Supporting information for:

**Copper(I)-Fesulphos Lewis Acid Catalysts for
Enantioselective Mannich-Type Reaction of *N*-Sulfonyl
Imines**

*Alvaro Salvador González, Ramón Gómez Arrayás and Juan C. Carretero**

Departamento de Química Orgánica. Facultad de Ciencias. Universidad Autónoma de Madrid.
28049. Madrid. Spain.

juancarlos.carretero@uam.es

Table of Contents

Experimental Section	3
General Methods	3
Typical procedure for the preparation of aromatic aldimines ..	3
Preparation of aliphatic aldimines	7
Typical procedure for the Mannich reaction	8
Typical procedure for the deprotection of sulfonamides	18
References	19
X-ray data of 4e	20
NMR-Spectra	29

Experimental Section

General methods.

All the reactions were carried out in anhydrous solvents and under nitrogen atmosphere. Melting points were taken in open-end capillary tubes. NMR spectra were recorded [300 MHz (^1H), 75 MHz (^{13}C)] at room temperature in CDCl_3 , with internal CHCl_3 as the reference (7.26 ppm for ^1H and 77.0 ppm for ^{13}C). For fluoro containing compounds the observed list of peaks is given as the ^{13}C NMR data. Peaks of IR spectra are reported in cm^{-1} . Mass spectra (MS) were determined at an ionizing voltage of 70 eV. CH_2Cl_2 and THF, DMF and toluene were dried and stored over microwave-activated 4Å molecular sieves. Flash column chromatography was performed using silica gel (230-400 mesh).

Typical procedure for the preparation of *N*-(2-thienylsulfonyl)aryl

aldimines. 2-Thiophenesulfonamide, *N*-phenylmethylene

(2e).ⁱ A mixture of 2-thiophenesulfonamide (1.58 g, 10 mmol), benzaldehyde (1.0 mL, 10 mmol), activated MS 4Å and a catalytic amount of Amberlist-15 in dry toluene

(10 mL) was heated at 120 °C in a sealed tube for 12 h. The mixture was allowed to reach room temperature, filtered through a pad of Celite and concentrated. The resulting light brown residue was triturated with a 1:1 mixture of *n*-hexane- Et_2O and filtered to afford **2e** as a white solid; yield: 2.3 g (93%); mp = 108-109 °C. ^1H NMR: δ 9.00 (s, 1H), 7.95 (d, J = 8.1 Hz, 2H), 7.80 (dd, J = 1.3, 3.7 Hz, 1H), 7.71 (dd, J = 1.3, 4.9 Hz, 1H), 7.63 (t, J = 8.1 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.14 (dd, J = 3.3, 4.9 Hz, 1H). ^{13}C RMN: δ 170.2, 138.5, 135.1, 134.1, 133.9, 132.1, 131.4, 129.1, 127.7. IR (NaCl): 3098, 1601, 1321, 1151. Anal. Calcd for $\text{C}_6\text{H}_7\text{NO}_2\text{S}_2$: C, 52.57; H, 3.61; N, 5.57; S, 25.52. Found: C, 52.57; H, 3.79; N, 5.60; S, 25.60.

2-Thiophenesulfonamide, N-4-(fluorophenyl)methylene (5e). Following

the typical procedure, the reaction of 4-fluorobenzaldehyde (1.0 mL, 10 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **5e** as a white solid; yield: 1.90 g (71%); mp = 112-113 °C. ¹H NMR: δ 8.97 (s, 1H), 8.00 - 7.96 (m, 2H), 7.79 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.71 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.23 - 7.16 (m, 2H), 7.15 (dd, *J* = 3.7, 4.9 Hz, 1H). ¹³C NMR: δ 168.6, 167.0 (d, ¹*J*_{C-F} = 259.0 Hz), 138.5, 134.1 (d, ³*J*_{C-F} = 10.4 Hz), 133.9, 131.8, 128.6 (d, ⁴*J*_{C-F} = 2.7 Hz), 127.7, 116.7 (d, ²*J*_{C-F} = 22.5 Hz). IR (NaCl) : 1601, 1574, 1295, 1164.

2-Thiophenesulfonamide, N-(4-methoxyphenyl)methylene (6e). Following

the typical procedure, the reaction of 4-methoxybenzaldehyde (1.21 mL, 10 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **6e** as a white solid; yield: 2.3 g (83%); mp = 127-129 °C. ¹H NMR: δ 8.91 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.77 (dd, *J* = 1.3, 3.7 Hz), 7.67 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.12 (dd, *J* = 3.8, 4.9 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). ¹³C NMR: δ 169.3, 165.5, 139.3, 133.9, 133.6, 133.4, 127.6, 125.0, 114.7, 55.7. IR (NaCl): 3011, 1600, 1590, 1321, 1172.

2-Thiophenesulfonamide, N-(2-methylphenyl)methylene (7e). Following

the typical procedure, the reaction of 2-methylbenzaldehyde (1.44 mL, 10 mmol) and 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **7e** as a white solid; yield: 1.69 g (64%); mp = 107-108 °C. ¹H NMR: δ 9.31 (s, 1H), 8.03 (dd, *J* = 1.2, 6.6 Hz, 1H), 7.79 (dd, *J* = 1.3, 3.8 Hz, 1H), 7.70 (dd, *J* = 1.3, 4.99 Hz, 1H), 7.49 (dt, *J* = 1.4, 7.5 Hz, 1H), 7.32 - 7.27 (m, 2H), 7.14 (dd, *J* = 3.7, 4.9 Hz, 1H), 2.61

(s, 3H). ^{13}C NMR: δ 168.7, 142.4, 138.8, 134.8, 133.9, 133.8, 131.6, 130.8, 130.2, 127.6, 126.7, 30.8. IR (NaCl): 3119, 1649, 1324, 1153.

2-Thiophenesulfonamide, *N*-(3-methoxyphenyl)methylene (8e). Following

the typical procedure, the reaction of 3-methoxybenzaldehyde (1.22 mL, 10 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **8e** as a white solid; yield: 1.77 g (63%); mp = 103-105 °C.

^1H NMR: δ 8.96 (s, 1H), 7.79 (dd, J = 1.3, 3.7 Hz, 1H), 7.71 (dd, 1.2, 4.9 Hz, 1H), 7.49 - 7.43 (m, 3H), 7.19 - 7.18 (m, 1H), 7.15 (dd, J = 3.7, 4.9 Hz, 1H), 3.85 (s, 3H). ^{13}C -NMR: δ 170.2, 160.1, 134.2, 134.0, 133.4, 130.1, 127.7, 125.5, 122.4, 113.4, 112.0, 55.5.

2-Thiophenesulfonamide, *N*-(3-chlorophenyl)methylene (9e). Following

the typical procedure, the reaction of 3-chlorobenzaldehyde (1.20 mL, 10 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **9e** as a white solid; yield = 1.02 g (73%); mp = 98-100 °C. ^1H

NMR: δ 8.95 (s, 1H), 7.95 (t, J = 1.8 Hz, 1H), 7.81 - 7.78 (m, 2H), 7.73 (dd, J = 1.3, 4.9 Hz, 1H), 7.59 (dq, J = 1.1, 8.0 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.16 (dd, J = 3.7, 4.9 Hz, 1H). ^{13}C NMR: δ 168.6, 137.9, 135.5, 134.9, 134.4, 134.3, 133.8, 130.4, 130.3, 129.8, 127.8.

2-Thiophenesulfonamide, *N*-(1-naphtyl)methylene (10e). Following the

typical procedure, the reaction of 1-naphtaldehyde (1.56 g, 10 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **10e** as a pale yellow solid; yield: 1.83 g (61%); mp = 115-117 °C. ^1H NMR: δ 9.57 (s, 1H), 9.00

(d, J = 8.6 Hz, 1H), 8.15 (m, 2H), 7.92 (d, J = 8.1 Hz, 1H), 7.85 (dd, J = 1.2, 3.7 Hz, 1H), 7.72 - 7.67 (m, 2H), 7.63 - 7.56 (m, 2H), 7.15 (dd, J = 3.8, 4.9 Hz, 1H). ^{13}C NMR: δ 169.9, 138.8, 136.4, 135.5, 133.9, 133.8, 131.8, 129.1, 129.0, 127.7, 127.4, 127.0, 125.1, 124.8, 124.2. IR (NaCl): 3093, 1596, 1344, 1151.

