Supporting Information

Copper-Catalyzed Asymmetric Alkynylation of Cyclic N-sulfonyl Ketimines

Zheng Ling,a Sonia Singh,a,b Fang Xie,*a Liang Wua and Wanbin Zhang*a

a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China
Fax: (+)86-21-54743265; Phone: (+)86-21-54743265; E-mail: wanbin@sjtu.edu.cn
b On leave from Yazd Branch, Islamic Azad University.

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1. General Information

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

2. General procedure for the synthesis of cyclic N-sulfonyl $\alpha$-iminoesters 1 and characterization data$^{[1]}$

To a solution of tert-butylamine (15.0 mmol), triethylamine (20.0 mmol) and DMAP (1.0 mmol) in DCM in an ice bath was added 4-isopropylbenzene-1-sulfonyl chloride (10.0 mmol) dropwise. The mixture was stirred at room temperature overnight. It was washed with saturated sodium carbonate and brine. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic extracts were dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated in vacuo to give the crude product. Then the product was recrystallized to give the $N$-(tert-butyl)-4-isopropylbenzenesulfonamide as a solid.

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

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

Ethyl 5-isopropylbenzo[d]isothiazole-3-carboxylate 1,1-dioxide (1c), 0.85 g, 60% yield, white solid, m.p.: 84-85 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.11 (d, $J = 1.6$ Hz, 1H), 7.85 (d, $J =$
To a solution of L12 (4.2 mmol) in THF (65 mL) in an ice bath was added 60% NaH (14.7 mmol). The mixture was stirred at room temperature for 1 h. The suspension was cooled further to 0 °C and 1-iodopentane (6.3 mmol) was added. The cooling bath was removed and the suspension was stirred at room temperature for 20 h. It was washed with brine. The organic layer was separated, and the aqueous layer was extracted with DCM (three times). The combined organic extracts were dried over anhydrous Na2SO4. The solvent was evaporated in vacuo to give the crude product.

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

(4S,4'S)-2,2'-(undecane-6,6-diyl)bis(4-phenyl-4,5-dihydrooxazole) (L15), 1.41 g, 75% yield, colorless oil; 1H NMR (400 MHz, CDCl3): δ 7.34-7.31 (m, 4H), 7.28-7.24 (m, 6H), 5.24 (dd, J
=10.4, 8.0 Hz, 2H), 4.65 (dd, J = 10.0, 8.0 Hz, 2H), 4.12 (t, J = 8.0 Hz, 2H), 2.13-2.06 (m, 4H), 1.39-1.26 (m, 12H), 0.91-0.85 (t, J = 6.8 Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta\) 169.2, 142.4, 128.7, 127.5, 126.8, 75.0, 69.6, 46.3, 32.6, 32.0, 23.6, 22.5, 14.0; HRMS (ESI): calcd for C₂₉H₃₆N₂O₂ [M+H]⁺ 447.3012, found 447.3003.

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

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\[^{[a]}\] Isolated Yield; \[^{[b]}\] Determined by HPLC using a chiral Daicel column; \[^{[c]}\] The absolute configuration of 3aa was determined as \(R\) according to ref. [3]; \[^{[d]}\] 15 mol% L15 was added; \[^{[e]}\] Reacted for two days.
5. General procedure for Cu-catalyzed alkynylation of cyclic ketimines 1

\(\text{Cu(OAc)}_2 (1.8 \text{ mg, 10 mol %}), 5\text{Å MS (60 mg)} \) and \(\text{L15 (6.8 mg, 15 mol%)}\) were stirred in toluene (1.0 mL) at 90 °C for 1 h. Cyclic ketimines \(1a\) (23.9 mg, 0.1 mmol) and LiOAc (6.6 mg, 1.0 eq.) were added. After 15 min, ethynylbenzene \(2a\) (16.5 μL, 1.5 eq.) was added and stirred at 90 °C for 2 days. After completion, the reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na\(_2\)SO\(_4\). After concentration in vacuo, the residue was finally purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5 to 1:3) to give the product \(3\text{aa}\) as a yellow solid (30.0 mg, 88%).

![Chemical structure](image1)

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

\(\text{Cu(OAc)}_2 (1.8 \text{ mg, 10 mol %}), 5\text{Å MS (60 mg)} \) and \(\text{L15 (6.8 mg, 15 mol%)}\) were stirred in toluene (1.0 mL) at 105 °C for 1 h. Cyclic ketimines \(4\text{a}\) (23.9 mg, 0.1 mmol) and LiOAc (6.6 mg, 1.0 eq.) were added. After 15 min, ethynylbenzene \(2a\) (16.5 μL, 1.5 eq.) was added and stirred at 105 °C for 24 h. After completion, the reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na\(_2\)SO\(_4\). After concentration in vacuo, the residue was finally purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5 to 1:3) to give the product \(5\text{aa}\) as a yellow solid (25.4 mg, 74%).

The results of alkynylation of cyclic ketimines \(4\text{c}\) and \(4\text{d}\) are as follow.

