):

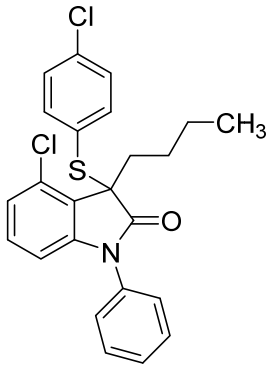
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 55% yield (231.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, J = 7.6 Hz, 2H, ArH), 7.33 (t, J = 7.6 Hz, 1H, ArH), 7.28 (s, 1H, ArH), 7.10 (s, 4H, ArH), 6.94 (d, J = 8.4 Hz, 1H, ArH), 6.90 (d, J = 8.4 Hz, 2H, ArH), 6.43 (d, J = 8.0 Hz, 1H, ArH), 2.41 (s, 3H, CH_3), 2.32-2.25 (m, 1H, CH_2), 2.19-2.08 (m, 1H, CH_2), 1.32-1.26 (m, 2H, CH_2), 1.24-1.09 (m, 2H, CH_2), 0.84 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 140.0, 136.8, 135.0, 133.2, 131.8, 128.6, 128.4, 128.0, 127.5, 127.3, 126.9, 125.1, 123.9, 108.0, 58.6, 34.1, 26.0, 21.7, 20.2, 12.8. HRMS (ESI) m/z: calcd for $C_{25}H_{25}ClNOS^+$ ($[M+H]^+$), 422.1340; found, 422.1340.



3-Butyl-6-chloro-3-((4-chlorophenyl)thio)-1-phenylindolin-2-one (4ac):

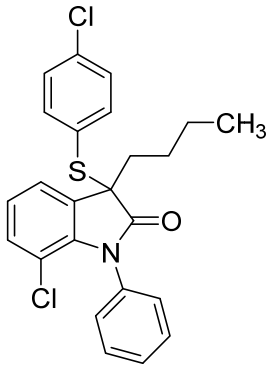
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether

/EtOAc =40/1, v/v) as a yellowish oily liquid in 82% yield (361.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 8.0 Hz, 2H, ArH), 7.40-7.36 (m, 2H, ArH), 7.15-7.13 (m, 5H, ArH), 6.86 (d, *J* = 7.6 Hz, 2H, ArH), 6.51 (s, 1H, ArH), 2.33-2.25 (m, 1H, CH_2), 2.15-2.08 (m, 1H, CH_2), 1.33-1.25 (m, 2H, CH_2), 1.21-1.06 (m, 2H, CH_2), 0.84 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 143.3, 136.8, 135.3, 133.3, 132.4, 128.7, 127.7, 127.5, 127.1, 126.7, 125.1, 124.3, 122.2, 108.8, 58.2, 34.0, 26.0, 21.6, 12.7. HRMS (ESI) m/z: calcd for $C_{24}H_{22}Cl_2NOS^+$ ($[M+H]^+$), 442.0794; found, 442.0783.



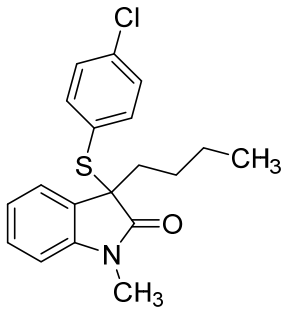
3-Butyl-4-chloro-3-((4-chlorophenyl)thio)-1-phenylindolin-2-one (4ad):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 68% yield (299.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H, ArH), 7.38-7.34 (m, 1H, ArH), 7.13-7.05 (m, 6H, ArH), 6.80 (d, *J* = 7.6 Hz, 2H, ArH), 6.36 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 1H, ArH), 2.66-2.59 (m, 1H, CH_2), 2.34-2.27 (m, 1H, CH_2), 1.38-1.26 (m, 2H, CH_2), 1.13-1.02 (m, 2H, CH_2), 0.85 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 143.9, 136.8, 135.2, 132.5, 130.5, 128.7, 128.5, 127.6, 127.4, 127.0, 125.3, 124.3, 123.3, 106.6, 59.9, 31.3, 26.6, 21.5, 12.7. HRMS (ESI) m/z: calcd for $C_{24}H_{22}Cl_2NOS^+$ ($[M+H]^+$), 442.0794; found, 442.0788.



3-Butyl-7-chloro-3-((4-chlorophenyl)thio)-1-phenylindolin-2-one (4ae):

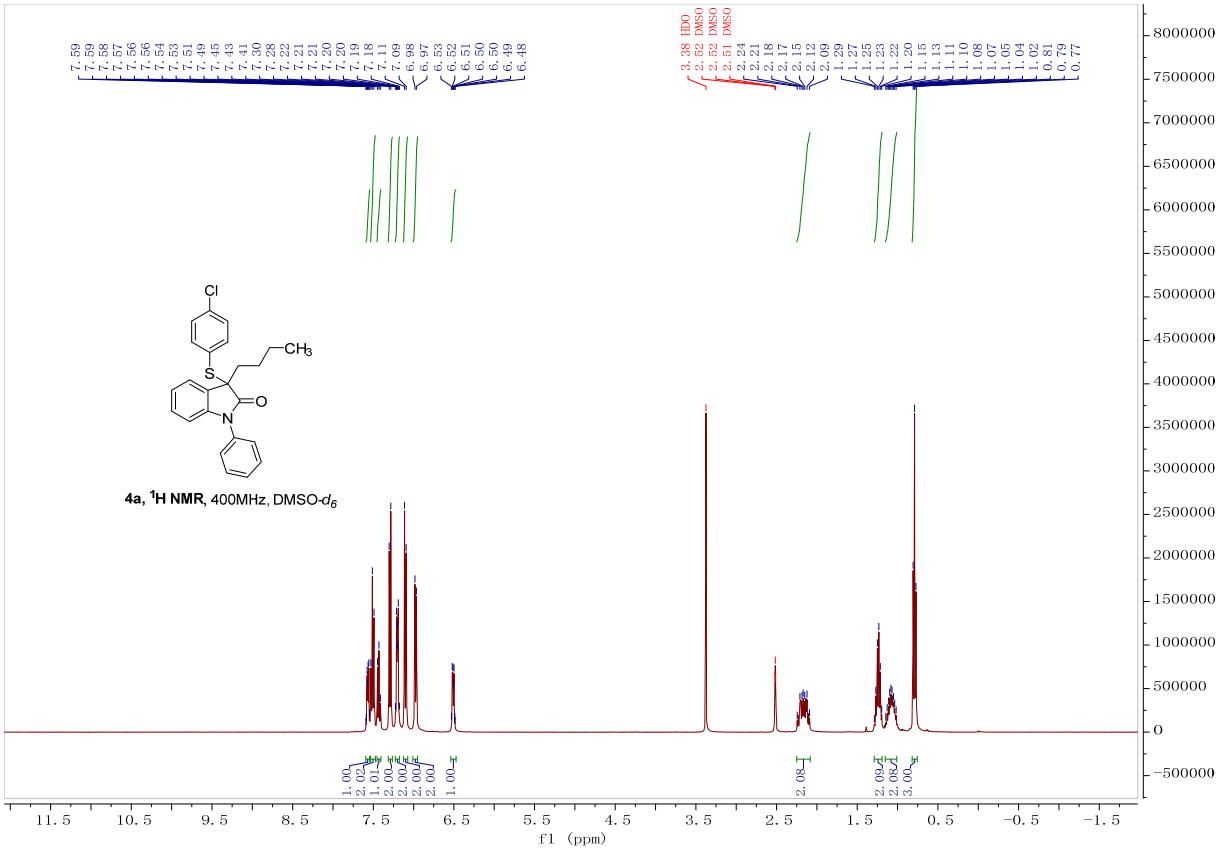
The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 57% yield (252.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H, ArH), 7.37-7.32 (m, 3H, ArH), 7.20-7.17 (m, 2H, ArH), 7.15-7.07 (m, 5H, ArH), 6.27 (d, *J* = 7.2 Hz, 1H, ArH), 2.33-2.26 (m, 1H, CH_2), 2.14-2.07 (m, 1H, CH_2), 1.34-1.27 (m, 2H, CH_2), 1.25-1.15 (m, 2H, CH_2), 0.85 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 136.9, 135.4, 133.9, 131.7, 130.1, 127.8(2), 127.7, 127.6, 126.9, 126.8, 122.7, 121.8, 114.9, 58.4, 34.4, 25.9, 21.6, 12.7. HRMS (ESI) m/z: calcd for $C_{24}H_{22}Cl_2NOS^+$ ($[M+H]^+$), 442.0794; found, 442.0784.



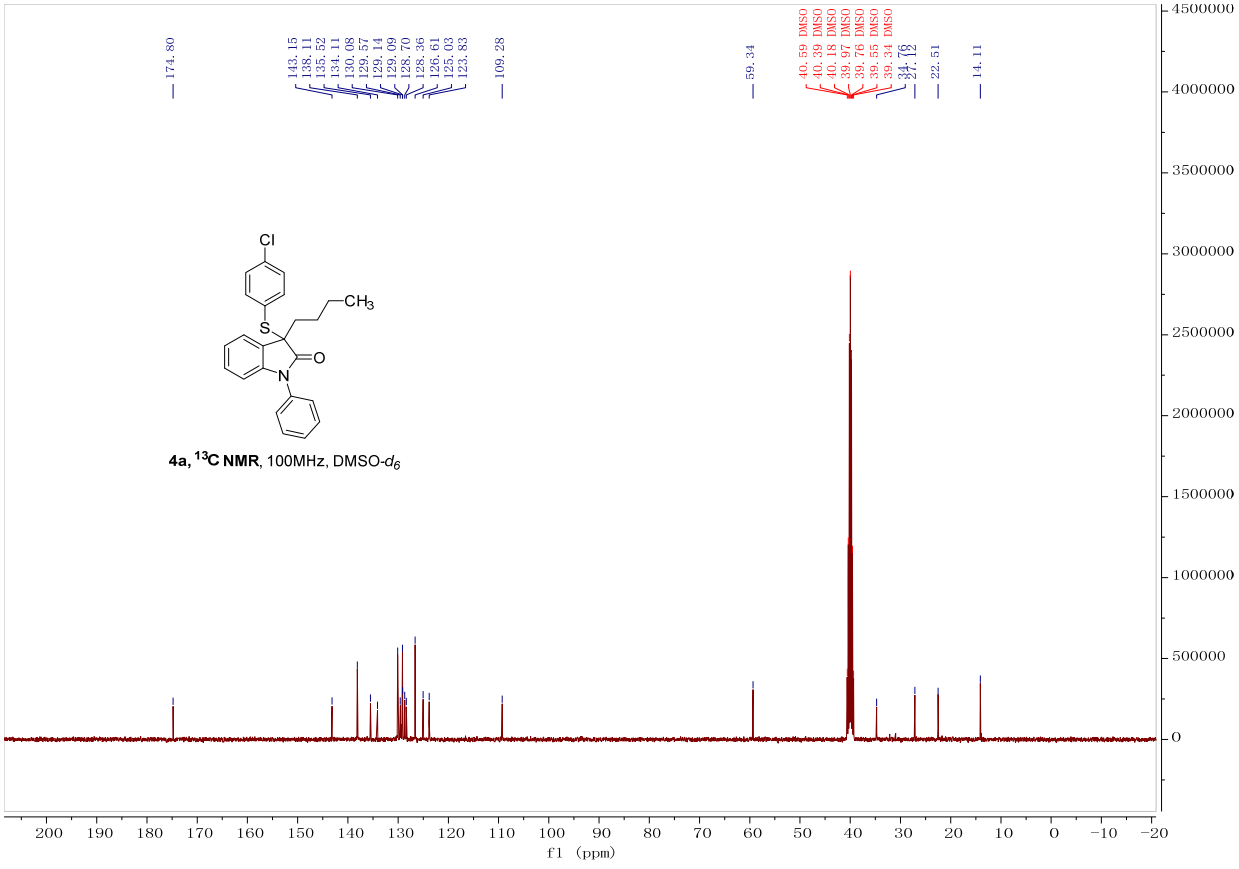
3-Butyl-3-((4-chlorophenyl)thio)-1-methylindolin-2-one (4af):

The title compound was isolated by silica-gel column chromatography (eluent: petroleum ether /EtOAc =40/1, v/v) as a yellowish oily liquid in 84% yield (290.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 1H, ArH), 7.20 (t, *J* = 7.6 Hz, 1H, ArH), 7.10 (t, *J* = 7.6 Hz, 1H, ArH), 7.05 (s, 4H, ArH), 6.55 (d, *J* = 7.6 Hz, 1H, ArH), 2.91 (s, 3H, CH_3), 2.22-2.03 (m, 2H, CH_2), 1.28-1.20 (m, 2H, CH_2), 1.11-0.96 (m, 2H, CH_2), 0.80 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 143.2, 137.6, 135.8, 129.6, 128.7, 128.3, 128.1, 124.1, 122.7, 108.0, 59.4, 34.6, 27.0, 26.1, 22.7, 13.8. HRMS (ESI) m/z: calcd for $C_{19}H_{20}ClNNaOS^+$ ($[M+Na]^+$), 368.0846; found, 368.0844.

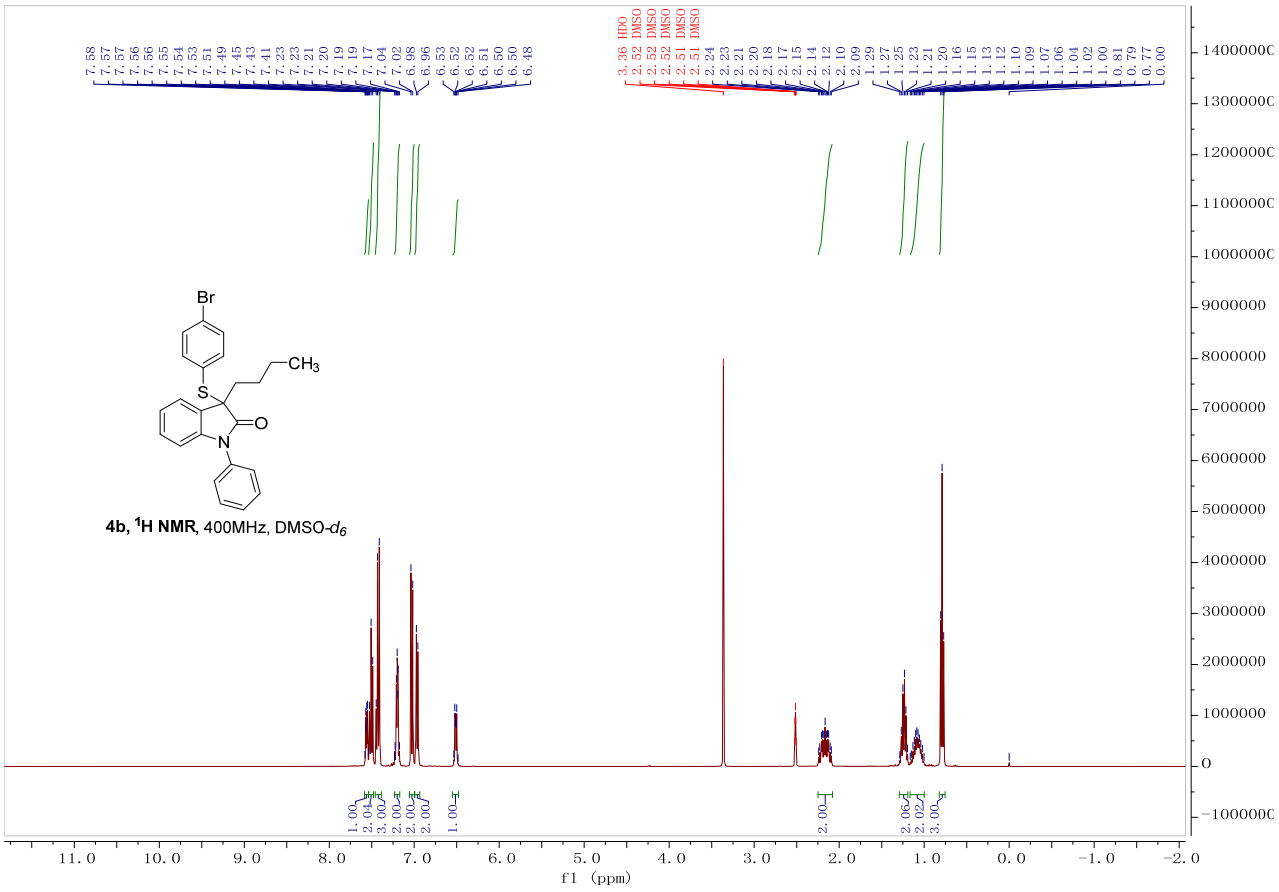
6. Spectroscopic data for C3-alkylated 3-thioxyindolin-2-one (4)

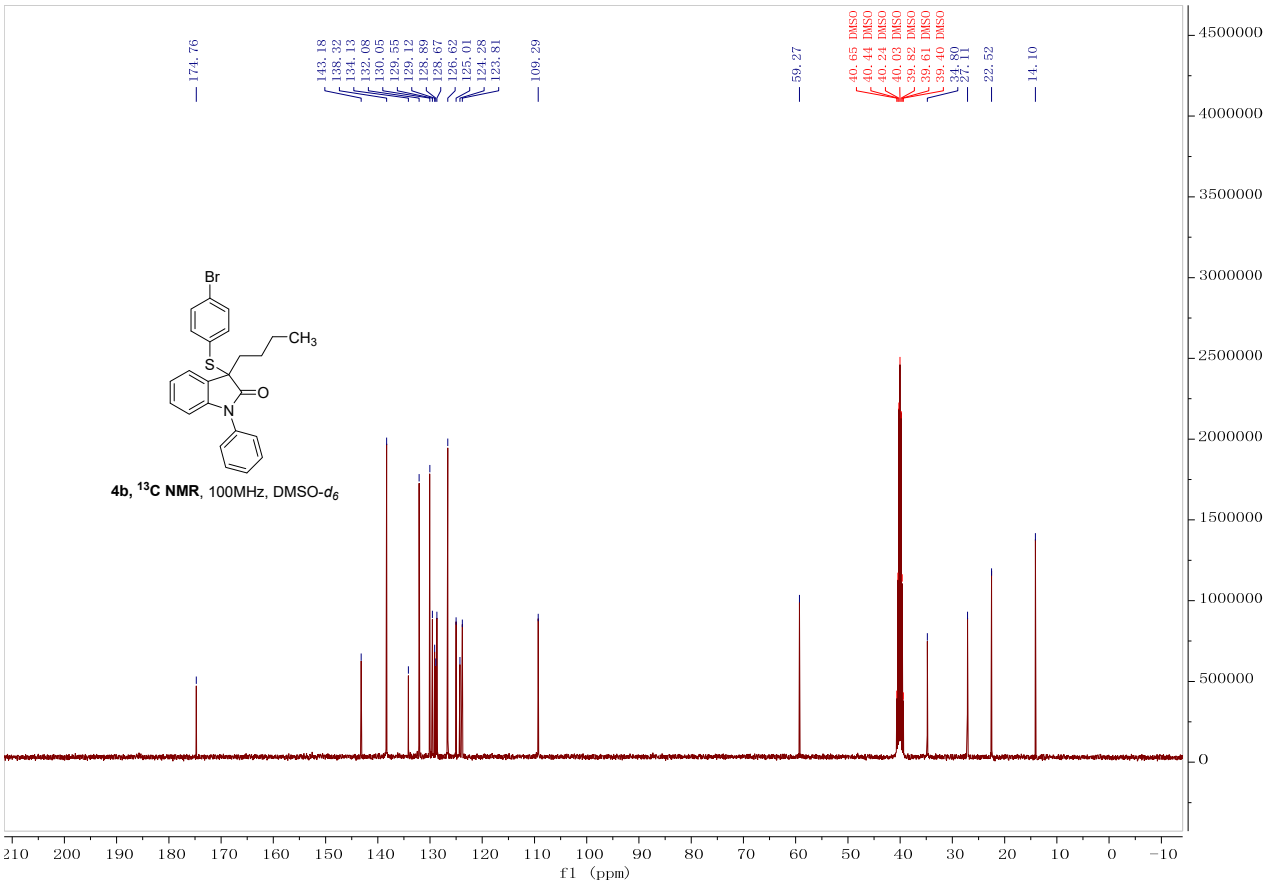


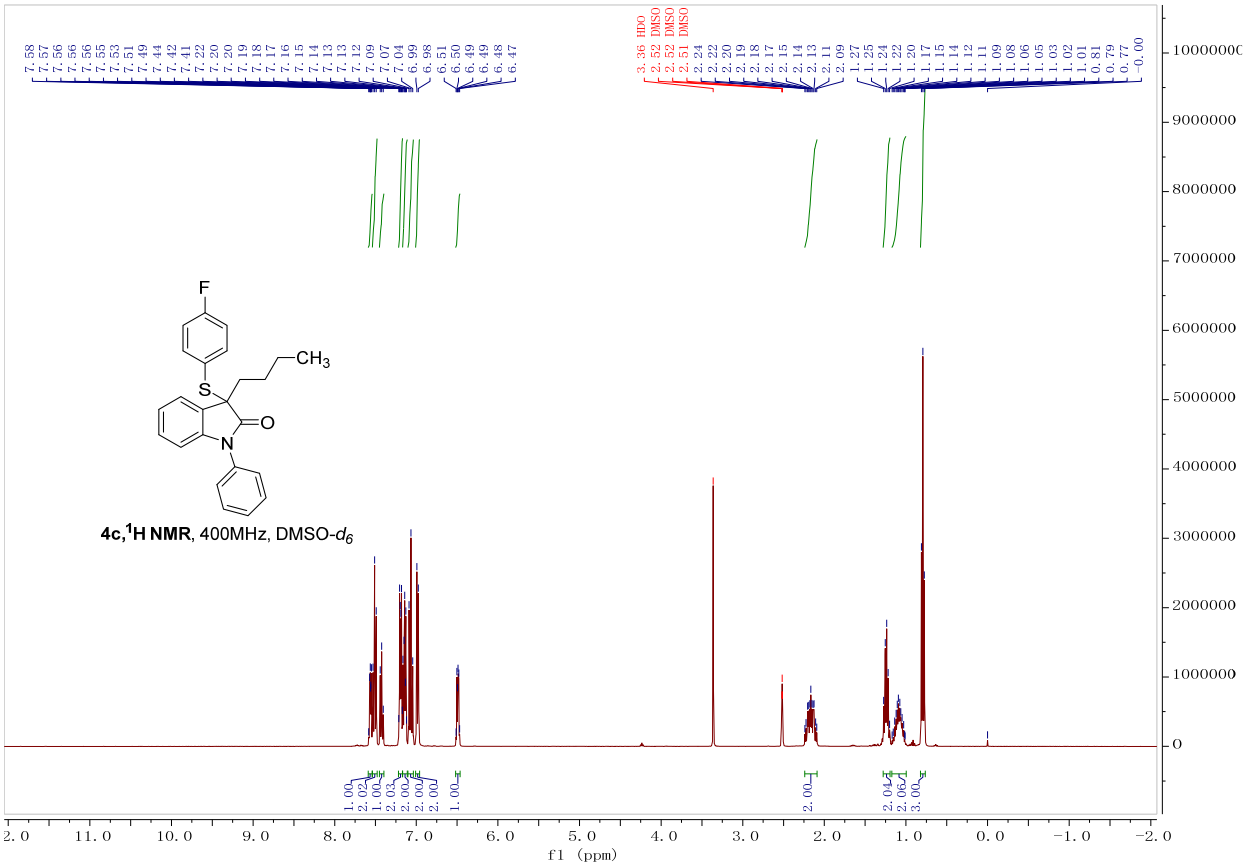
4a, ^{1}H NMR, 400MHz, DMSO-d_6



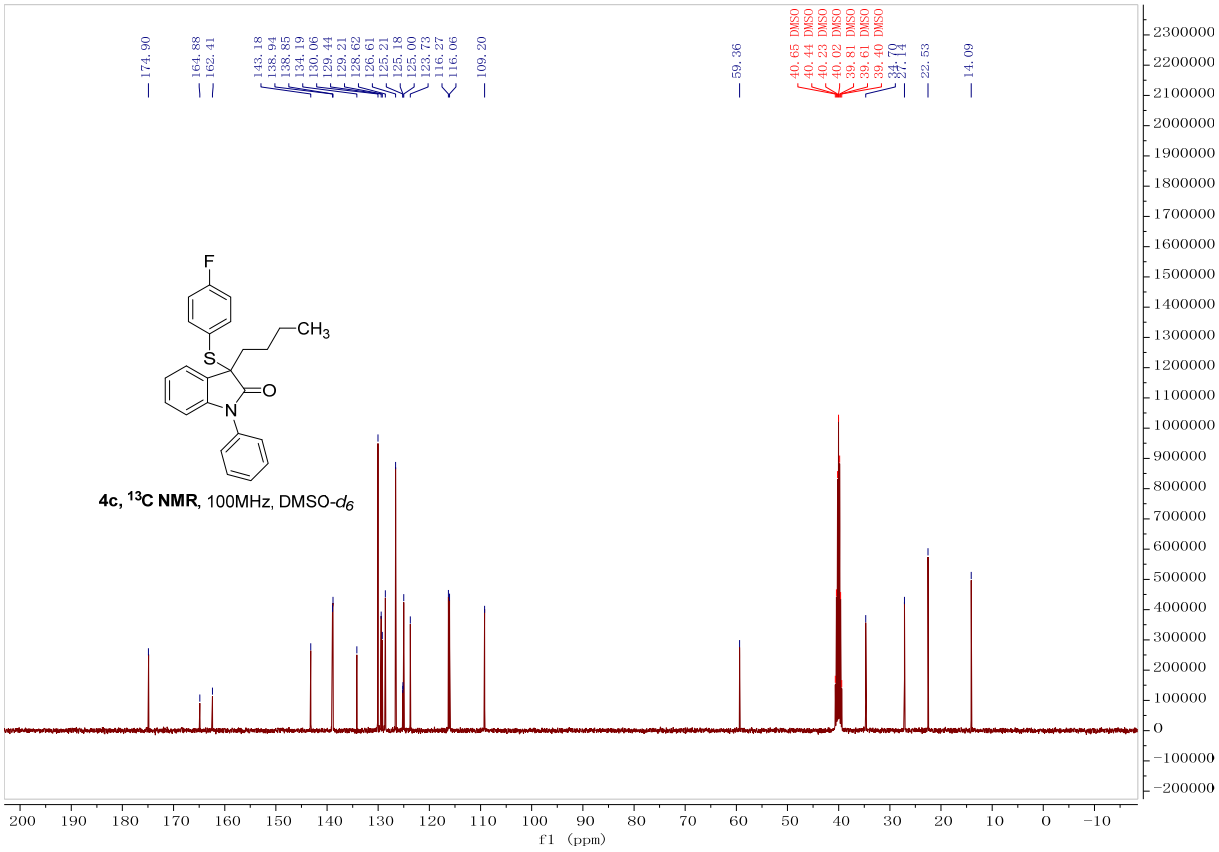
4a, ^{13}C NMR, 100MHz, DMSO-d_6


Br
S
CH3
O
N
4b, 1H NMR, 400MHz, DMSO-d6
f1 (ppm)

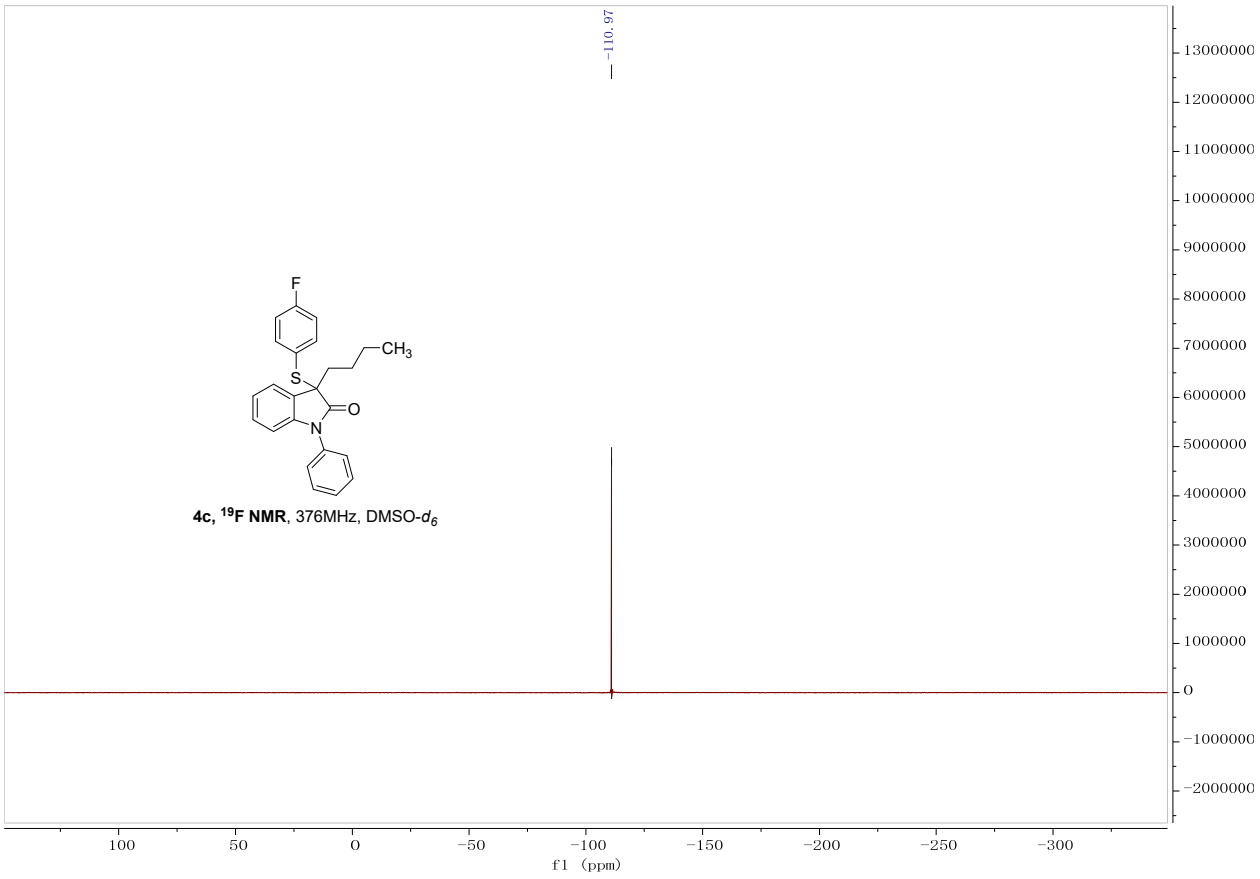

Br
S
CH3
O
N
4b, 13C NMR, 100MHz, DMSO-d6
f1 (ppm)



