Supporting Information for:

Enantioselective [2+2] Cycloaddition of *N*-Allenamides with Cyclic *N*-Sulfonylketimines: Access to Polysubstituted Azetidines Bearing Quaternary Stereocenters

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Contents:

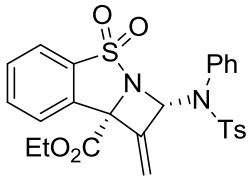
1. General information:

Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated by heating gun prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500MHz with TMS as internal standard. Anhydrous CH_2ClCH_2Cl were freshly distilled over calcium hydride. Melting points were measured on a Buchi Melting Point B-545 apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Agilent 6210 LCT (EI source) or Waters Xevo Q-Tof Mass Spectrometer (ESI source). Optical rotations were determined using a Rudolph Autopol IV polarimeter. HPLC analyses were performed using Waters 1525 chromatography. Chiralpak AD columns were purchased from Daicel Chemical Industries, LTD. Cellulose-2 column were purchased from Phenomenex. Flash column chromatography was carried out using silica gel (200-300 mesh). *N*-allenamides **1**[1] and **4**,[2] α-ketiminoesters **2**[3] and **6**[4] were synthesized according to the reported methods.

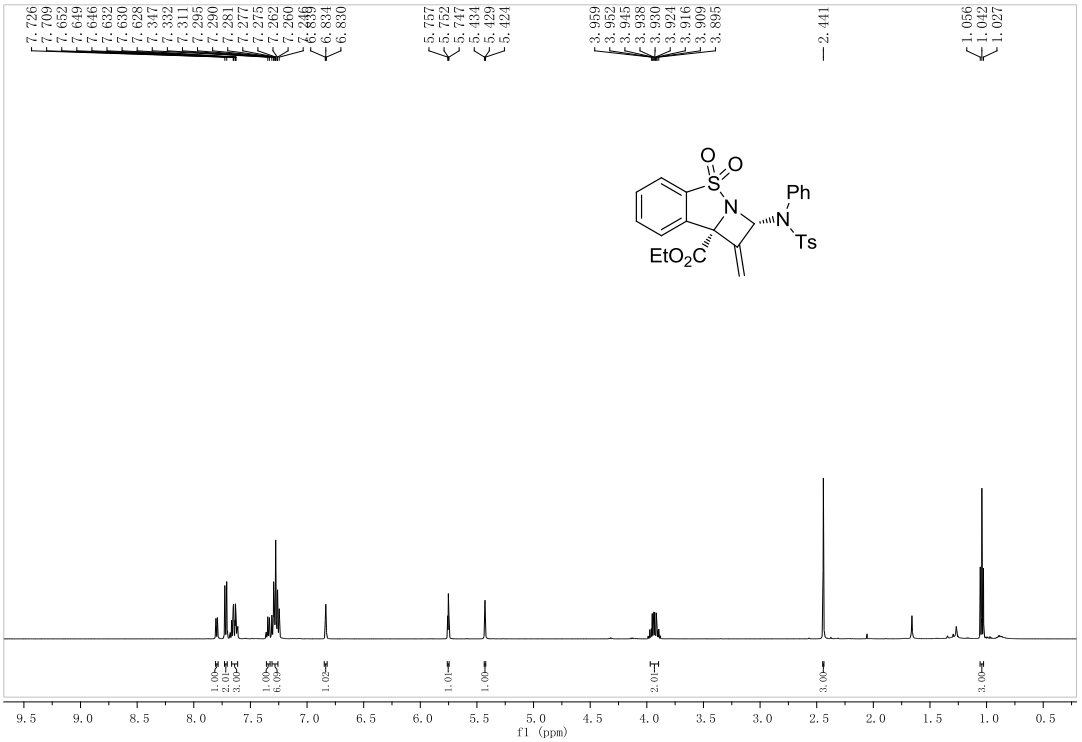
2. General procedure for asymmetric [2+2] cycloaddition reaction:

To a dried Schlenk tube was introduced activated 4Å molecular sieves (100 mg), $Ni(ClO_4)_2 \cdot H_2O$ (7.3 mg, 0.02 mmol), and **L4** (8.0 mg, 0.024 mmol) under N_2. 2.0 mL DCE was then added through a syringe. The resulting mixture was stirred at 25 °C for 1 h, after which cyclic *N*-sulfonyl α-ketiminoesters (0.2 mmol) and *N*-allenamides (0.3 mmol) were added under N_2. The mixture was stirred at 25 ℃ until the reaction was completed (monitored by TLC). The solvent was removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v) to afford the product.

Ethyl 2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3aa**)



Reaction time: 5 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; white solid, 82% yield, m.p. 130-132 ^{o}C, $[\alpha]_D^{15}$ = -4.0 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 51.1 min, t_{minor} = 47.0 min]; 1H NMR (500 MHz, $CDCl_3$): δ 7.78-7.81 (m, 1H), 7.70-7.73 (m, 2H), 7.60-7.67 (m, 3H), 7.32-7.35 (m, 1H), 7.26-7.32 (m, 6H), 6.83 (t, *J* = 2.5 Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.43 (t, *J* = 2.5 Hz, 1H), 3.89-3.96 (m, 2H), 2.44 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 144.2, 140.9, 136.3, 135.8, 135.6, 134.2, 134.1, 133.2, 131.0, 129.4, 129.0, 128.5, 128.4, 124.6, 122.3, 114.9, 80.1, 76.1, 62.5, 21.6, 13.8. HRMS m/z (ESI+): Calculated for $C_{26}H_{25}N_2O_6S_2$ ($[M+H]^+$) 525.1149, found 525.1148.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1.042
1.027
O
O
S
N
Ph
N
Ts
EtO2C
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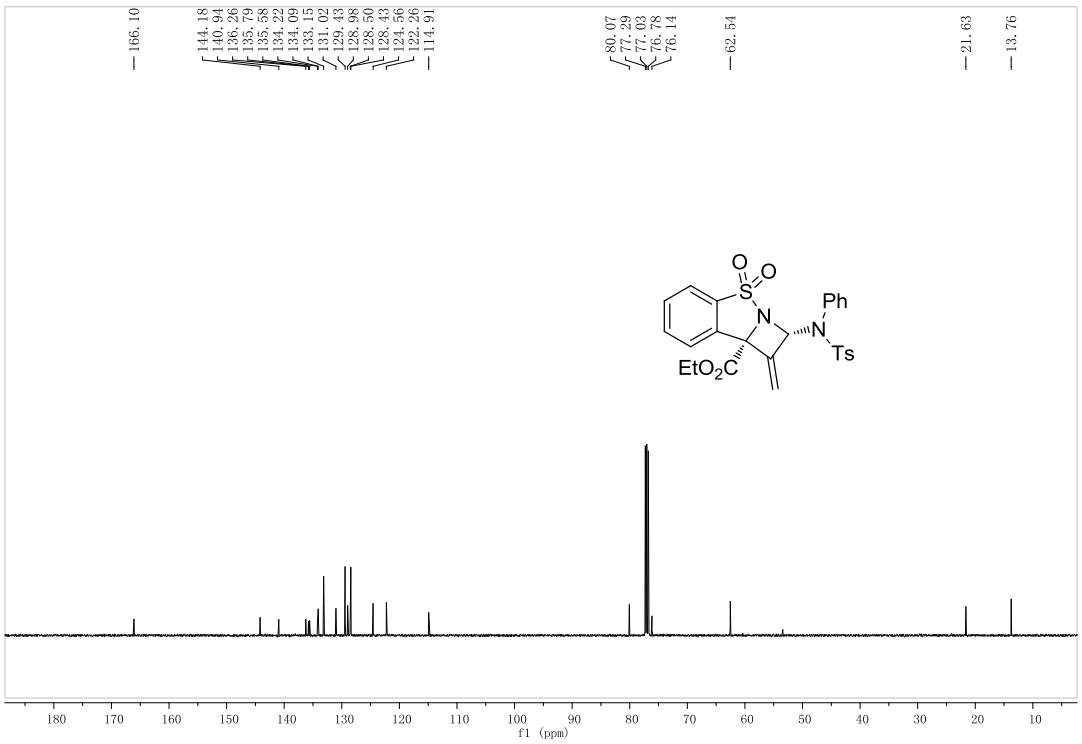
2.01
3.04
1.00
6.09
1.02
1.01
1.00
2.01
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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77.03
76.78
76.14
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S
N
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N
Ts
EtO2C
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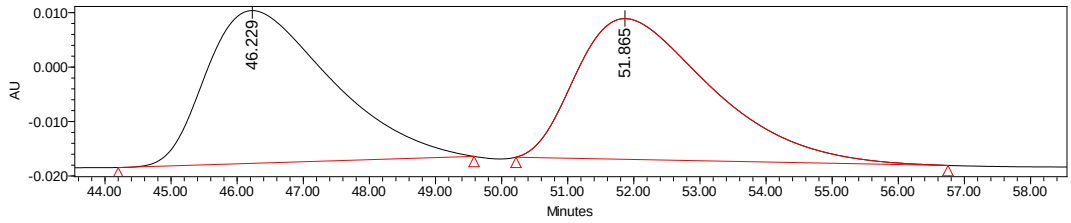
f1 (ppm)



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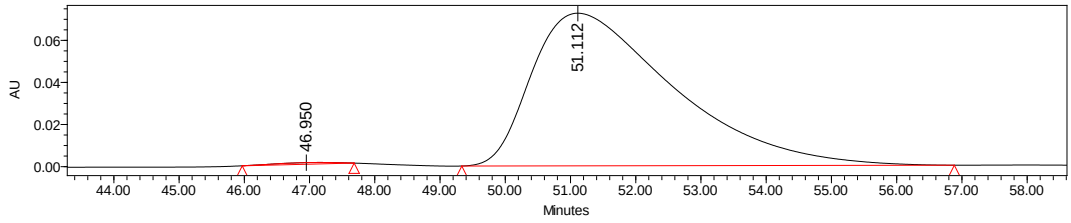
2	51.865	3667122	49.97	25837	47.94



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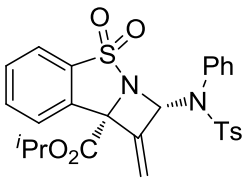
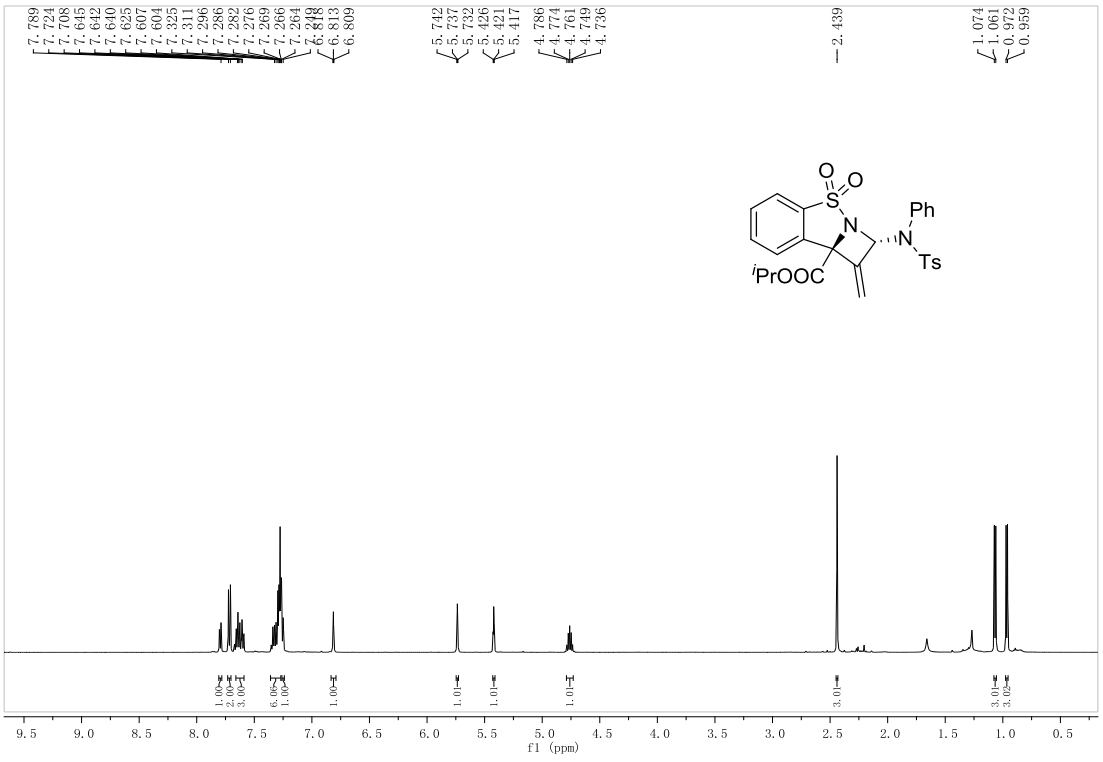
1	46.950	49012	0.45	778	1.06
2	51.112	10959179	99.55	72531	98.94

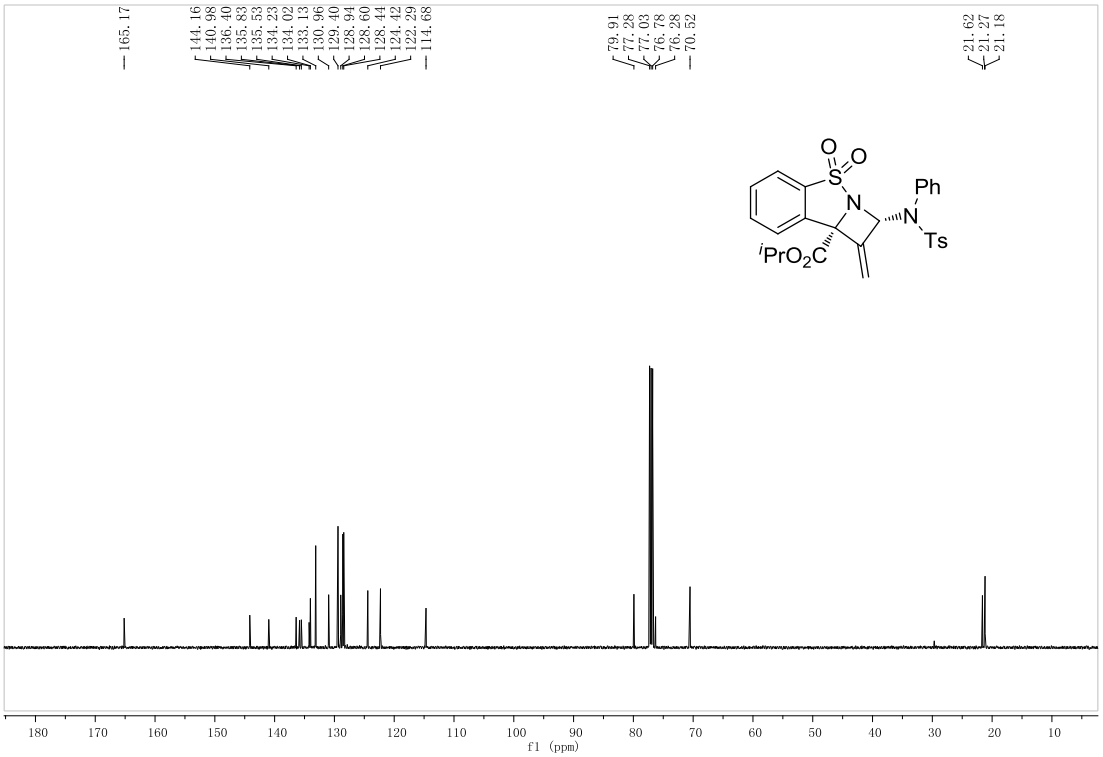
Isopropyl 2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ab**)

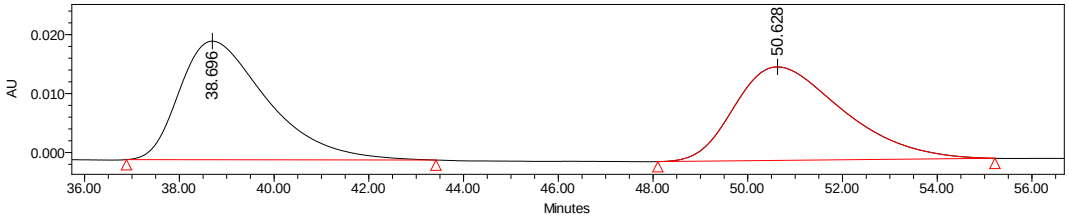


Reaction time: 5 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; light yellow solid, 75% yield, m.p. 110-112 ^{o}C, $[\alpha]_D^{15}$ = -1.2 (c =1.0 in CH_2Cl_2), 90% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 48.7 min, t_{minor} = 38.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.58-7.67 (m, 3H), 7.26-7.34 (m, 6H), 7.25 (t, *J* = 2.5 Hz, 1H), 6.81 (t, *J* = 2.5 Hz, 1H), 5.74 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.5 Hz, 1H), 4.76 (dt, *J* = 12.5, 6.0

Hz, 1H), 2.44 (s, 3H), 1.07 (d, J = 6.5 Hz, 3H), 0.97 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2, 144.2, 141.0, 136.4, 135.8, 135.5, 134.2, 134.0, 133.1, 131.0, 129.4, 128.9, 128.6, 128.4, 124.4, 122.3, 114.7, 79.9, 76.3, 70.5, 21.6, 21.3, 21.2. HRMS m/z (ESI+): Calculated for $C_{27}H_{27}N_2O_6S_2$ ($[M+H]^+$) 539.1305, found 539.1307.







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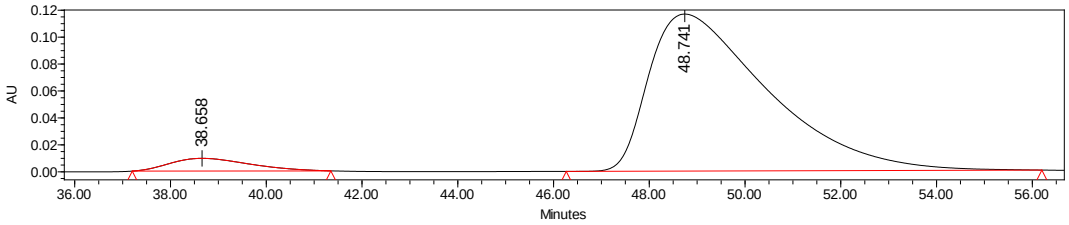

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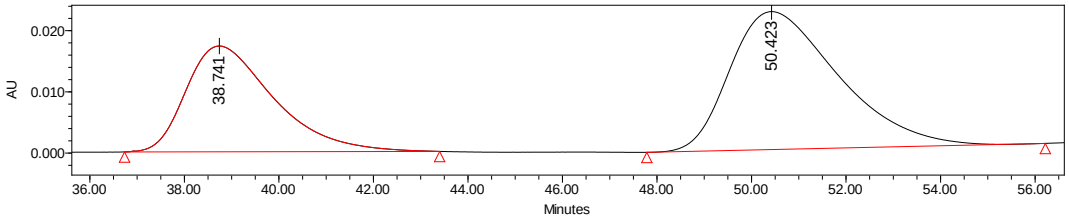
2	48.741	20124328	94.88	116576	92.52

Rac+Opt



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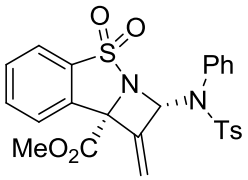
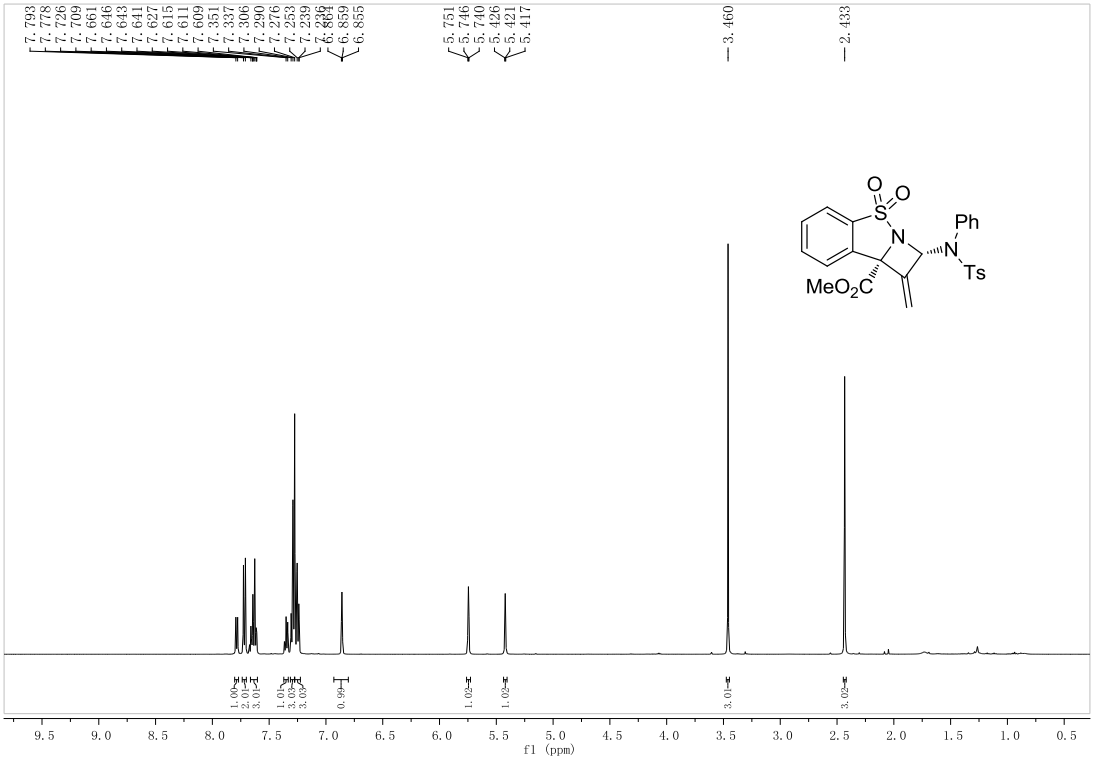
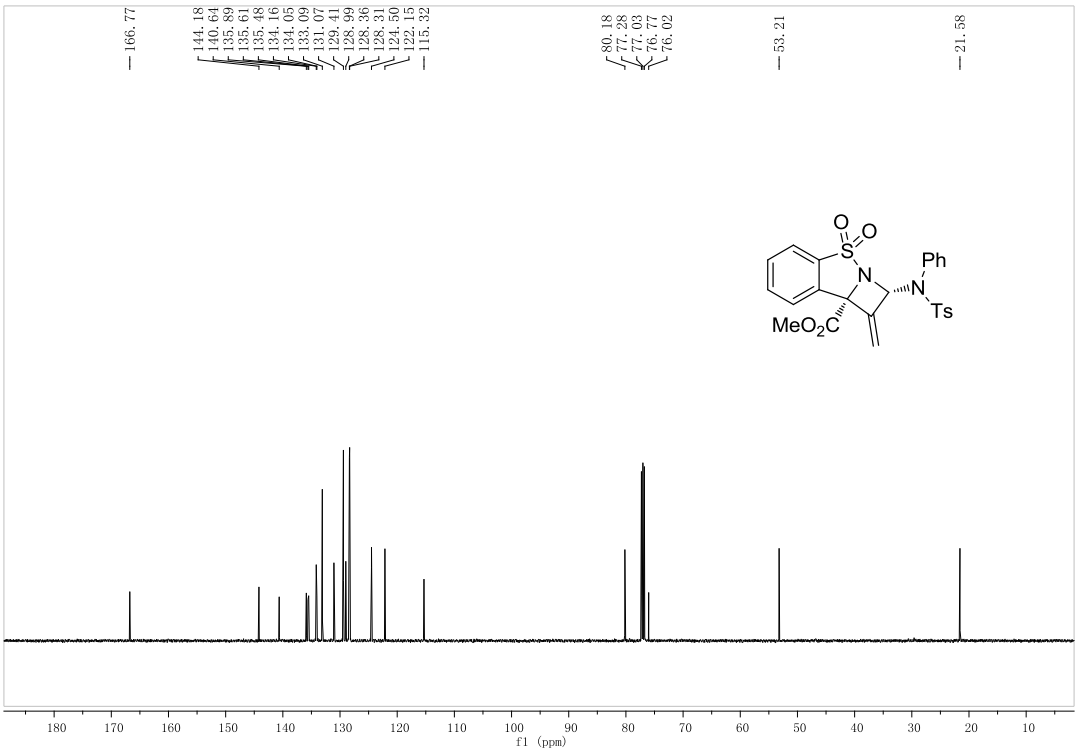
1	38.741	2221390	38.23	17281	43.39
2	50.423	3588826	61.77	22542	56.61

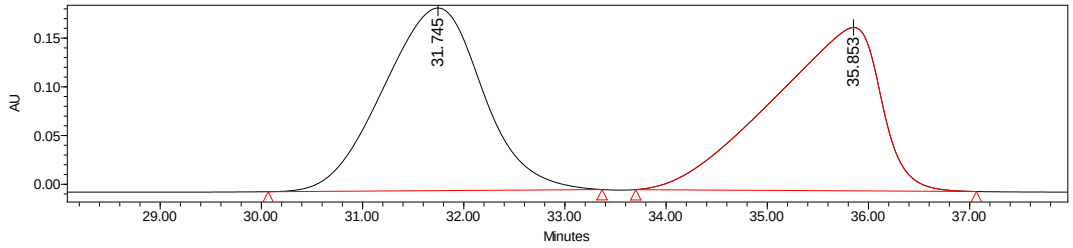
Methyl 2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ac**)



Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; light yellow solid, 76% yield, m.p. 152-154 ^{o}C, $[\alpha]_D^{15}$ = -6.4 (c =1.0 in CH_2Cl_2), 99% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 36.0 min, t_{minor} = 30.3 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.60-7.67 (m, 3H), 7.33-7.37 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 3H), 7.23-7.26 (m, 3H), 6.86 (t, *J* = 2.0 Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.0 Hz, 1H), 3.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 144.2, 140.6, 135.9, 135.6, 135.5, 134.2, 134.1, 133.1, 131.1, 129.4, 129.0, 128.4, 128.3, 124.5, 122.2, 115.3, 80.2, 76.0, 53.2, 21.6. HRMS m/z (ESI+): Calculated for $C_{25}H_{23}N_2O_6S_2$ ($[M+H]^+$) 511.0992, found 511.0997.







	Retention Time	Area	% Area	Height	% Height
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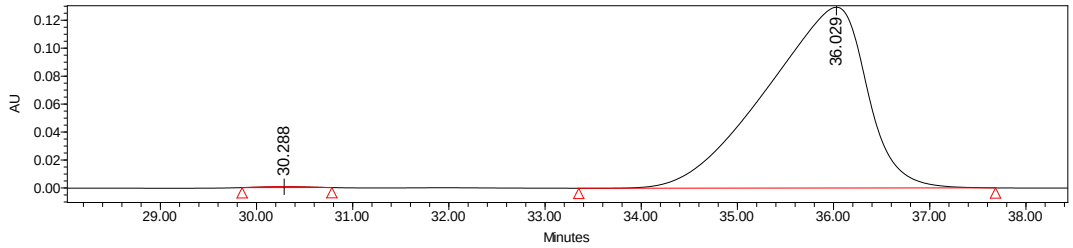
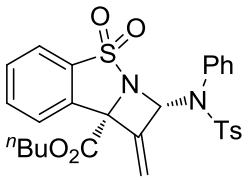
2	35.853	12487678	49.41	167584	47.25

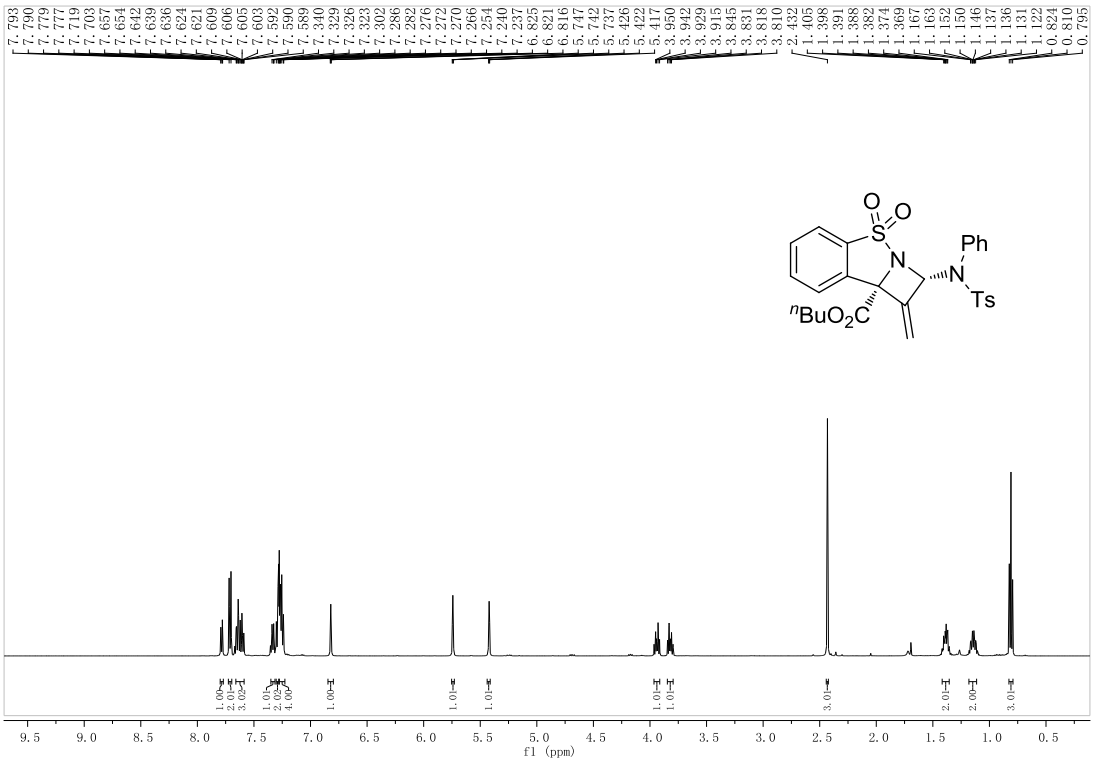


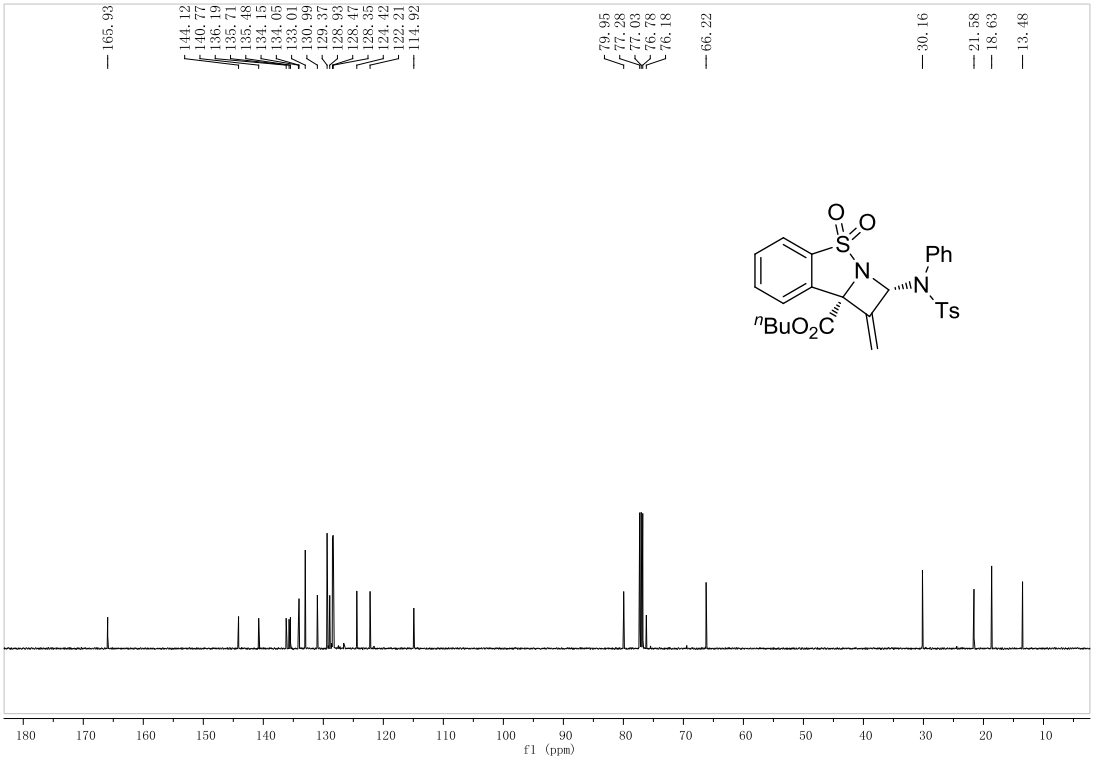
	Retention Time	Area	% Area	Height	% Height
1	30.288	21986	0.23	655	0.50
2	36.029	9434230	99.77	129358	99.50

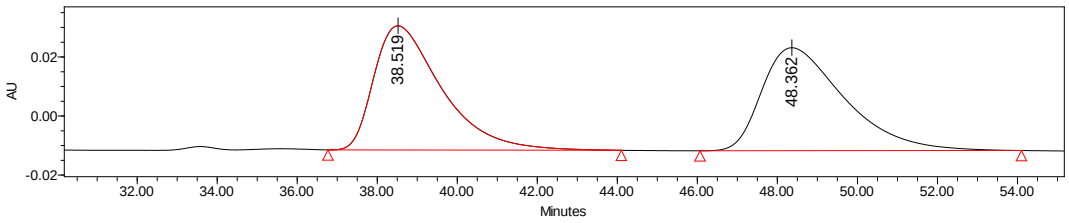
Butyl 2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ad**)



Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; colourless oil, 80% yield, $[\alpha]_D^{15}$ = -5.8 (c =1.0 in CH_2Cl_2), 98% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 46.1 min, t_{minor} =38.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.58-7.66 (m, 3H), 7.32-7.35 (m, 1H), 7.28-7.30 (m, 2H), 7.23-7.28 (m, 4H), 6.82 (t, *J* = 2.0 Hz, 1H), 5.74 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.0 Hz, 1H), 3.94 (dt, *J* = 10.5, 7.0 Hz, 1H), 3.82 (dt, *J* = 10.5, 7.0 Hz, 1H), 2.43 (s, 3H), 1.35-1.41 (m, 2H), 1.11-1.17 (m, 2H), 0.81 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 144.1, 140.8, 136.2, 135.7, 135.5, 134.2, 134.1, 133.0, 131.0, 129.4, 128.9, 128.5, 128.4, 124.4, 122.2, 114.9, 80.0, 76.2, 66.2, 30.2, 21.6, 18.6, 13.5. HRMS m/z (ESI+): Calculated for $C_{28}H_{29}N_2O_6S_2$ ($[M+H]^+$) 553.1462, found 553.1476.







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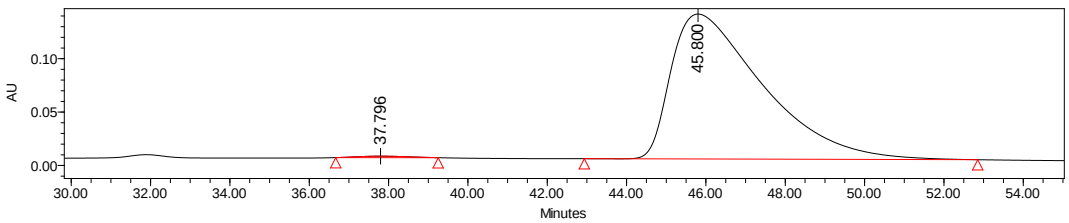
2	48.362	4995429	50.28	34875	45.34



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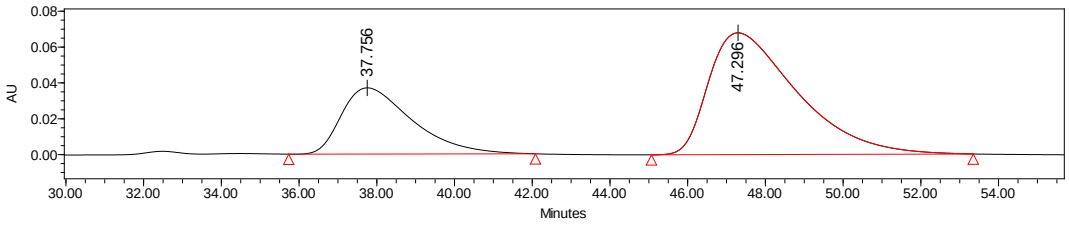
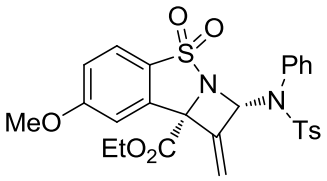
2	45.800	21780252	99.44	135733	99.00

Rac+Opt

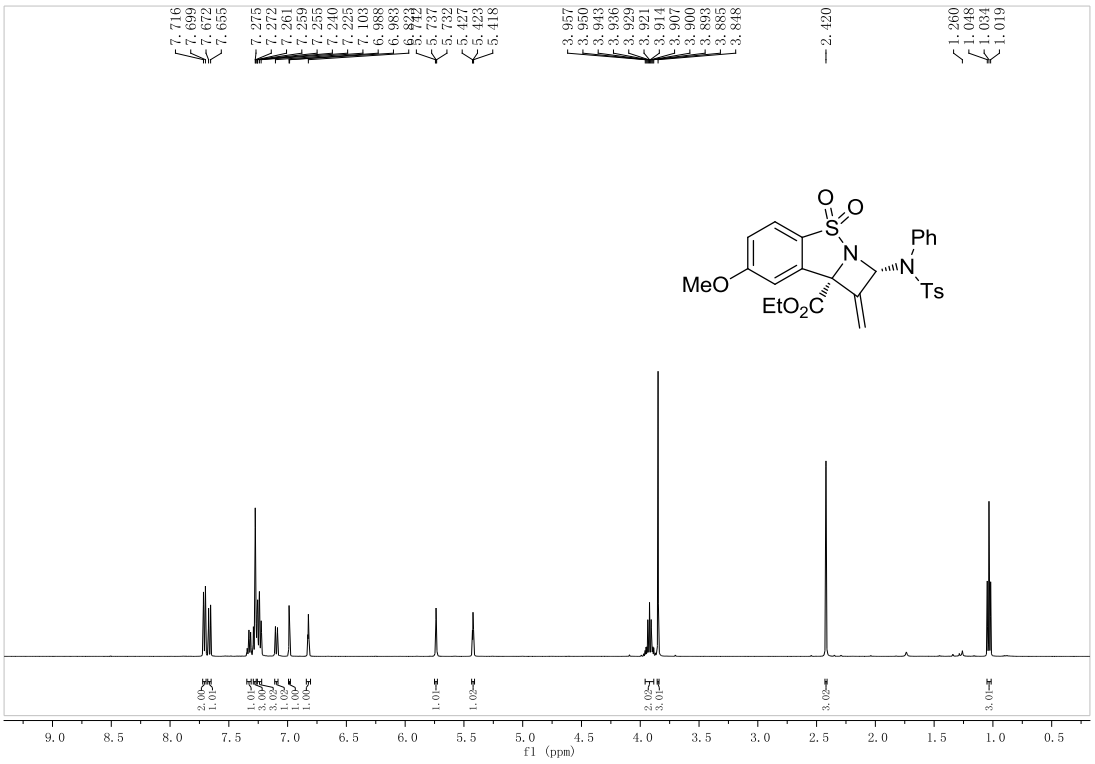


	Retention Time	Area	% Area	Height	% Height
1	37.756	4665690	30.29	36931	35.21
2	47.296	10740216	69.71	67946	64.79

Ethyl 7-methoxy-2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ae**)



Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.2; colourless oil, 77% yield, $[\alpha]_D^{15}$ = -7.4 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 70/30, 0.5 mL/min, 254 nm; t_{major} = 67.5 min, t_{minor} = 40.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.31-7.35 (m, 1H), 7.27-7.30 (m, 3H), 7.22-7.26 (m, 3H), 7.10 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.82 (t, *J* = 2.5 Hz, 1H), 5.74 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.0 Hz, 1H), 3.88-3.96 (m, 2H), 3.85 (s, 3H), 2.42 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 164.3, 144.1, 140.9, 138.7, 135.5, 134.2, 133.1, 129.3, 128.9, 128.4, 128.3, 127.7, 123.5, 117.9, 114.8, 108.2, 80.0, 75.6, 62.4, 56.0, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{27}H_{27}N_2O_7S_2$ ($[M+H]^+$) 555.1254, found 555.1249.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N
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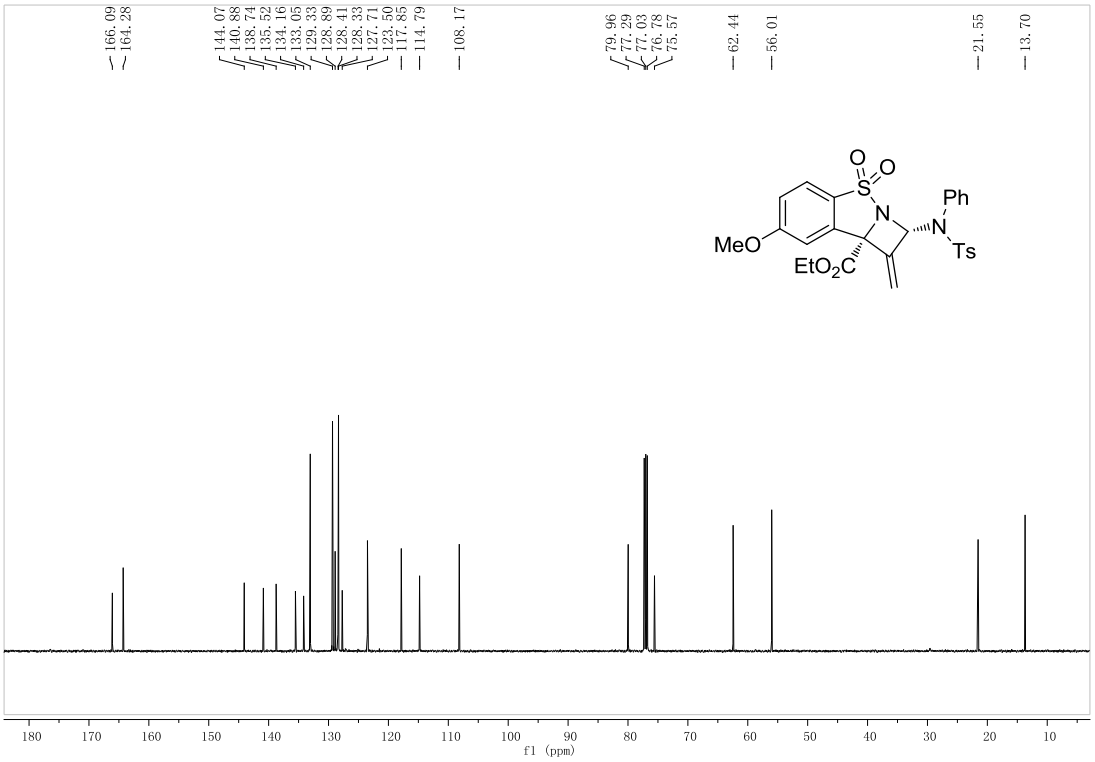
EtO2C
f1 (ppm)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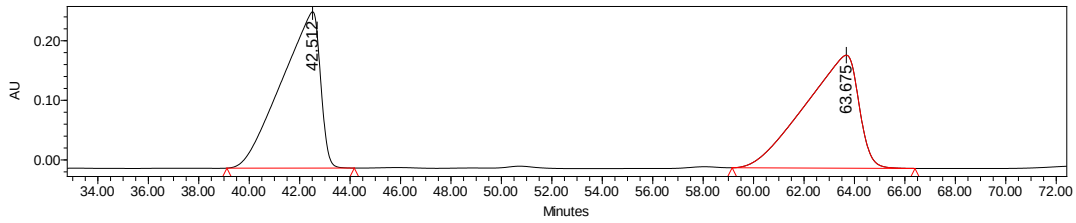
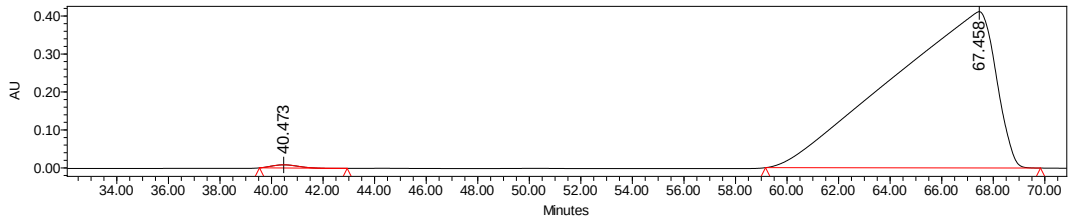
144.07
140.88
138.74
135.52
134.16
133.05
129.33
128.89
128.41
128.33
127.71
123.50
117.85
114.79
108.17
79.96
77.29
77.03
76.78
75.57
62.44
56.01
21.55
13.70
O
O
S
N
Ph
N
Ts
MeO
EtO2C
f1 (ppm)

