Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Rh(II)-catalyzed Doyle–Kirmse Reaction: Access to Unprotected 3-Allyl/3-allenyl-3-(thio)oxindoles

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Supporting Information

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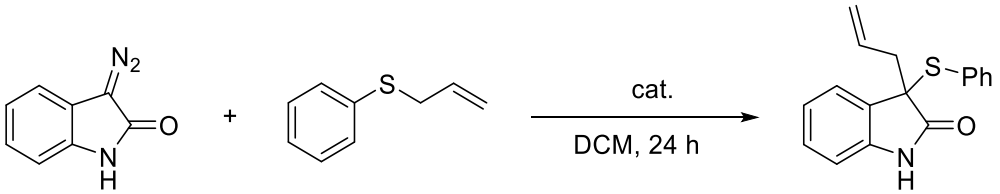
(A) General information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products.^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz Bruker spectrometers. Chemical shifts of ^{1}H were reported in part per million relatives to the TMS peak (δ 0.0). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint. (quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (*virt.*). High resolution mass spectra (HRMS) data were measured on a ESI-microTOF Ⅱ. Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Further visualization was achieved by staining with iodine, or $KMnO_4$ followed by heating on a hot plate. Flash column chromatography was performed on silica gel 60 Å, 10–40 μm.

The catalyst $Rh_2(esp)_2$ was prepared following the literature procedure.[1]

(B) Reaction condition optimization

B-1 Screening of catalysts

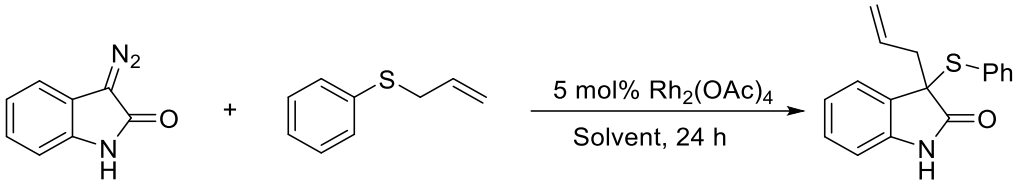


1a **2a** **3a**

Entry [a]	Catalyst (5 mol%)	Solvent	T (℃)	Yield(%) [b]
1	I_2	DCM	r.t.	0
2	$Fe(acac)_2$	DCM	r.t.	0
3	$Cu(OAc)_2$	DCM	r.t.	<5
4	$Cu(acac)_2$	DCM	r.t.	<5
5 [c]	$Cu_2(OAc)_4$	DCM	r.t.	<5
6 [d]	$Cu_2(OAc)_4$	DCM	r.t.	19
7	Hemin	DCM	r.t.	<5
8	$Rh_2(OAc)_4$	DCM	r.t.	25
9	$(Ph_3CCOO)_4Rh_2$	DCM	r.t.	19

a. Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** and 5 mol% catalyst in DCM (1.5 mL) at room temperature was stirred for 24 h. *b*. Isolated yield. *c*. 10 mol% $Cu_2(OAc)_4$ was used. *d*.10 mol% $Cu_2(OAc)_4$ and 20 mol% 1,10-phen were used.

B-2 Screening of solvents

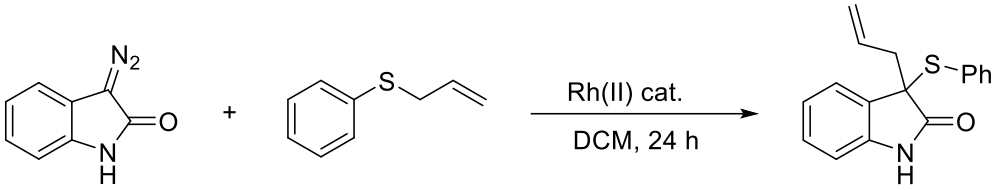


1a **2a** **3a**

Entry [a]	Catalyst (5 mol%)	Solvent	T (℃)	Yield(%) [b]
1	$Rh_2(OAc)_4$	DCM	r.t.	25
2	$Rh_2(OAc)_4$	DMF	r.t.	15
3	$Rh_2(OAc)_4$	H_2O	r.t.	<5
4	$Rh_2(OAc)_4$	THF	r.t.	18
5	$Rh_2(OAc)_4$	DMSO	r.t.	<5

a. Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** and 5 mol% catalyst in solvent (1.5 mL) at room temperature was stirred for 24 h. *b*. Isolated yield.

B-3 Optimization of catalysts and equivalents

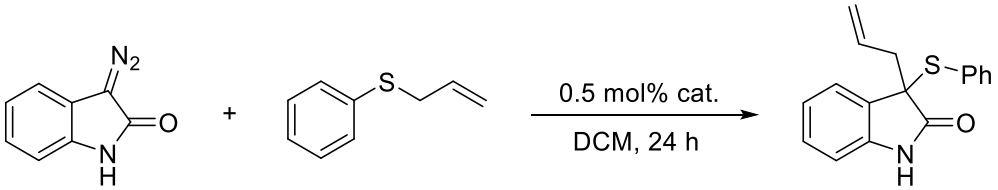


1a **2a** **3a**

Entry [a]	Catalyst	Catalyst loading	T (℃)	Yield(%) [b]
1	$Rh_2(OAc)_4$	5 mol%	r.t.	25
2	$Rh_2(esp)_2$	5 mol%	r.t.	89
3c	$Rh_2(esp)_2$	2.5 mol%	r.t.	88
4d	$Rh_2(esp)_2$	1 mol%	r.t.	90
5e	$Rh_2(esp)_2$	0.5 mol%	r.t.	89

a. Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** and catalyst in DCM (1.5 mL) at room temperature was stirred for 24 h. *b*. Isolated yield.

B-4 Further systematic optimization



1a **2a** **3a**

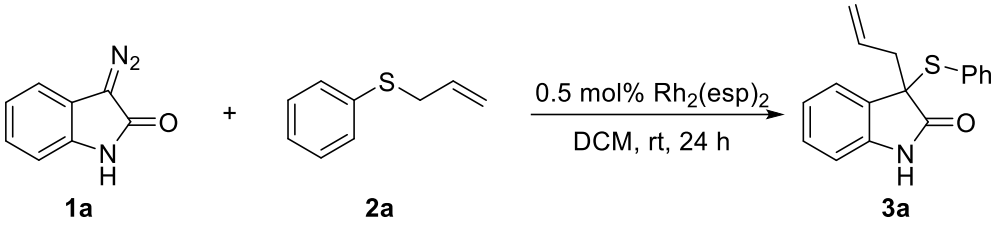
Entry [a]	Catalyst	Solvent	T (℃)	Yield(%) [b]
1	$Rh_2(esp)_2$	DCM	r.t.	89
2 [c,d]	$Rh_2(esp)_2$	DCM	30	93
3 [c,d,e]	$Rh_2(esp)_2$	DCM	30	97

a. Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** and 0.5 mol% $Rh_2(esp)_2$ in DCM (1.5 mL) at room temperature was stirred for 24 h. *b*. Isolated yield. *c*. 3.0 mL DCM was used. *d*. the ratio of **1a** 0.2 mmol, **2a** 0.24 mmol in 3.0

mL DCM and the reaction was performed at 30℃. *e*. Diazooxidoles was added in three portions over 30 min.

(C) Mechanistic studies

Mechanistic experiments – addition of a trapping agent (TEMPO and BHT)



1a **2a** **3a**

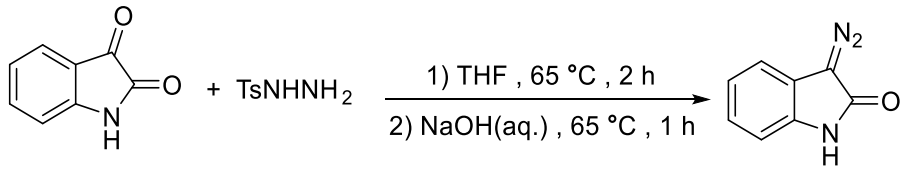
Entry [a]	conditions	Yield(%) [b]
1	**No trapping agent**	93
2 [c]	1.0 eq. TEMPO	88
3 [d]	1.0 eq. BHT	85

a. Reaction conditions: 0.2 mmol **1a**, 0.2 mmol **2a** and 0.5 mol% $Rh_2(esp)_2$ in DCM (1.5 mL) at room temperature was stirred for 24 h. *b*. Assay of intact 1,3,5-trimethoxybenzene as a function of the NMR yield of **3a**. *c*. 0.2 mmol **1a**, 0.2 mmol **2a**, 1.0 eq. TEMPO and 0.5 mol% $Rh_2(esp)_2$ in DCM (1.5 mL) at room temperature was stirred for 24 h. *d*. 0.2 mmol **1a**, 0.2 mmol **2a**, 1.0 eq. BHT and 0.5 mol% $Rh_2(esp)_2$ in DCM (1.5 mL) at room temperature was stirred for 24 h.

(D) General procedures for preparation of diazo compounds and allyl sulfides

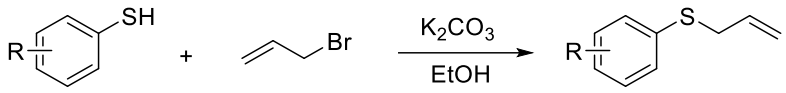
D-1. Procedures for preparation of diazo compounds

Diazo compounds were prepared via diazo transfer with $TsNHNH_2$ according to the literature procedure.[2]



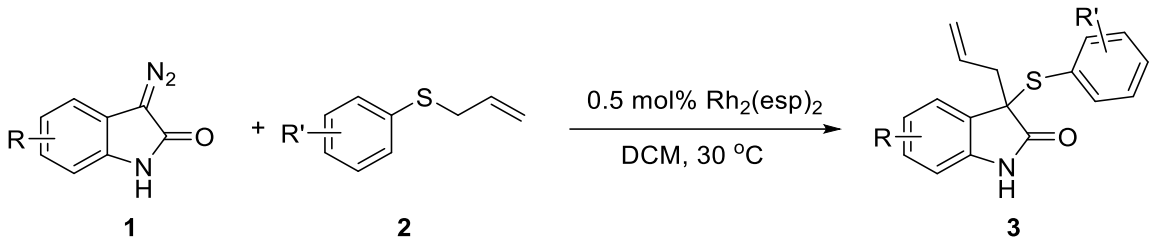
A mixture of isatin (10 mmol) and $TsNHNH_2$ (1.1 eq.) in THF (50 mL) was stirred at 65 ℃ for 2 h, then cooled at room temperature. The mixture solvent was concentrated under reduced pressure, and the pure tosylhydrazone was precipitated from MeOH (30 mL) solution. Then tosylhydrazone and aq. NaOH (0.2 N) solution was added in a round-bottomed flask, and the mixture was stirred at 65 ℃ for 2 h. Water (30 mL) and EtOAc (30 mL) were added and the organic layer was separated. The collected organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give the crude products without further purification. The observed characterization data are consistent with those previously reported.[2]

D-2. Procedures for preparation of allylic thioether [3]



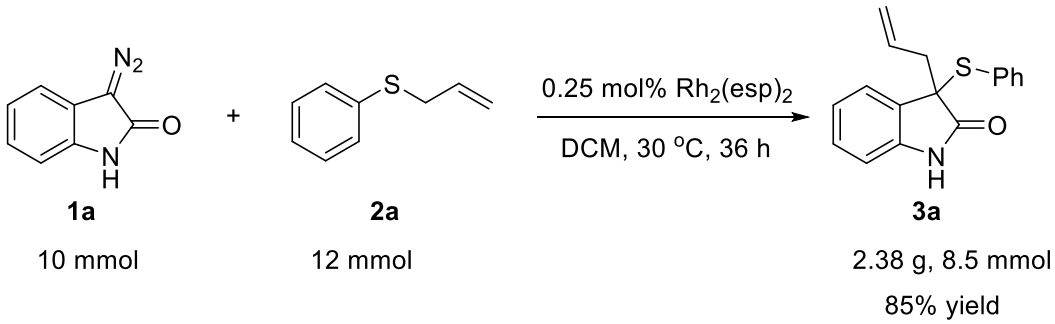
Allyl bromide/ benzyl bromide were added to an enthanolic solution of thiophenol/thiol (3 mmol), K_2CO_3 (3.6 mmol) at r.t., and the resulting mixture was stirred for 12 h. The resulting mixture was concentrated and extracted with CH_2Cl_2. Then the extract was purified by column chromatography (petroleum ether) to afford the desired sulfide. The observed characterization data are consistent with those previously reported.[3]

(E) General procedure for [2,3]-sigmatropic rearrangement reactions



Sulfide **2** (0.24 mmol, 1.2 eq.) was added into 3 mL DCM solution of 0.5 mol% $Rh_2(esp)_2$ (0.8 mg, 1.0 μmol), followed by adding 0.2 mmol diazo reagent **1** in three portions over 30 min. Then the reaction vial was stirred for 24 hours under 30 ℃. After completing the reaction confirmed by TLC, the mixture was subjected to a short silica gel column directly using PE/EA as elute to give the corresponding product **3**.

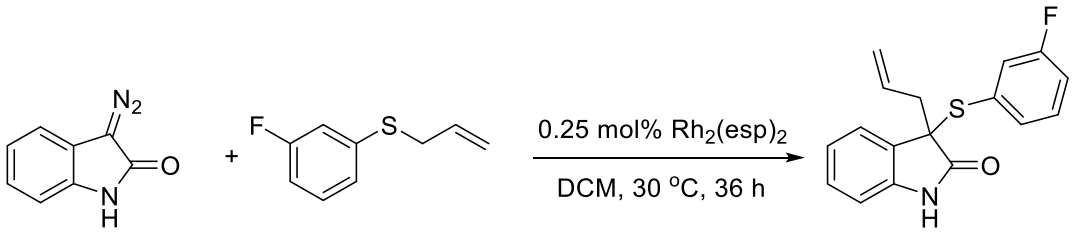
(F) Scale-up synthesis of 3,3-disubstituted oxindoles



A 100 mL round-bottomed flask was charged with a stir bar. allyl(phenyl)sulfane (12 mmol, 1.8 g, 1.2 eq.) was added into 50 mL DCM solution of 0.25 mol% $Rh_2(esp)_2$ (19 mg, 0.025 mmol), followed by adding 3-diazoindolin-2-one (10 mmol, 1.59 g) in five portions over 30 min. Then the reaction vial was stirred for 36 hours under 30 ℃. After completing the reaction confirmed by TLC,

the organic layer was further concentrated *in vacuo*. The mixture was subjected to silica gel, and eluted by petroleum ether to give the desired product 2.53g, the yield up to 85%.

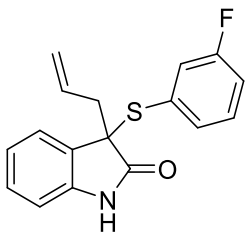
(G) Reactions with low catalyst loading for TON calculation



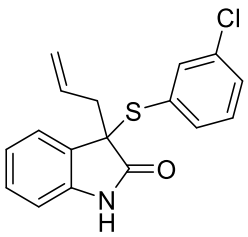
1a 10 mmol

2a 12 mmol

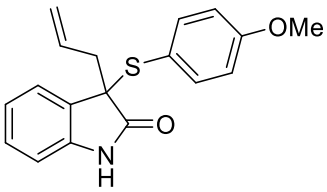
3a 2.53g, 9 mmol, 90% yield



0.01 mol% cat., 37% yield.
TON: 3700



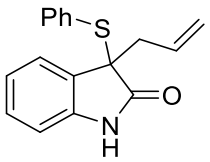
0.05 mol% cat., 66% yield.
TON: 1320



0.05 mol% cat., 48% yield.
TON: 960

(H) Analytical data of products

3-allyl-3-(phenylthio)indolin-2-one (3a)



3a

A light yellow solid, 97% yield.

M.P. : 156.2℃ ~ 159.1℃.

TLC: R_f = 0.45 (Hexane/EtOAc = 3:1).

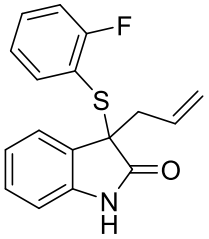
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (br s, 1H), 7.30 – 7.25 (m, 1H), 7.20 – 7.11 (m, 4H), 7.10 – 7.04 (m, 1H), 7.04 – 6.95 (m, 3H), 6.64 – 6.57 (m, 1H), 5.52 – 5.36 (m, 1H), 5.05 – 4.94 (m, 1H), 4.93 – 4.84 (m, 1H), 2.83 – 2.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 140.5, 136.6, 131.3, 129.9, 129.6, 129.4, 128.8, 128.5, 124.9, 122.7, 119.9, 109.9, 59.0, 39.7.

IR(KBr/cm^{-1}) 3223.9, 2924.6, 2857.1, 1721.2, 1680.6, 1486.0, 1311.5, 1196.5, 929.5, 749.9, 609.5.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{15}NOSNa^+$ [M+Na]$^+$: 304.0771, found: 304.0767.

3-allyl-3-((2-fluorophenyl)thio)indolin-2-one (3b)



3b

A white solid, 93% yield.

M.P. : 126.7℃ ~ 129.5℃.

TLC: R_f = 0.35 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.28 – 7.19 (m, 2H), 7.19 – 7.10 (m, 1H), 7.10 – 7.01 (m, 1H), 6.99 – 6.90 (m, 1H), 6.87 – 6.78 (m, 2H), 6.71 – 6.64 (m, 1H), 5.50 – 5.35 (m, 1H), 4.98 (dq, *J* = 17.0, 1.4 Hz, 1H), 4.92 – 4.83 (m, 1H), 2.90 – 2.74 (m, 2H).

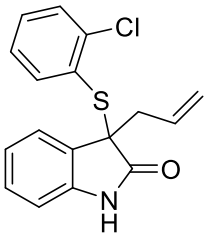
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 163.8 (d, *J* = 249.1 Hz), 140. 7 (d, *J* = 2.5 Hz), 139.2, 132.2 (d, *J* = 8.2 Hz), 131.2, 129.0, 128.9, 124.9, 124.1 (d, *J* = 4.0 Hz), 122.6, 120.0, 116.6 (d, *J* = 18.4 Hz), 115.7 (d, *J* = 23.8 Hz), 110.1, 58.5, 39.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -104.3.

IR(KBr/cm^{-1}) 3431.6, 3242.0, 1718.3, 1683.5, 1620.8, 147.0, 1261.5, 753.0, 607.8.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}FNOSNa^+$ [M+Na]$^+$: 322.0672, found: 322.0672.

3-allyl-3-((2-chlorophenyl)thio)indolin-2-one (3c)



3c

A white solid, 92% yield.

M.P. : 135.3℃ ~ 136.9℃.

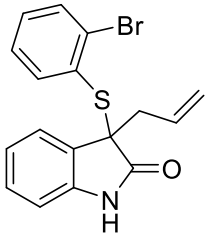
TLC: R_f = 0.40 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.34 – 7.29 (m, 1H), 7.25 – 7.17 (m, 2H), 7.11 – 7.04 (m, 2H), 6.97 – 6.87 (m, 2H), 6.74 – 6.67 (m, 1H), 5.48 – 5.34 (m, 1H), 5.03 – 4.93 (m, 1H), 4.91 – 4.84 (m, 1H), 2.94 – 2.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 140.7, 140.2, 138.4, 131.1, 130.7, 129.9, 129.2, 129.1, 128.7, 126.7, 125.0, 122.5, 120.1, 110.2, 58.8, 39.9.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}ClNOSNa^+$ [M+Na]$^+$: 338.0377, found: 338.0379.

3-allyl-3-((2-bromophenyl)thio)indolin-2-one (3d)



3d

A white solid, 89% yield.

M.P. : 133.8℃ ~ 136.2℃.

TLC: R_f = 0.38 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.43 – 7.37 (m, 1H), 7.37 – 7.31 (m, 1H), 7.26 – 7.20 (m, 1H), 7.11 – 7.03 (m, 1H), 7.01 – 6.94 (m, 2H), 6.94 – 6.88 (m, 1H), 6.74 – 6.69 (m, 1H), 5.05 – 4.93 (m, 1H), 4.91 – 4.83 (m, 1H), 2.96 – 2.76 (m, 2H).

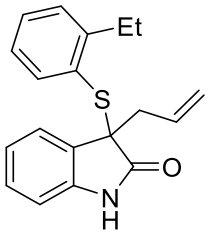
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 140.7, 137.9, 133.2, 131.5, 131.3, 131.1, 130.6, 129.1, 128.6, 127.4, 125.1, 122.6, 120.1, 110.2, 58.9, 40.0.

IR(KBr/cm^{-1}) 3217.3, 1723.4, 1686.2, 1619.9, 1472.8, 1332.6, 1239.9, 1020.6, 747.8, 672.2.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{79}BrNOSNa^+$ $[M+Na]^+$: 381.9872, found: 381.9873.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{81}BrNOSNa^+$ $[M+Na]^+$: 383.9851, found: 383.9852.

3-allyl-3-((2-ethylphenyl)thio)indolin-2-one (3e)



3e

A white solid, 95% yield.

M.P. : 118.5℃ ~ 120.3℃.

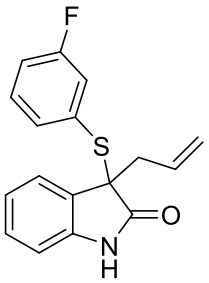
TLC: R_f = 0.62 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 – 9.00 (m, 1H), 7.19 – 7.12 (m, 1H), 7.12 – 6.95 (m, 4H), 6.94 – 6.86 (m, 1H), 6.86 – 6.77 (m, 1H), 6.70 – 6.60 (m, 1H), 5.46 – 5.28 (m, 1H), 5.02 – 4.90 (m, 1H), 4.89 – 4.79 (m, 1H), 2.91 – 2.74 (m, 2H), 2.74 – 2.53 (m, 2H), 1.01 – 0.92 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 148.6, 139.7, 136.6, 130.3, 128.8, 128.4, 127.7, 127.6, 127.3, 124.6, 123.6, 121.3, 118.6, 109.0, 57.7, 57.7, 38.8, 26.1, 14.7.

HRMS (ESI+): *m/z* calcd for $C_{19}H_{19}NOSNa^+$ $[M+Na]^+$: 332.1080, found: 332.1085.

3-allyl-3-((3-fluorophenyl)thio)indolin-2-one (3f)



3f

A white solid, 99% yield.

M.P. : 88.9℃ ~ 90.1℃.

TLC: R_f = 0.62 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.30 – 7.24 (m, 1H), 7.12 – 7.05 (m, 1H), 7.03 – 6.94 (m, 3H), 6.88 – 6.80 (m, 2H), 6.69 – 6.63 (m, 1H), 5.51 – 5.36 (m, 1H), 5.06 – 4.95 (m, 1H), 4.94 – 4.85 (m, 1H), 2.83 – 2.72 (m, 2H).

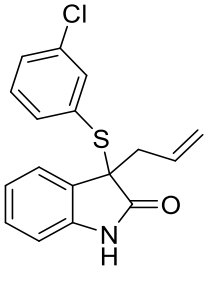
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 163.2, 160.7, 140.6, 132.1, 132.1, 131.5, 131.4, 131.0, 129.7, 129.6, 129.4, 129.1, 124.8, 123.1, 122.9, 122.8, 120.1, 116.8, 116.6, 110.2, 59.1, 39.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4.

IR(KBr/cm^{-1}) 3241.7, 1726.2, 1686.1, 1470.1, 1261.6, 1095.2, 801.9, 747.3, 680.8.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}FNOSNa^+$ $[M+Na]^+$: 322.0672, found: 322.0672.

3-allyl-3-((3-chlorophenyl)thio)indolin-2-one (3g)



3g

A white solid, 99% yield.

M.P. : 187.2℃ ~ 189.7℃.

TLC: R_f = 0.60 (Hexane/EtOAc = 3:1).

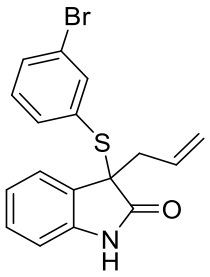
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 – 8.80 (m, 1H), 7.27 (d, J = 7.4 Hz, 1H), 7.15 – 7.05 (m, 4H), 7.04 – 6.97 (m, 1H), 6.97 – 6.90 (m, 1H), 6.70 – 6.63 (m, 1H), 5.50 – 5.36 (m, 1H), 5.04 – 4.94 (m, 1H), 4.93 – 4.86 (m, 1H), 2.84 – 2.70 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 140.6, 136.0, 134.5, 133.9, 131.3, 131.0, 129.7, 129.5, 129.4, 129.2, 124.8, 122.8, 120.1, 110.3, 59.0, 39.6.

IR(KBr/cm^{-1}) 3177.3, 1720.7, 1678.2, 1618.9, 1471.9, 1261.4, 1098.2, 1023.1, 802.9, 681.6, 617.7.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}ClNOSNa^+$ $[M+Na]^+$: 338.0377, found: 338.0379.

3-allyl-3-((3-bromophenyl)thio)indolin-2-one (3h)



3h

A white solid, 91% yield.

M.P. : 135.7℃ ~ 138.7℃.

TLC: R_f = 0.57 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (br s, 1H), 7.39 – 7.30 (m, 3H), 7.24 – 7.14 (m, 2H), 7.12 – 7.04 (m, 1H), 6.97 – 7.14 (m, 1H), 7.00– 6.91 (m, 1H), 5.60 – 5.40 (m, 1H), 5.12 – 5.03 (m, 1H), 5.02 – 4.95 (m, 1H), 2.91 – 2.79 (m, 2H).

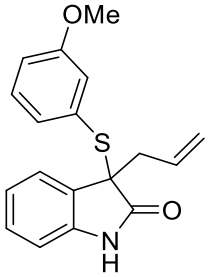
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 140.5, 138.8, 134.8, 132.5, 131.5, 130.9, 129.7, 129.3, 129.1, 124.8, 122.8, 121.8, 120.0, 110.1, 58.9, 39.5.

IR(KBr/cm^{-1}) 3173.1, 1721.3, 1676.9, 1471.2, 1231.9, 926.1, 755.2, 681.6.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{79}BrNOSNa^+$ $[M+Na]^+$: 381.9872, found: 381.9874.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{81}BrNOSNa^+$ $[M+Na]^+$: 383.9851, found: 383.9850.

3-allyl-3-((3-methoxyphenyl)thio)indolin-2-one (3i)



3i

A white solid, 79% yield.

M.P. : 140.9℃ ~ 142.4℃.

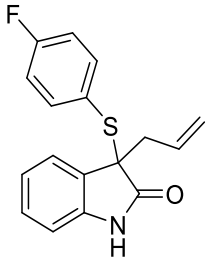
TLC: R_f = 0.56 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 – 8.82 (m, 1H), 7.32 – 7.25 (m, 1H), 7.11 – 7.02 (m, 1H), 7.03 – 6.95 (m, 1H), 6.94 – 6.86 (m, 1H), 6.83 – 6.75 (m, 1H), 6.73 – 6.58 (m, 3H), 5.50 – 5.35 (m, 1H), 5.04 – 4.94 (m, 1H), 4.94 – 4.85 (m, 1H), 3.46 (s, 3H), 2.98 – 2.58 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 159.1, 140.7, 131.2, 130.4, 130.0, 129.2, 128.8, 128.6, 124.8, 122.6, 120.4, 119.9, 116.4, 110.1, 59.1, 55.2, 39.8.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}NO_2SNa^+$ $[M+Na]^+$: 334.0872, found: 334.0872.

3-allyl-3-((4-fluorophenyl)thio)indolin-2-one (3j)



3j

A white solid, 96% yield.

M.P. : 100.1℃ ~ 102.6℃.

TLC: R_f = 0.55 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (br s, 1H), 7.32 – 7.24 (m, 1H), 7.16 – 7.05 (m, 3H), 6.72 – 6.95 (m, 1H), 6.73 – 6.60 (m, 3H), 5.48– 5.35 (m, 1H), 5.04 – 4.39 (m, 1H), 4.91 – 4.84 (m, 1H), 2.82 – 2.69 (m, 2H).

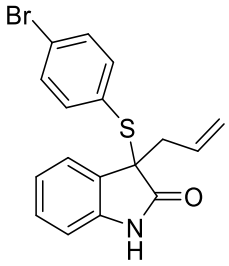
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 165.0, 162.5, 140.6, 138.7, 138.6, 131.1, 129.6, 129.0, 124.8, 124.7, 124.6, 122.8, 120.0, 115.8, 115.5, 110.1, 59.1, 39.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.8.

IR(KBr/cm^{-1}) 3184.1, 1724.2, 1685.1, 1619.3, 1488.7, 1229.9, 826.7, 756.5, 681.9.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}NOSNa^+$ $[M+Na]^+$: 322.0672, found: 322.0672.

3-allyl-3-((4-bromophenyl)thio)indolin-2-one (3k)



3k

A white solid, 85% yield.

M.P. : 116.2℃ ~ 118.5℃.

TLC: R_f = 0.55 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 – 8.96 (m, 1H), 7.40 – 7.33 (m, 1H), 7.24 – 7.14 (m, 3H), 7.13 – 7.03 (m, 3H), 6.77 – 6.69 (m, 1H), 5.58 – 5.42 (m, 1H), 5.11– 5.02 (m, 1H), 5.00 – 4.93 (m, 1H), 2.92 – 2.75 (m, 2H).

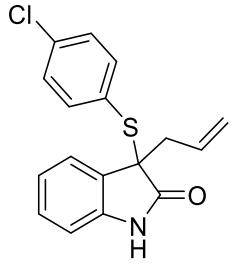
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 178.4, 140.5, 138.0, 131.7, 131.0, 129.5, 129.1, 128.5, 124.8, 124.5, 122.8, 120.1, 110.2, 59.0, 39.6.

IR(KBr/cm^{-1}) 3164.7, 1728.1, 1686.1, 1471.2, 1233.5, 1011.2, 815.7, 751.3.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{79}BrNOSNa^+$ $[M+Na]^+$: 381.9872, found: 381.9874.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{81}BrNOSNa^+$ $[M+Na]^+$: 383.9851, found: 383.9850.

3-allyl-3-((4-chlorophenyl)thio)indolin-2-one (3l)



3l

A white solid, 91% yield.

M.P. : 117.8℃ ~ 120.8℃.

TLC: R_f = 0.66 (Hexane/EtOAc = 3:1).

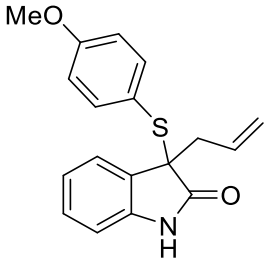
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 – 8.88 (m, 1H), 7.33 – 7.24 (m, 1H), 7.13 – 7.03 (m, 3H), 7.03 – 6.92 (m, 3H), 6.70 – 6.62 (m, 1H), 5.51 – 5.35 (m, 1H), 5.06 – 4.94 (m, 1H), 4.91 – 4.85 (m, 1H), 2.83 – 2.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 140.6, 140.6, 137.7, 136.1, 131.0, 129.5, 129.1, 128.7, 127.9, 124.8, 122.8, 120.0, 110.2, 59.0, 39.6.

IR(KBr/cm^{-1}) 2429.9, 3159.2, 1728.8, 1684.9, 1472.7, 1234.6, 1096.9, 819.5 , 750.7, 614.6.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}ClNOSNa^+$ $[M+Na]^+$: 338.0377, found: 338.0380.

3-allyl-3-((4-methoxyphenyl)thio)indolin-2-one (3m)



3m

A white solid, 99% yield.

TLC: R_f = 0.60 (Hexane/EtOAc = 3:1).

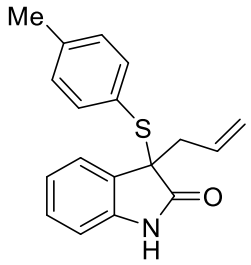
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 – 8.91 (m, 1H), 7.30 – 7.22 (m, 1H), 7.11 – 7.03 (m, 3H), 7.02 – 6.92 (m, 1H), 6.68 – 6.60 (m, 1H), 6.55 – 6.47 (m, 2H), 5.52 – 5.27 (m, 1H), 5.06 – 4.79 (m, 2H), 3.58 (s, 3H), 2.82 – 2.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 160.8, 140.7, 138.2, 131.4, 130.0, 128.7, 124.8, 122.5, 120.1, 119.7, 114.0, 110.1, 110.1, 59.0, 55.2, 39.4.

IR(KBr/cm^{-1}) 3201.1, 2962.3, 1725.6, 1683.7, 1256.4, 1099.4, 1027.1, 801.1, 748.9, 677.9.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}NO_2SNa^+$ $[M+Na]^+$: 334.0872, found: 334.0876.

3-allyl-3-(p-tolylthio)indolin-2-one (3n)



3n

A white solid, 95% yield.

TLC: R_f = 0.46 (Hexane/EtOAc = 3:1).

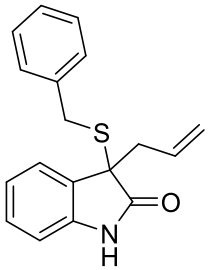
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.36 – 7.32 (m, 1H), 7.16 – 7.09 (m, 3H), 7.08 – 7.01 (m, 1H), 6.91 – 6.84 (m, 2H), 6.72 (d, *J* = 7.7 Hz, 1H), 5.56 – 5.44 (m, 1H), 5.05 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.93 (dd, *J* = 10.1, 1.8 Hz, 1H), 2.91 – 2.80 (m, 2H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 140.7, 139.7, 136.5, 131.3, 129.9, 129.3, 128.7, 125.8, 124.8, 122.5, 119.7, 110.1, 58.8, 39.6, 21.3.

IR(KBr/cm^{-1}) 3157.2, 1726.7, 1682.6, 1471.4, 1234.5, 926.3, 752.7, 683.2.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}NOSNa^+$ $[M+Na]^+$: 318.0923, found: 318.0925.

3-allyl-3-(benzylthio)indolin-2-one (3o)



3o

A white solid, 62% yield.

M.P. : 99.8℃ ~ 101.1℃.

TLC: R_f = 0.38 (Hexane/EtOAc = 3:1).

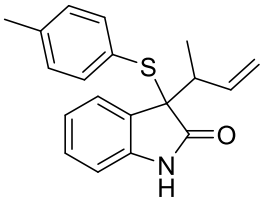
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.37 – 7.31 (m, 1H), 7.28 – 7.21 (m, 1H), 7.21 – 7.05 (m, 6H), 6.98 – 6.90 (m, 1H), 5.63 – 5.48 (m, 1H), 5.12 – 5.03 (m, 1H), 5.02 – 4.93 (m, 1H), 3.71 – 3.54 (m, 2H), 2.85 – 2.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 140.7, 136.7, 131.1, 129.5, 129.2, 129.1, 128.4, 127.2, 124.7, 123.0, 119.9, 110.4, 55.5, 40.3, 33.7.

IR(KBr/cm^{-1}) 3152.6, 3089.6, 1721.4, 1679.5, 1620.3, 1472.9, 1333.8, 754.1, 703.4, 686.7.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}NOSNa^+$ $[M+Na]^+$: 318.0923, found: 318.0923.

3-(but-3-en-2-yl)-3-(p-tolylthio)indolin-2-one (3p)



3p

A white solid, 90% yield.
M.P. : 155.5℃ ~ 156.7℃.
TLC: R_f = 0.41 (Hexane/EtOAc = 3:1).

Major diastereoisomer

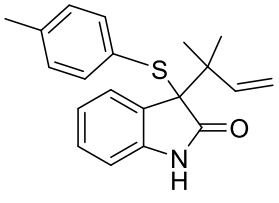
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.39 – 7.32 (m, 1H), 7.12 – 7.02 (m, 1H), 7.02 – 6.92 (m, 3H), 6.82 – 6.72 (m, 2H), 6.65 – 6.52 (m, 1H), 6.25 – 6.06 (m, 1H), 5.23 – 5.16 (m, 1H), 5.19 – 5.13 (m, 1H), 3.04 – 2.92 (m, 1H), 2.12 (s, 3H), 0.82 (d, *J* = 6.8 Hz, 3H).

Minor diastereoisomer

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.42 – 7.33 (m, 1H), 7.10 – 7.02 (m, 1H), 7.02 – 6.93 (m, 3H), 6.84 – 6.71 (m, 1H), 6.61 – 6.54 (m, 1H), 5.66 – 5.52 (m, 1H), 5.08 – 4.99 (m, 1H), 4.92 – 4.83 (m, 1H), 2.93 – 2.85 (m, 1H), 2.12 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR δ 178.63, 140.85, 140.79, 139.51, 139.46, 137.70, 137.31, 136.35, 129.53, 129.26, 129.13, 128.66, 126.06, 125.78, 125.34, 122.49, 122.43, 117.63, 117.15, 109.85, 109.79, 63.09, 44.09, 42.78, 21.33, 16.01, 15.57.
IR(KBr/cm^{-1}) 3233.9, 1723.4, 1684.9, 1617.8, 1470.6, 1393.5, 1327.7, 1229.6, 926.3, 806.0, 749.9
HRMS (ESI+): *m/z* calcd for $C_{19}H_{19}NNaOS^+$ $[M+Na]^+$: 332.1080, found: 332.1082.

Compound **3p** was synthesized using racemic methyl 2-benzamido-4-phenylbutanoate following the *general procedure*. The diastereoselectivity was 2.5:1, which determined from ^{1}H NMR analysis of product. The two diastereoisomers were not separated by column chromatography.

3-(2-methylbut-3-en-2-yl)-3-(p-tolylthio)indolin-2-one (3q)

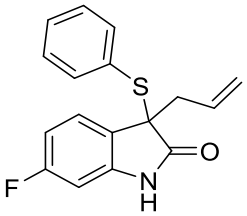


3q

A white solid, 99% yield.
M.P. : 167.5℃ ~ 168.1℃.
TLC: R_f = 0.45 (Hexane/EtOAc = 3:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.12 – 6.95 (m, 4H), 6.86 – 6.73 (m, 2H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.34 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.15 (d, *J* = 10.7 Hz, 1H), 5.08 (d, *J* = 17.4 Hz, 1H), 2.17 (s, 3H), 1.41 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 142.8, 140.8, 139.1, 136.4, 129.7, 129.1, 128.4, 127.3, 126.2, 121.7, 114.0, 109.4, 66.8, 43.3, 23.8, 22.3, 21.3.
IR(KBr/cm^{-1}) 3276.0, 1719.9, 1681.2, 1616.9, 1469.3, 1390.1, 1183.1, 926.3, 807.9, 746.2.
HRMS (ESI+): *m/z* calcd for $C_{20}H_{21}NNaOS^+$ $[M+Na]^+$: 346.1236, found: 346.1236.

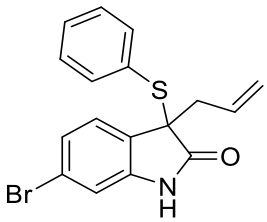
3-allyl-6-fluoro-3-(phenylthio)indolin-2-one (3r)



3r

A white solid, 98% yield.
M.P. : 126.3℃ ~ 129.5℃.
TLC: R_f = 0.58 (Hexane/EtOAc = 3:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 – 9.00 (m, 1H), 7.26 – 7.10 (m, 4H), 7.09 – 6.97 (m, 2H), 6.74 – 6.61 (m, 1H), 6.45 – 6.34 (m, 1H), 5.49 – 5.33 (m, 1H), 5.03 – 4.94 (m, 1H), 4.93 – 4.86 (m, 1H), 2.81 – 2.69 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 163.0 (d, *J* = 246.2 Hz), 141.9 (d, *J* = 12.2 Hz), 136.6, 131.0, 129.8, 129.2, 128.6, 126.0 (d, *J* = 9.8 Hz), 125.2 (d, *J* = 2.9 Hz), 120.1, 109.2 (d, *J* = 22.7 Hz), 98.7 (d, *J* = 27.2 Hz), 58.6, 39.7.
IR(KBr/cm-1) 3430.3, 3208.2, 3072.9, 1723.7, 1684.2, 1622.1, 1499.2, 1335.9, 1139.4, 1103.5, 750.9.
HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}FNOSNa^+$ $[M+Na]^+$: 322.0672, found: 322.0673.