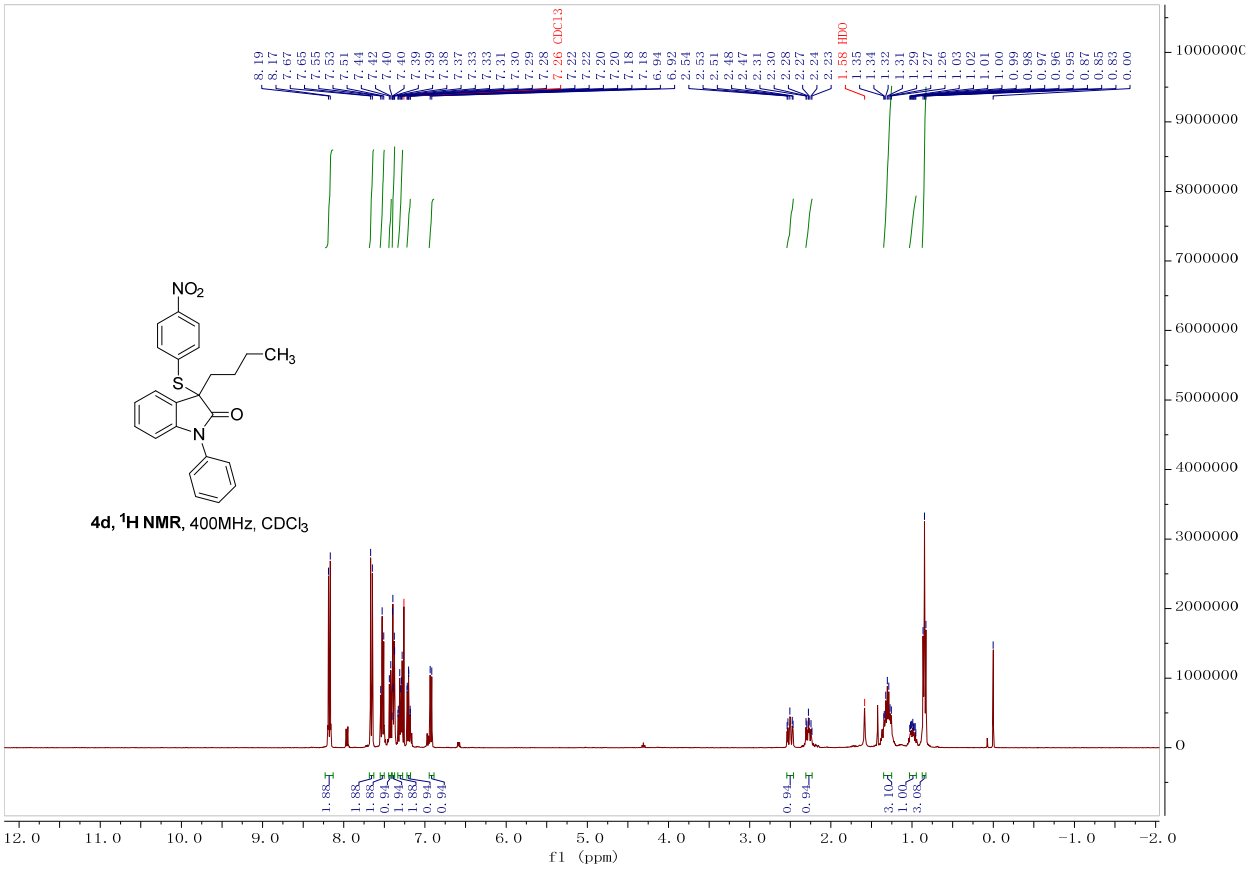
4c,^{1}H NMR, 400MHz, DMSO-d_6



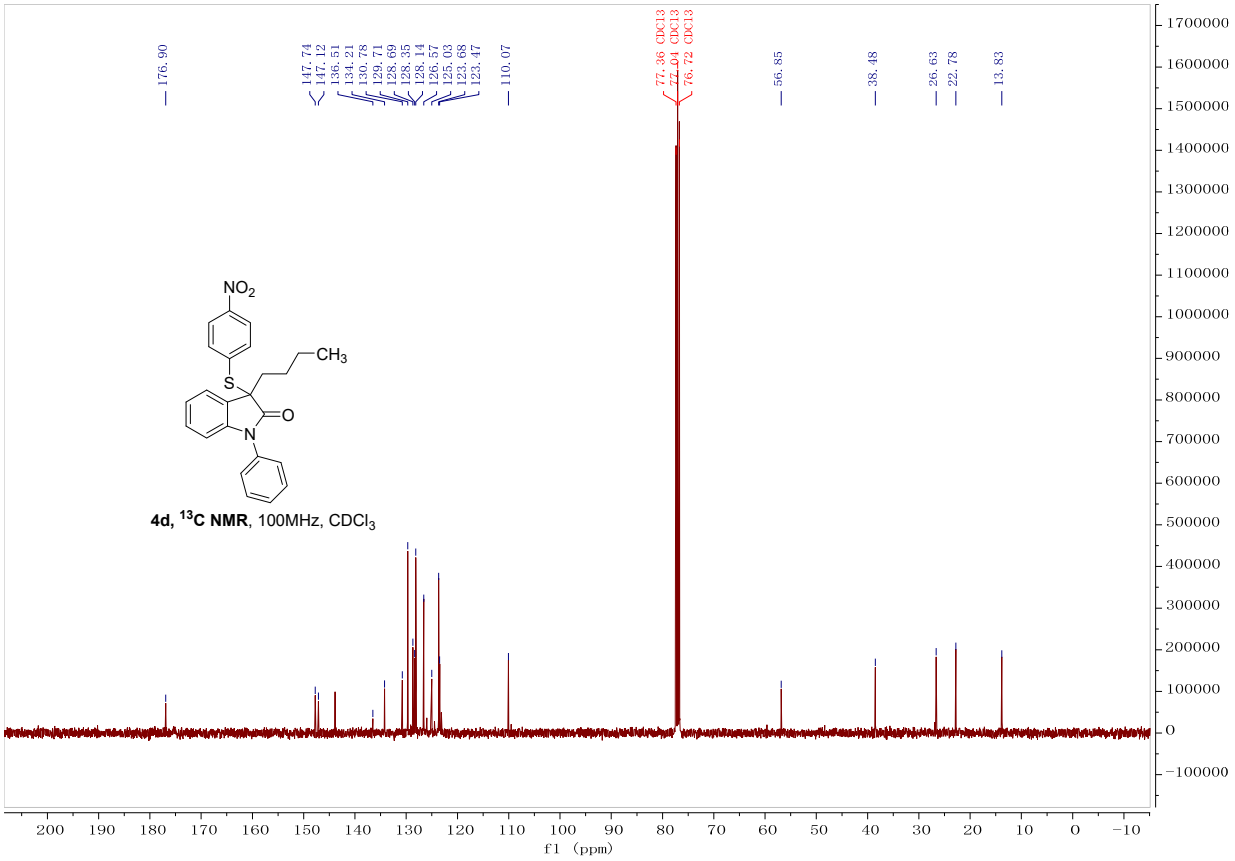
4c, ^{13}C NMR, 100MHz, DMSO-d_6



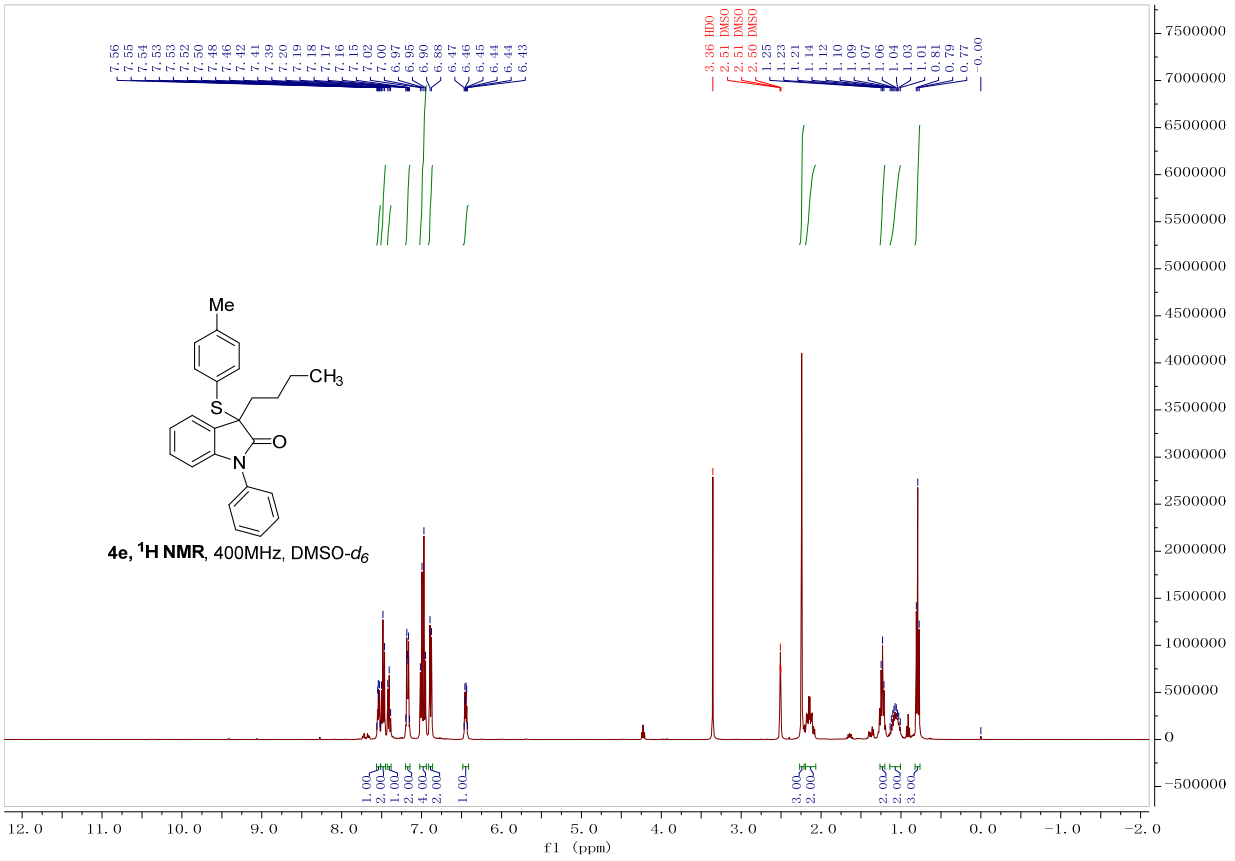
4c, ^{19}F NMR, 376MHz, DMSO-d_6



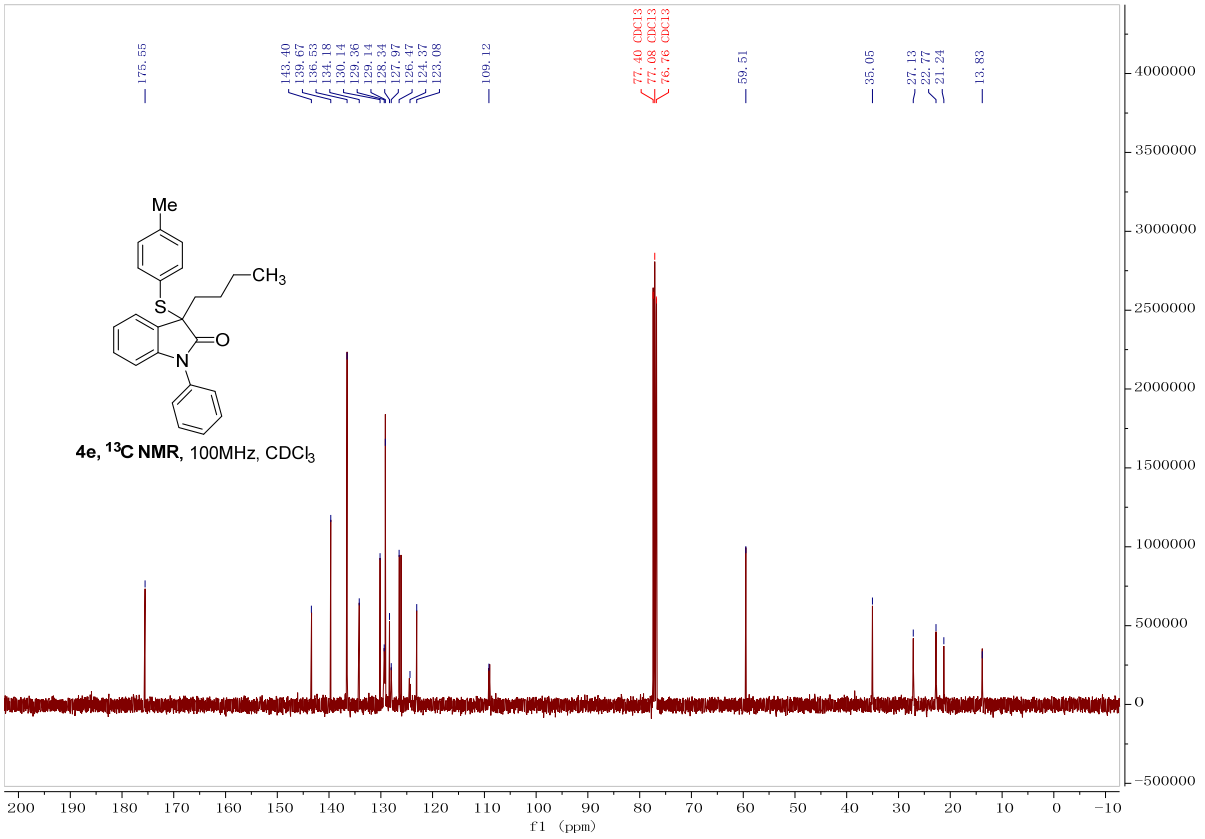
4d, ^{1}H NMR, 400MHz, $CDCl_3$



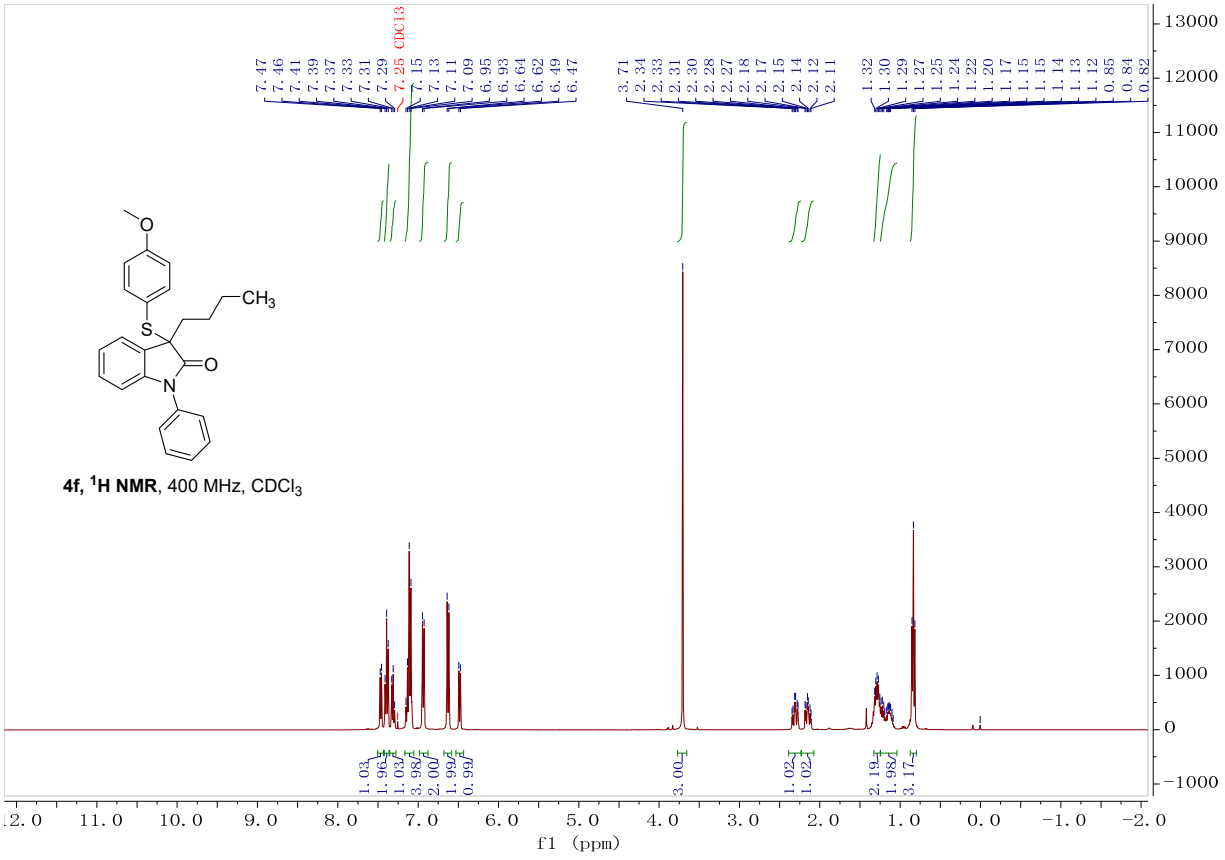
4d, ^{13}C NMR, 100MHz, $CDCl_3$



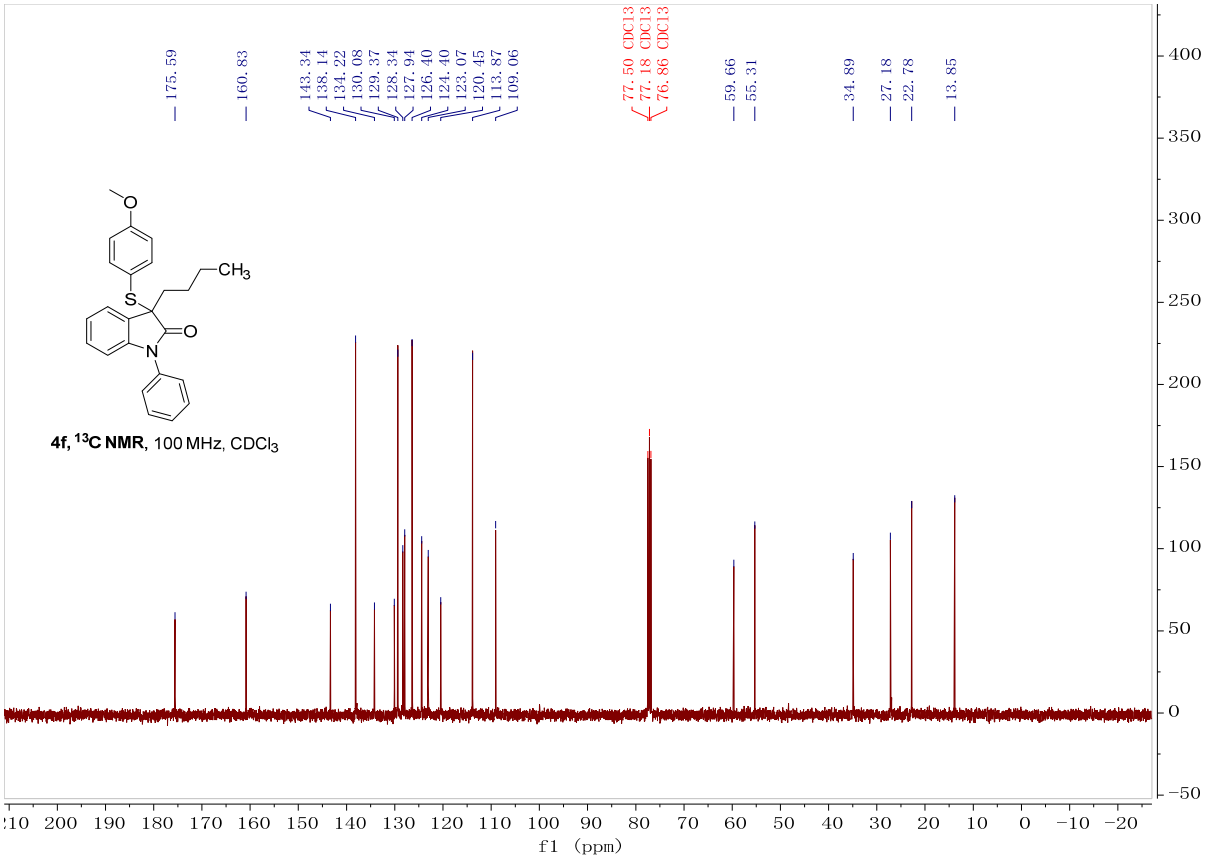
4e, ^{1}H NMR, 400MHz, DMSO-d_6



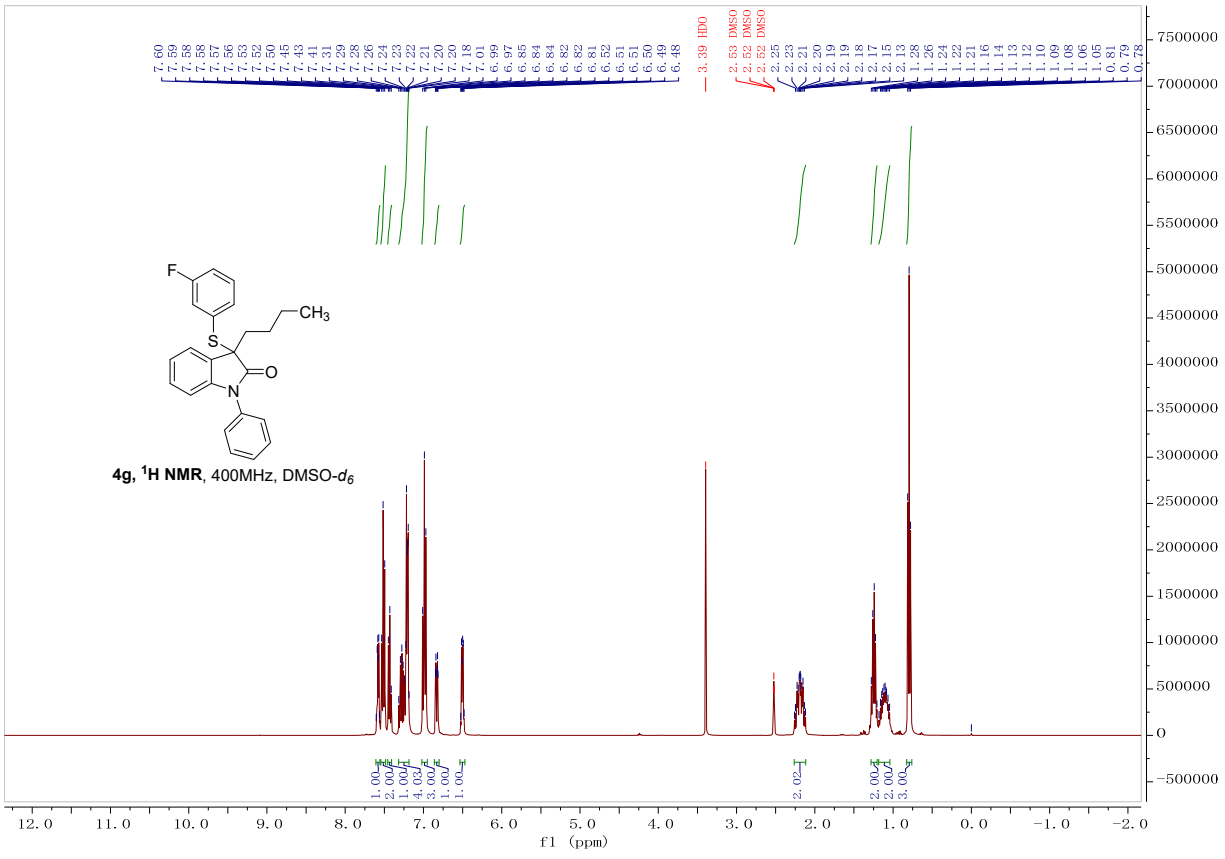
4e, ^{13}C NMR, 100MHz, $CDCl_3$



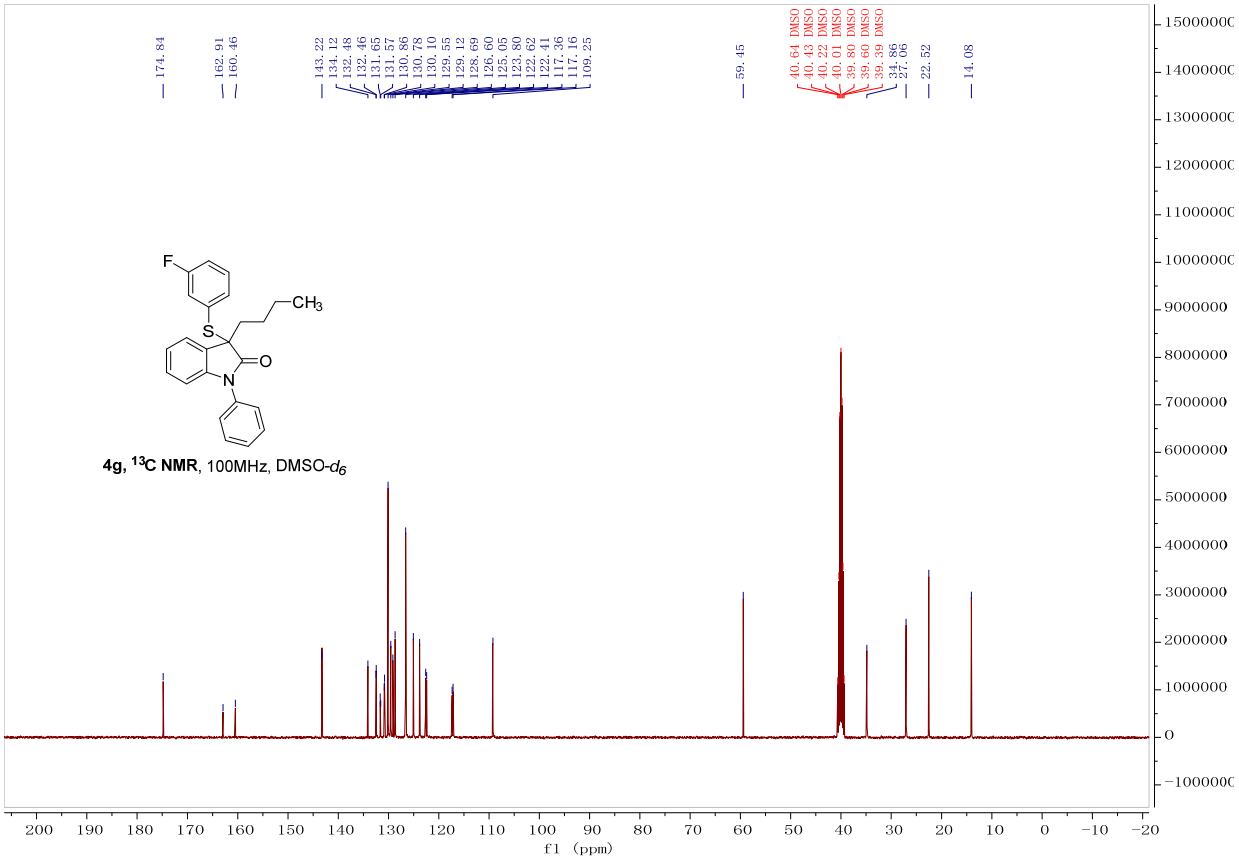
4f, ^{1}H NMR, 400 MHz, $CDCl_3$



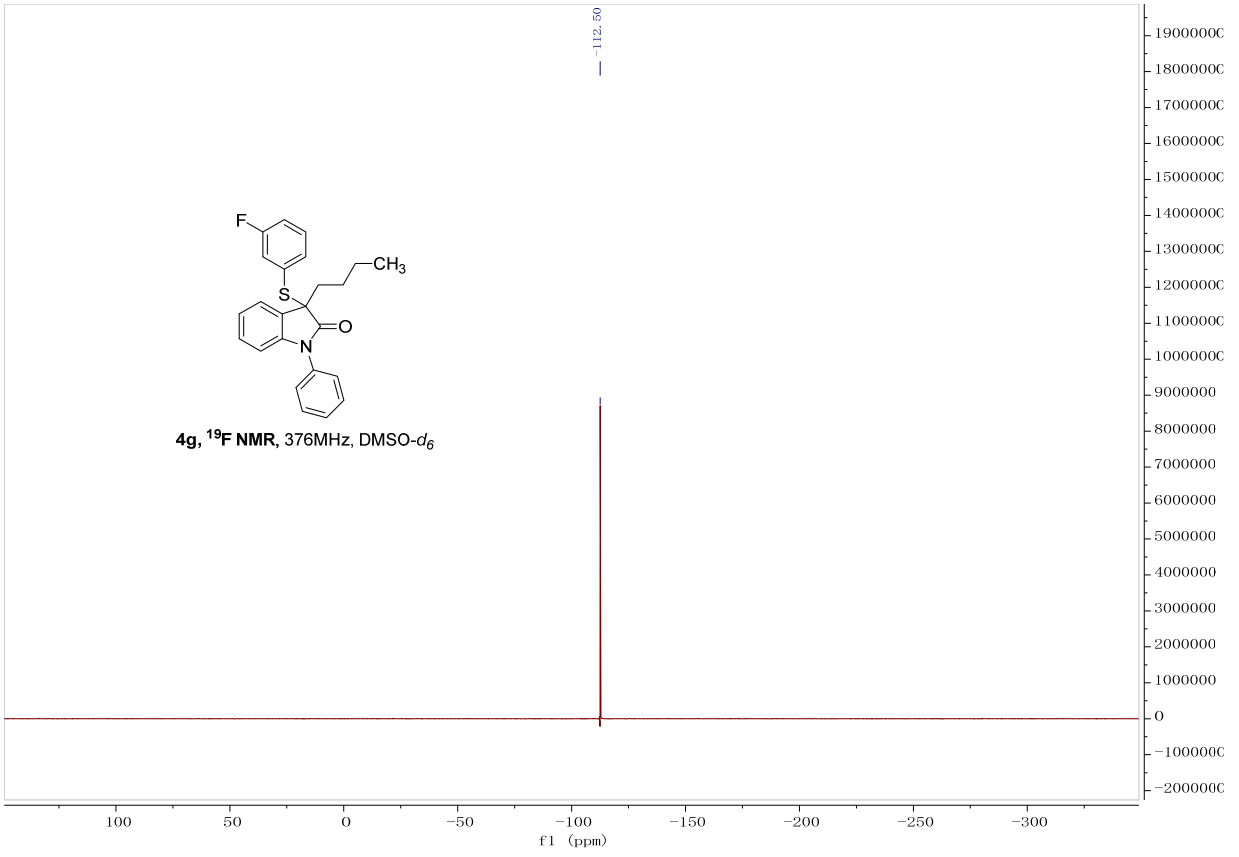
4f, ^{13}C NMR, 100 MHz, $CDCl_3$



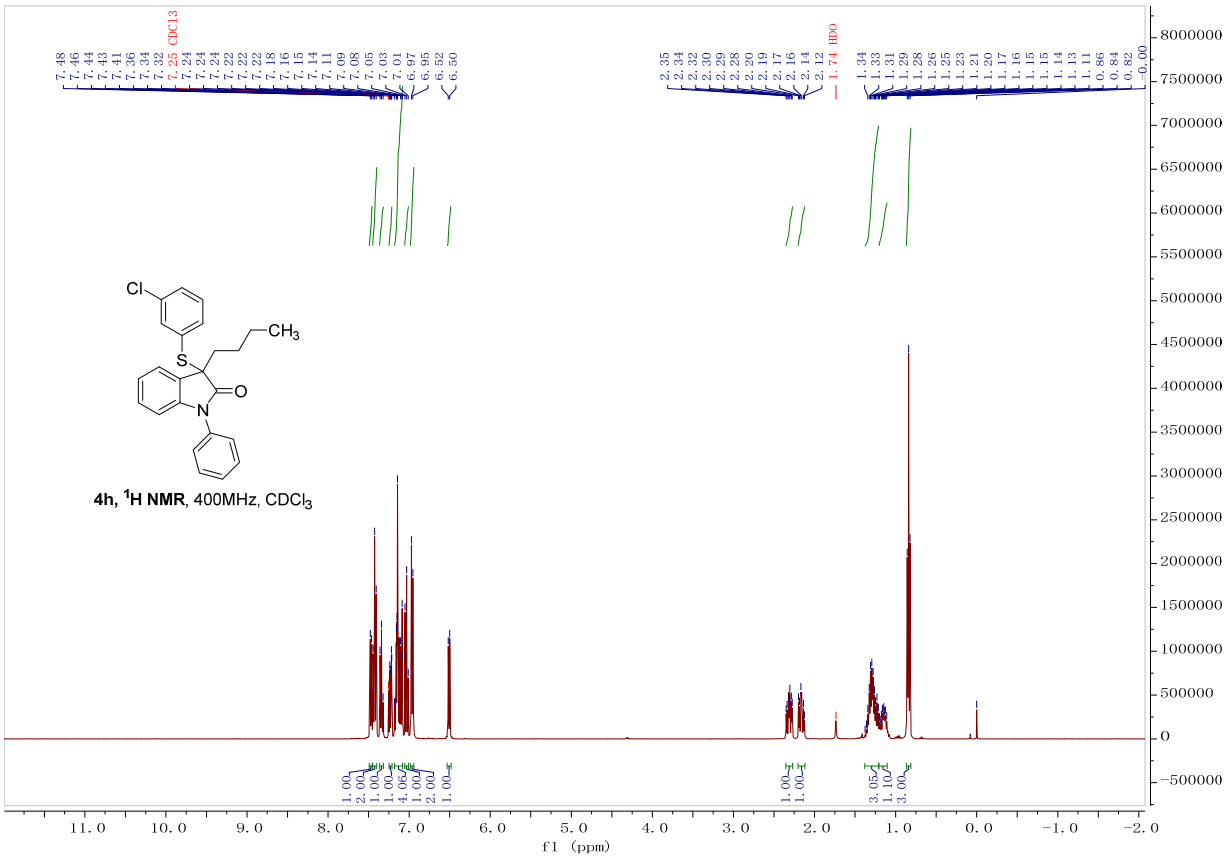
4g, ^{1}H NMR, 400MHz, DMSO-d_6

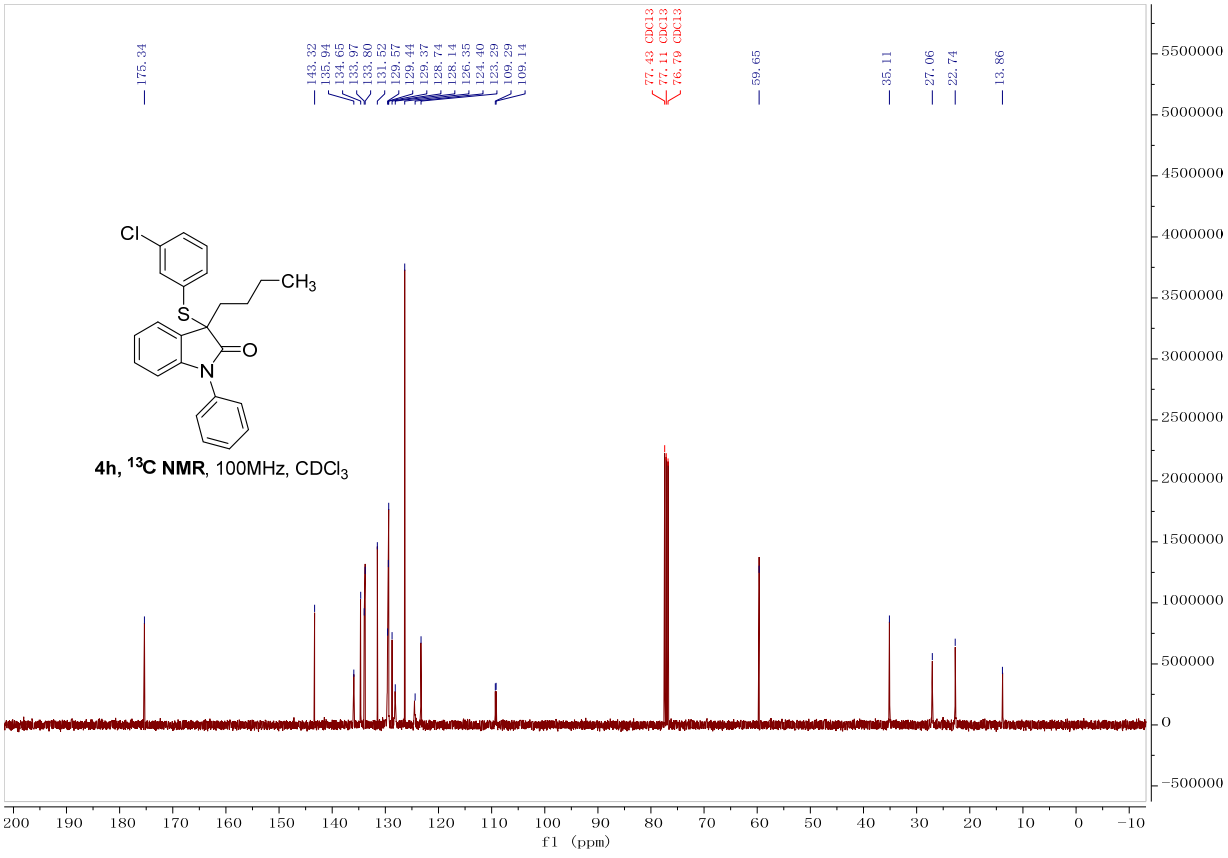


