

Experimental Procedures and Characterization Data
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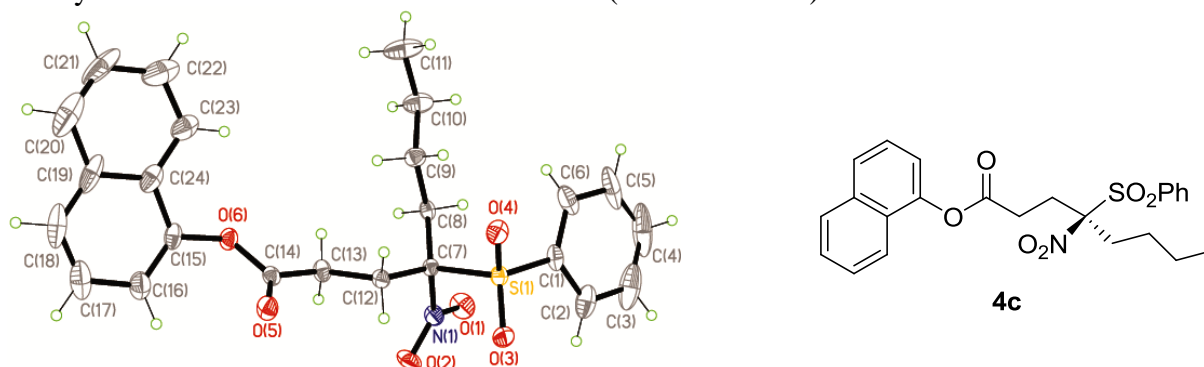
**Enantioselective Synthesis of γ -Tetrasubstituted γ -Nitro- γ -sulfonyl Carboxylates and Amides via
L-*tert*-Leucine-Derived-Squaramide Catalyzed Conjugate Addition of α -Nitrosulfones to
Acrylates and Acrylamides**

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Table S1. Crystal data and structure refinement for **4c** (CCDC 971336)



Identification code	inn-4-ksb-ns-ac	
Empirical formula	C ₂₄ H ₂₅ N O ₆ S	
Formula weight	455.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.600(4) Å	$\alpha = 90^\circ$.
	b = 12.434(5) Å	$\beta = 90^\circ$.
	c = 16.898(6) Å	$\gamma = 90^\circ$.
Volume	2227.2(15) Å ³	
Z	4	
Density (calculated)	1.358 Mg/m ³	
Absorption coefficient	0.186 mm ⁻¹	
F(000)	960	
Crystal size	0.48 x 0.34 x 0.27 mm ³	
Theta range for data collection	3.84 to 25.36°.	
Index ranges	-10 <= h <= 12, -14 <= k <= 10, -20 <= l <= 20	
Reflections collected	17141	

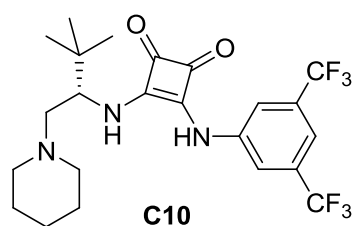
Independent reflections	4049 [R(int) = 0.0559]
Completeness to theta = 25.36°	99.2 %
Absorption correction	Numerical
Max. and min. transmission	0.9510 and 0.9160
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4049 / 0 / 290
Goodness-of-fit on F ²	1.032
Final R indices [I > 2σ(I)]	R1 = 0.0381, wR2 = 0.0867
R indices (all data)	R1 = 0.0419, wR2 = 0.0885
Absolute structure parameter	0.01(7)
Largest diff. peak and hole	0.260 and -0.244 e.Å ⁻³

Experimental

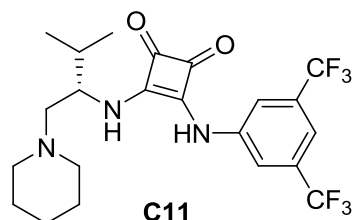
General Experimental Details. The melting points recorded are uncorrected. NMR spectra (¹H and ¹H decoupled ¹³C) were recorded with TMS as the internal standard. The coupling constants (*J* values) are given in Hz. High resolution mass spectra were recorded under ESI Q-TOF conditions. Enantioselectivities were determined using a chiral HPLC equipped with a PDA-detector. Specific rotations were measured for solutions of samples of known concentrations in CHCl₃ using a polarimeter equipped with a sodium vapor lamp. X-ray data were collected on a diffractometer equipped with Mo Kα radiation. The structure was solved by direct methods shelxs97 and refined by full-matrix least squares against F² using shelxl97 software. Catalysts **C1-C9**,¹⁻² Nitrosulfones **2a-g**,³ acrylates **1a-n**,⁴ acrylamide **5c-e**⁵ and enone **5a**⁶ were prepared following the procedures reported in the literature. Other electron deficient alkenes such as **5b**, **5f-h** and **1o-p** are commercially available.

General procedure for the synthesis of catalysts C10-12. To a solution of 3-methoxy-4-(arylamino)cyclobut-3-ene-1,2-dione (678 mg, 2.00 mmol) in dry DCM (10 ml) was slowly added a solution of diamine² (2.00 mmol) in dry DCM (10 ml) at rt. The reaction mixture was stirred for 4 h and the resulting precipitate was isolated by filtration. The residue was washed with ether (10 ml) and dried in vacuo to afford catalyst **C** as a white solid.

(S)-3-(3,5-Bis(trifluoromethyl)phenylamino)-4-(3,3-dimethyl-1-(piperidin-1-yl)butan-2-ylamino)cyclobut-3-ene-1,2-dione (C10). Colorless solid; Yield 736 mg, 75%; mp 257-259 °C; ν_{\max} (film)/cm⁻¹ 3205m, 3149m, 2942m, 1796m, 1662m, 1576vs, 1464s, 1376vs, 1275vs, 1196m, 1174m, 1127vs, 940w, 882w, 749w, 683w; δ_{H} (400 MHz; DMSO-d₆) 0.84 (9H, s), 1.15-1.42 (6H, m), 2.06-2.20 (2H, m), 2.25 (1H, t, *J* 11.8 Hz), 2.32-2.50 (3H, m), 3.92 (1H, t, *J* 8.6 Hz), 7.50-7.58 (2H, br unresolved), 7.99 (2H, s), 9.99 (1H, br s); δ_{C} (100 MHz; DMSO-d₆) 23.9, 25.7, 26.1, 33.8, 54.2, 58.9, 60.5, 114.6, 117.9, 123.2 (q, *J*_{C-F} 271.0 Hz), 131.4 (q, *J*_{C-F} 33.0 Hz), 141.2, 161.6, 170.7, 180.1, 184.6; HRMS (ES⁺, Ar) calcd for C₂₃H₂₇F₆N₃O₂Na (MNa⁺, 100), 514.1900, found 514.1890; $[\alpha]_{\text{D}}^{26} +49.47$ (c 0.5 in DMSO).

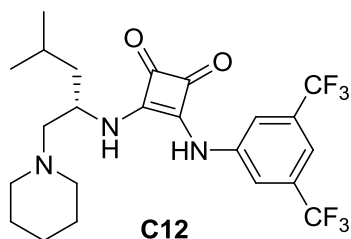


(S)-3-(3,5-bis(trifluoromethyl)phenylamino)-4-(3-methyl-1-(piperidin-1-yl)butan-2-ylamino)cyclobut-3-ene-1,2-dione (C11). Colorless solid; Yield 801 mg, 84%; mp 219-220 °C; ν_{\max} (film)/cm⁻¹ 3210s, 3156s, 2941s, 2857w, 2784w, 1800s, 1671s, 1579vs, 1458vs, 1381vs, 1277vs, 1336w, 1277vs, 1214w, 1181s, 1123vs,



999w, 942m, 885w, 752m; δ_{H} (400 MHz; DMSO- d_6) 0.88 (3H, d, J 6.8 Hz), 0.89 (3H, d, J 6.8 Hz), 1.24-1.46 (6H, m), 1.77-1.90 (1H, septet, J 6.8 Hz), 2.16-2.28 (2H, m), 2.29-2.39 (m, 3H), 2.39-2.47 (m, 1H), 4.05-4.17 (br unresolved, 1H), 7.51-7.59 (1H, br s), 7.61 (1H, s), 8.04 (2H, s), 9.78-10.40 (1H, br s); δ_{C} (100 MHz; DMSO- d_6) 16.9, 19.4, 24.0, 25.8, 30.6, 54.4, 57.2, 61.2, 114.7, 118.1, 123.3 (q, $J_{\text{C-F}}$ 271.0 Hz), 131.5 (q, $J_{\text{C-F}}$ 33.0 Hz), 141.3, 162.0, 170.6, 180.4, 184.7; HRMS (ES $^+$, Ar) calcd for C₂₂H₂₆F₆N₃O₂ (MH $^+$, 100) 478.1924, found 478.1923; $[\alpha]_{\text{D}}^{26}$ +14.22 (c 0.5 in Acetone).

