Supporting Information for

**Synthesis of Chiral Benzofuran-derived β -amino ester derivatives
induced by *N*-tert-butanefulfinamide**

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1. General Information:

General: DMF was dried over CaH_2 . chiral imines **1** were prepared from *N*-tert-butanefulfonamide and salicylaldehydes under microwave irradiation in the presence KHSO_4 . Compounds were visualized on analytical thin layer chromatograms (TLC) by UV light (254 nm). ^1H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively) with TMS as an internal standard. Chemical shifts are given in ppm relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants *J* are reported in Hz. IR spectra (Film) were recorded on a FT-IR spectrometer in the range of 400–4000 cm^{-1} . MS spectra were measured using the ESI method of ionization.

2. Typical Procedure for Preparation of product 3a:

K_2CO_3 (278 mg, 1 mmol, 2 equiv.) and diethyl bromomalonate **2** (192 mg, 1.2 mmol, 1.2 equiv.) were added into a solution of (*R, E*)-*N*-(2-hydroxybenzylidene)-2-methylpropane-2-sulfonamide **1a** (225 mg, 1.0 mmol, 1.0 equiv.) in dry *N,N*-dimethylformamide (5 mL). The mixture was stirred at 70 °C until the complete consumption of the **1a**, as monitored by TLC. The solid was filtered and the filtrate was diluted with water, then extracted with ethyl acetate 3 times (15 mL), the organic phase was combined and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (EtOAc/hexanes, 1:5) to give pure **3a** (298.7 mg, 78 %).

3. Procedure for Preparation of product 5:

The substrate **3a** (0.2 mmol) was treated with HCl/MeOH (4M, 1 mL), and the mixture was stirred at r.t. until all the starting material has been consumed. The solvent was removed under reduced pressure, the residue was taken up in DCM (5 mL) and cooled to 0 °C. Et_3N (0.10 mL, 0.71 mmol), cat. DMAP and Ac_2O (0.045 mL, 0.47 mmol) were added successively. The mixture

was allowed to warm to r.t. and stirred overnight, quenched by water (10 mL), and extracted with ether (40 mL). The organic phase was washed with sat. aq. NaHCO₃, brine, dried (Na₂SO₄), filtered and concentrated. The residue was purified by silica gel flash column chromatography to afford **5**.

4. Analytical data of products **3a** – **3j**

Diethyl 3-((*R*)-*tert*-butylsulfinamido)-(*S*)-benzofuran-2,2(3H)-dicarboxylate (3a**).** White solid, m.p. 136-137 °C, $[\alpha]_D^{20} +82.0$ (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 7.58 (d, *J*=7.5 Hz, 1H), 7.27 (t, *J*=7.5 Hz, 1H), 7.03 (t, *J*=7.5 Hz, 1H), 6.96 (d, *J*=7.5 Hz, 1H), 5.85 (d, *J*=9.5 Hz, 1H), 4.42~4.13 (m, 4H), 3.62 (d, *J*=9.5 Hz, 1H), 1.31 (q, *J*=14.0, 7.0 Hz, 6H), 1.19 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz) δ : 116.6, 165.3, 157.6, 130.7, 126.5, 125.4, 123.0, 110.6, 92.2, 63.9, 62.9, 62.5, 56.2, 22.6, 14.0, 13.9. IR (KBr) ν /cm⁻¹: 3291, 2985, 2927, 1737, 1602, 1467, 1417, 1391, 1367, 1297, 1249, 1218, 1099, 1071, 1012, 857, 759. HRMS (ESI) calcd for C₁₈H₂₆NO₆S, 384.1481 (M+H)⁺; Found, 384.1482.

Diethyl-((*R*)-*tert*-butylsulfinamido)-5-(*S*)-fluorobenzofuran-2,2(3H)-dicarboxylate (3b**).** White solid, m.p. 120-121 °C, $[\alpha]_D^{20} +112.0$ (*c* 1.05, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 7.24 (dd, *J*=7.5, 2.5 Hz, 1H), 6.89 (td, *J*=7.5, 2.5 Hz, 1H), 6.81 (dd, *J*=7.5, 2.5 Hz, 1H), 5.74 (d, *J*=9.5 Hz, 1H), 4.35~4.06 (m, 4H), 3.57 (d, *J*=9.5 Hz, 1H), 1.24 (q, *J*=14.0, 7.0 Hz, 6H), 1.13 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz) δ : 166.4, 165.1, 159.5, 157.6, 153.4, 126.7, 117.6, 113.5, 111.3, 111.2, 92.8, 64.0, 63.0, 62.6, 56.3, 22.6, 14.0, 13.9. IR (KBr) ν /cm⁻¹: 3293, 2986, 2926, 1738, 1485, 1445, 1415, 1390, 1367, 1294, 1247, 1213, 1139, 1103, 1067, 867, 829, 774, 738. HRMS (ESI) calcd for C₁₈H₂₅FNO₆S, 402.1387 (M+H)⁺; Found, 402.1381.

