

Palladium-Catalyzed Domino Cyclization/Direct Functionalization Involving the Insertion of SO₂

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Experimental procedures and compound characterization

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I. General information

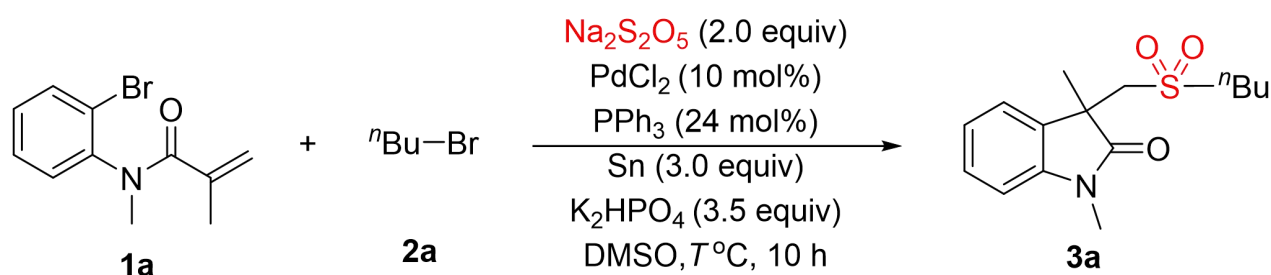
All NMR spectra were acquired on AV-400 MHz and AV-600 MHz spectrometers. ^1H NMR chemical shifts were recorded relative to CDCl_3 as the internal reference (CDCl_3 : δ 7.26). ^{13}C NMR chemical shifts were recorded relative to CDCl_3 as the internal standard (CDCl_3 : δ 77.16). Melting points were determined with XRC-1 and are uncorrected. High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI).

Unless noted otherwise, commercially available chemicals were used as received without purification. Alkenyl bromoarenes **1** were synthesized according to the literature procedures.^[1] All catalytic experiments were carried out using ultra dry solvents purchased from J&K Scientific. The GC internal standard, $n\text{-C}_{12}\text{H}_{26}$ was degassed with nitrogen and dried over activated 4 Å molecular sieve beads before use. Gas chromatography (GC) analysis was performed on a Agilent8890B GC System with Agilent J & W GC column DB-5MS-UI.

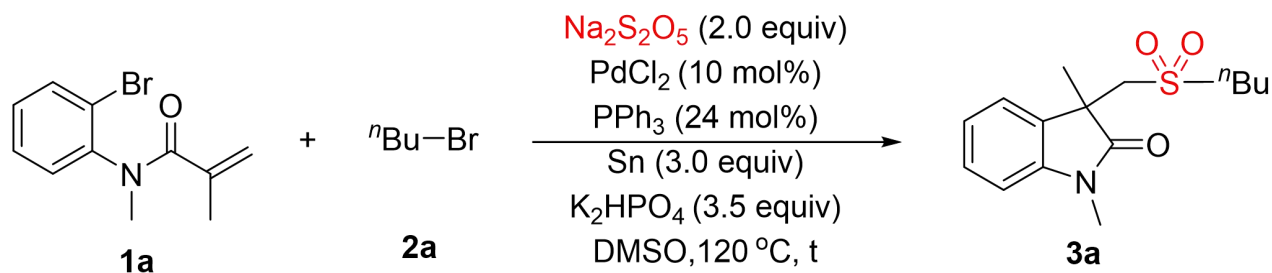
II. Condition optimization for the palladium-catalyzed domino cyclization/alkylsulfonylation

A typical procedure: In a nitrogen-filled glove box, **1a** (25.4 mg, 0.1 mmol, 1.0 equiv), $\text{Na}_2\text{S}_2\text{O}_5$ (38 mg, 0.2 mmol, 2.0 equiv), Pd catalyst (0.01 mmol, 10 mol%), PPh_3 (6.3 mg, 0.024 mmol, 24 mol%), reductive metal (0.3 mmol, 3 equiv), base (0.35 mmol, 3.5 equiv) and solvent (0.8 mL) were added to a 10-mL Schlenk tube. After stirring at room temperature for 1 min, 1-bromobutane **2a** (32 μL , 0.3 mmol, 3.0 equiv) and GC standard $n\text{-C}_{12}\text{H}_{26}$ (10 μL) was added. The reaction mixture was stirred at 120 °C for 48 h and then diluted with 3 mL of EtOAc. Aliquots were taken from the organic phase, and passed through a short plug of silica gel with EtOAc washing (about 1.5 mL). The filtrate was subjected to GC analysis to determine the yield of the product **3a**.

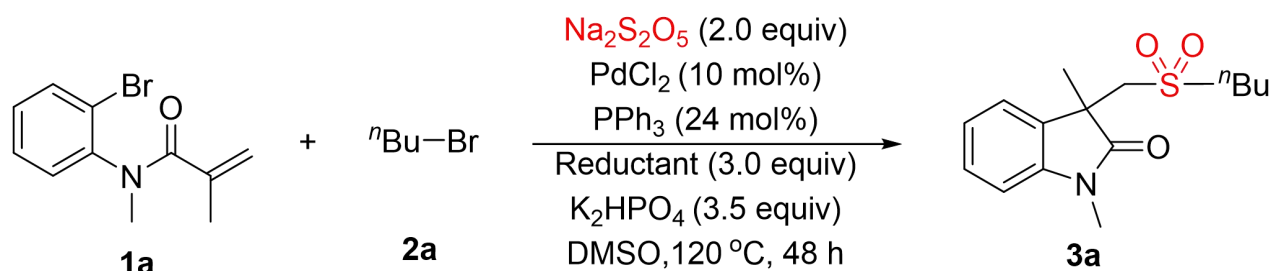
Table S1. The effect of temperature.



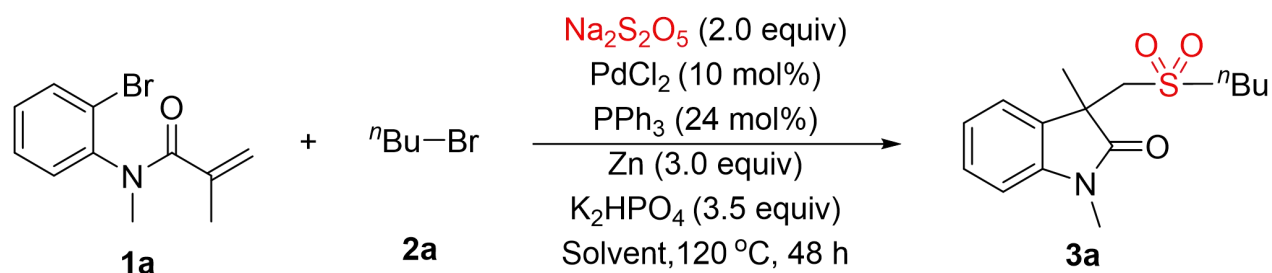
Entry	T	Yield 3a (%)
1	80	14
2	100	24
3	110	26
4	120	34
5	130	30

Table S2. The effect of reaction time.

Entry	t	Yield 3a (%)
1	10 h	34
2	24 h	38
3	48 h	45
4	72 h	46

Table S3. The effect of reductive metal.

Entry	Reductant	Yield 3a (%)
1	Sn	45
2	Zn	60
3	Mg	0
4	Mn	22
5	Fe	0

Table S4. The effect of solvent.

Entry	Solvent	Yield 3a (%)
1	toluene	0

2	1,4-dioxane	10
3	DCE	0
4	DMF	54
5	DMSO	60
6	DMA	51

Table S5. The effect of base.



Entry	Base	Yield 3a (%)
1	K_3PO_4	31
2	KH_2PO_4	50
3	KOPh	45
4	K_2CO_3	35
5	KHCO_3	42
6	NaHCO_3	47
7	DBU	55
8	Et_3N	44
9	DIPEA	40
10	K_2HPO_4	60

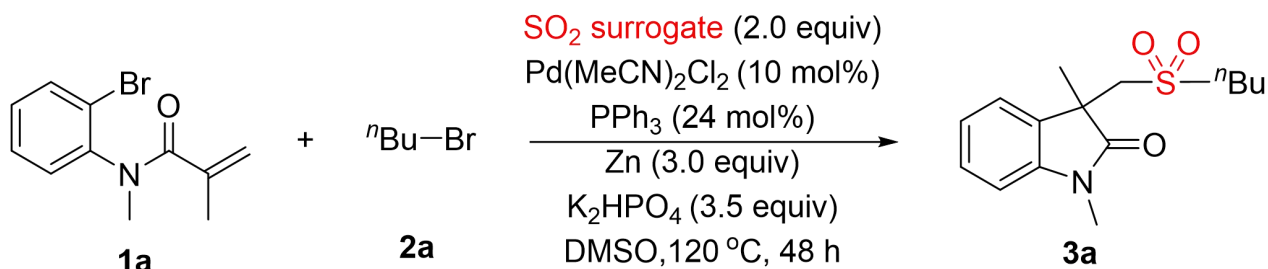
Table S6. The effect of catalyst.



Entry	Catalyst	Yield 3a (%)
1	PdCl_2	60
2	$\text{Pd}(\text{OAc})_2$	56

3	Pd(dba) ₂	65
4	Pd(PPh ₃) ₄	64
5	Pd(dppf) ₂ Cl ₂	50
6	Pd(MeCN)₂Cl₂	75
7	Ni(cod) ₂	0

Table S7. The effect of sulfur dioxide source.



Entry	SO ₂ surrogate	Yield 3a (%)
1	DABSO	72
2	K ₂ S ₂ O ₅	70
3	Na₂S₂O₅	75
4 ^a	Na ₂ S ₂ O ₈	0

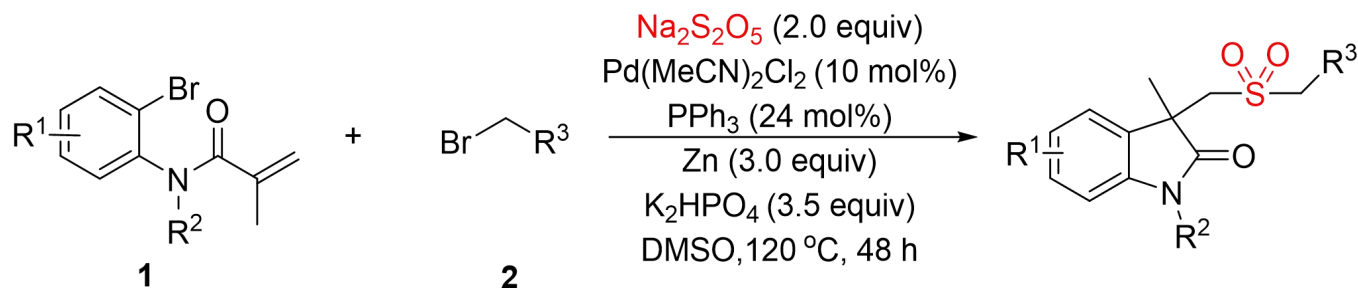
^a 0.9 equiv of **1a** was recovered.

Table S8. The effect of phase transfer catalyst.

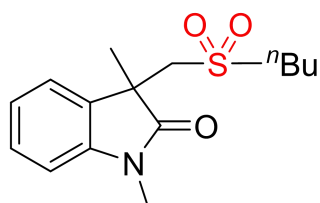


Entry	Additive	Yield 3a (%)
1	Bu ₄ NBr	70
2	Bu ₄ NCl	68
3	Bu ₄ NI	62
4	-	75

III. General procedure for the palladium-catalyzed domino cyclization/alkylsulfonylation



A typical procedure: In a nitrogen-filled glove box, compound **1** (0.2 mmol, 1.0 equiv), $\text{Na}_2\text{S}_2\text{O}_5$ (76 mg, 0.4 mmol, 2.0 equiv), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (5.2 mg, 0.02 mmol, 10 mol%), PPh_3 (12.6 mg, 0.048 mmol, 24 mol%), Zn dust (39.6 mg, 0.6 mmol, 3 equiv), K_2HPO_4 (121.9 mg, 0.7 mmol, 3.5 equiv) and DMSO (1.0 mL) were added to a 10-mL Schlenk tube. After stirring at room temperature for 1 min, alkyl bromide **2** (0.6 mmol, 3.0 equiv) was added. The reaction mixture was stirred at 120 °C for 48 h. The reaction mixture was cooled to room temperature and then extracted with EtOAc. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph.



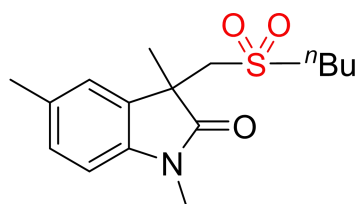
3-((Butylsulfonyl)methyl)-1,3-dimethylindolin-2-one (**3a**)^[2]

The product was isolated by flash chromatography (Petroleum ether/EtOAc = 2:1, V/V) as white solid. 70% yield. M.p.: 70-72 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.37-7.31 (m, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 3.63 (d, $J = 14.4$ Hz, 1H), 3.52 (d, $J = 14.4$ Hz, 1H), 3.25 (s, 3H), 2.72-2.60 (m, 2H), 1.74-1.64 (m, 2H), 1.45 (s, 3H), 1.39-1.29 (m, 2H), 0.87 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3): δ 178.1, 143.5, 130.4, 129.1, 123.7, 122.7, 108.9, 58.6, 55.1, 45.6, 26.8, 25.2, 23.8, 21.7, 13.6.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{21}\text{NNaO}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 318.1134, found 318.1126.



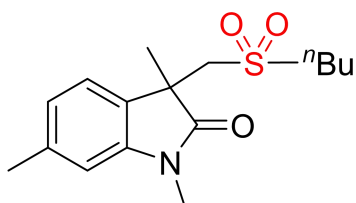
3-((Butylsulfonyl)methyl)-1,3,5-trimethylindolin-2-one (**3b**)

The product was isolated by flash chromatography (Petroleum ether/EtOAc = 2:1, V/V) as white solid. 87% yield. M.p.: 105-106 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.17 (s, 1H), 7.13 (d, $J = 8$ Hz, 1H), 6.79 (d, $J = 8$ Hz, 1H), 3.61 (d, $J = 14.4$ Hz, 1H), 3.50 (d, $J = 14.4$ Hz, 1H), 3.23 (s, 3H), 2.73-2.59 (m, 2H), 2.35 (s, 3H), 1.73-1.64 (m, 2H), 1.44 (s, 3H), 1.39-1.29 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 141.1, 132.2, 130.5, 129.4, 124.4, 108.6, 58.6, 55.0, 45.7, 26.8, 25.2, 23.9, 21.7, 21.3, 13.6.

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 310.1471, found 310.1462.



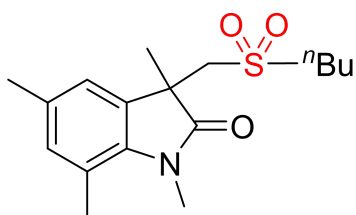
3-((Butylsulfonyl)methyl)-1,3,6-trimethylindolin-2-one (3c)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 87% yield. M.p.: 72-73 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.24 (d, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 6.72 (s, 1H), 3.60 (d, $J = 14.4$ Hz, 1H), 3.49 (d, $J = 14.4$ Hz, 1H), 3.23 (s, 3H), δ 2.73-2.61 (m, 2H), 2.39 (s, 3H), 1.72-1.65 (m, 2H), 1.43 (s, 3H), 1.39-1.30 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.4, 143.5, 139.3, 127.4, 123.4, 123.2, 109.8, 58.7, 55.0, 45.4, 26.7, 25.2, 23.8, 22.0, 21.7, 13.6.

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 310.1471, found 310.1462.



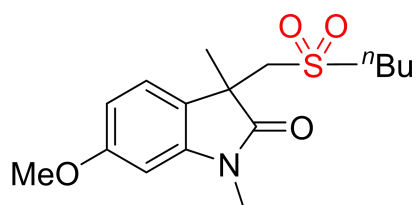
3-((Butylsulfonyl)methyl)-1,3,5,7-tetramethylindolin-2-one (3d)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 90% yield. M.p.: 106-108 °C.

^1H NMR (400 MHz, CDCl_3): δ 6.96 (s, 1H), 6.86 (s, 1H), 3.60 (d, $J = 14.8$ Hz, 1H), 3.50 (s, 3H), 3.46 (d, $J = 14.8$ Hz, 1H), 2.71-2.56 (m, 2H), 2.54 (s, 3H), 2.29 (s, 3H), 1.76-1.62 (m, 2H), 1.40 (s, 3H), 1.38-1.28 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.7, 138.9, 133.3, 132.0, 131.1, 122.0, 120.3, 58.9, 55.0, 45.1, 30.1, 25.7, 23.9, 21.7, 20.9, 19.1, 13.6.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{26}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 324.1628, found 324.1615



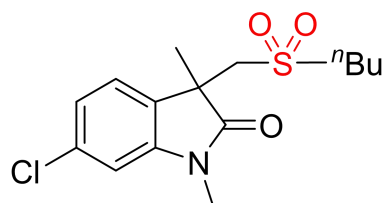
3-((Butylsulfonyl)methyl)-1,3-dimethyl-2-oxo-6-(oxo- λ^6 -methyl)indoline (3e)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 73% yield. M.p.: 92-93 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.27-7.25 (m, 1H), 6.60 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.47 (d, $J = 2.4$ Hz, 1H), 3.83 (s, 3H), 3.50 (d, $J = 14.4$ Hz, 1H), 3.48 (d, $J = 14.4$ Hz, 1H), 3.23 (s, 3H), 2.74-2.62 (m, 2H), 1.73-1.65 (m, 2H), 1.43 (s, 3H), 1.40-1.31 (m, 2H), 0.88 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.7, 160.9, 144.8, 124.4, 122.1, 106.6, 96.8, 58.7, 55.6, 55.1, 45.1, 26.8, 25.2, 23.8, 21.7, 13.6.

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_4\text{S}$ [$\text{M}+\text{H}^+$]: 326.1421, found 326.1407



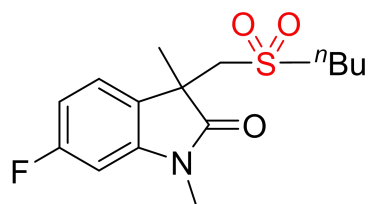
3-((Butylsulfonyl)methyl)-6-chloro-1,3-dimethylindolin-2-one (3f)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 67 % yield. M.p.: 76-77 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.29 (d, $J = 8$ Hz, 1H), 7.07 (dd, $J = 7.6, 1.6$ Hz, 1H), 6.89 (d, $J = 1.6$ Hz, 1H), 3.62 (d, $J = 14.4$ Hz, 1H), 3.50 (d, $J = 14.4$ Hz, 1H), 3.23 (s, 3H), 2.82-2.70 (m, 2H), 1.74-1.67 (m, 2H), 1.43 (s, 3H), 1.40-1.33 (m, 2H), 0.89 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 178.1, 144.6, 134.9, 128.8, 124.8, 122.5, 109.6, 58.3, 55.3, 45.3, 26.8, 25.2, 23.8, 21.7, 13.6.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{21}\text{ClNO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 330.0925, found 330.0911



3-((Butylsulfonyl)methyl)-6-fluoro-1,3-dimethylindolin-2-one (3g)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as yellow oil. 80 % yield.

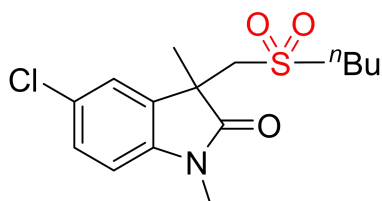
^1H NMR (400 MHz, CDCl_3): δ 7.30 (dd, $J = 8, 5.2$ Hz, 1H), 6.80-6.75 (m, 1H), 6.63 (dd, $J = 8.8, 2$ Hz, 1H),

3.62 (d, $J = 14.4$ Hz, 1H), 3.50 (d, $J = 14.4$ Hz, 1H), 3.23 (s, 3H), 2.80-2.68 (m, 2H), 1.74-1.66 (m, 2H), 1.43 (s, 3H), 1.40-1.33 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.5, 163.5 (d, $J = 247.0$ Hz), 145.1 (d, $J = 11.7$ Hz), 125.7 (d, $J = 3.1$ Hz), 124.9 (d, $J = 9.8$ Hz), 108.8 (d, $J = 22.6$ Hz), 97.8 (d, $J = 27.7$ Hz), 58.4, 55.2, 45.2, 26.9, 25.2, 23.8, 21.7, 13.6.

^{19}F NMR (377 MHz, CDCl_3): δ -110.9.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{21}\text{FNO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 314.1221, found 314.1207.



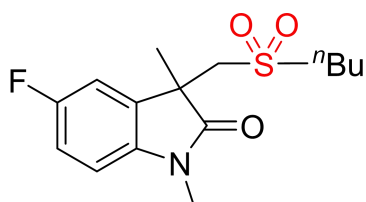
3-((Butylsulfonyl)methyl)-5-chloro-1,3-dimethylindolin-2-one (3h)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 65% yield. M.p.: 101-103 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.34 (d, $J = 1.6$ Hz, 1H), 7.30 (dd, $J = 8.4, 1.6$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 3.63 (d, $J = 14.4$ Hz, 1H), 3.50 (d, $J = 14.4$ Hz, 1H), 3.23 (s, 3H), 2.81-2.68 (m, 2H), 1.74-1.67 (m, 2H), 1.44 (s, 3H), 1.41-1.33 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 177.6, 142.0, 132.2, 129.0, 128.1, 124.3, 109.8, 58.3, 55.3, 45.8, 26.9, 25.1, 23.9, 21.7, 13.6.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{20}\text{ClNNaO}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 352.0745, found 352.0762.



3-((Butylsulfonyl)methyl)-5-fluoro-1,3-dimethylindolin-2-one (3i)

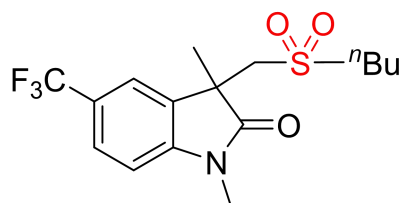
The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as yellow oil. 76% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.15 (dd, $J = 7.6, 2.4$ Hz, 1H), 7.05-7.00 (m, 1H), 6.81 (dd, $J = 8.4, 4$ Hz, 1H), 3.63 (d, $J = 14.4$ Hz, 1H), 3.49 (d, $J = 14.4$ Hz, 1H), 3.24 (s, 3H), 2.83-2.71 (m, 2H), 1.75-1.67 (m, 2H), 1.45 (s, 3H), 1.41-1.33 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 177.8, 159.3 (d, $J = 242.2$ Hz), 139.3 (d, $J = 1.9$ Hz), 132.1 (d, $J = 8.0$ Hz), 115.3 (d, $J = 23.4$ Hz), 112.1 (d, $J = 25.0$ Hz), 109.3 (d, $J = 8.3$ Hz), 58.2, 55.2, 46.0, 26.9, 25.1, 23.8, 21.7, 13.6.

^{19}F NMR (377 MHz, CDCl_3): δ -120.0.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{21}\text{FNO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 314.1221, found 314.1208.



3-((Butylsulfonyl)methyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one (3j)

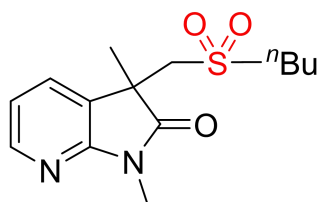
The product was isolated by flash chromatography (Petroleum ether/EtOAc =3:1, V/V) as yellow oil. 62% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.63-7.60 (m, 2H), 6.97 (d, $J = 8$ Hz, 1H), 3.67 (d, $J = 14.4$ Hz, 1H), 3.56 (d, $J = 14.4$ Hz, 1H), 3.28 (s, 3H), 2.78-2.66 (m, 2H), 1.73-1.65 (m, 2H), 1.47 (s, 3H), 1.40-1.31 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 177.8, 146.4, 131.0, 126.7 (q, $J = 4.04$ Hz), 124.8 (q, $J = 33.0$ Hz), 124.3 (q, $J = 407.9$ Hz), 120.8 (q, $J = 3.7$ Hz), 108.6, 58.2, 55.2, 45.4, 26.9, 25.0, 23.7, 21.6, 13.4.

^{19}F NMR (377 MHz, CDCl_3): δ -61.4.

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 364.1189, found 364.1178.



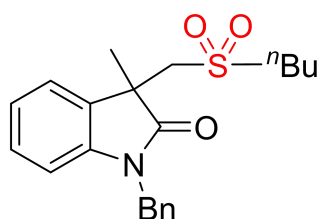
3-((Butylsulfonyl)methyl)-1,3-dimethyl-1,3-dihydro-2H-pyrrolo[2,3-b]pyridin-2-one (3k)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =1:1, V/V) as yellow oil. 48% yield.

^1H NMR (400 MHz, CDCl_3): δ 8.23 (dd, $J = 5.2, 0.8$ Hz, 1H), 7.69-7.67 (m, 1H), 7.01 (dd, $J = 7.2, 5.6$ Hz, 1H), 3.61 (d, $J = 14.0$ Hz, 1H), 3.52 (d, $J = 14.4$ Hz, 1H), 3.33 (s, 3H), 2.92-2.80 (m, 2H), 1.77-1.70 (m, 2H), 1.50 (s, 3H), 1.45-1.36 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 177.9, 156.5, 147.8, 131.9, 125.2, 118.4, 57.7, 55.4, 45.3, 25.9, 24.5, 23.8, 21.7, 13.6.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{NaO}_3\text{S}$ [$\text{M}+\text{Na}^+$]: 319.1087, found 319.1077.



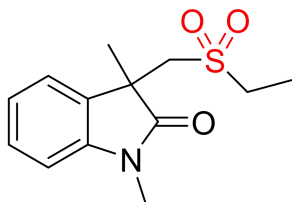
1-Benzyl-3-((butylsulfonyl)methyl)-3-methylindolin-2-one (3l)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =1:1, V/V) as yellow oil. 57% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.38 (d, $J = 7.6$ Hz, 1H), 7.36-7.24 (m, 5H), 7.22-7.18 (m, 1H), 7.09-7.05 (m, 1H), 6.75 (d, $J = 7.6$ Hz, 1H), 5.05 (d, $J = 16.0$ Hz, 1H), 4.87 (d, $J = 16.0$ Hz, 1H), 3.70 (d, $J = 14.4$ Hz, 1H), 3.57 (d, $J = 14.4$ Hz, 1H), 2.77-2.66 (m, 2H), 1.75-1.67 (m, 2H), 1.52 (s, 3H), 1.39-1.30 (m, 2H), 0.88 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.2, 142.5, 135.8, 130.5, 128.9, 127.7, 127.4, 123.7, 122.7, 110.0, 58.4, 55.1, 45.7, 44.3, 25.8, 23.8, 21.7, 13.6.

HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 372.1628, found 372.1622.



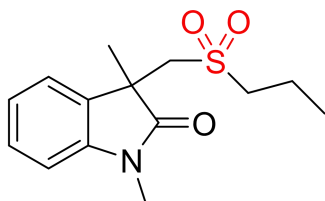
3-((Ethylsulfonyl)methyl)-1,3-dimethylindolin-2-one (4a)^[3]

The product was isolated by flash chromatography (Petroleum ether/EtOAc =1:1, V/V) as yellow oil. 62% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.35 (dd, $J = 16, 7.6$ Hz, 2H), 7.11 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 8$ Hz, 1H), 3.63 (d, $J = 14.4$ Hz, 1H), 3.52 (d, $J = 14.4$ Hz, 1H), 3.26 (s, 3H), 2.78-2.60 (m, 2H), 1.45 (s, 3H), 1.27 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 143.4, 130.4, 129.1, 123.6, 122.7, 108.9, 57.8, 49.6, 45.6, 26.7, 25.2, 6.5.

HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 268.1002, found 268.0991.



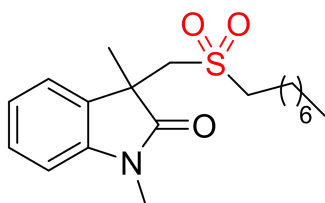
1,3-Dimethyl-3-((propylsulfonyl)methyl)indolin-2-one (4b)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =1:1, V/V) as white solid. 64% yield. M.p.: 106-108 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.37-7.32 (m, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 3.62 (d, $J = 14.4$ Hz, 1H), 3.52 (d, $J = 14.4$ Hz, 1H), 3.25 (s, 3H), 2.71-2.58 (m, 2H), 1.79-1.69 (m, 2H), 1.45 (s, 3H), 0.96 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 143.5, 130.4, 129.1, 123.6, 122.7, 108.9, 58.6, 57.0, 45.6, 26.7, 25.1, 15.8, 13.1.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 282.1156, found 282.1151.



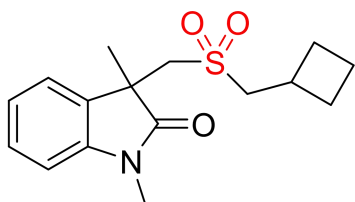
1,3-Dimethyl-3-((octylsulfonyl)methyl)indolin-2-one (4c)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 64% yield. M.p.: 68-70 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36-7.31 (m, 2H), 7.12-7.08 (m, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 3.63 (d, $J = 14.4$ Hz, 1H), 3.52 (d, $J = 14.4$ Hz, 1H), 3.25 (s, 3H), 2.70-2.58 (m, 2H), 1.72-1.64 (m, 2H), 1.45 (s, 3H), 1.27-1.20 (m, 10H), 0.86 (t, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.0, 143.5, 130.4, 129.1, 123.7, 122.6, 108.9, 58.6, 55.3, 45.6, 31.8, 29.0, 28.4, 26.7, 25.1, 22.7, 21.8, 14.2.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{30}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 352.1941, found 352.1928.



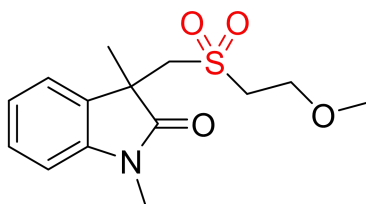
3-(((Cyclobutylmethyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (4d)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V / V) as white solid. 65% yield. M.p.: 102-103 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.38-7.31 (m, 2H), 7.10 (t, $J = 7.2$ Hz, 1H), 6.89 (d, $J = 8.0$ Hz, 1H), 3.56 (d, $J = 14.4$ Hz, 1H), 3.47 (d, $J = 14.4$ Hz, 1H), 3.25 (s, 3H), 2.84-2.82 (m, 2H), 2.81-2.73 (m, 1H), 2.18-2.11 (m, 2H), 1.99-1.87 (m, 1H), 1.85-1.74 (m, 3H), 1.44 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.1, 143.4, 130.5, 129.0, 123.8, 122.7, 108.8, 61.1, 59.3, 45.6, 29.2, 28.7, 28.6, 26.7, 25.1, 19.4.

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 308.1315, found 308.1302.



3-(((2-Methoxyethyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (4e)

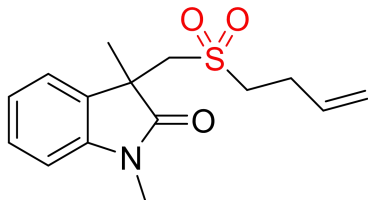
The product was isolated by flash chromatography (Petroleum ether/EtOAc =1:1, V/V) as yellow oil. 62% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.39-7.31 (m, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.89 (d, $J = 7.6$ Hz, 1H), 3.78-3.64

(m, 4H), 3.39 (s, 3H), 3.25 (s, 3H), 2.88 (t, $J = 5.2$ Hz, 2H), 1.44 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.3, 143.6, 130.3, 129.0, 124.1, 122.5, 108.8, 66.3, 60.8, 59.2, 55.5, 45.7, 26.7, 25.2.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_4\text{S}$ [$\text{M}+\text{H}^+$]: 298.1108, found 298.1098.



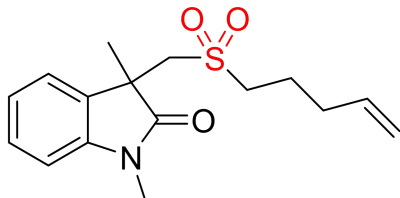
3-((But-3-en-1-ylsulfonyl)methyl)-1,3-dimethylindolin-2-one (4f)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 60% yield. M.p.: 90-91 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.37-7.32 (m, 2H), 7.11 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 8$ Hz, 1H), 5.76-5.66 (m, 1H), 5.09-5.04 (m, 2H), 3.66 (d, $J = 14.4$ Hz, 1H), 3.55 (d, $J = 14.8$ Hz, 1H), 3.26 (s, 3H), 2.82-2.69 (m, 2H), 2.49-2.43 (m, 2H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 145.9, 143.5, 135.7, 133.9, 130.4, 129.2, 123.7, 122.7, 117.5, 108.9, 59.0, 54.4, 45.6, 26.8, 26.0, 25.2.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]; 294.1158, found 294.1147.



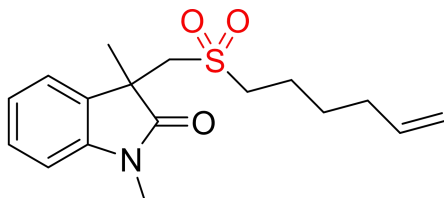
1,3-Dimethyl-3-((pent-4-en-1-ylsulfonyl)methyl)indolin-2-one (4g)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as white solid. 62% yield. M.p.: 93-94 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.36-7.32 (m, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 5.71-5.61 (m, 1H), 5.01-4.97 (m, 2H), 3.63 (d, $J = 14.8$ Hz, 1H), 3.52 (d, $J = 14.8$ Hz, 1H), 3.25 (s, 3H), 2.71-2.58 (m, 2H), 2.10-2.01 (m, 2H), 1.88-1.75 (m, 2H), 1.45 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 143.4, 136.3, 130.3, 129.1, 123.7, 122.7, 116.7, 108.9, 58.8, 54.5, 45.6, 32.1, 26.7, 25.1, 20.9.

HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{22}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 308.1315, found 308.1308.



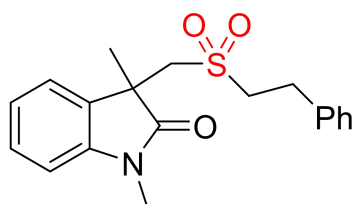
3-((Hex-5-en-1-ylsulfonyl)methyl)-1,3-dimethylindolin-2-one (4h)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =1:1, V/V) as yellow oil. 65% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.37-7.32 (m, 2H), 7.13-7.09 (m, 1H), 6.90 (d, $J = 8$ Hz, 1H), 5.78-5.68 (m, 1H), 5.02-4.95 (m, 2H), 3.62 (d, $J = 14.8$ Hz, 1H), 3.52 (d, $J = 14.8$ Hz, 1H), 3.26 (s, 3H), 2.73-2.61 (m, 2H), 2.04-1.99 (m, 2H), 1.76-1.70 (m, 2H), 1.45 (s, 3H), 1.43-1.37 (m, 2H).

^{13}C NMR (151 MHz, CDCl_3): δ 178.0, 143.5, 137.6, 130.4, 129.1, 123.6, 122.7, 115.5, 108.9, 58.7, 55.1, 45.6, 33.1, 27.6, 26.8, 25.1, 21.3.

HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 322.1471, found 322.1460.



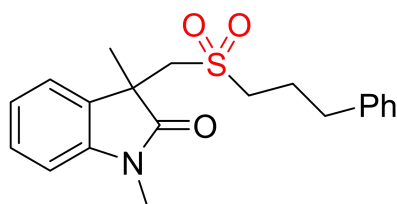
1,3-Dimethyl-3-((phenethylsulfonyl)methyl)indolin-2-one (4i)

The product was isolated by flash chromatography (Petroleum ether/EtOAc =3:1, V/V) as white solid. 73% yield. M.p.: 125-126 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.37-7.22 (m, 5H), 7.14-7.09 (m, 3H), 6.91 (d, $J = 8$ Hz, 1H), 3.61 (d, $J = 14.4$ Hz, 1H), 3.46 (d, $J = 14.8$ Hz, 1H), 3.26 (s, 3H), 3.04-2.94 (m, 4H), 1.44 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 143.5, 137.6, 130.3, 129.2, 129.0, 128.6, 127.1, 123.7, 122.7, 109.0, 59.0, 56.6, 45.6, 28.0, 26.8, 25.1.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 344.1315, found 344.1305.



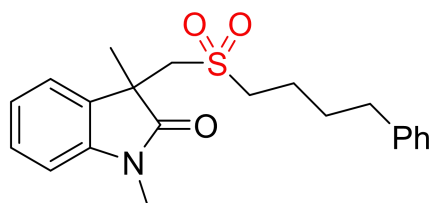
1,3-Dimethyl-3-(((3-phenylpropyl)sulfonyl)methyl)indolin-2-one (4j)

The product was isolated by flash chromatography ((Petroleum ether/EtOAc = 2:1, V/V) as yellow oil. 85% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.34-7.26 (m, 4H), 7.32-7.20 (m, 1H), 7.12-7.10 (m, 2H), 7.08-7.04 (m, 1H), 6.88 (d, $J = 8$ Hz, 1H), 3.61 (d, $J = 14.4$ Hz, 1H), 3.49 (d, $J = 14.4$ Hz, 1H), 3.23 (s, 3H), 2.71-2.58 (m, 4H), 2.10-1.98 (m, 2H), 1.43 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 143.4, 139.9, 130.3, 129.1, 128.8, 128.5, 126.6, 123.6, 122.7, 108.9, 55.8, 54.4, 45.6, 34.2, 26.7, 25.1, 23.4.

HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_3\text{S}$ [$\text{M}+\text{H}^+$]: 358.1471, found 358.1466.



1,3-Dimethyl-3-(((4-phenylbutyl)sulfonyl)methyl)indolin-2-one (4k)

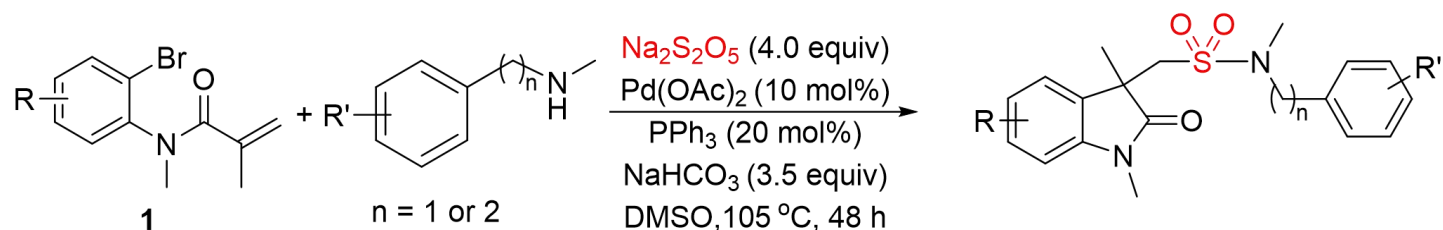
The product was isolated by flash chromatography (Petroleum ether/EtOAc =2:1, V/V) as yellow oil. 80% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.35-7.26 (m, 4H), 7.21-7.17 (m, 1H), 7.14-7.07 (m, 3H), 6.90 (d, *J* = 8 Hz, 1H), 3.62 (d, *J* = 14.8 Hz, 1H), 3.50 (d, *J* = 14.4 Hz, 1H), 3.25 (s, 3H), 2.73-2.52 (m, 4H), 1.77-1.60 (m, 4H), 1.44 (s, 3H).

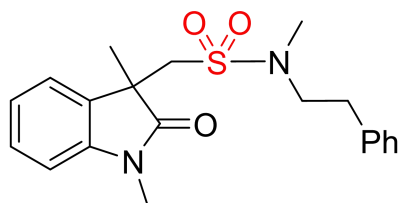
¹³C NMR (101 MHz, CDCl₃): δ 178.0, 143.5, 141.3, 129.1, 128.5, 128.4, 126.2, 123.6, 122.7, 108.9, 58.7, 55.0, 45.5, 35.3, 30.1, 26.7, 25.1, 21.4.

HRMS (ESI): calcd for C₂₁H₂₆NO₃S [M+H⁺]: 372.1628, found 372.1629.

IV. General procedure for the palladium-catalyzed domino cyclization/aminosulfonylation



A typical procedure: In a nitrogen-filled glove box, compound **1** (0.2 mmol, 1.0 equiv), amine (0.52 mmol, 2.6 equiv), Na₂S₂O₅ (152 mg, 0.4 mmol, 4.0 equiv), Pd(OAc)₂ (4.5 mg, 0.02 mmol, 10 mol%), PPh₃ (10.5 mg, 0.04 mmol, 20 mol%), NaHCO₃ (58.8 mg, 0.7 mmol, 3.5 equiv) and DMSO (1.0 mL) were added to a 10-mL Schlenk tube. The reaction mixture was stirred at 105 °C for 48 h. The reaction mixture was cooled to room temperature and then extracted with EtOAc. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph.



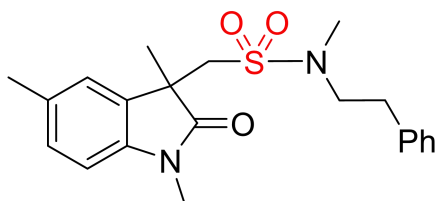
1-(1,3-Dimethyl-2-oxindolin-3-yl)-N-methyl-N-phenethylmethanesulfonamide (6a)^[4]

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 86% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.35-7.16 (m, 7H), 7.10 (td, *J* = 7.2, 1.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.38 (d, *J* = 14.4 Hz, 1H), 3.26-3.16 (m, 6H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.68 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.0, 141.8, 138.4, 132.3, 129.1, 128.8, 128.7, 128.1, 126.8, 124.8, 109.5, 55.7, 51.4, 45.9, 34.9, 34.4, 26.8, 24.9.

HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 395.1405. Found: 395.1396.



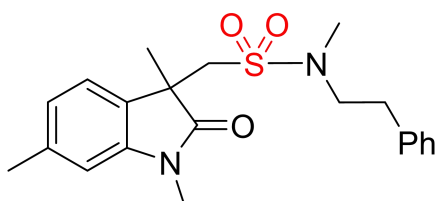
***N*-Methyl-*N*-phenethyl-1-(1,3,5-trimethyl-2-oxindolin-3-yl)methanesulfonamide (6b)^[4]**

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 82% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.31-7.27 (m, 2H), 7.24-7.20 (m, 1H), 7.18-7.16 (m, 3H), 7.09 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.40 (d, J = 14.4 Hz, 1H), 3.25-3.17 (m, 3H), 3.20 (s, 3H), 2.80 (t, J = 7.6 Hz, 2H), 2.67 (s, 3H), 2.36 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.3, 140.8, 138.5, 132.1, 130.7, 129.0, 128.7, 126.7, 125.1, 108.3, 55.8, 51.4, 45.8, 35.0, 34.4, 26.7, 25.1, 21.3.

HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 387.1742. Found: 387.1750.



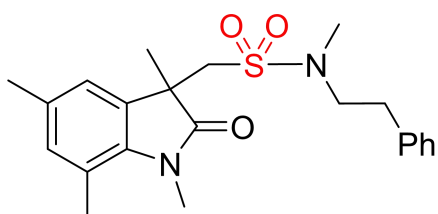
***N*-Methyl-*N*-phenethyl-1-(1,3,6-trimethyl-2-oxindolin-3-yl)methanesulfonamide (6c)^[4]**

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 76% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.31-7.27 (m, 2H), 7.24-7.20 (m, 2H), 7.18-7.16 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 3.37 (d, J = 14.4 Hz, 1H), 3.25-3.14 (m, 3H), 3.21 (s, 3H), 2.80 (t, J = 7.6 Hz, 2H), 2.69 (s, 3H), 2.37 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.7, 143.3, 138.9, 138.4, 129.0, 128.7, 127.6, 126.7, 124.0, 123.2, 109.5, 55.8, 51.3, 45.5, 35.0, 34.4, 26.6, 25.0, 22.0.

HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 409.1562. Found: 409.1573.



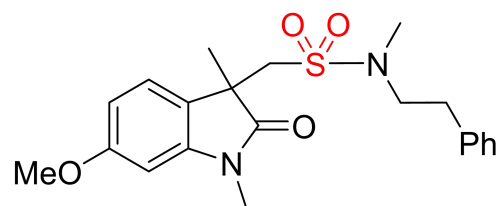
***N*-Methyl-*N*-phenethyl-1-(1,3,5,7-tetramethyl-2-oxindolin-3-yl)methanesulfonamide (6d)**

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 82% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.31-7.28 (m, 2H), 7.24-7.20 (m, 1H), 7.17 (d, $J = 7.6$ Hz, 2H), 6.95 (s, 1H), 6.81 (s, 1H), 3.47 (s, 3H), 3.43 (d, $J = 14.4$ Hz, 1H), 3.20-3.15 (m, 3H), 2.80 (t, $J = 8.0$ Hz, 2H), 2.67 (s, 3H), 2.49 (s, 3H), 2.30 (s, 3H), 1.32 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 179.0, 138.6, 138.5, 133.0, 131.9, 131.3, 129.0, 128.7, 126.7, 122.6, 119.9, 56.2, 51.3, 45.2, 35.1, 34.4, 30.1, 25.7, 21.0, 19.0.

HRMS (ESI): Calcd for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 401.1899. Found: 401.1897.



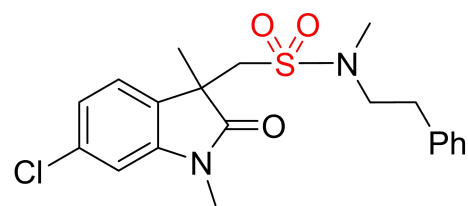
1-(6-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-N-methyl-N-phenethylmethanesulfonamide (6e)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 74% yield.

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ 7.29 (t, $J = 7.2$ Hz, 2H), 7.25-7.21 (m, 2H), 7.17 (d, $J = 7.2$ Hz, 2H), 6.60 (dd, $J = 7.8, 1.8$ Hz, 1H), 6.43 (d, $J = 2.4$ Hz, 1H), 3.81 (s, 3H), 3.34 (d, $J = 14.4$ Hz, 1H), 3.28-3.19 (m, 2H), 3.20 (s, 3H), 3.14 (d, $J = 14.4$ Hz, 1H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.70 (s, 3H), 1.35 (s, 3H).

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 179.0, 160.6, 144.5, 138.5, 129.0, 128.7, 126.7, 125.0, 122.5, 106.5, 96.6, 55.9, 55.6, 51.4, 45.3, 35.1, 34.5, 26.7, 25.1.

HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 403.1692. Found: 403.1699.



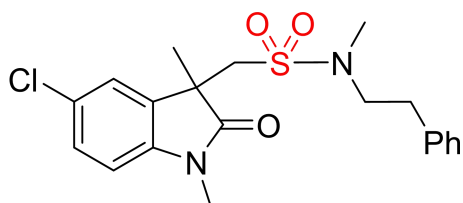
1-(6-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-N-methyl-N-phenethylmethanesulfonamide (6f)^[4]

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 91% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32-7.28 (m, 2H), 7.26-7.17 (m, 4H), 7.06 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.86 (d, $J = 2.0$ Hz, 1H), 3.34-3.22 (m, 3H), 3.20 (s, 3H), 3.10 (d, $J = 14.0$ Hz, 1H), 2.82 (t, $J = 7.6$ Hz, 2H), 2.71 (s, 3H), 1.34 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.4, 144.4, 138.4, 134.6, 129.0, 128.7, 126.8, 125.3, 122.5, 109.3, 55.6, 51.3, 45.5, 34.9, 34.4, 26.8, 24.8.

HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{24}\text{ClN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 407.1196, found 407.1191.



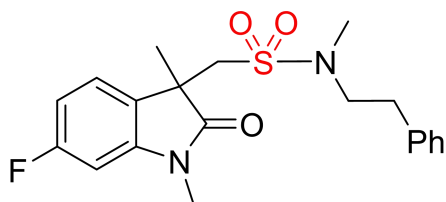
1-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-N-methyl-N-phenethylmethanesulfonamide (6g)^[4]

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 82% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.32-7.26 (m, 4H), 7.25-7.18 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 1H), 3.34 (d, *J* = 14.4 Hz, 1H), 3.31-3.23 (m, 2H), 3.21 (s, 3H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.70 (s, 3H), 1.34 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 178.0, 141.9, 138.4, 132.4, 129.1, 128.8, 128.7, 128.0, 126.8, 124.8, 109.5, 55.7, 51.4, 45.9, 35.0, 34.4, 26.8, 24.9.

HRMS (ESI): calcd for C₂₀H₂₄ClN₂O₃S [M+H]⁺407.1196, found 407.1181.



1-(6-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)-N-methyl-N-phenethylmethanesulfonamide (6h)

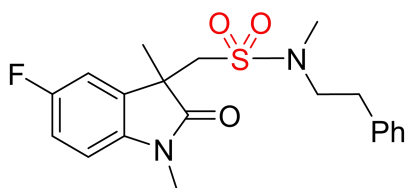
The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 72% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.32-7.23 (m, 4H), 7.21-7.17 (m, 2H), 6.80-6.75 (m, 1H), 6.61 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.35-3.23 (m, 2H), 3.32 (d, *J* = 14.0 Hz, 1H), 3.21 (s, 3H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.71 (s, 3H), 1.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 178.8, 163.4 (d, *J* = 246.5 Hz), 144.8 (d, *J* = 11.6 Hz), 138.4, 128.9 (d, *J* = 30.1 Hz), 126.8, 125.8 (d, *J* = 3.0 Hz), 125.4 (d, *J* = 10.1 Hz), 108.8 (d, *J* = 22.5 Hz), 97.4 (d, *J* = 27.7 Hz), 55.7, 51.4, 45.4, 35.0, 34.4, 26.8, 25.0.

¹⁹F NMR (377 MHz, CDCl₃): δ -111.5.

HRMS (ESI): Calcd for C₂₀H₂₄FN₂O₃S [M+H]⁺ 391.1492. Found: 391.1504.



1-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)-N-methyl-N-phenethylmethanesulfonamide (6i)^[4]

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 60%

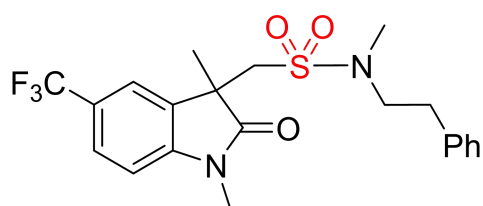
yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.32-7.28 (m, 2H), 7.26-7.18 (m, 3H), 7.11 (dd, $J = 8.0, 2.4$ Hz, 1H), 7.00 (td, $J = 8.8, 2.4$ Hz, 1H), 6.78 (dd, $J = 8.4, 4.0$ Hz, 1H), 3.35-3.23 (m, 3H), 3.21 (s, 3H), 3.10 (d, $J = 14.0$ Hz, 1H), 2.82 (t, $J = 7.6$ Hz, 2H), 2.72 (s, 3H), 1.35 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.1, 159.0 (d, $J = 241.4$ Hz), 139.1, 138.4, 132.3 (d, $J = 8.3$ Hz), 128.9 (d, $J = 31.7$ Hz), 126.8, 115.0 (d, $J = 23.5$ Hz), 112.6 (d, $J = 25.1$ Hz), 109.0 (d, $J = 8.1$ Hz), 55.6, 51.4, 46.2, 35.0, 34.4, 26.9, 24.9.

$^{19}\text{F NMR}$ (377 MHz, CDCl_3): δ -120.2.

HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{24}\text{FN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 391.1492, found 225.1287.



1-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-*N*-methyl-*N*-phenethylmethanesulfonamide (6j)

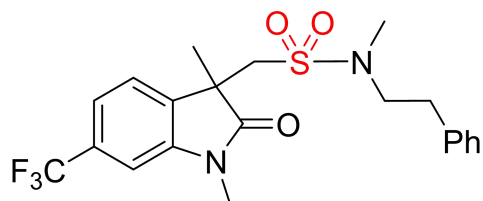
The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 82% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.59-7.55 (m, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.25-7.17 (m, 3H), 6.93 (d, $J = 8.0$ Hz, 1H), 3.37 (d, $J = 14.0$ Hz, 1H), 3.31-3.18 (m, 2H), 3.26 (s, 3H), 3.13 (d, $J = 14.4$ Hz, 1H), 2.80 (t, $J = 7.6$ Hz, 2H), 2.67 (s, 3H), 1.36 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.4, 146.3, 138.4, 131.3, 129.1, 128.8, 126.8, 126.5 (q, $J = 4.2$ Hz), 124.8 (q, $J = 32.8$ Hz), 124.5 (q, $J = 272.3$ Hz), 121.4 (q, $J = 3.7$ Hz), 108.4, 55.8, 51.3, 45.7, 34.9, 34.3, 26.9, 24.9.

$^{19}\text{F NMR}$ (377 MHz, CDCl_3): δ -61.3.

HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 441.1460, found 441.1452.