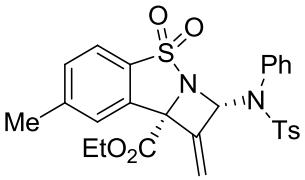


	Retention Time	Area	% Area	Height	% Height
1	42.512	28046048	49.84	262358	58.06
2	63.675	28223684	50.16	189537	41.94



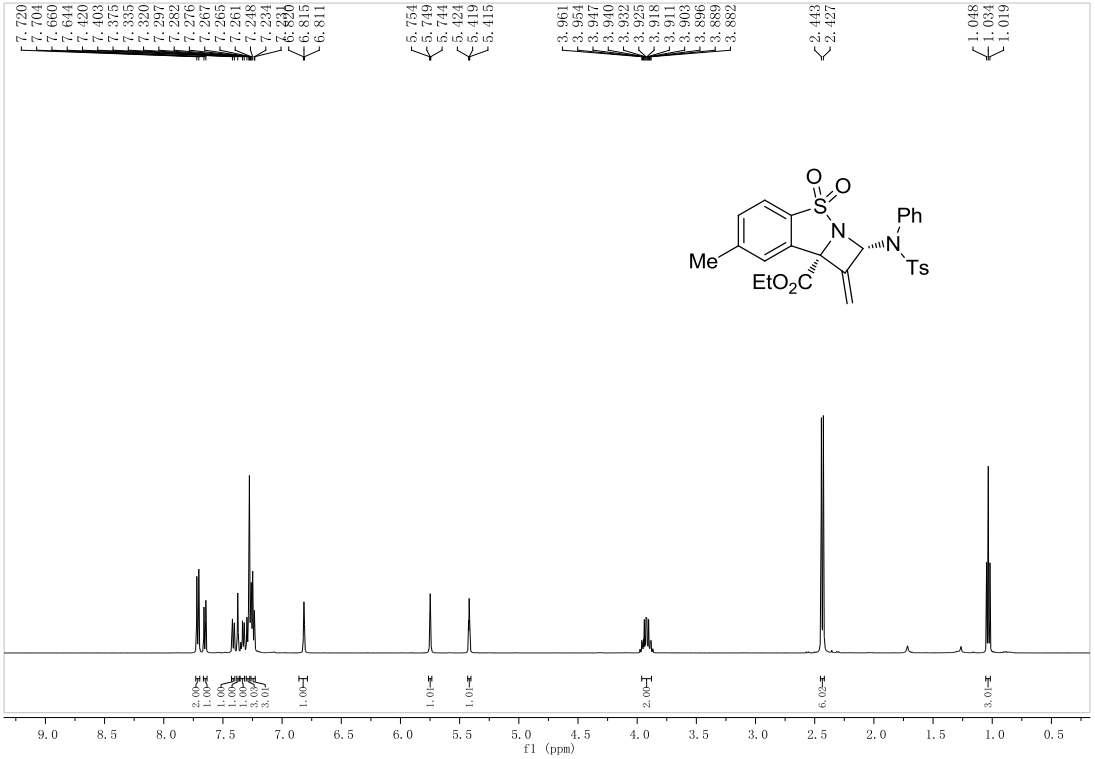
	Retention Time	Area	% Area	Height	% Height
1	40.473	549558	0.47	8142	1.94
2	67.458	116200465	99.53	411839	98.06

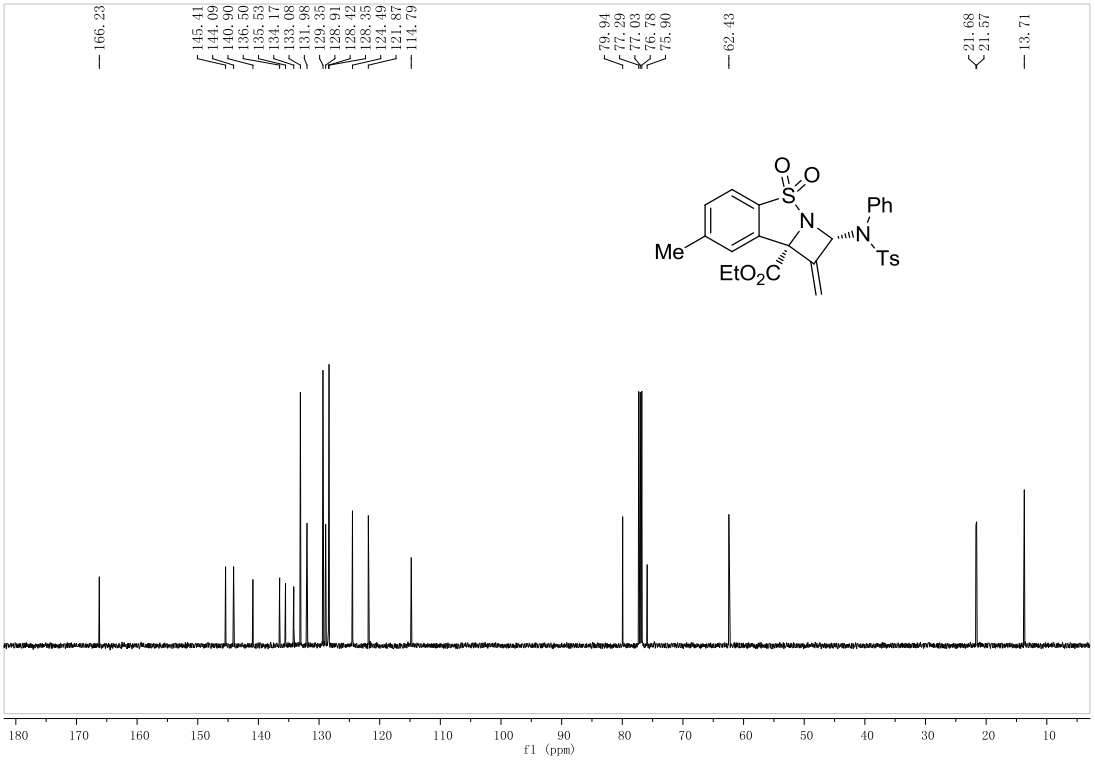
Ethyl 7-methyl-2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide **(3af)**

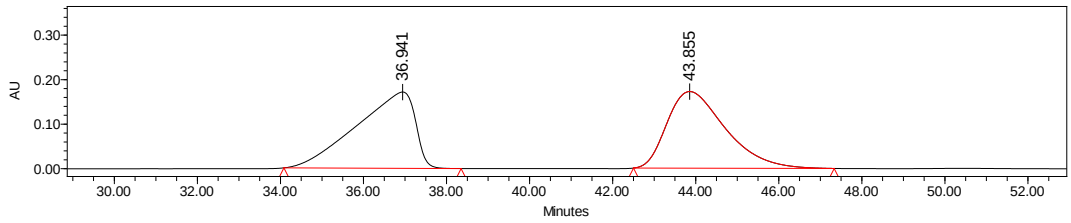


Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; colourless oil, 73% yield, $[\alpha]_D^{15}$ = -3.2 (c =1.0 in CH_2Cl_2), 97% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 43.8 min, t_{minor} = 36.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.37 (s, 1H), 7.31-7.35 (m, 1H), 7.27-7.30 (m, 3H), 7.27-7.30 (m, 3H), 6.82 (t, *J* = 2.5 Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.5 Hz, 1H), 3.88-

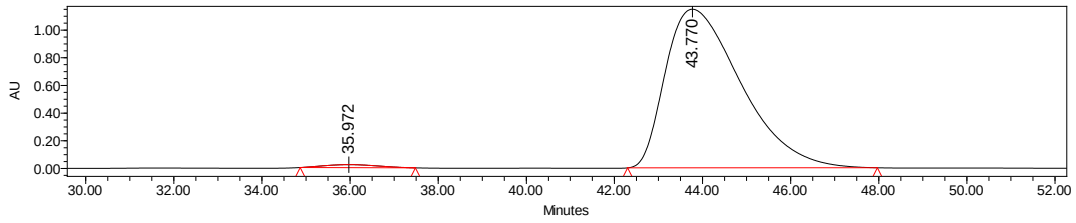
3.97 (m, 2H), 2.44 (d, J = 8.0 Hz, 6H), 1.03 (t, J = 7.0Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 145.4, 144.1, 140.9, 136.5, 135.5, 134.2, 133.1, 132.0, 129.4, 128.9, 128.4, 128.3, 124.5, 121.9, 114.8, 79.9, 75.9, 62.4, 21.7, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{27}H_{27}N_2O_6S_2$ ([M+H]$^+$) 539.1305, found 539.1304.





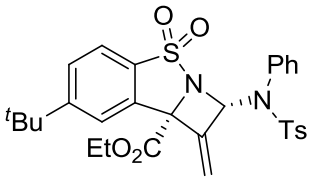


	Retention Time	Area	% Area	Height	% Height
1	36.941	17120808	50.13	172115	49.85
2	43.855	17034593	49.87	173120	50.15



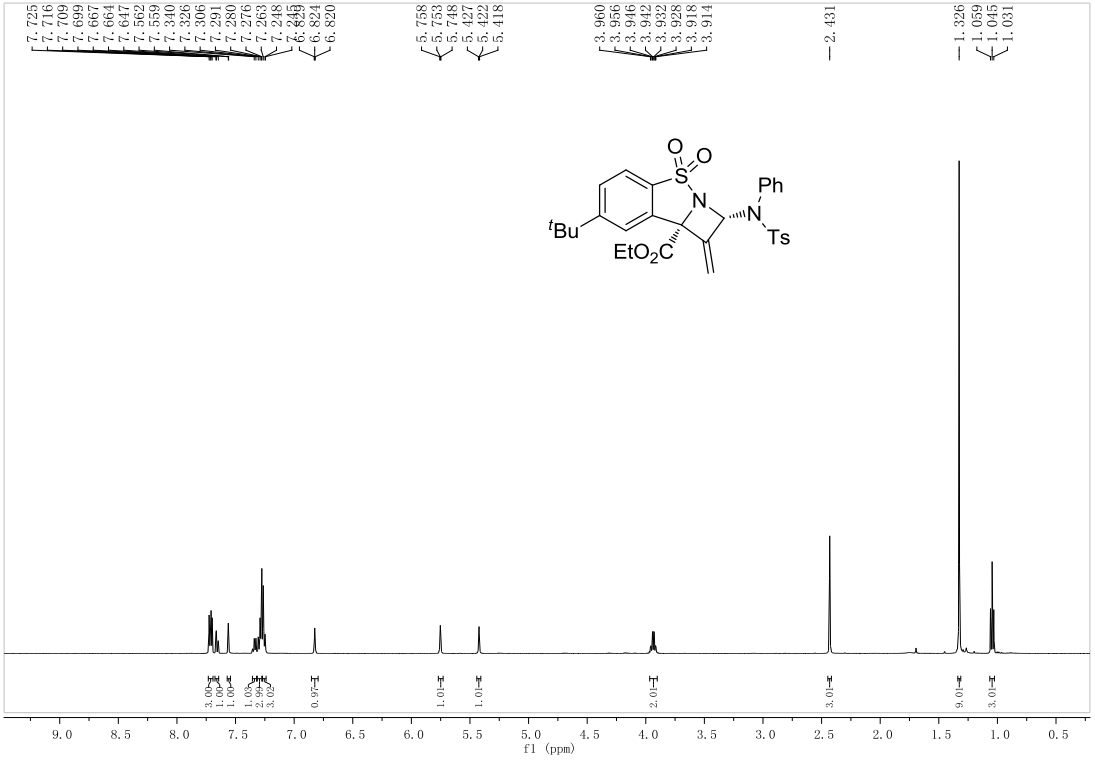
	Retention Time	Area	% Area	Height	% Height
1	35.972	1986316	1.42	22933	1.96
2	43.770	137587016	98.58	1149333	98.04

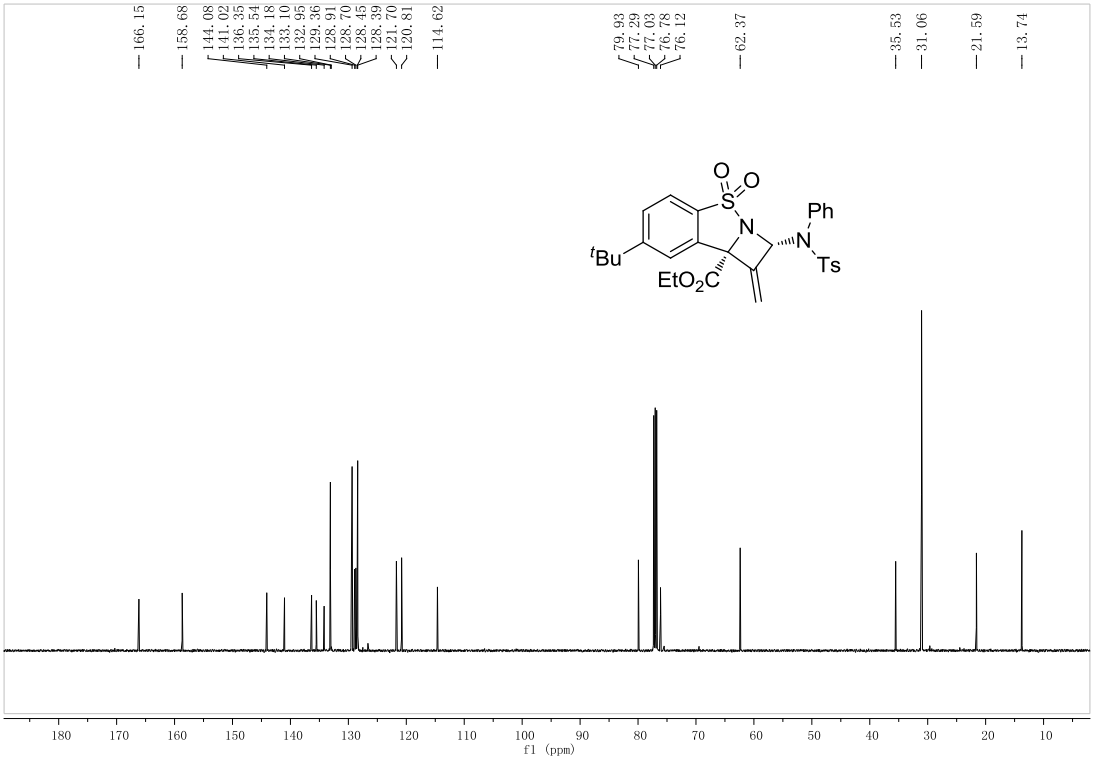
Ethyl 7-(tert-butyl)-2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ag**)

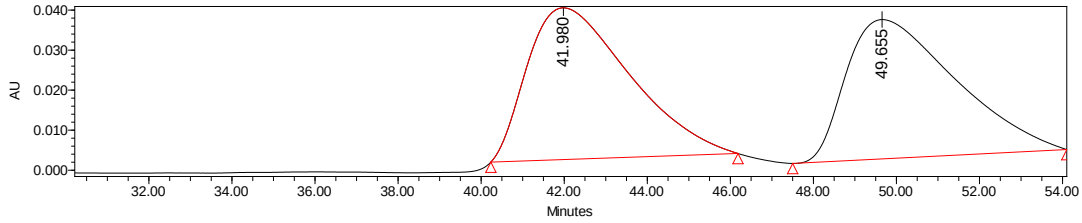


Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; light yellow solid, 70% yield, m.p. 196-198 ^{o}C, $[\alpha]_D^{15}$ = -0.4 (c =1.0 in CH_2Cl_2), 98% ee [Lux 5uCellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 38.6 min, t_{minor} = 50.9 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 8.0, 4.5 Hz, 3H), 7.66 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.32-7.36 (m, 1H), 7.27-7.31 (m, 3H), 7.24-7.27 (m, 3H), 6.82 (t, *J* = 2.0 Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.5

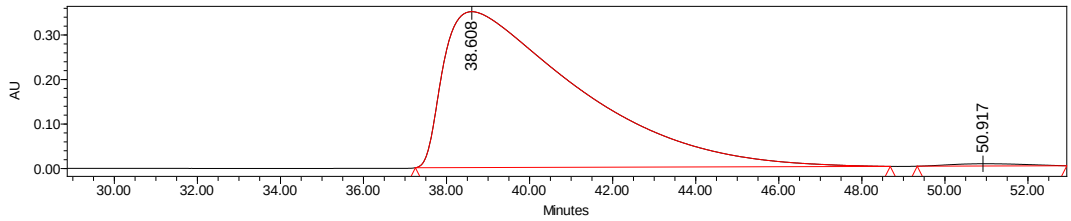
Hz, 1H), 3.93 (tt, *J* = 7.0, 3.5 Hz, 2H), 2.43 (s, 3H), 1.33 (s, 9H), 1.04 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 158.7, 144.1, 141.0, 136.4, 135.5, 134.2, 133.1, 133.0, 129.4, 128.9, 128.7, 128.5, 128.4, 121.7, 120.8, 114.6, 79.9, 76.1, 62.4, 35.5, 31.1, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{30}H_{33}N_2O_6S_2$ ($[M+H]^+$) 581.1775, found 581.1795.





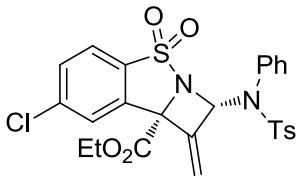


	Retention Time	Area	% Area	Height	% Height
1	41.980	6706196	51.87	38973	53.20
2	49.655	6223790	48.13	34291	46.80



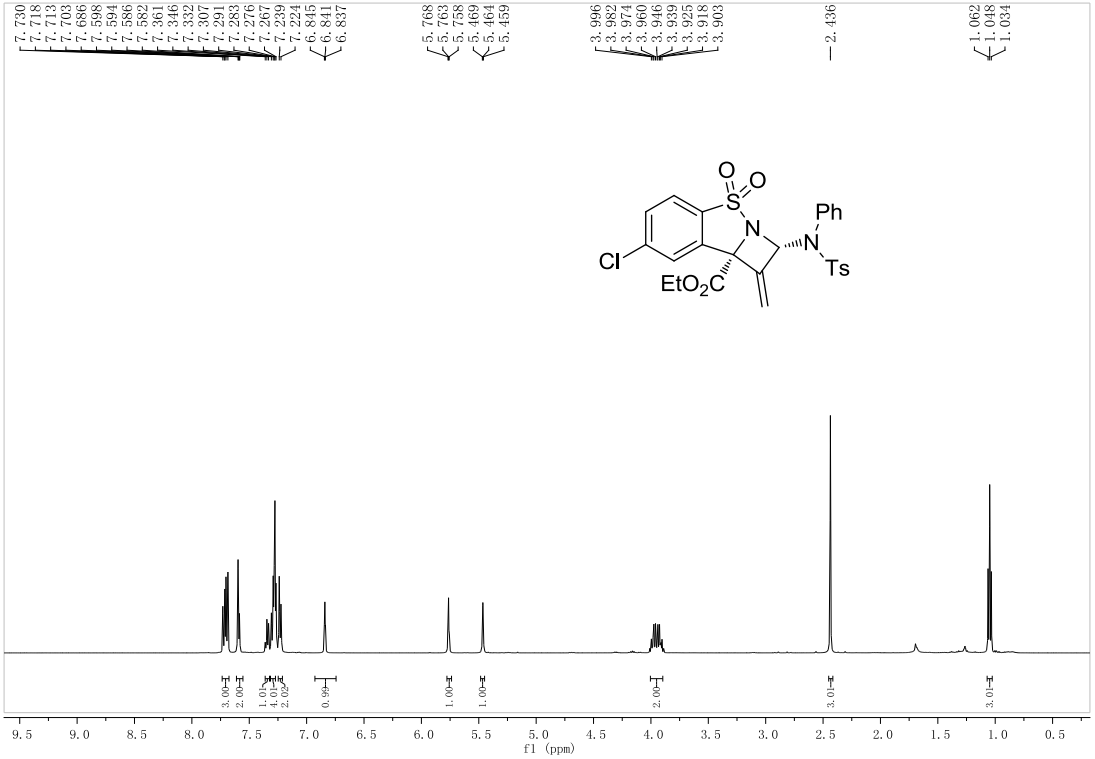
	Retention Time	Area	% Area	Height	% Height
1	38.608	78969089	99.19	350209	98.55
2	50.917	645799	0.81	5150	1.45

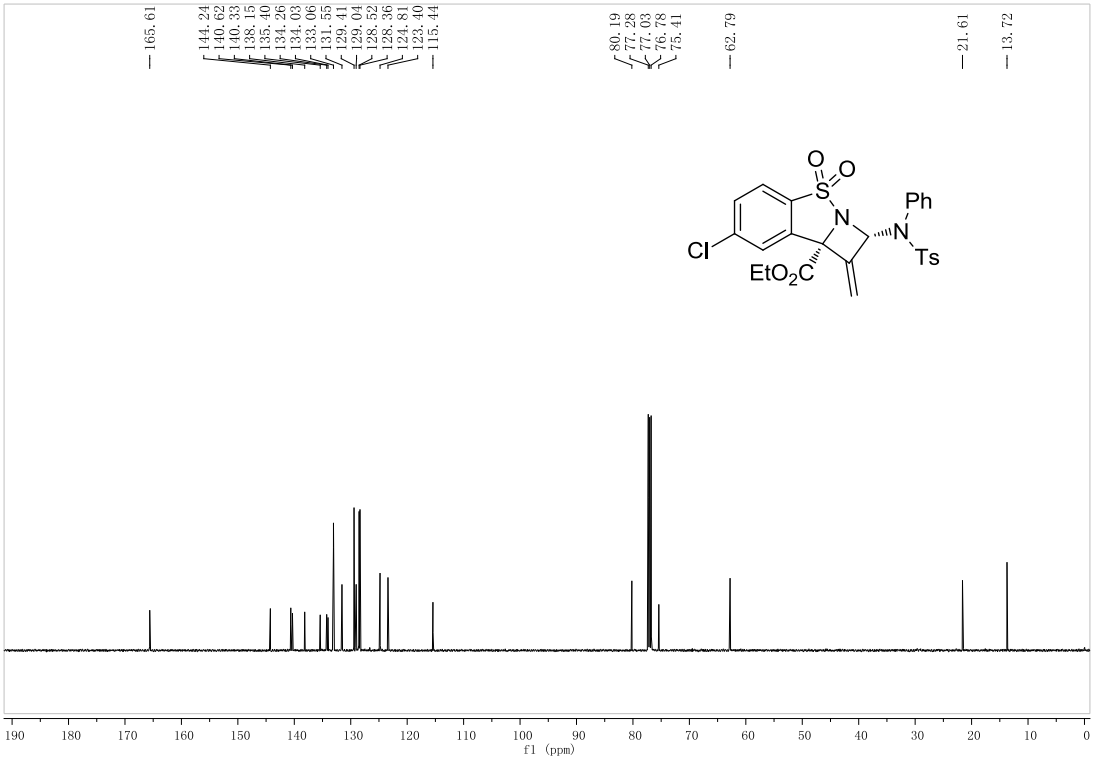
Ethyl 7-chloro-2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ah**)

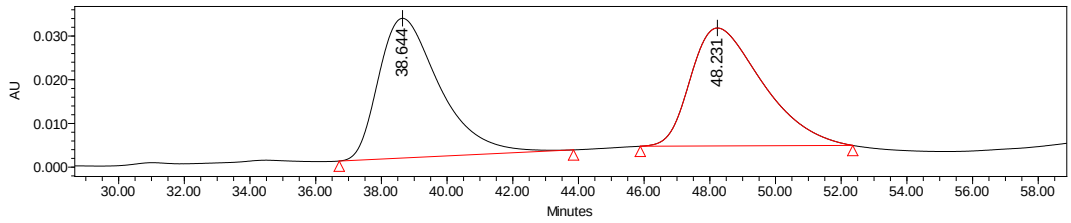


Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.5; light yellow solid, 64% yield, m.p. 191-193 ^{o}C, $[\alpha]_D^{15}$ = -3.5 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 45.4 min, t_{minor} = 38.1 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68-7.74 (m, 3H), 7.59 (dd, *J* = 6.0, 2.0 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.27-7.74 (m, 4H), 7.23 (d, *J* = 7.5 Hz, 2H), 6.84 (t, *J* = 2.0 Hz, 1H), 5.76 (t, *J* = 2.5 Hz, 1H), 5.46 (t, *J* = 2.5 Hz, 1H), 3.90-4.00 (m, 2H),

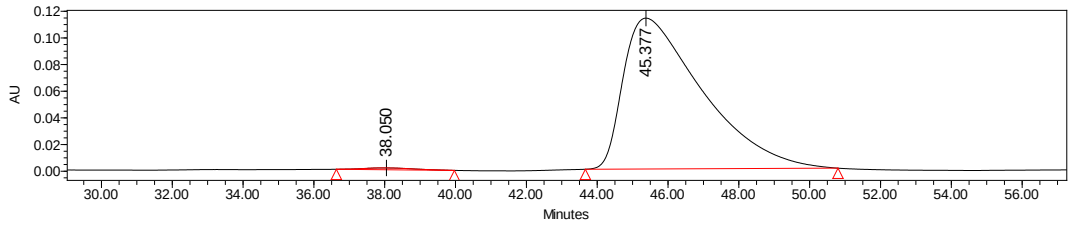
2.44 (s, 3H), 1.05 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 144.2, 140.6, 140.3, 138.2, 135.4, 134.3, 134.0, 133.1, 131.6, 129.4, 129.0, 128.5, 128.4, 124.8, 123.4, 115.4, 80.2, 75.4, 62.8, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{26}H_{24}ClN_2O_6S_2$ ($[M+H]^+$) 559.0759, found 559.0761.





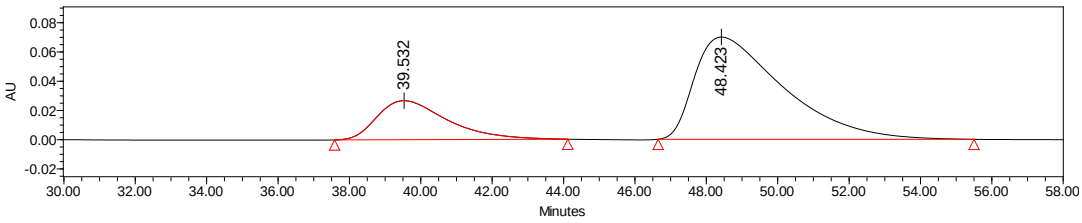


	Retention Time	Area	% Area	Height	% Height
1	38.644	4106360	49.29	31931	54.05
2	48.231	4224879	50.71	27150	45.95



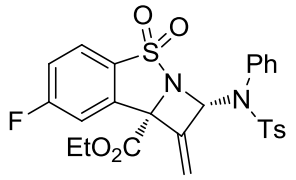
	Retention Time	Area	% Area	Height	% Height
1	38.050	87731	0.50	1095	0.96
2	45.377	17546678	99.50	113192	99.04

Rac+Opt

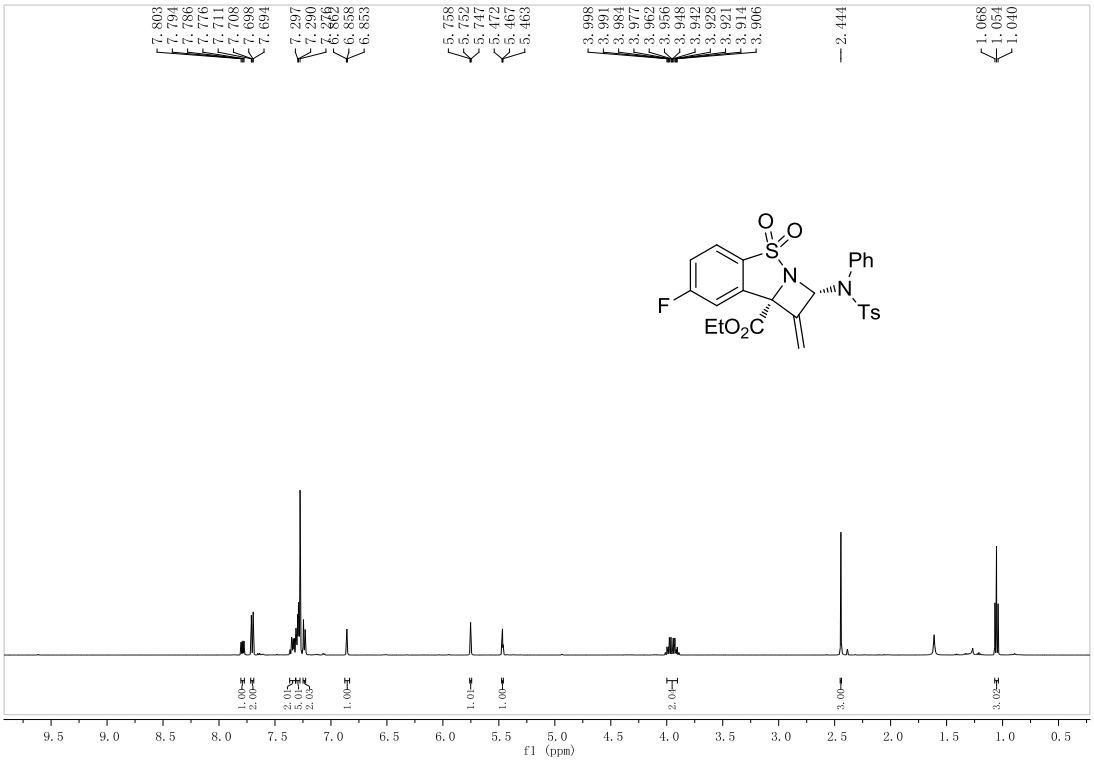


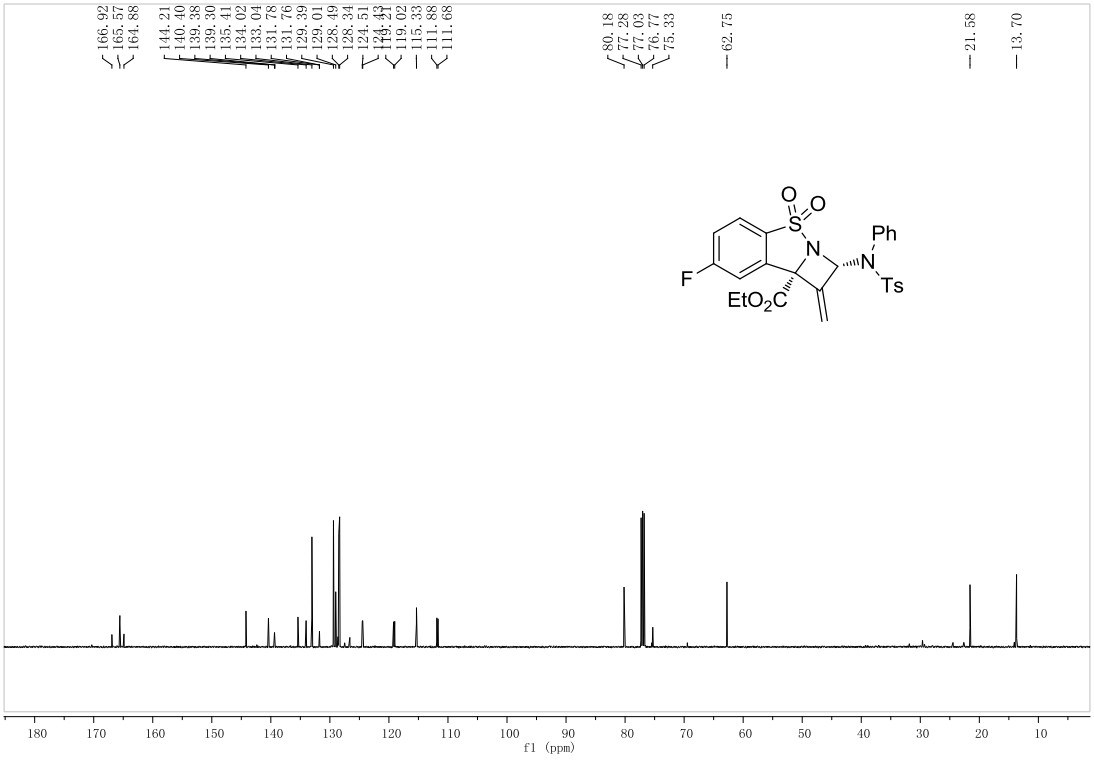
	Retention Time	Area	% Area	Height	% Height
1	39.532	3645527	23.23	26723	27.65
2	48.423	12046971	76.77	69908	72.35

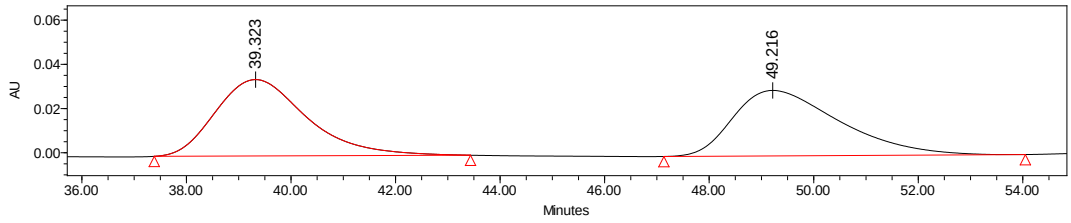
Ethyl 7-fluoro-2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ai**)



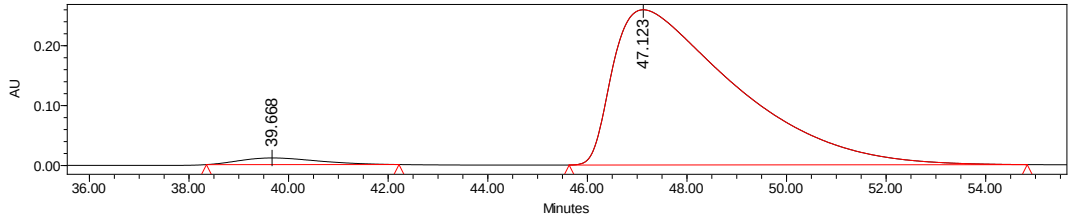
Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; white solid, 70% yield, m.p. 167-169 ^{o}C, $[\alpha]_D^{15}$ = -4.4 (c =1.0 in CH_2Cl_2), 95% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 47.1 min, t_{minor} = 39.7 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (dd, *J* = 8.5, 4.5 Hz, 1H), 7.69-7.72 (m, 2H), 7.32-7.37 (m, 2H), 7.27-7.32 (m, 5H), 7.22-7.26 (m, 2H), 6.86 (t, *J* = 2.5 Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.47 (t, *J* = 2.5 Hz, 1H), 3.89-4.00 (m, 2H), 2.44 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9 (d, *J* = 255.0 Hz), 165.6, 144.2, 140.4, 139.3 (d, *J* = 9.4 Hz), 135.4, 134.0, 133.0, 131.8, 129.4, 129.0, 128.4 (d, *J* = 18.8 Hz), 126.6, 124.5 (d, *J* = 10.1 Hz), 119.1 (d, *J* = 23.8 Hz), 115.3, 111.8 (d, *J* = 25.0 Hz), 80.2, 75.3, 62.8, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{26}H_{24}FN_2O_6S_2$ ($[M+H]^+$) 543.1054, found 543.1077.





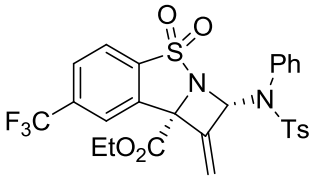


	Retention Time	Area	% Area	Height	% Height
1	39.323	4192642	50.03	34581	53.87
2	49.216	4187791	49.97	29615	46.13

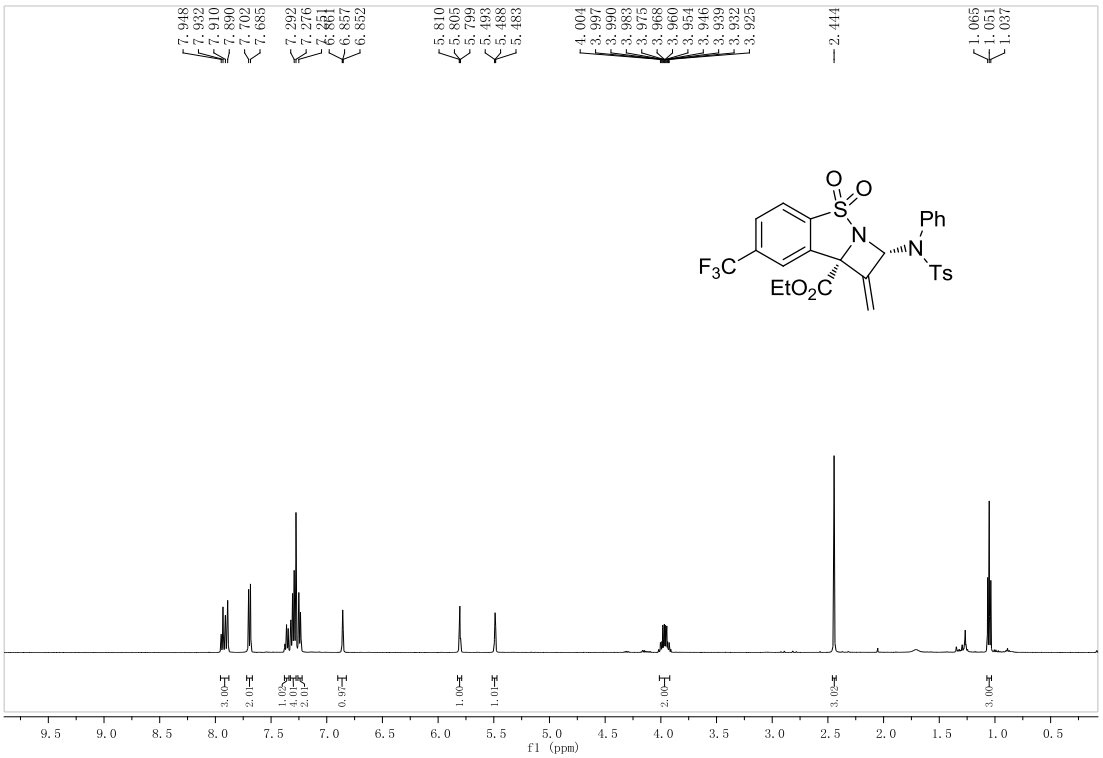


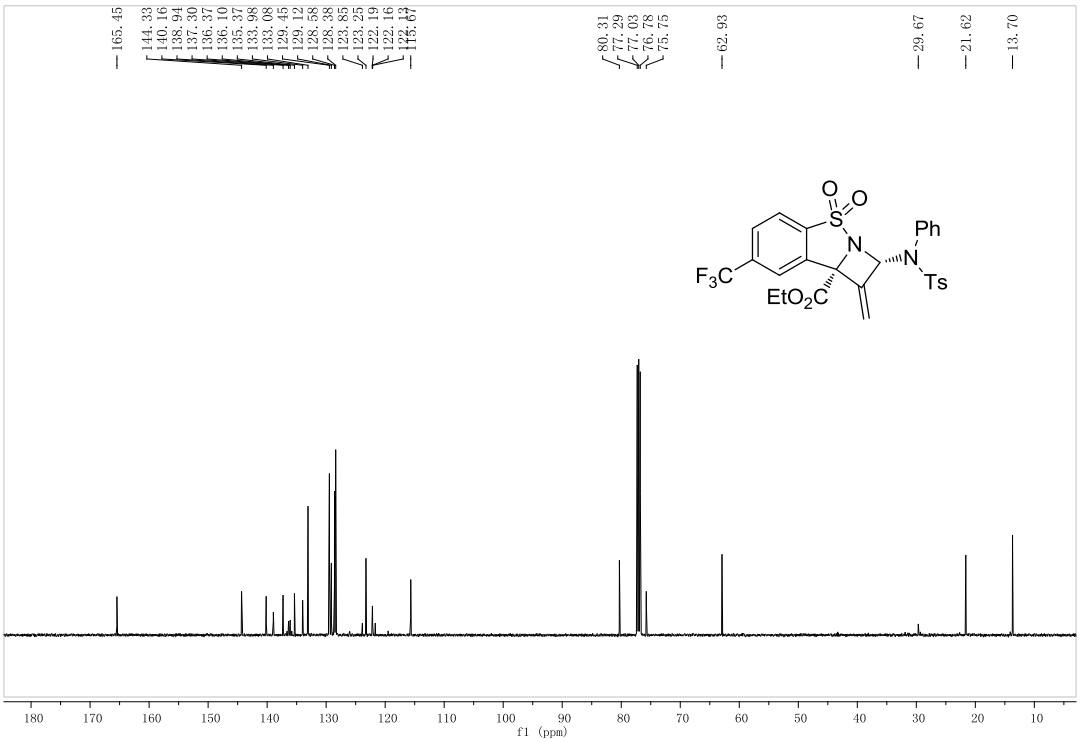
	Retention Time	Area	% Area	Height	% Height
1	39.668	1203582	2.65	11080	4.10
2	47.123	44198436	97.35	259200	95.90

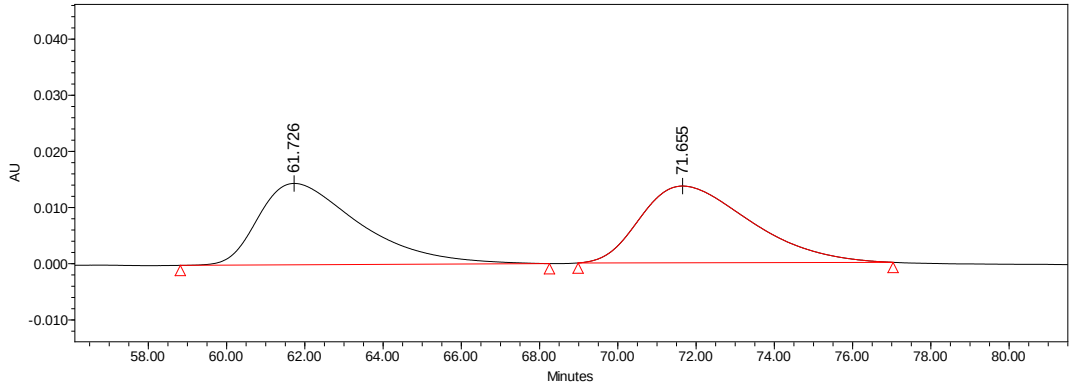
Ethyl 2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-7-(trifluoromethyl)-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3aj**)



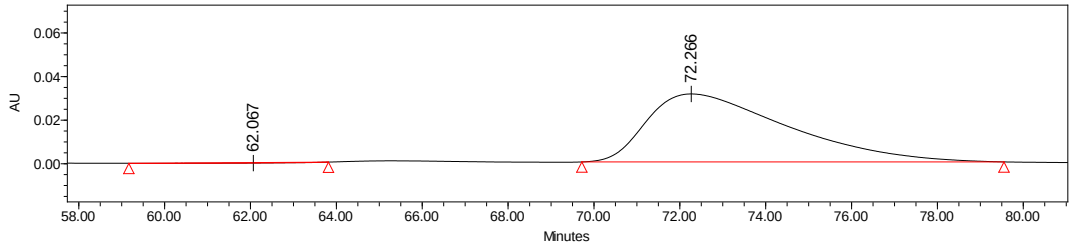
Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.5; colourless oil, 52% yield, $[\alpha]_D^{15}$ = -2.2 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5uCellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 90/10, 0.7 mL/min, 254 nm; t_{major} = 72.3 min, t_{minor} = 62.1 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 21.0, 10.0 Hz, 3H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.34-7.38 (m, 1H), 7.30 (dd, *J* = 15.5, 8.0 Hz, 4H), 7.23-7.26 (m, 2H), 6.86 (t, *J* = 2.0 Hz, 1H), 5.80 (t, *J* = 2.5 Hz, 1H), 5.49 (t, *J* = 2.5 Hz, 1H), 3.92-4.01 (m, 2H), 2.44 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 144.3, 140.2, 138.9, 137.3, 136.2 (q, *J* = 33.8 Hz), 135.4, 134.0, 133.1, 129.5, 129.1, 128.6, 128.4, 123.3, 123.0 (q, *J* = 211.3 Hz), 122.2, 122.1, 115.7, 80.3, 75.8, 62.9, 29.7, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{27}H_{24}F_3N_2O_6S_2$ ($[M+H]^+$) 593.1022, found 593.1019.





