Electronic Supplementary Material (ESI) for Chemical Communications

Enantioselective Synthesis of α-Nitro-δ-ketosulfones via a Quinine-Squaramide Catalyzed Conjugate Addition of α-Nitrosulfones to Enones

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1. Table S1. Crystal data and structure refinement for **4i** (CCDC 946574).

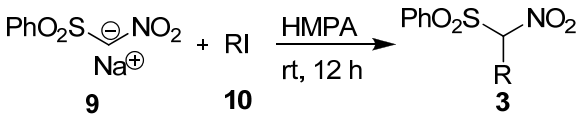
Identification code	inn-3-ksb-156b	
Empirical formula	C17 H16 Br N O5 S	
Formula weight	426.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.6053(9) Å	α = 90°
	b = 9.7866(9) Å	β = 90°
	c = 23.4727(18) Å	γ = 90°
Volume	1747.1(3) Å3	
Z	4	
Density (calculated)	1.621 Mg/m3	
Absorption coefficient	2.500 mm^{-1}	
F(000)	864	
Crystal size	0.15 x 0.15 x 0.09 mm^3	
Theta range for data collection	3.19 to 25.35°.	
Index ranges	-9<=h<=6, -11<=k<=11, -28<=l<=23	
Reflections collected	13569	
Independent reflections	3180 [R(int) = 0.1051]	
Completeness to theta = 25.35°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8063 and 0.7055	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3180 / 0 / 227	
Goodness-of-fit on F^2	0.941	

Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0615
R indices (all data)	R1 = 0.0319, wR2 = 0.0630
Absolute structure parameter	-0.014(7)
Largest diff. peak and hole	0.547 and -0.424 e.Å-3

2. General Experimental Details

The melting points recorded are uncorrected. NMR spectra (^{1}H and ^{1}H decoupled ^{13}C) 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 chiral HPLC equipped with a PDA-detector. Specific rotations were measured for solutions of samples of known concentrations in $CHCl_3$ using a polarimeter equipped with a sodium vapor lamp. Catalysts **C1-C7** were prepared by literature methods.[1-6] Nitrosulfones **3a**, **3d**, **3f** and **3g** are known in the literature and were prepared by general procedure reported in the literature.[7] Nitrosulfones **3b, 3c** and **3e** are new and were prepared by a general procedure reported in the literature.[7] Enones **2a-o** are known in the literature.[8-14]

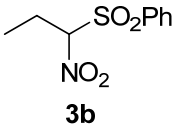
3. General procedure for the preparation of nitrosulfones 2[7]



9 **10** **3**

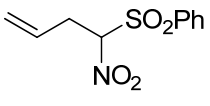
To a stirred solution of sodium salt of (nitromethylsulfonyl)benzene **9** (4.56 g, 20.44 mmol) in HMPA (10.3 g, 10 ml), alkyl iodide **10** (40.88 mmol) was added at rt under N_2 atmosphere and the stirring continued for 12 h at rt. The reaction mixture was diluted with diethyl ether and ice-water and then quenched with 3 N HCl. The aqueous layer was extracted with diethyl ether (3 × 50 ml). The combine organic layer was washed with 5% NaOH solution (3 × 50 ml). The combined basic solution was acidified and washed with diethyl ether (3 × 50 ml) and the organic layer was dried over anhyd sodium sulfate. The solvent was removed under reduced pressure and the crude nitrosulfone **3** was purified by silica gel column chromatography using EtOAc and pet ether (15-40%, gradient elution) as eluent.

(1-Nitropropylsulfonyl)benzene (3b). Colorless solid; Yield 2.0 g, 43%; mp 57-58 ^oC; ν_{max}(film)/cm^{-1} 2985s, 2952m, 1553vs, 1449m, 1332vs, 1316vs, 1180m, 1157vs, 1123m, 1083s, 888w, 811m, 762w, 723w, 690w; δ_H(400 MHz; $CDCl_3$) 1.06 (3H, t, *J* 7.4), 2.14-2.27 (1H, m), 2.28-2.40 (1H, m), 5.43 (1H, dd, *J* 11.2, 3.5), 7.63 (2H, t, *J* 7.5), 7.77 (1H, tt, *J* 7.5, 1.2), 7.89 (2H, dd, *J* 7.5, 1.2); δ_C(100 MHz; $CDCl_3$) 10.1, 22.1, 103.7, 129.7, 130.1, 134.0, 135.7; MS (ES+, Ar) m/z (rel intensity) 253 ([MNa+1]$^+$, 16), 252 ([MNa]$^+$, 100), 249 (14), 197 (10), 141 (6); HRMS (ES+, Ar) calcd for $C_9H_{11}NO_4SNa$ (MNa^+) 252.0306, found 252.0302.



3b

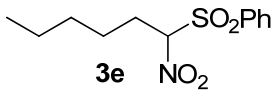
(1-Nitrohexylsulfonyl)benzene (3c). Colorless oil; Yield 1.86 g, 39%; ν_{max}(neat)/cm^{-1} 3069w, 2985m, 2901w, 1644w, 1563vs, 1449m, 1433m, 1339vs, 1226s, 1158vs, 1084m, 1024w, 998m, 935s, 847m, 759s, 737w, 722m, 687m, 644w, 592s, 532m; δ_H(400 MHz; $CDCl_3$) 2.92 (1H, ddd, *J* 15.0, 11.4, 7.7), 3.00-3.08 (1H, m), 5.18-5.21 (1H,



3c

m), 5.22-5.25 (1H, m), 5.55 (1H, dd, *J* 11.4, 3.4), 5.59-5.71 (1H, m), 7.63 (2H, t, *J* 7.9), 7.78 (1H, tt, *J* 7.9, 1.2), 7.90 (2H, dd, *J* 7.9, 1.2); δ_C(100 MHz; $CDCl_3$) 32.0, 101.3, 121.9, 128.4, 129.8, 130.1, 133.9, 135.8; HRMS (ES+, Ar) calcd for $C_{10}H_{11}NO_4SNa$ (MNa^+) 264.0301, found 264.0301.

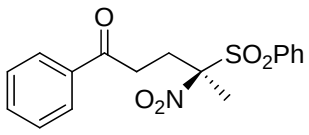
(1-Nitrohexylsulfonyl)benzene (3e). Colorless oil; Yield 2.21 g, 40%; ν_{max}(neat)/cm^{-1} 3068w, 2959vs, 2933vs, 2872s, 1562vs, 1449m, 1339vs, 1216m, 1157vs, 1083m, 891w, 842m, 757s, 723s, 689s, 597s, 535s; δ_H(400 MHz; $CDCl_3$) 0.87 (3H, t, *J* 7.0), 1.23-1.43 (6H, m), 2.15-2.30 (2H, m), 5.49 (1H, dd, *J* 10.5, 4.2), 7.63 (2H, t, *J* 7.9), 7.77 (1H, tt, *J* 7.9, 1.2), 7.89 (2H, dd, *J* 7.9, 1.2); δ_C(100 MHz; $CDCl_3$) 13.9, 22.2, 25.1, 27.9, 30.8, 102.5, 129.7, 130.2, 134.1, 135.6; MS (ES+, Ar) m/z (rel intensity) 295 ($[MNa+1]^+$, 17), 294 ($[MNa]^+$, 100), 291 (14), 289 (8), 242 (11), 197 (9), 170 (7), 141 (10); HRMS (ES+, Ar) calcd for $C_{12}H_{17}NO_4SNa$ (MNa^+) 294.0776, found 294.0782.