1-(1,3-Dimethyl-2-oxo-6-(trifluoromethyl)indolin-3-yl)-*N*-methyl-*N*-phenethylmethanesulfonamide (6k)

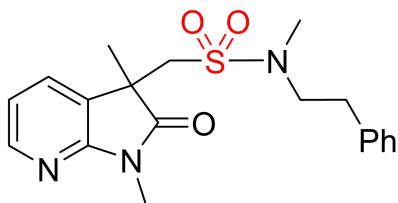
The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as yellow-green oil. 72% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.44 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 7.32-7.28 (m, 2H), 7.25-7.17 (m, 3H), 7.07 (s, 1H), 3.36-3.21 (m, 3H), 3.26 (s, 3H), 3.12 (d, $J = 14.0$ Hz, 1H), 2.82 (t, $J = 7.6$ Hz, 2H), 2.73 (s, 3H), 1.37 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.2, 143.9, 138.4, 134.5, 131.2 (q, $J = 32.7$ Hz), 129.1, 128.8, 126.8, 124.6, 124.1 (q, $J = 273.5$ Hz), 119.7 (q, $J = 3.9$ Hz), 105.3 (q, $J = 3.7$ Hz), 55.5, 51.4, 45.8, 34.9, 34.4, 26.8, 24.8.

^{19}F NMR (377 MHz, CDCl_3): δ -62.4.

HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 441.1460. found 441.1453.



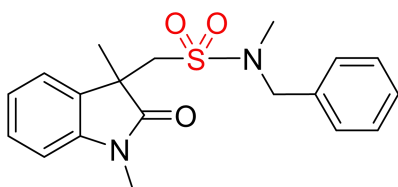
1-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)-N-methyl-N-phenethylmethanesulfonamide (6l)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 54% yield.

^1H NMR (600 MHz, CDCl_3): δ 8.21 (d, $J = 4.2$ Hz, 1H), 7.64 (d, $J = 6.6$ Hz, 1H), 7.29-7.27 (m, 2H), 7.23-7.17 (m, 3H), 7.01-6.98 (m, 1H), 3.34-3.26 (m, 2H), 3.31 (s, 3H), 3.22 (d, $J = 14.4$ Hz, 1H), 3.10 (d, $J = 14.4$ Hz, 1H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.74 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.1, 156.5, 147.6, 138.3, 132.3, 129.0, 128.8, 126.8, 125.2, 118.3, 55.1, 51.4, 45.5, 34.9, 34.4, 25.8, 24.1.

HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_3\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 317.1538. Found: 317.1531.



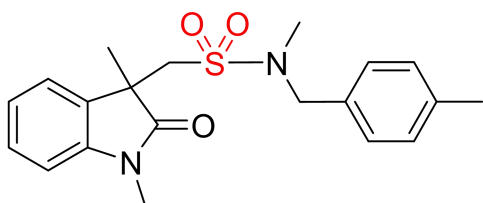
N-Benzyl-1-(1,3-dimethyl-2-oxoindolin-3-yl)-N-methylmethanesulfonamide (8a)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 84% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, $J = 7.2$ Hz, 1H), 7.36-7.24 (m, 6H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 4.10 (d, $J = 14.4$ Hz, 1H), 4.01 (d, $J = 14.4$ Hz, 1H), 3.63 (d, $J = 14.0$ Hz, 1H), 3.50 (d, $J = 14.0$ Hz, 1H), 3.27 (s, 3H), 2.59 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.4, 143.3, 135.8, 130.7, 128.9, 128.8, 128.4, 128.0, 124.3, 122.8, 108.7, 56.0, 53.5, 45.9, 33.8, 26.8, 25.1.

HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 359.1429. Found: 359.1433.



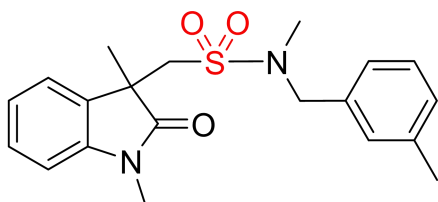
1-(1,3-Dimethyl-2-oxoindolin-3-yl)-N-methyl-N-(4-methylbenzyl)methanesulfonamide (8b)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 86% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.41 (d, $J = 7.6$ Hz, 1H), 7.33 (td, $J = 8.0, 0.8$ Hz, 1H), 7.15-7.10 (m, 5H), 6.90 (d, $J = 8.0$ Hz, 1H), 4.06 (d, $J = 14.8$ Hz, 1H), 3.98 (d, $J = 14.4$ Hz, 1H), 3.61 (d, $J = 14.4$ Hz, 1H), 3.48 (d, $J = 14.4$ Hz, 1H), 3.27 (s, 3H), 2.58 (s, 3H), 2.32 (s, 3H), 1.46 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.4, 143.3, 137.8, 132.7, 130.7, 129.4, 128.9, 128.4, 124.3, 122.8, 108.7, 56.0, 53.2, 45.9, 33.7, 26.8, 25.1, 21.2.

HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 395.1405. Found: 395.1423.



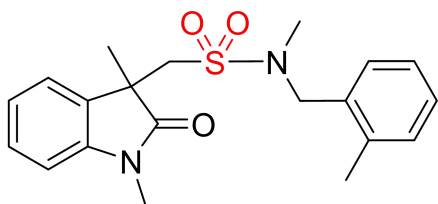
1-(1,3-Dimethyl-2-oxoindolin-3-yl)-N-methyl-N-(3-methylbenzyl)methanesulfonamide (8c)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 80% yield.

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42 (d, $J = 7.2$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.21-7.12 (m, 2H), 7.09-7.02 (m, 3H), 6.90 (d, $J = 8.0$ Hz, 1H), 4.06 (d, $J = 14.4$ Hz, 1H), 3.97 (d, $J = 14.8$ Hz, 1H), 3.62 (d, $J = 14.0$ Hz, 1H), 3.49 (d, $J = 14.0$ Hz, 1H), 3.27 (s, 3H), 2.59 (s, 3H), 2.31 (s, 3H), 1.46 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 178.4, 143.3, 138.5, 135.7, 130.7, 129.1, 128.9, 128.8, 128.6, 125.5, 124.3, 122.8, 108.7, 55.9, 53.4, 45.9, 33.8, 26.8, 25.1, 21.5.

HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 373.1586. Found: 373.1581.



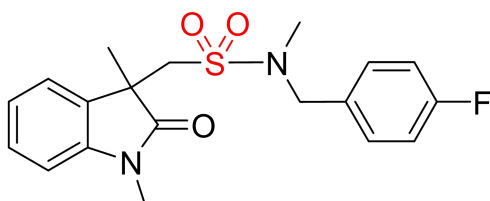
1-(1,3-Dimethyl-2-oxoindolin-3-yl)-N-methyl-N-(2-methylbenzyl)methanesulfonamide (8d)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 87% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, $J = 7.6$ Hz, 1H), 7.34 (td, $J = 7.6, 1.2$ Hz, 1H), 7.21-7.12 (m, 5H), 6.91 (d, $J = 8.0$ Hz, 1H), 4.13 (d, $J = 14.4$ Hz, 1H), 4.01 (d, $J = 14.4$ Hz, 1H), 3.64 (d, $J = 14.0$ Hz, 1H), 3.52 (d, $J = 14.0$ Hz, 1H), 3.27 (s, 3H), 2.60 (s, 3H), 2.27 (s, 3H), 1.49 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.4, 143.3, 137.0, 133.3, 130.7, 129.0, 128.9, 128.0, 126.2, 124.3, 122.7, 108.7, 54.9, 51.4, 45.8, 33.8, 26.7, 25.0, 19.2.

HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 373.1586. Found: 373.1579.



1-(1,3-Dimethyl-2-oxoindolin-3-yl)-N-(4-fluorobenzyl)-N-methylmethanesulfonamide (8e)

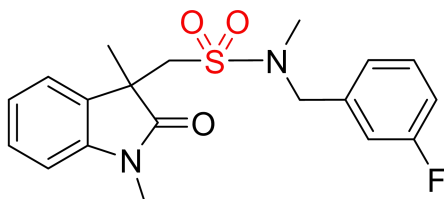
The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 76% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.41 (t, $J = 7.6$ Hz, 1H), 7.34 (td, $J = 7.6, 1.2$ Hz, 1H), 7.23-7.20 (m, 2H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.99 (t, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 7.6$ Hz, 1H), 4.05 (d, $J = 14.8$ Hz, 1H), 3.96 (d, $J = 14.8$ Hz, 1H), 3.63 (d, $J = 14.0$ Hz, 1H), 3.50 (d, $J = 14.0$ Hz, 1H), 3.27 (s, 3H), 2.57 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.3, 162.6 (d, $J = 247.2$ Hz), 143.3, 131.6 (d, $J = 3.1$ Hz), 130.6, 130.1 (d, $J = 8.2$ Hz), 128.9, 124.2, 122.8, 115.6 (d, $J = 21.6$ Hz), 108.7, 56.0, 52.7, 45.9, 33.7, 26.8, 25.2.

^{19}F NMR (377 MHz, CDCl_3): δ -114.4.

HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{22}\text{FN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 377.1335. Found: 377.1329.



1-(1,3-Dimethyl-2-oxoindolin-3-yl)-N-(3-fluorobenzyl)-N-methylmethanesulfonamide (8f)

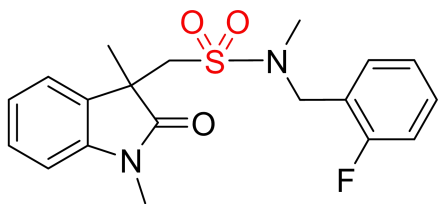
The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 75% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, $J = 7.2$ Hz, 1H), 7.34 (td, $J = 7.6, 0.8$ Hz, 1H), 7.30-7.24 (m, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.98-6.90 (m, 3H), 4.06 (d, $J = 15.2$ Hz, 1H), 3.98 (d, $J = 15.2$ Hz, 1H), 3.65 (d, $J = 14.0$ Hz, 1H), 3.51 (d, $J = 14.0$ Hz, 1H), 3.27 (s, 3H), 2.61 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.3, 163.1 (d, $J = 247.8$ Hz), 143.3, 138.5 (d, $J = 7.1$ Hz), 130.6, 130.3 (d, $J = 8.3$ Hz), 129.0, 124.2, 123.8 (d, $J = 2.9$ Hz), 122.8, 115.2 (d, $J = 18.5$ Hz), 114.9 (d, $J = 17.9$ Hz), 108.7, 56.1, 52.9, 45.9, 33.9, 26.8, 25.2.

^{19}F NMR (377 MHz, CDCl_3): δ -112.7.

HRMS (ESI): Calcd for C₁₉H₂₂FN₂O₃S [M+H]⁺ 377.1335. Found: 377.1343.



1-(1,3-Dimethyl-2-oxoindolin-3-yl)-N-(2-fluorobenzyl)-N-methylmethanesulfonamide (8g)

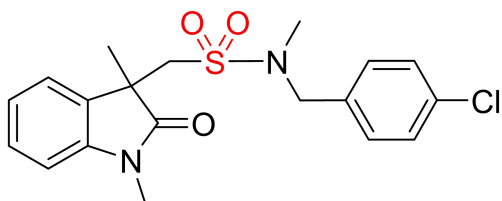
The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 70% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.37-7.31 (m, 2H), 7.28-7.22 (m, 1H), 7.14-7.08 (m, 2H), 7.04-6.99 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 14.8 Hz, 1H), 4.08 (d, *J* = 15.2 Hz, 1H), 3.65 (d, *J* = 14.4 Hz, 1H), 3.51 (d, *J* = 14.0 Hz, 1H), 3.27 (s, 3H), 2.62 (s, 3H), 1.45 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 178.3, 161.1 (d, *J* = 247.2 Hz), 143.3, 130.7 (d, *J* = 3.9 Hz), 130.6, 129.8 (d, *J* = 8.2 Hz), 128.9, 124.7 (d, *J* = 3.6 Hz), 124.2, 122.9 (d, *J* = 14.3 Hz), 122.8, 115.4 (d, *J* = 21.6 Hz), 108.7, 56.3, 46.4, 45.8, 34.0, 26.7, 25.1.

¹⁹F NMR (377 MHz, CDCl₃): δ -119.1.

HRMS (ESI): Calcd for C₁₉H₂₂FN₂O₃S [M+H]⁺ 377.1335. Found: 377.1330.



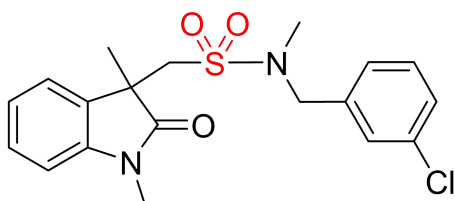
N-(4-Chlorobenzyl)-1-(1,3-dimethyl-2-oxoindolin-3-yl)-N-methylmethanesulfonamide (8h)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 96% yield.

¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.19-7.12 (m, 3H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.04 (d, *J* = 14.8 Hz, 1H), 3.96 (d, *J* = 14.8 Hz, 1H), 3.63 (d, *J* = 14.0 Hz, 1H), 3.50 (d, *J* = 14.0 Hz, 1H), 3.27 (s, 3H), 2.58 (s, 3H), 1.46 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 178.3, 143.3, 134.4, 133.9, 130.6, 129.7, 128.9, 124.2, 122.8, 108.7, 56.1, 52.8, 45.9, 33.8, 26.8, 25.2.

HRMS (ESI): calcd for C₁₉H₂₂ClN₂O₃S [M+H]⁺ 393.1040. found 393.1048.



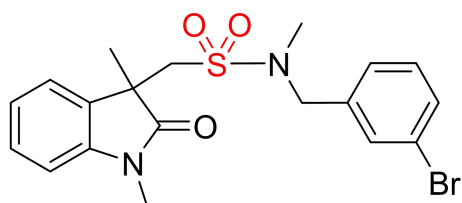
N-(3-Chlorobenzyl)-1-(1,3-dimethyl-2-oxoindolin-3-yl)-N-methylmethanesulfonamide (8i)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 86% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.40 (d, $J = 7.6$ Hz, 1H), 7.34 (td, $J = 7.6, 0.8$ Hz, 1H), 7.24-7.21 (m, 3H), 7.16-7.13 (m, 2H), 6.91 (d, $J = 7.6$ Hz, 1H), 4.03 (d, $J = 14.8$ Hz, 1H), 3.95 (d, $J = 15.2$ Hz, 1H), 3.65 (d, $J = 14.4$ Hz, 1H), 3.52 (d, $J = 14.0$ Hz, 1H), 3.27 (s, 3H), 2.59 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.3, 143.3, 138.0, 134.6, 130.6, 130.1, 128.9, 128.3, 128.2, 126.4, 124.1, 122.8, 108.7, 56.1, 52.9, 45.8, 33.9, 26.8, 25.2.

HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{22}\text{ClN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 393.1040. found 393.1034.



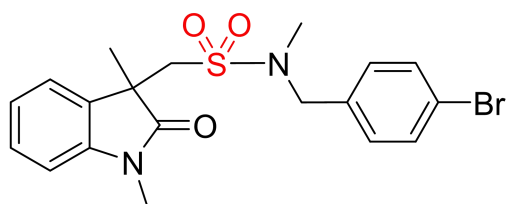
***N*-(3-Bromobenzyl)-1-(1,3-dimethyl-2-oxoindolin-3-yl)-*N*-methylmethanesulfonamide (8j)**

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 54% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.41-7.38 (m, 3H), 7.34 (td, $J = 8.0, 1.2$ Hz, 1H), 7.20-7.12 (m, 3H), 6.91 (d, $J = 7.6$ Hz, 1H), 4.03 (d, $J = 14.8$ Hz, 1H), 3.95 (d, $J = 14.8$ Hz, 1H), 3.65 (d, $J = 14.4$ Hz, 1H), 3.51 (d, $J = 14.4$ Hz, 1H), 3.27 (s, 3H), 2.60 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.3, 143.3, 138.3, 131.3, 131.2, 130.6, 130.4, 129.0, 126.9, 124.2, 122.8, 108.8, 56.2, 52.9, 45.9, 33.9, 26.8, 25.2.

HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{22}\text{BrN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 437.0535. Found: 437.0528.



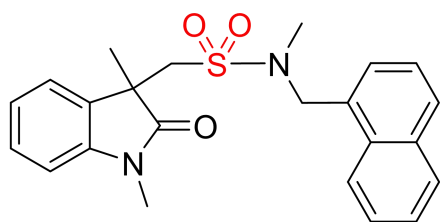
***N*-(4-Bromobenzyl)-1-(1,3-dimethyl-2-oxoindolin-3-yl)-*N*-methylmethanesulfonamide (8k)**

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 43% yield.

^1H NMR (400 MHz, CDCl_3): δ 7.43-7.40 (m, 3H), 7.34 (td, $J = 7.6, 0.8$ Hz, 1H), 7.16-7.11 (m, 3H), 6.91 (d, $J = 8.0$ Hz, 1H), 4.02 (d, $J = 14.8$ Hz, 1H), 3.94 (d, $J = 14.8$ Hz, 1H), 3.64 (d, $J = 14.4$ Hz, 1H), 3.51 (d, $J = 14.4$ Hz, 1H), 3.27 (s, 3H), 2.58 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.3, 143.3, 134.9, 131.9, 130.6, 130.0, 128.9, 124.2, 122.8, 122.0, 108.7, 56.1, 52.8, 45.8, 33.8, 26.8, 25.2.

HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{22}\text{BrN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 437.0535. Found: 437.0526.



1-(1,3-Dimethyl-2-oxoindolin-3-yl)-N-methyl-N-(naphthalen-1-ylmethyl)methanesulfonamide (**8i**)

The product was isolated by flash chromatography (petroleum ether/EtOAc = 2/1, v/v) as colorless oil. 54% yield.

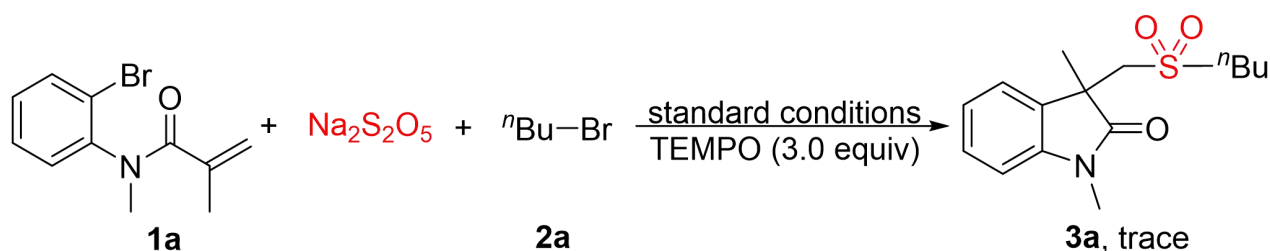
^1H NMR (400 MHz, CDCl_3): δ 8.17-8.15 (m, 1H), 7.86-7.80 (m, 2H), 7.52-7.47 (m, 3H), 7.43-7.35 (m, 3H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.93 (d, $J = 7.6$ Hz, 1H), 4.62 (d, $J = 14.0$ Hz, 1H), 4.51 (d, $J = 14.0$ Hz, 1H), 3.68 (d, $J = 14.0$ Hz, 1H), 3.57 (d, $J = 14.0$ Hz, 1H), 3.29 (s, 3H), 2.60 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 178.5, 143.4, 134.0, 131.7, 130.8, 130.7, 129.1, 129.0, 128.7, 127.4, 126.7, 126.1, 125.2, 124.3, 123.9, 122.8, 108.8, 54.7, 51.9, 45.8, 33.9, 26.8, 25.0.

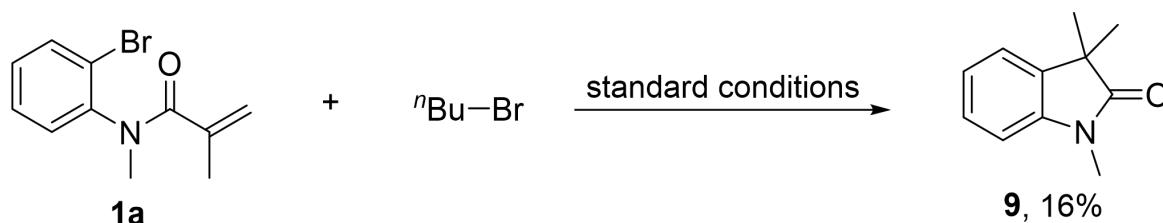
HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 409.1586. Found: 409.1580.

V. Mechanistic study

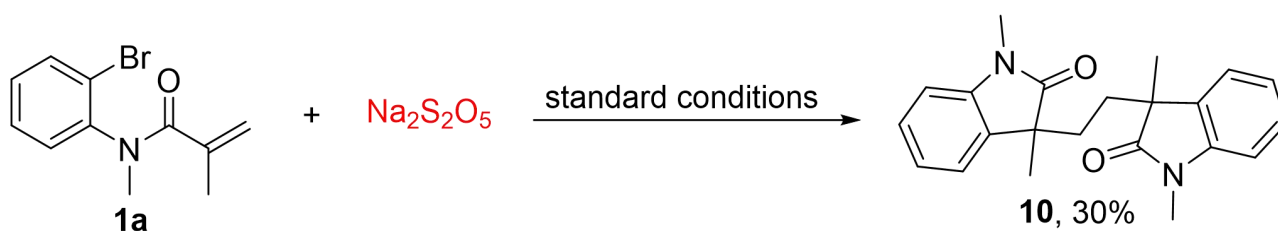
(1) The control experiments



In a nitrogen-filled glove box, **1a** (25.4 mg, 0.1 mmol, 1.0 equiv), $\text{Na}_2\text{S}_2\text{O}_5$ (38 mg, 0.2 mmol, 2.0 equiv), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (2.6 mg, 0.01 mmol, 10 mol%), PPh_3 (6.3 mg, 0.024 mmol, 24 mol%), Zn dust (19.6 mg, 0.3 mmol, 3 equiv), K_2HPO_4 (61 mg, 0.35 mmol, 3.5 equiv), TEMPO (46.9 mg, 0.30 mmol, 3.0 equiv), and DMSO (0.8 mL) were added to a 10-mL Schlenk tube. After stirring at room temperature for 1 min, 1-bromobutane **2a** (32 μL , 0.3 mmol, 3.0 equiv) and GC standard $n\text{-C}_{12}\text{H}_{26}$ (10 μL) was added. The reaction mixture was stirred at 120 $^\circ\text{C}$ for 48 h and then diluted with 3 mL of EtOAc. Aliquots were taken from the organic phase, and passed through a short plug of silica gel with EtOAc washing (about 1.5 mL). The filtrate was subjected to GC analysis to determine the yield of the product **3a**. GC analysis showed that trace amount of **3a** was obtained.



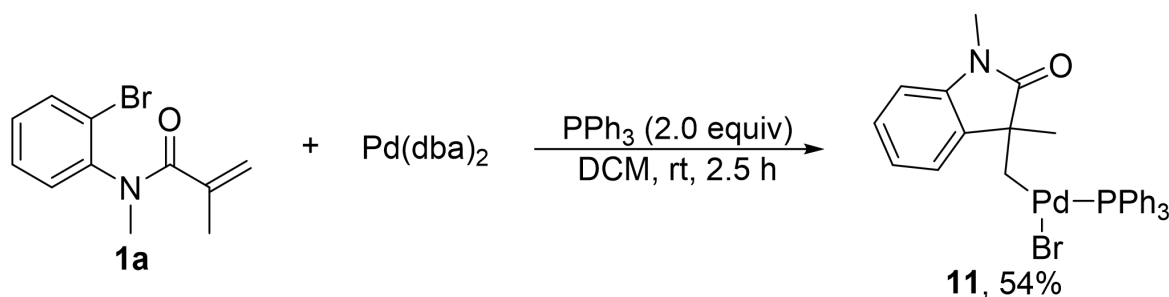
In a nitrogen-filled glove box, **1a** (50.8 mg, 0.2 mmol, 1.0 equiv), Pd(MeCN)₂Cl₂ (5.2 mg, 0.02 mmol, 10 mol%), PPh₃ (12.6 mg, 0.048 mmol, 24 mol%), Zn dust (39.6 mg, 0.6 mmol, 3 equiv), K₂HPO₄ (122 mg, 0.7 mmol, 3.5 equiv), 1-bromobutane **2a** (64 μL, 0.6 mmol, 3.0 equiv), and DMSO (1.0 mL) were added to a 10-mL Schlenk tube. The reaction mixture was stirred at 120 °C for 48 h. The reaction mixture was cooled to room temperature and then extracted with EtOAc. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph to afford **9** in 16% yield. ¹H NMR (600 MHz, CDCl₃): δ 7.28-7.25 (m, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.06 (td, *J* = 7.8, 1.2 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 1.37 (s, 6H). The ¹H NMR data matched that reported in the literature.^[5]



In a nitrogen-filled glove box, **1a** (50.8 mg, 0.2 mmol, 1.0 equiv), Na₂S₂O₅ (76 mg, 0.4 mmol, 2.0 equiv), Pd(MeCN)₂Cl₂ (5.2 mg, 0.02 mmol, 10 mol%), PPh₃ (12.6 mg, 0.048 mmol, 24 mol%), Zn dust (39.6 mg, 0.6 mmol, 3 equiv), K₂HPO₄ (122 mg, 0.7 mmol, 3.5 equiv), and DMSO (1.0 mL) were added to a 10-mL Schlenk tube. The reaction mixture was stirred at 120 °C for 48 h. The reaction mixture was cooled to room temperature and then extracted with EtOAc. The solvent was removed under reduced pressure and the crude product was purified by flash chromatograph to afford dimer **10** in 30% yield (d.r., 1:1). ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.24 (m, 2H), 7.13 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.07 (td, *J* = 7.6, 1.2 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 3.21 (s, 6H), 1.47-1.40 (m, 4H), 1.21 (s, 6H). Diastereoisomer: ¹H NMR (400 MHz, CDCl₃): δ 7.25 (td, *J* = 7.6, 1.6 Hz, 2H), 7.03 (td, *J* = 7.2, 0.8 Hz, 2H), 6.99 (dd, *J* = 7.2, 1.2 Hz, 2H), 6.81 (dt, *J* = 8.0, 0.8 Hz, 2H), 3.18 (s, 6H), 1.77-1.63 (m, 2H), 1.40-1.31 (m, 2H), 1.25 (s, 6H). The ¹H NMR data matched those reported in the literature.^[6]

(2) The synthesis and catalytic reaction of metalated Pd(II) complex

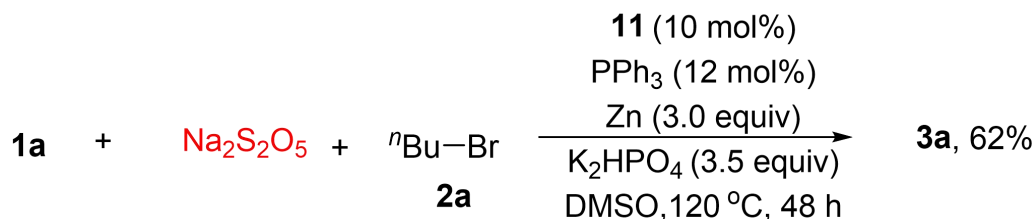
1) Synthesis of metalated Pd(II) complex 11



A Schlenk tube with a magnetic stir bar was charged with Pd(dba)₂ (100 mg, 0.176 mmol), PPh₃ (92 mg, 0.352

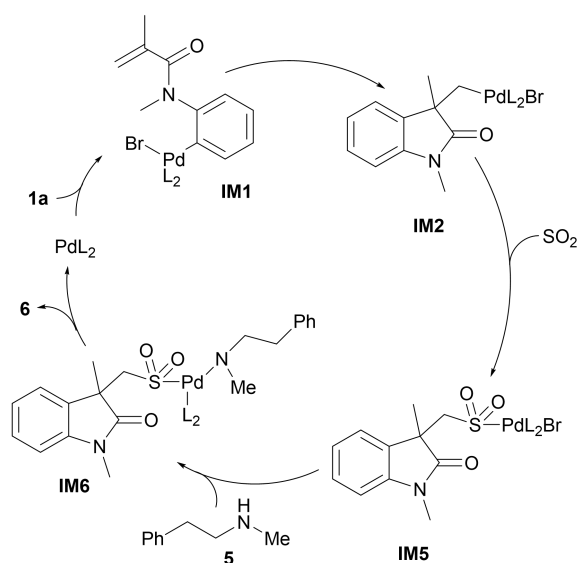
mmol), **1a** (50.8 mg, 0.20 mmol, 1.1 equiv), and CH₂Cl₂ (1.0 mL) under an N₂ atmosphere. The resulting mixture was stirred at room temperature for 2.5 h, and then Et₂O (10 mL) was added. The resulting suspension was filtered, and the solid was washed with Et₂O (2 × 1 mL) and N₂-dried to give compound **11** as a gray solid in 54% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.77-7.74 (m, 6H), 7.46-7.38 (m, 9H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.84-6.80 (m, 2H), 3.29 (s, 3H), 1.84 (s, 3H), 1.62 (m, 1H), 1.01 (t, *J* = 7.8 Hz, 1H). HRMS (ESI): calcd for C₂₉H₂₇NOPPd [M-Br]⁺ 542.0865, found 542.0865.

2) Complex **11**-catalyzed domino cyclization/alkylsulfonylation



In a nitrogen-filled glove box, **1a** (25.4 mg, 0.1 mmol, 1.0 equiv), Na₂S₂O₅ (38 mg, 0.2 mmol, 2.0 equiv), complex **11** (6.2 mg, 0.01 mmol, 10 mol%), PPh₃ (3.2 mg, 0.012 mmol, 12 mol%), Zn dust (19.6 mg, 0.3 mmol, 3 equiv), K₂HPO₄ (61 mg, 0.35 mmol, 3.5 equiv), and DMSO (0.8 mL) were added to a 10-mL Schlenk tube. After stirring at room temperature for 1 min, 1-bromobutane **2a** (32 μL, 0.3 mmol, 3.0 equiv) and GC standard *n*-C₁₂H₂₆ (10 μL) was added. The reaction mixture was stirred at 120 °C for 48 h and then diluted with 3 mL of EtOAc. Aliquots were taken from the organic phase, and passed through a short plug of silica gel with EtOAc washing (about 1.5 mL). The filtrate was subjected to GC analysis to determine the yield of the product **3a**. GC analysis showed that 62% yield of **3a** was obtained.

(3) Plausible mechanistic pathway for the palladium-catalyzed domino cyclization/aminosulfonylation

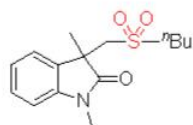


Scheme S1. The plausible mechanism for the formation of product **6**.

VI. Reference

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- [2] D. Xia, T. Miao, P. Li, L. Wang, *Chem. Asian J.* **2015**, *10*, 1919-1925.
- [3] Y.-Y. Jiang, S. Liang, C.-C. Zeng, L.-M. Hua, B.-G. Sun, *Green Chem.* **2016**, *18*, 6311-6319.
- [4] H. Lv, X. He, L. Shen, X. Zhang, Z. Lian, *Adv. Synth. Catal.* **2022**, *364*, 2729-2734.
- [5] C. Liu, D. Liu, W. Zhang, L. Zhou, A. Lei, *Org. Lett.* **2013**, *15*, 6166-6169.
- [6] K. Wang, Z. Ding, Z. Zhou, W. Kong, *J. Am. Chem. Soc.* **2018**, *140*, 12364-12368.

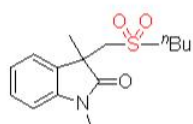
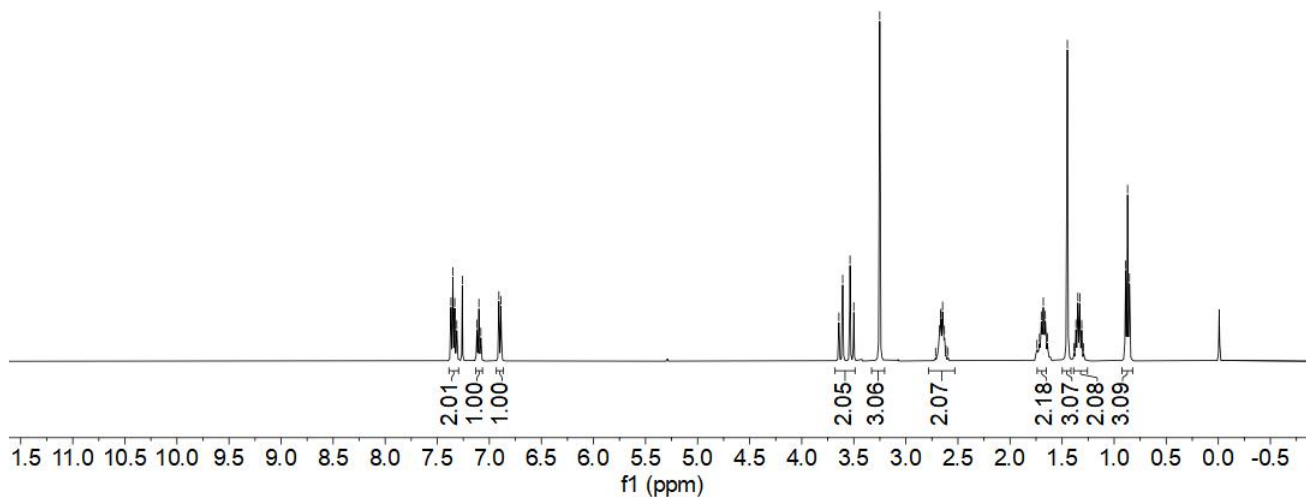
VII. Copies of NMR spectra



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7.100
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6.908
6.889

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3.536
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2.667
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2.647
2.630
2.615
2.595

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0.871



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122.694

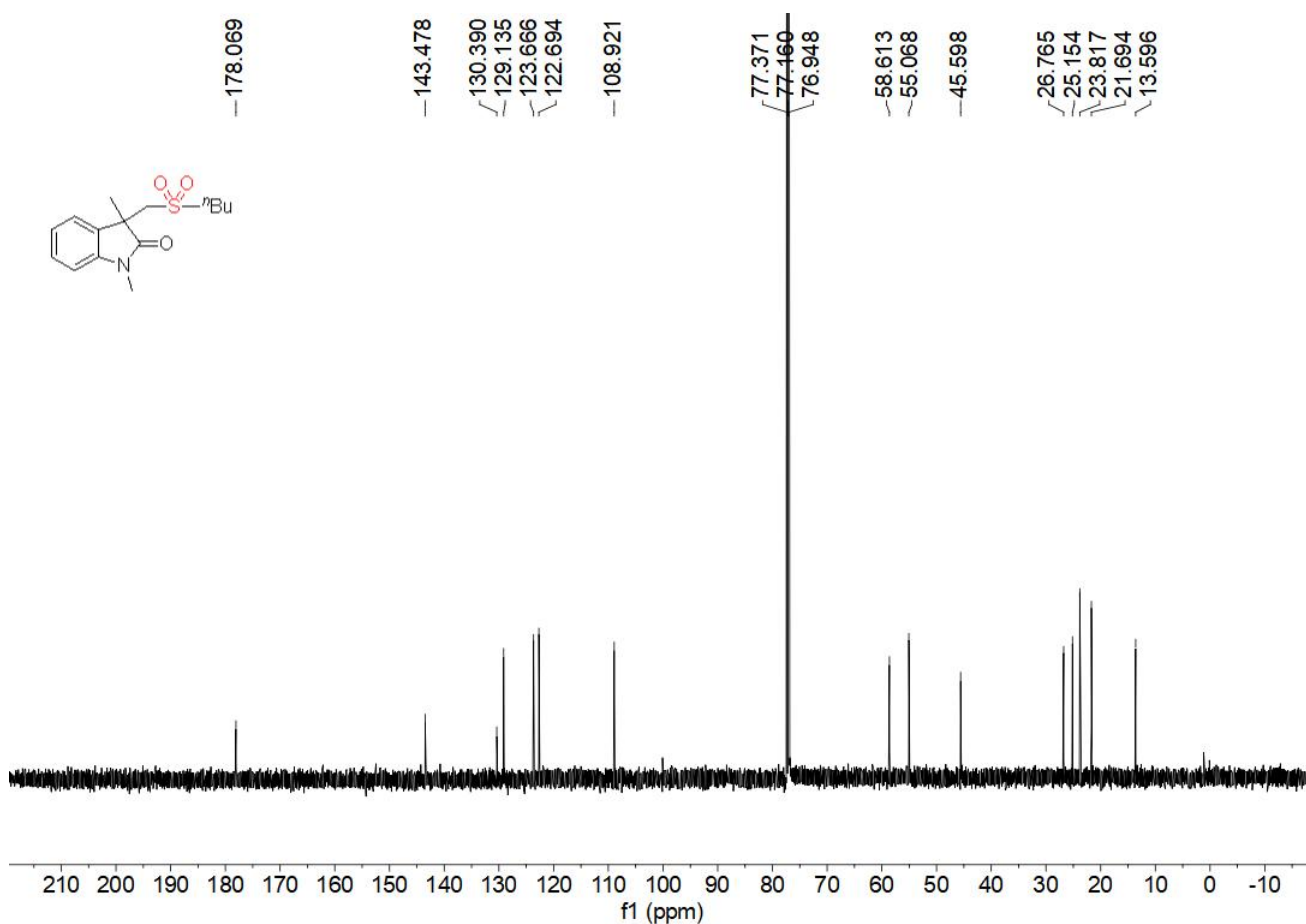
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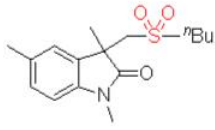
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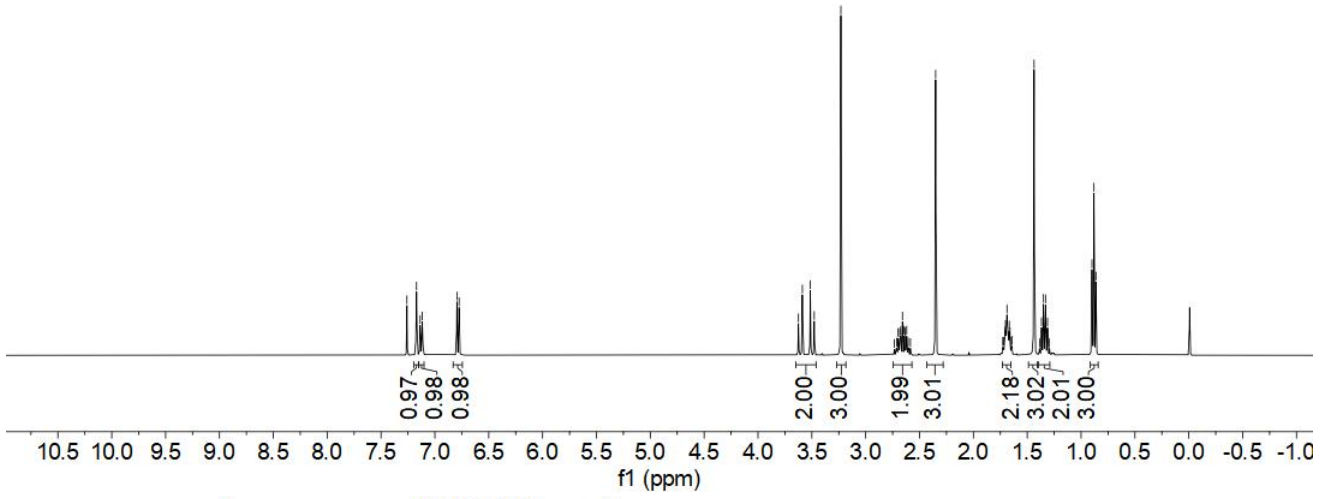
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25.154
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21.694
13.596





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7.117
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6.775
3.624
3.588
3.514
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26.763

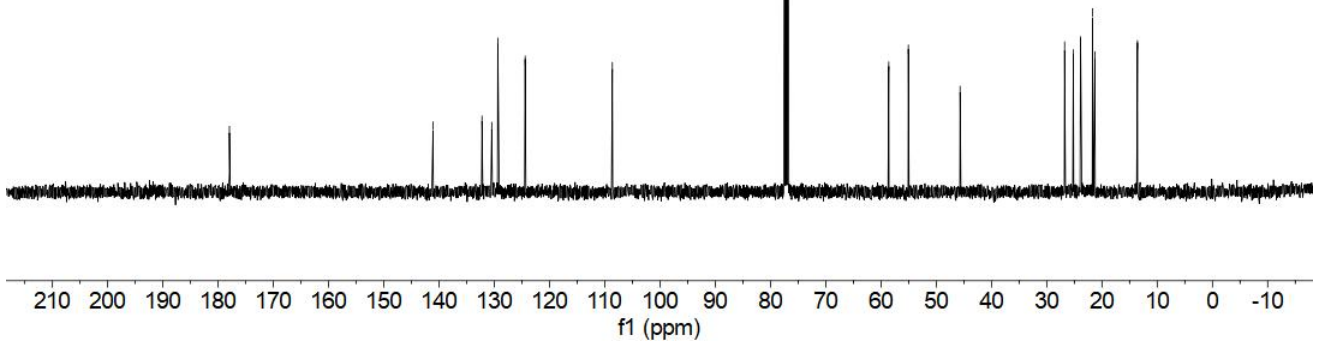
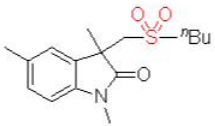
25.183

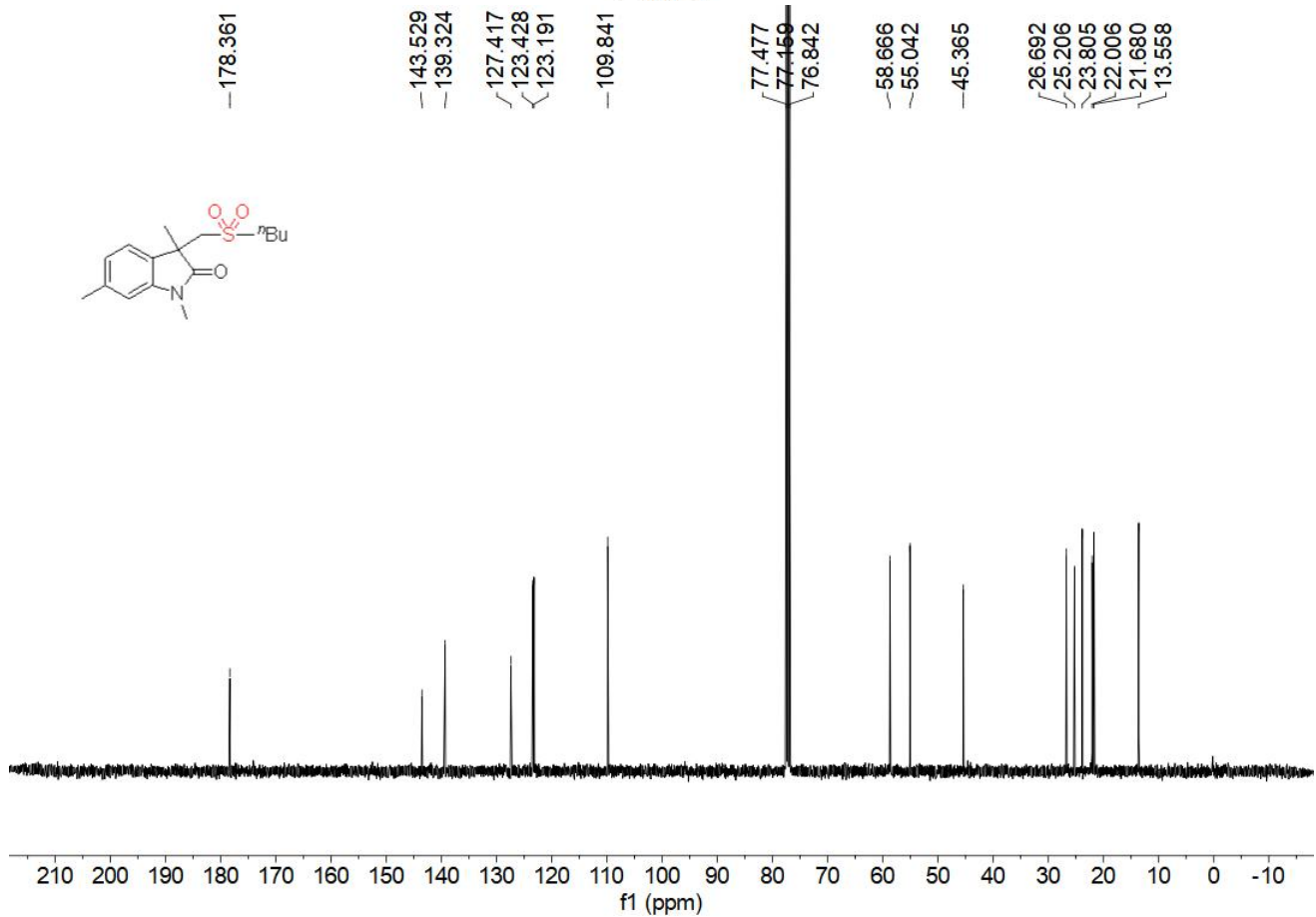
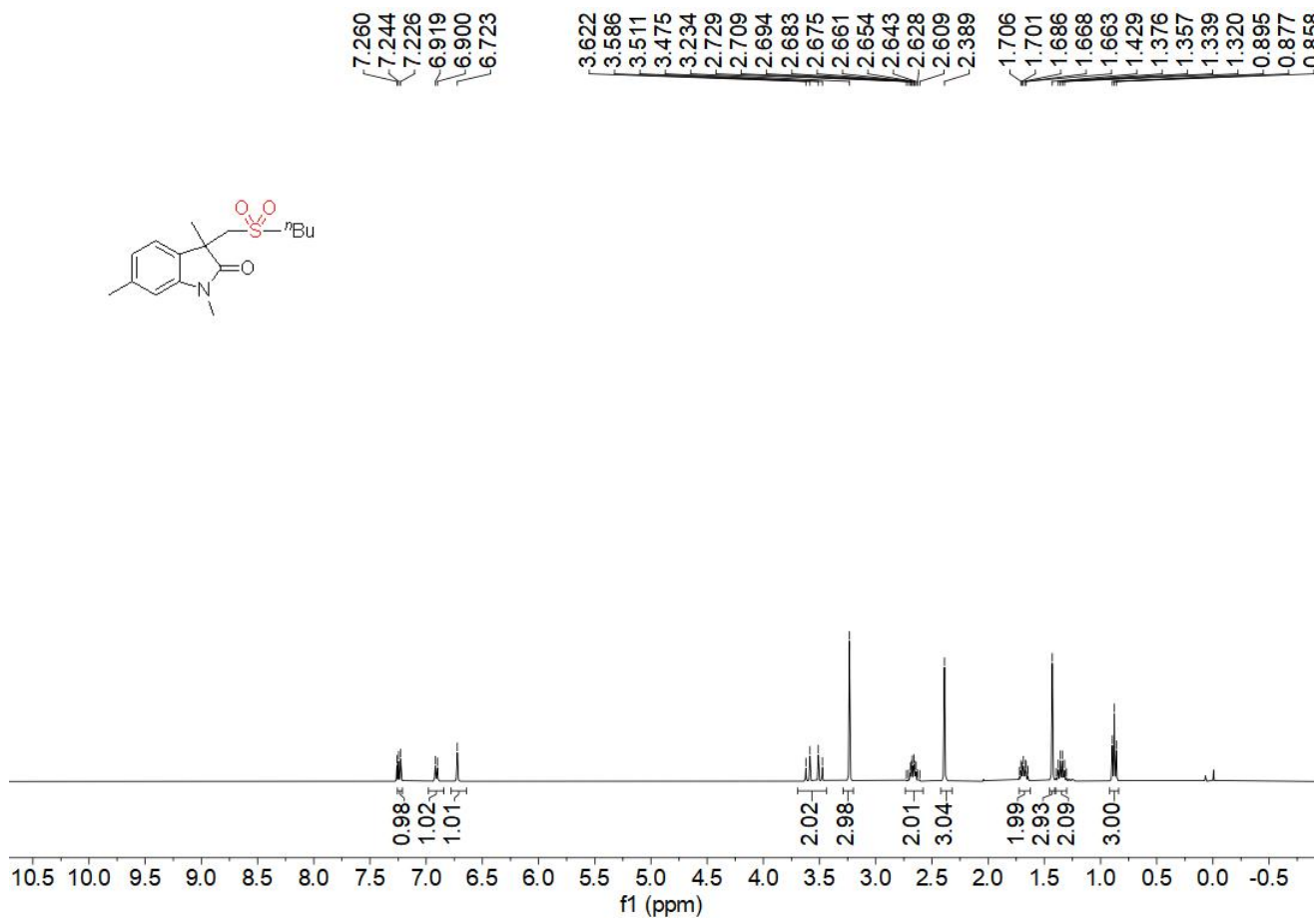
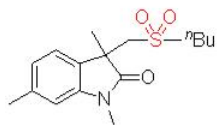
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21.701

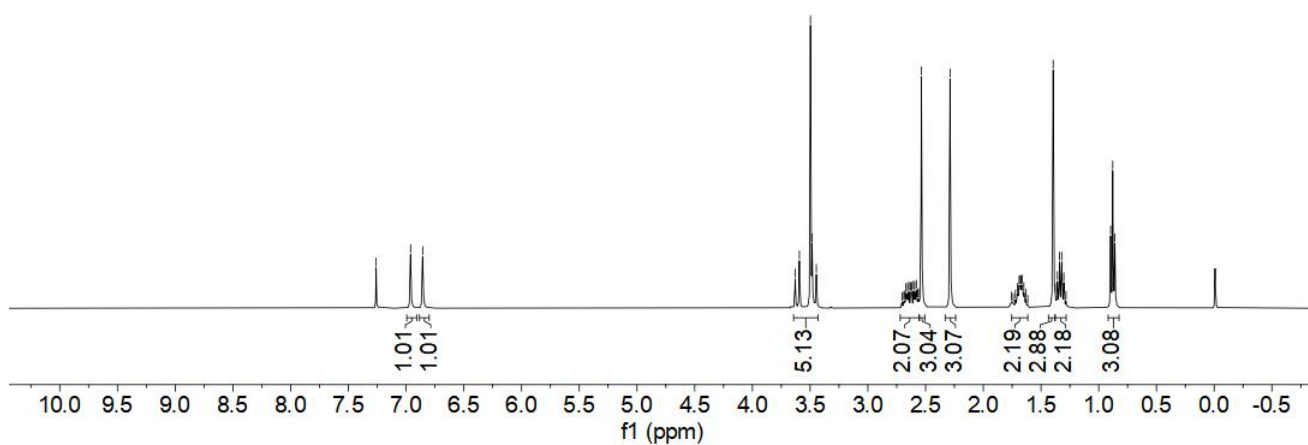
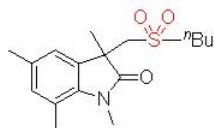
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13.576

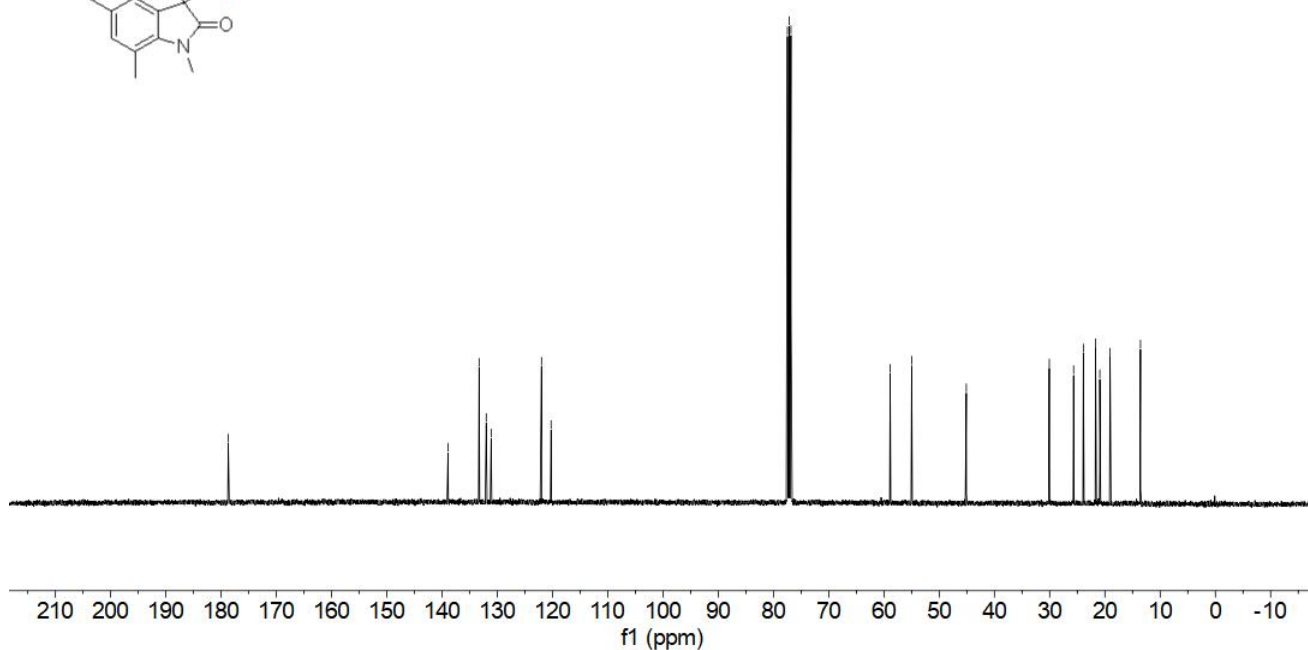
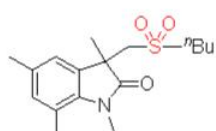