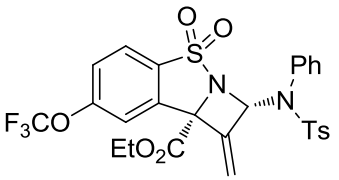


	Retention Time	Area	% Area	Height	% Height
1	61.726	2303726	47.43	13865	50.96
2	71.655	2553620	52.57	13342	49.04

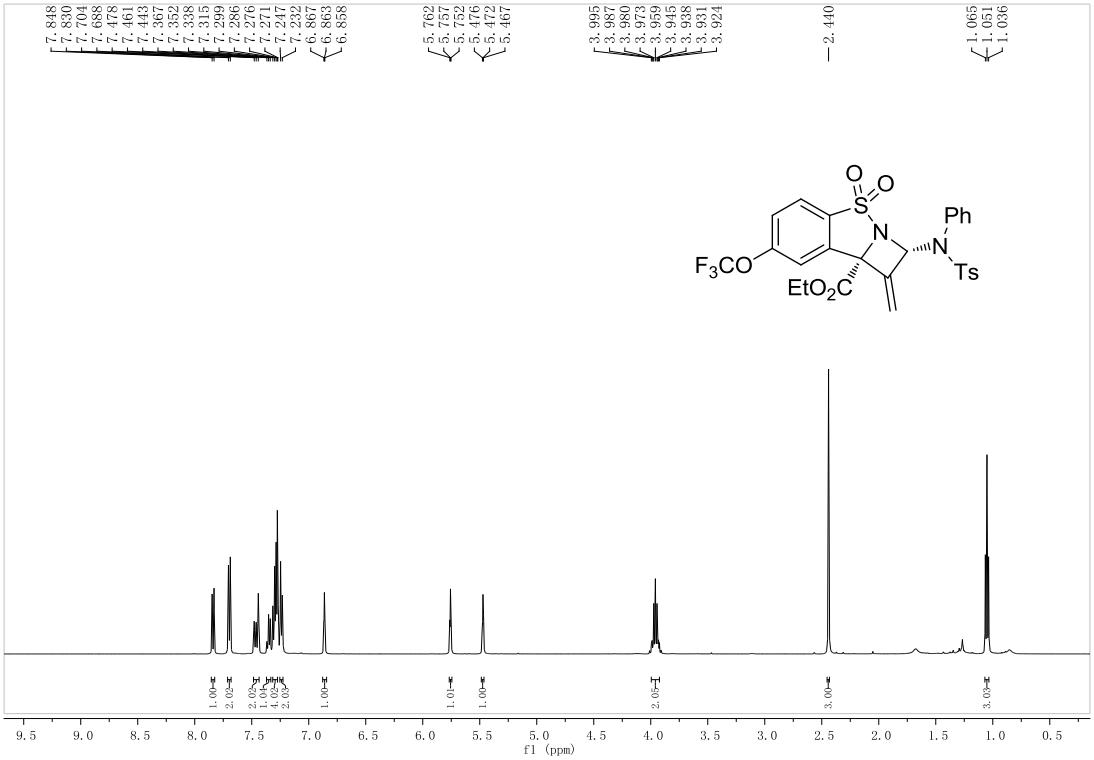


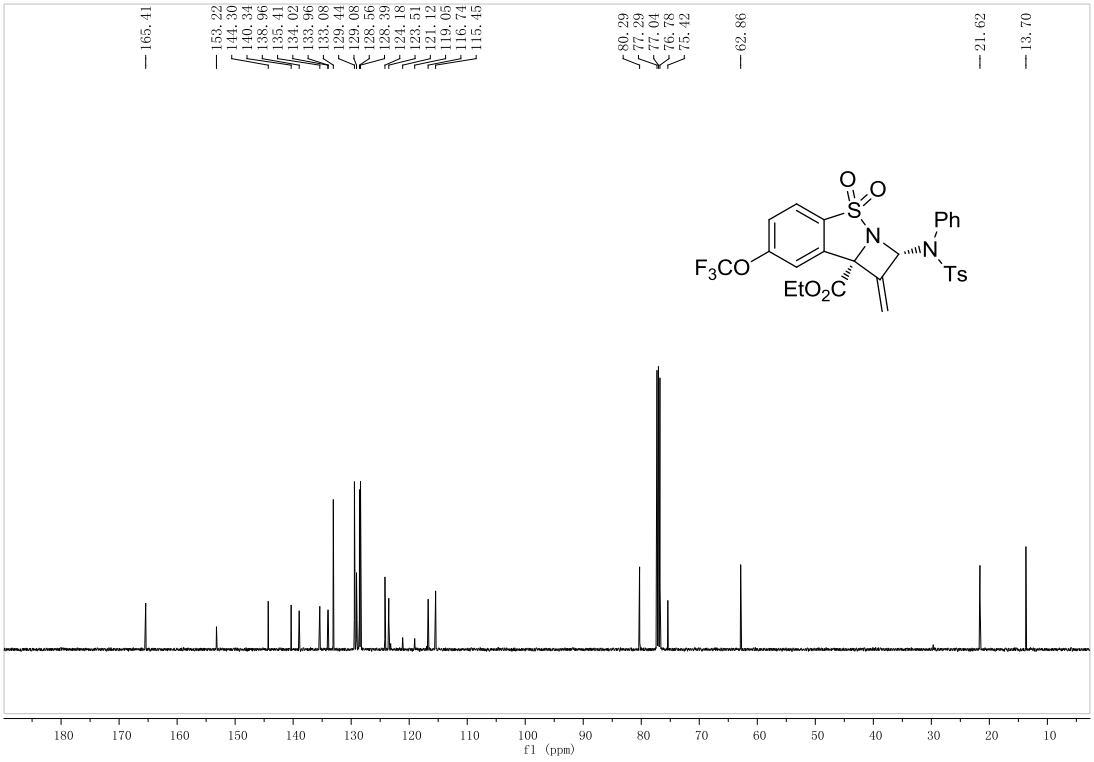
	Retention Time	Area	% Area	Height	% Height
1	62.067	44050	0.62	-234	0.74
2	72.266	7093834	99.38	31202	99.26

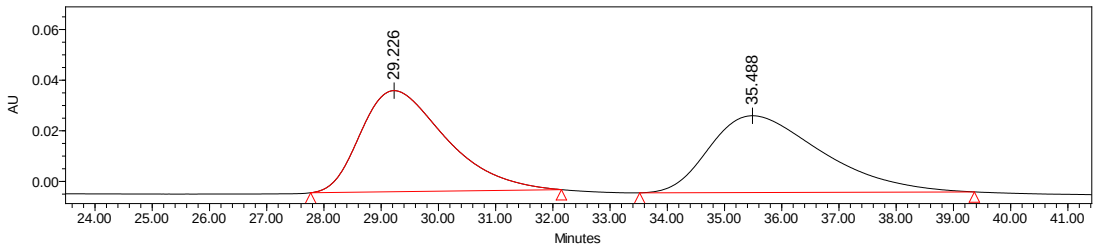
Ethyl 2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-7-(trifluoromethoxy)-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ak**)



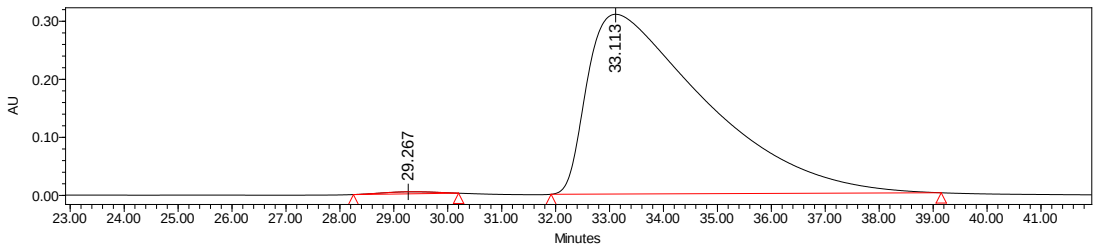
Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; light yellow oil, 55% yield, $[\alpha]_D^{15}$ = -0.6 (c =1.0 in CH_2Cl_2), 98% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 33.1 min, t_{minor} = 29.3 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.44-7.48 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (dd, *J* = 14.5, 6.5 Hz, 4H), 7.24 (d, *J* = 7.5 Hz, 2H), 6.86 (t, *J* = 2.5 Hz, 1H), 5.76 (t, *J* = 2.5 Hz, 1H), 5.47 (t, *J* = 2.5 Hz, 1H), 3.92-4.00 (m, 2H), 2.44 (s, 3H), 1.05 (t, *J* = 7.0Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 153.2, 144.3, 140.3, 139.0, 135.4, 134.02, 133.96, 133.1, 129.4, 129.1, 128.6, 128.4, 124.2, 123.5, 120.1 (q, *J* = 258.8 Hz), 119.1, 116.7, 115.5, 80.3, 75.4, 62.9, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{27}H_{24}F_3N_2O_7S_2$ ($[M+H]^+$) 609.0972, found 609.0986.





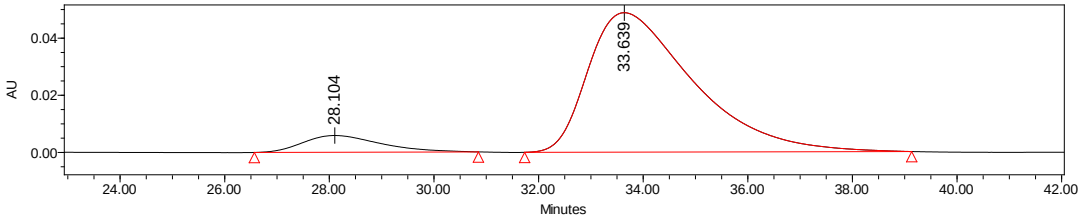


	Retention Time	Area	% Area	Height	% Height
1	29.226	4396167	50.63	40615	57.08
2	35.488	4287157	49.37	30541	42.92



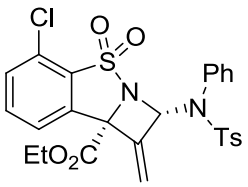
	Retention Time	Area	% Area	Height	% Height
1	29.267	238550	0.50	3544	1.13
2	33.113	47318785	99.50	309619	98.87

Rac+Opt

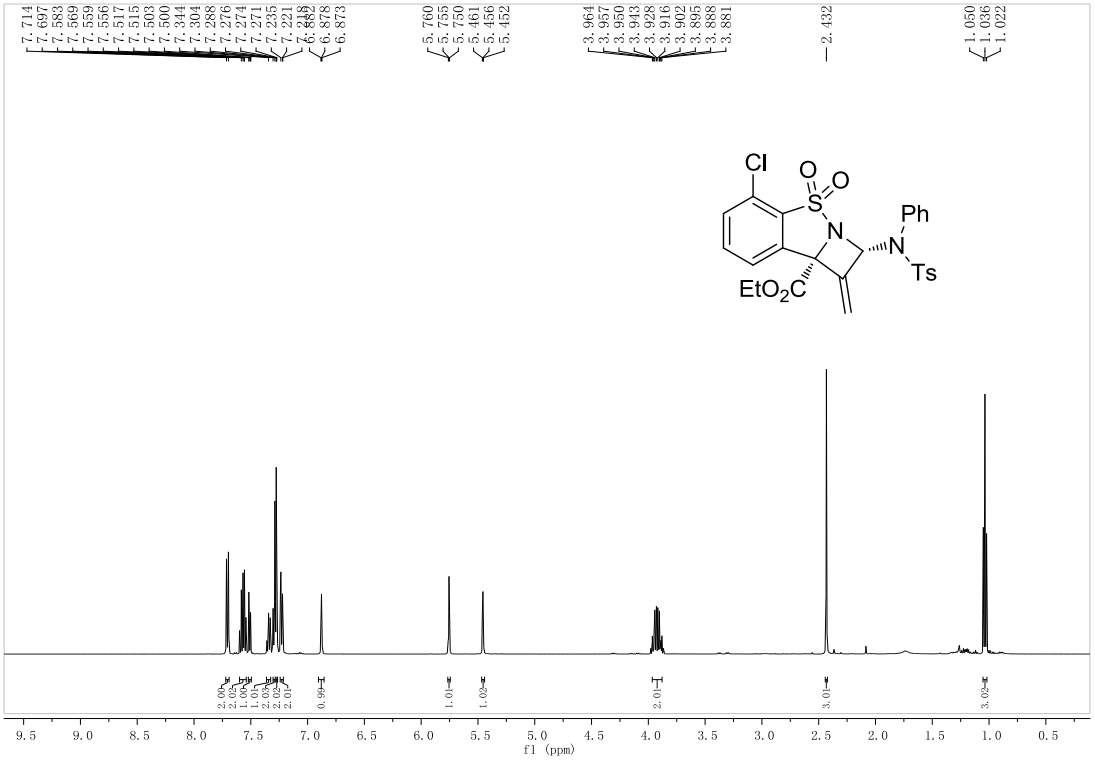


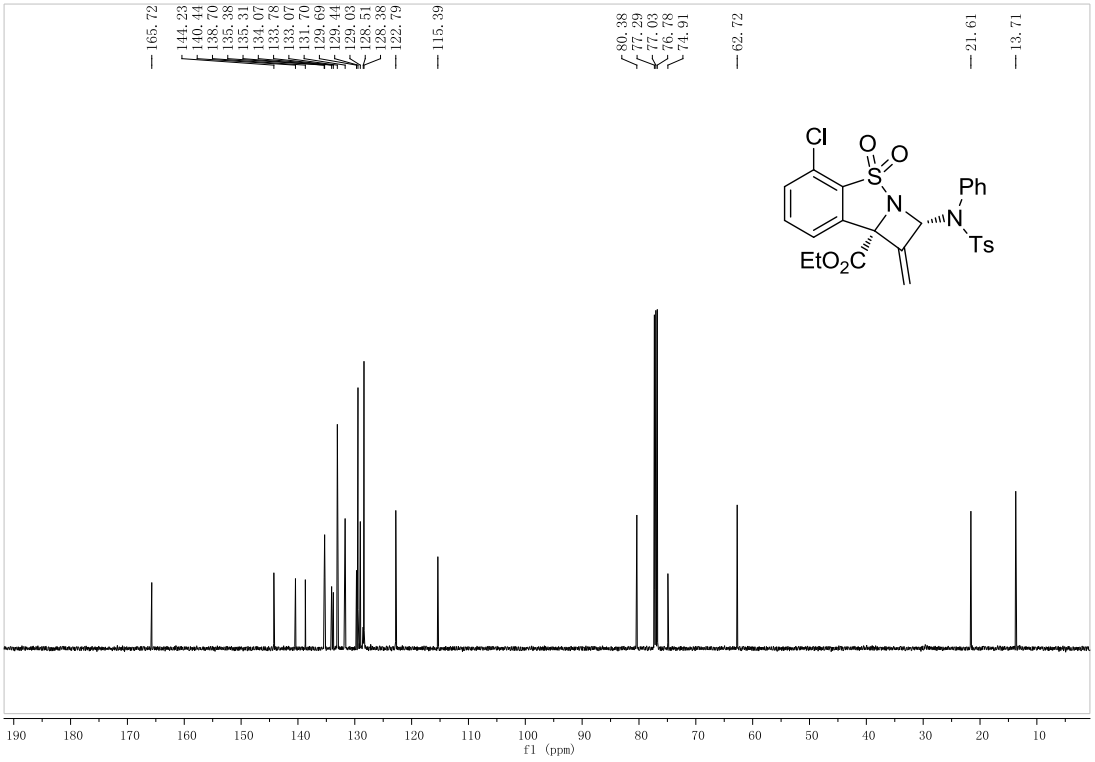
	Retention Time	Area	% Area	Height	% Height
1	28.104	603597	8.13	5865	10.73
2	33.639	6817606	91.87	48797	89.27

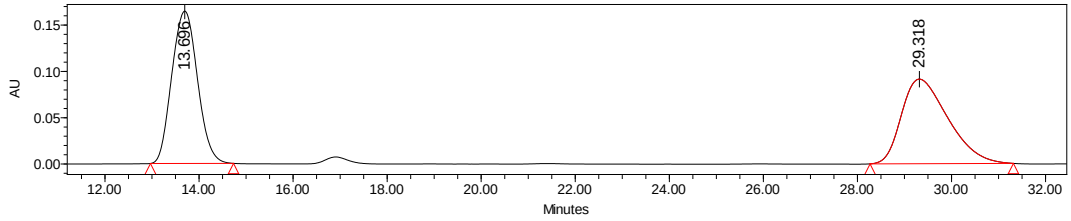
Ethyl 5-chloro-2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3al**)



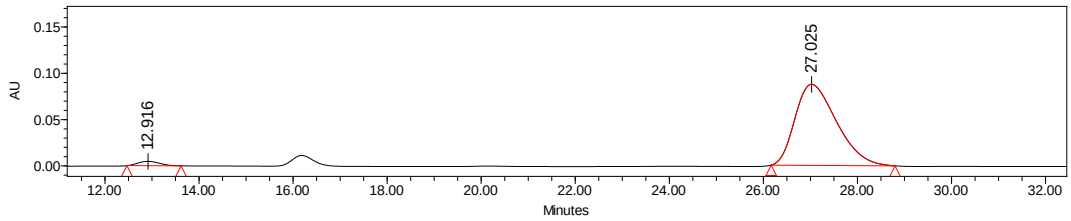
Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; yellow solid, 64% yield, m.p. 110-112 ^{o}C, $[\alpha]_D^{15}$ = -23 (c =1.0 in CH_2Cl_2), 94% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 27.0 min, t_{minor} = 12.9 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.53-7.60 (m, 2H), 7.51 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.32-7.37 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.27-7.29 (m, 2H), 7.21-7.25 (m, 2H), 6.88 (t, *J* = 2.5 Hz, 1H), 5.76 (t, *J* = 2.5 Hz, 1H), 5.46 (t, *J* = 2.5 Hz, 1H), 3.88-3.97 (m, 2H), 2.43 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 144.2, 140.4, 138.7, 135.4, 135.3, 134.1, 133.8, 133.1, 131.7, 129.7, 129.4, 129.0, 128.5, 128.4, 122.8, 115.4, 80.4, 74.9, 62.7, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{26}H_{24}ClN_2O_6S_2$ ($[M+H]^+$) 559.0759, found 559.0759.


7.714
7.697
7.583
7.569
7.559
7.556
7.517
7.515
7.503
7.500
7.344
7.304
7.288
7.276
7.274
7.271
7.235
7.221
6.878
6.873
5.760
5.755
5.750
5.461
5.456
5.452
3.964
3.957
3.950
3.943
3.928
3.916
3.902
3.895
3.888
3.881
2.432
1.050
1.036
1.022
Cl
O
O
S
N
Ph
N
Ts
EtO2C
2.00
2.05
1.05
1.03
2.02
2.07
0.99
1.01
1.02
2.01
3.01
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


165.72
144.23
140.44
138.70
135.38
135.31
134.07
133.78
133.07
131.70
129.69
129.44
129.03
128.51
128.38
122.79
115.39
80.38
77.29
77.03
76.78
74.91
62.72
21.61
13.71
Cl
O
O
S
N
Ph
N
Ts
EtO2C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

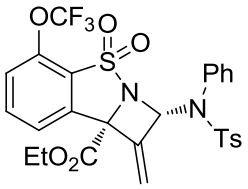


	Retention Time	Area	% Area	Height	% Height
1	13.696	6259622	49.69	164645	64.23
2	29.318	6337304	50.31	91703	35.77



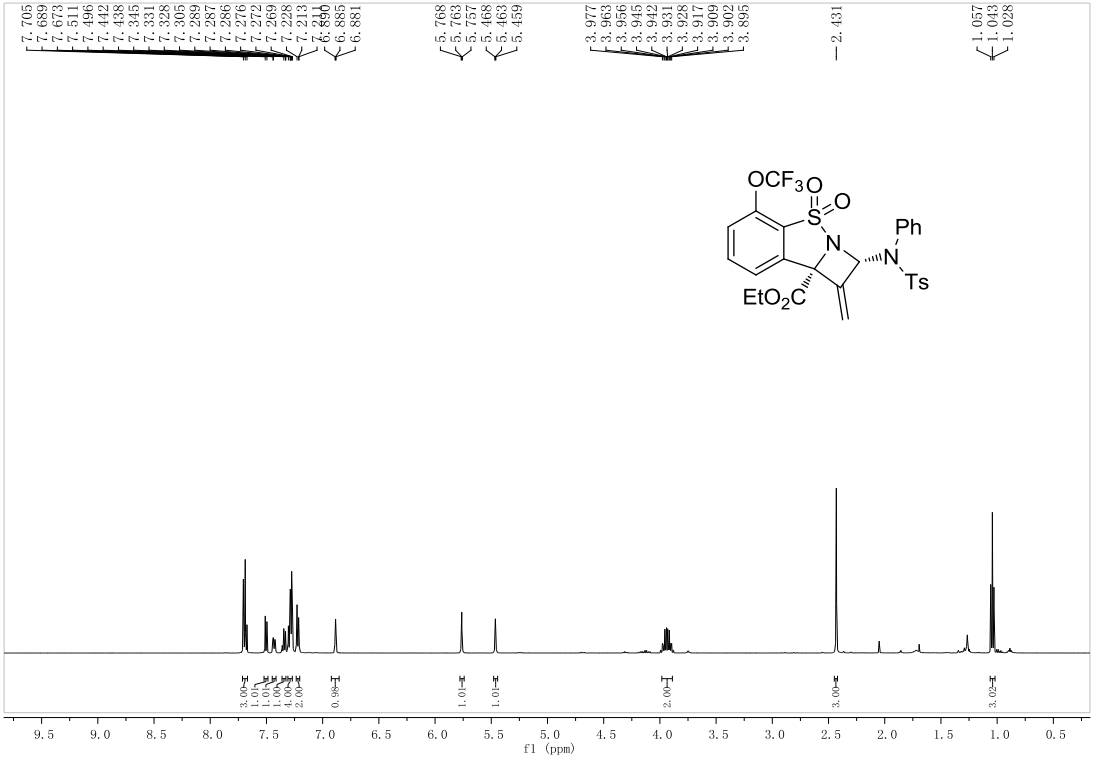
	Retention Time	Area	% Area	Height	% Height
1	12.916	150356	2.73	4668	5.07
2	27.025	5362009	97.27	87492	94.93

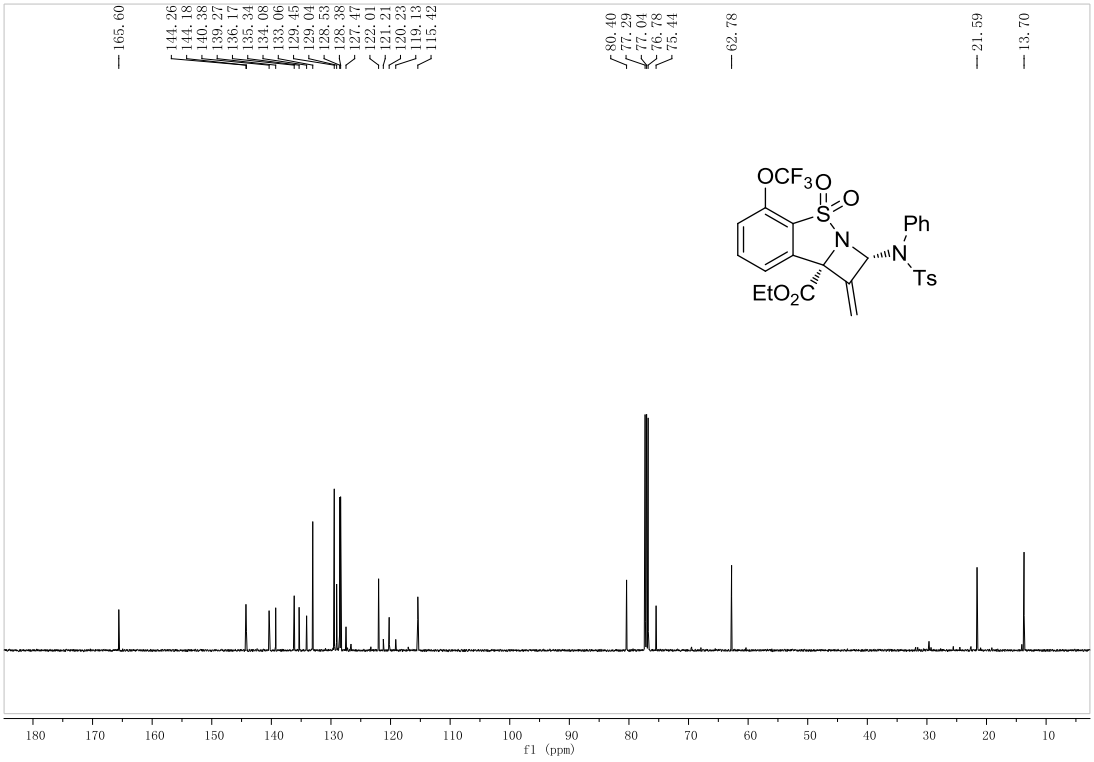
Ethyl 2-((4-methyl-N-phenylphenyl)sulfonamido)-1-methylene-5-(trifluoromethoxy)-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide **(3am)**

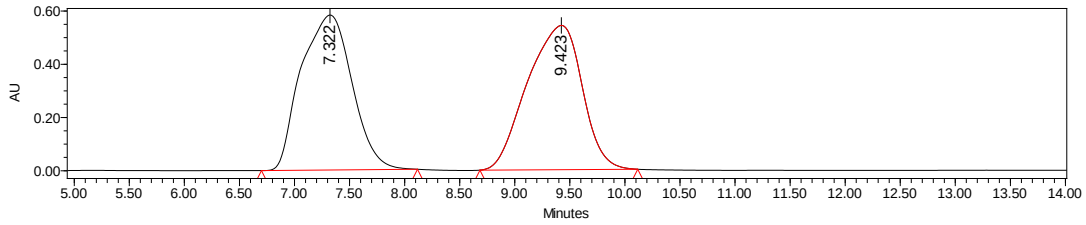


Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; light yellow solid, 76% yield, m.p. 134-136 ^{o}C, $[\alpha]_D^{15}$ = -10.8 (c =1.0 in CH_2Cl_2), 93% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{major} = 9.2 min, t_{minor} = 7.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (t, *J* = 8.0 Hz, 3H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.32-7.37 (m, 1H), 7.27-7.31 (m, 4H), 7.20-7.23 (m, 2H), 6.89 (t, *J* = 2.0 Hz, 1H), 5.76 (t, *J* = 2.5 Hz, 1H), 5.46 (t, *J* = 2.5 Hz,

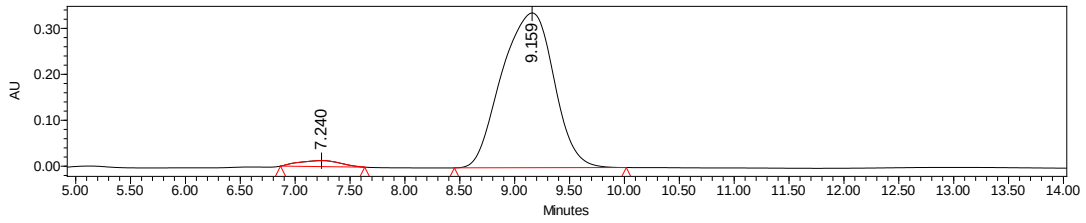
1H), 3.89-3.98 (m, 2H), 2.43 (s, 3H), 1.04 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 144.3, 144.2, 140.4, 139.3, 136.2, 135.3, 134.1, 133.1, 129.5, 129.0, 128.5, 128.4, 127.5, 122.0, 120.23, 120.17 (q, J = 260.0 Hz), 115.4, 80.4, 75.4, 62.8, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{27}H_{24}F_3N_2O_7S_2$ ($[M+H]^+$) 609.0972, found 609.0979.





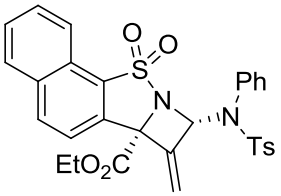


	Retention Time	Area	% Area	Height	% Height
1	7.322	18449284	49.36	578515	51.57
2	9.423	18926146	50.64	543285	48.43



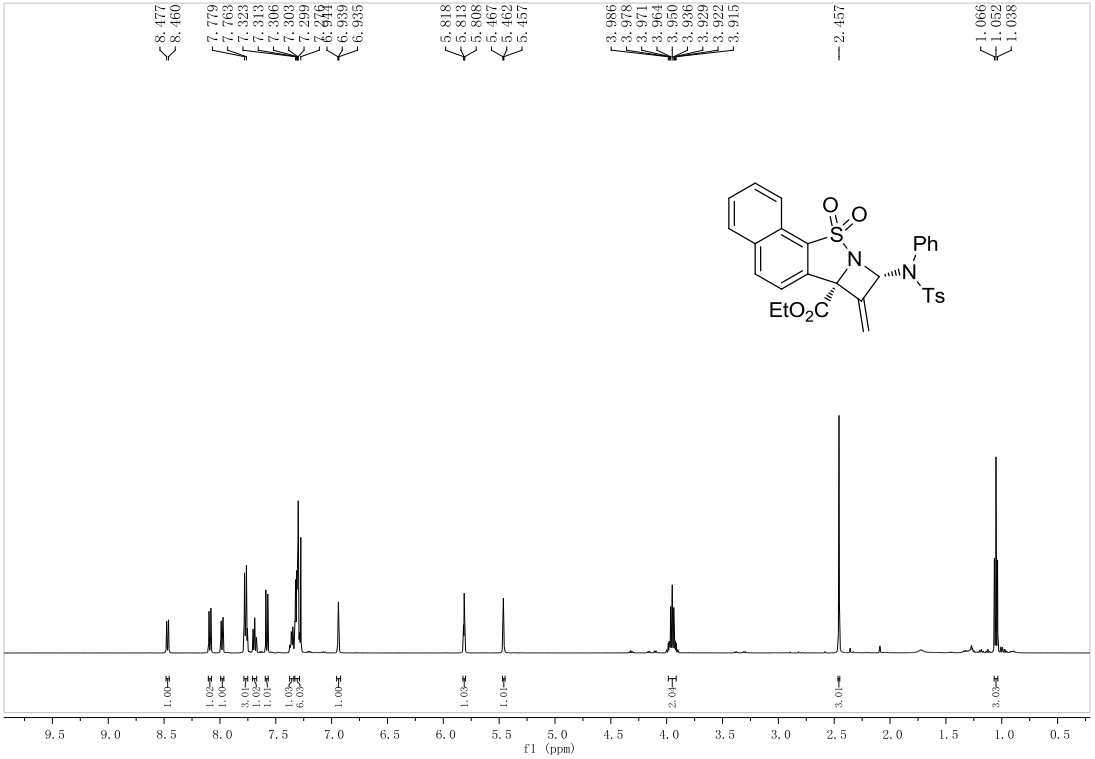
	Retention Time	Area	% Area	Height	% Height
1	7.240	343676	2.99	13043	3.73
2	9.159	11152147	97.01	337056	96.27

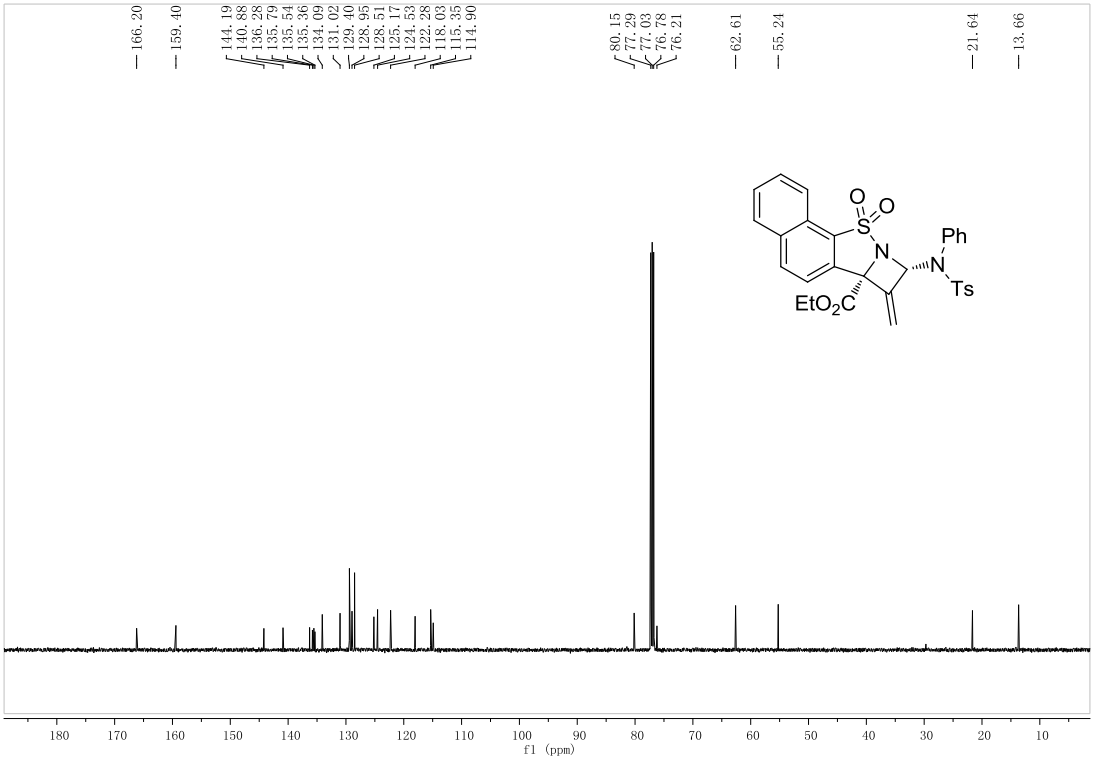
Ethyl 8-((4-methyl-N-phenylphenyl)sulfonamido)-7-methylene-7,8-dihydro-6bH-azeto[1,2-b]naphtho[2,1-d]isothiazole-6b-carboxylate 10,10-dioxide (**3an**)

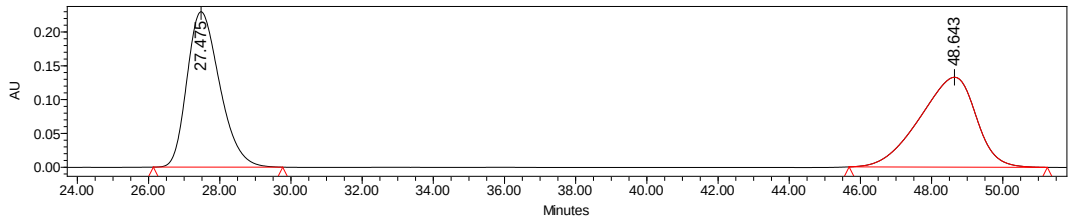


Reaction time: 5 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; light yellow solid, 70% yield, m.p. 162-164 ^{o}C, $[\alpha]_D^{15}$ = -75.0 (c =1.0 in CH_2Cl_2), 94% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{major} =51.0 min, t_{minor} = 28.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.75-7.79 (m, 3H), 7.67-7.71 (m, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.34-7.37 (m, 1H), 7.29-7.33 (m, 6H), 6.94 (t, *J* = 2.5 Hz, 1H), 5.81 (t, *J*

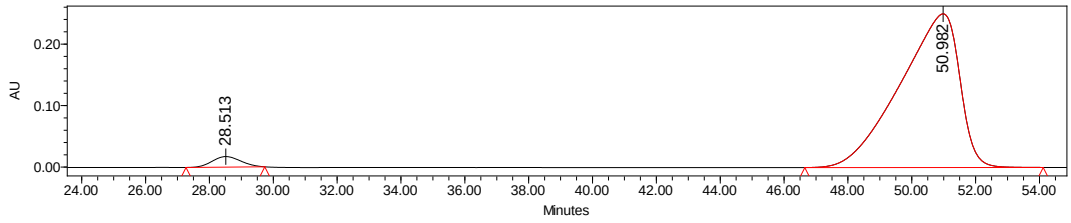
= 2.5 Hz, 1H), 5.46 (t, *J* = 2.5 Hz, 1H), 3.91-3.99 (m, 2H), 2.46 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 159.4, 144.2, 140.9, 136.3, 135.8, 135.5, 135.4, 134.1, 131.0, 129.4, 129.0, 128.5, 125.2, 124.5, 122.3, 118.0, 115.4, 114.9, 80.2, 76.2, 62.6, 55.2, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{30}H_{27}N_2O_6S_2$ ($[M+H]^+$) 575.1305, found 575.1292.





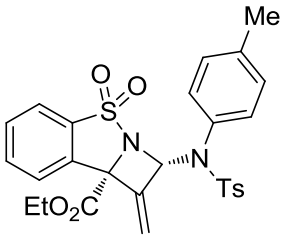


	Retention Time	Area	% Area	Height	% Height
1	27.475	14668336	49.99	229839	63.36
2	48.643	14672164	50.01	132918	36.64



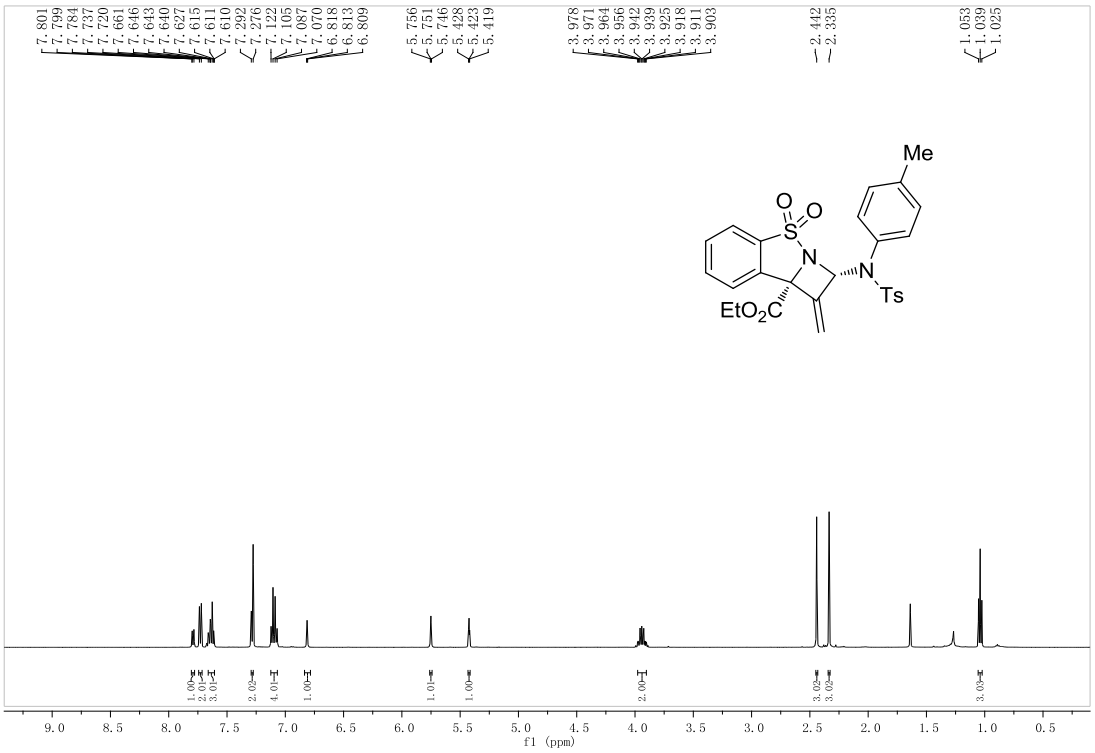
	Retention Time	Area	% Area	Height	% Height
1	28.513	985069	2.97	16550	6.24
2	50.982	32146204	97.03	248806	93.76

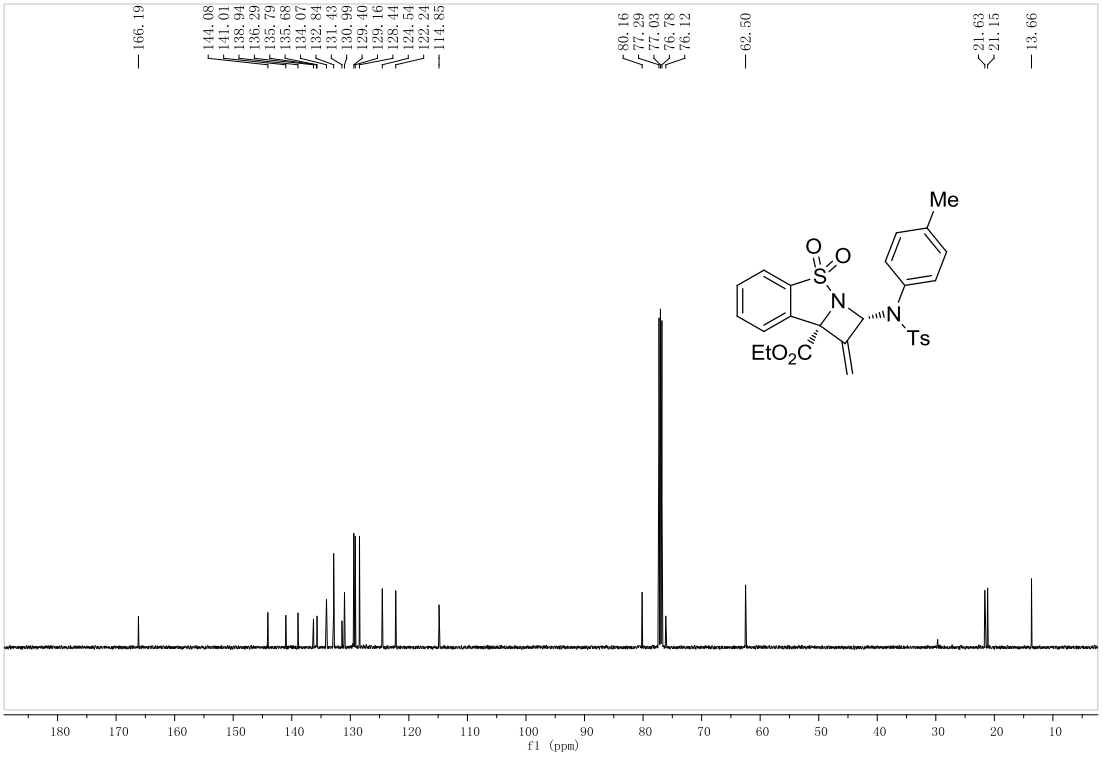
Ethyl 2-((4-methyl-N-(p-tolyl)phenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ba**)

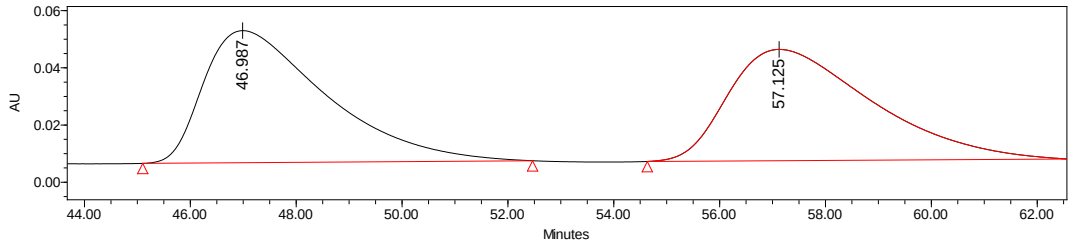


Reaction time: 2.5 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; light yellow solid, 75% yield, m.p. 176-178 ^{o}C, $[\alpha]_D^{15}$ = 16.3 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 53.6 min, t_{minor} =45.8 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78-7.81 (m, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.61-7.67 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10 (q, *J* = 8.5 Hz, 4H), 6.81 (t,

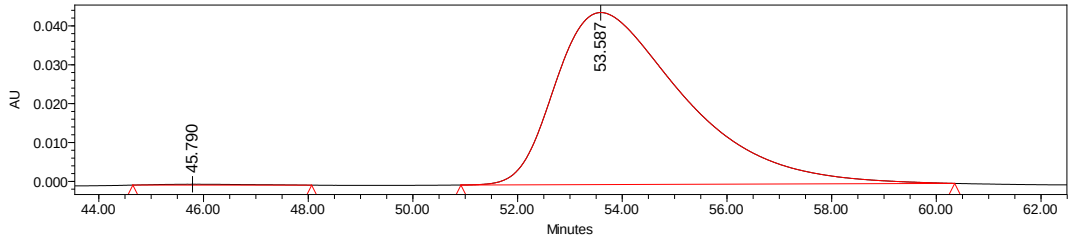
J = 2.5 Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.5 Hz, 1H), 3.94 (m, 2H), 2.44 (s, 3H), 2.34 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 144.1, 141.0, 138.9, 136.3, 135.8, 135.7, 134.1, 132.8, 131.4, 131.0, 129.4, 129.2, 128.4, 124.5, 122.2, 114.9, 80.2, 76.1, 62.5, 21.6, 21.2, 13.7. HRMS m/z (ESI+): Calculated for $C_{27}H_{27}N_2O_6S_2$ ($[M+H]^+$) 539.1305, found 539.1301.