2-Thiophenesulfonamide, N-(2-naphtyl)methylene (11e). Following the

11e

typical procedure, the reaction of 2-naphtaldehyde (1.56 g, 10 mmol) and 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **11e** as a white solid; yield: 2.61 g (87%); mp = 121-123 °C. ¹H NMR: δ 9.15 (s, 1H), 8.35 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.97-7.87 (m, 3H), 7.83 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.72 (dd, *J* = 3.7, 4.9 Hz, 1H), 7.67 - 7.56 (m, 2H), 7.17 - 7.14 (m, 2H). ¹³C NMR: δ 170.1, 138.7, 136.6, 136.4, 134.1, 133.9, 132.6, 131.7, 129.9, 129.5, 129.3, 129.1, 128.0, 127.7, 127.3, 124.1.

2-Thiophenesulfonamide, N-(2-furyl)methylene (12e). Following the

12e

typical procedure, the reaction of 2-furfural (0.83 mL, 10 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **12e** as a brown solid; yield: 1.78 g (74%); mp = 112-114 °C. ¹H NMR: δ 8.77 (s, 1H), 7.76 (d, *J* = 1.1 Hz, 1H), 7.75 (d, *J* = 1.3 Hz, 1H), 7.68 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.38 (dd, *J* = 0.5, 3.7 Hz, 1H), 7.11 (dd, *J* = 3.7, 4.9 Hz, 1H), 6.65 (dd, *J* = 1.7, 3.5 Hz, 1H). ¹³C NMR: δ 155.6, 150.1, 148.8, 138.5, 134.1, 133.9, 127.7, 125.3, 113.8. IR (NaCl): 3098, 1594, 1520, 1274, 1210.

2-Thiophenesulfonamide, N-[(2E)-3-phenylprop-2-en-1-ylidene (13e).

13e

Following the typical procedure, the reaction of cinnamaldehyde (1.25 mL, 10 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **13e** as white solid; yield: 1.46 g (53%); mp = 105-107 °C. ¹H NMR: δ 8.76 (d, *J* = 9.4 Hz, 1H), 7.76 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.70 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.58 - 7.55 (m, 2H), 7.51 (d, *J* = 15.8 Hz, 1H), 7.47 - 7.41 (m, 3H), 7.14 (dd, *J* = 3.7, 4.9 Hz, 1H), 7.02 (dd, *J* = 9.4, 15.8 Hz, 1H). ¹³C NMR: δ 171.0, 154.3, 138.9, 134.1, 133.9, 133.8, 132.8, 131.8, 129.2, 128.7, 127.7, 124.6. IR (NaCl): 3091, 2310, 2915, 1630, 1596.

2-Thiophenesulfonamide, *N*-[(2*E*)-3-(2-furyl)prop-2-en-1-ylidene (14e**).**

Following the typical procedure, the reaction of 3-(2-furyl)acrolein (1.22 g, 10.0 mmol) with 2-thiophenesulfonamide (1.58 g, 10 mmol) gave **14e** as a brown solid; yield = 1.63 g (61%); mp = 115-116 °C. ¹H NMR: δ 8.70 (d, *J* = 9.6 Hz, 1H), 7.78 (dd, *J* = 1.1, 3.7 Hz, 1H), 7.72 (dd, *J* = 1.1, 4.9 Hz, 1H), 7.62 (d, *J* = 1.1 Hz, 1H), 7.32 (d, *J* = 2.7 Hz, 1H), 7.16 (dd, *J* = 3.7, 4.9 Hz, 1H), 6.90 (dd, *J* = 9.6, 15.5 Hz, 1H), 6.84 (d, *J* = 3.4 Hz, 1H), 6.58 (dd, *J* = 1.7, 3.4 Hz, 1H). ¹³C NMR: δ 170.3, 150.9, 147.8, 146.7, 138.9, 133.7, 133.6, 127.6, 122.1, 117.8, 113.1.

Preparation of aliphatic imines. Aliphatic imines were prepared according to the procedure described in the bibliography:ⁱⁱ

2-Thiophenesulfonamide, *N*-(cyclohexyl)methylene (15e**).** A solution of sodium phenylsulfinate (1.90 g, 10 mmol), 2-thiophenesulfonamide (1.58 g, 10 mmol) and cyclohexanecarbaldehyde (1.14 mL, 10 mmol) was stirred at room temperature in a mixture of formic acid (15 mL) and H₂O (15 mL) for 24 hours. The resulting suspension was filtered and the solid was successively washed with water (2 x 10 mL) to afford **I** as a white solid; yield: 2.92 g (74%). To a solution of **I** (2.90 mg, 7 mmol) in CH₂Cl₂ (10 mL) at room temperature was added sat. aq solution of Na₂CO₃ (100 mL). The reaction mixture was vigorously stirred at room temperature for 2 h, then the aqueous phase was extracted with CH₂Cl₂ (2 x 20 mL) and the combined organic phase was dried (MgSO₄) and concentrated to afford **15e** as colourless oil; yield: 1.78 g (46%). ¹H NMR: δ 8.40 (d, *J* = 4.3 Hz, 1H), 7.70-7.67 (m, 2H), 7.10 (dd, *J* = 4.0, 4.7 Hz, 1H), 2.45 - 2.41 (m, 1H), 1.83 - 1.61 (m, 5H), 1.35-1.14 (m,

5H). ^{13}C NMR: δ 181.1, 137.7, 134.1, 134.0, 127.6, 28.1, 25.4, 25.1, 24.8.

Typical procedure for the catalytic enantioselective Mannich reaction:

(*R*)-*S*-tert-butyl

3-phenyl-3-[(2-

thienyl)sulfonyl]amino-3-propanethioate (**4e**). A

solution of complex $[\mathbf{1} \cdot \text{CuBr}]_2$ (7.8 mg, 0.022 mmol)

and AgClO_4 (2.2 mg, 0.011 mmol) in CH_2Cl_2 (0.6 mL) was

stirred in the dark at room temperature under argon for 2 h and treated with a solution of imine **2e** (27.0 mg, 0.11 mmol) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred at room temperature for 5 min before it was treated with the silyl enol ether **3** (81.8 mg, 0.33 mmol) at room temperature. Once the reaction is finished (TLC monitoring), H_2O (1.5 mL) was added and the mixture was stirred for 5 min at room temperature. The organic phase was separated and the aqueous phase was washed with CH_2Cl_2 (2 x 5 mL). The combined organic phase was dried (MgSO_4) and concentrated. The residue was purified by flash chromatography (*n*-hexane-EtOAc 4:1) to afford **4e** as a white solid; yield: 33.7 mg (80%), 91% ee. Recrystallization from hexane- CH_2Cl_2 gave the product with >99% ee; mp = 107-109 °C. $[\alpha]_{\text{D}}^{20} = +84$ (*c* 0.6, CHCl_3), >99% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245 nm; (*S*)-**4e** t_{R} = 20.6 min; (*R*)-**4e** t_{R} = 32.7 min]. ^1H NMR: δ 7.46 (dd, J = 1.3, 5.0 Hz, 1H), 7.40 (dd, J = 1.3, 3.7 Hz, 1H), 7.22 - 7.18 (m, 3H), 7.14 - 7.11 (m, 2H), 6.92 (dd, J = 3.7, 4.9 Hz, 1H), 5.88 (bd, J = 6.4 Hz, 1H), 4.78 (q, J = 6.5 Hz, 1H), 2.93 (dd, J = 6.5, 15.1 Hz, 1H), 2.84 (dd, J = 6.5, 15.1 Hz, 1H), 1.34 (s, 9H). ^{13}C RMN: δ 197.9, 141.3, 138.8, 132.3, 131.8, 128.5, 127.8, 127.1, 126.4, 55.5, 49.9, 48.8, 29.5. MS (FAB+) m/z : 384.1 [$\text{M}^+ + 1$] (35), 349.1 (19), 252 (92), 154.1 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}_3$: C: 53.23, H: 5.52, N: 3.65, S: 25.08 Found: C: 53.05, H: 5.57, N: 3.69, S: 24.99.