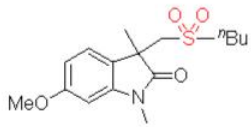


7.260
6.961
6.857
3.630
3.593
3.497
3.483
3.446
2.705
2.689
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2.595
2.580
2.569
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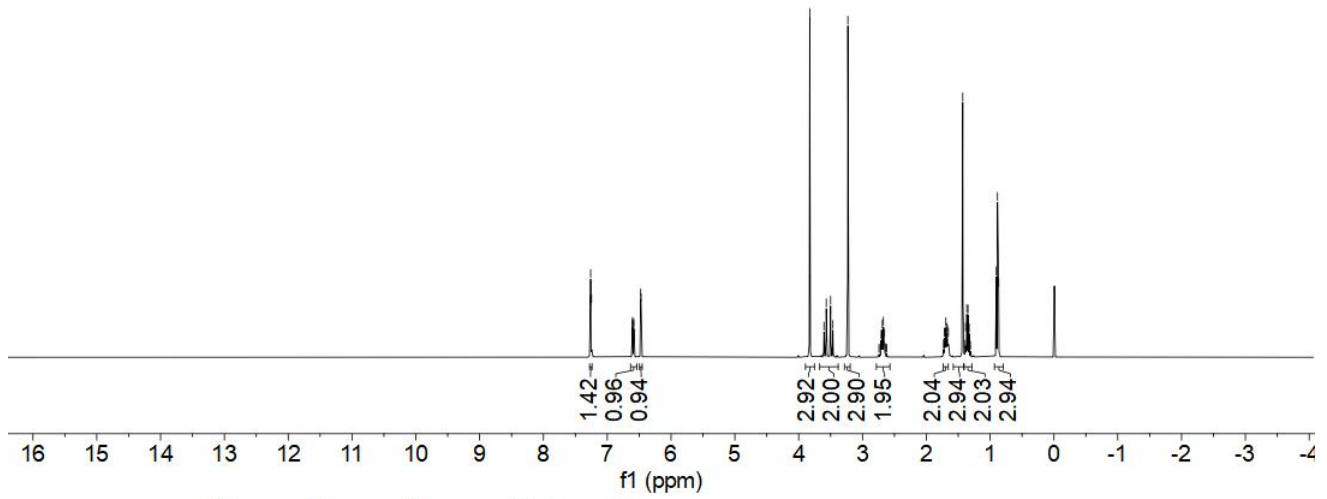


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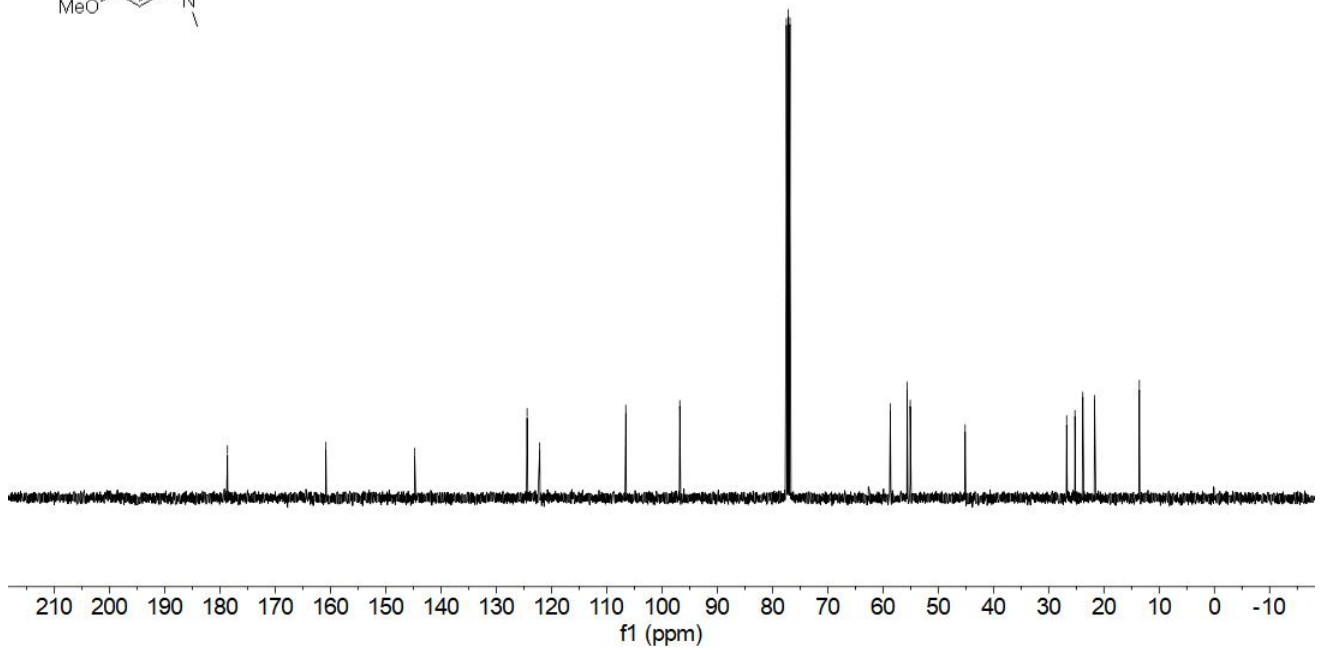
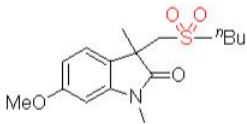


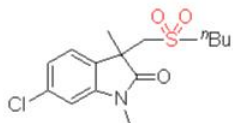


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6.583
6.476
6.470
3.827
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3.568
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3.464
3.229
2.742
2.722
2.708
2.689
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2.620
1.730
1.714
1.710
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0.866



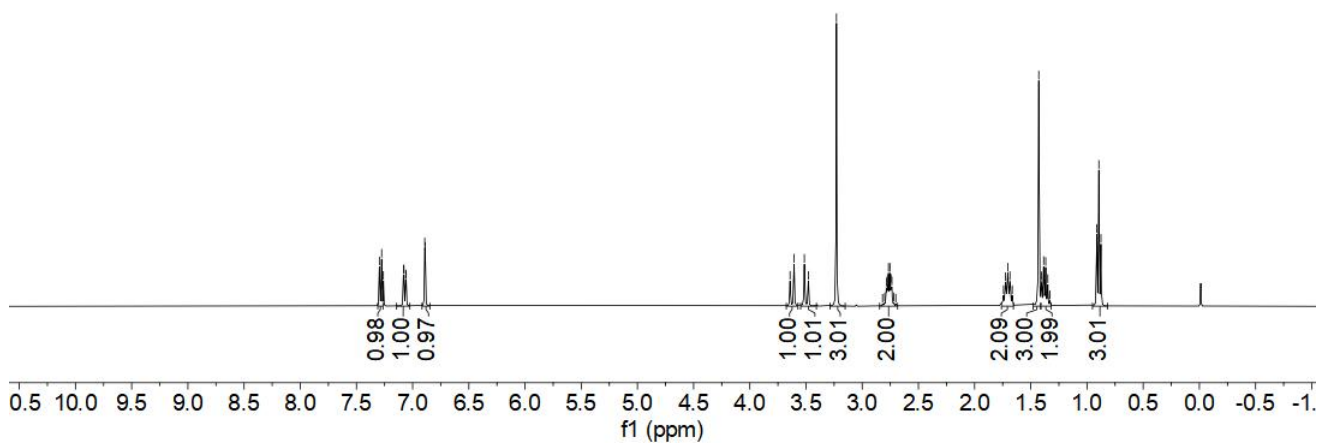
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23.831
21.701
13.590





7.296
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7.081
7.077
7.062
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6.888

3.642
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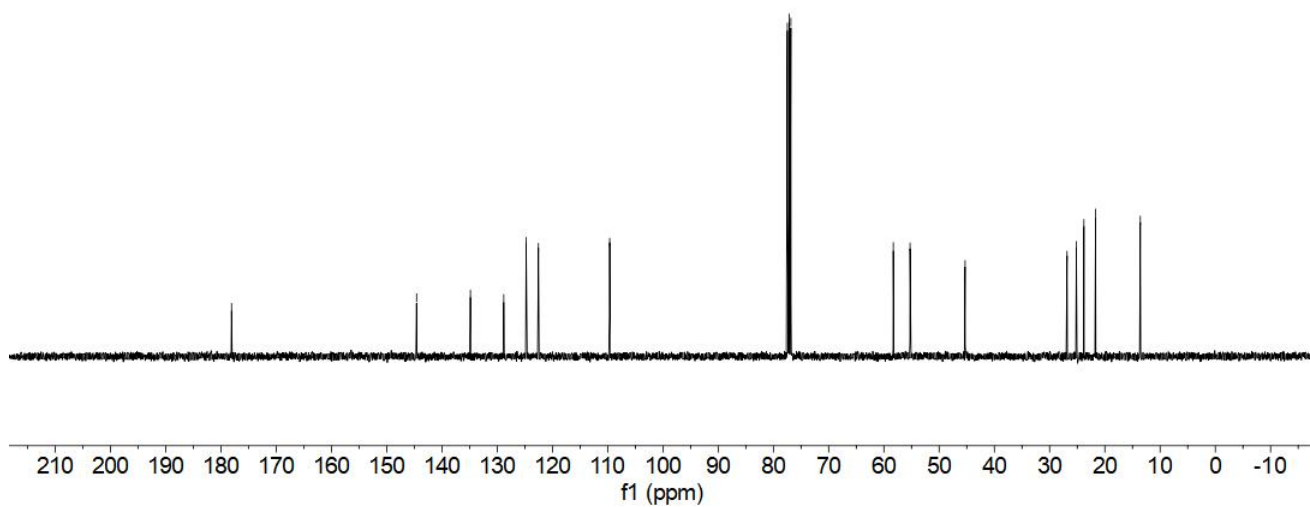
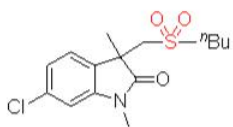
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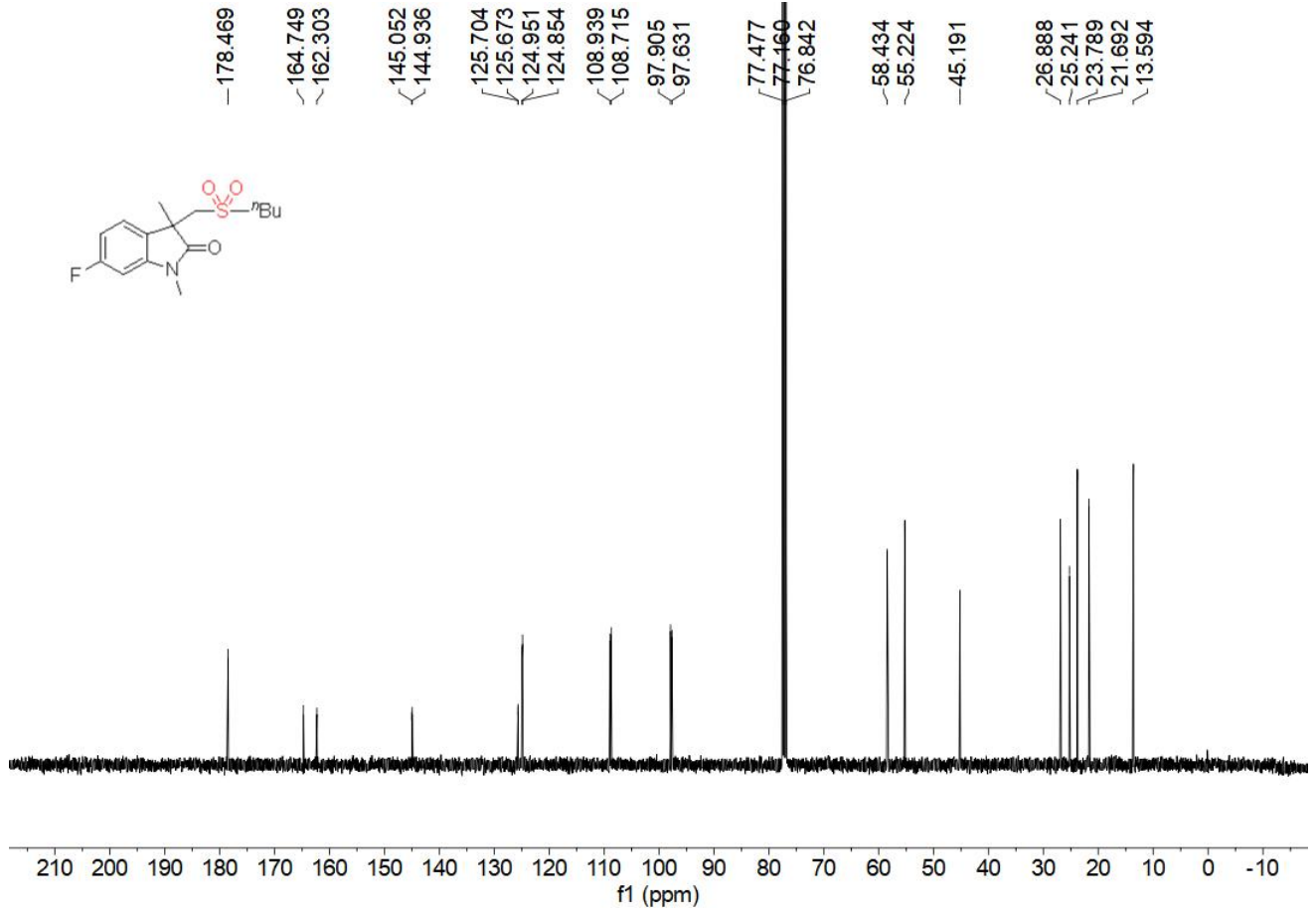
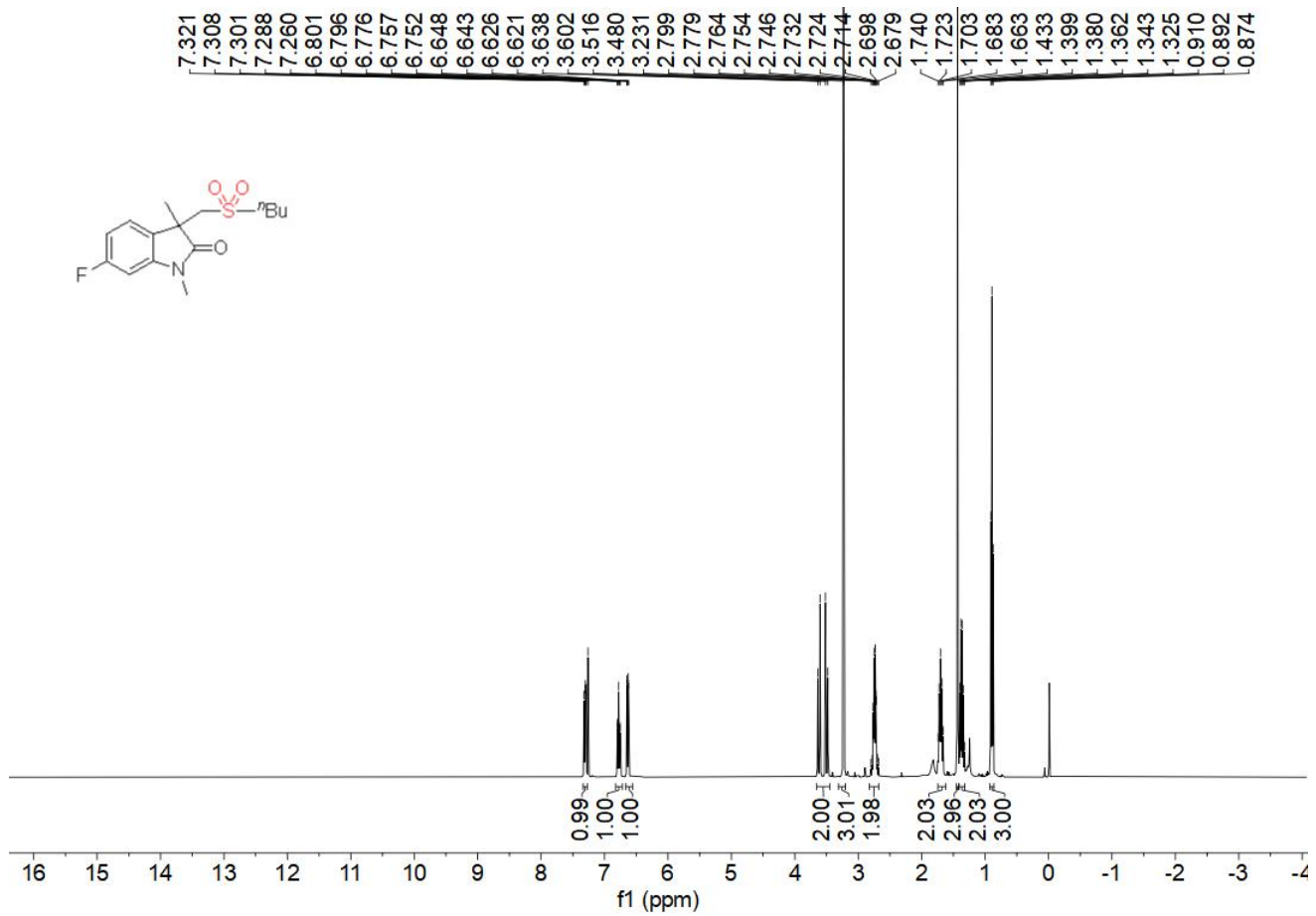
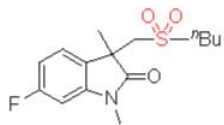
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23.790

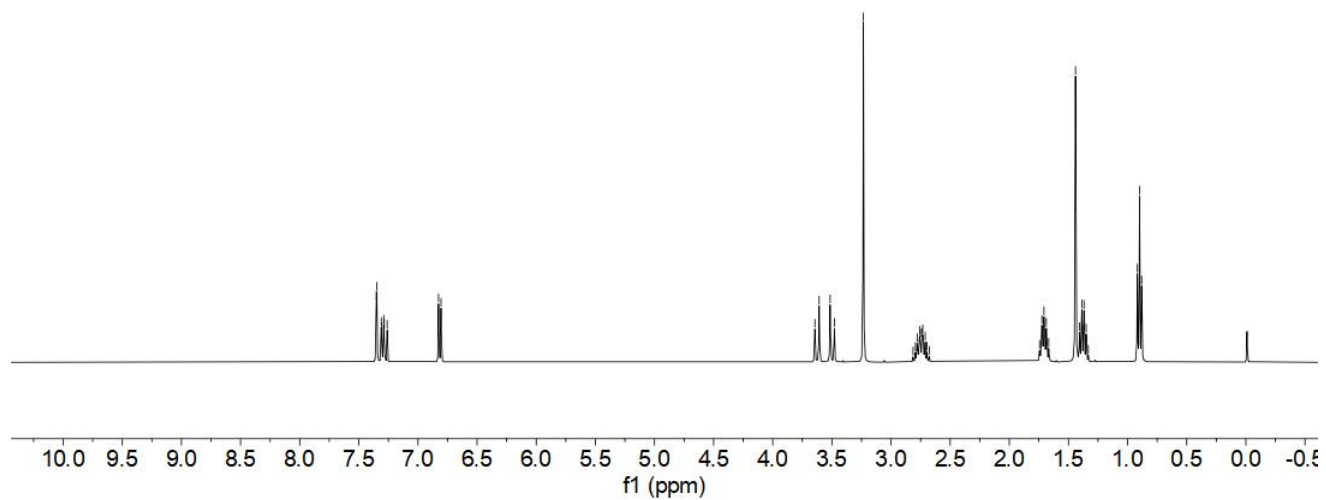
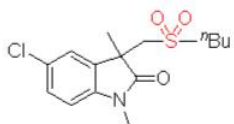
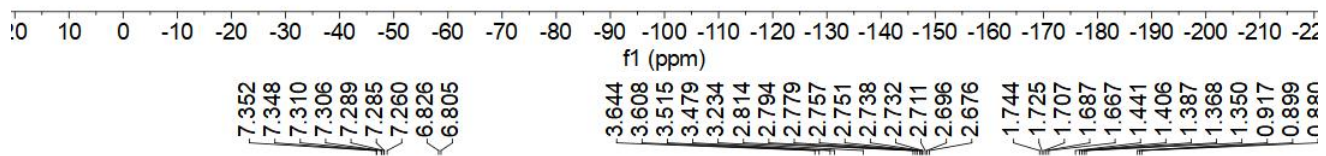
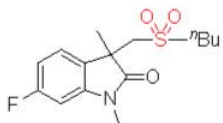
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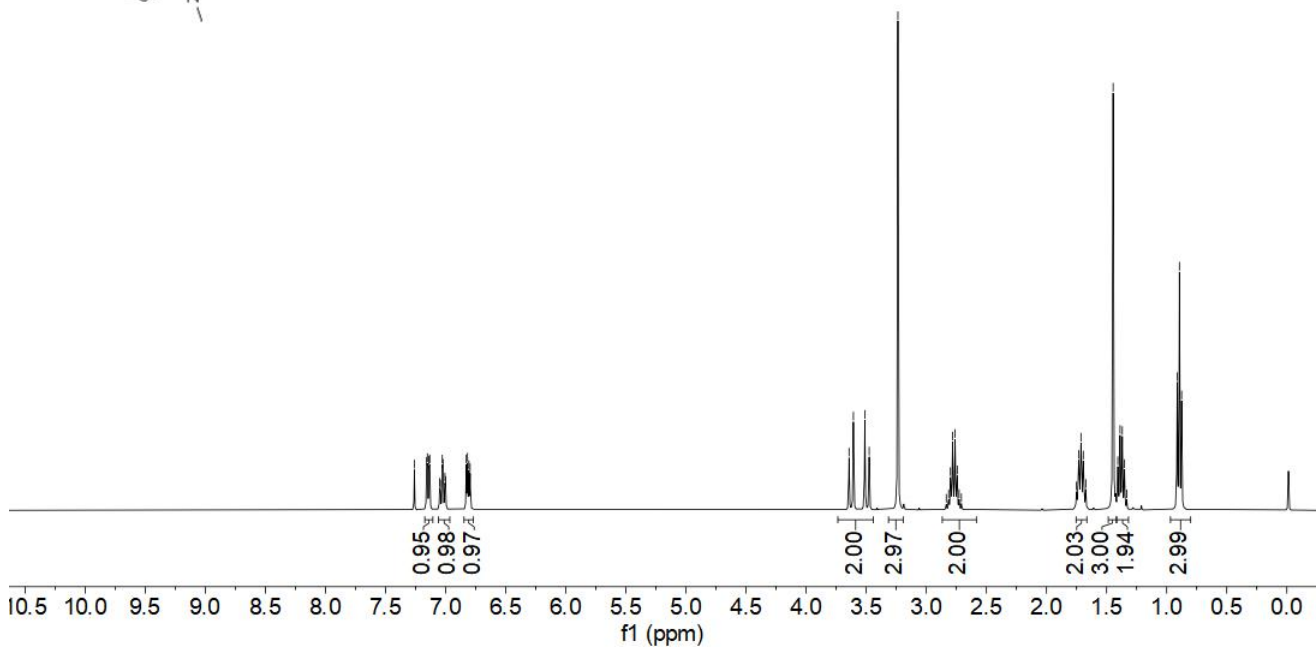
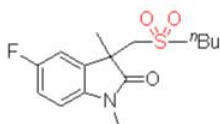
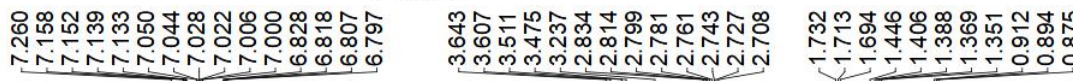
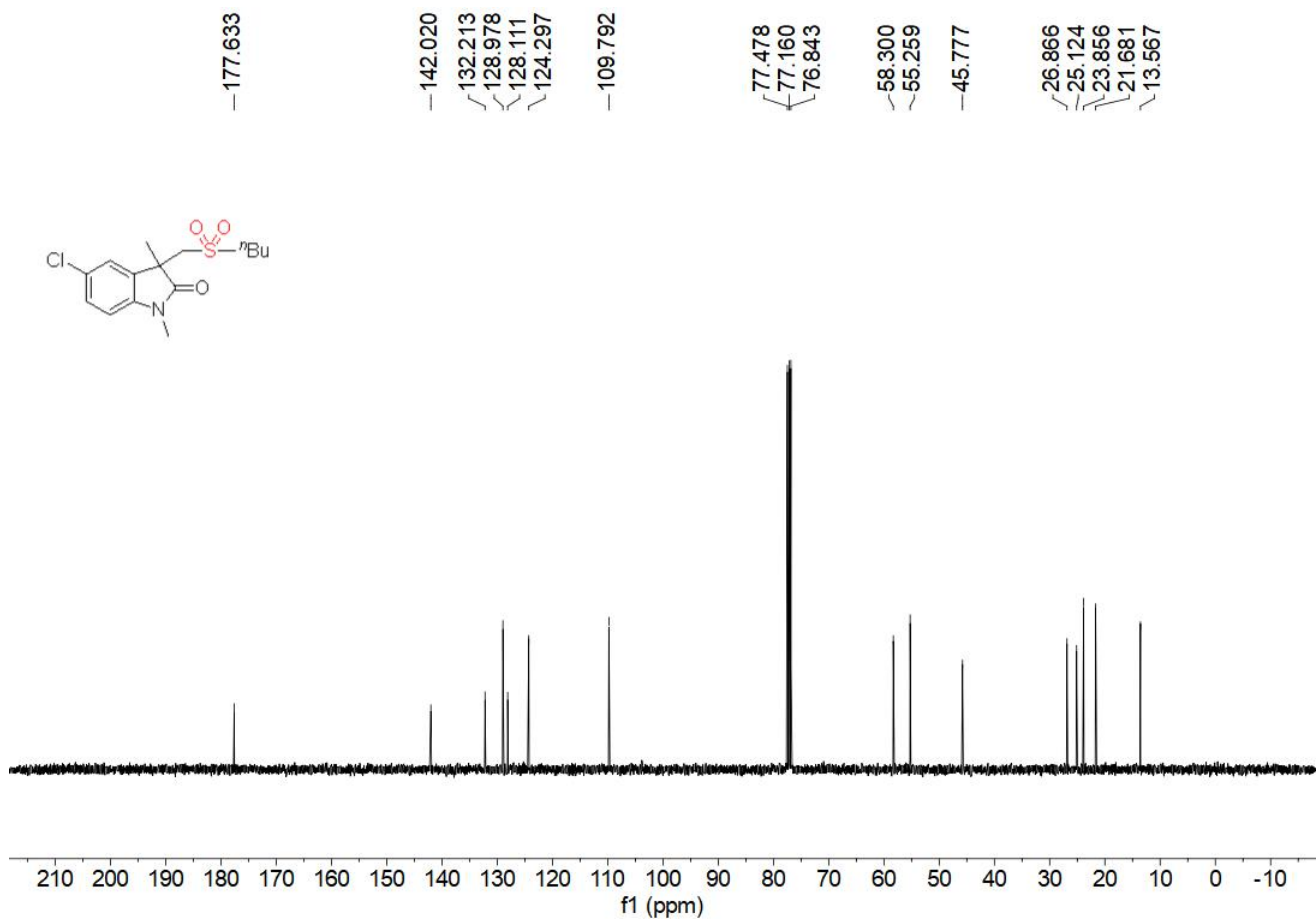
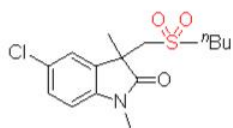
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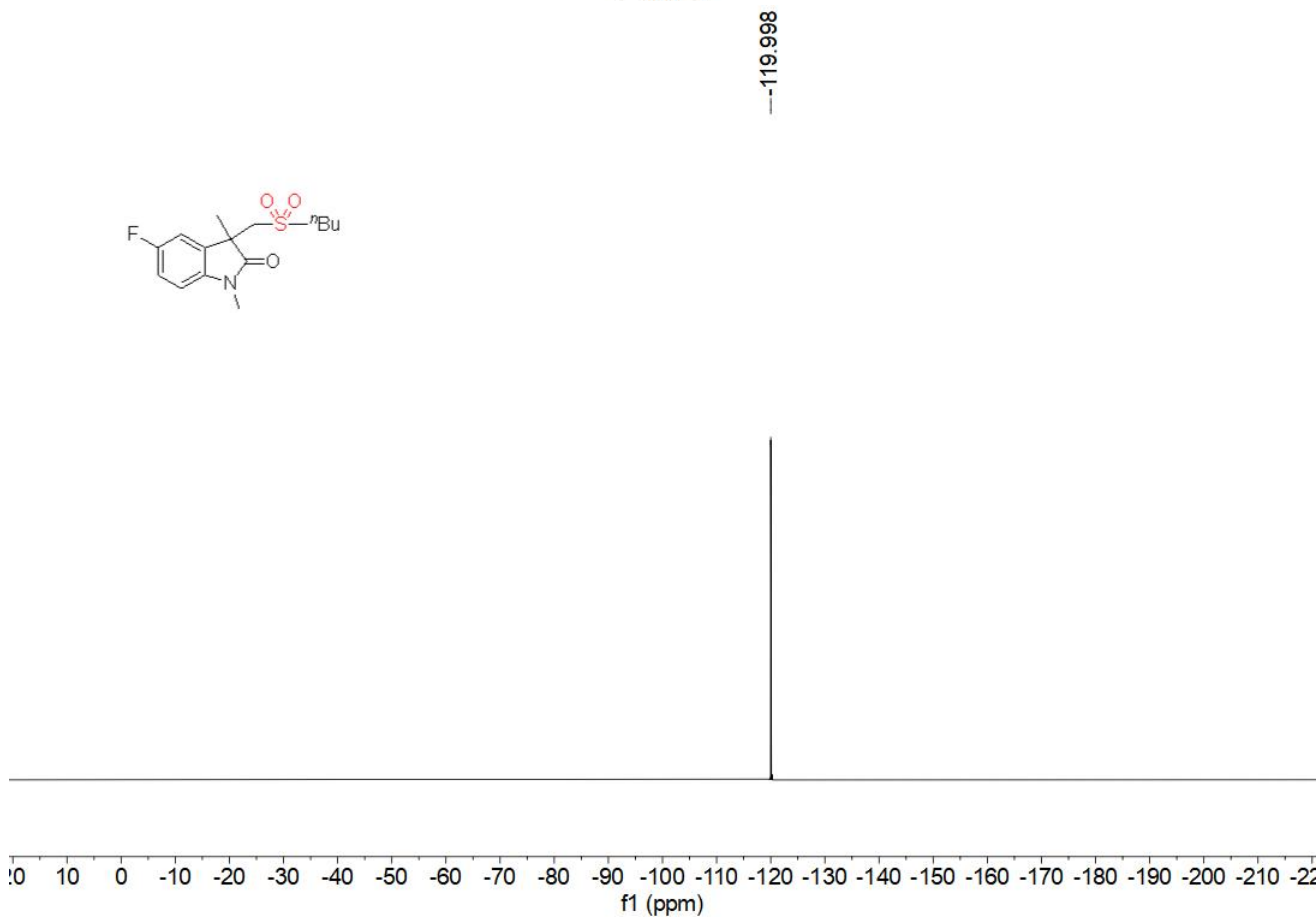
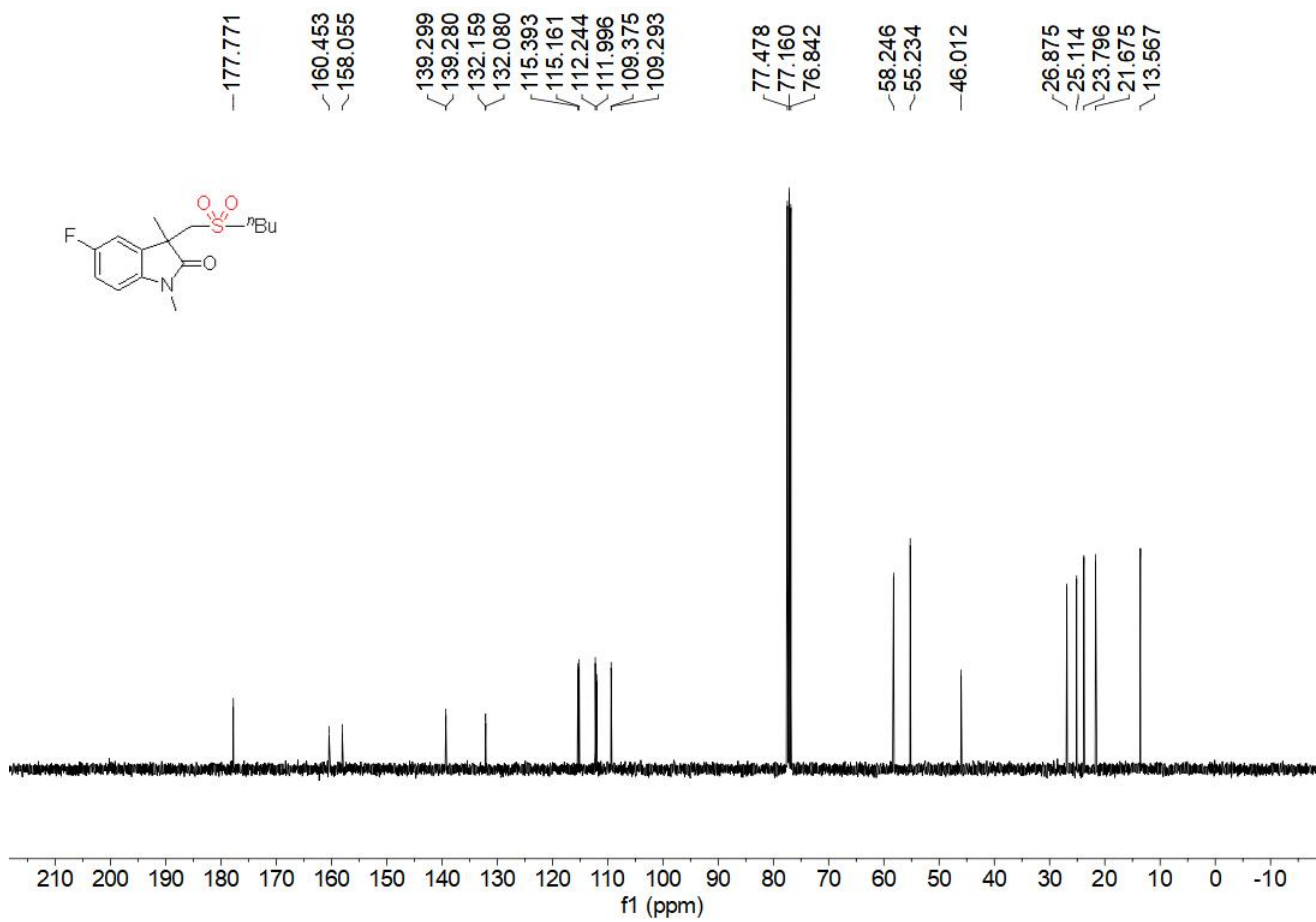


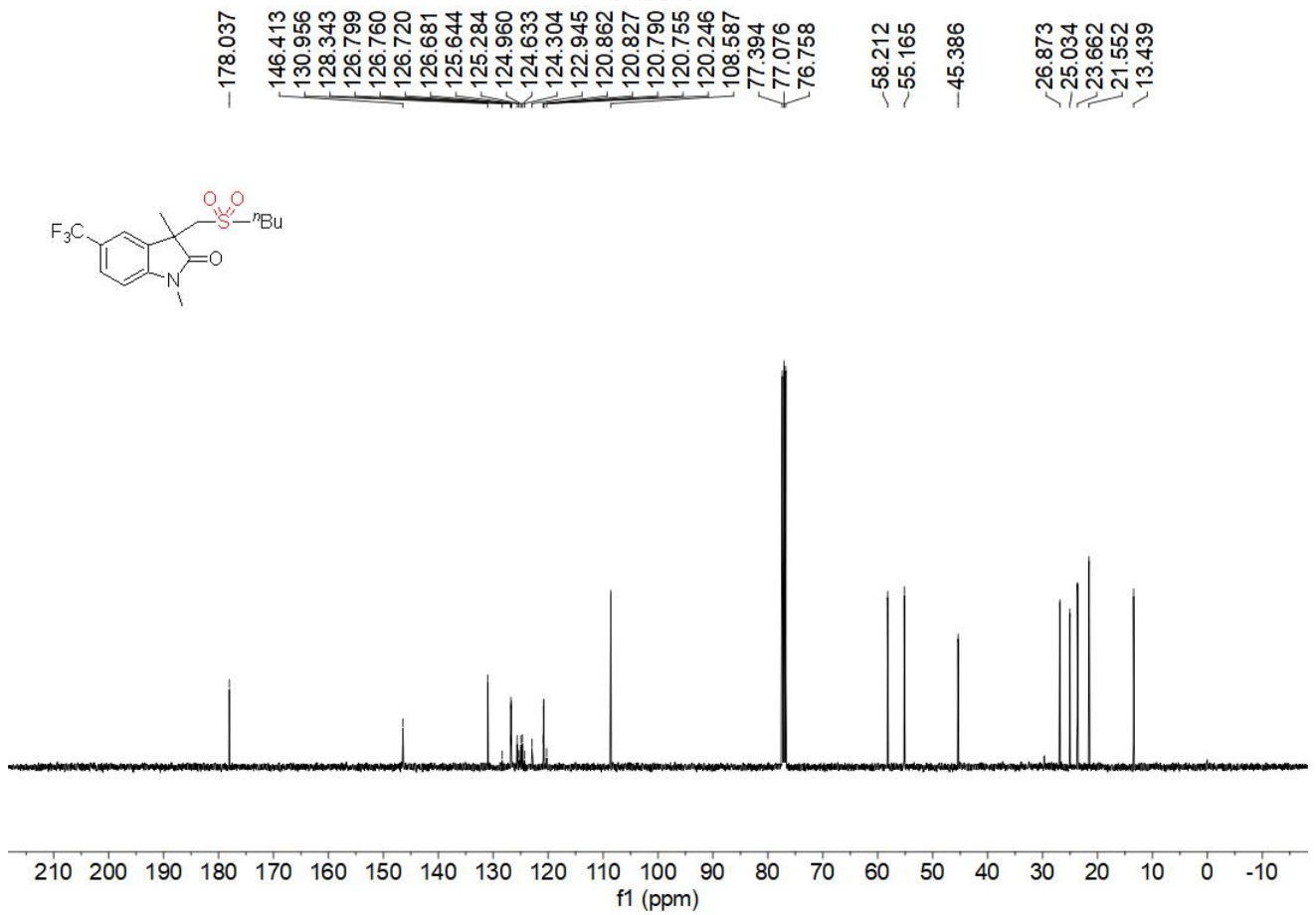
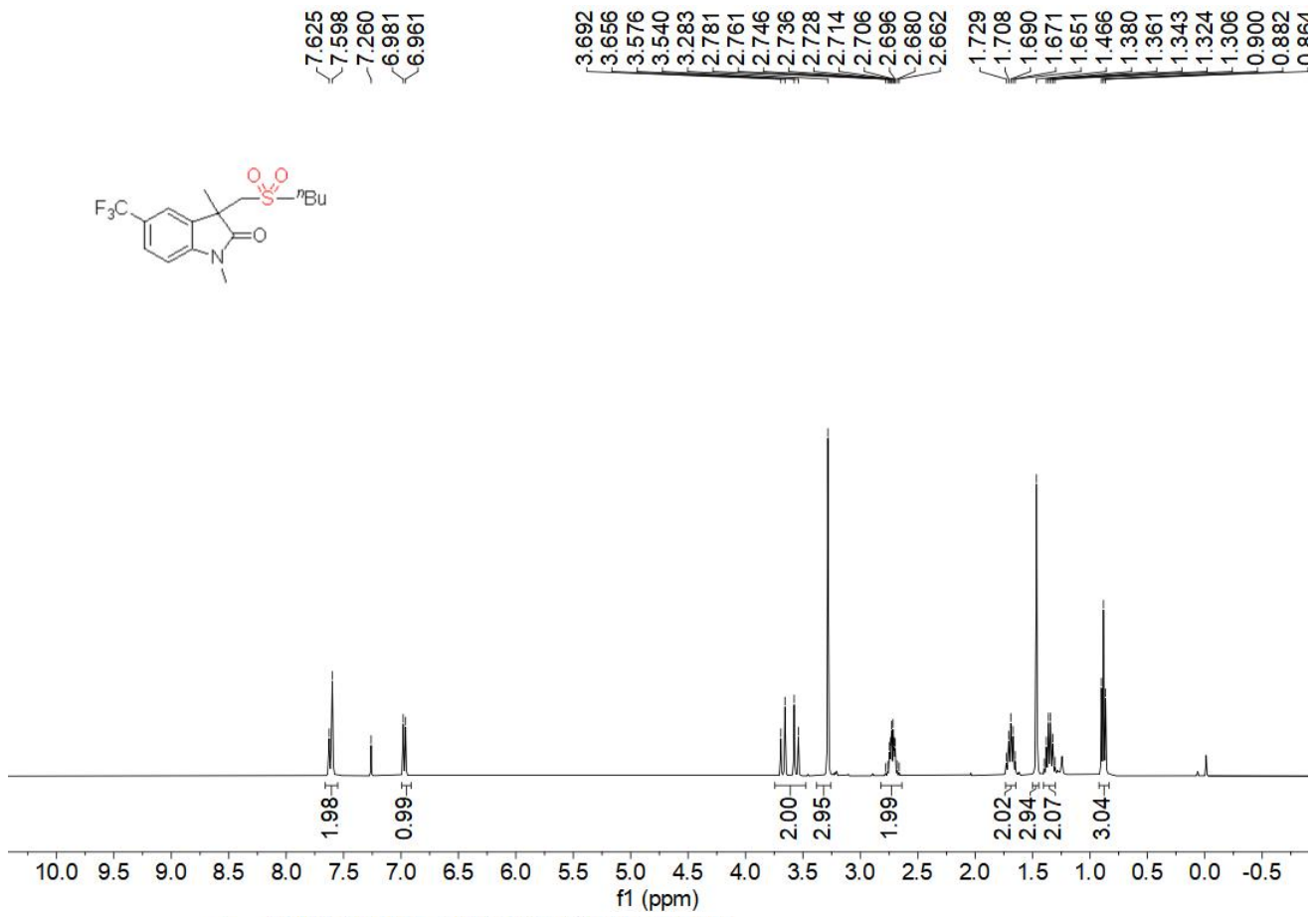


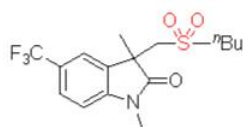
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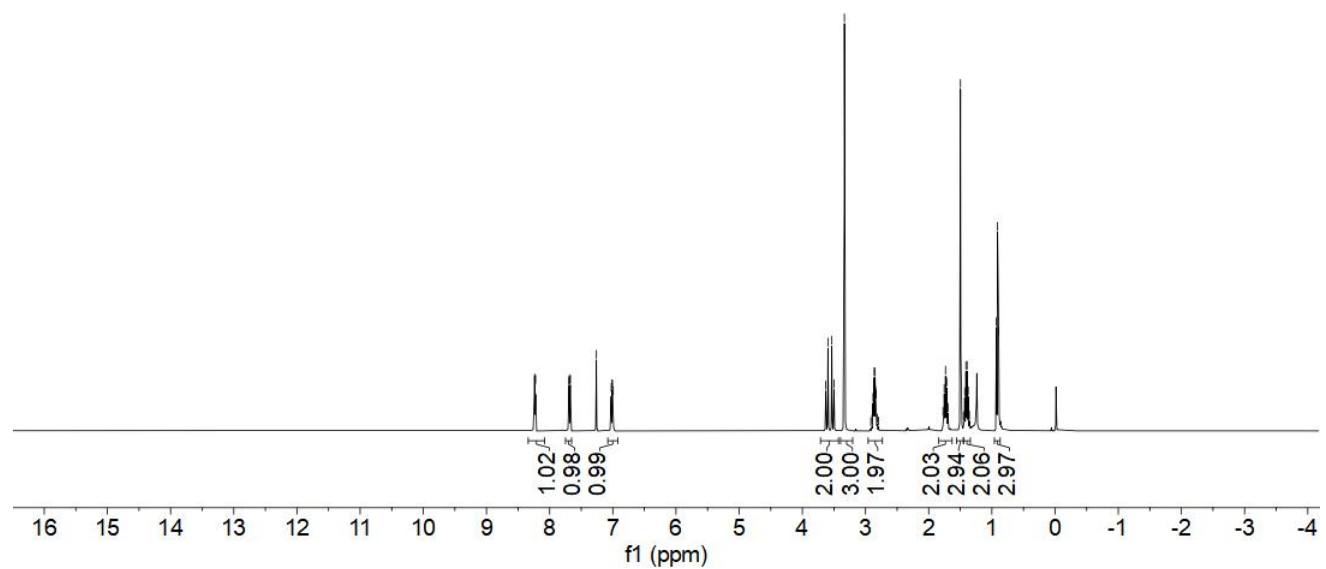
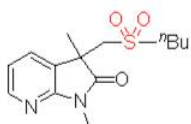
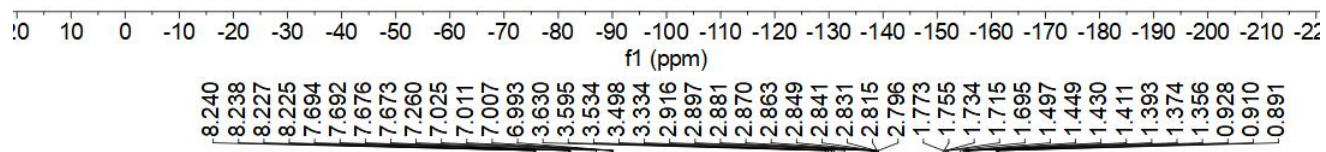


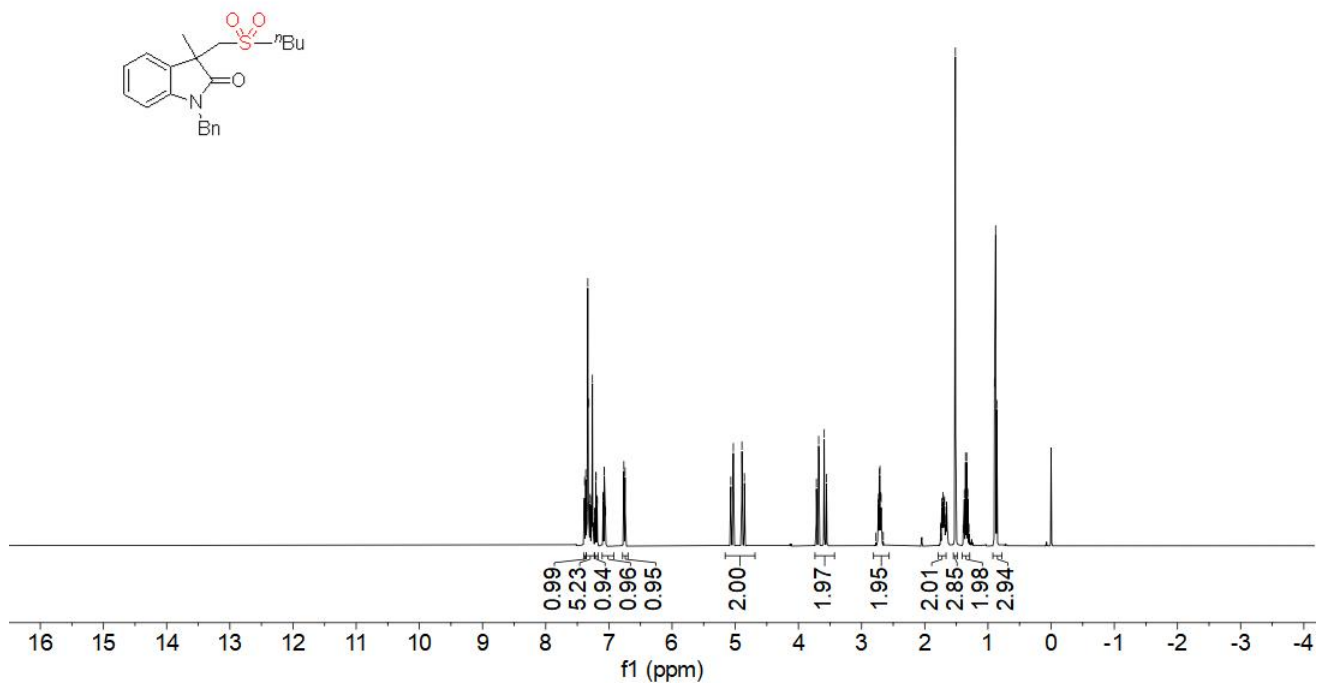
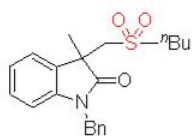
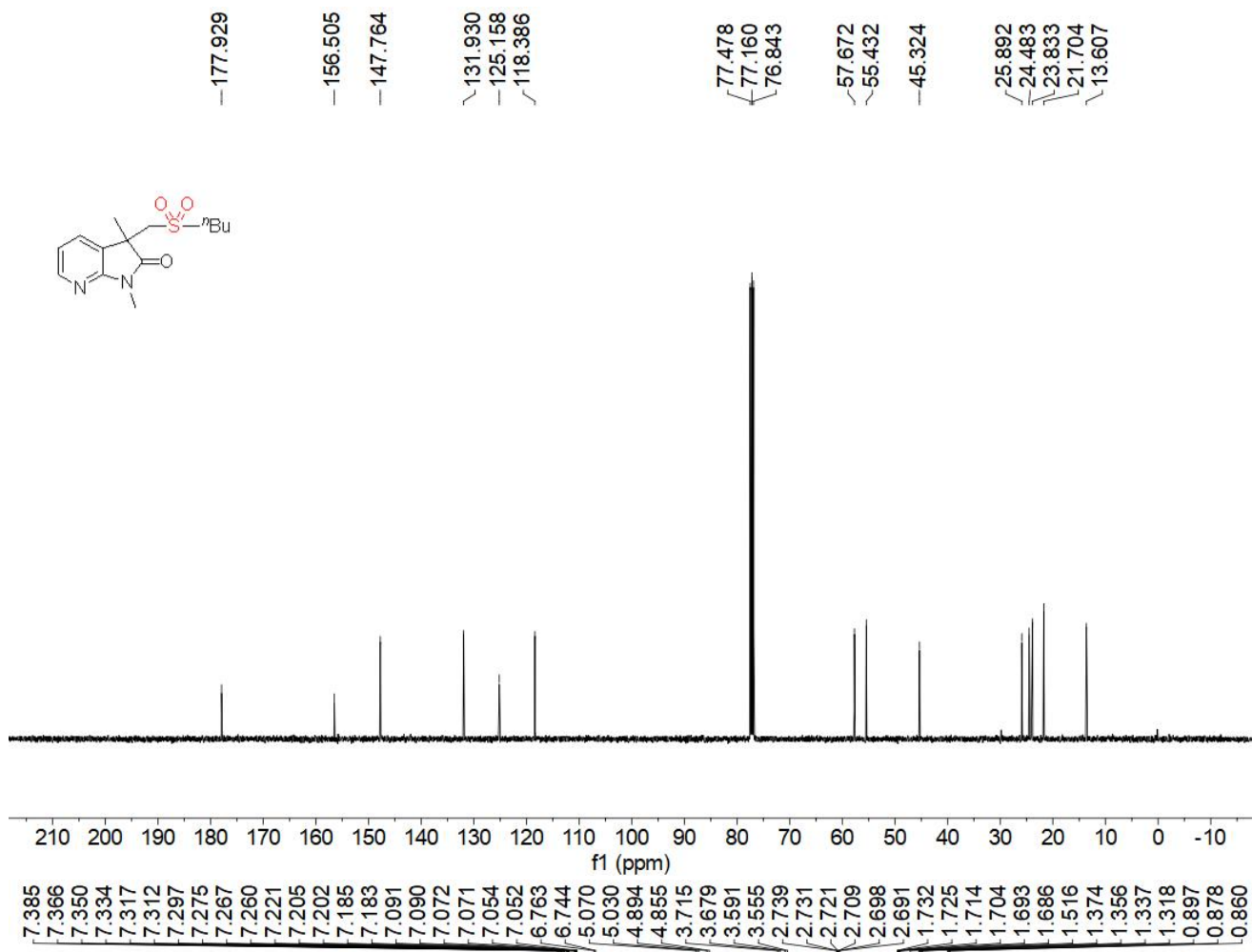
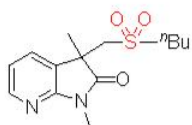


