Supporting Information

Facile Synthesis of Chiral ε-Sultams via Organocatalytic Aza-Friedel-Crafts Reaction

Table of Contents

1. General and Materials.................................................................S1
2. Organocatalytic Aza-Friedel-Crafts Reaction..............................S1-5
3. Determination of Absolute Configuration................................S6
4. References....................................................................................S6
5. Copies of NMR and HPLC.............................................................S7-54
1. General and Materials

**General:** All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. $^1$H NMR, $^{13}$C NMR spectra were recorded at room temperature in CDCl$_3$ and DMSO on 400 MHz instrument with TMS as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis.

**Materials:** The seven-membered cyclic N-sulfonylimines 1 could be synthesized according to the known literature procedures.$^1$ A variety of naphthols were synthesized according to the known literature procedures.$^2$

2. Organocatalytic Aza-Friedel-Crafts Reaction

A reaction mixture of seven-membered cyclic N-sulfonylimines 1 (0.20 mmol), naphthols or phenols 2 (0.30 mmol) and organocatalyst (0.02 mmol, 10 mol%) in chloroform (12 mL) was stirred at 0 °C for 4-72 h. Then the solvent was removed under the reduced pressure. Flash chromatography on silica gel using hexanes/ethyl acetate as the eluent gave the chiral products 3.

(RS)-(-)-7-(1-Hydroxynaphthalen-2-yl)-6,7-dihydrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3aa): 74 mg, 95% yield, yellow solid, mp 169-170 °C, new compound, $R_f$ = 0.60 (hexanes/ethyl acetate 3/1), 89% ee, $[\alpha]_{20}^D = -137.90$ (c 1.72, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.38-8.28 (m, 1H), 8.13 (brs, 1H), 8.04 (d, $J = 7.7$ Hz, 1H), 7.76 ($J = 7.2$ Hz, 1H), 7.73-7.66 (m, 1H), 7.65-7.55 (m, 2H), 7.52-7.44 (m, 2H), 7.42-7.36 (m, 2H), 7.24-7.18 (m, 2H), 6.97 (d, $J = 7.8$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 5.61 (d, $J = 2.7$ Hz, 1H), 5.35 (d, $J = 2.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.3, 140.0, 139.2, 135.6, 134.6, 134.1, 132.9, 130.4, 129.8, 129.5, 129.4, 129.3, 129.0, 127.5, 127.2, 126.6, 126.5, 125.8, 125.5, 122.5, 120.3, 114.4, 61.2. HPLC: Chiracel AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 15.0 min and 17.6 min (major). HRMS Calculated for C$_{23}$H$_{18}$NO$_3$S [M+H]$^+$ 388.1002, found: 388.1002.

(RS)-(-)-7-(1-Hydroxy-4-methoxynaphthalen-2-yl)-6,7-dihydrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3ab): 78 mg, 93% yield, brown solid, mp 163-164 °C, new compound, $R_f$ = 0.60 (hexanes/ethyl acetate 3/1), 92% ee, $[\alpha]_{20}^D = -129.99$ (c 0.68, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.32 (d, $J = 6.2$ Hz, 1H), 8.24-8.11 (m, 2H), 7.91-7.83 (m, 1H), 7.77-7.67 (m, 2H), 7.62-7.54 (m, 2H), 7.53-7.46 (m, 2H), 7.38-7.28 (m, 2H), 7.11 (d, $J = 7.5$ Hz, 1H), 6.26 (brs, 1H), 5.72 (s, 1H), 5.37 (s, 1H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 145.4, 140.0, 139.2, 135.8, 134.0, 133.0, 130.4, 129.8, 129.5, 129.5, 129.3, 128.9, 126.6,
126.4, 126.3, 126.3, 122.1, 121.7, 104.0, 61.1, 55.7. HPLC: Chiracel AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 14.5 min and 20.5 min (major). HRMS Calculated for C_{25}H_{22}NO_{4}S [M+H]⁺ 432.1264, found: 432.1262.

