Cobalt-Promoted Synthesis of Sulfurated Oxindoles *via* Radical Annulation of *N*-arylacrylamides with Disulfides

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Supporting Information

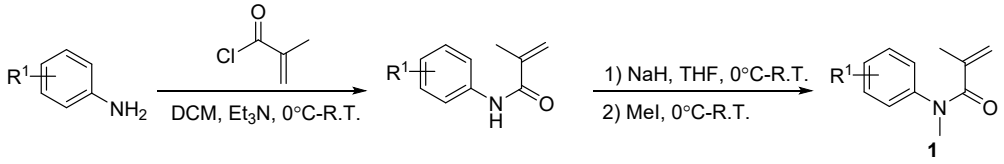
1. General information

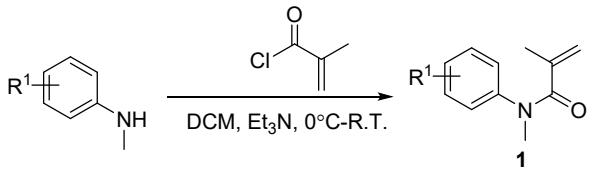
Unless otherwise stated, all the commercial reagents and solvents were used as such without further purification. The flash column chromatography was carried out over silica gel (200-300 mesh). ^{1}H and ^{13}C and spectra were recorded on a Bruker Avance NEO 400/600 MHz spectrometer. Chemical shifts in ^{1}H-NMR spectra were reported in parts per million (ppm) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra were reported relative to the central line of the chloroform signal (δ = 77.06 ppm). ^{1}H-NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C-NMR spectral data are reported in terms of chemical shift (δ, ppm) and multiplicity. Peaks were labeled as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). ^{19}F NMR were recorded on a Bruker Avance NEO 400/600 MHz spectrometer. High resolution mass spectra were performed on Waters G2-XSQ-Tof mass spectrometer. Melting points were determined on a Tektronix X-4 melting point apparatus. Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Typical procedures for the synthesis of substrates

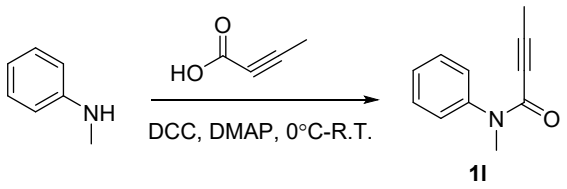
N-arylacrylamides **1** were prepared according to previous literatures.[1-4]

Method A: Substrate **1** were prepared according to literature.[1-3]

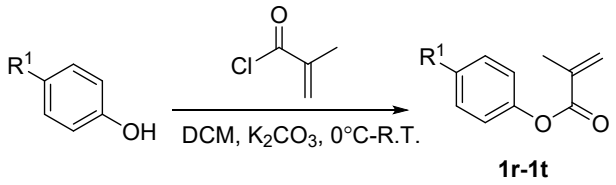




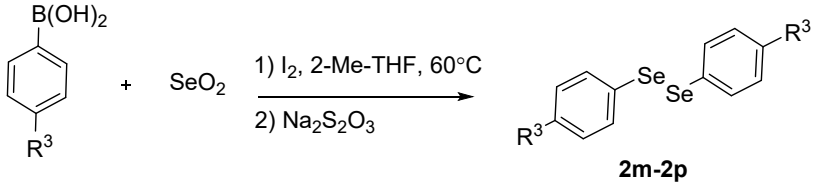
Method B: Substrate **1l** was prepared according to literature.[4]



Substrate **1r-1t** were prepared according to literature.[5]

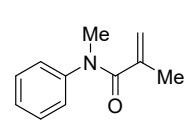


Substrate **2m-2p** were prepared according to literature.[6]



3. Chemical structures of the substrates 1 and 2

Table 1. Chemical structures of **1**



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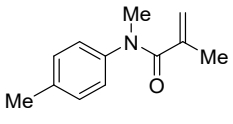

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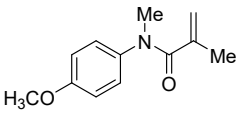

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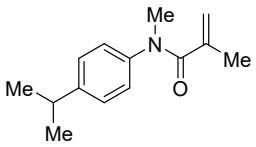

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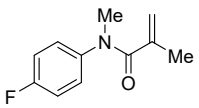

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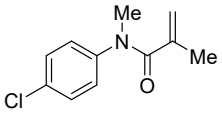

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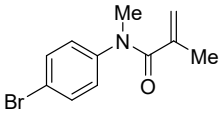

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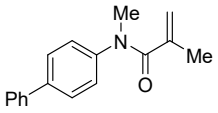

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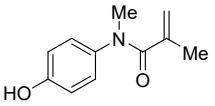

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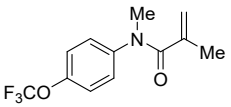

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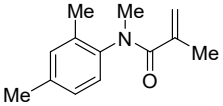

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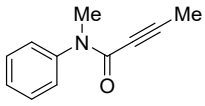

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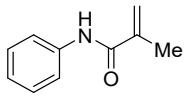

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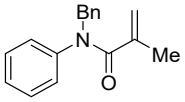

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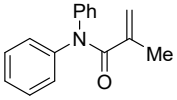

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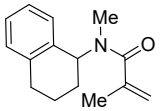

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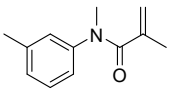

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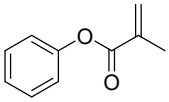

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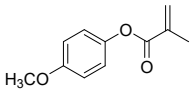

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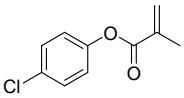
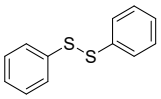


1t

Table 2. Chemical structures of **2**



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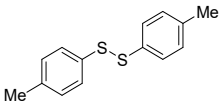

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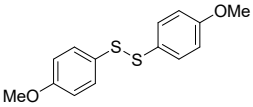

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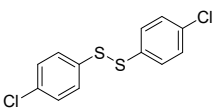

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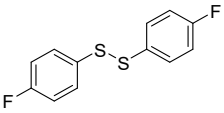

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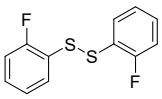

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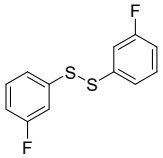

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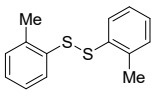

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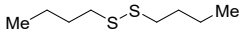

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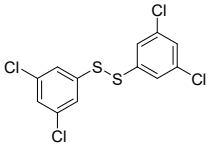

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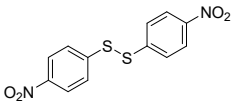

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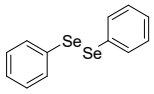

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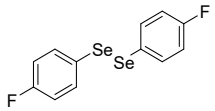

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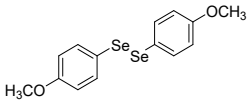

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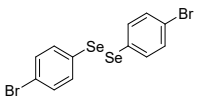

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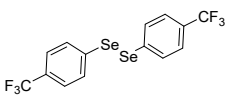
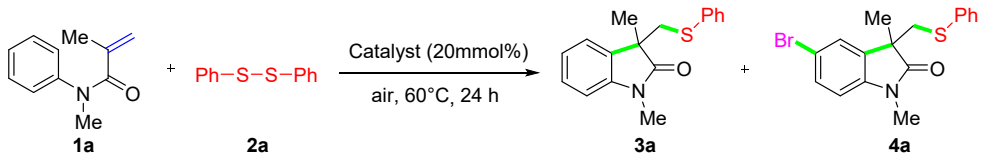


2p

4. The Optimization Reaction Conditions

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



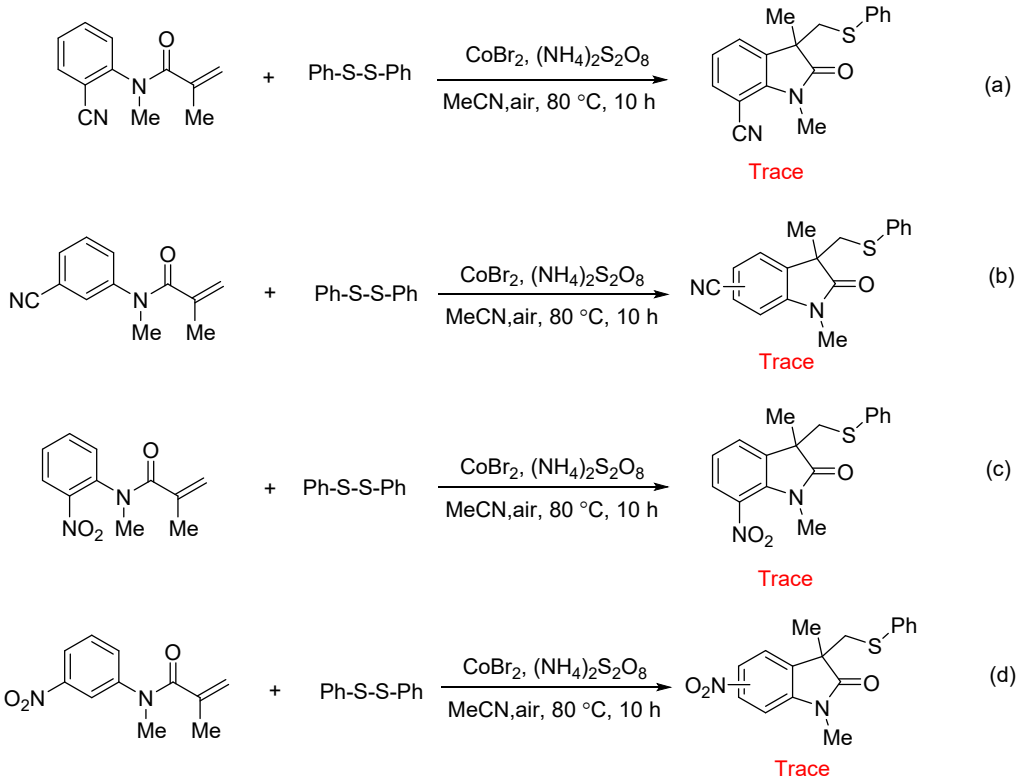
Entry	Catalyst	Oxidant	Solvent	Yield(%)[b]	
				3a	**4a**
1	$FeBr_3$	-	MeCN	trace	trace
2	$FeBr_3$	$(NH_4)_2S_2O_8$	MeCN	51	15
3	$FeCl_3$	$(NH_4)_2S_2O_8$	MeCN	NR[c]	NR
4	$FeCl_2$	$(NH_4)_2S_2O_8$	MeCN	NR	NR
5	$Fe(OAc)_3$	$(NH_4)_2S_2O_8$	MeCN	NR	NR
6	$CuBr_2$	$(NH_4)_2S_2O_8$	MeCN	40	12
7	CuBr	$(NH_4)_2S_2O_8$	MeCN	32	trace
8		$(NH_4)_2S_2O_8$	MeCN	NR	NR
9		$(NH_4)_2S_2O_8$	MeCN	41	trace
10	CuI	$(NH_4)_2S_2O_8$	MeCN	trace	
11	$CuCl_2$	$(NH_4)_2S_2O_8$	MeCN		trace
12	$CoCl_2$	$(NH_4)_2S_2O_8$	MeCN	22	
13	$NiBr_2$	$(NH_4)_2S_2O_8$	MeCN	66	trace
14	$CoBr_2$	$(NH_4)_2S_2O_8$	MeCN	NR	
15	$Co(OAc)_2$	$Na_2S_2O_8$	MeCN	23	12
16	KBr	$K_2S_2O_8$	MeCN	47	NR
	$CoBr_2$			54	trace
	$CoBr_2$				18
17	$CoBr_2$	$(NH_4)_2S_2O_8$	MeOH	trace	trace
18	$CoBr_2$	$(NH_4)_2S_2O_8$	1,4-dioxane	trace	trace
19	$CoBr_2$	$(NH_4)_2S_2O_8$	DCE	12	trace
20	$CoBr_2$	$(NH_4)_2S_2O_8$	DMF	trace	trace
21	$CoBr_2$	$(NH_4)_2S_2O_8$	toluene	trace	trace
22[d]	$CoBr_2$	$(NH_4)_2S_2O_8$	MeCN	69	14
23[e]	$CoBr_2$	$(NH_4)_2S_2O_8$	MeCN	73	19
24[e]	$CoBr_2$ (10mmol%)	$(NH_4)_2S_2O_8$	MeCN	42	5

25[e]	$CoBr_2$ (30mmol%)	$(NH_4)_2S_2O_8$	MeCN	58	29
26[e]	$CoBr_2$	$(NH_4)_2S_2O_8$ (0.36mmol)	MeCN	85	10
27[e]	$CoBr_2$	$(NH_4)_2S_2O_8$ (0.42mmol)	MeCN	76	16
28[e, f]	$CoBr_2$	$(NH_4)_2S_2O_8$ (0.36mmol)	MeCN	59	11
29[d]	$CoBr_2$ (50mmol%)	$(NH_4)_2S_2O_8$ (0.6mmol)	MeCN	trace	83

[a] Reaction conditions: **1a** (0.30 mmol), **2a** (0.15 mmol), catalyst (20 mmol%), oxidant (0.30 mmol), solvent (1.0 mL), 60 ℃, air, 24 h (an oil bath). [b] Isolated yield based on **1a**. [c] NR means no reaction. [d] The reaction was performed at 80 ℃, 12 h (an oil bath). [e] The reaction was performed at 100 ℃ (an oil bath), 8h. [f] The reaction was performed under an Ar atmosphere.

5. Substrate scope of *N*-aryacrylamides bearing electron-withdrawing groups.

Several *N*-aryacrylamides bearing electron-withdrawing groups attached to the *ortho* and *meta*-positions of aryl ring have been investigated to evaluate the effects of electrotropy and steric hindrance on the reaction. Unfortunately, traces of sulfurated products were noticed when the strong electron-withdrawing group (CN, NO_2) substituted *N*-aryacrylamides were performed, and the potential causes are still being investigated in our lab (Scheme 1).



Scheme 1. Reactivity of *N*-aryacrylamides with electron-withdrawing substitutents.

6. General procedure for the cobalt-catalyzed synthesis of sulfurated oxindoles.

A reaction flask (10.0 mL) was charged with *N*-arylacrylamide (0.3 mmol), disulphide (0.15 mmol), $CoBr_2$ (0.06 mmol) and $(NH_4)_2S_2O_8$ (0.36 mmol) in MeCN (1.0 mL). The resulting reaction mixture was heated at 80-100 °C in an oil bath for 10-12 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and removed the solvent under reduced pressure. The crude product was purified *via* flash column chromatography (PE/EA = 4:1 to 1:1) to give the corresponding substituted sulfurated oxindole.

1,3-Dimethyl-3-((phenylthio)methyl)indolin-2-one (3a)[7]: colourless oil; 72 mg, yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 1H), 7.22-7.09 (m, 6H), 7.00-6.96 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.44-3.34 (m, 2H), 3.21 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 143.4, 136.2, 132.3, 130.5, 128.7, 128.3, 126.5, 123.3, 122.5, 108.0, 49.0, 42.8, 26.3, 23.0. HRMS (ESI) m/z: calcd for $C_{17}H_{18}NOS$ $[M + H]^+$ 284.1109; Found 284.1104.

1,3-Dimethyl-3-((p-tolylthio)methyl)indolin-2-one (3b)[7]: colourless oil; 78 mg, yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.03-6.94 (m, 3H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.40-3.30 (m, 2H), 3.21 (s, 3H), 2.27 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 143.4, 136.6, 132.5, 132.4, 131.2, 129.5, 128.2, 123.3, 122.5, 108.0, 49.1, 43.5, 26.3, 23.0, 21.0. HRMS (ESI) m/z: calcd for $C_{18}H_{20}NOS$ $[M + H]^+$ 298.1266; Found 298.1264.

3-(((4-Methoxyphenyl)thio)methyl)-1,3-dimethylindolin-2-one (3c)[7]: colourless oil; 85 mg, yield: 90%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 15.4, 8.0 Hz, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 3.31 (d, *J* = 1.1 Hz, 2H), 3.21 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.1, 159.0, 143.5, 133.9, 132.4, 128.2, 126.5, 123.3, 122.5, 114.3, 108.0, 55.3, 49.3, 44.6, 26.3, 23.2.HRMS (ESI) m/z: calcd for $C_{18}H_{20}NO_2S$ $[M + H]^+$ 314.1215; Found 314.1217.

3-(((4-Chlorophenyl)thio)methyl)-1,3-dimethylindolin-2-one (3d)[7]: colourless oil; 74 mg, yield: 78%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (td, *J* = 7.7, 1.2 Hz, 1H), 7.16-7.07 (m, 5H), 7.01-6.93 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.39-3.34 (m, 2H), 3.21 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.9, 143.5, 134.6, 132.6, 132.1, 132.0, 128.8, 128.4, 123.3, 122.6, 108.1, 49.1, 43.0, 26.3, 23.1. HRMS (ESI) m/z: calcd for $C_{17}H_{18}ClNOS$ $[M + H]^+$ 318.0719; Found 318.0714.

1,3-Dimethyl-3-(((4-nitrophenyl)thio)methyl)indolin-2-one (3e): yellow oil; 39 mg, yield: 40%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.38 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.29-7.22 (m, 3H), 7.18 (d, *J* = 1.9 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 3.46 (s, 2H), 3.21 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.0, 145.8, 145.7, 142.5, 133.5, 131.5, 128.5, 126.7, 123.8, 115.4, 109.7, 49.2, 41.0, 26.5, 22.9. HRMS (ESI) m/z: calcd for $C_{17}H_{18}N_2O_3S$ $[M + H]^+$ 329.0960; Found 329.0958.

3-Methyl-3-((phenylthio)methyl)indolin-2-one (3f): colourless oil; 61 mg, yield: 76%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.36-7.32 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.20-7.14 (m, 2H), 3.75 (d, *J* = 13.9 Hz, 1H), 3.57 (d, *J* = 13.9 Hz, 1H), 1.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 136.9, 135.6,

130.9, 129.0, 129.0, 127.0, 125.1, 120.2, 73.5, 47.7, 29.3. HRMS (ESI) m/z: calcd for $C_{16}H_{16}NOS$ $[M + H]^+$ 270.0953; Found 270.0948.

1-Benzyl-3-methyl-3-((phenylthio)methyl)indolin-2-one (3g): colourless oil; 86 mg, yield: 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.31-7.28 (m, 2H), 7.27-7.23 (m, 2H), 7.21-7.17 (m, 2H), 7.17-7.08 (m, 5H), 6.90 (td, *J* = 7.5, 1.0 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.05 (d, *J* = 15.8 Hz, 1H), 4.82 (d, *J* = 15.8 Hz, 1H), 3.50 (d, *J* = 12.7 Hz, 1H), 3.45 (d, *J* = 12.7 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.2, 142.5, 136.3, 135.8, 132.2, 130.5, 128.7, 128.7, 128.1, 127.6, 127.3, 126.4, 123.3, 122.5, 109.2, 49.2, 43.9, 42.8, 23.5. HRMS (ESI) m/z: calcd for $C_{23}H_{21}NOS$ $[M + H]^+$ 360.1422; Found 360.1425.

1,3,5-Trimethyl-3-((phenylthio)methyl)indolin-2-one (3h): colourless oil; 77 mg, yield: 86%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20-7.09 (m, 5H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.91 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.40-3.35 (m, 2H), 3.20 (s, 3H), 2.24 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.0, 141.1, 136.2, 132.2, 132.0, 130.6, 128.6, 128.5, 126.4, 124.3, 107.7, 49.2, 42.9, 26.3, 23.1, 21.1. HRMS (ESI) m/z: calcd for $C_{18}H_{20}NOS$ $[M + H]^+$ 298.1266; Found 298.1261.

5-Methoxy-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3i): colourless oil; 85 mg, yield: 90%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20-7.14 (m, 4H), 7.14-7.11 (m, 1H), 6.81-6.73 (m, 3H), 3.71 (s, 3H), 3.41-3.33 (m, 2H), 3.19 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.7, 156.0, 137.0, 136.2, 133.6, 130.7, 128.7, 126.5, 112.6, 110.8, 108.3, 55.7, 49.6, 42.8, 26.4, 23.1. HRMS (ESI) m/z: calcd for $C_{18}H_{20}NO_2S$ $[M + H]^+$ 314.1215; Found 314.1215.

5-Isopropyl-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3j): colourless oil; 89 mg, yield: 91%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.07 (m, 6H), 7.06 (d, *J* = 1.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.40 (d, *J* = 12.9 Hz, 1H), 3.35 (d, *J* = 12.9 Hz, 1H), 3.20 (s, 3H), 2.81 (hept, *J* = 6.9 Hz, 1H), 1.44 (s, 3H), 1.19 (dd, *J* = 12.3, 6.9 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.1, 143.3, 141.3, 136.4, 132.3, 130.4, 128.7, 126.4, 125.8, 121.7, 107.7, 49.2, 42.9, 33.8, 26.3, 24.2, 24.2, 22.9. HRMS (ESI) m/z: calcd for $C_{20}H_{24}NOS$ $[M + H]^+$ 326.1579; Found 326.1575.

5-Fluoro-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3k): colourless oil; 74 mg, yield: 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.11 (m, 5H), 6.98-6.92 (m, 1H), 6.87 (dd, *J* = 8.0, 2.6 Hz, 1H), 6.75 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.41-3.33 (m, 2H), 3.20 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.7, 159.2 (d, *J* = 240.9 Hz), 139.4, 135.8, 133.9 (d, *J* = 7.7 Hz), 130.8, 128.8, 126.8, 114.4 (d, *J* = 23.0 Hz), 111.7 (d, *J* = 25.0 Hz), 108.4 (d, *J* = 8.6 Hz), 49.7, 42.7, 26.4, 23.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.2. HRMS (ESI) m/z: calcd for $C_{17}H_{17}FNOS$ $[M + H]^+$ 302.1015; Found 302.1017.

5-Chloro-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3l)[8]: colourless oil; 78 mg, yield: 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.17 (m, 5H), 7.05 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.36 (s, 2H), 3.20 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.6, 142.1, 135.6, 133.9, 130.9, 128.8, 128.2, 127.9, 126.9, 124.0, 108.9, 49.6, 42.7, 26.4, 23.0. HRMS (ESI) m/z: calcd for $C_{17}H_{17}ClNOS$ $[M + H]^+$ 318.0719; Found 318.0719.

5-Bromo-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3m): colourless oil; 87 mg, yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.17 (dd, *J* =

3.5, 1.5 Hz, 6H), 6.71 (d, *J* = 8.3 Hz, 1H), 3.36 (s, 2H), 3.19 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 142.6, 135.6, 134.2, 131.1, 130.9, 128.8, 126.9, 126.8, 115.2, 109.4, 49.6, 42.8, 26.4, 23.0. HRMS (ESI) m/z: calcd for $C_{17}H_{17}BrNOS$ $[M + H]^+$ 362.0214; Found 362.0212.

1,3-Dimethyl-5-phenyl-3-((phenylthio)methyl)indolin-2-one (3n): colourless oil; 97 mg, yield: 90%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.46-7.38 (m, 4H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 3.46-3.40 (m, 2H), 3.27 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.1, 142.9, 140.9, 136.0, 136.0, 132.8, 130.7, 128.7, 128.7, 127.1, 126.9, 126.9, 126.6, 122.5, 108.2, 49.5, 42.9, 26.4, 23.1. HRMS (ESI) m/z: calcd for $C_{23}H_{22}NOS$ $[M + H]^+$ 360.1422; Found 360.1425.

5-Hydroxy-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3o): pink solid; 63 mg, yield: 70%; mp: 52-53 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.05 (s, 1H), 7.23 (dt, *J* = 15.1, 7.3 Hz, 4H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.83-6.79 (m, 2H), 6.67 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.52 (d, *J* = 12.3 Hz, 1H), 3.26 (d, *J* = 12.3 Hz, 1H), 3.06 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 178.0, 153.7, 136.7, 135.7, 133.5, 129.3, 129.2, 126.4, 114.4, 111.9, 109.2, 48.9, 41.0, 26.5, 23.8. HRMS (ESI) m/z: calcd for $C_{17}H_{18}NO_2S$ $[M + H]^+$ 300.1058; Found 300.1057.

1,3-Dimethyl-3-((phenylthio)methyl)-5-(trifluoromethyl)indolin-2-one (3p): colourless oil; 83 mg, yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.09 (m, 6H), 7.04 (d, *J* = 1.3 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.37 (d, *J* = 1.7 Hz, 2H), 3.21 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 144.7, 142.1, 135.6, 133.8, 130.8, 128.8, 126.9, 121.3, 117.5, 108.3, 49.6, 42.7, 26.4, 22.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ -58.3. HRMS (ESI) m/z: calcd for $C_{18}H_{17}F_3NO_2S$ $[M + H]^+$ 368.0932; Found 368.0931.

1,3,4-Trimethyl-3-((phenylthio)methyl)indolin-2-one /1,3,6-trimethyl-3-((phenylthio)methyl)indolin-2-one (1.5:1) (***3q:3q'***): colourless oil; 64 mg, yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 7.24-7.19 (m, 3H), 7.18 (dd, *J* = 2.0, 1.3 Hz, 2H), 7.17 (d, *J* = 1.0 Hz, 1H), 7.16 (d, *J* = 0.8 Hz, 1H), 7.15 (d, *J* = 1.1 Hz, 1H), 7.13-7.10 (m, 2H), 7.03 (tt, *J* = 6.8, 1.2 Hz, 3H), 6.80 (s, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.58-3.50 (m, 1H), 3.36 (d, *J* = 1.8 Hz, 2H), 3.21 (s, 3H), 3.17 (s, 2H), 2.41 (s, 3H), 2.22 (s, 2H), 1.62 (s, 3H), 1.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 144.9, 144.5, 143.0, 138.9, 138.3, 138.1, 136.5, 135.9, 135.1, 131.5, 130.9, 130.7, 130.6, 129.0, 128.9, 128.7, 128.6, 127.0, 126.9, 126.6, 125.3, 125.3, 110.5, 106.7, 50.6, 49.1, 42.9, 41.3, 26.4, 26.3, 23.0, 22.2, 21.4. HRMS (ESI) m/z: calcd for $C_{18}H_{20}NOS$ $[M + H]^+$ 298.1266; Found 298.1264.

1,3,5,7-Tetramethyl-3-((phenylthio)methyl)indolin-2-one (3r): colourless oil; 78 mg, yield: 84%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.15 (m, 4H), 7.14-7.09 (m, 1H), 6.77 (d, *J* = 11.0 Hz, 2H), 3.47 (s, 3H), 3.35 (s, 2H), 2.54 (s, 3H), 2.19 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.7, 138.8, 136.3, 133.0, 132.4, 131.8, 130.6, 128.6, 126.4, 122.0, 119.3, 48.5, 43.1, 29.6, 23.5, 20.8, 18.9. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NOS$ $[M + H]^+$ 312.1422; Found 312.1425.

1,3,5-Trimethyl-3-((p-tolylthio)methyl)indolin-2-one (3s)[7]: colourless oil; 78 mg, yield: 84%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09-7.02 (m, 3H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.89

(s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 3.36-3.30 (m, 2H), 3.20 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.1, 141.1, 136.5, 132.5, 132.3, 131.9, 131.3, 129.4, 128.4, 124.3, 107.7, 49.3, 43.5, 26.3, 23.1, 21.1, 21.0. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NOS$ $[M + H]^+$ 312.1422; Found 312.1425.

3-(((4-Methoxyphenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3t): colourless oil; 84 mg, yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.06 (m, 2H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.86 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.71-6.65 (m, 2H), 3.76 (s, 3H), 3.29 (s, 2H), 3.20 (s, 3H), 2.24 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 158.9, 141.2, 133.9, 132.3, 131.9, 128.4, 126.6, 124.2, 114.2, 107.7, 55.3, 49.5, 44.5, 26.3, 23.3, 21.1. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NO_2S$ $[M + H]^+$ 328.1371; Found 328.1376.

3-(((4-Chlorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3u): colourless oil; 79 mg, yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.01 (m, 5H), 6.83 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.34 (s, 2H), 3.20 (s, 3H), 2.23 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 141.1, 134.6, 132.5, 132.2, 132.1, 132.0, 128.7, 128.5, 124.2, 107.8, 49.4, 43.2, 26.3, 23.2, 21.0. HRMS (ESI) m/z: calcd for $C_{18}H_{19}ClNOS$ $[M + H]^+$ 332.0876; Found 332.0878.

3-(((4-Fluorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3v): colourless oil; 82 mg, yield: 87%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15-7.08 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.88-6.80 (m, 3H), 6.74 (d, *J* = 7.9 Hz, 1H), 3.33 (d, *J* = 2.1 Hz, 2H), 3.21 (s, 3H), 2.24 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.0, 161.9 (d, *J* = 247.3 Hz), 141.2, 133.6 (d, *J* = 7.7 Hz), 132.1, 132.0, 131.1 (d, *J* = 4.0 Hz), 128.5, 124.2, 115.6 (d, *J* = 21.8 Hz), 107.8, 49.5, 44.0, 26.3, 23.2, 21.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.2. HRMS (ESI) m/z: calcd for $C_{18}H_{19}FNOS$ $[M + H]^+$ 316.1171; Found 316.1170.

3-(((2-Fluorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3w): colourless oil; 85 mg, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.09 (m, 1H), 7.06 (td, *J* = 7.6, 1.8 Hz, 1H), 7.00 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1H), 6.95-6.86 (m, 2H), 6.84 (s, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 3.31 (d, *J* = 13.2 Hz, 1H), 3.20 (s, 3H), 2.19 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 161.7 (d, *J* = 245.6 Hz), 141.2, 133.6, 132.0, 131.9, 128.9, 128.8, 128.5, 124.1 (d, *J* = 3.7 Hz), 124.0, 122.5 (d, *J* = 17.5 Hz), 115.4 (d, *J* = 22.7 Hz), 107.7, 49.5, 41.6 (d, *J* = 2.9 Hz), 26.3, 23.2, 21.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.3. HRMS (ESI) m/z: calcd for $C_{18}H_{19}FNOS$ $[M + H]^+$ 316.1171; Found 316.1169.

3-(((3-Fluorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3x): colourless oil; 75 mg, yield: 79%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (td, *J* = 8.0, 6.1 Hz, 1H), 7.05 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1H), 6.95 (ddd, *J* = 7.9, 1.7, 0.9 Hz, 1H), 6.89 (s, 1H), 6.85-6.77 (m, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 3.37 (d, *J* = 2.7 Hz, 2H), 3.21 (s, 3H), 2.24 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.9, 163.3, 161.6, 141.1, 138.6, 138.5, 132.1, 132.0, 129.9, 129.8, 128.6, 125.8, 124.2, 117.2, 117.0, 113.4, 113.3, 107.8, 49.2, 42.6, 26.3, 23.1, 21.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.8. HRMS (ESI) m/z: calcd for $C_{18}H_{19}FNOS$ $[M + H]^+$ 316.1171; Found 316.1172.

1,3,5-Trimethyl-3-((o-tolylthio)methyl)indolin-2-one (3y): colourless oil; 71 mg, yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1H), 7.04 (q, *J* = 2.6, 2.0 Hz, 4H), 6.92 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 3.33 (s, 2H), 3.19 (s, 3H), 2.24 (s, 3H), 2.20 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 141.1, 138.9, 135.3, 132.3, 132.0, 130.9,

129.9, 128.4, 126.5, 126.2, 124.2, 107.7, 49.2, 42.2, 26.3, 23.3, 21.1, 20.5. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NOS$ $[M + H]^+$ 312.1422; Found 312.1424.

3-(((3,5-Dichlorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3z): pale yellow oil; 79 mg, yield: 72%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.10-7.03 (m, 2H), 6.96 (d, *J* = 1.8 Hz, 2H), 6.82 (s, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 3.35 (d, *J* = 2.2 Hz, 2H), 3.22 (s, 3H), 2.22 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.6, 141.1, 139.6, 134.6, 132.0, 131.6, 128.9, 128.4, 126.5, 124.1, 107.8, 49.3, 42.6, 26.3, 23.0, 21.0. HRMS (ESI) m/z: calcd for $C_{18}H_{18}Cl_2NOS$ $[M + H]^+$ 366.0486; Found 366.0489.

(Z)-1-Methyl-3-(1-(phenylthio)ethylidene)indolin-2-one (3aa): yellow oil; 40 mg, yield: 47%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.6, 7.1, 1.5 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.21 (d, *J* = 3.8 Hz, 4H), 7.15–7.08 (m, 1H), 3.75 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 152.2, 139.6, 136.7, 131.2, 128.9, 127.6, 126.4, 125.7, 125.5, 122.3, 121.0, 114.5, 30.6, 18.4. HRMS (ESI) m/z: calcd for $C_{17}H_{16}NOS$ $[M + H]^+$ 282.0953; Found 282.0963.

3-((Butylthio)methyl)-1,3,5-trimethylindolin-2-one (3ab): colourless oil; 61 mg, yield: 73%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.1 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 1H), 3.21 (s, 3H), 3.01 (d, *J* = 13.0 Hz, 1H), 2.90 (d, *J* = 13.0 Hz, 1H), 2.41-2.29 (m, 5H), 1.47-1.36 (m, 5H), 1.33-1.22 (m, 3H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 141.2, 133.0, 131.9, 128.4, 123.9, 107.8, 49.3, 40.2, 33.5, 31.8, 26.3, 23.0, 21.8, 21.2, 13.6. HRMS (ESI) m/z: calcd for $C_{14}H_{24}NOS$ $[M + H]^+$ 278.1579; Found 278.1581.

1,3,5-Trimethyl-3-((phenylselanyl)methyl)indolin-2-one (3ac)[9]: pale yellow oil; 85 mg, yield: 82%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 2H), 7.19-7.11 (m, 3H), 7.04 (ddd, *J* = 7.9, 1.8, 0.9 Hz, 1H), 6.84 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.40-3.24 (m, 2H), 3.21 (s, 3H), 2.21 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 141.0, 133.6, 132.7, 132.0, 130.2, 128.7, 128.5, 127.0, 124.0, 107.7, 49.2, 36.1, 26.3, 23.7, 21.1. HRMS (ESI) m/z: calcd for $C_{18}H_{20}NOSe$ $[M + H]^+$ 346.0710; Found 346.0712.

3-(((4-Fluorophenyl)selanyl)methyl)-1,3,5-trimethylindolin-2-one (3ad): pale yellow oil; 85mg, yield: 78%; ^1H NMR (600 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 7.05 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H), 6.85-6.78 (m, 2H), 6.77 (s, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 3.33-3.24 (m, 2H), 3.22 (s, 3H), 2.21 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.2, 163.1, 161.5, 141.0, 136.1, 136.1, 132.5, 132.0, 128.5, 124.5, 123.9, 115.9, 115.7, 107.8, 49.4, 36.7, 26.3, 23.9, 21.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.8. HRMS (ESI) m/z: calcd for $C_{18}H_{19}FNOSe$ $[M + H]^+$ 364.0616; Found 364.0615.

3-(((4-Bromophenyl)selanyl)methyl)-1,3,5-trimethylindolin-2-one (3ae): pale yellow oil; 91 mg, yield: 72%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 2H), 7.12-7.07 (m, 2H), 7.03 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1H), 6.79-6.69 (m, 2H), 3.36-3.24 (m, 2H), 3.21 (s, 3H), 2.21 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 141.0, 135.3, 132.3, 132.1, 131.7, 128.9, 128.5, 123.9, 121.4, 107.8, 49.3, 36.3, 26.3, 23.8, 21.0. HRMS (ESI) m/z: calcd for $C_{18}H_{19}BrNOSe$ $[M + H]^+$ 423.9815; Found 423.9812.

3-(((4-Methoxyphenyl)selanyl)methyl)-1,3,5-trimethylindolin-2-one (3af): pale yellow oil; 93 mg, yield: 83%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 2H), 7.04 (ddd, *J* = 7.9, 1.7, 0.9 Hz, 1H), 6.81 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.69-6.64 (m, 2H), 3.76 (s,

3H), 3.25 (d, *J* = 2.8 Hz, 2H), 3.22 (s, 3H), 2.22 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 159.2, 141.1, 136.0, 132.7, 131.9, 128.4, 124.0, 120.3, 114.4, 107.7, 55.2, 49.4, 36.8, 26.3, 23.9, 21.1. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NO_2Se$ $[M + H]^+$ 376.0816; Found 376.0807.

1,3,5-Trimethyl-3-(((4-(trifluoromethyl)phenyl)selanyl)methyl)indolin-2-one (3ag): yellow oil; 56 mg, yield: 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 4H), 7.03 (ddd, *J* = 7.9, 1.7, 0.9 Hz, 1H), 6.78 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.41-3.33 (m, 2H), 3.21 (s, 3H), 2.17 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 141.0, 135.3, 133.0, 132.3, 132.1, 129.1, 128.8, 128.6, 125.4, 125.38, 125.3, 125.3, 125.3, 123.9, 122.7, 107.9, 49.2, 35.8, 26.3, 23.7, 20.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.65. HRMS (ESI) m/z: calcd for $C_{19}H_{19}F_3NOSe$ $[M + H]^+$ 414.0584; Found 414.0583.

***3-Methyl-3-((phenylthio)methyl)benzofuran-2(3H)-one (3ah)*:** colourless oil; 44 mg, yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.37-7.32 (m, 2H), 7.31-7.27 (m, 1H), 7.26 (td, *J* = 1.9, 1.2 Hz, 1H), 7.23-7.21 (m, 1H), 6.96-6.88 (m, 2H), 3.58 (d, *J* = 13.7 Hz, 1H), 3.38 (d, *J* = 13.7 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 150.4, 135.7, 130.6, 129.7, 129.5, 129.1, 126.9, 126.6, 126.3, 121.1, 49.2, 45.0, 25.7. HRMS (ESI) m/z: calcd for $C_{16}H_{15}O_2S$ $[M + H]^+$ 271.0793; Found 271.0783.

***5-Methoxy-3-methyl-3-((phenylsulfonyl)methyl)benzofuran-2(3H)-one* (3ai):** colourless oil; 73 mg, yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.42 (m, 2H), 7.31-7.25 (m, 2H), 7.24-7.18 (m, 1H), 6.83 (d, *J* = 2.4 Hz, 3H), 3.79 (s, 3H), 3.57 (d, *J* = 13.7 Hz, 1H), 3.36 (d, *J* = 13.7 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 157.6, 143.8, 135.7, 130.6, 129.1, 126.8, 122.0, 121.9, 114.6, 114.5, 75.3, 55.6, 45.0, 25.7. HRMS (ESI) m/z: calcd for $C_{17}H_{17}O_5S$ $[M + H]^+$ 333.0797; Found 333.0797.

***5-Chloro-3-methyl-3-((phenylsulfonyl)methyl)benzofuran-2(3H)-one* (3aj):** colourless oil; 73 mg, yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.41 (m, 2H), 7.31-7.27 (m, 3H), 7.25-7.19 (m, 1H), 6.85-6.77 (m, 2H), 3.57 (d, *J* = 13.9 Hz, 1H), 3.35 (d, *J* = 13.9 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 148.8, 135.4, 131.7, 130.7, 129.5, 129.2, 127.0, 122.6, 75.4, 45.0, 25.6. HRMS (ESI) m/z: calcd for $C_{16}H_{14}ClO_4S$ $[M + H]^+$ 337.0301; Found 337.0298.

7. General procedure for the synthesis of 4a-4h.

A reaction flask (10.0 mL) was charged with *N*-methyl-*N*-phenylmethacrylamide (0.3 mmol), disulphide (0.15 mmol), $CoBr_2$ (0.15 mmol) and $(NH_4)_2S_2O_8$ (0.6 mmol) in MeCN (1.0 mL). The resulting reaction mixture was heated at 80 °C in an oil bath for 12 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and removed the solvent under reduced pressure. The crude product was purified *via* flash column chromatography (PE/EA = 4:1) to give the corresponding 5-bromo substituted sulfurated oxindole.

5-Bromo-1,3-dimethyl-3-((phenylthio)methyl)indoline (4a): colourless oil; 78 mg, yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.17 (dd, *J* = 3.5, 1.5 Hz, 6H), 6.71 (d, *J* = 8.3 Hz, 1H), 3.36 (s, 2H), 3.19 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 142.6, 135.6, 134.2, 131.1, 130.9, 128.8, 126.9, 126.8, 115.2,

109.4, 49.6, 42.8, 26.4, 23.0. HRMS (ESI) m/z: calcd for $C_{17}H_{17}BrNOS$ $[M + H]^+$ 362.0214; Found 362.0212.

5-Bromo-1,3-dimethyl-3-((p-tolylthio)methyl)indolin-2-one (4b)[7]: colourless oil; 97 mg, yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.05–6.93 (m, 4H), 6.70 (d, *J* = 8.3 Hz, 1H), 3.32 (s, 2H), 3.20 (s, 3H), 2.29 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 142.6, 137.1, 134.3, 131.9, 131.6, 130.9, 129.6, 126.8, 115.2, 109.3, 49.8, 43.4, 26.4, 23.1, 21.1. HRMS (ESI) m/z: calcd for $C_{18}H_{19}BrNOS$ $[M + H]^+$ 376.0371; Found 376.0370.

5-Bromo-3-(((4-methoxyphenyl)thio)methyl)-1,3-dimethylindolin-2-one (4c): colourless oil; 106 mg, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.10-7.00 (m, 3H), 6.74-6.66 (m, 3H), 3.78 (s, 3H), 3.32-3.22 (m, 2H), 3.21 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 159.2, 142.6, 134.3, 134.0, 130.9, 126.7, 125.9, 115.2, 114.4, 109.3, 55.3, 49.9, 44.3, 26.4, 23.2. HRMS (ESI) m/z: calcd for $C_{18}H_{19}BrNO_2S$ $[M + H]^+$ 392.0320; Found 392.0316.

5-Bromo-3-(((4-chlorophenyl)thio)methyl)-1,3-dimethylindoline (4d): colourless oil; 92 mg, yield: 80%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.15-7.11 (m, 3H), 7.08-7.04 (m, 2H), 6.71 (d, *J* = 8.3 Hz, 1H), 3.36-3.31 (m, 2H), 3.19 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.3, 142.6, 134.1, 134.0, 133.1, 132.3, 131.1, 128.9, 126.8, 115.3, 109.5, 49.7, 43.0, 26.4, 23.1. HRMS (ESI) m/z: calcd for $C_{17}H_{16}BrClNOS$ $[M + H]^+$ 395.9825; Found 395.9822.

5-Bromo-3-((butylthio)methyl)-1,3-dimethylindolin-2-one (4e): colourless oil; 77 mg, yield: 75%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.38 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 3.21 (s, 3H), 2.99 (d, *J* = 13.1 Hz, 1H), 2.89 (d, *J* = 13.1 Hz, 1H), 2.41-2.30 (m, 2H), 1.46-1.38 (m, 5H), 1.30 (dt, *J* = 14.7, 7.3 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.0, 142.6, 135.1, 131.0, 126.4, 115.2, 109.5, 49.6, 40.0, 33.7, 31.8, 26.4, 22.8, 21.8, 13.6. HRMS (ESI) m/z: calcd for $C_{15}H_{21}BrNOS$ $[M + H]^+$ 342.0527; Found 342.0523.

5-Bromo-3-(((3,5-dichlorophenyl)thio)methyl)-1,3-dimethylindoline (4f): colourless oil; 91 mg, yield: 73%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.14 (t, *J* = 1.9 Hz, 1H), 7.09 (d, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 1.8 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 1H), 3.38-3.32 (m, 2H), 3.22 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 142.6, 138.9, 134.8, 133.6, 131.5, 128.6, 127.2, 126.7, 115.3, 109.5, 42.5, 26.4, 23.0. HRMS (ESI) m/z: calcd for $C_{17}H_{15}BrCl_2NOS$ $[M + H]^+$ 429.9435; Found 429.9424.

5-Bromo-3-methyl-1-phenyl-3-((phenylthio)methyl)indolin-2-one (4g): colourless oil; 104 mg, yield: 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.8 Hz, 2H), 7.45-7.36 (m, 3H), 7.26 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.22-7.14 (m, 6H), 6.69 (d, *J* = 8.4 Hz, 1H), 3.50-3.43 (m, 2H), 1.53 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 142.7, 135.6, 134.3, 133.9, 131.0, 131.0, 129.7, 128.8, 128.3, 127.0, 126.9, 126.7, 115.6, 110.8, 49.82 , 43.54 , 23.3. HRMS (ESI) m/z: calcd for $C_{22}H_{19}BrNOS$ $[M + H]^+$ 424.0371; Found 424.0359.

8-Bromo-1-methyl-1-((phenylthio)methyl)-5,6-dihydro-4H-pyrrolo[3,2,1-iJ]quinolin-2(1H)-one (4h): colourless oil; 96 mg, yield: 83%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23-7.10 (m, 6H), 7.05 (s, 1H), 3.69 (dd, *J* = 12.9, 6.5 Hz, 2H), 3.41-3.30 (m, 2H), 2.82-2.70 (m, 2H), 2.04-1.97 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.3, 138.2, 135.7, 132.7, 130.8, 129.9, 128.8, 126.8, 124.7, 121.8, 114.8, 50.7, 42.5, 38.8, 24.4, 22.7, 21.0. HRMS (ESI) m/z: calcd for $C_{19}H_{19}BrNOS$ $[M + H]^+$ 388.0371; Found 388.0375.

1,3-Dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (5). To a solution of **3a** (0.3 mmol) in CH_2Cl_2 (2.0 mL) was added *m*-chloroperbenzoic acid (0.9 mmol) portion wise at 0 ℃. The mixture was stirred for 4 h until complete consumption of the starting material. Saturated aqueous $NaHCO_3$ solution was added and the resulting mixture was extracted with CH_2Cl_2 (10 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography (PE/EA=1:1) to give the desired product **5** as a white soild (77 mg, 81%). Mp: 145-147 ℃; ^{1}H NMR (600 MHz, CDCl3) δ 7.58-7.48 (m, 3H), 7.41-7.36 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.90 (td, *J* = 7.6, 1.0 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.88 (d, *J* = 14.7 Hz, 1H), 3.69 (d, *J* = 14.6 Hz, 1H), 3.17 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 143.3, 139.9, 133.4, 129.5, 128.9, 128.6, 127.8, 124.1, 122.6, 108.4, 61.9, 45.6, 26.6, 25.5. HRMS (ESI) m/z: calcd for $C_{17}H_{18}NO_3S$ $[M + H]^+$ 316.1007; Found 316.1006.

1,3-Dimethyl-3-((phenylsulfinyl)methyl)indolin-2-one (6). To a stirred solution of **3a** (0.3 mmol) in CH_3COOH (2.0 mL) at room temperature was added 30% H_2O_2 (aq. 0.6 mmol, 0.061 mL, 2.0 eq). The mixture was stirred at 50 ℃ for 6 h until complete consumption of the starting material. The mixture was washed with 1.0 M NaOH solution (2.0 mL) and the resulting mixture was extracted with EtOAc (10 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography (PE/EA=1:2) to give the desired product **6** as a colourless oil (76 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.52 (m, 2H), 7.46 (q, *J* = 2.6, 1.9 Hz, 10H), 7.35 (qd, *J* = 7.9, 1.3 Hz, 2H), 7.14 (dtd, *J* = 17.3, 7.5, 1.0 Hz, 2H), 6.90 (dd, *J* = 7.8, 3.3 Hz, 2H), 3.38 (dd, *J* = 13.5, 2.1 Hz, 2H), 3.29-3.14 (m, 7H), 3.03 (d, *J* = 13.4 Hz, 1H), 1.57 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 144.5, 144.1, 143.1, 142.9, 131.2, 131.1, 131.0, 129.3, 129.2, 128.9, 124.4, 124.2, 124.0, 124.0, 123.0, 122.7, 108.6, 108.5, 65.8, 65.6, 46.8, 46.5, 26.6, 26.4, 24.5, 24.0. HRMS (ESI) m/z: calcd for $C_{17}H_{18}NO_2S$ $[M + H]^+$ 300.1058; Found 300.1058.

1,3-Dimethyl-3-((phenylthio)methyl)indoline (7). To a solution of **3a** in dry THF (3.0 mL) under an inert atmosphere (N_2) was added $LiAlH_4$ (34 mg; 3.0 eq.). The reaction mixture was stirred at refluxed for 8 h. Then, the excess $LiAlH_4$ was carefully hydrolyzed with NaOH solution (1.0 M, 10 mL). The aqueous layer is extracted with EtOAc (20 mL ×3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified *via* flash column chromatography (PE/EA=4:1) to give the final product **7** as a colourless oil (68 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.23 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.13 (ddt, *J* = 7.9, 6.4, 1.2 Hz, 2H), 7.07 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 3.46 (d, *J* = 9.1 Hz, 1H), 3.24-3.16 (m, 2H), 3.00 (d, *J* = 9.2 Hz, 1H), 2.75 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 137.8, 136.4, 128.8, 128.3, 125.7, 122.4, 118.0, 107.6, 67.1, 45.0, 44.2, 35.7, 24.0. HRMS (ESI) m/z: calcd for $C_{17}H_{20}NS$ $[M + H]^+$ 270.1316; Found 270.1321.

8. References

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(2) H.-L. Wei, T. Piou, J. Dufour, L. Neuville and J. Zhu, *Org. Lett.*, 2011, **13**, 2244-2247.
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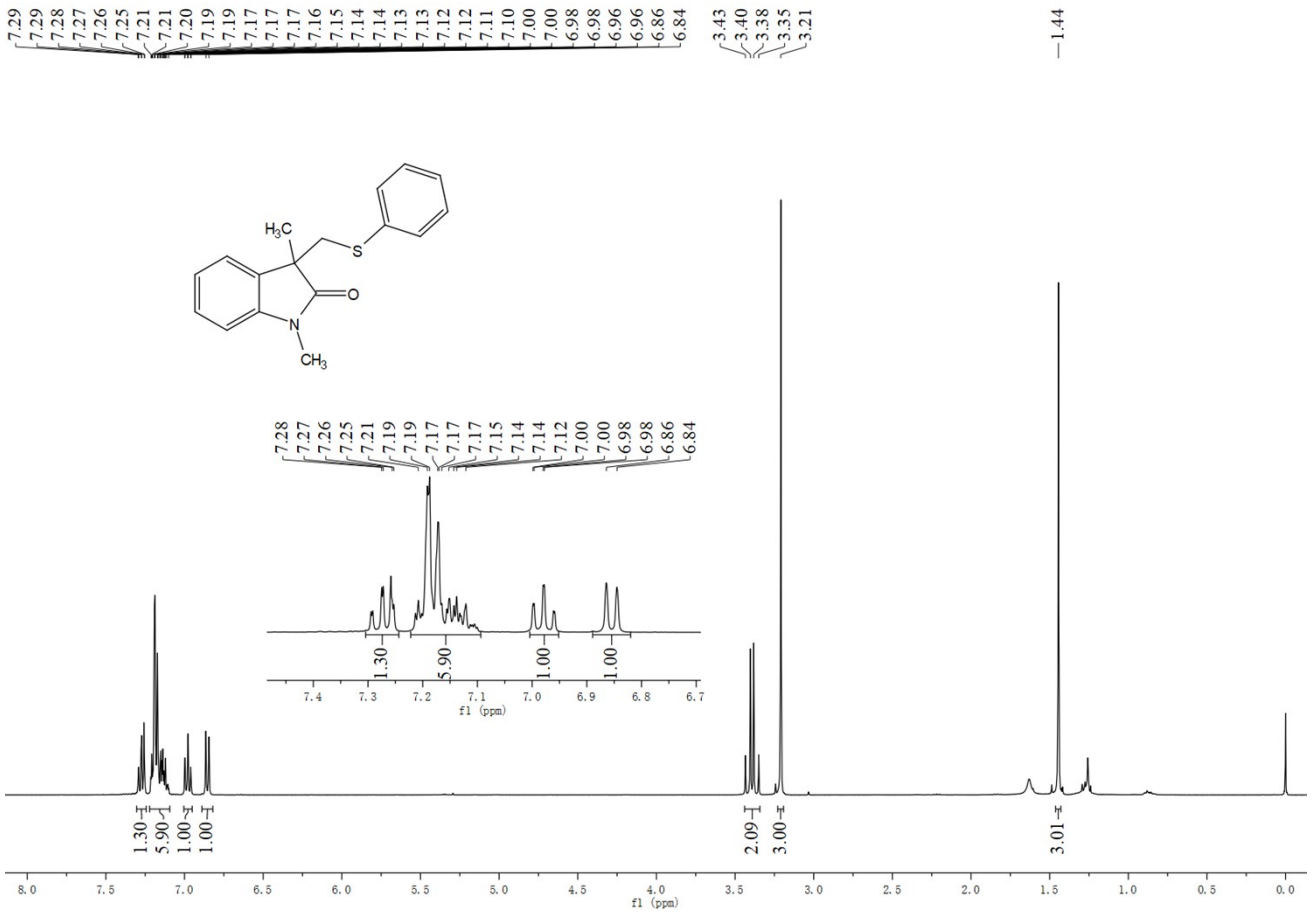
(4) C.-S. Wang, T. Roisnel, P. H. Dixneuf, J.-F. Soulé, *Adv. Synth. Catal.,* 2019, **361**, 445-450.
(5) M. Klussmann, E. Boess, S. Karanestora, A.-E. Bosnidou, B. Schweitzer-Chaput and M. Hasenbeck, *Synlett.*, 2015, **26**, 1973-1976.
(6) D. Kommula, Q. Li, S. Ning, W. Liu, Q. Wang and Z. K. Zhao, *Synth Commun.*, 2020, **50**, 1026-1034.
(7) F.-X. Wang and S.-K. Tian, *J. Org. Chem.*, 2015, **80**, 12697-12703.
(8) D.-L. Kong, J.-X. Du, W.-M. Chu, C.-Y. Ma, J.-Y. Tao and W.-H. Feng, *Molecules.*, 2018, **23**, 2727.
(9) X.-Y. Wang, Y.-F. Zhong, Z.-Y. Mo, S.-H. Wu, Y.-L. Xu, H.-T. Tang, Y.-M. Pan, *Adv. Synth. Catal.,* 2021, ***363***, 208-214.

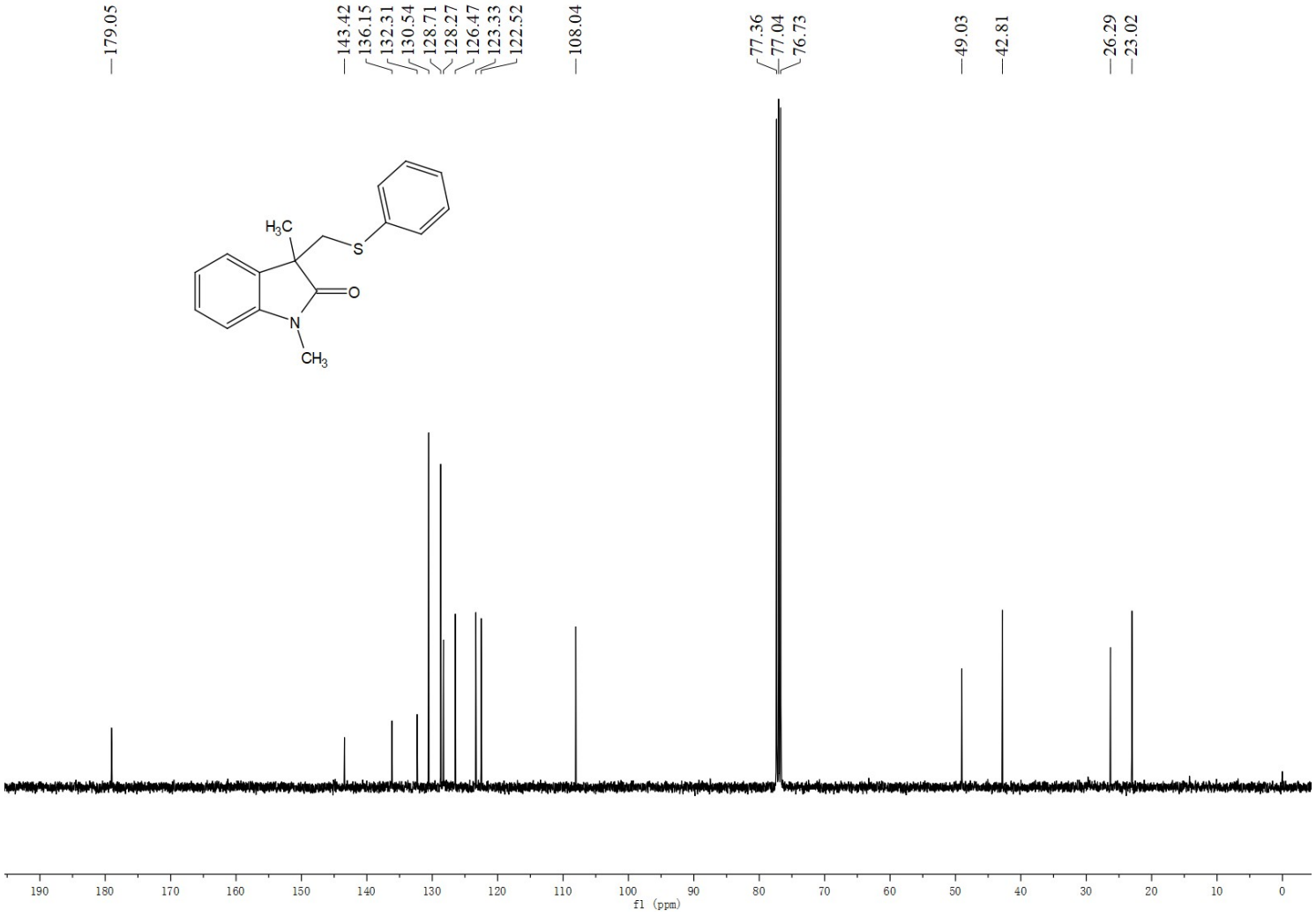
9. ^{1}H NMR, ^{13}C NMR and HRMS spectra of the synthesized compounds

1,3-Dimethyl-3-((phenylthio)methyl)indolin-2-one (3a)

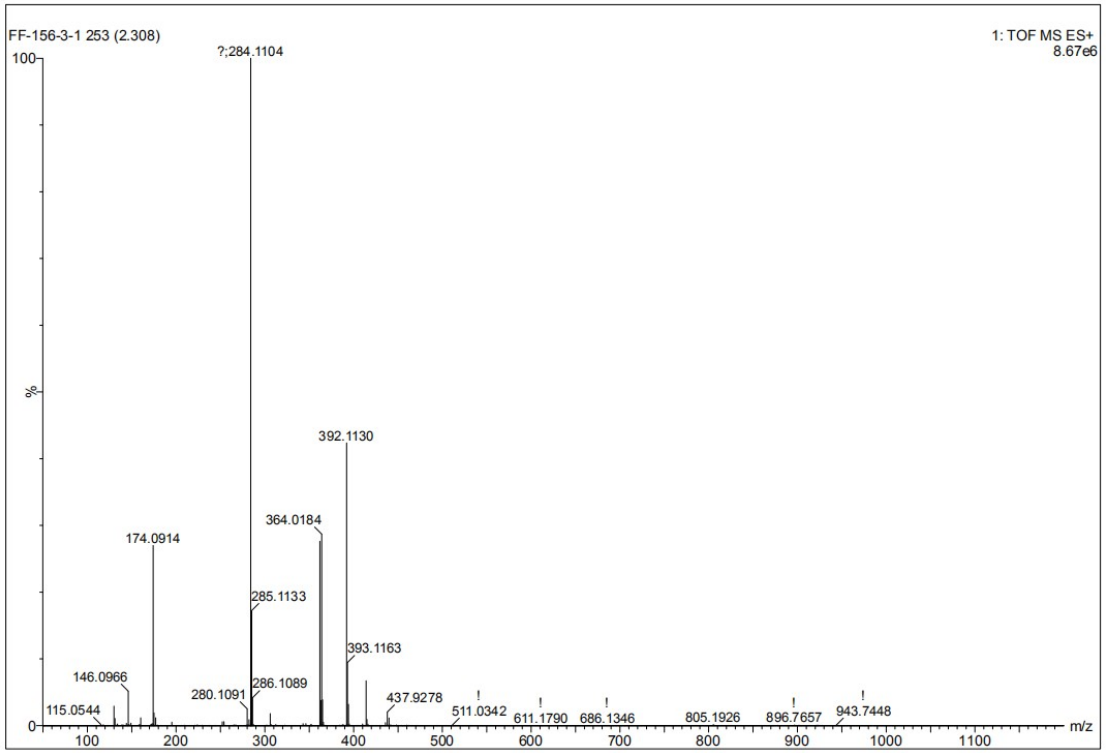
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (400 MHz, $CDCl_3$)

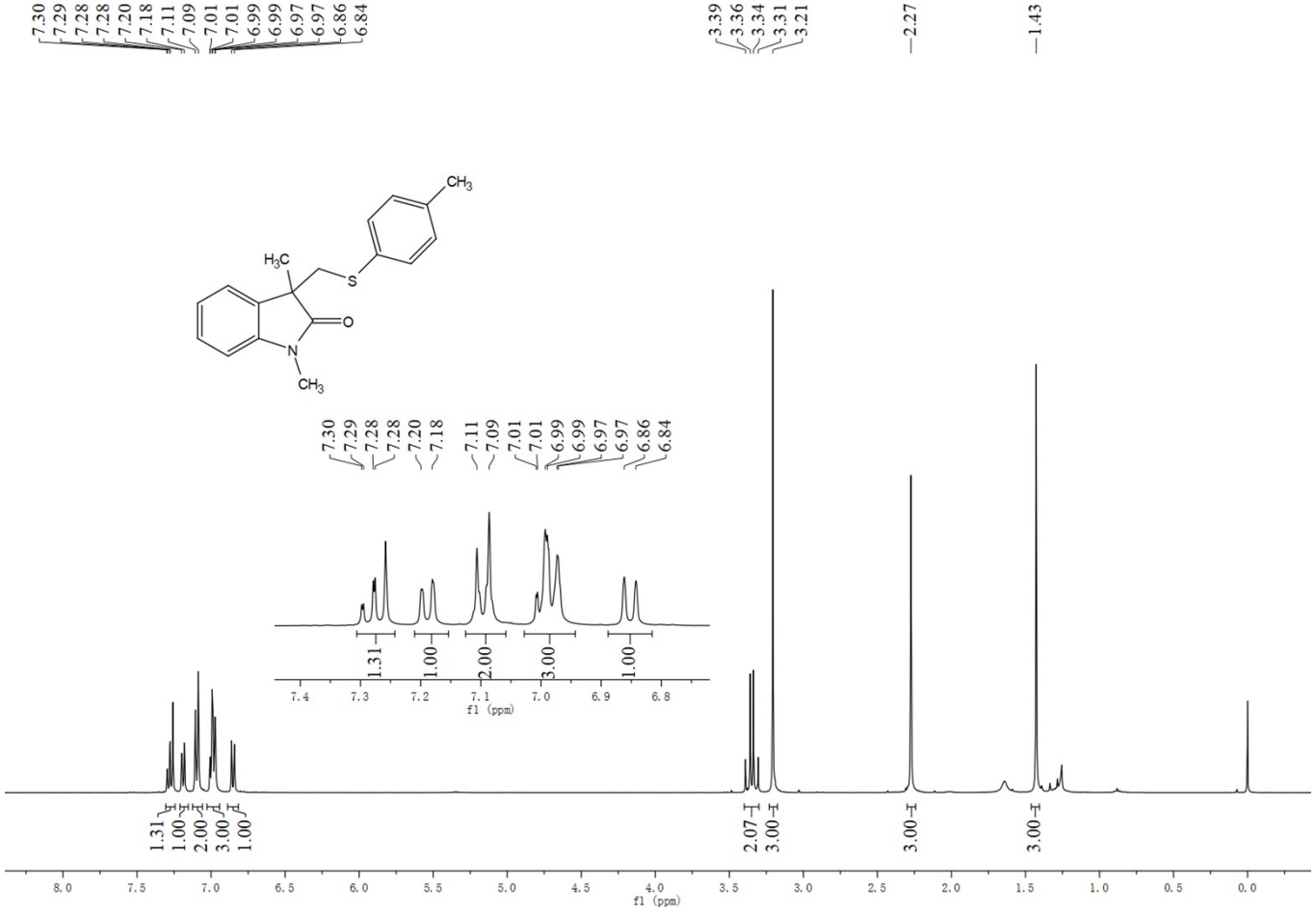


HRMS (ESI)

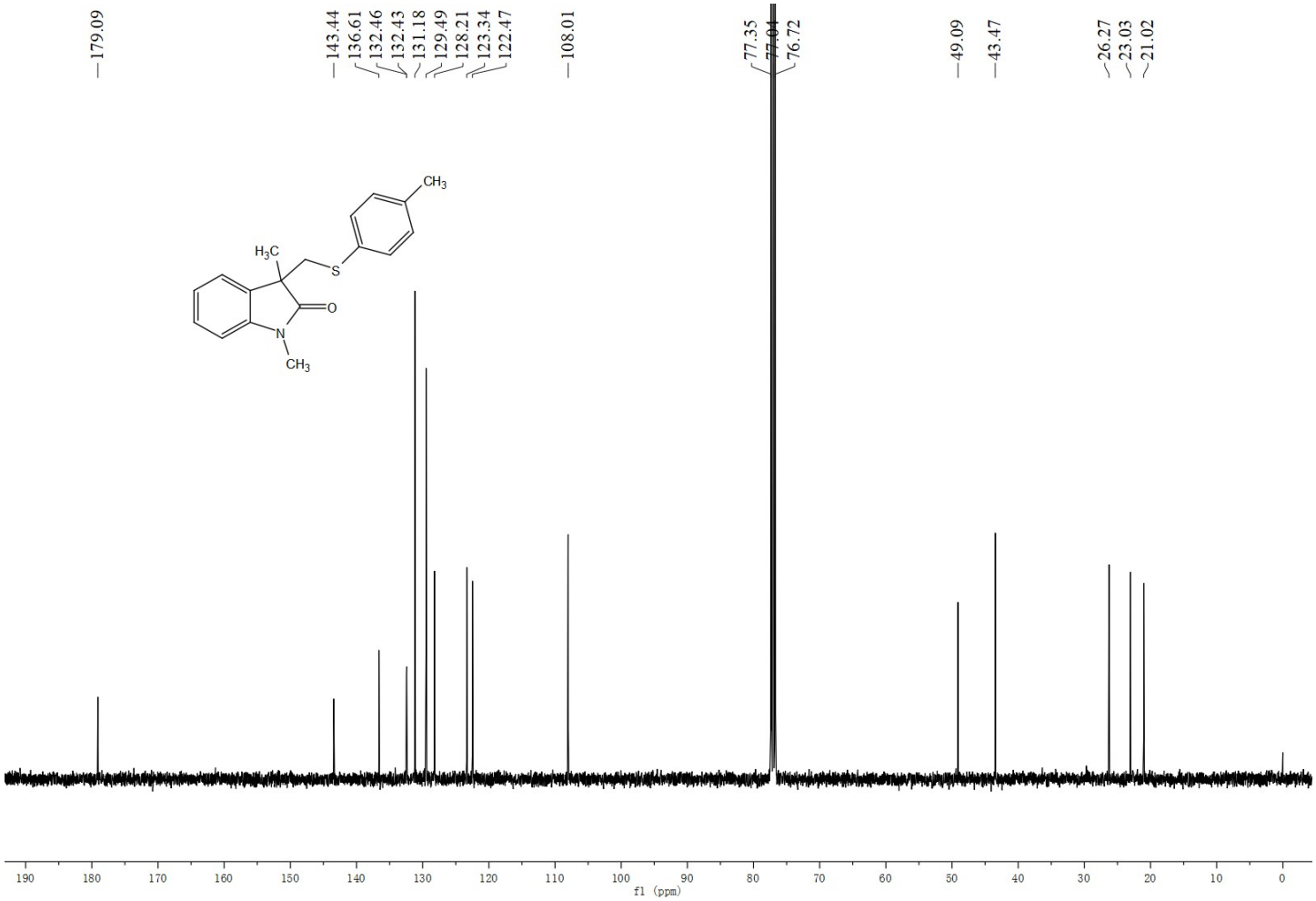

FF-156-3-1 253 (2.308)
1: TOF MS ES+
8.67e6
100
%
0
?;284.1104
392.1130
364.0184
174.0914
285.1133
393.1163
146.0966
280.1091
286.1089
437.9278
511.0342
611.1790
686.1346
805.1926
896.7657
943.7448
115.0544
100
200
300
400
500
600
700
800
900
1000
1100
m/z

1,3-Dimethyl-3-((p-tolylthio)methyl)indolin-2-one (3b)

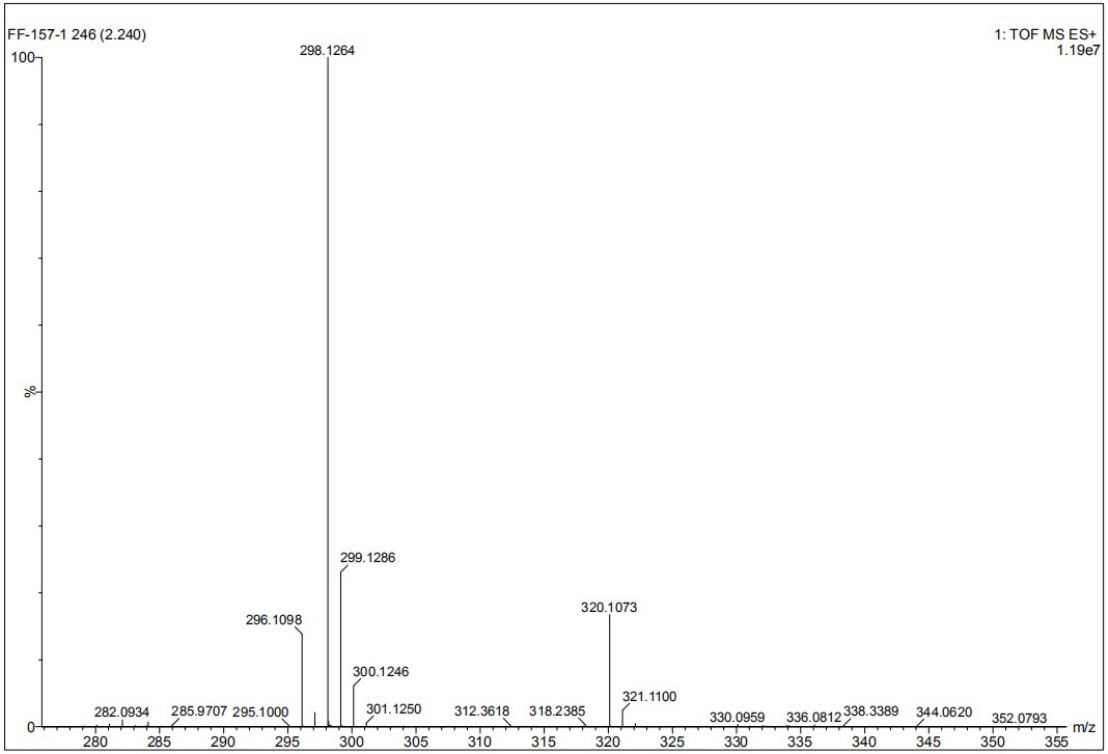
^{1}H NMR (400 MHz, $CDCl_3$)