(R)-*S*-tert-Butyl

3-[(4-methylphenyl)sulfonyl]amino-3-

phenylpropanethioate (4c).

Following the typical procedure, the reaction of imine **2c** (28,5 mg, 0.11 mmol) with **3** (81 mg, 0.33 mmol) gave **4c** as a white solid after chromatographic purification (*n*-hexane-EtOAc 4:1); yield: 16.7 mg (39%); mp = 115-116 °C. $[\alpha]_D^{20} = -8$ (*c* 0.2, CHCl₃), 90% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245 nm; (*S*)-**4c** t_R = 20.6 min; (*R*)-**4c** t_R = 23.8 min]. ¹H NMR: δ 7.93-7.90 (m, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.48 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 8.3 Hz, 2H), 7.08 (dd, J = 3.6, 6.6 Hz, 2H), 5.71 (bd, J = 6.8 Hz, 1H), 4.68 (q, J = 6.6 Hz, 1H), 2.90 (dd, J = 6.7, 15.1 Hz, 1H), 2.78 (dd, J = 5.9, 15.1 Hz, 1H), 2.36 (s, 3H), 1.33 (s, 9H). ¹³C RMN: δ 197.9, 131.3, 129.8, 129.4, 128.4, 128.0, 127.6, 127.1, 126.5, 55.2, 50.1, 48.7, 29.5, 21.4.

(R)-*S*-tert-Butyl

3-[2-pyridylsulfonyl]amino-3-phenylpropanethioate

(4d).

Following the typical procedure, the reaction of imine **2d** (27.0 mg, 0.11 mmol) with **3** (81 mg, 0.33 mmol) gave **4d** as a white solid after chromatographic purification (*n*-hexanes-EtOAc 3:1); yield: 26.9 mg (65 %); mp = 102-104 °C. $[\alpha]_D^{20} = -6$ (*c* 0.2, CHCl₃), 39% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245 nm; (*R*)-**4d** t_R = 31.7 min; (*S*)-**4d** t_R = 41.3 min]. ¹H NMR: δ 8.56 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.70 (dt, J = 1.8, 7.2 Hz, 1H), 7.36 - 7.32 (m, 1H), 7.14 - 7.06 (m, 5H), 6.07 (d, J = 7.4 Hz, 1H), 4.90 (q, J = 6.2 Hz, 1H), 3.01 (dd, J = 6.2, 15.3 Hz, 1H), 2.93 (dd, J = 6.2, 15.3 Hz, 1H), 1.34 (s, 9H). ¹³C RMN: δ 197.6, 157.7, 149.8, 138.8, 137.5, 128.3, 127.6, 126.7, 126.3, 122.0, 55.6, 50.0, 48.8, 29.5. MS (FAB+) m/z : 379.0 (100) [$M^+ + 1$], 289.0 (14.6), 247 (40.7), 185 (11.1), 159 (60.7), 131 (40.8).

(R)-*S*-*tert*-Butyl

3-(4-fluorophenyl)-3-[(2-

thienylsulfonyl)amino]propanethioate

(16e).

Following the typical procedure, the reaction of imine **5e** (22.7 mg, 0.11 mmol) with **3** (81.1 mg, 0.33 mmol) gave **16e** as a pale yellow solid after chromatographic purification (*n*-hexane-EtOAc 3:1); yield: 26.4 mg (60 %); mp = 127-129 °C. $[\alpha]_D^{20} +34$ (*c* 0.5, CHCl₃), 82% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 254.4 nm; (*S*)-**16e** t_R = 25.5 min; (*R*)-**16e** t_R = 30.5 min]. ¹H NMR: δ 7.48 (dd, *J* = 1.3, 4.8 Hz, 1H), 7.40 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.14 - 7.09 (m, 2H), 6.95 - 6.87 (m, 3H), 5.93 (bd, *J* = 6.7 Hz, 1H), 4.77 (q, *J* = 6.0 Hz, 1H), 2.90 (dd, *J* = 6.6, 15.3 Hz, 1H), 2.81 (dd, *J* = 6.0, 15.3 Hz, 1H), 1.35 (s, 9H). ¹³C NMR: δ 198.0, 162.1 (d, ¹*J*_{C-F} = 245.3 Hz), 141.2, 134.5 (d, ⁴*J*_{C-F} = 3.3 Hz), 132.4, 131.9, 128.2 (d, ³*J*_{C-F} = 8.2 Hz), 127.1, 115.4 (²*J*_{C-F} = 21.4 Hz), 54.8, 49.8, 40.9, 29.4.

(R)-*S*-*tert*-Butyl

3-(4-methoxyphenyl)-3-[(2-

thienylsulfonyl)amino]propanethioate

(17e).

Following the typical procedure, the reaction of imine **6e** (30.9 mg, 0.11 mmol) with **3** (81.1 mg, 0.33 mmol) gave **17e** as a white solid after chromatographic purification (*n*-hexane-EtOAc 5:1); yield: 26.3 mg (58 %); mp = 106-108 °C. $[\alpha]_D^{20} = +12$ (*c* 0.6, CHCl₃), 81% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245 nm; (*S*)-**17e** t_R = 21.1 min; (*R*)-**17e** t_R = 24.5 min]. ¹H NMR: δ 7.48 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.40 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.94 (dd, *J* = 3.7, 4.9 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.77 (bd, *J* = 6.7 Hz, 1H), 4.73 (q, *J* = 6.4 Hz, 1H), 3.75 (s, 3H), 2.93 (dd, *J* = 6.5, 15.1 Hz, 1H), 2.83 (dd, *J* = 15.9, 15.2 Hz, 1H), 1.35. ¹³C NMR: δ 198.0, 159.1, 141.4, 132.3, 131.8, 130.9, 127.7, 127.1, 113.4, 55.2, 55.0, 50.0, 48.8, 29.5.

(R)-*S*-*tert*-Butyl

3-(2-methylphenyl)-3-[(2-

thienylsulfonyl)amino]propanethioate (**18e**). Following the typical procedure, the reaction of the imine **7e** (29.1 mg, 0.11 mmol) with **3** (81 mg, 0.33 mmol) afforded **18e** as a white solid after chromatographic

purification (*n*-hexane-EtOAc 6:1); yield: 33.6 mg (77 %); mp = 107-109 °C. $[\alpha]_D^{20} = -23$ (*c* 0.5, CHCl₃), 93% ee. HPLC Daicel Chiralpack AD [hexane/ *i*-PrOH 70:30; 1 mL/min; 245 nm; (*S*)-**18e** t_R = 9.8 min; (*R*)-**18e** t_R = 13.9 min]. ¹H NMR: δ 7.44 (dd, *J* = 1.3, 5.0 Hz, 1H), 7.36 (dd, *J* = 1.3, 3.8 Hz, 1H), 7.15 - 7.13 (m, 1H), 7.09 - 7.03 (m, 3H), 6.90 (dd, *J* = 3.8, 5.0 Hz, 1H), 5.70 (bd, *J* = 6.8 Hz, 1H), 5.04 (q, *J* = 6.5 Hz, 1H), 2.89 (dd, *J* = 6.9, 14.9 Hz, 1H), 2.82 (dd, *J* = 6.9, 14.9 Hz, 1H), 2.25 (s, 3H), 1.35 (s, 9H). ¹³C NMR: δ 197.7, 141.2, 136.9, 134.7, 132.2, 131.8, 130.5, 127.7, 127.1, 126.3, 126.0, 51.7, 49.5, 48.7, 29.5, 19.0.

