

Supporting Information

Copper-Catalyzed Asymmetric Alkynylation of Cyclic *N*-sulfonyl Ketimines

Zheng Ling,^a Sonia Singh,^{a,b} Fang Xie,^{*a} Liang Wu^a and Wanbin Zhang^{*a}

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

Fax: (+)86-21-54743265; Phone: (+)86-21-54743265; E-mail: wanbin@sjtu.edu.cn

^b On leave from Yazd Branch, Islamic Azad University.

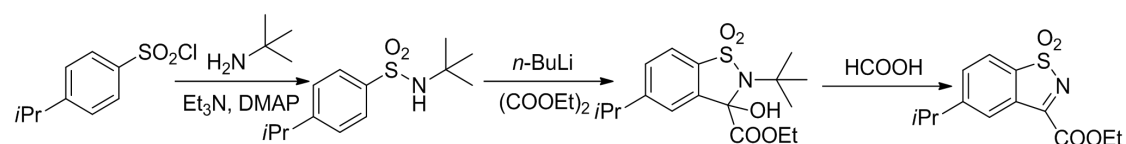
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1. General Information

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. High resolution mass spectrum (HRMS) was performed at the Analysis Center of Shanghai Jiao Tong University. Enantioselectivity was measured by high performance liquid chromatography (HPLC) using Daicel Chiralcel AY, OD-H and AD-H columns with *n*-hexane/*i*-PrOH as an eluent. Column chromatography was performed using 100–200 mesh silica gel. Melting point was measured with SGW X-4 micro melting point apparatus. All commercially available substrates were used as received.

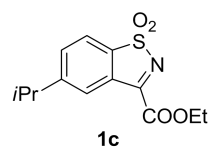
2. General procedure for the synthesis of cyclic *N*-sulfonyl α -iminoesters **1** and characterization data ^[1]



To a solution of *tert*-butylamine (15.0 mmol), triethylamine (20.0 mmol) and DMAP (1.0 mmol) in DCM in an ice bath was added 4-isopropylbenzene-1-sulfonyl chloride (10.0 mmol) dropwise. The mixture was stirred at room temperature overnight. It was washed with saturated sodium carbonate and brine. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic extracts were dried over anhydrous Na_2SO_4 . The solvent was evaporated in vacuo to give the crude product. Then the product was recrystallized to give the *N*-(*tert*-butyl)-4-isopropylbenzenesulfonamide as a solid.

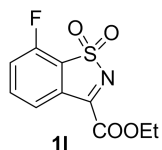
Butyllithium (10.0 mmol) was added dropwise over a 20 min period to a cold (0 °C), mechanically stirred solution of the *N*-(*tert*-butyl)-4-isopropylbenzenesulfonamide (5.0 mmol) in anhydrous THF (25 mL) under a dry nitrogen atmosphere. After stirring an additional 25 min at 0 °C a precipitate formed. The suspension was cooled further to -78 °C and diethyl oxalate (15.0 mmol) was added. The cooling bath was removed and the suspension was stirred at ambient temperature for 3 h. The reaction was quenched with 10% HCl (15 mL) and added to water (80 mL). The organics were extracted with ethyl acetate (80 mL). The ether acetate phase was washed with brine (80 mL). The solvent was removed and the crude product was obtained used directly in the next step.

To the product obtained above, formic acid (20 mL) was added and the suspension was stirred at room temperature under a dry nitrogen atmosphere. After 5 min dissolution occurred. After 20 h the solution was concentrated and the resultant solid was dissolved in DCM and concentrated (three times) to remove traces of formic acid. The crude product was further purified by flash chromatography (PE:EA = 5:1) to give **1c**.

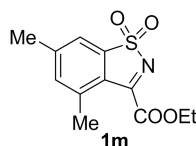


Ethyl 5-isopropylbenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**1c**), 0.85 g, 60% yield, white solid, m.p.: 84–85 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, J = 1.6 Hz, 1H), 7.85 (d, J =

1.6 Hz, 1H), 7.62 (dd, $J=7.2$, 1.6 Hz, 1H), 4.55 (q, $J=7.2$ Hz, 2H), 3.12-3.05 (m, 1H), 1.48 (t, $J=7.2$ Hz, 3H), 1.31 (d, $J=7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 160.6, 160.2, 156.7, 137.7, 132.4, 128.9, 125.6, 123.0, 63.8, 34.6, 23.7, 14.0; HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 282.0800, found 282.0810.

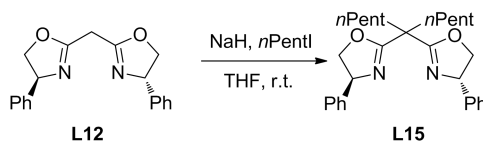


3-ethoxycarbonyl-2-fluorobenzo[d]isothiazole 1,1-dioxide (**11**). 0.76 g, 59% yield, white solid, m.p.: 117~118 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, $J=7.6$ Hz, 1H), 7.80-7.75 (m, 1H), 7.48-7.44 (m, 1H), 4.55 (q, $J=7.2$ Hz, 2H), 1.49 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 158.9 (d, $J=3.0$ Hz), 157.2 (d, $J=263.6$ Hz), 137.4 (d, $J=6.9$ Hz), 131.0 (d, $J=2.0$ Hz), 126.3 (d, $J=20.2$ Hz), 123.5 (d, $J=3.5$ Hz), 122.2 (d, $J=19.6$ Hz), 64.0, 14.0; HRMS (ESI): calcd for $\text{C}_{10}\text{H}_9\text{NO}_4\text{SF}$ $[\text{M}+\text{H}]^+$ 258.0236, found 258.0221.



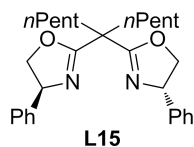
3-ethoxycarbonyl-5,7-dimethylbenzo[d]isothiazole 1,1-dioxide (**1m**). 0.72 g, 54% yield, white solid, m.p.: 132~133 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.29 (s, 1H), 4.54 (q, $J=7.2$ Hz, 2H), 2.49 (s, 3H), 2.44 (s, 3H), 1.46 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.81, 162.80, 146.5, 140.4, 137.3, 137.2, 124.0, 121.8, 63.8, 21.6, 18.7, 13.9; HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 268.0644, found 268.0637.

3. General procedure for the synthesis of L15 and characterization data^[2]



To a solution of **L12** (4.2 mmol) in THF (65 mL) in an ice bath was added 60% NaH (14.7 mmol). The mixture was stirred at room temperature for 1 h. The suspension was cooled further to 0 °C and 1-iodopentane (6.3 mmol) was added. The cooling bath was removed and the suspension was stirred at room temperature for 20 h. It was washed with brine. The organic layer was separated, and the aqueous layer was extracted with DCM (three times). The combined organic extracts were dried over anhydrous Na_2SO_4 . The solvent was evaporated in vacuo to give the crude product.

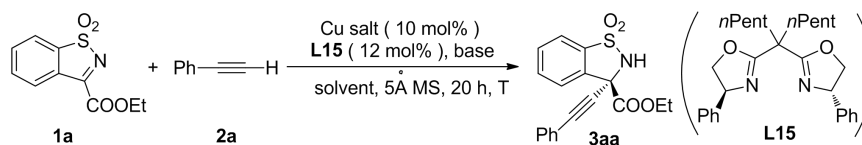
To the product obtained above, redo above step to give the crude product. Then it was further purified by flash chromatography (PE:EA = 5:1) to give **L15**.



(4*S*,4'*S*)-2,2'-(undecane-6,6-diyl)bis(4-phenyl-4,5-dihydrooxazole) (**L15**), 1.41 g, 75% yield, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.31 (m, 4H), 7.28-7.24 (m, 6H), 5.24 (dd, J

=10.4, 8.0 Hz, 2H), 4.65 (dd, $J = 10.0, 8.0$ Hz, 2H), 4.12 (t, $J = 8.0$ Hz, 2H), 2.13-2.06 (m, 4H), 1.39-1.26 (m, 12H), 0.91-0.85 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.2, 142.4, 128.7, 127.5, 126.8, 75.0, 69.6, 46.3, 32.6, 32.0, 23.6, 22.5, 14.0; HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{39}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 447.3012, found 447.3003.

4. Optimization reaction conditions^{[a],[b],[c]}

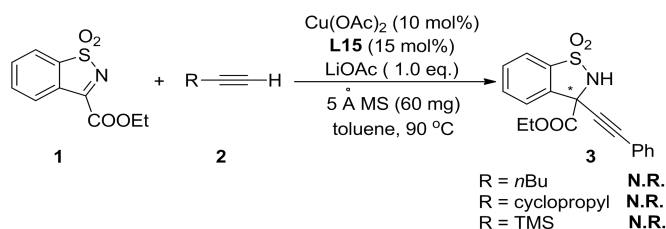


entry	Cu salt	base	solvent	T (°C)	yield (%)	ee (%)
1	-	LiOAc	toluene	80	N.R.	-
2	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	-	toluene	80	N.R.	-
3	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	Li_2CO_3	toluene	80	54	68
4	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	Na_2CO_3	toluene	80	31	66
5	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	NaOAc	toluene	80	trace	-
6	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	KOAc	toluene	80	trace	-
7	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	K_3PO_4	toluene	80	40	60
8	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	LiOAc	toluene	80	53	85
9	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	LiOAc	DCE	80	42	73
10	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	LiOAc	1,4-dioxane	80	trace	-
11	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	LiOAc	$\text{C}_6\text{H}_5\text{OCH}_3$	80	28	38
12	$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	LiOAc	toluene	80	43	50
13	$\text{Cu}(\text{CH}_3\text{CN})_4\text{ClO}_4$	LiOAc	toluene	80	39	55
14	CuBr	LiOAc	toluene	80	trace	-
15	$\text{Cu}(\text{Me}_2\text{S})\text{Br}$	LiOAc	toluene	80	trace	-
16	CuBr_2	LiOAc	toluene	80	trace	-
17	CuCl	LiOAc	toluene	80	47	81
18	$\text{Cu}(\text{OTf})_2$	LiOAc	toluene	80	trace	-
19	$(\text{CuOTf})_2 \cdot \text{C}_6\text{H}_6$	LiOAc	toluene	80	trace	-
20	$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	LiOAc	toluene	80	40	75
21	$\text{Cu}(\text{acac})_2$	LiOAc	toluene	80	74	73
22	$\text{Cu}(\text{OAc})_2$	LiOAc	toluene	80	37	89
23 ^[d]	$\text{Cu}(\text{OAc})_2$	LiOAc	toluene	80	41	96
24 ^[e]	$\text{Cu}(\text{OAc})_2$	LiOAc	toluene	80	67	96
25 ^[e]	$\text{Cu}(\text{OAc})_2$	LiOAc	toluene	90	88	96

[a] Isolated Yield; [b] Determined by HPLC using a chiral Daicel column; [c] The absolute configuration of **3aa** was determined as *R* according to ref. [3]; [d] 15 mol% **L15** was added; [e] Reacted for two days.

5. General procedure for Cu-catalyzed alkylation of cyclic ketimines 1

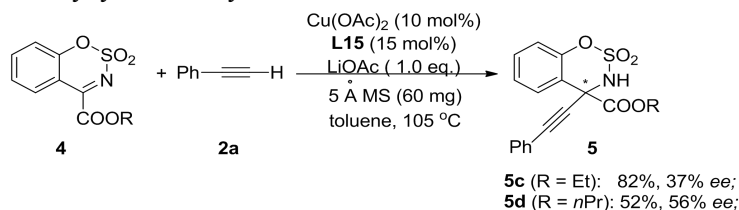
Cu(OAc)₂ (1.8 mg, 10 mol %), 5 Å MS (60 mg) and **L15** (6.8 mg, 15 mol%) were stirred in toluene (1.0 mL) at 90 °C for 1 h. Cyclic ketimines **1a** (23.9 mg, 0.1 mmol) and LiOAc (6.6 mg, 1.0 eq.) were added. After 15 min, ethynylbenzene **2a** (16.5 μL, 1.5 eq.) was added and stirred at 90 °C for 2 days. After completion, the reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na₂SO₄. After concentration in vacuo, the residue was finally purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5 to 1:3) to give the product **3aa** as a yellow solid (30.0 mg, 88%).



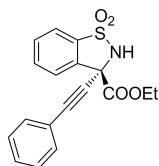
6. General procedure for Cu-catalyzed alkylation of cyclic ketimines 4

Cu(OAc)₂ (1.8 mg, 10 mol %), 5 Å MS (60 mg) and **L15** (6.8 mg, 15 mol%) were stirred in toluene (1.0 mL) at 105 °C for 1 h. Cyclic ketimines **4a** (23.9 mg, 0.1 mmol) and LiOAc (6.6 mg, 1.0 eq.) were added. After 15 min, ethynylbenzene **2a** (16.5 μL, 1.5 eq.) was added and stirred at 105 °C for 24 h. After completion, the reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na₂SO₄. After concentration in vacuo, the residue was finally purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5 to 1:3) to give the product **5aa** as a yellow solid (25.4 mg, 74%).

The results of alkylation of cyclic ketimines **4c** and **4d** are as follow.



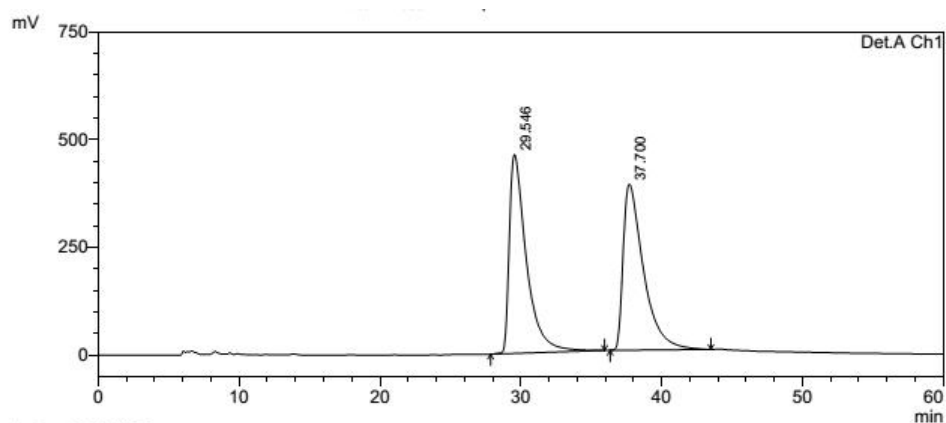
7. Characterization data and HPLC of addition products



(*R*)-ethyl 3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3aa**), 30.0 mg, 88% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.37-7.29 (m, 3H), 5.90 (br, 1H), 4.43-4.34 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H).^[3]

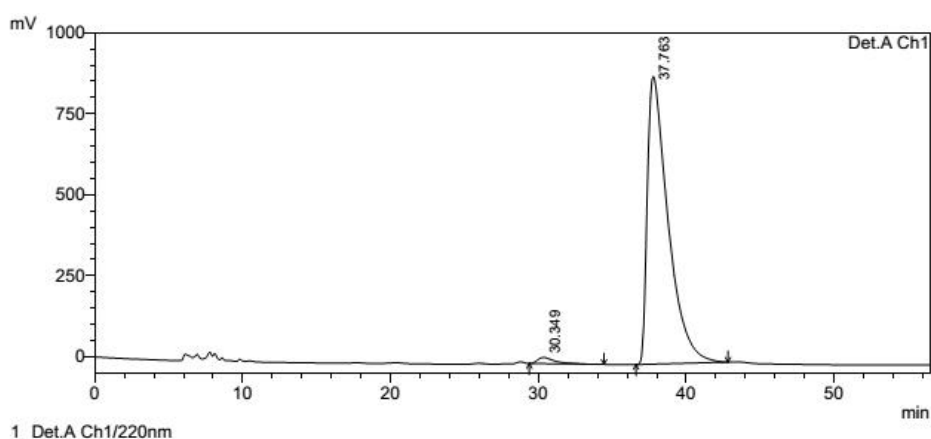
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 30.3 min; 37.7 min (major), 96% ee, [α]²⁵: 45.539 (c

0.25, CHCl₃).



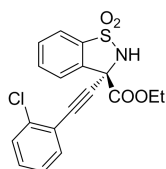
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
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Total		77634711	847318	100.000	100.000



PeakTable

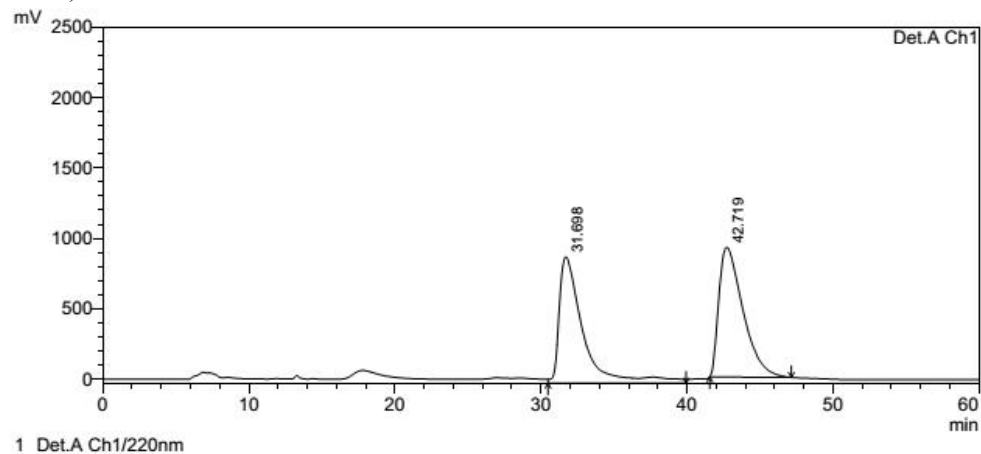
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.349	1602717	19415	1.820	2.140
2	37.763	86460999	887614	98.180	97.860
Total		88063716	907029	100.000	100.000



(*R*)-ethyl 3-((2-chlorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3ab**), 30.8 mg, 82% yield, yellow solid, m.p.: 89-90 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 7.6, 1.2 Hz, 1H), 7.65 (td, *J* = 8.0, 0.8 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.30 (td, *J* = 7.6, 2.0 Hz, 1H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 5.90 (br, 1H), 4.45-4.34 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 136.6, 135.6, 134.2, 133.9, 133.6, 131.1, 130.4, 129.4, 126.5,

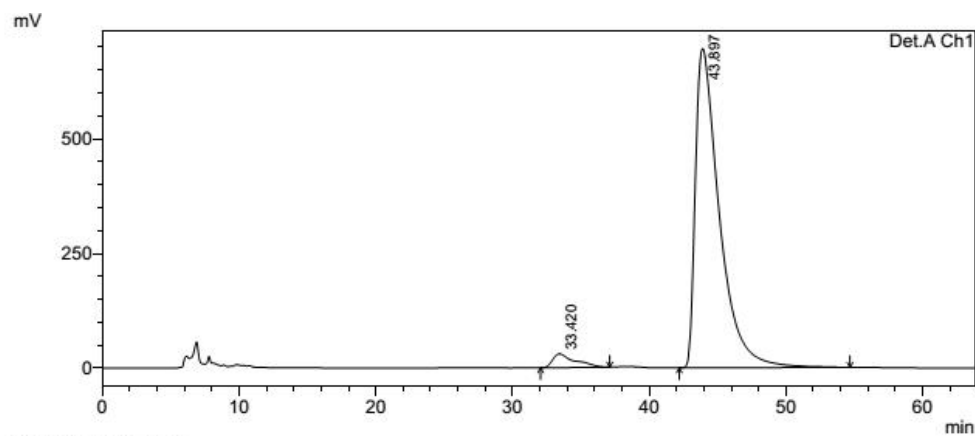
126.3, 121.4, 121.2, 89.2, 82.3, 64.7, 61.8, 14.0; HRMS (ESI): calcd for C₁₈H₁₅NO₄Cl [M+H]⁺ 376.0410, found 376.0419.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 33.4 min; 43.8 min (major), 92% *ee*, [α]²⁵: 19.973 (c 0.20, CHCl₃).



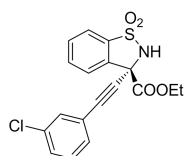
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1	31.698	102011842	896865	49.121	49.331
2	42.719	105663619	921205	50.879	50.669
Total		207675461	1818071	100.000	100.000



PeakTable

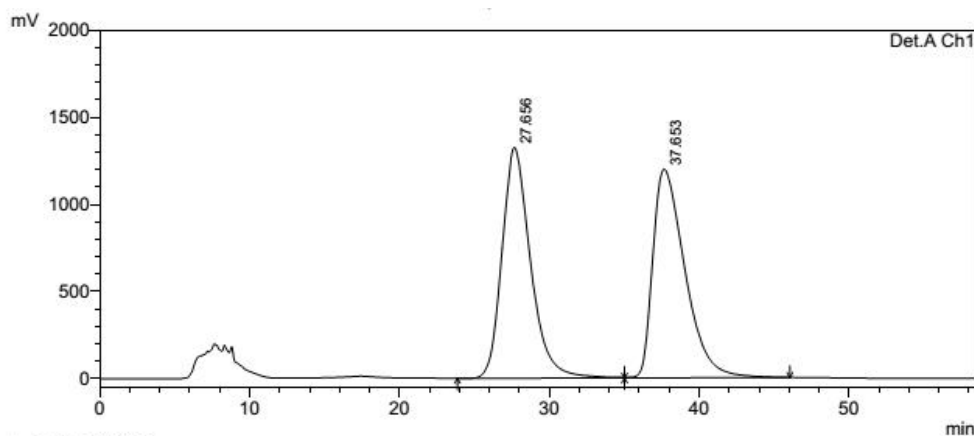
Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.420	3420231	29983	3.865	4.127
2	43.897	85072513	696608	96.135	95.873
Total		88492744	726591	100.000	100.000



(*R*)-ethyl 3-((3-chlorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3ac**), 30.0 mg, 80% yield, yellow solid, m.p.: 93-94 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.91

(d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.74 (td, $J = 7.6, 1.6$ Hz, 1H), 7.66 (td, $J = 7.2, 0.8$ Hz, 1H), 7.43 (t, $J = 1.6$ Hz, 1H), 7.34-7.30 (m, 2H), 7.24 (t, $J = 8.0$ Hz, 1H), 5.90 (br, 1H), 4.45-4.36 (m, 2H), 1.38 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 135.7, 134.3, 134.2, 134.0, 131.9, 131.2, 130.2, 129.7, 129.6, 126.0, 122.7, 121.5, 85.4, 83.9, 64.8, 61.6, 14.0; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_4\text{SCl}$ $[\text{M}+\text{H}]^+$ 376.0410, found 376.0424.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 28.9 min; 39.0 min (major), 85% *ee*, $[\alpha]^{25}$: 22.690 (c 0.25, CHCl_3).

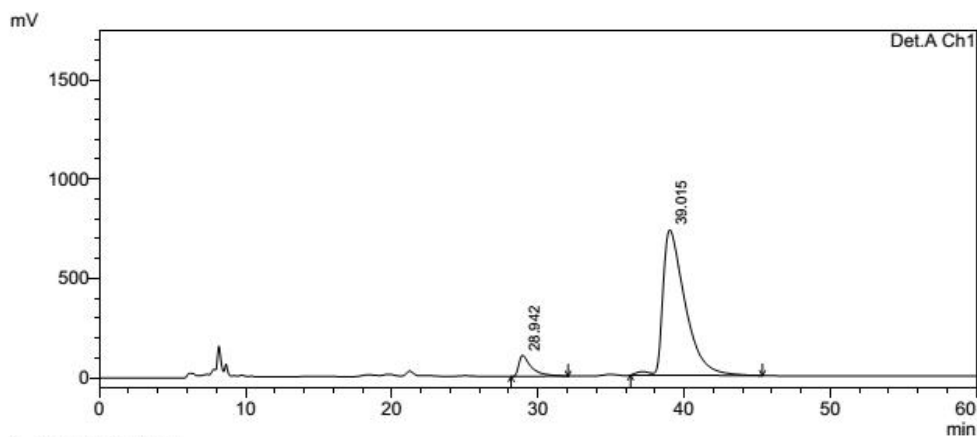


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.656	175190153	1324878	49.578	52.525
2	37.653	178171618	1197520	50.422	47.475
Total		353361772	2522398	100.000	100.000

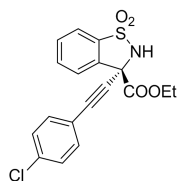


1 Det.A Ch1/220nm

PeakTable

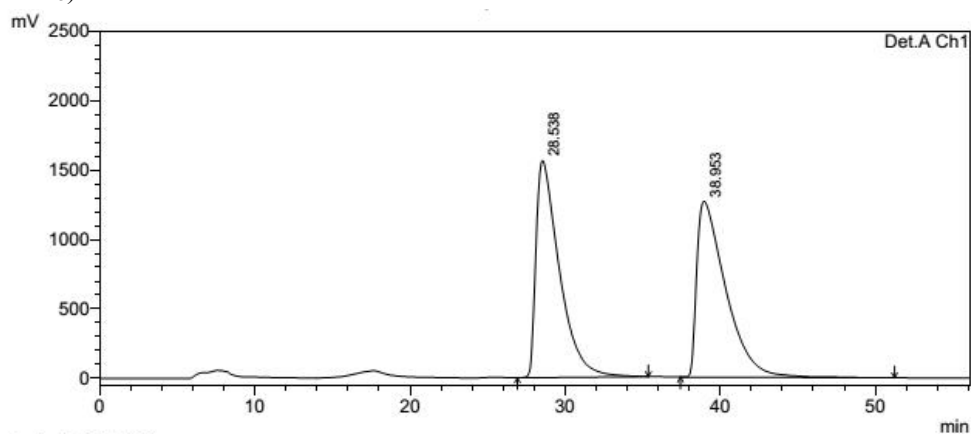
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.942	6324209	106325	7.543	12.687
2	39.015	77512890	731759	92.457	87.313
Total		83837099	838084	100.000	100.000



(*R*)-ethyl 3-((4-chlorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3ad**), 31.9 mg, 85% yield, yellow solid, m.p.: 122-123 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.6, 1H), 7.65 (t, *J* = 7.6, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.90 (br, 1H), 4.43-4.36 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 135.7, 135.6, 134.2, 134.0, 133.2, 131.0, 128.7, 126.0, 121.4, 119.5, 85.2, 84.3, 64.7, 61.8, 14.0; HRMS (ESI): calcd for C₁₈H₁₅NO₄SCl [M+H]⁺ 376.0410, found 376.0413.

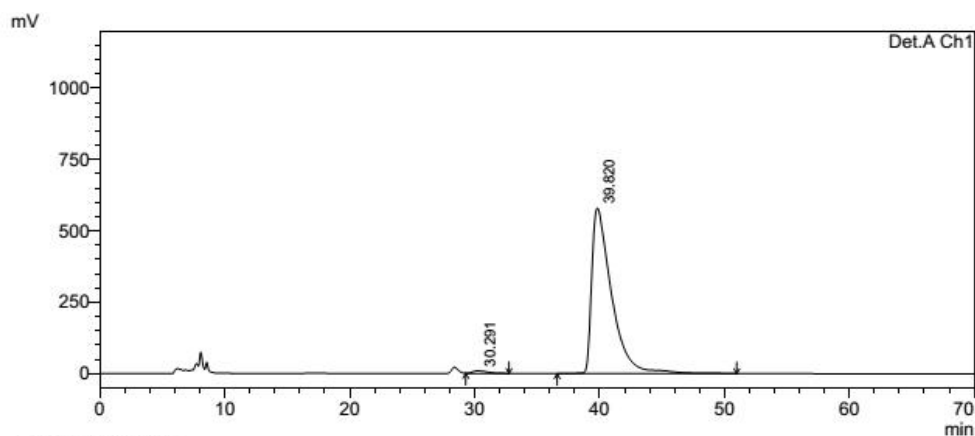
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 30.2 min; 39.8 min (major), 98% *ee*, [α]²⁵: 27.963 (c 0.20, CHCl₃).



1 Det.A Ch1/220nm

PeakTable

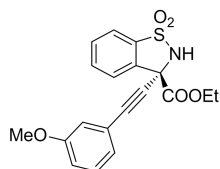
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.538	164030035	1562129	49.944	55.233
2	38.953	164396007	1266138	50.056	44.767
Total		328426042	2828267	100.000	100.000



1 Det.A Ch1/220nm

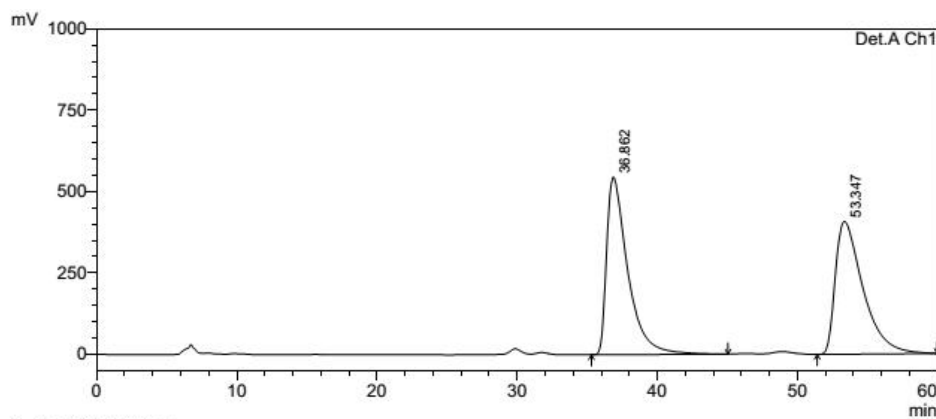
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.291	734007	8956	1.131	1.521
2	39.820	64152386	579818	98.869	98.479
Total		64886393	588774	100.000	100.000



(*R*)-ethyl 3-((3-methoxyphenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3ae**), 24.1 mg, 65% yield, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.74 (td, $J = 7.6$, 1.2 Hz, 1H), 7.64 (td, $J = 7.6$, 0.8 Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 7.6$ Hz, 1H), 6.95-6.89 (m, 2H), 5.86 (br, 1H), 4.45-4.33 (m, 2H), 3.78 (s, 3H), 1.37 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.8, 159.2, 135.8, 134.2, 133.9, 131.9, 129.4, 126.1, 124.5, 122.0, 121.3, 116.8, 116.1, 85.4, 84.0, 64.6, 61.8, 55.3, 14.0; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$ 372.0906, found 372.0900.

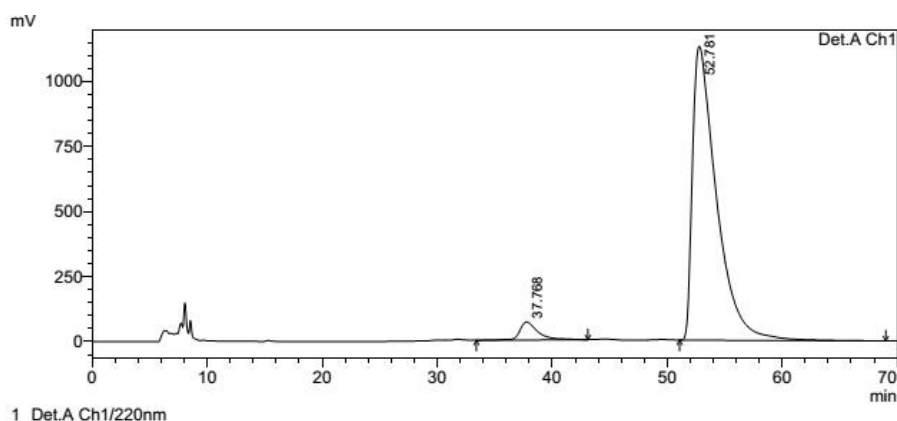
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 37.7 min; 52.7 min (major), 91% *ee*, $[\alpha]^{25}$: 25.965 (c 0.20, CHCl_3).