![Chemical structure](image2)

7. Characterization data and HPLC of addition products

(R)-ethyl 3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3\text{aa}), 30.0 mg, 88% yield; 1H NMR (400 MHz, CDCl\(_3\)): δ 7.93 (d, \(J = 7.6\) Hz, 1H), 7.79 (d, \(J = 7.6\) Hz, 1H), 7.73 (t, \(J = 7.6\) Hz, 1H), 7.64 (t, \(J = 7.6\) Hz, 1H), 7.43 (d, \(J = 6.8\) Hz, 2H), 7.37-7.29 (m, 3H), 5.90 (br, 1H), 4.43-4.34 (m, 2H), 1.37 (t, \(J = 7.2\) Hz, 3H).[3]

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 30.3 min; 37.7 min (major), 96% ee, \([\alpha]^2\): 45.539 (c
(R)-ethyl 3-((2-chlorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ab), 30.8 mg, 82% yield, yellow solid, m.p.: 89-90 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 7.6\) Hz, 1H), 7.80 (d, \(J = 8.0\) Hz, 1H), 7.73 (td, \(J = 7.6, 1.2\) Hz, 1H), 7.65 (td, \(J = 8.0, 0.8\) Hz, 1H), 7.46 (dd, \(J = 7.6, 1.6\) Hz, 1H), 7.39 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.30 (td, \(J = 7.6, 2.0\) Hz, 1H), 7.21 (td, \(J = 7.6, 1.2\) Hz, 1H), 5.90 (br, 1H), 4.45-4.34 (m, 2H), 1.39 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 166.7, 136.6, 135.6, 134.2, 133.9, 133.6, 131.1, 130.4, 129.4, 126.5,
126.3, 121.4, 121.2, 89.2, 82.3, 64.7, 61.8, 14.0; HRMS (ESI): calcd for C\textsubscript{18}H\textsubscript{15}NO\textsubscript{4}SCl [M+H]\textsuperscript{+} 376.0410, found 376.0419.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 33.4 min; 43.8 min (major), 92% ee, \([\alpha]\)\textsuperscript{25}: 19.973 (c 0.20, CHCl\textsubscript{3}).

(R)-ethyl 3-((3-chlorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ac), 30.0 mg, 80% yield, yellow solid, m.p.: 93-94 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.91
(d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.74 (td, J = 7.6, 1.6 Hz, 1H), 7.66 (td, J = 7.2, 0.8 Hz, 1H), 7.43 (t, J = 1.6 Hz, 1H), 7.34-7.30 (m, 2H), 7.24 (t, J = 8.0 Hz, 1H), 5.90 (br, 1H), 4.45-4.36 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); $^1$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.6, 135.7, 134.3, 134.2, 134.0, 131.9, 131.2, 130.2, 129.7, 129.6, 126.0, 122.7, 121.5, 85.4, 83.9, 64.8, 61.6, 14.0; HRMS (ESI): calcld for C$_{18}$H$_{15}$NO$_4$SCl [M+H]$^+$ 376.0410, found 376.0424.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 28.9 min; 39.0 min (major), 85% ee, $[\alpha]^{25}$: 22.690 (c 0.25, CHCl$_3$).
(R)-ethyl 3-((4-chlorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ad), 31.9 mg, 85% yield, yellow solid, m.p.: 122-123 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.73 (t, J = 7.6, 1H), 7.65 (t, J = 7.6, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.90 (br, 1H), 4.43-4.36 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 135.7, 135.6, 134.2, 134.0, 133.2, 131.0, 128.7, 126.0, 121.4, 119.5, 85.2, 84.3, 64.7, 61.8, 14.0; HRMS (ESI): calcd for C_{18}H_{15}NO_{4}SCl [M+H]^+ 376.0410, found 376.0413.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 30.2 min; 39.8 min (major), 98% ee, [α]²⁵: 27.963 (c 0.20, CHCl₃).
(R)-ethyl 3-((3-methoxyphenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ae), 24.1 mg, 65% yield, yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J$ = 7.6 Hz, 1H), 7.79 (d, $J$ = 8.0 Hz, 1H), 7.74 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.64 (td, $J$ = 7.6, 0.8 Hz, 1H), 7.21 (t, $J$ = 7.6 Hz, 1H), 7.03 (d, $J$ = 7.6 Hz, 1H), 6.95-6.89 (m, 2H), 5.86 (br, 1H), 4.45-4.33 (m, 2H), 3.78 (s, 3H), 1.37 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.8, 159.2, 135.8, 134.2, 133.9, 131.9, 129.4, 126.1, 124.5, 122.0, 121.3, 116.8, 116.1, 85.4, 84.0, 64.6, 61.8, 55.3, 14.0; HRMS (ESI): calcd for C$_{19}$H$_{18}$NO$_5$S [M+H]$^+$ 372.0906, found 372.0900.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 37.7 min; 52.7 min (major), 91% ee, $[\alpha]^{25}$ 25.965 (c 0.20, CHCl$_3$).
**(R)-ethyl 3-((4-bromophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3af)**, 32.7 mg, 78% yield, yellow solid, m.p.: 126-127 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.90 (d, \(J = 7.6\) Hz, 1H), 7.80 (d, \(J = 8.0\) Hz, 1H), 7.73 (td, \(J = 7.2, 1.2\) Hz, 1H), 7.65 (td, \(J = 7.6, 0.8\) Hz, 1H), 7.46-7.31 (m, 2H), 7.30-7.28 (m, 2H), 5.86 (br, 1H), 4.44-4.35 (m, 2H), 1.37 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 166.6, 135.7, 134.2, 133.9, 133.4, 131.7, 131.2, 126.0, 124.0, 121.4, 120.0, 85.3, 84.3, 64.7, 61.7, 14.0; HRMS (ESI): calcd for C\(_{18}\)H\(_{15}\)NO\(_4\)SBr [M+H]\(^+\) 419.9905, found 419.9899.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 32.1 min; 42.3 min (major), 98% ee, \([\alpha]^{25}\): 19.973 (c 0.20, CHCl\(_3\)).
(R)-ethyl 3-((4-fluorophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ag), 25.1 mg, 70% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 (td, J = 7.6, 1.2 Hz, 1H), 7.65 (td, J = 8.0, 0.8 Hz, 1H), 7.44-7.40 (m, 2H), 7.00-6.98 (m, 2H), 5.86 (br, 1H), 4.45-4.33 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.8, 165.6 (d, J = 249.7 Hz), 135.9, 134.3, 134.1 (d, J = 8.5 Hz), 133.9, 131.1, 126.0, 121.3, 117.1 (d, J = 3.5 Hz), 115.7 (d, J = 22.1 Hz), 84.4, 84.0, 64.6, 61.7, 14.0; HRMS (ESI): calcd for C₁₈H₁₅NO₄SF [M+H]+ 360.0706, found 360.0714.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 29.0 min; 36.7 min (major), 93% ee, [α]²⁵: 24.967 (c 0.20, CHCl₃).
(R)-ethyl 3-((4-(trifluoromethyl)phenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ah), 37.2 mg, 91% yield; 'H NMR (400 MHz, CDCl₃): δ 7.91 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.66 (t, J = 7.2, Hz, 1H), 7.58-7.53 (m, 4H), 5.91 (br, 1H), 4.45-4.37 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H).[^3]