(-)-7-(4-Ethoxy-1-hydroxynaphthalen-2-yl)-6,7-dihyrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3ac): 82 mg, 95% yield, yellow solid, mp 163-164 °C, new compound, R_f = 0.70 (hexanes/ethyl acetate 3/1), 90% ee, [α]_{D}^{20} = -113.59 (ε 5.00, CHCl3). ^1H NMR (400 MHz, CDCl3) δ 8.18 (d, J = 6.9 Hz, 1H), 8.14-8.08 (m, 1H), 8.06-7.95 (m, 1H), 7.79-7.70 (m, 1H), 7.63-7.55 (m, 2H), 7.47-7.40 (m, 2H), 7.39-7.31 (m, 2H), 7.27-7.12 (m, 2H), 6.96 (d, J = 7.8 Hz, 1H), 6.11 (brs, 1H), 5.66 (s, 1H), 5.19 (s, 1H), 3.86 (q, J = 6.7 Hz, 2H), 1.33 (t, J = 6.9 Hz, 3H). ^13C NMR (100 MHz, CDCl3) δ 148.7, 145.4, 140.0, 139.2, 135.9, 134.0, 133.0, 129.8, 129.5, 129.2, 128.9, 126.6, 124.5, 122.1, 120.9, 105.0, 64.1, 61.0, 14.8. HPLC: Chiracel AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 12.4 min and 15.9 min (major). HRMS Calculated for C_{25}H_{22}NO_{4}S [M+H]⁺ 432.1264, found: 432.1262.

(-)-7-(1-Hydroxy-4-isopropoxynaphthalen-2-yl)-6,7-dihyrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3ad): 87 mg, 98% yield, yellow solid, mp 157-158 °C, new compound, R_f = 0.65 (hexanes/ethyl acetate 3/1), 92% ee, [α]_{D}^{20} = -111.59 (ε 0.50, CHCl3). ^1H NMR (400 MHz, CDCl3) δ 8.19-8.15 (m, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.72-7.65 (m, 1H), 7.61-7.48 (m, 2H), 7.45-7.27 (m, 4H), 7.26-6.98 (m, 2H), 6.89 (d, J = 7.8 Hz, 1H), 6.13 (brs, 1H), 5.80 (s, 1H), 5.11 (s, 1H), 4.42-4.15 (m, 1H), 1.18 (dd, J = 11.5, 6.1 Hz, 6H). ^13C NMR (100 MHz, CDCl3) δ 147.4, 145.6, 140.0, 139.2, 135.9, 134.0, 130.4, 129.7, 129.5, 129.3, 128.9, 127.7, 126.5, 126.4, 126.2, 122.2, 122.0, 108.1, 71.7, 60.9, 22.2, 22.2. HPLC: Chiracel OD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 90/10, flow = 0.7 mL/min, retention time 26.6 min and 32.2 min (major). HRMS Calculated for C_{26}H_{24}NO_{4}S [M+H]⁺ 446.1421, found: 446.1424.

(-)-7-(4-Cyclohexyloxy-1-hydroxynaphthalen-2-yl)-6,7-dihyrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3ae): 87 mg, 90% yield, yellow solid, mp 160-161 °C, new compound, R_f = 0.50 (hexanes/ethyl acetate 3/1), 92% ee, [α]_{D}^{20} = -105.59 (ε 0.50, CHCl3). ^1H NMR (400 MHz, CDCl3) δ 8.32 (d, J = 8.0 Hz, 1H), 8.28-8.22 (m, 1H), 8.17-8.12 (m, 1H), 7.91-7.85 (m, 1H), 7.78-7.66 (m, 2H), 7.62-7.44 (m, 4H), 7.37-7.27 (m, 2H), 7.12 (d, J = 7.8 Hz, 1H), 6.37 (brs, 1H), 5.74 (s, 1H), 5.37 (s, 1H), 4.82-4.19 (m, 1H), 1.98-1.74 (m, 2H), 1.67-1.49 (m, 2H), 1.39-1.31 (m, 2H). ^13C NMR (100 MHz, CDCl3) δ 147.2, 145.7, 140.0, 139.2, 135.9, 134.0, 133.0, 129.7, 129.6, 129.5, 129.3, 128.9, 127.9, 126.6, 126.5, 126.4, 126.2, 122.3, 122.1, 108.2, 61.1, 31.8, 31.8, 25.6, 23.7. HPLC: Chiracel AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 14.6 min and 27.2 min (major). HRMS Calculated for C_{29}H_{28}NO_{4}S [M+H]⁺ 486.1734, found: 486.1737.