Detector A Ch1 220nm

PeakTable

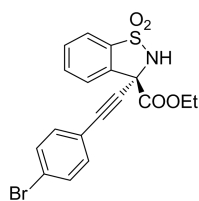
Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.862	57340963	545984	50.511	57.244
2	53.347	56180063	407792	49.489	42.756
Total		113521025	953775	100.000	100.000



Detector A Ch1 220nm

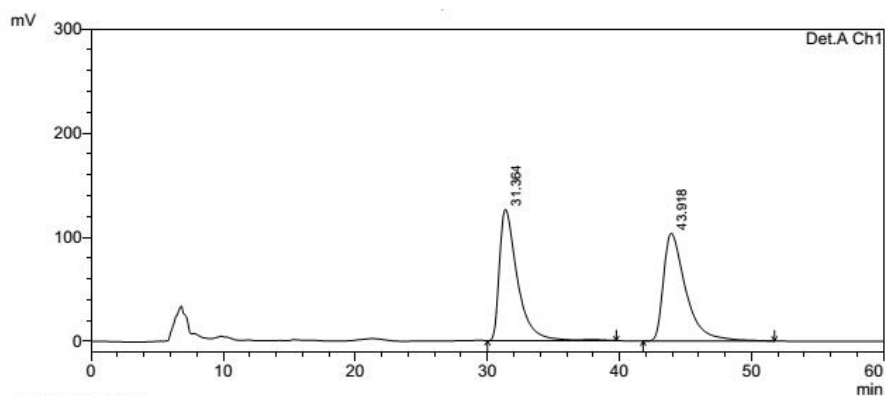
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.768	7672662	69183	4.457	5.767
2	52.781	164475763	1130399	95.543	94.233
Total		172148425	1199582	100.000	100.000



(*R*)-ethyl 3-((4-bromophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3af**), 32.7 mg, 78% yield, yellow solid, m.p.: 126-127 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 7.2, 1.2 Hz, 1H), 7.65 (td, *J* = 7.6, 0.8 Hz, 1H), 7.46-7.43 (m, 2H), 7.30-7.28 (m, 2H), 5.86 (br, 1H), 4.44-4.35 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 135.7, 134.2, 133.9, 133.4, 131.7, 131.2, 126.0, 124.0, 121.4, 120.0, 85.3, 84.3, 64.7, 61.7, 14.0; HRMS (ESI): calcd for C₁₈H₁₅NO₄SBr [M+H]⁺ 419.9905, found 419.9899.

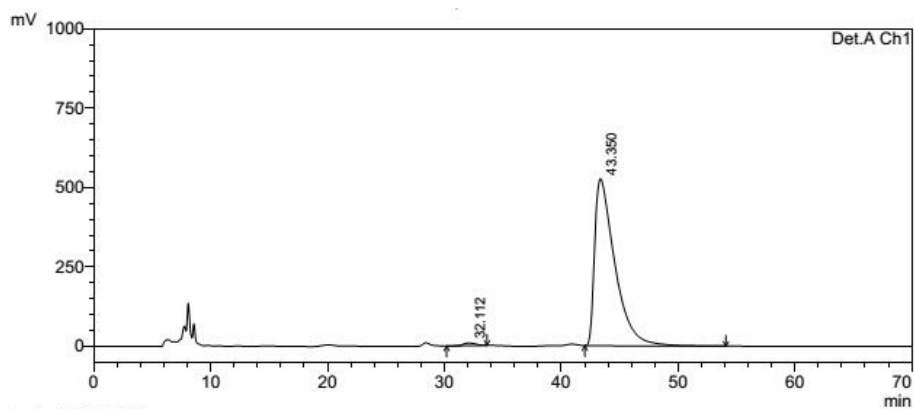
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 32.1 min; 42.3 min (major), 98% *ee*, [α]_D²⁵: 19.973 (c 0.20, CHCl₃).



PeakTable

Detector A Ch1 220nm

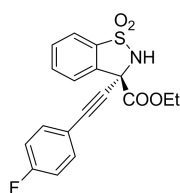
Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.364	11998298	126052	49.634	54.927
2	43.918	12175349	103439	50.366	45.073
Total		24173647	229491	100.000	100.000



PeakTable

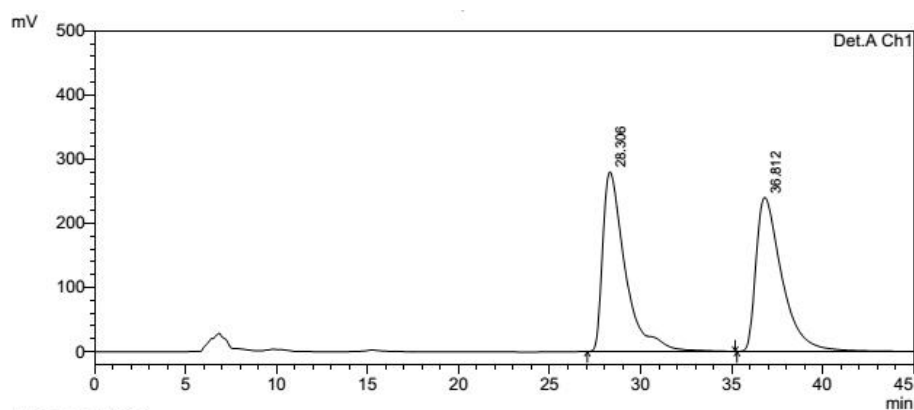
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.112	658224	8493	1.031	1.590
2	43.350	63170510	525650	98.969	98.410
Total		63828734	534143	100.000	100.000



(*R*)-ethyl 3-((4-fluorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3ag**), 25.1 mg, 70% yield, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.73 (td, $J = 7.6, 1.2$ Hz, 1H), 7.65 (td, $J = 8.0, 0.8$ Hz, 1H), 7.44-7.40 (m, 2H), 7.00-6.98 (m, 2H), 5.86 (br, 1H), 4.45-4.33 (m, 2H), 1.37 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.8, 165.6 (d, $J = 249.7$ Hz), 135.9, 134.3, 134.1 (d, $J = 8.5$ Hz), 133.9, 131.1, 126.0, 121.3, 117.1 (d, $J = 3.5$ Hz), 115.7 (d, $J = 22.1$ Hz), 84.4, 84.0, 64.6, 61.7, 14.0; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_4\text{SF}$ $[\text{M}+\text{H}]^+$ 360.0706, found 360.0714.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 29.0 min; 36.7 min (major), 93% *ee*, $[\alpha]^{25}$: 24.967 (c 0.20, CHCl_3).

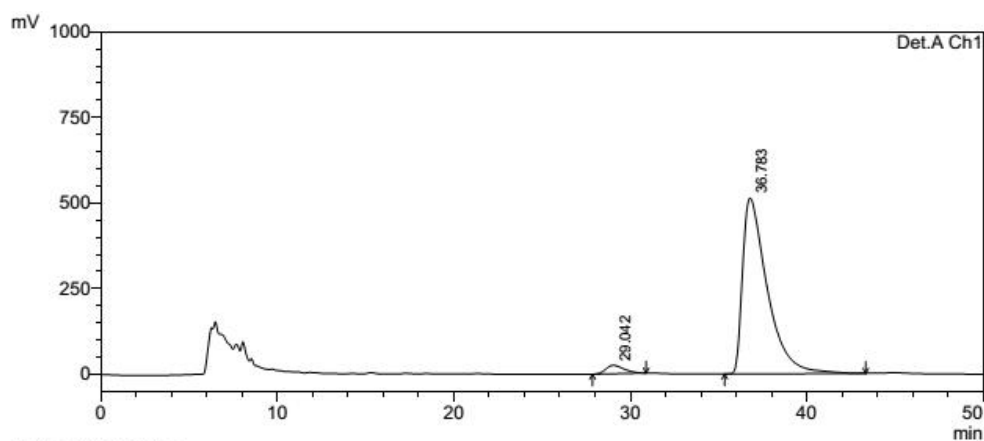


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.306	24156729	279752	50.452	53.830
2	36.812	23723804	239946	49.548	46.170
Total		47880533	519698	100.000	100.000

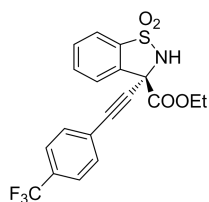


1 Det.A Ch1/220nm

PeakTable

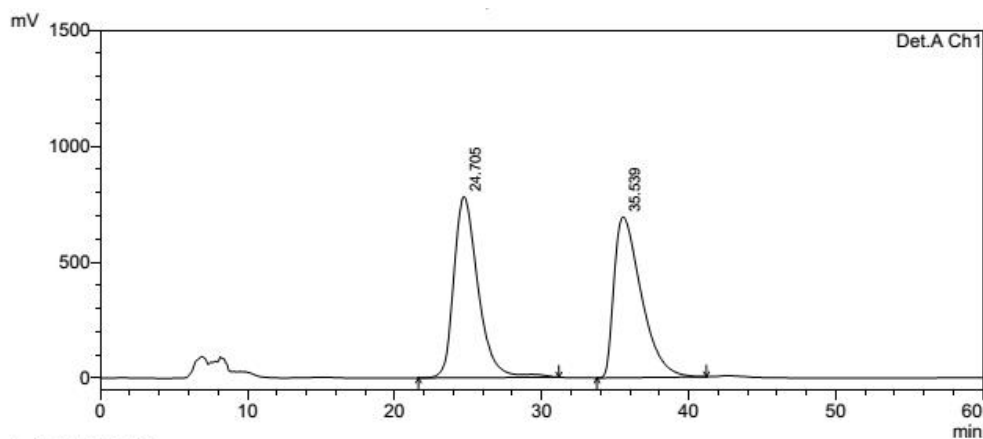
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.042	1755670	24532	3.398	4.557
2	36.783	49913747	513804	96.602	95.443
Total		51669417	538336	100.000	100.000



(*R*)-ethyl 3-((4-(trifluoromethyl)phenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3ah**), 37.2 mg, 91% yield; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.58-7.53 (m, 4H), 5.91 (br, 1H), 4.45-4.37 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H).^[3]

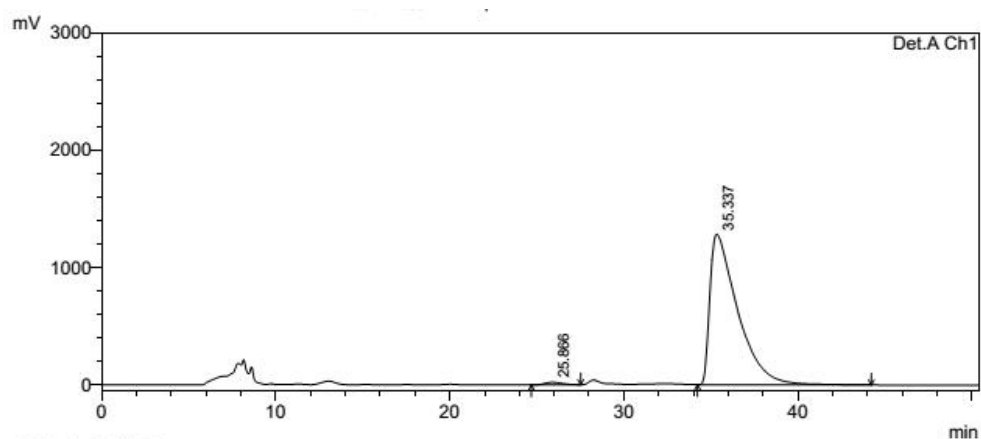
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 25.8 min; 35.3 min (major), 98% *ee*, [α]²⁵: 40.945 (c 0.20, CHCl₃).



PeakTable

Detector A Ch1 220nm

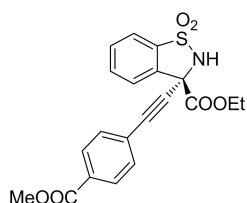
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.705	89721128	781717	50.119	53.011
2	35.539	89294737	692929	49.881	46.989
Total		179015865	1474646	100.000	100.000



PeakTable

Detector A Ch1 220nm

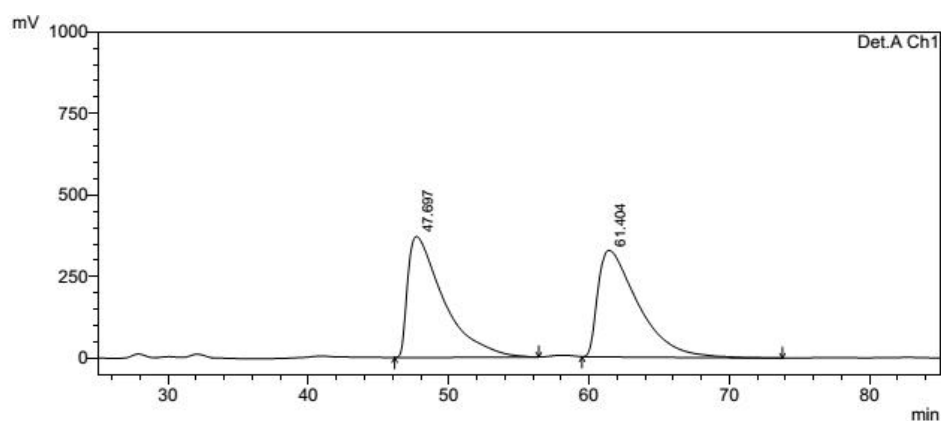
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.866	1550381	21666	1.081	1.661
2	35.337	141904923	1282679	98.919	98.339
Total		143455303	1304345	100.000	100.000



(*R*)-ethyl 3-((4-(methoxycarbonyl)phenyl)ethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ai**), 37.1 mg, 93% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 5.93 (br, 1H), 4.43-4.38 (m, 2H), 3.91 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 166.3, 135.6, 134.2, 134.0, 132.0, 131.2, 130.6, 129.5, 126.0, 125.6, 121.5, 86.9, 84.5, 64.8, 61.7, 52.4, 14.0; HRMS (ESI): calcd for C₂₀H₁₈NO₆S [M+H]⁺ 400.0855, found 400.0847.

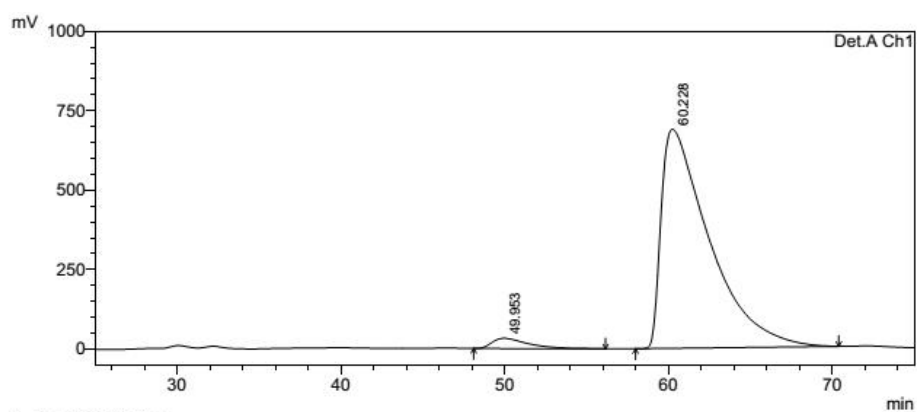
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol =

85/15; flow = 0.5 mL/min; Retention time: 49.9 min; 60.2 min (major), 98% *ee*, $[\alpha]^{25}$: 39.512 (c 0.46, CHCl₃).



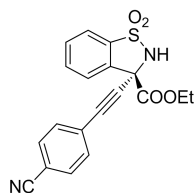
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.697	65997003	370502	50.230	53.180
2	61.404	65392933	326195	49.770	46.820
Total		131389935	696698	100.000	100.000



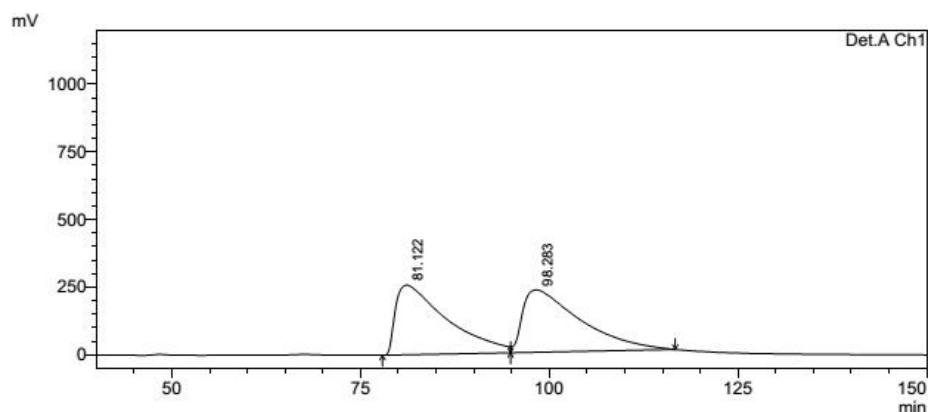
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.953	4981571	32365	3.413	4.484
2	60.228	140964132	689396	96.587	95.516
Total		145945703	721760	100.000	100.000



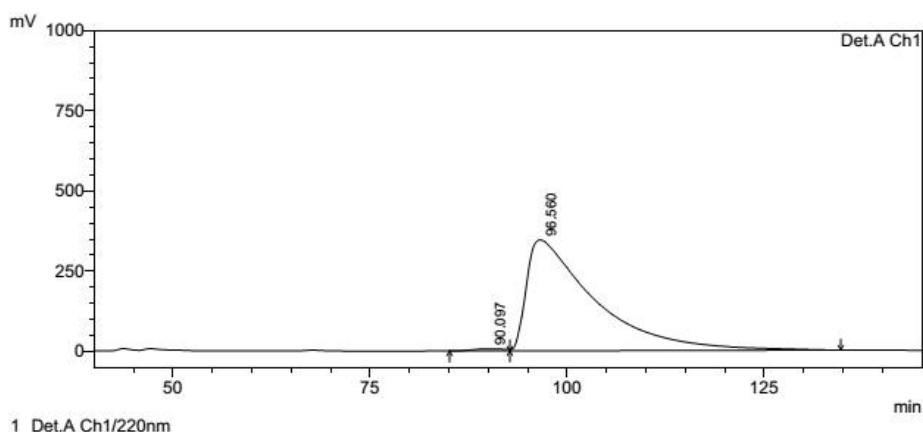
(*R*)-ethyl 3-((4-cyanophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3aj**), 34.4 mg, 94% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 7.6, 1.2 Hz, 1H), 7.66 (td, *J* = 8.0, 0.8 Hz, 1H), 7.60-7.58 (m, 2H), 7.52-7.50 (m, 2H), 5.94 (br, 1H), 4.45-4.37 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.4, 135.4, 134.3, 134.1, 132.6, 132.0, 131.4, 125.9, 125.8, 121.6, 118.1, 112.8, 88.4, 83.4, 64.9, 61.5, 14.0; HRMS (ESI): calcd for C₁₉H₁₅N₂O₄S [M+H]⁺ 367.0753, found 367.0763.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 90.0 min; 96.5 min (major), 98% *ee*, $[\alpha]^{25}$: 16.286 (c 0.65, CHCl₃).



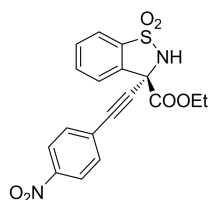
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	81.122	121033750	257740	49.692	52.773
2	98.283	122532685	230650	50.308	47.227
Total		243566435	488390	100.000	100.000



PeakTable

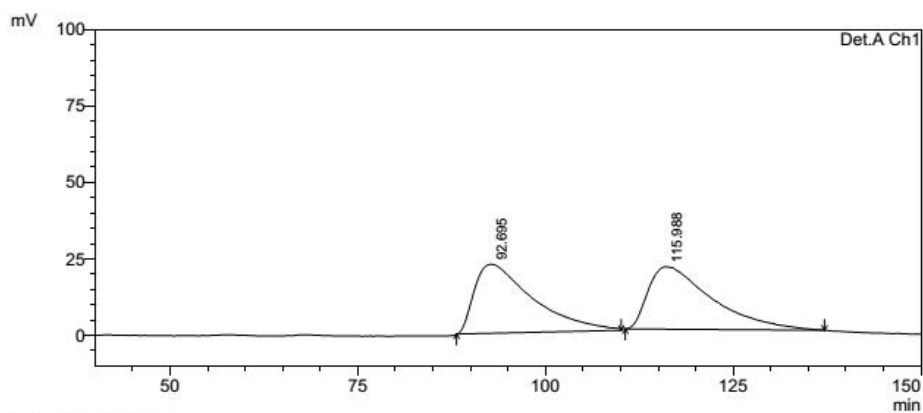
Peak#	Ret. Time	Area	Height	Area %	Height %
1	90.097	1819004	6343	0.868	1.804
2	96.560	207710587	345270	99.132	98.196
Total		209529591	351614	100.000	100.000



(*R*)-ethyl 3-((4-nitrophenyl)ethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ak**), 34.7 mg, 90% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 8.18-8.15 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74 (td, *J* = 7.2, 1.2 Hz, 1H), 7.67 (td, *J* = 7.6, 1.2 Hz, 1H), 7.60-7.57 (m, 2H), 5.96 (br, 1H), 4.46-4.38 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.3, 147.8, 135.3, 134.3, 134.1, 132.9, 131.4, 127.8, 125.8, 123.6, 121.6, 89.1, 83.1, 65.0, 61.5, 14.0; HRMS (ESI): calcd for C₁₈H₁₅N₂O₆S [M+H]⁺ 387.0651, found

387.0664.

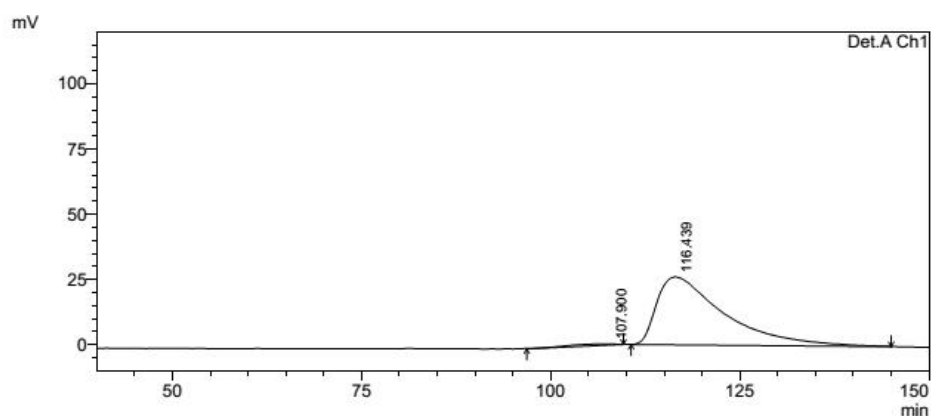
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 107.9 min; 116.4 min (major), 96% *ee*, $[\alpha]_D^{25}$: 32.684 (c 0.22, CHCl₃).



1 Det.A Ch1/220nm

PeakTable

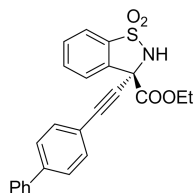
Peak#	Ret. Time	Area	Height	Area %	Height %
1	92.695	12168049	22536	50.234	52.499
2	115.988	12054705	20391	49.766	47.501
Total		24222755	42928	100.000	100.000



1 Det.A Ch1/220nm

PeakTable

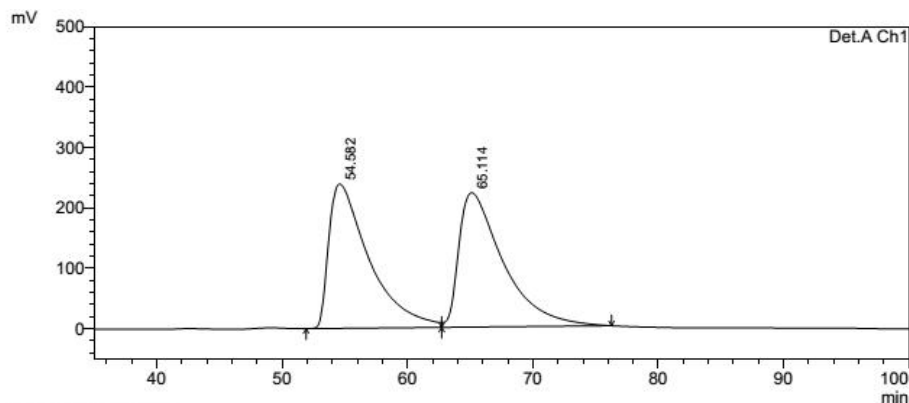
Peak#	Ret. Time	Area	Height	Area %	Height %
1	107.900	299126	460	1.833	1.730
2	116.439	16024015	26098	98.167	98.270
Total		16323141	26558	100.000	100.000



(*R*)-ethyl 3-([1,1'-biphenyl]-4-ylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3a1**), 31.3 mg, 75% yield, yellow solid, m.p.: 95-96 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.81-7.80 (m, 1H), 7.73 (td, *J* = 7.2, 0.8 Hz, 1H), 7.64 (td, *J* = 7.6, 0.8 Hz, 1H), 7.57-7.48 (m, 6H), 7.46-7.41 (m, 2H), 7.37-7.33 (m, 1H), 5.90 (br, 1H), 4.46-4.33 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 142.2, 140.0, 136.0, 134.2,

133.9, 132.5, 131.1, 128.9, 127.9, 127.1, 127.0, 126.2, 121.4, 119.9, 85.4, 84.8, 65.0, 61.9, 14.0;
 HRMS (ESI): calcd for C₂₄H₂₀NO₄S [M+H]⁺ 418.1113, found 418.1110.

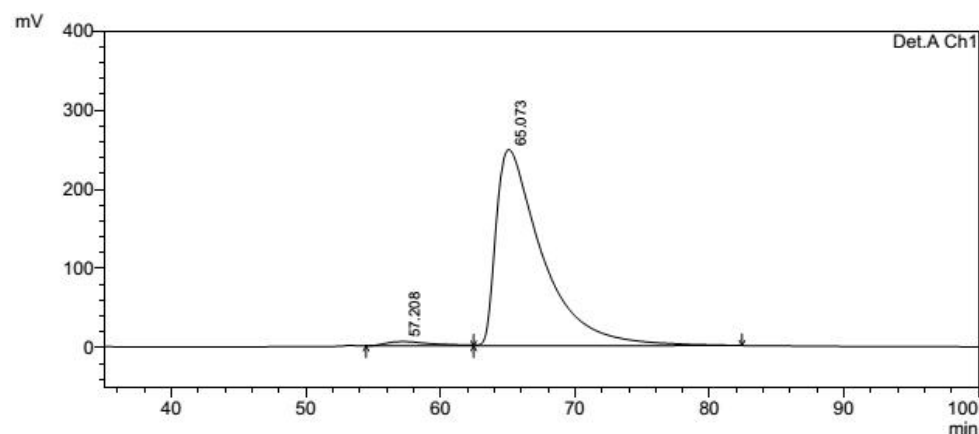
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 57.2 min; 65.1 min (major), 96% *ee*, [α]_D²⁵: 29.461 (c 0.40, CHCl₃).



1 Det.A Ch1/220nm

PeakTable

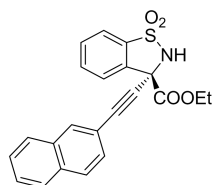
Peak#	Ret. Time	Area	Height	Area %	Height %
1	54.582	53550536	238932	49.375	51.787
2	65.114	54907293	222446	50.625	48.213
Total		108457828	461378	100.000	100.000



1 Det.A Ch1/220nm

PeakTable

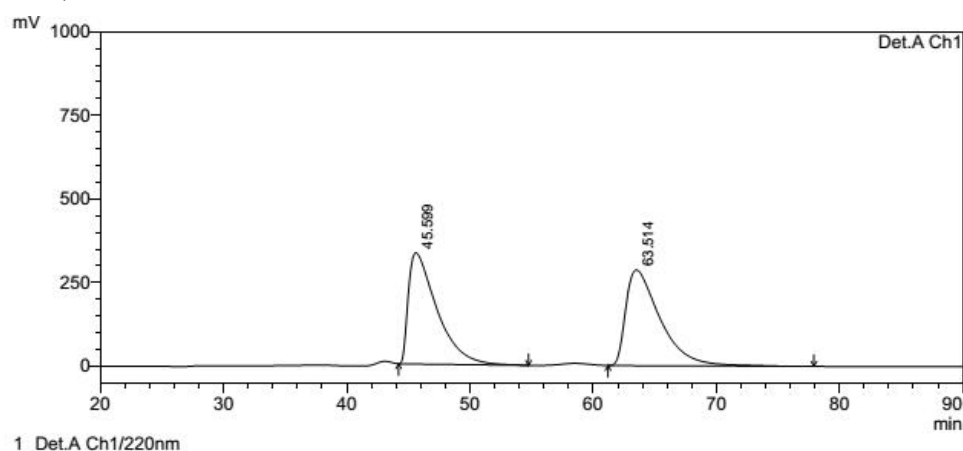
Peak#	Ret. Time	Area	Height	Area %	Height %
1	57.208	1358870	5686	2.230	2.244
2	65.073	59585268	247704	97.770	97.756
Total		60944138	253389	100.000	100.000



(*R*)-ethyl 3-(naphthalen-2-ylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3am**), 23.0 mg, 59% yield, yellow solid, m.p.: 103-104 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.98-7.97 (m, 2 H), 7.82-7.73 (m, 5 H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.50-7.44 (m, 3H), 5.94 (br, 1H), 4.46-4.37 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 136.0, 134.3, 134.0, 133.2, 132.7, 132.5, 131.1, 128.1, 127.9, 127.8, 127.3, 126.8, 126.2, 121.4, 118.3, 85.8,

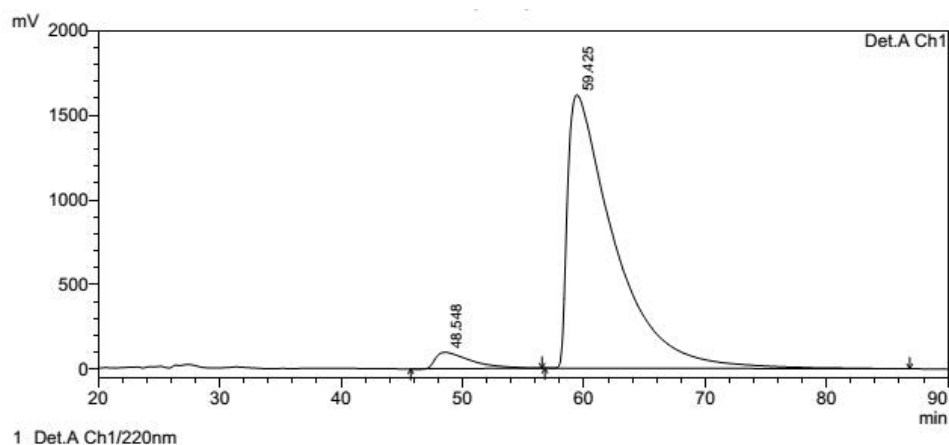
84.5, 64.6, 61.9, 14.0; HRMS (ESI): calcd for C₂₂H₁₈NO₄S [M+H]⁺ 392.0957, found 392.0949.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 48.5 min; 59.4 min (major), 91% *ee*, [α]_D²⁵: 24.178 (c 0.19, CHCl₃).



