Asymmetric Decarboxylative Claisen Rearrangement Reactions of Sulfoximine-substituted Allylic Tosylacetic esters.

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SUPPORTING INFORMATION

General experimental:

All reactions were monitored by ^1H NMR or by thin-layer chromatography using precoated aluminium-backed plates (Merck Kieselgel 60 F254) and are visualised by UV light and/or vaporisation of a solution of KMnO_4 . Merck Kieselgel silica gel (230–400 mesh) was used for flash chromatography.

• Preparation of sulfoximines 3a–g , 4a–b , 6	S3–S8
• General procedure for the carboxylation, preparation of acids 7a–h	S9–S12
• General procedure for the esterification, preparation of esters 8a–n	S13–S22
• Decarboxylative Claisen rearrangement reaction	S23–S36
• NMR spectra for the rearranged products 9a–f , 9h–j , 9m–n	S37–S49
• Crystal data and structure refinement for (<i>S_S</i> , 2 <i>S</i>)- 9i and (<i>S_S</i> , 3 <i>R</i>)- 9m	S50–S53

Preparation of (±)-*S*-methyl-*S*-phenylsulfoximine 3a.

For the preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(4-toluenesulfonyl)sulfilimine, see: Johnson, C. R.; Mori, K.; Nakanishi, A. *J. Org. Chem.* **1979**, 44, 2065–2067.

For conversion of the sulfilimine into (±)-*S*-methyl-*S*-phenyl-*N*-(4-toluenesulfonyl)sulfoximine, see: Veale, H. S.; Levin, J.; Swern, D. *Tetrahedron. Lett.* **1978**, 503–506.

For the detosylation of the protected sulfoximine, see: Cram, D. J.; Day, J.; Rayner, D. R.; Von Schriltz, D. M.; Duchamp, D. J.; Garwood, D. C. *J. Am. Chem. Soc.* **1970**, 92, 7369–7384.

Resolution of (±)-*S*-methyl-*S*-phenylsulfoximine 3a, preparation of (+)-(*S*_S)-*S*-methyl-*S*-phenylsulfoximine (*S*_S)-3a.

Brandt, J; Gäis, H.-J. *Tetrahedron: Asymmetry* **1997**, 8, 909–912.

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(4-toluenesulfonyl)sulfoximine 3b.

Johnson, C. R.; Kirchoff, R. A.; Reischer, R. J.; Katekar, G. F. *J. Am. Chem. Soc.* **1973**, 95, 4287–4291.

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine 3c.

Craig, D; Geach, N. J.; Pearson, C. J.; Slawin, A. M. Z., White, A. J. P., Williams, D. J. *Tetrahedron* **1995**, *51*, 6071–6098.

Preparation of (+)-(*S*_S)-*S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S*_S)-3c.

Trost, B. M.; Matsuoka, R. T. *Synlett* **1992**, 27–30.

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine 3d.

To a solution of (±)-*S*-methyl-*S*-phenylsulfoximine **3a** (547 mg, 3.53 mmol) in pyridine (2 mL) was added, at 0 °C under N₂, 1-naphthalenesulfonyl chloride (800 mg, 3.53 mmol, 1 equiv). The reaction was stirred 15 h at room temperature and then diluted with CH₂Cl₂, washed with a 5% aqueous solution of CuSO₄, an aqueous solution of NaHCO₃, brine, dried (MgSO₄), and concentrated under reduced pressure. Recrystallisation gave (±)-*S*-methyl-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine **3d** (891 mg, 73%) as a colorless solid: mp 143–144 °C (EtOH); R_f 0.26 (50% EtOAc–petroleum ether); ¹H NMR (270 MHz, CDCl₃) δ 8.84 (1H, d, *J* 8.5 Hz), 8.17 (1H, d, *J* 7.0 Hz), 7.95 (1H, d, *J* 8.5 Hz), 7.85 (3H, m), 7.53 (6H, m), 3.34 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 138.9, 137.8, 134.4, 134.2, 133.8, 129.6, 128.7,

127.9, 127.4, 127.3, 126.7, 125.8, 124.2, 46.4; MS (CI) m/z : 363 $[M+NH_4]^+$, 346 $[M+H]^+$; HMRS (CI) m/z calcd for $[C_{17}H_{15}NO_3S_2+NH_4]^+$: 346.0572, found: 346.0564; Anal. calcd for $C_{17}H_{15}NO_3S_2$: C, 59.11; H, 4.38; N, 4.05; found: C, 59.11; H, 4.30; N, 3.96.

Preparation of ($\pm$)-*S*-methyl-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine **3e.**

Craig, D; Geach, N. J.; Pearson, C. J.; Slawin, A. M. Z., White, A. J. P., Williams, D. J. *Tetrahedron* **1995**, *51*, 6071–6098.

Preparation of ($\pm$)-*S*-methyl-*S*-phenyl-*N*-[2-(trifluoromethoxy)benzenesulfonyl]-sulfoximine **3f.**

To a solution of ($\pm$)-*S*-methyl-*S*-phenylsulfoximine **3a** (280 mg, 1.81 mmol) in pyridine (5 mL) was added, at 0 °C under N_2 , 2-(trifluoromethoxy)benzenesulfonyl chloride (470 mg, 1.81 mmol, 1 equiv). The reaction was heated at 70 °C for 2 h, then allowed to cool and diluted with CH_2Cl_2 , washed with a 5% aqueous solution of $CuSO_4$, an aqueous solution of $NaHCO_3$, brine, dried ($MgSO_4$), and concentrated under reduced pressure. Recrystallisation gave ($\pm$)-*S*-methyl-*S*-phenyl-*N*-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine **3f** (495 mg, 72%) as a colorless solid: mp 90–92 °C (EtOH); R_f 0.38 (50% EtOAc–petroleum ether); ^{19}F NMR (376 MHz, $CDCl_3$) δ 54.7 (3F, d, J 1.5 Hz, CF_3), 1H NMR (270 MHz, $CDCl_3$) δ 7.99 (3H, m), 7.68 (1H, t, J 7.0 Hz), 7.57 (3H, m), 7.33 (2H, m), 3.42 (3H, s); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 146.2, 138.2, 135.7, 134.6, 134.0, 129.8, 127.4, 126.4, 120.5 (q, J 252.0 Hz, CF_3), 120.4, 46.6; MS (CI) m/z : 397 $[M+NH_4]^+$, 380 $[M+H]^+$; HMRS (CI) m/z calcd for $[C_{14}H_{12}F_3NO_4S_2+NH_4]^+$: 397.0504, found: 397.0485; Anal. calcd for $C_{14}H_{12}F_3NO_4S_2$: C, 44.32; H, 3.19; N, 3.69; found: C, 44.50; H, 3.06; N, 3.57.

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl] sulfoximine 3g.

To a solution of (±)-*S*-methyl-*S*-phenylsulfoximine **3a** (307 mg, 1.98 mmol) in pyridine (2 mL) was added, at 0 °C under N₂, 2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl chloride (738 mg, 1.98 mmol, 1 equiv). The reaction was stirred 20 h at room temperature and then diluted with CH₂Cl₂, washed with a 5% aqueous solution of CuSO₄, an aqueous solution of NaHCO₃, brine, dried (MgSO₄), and concentrated under reduced pressure. Recrystallisation from absolute EtOH gave (±)-*S*-methyl-*S*-phenyl-*N*-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl] sulfoximine **3g** (693 mg, 71%) as a colorless solid, mp 118–120 °C (EtOH); R_f 0.39 (50% EtOAc–petroleum ether); ¹⁹F NMR (376 MHz, CDCl₃) δ 72.5 (3F, t, *J* 8.5 Hz), -73.0 (3F, t, *J* 8.0 Hz); ¹H NMR (270 MHz, CDCl₃) δ 7.96 (2H, d, *J* 7.0 Hz), 7.68 (1H, tt, *J* 2.0, 7.5 Hz), 7.56 (2H, m), 7.46 (1H, d, *J* 3.0 Hz), 4.45 (2H, qd, *J* 3.0, 8.0 Hz), 4.29 (2H, q, *J* 8.0 Hz), 3.41 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 152.3, 150.1, 138.1, 134.6, 129.8, 127.5, 123.3 (q, *J* 278.0 Hz, CF₃), 123.1 (q, *J* 278.0 Hz, CF₃), 121.4, 118.5, 115.2, 68.7 (q, *J* 36.0 Hz), 66.5 (q, *J* 36.0), 46.4; MS (CI) *m/z*: 509 [M+NH₄]⁺, 492 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₁₇H₁₅F₆NO₅S₂+H]⁺: 492.0296, found: 492.0311; Anal. calcd for C₁₇H₁₅F₆NO₅S₂: C, 41.55; H, 3.08; N, 2.86; found: C, 41.68; H, 2.99; N, 2.68.

Preparation of (±)-*S*-mesityl-*S*-methylsulfoximine 4a.

For the preparation of *S*-methyl-*S*-mesitylsulfoxide, see: Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc.* **1973**, 95, 7418–7423.

For the oxidation of sulfoxide into *S*-methyl-*S*-mesityl sulfoximine, see: Johnson, C.R.; Haake, M.; Schroeck, C.W. *J. Am. Chem. Soc.* **1970**, 92, 6594–6598.

Preparation of (±)-*S*-mesityl-*S*-methyl-*N*-(4-toluenesulfonyl)sulfoximine 4b.

To a solution of (±)-*S*-methyl-*S*-mesitylsulfoximine **4a** (393 mg, 1.99 mmol) in pyridine (5 mL) was added, at room temperature under N₂, 4-toluenesulfonyl chloride (380 mg, 1.99 mmol, 1 equiv). The reaction was heated at 70 °C for 7h, then allowed to cool to room temperature and diluted with CH₂Cl₂, washed with a 5% aqueous solution of CuSO₄, an aqueous solution of NaHCO₃, brine, dried (MgSO₄), and concentrated under reduced pressure. Recrystallisation gave (±)-*S*-methyl-*S*-mesityl-*N*-(4-toluenesulfonyl)sulfoximine **4b** (364 mg, 52%) as a brown solid, mp 165–167 °C (EtOH); *R*_f 0.28 (33% EtOAc–petroleum ether); ¹H NMR (270 MHz, CDCl₃) δ 7.77 (2H, d, *J* 8.5 Hz), 7.21 (2H, d, *J* 8.5 Hz, 2H), 6.95 (2H, s, 2H), 3.41 (3H, s), 2.65 (6H, s), 2.37 (3H, s, CH₃-*para* Ts), 2.29 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 144.0, 142.6, 140.9, 139.7, 133.0, 129.2, 126.7, 46.7, 23.0, 21.6, 21.0; MS (CI) *m/z*: 369 [M+NH₄]⁺, 352 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₁₇H₂₁NO₃S₂+H]⁺: 352.1041, found: 352.1054; Anal. calcd for C₁₇H₂₁NO₃S₂: C, 58.03; H, 6.02; N, 4.00; found: C, 57.93; H, 6.04; N, 3.89.

Preparation of (±)-*S*-methyl-*S*-(2-pyridyl)-*N*-(4-toluenesulfonyl)sulfoximine **6**.

For the preparation of sulfilimine **5**, see: Furukawa, N.; Takahashi, F.; Kawai, T.; Kishimoto, K.; Ogawa, S.; Oae, S. *Phosphorus, Sulfur and the Related Elements* **1983**, *16*, 167–180.