3-allyl-6-bromo-3-(phenylthio)indolin-2-one (3s)



3s

A white solid, 92% yield.
M.P. : 157.5℃ ~ 160.0℃.
TLC: R_f = 0.48 (Hexane/EtOAc = 3:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.20 – 7.13 (m, 3H), 7.13 – 7.07 (m, 2H), 7.07 – 7.00 (m, 2H), 6.85 – 6.80 (m, 1H), 5.45 – 5.32 (m, 1H), 5.02 – 4.92 (m, 1H), 4.93 – 4.85 (m, 1H), 2.76 (d, *J* = 7.3 Hz, 2H).

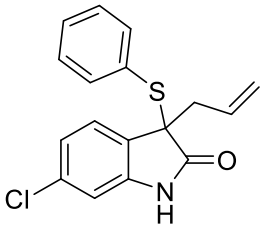
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 141.8, 136.6, 130.9, 129.8, 129.0, 128.8, 128.7, 126.1, 125.6, 122.3, 120.2, 113.6, 58.7, 39.6.

IR(KBr/cm^{-1}) 3143.8, 3074.9, 1726.8, 1683.6, 1612.6, 1478.3, 1329.5, 1236.3.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{79}BrNOSNa^+$ $[M+Na]^+$: 381.9872, found: 381.9872.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{81}BrNOSNa^+$ $[M+Na]^+$: 383.9851, found: 383.9852.

3-allyl-6-chloro-3-(phenylthio)indolin-2-one (3t)



3t

A white solid, 57% yield and 64% yield in DCM and DCE, respectively.

TLC: R_f = 0.50 (Hexane/EtOAc = 3:1).

M.P. : 148.6℃ ~ 150.7℃.

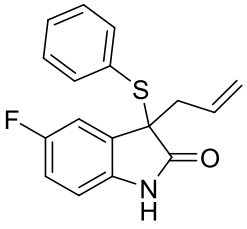
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.95 (s, 1H), 7.30 – 7.19 (m, 4H), 7.17 – 7.09 (m, 2H), 7.09 – 7.00 (m, 1H), 6.77 – 6.70 (m, 1H), 5.59 – 5.37 (m, 1H), 5.15 – 4.93 (m, 2H), 2.84 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 141.6, 136.6, 134.4, 130.9, 129.9, 129.0, 128.7, 128.3, 125.8, 122.7, 120.2, 110.7, 58.6, 39.7.

IR(KBr/cm^{-1}) 3432.4, 3137.7, 1726.4, 1683.3, 1616.8, 1485.1, 1439.2, 1330.0, 1238.1, 1066.4, 924.3, 748.1, 696.1, 620.3.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}ClNOSNa^+$ $[M+Na]^+$: 338.0377, found: 338.0377.

3-allyl-5-fluoro-3-(phenylthio)indolin-2-one (3u)



3u

A white solid, 92% yield.

M.P. : 150.0℃ ~ 152.2℃.

TLC: R_f = 0.36 (Hexane/EtOAc = 3:1).

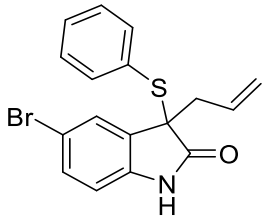
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 – 8.96 (m, 1H), 7.21 – 7.07 (m, 3H), 7.07 – 6.90 (m, 3H), 6.82 – 6.69 (m, 1H), 6.65 – 6.47 (m, 1H), 5.50 – 5.34 (m, 1H), 5.06 – 4.94 (m, 1H), 4.94 – 4.85 (m, 1H), 2.83 – 2.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 159.1 (d, *J* = 240.9 Hz), 136.5, 131.6 (d, *J* = 8.1 Hz), 130.8, 129.8, 129.0, 128.6, 120.3, 115.4 (d, *J* = 23.6 Hz), 112.5 (d, *J* = 24.9 Hz), 110.7 (d, *J* = 8.2 Hz), 59.4, 59.4, 39.7.

IR(KBr/cm^{-1}) 3222.9, 2924.6, 1721.2, 1680.6, 1486.0, 776.3, 750.0, 609.5.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}FNOSNa^+$ $[M+Na]^+$: 322.0672, found: 322.0675.

3-allyl-5-bromo-3-(phenylthio)indolin-2-one (3v)



3v

A white solid, 92% yield.

M.P. : 156.3℃ ~ 159.0℃.

TLC: R_f = 0.32 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 – 9.12 (m, 1H), 7.38 – 7.31 (m, 1H), 7.23 – 7.09 (m, 4H), 7.07 – 6.98 (m, 2H), 6.57 – 6.48 (m, 1H), 5.48 – 5.33 (m, 1H), 5.04 – 4.94 (m, 1H), 4.94 – 4.85 (m, 1H), 2.75 (d, *J* = 7.3 Hz, 2H).

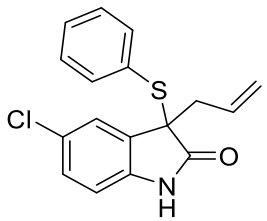
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 139.6, 136.6, 132.0, 131.7, 130.7, 129.8, 128.9, 128.7, 127.9, 120.3, 115.2, 111.6, 59.0, 39.6.

IR(KBr/cm^{-1}) 3397.2, 3241.5, 3074.9, 2922.9, 1722.3, 1683.7, 1307.7, 1184.3, 1126.6, 750.8, 611.4.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{79}BrNOSNa^+$ $[M+Na]^+$: 381.9872, found: 381.9872.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{81}BrNOSNa^+$ $[M+Na]^+$: 383.9851, found: 383.9852.

3-allyl-5-chloro-3-(phenylthio)indolin-2-one (3w)



3w

A white solid, 99% yield.

M.P. : 186.2℃ ~ 188.6℃.

TLC: R_f = 0.29 (Hexane/EtOAc = 3:1).

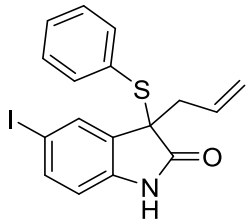
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.34 – 7.28 (m, 1H), 7.28 – 7.20 (m, 3H), 7.15 – 7.07 (m, 3H), 6.69 – 6.61 (m, 1H), 5.57 – 5.40 (m, 1H), 5.13 – 5.04 (m, 1H), 5.01 – 4.94 (m, 1H), 2.90 – 2.77 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 139.1, 136.6, 131.7, 130.8, 129.8, 128.9, 128.9, 128.7, 128.0, 125.1, 120.3, 111.1, 59.1, 39.6.

IR(KBr/cm^{-1}) 3234.2, 1722.0, 1682.9, 1616.8, 1477.3, 1439.2, 1308.1, 1184.9, 996.5, 928.2, 821.4, 751.3, 694.1.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}ClNOSNa^+$ $[M+Na]^+$: 338.0377, found: 338.0378.

3-allyl-5-iodo-3-(phenylthio)indolin-2-one (3x)



3x

A yellow solid, 95% yield.

M.P. : 162.5℃ ~ 163.5℃.

TLC: R_f = 0.46 (Hexane/EtOAc = 3:1).

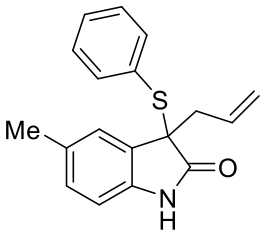
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.69 – 7.58 (m, 1H), 7.53 – 7.44 (m, 1H), 7.35 – 7.23 (m, 3H), 7.22 – 7.10 (m, 2H), 6.57 – 6.45 (m, 1H), 5.59 – 5.45 (m, 1H), 5.18 – 5.07 (m, 1H), 5.07 – 4.97 (m, 1H), 2.96 – 2.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 140.1, 137.6, 136.7, 133.7, 132.4, 130.8, 129.9, 129.0, 128.7, 120.4, 112.0, 85.0, 58.8, 39.6.

IR(KBr/cm^{-1}) 3430.3, 3198.6, 2923.5, 1721.4, 1685.3, 1613.2, 1472.3, 1435.2, 1307.4, 1183.3, 918.8, 815.6.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}INOSNa^+$ $[M+Na]^+$: 429.9733, found: 429.9735.

3-allyl-5-methyl-3-(phenylthio)indolin-2-one (3y)



3y

A white solid, 88% yield.

M.P. : 147.6℃ ~ 150.2℃.

TLC: R_f = 0.39 (Hexane/EtOAc = 3:1).

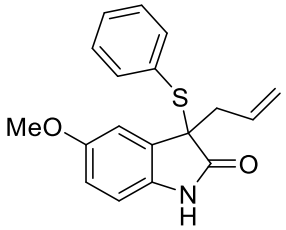
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 – 8.76 (m, 1H), 7.19 – 7.11 (m, 3H), 7.08 – 7.05 (m, 1H), 7.04 – 6.97 (m, 2H), 6.93 – 6.82 (m, 1H), 6.58 – 6.47 (m, 1H), 5.50 – 5.35 (m, 1H), 5.04 – 4.95 (m, 1H), 4.91 – 4.83 (m, 1H), 2.76 (dt, *J* = 7.2, 1.2 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.68, 138.22, 136.55, 132.07, 131.37, 129.80, 129.52, 129.49, 129.24, 128.46, 125.38, 119.73, 109.75, 58.90, 39.71, 21.31.

IR (KBr/cm^{-1}) 3218.8, 3072.3, 2917.7, 2857.6, 1718.3,1678.1,1490.5, 1314.7, 1207.3, 752.8, 694.7.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}NOSNa^+$ $[M+Na]^+$: 318.0923, found: 318.0923.

3-allyl-5-methoxy-3-(phenylthio)indolin-2-one (3z)



3z

A white solid, 90% yield.

M.P. : 96.4℃ ~ 98.2℃.

TLC: R_f = 0.32 (Hexane/EtOAc = 3:1).

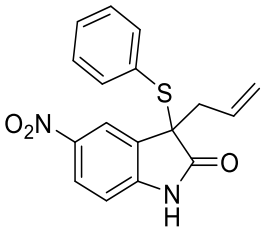
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 – 8.81 (m, 1H), 7.21 – 7.10 (m, 3H), 7.05 – 6.96 (m, 2H), 6.89 – 6.82 (m, 1H), 6.65 – 6.58 (m, 1H), 6.58 – 6.51 (m, 1H), 5.51 – 5.36 (m, 1H), 5.04 – 4.94 (m, 1H), 4.94 – 4.83 (m, 1H), 3.72 (s, 3H), 2.84 – 2.69 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 155.9, 136.5, 134.1, 131.2, 131.1, 129.5, 129.4, 128.5, 119.9, 113.9, 111.4, 110.5, 59.4, 55.9, 39.8.

IR (KBr/cm^{-1}) 3206.5, 2929.9, 2833.3, 17323.2, 1682.4,1488.4, 1204.8, 1029.5, 747.3, 688.5.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}NO_2SNa^+$ $[M+Na]^+$: 334.0872, found: 334.0873.

3-allyl-5-nitro-3-(phenylthio)indolin-2-one (3aa)



3aa

A yellow solid, 28% yield and 87% yield in DCM and DCE respectively.

M.P. : 197.6℃ ~ 200.2℃.

TLC: R_f = 0.27 (Hexane/EtOAc = 3:1).

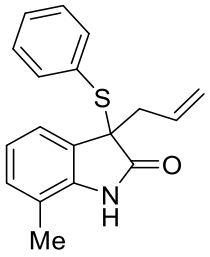
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 1H), 8.06 – 7.96 (m, 1H), 7.24 – 7.13 (m, 3H), 7.13 – 7.01 (m, 2H), 6.68 – 6.60 (m, 1H), 5.48 – 5.34 (m, 1H), 5.08 – 4.99 (m, 1H), 4.98 – 4.91 (m, 1H), 2.82 (dd, *J* = 7.3, 1.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 146.9, 143.2, 136.6, 131.0, 130.3, 130.0, 128.8, 128.5, 125.7, 120.7, 109.5, 58.7, 39.4.

IR(KBr/cm^{-1}) 3206.0, 2922.4, 2855.2, 1726.2, 1690.9, 1623.5, 1518.7, 1251.6, 1100.1, 753.4.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}N_2O_3SNa^+$ $[M+Na]^+$: 349.0617, found: 349.0622.

3-allyl-7-methyl-3-(phenylthio)indolin-2-one (3ab)



3ab

A white solid, 97% yield.

M.P. : 107.1℃ ~ 108.2℃.

TLC: R_f = 0.48 (Hexane/EtOAc = 3:1).

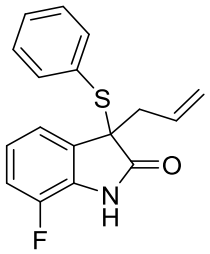
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 – 9.16 (m, 1H), 7.21 – 7.10 (m, 3H), 7.06 (d, *J* = 4.3 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.91 – 6.85 (m, 2H), 5.49 – 5.36 (m, 1H), 4.97 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.87 (dd, *J* = 10.1, 1.8 Hz, 1H), 2.82 – 2.71 (m, 2H), 2.10 – 2.01 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.21, 139.56, 136.63, 131.54, 130.09, 129.51, 129.47, 129.28, 128.35, 122.51, 122.15, 119.62, 119.54, 59.04, 39.50, 16.43.

IR(KBr/cm^{-1}) 3394.4, 3240.4, 1722.1, 1683.8, 1615.6, 1474.2, 1437.8, 1307.2, 1184.4, 996.2, 932.8, 828.9, 751.7, 691.8.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{17}NOSNa^+$ $[M+Na]^+$: 318.0923, found: 318.0925.

3-allyl-7-fluoro-3-(phenylthio)indolin-2-one (3ac)



3ac

A white solid, 67% yield.

M.P. : 76.8℃ ~ 78.0℃.

TLC: R_f = 0.42 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.28 – 7.22 (m, 3H), 7.18 – 7.14 (m, 1H), 7.14 – 7.08 (m, 2H), 7.05 – 6.99 (m, 1H), 6.95 – 6.89 (m, 1H), 5.55 – 5.42 (m, 1H), 5.11 – 5.03 (m, 1H), 5.00 – 4.94 (m, 1H), 2.95 – 2.80 (m, 2H).

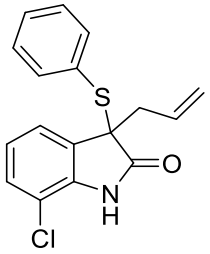
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 146.9 (d, *J* = 245.0 Hz), 136.6, 132.7 (d, *J* = 3.0 Hz), 130.9, 129.8, 129.0, 128.6, 127.9 (d, *J* = 12.1 Hz), 123.2 (d, *J* = 5.8 Hz), δ120.6 (d, *J* = 3.4 Hz), 120.2, 115.8 (d, *J* = 17.2 Hz), 59.2, 39.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -133.6.

IR(KBr/cm^{-1}) 3425.5, 3197.9, 1722.7, 1640.1, 1493.2, 1323.4, 1200.4, 924.9, 779.2, 729.2, 694.1.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}FNOSNa^+$ $[M+Na]^+$: 322.0672, found: 322.0673.

3-allyl-7-chloro-3-(phenylthio)indolin-2-one (3ad)



3ad

A white solid, 93% yield.

TLC: R_f = 0.52 (Hexane/EtOAc = 3:1).

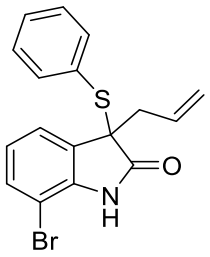
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.29 – 7.20 (m, 4H), 7.18 – 7.09 (m, 3H), 7.04 – 6.97 (m, 1H), 5.57 – 5.44 (m, 1H), 5.12 – 5.05 (m, 1H), 5.03 – 4.96 (m, 1H), 2.93 – 2.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 138.2, 136.7, 131.4, 130.9, 129.9, 128.9, 128.7, 128.6, 123.5, 123.2, 120.3, 115.0, 59.7, 39.6.

IR(KBr/cm^{-1}) 3420.0, 3151.7, 3076.2, 1721.5, 1619.4, 1474.6, 1323.0, 1174.6, 1143.5, 753.7, 707.9.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}ClNOSNa^+$ $[M+Na]^+$: 338.0377, found: 338.0379.

3-allyl-7-bromo-3-(phenylthio)indolin-2-one (3ae)



3ae

A white solid, 50% yield.

TLC: R_f = 0.55 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.32 – 7.22 (m, 5H), 7.18 – 7.13 (m, 2H), 6.98 – 6.92 (m, 1H), 5.59 – 5.46 (m, 1H), 5.12 – 5.04 (m, 1H), 5.04 – 4.98 (m, 1H), 2.92 – 2.77 (m, 2H).

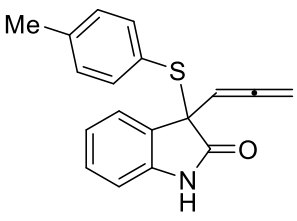
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 139.7, 136.6, 131.4, 131.2, 130.9, 129.9, 128.9, 128.6, 123.8, 123.8, 120.3, 102.7, 60.0, 39.6.

IR(KBr/cm^{-1}) 3432.2, 3181.7, 1721.7, 1615.6, 1472.1, 1320.3, 1134.1, 753.1, 696.6.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{79}BrNOSNa^+$ $[M+Na]^+$: 381.9872, found: 381.9872.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{14}{}^{81}BrNOSNa^+$ $[M+Na]^+$: 383.9851, found: 383.9851.

3-(propa-1,2-dien-1-yl)-3-(p-tolylthio)indolin-2-one (5a)



5a

A white solid, 92% yield.

M.P. : 145.5℃ ~ 147.6℃.

TLC: R_f = 0.55 (Hexane/EtOAc = 3:1).

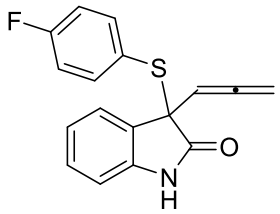
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (br s, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.13 (m, 3H), 7.12 – 7.02 (m, 1H), 7.00 – 6.90 (m, 2H), 6.82 – 6.71 (m, 1H), 5.67 (t, *J* = 6.6 Hz, 1H), 5.00 (dd, *J* = 11.6, 6.6 Hz, 1H), 4.89 (dd, *J* = 11.6, 6.6 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 177.0, 140.1, 139.9, 136.7, 129.5, 129.4, 128.9, 126.2, 126.0, 122.5, 110.1, 89.4, 79.6, 57.4, 21.4.

IR(KBr/cm^{-1}) 3446.5, 3242.7, 1955.3, 1724.0, 1691.4, 1620.7, 1472.4, 1398.5, 1328.3, 1211.1, 841.0, 811.9, 746.7.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{15}NNaOS^+$ $[M+Na]^+$: 316.0767, found: 316.0767.

3-((4-fluorophenyl)thio)-3-(propa-1,2-dien-1-yl)indolin-2-one (5b)



5b

A white solid, 98% yield.

M.P. : 134.6℃ ~ 136.4℃.

TLC: R_f = 0.53 (Hexane/EtOAc = 3:1).

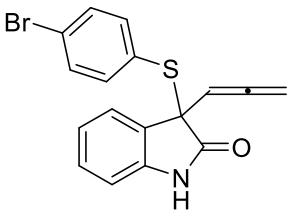
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.24 – 7.20 (m, 1H), 7.20 – 7.08 (m, 3H), 7.03 – 6.96 (m, 1H), 6.78 – 6.70 (m, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 5.56 (t, *J* = 6.6 Hz, 1H), 4.92 (dd, *J* = 11.7, 6.6 Hz, 1H), 4.81 (dd, *J* = 11.7, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 176.8, 164.0 (d, *J* = 250.8 Hz), 139.9, 138.9 (d, *J* = 8.7 Hz), 129.2, 129.2, 126.0, 125.1 (d, *J* = 3.4 Hz), 122.7, 115.7 (d, *J* = 21.7 Hz), 110.4, 89.1, 79.8, 57.5.

IR(KBr/cm^{-1}) 3166.5, 1956.8, 1730.1, 1684.4, 1618.5, 1488.4, 1470.7, 1228.8, 829.6, 819.5, 755.6.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{12}FNNaOS^+$ $[M+Na]^+$: 320.0516, found: 320.0517.

3-((4-bromophenyl)thio)-3-(propa-1,2-dien-1-yl)indolin-2-one (5c)



5c

A white solid, 82% yield.

TLC: R_f = 0.51 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (br s, 1H), 7.25 – 7.21 (m, 1H), 7.21 – 7.16 (m, 2H), 7.16 – 7.10 (m, 1H), 7.07 – 7.02 (m, 2H), 7.02 – 6.97 (m, 1H), 6.71 – 6.65 (m, 1H), 5.56 (t, *J* = 6.6 Hz, 1H), 4.93 (dd, *J* = 11.7, 6.6 Hz, 1H), 4.82 (dd, *J* = 11.7, 6.6 Hz, 1H).

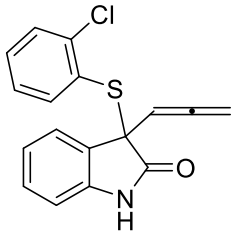
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 176.4, 139.8, 138.2, 131.8, 129.3, 129.1, 128.9, 126.0, 124.9, 122.7, 110.2, 89.2, 79.9, 57.4.

IR(KBr/cm^{-1}) 3225.3, 1950.1, 1725.1, 1690.5, 1620.7, 1471.9, 1392.5, 1328.5, 1212.8, 1068.8, 1010.7, 851.3, 814.6, 745.1.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{12}{}^{79}BrNNaOS^+$ $[M+Na]^+$: 381.9695, found: 381.9696.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{12}{}^{81}BrNNaOS^+$ $[M+Na]^+$: 379.9715, found: 379.9717.

3-((2-chlorophenyl)thio)-3-(propa-1,2-dien-1-yl)indolin-2-one (5d)



5d

A white solid, 96% yield.

TLC: R_f = 0.60 (Hexane/EtOAc = 3:1).

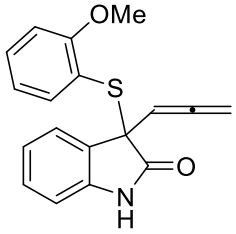
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.44 – 7.38 (m, 1H), 7.27 – 7.21 (m, 1H), 7.17 – 7.09 (m, 3H), 7.04 – 6.97 (m, 1H), 6.96 – 6.89 (m, 1H), 6.76 – 6.70 (m, 1H), 5.62 (t, *J* = 6.6 Hz, 1H), 4.91 (dd, *J* = 11.7, 6.6 Hz, 1H), 4.78 (dd, *J* = 11.7, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3, 176.7, 140.6, 139.9, 138.7, 131.0, 130.0, 129.4, 129.3, 128.4, 126.7, 126.2, 122.5, 110.2, 89.5, 79.7, 57.3.

IR(KBr/cm^{-1}) 3173.6, 1950.2, 1721.5, 1682.0, 1621.1, 1473.3, 1448.0, 1333.2, 1208.8, 891.5, 851.7, 747.4, 672.2.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{12}ClNNaOS^+$ $[M+Na]^+$: 336.0220, found: 336.0222.

3-((2-methoxyphenyl)thio)-3-(propa-1,2-dien-1-yl)indolin-2-one (5e)



5e

A white solid, 92% yield.

M.P. : 148.0℃ ~ 149.7℃.

TLC: R_f = 0.60 (Hexane/EtOAc = 3:1).

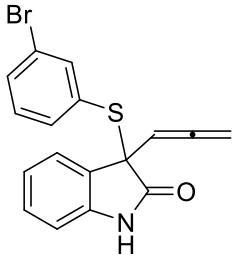
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (s, 1H), 7.35 – 7.25 (m, 1H), 7.21 – 7.13 (m, 1H), 7.13 – 7.08 (m, 1H), 7.08 – 7.00 (m, 1H), 6.90 – 6.83 (m, 1H), 6.70 – 6.64 (m, 2H), 6.61 (d, *J* = 8.2 Hz, 1H), 5.63 (t, *J* = 6.6 Hz, 1H), 4.89 (dd, *J* = 11.6, 6.6 Hz, 1H), 4.78 (dd, *J* = 11.6, 6.6 Hz, 1H), 3.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1, 177.4, 161.0, 139.9, 139.2, 131.8, 129.0, 128.7, 126.1, 121.9, 120.4, 117.9, 110.7, 109.8, 89.8, 79.6, 57.3, 55.4.

IR(KBr/cm^{-1}) 3266.3, 1953.3, 1719.9, 1683.2, 1670.0, 1472.5, 1274.8, 1247.7, 1023.5, 863.9, 757.1, 700.1.

HRMS (ESI+): *m/z* calcd for $C_{18}H_{15}NNaO_2S^+$ $[M+Na]^+$: 332.0716, found: 332.0718.

3-((3-bromophenyl)thio)-3-(propa-1,2-dien-1-yl)indolin-2-one (5f)



5f

A white solid, 93% yield.

M.P. : 149.2℃ ~ 151.3℃.

TLC: R_f = 0.56(Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (br s, 1H), 7.38 – 7.27 (m, 2H), 7.23 – 7.10 (m, 3H), 7.04 – 6.97 (m, 1H), 6.97 – 6.89 (m, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 5.57 (t, *J* = 6.6 Hz, 1H), 4.95 (dd, *J* = 11.7, 6.6 Hz, 1H), 4.83 (dd, *J* = 11.8, 6.6 Hz, 1H).

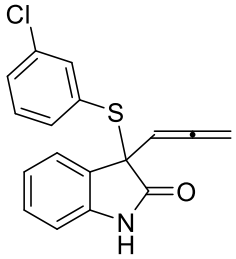
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 176.4, 139.8, 139.1, 135.2, 132.8, 131.9, 129.8, 129.4, 128.9, 126.0, 122.7, 121.9, 110.2, 89.1, 79.9, 57.5.

IR(KBr/cm^{-1}) 3240.8, 1950.0, 1723.7, 1691.1, 1620.9, 1473.4, 1394.7, 1211.3, 1093.8, 1014.5, 852.5, 818.0, 744.6.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{12}{}^{79}BrNNaOS^+$ $[M+Na]^+$: 379.9715, found: 379.9715.

HRMS (ESI+): *m/z* calcd for $C_{17}H_{12}{}^{81}BrNNaOS^+$ $[M+Na]^+$: 381.9695, found: 381.9694.

3-((3-chlorophenyl)thio)-3-(propa-1,2-dien-1-yl)indolin-2-one (5g)



5g

A white solid, 89% yield.

M.P. : 146.7℃ ~ 148.1℃.

TLC: R_f = 0.53 (Hexane/EtOAc = 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (br s, 1H), 7.25 – 7.08 (m, 5H), 7.04 – 6.96 (m, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.57 (t, *J* = 6.6 Hz, 1H), 4.95 (dd, *J* = 11.8, 6.6 Hz, 1H), 4.83 (dd, *J* = 11.8, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 176.4, 139.8, 139.8, 136.3, 134.8, 134.0, 131.6, 130.0, 129.5, 129.3, 129.0, 126.0, 122.7, 110.2, 110.1, 89.1, 79.9, 57.4.

IR(KBr/cm^{-1}) 3160.3, 1950.1, 1724.3, 1680.8, 1620.5, 1471.3, 1397.2, 1217.0, 853.7, 780.7, 756.5.
HRMS (ESI+): *m/z* calcd for $C_{17}H_{12}ClNNaOS^+$ $[M+Na]^+$: 336.0220, found:336.0221.

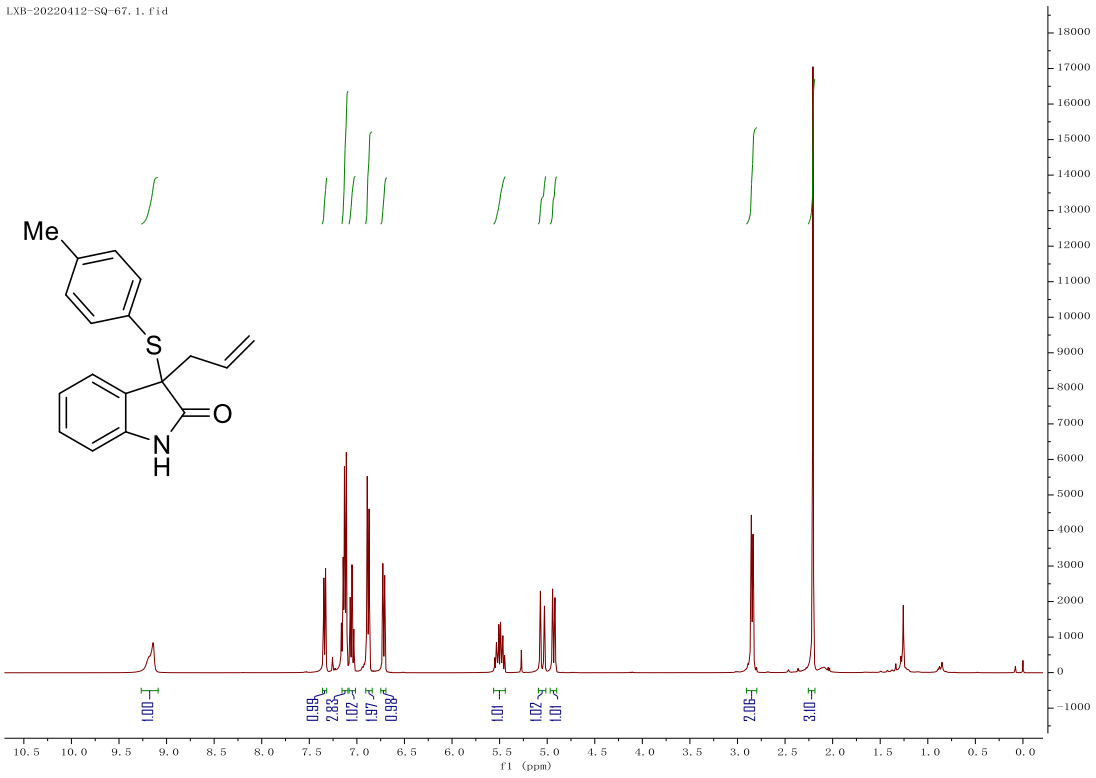
(I). References

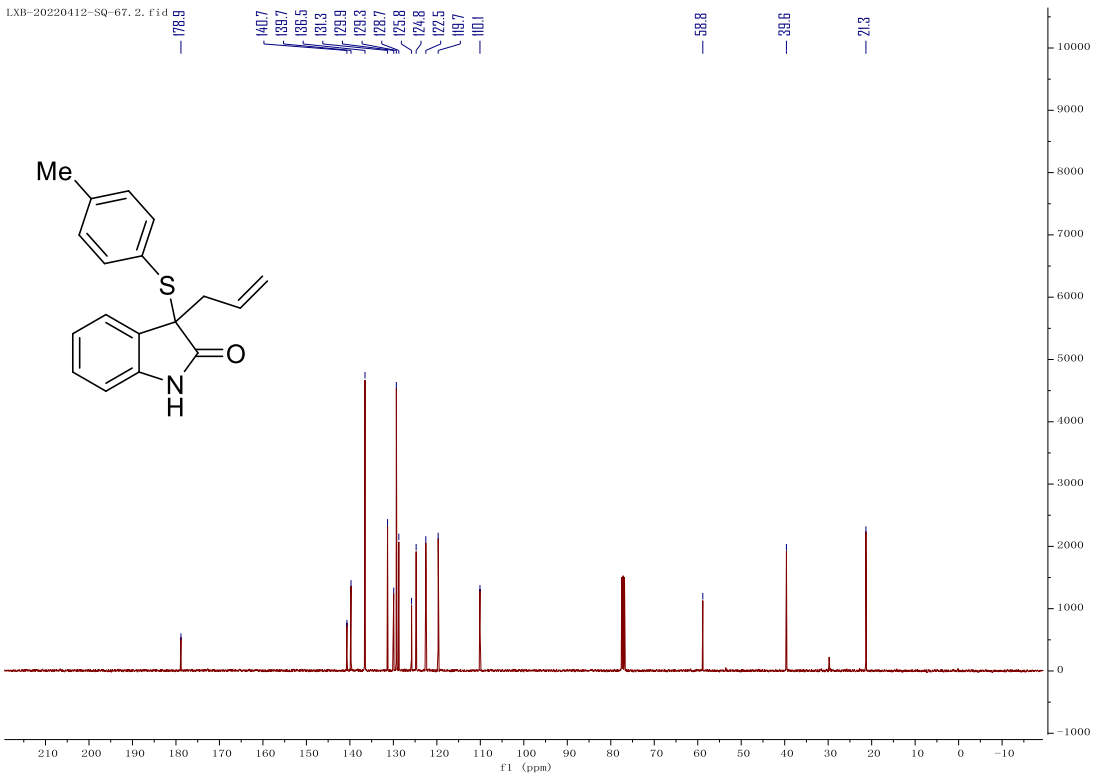
1. C. G. Espino, K. W. Fiori, M. Kim, J. Du Bois, *J. Am. Chem. Soc.*, 2004, **126**, 15378.

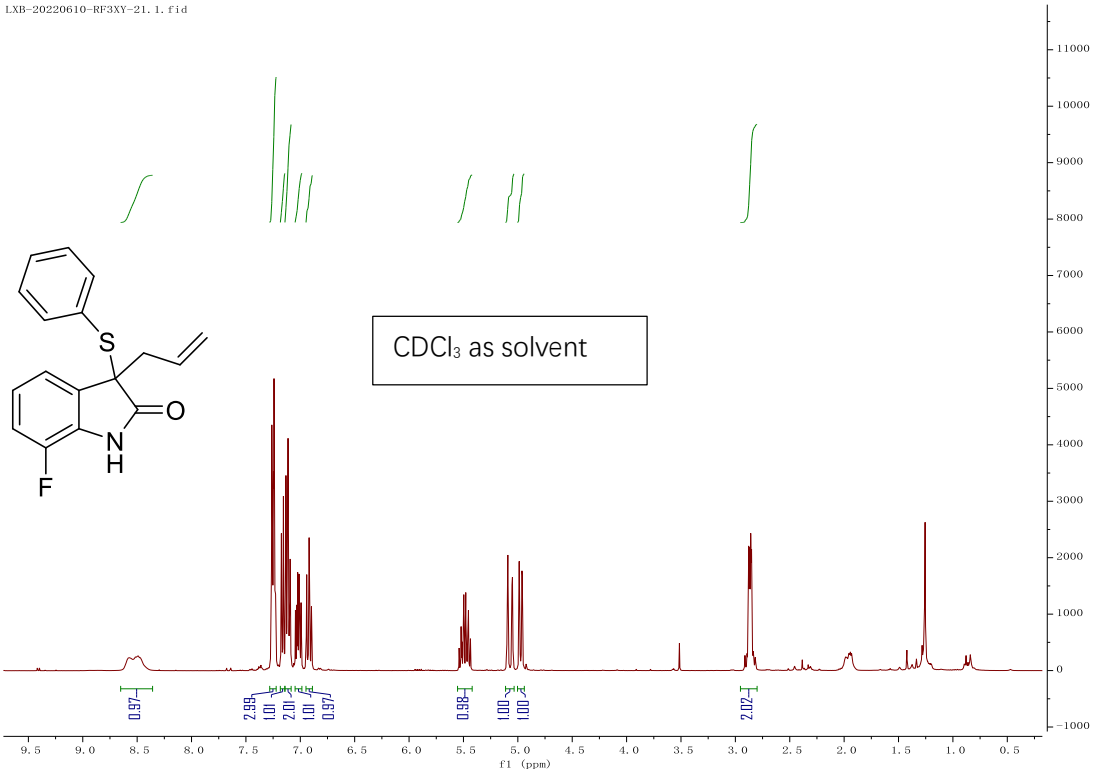
2. B. Ma, P. Wu, X. Wang, Z. Y. Wang, H.-X. Lin, H.-X. Dai, *Angew. Chem., Int. Ed.*, 2019, **58**, 13335.

3. (a) X. F. Xu, C. Li, Z. H. Tao, Y. J. Pan, *Green Chem.*, 2017, **19**, 1245; (b) M. P. Gogoi, R. Vanjari, B. Prabagar, S. Yang, S. Dutta, R. K. Mallick, V. Gandon, A. K. Sahoo, *Chem. Commun.*, 2021, **57**, 7521.