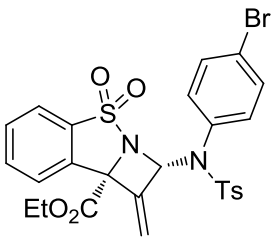


	Retention Time	Area	% Area	Height	% Height
1	46.987	7400891	50.15	46191	54.27
2	57.125	7357154	49.85	38919	45.73



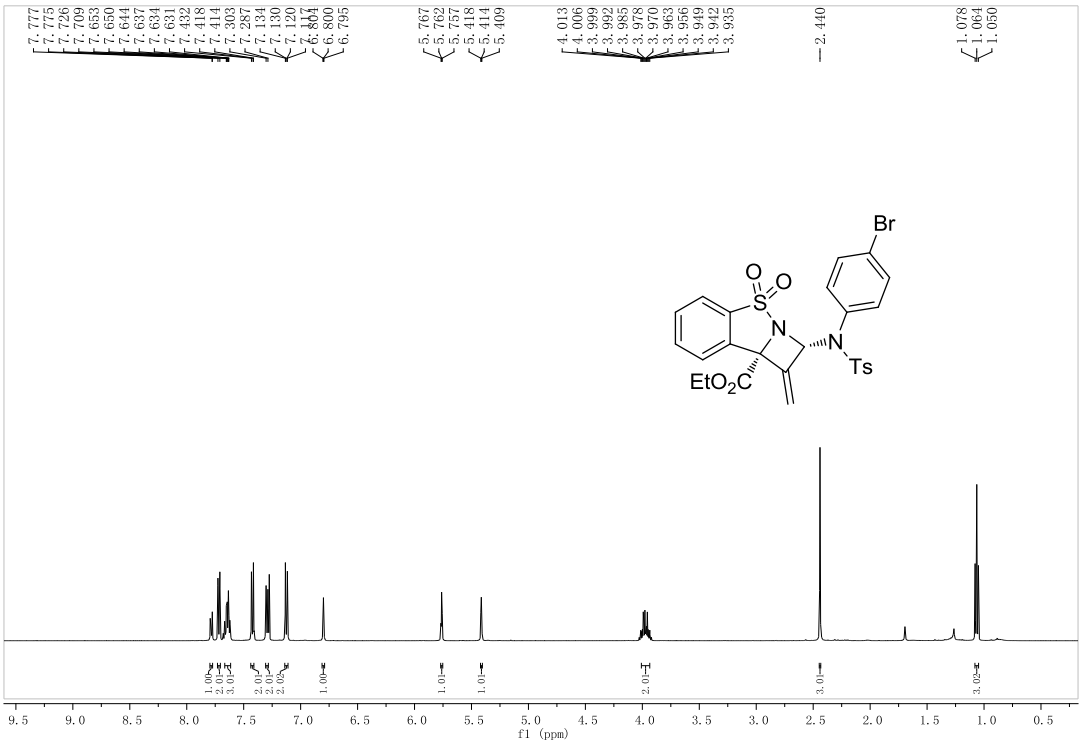
	Retention Time	Area	% Area	Height	% Height
1	45.790	50175	0.65	328	0.74
2	53.587	7670105	99.35	44263	99.26

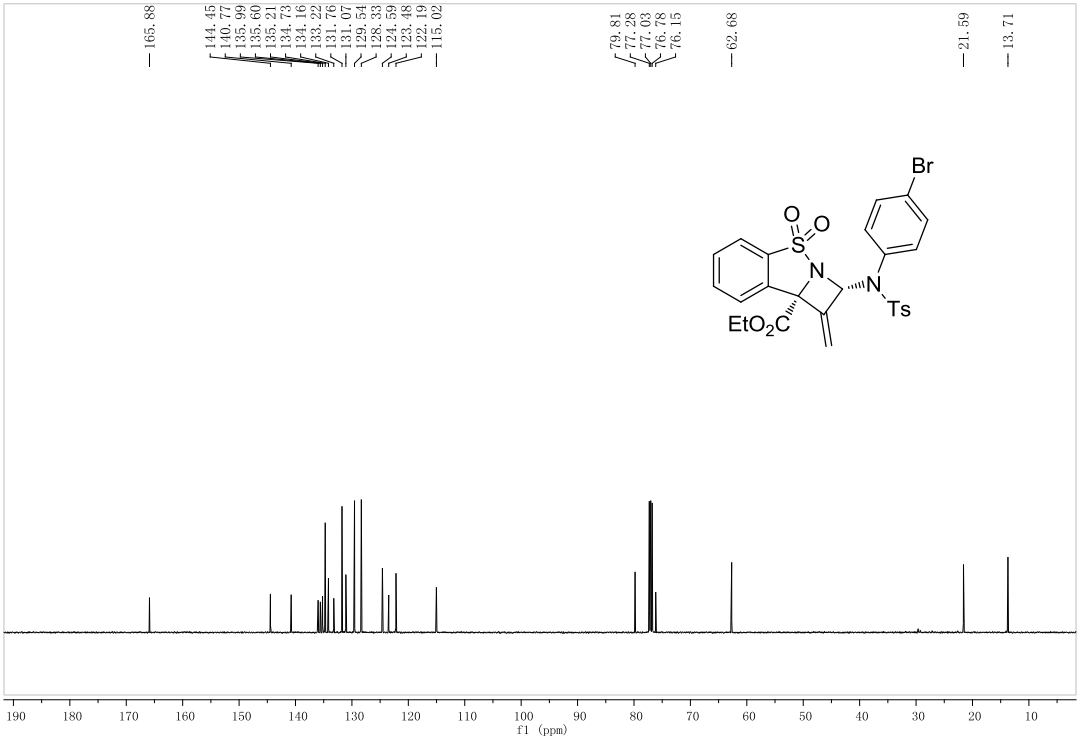
Ethyl 2-((N-(4-bromophenyl)-4-methylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ca**)

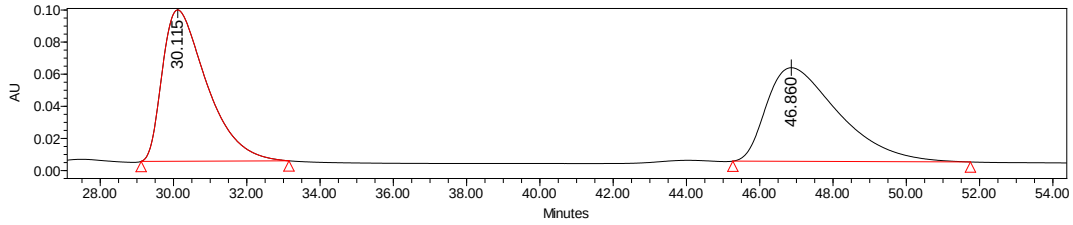


Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; light yellow solid, 67% yield, m.p. 130-132 ^{o}C, $[\alpha]_D^{15}$ = 2.0 (c =1.0 in CH_2Cl_2), 97% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 46.9 min, t_{minor} = 30.9 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.80 (m, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.61-7.67 (m, 3H), 7.40-7.44 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.11-7.15 (m, 2H),

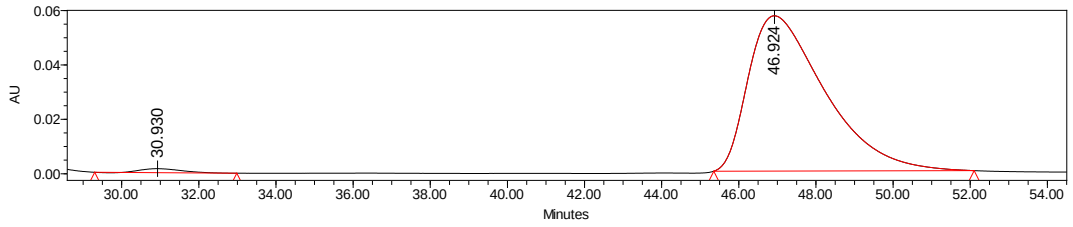
6.80 (t, J = 2.0 Hz, 1H), 5.76 (t, J = 2.5 Hz, 1H), 5.41 (t, J = 2.5 Hz, 1H), 3.93-4.02 (m, 2H), 2.44 (s, 3H), 1.06 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 144.5, 140.8, 136.0, 135.6, 135.2, 134.7, 134.2, 133.2, 131.8, 131.1, 129.5, 128.3, 124.6, 123.5, 122.2, 115.0, 79.8, 76.2, 62.7, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{27}H_{24}BrN_2O_6S_2$ ($[M+H]^+$) 603.0254, found 603.0257.





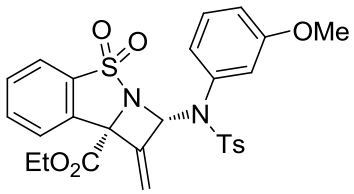


	Retention Time	Area	% Area	Height	% Height
1	30.115	8091519	50.12	94803	61.82
2	46.860	8054285	49.88	58548	38.18



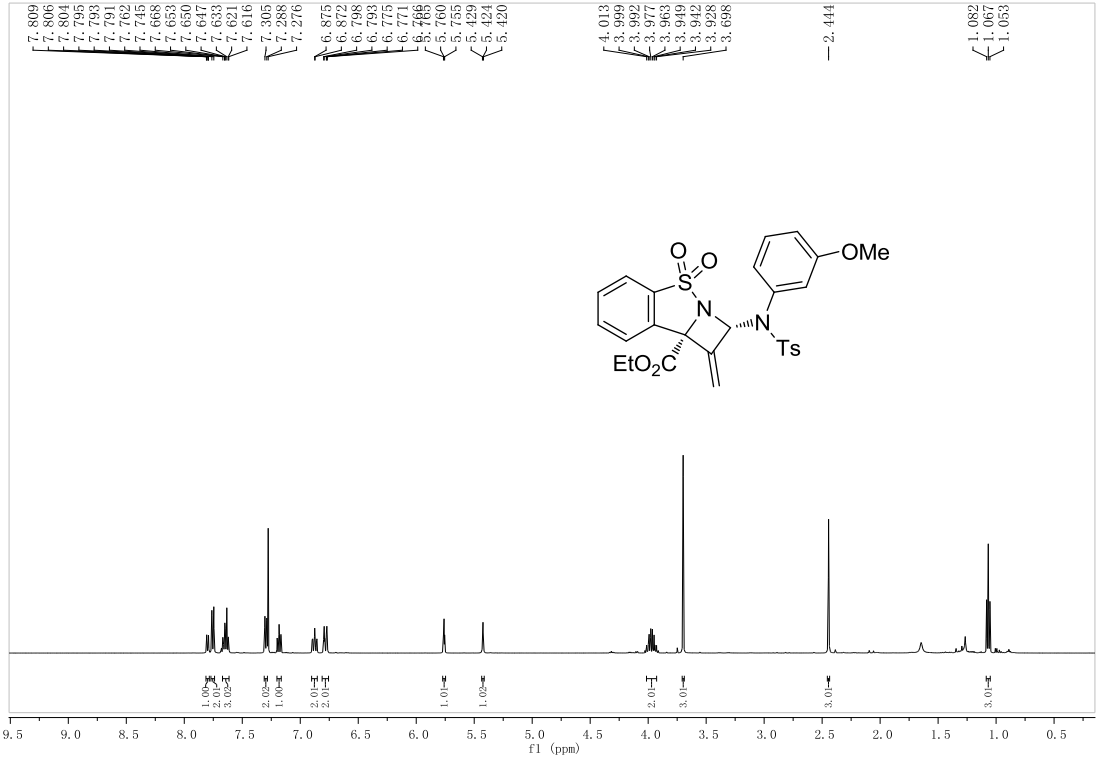
	Retention Time	Area	% Area	Height	% Height
1	30.930	114456	1.43	1472	2.51
2	46.924	7885985	98.57	57085	97.49

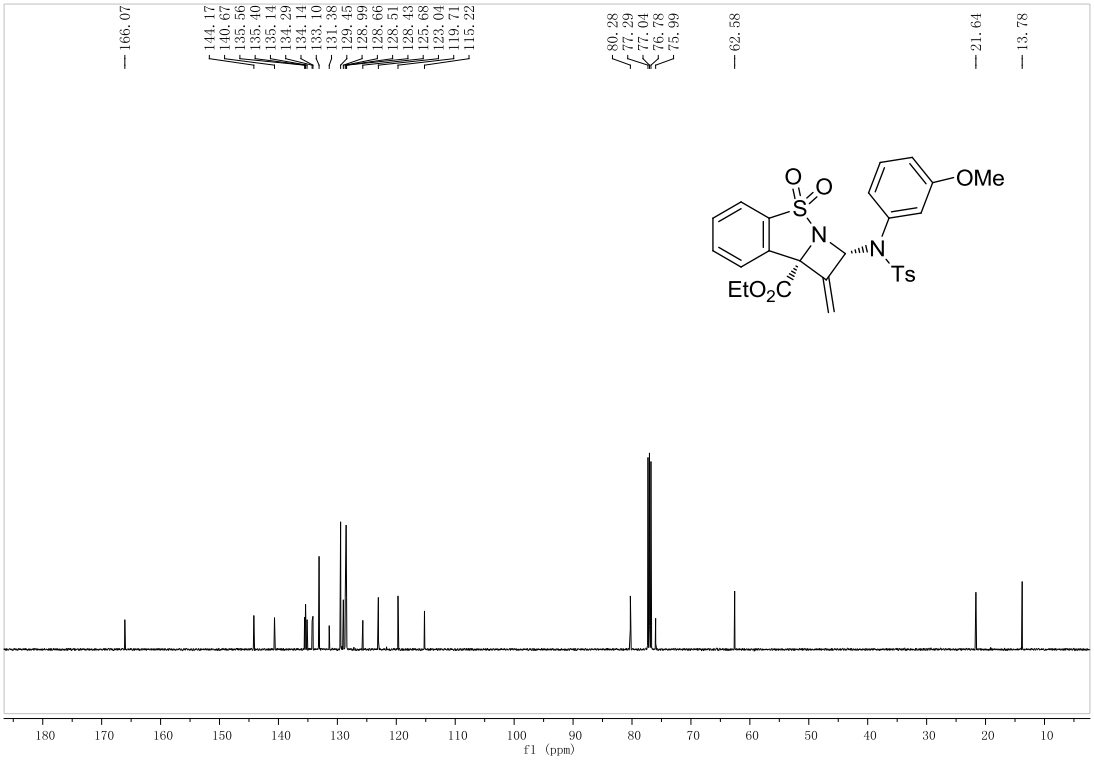
Ethyl 2-((N-(3-methoxyphenyl)-4-methylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3da**)

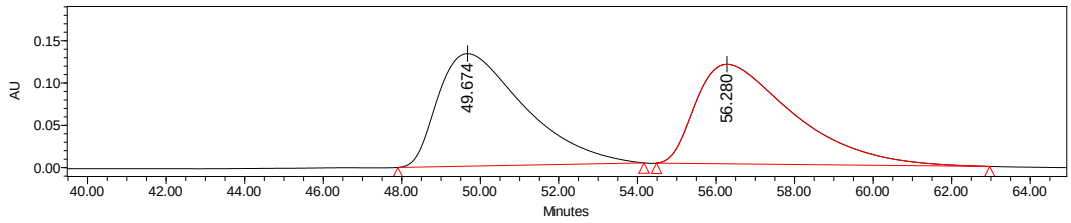


Reaction time: 2 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; light yellow solid, 78% yield, m.p. 96-98 ^{o}C, $[\alpha]_D^{15}$ = -4.0 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 55.9 min, t_{minor} = 49.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.81 (m, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.61-7.67 (m, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.85-6.90 (m, 2H), 6.78 (dt, *J* = 11.0, 2.5 Hz, 2H), 5.76 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.5 Hz, 1H),

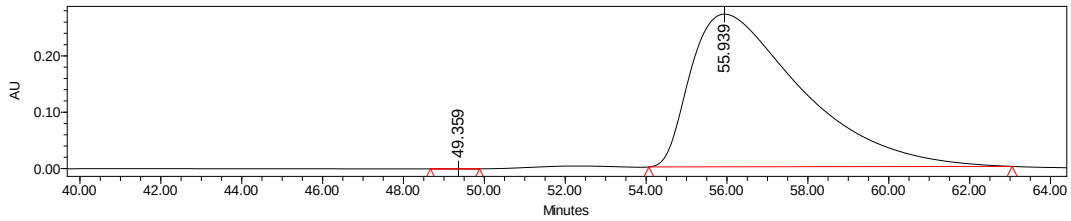
3.92-4.02 (m, 2H), 3.70 (s, 3H), 2.44 (s, 3H), 1.07 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 144.2, 140.8, 135.6, 135.4, 135.1, 134.3, 134.1, 133.1, 131.4, 129.5, 129.0, 128.7, 128.5, 128.4, 125.7, 123.0, 119.7, 115.2, 80.3, 76.0, 62.6, 21.6, 13.8. HRMS m/z (ESI+): Calculated for $C_{27}H_{27}N_2O_7S_2$ ($[M+H]^+$) 555.1254, found 555.1250.





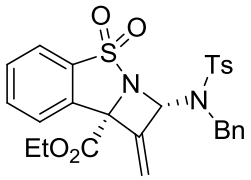


	Retention Time	Area	% Area	Height	% Height
1	49.674	20324451	49.83	132957	53.02
2	56.280	20465282	50.17	117794	46.98



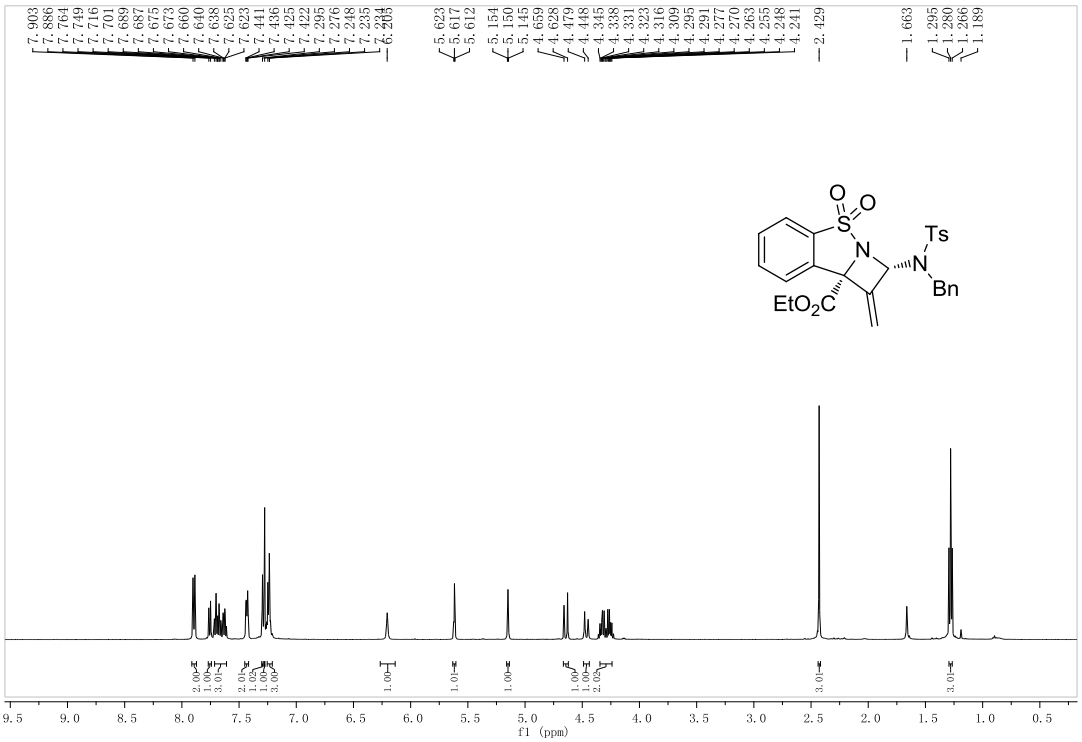
	Retention Time	Area	% Area	Height	% Height
1	49.359	3008	0.01	-59	0.02
2	55.939	51760505	99.99	271111	99.98

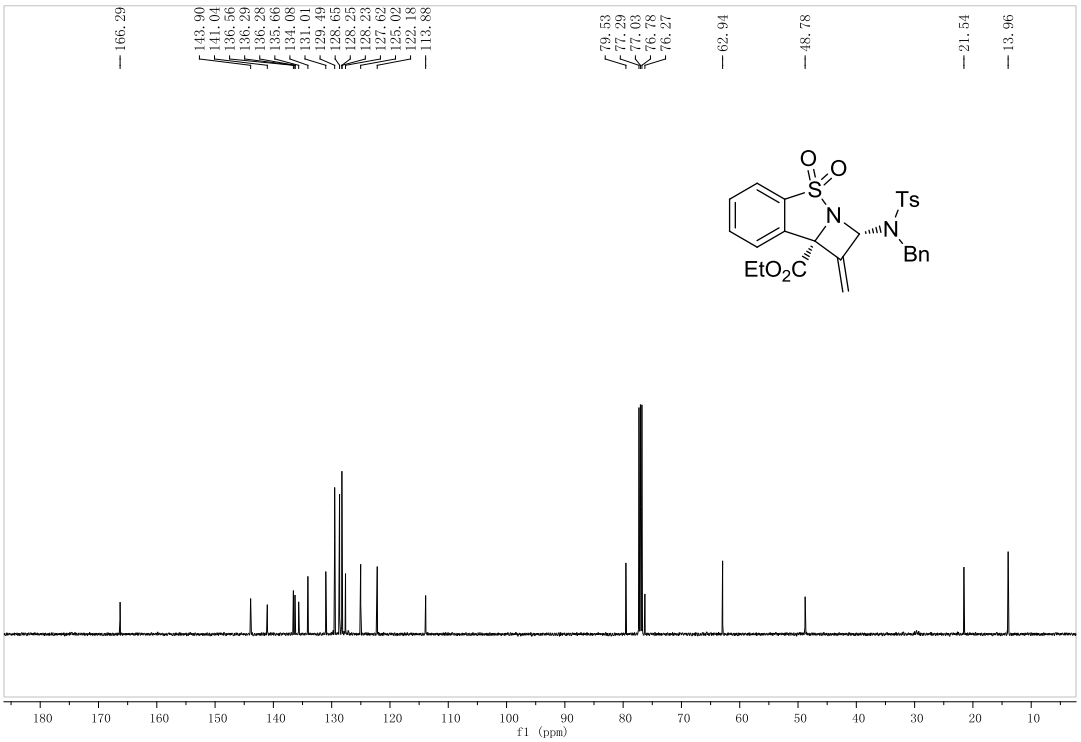
Ethyl 2-((N-benzyl-4-methylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ea**)

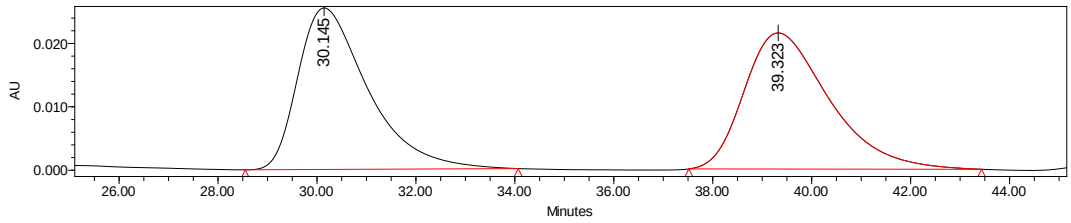


Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; light yellow solid, 71% yield, m.p. 126-128 ^{o}C $[\alpha]_D^{15}$ = 1.7 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm ×0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 38.1 min, t_{minor} = 30.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.60-7.72 (m, 3H), 7.43 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.30 (s, 1H), 7.28 (s, 1H), 7.23 (dt, *J* = 6.5, 5.0 Hz, 3H), 6.21 (s, 1H), 5.62 (t, *J* = 2.5 Hz, 1H), 5.15 (t, *J* = 2.5 Hz, 1H),

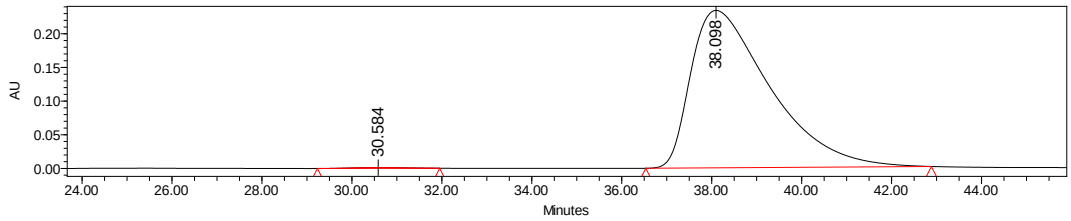
4.64 (d, *J* = 15.5 Hz, 1H), 4.46 (d, *J* = 15.5 Hz, 1H), 4.24-4.35 (m, 2H), 2.43 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 143.9, 141.0, 136.6, 136.3, 136.2, 135.7, 134.1, 131.0, 129.5, 128.7, 128.3, 128.2, 127.6, 125.0, 122.2, 113.9, 79.5, 76.3, 62.9, 48.8, 21.5, 14.0. HRMS m/z (ESI+): Calculated for $C_{27}H_{26}N_2NaO_6S_2$ ([M+Na]$^+$) 561.1124, found 561.1124.





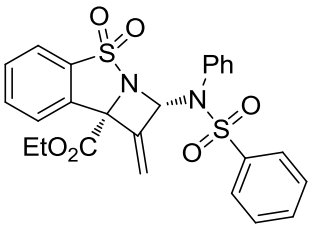


	Retention Time	Area	% Area	Height	% Height
1	30.145	2495188	49.10	25464	54.14
2	39.323	2586398	50.90	21569	45.86



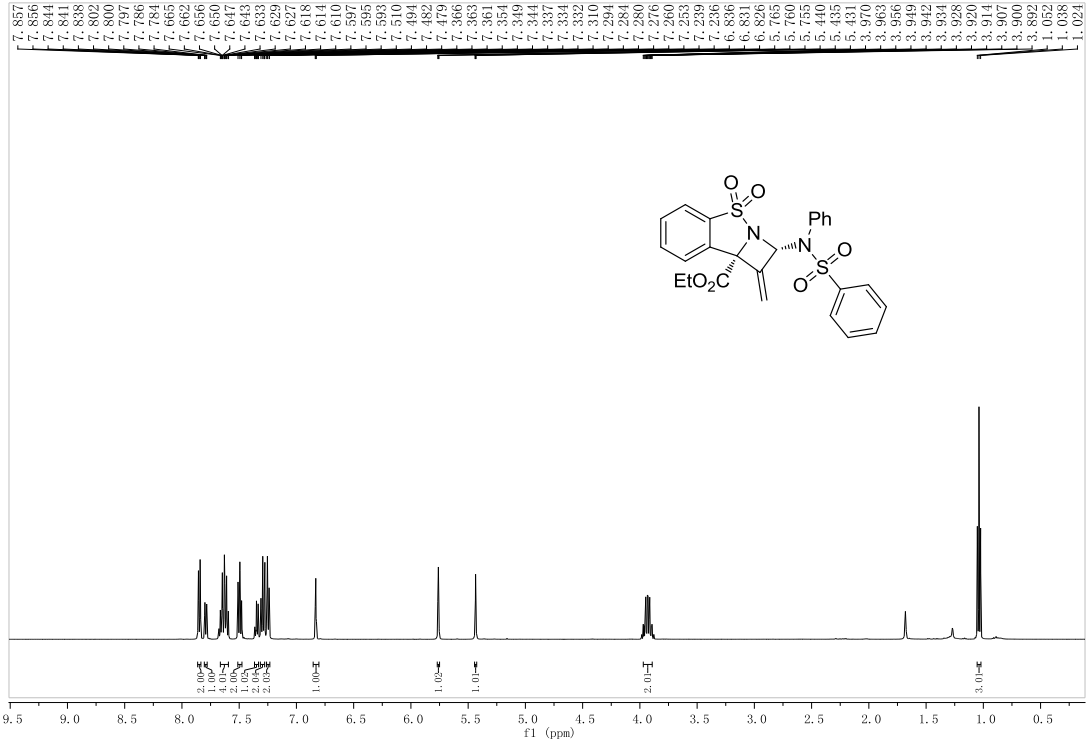
	Retention Time	Area	% Area	Height	% Height
1	30.584	94421	0.33	1144	0.49
2	38.098	28569714	99.67	233830	99.51

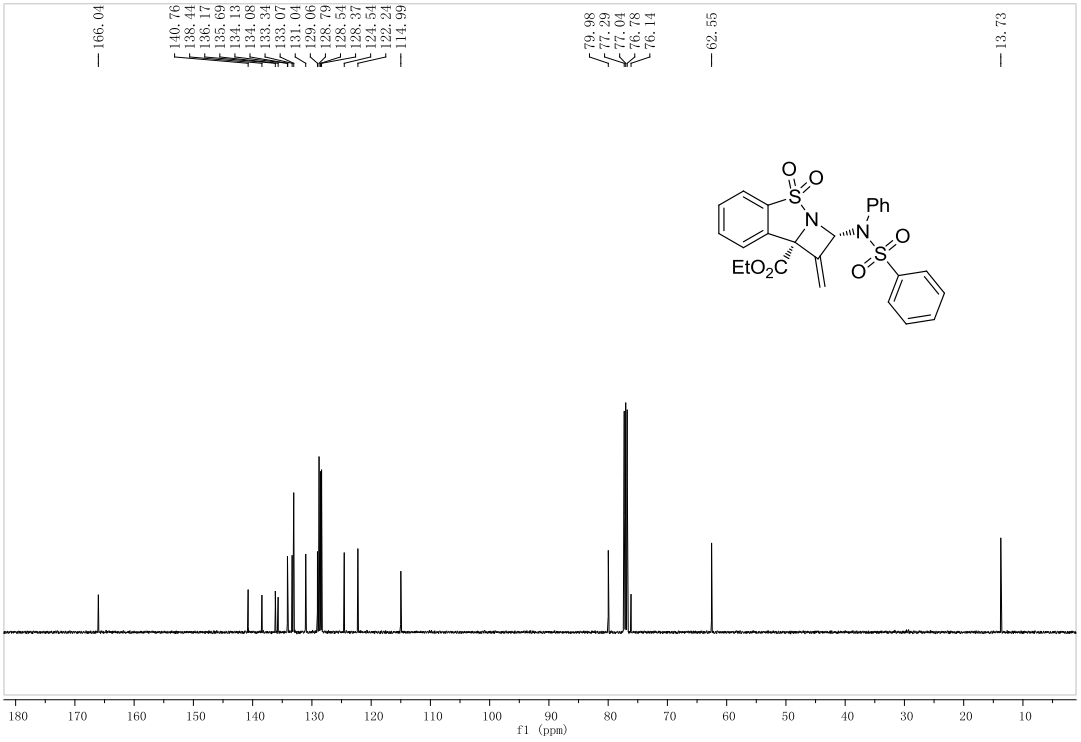
Ethyl 1-methylene-2-(N-phenylphenylsulfonamido)-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3fa**)

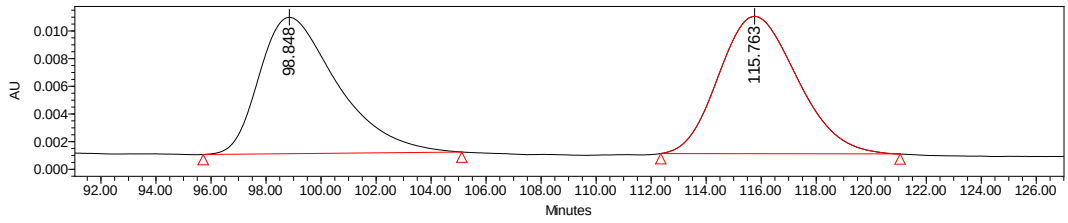


Reaction time: 2 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; colourless oil, 70% yield, $[\alpha]_D^{15}$ = -9.0 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 90/10, 0.8 mL/min, 254 nm; t_{major} = 119.9 min, t_{minor} = 105.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83-7.86 (m, 2H), 7.78-7.81 (m, 1H), 7.59-7.67 (m, 4H), 7.47-7.52 (m, 2H), 7.33-7.37 (m, 1H), 7.27-7.32 (m, 2H), 7.23-7.27 (m, 2H), 6.83 (t, *J* = 2.5 Hz, 1H), 5.76 (t, *J* = 2.5 Hz, 1H), 5.44 (t, *J* = 2.5 Hz, 1H), 3.87-3.99

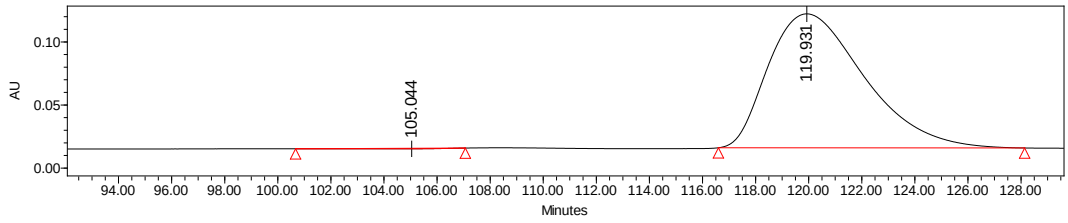
(m, 2H), 1.04 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 140.8, 138.4, 136.2, 135.7, 134.1, 134.0, 133.3, 133.1, 131.0, 129.1, 128.8, 128.5, 128.4, 124.5, 122.2, 115.0, 80.0, 76.1, 62.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{25}H_{23}N_2O_6S_2$ ($[M+H]^+$) 511.0992, found 511.0991.





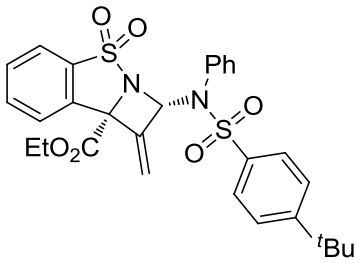


	Retention Time	Area	% Area	Height	% Height
1	98.848	1893381	48.50	9727	49.32
2	115.763	2010410	51.50	9996	50.68



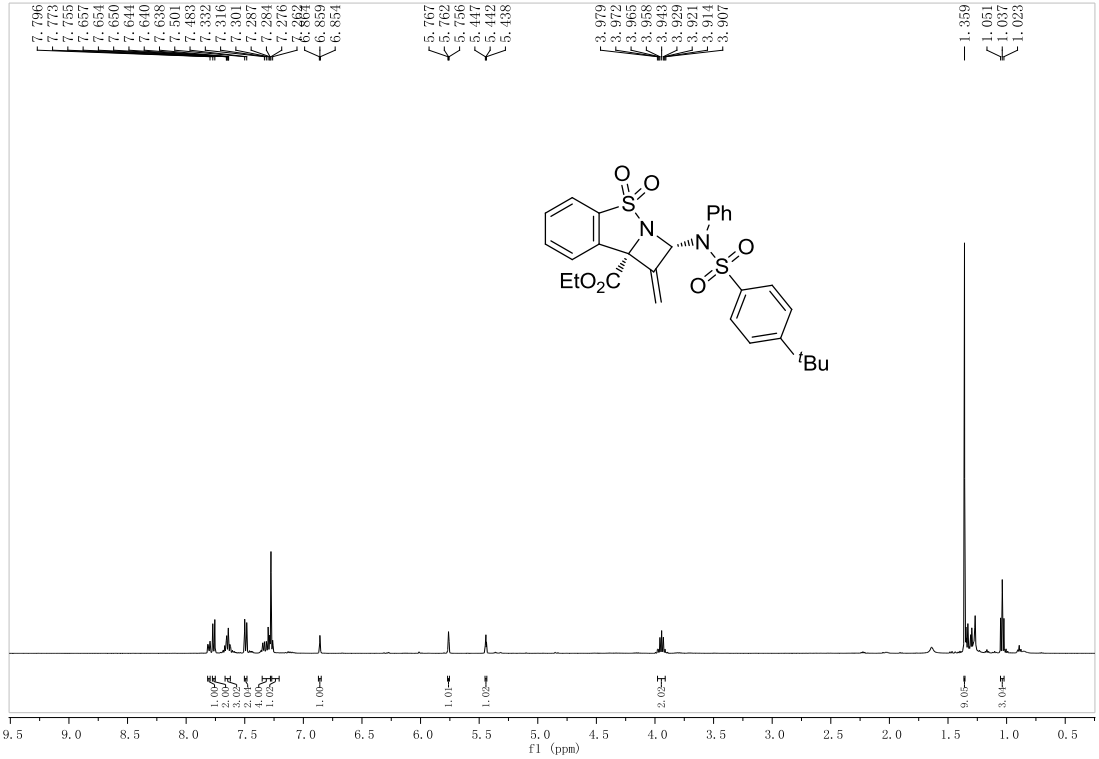
	Retention Time	Area	% Area	Height	% Height
1	105.044	84069	0.31	-385	0.36
2	119.931	26714091	99.69	106188	99.64

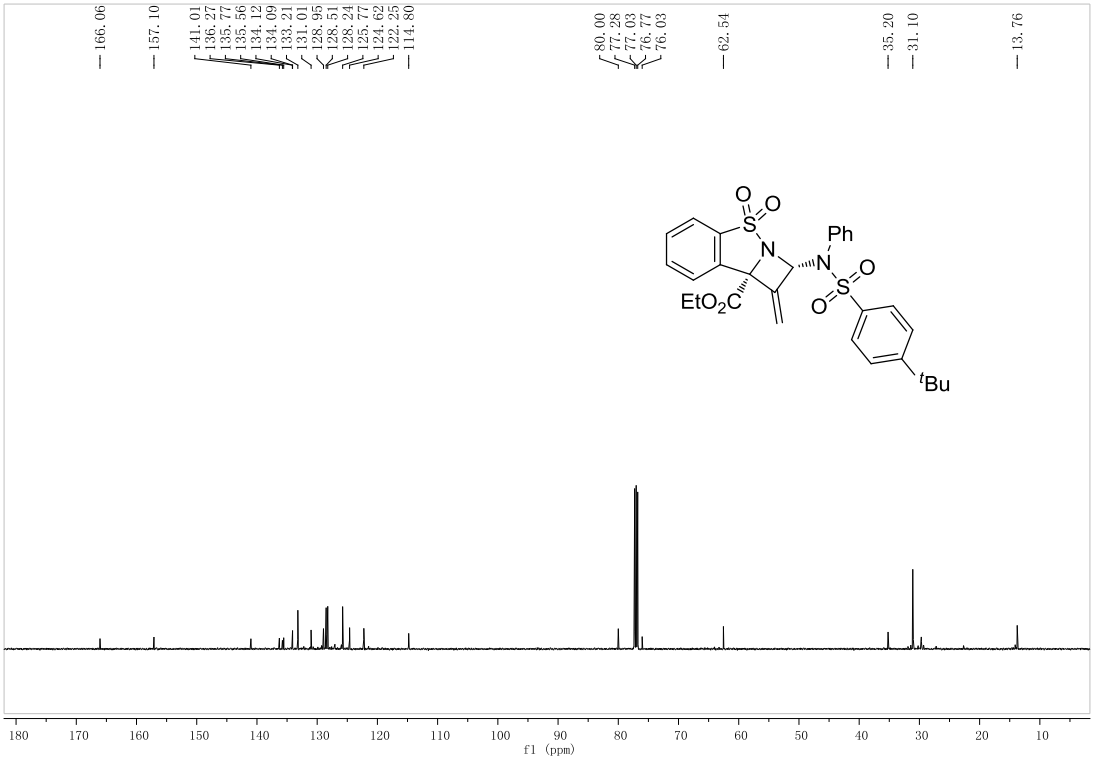
Ethyl 2-((4-(tert-butyl)-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ga**)

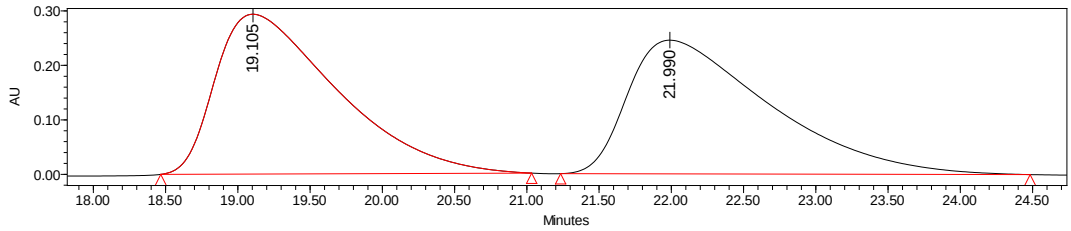


Reaction time: 2 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; white solid, 80% yield, m.p. 106-108 ^{o}C, $[\alpha]_D^{15}$ = -1.8 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-1 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 19.0 min, t_{minor} = 21.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.75-7.78 (m, 2H), 7.62-7.68 (m, 3H), 7.48-7.51 (m, 2H), 7.28-7.35 (m, 4H), 7.26 (d, *J* = 2.0 Hz,

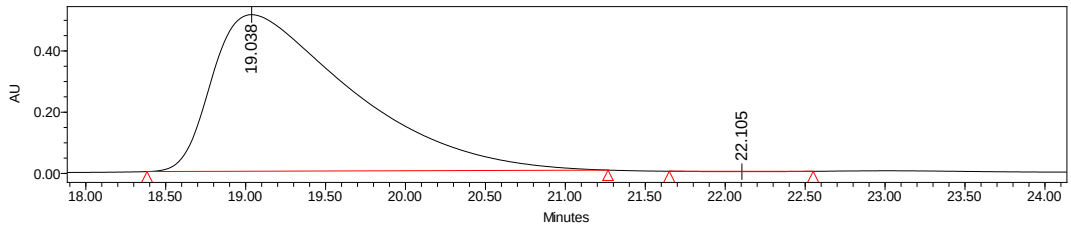
1H), 6.86 (t, *J* = 2.5 Hz, 1H), 5.76 (t, *J* = 2.5 Hz, 1H), 5.44 (t, *J* = 2.5 Hz, 1H), 3.90-3.98 (m, 2H), 1.36 (s, 9H), 1.04 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 157.1, 141.0, 136.3, 135.8, 135.6, 134.1, 134.0, 133.2, 131.0, 129.0, 128.5, 128.2, 125.8, 124.6, 122.3, 114.8, 80.0, 76.0, 62.5, 35.2, 31.1, 13.8. HRMS m/z (ESI+): Calculated for $C_{29}H_{31}N_2O_6S_2$ ([M+H]$^+$) 567.1618, found 567.1613.