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 25.8 min; 35.3 min (major), 98% ee, [α]²³: 40.945 (c 0.20, CHCl₃).
(R)-ethyl 3-((4-(methoxycarbonyl)phenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxy late 1,1-dioxide (3ai), 37.1 mg, 93% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 5.93 (br, 1H), 4.43-4.38 (m, 2H), 3.91 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 166.3, 135.6, 134.2, 134.0, 132.0, 131.2, 130.6, 129.5, 126.0, 125.6, 121.5, 86.9, 84.5, 64.8, 61.7, 52.4, 14.0; HRMS (ESI): calcld for C₂₀H₁₈NO₅S [M+H]^+ 400.0855, found 400.0847.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = .
85/15; flow = 0.5 mL/min; Retention time: 49.9 min; 60.2 min (major), 98% ee, [α]$_D^{25}$: 39.512 (c 0.46, CHCl$_3$).

(R)-ethyl 3-((4-cyanophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxi- 
(3aj), 34.4 mg, 94% yield, yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.89 (d, $J$ = 8.0 Hz, 
1H), 7.80 (d, $J$ = 8.0 Hz, 1H), 7.73 (td , $J$ = 7.6, 1.2 Hz, 1H), 7.66 (td, $J$ = 8.0, 0.8 Hz, 1H), 
7.60-7.58 (m, 2H), 7.52-7.50 (m, 2H), 5.94 (br, 1H), 4.45-4.37 (m, 2H), 1.38 (t, $J$ = 7.2 Hz, 3H); 
$^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.4, 135.4, 134.3, 134.1, 132.6, 132.0, 131.4, 125.9, 125.8, 
121.6, 118.1, 112.8, 88.4, 83.4, 64.9, 61.5, 14.0; HRMS (ESI): caleed for C$_{19}$H$_{15}$N$_2$O$_4$S [M+H]$^+$ 
367.0753, found 367.0763.
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 90.0 min; 96.5 min (major), 98% ee, \([\alpha]^2_{25}\): 16.286 (c 0.65, CHCl₃).

(R)-ethyl 3-((4-nitrophenyl)ethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ak), 34.7 mg, 90% yield, yellow oil; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 8.18-8.15 (m, 2H), 7.81 (d, \(J = 8.0\) Hz, 1H), 7.74 (td, \(J = 7.2, 1.2\) Hz, 1H), 7.67 (td, \(J = 7.6, 1.2\) Hz, 1H), 7.67-7.57 (m, 2H), 5.96 (br, 1H), 4.46-4.38 (m, 2H), 1.39 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta\) 166.3, 147.8, 135.3, 134.3, 134.1, 132.9, 131.4, 127.8, 125.8, 123.6, 121.6, 89.1, 83.1, 65.0, 61.5, 14.0; HRMS (ESI): calcd for C₁₆H₁₃N₂O₆S [M+H]^+ 387.0651, found
HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 107.9 min; 116.4 min (major), 96% ee, \([\alpha]^{25}_D: 32.684\) (c 0.22, CHCl). 

\[ \text{(R)-ethyl 3-[[1',1'-biphenyl]-4-ylethynyl]-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3aI), 31.3 mg, 75% yield, yellow solid, m.p.: 95-96 °C; } \]

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta 7.94 (d, J = 8.0 Hz, 1H), 7.81-7.80 (m, 1H), 7.73 (td, J = 7.2, 0.8 Hz, 1H), 7.64 (td, J = 7.6, 0.8 Hz, 1H), 7.57-7.48 (m, 6H), 7.46-7.41 (m, 2H), 7.37-7.33 (m, 1H), 5.90 (br, 1H), 4.46-4.33 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); \]

\[ ^13C \text{NMR (100 MHz, CDCl}_3\text{): } \delta 166.9, 142.2, 140.0, 136.0, 134.2, \]
133.9, 132.5, 131.1, 128.9, 127.9, 127.1, 127.0, 126.2, 121.4, 119.9, 85.4, 84.8, 65.0, 61.9, 14.0; HRMS (ESI): calcd for C_{24}H_{20}NO_{4}S [M+H]^+ 418.1113, found 418.1110.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 57.2 min; 65.1 min (major), 96% ee, $[\alpha]_{25}^{25}$: 29.461 (c 0.40, CHCl3).