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

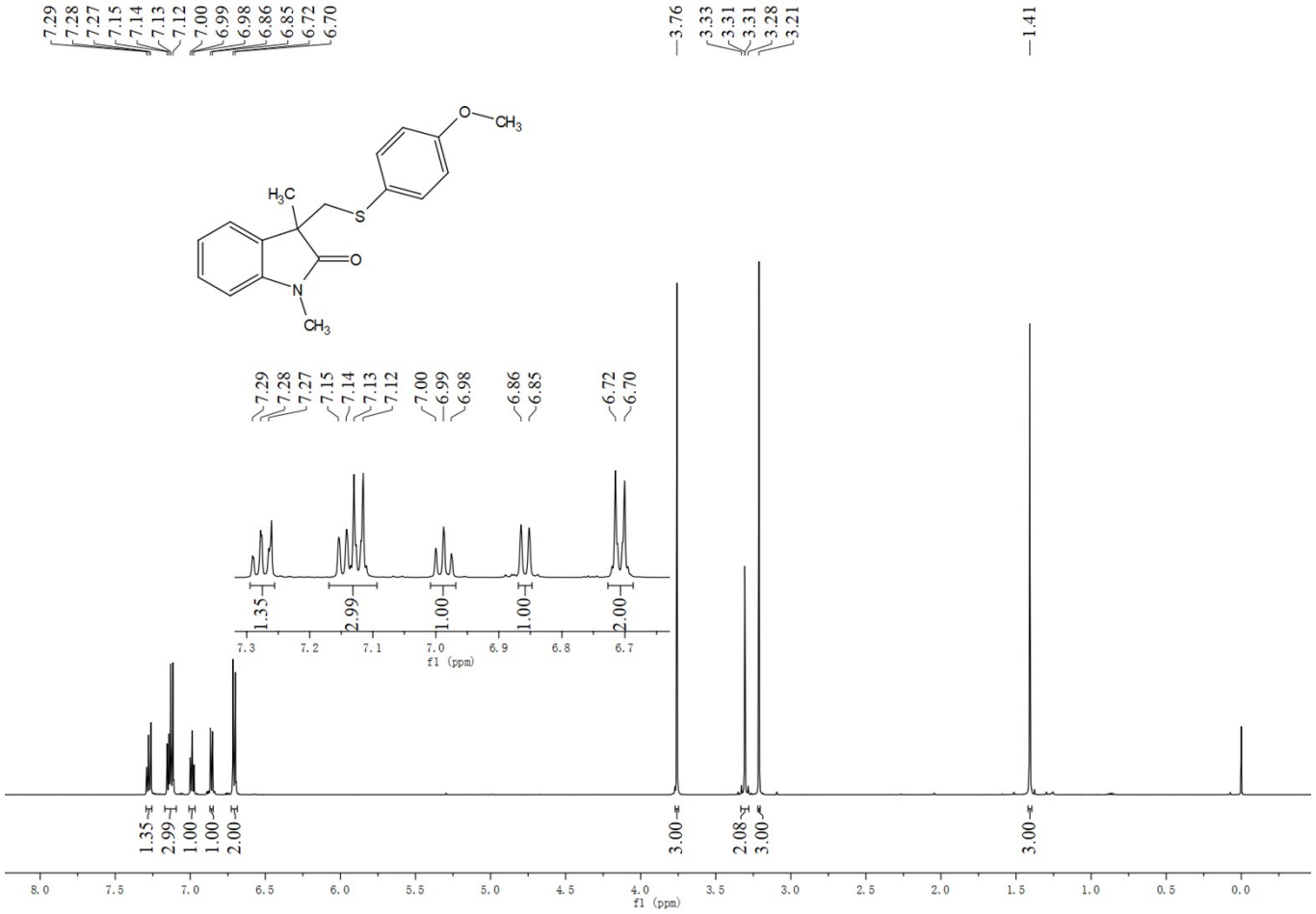


HRMS (ESI)

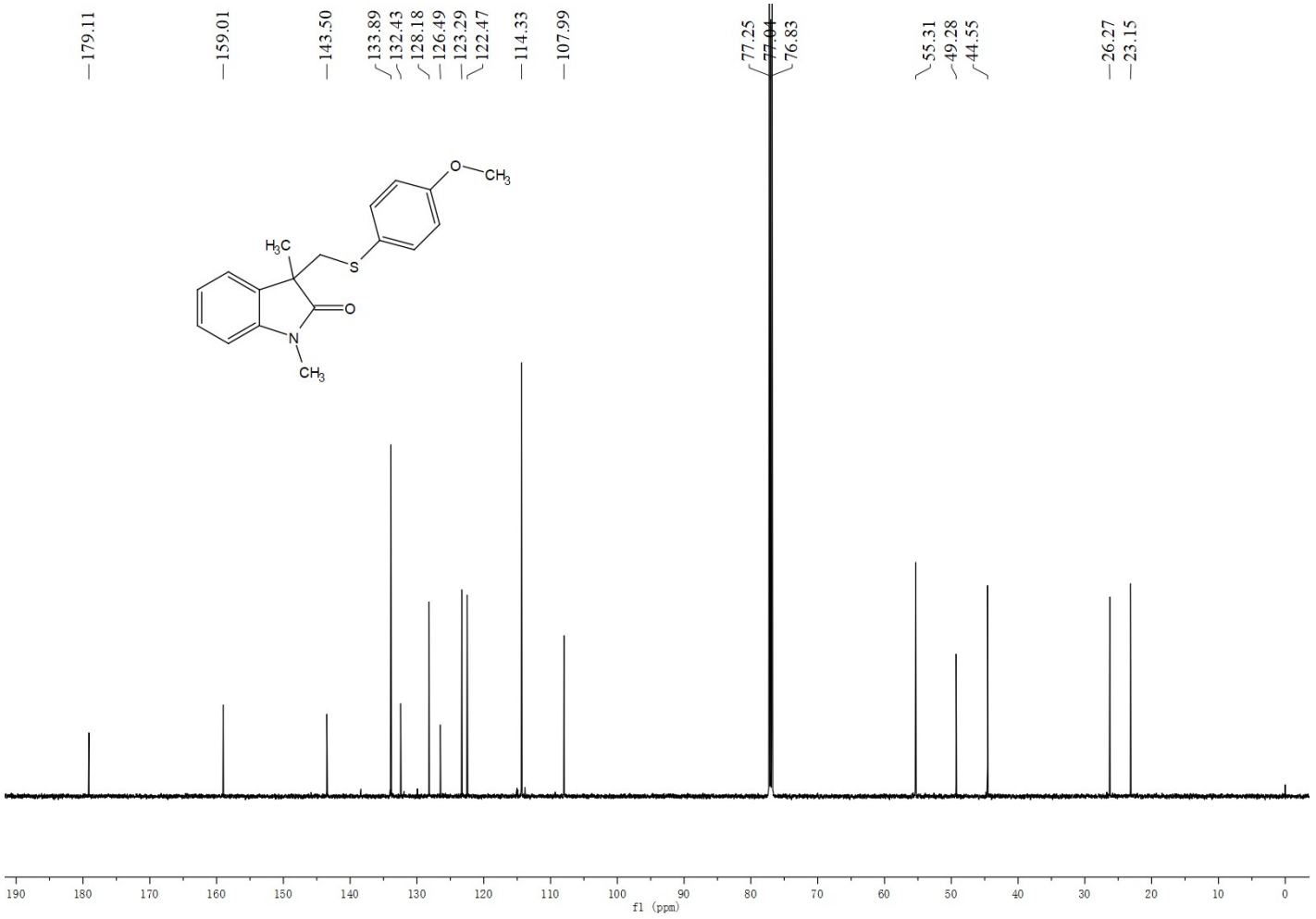

FF-157-1 246 (2.240)
1: TOF MS ES+
1.19e7
100
%
0
298.1264
299.1286
296.1098
320.1073
300.1246
321.1100
282.0934
285.9707
295.1000
301.1250
312.3618
318.2385
330.0959
336.0812
338.3389
344.0620
352.0793
m/z
280
285
290
295
300
305
310
315
320
325
330
335
340
345
350
355

3-(((4-Methoxyphenyl)thio)methyl)-1,3-dimethylindolin-2-one (3c)

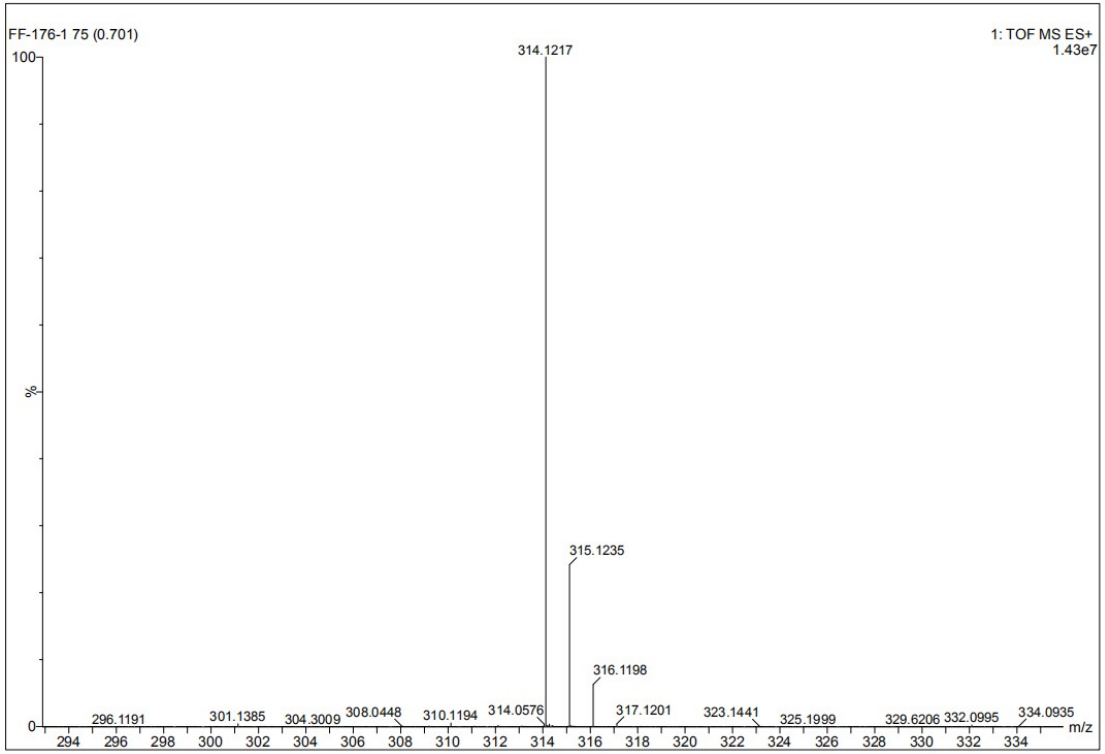
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

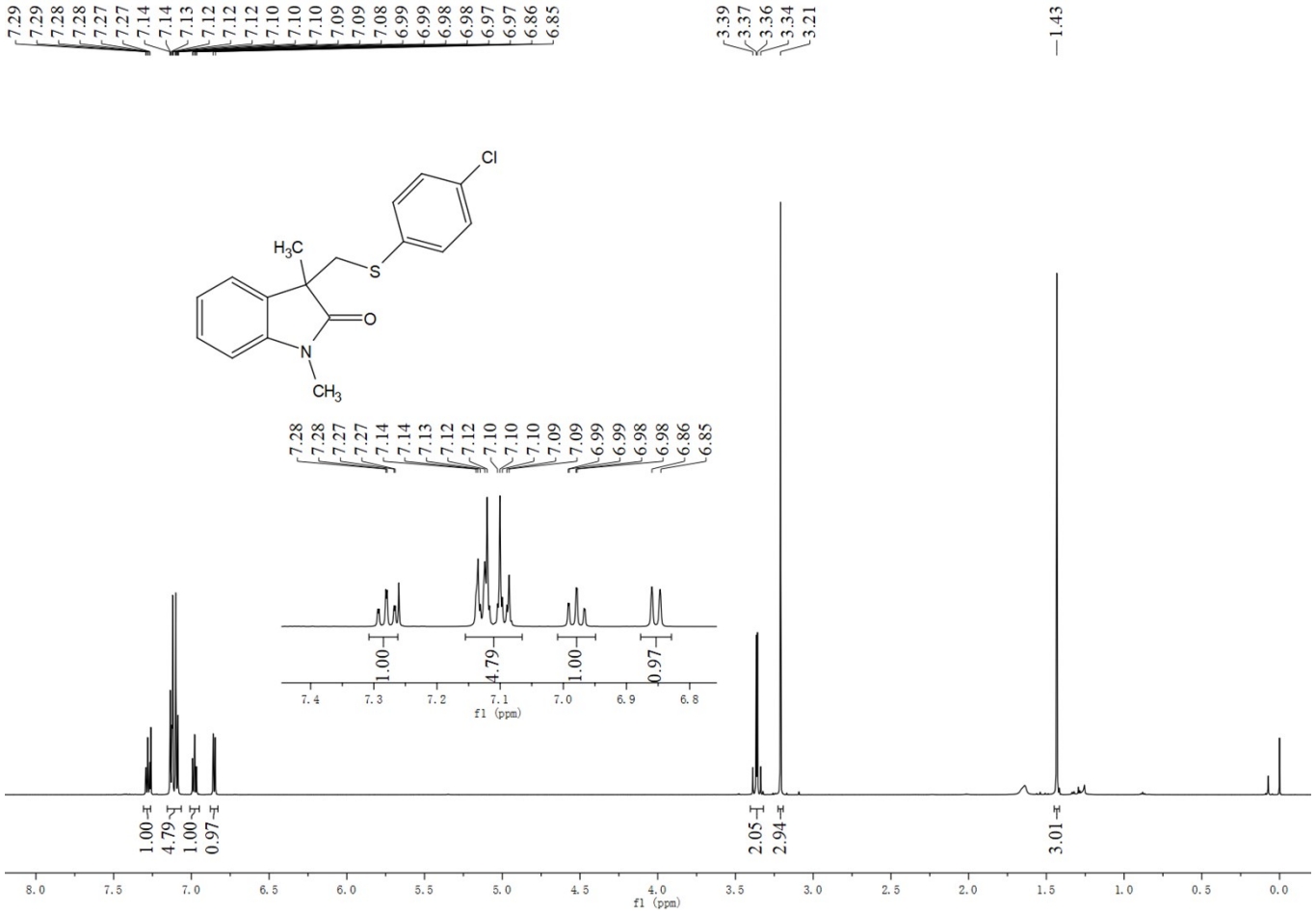


HRMS (ESI)

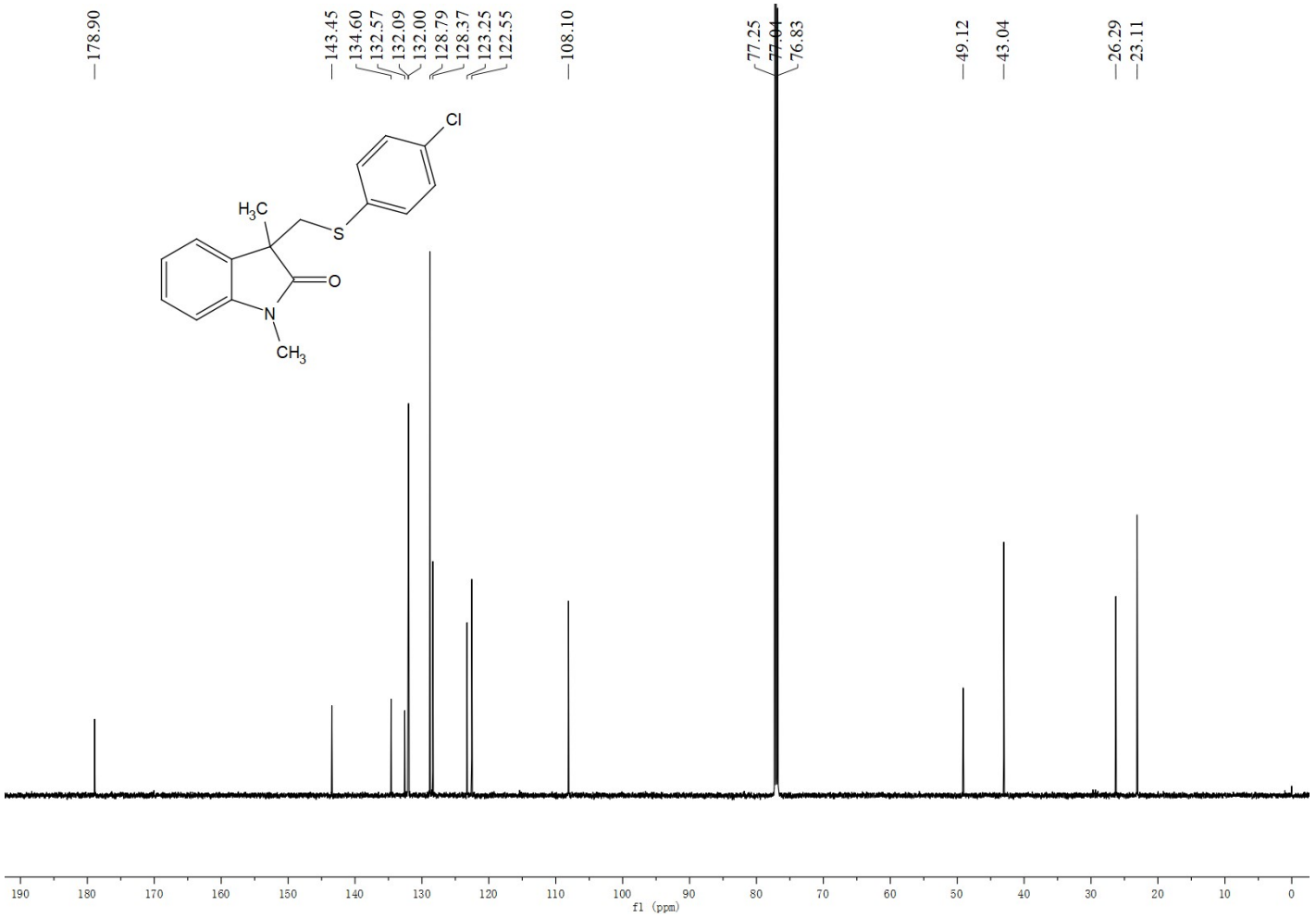

FF-176-1 75 (0.701)
1: TOF MS ES+
1.43e7
100
%
0
314.1217
315.1235
316.1198
296.1191
301.1385
304.3009
308.0448
310.1194
314.0576
317.1201
323.1441
325.1999
329.6206
332.0995
334.0935
m/z
294
296
298
300
302
304
306
308
310
312
314
316
318
320
322
324
326
328
330
332
334

3-(((4-Chlorophenyl)thio)methyl)-1,3-dimethylindolin-2-one (3d)

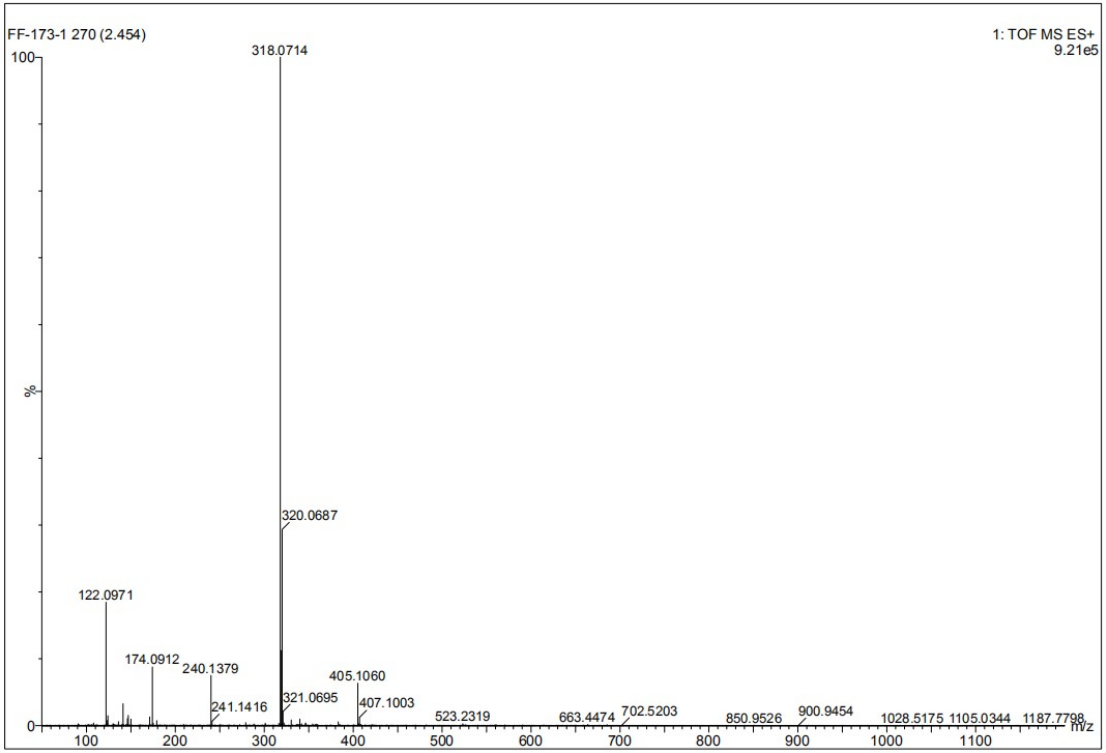
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

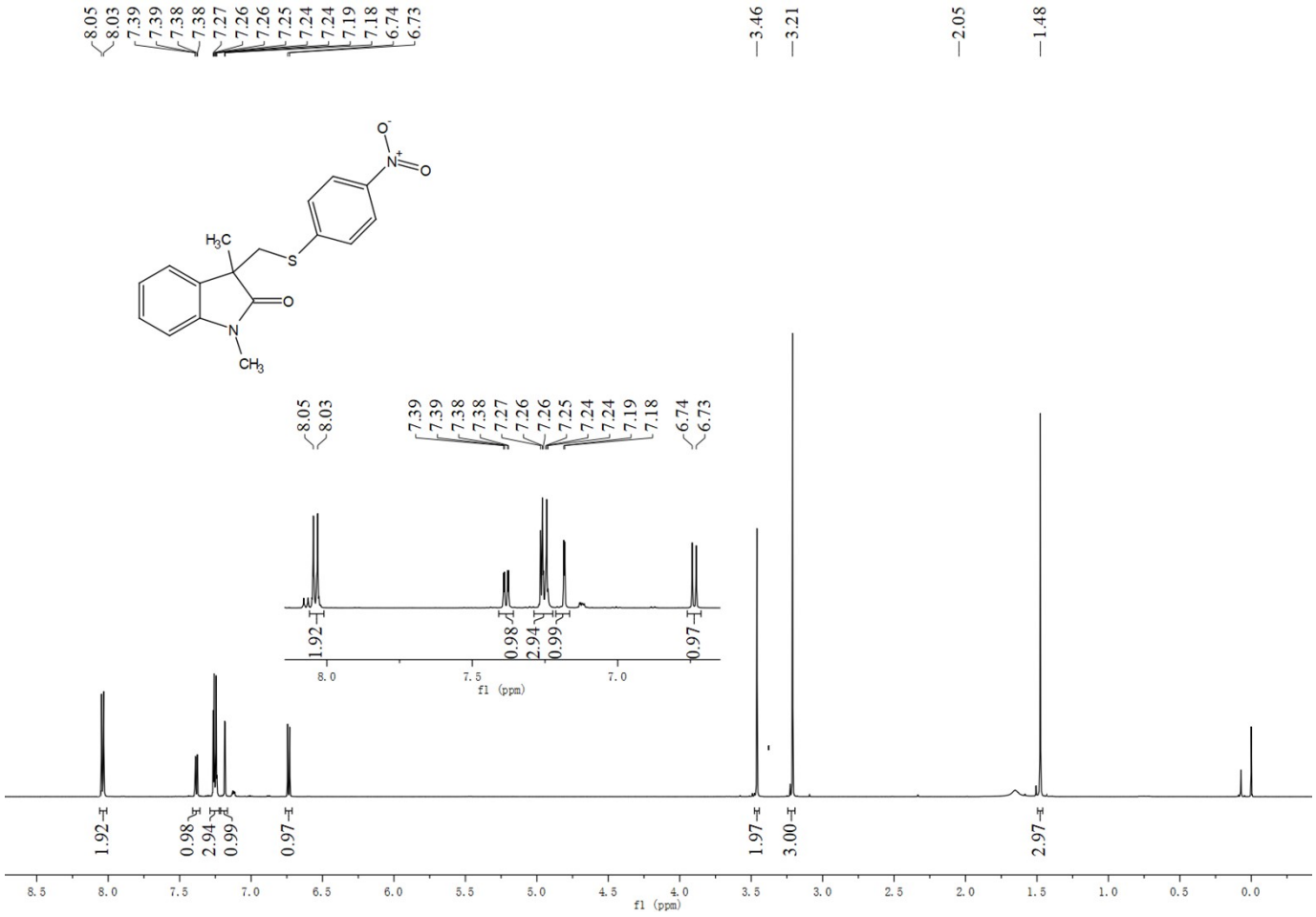


HRMS (ESI)

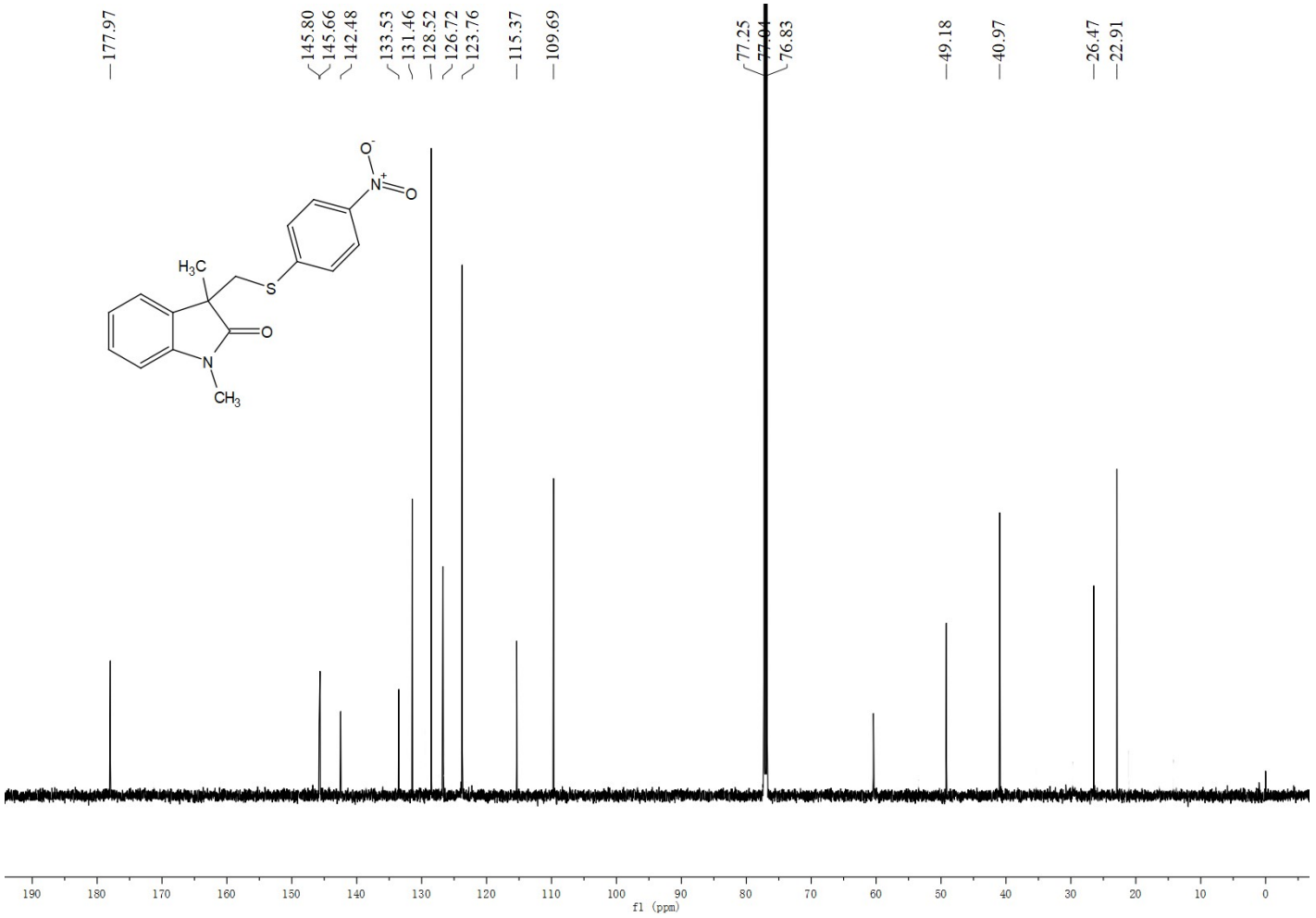

FF-173-1 270 (2.454)
1: TOF MS ES+
9.21e5
100
%
0
318.0714
320.0687
122.0971
174.0912
240.1379
241.1416
321.0695
405.1060
407.1003
523.2319
663.4474
702.5203
850.9526
900.9454
1028.5175
1105.0344
1187.7798
100
200
300
400
500
600
700
800
900
1000
1100
m/z

1,3-Dimethyl-3-(((4-nitrophenyl)thio)methyl)indolin-2-one (3e)

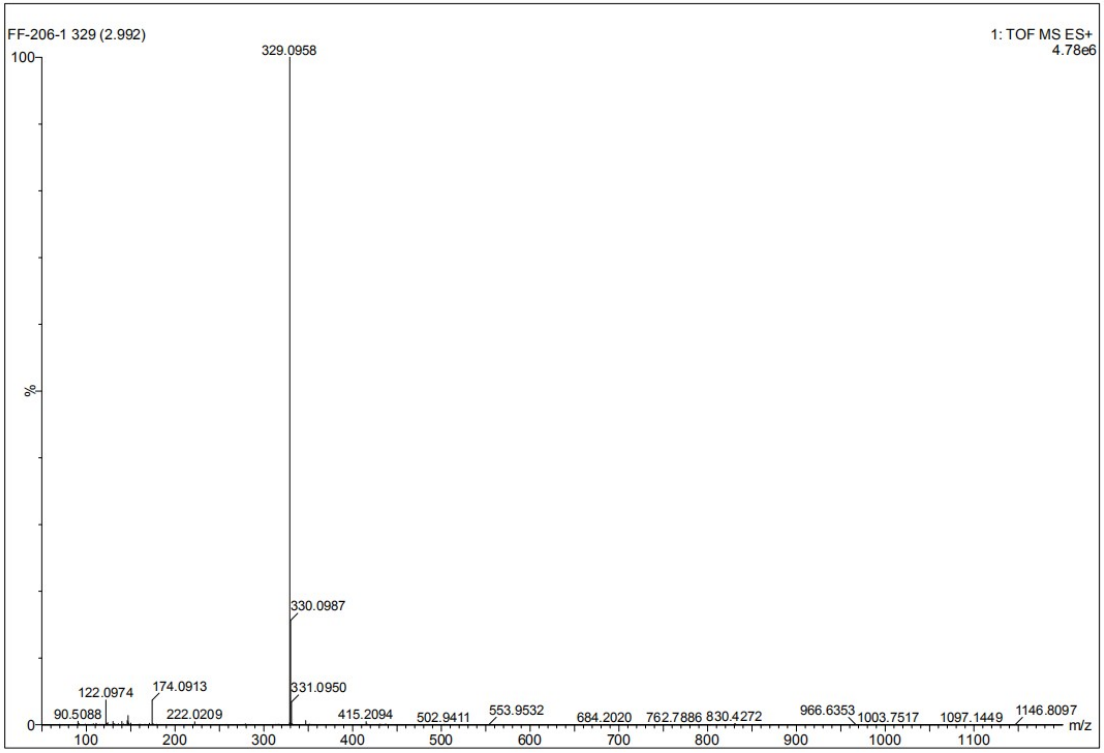
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

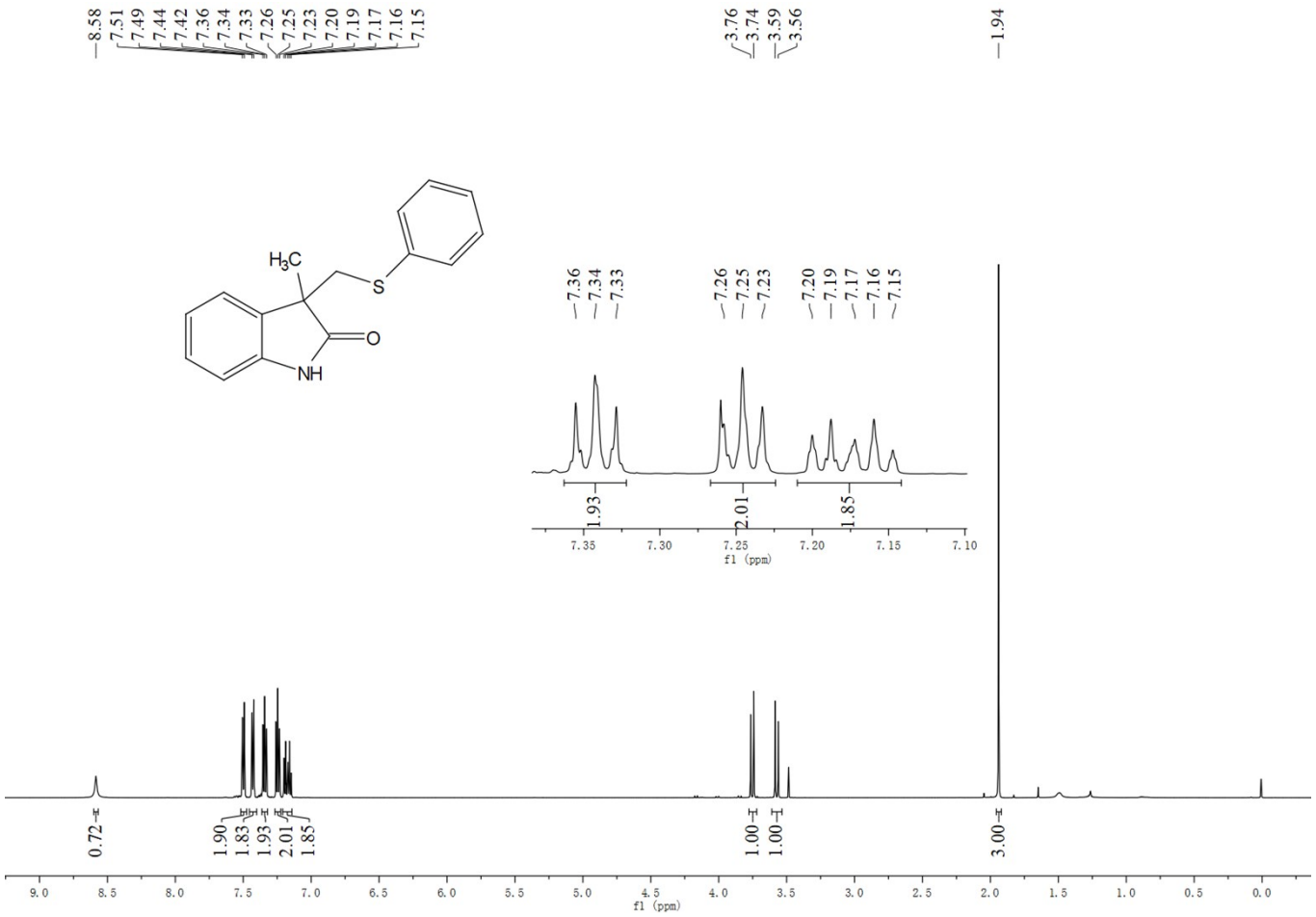


HRMS (ESI)

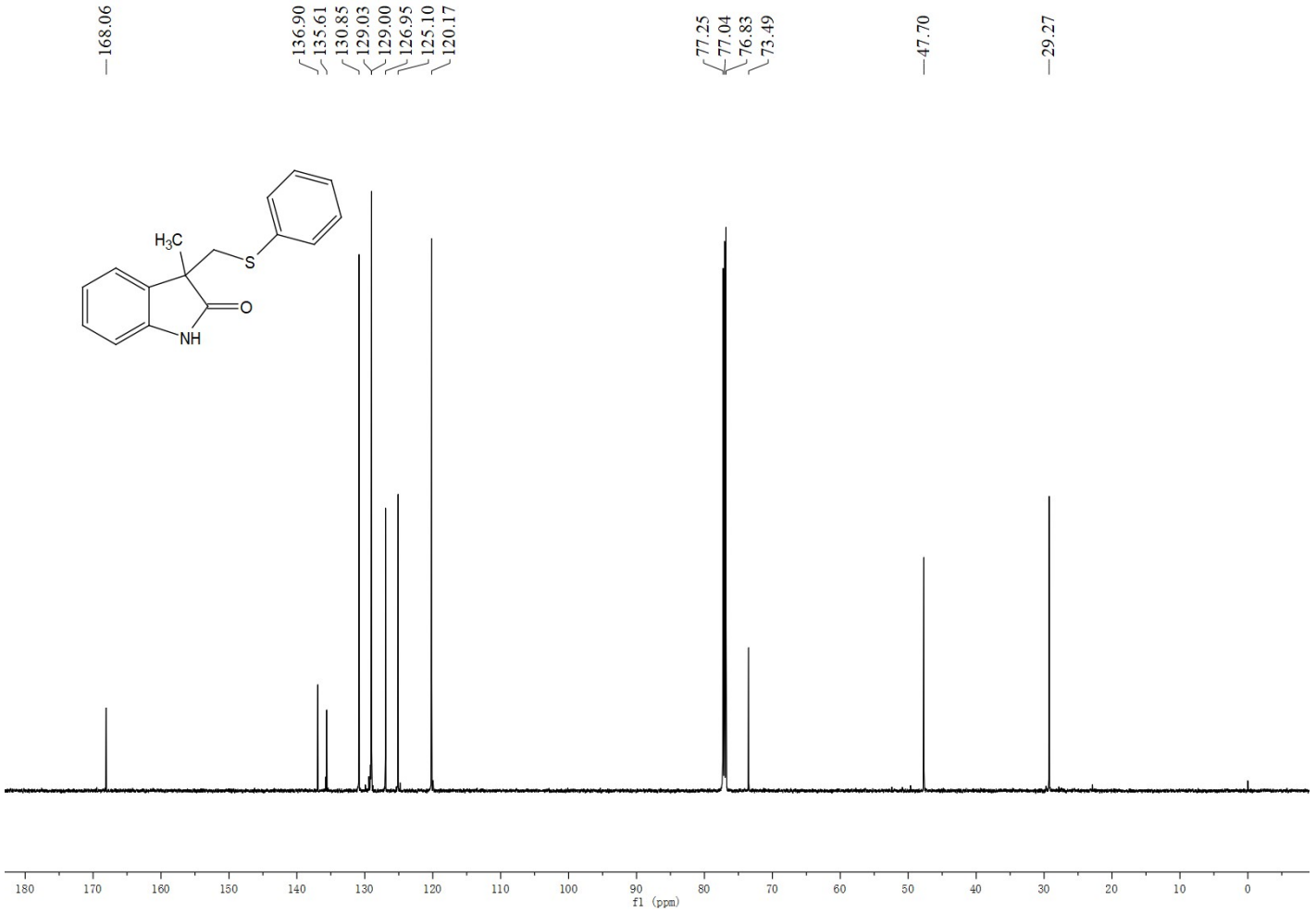

FF-206-1 329 (2.992)
1: TOF MS ES+
4.78e6
100
%
0
329.0958
330.0987
331.0950
122.0974
174.0913
90.5088
222.0209
415.2094
502.9411
553.9532
684.2020
762.7886
830.4272
966.6353
1003.7517
1097.1449
1146.8097
m/z
100
200
300
400
500
600
700
800
900
1000
1100

3-Methyl-3-((phenylthio)methyl)indolin-2-one (3f)

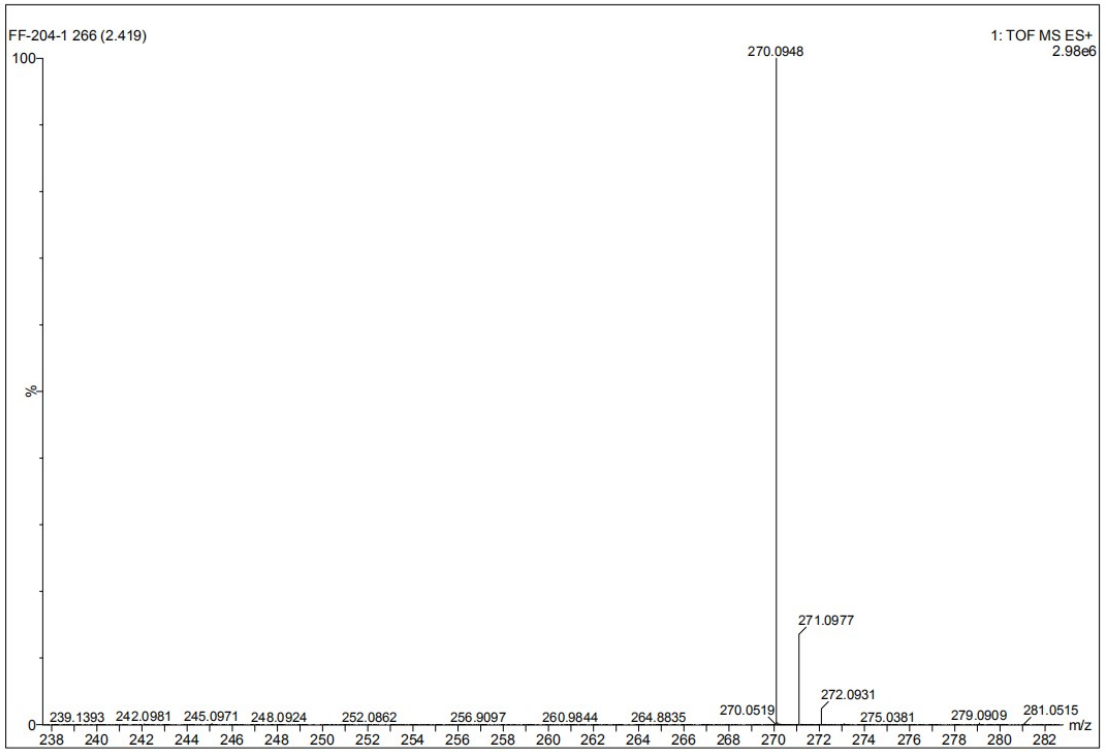
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)



HRMS (ESI)


FF-204-1 266 (2.419)
1: TOF MS ES+
2.98e6
100
%
0
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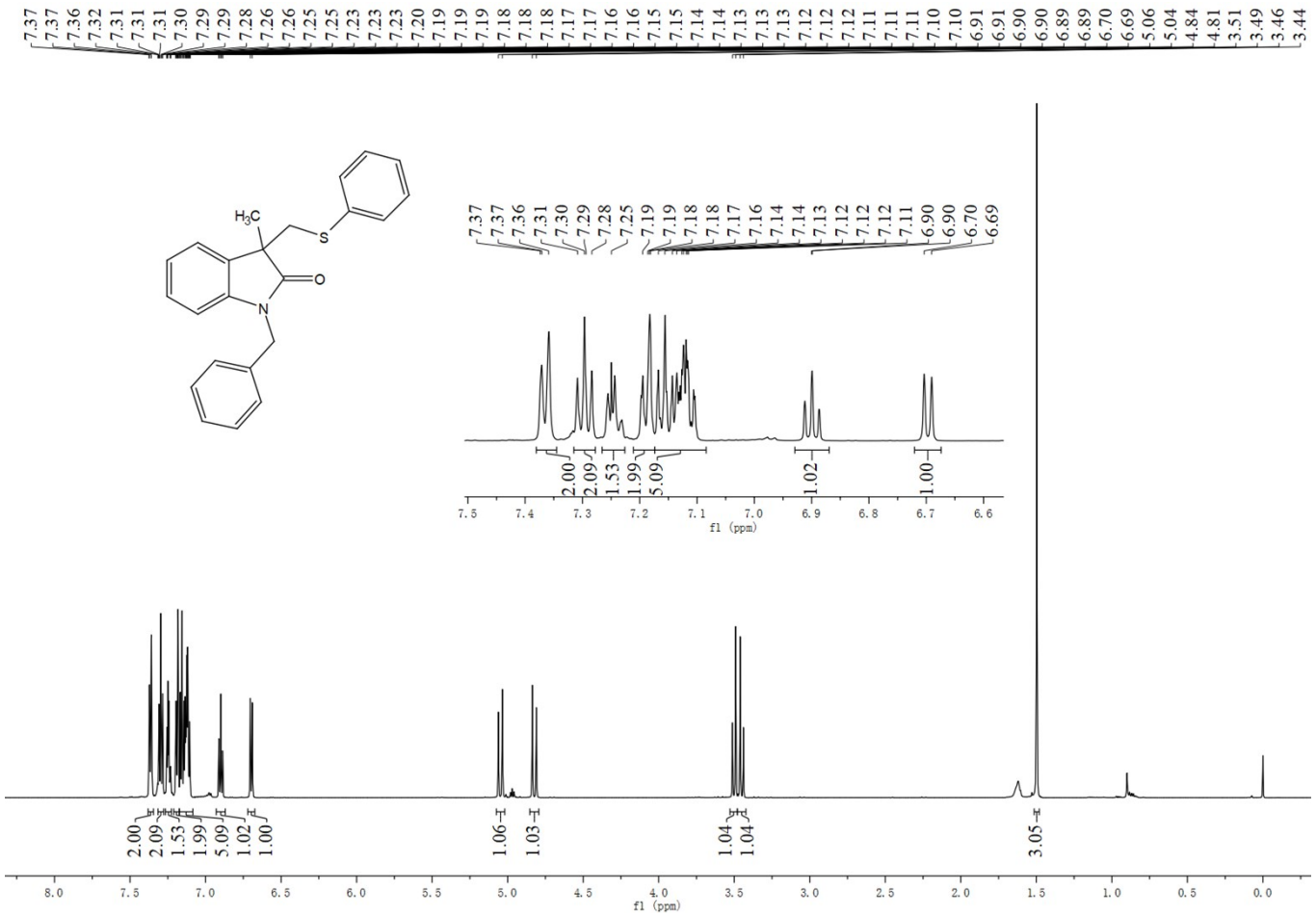
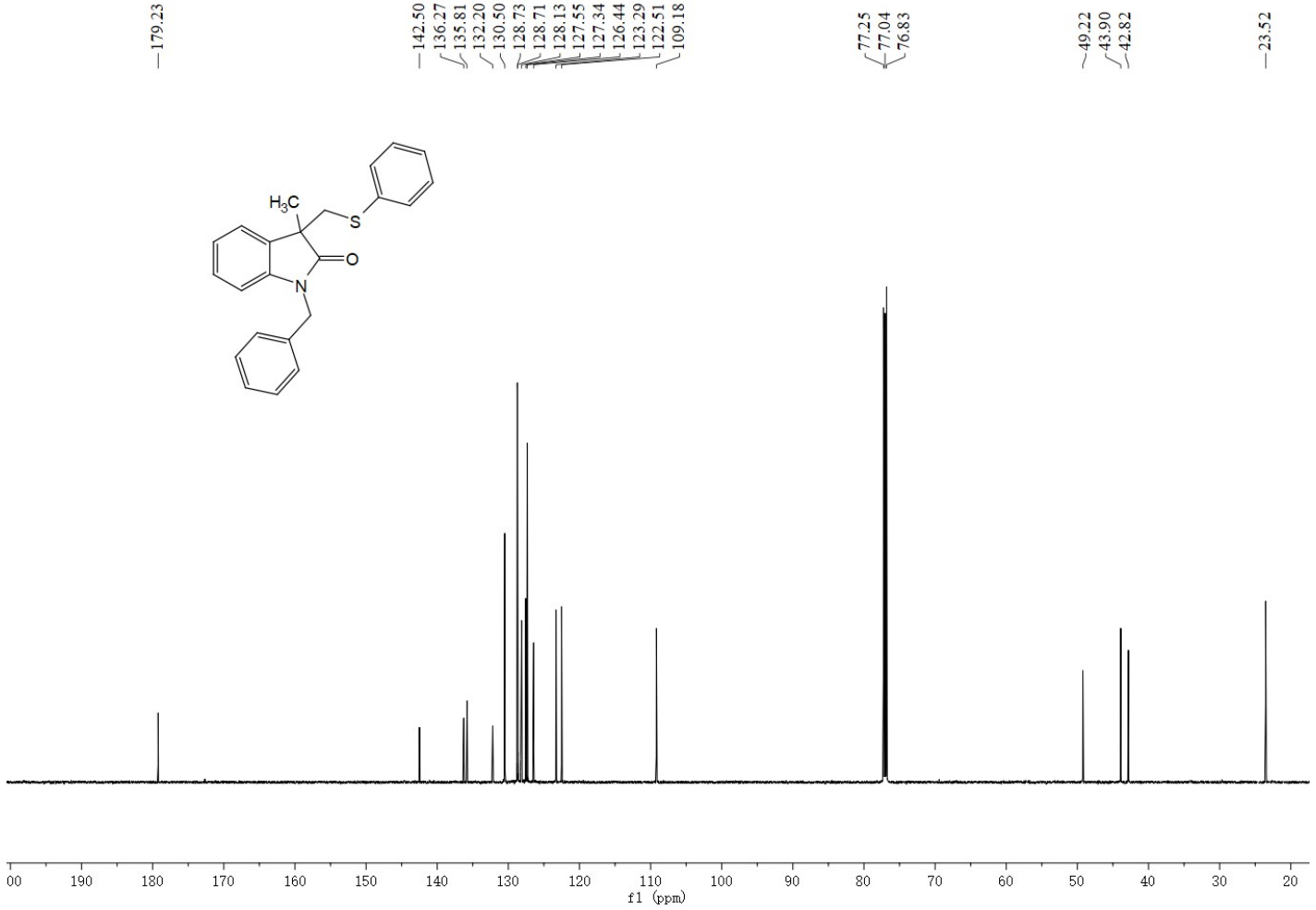
271.0977
272.0931
239.1393
242.0981
245.0971
248.0924
252.0862
256.9097
260.9844
264.8835
270.0519
275.0381
279.0909
281.0515
m/z
238 240 242 244 246 248 250 252 254 256 258 260 262 264 266 268 270 272 274 276 278 280 282

1-Benzyl-3-methyl-3-((phenylthio)methyl)indolin-2-one (3g)

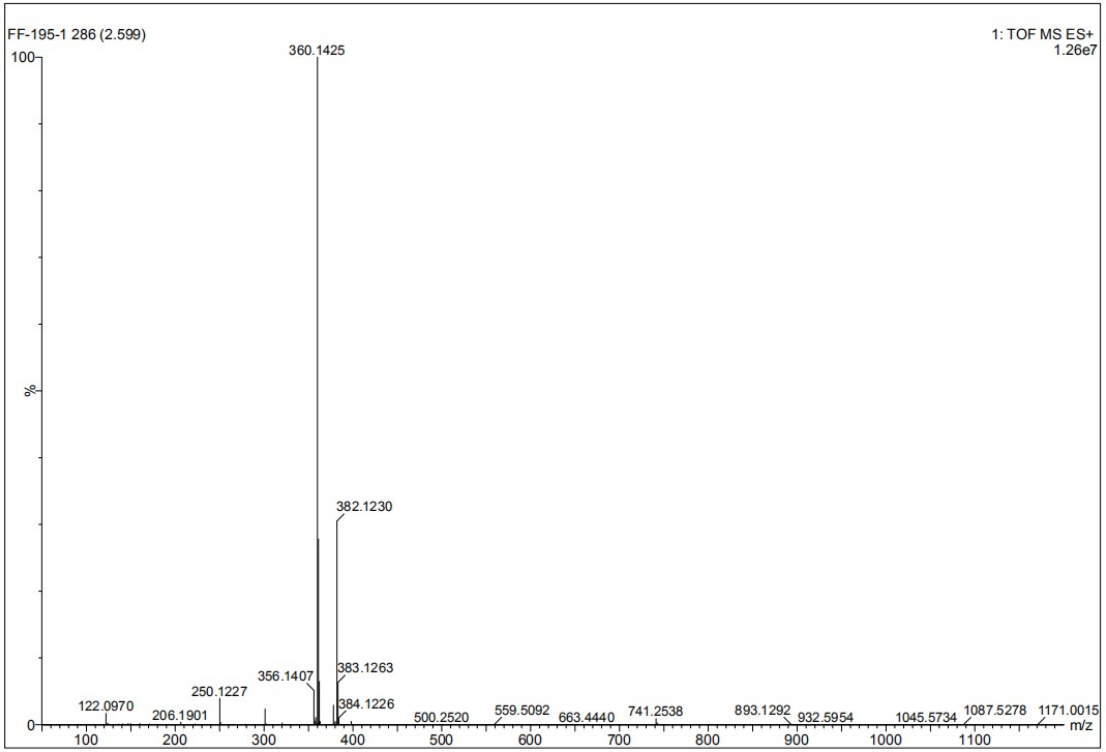
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

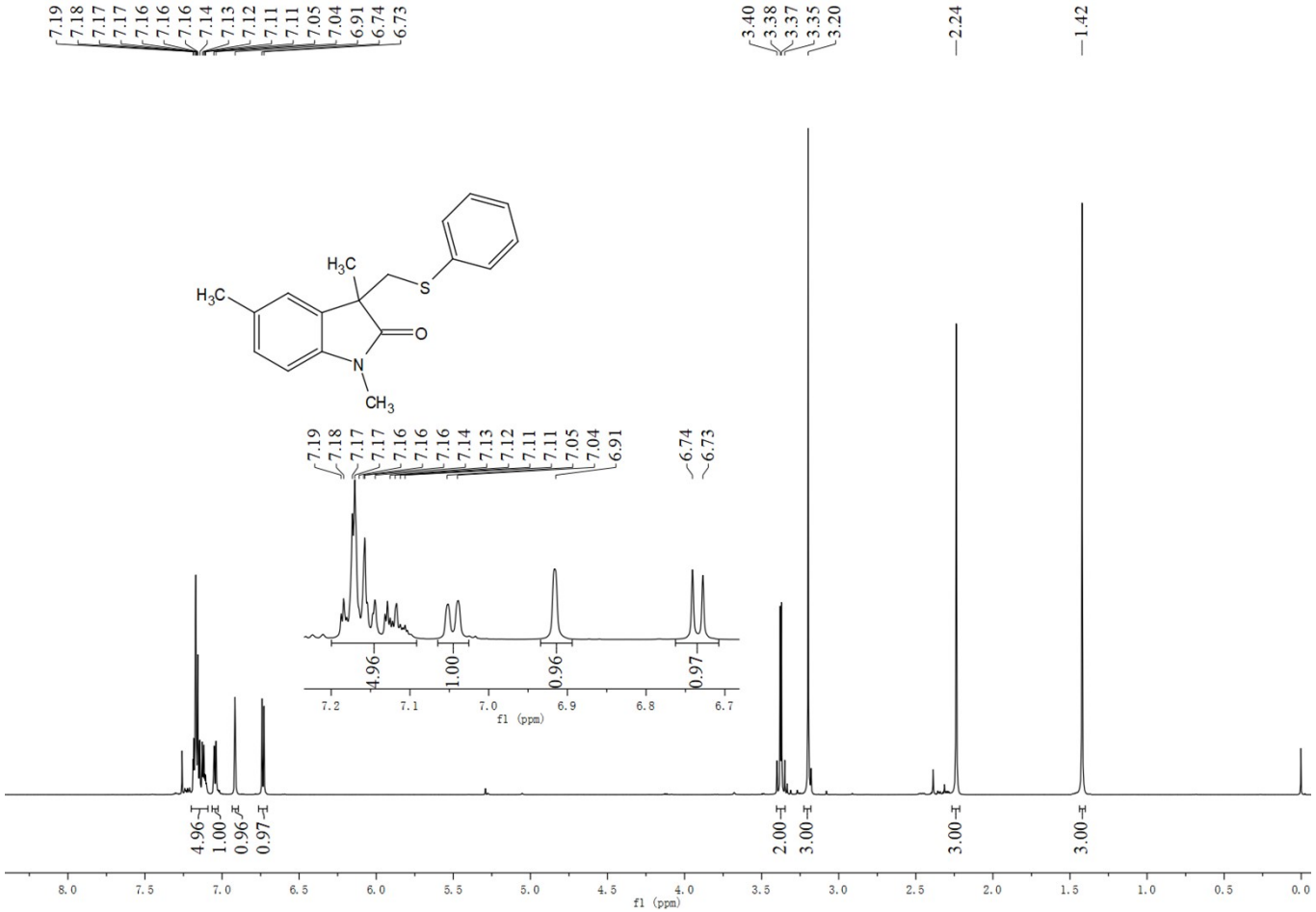


HRMS (ESI)

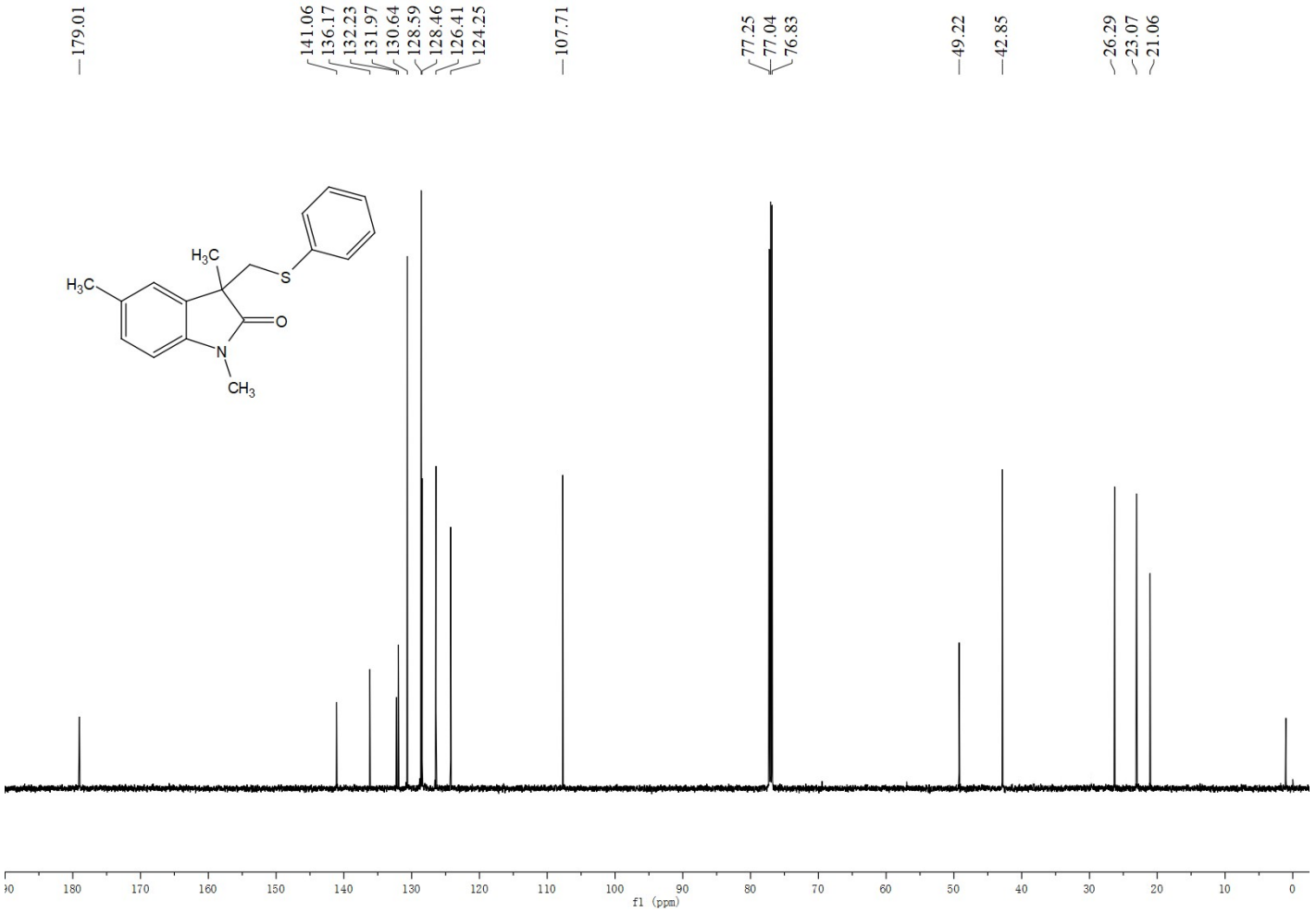

FF-195-1 286 (2.599)
1: TOF MS ES+
1.26e7
100
%
0
360.1425
382.1230
383.1263
356.1407
384.1226
250.1227
122.0970
206.1901
500.2520
559.5092
663.4440
741.2538
893.1292
932.5954
1045.5734
1087.5278
1171.0015
m/z
100
200
300
400
500
600
700
800
900
1000
1100

1,3,5-Trimethyl-3-((phenylthio)methyl)indolin-2-one (3h)

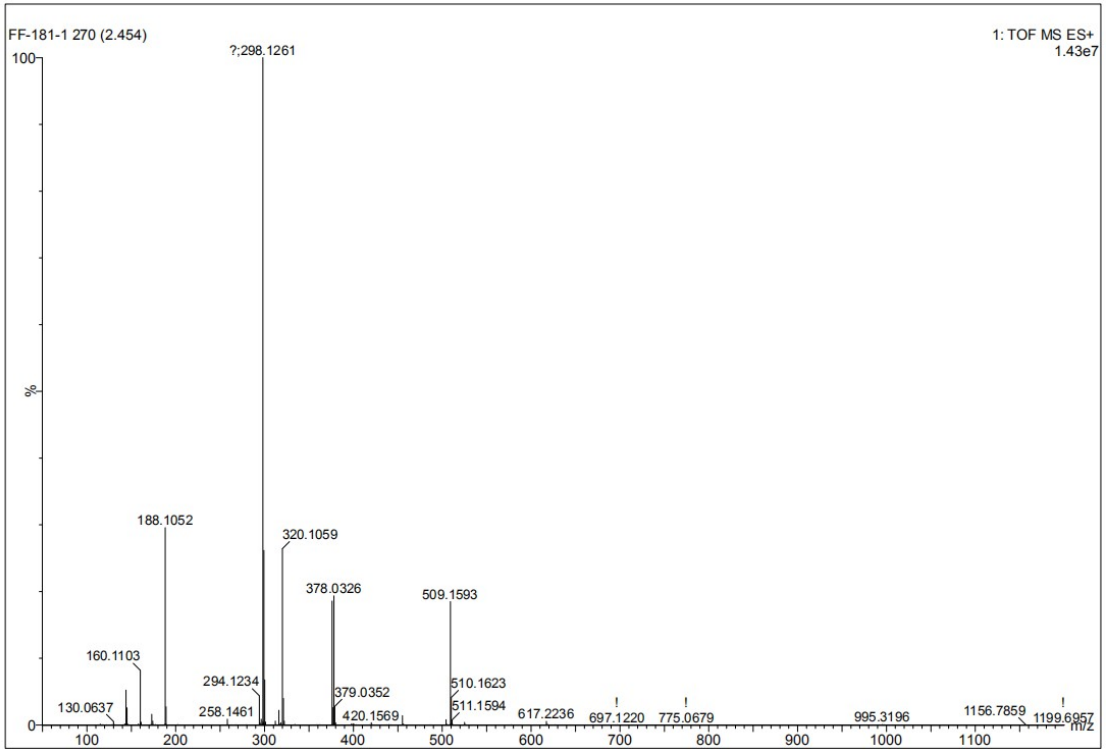
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

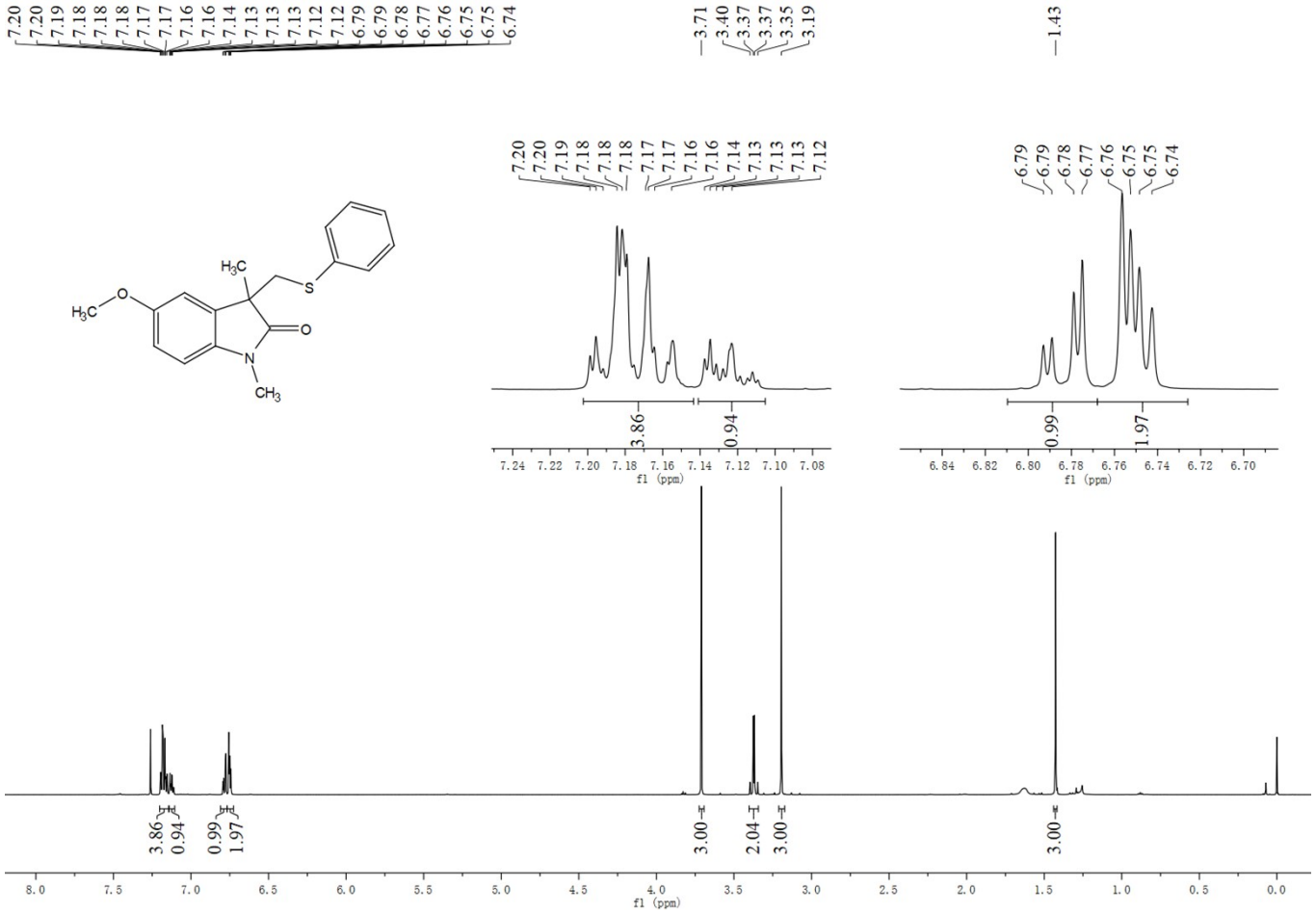


HRMS (ESI)

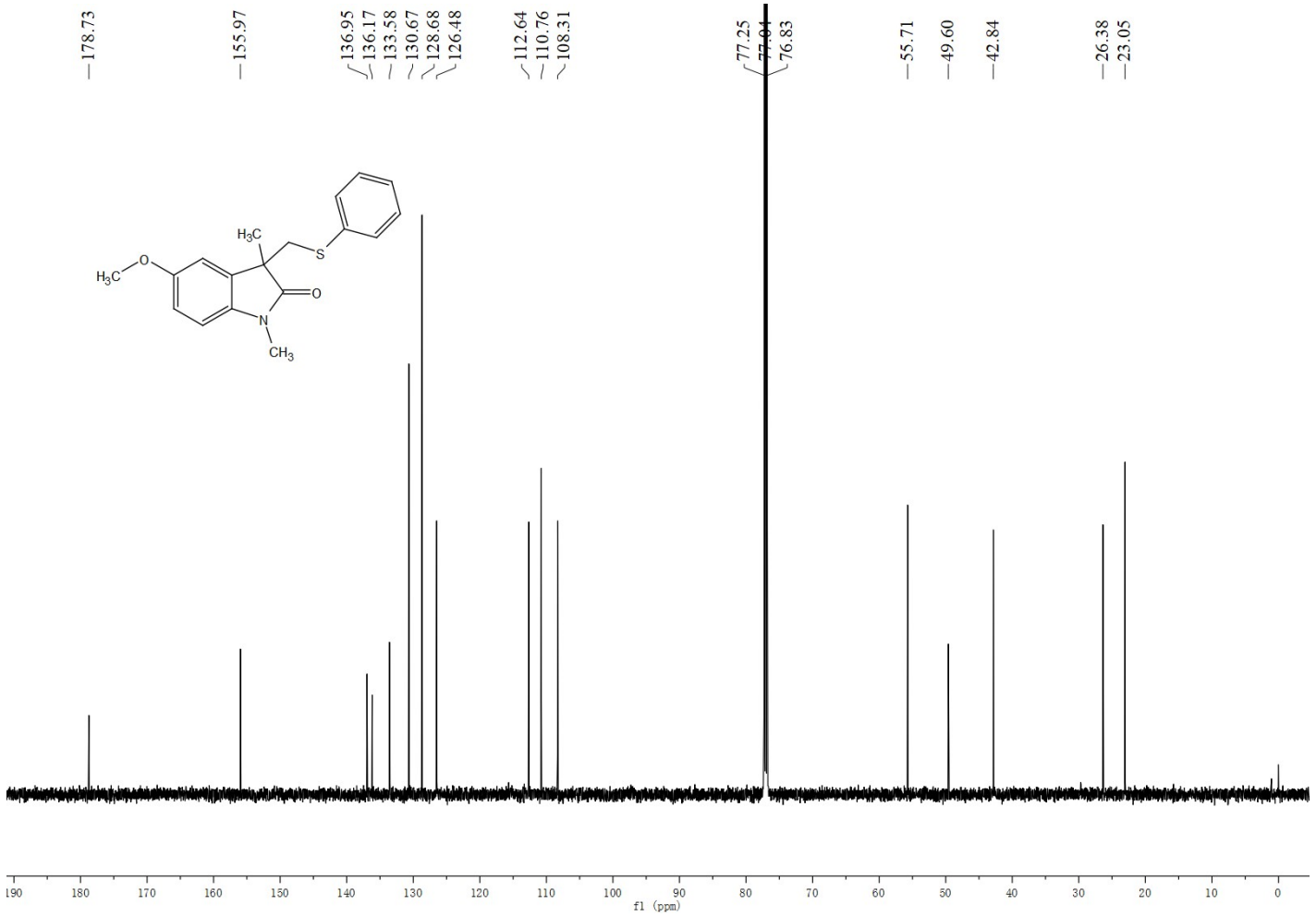

FF-181-1 270 (2.454)
1: TOF MS ES+
1.43e7
?:298.1261
188.1052
320.1059
378.0326
509.1593
160.1103
294.1234
510.1623
379.0352
511.1594
130.0637
258.1461
420.1569
617.2236
697.1220
775.0679
995.3196
1156.7859
1199.6957
%
m/z

5-Methoxy-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3i)

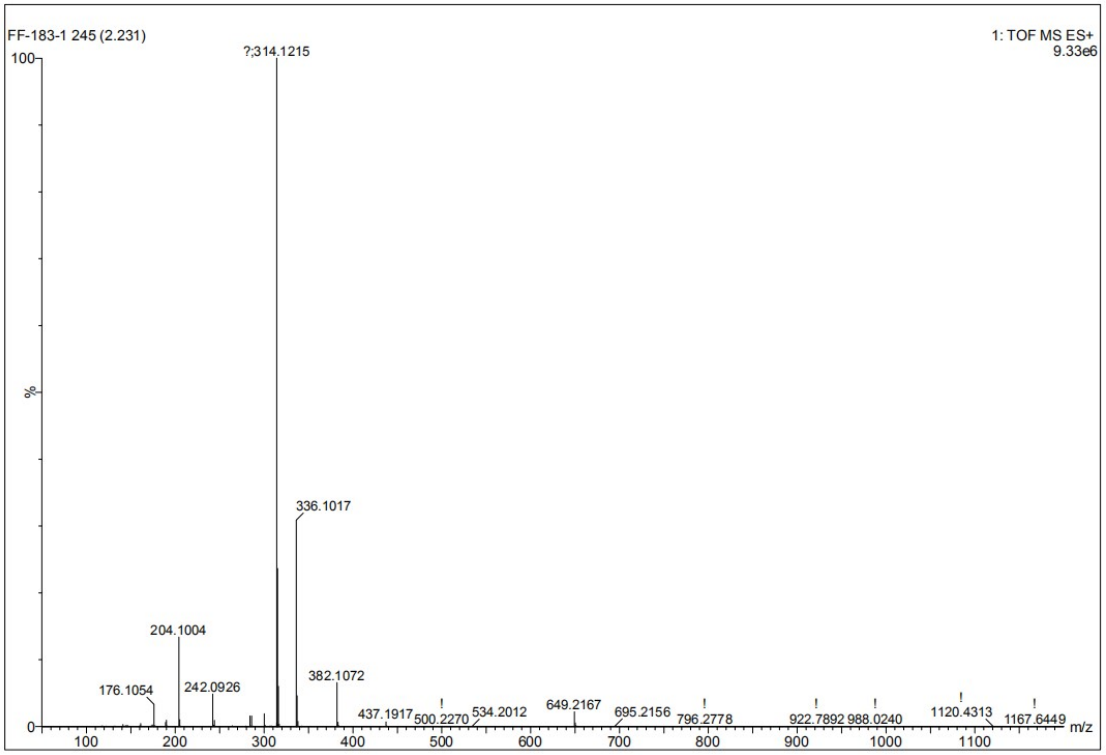
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