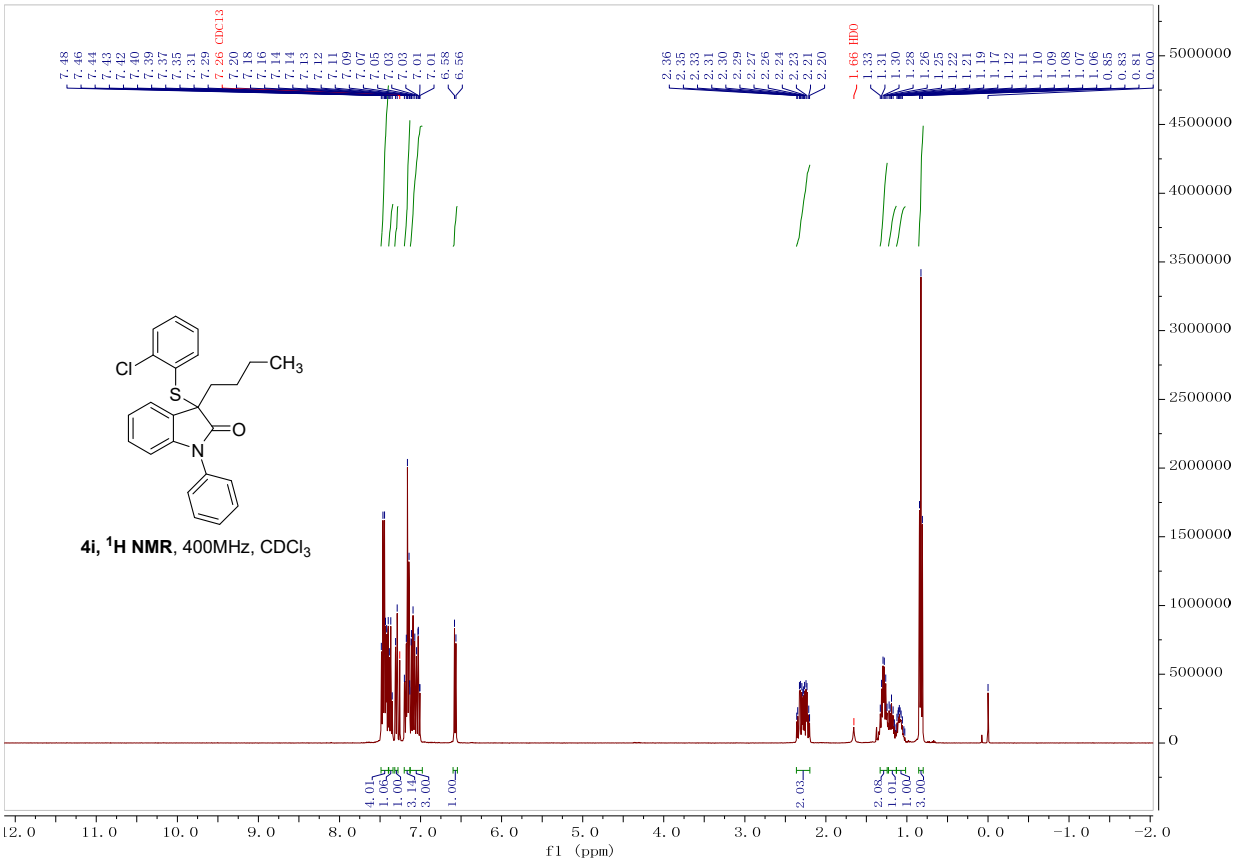
4g, ^{13}C NMR, 100MHz, DMSO-d_6



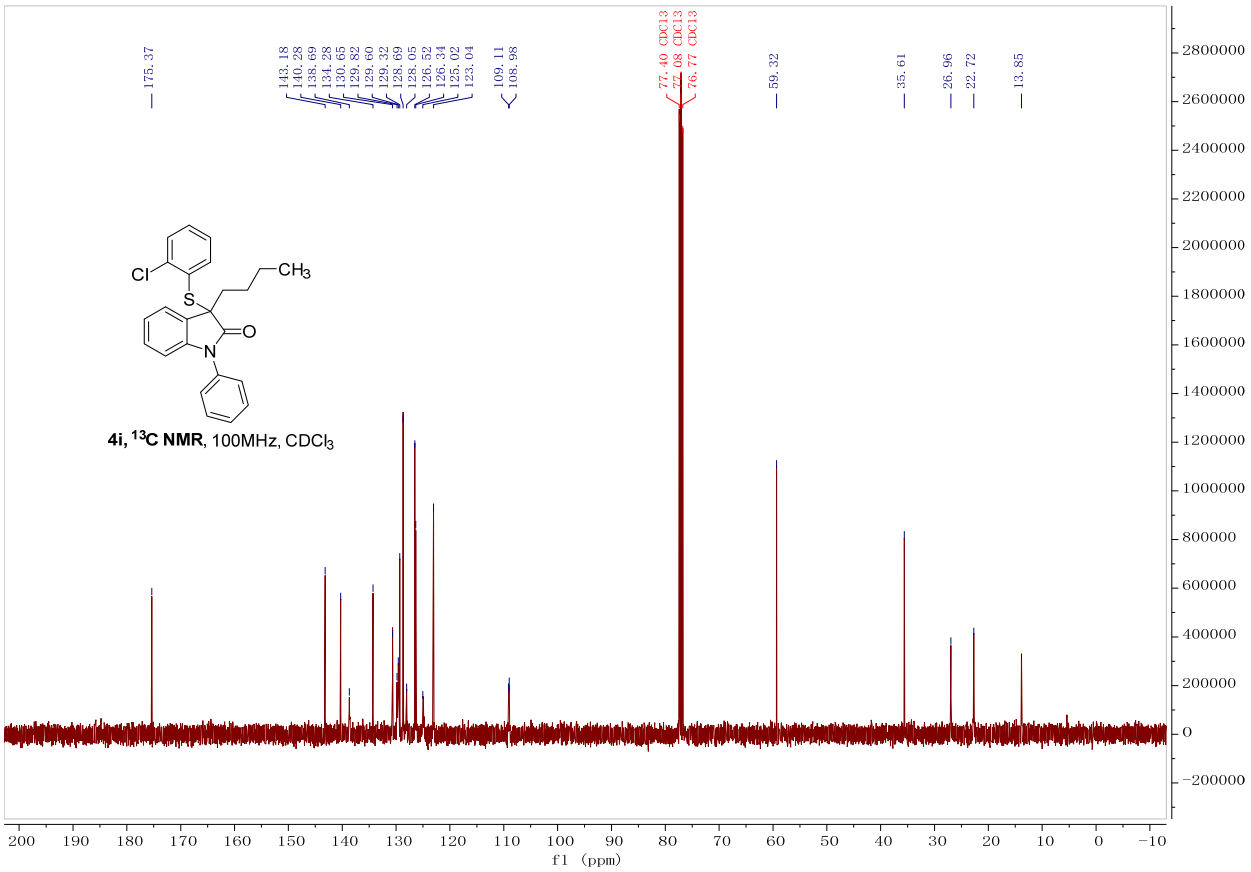
4g, ^{19}F NMR, 376MHz, DMSO-d_6


Cl
CH3
S
O
N
4h, 1H NMR, 400MHz, CDCl3
f1 (ppm)

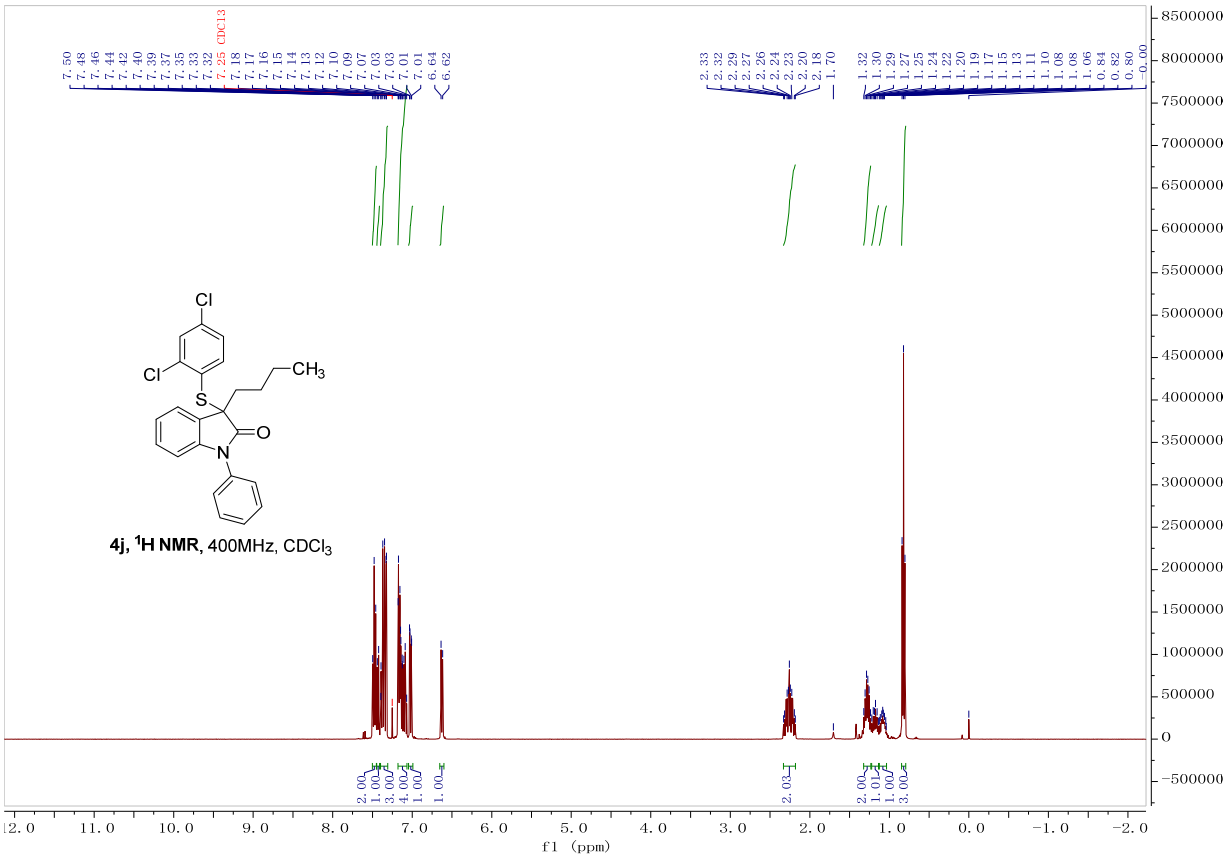

Cl
CH3
S
O
N
4h, 13C NMR, 100MHz, CDCl3
f1 (ppm)

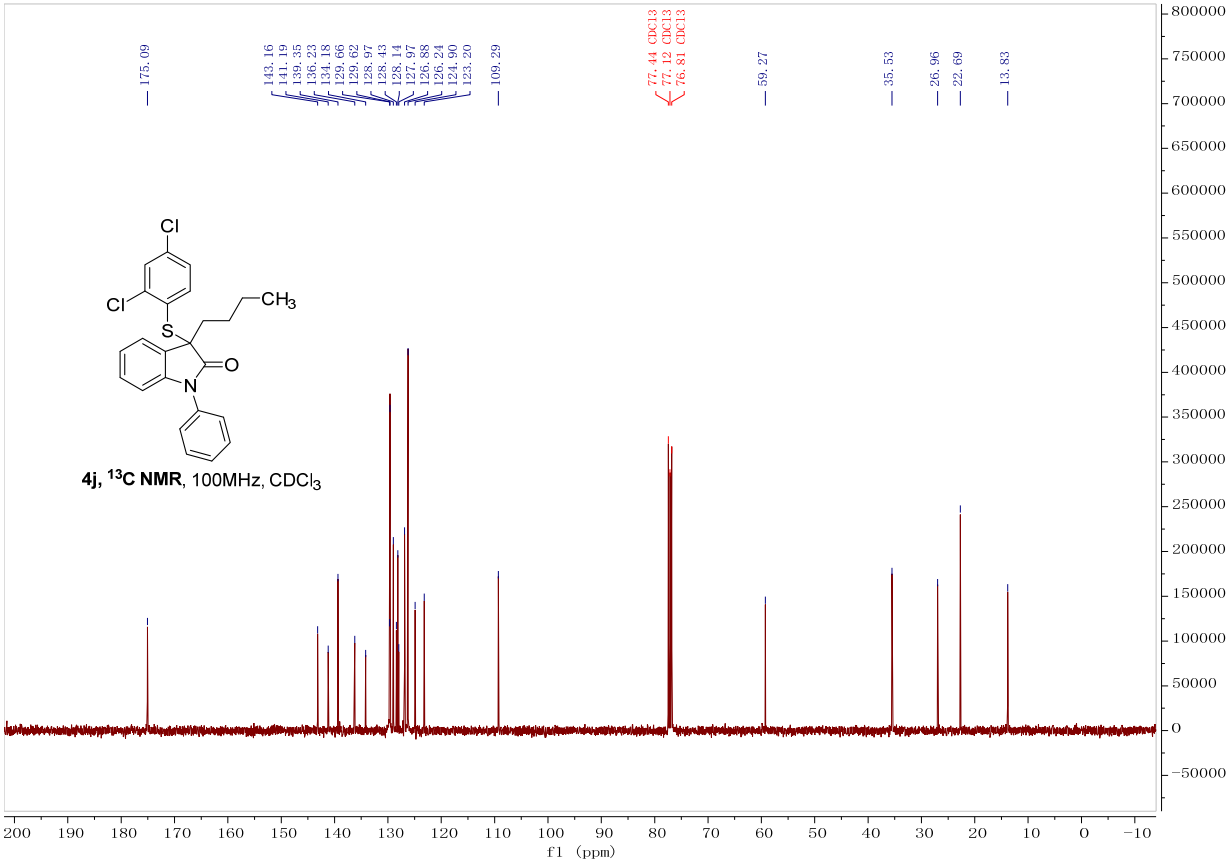


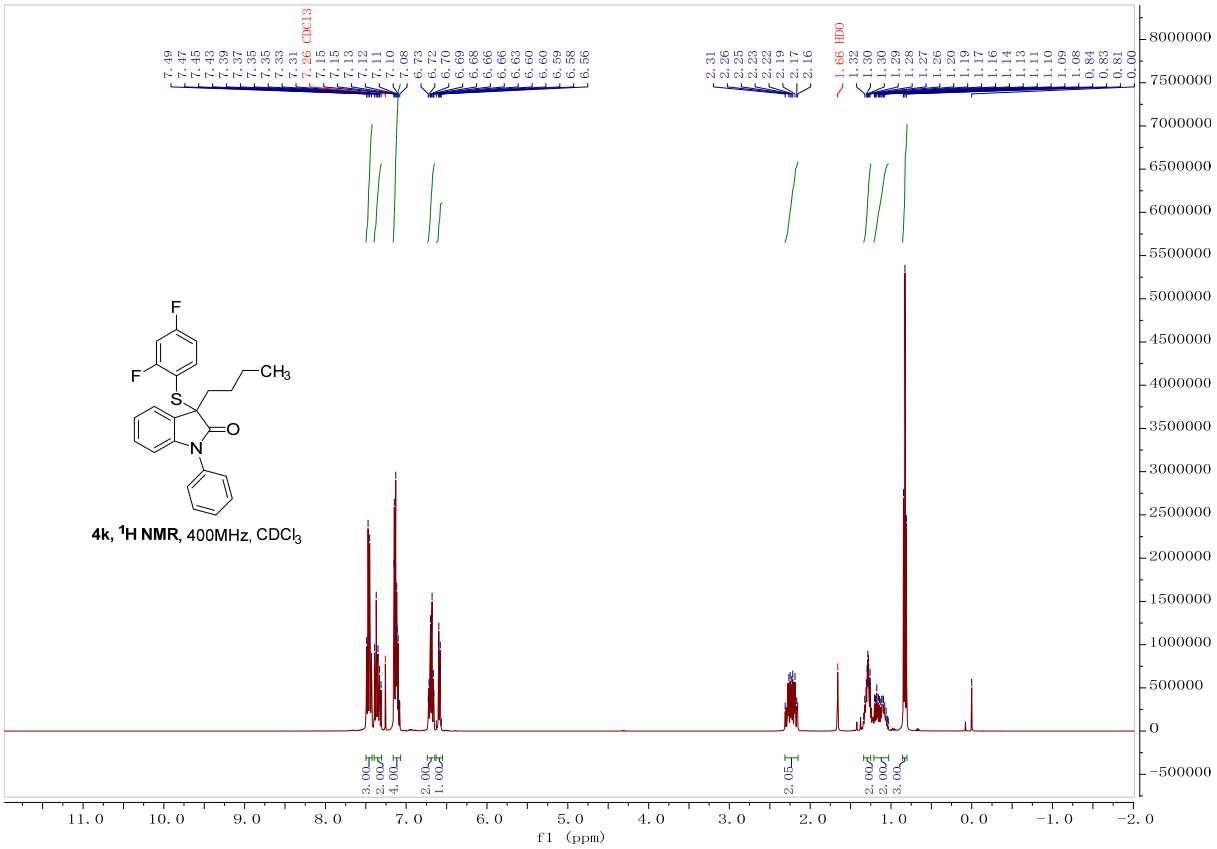
4i, ^{1}H NMR, 400MHz, $CDCl_3$

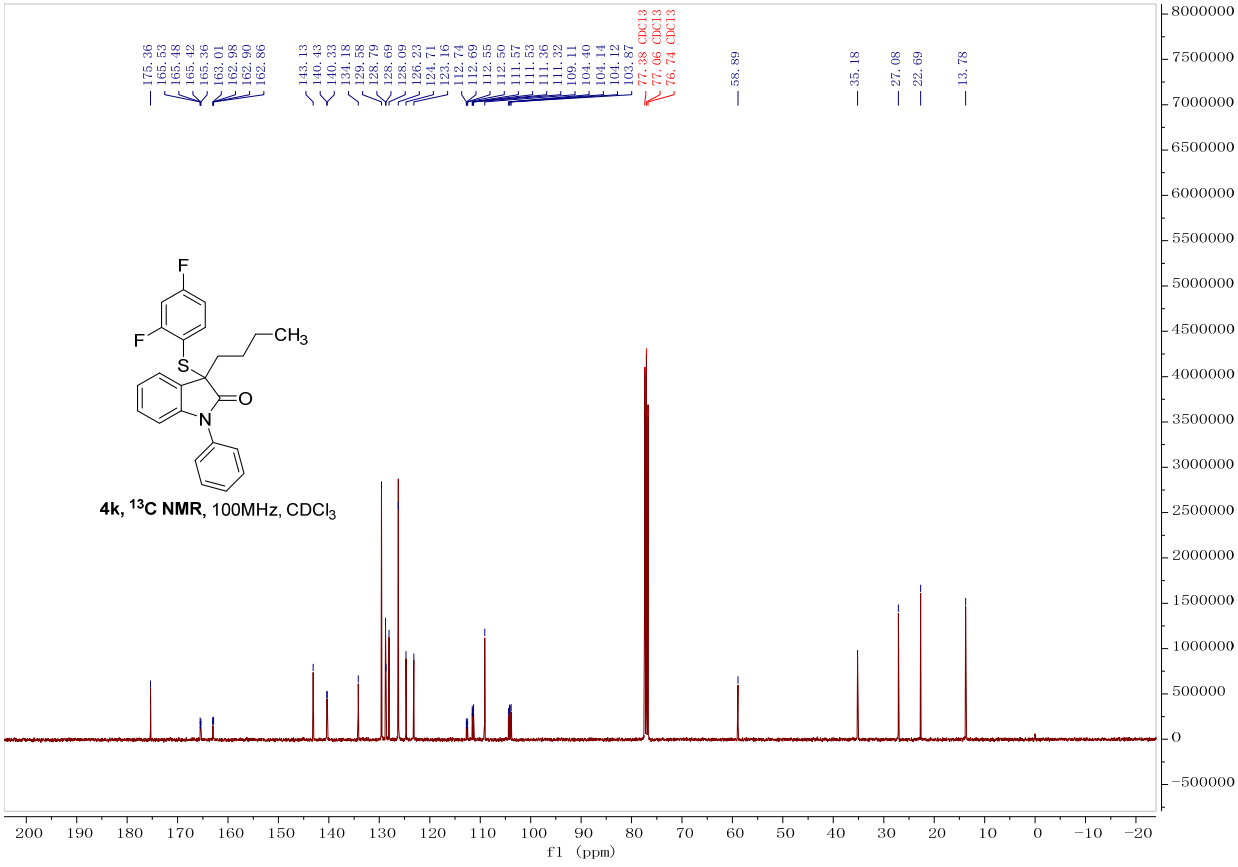


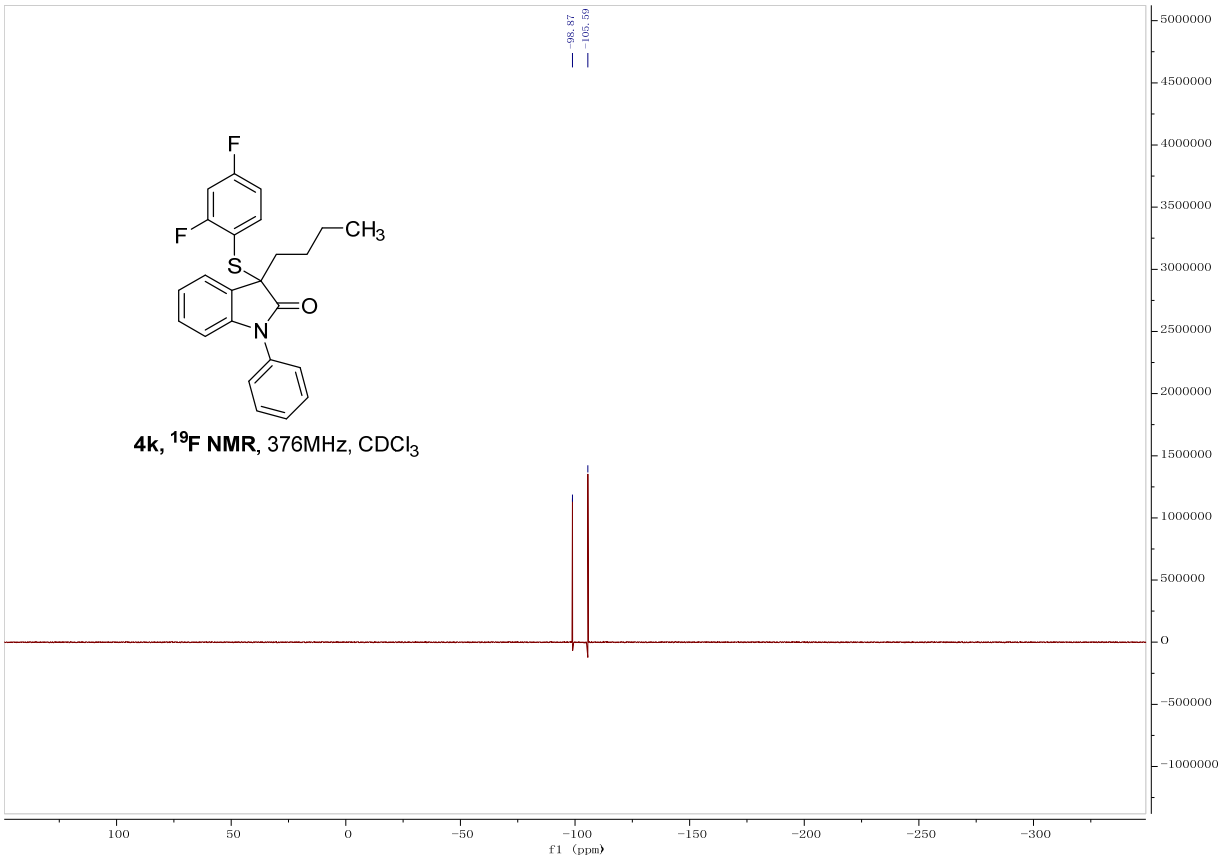
4i, ^{13}C NMR, 100MHz, $CDCl_3$


Cl
Cl
S
CH3
O
N
4j, 1H NMR, 400MHz, CDCl3
f1 (ppm)

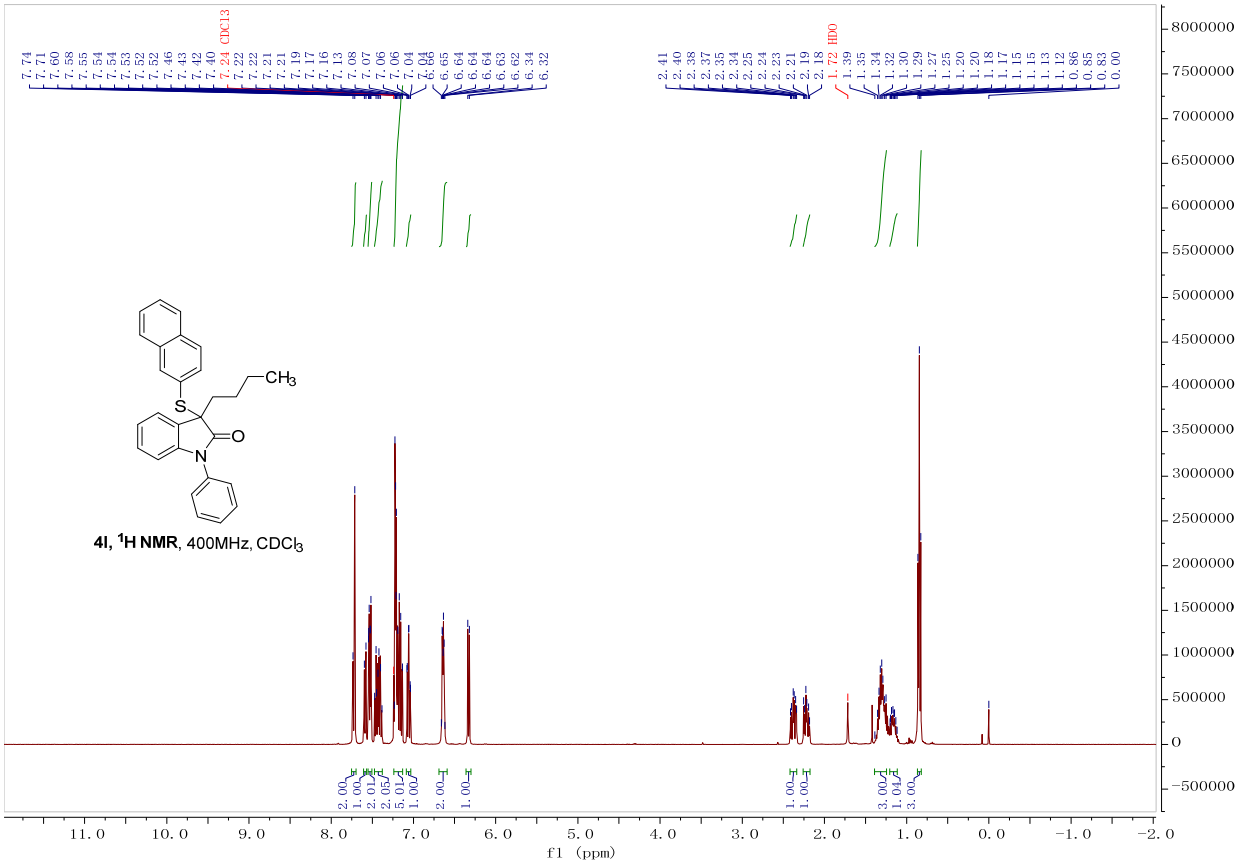

Cl
Cl
S
CH3
O
N
4j, 13C NMR, 100MHz, CDCl3
f1 (ppm)


F
F
S
CH3
O
N
4k, 1H NMR, 400MHz, CDCl3
f1 (ppm)

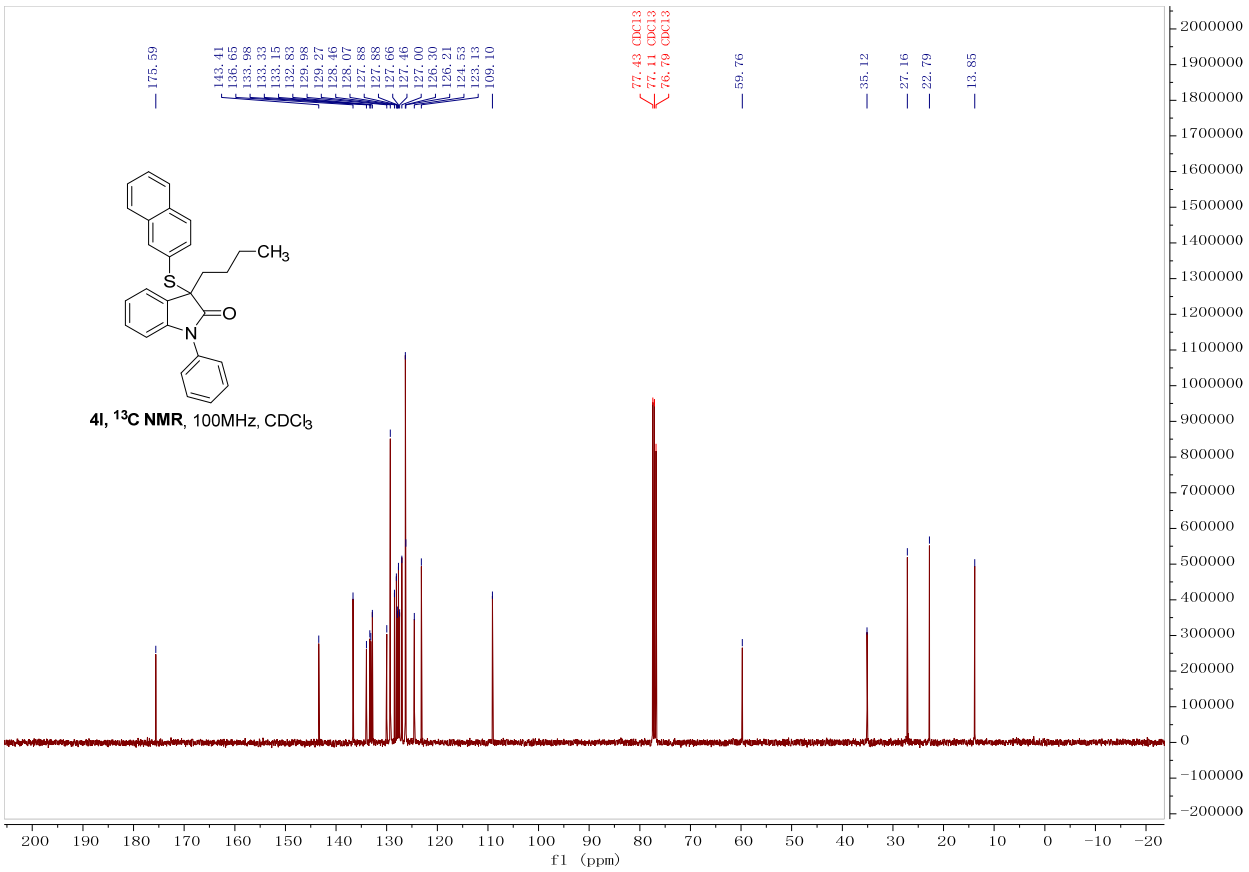

F
F
S
CH3
O
N
4k, 13C NMR, 100MHz, CDCl3
f1 (ppm)