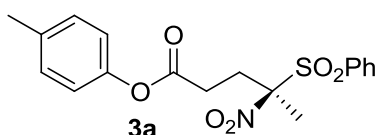
(S)-3-(3,5-bis(trifluoromethyl)phenylamino)-4-(4-methyl-1-(piperidin-1-yl)pentan-2-ylamino)cyclobut-3-ene-1,2-dione (C12). Colorless solid;



Yield 786 mg, 80%; mp 205-207 °C; ν_{max} (film)/cm $^{-1}$ 3204m, 3151m, 3082w, 2938s, 2799w, 1797s, 1665s, 1586vs, 1456vs, 1377vs, 1330w, 1275vs, 1230w, 1194s, 1173m, 1128s, 999w, 941m, 883m, 862w, 744m, 728m, 700m; δ_{H} (400 MHz; DMSO- d_6) 0.85 (3H, d, J 6.6 Hz), 0.88 (3H, d, J 6.6 Hz), 1.25-1.50 (8H, m), 1.66 (1H, m), 2.15-2.36 (4H, m), 2.36-2.47 (2H, m), 4.21-4.34 (1H, br m), 7.55 (1H, br s), 7.60 (1H, s), 8.00 (2H, s), 10.10 (1H, br s); δ_{C} (100 MHz; DMSO- d_6) 21.2, 23.2, 23.9, 24.3, 25.7, 42.1, 50.8, 54.4, 64.2, 114.5, 118.0, 123.2 (q, $J_{\text{C-F}}$ 271.0 Hz), 131.4 (q, $J_{\text{C-F}}$ 33.0 Hz), 141.2, 161.8, 170.1, 180.2, 184.7; HRMS (ES $^+$, Ar) calcd for C₂₃H₂₈F₆N₃O₂ (MH $^+$) 492.2080, found 492.2088; $[\alpha]_{\text{D}}^{26}$ -30.59 (c 0.5 in Acetone).

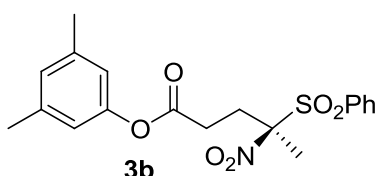
General procedure for the addition of nitrosulfone 2 to acrylate 1 and other electron deficient alkenes 5. To a solution of nitrosulfone 2 (0.4 mmol) and catalyst C10 (0.02 mmol, 9.9 mg) in mesitylene (0.8 ml) was added acrylate 1 (0.6 mmol) at rt. The reaction mixture was stirred at rt and monitored by TLC. The residue was purified by silica gel column chromatography using pet ether-EtOAc (18-40%) as eluent.

(R)-*p*-Tolyl 4-nitro-4-(phenylsulfonyl)pentanoate (3a).⁷ Colorless solid; Yield 148 mg, 98%; mp 98-99 °C (lit⁷ 98-99 °C); ν_{max} (film)/cm $^{-1}$ 3065m, 3034m,



2925s, 2874m, 1756vs, 1551s, 1508m, 1448s, 1384m, 1315vs, 1192vs, 1172vs, 1105w, 916m, 846s, 756s, 730s, 607m; δ_{H} (400 MHz; CDCl₃) 2.00 (3H, s), 2.34 (s, 3H), 2.52-2.63 (m, 1H), 2.72 (2H, dt, J 13.0, 5.0 Hz), 2.82-2.93 (1H, m), 6.93 (2H, d, J 8.3 Hz), 7.17 (2H, d, J 8.3 Hz), 7.61 (2H, t, J 7.8 Hz), 7.77 (1H, t, J 7.8 Hz), 7.88 (2H, d, J 7.8 Hz); δ_{C} (100 MHz; CDCl₃) 17.3, 21.0, 28.8, 28.9, 106.0, 121.1, 129.4, 130.1, 131.2, 132.5, 135.7, 136.0, 148.2, 170.0; MS (ES $^+$, Ar) m/z (rel intensity) 401 ([MNa+1] $^+$, 23), 400 (MNa $^+$, 100), 397 (28), 395 (22), 378 (23), 270 (31); HRMS (ES $^+$, Ar) calcd for C₁₈H₁₉NO₆SNa (MNa $^+$) 400.0831, found 400.0817; $[\alpha]_{\text{D}}^{25}$ +31.43 (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 258 nm), t_{R} (major) = 85.4 min, t_{R} (minor) = 81.9 min; 92% ee. The experimental data are consistent with those reported in the literature (3a was earlier prepared by addition of nitrosulfone to vinyl ketone followed by *m*-CPBA oxidation).⁷

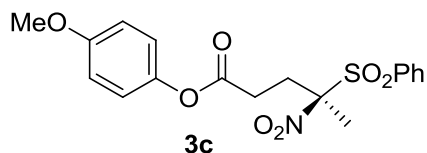
(R)-3,5-Dimethylphenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3b). Colorless sticky oil;



Yield 152 mg, 97%; ν_{max} (neat)/cm $^{-1}$ 3065w, 2923w, 2870w, 1757s, 1618w, 1589w, 1555s, 1449w, 1385w, 1335m, 1314w, 1288w, 1157vs, 1076w, 848w, 759w, 688w, 603w; δ_{H} (400 MHz; CDCl₃) 2.00 (3H, s), 2.31 (6H, s), 2.57 (1H, ddd, J 13.3, 10.2, 5.4 Hz), 2.67-2.77 (2H, m), 2.88 (1H,

ddd, J 13.0, 9.1, 5.4 Hz), 6.68 (2H, s), 6.87 (1H, s), 7.61 (2H, t, J 7.9 Hz), 7.76 (1H, tt, J 7.9, 1.1 Hz), 7.89 (2H, dd, J 7.9, 1.1 Hz); δ_C (100 MHz; CDCl₃) 17.3, 21.3, 28.7, 28.8, 106.0, 118.9, 127.9, 129.4, 131.1, 132.4, 135.6, 139.5, 150.3, 170.0; HRMS (ES⁺, Ar) calcd for C₁₉H₂₁NO₆SNa (MNa⁺) 414.0982, found 414.0985; $[\alpha]_D^{25}$ +28.81 (c 1.0, CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 258 nm), t_R (major) = 83.1 min, t_R (minor) = 71.7 min; 91% ee.

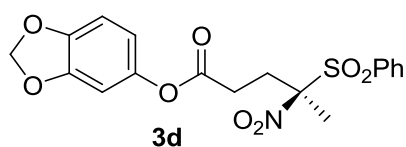
(R)-4-Methoxyphenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3c). Colorless solid; Yield 148



mg, 94%; mp 73-75 °C; ν_{\max} (film)/cm⁻¹ 2931w, 2841w, 1747vs, 1553m, 1507m, 1453w, 1440w, 1385w, 1328m, 1315m, 1298m, 1255w, 1199s, 1169s, 1153s, 1103w, 1073w, 1029w, 845m, 525m; δ_H (400 MHz; CDCl₃) 1.98 (3H, s), 2.56

(1H, ddd, J 12.9, 9.6, 5.9 Hz), 2.66-2.76 (2H, m), 2.87 (1H, ddd, J 13.7, 9.5, 5.9 Hz), 3.77 (3H, s), 6.87, 6.97 (4H, ABq, J 9.0 Hz), 7.60 (2H, t, J 7.6 Hz), 7.76 (1H, t, J 7.6 Hz), 7.88 (2H, d, J 7.6 Hz); δ_C (100 MHz; CDCl₃) 17.3, 28.7, 28.8, 55.7, 106.0, 114.6, 122.2, 129.4, 131.1, 132.5, 135.6, 143.9, 157.5, 170.1; HRMS (ES⁺, Ar) calcd for C₁₈H₁₉NO₇SNa (MNa⁺) 416.0774, found 416.0774; $[\alpha]_D^{25}$ +34.42 (c 1.0 in CHCl₃); HPLC: Chiralpak IA (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 98.5 min, t_R (minor) = 102.0 min; 91% ee.