3e

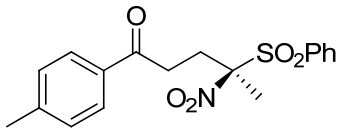
4. General procedure for the addition of nitrosulfone 3 to vinylketone 2. To a solution of nitrosulfone **3** (0.5 mmol) and catalyst **C6** (0.7 mg, 0.001 mmol, 0.2 mol %) in toluene (2 ml) was added vinyl ketone **2** (0.75 mmol) at –60 °C. The reaction mixture was stirred at specified temperature and monitored by TLC. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using pet ether-EtOAc (18-40%, gradient elution) as eluent.

4-Nitro-1-phenyl-4-(phenylsulfonyl)pentan-1-one (4a). Colorless solid; Yield 170 mg, 98%; mp 123-125 °C; ν_{max}(film)/cm^{-1} 3058w, 2922w, 1687vs, 1557s, 1447m, 1327vs, 1318s, 1293m, 1218m, 1156s, 1077m, 848m, 743m, 689m, 610m; δ_H(400 MHz; $CDCl_3$) 1.99 (3H, s), 2.72-2.87 (2H, m), 3.05 (2H, ABqdd, *J* 17.5, 9.2, 6.0), 7.46 (2H, t, *J* 7.6 Hz), 7.59 (1H, tt, *J* 7.9, 1.1), 7.62 (2H, t, *J* 7.9), 7.77 (1H, tt, *J* 7.5, 1.1), 7.91 (4H, dd, *J* 7.9, 1.1); δ_C(100 MHz; $CDCl_3$) 17.7, 28.4, 32.7, 106.6, 128.2, 129.0, 129.4, 131.3, 132.8, 133.9, 135.6, 136.1, 196.7; MS (ES+, Ar) m/z (rel intensity) 350 ($[MH+2]^+$, 8), 349($[MH+1]^+$, 24), 348 (MH^+, 100), 326 (10), 301 (15), 297 (12); HRMS (ES+, Ar) calcd for $C_{17}H_{18}NO_5S$ (MH^+) 348.0906, found 348.0918; $[\alpha]^{25}_D$ +29.12 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 30.8 min, t_R (minor) = 33.6 min; >99% ee.



4a

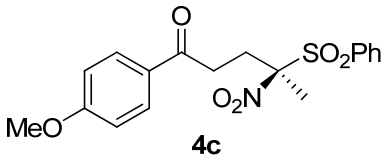
4-Nitro-4-(phenylsulfonyl)-1-p-tolylpentan-1-one (4b). Colorless solid; Yield 179 mg, 99%; mp 132-134 °C; ν_{max}(film)/cm^{-1} 2921w, 1671s, 1608w, 1548vs, 1448w, 1439w, 1328m, 1310m, 1154s, 1073w, 982w, 790w; δ_H(400 MHz; $CDCl_3$) 1.99 (3H, s), 2.40 (3H, s), 2.78 (2H, ABqdd, *J* 14.8, 9.1, 6.0), 3.01 (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; $CDCl_3$) 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; MS (ES+, Ar) m/z (rel intensity) 364 ($[MH+2]^+$, 9), 363 ($[MH+1]^+$, 23), 362 (MH^+, 100), 315 (12), 173 (7); HRMS (ES+, Ar) calcd for $C_{18}H_{20}NO_5S$ (MH^+) 362.1062, found 362.1050; $[\alpha]^{25}_D$ +28.3 (*c* 1.0 in



4b

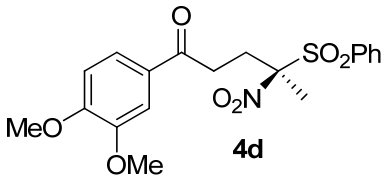
$CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 39.4 min, t_R (minor) = 41.6 min; 96% ee.

1-(4-Methoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4c). Colorless solid; Yield 186 mg, 98%; mp 136-138 °C; ν_{max}(film)/cm^{-1} 3060w, 2940w, 2841w, 1674s, 1602vs, 1576m, 1551s, 1510m, 1449m, 1421w, 1336s, 1314m, 1260m, 1218w, 1177s, 1155vs, 1076m, 1025m, 982w, 844m, 762w, 688w, 614w; δ_H(400 MHz; $CDCl_3$) 1.98 (3H, s), 2.77 (2H, ABqdd, *J* 14.9, 9.3, 5.9), 2.98 (2H, ABqdd, *J* 17.2, 9.3, 5.9), 3.85 (3H, s), 6.91 (2H, d, *J* 8.9), 7.61 (2H, t, *J* 7.7), 7.75 (1H, tt, *J* 7.7, 1.0), 7.87 (2H, d, *J* 8.9), 7.89 (2H, dd, *J* 7.7, 1.0); δ_C(100 MHz; $CDCl_3$) 17.5, 28.6, 32.3, 55.7, 106.7, 114.1, 129.2, 129.4, 130.5, 131.3, 132.8, 135.6, 164.1, 195.1; MS (ES+, Ar) m/z (rel intensity) 380 ([MH+2]$^+$, 10), 379 ([MH+1]$^+$, 25), 378 (MH$^+$, 100), 353 (4), 331 (3), 270 (6); HRMS (ES+, Ar) calcd for $C_{18}H_{20}NO_6S$ (MH$^+$) 378.1011, found 378.1007; $[\alpha]^{25}_D$ +27.36 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 29.7 min, t_R (minor) = 33.6 min; 99% ee.



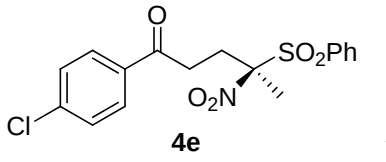
4c

1-(3,4-Dimethoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4d). Colorless solid; Yield 203 mg, 99%; mp 139-140 °C; ν_{max}(film)/cm^{-1} 3065w, 3004w, 2937w, 2842w, 1676m, 1596m, 1586m, 1552vs, 1516m, 1449m, 1420m, 1385w, 1334s, 1313m, 1266vs, 1201w, 1155vs, 1076m, 1022m, 999w, 878w, 849w, 765m, 737w, 720w, 689w, 608m; δ_H(400 MHz; $CDCl_3$) 1.99 (3H, s), 2.79 (2H, ABqdd, *J* 14.8, 9.0, 6.2), 2.99 (2H, ABqdd, *J* 17.0, 9.0, 6.2), 3.91 (3H, s), 3.94 (3H, s), 6.87 (1H, d, *J* 8.4), 7.46 (1H, d, *J* 2.0), 7.51 (1H, dd, *J* 8.4, 2.0), 7.62 (2H, t, *J* 7.9), 7.77 (1H, td, *J* 7.9, 1.0), 7.90 (2H, dd, *J* 7.9, 1.0); δ_C(100 MHz; $CDCl_3$) 17.6, 28.7, 32.2, 56.2, 56.3, 106.7, 110.1, 110.2, 122.9, 129.3, 129.4, 131.2, 132.8, 135.5, 149.3, 153.9, 195.3; MS (ES+, Ar) m/z (rel intensity) 410 ([MH+2]$^+$, 8), 409 ([MH+1]$^+$, 22), 408 (MH$^+$, 100), 270 (6); HRMS (ES+, Ar) calcd for $C_{19}H_{22}NO_7S$ (MH$^+$) 408.1117, found 408.1100; $[\alpha]^{25}_D$ +30.89 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 38.2 min, t_R (minor) = 42.1 min; 96% ee.