(R)-*S*-*tert*-Butyl

3-(3-methoxyphenyl)-3-[(2-

thienylsulfonyl)amino]propanethioate (**19e**). Following the typical procedure, the reaction of the imine **8e** (30.9 mg, 0.11 mmol) with **3** (81.1 mg, 0.33 mmol) afforded **19e** as a yellow solid after chromatographic

purification (*n*-hexane-EtOAc 3:1); yield: 41.3 mg (91 %), 83% ee. Recrystallization from hexane-CH₂Cl₂ gave the product with 94% ee; mp = 112-114 °C. $[\alpha]_D^{20} = +43$ (*c* 0.5, CHCl₃). HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245 nm; (*S*)-**19e** t_R = 27.9 min; (*R*)-**19e** t_R = 39.4 min]. ¹H NMR: δ 7.47 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.40 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.92 (dd, *J* = 3.7, 4.9 Hz, 1H), 6.75 - 6.70 (m, 2H), 6.64 (t, *J* = 2 Hz, 1H), 5.88 (bd, *J* = 6.8 Hz, 1H), 4.76 (q, *J* = 6.4 Hz, 1H), 3.71 (s, 3H), 2.93 (dd, *J* = 6.4, 15.2 Hz, 1H), 2.84 (dd, *J* = 5.8, 15.2 Hz, 1H), 1.36 (s, 9H). ¹³C NMR: δ 197.9, 159.6, 132.4, 131.8, 129.5, 127.1, 118.7, 113.6, 111.8, 55.4, 55.1, 49.9, 48.8, 29.5.

(R)-*S*-tert-Butyl

3-(3-chlorophenyl)-3-[(2-

thienylsulfonyl)amino]propanethioate (20e). Following

the typical procedure, the reaction of the imine **9e** (31.2 mg, 0.11 mmol) with **3** (81.1 mg, 0.33 mmol)

afforded **20e** as a white solid after chromatographic

purification (*n*-hexane-EtOAc 4:1); yield: 36.7 mg (80%), 88% ee.

Recrystallization from hexane-CH₂Cl₂ gave the product with 98% ee; mp =

114-116 °C. $[\alpha]_D^{20} = +294$ (*c* 0.7, CHCl₃). HPLC Daicel Chiralpack AD

[hexane/*i*-PrOH 90:10; 1 mL/min; 254.1 nm; (*S*)-**20e** *t_R* = 16.5 min; (*R*)-**20e**

t_R = 21.2 min]. ¹H NMR: δ 7.49 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.40 (dd, *J* =

1.3, 3.7 Hz, 1H), 7.19 - 7.13 (m, 2H), 7.09 (s, 1H), 7.06 - 7.03 (m,

1H), 6.94 (dd, *J* = 3.7, 4.9 Hz, 1H), 5.97 (bd, *J* = 6.8 Hz, 1H), 4.75

(q, *J* = 6.1 Hz, 1H), 2.87 (dd, *J* = 6.8, 15.3 Hz, 1H), 2.80 (dd, *J* =

5.5, 15.3 Hz, 1H), 1.36 (s, 9H). ¹³C NMR: δ 197.9, 141.1, 134.4, 132.4,

132.0, 129.7, 128.0, 127.1, 126.7, 124.7, 124.6, 55.0, 49.5, 49.1,

29.5.

(R)-*S*-tert-Butyl

3-(1-naphthyl)-3-[(2-

thienylsulfonyl)amino]propanethioate (21e). Following

the typical procedure, the reaction of the imine **10e** (31.2 mg, 0.11 mmol) with **3** (81.1 mg, 0.33 mmol)

afforded **21e** as a white solid after chromatographic

purification (*n*-hexane-EtOAc 6:1); yield: 40.7 mg (86%); mp = 101-102

°C. $[\alpha]_D^{20} = -58$ (*c* 0.5, CHCl₃), 88% ee. HPLC Daicel Chiralpack AD

[hexane/*i*-PrOH 85:15; 0.5 mL/min; 210 nm; (*S*)-**21e** *t_R* = 61.8 min; (*R*)-**21e**

t_R = 80.59 min]. ¹H NMR: δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.8

Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.54 - 7.45 (m, 2H), 7.42 - 7.37

(m, 2H), 7.34 - 7.29 (m, 2H), 6.82 (dd, *J* = 3.7, 4.9 Hz, 1H), 5.98

(bd, *J* = 6.8 Hz, 1H), 5.64 (q, *J* = 6.4 Hz, 1H), 3.07 (dd, *J* = 6.4, 15

Hz, 1H), 3.07 (dd, *J* = 5.8, 15 Hz, 1H), 1.33 (s, 9H). ¹³C NMR: δ 197.9,

141.0, 134.3, 133.7, 132.4, 131.8, 129.9, 129.0, 128.5, 127.0, 126.6,

125.7, 125.1, 124.3, 122.1, 51.8, 49.5, 48.8, 29.5.

(R)-*S*-*tert*-Butyl

3-(2-naphthyl)-3-[(2-

thienylsulfonyl)amino]propanethioate (22e).

22e

Following the typical procedure, the reaction between the imine **11e** (34.6 mg, 0.11 mmol) with **3** (81.8 mg, 0.33 mmol) afforded **22e** as a yellow solid after chromatographic purification (*n*-hexane-EtOAc 5:1); yield: 33.6 mg (71%); mp = 109-110 °C. $[\alpha]_D^{20} = +32$ (*c* 0.5, CHCl₃), 91% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 254 nm; (*S*)-**22e** t_R = 29.3 min; (*R*)-**22e** t_R = 58.3 min]. ¹H NMR: δ 7.65-7.56 (m, 3H), 7.46 (s, 1H), 7.35-7.24 (m, 2H), 7.24 (s, 1H), 7.12 (s, 1H), 7.10 (d, *J* = 1.8 Hz, 1H), 6.68 (dd, *J* = 3.7, 4.9 Hz, 1H), 5.87 (bd, *J* = 7.2 Hz, 1H), 4.83 (q, *J* = 6.4 Hz, 1H), 2.89 (dd, *J* = 5.8, 15.2 Hz, 1H), 2.80 (dd, *J* = 5.8, 15.2 Hz, 1H), 1.29 (s, 9H). ¹³C NMR: δ 197.9, 141.4, 136.2, 133.0, 132.8, 132.4, 131.8, 128.4, 127.9, 127.5, 127.0, 126.3, 126.1, 125.7, 124.0, 55.7, 49.9, 48.9, 29.5. EI⁺MS : 326(31), 252(100), 147 (49), 104 (40).

(R)-*S*-*tert*-Butyl

3-(2-furyl)-3-[(2-

thienylsulfonyl)amino]propanethioate (23e). Following

23e

the typical procedure, the reaction of the imine **12e** (26.5 mg, 0.11 mmol) with **3** (81.8 mg, 0.33 mmol) afforded **23e** as a brown solid after chromatographic purification (*n*-hexane-EtOAc 3:1); yield: 35.7 mg (87%); mp = 101-102 °C. $[\alpha]_D^{20} = +12$ (*c* 0.2, CHCl₃), 49% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245 nm; (*S*)-**23e** t_R = 21.3 min; (*R*)-**23e** t_R = 28.0 min]. ¹H NMR: δ 7.52-7.50 (m, 2H), 7.21 (t, *J* = 0.8 Hz, 1H), 6.99 (dd, *J* = 3.8, 4.9 Hz, 1H), 6.18 (dd, *J* = 1.8, 3.1 Hz, 1H), 6.05 (dd, *J* = 0.8, 3.2 Hz, 1H), 5.69 (bd, *J* = 8.6 Hz, 1H), 4.89 (dt, *J* = 6.1, 8.5 Hz, 1H), 3.03 (dd, *J* = 5.7, 15.4 Hz, 1H), 2.90 (dd, *J* = 6.2, 15.5 Hz, 1H), 1.39 (s, 9H). ¹³C NMR: δ 197.3, 151.2, 142.2, 141.4, 132.3, 131.9, 127.1, 110.3, 107.4, 49.1, 48.8, 47.5, 29.5.