(-)-7-(4-Butoxy-1-hydroxynaphthalen-2-yl)-6,7-dihyrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3af): 87 mg, 95% yield, yellow solid, mp 128-129 °C, new compound, R_f = 0.80 (hexanes/ethyl acetate 3/1), 91% ee, [α]_{D}^{20} = -99.24 (ε 0.40, CHCl3). ^1H NMR (400 MHz, CDCl3) δ 8.30 (d, J = 7.2 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.90-7.82 (m, 1H), 7.81-7.60
(m, 3H), 7.59-7.43 (m, 4H), 7.34-7.29 (m, 1H), 7.08 (d, J = 7.6 Hz, 1H),
6.20 (brs, 1H), 5.85 (s, 1H), 5.30 (s, 1H), 3.98-3.83 (m, 2H), 1.88-1.76 (m,
2H), 1.60-1.48 (m, 2H), 0.99 (t, J = 7.4 Hz, 1H).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25-8.16 (m, 1H), 7.87 (d, $J$ = 7.4 Hz, 1H),
7.67-7.61 (m, 2H), 7.55-7.36 (m, 5H), 7.31-7.25 (m, 2H), 7.15-7.11 (m, 1H),
6.88 (d, $J$ = 7.8 Hz, 1H), 6.63 (brs, 1H), 5.81 (s, 1H), 5.17 (d, $J$ = 2.7 Hz, 1H),
2.15 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.9, 150.3, 140.0, 139.6, 139.2, 135.7, 134.1, 132.5, 130.3, 129.9, 129.5, 129.4, 129.3, 128.9, 127.7, 127.6, 126.6, 126.3, 126.3, 123.0, 120.9, 118.4, 113.6, 60.8, 20.8. HPLC: Chiracel AD-H column, 254
nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 11.4 min and 14.6 min
(major). HRMS Calculated for C$_{25}$H$_{20}$NO$_5$S [M+H]$^+$ 446.1057, found: 446.1042.

(-)-3-(5,5-Dioxido-6,7-dihydropyrido[4,3-d]pyrimidin-7-yl)acetylacetate (3ag): 87 mg, 98% yield, white solid, mp 175-176 °C, new compound, R$_f$ = 0.50
(hexanes/ethyl acetate 3/1), 86% ee, $[\alpha]^20_D$ = -103.39 (c 0.50, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$ = 8.2 Hz, 1H), 8.32 (brs, 1H), 8.18 (d, $J$
= 8.2 Hz, 1H), 7.89-7.82 (m, 1H), 7.74-7.59 (m, 4H), 7.53-7.43 (m, 2H), 7.36-7.29 (m, 1H),
7.08-7.00 (m, 2H), 5.75 (d, $J$ = 2.9 Hz, 1H), 5.37 (d, $J$ = 3.0 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.4, 140.0, 139.0, 135.5, 134.2, 132.4, 131.5, 130.4, 129.9, 129.5, 129.4, 129.0, 127.7, 127.6, 126.6, 126.3, 126.3, 123.0, 120.9, 118.4, 113.6, 60.8, 20.8. HPLC: Chiracel AD-H column, 254
nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 10.2 min and 12.6 min
(major). HRMS Calculated for C$_{25}$H$_{20}$NO$_5$S [M+H]$^+$ 446.1057, found: 446.1042.