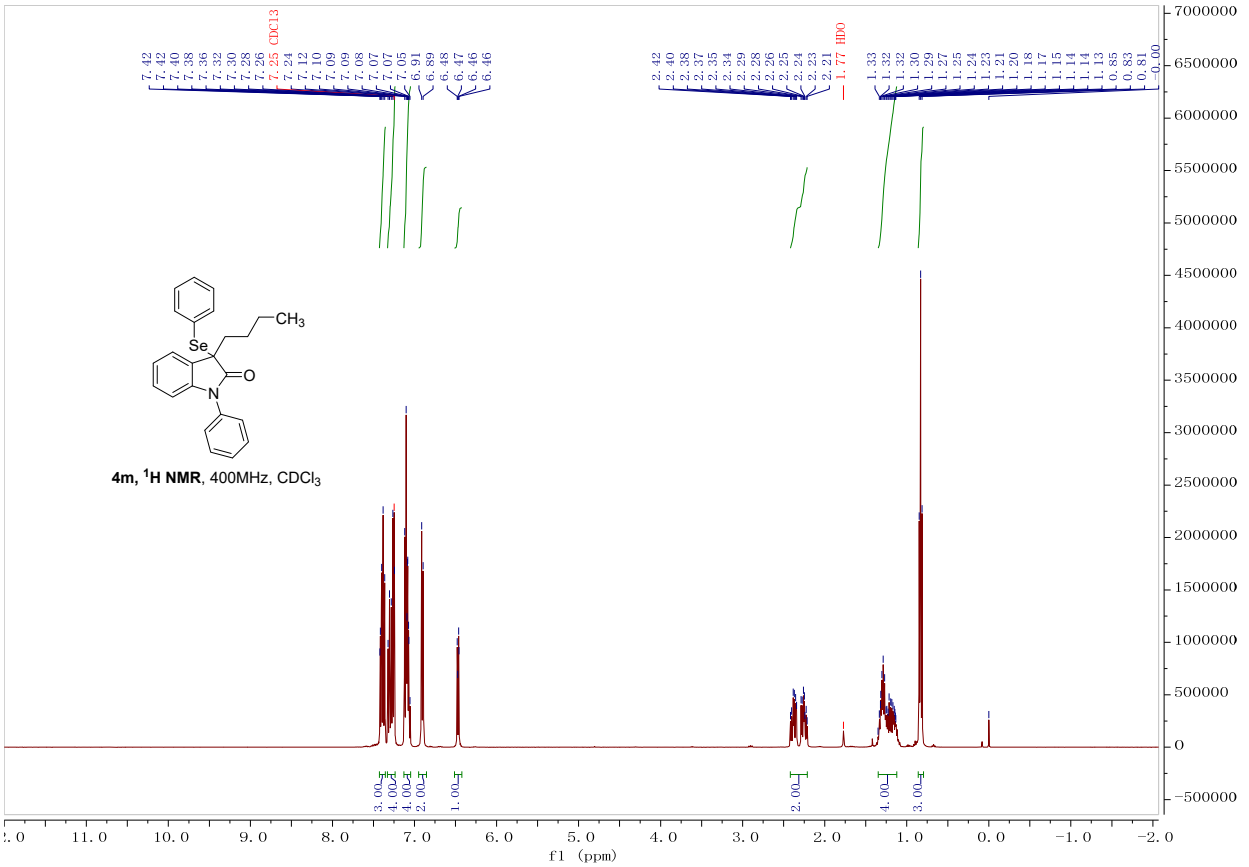
4k, ^{19}F NMR, 376MHz, $CDCl_3$



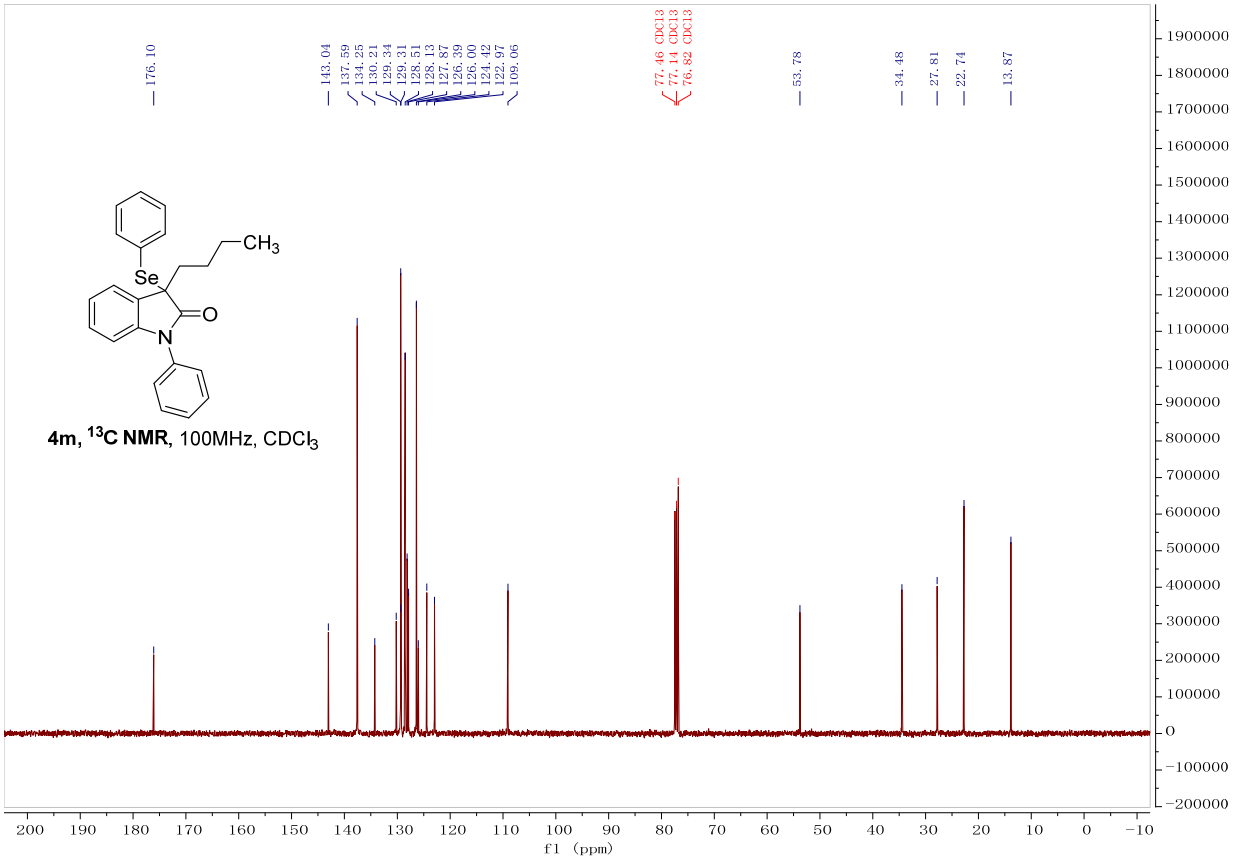
4l, ^{1}H NMR, 400MHz, $CDCl_3$



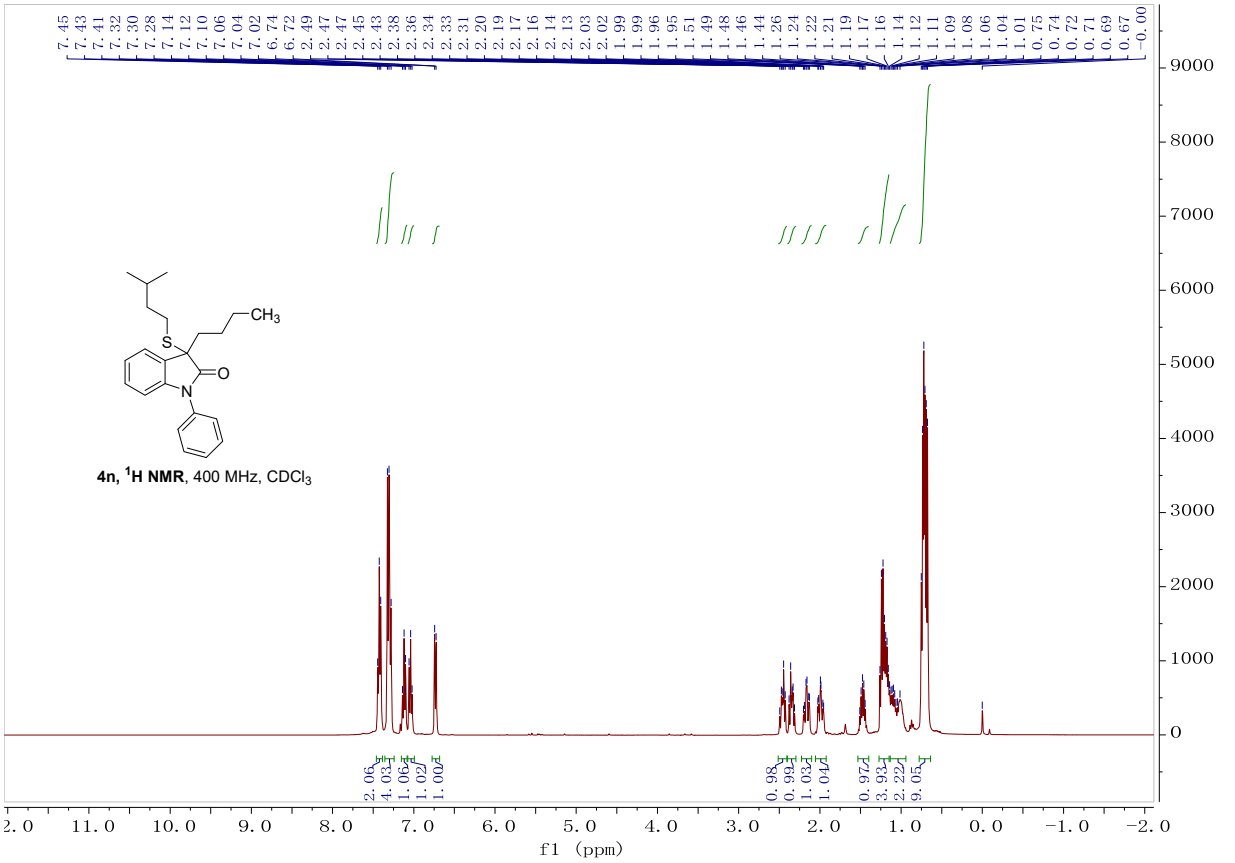
4l, ^{13}C NMR, 100MHz, $CDCl_3$



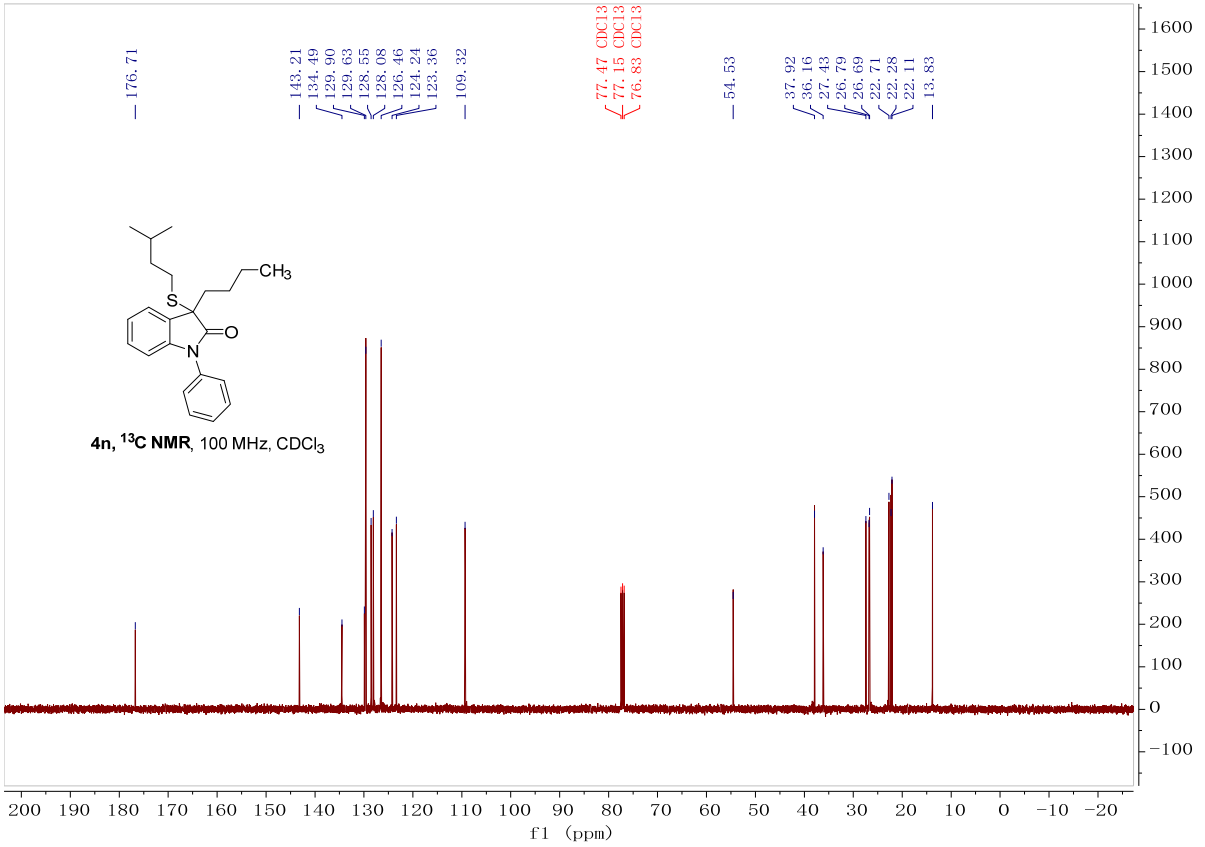
4m, ^{1}H NMR, 400MHz, $CDCl_3$



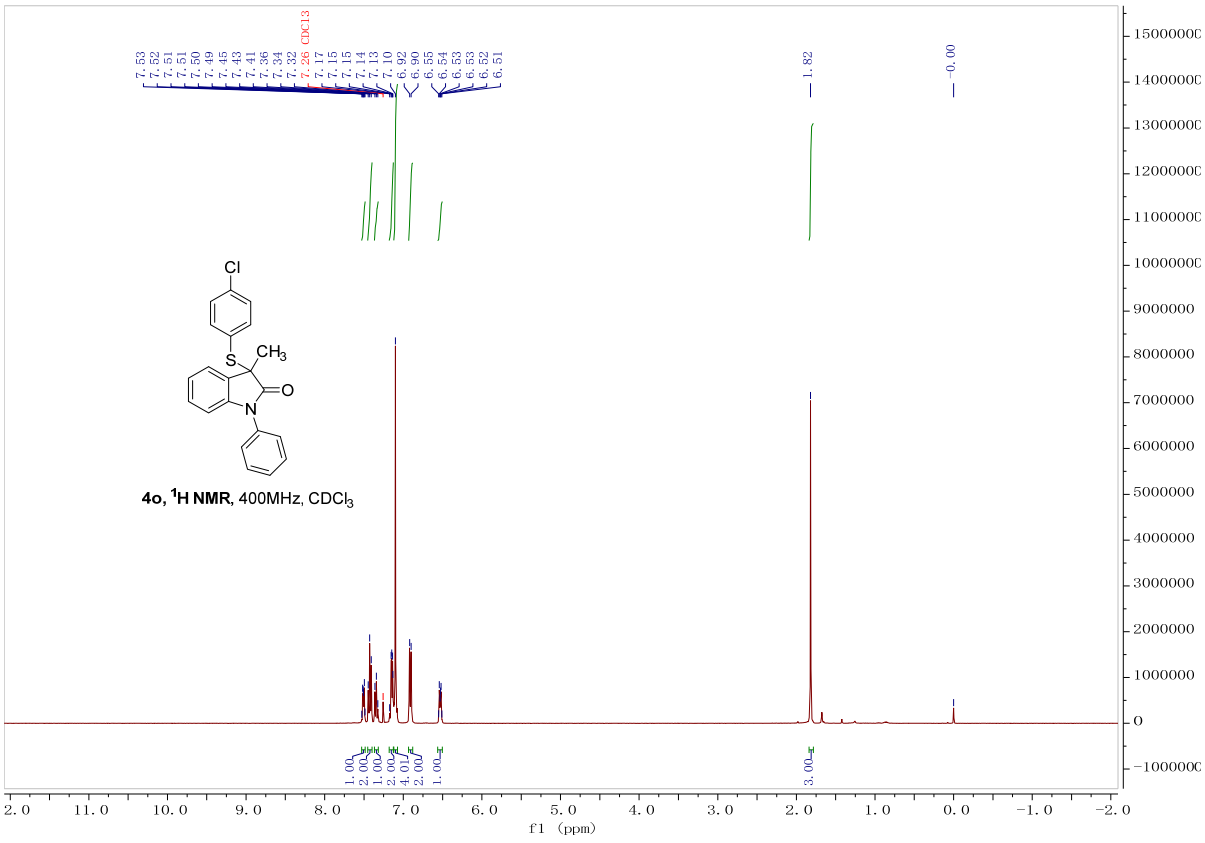
4m, **^{13}C NMR**, 100MHz, $CDCl_3$



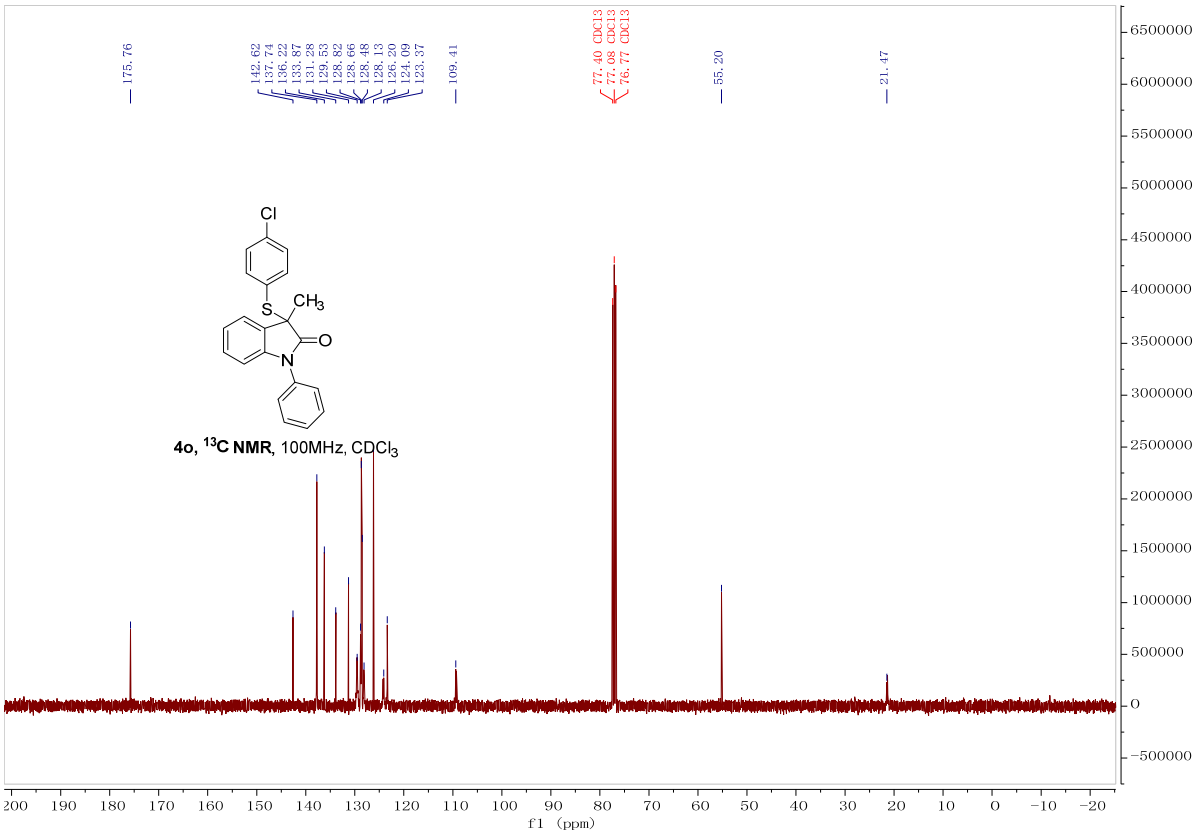
4n, **^{1}H NMR**, 400 MHz, $CDCl_3$



4n, ^{13}C NMR, 100 MHz, $CDCl_3$



4o, ^{1}H NMR, 400MHz, $CDCl_3$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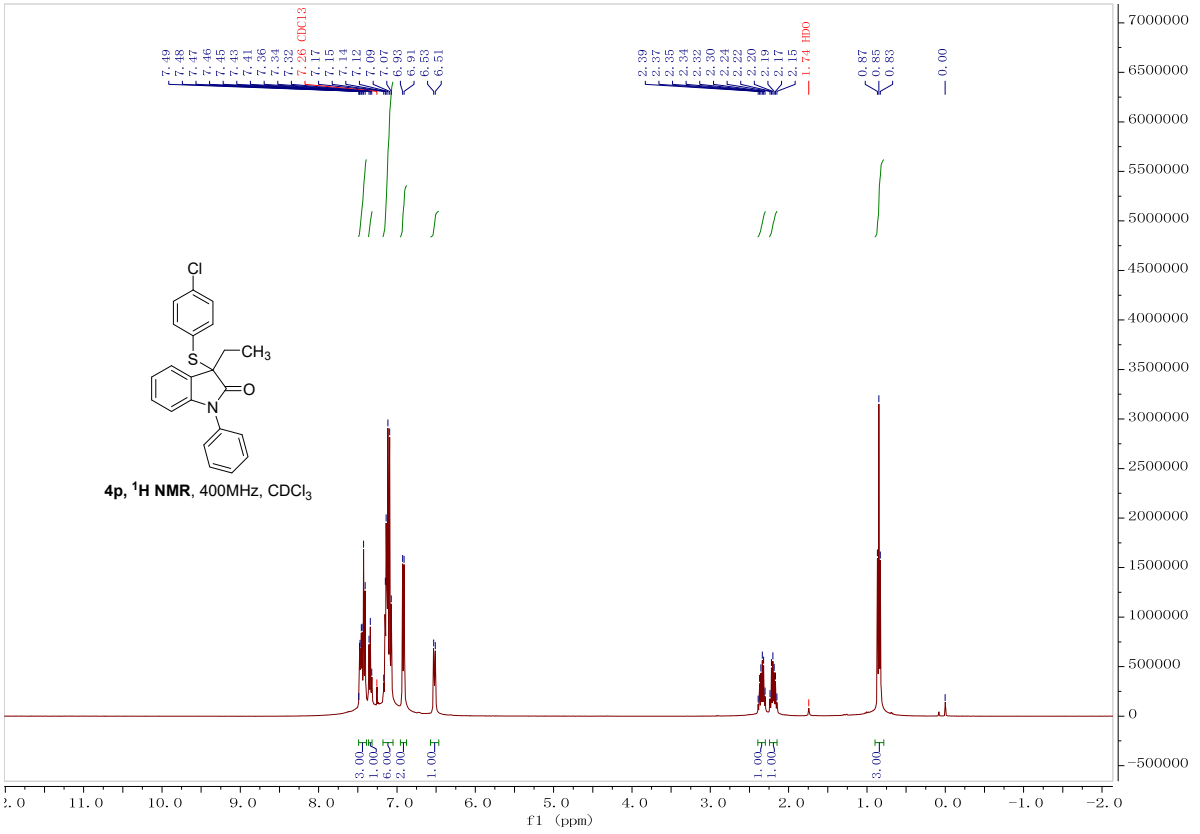
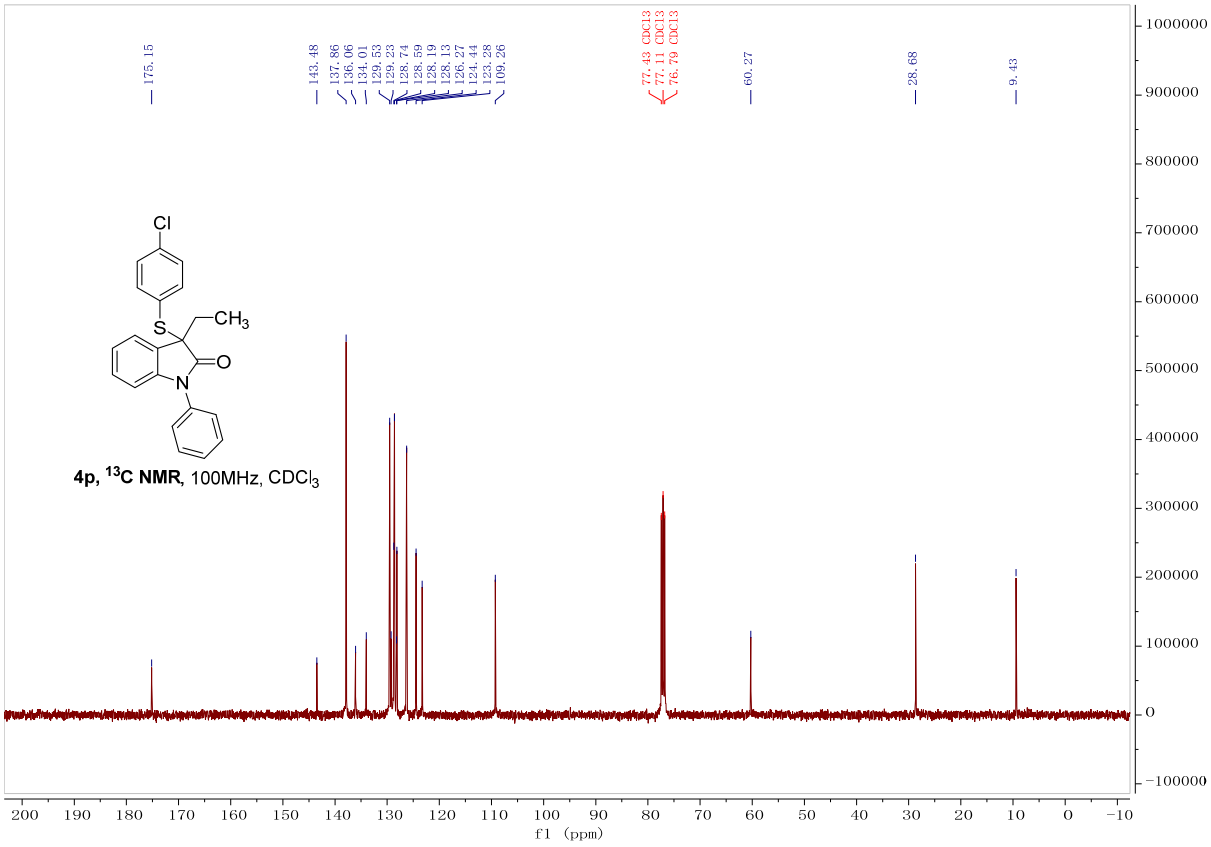
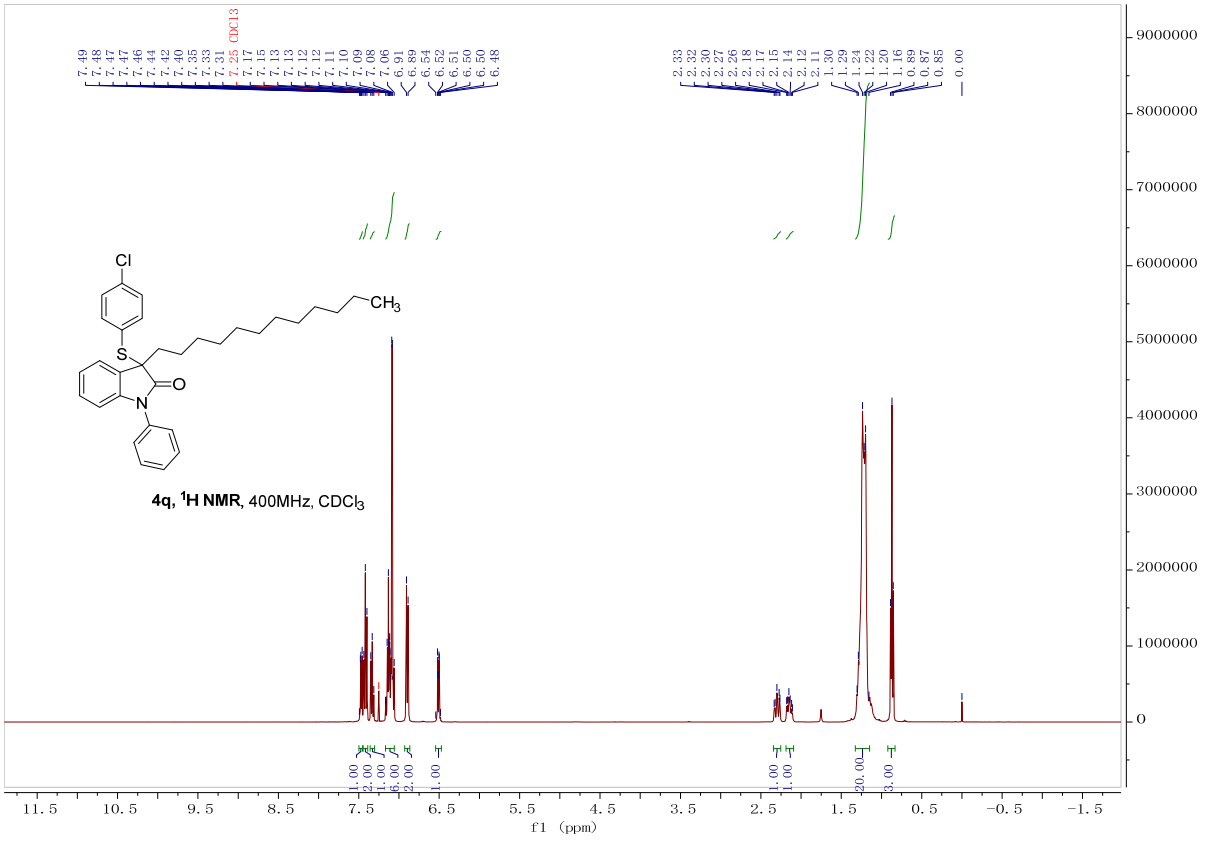
136.22
133.87
131.28
129.53
128.82
128.66
128.48
128.13
126.20
124.09
123.37
109.41
77.40 CDCl3
77.08 CDCl3
76.77 CDCl3
55.20
21.47
Cl
S
CH3
O
N
4o, 13C NMR, 100MHz, CDCl3
f1 (ppm)