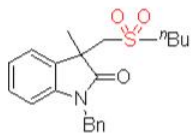




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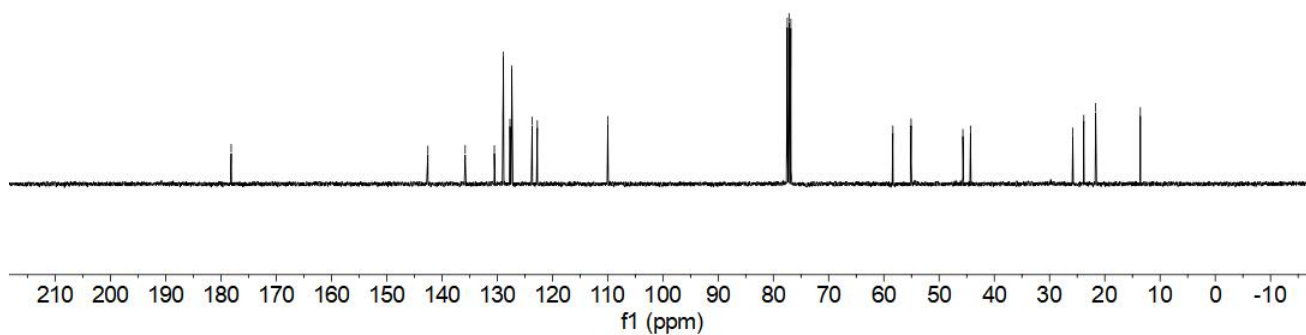
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77.160
76.842

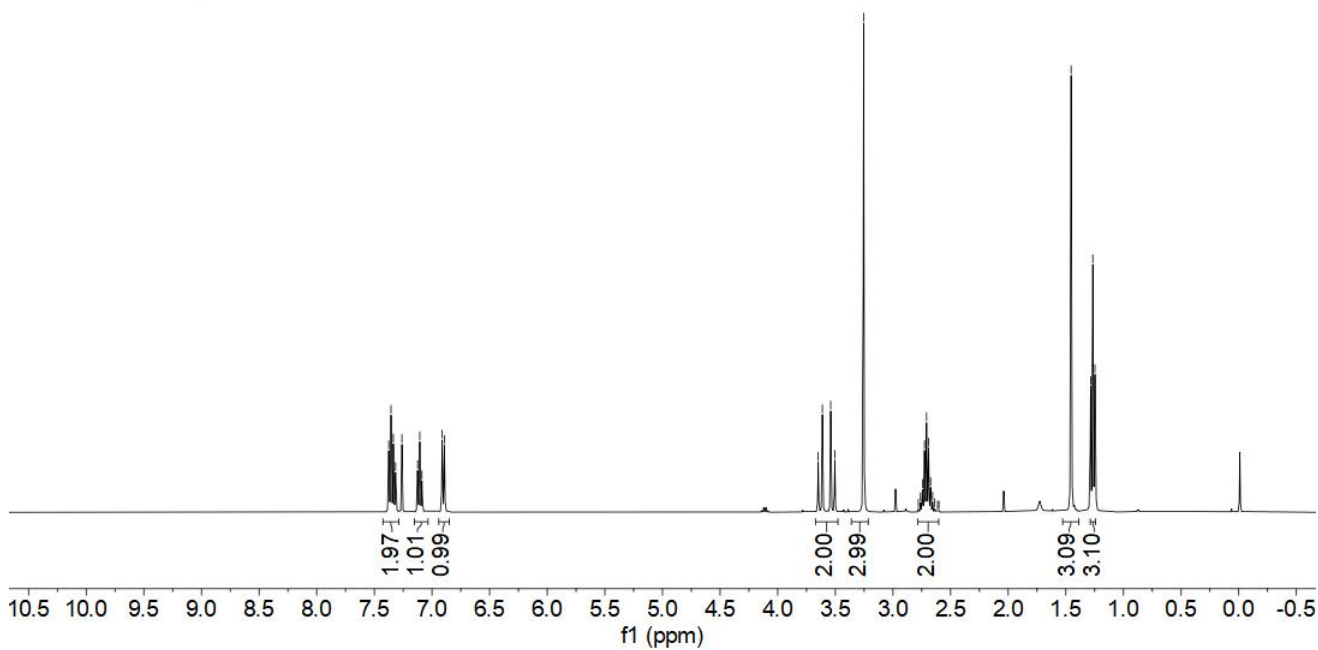
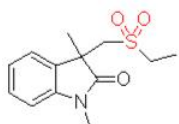
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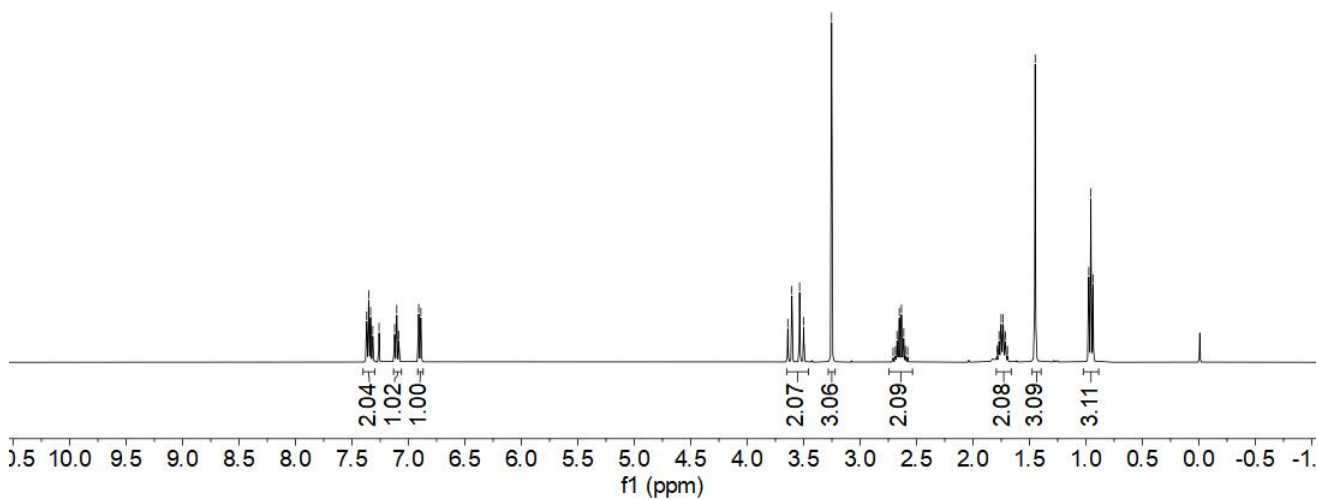
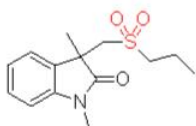
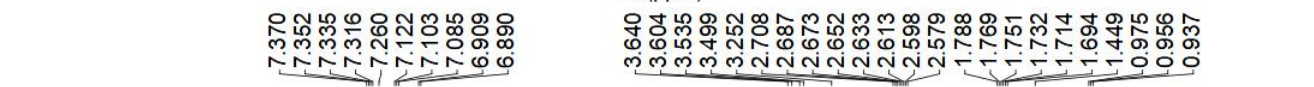
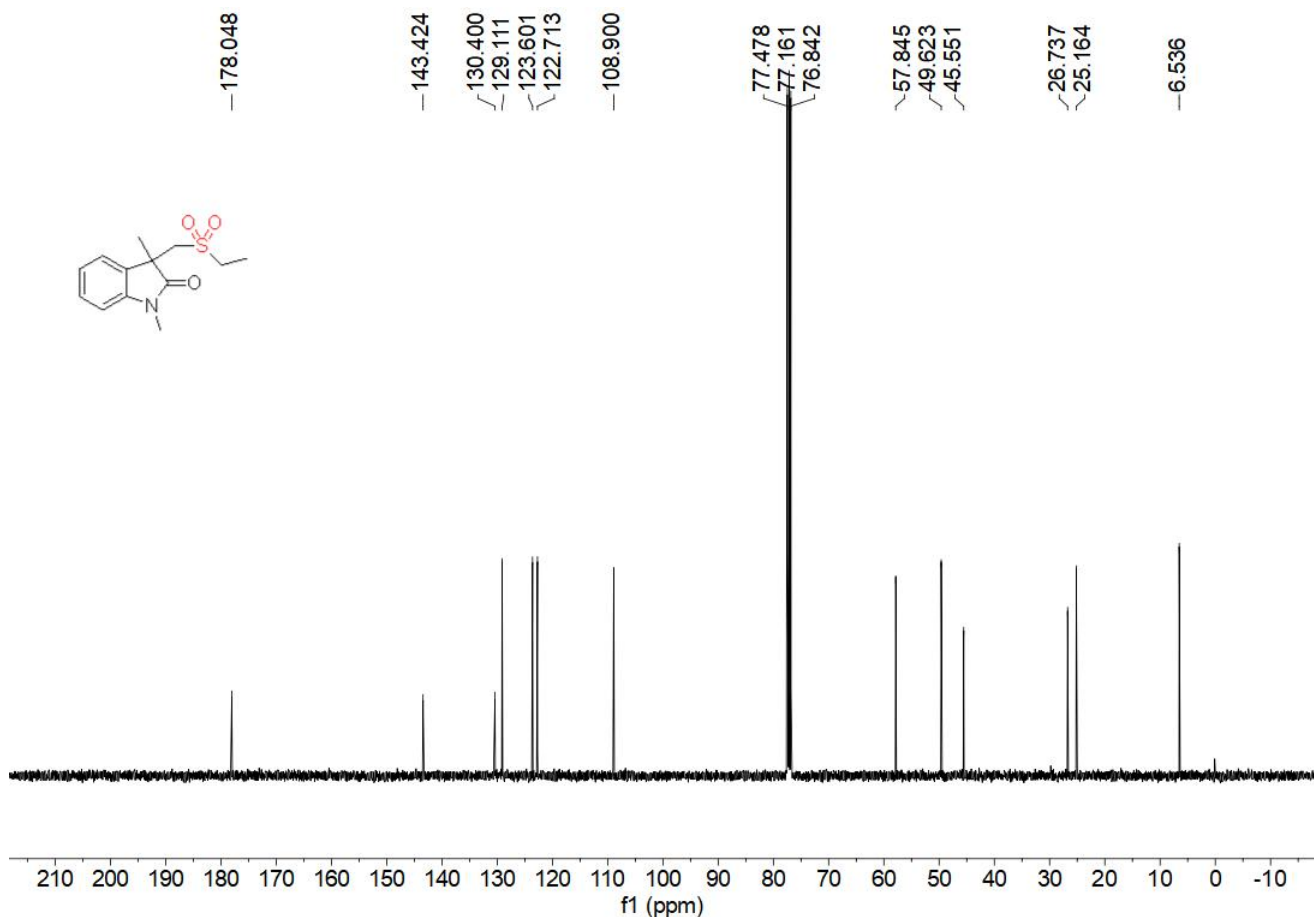
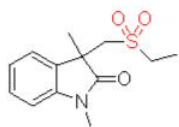
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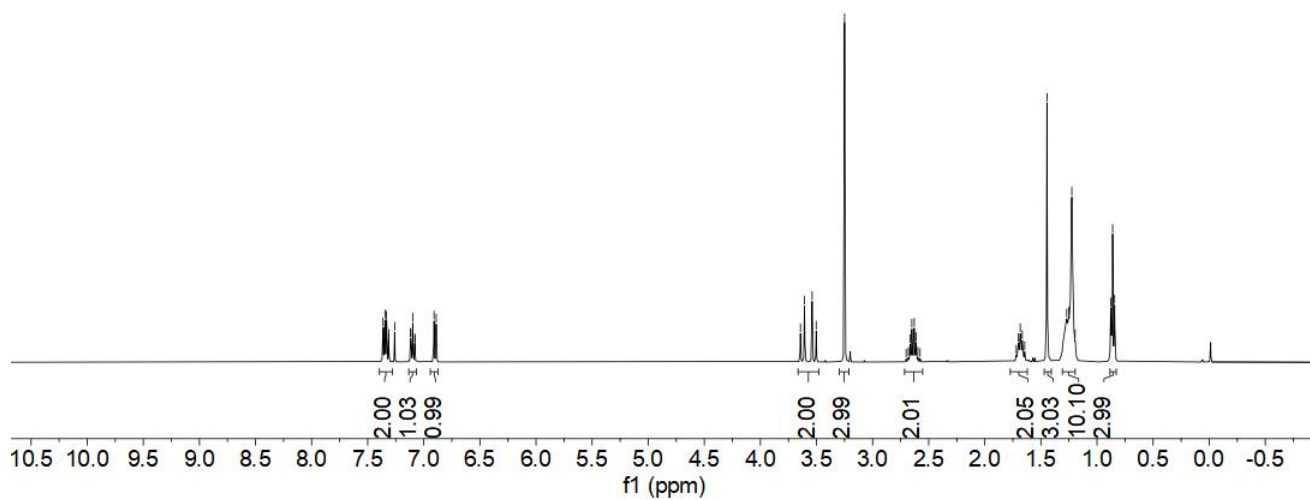
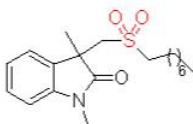
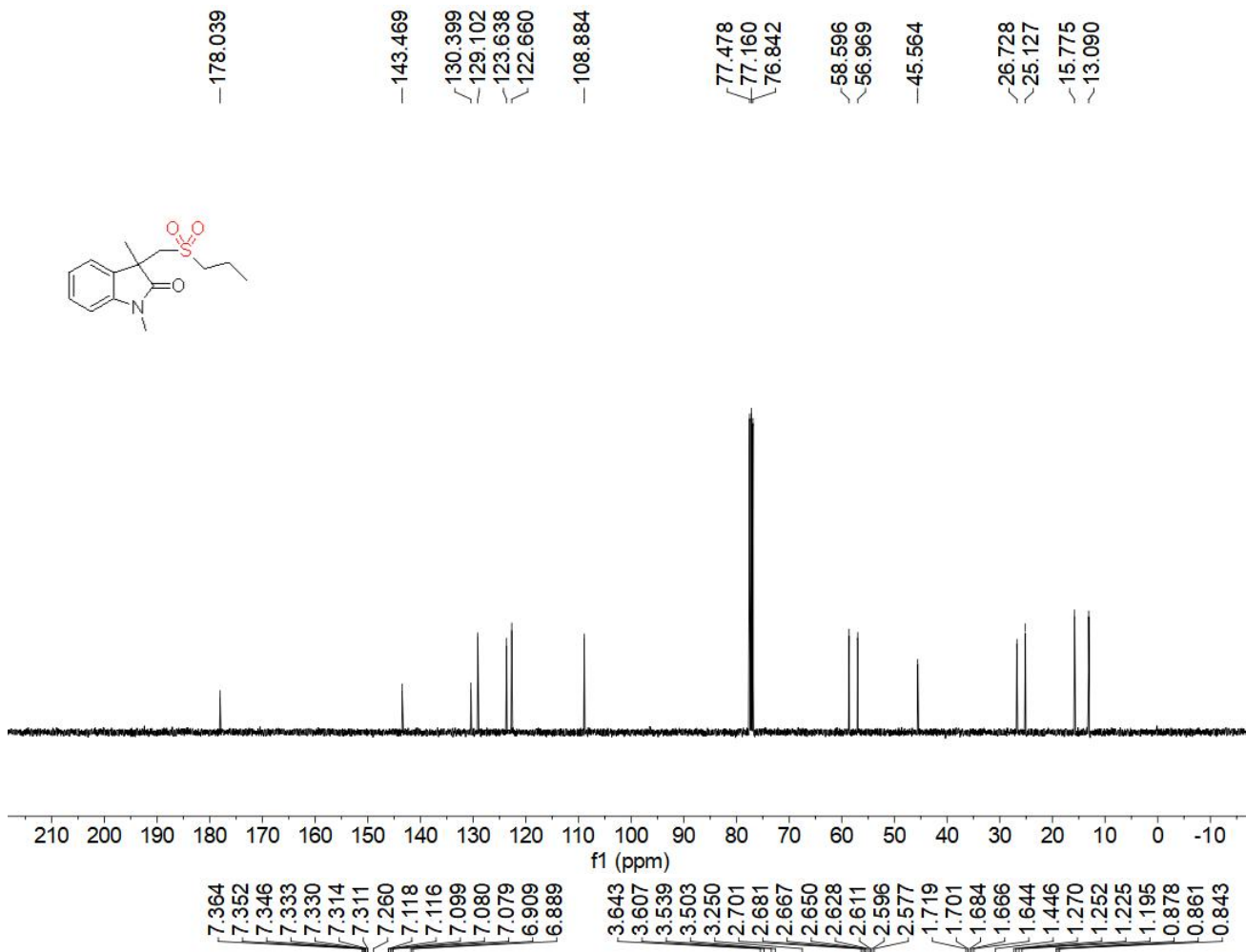
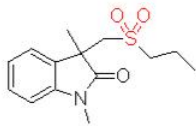


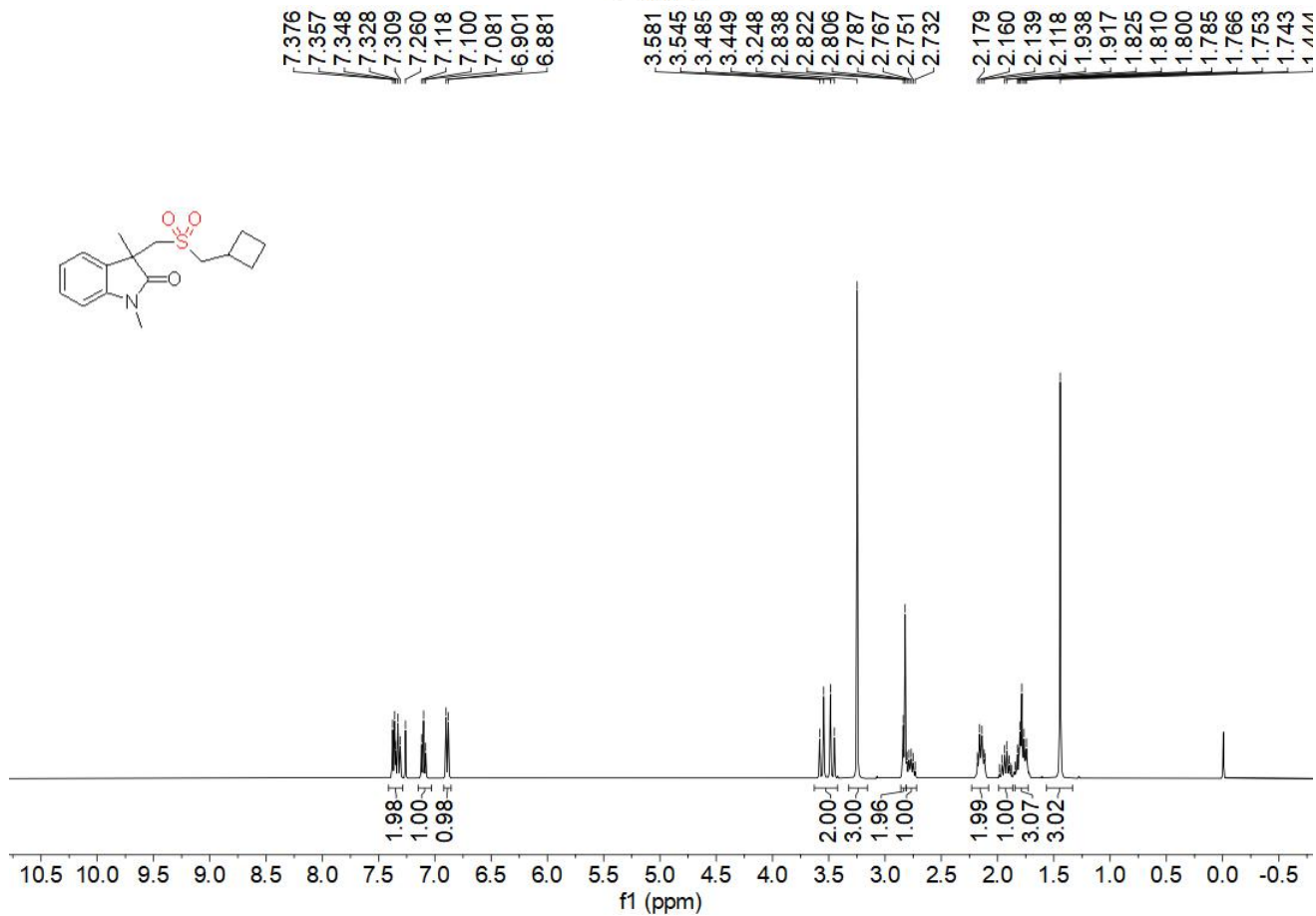
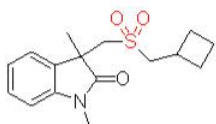
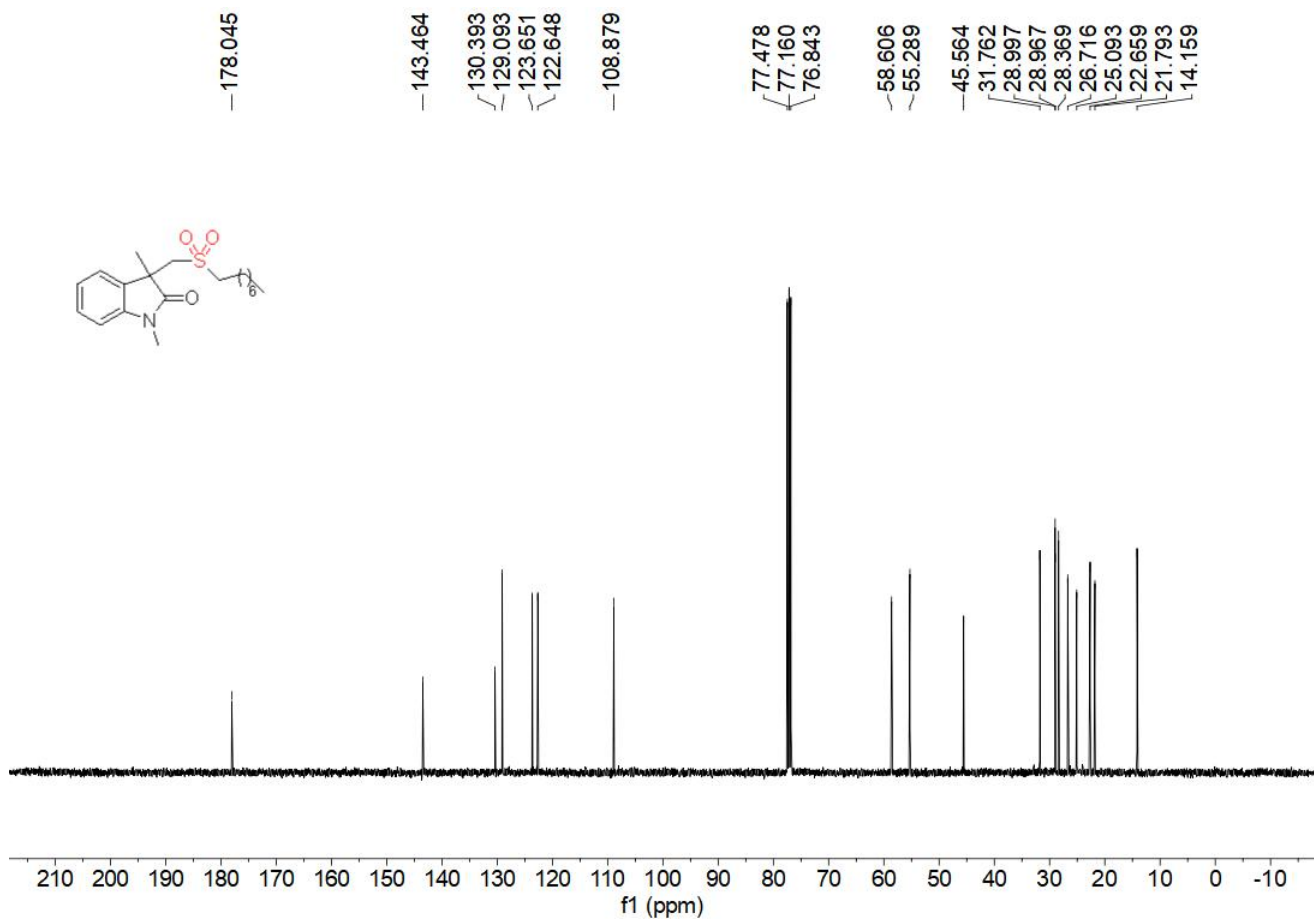
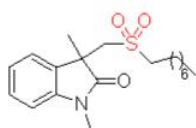
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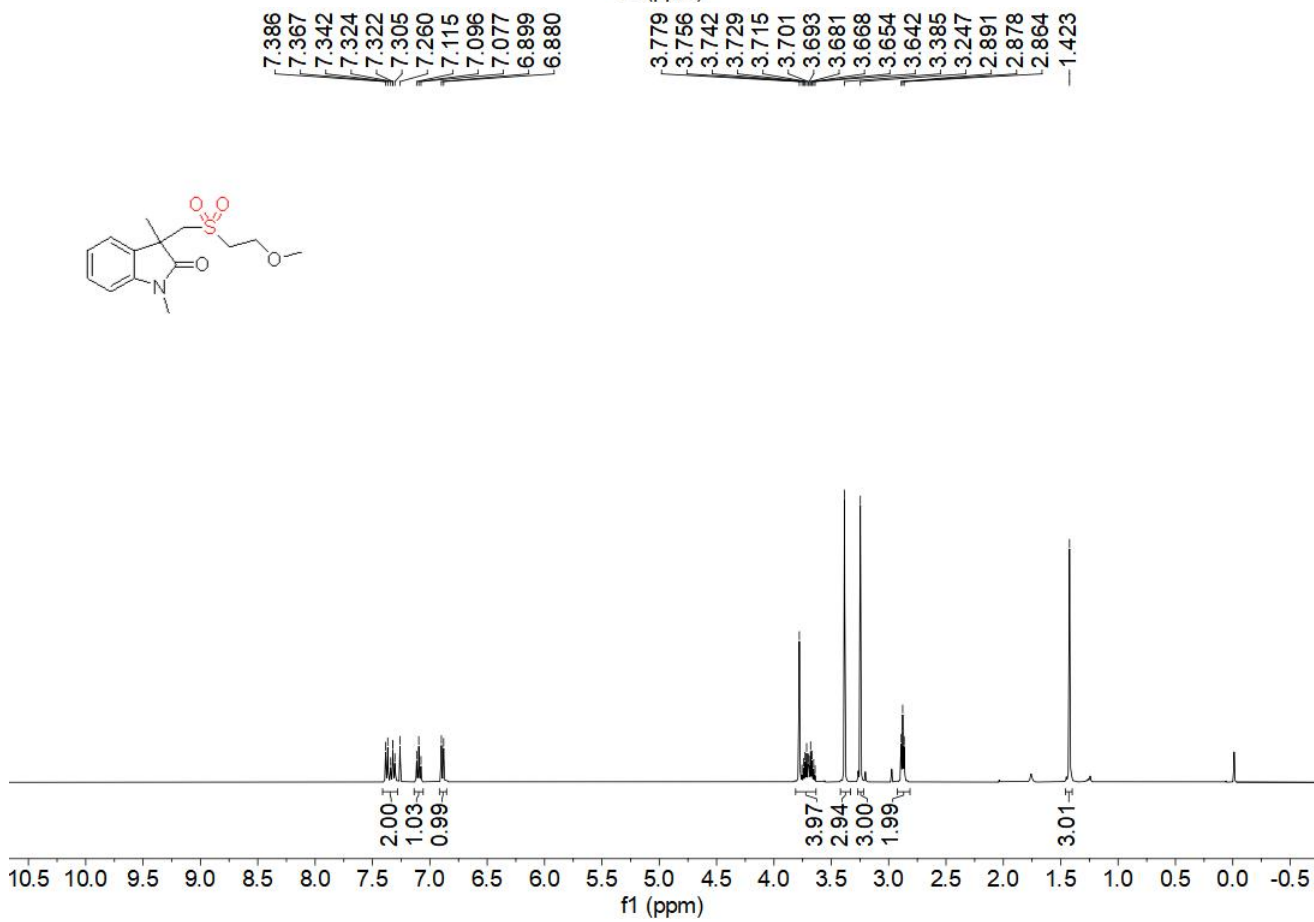
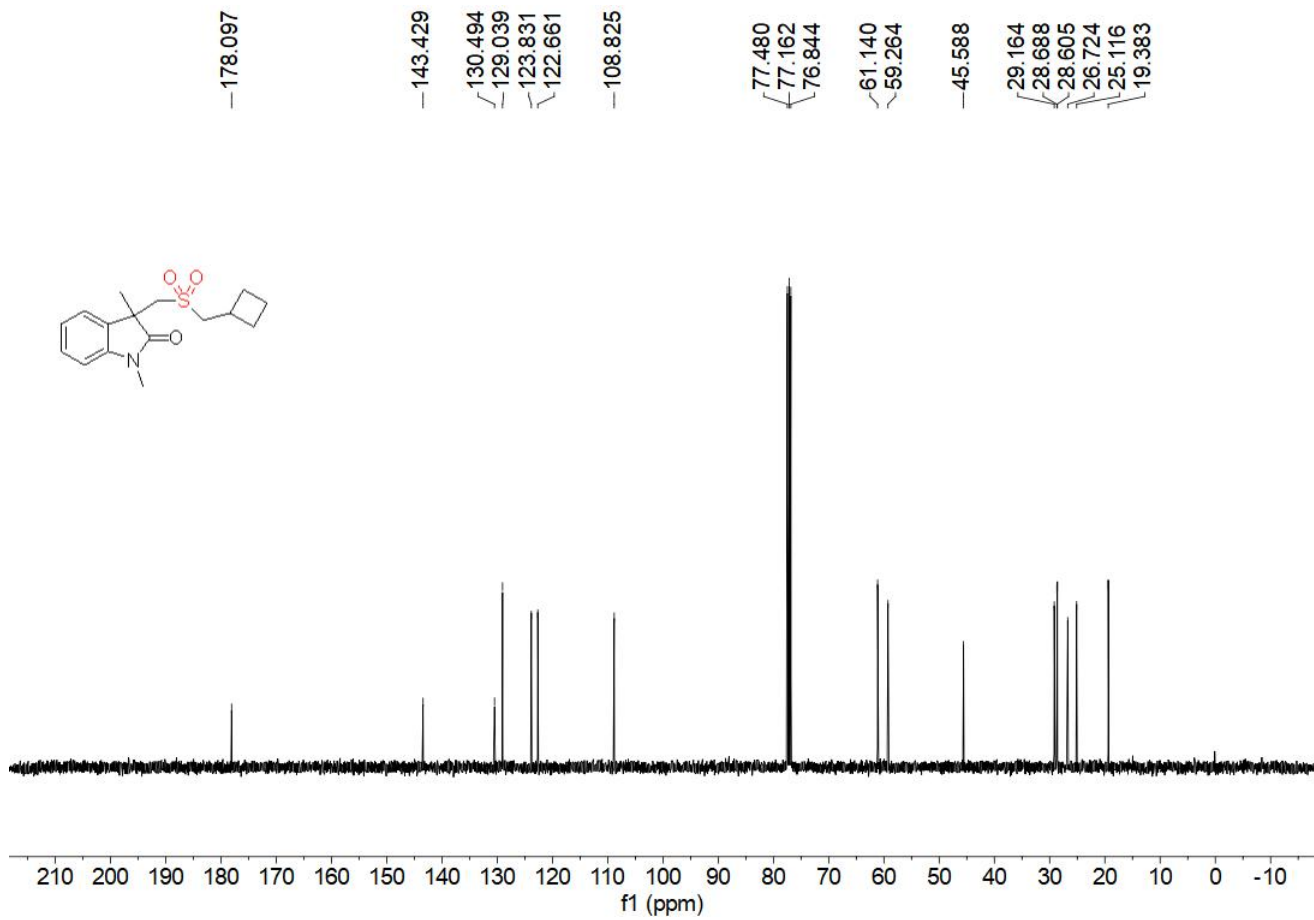
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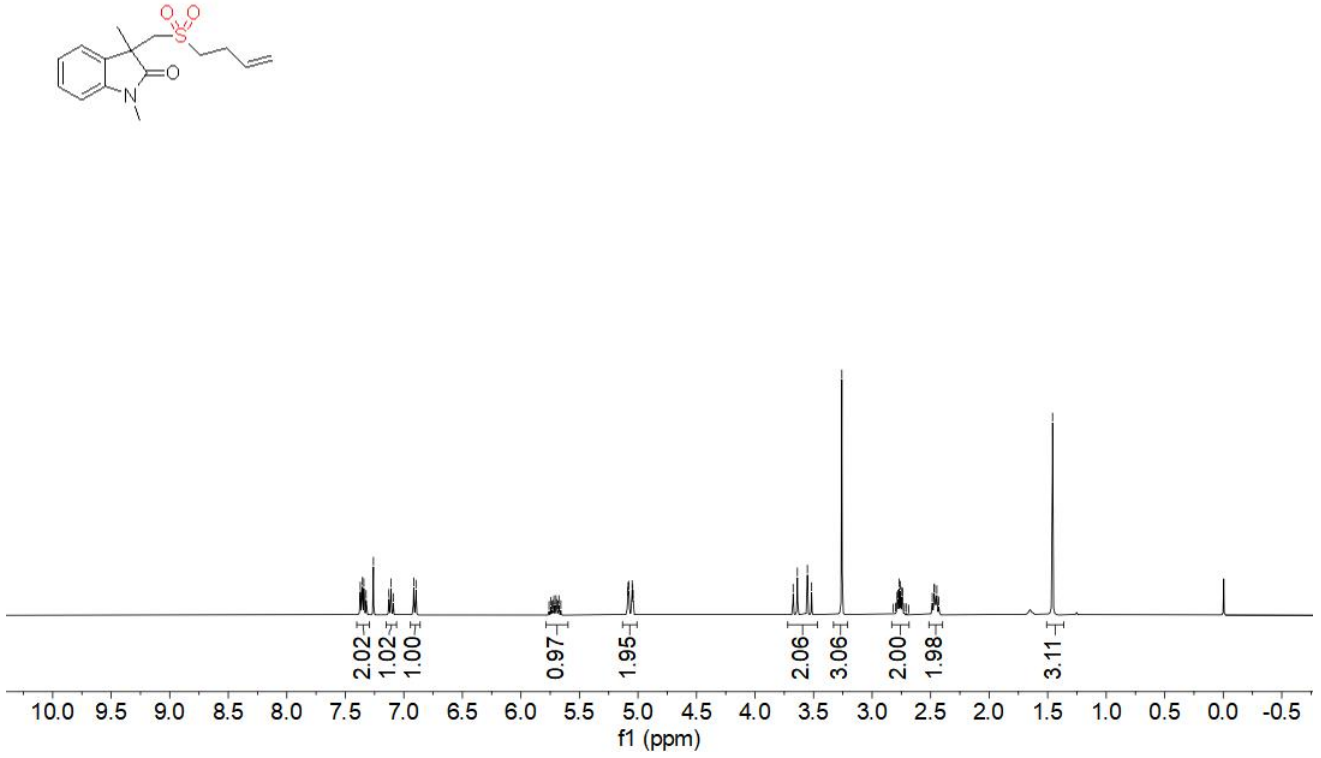
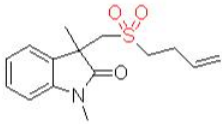
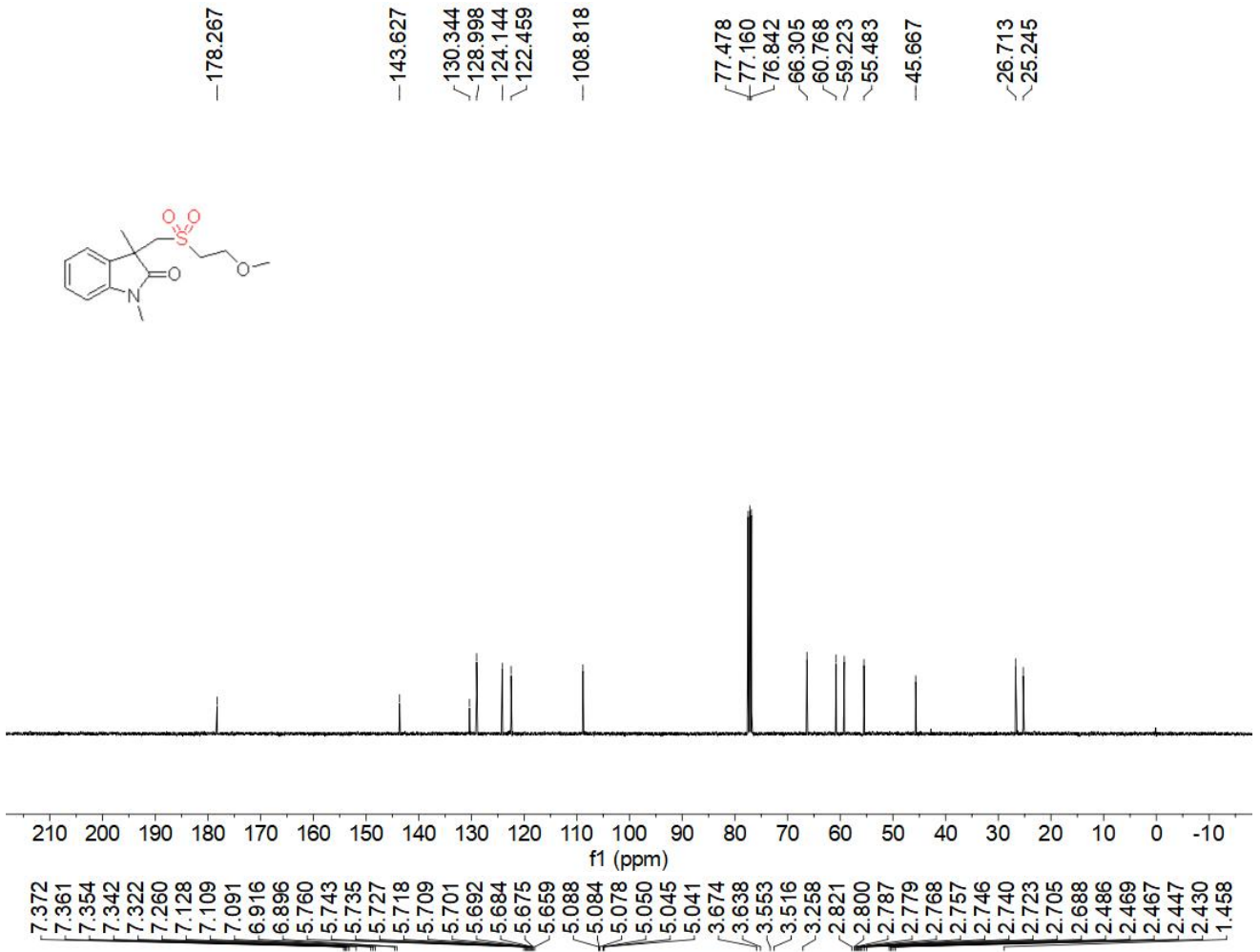
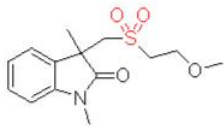


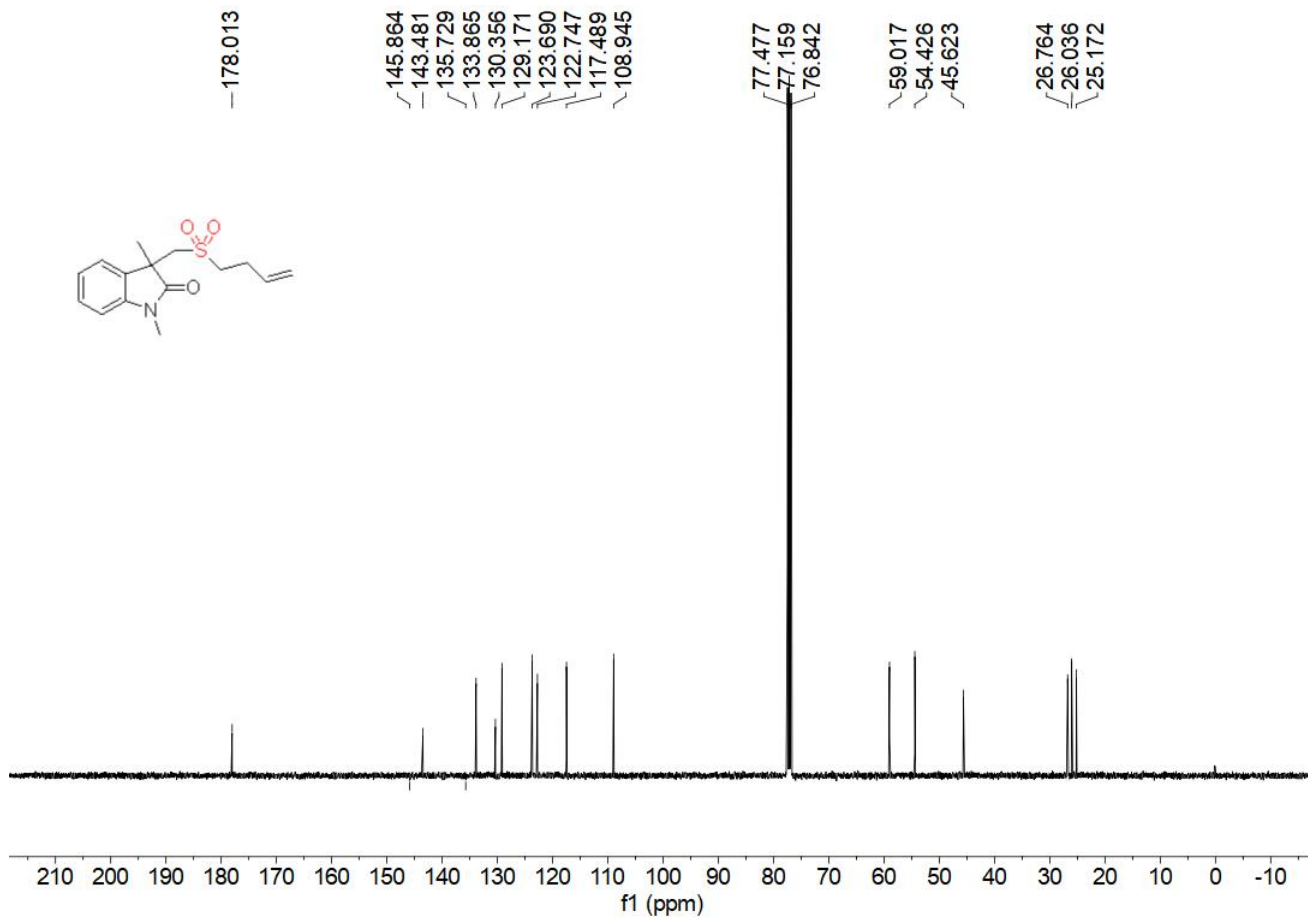
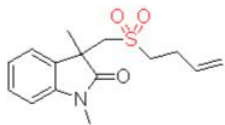




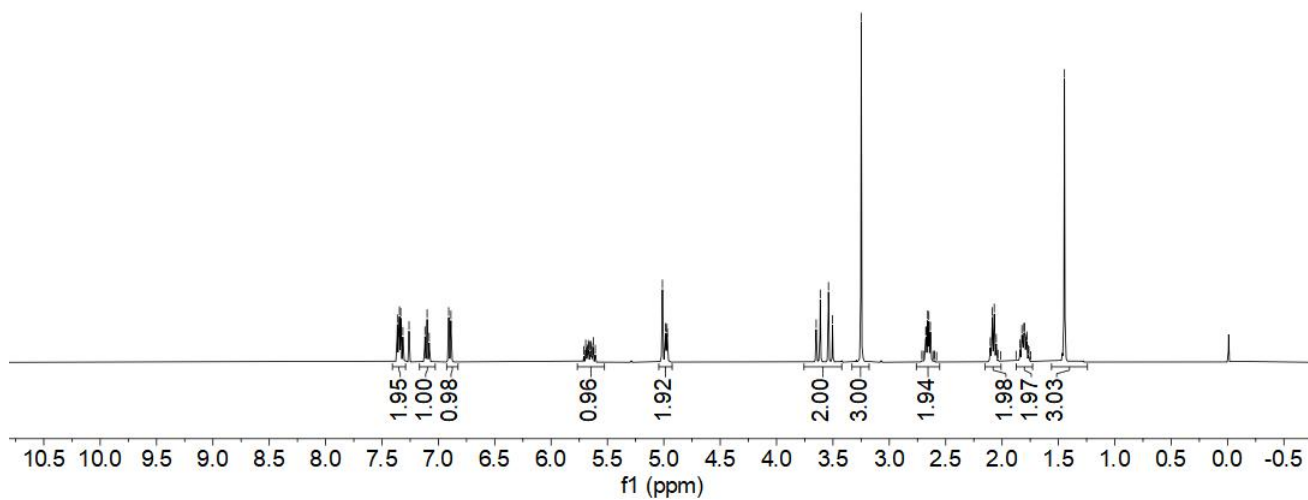
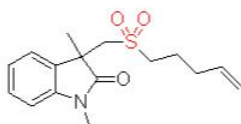


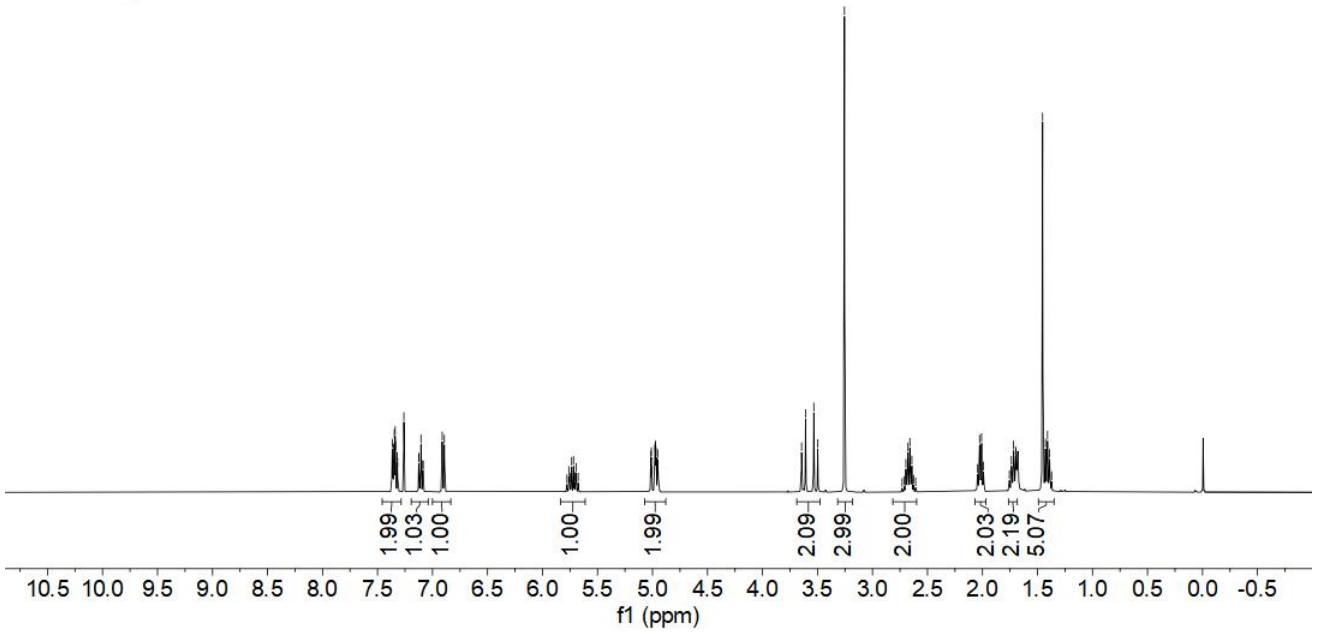
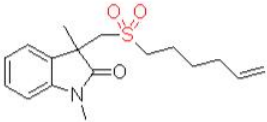
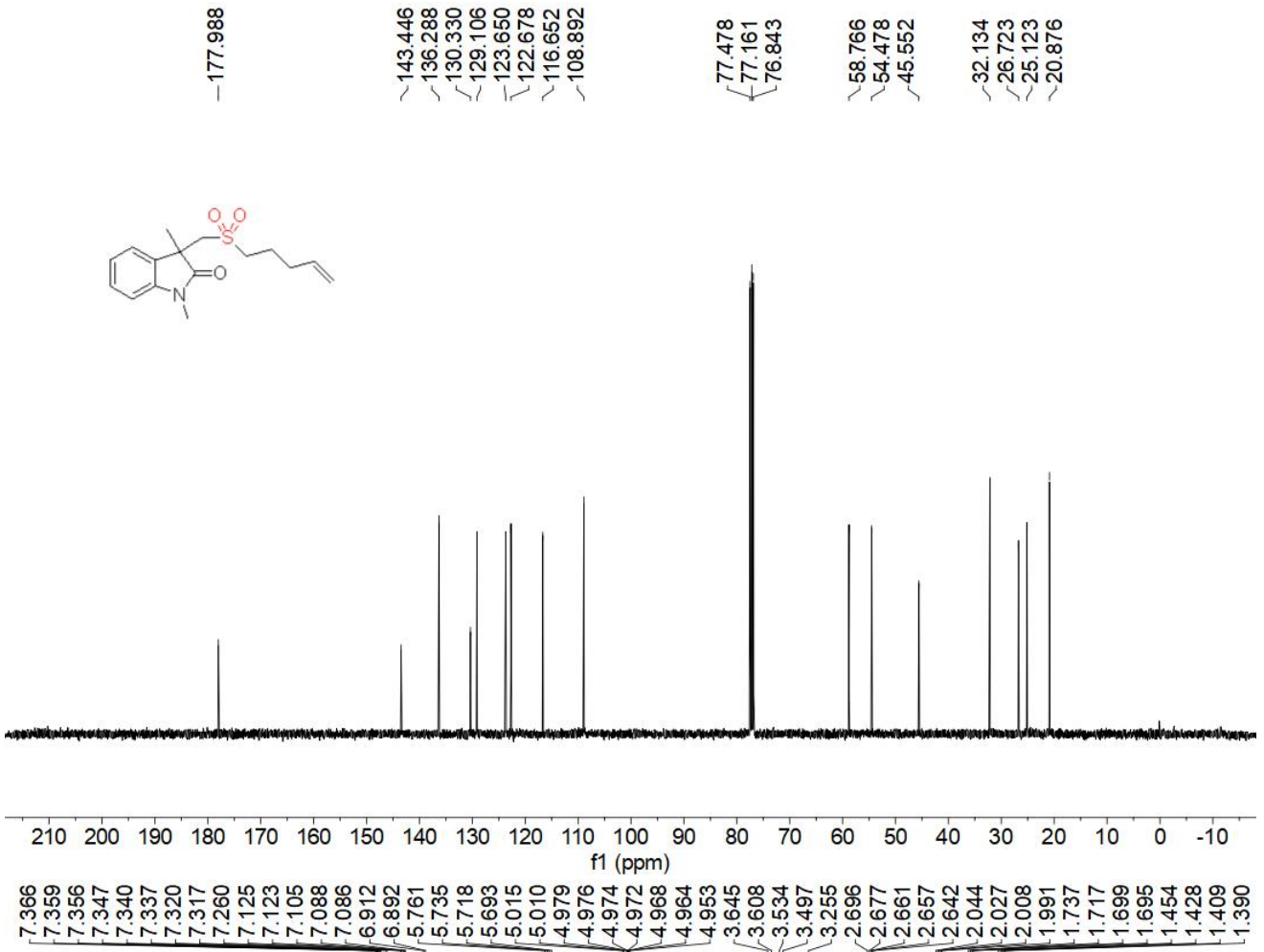
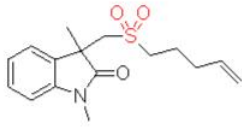