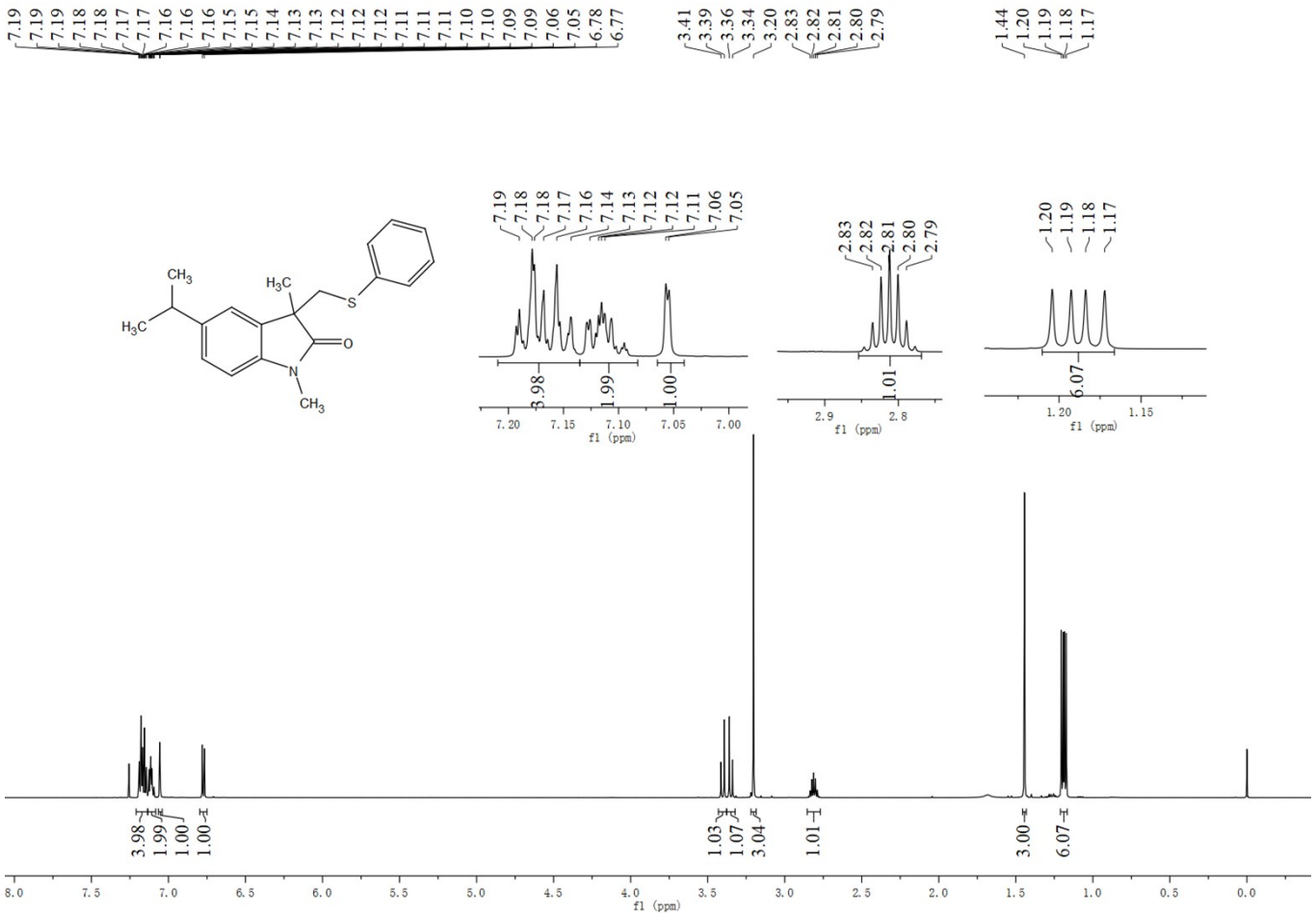


HRMS (ESI)

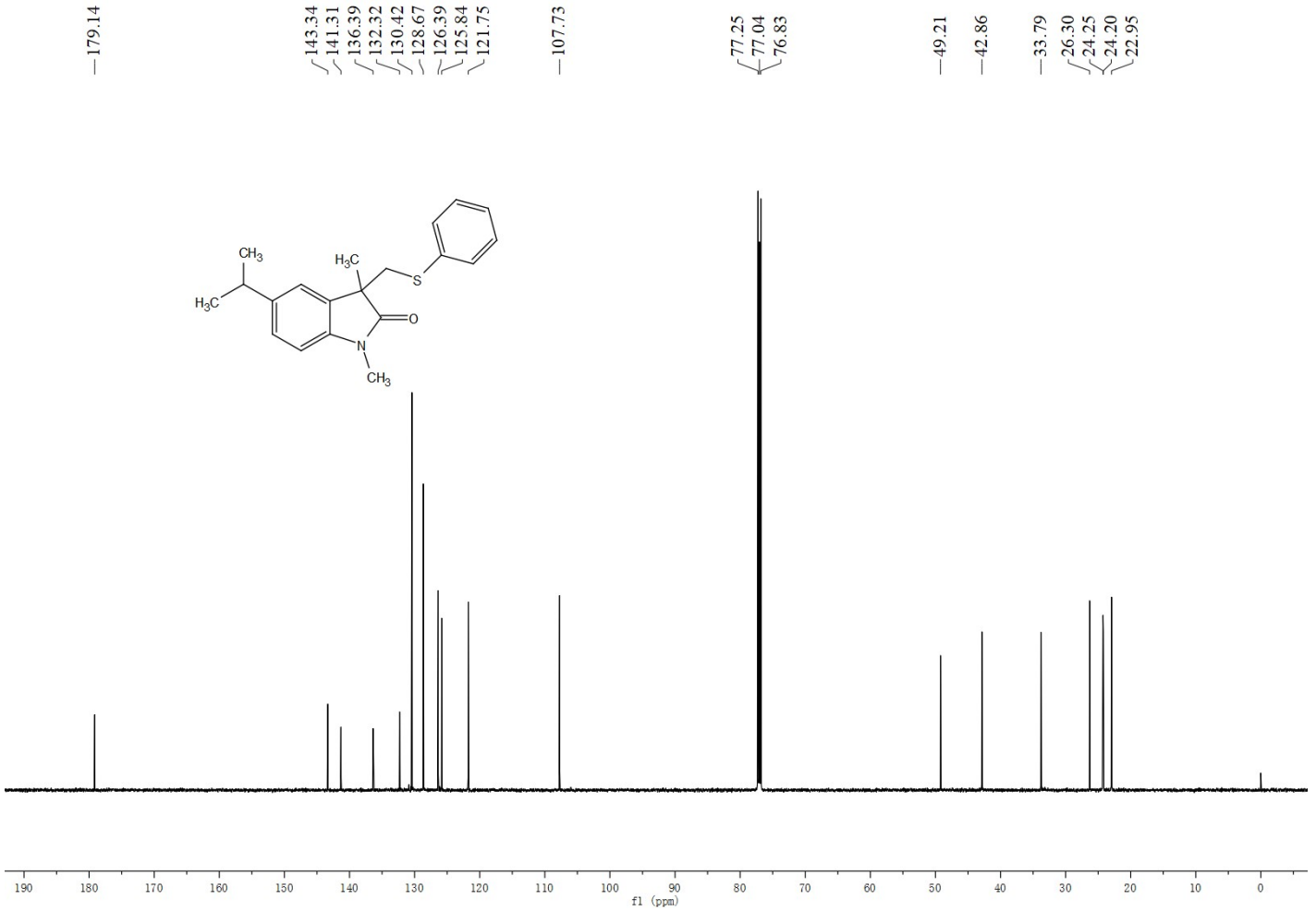

FF-183-1 245 (2.231)
1: TOF MS ES+
9.33e6
100
%
0
?;314.1215
336.1017
204.1004
382.1072
176.1054
242.0926
437.1917
500.2270
534.2012
649.2167
695.2156
796.2778
922.7892
988.0240
1120.4313
1167.6449
100
200
300
400
500
600
700
800
900
1000
1100
m/z

5-Isopropyl-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3j)

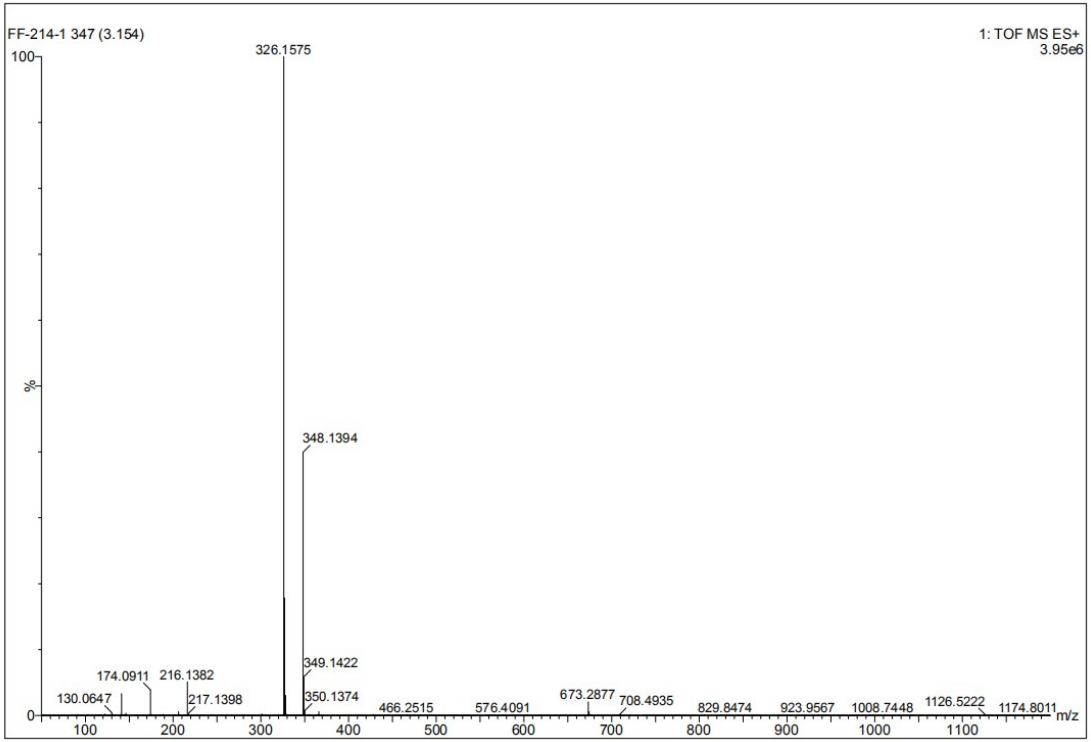
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

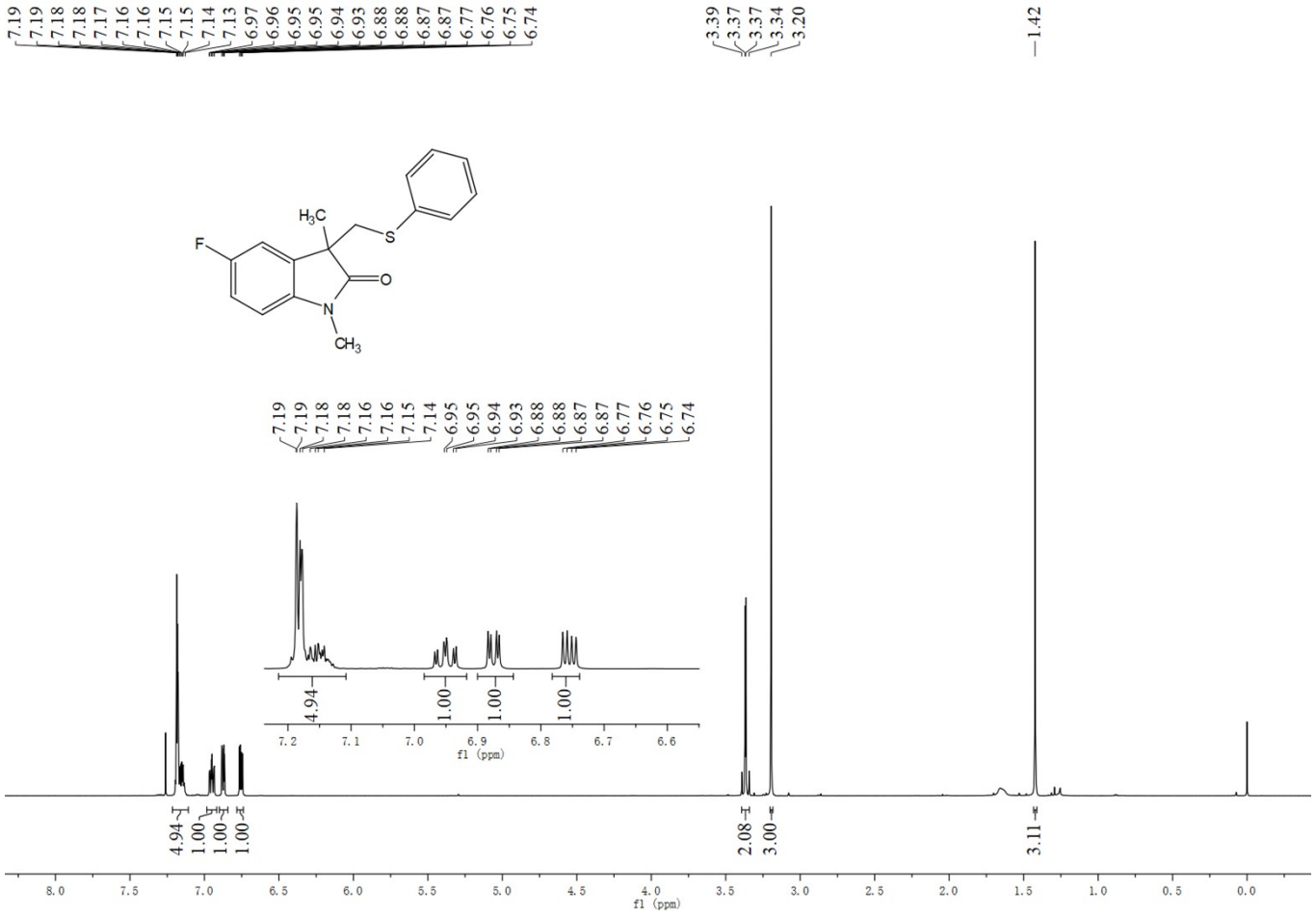


HRMS (ESI)

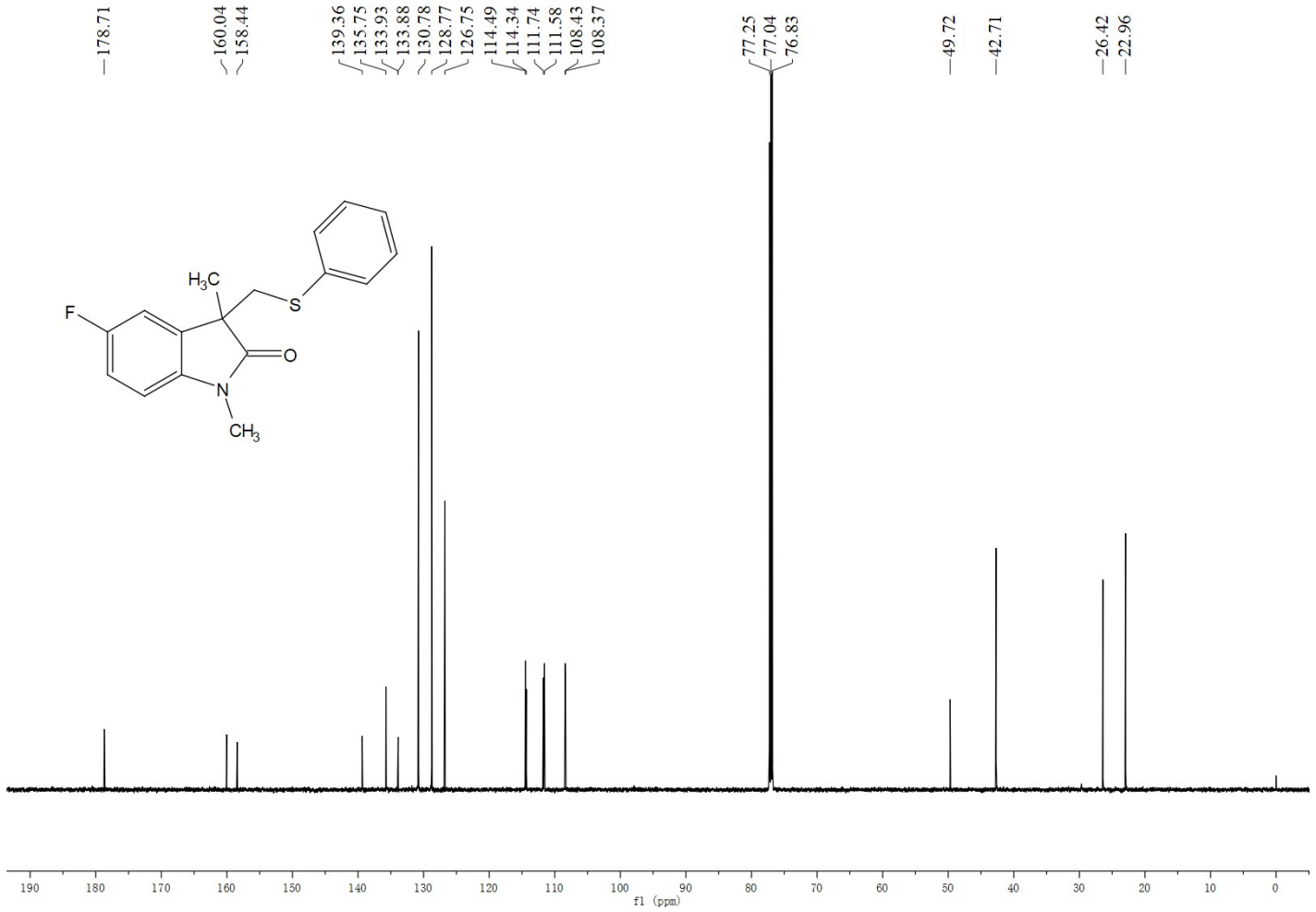

FF-214-1 347 (3.154)
1: TOF MS ES+
3.95e6
100
%
0
326.1575
348.1394
349.1422
174.0911
216.1382
130.0647
217.1398
350.1374
466.2515
576.4091
673.2877
708.4935
829.8474
923.9567
1008.7448
1126.5222
1174.8011
100
200
300
400
500
600
700
800
900
1000
1100
m/z

5-Fluoro-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3k)

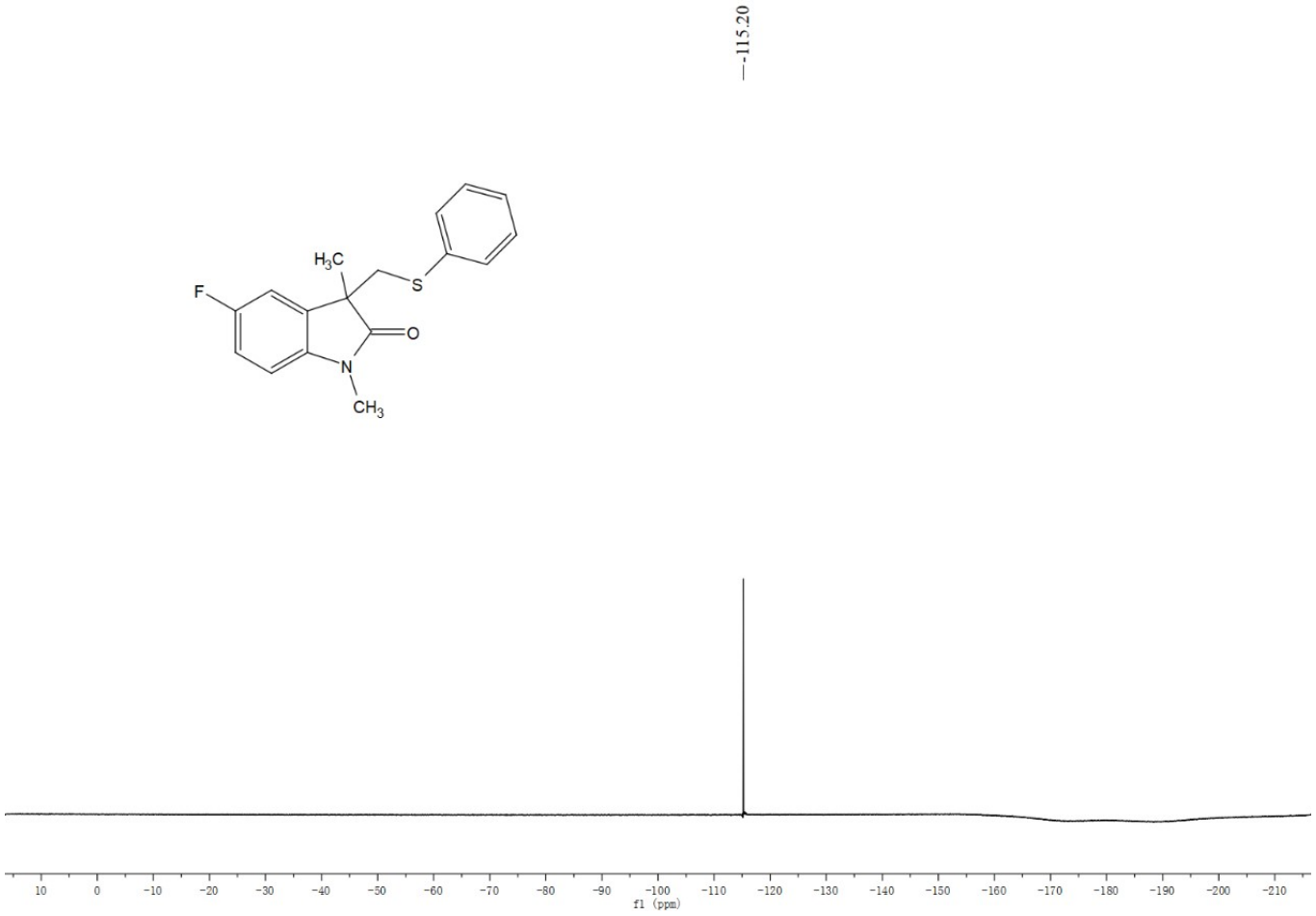
^{1}H NMR (600 MHz, $CDCl_3$)



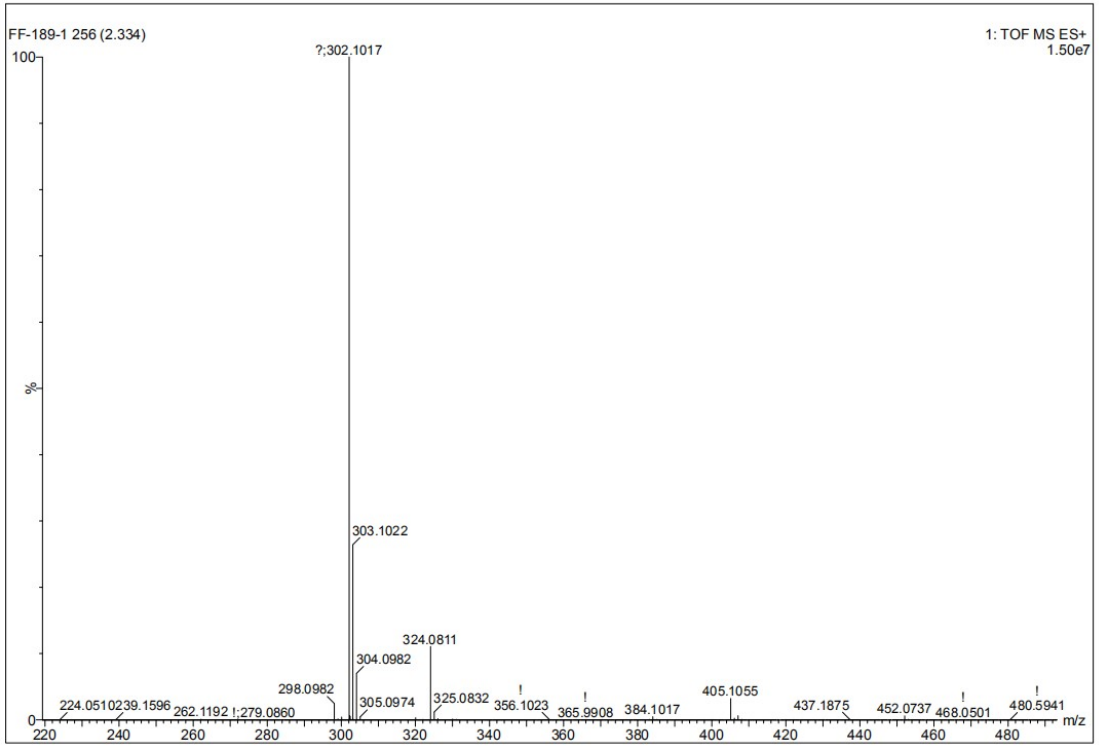
^{13}C NMR (150 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

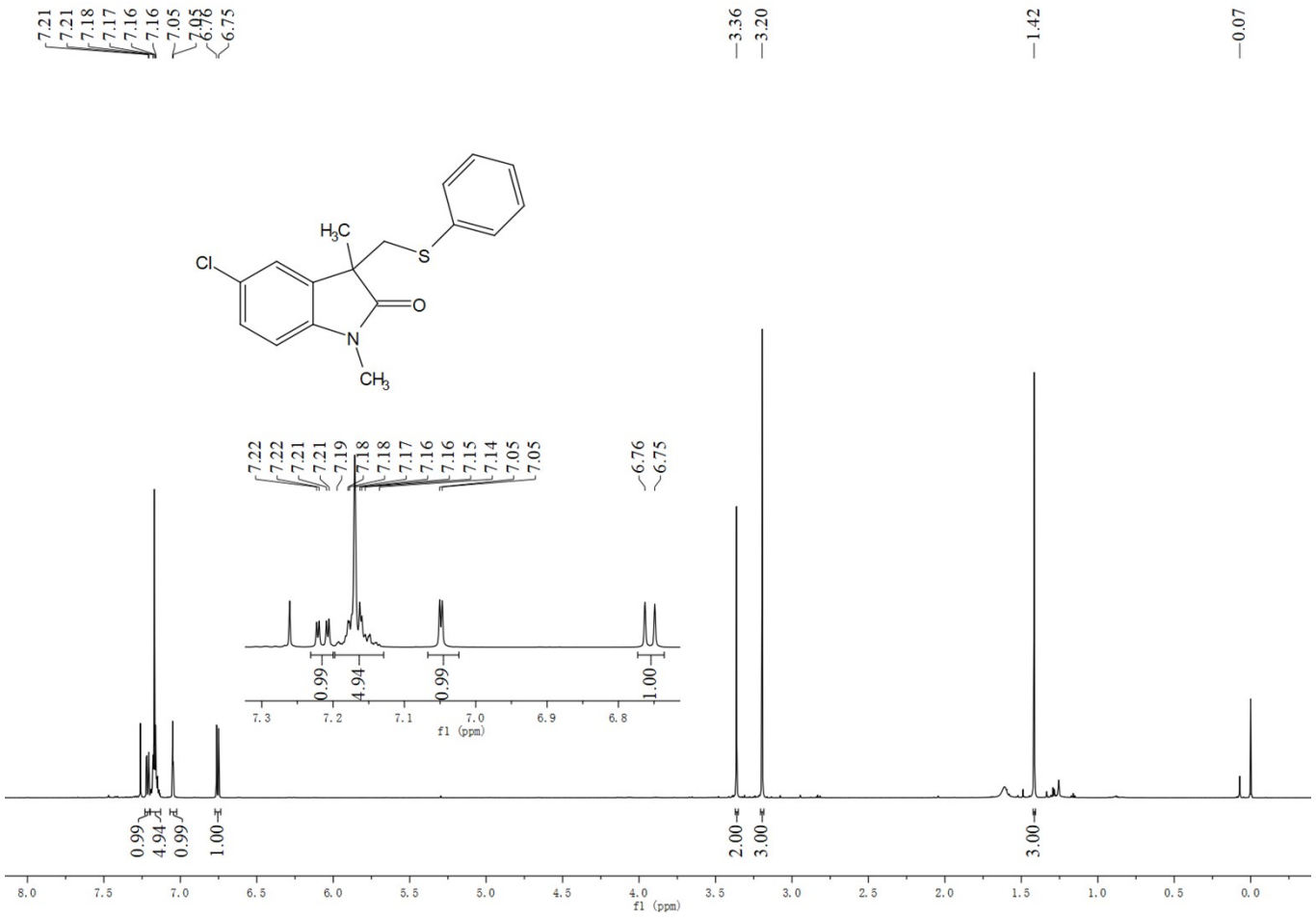


HRMS (ESI)

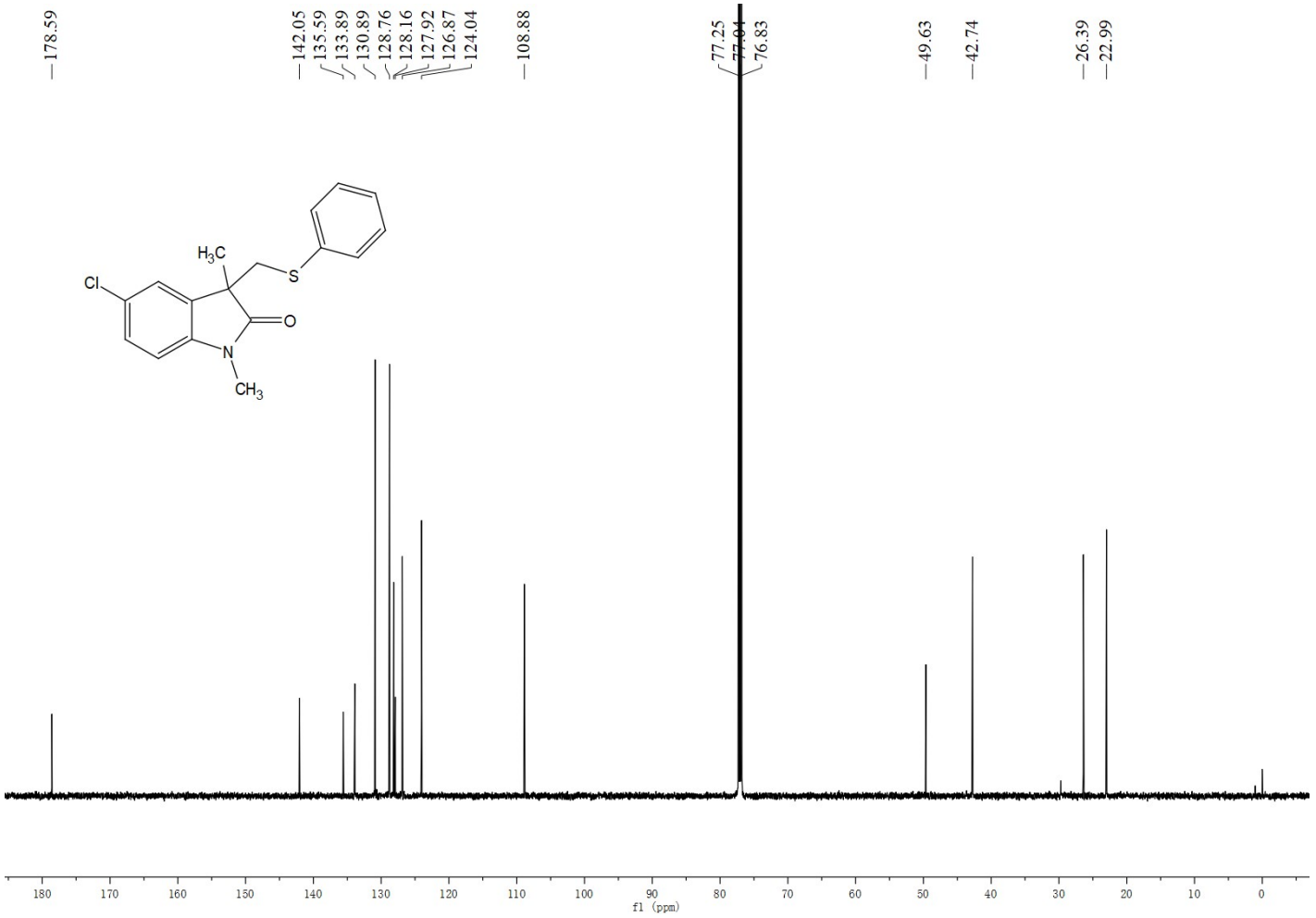

FF-189-1 256 (2.334)
1: TOF MS ES+
1.50e7
100
%
0
?;302.1017
303.1022
324.0811
304.0982
298.0982
305.0974
325.0832
224.0510
239.1596
262.1192
279.0860
356.1023
365.9908
384.1017
405.1055
437.1875
452.0737
468.0501
480.5941
220
240
260
280
300
320
340
360
380
400
420
440
460
480
m/z

5-Chloro-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3l)

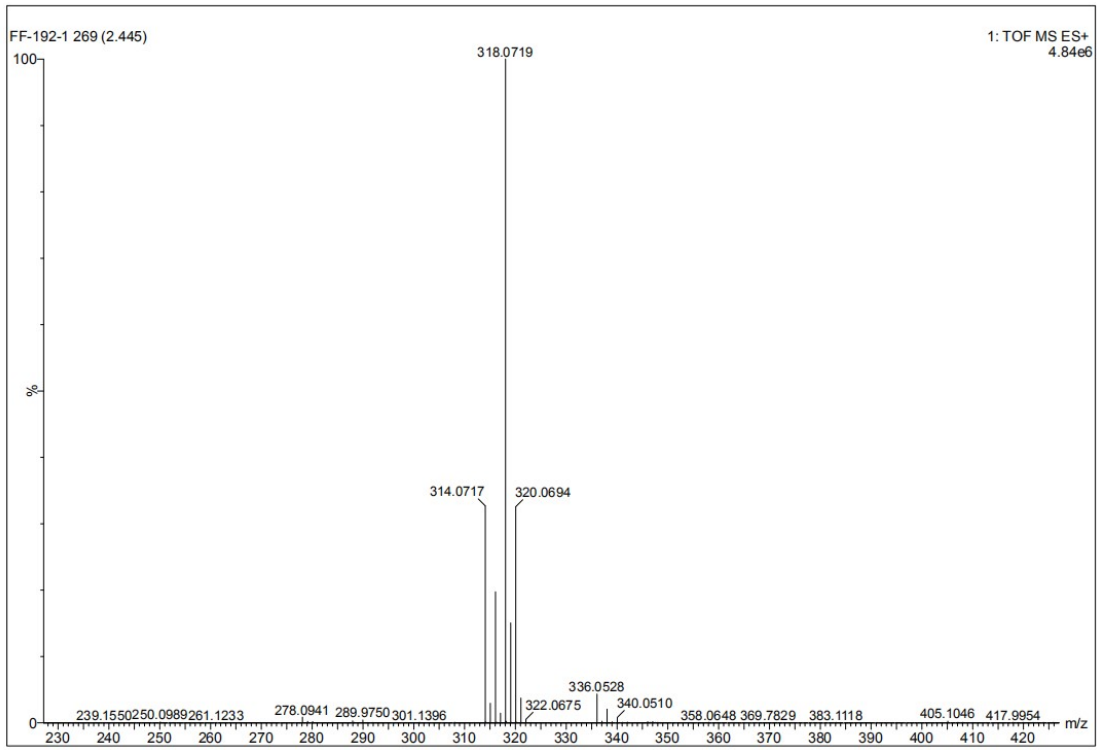
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

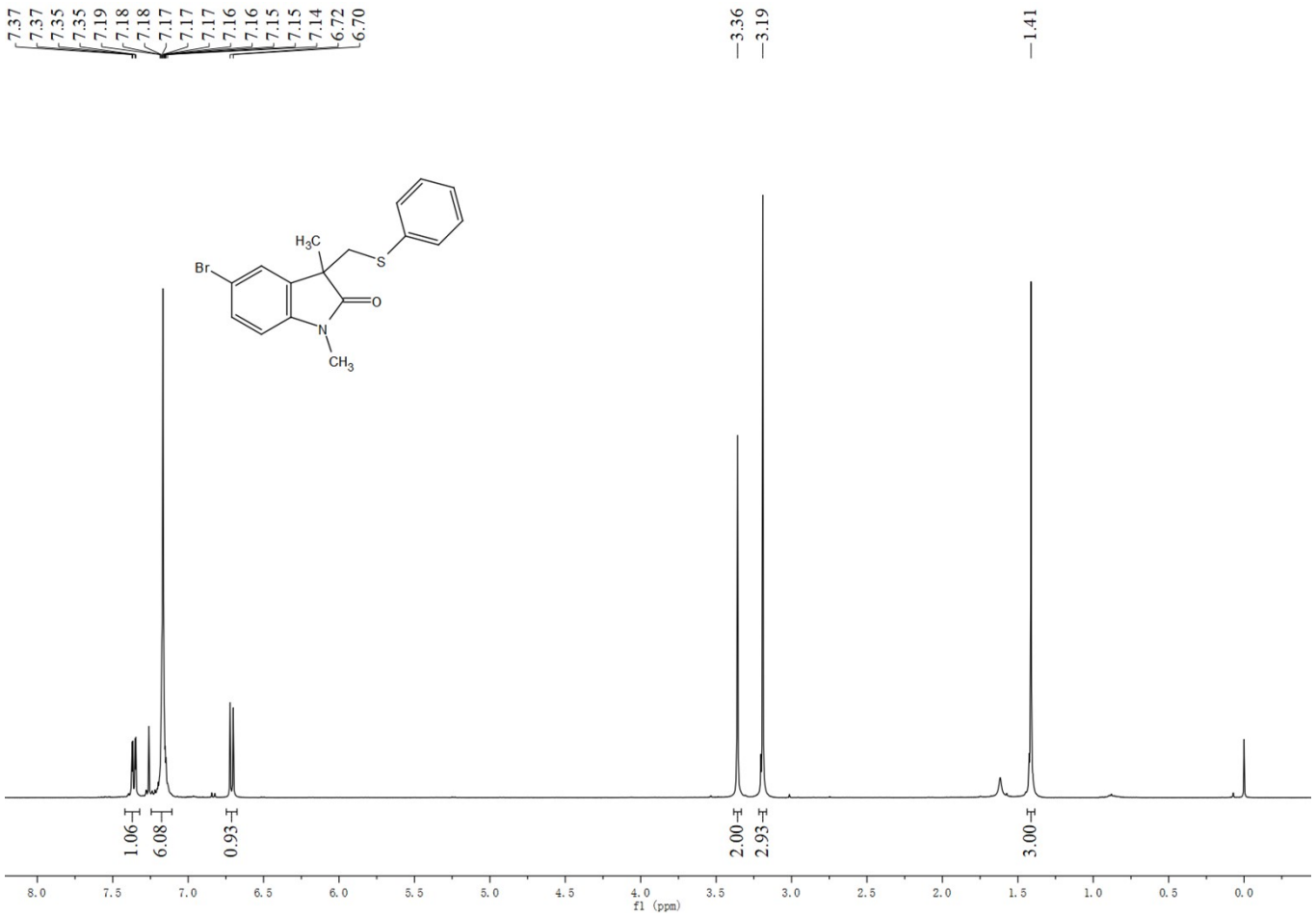


HRMS (ESI)

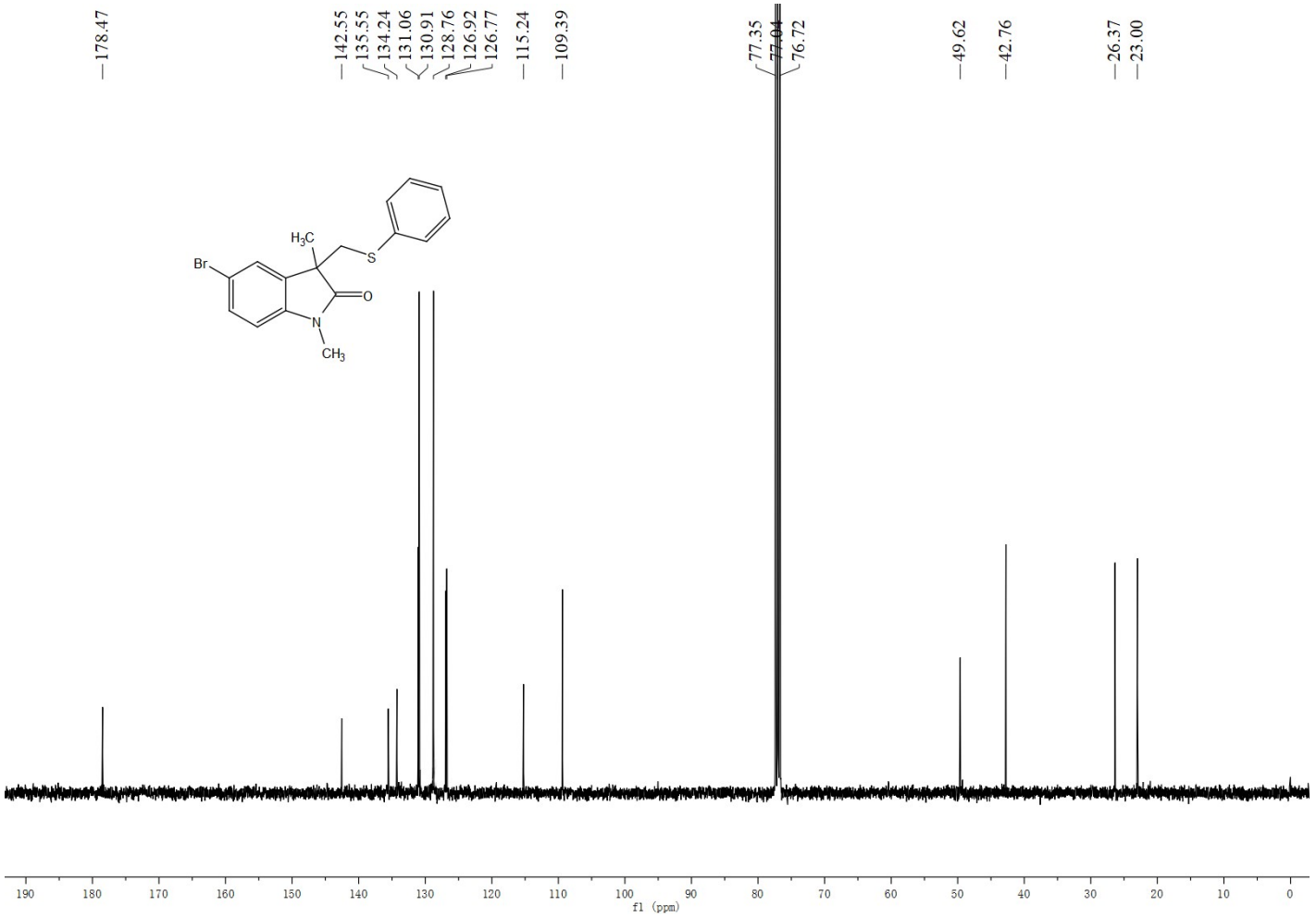

FF-192-1 269 (2.445)
1: TOF MS ES+
4.84e6
100
%
0
318.0719
314.0717
320.0694
336.0528
322.0675
340.0510
239.1550
250.0989
261.1233
278.0941
289.9750
301.1396
358.0648
369.7829
383.1118
405.1046
417.9954
m/z
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
380
390
400
410
420

5-Bromo-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3m)

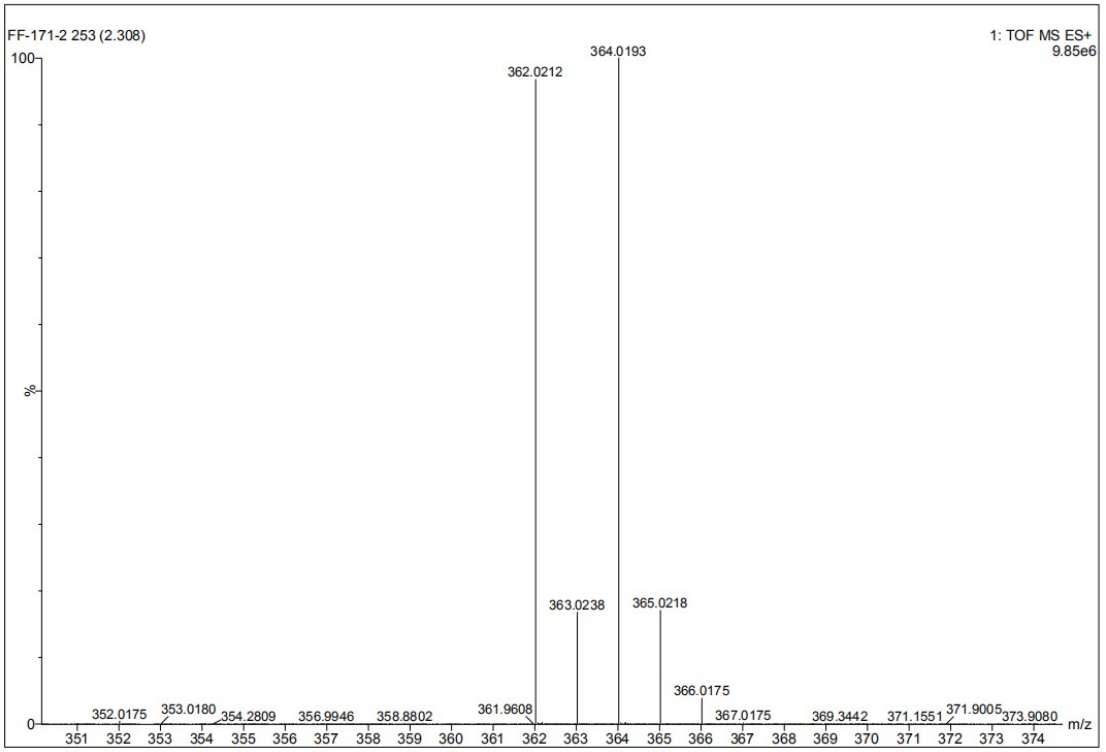
^{1}H NMR (400 MHz, $CDCl_3$)



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

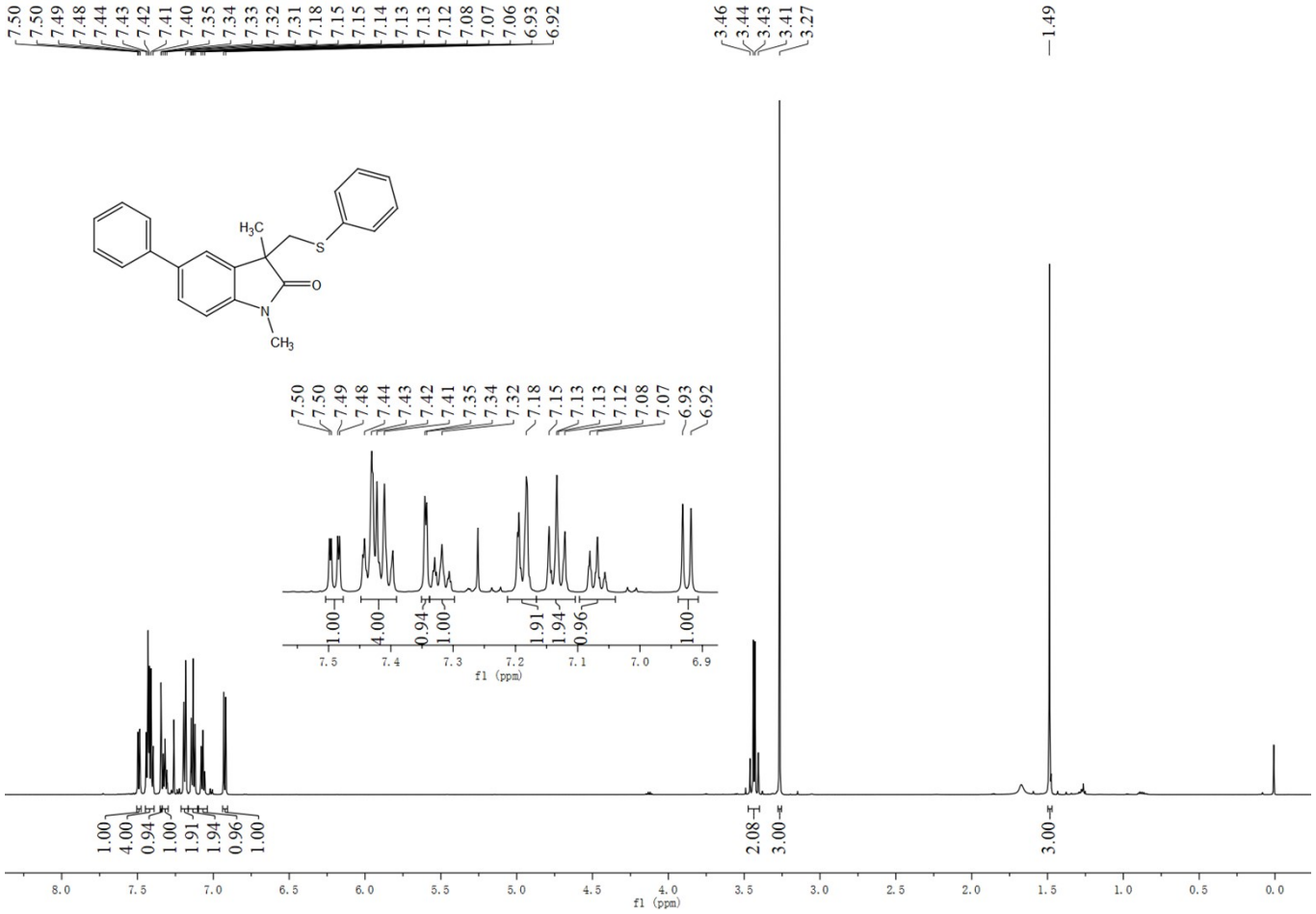


HRMS (ESI)

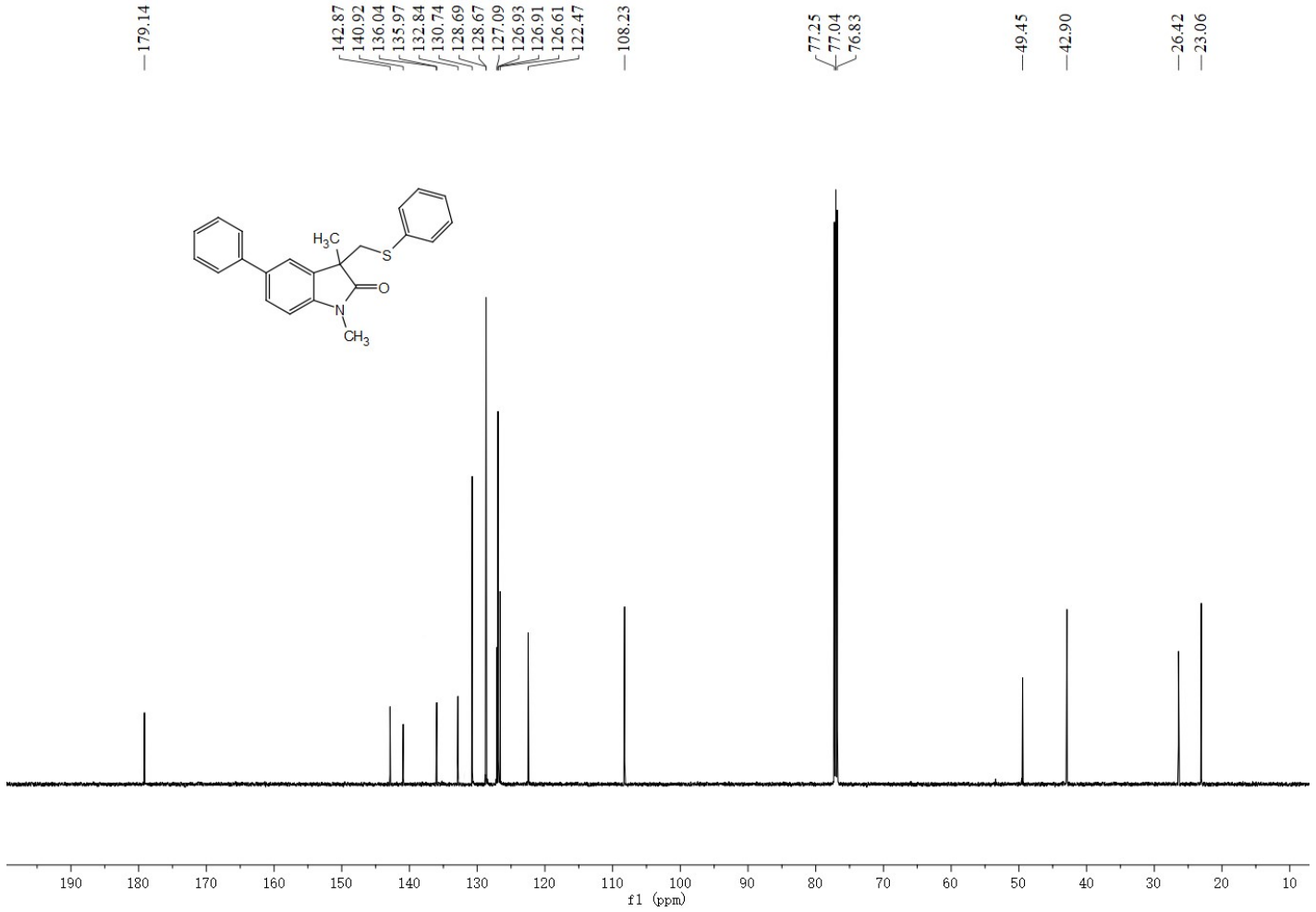

FF-171-2 253 (2.308)
1: TOF MS ES+
9.85e6
100
%
0
362.0212
364.0193
363.0238
365.0218
366.0175
352.0175
353.0180
354.2809
356.9946
358.8802
361.9608
367.0175
369.3442
371.1551
371.9005
373.9080
m/z
351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374

1,3-Dimethyl-5-phenyl-3-((phenylthio)methyl)indolin-2-one (3n)

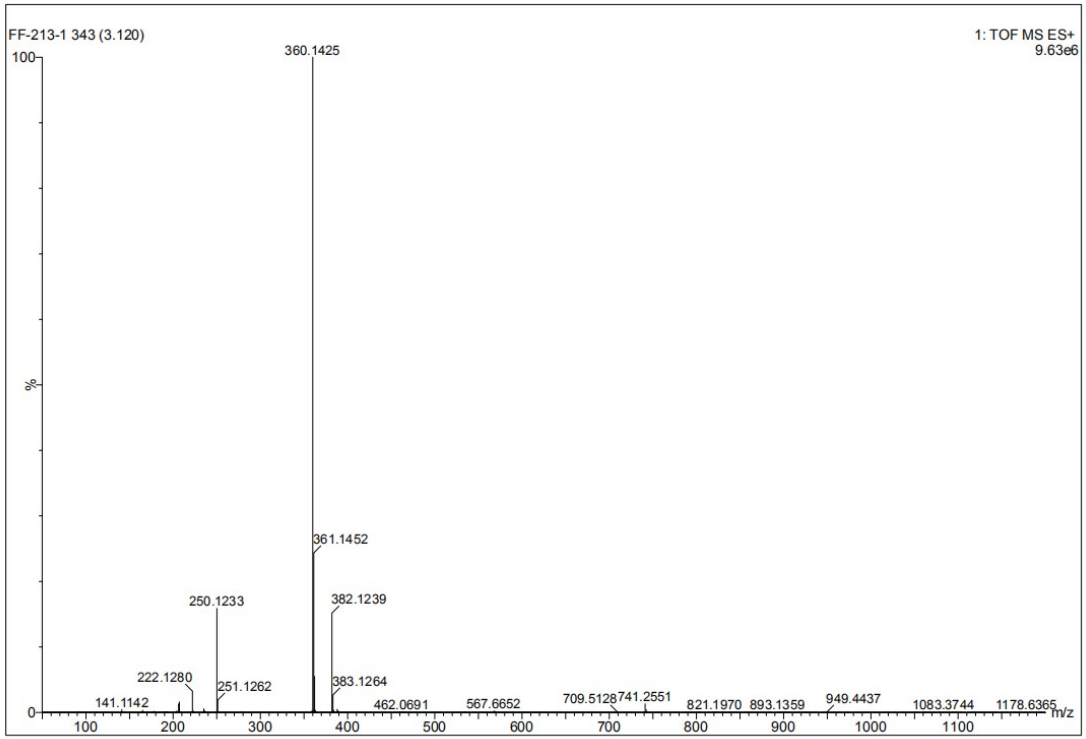
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

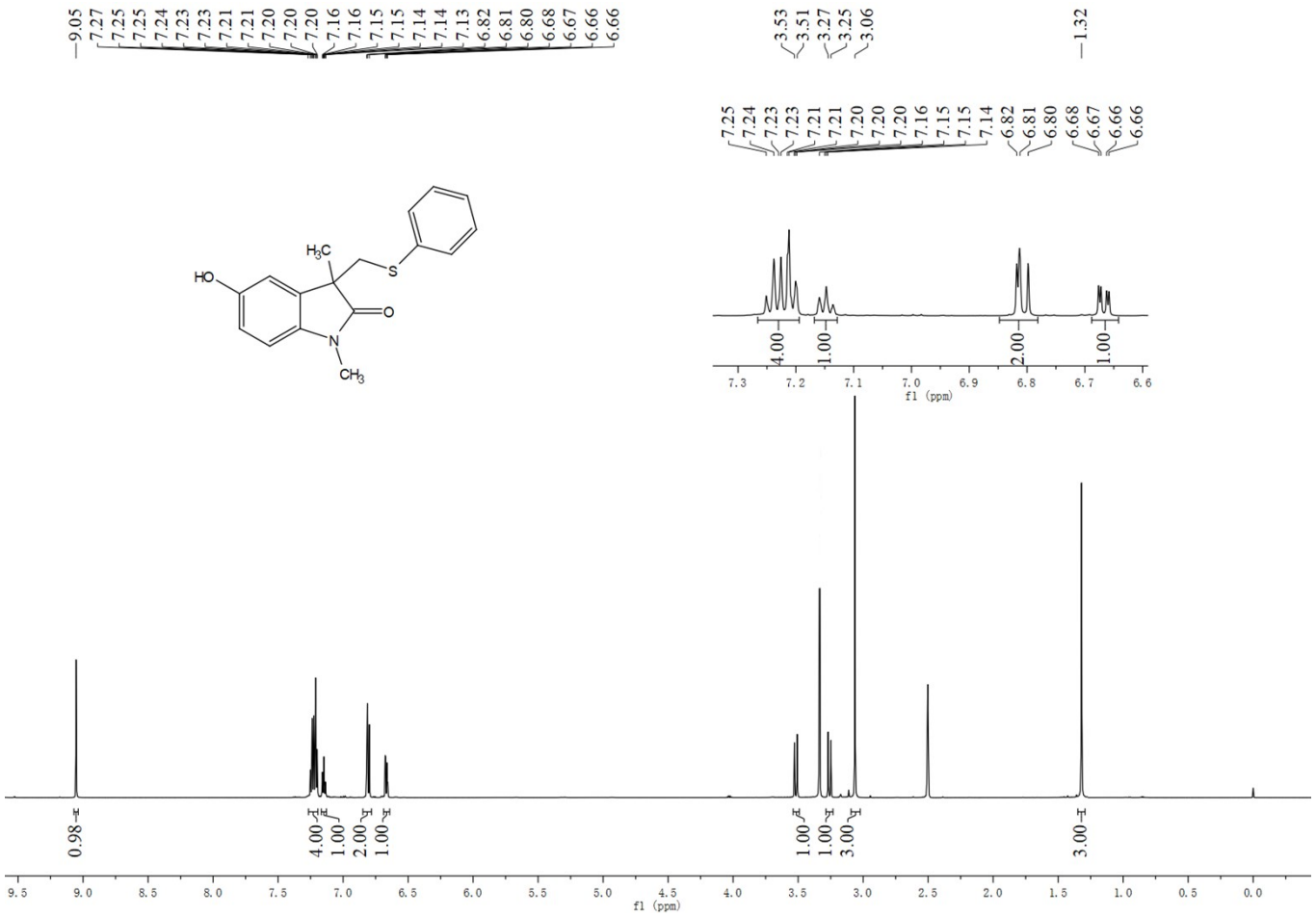


HRMS (ESI)

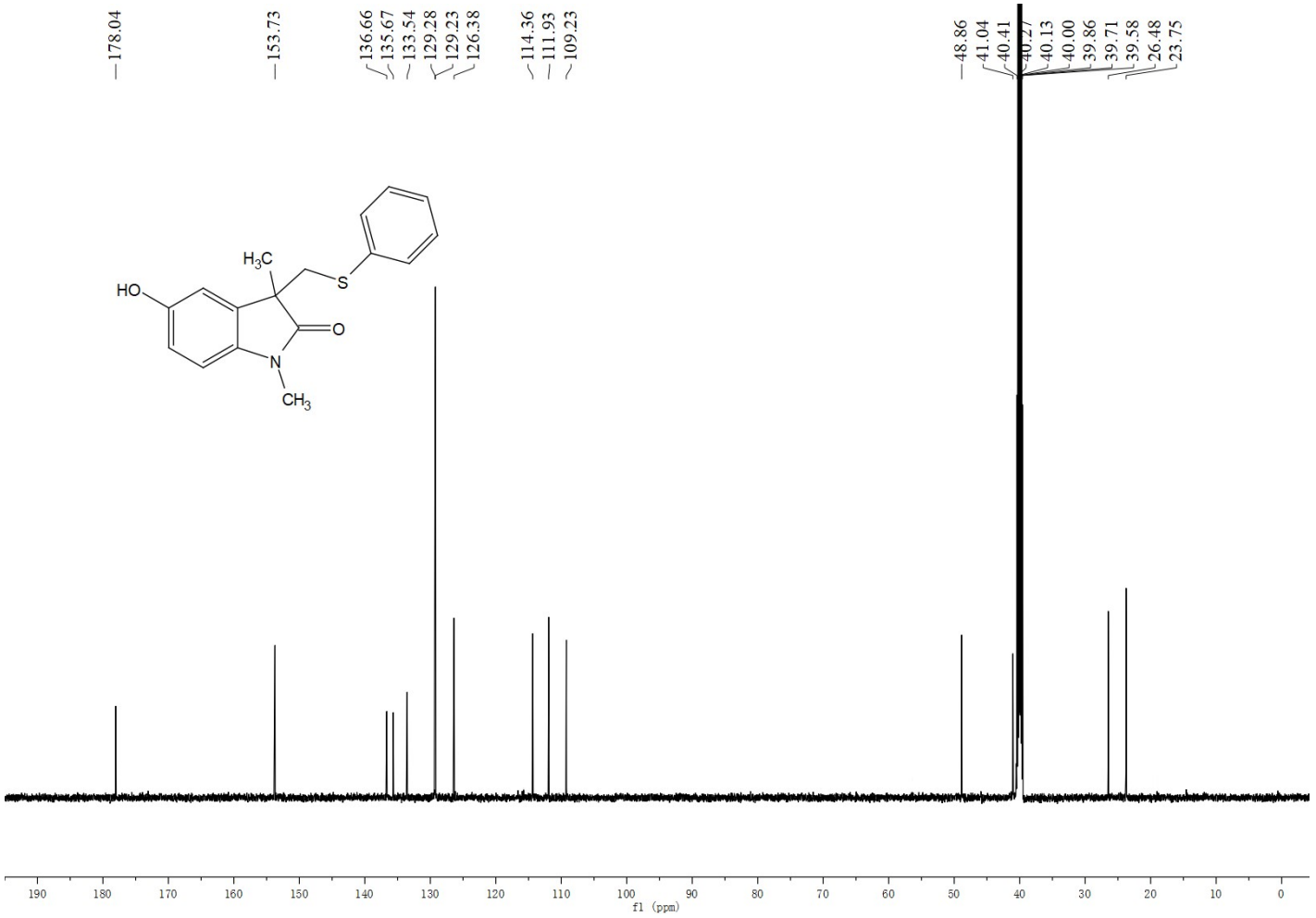

FF-213-1 343 (3.120)
1: TOF MS ES+
9.63e6
100
%
0
360.1425
361.1452
250.1233
382.1239
222.1280
251.1262
383.1264
141.1142
462.0691
567.6652
709.5128
741.2551
821.1970
893.1359
949.4437
1083.3744
1178.6365
100
200
300
400
500
600
700
800
900
1000
1100
m/z

5-Hydroxy-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (3o)

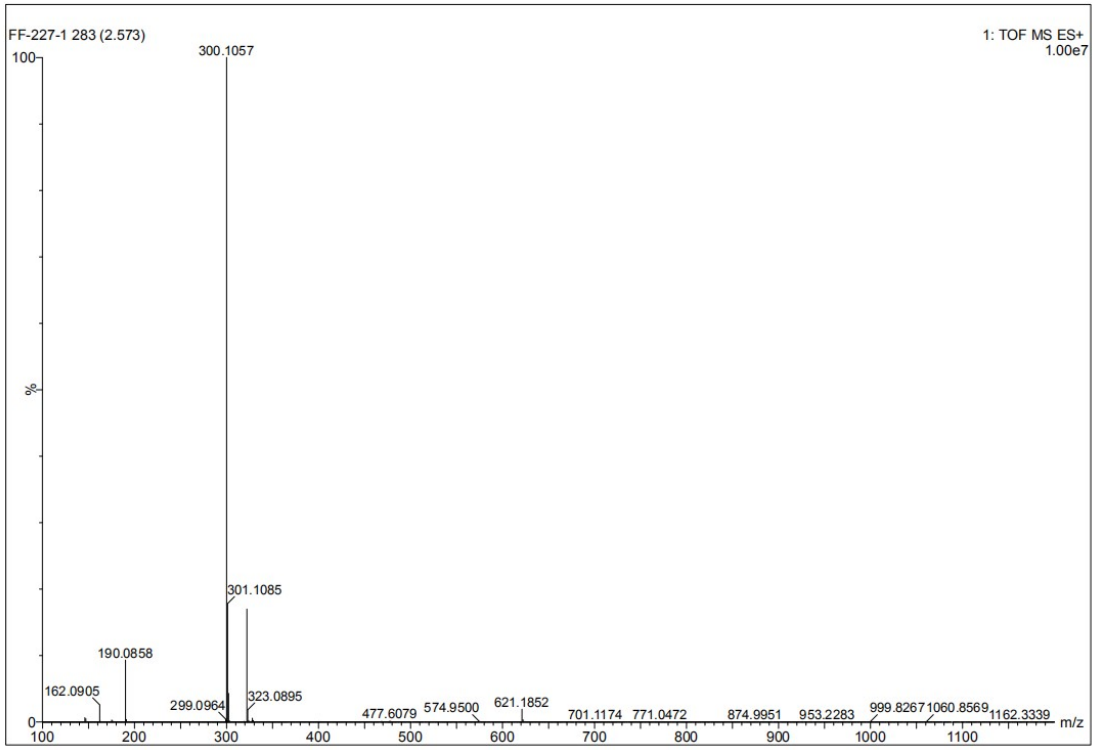
^{1}H NMR (600 MHz, DMSO-d_6)



^{13}C NMR (150 MHz, DMSO-d_6)

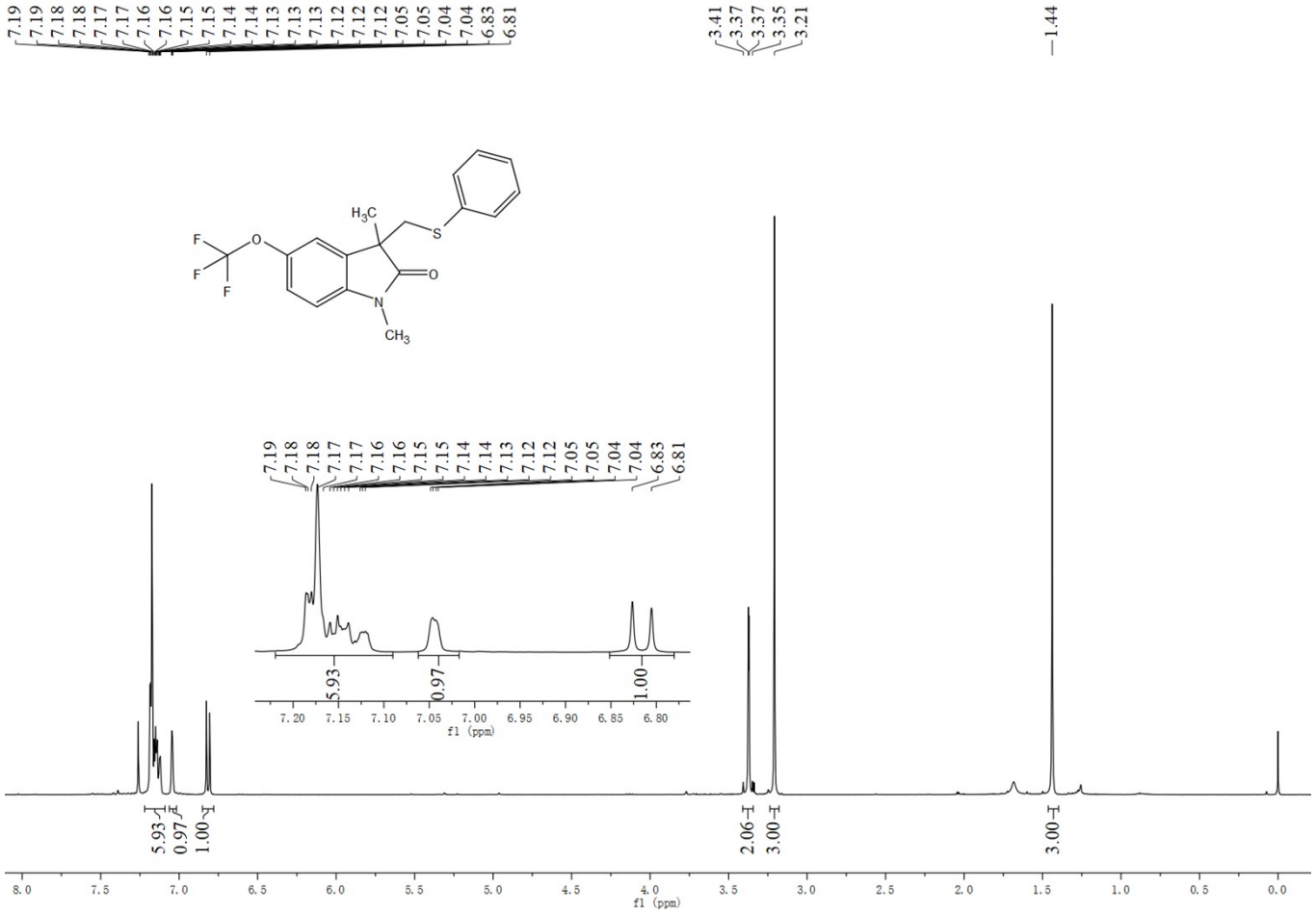


HRMS (ESI)

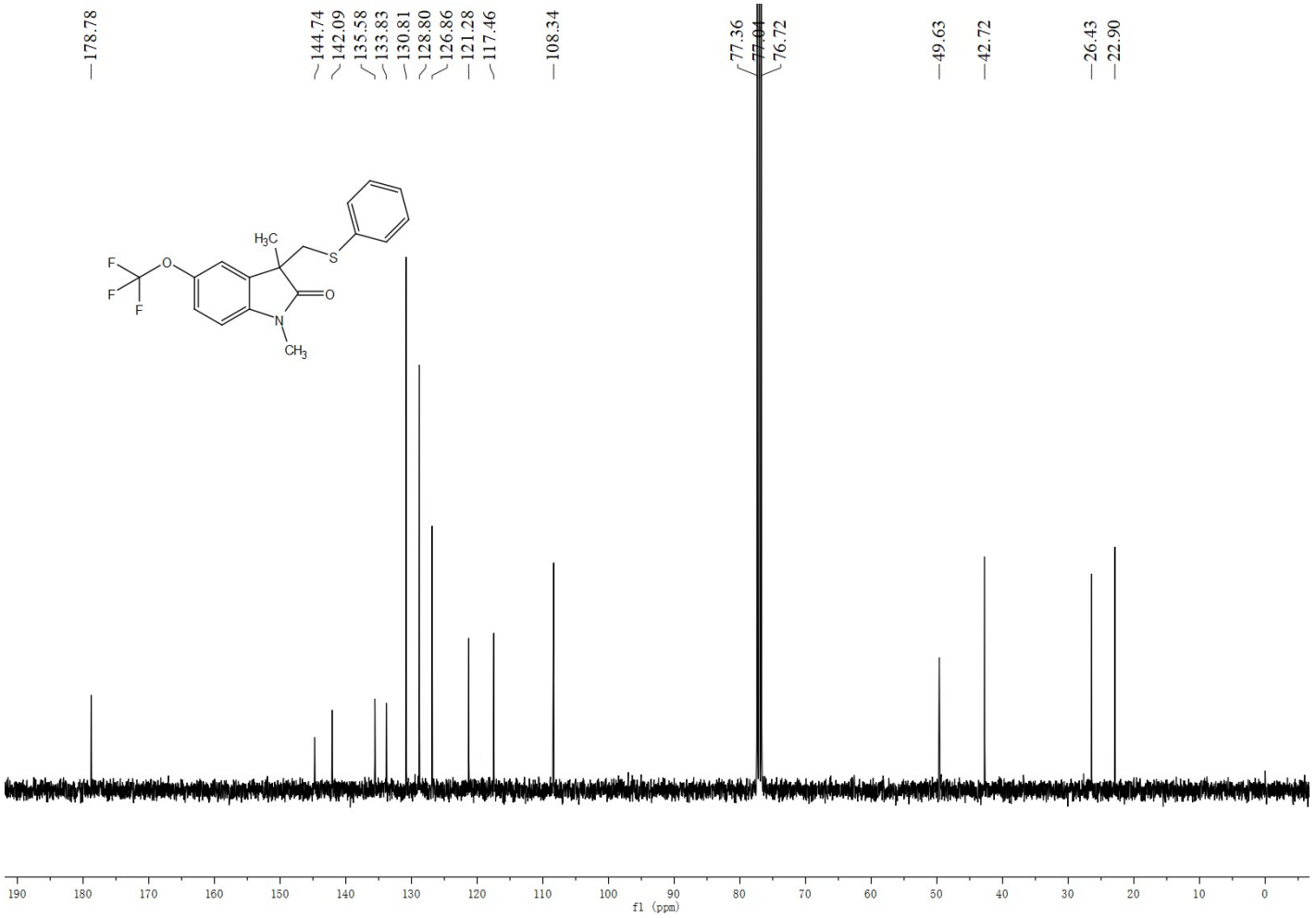

FF-227-1 283 (2.573)
1: TOF MS ES+
1.00e7
100
%
0
300.1057
301.1085
190.0858
162.0905
299.0964
323.0895
477.6079
574.9500
621.1852
701.1174
771.0472
874.9951
953.2283
999.8267
1060.8569
1162.3339
100
200
300
400
500
600
700
800
900
1000
1100
m/z