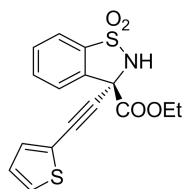
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.599	53775307	332914	49.199	53.805
2	63.514	55525435	285831	50.801	46.195
Total		109300742	618746	100.000	100.000



PeakTable

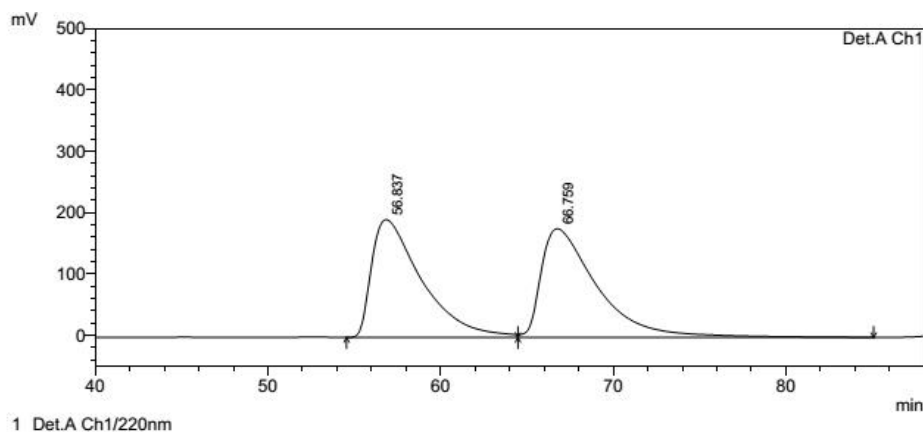
Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.548	19647465	97167	4.340	5.679
2	59.425	433100103	1613879	95.660	94.321
Total		452747568	1711047	100.000	100.000



(*R*)-ethyl 3-(thiophen-2-ylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3an**), 28.1 mg, 81% yield, yellow solid, m.p.: 93-94 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 7.6 Hz, 1 H), 7.79 (d, *J* = 7.6 Hz, 1 H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 4.6, 1.2 Hz, 1H), 7.27-7.26 (m, 1H), 6.98-6.96 (m, 1H), 5.85 (br, 1H), 4.46-4.33 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 135.6, 134.2, 134.0, 133.8, 131.1,

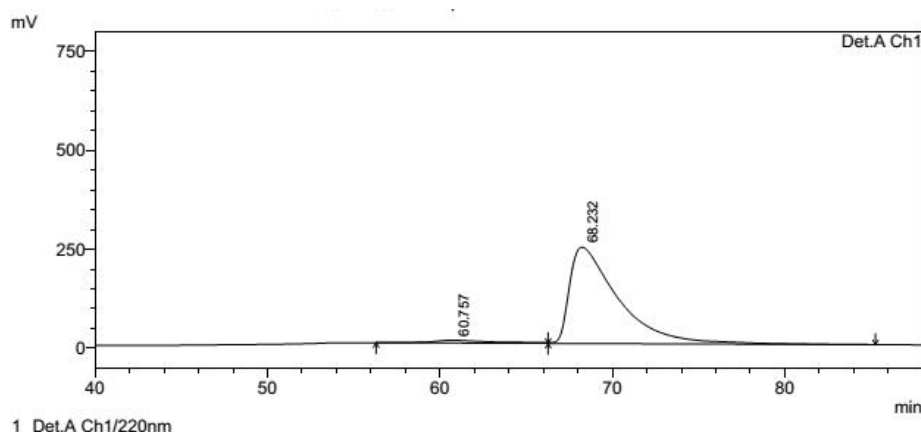
128.6, 127.1, 126.1, 121.4, 120.8, 87.9, 79.0, 64.7, 61.9, 14.0; HRMS (ESI): calcd for C₁₆H₁₄NO₄S₂ [M+H]⁺ 348.0364, found 348.0357.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 60.7 min; 68.2 min (major), 93% *ee*, [α]_D²⁵: 35.785 (c 0.24, CHCl₃).



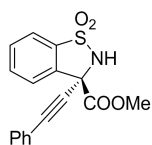
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	56.837	38819266	191962	49.238	51.994
2	66.759	40020611	177241	50.762	48.006
Total		78839877	369203	100.000	100.000



Detector A Ch1 220nm

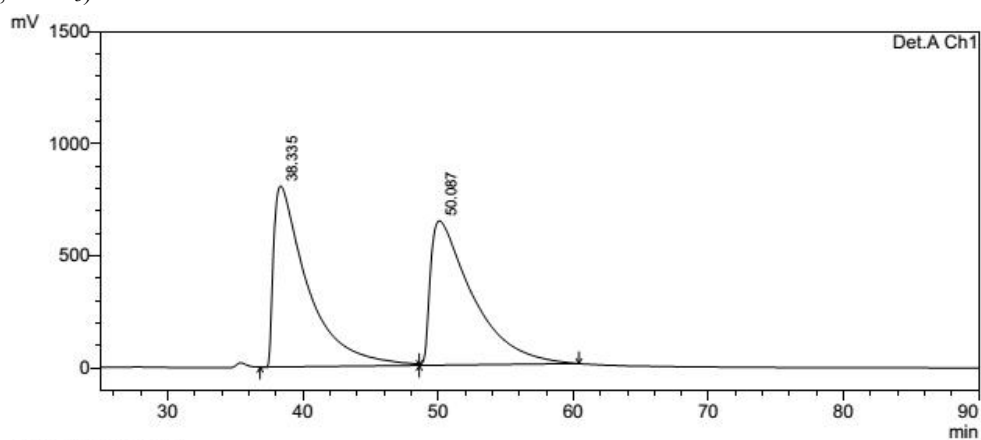
Peak#	Ret. Time	Area	Height	Area %	Height %
1	60.757	1775134	6854	3.571	2.740
2	68.232	47930678	243279	96.429	97.260
Total		49705812	250133	100.000	100.000



(*R*)-methyl 3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ba**), 29.4 mg, 90% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.92 (td, *J* = 7.2, 0.8 Hz, 1H), 7.80-7.78 (m, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.65 (td, *J* = 7.6, 0.8 Hz, 1H), 7.45-7.42 (m, 2H), 7.37-7.28 (m, 3H), 5.87 (br, 1H), 3.94 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.4, 135.8, 134.2, 134.0, 132.1, 131.1, 129.5, 128.3, 126.2, 121.3, 121.0, 85.7, 84.0, 61.8, 55.0; HRMS (ESI):

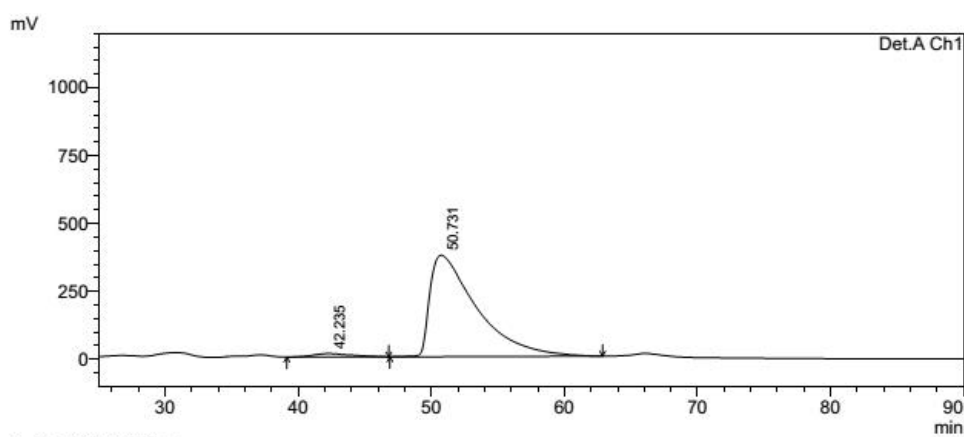
calcd for C₁₇H₁₄NO₄S [M+H]⁺ 328.0644, found 328.0653.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 42.2 min; 50.7 min (major), 95% *ee*, [α]_D²⁵: 10.796 (c 0.185, CHCl₃).



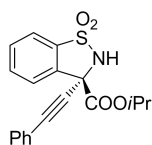
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.335	142160079	806885	50.380	55.635
2	50.087	140015380	643446	49.620	44.365
Total		282175459	1450332	100.000	100.000



PeakTable

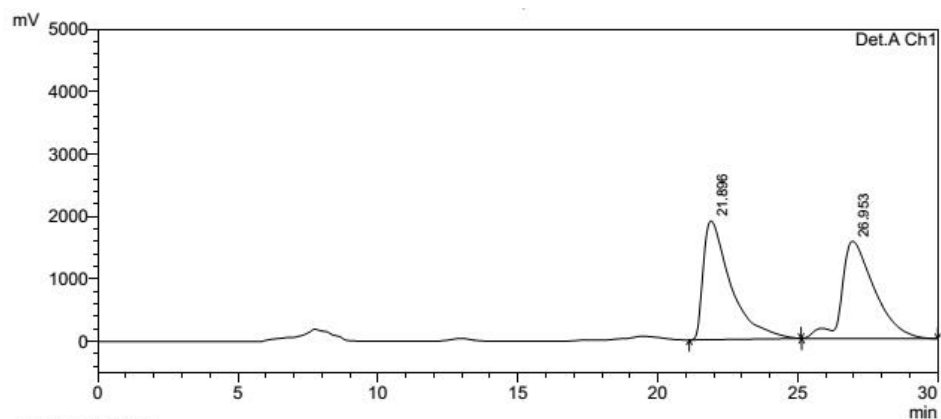
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.235	2555627	12684	2.720	3.283
2	50.731	91415162	373703	97.280	96.717
Total		93970790	386388	100.000	100.000



(*R*)-isopropyl 3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ca**), 27.0 mg, 76% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.71 (td, *J* = 7.6, 1.2 Hz, 1H), 7.63 (td, *J* = 7.6, 1.2 Hz, 1H), 7.43-7.40 (m, 2H), 7.35-7.28 (m, 3H), 5.87 (br, 1H), 5.20-5.14 (m, 1H), 1.40 (d, *J* = 6.0 Hz, 3H), 1.31 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.3, 136.0, 134.3, 133.8, 132.0, 131.0, 129.3, 128.4,

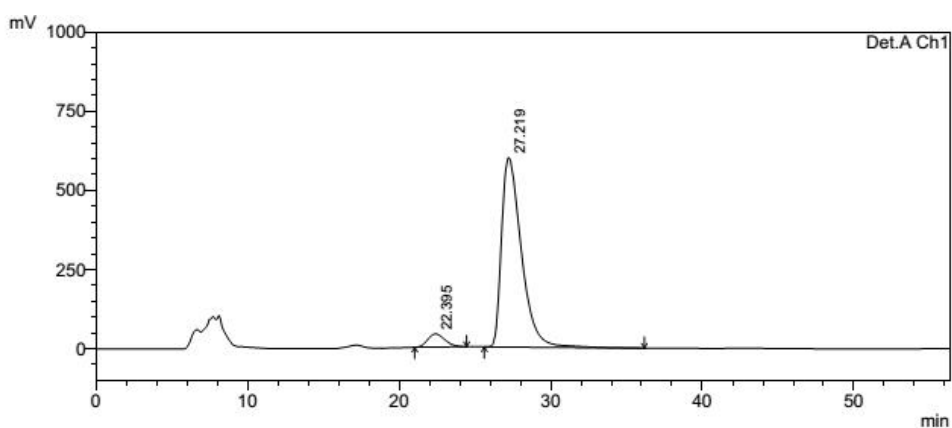
126.0, 121.3, 121.1, 85.3, 84.3, 73.0, 61.9, 21.5, 21.4; HRMS (ESI): calcd for C₁₉H₁₈NO₄S [M+H]⁺ 356.0957, found 356.0949.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 22.4 min; 27.2 min (major), 89% *ee*, [α]_D²⁵: 45.495 (c 0.36, CHCl₃).



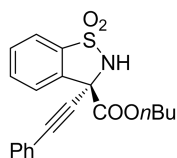
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.896	130421667	1903407	50.616	54.923
2	26.953	127247100	1562189	49.384	45.077
Total		257668767	3465596	100.000	100.000



PeakTable

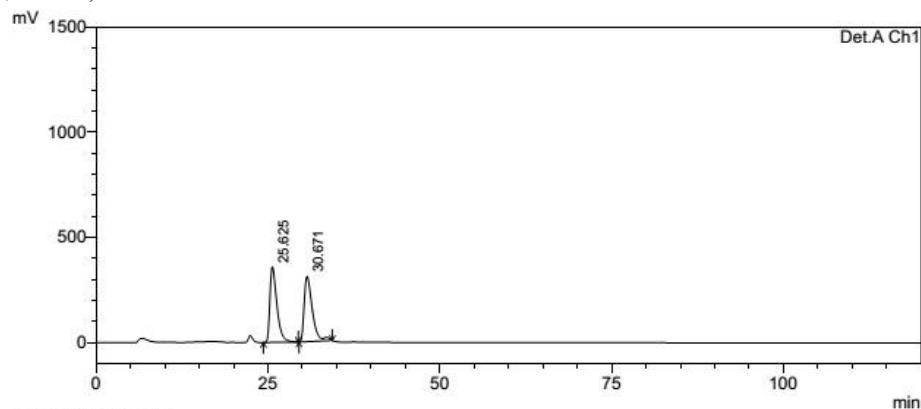
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.395	3238140	41220	5.599	6.446
2	27.219	54597801	598217	94.401	93.554
Total		57835941	639438	100.000	100.000



(*R*)-butyl 3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3da**), 29.5 mg, 80% yield, yellow solid, m.p.: 116-118 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.92(d, *J* = 8.0 Hz, 1H), 7.80(t, *J* = 6.8 Hz, 1H), 7.72 (td, *J* = 7.6, 1.2 Hz, 1H), 7.64 (td, *J* = 7.6, 0.8Hz, 1H), 7.44-7.41 (m, 2H), 7.36-7.28 (m, 3H), 5.87 (br, 1H), 4.41-4.25 (m, 2H), 1.76-1.69 (m, 2H), 1.48-1.38 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 135.8, 134.2,

133.8, 132.0, 131.0, 129.3, 128.3, 126.1, 121.3, 121.0, 85.4, 84.2, 68.3, 61.8, 60.4, 30.3, 19.0, 13.6; HRMS (ESI): calcd for C₂₀H₂₀NO₄S [M+H]⁺ 370.1113, found 370.1110.

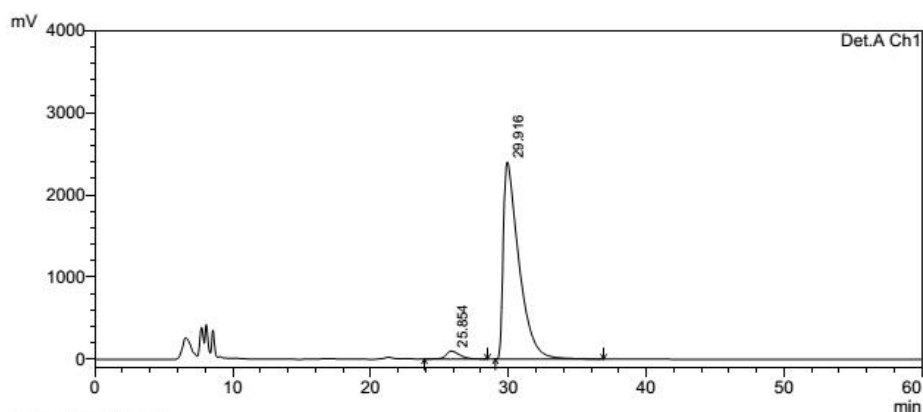
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 25.8 min; 29.9 min (major), 93% *ee*, [α]_D²⁵: 89.024 (c 0.175, CHCl₃).



1 Det.A Ch1/220nm

PeakTable

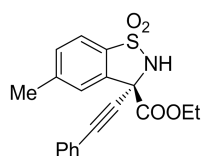
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.625	25538102	359475	50.076	53.675
2	30.671	25460936	310252	49.924	46.325
Total		50999038	669727	100.000	100.000



1 Det.A Ch1/220nm

PeakTable

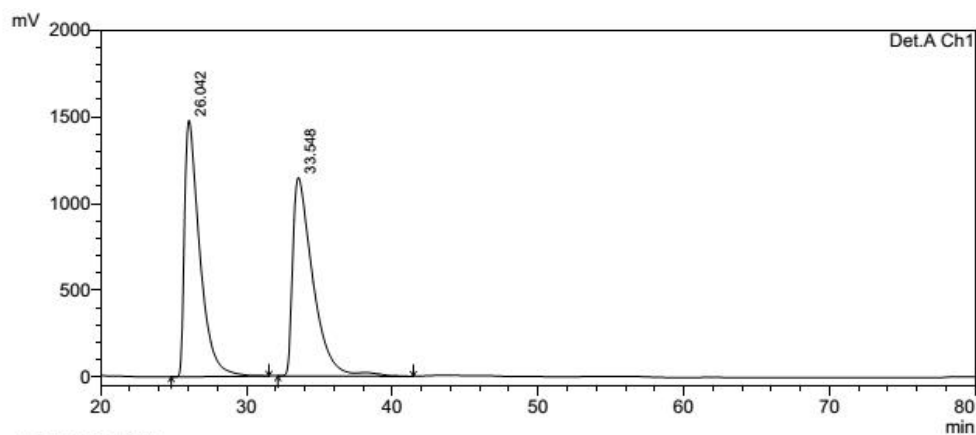
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.854	6606702	95728	3.374	3.839
2	29.916	189223208	2397819	96.626	96.161
Total		195829910	2493547	100.000	100.000



(*R*)-ethyl 5-methyl-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3ea**), 27.0 mg, 76% yield, yellow solid, m.p.: 115-117 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.68-7.65 (m, 2H), 7.46-7.42 (m, 3H), 7.36-7.30 (m, 3H), 5.84 (br, 1H), 4.44-4.35 (m, 2H), 2.51 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 145.2, 136.2, 134.5, 132.1, 131.6, 129.4, 128.4, 126.2, 121.1, 121.0, 85.3, 84.4, 64.5, 61.7, 22.0, 14.0; HRMS (ESI): calcd for

C₁₉H₁₈NO₄S [M+H]⁺ 356.0957, found 356.0969.

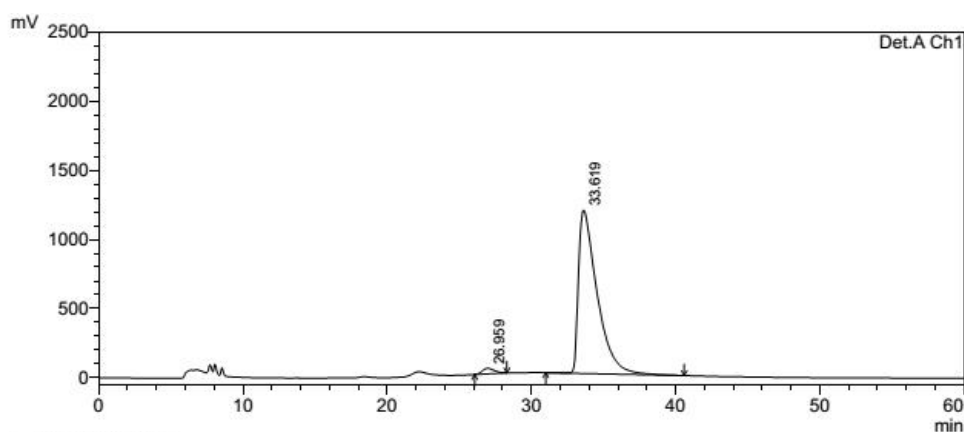
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 26.9 min; 33.6 min (major), 96% *ee*, [α]_D²⁵: 64.404 (c 0.49, CHCl₃).



1 Det.A Ch1/220nm

PeakTable

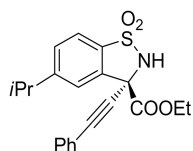
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.042	107872822	1478635	49.477	56.390
2	33.548	110154476	1143511	50.523	43.610
Total		218027298	2622146	100.000	100.000



1 Det.A Ch1/220nm

PeakTable

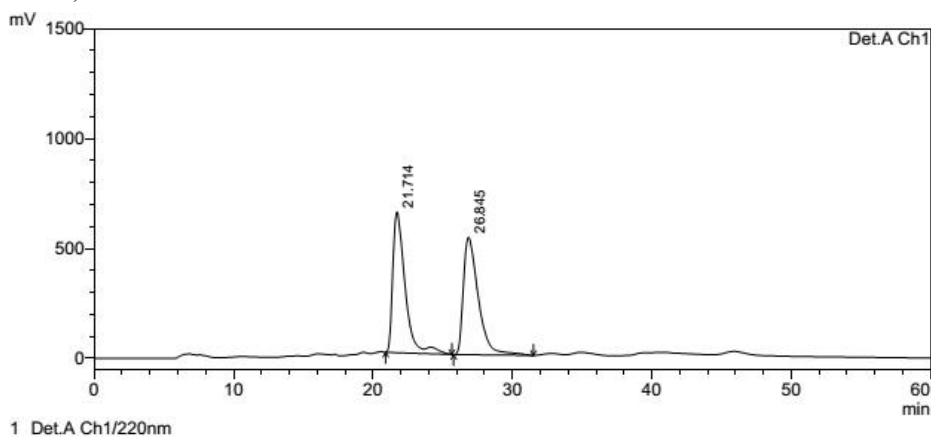
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.959	2291604	39751	2.114	3.257
2	33.619	106133038	1180753	97.886	96.743
Total		108424643	1220503	100.000	100.000



(*R*)-ethyl 5-isopropyl-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3fa**), 26.8mg, 70% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 1.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.50-7.42 (m, 3H), 7.35-7.28 (m, 3H), 5.82 (br, 1H), 4.41-4.37 (m, 2H), 3.10-3.03 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz,

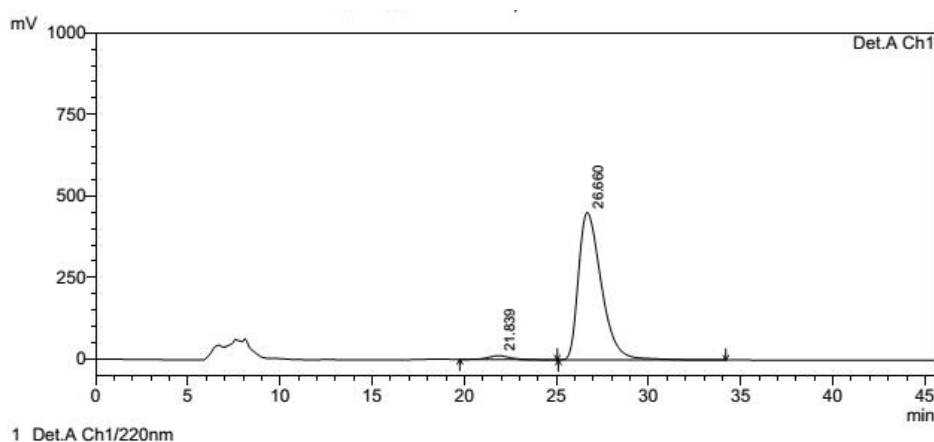
CDCl₃): δ 167.0, 156.0, 136.2, 132.0, 131.8, 129.7, 129.3, 128.3, 123.7, 121.2, 121.1, 85.3, 84.5, 64.4, 61.8, 34.5, 23.9, 23.6, 14.0; HRMS (ESI): calcd for C₂₁H₂₂NO₄S [M+H]⁺ 384.1270, found 384.1254.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 21.8 min; 26.6 min (major), 95% *ee*, [α]_D²⁵: 89.024 (c 0.175, CHCl₃).



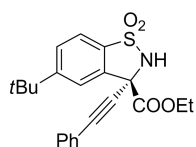
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.714	39686310	641003	49.932	54.534
2	26.845	39794964	534415	50.068	45.466
Total		79481274	1175418	100.000	100.000



PeakTable

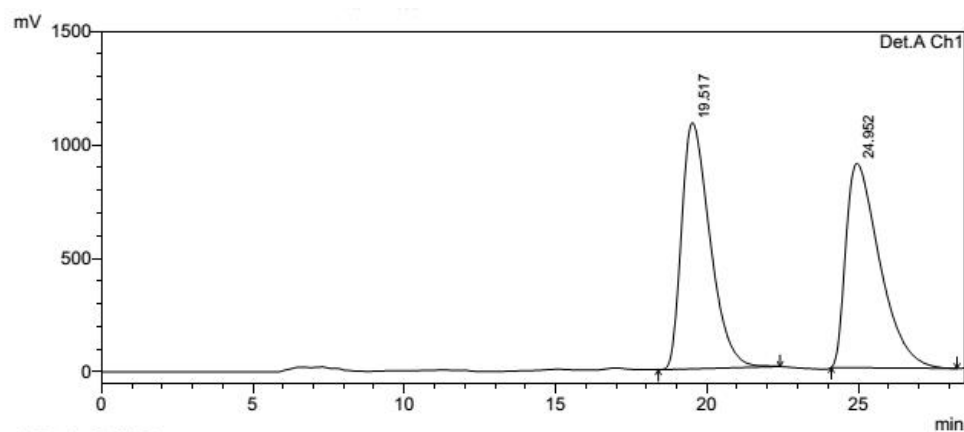
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.839	1022784	11971	2.548	2.582
2	26.660	39124439	451614	97.452	97.418
Total		40147223	463585	100.000	100.000



(*R*)-ethyl 5-(*tert*-butyl)-3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ga**), 22.2 mg, 56% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.90(d, *J* = 1.2 Hz, 1H), 7.72-7.65 (m, 2H), 7.45-7.42 (m, 2H), 7.36-7.29 (m, 3H), 5.86 (br, 1H), 4.46-4.33 (m, 2H),

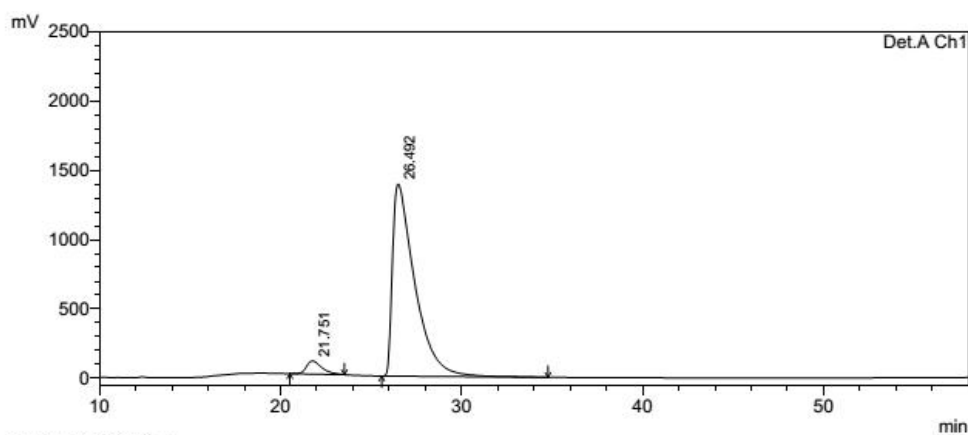
1.38-1.35 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 158.3, 136.0, 132.0, 131.4, 129.3, 128.6, 128.3, 122.7, 121.2, 121.9, 85.3, 84.5, 64.3, 61.8, 35.6, 31.2, 14.0; HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 398.1426, found 398.1418.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 21.8 min; 26.5 min (major), 91% *ee*, $[\alpha]_D^{25}$: 52.525 (c 0.27, CHCl_3).



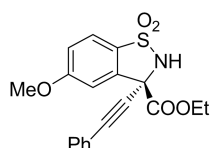
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.517	70764576	1084260	50.262	54.633
2	24.952	70025952	900351	49.738	45.367
Total		140790528	1984611	100.000	100.000



PeakTable

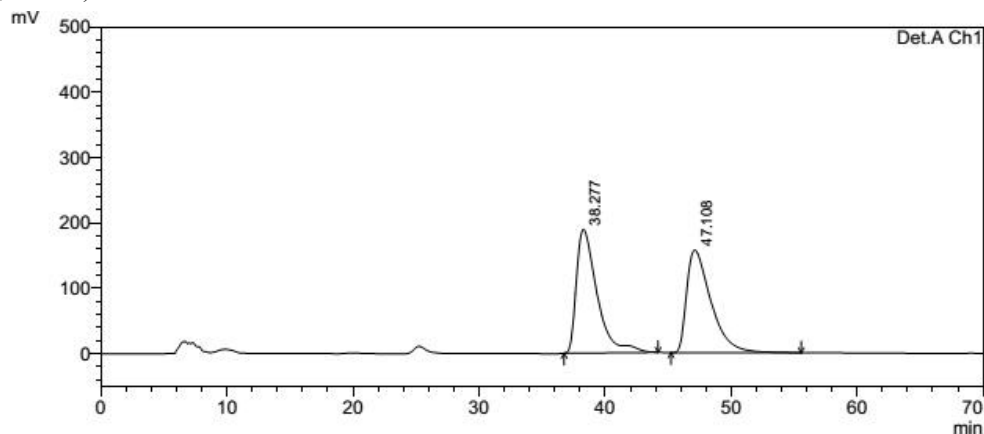
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.751	5686143	94432	4.565	6.384
2	26.492	118881378	1384809	95.435	93.616
Total		124567521	1479241	100.000	100.000



(*R*)-ethyl 5-methoxy-3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ha**), 26.0 mg, 70% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, J = 8.0 Hz, 1H),

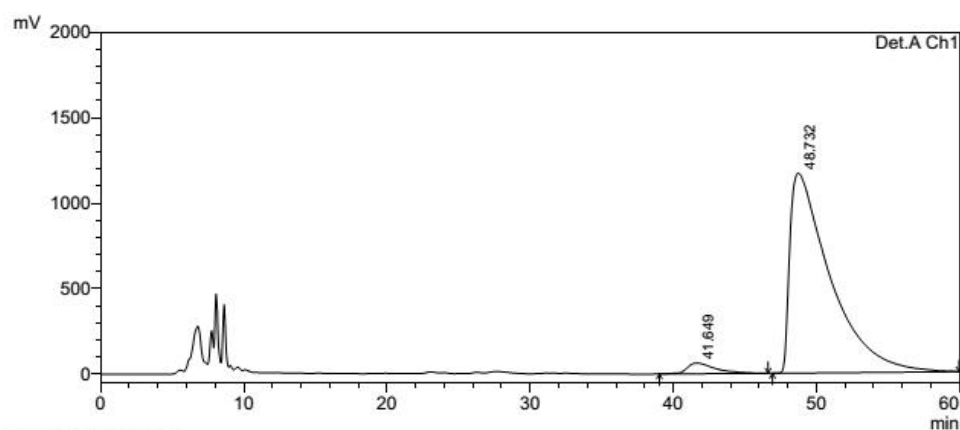
7.45-7.42 (m, 2H), 7.35-7.28 (m, 4H), 7.12 (dd, $J = 8.0, 2.0$ Hz, 1H), 5.85 (br, 1H), 4.42-4.37 (m, 2H), 3.91 (s, 3H), 1.37 (t, $J = 6.8$ Hz, 3H).^[3]

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 41.6 min; 48.7 min (major), 93% *ee*, $[\alpha]^{25}$: 77.791 (c 0.285, CHCl₃).