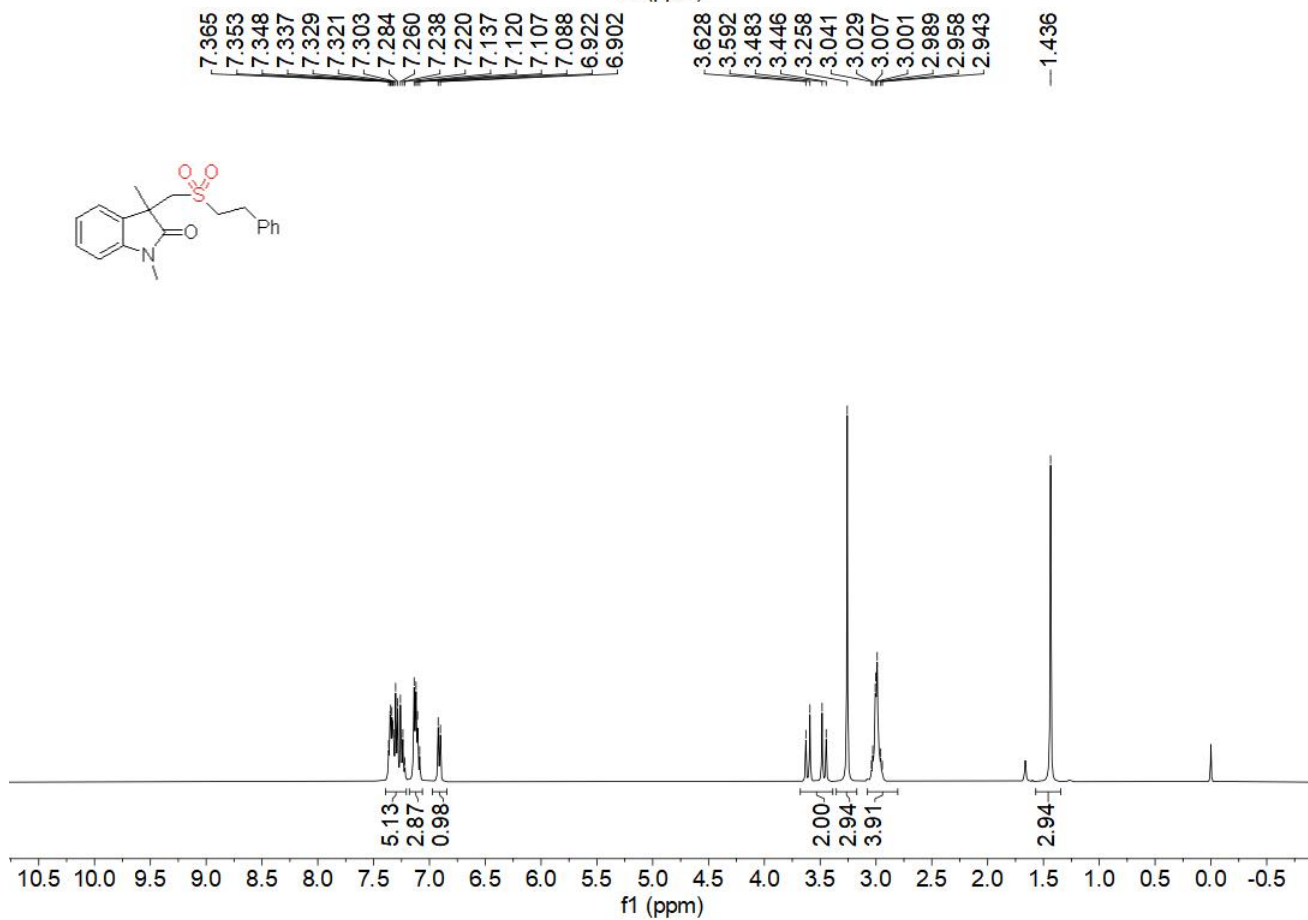
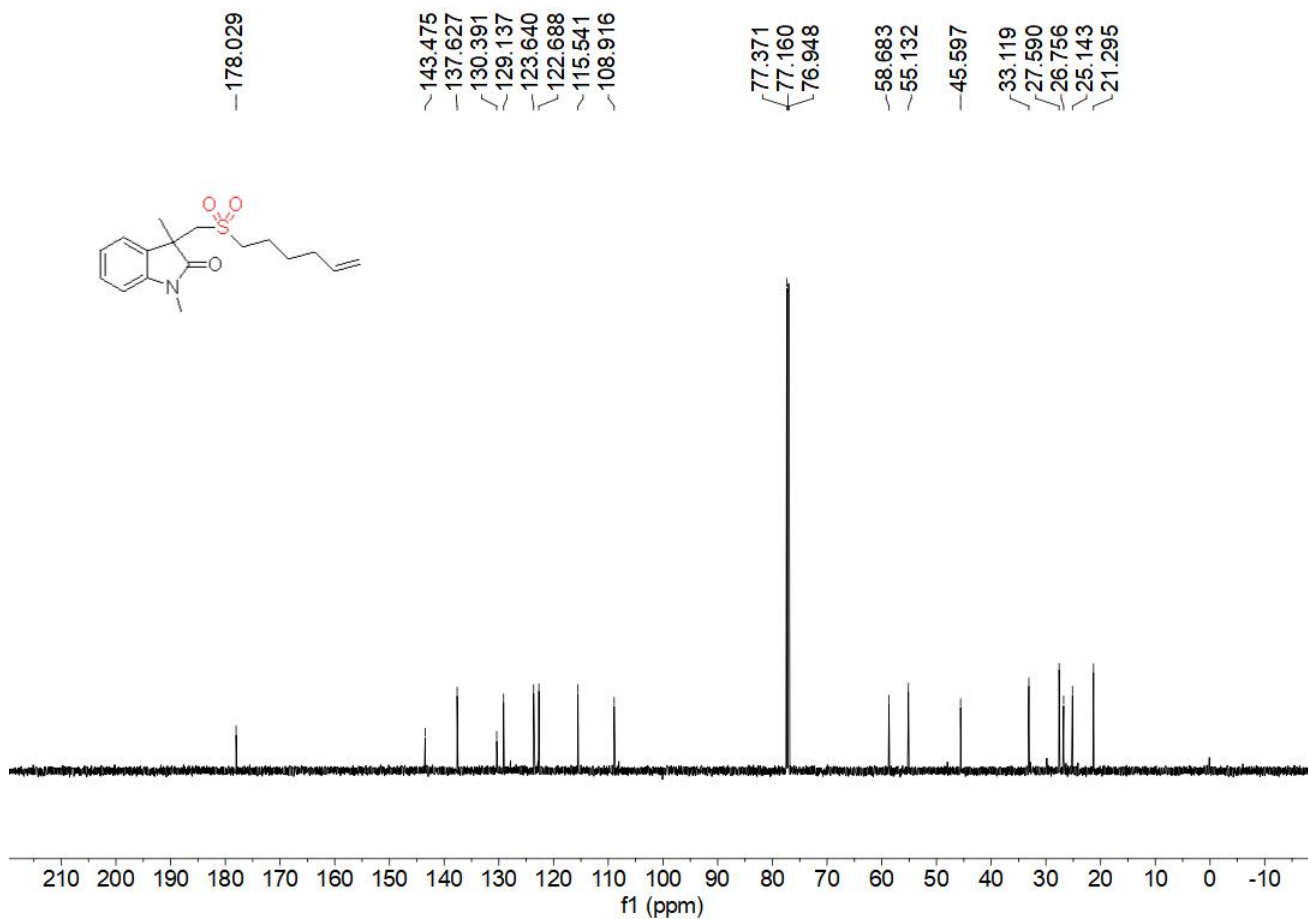


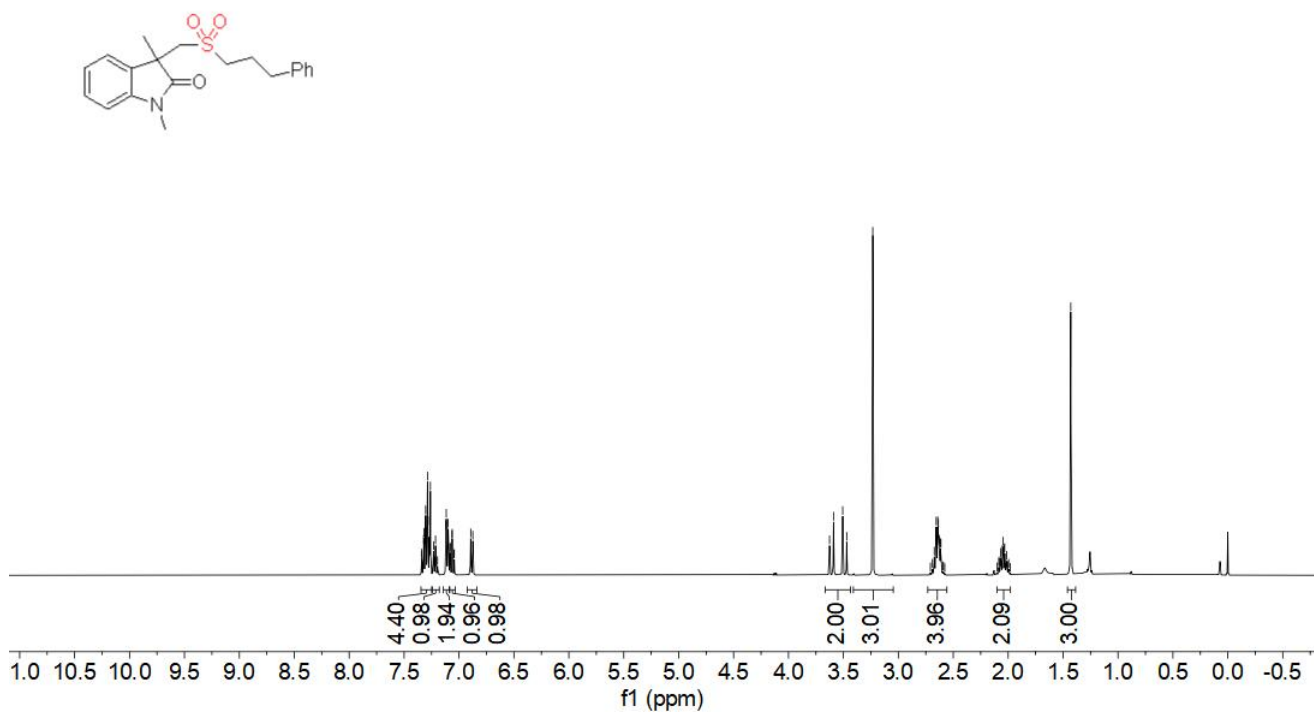
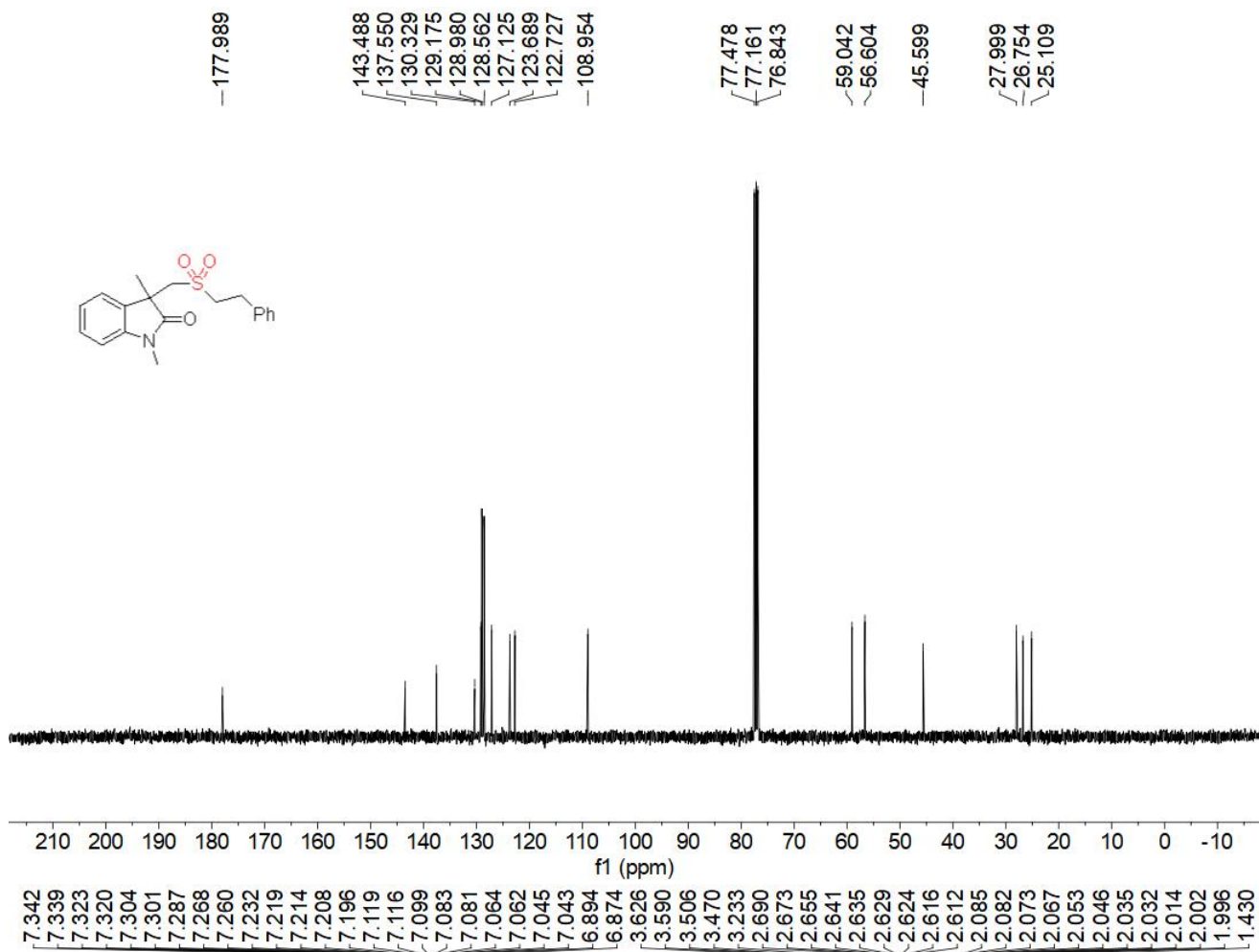


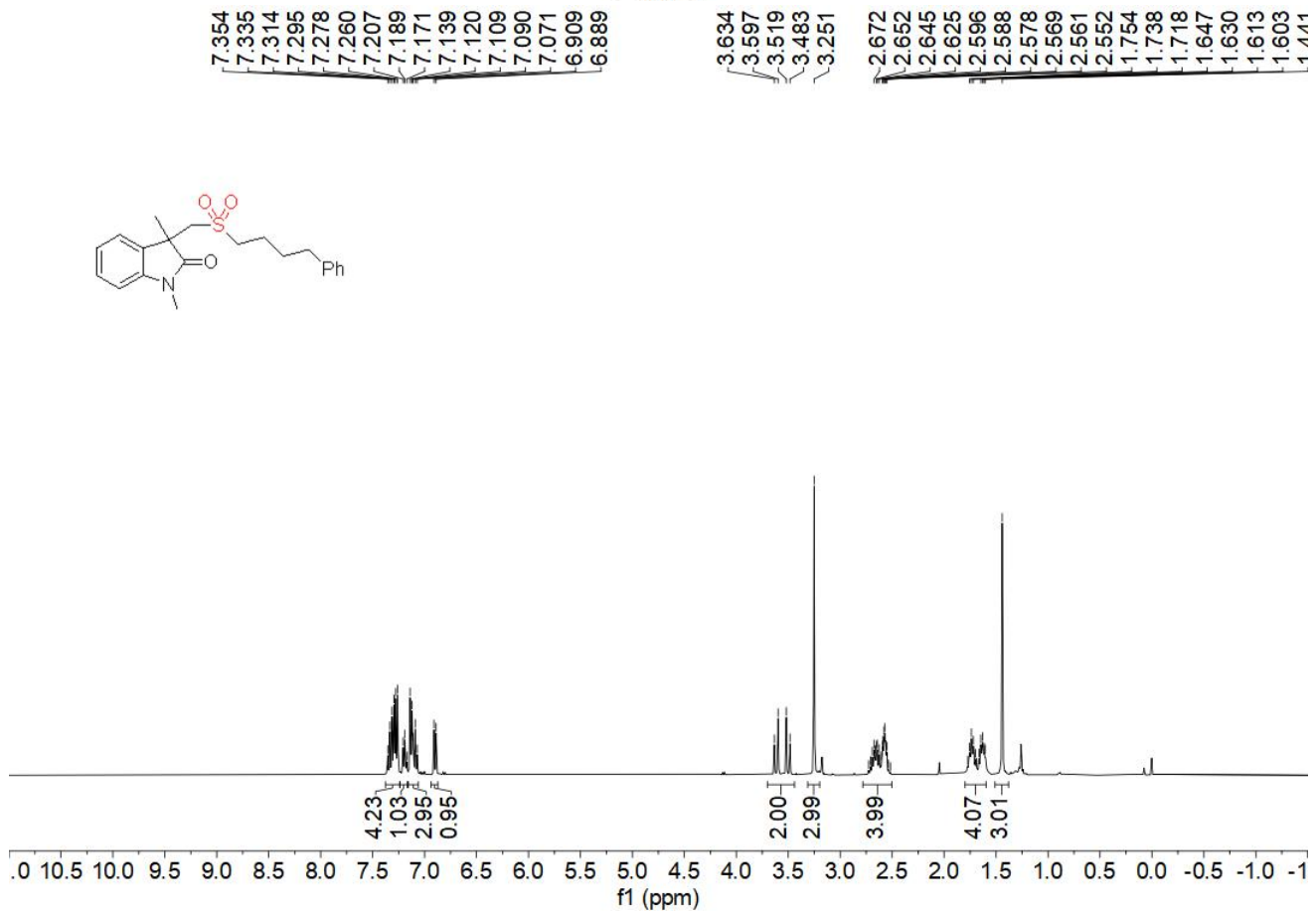
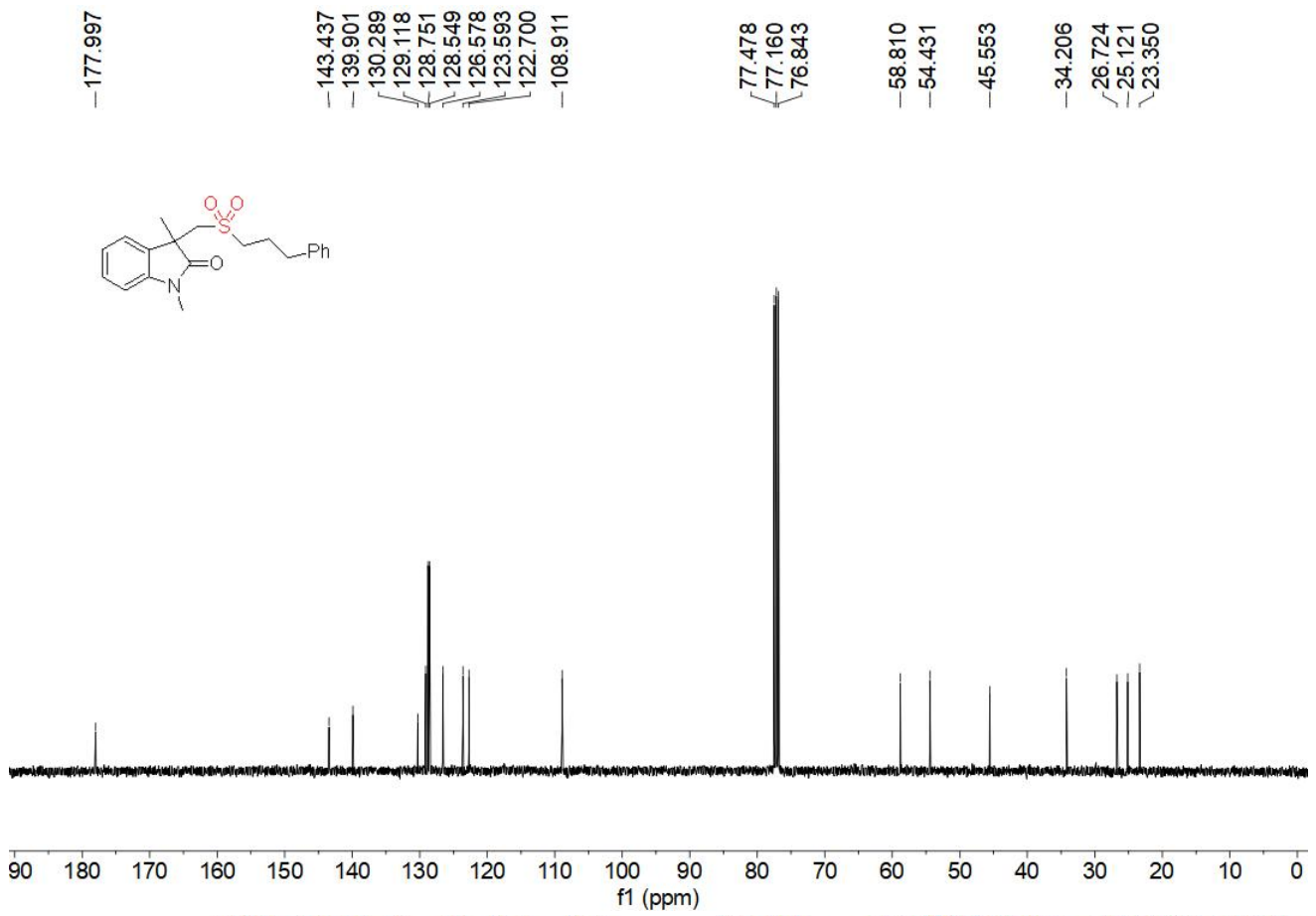
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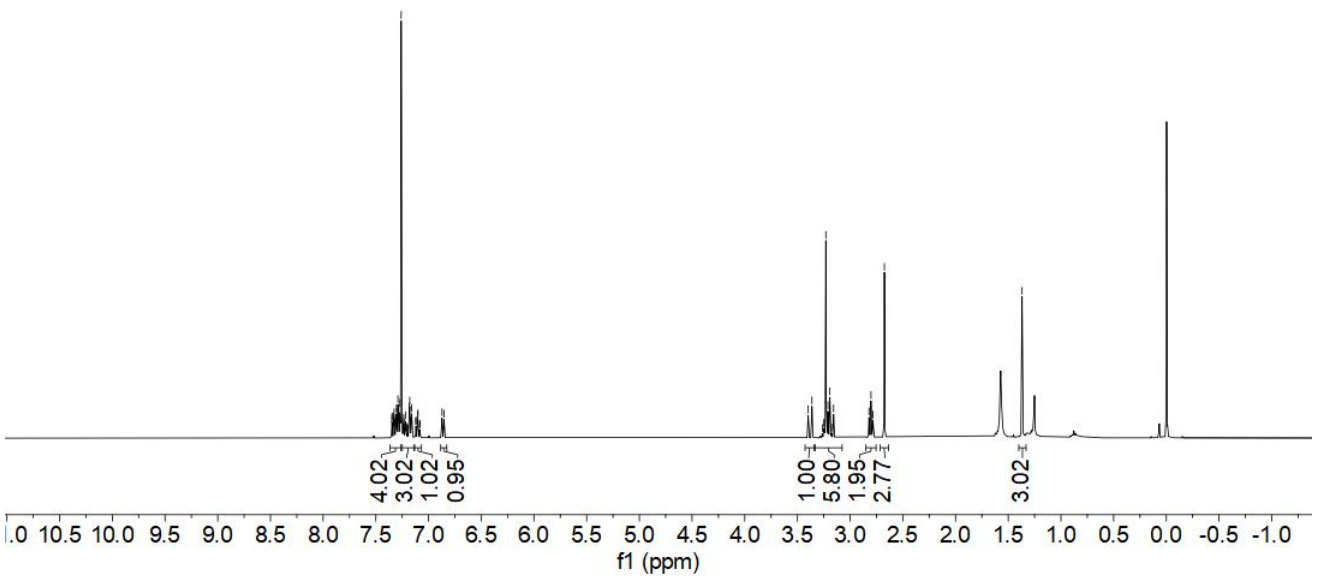
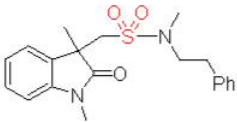
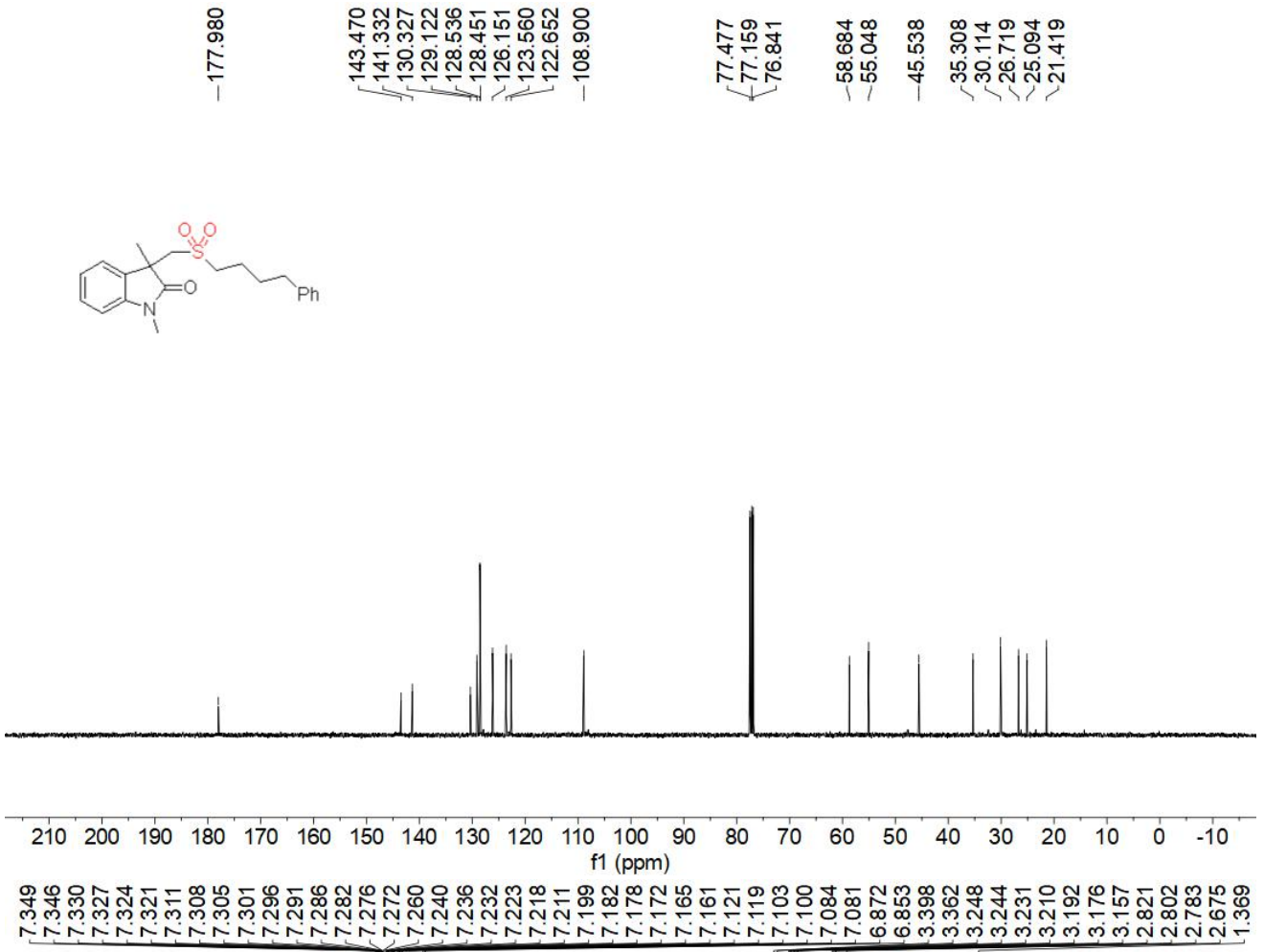
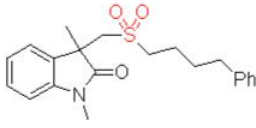


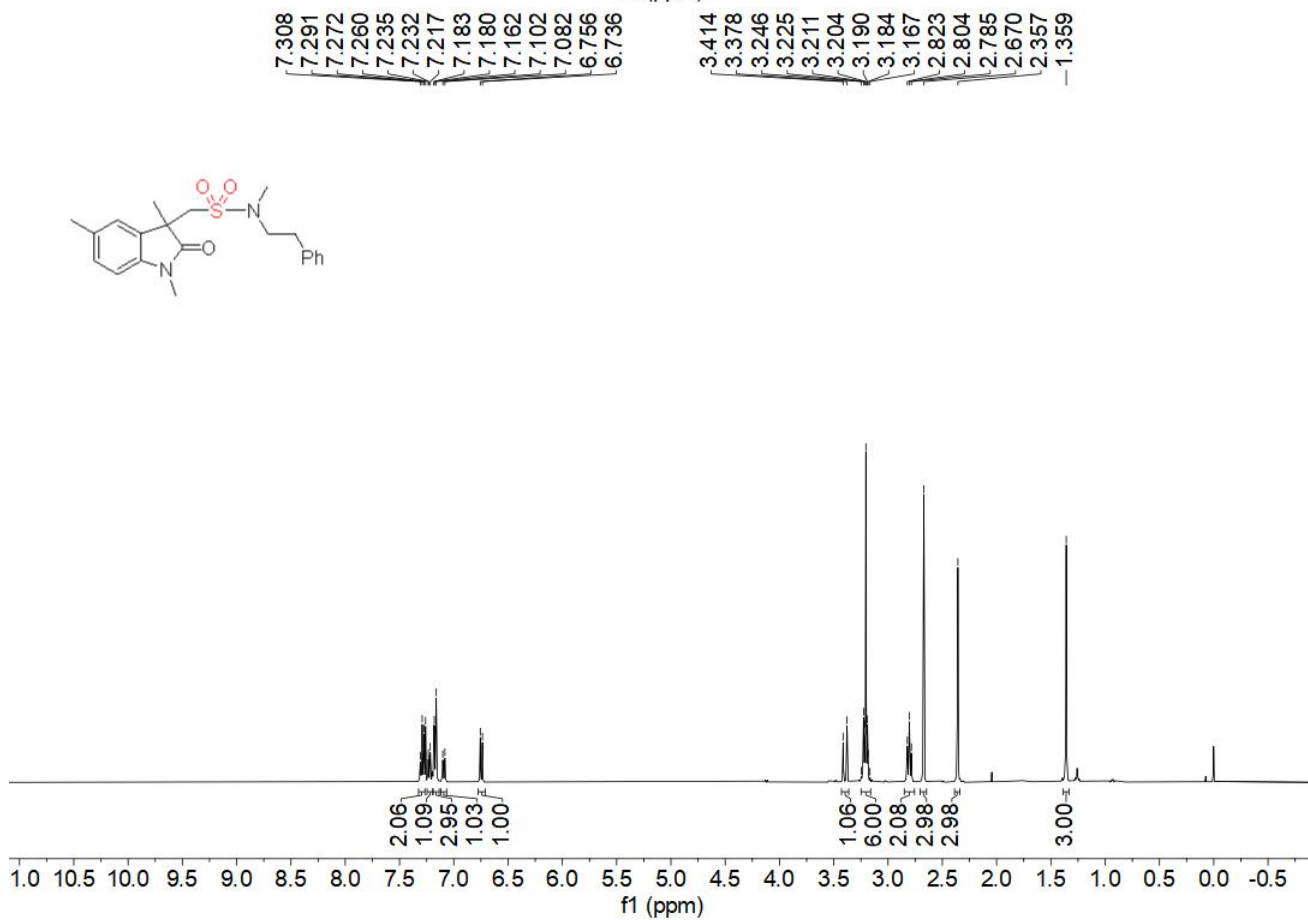
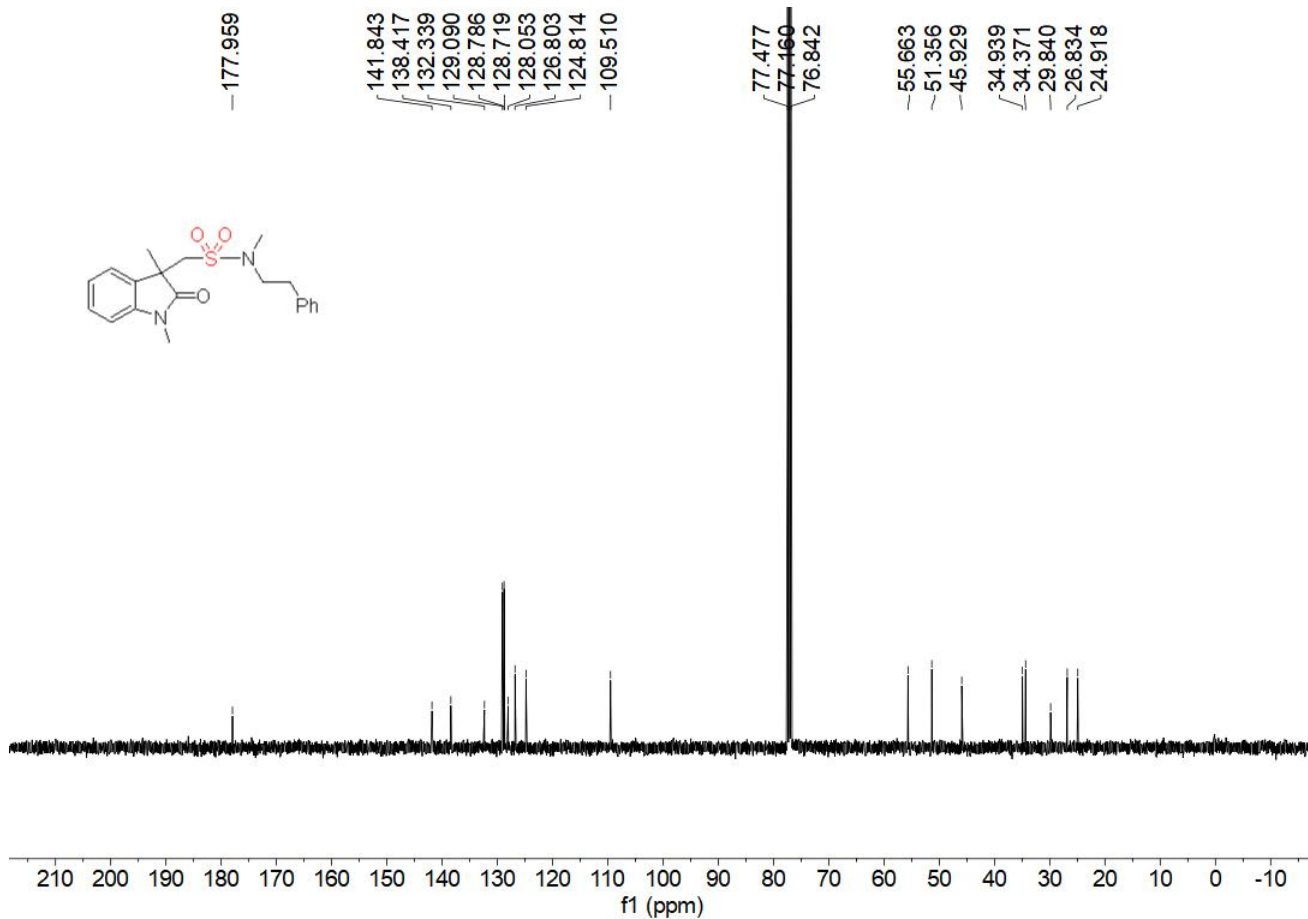


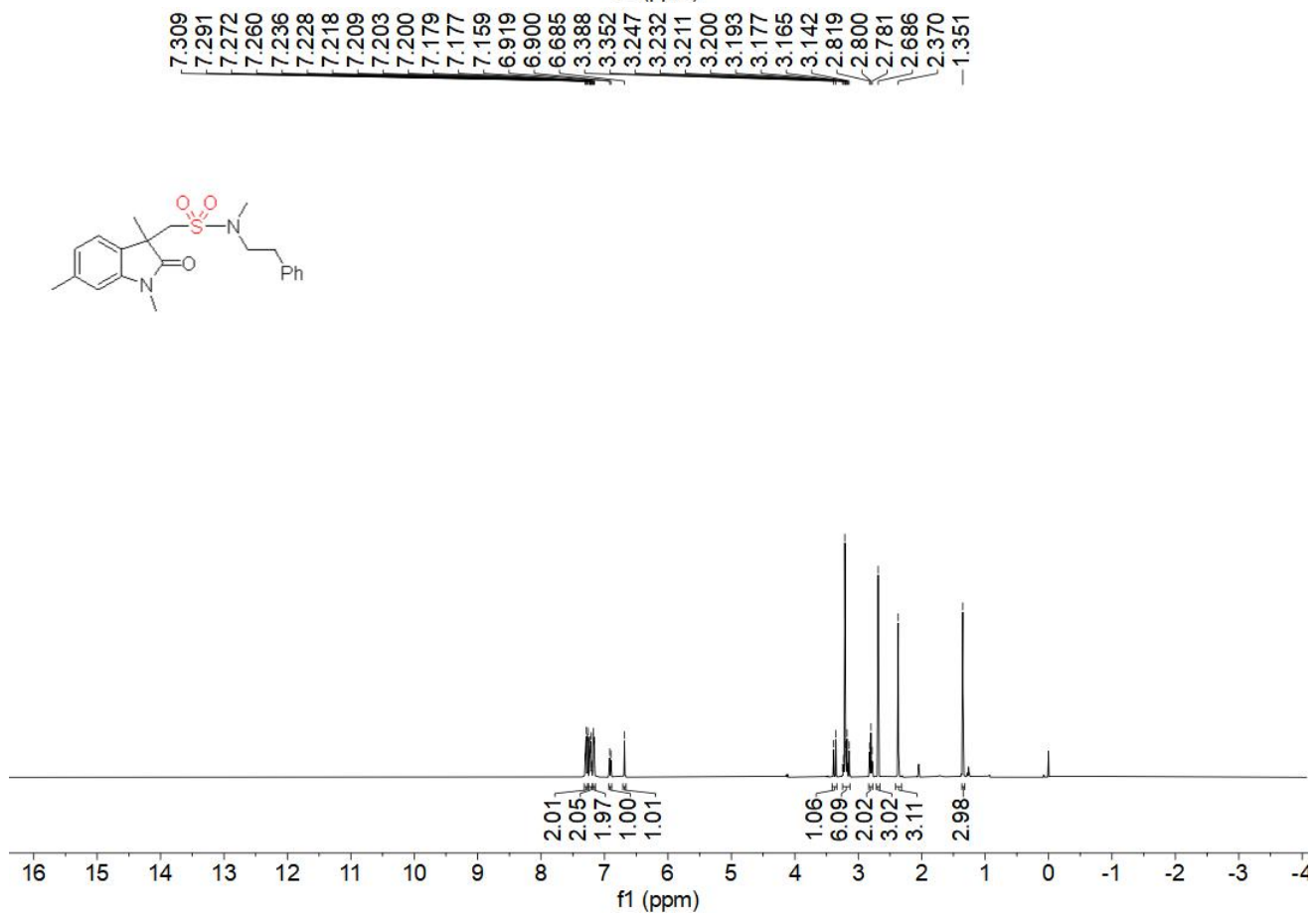
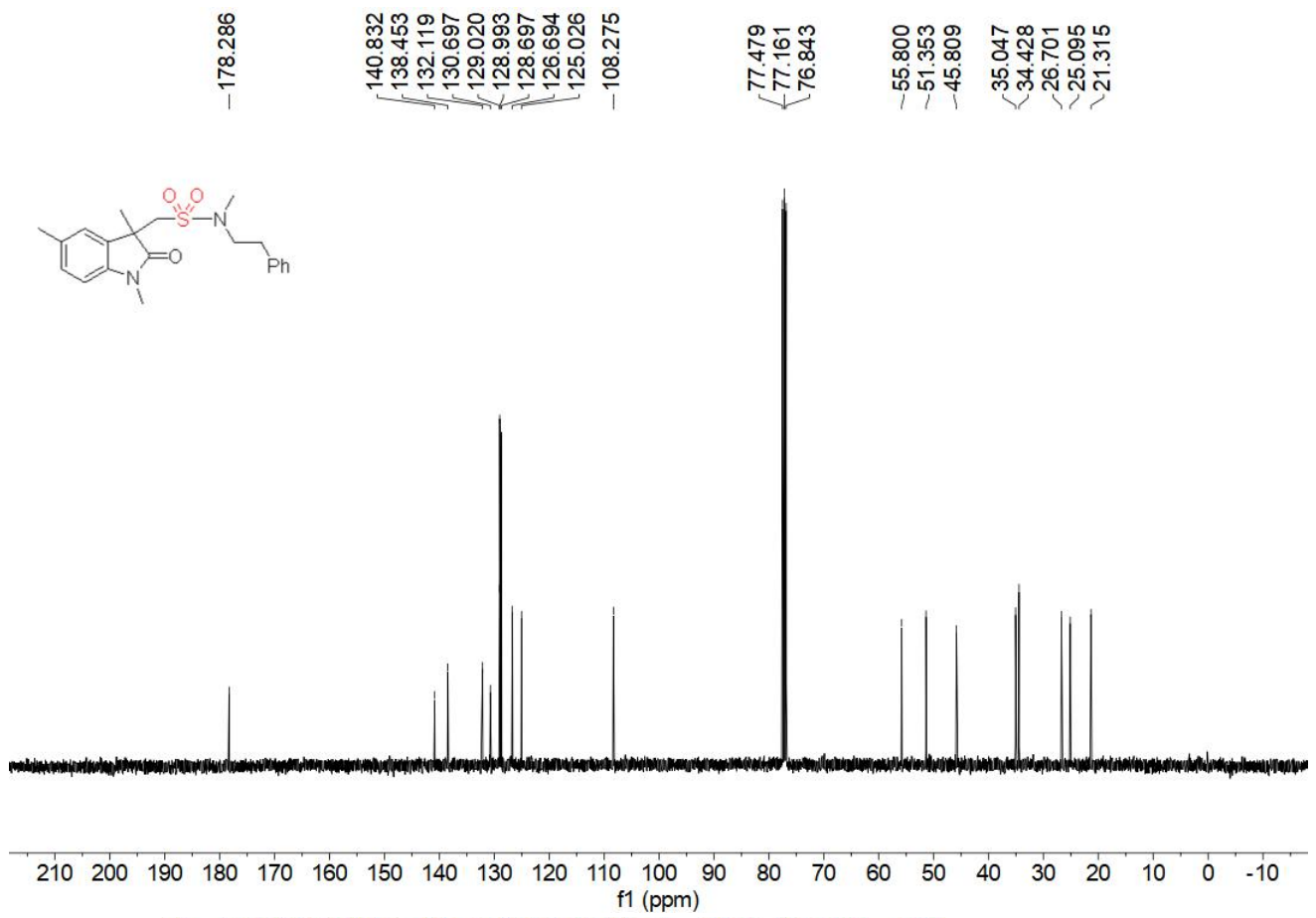


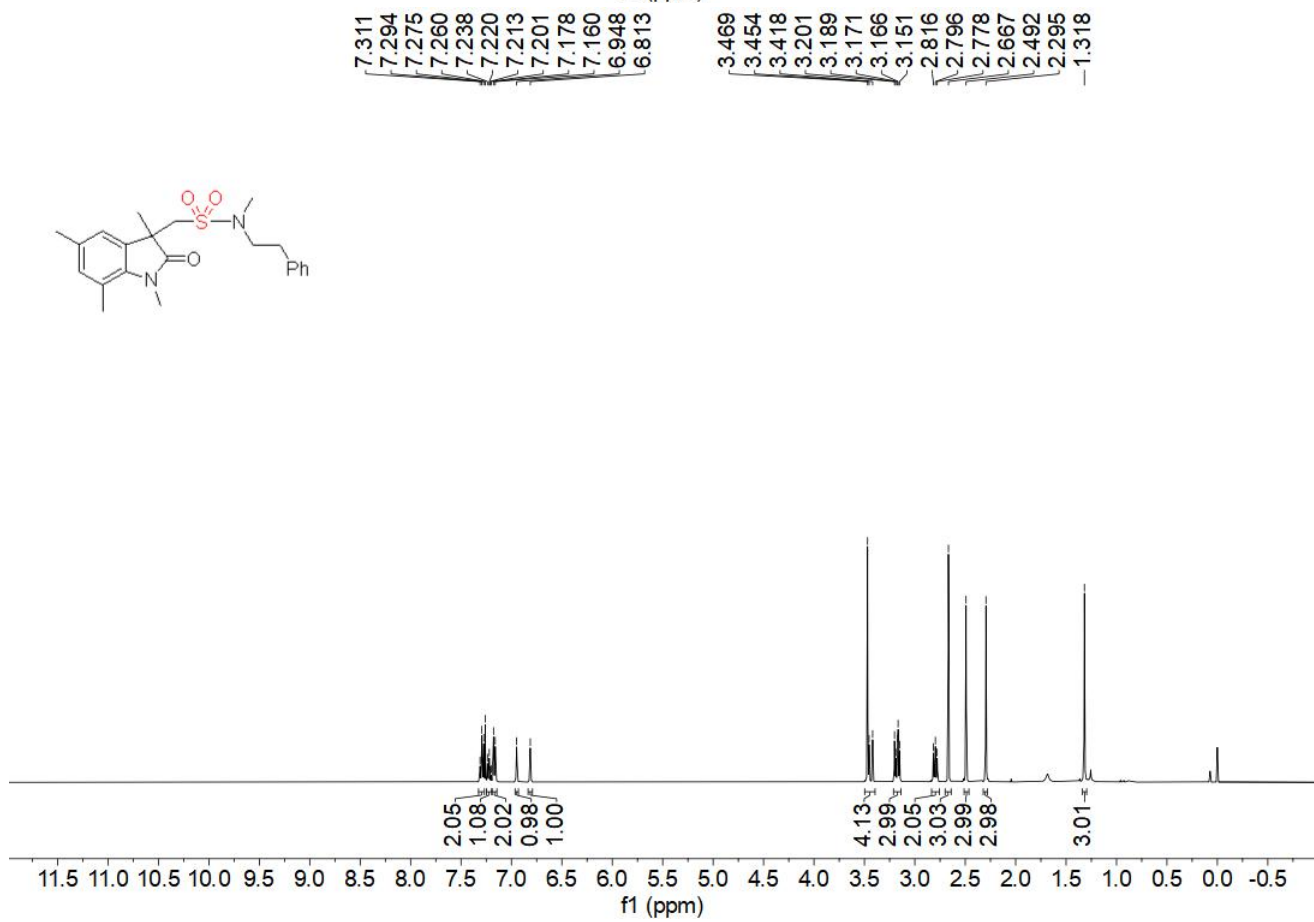
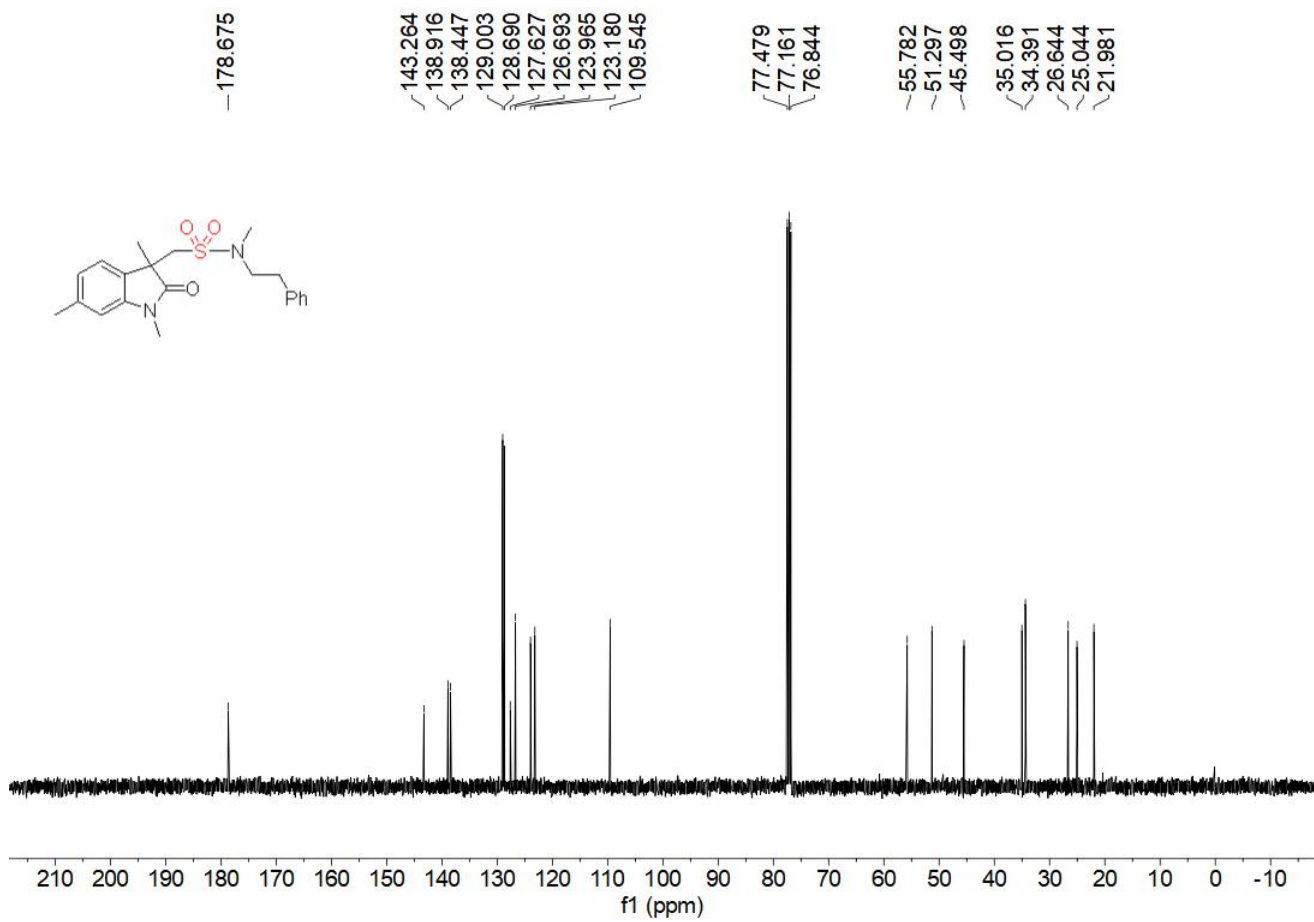