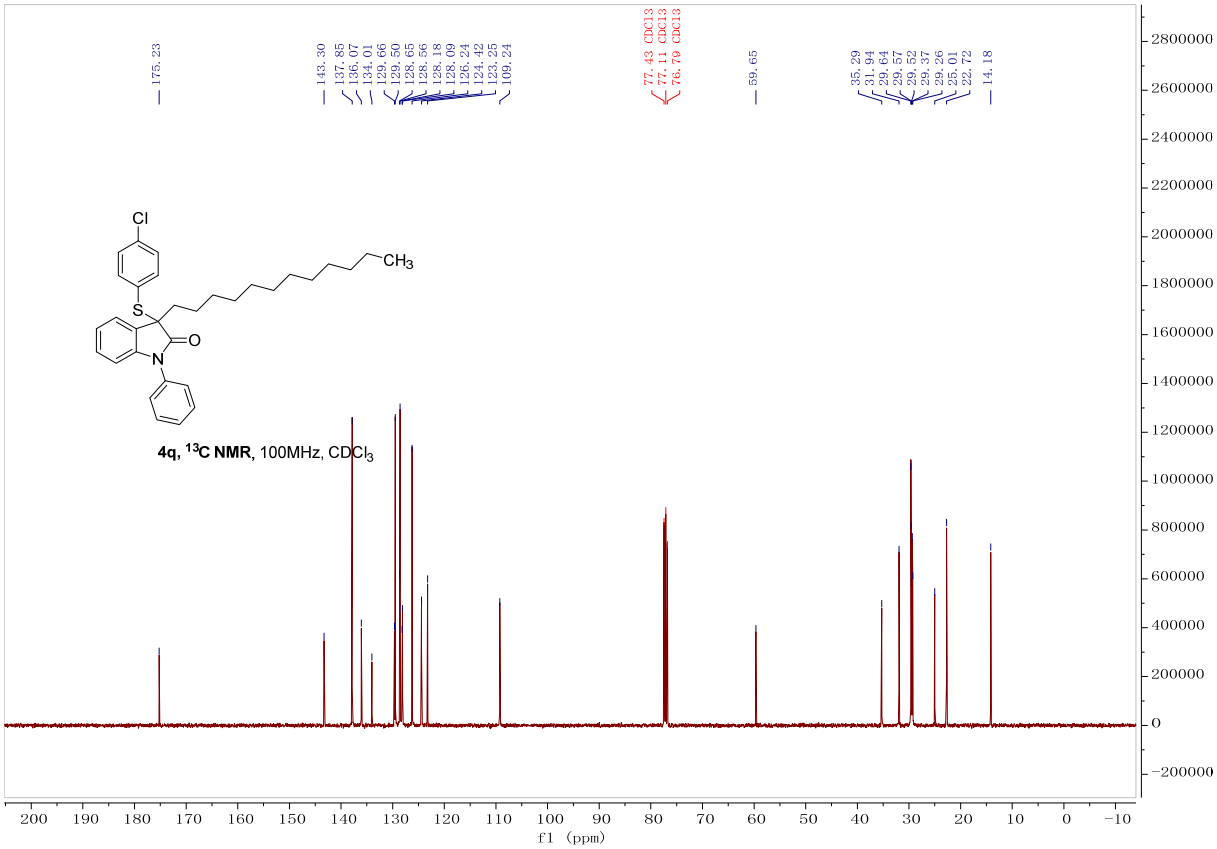

7.49
7.48
7.47
7.46
7.45
7.43
7.41
7.36
7.34
7.32
7.26 CDCl3
7.17
7.15
7.14
7.12
7.09
7.07
6.93
6.91
6.53
6.51
2.39
2.37
2.35
2.34
2.32
2.30
2.24
2.22
2.20
2.19
2.17
2.15
1.74 HDO
0.87
0.85
0.83
0.00
Cl
S
CH3
O
N
4p, 1H NMR, 400MHz, CDCl3
3.00
1.00
6.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)



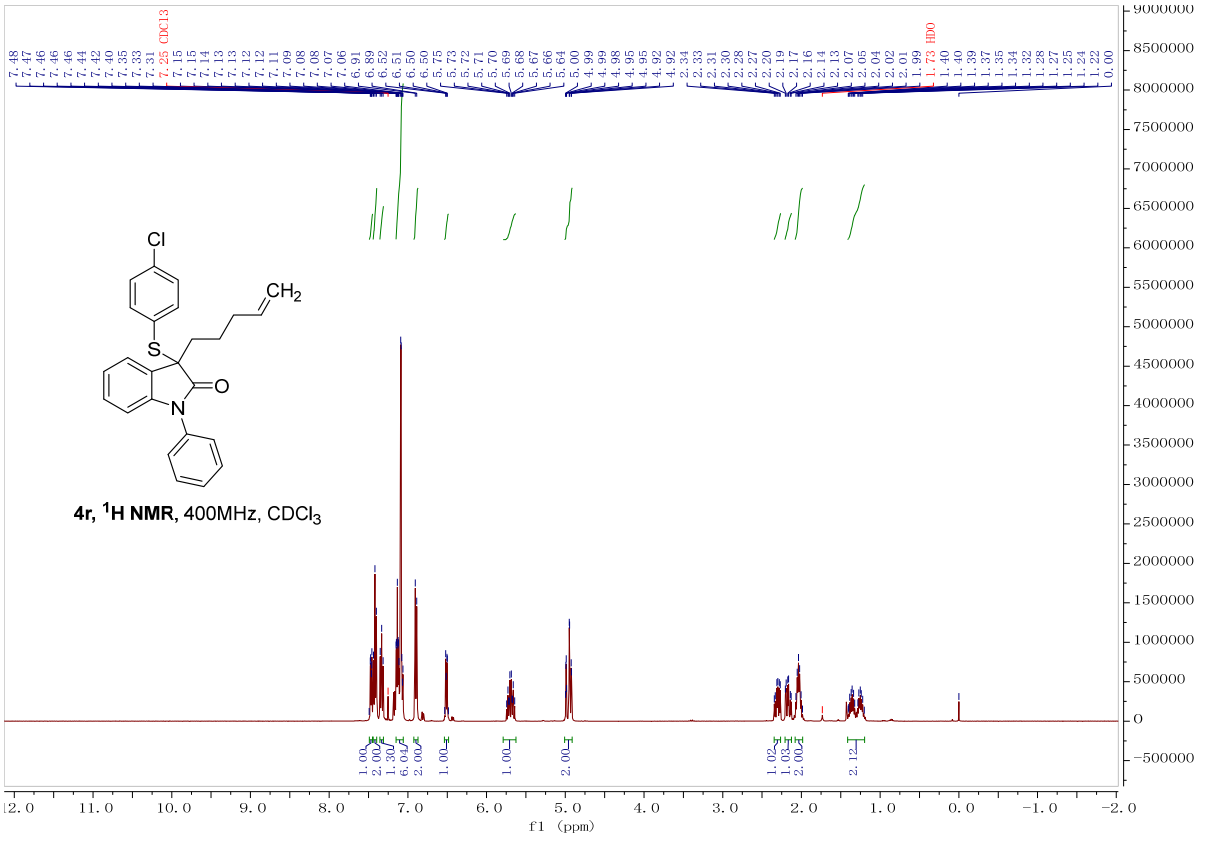
4p, ^{13}C NMR, 100MHz, $CDCl_3$



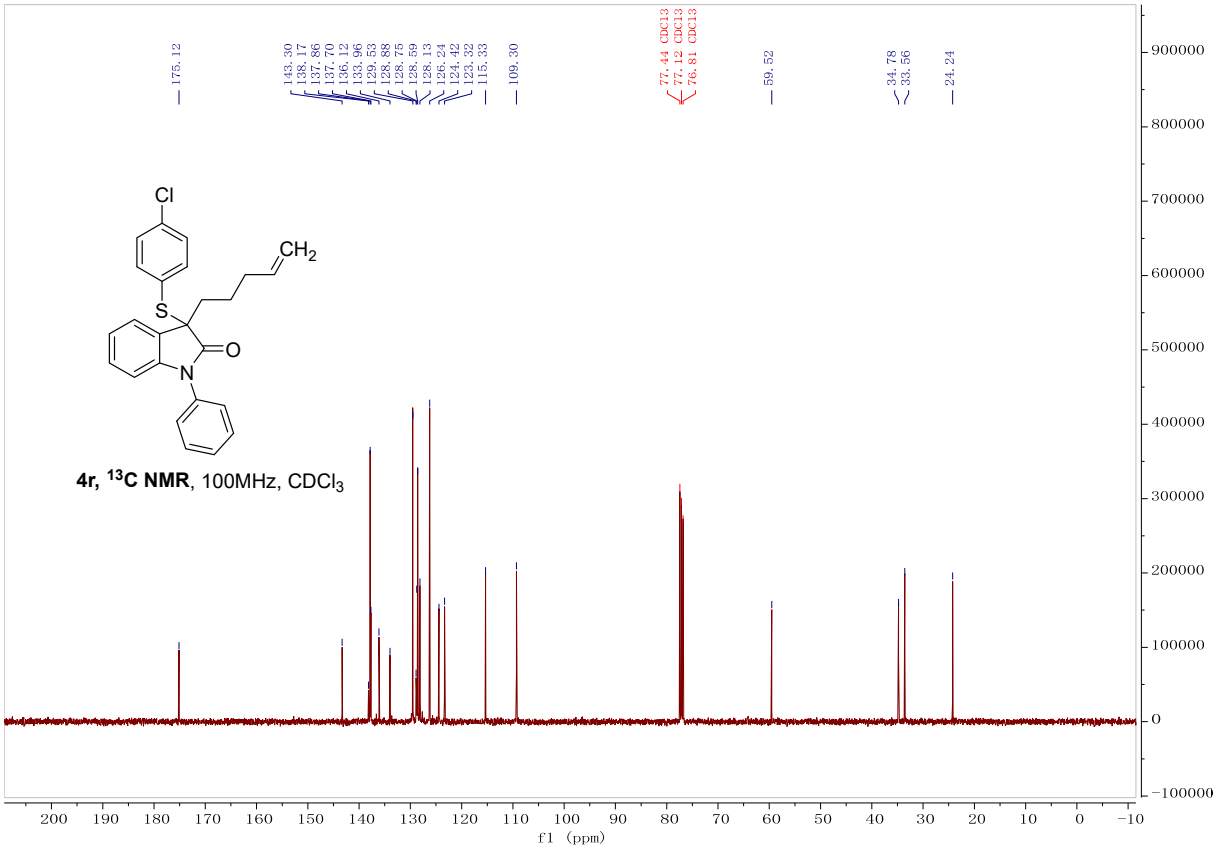
4q, ^{1}H NMR, 400MHz, $CDCl_3$



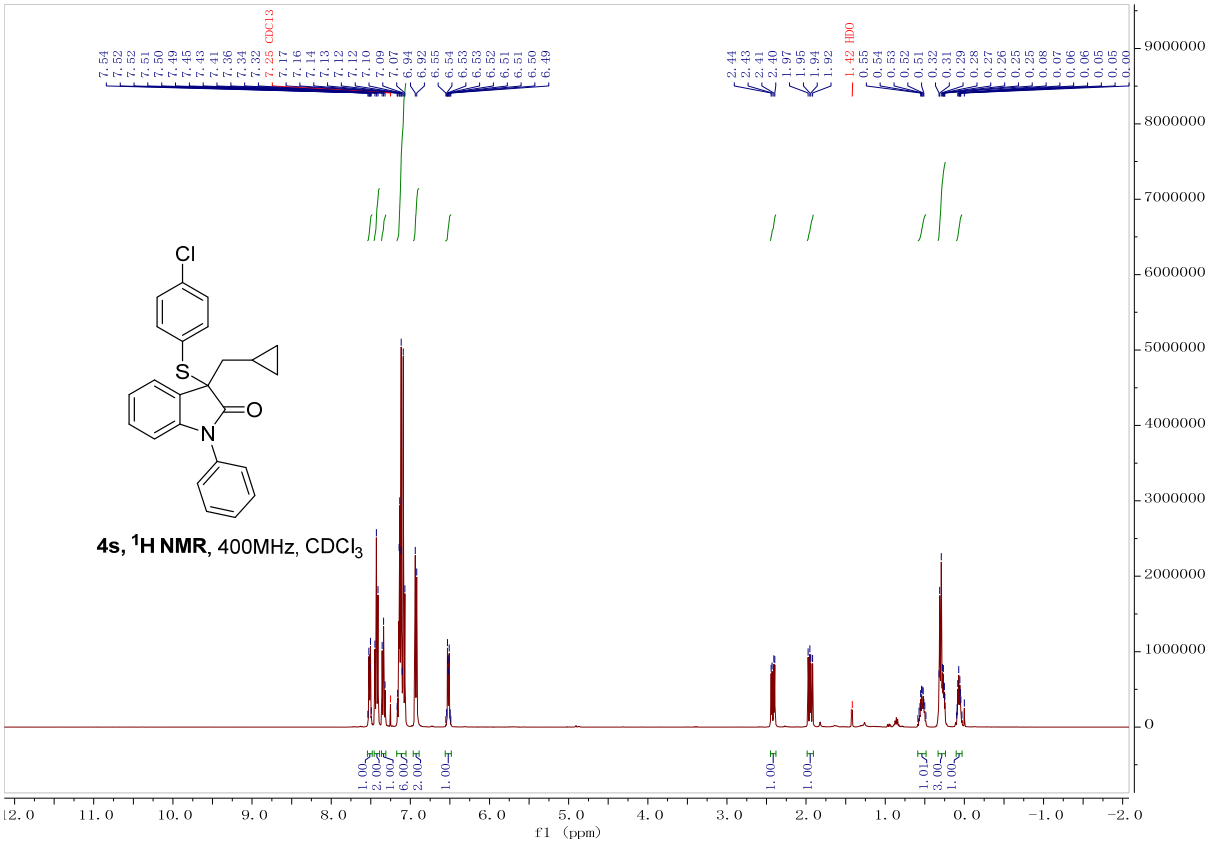
4q, ^{13}C NMR, 100MHz, $CDCl_3$



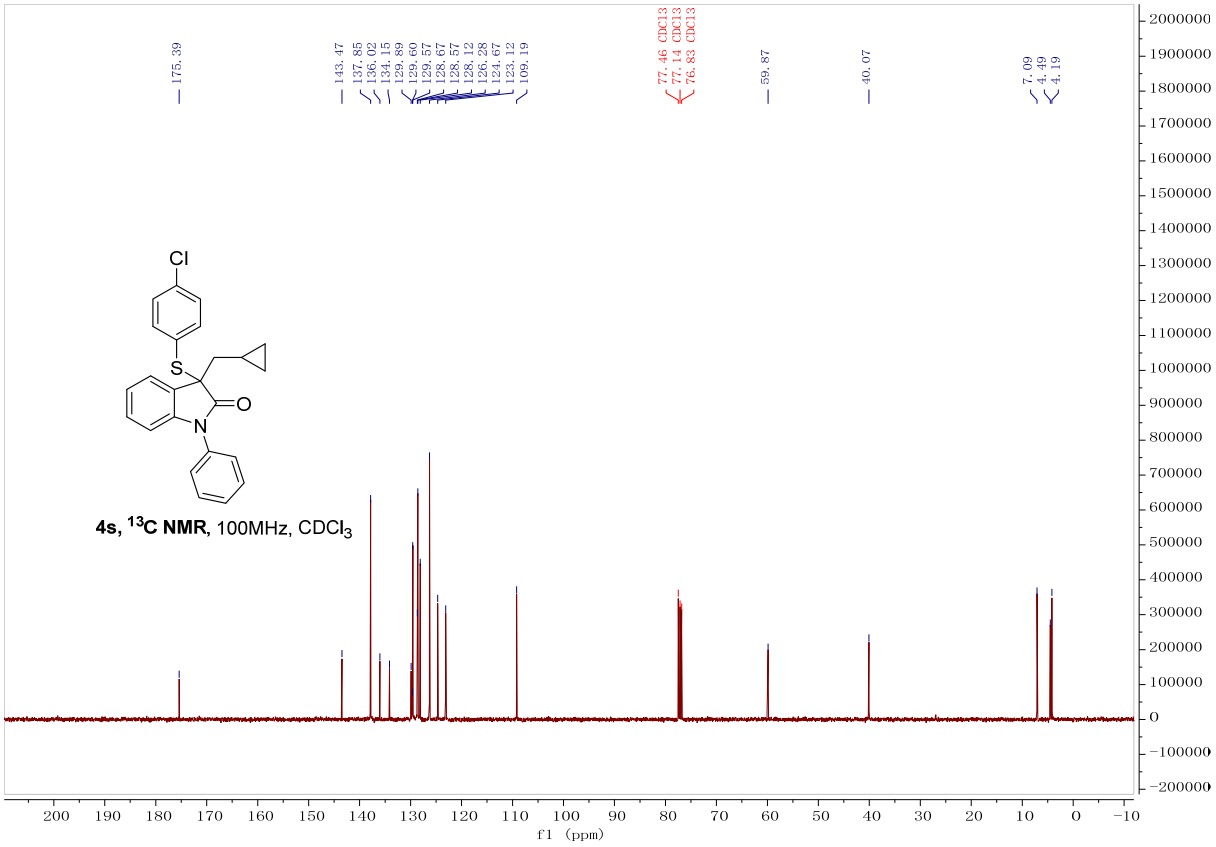
4r, ^{1}H NMR, 400MHz, $CDCl_3$



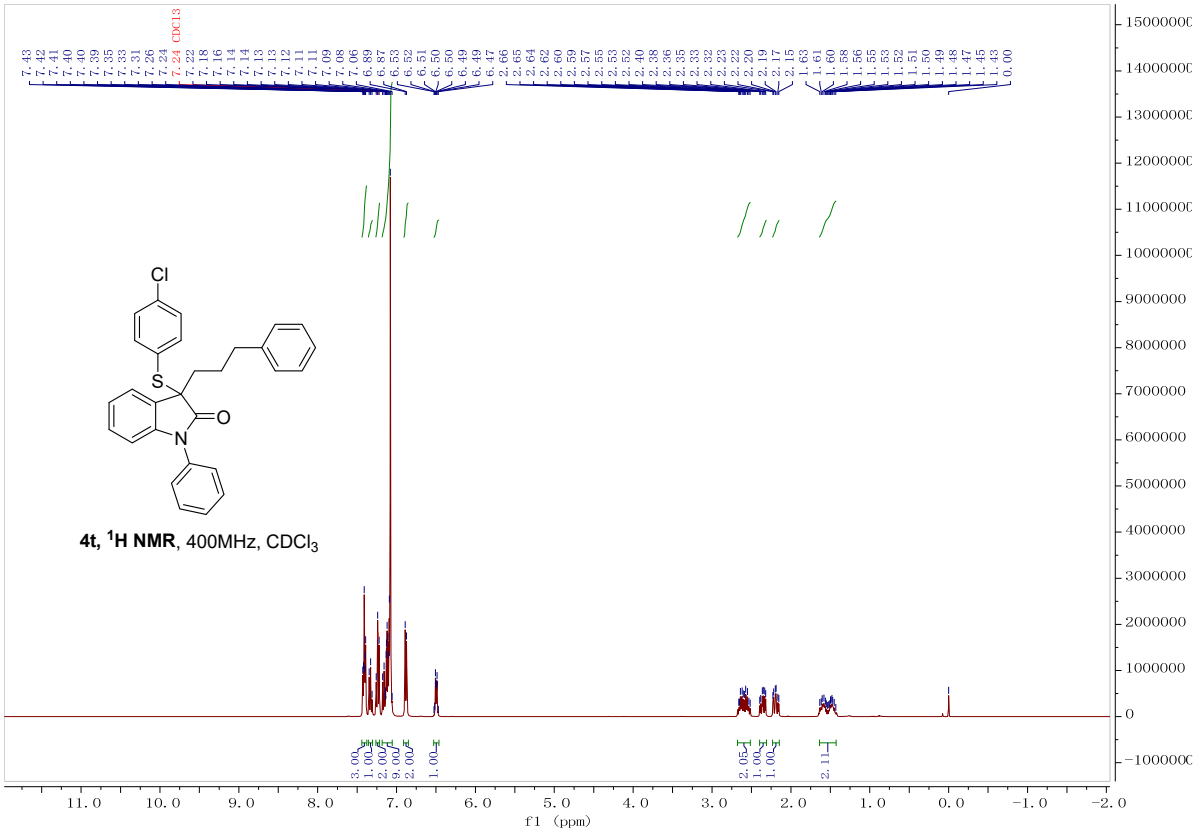
4r, ^{13}C NMR, 100MHz, $CDCl_3$



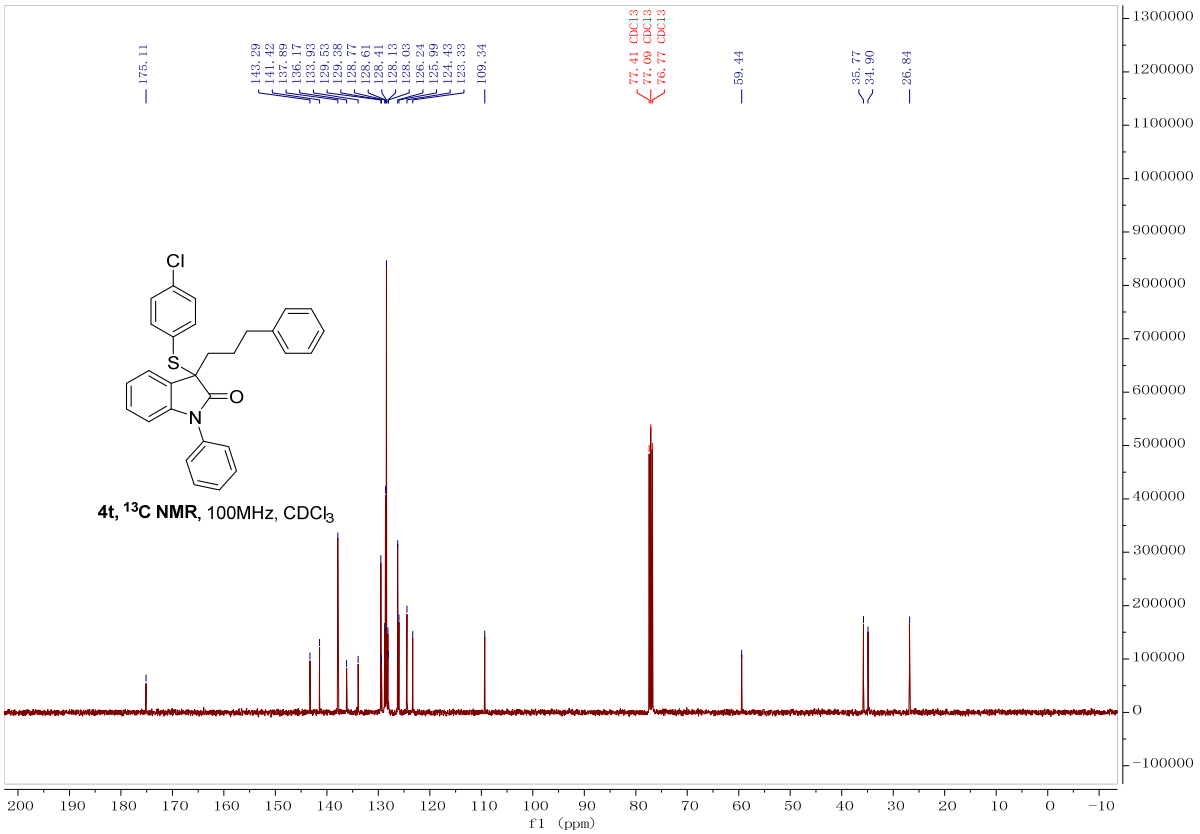
4s, ^{1}H NMR, 400MHz, $CDCl_3$



4s, ^{13}C NMR, 100MHz, $CDCl_3$



4t, ^{1}H NMR, 400MHz, $CDCl_3$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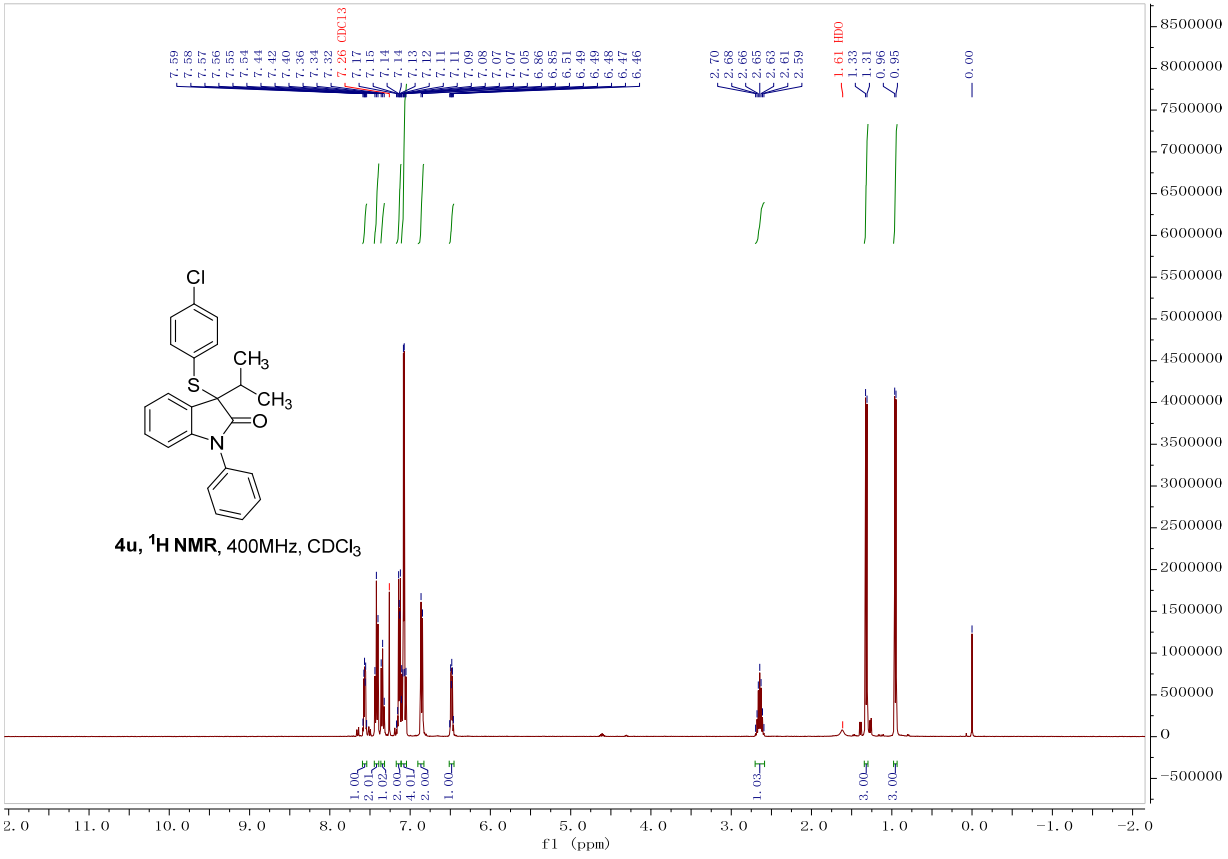
133.93
129.53
129.38
128.77
128.61
128.41
128.13
128.03
126.24
125.99
124.43
123.33
109.34
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
59.44
35.77
34.90
26.84
Cl
S
O
N
4t, 13C NMR, 100MHz, CDCl3
f1 (ppm)


7.59
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7.56
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7.54
7.44
7.42
7.40
7.36
7.34
7.32
7.26 CDCl3
7.17
7.15
7.14
7.14
7.13
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7.09
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7.07
7.05
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6.48
6.47
6.46
2.70
2.68
2.66
2.65
2.63
2.61
2.59
1.61 HDO
1.33
1.31
0.96
0.95
0.00
Cl
S
CH3
CH3
O
N
4u, 1H NMR, 400MHz, CDCl3
1.00
2.01
1.02
2.00
4.01
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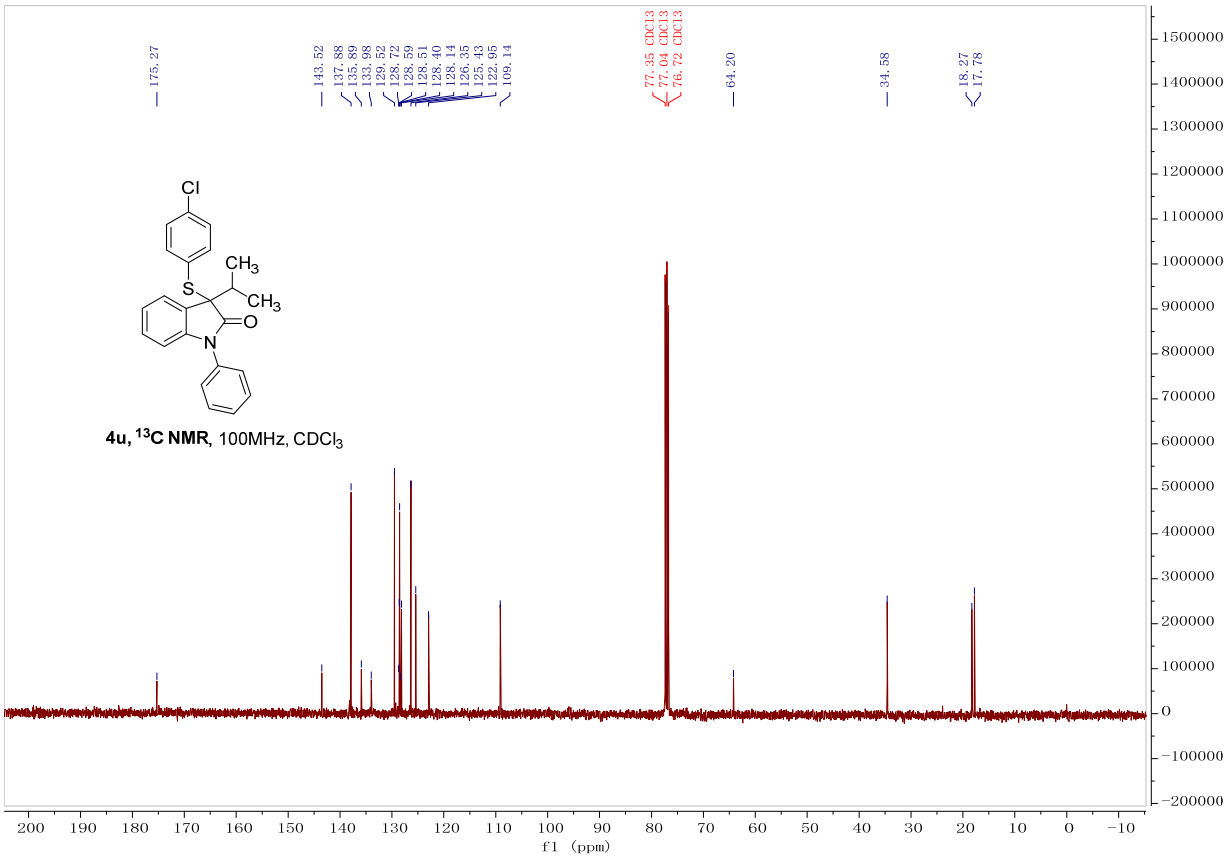
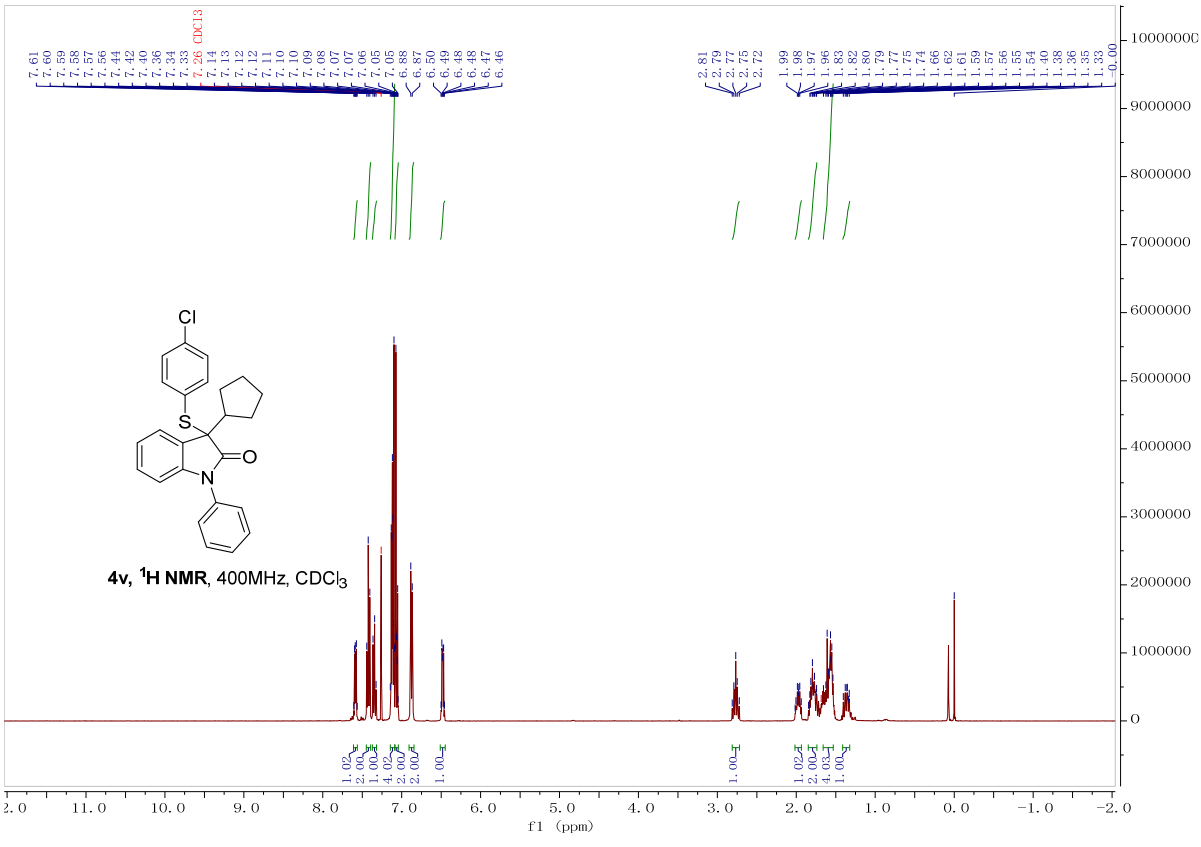
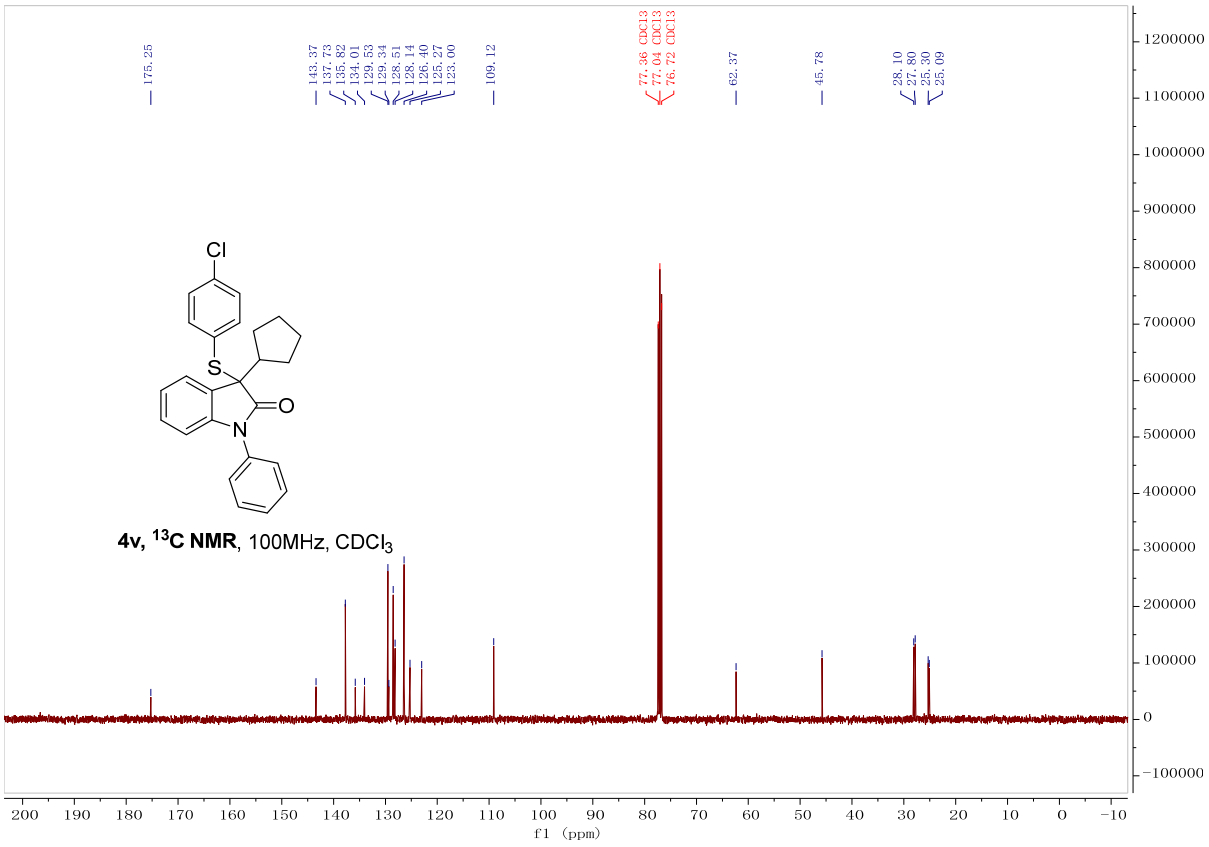
1.00
1.03
3.00
3.00
f1 (ppm)