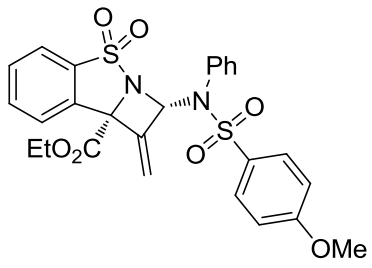


	Retention Time	Area	% Area	Height	% Height
1	19.105	17142762	50.55	293482	54.45
2	21.990	16767226	49.45	245530	45.55



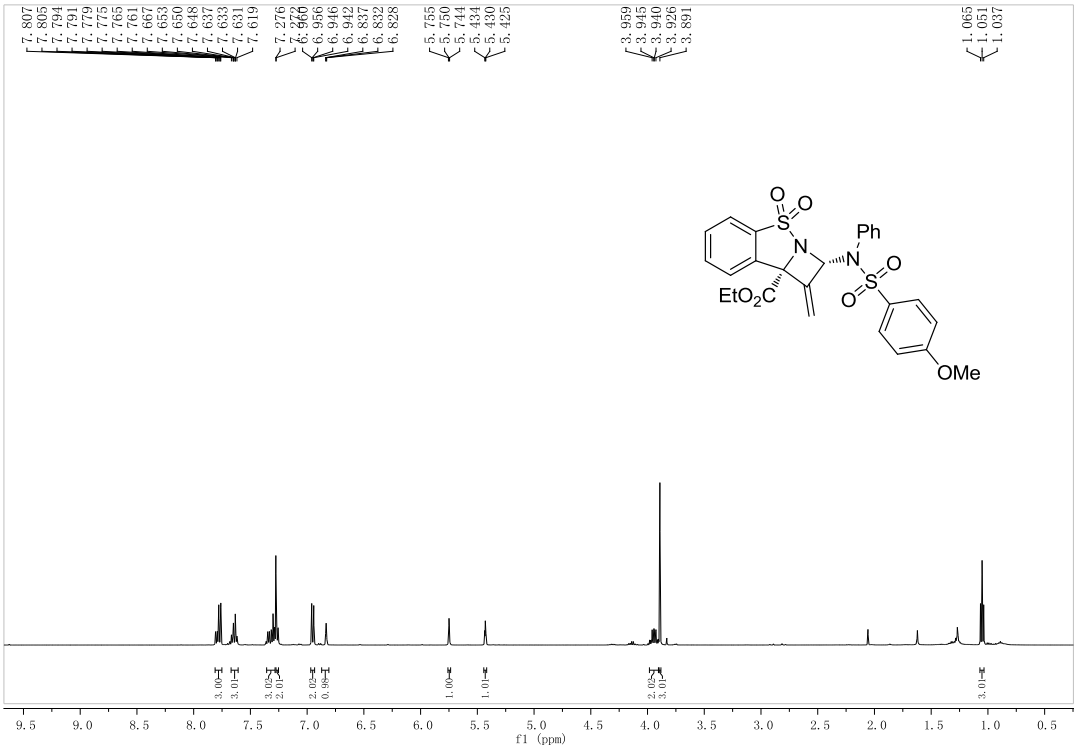
	Retention Time	Area	% Area	Height	% Height
1	19.038	30581333	99.71	509758	99.55
2	21.567	87695	0.29	-2324	0.45

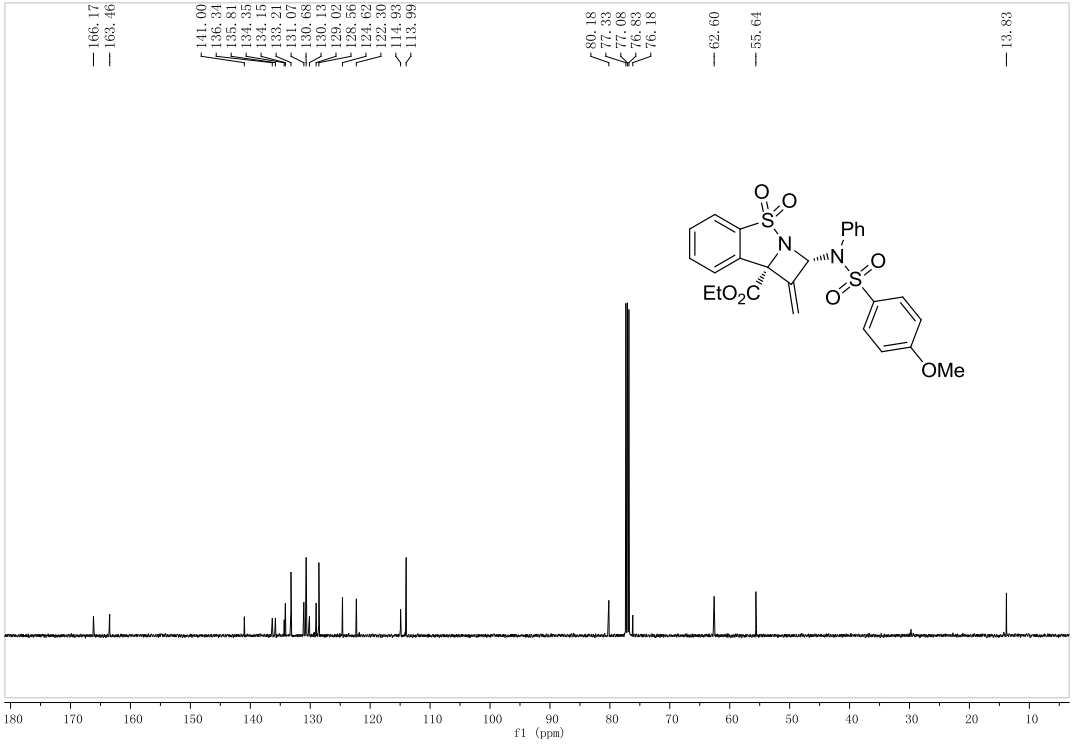
Ethyl 2-((4-methoxy-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ha**)

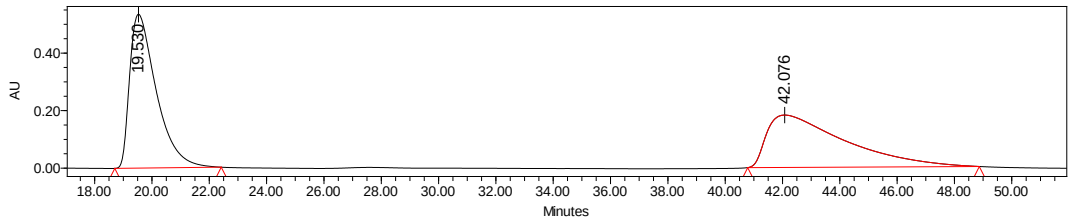


Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.2; light yellow solid, 70% yield, m.p. 134-136 ^{o}C, $[\alpha]_D^{15}$ = -4.6 (c =1.0 in CH_2Cl_2), 94% ee [Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 19.6 min, t_{minor} = 42.8 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.81 (m, 3H), 7.61-7.67 (m, 3H), 7.28-7.35 (m, 3H), 7.25-7.28 (m, 2H), 6.94-6.97 (m, 2H), 6.83 (t, *J* = 2.5 Hz, 1H),

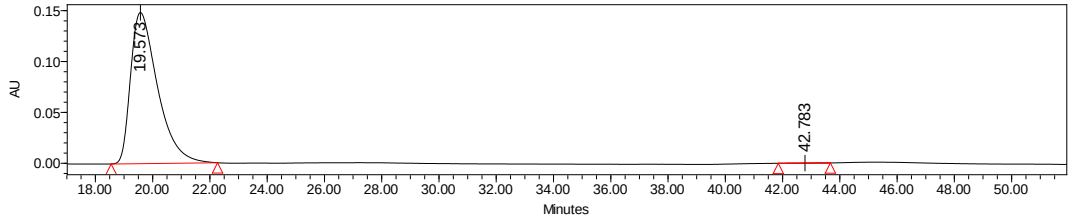
5.75 (t, *J* = 2.5 Hz, 1H), 5.43 (t, *J* = 2.5 Hz, 1H), 3.92-3.96 (m, 2H), 3.89 (s, 3H), 1.05 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 163.5, 141.0, 136.3, 135.8, 134.4, 134.2, 133.2, 131.1, 130.7, 130.1, 129.0, 128.6, 124.6, 122.3, 114.9, 114.0, 80.2, 76.2, 62.6, 55.6, 13.8. HRMS m/z (ESI+): Calculated for $C_{26}H_{25}N_2O_7S_2$ ($[M+H]^+$) 541.1098, found 541.1095.





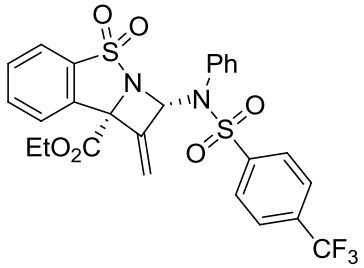


	Retention Time	Area	% Area	Height	% Height
1	19.530	34792332	49.52	535414	74.43
2	42.076	35467783	50.48	183961	25.57



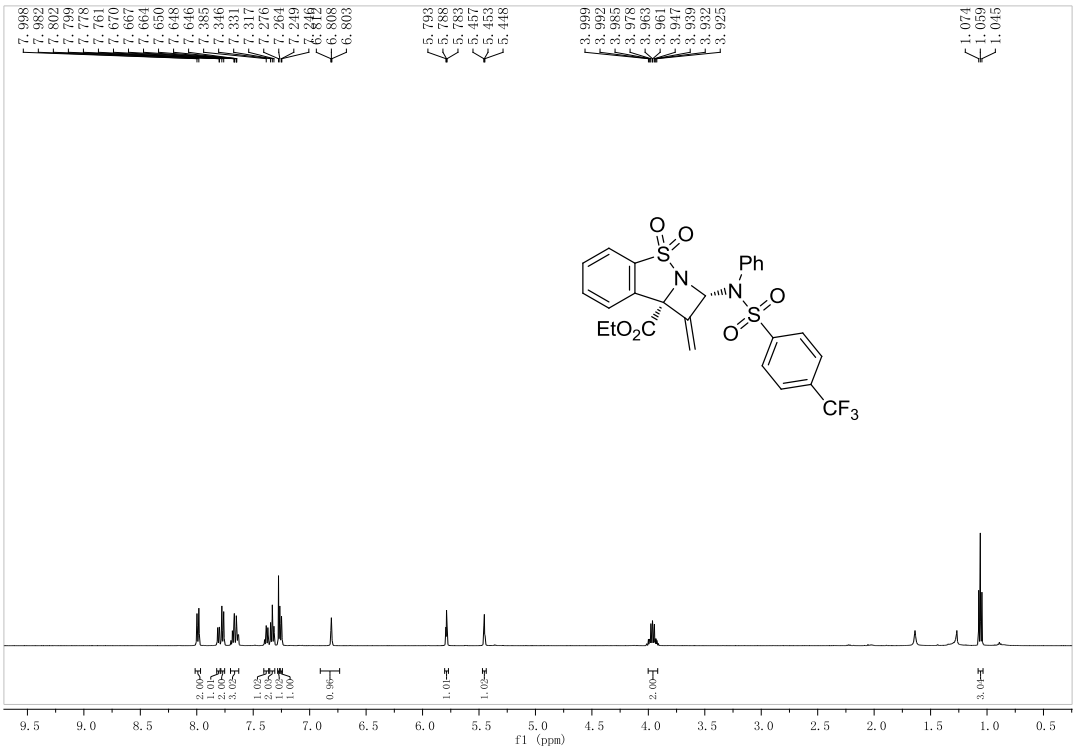
	Retention Time	Area	% Area	Height	% Height
1	19.573	9727954	99.99	148523	99.98
2	42.783	1149	0.01	-28	0.02

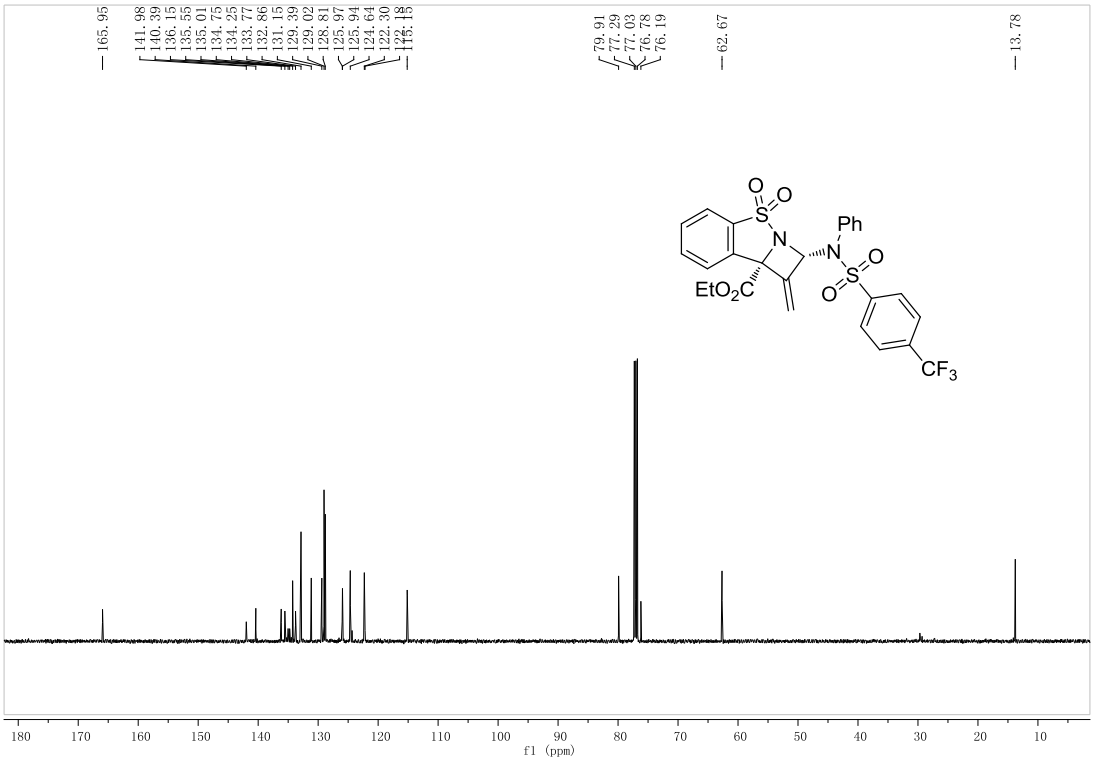
Ethyl 1-methylene-2-((N-phenyl-4-(trifluoromethyl)phenyl)sulfonamido)-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ia**)

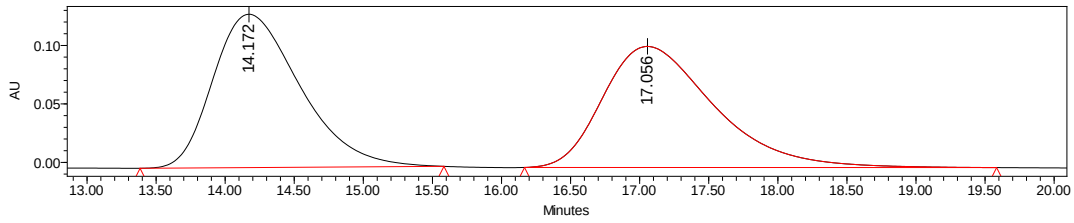


Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.5; light yellow solid, 66% yield, m.p. 158-160 ^{o}C , $[\alpha]_D^{15}$ = -13.6 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 14.3 min, t_{minor} = 17.1 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.81 (dd, *J* = 6.5, 1.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.62-7.70 (m, 3H), 7.36-7.41 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 6.81 (t, *J* = 2.5 Hz,

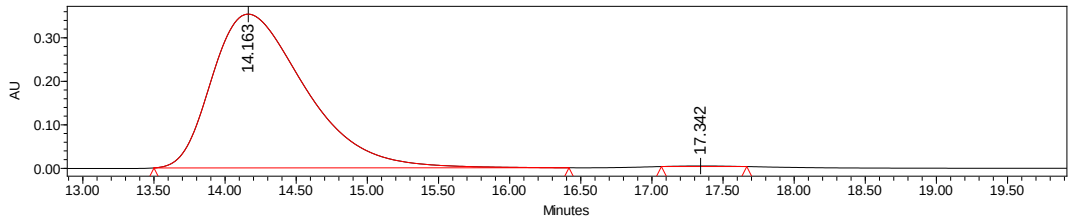
1H), 5.79 (t, *J* = 2.5 Hz, 1H), 5.45 (t, *J* = 2.5 Hz, 1H), 3.92–4.00 (m, 2H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 142.0, 140.4, 136.2, 135.6, 134.9 (q, *J* = 32.5 Hz), 134.3, 133.8, 132.9, 131.2, 129.4, 129.0, 128.8, 126.0 (q, *J* = 3.8 Hz), 124.6, 124.4, 122.2 (q, *J* = 15.0 Hz), 115.2, 79.9, 76.2, 62.7, 13.8. HRMS m/z (ESI+): Calculated for $C_{26}H_{22}F_3N_2O_6S_2$ ([M+H]$^+$) 579.0866, found 579.0863.





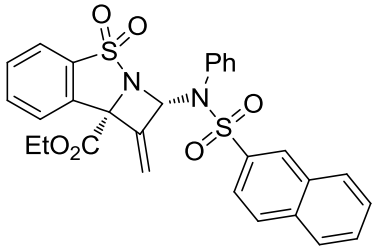


	Retention Time	Area	% Area	Height	% Height
1	14.172	5745164	49.75	131137	55.88
2	17.056	5803213	50.25	103544	44.12



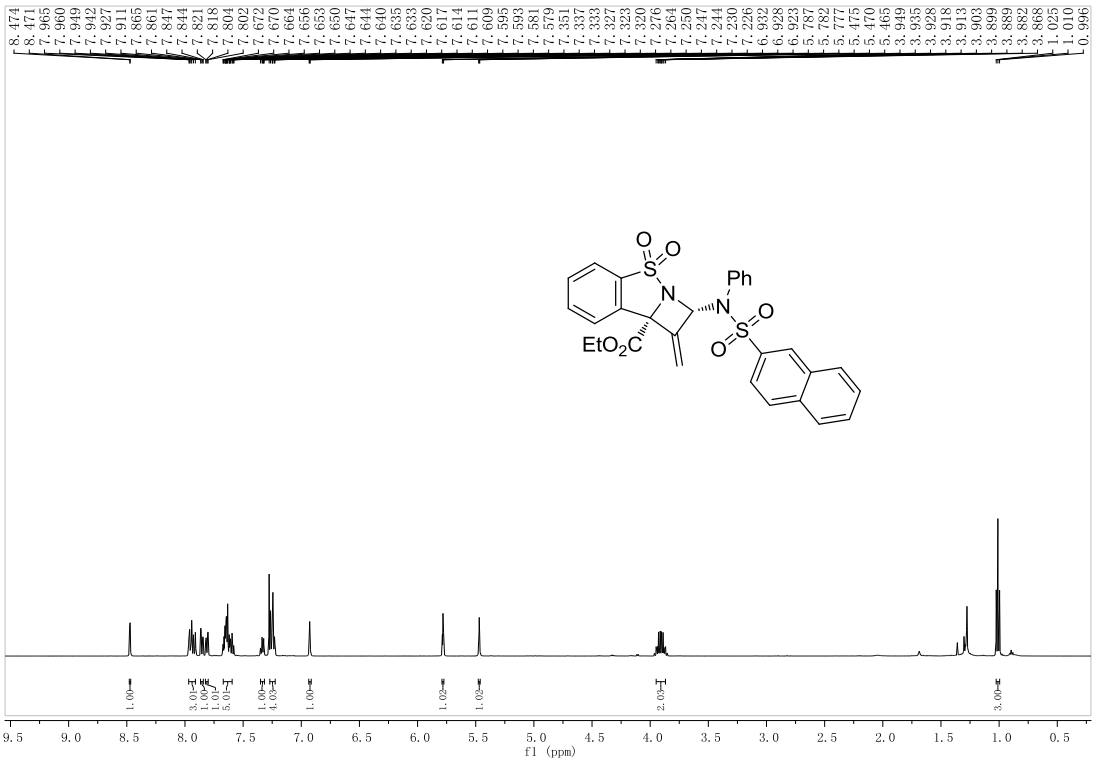
	Retention Time	Area	% Area	Height	% Height
1	14.163	15632079	99.91	350944	99.80
2	17.342	14029	0.09	709	0.20

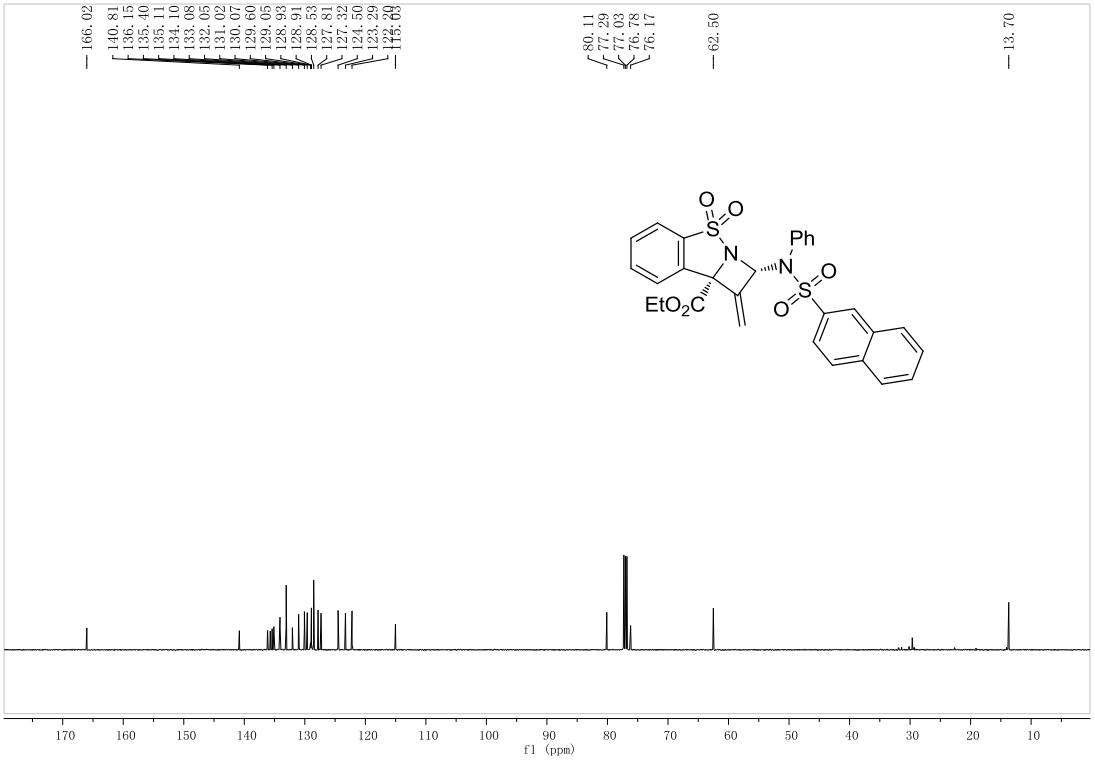
Ethyl 1-methylene-2-(N-phenylnaphthalene-2-sulfonamido)-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ja**)

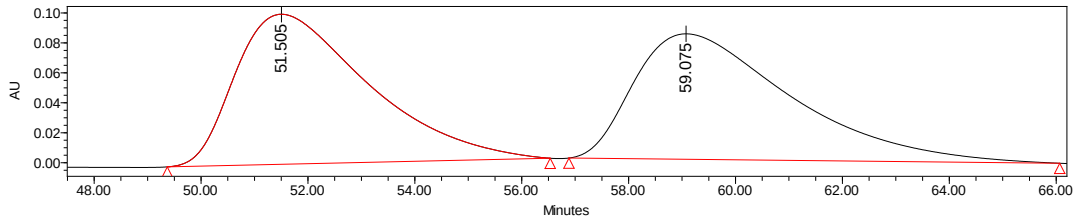


Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; light yellow solid, 80% yield, m.p. 146-148 ^{o}C $[\alpha]_D^{15}$ = -1.8 (c =1.0 in CH_2Cl_2), 94% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 50.9 min, t_{minor} = 59.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (d, *J* = 1.5 Hz, 1H), 7.91-7.97 (m, 3H), 7.85 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.57-7.68 (m, 5H), 7.31-7.36 (m, 1H), 7.22-7.27 (m, 4H), 6.93 (t, *J* = 2.5 Hz, 1H), 5.78 (t, *J* = 2.5 Hz, 1H),

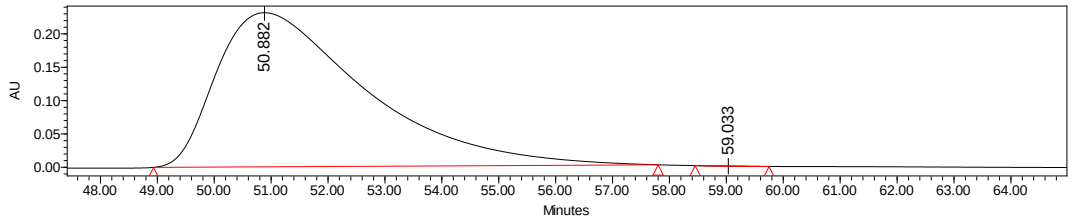
5.47 (t, *J* = 2.5 Hz, 1H), 3.86-3.95 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 140.8, 136.2, 135.7, 135.4, 135.1, 134.1, 134.0, 133.1, 132.1, 131.0, 130.1, 129.6, 129.1, 129.0, 128.9, 128.5, 127.8, 127.3, 124.5, 123.3, 122.2, 115.0, 80.1, 76.2, 62.5, 13.7. HRMS m/z (ESI+): Calculated for $C_{29}H_{25}N_2O_6S_2$ ($[M+H]^+$) 561.1149, found 561.1143.





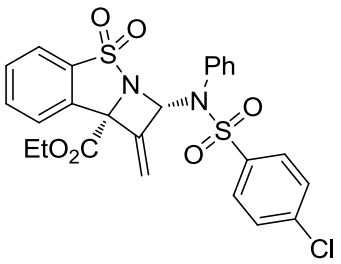


	Retention Time	Area	% Area	Height	% Height
1	51.505	17369264	50.43	100154	54.47
2	59.075	17069954	49.57	83724	45.53



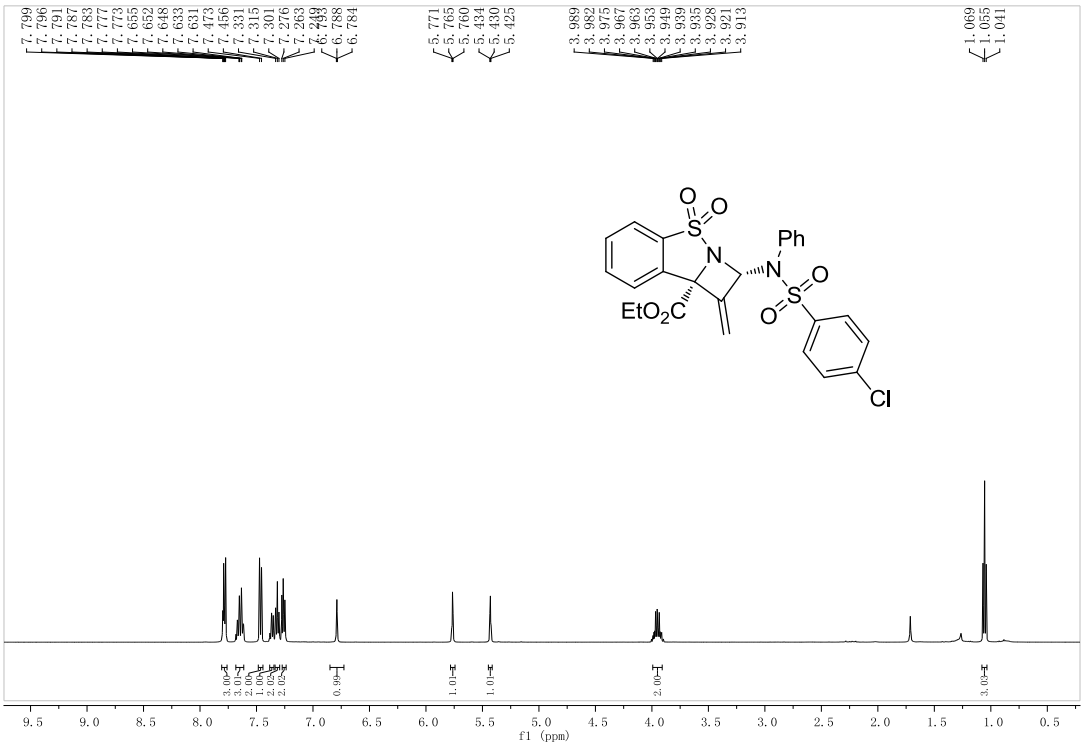
	Retention Time	Area	% Area	Height	% Height
1	50.882	42452720	99.93	231722	99.84
2	59.033	29180	0.07	-360	0.16

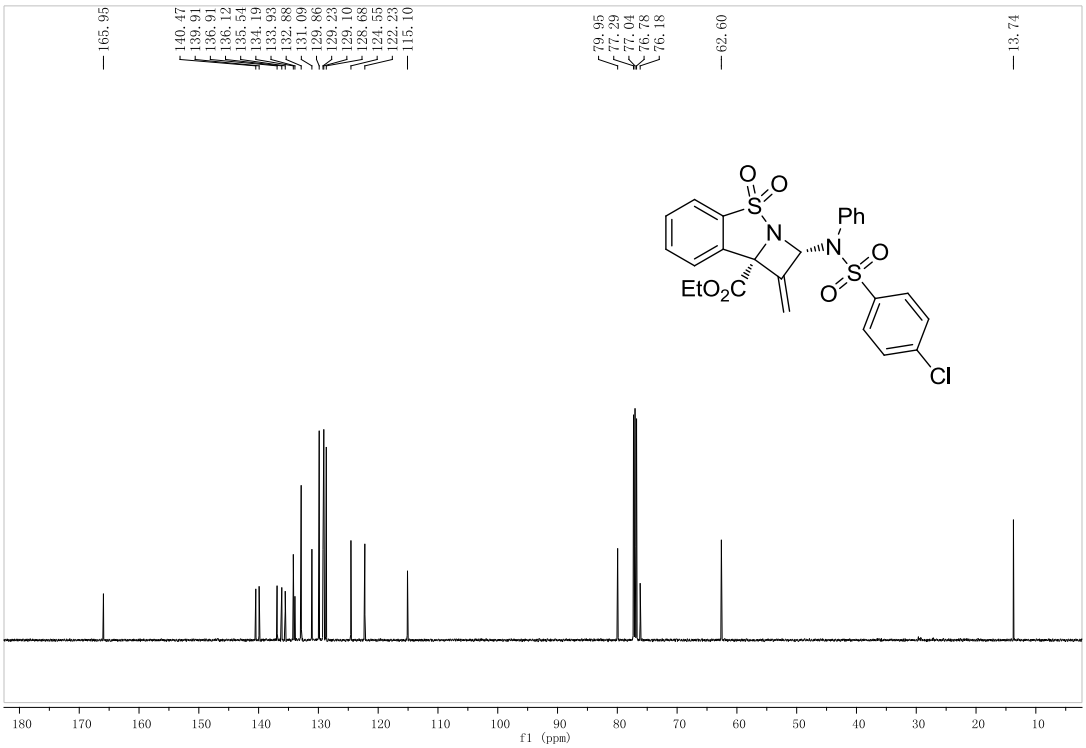
Ethyl 2-((4-chloro-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ka**)

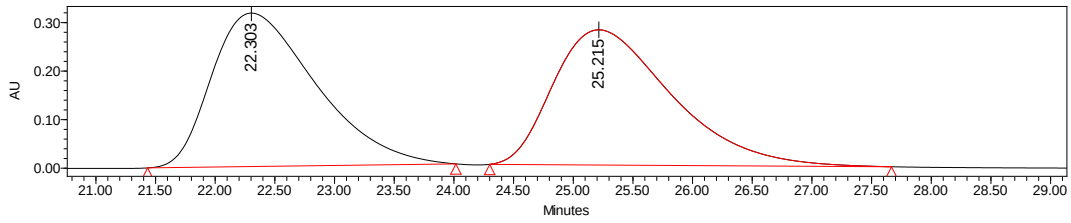


Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.5; light yellow solid, 72% yield, m.p. 116-118 ^{o}C , $[\alpha]_D^{15}$ = 8.0 (c =1.0 in CH_2Cl_2), 98% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 22.1 min, t_{minor} = 25.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.80 (m, 3H), 7.61-7.69 (m, 3H), 7.45-7.48 (m, 2H), 7.34-7.39 (m, 1H), 7.32 (t, *J* = 7.0 Hz, 2H), 7.24-7.27 (m, 2H),

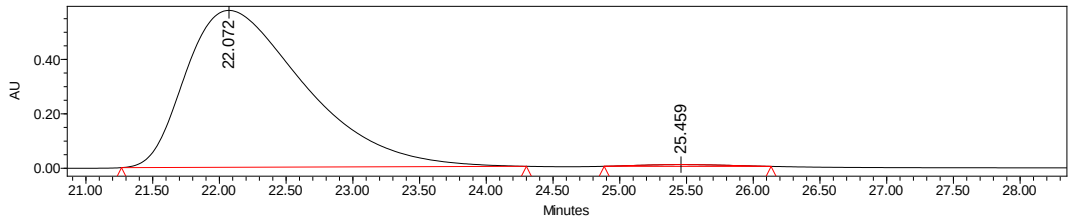
6.79 (t, *J* = 2.5 Hz, 1H), 5.77 (t, *J* = 2.5 Hz, 1H), 5.43 (t, *J* = 2.5 Hz, 1H), 3.91-3.99 (m, 2H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 140.5, 139.9, 136.9, 136.1, 135.5, 134.2, 133.9, 132.9, 131.1, 129.9, 129.2, 129.1 128.7, 124.6, 122.2, 115.1, 80.0, 76.2, 62.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{25}H_{22}ClN_2O_6S_2$ ($[M+H]^+$) 545.0602, found 545.0605.





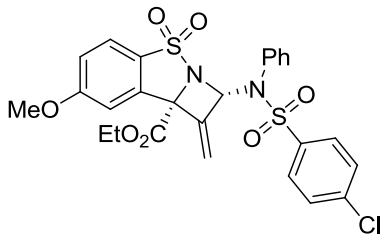


	Retention Time	Area	% Area	Height	% Height
1	22.303	19194862	49.95	316303	53.17
2	25.215	19229797	50.05	278555	46.83



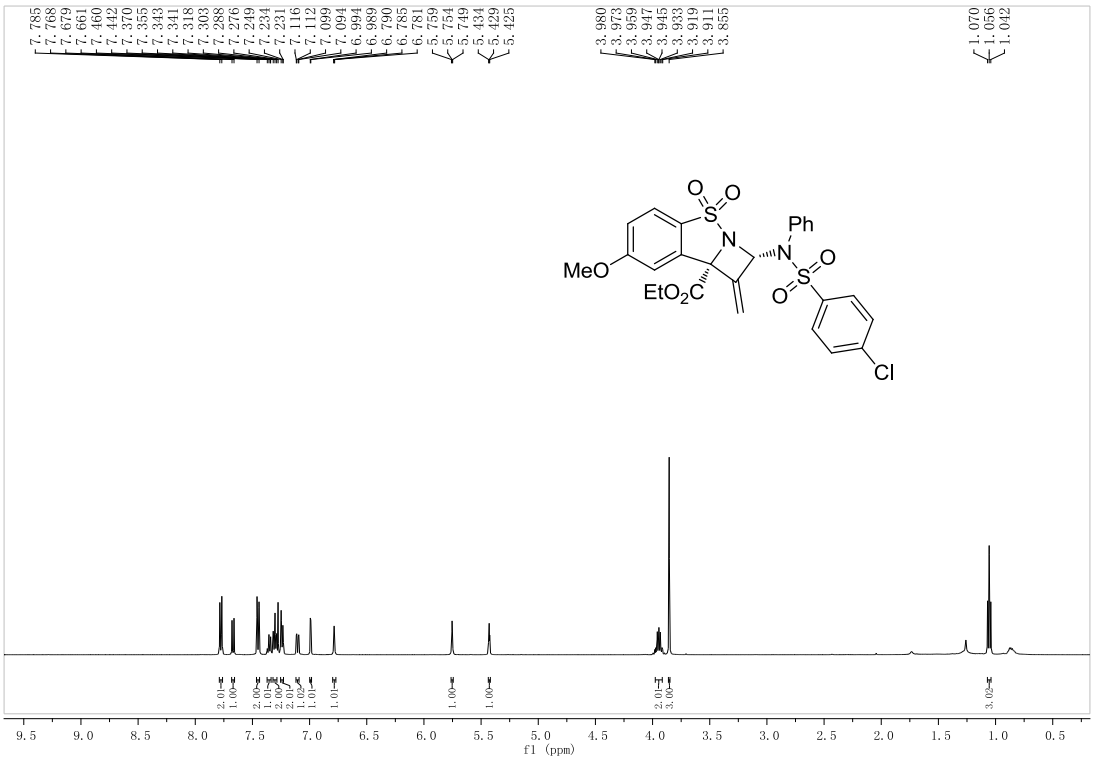
	Retention Time	Area	% Area	Height	% Height
1	22.072	35686750	99.06	576982	98.78
2	25.459	340350	0.94	7109	1.22

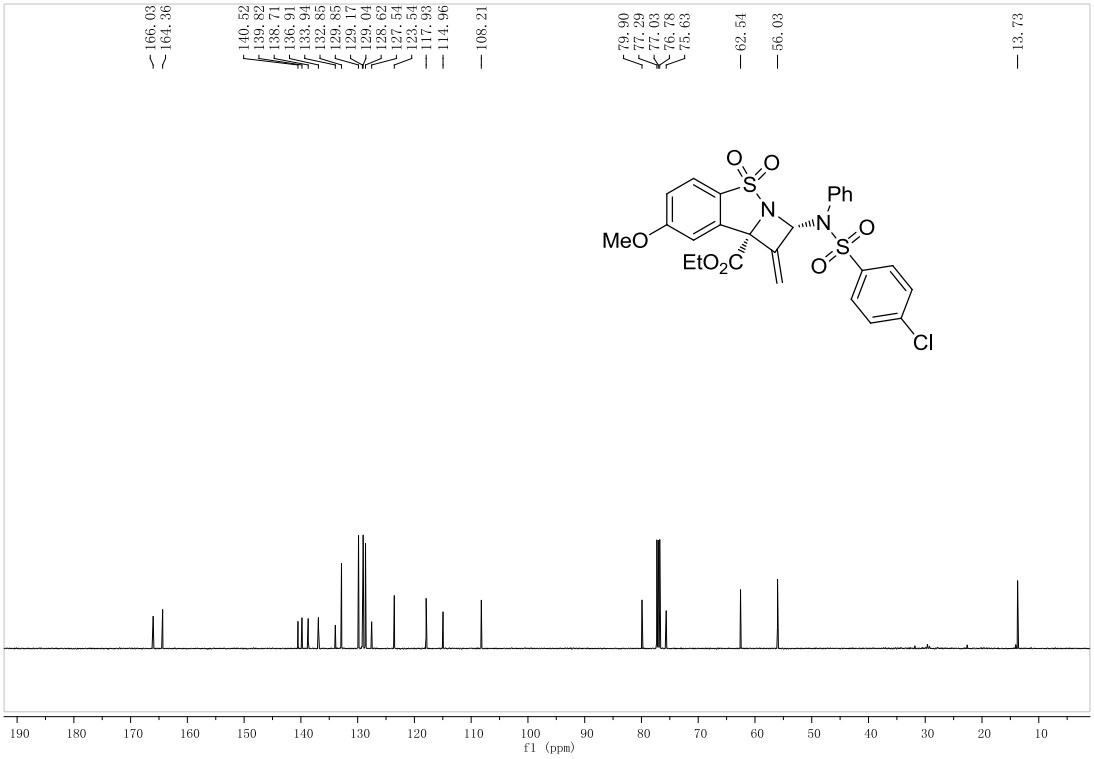
Ethyl 2-((4-chloro-N-phenylphenyl)sulfonamido)-7-methoxy-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3ke**)

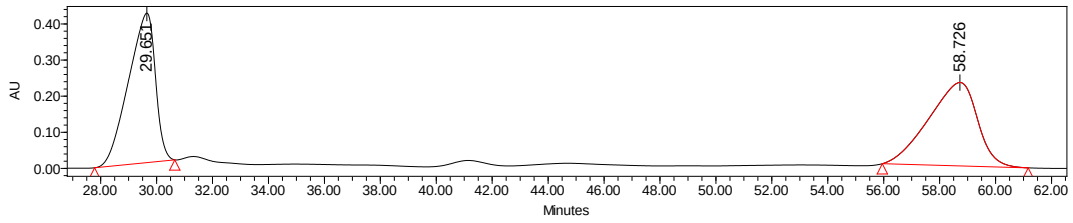


Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.3; white solid, 75% yield, m.p. 141-143 ^{o}C, $[\alpha]_D^{15}$ = 12.9 (c =1.0 in CH_2Cl_2), 99% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 62.2 min, t_{minor} = 29.2 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.34-7.38 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23-7.25 (m, 2H), 7.11 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.79 (t, *J* = 2.5

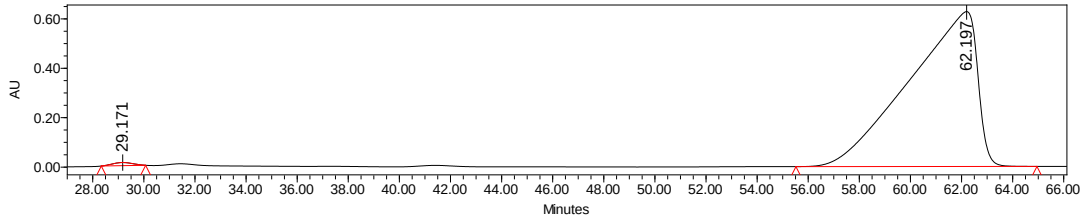
Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.43 (t, *J* = 2.5 Hz, 1H), 3. 91-3.99 (m, 2H), 3.86 (s, 3H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 164.4, 140.5, 139.8, 138.7, 136.9, 133.9, 132.9, 129.9, 129.2, 129.0 128.6, 127.5, 123.5, 117.9, 115.0, 108.2, 79.9, 75.6, 62.5, 56.0, 13.7. HRMS m/z (ESI+): Calculated for $C_{25}H_{24}ClN_2O_7S_2$ ([M+H]$^+$) 575.0708, found 575.0710.





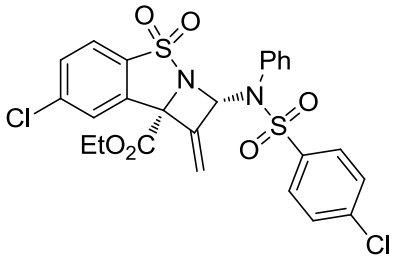


	Retention Time	Area	% Area	Height	% Height
1	29.651	27703284	49.73	414022	64.19
2	58.726	28007489	50.27	230939	35.81



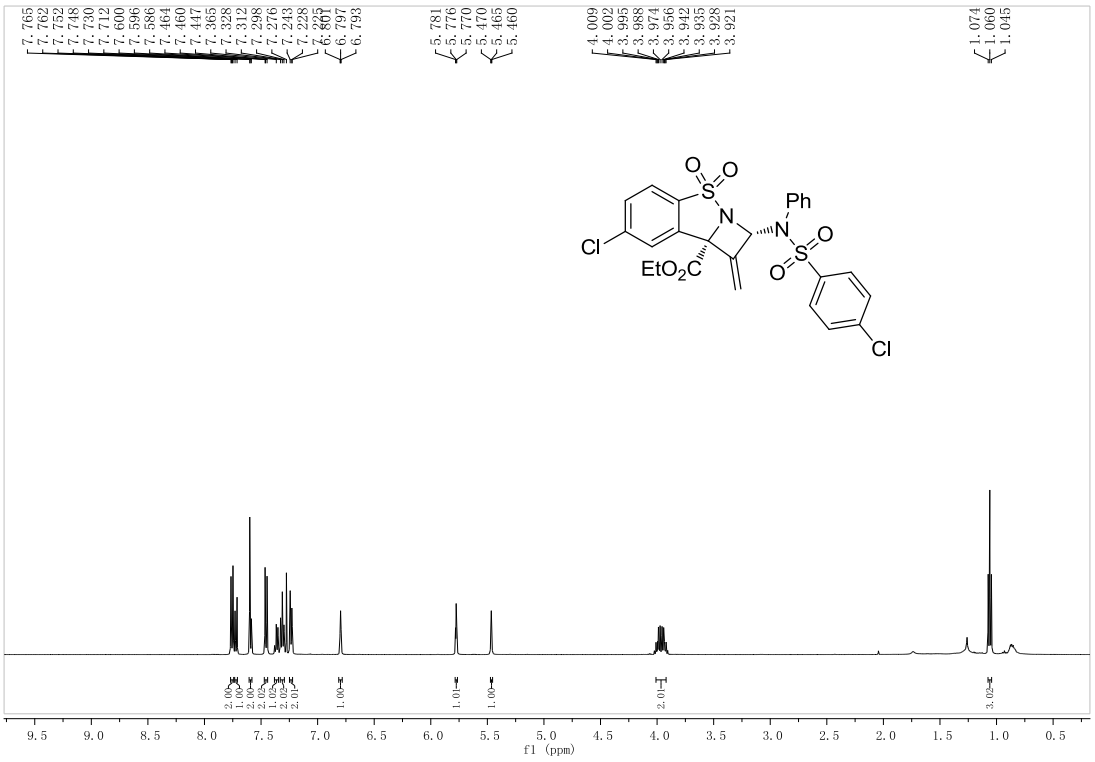
	Retention Time	Area	% Area	Height	% Height
1	29.171	594335	0.51	11549	1.81
2	62.197	116129370	99.49	625776	98.19

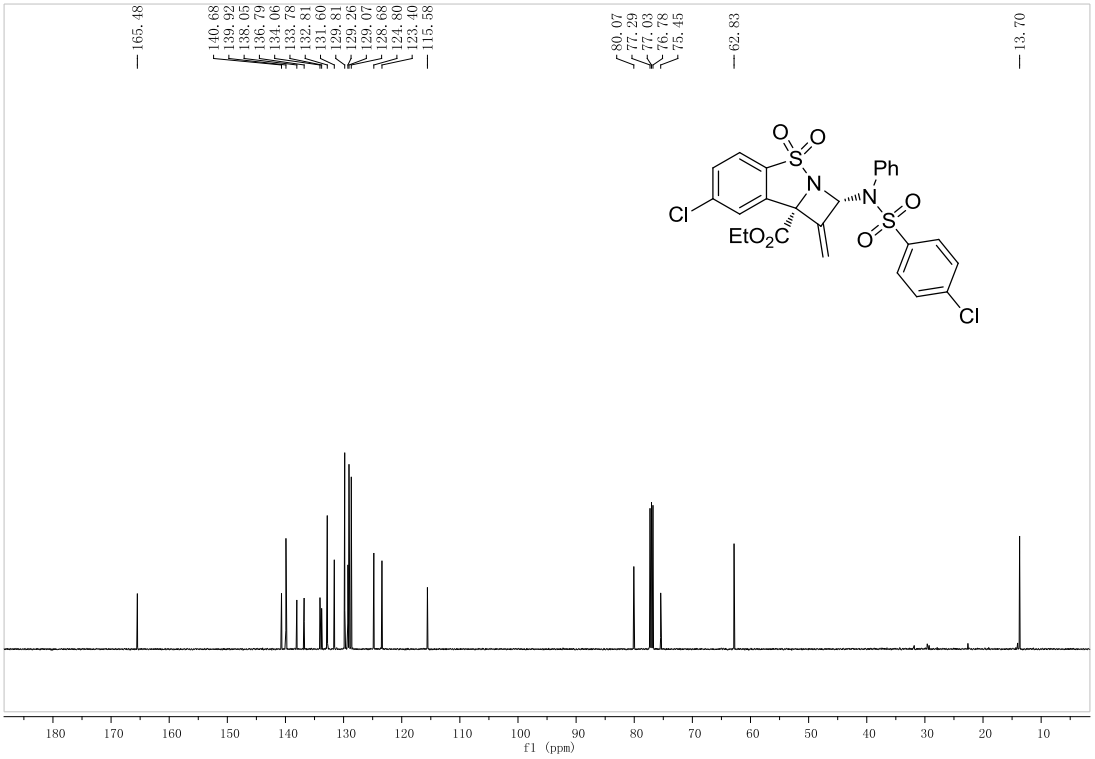
Ethyl 7-chloro-2-((4-chloro-N-phenylphenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3kh**)

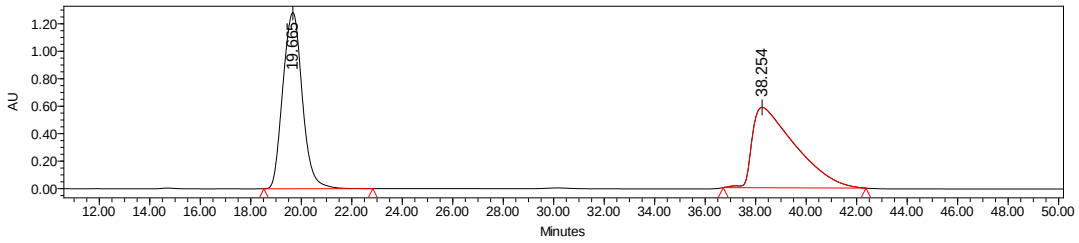


Reaction time: 4 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; white solid, 90% yield, m.p. 138-140 ^{o}C, $[\alpha]_D^{15}$ = 12.9 (c =1.0 in CH_2Cl_2), 98% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 38.4 min, t_{minor} = 19.8 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.78 (m, 2H), 7.71-7.74 (m, 1H), 7.59 (dd, *J* = 7.0, 2.0 Hz, 2H), 7.44-7.47 (m, 2H), 7.35-7.39 (m, 1H), 7.31 (t, *J* = 7.5 Hz,

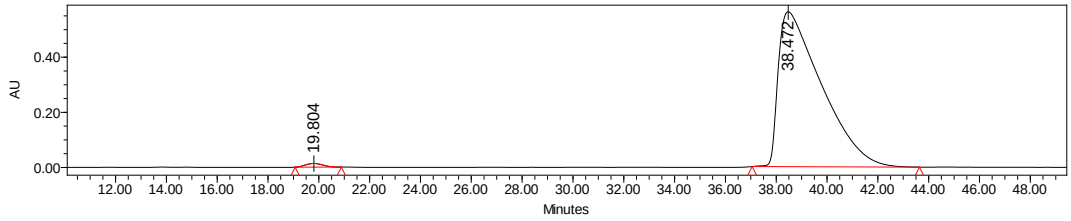
2H), 7.22-7.25 (m, 2H), 6.80 (t, *J* = 2.5 Hz, 1H), 5.78 (t, *J* = 2.5 Hz, 1H), 5.47 (t, *J* = 2.5 Hz, 1H), 3.92-4.01 (m, 2H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 140.7, 139.9, 138.1, 136.8, 134.1, 133.8, 132.8, 131.6, 129.8, 129.3, 129.1, 128.7, 124.8, 123.4, 115.6, 80.1, 75.5, 62.8, 13.7. HRMS m/z (ESI+): Calculated for $C_{25}H_{21}Cl_2N_2O_6S_2$ ([M+H]$^+$) 579.0213, found 579.0236.