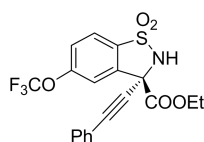
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.277	21657255	189457	50.620	54.633
2	47.108	21126946	157326	49.380	45.367
Total		42784201	346784	100.000	100.000



PeakTable

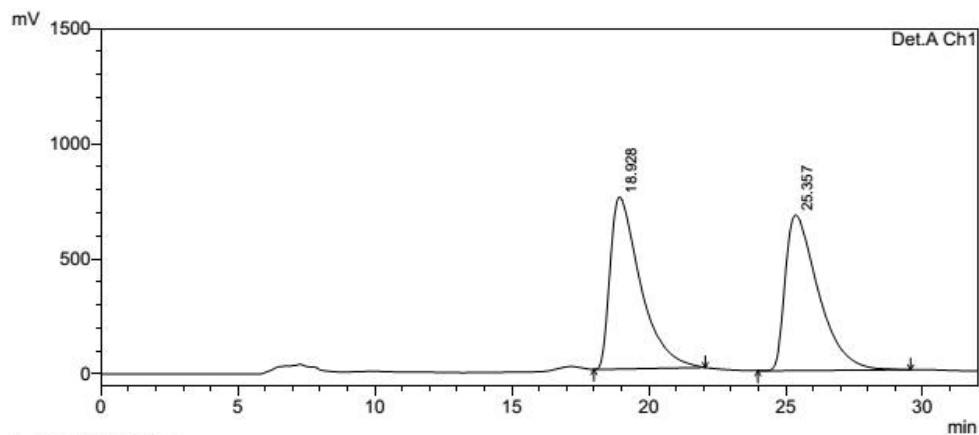
Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.649	8661680	62824	3.635	5.100
2	48.732	229609479	1168901	96.365	94.900
Total		238271159	1231725	100.000	100.000



(*R*)-ethyl 3-(phenylethynyl)-5-(trifluoromethoxy)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ia**), 40.3 mg, 95% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 1.2$ Hz, 1H), 7.50-7.42 (m, 3H), 7.40-7.30 (m, 3H), 5.98 (br, 1H), 4.41 (q, $J = 6.8$ Hz, 2H), 1.38 (t, $J = 6.8$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.2, 153.0 (q, $J = 1.8$ Hz), 138.6, 132.5, 132.1, 129.6, 128.4, 123.7 (q, $J = 0.8$ Hz), 123.3, 122.7 (q, $J = 258.5$ Hz), 120.7,

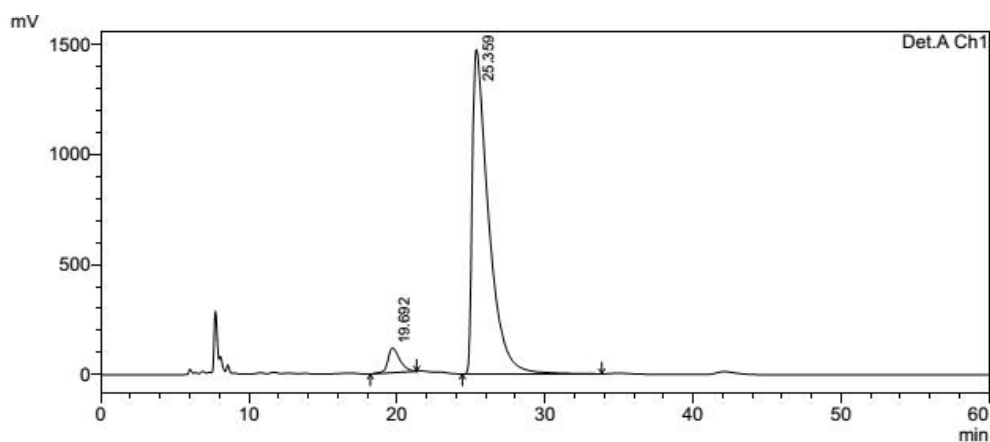
118.3, 86.1, 83.4, 64.9, 61.3, 13.9; HRMS (ESI): calcd for C₁₉H₁₅NO₅SF₃ [M+H]⁺ 426.0623, found 426.0637.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 19.7 min; 25.3 min (major), 90% *ee*, [α]²⁵: 57.399 (c 0.515, CHCl₃).



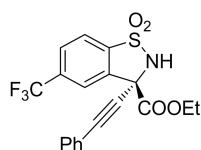
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.928	57529790	747728	50.333	52.546
2	25.357	56769426	675277	49.667	47.454
Total		114299216	1423005	100.000	100.000



PeakTable

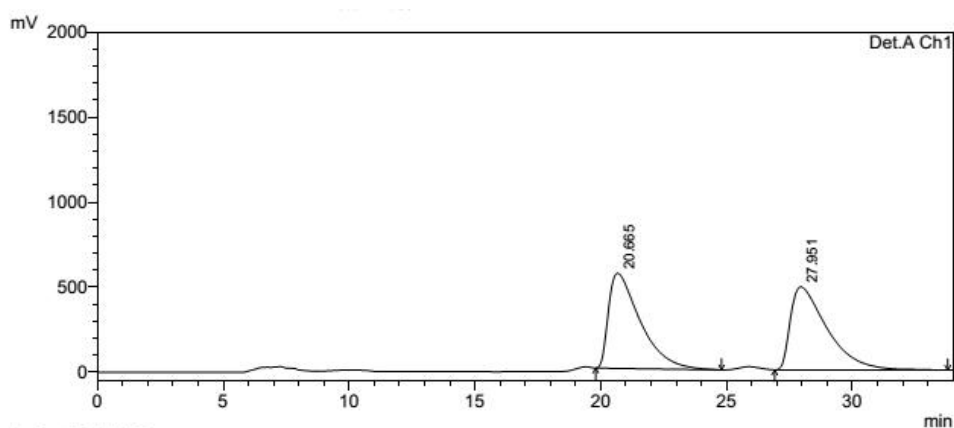
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.692	6253780	112677	5.239	7.092
2	25.359	113121966	1476209	94.761	92.908
Total		119375746	1588886	100.000	100.000



(*R*)-ethyl 3-(phenylethynyl)-5-(trifluoromethyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3ja**), 39.7 mg, 97% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 8.19 (d, *J* =

0.8 Hz, 1H), 7.92-7.91 (m, 2H), 7.46-7.43 (m, 2H), 7.39-7.30 (m, 3H), 6.00 (br, 1H), 4.43 (q, $J = 6.8$ Hz, 2H), 1.39 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.1, 137.6, 137.0, 136.0 (q, $J = 33.4$ Hz), 132.1, 129.7, 128.4, 128.3 (q, $J = 3.5$ Hz), 125.6 (q, $J = 271.9$ Hz), 123.7 (q, $J = 4.0$ Hz), 122.2, 120.6, 86.3, 83.2, 64.9, 61.6, 13.9; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_4\text{SF}_3$ $[\text{M}+\text{H}]^+$ 410.0674, found 410.0666.

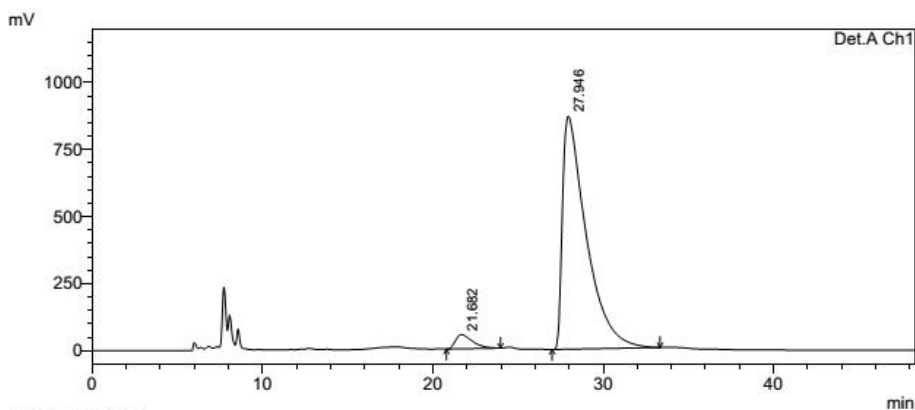
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 21.7 min; 27.9 min (major), 92% *ee*, $[\alpha]^{25}$: 46.049 (c 0.36, CHCl_3).



PeakTable

Detector A Ch1 220nm

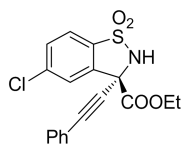
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.665	49297586	560434	49.750	53.400
2	27.951	49792877	489076	50.250	46.600
Total		99090463	1049511	100.000	100.000



PeakTable

Detector A Ch1 220nm

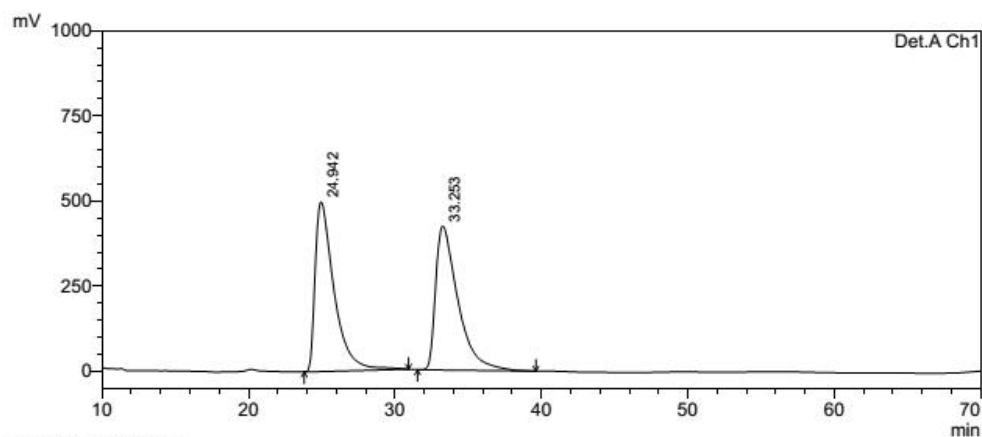
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.682	3671742	52780	4.174	5.724
2	27.946	84291022	869259	95.826	94.276
Total		87962764	922040	100.000	100.000



(*R*)-ethyl 5-chloro-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dio-

xide (**3ka**), 35.2 mg, 94% yield; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.89 (d, $J=1.6$ Hz, 1H), 7.72 (d, $J=8.0$ Hz, 1H), 7.61 (dd, $J=8.0, 2.0$ Hz, 1H), 7.46-7.44 (m, 2H), 7.37-7.30 (m, 3H), 5.89 (br, 1H), 4.47-4.37 (m, 2H), 1.39 (t, $J=7.2$ Hz, 3H).^[3]

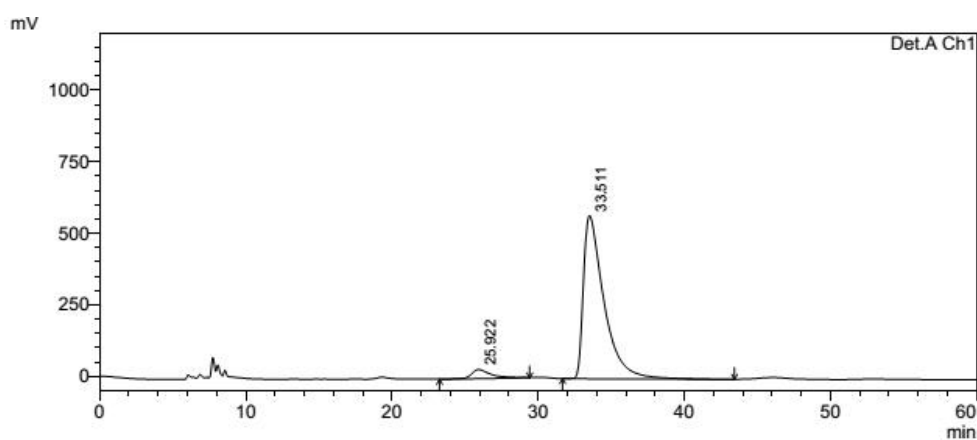
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 25.9 min; 35.5 min (major), 90% *ee*, $[\alpha]_D^{25}$: 67.909 (c 0.20, CHCl_3).



1 Det.A Ch1/220nm

PeakTable

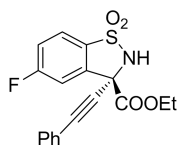
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.942	44843952	497635	50.108	54.080
2	33.253	44650592	422554	49.892	45.920
Total		89494543	920188	100.000	100.000



1 Det.A Ch1/220nm

PeakTable

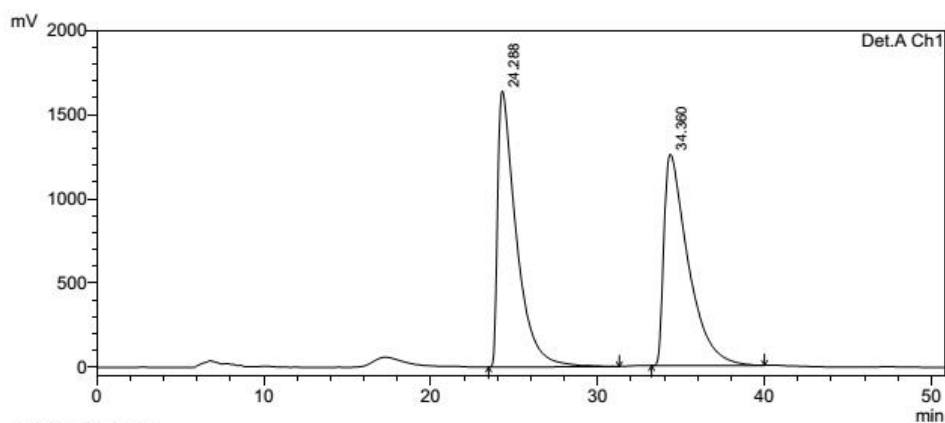
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.922	3012368	31682	5.114	5.270
2	33.511	55890155	569452	94.886	94.730
Total		58902523	601134	100.000	100.000



(*R*)-ethyl 5-fluoro-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**3la**), 33.3 mg, 93% yield, yellow solid, m.p.: 93-94 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.90 (dd, $J=8.0, 4.8$ Hz, 1H), 7.59 (dd, $J=8.0, 2.0$ Hz, 1H), 7.45-7.43 (m, 2H), 7.37-7.29 (m, 4H), 5.93

(br, 1H), 4.48-4.36 (m, 2H), 1.39 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.3, 165.8 (d, $J = 254.9$ Hz), 139.1 (d, $J = 9.4$ Hz), 132.0, 130.4 (d, $J = 2.9$ Hz), 129.6, 128.4, 123.6 (d, $J = 9.8$ Hz), 120.8, 119.2 (d, $J = 24.0$ Hz), 113.4, 85.9, 83.5, 64.8, 61.2, 14.0; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_4\text{SF}$ $[\text{M}+\text{H}]^+$ 360.0706, found 360.0720.

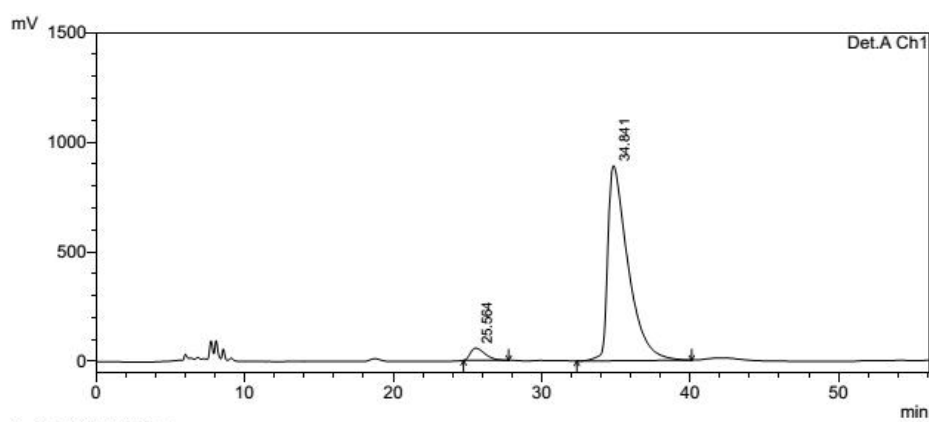
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 85/15; flow = 0.5 mL/min; Retention time: 25.5 min; 34.8 min (major), 91% *ee*, $[\alpha]^{25}$: 47.583 (c 0.34, CHCl_3).



PeakTable

Detector A Ch1 220nm

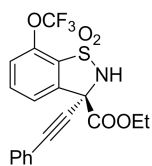
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.288	127913884	1638568	50.211	56.608
2	34.360	126838385	1256003	49.789	43.392
Total		254752269	2894572	100.000	100.000



PeakTable

Detector A Ch1 220nm

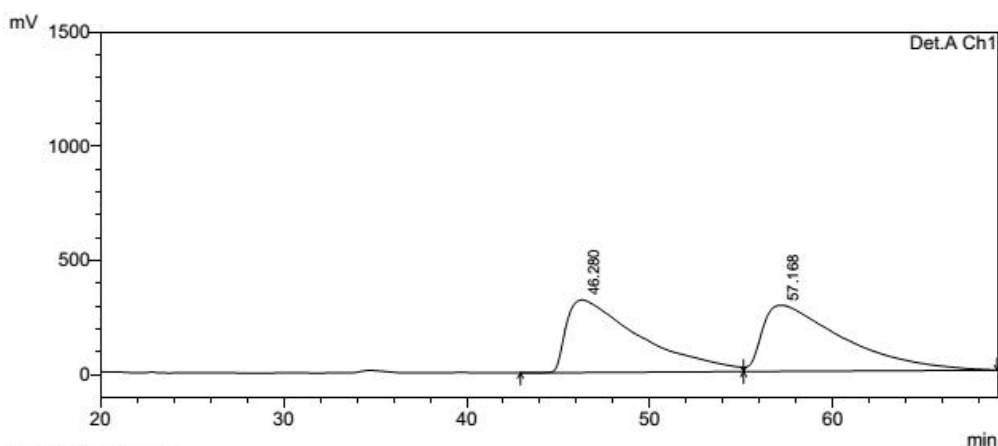
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.564	3863013	55866	4.360	5.906
2	34.841	84734141	890129	95.640	94.094
Total		88597153	945995	100.000	100.000



(*R*)-ethyl 3-(phenylethynyl)-7-(trifluoromethoxy)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate **(3ma)**, 34.8 mg, 82% yield, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, J

=7.6 Hz, 1H), 7.75 (t, J =8.0Hz, 1H), 7.46-7.29 (m, 3H), 7.39-7.29 (m, 3H), 5.98 (br, 1H), 4.46-4.37 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.3, 143.5 (q, J =2.0 Hz), 139.2, 135.7, 132.0, 129.5, 128.3, 126.4, 123.6, 123.1 (q, J =283.4 Hz), 120.8, 120.7 (q, J =1.7 Hz), 86.0, 83.5, 64.8, 61.2, 14.0; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_5\text{SF}_3$ $[\text{M}+\text{H}]^+$ 426.0623, found 426.0631.

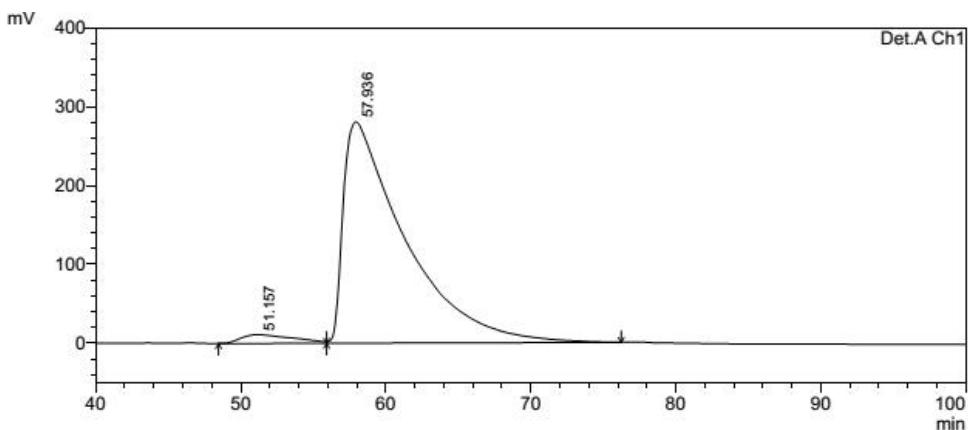
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 51.2 min; 57.9 min (major), 94% *ee*, $[\alpha]^{25}$: 17.669 (c 0.26, CHCl_3).



PeakTable

Detector A Ch1 220nm

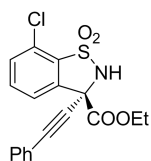
Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.280	89002608	318532	50.022	52.334
2	57.168	88922727	290123	49.978	47.666
Total		177925335	608654	100.000	100.000



PeakTable

Detector A Ch1 220nm

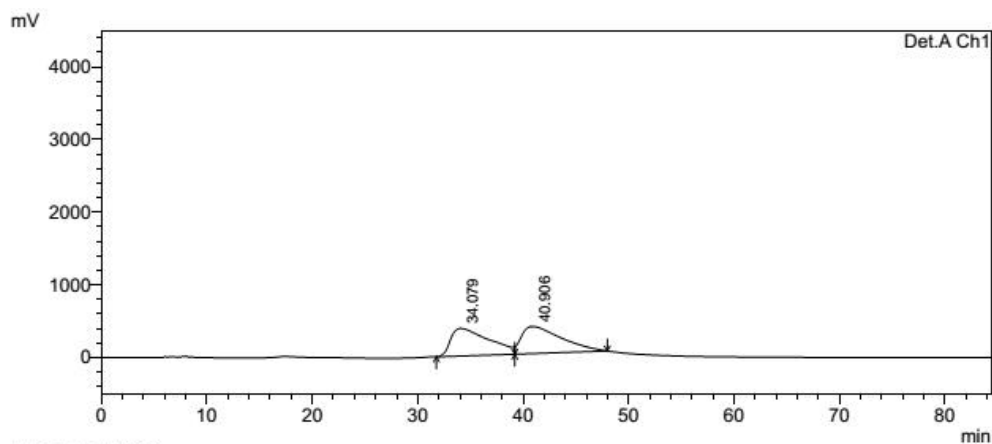
Peak#	Ret. Time	Area	Height	Area %	Height %
1	51.157	2806926	11233	3.260	3.846
2	57.936	83294769	280817	96.740	96.154
Total		86101695	292050	100.000	100.000



(*R*)-ethyl 7-chloro-3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3na**), 30.0 mg, 80% yield, yellow solid, m.p.: 96-97 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.82

(dd, $J = 8.0, 0.8$ Hz, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.56 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.44-7.41 (m, 2H), 7.38-7.28 (m, 3H), 6.00 (br, 1H), 4.46-4.34 (m, 2H), 1.38 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.4, 138.6, 134.9, 132.4, 132.0, 131.8, 129.5, 128.9, 128.3, 124.3, 120.8, 85.8, 83.7, 64.8, 60.7, 13.9; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 376.0410, found 376.0421.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 37.0 min; 41.3 min (major), 94% *ee*, $[\alpha]^{25}$: -5.463 (c 0.585, CHCl_3).

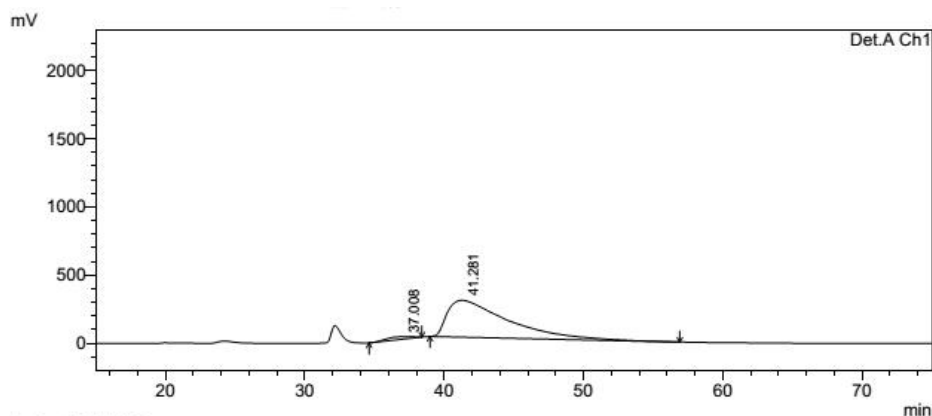


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.079	95113709	380559	49.221	50.518
2	40.906	98125903	372752	50.779	49.482
Total		193239612	753311	100.000	100.000

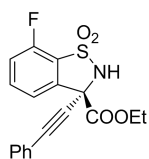


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

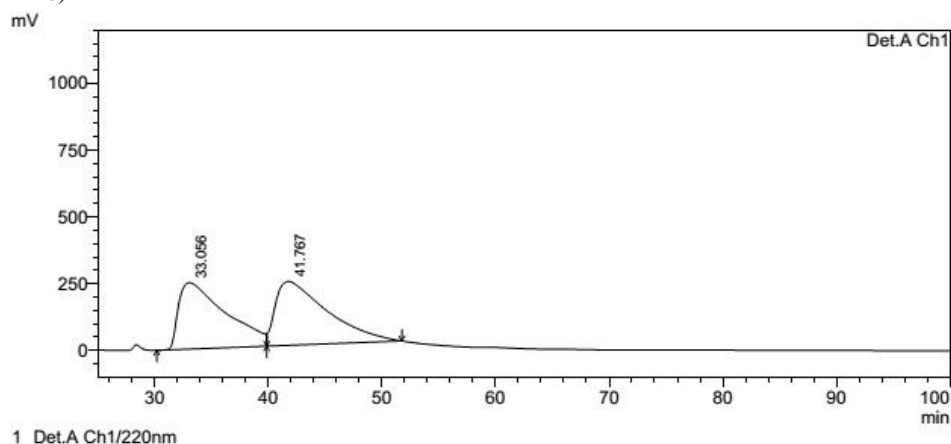
Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.008	2517086	18801	2.969	6.495
2	41.281	82247924	270679	97.031	93.505
Total		84765009	289480	100.000	100.000



(*R*)-ethyl 7-fluoro-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dio-

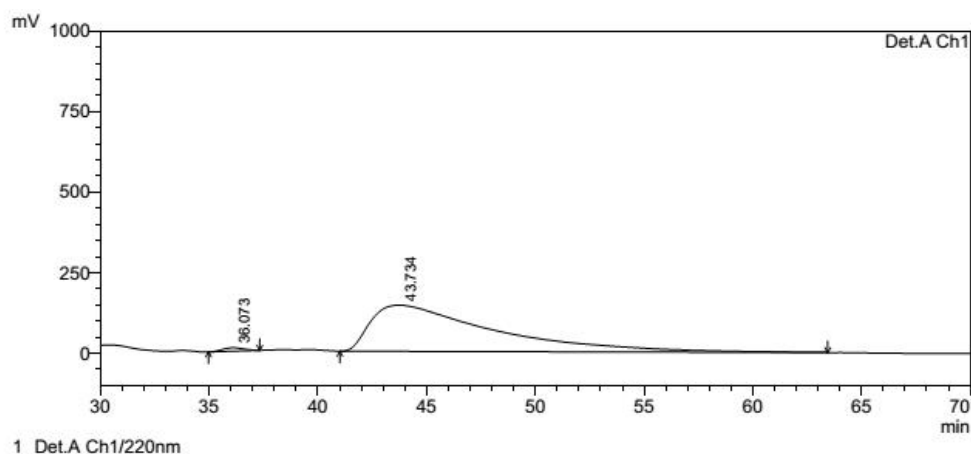
xide (**30a**), 27.3 mg, 76% yield, yellow solid, m.p.: 70-72 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.72-7.69 (m, 2H), 7.44-7.42 (m, 2H), 7.38-7.26 (m, 4H), 6.00 (br, 1H), 4.47-4.35 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.4, 156.0 (d, *J* = 258.5 Hz), 139.2, 136.3 (d, *J* = 7.0 Hz), 132.0, 129.5, 128.4, 122.7 (d, *J* = 20.1 Hz), 121.6 (d, *J* = 4.2 Hz), 120.9, 117.9 (d, *J* = 18.3 Hz), 85.9, 83.6, 64.8, 61.6, 13.9; HRMS (ESI): calcd for C₁₈H₁₅NO₄SF [M+H]⁺ 360.0706, found 360.0719.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 36.1 min; 43.7 min (major), 98% *ee*, [α]_D²⁵: 41.373 (c 0.42, CHCl₃).



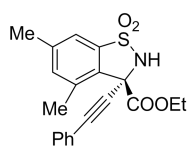
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.056	71319637	248706	48.449	50.935
2	41.767	75887272	239575	51.551	49.065
Total		147206909	488281	100.000	100.000



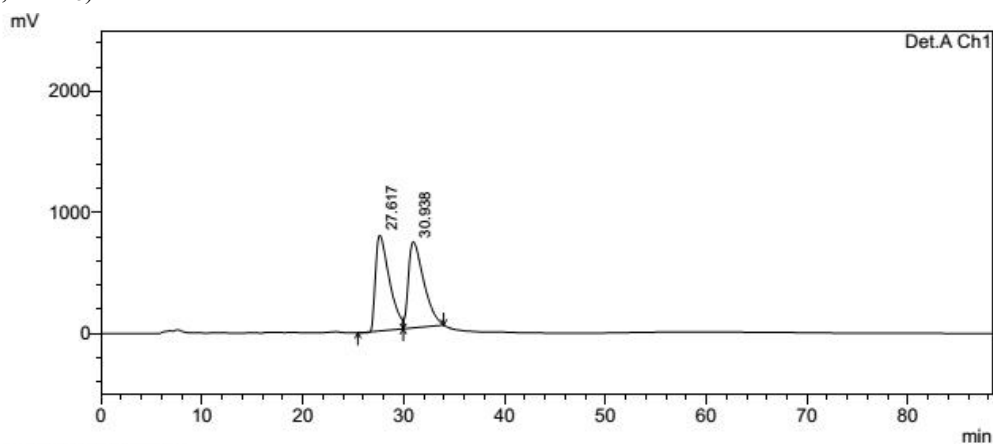
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.073	710787	10697	1.244	6.940
2	43.734	56449347	143445	98.756	93.060
Total		57160133	154142	100.000	100.000



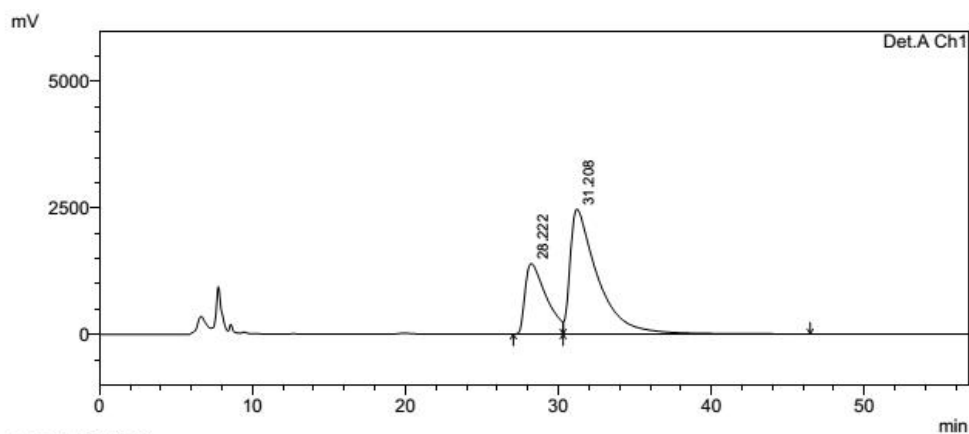
(*R*)-ethyl 4,6-dimethyl-3-(phenylethynyl)-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**3pa**), 22.8 mg, 62% yield, yellow solid, m.p.: 112-114 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.42 (m, 3H), 7.38-7.29 (m, 4H), 5.44 (br, 1H), 4.33-4.27 (m, 2H), 2.56 (s, 3H), 2.43 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 141.7, 137.2, 136.4, 134.4, 131.9, 130.5, 129.4, 128.4, 121.0, 119.2, 87.4, 82.8, 63.9, 62.0, 21.1, 18.8, 13.9; HRMS (ESI): calcd for C₂₀H₂₀NO₄S [M+H]⁺ 370.1113, found 370.1110.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 28.2 min; 31.2 min (major), 40% *ee*, [α]_D²⁵: 10.241 (c 0.55, CHCl₃).