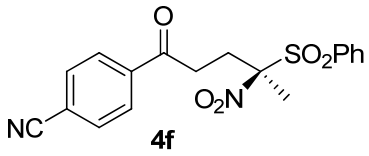
4d

1-(4-Chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4e). Colorless solid; Yield 188 mg, 98%; mp 141-143 °C; ν_{max}(film)/cm^{-1} 2923w, 1689m, 1590m, 1553vs, 1449w, 1401w, 1334m, 1213w, 1155s, 1093w, 1076w, 986w, 849w, 722w, 688w, 607w; δ_H(400 MHz; $CDCl_3$) 1.97 (3H, s), 2.79 (2H, ABqdd, *J* 15.0, 9.5, 5.7), 3.04 (2H, ABqdd, *J* 17.6, 9.5, 5.7), 7.42 (2H, d, *J* 8.6), 7.61 (2H, t, *J* 7.5), 7.76 (1H, t, *J* 7.5), 7.84 (2H, d, *J* 8.6), 7.88 (2H, d, *J* 7.5); δ_C(100 MHz; $CDCl_3$) 17.8, 28.3, 32.7, 106.4, 129.3, 129.4, 129.6, 131.2, 132.7, 134.4, 135.6, 140.3, 195.5; MS (ES+, Ar) m/z (rel intensity) 385 ([MH+3]$^+$, 9), 384 ([MH+2]$^+$, 44), 383 ([MH+1]$^+$, 24), 382 (MH$^+$, 100), 337 (7), 335 (19); HRMS (ES+, Ar) calcd for $C_{17}H_{17}NO_5ClS$ (MH$^+$) 382.0516, found 382.0516; $[\alpha]^{25}_D$ +29.39 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 42.8 min, t_R (minor) = 48.4 min; >99% ee.



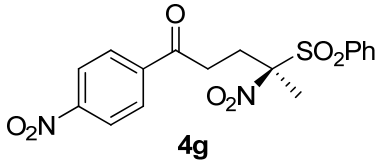
4e

4-(4-Nitro-4-(phenylsulfonyl)pentanoyl)benzonitrile (4f). Colorless solid; Yield 185 mg, 99%; mp 139-141 °C; ν_{max}(film)/cm^{-1} 3094w, 2919w, 2231m, 1687s, 1547s, 1310s, 1214w, 1158s, 1074w, 993w, 847m, 687w, 606s; δ_H(400 MHz; $CDCl_3$) 1.96 (3H, s), 2.81 (2H, ABqdd, *J* 15.1, 9.6, 5.6), 3.11 (2H, ABqdd, *J* 17.9, 9.6, 5.6), 7.62 (2H, t, *J* 7.8), 7.74-7.79 (3H, m), 7.88 (2H, dd, *J* 7.8, 1.2), 8.00 (2H, d, *J* 8.4); δ_C(100 MHz; $CDCl_3$) 18.2, 28.1, 33.2, 106.2, 117.0, 117.9, 128.6, 129.5, 131.2, 132.7, 132.8, 135.7, 139.0, 195.5; MS (ES+, Ar) m/z (rel intensity) 395 (MNa^+, 80), 375 ($[MH+2]^+$, 9), 374 ($[MH+1]^+$, 24), 373 ($[MH]^+$, 100), 327 (10), 326 (46), 315 (11), 125 (12); HRMS (ES+, Ar) calcd for $C_{18}H_{17}N_2O_5S$ (MH^+) 373.0858, found 373.0858; $[\alpha]^{25}_D$ +32.80 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 42.0 min, t_R (minor) = 47.7 min; >99% ee.



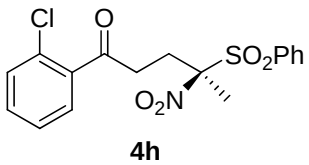
4f

4-Nitro-1-(4-nitrophenyl)-4-(phenylsulfonyl)pentan-1-one (4g). Colorless solid; Yield 194 mg, 99%; mp 155-157 °C; ν_{max}(film)/cm^{-1} 3111w, 3076w, 2920w, 2866w, 1698s, 1604w, 1553vs, 1527vs, 1449w, 1347vs, 1334s, 1318s, 1209m, 1155s, 1076m, 989w, 857w, 740m, 688w, 606m; δ_H(400 MHz; $CDCl_3$) 1.98 (3H, s), 2.84 (2H, ABqdd, *J* 15.1, 9.4, 5.7), 3.17 (2H, ABqdd, *J* 17.9, 9.4, 5.7), 7.63 (2H, tt, *J* 7.7, 1.3), 7.78 (2H, tt, *J* 7.7, 1.3), 7.90 (1H, dd, *J* 7.7, 1.3), 8.08 (2H, d, *J* 9.0), 8.30 (2H, d, *J* 9.0); δ_C(100 MHz; $CDCl_3$) 18.4, 28.1, 33.5, 106.2, 124.2, 129.3, 129.5, 131.3, 132.8, 135.7, 140.5, 150.8, 195.3; MS (ES+, Ar) m/z (rel intensity) 395 ($[MH+2]^+$, 9), 394 ($[MH+1]^+$, 22), 393 (MH^+, 100), 360 (25), 346 (23), 339 (15), 338 (61), 256 (7), 214 (12), 158 (15), 125 (7); HRMS (ES+, Ar) calcd for $C_{17}H_{17}N_2O_7S$ (MH^+) 393.0756, found 393.0758; $[\alpha]^{25}_D$ +31.36 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 39.5 min, t_R (minor) = 51.3 min; 99% ee.



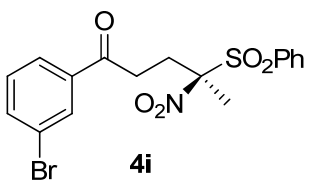
4g

1-(2-Chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4h). Colorless solid; Yield 186 mg, 97%; mp 83-85 °C; ν_{max}(film)/cm^{-1} 3061w, 2920w, 1702m, 1589w, 1552vs, 1448w, 1434w, 1385w, 1332m, 1314m, 1267m, 1213w, 1156s, 1074m, 1039w, 986w, 847w, 751s; δ_H(400 MHz; $CDCl_3$) 1.97 (3H, s), 2.78 (2H, ABqdd, *J* 15.1, 9.8, 5.3), 3.05 (2H, ABqdd, *J* 17.8, 9.8, 5.3), 7.29-7.37 (1H, m), 7.38-7.45 (3H, m), 7.62 (2H, t, *J* 7.8), 7.77 (1H, t, *J* 7.8), 7.88 (2H, d, *J* 7.8); δ_C(100 MHz; $CDCl_3$) 17.6, 28.3, 37.0, 106.3, 127.3, 129.2, 129.4, 130.9, 131.1, 131.2, 132.5, 132.7, 135.6, 138.3, 199.6; MS (ES+, Ar) m/z (rel intensity) 385 ($[MH+3]^+$, 10), 384 ($[MH+2]^+$, 43), 383 ($[MH+1]^+$, 24), 382 (MH^+, 100), 337 (7), 335 (17), 195 (6), 193 (15), 158 (9); HRMS (ES+, Ar) calcd for $C_{17}H_{17}NO_5SCl$ (MH^+) 382.0516, found 382.0516; $[\alpha]^{25}_D$ +12.33 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack AD-H (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 20.4 min, t_R (minor) = 22.1 min; 98% ee.