To a suspension of (±)-*S*-methyl-*S*-(2-pyridyl)-*N*-(4-toluenesulfonyl)sulfilimine **5** (102 mg, 0.35 mmol) and RuO₂·xH₂O (1 mg, 0.007 mmol, 0.02 equiv) in a CCl₄–MeCN mixture (1:1, 2 mL) was added a solution of NaIO₄ (148 mg, 0.69 mmol, 2 equiv) in H₂O (2 mL). After 1 h of stirring at rt, the two layers were separated. The aqueous layer was extracted several times with CH₂Cl₂, the organic layers were combined and stirred overnight with *i*-PrOH (1 mL). The solution was then filtered through Celite and the filtrate was dried (MgSO₄). Evaporation

of the solvent under reduced pressure and chromatography on silica gel (40% ether-CH₂Cl₂) afforded (*±*)-*S*-methyl-*S*-(2-pyridyl)-*N*-(4-toluenesulfonyl)sulfoximine **6** (96 mg, 89%) as a colorless solid, mp 134–136 °C (Et₂O); *R*_f 0.62 (100% EtOAc); ¹H NMR (270 MHz, CDCl₃) δ 8.67 (1H, d, *J* 4.5 Hz, H-*meta* pyridine), 8.21 (1H, d, *J* 9.5 Hz, H pyridine), 7.97 (1H, dt, *J* 1.5, 7.5 Hz, H pyridine), 7.79 (2H, d, *J* 8.5 Hz), 7.57 (1H, ddd, *J* 1.0, 4.5, 7.5 Hz), 7.22 (2H, d, *J* 8.5 Hz), 3.52 (3H, s), 2.37 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 150.2, 143.0, 140.5, 138.6, 129.3, 128.0, 126.7, 123.0, 41.6, 21.6; MS (CI) *m/z*: 311 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₁₃H₁₄N₂O₃S₂+H]⁺: 311.0524, found: 311.0525; Anal. calcd for C₁₃H₁₄N₂O₃S₂: C, 50.30; H, 4.55; N, 9.06; found: C, 50.15; H, 4.36; N, 8.94.

General procedure for carboxylation: A solution of sulfoximine **3b–g**, **4b** or **6** in THF at –78 °C under N₂ was treated with *n*-BuLi in hexanes (1.1 equiv). After stirring for 1 h at this temperature, dry CO₂ was bubbled through the solution for 30 min. The cooling bath was then removed, the solution was diluted with CH₂Cl₂ or a solution of hexane and ether (1:1), hydrolysed with water and the two layers were separated. The aqueous layer was acidified with aq HCl until a colorless precipitate appeared. The suspension was extracted several times with CH₂Cl₂ or a solution of hexane and ether (1:1), the organic layer was then dried (MgSO₄), concentrated under reduced pressure, and dried *in vacuo* to give acids **7a–h** which were used in the next step without further purification.

(±)-*S*-Carboxymethyl-*S*-phenyl-*N*-(4-toluenesulfonyl)sulfoximine 7a.

According to the general procedure, a solution of (±)-*S*-methyl-*S*-phenyl-*N*-(4-toluenesulfonyl)sulfoximine **3b** (752 mg, 2.43 mmol) in THF (9 mL) reacted with *n*-BuLi (1.95 mL, 2.68 mmol, 1.1 equiv) and CO₂. After work-up (extraction with CH₂Cl₂), (±)-*S*-carboxymethyl-*S*-phenyl-*N*-(4-toluenesulfonyl)sulfoximine **7a** (680 mg, 79%) was obtained as a colorless oil; ¹H NMR (270 MHz, CDCl₃) δ 7.93 (2H, d, *J* 8.0 Hz), 7.78 (2H, d, *J* 8.0 Hz), 7.60 (1H, t, *J* 8.0 Hz), 7.47 (2H, d, *J* 8.0 Hz), 7.19 (2H, d, *J* 8.0 Hz), 7.09 (1H, bs), 4.68 (1H, d, *J* 15.0 Hz), 4.58 (1H, d, *J* 15.0 Hz), 2.32 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 163.5, 143.5, 140.0, 135.6, 135.1, 129.6, 129.5, 128.7, 126.7, 61.3, 21.6.

(+)-(*S*_S)-*S*-Carboxymethyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S*_S)-7b.

According to the general procedure, a solution of (+)-(*S*_S)-*S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S*_S)-**3c** (270 mg, 0.64 mmol) in THF (5 mL) reacted with *n*-BuLi (440 μL, 0.70 mmol, 1.1 equiv) and CO₂. After work-up (extraction with a 1:1 mixture of diethyl ether and hexane), (+)-(*S*_S)-*S*-carboxymethyl-*S*-mesityl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S*_S)-**7b** (238 mg, 80%) was obtained as a colorless oil; [α]_D²⁰ +46.1 (*c* 0.76, CHCl₃); ¹H NMR (270 MHz, CDCl₃) δ 9.22 (1H, bs), 8.00 (2H, d, *J* 7.0 Hz), 7.68 (1H, t, *J* 7.5 Hz), 7.55 (2H, t, *J* 7.0 Hz), 7.10 (2H, s), 4.69 (1H, d, *J* 15.0 Hz), 4.62 (1H, d, *J* 15.0 Hz), 4.32 (2H, sept, *J* 6.5 Hz), 2.85 (1H, sept, *J* 6.5 Hz), 1.22 (6H, d, *J* 6.5 Hz), 1.21 (6H, d, *J* 6.5 Hz), 1.16 (6H, d, *J* 6.5 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 164.1, 152.2, 149.2, 135.0, 129.7, 129.6, 128.7, 127.1, 123.6, 61.9, 34.2, 29.4, 24.8, 24.6, 23.7.

(±)-*S*-Carboxymethyl-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine 7c.

According to the general procedure, a solution of (±)-*S*-methyl-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine **3d** (848 mg, 2.46 mmol) in THF (20 mL) reacted with *n*-BuLi (1.9 mL, 2.70 mmol, 1.1 equiv) and CO₂. After work-up (extraction with CH₂Cl₂), (±)-*S*-carboxymethyl-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine **7c** (496 mg, 52%) was obtained as a colorless oil; ¹H NMR (270 MHz, CDCl₃) δ 9.90 (1H, bs), 8.79 (1H, d, *J* 8.5 Hz), 8.18 (1H, d, *J* 7.5 Hz), 7.95 (1H, d, *J* 8.0 Hz), 7.84 (3H, m), 7.40 (6H, m), 4.68 (1H, d, *J* 15.0 Hz), 4.54 (1H, d, *J* 15.0 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 163.5, 138.5, 135.6, 134.9, 134.1, 129.5, 128.7, 128.6, 128.3, 128.0, 127.5, 126.8, 125.6, 124.2, 67.9.

(±)-*S*-Carboxymethyl-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine 7d.

According to the general procedure, a solution of (±)-*S*-methyl-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine **3e** (280 mg, 0.98 mmol) in THF (3 mL) reacted with *n*-BuLi (767 μL, 1.07 mmol, 1.1 equiv) and CO₂. After work-up (extraction with CH₂Cl₂), (±)-*S*-carboxymethyl-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine **7d** (79 mg, 24%) was obtained as a pale yellow oil; ¹H NMR (270 MHz, CDCl₃) δ 8.25 (1H, bs), 8.03 (2H, d, *J* 7.5 Hz), 7.78 (1H, t, *J* 7.5 Hz), 7.07 (2H, t, *J* 7.5 Hz), 4.64 (2H, d, *J* 2.0 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 163.2, 136.0, 134.9, 130.1, 128.7, 127.4, 119.1 (q, *J* 325.0 Hz, CF₃), 61.6.

(±)-S-Carboxymethyl-S-phenyl-N-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine 7e.

According to the general procedure, a solution of (±)-S-methyl-S-phenyl-N-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine **3f** (429 mg, 1.13 mmol) in THF (8 mL) reacted with *n*-BuLi (889 μ L, 1.24 mmol, 1.1 equiv) and CO₂. After work-up (extraction with CH₂Cl₂), (±)-S-carboxymethyl-S-phenyl-N-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine **7e** (200 mg, 42%) was obtained as a colorless oil; ¹H NMR (270 MHz, CDCl₃) δ 8.67 (1H, bs), 7.99 (3H, m), 7.68 (1H, t, *J* 7.5 Hz), 7.54 (3H, t, *J* 8.0 Hz), 7.32 (2H, m), 4.70 (1H, d, *J* 15.0 Hz), 4.58 (1H, d, *J* 15.0 Hz, CHaHbCO₂); ¹³C NMR (67.5 MHz, CDCl₃) δ 163.8, 146.1, 135.5, 135.2, 134.4, 129.8, 129.6, 129.4, 128.7, 126.6, 125.0, 120.5, 120.4 (q, *J* 261.0 Hz, CF₃), 66.0.

(±)-S-Carboxymethyl-S-phenyl-N-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]sulfoximine 7f.

According to the general procedure, a solution of (±)-S-methyl-S-phenyl-N-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]sulfoximine **3g** (545 mg, 1.11 mmol) in THF (10 mL) reacted with *n*-BuLi (1.0 mL, 1.22 mmol, 1.1 equiv) and CO₂. After work-up (extraction with CH₂Cl₂), (±)-S-carboxymethyl-S-phenyl-N-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]sulfoximine **7f** (60 mg, 10%) was obtained as a colorless oil; ¹H NMR (270 MHz, CDCl₃) δ 7.98 (2H, d, *J* 7.5 Hz), 7.70 (1H, t, *J* 7.5 Hz), 7.56 (2H, t, *J* 8.0 Hz), 7.48 (1H, d, *J* 3.5 Hz), 7.07 (2H, m), 4.68 (1H, d, *J* 15.0 Hz), 4.59 (1H, d, *J* 15.0 Hz), 4.43 (2H, m), 4.30 (2H, q, *J* 8.0 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 163.6, 152.3, 150.1, 135.6, 135.3, 135.0, 133.9, 129.6, 128.7, 125.2, 121.9, 119.6 (q, *J* 285.0 Hz, CF₃), 118.9 (q, *J* 285.0 Hz, CF₃), 118.1, 115.2, 68.3 (q, *J* 36.0 Hz), 66.6 (q, *J* 36.0 Hz), 61.0.

(±)-S-Carboxymethyl-S-mesityl-N-(4-toluenesulfonyl)sulfoximine 7g.

According to the general procedure, a solution of (±)-S-methyl-S-mesityl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine **4b** (225 mg, 0.64 mmol) in THF (5 mL) reacted with *n*-BuLi (440 μ L, 0.70 mmol, 1.1 equiv) and CO₂. After work-up (extraction with a 1:1 mixture of diethyl ether and hexane), (±)-S-carboxymethyl-S-mesityl-N-(4-toluenesulfonyl)sulfoximine **7g** (102 mg, 42%) was obtained as a colorless oil; ¹H NMR (270 MHz, CDCl₃) δ 7.74 (2H, d, *J* 8.0 Hz), 7.50 (1H, bs), 7.19 (2H, d, *J* 8.0 Hz), 6.92 (2H, s), 4.76 (1H, d, *J* 15.0 Hz), 4.47 (1H, d, *J* 15.0 Hz), 2.59 (6H, s), 2.36 (3H, s), 2.26 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 164.0, 144.7, 143.1, 140.5, 133.1, 129.3, 126.7, 61.4, 22.8, 21.6, 21.1.

(±)-S-Carboxymethyl-S-(2-pyridyl)-N-(4-toluenesulfonyl)sulfoximine 7h.

According to the general procedure, a solution of (±)-S-methyl-S-(2-pyridyl)-N-(4-toluenesulfonyl)sulfoximine **6** (1.5 g, 4.43 mmol) in THF (15 mL) reacted with *n*-BuLi (3.48 mL, 4.88 mmol, 1.1 equiv) and CO₂. After work-up (extraction with CH₂Cl₂), (±)-S-carboxymethyl-S-(2-pyridyl)-N-(4-toluenesulfonyl)sulfoximine **7h** (1.03 g, 61%) was obtained as a pale solid; ¹H NMR (270 MHz, CDCl₃) δ 9.15 (1H, bs), 8.67 (1H, d, *J* 8.0 Hz), 8.19 (1H, d, *J* 8.0 Hz), 7.98 (1H, td, *J* 5.0, 9.0 Hz), 7.78 (2H, d, *J* 8.0 Hz), 7.58 (1H, dd, *J* 5.0, 9.0 Hz), 7.23 (2H, d, *J* 8.0 Hz), 4.95 (1H, d, *J* 15.5 Hz), 4.81 (1H, d, *J* 15.5 Hz), 2.38 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 163.7, 154.7, 150.2, 143.3, 140.1, 138.8, 129.4, 128.2, 126.7, 124.1, 56.5, 21.6.