Diethyl 5-chloro-3-((*R*)-*tert*-butylsulfonamido)-(*S*)-benzofuran-2,2(3H)-dicarboxylate (3c).

White solid, m.p. 120-121 °C, $[\alpha]_D^{20} +85.3$ (*c* 1.10, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 7.51 (s, 1H), 7.16 (d, *J*=8.0 Hz, 1H), 6.82 (d, *J*=8.0 Hz, 1H), 5.75 (d, *J*=10.0 Hz, 1H), 4.34~4.07 (m, 4H), 3.58 (d, *J*=10.0 Hz, 1H), 1.25 (q, *J*=15.0, 7.5 Hz, 6H), 1.15 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz) δ : 166.2, 165.0, 156.2, 130.8, 127.8, 127.2, 126.5, 111.7, 92.6, 63.8, 63.0, 62.7, 56.3, 22.6, 18.4, 14.0, 13.9. IR (KBr) ν/cm^{-1} : 3288, 2984, 2925, 2858, 2025, 1756, 1737, 1492, 1468, 1364, 1283, 1252, 1214, 1097, 1073, 822. HRMS (ESI) calcd for C₁₈H₂₅ClNO₆S, 418.1091 (M+H)⁺; Found, 418.1109.

Diethyl 5-bromo-3-((*R*)-*tert*-butylsulfonamido)-(*S*)-benzofuran-2,2(3H)-dicarboxylate (3d).

White solid, m.p. 105-106 °C, $[\alpha]_D^{20} +48.5$ (*c* 1.06, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 7.63 (d, *J*=1.5 Hz, 1H), 7.30 (dd, *J*=8.5, 1.5 Hz, 1H), 6.77 (d, *J*=8.5 Hz, 1H), 5.75 (d, *J*=9.5 Hz, 1H), 4.34~4.06 (m, 4H), 3.58 (d, *J*=9.5 Hz, 1H), 1.24 (dd, *J*=15.0, 7.5 Hz, 6H), 1.13 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ : 166.2, 165.0, 156.8, 133.7, 129.3, 127.7, 114.9, 112.3, 92.6, 63.7, 63.1, 62.7, 56.4, 29.7, 22.6, 14.0, 13.9. IR (KBr) ν/cm^{-1} : 3285, 2926, 2856, 1736, 1470, 1416, 1367, 1304, 1248, 1214, 1179, 1096, 1069, 823, 659. HRMS (ESI) calcd for C₁₈H₂₅BrNO₆S, 462.0586 (M+H)⁺; Found, 462.0588.

Diethyl 3-((*R*)-*tert*-butylsulfonamido)-5-methyl-(*S*)-benzofuran-2,2(3H)-dicarboxylate (3e).

White solid, m.p. 122-123 °C, $[\alpha]_D^{20} +118.0$ (*c* 0.975, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 7.36 (s, 1H), 7.06 (d, *J*=8.0 Hz, 1H), 6.84 (d, *J*=8.0 Hz, 1H), 5.81 (d, *J*=9.5 Hz, 1H), 4.41~4.11 (m, 4H), 3.60 (d, *J*=9.5 Hz, 1H), 2.30 (s, 3H), 1.33-1.28 (m, 6H), 1.19 (s, 9H). ¹³C NMR (CDCl₃, 125

MHz) δ : 166.7, 165.4, 155.6, 132.6, 131.3, 126.6, 125.3, 110.2, 92.4, 64.1, 62.8, 62.4, 56.2, 29.7, 22.6, 20.8, 14.0, 13.9. IR (KBr) ν/cm^{-1} : 3287, 2984, 2925, 2858, 2025, 1756, 1737, 1492, 1468, 1364, 1283, 1252, 1214, 1097, 1073, 822. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_6\text{S}$, 398.1637 ($\text{M}+\text{H}$)⁺; Found, 398.1637.

Diethyl 3-((*R*)-*tert*-butylsulfinamido)-5-hydroxy-(*S*)-benzofuran-2,2(3H)-dicarboxylate (3f).

White solid, m.p. 183-184 °C, $[\alpha]_{\text{D}}^{20} +80.3$ (c 1.07, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : 7.08 (d, $J=2.5$ Hz, 1H), 6.85~6.80 (m, 1H), 6.76~6.74 (m, 1H), 5.73 (d, $J=10.0$ Hz, 1H), 4.40 (m, 4H), 4.04 (d, $J=10.0$ Hz, 1H), 1.32~1.29 (m, 6H), 1.19 (s, 9H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 166.9, 165.3, 152.7, 150.7, 125.6, 118.0, 112.6, 111.2, 92.6, 64.6, 62.9, 62.4, 56.6, 29.7, 22.7, 14.1, 14.0. IR (KBr) ν/cm^{-1} : 3299, 2982, 2927, 2025, 1760, 1729, 1495, 1465, 1370, 1306, 1207, 1096, 1033, 817. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_7\text{S}$, 400.1430 ($\text{M}+\text{H}$)⁺; Found, 400.1432.