(R)-ethyl 3-(naphthalen-2-ylethynyl)-2,3-dihydro[1,1-dioxide (3am), 23.0 mg, 59% yield, yellow solid, m.p.: 103-104 °C; $^1$H NMR (400 MHz, CDCl3): $\delta$ 7.98-7.97 (m, 2 H), 7.82-7.73 (m, 5 H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.50-7.44 (m, 3H), 5.94 (br, 1H), 4.46-4.37 (m, 2H), 1.40 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3): $\delta$ 166.9, 136.0, 134.3, 134.0, 133.2, 132.7, 132.5, 131.1, 128.1, 127.9, 127.8, 127.3, 126.8, 126.2, 121.4, 118.3, 85.8,
84.5, 64.6, 61.9, 14.0; HRMS (ESI): calcd for C_{22}H_{18}NO_{4}S [M+H]^+ 392.0957, found 392.0949.

HPLC: Daicel Chiraleel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 48.5 min; 59.4 min (major), 91% ee, [α]^22: 24.178 (c 0.19, CHCl3).

(R)-ethyl 3-(thiophen-2-ylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3an), 28.1 mg, 81% yield, yellow solid, m.p.: 93-94 °C; 1H NMR (400 MHz, CDCl3): δ 7.91 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.31 (dd, J = 4.6, 1.2 Hz, 1H), 7.27-7.26 (m, 1H), 6.98-6.96 (m, 1H), 5.85 (br, 1H), 4.46-4.33 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 166.6, 135.6, 134.2, 134.0, 133.8, 131.1,
128.6, 127.1, 126.1, 121.4, 120.8, 87.9, 79.0, 64.7, 61.9, 14.0; HRMS (ESI): calcd for C_{16}H_{14}NO_{4}S_{2} [M+H]^+: 348.0364, found 348.0357.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 90/10; flow = 0.5 mL/min; Retention time: 60.7 min; 68.2 min (major), 93% ee, [$\alpha$]^{25}: 35.785 (c 0.24, CHCl$_3$).

(R)-methyl 3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ba), 29.4 mg, 90% yield, yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (td, $J$ = 7.2, 0.8 Hz, 1H), 7.80-7.78 (m, 1H), 7.34 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.65 (td, $J$ = 7.6, 0.8 Hz, 1H), 7.45-7.42 (m, 2H), 7.37-7.28 (m, 3H), 5.87 (br, 1H), 3.94 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.4, 135.8, 134.2, 134.0, 132.1, 131.1, 129.5, 128.3, 126.2, 121.3, 121.0, 85.7, 84.0, 61.8, 55.0; HRMS (ESI):
calcd for C_{17}H_{14}NO_{3}S [M+H]^+ 328.0644, found 328.0653.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/05; flow = 0.5 mL/min; Retention time: 42.2 min; 50.7 min (major), 95% ee, [α]^{25}_{D}: 10.796 (c 0.185, CHCl_{3}).

(R)-isopropyl 3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ca), 27.0 mg, 76% yield, yellow oil; ^1H NMR (400 MHz, CDCl_{3}): δ 7.91 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.71 (td, J = 7.6, 1.2 Hz, 1H), 7.63 (td, J = 7.6, 1.2 Hz, 1H), 7.43-7.40 (m, 2H), 7.35-7.28 (m, 3H), 5.87 (br, 1H), 5.20-5.14 (m, 1H), 1.40 (d, J = 6.0 Hz, 3H), 1.31 (d, J = 6.0 Hz, 3H); ^13C NMR (100 MHz, CDCl_{3}): δ 166.3, 136.0, 134.3, 133.8, 132.0, 131.0, 129.3, 128.4,
126.0, 121.3, 121.1, 85.3, 84.3, 73.0, 61.9, 21.5, 21.4; HRMS (ESI): calcd for C_{19}H_{18}NO_{3}S [M+H]^+ 356.0957, found 356.0949.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/05; flow = 0.5 mL/min; Retention time: 22.4 min; 27.2 min (major), 89% ee, [α]^{25}_D: 45.495 (c 0.36, CHCl₃).

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(R)-butyl 3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3da), 29.5 mg, 80% yield, yellow solid, m.p.: 116-118 °C; {\textsuperscript{1}}H NMR (400 MHz, CDCl₃): δ 7.92(d, J = 8.0 Hz, 1H), 7.80(t, J = 6.8 Hz, 1H), 7.72 (td, J = 7.6, 1.2 Hz, 1H), 7.64 (td, J = 7.6, 0.8Hz, 1H), 7.44-7.41 (m, 2H), 7.36-7.28 (m, 3H), 5.87 (br, 1H), 4.41-4.25 (m, 2H), 1.76-1.69 (m, 2H), 1.48-1.38 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); {\textsuperscript{13}}C NMR (100 MHz, CDCl₃): δ 166.9, 135.8, 134.2,
133.8, 132.0, 131.0, 129.3, 128.3, 126.1, 121.3, 121.0, 85.4, 84.2, 68.3, 61.8, 60.4, 30.3, 19.0, 13.6; HRMS (ESI): calcd for C_{20}H_{20}NO_4S [M+H]^+ 370.1113, found 370.1110.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/05; flow = 0.5 mL/min; Retention time: 25.8 min; 29.9 min (major), 93% ee, [\(\alpha\)]^{25} = 89.024 (c 0.175, CHCl_3).