General procedure for the esterification of acids 7: A solution of acid **7**, allylic alcohol (1 equiv) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) (1 equiv) in CH₂Cl₂ was stirred 1 h at 0 °C and 15 h at room temperature under N₂. The solution was then diluted with CH₂Cl₂, washed with water and dried (MgSO₄). Evaporation of the solvent under reduced pressure and chromatography on silica gel afforded the corresponding ester **8**.

(±)-S-(3-Phenyl-2-propenyloxycarbonylmethyl)-S-phenyl-N-(4-toluenesulfonyl)sulfoximine 8a.

According to the general procedure, (±)-S-carboxymethyl-S-phenyl-N-(4-toluenesulfonyl)sulfoximine **7a** (229 mg, 0.649 mmol) was esterified with cinnamyl alcohol (90 mg, 0.649 mmol, 1 equiv), and EDCI (124 mg, 0.649 mmol, 1 equiv) in CH₂Cl₂ (3 mL). Chromatography (50% EtOAc–petroleum ether) yielded (±)-S-(3-phenyl-2-propenyloxycarbonylmethyl)-S-phenyl-N-(4-toluenesulfonyl)sulfoximine **8a** (243 mg, 79%) as a colorless solid, mp 95–97 °C (EtOH); *R_f* 0.20 (25% EtOAc–petroleum ether); IR ν_{CO} (film) 1742 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.97 (2H, d, *J* 8.0 Hz), 7.87 (2H, d, *J* 8.0 Hz), 7.62 (1H, t, *J* 8.0 Hz), 7.49 (2H, t, *J* 8.0 Hz), 7.33–7.22 (7H, m), 6.57 (1H, d, *J* 16.0 Hz), 6.07 (1H, td, *J* 6.5, 16.0), 4.80 (1H, d, *J* 14.5 Hz), 4.68 (2H, d, *J* 6.5 Hz), 4.61 (1H, d, *J* 14.5 Hz), 2.37 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) 161.5, 143.2, 135.9, 134.9, 129.5, 129.4, 128.8, 128.7, 128.5, 126.8, 121.3, 67.1, 61.5, 21.6; Anal. calcd for C₂₄H₂₃NO₅S₂: C, 61.39; H, 4.94; N, 2.98; found: C, 61.47; H, 4.88; N, 2.93.

(+)-(S_S)-S-Phenyl-S-(3-phenyl-2-propenyloxycarbonylmethyl)-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-8b.

According to the general procedure, (+)-(S_S)-S-carboxymethyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-**7b** (610 mg, 1.31 mmol) was esterified with cinnamyl alcohol (176 mg, 1.31 mmol, 1 equiv), and EDCI (251 mg, 1.31 mmol, 1 equiv) in

CH₂Cl₂ (10 mL). Chromatography (35% EtOAc–petroleum ether) yielded (+)-(*S_S*)-*S*-phenyl-*S*-(3-phenyl-2-propenyloxycarbonylmethyl)-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-**8b** (550 mg, 72%) as a colorless oil, *R_f* 0.67 (33% EtOAc–petroleum ether); [α]_D²⁰ +24.9 (*c* 1.00, acetone); IR ν_{CO} (film) 1743 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.97 (2H, d, *J* 8.0 Hz), 7.60 (1H, t, *J* 7.5 Hz), 7.47 (2H, t, *J* 8.0 Hz), 7.32 (5H, m, Ph), 7.13 (2H, s), 6.57 (1H, d, *J* 16.0 Hz), 6.09 (1H, td, *J* 7.0, 16.0 Hz), 4.74 (1H, d, *J* 14.5 Hz), 4.67 (2H, d, *J* 7.0 Hz), 4.64 (1H, d, *J* 14.5 Hz), 4.39 (2H, sept, *J* 6.5 Hz), 2.86 (1H, sept, *J* 6.5 Hz), 1.22 (6H, d, *J* 6.5 Hz), 1.21 (6H, d, *J* 6.5 Hz), 1.16 (6H, d, *J* 6.5 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.5, 152.3, 149.1, 137.5, 137.1, 136.4, 135.8, 135.7, 134.8, 129.4, 128.7, 128.5, 126.8, 123.5, 121.5, 67.0, 62.0, 34.2, 29.4, 24.8, 24.7, 23.7; Anal. calcd for C₃₂H₃₉NO₅S₂: C, 66.06; H, 6.76; N, 2.34; found: C, 65.93; H, 6.81; N, 2.34.

(±)-*S*-Phenyl-*S*-(3-phenyl-2-propenyloxycarbonylmethyl)-*N*-1-naphthalenesulfonyl-sulfoximine 8c.

According to the general procedure, (±)-*S*-carboxymethyl-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine **7c** (496 mg, 1.27 mmol) was esterified with cinnamyl alcohol (170 mg, 1.27 mmol, 1 equiv), and EDCI (216 mg, 1.27 mmol, 1 equiv) in CH₂Cl₂ (10 mL). Chromatography (40% EtOAc–petroleum ether) yielded (±)-*S*-phenyl-*S*-(3-phenyl-2-propenyloxycarbonylmethyl)-*N*-(1-naphthalenesulfonyl)sulfoximine **8c** (374 mg, 58%) as a colorless moss, *R_f* 0.32 (25% EtOAc–petroleum ether); IR ν_{CO} (film) 1743 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 8.86 (1H, d, *J* 8.5 Hz), 8.26 (1H, dd, *J* 1.0, 7.5 Hz), 7.96 (1H, d, *J* 8.0 Hz), 7.85 (3H, m), 7.59 (1H, ddd, *J* 1.5, 7.0, 8.5 Hz), 7.53 (2H, m), 7.35 (3H, m), 7.29 (5H, m, 5H), 6.48 (1H, d, *J* 16.0 Hz), 5.94 (1H, td, *J* 6.5, 16.0 Hz), 4.71 (1H, d, *J* 14.5), 4.61 (1H, d, *J* 14.5 Hz), 4.56 (2H, dt, *J* 1.0, 6.5 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.2, 138.9, 135.8, 135.7, 134.9, 134.2, 134.0, 129.4, 128.8, 128.6, 128.4, 128.0, 127.5, 126.8, 125.7, 124.2, 121.3, 67.1, 61.5; Anal. calcd for C₂₇H₂₃NO₅S₂: C, 64.14; H, 4.59; N, 2.77; found: C, 64.27; H, 4.39; N, 2.69.

(±)-S-Phenyl-S-(3-phenyl-2-propenyloxycarbonylmethyl)-N-(trifluoromethylsulfonyl)sulfoximine 8d.

According to the general procedure, (±)-S-carboxymethyl-S-phenyl-N-(trifluoromethylsulfonyl)sulfoximine **7d** (160 mg, 0.483 mmol) was esterified with cinnamyl alcohol (65 mg, 0.483 mmol, 1 equiv), and EDCI (93 mg, 0.483 mmol, 1 equiv) in CH₂Cl₂ (2 mL). Chromatography (40% EtOAc–petroleum ether) yielded (±)-S-phenyl-S-(3-phenyl-2-propenyloxycarbonylmethyl)-N-(trifluoromethylsulfonyl)sulfoximine **8d** (109 mg, 50%) as a colorless oil, *R_f* 0.32 (25% EtOAc–petroleum ether); IR ν_{CO} (film) 1743 cm⁻¹; ¹⁹F NMR (376 MHz, CDCl₃) δ -77.7 (3F, s, CF₃); ¹H NMR (270 MHz, CDCl₃) δ 8.01 (2H, d, *J* 8.0 Hz), 7.73 (1H, t, *J* 8.0 Hz), 7.58 (2H, t, *J* 8.0 Hz), 7.34 (5H, m), 6.61 (1H, d, *J* 16.0 Hz), 6.12 (1H, td, *J* 6.5, 16.0 Hz), 4.74 (2H, d, *J* 6.5 Hz), 4.67 (2H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 160.4, 136.4, 135.9, 135.6, 134.9, 129.9, 128.8, 128.7, 126.8, 120.9, 67.7, 61.9, CF₃ not observed; MS (CI) *m/z*: 465 [M+NH₄]⁺; HMRS (CI) *m/z* calcd for [C₁₈H₁₆F₃NO₅S₂+NH₄]⁺: 465.0766, found: 465.0748.

(±)-S-Phenyl-S-(3-phenyl-2-propenyloxycarbonylmethyl)-N-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine 8e.

According to the general procedure, (±)-S-carboxymethyl-S-phenyl-N-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine **7e** (184 mg, 0.43 mmol) was esterified with cinnamyl alcohol (58 mg, 0.43 mmol, 1 equiv), and EDCI (82 mg, 0.43 mmol, 1 equiv) in CH₂Cl₂ (2 mL). Chromatography (40% EtOAc–petroleum ether) yielded (±)-S-phenyl-S-(3-phenyl-2-propenyloxycarbonylmethyl)-N-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine **8e** (133 mg, 57%) as a colorless oil, *R_f* 0.65 (50% EtOAc–petroleum ether); IR ν_{CO} (film) 1746 cm⁻¹; ¹⁹F NMR (376 MHz, CDCl₃) δ -54.8 (3F, s); ¹H NMR (270 MHz, CDCl₃) δ 8.07 (1H, d, *J* 8.0 Hz), 7.99 (2H, d, *J* 7.5 Hz), 7.62 (1H, q, *J* 7.5 Hz), 7.51 (2H, q, *J* 7.5 Hz), 7.33 (8H, m), 6.57 (1H, d, *J* 15.5 Hz), 6.08 (1H, td, *J* 6.5, 15.5 Hz), 4.80 (1H, d, *J* 14.5 Hz), 4.68 (2H, d, *J* 6.5 Hz), 4.61 (1H, d, *J* 14.5 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.1, 135.9, 135.0, 134.2,

129.8, 129.5, 128.7, 128.5, 126.8, 126.4, 121.3, 120.5, 67.2, 61.6, CF₃ not observed; MS (CI) m/z: 557 [M+NH₄]⁺; HMRS (CI) m/z calcd for [C₂₄H₂₀F₃O₆NS₂+NH₄]⁺: 557.1028, found: 557.1023; Anal. calcd for C₂₄H₂₀F₃NO₆S₂: C, 53.42; H, 3.74; N, 2.61; found: C, 53.53; H, 3.81; N, 2.58.

(±)-S-Phenyl-S-(3-phenyl-2-propenyloxycarbonylmethyl)-N-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]sulfoximine 8f.