(J) ^{1}H and ^{13}C NMR spectra data of all products



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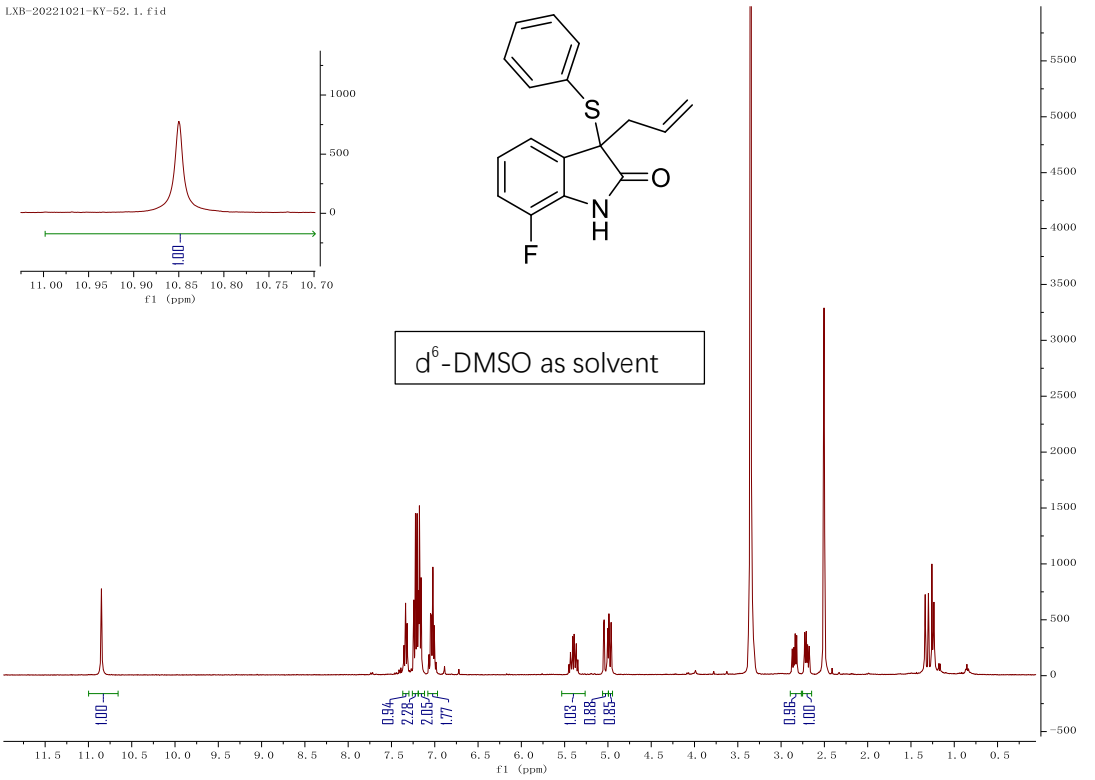
CDCl3 as solvent
S
O
N
H
F
f1 (ppm)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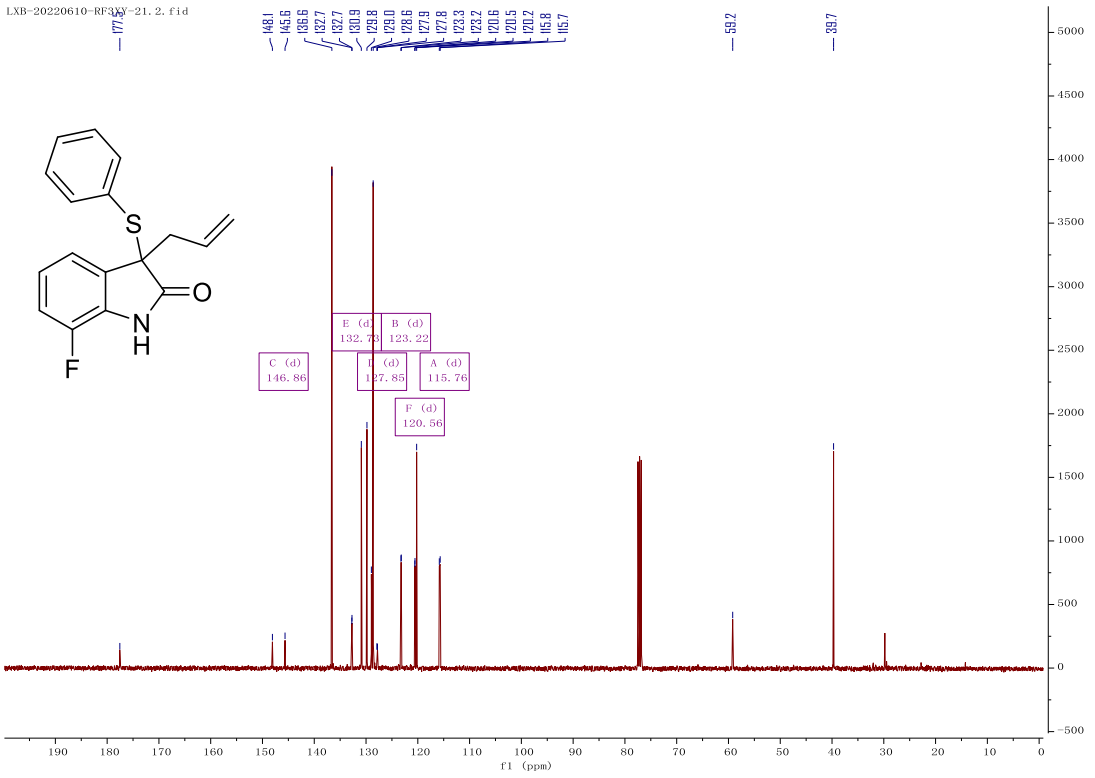
d6-DMSO as solvent
S
O
N
H
F
f1 (ppm)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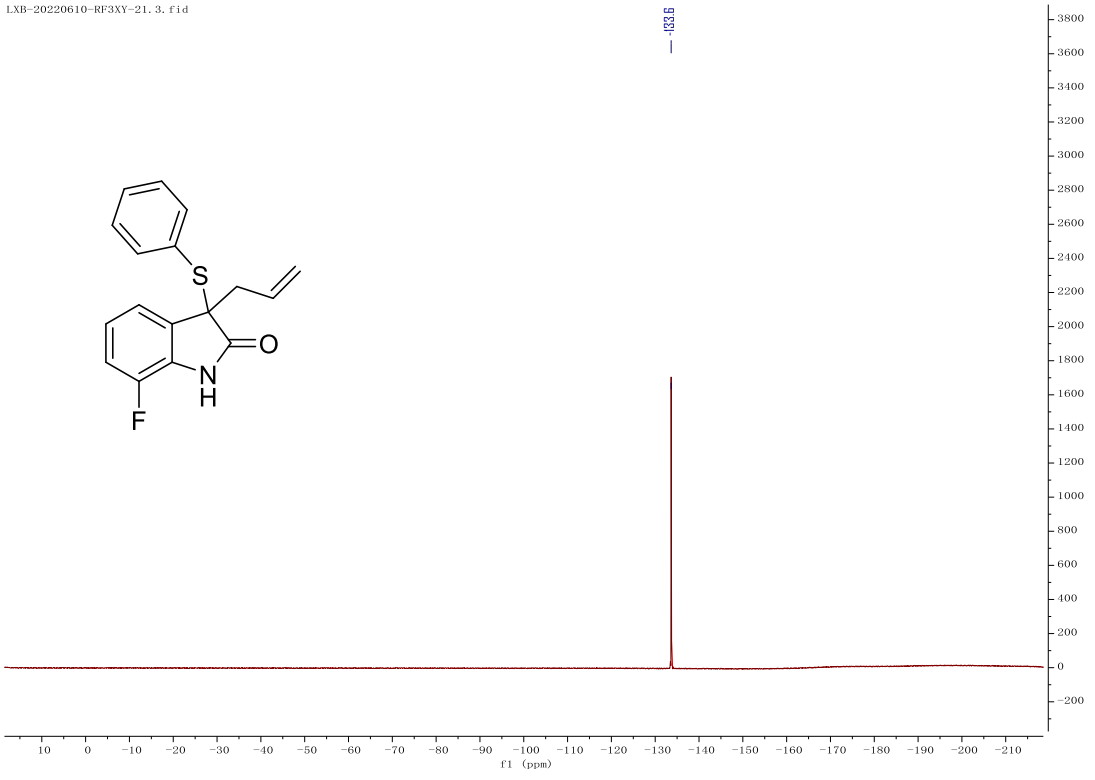
148.1
145.6
136.6
132.7
132.7
130.9
129.8
129.0
128.6
127.9
127.8
123.3
123.2
120.6
120.5
120.2
115.8
115.7
59.2
39.7
E (d)
132.73
B (d)
123.22
C (d)
146.86
D (d)
127.85
A (d)
115.76
F (d)
120.56
S
O
N
H
F
f1 (ppm)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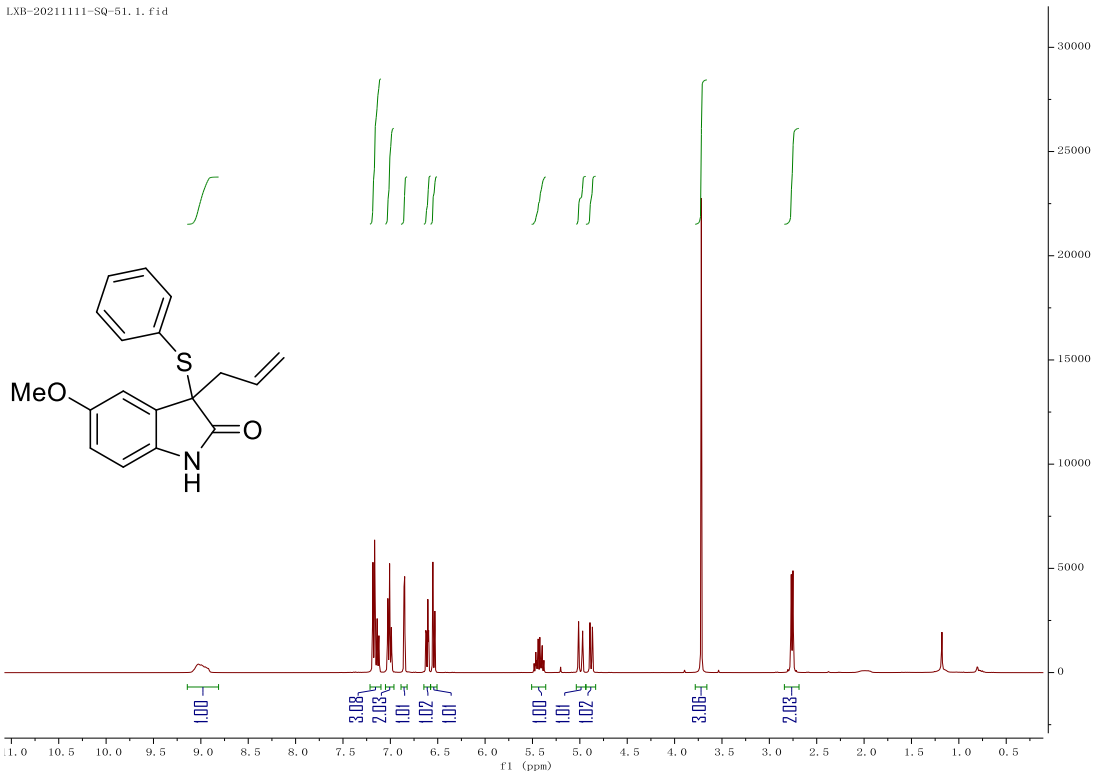
S
O
N
H
F
f1 (ppm)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MeO
S
O
N
H
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1.01
1.02
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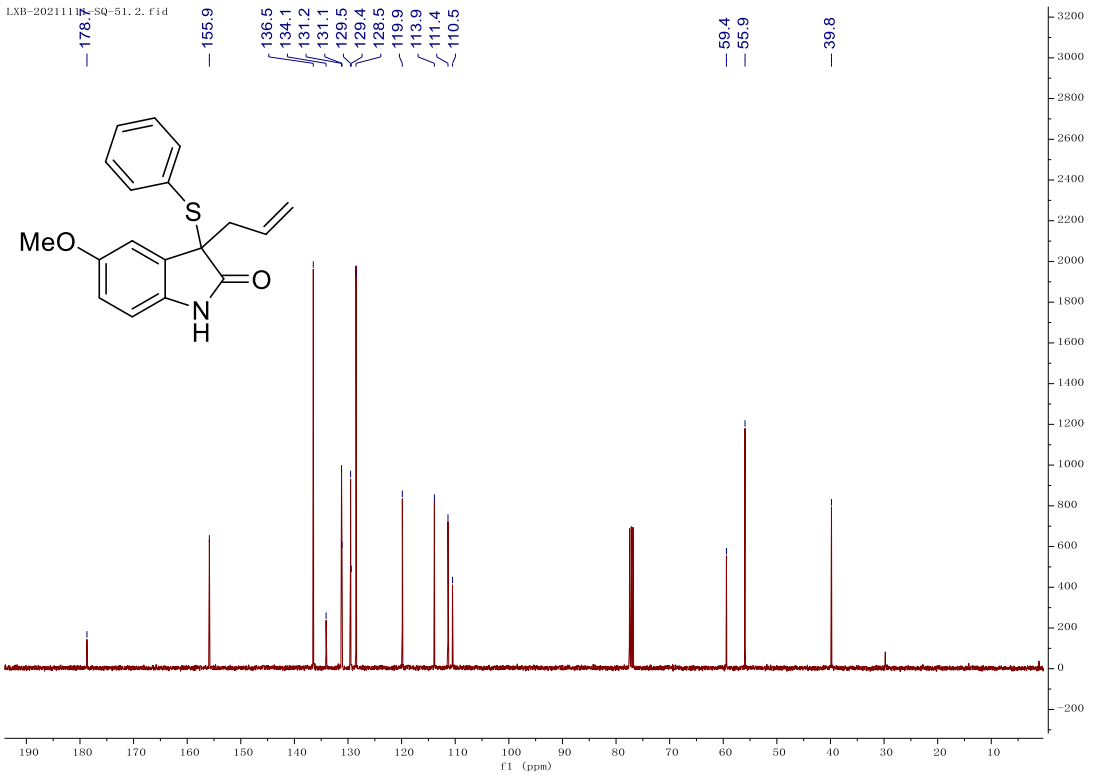
1.01
1.02
3.06
2.03
f1 (ppm)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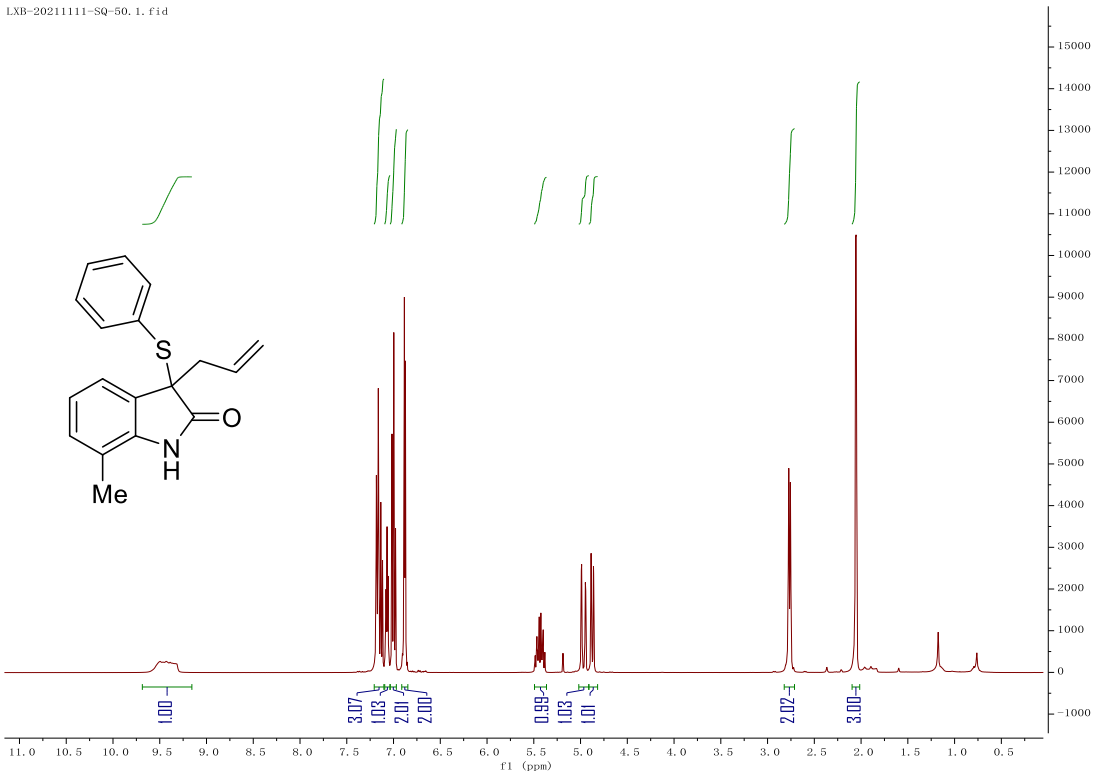
155.9
136.5
134.1
131.2
131.1
129.5
129.4
128.5
119.9
113.9
111.4
110.5
59.4
55.9
39.8
MeO
S
O
N
H
f1 (ppm)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S
O
N
H
Me
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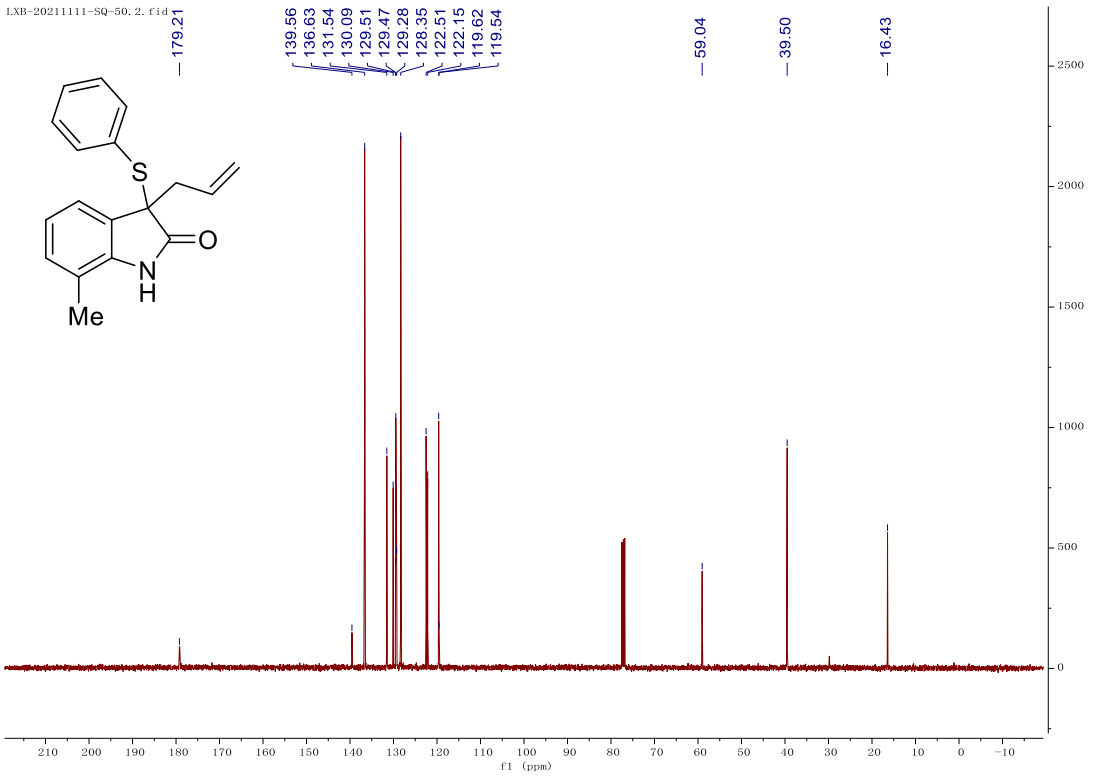
3.07
1.03
2.01
2.00
0.99
1.03
1.01
2.02
3.00
f1 (ppm)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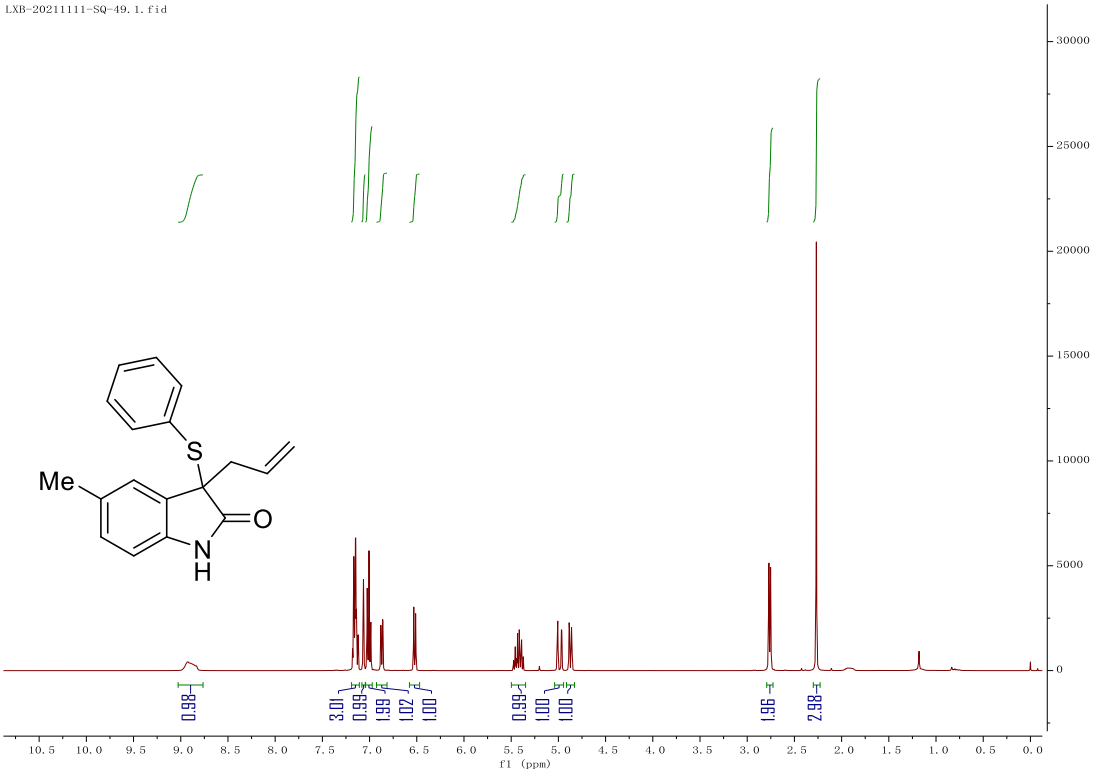
139.56
136.63
131.54
130.09
129.51
129.47
129.28
128.35
122.51
122.15
119.62
119.54
59.04
39.50
16.43
S
O
N
H
Me
f1 (ppm)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S
O
N
H
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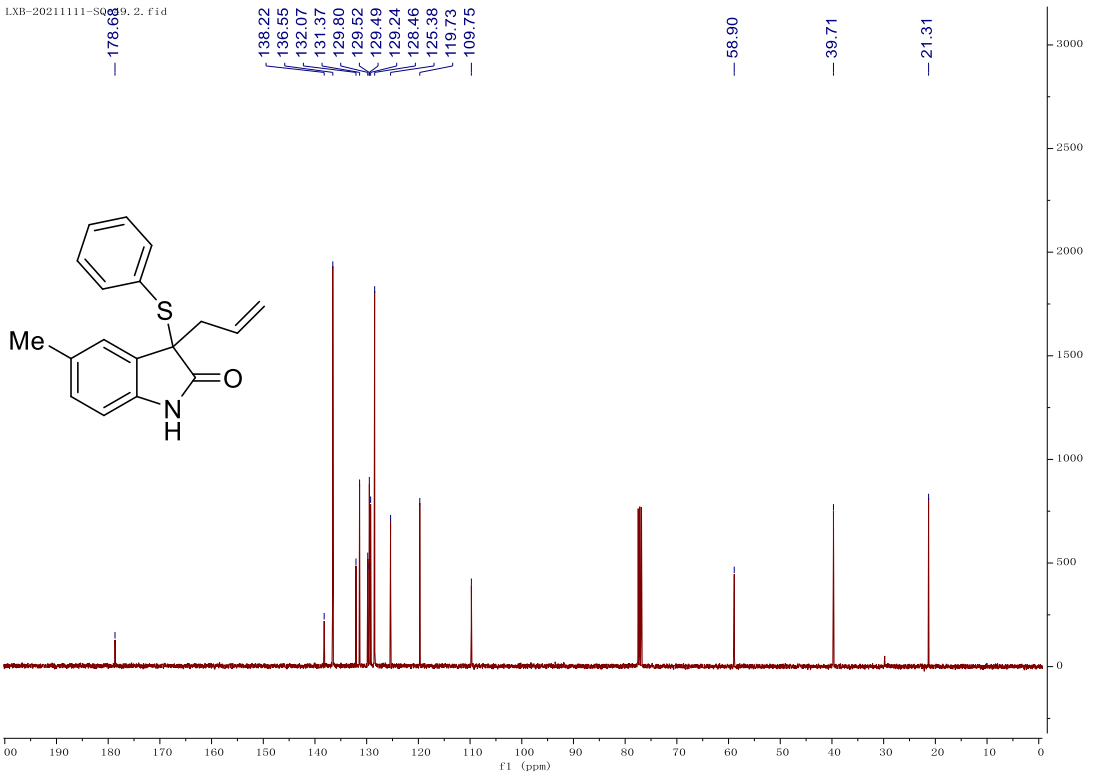
0.99
1.99
1.02
1.00
0.99
1.00
1.00
1.96
2.98
f1 (ppm)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129.49
129.24
128.46
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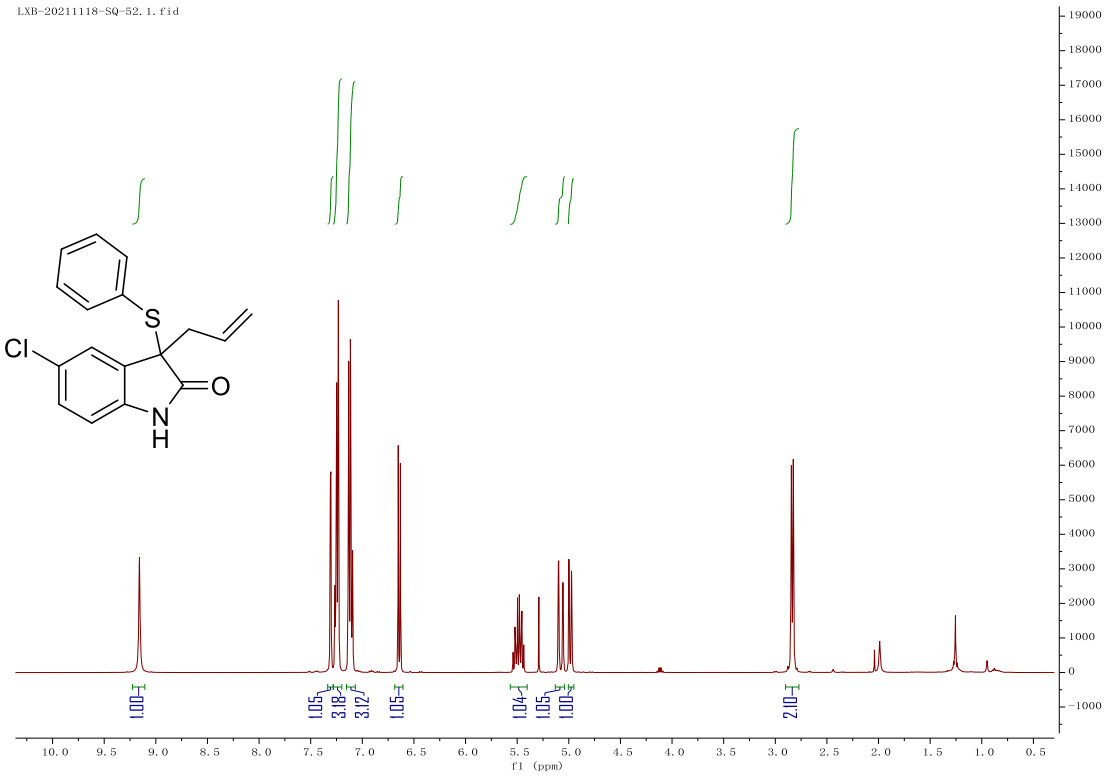
119.73
109.75
58.90
39.71
21.31
Me
S
O
N
H
f1 (ppm)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Cl
S
O
N
H
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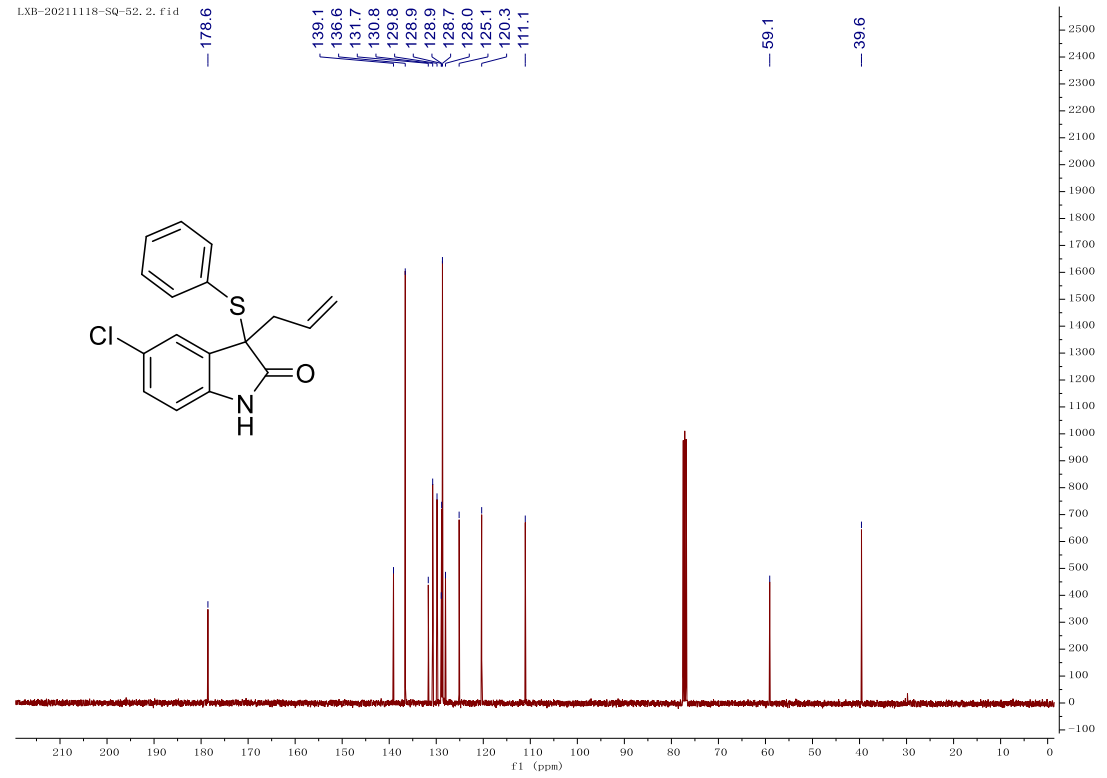
3.18
3.12
1.05
1.04
1.05
1.00
2.10
f1 (ppm)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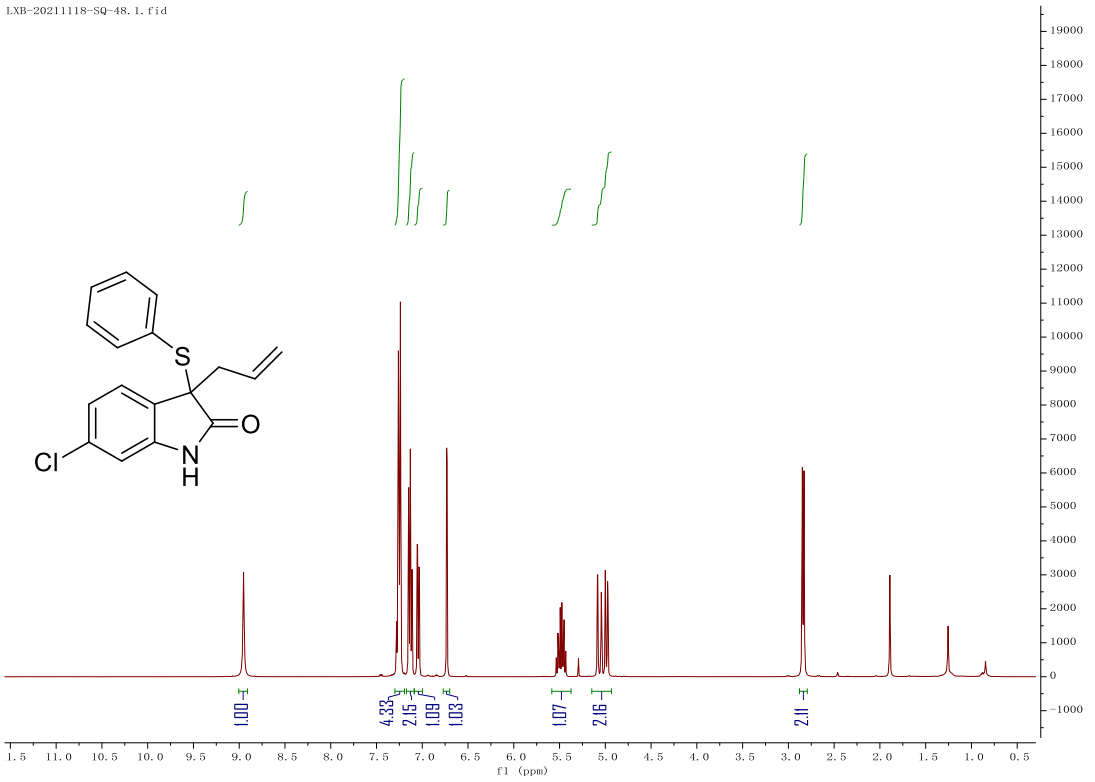
139.1
136.6
131.7
130.8
129.8
128.9
128.9
128.7
128.0
125.1
120.3
111.1
59.1
39.6
Cl
S
O
N
H
f1 (ppm)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S
O
N
H
Cl
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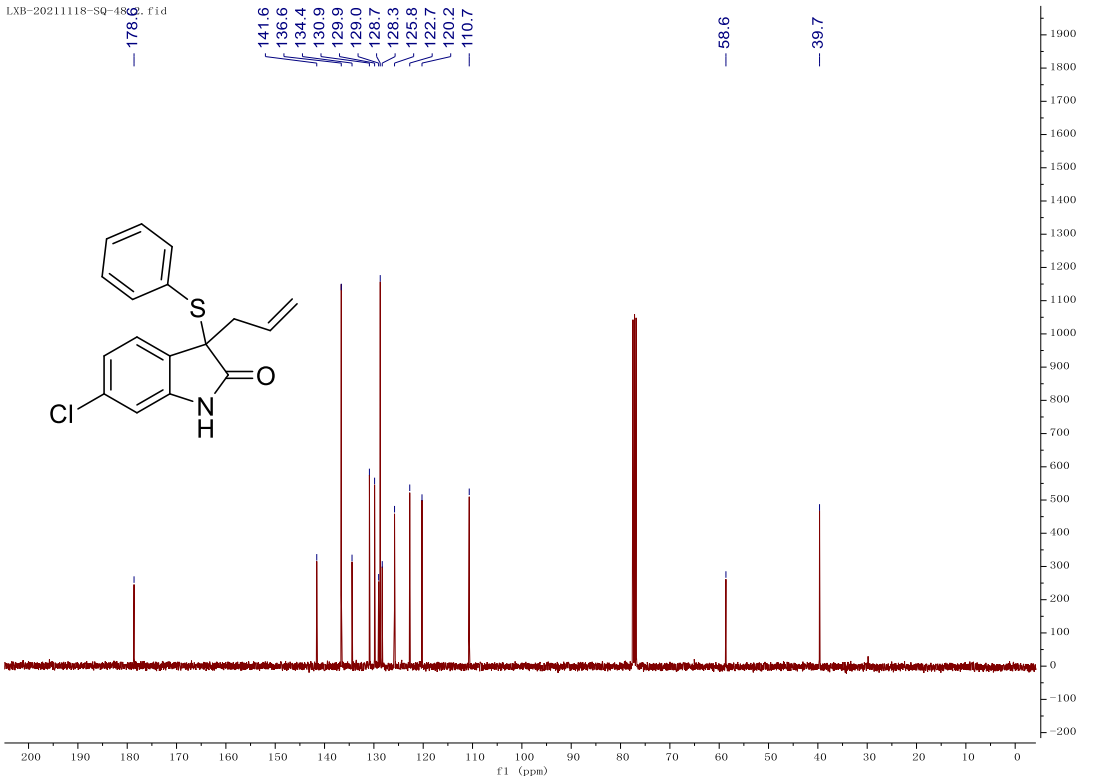
1.09
1.03
1.07
2.16
2.11
f1 (ppm)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130.9
129.9
129.0
128.7
128.3
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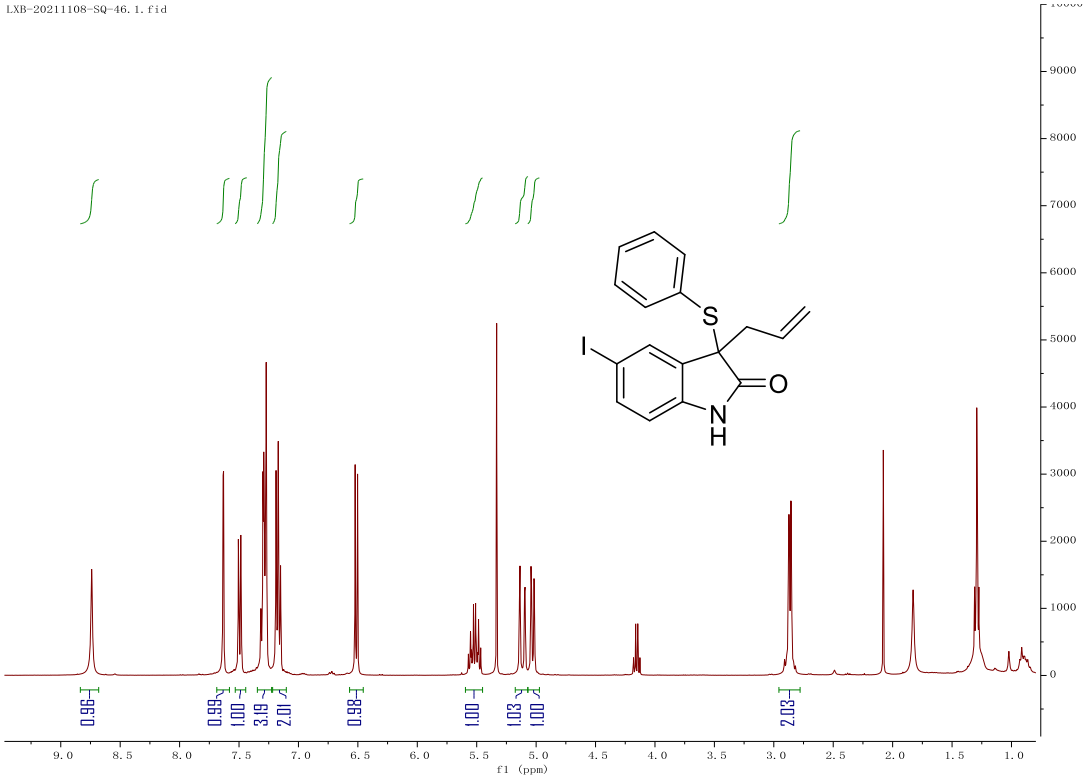
120.2
110.7
58.6
39.7
S
O
N
H
Cl
f1 (ppm)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3.19
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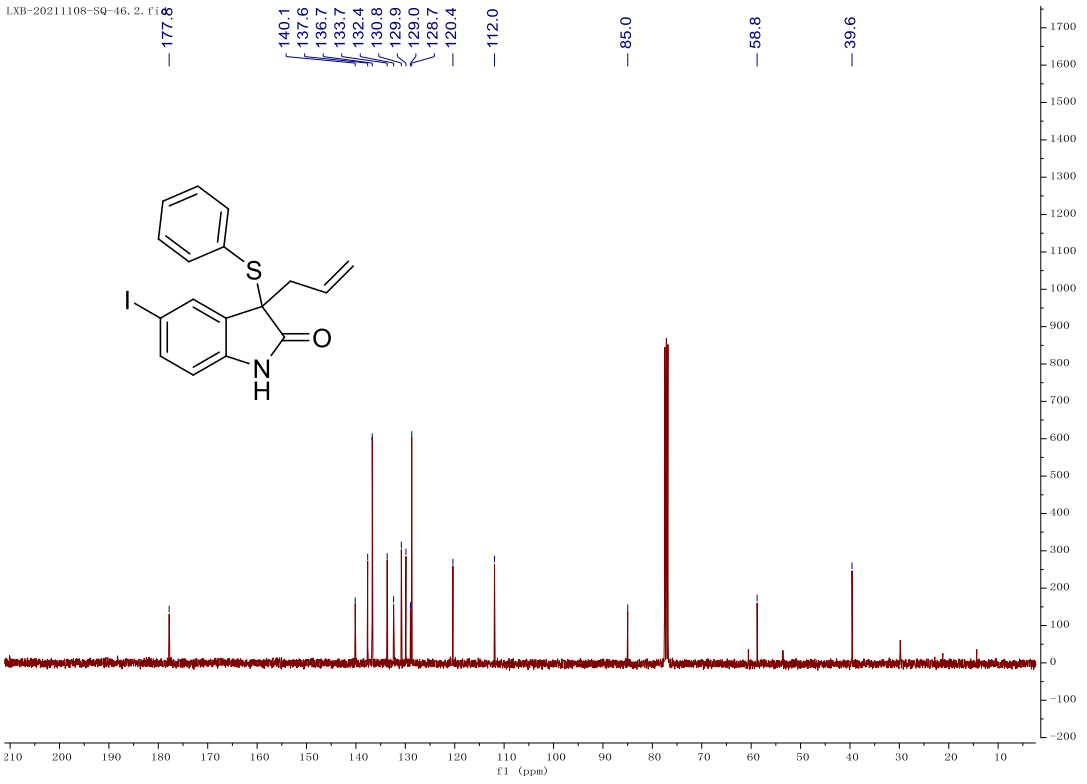
0.98
1.00
1.03
1.00
2.03
f1 (ppm)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140.1
137.6
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129.9
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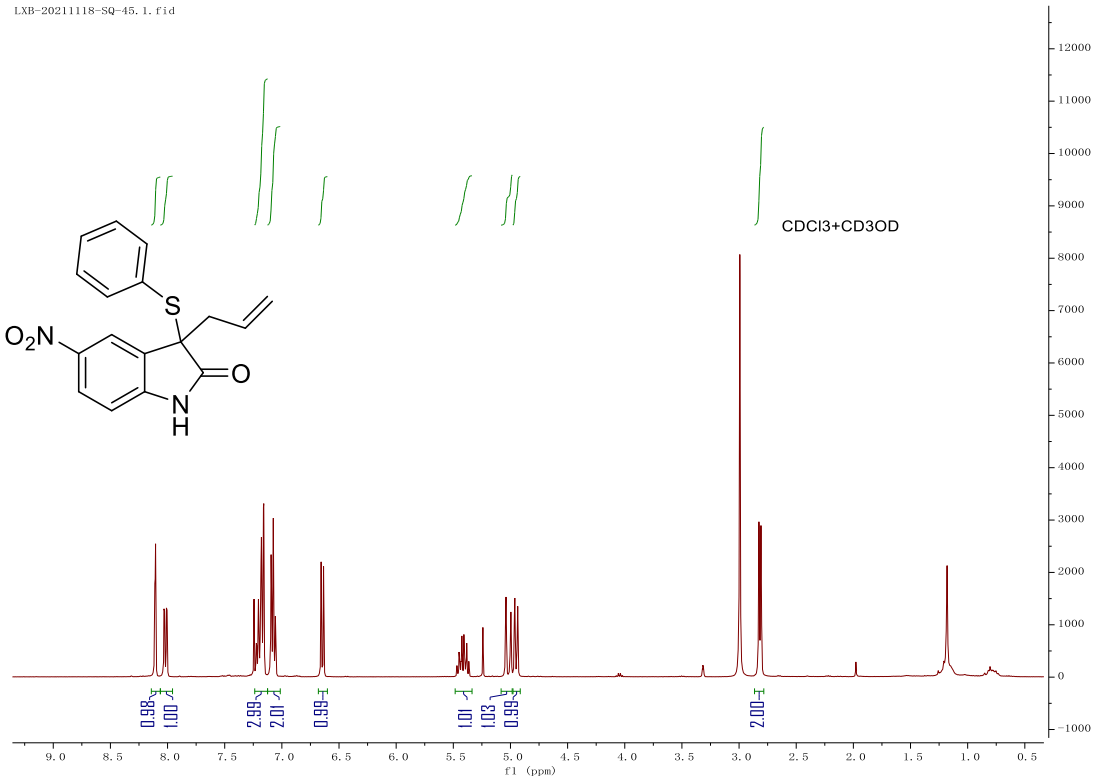
112.0
85.0
58.8
39.6
f1 (ppm)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CDCl3+CD3OD
O2N
S
O
N
H
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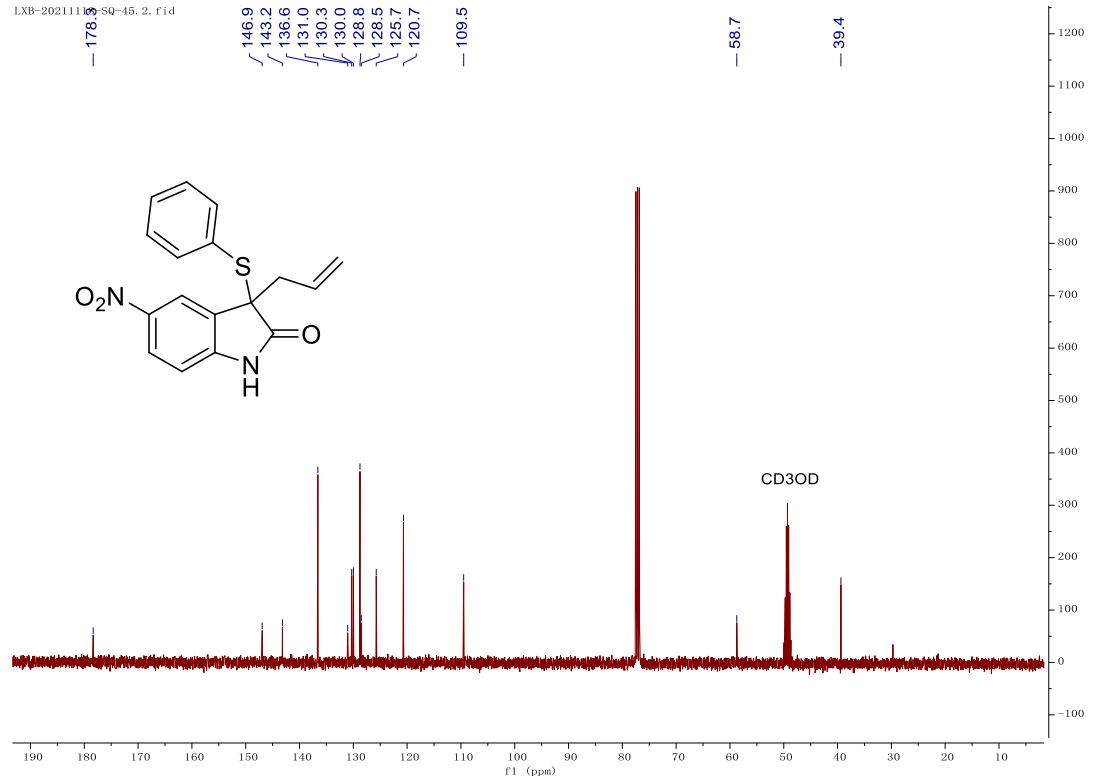
2.01
0.99
1.01
1.03
0.99
2.00
f1 (ppm)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146.9
143.2
136.6
131.0
130.3
130.0
128.8
128.5
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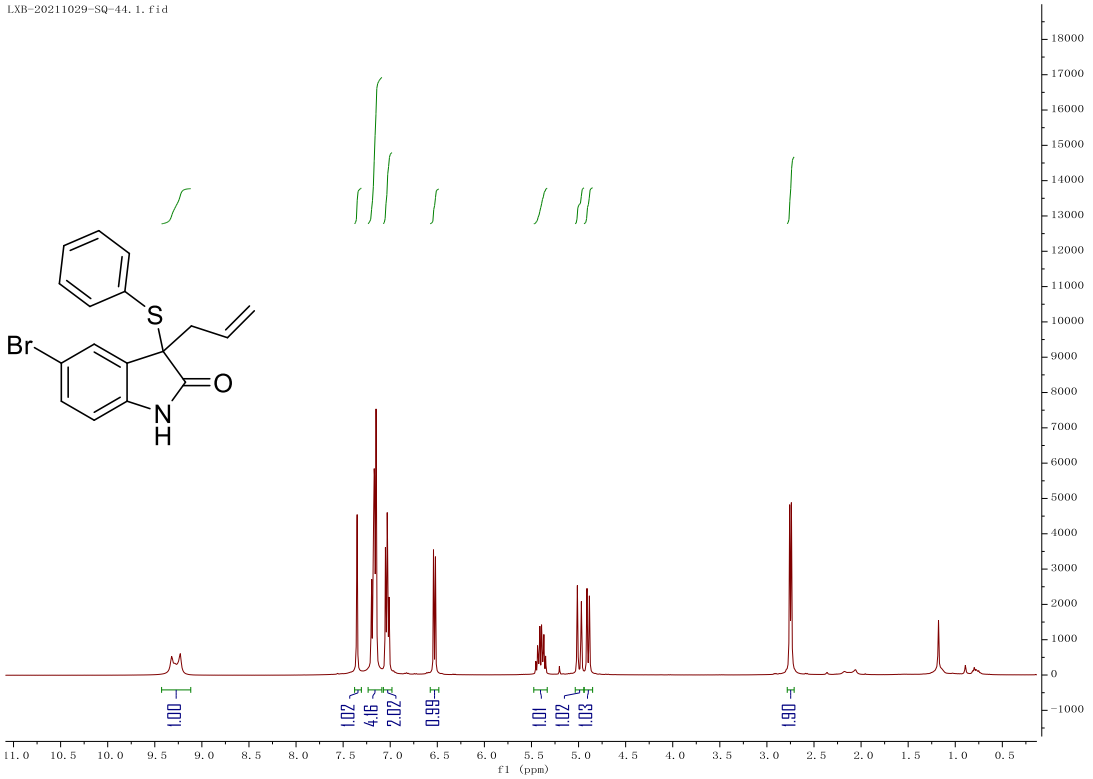
120.7
109.5
58.7
39.4
CD3OD
O2N
S
O
N
H
f1 (ppm)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Br
S
O
N
H
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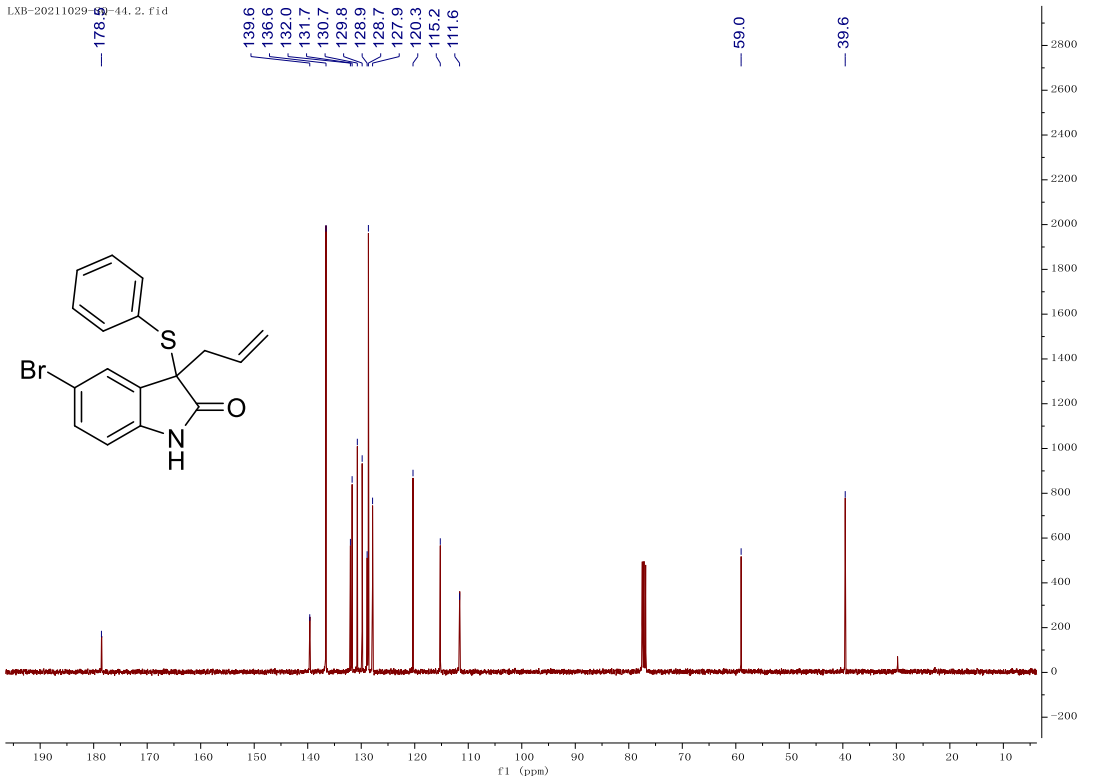
4.16
2.02
0.99
1.01
1.02
1.03
1.90
f1 (ppm)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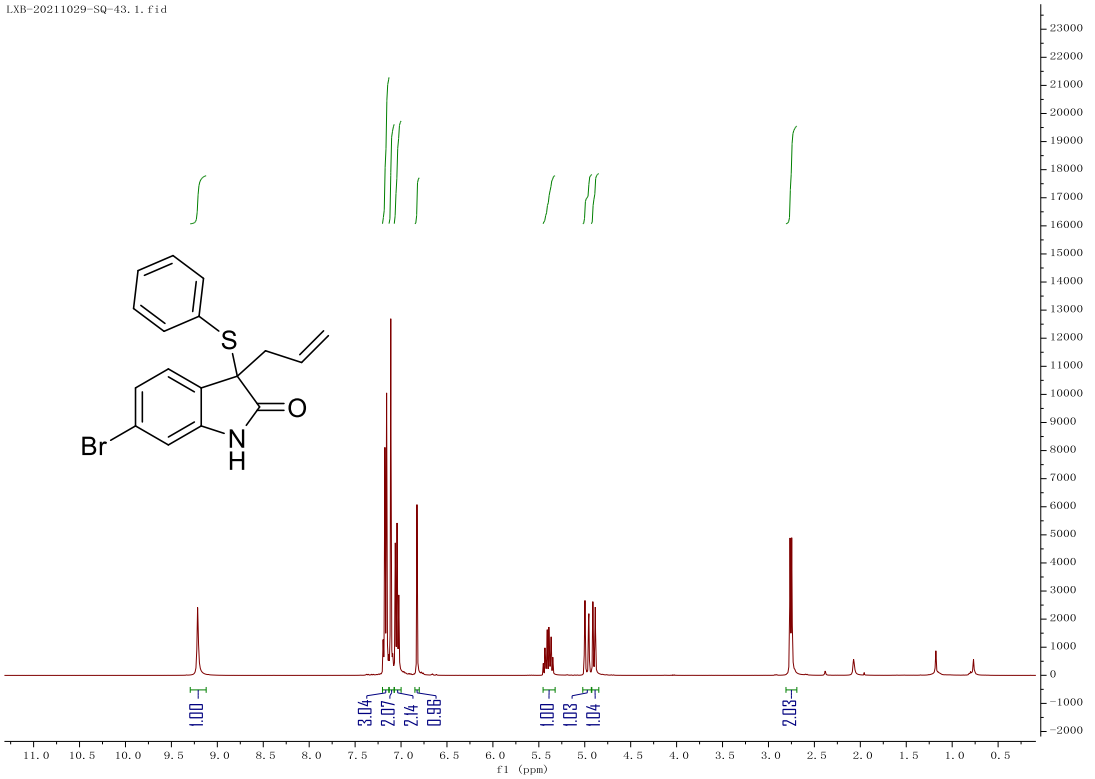
120.3
115.2
111.6
59.0
39.6
Br
S
O
N
H
f1 (ppm)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O
N
H
Br
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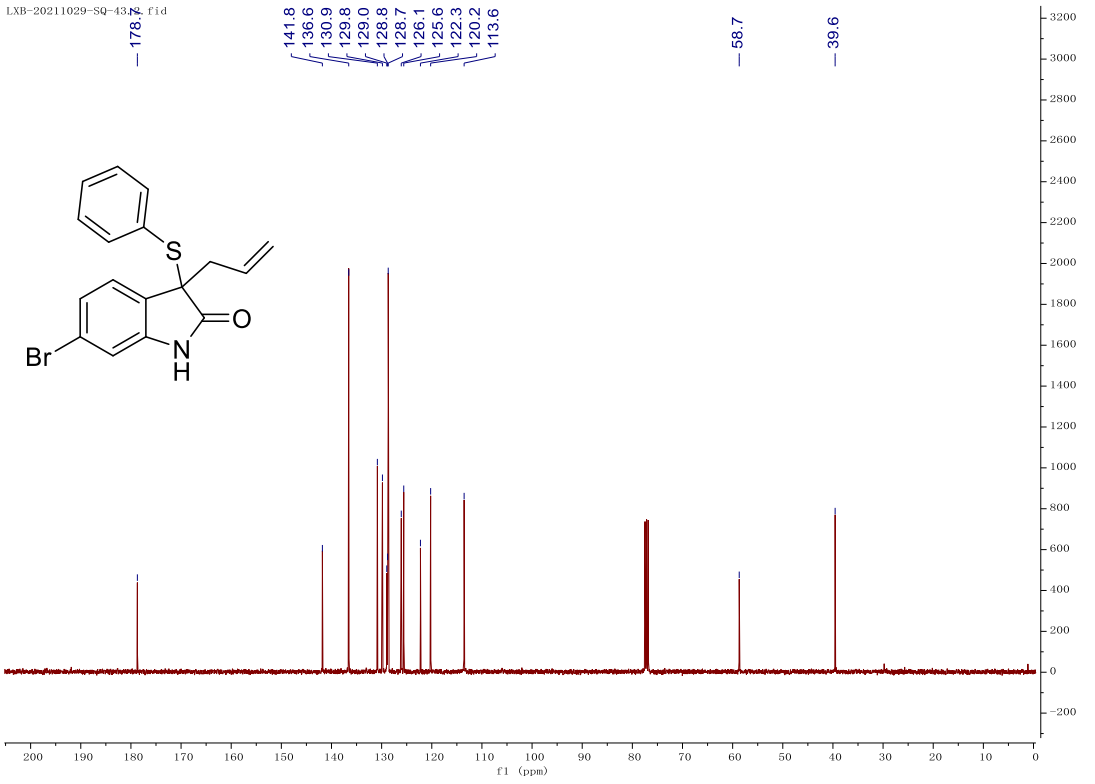
1.00
1.03
1.04
2.03
f1 (ppm)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141.8
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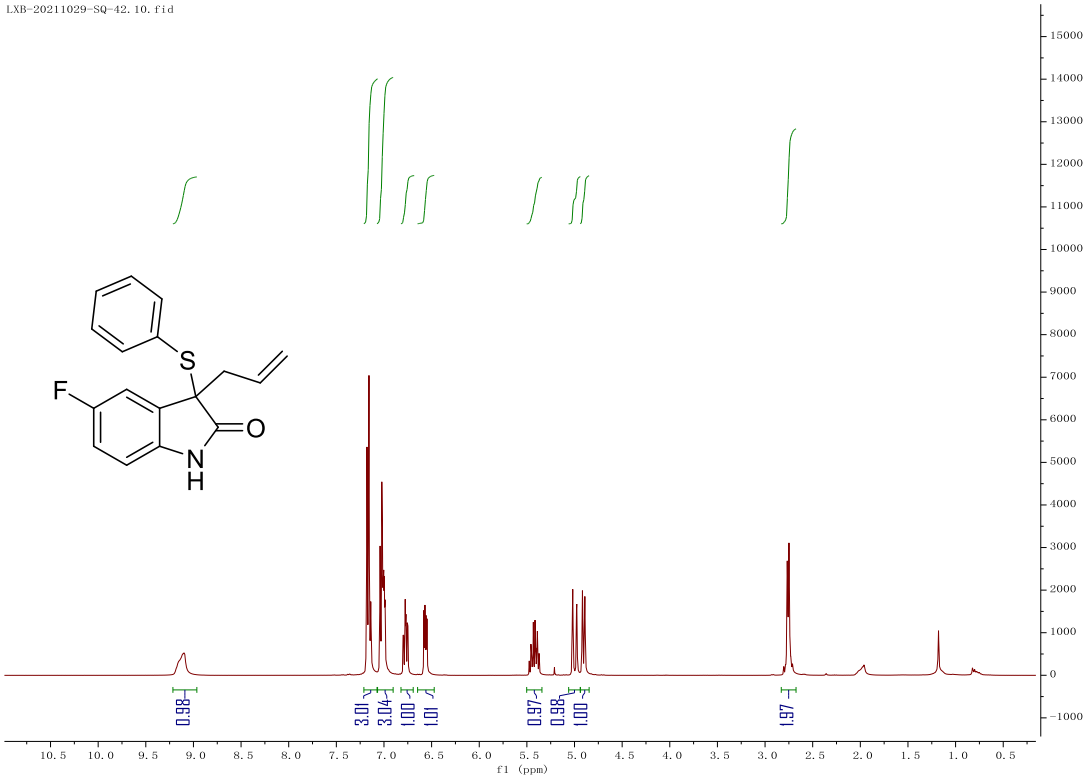
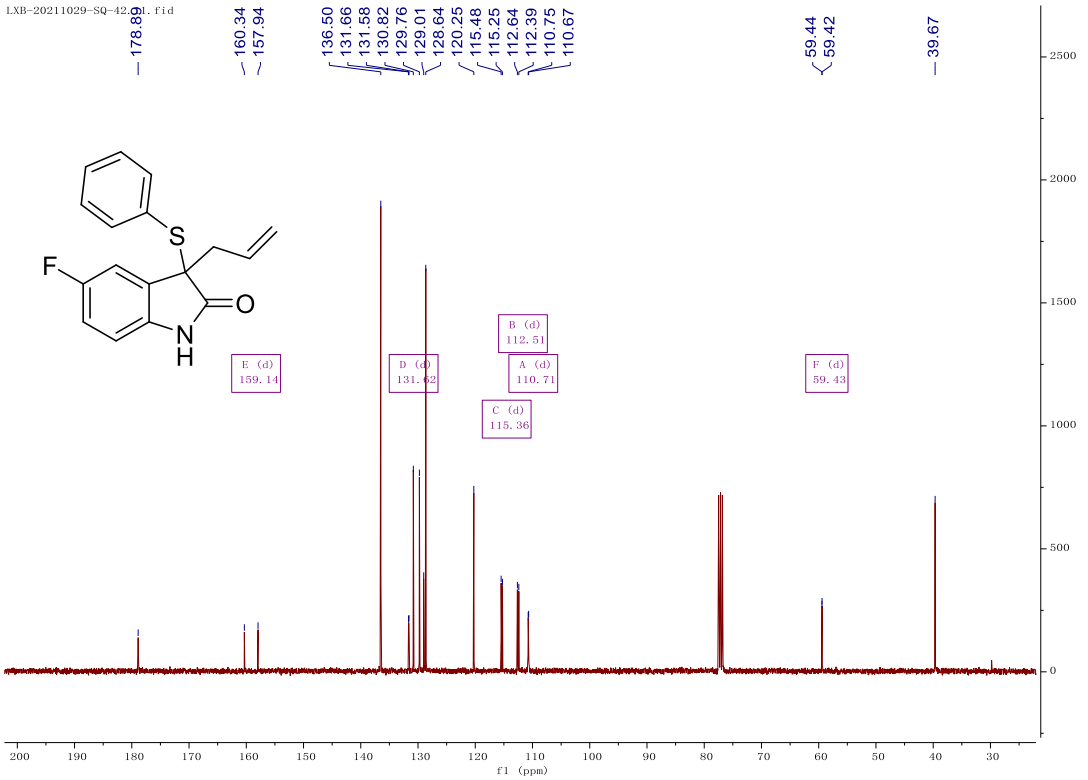
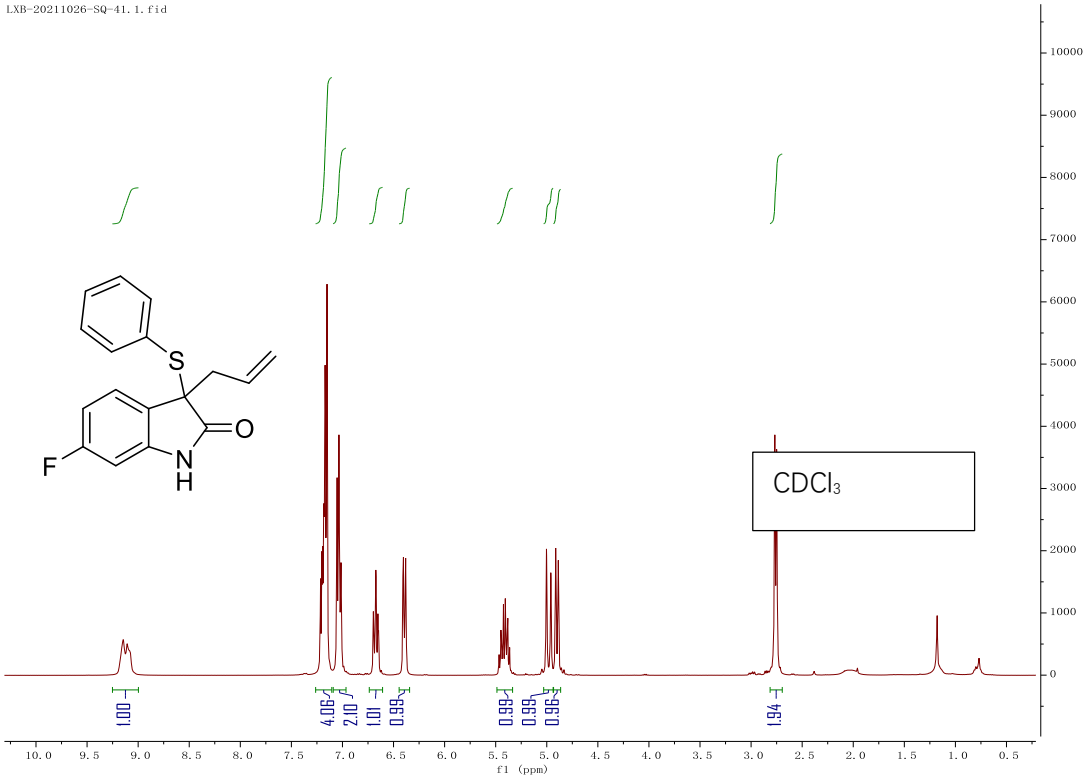
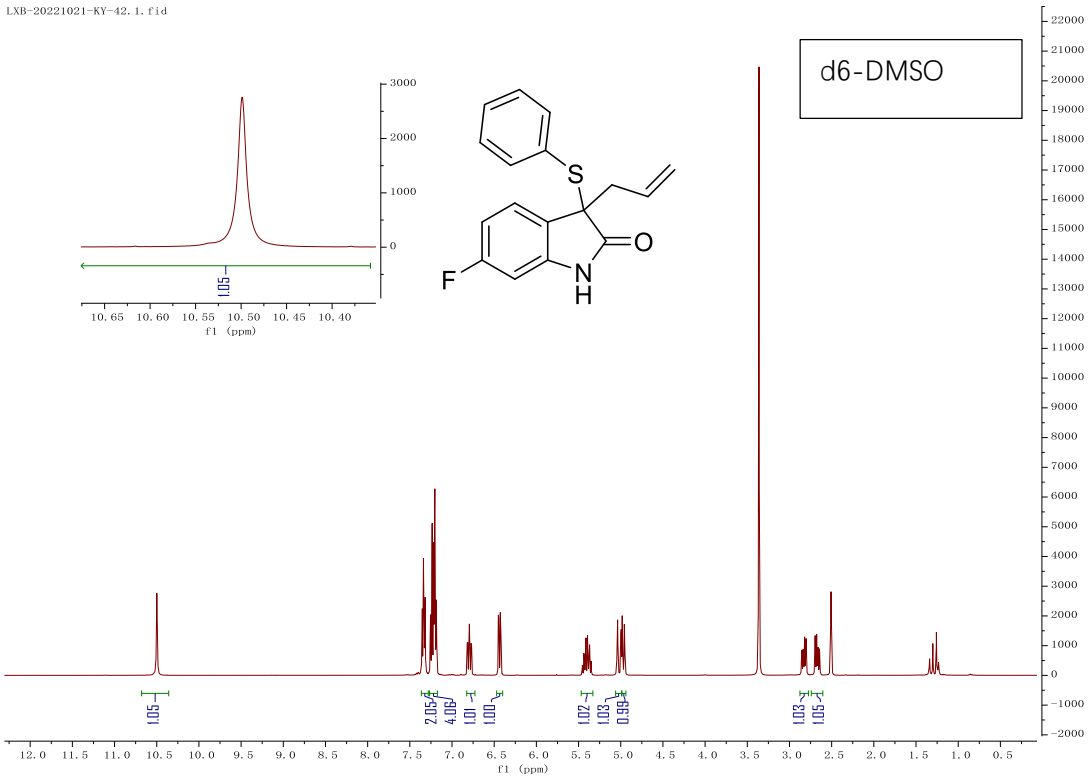
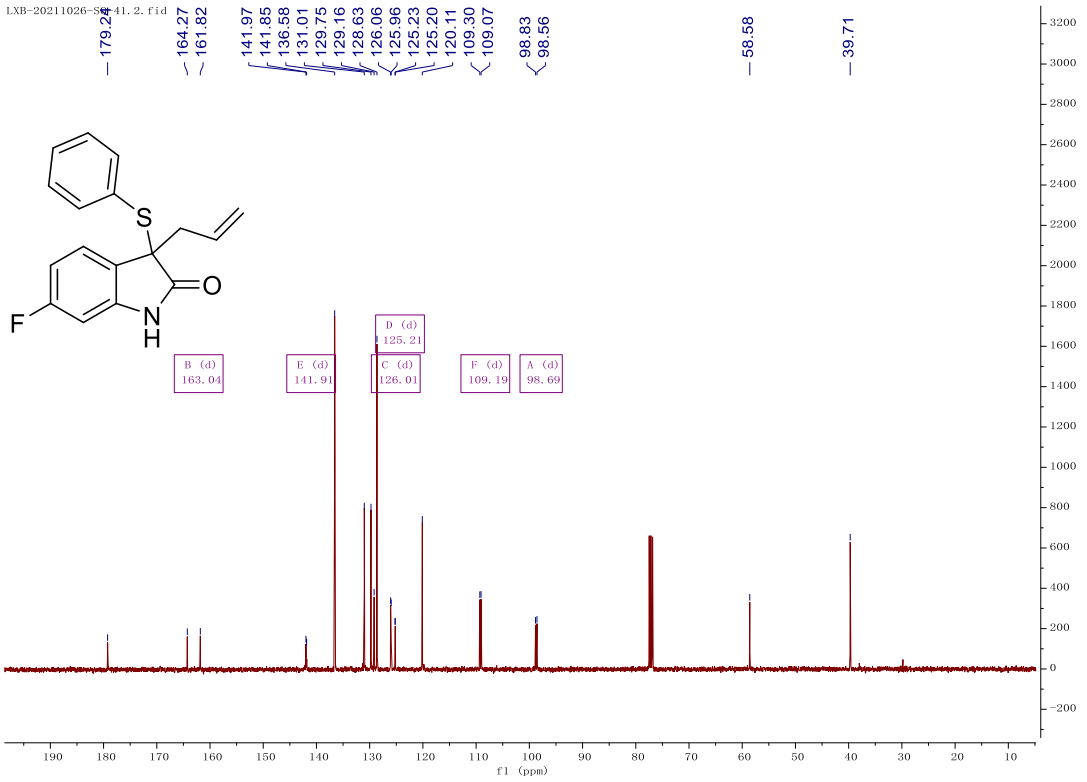
128.7
126.1
125.6
122.3
120.2
113.6
58.7
39.6
S
O
N
H
Br
f1 (ppm)