(*R*)-*S*-*tert*-Butyl

(4*E*)-5-phenyl-3-(2-thienylsulfonyl)amino-4-

24e

pentenethioate (**24e**). Following the typical procedure, the reaction of the imine **13e** (30.5 mg, 0.11 mmol) with **3** (81.8 mg, 0.33 mmol) afforded **24e** as a white solid after chromatographic purification

(*n*-hexane-EtOAc 3:1); yield: 17.9 mg, (40 %); mp = 104-105 °C. $[\alpha]_D^{20} = +12$ (*c* 0.2, CHCl₃), 71% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 254.4 nm; (*S*)-**24e** t_R = 21.7 min; (*R*)-**24e** t_R = 34.2 min]. ¹H NMR: δ 7.54 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.45 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.25 - 7.14 (m, 5H), 6.94 (dd, *J* = 3.7, 4.9 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.54 (bd, *J* = 7.9 Hz, 1H), 4.36-4.28 (m, 1H), 2.75 (dd, *J* = 0.9, 5.2 Hz, 1H), 1.37 (s, 9H). ¹³C NMR: δ 198.4, 135.9, 135.1, 132.4, 132.3, 131.8, 130.1, 128.5, 127.9, 127.3, 126.5, 53.7, 49.1, 48.5, 29.6.

(*R*)-*S*-*tert*-Butyl

(4*E*)-5-(2-furyl)-3-(2-thienylsulfonyl)amino-4-

25e

pentenethioate (**25e**). Following the typical procedure, the reaction of the imine **14e** (30.5 mg, 0.11 mmol) with **3** (81.8 mg, 0.33 mmol) afforded **25e** as a white solid after chromatographic purification

(*n*-hexane-EtOAc 4:1); yield: 36.4 mg (83 %); mp = 97-99 °C. $[\alpha]_D^{20} = +21$ (*c* 0.2, CHCl₃), 60% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 254.4 nm; (*S*)-**25e** t_R = 25.6 min; (*R*)-**25e** t_R = 29.5 min]. ¹H NMR: δ 7.59 (d, *J* = 1.3, Hz, 1H), 7.52 (d, *J* = 3.1 Hz, 1H), 7.30 (d, *J* = 1.1 Hz, 1H), 7.00 (dd, *J* = 1.1, 3.1 Hz, 1H), 6.31 (dd, *J* = 6.8, 15.8 Hz, 1H), 6.29 (dd, *J* = 6.7, 15.8 Hz, 1H), 5.97- 5.89 (m, 2H), 5.56 (bd, *J* = 6.9 Hz, 1H), 4.31-4.39 (m, 1H), 2.68 (d, *J* = 6.4 Hz, 1H), 1.39 (s, 9H).

(R)-*S*-tert-Butyl

3-cyclohexyl-3-[(2-

26e

thienylsulfonyl)aminol]propanethioate (26e). Following

the typical procedure for the catalytic asymmetric Mannich reaction, the reaction between the imine **15e** (30.5 mg, 0.11 mmol) and the silyl enol ether **3** (81.8 mg, 0.33 mmol) afforded **26e** after chromatographic purification (*n*-hexanes:EtOAc : 3:1) as a white solid; yield = 29.9 mg (70%); 76% ee. Recrystallization from hexane-CH₂Cl₂ gave the product with 88% ee; mp 104-105 °C. $[\alpha]_D^{20} = -123$ (*c* 0.6, CHCl₃). HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 254.4 nm; (*S*)-**26e** t_R = 21.7 min; (*R*)-**26e** t_R = 34.2 min]. ¹H NMR: δ 7.60 (dd, *J* = 1.3, 3.7 Hz, 1H), 7.56 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.06 (dd, *J* = 3.7, 4.9 Hz, 1H), 5.33 (bd, *J* = 8.9 Hz, 1H), 3.43 - 3.34 (m, 1H), 2.64 (dd, *J* = 4.4 Hz, 15.9 Hz, 1H), 2.44 (dd, *J* = 5.8, 15.9 Hz, 1H), 1.83 - 1.48 (m, 2H), 1.20 - 1.09 (m, 2H). ¹³C NMR: δ 198.9, 131.9, 131.6, 130.1, 127.3, 56.7, 48.7, 44.8, 29.7, 29.4, 29.0, 26.1, 26.0. MS (EI) *m/z*: 258 (100) [*M*⁺-SO₂-(2-thienyl)], 242 (21), 190 (36), 176(31), 147(45), 95 (25).

(R) Methyl 3-phenyl-3-[(2-thienylsulfonyl)aminol]propanoate (27e).

27e

Following the typical procedure, the reaction of the imine **2e** (111.2 mg, 0.44 mmol) with the *tert*-butyldimethylsilyl enol ether of methyl acetate (288 μl, 1.32 mmol) afforded **27e** after chromatographic purification (*n*-hexanes:EtOAc : 5:1) as a light yellow solid; yield: 135 mg, (75%). mp = 123-125 °C. $[\alpha]_D^{20} = +209$ (*c* 0.7, CHCl₃), 80% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245.4 nm; (*S*)-**27e** t_R = 25.4 min; (*R*)-**27e** t_R = 30.0 min]. ¹H NMR: δ 7.45 (dd, *J* = 1.1, 4.9 Hz, 1H), 7.40 (dd, *J* = 1.1, 3.7 Hz, 1H), 7.20 - 7.12 (m, 5H), 6.91 (dd, *J* = 3.7, 4.9 Hz, 1H), 6.06 (bd, *J* = 7.8 Hz, 1H), 4.83 (q, *J* = 6.5 Hz, 1H), 3.56 (s, 3H), 2.88 (dd, *J* = 6.3, 15.9 Hz, 1H), 2.79 (dd, *J* = 6.3, 15.9 Hz, 1H). ¹³C NMR: δ 170.9, 141.3, 139.0, 132.3,

131.8, 128.5, 127.8, 127.1, 126.2, 54.6, 51.8, 41.1. MS (EI): m/z 325 (8.5) $[M^+]$, 294 (49.4), 252 (80.2), 178 (100), 146 (93).

(S) Methyl 2,2-dimethyl-3-phenyl-3-[(2-thienylsulfonyl)amino]propanoate (28e).

Following the typical procedure, the reaction of the imine **2e** (111.2 mg, 0.44 mmol) with the *tert*-butyldimethylsilyl enol ether of methyl isobutyrate (288 μ l, 1.32 mmol) afforded **28e** after chromatographic purification (*n*-hexanes:EtOAc : 4:1) as a light yellow solid; yield: 119 mg (77%); mp = 127–129 °C. $[\alpha]_D^{20} = +146$ (*c* 0.5, CHCl_3), 86 %ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 245.4 nm; (*R*)-**28e** t_R = 16.0 min; (*S*)-**28e** t_R = 19.1 min]. ^1H NMR: δ 7.30 (dd, J = 1.2, 4.9 Hz, 1H), 7.16 – 7.12 (m, 4H), 7.01 – 6.97 (m, 2H), 6.72 (dd, J = 3.7, 4.9 Hz, 1H), 6.72 (bs, 1H), 4.42 (s, 1H), 3.65 (s, 3H), 1.37 (s, 3H), 1.11 (s, 3H). ^{13}C NMR: δ 176.4, 141.7, 136.9, 131.8, 131.2, 127.9, 127.7, 127.6, 126.7, 65.0, 52.1, 47.0, 24.8, 22.5. EI $^+$ MS: 353 (43), 294 (100), 279 (67), 266 (50). Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_4\text{S}_2$: C, 54.37; H, 5.42; N, 3.96; S, 18.14. Found: C, 54.59; H, 5.59; N, 3.83; S, 18.30.

(R) 1,3-Diphenyl-3-(2-thienylsulfonyl)amino-1-propanone (29e).

Following the typical procedure, the reaction of the imine **2e** (111.2 mg, 0.44 mmol) with the trimethylsilyl enol ether of acetophenone (288 μ l, 1.32 mmol) afforded **29e** after chromatographic purification (*n*-hexanes:EtOAc : 5:1) as a light yellow solid; yield: 116 mg (71%); mp = 105–107 °C. $[\alpha]_D^{20} = +33$ (*c* 0.2, CHCl_3), 93% ee. HPLC Daicel Chiralpack OD [hexane/*i*-PrOH 90:10; 1 mL/min; 245.4 nm; (*R*)-**29e** t_R = 35.5 min; (*S*)-**29e** t_R = 55.8 min]. ^1H NMR: δ 7.84 – 7.81 (m, 2H), 7.55 (dt, J = 2.0, 7.4 Hz, 1H), 7.48 – 7.39 (m, 4H), 7.20 (m, 5H), 6.93 (dd, J = 3.7, 4.9 Hz, 1H), 5.96 (bd, J = 7.0 Hz, 1H), 4.98 (q, J = 6.2 Hz, 1H), 3.64 (dd, J = 5.4, 17.3 Hz, 1H), 3.49 (dd, J = 6.2,

17.3, 1H). ^{13}C NMR: δ 197.7, 141.2, 139.6, 133.6, 132.4, 131.8, 128.7, 128.6, 128.0, 127.1, 126.6, 54.7, 44.6. EI^+ MS: 251(20), 210(24), 207(57), 147(100). Elemental Analysis Calcd: C: 61.43, H: 4.61, N: 3.77, S: 15.31 Found: C: 61.14, H: 5.11, N: 3.39, S: 15.2.