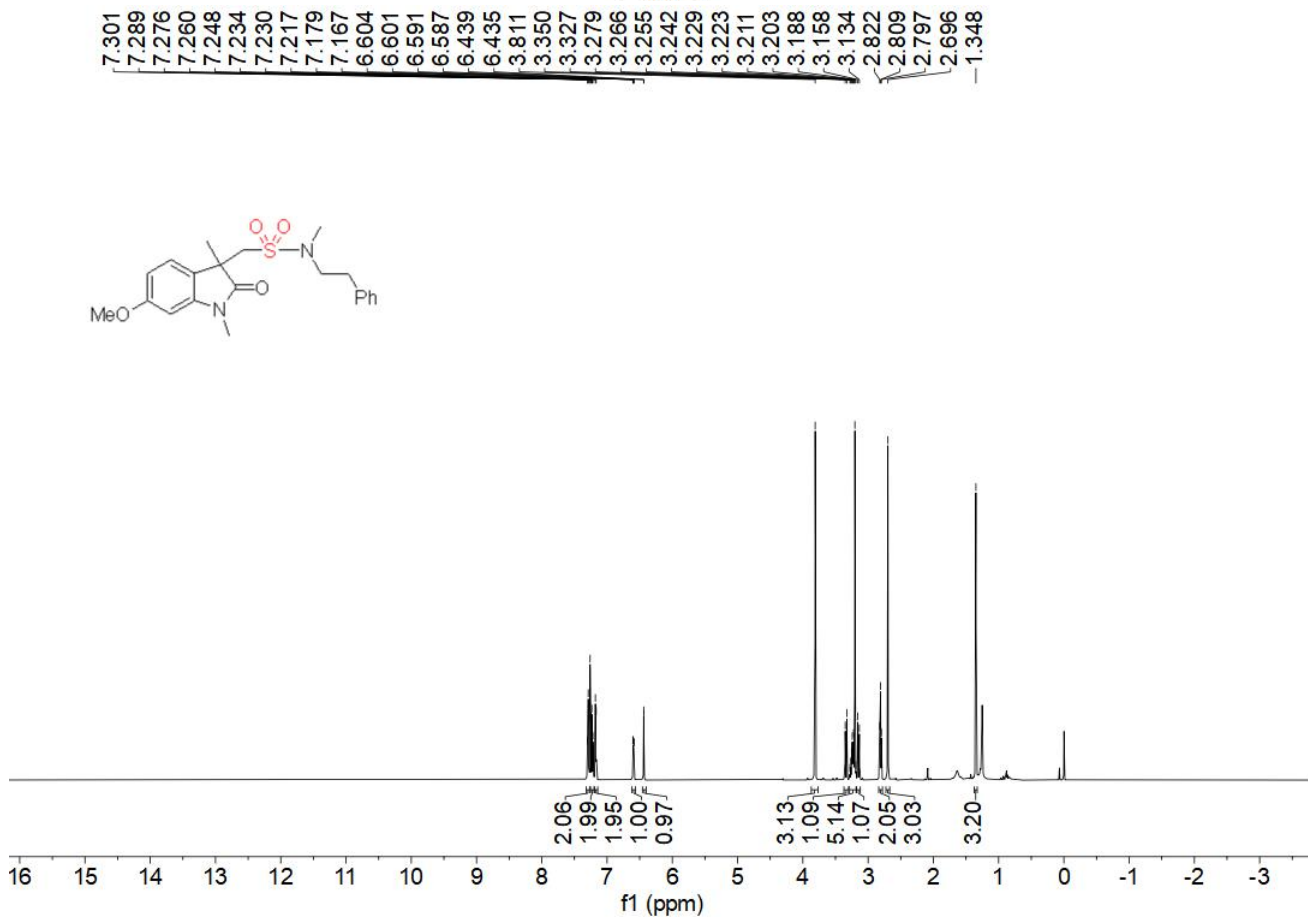
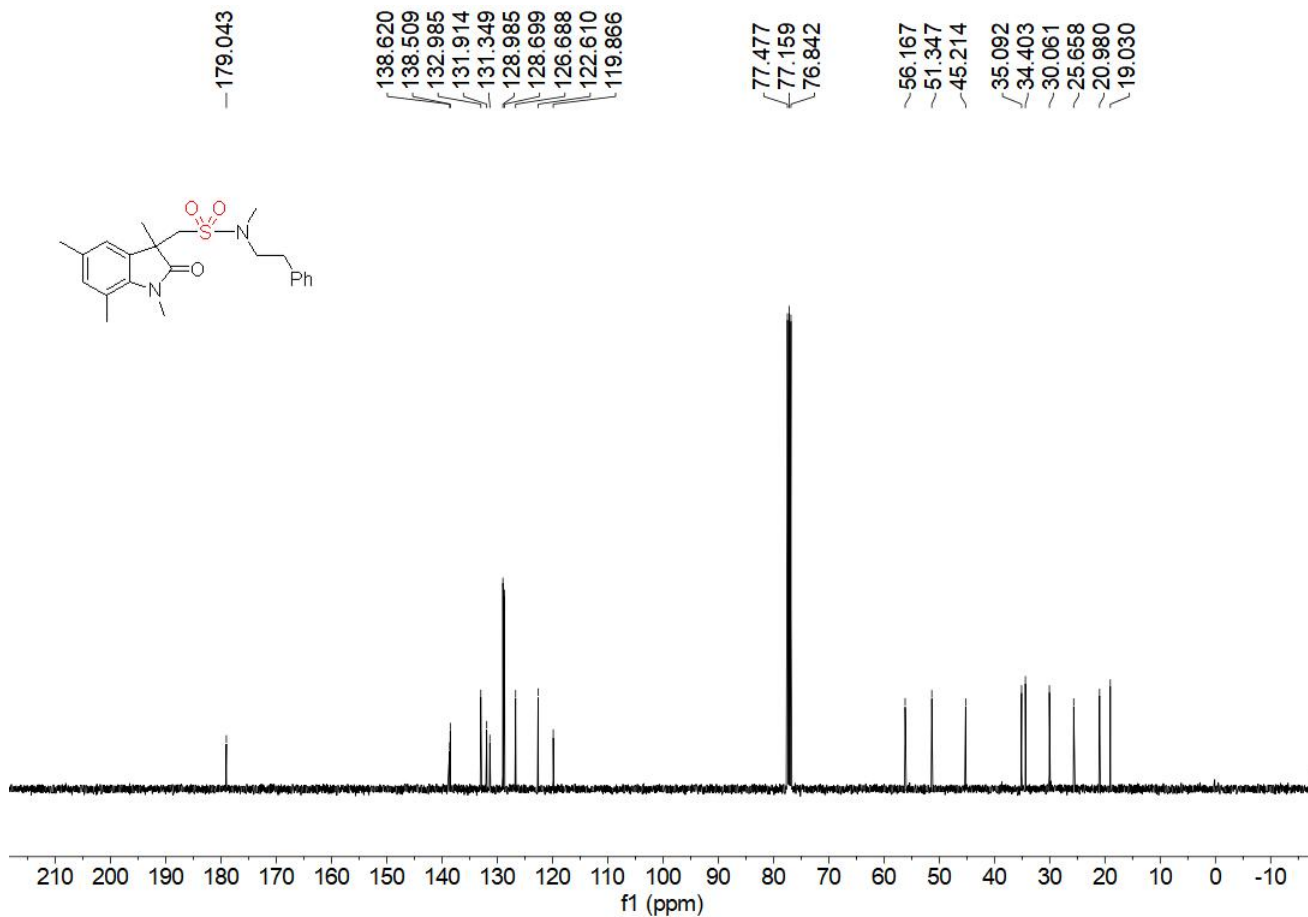


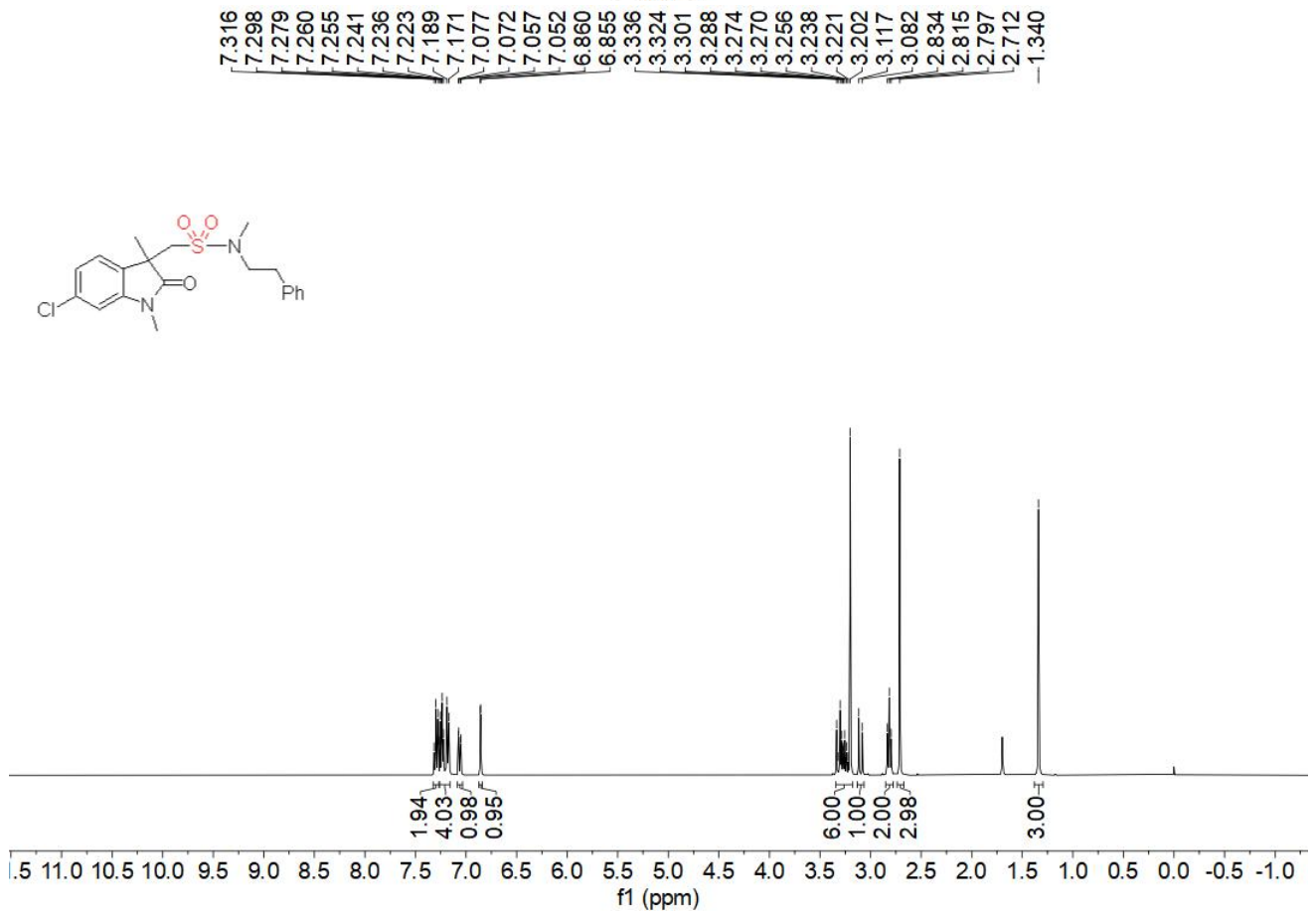
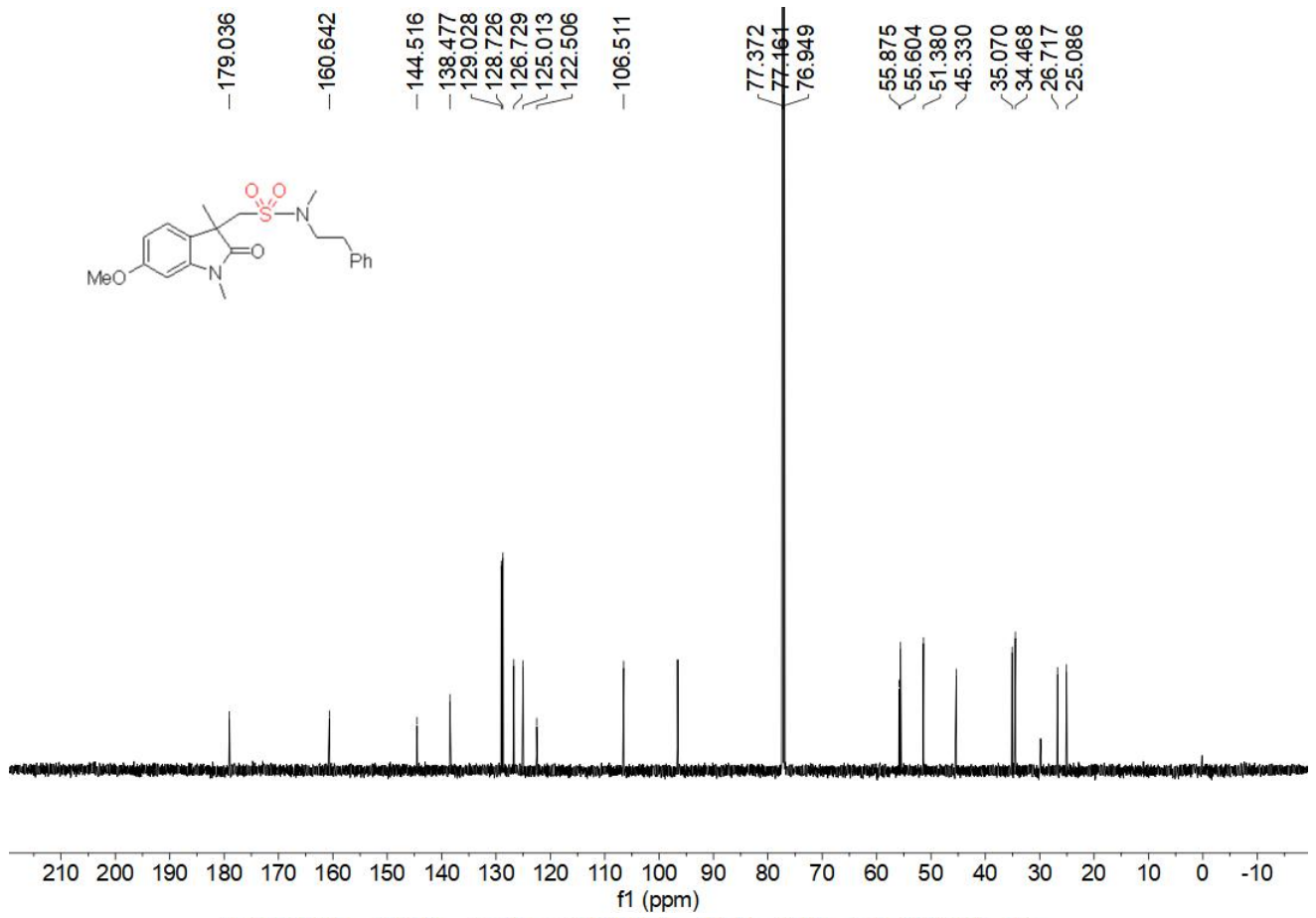


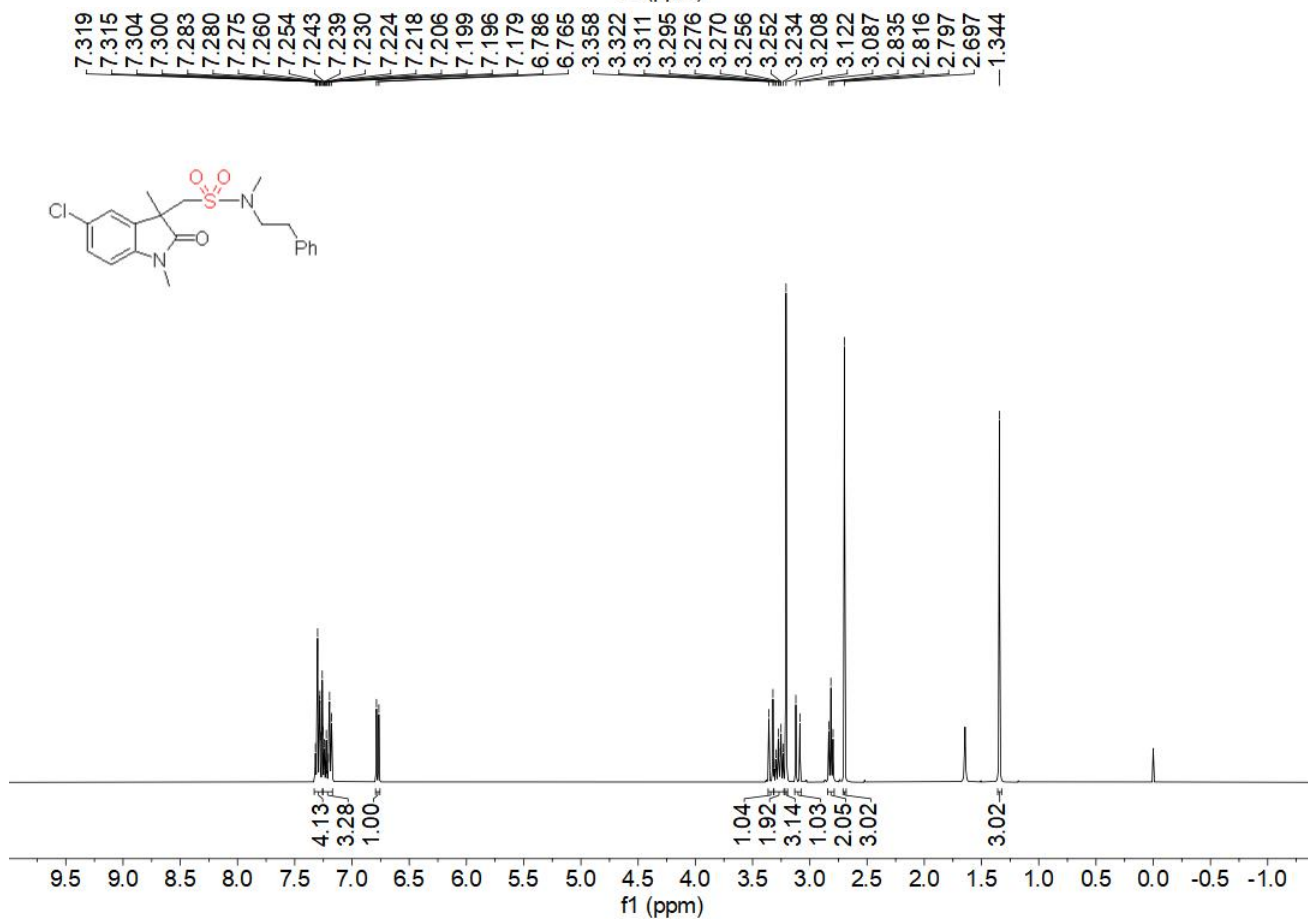
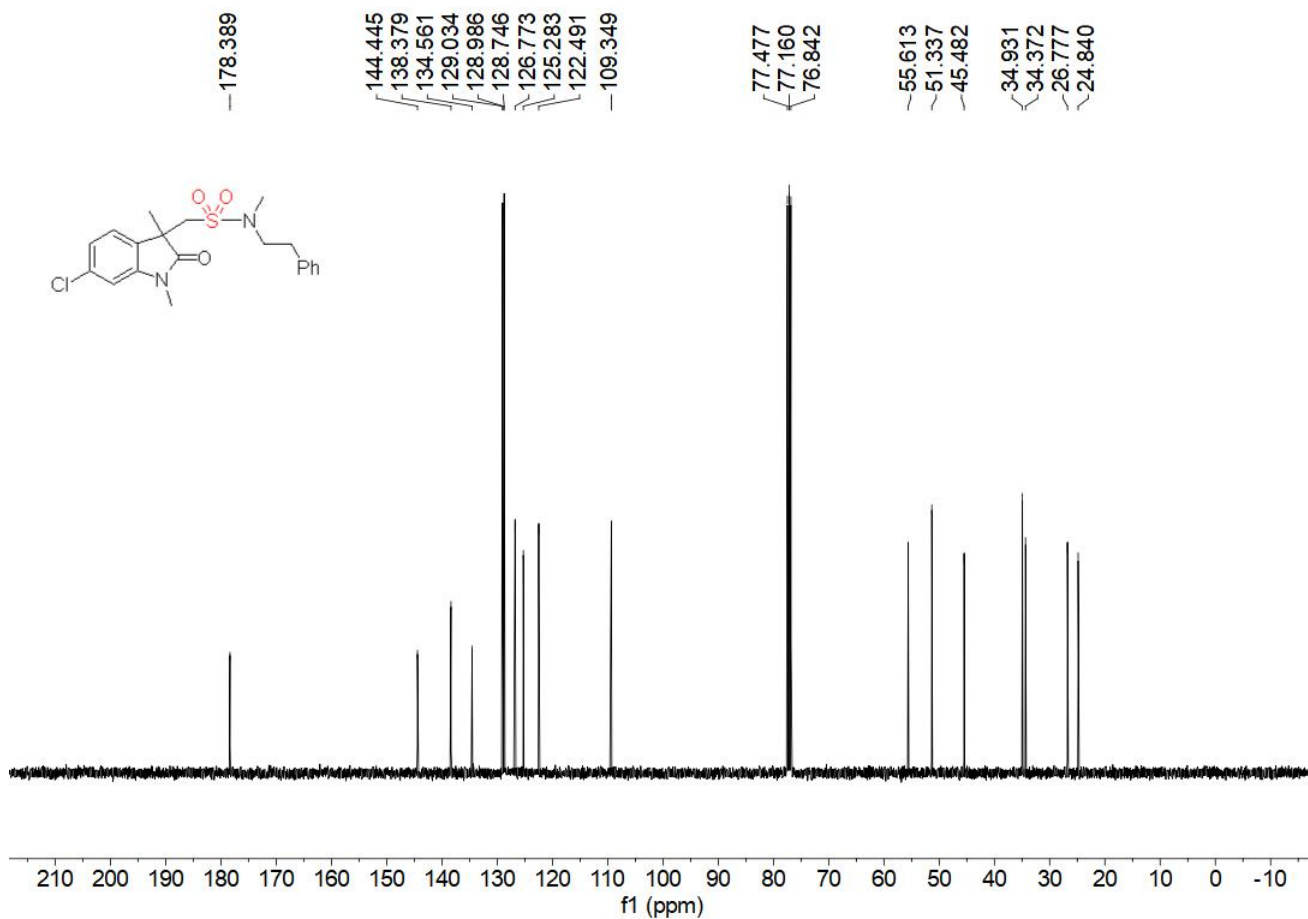


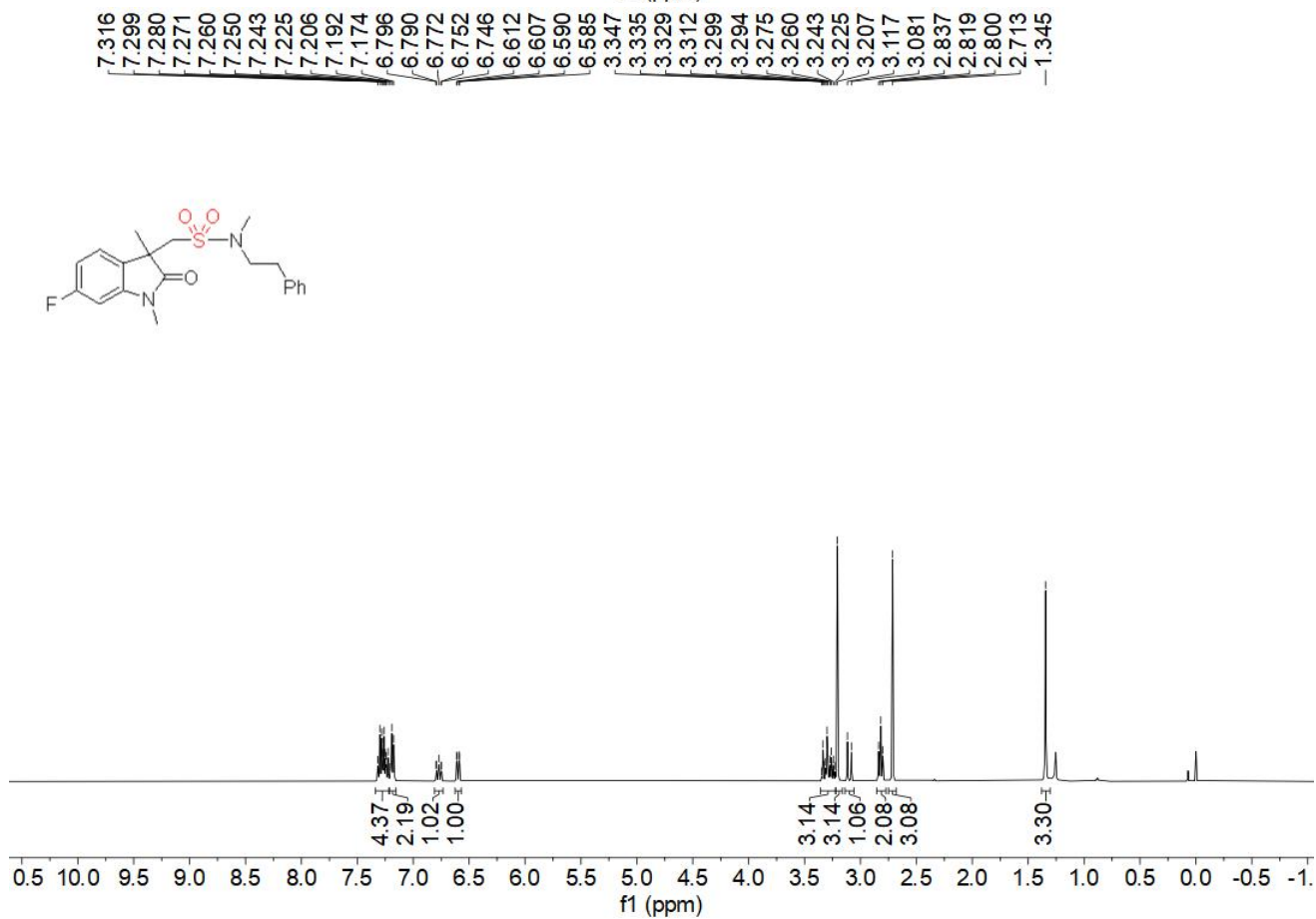
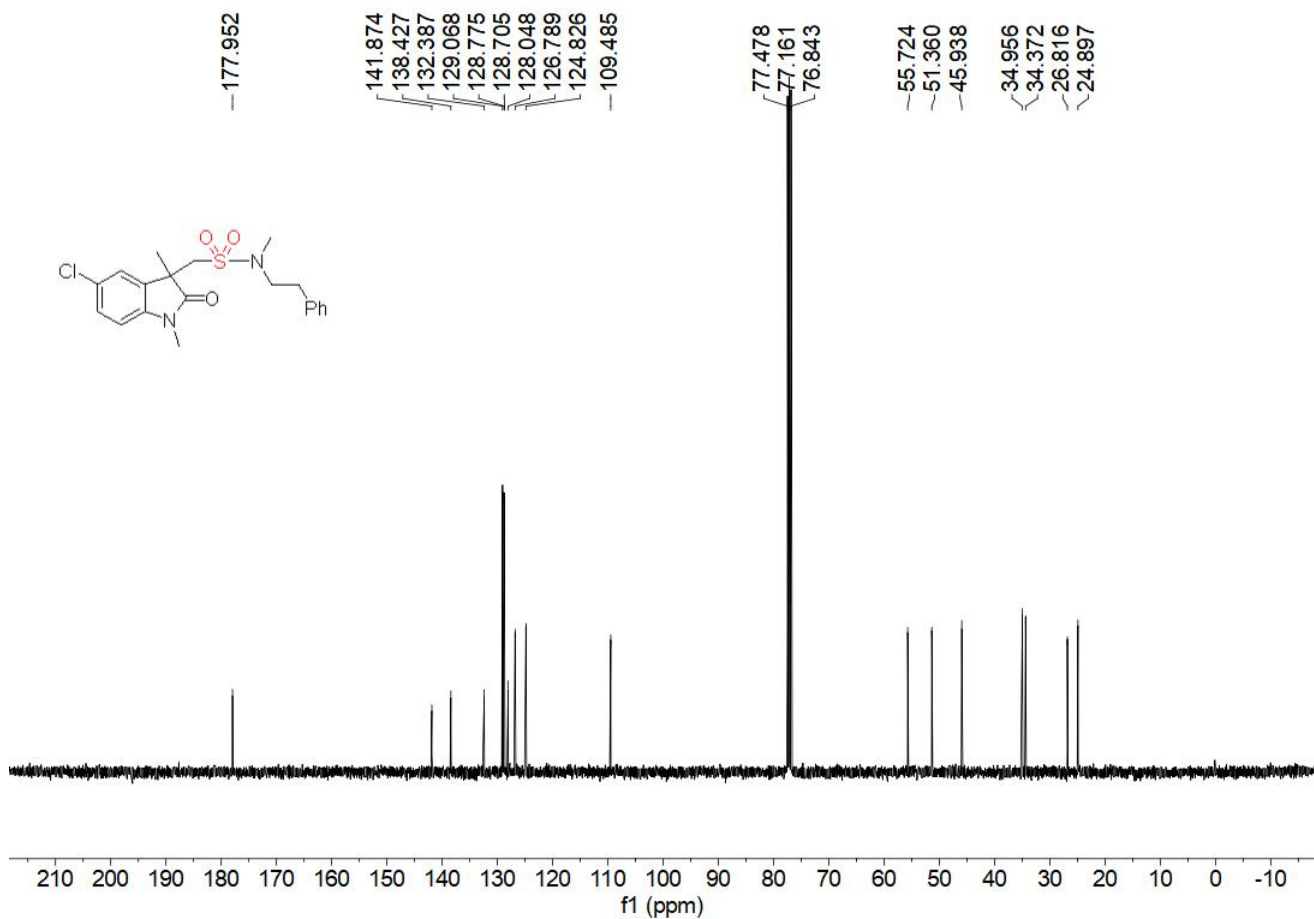


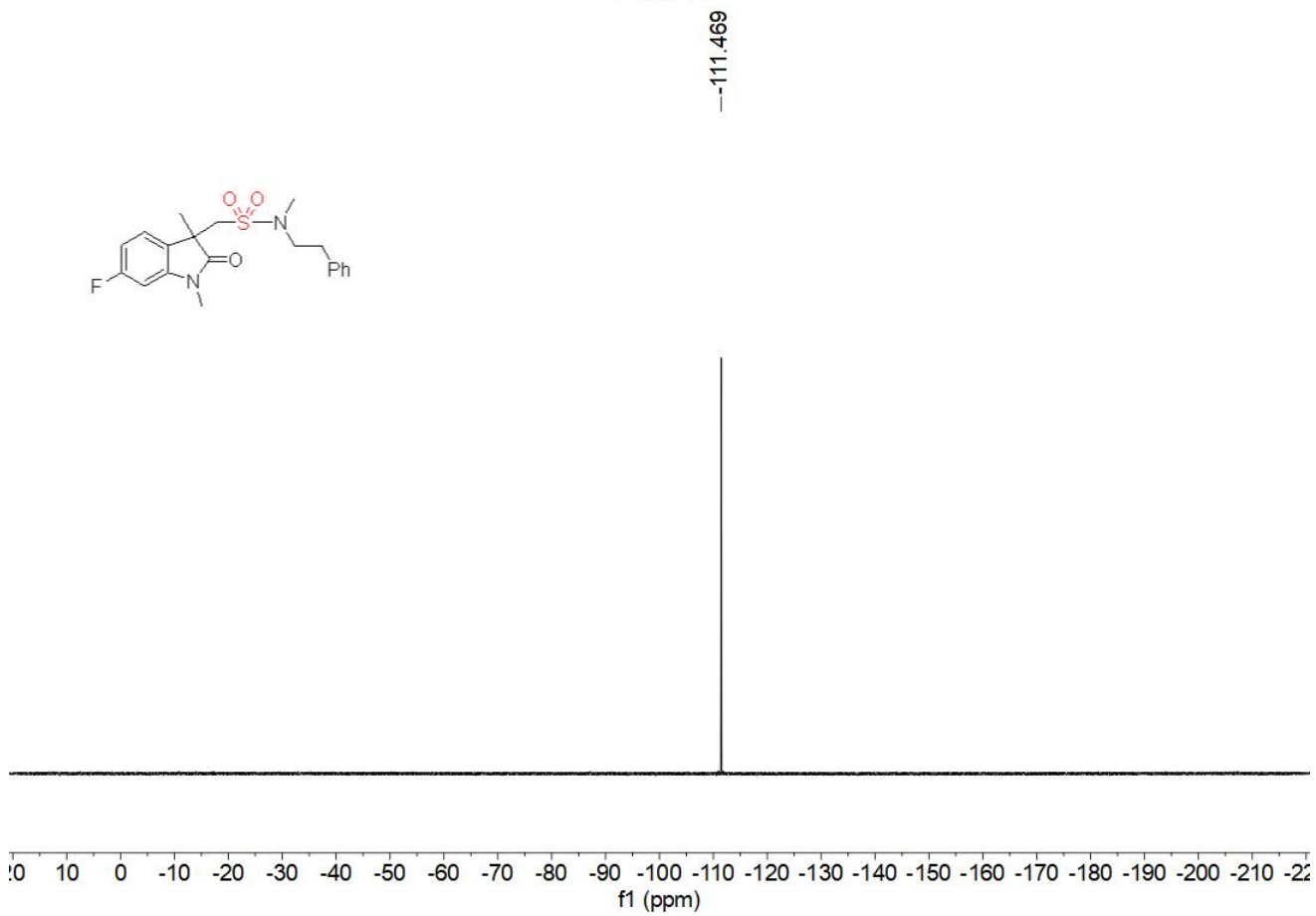
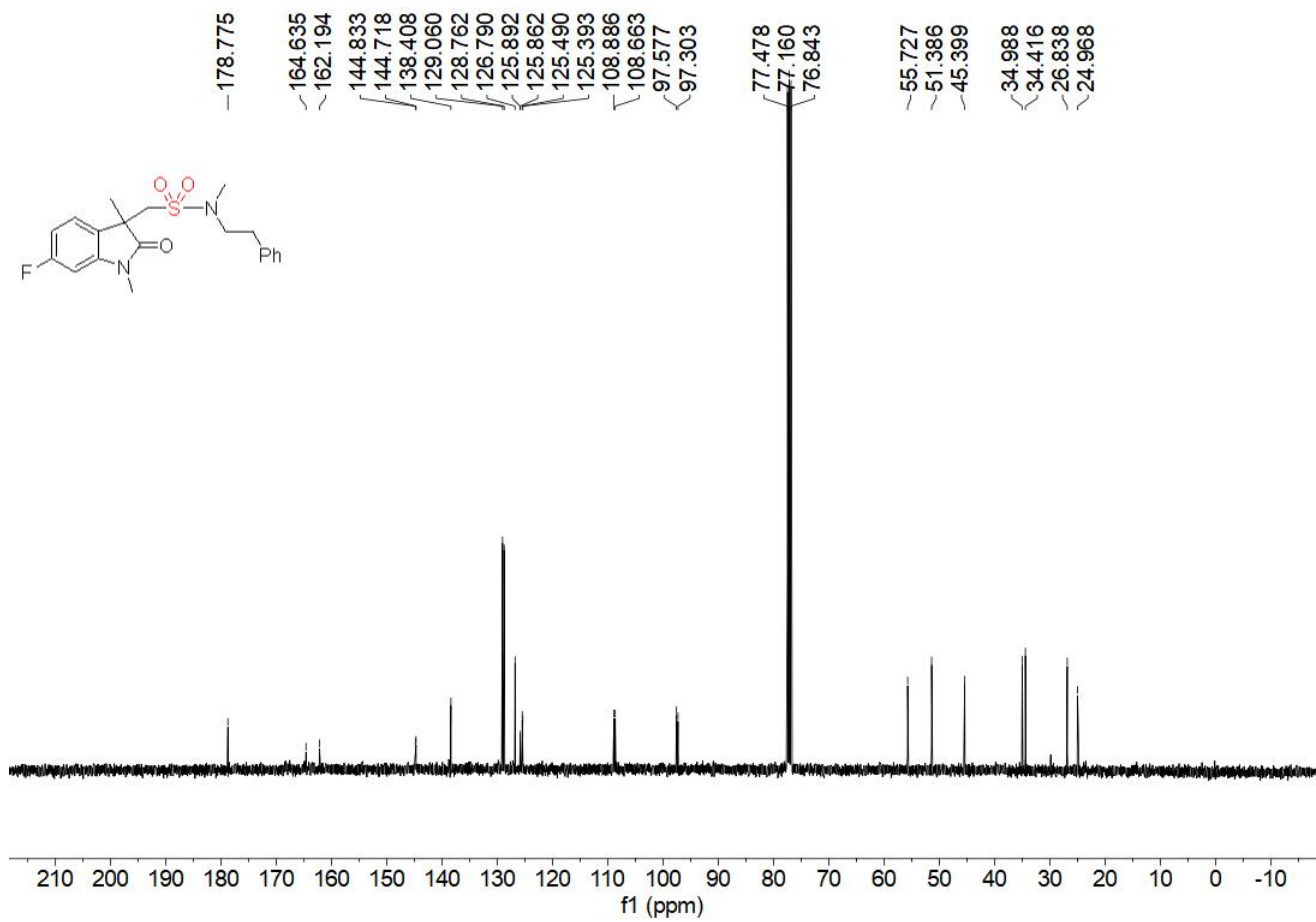




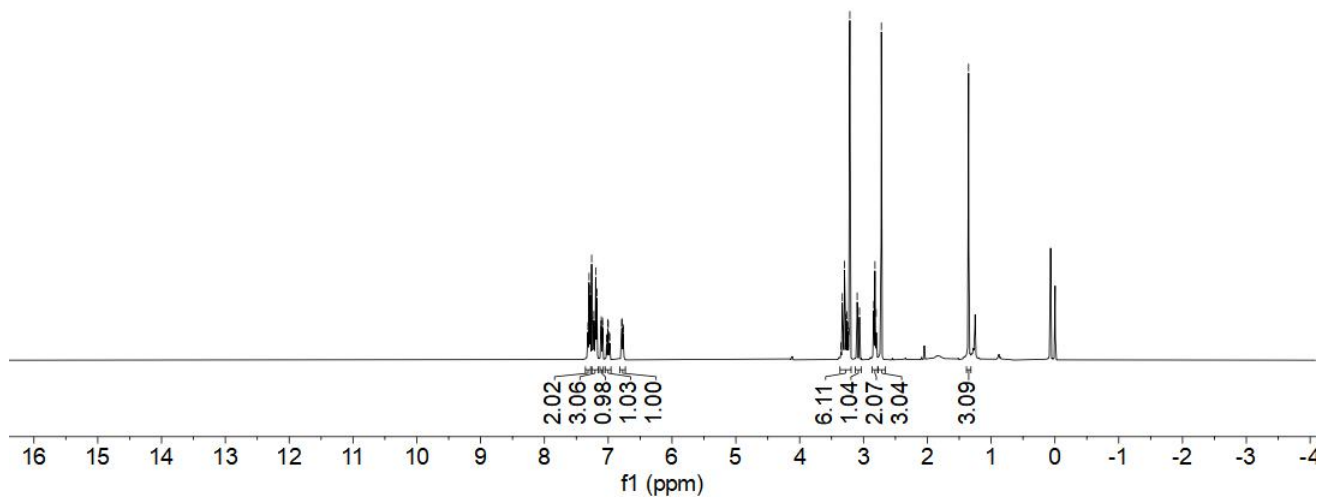
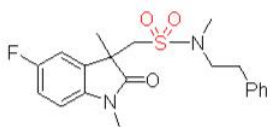




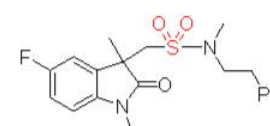
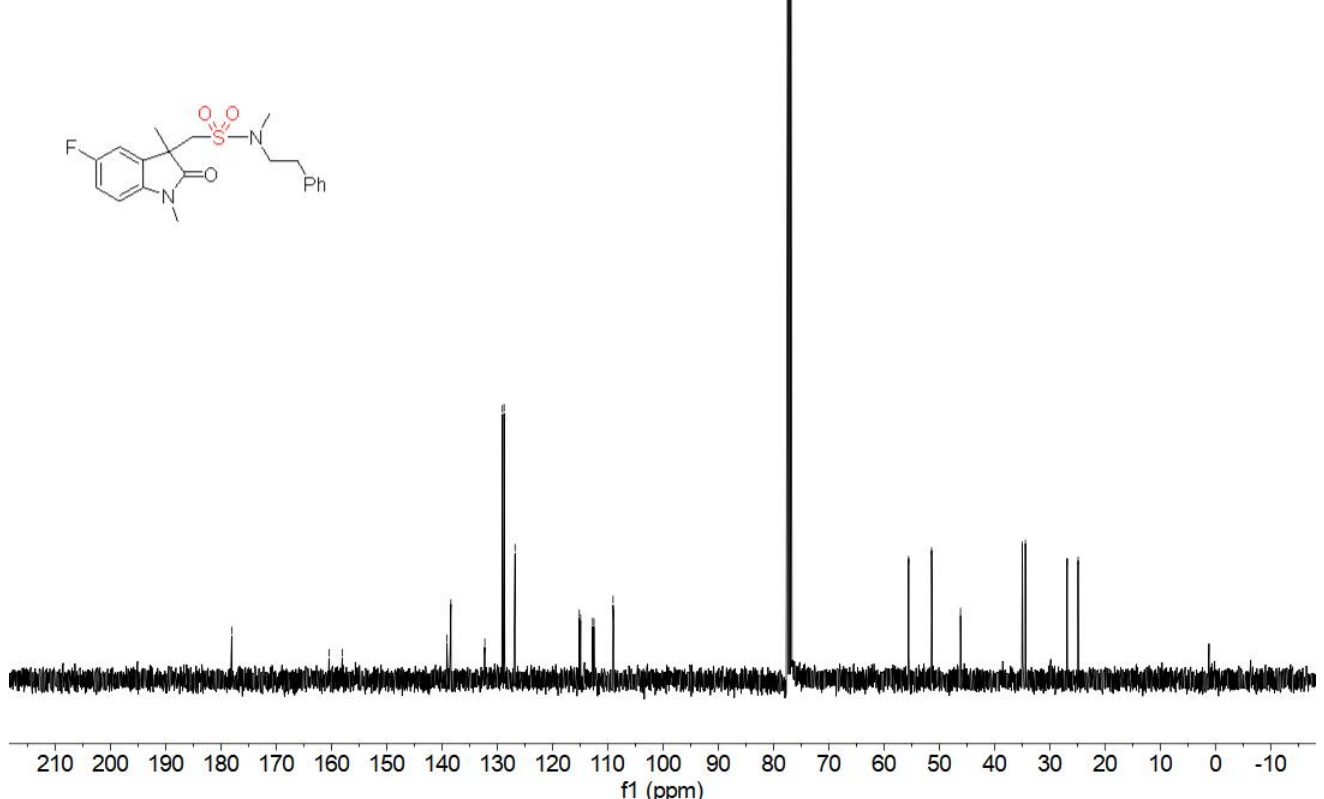




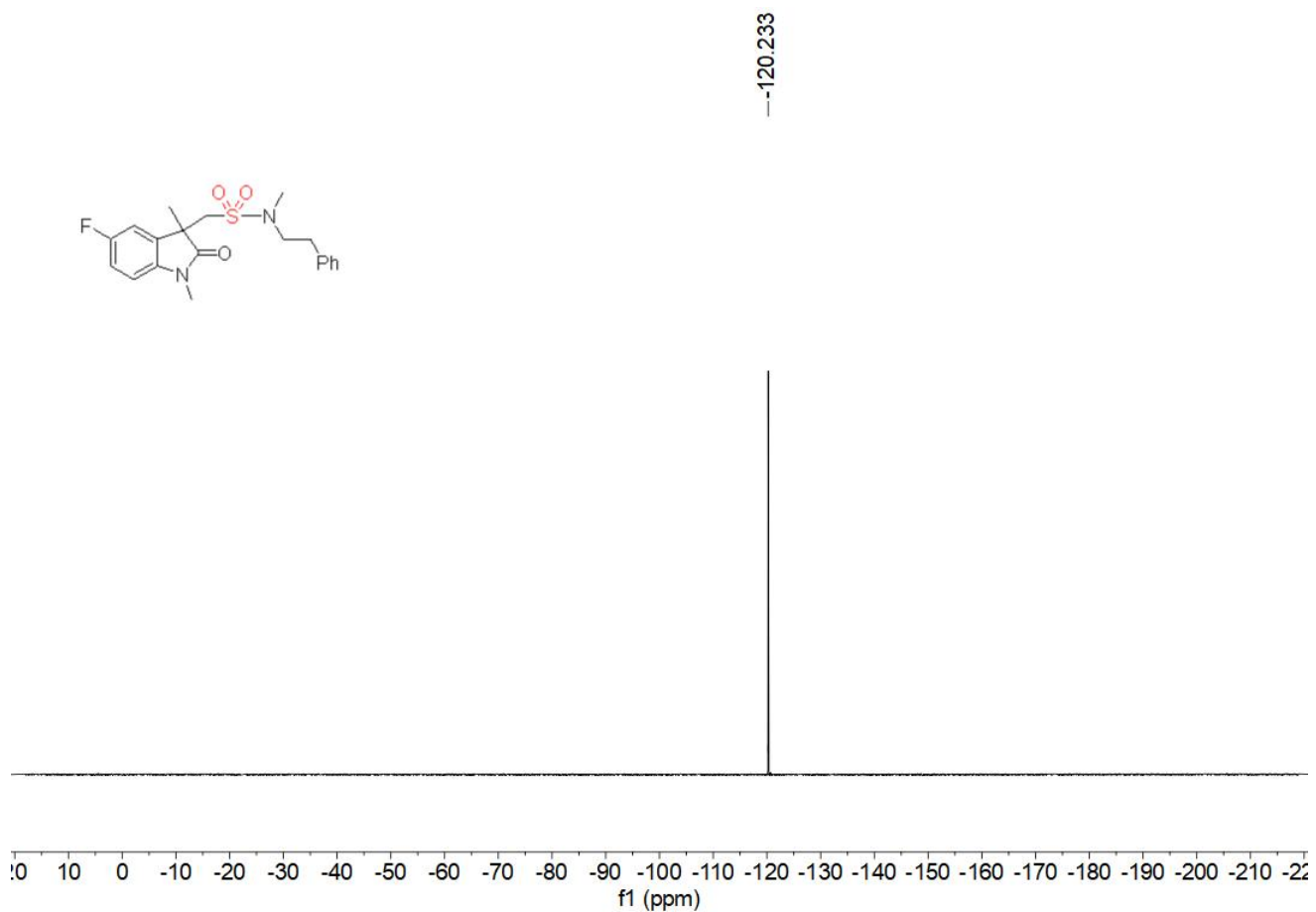
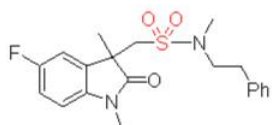
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7.027
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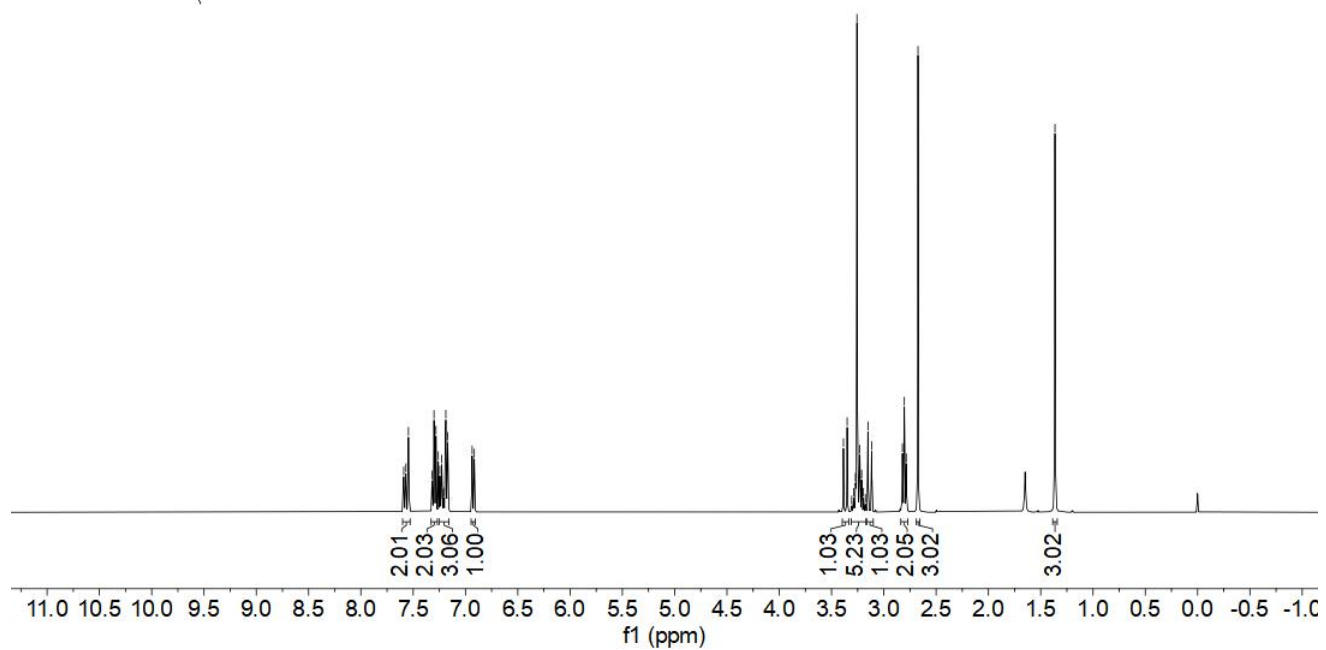
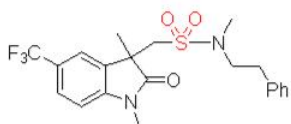
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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



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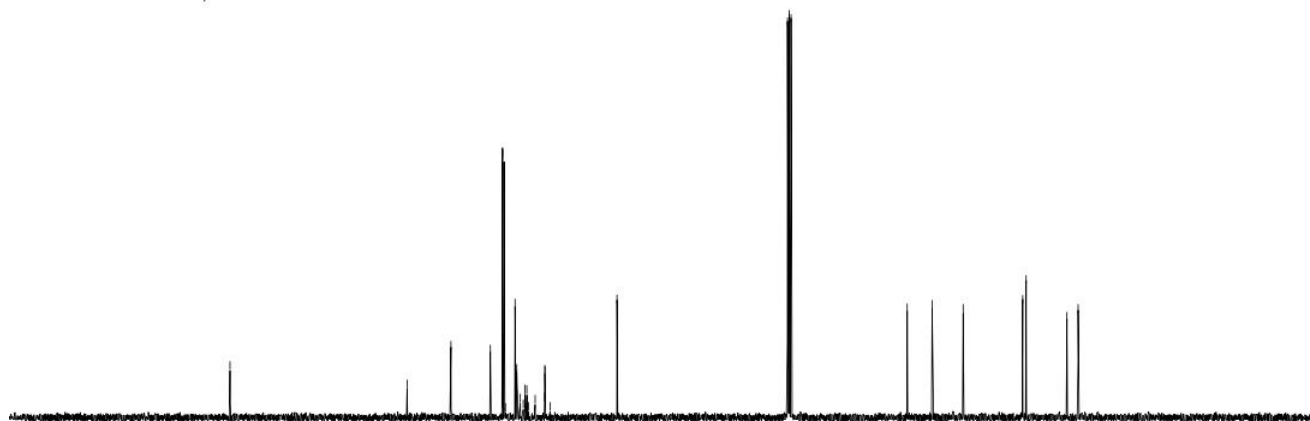
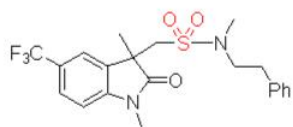
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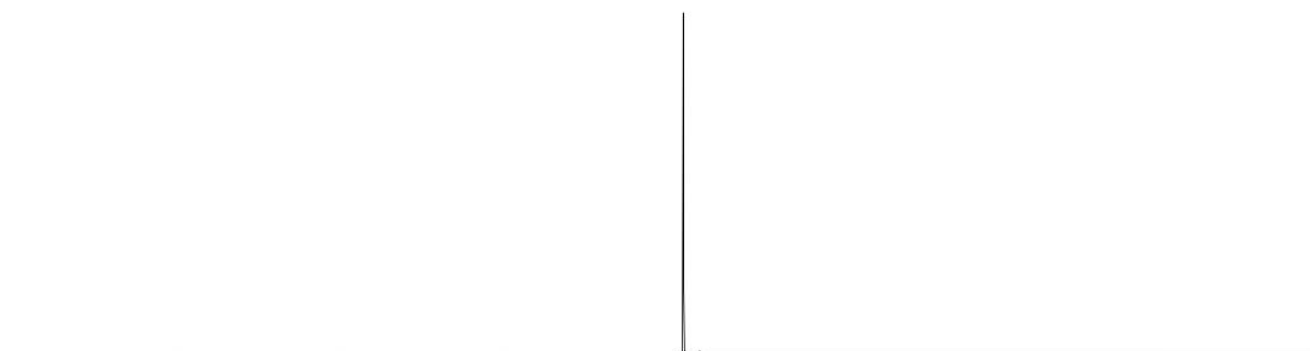
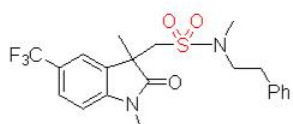
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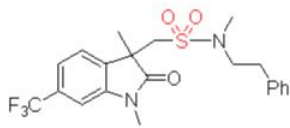
f1 (ppm)

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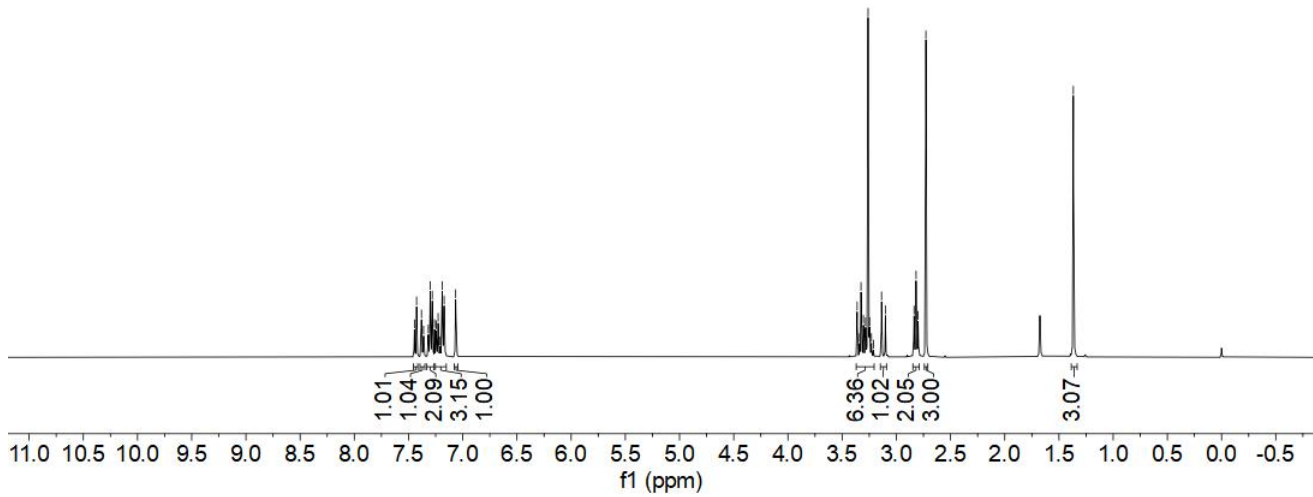
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f1 (ppm)