1,3-Dimethyl-3-((phenylthio)methyl)-5-(trifluoromethoxy)indolin-2-one (3p)

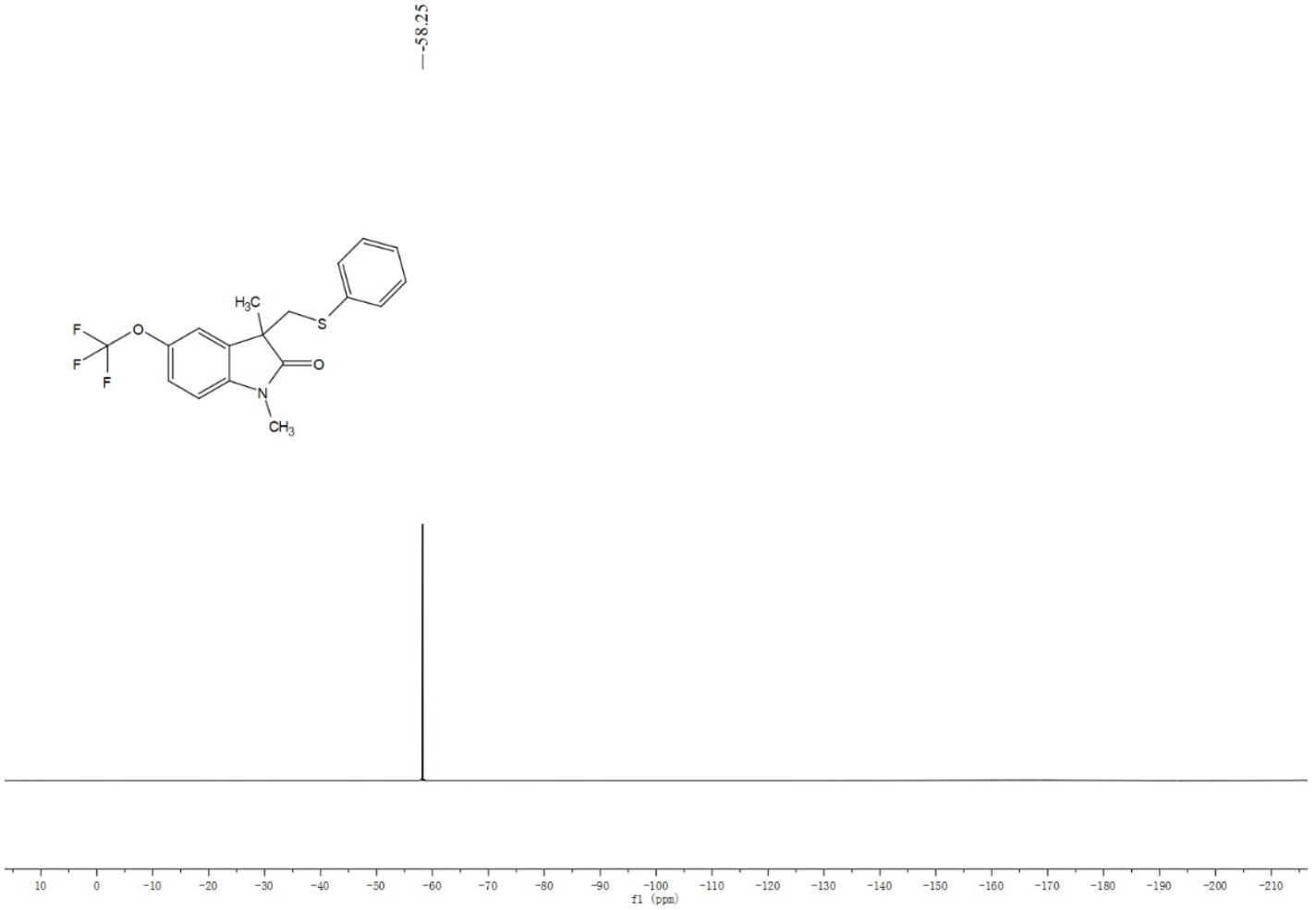
^{1}H NMR (400 MHz, $CDCl_3$)



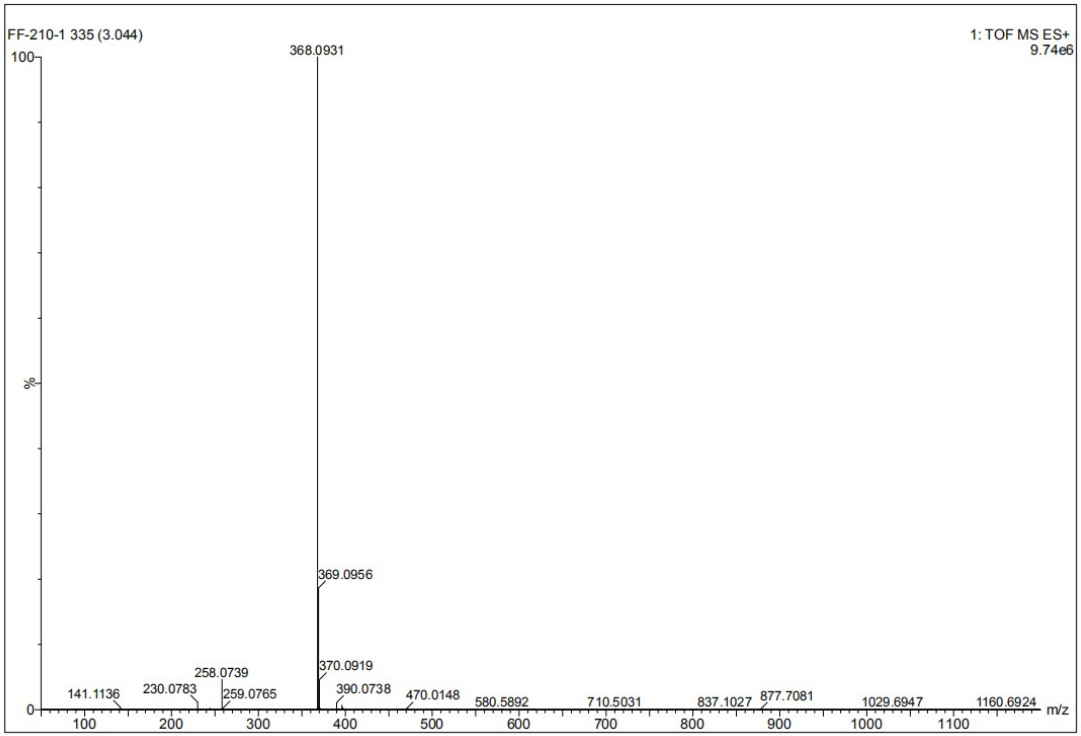
^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

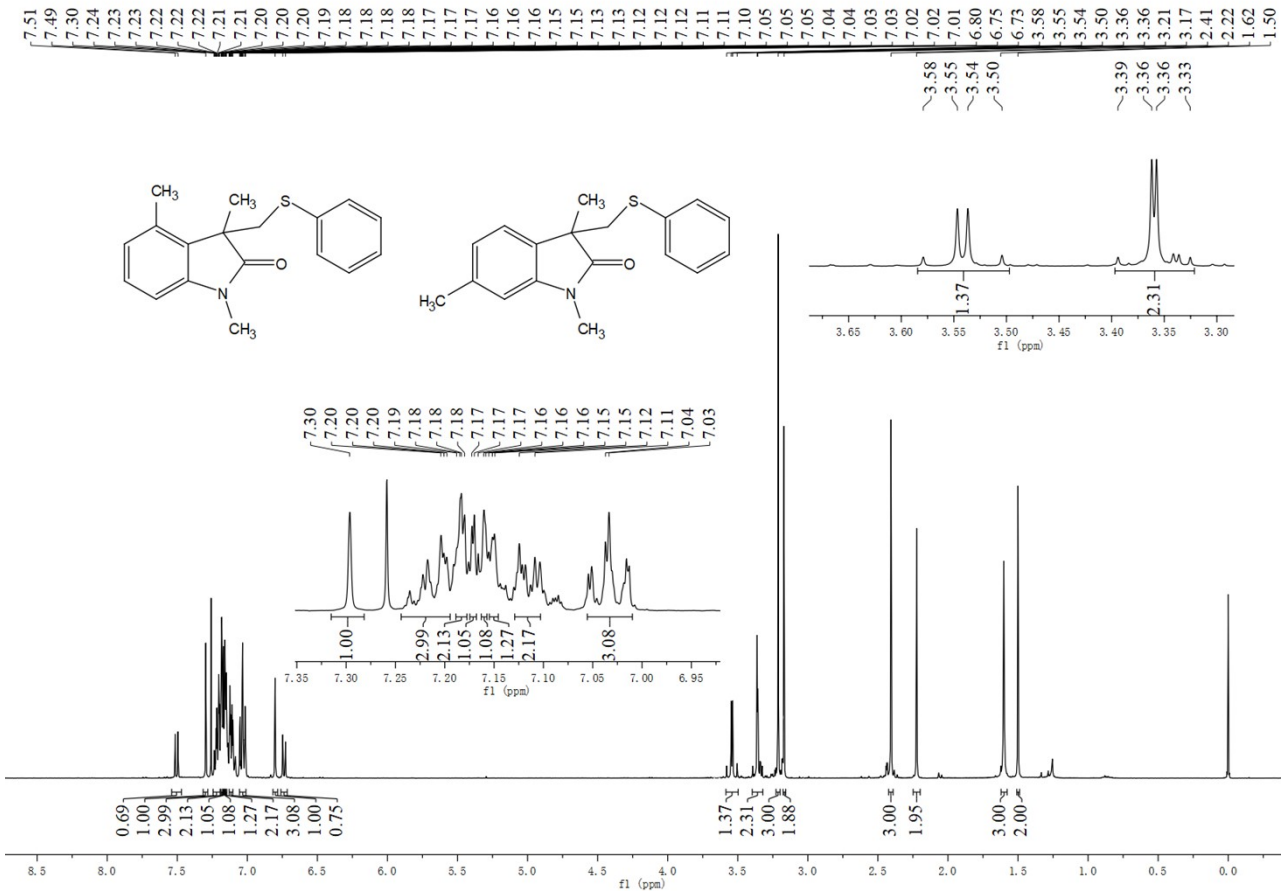


HRMS (ESI)

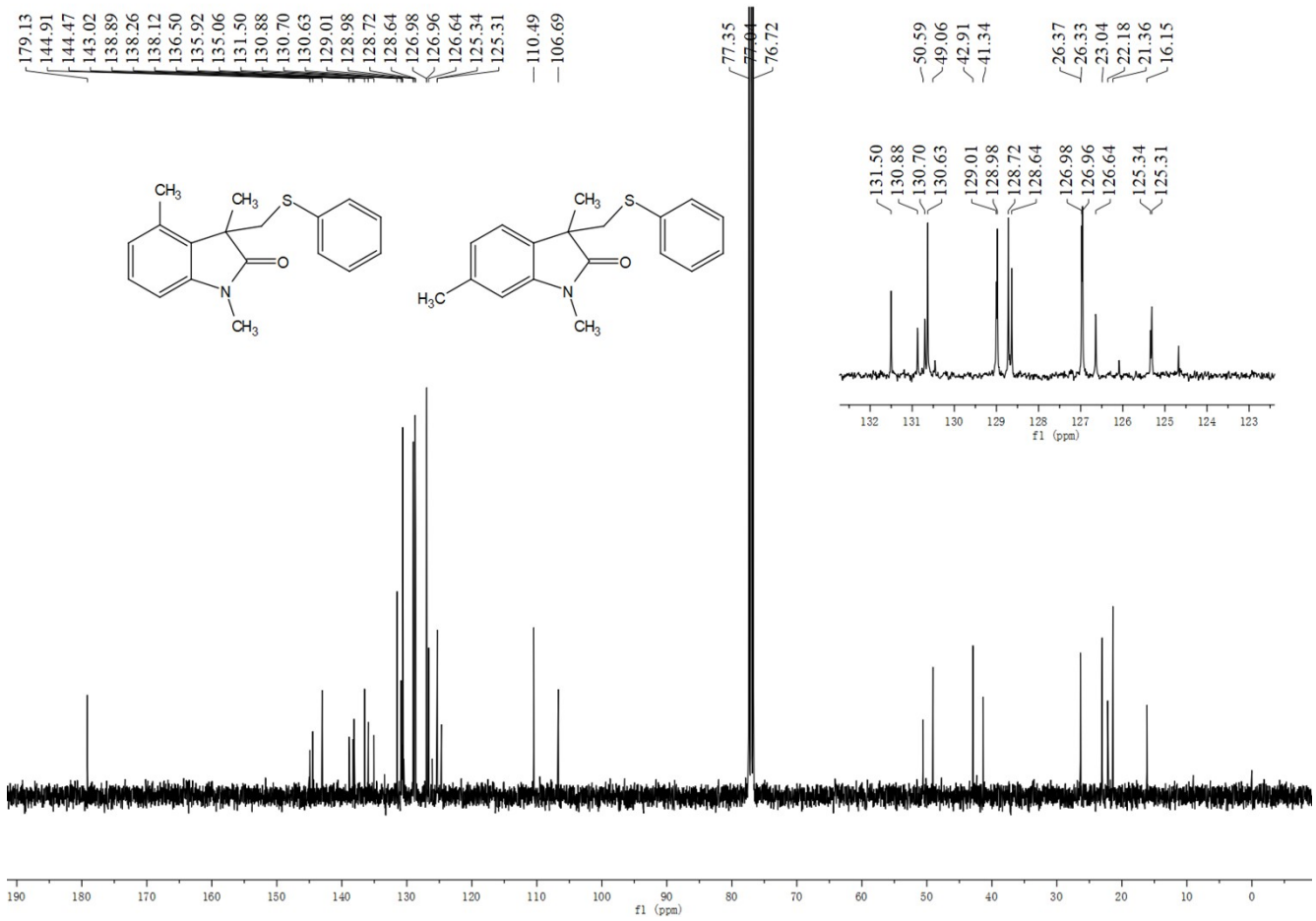

FF-210-1 335 (3.044)
1: TOF MS ES+
9.74e6
100
%
0
368.0931
369.0956
370.0919
258.0739
141.1136
230.0783
259.0765
390.0738
470.0148
580.5892
710.5031
837.1027
877.7081
1029.6947
1160.6924
100
200
300
400
500
600
700
800
900
1000
1100
m/z

1,3,4-Trimethyl-3-((phenylthio)methyl)indolin-2-one /1,3,6-trimethyl-3-((phenylthio)methyl)indolin-2-one (1.5:1) (3q:3q')

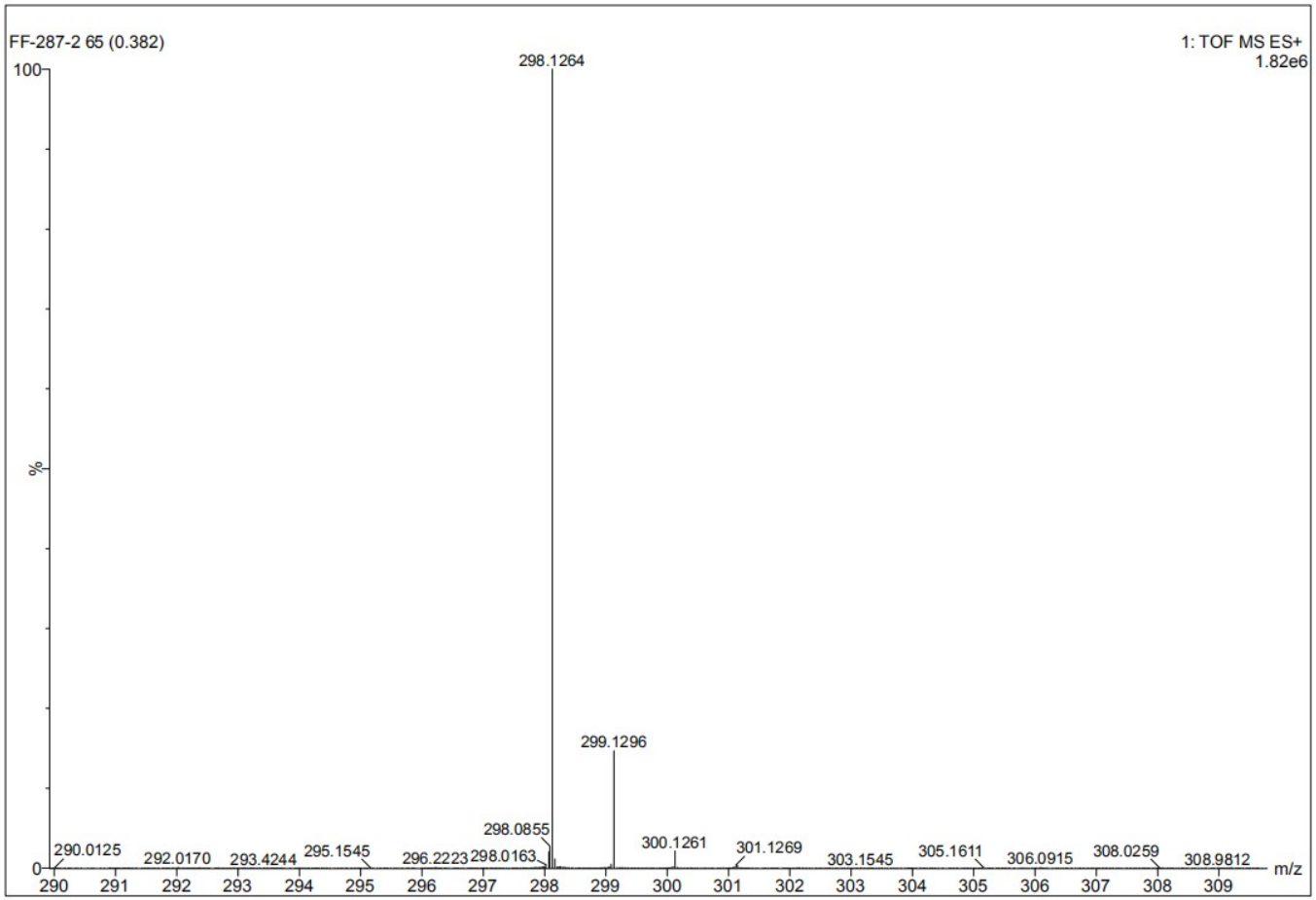
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

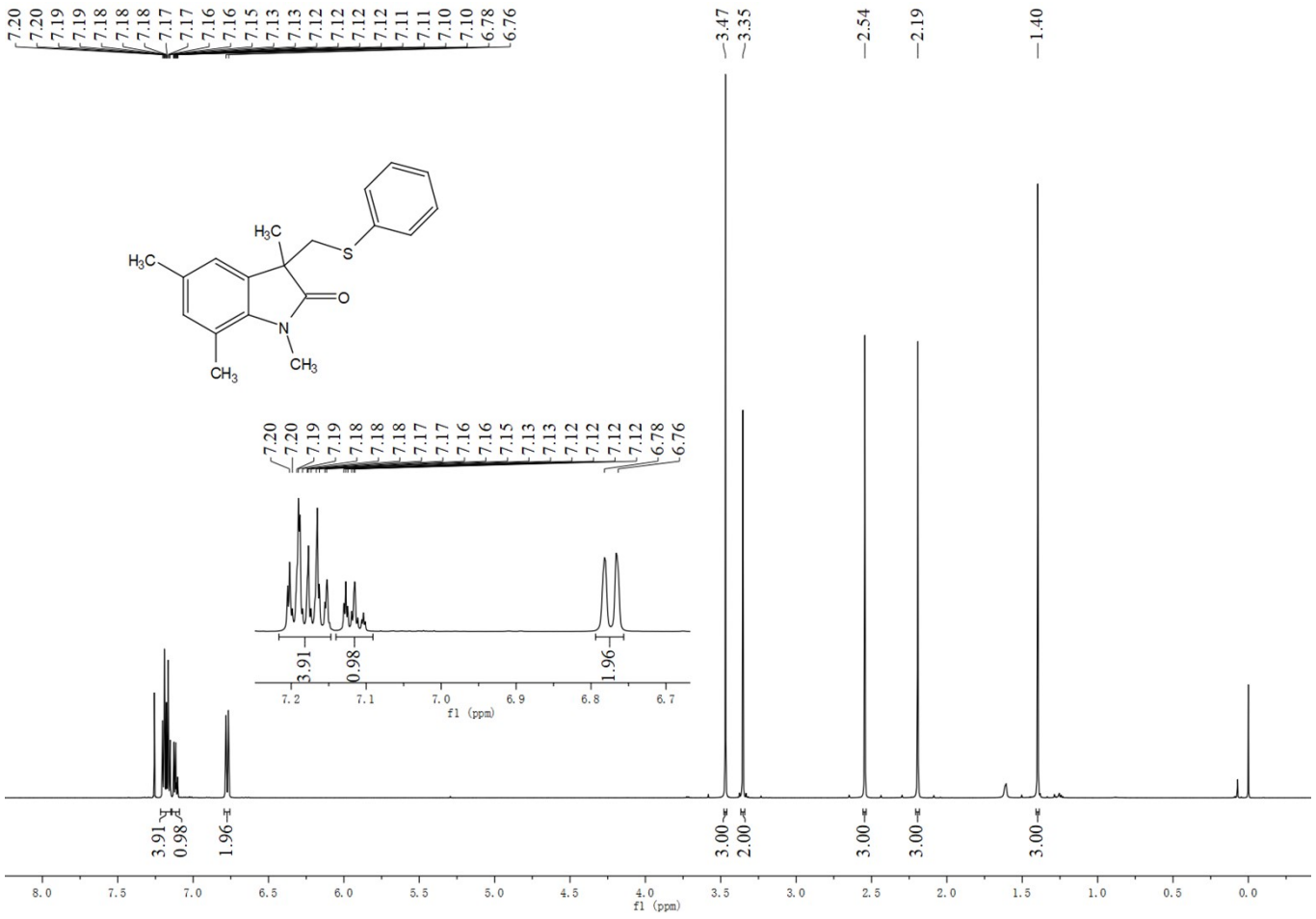


HRMS (ESI)

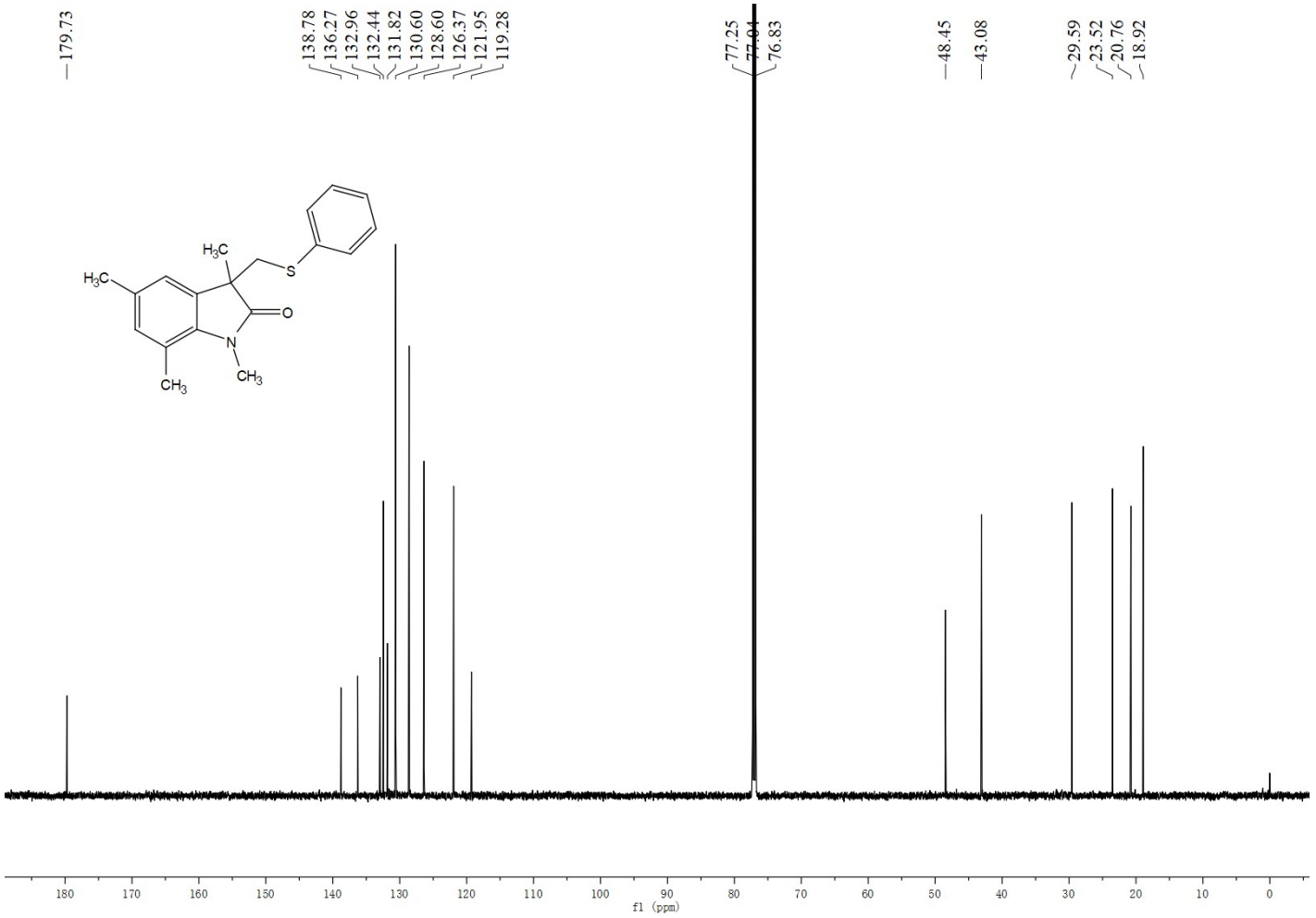

FF-287-2 65 (0.382)
1: TOF MS ES+
1.82e6
100
%
0
298.1264
299.1296
298.0855
290.0125
292.0170
293.4244
295.1545
296.2223
298.0163
300.1261
301.1269
303.1545
305.1611
306.0915
308.0259
308.9812
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
m/z

1,3,5,7-Tetramethyl-3-((phenylthio)methyl)indolin-2-one (3r)

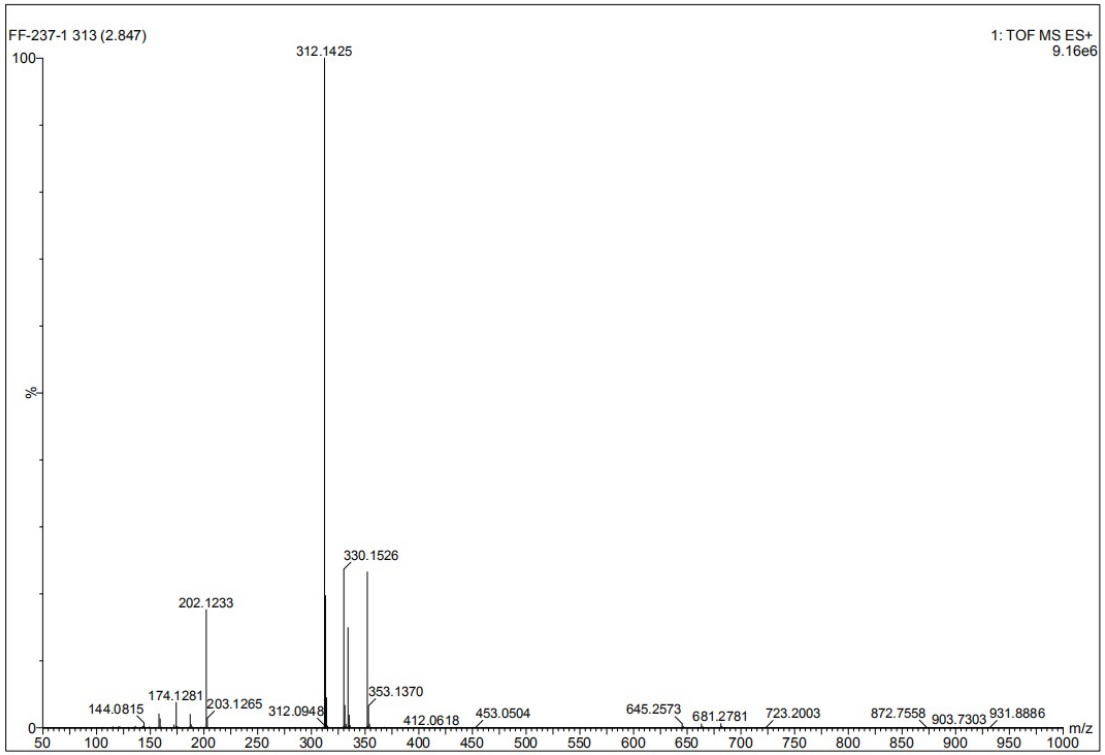
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

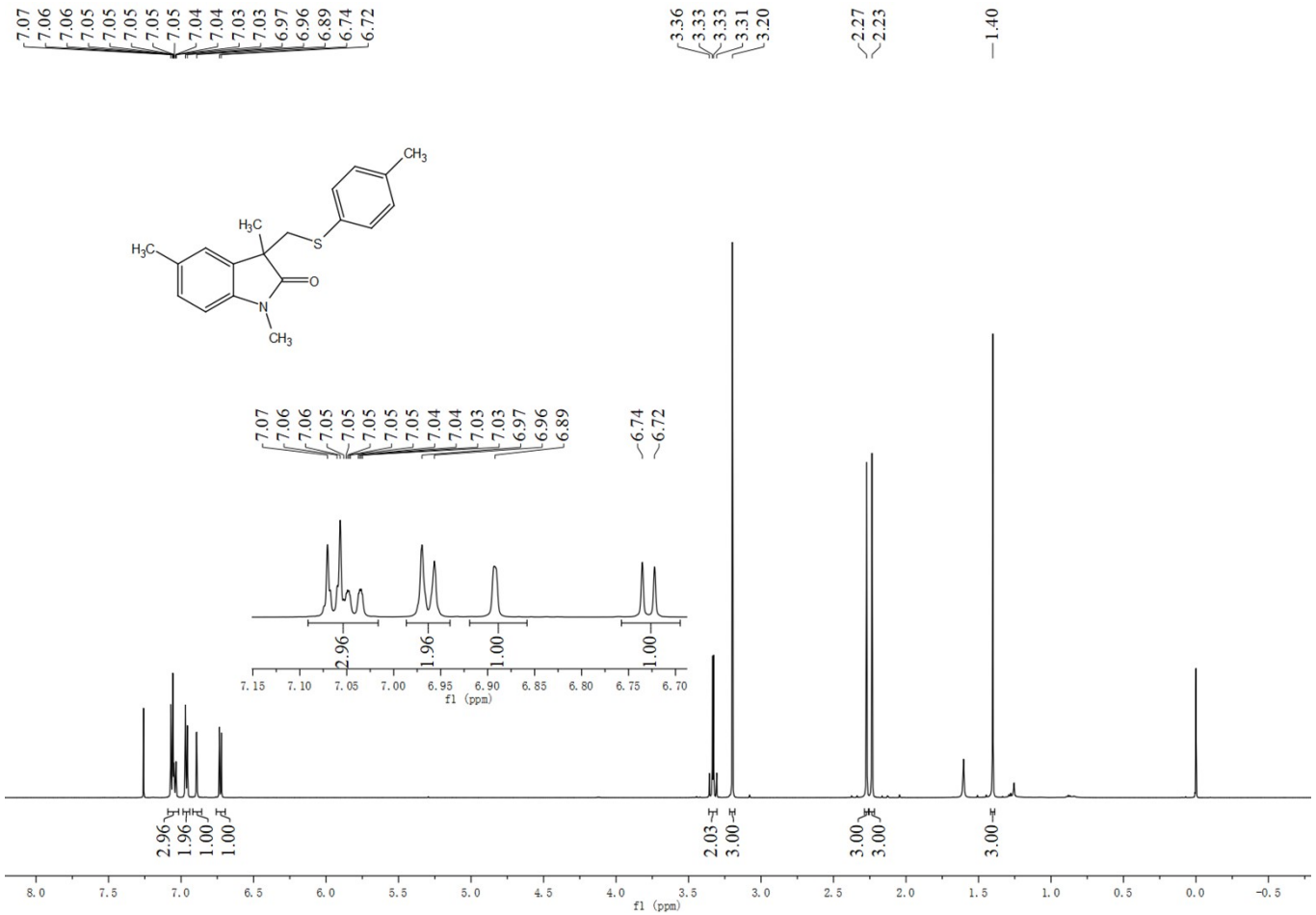


HRMS (ESI)

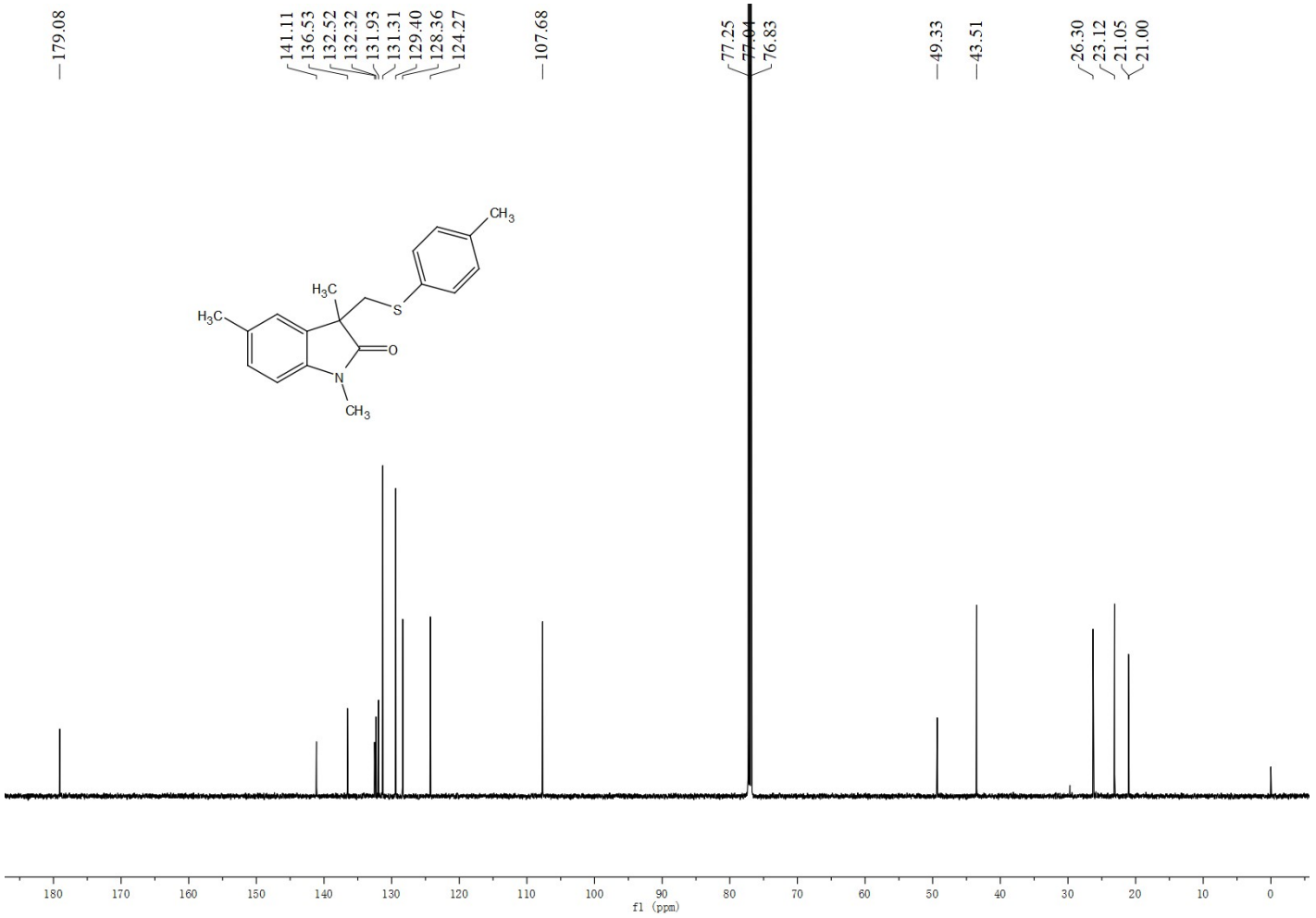

FF-237-1 313 (2.847)
1: TOF MS ES+
9.16e6
100
%
0
312.1425
330.1526
202.1233
353.1370
174.1281
144.0815
203.1265
312.0948
412.0618
453.0504
645.2573
681.2781
723.2003
872.7558
903.7303
931.8886
m/z
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000

1,3,5-Trimethyl-3-((p-tolylthio)methyl)indolin-2-one (3s)

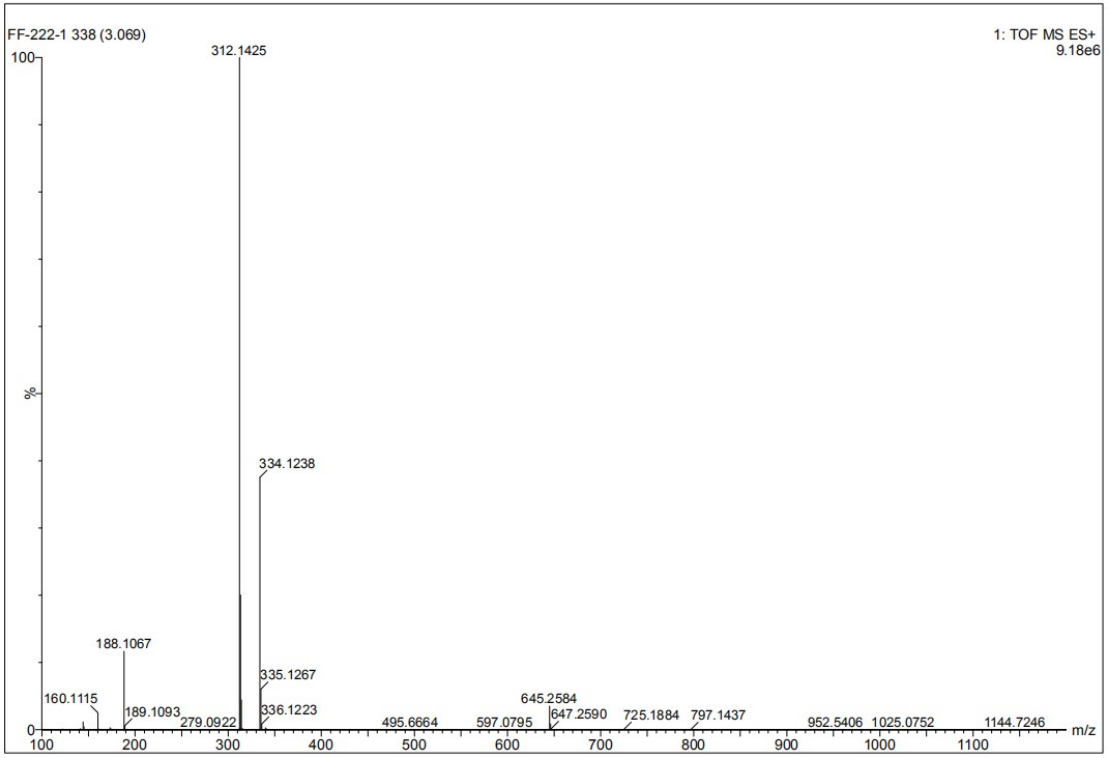
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

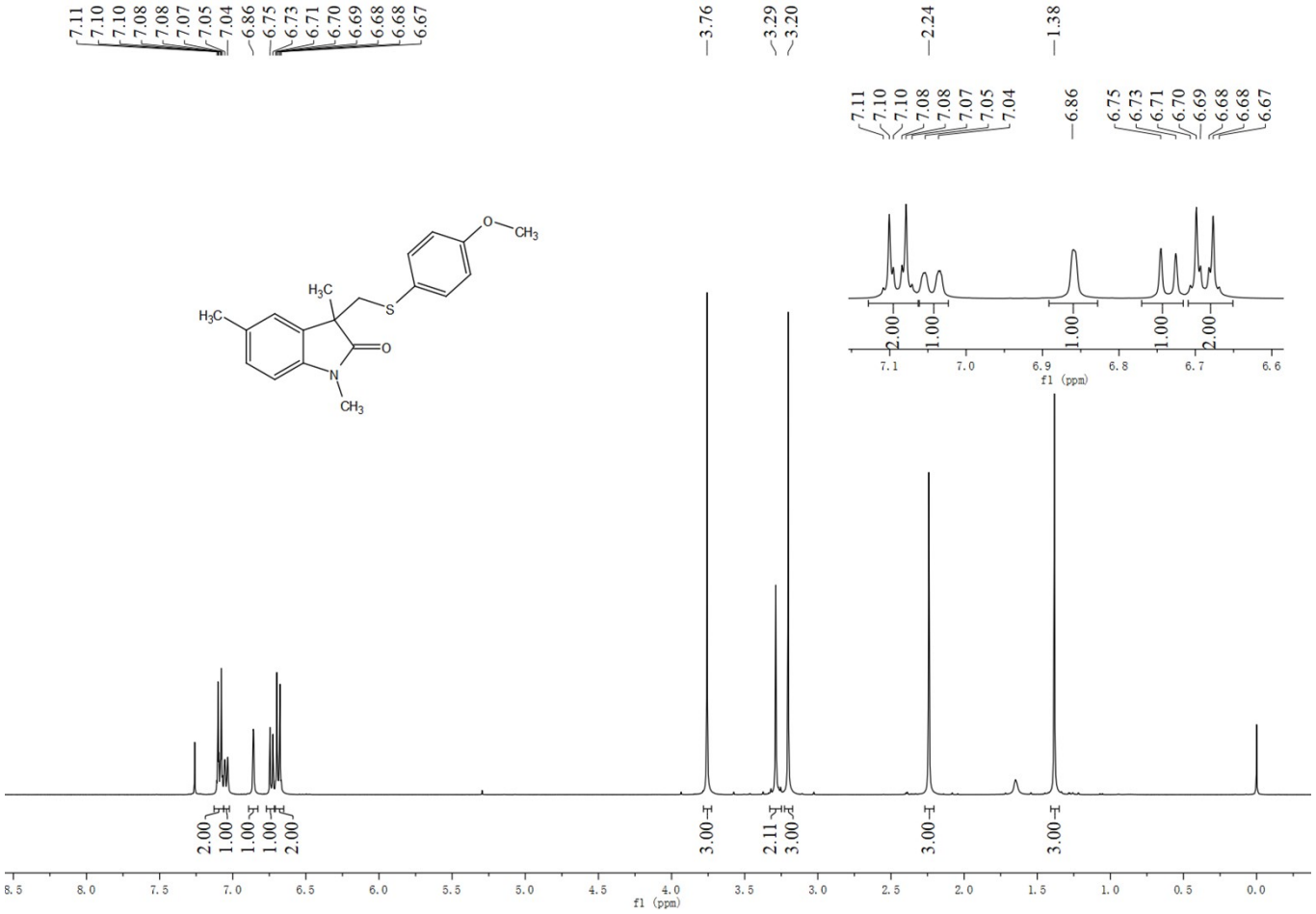


HRMS (ESI)

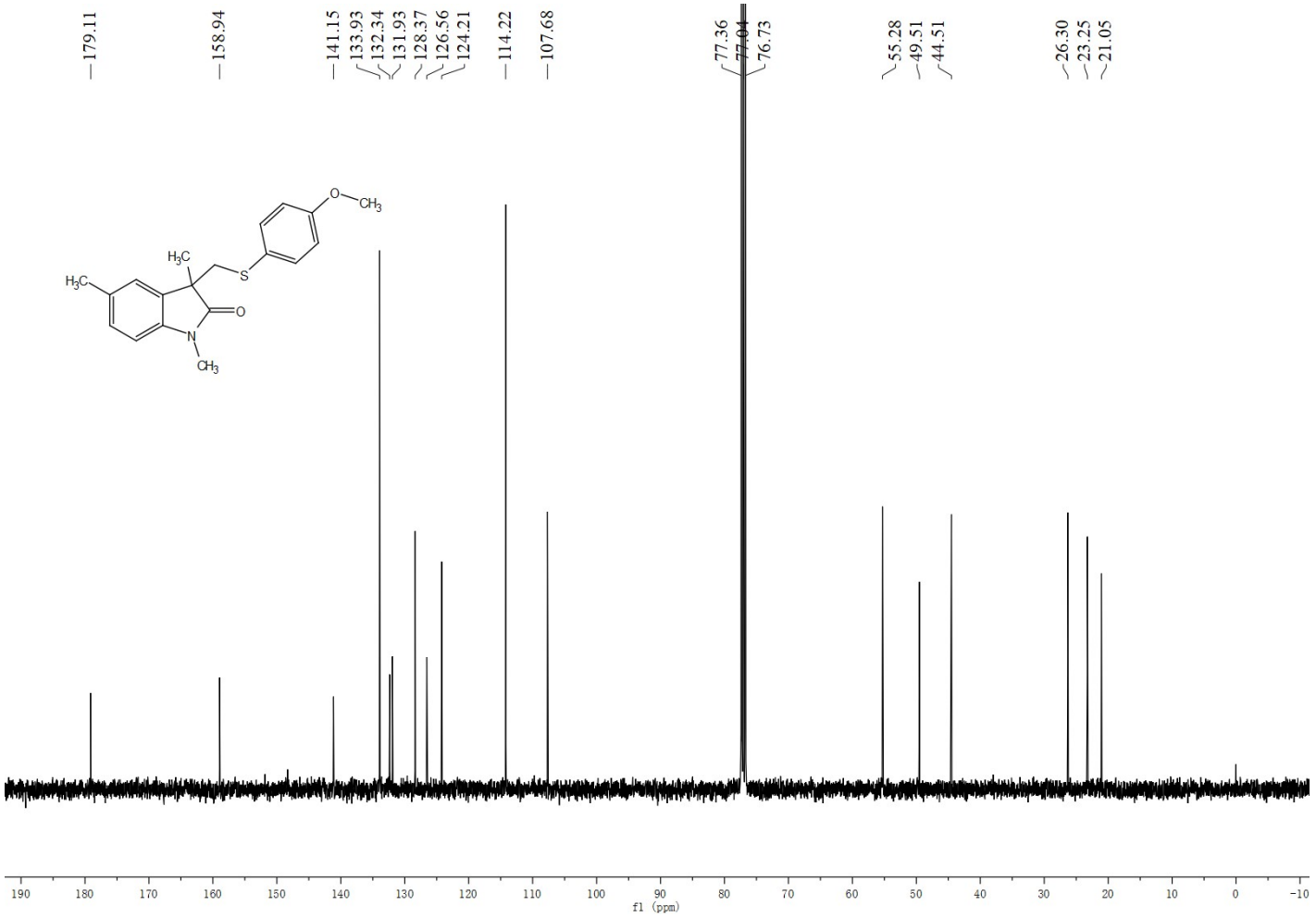

FF-222-1 338 (3.069)
1: TOF MS ES+
9.18e6
100
%
0
312.1425
334.1238
188.1067
335.1267
160.1115
189.1093
336.1223
279.0922
495.6664
597.0795
645.2584
647.2590
725.1884
797.1437
952.5406
1025.0752
1144.7246
m/z
100
200
300
400
500
600
700
800
900
1000
1100

3-(((4-Methoxyphenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3t)

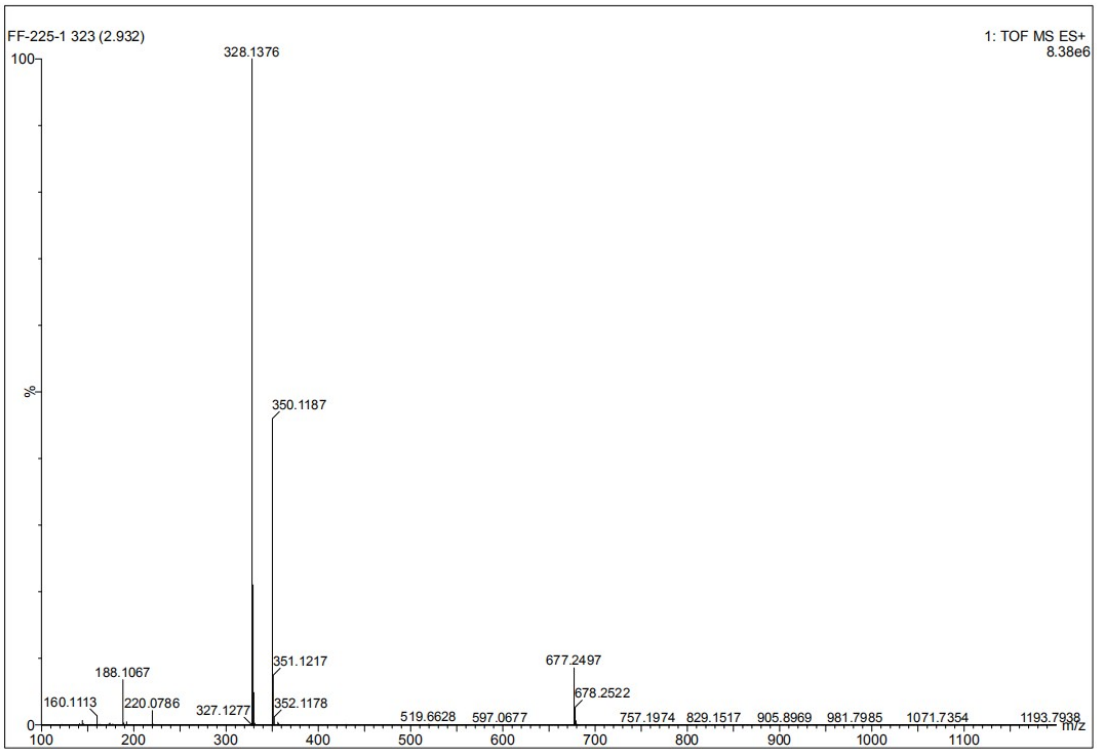
^{1}H NMR (400 MHz, $CDCl_3$)



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

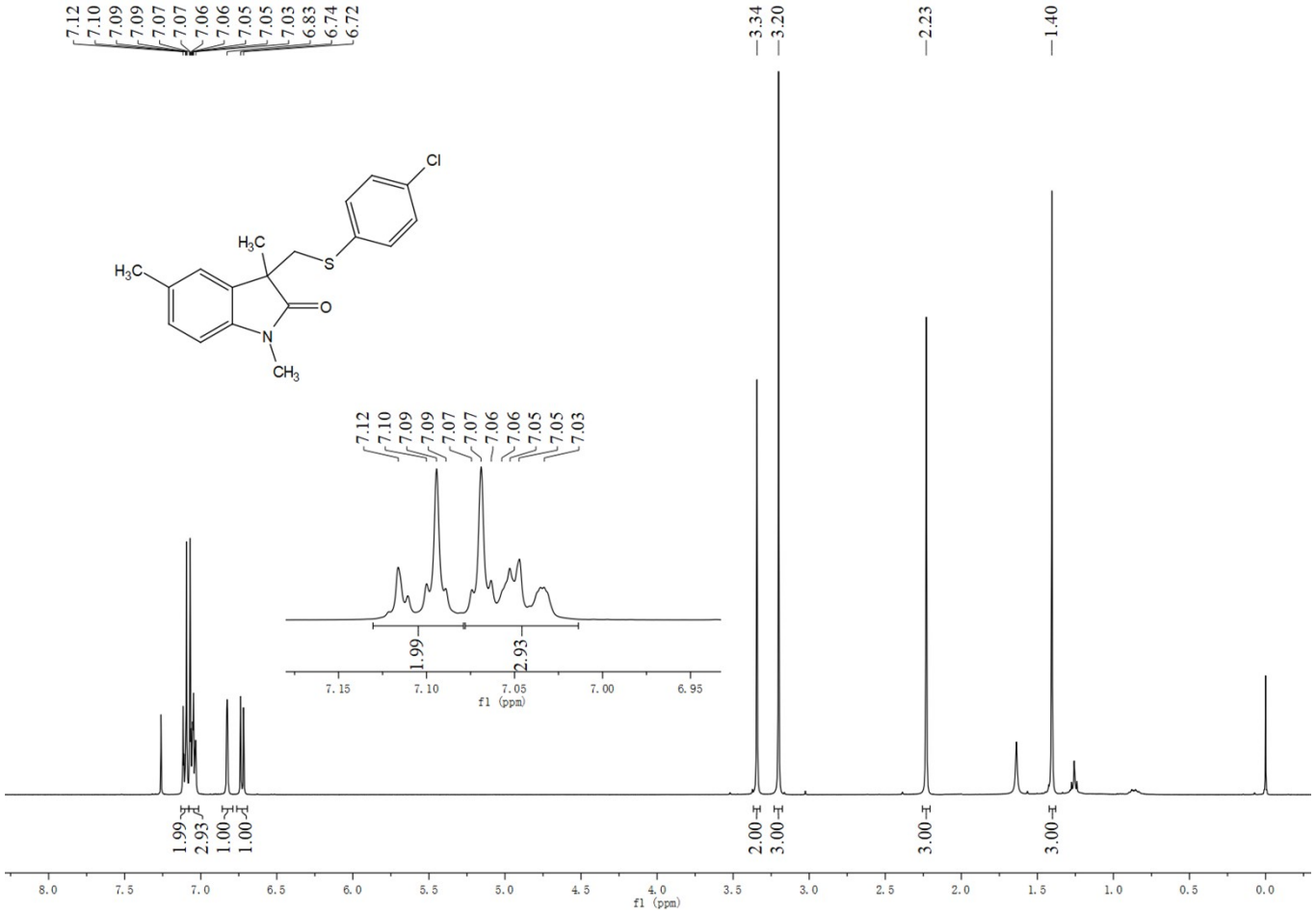


HRMS (ESI)

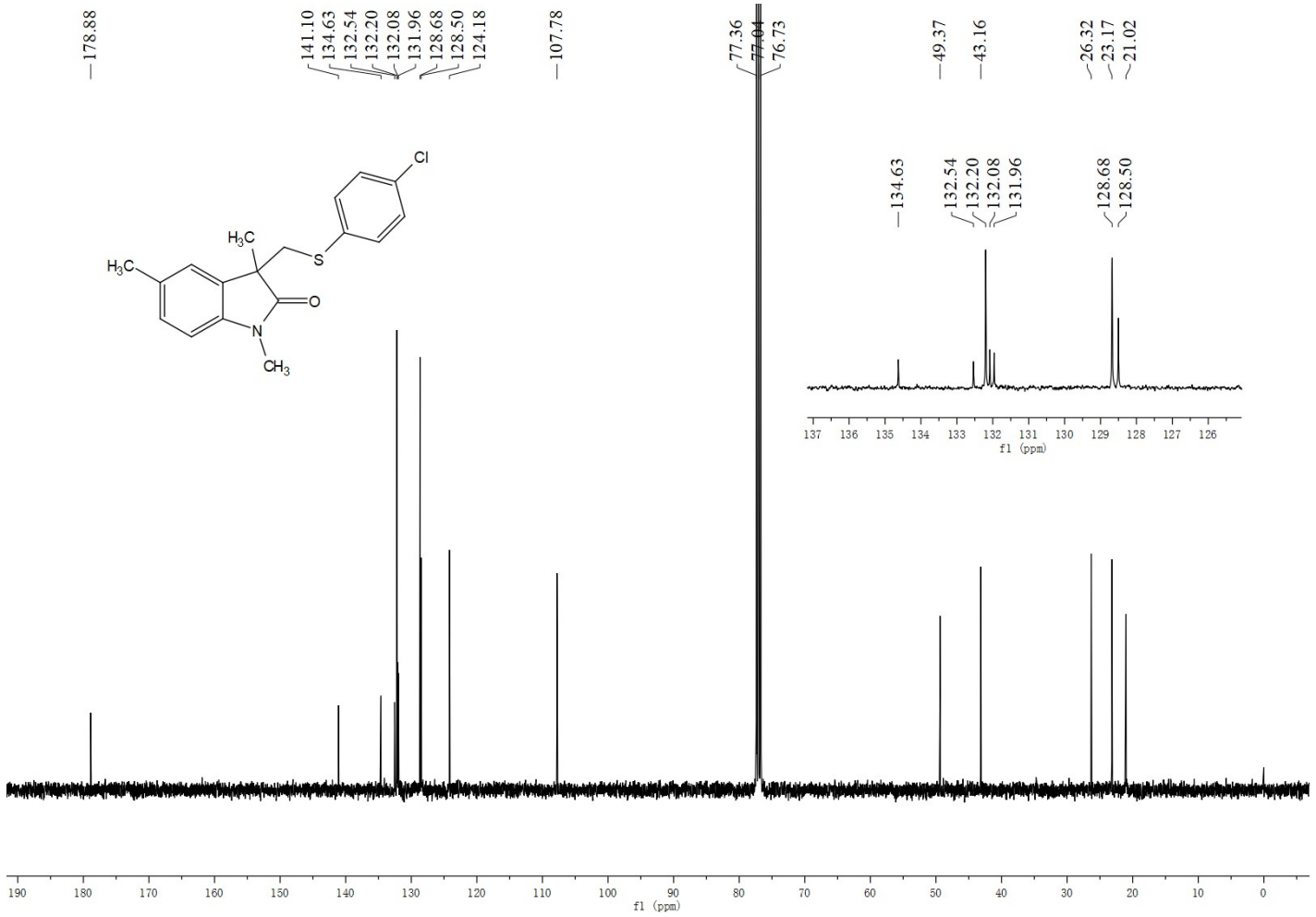

FF-225-1 323 (2.932)
1: TOF MS ES+
8.38e6
100
%
0
328.1376
350.1187
351.1217
352.1178
188.1067
160.1113
220.0786
327.1277
519.6628
597.0677
677.2497
678.2522
757.1974
829.1517
905.8969
981.7985
1071.7354
1193.7938
100
200
300
400
500
600
700
800
900
1000
1100
m/z

3-(((4-Chlorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3u)

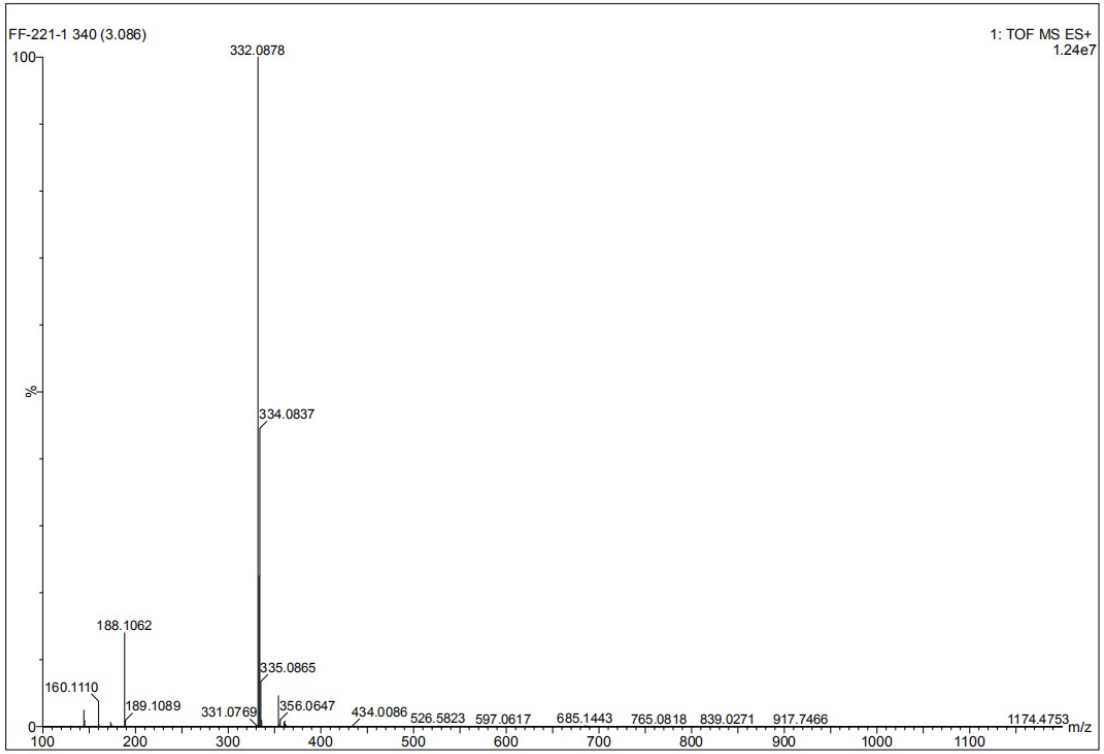
^{1}H NMR (400 MHz, $CDCl_3$)



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

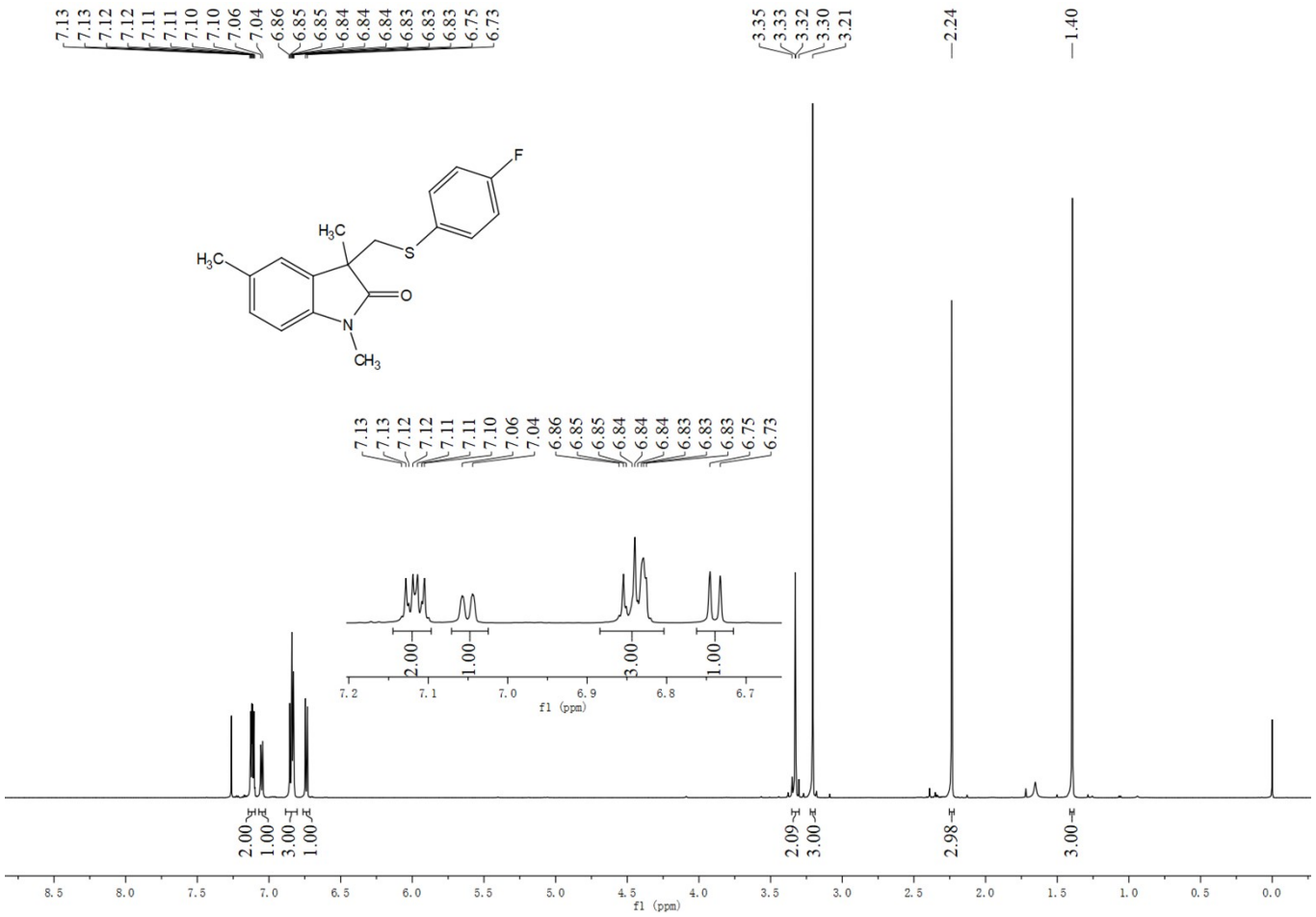


HRMS (ESI)

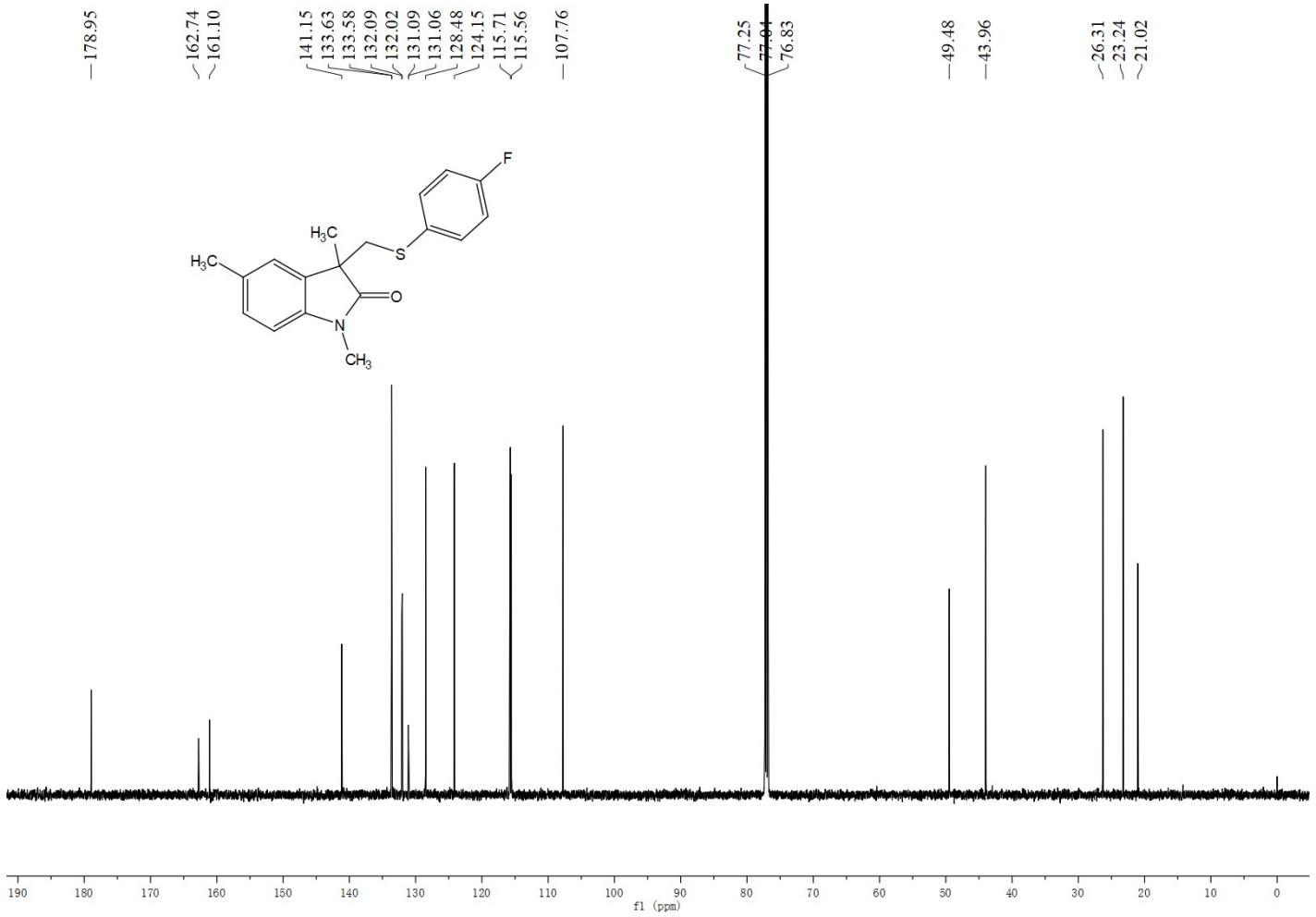

FF-221-1 340 (3.086)
1: TOF MS ES+
1.24e7
100
%
0
332.0878
334.0837
188.1062
335.0865
160.1110
189.1089
331.0769
356.0647
434.0086
526.5823
597.0617
685.1443
765.0818
839.0271
917.7466
1174.4753
m/z
100
200
300
400
500
600
700
800
900
1000
1100

3-(((4-Fluorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3v)

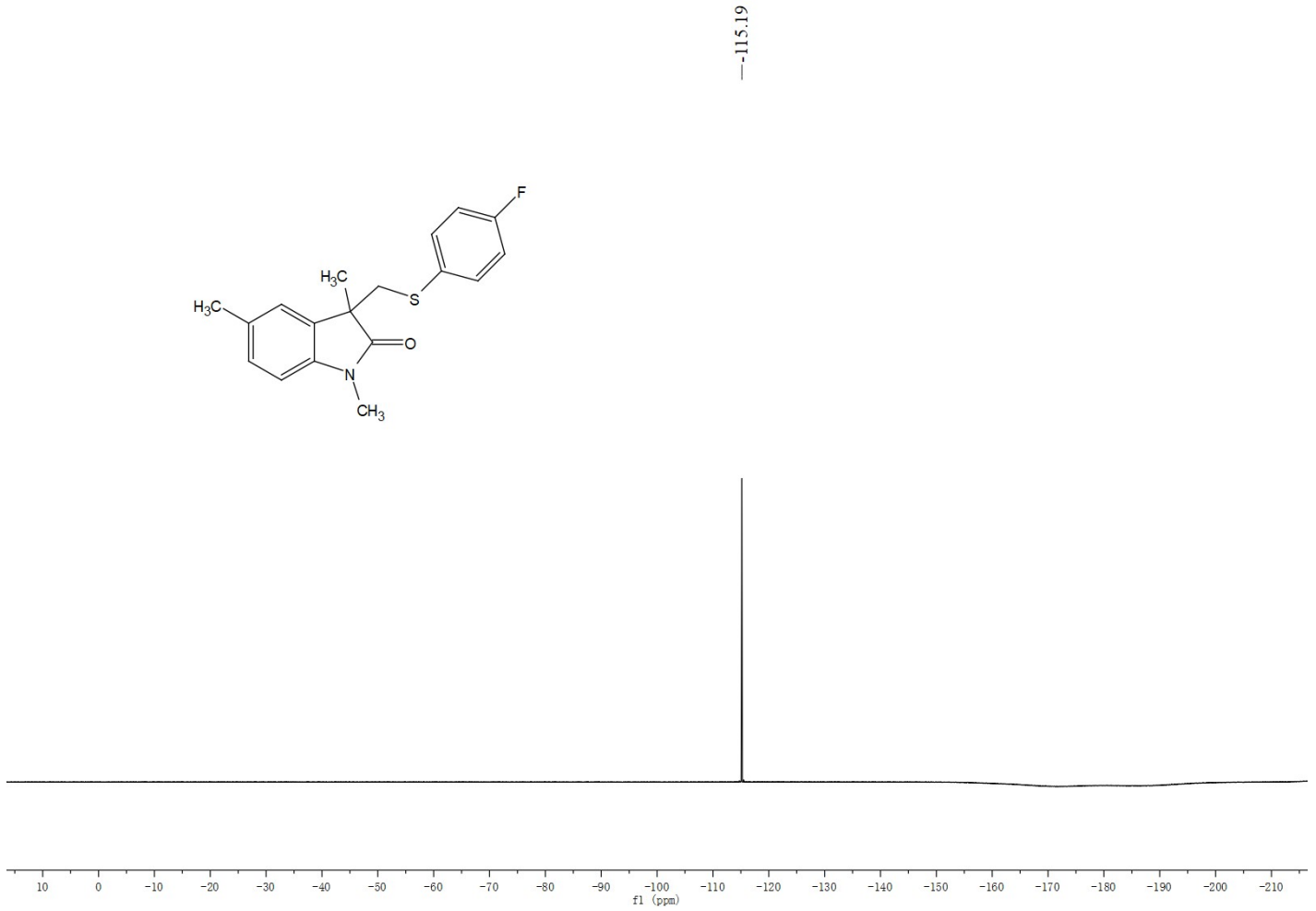
^{1}H NMR (600 MHz, $CDCl_3$)