(-)-7-(4-Cloro-1-hydroxynaphthalen-2-yl)-6,7-dihydropyrido[4,3-d]pyrimidin-7-
odioxide (3ah): 80 mg, 95% yield, yellow solid, mp 248-249 °C, new compound, R$_f$ = 0.80
(hexanes/ethyl acetate 3/1), 78% ee, $[\alpha]^20_D$ = -102.78 (c 1.58, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (d, $J$ = 8.1 Hz, 1H), 8.37 (brs, 1H),
8.19-8.10 (m, 2H), 7.90-7.84 (m, 1H), 7.74-7.59 (m, 4H), 7.53-7.43 (m, 2H), 7.36-7.29 (m, 1H),
7.06 (d, $J$ = 7.8 Hz, 1H), 5.73 (d, $J$ = 2.8 Hz, 1H), 5.40 (d, J = 3.0 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.3, 140.0, 139.0, 135.5, 134.2, 132.4, 131.5, 130.4, 129.9, 129.5, 129.4, 129.3, 128.2, 126.7, 126.5, 126.2, 124.1, 123.1, 123.0, 114.6, 60.7. HPLC: Chiracel AD-H column, 254
nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 10.4 min and 12.3 min
(major). HRMS Calculated for C$_{23}$H$_{17}$ClNO$_3$S [M+H]$^+$ 422.0609, found: 422.0609.

(-)-7-(4-Bromo-1-hydroxynaphthalen-2-yl)-6,7-dihydropyrido[4,3-d]pyrimidin-7-
odioxide (3ai): 91 mg, 98% yield, yellow solid, mp 247-248 °C, new compound, R$_f$ = 0.80
(hexanes/ethyl acetate 3/1), 74% ee, $[\alpha]^20_D$ = -85.73 (c 1.62, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.45 (d, $J$ = 8.2 Hz, 1H), 8.37 (brs, 1H),
8.19-8.10 (m, 2H), 7.90-7.84 (m, 1H), 7.74-7.59 (m, 4H), 7.53-7.43 (m, 2H), 7.36-7.29 (m, 1H),
7.06 (d, $J$ = 7.8 Hz, 1H), 5.73 (d, $J$ = 2.8 Hz, 1H), 5.40 (d, J = 3.0 Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.3, 140.0, 139.1, 135.6, 134.3, 132.7, 132.2, 130.5, 130.0, 129.7, 129.6, 129.4, 129.3, 129.1, 128.9, 128.6, 126.8, 126.7, 126.6, 126.3, 123.1, 113.1, 60.9. HPLC: Chiracel AD-H column, 254
nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 10.4 min and 12.3 min
(major). HRMS Calculated for C$_{23}$H$_{17}$BrNO$_3$S [M+H]$^+$ 466.0107, found: 466.0106.

(-)-7-(1-Hydroxy-3-methoxynaphthalen-2-yl)-6,7-dihydropyrido[4,3-d]pyrimidin-7-
odioxide (3aj): 80 mg, 96% yield, yellow solid, mp 168-169 °C, new compound, R$_f$ = 0.55
(hexanes/ethyl acetate 3/1), 89% ee, \([\alpha]^{20}_D = -106.92\) (c 0.52, CHCl3). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 8.82 (s, 1H), 8.33 (d, \(J = 8.4\) Hz, 1H), 8.12 (dd, \(J = 7.8, 1.1\) Hz, 1H), 7.89-7.82 (m, 1H), 7.75-7.64 (m, 3H), 7.54-7.45 (m, 3H), 7.44-7.38 (m, 1H), 7.35-7.29 (m, 1H), 7.12 (d, \(J = 7.8\) Hz, 1H), 6.68 (brs, 1H), 6.03 (d, \(J = 3.1\) Hz, 1H), 5.55 (d, \(J = 3.1\) Hz, 1H), 3.66 (s, 3H). \(^1\)C NMR (100 MHz, CDCl3) \(\delta\) 154.5, 154.2, 140.3, 139.6, 135.6, 134.8, 134.2, 132.3, 130.3, 129.8, 129.4, 129.3, 129.1, 128.8, 127.8, 126.7, 126.2, 123.4, 122.7, 121.3, 106.8, 97.8, 55.6, 53.9. HPLC: Chiracel AD-H column, 254 nm, 30 °C, \(n\)-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 15.8 min and 18.3 min (major). HRMS Calculated for C24H20NO4S \([M+H]^+\) 418.1108, found: 418.1108.