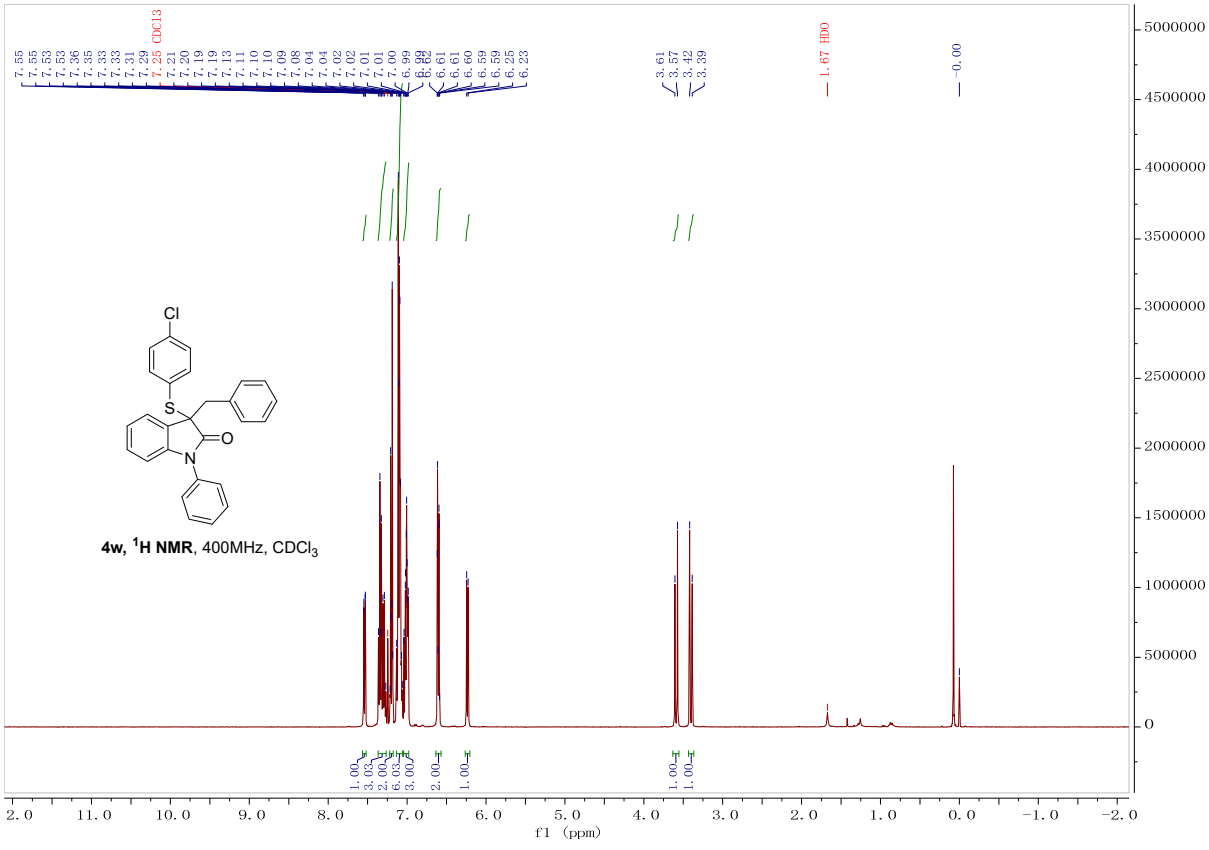


4u, ^{13}C NMR, 100MHz, $CDCl_3$



4v, ^{1}H NMR, 400MHz, $CDCl_3$


175.25
143.37
137.73
135.82
134.01
129.53
129.34
128.51
128.14
126.40
125.27
123.06
109.12
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
62.37
45.78
28.10
27.80
25.30
25.09
Cl
S
O
N
4v, 13C NMR, 100MHz, CDCl3
f1 (ppm)


7.55
7.53
7.36
7.35
7.33
7.31
7.29
7.25 CDCl3
7.21
7.20
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7.11
7.10
7.09
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7.04
7.02
7.01
7.00
6.99
6.61
6.60
6.59
6.25
6.23
3.61
3.57
3.42
3.39
1.67 HDO
-0.00
1.00
3.03
2.00
6.03
3.00
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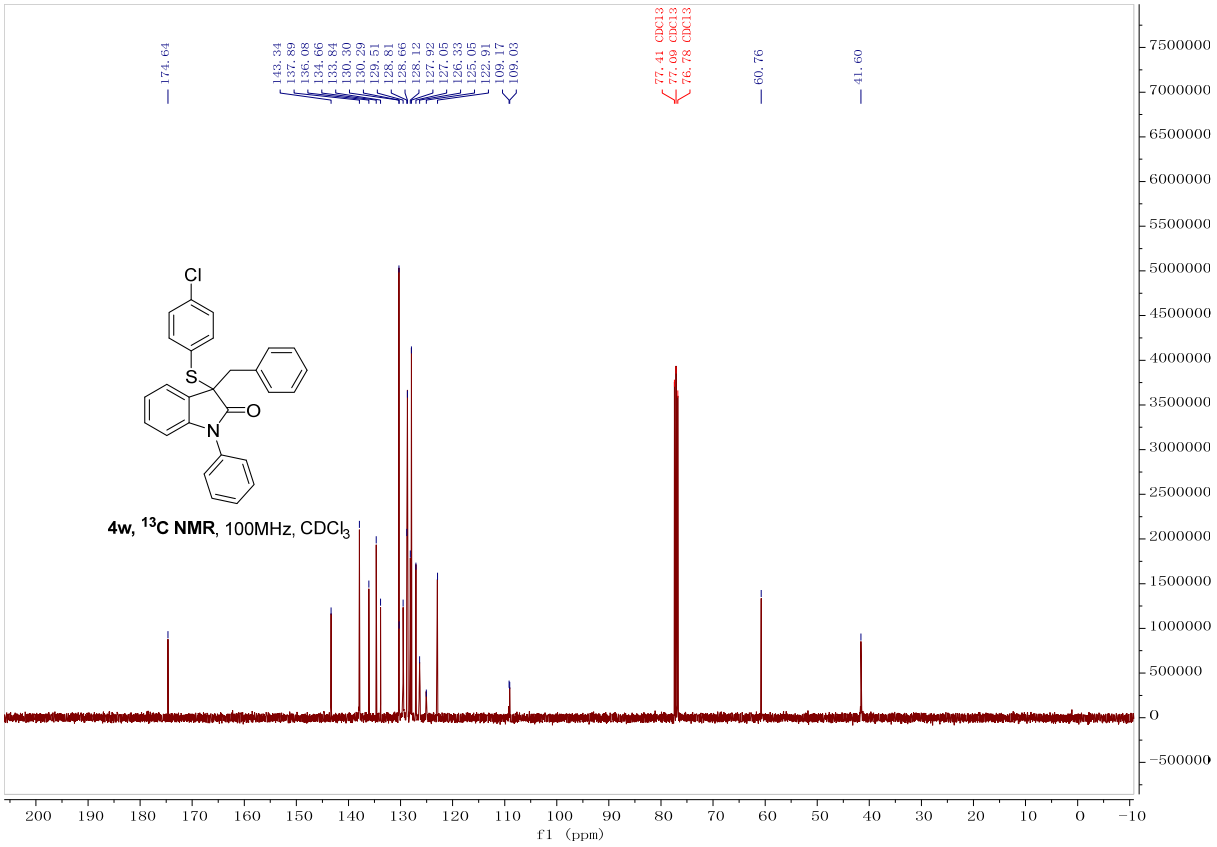
1.00
1.00
1.00
Cl
S
O
N
4w, 1H NMR, 400MHz, CDCl3
f1 (ppm)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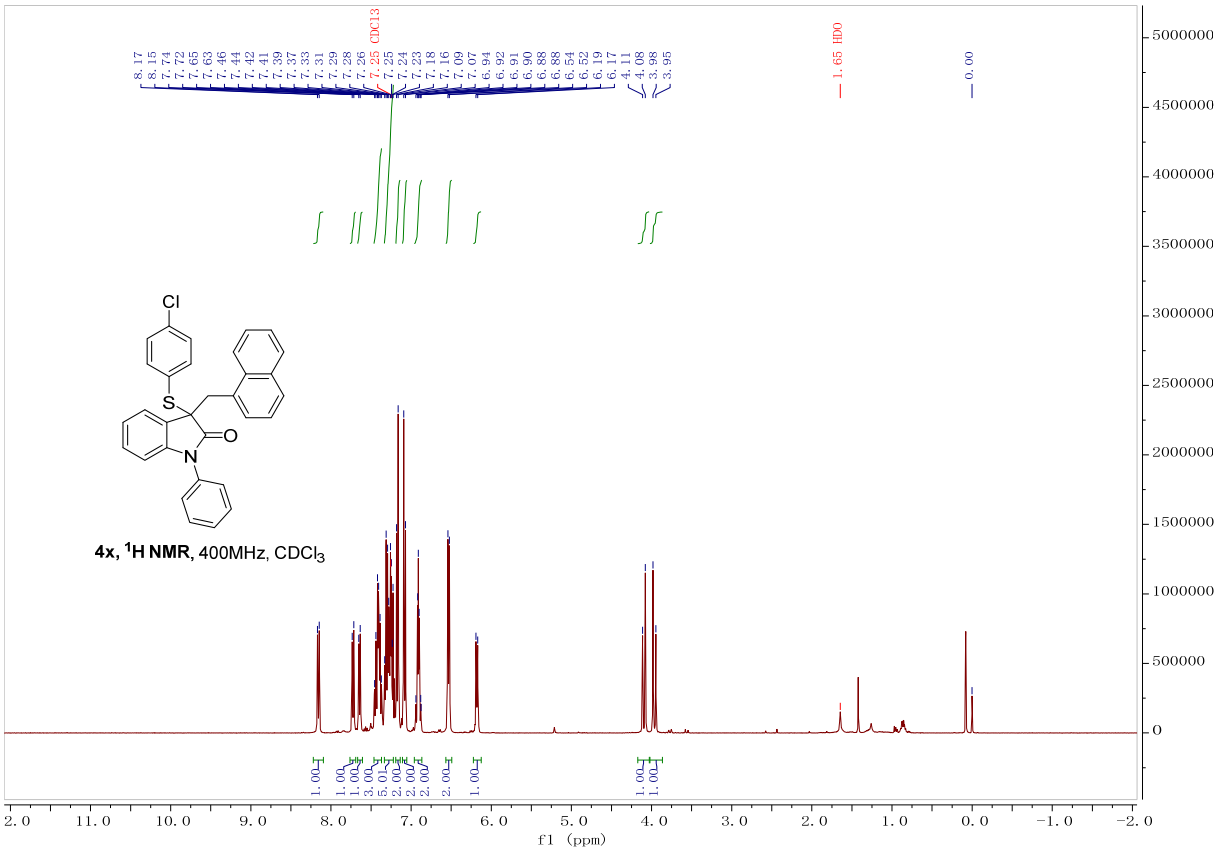
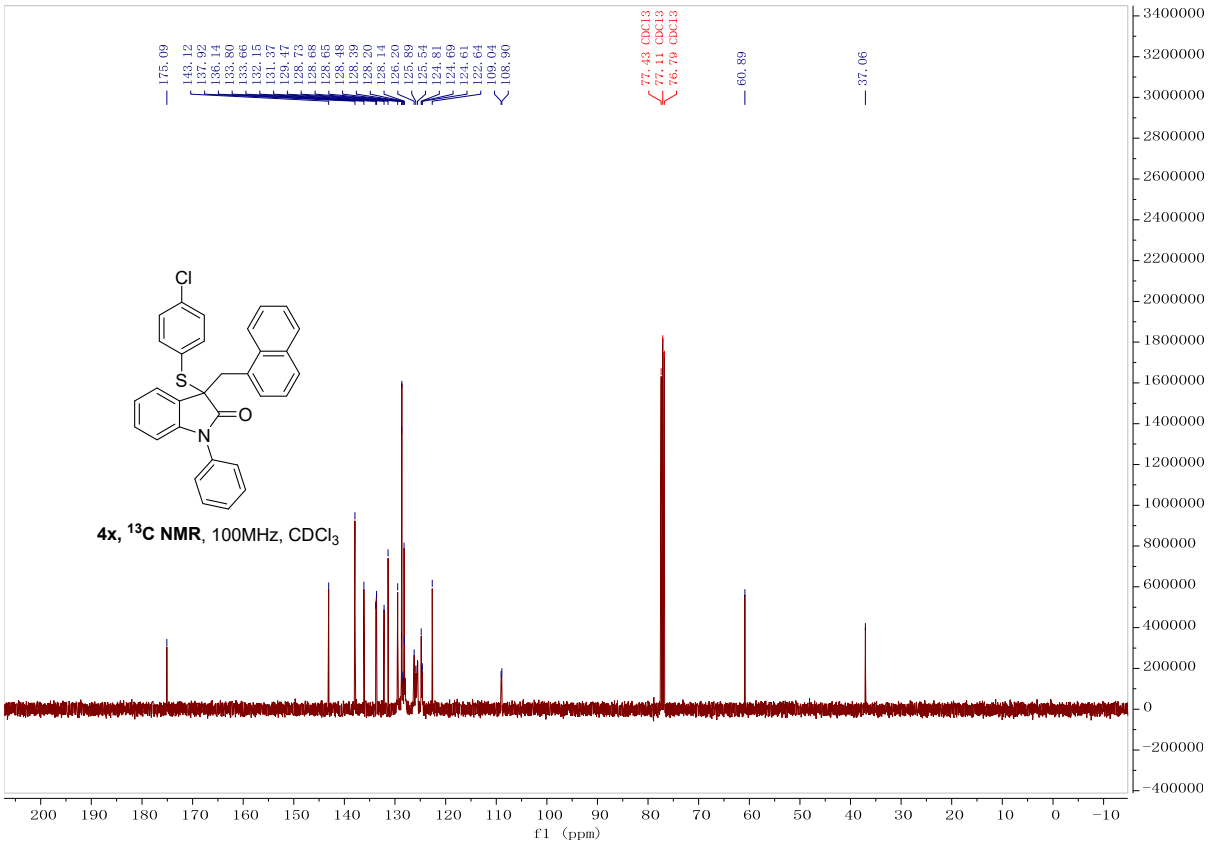
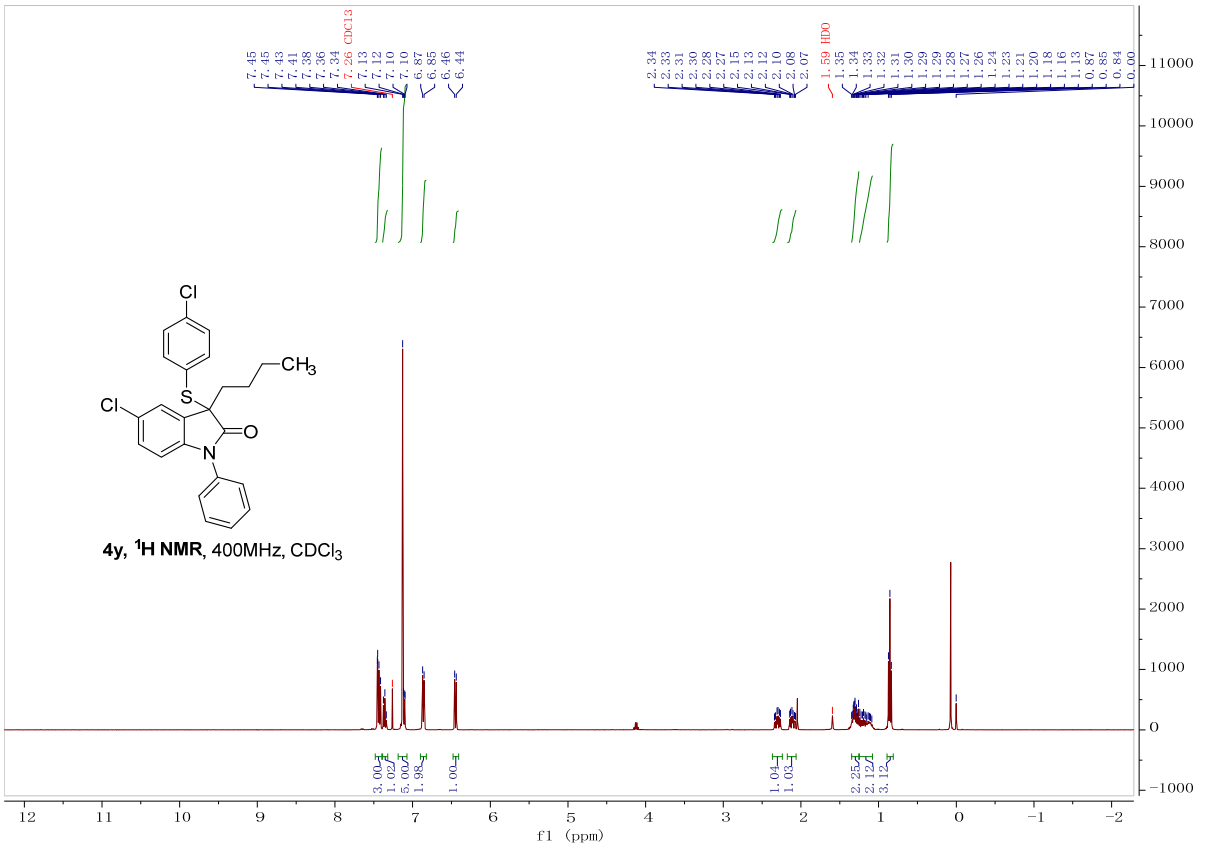
128.81
128.66
128.12
127.92
127.05
126.33
125.05
122.91
109.17
109.03
77.41 CDCl3
77.09 CDCl3
76.78 CDCl3
60.76
41.60
Cl
S
O
N
4w, 13C NMR, 100MHz, CDCl3
f1 (ppm)

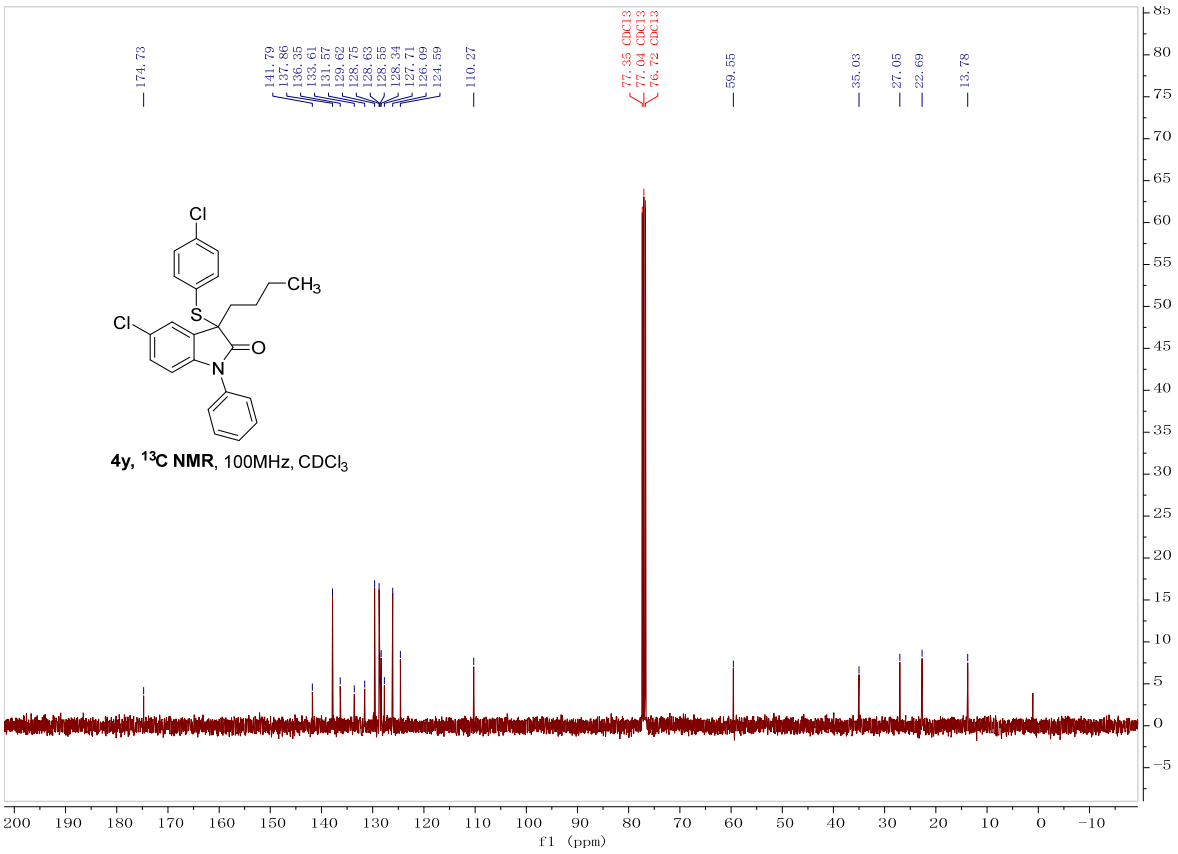

8.17
8.15
7.74
7.72
7.65
7.63
7.46
7.44
7.42
7.41
7.39
7.37
7.33
7.31
7.29
7.28
7.26 CDCl3
7.25
7.24
7.23
7.18
7.16
7.09
7.07
6.94
6.92
6.91
6.90
6.88
6.54
6.52
6.19
6.17
4.11
4.08
3.98
3.95
1.65 HDO
0.00
Cl
S
O
N
4x, 1H NMR, 400MHz, CDCl3
f1 (ppm)