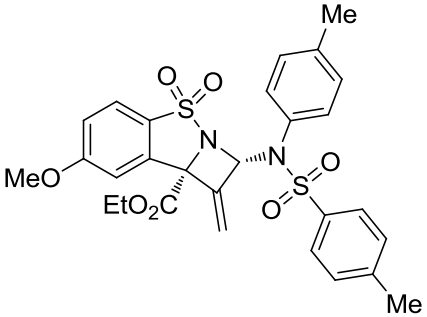


	Retention Time	Area	% Area	Height	% Height
1	19.665	68372194	49.19	1281806	68.50
2	38.254	70613166	50.81	589540	31.50



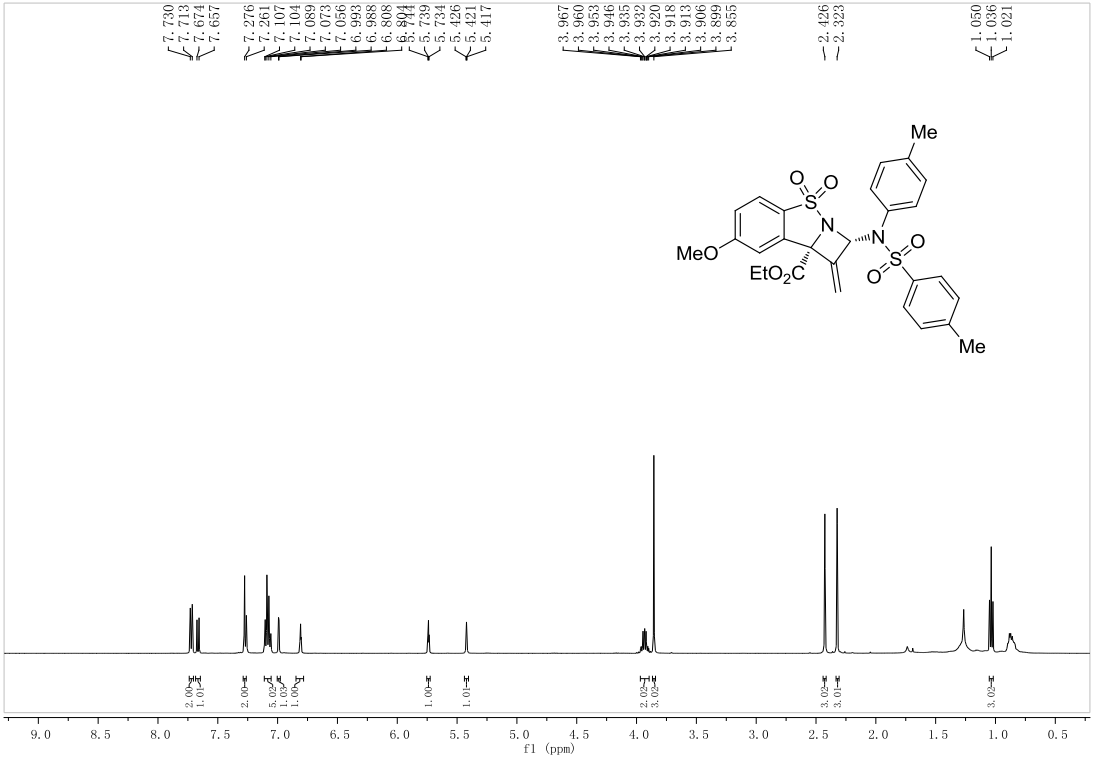
	Retention Time	Area	% Area	Height	% Height
1	19.804	625615	0.93	13269	2.31
2	38.472	66477193	99.07	562077	97.69

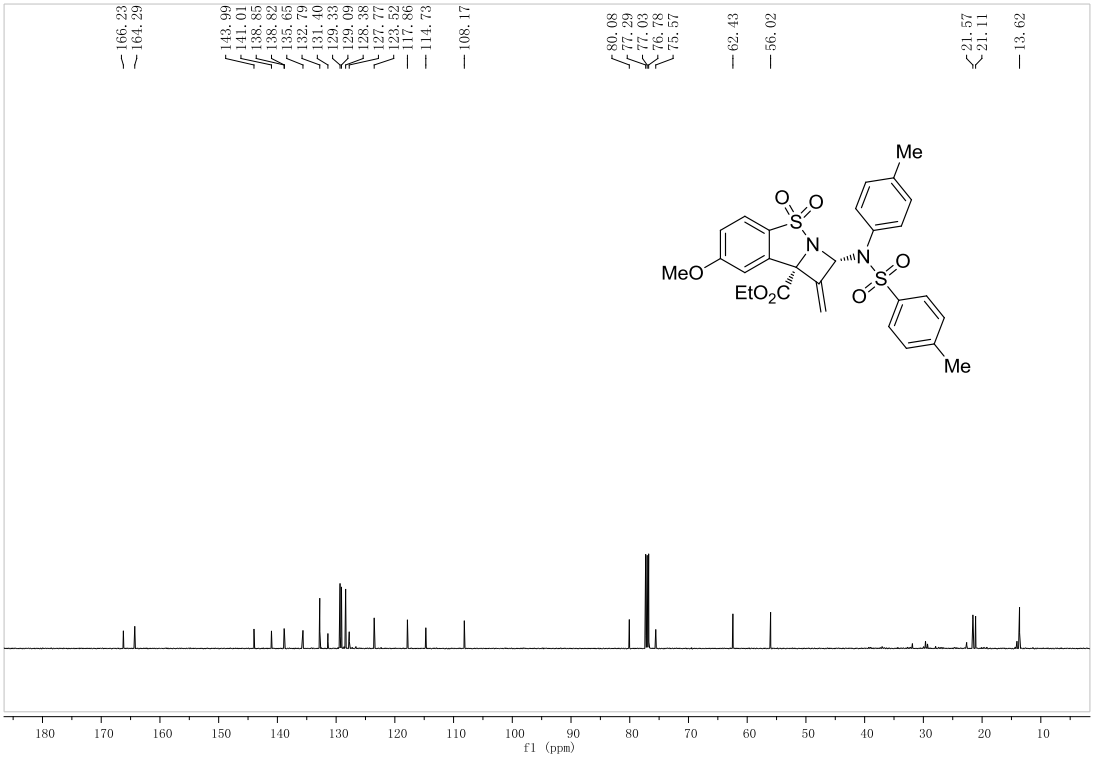
Ethyl 7-methoxy-2-((4-methyl-N-(p-tolyl)phenyl)sulfonamido)-1-methylene-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3be**)

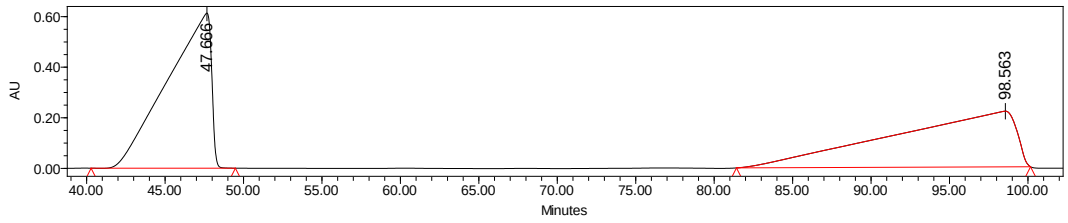


Reaction time: 3 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.2; light yellow solid, 85% yield, m.p. 195-197 ^{o}C, $[\alpha]_D^{15}$ = 20.7 (c =1.0 in CH_2Cl_2), 98% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 98.6 min, t_{minor} = 43.7 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.28 (s, 2H), 7.05-7.11 (m, 5H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.81 (t, *J* = 2.0 Hz,

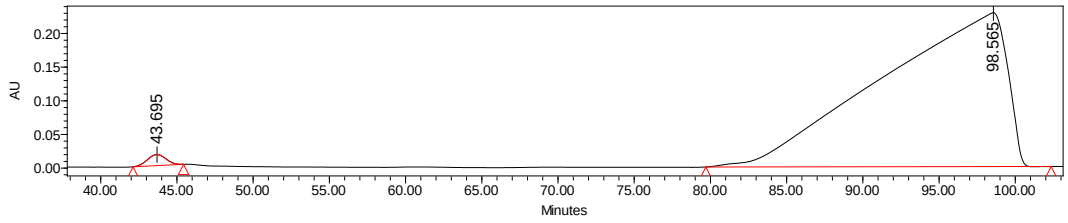
1H), 5.74 (t, *J* = 2.5 Hz, 1H), 5.42 (t, *J* = 2.5 Hz, 1H), 3.89-3.97 (m, 2H), 3.86 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 164.3, 144.0, 141.0, 138.9, 138.8, 135.7, 132.8, 131.4, 129.3, 129.1, 128.4, 127.8, 123.5, 117.9, 114.7, 108.2, 80.1, 75.6, 62.4, 56.0, 21.5, 21.1, 13.6. HRMS m/z (ESI+): Calculated for $C_{28}H_{29}N_2O_7S_2$ ($[M+H]^+$) 569.1411, found 569.1415.





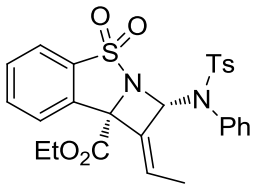


	Retention Time	Area	% Area	Height	% Height
1	47.666	119708434	49.58	613503	73.59
2	98.563	121713702	50.42	220185	26.41



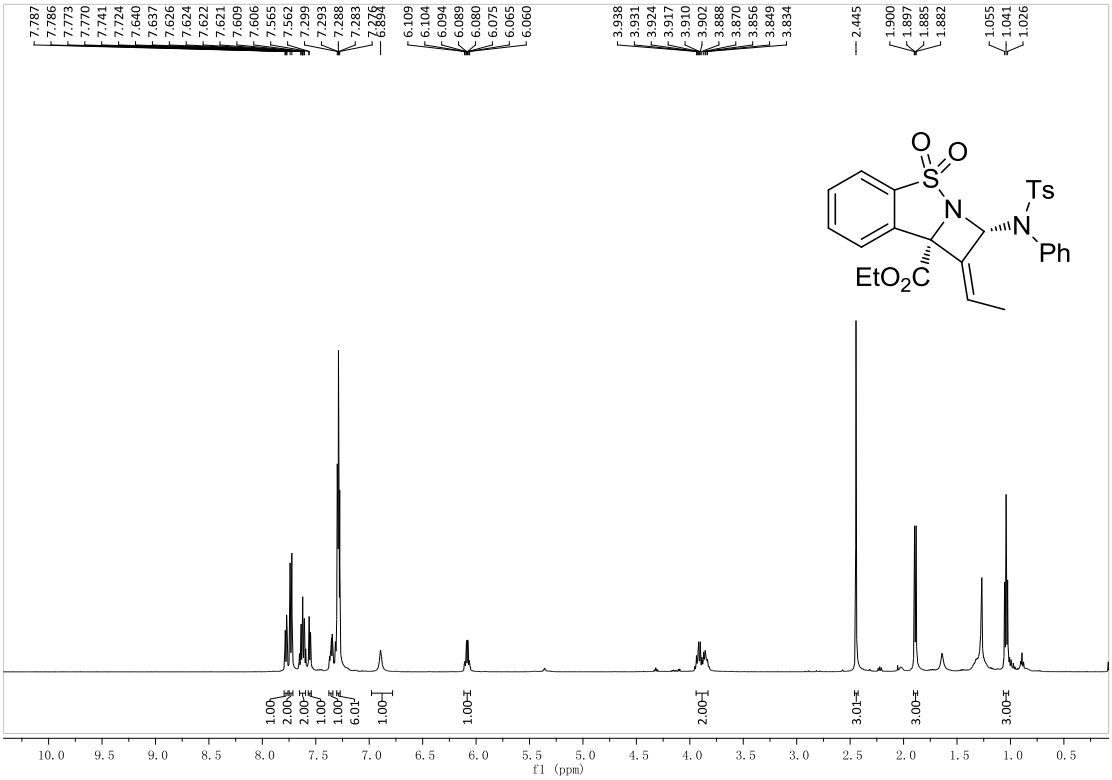
	Retention Time	Area	% Area	Height	% Height
1	43.695	1367011	1.03	16295	6.64
2	98.565	131548258	98.97	228931	93.36

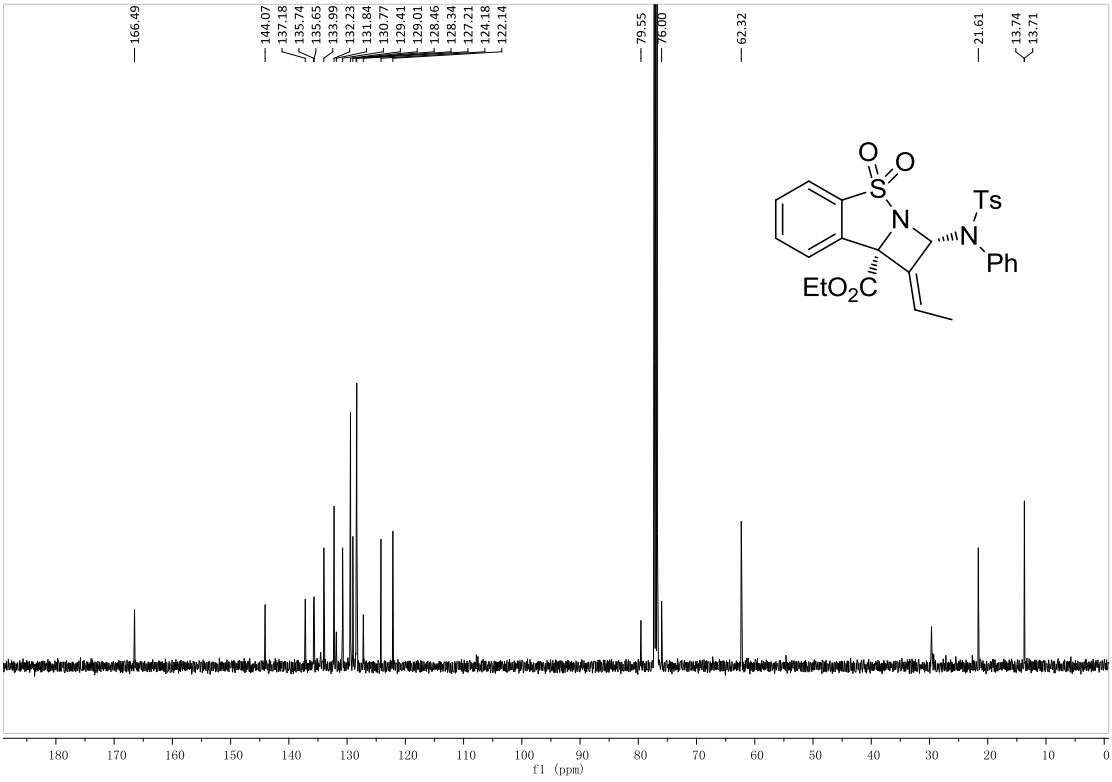
Ethyl 1-ethylidene-2-(4-methyl-N-phenylphenylsulfonamido)-2,8b-dihydro-1H-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**3la**)

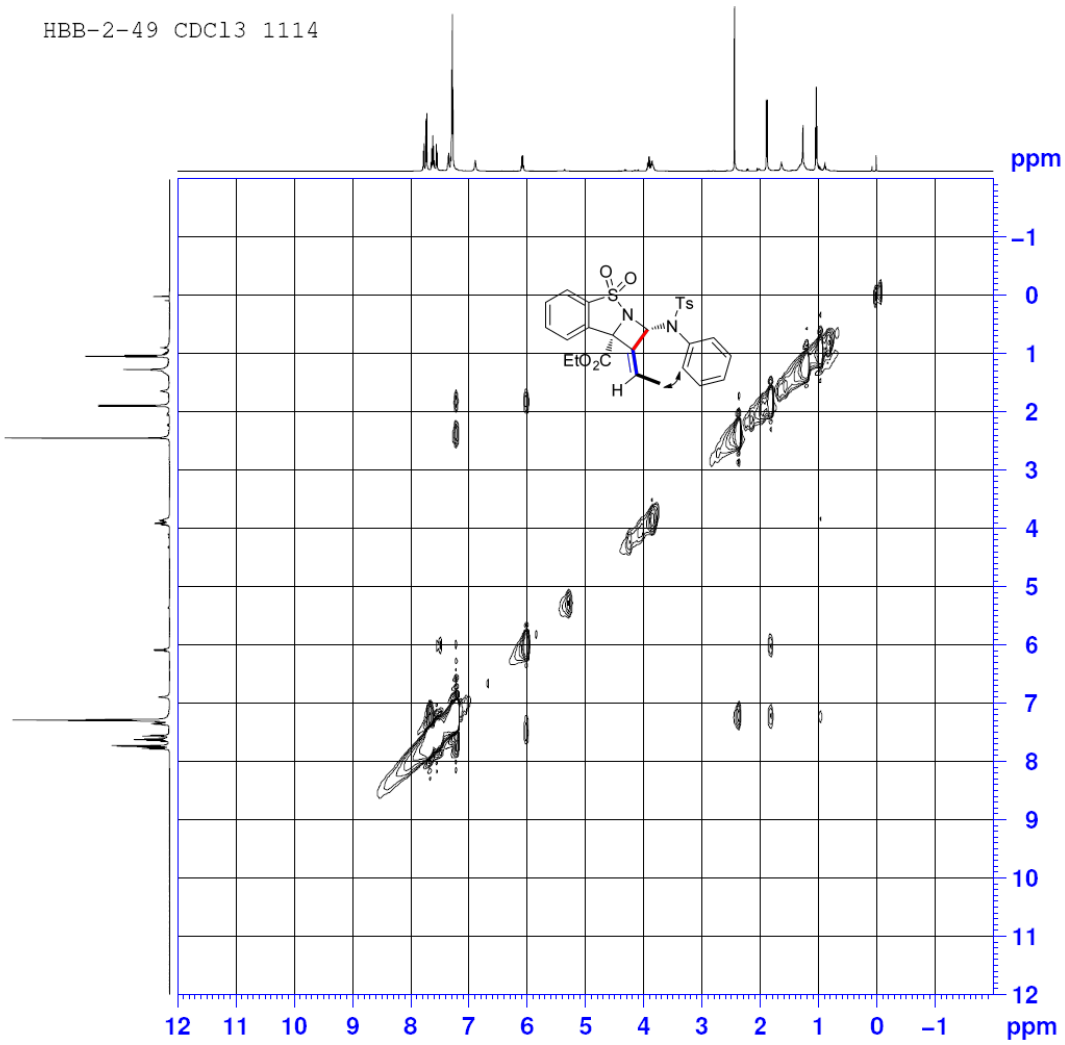


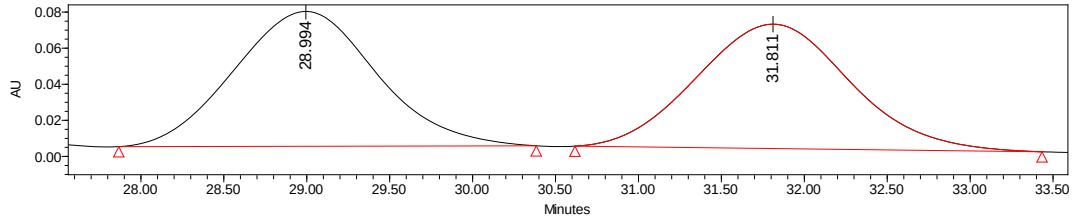
Reaction time: 3.5 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v), Rf: 0.4; yellow oil, 75% yield, $[\alpha]_D^{25}$= -2.0 (*c* 1.0, CH_2Cl_2), 95% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 29.4 min, t_{minor} =32.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.79 (m, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.59-7.66 (m, 2H), 7.56 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.34-7.37 (m, 1H), 7.27-7.30 (m, 6H), 6.89 (s, 1H), 6.06-6.11 (m, 1H), 3.83-3.94 (m, 2H), 2.45 (s, 3H), 1.89 (dd, *J* = 7.5, 1.5 Hz,

3H), 1.04 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 144.1, 137.2, 135.74, 137.65, 134.0, 132.2, 131.8, 130.8, 129.4, 129.0, 128.5, 128.3, 127.2, 124.2, 122.1, 79.6, 76.0, 62.3, 21.6, 13.74, 13.71. HRMS m/z (ESI+): Calculated for $C_{27}H_{27}N_2O_6S_2$ ($[M+H]^+$) 539.1305, found 539.1272.

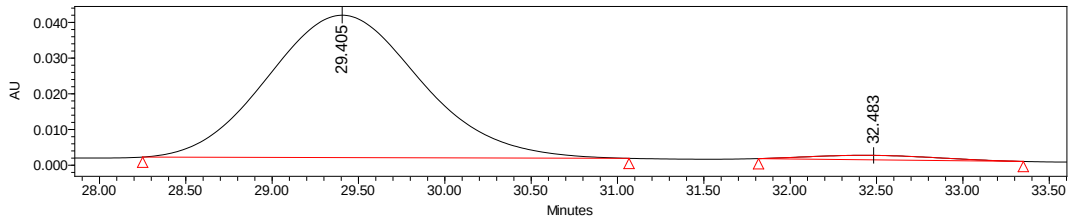






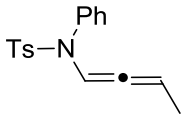


	Retention Time	Area	% Area	Height	% Height
1	28.994	4465057	50.16	74727	52.01
2	31.811	4436511	49.84	68941	47.99

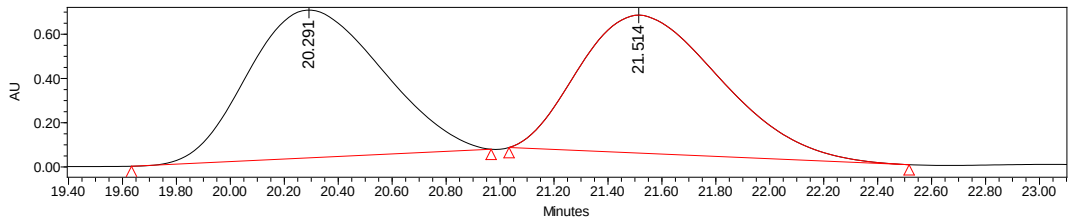


	Retention Time	Area	% Area	Height	% Height
1	29.405	2505096	97.43	40130	96.90
2	32.483	66020	2.57	1284	3.10

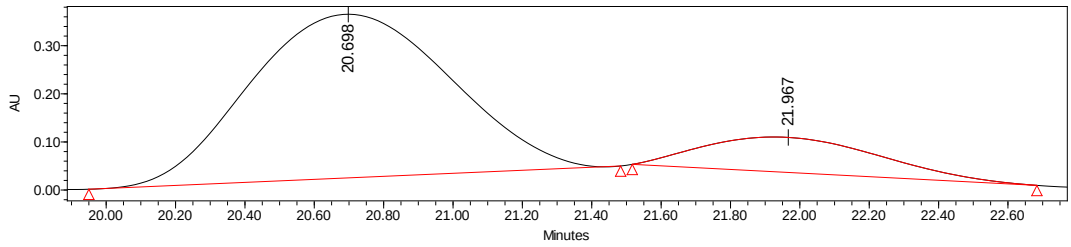
N-(Buta-1,2-dien-1-yl)-4-methyl-N-phenylbenzenesulfonamide (**1l**)



Reaction time: 3.5 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v), Rf: 0.7; yellow oil, 70% yield, $[\alpha]_D^{25}$= -4.3 (*c* 1.0, CH_2Cl_2), 68% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 20.7 min, t_{minor} = 22.0 min].

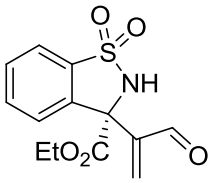


	Retention Time	Area	% Area	Height	% Height
1	20.291	23028980	50.28	668171	51.71
2	21.514	22774677	49.72	623904	48.29

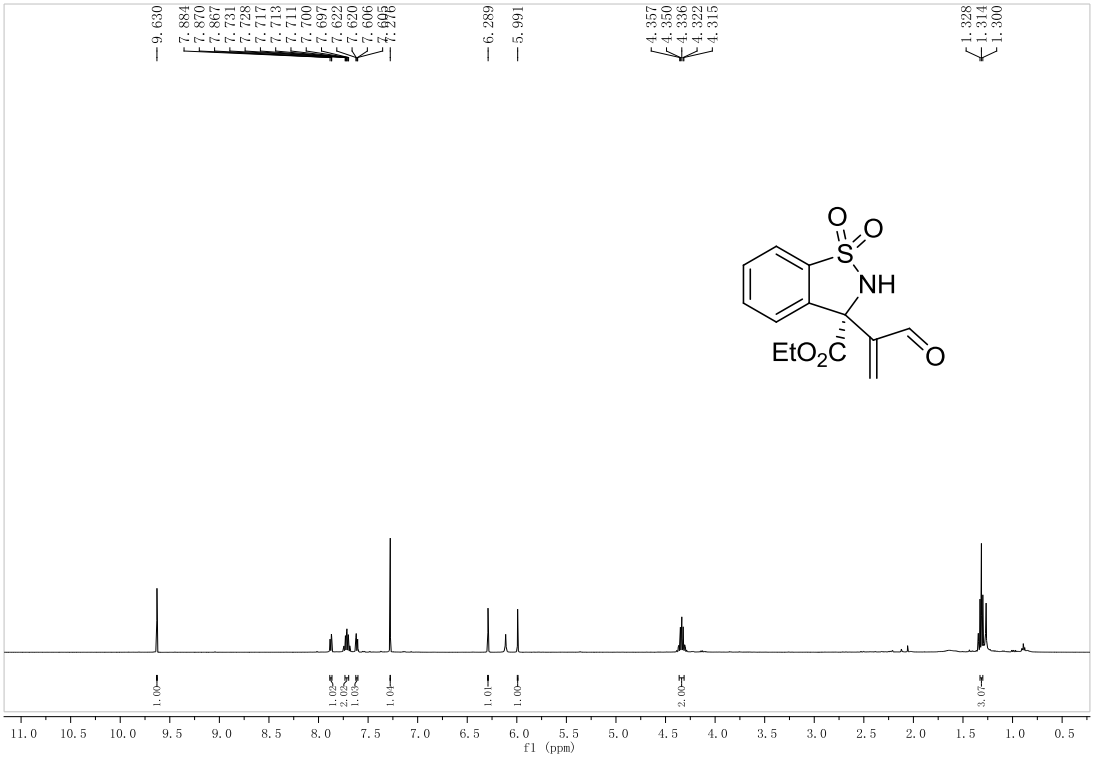


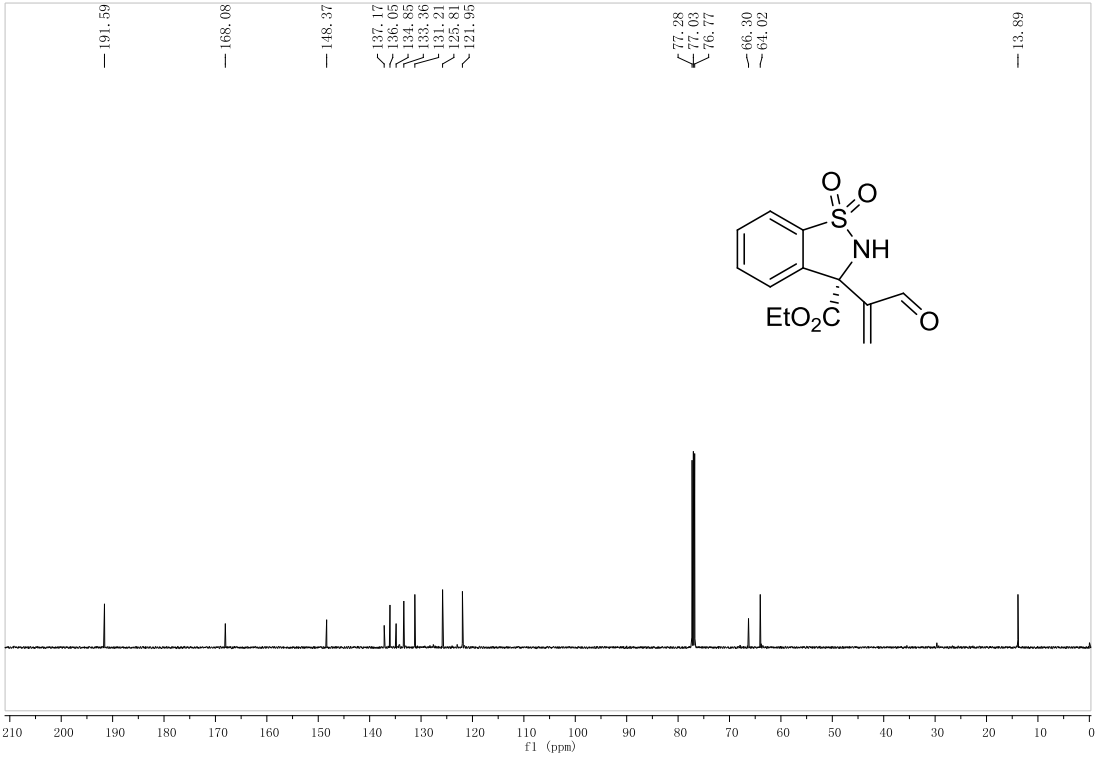
	Retention Time	Area	% Area	Height	% Height
1	20.698	13615837	83.93	340237	82.36
2	21.967	2607938	16.07	72878	17.64

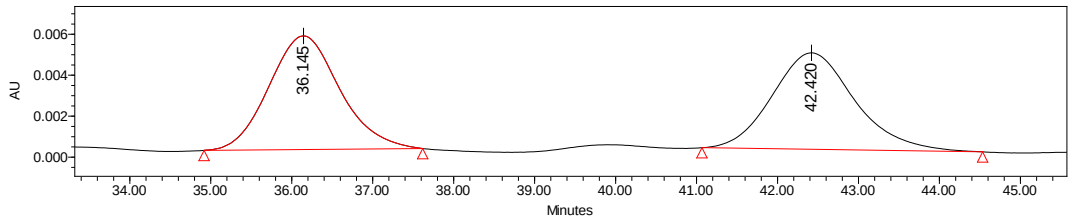
Ethyl 3-(3-oxoprop-1-en-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**5a**)



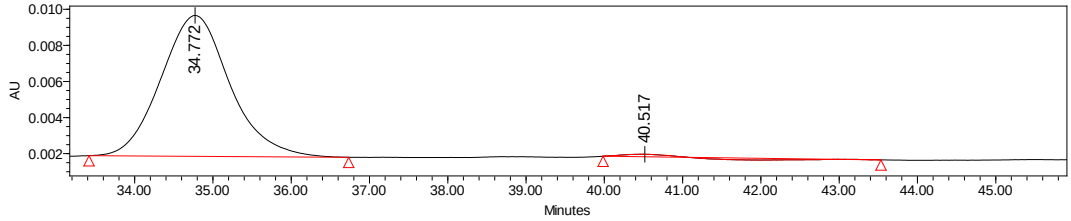
Reaction time: 8 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:2 (v/v), Rf: 0.5; light yellow oil, 62% yield, $[\alpha]_D^{25}$ = -210.6 (c =1.0 in CH_2Cl_2), 94% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 34.8 min, t_{minor} = 40.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.86-7.89 (m, 1H), 7.69-7.74 (m, 2H), 7.60-7.63 (m, 1H), 7.28 (s, 1H), 6.29 (s, 1H), 5.99 (s, 1H), 4.31-4.36 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.6, 168.1, 148.4, 137.2, 136.1, 134.9, 133.4, 131.2, 125.8, 122.0, 66.3, 64.0, 13.9. HRMS m/z (ESI+): Calculated for $C_{13}H_{14}NO_5S$ ($[M+H]^+$) 296.0587, found 296.0582.


9.630
7.884
7.870
7.867
7.731
7.728
7.717
7.713
7.711
7.700
7.697
7.622
7.620
7.606
6.289
5.991
4.357
4.350
4.336
4.322
4.315
1.328
1.314
1.300
O
O
S
NH
EtO2C
O
f1 (ppm)


191.59
168.08
148.37
137.17
136.05
134.85
133.36
131.21
125.81
121.95
77.28
77.03
76.77
66.30
64.02
13.89
O
O
S
NH
EtO2C
O
f1 (ppm)

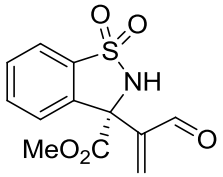


	Retention Time	Area	% Area	Height	% Height
1	36.145	337596	50.33	5545	54.08
2	42.420	333144	49.67	4709	45.92



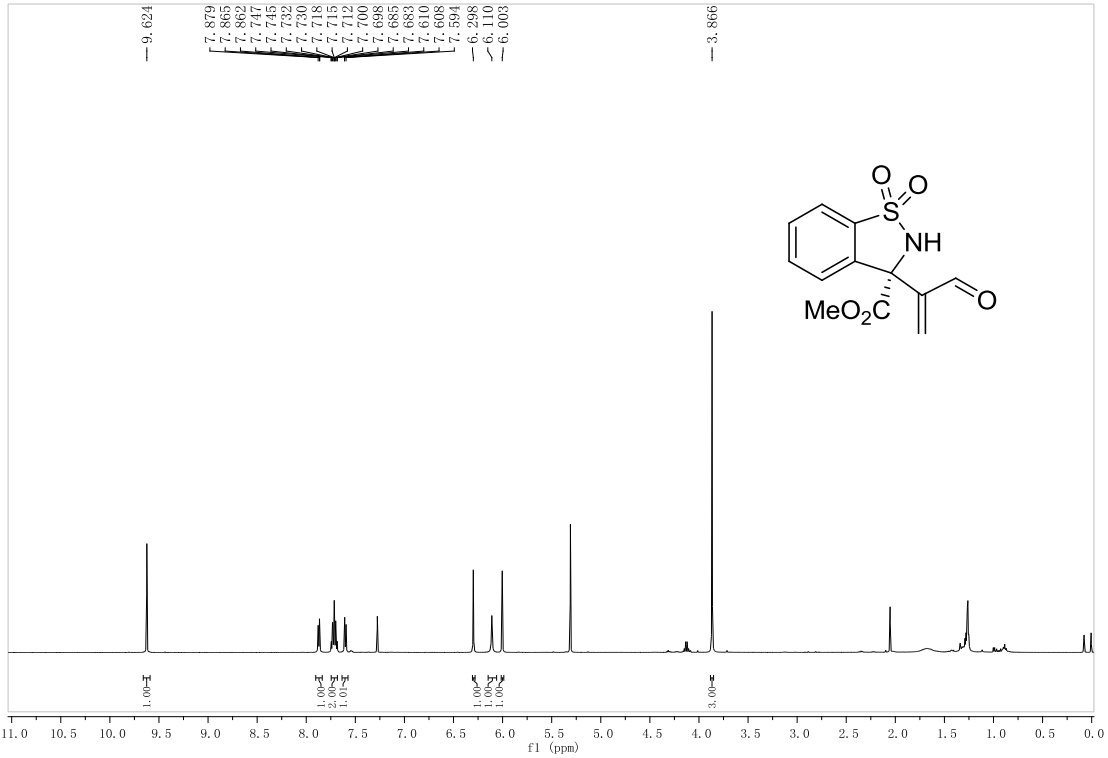
	Retention Time	Area	% Area	Height	% Height
1	34.772	483391	97.34	7834	97.27
2	40.517	13207	2.66	220	2.73

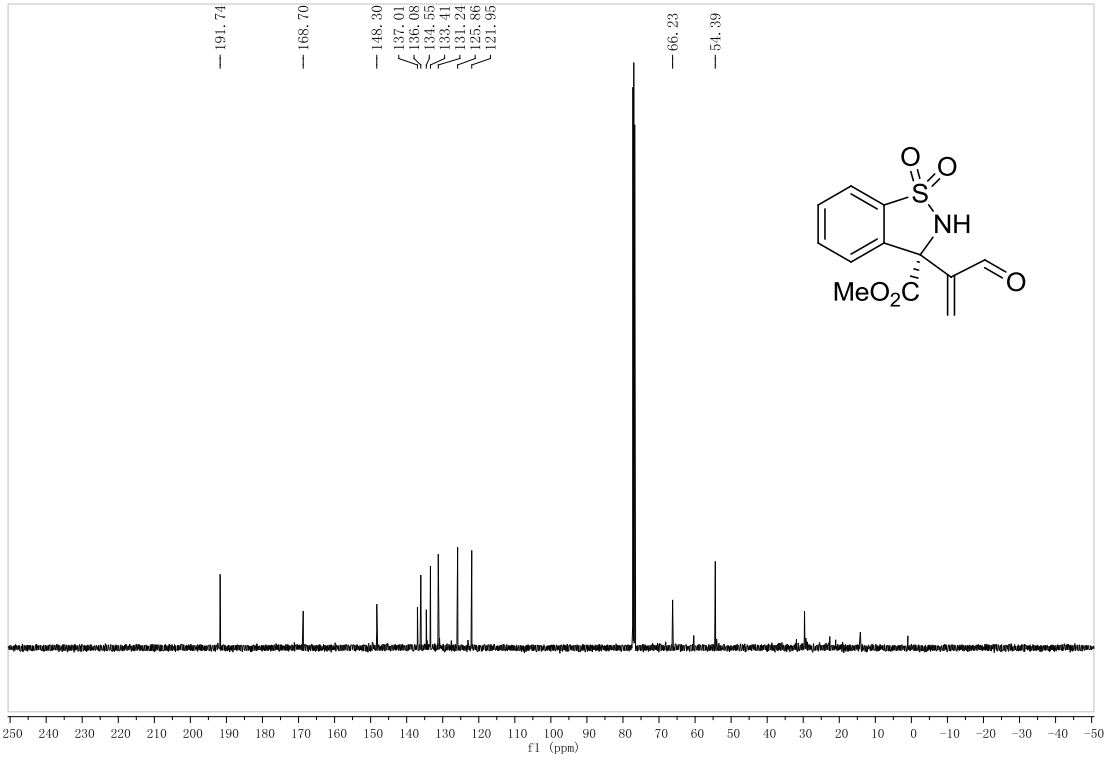
Methyl 3-(3-oxoprop-1-en-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**5b**)

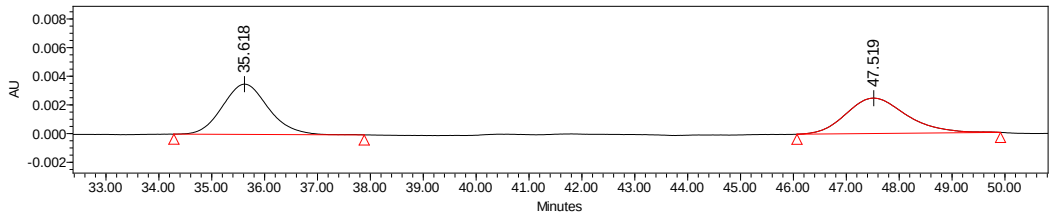


Reaction time: 8 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:2 (v/v), Rf: 0.5; yellow oil, 65% yield, $[\alpha]_D^{25}$= -131.2 (*c* 1.0, CH_2Cl_2), 95% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 35.4 min, t_{minor} = 46.7 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.86-7.88 (m, 1H), 7.68-7.75 (m, 2H), 7.59-7.61 (m, 1H), 6.30 (s, 1H), 6.11 (s, 1H), 6.00 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 168.7, 148.3, 137.0, 136.1, 134.6, 133.4, 131.2, 125.9, 122.0,

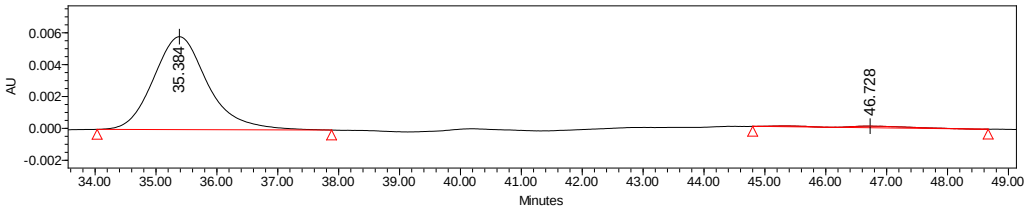
66.2, 54.4. HRMS m/z (ESI+): Calculated for $C_{12}H_{12}NO_5S$ ($[M+H]^+$) 282.0431, found 282.0431.