(-)-7-(1-Hydroxy-5-methoxynaphthalen-2-yl)-6,7-dihydrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3ak): 81 mg, 97% yield, yellow solid, mp 276-277 °C, new compound, \(R_f = 0.50\) (hexanes/ethyl acetate 5/1), 89% ee, \([\alpha]^{20}_D = -78.46\) (c 0.52, EtOAc). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 8.12-7.98 (m, 2H), 7.87 (d, \(J = 8.4\) Hz, 1H), 7.78-7.72 (m, 1H), 7.67-7.52 (m, 3H), 7.42-7.34 (m, 3H), 7.29-7.08 (m, 1H), 6.95 (d, \(J = 7.8\) Hz, 1H), 6.87-6.78 (m, 2H), 5.62 (s, 1H), 5.34 (s, 1H), 3.91 (s, 3H). \(^1\)C NMR (100 MHz, CDCl3) \(\delta\) 155.2, 152.1, 140.0, 139.3, 135.8, 134.1, 132.8, 130.4, 129.8, 129.5, 129.3, 128.9, 126.9, 126.6, 125.9, 125.6, 114.9, 114.6, 114.5, 105.2, 61.3, 55.6. HPLC: Chiracel OD-H column, 254 nm, 30 °C, \(n\)-Hexane/i-PrOH = 70/30, flow = 1.0 mL/min, retention time 10.9 min (major) and 15.5 min. HRMS Calculated for C24H20NO4S \([M+H]^+\) 418.1108, found: 418.1104.

(-)-7-(2-Hydroxynaphthalen-1-yl)-6,7-dihydrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3al): 74 mg, 95% yield, yellow solid, mp 150-151 °C, new compound, \(R_f = 0.50\) (hexanes/ethyl acetate 3/1), 82% ee, \([\alpha]^{20}_D = -111.70\) (c 0.76, CHCl3). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 8.64 (brs, 1H), 8.07 (d, \(J = 7.6\) Hz, 1H), 7.91-7.83 (m, 1H), 7.81-7.69 (m, 2H), 7.68-7.61 (m, 2H), 7.48-7.39 (m, 2H), 7.23-7.15 (m, 4H), 7.10-6.98 (m, 2H), 6.06 (s, 1H), 5.58 (s, 1H). \(^1\)C NMR (100 MHz, CDCl3) \(\delta\) 155.5, 140.1, 139.2, 135.5, 134.4, 132.2, 131.4, 131.3, 130.2, 130.0, 129.7, 129.3, 129.2, 129.1, 129.0, 128.9, 127.2, 126.9, 123.4, 120.6, 119.9, 111.4, 56.3. HPLC: Chiracel AD-H column, 254 nm, 30 °C, \(n\)-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 14.8 min (major) and 20.4 min. HRMS Calculated for C23H18NO3S \([M+H]^+\) 388.1002, found: 388.1000.

(-)-7-(6-Hydroxybenzo[d][1,3]dioxol-5-yl)-6,7-dihydrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (3am): 72 mg, 94% yield, yellow solid, mp 167-168 °C, new compound, \(R_f = 0.45\) (hexanes/ethyl acetate 2/1), 63% ee, \([\alpha]^{20}_D = -46.87\) (c 0.64, MeOH). \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.16 (s, 1H), 8.25 (s, 1H), 7.93 (d, \(J = 7.6\) Hz, 1H), 7.88-7.82 (m, 1H), 7.78-7.64 (m, 2H), 7.43-7.37 (m, 2H), 7.33-7.23 (m, 1H), 7.03 (s, 1H), 6.76 (d, \(J = 7.6\) Hz, 1H), 6.42 (s, 1H), 5.98 (d, \(J = 2.4\) Hz, 2H), 5.35 (s, 1H). \(^1\)C NMR (100 MHz, DMSO) \(\delta\) 149.3, 147.3, 140.4, 140.3, 138.8, 138.1, 137.7, 133.8, 130.6, 129.3, 129.3, 128.9, 128.4, 125.5, 117.2, 108.6, 101.4, 98.1, 53.8. HPLC: Chiracel AD-H column, 254 nm, 30 °C, \(n\)-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 28.1 min and 34.8 min (major). HRMS Calculated for C20H16NO3S \([M+H]^+\) 382.0744, found: 382.0740.