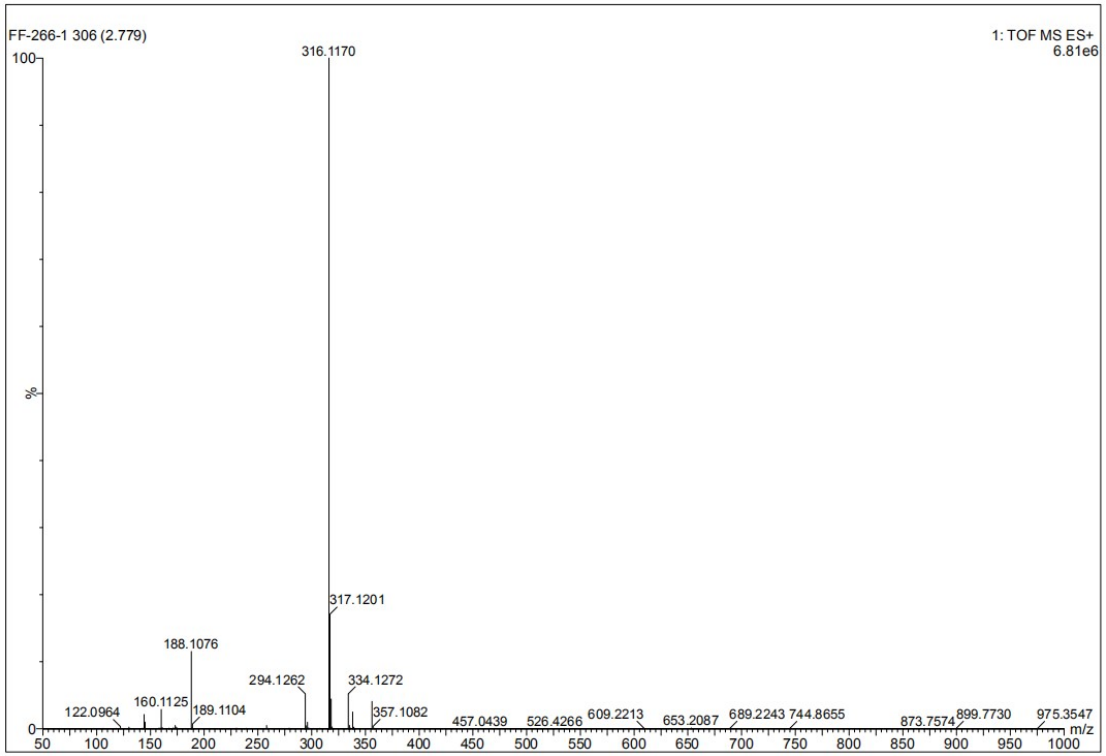
^{13}C NMR (150 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

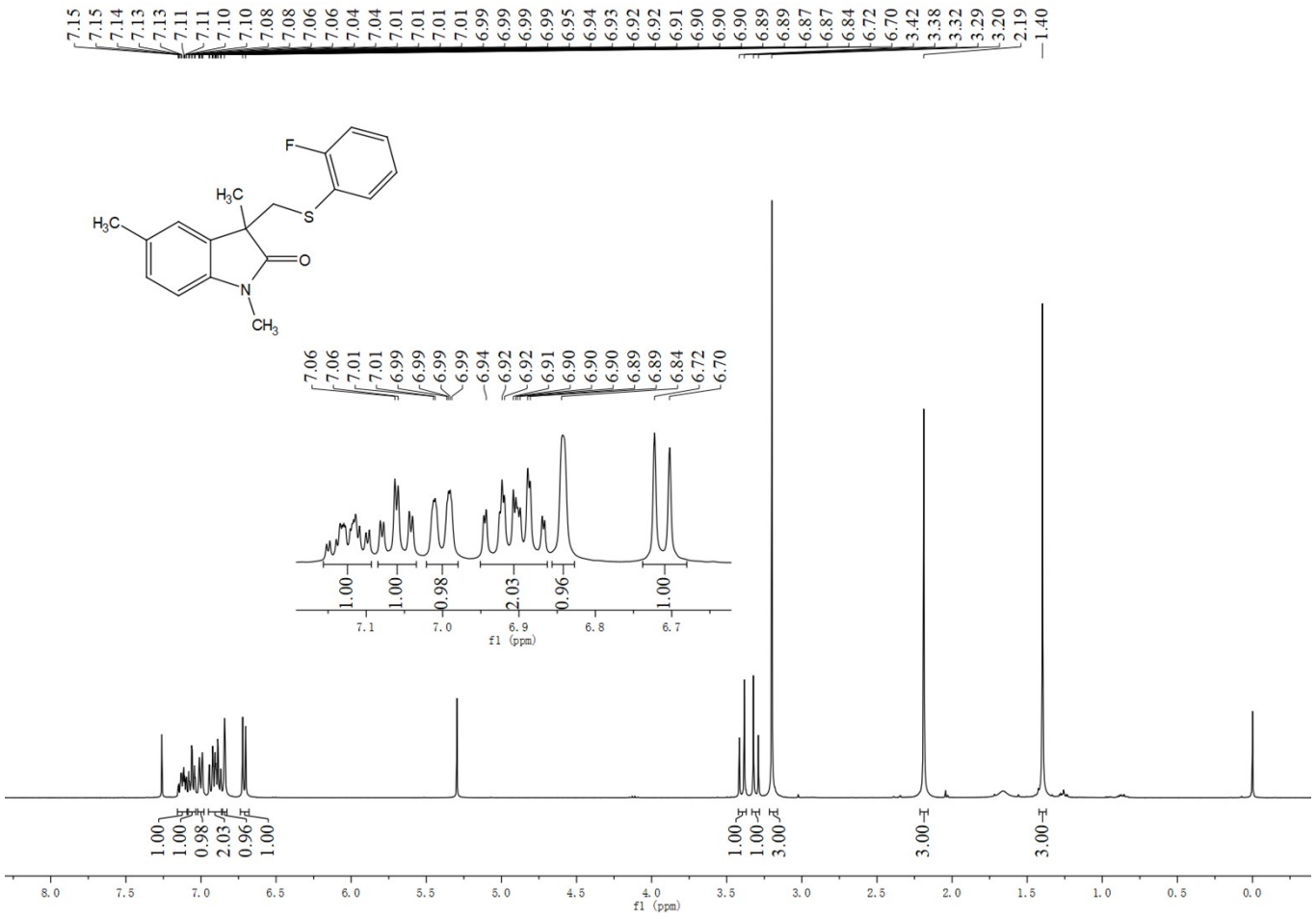


HRMS (ESI)

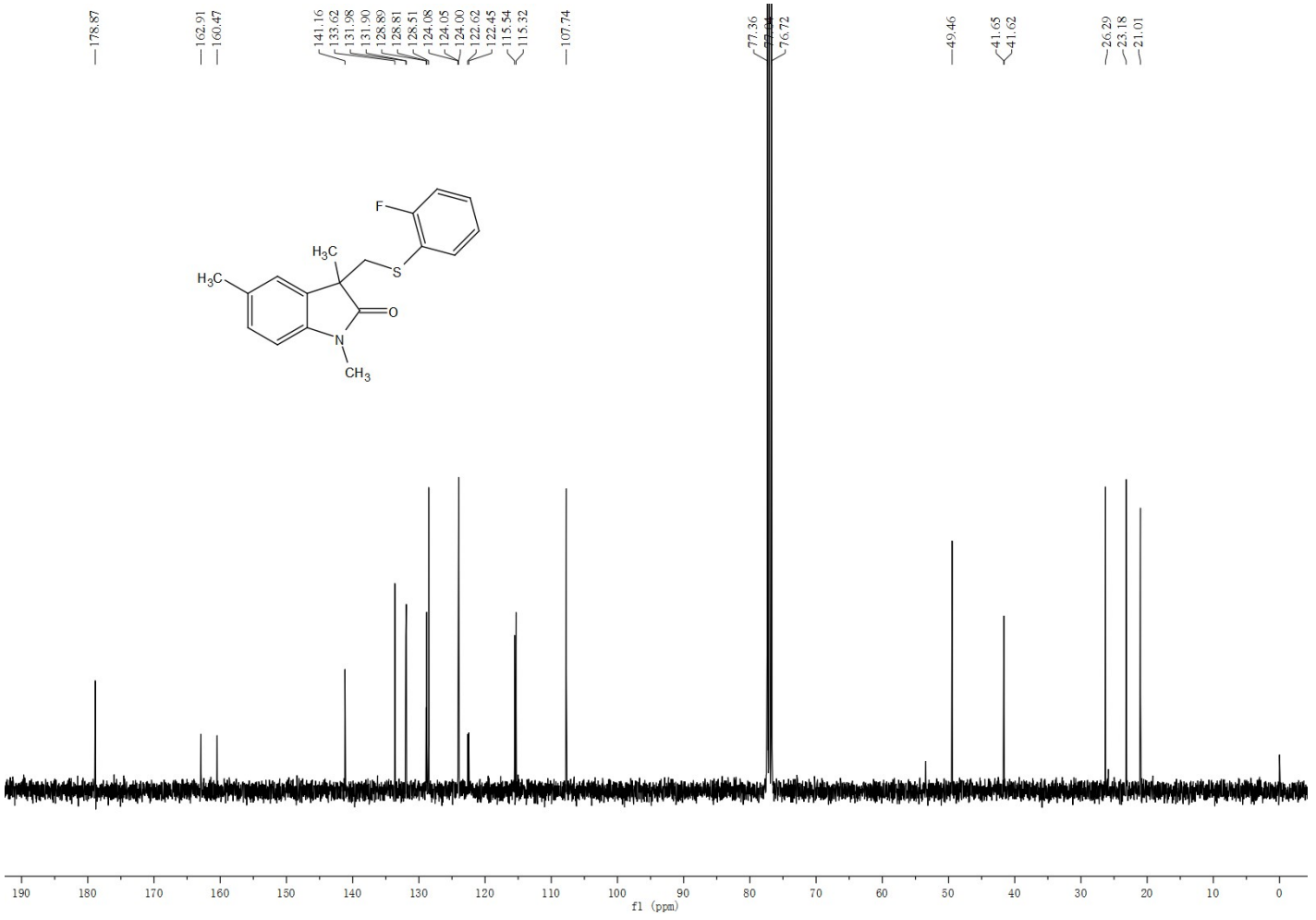

FF-266-1 306 (2.779)
1: TOF MS ES+
6.81e6
100
%
0
316.1170
317.1201
188.1076
294.1262
334.1272
160.1125
122.0964
189.1104
357.1082
457.0439
526.4266
609.2213
653.2087
689.2243
744.8655
873.7574
899.7730
975.3547
m/z
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000

3-(((2-Fluorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3w)

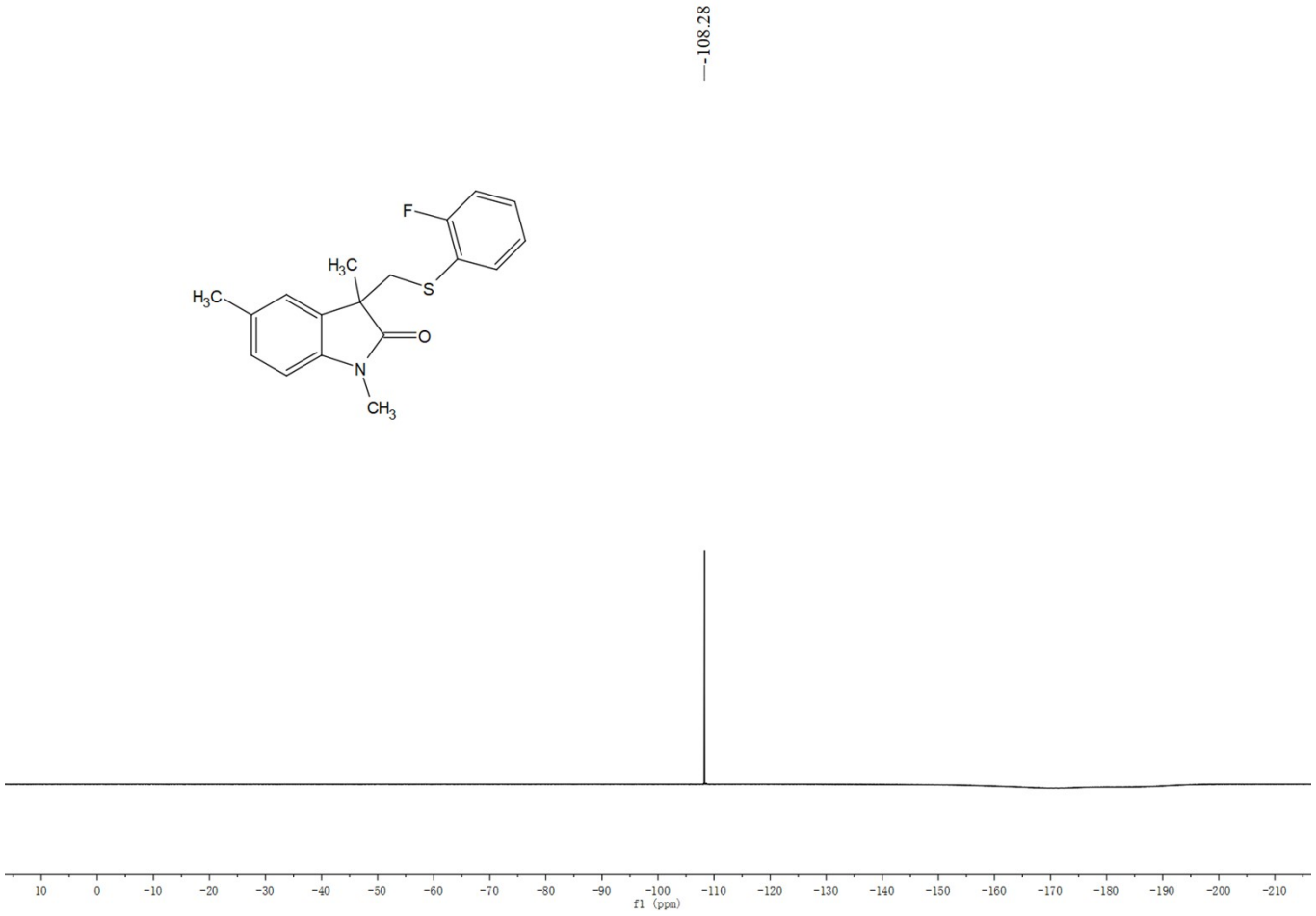
^{1}H NMR (400 MHz, $CDCl_3$)



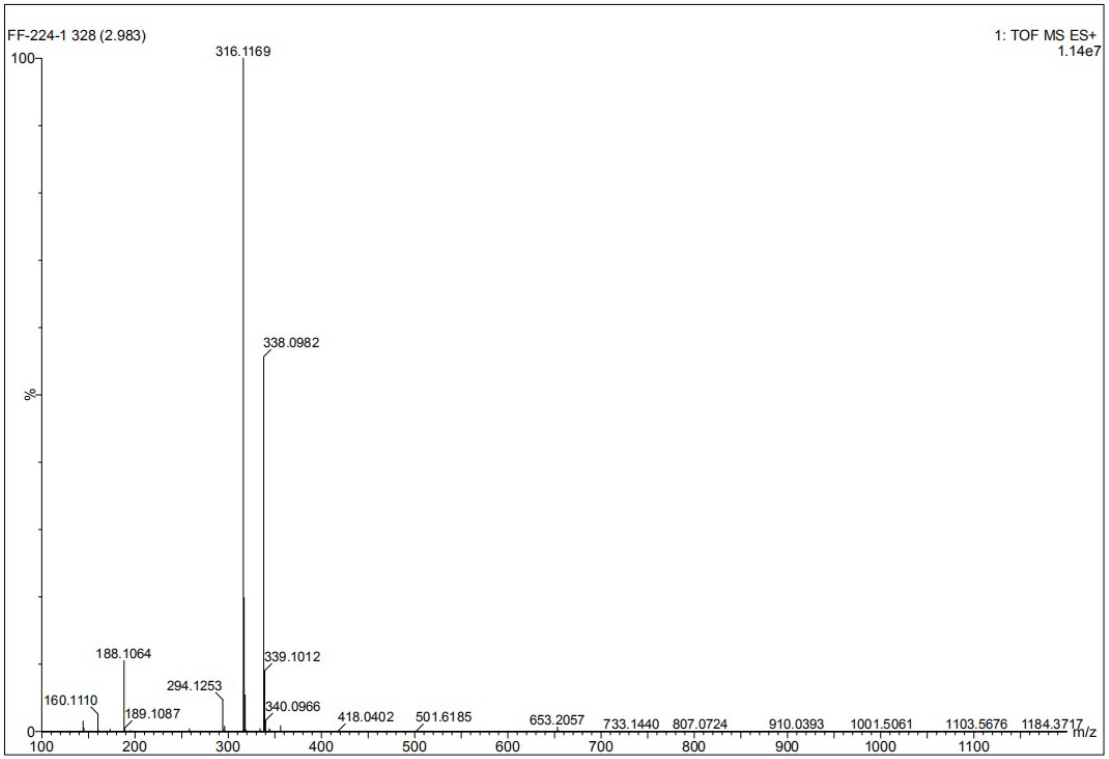
^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

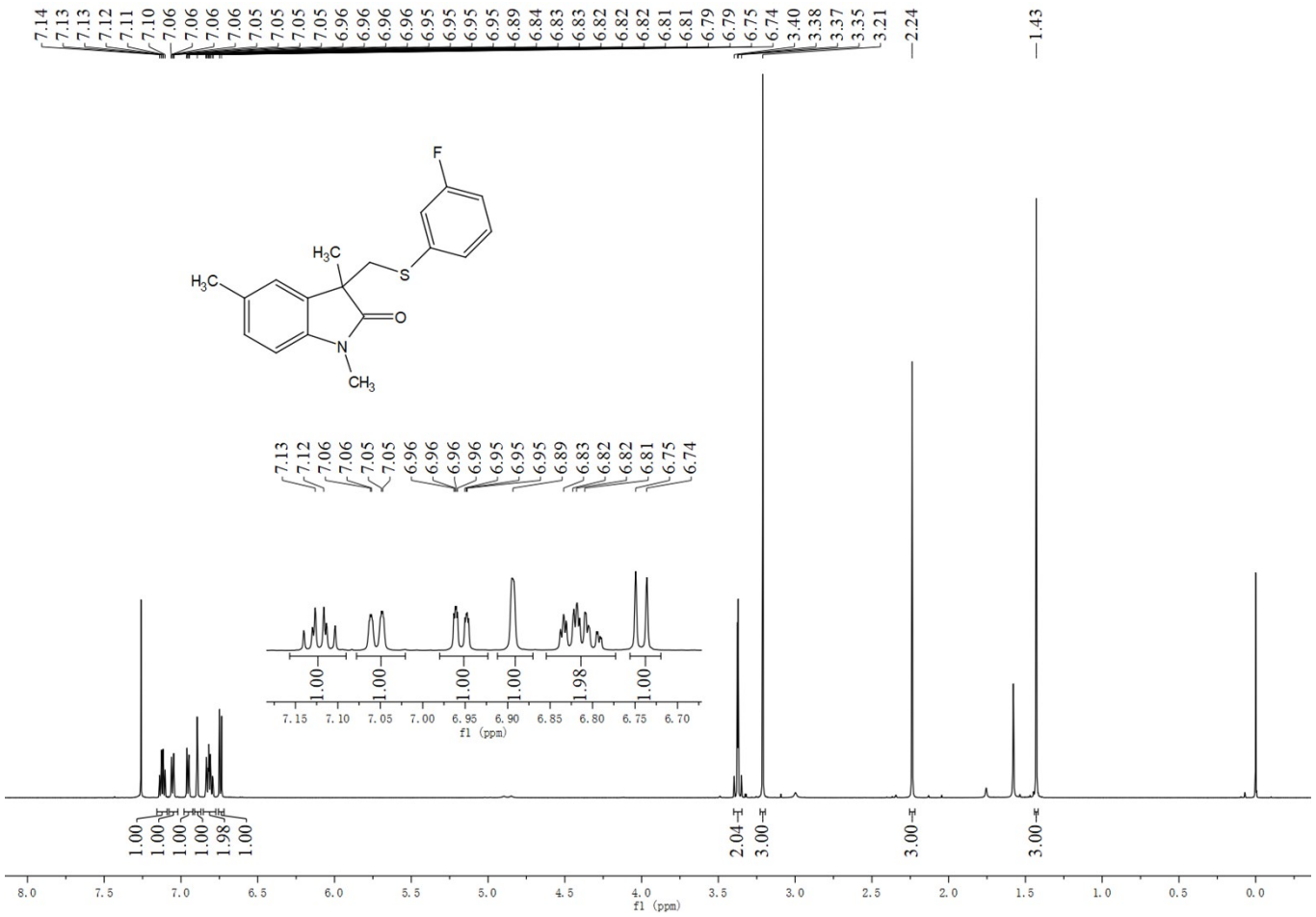


HRMS (ESI)

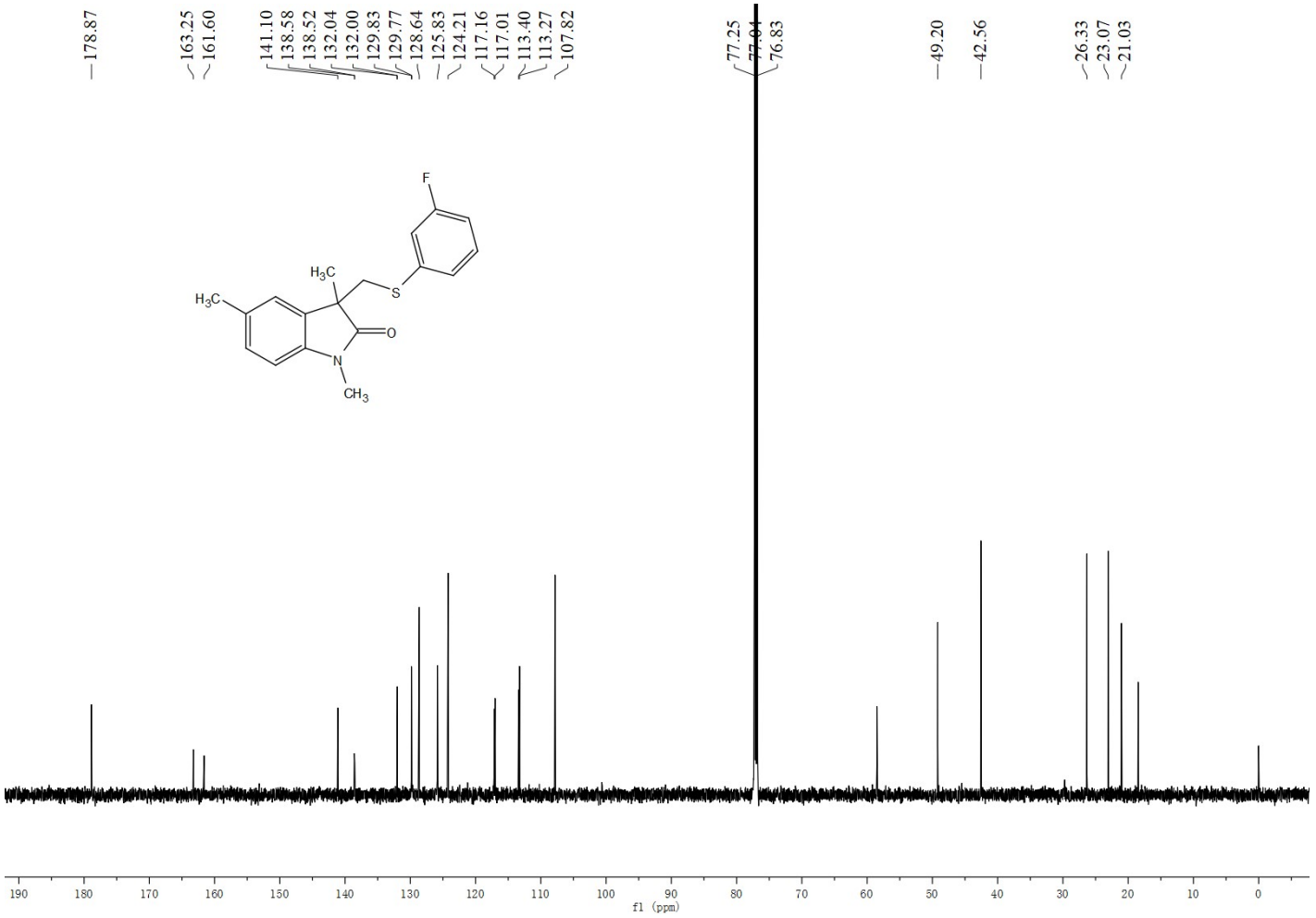

FF-224-1 328 (2.983)
1: TOF MS ES+
1.14e7
316.1169
338.0982
339.1012
340.0966
188.1064
294.1253
160.1110
189.1087
418.0402
501.6185
653.2057
733.1440
807.0724
910.0393
1001.5061
1103.5676
1184.3717
%
m/z

3-(((3-Fluorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3x)

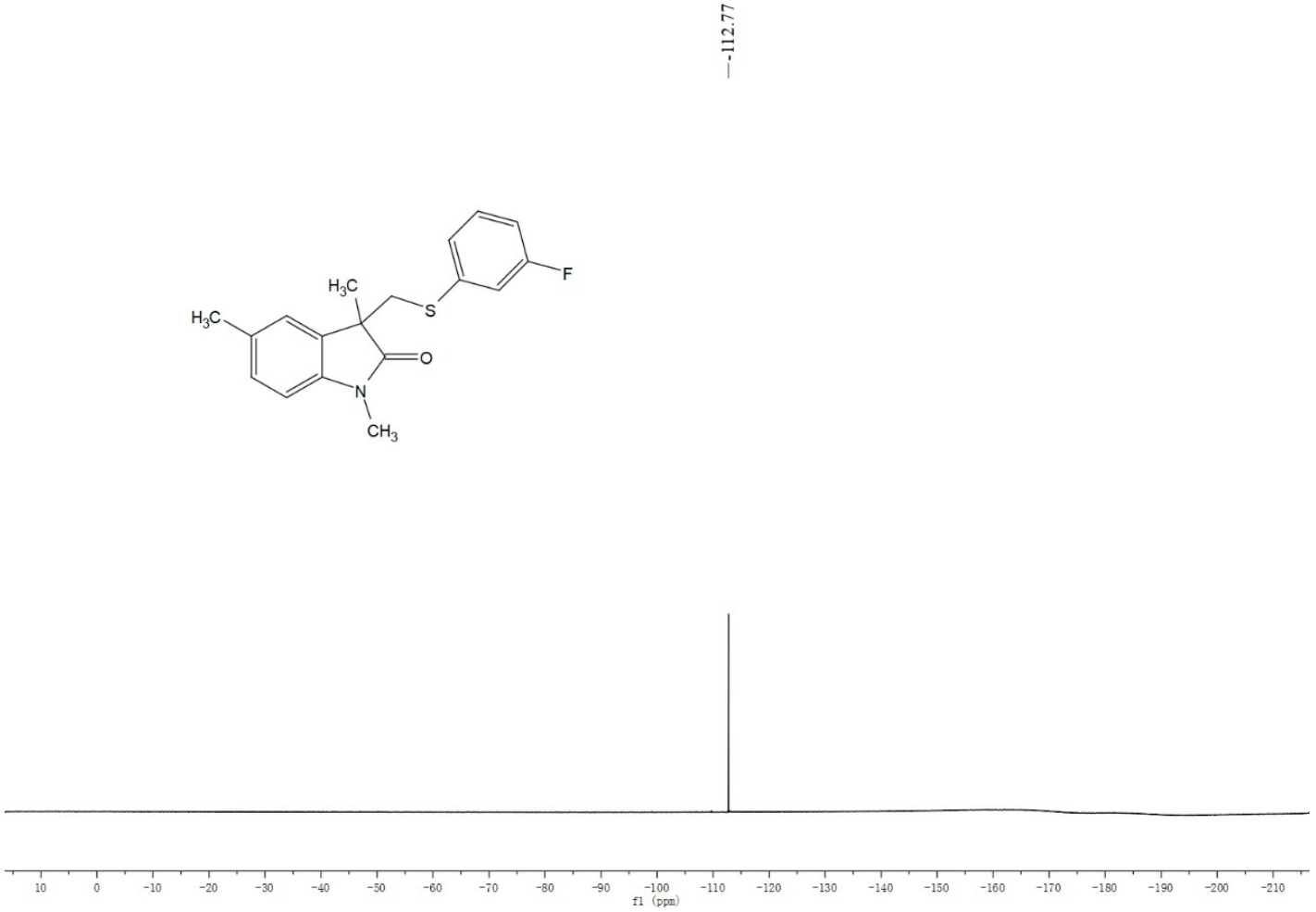
^{1}H NMR (600 MHz, $CDCl_3$)



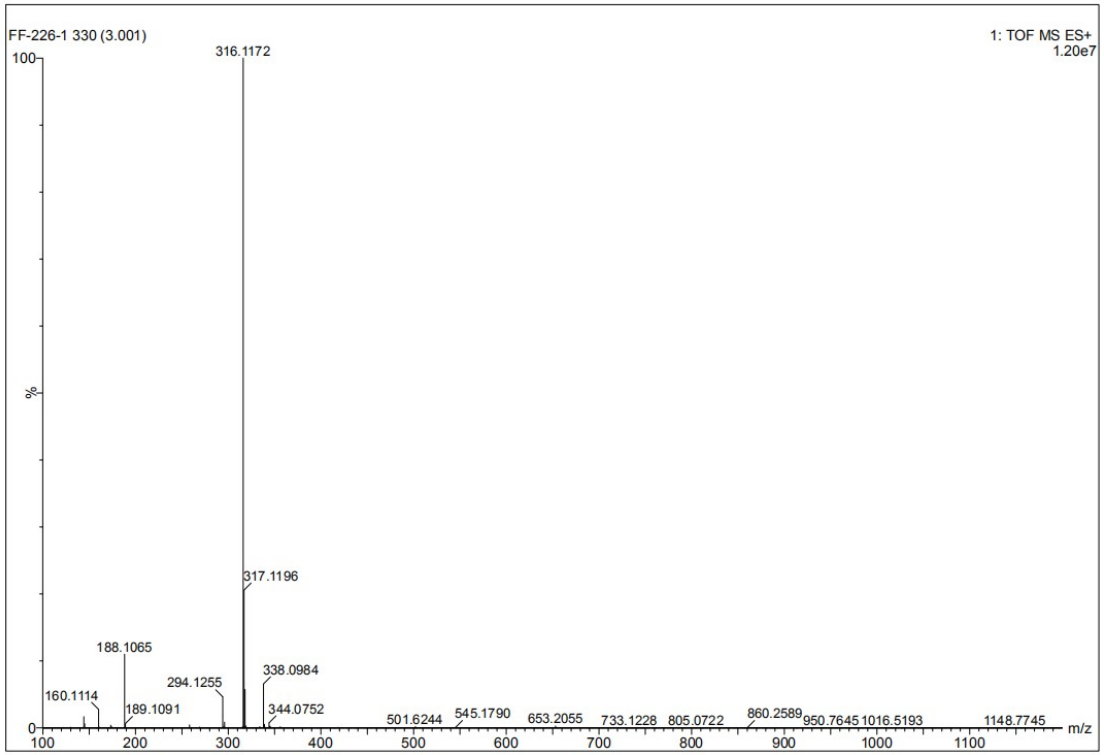
^{13}C NMR (150 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

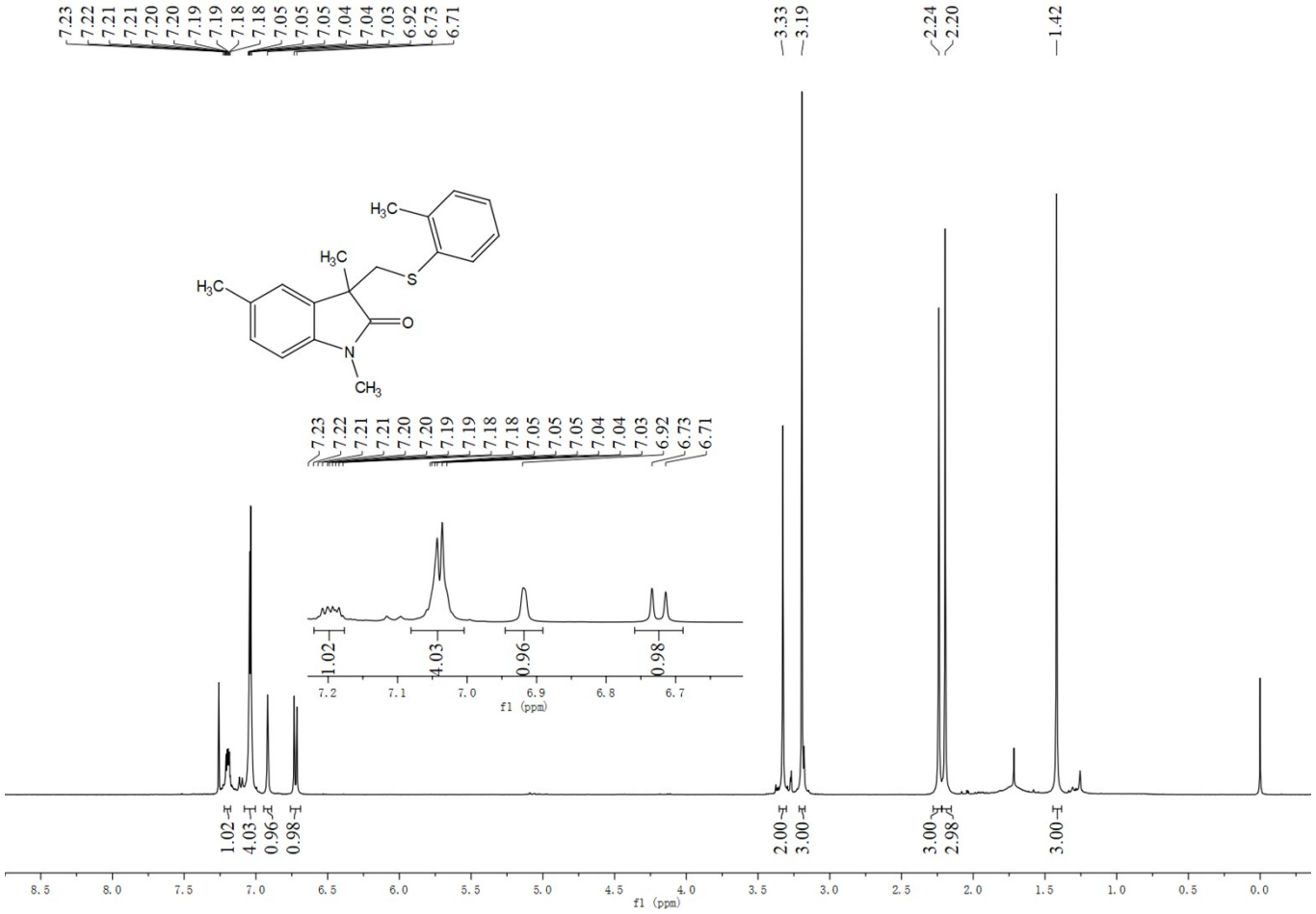


HRMS (ESI)

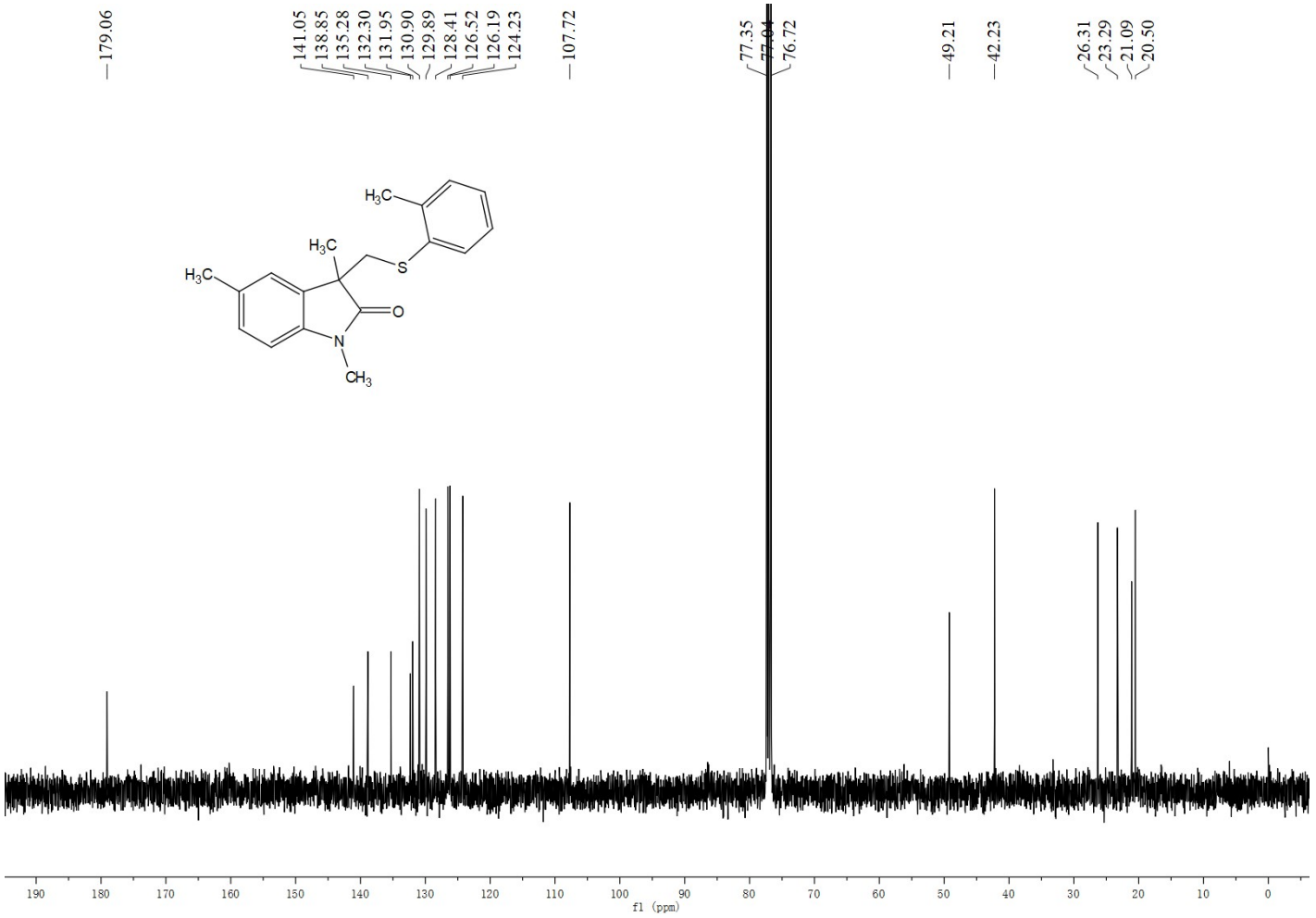

FF-226-1 330 (3.001)
1: TOF MS ES+
1.20e7
100
%
0
316.1172
317.1196
188.1065
338.0984
294.1255
160.1114
189.1091
344.0752
501.6244
545.1790
653.2055
733.1228
805.0722
860.2589
950.7645
1016.5193
1148.7745
m/z
100
200
300
400
500
600
700
800
900
1000
1100

1,3,5-Trimethyl-3-((o-tolylthio)methyl)indolin-2-one (3y)

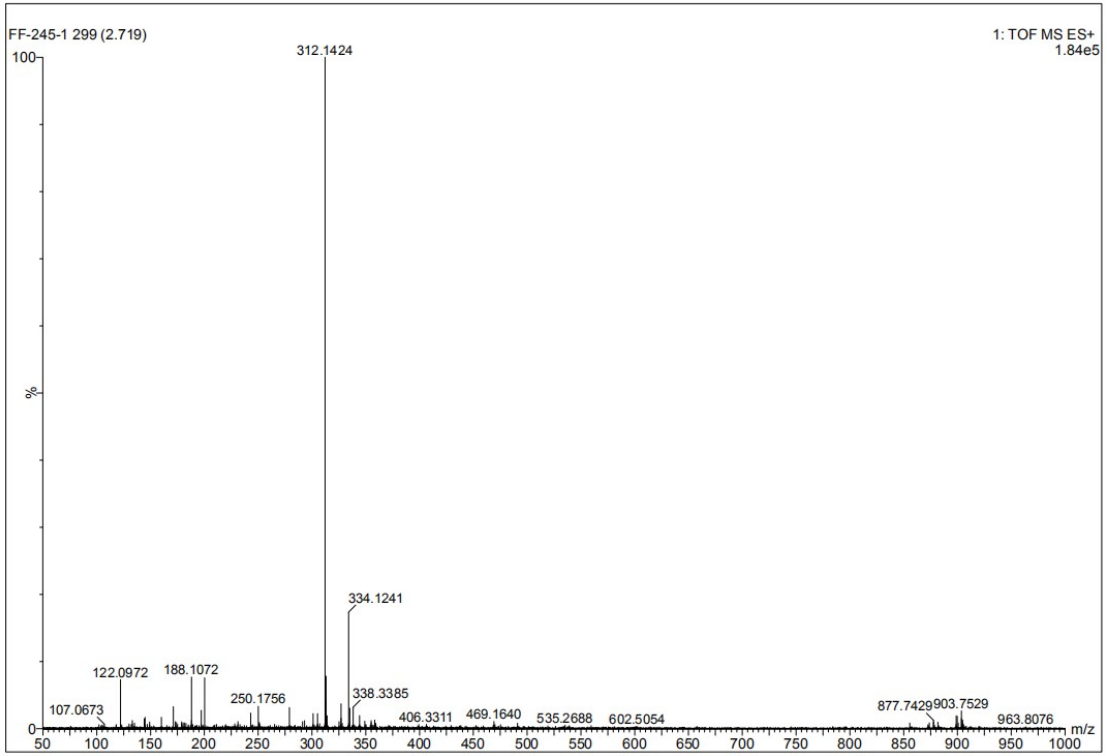
^{1}H NMR (400 MHz, $CDCl_3$)



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

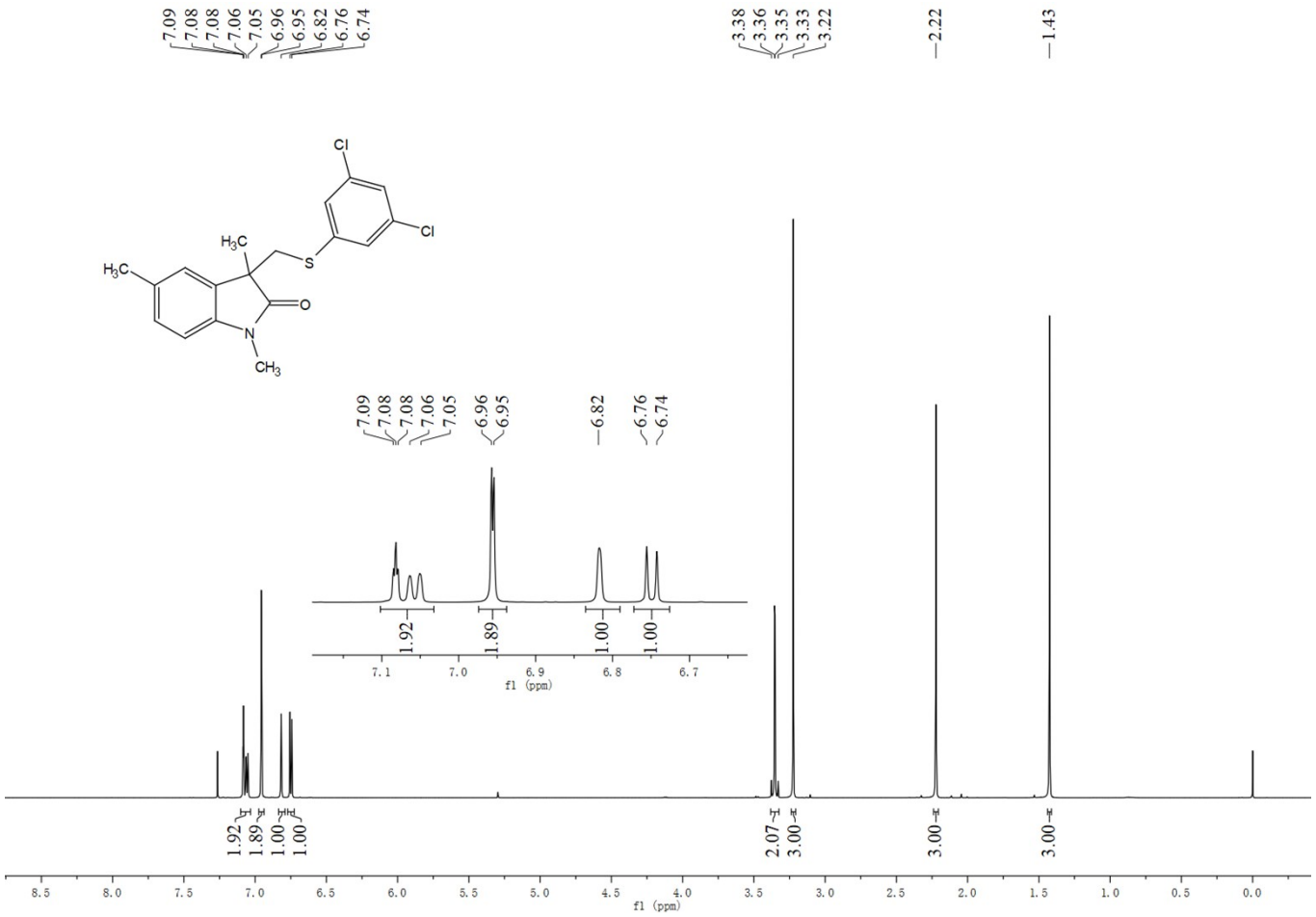


HRMS (ESI)

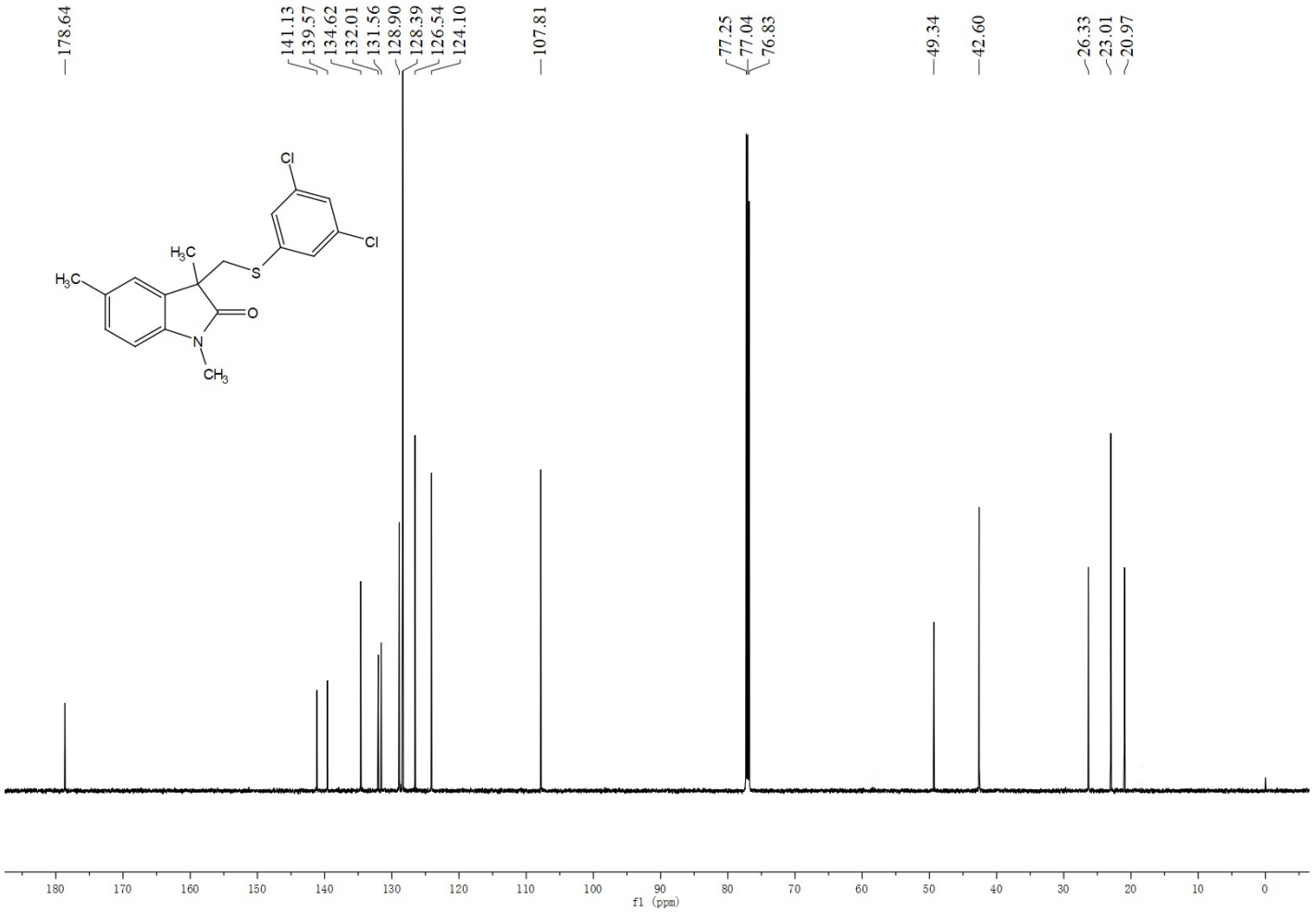

FF-245-1 299 (2.719)
1: TOF MS ES+
1.84e5
100
%
0
312.1424
334.1241
122.0972
188.1072
250.1756
338.3385
107.0673
406.3311
469.1640
535.2688
602.5054
877.7429
903.7529
963.8076
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

3-(((3,5-Dichlorophenyl)thio)methyl)-1,3,5-trimethylindolin-2-one (3z)

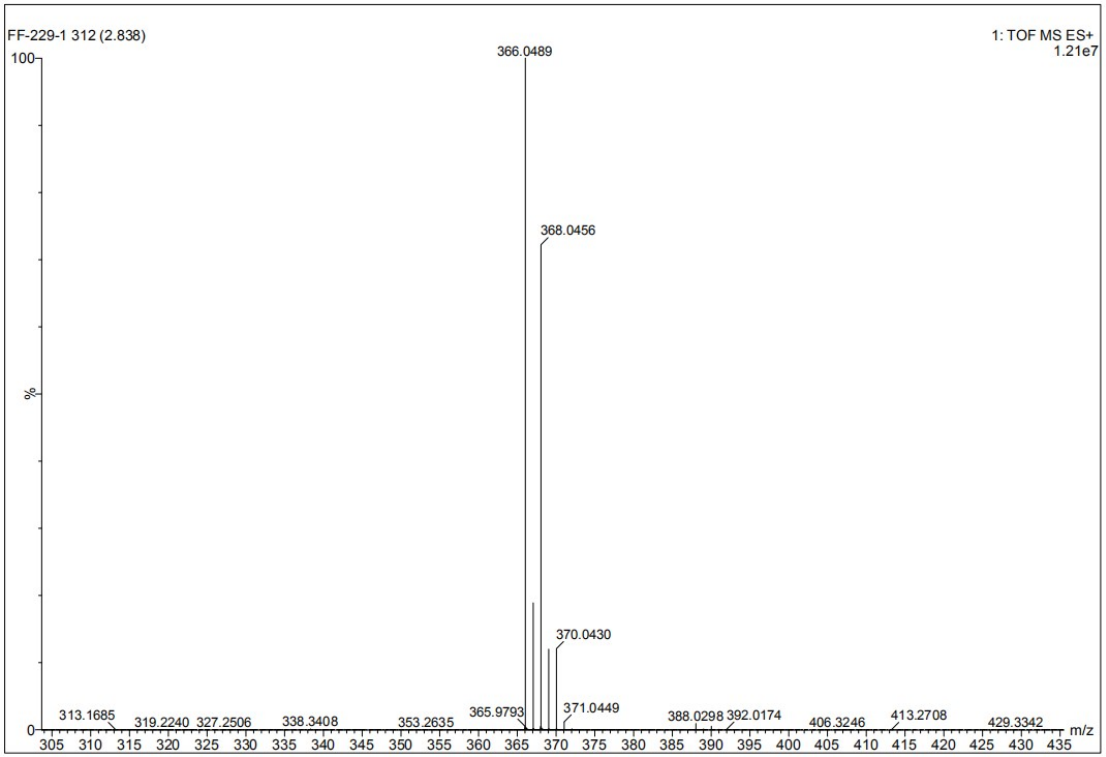
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

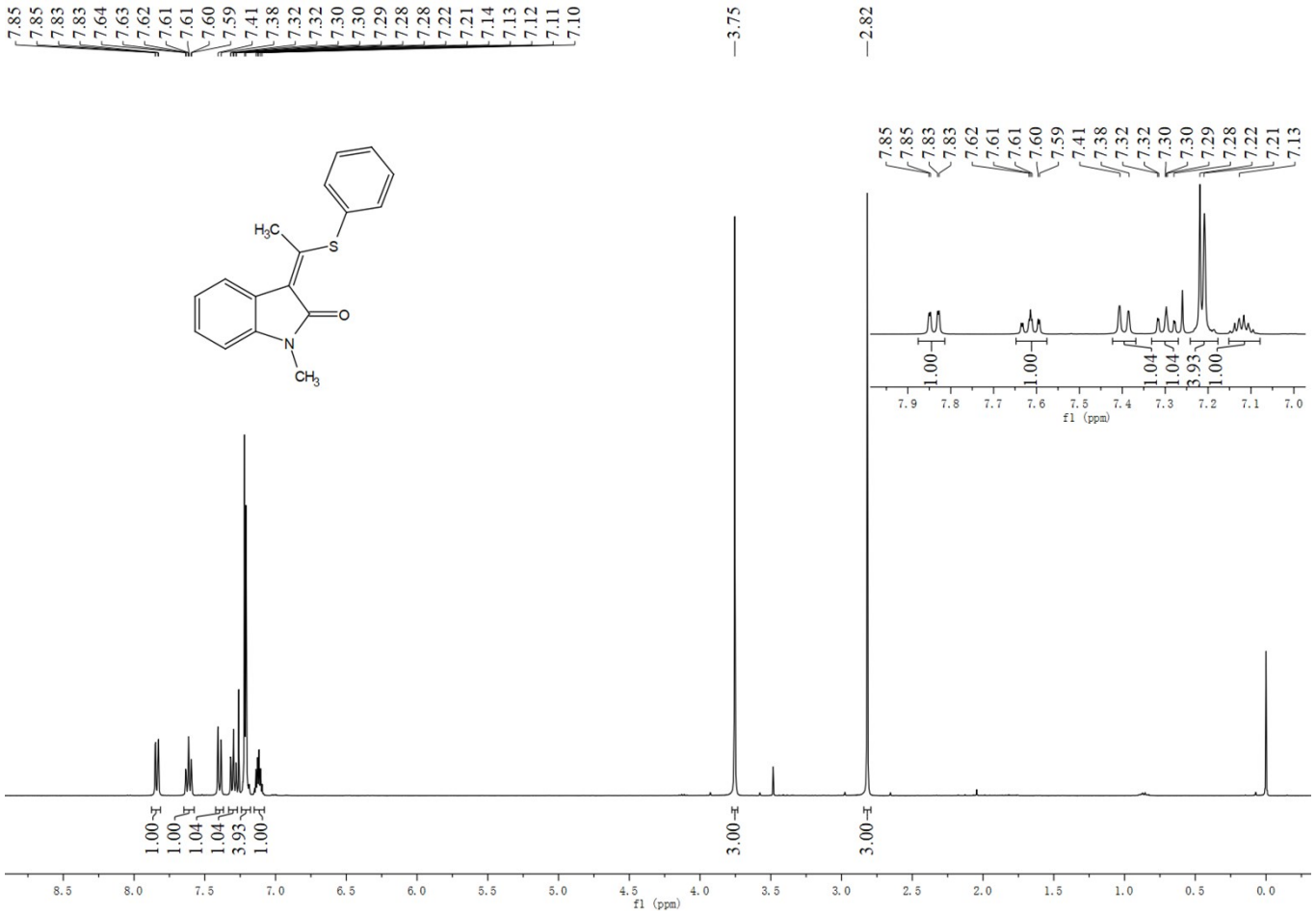


HRMS (ESI)

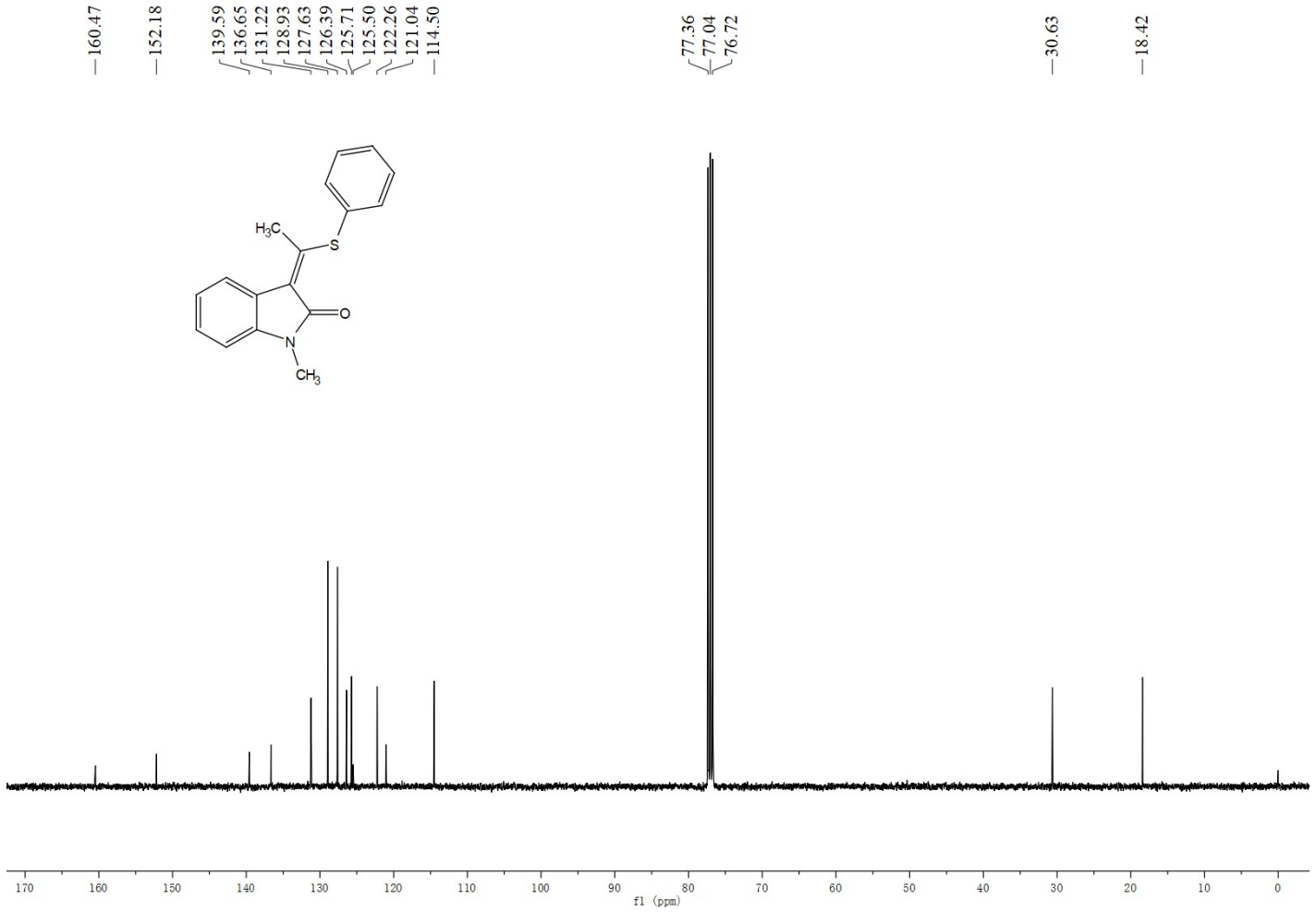

FF-229-1 312 (2.838)
1: TOF MS ES+
1.21e7
100
%
0
366.0489
368.0456
370.0430
371.0449
313.1685
319.2240
327.2506
338.3408
353.2635
365.9793
388.0298
392.0174
406.3246
413.2708
429.3342
m/z
305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435

(*Z*)-1-Methyl-3-(1-(phenylthio)ethylidene)indolin-2-one (3aa)

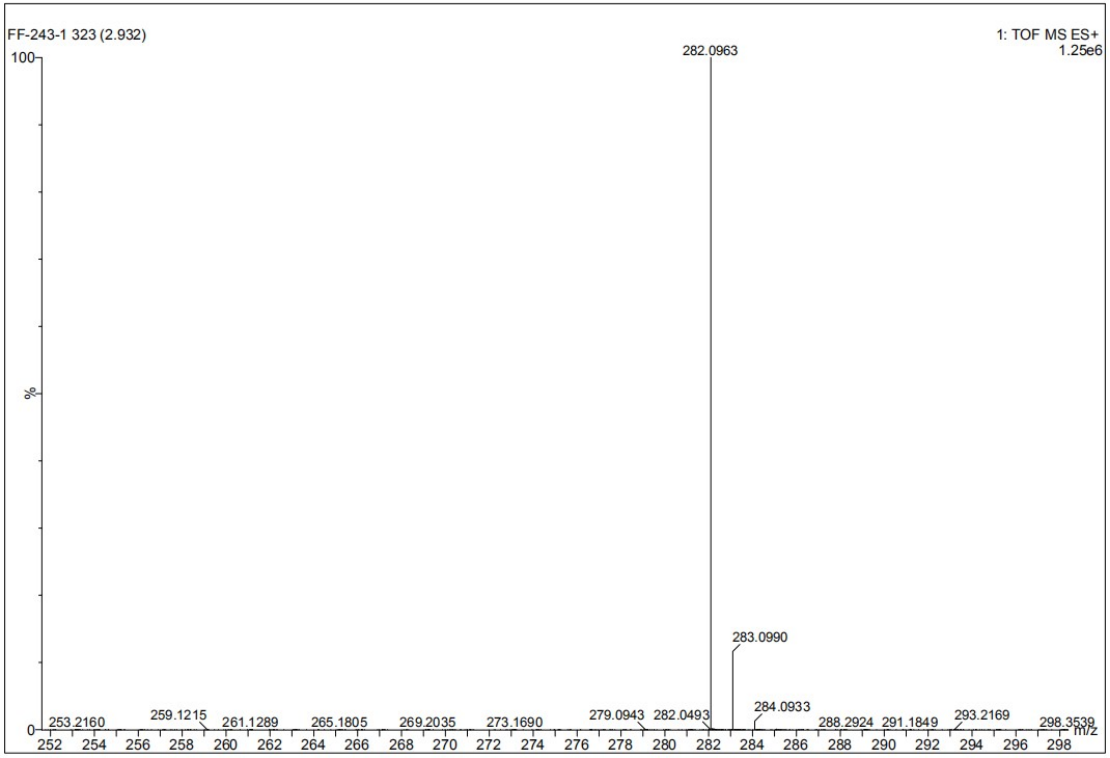
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, CDCl^{3})

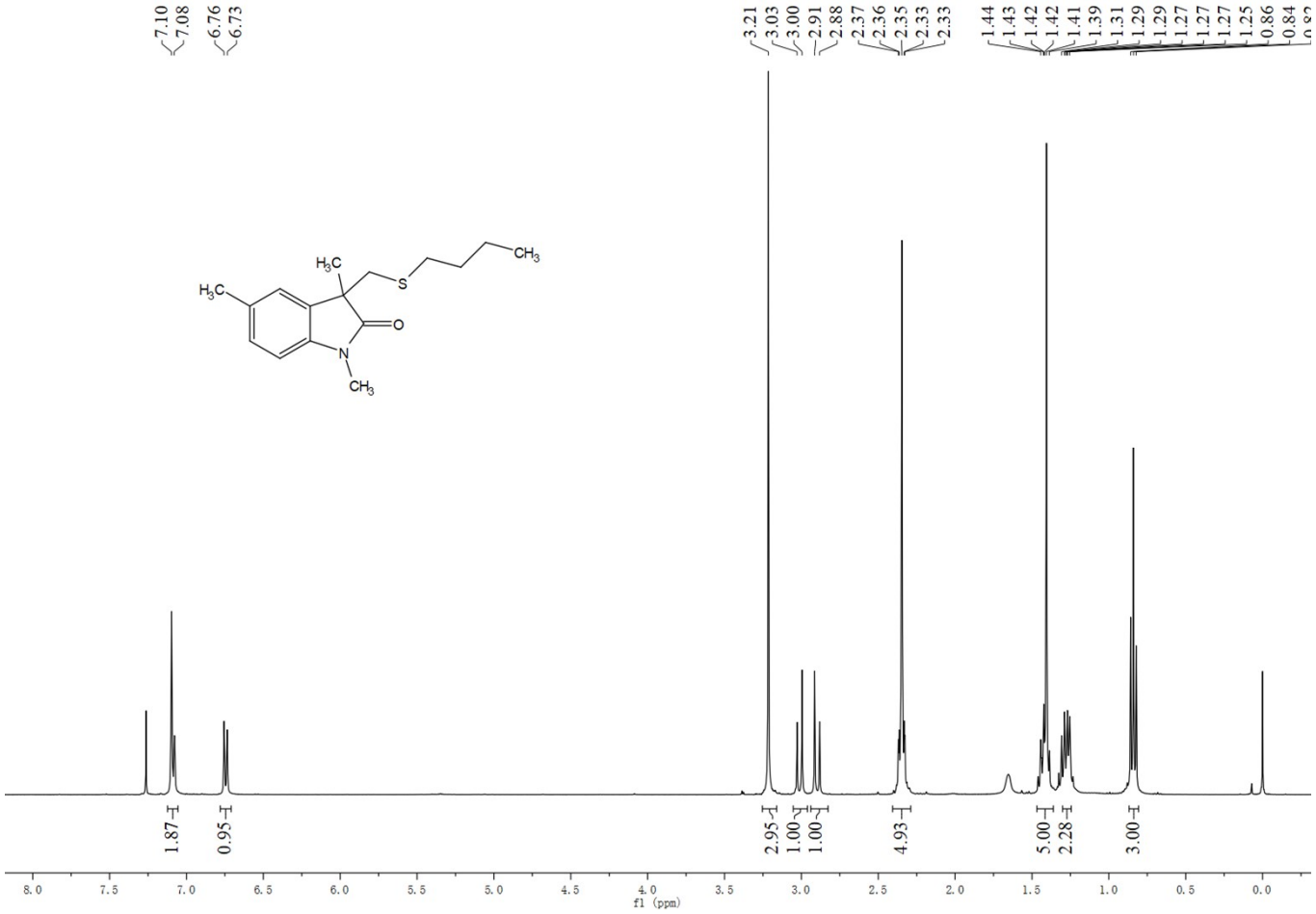


HRMS (ESI)

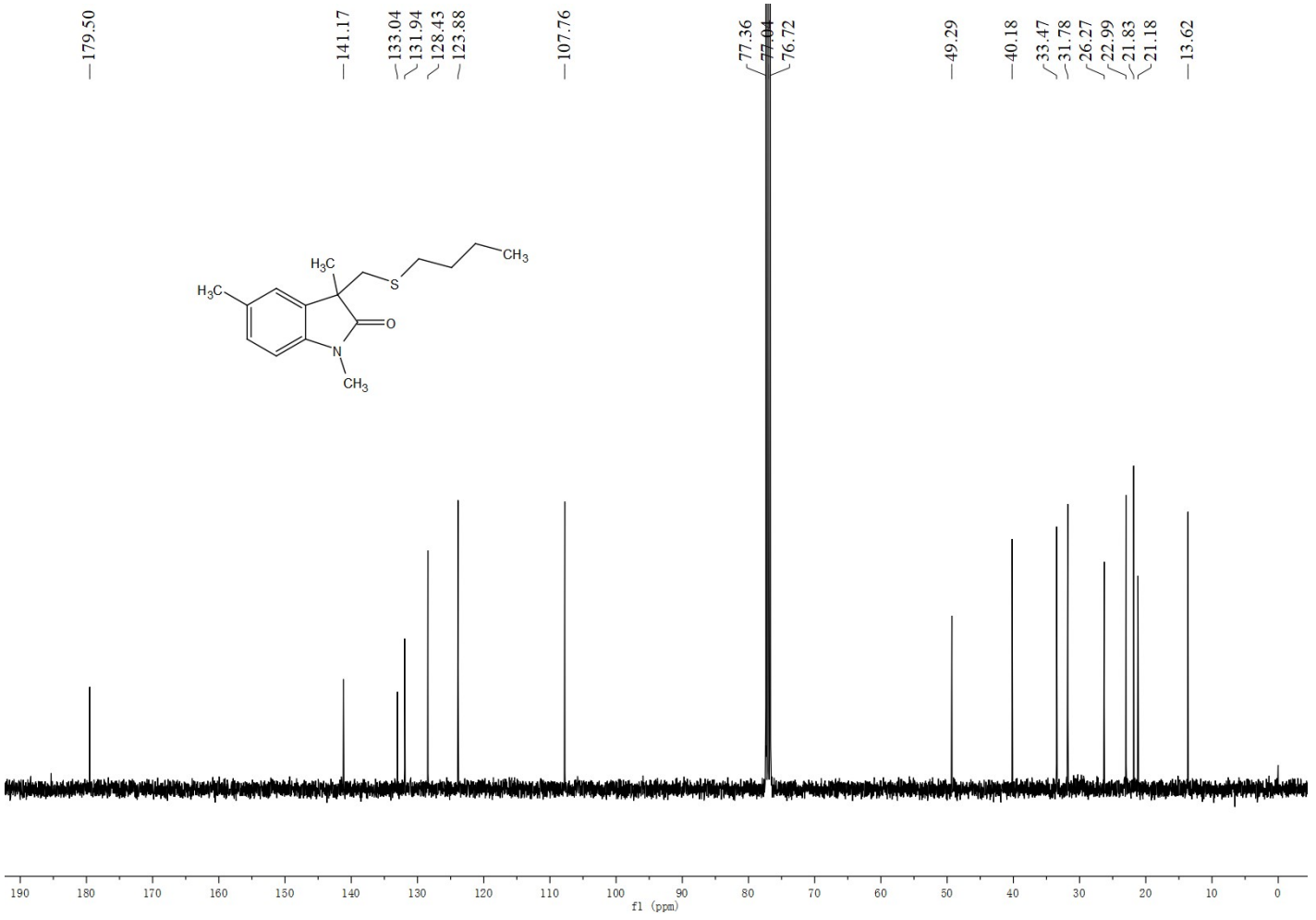

FF-243-1 323 (2.932)
1: TOF MS ES+
1.25e6
100
%
0
282.0963
283.0990
284.0933
253.2160
259.1215
261.1289
265.1805
269.2035
273.1690
279.0943
282.0493
288.2924
291.1849
293.2169
298.3539
m/z
252 254 256 258 260 262 264 266 268 270 272 274 276 278 280 282 284 286 288 290 292 294 296 298

3-((Butylthio)methyl)-1,3,5-trimethylindolin-2-one (3ab)