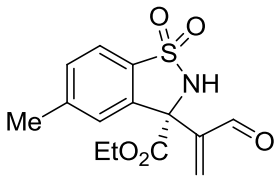


	Retention Time	Area	% Area	Height	% Height
1	35.618	205684	50.91	3475	58.44
2	47.520	198356	49.09	2471	41.56



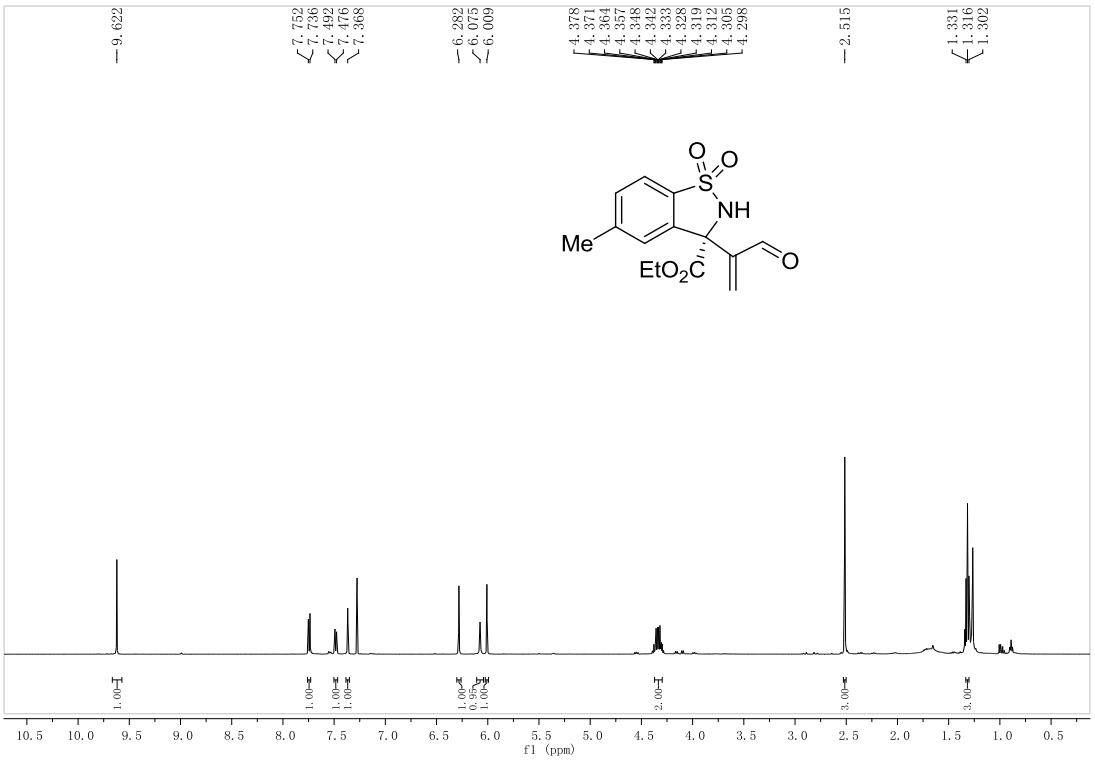
	Retention Time	Area	% Area	Height	% Height
1	35.384	361145	97.53	5830	98.26
2	46.728	9161	2.47	103	1.74

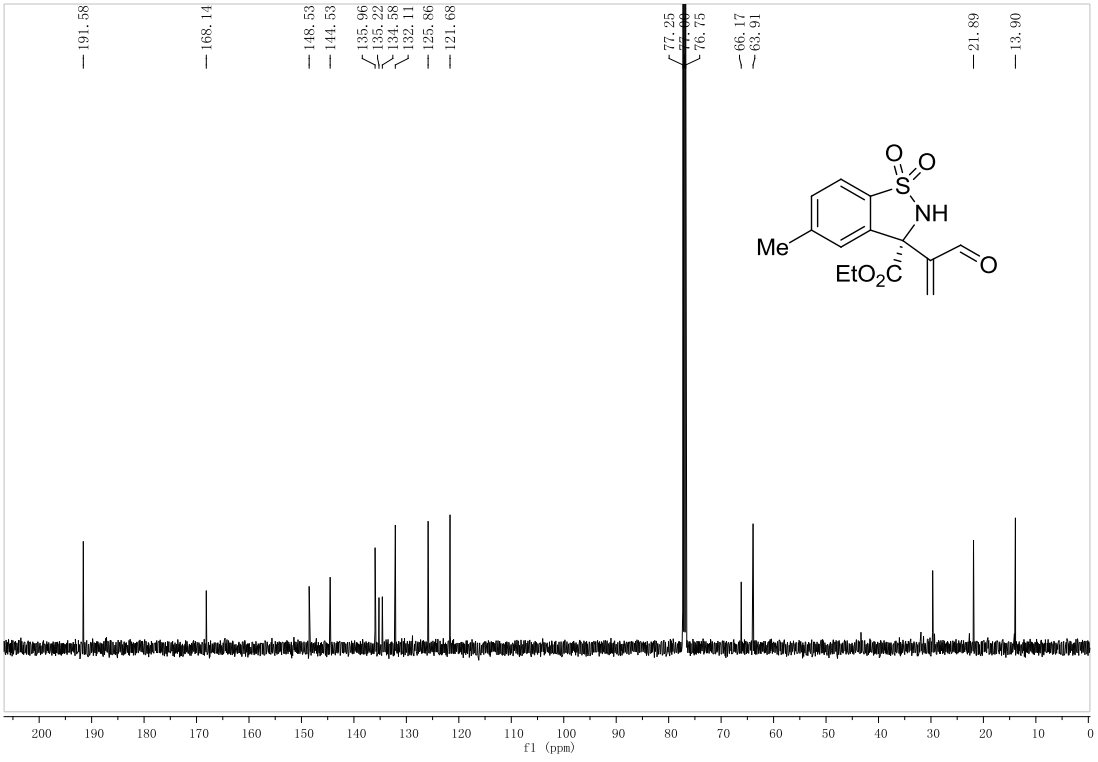
Ethyl 5-methyl-3-(3-oxoprop-1-en-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**5c**)

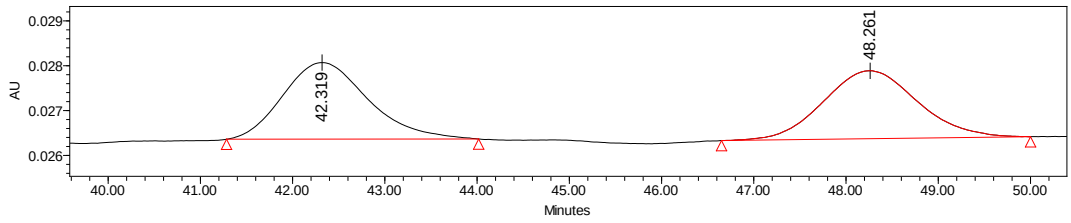


Reaction time: 12 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:2 (v/v), Rf: 0.5; yellow oil, 60% yield, $[\alpha]_D^{25}$= -299.0 (*c* 1.0, CH_2Cl_2), 90% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 41.8 min, t_{minor} =47.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 6.28 (s, 1H), 6.08 (s, 1H), 6.01 (s, 1H), 4.29-4.38 (m, 2H), 2.51 (s, 3H), 1.32 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 168.1, 148.5,

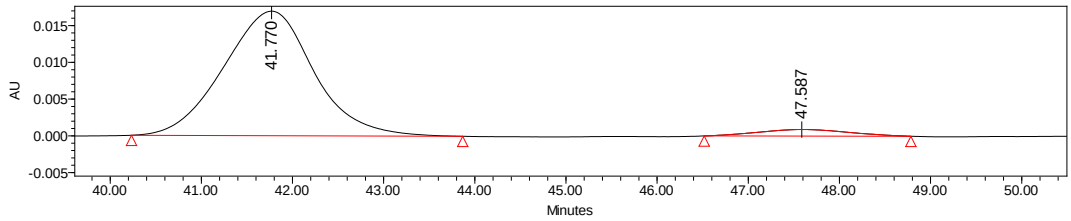
144.5, 136.0, 135.2, 134.6, 132.1, 125.9, 121.7, 66.2, 63.9, 21.9, 13.9. HRMS m/z (ESI+): Calculated for $C_{14}H_{16}NO_5S$ ($[M+H]^+$) 310.0744, found 310.0742.





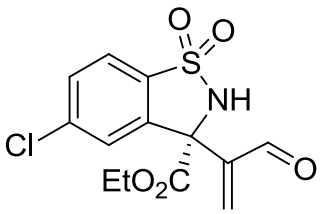


	Retention Time	Area	% Area	Height	% Height
1	42.319	109389	50.52	1707	52.96
2	48.261	107116	49.48	1516	47.04



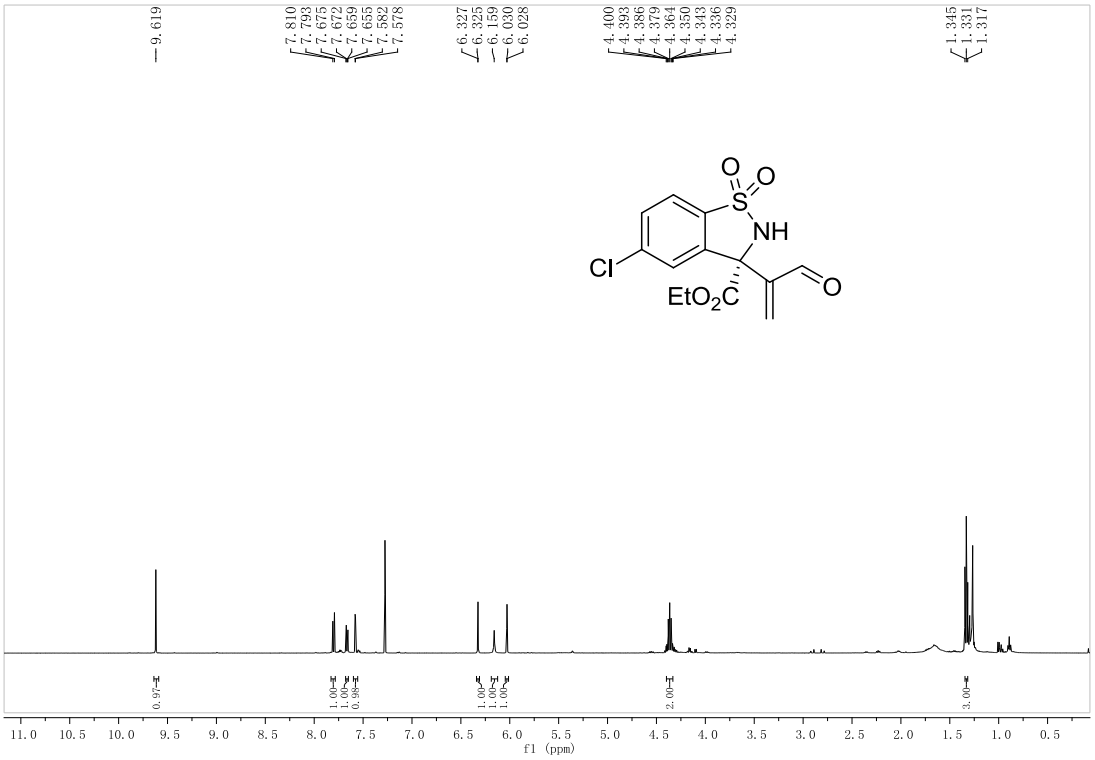
	Retention Time	Area	% Area	Height	% Height
1	41.770	1191609	95.19	17052	95.08
2	47.587	60236	4.81	882	4.92

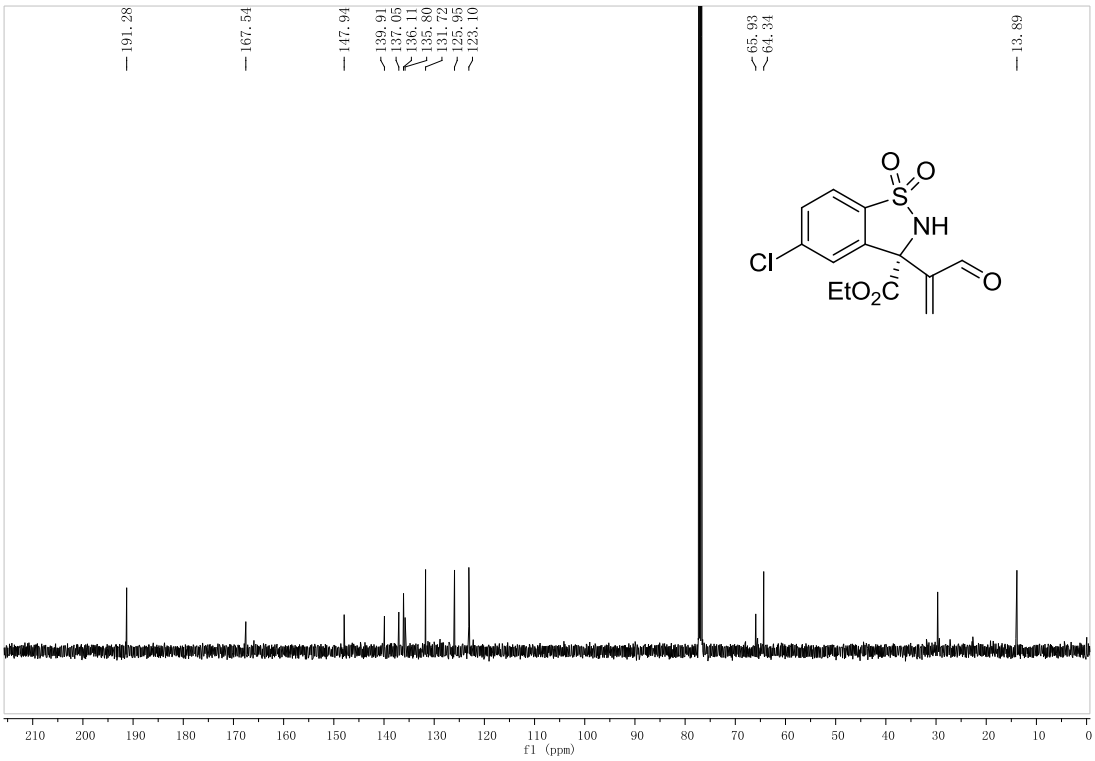
Ethyl 5-chloro-3-(3-oxoprop-1-en-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**5d**)

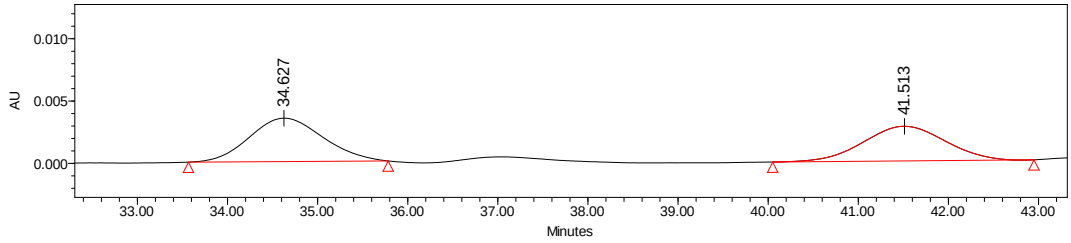


Reaction time: 12 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:2 (v/v), Rf: 0.5; yellow oil, 56% yield, $[\alpha]_D^{25}$= -172.0 (*c* 1.0, CH_2Cl_2), 86% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 34.8 min, t_{minor} = 41.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 6.33 (d, *J* = 1.0 Hz, 1H), 6.16 (s, 1H), 6.03 (d, *J* = 1.0 Hz, 1H), 4.32-4.40 (m, 2H), 1.32 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz,

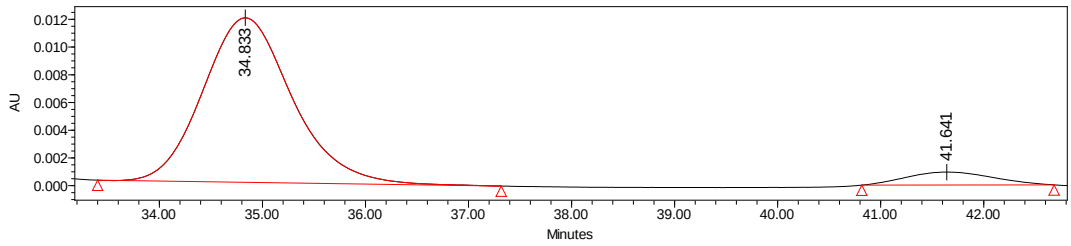
$CDCl_3$) δ 191.3, 167.5, 147.9, 139.9, 137.1, 136.1, 135.8, 131.7, 126.0, 123.1, 65.9, 64.3, 13.9. HRMS m/z (ESI+): Calculated for $C_{13}H_{13}ClNO_5S$ ($[M+H]^+$) 330.0197, found 330.0186.





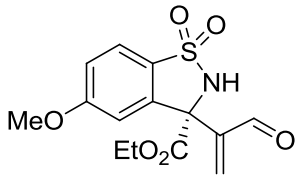


	Retention Time	Area	% Area	Height	% Height
1	34.627	180594	50.87	3343	54.71
2	41.513	174443	49.13	2767	45.29



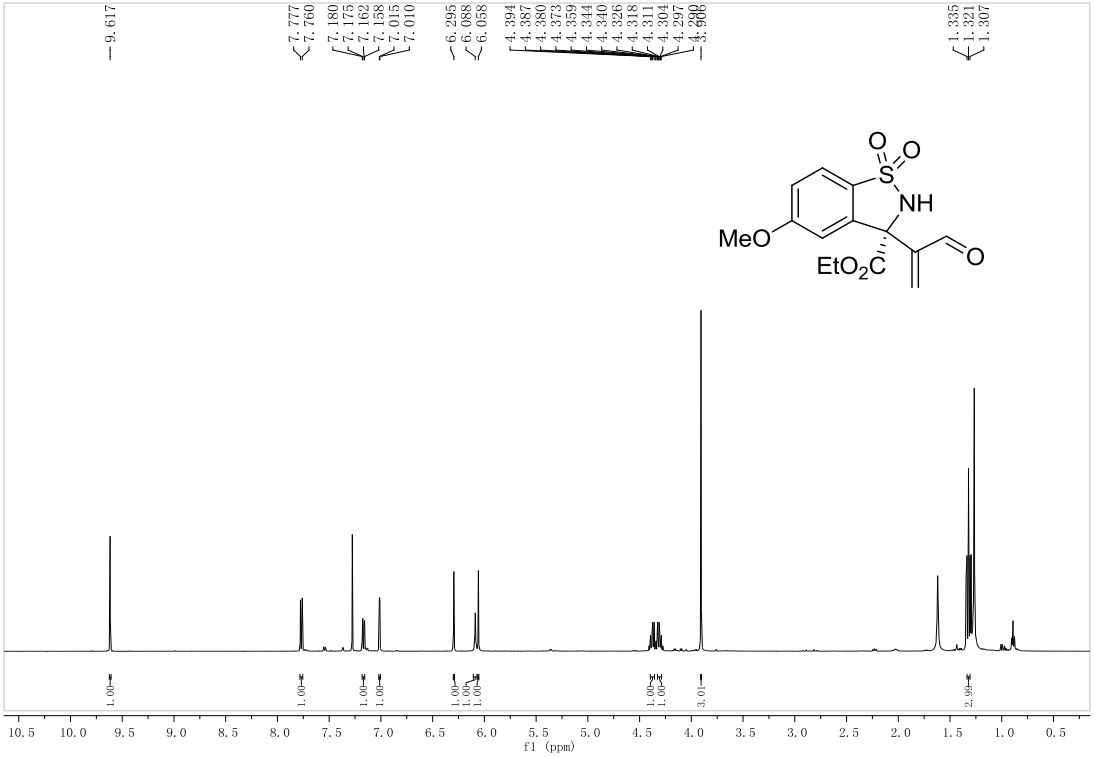
	Retention Time	Area	% Area	Height	% Height
1	34.833	715525	92.91	11871	92.68
2	41.641	54627	7.09	937	7.32

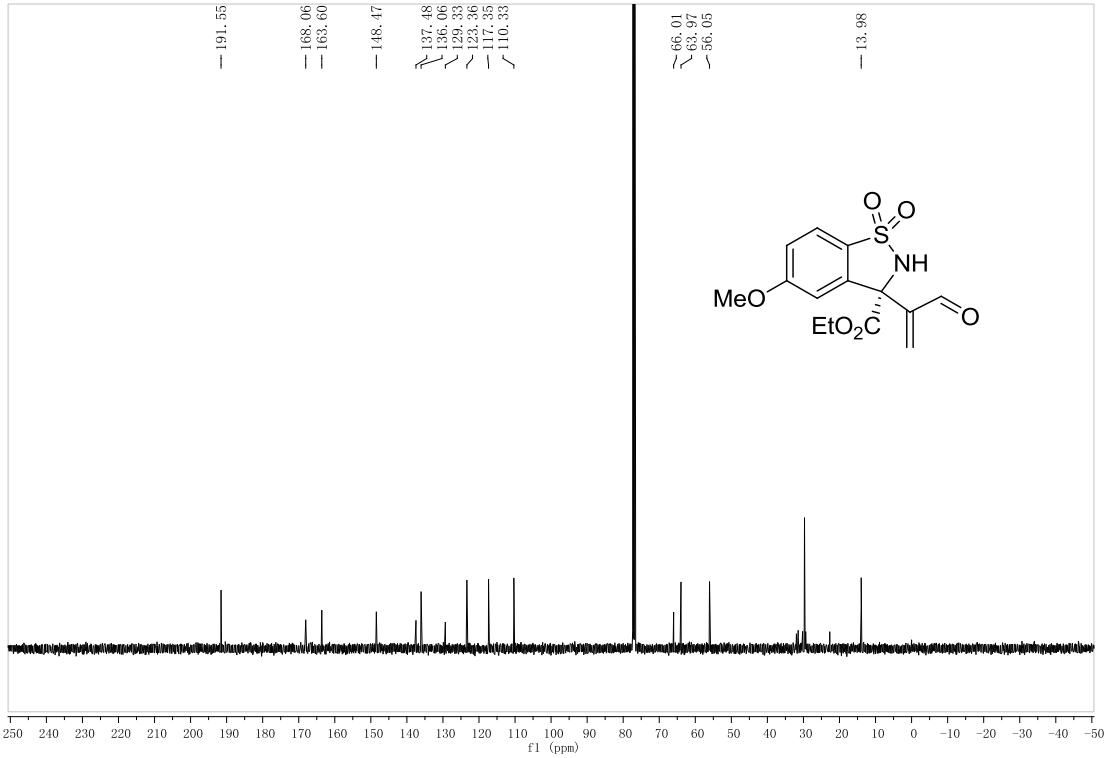
Ethyl 5-methoxy-3-(3-oxoprop-1-en-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**5e**)

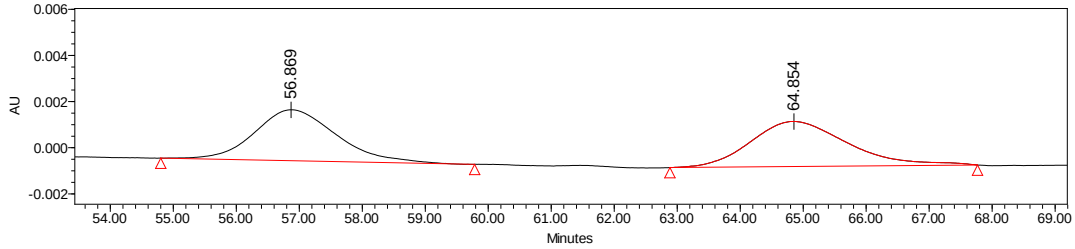


Reaction time: 12 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:2 (v/v), Rf: 0.4; yellow oil, 44% yield, $[\alpha]_D^{25}$= -98.9 (*c* 1.0, CH_2Cl_2), 83% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 59.8 min, t_{minor} =66.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.17 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.30 (s, 1H), 6.09 (s, 1H), 6.06 (s, 1H), 4.35-

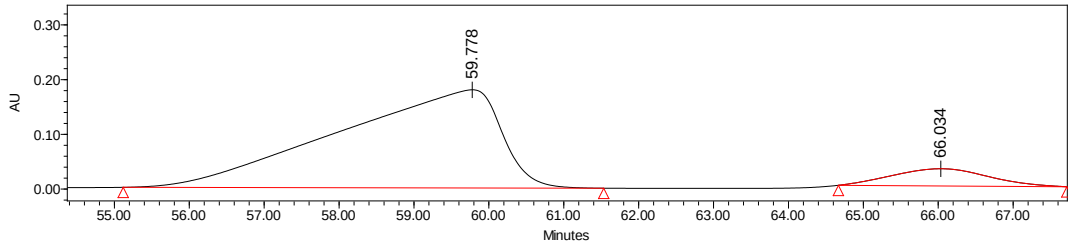
4.40 (m, 1H), 4.29-4.33 (m, 1H), 3.91 (s, 3H), 1.31 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 168.1, 163.6, 148.5, 137.5, 136.1, 129.3, 123.4, 117.4, 110.3, 66.0, 64.0, 56.1, 14.0. HRMS m/z (ESI+): Calculated for $C_{14}H_{16}NO_6S$ ($[M+H]^+$) 326.0693, found 326.0695.





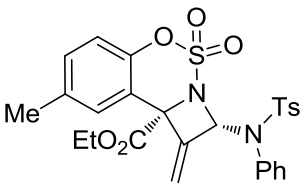


	Retention Time	Area	% Area	Height	% Height
1	56.871	196270	49.47	2194	53.19
2	64.854	200457	50.53	1931	46.81



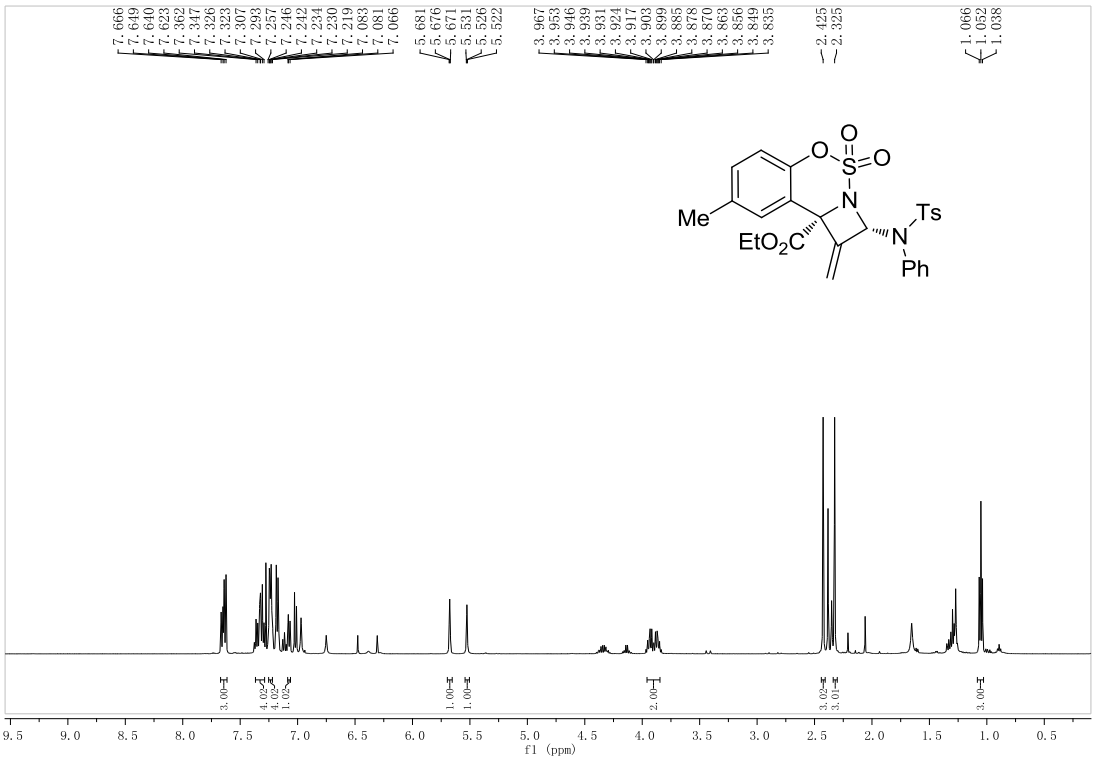
	Retention Time	Area	% Area	Height	% Height
1	59.778	27157642	91.33	179363	85.58
2	66.034	2578507	8.67	30223	14.42

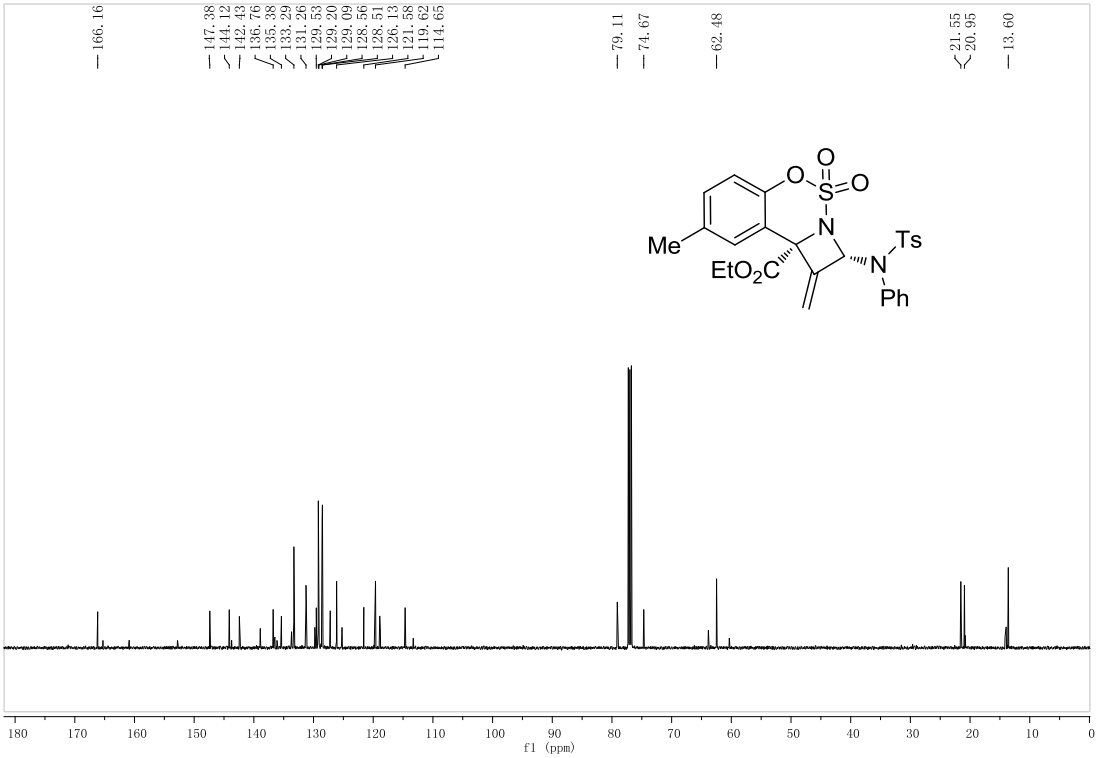
Ethyl 8-methyl-2-(4-methyl-N-phenylphenylsulfonamido)-1-methylene-2,9b-dihydro-1H-azeto[1,2-c]benzo[e][1,2,3]oxathiazine-9b-carboxylate 4,4-dioxide (**7a**)

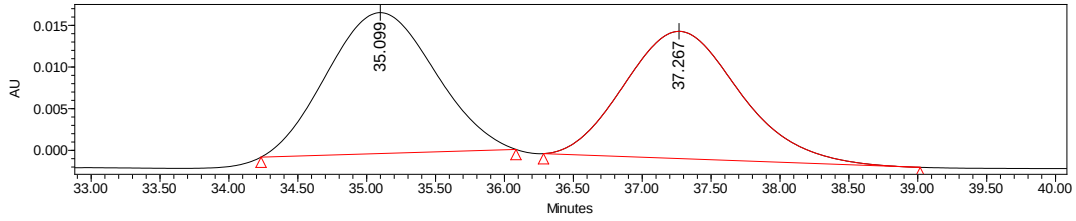


Reaction time: 12 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:5 (v/v), Rf: 0.4; yellow oil, 70% yield (there was a little part decomposed to the ring-opening acrylaldehyde product in the silica gel), $[\alpha]_D^{25}$= -5.2 (*c* 1.0, CH_2Cl_2), 92% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 95/5, 0.8 mL/min, 254 nm; t_{major} = 39.5 min, t_{minor} =36.5 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 13.0, 8.0 Hz, 3H), 7.29-7.37 (m, 4H), 7.21-7.26 (m, 4H), 7.06-7.09 (m, 1H), 5.68 (t, *J* = 2.5 Hz, 1H), 5.53 (t, *J* = 2.5

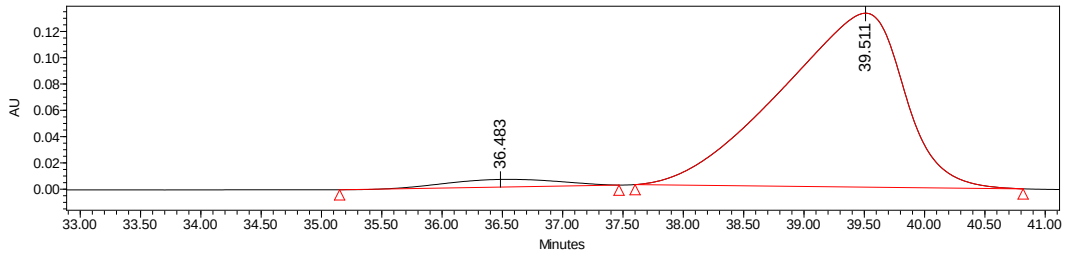
Hz, 1H), 3.83-3.97 (m, 2H), 2.43 (s, 3H), 2.33 (s, 3H), 1.05 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 147.4, 144.1, 142.4, 136.8, 135.4, 133.3, 131.3, 129.5, 129.2, 129.1, 128.6, 128.5, 126.1, 121.6, 119.6, 114.7, 79.1, 74.7, 62.5, 21.6, 21.0, 13.6. HRMS m/z (ESI+): Calculated for $C_{30}H_{32}N_2O_7S_2$ ($[M+H]^+$) 555.1254, found 555.1262.





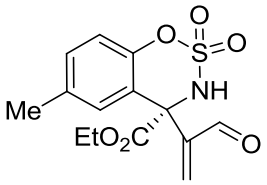


	Retention Time	Area	% Area	Height	% Height
1	35.099	916810	50.77	16906	52.56
2	37.267	889158	49.23	15261	47.44



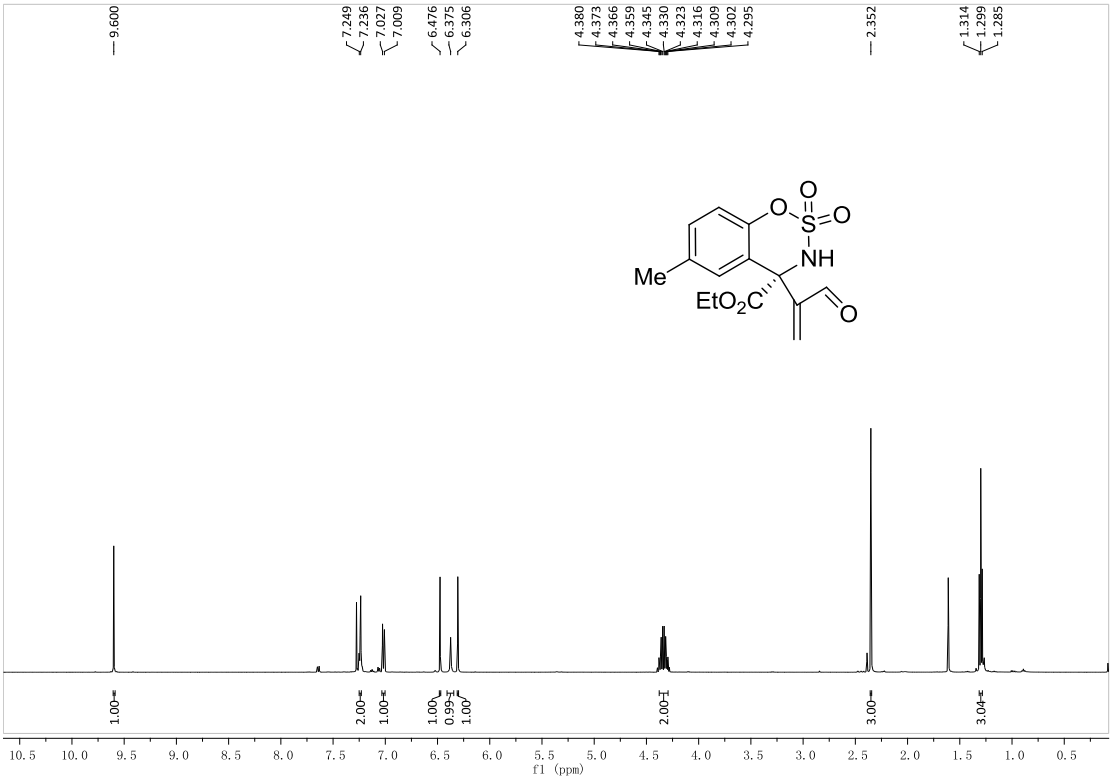
	Retention Time	Area	% Area	Height	% Height
1	36.483	380754	3.89	5881	4.26
2	39.511	9417508	96.11	132247	95.74

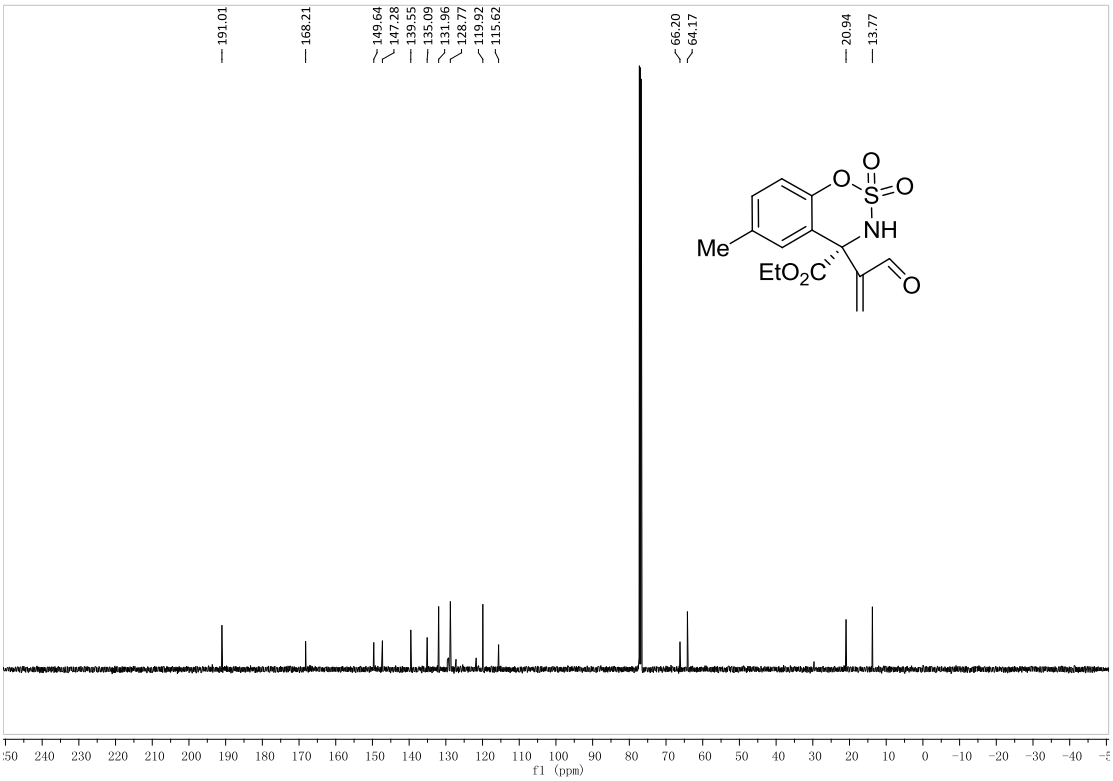
Ethyl 6-methyl-4-(3-oxoprop-1-en-2-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (**8a**)



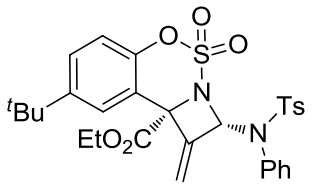
It was difficult to obtain a pure NMR spectrum due to the impurity in compound **7a**. Compound **7a** was therefore changed to **8a** through hydrolysis reaction by adding TsOH catalyst after the [2+2] reaction. Compound **8a** was purified by chromatography on silica gel, eluting with ethyl acetate/ dichloromethane/petroleum ether: 0.1/2/4 (v/v), Rf: 0.5; yellow oil, 65% yield for two steps, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.23-7.25 (m, 2H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.48 (s, 1H), 6.37

(s, 1H), 6.31 (s, 1H), 4.29-4.38 (m, 2H), 2.35 (s, 3H), 1.30 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 168.2, 149.6, 147.3, 139.6, 135.1, 132.0, 128.8, 119.9, 115.6, 66.2, 64.2, 20.9, 13.8.

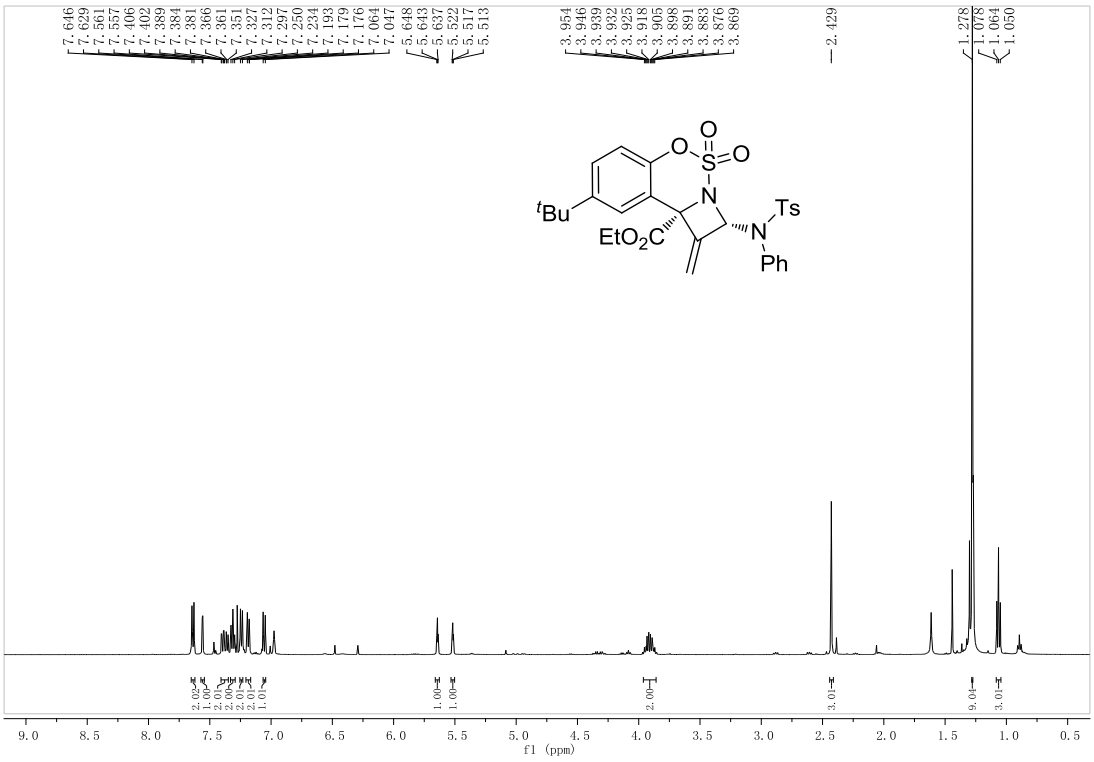


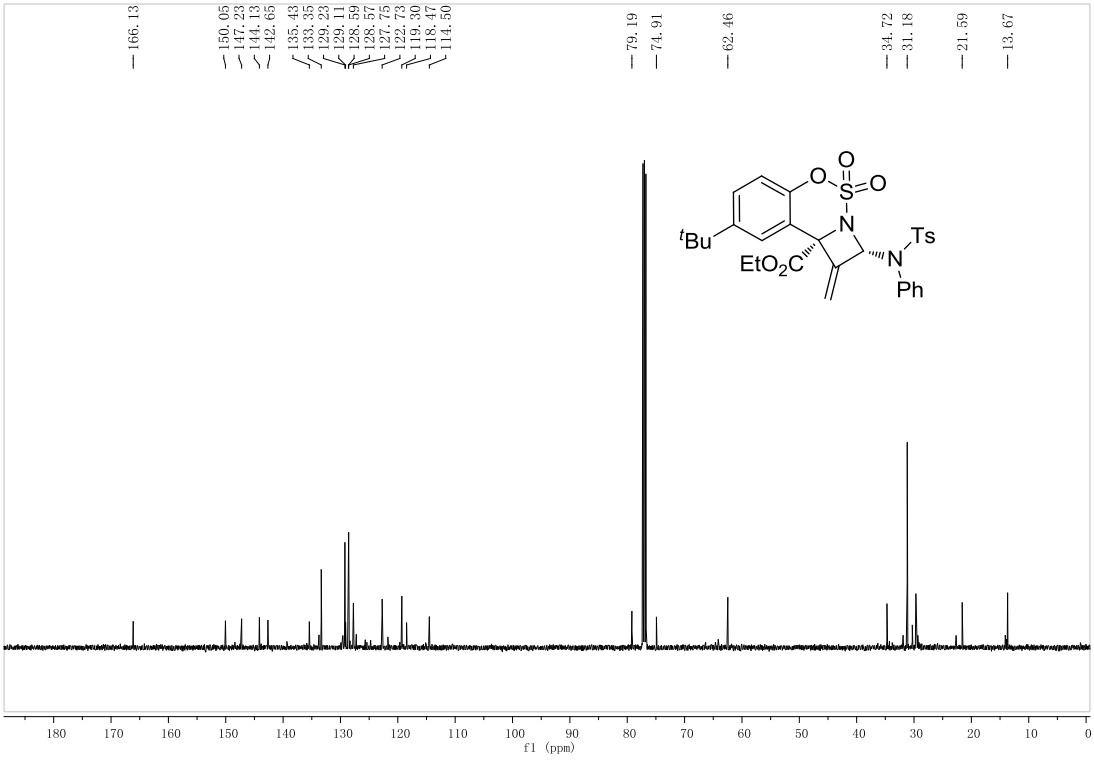


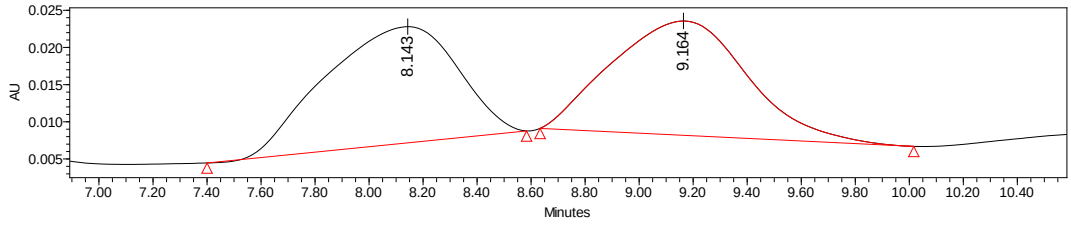
Ethyl 8-(tert-butyl)-2-(4-methyl-N-phenylphenylsulfonamido)-1-methylene-2,9b-dihydro-1H-azeto[1,2-c]benzo[e][1,2,3]oxathiazine-9b-carboxylate 4,4-dioxide (**7b**)



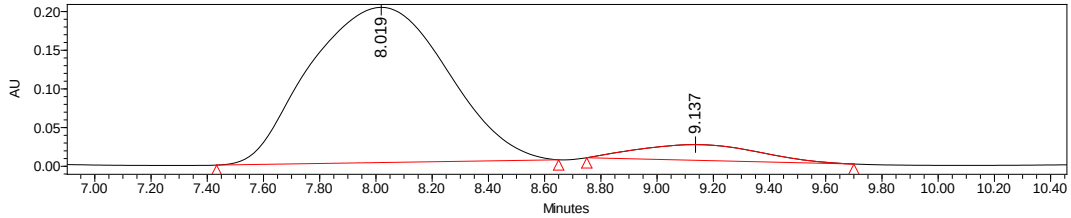
Reaction time: 12 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:7 (v/v), Rf: 0.5; yellow oil, 72% yield, $[\alpha]_D^{25}$= -4.3 (*c* 1.0, CH_2Cl_2), 84% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 9.1 min, t_{minor} = 8.0 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.35-7.41 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17-7.20 (m, 2H), 7.06 (d, *J* = 8.5 Hz, 1H), 5.64 (t, *J* = 2.5 Hz, 1H), 5.52 (t, *J* = 2.5 Hz, 1H), 3.86-3.96 (m, 2H), 2.43 (s, 3H), 1.28 (s, 9H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 150.1, 147.2, 144.1, 142.7, 135.4, 133.4, 129.2, 129.1, 128.59, 128.57, 127.8, 122.7, 119.3, 118.5, 114.5, 79.2, 74.9, 62.5, 34.7, 31.2, 21.6, 13.7. HRMS m/z (ESI+): Calculated for $C_{30}H_{32}N_2O_7S_2$ ($[M+H]^+$) 597.1724, found 597.1733.