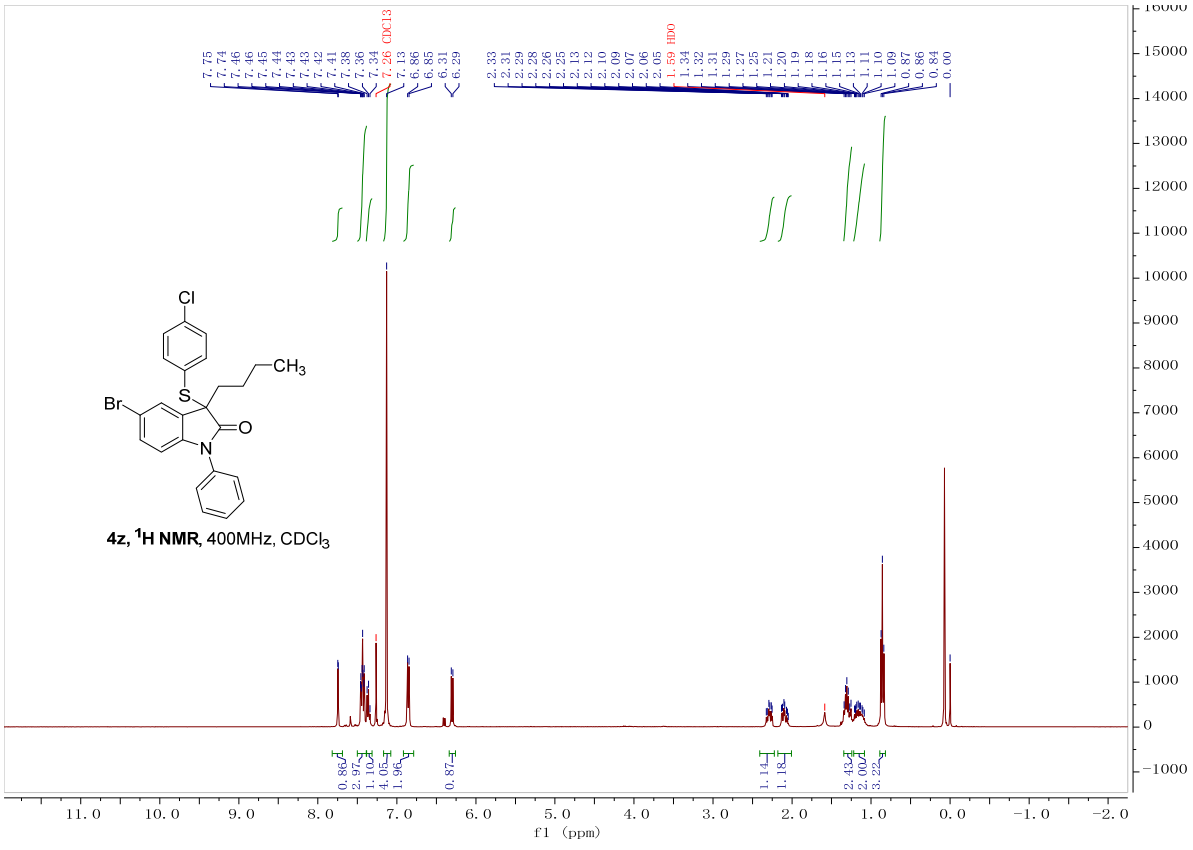
4x, ^{13}C NMR, 100MHz, $CDCl_3$



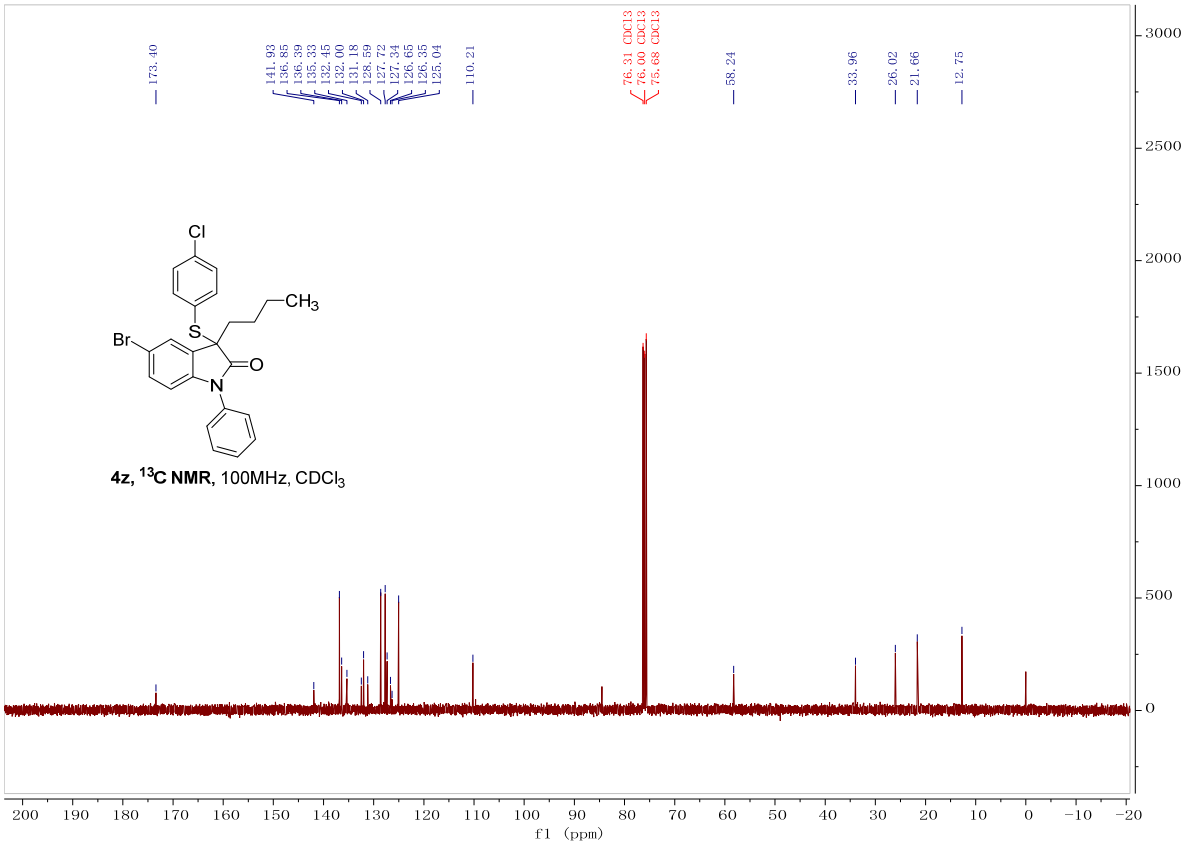
4y, ^{1}H NMR, 400MHz, $CDCl_3$



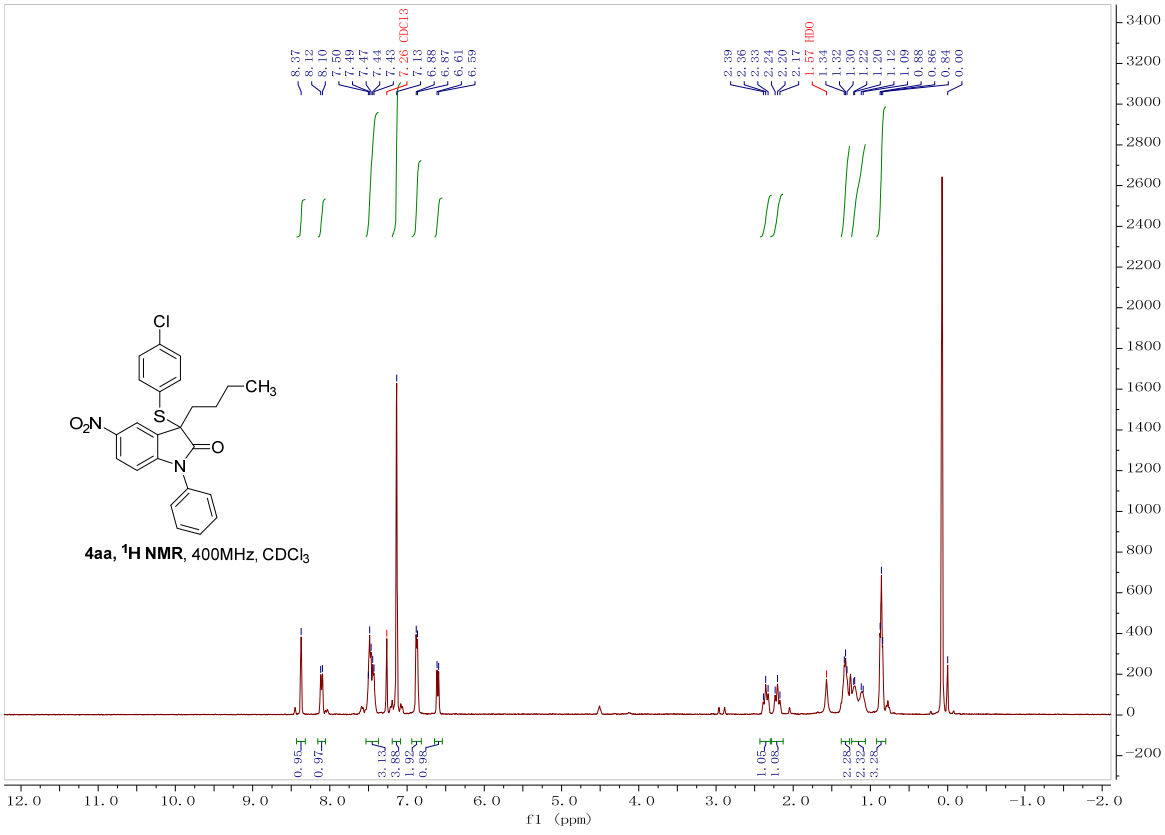
4y, ^{13}C NMR, 100MHz, $CDCl_3$



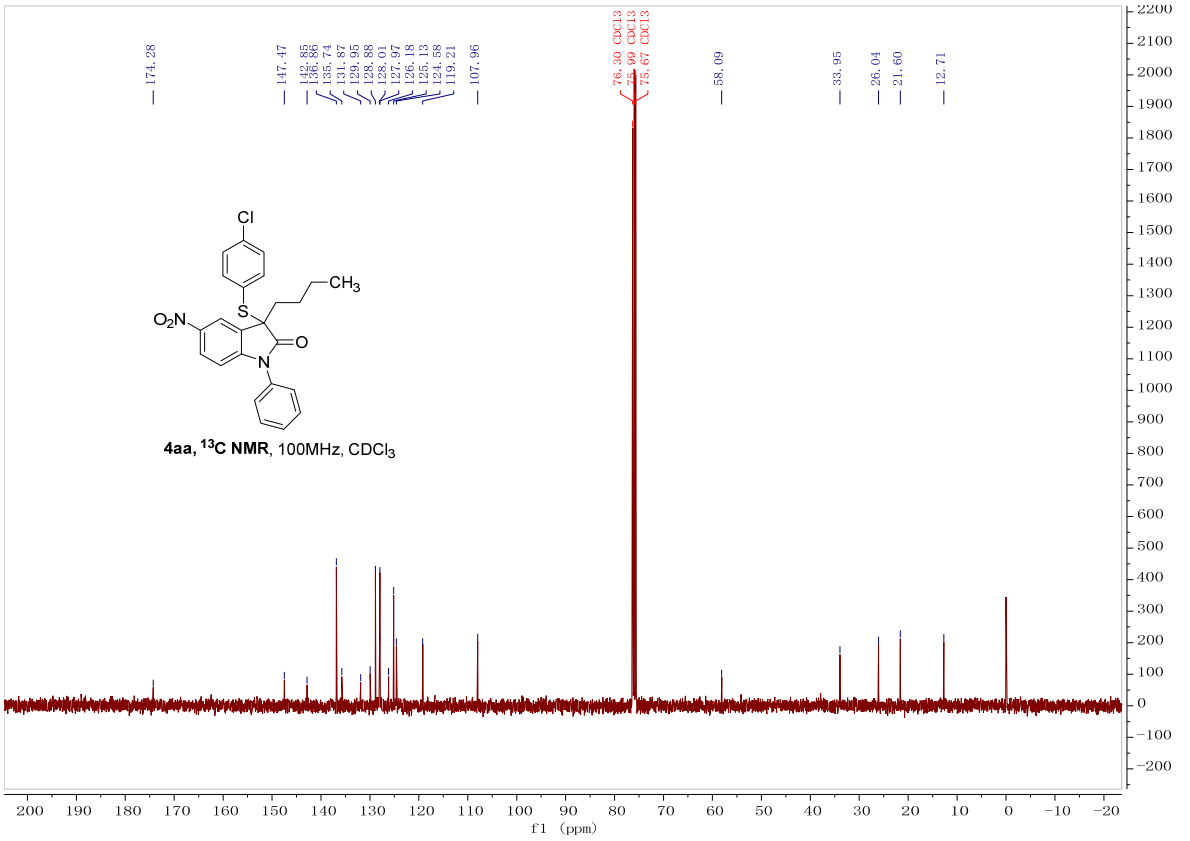
4z, ^{1}H NMR, 400MHz, $CDCl_3$



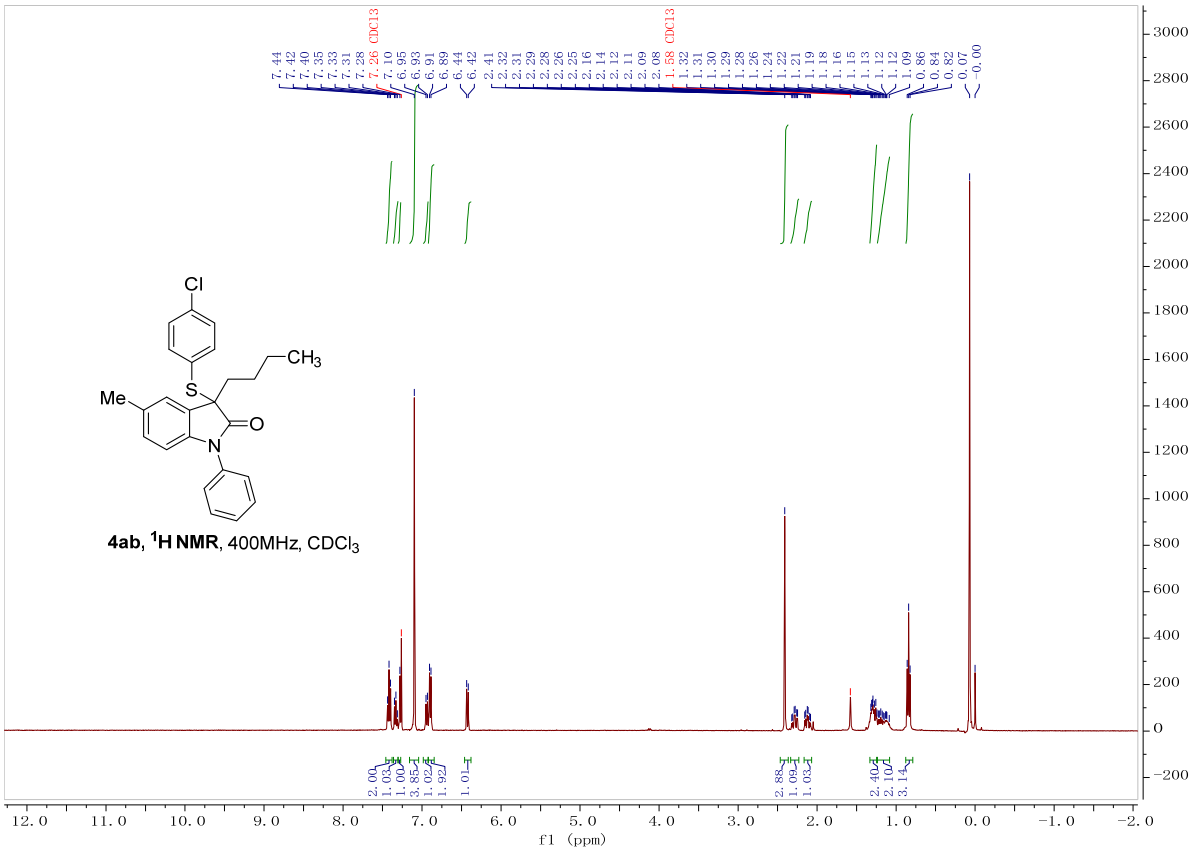
4z, ^{13}C NMR, 100MHz, $CDCl_3$



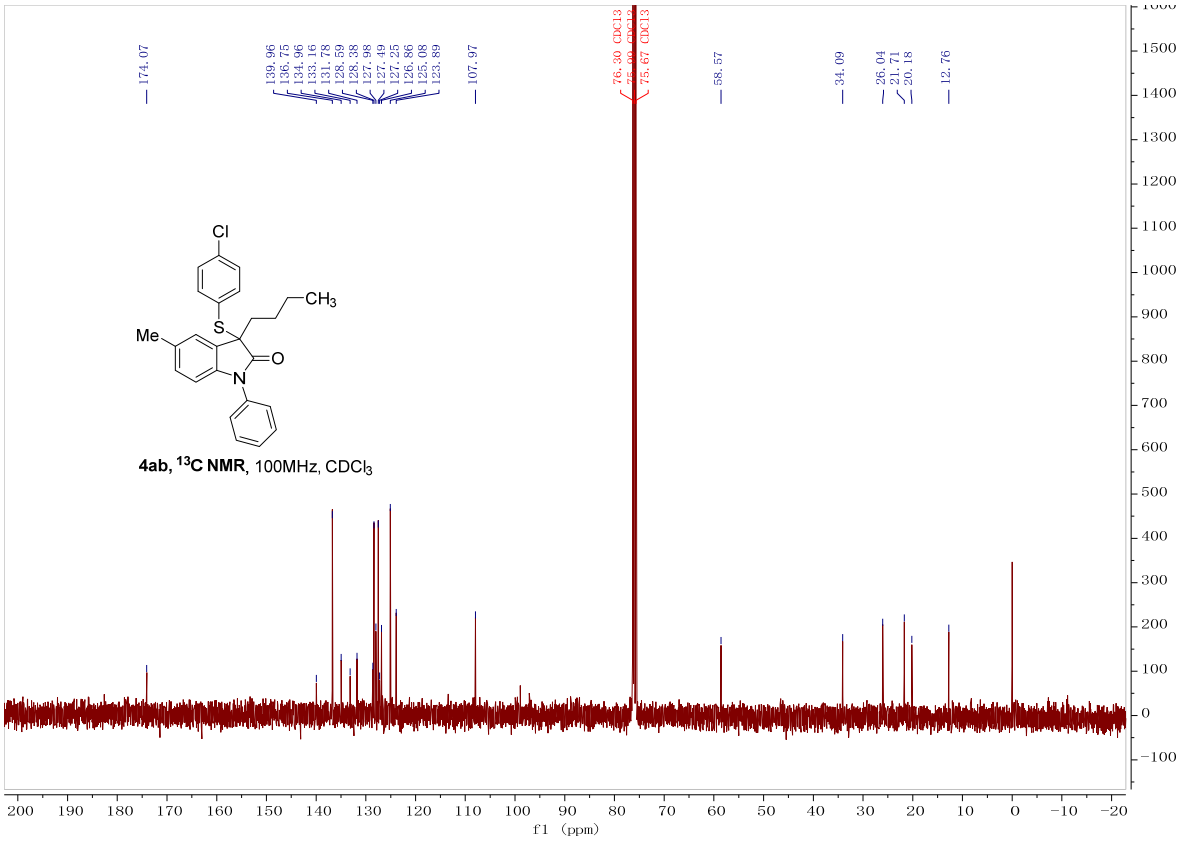
4aa, ^{1}H NMR, 400MHz, $CDCl_3$



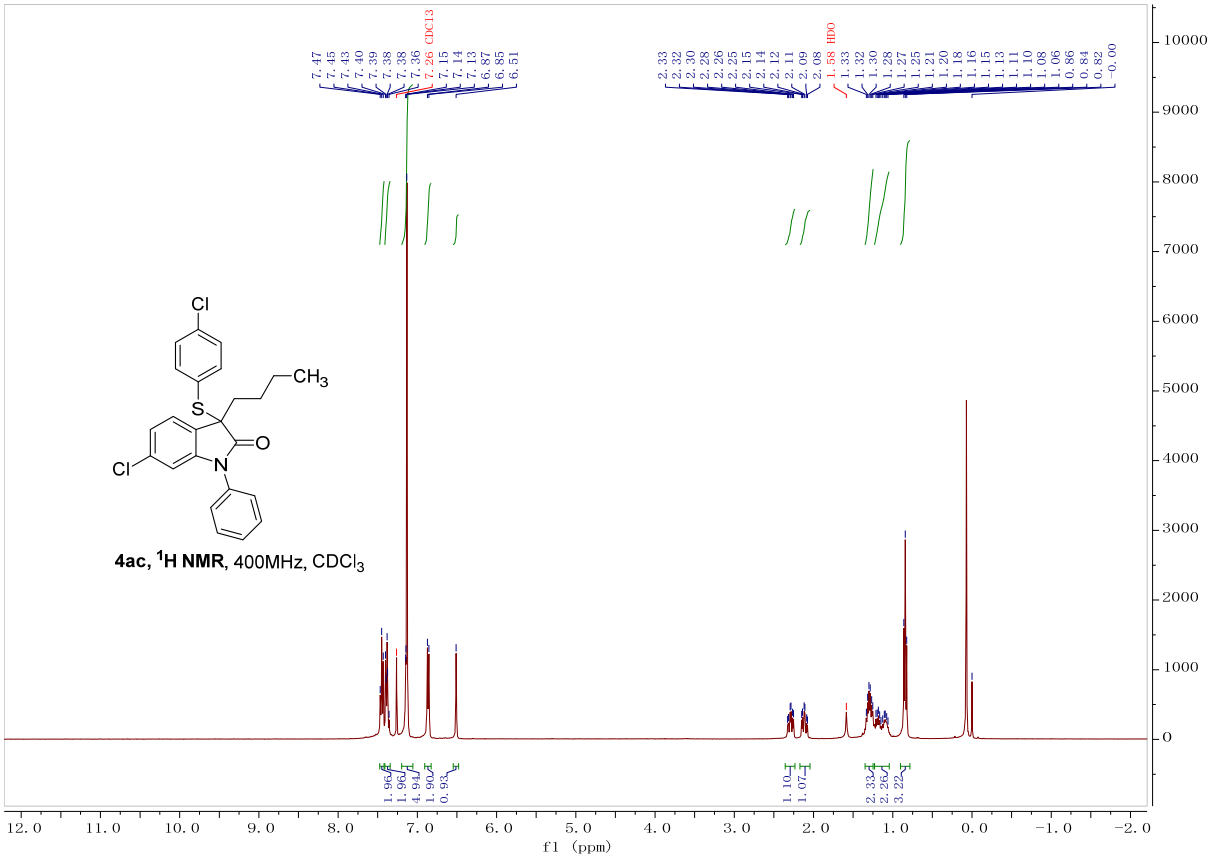
4aa, ^{13}C NMR, 100MHz, $CDCl_3$



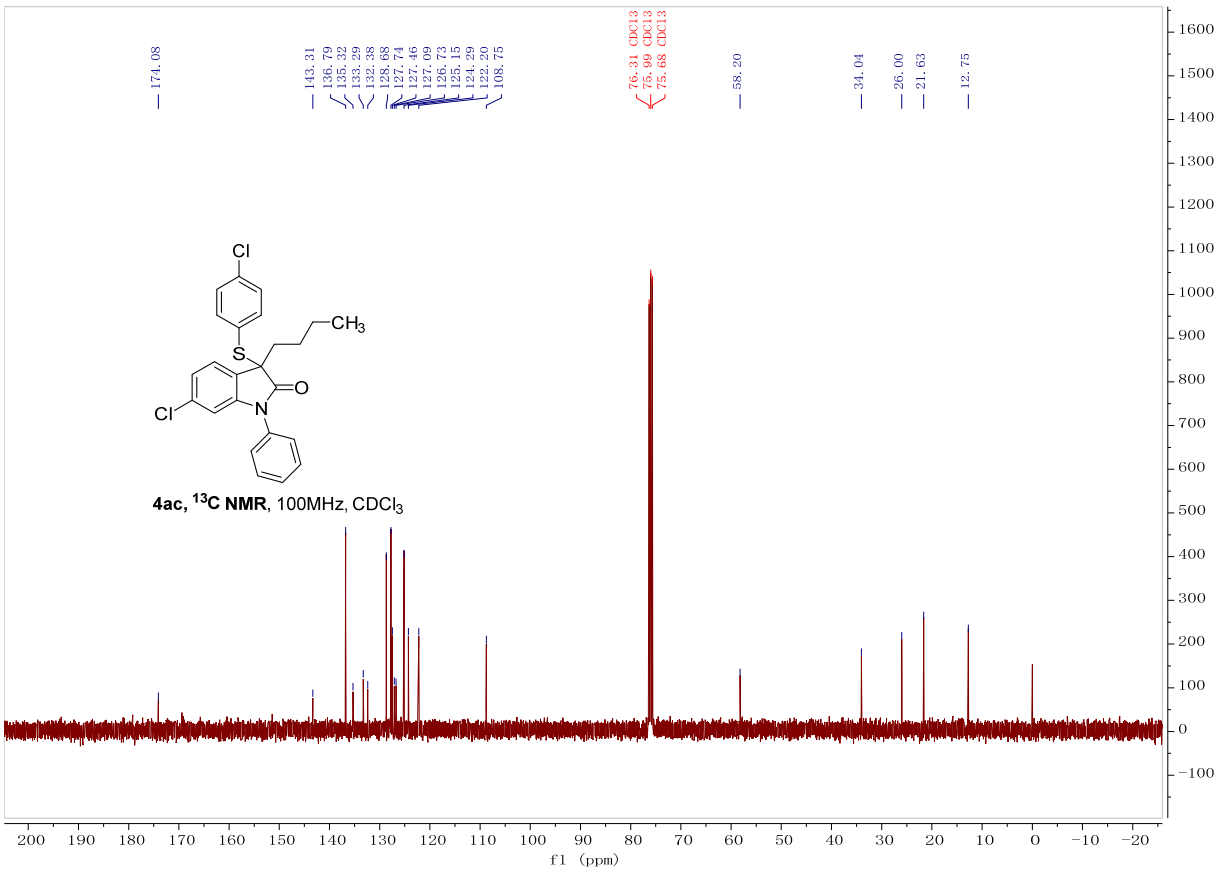
4ab, ^{1}H NMR, 400MHz, $CDCl_3$



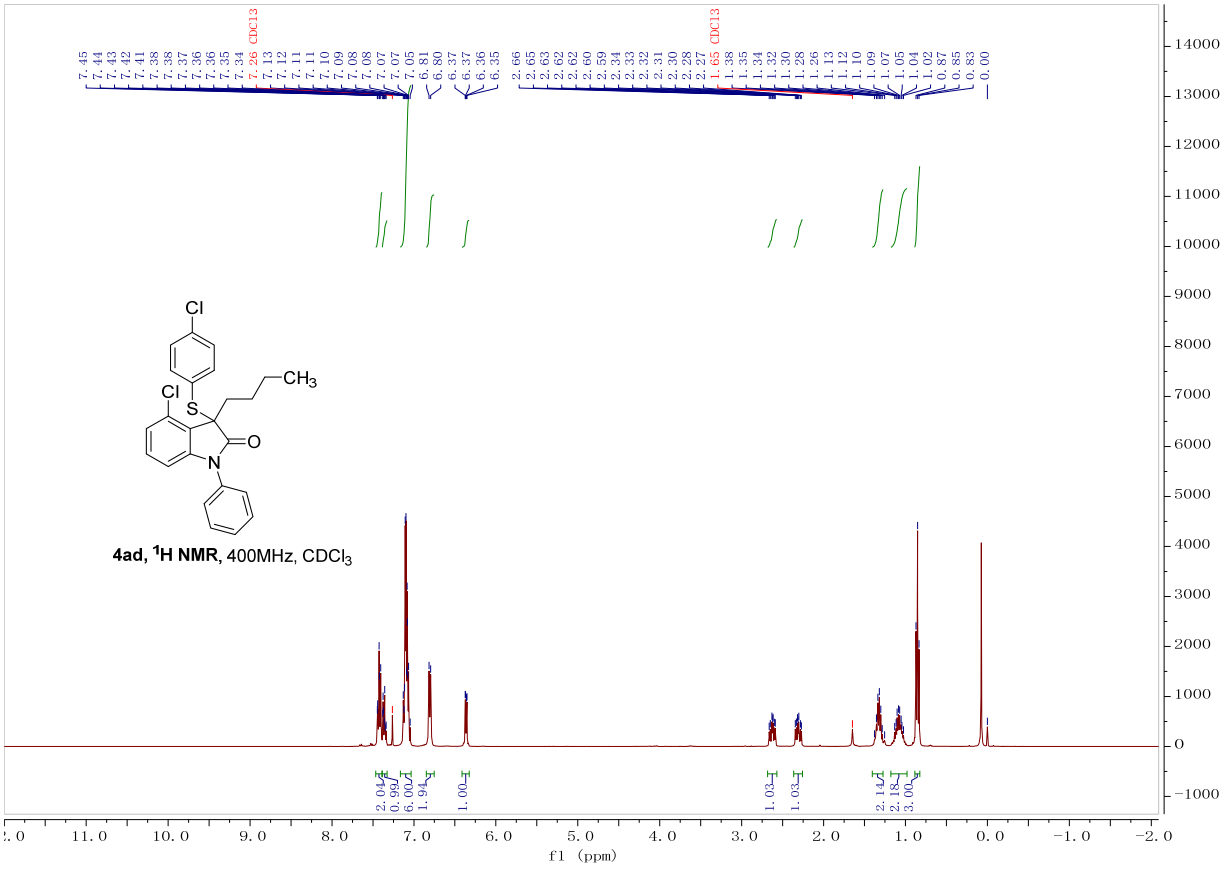
4ab, ^{13}C NMR, 100MHz, $CDCl_3$



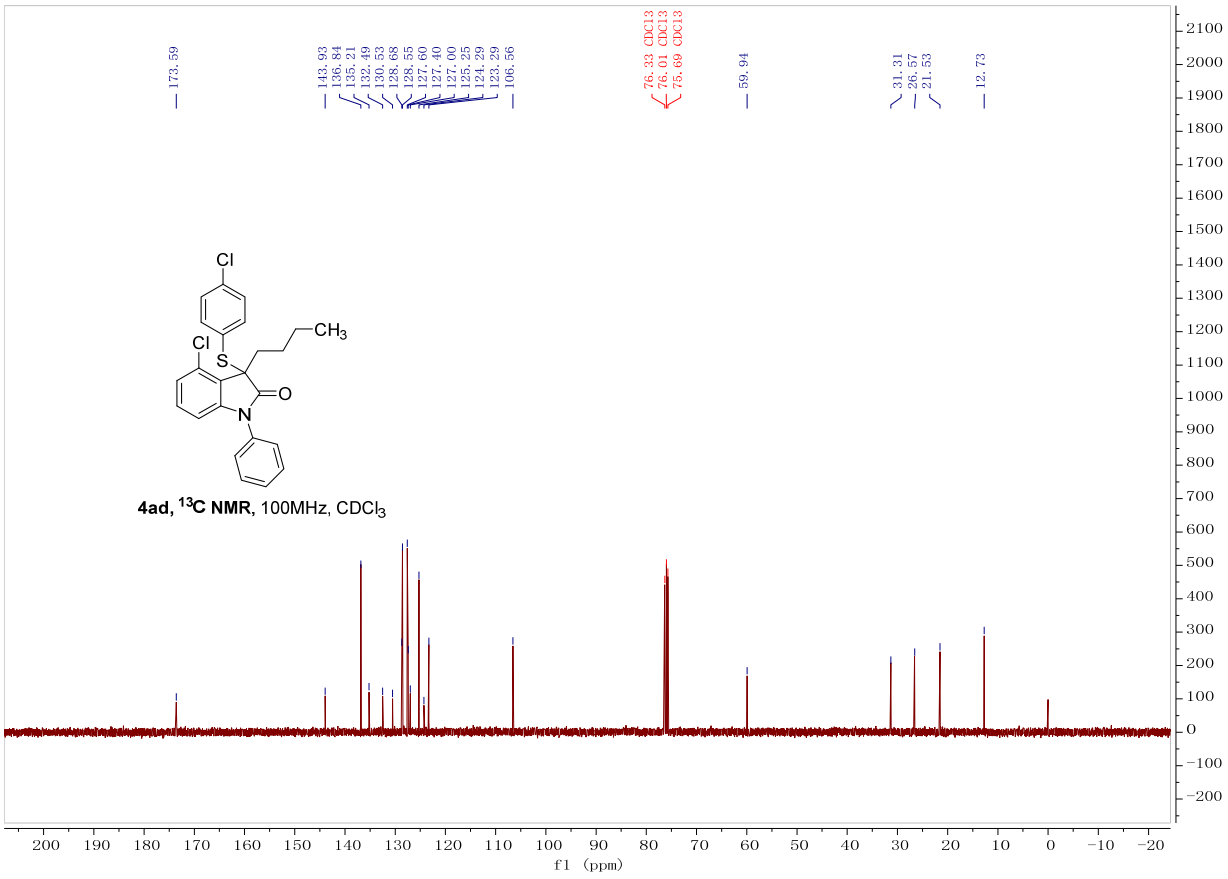
4ac, ^{1}H NMR, 400MHz, $CDCl_3$



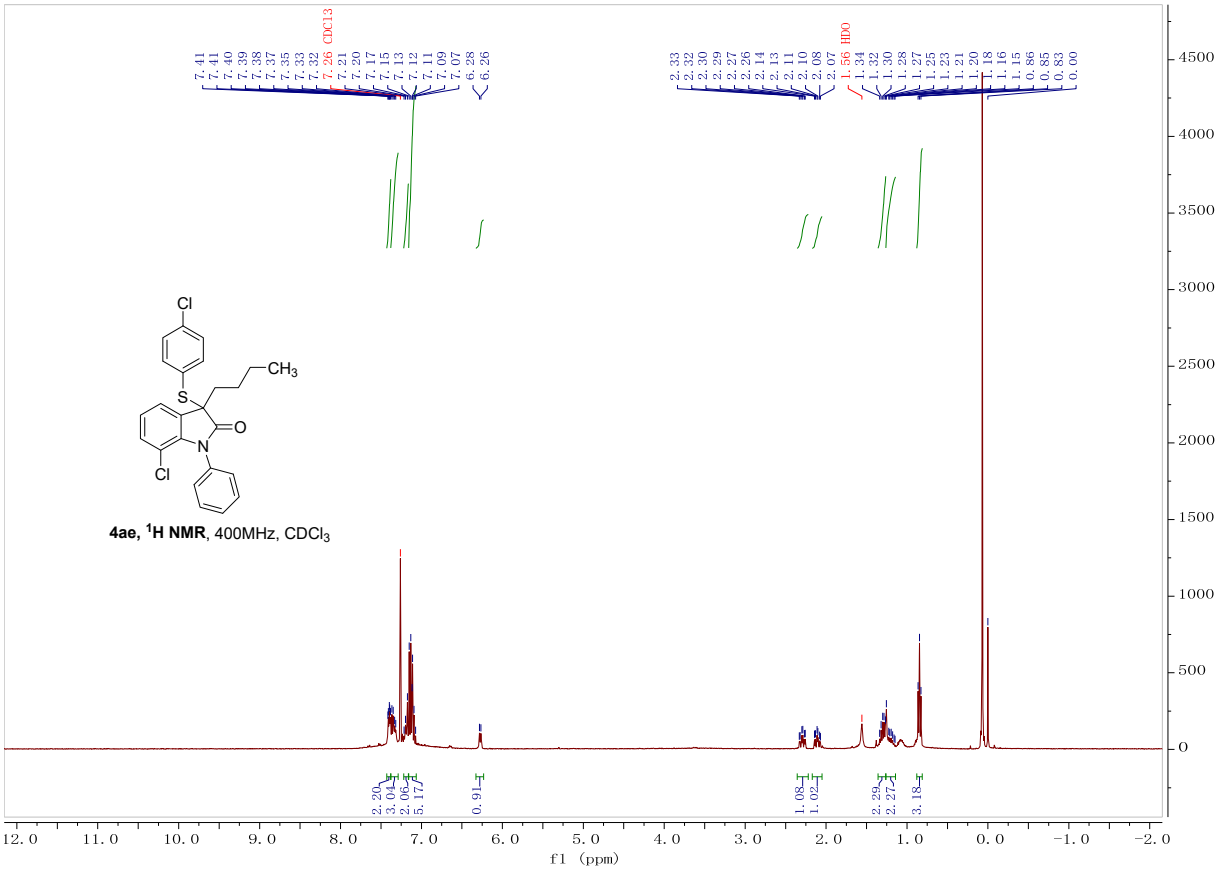
4ac, ^{13}C NMR, 100MHz, $CDCl_3$



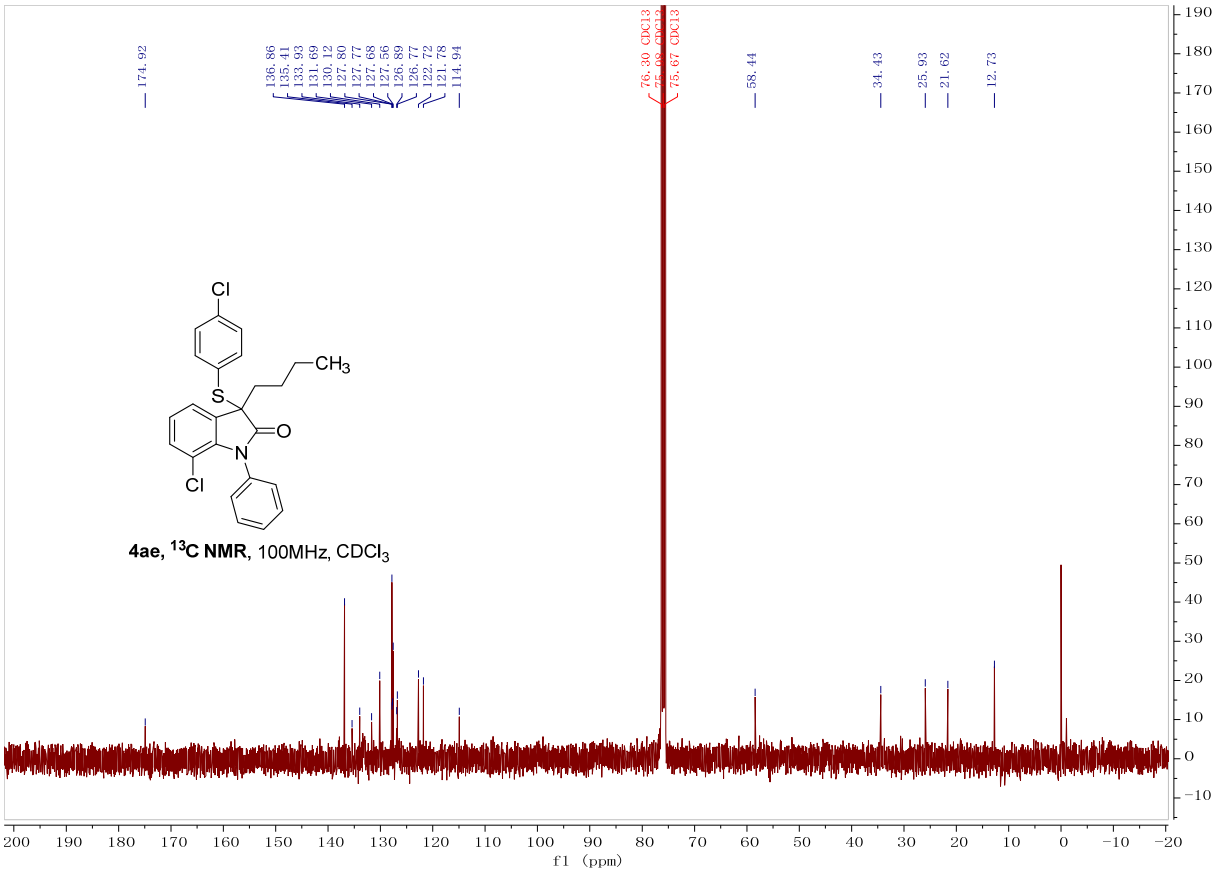
4ad, ^{1}H NMR, 400MHz, $CDCl_3$



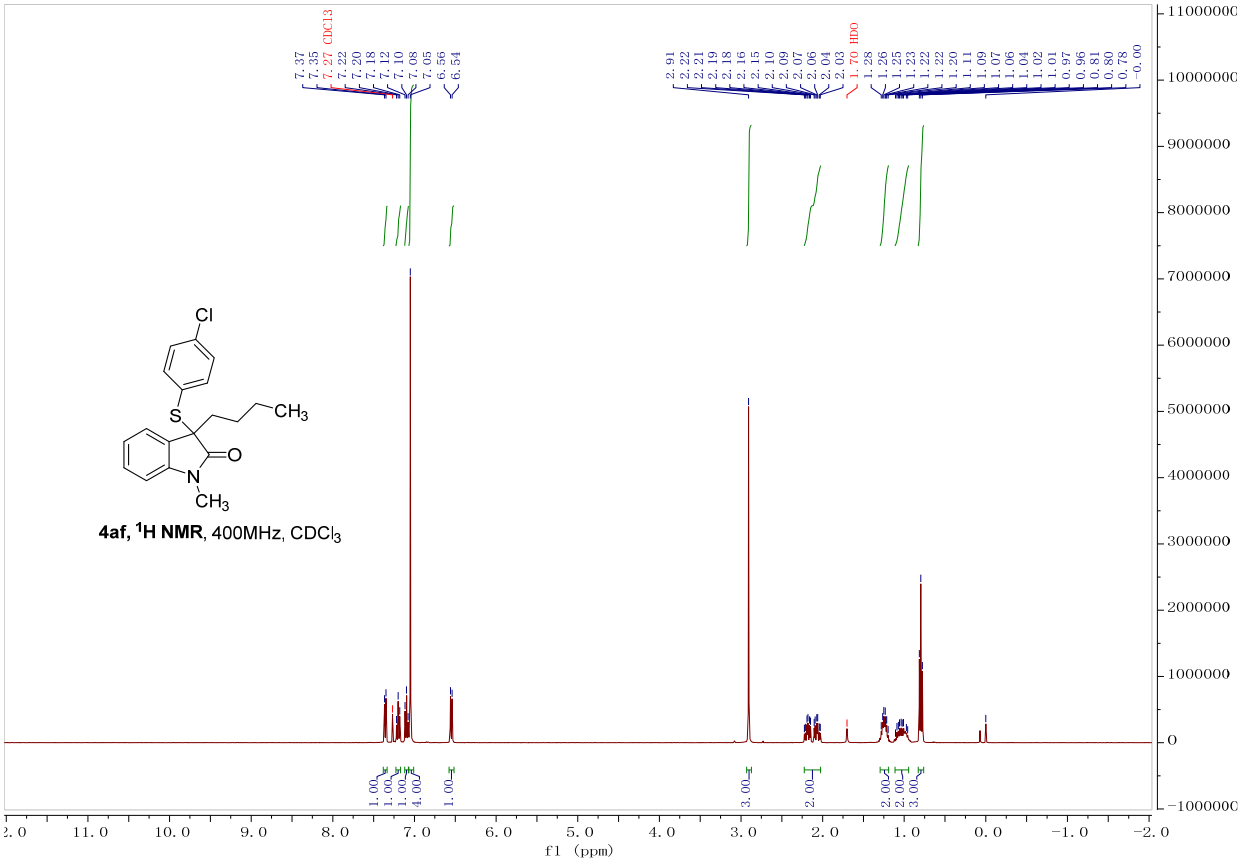
4ad, ^{13}C NMR, 100MHz, $CDCl_3$