According to the general procedure, (±)-S-carboxymethyl-S-phenyl-N-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]sulfoximine **7f** (168 mg, 0.31 mmol) was esterified with cinnamyl alcohol (42 mg, 0.31 mmol, 1 equiv), and EDCI (58 mg, 0.31 mmol, 1 equiv) in CH₂Cl₂ (2 mL). Chromatography (40% EtOAc–petroleum ether) yielded (±)-S-phenyl-S-(3-phenyl-2-propenyloxycarbonylmethyl)-N-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]-sulfoximine **8f** (100 mg, 50%) as a colorless oil, R_f 0.24 (25% EtOAc–petroleum ether); IR ν_{CO} (film) 1744 cm⁻¹; ¹⁹F NMR (376 MHz, CDCl₃) δ -72.7 (3F, t, *J* 8.5 Hz), -73.2 (3F, t, *J* 8.0 Hz); ¹H NMR (270 MHz, CDCl₃) δ 7.98 (2H, td, *J* 1.5, 8.0 Hz), 7.63 (1H, tt, *J* 1.5, 7.5 Hz), 7.50 (3H, m), 7.33 (5H, m), 7.08 (2H, m), 6.56 (1H, d, *J* 16.0 Hz), 6.07 (1H, m), 4.78 (1H, d, *J* 14.5 Hz), 4.68 (2H, dd, *J* 1.0, 6.5 Hz), 4.58 (1H, d, *J* 14.5 Hz), 4.44 (2H, m), 4.32 (2H, q, *J* 8.0 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.3, 152.4, 150.1, 135.8, 135.0, 134.6, 129.5, 128.8, 128.5, 126.8, 121.7, 121.3, 118.6, 115.1, 68.7 (q, *J* 35.0 Hz), 67.2, 66.5 (q, *J* 36.0 Hz), 61.4, 2 CF₃ not observed; MS (CI) m/z: 669 [M+NH₄]⁺.

(±)-S-(Acetic acid 3-phenyl allyl ester)-S-mesityl-N-(4-toluenesulfonyl)sulfoximine 8g.

According to the general procedure, (±)-S-carboxymethyl-S-mesityl-N-(4-toluenesulfonyl)sulfoximine **7g** (100 mg, 0.26 mmol) was esterified with cinnamyl alcohol

(37 mg, 0.26 mmol, 1 equiv), and EDCI (50 mg, 0.26 mmol, 1 equiv) in CH₂Cl₂ (2 mL). Chromatography (25% EtOAc–petroleum ether) yielded (±)-*S*-phenyl-*S*-(3-phenyl-2-propenyloxycarbonylmethyl)-*N*-(4-toluenesulfonyl)sulfoximine **8g** (65 mg, 49%) as a colorless oil, *R*_f 0.74 (33% EtOAc–petroleum ether); IR ν_{CO} (film) 1742 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.80 (2H, d, *J* 8.5 Hz), 7.28 (9H, m), 6.50 (1H, d, *J* 15.5 Hz), 5.93 (1H, td, *J* 6.5, 15.5 Hz), 4.83 (1H, d, *J* 14.5 Hz), 4.62 (2H, d, *J* 7.5 Hz), 4.58 (1H, d, *J* 14.5 Hz), 2.63 (6H, s), 2.37 (3H, s), 2.18 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.7, 144.5, 140.5, 135.9, 133.1, 129.3, 128.7, 128.5, 126.7, 126.5, 121.1, 67.1, 61.8, 22.9, 21.6, 21.1; MS (CI) *m/z*: 529 [M+NH₄]⁺; HMRS (CI) *m/z* calcd for [C₂₇H₂₉O₅NS₂+NH₄]⁺: 529.1831, found: 529.1839; Anal. calcd for C₂₇H₂₉O₅NS₂: C, 63.38; H, 5.71; N, 2.75; found: C, 63.26; H, 5.62; N, 2.69.

(±)-*S*-(2-Pyridyl)-*S*-(3-phenyl-2-propenyloxycarbonylmethyl)-*N*-(4-toluenesulfonyl)-sulfoximine **8h.**

According to the general procedure, (±)-*S*-carboxymethyl-*S*-(2-pyridyl)-*N*-(4-toluenesulfonyl)sulfoximine **7h** (950 mg, 2.48 mmol) was esterified with cinnamyl alcohol (333 mg, 2.48 mmol, 1 equiv), and EDCI (476 mg, 2.48 mmol, 1 equiv) in CH₂Cl₂ (10 mL). Chromatography (35% diethyl ether–dichloromethane) yielded (±)-*S*-(2-pyridyl)-*S*-(3-phenyl-2-propenyloxycarbonylmethyl)-*N*-(4-toluenesulfonyl)sulfoximine **8h** (485 mg, 42%) as a colorless solid: mp 104–105 °C (Et₂O); *R*_f 0.13 (33% EtOAc–petroleum ether); IR ν_{CO} (film) 1743 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 8.64 (1H, d, *J* 4.5 Hz), 8.15 (1H, d, *J* 8.0 Hz), 7.83 (3H, m), 7.47 (1H, m), 7.25 (7H, m), 6.51 (1H, d, *J* 16.0 Hz), 6.03 (1H, td, *J* 6.0, 16.0 Hz), 5.06 (1H, d, *J* 15.5 Hz), 4.84 (1H, d, *J* 15.5 Hz), 4.65 (2H, d, *J* 6.5 Hz), 2.35 (3H, s); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.4, 154.9, 150.2, 143.2, 140.3, 138.5, 135.8, 135.6, 129.4, 128.8, 128.5, 128.1, 126.8, 123.8, 121.3, 67.0, 56.2, 21.6. Anal. calcd for C₂₃H₂₂N₂O₅S₂: C, 58.71; H, 4.71; N, 5.98; found: C, 58.64; H, 4.64; N, 5.86.

(+)-(S_S)-S-Phenyl-S-[3-(4-nitrophenyl)-2-propenyloxycarbonylmethyl]-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-8i.

According to the general procedure, (+)-*S*-carboxymethyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-**7b** (884 mg, 1.90 mmol) was esterified with 4-nitrocinnamyl alcohol (340 mg, 1.90 mmol, 1 equiv), and EDCI (364 mg, 1.90 mmol, 1 equiv) in CH₂Cl₂ (10 mL). Chromatography (40% EtOAc–petroleum ether) yielded (+)-(S_S)-*S*-phenyl-*S*-[3-(4-nitrophenyl)-2-propenyloxycarbonylmethyl]-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (+)-(S_S)-**8i** (834 mg, 70%) as a pale yellow moss, *R*_f 0.22 (25% EtOAc–petroleum ether); [α]_D²⁰ +35.4 (*c* 0.82, acetone); IR ν_{CO} (film) 1748 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 8.19 (2H, d, *J* 8.0 Hz), 7.98 (2H, d, *J* 8.0 Hz), 7.66 (1H, td, *J* 1.0, 7.0 Hz), 7.53 (4H, t, *J* 6.0), 7.10 (2H, s), 6.73 (1H, d, *J* 16.0 Hz), 6.33 (1H, td, *J* 6.0, 16.0 Hz), 4.77 (2H, d, *J* 6.0 Hz), 4.72 (2H, s), 4.37 (2H, sept, *J* 6.5 Hz), 2.85 (1H, sept, *J* 6.5 Hz), 1.25 (6H, d, *J* 6.5 Hz), 1.21 (6H, d, *J* 6.5 Hz), 1.16 (6H, d, *J* 6.5 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.5, 152.4, 149.1, 142.4, 136.5, 134.8, 132.2, 129.4, 128.7, 127.4, 126.5, 124.1, 123.6, 66.1, 61.9, 34.2, 29.4, 24.8, 24.6, 23.7; Anal. calcd for C₃₂H₃₈N₂O₇S₂: C, 61.30; H, 6.11; N, 4.21; found: C, 61.08; H, 6.36; N, 4.21.

(+)-(S_S)-S-(2-*E*-Hexenyloxycarbonylmethyl)-S-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-8j.

According to the general procedure, (+)-(S_S)-S-carboxymethyl-S-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-**7b** (875 mg, 1.88 mmol) was esterified with *E*-2-hexen-1-ol (222 μL, 1.88 mmol, 1 equiv), and EDCI (360 mg, 1.88 mmol, 1 equiv) in CH₂Cl₂ (15 mL). Chromatography (25% EtOAc–petroleum ether) yielded (+)-(S_S)-S-(2-hexenyloxycarbonylmethyl)-S-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-**8j** (742 mg, 72%) as a colorless oil, *R*_f 0.30 (33% EtOAc–petroleum ether); [α]_D²⁰ +34.8 (*c* 1.06, acetone); IR ν_{CO} (film) 1743 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.98 (2H, dd, *J* 1.5, 8.5 Hz), 7.69 (1H, tt, *J* 1.0, 7.5 Hz), 7.56 (2H, tt, *J* 1.5, 7.5 Hz), 7.09 (2H, s), 5.69 (1H, td, *J* 6.5, 15.5 Hz), 5.36 (1H, tdd, *J* 1.5, 6.5, 15.5 Hz), 4.72 (1H, d, *J* 14.5 Hz), 4.53 (1H, d, *J* 14.5 Hz), 4.44 (2H, dd, *J* 1.0, 6.5 Hz), 4.36 (2H, sept, *J* 6.5 Hz), 2.85 (1H, sept, *J* 6.5 Hz), 1.97 (2H, q, *J* 7.0 Hz), 1.36 (2H, sext, *J* 7.0 Hz), 1.24 (6H, d, *J* 6.5 Hz), 1.22 (6H, d, *J* 6.5 Hz), 1.17 (6H, d, *J* 6.5 Hz), 0.87 (3H, t, *J* 7.0 Hz, CH₂-CH₃); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.5, 152.2, 149.1, 138.0, 137.2, 136.6, 134.7, 129.3, 128.8, 123.5, 122.5, 67.3, 62.0, 34.3, 34.2, 29.3, 24.8, 24.6, 23.7, 22.0, 13.7; Anal. calcd for C₂₉H₄₁NO₅S₂: C, 63.59; H, 7.54; N, 2.56; found: C, 63.66; H, 7.62; N, 2.55.

(+)-(S_S)-S-(2-Z-Hexenyloxycarbonylmethyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-8k.

According to the general procedure, (+)-(S_S)-S-carboxymethyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-7b (229 mg, 0.49 mmol) was esterified with Z-2-hexen-1-ol (58 μ L, 0.49 mmol, 1 equiv), and EDCI (94 mg, 0.49 mmol, 1 equiv) in CH₂Cl₂ (3 mL). Chromatography (35% EtOAc–petroleum ether) yielded (+)-(S_S)-S-(2-Z-hexenyloxycarbonylmethyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-8k (192 mg, 72%) as a colorless oil, *R_f* 0.30 (25% EtOAc–petroleum ether); [α]_D²⁰ +31.1 (*c* 1.03, acetone); IR ν_{CO} (film) 1743 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.99 (2H, dd, *J* 1.0, 7.5 Hz), 7.63 (1H, tt, *J* 1.0, 7.5 Hz), 7.56 (2H, t, *J* 8.0 Hz), 7.10 (2H, s), 5.60 (1H, m), 5.32 (1H, m), 4.73 (1H, d, *J* 14.5 Hz), 4.56 (2H, d, *J* 5.0 Hz), 4.53 (1H, d, *J* 14.5 Hz), 4.36 (2H, sept, *J* 6.5 Hz), 2.85 (1H, sept, *J* 6.5 Hz), 1.98 (2H, q, *J* 7.0 Hz), 1.30 (2H, sext, *J* 7.0 Hz), 1.24 (6H, d, *J* 6.5 Hz), 1.22 (6H, d, *J* 6.5 Hz), 1.18 (6H, d, *J* 6.5 Hz), 0.85 (3H, t, *J* 7.0 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 161.6, 152.2, 149.2, 136.7, 136.4, 134.7, 129.4, 128.8, 123.5, 122.0, 62.3, 61.9, 34.2, 29.5, 29.3, 24.7, 24.6, 23.7, 22.5, 13.7; Anal. calcd for C₂₉H₄₁NO₅S₂: C, 63.59; H, 7.54; N, 2.56; found: C, 63.62; H, 7.50; N, 2.40.

(+)-(S_S)-S-(2-Methyl-3-phenyl-2-propenyloxycarbonylmethyl)-S-Phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-8l.