S4
(-)-9-Chloro-7-(1-hydroxynaphthalen-2-yl)-6,7-dihy do ribenzo[df][1,2]thiazepine 5,5-dioxide (3ba): 80 mg, 95% yield, white solid, mp 237-238 °C, new compound, R<sub>t</sub> = 0.75 (hexanes/ethyl acetate 3/1), 86% ee, [α]<sup>20</sup> = -91.38 (c 0.36, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.46-8.35 (m, 1H), 8.13 (d, <i>J</i> = 7.4 Hz, 1H), 8.05 (brs, 1H), 7.91-7.78 (m, 2H), 7.74-7.67 (m, 2H), 7.64-7.56 (m, 2H), 7.50-7.45 (m, 1H), 7.44-7.35 (m, 2H), 7.02 (d, <i>J</i> = 1.8 Hz, 1H), 6.99-6.93 (m, 1H), 5.70 (d, <i>J</i> = 2.5 Hz, 1H), 5.40 (d, <i>J</i> = 2.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.1, 138.5, 138.2, 135.7, 135.6, 134.8, 134.8, 134.2, 130.5, 130.3, 130.1, 129.6, 129.3, 127.5, 127.4, 126.7, 126.2, 125.9, 125.5, 122.5, 120.6, 113.6, 60.8. HPLC: Chiracel AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 12.1 min and 21.0 min (major). HRMS Calculated for C<sub>23</sub>H<sub>17</sub>ClNO<sub>3</sub>S [M+H]<sup>+</sup> 422.0612, found: 422.0615.

(-)-7-(1-Hydroxynaphthalen-2-yl)-9-methoxy-6,7-dihy drodibenzo[df][1,2]thiazepine 5,5-dioxide (3ca): 82 mg, 98% yield, white solid, mp 276-277 °C, new compound, R<sub>f</sub> = 0.70 (hexanes/ethyl acetate 3/1), 90% ee, [α]<sup>20</sup> = -65.19 (c 0.52, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.26 (dd, <i>J</i> = 6.1, 3.3 Hz, 1H), 8.09 (brs, 1H), 7.97 (d, <i>J</i> = 7.7 Hz, 1H), 7.73-7.62 (m, 2H), 7.59-7.47 (m, 2H), 7.46-7.38 (m, 2H), 7.27-7.17 (m, 2H), 6.90-6.75 (m, 2H), 6.49 (d, <i>J</i> = 2.5 Hz, 1H), 5.60 (d, <i>J</i> = 2.8 Hz, 1H), 5.27 (d, <i>J</i> = 2.8 Hz, 1H), 3.53 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.5, 152.3, 139.2, 135.5, 134.7, 134.3, 134.1, 132.2, 130.6, 130.3, 128.4, 127.4, 127.2, 126.7, 126.4, 125.8, 125.6, 122.6, 120.3, 116.4, 114.1, 61.3, 55.2. HPLC: Chiracel AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 18.2 min and 36.2 min (major). HRMS Calculated for C<sub>24</sub>H<sub>20</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 418.1108, found: 418.1105.