4h

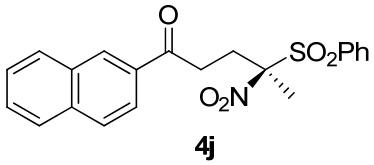
1-(3-Bromophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4i). Colorless solid; Yield 210 mg, 99%; mp 145-147 °C; ν_{max}(film)/cm^{-1} 3062w, 2923w, 1690s, 1557s, 1542s, 1449w, 1423w, 1385w, 1367w, 1335s, 1314m, 1292m, 1208m, 1156vs, 1110w, 1074m, 997w, 906w, 849w, 761m, 751m, 689w, 610m; δ_H(400 MHz; $CDCl_3$) 1.98 (3H, s), 2.79 (2H, ABqdd, *J*



4i

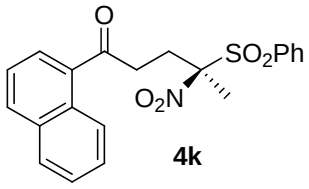
14.9, 9.5, 5.6), 3.04 (2H, ABqdd, *J* 17.7, 9.5, 5.6), 7.34 (1H, t, *J* 7.9), 7.62 (2H, t, *J* 7.8), 7.69 (1H, ddd, *J* 7.9, 1.8, 1.0), 7.77 (1H, tt, *J* 7.8, 1.2), 7.82 (1H, td, *J* 7.9, 1.0), 7.89 (2H, dd, *J* 7.8, 1.2), 8.01 (1H, t, *J* 1.8); δ_C(100 MHz; $CDCl_3$) 17.9, 28.2, 32.9, 106.4, 123.3, 126.7, 129.5, 130.6, 131.2, 131.3, 132.8, 135.6, 136.7, 137.8, 195.4; MS (ES+, Ar) m/z (rel intensity) 429 ($[MH+3]^+$, 22), 428 ($[MH+2]^+$, 100), 427 ($[MH+1]^+$, 20), 426 (MH^+, 98), 381 (12), 379 (12), 378 (19), 297 (6), 239 (9), 237 (8); HRMS (ES+, Ar) calcd for $C_{17}H_{17}NO_5SBr$ (MH^+) 426.0011, found 426.0013; $[\alpha]^{25}_D$ +28.27 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 32.2 min, t_R (minor) = 37.0 min; >99% ee.

1-(Naphthalen-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4j). Colorless solid; Yield 195 mg, 98%; mp 156-158 °C; ν_{max}(film)/cm^{-1} 3061w, 2919w, 1682vs, 1626w, 1550vs, 1468w, 1449m, 1385m, 1332vs, 1314s, 1175m, 1155vs, 1076m, 756m, 688m, 607m; δ_H(400 MHz; $CDCl_3$) 2.03 (3H, s), 2.86 (2H, ABqdd, *J* 14.9, 9.4, 5.9), 3.18 (2H, ABqdd, *J* = 17.4, 9.4, 5.9), 7.55 (1H, td, *J* 8.1, 1.2), 7.57-7.63 (3H, m), 7.75 (1H, tt, *J* 7.5, 1.0), 7.86 (2H, d, *J* 7.9), 7.87 (1H, d, *J* 8.6), 7.90-7.97 (3H, m), 8.39 (1H, s); δ_C(100 MHz; $CDCl_3$) 17.6, 28.5, 32.7, 106.7, 123.6, 127.1, 127.9, 128.8, 129.0, 129.4, 129.7, 130.0, 131.2, 132.5, 132.8, 133.4, 135.6, 135.9, 196.5; MS (ES+, Ar) m/z (rel intensity) 400 ($[MH+2]^+$, 9), 399 ($[MH+1]^+$, 26), 398 (MH^+, 100), 397 (7), 351 (9), 209 (24), 207 (10); HRMS (ES+, Ar) calcd for $C_{21}H_{20}NO_5S$ (MH^+) 398.1062, found 398.1062; $[\alpha]^{25}_D$ +18.25 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack AD-H (pet ether/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 28.9 min, t_R (minor) = 32.3 min; 99% ee.



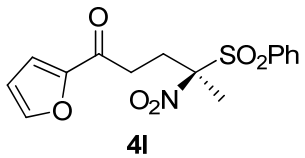
4j

1-(Naphthalen-1-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4k). Colorless solid; Yield 197 mg, 99%; mp 128-130 °C; ν_{max}(film)/cm^{-1} 3091m, 3063m, 3013w, 2945w, 2925w, 2871w, 1677vs, 1595w, 1580w, 1546vs, 1508s, 1447s, 1382m, 1362w, 1327vs, 1315vs, 1235m, 1215m, 1178s, 1155vs, 1099s, 1073s, 1024w, 998w, 970w, 946m, 870w, 847m, 793s, 777vs, 759m, 737m, 717m, 687m, 653w, 606s, 559m, 519m; δ_H(400 MHz; $CDCl_3$) 2.01 (3H, s), 2.88 (2H, ABqdd, *J* 14.9, 9.4, 5.7), 3.14 (2H, ABqdd, *J* 17.4, 9.4, 5.7), 7.48 (1H, t, *J* 8.1), 7.54 (1H, t, *J* 7.8), 7.58 (1H, td, *J* 7.8, 1.0), 7.62 (2H, t, *J* 7.9), 7.77 (1H, t, *J* 7.9), 7.84 (1H, dd, *J* 7.8, 1.0 Hz), 7.87 (1H, d, *J* 7.8), 7.92 (2H, dd, *J* 7.9, 1.2), 8.00 (1H, d, *J* 8.1), 8.61 (1H, d, *J* 8.1); δ_C(100 MHz; $CDCl_3$) 17.7, 28.7, 35.8, 106.6, 124.5, 125.7, 126.8, 128.2, 128.5, 128.7, 129.4, 130.2, 131.3, 132.8, 133.7, 134.1, 134.6, 135.6, 200.3; MS (ES+, Ar) m/z (rel intensity) 420 (MNa^+, 55), 400 ($[MH+2]^+$, 10), 399 ($[MH+1]^+$, 28), 398 (MH^+, 100), 297 (10), 288 (11), 270 (7), 251 (25); HRMS (ES+, Ar) calcd for $C_{21}H_{20}NO_5S$ (MH^+) 398.1062, found 398.1078; $[\alpha]^{25}_D$ +36.98 (*c* 1.0 in $CHCl_3$); HPLC: Chiralcel OD-H (pet ether/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 43.1 min, t_R (minor) = 57.6 min; 72% ee.