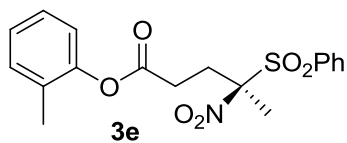
(R)-Benzo[d][1,3]dioxol-5-yl 4-nitro-4-(phenylsulfonyl)pentanoate (3d). Colorless solid;



Yield 160 mg, 99%; mp 117-118 °C; ν_{\max} (film)/cm⁻¹ 3068w, 2989w, 2900m, 1758s, 1582w, 1554s, 1502m, 1484s, 1448m, 1386w, 1333s, 1315m, 1248m, 1159vs, 1075w, 1037m, 930m, 848w, 758m, 721w, 689w, 605w; δ_H (400 MHz; CDCl₃) 1.97

(3H, s), 2.55 (1H, ddd, J 13.2, 8.7, 4.5 Hz), 2.65-2.75 (2H, m), 2.85 (1H, ddd, J 14.5, 8.7, 5.0 Hz), 5.95 (2H, s), 6.48 (1H, dd, J 8.4, 2.3 Hz), 6.56 (1H, d, J 2.3 Hz), 6.74 (1H, d, J 8.4 Hz), 7.60 (2H, t, J 7.6 Hz), 7.76 (1H, t, J 7.6 Hz), 7.87 (2H, d, J 7.6 Hz); δ_C (100 MHz; CDCl₃) 17.4, 28.7, 28.8, 101.9, 103.5, 105.9, 108.1, 113.8, 129.4, 131.1, 132.4, 135.7, 144.6, 145.6, 148.1, 170.1; HRMS (ES⁺, Ar) calcd for C₁₈H₁₇NO₈SNa (MNa⁺) 430.0567, found 430.0566; $[\alpha]_D^{25}$ +34.26 (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 250 nm), t_R (major) = 123.8 min, t_R (minor) = 118.6 min; 90% ee.

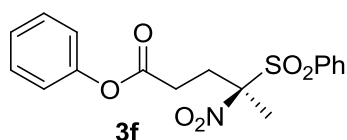
(R)-o-Tolyl 4-nitro-4-(phenylsulfonyl)pentanoate (3e). Colorless solid; Yield 148 mg, 98%;



mp 93-94 °C; ν_{\max} (film)/cm⁻¹ 3067w, 3026w, 2923w, 1758s, 1583w, 1555s, 1491w, 1449w, 1385w, 1334s, 1314m, 1251w, 1223m, 1156vs, 1111w, 1076w, 948w, 917w, 848w, 752m, 720w, 688w, 617w, 603w; δ_H (400 MHz; CDCl₃) 2.01 (3H, s), 2.14 (3H,

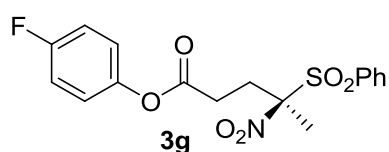
s), 2.61 (1H, ddd, J 16.5, 9.6, 5.4 Hz), 2.74 (1H, ddd, J 16.5, 10.9, 4.6 Hz), 2.77 (1H, ddd, J 15.6, 9.6, 4.6 Hz), 2.90 (1H, ddd, J 15.6, 10.9, 5.4 Hz), 6.98 (1H, dd, J 7.6, 1.5 Hz), 7.15 (1H, td, J 7.6, 1.5 Hz), 7.18 (1H, dd, J 7.6, 1.5 Hz), 7.22 (1H, td, J 7.6, 1.5 Hz), 7.61 (2H, t, J 8.0 Hz), 7.77 (1H, tt, J 8.0, 1.1 Hz), 7.89 (2H, dd, J 8.0, 1.1 Hz); δ_C (100 MHz; CDCl₃) 16.3, 17.4, 28.6, 28.9, 106.0, 121.7, 126.4, 127.1, 129.4, 129.9, 131.2, 131.3, 132.5, 135.7, 149.1, 169.5; HRMS (ES⁺, Ar) calcd for C₁₈H₁₉NO₆SNa (MNa⁺) 400.0825, found 400.0825; $[\alpha]_D^{25}$ +27.35 (c 1.0 in CHCl₃); HPLC: Chiralpak AD-H (pet ether/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 250 nm), t_R (major) = 61.2 min, t_R (minor) = 70.3 min; 84% ee.

(R)-Phenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3f). Colorless solid; Yield 140 mg, 97%;



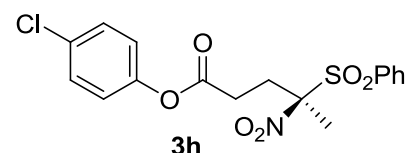
mp 110-112 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3067w, 2950w, 1758vs, 1583w, 1592w, 1554vs, 1493w, 1449w, 1386m, 1334vs, 1315s, 1197s, 1156s, 1075m, 943w, 848w, 754m, 688w, 610w; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.00 (3H, s), 2.59 (1H, ddd, J 16.3, 10.4, 5.6 Hz), 2.72 (1H, ddd, J 16.3, 10.6, 4.9 Hz), 2.75 (1H, ddd, J 15.6, 10.4, 4.9 Hz), 2.89 (1H, ddd, J 15.6, 10.6, 5.6 Hz), 7.06 (2H, dd, J 7.7, 1.0 Hz), 7.24 (1H, tt, J 7.7, 1.0 Hz), 7.38 (2H, t, J 7.7 Hz), 7.61 (2H, t, J 7.9 Hz), 7.63 (1H, tt, J 7.9, 1.1 Hz), 7.91 (2H, dd, J 7.9, 1.1 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.4, 28.8 ($\times 2$), 106.0, 121.4, 126.3, 129.4, 129.6, 131.2, 132.5, 135.7, 150.4, 169.8; HRMS (ES^+ , Ar) calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_6\text{SNa}$ (MNa^+) 386.0669, found 386.0665; $[\alpha]_{\text{D}}^{25} +30.64$ (c 1.0 in CHCl_3); HPLC: Lux cellulose-1 (pet ether/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 258 \text{ nm}$), t_{R} (major) = 67.4 min, t_{R} (minor) = 65.4 min; 89% ee.

(R)-4-Fluorophenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3g). Colorless solid; Yield 148



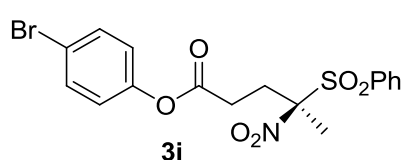
mg, 97%; mp 101-103 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3071w, 2931w, 2868w, 1757vs, 1547m, 1502m, 1448w, 1388w, 1331s, 1316s, 1251w, 1188s, 1158s, 1089w, 1076w, 916w, 847w, 762s; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.99 (3H, s), 2.58 (1H, ddd, J 16.5, 10.6, 5.5 Hz), 2.71 (1H, ddd, J 16.5, 10.8, 4.7 Hz), 2.74 (1H, ddd, J 15.7, 10.6, 4.7 Hz), 2.89 (1H, ddd, J 15.7, 10.8, 5.5 Hz), 6.98-7.08 (4H, m), 7.61 (2H, t, J 7.9 Hz), 7.77 (1H, tt, J 7.9, 1.1 Hz), 7.88 (2H, dd, J 7.9, 1.1 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.5, 28.7 ($\times 2$), 105.9, 116.3 (d, $J_{\text{C-F}}$ 23.0 Hz), 122.9 (d, $J_{\text{C-F}}$ 9.0 Hz), 129.5, 131.2, 132.4, 135.7, 146.2 (d, $J_{\text{C-F}}$ 3.0 Hz), 160.4 (d, $J_{\text{C-F}}$ 244.0 Hz), 169.8; $\delta_{\text{F}}(470 \text{ MHz}; \text{CDCl}_3)$ 116.37 (tt, J 8, 4.0 Hz); HRMS (ES^+ , Ar) calcd for $\text{C}_{17}\text{H}_{16}\text{FNO}_6\text{SNa}$ (MNa^+) 404.0575, found 404.0581; $[\alpha]_{\text{D}}^{25} +27.41$ (c 1.0 in CHCl_3); HPLC: chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, $\lambda = 250 \text{ nm}$), t_{R} (major) = 51.3 min, t_{R} (minor) = 48.2 min; 86% ee.