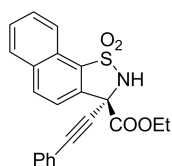
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.617	75344749	789772	49.946	52.649
2	30.938	75508941	710301	50.054	47.351
Total		150853691	1500073	100.000	100.000



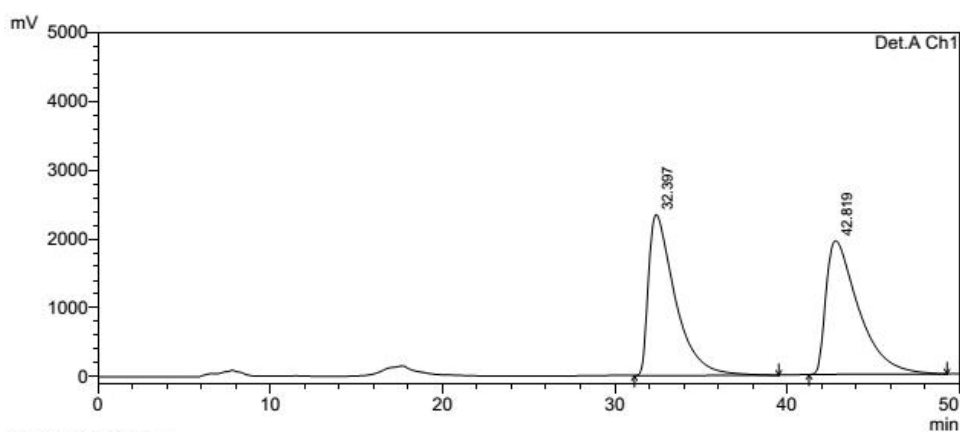
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.222	132624662	1394083	29.943	36.080
2	31.208	310294413	2469833	70.057	63.920
Total		442919075	3863915	100.000	100.000



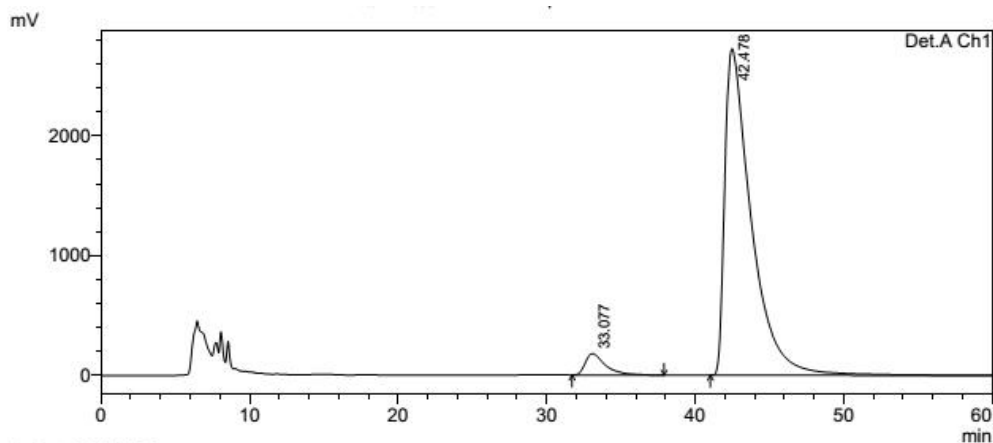
(*R*)-ethyl 3-(phenylethynyl)-2,3-dihydro-naphtho[2,1-*d*]isothiazole-3-carboxylate 1,1-dioxide (**3qa**), 34.0 mg, 87% yield, yellow solid, m.p.: 116-118 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77-7.67 (m, 2H), 7.45-7.43 (m, 2H), 7.35-7.28 (m, 3H), 6.00 (br, 1H), 4.45-4.36 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 135.0, 134.8, 134.1, 132.0, 129.7, 129.5, 129.4, 128.64, 128.63, 128.4, 125.0, 123.3, 121.4, 121.1, 85.8, 84.1, 64.6, 61.9, 14.0; HRMS (ESI): calcd for C₂₂H₁₈NO₄S [M+H]⁺ 392.0957, found 392.0949.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/05; flow = 0.5 mL/min; Retention time: 33.1 min; 42.4 min (major), 91% *ee*, [α]_D²⁵: -26.631 (c 0.285, CHCl₃).



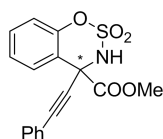
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.397	251505891	2336606	49.580	54.643
2	42.819	255769249	1939552	50.420	45.357
Total		507275140	4276158	100.000	100.000



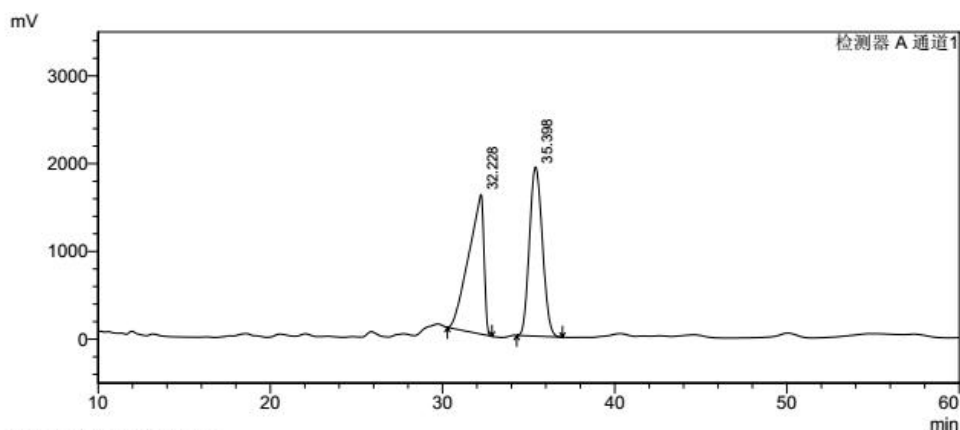
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.077	16906734	178591	4.736	6.146
2	42.478	340064900	2727070	95.264	93.854
Total		356971634	2905661	100.000	100.000



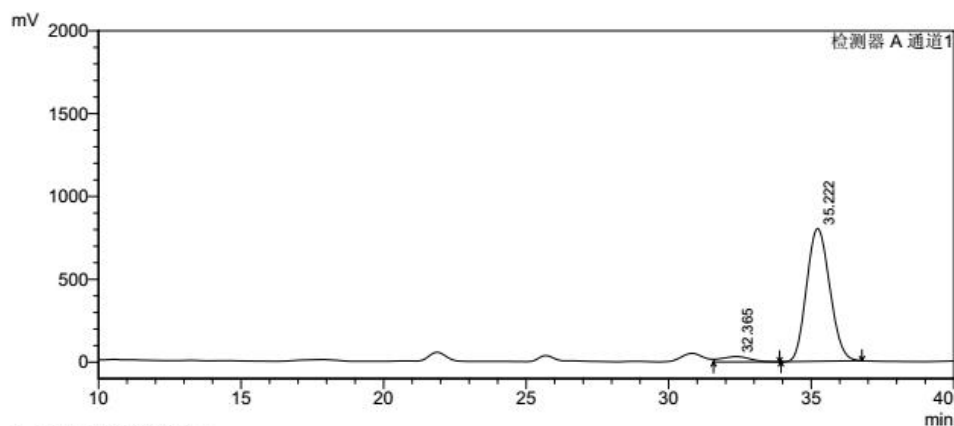
Methyl 4-(phenylethynyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (**5a**), 25.4 mg, 74% yield, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.87-7.84 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.49-7.45 (m, 2H), 7.44-7.39 (m, 1H), 7.37-7.27 (m, 4H), 7.09-7.05 (dd, $J = 8.0, 1.2$ Hz, 1H), 3.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.6, 149.7, 132.1, 131.2, 129.48, 129.46, 128.4, 125.9, 121.0, 119.5, 119.1, 86.5, 84.1, 62.2, 55.3; HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$ 344.0593, found 344.0581.

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 32.2 min; 35.4 min (major), 91% *ee*, $[\alpha]_D^{25}$: 7.714 (c 0.245, CHCl_3).



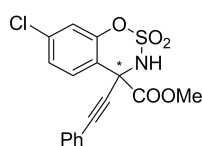
峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	32.228	97991323	1591888	49.331	45.242
2	35.398	100647151	1926731	50.669	54.758
总计		198638474	3518619	100.000	100.000



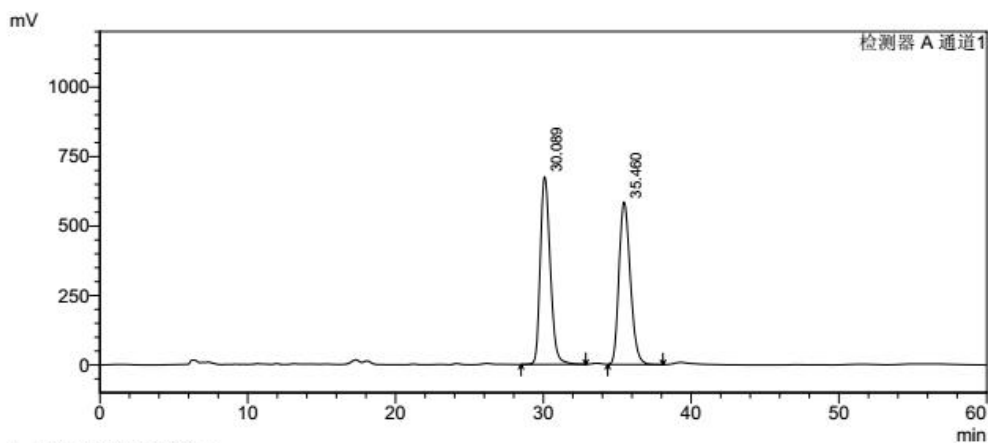
峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	32.365	2208965	31808	4.641	3.817
2	35.222	45389424	801449	95.359	96.183
总计		47598389	833257	100.000	100.000



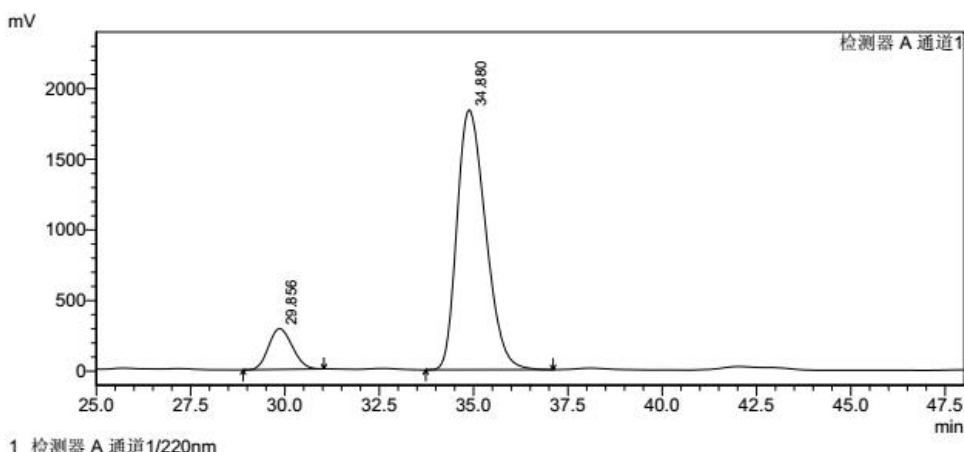
Methyl 7-chloro-4-(phenylethynyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (**5b**), 30.5 mg, 81% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.78 (d, *J* = 8.8 Hz, 1H), 7.48-7.44 (m, 2H), 7.40-7.26 (m, 4H), 7.11-7.09 (d, *J* = 2.0 Hz, 1H), 3.97 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 167.3, 149.9, 136.7, 132.1, 130.6, 129.6, 128.4, 126.3, 120.8, 119.6, 117.7, 86.9, 83.6, 61.9, 55.4; HRMS (ESI): calcd for C₁₇H₁₃NO₅SCl [M+H]⁺ 378.0203, found 378.0217.

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 30.1 min; 35.5 min (major), 77% *ee*, [α]_D²⁵: 3.026 (c 0.33, CHCl₃).



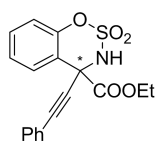
峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	30.089	31663467	675518	50.305	53.596
2	35.460	31279089	584860	49.695	46.404
总计		62942556	1260378	100.000	100.000



峰表

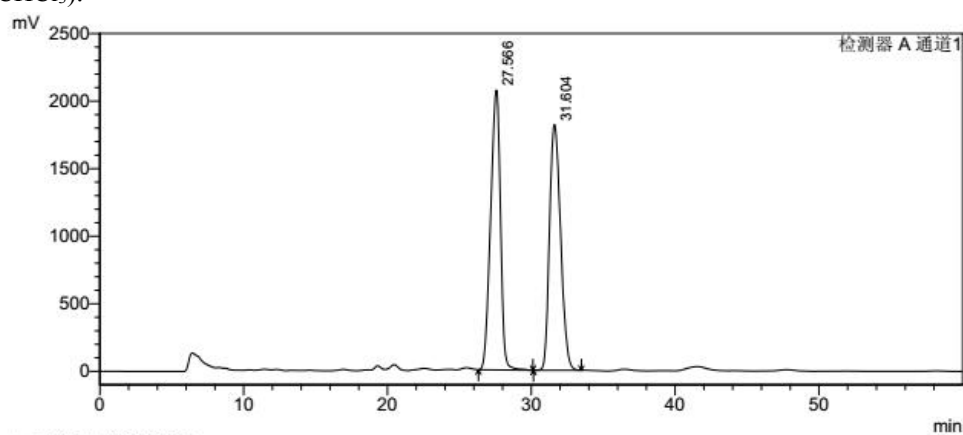
峰#	保留时间	面积	高度	面积 %	高度 %
1	29.856	12661622	288506	11.540	13.565
2	34.880	97054303	1838328	88.460	86.435
总计		109715924	2126834	100.000	100.000



Ethyl 4-(phenylethynyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxi de

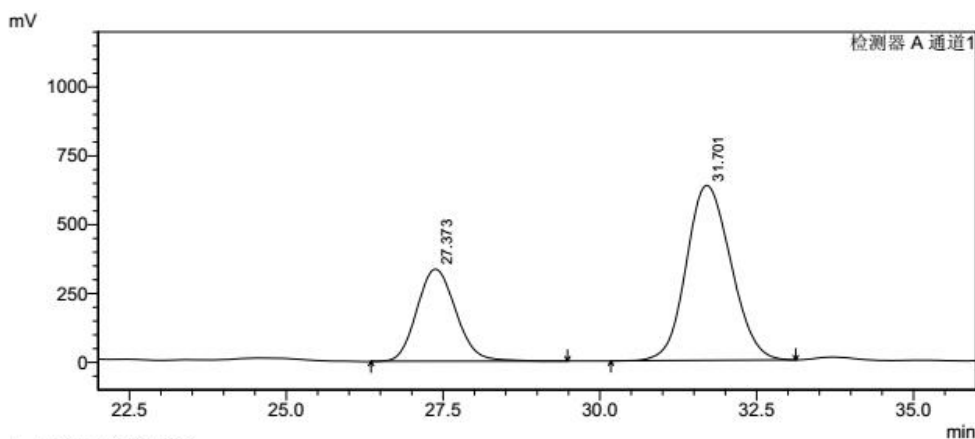
(5c), 28.5 mg, 82% yield, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.88-7.85 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.49-7.45 (m, 2H), 7.44-7.39 (m, 1H), 7.37-7.27 (m, 4H), 7.08-7.06 (dd, $J = 8.0, 1.2$ Hz, 1H), 4.45-4.36 (m, 2H), 1.40-1.36 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 149.7, 132.1, 131.1, 129.40, 129.39, 128.4, 125.8, 121.1, 119.5, 119.2, 86.3, 84.4, 64.9, 62.2, 13.9; HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$ 358.0749, found 358.0760.

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 27.6 min; 31.6 min (major), 37% *ee*, $[\alpha]^{25}$: -0.110 (c 0.73, CHCl_3).



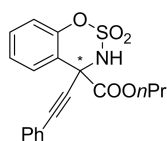
峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	27.566	98230384	2071310	50.258	53.246
2	31.604	97223338	1818794	49.742	46.754
总计		195453722	3890104	100.000	100.000



峰表

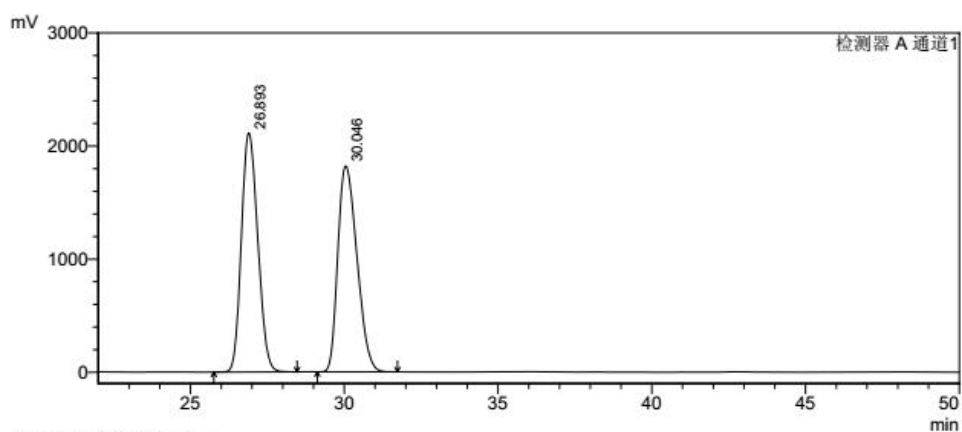
峰#	保留时间	面积	高度	面积 %	高度 %
1	27.373	14417227	334430	31.398	34.478
2	31.701	31499809	635551	68.602	65.522
总计		45917036	969982	100.000	100.000



Propyl 4-(phenylethynyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxi de

(**5d**), 19.3 mg, 52% yield, yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.89-7.86 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.48-7.45 (m, 2H), 7.43-7.38 (m, 1H), 7.36-7.28 (m, 4H), 7.08-7.05 (dd, $J = 8.0, 1.2$ Hz, 1H), 4.40-4.24 (m, 2H), 1.82-1.73 (m, 2H), 1.02-0.98 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.5, 150.0, 132.2, 131.3, 129.7, 129.6, 128.6, 125.9, 121.4, 119.7, 119.5, 86.3, 84.8, 70.5, 62.4, 22.0, 10.5; HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$ 372.0906, found 372.0920.

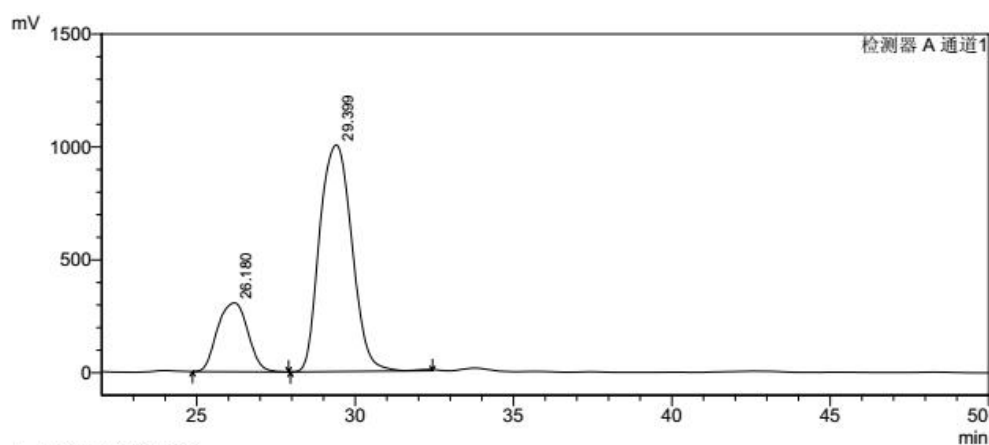
HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 26.9 min; 30.0 min (major), 56% *ee*, $[\alpha]_D^{25}$: 1.135 (c 0.88, CHCl_3).



1 检测器 A 通道1/220nm

峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.893	78191158	2114430	49.856	53.723
2	30.046	78641390	1821356	50.144	46.277
总计		156832548	3935786	100.000	100.000

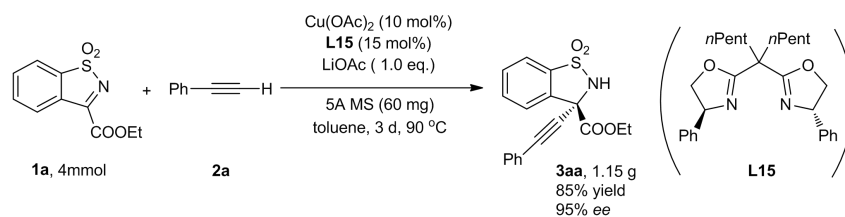


1 检测器 A 通道1/220nm

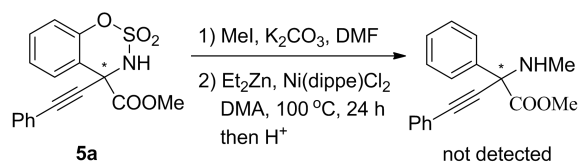
峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.180	20337252	304978	22.198	23.297
2	29.399	71280430	1004100	77.802	76.703
总计		91617682	1309078	100.000	100.000

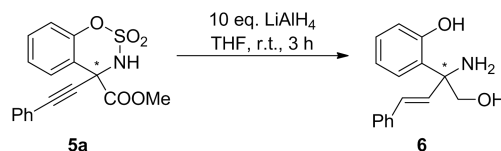
8. General Procedure for the derivatives of **3aa** and **5a**.



$\text{Cu}(\text{OAc})_2$ (72 mg, 10 mol %), 5Å MS (2.4 g) and **L15** (0.272 g, 15 mol%) were stirred in toluene (40.0 mL) at 90 °C for 1 h. Cyclic ketimines **1a** (0.956 g, 4.0 mmol) and LiOAc (0.264 g, 1.0 eq.) were added. After 15 min, ethynylbenzene **2a** (0.66 mL, 1.5 eq.) was added and stirred at 90 °C for 3 days. After completion, the reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na_2SO_4 . After concentration in vacuo, the residue was finally purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5 to 1:3) to give the product **3aa** as a yellow solid (1.159 g, 85%).



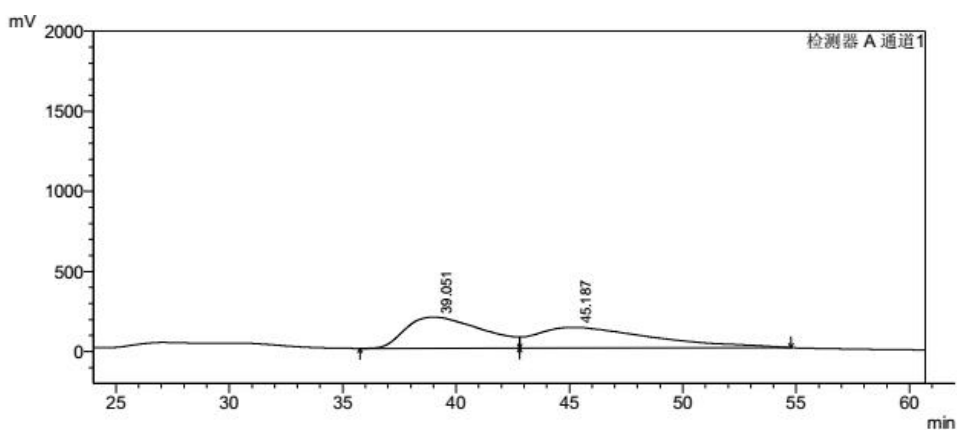
We tried to remove SO_2 group according to ref. 4, but no desired product was detected.



To a solution of the alkenylation product **5a** (34.3 mg, 0.1 mmol) in THF (1.0 mL) at room temperature was added LiAlH_4 (1.0 N in THF, 1.0 mL, 1.0 mmol) dropwise over 2 mins and stirred at room temperature for 3 hours. The reaction was quenched carefully with EtOAc (2.0 mL) followed by EtOH (2.0 mL). The solution was concentrated in vacuo. The residue was purified by column chromatography (PE/EA = 2:1) to give the product **6**.

E-(*R*)-2-(2-amino-1-hydroxy-4-phenylbut-3-en-2-yl)phenol (**6**), 23.9 mg, 94% yield, yellow oil; ^1H NMR (400 MHz CDCl_3): δ 7.44-7.38 (m, 2H), 7.36-7.30 (m, 2H), 7.29-7.24 (m, 1H), 7.22-7.16 (m, 1H), 7.11 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.88 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.80 (td, $J = 7.6, 1.2$ Hz, 1H), 6.58 (d, $J = 16.4$ Hz, 1H), 6.43 (d, $J = 16.4$ Hz, 1H), 4.10 (d, $J = 11.2$ Hz, 1H), 3.79 (d, $J = 11.2$ Hz, 1H); ^{13}C NMR (100 MHz CDCl_3) δ 158.9, 136.4, 131.8, 130.5, 129.8, 128.9, 128.3, 127.5, 126.8, 124.9, 119.2, 118.4, 68.0, 62.3; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 256.1338, found 256.1333.

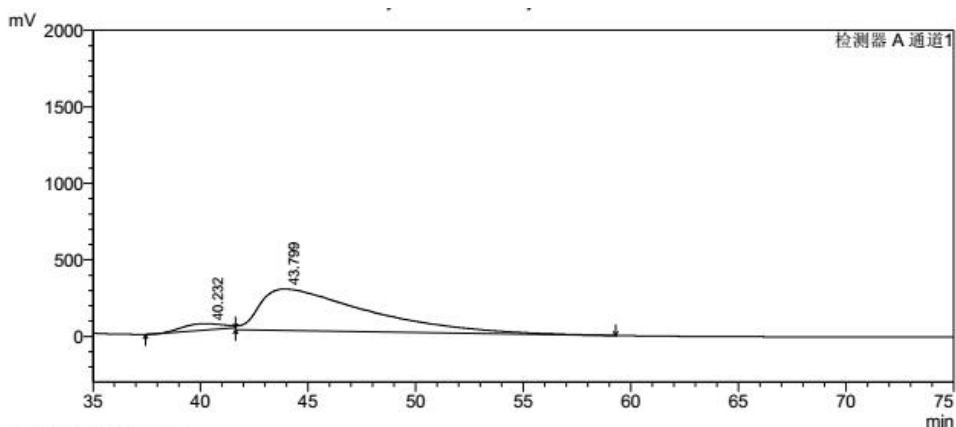
HPLC: Daicel Chiralcel AY column (250 mm); detected at 210 nm; hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 39.1 min; 45.2 min (major), 90% *ee*, $[\alpha]^{25}$: -8.929 (c 1.70, CHCl_3).



峰表

Detector A Ch1 210nm

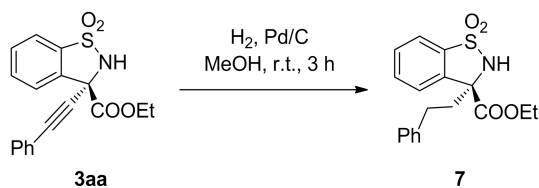
峰#	保留时间	面积	高度	面积 %	高度 %
1	39.051	46168806	194224	50.102	60.105
2	45.187	45980044	128917	49.898	39.895
总计		92148850	323142	100.000	100.000



峰表

Detector A Ch1 210nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	40.232	5413039	40540	5.385	13.052
2	43.799	95114656	270061	94.615	86.948
总计		100527696	310601	100.000	100.000

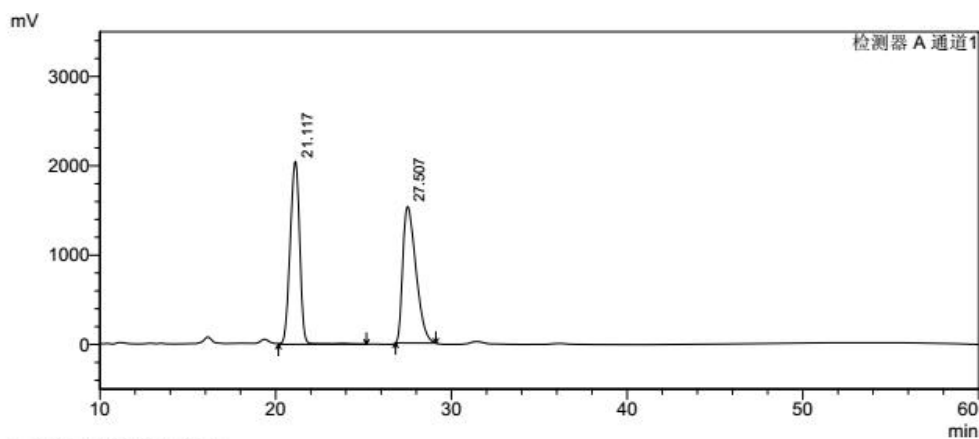


To a solution of **3aa** (34.1 mg, 0.1 mmol) in MeOH (1.0 mL) was added Pd/C (10 wt% of Pd, 16.0 mg), the mixture was stirred at room temperature for 3 hours and then filtrated off to removed the catalyst. After concentration under reduced pressure, the residue obtained was purified by column chromatography (PE:EA = 4:1) to give **7**.

(*R*)-ethyl 3-phenethyl-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**7**), 34.2 mg, 99% yield, colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.79-7.76 (d, *J* = 7.6 Hz, 1H), 7.73-7.69 (d, *J* = 8.0 Hz, 1H), 7.67-7.56 (m, 2H), 7.29-7.23 (m, 2H), 7.21-7.12 (m, 3H), 5.87 (br, 1H), 4.30-4.21 (m,

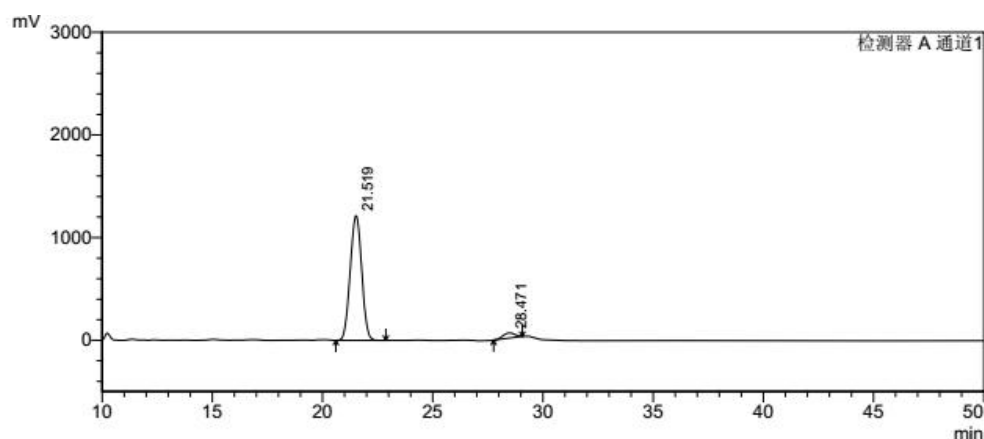
2H), 2.80-2.61 (m, 2H), 2.58-2.48 (m, 1H), 2.36-2.26 (m, 1H), 1.37-1.31 (t, $J = 7.2$ Hz, 3H).^[1b]

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 80/20; flow = 1.0 mL/min; Retention time: 21.1 min (major); 27.5 min, 92% *ee*, $[\alpha]_D^{25}$: 12.689 (c 0.85, CHCl₃).