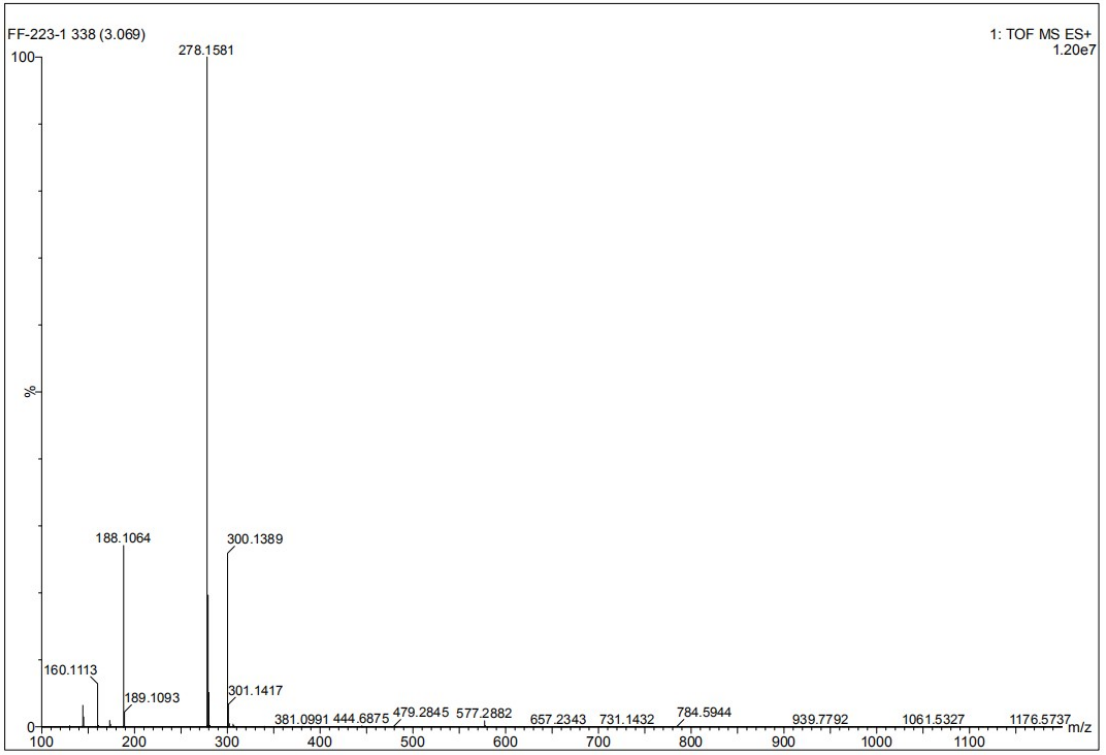
^{1}H NMR (400 MHz, $CDCl_3$)



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

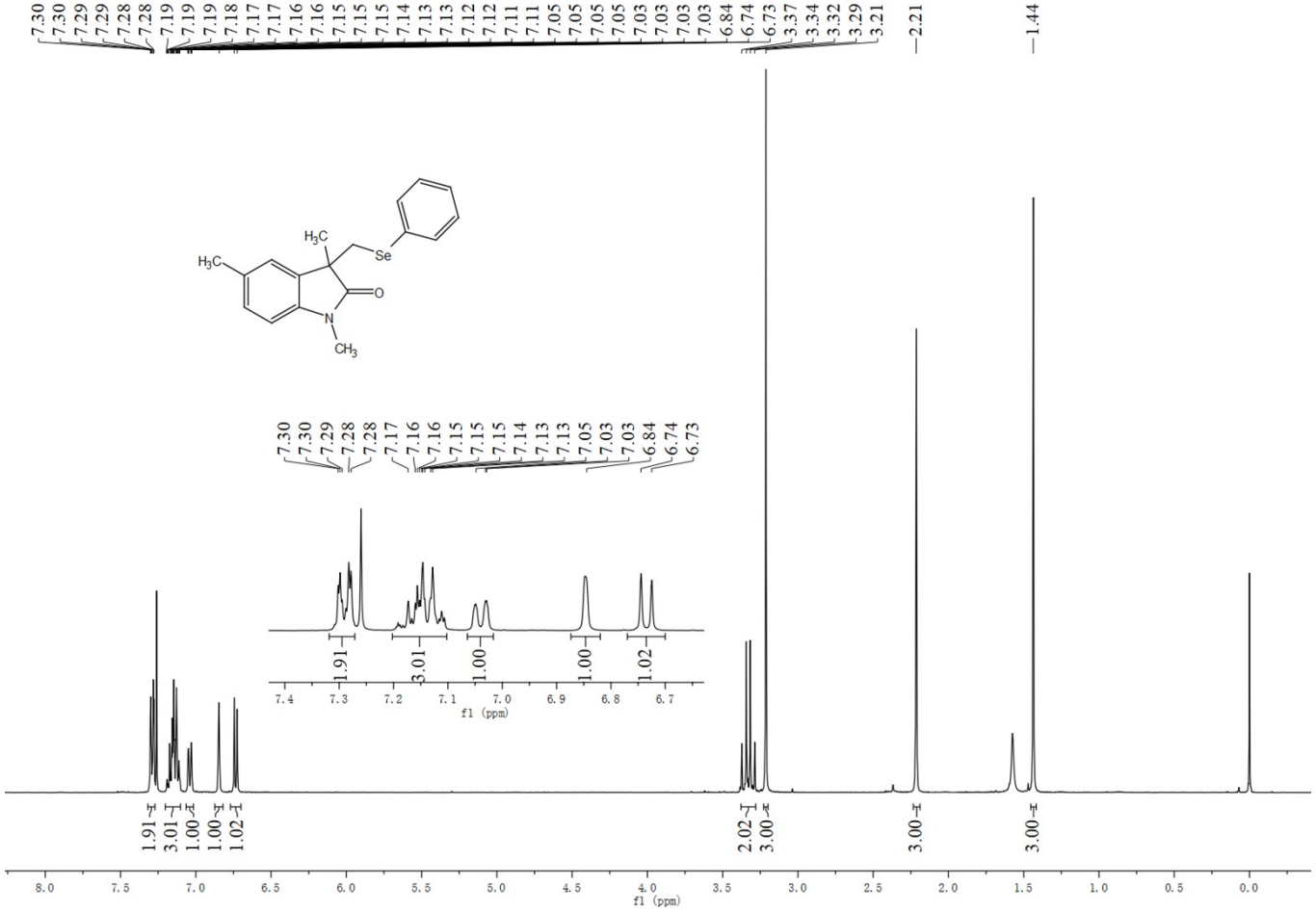


HRMS (ESI)

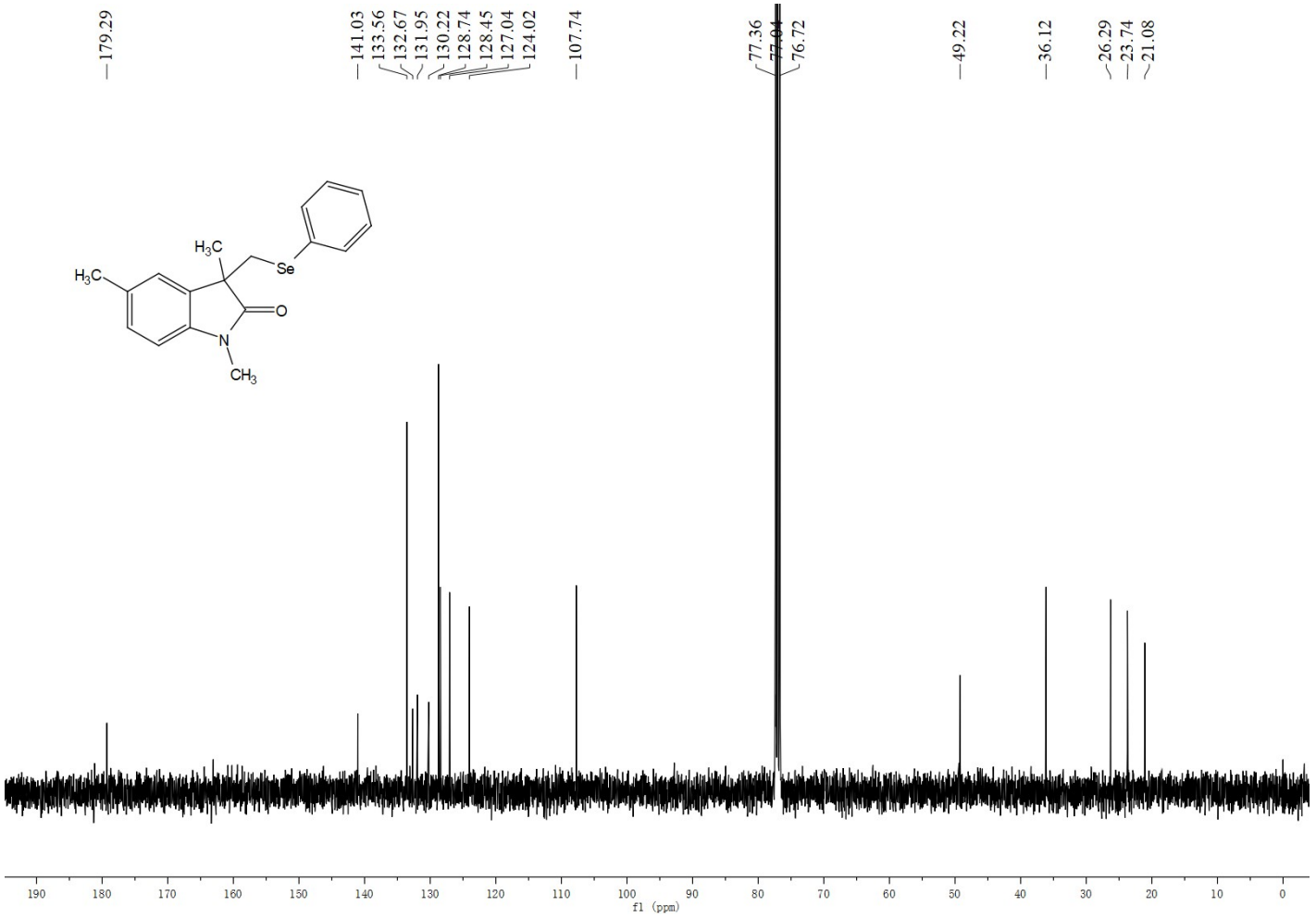

FF-223-1 338 (3.069)
1: TOF MS ES+
1.20e7
278.1581
188.1064
300.1389
160.1113
189.1093
301.1417
381.0991 444.6875 479.2845 577.2882 657.2343 731.1432 784.5944 939.7792 1061.5327 1176.5737
%
m/z

1,3,5-Trimethyl-3-((phenylselanyl)methyl)indolin-2-one (3ac)

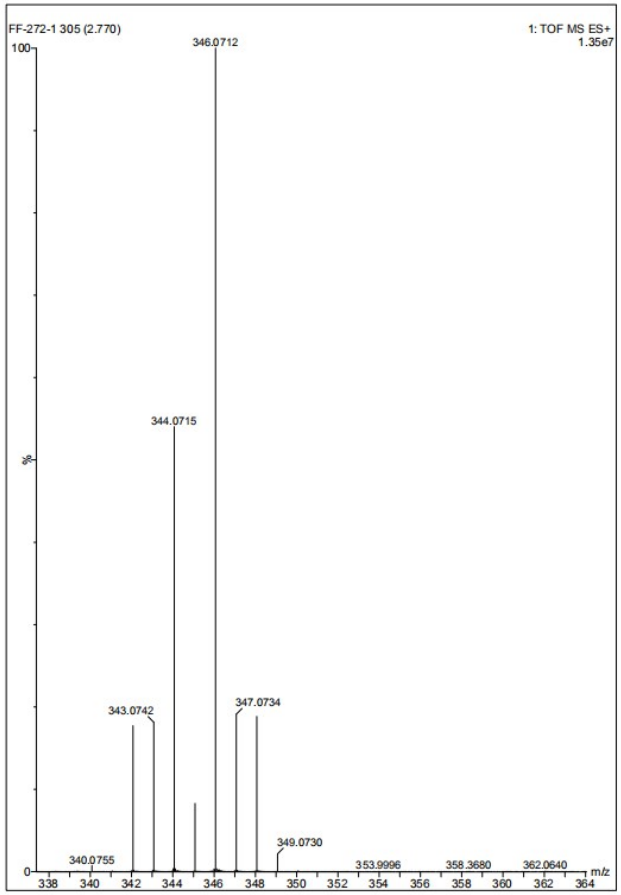
^{1}H NMR (400 MHz, $CDCl_3$)



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

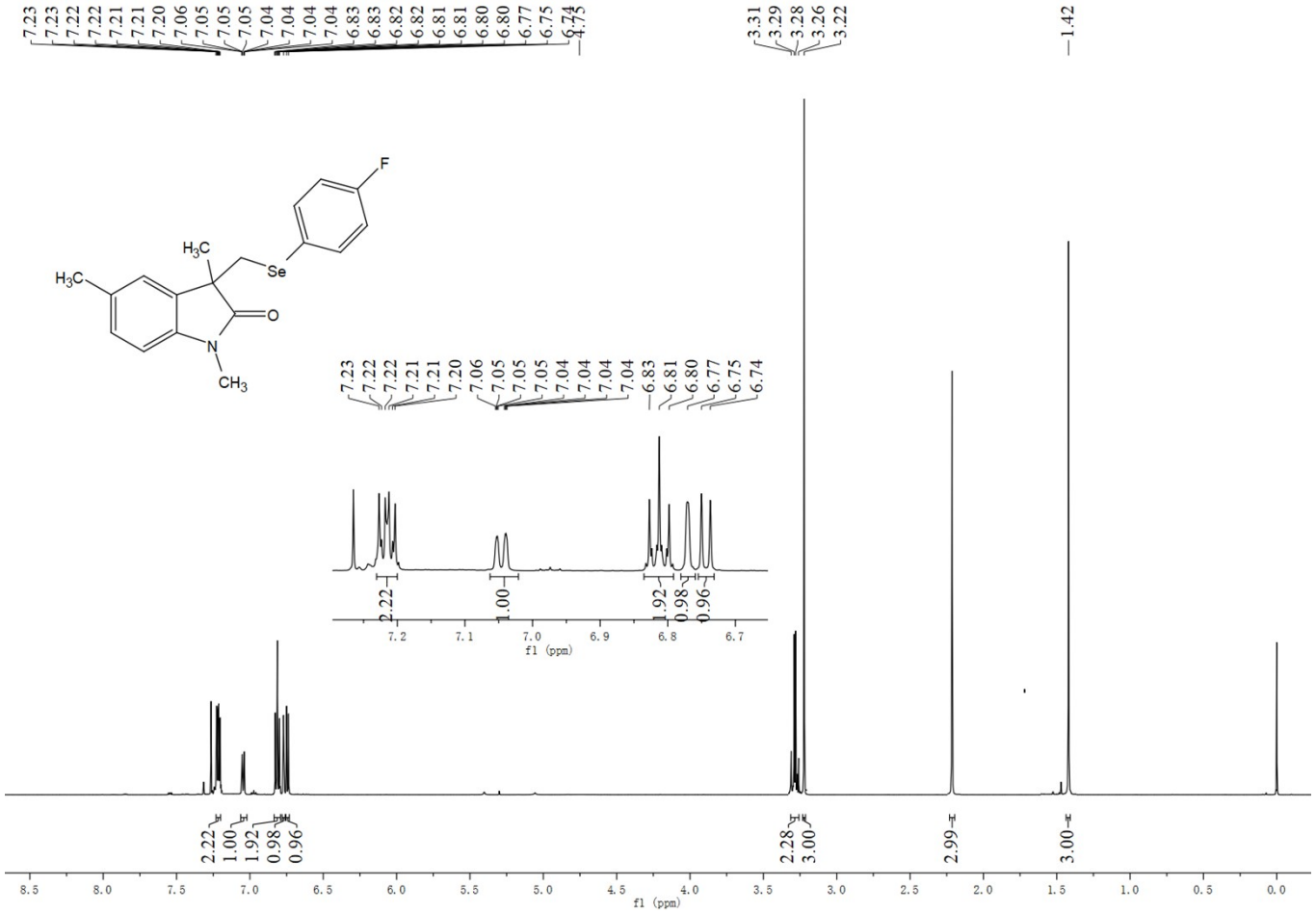


HRMS (ESI)

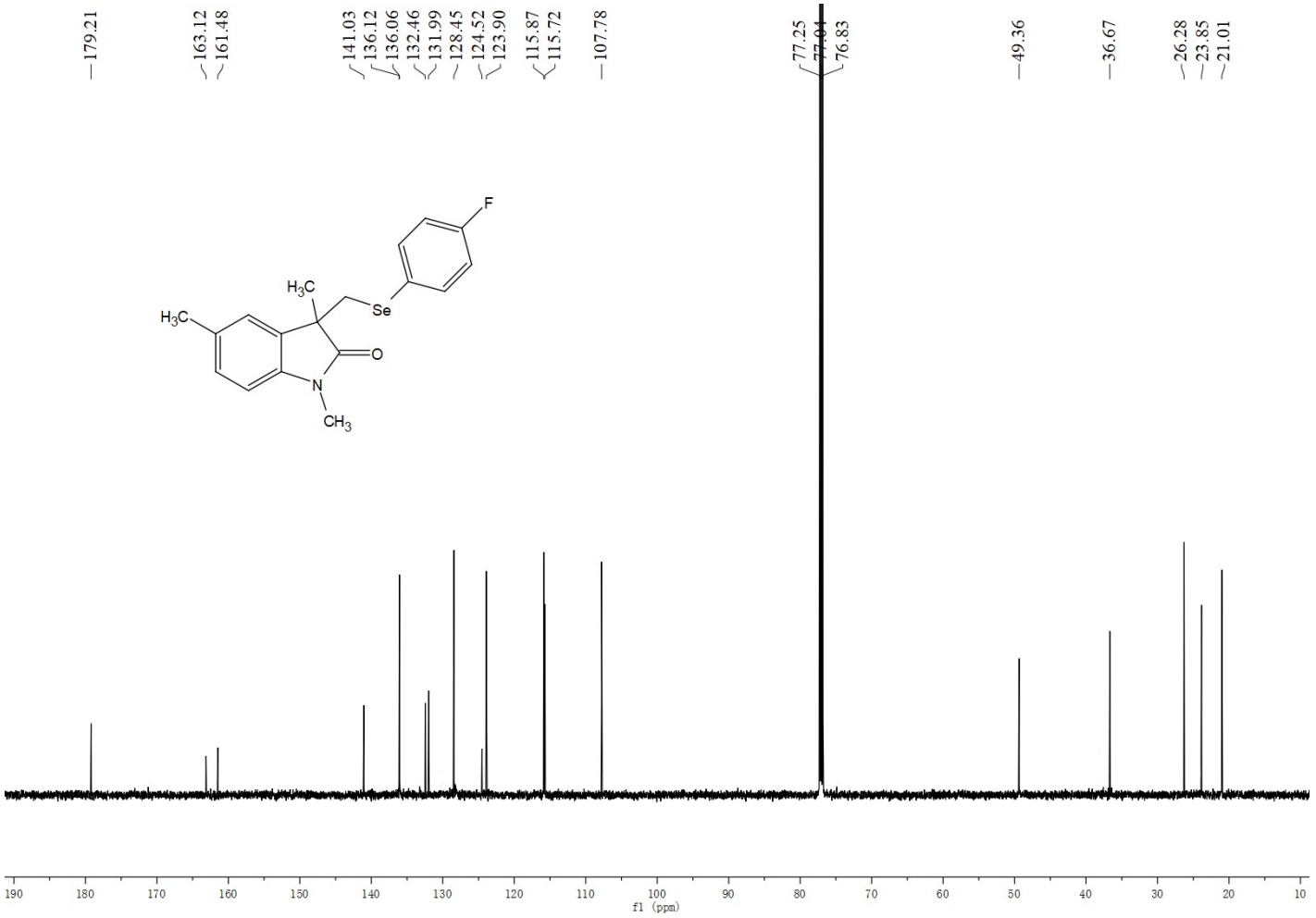

FF-272-1 305 (2.770)
1: TOF MS ES+
1.35e7
100
%
0
346.0712
344.0715
343.0742
347.0734
349.0730
340.0755
353.9996
358.3680
362.0640
m/z
338
340
342
344
346
348
350
352
354
356
358
360
362
364

3-(((4-Fluorophenyl)selanyl)methyl)-1,3,5-trimethylindolin-2-one (3ad)

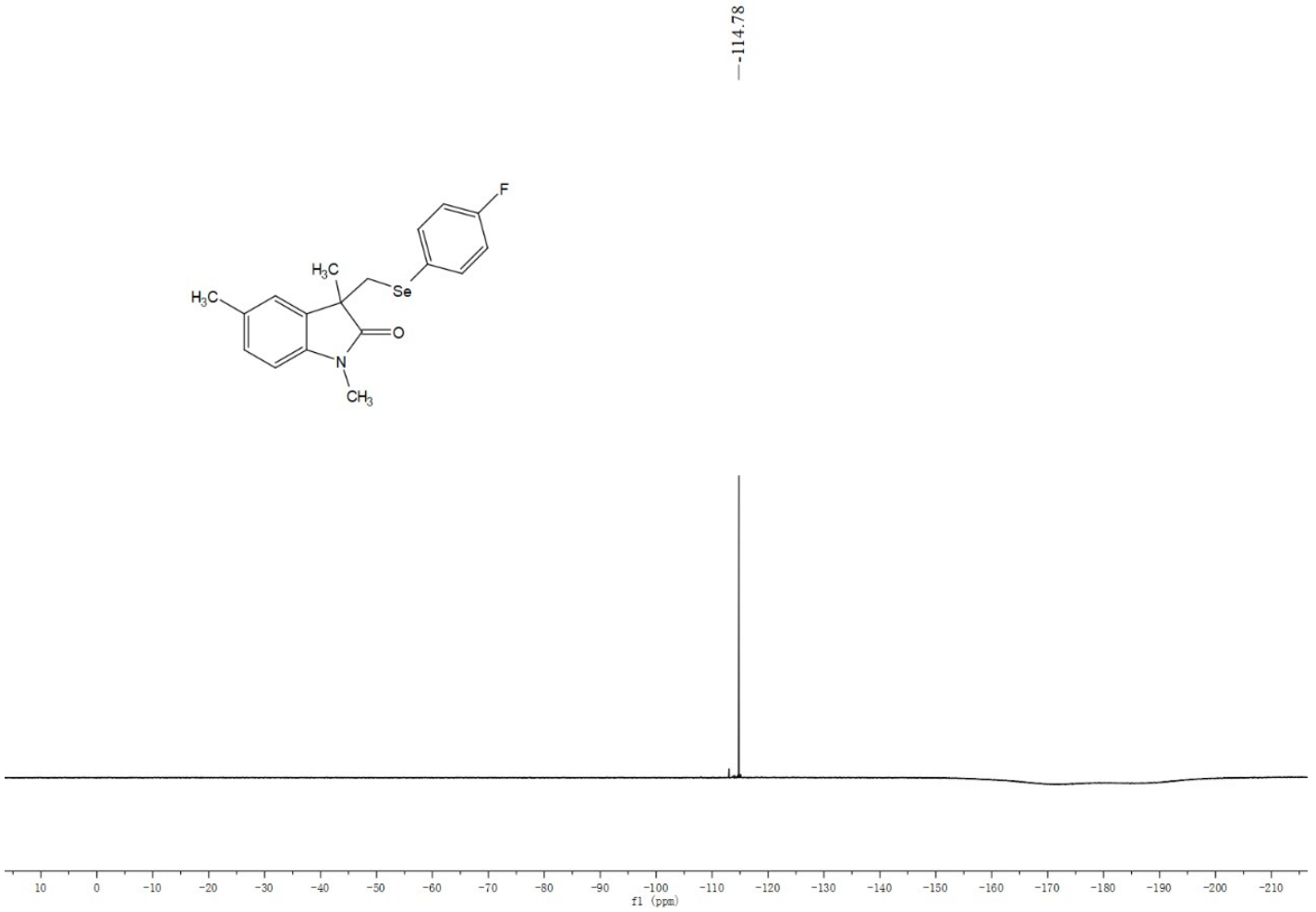
^{1}H NMR (600 MHz, $CDCl_3$)



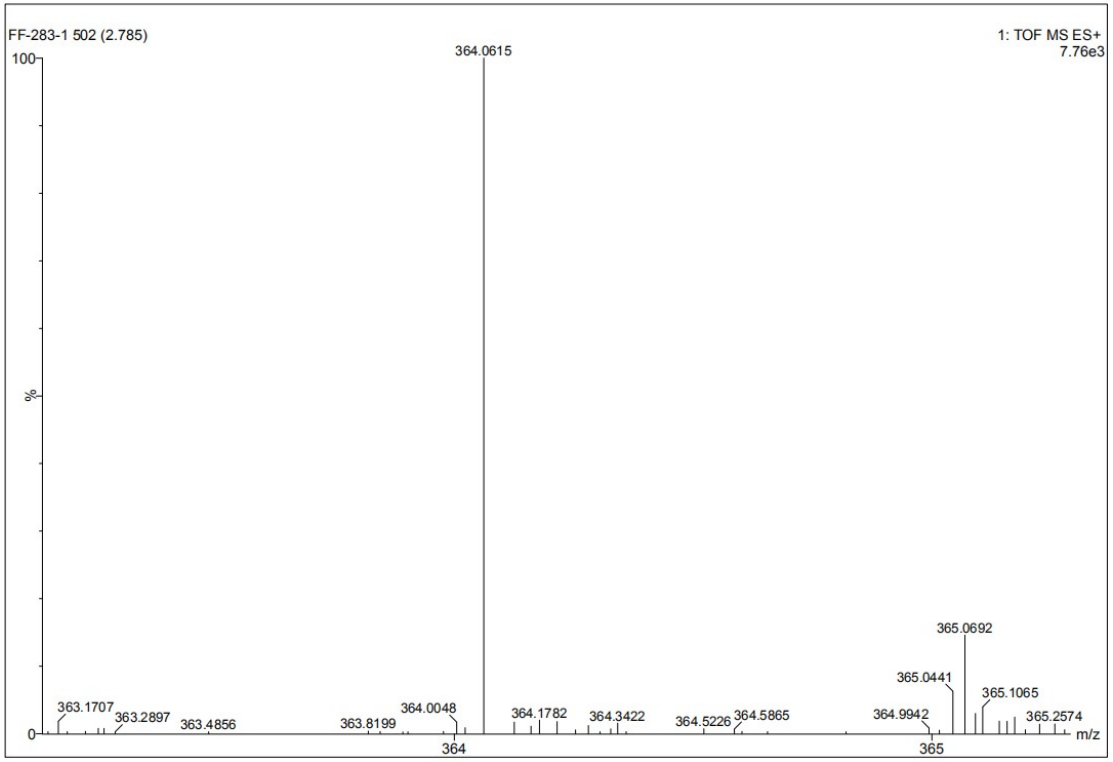
^{13}C NMR (150 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

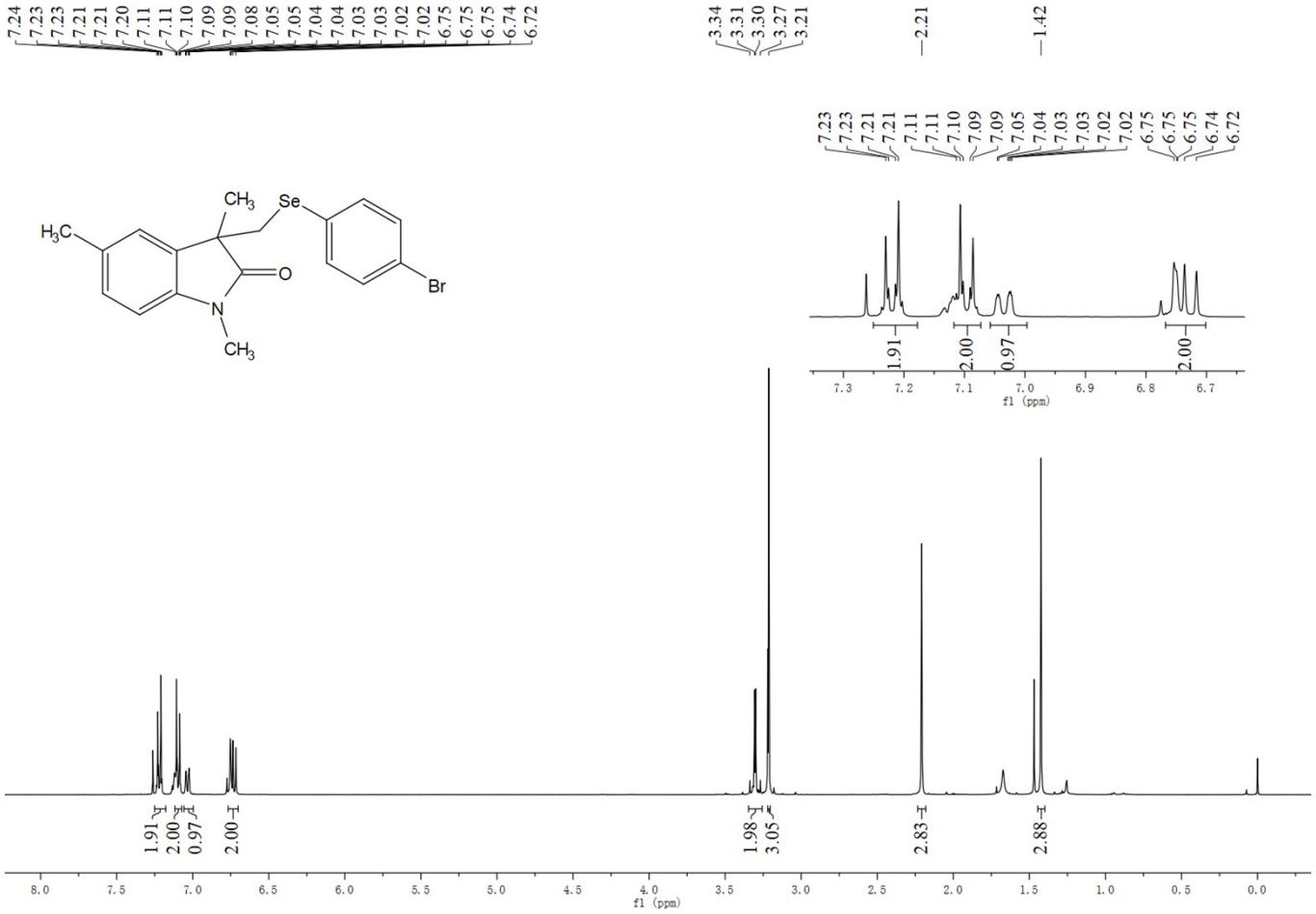


HRMS (ESI)

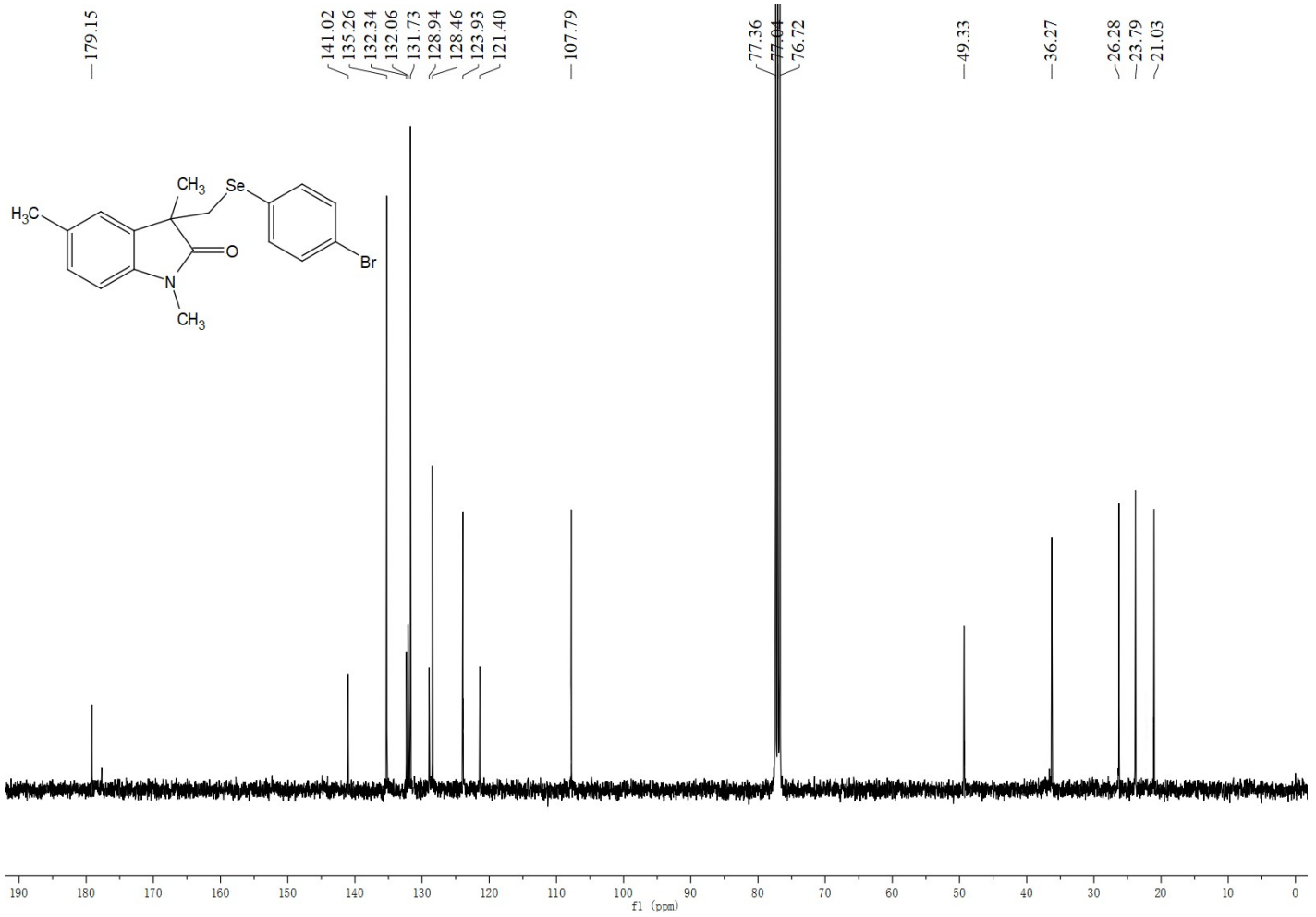

FF-283-1 502 (2.785)
1: TOF MS ES+
7.76e3
100
%
0
364.0615
365.0692
365.0441
365.1065
365.2574
363.1707
363.2897
363.4856
363.8199
364.0048
364.1782
364.3422
364.5226
364.5865
364.9942
364
365
m/z

3-(((4-Bromophenyl)selanyl)methyl)-1,3,5-trimethylindolin-2-one (3ae)

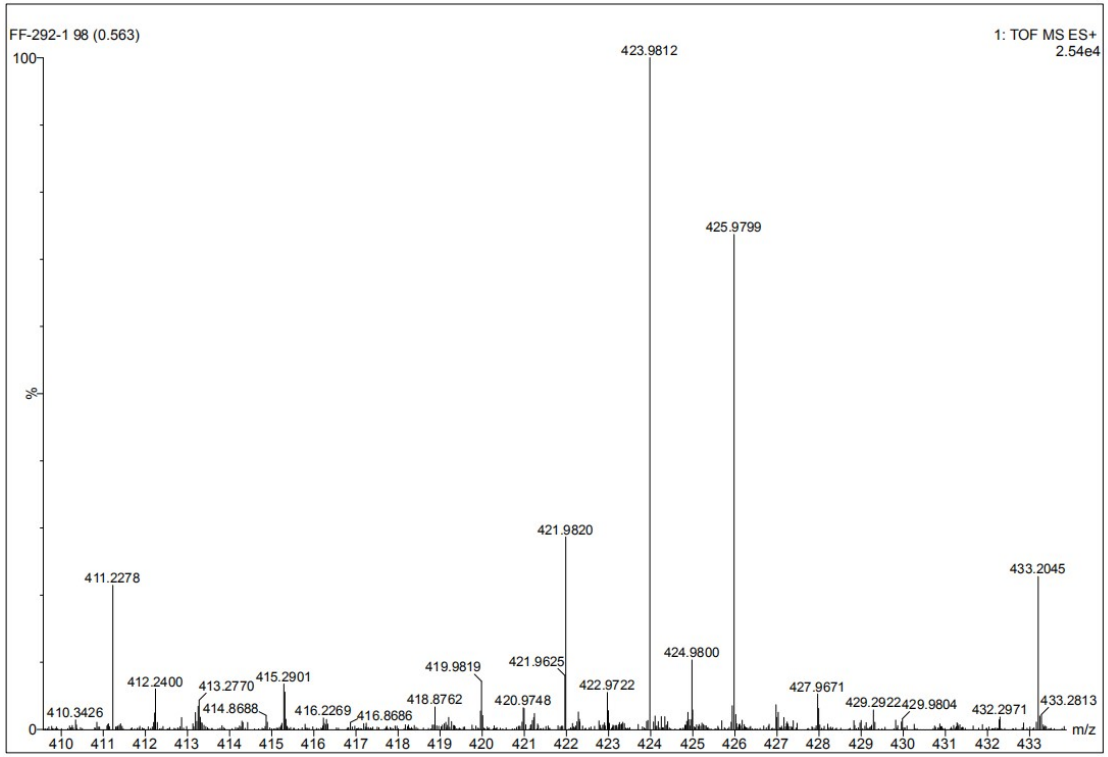
^{1}H NMR (400 MHz, $CDCl_3$)



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

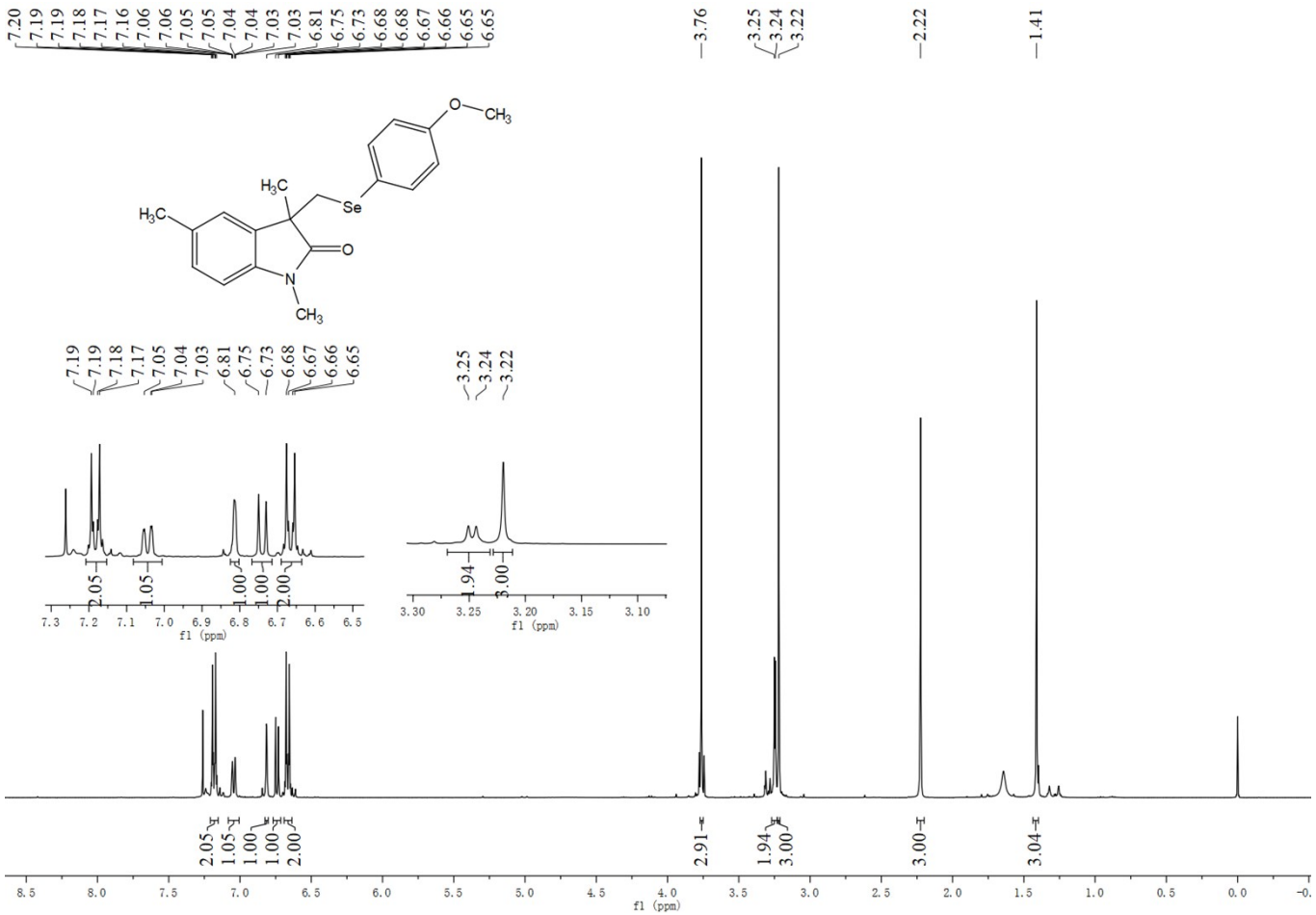


HRMS (ESI)

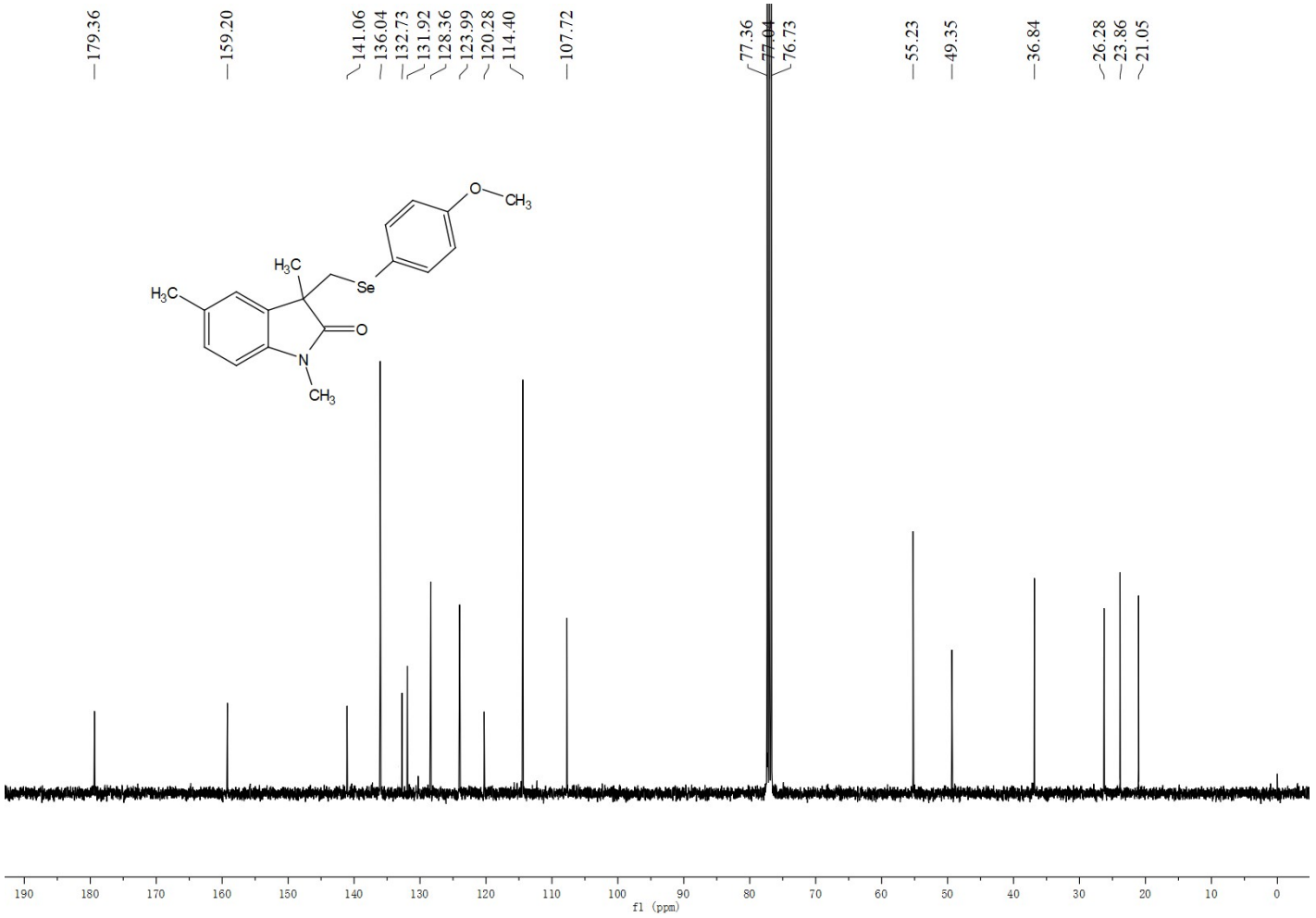

FF-292-1 98 (0.563)
1: TOF MS ES+
2.54e4
100
%
0
423.9812
425.9799
421.9820
411.2278
433.2045
424.9800
421.9625
419.9819
412.2400
413.2770
415.2901
422.9722
427.9671
414.8688
418.8762
420.9748
429.2922
429.9804
410.3426
416.2269
416.8686
432.2971
433.2813
m/z
410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433

3-(((4-Methoxyphenyl)selanyl)methyl)-1,3,5-trimethylindolin-2-one (3af)

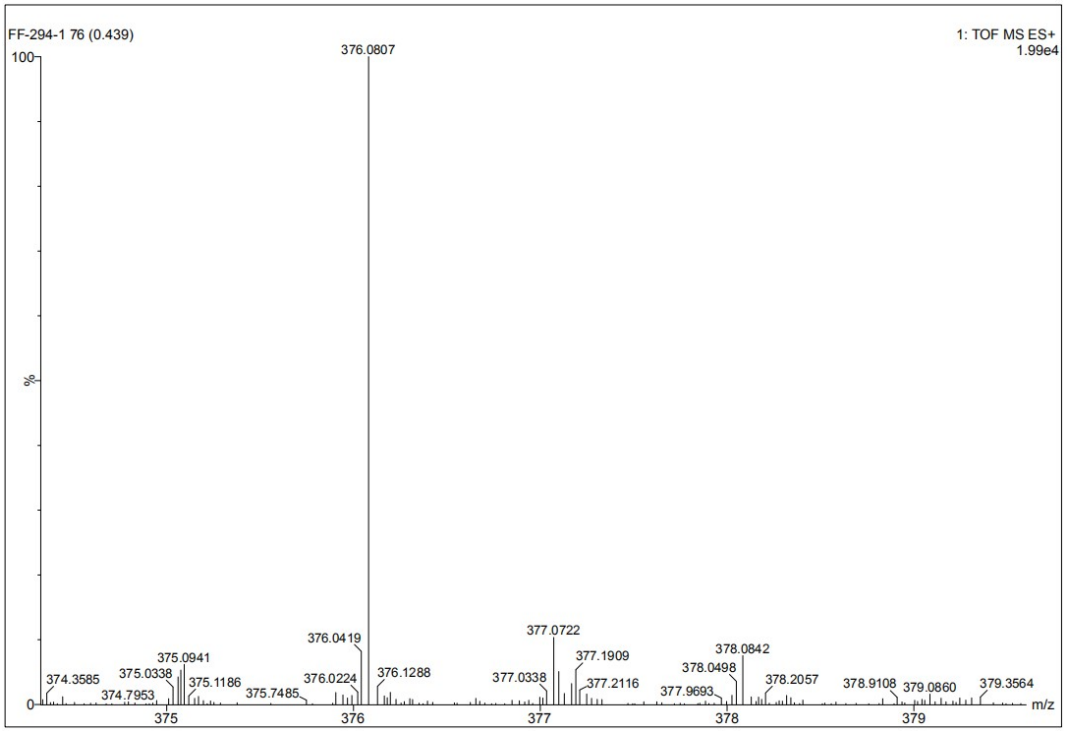
^{1}H NMR (400 MHz, $CDCl_3$)



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

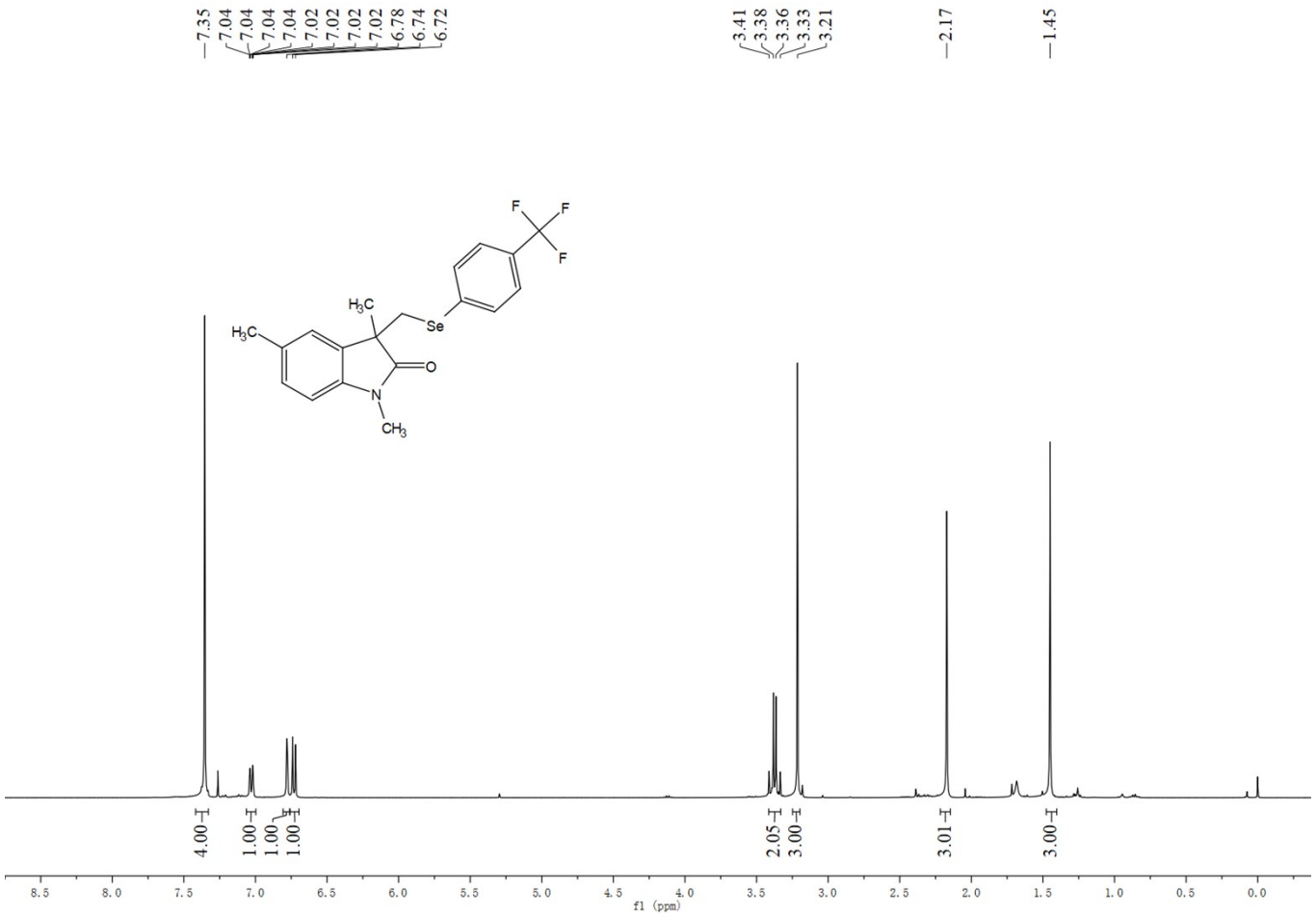


HRMS (ESI)

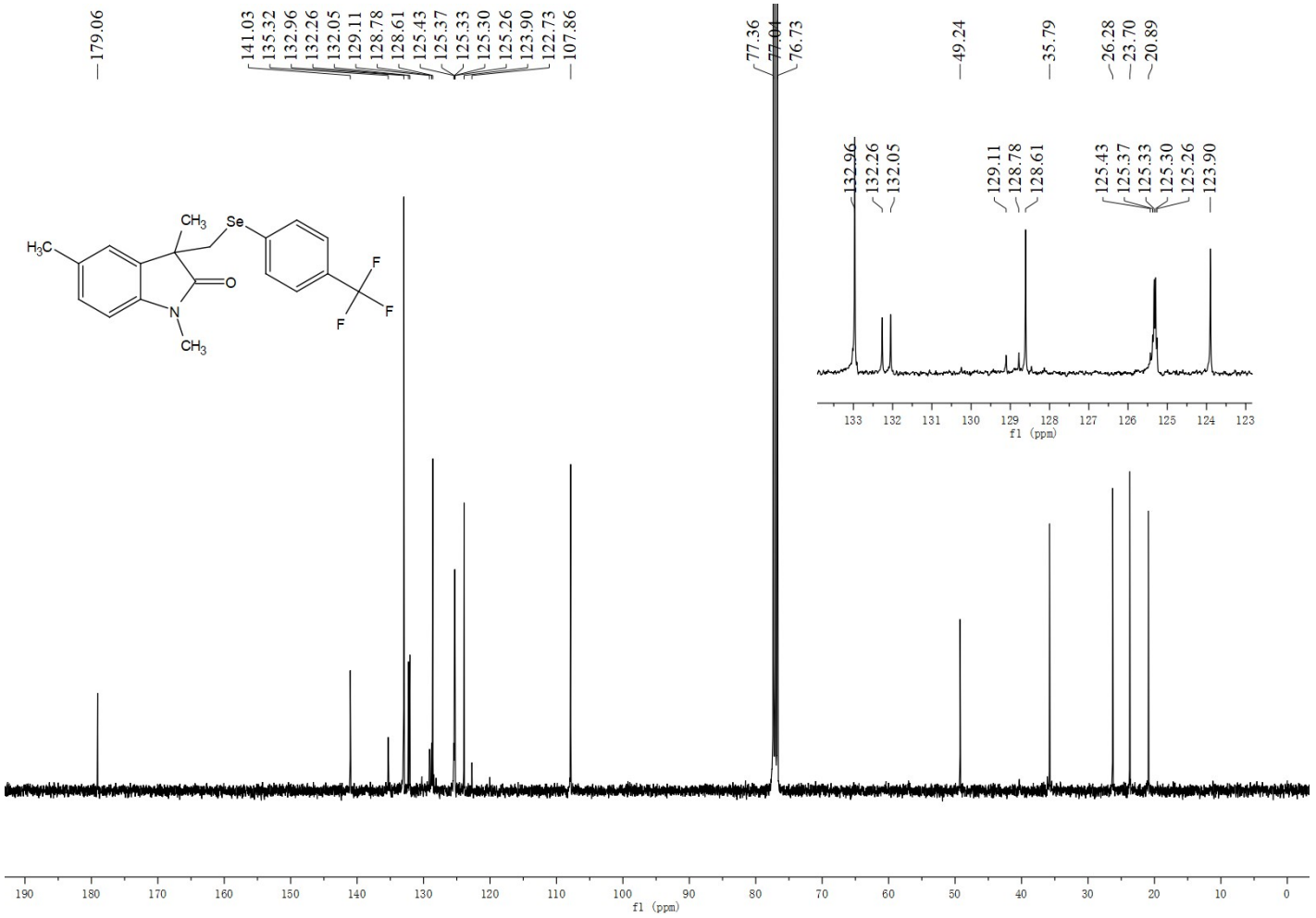

FF-294-1 76 (0.439)
1: TOF MS ES+
1.99e4
100
%
0
376.0807
376.0419
377.0722
377.1909
378.0842
375.0941
375.0338
374.3585
375.1186
374.7953
376.0224
376.1288
375.7485
377.0338
377.2116
378.0498
377.9693
378.2057
378.9108
379.0860
379.3564
m/z
375
376
377
378
379

1,3,5-Trimethyl-3-(((4-(trifluoromethyl)phenyl)selanyl)methyl)indolin-2-one (3ag)

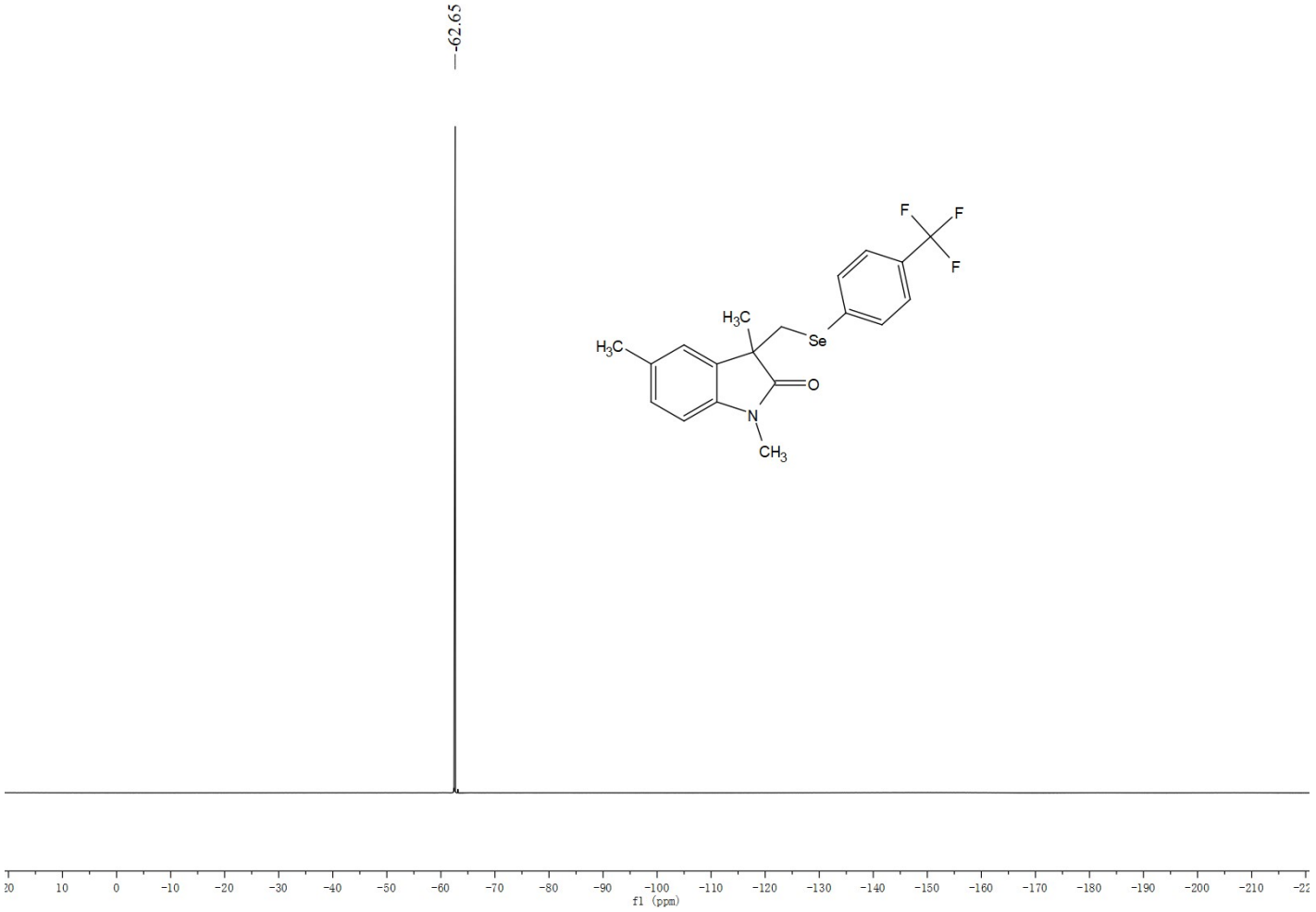
^{1}H NMR (400 MHz, $CDCl_3$)



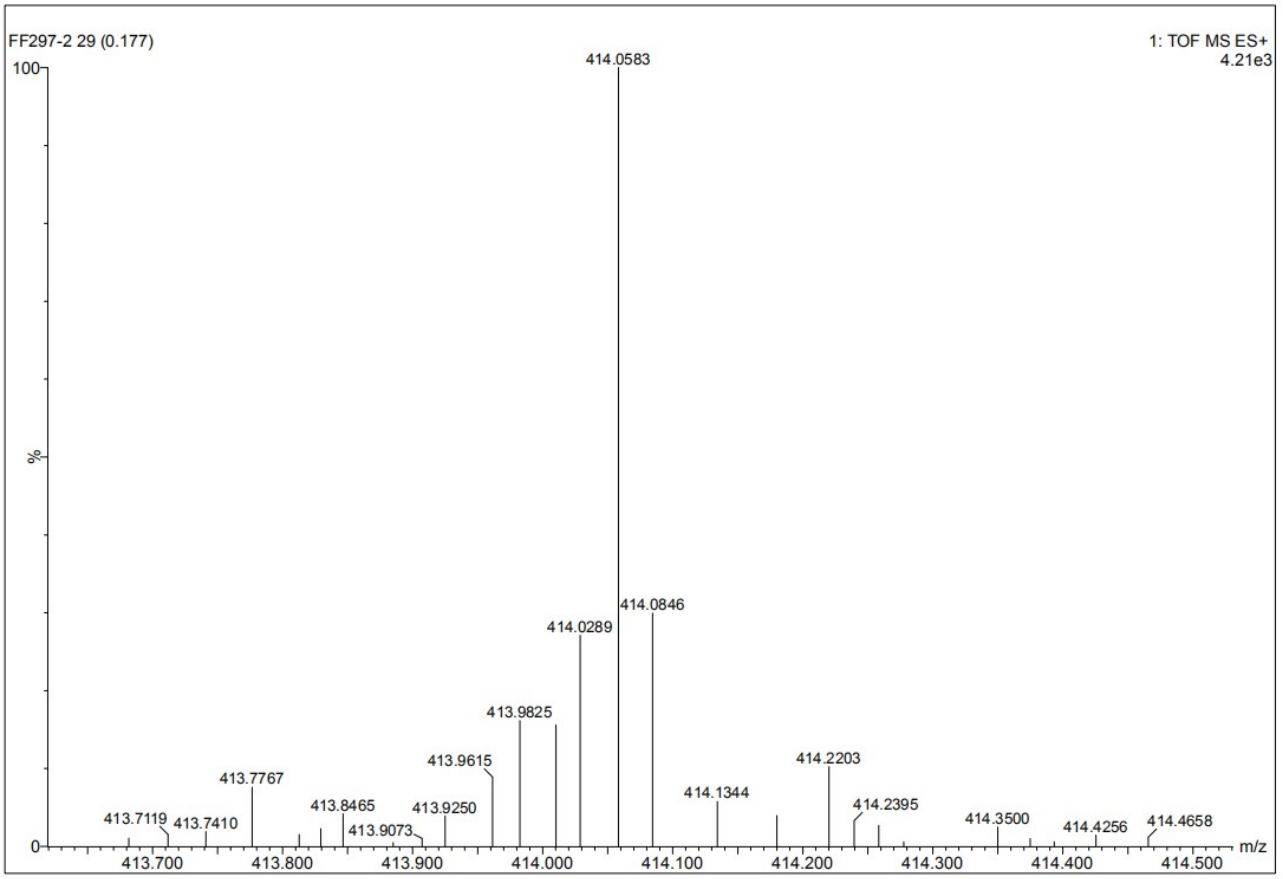
^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)

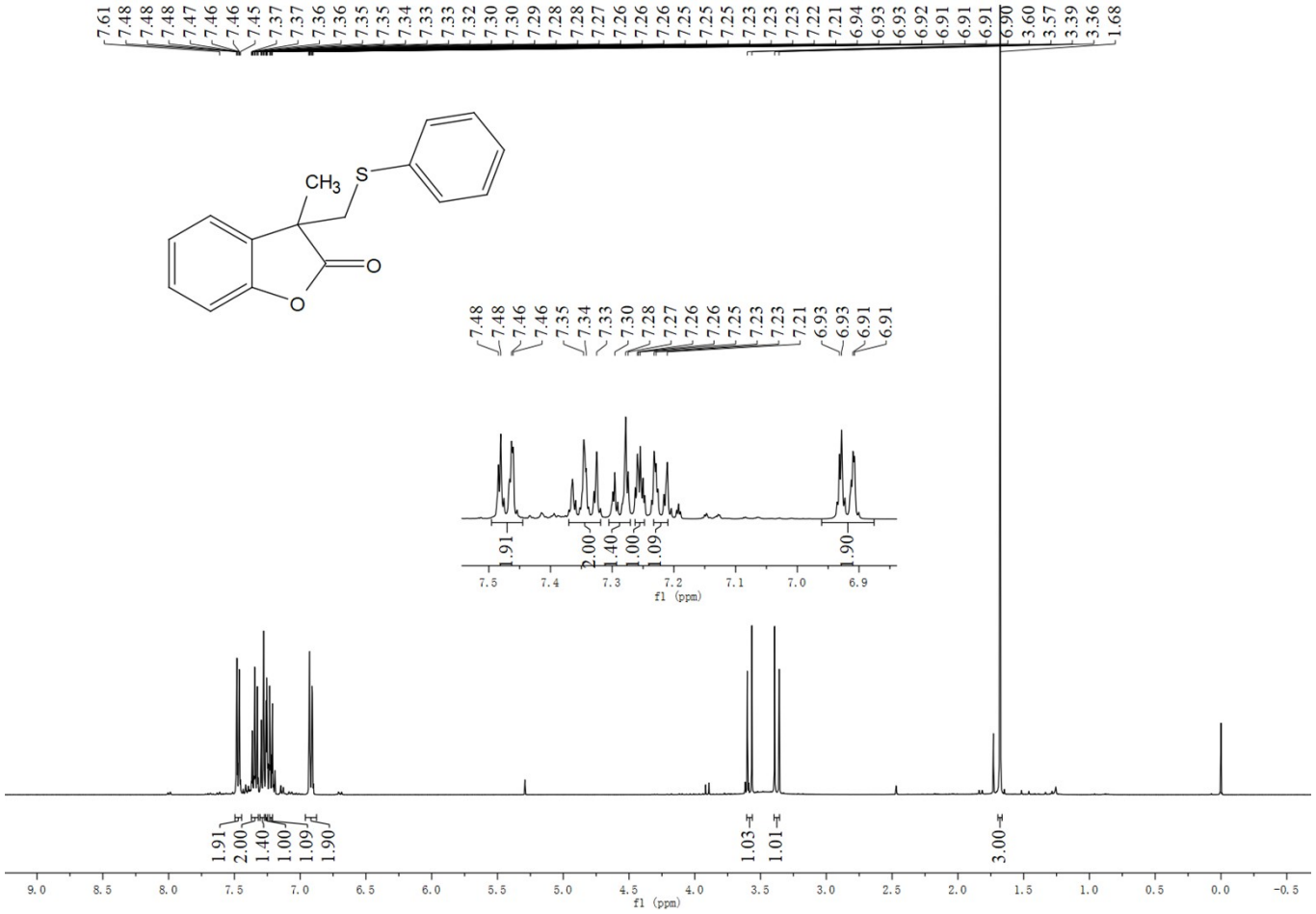


HRMS (ESI)

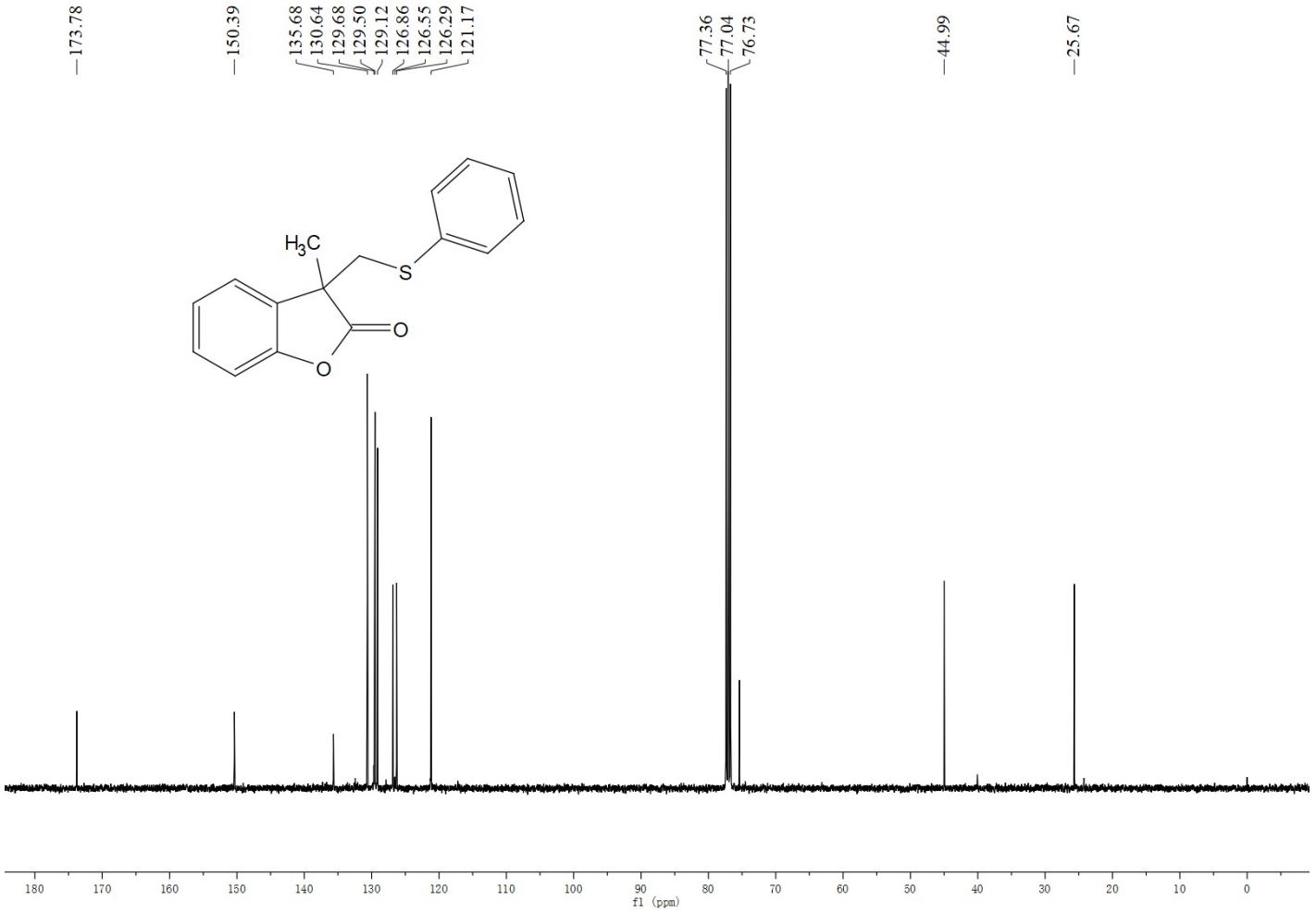

FF297-2 29 (0.177)
1: TOF MS ES+
4.21e3
100
%
0
414.0583
414.0846
414.0289
413.9825
413.9615
413.7767
414.2203
414.1344
414.2395
413.8465
413.9250
413.7119
413.7410
413.9073
414.3500
414.4256
414.4658
m/z
413.700
413.800
413.900
414.000
414.100
414.200
414.300
414.400
414.500

3-Methyl-3-((phenylthio)methyl)benzofuran-2(3*H*)-one (3ah)