(R)-4-Chlorophenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3h). Colorless solid; Yield 152



mg, 96%; mp 89-90 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3098w, 3069w, 2930w, 1760s, 1583w, 1554s, 1487m, 1449w, 1386w, 1334s, 1314m, 1202s, 1156vs, 1087m, 1076m, 1015w, 847w, 757w, 688w, 605w; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.98 (3H, s), 2.59 (1H, ddd, J 16.5, 10.7, 5.5 Hz), 2.72 (1H, ddd, J 16.5, 10.8, 4.6 Hz), 2.75 (1H, ddd, J 15.7, 10.7, 4.6 Hz), 2.89 (1H, ddd, J 15.7, 10.8, 5.5 Hz), 7.01 (2H, d, J 8.8 Hz), 7.33 (2H, d, J 8.8 Hz), 7.61 (2H, t, J 7.9 Hz), 7.77 (1H, tt, J 7.9, 1.1 Hz), 7.88 (2H, dd, J 7.9, 1.1 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.6, 28.7, 28.8, 105.9, 122.8, 129.5, 129.7, 131.2, 131.6, 132.5, 135.7, 148.9, 169.6; HRMS (ES^+ , Ar) calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_6\text{SNa}$ (MNa^+) 420.0279, found 420.0285; $[\alpha]_{\text{D}}^{25} +32.92$ (c 1.0 in CHCl_3); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 258 \text{ nm}$), t_{R} (major) = 93.6 min, t_{R} (minor) = 85.5 min; 85% ee.

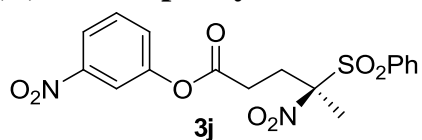
(R)-4-Bromophenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3i). Colorless solid; Yield 176



mg, 99%; mp 101-103 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3060w, 2930w, 2863w, 1759s, 1553s, 1484w, 1449w, 1382w, 1333m, 1311m, 1201m, 1155vs, 1074w, 913w, 847w, 752m; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 1.99 (3H, s), 2.60 (1H, ddd, J 16.5, 10.7, 5.5 Hz), 2.72 (1H, ddd, J 16.5, 10.8, 4.5 Hz), 2.75 (1H, ddd, J 15.6, 10.7, 4.5 Hz), 2.88 (1H, ddd, J 15.6, 10.8, 5.5 Hz), 6.95 (2H, d, J 8.9 Hz), 7.49 (2H, d, J 8.9 Hz), 7.62 (2H, t, J 7.9 Hz), 7.78 (1H, tt, J 7.9, 1.2 Hz), 7.88 (2H, dd, J 7.9, 1.2 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.6, 28.8 ($\times 2$), 105.9, 119.4, 123.3, 129.5, 131.2, 132.5, 132.7, 135.7, 149.4, 169.5; HRMS (ES^+ , Ar) calcd for $\text{C}_{17}\text{H}_{16}\text{BrNO}_6\text{SNa}$ (MNa^+) 463.9774, found 463.9761; $[\alpha]_{\text{D}}^{25} +32.60$

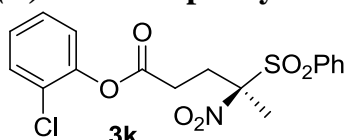
(c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 250 nm), *t*_R (major) = 67.2 min, *t*_R (minor) = 62.5 min; 84% ee.

(R)-3-Nitrophenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3j). Colorless solid; Yield 140



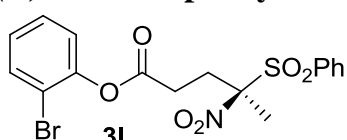
mg, 86%; mp 103-105 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3098w, 2931w, 2873w, 1767s, 1553s, 1532s, 1477w, 1449w, 1384w, 1352s, 1335s, 1210m, 1155s, 1076w, 814w, 759w, 744w, 611w; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.00 (3H, s), 2.68 (1H, ddd, *J* 13.9, 9.3, 4.3 Hz), 2.72-2.88 (2H, m), 2.92 (1H, ddd, *J* 13.0, 9.3, 4.5 Hz), 7.44 (1H, ddd, *J* 8.2, 2.2, 1.0 Hz), 7.57 (1H, t, *J* 8.2 Hz), 7.63 (2H, t, *J* 7.9 Hz), 7.79 (1H, tt, *J* 7.9, 1.2 Hz), 7.89 (2H, dd, *J* 7.9, 1.2 Hz), 7.98 (1H, t, *J* 2.2 Hz), 8.12 (1H, ddd, *J* 7.5, 2.2, 1.0 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.8, 28.7, 28.8, 105.8, 117.3, 121.3, 128.0, 129.5, 130.4, 131.2, 132.5, 135.8, 148.9, 150.6, 169.3; HRMS (ES⁺, Ar) calcd for C₁₇H₁₆N₂O₈SNa (MNa⁺) 431.0520, found 431.0516; $[\alpha]_{\text{D}}^{25} +32.72$ (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 250 nm), *t*_R (major) = 74.2 min, *t*_R (minor) = 67.6 min; 92% ee.

(R)-2-Chlorophenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3k). Colorless solid; Yield 150



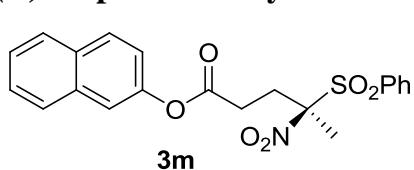
mg, 94%; mp 97-99 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3070w, 2929w, 2873w, 1767vs, 1583m, 1555vs, 1477m, 1449m, 1386m, 1334s, 1315m, 1217m, 1155vs, 1076w, 1063w, 916w, 848w, 831w, 755s, 688m, 604m; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.00 (3H, s), 2.59-2.69 (1H, m), 2.71-2.85 (2H, m), 2.86-2.96 (1H, m), 7.11 (1H, dd, *J* 7.8, 1.6 Hz), 7.19 (1H, td, *J* 7.8, 1.6 Hz), 7.27 (1H, td, *J* 7.8, 1.6 Hz), 7.42 (1H, dd, *J* 7.8, 1.6 Hz), 7.62 (2H, t, *J* 7.9 Hz), 7.75 (1H, tt, *J* 7.9, 1.1 Hz), 7.88 (2H, dd, *J* 7.9, 1.1 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.3, 28.5, 28.8, 105.9, 123.6, 126.7, 127.5, 128.0, 129.4, 130.4, 131.1, 132.4, 135.7, 146.6, 168.9; HRMS (ES⁺, Ar) calcd for C₁₇H₁₆ClNO₆SNa (MNa⁺) 420.0279, found 420.0274; $[\alpha]_{\text{D}}^{25} +28.80$ (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 250 nm), *t*_R (major) = 55.5 min, *t*_R (minor) = 54.5 min; 94% ee.

(R)-2-Bromophenyl 4-nitro-4-(phenylsulfonyl)pentanoate (3l). Colorless solid; Yield 166



mg, 94%; mp 81-83 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3067w, 3026w, 2921w, 1767s, 1582w, 1554s, 1471m, 1448m, 1385w, 1334s, 1314m, 1249w, 1212m, 1155s, 1075w, 1046w, 848w, 828w, 754m, 720w, 688w, 604w; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.02 (3H, s), 2.65 (1H, ddd, *J* 16.4, 10.9, 5.3 Hz), 2.76 (1H, ddd, *J* 16.4, 10.2, 4.3 Hz), 2.80 (1H, ddd, *J* 15.6, 10.9, 4.3 Hz), 2.92 (1H, ddd, *J* 15.6, 10.2, 5.3 Hz), 7.11 (1H, dd, *J* 7.9, 1.5 Hz), 7.14 (1H, td, *J* 7.9, 1.5 Hz), 7.33 (1H, td, *J* 7.9, 1.5 Hz), 7.60 (1H, dd, *J* 7.9, 1.5 Hz), 7.62 (2H, t, *J* 7.7 Hz), 7.78 (1H, tt, *J* 7.7, 1.2 Hz), 7.89 (2H, dd, *J* 7.7, 1.2 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 17.4, 28.7, 28.9, 106.0, 116.1, 123.7, 127.9, 128.8, 129.5, 131.3, 132.5, 133.6, 135.7, 147.9, 169.0; HRMS (ES⁺, Ar) calcd for C₁₇H₁₆BrNO₆SNa (MNa⁺) 463.9774, found 463.9773; $[\alpha]_{\text{D}}^{25} +21.69$ (c 1.0 in CHCl₃); HPLC: Chiralpak AD-H (pet ether/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 250 nm), *t*_R (major) = 80.5 min, *t*_R (minor) = 100.9 min; 91% ee.