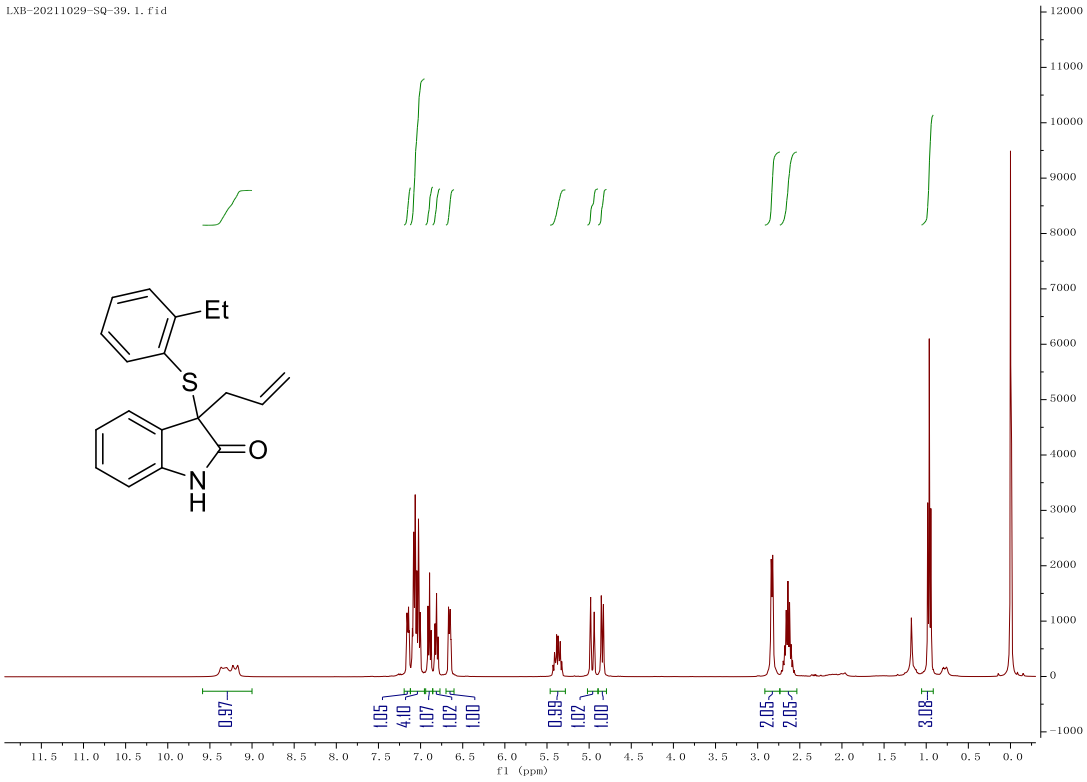

LXB-20211029-SQ-42.10.fid
S
F
O
N
H
0.98
3.01
3.04
1.00
1.01
0.97
0.98
1.00
1.97
f1 (ppm)

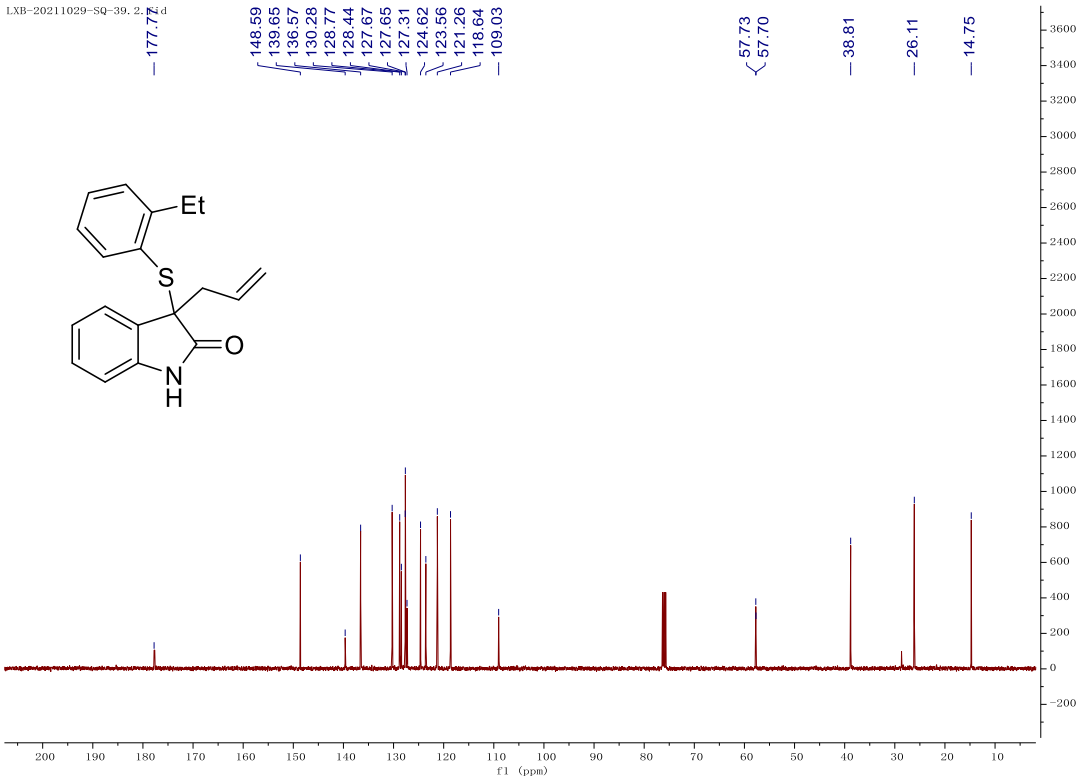

LXB-20211029-SQ-42.11.fid
178.89
160.34
157.94
136.50
131.66
131.58
130.82
129.76
129.01
128.64
120.25
115.48
115.25
112.64
112.39
110.75
110.67
59.44
59.42
39.67
S
F
O
N
H
E (d)
159.14
D (d)
131.62
B (d)
112.51
A (d)
110.71
C (d)
115.36
F (d)
59.43
f1 (ppm)

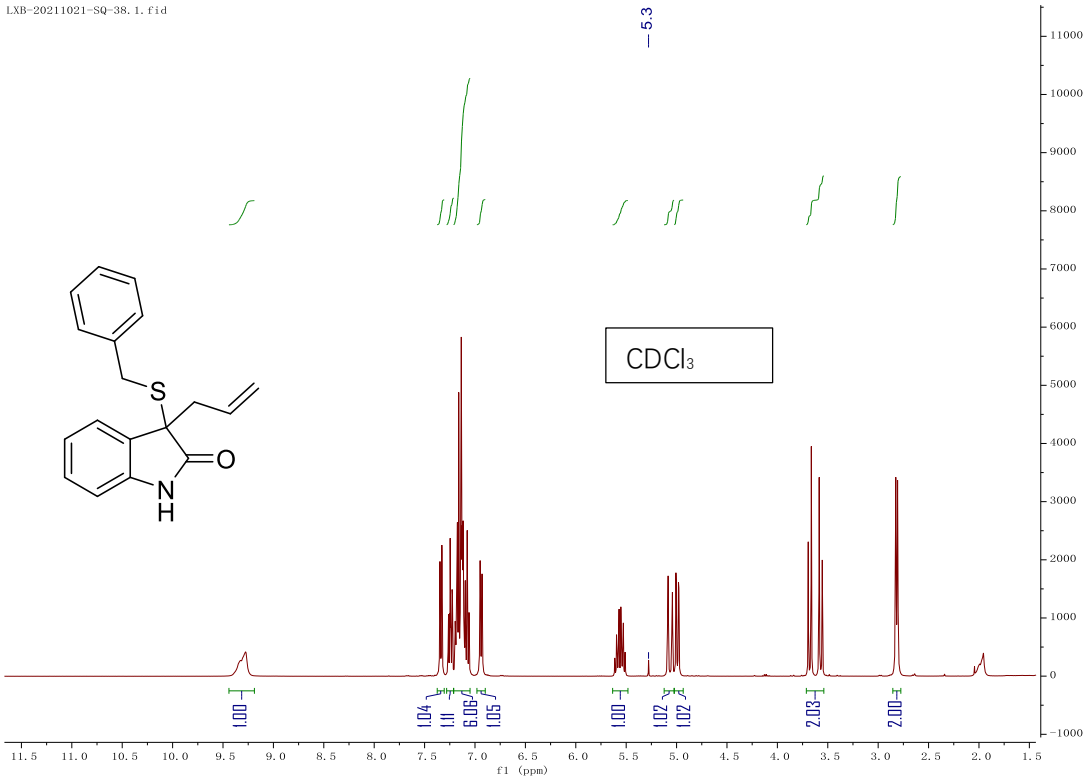

LXB-20211026-SQ-41.1.fid
CDCl3
1.00
4.06
2.10
1.01
0.99
0.99
0.99
0.96
1.94
f1 (ppm)