According to the general procedure, (+)-(S_S)-S-carboxymethyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-7b (335 mg, 0.72 mmol) was esterified with *E*-2-methyl-3-phenyl-2-propen-1-ol (104 μ L, 0.72 mmol, 1 equiv), and EDCI (138 mg, 0.72 mmol, 1 equiv) in CH₂Cl₂ (5 mL). Chromatography (25% EtOAc–petroleum ether) yielded (+)-(S_S)-S-(2-methyl-3-phenyl-2-propenyloxycarbonylmethyl)-S-phenyl-N-(2,4,6-triisopropylphenyl-

sulfonyl)sulfoximine (*S_S*)-**8l** (198 mg, 46%) as a colorless oil, *R_f* 0.64 (25% EtOAc–petroleum ether); $[\alpha]_D^{20} +33.4$ (*c* 0.96, acetone); IR ν_{CO} (film) 1743 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.99 (2H, d, *J* 7.5 Hz), 7.65 (1H, t, *J* 7.5 Hz), 7.53 (2H, t, *J* 8.0 Hz), 7.30 (5H, m, Ph), 7.10 (2H, s), 6.43 (1H, s), 4.81 (1H, d, *J* 14.5 Hz), 4.60 (1H, d, *J* 14.5 Hz), 4.59 (2H, s), 4.37 (2H, sept, *J* 6.5 Hz), 2.85 (1H, sept, *J* 6.5 Hz), 1.77 (3H, d, *J* 1.0 Hz), 1.24 (6H, d, *J* 6.5 Hz), 1.22 (6H, d, *J* 6.5 Hz), 1.17 (6H, d, *J* 6.5 Hz); ^{13}C NMR (67.5 MHz, CDCl_3) δ 161.6, 152.3, 149.2, 137.2, 136.6, 134.8, 131.4, 130.0, 129.4, 129.0, 128.7, 128.3, 127.1, 123.6, 72.5, 62.0, 34.2, 29.4, 24.8, 24.7, 23.7, 15.6; Anal. calcd for $\text{C}_{33}\text{H}_{41}\text{NO}_5\text{S}_2$: C, 66.52; H, 6.94; N, 2.35; found: C, 66.66; H, 6.81; N, 2.23.

(+)-(S_S)-S-(3,7-Dimethylocta-2,6-dienyloxycarbonylmethyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-8m**.**

According to the general procedure, (+)-(*S_S*)-S-carboxymethyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-**7b** (455 mg, 0.98 mmol) was esterified with geraniol (170 μL , 0.98 mmol, 1 equiv), and EDCI (187 mg, 0.98 mmol, 1 equiv) in CH_2Cl_2 (5 mL). Chromatography (30% EtOAc–petroleum ether) yielded (+)-(*S_S*)-S-(3,7-dimethylocta-2,6-dienyloxycarbonylmethyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-**8m** (370 mg, 63%) as a colorless oil, *R_f* 0.20 (20% EtOAc–petroleum ether); $[\alpha]_D^{20} +30.9$ (*c* 0.97, acetone); IR ν_{CO} (film) 1744 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.99 (2H, d, *J* 7.5 Hz), 7.68 (1H, t, *J* 7.5 Hz), 7.55 (1H, t, *J* 7.5 Hz), 7.10 (2H, s), 5.15 (1H, t, *J* 7.0 Hz), 5.04 (1H, *J* 7.0 Hz), 4.72 (1H, d, *J* 14.5 Hz), 4.53 (2H, d, *J* 7.5 Hz), 4.52 (1H, d, *J* 14.5 Hz), 4.36 (2H, sept, *J* 6.5 Hz), 2.85 (1H, sept, *J* 6.5 Hz), 2.00 (4H, m), 1.66 (3H, s), 1.60 (3H, s), 1.58 (3H, s), 1.24 (6H, d, *J* 6.5 Hz), 1.22 (6H, d, *J* 6.5 Hz), 1.18 (6H, d, *J* 6.5 Hz); ^{13}C NMR (67.5 MHz, CDCl_3) δ 161.7, 152.2, 149.1, 143.9, 137.2, 136.7, 134.7, 132.1, 129.3, 128.8, 123.6, 123.5, 116.9, 63.4, 62.0, 34.6, 34.2, 29.3, 26.3, 25.8, 24.8, 24.6, 23.7, 17.8, 16.6; Anal. calcd for $\text{C}_{33}\text{H}_{47}\text{NO}_5\text{S}_2$: C, 65.86; H, 7.87; N, 2.33; found: C, 65.87; H, 7.92; N, 2.17.

(+)-(S_S)-S-(Pent-3-en-2-yloxy carbonylmethyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-8n.

According to the general procedure, (+)-(S_S)-S-carboxymethyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-**7b** (335 mg, 0.72 mmol) was esterified with (±)-*E*-3-propen-2-ol (74 μL, 0.72 mmol, 1 equiv), and EDCI (138 mg, 0.72 mmol, 1 equiv) in CH₂Cl₂ (5 mL). Chromatography (25% EtOAc–petroleum ether) yielded a 1:1 diastereoisomeric mixture of (+)-(S_S)-S-(pent-3-en-2-yloxy carbonylmethyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-**8n** (245 mg, 64%) as a colorless oil, *R_f* 0.23 (25% EtOAc–petroleum ether); IR ν_{CO} (film) 1740 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.98 (2H, d, *J* 8.0 Hz), 7.68 (1H, t, *J* 7.5 Hz), 7.56 (2H, t, *J* 8.0 Hz), 7.09 (2H, s), 5.62 (1H, m), 5.30 (1H, m), 5.22 (1H, sext, *J* 6.5 Hz), 4.69 (1H, dd, *J* 6.5, 14.5 Hz), 4.48 (1H, dd, *J* 1.0, 14.5 Hz), 4.36 (2H, sept, *J* 6.5 Hz), 2.85 (1H, sept, *J* 6.5 Hz), 1.64 (3H, d, *J* 7.0 Hz), 1.24 (6H, d, *J* 6.5 Hz), 1.22 (6H, d, *J* 6.5 Hz), 1.18 (6H, d, *J* 6.5 Hz), 1.16 (3H, d, *J* 6.5 Hz); ¹³C NMR (67.5 MHz, CDCl₃) δ 160.9, 152.2, 149.1, 137.1, 136.7, 134.6, 129.8, 129.5, 129.3, 128.8, 123.5, 74.3, 62.2, 62.1, 34.2, 29.3, 24.8, 24.7, 23.7, 20.0, 17.7; Anal. calcd for C₂₈H₃₉NO₅S₂: C, 63.00; H, 7.36; N, 2.62; found: C, 63.07; H, 7.28; N, 2.72.

General procedure for the decarboxylative Claisen rearrangement reaction: A solution of sulfoximine **8a–h**, *N,O*-bis(trimethylsilyl)acetamide (BSA) (0.25 equiv) and KOAc (0.1 equiv) in toluene was heated at reflux under N₂. After completion of the reaction (reaction monitored by TLC or NMR ¹H), the solution was cooled to room temperature. Evaporation of the solvent under reduced pressure and chromatography on silica gel afforded the rearranged product **9a–h** as an inseparable mixture of diastereoisomers.*

(S_S^{*},S^{*})-S-(2-Phenylbut-3-enyl)-S-phenyl-N-(4-toluenesulfonyl)sulfoximine and **(S_S^{*},R^{*})-S-(2-phenylbut-3-enyl)-S-phenyl-N-(4-toluenesulfonyl)sulfoximine (±)-**9a**.**

According to the general procedure, **8a** (90 mg, 0.190 mmol) reacted with BSA (11 μL, 0.047 mmol, 0.25 equiv) and KOAc (2 mg, 0.019 mmol, 0.1 equiv) in toluene (1 mL) for 2 h. Chromatography (50% EtOAc–petroleum ether) yielded *(S_S^{*},S^{*})-S-(2-phenyl-but-3-enyl)-S-phenyl-N-(4-toluenesulfonyl)sulfoximine* and *(S_S^{*},R^{*})-S-(2-phenyl-but-3-enyl)-S-phenyl-N-(4-toluenesulfonyl)sulfoximine* (±)-**9a** (69 mg, 85%, mixture 70:30 determined by ¹H NMR) as a colorless solid, *R_f* 0.33 (25% EtOAc–petroleum ether); ¹H NMR (400 MHz, toluene-*d*₈) δ 8.05 (d, *J* 8.0 Hz) major isomer, 8.04 (d, *J* 8.0 Hz) minor isomer, 7.54 (d, *J* 8.0 Hz), 7.47 (d, *J* 8.0 Hz), 6.90–6.54 (10H, m), 5.52 (1H, m), 4.72 (s), 4.69 (s), 4.66 (1H, d, *J* 6.0 Hz), 4.08 (dd, *J* 6.0, 14.5 Hz), 3.99 (dd, *J* 6.5, 13.5 Hz), 3.84 (dd, *J* 6.5, 14.5 Hz), 3.77 (dd, *J* 7.0, 13.5 Hz), 3.67 (dd, *J* 7.0, 14.5 Hz), 3.49 (dd, *J* 7.5, 14.5 Hz), 1.87 (s) minor isomer, 1.86 (s) major isomer); ¹³C NMR (100 MHz, toluene-*d*₈) δ 142.6 and 142.5, 142.1, 140.0 and 139.9, 138.7 and 138.2 (CH=CH₂), 133.4 and 133.3, 129.5, 129.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.2, 127.7 and 127.1, 116.3 and 116.0, 62.6 and 62.1, 45.4 and 44.8, 21.1 MS (CI) *m/z*: 443 [M+NH₄]⁺, 426 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₂₃H₂₃NO₃S₂+H]⁺: 426.1198, found: 426.1206; Anal. calcd for C₂₃H₂₃NO₃S₂: C, 64.91; H, 5.45; N, 3.31; found: C, 64.87; H, 5.70; N, 3.24.

(S_S,S)-S-(2-Phenylbut-3-enyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and **(S_S,R)-S-(2-phenylbut-3-enyl)-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (S_S)-**9b**.**

* the protons allowing the determination of the diastereoisomeric ratio are indicated in blue.

According to the general procedure, (*S_S*)-**8b** (475 mg, 0.816 mmol) reacted with BSA (50 μ L, 0.204 mmol, 0.25 equiv) and KOAc (9 mg, 0.082 mmol, 0.1 equiv) in toluene (4 mL) for 1h30 h. Chromatography (35% EtOAc–petroleum ether) yielded (*S_S*,*S*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S*,*R*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-**9b** (420 mg, 91%, mixture 82:18 determined by ^1H NMR) as a colorless solid, R_f 0.68 (25% EtOAc–petroleum ether); ^1H NMR (400 MHz, toluene- d_8) δ 7.48 (d, J 7.5 Hz), 7.41 (d, J 7.5 Hz,), 6.95–6.50 (10H, m), 5.55 (ddd, J 7.0, 10.0, 17.0 Hz), 5.50 (ddd, J 6.5, 13.5, 17.0 Hz), 4.86 (sept, J 6.5 Hz, 2 $\text{CH}(\text{CH}_3)_2$ -*ortho* major isomer), 4.70 (m), 4.68 (m), 4.66 (d, J 17.0 Hz), 4.20 (m, 2 $\text{CH}(\text{CH}_3)_2$ -*ortho* minor isomer), 4.08 (dd, J 6.0, 15.0 Hz), 4.01 (dd, J 6.5, 13.5 Hz), 3.81 (dd, J 6.0, 14.5 Hz AB system), 3.76 (m), 3.66 (dd, J 7.0, 14.5 Hz AB system), 3.54 (dd, J 7.5, 14.5 Hz), 2.60 (1H, m), 1.37 (d, J 6.5 Hz, $\text{CH}(\text{CH}_3)_2$ -*ortho* major isomer), 1.36 (d, J 6.5 Hz, $\text{CH}(\text{CH}_3)_2$ -*ortho* minor isomer), 1.29 (d, J 6.5 Hz, $\text{CH}(\text{CH}_3)_2$ -*ortho* major isomer), 1.20 (d, J 6.5 Hz, $\text{CH}(\text{CH}_3)_2$ -*ortho* minor isomer), 1.06 (6H, m); ^{13}C NMR (100 MHz, toluene- d_8) δ 151.8 (*C*-*para* triisopropylphenyl), 149.6 (2*C*-*ortho* triisopropylphenyl), 140.1 and 140.0, 138.8 and 138.5 ($\text{CH}=\text{CH}_2$), 133.3 and 133.2, 129.2, 128.8, 128.7, 128.4, 128.1, 123.5, 116.3 and 116.2 ($\text{CH}=\text{CH}_2$), 62.9 and 62.5 (SOCH_2), 45.3 and 44.8 (CHPh), 34.5 ($\text{CH}(\text{CH}_3)_2$ -*para*), 29.7 and 29.4 (2 $\text{CH}(\text{CH}_3)_2$ -*ortho*), 25.1 and 25.0 and 23.8 (3 $\text{CH}(\text{CH}_3)_2$); MS (CI) m/z : 555 $[\text{M}+\text{NH}_4]^+$, 538 $[\text{M}+\text{H}]^+$; HMRS (CI) m/z calcd for $[\text{C}_{31}\text{H}_{39}\text{NO}_3\text{S}_2+\text{H}]^+$: 538.2450, found: 538.2451; Anal. calcd for $\text{C}_{31}\text{H}_{39}\text{NO}_3\text{S}_2$: C, 69.24; H, 7.31; N, 2.60; found: C, 69.32; H, 7.06; N, 2.42. Small amount of the major isomer crystallized in absolute ethanol.