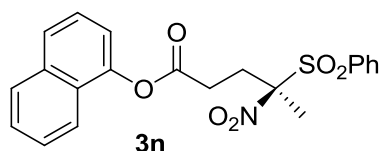
(R)-Naphthalen-2-yl 4-nitro-4-(phenylsulfonyl)pentanoate (3m). Colorless solid; Yield 148



mg, 90%; mp 139-142 °C; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2928w, 2852w, 1758m, 1554m, 1449w, 1386w, 1334w, 1210w, 1157vs, 1075w, 759s; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.03 (3H, s), 2.66 (1H, ddd, *J* 16.5, 10.8, 5.5 Hz), 2.76 (1H, ddd, *J* 16.5, 10.9, 4.4 Hz), 2.81 (1H, ddd, *J* 15.7, 10.8, 4.4 Hz), 2.93 (1H, ddd, *J* 15.7, 10.9, 5.5 Hz), 7.19 (2H, dd, *J* 8.9, 2.3 Hz), 7.48 (1H, td, *J* 7.0, 1.7 Hz), 7.51 (1H, td, *J* 7.0, 1.7

H_z), 7.54 (1H, d, *J* 2.3 Hz), 7.63 (2H, t, *J* 8.1 Hz), 7.78 (1H, tt, *J* 8.1, 1.1 Hz), 7.78-7.82 (1H, m), 7.83-7.86 (1H, m), 7.85 (1H, d, *J* 8.9 Hz), 7.91 (2H, dd, *J* 8.1, 1.1 Hz); δ_{C} (100 MHz; CDCl₃) 17.5, 28.9, 106.0, 118.5, 120.8, 126.1, 126.9, 127.8, 127.9, 129.5, 129.7, 131.2, 131.7, 132.5, 133.8, 135.7, 148.1, 170.0; HRMS (ES⁺, Ar) calcd for C₂₁H₁₉NO₆SNa (MNa⁺) 436.0825, found 436.0824; $[\alpha]_{\text{D}}^{25} +41.79$ (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 250$ nm), t_{R} (major) = 51.4 min, t_{R} (minor) = 39.9 min; 86% ee.

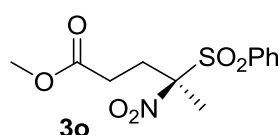
(R)-Naphthalen-1-yl 4-nitro-4-(phenylsulfonyl)pentanoate (3n). Colorless sticky oil; Yield



155 mg, 94%; ν_{max} (neat)/cm⁻¹ 3065w, 2947w, 1761s, 1598w, 1554s, 1448w, 1387m, 1334s, 1225w, 1155vs, 1113w, 1076w, 773m; δ_{H} (400 MHz; CDCl₃) 2.03 (3H, s), 2.72-2.87 (m, 2H), 2.89-3.04 (2H, m), 7.25 (1H, dd, *J* 7.9, 0.7 Hz), 7.46 (1H, t, *J* 7.9 Hz), 7.79-7.83 (1H, m), 7.85-7.90 (1H, m), 7.91 (2H, dd, *J*

7.9, 0.9 Hz); δ_{C} (100 MHz; CDCl₃) 17.4, 28.6, 28.9, 105.9, 118.0, 120.9, 125.4, 126.4, 126.5, 126.6, 126.7, 128.2, 129.4, 131.1, 132.4, 134.6, 135.6, 146.2, 169.8; HRMS (ES⁺, Ar) calcd for C₂₁H₁₉NO₆SNa (MNa⁺) 436.0825, found 436.0823; $[\alpha]_{\text{D}}^{25} +22.77$ (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, $\lambda = 250$ nm), t_{R} (major) = 130.7 min, t_{R} (minor) = 148.5 min; 93% ee.

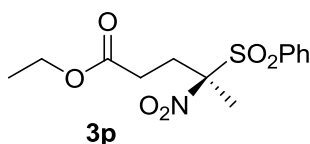
(R)-Methyl 4-nitro-4-(phenylsulfonyl)pentanoate (3o). Colorless oil; Yield 110 mg, 91%;



ν_{max} (neat)/cm⁻¹ 3020w, 2954w, 1739vs, 1583w, 1553vs, 1448m, 1385w, 1333s, 1314m, 1202m, 1178m, 1155s, 1076w, 998vw, 931vw, 847w, 758m, 721w, 689w, 607m, 550w; δ_{H} (400 MHz; CDCl₃) 1.93 (3H, s), 2.30 (1H, ddd, *J* 16.2, 10.3, 5.8 Hz), 2.45 (1H, ddd, *J* 16.2, 10.2, 5.4 Hz), 2.59 (1H, ddd, *J* 15.4, 10.3, 5.4 Hz), 2.75 (1H, ddd, *J* 15.4, 10.2,

5.8 Hz), 3.67 (3H, s), 7.60 (2H, t, *J* 7.9 Hz), 7.76 (1H, tt, *J* 7.9, 1.1 Hz), 7.85 (2H, dd, *J* 7.9, 1.1 Hz); δ_{C} (100 MHz; CDCl₃) 17.1, 28.4, 28.9, 52.3, 106.1, 129.4, 131.2, 132.5, 135.6, 171.6; HRMS (ES⁺, Ar) calcd for C₁₂H₁₅NO₆SNa (MNa⁺) 324.0512, found 324.0512; $[\alpha]_{\text{D}}^{25} +18.84$ (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, $\lambda = 250$ nm), t_{R} (major) = 71.9 min, t_{R} (minor) = 32.1 min; 94% ee.

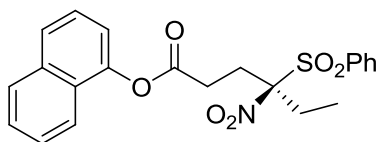
(R)-Ethyl 4-nitro-4-(phenylsulfonyl)pentanoate (3p). Colorless solid; Yield 125 mg, 99%;



mp 69-71 °C; ν_{max} (film)/cm⁻¹ 3067w, 2984m, 2942w, 1733vs, 1583w, 1555vs, 1449m, 1384w, 1334s, 1314m, 1263vw, 1191m, 1156s, 1112w, 1095w, 1076m, 1022w, 999w, 919w, 846m, 757m, 721m, 689m, 607m, 552w, 553w; δ_{H} (400 MHz; CDCl₃) 1.24 (3H, t, *J* 7.1 Hz), 1.94 (3H, s), 2.30 (1H, ddd, *J* 16.2, 10.3, 5.8 Hz), 2.45 (1H, ddd,

J 16.2, 10.2, 5.4 Hz), 2.59 (1H, ddd, *J* 15.3, 10.3, 5.4 Hz), 2.75 (1H, ddd, *J* 15.3, 10.2, 5.8 Hz), 4.12 (2H, q, *J* 7.1 Hz), 7.61 (2H, t, *J* 8.1 Hz), 7.76 (1H, tt, *J* 8.1, 1.2 Hz), 7.86 (2H, dd, *J* 8.1, 1.2 Hz); δ_{C} (100 MHz; CDCl₃) 14.3, 17.1, 28.7, 29.0, 61.4, 106.2, 129.4, 131.2, 132.6, 135.6, 171.1; HRMS (ES⁺, Ar) calcd for C₁₃H₁₇NO₆SNa (MNa⁺) 338.0669, found 338.0669; $[\alpha]_{\text{D}}^{25} +18.57$ (c 1.0 in CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, $\lambda = 250$ nm), t_{R} (major) = 46.7 min, t_{R} (minor) = 28.3 min; 95% ee.