4k

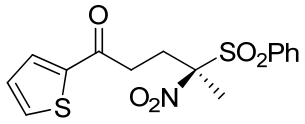
1-(Furan-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-one (4l). Colorless solid; Yield 162 mg, 96%; mp 112-113 °C; ν_{max}(film)/cm^{-1} 2923m, 2852w, 1671s, 1567w, 1549s, 1469m, 1446w, 1396w, 1384w, 1335s, 1313m, 1248w, 1158s, 1074w, 1066w, 1024w, 990w, 916w, 845w, 763 (s), 719 (w), 687 (w), 607 (m); δ_H(400 MHz; $CDCl_3$) 1.97 (3H, s), 2.75 (2H, ABqdd, *J* 15.2, 9.7, 5.7), 2.91 (2H, ABqdd, *J* 17.0, 9.7, 5.7), 6.53 (1H, dd, *J* 3.6, 1.5),



4l

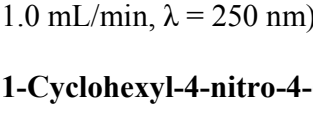
7.19 (1H, dd, *J* 3.6, 0.4), 7.57 (1H, dd, *J* 1.5, 0.4), 7.61 (2H, t, *J* 8.6), 7.76 (1H, tt, *J* 8.6, 1.2 Hz), 7.88 (2H, dd, *J* 8.6, 1.2); δ_C(100 MHz; $CDCl_3$) 17.5, 27.9, 32.5, 106.5, 112.7, 117.7, 129.4, 131.2, 132.7, 135.6, 146.9, 152.0, 185.8; MS (ES+, Ar) m/z (rel intensity) 340 ($[MH+2]^+$, 9), 339 ($[MH+1]^+$, 20), 338 (MH^+, 100), 291 (9), 223 (15), 195 (9), 149 (27), 125 (24); HRMS (ES+, Ar) calcd for $C_{15}H_{16}NO_6S$ (MH^+) 338.0698, found 338.0692; $[\alpha]^{25}_D$ +15.56 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack AD-H (pet ether/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 268 nm), t_R (major) = 17.9 min, t_R (minor) = 19.9 min; 99% ee.

4-Nitro-4-(phenylsulfonyl)-1-(thiophen-2-yl)pentan-1-one (4m). Colorless solid; Yield 171 mg, 97%; mp 146-148 °C; ν_{max}(film)/cm^{-1} 2923s, 2853m, 1661s, 1552s, 1520w, 1449w, 1416m, 1386w, 1331s, 1314m, 1219w, 1155s, 1075w, 998w, 936w, 853w, 760s, 738m, 689w, 606w; δ_H(400 MHz; $CDCl_3$) 1.98 (3H, s), 2.79 (2H, ABqdd, *J* 14.8, 9.0, 6.2), 2.99 (2H, ABqdd, *J* 16.8, 9.0, 6.2), 7.13 (1H, dd *J* 3.8, 4.9), 7.62 (2H, t, *J* 7. 8), 7.67 (1H, dd, *J* 4.9, 1.0), 7.69 (1H, dd, *J* 3.8, 1.0), 7.77 (1H, tt, *J* 7.8, 1.0), 7.89 (2H, dd, *J* 7.8, 1.0 Hz); δ_C(100 MHz; $CDCl_3$) 17.6, 28.5, 33.3, 106.5, 128.5, 129.5, 131.3, 132.5, 134.6, 135.6, 143.2, 189.6; MS (ES+, Ar) m/z (rel intensity) 376 (MNa^+, 95), 356 ($[MH+2]^+$, 13), 355 ($[MH+1]^+$, 22), 354 (MH^+, 100), 307 (11), 297 (15), 270 (10), 223 (9), 205 (37), 165 (14); HRMS (ES+, Ar) calcd for $C_{15}H_{16}NO_5S_2$ (MH^+) 354.0470, found 354.0471; $[\alpha]^{25}_D$ +25.48 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack AD-H (pet ether/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 18.4 min, t_R (minor) = 21.1 min; 97% ee.



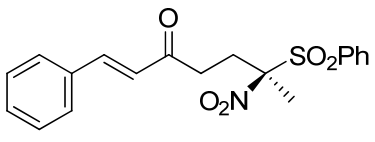
4m

1-Cyclohexyl-4-nitro-4-(phenylsulfonyl)pentan-1-one (4n). Colorless solid; Yield 151 mg, 86%; mp 93-95 °C; ν_{max}(film)/cm^{-1} 2928m, 2854w, 1709m, 1553s, 1447m, 1385vw, 1330s, 1315m, 1267w, 1155s, 1074m, 1025vw, 999vw, 848w, 755m, 722w, 689w, 606m; δ_H(400 MHz; $CDCl_3$) 1.13-1.34 (5H, m), 1.60-1.67 (1H, m), 1.70-1.82 (4H, m), 1.90 (3H, s), 2.25-2.33 (1H, m), 2.36-2.48 (1H, m), 2.50-2.64 (3H, m), 7.60 (2H, t, *J* 8.3), 7.75 (1H, tt, *J* 8.3, 1.2), 7.86 (2H, dd, *J* 8.3, 1.2); δ_C(100 MHz; $CDCl_3$) 17.4, 25.6 (× 2), 25.8, 28.0, 28.5, 28.6, 34.4, 50.9, 106.5, 129.4, 131.2, 132.8, 135.5, 210.5; MS (ES+, Ar) m/z (rel intensity) 376 (MNa^+, 98), 356 ($[MH+2]^+$, 9), 355 ($[MH+1]^+$, 23), 354 (MH^+, 100), 307 (9); HRMS (ES+, Ar) calcd for $C_{17}H_{24}NO_5S$ (MH^+) 354.1375, found 354.1378; $[\alpha]^{25}_D$ +17.31 (*c* 1.0 in $CHCl_3$); HPLC: Chiral cell OD-H (pet ether/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 14.0 min, t_R (minor) = 12.3 min; 91% ee.



4n

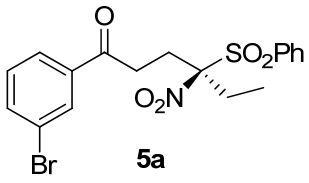
(*E*)-6-Nitro-1-phenyl-6-(phenylsulfonyl)hept-1-en-3-one (4o). Colorless solid; Yield 183 mg, 98%; mp 103-105 °C; ν_{max}(film)/cm^{-1} 3063w, 3028vw, 2922vw, 2872vw, 1692m, 1664m, 1612m, 1577w, 1552s, 1495w, 1449m, 1384w, 1332s, 1314m, 1182m, 1155s, 1112w, 1074m, 999w, 978w, 847w, 743m, 721m, 689m, 606m; δ_H(400 MHz; $CDCl_3$) 1.95 (3H, s), 2.64-2.86 (4H, m), 6.69 (1H, d, *J* 16.2), 7.34-7.39 (3H, m), 7.49-7.52 (2H, m), 7.53 (1H, d, *J* 16.2), 7.58 (2H, t, *J* 7.8), 7.74 (1H, t, *J* 7.8), 7.87 (2H, dd, *J* 7.8, 1.3); δ_C(100 MHz; $CDCl_3$) 17.4, 28.1, 34.6, 106.5, 125.2, 128.5, 129.1, 129.3, 131.0, 131.1, 132.7, 134.1, 135.5, 143.7, 196.4; MS (ES+, Ar) m/z (rel intensity) 396 (MNa^+, 30), 376 ($[MH+2]^+$, 9), 375 ($[MH+1]^+$, 28), 374 (MH^+, 100), 270 (16); HRMS (ES+, Ar) calcd for $C_{19}H_{20}NO_5S$ (MH^+) 374.1062, found 374.1059; $[\alpha]^{25}_D$ +25.49 (*c* 1.0



4o

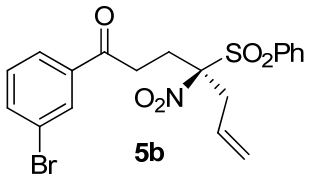
in $CHCl_3$); HPLC: Chiralpack IC (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 284 nm), t_R (major) = 35.3 min, t_R (minor) = 32.2 min; 97% ee.