(R)-ethyl 5-methyl-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ea), 27.0 mg, 76% yield, yellow solid, m.p.: 115-117 \(\degree\)C; \(^1H\) NMR (400 MHz, CDCl_3): \(\delta\) 7.68-7.65 (m, 2H), 7.46-7.42 (m, 3H), 7.36-7.30 (m, 3H), 5.84 (br, 1H), 4.44-4.35 (m, 2H), 2.51 (s, 3H), 1.37 (t, \(J = 7.2\) Hz, 3H); \(^{13}C\) NMR (100 MHz, CDCl_3): \(\delta\) 166.7, 145.2, 136.2, 134.5, 132.1, 131.6, 129.4, 128.4, 126.2, 121.1, 121.0, 85.3, 84.4, 64.5, 61.7, 22.0, 14.0; HRMS (ESI): calcd for
C\textsubscript{19}H\textsubscript{18}NO\textsubscript{4}S [M+H]\textsuperscript{+} 356.0957, found 356.0969.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 26.9 min; 33.6 min (major), 96\% ee, [\(\alpha\)]\textsubscript{D}: 64.404 (c 0.49, CHCl\textsubscript{3}).

(R)-ethyl 5-isopropyl-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3f), 26.8mg, 70\% yield, yellow oil; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.72 (d, \(J = 1.2\) Hz, 1H), 7.69 (d, \(J = 8.0\) Hz, 1H), 7.50-7.42 (m, 3H), 7.35-7.28 (m, 3H), 5.82 (br, 1H), 4.41-4.37 (m, 2H), 3.10-3.03 (m, 1H), 1.36 (t, \(J = 7.2\) Hz, 3H), 1.30 (d, \(J = 6.8\) Hz, 6H); \(^{13}\)C NMR (100 MHz,
CDCl₃): δ 167.0, 156.0, 136.2, 132.0, 128.3, 123.7, 121.2, 121.1, 85.3, 84.5, 64.4, 61.8, 34.5, 23.9, 23.6, 14.0; HRMS (ESI): calcd for C₂₁H₂₂NO₄S [M+H]⁺ 384.1270, found 384.1254.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 21.8 min; 26.6 min (major), 95% ee, [α]²⁵: 89.024 (c 0.175, CHCl₃).

(R)-ethyl 5-(tert-butyl)-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ga), 22.2 mg, 56% yield, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.90(d, J = 1.2 Hz, 1H), 7.72-7.65 (m, 2H), 7.45-7.42 (m, 2H), 7.36-7.29 (m, 3H), 5.86 (br, 1H), 4.46-4.33 (m, 2H), 4.39-4.32 (m, 2H), 4.29-4.25 (m, 2H), 4.04-3.99 (m, 2H), 3.51-3.47 (m, 2H), 2.22-2.17 (m, 2H), 1.37-1.32 (m, 2H), 1.18-1.13 (m, 2H), 1.05-1.00 (m, 2H), 0.87-0.83 (m, 2H), 0.83-0.78 (m, 2H), 0.78-0.74 (m, 2H), 0.74-0.70 (m, 2H), 0.69-0.65 (m, 2H), 0.65-0.61 (m, 2H), 0.61-0.57 (m, 2H), 0.57-0.53 (m, 2H), 0.53-0.49 (m, 2H), 0.49-0.45 (m, 2H), 0.45-0.41 (m, 2H), 0.41-0.37 (m, 2H), 0.37-0.33 (m, 2H), 0.33-0.29 (m, 2H), 0.29-0.25 (m, 2H), 0.25-0.21 (m, 2H), 0.21-0.17 (m, 2H), 0.17-0.13 (m, 2H), 0.13-0.09 (m, 2H), 0.09-0.05 (m, 2H), 0.05-0.01 (m, 2H).
1.38-1.35 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.0, 158.3, 136.0, 132.0, 131.4, 129.3, 128.6, 128.3, 122.7, 121.2, 121.9, 85.3, 84.5, 64.3, 61.8, 35.6, 31.2, 14.0; HRMS (ESI): calc for C$_{22}$H$_{24}$NO$_4$S [M+H]+ 398.1426, found 398.1418.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 21.8 min; 26.5 min (major), 91% ee, $[\alpha]^{25}_D$: 52.525 (c 0.27, CHCl$_3$).

$^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.68 (d, $J$ = 8.0 Hz, 1H), 7.57 (d, $J$ = 8.0 Hz, 1H), 7.51 (s, 1H), 7.40-7.25 (m, 5H), 7.18 (t, $J$ = 8.0 Hz, 2H), 7.08 (s, 1H), 6.28 (s, 1H), 4.15 (br q, $J$ = 7.0 Hz, 2H), 3.79 (s, 3H), 1.14 (t, $J$ = 7.0 Hz, 3H), 0.96 (t, $J$ = 7.0 Hz, 3H).
7.45-7.42 (m, 2H), 7.35-7.28 (m, 4H), 7.12 (dd, J = 8.0, 2.0 Hz, 1H), 5.85 (br, 1H), 4.42-4.37 (m, 2H), 3.91 (s, 3H), 1.37 (t, J = 6.8 Hz, 3H).[3]

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 41.6 min; 48.7 min (major), 93% ee, [α]23: 77.79 (c 0.285, CHCl3).