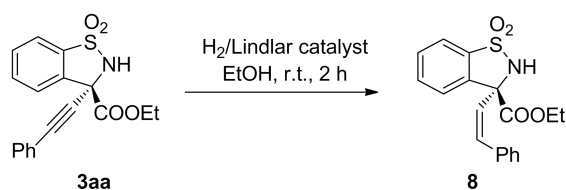
峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	21.117	77362252	2047441	49.207	57.282
2	27.507	79854274	1526857	50.793	42.718
总计		157216527	3574298	100.000	100.000



峰表

峰#	保留时间	面积	高度	面积 %	高度 %
1	21.519	43933201	1214951	95.941	96.040
2	28.471	1858535	50100	4.059	3.960
总计		45791736	1265052	100.000	100.000

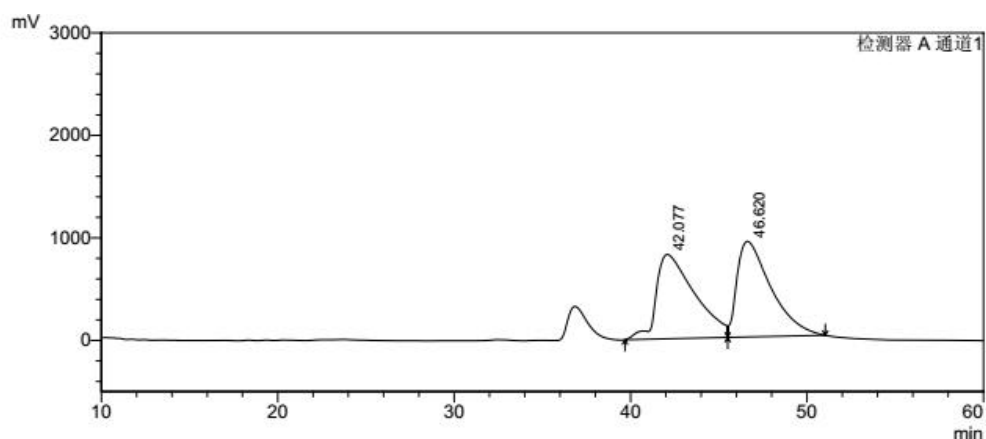


To a solution of **3aa** (34.1 mg, 0.1 mmol) in EtOH (1.0 mL) was added Lindlar catalyst (5 wt% of Pd, 78.0 mg), the mixture was stirred at room temperature for 2 hours and then filtrated off

to removed the catalyst. After concentration under reduced pressure, the residue obtained was purified by column chromatography (PE:EA = 4:1) to give **8**.

Z-(*R*)-ethyl 3-styryl-2,3-dihydrobenzo[*d*]isothiazole-3-carboxylate 1,1-dioxide (**8**), 31.2 mg, 91% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.76-7.74 (d, *J* = 8.0 Hz, 1H), 7.71-7.68 (d, *J* = 7.2 Hz, 1H), 7.65-7.55 (m, 2H), 7.35-7.21 (m, 5H), 6.85-6.82 (d, *J* = 11.6 Hz, 1H), 5.92-5.89 (d, *J* = 11.6 Hz, 1H), 4.00-3.91 (m, 1H), 3.76-3.67 (m, 1H), 1.12-1.08 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 169.2, 139.0, 135.3, 135.1, 135.0, 133.6, 130.6, 129.2, 128.6, 128.3, 128.0, 125.5, 121.3, 66.9, 63.6, 13.7.; HRMS (ESI): calcd for C₁₈H₁₈NO₄S [M+H]⁺ 344.0957, found 344.0944.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 30.1 min (major); 35.5 min, 94% *ee*, [α]²⁵: 21.826 (c 0.97, CHCl₃).

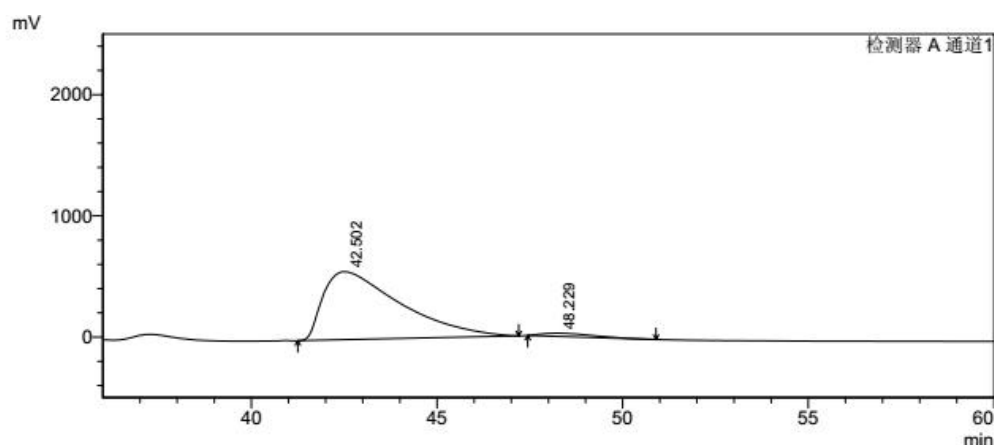


1 检测器 A 通道1/220nm

峰表

检测器 A Ch1 220nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	42.077	124443390	822000	49.829	46.851
2	46.620	125299726	932498	50.171	53.149
总计		249743116	1754498	100.000	100.000



1 检测器 A 通道1/220nm

峰表

检测器 A Ch1 220nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	42.502	80840601	560760	96.892	95.521
2	48.229	2593116	26292	3.108	4.479
总计		83433717	587052	100.000	100.000

9. References

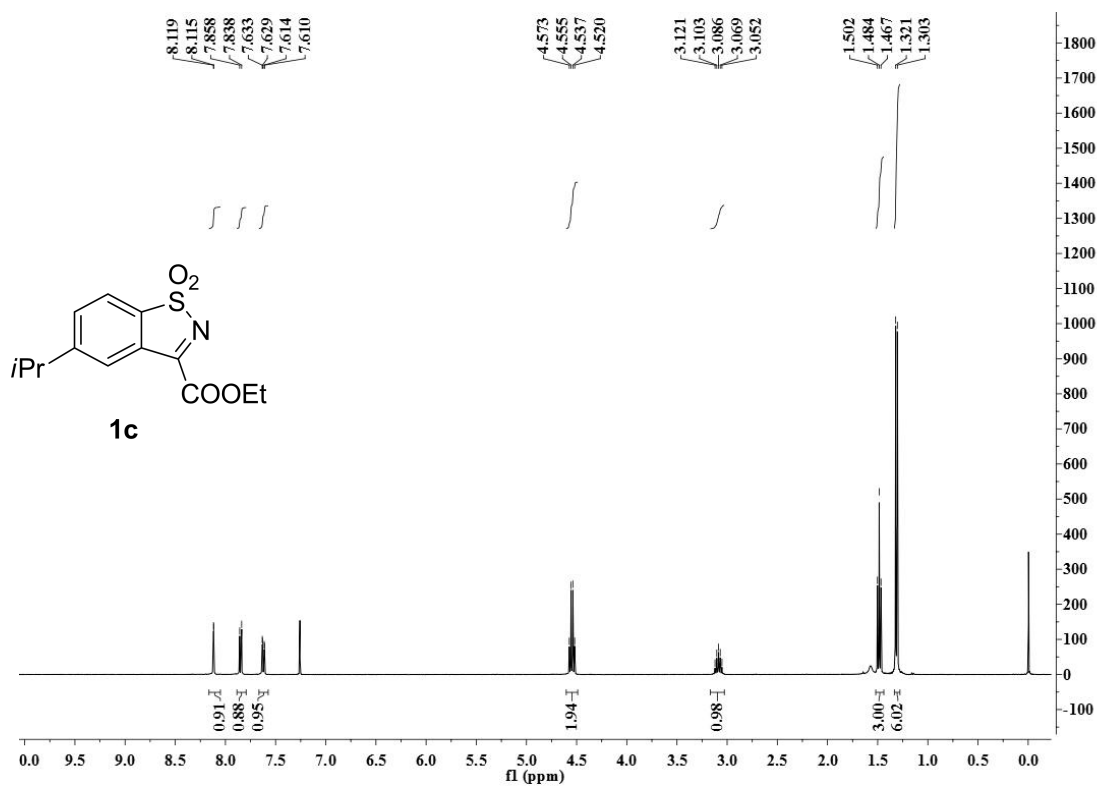
[1] (a) H. Wang, T. Jiang, M.-H. Xu *J. Am. Chem. Soc.*, 2013, **135**, 971; (b) R.-R. Liu, D.-J. Wang, L. Wu, B. Xiang, G.-Q. Zhang, J.-R. Gao, Y.-X. Jia, *ACS Catal.*, 2015, **5**, 6524; (c) M. Quan, G. Yang, F. Xie, I. D. Gridnev, W. Zhang, *Org. Chem. Front.*, 2015, **2**, 398.

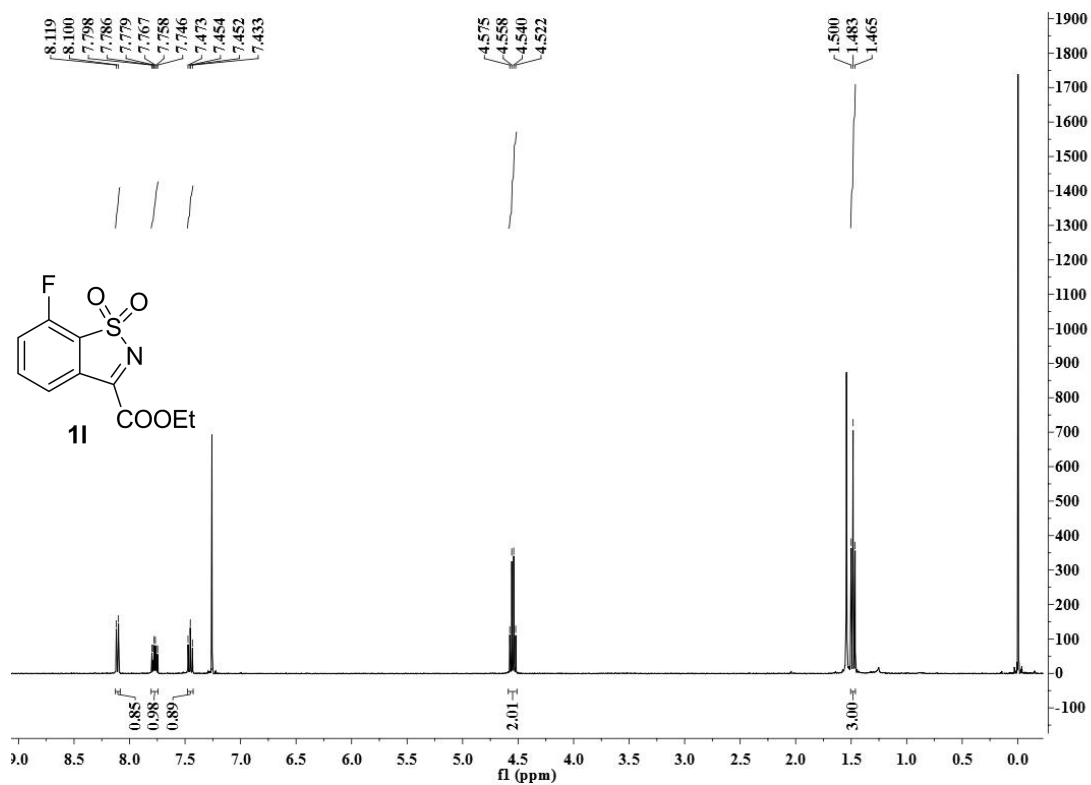
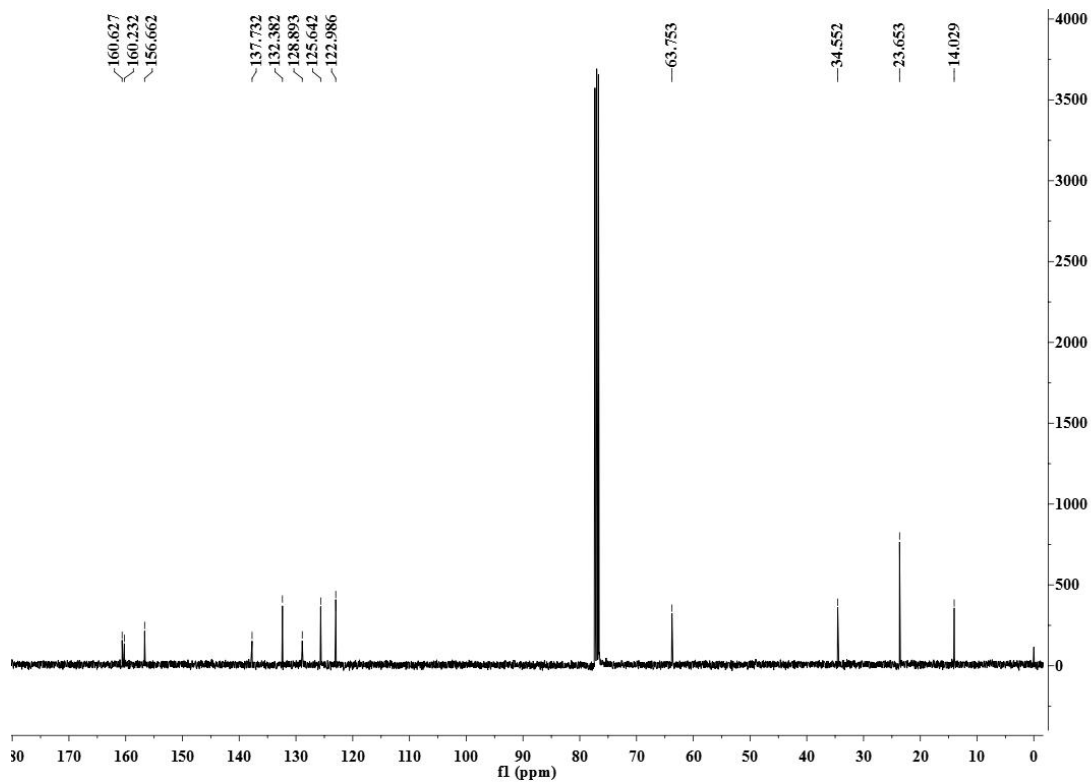
[2] J. Bayardon, D. Sinou, *J. Org. Chem.*, 2004, **69**, 3121.

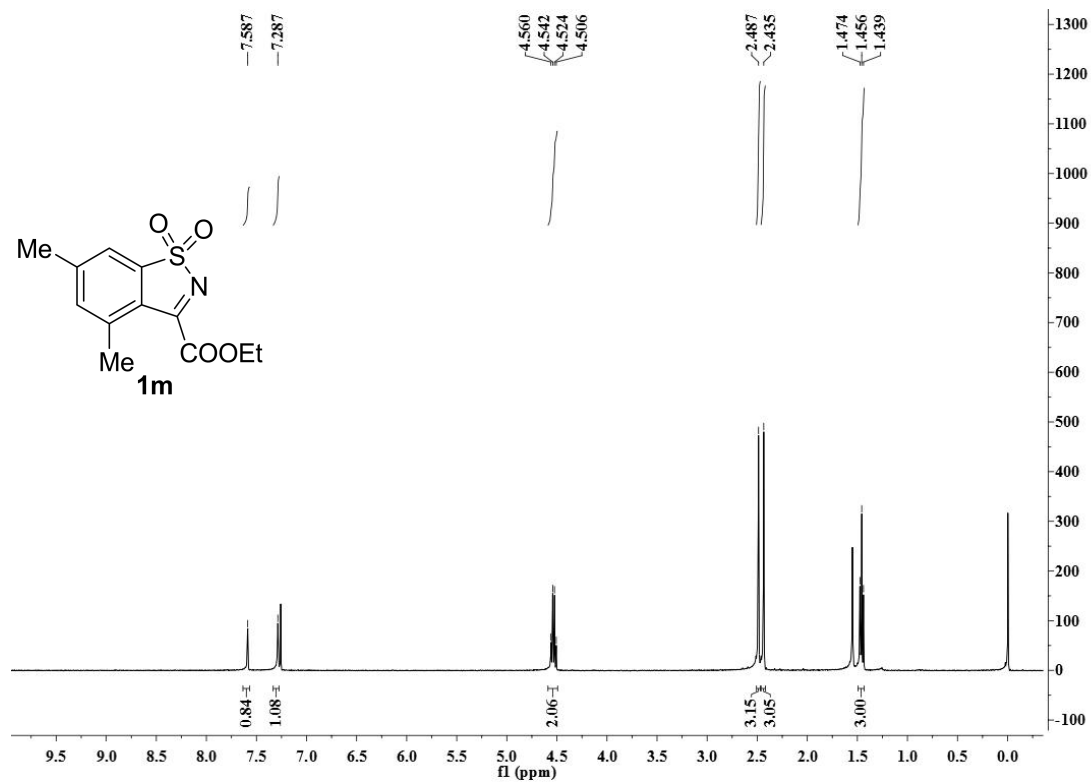
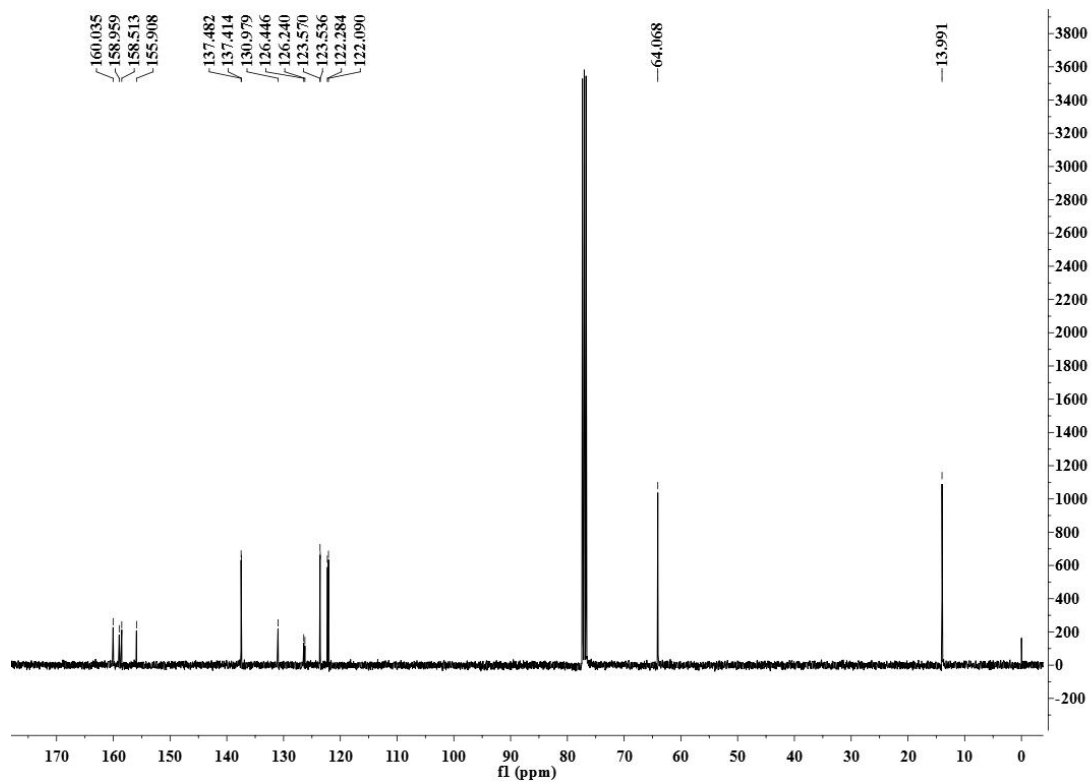
[3] K. Morisaki, M Sawa, R. Yonesaki, H. Morimoto, K. Mashima, T. Ohshima, *J. Am. Chem. Soc.*, 2016, **138**, 6194.

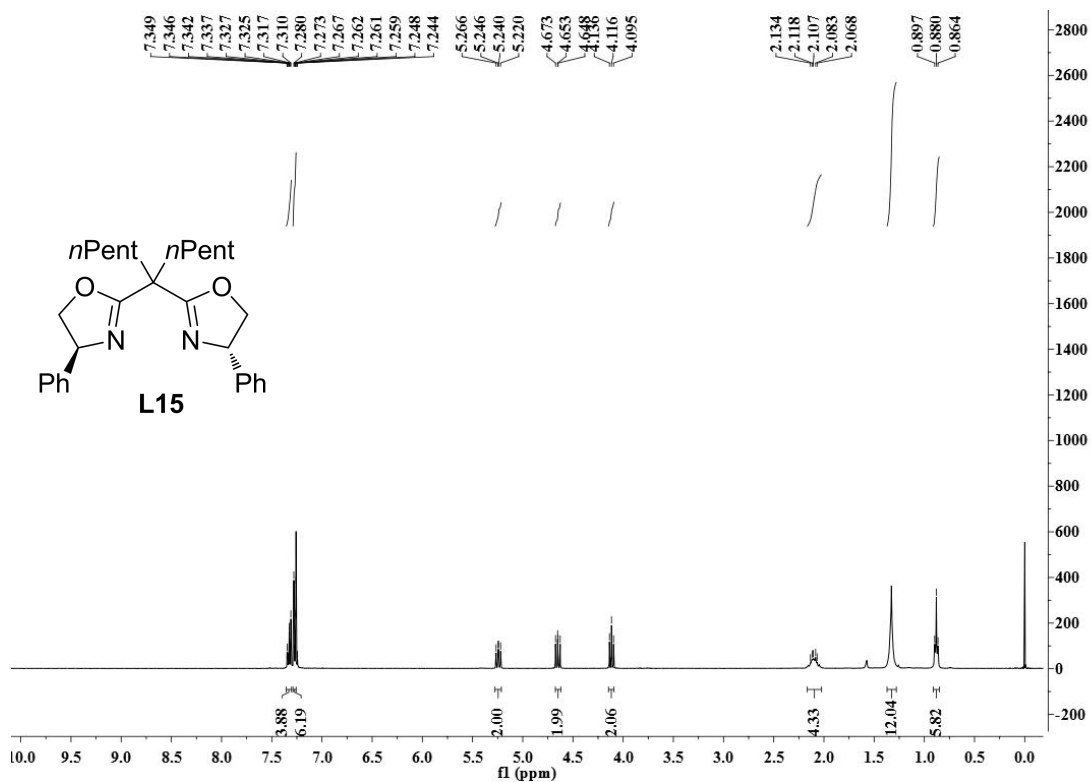
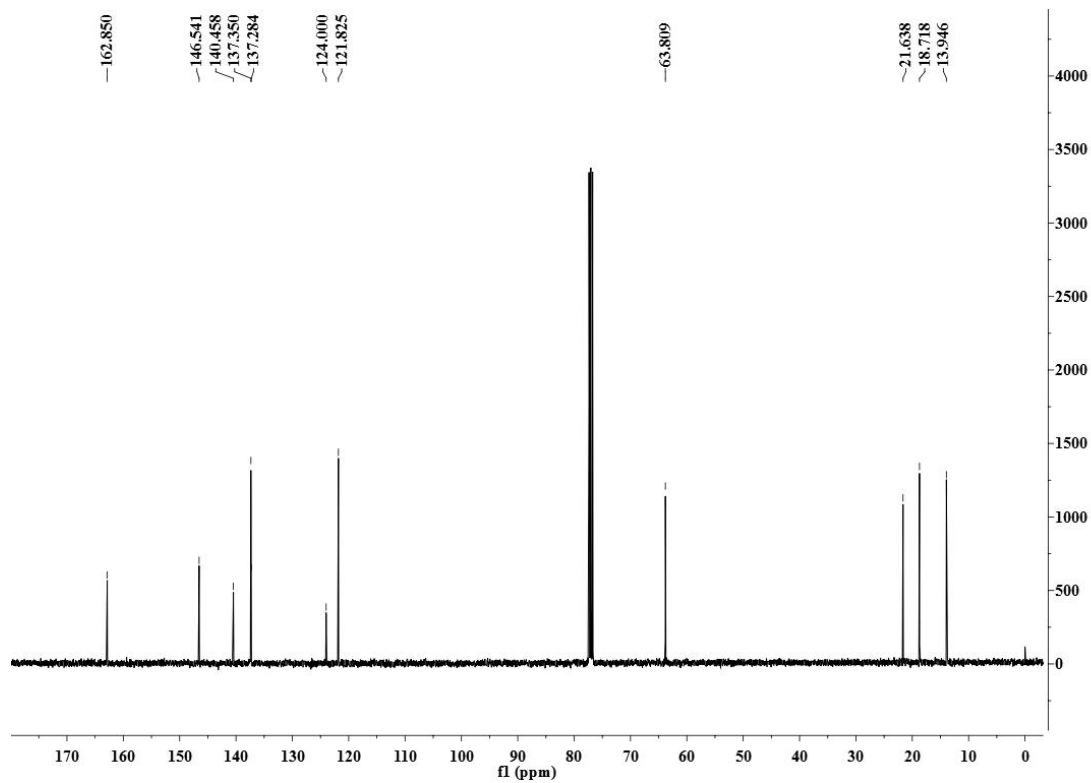
[4] R. Takechi, T. Nishimura, *Org. Biomol. Chem.*, 2015, **13**, 4918.

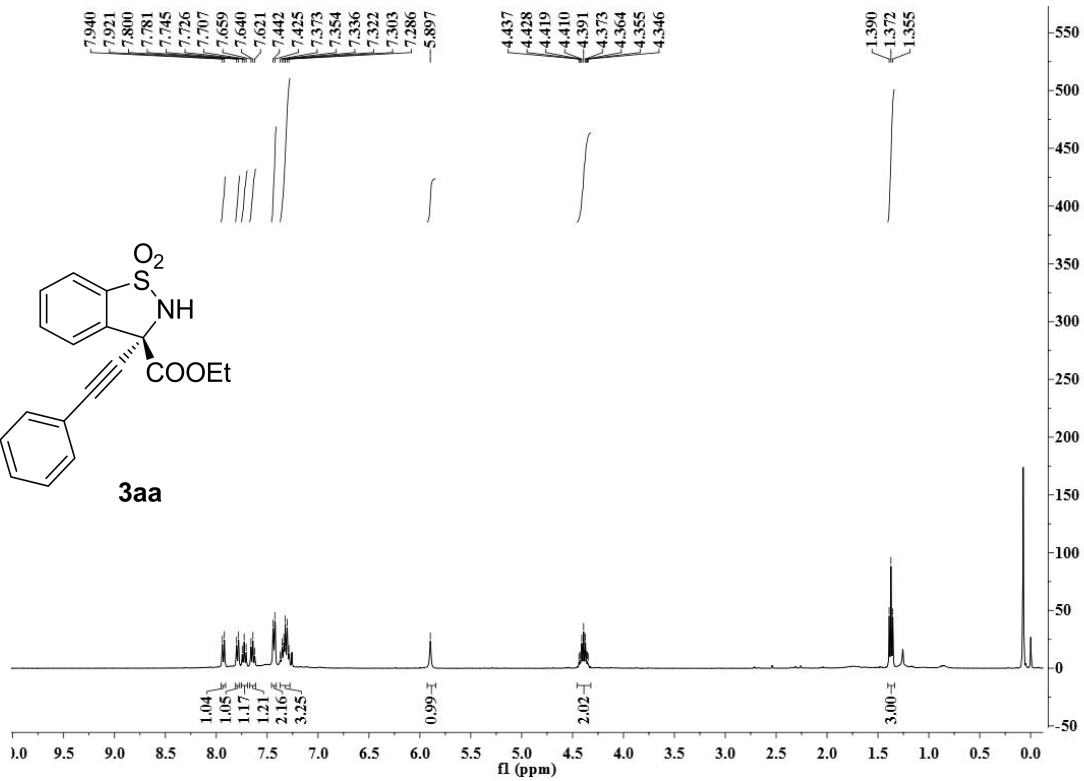
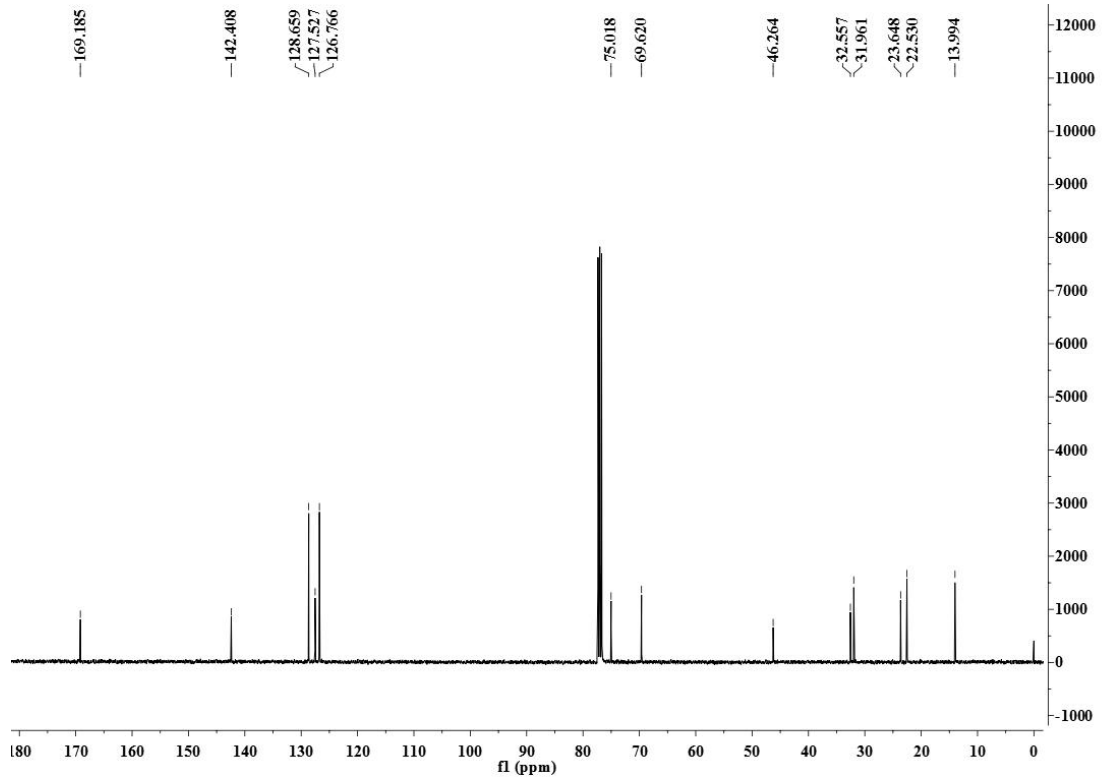
10. Copies of ^1H NMR and ^{13}C NMR spectra