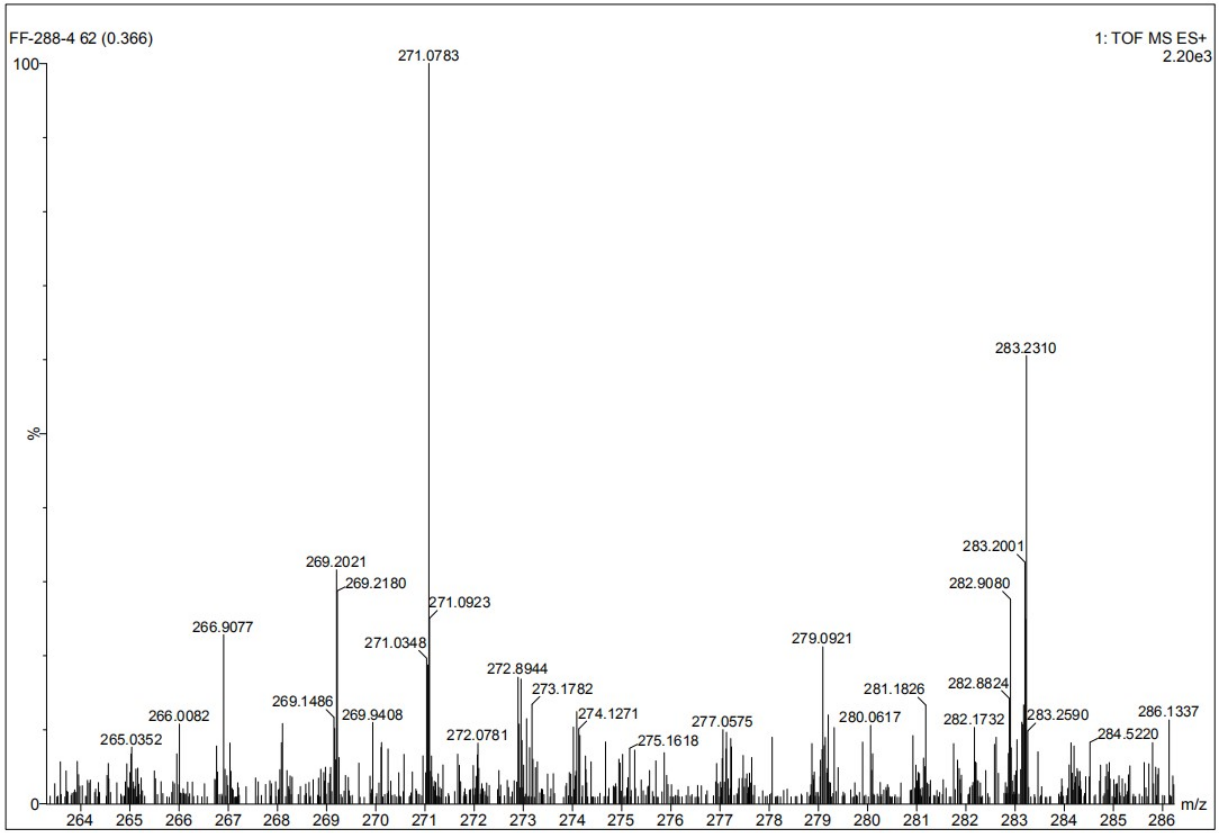
^{1}H NMR (400 MHz, $CDCl_3$)



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

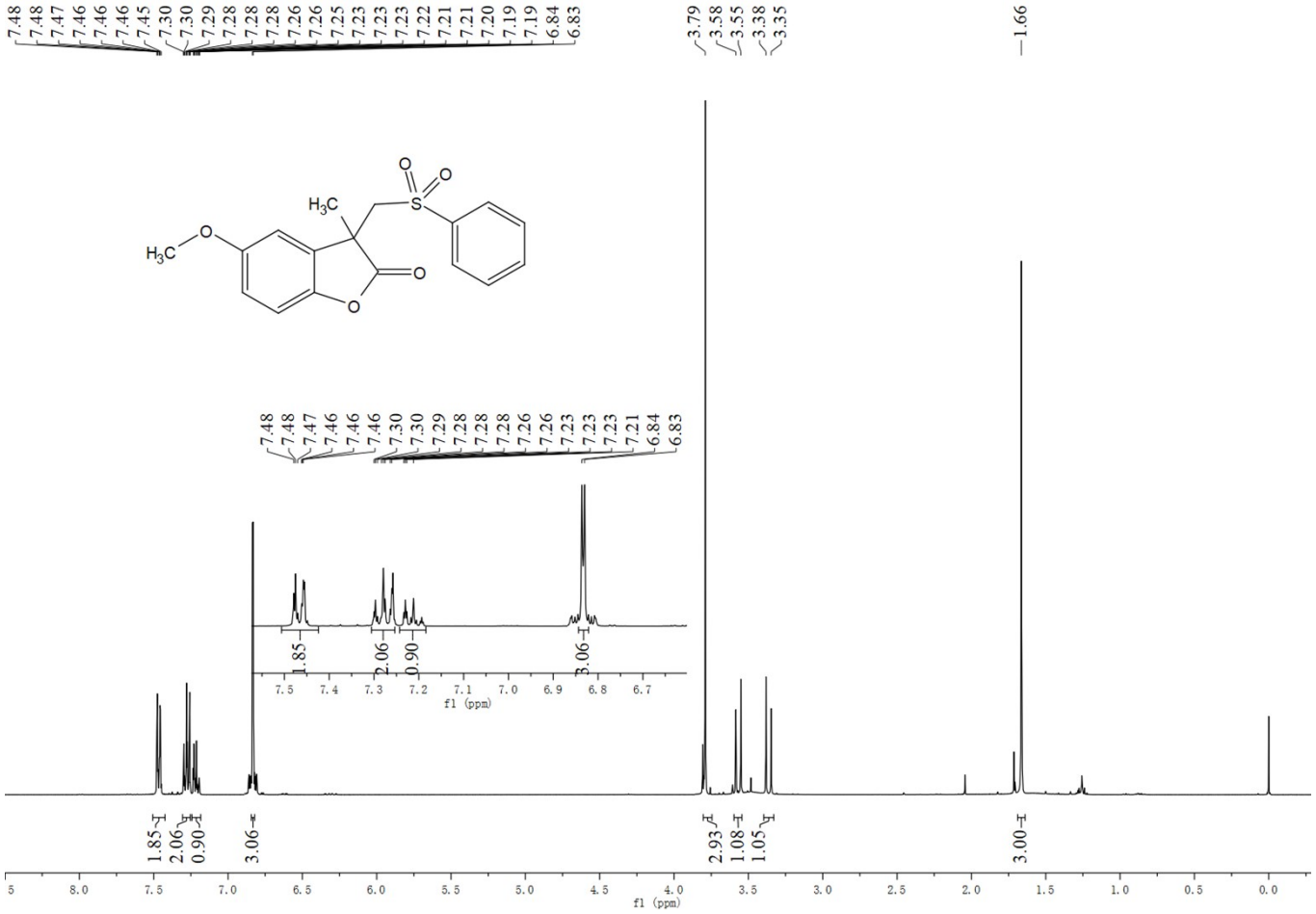


HRMS (ESI)

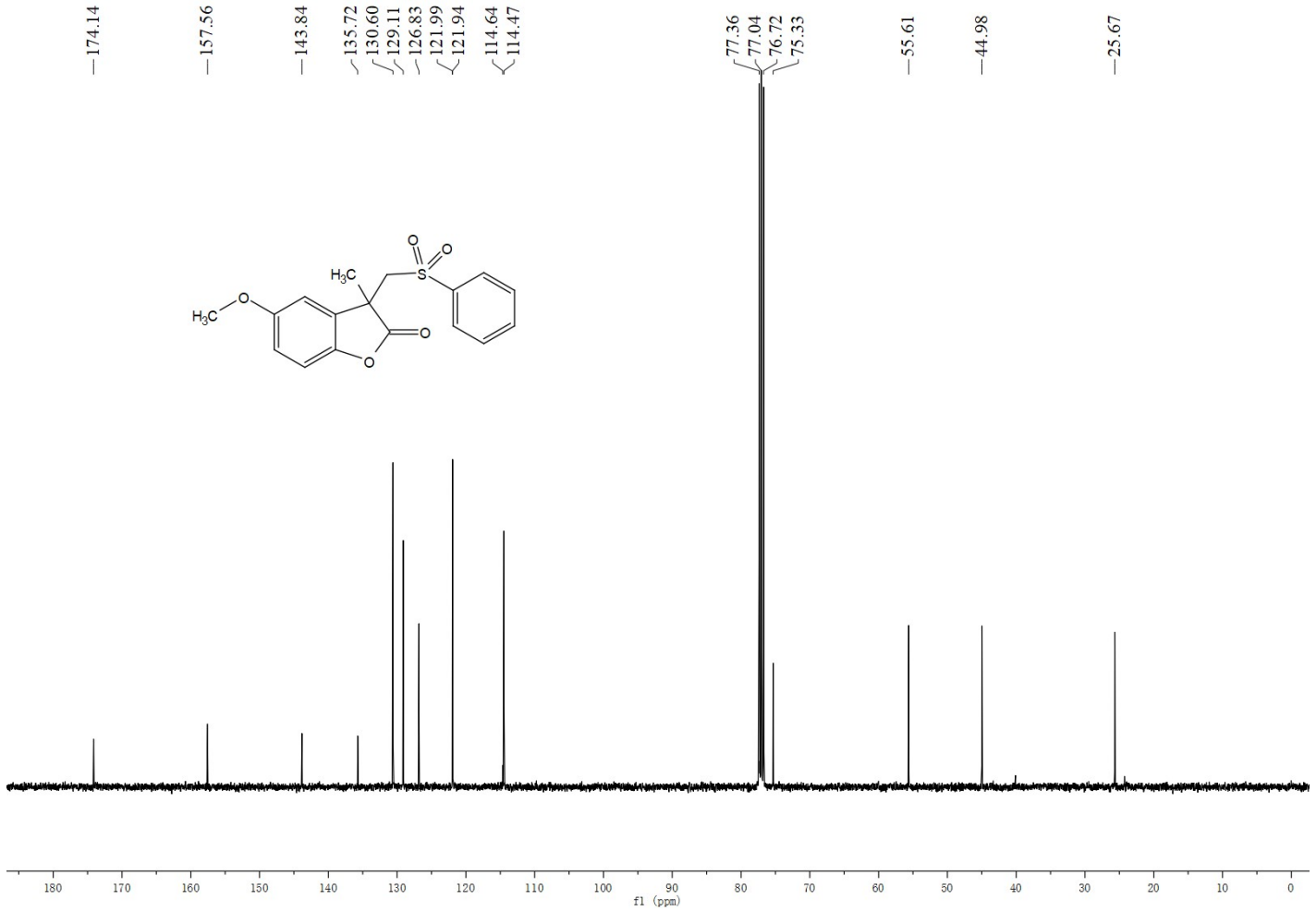

FF-288-4 62 (0.366)
1: TOF MS ES+
2.20e3
100
%
0
271.0783
283.2310
283.2001
282.9080
269.2021
269.2180
271.0923
266.9077
271.0348
279.0921
272.8944
273.1782
282.8824
281.1826
269.1486
266.0082
269.9408
274.1271
277.0575
280.0617
282.1732
283.2590
286.1337
265.0352
272.0781
275.1618
284.5220
264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286
m/z

5-Methoxy-3-methyl-3-((phenylsulfonyl)methyl)benzofuran-2(3*H*)-one (3ai)

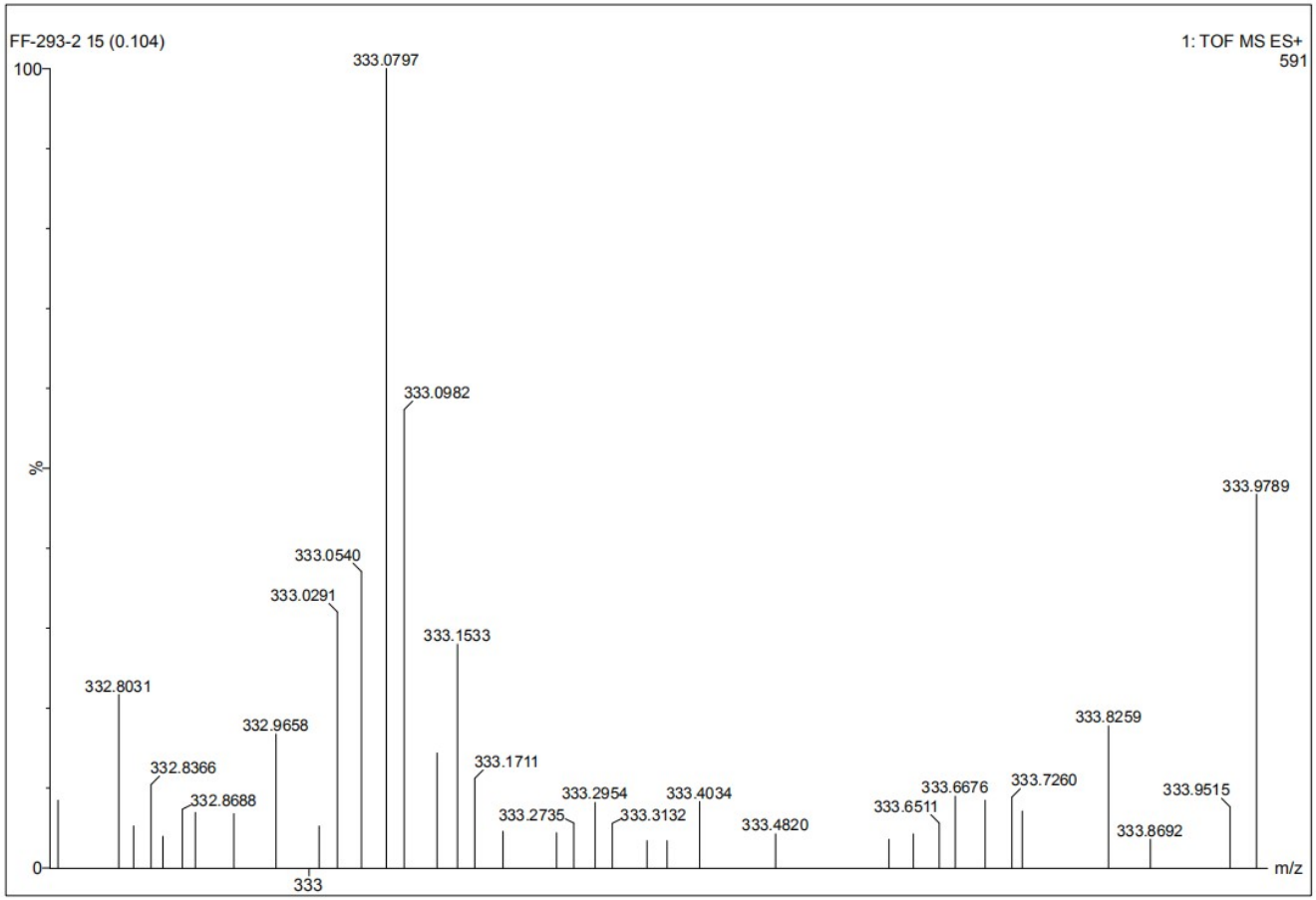
^{1}H NMR (400 MHz, $CDCl_3$)



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

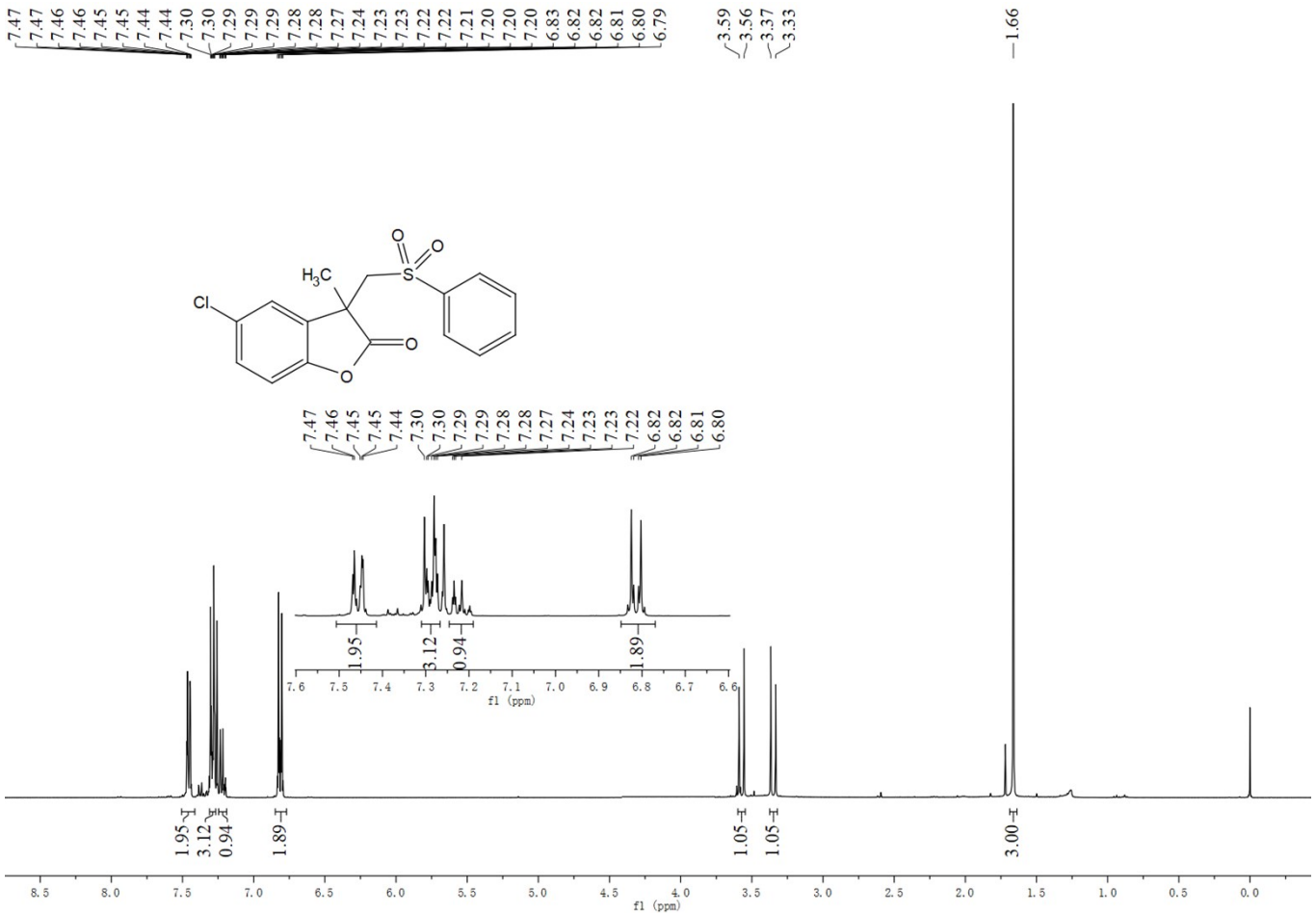


HRMS (ESI)

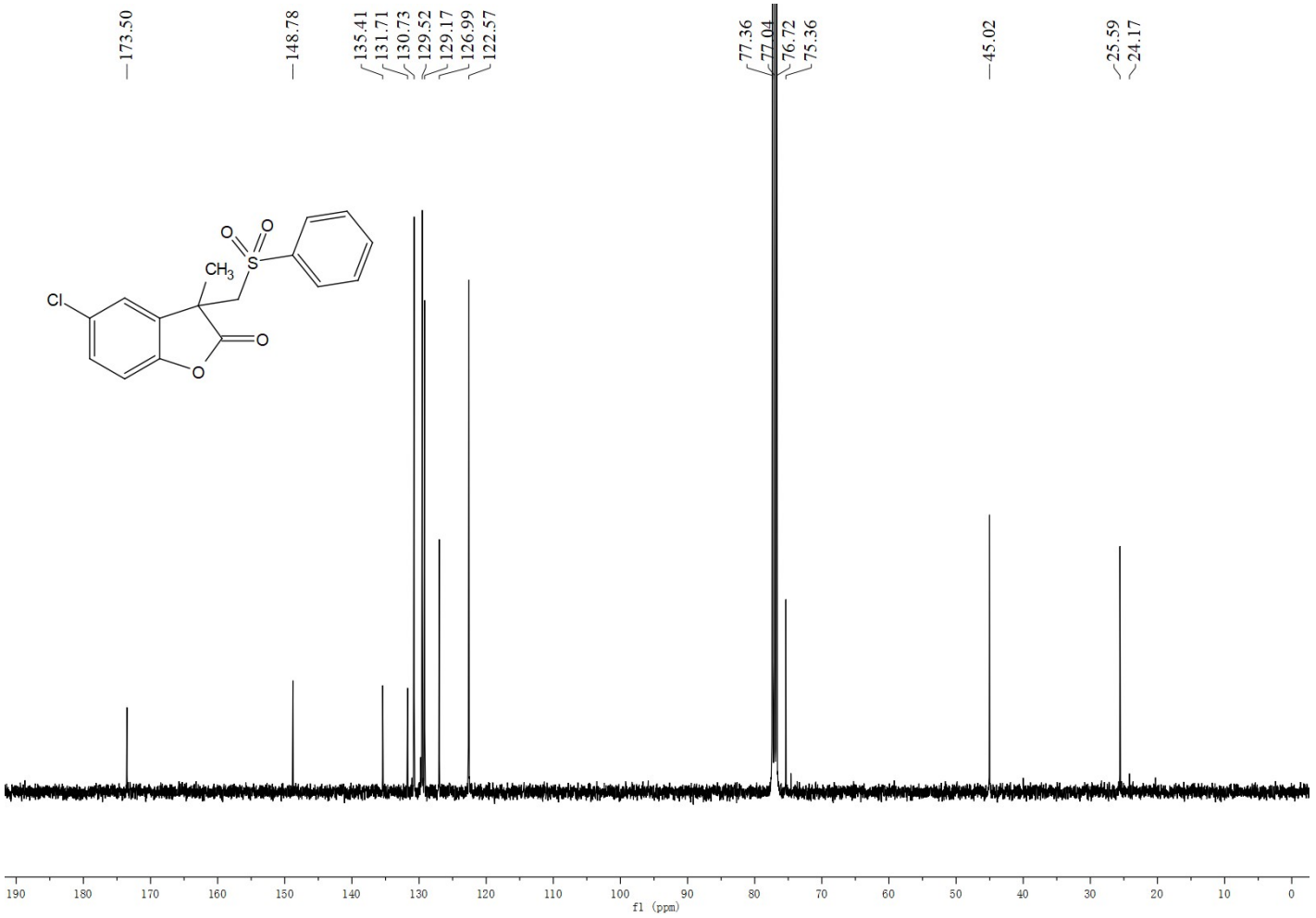

FF-293-2 15 (0.104)
1: TOF MS ES+
591
100
%
0
333
m/z
333.0797
333.0982
333.9789
333.0540
333.0291
333.1533
332.8031
332.9658
333.8259
333.1711
332.8366
332.8688
333.2954
333.4034
333.7260
333.6676
333.9515
333.2735
333.3132
333.6511
333.4820
333.8692

5-Chloro-3-methyl-3-((phenylsulfonyl)methyl)benzofuran-2(3*H*)-one (3aj)

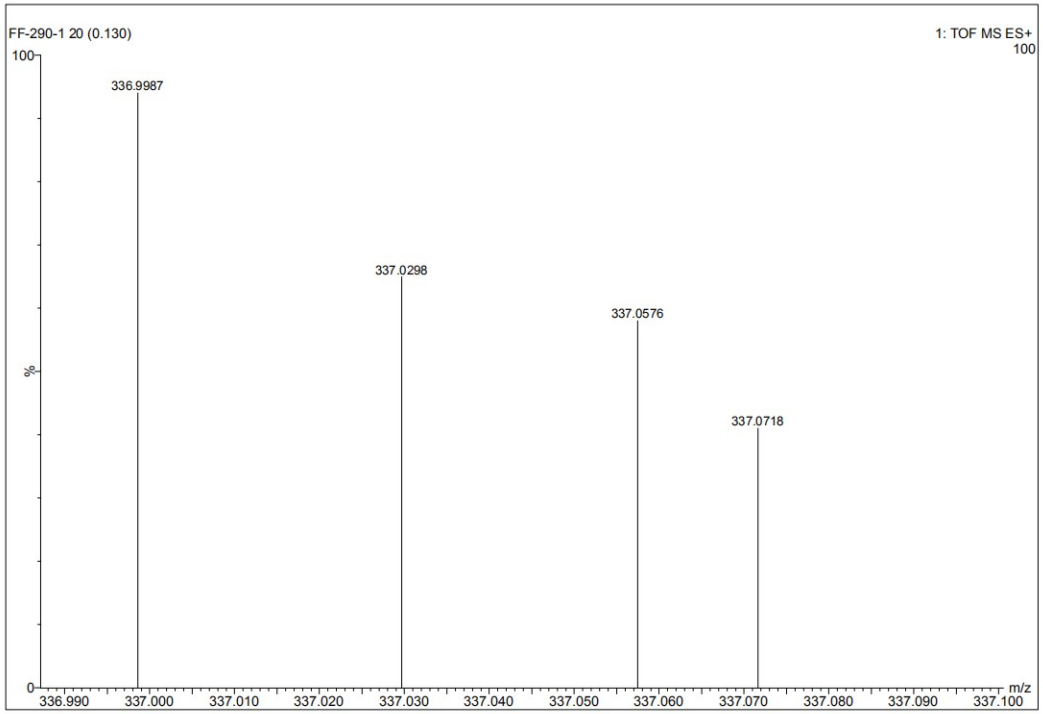
^{1}H NMR (400 MHz, $CDCl_3$)



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

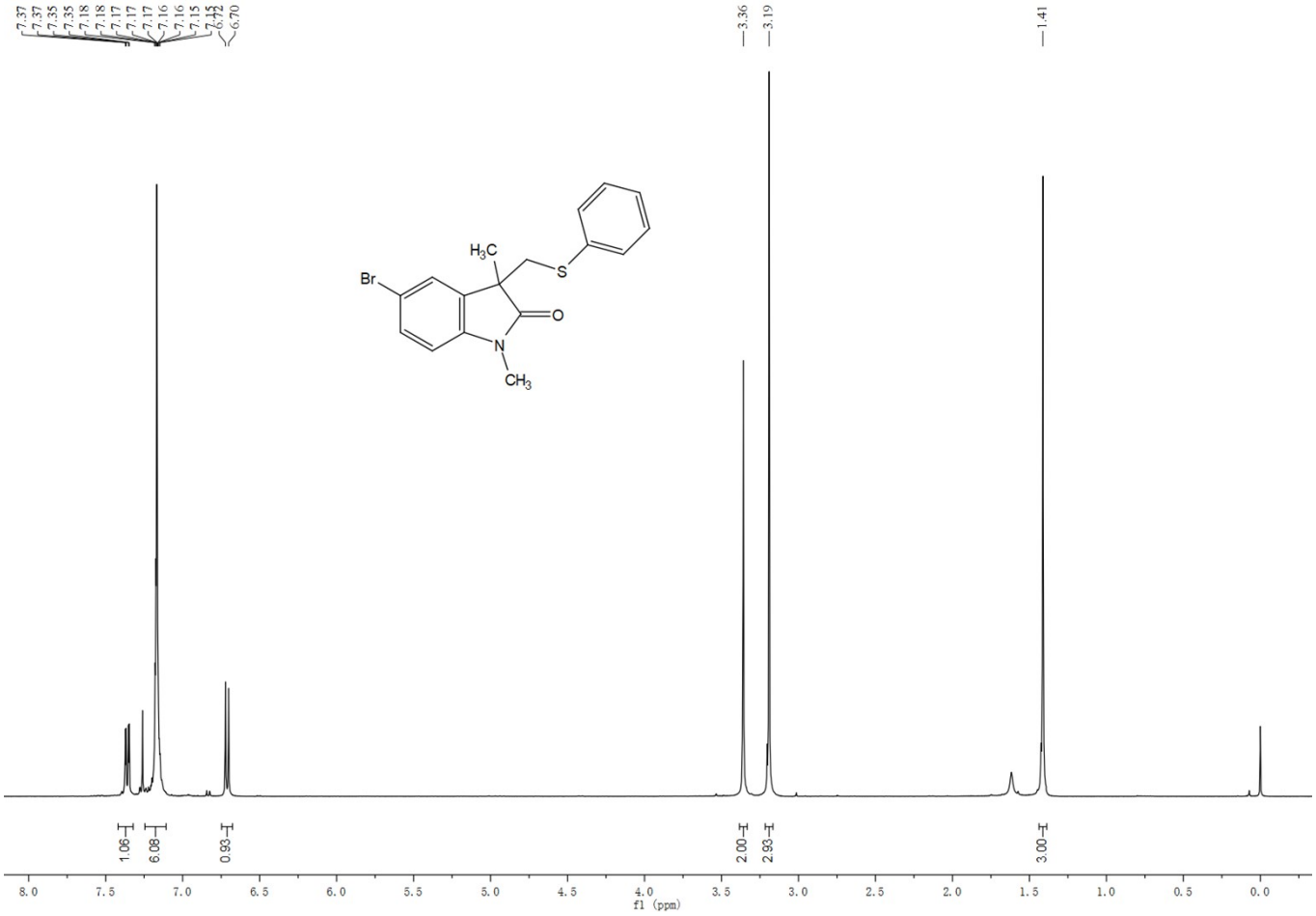


HRMS (ESI)

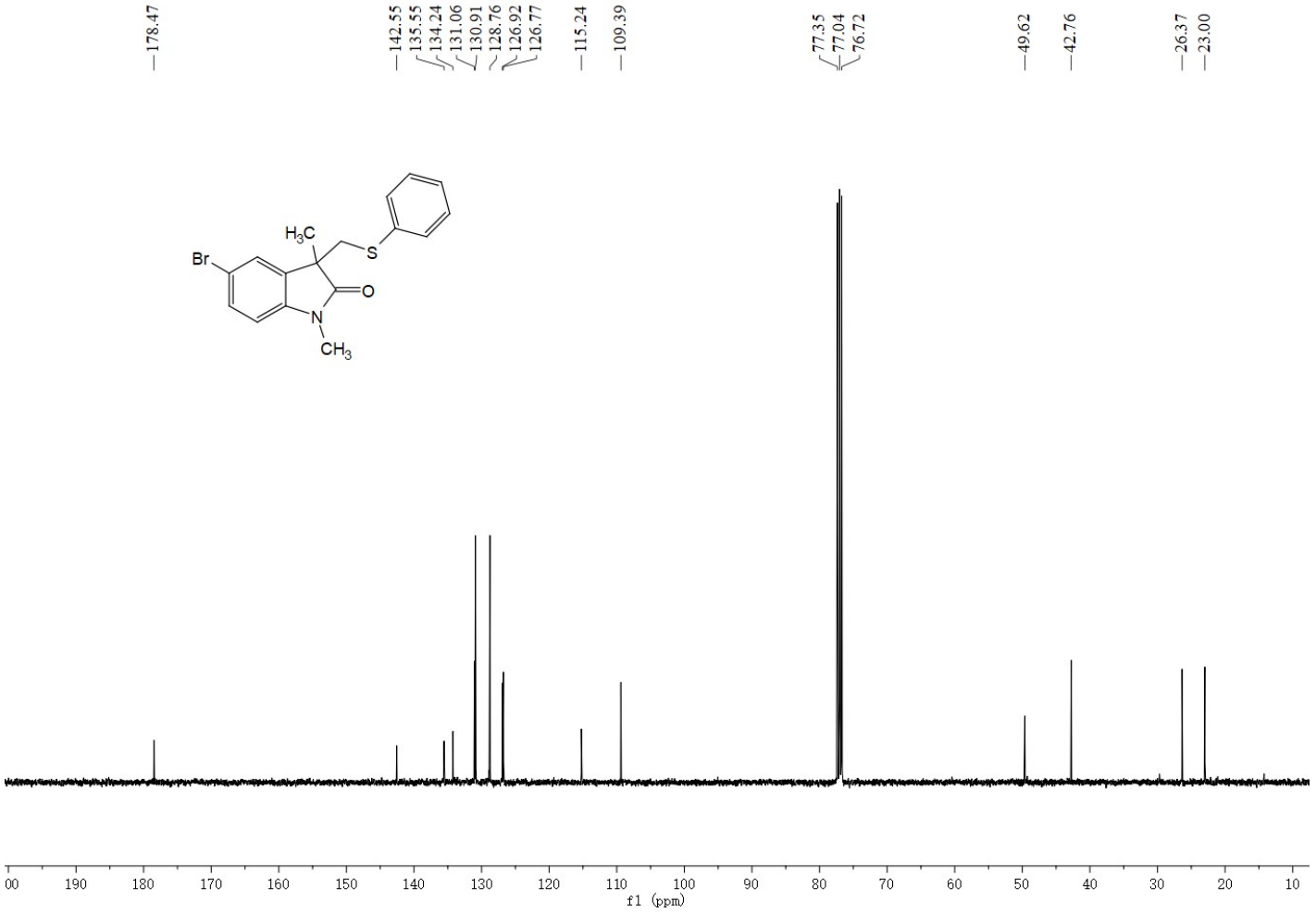

FF-290-1 20 (0.130)
1: TOF MS ES+
100
100
336.9987
337.0298
337.0576
337.0718
%
0
m/z
336.990
337.000
337.010
337.020
337.030
337.040
337.050
337.060
337.070
337.080
337.090
337.100

5-Bromo-1,3-dimethyl-3-((phenylthio)methyl)indolin-2-one (4a)

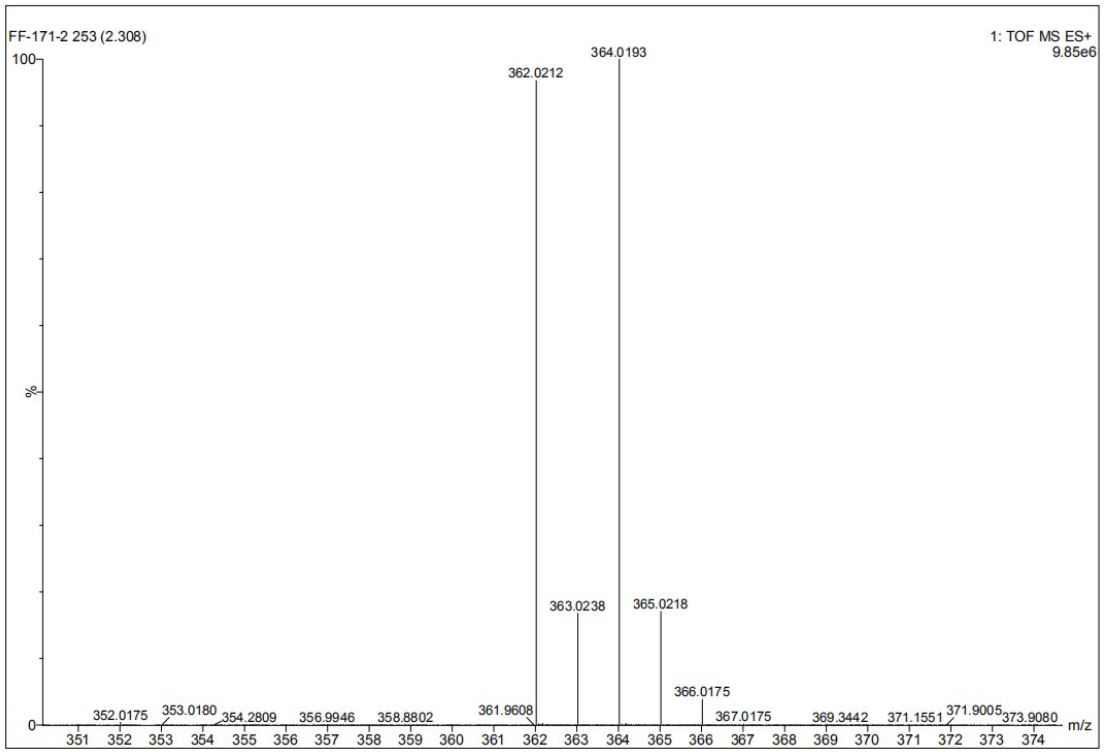
^{1}H NMR (400 MHz, $CDCl_3$)



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

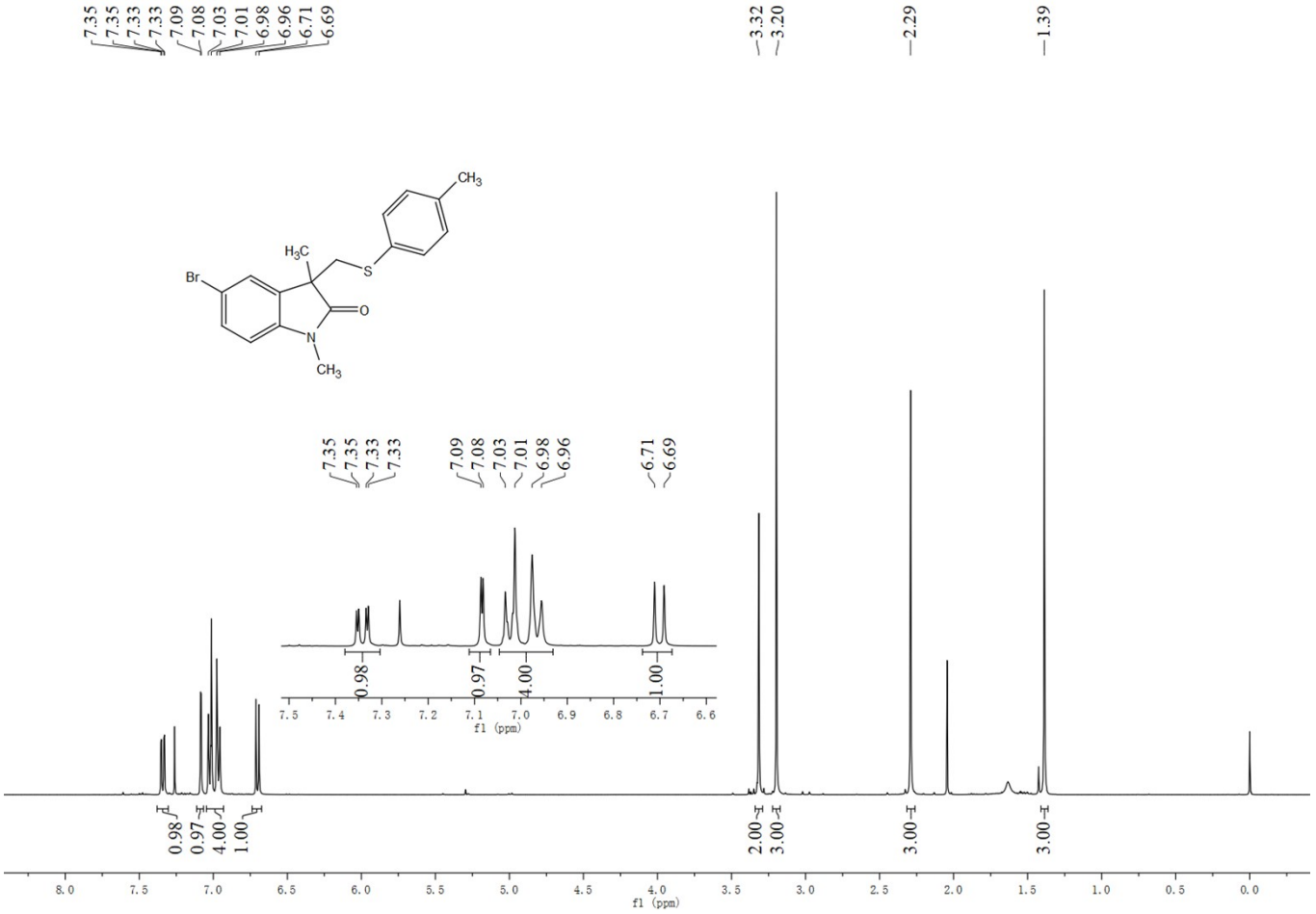


HRMS (ESI)

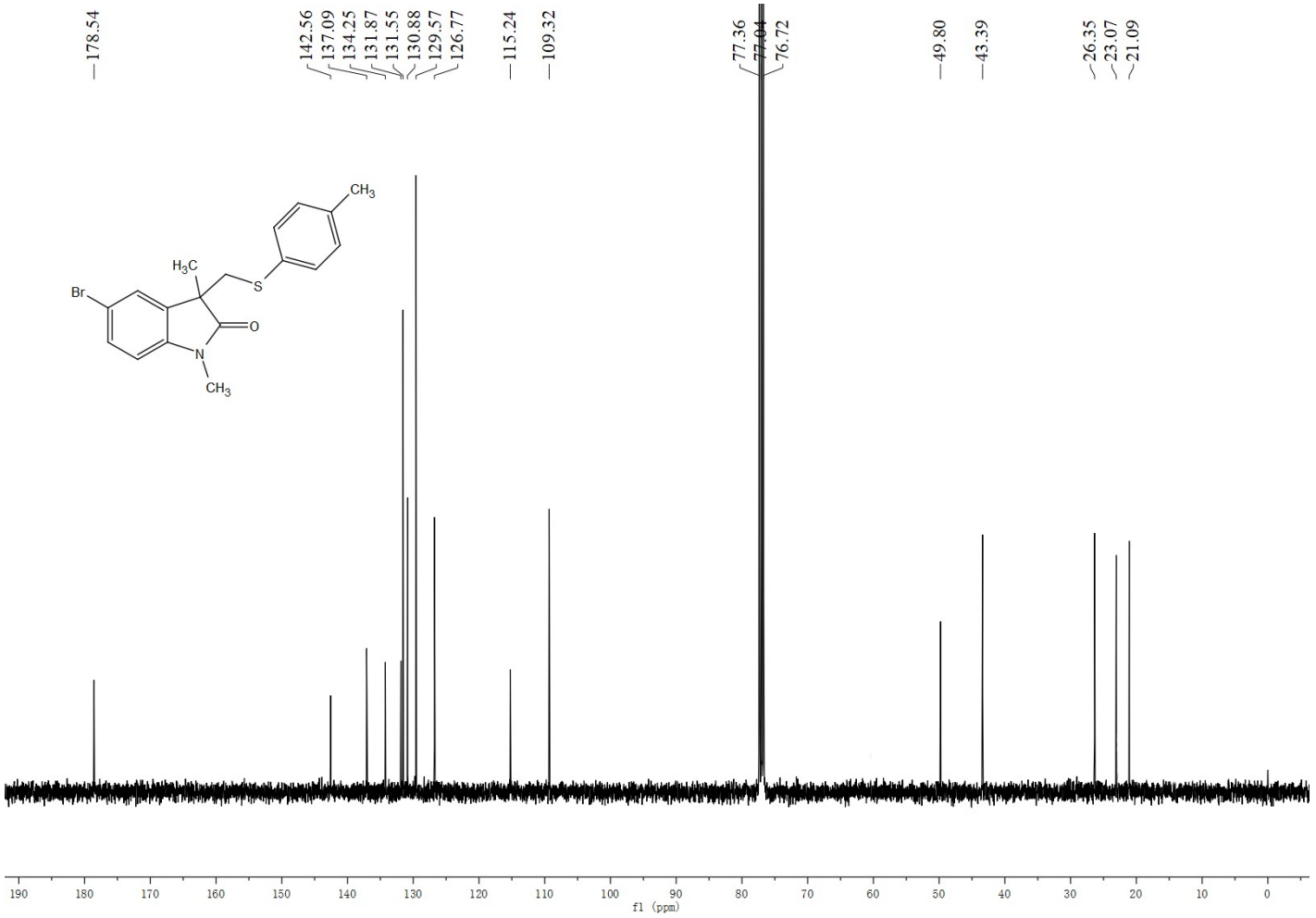

FF-171-2 253 (2.308)
1: TOF MS ES+
9.85e6
100
%
0
362.0212
364.0193
363.0238
365.0218
366.0175
352.0175
353.0180
354.2809
356.9946
358.8802
361.9608
367.0175
369.3442
371.1551
371.9005
373.9080
m/z
351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374

5-Bromo-1,3-dimethyl-3-((*p*-tolylthio)methyl)indolin-2-one (4b)

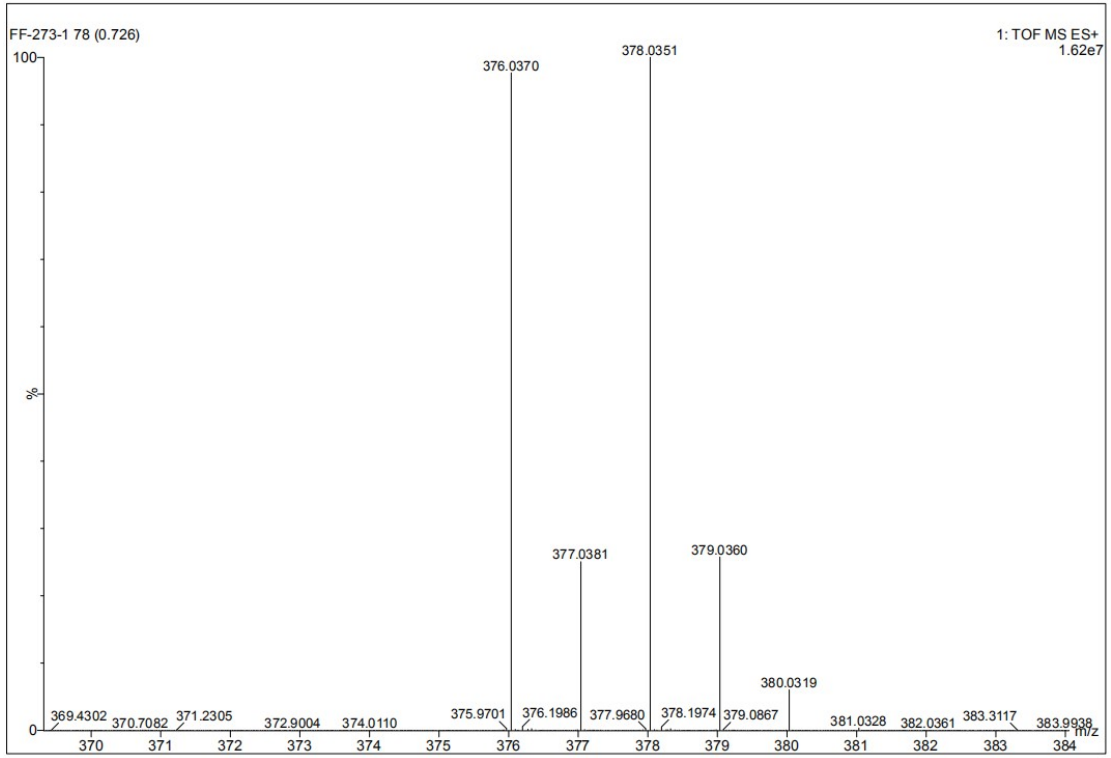
^{1}H NMR (400 MHz, $CDCl_3$)



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

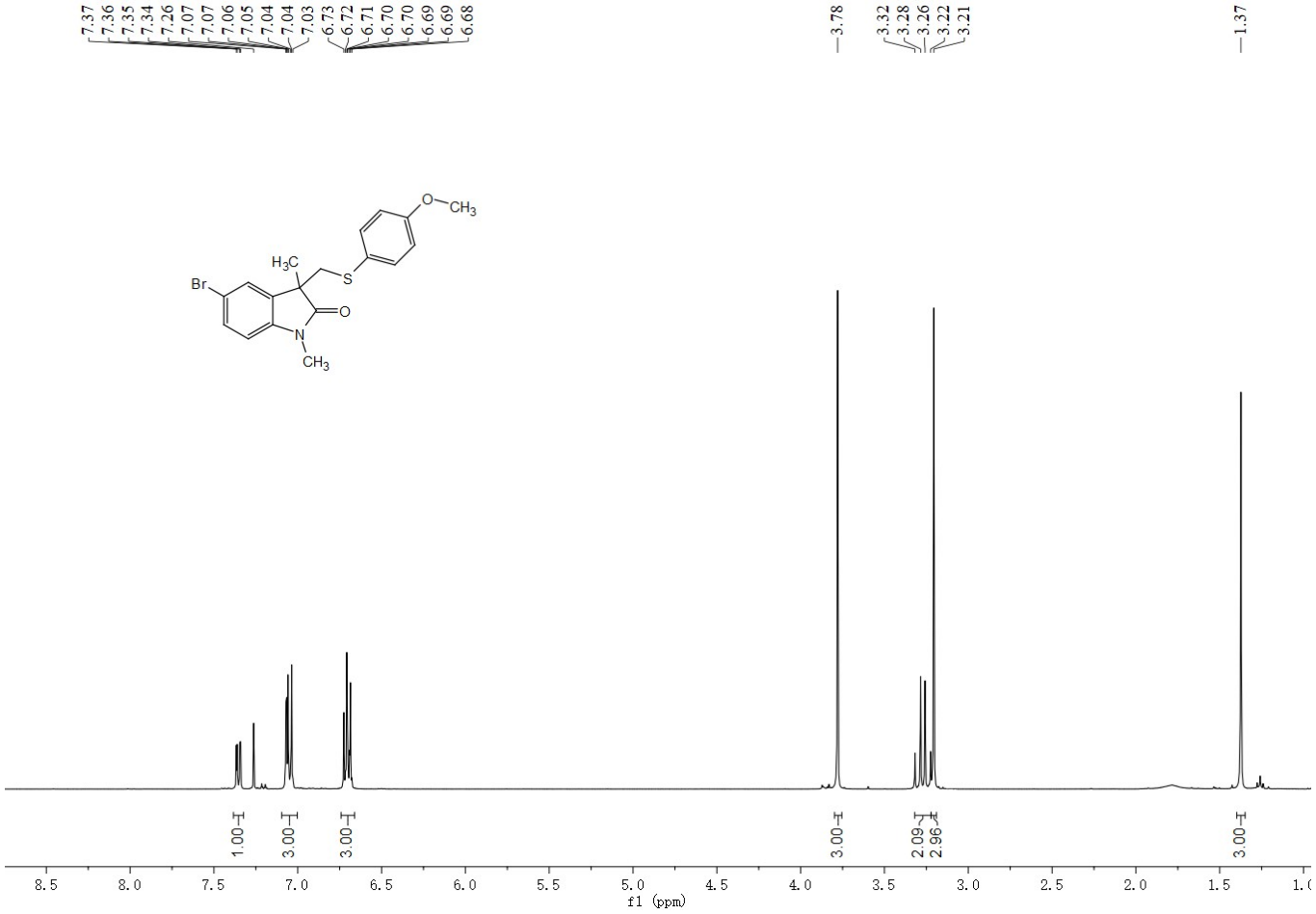


HRMS (ESI)

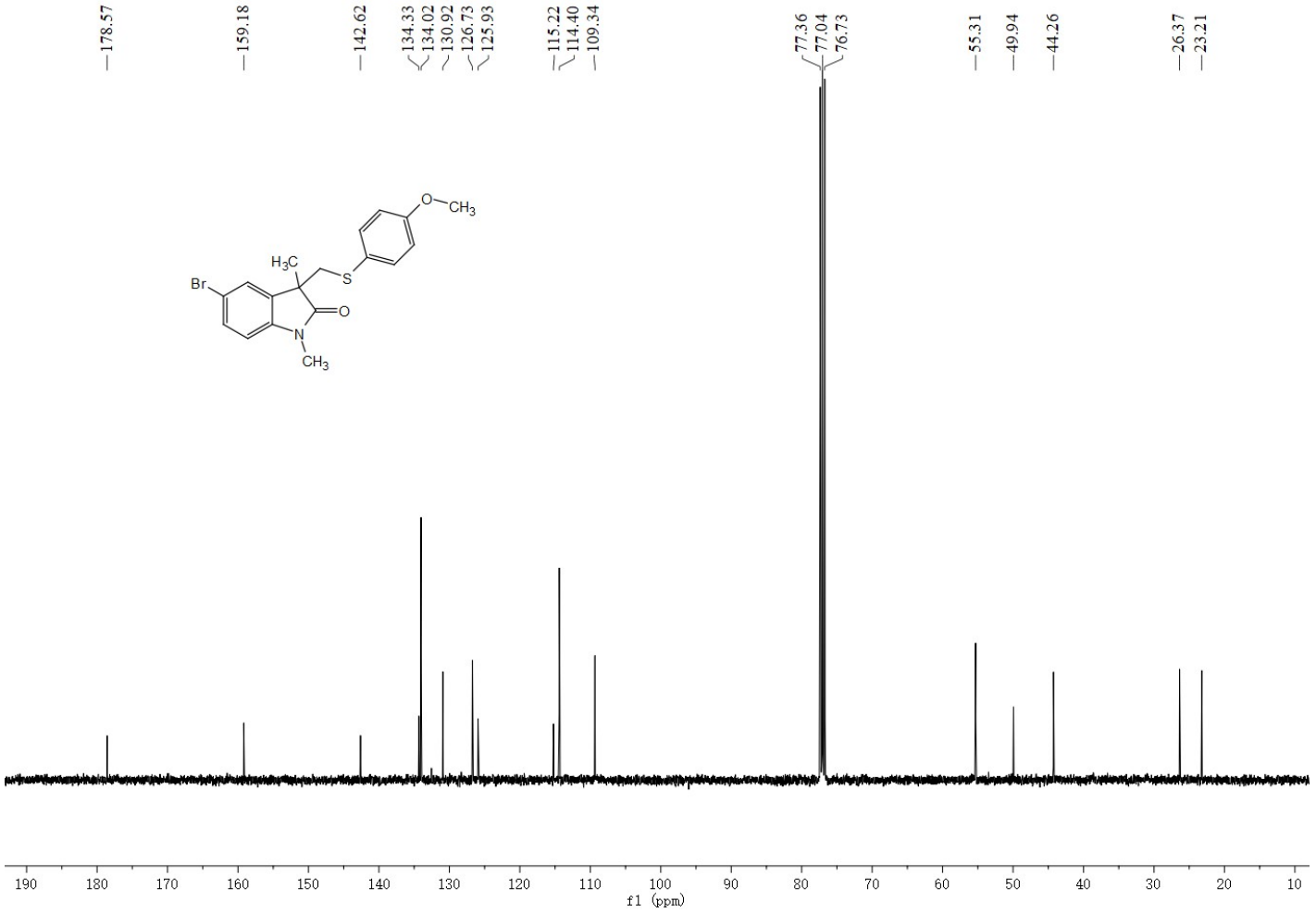

FF-273-1 78 (0.726)
1: TOF MS ES+
1.62e7
100
%
0
376.0370
378.0351
377.0381
379.0360
380.0319
369.4302
370.7082
371.2305
372.9004
374.0110
375.9701
376.1986
377.9680
378.1974
379.0867
381.0328
382.0361
383.3117
383.9938
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
m/z

5-Bromo-3-(((4-methoxyphenyl)thio)methyl)-1,3-dimethylindolin-2-one (4c)

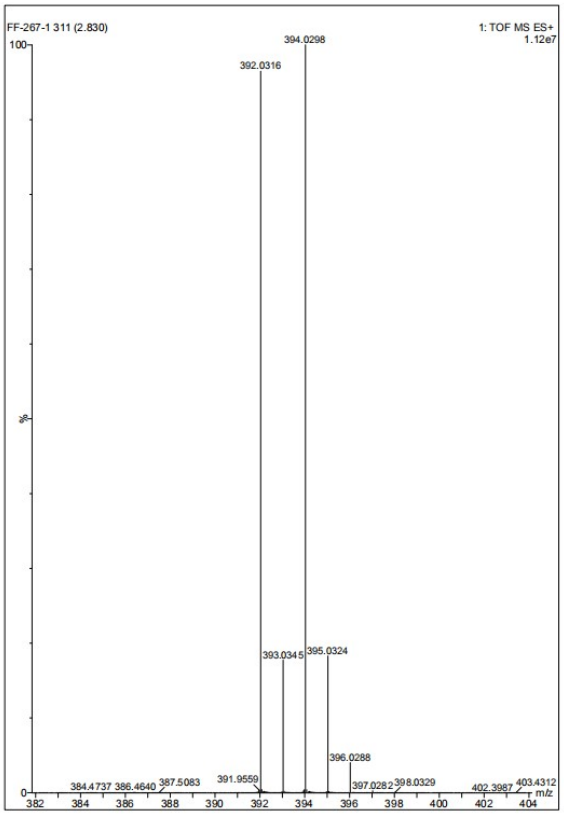
^{1}H NMR (400 MHz, $CDCl_3$)



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

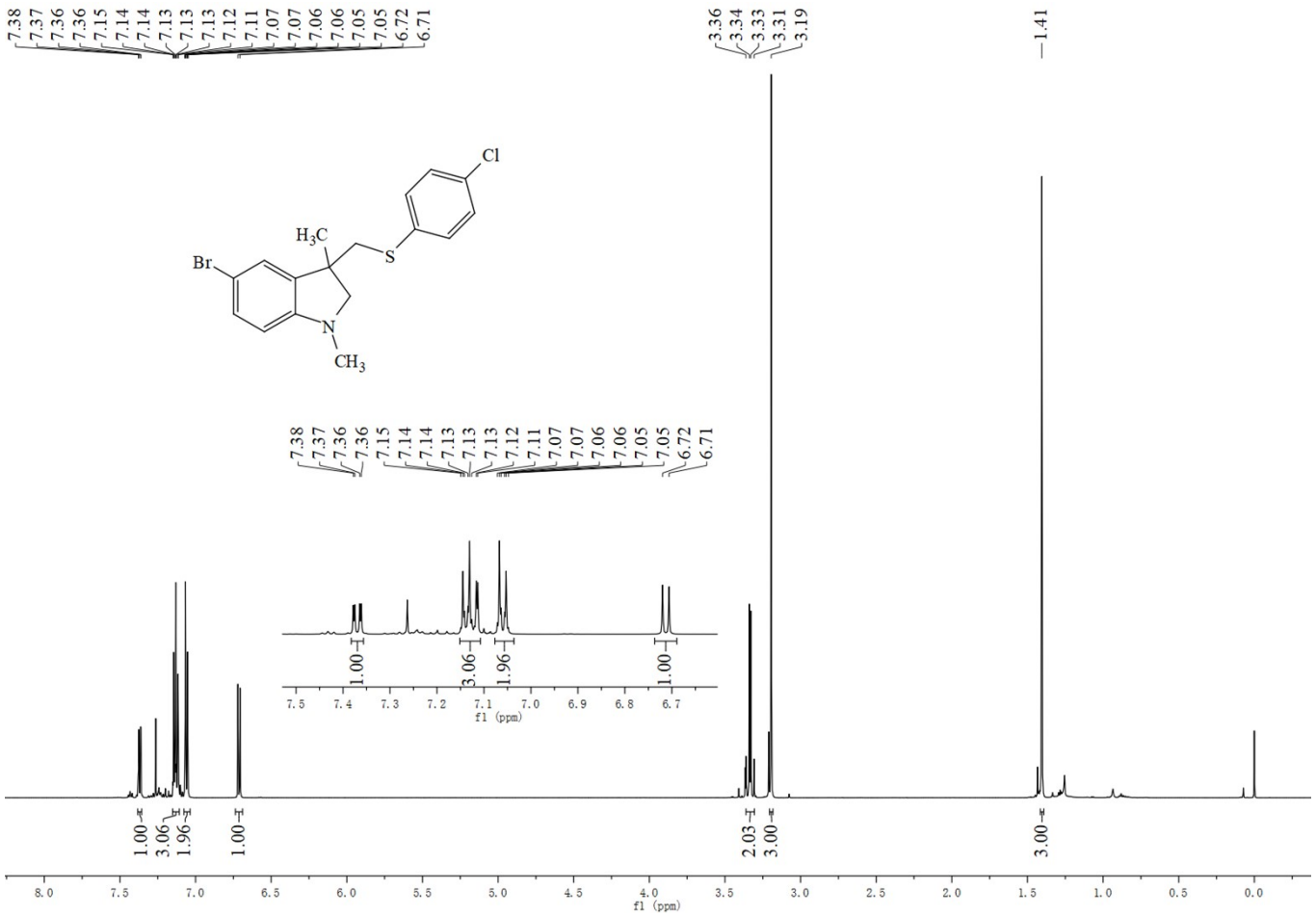


HRMS (ESI)

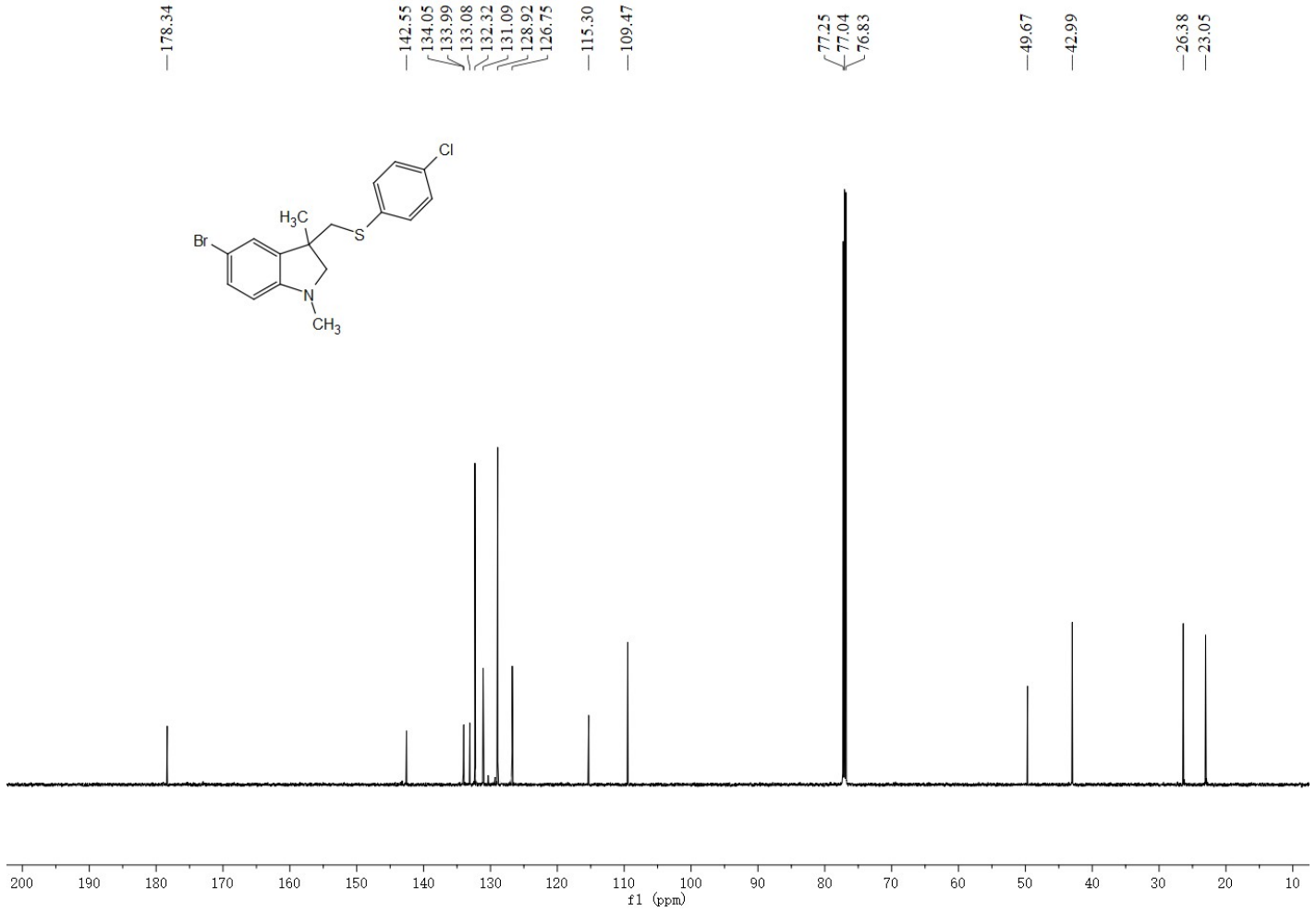

FF-267-1 311 (2.830)
1: TOF MS ES+
1.12e7
100
%
0
394.0298
392.0316
393.0345
395.0324
396.0288
384.4737
386.4640
387.5083
391.9559
397.0282
398.0329
402.3987
403.4312
m/z
382
384
386
388
390
392
394
396
398
400
402
404

5-Bromo-3-(((4-chlorophenyl)thio)methyl)-1,3-dimethylindolin-2-one (4d)

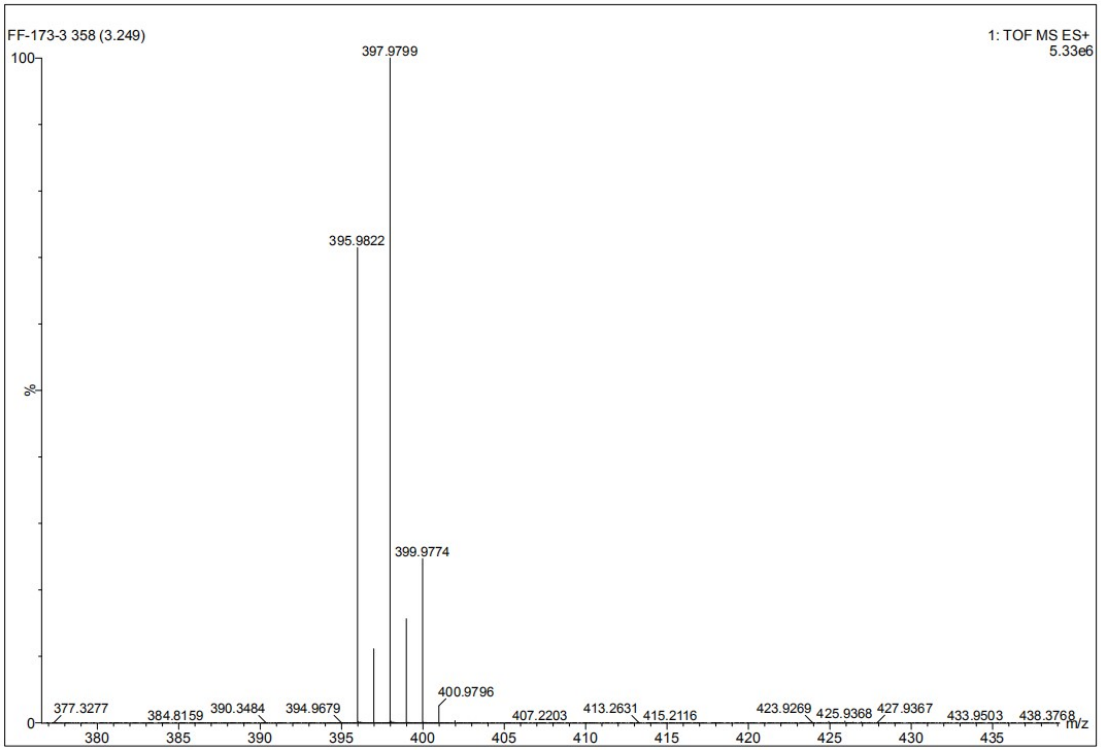
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

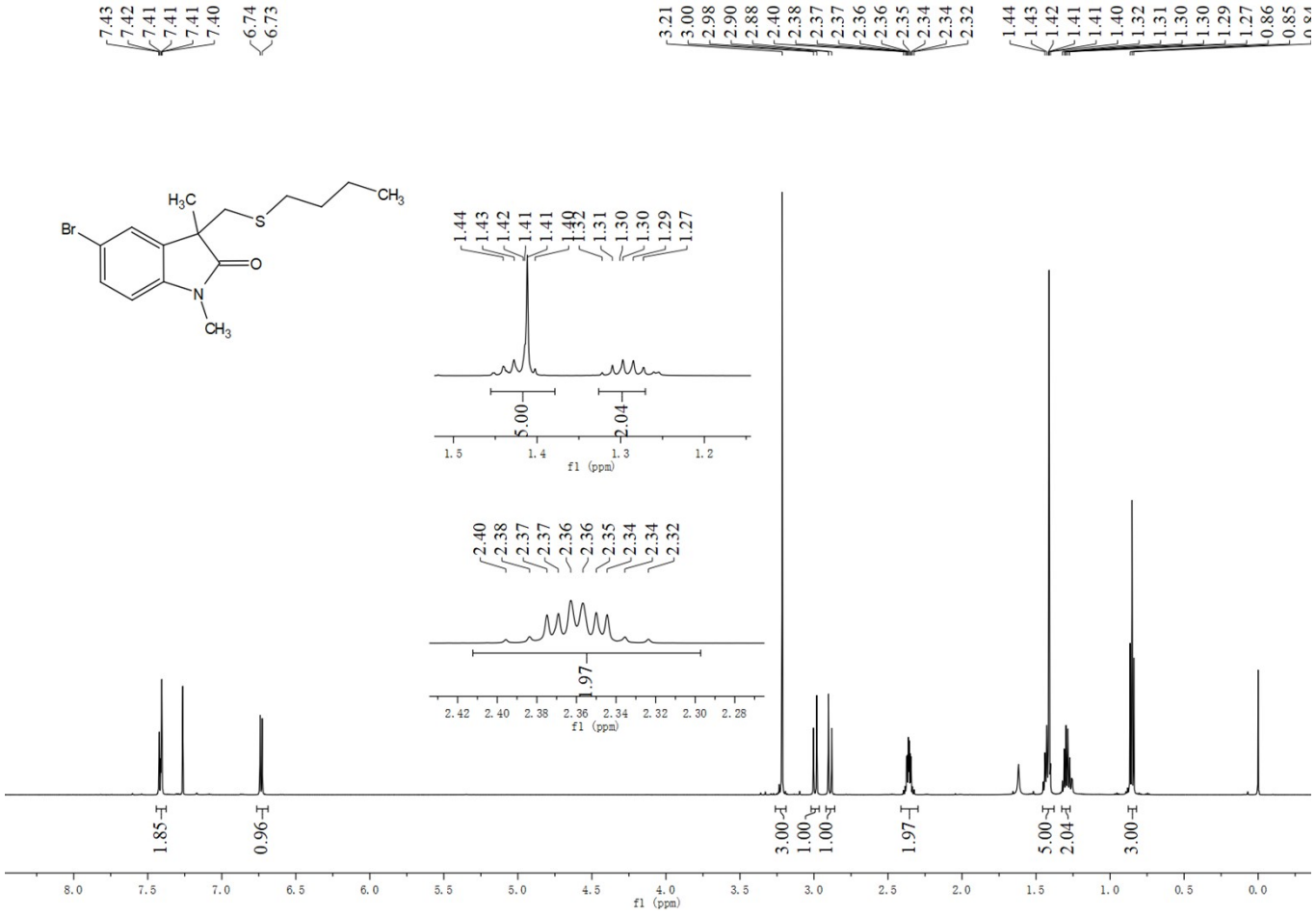


HRMS (ESI)

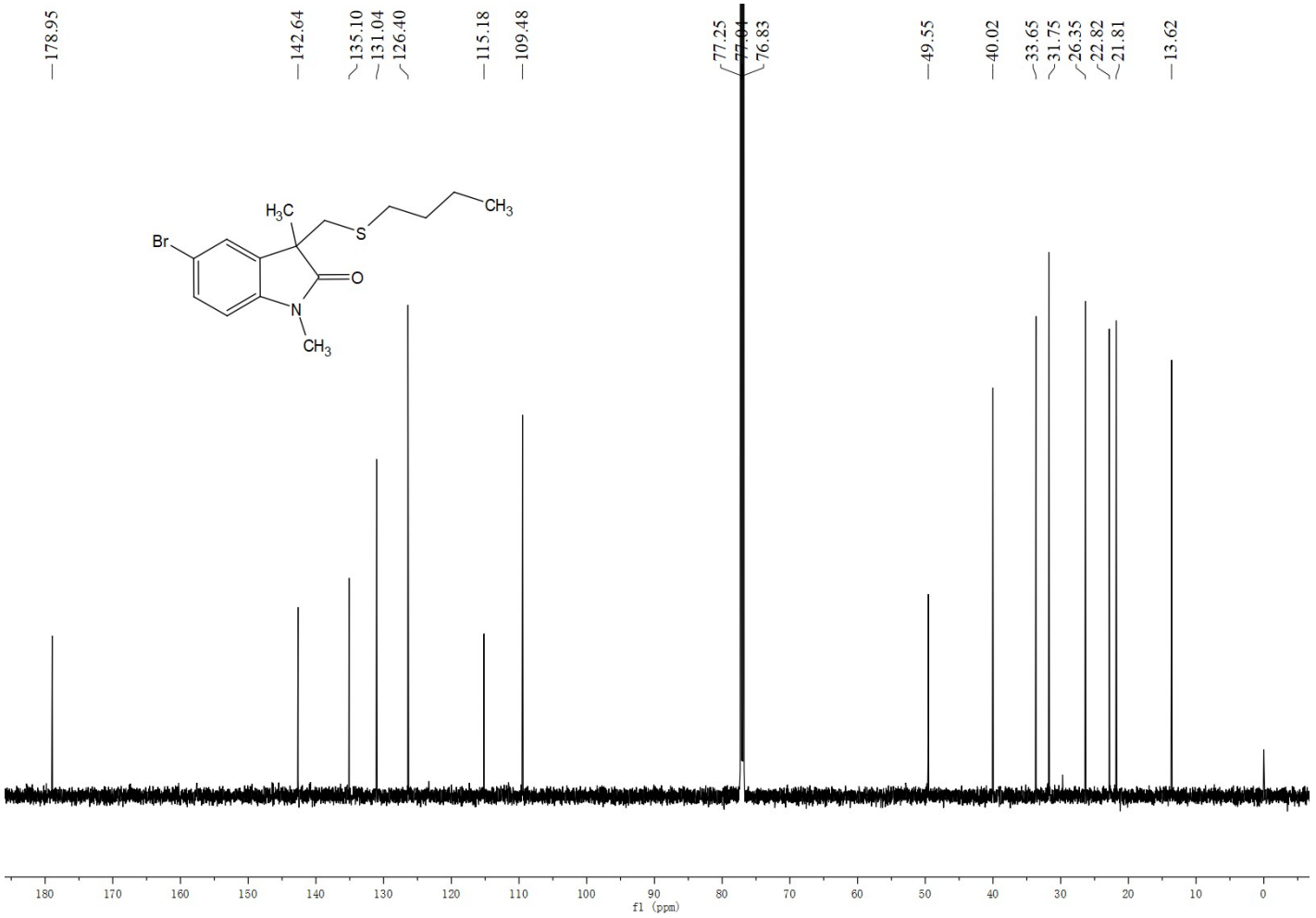

FF-173-3 358 (3.249)
1: TOF MS ES+
5.33e6
100
%
0
397.9799
395.9822
399.9774
400.9796
377.3277
384.8159
390.3484
394.9679
407.2203
413.2631
415.2116
423.9269
425.9368
427.9367
433.9503
438.3768
380
385
390
395
400
405
410
415
420
425
430
435
m/z