(R)-ethyl 3-(phenylethynyl)-5-(trifluoromethoxy)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ia), 40.3 mg, 95% yield, yellow oil; 1H NMR (400 MHz, CDCl3): δ 7.83 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 1.2 Hz, 1H), 7.50-7.42 (m, 3H), 7.40-7.30 (m, 3H), 5.98 (br, 1H), 4.41 (q, J = 6.8 Hz, 2H), 1.38 (t, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 166.2, 153.0 (q, J = 1.8 Hz), 138.6, 132.5, 132.1, 129.6, 128.4, 123.7 (q, J = 0.8 Hz), 123.3, 122.7 (q, J = 258.5 Hz), 120.7,
118.3, 86.1, 83.4, 64.9, 61.3, 13.9; HRMS (ESI): calcd for C_{19}H_{15}NO_{5}SF_{3} [M+H]^+ 426.0623, found 426.0637.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 19.7 min; 25.3 min (major), 90% ee, [α]^{25}: 57.399 (c 0.515, CHCl_{3}).

(R)-ethyl 3-(phenylethynyl)-5-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ja), 39.7 mg, 97% yield, yellow oil; ^1H NMR (400 MHz, CDCl_{3}): δ 8.19 (d, J =
0.8 Hz, 1H), 7.92-7.91 (m, 2H), 7.46-7.43 (m, 2H), 7.39-7.30 (m, 3H), 6.00 (br, 1H), 4.43 (q, J = 6.8 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.1, 137.6, 137.0, 136.0 (q, J = 33.4 Hz), 132.1, 129.7, 128.4, 128.3 (q, J = 3.5 Hz), 125.6 (q, J = 271.9 Hz), 123.7 (q, J = 4.0 Hz), 122.2, 120.6, 86.3, 83.2, 64.9, 61.6, 13.9; HRMS (ESI): calcd for C$_{19}$H$_{15}$NO$_5$S$_3$ [M+H]$^+$ 410.0674, found 410.0666.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 21.7 min; 27.9 min (major), 92% ee, $[\alpha]^{25}$: 46.049 (c 0.36, CHCl$_3$).

(R)-ethyl 5-chloro-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dio-
xide (3ka), 35.2 mg, 94% yield; 1H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 1.6 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.61 (dd, J = 8.0, 2.0 Hz, 1H), 7.46-7.44 (m, 2H), 7.37-7.30 (m, 3H), 5.89 (br, 1H), 4.47-4.37 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H). [3]

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 25.9 min; 35.5 min (major), 90% ee, [α]²³: 67.909 (c 0.20, CHCl₃).

(R)-ethyl 5-fluoro-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3la), 33.3 mg, 93% yield, yellow solid, m.p.: 93-94 °C; 1H NMR (400 MHz, CDCl₃): δ 7.90 (dd, J = 8.0, 4.8 Hz, 1H), 7.59 (dd, J = 8.0, 2.0 Hz, 1H), 7.45-7.43 (m, 2H), 7.37-7.29 (m, 4H), 5.93
(1H), 4.48-4.36 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 166.3, 165.8 (d, J = 254.9 Hz), 139.1 (d, J = 9.4 Hz), 132.0, 130.4 (d, J = 2.9 Hz), 129.6, 128.4, 123.6 (d, J = 9.8 Hz), 120.8, 119.2 (d, J = 24.0 Hz), 113.4, 85.9, 83.5, 64.8, 61.2, 14.0; HRMS (ESI): calcd for C18H16NO3SF [M+H]+ 360.0706, found 360.0720.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 85/15; flow = 0.5 mL/min; Retention time: 25.5 min; 34.8 min (major), 91% ee, [α]25: 47.583 (c 0.34, CHCl3).

(R)-ethyl 3-(phenylethynyl)-7-(trifluoromethoxy)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3ma), 34.8 mg, 82% yield, yellow oil; 1H NMR (400 MHz, CDCl3): δ 7.82 (d, J
=7.6 Hz, 1H), 7.75 (t, J =8.0Hz, 1H), 7.46-7.29 (m, 3H), 7.39-7.29 (m, 3H), 5.98 (br, 1H), 4.46-4.37 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 166.3, 143.5 (q, \(J =2.0\) Hz), 139.2, 135.7, 132.0, 129.5, 128.3, 126.4, 123.6, 123.1 (q, \(J =283.4\) Hz), 120.8, 120.7 (q, \(J =1.7\) Hz), 86.0, 83.5, 64.8, 61.2, 14.0; HRMS (ESI): calcld for C\(_{19}\)H\(_{15}\)NO\(_5\)SF\(_3\) [M+H]\(^{+}\) 426.0623, found 426.0631.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/05; flow = 0.5 mL/min; Retention time: 51.2 min; 57.9 min (major), 94% ee, \([\alpha]\)\(^{25}\) = 17.669 (c 0.26, CHCl\(_3\)).

(R)-ethyl 7-chloro-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3na), 30.0 mg, 80% yield, yellow solid, m.p.: 96-97 °C; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.82
(dd, J = 8.0, 0.8 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.0, 0.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.38-7.28 (m, 3H), 6.00 (br, 1H), 4.46-4.34 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.4, 138.6, 134.9, 132.4, 132.0, 131.8, 129.5, 128.9, 128.3, 124.3, 120.8, 85.8, 83.7, 64.8, 60.7, 13.9; HRMS (ESI): calcd for C$_{18}$H$_{15}$NO$_4$SCl [M+H]$^+$ 376.0410, found 376.0421.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/05; flow = 0.5 mL/min; Retention time: 37.0 min; 41.3 min (major), 94% ee, [α]$^2_{25}$: -5.463 (c 0.585, CHCl$_3$).