(R) 3-Phenyl-1-(4-methoxyphenyl)-3-(2-thienylsulfonyl)amino-1-propanone (30e).

Following the typical procedure, the reaction of the imine **2e** (27.0 mg, 0.11 mmol) with the trimethylsilyl enol ether of 4-methoxyacetophenone (73.9 mg, 0.33 mmol) afforded **30e** after chromatographic purification (*n*-hexanes:EtOAc : 4:1) as a yellow solid; yield: 35.2 mg (80%); mp = 96-98 °C. $[\alpha]_{\text{D}}^{20} = -46$ (*c* 0.6, CHCl_3), 85% ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 254.1 nm; (*S*)-**30e** $t_{\text{R}} = 88.1$ min; (*R*)-**30e** $t_{\text{R}} = 94.0$ min]. ^1H NMR: δ 7.79 (d, $J = 8.8$ Hz, 2H), 7.45 (dd, $J = 1.1, 4.9$ Hz, 1H), 7.42 (dd, $J = 1.1, 3.7$ Hz, 1H), 7.21-7.17 (m, 5H), 6.91 (dd, $J = 3.8, 4.9$ Hz, 1H), 6.87 (d, $J = 8.8$ Hz, 2H), 6.14 (bd, $J = 7.0$ Hz, 1H), 4.96 (q, $J = 6.0$ Hz, 1H), 3.84 (s, 3H), 3.54 (dd, $J = 5.5, 17.0$ Hz, 1H), 3.40 (dd, $J = 6.1, 17.0$ Hz, 1H). ^{13}C NMR: δ 196.2, 163.9, 141.1, 139.8, 132.4, 131.8, 130.4, 129.5, 128.6, 127.7, 127.2, 126.6, 113.8, 55.5, 54.9, 44.2. MS (FAB^+): 402 (35) [$\text{M}^+ + 1$], 252 (33), 154 (63), 135 (100), 106 (10), 77 (17). HRMS calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_4\text{S}_2$ 402.0824; found 402.0834.

(R) 3-Phenyl-1-(2-naphthyl)-3-(2-thienylsulfonyl)amino-1-propanone (31e).

Following the typical procedure, the reaction of the imine **2e** (27.0 mg, 0.11 mmol) with the trimethylsilyl enol ether of acetophenone (78.8 mg, 0.33 mmol) afforded **31e** after chromatographic purification (*n*-hexanes:EtOAc : 6:1) as a white solid; yield: 41.7mg (90%); mp = 115 - 117 °C. $[\alpha]_{\text{D}}^{20} = -134$ (*c* 0.5, CHCl_3), 86 %ee. HPLC Daicel Chiralpack AD [hexane/*i*-PrOH 90:10; 1 mL/min; 254.1 nm; (*S*)-**31e** $t_{\text{R}} = 16.2$ min; (*R*)-**31e** $t_{\text{R}} = 20.1$ min]. ^1H -NMR

(300 MHz): δ 8.34 (s, 1H), 7.93 - 7.82 (m, 4H), 7.62 - 7.52 (m, 2H), 7.46 - 7.44 (m, 2H), 7.24 - 7.18 (m, 5H), 6.92 (dd, J = 3.8, 4.9 Hz, 1H), 6.00 (bd, J = 6.9 Hz, 1H), 5.04 (q, J = 6.2 Hz, 1H), 3.78 (dd, J = 5.7, 17.7 Hz, 1H), 3.62 (dd, J = 6.1, 17.7 Hz, 1H). ^{13}C -NMR (75 MHz): δ 197.6, 141.2, 139.6, 135.7, 133.6, 132.5, 132.3, 131.9, 130.0, 129.6, 128.8, 128.8, 128.6, 128.5, 127.8, 127.7, 127.1, 126.9, 126.6, 123.4, 54.8, 44.6.

Typical procedure for the deprotection of the 2-thienylsulfonamides:

(R) Methyl 3-amino-3-phenylpropanoate (32).ⁱⁱⁱ A solution of a >99% ee sample of **27e** (50 mg, 0.13 mmol) and Mg (31 mg, 1.3 mmol) in MeOH (5 mL) was stirred for 5 h at room temperature. Once the reaction was finished (TLC monitoring with EtOAc as eluent), the mixture was concentrated to dryness. The solid residue was dissolved in CH_2Cl_2 (10 mL) and washed with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) and the combined organic phase was dried (MgSO_4) and concentrated. The residue was purified by flash chromatography (EtOAc) to afford **32** as a colourless oil; yield: 19.3 mg (83%). $[\alpha]_{\text{D}}^{20}$ = +16 (c 0.5, CHCl_3), >99% ee. {litⁱⁱⁱ $[\alpha]_{\text{D}}^{20}$ = +20.9 (c 1.05, CHCl_3), enantiopure}. HPLC Daicel Chiralpack AS-H [hexane/ *i*-PrOH 60:40; 0.8 mL/min; 210 nm; (*S*)-**32** t_{R} = 6.7 min; (*R*)-**32** t_{R} = 9.2 min]. ^1H NMR: δ 7.37-7.25 (m, 5H), 4.28 (t, J = 6.5 Hz, 1H), 3.68 (s, 3H), 2.68 (s, 1H), 2.66 (s, 1H), 1.70 (bs, 2H). ^{13}C NMR: δ 172.5, 128.6, 128.5, 127.4, 126.2, 52.6, 51.7, 43.9.

(R) Methyl 3-amino-3(3-chlorophenyl)propanoate (33). Following the typical procedure, the reaction of a >99% ee sample of **20e** (50 mg, 0.12 mmol) with Mg (29.1 mg, 1.2 mmol) afforded after chromatographic purification (EtOAc) **33** as a colourless oil; yield: 21.7 mg (84%). $[\alpha]_{\text{D}}^{20}$ = + 9 (c 1, CHCl_3), >99% ee. ^1H NMR: δ 7.20-7.08 (m, 2H), 7.12 (s, 1H), 7.10-7.05 (m, 1H), 4.32 (bs, 1H), 3.70 (s, 3H), 2.70

(bs, 2H). ^{13}C NMR: δ 175.6, 129.7, 129.1, 128.6, 128.5, 127.4, 126.2, 52.6, 51.7, 43.9.

(R) Methyl 3-amino-2,2-dimethyl-3-phenylpropanoate

(34).^{iv} Following the typical procedure, the reaction of a 86% ee sample of **28e** (50 mg, 0.14 mmol) with Mg (34 mg, 1.4 mmol) afforded after chromatographic purification (EtOAc) **34** as a colourless oil; yield: 24.9 mg (87%). $[\alpha]_{\text{D}}^{20} = +26$ (c 0.33, 1N aq HCl), 86% ee {lit^{Error! Bookmark not defined.} $[\alpha]_{\text{D}}^{20} = +34.2$, 98% ee}. HPLC Daicel Chiralpack AS-H [hexane/*i*-PrOH 60:40; 0.8 mL/min; 210 nm; (*S*)-**34** $t_{\text{R}} = 5.2$ min; (*R*)-**34** $t_{\text{R}} = 96.1$ min] ^1H NMR: δ 7.30–7.25 (m, 5H), 4.32 (bs, 1H), 3.69 (s, 3H), 1.15 (s, 3H), 1.09 (s, 3H). ^{13}C NMR: δ 177.8, 128.5, 128.1, 127.8, 127.3, 51.8, 51.4, 29.7, 23.6, 19.4.