(+)-10-Chloro-7-(1-hydroxynaphthalen-2-yl)-6,7-dihy drodibenzo[df][1,2]thiazepine 5,5-dioxide (3da): 76 mg, 90% yield, pink solid, mp 267-268 °C, new compound, R<sub>t</sub> = 0.70 (hexanes/ethyl acetate 3/1), 84% ee, [α]<sup>20</sup> = 46.09 (c 0.64, DMSO). <sup>1</sup>H NMR (400 MHz, DMSO) δ 9.44 (s, 1H), 8.52 (s, 1H), 8.10 (d, <i>J</i> = 8.2 Hz, 1H), 7.98 (d, <i>J</i> = 7.7 Hz, 1H), 7.84-7.81 (m, 3H), 7.60 (d, <i>J</i> = 8.5 Hz, 1H), 7.56-7.43 (m, 3H), 7.31 (dd, <i>J</i> = 8.4, 2.2 Hz, 1H), 6.64 (d, <i>J</i> = 8.2 Hz, 1H), 5.70 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO) δ 149.7, 142.7, 138.2, 137.3, 136.9, 134.3, 133.9, 133.5, 130.8, 130.5, 130.0, 128.8, 128.7, 128.3, 126.7, 126.7, 125.7, 125.5, 122.4, 120.5, 120.0, 53.8. HPLC: Chiracel AD-H column, 254 nm, 30 °C, n-Hexane/i-PrOH = 80/20, flow = 1.0 mL/min, retention time 14.4 min and 21.7 min (major). HRMS Calculated for C<sub>23</sub>H<sub>17</sub>ClNO<sub>3</sub>S [M+H]<sup>+</sup> 422.0612, found: 422.0613.
3. Determination of Absolute Configuration

To determine the absolute configuration of (-)-7-(1-hydroxynaphthalen-2-yl)-6,7-dihydrodibenzo[d,f][1,2]thiazepine 5,5-dioxide (-)-3aa (89% ee), firstly, (-)-3aa was upgraded to >99% ee by recrystallization with n-hexane/ethyl acetate. Then, n-hexane was added into the solution of (-)-3aa (>99% ee) in dichloromethane, then the solution was slowly evaporated and single crystal of (-)-3aa was obtained after 2 days. The crystal was grown from the solution, which is suitable for X-ray diffraction analysis. The structure in Figure S1 showed that the absolute configuration of (-)-3aa is R [CCDC 1892454] contains the structure and supplementary crystallographic data for (R)-(−)-3aa. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

![Figure S1. X-ray Crystallographic Analysis of Sultam (R)-(−)-3aa](image)

4. References


5. Copy of NMR and HPLC

1H NMR ZZ-3-39 in CDCl3

3aa 1H NMR (400 MHz, CDCl₃)
$^{13}$C NMR ZZ-3-39 IN CDCl$_3$

3aa $^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR ZZ-3.54 in CDCl₃

3ab ¹H NMR (400 MHz, CDCl₃)
$\text{S10}$

$13C\text{ NMR ZZ-3-54 in CDCl}_3$

$3ab\ 13C\text{ NMR (100 MHz, CDCl}_3)$
$^1$H NMR ZZ-3-73 in CDCl$_3$
$^{13}$C NMR ZZ-3-73 in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)

S12
1H NMR ZZ-3-75 in CDCl₃

3ad 1H NMR (400 MHz, CDCl₃)
$^{13}$C NMR ZZ-3-75 in CDCl$_3$

3ad $^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR ZZ-3-82 in CDCl3

3ae 1H NMR (400 MHz, CDCl3)
$^{13}$C NMR ZZ-3-B2 in CDCl$_3$

3ae $^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR ZZ-3-83 in CDCl₃

3af ¹H NMR (400 MHz, CDCl₃)
$^{13}$C NMR of 3af in CDCl$_3$
$^{13}$C NMR ZZ-3-89 in CDCl$_3$
1H NMR ZZ-3-53 in CDCl3

3ah 1H NMR (400 MHz, CDCl3)
$^{13}$C NMR ZZ-3-53 in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR ZZ-3-65A in CDCl$_3$

$^{1}H$ NMR (400 MHz, CDCl$_3$)

![Chemical Structure](image)

0.83, 1.05, 1.20, 1.45, 1.65, 2.10, 2.54, 2.76, 4.08, 4.16, 7.00, 7.10, 7.20, 7.30, 7.40, 7.50, 8.50, 8.60, 9.50 ppm
$^{13}$C NMR ZZ-3-65A in CDCl$_3$
$^{1}$H NMR ZZ-3-98 in CDCl$_3$
$^{13}$C NMR ZZ-3-98 in CDCl$_3$
$^1$H NMR ZZ-3.95 in CDCl$_3$