(R)-ethyl 7-fluoro-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dio-
xide (3oa), 27.3 mg, 76% yield, yellow solid, m.p.: 70-72 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.72-7.69 (m, 2H), 7.44-7.42 (m, 2H), 7.38-7.26 (m, 4H), 6.00 (br, 1H), 4.47-4.35 (m, 2H), 1.38 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.4, 156.0 (d, $J = 258.5$ Hz), 139.2, 136.3 (d, $J = 7.0$ Hz), 132.0, 129.5, 128.4, 122.7 (d, $J = 20.1$ Hz), 121.6 (d, $J = 4.2$ Hz), 120.9, 117.9 (d, $J = 18.3$ Hz), 85.9, 83.6, 64.8, 61.6, 13.9; HRMS (ESI): calcd for C$_{18}$H$_{15}$NO$_4$SF [M+H]$^+$ 360.0706, found 360.0719.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/05; flow = 0.5 mL/min; Retention time: 36.1 min; 43.7 min (major), 98% ee, $[\alpha]_D^{25}$: 41.373 (c 0.42, CHCl$_3$).
(R)-ethyl 4,6-dimethyl-3-(phenylethynyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (3pa), 22.8 mg, 62% yield, yellow solid, m.p.: 112-114 °C; 1H NMR (400 MHz, CDCl3): δ 7.45-7.42 (m, 3H), 7.38-7.29 (m, 4H), 5.44 (br, 1H), 4.33-4.27 (m, 2H), 2.56 (s, 3H), 2.43 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3): δ 166.7, 141.7, 137.2, 136.4, 134.4, 131.9, 130.5, 129.4, 128.4, 121.0, 119.2, 87.4, 82.8, 82.3, 63.9, 62.0, 21.1, 18.8, 13.9; HRMS (ESI): caled for C20H20NO4S [M+H]+ 370.1113, found 370.1110.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/05; flow = 0.5 mL/min; Retention time: 28.2 min; 31.2 min (major), 40% ee, [α]25: 10.241 (c 0.55, CHCl3).
(R)-ethyl 3-(phenylethynyl)-2,3-dihyronaphtho[2,1-d]isothiazole-3-carboxylate 1,1-dioxide (3qa), 34.0 mg, 87% yield, yellow solid, m.p.: 116-118 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.41 (d, $J = 8.0$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.77-7.67 (m, 2H), 7.45-7.43 (m, 2H), 7.35-7.28 (m, 3H), 6.00 (br, 1H), 4.45-4.36 (m, 2H), 1.38 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 166.9, 135.0, 134.8, 134.1, 132.0, 129.7, 129.5, 129.4, 128.64, 128.63, 128.4, 125.0, 123.3, 121.4, 121.1, 85.8, 84.1, 64.6, 61.9, 14.0; HRMS (ESI): calcd for C$_{22}$H$_{18}$N$\text{O}_4$S [M+H]$^+$ 392.0957, found 392.0949.

HPLC: Daicel Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/5; flow = 0.5 mL/min; Retention time: 33.1 min; 42.4 min (major), 91% ee, [\(\alpha\)]$_{25}^\circ$ -26.631 (c 0.285, CHCl$_3$).
Methyl 4-(phenylethynyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (5a), 25.4 mg, 74% yield, yellow oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.87-7.84 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.49-7.45 (m, 2H), 7.44-7.39 (m, 1H), 7.37-7.27 (m, 4H), 7.09-7.05 (dd, $J = 8.0, 1.2$ Hz, 1H), 3.97 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.6, 149.7, 132.1, 131.2, 129.48, 129.46, 128.4, 125.9, 121.0, 119.5, 119.1, 86.5, 84.1, 62.2, 55.3; HRMS (ESI): calcd for C$_{17}$H$_{14}$NO$_5$S [M+H]$^+$ 344.0593, found 344.0581.

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 90/10; flow = 0.5 mL/min; Retention time: 32.2 min; 35.4 min (major), 91% ee, $[a]_{25}^{25}$: 7.714 (c 0.245, CHCl$_3$).
Methyl 7-chloro-4-(phenylethynyl)-3,4-dihydrobenzo[e][1,2,3]oxathiazine-4-carboxylate 2,2-dioxide (5b), 30.5 mg, 81% yield, yellow oil; 1H NMR (400 MHz, CDCl3): δ 7.81-7.78 (d, J = 8.8 Hz, 1H), 7.48-7.44 (m, 2H), 7.40-7.26 (m, 4H), 7.11-7.09 (d, J = 2.0 Hz, 1H), 3.97 (s, 1H); 13C NMR (100 MHz, CDCl3): δ 167.3, 149.9, 136.7, 132.1, 130.6, 129.6, 128.4, 126.3, 120.8, 119.6, 117.7, 86.9, 83.6, 61.9, 55.4; HRMS (ESI): calcd for C17H13NO5SCl [M+H]+ 378.0203, found 378.0217.

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 90/10; flow = 0.5 mL/min; Retention time: 30.1 min; 35.5 min (major), 77% ee, [α]25: 3.026 (c 0.33, CHCl3).