1-(3-Bromophenyl)-4-nitro-4-(phenylsulfonyl)hexan-1-one (5a). Colorless solid; Yield 211 mg, 96%; mp 103-105 °C; ν_{max}(film)/cm^{-1} 3066w, 2982w, 2950w, 1692s, 1555s, 1448m, 1422m, 1329vs, 1314vs, 1208s, 1151s, 1076m, 998w, 739m, 688w, 616m; δ_H(400 MHz; $CDCl_3$) 1.02 (3H, t, *J* 7.4), 2.34 (2H, ABqq, *J* 14.8, 7.4), 2.67 (1H, ddd, *J* 15.7, 11.3, 4.6), 3.03 (1H, ddd, *J* 15.7, 11.2, 4.1), 3.29 (1H, ddd, *J* 18.0, 11.2, 4.6), 3.51(1H, ddd, *J* 18.0, 11.3, 4.1), 7.37 (1H, t, *J* 8.0), 7.62 (2H, t, *J* 7.8), 7.71 (1H, dt, *J* 8.0, 0.9), 7.77 (1H, t, *J* 7.8), 7.89 (2H, d, partially overlapped with another doublet, *J* 7.8), 7.92 (1H, d, partially overlapped with another doublet, *J* 8.0), 8.11 (1H, t, *J* 0.9); δ_C(100 MHz; $CDCl_3$) 8.3, 24.9, 27.2, 33.4, 109.7, 123.3, 126.8, 129.3, 130.5, 131.2, 133.7, 135.5, 136.5, 138.1, 196.1; MS (ES+, Ar) m/z (rel intensity) 443 ($[MH+3]^+$, 26), 442 ($[MH+2]^+$, 99), 441 ($[MH+1]^+$, 36), 440 (MH^+, 100), 397 (14), 396 (51), 395 (12), 394 (46), 290 (40), 289 (28), 259 (29), 257(24), 127 (15), 125 (17); HRMS (ES+, Ar) calcd for $C_{18}H_{18}NO_5SBrNa$ (MNa^+) 461.9980, found 461.9981; $[\alpha]^{25}_D$ +29.29 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack AD-H (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 19.8 min, t_R (minor) = 17.8 min; 85% ee.



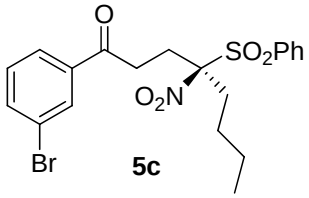
5a

1-(3-Bromophenyl)-4-nitro-4-(phenylsulfonyl)hept-6-en-1-one (5b). Colorless solid; Yield 224 mg, 99%; mp 141-142 °C; IR (film, cm^{-1}) ν_{max}(film)/cm^{-1} 3069w, 2924w, 1692s, 1555s, 1421m, 1333s, 1314s, 1208s, 1150s, 1081w, 997w, 936w, 755m, 722m, 688m, 606m; δ_H(400 MHz; $CDCl_3$) 2.67 (1H, ddd, *J* 15.6, 11.3, 4.6), 2.97 (1H, ddd, *J* 15.6, 11.2, 4.2), 3.07 (2H, ABqd, *J* 14.9, 7.1), 3.26 (1H, ddd, *J* 17.9, 11.2, 4.6), 3.48 (1H, ddd, *J* 17.9, 11.3, 4.2), 5.25 (1H, dd, *J* 17.2, 1.2), 5.27 (1H, dd, *J* 10.1, 1.2), 5.68 (1H, ddd, *J* 17.2, 10.1, 7.1), 7.36 (1H, t, *J* 7.9), 7.63 (2H, t, *J* 7.7), 7.71 (1H, ddd, *J* 7.9, 1.7, 0.8), 7.78 (1H, t, *J* 7.7), 7.87-7.92 (3H, m), 8.08 (1H, t, *J* 1.7); δ_C(100 MHz; $CDCl_3$) 25.7, 33.2, 37.8, 108.3, 122.9, 123.3, 126.8, 128.2, 129.4, 130.5, 131.2, 131.3, 133.4, 135.7, 136.5, 138.1, 196.0; MS (ES+, Ar) m/z (rel intensity) 455 ($[MH+3]^+$, 23), 454 ($[MH+2]^+$, 100), 453 ($[MH+1]^+$, 24), 452 (MH^+, 95), 289 (11), 287 (14), 265 (17), 263 (19), 241 (13), 239 (17), 231 (23); HRMS (ES+, Ar) calcd for $C_{19}H_{19}NO_5SBr$ (MH^+) 452.0167, found 452.0163; $[\alpha]^{25}_D$ +38.43 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IC (pet ether/*i*-PrOH = 95/5, flow rate 0.75 mL/min, λ = 250 nm), t_R (major) = 36.9 min, t_R (minor) = 34.5 min; >99% ee.



5b

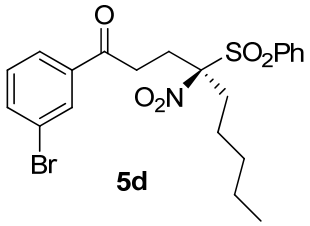
1-(3-Bromophenyl)-4-nitro-4-(phenylsulfonyl)octan-1-one (5c). Colorless oil; Yield 218 mg, 93%; ν_{max}(film)/cm^{-1} 3067w, 2960s, 2933s, 2874m, 1692s, 1556s, 1448m, 1422m, 1330s, 1314s, 1208m, 1150m, 1081m, 997w, 738m, 721m, 689m, 621w; δ_H(400 MHz; $CDCl_3$) 0.87 (3H, t, *J* 7.3), 1.06-1.18 (1H, m), 1.23-1.38 (2H, m), 1.46-1.59 (1H, m), 2.26 (2H, ABqdd, *J* 14.5, 12.1, 4.6), 2.67 (1H, ddd, *J* 15.6, 11.4, 4.6), 3.00 (1H, ddd, *J* 15.6, 11.3, 4.1), 3.26 (1H, ddd, *J* 17.9, 11.3, 4.6), 3.50 (1H, ddd, *J* 17.9, 11.4, 4.1), 7.36 (1H, t, *J* 7.9), 7.61 (2H, t, *J* 7.7), 7.70 (1H, ddd, *J* 7.9, 1.6, 0.8), 7.76 (1H, t, *J* 7.7), 7.85-7.93 (3H, m), 8.09 (1H, t, *J* 1.6); δ_C(100 MHz; $CDCl_3$) 13.7, 22.7, 25.4, 25.7, 33.1, 33.4, 109.3, 123.2, 126.8, 129.3, 130.5, 131.2 (× 2), 133.6,