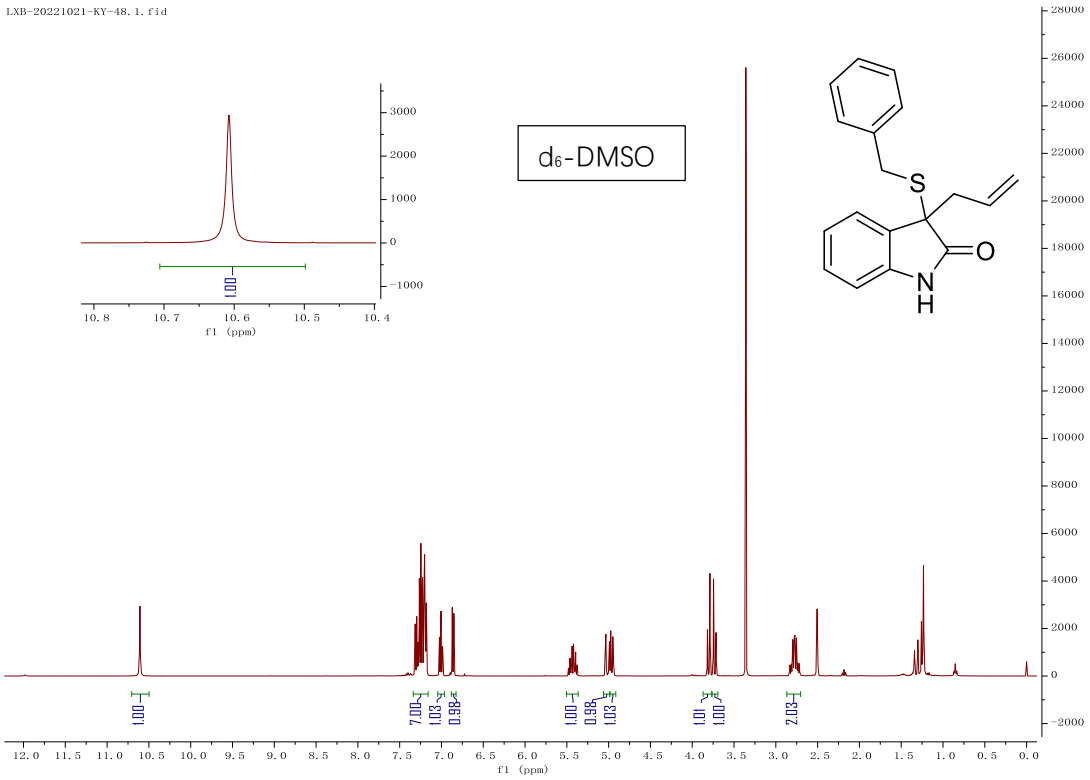

LXB-20221021-KY-42.1.fid
d6-DMSO
1.05
1.05
2.05
4.08
1.01
1.00
1.02
1.03
0.99
1.03
1.05
f1 (ppm)

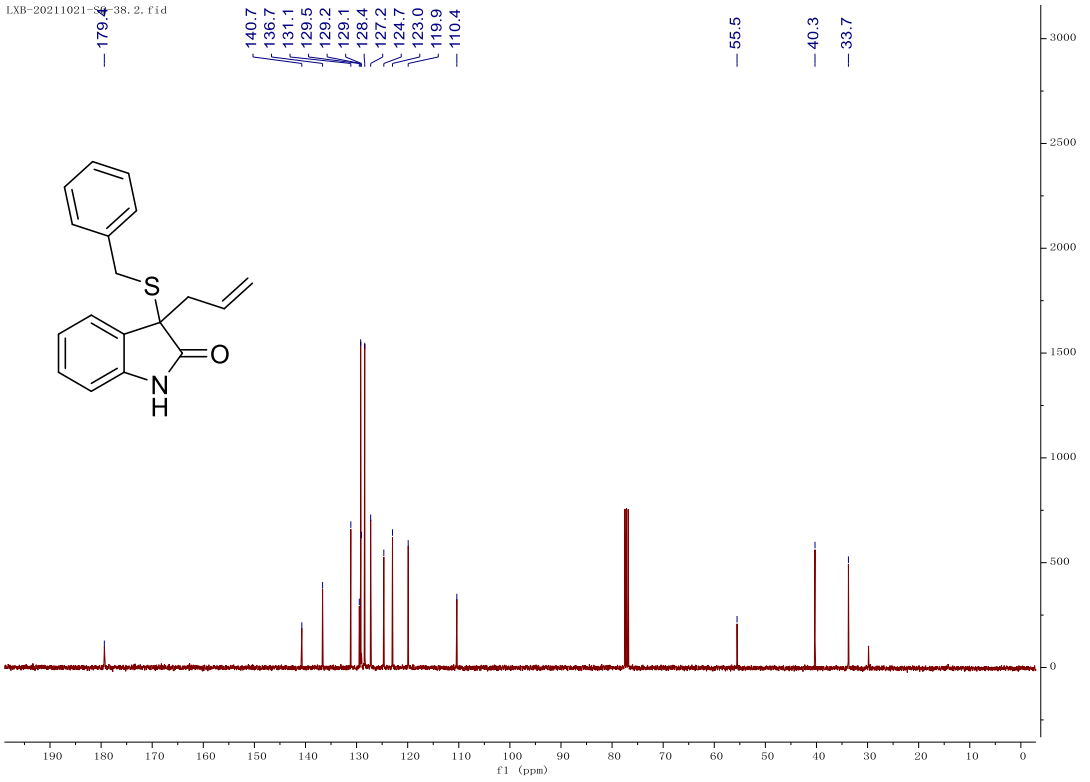

LXB-20211026-SQ-41.2.fid
179.24
164.27
161.82
141.97
141.85
136.58
131.01
129.75
129.16
128.63
126.06
125.96
125.23
125.20
120.11
109.30
109.07
98.83
98.56
58.58
39.71
S
O
N
H
F
B (d) 163.04
E (d) 141.91
D (d) 125.21
C (d) 126.01
F (d) 109.19
A (d) 98.69
f1 (ppm)

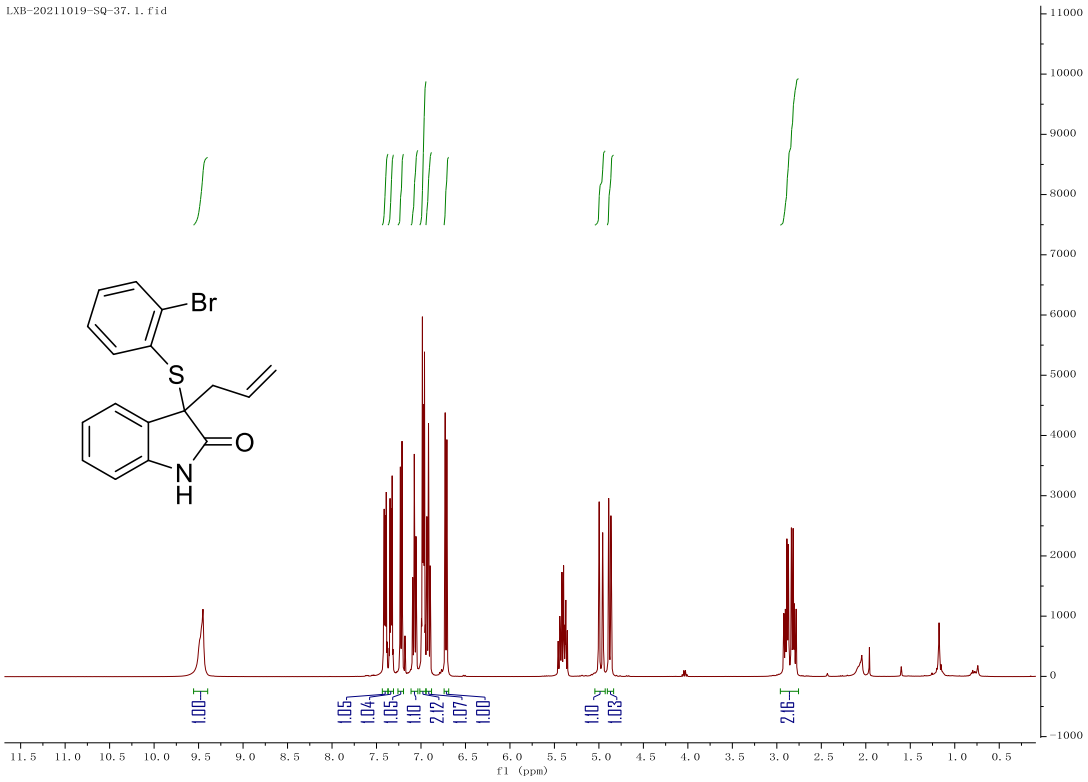

LXB-20211029-SQ-39.1.fid
Et
S
O
N
H
0.97
1.05
4.10
1.07
1.02
1.00
0.99
1.02
1.00
2.05
2.05
3.08
f1 (ppm)

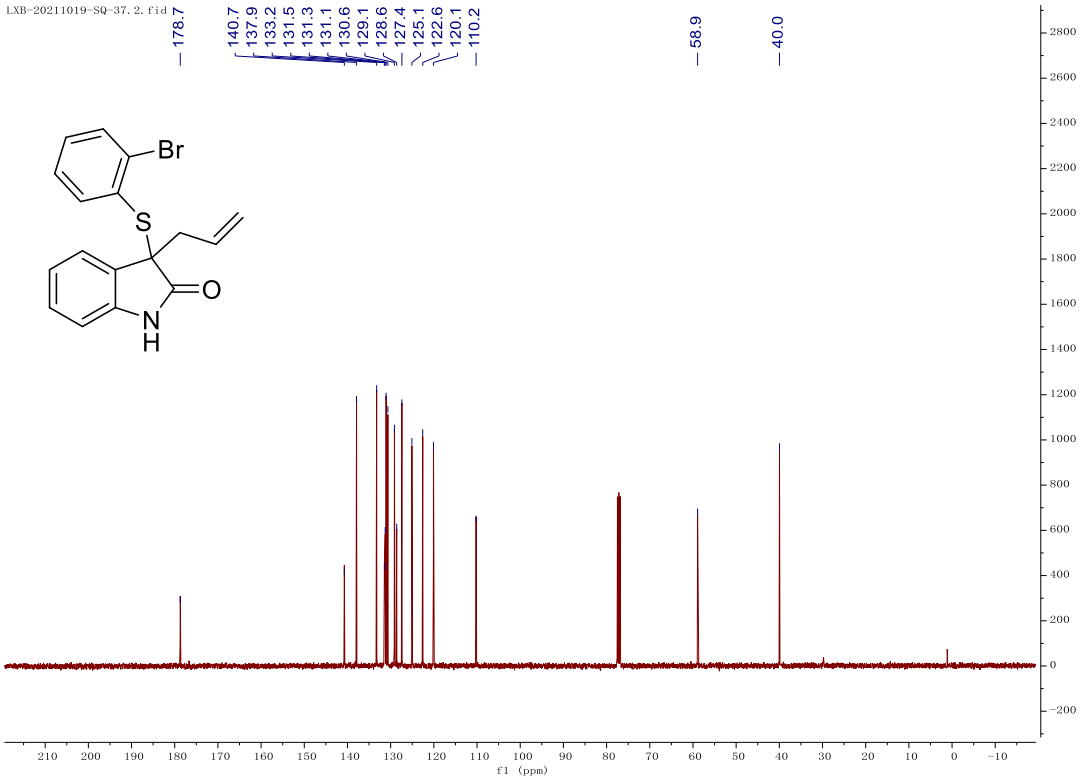

LXB-20211029-SQ-39.2.fid
177.77
148.59
139.65
136.57
130.28
128.77
128.44
127.67
127.65
127.31
124.62
123.56
121.26
118.64
109.03
57.73
57.70
38.81
26.11
14.75
Et
S
O
N
H
f1 (ppm)

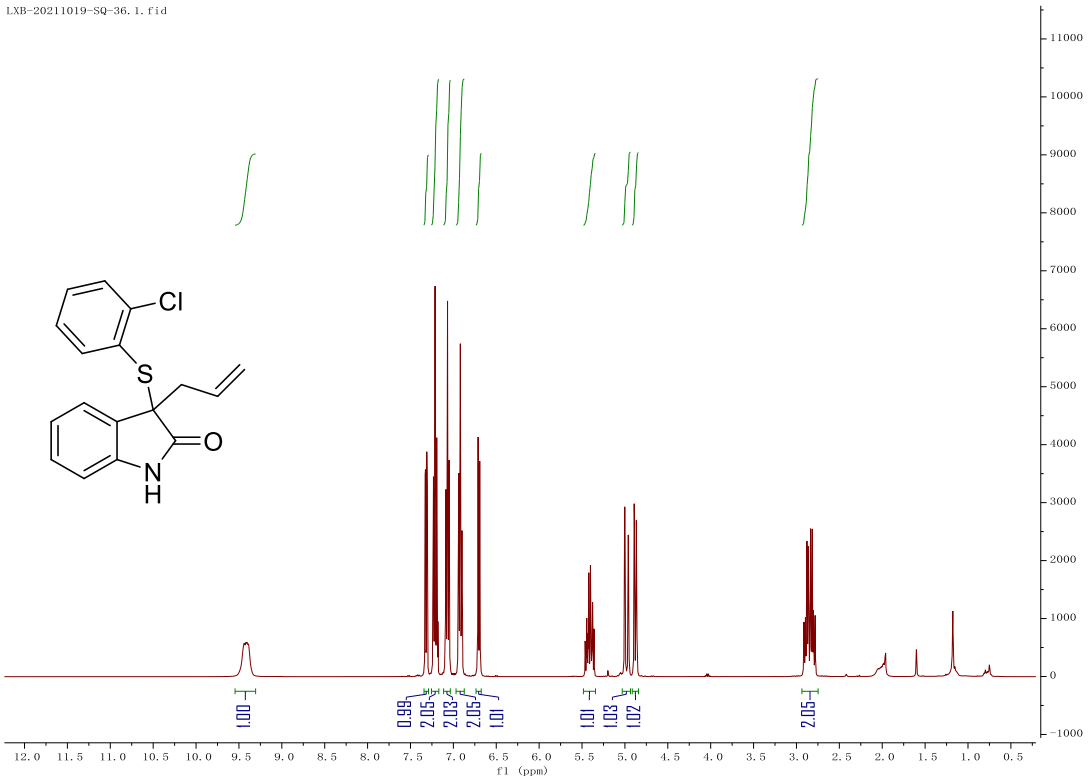

LXB-20211021-SQ-38.1.fid
5.3
CDCl3
S
O
N
H
1.00
1.04
1.11
6.08
1.05
1.00
1.02
1.02
2.03
2.00
f1 (ppm)

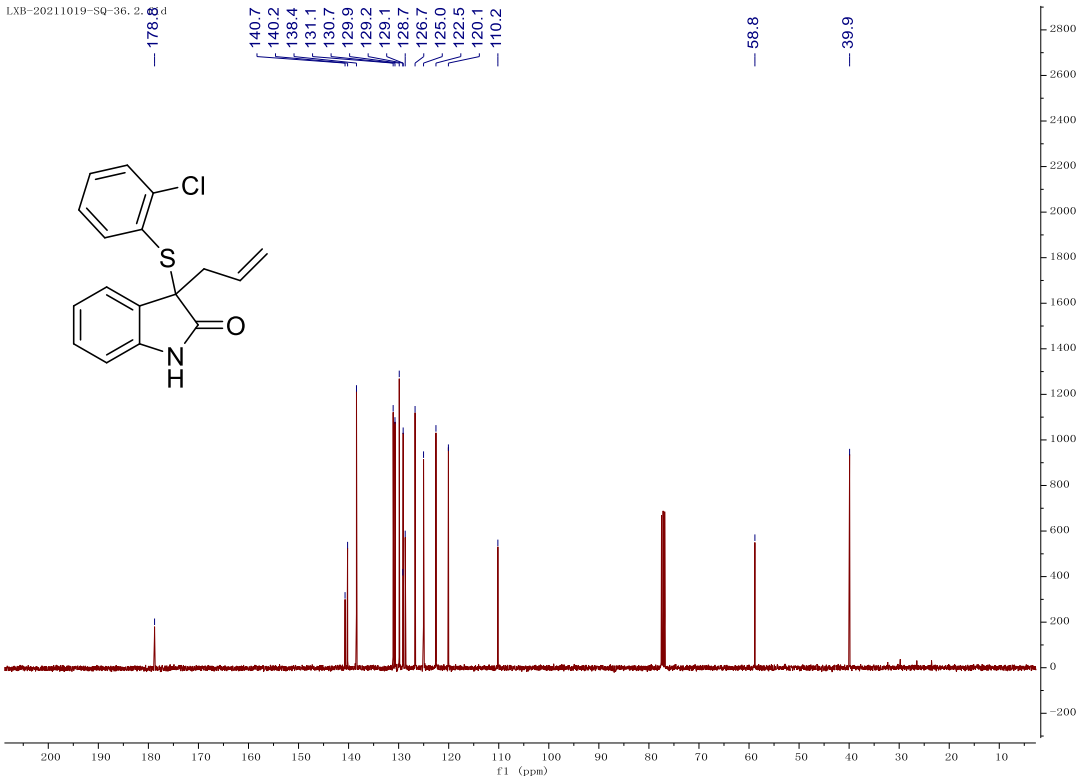

LXB-20221021-KY-48.1.fid
d6-DMSO
f1 (ppm)

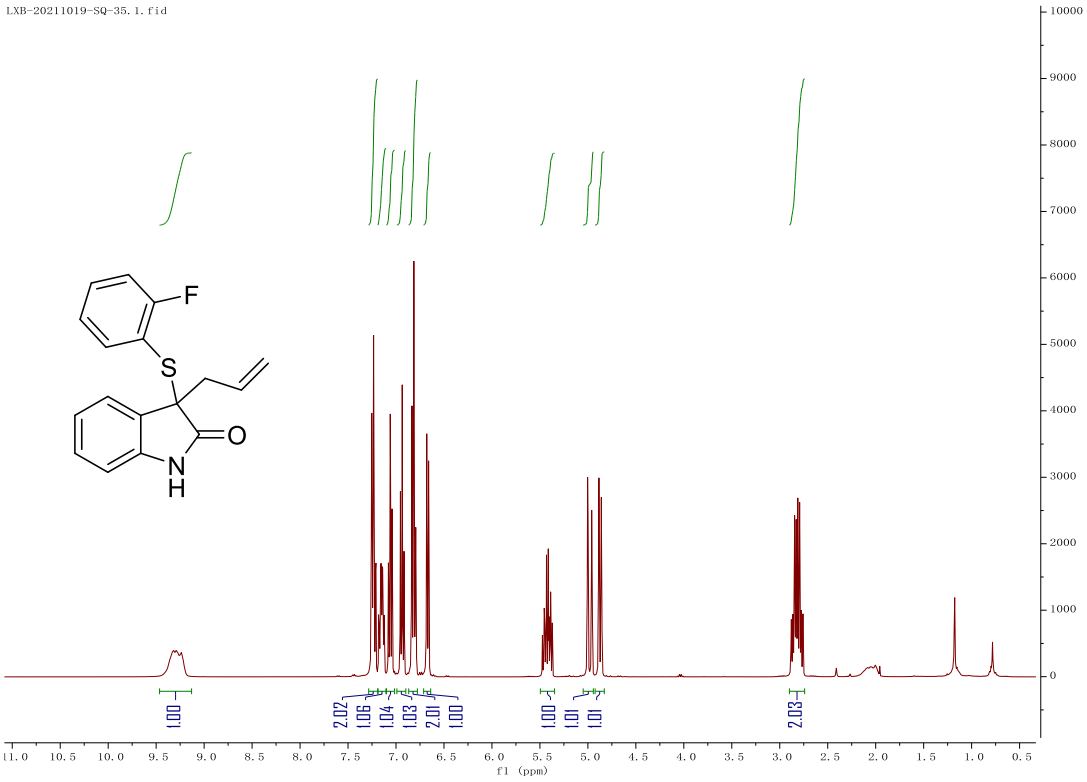

LXB-20211021-SB-38.2.fid
179.4
140.7
136.7
131.1
129.5
129.2
129.1
128.4
127.2
124.7
123.0
119.9
110.4
55.5
40.3
33.7
f1 (ppm)

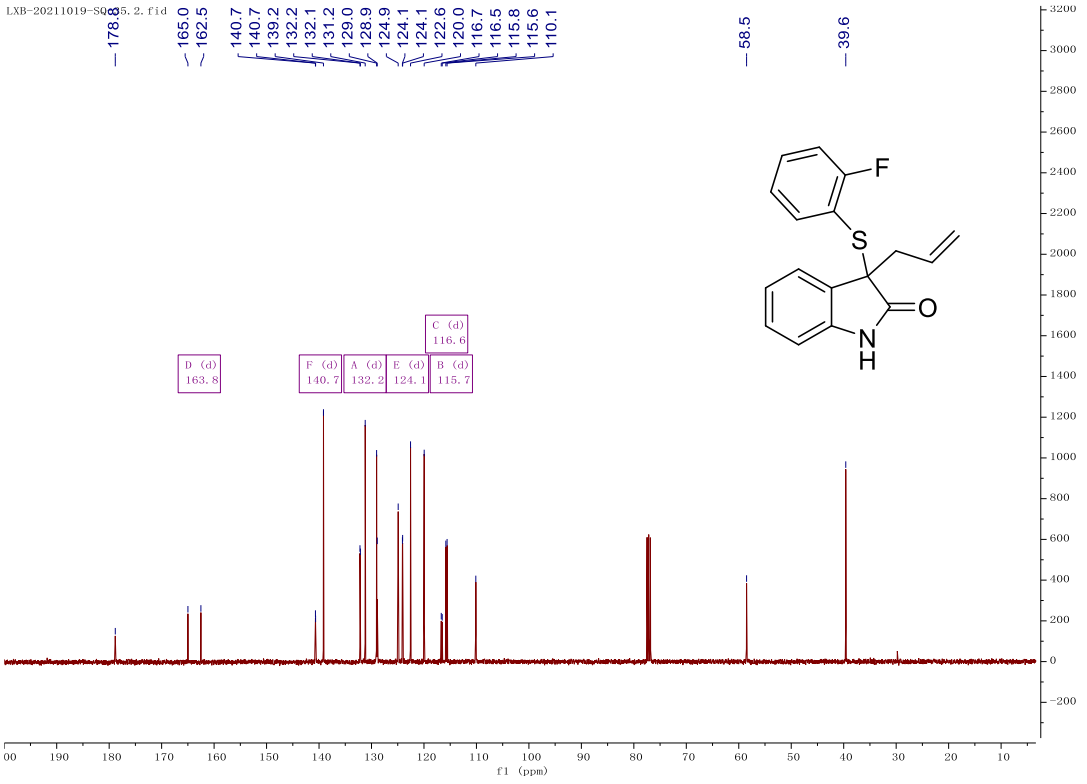

LXB-20211019-SQ-37.1.fid
Br
S
O
N
H
1.00
1.05
1.04
1.05
1.10
2.12
1.07
1.00
1.10
1.03
2.16
f1 (ppm)

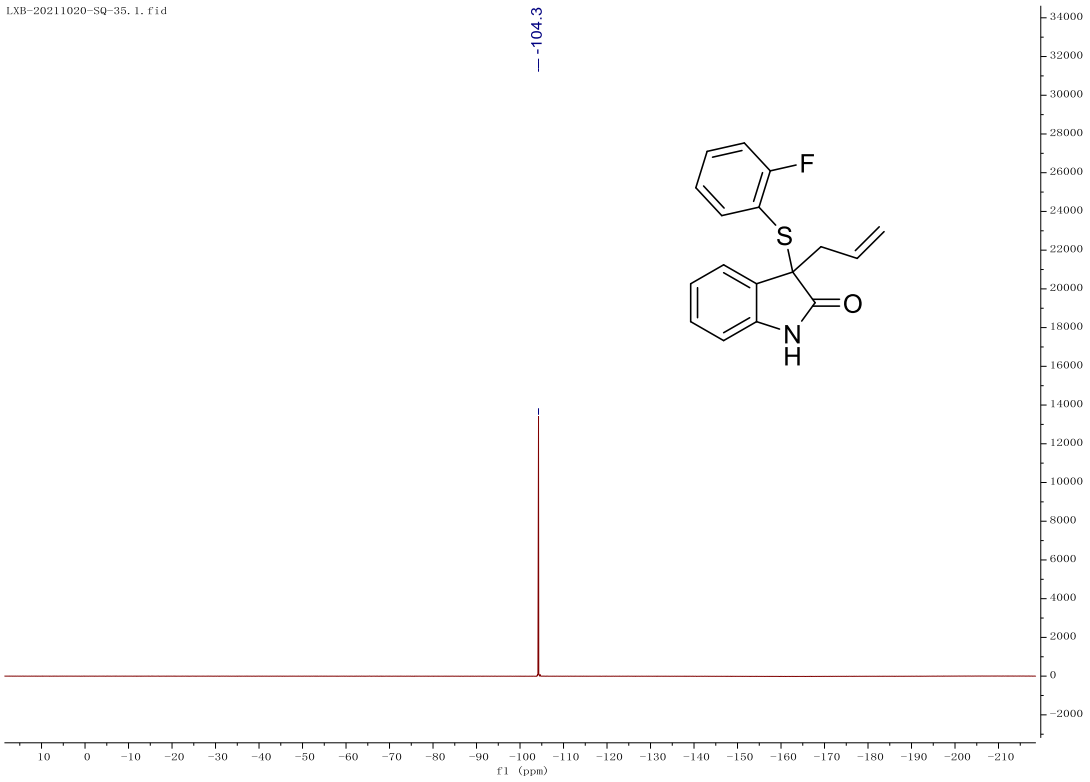

LXB-20211019-SQ-37.2.fid
178.7
140.7
137.9
133.2
131.5
131.3
131.1
130.6
129.1
128.6
127.4
125.1
122.6
120.1
110.2
58.9
40.0
Br
S
O
N
H
f1 (ppm)

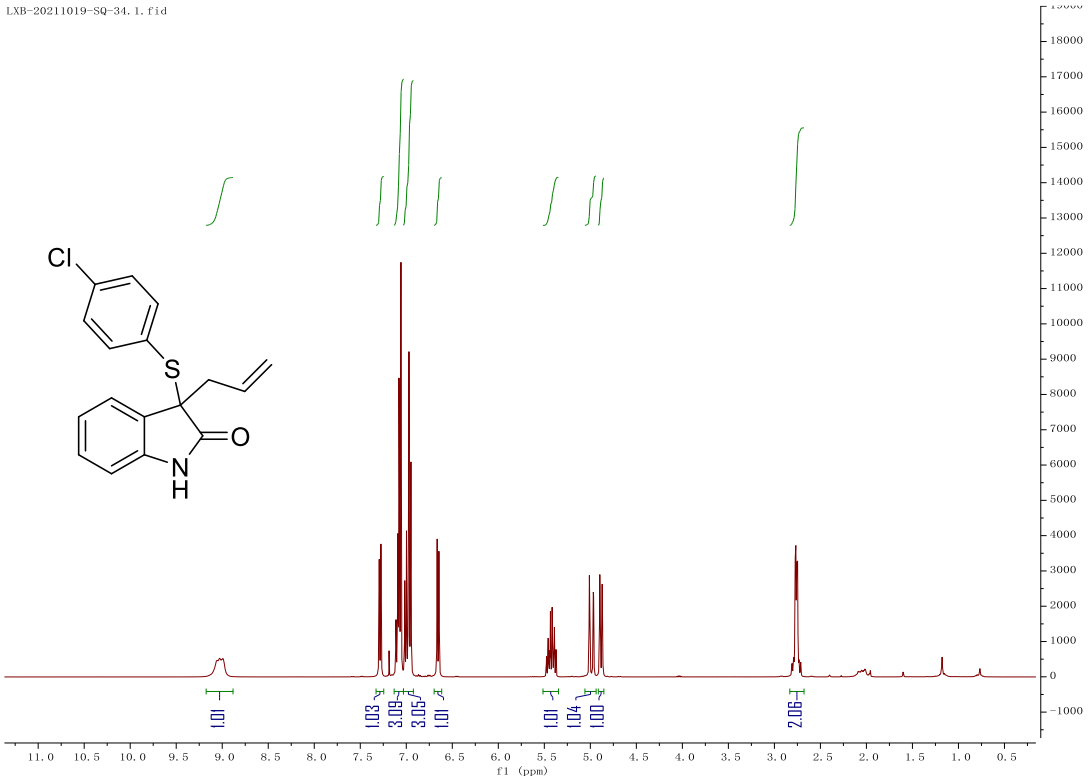

LXB-20211019-SQ-36.1.fid
Cl
S
O
N
H
1.00
0.99
2.05
2.03
2.05
1.01
1.01
1.03
1.02
2.05
f1 (ppm)

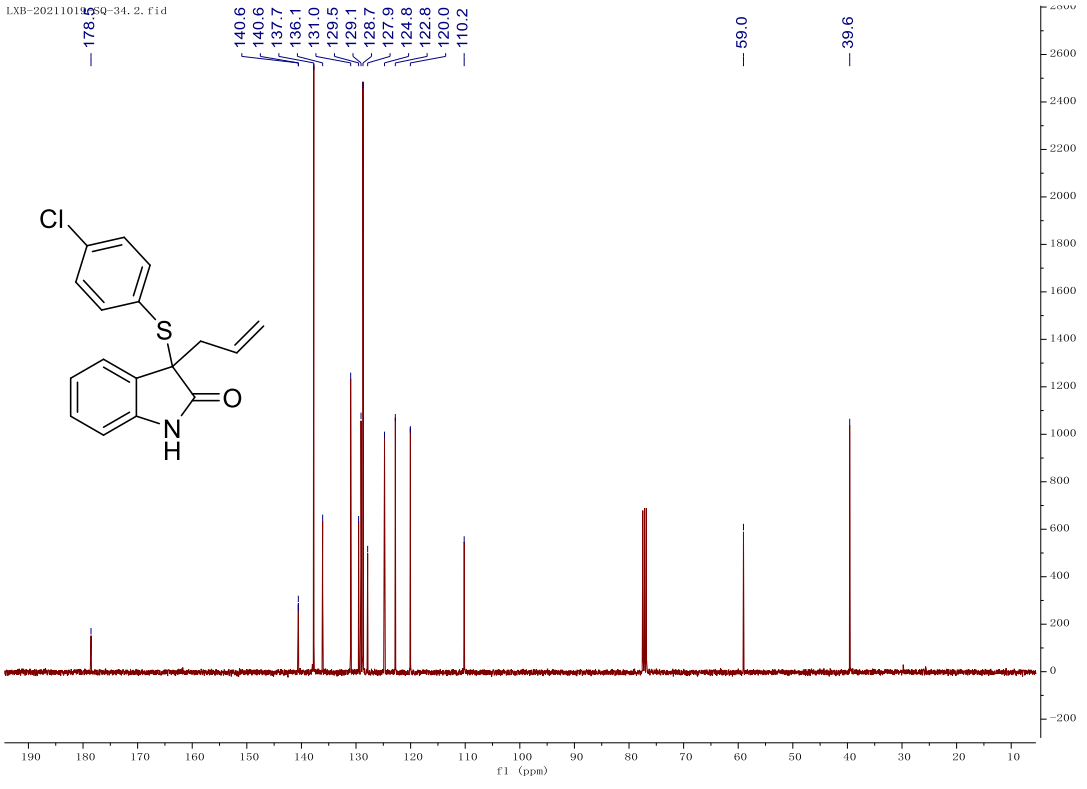

LXB-20211019-SQ-36.2.fid
178.8
140.7
140.2
138.4
131.1
130.7
129.9
129.2
129.1
128.7
126.7
125.0
122.5
120.1
110.2
58.8
39.9
Cl
S
O
N
H
f1 (ppm)

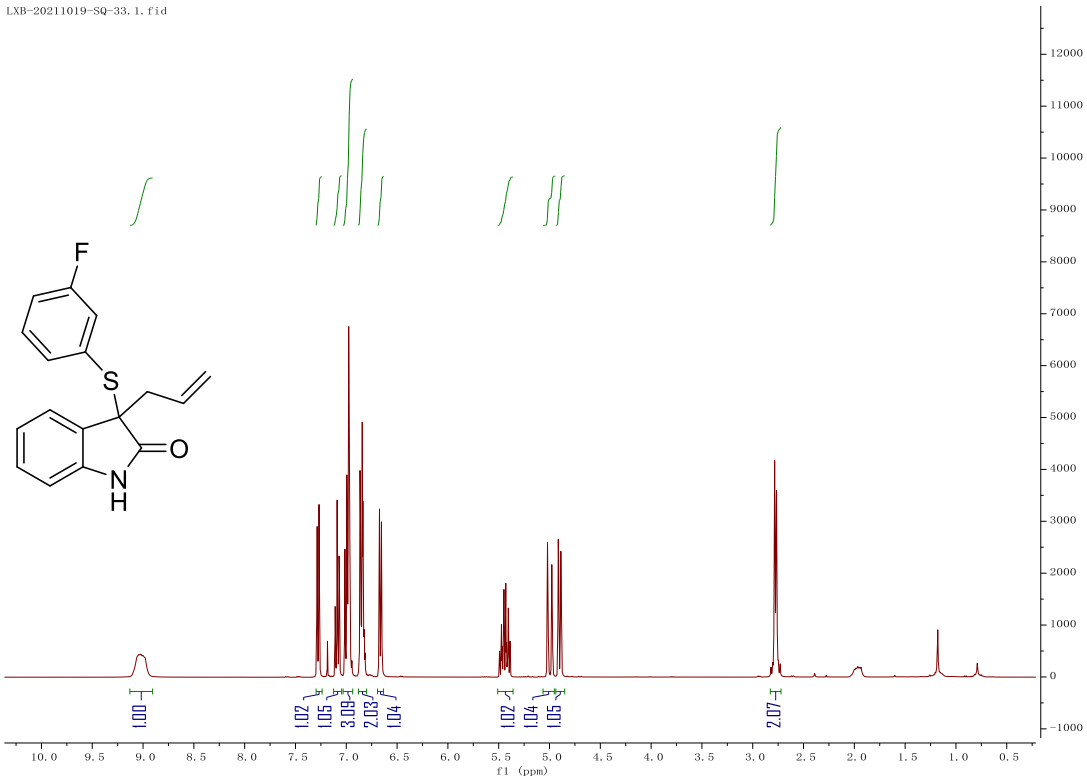

LXB-20211019-SQ-35.1.fid
F
S
O
N
H
1.00
2.02
1.06
1.04
1.03
2.01
1.00
1.00
1.01
1.01
2.03
f1 (ppm)

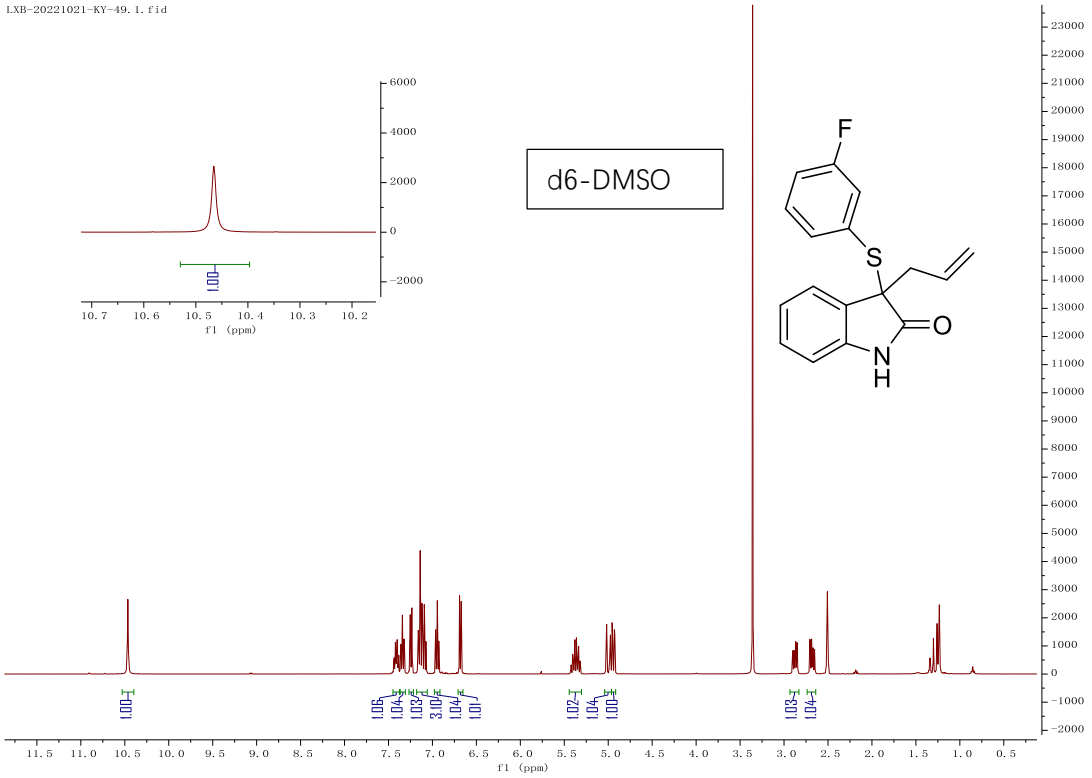

LXB-20211019-SQ-35.2.fid
178.3
165.0
162.5
140.7
140.7
139.2
132.2
132.1
131.2
129.0
128.9
124.9
124.1
124.1
122.6
120.0
116.7
116.5
115.8
115.6
110.1
58.5
39.6
C (d) 116.6
D (d) 163.8
F (d) 140.7
A (d) 132.2
E (d) 124.1
B (d) 115.7
F
S
O
N
H
f1 (ppm)