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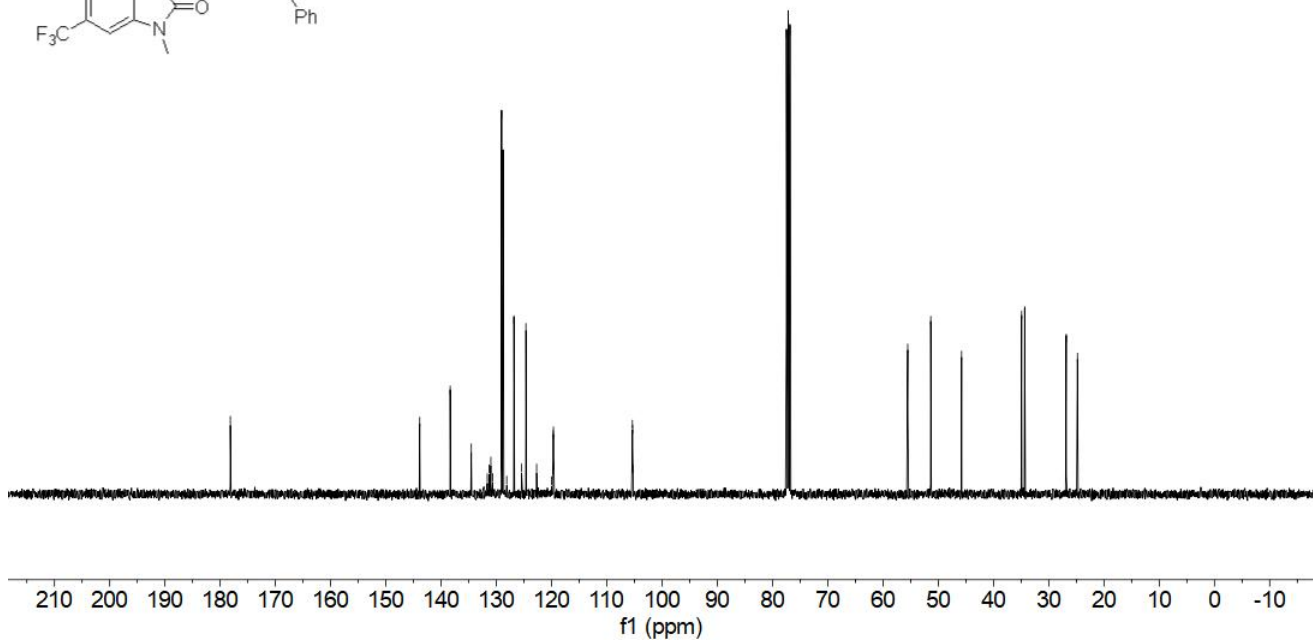
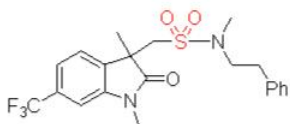


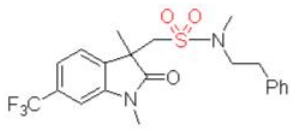
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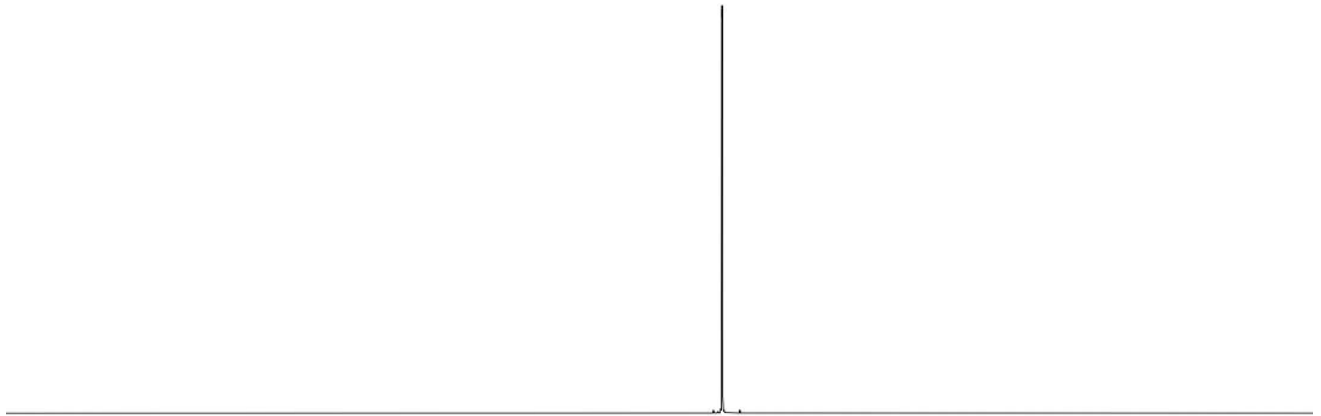
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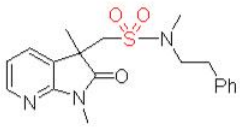


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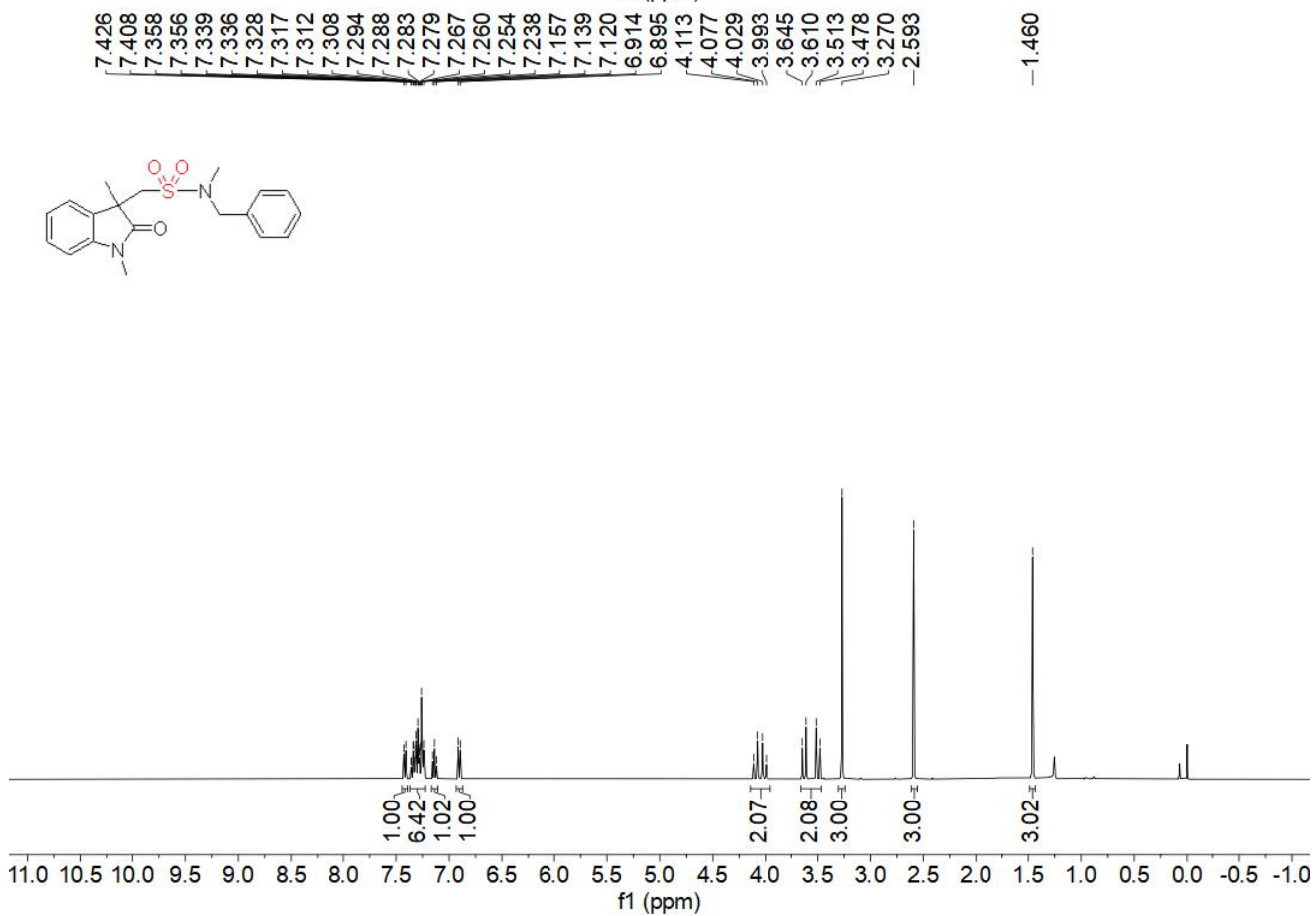
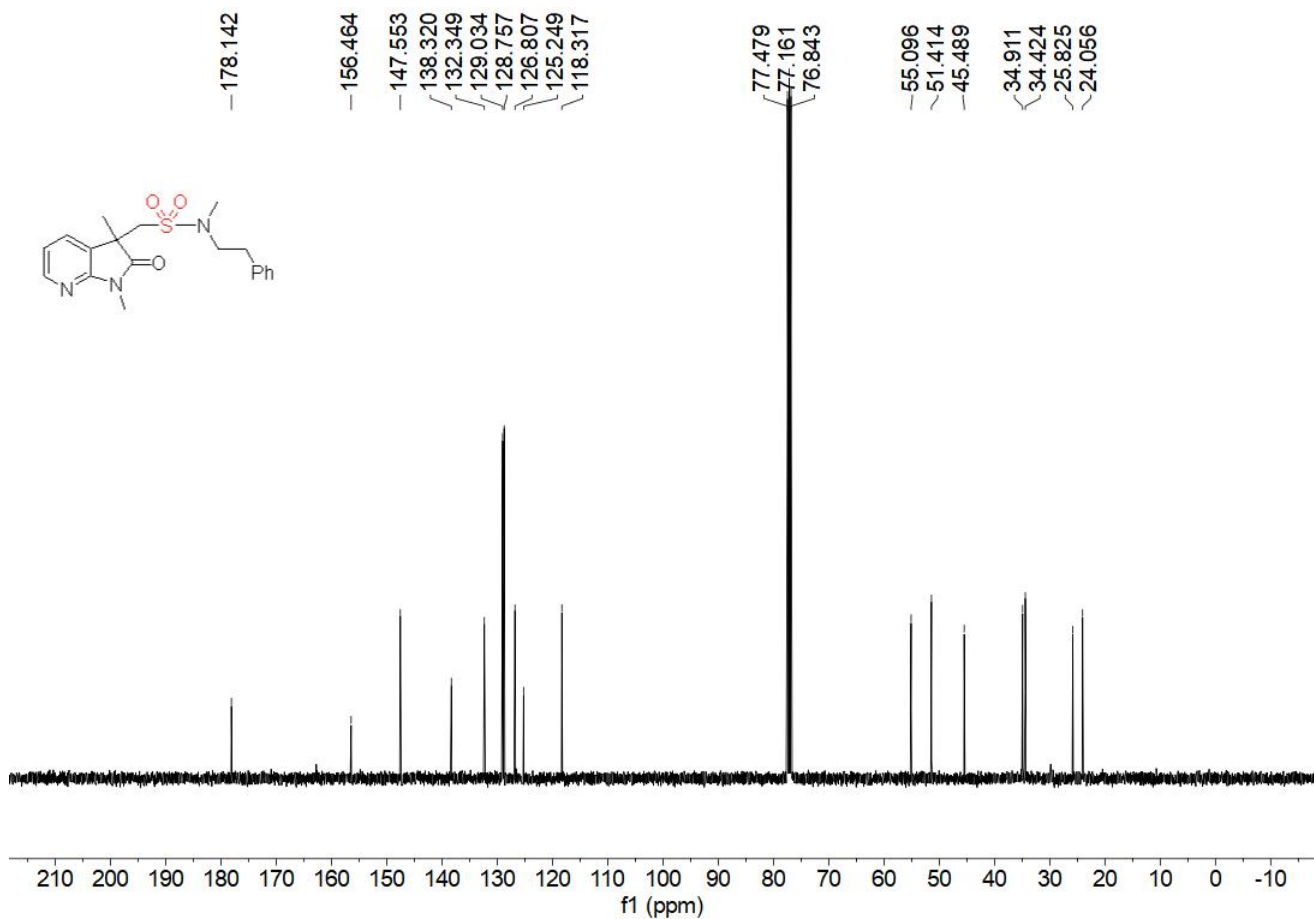
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f1 (ppm)

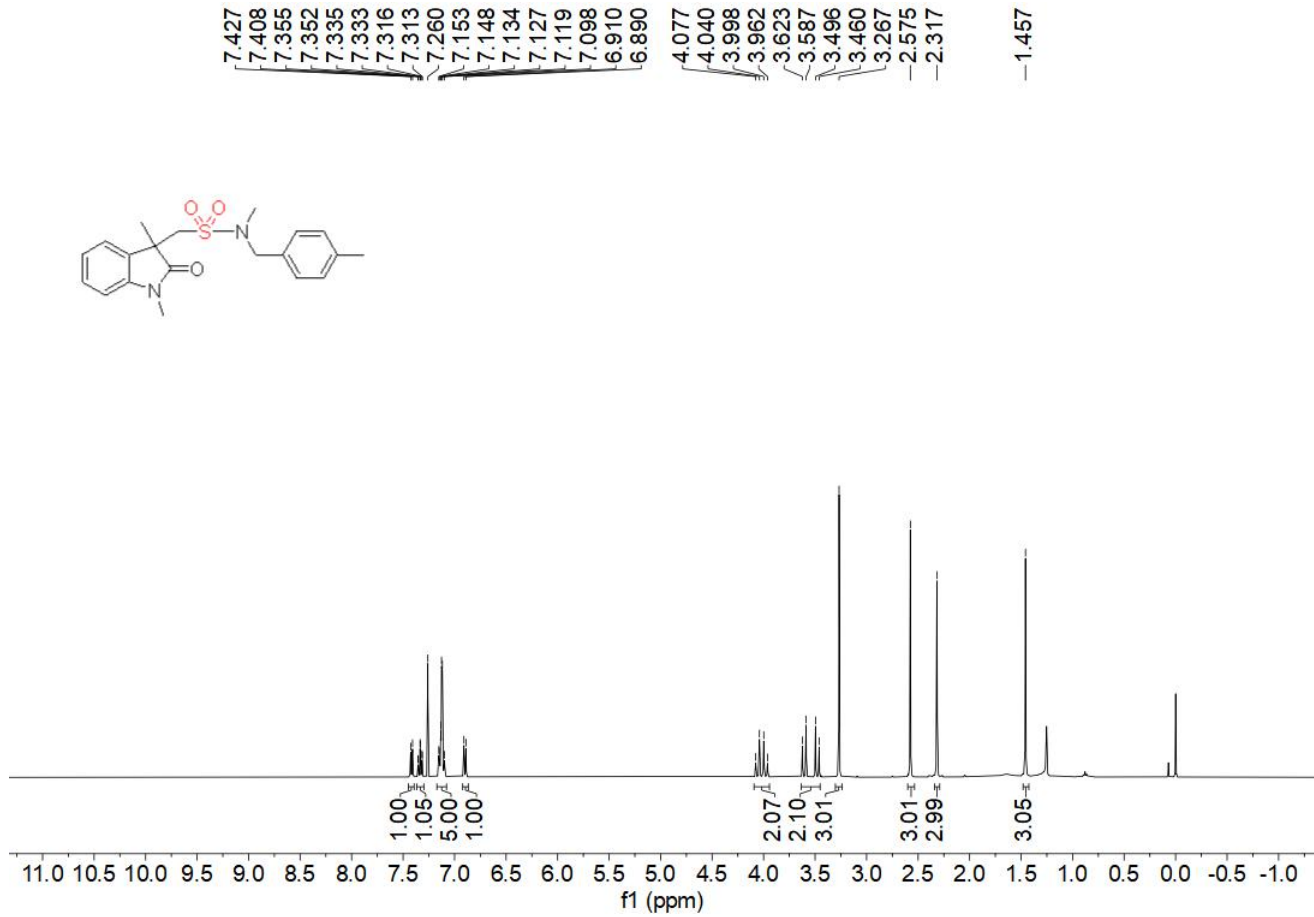
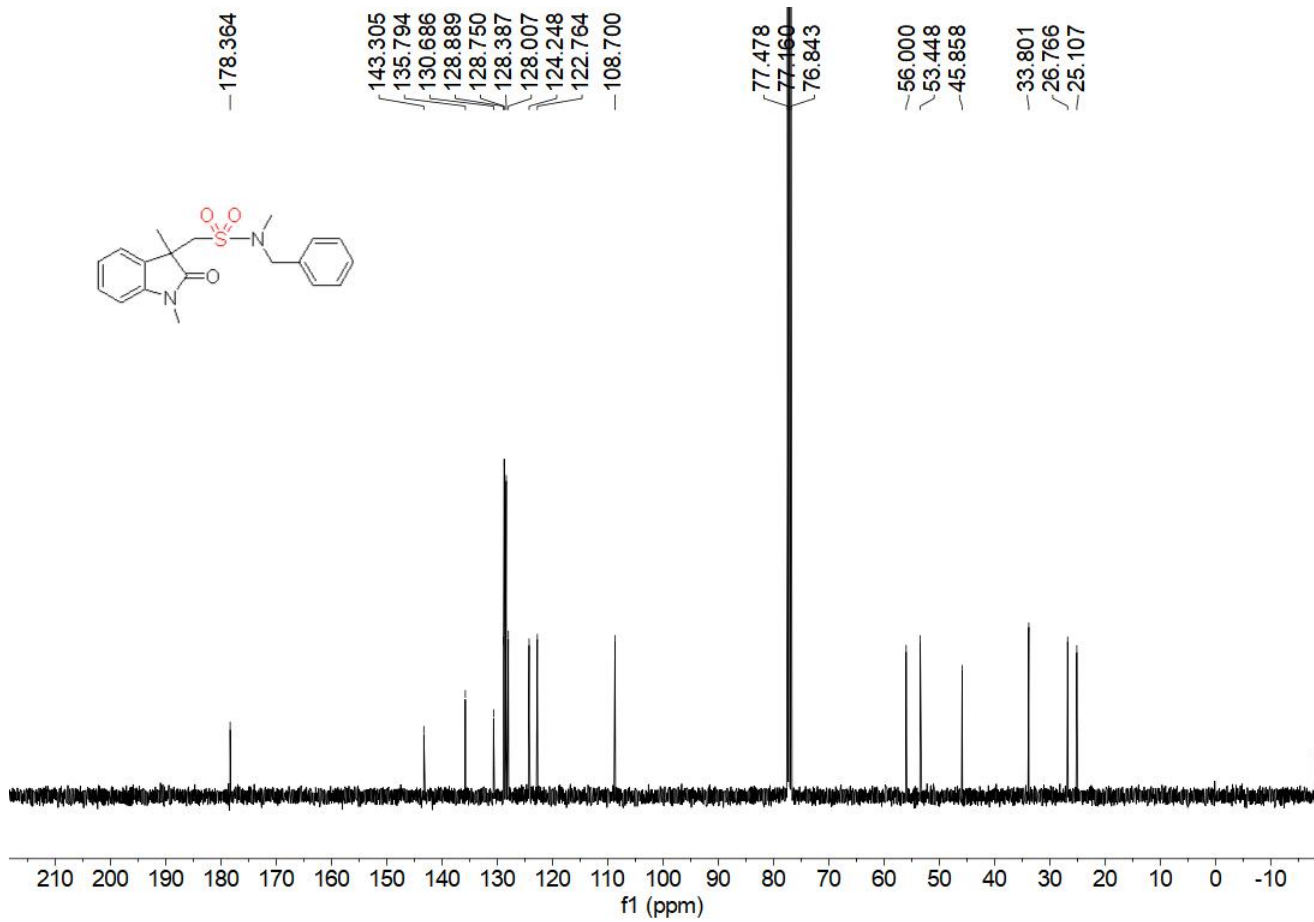
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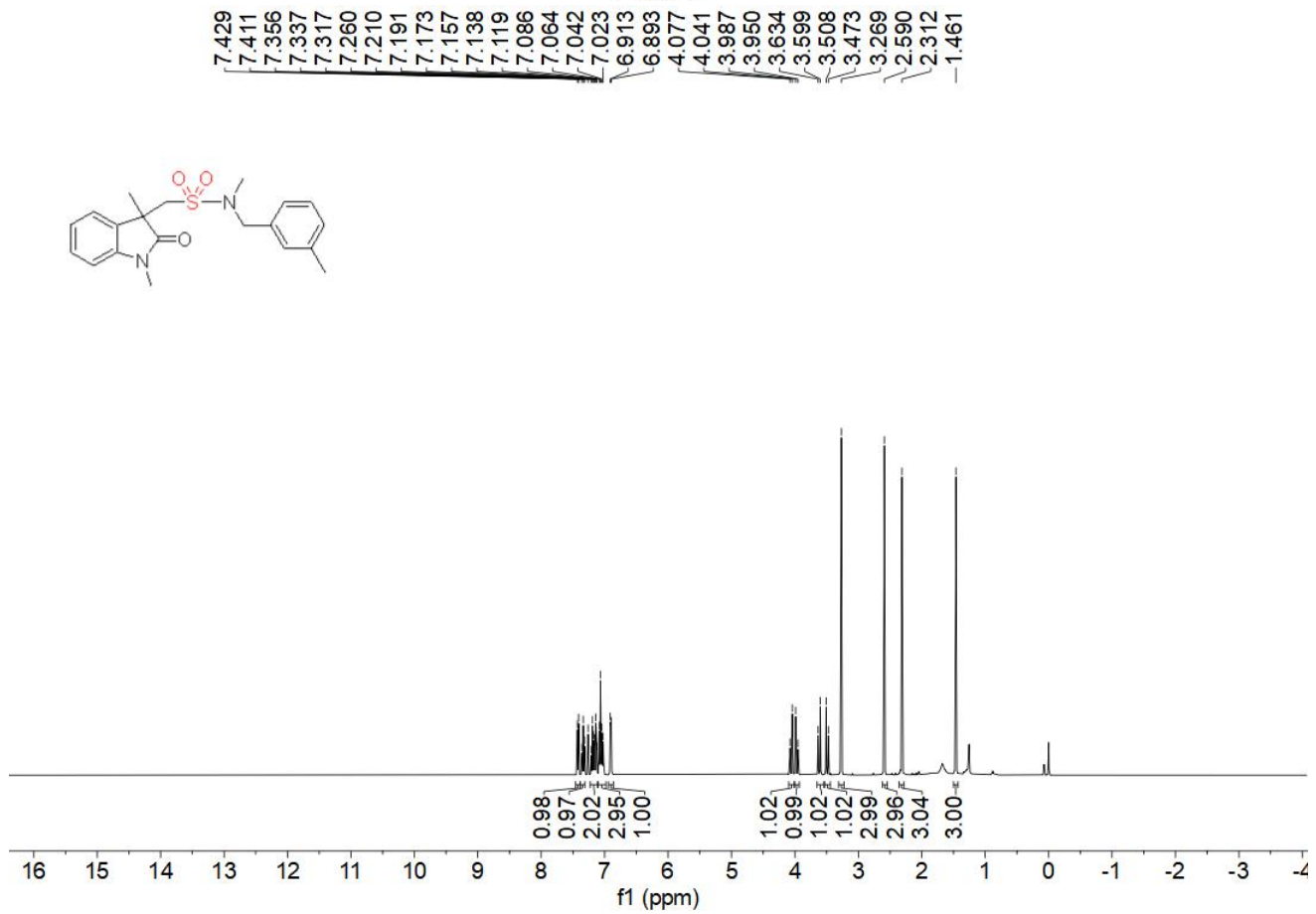
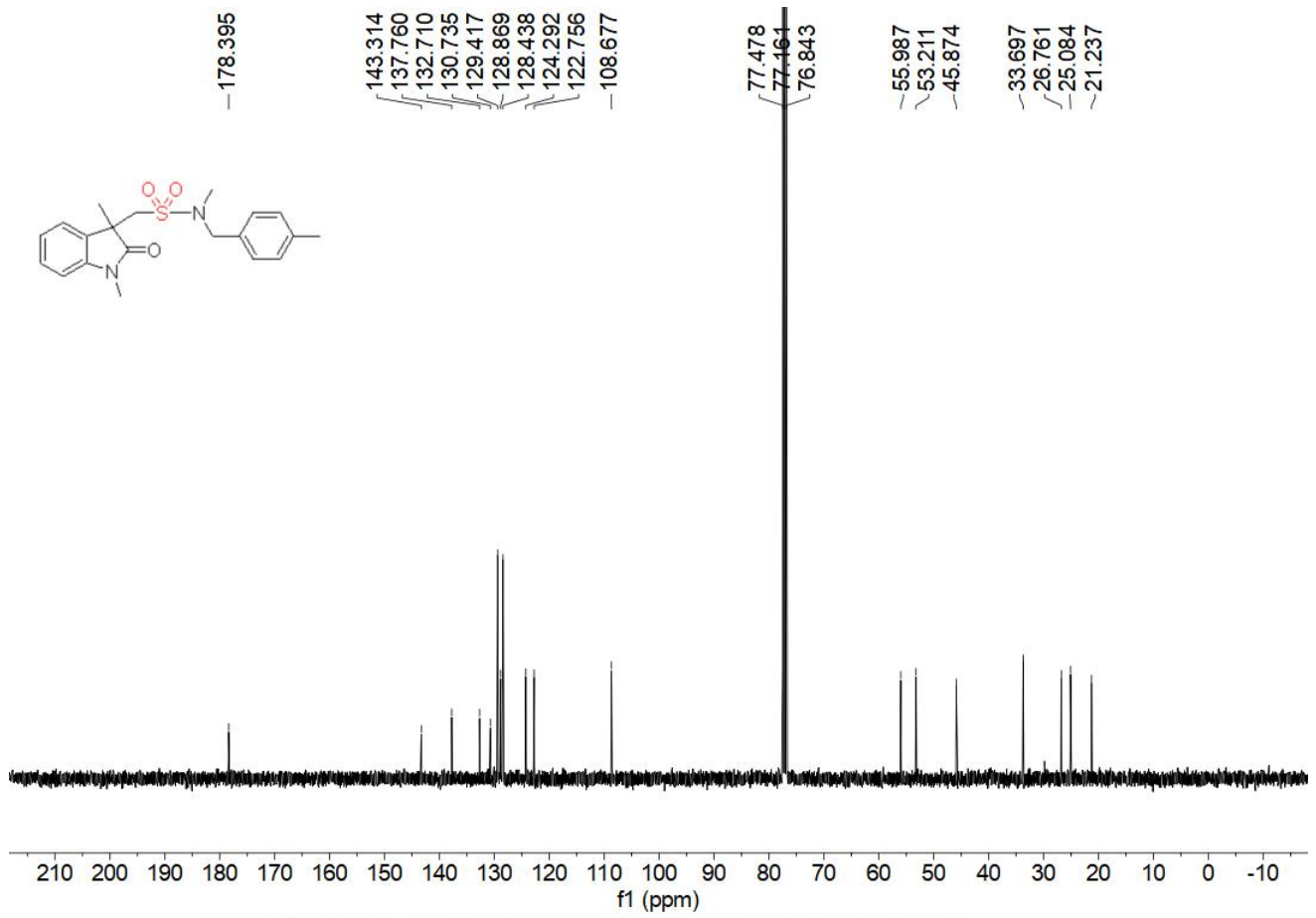


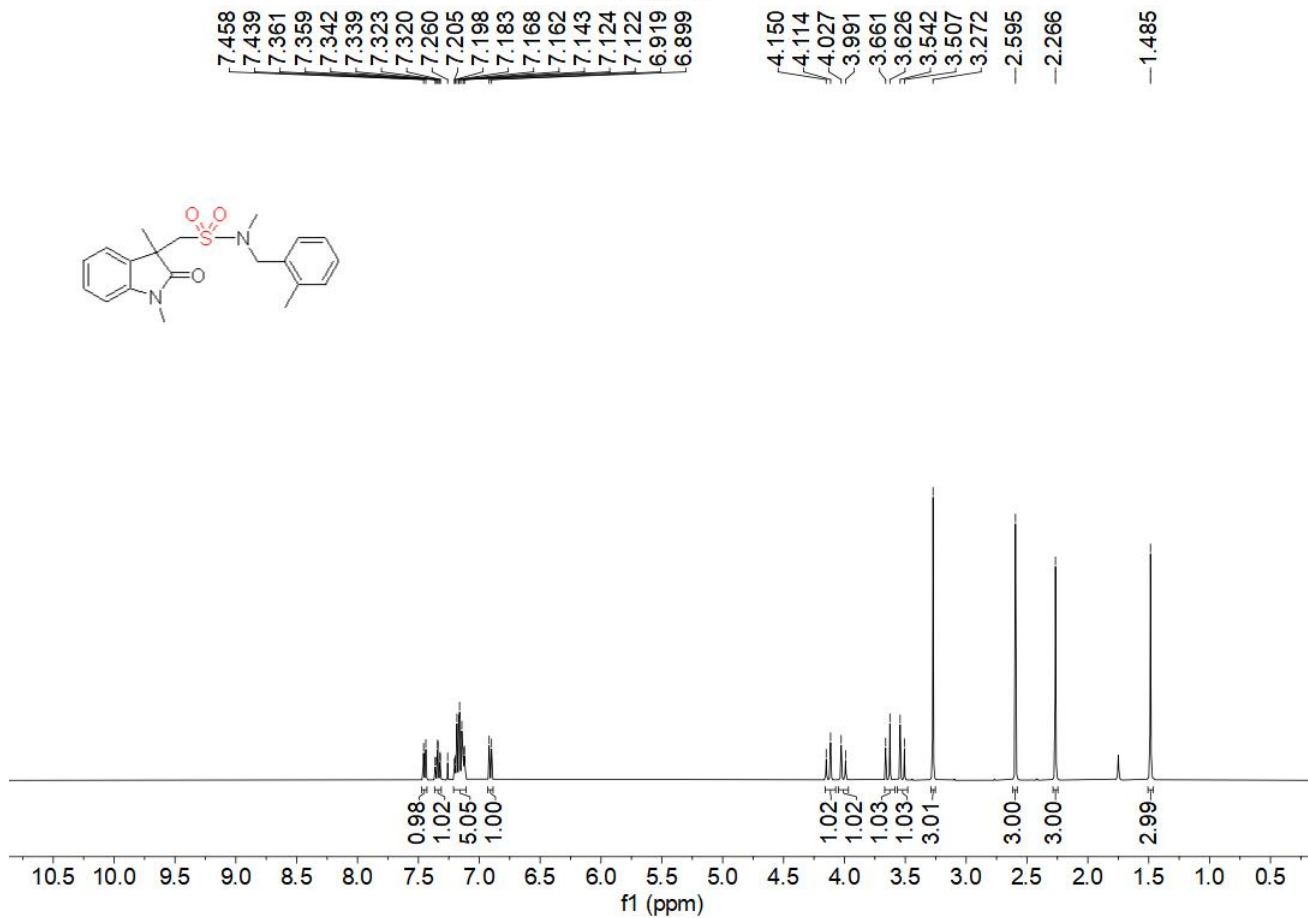
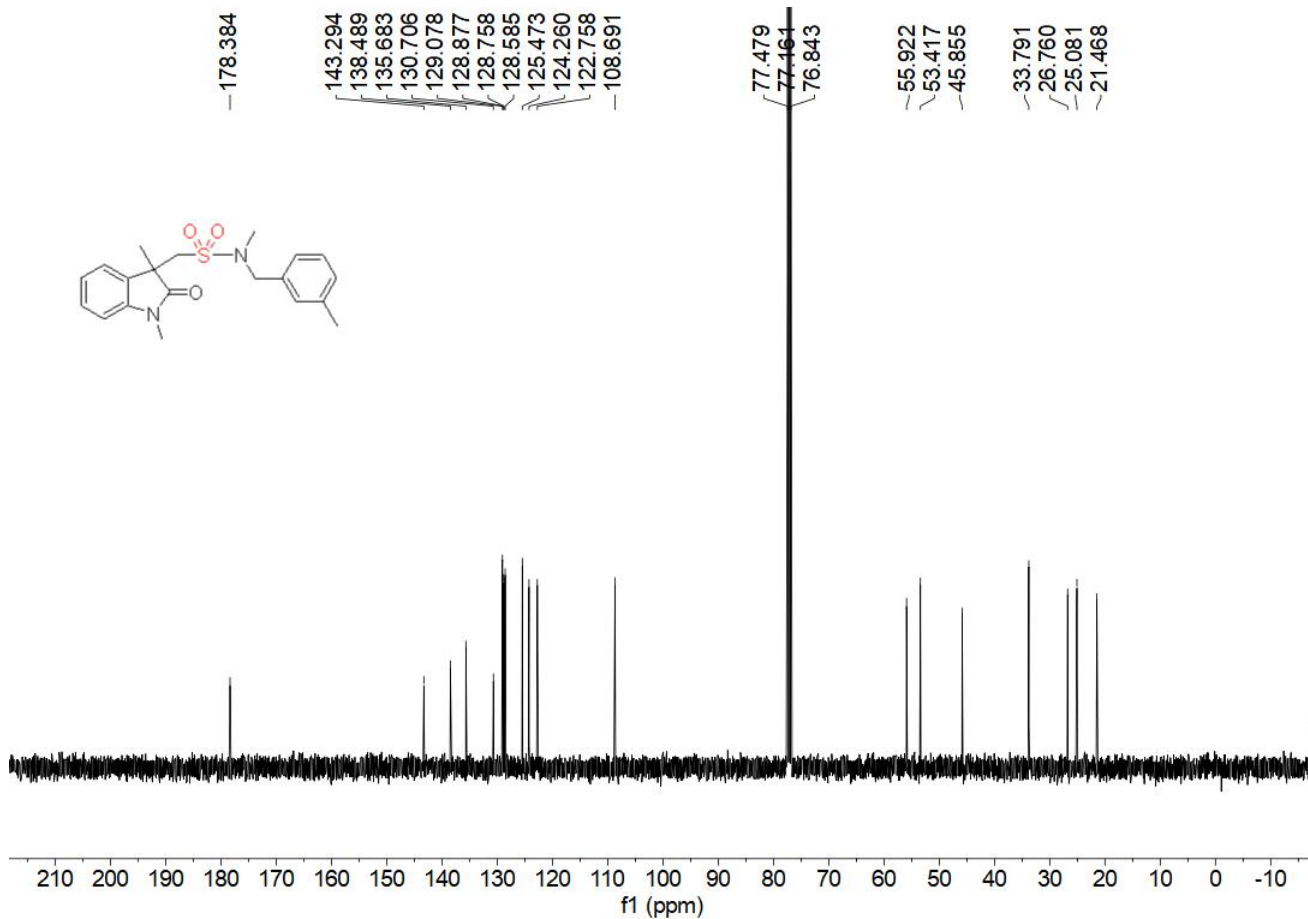
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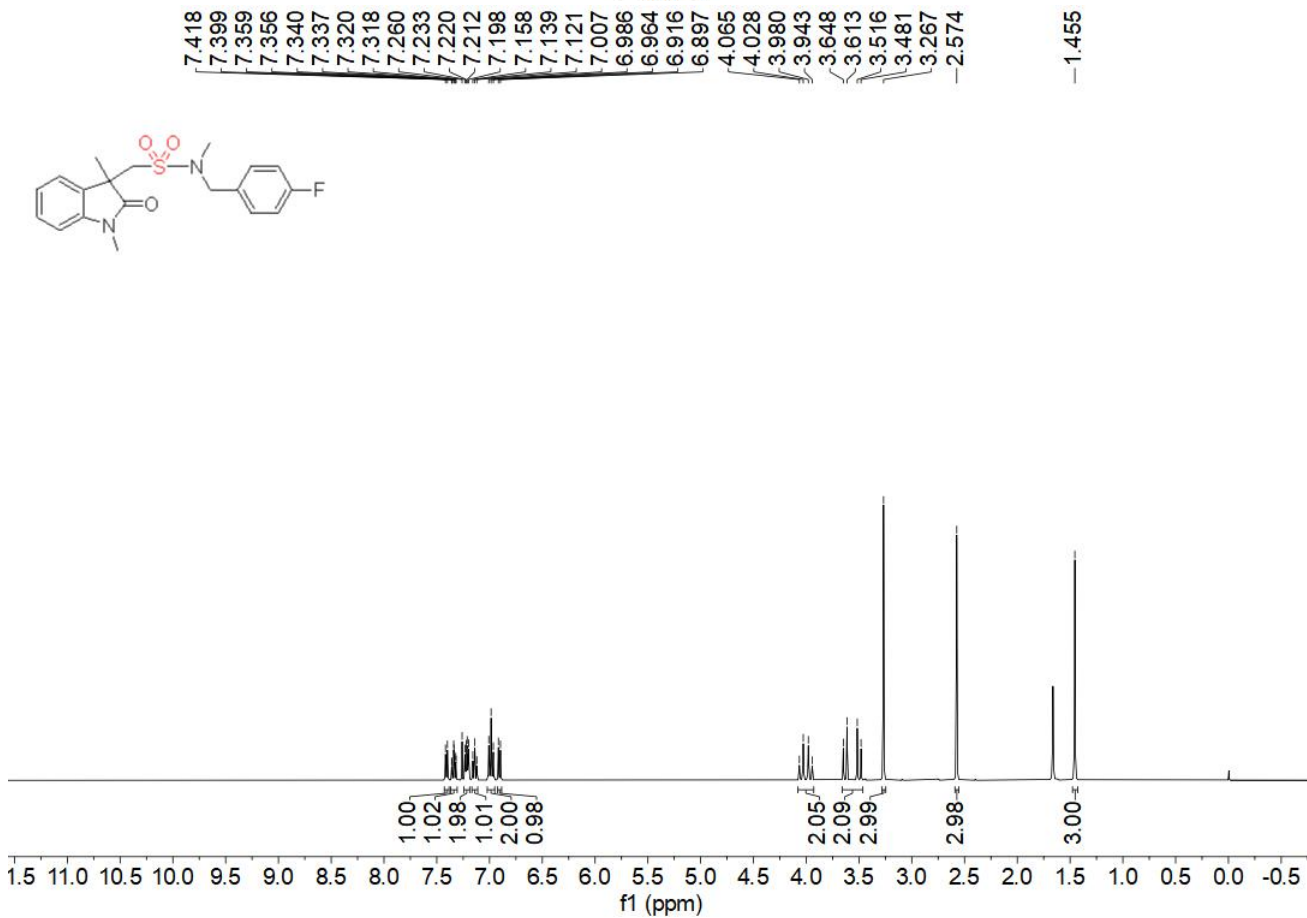
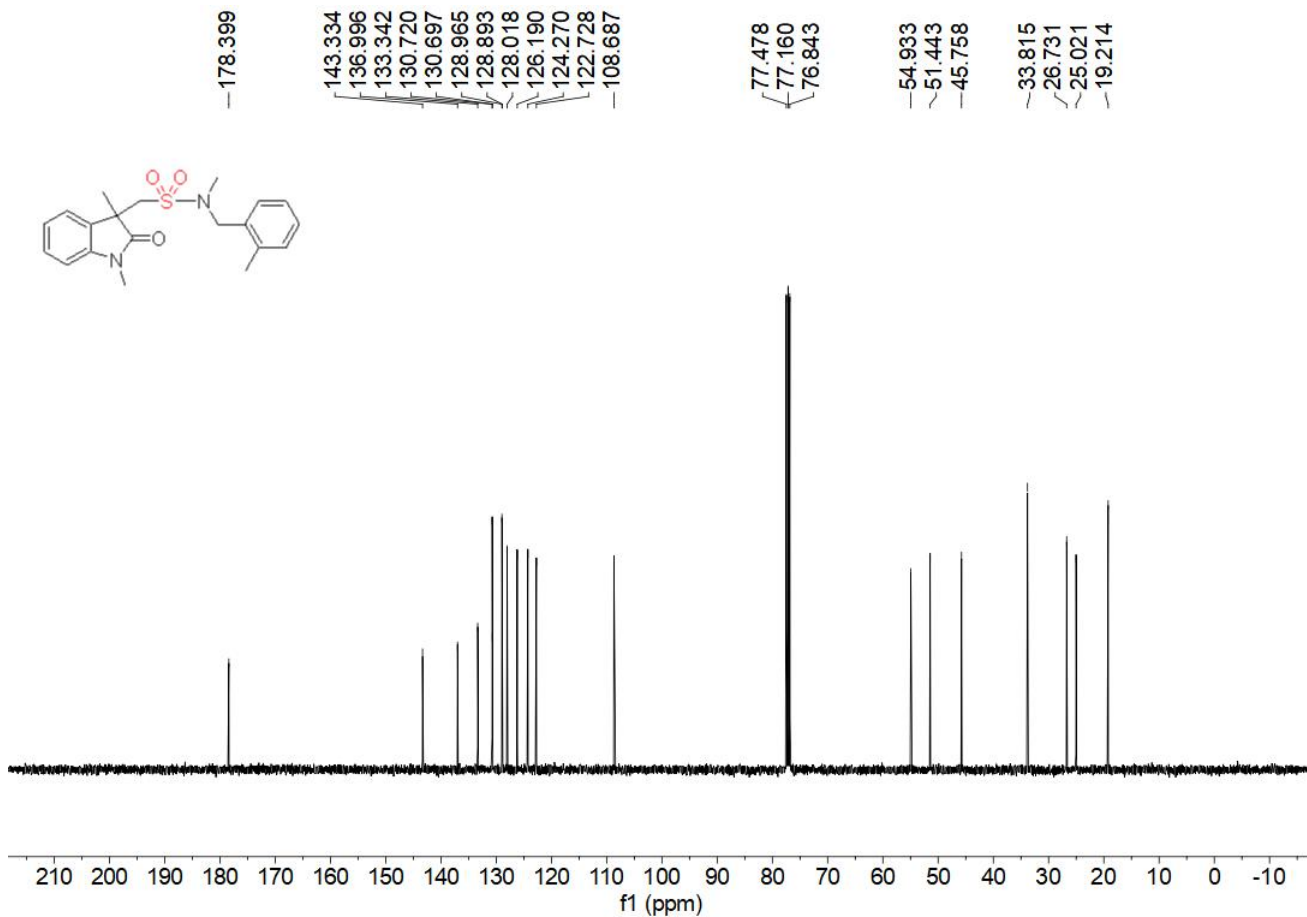
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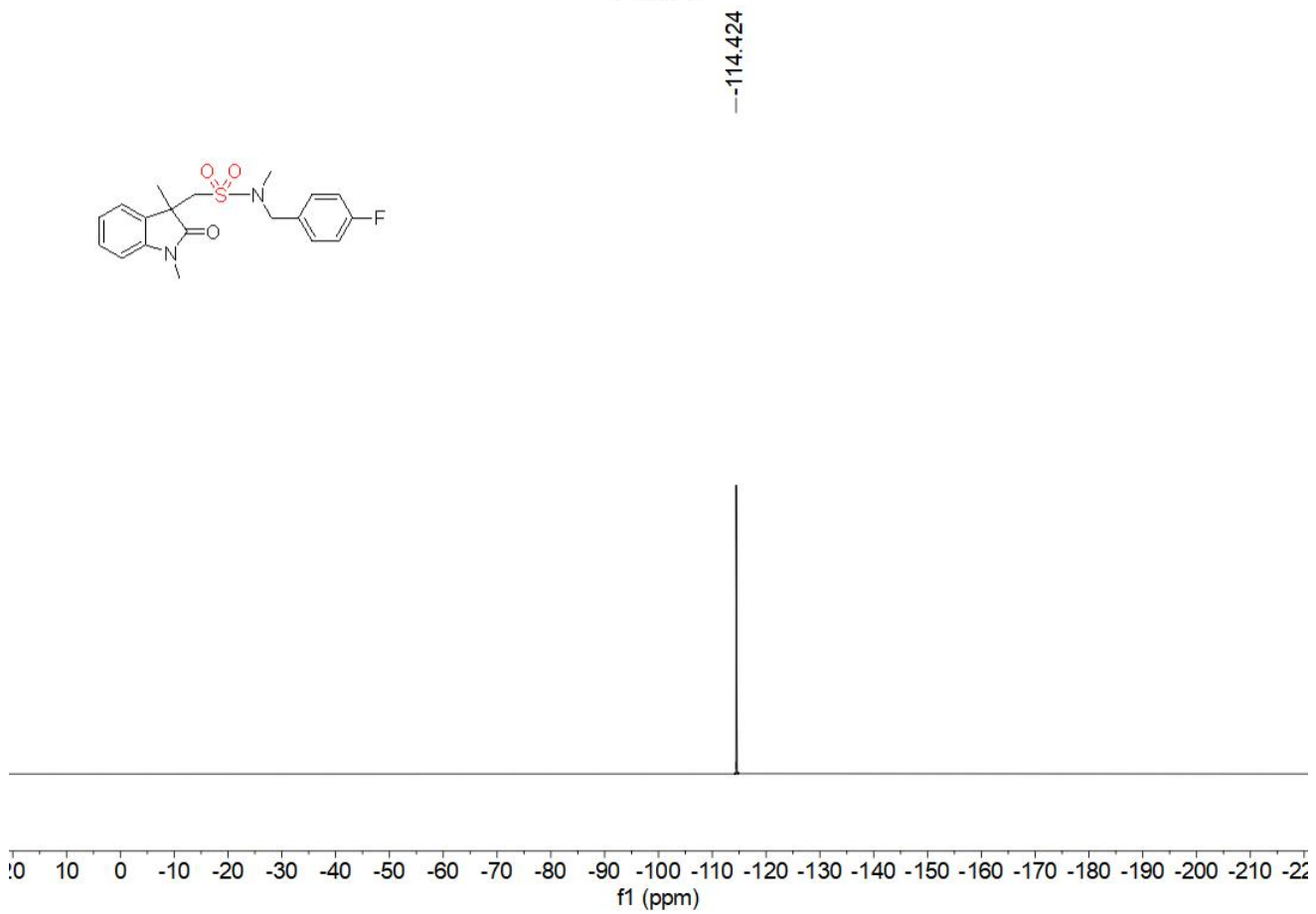
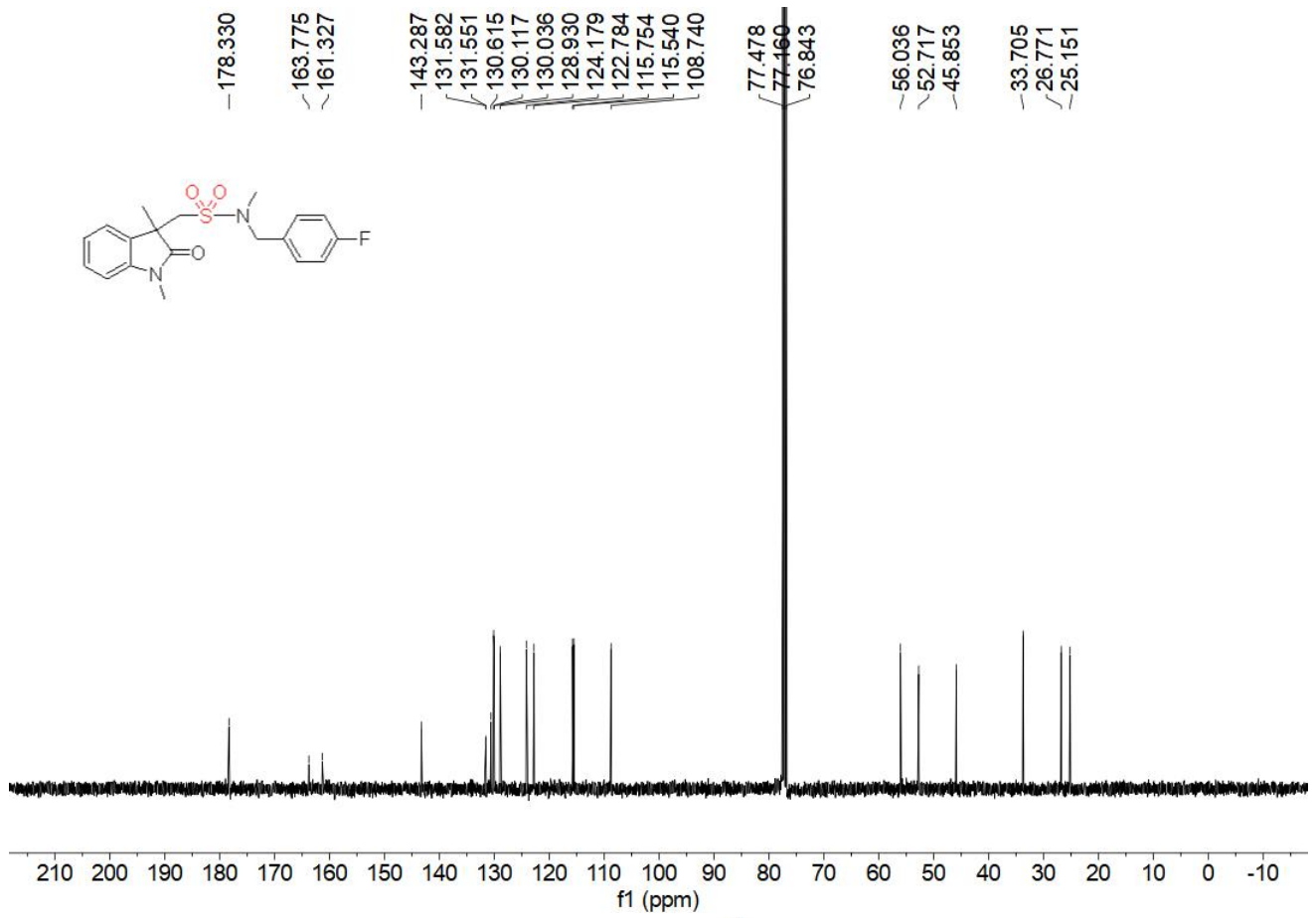