5c

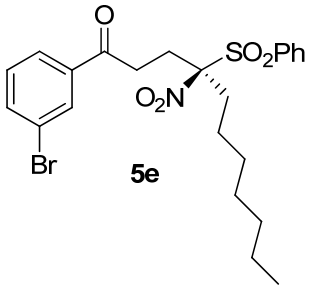
135.5, 136.5, 138.1, 196.1; MS (ES+, Ar) m/z (rel intensity) 471 ($[MH+3]^+$, 24), 470 ($[MH+2]^+$, 100), 469 ($[MH+1]^+$, 23), 468 (MH^+, 91), 425 (23), 423 (28), 421 (24), 397 (18), 282 (12), 281 (46), 280 (14), 279 (51), 247 (38), 242 (22); HRMS (ES+, Ar) calcd for $C_{20}H_{23}NO_5SBr$ (MH^+) 468.0480, found 468.0482; $[\alpha]^{25}_D$ +21.70 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 14.9 min, t_R (minor) = 16.6 min; 95% ee.

1-(3-Bromophenyl)-4-nitro-4-(phenylsulfonyl)nonan-1-one (5d). Colorless solid; Yield 236 mg, 98%; mp 96-98 °C; ν_{max}(film)/cm^{-1} 3067w, 2956s, 2933s, 2872m, 1692s, 1555s, 1447m, 1422m, 1330vs, 1314s, 1209m, 1149m, 1081w, 738m, 689m; δ_H(400 MHz; $CDCl_3$) 0.85 (3H, t, *J* 7.1), 1.08-1.20 (1H, m), 1.21-1.32 (4H, m), 1.48-1.59 (1H, m), 2.25 (2H, ABqdd, *J* 14.6, 12.0, 4.6), 2.67 (1H, ddd, *J* 15.7, 11.4, 4.6), 3.01 (1H, ddd, *J* 15.7, 11.3, 4.1), 3.27 (1H, ddd, *J* 18.0, 11.3, 4.6), 3.51 (1H, ddd, *J* 18.0, 11.4, 4.1), 7.37 (1H, t, *J* 8.0), 7.62 (2H, t, *J* 7.9), 7.72 (1H, ddd, *J* 8.0, 1.8, 1.0), 7.77 (1H, tt, *J* 7.9, 1.1), 7.89 (2H, dd, *J* 7.9, 1.1), 7.92 (1H, dt, *J* 8.0, 1.0), 8.11 (1H, t, *J* 1.8); δ_C(100 MHz; $CDCl_3$) 14.0, 22.3, 23.4, 25.5, 31.7, 33.5 (× 2), 109.4, 123.3, 126.9, 129.3, 130.5, 131.2, 131.3, 133.7, 135.5, 136.5, 138.1, 196.2; MS (ES+, Ar) m/z (rel intensity) 485 ($[MH+3]^+$, 25), 484 ($[MH+2]^+$, 100), 483 ($[MH+1]^+$, 24), 482 (MH^+, 99), 438 (7), 437 (31), 436 (7), 435 (30), 296 (9), 295 (39), 294 (9), 293 (240), 261 (26); HRMS (ES+, Ar) calcd for $C_{21}H_{25}NO_5SBr$ (MH^+) 482.0637, found 482.0652; $[\alpha]^{25}_D$ +16.78 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IC (pet ether/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 250 nm), t_R (major) = 18.7 min, t_R (minor) = 20.0 min; 95% ee.



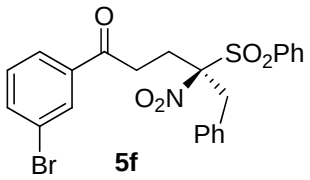
5d

1-(3-Bromophenyl)-4-nitro-4-(phenylsulfonyl)undecan-1-one (5e). Colorless oil; Yield 229 mg, 90%; ν_{max}(neat)/cm^{-1} 3067w, 2931vs, 2858s, 1692s, 1558s, 1449m, 1334vs, 1208m, 1150s, 1083m, 839w, 756m, 722m, 688m, 621w, 603w; δ_H(400 MHz; $CDCl_3$) 0.84 (3H, t, *J* 6.8), 1.08-1.30 (9H, m), 1.48-1.58 (1H, m), 2.25 (2H, ABqdd, *J* 14.5, 12.0, 4.6), 2.67 (1H, ddd, *J* 15.6, 11.3, 4.6), 3.01 (1H, ddd, *J* 15.6, 11.2, 4.1), 3.27 (1H, ddd, *J* 17.9, 11.2, 4.6), 3.51 (1H, ddd, *J* 17.9, 11.3, 4.1), 7.37 (1H, t, *J* 7.9), 7.62 (2H, t, *J* 7.8 Hz), 7.72 (1H, dd, *J* 7.9, 0.9), 7.77 (1H, t, *J* 7.8), 7.89 (2H, dd, *J* 7.8), 7.92 (1H, d, *J* 7.9, 0.9), 8.11 (1H, t, *J* 0.9); δ_C(100 MHz; $CDCl_3$) 14.2, 22.7, 23.7, 25.4, 28.9, 29.5, 31.7, 33.5, 109.4, 123.3, 126.9, 129.3, 130.5, 131.2, 131.3, 133.7, 135.5, 136.6, 138.1, 196.2; MS (ES+, Ar) m/z (rel intensity) 513 ($[MH+3]^+$, 21), 512 ($[MH+2]^+$, 95), 511 ($[MH+1]^+$, 29), 510 ($[MH]^+$, 100), 465 (11), 463 (11), 125 (24); HRMS (ES+, Ar) calcd for $C_{23}H_{28}NO_5SBrNa$ (MNa^+) 532.0767, found 532.0764; $[\alpha]^{25}_D$ +2.34 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IC (pet ether/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 250 nm), t_R (major) = 22.4 min, t_R (minor) = 24.6 min; 50% ee.



5e

1-(3-Bromophenyl)-4-nitro-5-phenyl-4-(phenylsulfonyl)pentan-1-one (5f). Colorless solid; Yield 239 mg, 95%; mp 133-135 °C; ν_{max}(film)/$cm^{-1,}$ 3066w, 3032w, 2929w, 1692s, 1583w, 1556s, 1497w, 1448m, 1422m, 1372w, 1332s, 1314s, 1210s, 1147s, 1081m, 1032w, 997w, 904w, 850w, 757s, 719m, 701m, 687w, 605m, 542m, 524m; δ_H(400 MHz; $CDCl_3$) 2.74

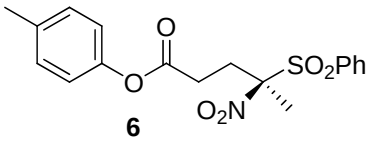


5f

(2H, t, *J* 7.7), 3.35 (2H, ABqt, *J* 18.9, 7.7), 3.48 (2H, ABq, *J* 14.1), 7.02-7.06 (2H, m), 7.25-7.29 (3H, m), 7.32 (1H, t, *J* 7.9), 7.64-7.70 (3H, m), 7.78-7.83 (2H, m), 7.99 (1H, t, *J* 1.7), 8.02 (2H, dd, *J* 8.4, 1.0); δ_C(100 MHz; $CDCl_3$) 25.8, 33.4, 41.7, 109.2, 123.1, 126.7, 128.8, 129.4 (× 2), 130.1, 130.4, 131.1, 131.3, 131.7, 134.2, 135.6, 136.3, 138.2, 196.3; MS (ES+, Ar) m/z (rel intensity) 505 ($[MH+3]^+$, 25), 504 ($[MH+2]^+$, 100), 503 ($[MH+1]^+$, 27), 502 (MH^+, 90), 457 (42), 455 (38), 425 (18), 397 (16), 316 (12), 315 (49), 314 (15), 313 (47), 282 (18), 281 (85), 125 (16); HRMS (ES+, Ar) calcd for $C_{23}H_{21}NO_5SBr$ (MH^+) 502.0324, found 502.0331; $[\alpha]^{25}_D$ +42.47 (*c* 1.0 in $CHCl_3$); HPLC: Chiralpack IA (pet ether/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 250 nm), t_R (major) = 31.7 min, t_R (minor) = 23.3 min; 96% ee.