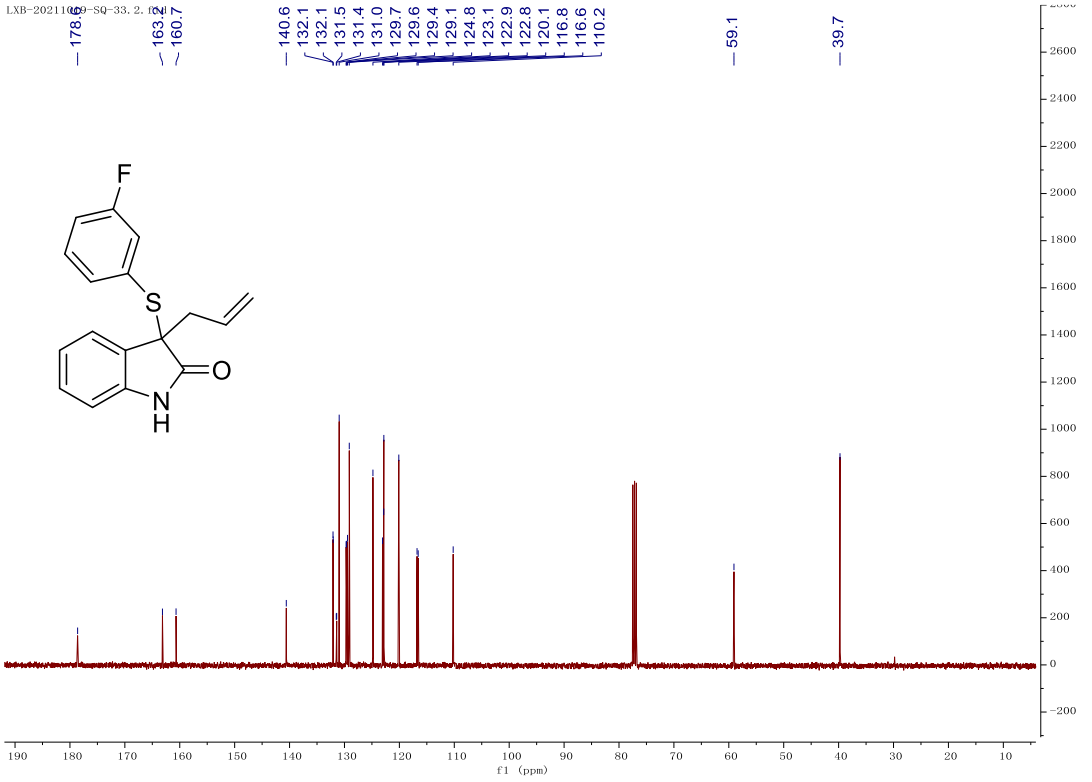

LXB-20211020-SQ-35.1.fid
-104.3
F
S
O
N
H
f1 (ppm)

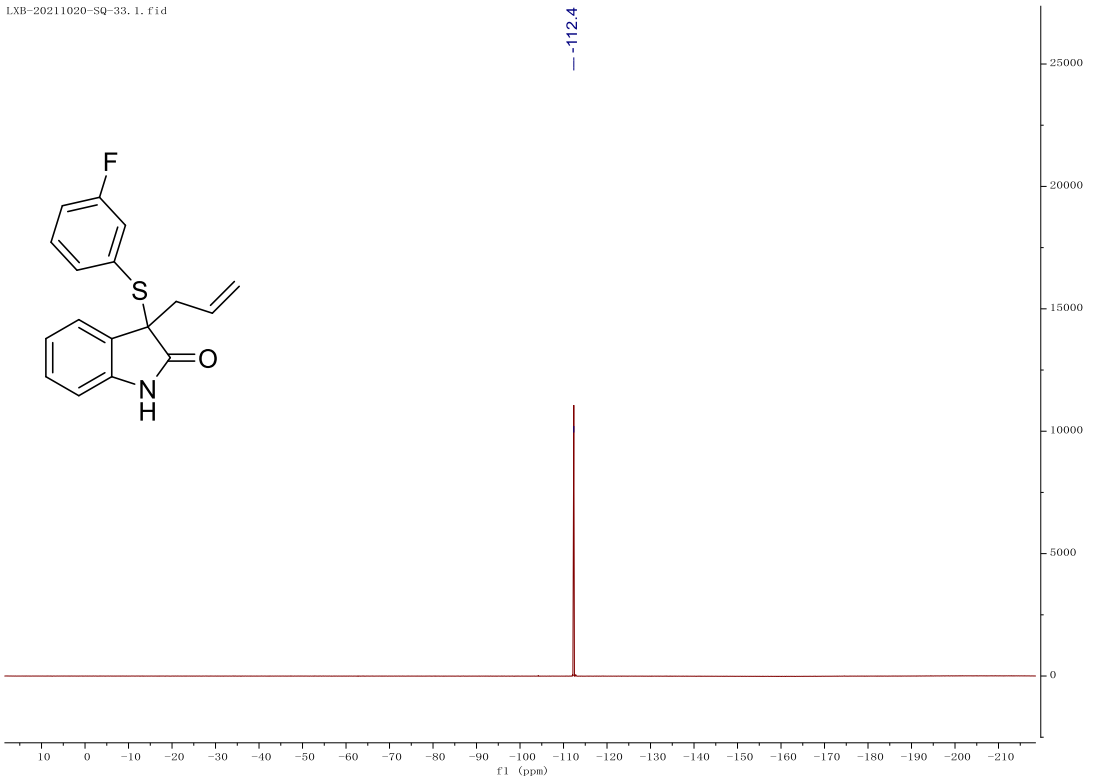

LXB-20211019-SQ-34.1.fid
Cl
S
O
N
H
1.01
1.03
3.09
3.05
1.01
1.01
1.04
1.00
2.06
f1 (ppm)

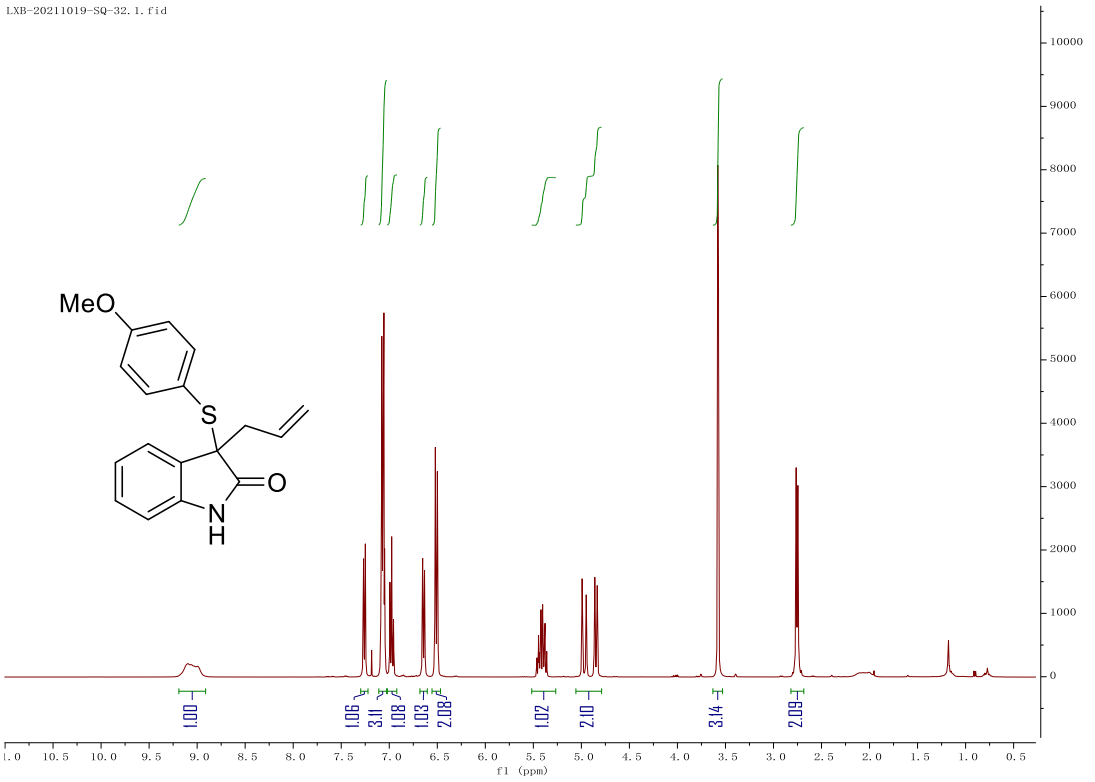

LXB-20211019-SQ-34.2.fid
178.5
140.6
140.6
137.7
136.1
131.0
129.5
129.1
128.7
127.9
124.8
122.8
120.0
110.2
59.0
39.6
Cl
S
O
N
H
f1 (ppm)

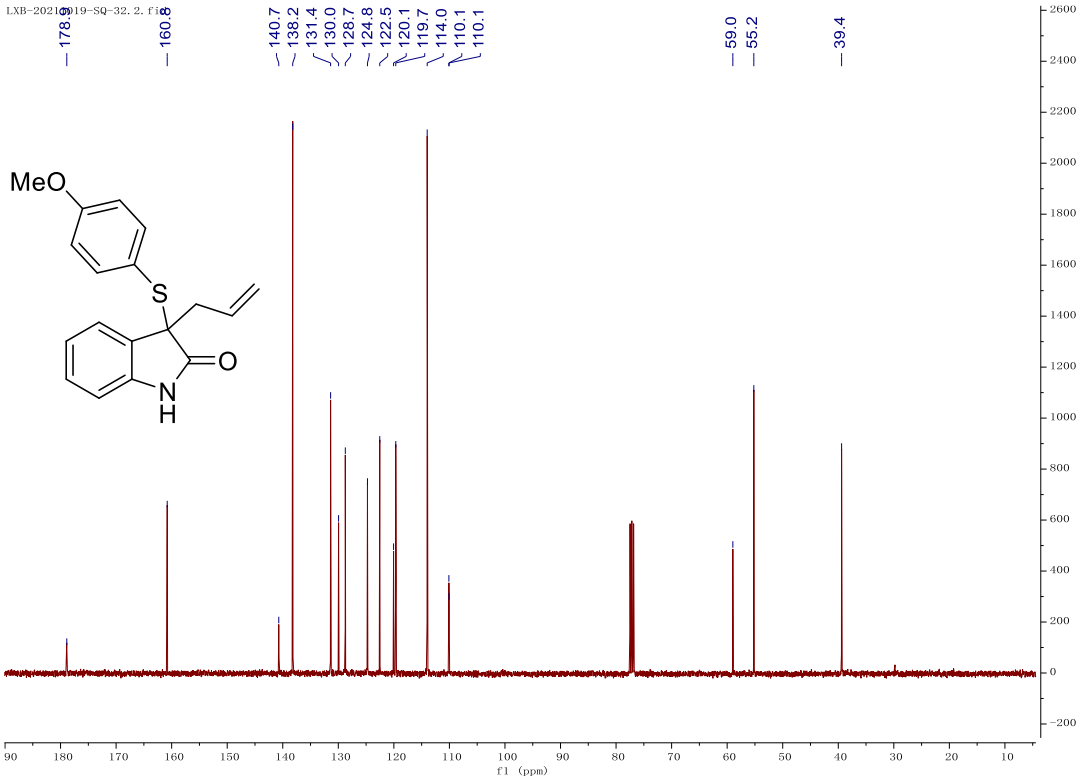

LXB-20211019-SQ-33.1.fid
F
S
O
N
H
1.00
1.02
1.05
3.09
2.03
1.04
1.02
1.04
1.05
2.07
f1 (ppm)

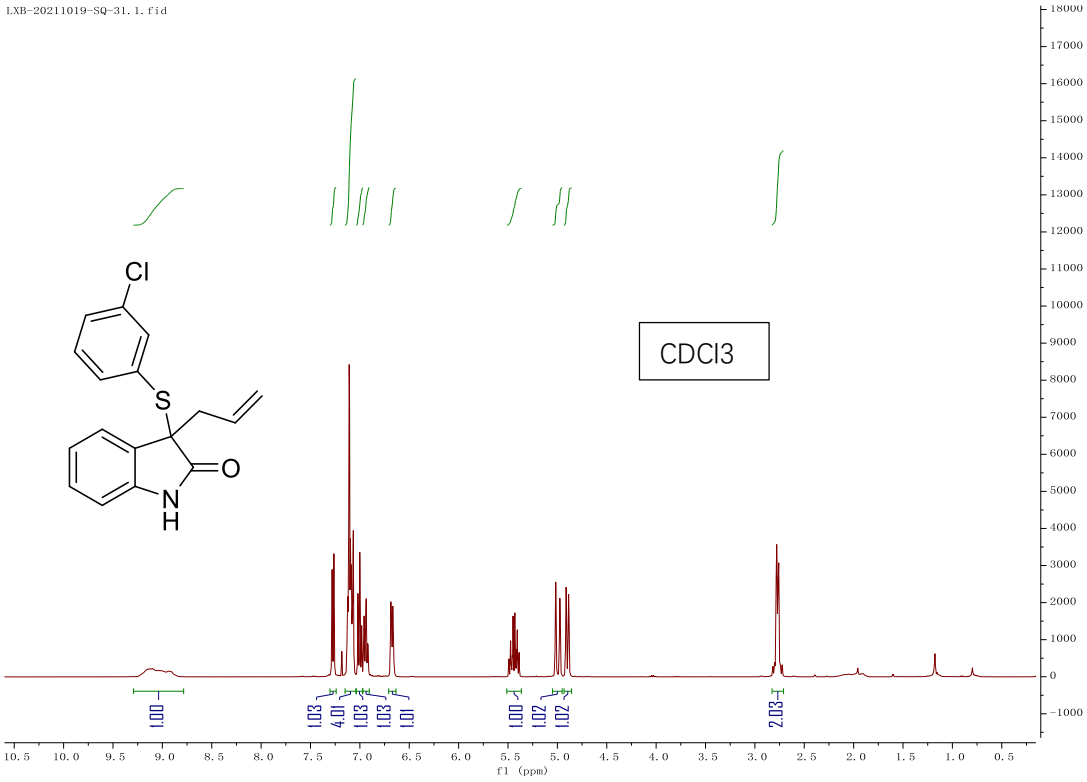

LXB-20221021-KY-49.1.fid
d6-DMSO
F
S
O
N
H
f1 (ppm)

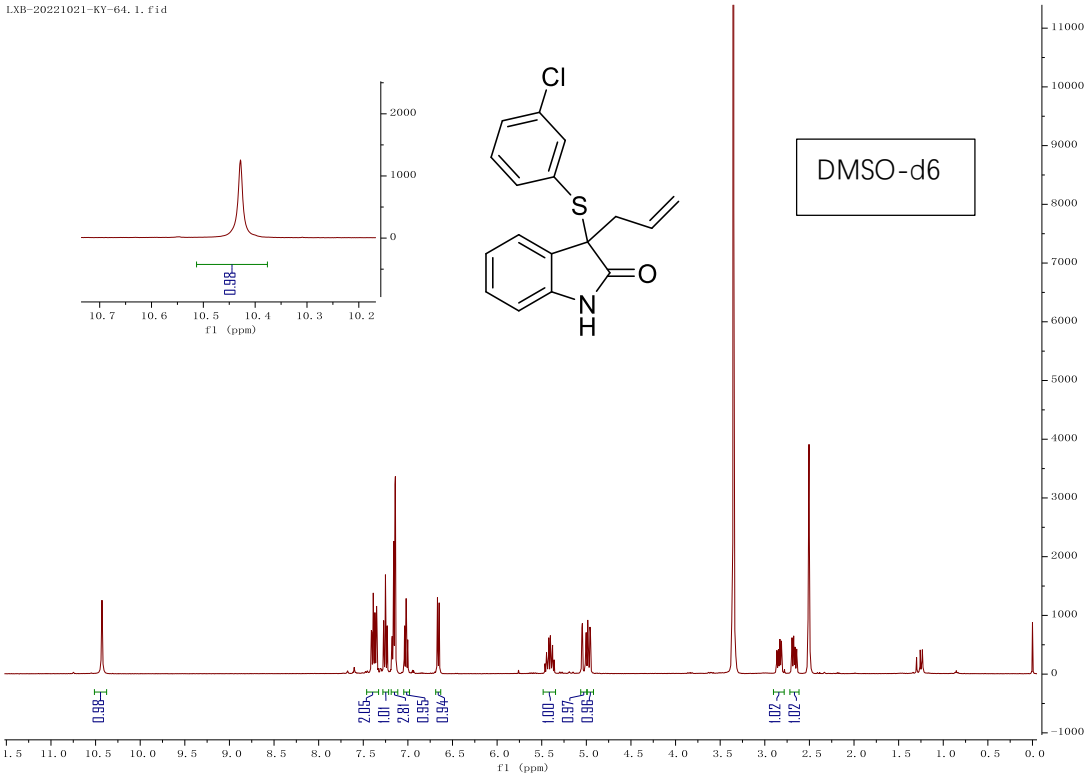

178.6
163.2
160.7
140.6
132.1
132.1
131.5
131.4
131.0
129.7
129.6
129.4
129.1
124.8
123.1
122.9
122.8
120.1
116.8
116.6
110.2
59.1
39.7
F
S
O
N
H
f1 (ppm)

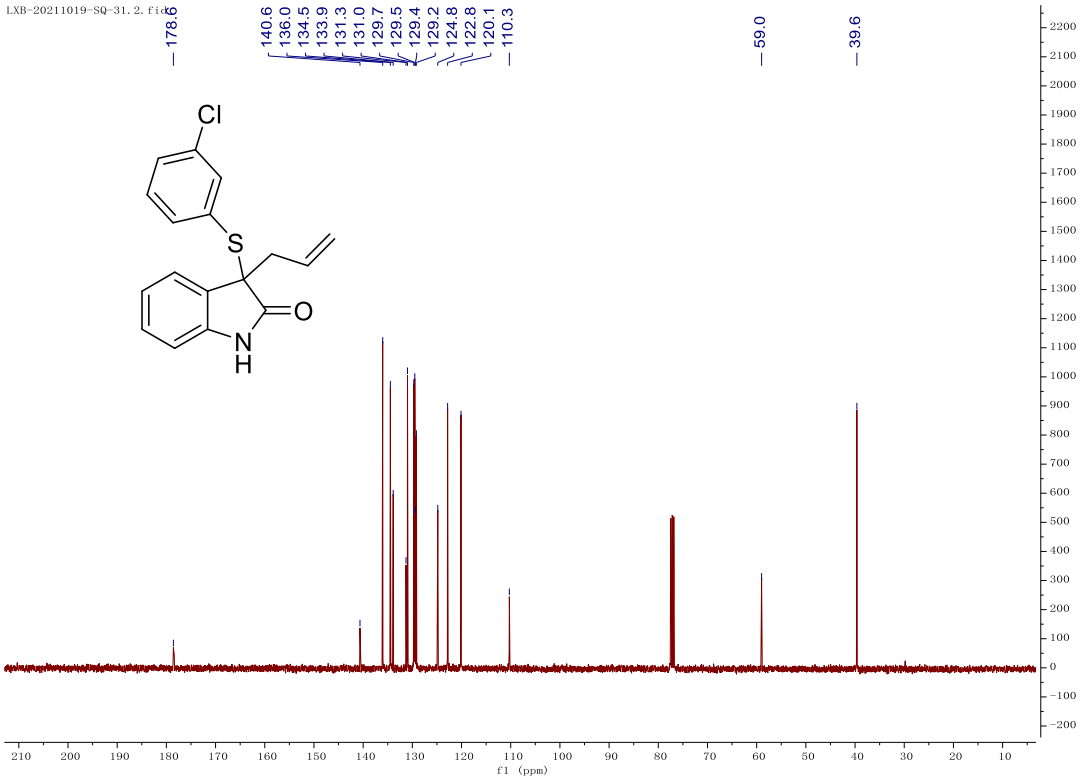

LXB-20211020-SQ-33.1.fid
-112.4
F
S
O
N
H
25000
20000
15000
10000
5000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

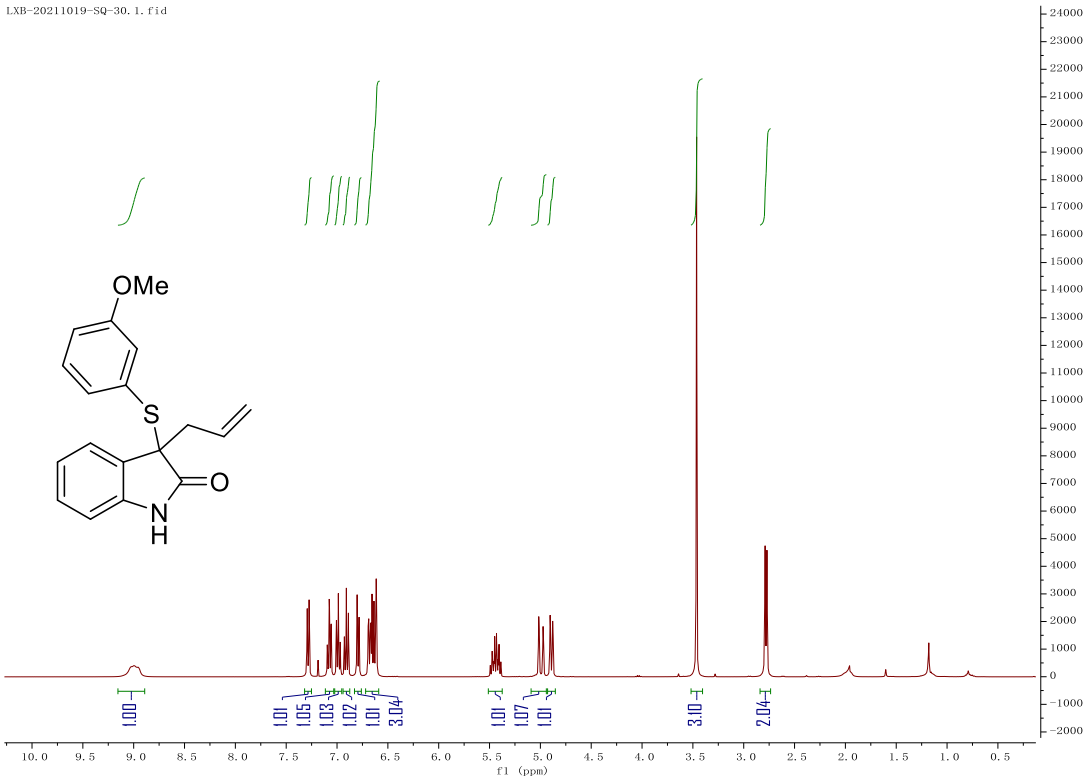

LXB-20211019-SQ-32.1.fid
MeO
S
O
N
H
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.00
1.06
3.11
1.08
1.03
2.08
1.02
2.10
3.14
2.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

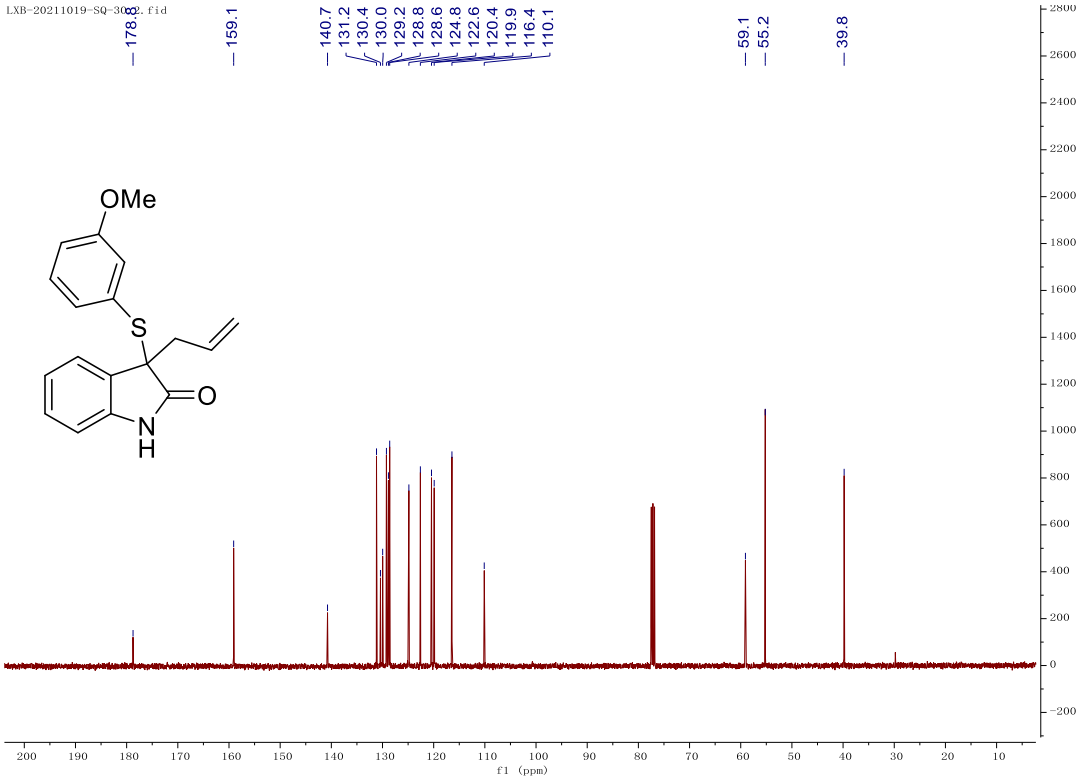

LXB-20211019-SQ-32.2.fid
178.9
160.8
140.7
138.2
131.4
130.0
128.7
124.8
122.5
120.1
119.7
114.0
110.1
110.1
59.0
55.2
39.4
MeO
S
O
N
H
f1 (ppm)

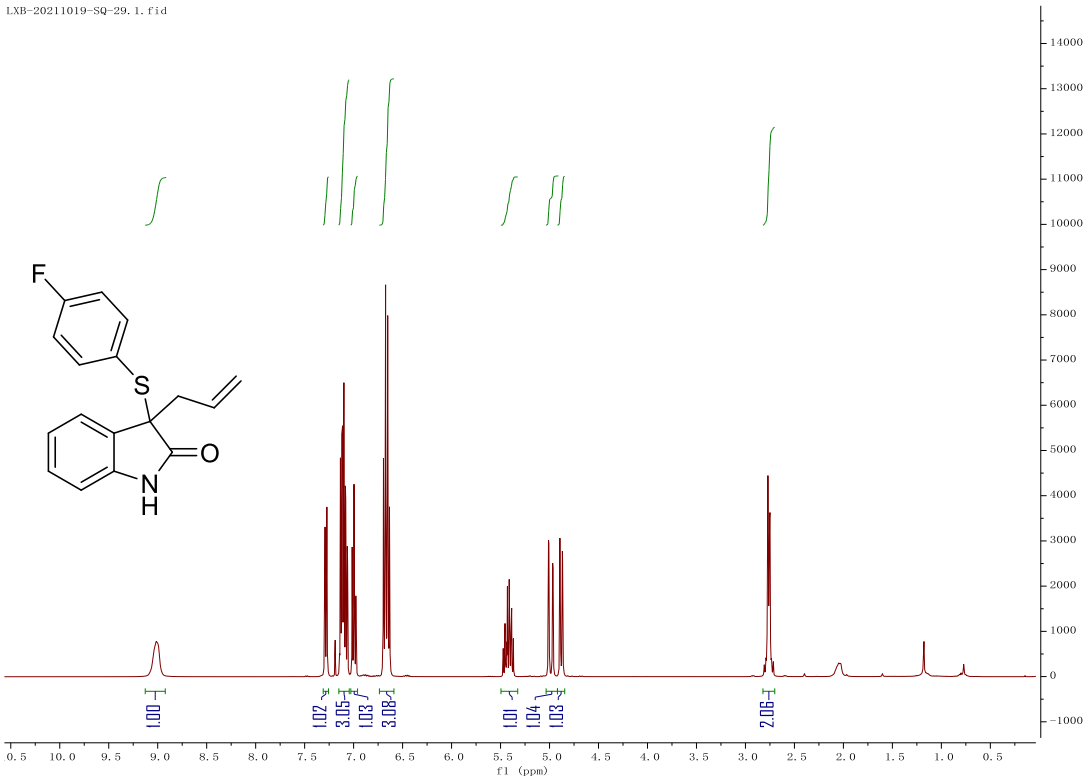

LXB-20211019-SQ-31.1.fid
Cl
S
O
N
H
CDCl3
1.00
1.03
4.01
1.03
1.03
1.01
1.00
1.02
1.02
2.03
f1 (ppm)

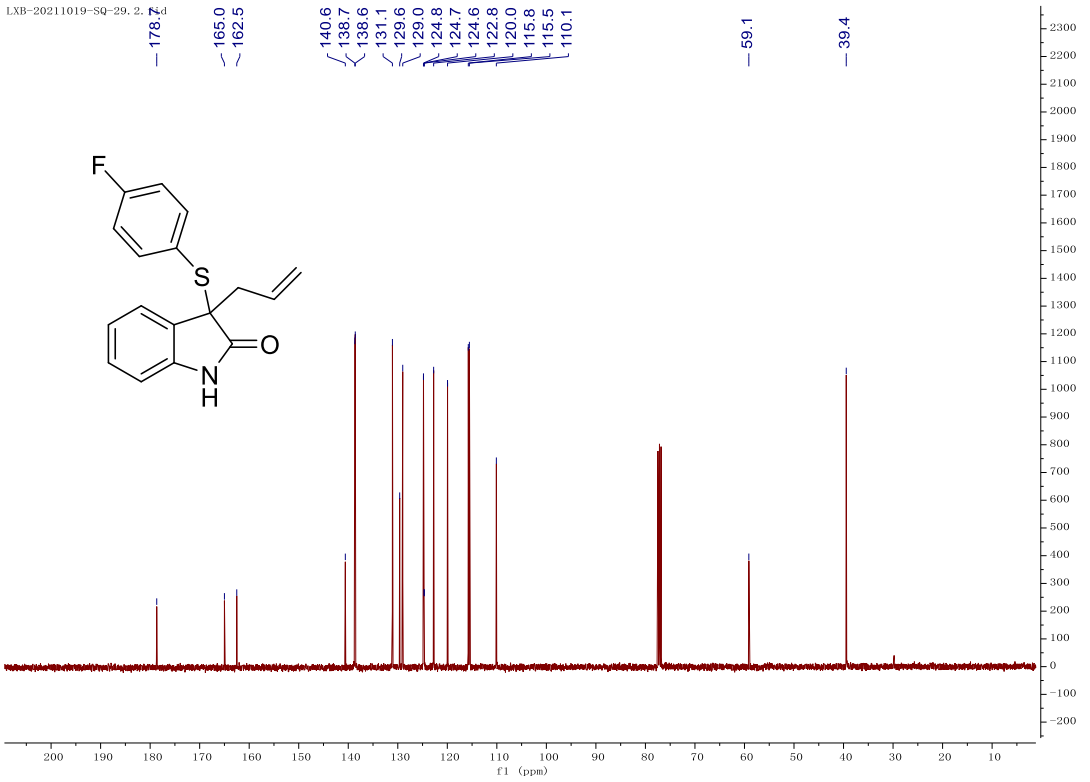

LXB-20221021-KY-64.1.fid
DMSO-d6
Cl
S
O
N
H
f1 (ppm)

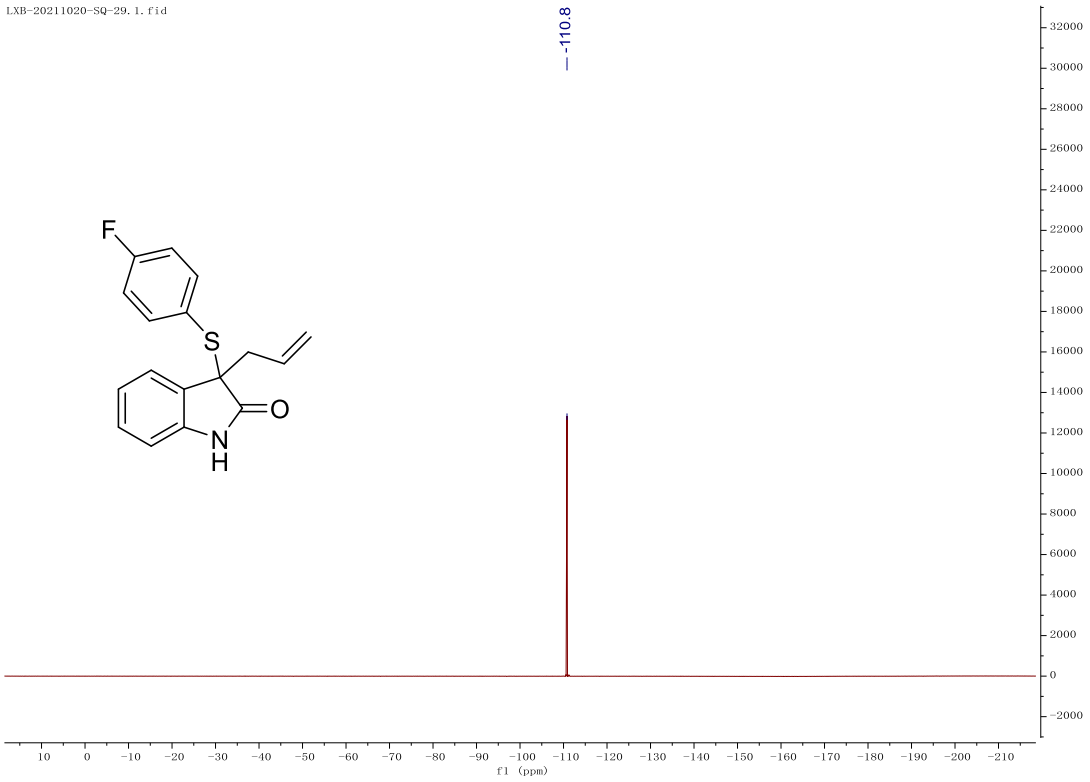

LXB-20211019-SQ-31.2.fid
178.6
140.6
136.0
134.5
133.9
131.3
131.0
129.7
129.5
129.4
129.2
124.8
122.8
120.1
110.3
59.0
39.6
Cl
S
O
N
H
f1 (ppm)

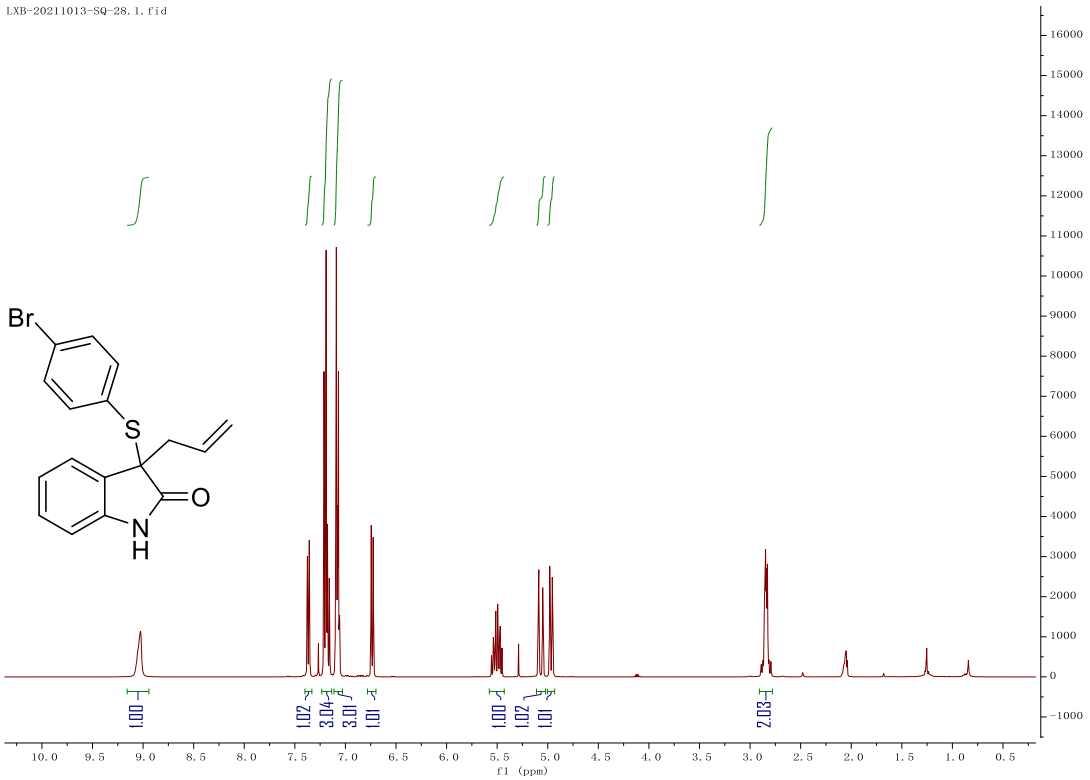

LXB-20211019-SQ-30.1.fid
OMe
S
O
N
H
1.00
1.01
1.05
1.03
1.02
1.01
3.04
1.01
1.07
1.01
3.10
2.04
f1 (ppm)

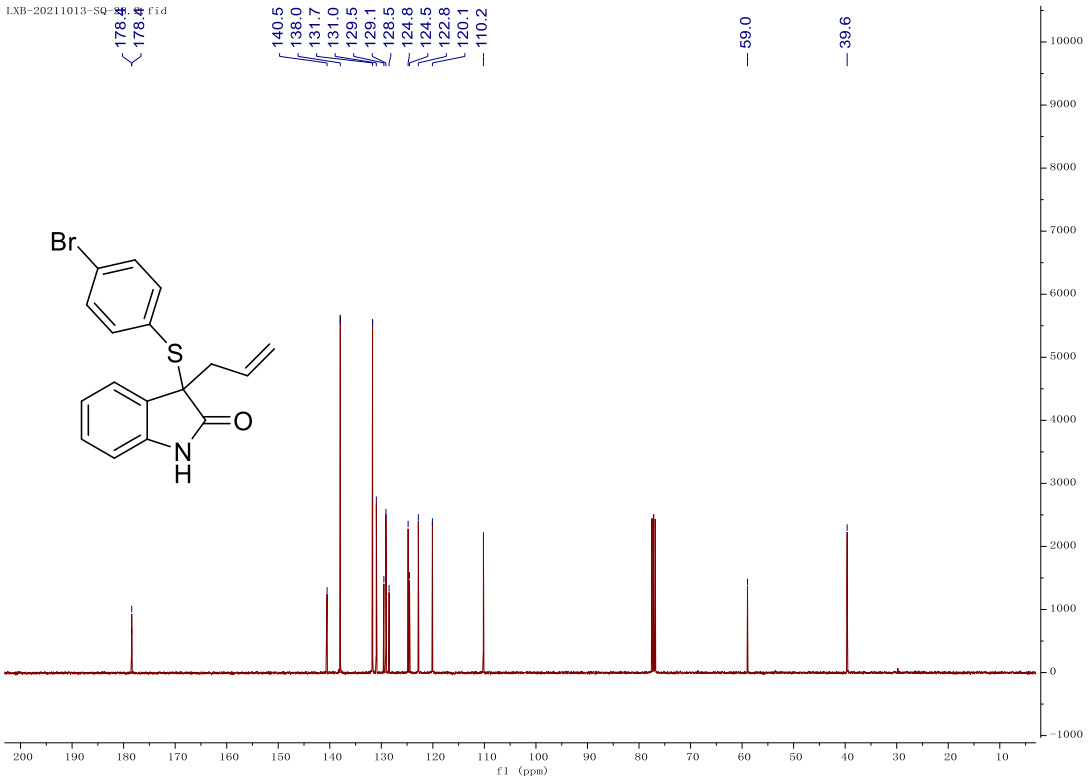

LXB-20211019-SQ-30B.fid
178.8
159.1
140.7
131.2
130.4
130.0
129.2
128.8
128.6
124.8
122.6
120.4
119.9
116.4
110.1
59.1
55.2
39.8
OMe
S
O
N
H
f1 (ppm)