5-Bromo-3-((butylthio)methyl)-1,3-dimethylindolin-2-one (4e)

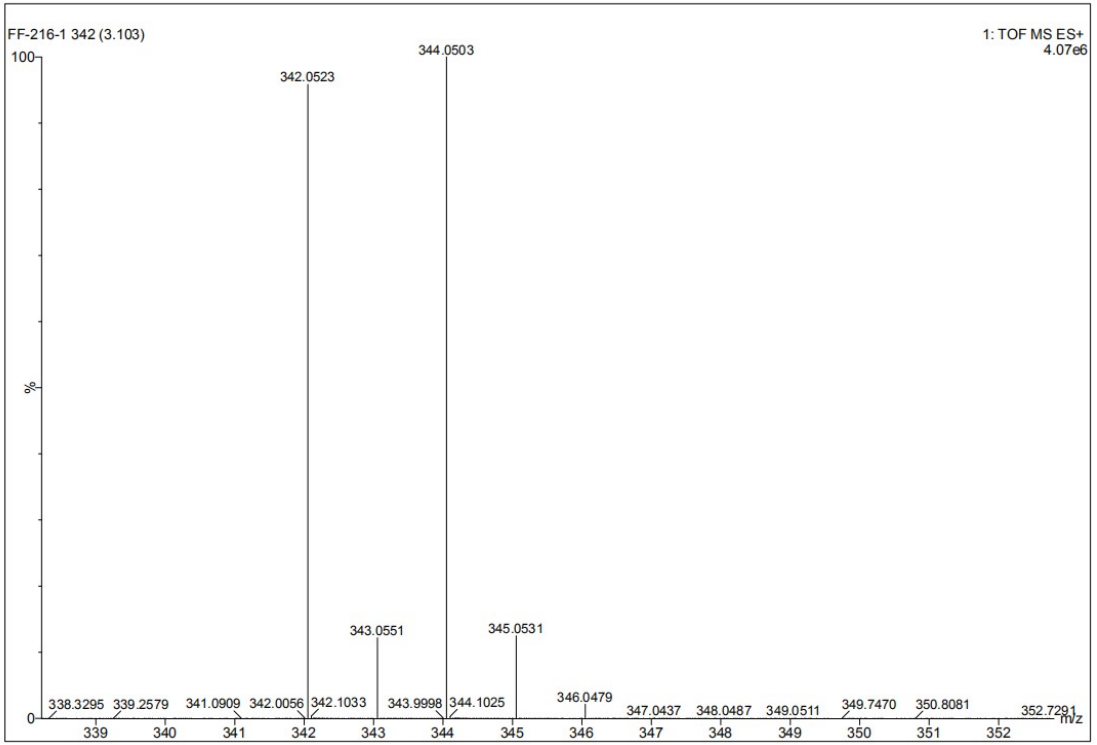
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

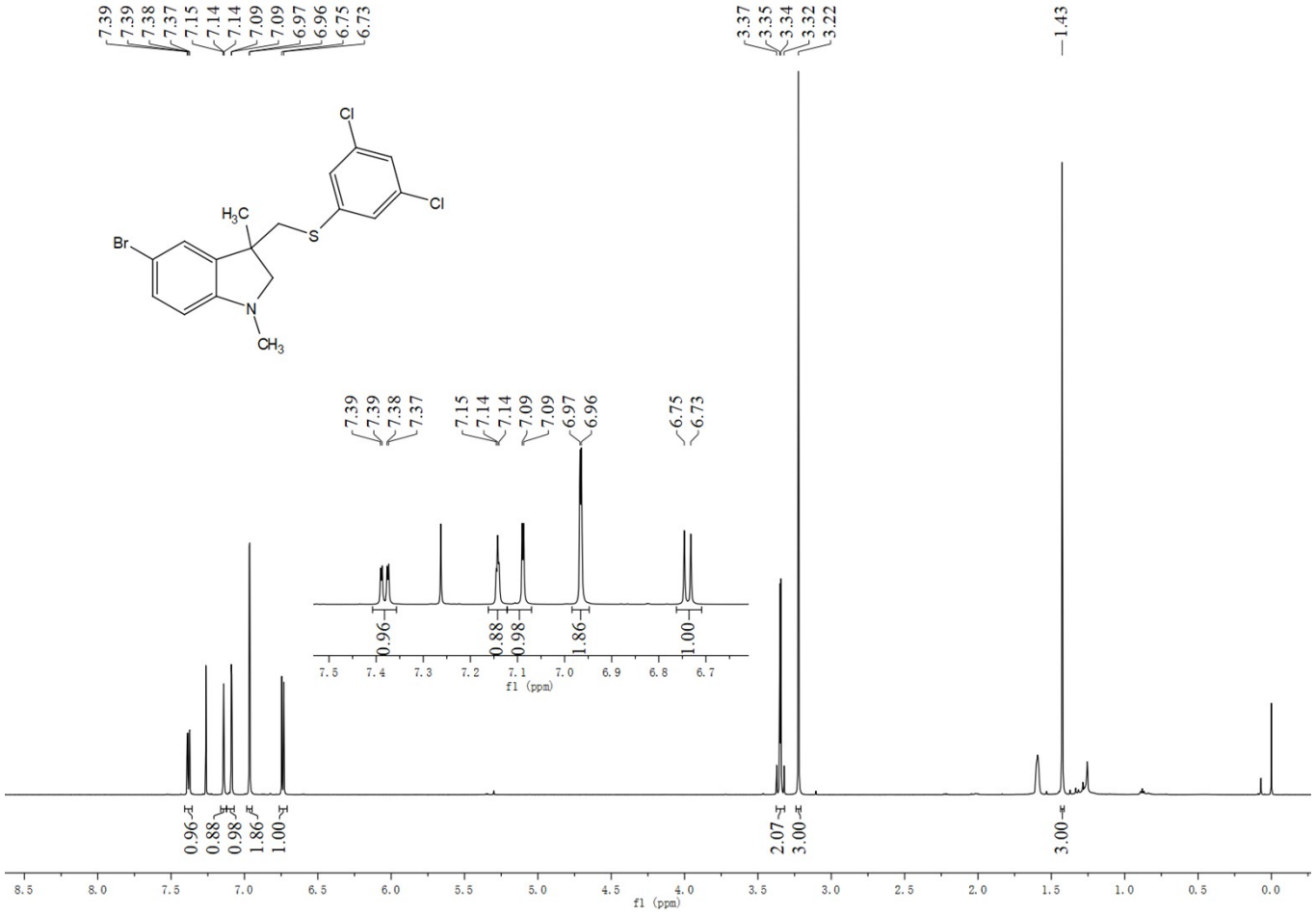


HRMS (ESI)

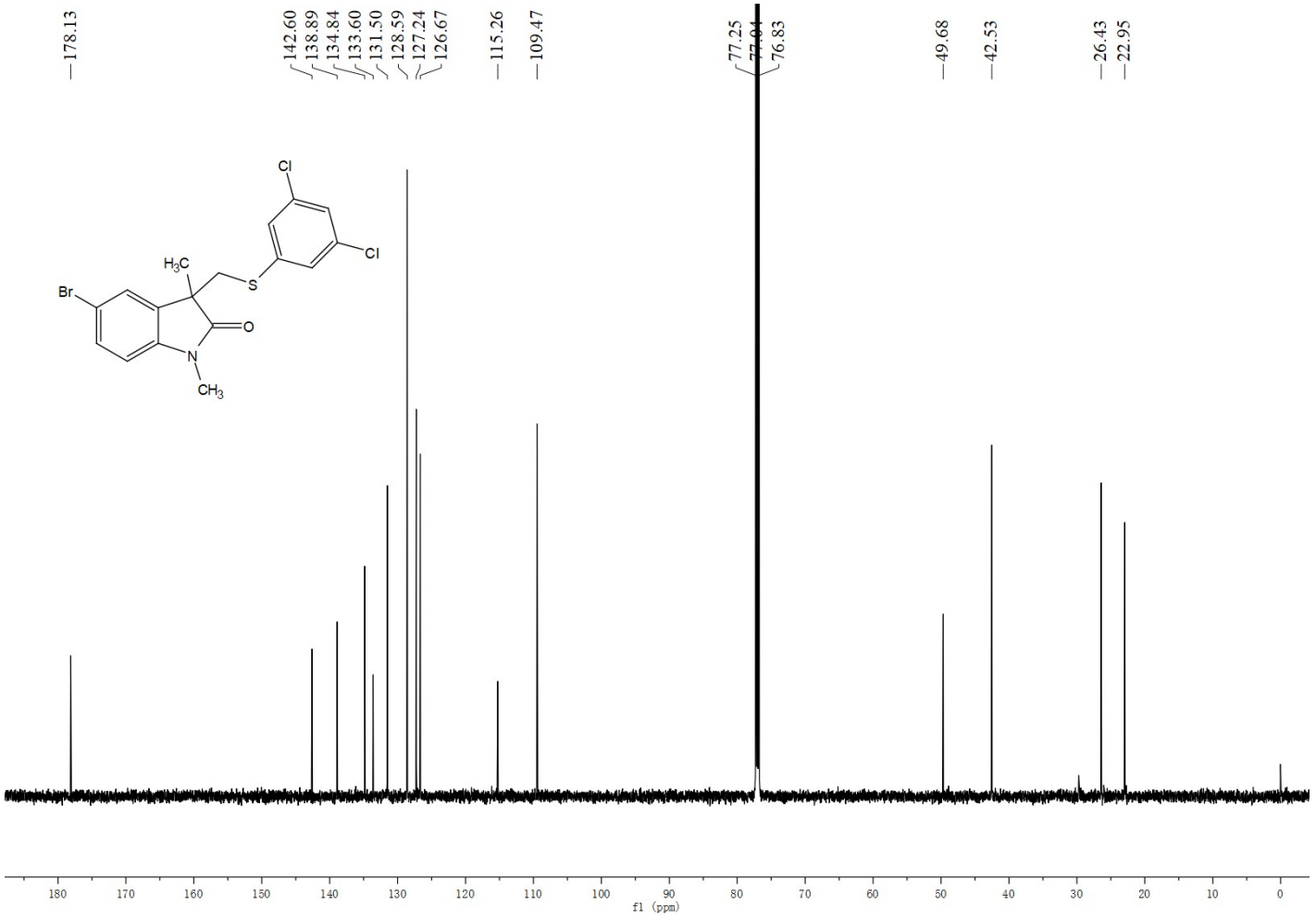

FF-216-1 342 (3.103)
1: TOF MS ES+
4.07e6
100
%
0
344.0503
342.0523
343.0551
345.0531
338.3295
339.2579
341.0909
342.0056
342.1033
343.9998
344.1025
346.0479
347.0437
348.0487
349.0511
349.7470
350.8081
352.7291
339
340
341
342
343
344
345
346
347
348
349
350
351
352
m/z

5-Bromo-3-(((3,5-dichlorophenyl)thio)methyl)-1,3-dimethylindolin-2-one (4f)

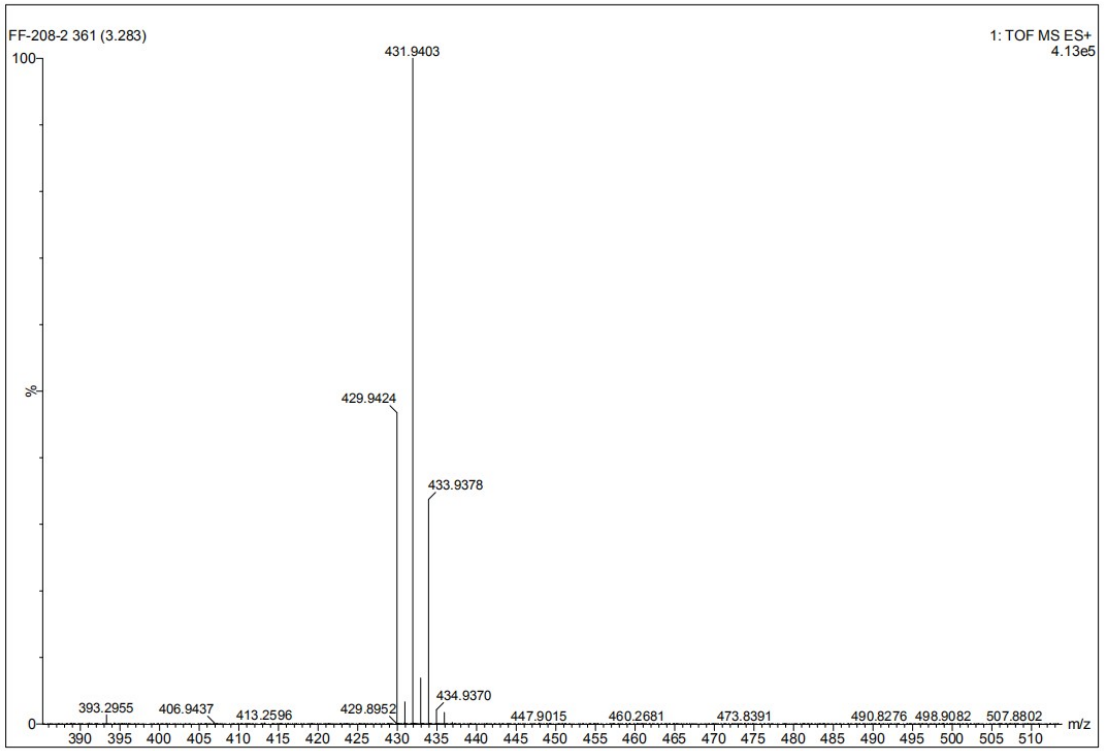
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

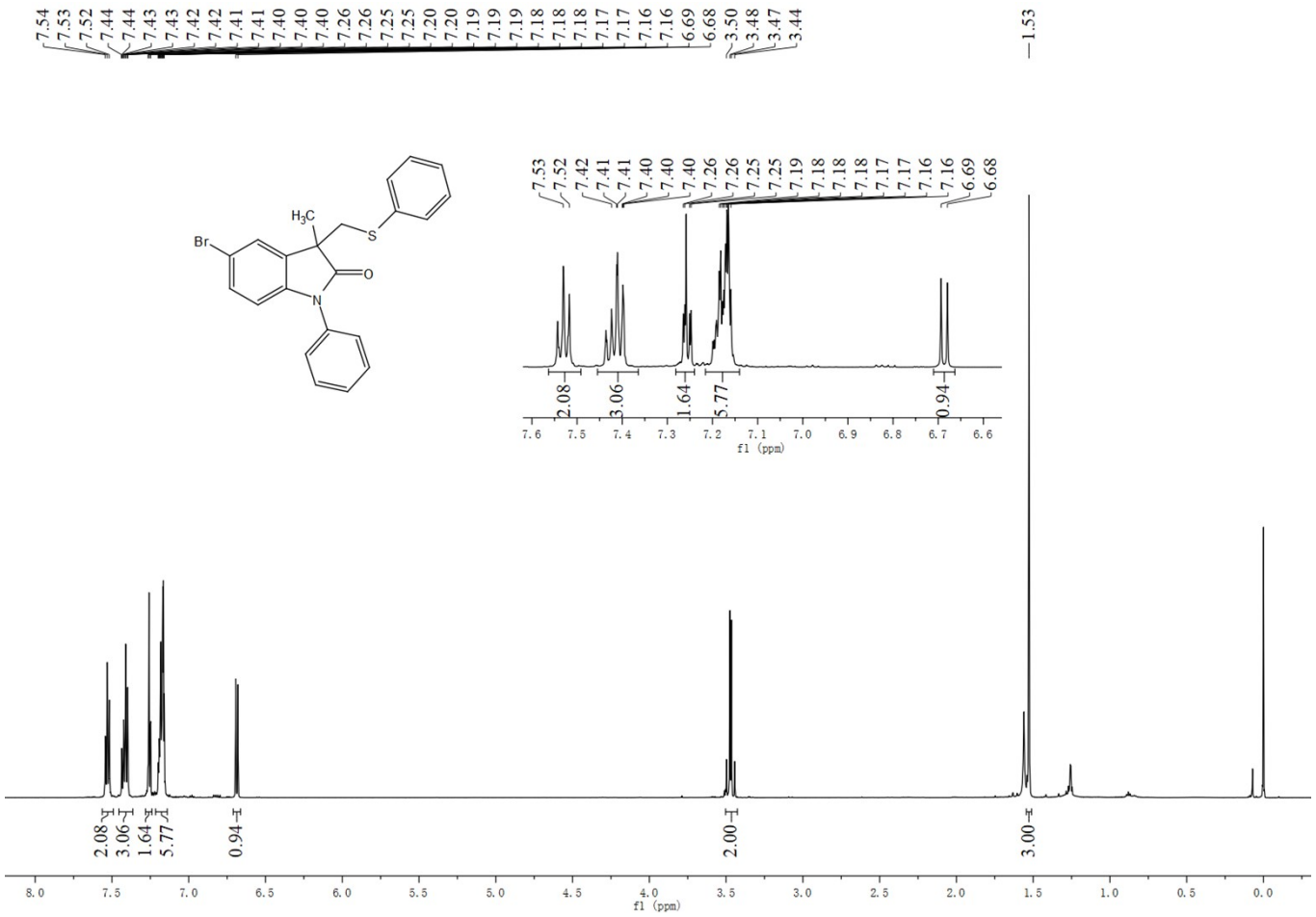


HRMS (ESI)

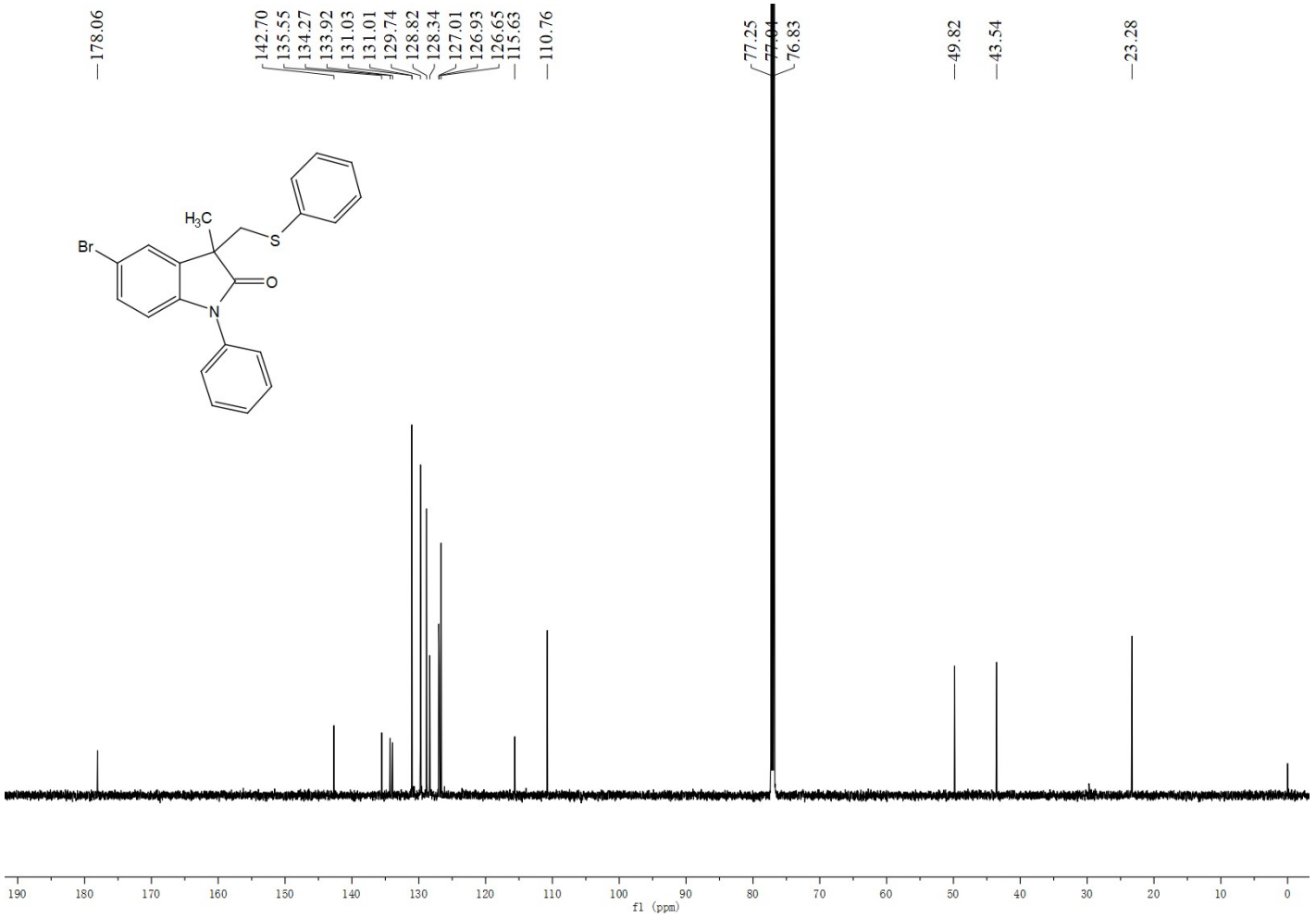

FF-208-2 361 (3.283)
1: TOF MS ES+
4.13e5
100
%
0
431.9403
429.9424
433.9378
434.9370
393.2955
406.9437
413.2596
429.8952
447.9015
460.2681
473.8391
490.8276
498.9082
507.8802
m/z
390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510

5-Bromo-3-methyl-1-phenyl-3-((phenylthio)methyl)indolin-2-one (4g)

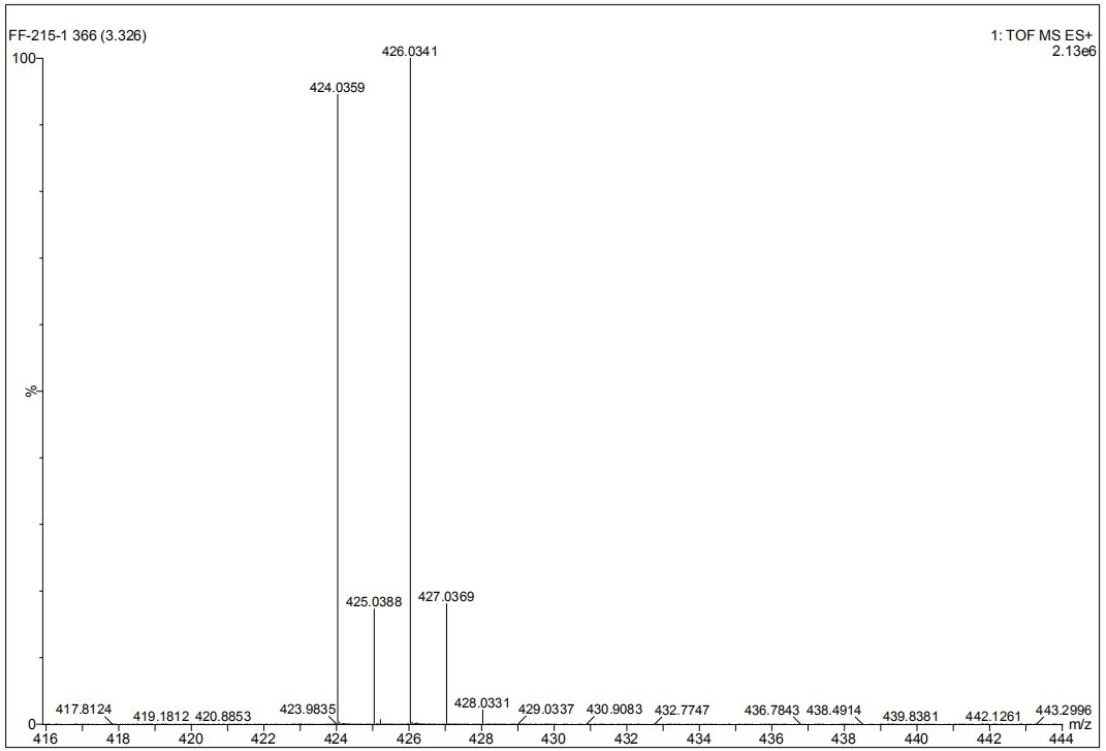
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

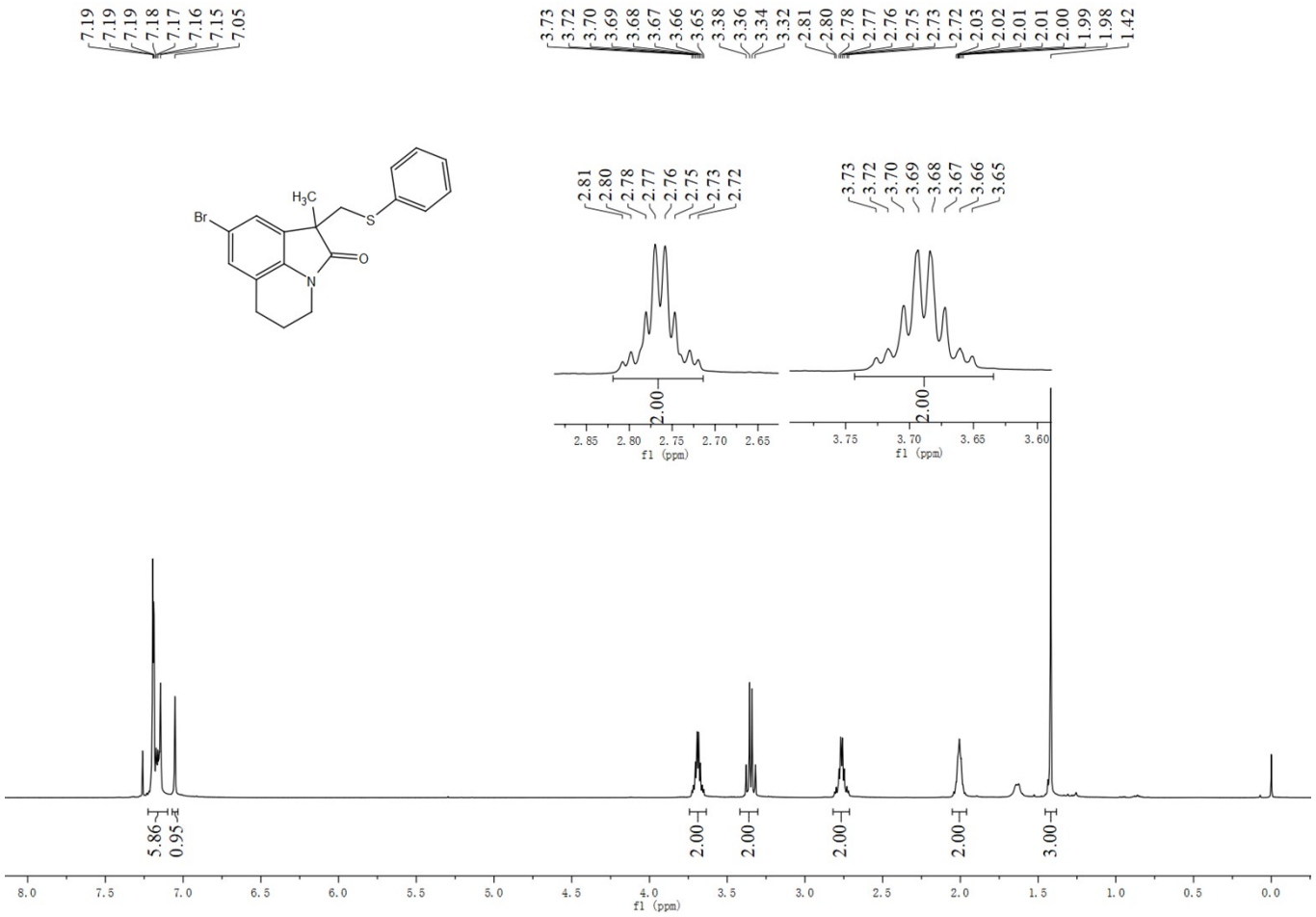


HRMS (ESI)

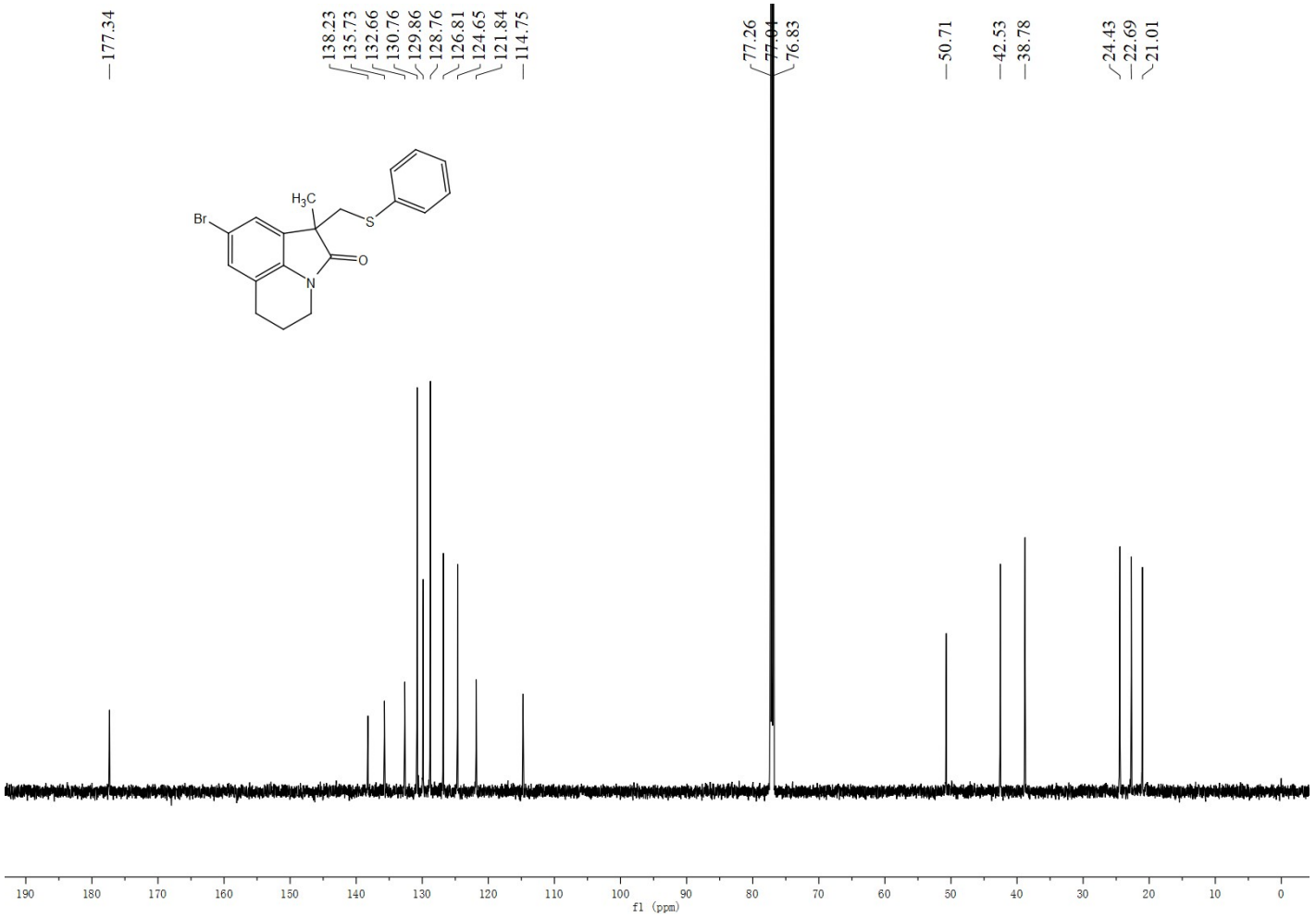

FF-215-1 366 (3.326)
1: TOF MS ES+
2.13e6
100
%
0
426.0341
424.0359
425.0388
427.0369
417.8124
419.1812
420.8853
423.9835
428.0331
429.0337
430.9083
432.7747
436.7843
438.4914
439.8381
442.1261
443.2996
m/z
416
418
420
422
424
426
428
430
432
434
436
438
440
442
444

8-Bromo-1-methyl-1-((phenylthio)methyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-iJ]quinolin-2(1*H*)-one (4h)

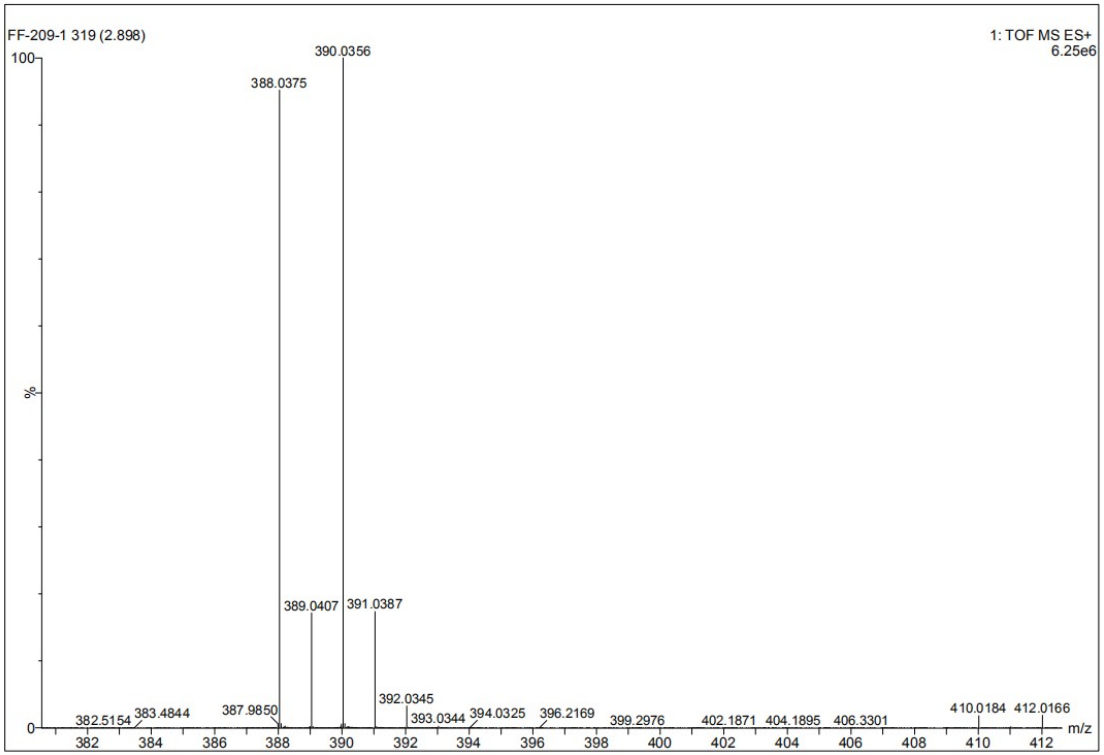
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

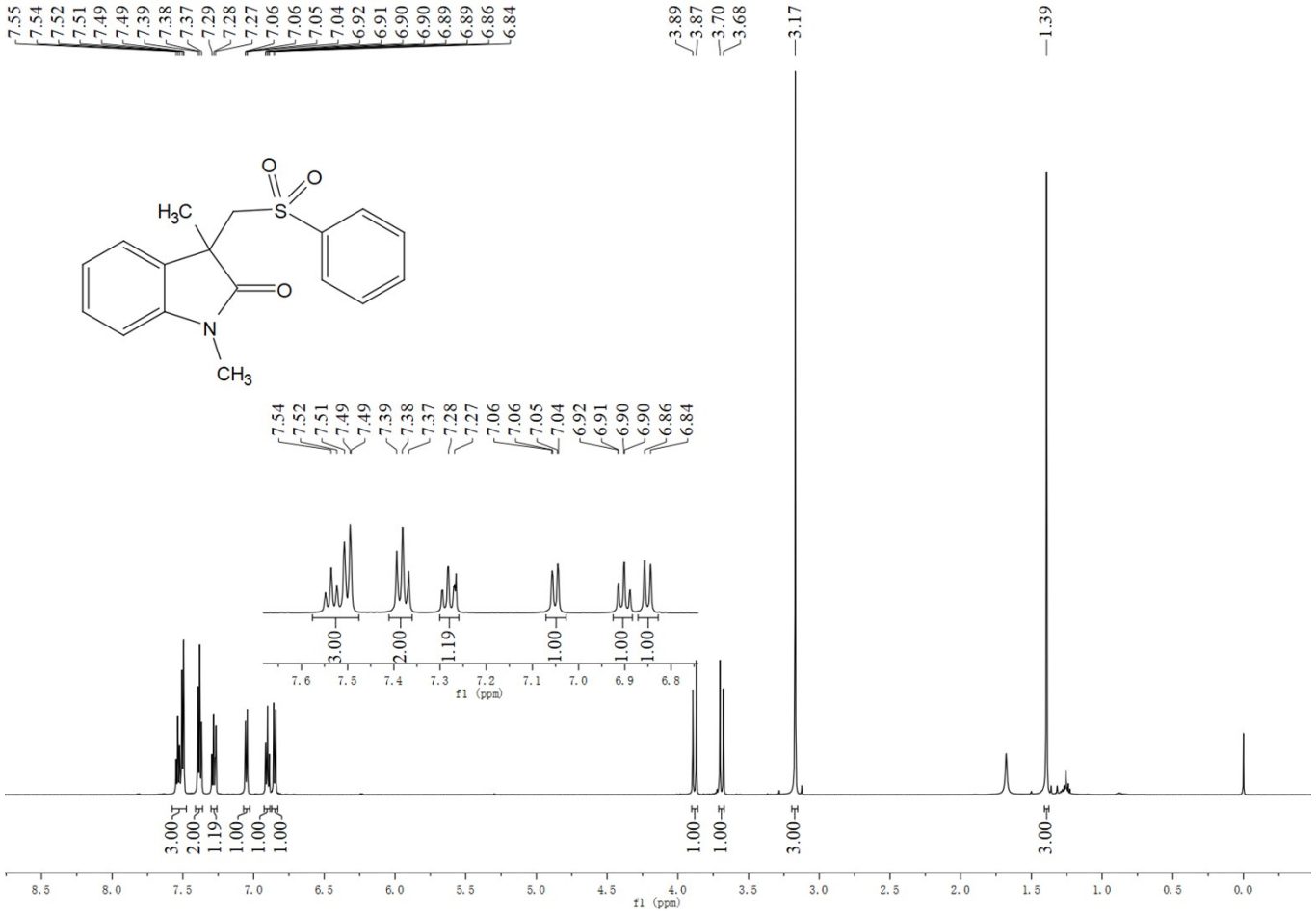


HRMS (ESI)

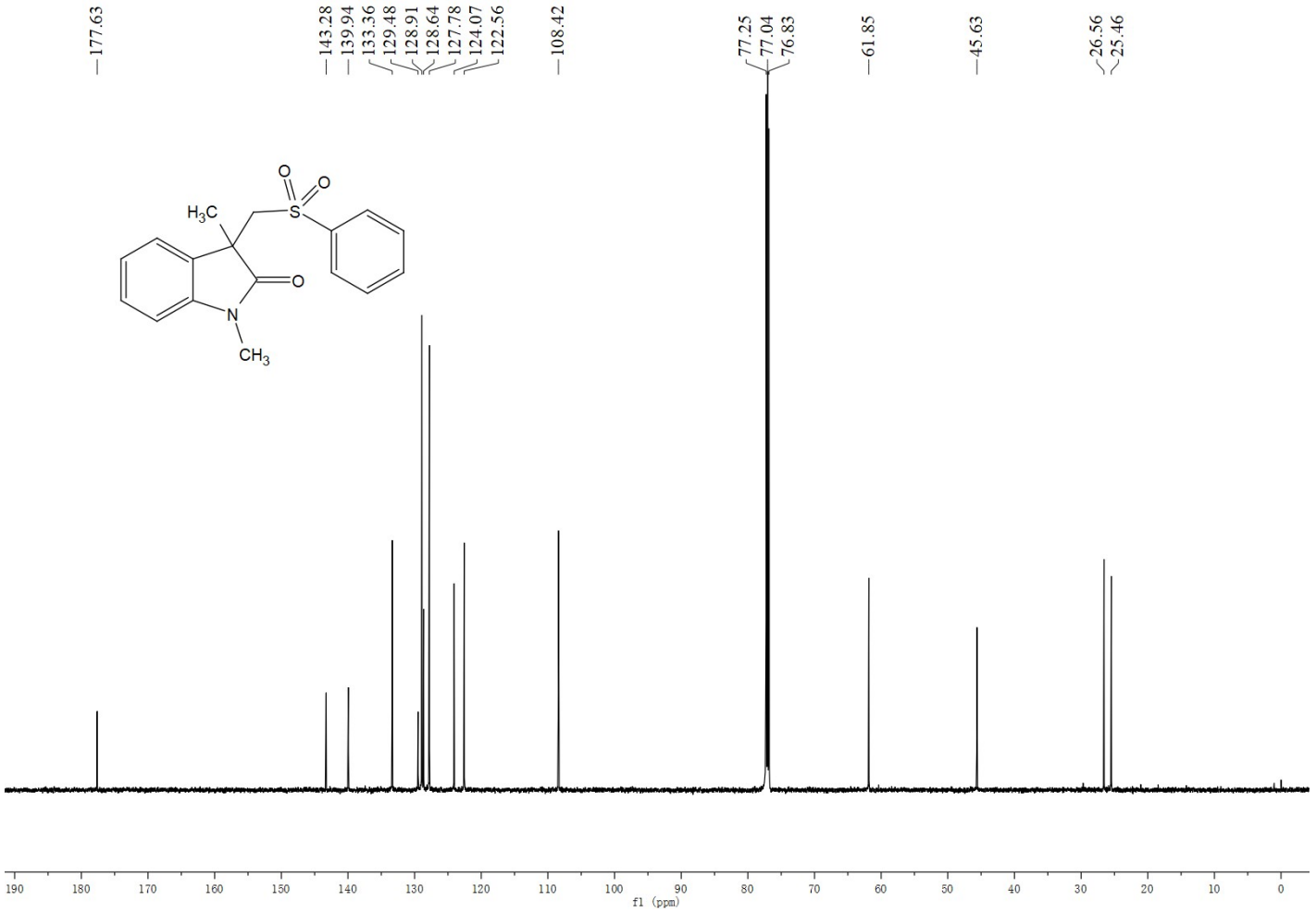

FF-209-1 319 (2.898)
1: TOF MS ES+
6.25e6
100
%
0
390.0356
388.0375
389.0407
391.0387
392.0345
382.5154
383.4844
387.9850
393.0344
394.0325
396.2169
399.2976
402.1871
404.1895
406.3301
410.0184
412.0166
m/z
382
384
386
388
390
392
394
396
398
400
402
404
406
408
410
412

1,3-Dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (5)

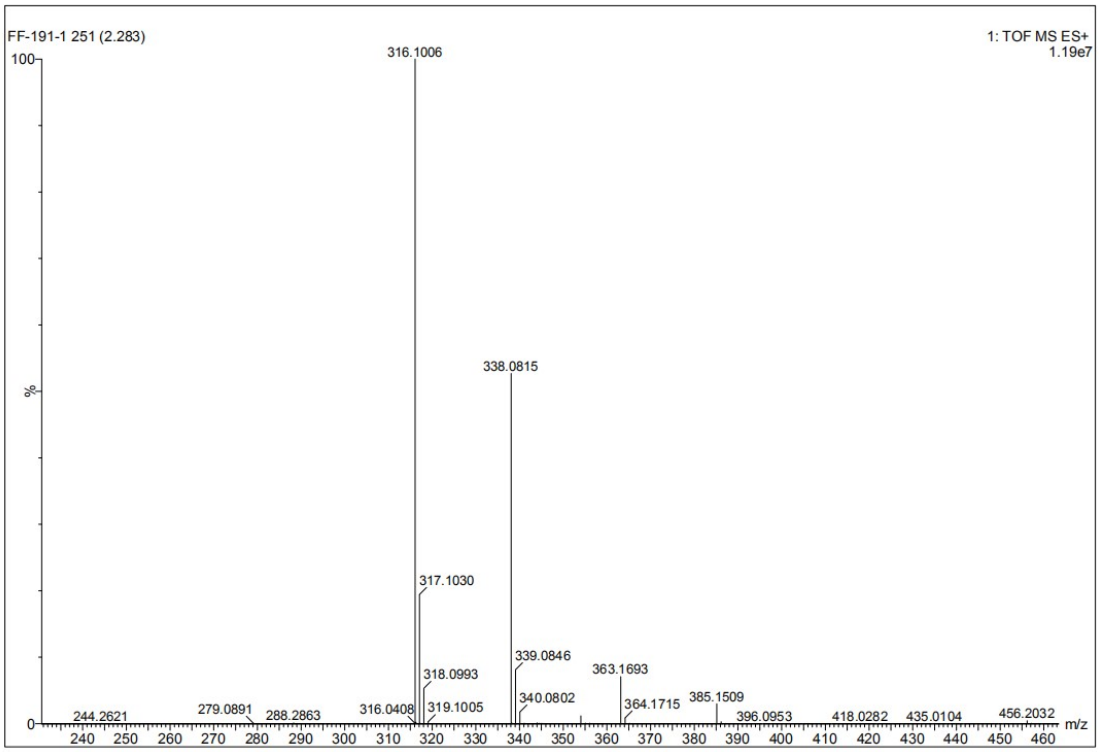
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

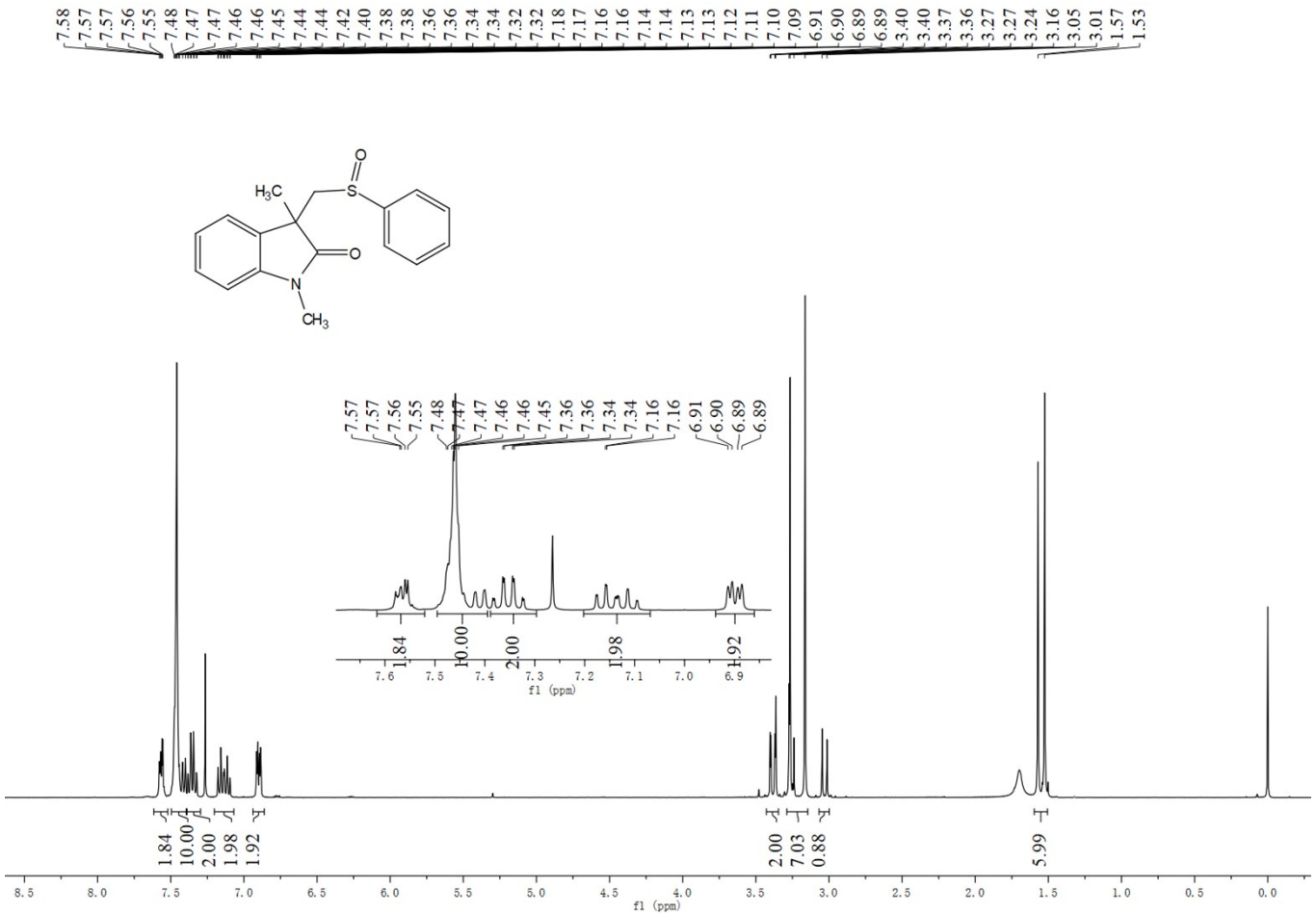


HRMS (ESI)

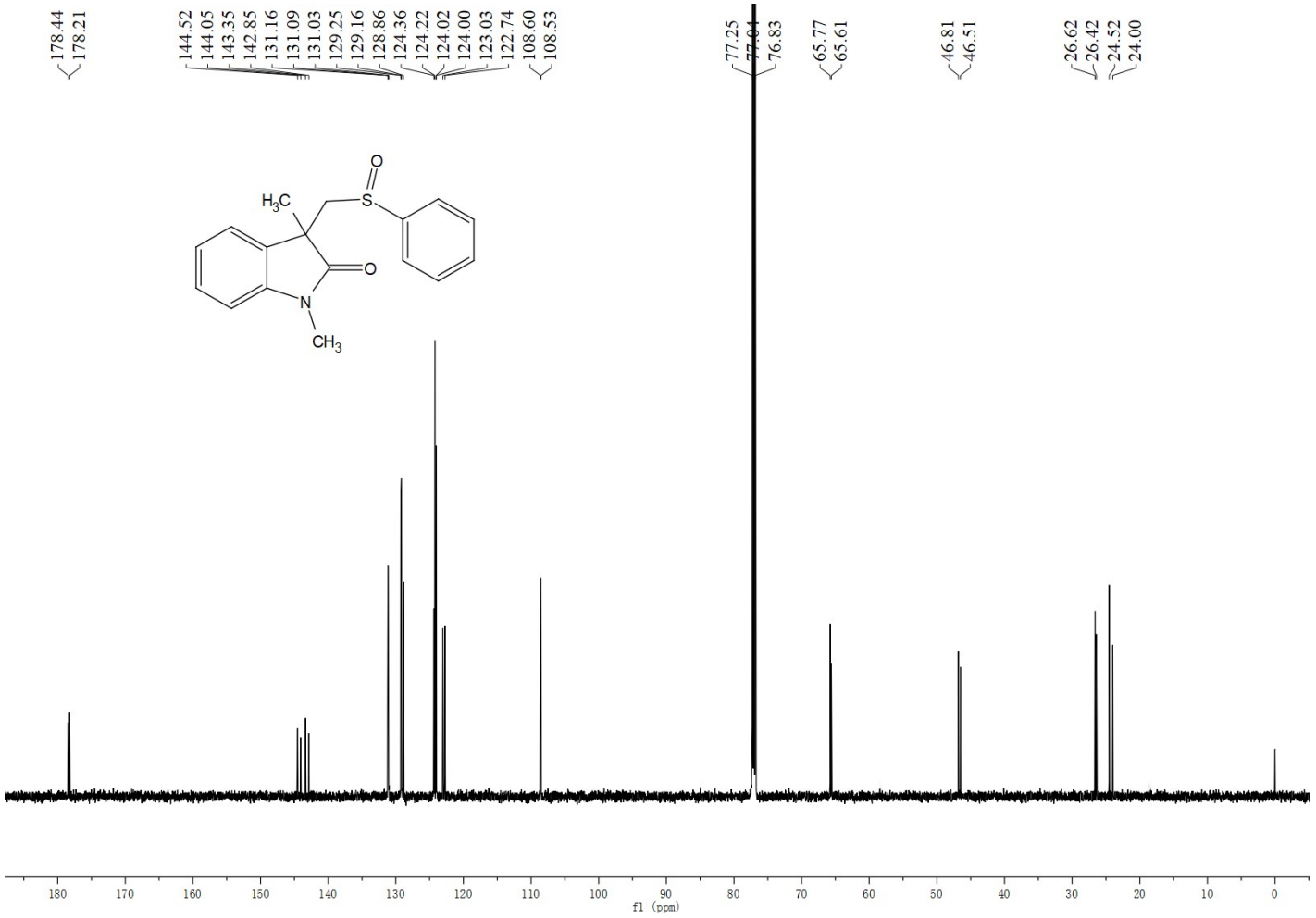

FF-191-1 251 (2.283)
1: TOF MS ES+
1.19e7
100
%
0
316.1006
338.0815
317.1030
339.0846
318.0993
363.1693
340.0802
364.1715
385.1509
319.1005
316.0408
279.0891
288.2863
244.2621
396.0953
418.0282
435.0104
456.2032
240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460
m/z

1,3-Dimethyl-3-((phenylsulfinyl)methyl)indolin-2-one (6)

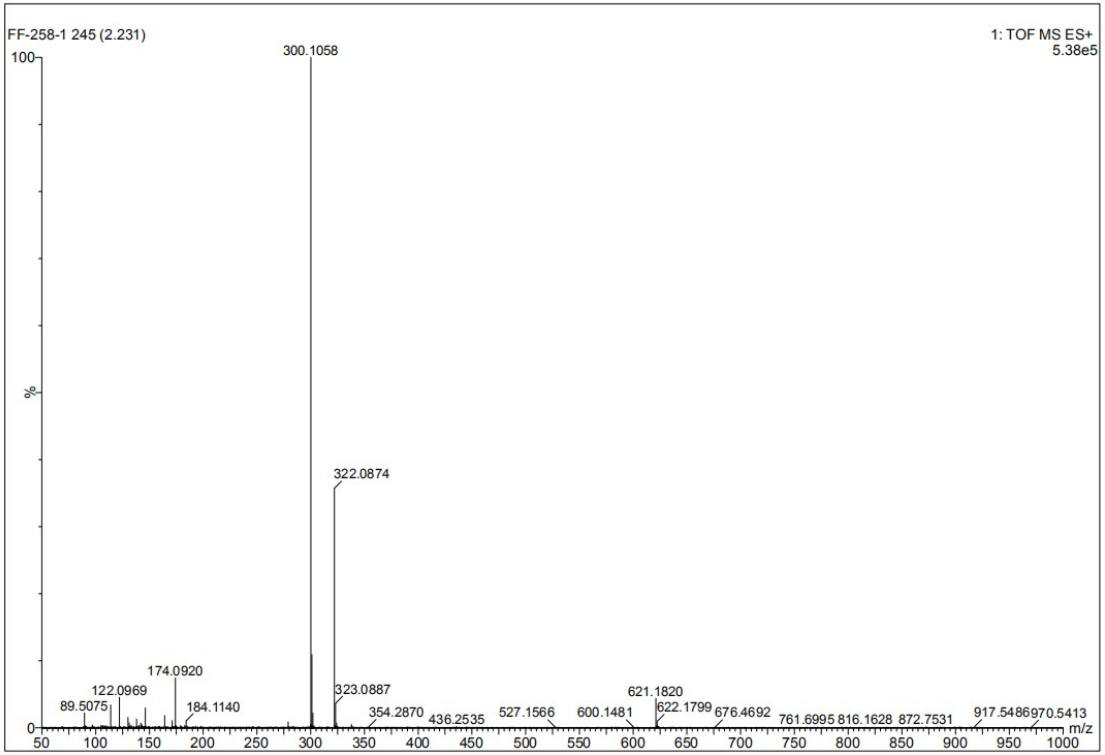
^{1}H NMR (400 MHz, $CDCl_3$)



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

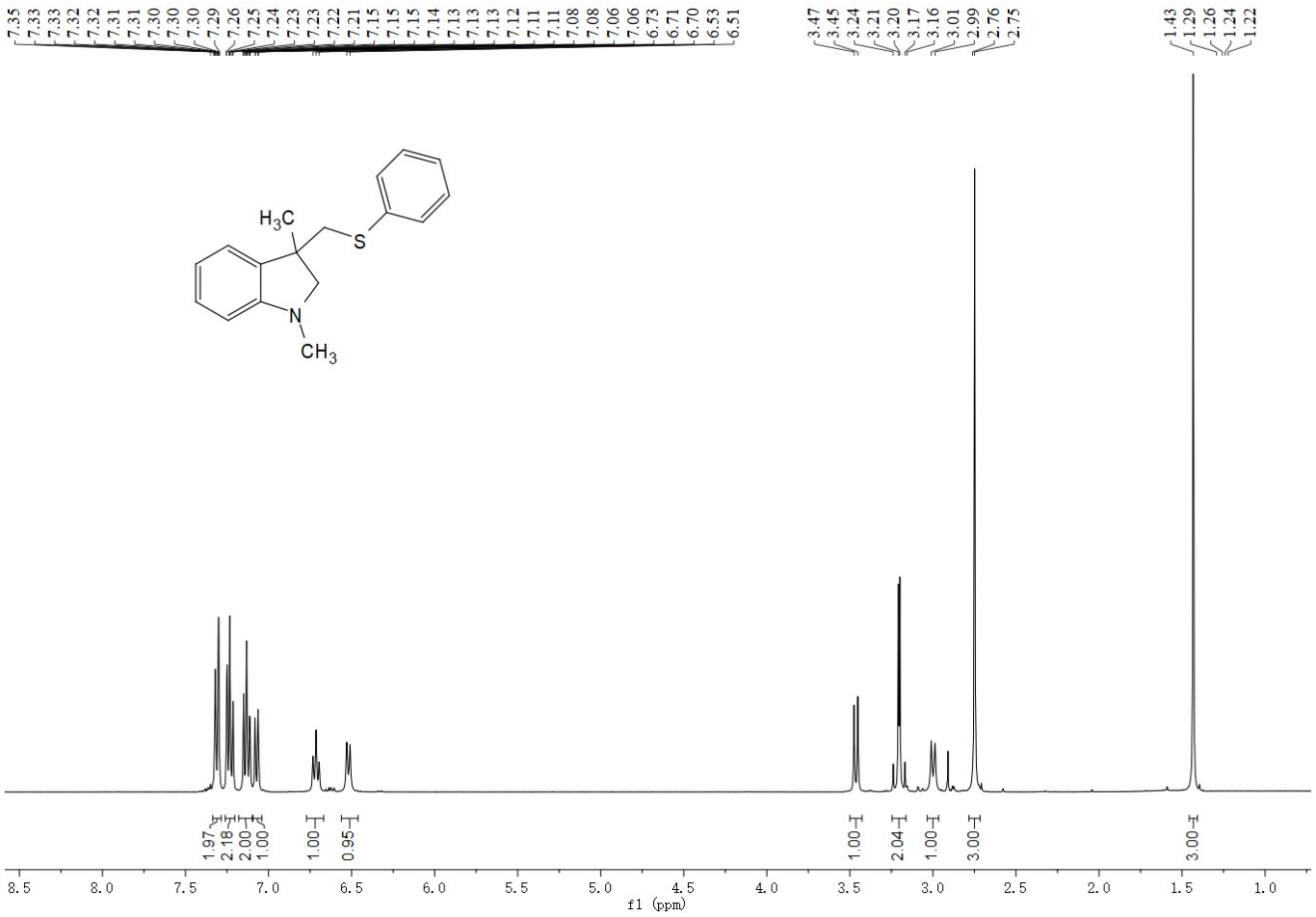


HRMS (ESI)

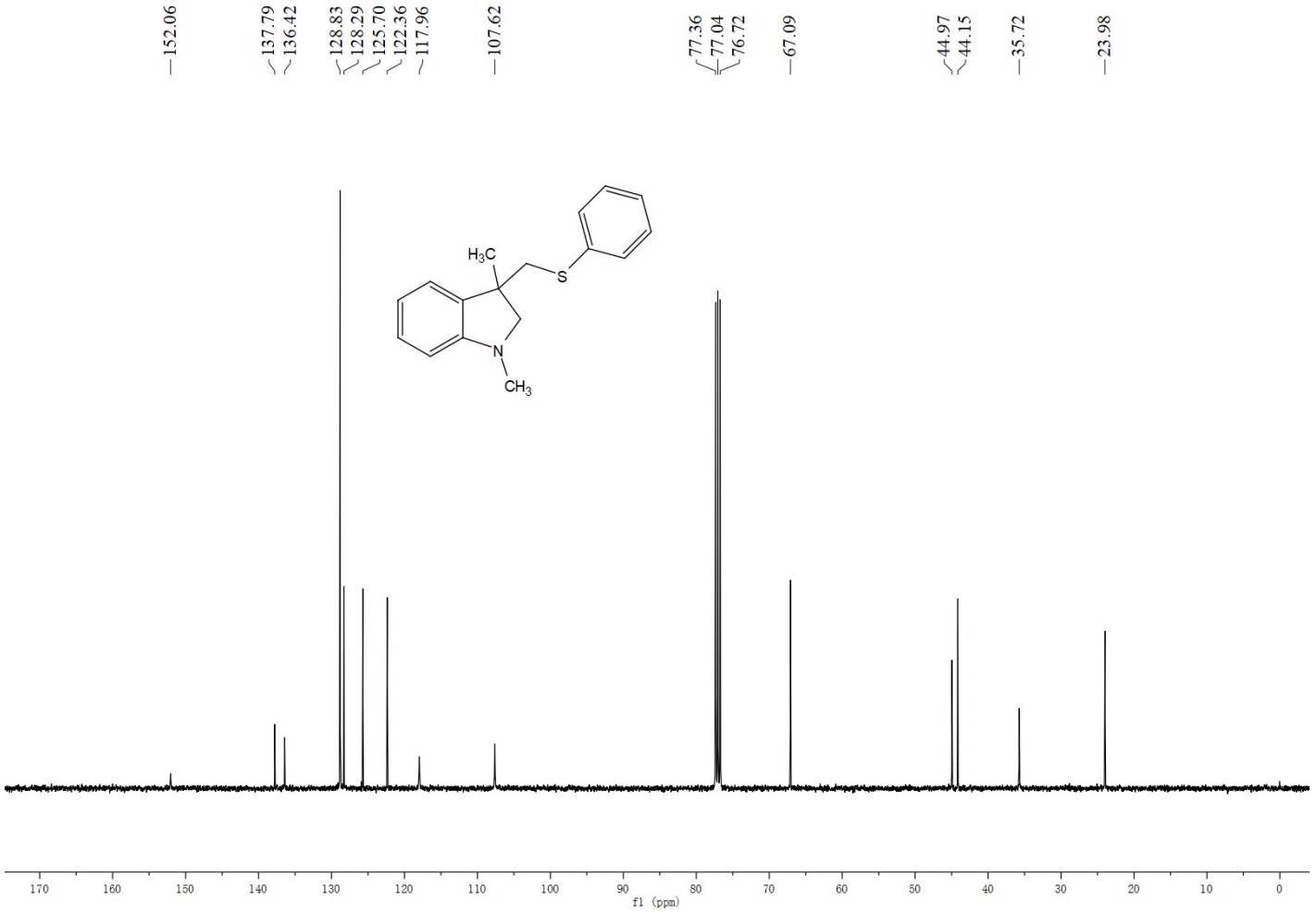

FF-258-1 245 (2.231)
1: TOF MS ES+
5.38e5
100
%
0
300.1058
322.0874
174.0920
122.0969
89.5075
184.1140
323.0887
354.2870
436.2535
527.1566
600.1481
621.1820
622.1799
676.4692
761.6995
816.1628
872.7531
917.5486
970.5413
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

1,3-Dimethyl-3-((phenylthio)methyl)indoline (7)

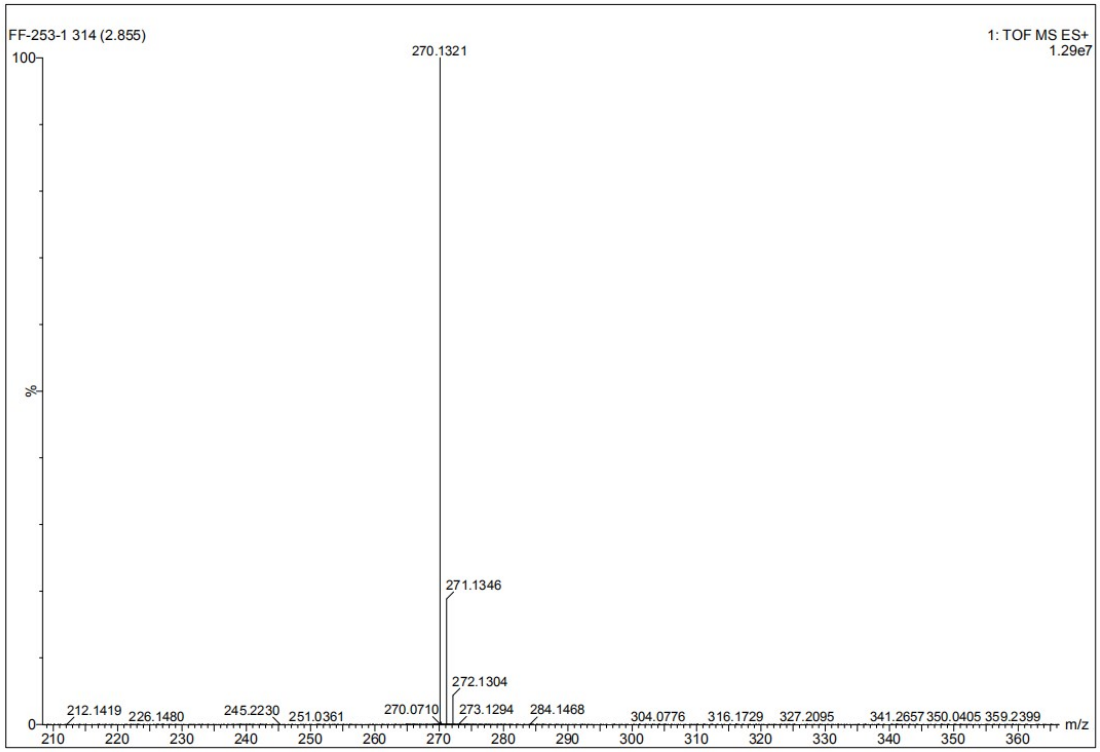
^{1}H NMR (400 MHz, $CDCl_3$)



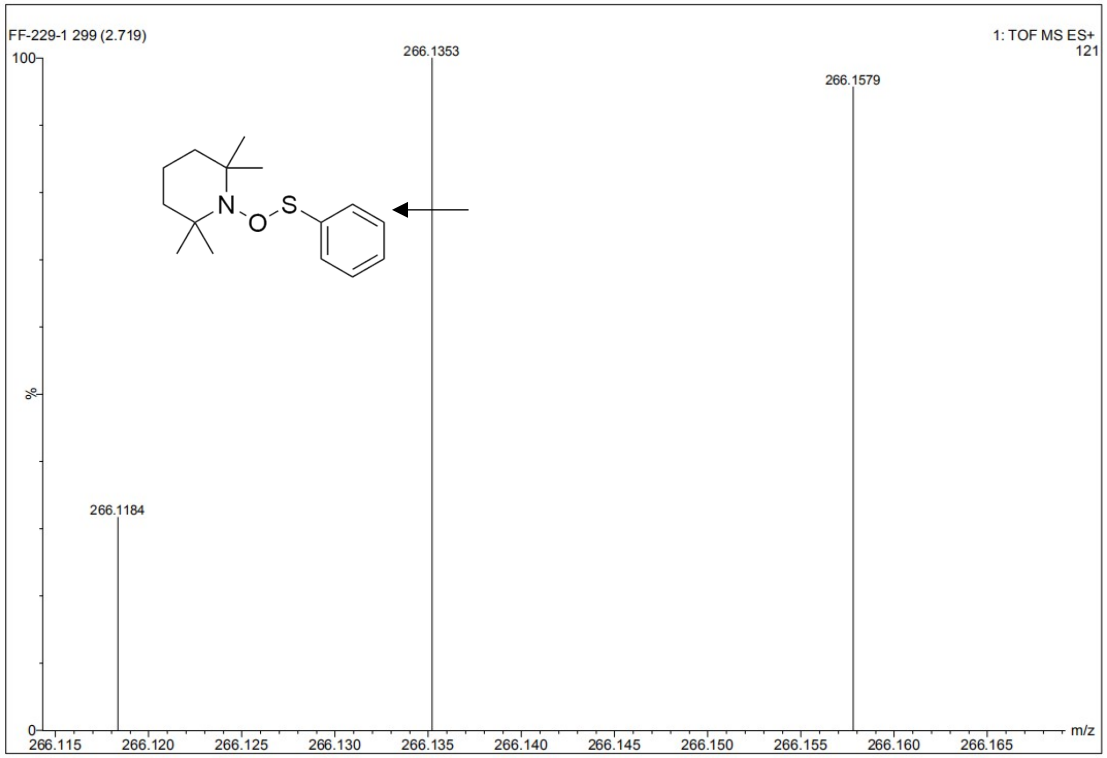
^{13}C NMR (100 MHz, $CDCl_3$)

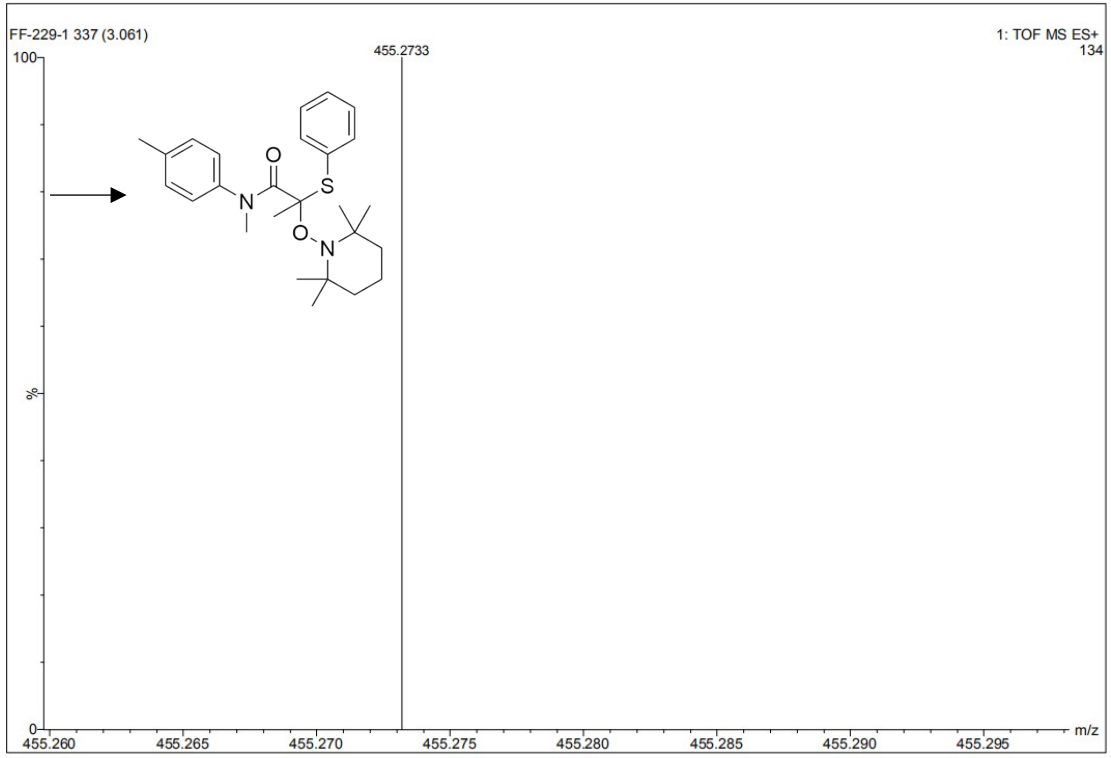


HRMS (ESI)


FF-253-1 314 (2.855)
1: TOF MS ES+
1.29e7
100
%
0
270.1321
271.1346
272.1304
212.1419
226.1480
245.2230
251.0361
270.0710
273.1294
284.1468
304.0776
316.1729
327.2095
341.2657
350.0405
359.2399
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
m/z

10. HRMS spectra of the control experiments




FF-229-1 337 (3.061)
1: TOF MS ES+
134
455.2733
100
%
0
455.260
455.265
455.270
455.275
455.280
455.285
455.290
455.295
m/z
O
S
N
O
N