Diethyl 3-((*R*)-*t*-butylsulfinamido)-6-methoxy-(*S*)-benzofuran-2,2(3H)-dicarboxylate (3g).

White solid, m.p. 125-126 °C, $[\alpha]_{\text{D}}^{20} +135.0$ (c 1.03, CHCl_3). ^1H NMR (CDCl_3 , 500 MHz) δ : ^1H NMR (CDCl_3 , 500 MHz) δ : 7.44 (d, $J=8.5$ Hz, 1H), 6.57 (dd, $J=8.5$, 2.0 Hz, 1H), 6.51 (d, $J=2.0$ Hz, 1H), 5.78 (d, $J=9.5$ Hz, 1H), 4.41~4.12 (m, 4H), 3.77 (s, 3H), 3.52 (d, $J=9.5$, 1H), 1.32-1.29 (m, 6H), 1.18 (s, 9H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 166.5, 165.3, 162.2, 159.0, 126.9, 117.4, 109.3, 96.6, 93.2, 63.6, 62.9, 62.5, 56.2, 55.6, 22.6, 14.1, 14.0. IR (KBr) ν/cm^{-1} : 3135, 2985, 2025, 1749, 1625, 1599, 1501, 1459, 1369, 1330, 1291, 1253, 1214, 1192, 1152, 1127, 1096, 1054, 854. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_7\text{S}$, 414.1586 ($\text{M}+\text{H}$)⁺; Found, 414.1585.

Diethyl 3-((*R*)-*tert*-butylsulfinamido)-7-methoxy-(*S*)-benzofuran-2,2(3H)-dicarboxylate (3h).

White solid, m.p. 121-122 °C, $[\alpha]_D^{20} +159.0$ (*c* 1.06, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 7.17 (d, *J*=8.0 Hz, 1H), 6.97 (t, *J*=8.0 Hz, 1H), 6.85 (d, *J*=8.0 Hz, 1H), 5.88 (d, *J*=9.5 Hz, 1H), 4.41~4.12 (m, 4H), 3.89 (s, 3H), 3.60 (d, *J*=9.5 Hz, 1H), 1.30 (dd, *J*=13.0, 6.5 Hz, 6H), 1.19 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz) δ : 166.6, 165.1, 146.2, 144.6, 126.5, 123.8, 117.9, 113.3, 92.6, 64.5, 62.9, 62.5, 56.3, 56.0, 22.6, 14.1, 14.0. IR (KBr) ν/cm^{-1} : 3283, 2975, 2927, 2025, 1774, 1736, 1623, 1595, 1496, 1463, 1399, 1103, 1067, 867, 829, 774, 738. HRMS (ESI) calcd for C₁₉H₂₈NO₇S, 414.1586 (M+H)⁺; Found, 414.1585.

Diethyl 5,7-Di-*t*-butyl-3-((*R*)-1,1-*t*-butylsulfinamido)-(S)-benzofuran-2,2(3H)-dicarboxylate (3i).

White solid, m.p. 97-98 °C, $[\alpha]_D^{20} +85.7$ (*c* 1.10, CHCl₃). ¹H NMR (CDCl₃, 500 MHz) δ : 7.46 (d, *J*=2.0 Hz, 1H), 7.22 (d, *J*=2.0 Hz, 1H), 5.81 (d, *J*=9.5 Hz, 1H), 4.36~4.26 (m, 4H), 3.77 (d, *J*=9.5 Hz, 1H), 1.39 (s, 9H), 1.29 (s, 15H), 1.21 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz) δ : 167.2, 165.6, 162.3, 153.5, 145.7, 132.9, 125.1, 124.5, 120.7, 92.1, 64.2, 63.2, 62.6, 62.2, 56.2, 34.7, 34.3, 31.7, 29.3, 22.6, 14.0, 13.9. IR (KBr) ν/cm^{-1} : 3315, 2985, 2025, 1749, 1625, 1599, 1501, 1459, 1369, 1330, 1291, 1253, 1214, 1192, 1152, 1127, 1096, 1054, 854. HRMS (ESI) calcd for C₂₆H₄₂NO₆S, 496.2733 (M+H)⁺; Found, 496.2747.

(S)-Diethyl 6-(diethylamino)-3-((*R*)-*t*-butylsulfinamido)benzofuran-2,2(3H)- dicarboxylate (3j).