3ak $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR ZZ-3-95 in CDC$_3$

3ak $^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR Z2-4.34 in CDCl3

3a1 \textsuperscript{1}H NMR (400 MHz, CDCl3)
$^{13}$C NMR ZZ-4-34 in CDCl$_3$

3a$\text{I}^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{1H NMR ZZ-4.35 in DMSO}$

$\text{3am } ^1\text{H NMR (400 MHz, DMSO)}$
$^{13}$C NMR ZZ-4-35 in DMSO

3am $^{13}$C NMR (100 MHz, DMSO)
1H NMR ZZ-3-88 in CDCl₃

3ba ¹H NMR (400 MHz, CHCl₃)
$^{13}$C NMR ZZ-3-88 in CDCl$_3$
$^1$H NMR ZZ-3-69 in CDCl$_3$

3ca $^1$H NMR (400 MHz, CHCl$_3$)
$^{13}$C NMR ZZ-3-69 in CDCl$_3$

$^{13}$C NMR (100 MHz, CHCl$_3$)
1H NMR ZZ-3-85 in DMSO

3da $^1$H NMR (400 MHz, DMSO)
$^{13}$C NMR ZZ-3-85 in DMSO

3da $^{13}$C NMR (100 MHz, DMSO)
Data File (C:\\CHEM321\\DATA120D-18VD000509.D)
Sample Name: vz-3-02

<table>
<thead>
<tr>
<th>Acq. Date &amp; Time</th>
<th>Location</th>
<th>Instrument</th>
<th>Acq. Method</th>
<th>Analysis Method</th>
<th>Sample Info</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/2/2008 11:20:20 PM</td>
<td>-</td>
<td>Instrument 1</td>
<td>Method DEF_111.M</td>
<td>Method DEF_111.M</td>
<td>AD-M, Benzene/1.0mL, 80/20, 1.0 mL/min, 30 °C, 254 nm</td>
</tr>
</tbody>
</table>

Sample 1

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Signal</th>
<th>Dilution</th>
<th>Multiplier</th>
<th>Multiplier &amp; Dilution Factor with INITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal 1: VDI A, Wavelength=254 nm</td>
<td>1.0000</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Peak RetTime Type Width Area Height Area %
<table>
<thead>
<tr>
<th># (main)</th>
<th>(main)</th>
<th>(main)</th>
<th>(main)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 10.647 BR 0.2818 6056.18994 379.0226 20.5311</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 15.916 BS 0.4711 6966.44593 223.7477 50.4909</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Totals: 1.3804E6 606.36000

*** End of Report ***

Data File (C:\\CHEM321\\DATA120D-18VD000509.D)
Sample Name: vz-3-02

<table>
<thead>
<tr>
<th>Acq. Date &amp; Time</th>
<th>Location</th>
<th>Instrument</th>
<th>Acq. Method</th>
<th>Analysis Method</th>
<th>Sample Info</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/2/2008 11:20:20 PM</td>
<td>-</td>
<td>Instrument 1</td>
<td>Method DEF_111.M</td>
<td>Method DEF_111.M</td>
<td>AD-M, Benzene/1.0mL, 80/20, 1.0 mL/min, 30 °C, 254 nm</td>
</tr>
</tbody>
</table>

Sample 1

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Signal</th>
<th>Dilution</th>
<th>Multiplier</th>
<th>Multiplier &amp; Dilution Factor with INITS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal 1: VDI A, Wavelength=254 nm</td>
<td>1.0000</td>
<td>1.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Peak RetTime Type Width Area Height Area %
<table>
<thead>
<tr>
<th># (main)</th>
<th>(main)</th>
<th>(main)</th>
<th>(main)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 10.674 BS 0.2813 316.51801 17.45981 4.3502</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 15.672 BS 0.4063 7003.4455 220.70457 55.4408</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Totals: 79321.96385 246.25380

*** End of Report ***