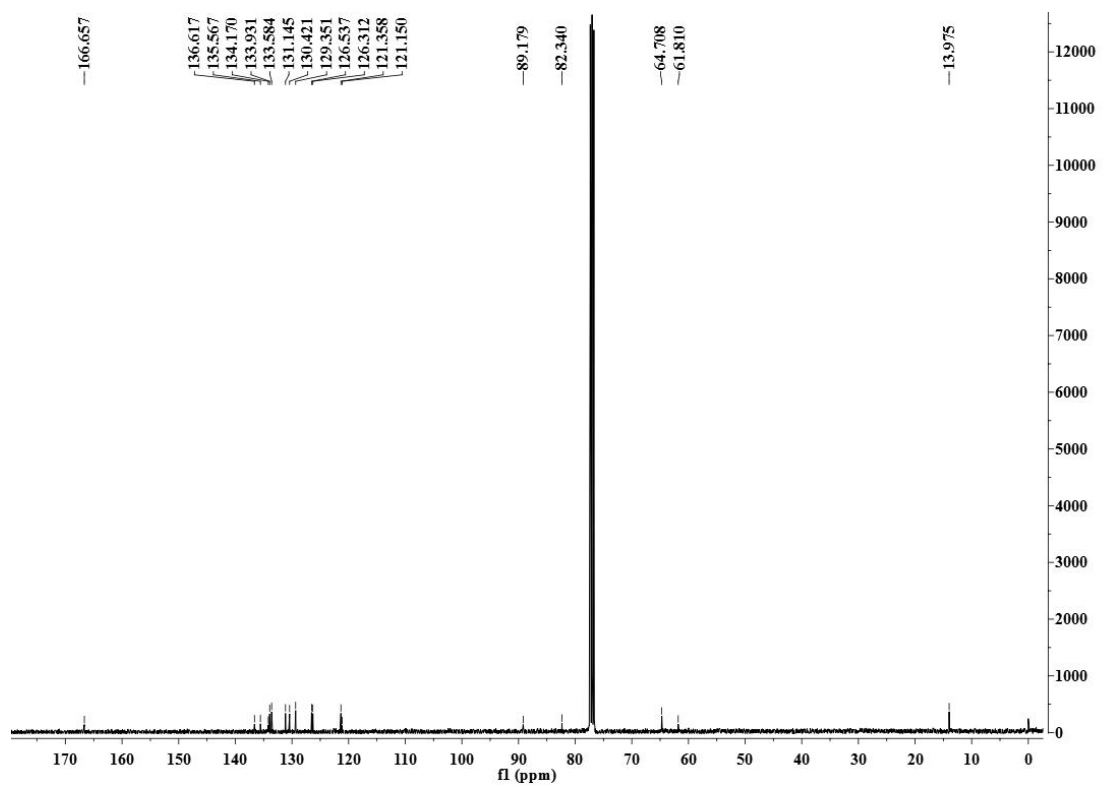
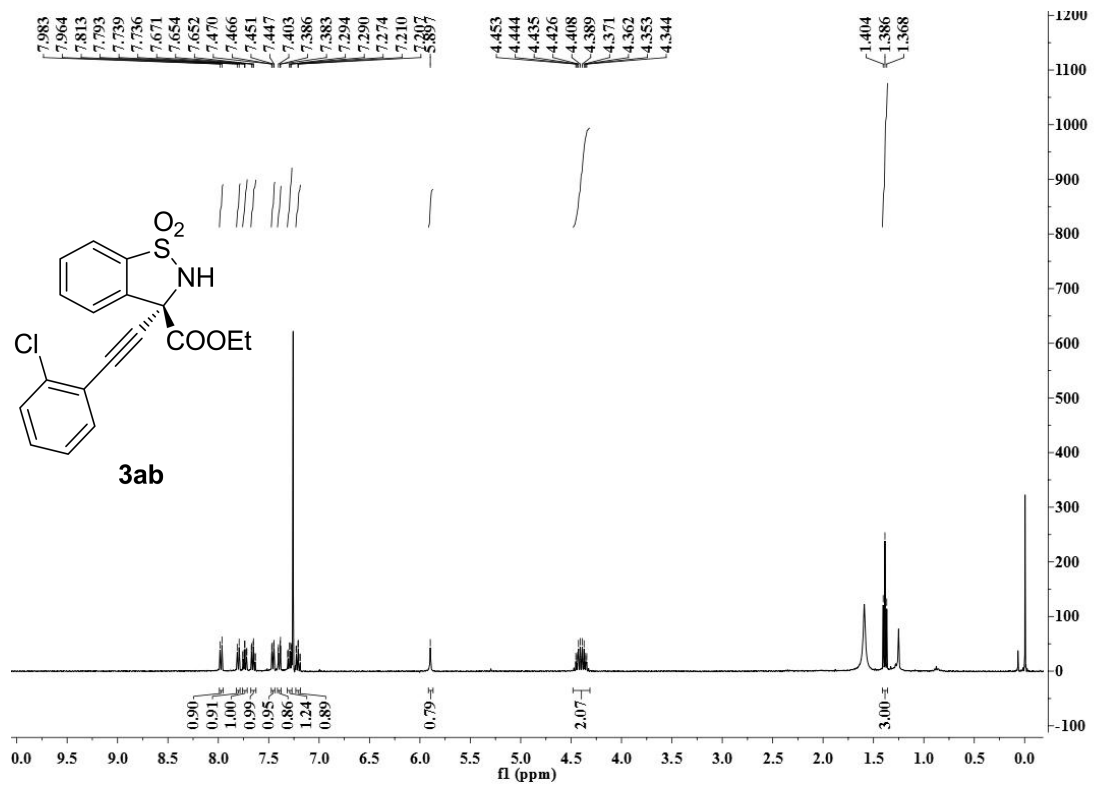


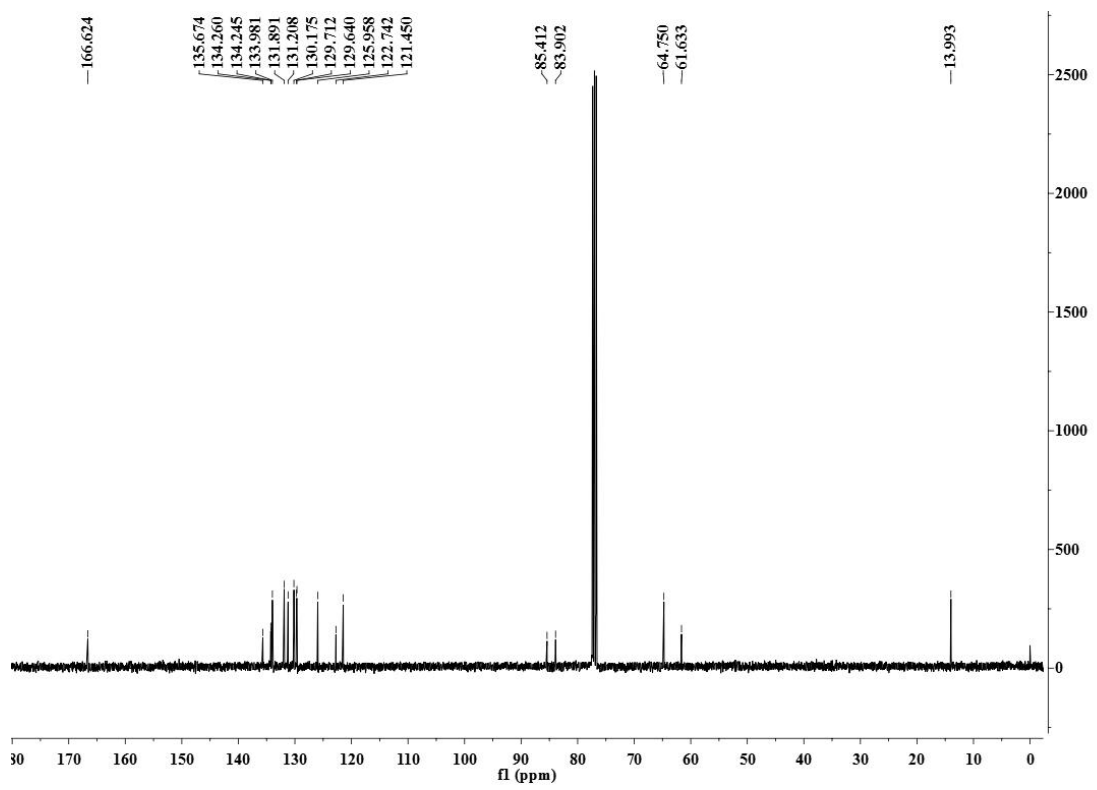
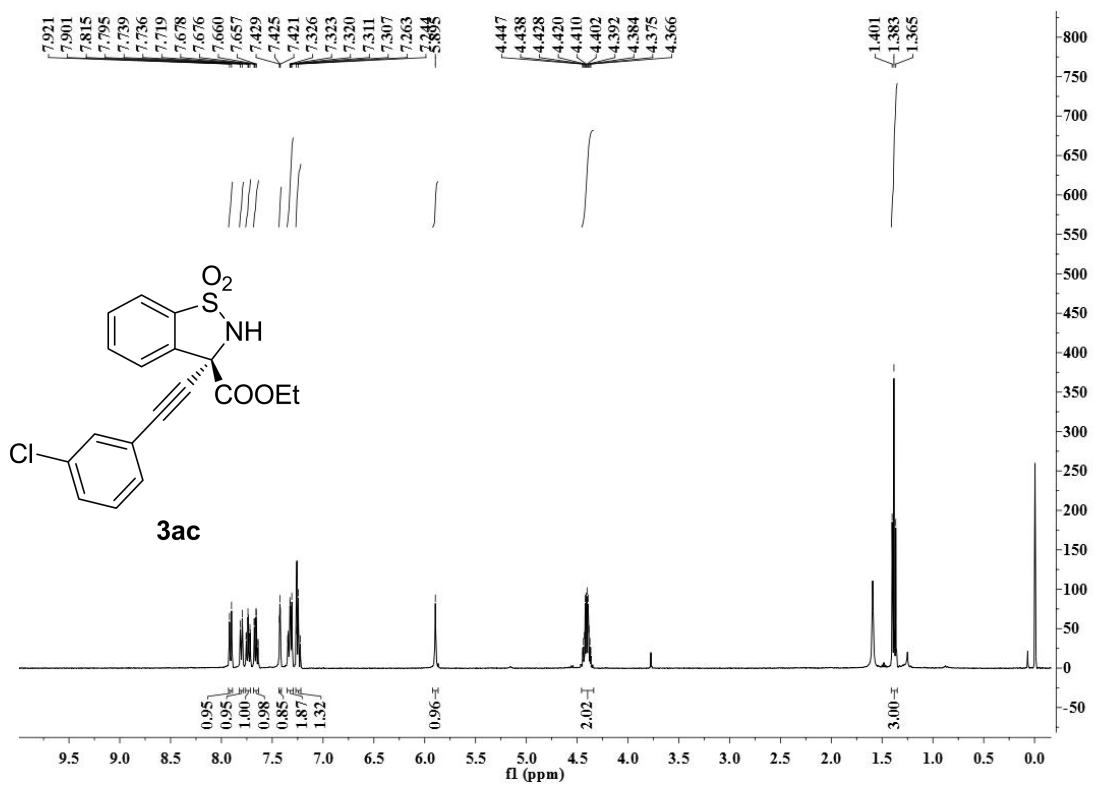


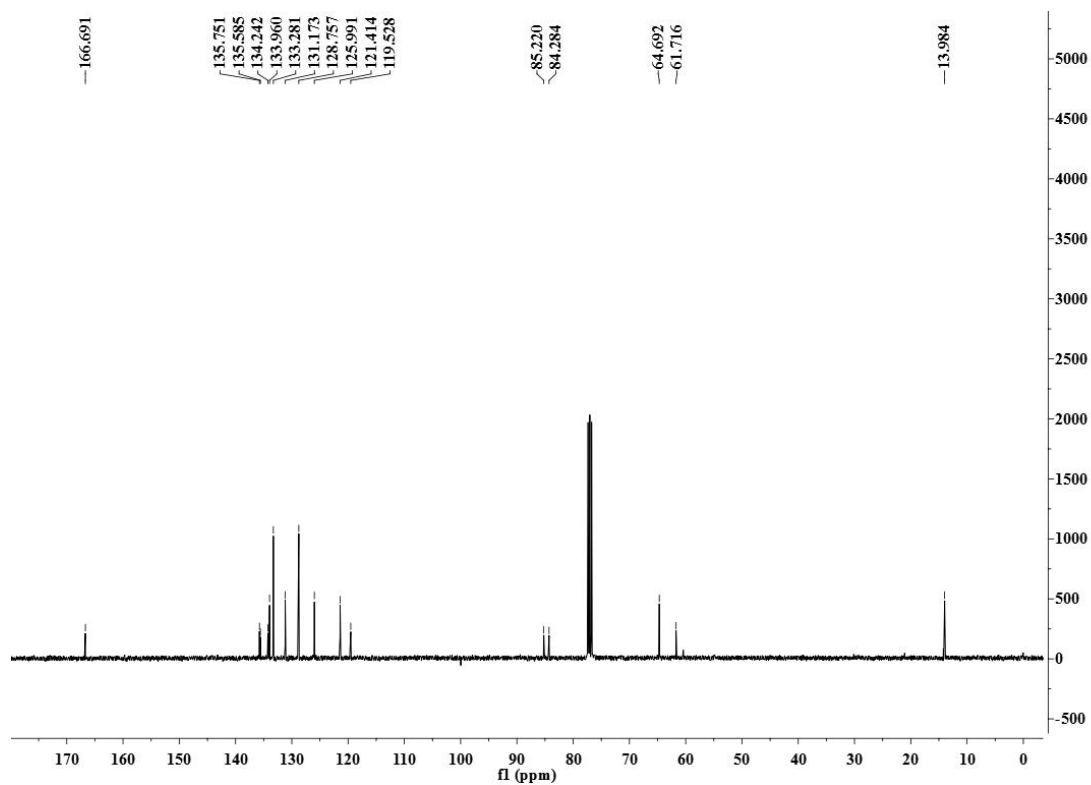
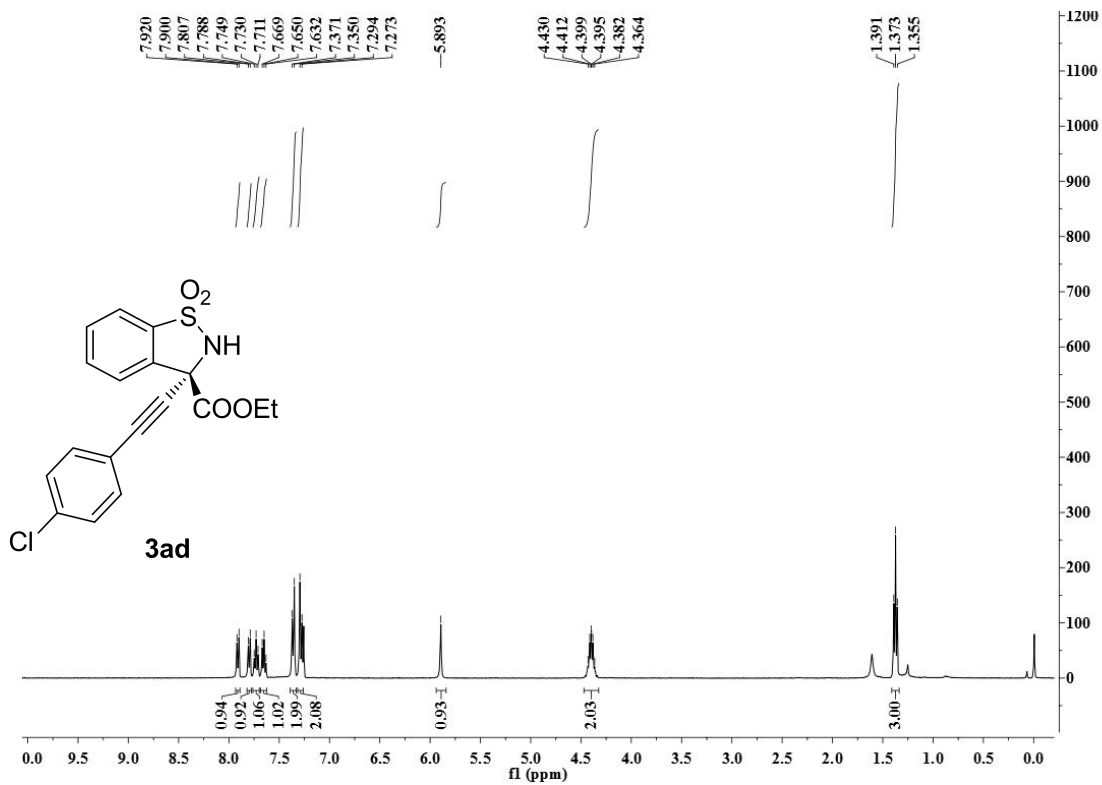


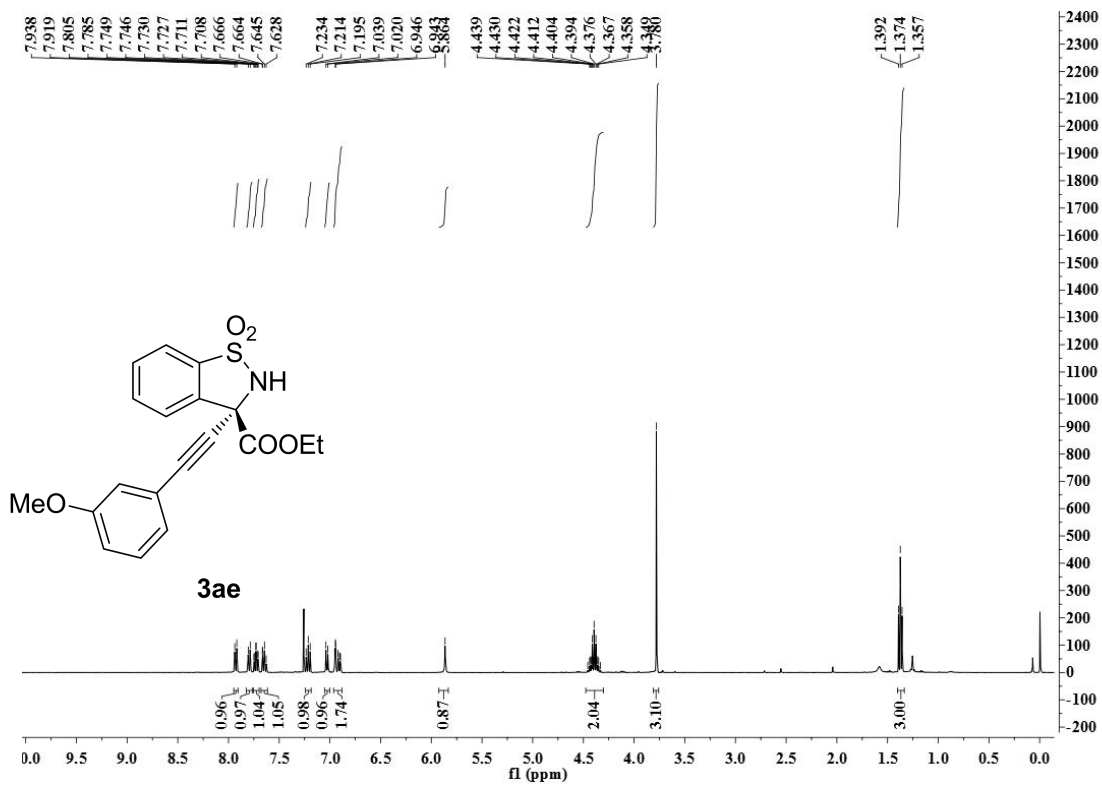


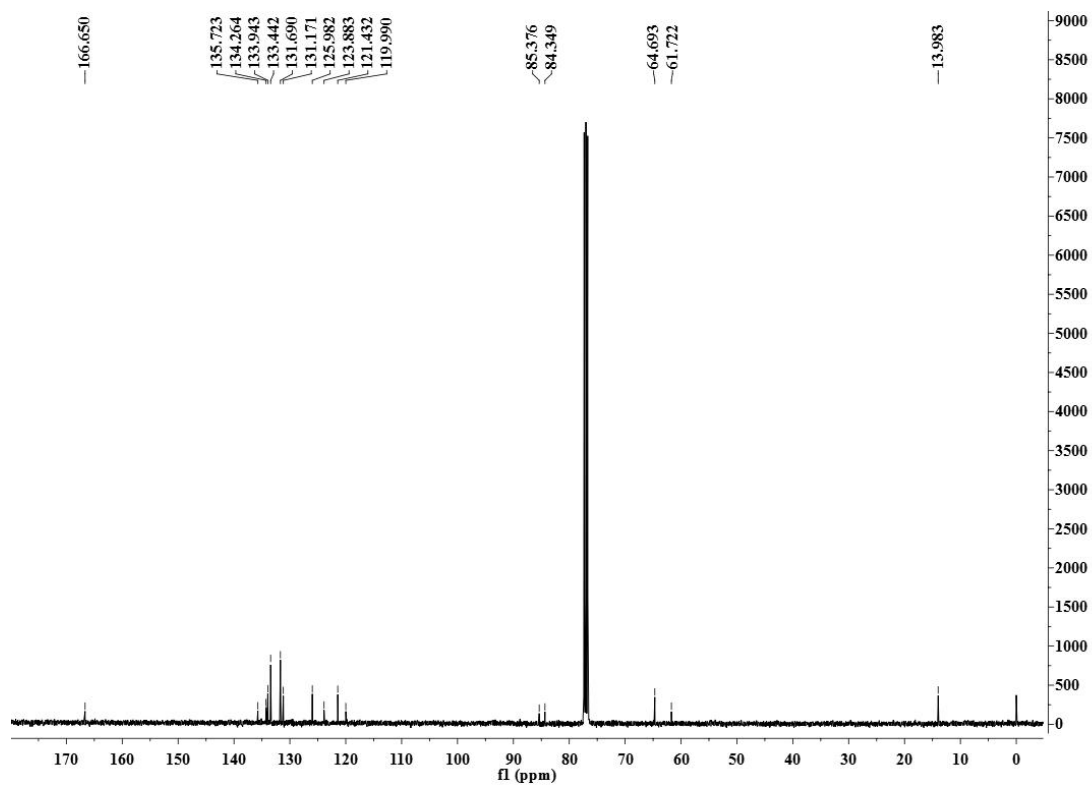
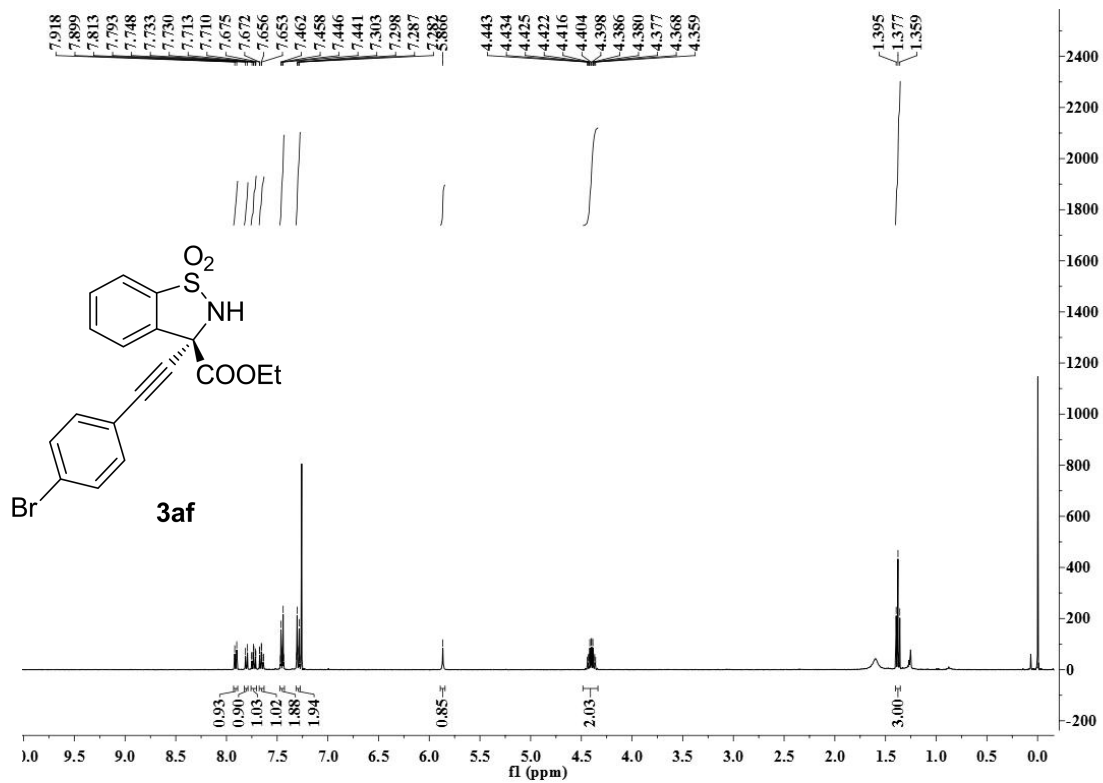


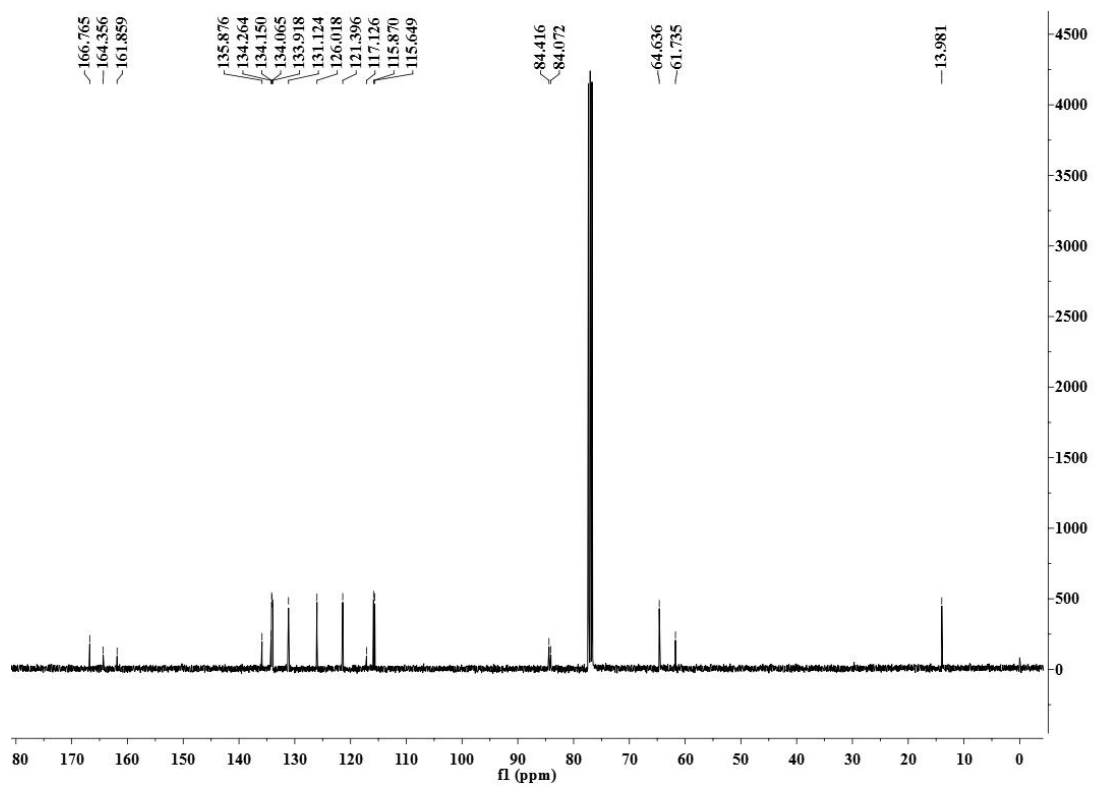
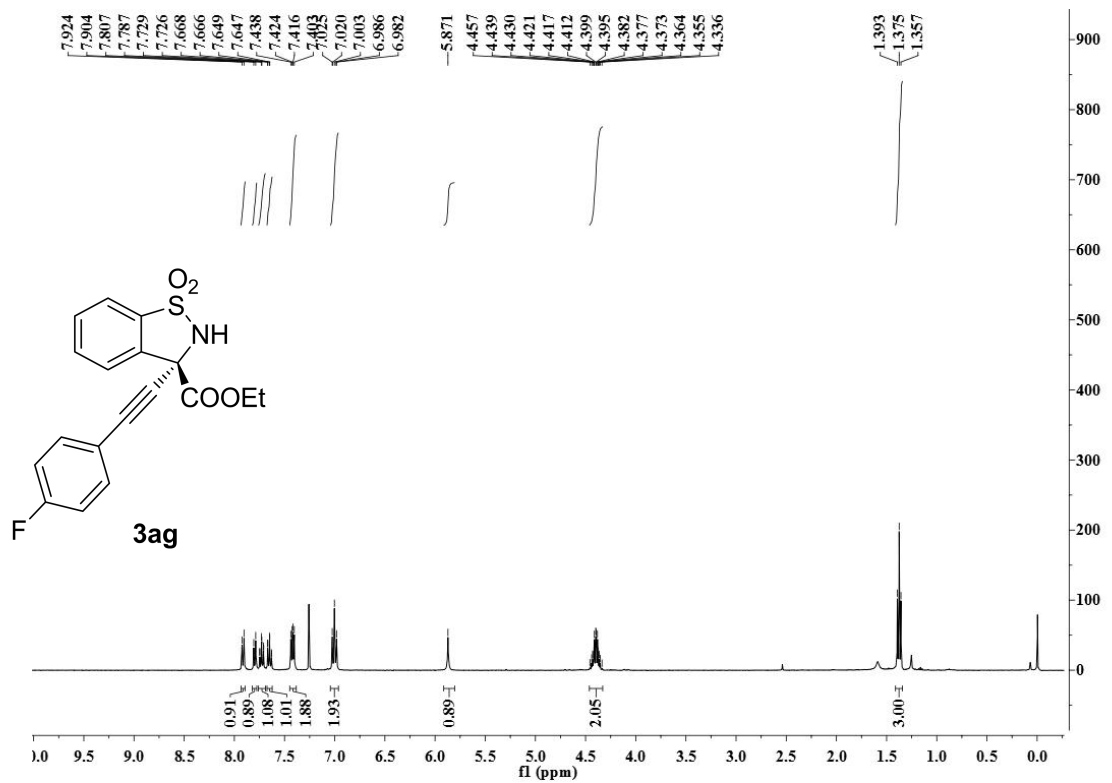