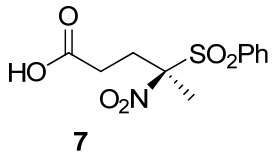
5. Synthetic applications of nitrosulfone 4b

p-Tolyl 4-nitro-4-(phenylsulfonyl)pentanoate (6). TFA (6.91 mmol, 200 µl) was added to a stirred solution of m-chloroperbenzoic acid (55-75%, 11.06 mmol, 3.2 g) in dichloromethane (9 ml) at rt and the stirring continued for 6 h. A solution of **4b** (500 mg, 1.38 mmol) in dichloromethane (3 ml) was added to the reaction mixture and stirring continued for another 14 h at rt. The reaction mixture was diluted with ether (15 ml), washed with sat solution of sodium sulphite (20 ml), sodium bicarbonate (20 ml), brine (10 ml) and dried over anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using EtOAc-pet ether (30%) as eluent to afford the ester **6.** Colorless solid; Yield 486 mg, 93%; mp 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; $CDCl_3$) 2.00 (3H, s), 2.34 (3H, s), 2.52-2.63 (1H, m), 2.72 (2H, td, *J* 13.0, 5.0), 2.82-2.93 (1H, m), 6.93 (2H, d, *J* 8.3), 7.17 (2H, d, *J* 8.3), 7.61 (2H, t, *J* 7.8), 7.77 (1H, t, *J* 7.8), 7.88 (2H, d, *J* 7.8); δ_C(100 MHz; $CDCl_3$) 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 $C_{18}H_{19}NO_6SNa$ (MNa^+) 400.0831, found 400.0817; $[\alpha]^{25}_D$ +35.73 (*c* 1.0 in $CHCl_3$); HPLC: Lux Cellulose-1 (pet ether/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 250 nm), t_R (major) = 65.7 min, t_R (minor) = 62.7 min; 99% ee.



6

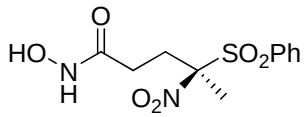
4-Nitro-4-(phenylsulfonyl)pentanoic acid (7). To a solution of **6** (150 mg, 0.40 mmol) in THF (5.0 ml) and H_2O (3.0 ml) was added $LiOH·H_2O$ (33 mg, 0.80 mmol) and the mixture was stirred at room temperature for 10 min. The mixture was acidified with 1 N HCl and extracted with Et_2O (3 × 15 ml). The combined extract was dried over anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using EtOAc-pet ether (90%) as eluent to afford the acid **7**. Colorless solid; Yield 96 mg, 84%; mp 153-154 °C; ν_{max}(film)/cm^{-1} 2929w, 2857vw, 1708s, 1554s, 1446m, 1332m, 1315m, 1231w, 1154m, 1075vw, 917vw, 846vw, 753vm, 687vw; δ_H(400 MHz; $CDCl_3$) 1.94 (3H, s), 2.39 (1H, ddd, *J* 16.3, 10.4, 5.7), 2.53 (1H, ddd, *J* 16.3, 10.2, 5.4), 2.61 (1H, ddd, *J* 15.2, 10.4, 5.4), 2.77 (1H, ddd, *J* 15.2, 10.2, 5.7), 7.62 (2H, t, *J* 7.7), 7.78 (1H, t, *J* 7.7), 7.86 (2H, d, *J* 7.7); δ_C(100 MHz; $CDCl_3$) 17.4, 28.5 (× 2), 105.9, 129.5, 131.2, 132.5, 135.7, 177.1; MS (ES+, Ar) m/z (rel



7

intensity) 290 ([MH+2]$^+$, 11), 289 ([MH+1]$^+$, 18), 288 (MH$^+$, 81), 287 (100), 273 (12), 295 (24), 246 (18), 185 (11), 149 (18), 137 (13), 125 (91); HRMS (ES+, Ar) calcd for $C_{11}H_{13}NO_6SNa$ (MNa^+) 310.0353, found 310.0356; $[\alpha]^{25}_D$ +21.35 (*c* 1.0 in $CHCl_3$).

***N*-hydroxy-4-nitro-4-(phenylsulfonyl)pentanamide (8).** To a solution of **6** (150 mg, 0.40 mmol) in EtOH-DCM (7:3, 7.0 ml) was added $HONH_2$·HCl (111 mg, 1.60 mmol, 4 equiv) and pyridine (130 µl, 1.60 mmol) and the mixture was stirred at room temperature for 12 h. The mixture was concentrated in vacuo and the residue was purified by silica gel column chromatography using EtOAc-pet ether (60%) as eluent to afford the amide **8**. Colorless sticky liquid; Yield 89 mg, 74%;



8

ν_{max}(neat)/cm^{-1} 3389brvs, 1655s, 1554vs, 1449w, 1386vw, 1332s, 1315m, 1218w, 1155m, 1075w, 768s, 721w; δ_H(400 MHz; $CDCl_3$) 1.85 (3H, s), 2.12 (1H, ddd, *J* 15.1, 10.1, 5.6), 2.37 (1H, ddd, *J* 15.1, 10.1, 5.1), 2.60 (1H, ddd, *J* 14.9, 10.2, 5.1), 2.77 (1H, ddd, *J* 14.9, 10.2, 5.6), 7.57 (2H, t, *J* 7.6), 7.72 (1H, t, *J* 7.6), 7.81 (2H, d, *J* 7.6); δ_C(100 MHz; $CDCl_3$) 17.4, 27.0, 28.8, 106.6, 129.6, 131.1, 132.3, 135.8, 169.7; MS (ES+, Ar) m/z (rel intensity) 290 ([MH+2]$^+$, 11), 289 ([MH+1]$^+$, 18), 288 (MH$^+$, 81), 287 (100), 273 (12), 295 (24), 246 (18), 185 (11), 149 (18), 137 (13), 125 (91); HRMS (ES+, Ar) calcd for $C_{11}H_{14}N_2O_6SNa$ (MNa^+) 325.0465, found 325.0460; $[\alpha]^{25}_D$ +12.71 (*c* 1.05 in $CHCl_3$); HPLC: Chiralpack AD-H (pet ether/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 216 nm), t_R (major) = 40.1 min, t_R (minor) = 45.2 min; >99% ee.

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