(R)-Naphthalen-1-yl 4-nitro-4-(phenylsulfonyl)hexanoate (4a). Colorless solid; Yield 170

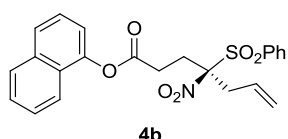


mg, 99%; mp 102-104 °C; ν_{max} (film)/cm⁻¹ 3065m, 2984m, 2949m, 2886w, 1760s, 1598m, 1582m, 1554s, 1509w, 1462m, 1448m, 1388m, 1331s, 1314s, 1259w, 1224m, 1152s, 1076m, 1038vw, 1014vw, 936w, 870w, 822m, 796m, 774s, 757s, 688m,

4a

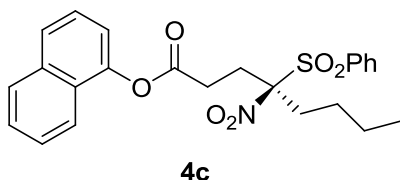
617m, 598m, 555m; δ_{H} (400 MHz; CDCl_3) 1.08 (3H, t, J 7.4 Hz), 2.39 (2H, ABqq, J 14.9, 7.4 Hz), 2.76-2.85 (1H, m), 3.05-3.16 (2H, m), 3.27-3.37 (1H, m), 7.30 (1H, dd, J 7.8, 0.8 Hz), 7.48 (1H, t, J 7.8 Hz), 7.53 (1H, td, J 7.5, 2.0 Hz), 7.55 (1H, td, J 7.5, 2.0 Hz), 7.61 (2H, t, J 8.1 Hz), 7.75 (1H, tt, J 8.1, 1.0 Hz), 7.77 (1H, dd, J 7.8, 0.8 Hz), 7.88 (1H, dd, J 7.5, 2.0 Hz), 7.89 (1H, dd, J 7.5, 2.0 Hz), 7.93 (2H, dd, J 8.1, 1.0 Hz); δ_{C} (100 MHz; CDCl_3) 8.3, 25.7, 26.6, 29.1, 109.3, 118.1, 121.1, 125.5, 126.4, 126.7 ($\times 2$), 126.8, 128.2, 129.3, 131.2, 133.4, 134.8, 135.5, 146.5, 170.5; HRMS (ES^+ , Ar) calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_6\text{SNa}$ (MNa^+) 450.0982, found 450.0988; $[\alpha]_{\text{D}}^{25} +28.23$ (c 1.0 in CHCl_3); HPLC: Lux Cellulose-1 (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 250$ nm), t_{R} (major) = 30.8 min, t_{R} (minor) = 24.6 min; 92% ee.

(S)-Naphthalen-1-yl 4-nitro-4-(phenylsulfonyl)hept-6-enoate (4b). Colorless solid; Yield



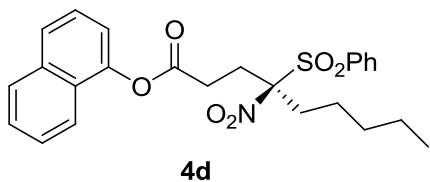
175 mg, 99%; mp 93-95 °C; ν_{max} (film)/ cm^{-1} 3065w, 2986vw, 1761s, 1599vw, 1555s, 1448w, 1385w, 1335s, 1315m, 1225w, 1151vs, 1082w, 936w, 800w, 739s, 688w, 611w, 554w; δ_{H} (400 MHz; CDCl_3) 2.80 (1H, ddd, J 16.9, 10.7, 4.2 Hz), 2.98-3.19 (4H, m), 3.30 (1H, ddd, J 16.9, 10.7, 4.2 Hz), 5.34 (1H, dd, J 17.8, 1.0 Hz), 5.35 (1H, dd, J 10.4, 1.0 Hz), 5.75 (1H, ddt, J 17.8, 10.4, 7.1 Hz), 7.27 (1H, d, J 7.6 Hz), 7.47 (1H, t, J 7.6 Hz), 7.50-7.56 (2H, m), 7.64 (2H, t, J 8.1 Hz), 7.76 (1H, d, J 7.6 Hz), 7.79 (1H, t, J 8.1, 1.1 Hz), 7.81-7.85 (1H, m), 7.86-7.91 (1H, m), 7.94 (2H, dd, J 8.1, 1.1 Hz); δ_{C} (100 MHz; CDCl_3) 26.5, 28.9, 37.2, 107.9, 118.1, 121.1, 123.1, 125.5, 126.4, 126.7 ($\times 2$), 126.8, 128.2 ($\times 2$), 129.5, 131.3, 133.2, 134.8, 135.7, 146.5, 170.4; HRMS (ES^+ , Ar) calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_6\text{SNa}$ (MNa^+) 462.0982, found 462.0982; $[\alpha]_{\text{D}}^{25} +27.30$ (c 1.0 in CHCl_3); HPLC: Lux Cellulose-1 (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 250$ nm), t_{R} (major) = 19.3 min, t_{R} (minor) = 17.4 min; 93% ee.

(R)-Naphthalen-1-yl 4-nitro-4-(phenylsulfonyl)octanoate (4c). Colorless solid; Yield 176 mg, 97%; mp 108-109 °C; ν_{max} (film)/ cm^{-1} 2961w, 2935w,



2873w, 1760s, 1646w, 1553s, 1509vw, 1448w, 1385w, 1331s, 1314m, 1259vw, 1225w, 1150vs, 1079w, 798m, 775m, 756m, 775s, 756s, 738s, 688m, 619w, 550w; δ_{H} (400 MHz; CDCl_3) 0.93 (3H, t, J 7.3 Hz), 1.16-1.27 (1H, m), 1.31-1.43 (2H, m), 1.54-1.65 (1H, m), 2.33 (2H, ABqdd, J 14.7, 11.6, 4.8 Hz), 2.72-2.85 (1H, m), 3.02-3.12 (2H, m), 3.25-3.39 (1H, m), 7.29 (1H, dd, J 7.8, 0.9 Hz), 7.48 (1H, t, J 7.8 Hz), 7.53 (1H, td, J 6.9, 1.9 Hz), 7.55 (1H, td, J 6.9, 2.0 Hz), 7.62 (2H, t, J 8.1 Hz), 7.77 (1H, tt overlap with dd, J 8.1, 1.1 Hz), 7.77 (1H, dd overlap with tt, J 7.8, 0.9 Hz), 7.84-7.91 (2H, m), 7.93 (2H, dd, J 8.1, 1.1 Hz), confirmed by ^1H - ^1H -COSY spectrum; δ_{C} (100 MHz; CDCl_3) 13.8, 22.8, 25.8, 26.3, 29.3, 32.5, 109.0, 118.2, 121.2, 125.5, 126.4, 126.7, 126.8 ($\times 2$), 128.3, 129.4, 131.2, 133.4, 134.8, 135.6, 146.5, 170.5; HRMS (ES^+ , Ar) calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_6\text{SNa}$ (MNa^+) 478.1295, found 478.1308; $[\alpha]_{\text{D}}^{25} +19.98$ (c 1.0 in CHCl_3); HPLC: Lux Cellulose-1 (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 250$ nm), t_{R} (major) = 18.7 min, t_{R} (minor) = 16.6 min; 92% ee.

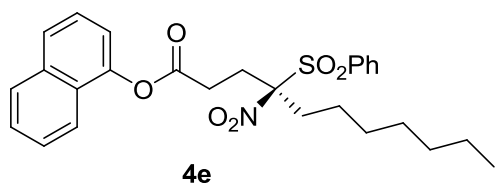
(R)-Naphthalen-1-yl 4-nitro-4-(phenylsulfonyl)nonanoate (4d). Colorless solid; Yield 179 mg, 95%; mp 99-100 °C; ν_{max} (film)/ cm^{-1} 2956w, 2934w,



2874w, 1762m, 1646w, 1553s, 1448w, 1385w, 1331m, 1225w, 1150vs, 1080w, 773w, 688w, 620w; δ_{H} (400 MHz; CDCl_3) 0.89 (3H, t, J 7.0 Hz), 1.16-1.42 (5H, m), 1.54-1.67 (1H, m), 2.32 (2H, ABqdd, J 14.7, 11.6, 4.5 Hz), 2.71-2.85 (1H, m), 3.03-3.14 (2H, m), 3.26-3.40 (1H, m), 7.29 (1H, d, J 7.8 Hz), 7.48 (1H, t, J 7.8 Hz), 7.53 (1H, td, J 6.8, 1.9 Hz), 7.55 (1H, td, J 6.8, 1.9 Hz), 7.62

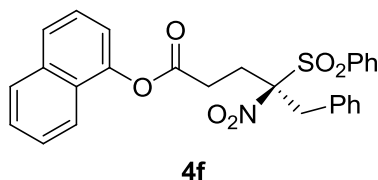
(2H, t, J 7.7 Hz), 7.76 (1H, tt overlap with d, J 7.7, 1.2 Hz), 7.77 (1H, d overlap with tt, J 7.8 Hz), 7.84-7.91 (2H, m), 7.93 (2H, dd, J 7.7, 1.2 Hz); δ_C (100 MHz; CDCl₃) 14.0, 22.3, 23.4, 26.2, 29.2, 31.6, 32.7, 108.9, 118.1, 121.1, 125.5, 126.4, 126.7, 126.8, 128.2, 129.4, 131.2, 133.4, 134.8, 135.6, 146.5, 170.5; HRMS (ES⁺, Ar) calcd for C₂₅H₂₇NO₆SNa (MNa⁺) 492.1451, found 492.1451; $[\alpha]_D^{25}$ +14.30 (c 1.0 in CHCl₃); HPLC: Lux Cellulose-1 (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 22.6 min, t_R (minor) = 19.3 min; 92% ee.