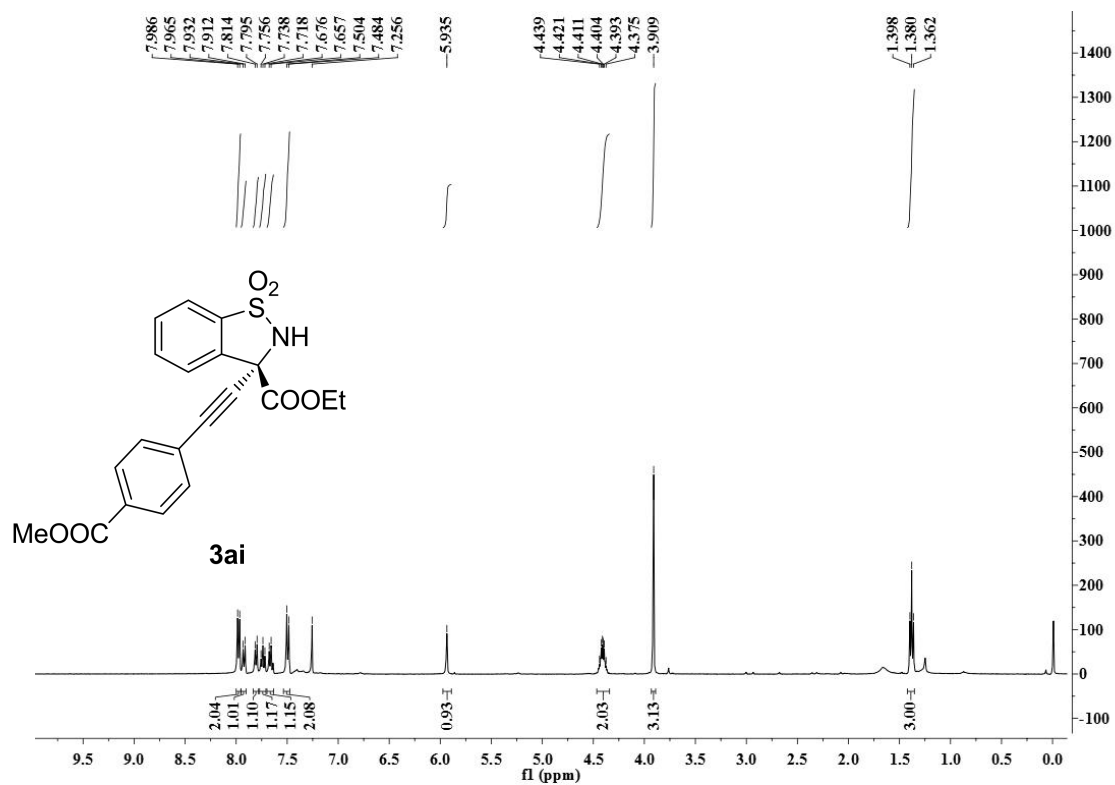
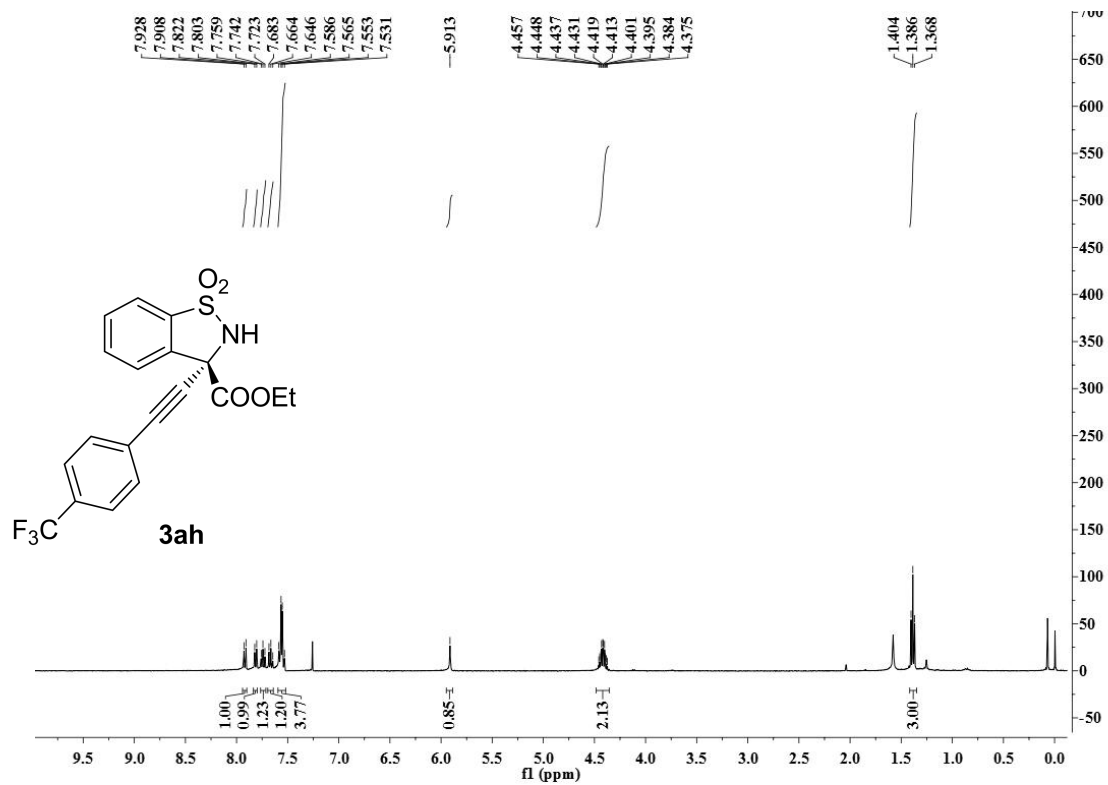


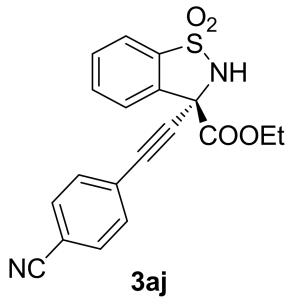
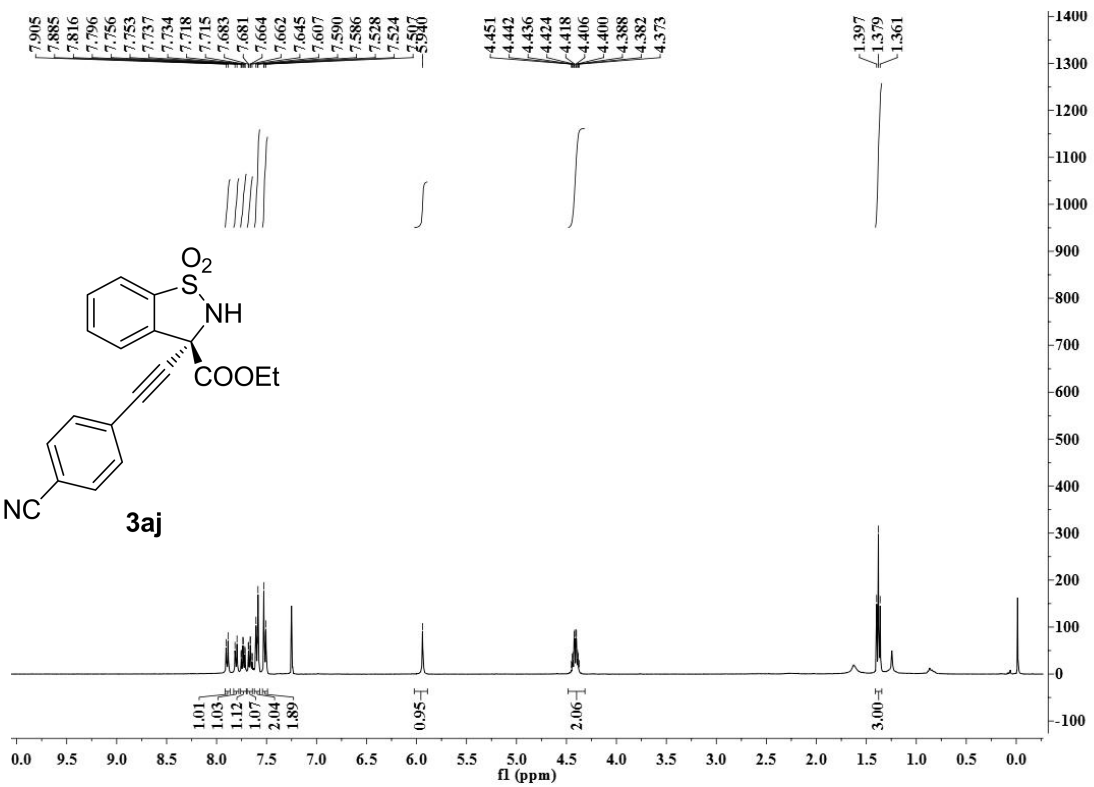
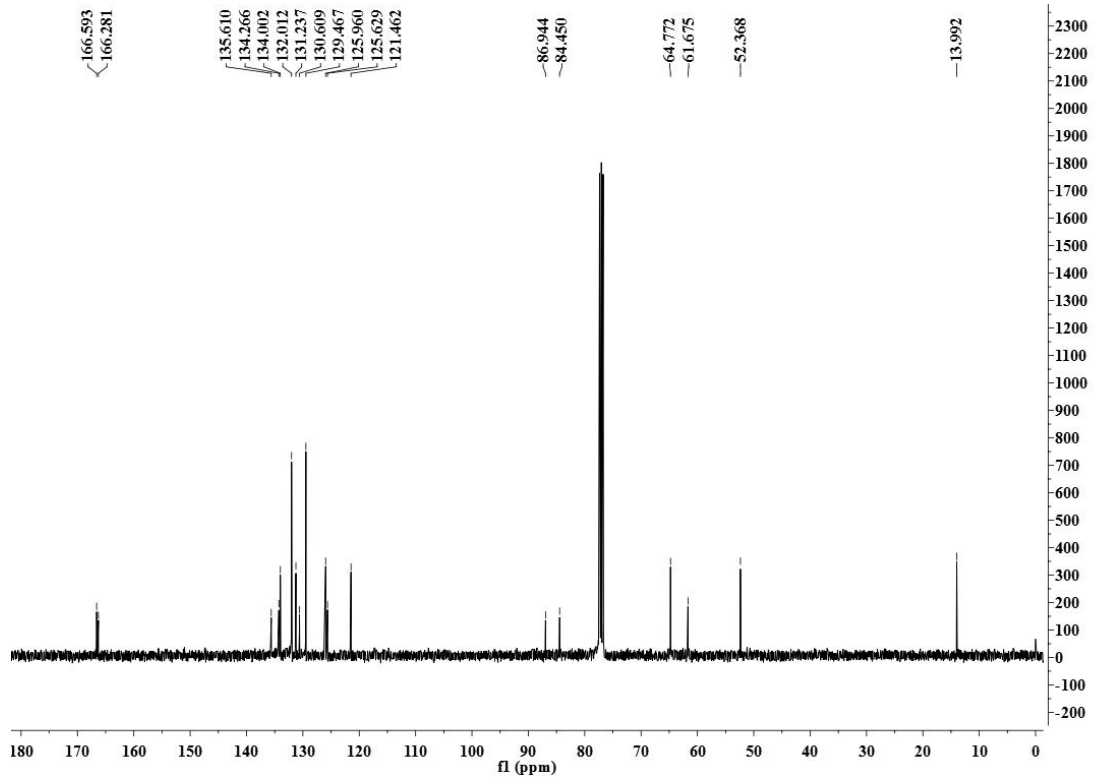


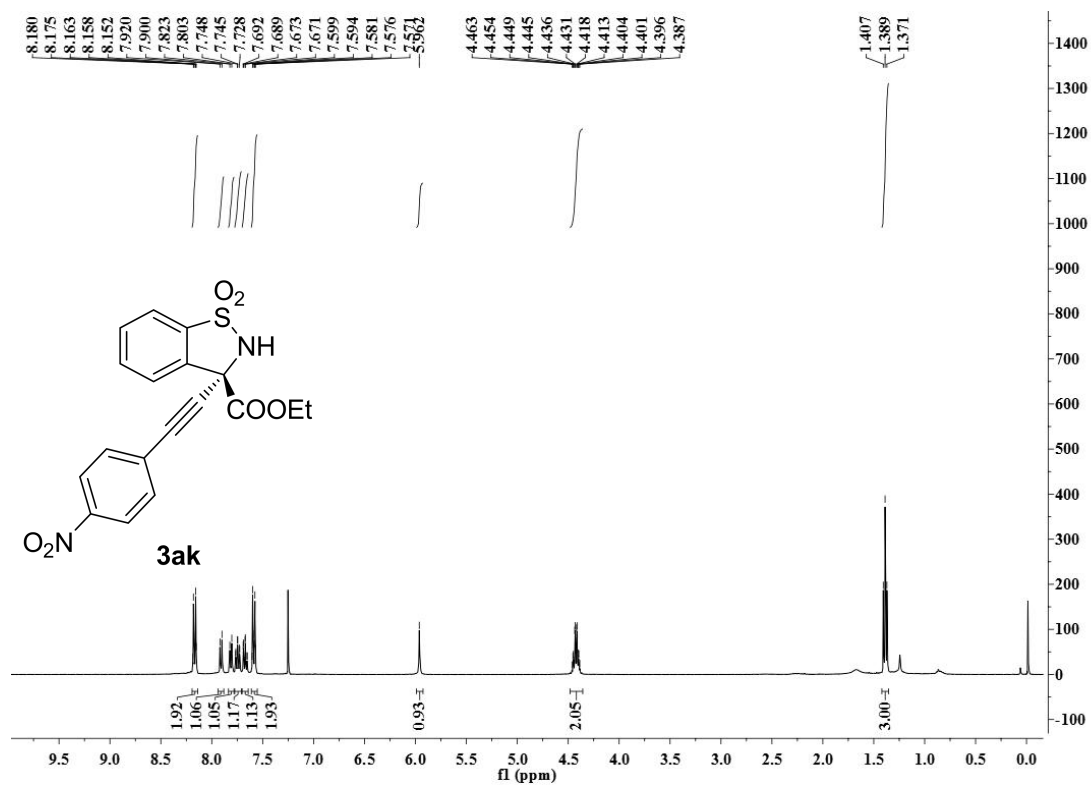
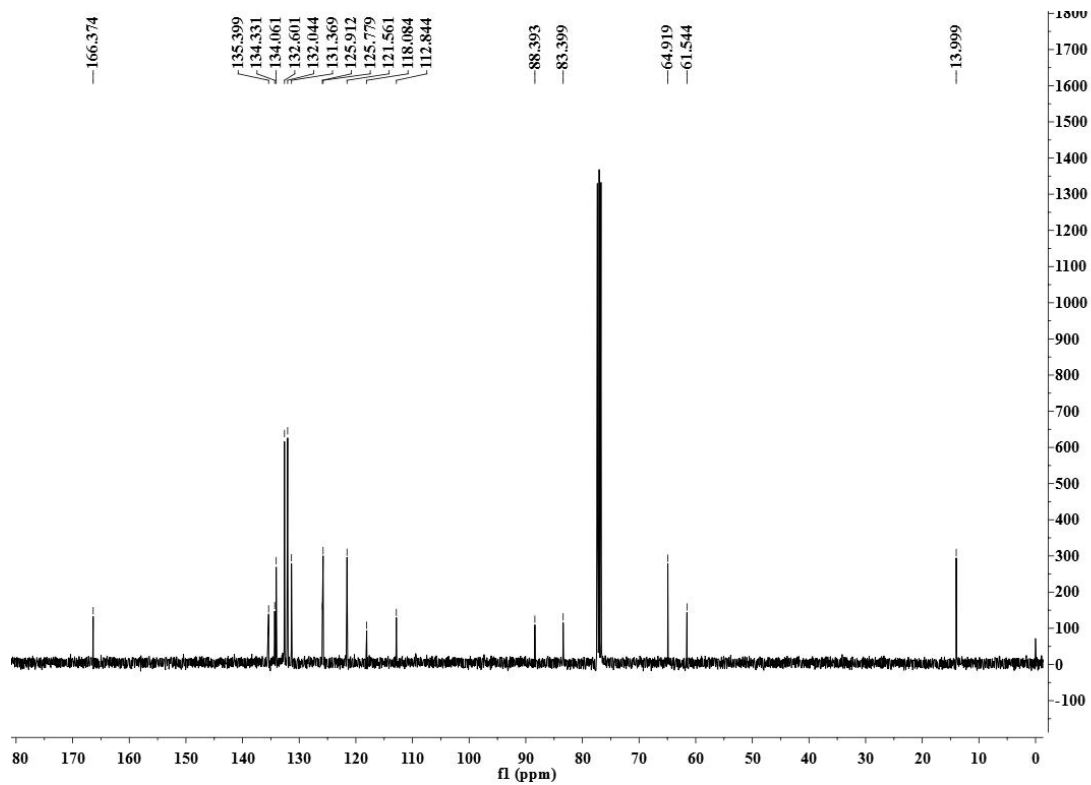


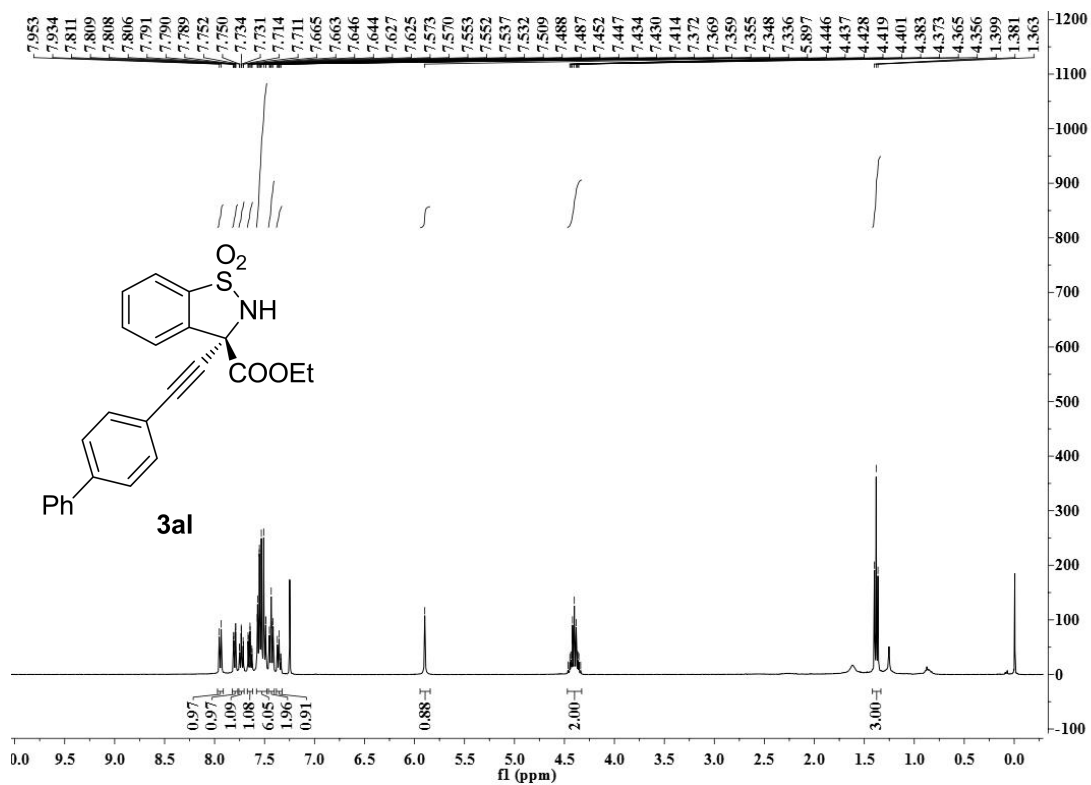
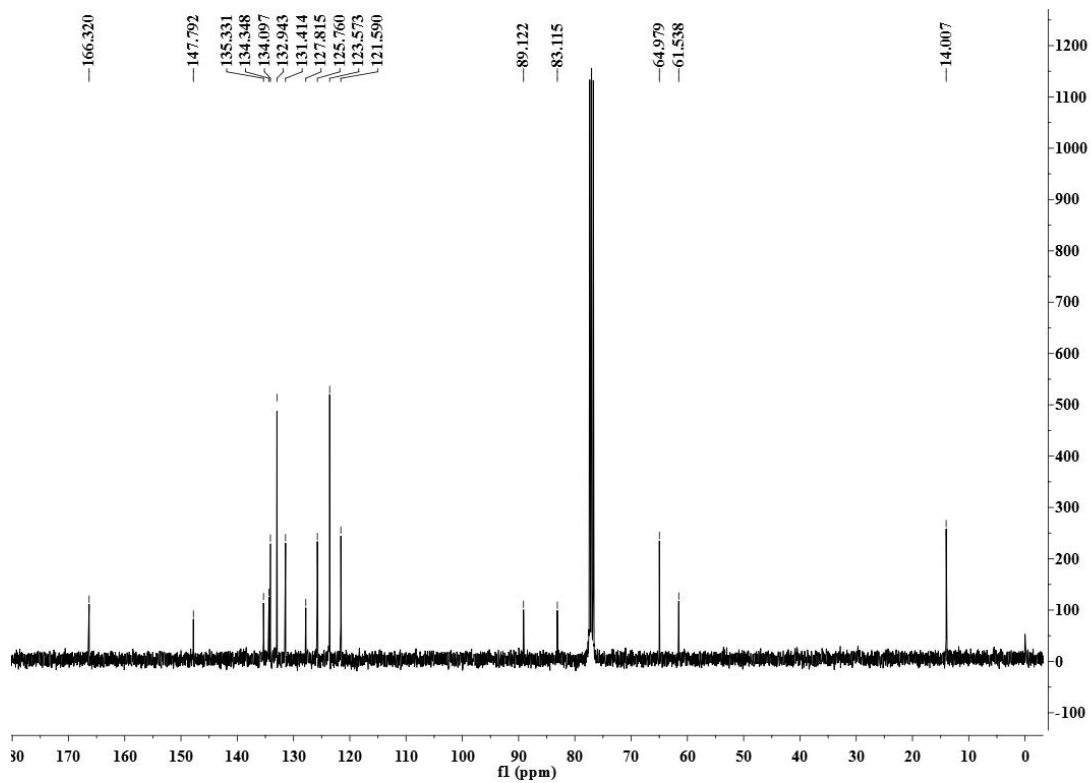


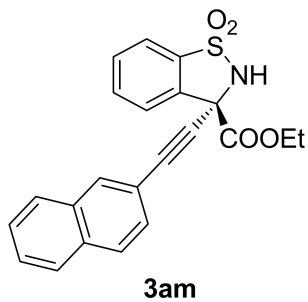
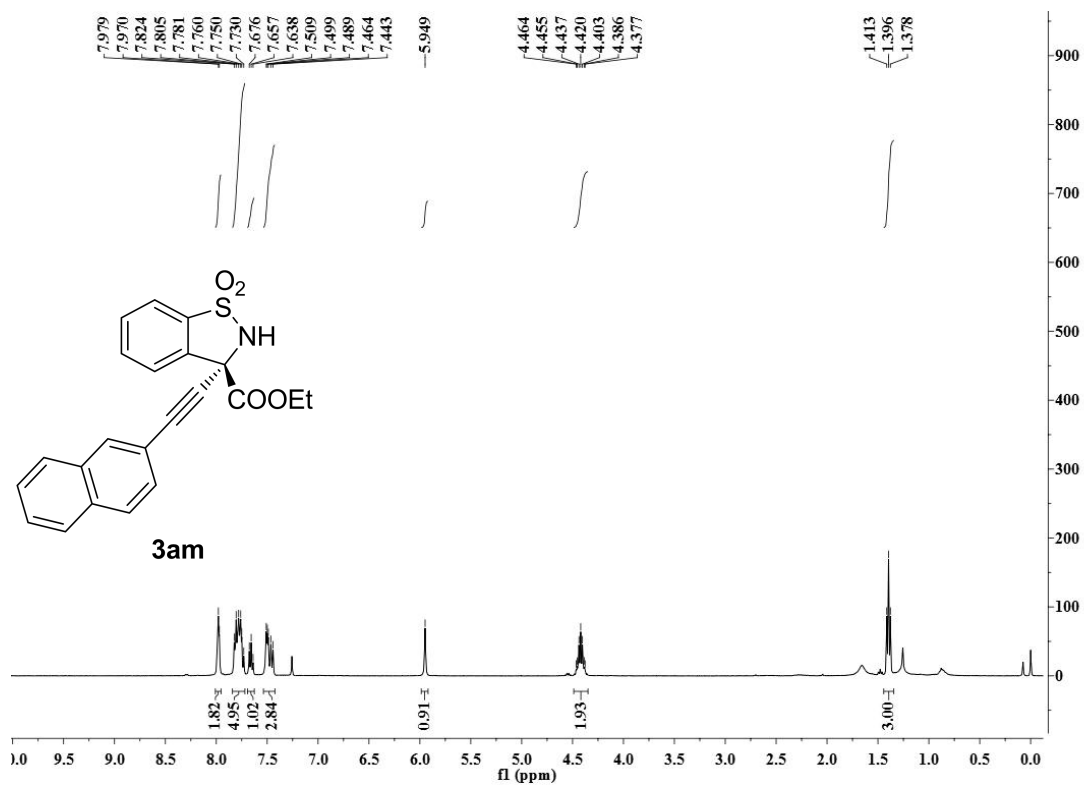
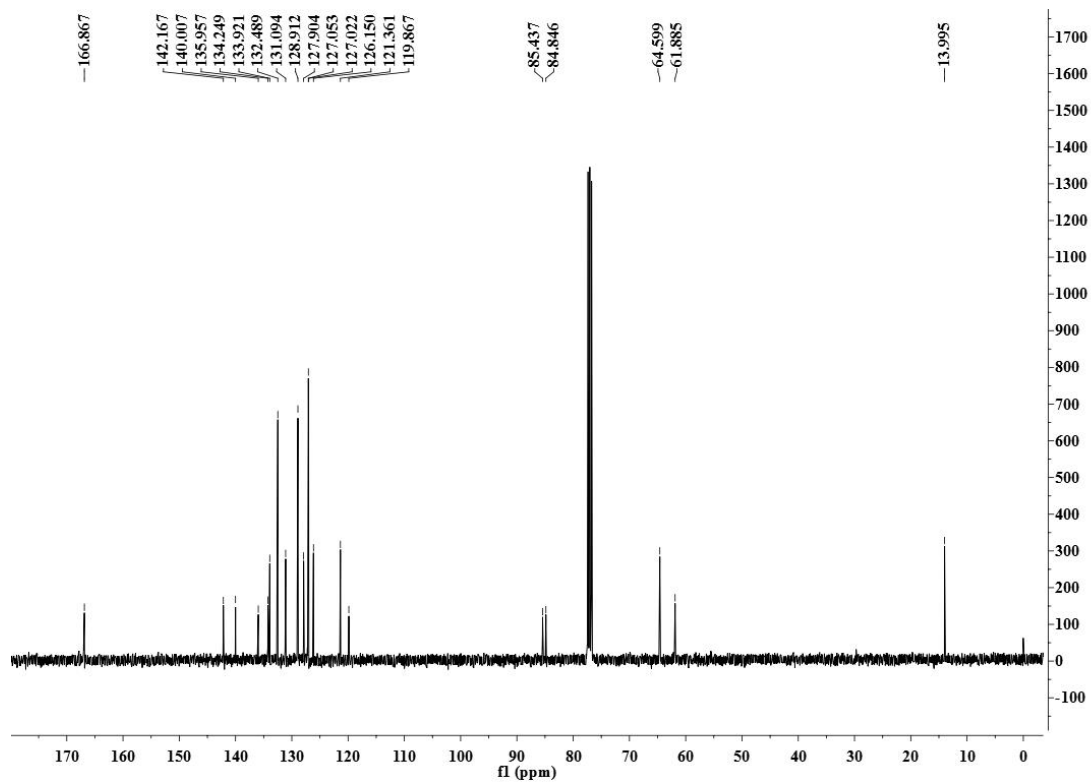


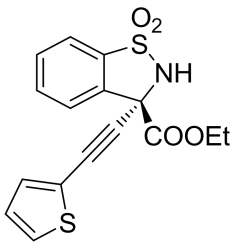
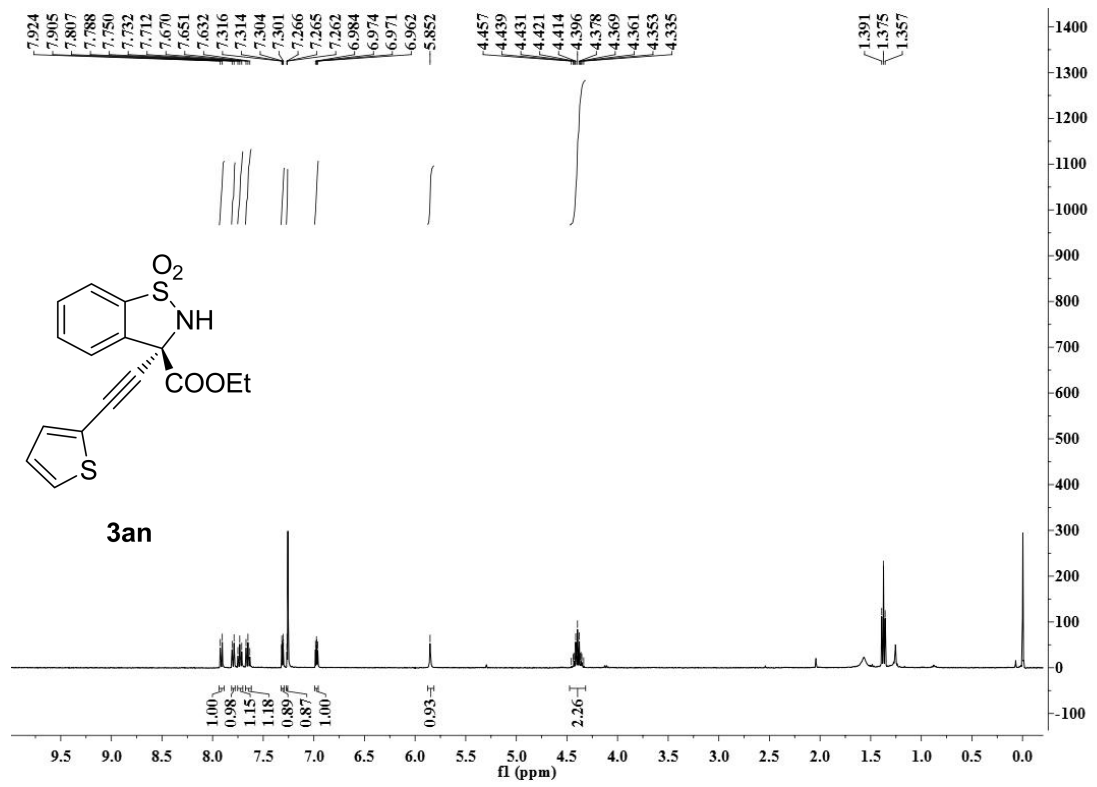
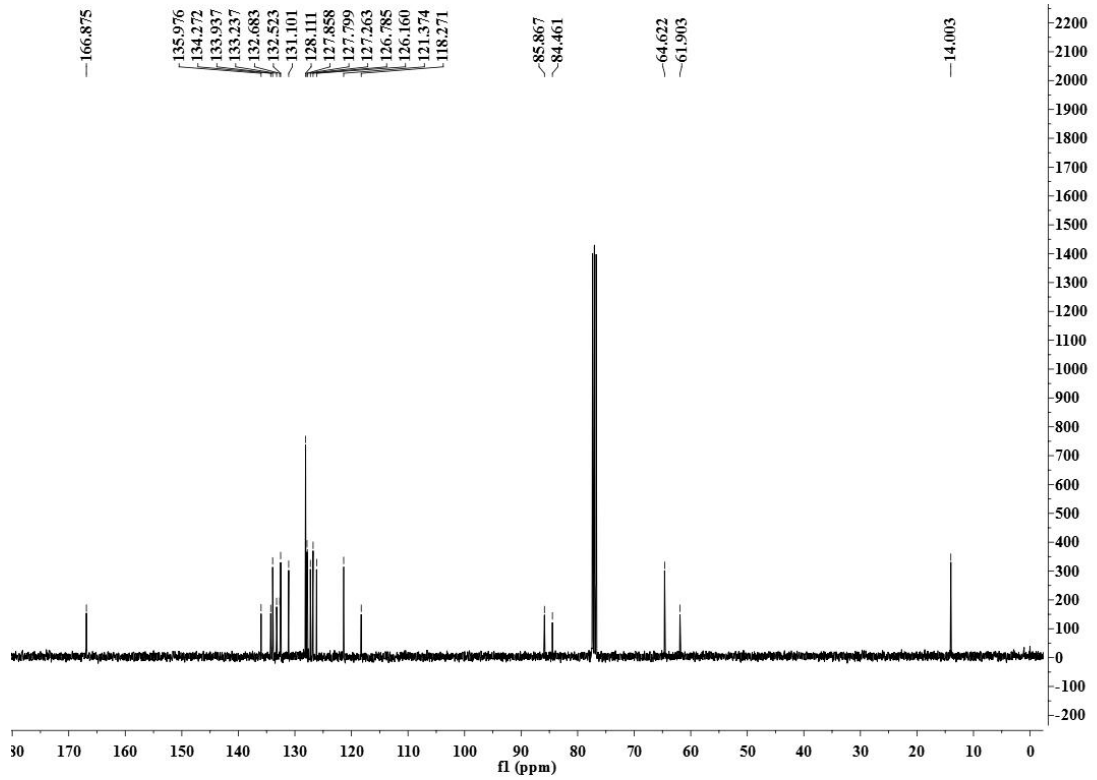












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