(*S_S^{*}*,*S^{*}*)-*S*-(2-Phenylbut-3-enyl)-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine and (*S_S^{*}*,*R^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine ($\pm$)-**9c**

According to the general procedure, (±)-**8c** (92 mg, 0.182 mmol) reacted with BSA (11 µL, 0.045 mmol, 0.25 equiv) and KOAc (1.5 mg, 0.018 mmol, 0.1 equiv) in toluene (1 mL) for 8 h. Chromatography (20% EtOAc–petroleum ether) yielded (*S_S**,*S**)-*S*-(2-phenyl-but-3-enyl)-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine and (*S_S**,*R**)-*S*-(2-phenyl-but-3-enyl)-*S*-phenyl-*N*-(1-naphthalenesulfonyl)sulfoximine (±)-**9c** (71 mg, 83%, mixture 75:25 determined by ¹H NMR) as a colorless solid, *R_f* 0.48 (20% EtOAc–petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.91 (d, *J* 8.5 Hz), 8.88 (d, *J* 8.5 Hz), 8.17 (d, *J* 7.5 Hz), 8.13 (d, *J* 7.5 Hz), 7.99 (1H, d, *J* 8.0 Hz), 7.89 (1H, d, *J* 8.0 Hz), 7.75 (1H, d, *J* 8.0 Hz), 7.70–6.80 (12H, m), 5.84 (ddd, *J* 7.0, 10.0, 17.0 Hz), 5.72 (ddd, *J* 6.5, 10.0, 17.5 Hz), 4.96 (d, *J* 10.0 Hz), 4.90 (d, *J* 17.0 Hz), 4.83 (d, *J* 10.0 Hz), 4.68 (d, *J* 17.0 Hz), 4.09 (dd, *J* 5.5, 14.5 Hz), 4.02 (q, *J* 7.0 Hz), 3.90 (q, *J* 7.0 Hz), 3.84 (d, *J* 7.0 Hz), 3.73 (dd, *J* 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 139.8 and 139.2, 137.5 and 137.2 (CH=CH₂), 134.0 and 133.8, 133.5, 129.2 and 129.1, 128.8, 128.7 and 128.6, 128.1 and 127.9, 127.7 and 127.6, 127.4 and 127.3, 126.5, 125.8, 124.1, 116.8 and 116.5 (CH=CH₂), 62.6 and 62.2 (SOCH₂), 44.3 and 43.8 (CHPh); Anal. calcd for C₂₆H₂₃NO₃S₂: C, 67.65; H, 5.02; N, 3.05; found: C, 67.49; H, 5.12; N, 3.07.

(*S_S^{*},S^{*}*)-*S*-(2-Phenyl-but-3-enyl)-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine and (*S_S^{*},R^{*}*)-*S*-(2-phenyl-but-3-enyl)-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine (±)-**9d**.

According to the general procedure, (±)-**8d** (70 mg, 0.157 mmol) reacted with BSA (9.5 μL, 0.039 mmol, 0.25 equiv) and KOAc (1.5 mg, 0.016 mmol, 0.1 equiv) in toluene (700 μL) for 7 h. Chromatography (35% EtOAc–petroleum ether) yielded (*S_S^{*},S^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine and (*S_S^{*},R^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine (±)-**9d** (20 mg containing ~ 10% of product of degradation, ~ 30% yield, mixture 66:34 determined by ¹⁹F NMR) as a yellow oil; *R_f* 0.55 (25% EtOAc–petroleum ether); ¹⁹F NMR (376 MHz, toluene-*d*₈) δ **–77.91 (s)**, **–78.01 (s)**; ¹H NMR (270 MHz, toluene-*d*₈) δ **7.30 (d, *J* 8.0 Hz)**, **7.19 (d, *J* 8.0 Hz)**, 7.10–6.35 (8H, m), 5.35 (1H, m), 4.72 (d, *J* 10.0 Hz), 4.65 (d, *J* 10.0 Hz), 4.62 (d, *J* 17.0 Hz), 4.58 (d, *J* 17.0 Hz), 3.77 (q, *J* 7.0 Hz), 3.70 (dd, *J* 6.0, 14.5 Hz), 3.58 (q, *J* 7.0 Hz), 3.37 (d, *J* 6.5 Hz), 3.15 (dd, *J* 8.0, 14.5 Hz); ¹³C NMR (125 MHz, toluene-*d*₈) δ 139.5 and 139.0, 137.9 and 137.5 (CH=CH₂), 134.3 and 134.0, 129.4, 129.2, 129.2, 128.8, 128.3, 128.0, 127.5 and 127.4, 117.0 and 116.5 (CH=CH₂), 62.8 and 62.2 (SOCH₂), 44.9 and 44.3 (CHPh), CF₃ not observed; MS (CI) *m/z*: 421 [M+NH₄]⁺; HMRS (CI) *m/z* calcd for [C₁₇H₁₆F₃NO₃S₂+NH₄]⁺: 421.0867, found: 421.0868.

(*S_S^{*},S^{*}*)-*S*-(2-Phenylbut-3-enyl)-*S*-phenyl-*N*-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine and (*S_S^{*},R^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine (±)-9e.

According to the general procedure, (±)-**8e** (111 mg, 0.206 mmol) reacted with BSA (12.5 μL, 0.051 mmol, 0.25 equiv) and KOAc (2 mg, 0.021 mmol, 0.1 equiv) in toluene (2 mL) for 8 h. Chromatography (35% EtOAc–petroleum ether) yielded (*S_S^{*},S^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine and (*S_S^{*},R^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-[2-(trifluoromethoxy)benzenesulfonyl]sulfoximine (±)-**9e** (65 mg, 64%, mixture 75:25 determined by ¹H NMR) as a colorless oil, *R_f* 0.53 (50% EtOAc–petroleum ether); ¹⁹F NMR (376 MHz, CDCl₃) δ –54.69 (d, *J* 1.5 Hz), –54.70 (d, *J* 1.5 Hz), –55.12 (d, *J* 1.5 Hz); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* 1.0, 8.0 Hz), 8.00 (dd, *J* 1.0, 8.0 Hz), 7.81 (d, *J* 7.5 Hz), 7.70 (d, *J* 7.5 Hz), 7.65–6.90 (10H, m), 5.87 (ddd, *J* 7.0, 10.0, 17.0 Hz), 5.79 (ddd, *J* 7.5, 10.0, 17.5 Hz), 5.00 (m), 4.94 (dd, *J* 10.0, 15.0 Hz), 4.21 (dd, *J* 5.5, 14.0 Hz), 4.05 (q, *J* 7.0 Hz), 3.94 (d, *J* 7.0 Hz), 3.93 (m), 3.83 (dd, *J* 8.0, 14.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 139.5 and 139.0, 137.8 and 137.6, 137.1 and 136.9, 135.9 and 135.8, 134.3, 133.9, 133.7, 129.7, 129.4, 129.3, 129.2, 128.8 and 128.7, 128.2, 128.0, 127.6, 127.5, 127.3, 126.5 and 126.3, 120.2 and 119.8, 116.9 and 116.7 (CH=CH₂), 62.6 and 62.1 (SOCH₂), 44.5 and 44.1 (CHPh), CF₃ not observed; MS (CI) *m/z*: 513 [M+NH₄]⁺, 496 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₂₃H₂₀F₃NO₄S₂+NH₄]⁺: 513.1130, found: 513.1118; Anal. calcd for C₂₃H₂₀F₃NO₄S₂: C, 55.79; H, 4.07; N, 2.84; found: C, 55.86; H, 3.99; N, 2.93.

(*S_S^{*},S^{*}*)-*S*-(2-Phenylbut-3-enyl)-*S*-phenyl-*N*-[2,5-bis(2,2,2trifluoroethoxy)benzenesulfonyl]sulfoximine and (*S_S^{*},R^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]sulfoximine (±)-9f.

According to the general procedure, (±)-**8f** (43 mg, 0.067 mmol) reacted with BSA (4 μL, 0.017 mmol, 0.25 equiv) and KOAc (1 mg, 0.007 mmol, 0.1 equiv) in toluene (400 μL) for 15 h. Chromatography (35% EtOAc–petroleum ether) yielded (*S_S^{*},S^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-[2,5-bis(2,2,2trifluoroethoxy)benzenesulfonyl]sulfoximine and (*S_S^{*},R^{*}*)-*S*-(2-phenylbut-3-enyl)-*S*-phenyl-*N*-[2,5-bis(2,2,2-trifluoroethoxy)benzenesulfonyl]sulfoximine (±)-**9f** (34 mg, 83%, mixture 78:22 determined by ¹⁹F NMR) as a colorless oil, *R_f* 0.49 (25% EtOAc–petroleum ether); ¹⁹F NMR (235 MHz, CDCl₃) δ **-77.75 (t, *J* 8.5 Hz)**, **-77.78 (t, *J* 8.5 Hz)**, -78.18 (t, *J* 8.5 Hz, CF₃); ¹H NMR (400 MHz, toluene-*d*₈) δ 7.51 (m), 7.47 (d, *J* 3 Hz), 7.43 (m), 6.86–6.65 (8H, m), 6.52 (1H, m), 6.34 (1H, m), 5.58 (m), 5.56 (ddd, *J* 3.0, 8.0, 13.0 Hz), 4.71 (d, *J* 17.0 Hz), 4.70 (d, *J* 10.0 Hz), 4.69 (m), 4.05 (q, *J* 7.0 Hz), 3.97 (2H, q, *J* 8.5 Hz), 3.95 (m), 3.78 (q, *J* 7.0 Hz), 3.65 (dd, *J* 6.5, 14.5 Hz AB system), 3.54 (dd, *J* 6.5, 14.5 Hz AB system), 3.43 (m), 3.35 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 152.7 and 152.5, 150.4 and 149.5, 140.0 and 139.8, 138.5 and 138.2 (CH=CH₂), 138.0, 136.9, 133.5 and 133.4, 129.2, 129.0, 128.9, 128.7, 128.5, 128.4, 128.2, 128.0, 127.2, 125.4, 123.6 (q, *J* 210 Hz, CF₃), 123.4 (q, *J* 220 Hz, CF₃), 121.3, 120.0, 116.4 and 116.1 (CH=CH₂), 114.5, 69.3 (q, *J* 35 Hz), 65.8 (q, *J* 35.0 Hz), 62.6 and 62.2 (SOCH₂), 45.0 and 44.6 (CHPh); MS (CI) *m/z*: 625 [M+NH₄]⁺, 608 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₂₆H₂₃F₆NO₅S₂+NH₄]⁺: 625.1266, found: 625.1267; Anal. calcd for C₂₆H₂₃F₆NO₅S₂: C, 51.39; H, 3.82; N, 2.32; found: C, 51.41; H, 3.70; N, 2.19.