(R)-Naphthalen-1-yl 4-nitro-4-(phenylsulfonyl)undecanoate (4e). Colorless solid; Yield



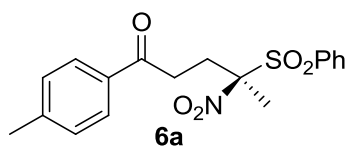
185 mg, 93%; mp 92-94 °C; ν_{\max} (film)/cm⁻¹ 2930w, 2857w, 1762m, 1648w, 1554m, 1448w, 1386w, 1332m, 1225w, 1151s, 1081w, 739m; δ_H (400 MHz; CDCl₃) 0.88 (3H, t, J 6.8 Hz), 1.18-1.40 (9H, m), 1.54-1.67 (1H, m), 2.32 (2H, ABqdd, J 14.6, 11.6, 4.6 Hz), 2.74-2.84 (1H, m), 3.02-3.13 (2H, m), 3.25-3.36 (1H, m), 7.29 (1H, dd, J 7.7, 0.7 Hz), 7.48 (1H, t, J 7.7 Hz), 7.53 (1H, td, J 6.9, 1.8 Hz), 7.55 (1H, td, J 6.9, 1.8 Hz), 7.62 (2H, t, J 7.9 Hz), 7.77 (1H, dd overlap with tt, J 7.7, 0.7 Hz), 7.77 (1H, tt overlap with dd, J 7.9, 1.2 Hz), 7.84-7.91 (2H, m), 7.93 (2H, dd, J 7.9, 1.2 Hz); δ_C (100 MHz; CDCl₃) 14.2, 22.7, 23.7, 26.2, 28.9, 29.3, 29.5, 31.7, 32.8, 108.9, 118.1, 121.1, 125.5, 126.4, 126.7 (\times 2), 126.8, 128.2, 129.4, 131.2, 133.4, 134.8, 135.6, 146.5, 170.6; HRMS (ES⁺, Ar) calcd for C₂₇H₃₁NO₆SNa (MNa⁺) 520.1764, found 520.1760; $[\alpha]_D^{25}$ +9.80 (c 1.0 in CHCl₃); HPLC: Lux Cellulose-1 (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 16.5 min, t_R (minor) = 20.0 min; 92% ee.

(S)-Naphthalen-1-yl 4-nitro-5-phenyl-4-(phenylsulfonyl)pentanoate (4f). Colorless solid;



Yield 193 mg, 98%; mp 151-153 °C; ν_{\max} (film)/cm⁻¹ 3063vw, 1761m, 1599vw, 1555m, 1448w, 1385w, 1332m, 1225w, 1150s, 1081w, 800w, 739m, 703w, 687w, 598w, 518vw; δ_H (400 MHz; CDCl₃) 2.79 (2H, ABqdd, J 15.8, 10.0, 6.2 Hz), 3.18 (1H, ddd, J 17.6, 10.0, 6.2 Hz), 3.33 (1H, ddd, J 17.6, 10.0, 6.2 Hz), 3.52 (2H, ABq, J 14.2 Hz), 7.03-7.11 (2H, m), 7.23 (1H, dd, J 7.8, 0.8 Hz), 7.28-7.33 (3H, m), 7.45 (1H, t, J 7.8 Hz), 7.49-7.55 (2H, m), 7.68 (2H, t, J 8.1 Hz), 7.74 (1H, dd, J 7.8, 0.8 Hz), 7.77-7.81 (1H, m), 7.81 (1H, tt overlap with m, J 8.1, 1.0 Hz), 7.84-7.90 (1H, m), 8.06 (2H, dd, J 8.1, 1.0 Hz); δ_C (100 MHz; CDCl₃) 26.7, 29.1, 41.5, 108.9, 118.1, 121.3, 125.5, 126.3, 126.6, 126.7, 126.8, 128.2, 128.8, 129.4 (\times 2), 130.0, 131.2, 131.7, 134.1, 134.8, 135.7, 146.6, 170.8; HRMS (ES⁺, Ar) calcd for C₂₇H₂₃NO₆SNa (MNa⁺) 512.1138, found 512.1138; $[\alpha]_D^{25}$ +30.02 (c 1.0 in CHCl₃); HPLC: Lux Cellulose-1 (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 16.2 min, t_R (minor) = 23.6 min; 83% ee.

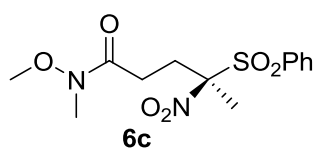
(R)-4-Nitro-4-(phenylsulfonyl)-1-p-tolylpentan-1-one (6a).⁷ Colorless solid; Yield 179 mg,



99%; mp 132-134 °C; ν_{\max} (film)/cm⁻¹ 2921w, 1671s, 1608w, 1548vs, 1448w, 1439w, 1328m, 1310m, 1154s, 1073w, 982w, 790w; δ_H (400 MHz; CDCl₃) 1.99 (3H, s), 2.40 (3H, s), 2.78 (2H, ABqdd, J 14.8, 9.1, 6.0), 3.01 (2H, ABqdd, J 17.4, 9.1, 6.0), 7.25 (2H, d, J 8.2), 7.62 (2H, t, J 7.8), 7.77 (1H, tt, J 7.8, 1.0), 7.80 (2H, d, J 8.2), 7.90 (2H, dd, J 7.8, 1.0); δ_C (100 MHz; CDCl₃) 17.6, 21.9, 28.5, 32.6, 106.7, 128.3, 129.4, 129.6, 131.3, 132.9, 133.7, 135.6, 144.8, 196.3; m/z (ES⁺, Ar) 364 ([MH+2]⁺, 9), 363 ([MH+1]⁺, 23), 362 (MH⁺, 100), 315 (12), 173 (7); HRMS (ES⁺, Ar) calcd for C₁₈H₂₀NO₅S (MH⁺) 362.1062, found 362.1050; $[\alpha]_D^{25}$ +28.3 (c 1.0 in CHCl₃); HPLC: Lux Amylose-2 (pet

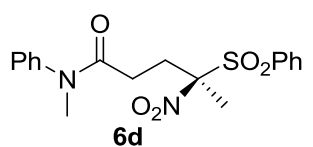
ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 51.3 min, t_R (minor) = 45.3 min; 96% ee.

(R)-*N*-Methoxy-*N*-methyl-4-nitro-4-(phenylsulfonyl)pentanamide (6c). Colorless oil; Yield



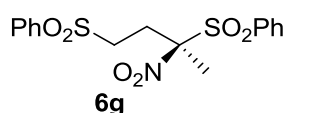
120 mg, 92%; ν_{\max} (neat)/cm⁻¹ 2942m, 1661vs, 1554s, 1448s, 1387s, 1334vs, 1157vs, 1075m, 998m, 915m, 848w, 732m, 690m, 607m; δ_H (500 MHz; CDCl₃) 1.97 (3H, s), 2.41 (1H, ddd, J 16.1, 10.2, 5.8 Hz), 2.53 (1H, ddd, J 16.1, 10.2, 5.2 Hz), 2.63 (1H, ddd, J 15.2, 10.2, 5.2 Hz), 2.71 (1H, ddd, J 15.2, 10.2, 5.8 Hz), 3.16 (3H, s), 3.64 (3H, s), 7.61 (2H, t, J 7.5 Hz), 7.76 (1H, tt, J 7.5, 1.2 Hz), 7.89 (2H, dd, J 7.5, 1.2 Hz); δ_C (125 MHz; CDCl₃) 17.1, 26.4, 29.0, 32.4, 61.5, 106.7, 129.4, 131.2, 132.8, 135.5, 171.5; HRMS (ES⁺, Ar) calcd for C₁₃H₁₈N₂O₆SK (MK⁺) 369.0517, found 369.0517; $[\alpha]_D^{25}$ +6.16 (c 1.0, CHCl₃); HPLC: Chiralpak AD-H (pet ether/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 212 nm), t_R (major) = 6.2 min, t_R (minor) = 9.0 min; 92% ee.

(R)-*N*-Methyl-4-nitro-*N*-phenyl-4-(phenylsulfonyl)pentanamidepentanamide (6d).