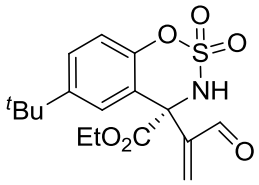


	Retention Time	Area	% Area	Height	% Height
1	8.143	537613	50.05	15640	50.42
2	9.164	536598	49.95	15377	49.58

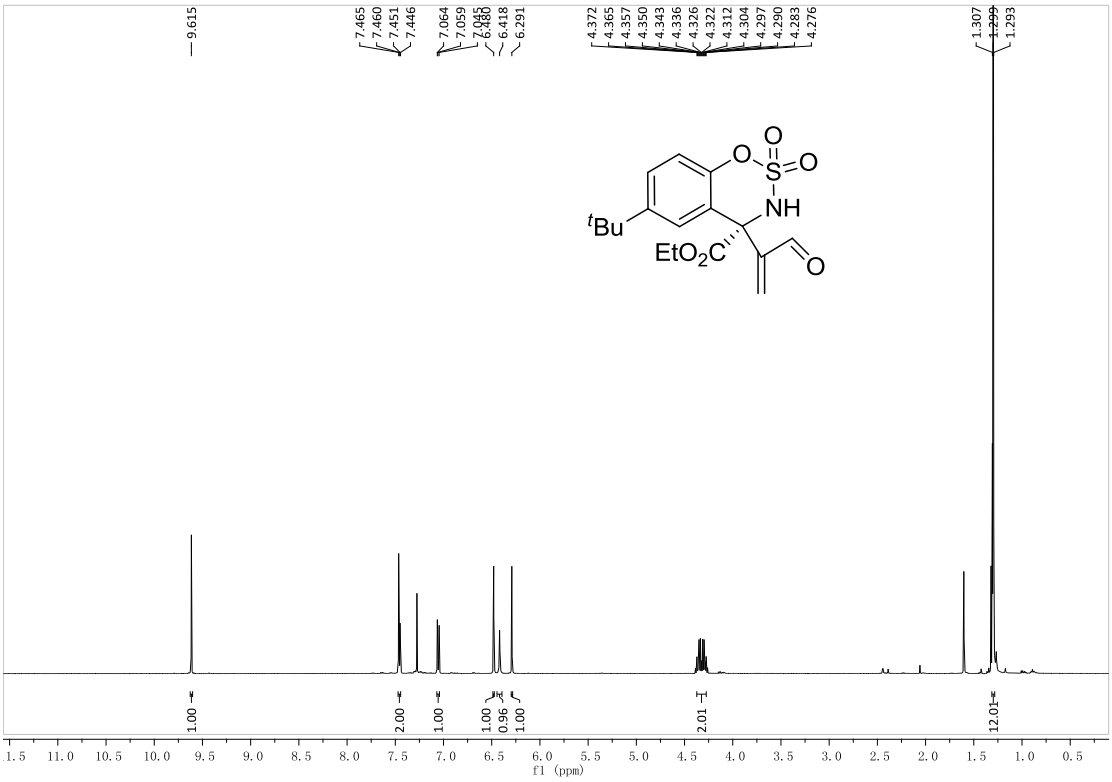


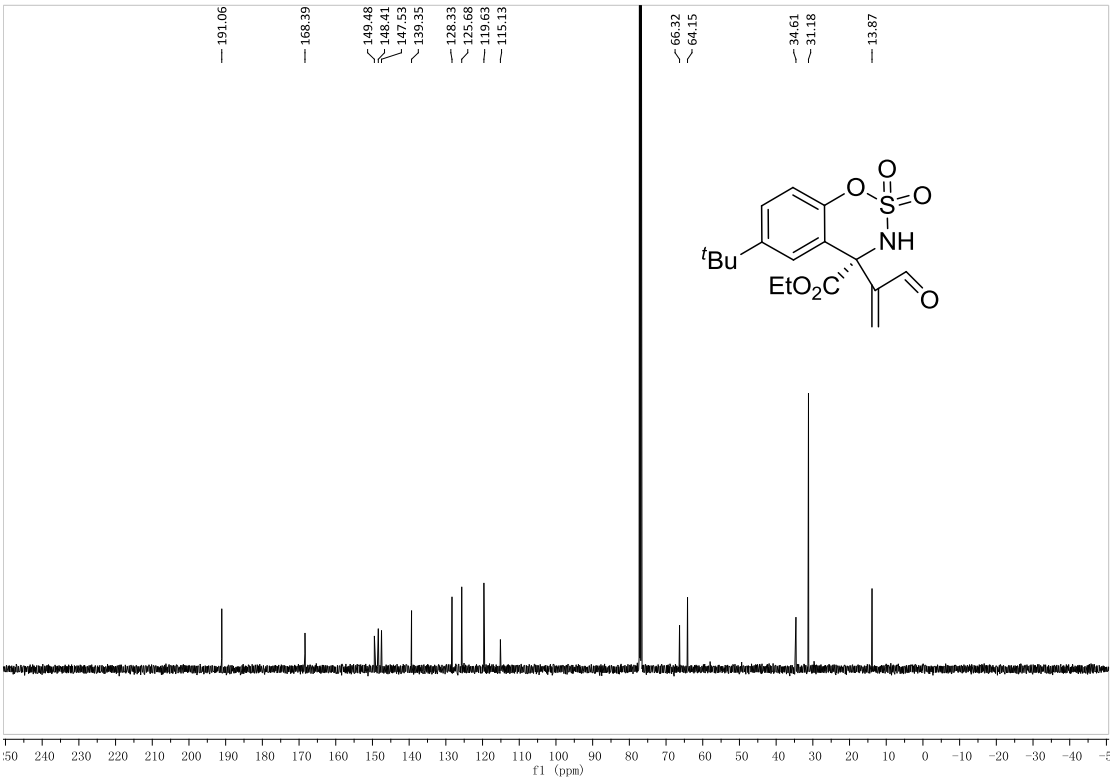
	Retention Time	Area	% Area	Height	% Height
1	8.019	6835282	91.98	200777	90.92
2	9.137	595823	8.02	20056	9.08

Ethyl 6-(tert-butyl)-4-(3-oxoprop-1-en-2-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (**8b**)

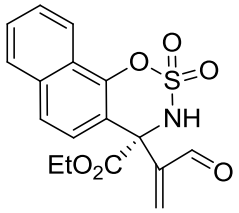


It was difficult to obtain a pure NMR spectrum due to the impurity in compound **7a**. Compound **7a** was therefore changed to **8a** through hydrolysis reaction by adding TsOH catalyst after the [2+2] reaction. Compound **8a** was purified by chromatography on silica gel, eluting with ethyl acetate/ dichloromethane/petroleum ether: 0.1/2/4 (v/v), Rf: 0.6; colorless oil, 63% yield for two steps, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.44-7.47 (m, 2H), 7.04-7.07 (m, 1H), 6.48 (s, 1H), 6.42 (s, 1H), 6.29 (s, 1H), 4.27-4.38 (m, 2H), 1.29-1.31 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.1, 168.4, 149.5, 148.4, 147.5, 139.4, 128.3, 125.7, 119.6, 115.1, 66.3, 64.2, 34.6, 31.2, 13.9.



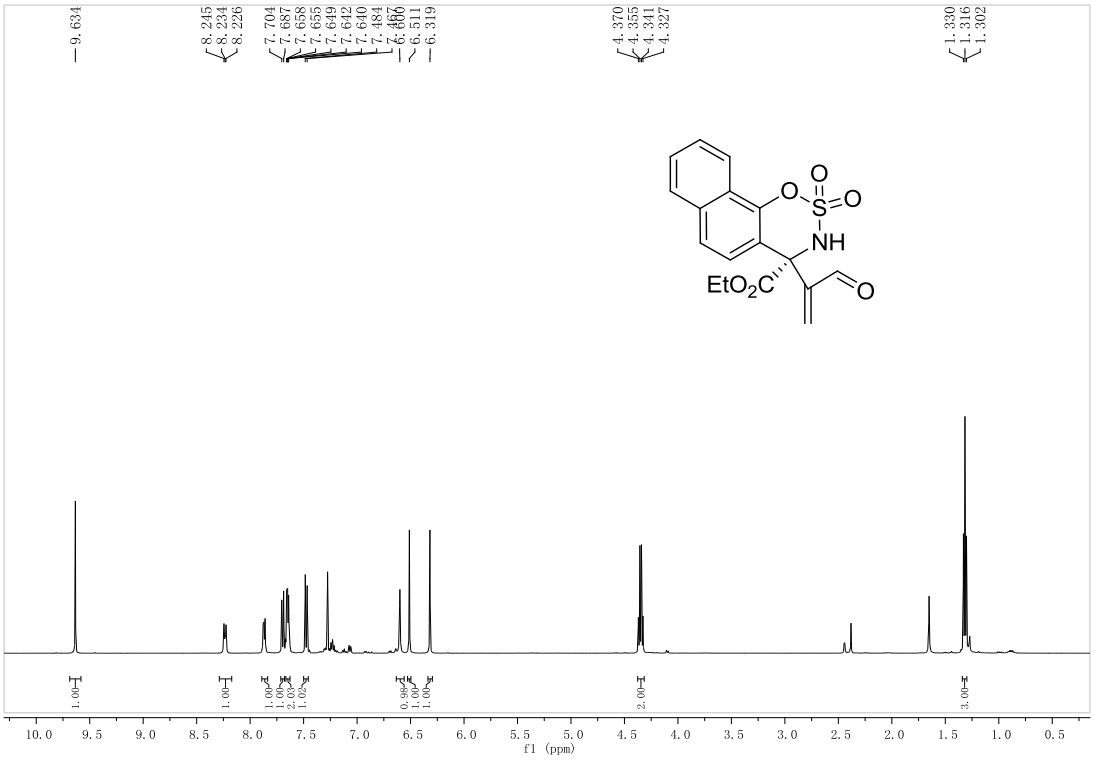


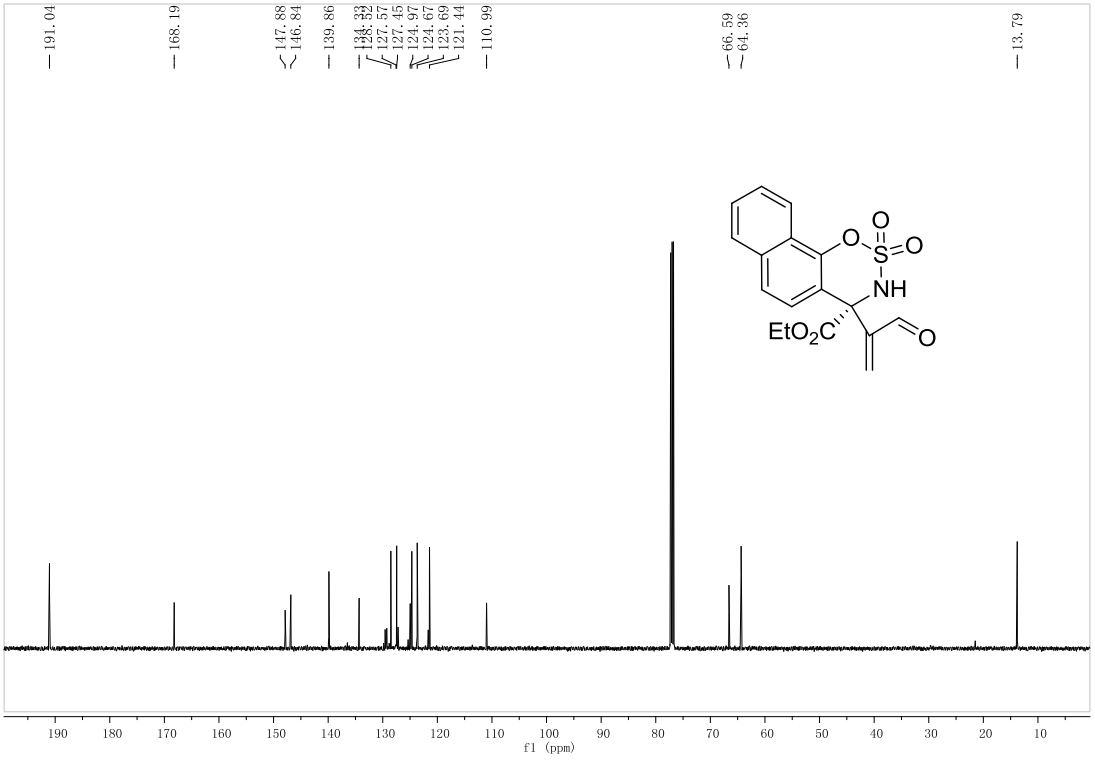
Ethyl 4-(3-oxoprop-1-en-2-yl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (**8c**)

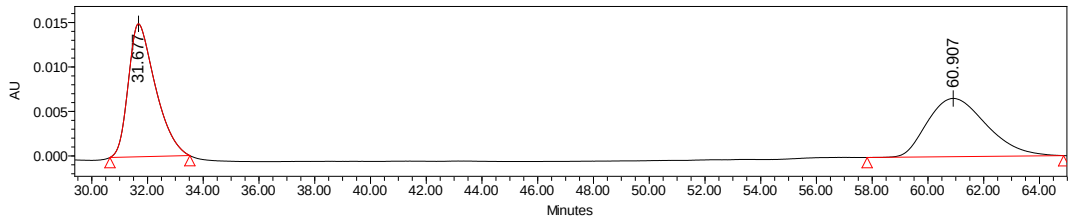


Reaction time: 14 hours. Purified by chromatography on silica gel, eluting with ethyl acetate/dichloromethane/petroleum ether = 0.1/2/4 (v/v), Rf: 0.4; yellow oil, 63% yield for two steps, $[\alpha]_D^{25}$= -10.7 (*c* 1.0, CH_2Cl_2), 82% ee [Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 58.8 min, t_{minor} = 31.8 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.22-8.25 (m, 1H), 7.87 (dd, *J* = 4.5, 3.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.64-7.67 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 6.60 (s, 1H), 6.51 (s, 1H), 6.32 (s, 1H), 4.35 (q, *J* = 7.5 Hz, 2H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.0, 168.2, 147.9, 146.8, 139.9, 134.3, 128.5, 127.6, 127.5, 125.0, 124.7, 123.7, 121.4, 111.0, 66.6, 64.4,

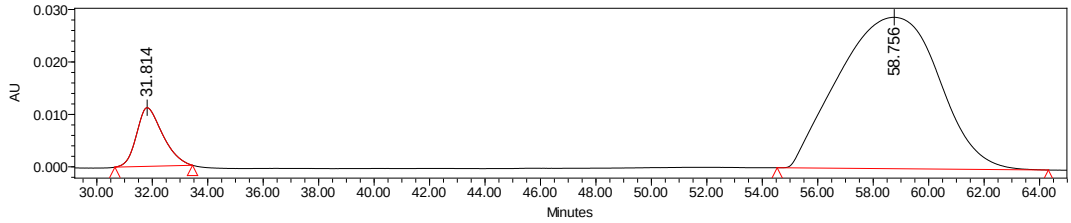
13.8. HRMS m/z (ESI+): Calculated for $C_{17}H_{15}NO_6S$ ($[M+H]^+$) 362.0693, found 362.0711.







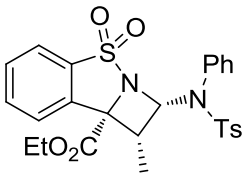
	Retention Time	Area	% Area	Height	% Height
1	31.677	1007996	51.08	14948	69.54
2	60.907	965302	48.92	6549	30.46



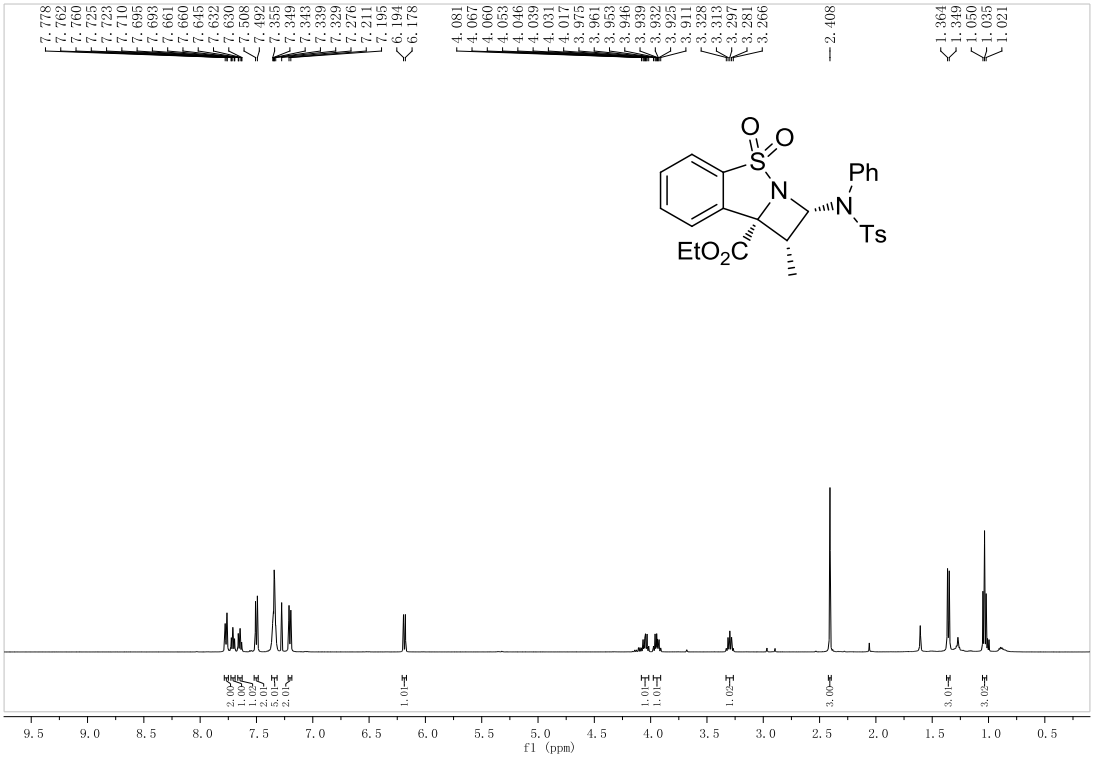
	Retention Time	Area	% Area	Height	% Height
1	31.814	738695	9.24	11205	27.97
2	58.756	7258817	90.76	28855	72.03

3. Synthetic transformations of compound 3aa:

Ethyl 1-methyl-2-((4-methyl-N-phenylphenyl)sulfonamido)-1,2-dihydro-8bH-azeto[1,2-b]benzo[d]isothiazole-8b-carboxylate 4,4-dioxide (**9**)



To a dried Schlenk tube was added Pd/C (40 mg, 0.02 mmol) and compound **3aa** (104.9 mg, 0.2 mmol), followed by the addition of 2.0 mL MeOH through a syringe. The resulting mixture was stirred under a H_2 balloon at room temperature for 12 h until the reaction was completed (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:3 (v/v) to afford compound **9**. colorless oil, 76% yield, $[\alpha]_D^{15}$ = -105.6 (c =1.0 in CH_2Cl_2), 97% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.7 mL/min, 254 nm; t_{major} = 63.4 min, t_{minor} = 70.6 min]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.79 (m, 2H), 7.69-7.73 (m, 1H), 7.62-7.67 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.32-7.36 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.19 (d, *J* = 8.0 Hz, 1H), 4.01-4.09 (m, 1H), 3.91-3.98 (m, 1H), 3.26-3.33 (m, 1H), 2.41 (s, 3H), 1.36 (d, *J* = 7.5 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 143.9, 138.7, 135.6, 135.4, 135.0, 134.1, 133.6, 130.8, 129.2, 128.7, 128.4, 128.3, 125.8, 122.0, 73.1, 72.4, 62.0, 46.2, 21.6, 13.9, 12.2. HRMS m/z (ESI+): Calculated for $C_{26}H_{27}N_2O_6S_2$ ($[M+H]^+$) 527.1305, found 527.1305.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7.762
7.760
7.725
7.723
7.710
7.695
7.693
7.661
7.660
7.645
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7.355
7.349
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7.276
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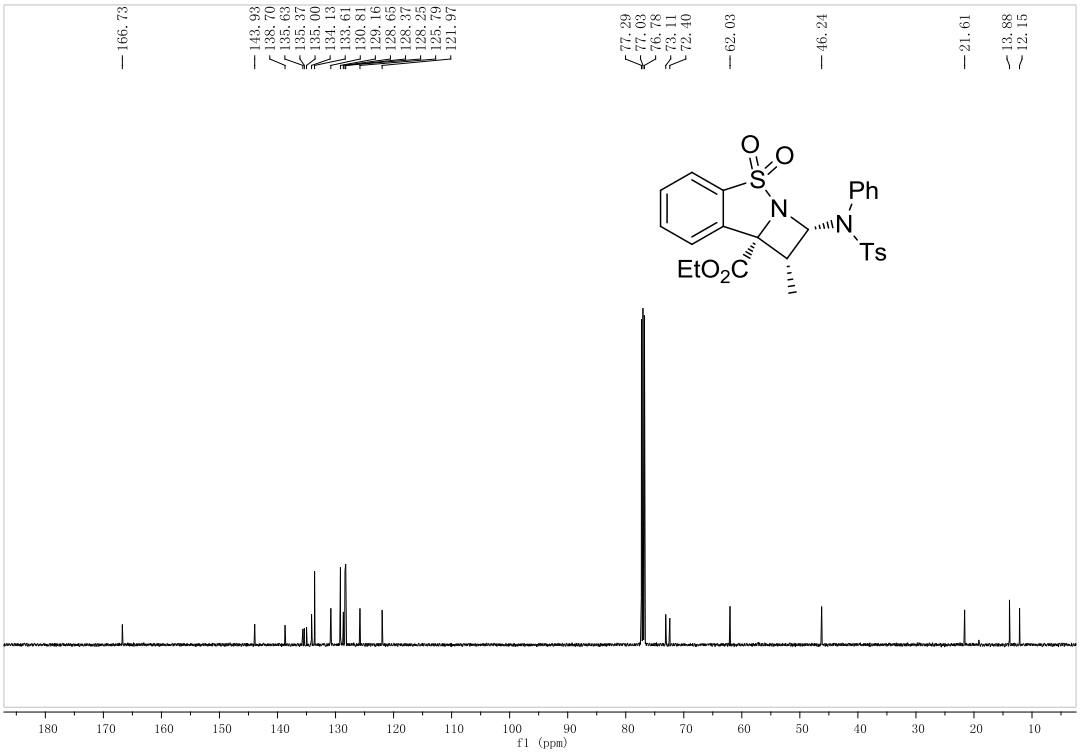
N
Ph
N
Ts
EtO2C
f1 (ppm)


166.73
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133.61
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129.16
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128.37
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125.79
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77.29
77.03
76.78
73.11
72.40
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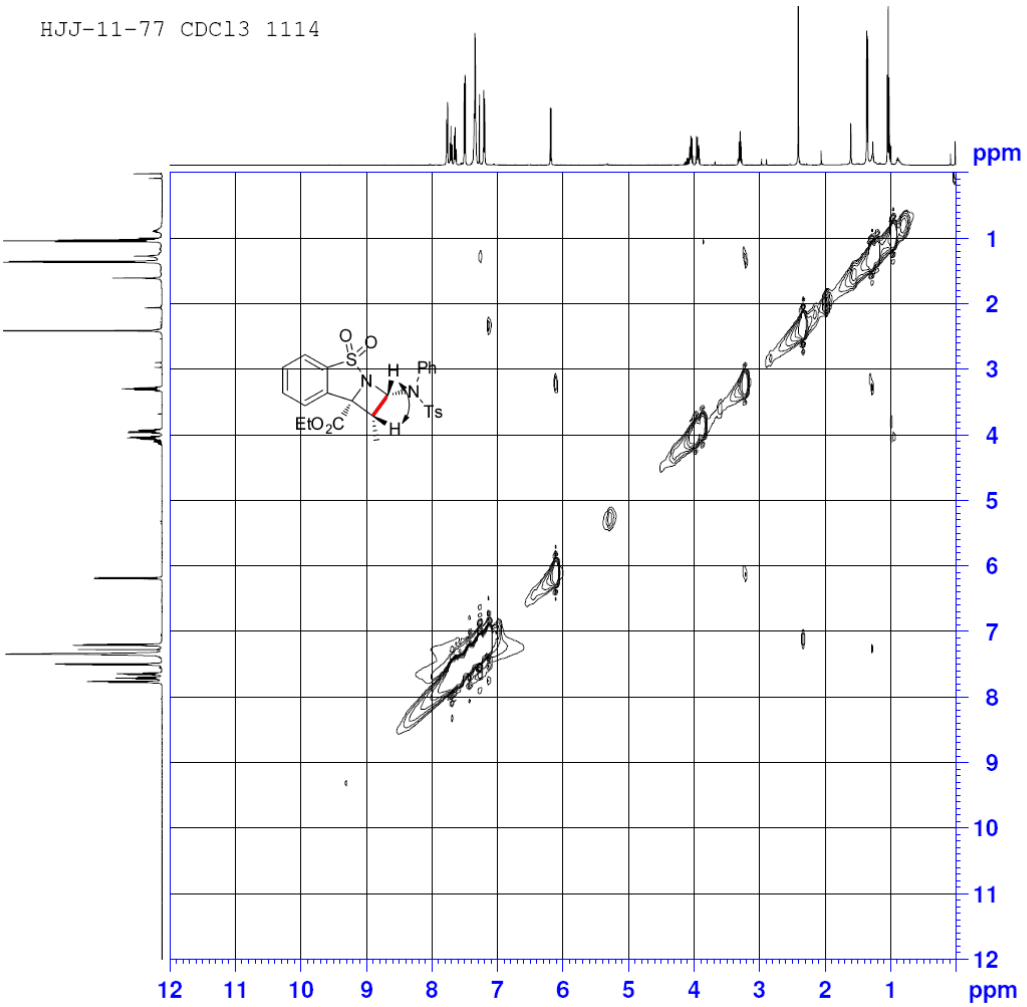
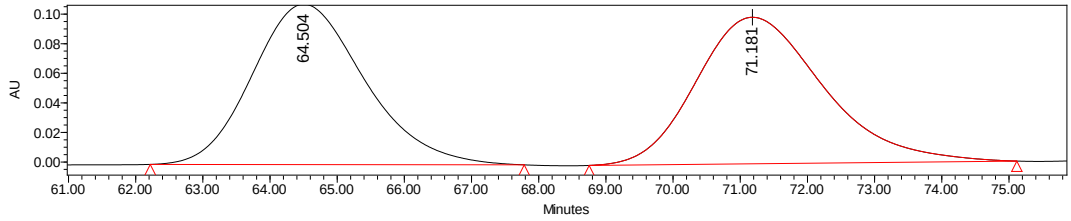
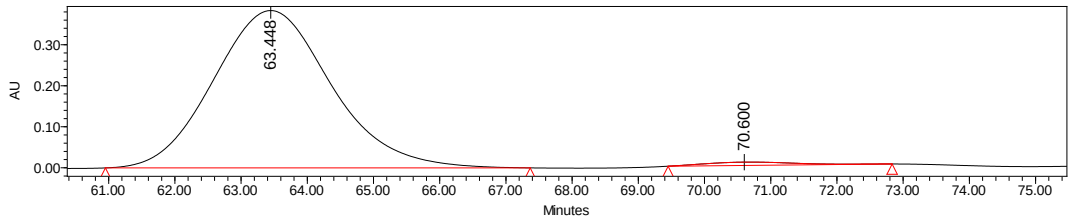
13.88
12.15
O
O
S
N
Ph
N
Ts
EtO2C
f1 (ppm)



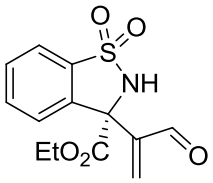


	Retention Time	Area	% Area	Height	% Height
1	64.504	12576557	49.08	108494	52.27
2	71.181	13050247	50.92	99075	47.73

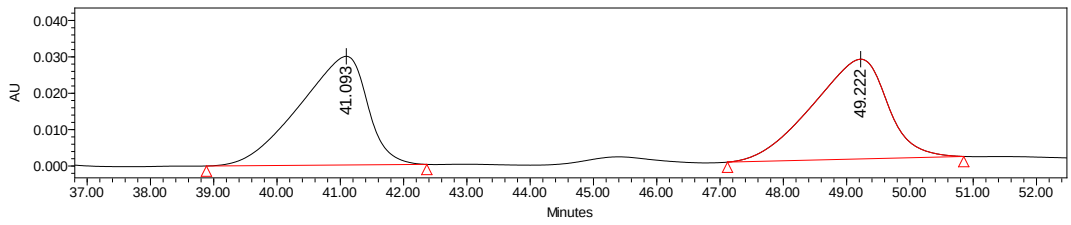


	Retention Time	Area	% Area	Height	% Height
1	63.448	46985613	98.44	382059	97.88
2	70.600	742757	1.56	8260	2.12

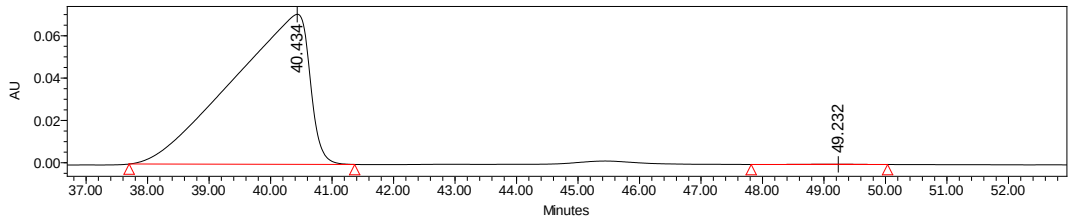
Ethyl 3-(3-oxoprop-1-en-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**5a**)



To a dried Schlenk tube was added TsOH·H_2O (3.8 mg, 0.02 mmol) and compound **3aa** (104.9 mg, 0.2 mmol) under N_2. 1.0 mL DCE solvent was then added through a syringe. The resulting mixture was stirred at 60 °C for 3.0 h until the reaction was completed (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:2 (v/v) to afford compound **5a**. Light yellow oil, 80% yield, $[\alpha]_D^{15}$ = -230.8 (c =1.0 in CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 40.3 min, t_{minor} = 49.2 min].

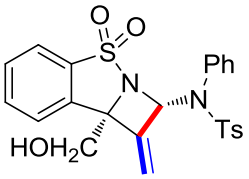


	Retention Time	Area	% Area	Height	% Height
1	41.093	2247758	49.71	29865	52.16
2	49.222	2273948	50.29	27395	47.84

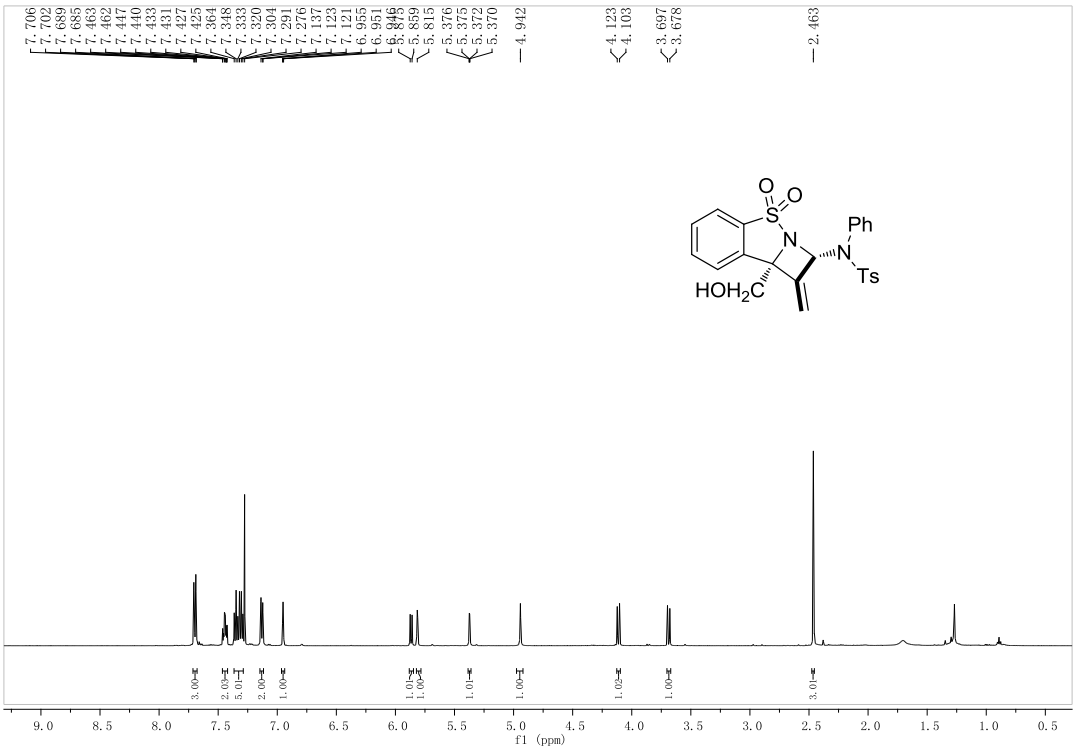


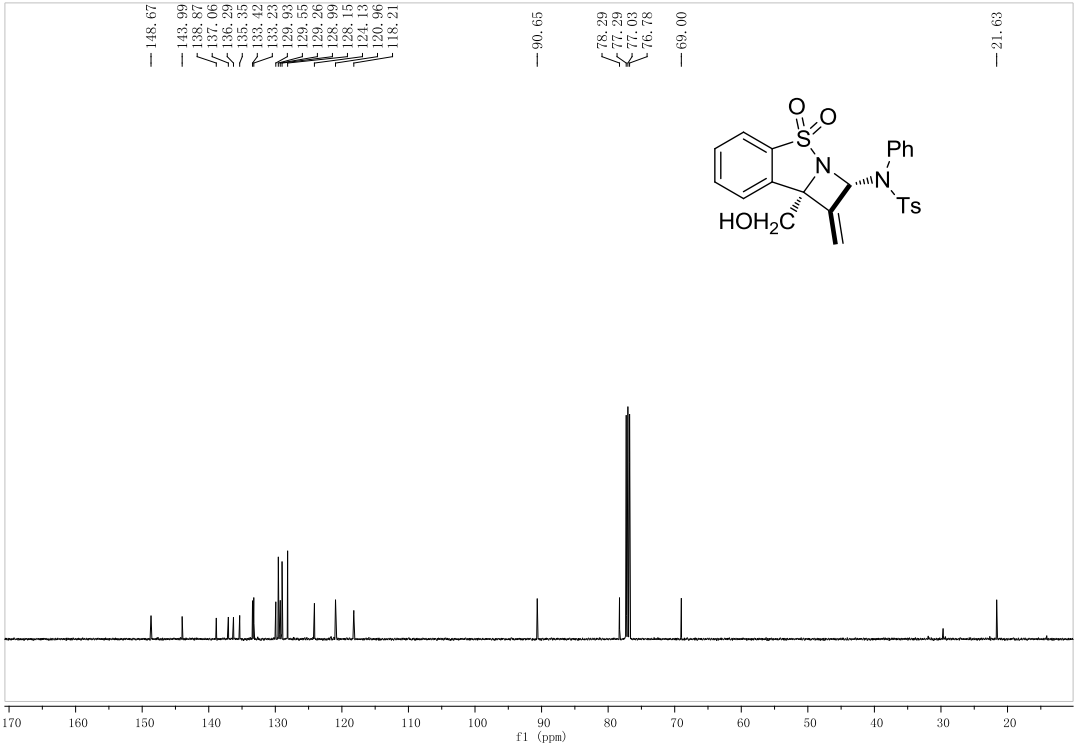
	Retention Time	Area	% Area	Height	% Height
1	40.434	6188245	99.88	70901	99.84
2	49.232	7469	0.12	113	0.16

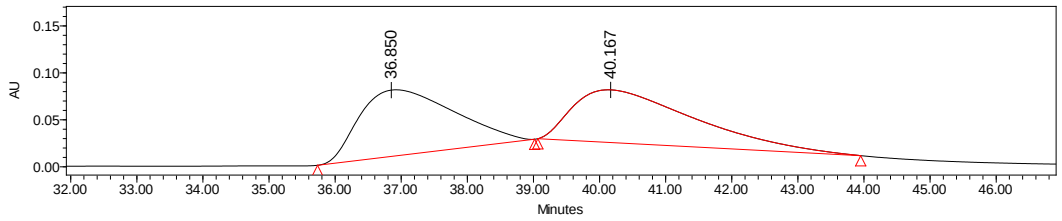
N-((8bS)-8b-(Hydroxymethyl)-1-methylene-4,4-dioxido-2,8b-dihydro-1H-azeto[1,2-b]benzo[d]isothiazol-2-yl)-4-methyl-N-phenylbenzenesulfonamide (**10**)



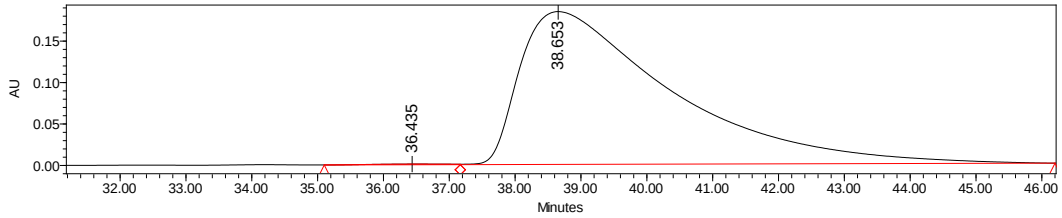
To a solution of **3aa** (104.9 mg, 0.2 mmol) in 2.0 mL THF was added 2.0 equiv. $LiAlH_4$ at 0 °C. The resulting mixture was then stirred at 25 °C for 1.0 h until the reaction was completed (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:1 (v/v) to afford compound **10**. light yellow solid, 90% yield, m.p. 116-118 °C, $[\alpha]_D^{15}$ = 17.7 (c 1.0, CH_2Cl_2), 99% ee [Lux 5u Cellulose-2 column (25 cm × 0.46 cm ID), n-hexane/i-PrOH = 80/20, 0.8 mL/min, 254 nm; t_{major} = 38.7 min, t_{minor} = 36.4 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.5, 2.0 Hz, 3H), 7.42-7.47 (m, 2H), 7.33 (dt, *J* = 21.0, 7.0 Hz, 5H), 7.12-7.14 (m, 2H), 6.95 (t, *J* = 2.0 Hz, 1H), 5.87 (d, *J* = 8.0 Hz, 1H), 5.81 (s, 1H), 5.37 (dd, *J* = 2.0, 1.0 Hz, 1H), 4.94 (s, 1H), 4.11 (d, *J* = 10.0 Hz, 1H), 3.69 (d, *J* = 9.5 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 144.0, 138.9, 137.1, 136.3, 135.4, 133.4, 133.2, 129.9, 129.6, 129.3, 129.0, 128.2, 124.1, 121.0, 118.2, 90.7, 78.3, 69.0, 21.6. HRMS m/z (ESI+): Calculated for $C_{24}H_{23}N_2O_5S_2$ ($[M+H]^+$) 483.1043, found 483.1052.


7.706
7.702
7.689
7.685
7.463
7.462
7.447
7.440
7.433
7.431
7.427
7.425
7.364
7.348
7.333
7.320
7.304
7.291
7.276
7.137
7.123
7.121
6.955
6.951
6.846
6.842
5.875
5.859
5.815
5.376
5.375
5.372
5.370
4.942
4.123
4.103
3.697
3.678
2.463
Ph
N
Ts
HOH2C
f1 (ppm)


148.67
143.99
138.87
137.06
136.29
135.35
133.42
133.23
129.93
129.55
129.26
128.99
128.15
124.13
120.96
118.21
90.65
78.29
77.29
77.03
76.78
69.00
21.63
Ph
N
Ts
HOH2C
f1 (ppm)

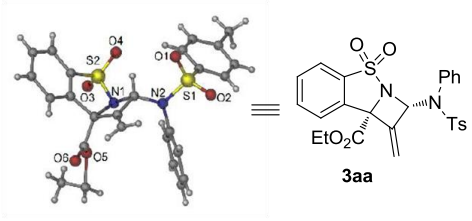


	Retention Time	Area	% Area	Height	% Height
1	36.850	6944893	50.41	70321	56.81
2	40.167	6831750	49.59	53472	43.19



	Retention Time	Area	% Area	Height	% Height
1	36.435	67635	0.23	832	0.45
2	38.653	29434220	99.77	184291	99.55

4. Crystal report of compound 3aa:



Bond precision:	C-C = 0.0053 A		Wavelength=0.71073
Cell:	a=8.7715(4)	b=15.9157(8)	c=36.3389(18)
	alpha=90	beta=90	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	5073.1(4)	5073.1(4)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C26 H24 N2 O6 S2	?
Sum formula	C26 H24 N2 O6 S2	C26 H24 N2 O6 S2
Mr	524.59	524.59
Dx,g cm-3	1.374	1.374
Z	8	8
Mu (mm-1)	0.254	0.254
F000	2192.0	2192.0
F000'	2194.99	
h,k,lmax	10,18,43	10,18,42
Nref	8959[5039]	8949
Tmin,Tmax	0.885,0.922	0.888,0.923
Tmin'	0.885	

Correction method= # Reported T Limits: Tmin=0.888 Tmax=0.923
AbsCorr = MULTI-SCAN

Data completeness= 1.78/1.00 Theta(max)= 25.010

R(reflections)= 0.0420(7514) wR2(reflections)= 0.1043(8949)

S = 1.065 Npar= 649

5. References:

1. S. Suárez-Pantiga, C. Hernández-Díaz, M. Piedrafita, E. Rubio and J. González, *Adv. Synth. Catal.* 2012, **354**, 1651.

2. L.-L. Wei, J. A. Mulder, H. Xiong, C. A. Zificsak, C. J. Douglas and R. P. Hsung, *Tetrahedron* 2001, **57**, 459.

3. H. Wang, T. Jiang and M.-H. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 971.

4. Q. An, J. Shen, N. Butt, D. Liu, Y. Liu, and W. Zhang, *Org. Lett.*, 2014, **16**, 4496.