White solid, m.p. 115-116 °C, $[\alpha]_D^{20} +91.5$ (*c* 1.12, CHCl₃). ¹H NMR (CDCl₃, 500 MHz), δ : 7.11 (d, *J*=8.5 Hz, 1H), 6.33 (d, *J*=8.5 Hz, 1H), 6.21 (s, 1H), 5.53 (d, *J*=9.0 Hz, 1H), 5.48 (d, *J*=9.0 Hz, 1H), 4.30~4.07 (m, 4H), 3.35~3.32 (m, 4H), 1.31~1.21 (m, 6H), 1.10 (s, 9H), 1.11~1.06 (m, 6H). ¹³C NMR (CDCl₃, 125 MHz), δ : 167.2, 165.3, 159.7, 150.1, 126.8, 111.9, 106.4, 92.9, 64.0, 62.8, 62.2, 55.9, 44.5, 23.1, 14.3, 14.2, 12.8. IR (KBr) ν/cm^{-1} : 3278, 2959, 2925, 2855, 2024, 1740,

1629, 1581, 1513, 1465, 1364, 1291, 1190, 1124, 1077, 966, 900, 860, 821, 792, 746, 608. HRMS (ESI) calcd for $C_{22}H_{35}N_2O_6S$, 455.2216 ($M+H$)⁺; Found, 455.2206.

(S)-diethyl 3-acetamidobenzofuran-2,2(3H)-dicarboxylate (5). White solid, m.p: 154~155 °C. $[\alpha]_D^{20}$ +214.0 (*c* 1.1, $CHCl_3$). 1H NMR ($CDCl_3$, 500 MHz) δ : 7.26~7.24 (m, 1H), 7.00~6.96 (m, 2H), 6.56 (d, *J*=9.5 Hz, 1H), 5.97 (d, *J*=9.5 Hz, 1H), 4.34~4.22 (m, 4H), 1.95 (s, 3H), 1.30~1.27 (m, 6H); ^{13}C NMR ($CDCl_3$, 125MHz) δ : 168.9, 165.9, 165.6, 158.0, 130.5, 125.2, 124.9, 122.7, 110.8, 91.4, 62.8, 62.6, 55.4, 23.1, 14.0, 13.9; IR (KBr) ν/cm^{-1} : 3240, 3039, 2984, 2024, 1768, 1739, 1657, 1602, 1524, 1482, 1371, 1279, 1238, 1181, 1094, 1043, 882, 851, 754, 701, 608, 491. HRMS (ESI) calcd for $C_{16}H_{20}NO_6$, 322.1291 ($M+H$)⁺; Found, 322.1291. HPLC: Chiralcel OD-H column, detected at 254 nm, eluent: n-hexane/2-propanol =90/10 (v/v), flow rate: 0.7 ml/min, t_1 = 9.3 min (minor), t_2 = 11.3 min (major), 95% ee.

5. Crystal data and structure refinement for 3b

Parameters	Values
Empirical formula	C18 H24 F N O6 S
Formula weight	401.44
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.6757(4) Å alpha = 90 deg. b = 11.6515(5) Å beta = 90 deg. c = 17.7548(8) Å gamma = 90 deg.
Volume	2001.61(15) Å ³
Z, Calculated density	4, 1.332 Mg/m ³
Absorption coefficient	0.204 mm ⁻¹
F(000)	848
Crystal size	0.36 x 0.33 x 0.3 mm
Theta range for data collection	2.09 to 28.32 deg.
Limiting indices	-11 ≤ h ≤ 12, -14 ≤ k ≤ 15, -23 ≤ l ≤ 22
Reflections collected / unique	25722 / 4930 [R(int) = 0.0280]
Completeness to theta	28.32 99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6411
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4930 / 0 / 249
Goodness-of-fit on F ²	1.020
Final R indices [I > 2σ(I)]	R1 = 0.0394, wR2 = 0.1049
R indices (all data)	R1 = 0.0516, wR2 = 0.1127
Absolute structure parameter	-0.06(7)
Largest diff. peak and hole	0.420 and -0.195 e.Å ⁻³

6. Copies of ^1H and ^{13}C NMR spectra of products 3a – 3j

Fig.2.17 The ^1H NMR Spectrum of compound 12o

图 2.17 化合物 12o 的 ^1H NMR 谱图

Fig. 2.18 The ¹³C NMR Spectrum of compound 12o

7.Copies of HPLC spectra of product 5

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.314	226082	6441	2.540	3.598
2	11.263	8674089	172556	97.460	96.402
Total		8900171	178997	100.000	100.000

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.150	5275400	147029	49.498	58.217
2	11.353	5382384	105523	50.502	41.783
Total		10657784	252553	100.000	100.000