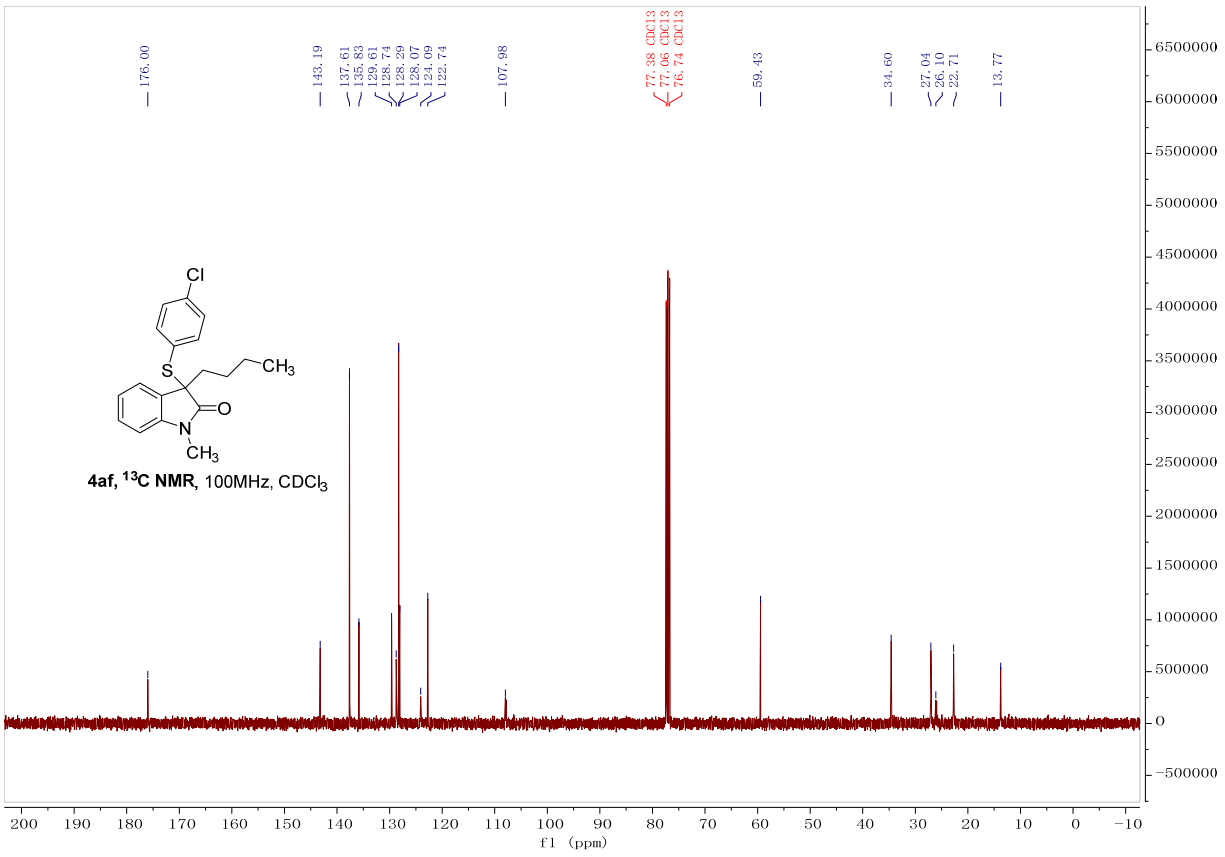
4ae, ^{1}H NMR, 400MHz, $CDCl_3$



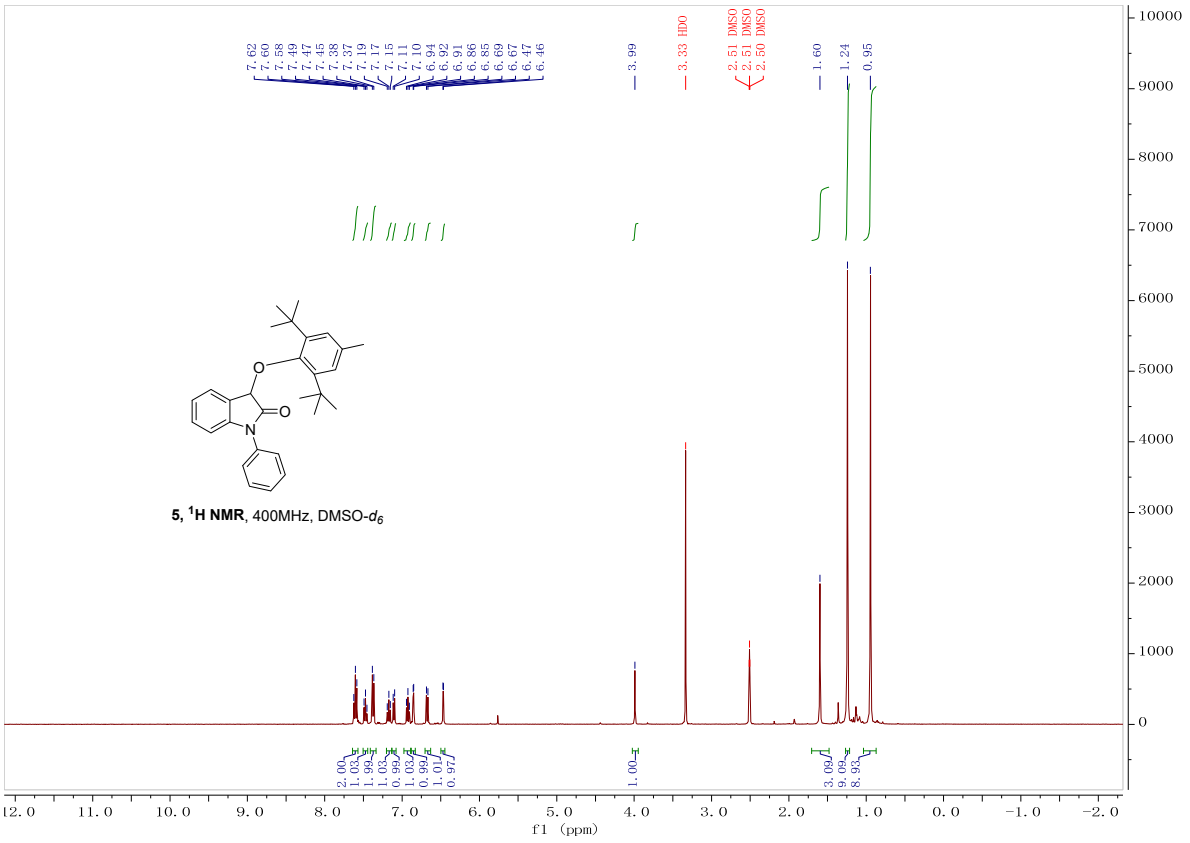
4ae, ^{13}C NMR, 100MHz, $CDCl_3$



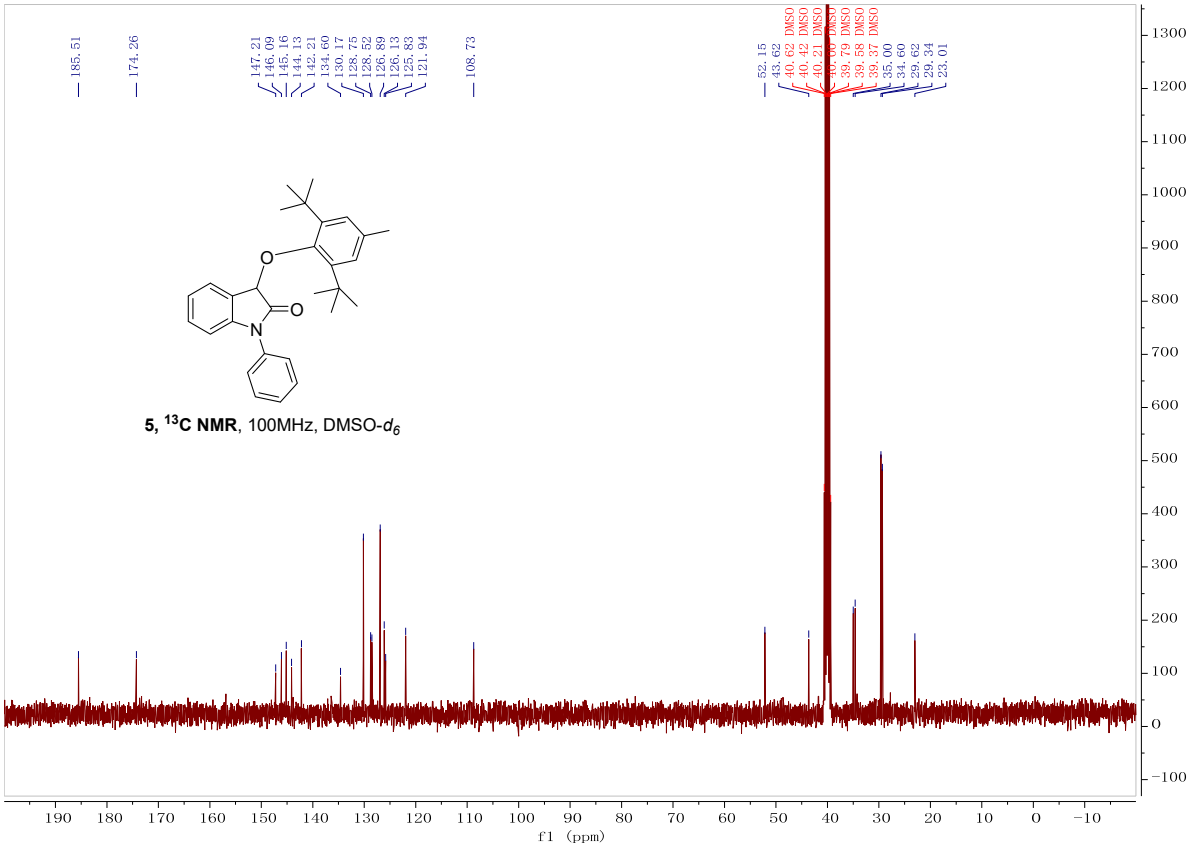
4af, ^{1}H NMR, 400MHz, $CDCl_3$


176.00
143.19
137.61
135.83
129.61
128.74
128.29
128.07
124.09
122.74
107.98
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
59.43
34.60
27.04
26.10
22.71
13.77
Cl
S
CH3
O
N
CH3
4af, 13C NMR, 100MHz, CDCl3
f1 (ppm)

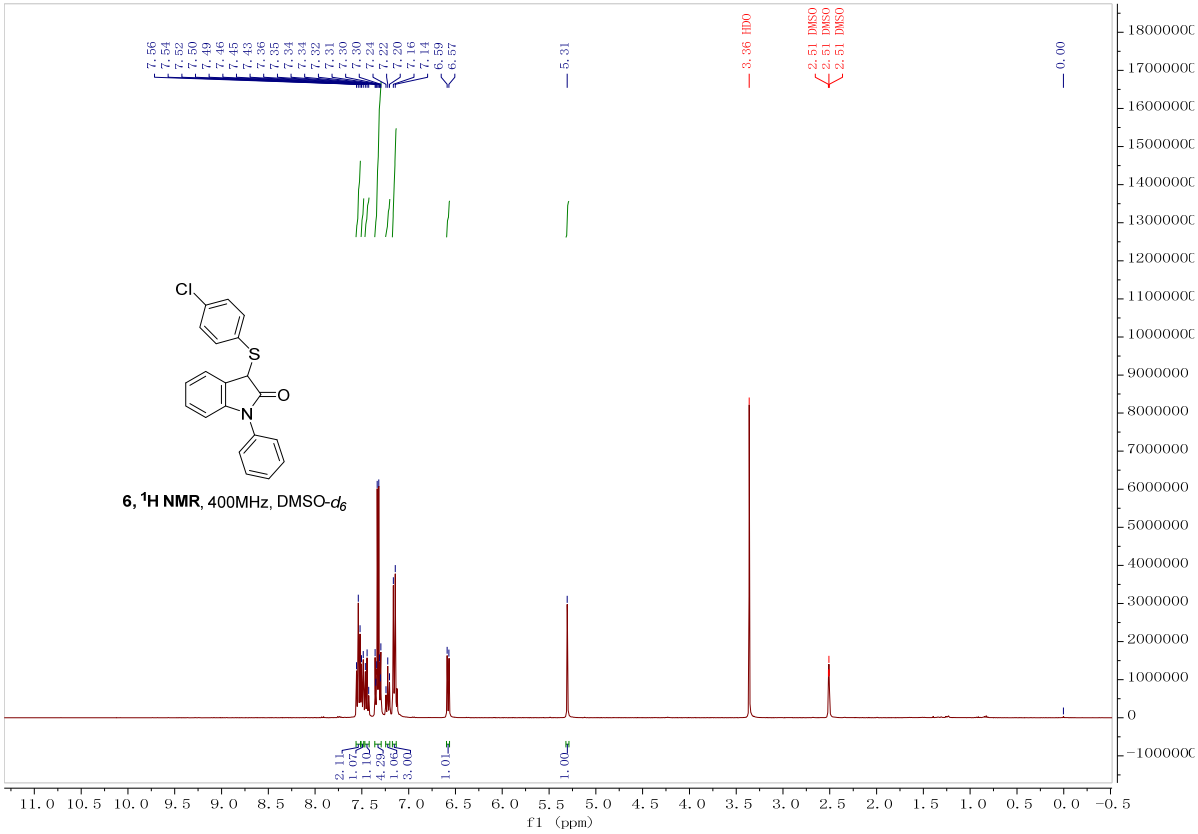
7. Spectroscopic data for compounds 5-8



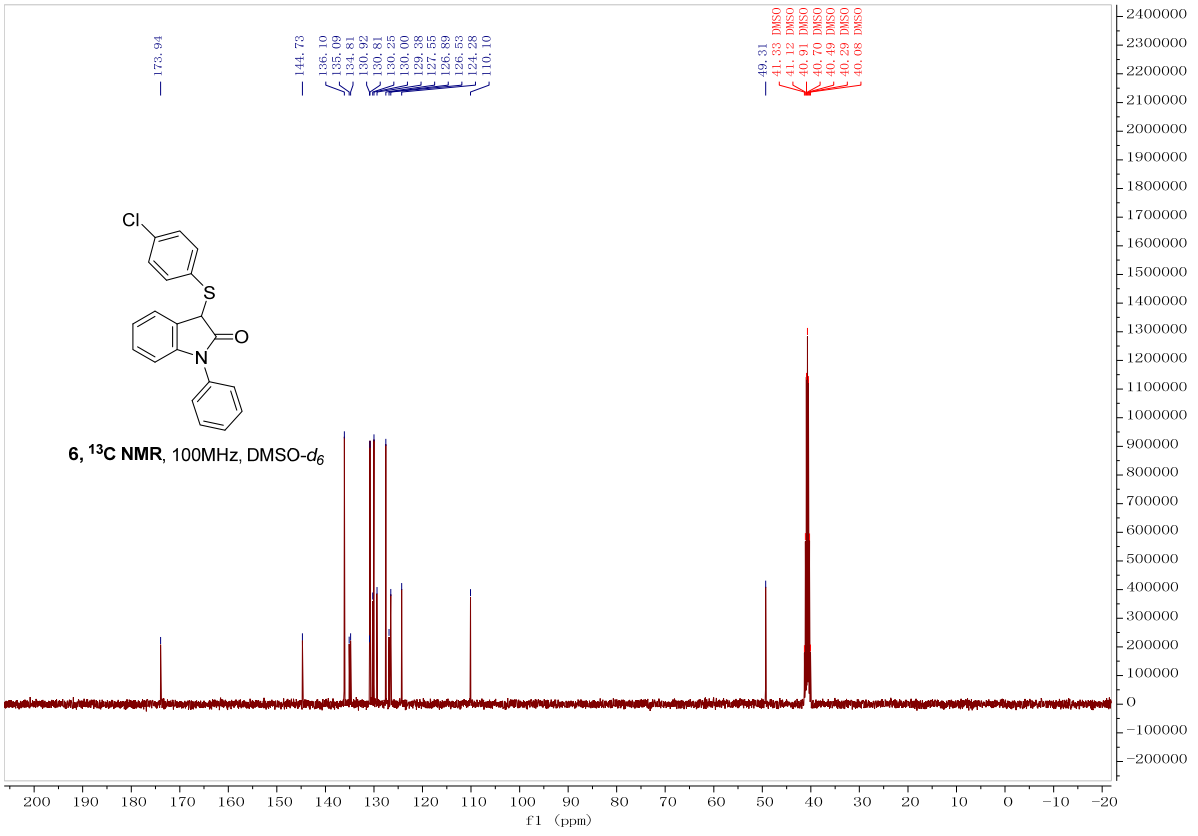
5, ^{1}H NMR, 400MHz, DMSO-d_6



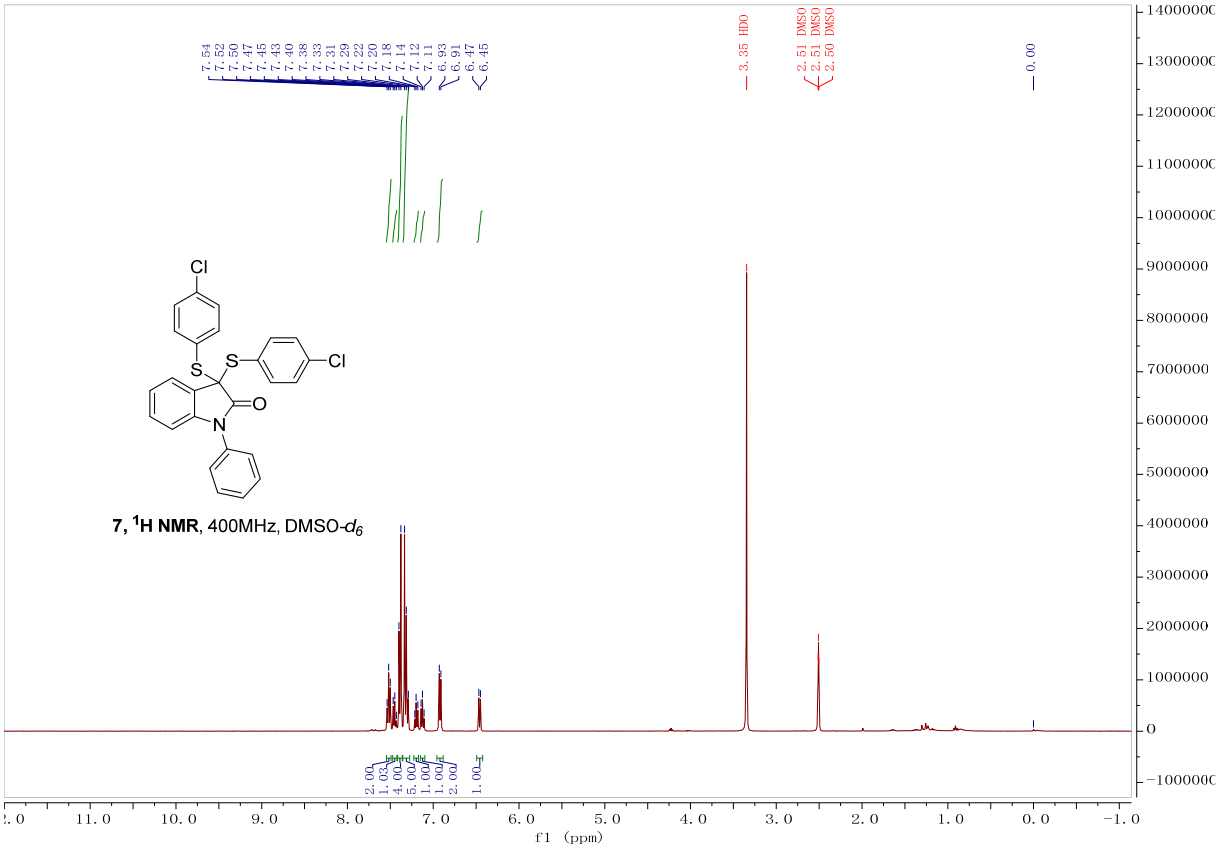
5, ^{13}C NMR, 100MHz, DMSO-d_6



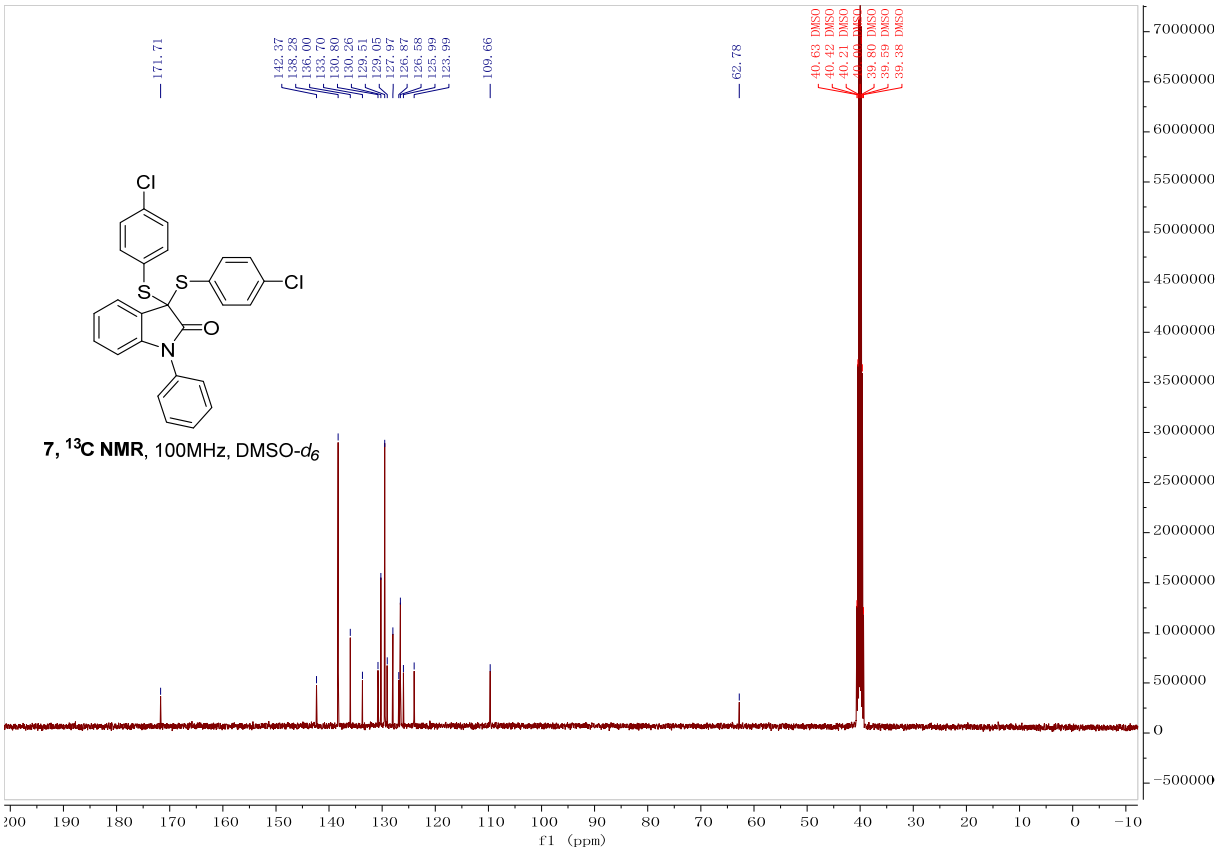
6, ^{1}H NMR, 400MHz, DMSO-d_6



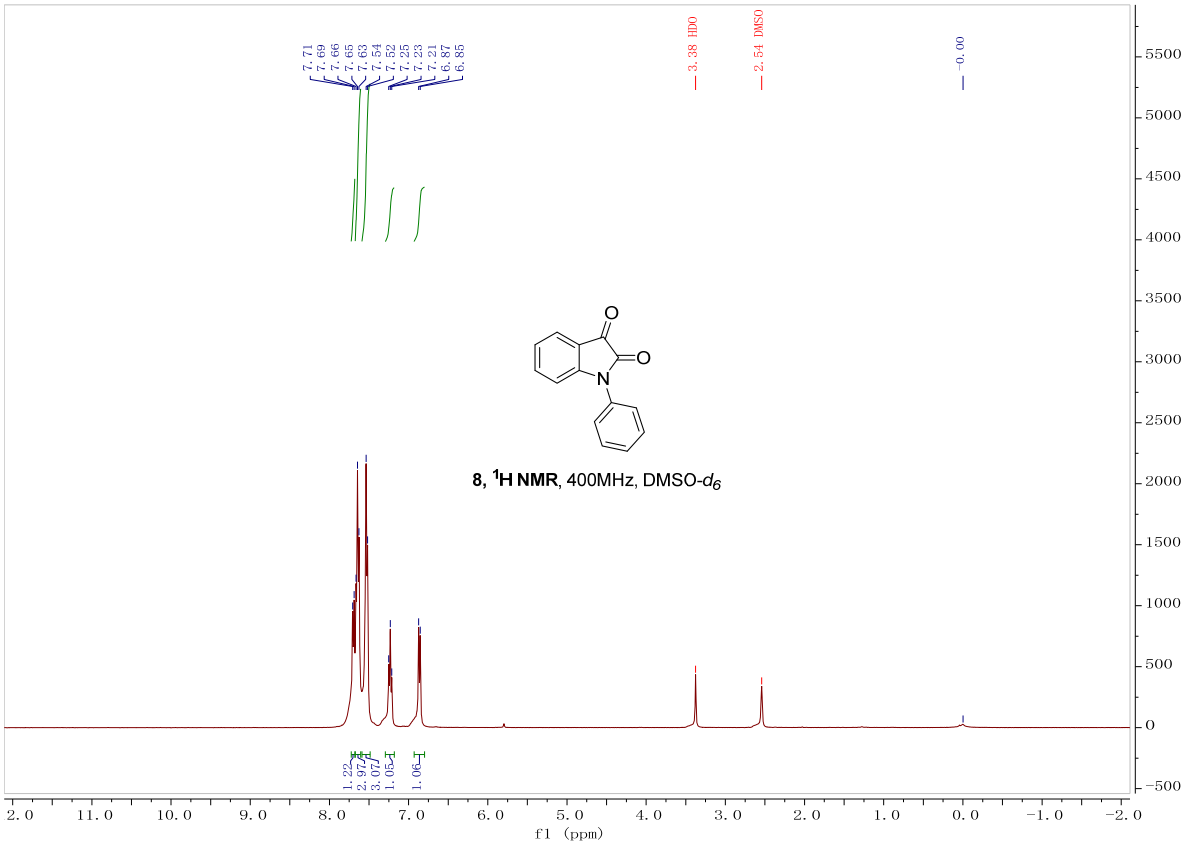
6, ^{13}C NMR, 100MHz, DMSO-d_6



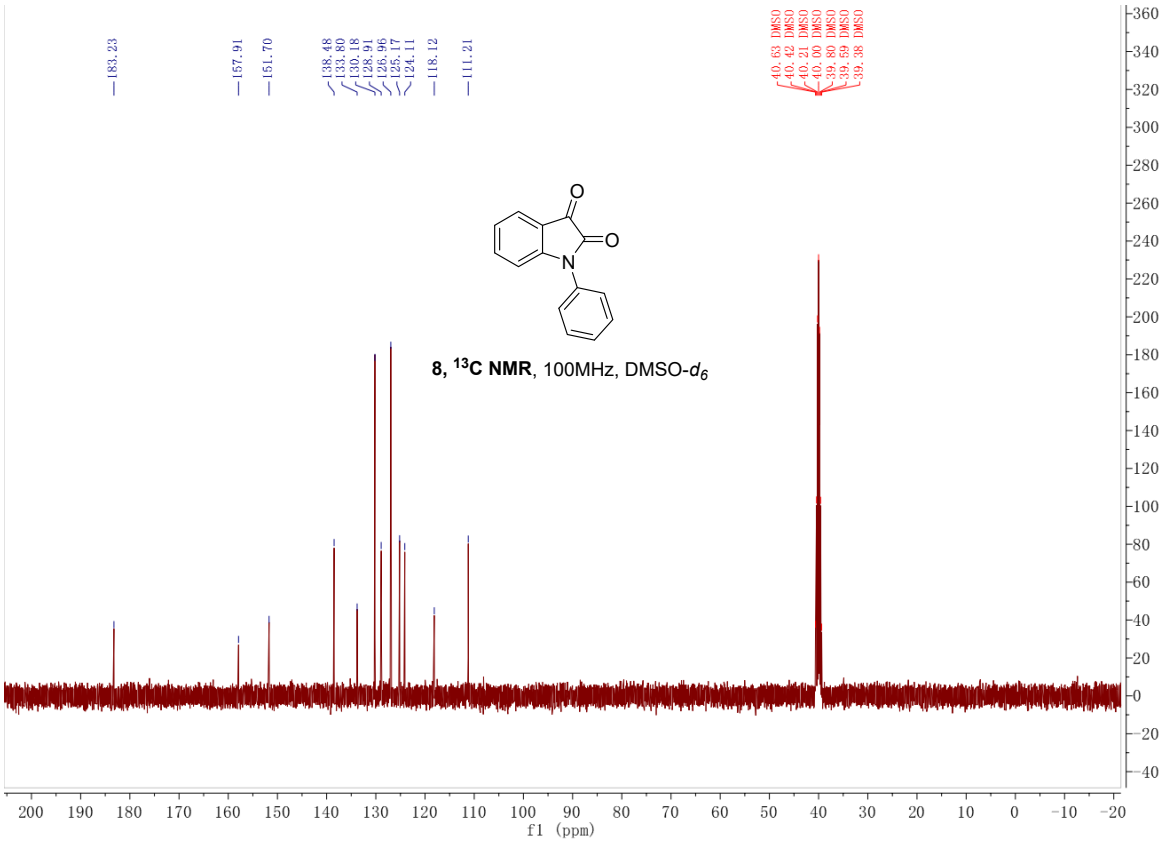
7, ^{1}H NMR, 400MHz, DMSO-d_6



7, ^{13}C NMR, 100MHz, DMSO-d_6



8, ^{1}H NMR, 400MHz, DMSO-d_6



8, ^{13}C NMR, 100MHz, DMSO-d_6