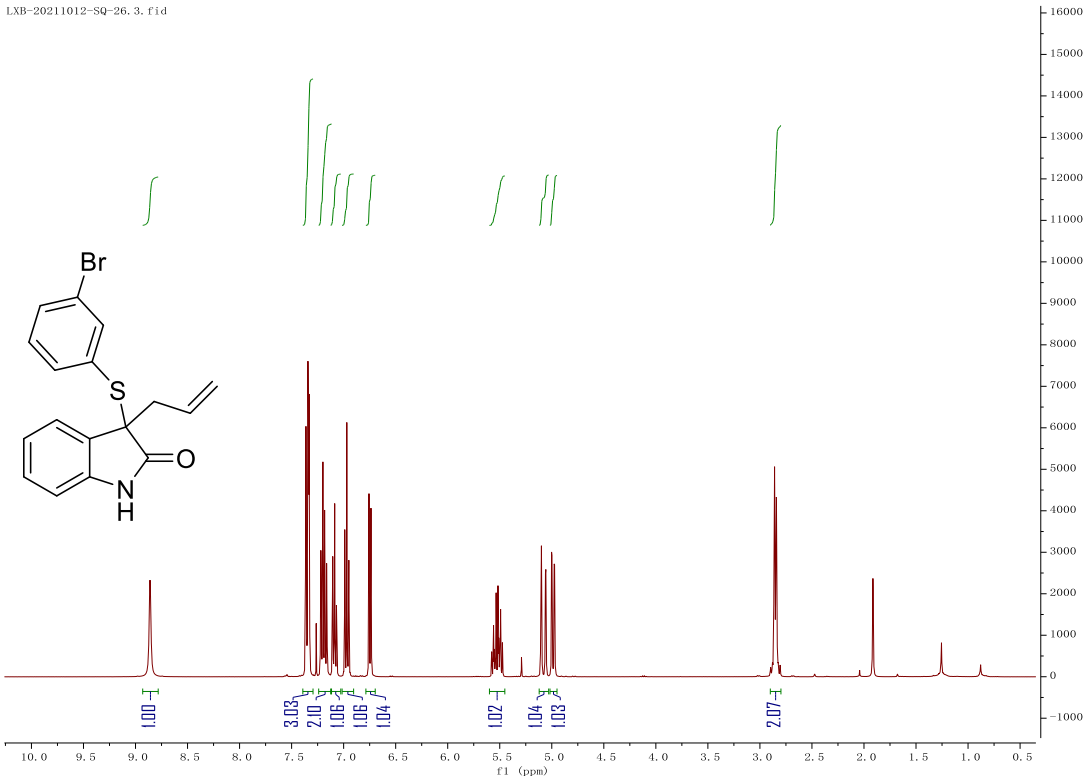

LXB-20211019-SQ-29.1.fid
F
S
O
N
H
1.00
1.02
3.05
1.03
3.08
1.01
1.04
1.03
2.06
f1 (ppm)

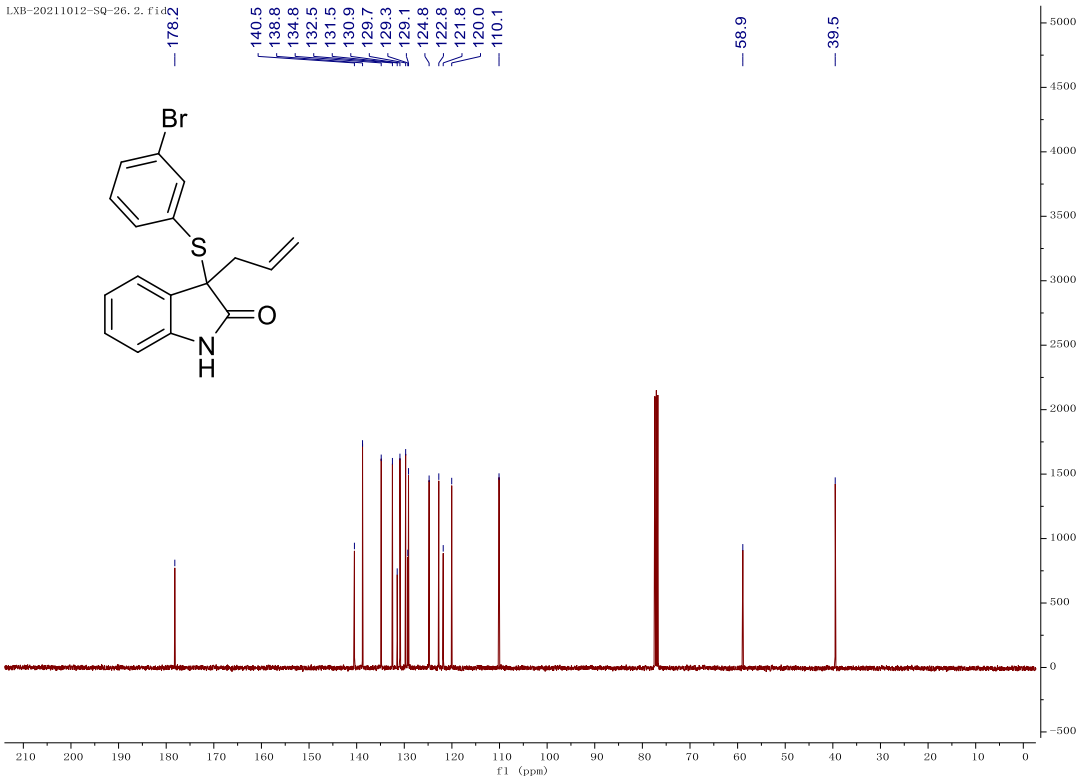

LXB-20211019-SQ-29.2.fid
178.7
165.0
162.5
140.6
138.7
138.6
131.1
129.6
129.0
124.8
124.7
124.6
122.8
120.0
115.8
115.5
110.1
59.1
39.4
F
S
O
N
H
f1 (ppm)

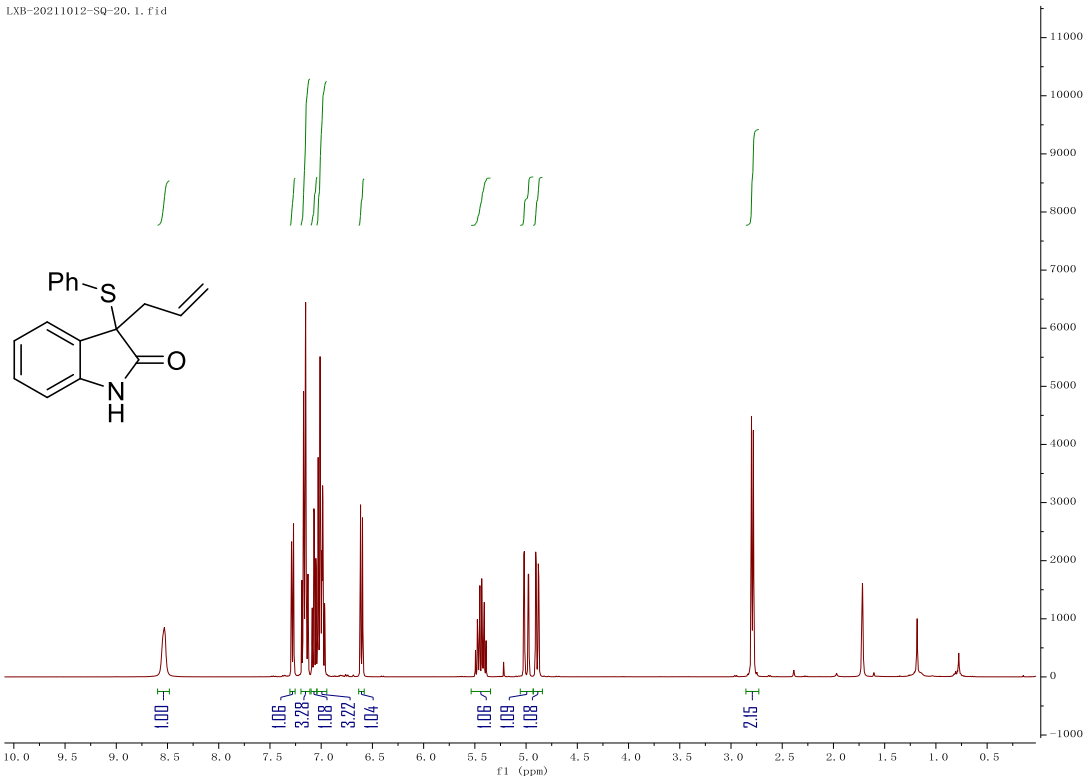

LXB-20211020-SQ-29.1.fid
-110.8
F
S
O
N
H
f1 (ppm)

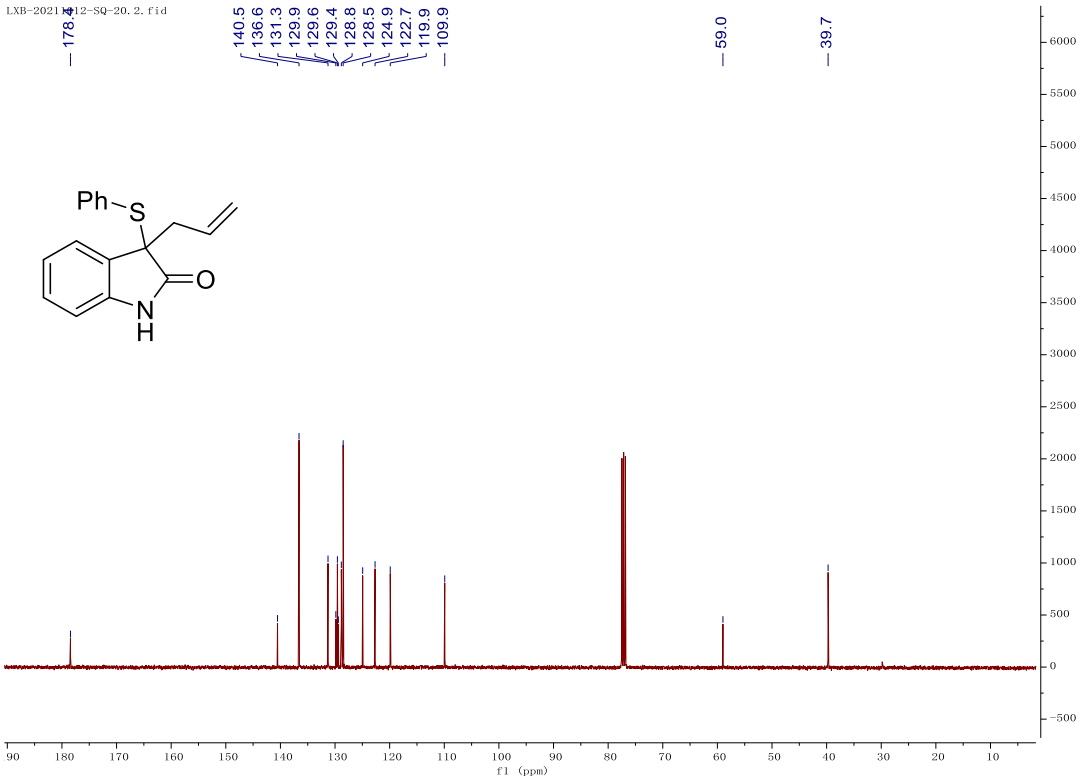

LXB-20211013-SQ-28.1.fid
Br
S
O
N
H
1.00
1.02
3.04
3.01
1.01
1.00
1.02
1.01
2.03
f1 (ppm)

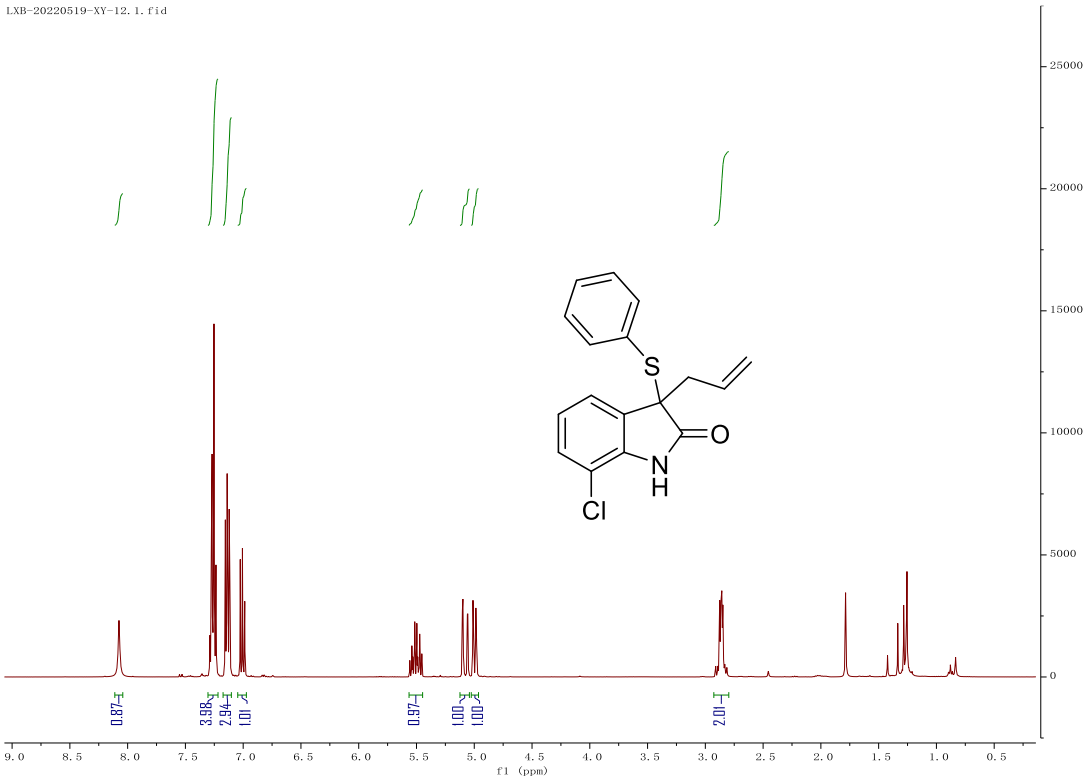

LXB-20211013-SQ-26.4.fid
178.4
178.4
140.5
138.0
131.7
131.0
129.5
129.1
128.5
124.8
124.5
122.8
120.1
110.2
59.0
39.6
Br
S
O
N
H
f1 (ppm)

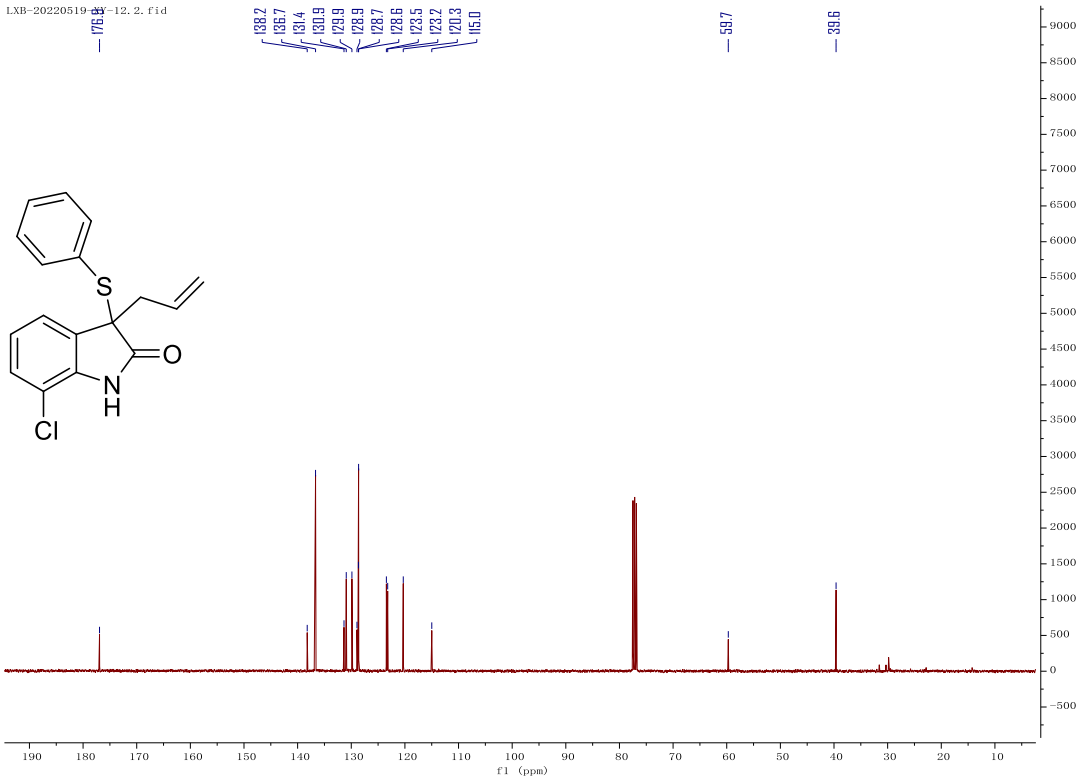

LXB-20211012-SQ-26.3.fid
Br
S
O
N
H
1.00
3.03
2.10
1.06
1.06
1.04
1.02
1.04
1.03
2.07
f1 (ppm)

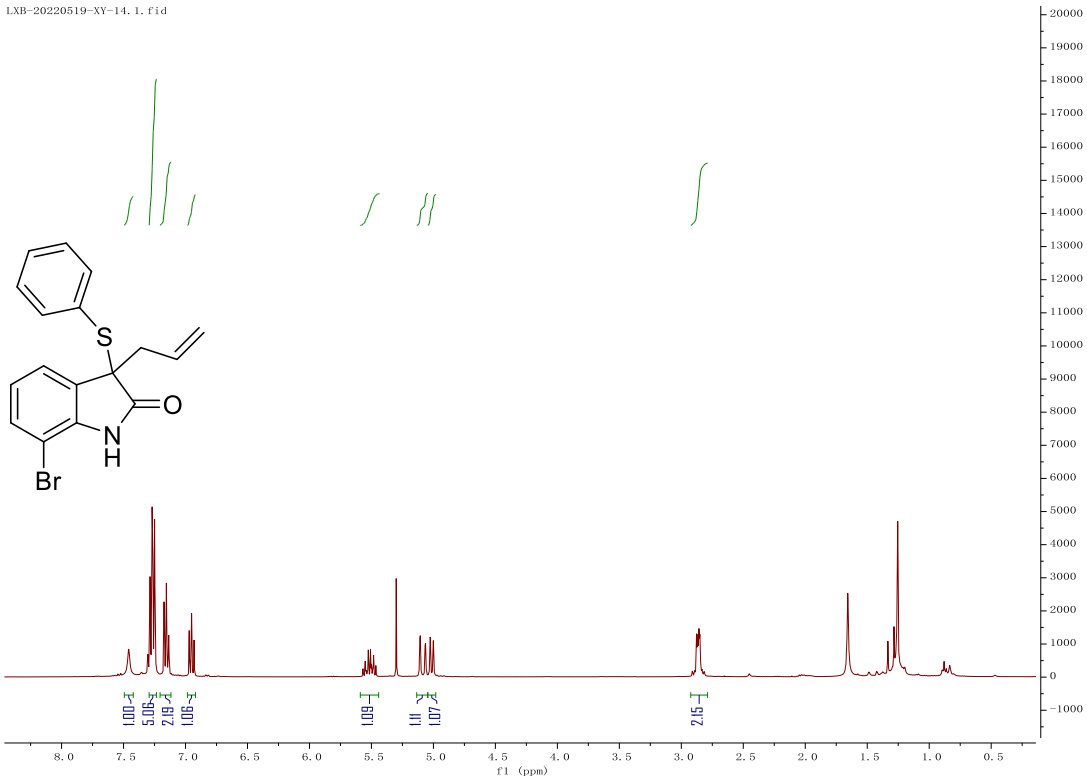

LXB-20211012-SQ-26.2.fid
178.2
140.5
138.8
134.8
132.5
131.5
130.9
129.7
129.3
129.1
124.8
122.8
121.8
120.0
110.1
58.9
39.5
Br
S
O
N
H
f1 (ppm)

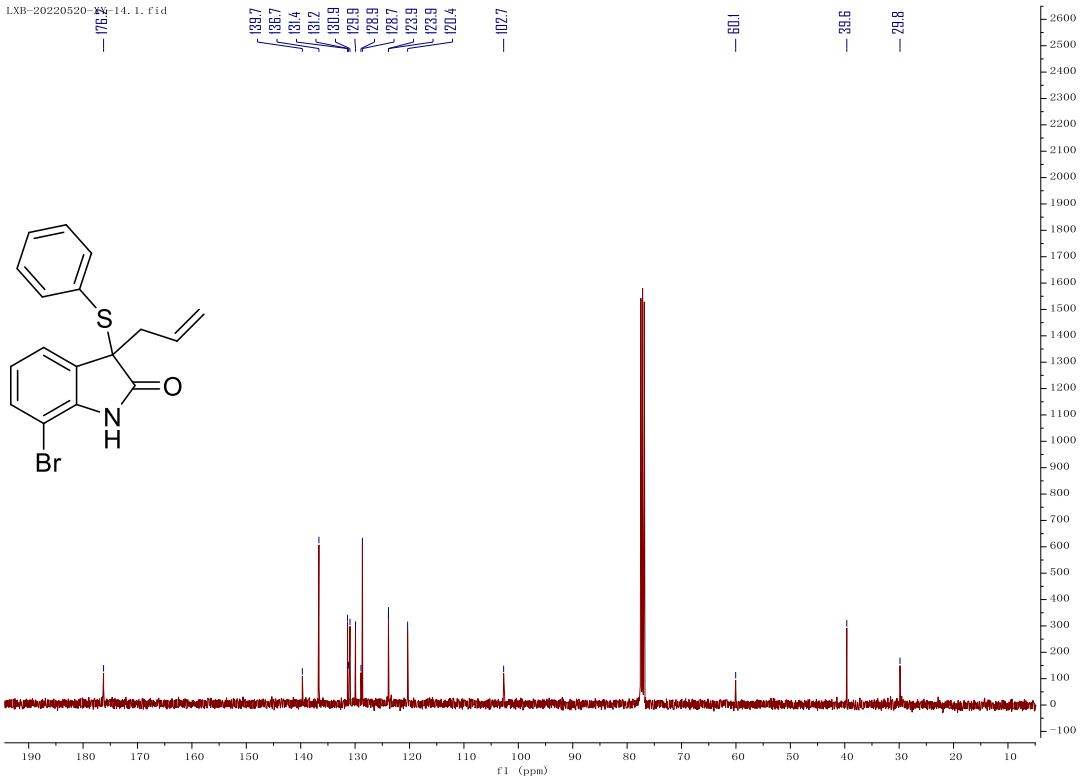

LXB-20211012-SQ-20.1.fid
Ph
S
O
N
H
1.00
1.06
3.28
1.08
3.22
1.04
1.06
1.09
1.08
2.15
f1 (ppm)

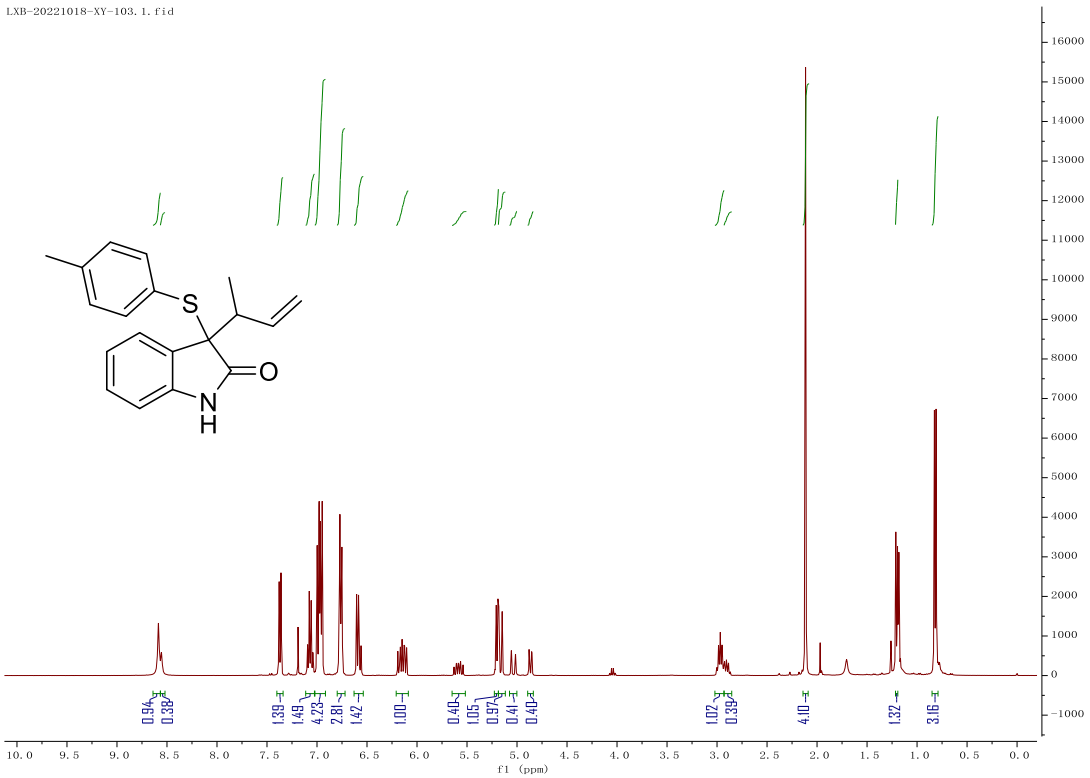

LXB-2021
178.4
140.5
136.6
131.3
129.9
129.6
129.4
128.8
128.5
124.9
122.7
119.9
109.9
59.0
39.7
Ph
S
O
N
H
f1 (ppm)

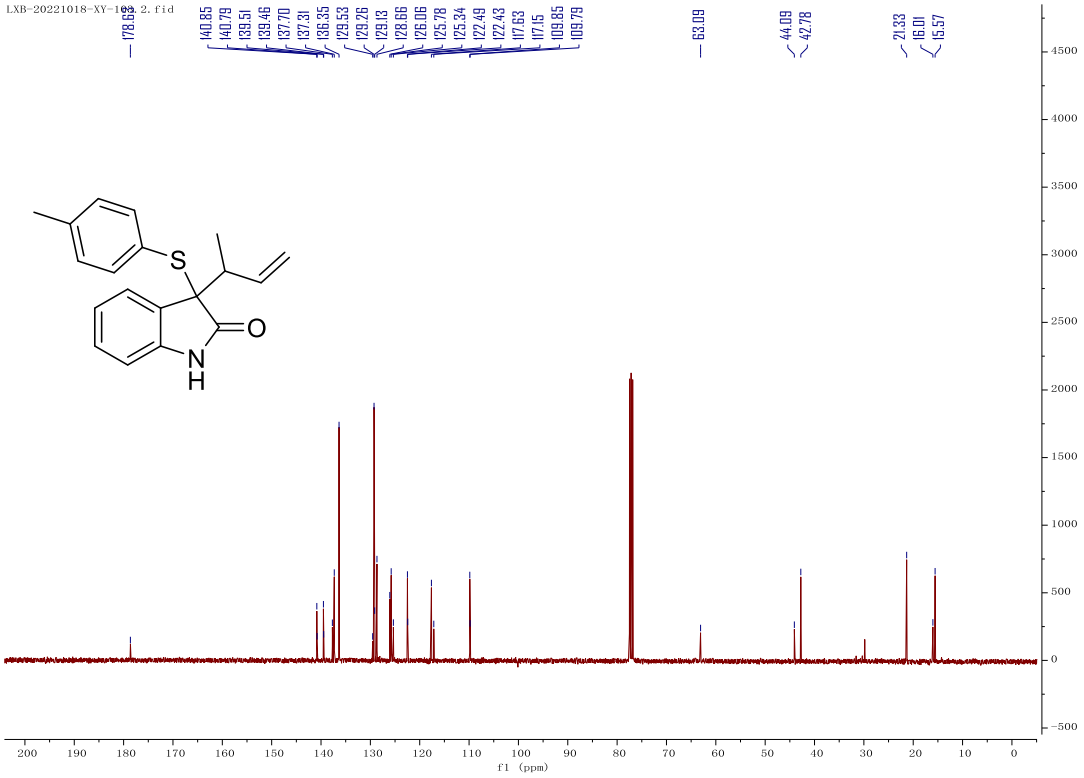

LXB-20220519-XY-12.1.fid
0.87
3.98
2.94
1.01
0.97
1.00
1.00
2.01
S
O
N
H
Cl
f1 (ppm)

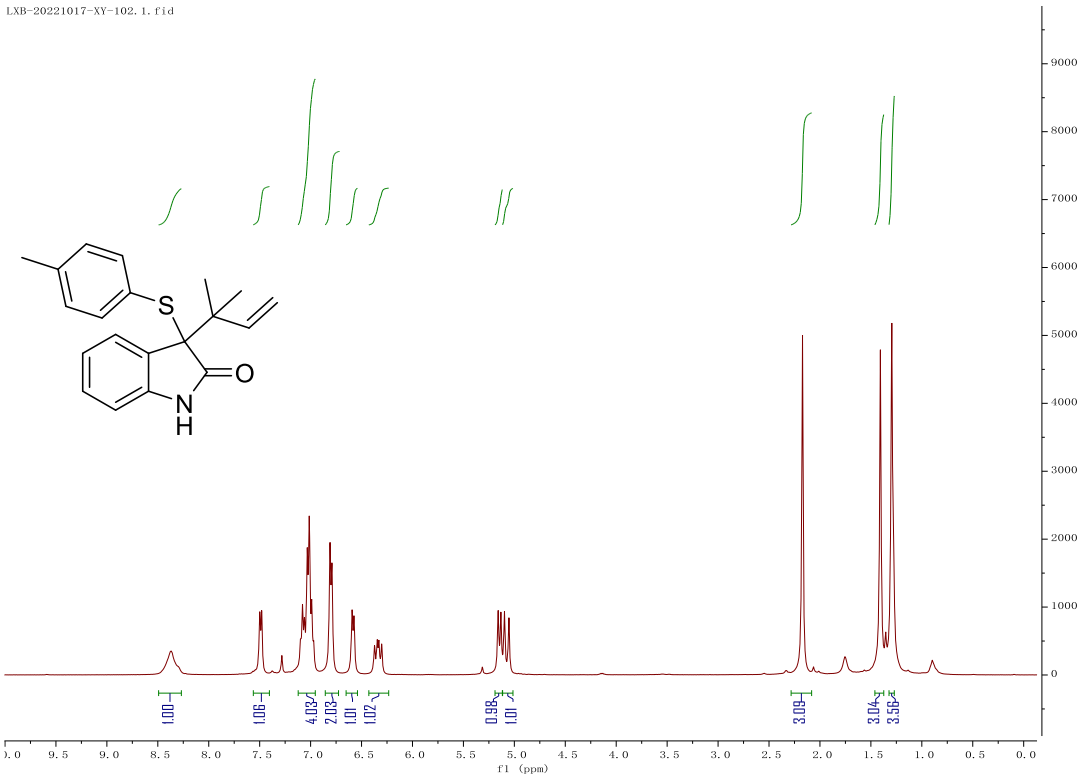

LXB-20220519-XY-12.2.fid
176.4
138.2
136.7
131.4
130.9
129.9
128.9
128.7
128.6
123.5
123.2
120.3
115.0
59.7
39.6
S
O
N
H
Cl
f1 (ppm)

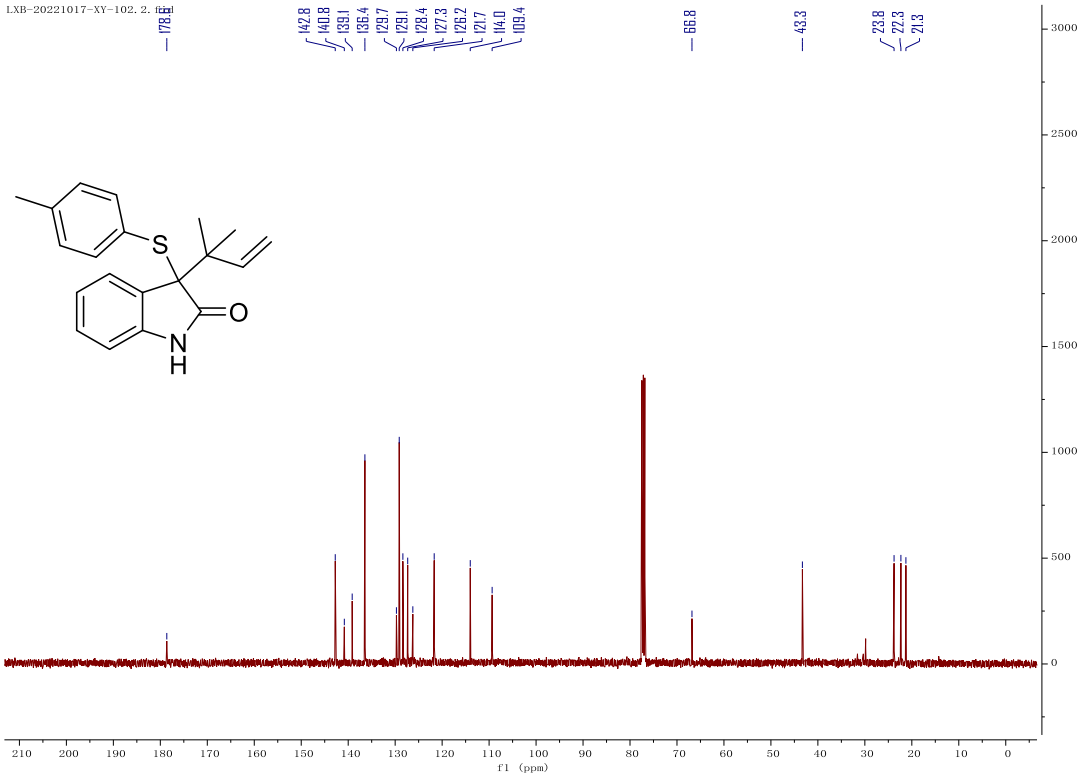

LXB-20220519-XY-14.1.fid
S
O
N
H
Br
1.00
5.06
2.19
1.06
1.09
1.11
1.07
2.15
f1 (ppm)

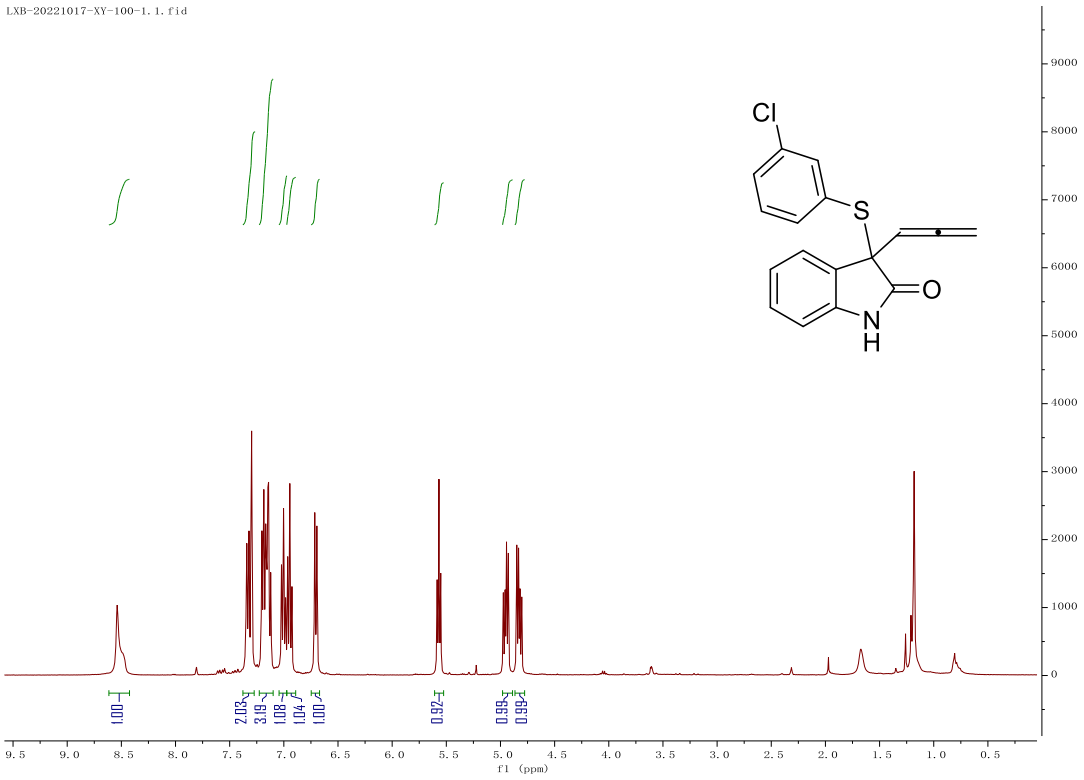

LXB-20220520-XY-14.1.fid
176.1
139.7
136.7
131.4
131.2
130.9
129.9
128.9
128.7
123.9
123.9
120.4
102.7
60.1
39.6
29.8
S
O
N
H
Br
f1 (ppm)

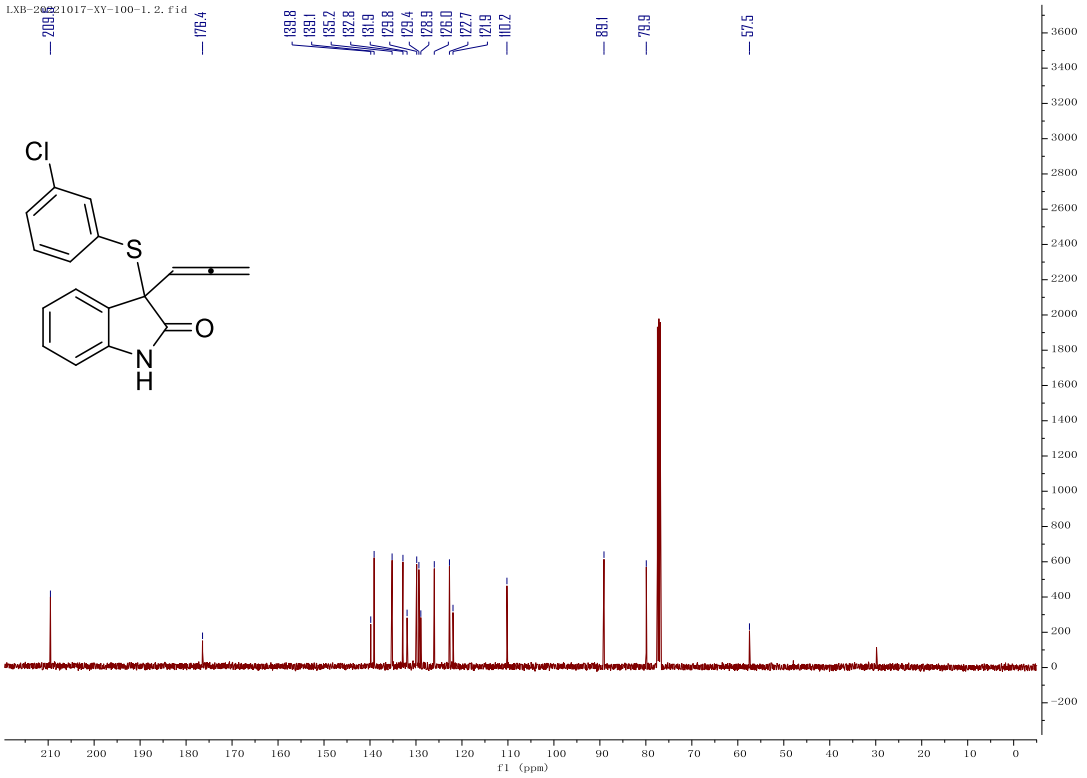

LXB-20221018-XY-103.1.fid
S
O
N
H
0.94
0.38
1.39
1.49
4.23
2.81
1.42
1.00
0.40
1.05
0.97
0.41
0.40
1.07
0.39
4.10
1.32
3.16
f1 (ppm)