References

- i) The N-sulfonylimines **2a–d** were prepared following the same experimental procedure. For previous preparation of **2c** see: Trost, B. M.; Christofer, M. J. *Org. Chem.* **1991**, *56*, 6468. For previous preparation of **2d**, see: Esquivias, J.; Gómez Arrayás, R.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 629.
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- (iii) Hata, S.; Iguchi, M.; Iwasawa, T.; Yamada, K.-i.; Tomioka, K. *Org. Lett.* **2004**, *6*, 1721.
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X-ray structure of 4e^v

X-Ray data for compound **4e**

Table 1. Crystal data and structure refinement for **4e**.

Empirical formula	C ₁₇ H ₂₁ N O ₃ S ₃
Formula weight	383.53
Temperature	446(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 9.84780(10) Å $\alpha = 90^\circ$. b = 10.32280(10) Å $\beta = 90^\circ$. c = 18.1098(2) Å $\gamma = 90^\circ$.
Volume	1840.99(3) Å ³
Z	4
Density (calculated)	1.384 Mg/m ³
Absorption coefficient	3.810 mm ⁻¹
F(000)	808
Crystal size	0.20 x 0.20 x 0.10 mm ³
Theta range for data collection	4.88 to 71.25°.
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 12, -22 ≤ l ≤ 20
Reflections collected	18402
Independent reflections	3521 [R(int) = 0.0349]

Completeness to theta = 71.25°	99.1 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3521 / 0 / 283
Goodness-of-fit on F ²	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1469
R indices (all data)	R1 = 0.0545, wR2 = 0.1482
Absolute structure parameter	0.02(3)
Largest diff. peak and hole	2.125 and -0.969 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for **4e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	3072(1)	3496(1)	1894(1)	20(1)
S(2)	7813(1)	3421(1)	1717(1)	21(1)
S(3)	1146(1)	5509(1)	2389(1)	36(1)
C(1)	1708(4)	3984(4)	2439(2)	22(1)
C(2)	962(3)	3171(3)	3043(2)	14(1)
C(3)	21(5)	4058(6)	3337(3)	39(1)
C(4)	20(3)	5290(3)	3067(2)	14(1)
C(5)	4814(4)	4136(4)	2975(2)	16(1)
C(6)	4307(4)	3887(4)	3752(2)	19(1)
C(7)	4648(5)	2746(4)	4119(2)	23(1)
C(8)	4127(5)	2504(5)	4819(2)	30(1)
C(9)	3283(4)	3388(5)	5160(2)	32(1)
C(10)	2961(4)	4537(5)	4806(2)	33(1)
C(11)	3473(4)	4794(5)	4099(2)	26(1)
C(12)	6380(4)	4162(4)	2938(2)	19(1)
C(13)	6816(4)	4576(4)	2170(2)	18(1)
C(14)	7992(4)	3966(4)	748(2)	22(1)
C(15)	8620(5)	5299(4)	692(2)	24(1)
C(16)	8983(6)	2959(5)	426(3)	35(1)

C(17)	6628 (5)	3895 (5)	374 (3)	28 (1)
N(1)	4311 (3)	3146 (3)	2454 (2)	17 (1)
O(1)	3445 (3)	4604 (3)	1468 (2)	27 (1)
O(2)	2722 (3)	2298 (3)	1534 (2)	29 (1)
O(3)	6470 (3)	5616 (2)	1903 (2)	20 (1)

Table 3. Bond lengths [Å] and angles [°] for **4e**.

S(1)-O(1)	1.428 (3)
S(1)-O(2)	1.440 (3)
S(1)-N(1)	1.627 (3)
S(1)-C(1)	1.741 (4)
S(2)-C(13)	1.749 (4)
S(2)-C(14)	1.851 (4)
S(3)-C(4)	1.670 (4)
S(3)-C(1)	1.671 (4)
C(1)-C(2)	1.561 (5)
C(2)-C(3)	1.407 (7)
C(2)-H(2)	0.9300
C(3)-C(4)	1.362 (7)
C(3)-H(3)	1.04 (6)
C(4)-H(4)	0.9300
C(5)-N(1)	1.477 (5)
C(5)-C(6)	1.515 (5)
C(5)-C(12)	1.544 (5)
C(5)-H(5)	0.83 (4)
C(6)-C(7)	1.394 (6)
C(6)-C(11)	1.395 (6)
C(7)-C(8)	1.391 (6)
C(7)-H(7)	0.90 (5)
C(8)-C(9)	1.380 (7)
C(8)-H(8)	0.88 (5)
C(9)-C(10)	1.385 (7)
C(9)-H(9)	0.87 (5)
C(10)-C(11)	1.400 (6)
C(10)-H(10)	0.95 (5)

C(11)-H(11)	0.93(5)
C(12)-C(13)	1.517(5)
C(12)-H(12A)	1.01(4)
C(12)-H(12B)	0.95(4)
C(13)-O(3)	1.225(5)
C(14)-C(17)	1.507(6)
C(14)-C(15)	1.512(6)
C(14)-C(16)	1.540(6)
C(15)-H(15A)	0.99(6)
C(15)-H(15B)	0.96(5)
C(15)-H(15C)	0.73(6)
C(16)-H(16A)	0.95(7)
C(16)-H(16B)	1.00(6)
C(16)-H(16C)	0.93(6)
C(17)-H(17A)	0.94(6)
C(17)-H(17B)	0.87(6)
C(17)-H(17C)	0.91(6)
N(1)-H(1)	0.8600

O(1)-S(1)-O(2)	120.31(19)
O(1)-S(1)-N(1)	108.73(17)
O(2)-S(1)-N(1)	105.75(18)
O(1)-S(1)-C(1)	105.87(19)
O(2)-S(1)-C(1)	108.71(19)
N(1)-S(1)-C(1)	106.80(17)
C(13)-S(2)-C(14)	106.90(19)
C(4)-S(3)-C(1)	93.00(19)
C(2)-C(1)-S(3)	112.9(3)
C(2)-C(1)-S(1)	127.2(3)
S(3)-C(1)-S(1)	119.8(2)
C(3)-C(2)-C(1)	103.0(3)
C(3)-C(2)-H(2)	128.5
C(1)-C(2)-H(2)	128.5
C(4)-C(3)-C(2)	118.2(4)
C(4)-C(3)-H(3)	104(3)
C(2)-C(3)-H(3)	137(3)
C(3)-C(4)-S(3)	112.9(3)
C(3)-C(4)-H(4)	123.5

S (3) -C (4) -H (4)	123.5
N (1) -C (5) -C (6)	111.4 (3)
N (1) -C (5) -C (12)	108.6 (3)
C (6) -C (5) -C (12)	111.9 (3)
N (1) -C (5) -H (5)	104 (3)
C (6) -C (5) -H (5)	111 (3)
C (12) -C (5) -H (5)	110 (3)
C (7) -C (6) -C (11)	119.6 (4)
C (7) -C (6) -C (5)	120.5 (4)
C (11) -C (6) -C (5)	119.9 (4)
C (8) -C (7) -C (6)	119.9 (4)
C (8) -C (7) -H (7)	121 (3)
C (6) -C (7) -H (7)	120 (3)
C (9) -C (8) -C (7)	120.7 (4)
C (9) -C (8) -H (8)	125 (3)
C (7) -C (8) -H (8)	115 (3)
C (8) -C (9) -C (10)	119.8 (4)
C (8) -C (9) -H (9)	117 (3)
C (10) -C (9) -H (9)	123 (3)
C (9) -C (10) -C (11)	120.2 (4)
C (9) -C (10) -H (10)	122 (3)
C (11) -C (10) -H (10)	117 (3)
C (6) -C (11) -C (10)	119.8 (4)
C (6) -C (11) -H (11)	123 (3)
C (10) -C (11) -H (11)	117 (3)
C (13) -C (12) -C (5)	109.1 (3)
C (13) -C (12) -H (12A)	106 (2)
C (5) -C (12) -H (12A)	113 (2)
C (13) -C (12) -H (12B)	108 (2)
C (5) -C (12) -H (12B)	110 (2)
H (12A) -C (12) -H (12B)	110 (3)
O (3) -C (13) -C (12)	122.0 (3)
O (3) -C (13) -S (2)	124.6 (3)
C (12) -C (13) -S (2)	113.4 (3)
C (17) -C (14) -C (15)	112.2 (4)
C (17) -C (14) -C (16)	111.2 (4)
C (15) -C (14) -C (16)	109.3 (4)
C (17) -C (14) -S (2)	109.0 (3)