(S_S^{},S^{*})-S-(2-Phenylbut-3-enyl)-S-(2-pyridyl)-N-(4-toluenesulfonyl)sulfoximine* and *(S_S^{*},R^{*})-S-(2-phenylbut-3-enyl)-S-(2-pyridyl)-N-(4-toluenesulfonyl)sulfoximine* (±)-**9h**.

According to the general procedure, (±)-**8h** (40 mg, 0.080 mmol) reacted with BSA (5 µL, 0.020 mmol, 0.25 equiv) and KOAc (1 mg, 0.008 mmol, 0.1 equiv) in toluene (400 µL) for 18 h. Chromatography (5% diethyl ether–dichloromethane) yielded *(S_S^{*},S^{*})-S-(2-phenylbut-3-enyl)-S-(2-pyridyl)-N-(4-toluenesulfonyl)sulfoximine* and *(S_S^{*},R^{*})-S-(2-phenylbut-3-enyl)-S-(2-pyridyl)-N-(4-toluenesulfonyl)sulfoximine* (±)-**9h** (20 mg containing ~ 10% of starting material, ~ 50%, mixture 68:32 determined by ¹H NMR) as a colorless oil, *R_f* 0.26 (50% EtOAc–petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* 4.0 Hz), 8.52 (d, *J* 4.0 Hz), 7.95–7.63 (3H, m), 7.45–6.90 (9H, m), 5.84 (ddd, *J* 7.0, 10.5, 17.0 Hz), 5.73 (ddd, *J* 7.5, 10.0, 17.5 Hz), 5.02 (d, *J* 10.0 Hz), 5.00 (d, *J* 17.0 Hz), 4.96 (d, *J* 17.0 Hz), 4.88 (d, *J* 10.0 Hz), 4.37 (dd, *J* 9.5, 14.5 Hz), 4.30 (dd, *J* 7.5, 14.5 Hz), 4.20 (dd, *J* 6.5, 14.5 Hz), 4.10 (1H, *J* 7.0 Hz), 4.09 (m), 2.39 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 155.6, 149.9 and 149, 142.7 and 142.6, 140.7, 139.4, 138.5 and 138.3, 138.0, 137.8, 137.4, 129.2, 128.7, 128.4, 128.1, 127.8, 127.3, 127.2, 127.1, 127.0, 126.6, 124.0 and 123.8, 116.7 and 116.3, 57.4 and 57.0, 44.5 and 43.8, 21.5; MS (CI) *m/z*: 444 [M+NH₄]⁺, 427 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₂₂H₁₉NO₃S₂+H]⁺: 427.1150, found: 427.1145.

(*S_S,S*)-*S*-[2-(4-Nitrophenyl)but-3-enyl]-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl) sulfoximine and (*S_S,R*)-*S*-[2-(4-nitrophenyl)but-3-enyl]-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-9i.

According to the general procedure, (*S_S*)-**8i** (358 mg, 0.57 mmol) reacted with BSA (35 μ L, 0.15 mmol, 0.25 equiv) and KOAc (6 mg, 0.06 mmol, 0.1 equiv) in toluene (4 mL) for 9 h. Chromatography (35% EtOAc–petroleum ether) yielded (*S_S,S*)-*S*-[2-(4-nitrophenyl)but-3-enyl]-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl) sulfoximine and (*S_S,R*)-*S*-[2-(4-nitrophenyl)but-3-enyl]-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl) sulfoximine (*S_S*)-**9i** (216 mg, 65%, mixture 78:22 determined by ^1H NMR) as a yellow solid, R_f 0.44 (25% EtOAc–petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J 8.5 Hz), 7.94 (d, J 8.5 Hz), 7.74 (d, J 7.5 Hz), 7.69 (d, J 8.0 Hz), 7.48 (1H, m), 7.38 (2H, m), 7.19 (2H, m), 7.10 (2H, s), 5.81 (1H, ddd, J 7.0, 10.0, 17.0 Hz), 5.10 (m), 5.07 (d, J 10.0 Hz), 4.99 (d, J 17.0 Hz), 4.93 (d, J 17.0 Hz), 4.37 (sept, J 6.5 Hz), 4.30–4.00 (m), 2.87 (m), 1.30–1.18 (m); ^{13}C NMR (100 MHz, CDCl_3) δ 152.1 (C-*para* triisopropylphenyl), 149.0 and 148.9 (C-*ortho* triisopropylphenyl), 147.0 and 146.8 (C-*ipso*, C-*para* $\text{C}_6\text{H}_4\text{NO}_2$), 137.2 and 136.6 ($\text{CH}=\text{CH}_2$), 134.1 and 134.0 (C-*para* SOPh), 129.3 (2C-*meta* SOPh), 128.8 (2C-*ortho* $\text{C}_6\text{H}_4\text{NO}_2$), 128.1 (2C-*ortho* SOPh), 123.8 and 123.7 and 123.4 (2C-*meta* $\text{C}_6\text{H}_4\text{NO}_2$, 2C-*meta* triisopropylphenyl), 117.9 ($\text{CH}=\text{CH}_2$), 62.2 and 62.0 (SOCH_2), 44.7 and 44.1 ($\text{CHC}_6\text{H}_4\text{NO}_2$), 34.1 ($\text{CH}(\text{CH}_3)_2$ -*para*), 29.8 and 29.3 (2 $\text{CH}(\text{CH}_3)_2$ -*ortho*), 24.7 and 24.5 and 23.6 (3 $\text{CH}(\text{CH}_3)_2$); MS (CI) m/z : 600 $[\text{M}+\text{NH}_4]^+$; HMRS (CI) m/z calcd for $[\text{C}_{31}\text{H}_{38}\text{N}_2\text{O}_5\text{S}_2+\text{NH}_4]^+$: 600.2566, found: 600.2584; Anal. calcd for $\text{C}_{31}\text{H}_{38}\text{N}_2\text{O}_5\text{S}_2$: C, 63.89; H, 6.57; N, 4.81; found: C, 63.84; H, 6.54; N, 4.71.

(*S_S,R*)-*S*-(2-Propylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S,S*)-*S*-(2-propylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S)-9j*.

Decarboxylative Claisen rearrangement reaction of (*S_S)-8j*: According to the the general procedure, (*S_S)-8j* (875 mg, 1.60 mmol) reacted with BSA (97 μ L, 0.40 mmol, 0.25 equiv) and KOAc (16 mg, 0.16 mmol, 0.1 equiv) in toluene (10 mL) for 6 h. Chromatography (25% EtOAc–petroleum ether) yielded (*S_S,R*)-*S*-(2-propylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S,S*)-*S*-(2-propylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S)-9j* (631 mg, 78%, mixture 75:25 determined by ^1H NMR) as a colorless oil; R_f 0.13 (25% EtOAc–petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J 8.0 Hz), 7.88 (d, J 8.0 Hz), 7.62 (1H, t, J 8.0 Hz), 7.52 (2H, q, J 8.0 Hz), 7.09 (2H, s), 5.40 (td, J 9.0, 17.0 Hz), 5.27 (td, J 10.0, 17.0 Hz), 4.87 (d, J 11.5 Hz), 4.80 (d, J 10.0 Hz), 4.75 (1H, dd, J 10.0, 14.0 Hz), 4.35 (2H, sept, J 7.0 Hz), 3.65 (dd, J 4.5, 14.5 Hz AB system), 3.52 (m), 3.41 (dd, J 8.0, 14.5 Hz AB system), 2.86 (1H, sept, J 7.0 Hz), 2.53 (1H, sext, J 4.5 Hz), 1.40 (m), 1.32–1.15 (m), 0.80 (t, J 7.0 Hz), 0.74 (t, J 7.5 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 148.8, 138.1 and 137.9, 137.4, 134.0 and 133.9, 129.2, 128.3, 123.5 and 123.2, 116.6 and 116.5, 62.6 and 62.4, 38.5 and 38.2, 36.5 and 36.3, 34.0, 29.8 and 29.1, 24.6 and 24.5 and 23.5, 19.4 and 19.3, 13.5; MS (CI) m/z : 521 $[\text{M}+\text{NH}_4]^+$, 504 $[\text{M}+\text{H}]^+$; HMRS (CI) m/z calcd for $[\text{C}_{28}\text{H}_{41}\text{NO}_3\text{S}_2+\text{NH}_4]^+$: 521.2872, found: 521.2868; Anal. calcd for $\text{C}_{28}\text{H}_{41}\text{NO}_3\text{S}_2$: C, 66.76; H, 8.20; N, 2.78; found: C, 66.81; H, 8.31; N, 2.83.

Decarboxylative Claisen rearrangement reaction of (*S_S)-8k*: According to the general procedure, (*S_S)-8k* (364 mg, 0.665 mmol) reacted with BSA (40 μ L, 0.166 mmol, 0.25 equiv) and KOAc (6 mg, 0.067 mmol, 0.1 equiv) in toluene (7 mL) for 8 h. Chromatography (25% EtOAc–petroleum ether) yielded (*S_S,R*)-*S*-(2-propylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S,S*)-*S*-(2-propylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S)-9j* (232 mg, 67%, mixture 13:87 determined by ^1H NMR) as a colorless oil; R_f 0.13 (25% EtOAc–petroleum ether); ^1H NMR (400 MHz,

CDCl₃) δ 7.94 (d, *J* 8.0 Hz), 7.90 (d, *J* 8.0 Hz), 7.65 (1H, q, *J* 7.5 Hz), 7.53 (2H, t, *J* 7.5 Hz, 2H-*meta* Ph), 7.17 (s, 2H), 7.10 (s, 2H), 5.40 (td, *J* 9.0, 17.5 Hz), 5.27 (td, *J* 8.0, 17.0 Hz), 4.78 (d, *J* 10.0 Hz), 4.73 (d, *J* 17.0 Hz), 4.37 (sept, *J* 7.0 Hz), 4.11 (sept, *J* 7.0 Hz), 3.66 (dd, *J* 4.5, 14.5 Hz), 3.55 (m), 3.41 (dd, *J* 7.5, 14.5 Hz), 2.87 (1H, sept, *J* 7.0 Hz), 2.50 (1H, m), 1.50–1.10 (20H), 0.81 (t, *J* 7.0 Hz), 0.75 (t, *J* 7.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 148.9, 138.2 and 138.0, 137.5, 134.0 and 133.9, 129.2, 128.7 and 128.5, 123.6 and 123.3, 116.6 and 116.5, 62.7 and 62.5, 38.6 and 38.3, 36.5 and 36.4, 34.0, 29.8 and 29.1, 24.6 and 24.5 and 23.5, 19.4 and 19.3, 13.5; MS (CI) *m/z*: 521 [M+NH₄]⁺, 504 [M+H]⁺; HMRS (CI) *m/z* calcd for [C₂₈H₄₁NO₃S₂+H]⁺: 504.2606, found: 504.2620; Anal. calcd for C₂₈H₄₁NO₃S₂: C, 66.76; H, 8.20; N, 2.78; found: C, 66.42; H, 7.97; N, 2.68.

(*S_S,S*)-*S*-(2-Phenyl-3-methylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S,R*)-*S*-(2-phenyl-3-methylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-9I.