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

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 90/10; flow = 0.5 mL/min; Retention time: 27.6 min; 31.6 min (major), 37% ee, \([\alpha]\)\textsuperscript{25} = -0.110 (c 0.73, CHCl\textsubscript{3}).
(5d), 19.3 mg, 52% yield, yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.89-7.86 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.48-7.45 (m, 2H), 7.43-7.38 (m, 1H), 7.36-7.28 (m, 4H), 7.08-7.05 (dd, \(J = 8.0, 1.2\) Hz, 1H), 4.40-4.24 (m, 2H), 1.82-1.73 (m, 2H), 1.02-0.98 (t, \(J = 7.2\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 167.5, 150.0, 132.2, 131.3, 129.7, 129.6, 128.6, 125.9, 121.4, 119.7, 119.5, 86.3, 84.8, 70.5, 62.4, 22.0, 10.5; HRMS (ESI): calcld for C\(_{19}\)H\(_{18}\)NO\(_5\)S [M+H]\(^+\) 372.0906, found 372.0920.

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 90/10; flow = 0.5 mL/min; Retention time: 26.9 min; 30.0 min (major), 56% ee, \([\alpha]\)\(^{25}\): 1.135 (c 0.88, CHCl\(_3\)).
8. General Procedure for the derivatives of 3aa and 5a.

Cu(OAc)$_2$ (72 mg, 10 mol %), 5Å MS (2.4 g) and L15 (0.272 g, 15 mol%) were stirred in toluene (40.0 mL) at 90 °C for 1 h. Cyclic ketimines 1a (0.956 g, 4.0 mmol) and LiOAc (0.264 g, 1.0 eq.) were added. After 15 min, ethynylbenzene 2a (0.66 mL, 1.5 eq.) was added and stirred at 90 °C for 3 days. After completion, the reaction mixture was cooled down to room temperature and then quenched with 10% aqueous HCl solution. The aqueous layer was extracted further with DCM three times; then the combined organic layer was dried over Na$_2$SO$_4$. After concentration in vacuo, the residue was finally purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:5 to 1:3) to give the product 3aa as a yellow solid (1.159 g, 85%).

We tried to remove SO$_2$ group according to ref. 4, but no desired product was detected.

To a solution of the alkenylation product 5a (34.3 mg, 0.1 mmol) in THF (1.0 mL) at room temperature was added LiAlH$_4$ (1.0 N in THF, 1.0 mL, 1.0 mmol) dropwise over 2 mins and stirred at room temperature for 3 hours. The reaction was quenched carefully with EtOAc (2.0 mL) followed by EtOH (2.0 mL). The solution was concentrated in vacuo. The residue was purified by column chromatography (PE/EA = 2:1) to give the product 6.

*E-(R)-2-(2-amino-1-hydroxy-4-phenylbut-3-en-2-yl)phenol (6)*, 23.9 mg, 94% yield, yellow oil; $^1$H NMR (400 MHz CDCl$_3$): δ 7.44-7.38 (m, 2H), 7.36-7.30 (m, 2H), 7.29-7.24 (m, 1H), 7.22-7.16 (m, 1H), 7.11 (dd, $J = 8.0$, 1.6 Hz, 1H), 6.88 (dd, $J = 8.0$, 1.2 Hz, 1H), 6.80 (td, $J = 7.6$, 1.2 Hz, 1H), 6.58 (d, $J = 16.4$ Hz, 1H), 6.43 (d, $J = 16.4$ Hz, 1H), 4.10 (d, $J = 11.2$ Hz, 1H), 3.79 (d, $J = 11.2$ Hz, 1H); $^{13}$C NMR (100 MHz CDCl$_3$) δ 158.9, 136.4, 131.8, 130.5, 129.8, 128.9, 128.3, 127.5, 126.8, 124.9, 119.2, 118.4, 68.0, 62.3; HRMS (ESI) calcd for C$_{16}$H$_{18}$NO$_2$ [M+H]$^+$ 256.1338, found 256.1333.

HPLC: Daicel Chiralcel AY column (250 mm); detected at 210 nm; hexane/i-propanol = 90/10; flow = 0.5 mL/min; Retention time: 39.1 min; 45.2 min (major), 90% ee, $[\alpha]^{25}$: -8.929 (c 1.70, CHCl$_3$).
To a solution of 3aa (34.1 mg, 0.1 mmol) in MeOH (1.0 mL) was added Pd/C (10 wt% of Pd, 16.0 mg), the mixture was stirred at room temperature for 3 hours and then filtrated off to removed the catalyst. After concentration under reduced pressure, the residue obtained was purified by column chromatography (PE:EA = 4:1) to give 7.

(R)-ethyl 3-phenethyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (7), 34.2 mg, 99% yield, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.79-7.76 (d, \(J = 7.6\) Hz, 1H), 7.73-7.69 (d, \(J = 8.0\) Hz, 1H), 7.67-7.56 (m, 2H), 7.29-7.23 (m, 2H), 7.21-7.12 (m, 3H), 5.87 (br, 1H), 4.30-4.21 (m,
2H), 2.80-2.61 (m, 2H), 2.58-2.48 (m, 1H), 2.36-2.26 (m, 1H), 1.37-1.31 (t, J = 7.2 Hz, 3H).\(^{[1b]}\)

HPLC: Daicel Chiralcel AD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 80/20; flow = 1.0 mL/min; Retention time: 21.1 min (major); 27.5 min, 92% ee, \([\alpha]_2^25\): 12.689 (c 0.85, CHCl₃).

To a solution of 3aa (34.1 mg, 0.1 mmol) in EtOH (1.0 mL) was added Lindlar catalyst (5 wt% of Pd, 78.0 mg), the mixture was stirred at room temperature for 2 hours and then filtrated off.
to removed the catalyst. After concentration under reduced pressure, the residue obtained was purified by column chromatography (PE:EA = 4:1) to give 8.

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

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


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