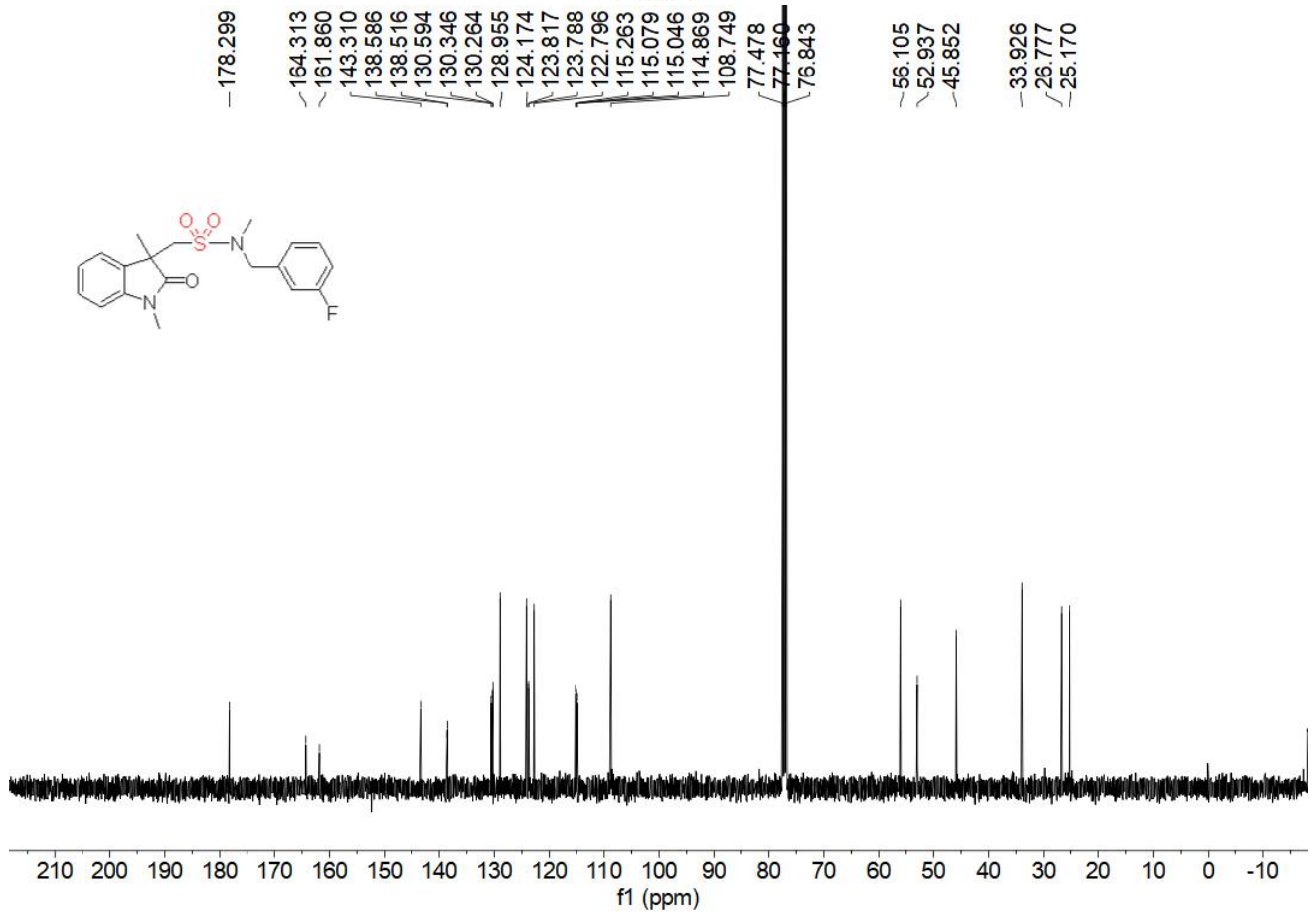
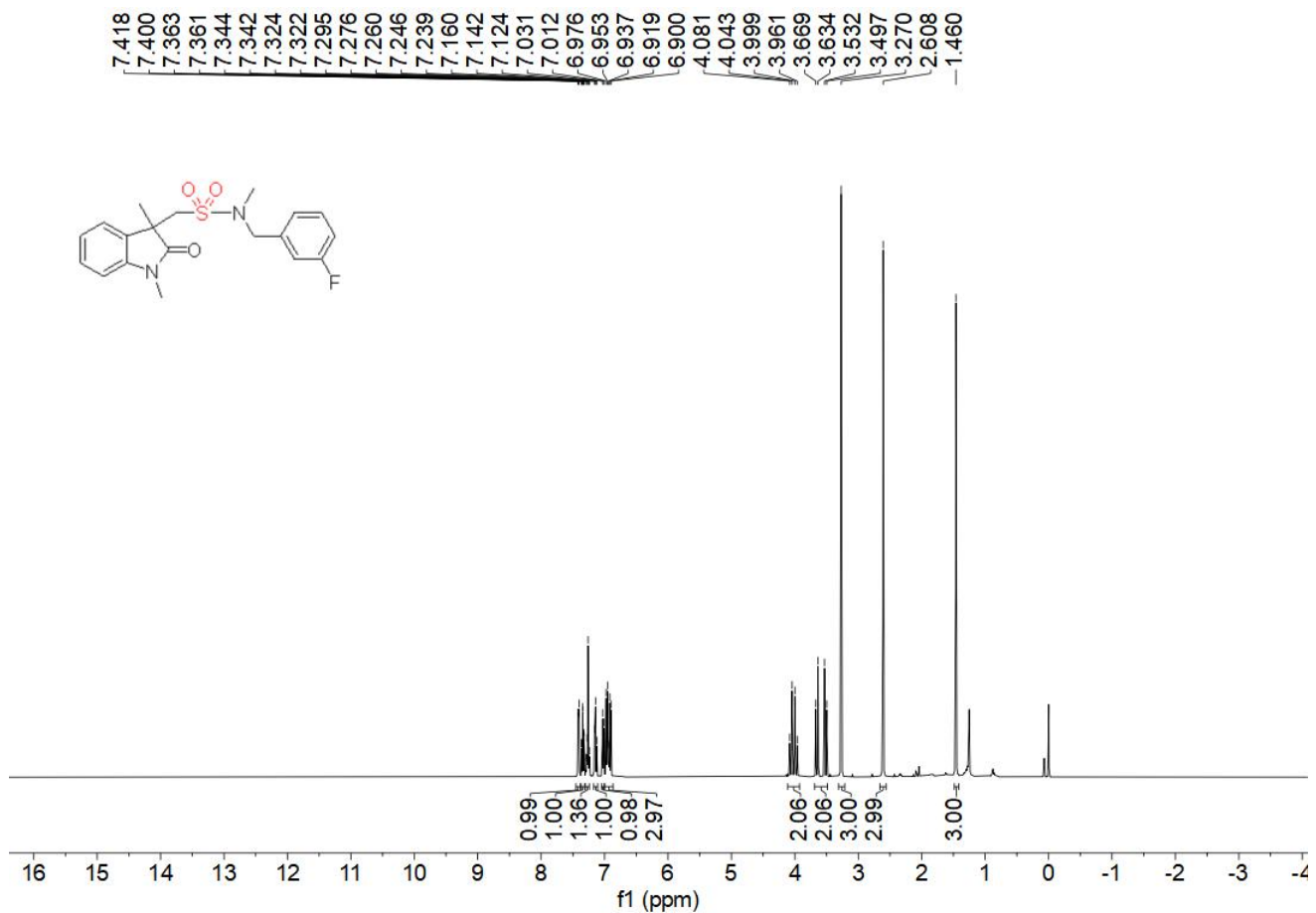


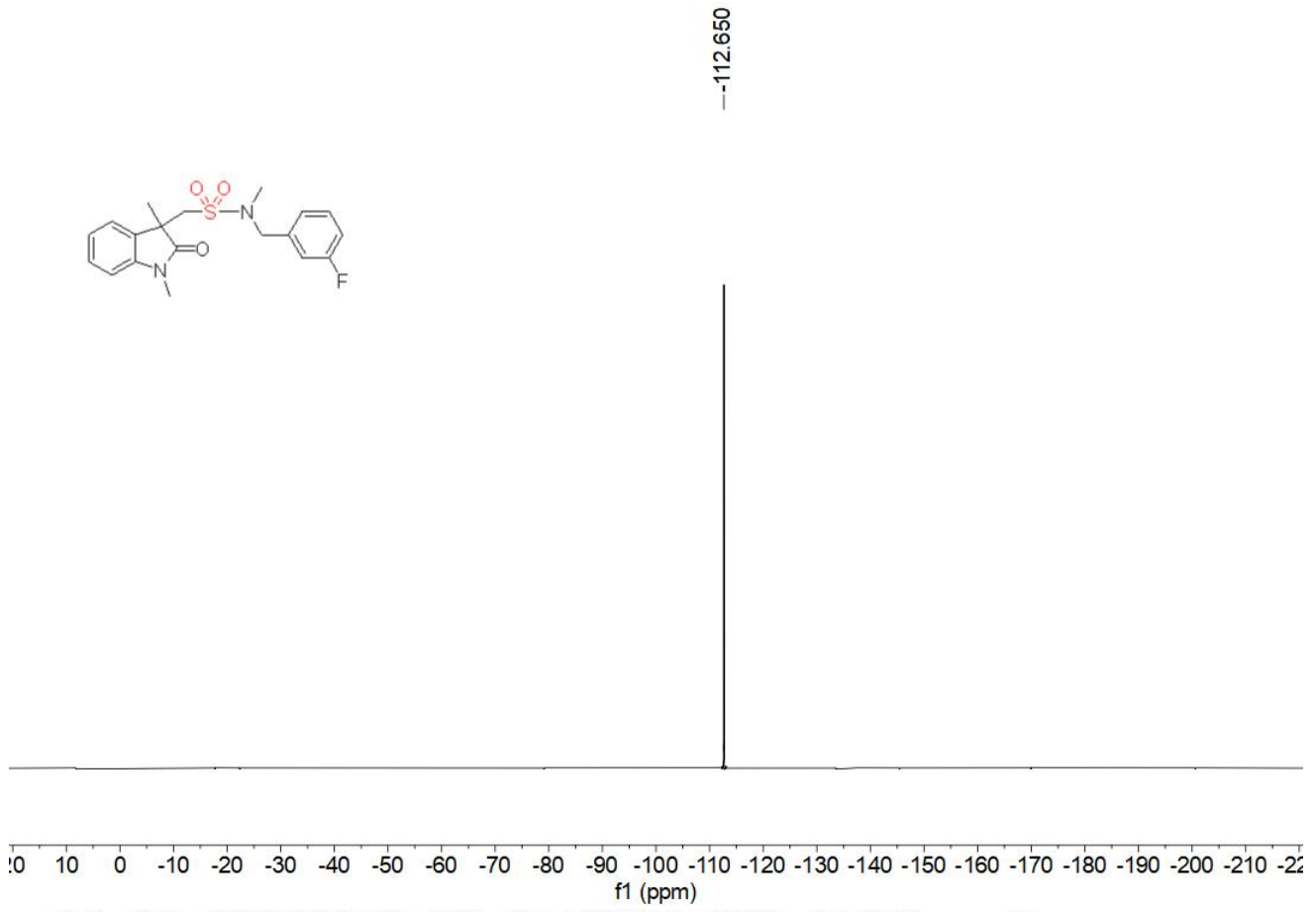
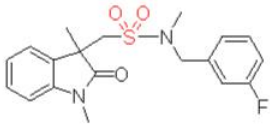




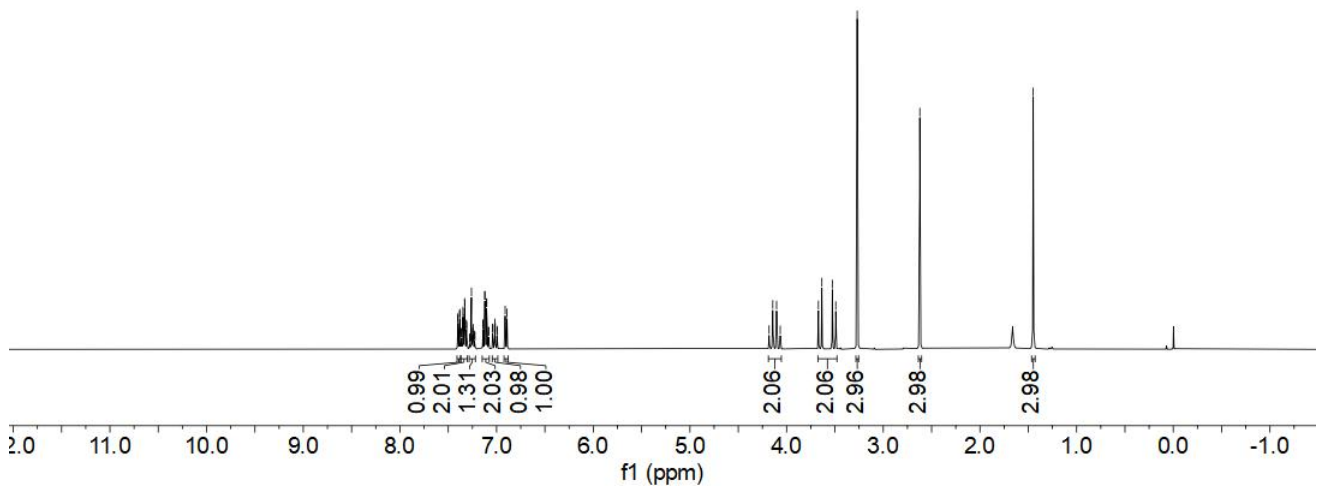
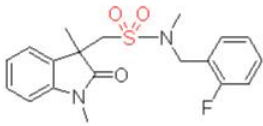




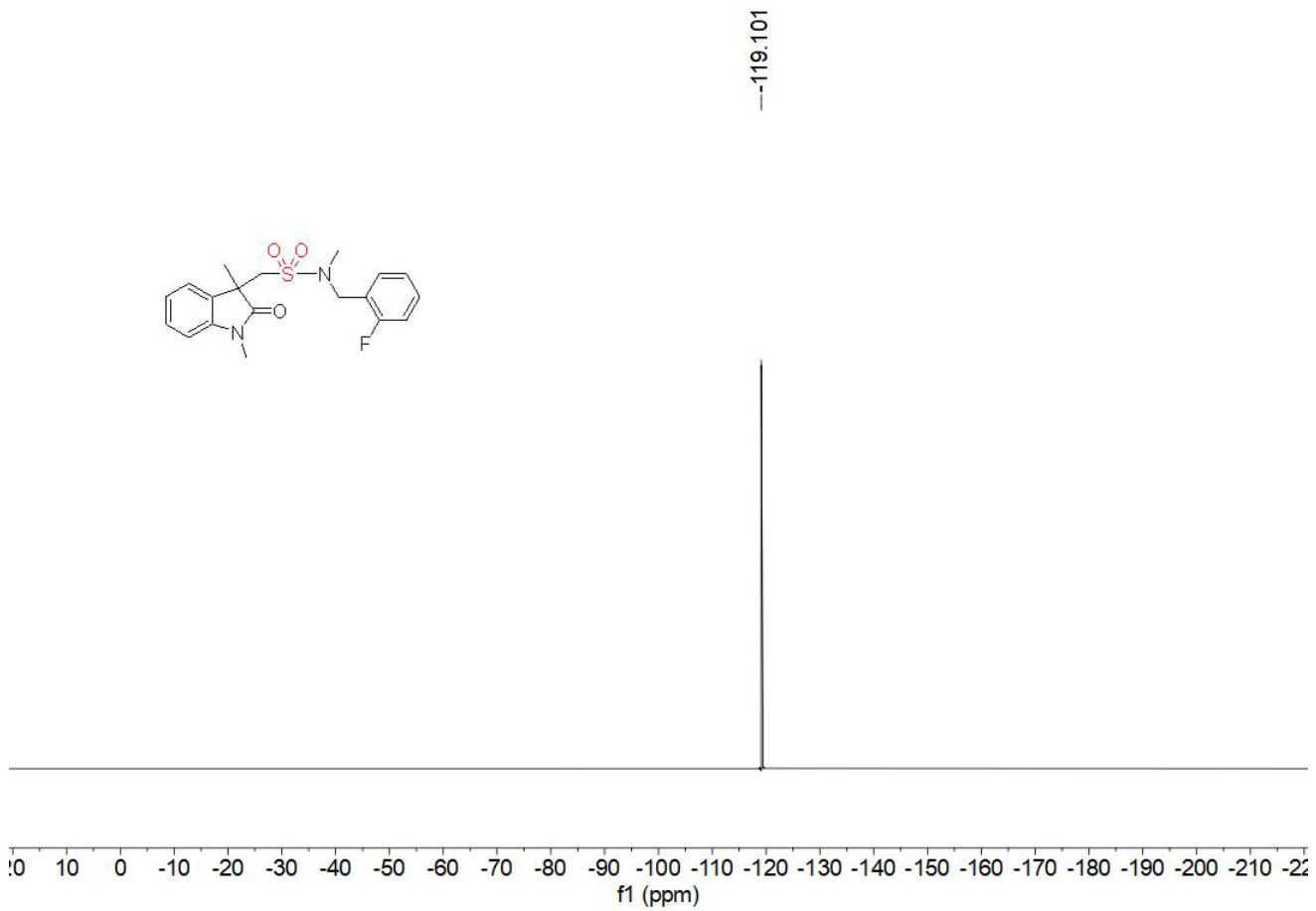
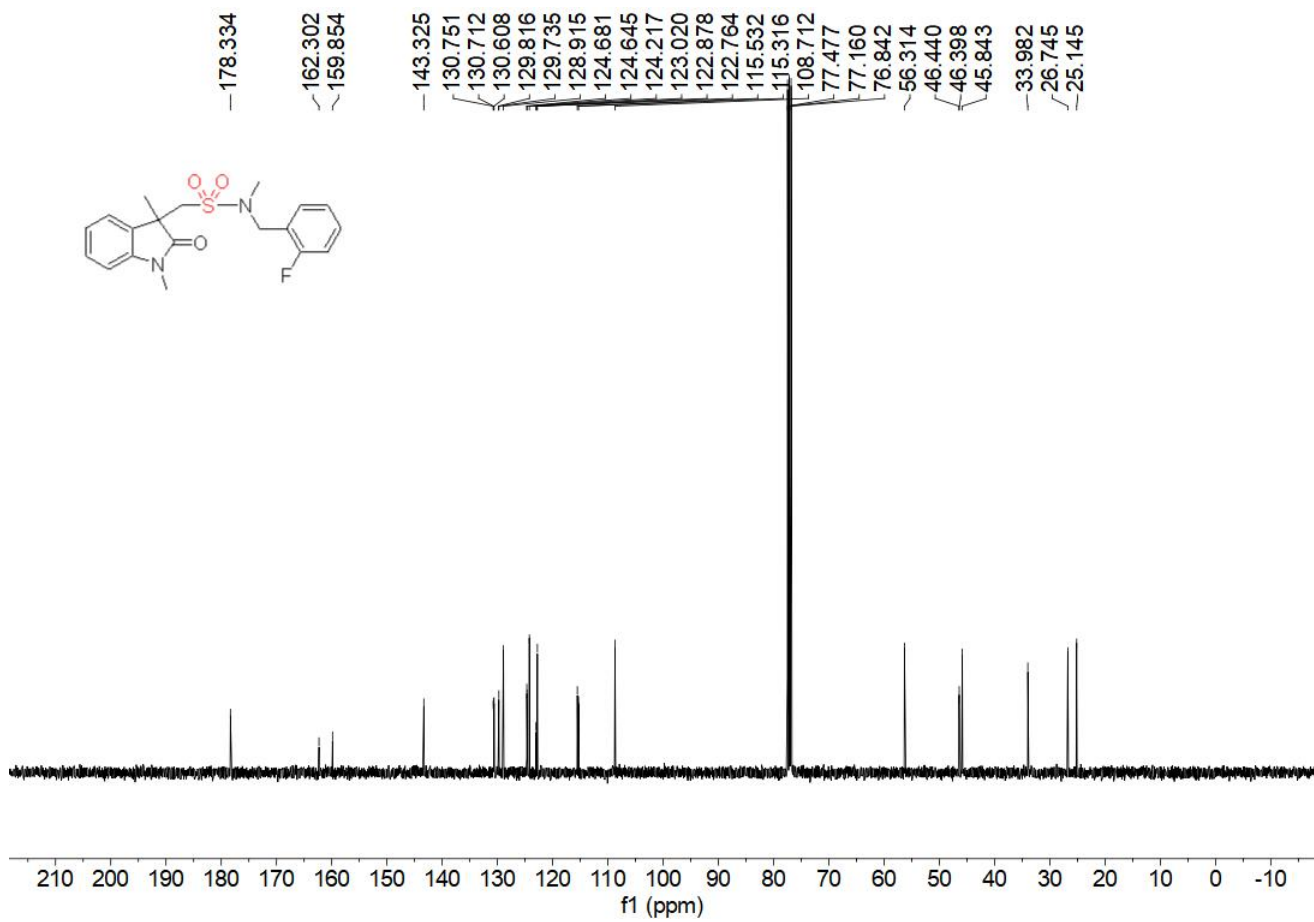


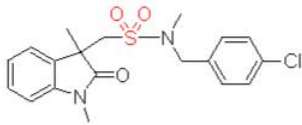


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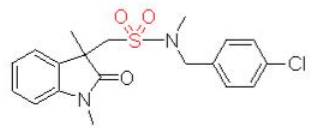
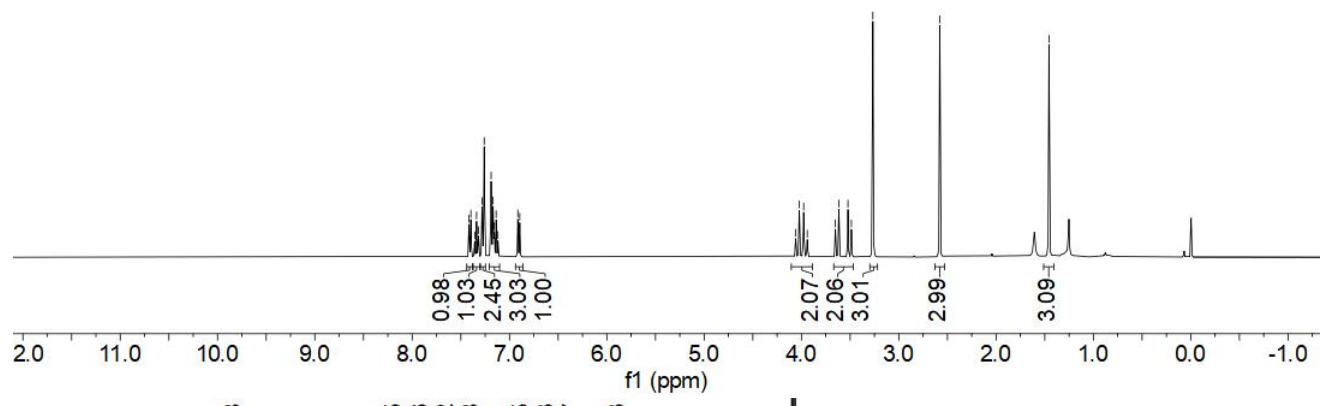


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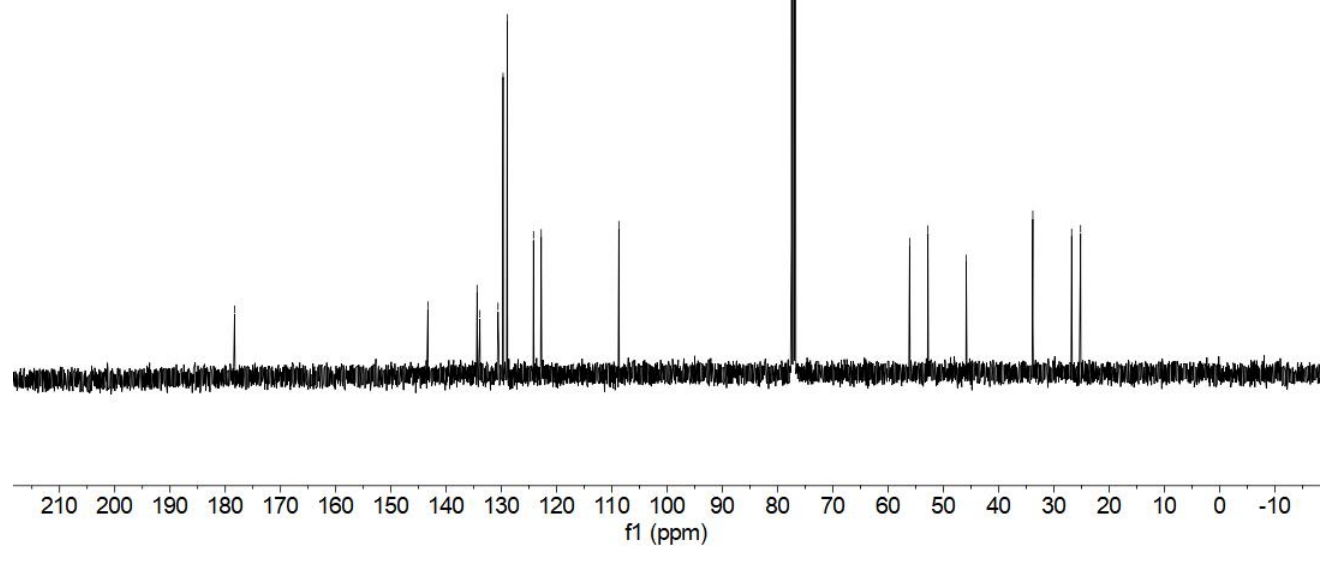




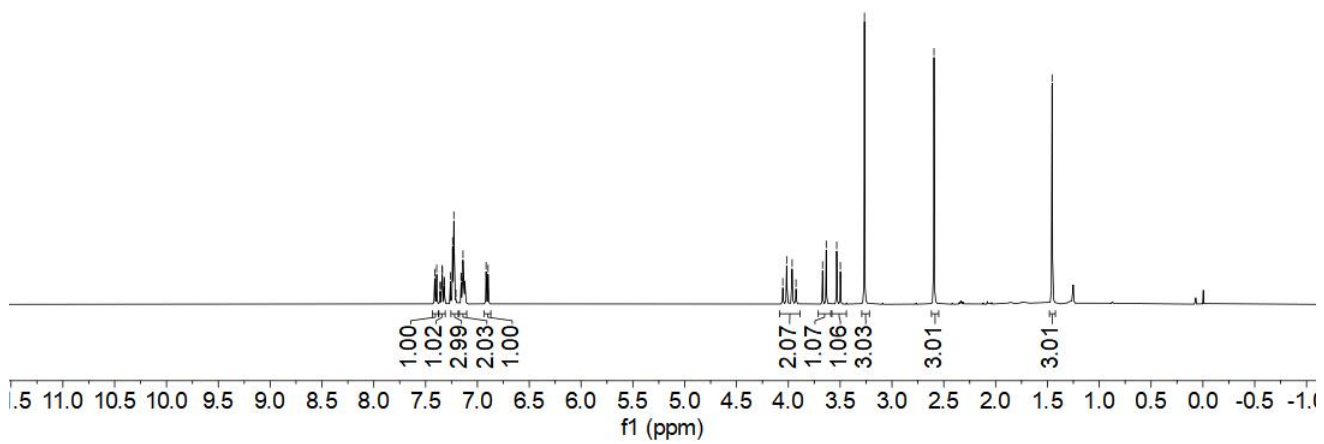
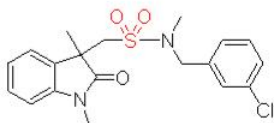
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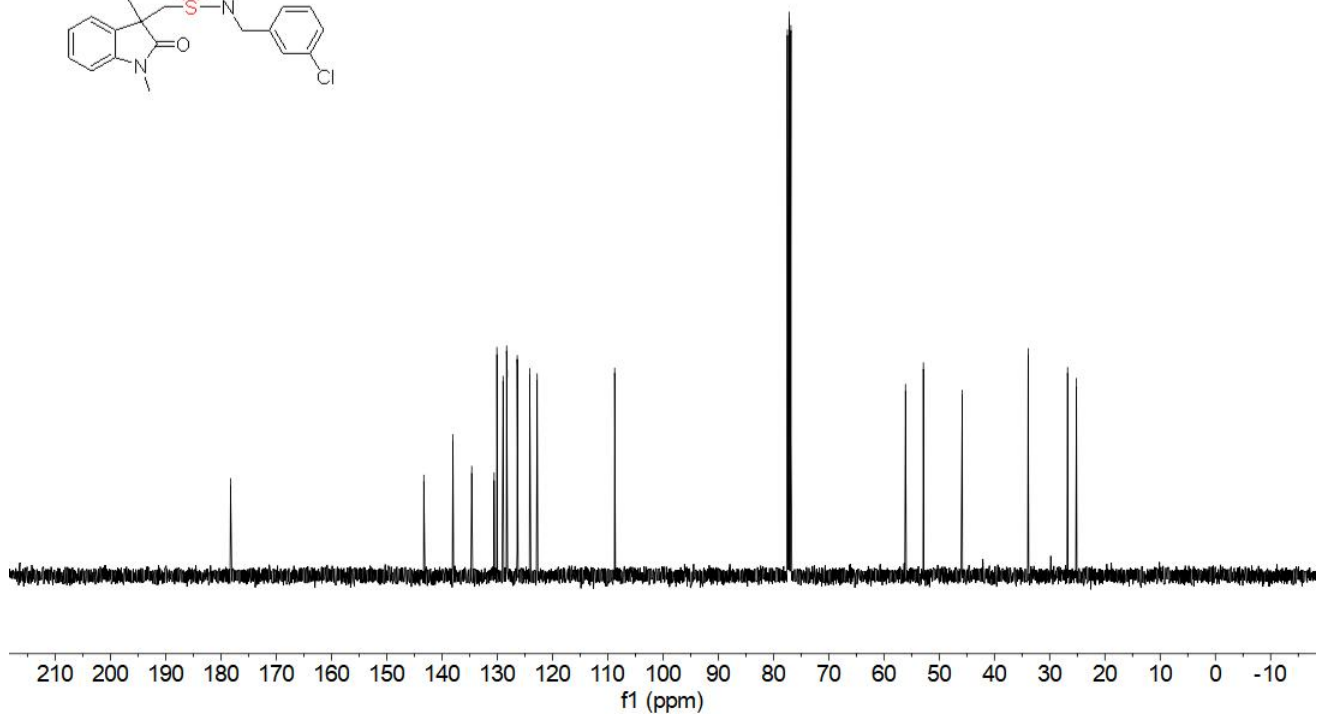
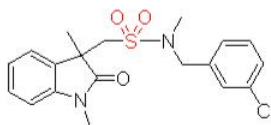
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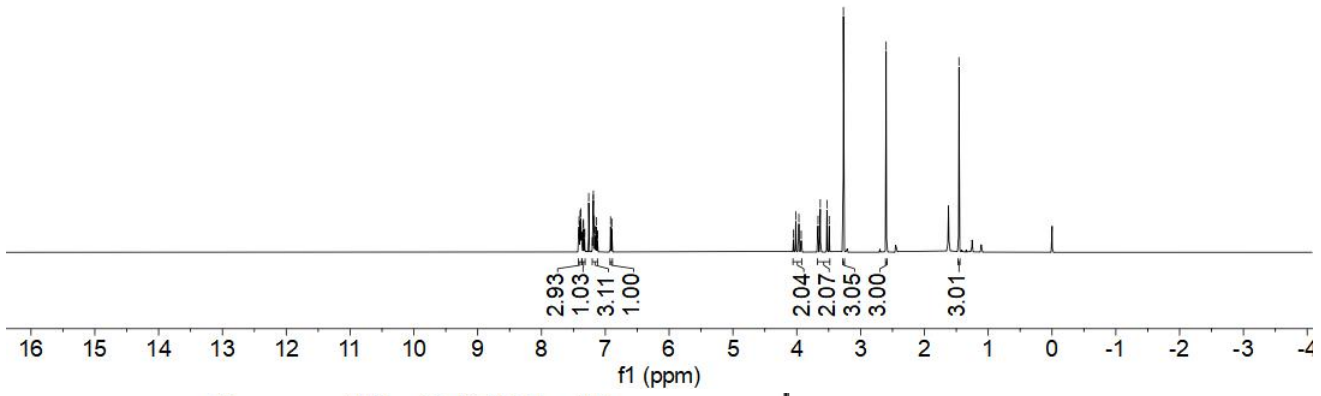
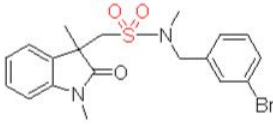
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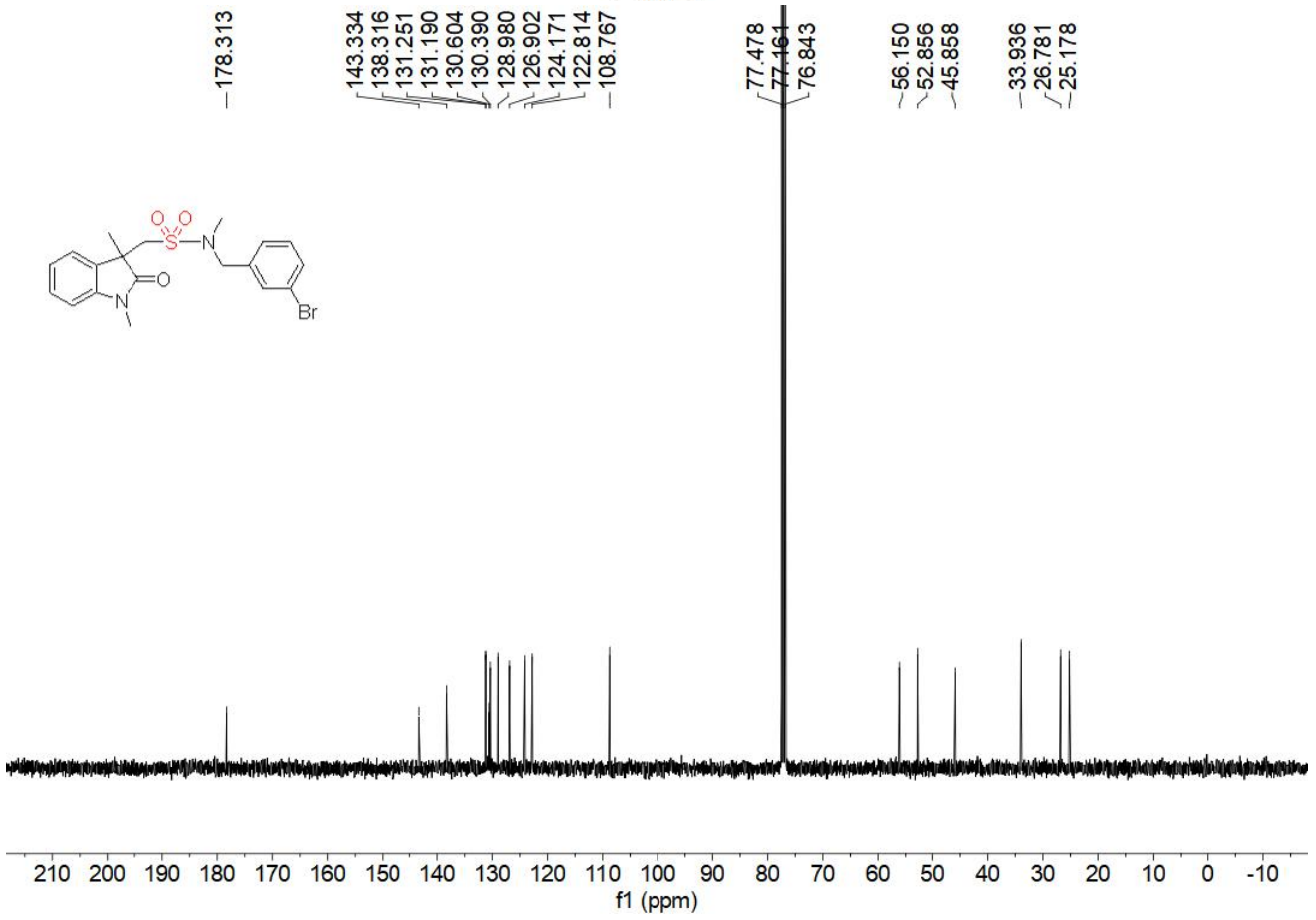
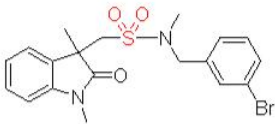
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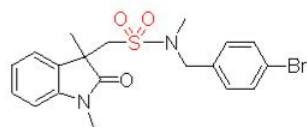


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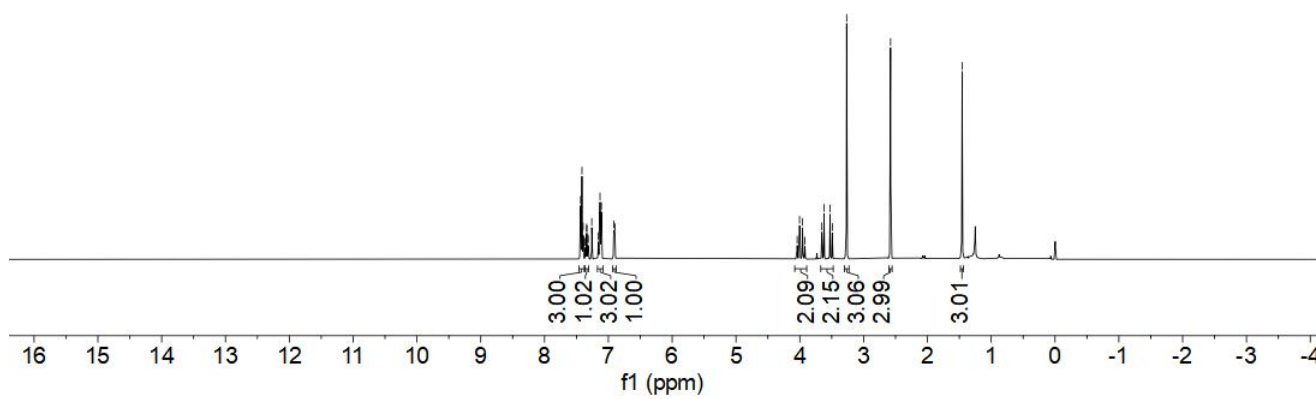


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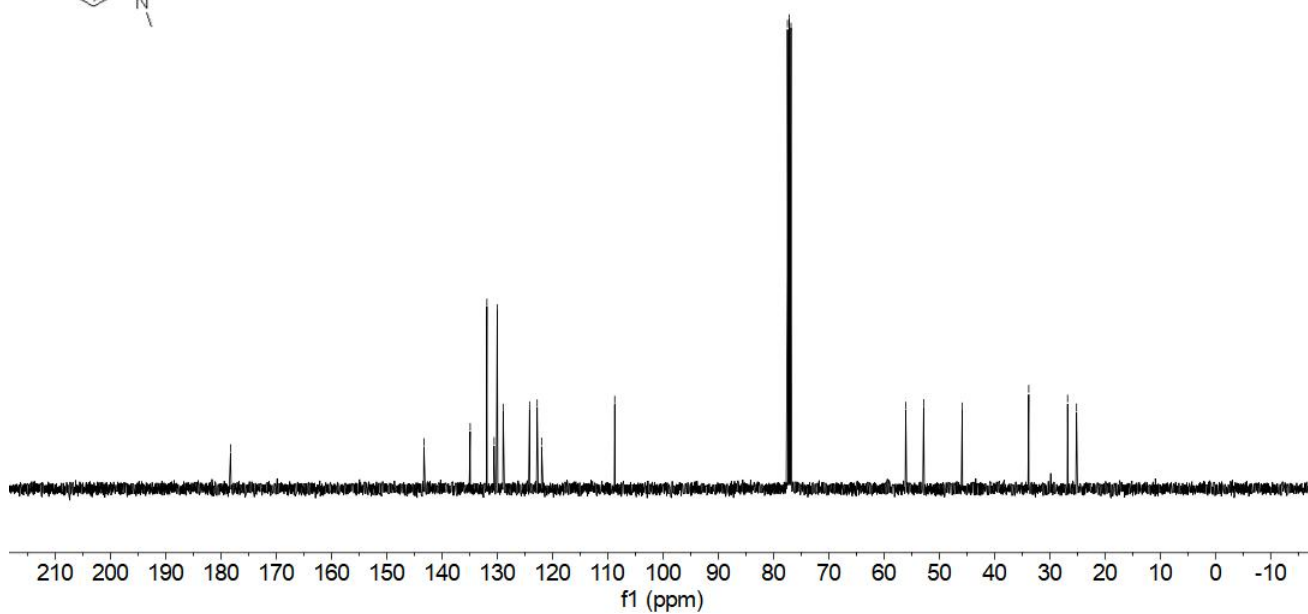
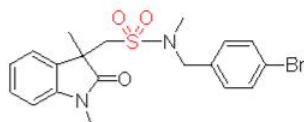




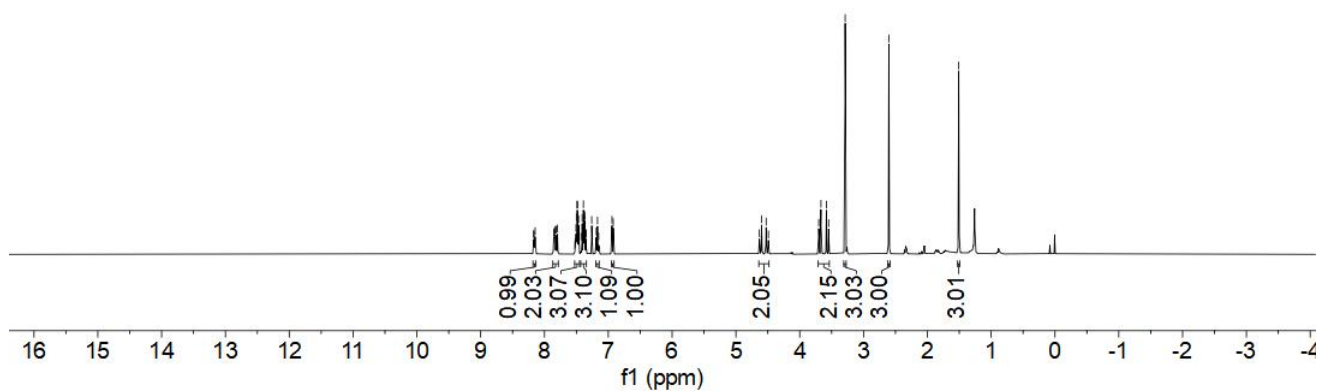
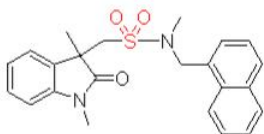
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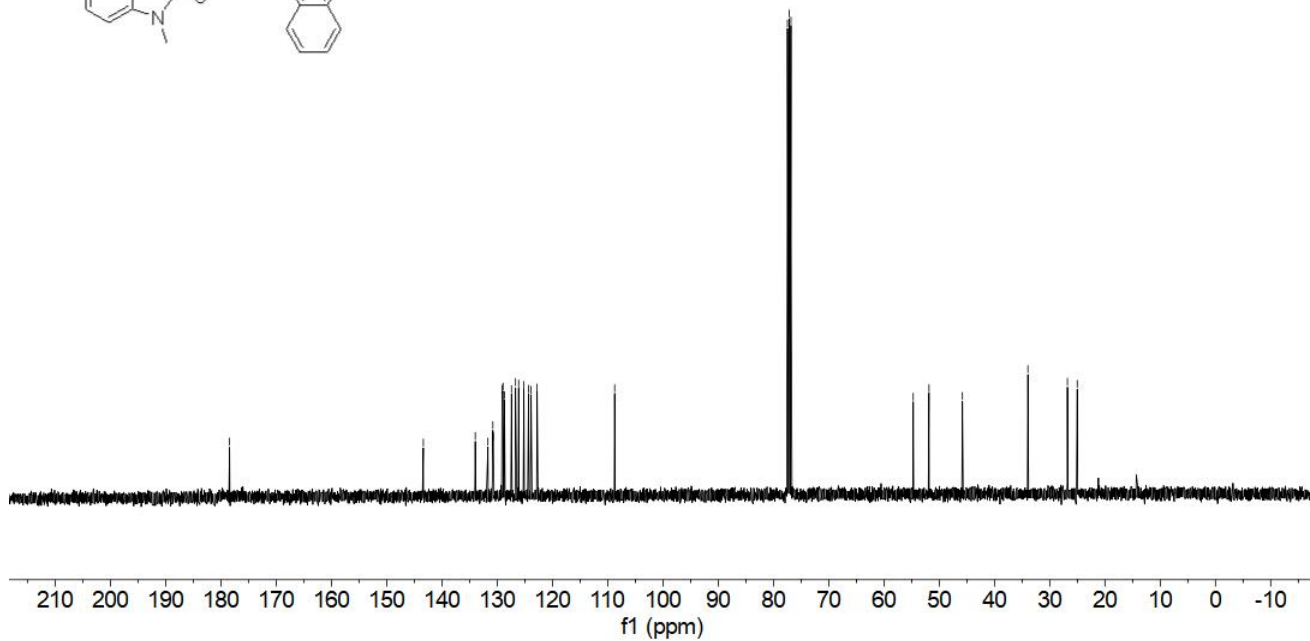
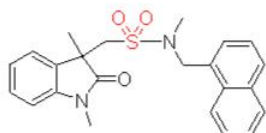


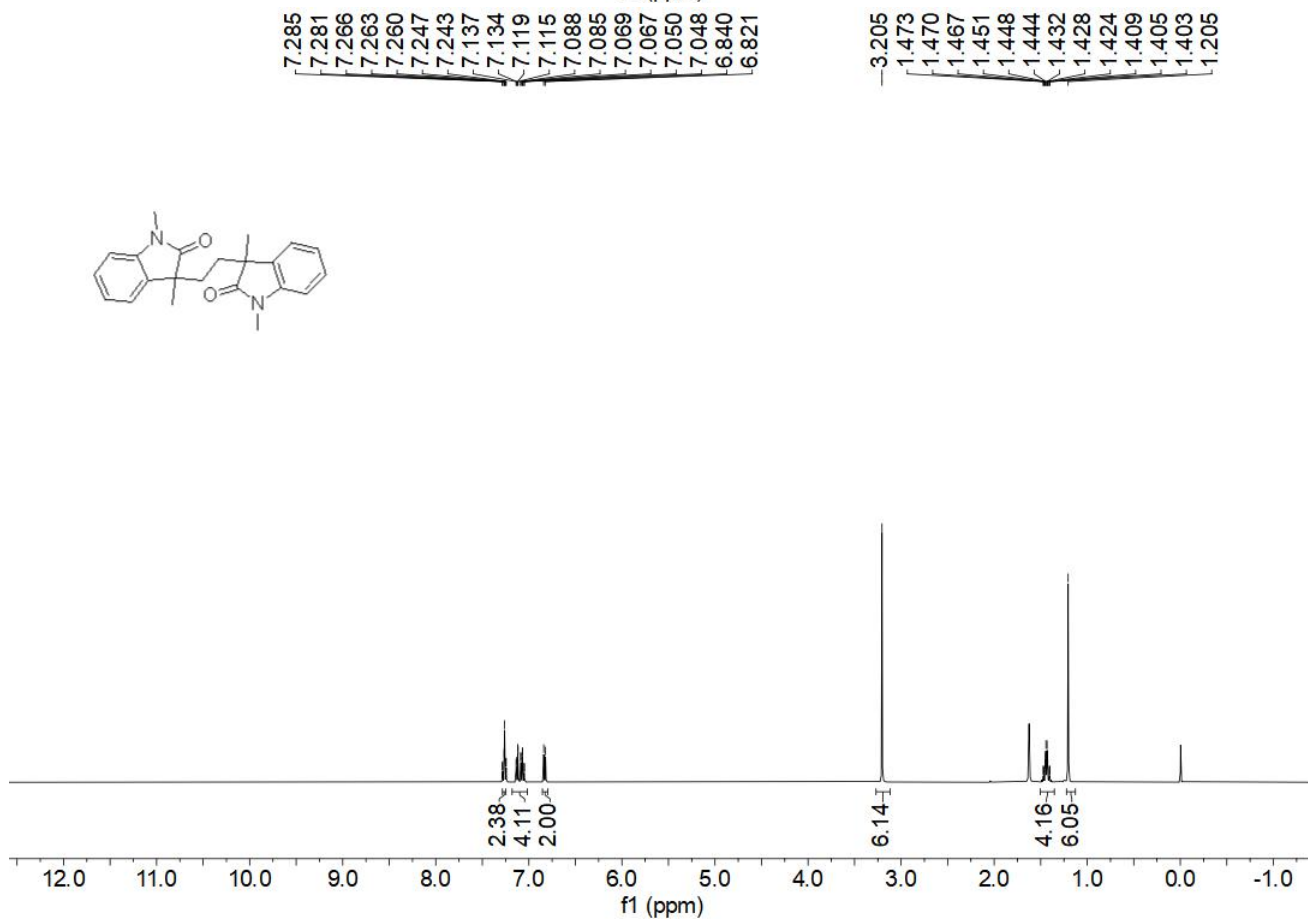
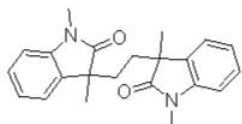
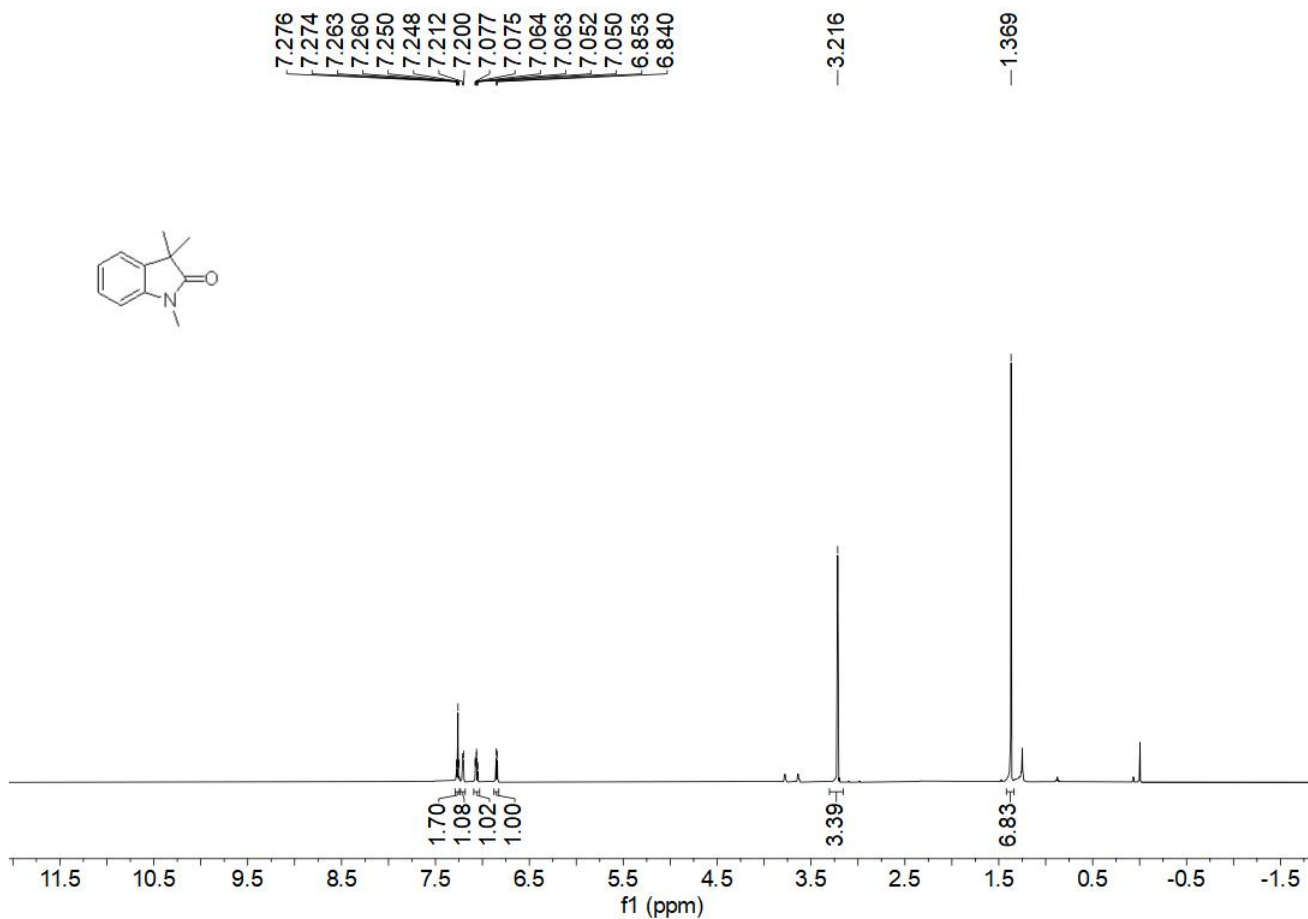
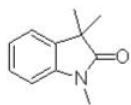
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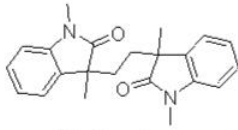
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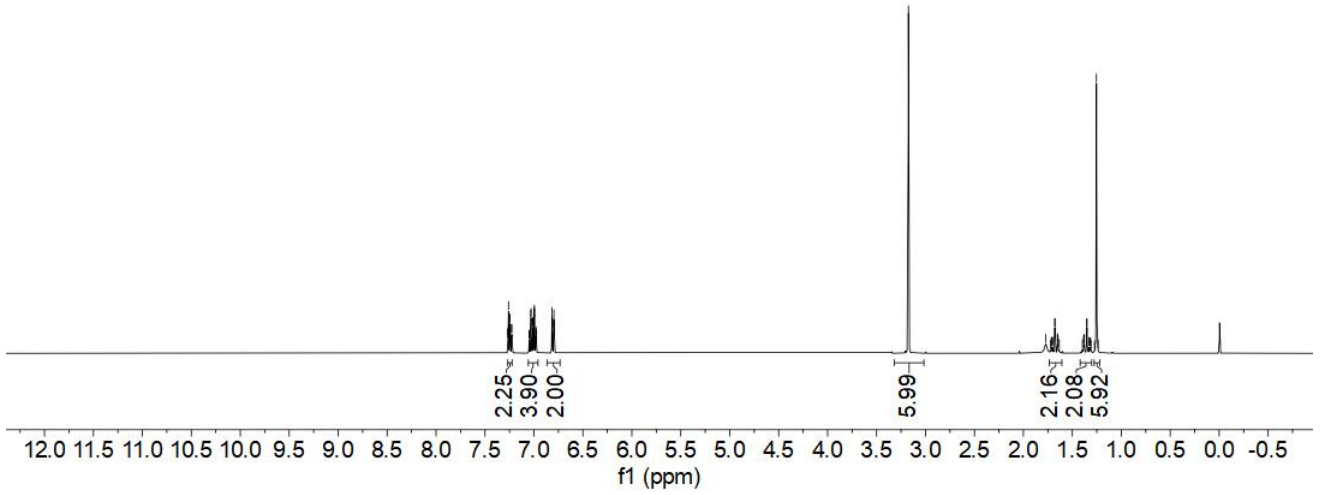




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1.645
1.633
1.397
1.385
1.380
1.377
1.353
1.350
1.329
1.320
1.315
1.309
1.254
1.238



Diastereoisomer



7.772
7.760
7.752
7.740
7.746
7.453
7.444
7.440
7.431
7.428
7.426
7.415
7.411
7.402
7.398
7.390
7.387
7.384
7.260
7.238
7.225
7.213
7.007
6.995
6.982
6.842
6.830
6.817
6.804
-3.286

-1.842
-1.599
1.018
1.005
0.992