According to the general procedure, (*S_S*)-**8I** (198 mg, 0.332 mmol) reacted with BSA (20 μ L, 0.083 mmol, 0.25 equiv) and KOAc (3 mg, 0.033 mmol, 0.1 equiv) in toluene (4 mL) for 8 h. Chromatography (25% EtOAc–petroleum ether) yielded (*S_S,S*)-*S*-(2-phenyl-3-methylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S,R*)-*S*-(2-phenyl-3-methylbut-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-**9I** (139 mg, 76%, mixture 75:25 determined by ¹H NMR) as a colorless oil, *R_f* 0.65 (25% EtOAc–petroleum ether); ¹H NMR (400 MHz, toluene-*d*₈) δ 7.49 (d, *J* 7.5 Hz), 7.40 (d, *J* 7.5 Hz), 7.15–6.35 (10H, m), 4.89 (sept, *J* 6.5 Hz), 4.53 (s), 4.48 (d, *J* 8.5 Hz), 4.35 (dd, *J* 4.0, 13.5 Hz), 4.23 (sept, *J* 7.0 Hz), 4.02 (m), 3.87 (dd, *J* 9.5, 16.0 Hz), 3.70 (m), 2.63 (1H, sept, *J* 7.0 Hz), 1.39 (d, *J* 7.0 Hz), 1.38 (d, *J* 7.0 Hz), 1.30 (d, *J* 7.0 Hz), 1.28 (s), 1.27 (s), 1.21 (d, *J* 7.0 Hz), 1.07 (d, *J* 7.0 Hz), 1.06 (d, *J* 7.0 Hz); ¹³C NMR (100 MHz, toluene-*d*₈) δ 151.7, 149.6, 145.1, 139.5 and 139.3, 138.5 and 138.4, 133.2 and 133.1, 128.8, 128.5, 128.3, 127.0, 123.5, 112.3 and 111.8, 61.6 and 61.3, 48.1 and 47.6, 34.5, 30.0 and 29.7, 25.1 and 25.0 and 24.9 and 23.8; MS (CI) *m/z*: 569 [M+NH₄]⁺, 552 [M+H]⁺; HMRS

(CI) m/z calcd for $[C_{32}H_{41}NO_3S_2+H]^+$: 552.2606, found: 552.2615; Anal. calcd for $C_{32}H_{41}NO_3S_2$: C, 69.65; H, 7.49; N, 2.53; found: C, 69.83; H, 7.37; N, 2.62.

(*S_S,R*)-*S*-(2,6-Dimethyl-2-ethenylhept-5-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S,S*)-*S*-(2,6-dimethyl-2-ethenylhept-5-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-9m.

According to the general procedure, (*S_S*)-**8m** (205 mg, 0.35 mmol) reacted with BSA (21 μ L, 0.16 mmol, 0.25 equiv) and KOAc (3 mg, 0.035 mmol, 0.1 equiv) in toluene (4 mL) for 6 h. Chromatography (20% EtOAc–petroleum ether) yielded (*S_S,R*)-*S*-(2,6-dimethyl-2-ethenylhept-5-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S,S*)-*S*-(2,6-dimethyl-2-ethenylhept-5-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-**9m** (165 mg, 84%, mixture 70:30 determined by 1H NMR) as a colorless oil, R_f 0.23 (25% EtOAc–petroleum ether); 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J 8.0 Hz), 7.87 (d, J 8.0 Hz), 7.62 (1H, t, J 7.0 Hz), 7.51 (2H, dd, J 5.0, 8.0 Hz), 7.08 (2H, s), 5.57 (dd, J 10.0, 17.0 Hz), 5.37 (dd, J 10.5, 17.0 Hz), 4.94 (1H, m, $CH=C(CH_3)_2$), 4.80 (2H, m), 3.88 (d, J 14.5 Hz AB system), 3.82 (d, J 14.5 Hz AB system), 3.46 (d, J 14.5 Hz AB system), 3.42 (d, J 14.5 Hz AB system), 2.86 (2H, sept, J 7.0 Hz), 1.80 (2H, m), 1.65 (s), 1.63 (s), 1.51 (3H, s), 1.40 (2H, m), 1.25–1.10 (21H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 149.0, 142.5 and 141.9, 139.3 and 139.1 and 137.5, 133.8, 132.0 and 131.9, 129.2 and 129.1, 128.4 and 128.3, 123.5 and 123.4 and 123.2, 114.1 and 113.7, 67.4, 41.4 and 40.8 and 40.2, 34.0, 29.2, 25.6, 24.7 and 24.6 and 23.6, 22.4 and 22.2, 21.2, 17.5; MS (CI) m/z : 575 $[M+NH_4]^+$, 558 $[M+H]^+$; HMRS (CI) m/z calcd for $[C_{32}H_{47}NO_3S_2+H]^+$: 558.3076, found: 558.3087.

A small amount of the major isomer crystallized in toluene. Anal. calcd for $C_{32}H_{47}NO_3S_2$: C, 68.89; H, 8.49; N, 2.52; found: C, 68.95; H, 8.63; N, 2.46.

(*S_S*,*R*)-*S*-(2-Methylpent-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S*,*S*)-*S*-(2-methylpent-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-9n**.**

According to the general procedure, (*S_S*)-**8n** (192 mg, 0.360 mmol) reacted with BSA (22 μ L, 0.090 mmol, 0.25 equiv) and KOAc (4 mg, 0.036 mmol, 0.1 equiv) in toluene (4 mL) for 8 h. Chromatography (20% EtOAc–petroleum ether) yielded (*S_S*,*R*)-*S*-(2-methylpent-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine and (*S_S*,*S*)-*S*-(2-methylpent-3-enyl)-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (*S_S*)-**9n** (165 mg, 94%, mixture 53:47 determined by ^1H NMR) as a colorless oil, R_f 0.40 (20% EtOAc–petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J 8.0 Hz), 7.90 (d, J 7.5 Hz), 7.64 (1H, q, J 7.0 Hz), 7.55 (2H, q, J 7.0 Hz), 7.10 (2H, s), 5.31 (qd, J 6.5, 14.5 Hz), 5.22 (qd, J 7.0, 15.0 Hz), 5.08 (dd, J 7.5, 15.5 Hz), 4.95 (dd, J 8.0, 15.5 Hz), 4.35 (2H, sept, J 7.5 Hz), 3.60 (dd, J 5.5 Hz, 14.5 Hz), 3.48 (dd, J 7.0, 14.5 Hz), 3.41 (dd, J 6.5, 13.5 Hz), 3.37 (dd, J 7.0, 14.5 Hz), 2.87 (1H, sept, J 7.5 Hz), 2.78 (quint, J 7.0 Hz), 2.65 (quint, J 7.0 Hz, CHCH_3), 1.48 (d, J 6.5 Hz), 1.40 (d, J 6.5 Hz), 1.25–1.20 (18H, m), 1.06 (d, J 7.0 Hz), 1.04 (d, J 7.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 151.7, 149.0, 138.0 and 137.8, 134.0 and 133.9, 132.7 and 132.5, 129.3 and 129.2, 128.3, 126.2 and 126.0, 123.3, 64.3 and 63.9, 34.1, 32.5 and 32.2, 29.2, 24.7 and 24.6 and 23.7, 20.9 and 20.6, 17.7 and 17.6; MS (CI) m/z : 507 $[\text{M}+\text{NH}_4]^+$, 490 $[\text{M}+\text{H}]^+$; HMRS (CI) m/z calcd for $[\text{C}_{27}\text{H}_{39}\text{NO}_3\text{S}_2+\text{NH}_4]^+$: 507.2715, found: 507.2692; Anal. calcd for $\text{C}_{27}\text{H}_{39}\text{NO}_3\text{S}_2$: C, 66.21; H, 8.03; N, 2.87; found: C, 66.14; H, 7.90; N, 2.79.

Decarboxylative Claisen rearrangement reaction of **8a**.

Decarboxylative Claisen rearrangement reaction of (*S_S*)-**8b**.

Decarboxylative Claisen rearrangement reaction of **8c**.

Decarboxylative Claisen rearrangement reaction of **8d**.

Decarboxylative Claisen rearrangement reaction of **8e**.

Decarboxylative Claisen rearrangement reaction of **8f**.

Decarboxylative Claisen rearrangement reaction of **8h**.

Decarboxylative Claisen rearrangement reaction of (*S_S*)-**8i**

Decarboxylative Claisen rearrangement reaction of (*S_S*)-**8j**

Decarboxylative Claisen rearrangement reaction of (*S_S*)-**8k**

Decarboxylative Claisen rearrangement reaction of (*S_S*)-**81**

Decarboxylative Claisen rearrangement reaction of (*S_S*)-**8m**

Decarboxylative Claisen rearrangement reaction of (*S_S*)-**8n**

Supplementary data: X-ray crystallography

Crystal data for (S_S,2S)-9i: C₃₁H₃₈N₂O₅S₂, *M* = 582.75, monoclinic, *P*2₁ (no. 4), *a* = 5.9105(5), *b* = 9.4071(8), *c* = 27.0869(19) Å, β = 94.813(7)°, *V* = 1500.7(2) Å³, *Z* = 2, *D_c* = 1.290 g cm⁻³, μ(Cu-Kα) = 1.948 mm⁻¹, *T* = 173 K, colourless tabular needles; 4300 independent measured reflections, *F*² refinement, *R*₁ = 0.060, *wR*₂ = 0.166, 4059 independent observed absorption-corrected reflections [*|F_o||* > 4σ(*|F_o||*), 2θ_{max} = 143°], 362 parameters. The absolute structure of (S_S, 2S)-9i was determined by a combination of *R*-factor tests [*R*₁⁺ = 0.0598, *R*₁⁻ = 0.0683] and by use of the Flack parameter [*x*⁺ = 0.00(3), *x*⁻ = 1.00(3)]. CCDC 268390.

Crystal data for (S_S, 3R)-9m: C₃₂H₄₇NO₃S₂, *M* = 557.83, triclinic, *P*1 (no. 1), *a* = 11.7597(9), *b* = 12.5439(8), *c* = 13.2635(9) Å, α = 108.493(6), β = 102.329(6), γ = 107.814(6)°, *V* = 1658.7(2) Å³, *Z* = 2 (there are two independent molecules, both of which have the same chirality), *D_c* = 1.117 g cm⁻³, μ(Mo-Kα) = 0.190 mm⁻¹, *T* = 173 K, colourless blocky needles; 13477 independent measured reflections, *F*² refinement, *R*₁ = 0.087, *wR*₂ = 0.243, 12748 independent observed absorption-corrected reflections [*|F_o||* > 4σ(*|F_o||*), 2θ_{max} = 65°], 721 parameters. The absolute structure of (S_S,3R)-9m could not be unambiguously determined crystallographically [*R*₁⁺ = 0.0872, *R*₁⁻ = 0.0875, *x*⁺ = 0.00(11)] and so was assigned by analogy with that of (S_S,2S)-9i. CCDC 268391.

Figures

Fig. S1 The molecular structure of (S_S,2S)-9i (50% probability ellipsoids).

Fig. S2 The molecular structure of one (A) of the two independent molecules present in the crystals of (S_S,3R)-9m (30% probability ellipsoids).

Fig. S3 The molecular structure of one (B) of the two independent molecules present in the crystals of (S_S,3R)-9m.

Fig. S4 The molecular structure of one (B) of the two independent molecules present in the crystals of (S_S,3R)-9m (30% probability ellipsoids).

Fig. S5 The molecular structure of one (**B**) of the two independent molecules present in the crystals of (*S_S*,3*R*)-**9m** showing the disorder present in one of the *iso*-propyl substituents and in the $-\text{CH}_2-\text{CH}=\text{CMe}_2$ side chain. (Note that the disorder does not effect the stereochemistry at either of the chiral centres.)

Fig. S1

Fig. S2

Fig. S3

Fig. S4

Fig. S5