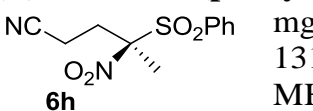
Colorless solid; mp 106-107 °C; Yield 80 mg, 53%; ν_{\max} (flim)/cm⁻¹ 2947w, 1649m, 1597w, 1555m, 1497w, 1449w, 1395w, 1335m, 1157m, 1076w, 910s, 848vw, 735s, 651m, 607w; δ_H (500 MHz; CDCl₃) 1.81 (3H, s), 1.99 (1H, ddd, J 15.7, 10.0, 5.7 Hz), 2.13 (1H, ddd, J 15.7, 10.0, 5.7 Hz), 2.61 (2H, ABqdd, J 14.9, 10.0, 5.7 Hz), 3.23 (3H, s), 7.11 (2H, d, J 7.4 Hz), 7.35 (1H, t, J 7.4 Hz), 7.40 (2H, t, J 7.4 Hz), 7.60 (2H, t, J 7.5 Hz), 7.75 (1H, tt, J 7.5, 1.2 Hz), 7.84 (2H, dd, J 7.5, 1.2 Hz); δ_C (125 MHz; CDCl₃) 16.8, 28.4, 29.9, 37.7, 106.7, 127.2, 128.5, 129.4, 130.3, 131.3, 132.8, 135.5, 143.3, 170.0; HRMS (ES⁺, Ar) calcd for C₁₈H₂₀N₂O₅SK (MK⁺) 415.0725, found 415.0723; $[\alpha]_D^{25}$ -23.86 (c 1.0, CHCl₃); HPLC: Chiralpak AD-H (pet ether/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 212 nm), t_R (major) = 9.6 min, t_R (minor) = 11.3 min; 96% ee.

((R)-3-Nitro-3-(phenylsulfonyl)butylsulfonyl)benzene (6g). Colorless solid; Yield 150 mg,



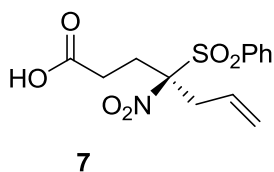
91%; mp 111-113 °C; ν_{\max} (film)/cm⁻¹ 3061vw, 2928vw, 1556m, 1448w, 1386vw, 1327m, 1266m, 1152s, 1083w, 1075w, 738vs, 704m, 610w, 535w; δ_H (400 MHz; DMSO-*d*₆) 1.86 (3H, s), 2.42 (1H, ddd, J 14.3, 12.0, 5.0 Hz), 2.62 (1H, ddd, J 14.3, 12.0, 3.9 Hz), 3.36 (1H, ddd, J 14.0, 12.0, 3.9 Hz), 3.65 (1H, ddd, J 14.0, 12.0, 5.0 Hz), 7.68 (2H, t, J 7.6 Hz), 7.73 (2H, t, J 7.8 Hz), 7.75-7.81 (3H, m), 7.85-7.94 (3H, m); δ_C (100 MHz; DMSO-*d*₆) 16.6, 26.4, 49.1, 105.2, 127.9, 129.7, 129.9, 130.7, 131.1, 134.4, 136.3, 137.9; HRMS (ES⁺, Ar) calcd for C₁₆H₁₇NO₆S₂Na (MNa⁺) 406.0389, found 406.0387; $[\alpha]_D^{25}$ -1.28 (c 1.0, CHCl₃); HPLC: Chiralpak IA (pet ether/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 216 nm), t_R (major) = 40.0 min, t_R (minor) = 48.1 min; 10% ee.

(R)-4-Nitro-4-(phenylsulfonyl)pentanenitrile (6h). Colorless solid; mp 81-82 °C; Yield 55

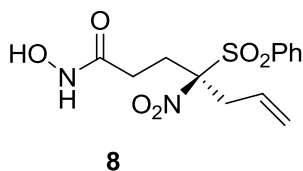


mg, 51%; ν_{\max} (film)/cm⁻¹ 3067m, 2870w, 2248m, 1544vs, 1433m, 1330s, 1310vs, 1283s, 1153s, 1072w, 960m, 842m, 811w, 718w, 686w; δ_H (500 MHz; CDCl₃) 1.97 (3H, s), 2.61 (2H, ABqdd, J 16.9, 9.0, 6.5 Hz), 2.68 (1H, ddd, J 15.0, 9.0, 6.5 Hz), 2.86 (1H, ddd, J 15.0, 9.0, 6.5 Hz), 7.64 (2H, t, J 8.0 Hz), 7.80 (1H, tt, J 8.0, 1.2 Hz), 7.85 (2H, dd, J 8.0, 1.2 Hz); δ_C (125 MHz; CDCl₃) 12.7, 17.9, 29.4, 105.0, 117.5, 129.7, 131.2, 132.0, 136.0; HRMS (ES⁺, Ar) calcd for C₁₁H₁₂N₂O₄SNa (MNa⁺) 291.0410, found 291.0404; $[\alpha]_D^{25}$ +2.77 (c 1.0, CHCl₃); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 216 nm), t_R (major) = 19.5 min, t_R (minor) = 17.5 min; 14% ee.

(S)-4-Nitro-4-(phenylsulfonyl)hept-6-enoic acid (7). To a solution of **4b** (220 mg, 0.50 mmol) in THF (5.0 ml) and H₂O (5.0 ml) was added LiOH·H₂O (42 mg, 1.0 mmol) and the mixture was stirred at room temperature for 15 min. The mixture was acidified with 1 N HCl and extracted with Et₂O (3 × 15 ml). The combined extract was dried over anhydrous sodium sulfate. The organic layer was concentrated in vacuo and the residue was purified by silica gel column chromatography using EtOAc-pet ether (90%) as eluent to afford the acid **7**. Red oil; Yield 141 mg, 90%; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3069brs, 2987brs, 1716vs, 1582m, 1554vs, 1441s, 1334vs, 1315s, 1230vw, 1151vs, 1082m, 999w, 937m, 854w, 758w, 721w, 688w, 608m, 565w, 545w; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 2.57-2.69 (2H, m), 2.77-2.96 (2H, m), 2.98-3.12 (2H, m), 5.27 (1H, dd, J 16.8, 1.2 Hz), 5.30 (1H, dd, J 10.1 1.2 Hz), 5.67 (1H, ddt, J 16.8, 10.1, 7.0 Hz), 7.62 (2H, t, J 7.9 Hz), 7.78 (1H, tt, J 7.9, 1.2 Hz), 7.88 (2H, dd, J 7.9, 1.2 Hz); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 26.0, 28.5, 36.9, 107.8, 123.0, 128.2, 129.5, 131.2, 133.1, 135.7, 177.4; HRMS (ES⁺, Ar) calcd for C₁₃H₁₅NO₆SNa (MNa⁺) 336.0512, found 336.0514; $[\alpha]_{\text{D}}^{25} +25.00$ (c 1.0 in CHCl₃).



(S)-N-hydroxy-4-nitro-4-(phenylsulfonyl)hept-6-enamide (8). To a solution of **4b** (317 mg, 0.72 mmol) in EtOH-DCM (10.5:4.5, 15.0 ml) was added HONH₂·HCl (187 mg, 2.89 mmol) and pyridine (233 μ l, 2.89 mmol) and the mixture was stirred at room temperature for 12 h. The mixture was evaporated in vacuo and the residue was purified by silica gel column chromatography using EtOAc-pet ether (60:40) as eluent to afford pure amide **8**. Colorless sticky liquid; Yield 194 mg, 82%; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3235brvs, 1662vs, 1583m, 1554s, 1448m, 1332s, 1315s, 1268m, 1150vs, 1081m, 999m, 937m, 894w, 853m, 757m, 739m, 689m, 607m, 543m; $\delta_{\text{H}}(500 \text{ MHz}; \text{CDCl}_3)$ 2.40-2.52 (1H, m), 2.61-2.74 (2H, m), 2.81-2.90 (1H, m), 2.97, 3.05 (2H, ABqd, J 15.0, 7.1 Hz), 5.22 (1H, d, J 15.1 Hz), 5.23 (1H, d, J 12.3 Hz), 5.60-5.70 (1H, m), 7.61 (2H, t, J 7.6 Hz), 7.76 (1H, t, J 7.6 Hz), 7.88 (2H, d, J 7.6 Hz); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 26.7, 27.3, 36.8, 108.4, 123.1, 128.0, 129.5, 131.2, 133.1, 135.7, 169.8; HRMS (ES⁺, Ar) calcd for C₁₃H₁₆N₂O₆SNa (MNa⁺) 351.0621, found 351.0626; $[\alpha]_{\text{D}}^{25} +26.19$ (c 1.0 in CHCl₃); HPLC: Chiralpak IC (pet ether/*i*-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 216 \text{ nm}$), t_{R} (major) = 11.4 min, t_{R} (minor) = 13.5 min; 94% ee.



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- C9**: Reference 32, main text.
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