C(15)-C(14)-S(2)	112.3(3)
C(16)-C(14)-S(2)	102.4(3)
C(14)-C(15)-H(15A)	112(3)
C(14)-C(15)-H(15B)	118(3)
H(15A)-C(15)-H(15B)	105(4)
C(14)-C(15)-H(15C)	118(4)
H(15A)-C(15)-H(15C)	101(5)
H(15B)-C(15)-H(15C)	100(5)
C(14)-C(16)-H(16A)	111(4)
C(14)-C(16)-H(16B)	100(3)
H(16A)-C(16)-H(16B)	104(5)
C(14)-C(16)-H(16C)	109(4)
H(16A)-C(16)-H(16C)	120(6)
H(16B)-C(16)-H(16C)	110(5)
C(14)-C(17)-H(17A)	104(4)
C(14)-C(17)-H(17B)	114(4)
H(17A)-C(17)-H(17B)	111(5)
C(14)-C(17)-H(17C)	112(3)
H(17A)-C(17)-H(17C)	119(5)
H(17B)-C(17)-H(17C)	97(5)
C(5)-N(1)-S(1)	119.8(2)
C(5)-N(1)-H(1)	120.1
S(1)-N(1)-H(1)	120.1

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4e**.
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
<hr/>						
S(1)	18(1)	29(1)	14(1)	3(1)	-2(1)	-4(1)
S(2)	23(1)	20(1)	21(1)	1(1)	3(1)	4(1)
S(3)	33(1)	34(1)	41(1)	-2(1)	-3(1)	1(1)

C(1)	17(2)	27(2)	20(2)	7(2)	-4(2)	-5(2)
C(2)	9(1)	16(1)	18(1)	-7(1)	-9(1)	6(1)
C(3)	25(2)	69(3)	22(2)	10(2)	-5(2)	-16(2)
C(4)	9(1)	16(1)	18(1)	-7(1)	-9(1)	6(1)
C(5)	17(2)	17(2)	16(2)	4(1)	-1(1)	1(1)
C(6)	16(2)	23(2)	16(2)	0(1)	0(1)	-4(2)
C(7)	27(2)	23(2)	19(2)	-1(2)	-2(2)	-5(2)
C(8)	43(3)	30(2)	16(2)	4(2)	-4(2)	-12(2)
C(9)	28(2)	52(3)	15(2)	-4(2)	3(2)	-20(2)
C(10)	21(2)	56(3)	21(2)	-7(2)	3(2)	0(2)
C(11)	20(2)	37(2)	20(2)	-3(2)	-3(2)	5(2)
C(12)	15(2)	22(2)	19(2)	4(2)	-2(1)	-2(1)
C(13)	15(2)	21(2)	19(2)	-1(1)	0(1)	-4(1)
C(14)	24(2)	25(2)	18(2)	0(2)	5(2)	-1(2)
C(15)	23(2)	24(2)	24(2)	-1(2)	4(2)	0(2)
C(16)	35(3)	40(3)	31(3)	-4(2)	6(2)	8(2)
C(17)	27(2)	33(2)	24(2)	-2(2)	-1(2)	-9(2)
N(1)	17(2)	17(2)	18(2)	0(1)	0(1)	1(1)
O(1)	24(1)	36(2)	20(1)	9(1)	-1(1)	-4(1)
O(2)	29(2)	38(2)	20(1)	-5(1)	-5(1)	-4(1)
O(3)	24(1)	16(1)	20(1)	1(1)	3(1)	3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4e**.

	x	y	z	U(eq)
H(2)	1105	2312	3176	17
H(4)	-549	5940	3242	17
H(1)	4671	2387	2447	21
H(3)	-670(60)	4090(60)	3770(30)	45(16)
H(5)	4500(40)	4830(40)	2810(20)	1(8)
H(7)	5190(50)	2160(50)	3900(30)	19(12)

H(8)	4390(40)	1770(50)	5020(20)	12(10)
H(9)	3090(50)	3250(40)	5620(30)	13(10)
H(10)	2550(50)	5240(50)	5060(30)	29(13)
H(11)	3250(50)	5590(50)	3890(30)	25(12)
H(12A)	6810(40)	3290(40)	3030(20)	5(9)
H(12B)	6720(40)	4780(40)	3280(20)	3(9)
H(15A)	8830(60)	5530(50)	170(30)	31(13)
H(15B)	9440(50)	5470(40)	960(30)	18(11)
H(15C)	8210(60)	5860(60)	800(30)	29(15)
H(16A)	9890(80)	3100(70)	590(40)	60(20)
H(16B)	9000(60)	3250(50)	-100(30)	34(14)
H(16C)	8600(60)	2140(60)	460(30)	35(15)
H(17A)	6820(60)	4050(60)	-130(30)	38(15)
H(17B)	6220(60)	3160(60)	430(30)	29(14)
H(17C)	6000(60)	4400(50)	600(30)	28(13)

Table 6. Torsion angles [°] for **4e**.

C(4)-S(3)-C(1)-C(2)	0.2(3)
C(4)-S(3)-C(1)-S(1)	-175.6(2)
O(1)-S(1)-C(1)-C(2)	-176.1(3)
O(2)-S(1)-C(1)-C(2)	53.4(4)
N(1)-S(1)-C(1)-C(2)	-60.3(4)
O(1)-S(1)-C(1)-S(3)	-1.0(3)
O(2)-S(1)-C(1)-S(3)	-131.6(2)
N(1)-S(1)-C(1)-S(3)	114.7(2)
S(3)-C(1)-C(2)-C(3)	0.8(4)
S(1)-C(1)-C(2)-C(3)	176.2(3)
C(1)-C(2)-C(3)-C(4)	-1.8(5)
C(2)-C(3)-C(4)-S(3)	2.1(5)
C(1)-S(3)-C(4)-C(3)	-1.2(3)
N(1)-C(5)-C(6)-C(7)	61.4(5)
C(12)-C(5)-C(6)-C(7)	-60.4(5)
N(1)-C(5)-C(6)-C(11)	-117.5(4)
C(12)-C(5)-C(6)-C(11)	120.7(4)
C(11)-C(6)-C(7)-C(8)	1.7(6)
C(5)-C(6)-C(7)-C(8)	-177.2(4)

C(6)-C(7)-C(8)-C(9)	-0.6(6)
C(7)-C(8)-C(9)-C(10)	-0.7(7)
C(8)-C(9)-C(10)-C(11)	0.9(7)
C(7)-C(6)-C(11)-C(10)	-1.5(6)
C(5)-C(6)-C(11)-C(10)	177.4(4)
C(9)-C(10)-C(11)-C(6)	0.2(6)
N(1)-C(5)-C(12)-C(13)	63.5(4)
C(6)-C(5)-C(12)-C(13)	-173.1(3)
C(5)-C(12)-C(13)-O(3)	58.5(5)
C(5)-C(12)-C(13)-S(2)	-120.5(3)
C(14)-S(2)-C(13)-O(3)	-8.4(4)
C(14)-S(2)-C(13)-C(12)	170.5(3)
C(13)-S(2)-C(14)-C(17)	-67.1(3)
C(13)-S(2)-C(14)-C(15)	57.9(3)
C(13)-S(2)-C(14)-C(16)	175.0(3)
C(6)-C(5)-N(1)-S(1)	103.4(3)
C(12)-C(5)-N(1)-S(1)	-132.8(3)
O(1)-S(1)-N(1)-C(5)	56.4(3)
O(2)-S(1)-N(1)-C(5)	-173.1(3)
C(1)-S(1)-N(1)-C(5)	-57.5(3)

Symmetry transformations used to generate equivalent atoms:

2d

7e

11e

13e

15e

18e

21e

24e

25e

26e

28e

29e