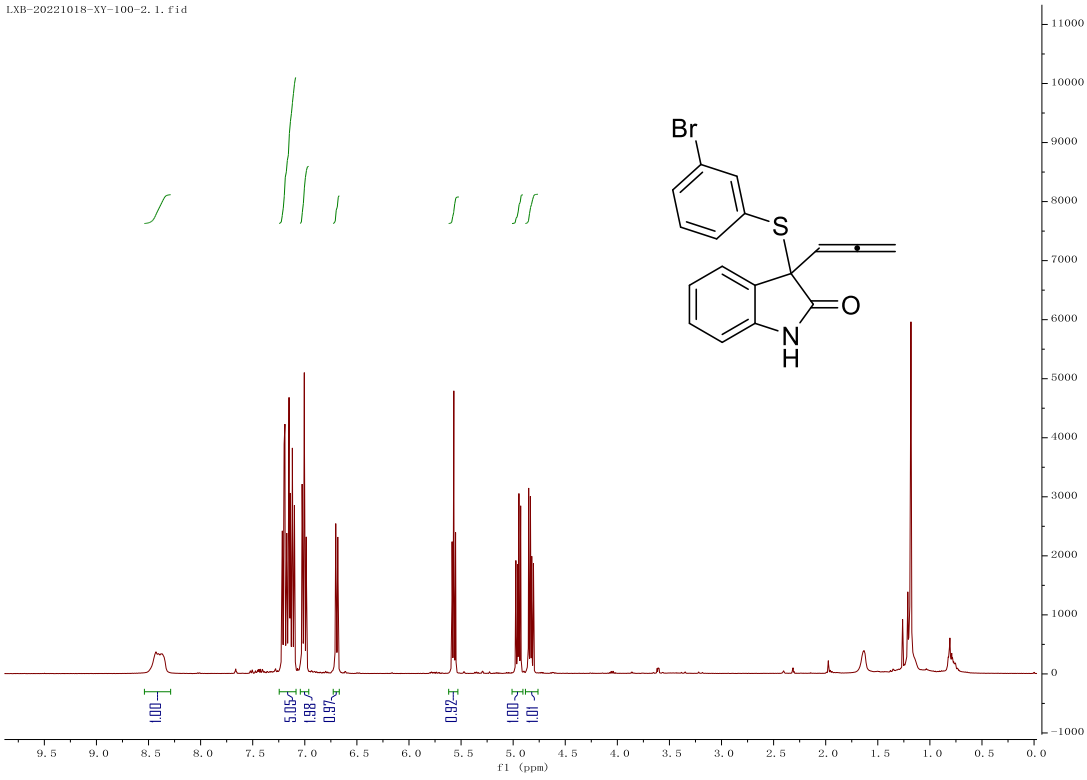

LXB-20221018-XY-102.2.fid
178.69
140.85
140.79
139.51
139.46
137.70
137.31
136.35
129.53
129.26
129.13
128.66
126.06
125.78
125.34
122.49
122.43
117.63
117.15
109.85
109.79
63.09
44.09
42.78
21.33
16.01
15.57
S
O
N
H
f1 (ppm)

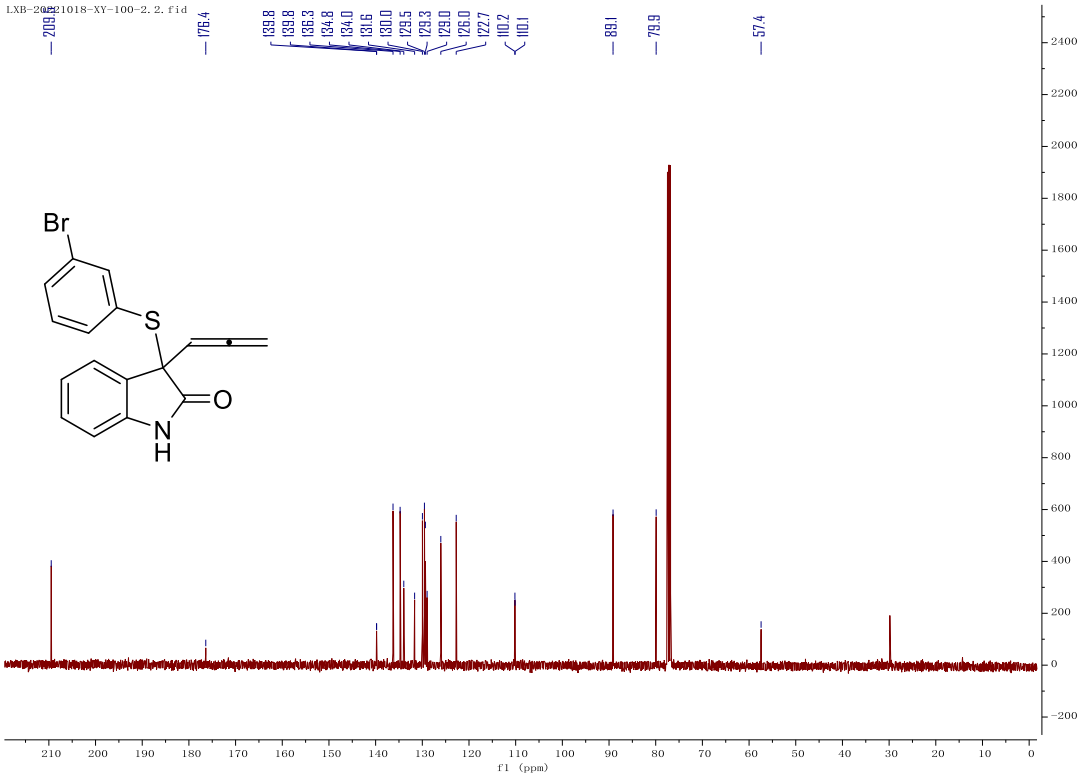

LXB-20221017-XY-102.1.fid
1.00
1.06
4.03
2.03
1.01
1.02
0.98
1.01
3.09
3.04
3.56
S
O
N
H
f1 (ppm)

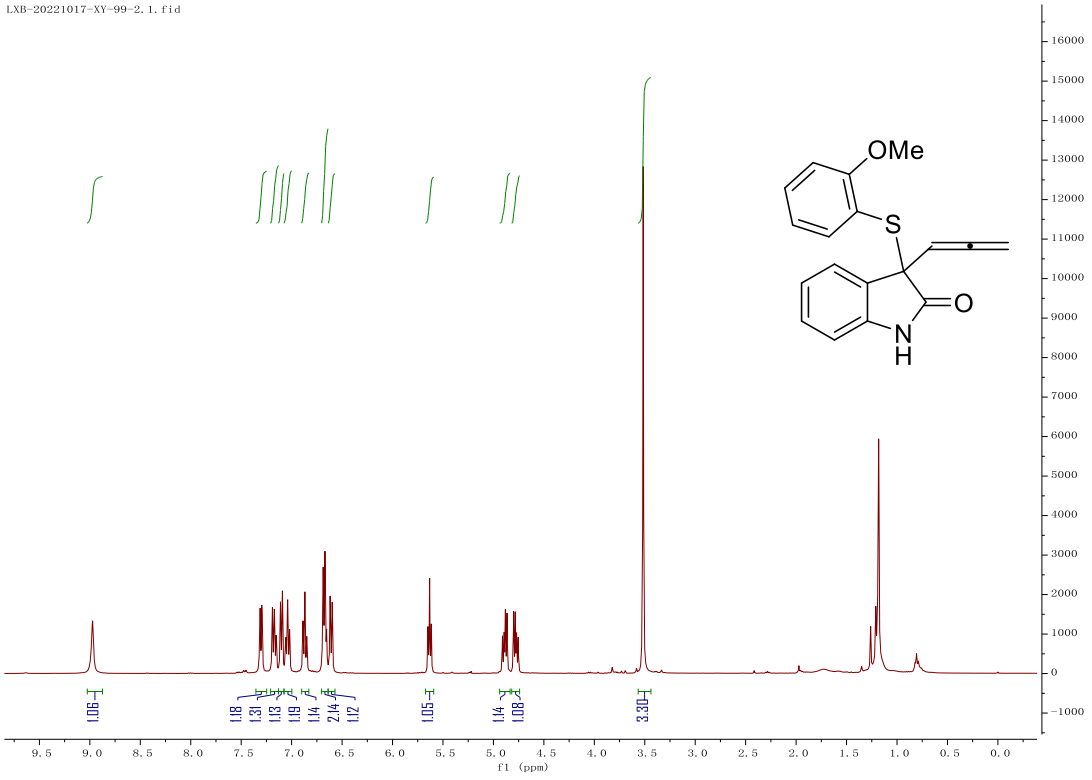

LXB-20221017-XY-102.2.fid
178.6
142.8
140.8
139.1
136.4
129.7
129.1
128.4
127.3
126.2
121.7
114.0
109.4
66.8
43.3
23.8
22.3
21.3
S
O
N
H
f1 (ppm)

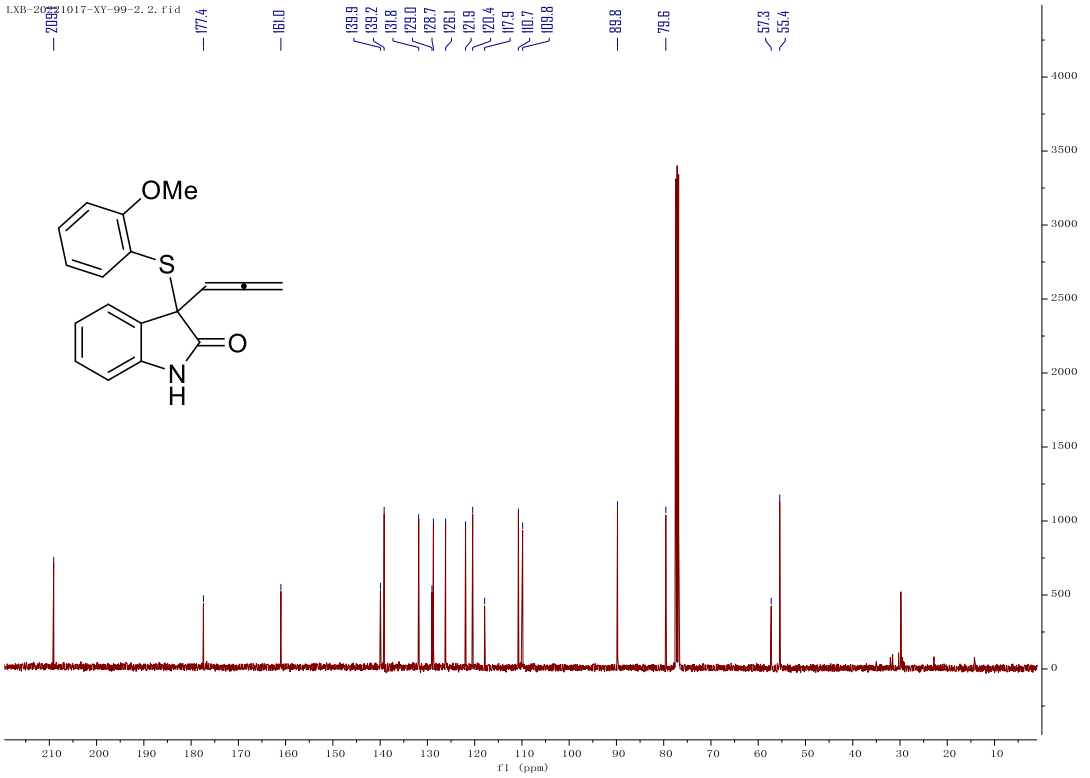

LXB-20221017-XY-100-1.1.fid
Cl
S
O
N
H
1.00
2.03
3.19
1.08
1.04
1.00
0.92
0.99
0.99
f1 (ppm)

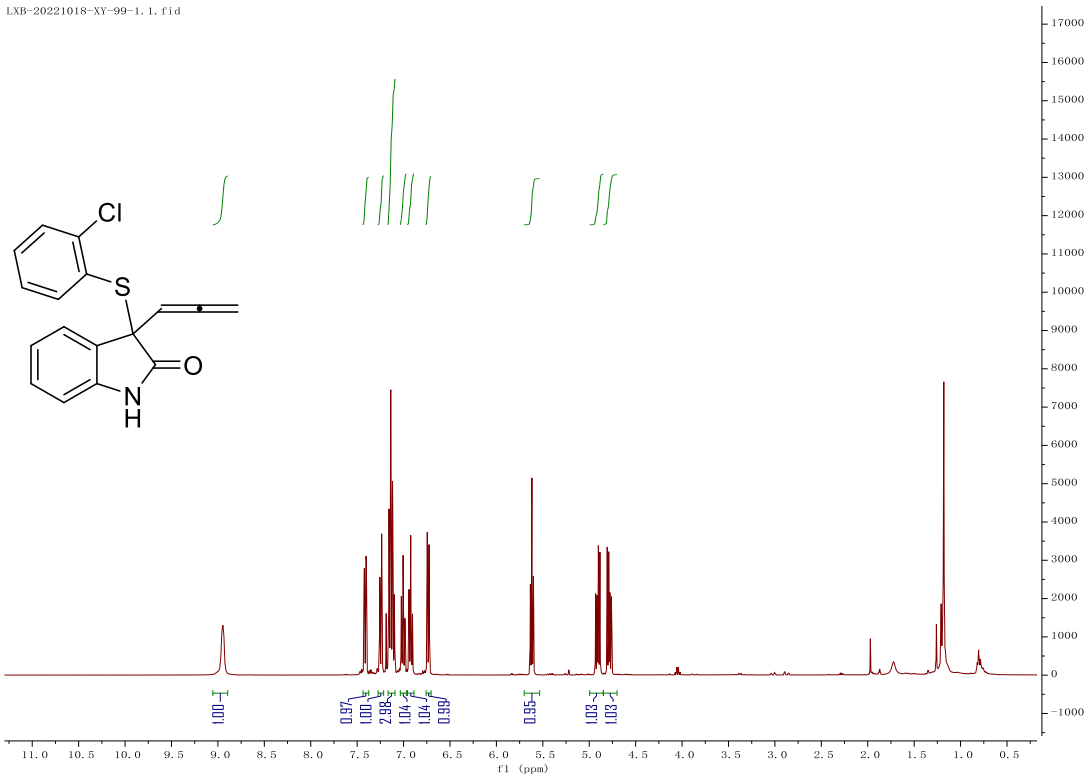

LXB-20221017-XY-100-1.2.fid
209.6
176.4
139.8
139.1
135.2
132.8
131.9
129.8
129.4
128.9
126.0
122.7
121.9
110.2
89.1
79.9
57.5
Cl
S
O
N
H
f1 (ppm)

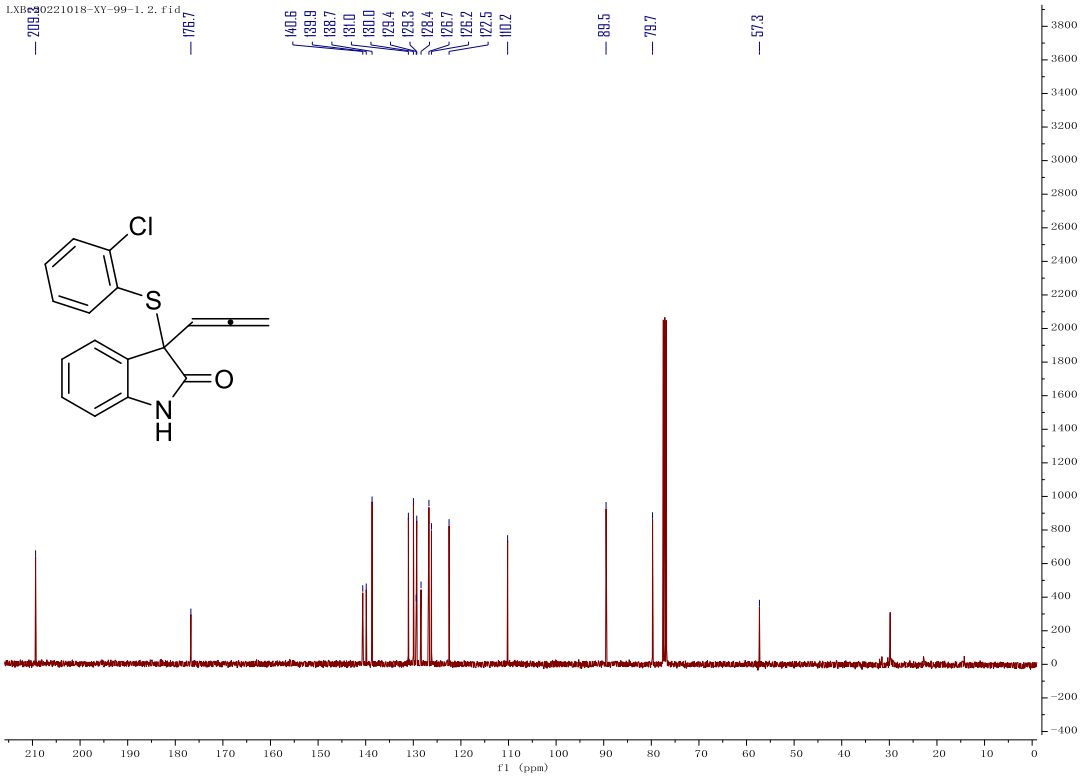

LXB-20221018-XY-100-2.1.fid
Br
S
O
N
H
1.00
5.05
1.98
0.97
0.92
1.00
1.01
f1 (ppm)

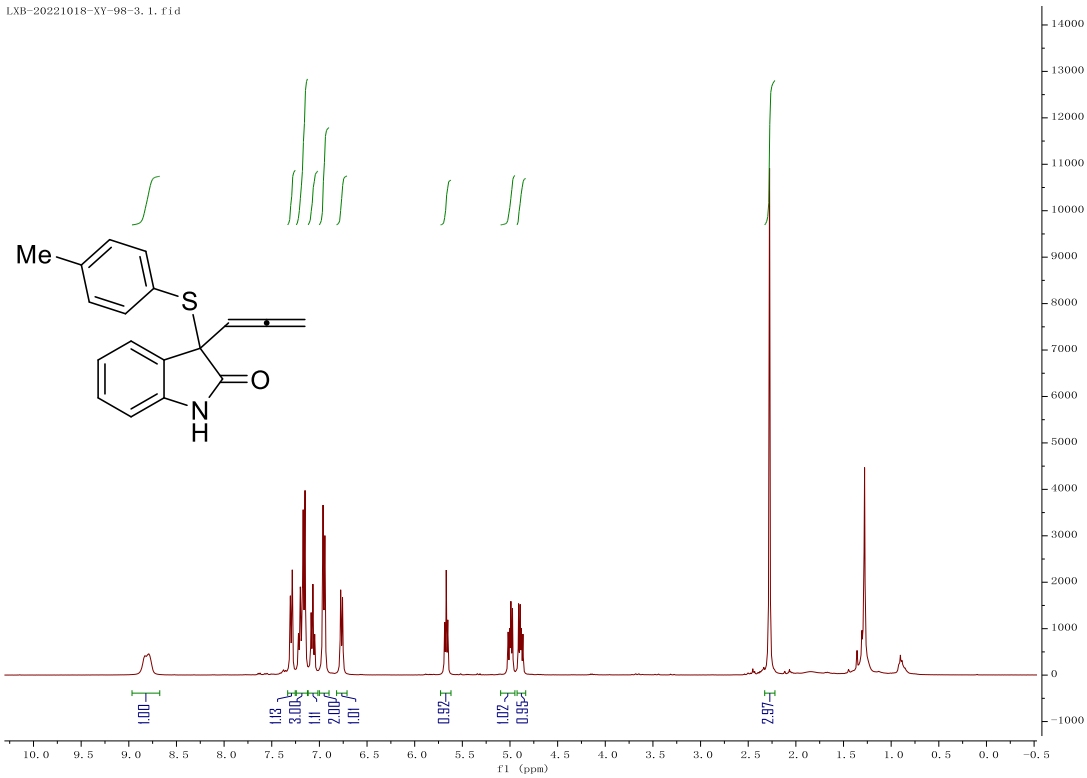

LXB-20221018-XY-100-2.2.fid
209.8
176.4
139.8
139.8
136.3
134.8
134.0
131.6
130.0
129.5
129.3
129.0
126.0
122.7
110.2
110.1
89.1
79.9
57.4
Br
S
O
N
H
f1 (ppm)

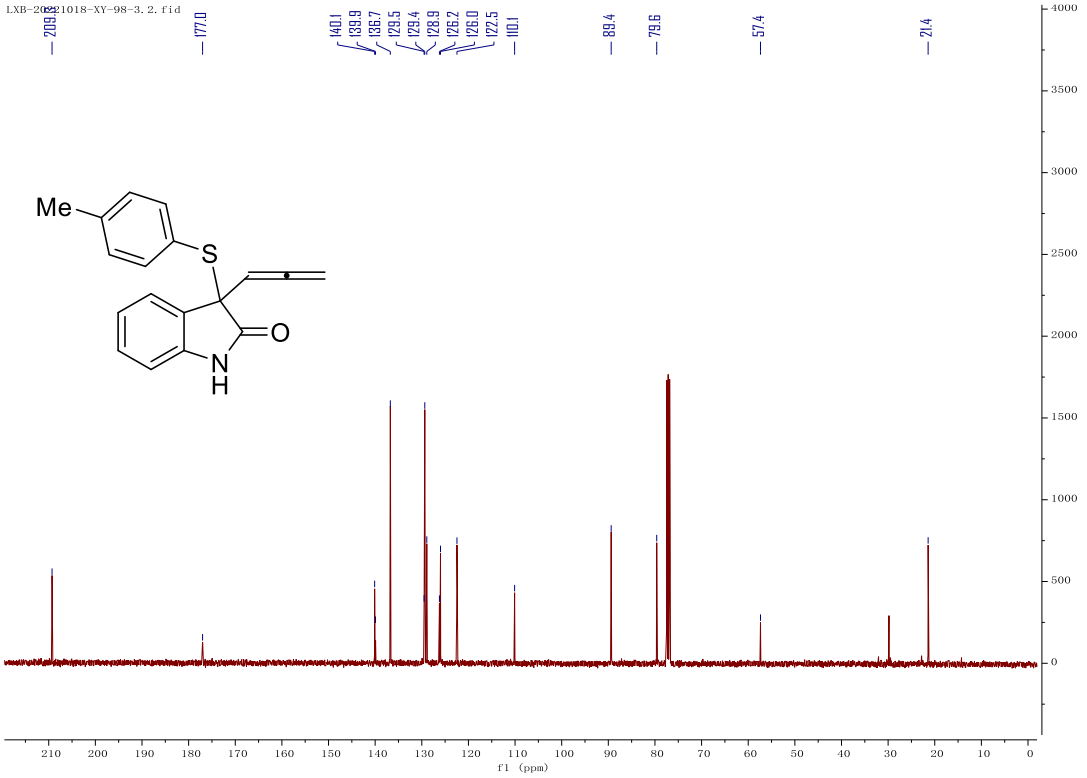

LXB-20221017-XY-99-2.1.fid
OMe
S
O
N
H
1.06
1.8
1.31
1.13
1.9
1.14
2.14
1.12
1.05
1.4
1.08
3.30
f1 (ppm)

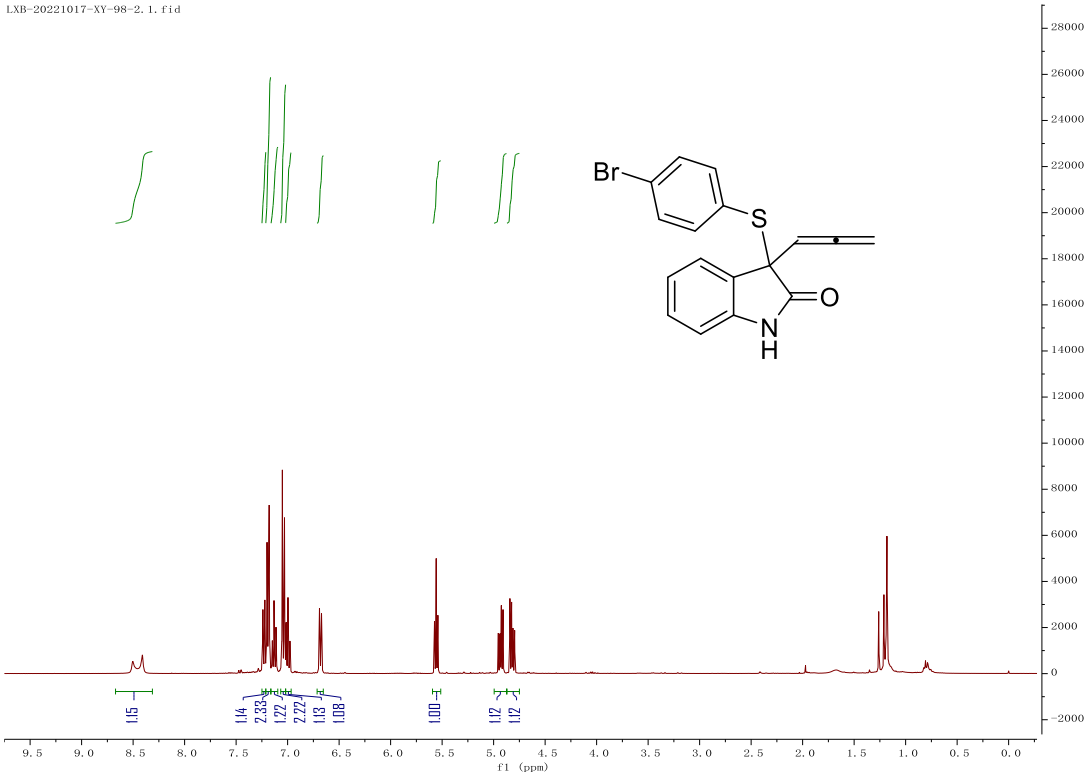

LXB-20221017-XY-99-2.2.fid
209.1
177.4
161.0
139.9
139.2
131.8
129.0
128.7
126.1
121.9
120.4
117.9
110.7
109.8
89.8
79.6
57.3
55.4
OMe
S
O
N
H
f1 (ppm)

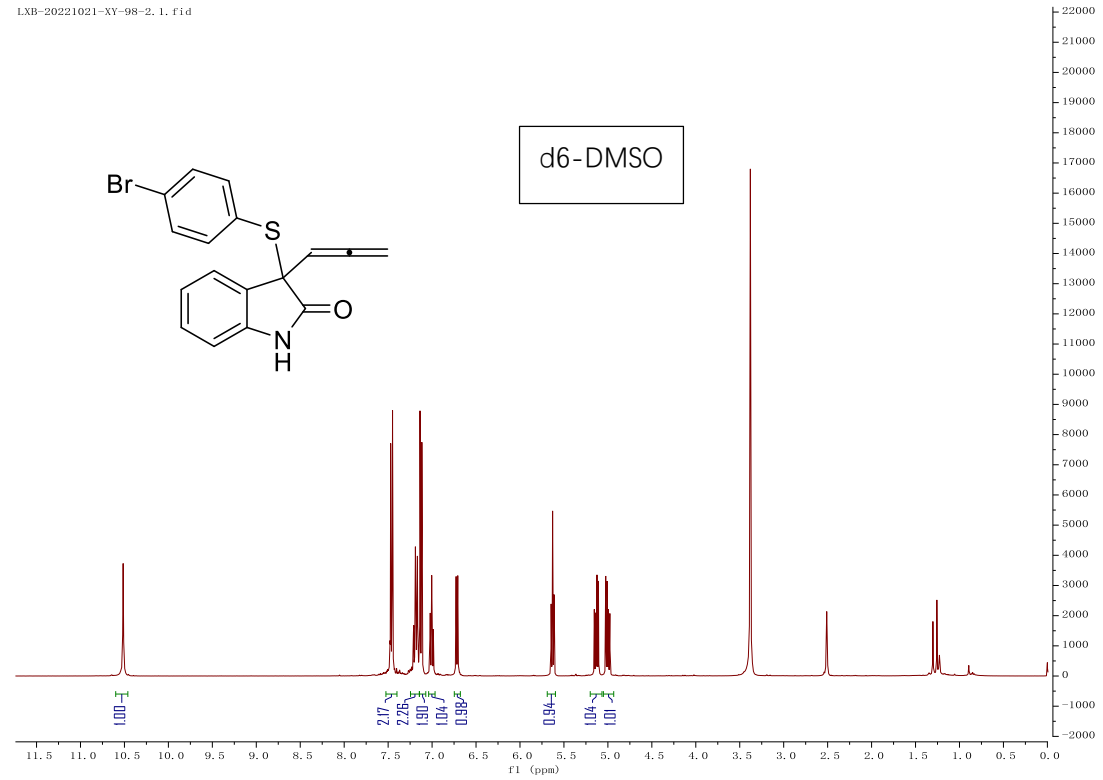

LXB-20221018-XY-99-1.1.fid
Cl
S
O
N
H
1.00
0.97
1.00
2.98
1.04
1.04
0.99
0.95
1.03
1.03
f1 (ppm)

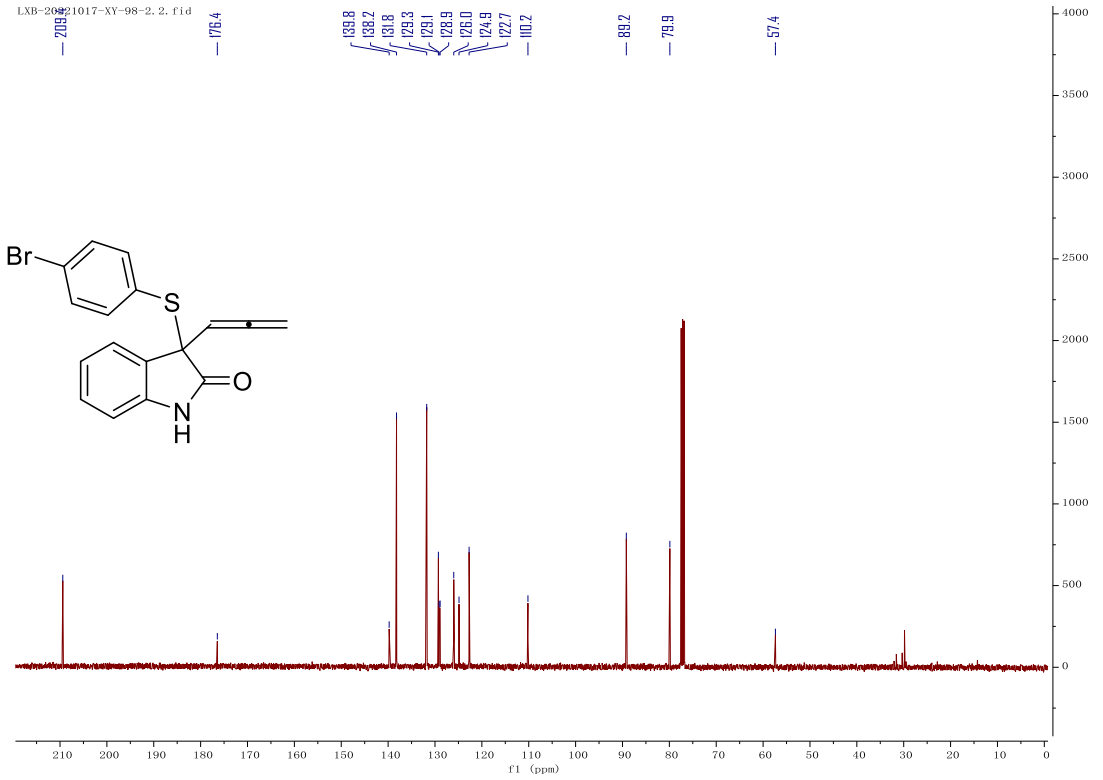

LXB-20221018-XY-99-1.2.fid
209.3
176.7
140.6
139.9
138.7
131.0
130.0
129.4
129.3
128.4
126.7
126.2
122.5
110.2
89.5
79.7
57.3
Cl
S
O
N
H
f1 (ppm)

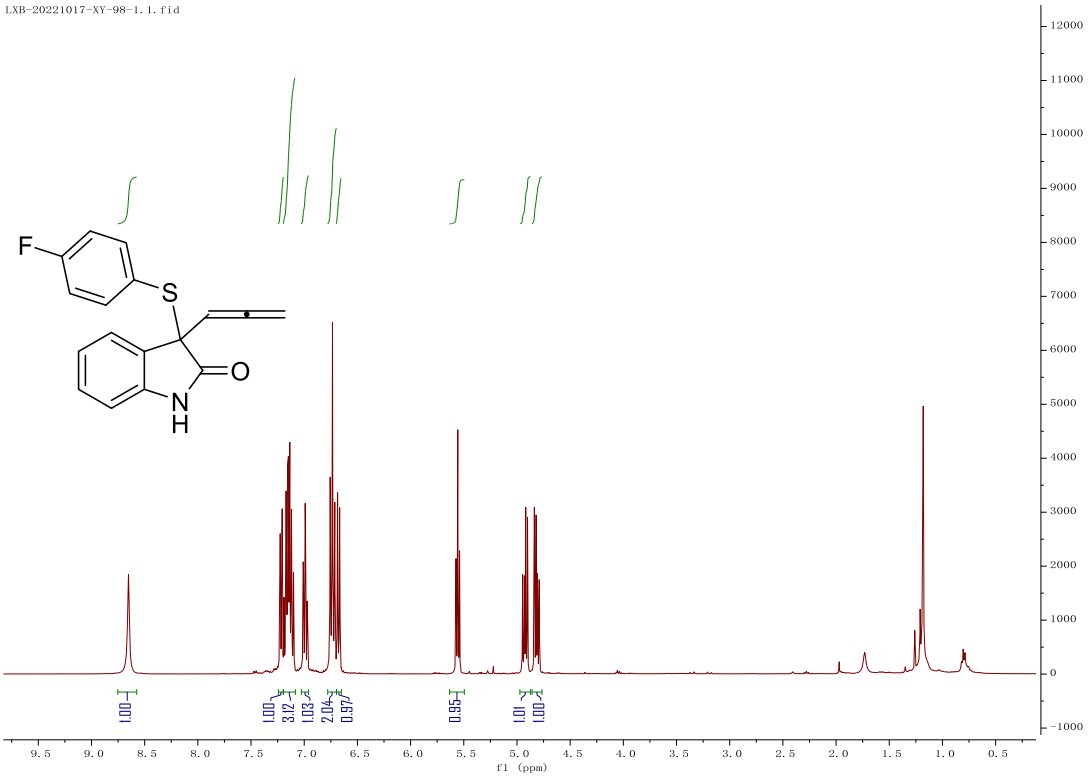

LXB-20221018-XY-98-3.1.fid
Me
S
O
N
H
1.00
1.13
3.00
1.11
2.00
1.01
0.92
1.02
0.95
2.97
f1 (ppm)

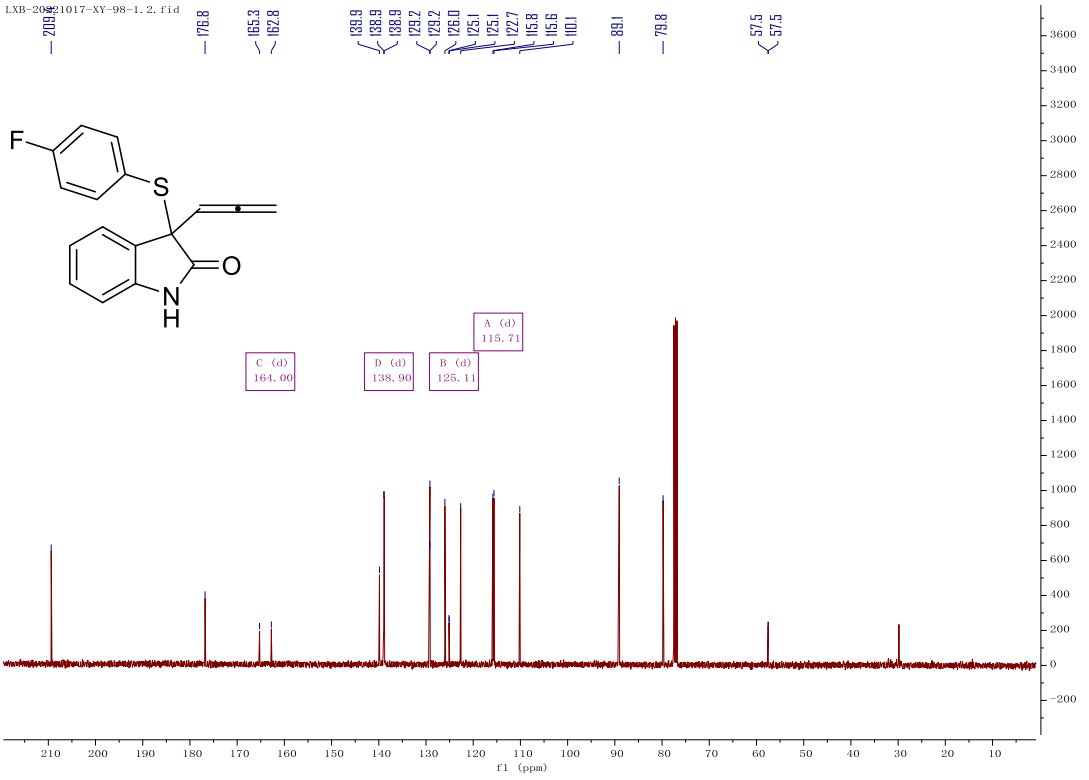

LXB-20221018-XY-98-3.2.fid
209.8
177.0
140.1
139.9
136.7
129.5
129.4
128.9
126.2
126.0
122.5
110.1
89.4
79.6
57.4
21.4
Me
S
O
N
H
f1 (ppm)


LXB-20221017-XY-98-2.1.fid
Br
S
O
N
H
1.15
1.14
2.38
1.22
2.22
1.13
1.08
1.00
1.12
1.12
f1 (ppm)


LXB-20221021-XY-98-2.1.fid
d6-DMSO
Br
S
O
N
H
1.00
2.17
2.26
1.90
1.04
0.98
0.94
1.04
1.01
f1 (ppm)


LXB-20221017-XY-98-2.2.fid
209.4
176.4
133.8
138.2
131.8
129.3
129.1
128.9
126.0
124.9
122.7
110.2
89.2
79.9
57.4
Br
S
O
N
H
f1 (ppm)


LXB-20221017-XY-98-1.1.fid
F
S
O
N
H
1.00
3.12
1.03
2.04
0.97
0.95
1.01
1.00
f1 (ppm)


LXB-20221017-XY-98-1.2.fid
209.4
176.8
165.3
162.8
139.9
138.9
138.9
129.2
129.2
126.0
125.1
125.1
122.7
115.8
115.6
110.1
89.1
79.8
57.5
57.5
F
S
O
N
H
A (d)
115.71
C (d)
164.00
D (d)
138.90
B (d)
125.11
f1 (ppm)