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SUPPORTING INFORMATION

Title: Direct Asymmetric α-Sulfamidation of α-Branched Aldehydes: A Novel Approach to Enamine Catalysis
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Ref. No.: O200600587

General methods. Flash chromatography (FC) was carried out using Merck silica gel 60 (230 – 400 mesh). TLC was carried out on silica gel coated aluminium sheets with fluorescence indicator (silica gel 60 F_{254}) by Merck. ^{1}H NMR spectra were recorded at 250 MHz on Bruker AC300, at 300 MHz on Bruker DP300 and at 400 MHz on Bruker DP400 and on Bruker AM400, the ^{13}C NMR spectra were recorded at 75 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm relative to the solvent residual peak[1] In case of a mixture of stereoisomeric products, the signals for the major product are printed in bold letters. Mass spectra were recorded on Kratos MS50, on Finnigan MAT 90 (EI-MS, HRMS), Thermo Quest Finnigan MAT 95 XL (EI-MS) or Kratos Concept 1H (FAB). Elemental analysis was carried out on Elementar Vario EL and on Heraeus CHN-O-Rapid. HPLC was performed on Agilent 1100 Series using Diacel Chiralpak AS (250 × 4.6 mm) or Diacel Chiracel OD (250 × 4.00 mm, 10μm). Rotational values were determined on a Perkin Elmer 241 Polarimeter at $\lambda = 589$ nm (sodium D-line). The concentration c is given in [g/100 ml]. *ee*'s and *de*'s were determined by comparison with the racemic products obtained

by application of DL-proline as catalyst. As the ratio of the integrals of HPLC or ^{19}F NMR signals for the enantiomers $E_{1,rac}$ and $E_{2,rac}$ in the racemic mixture was not always exactly 1:1, error margins for *ee*'s of non-racemic products were determined according to $\Delta ee = \{[(\delta ee/\delta E_1)*\Delta E_1]^2 + [(\delta ee/\delta E_2)*\Delta E_2]^2\}^{½}$ with $\Delta E_i = \delta E_{i,rac}*E_i$ and $\delta E_{i,rac} = [E_{i,rac} - (E_{1,rac}+E_{2,rac}/2)]/2$ (i = 1,2).

Materials. All reagents available from commercial sources (Acros, Aldrich, Fluka, Lancaster, Merck) were used without further purification. Sulfonyl azides were synthesised following known procedures.[2] Stroh-Rum was purchased from Stock Austria GmbH. Ionic Liquids [bmim][BF_4],[3] [capemim][BF_4][4] and [C_3OHmim][BF_4][5] were synthesised following known procedures. Ionic Liquids ECOENG 212™, ECOENG 1111P™, AMMOENG 100™, AMMOENG 102™ and AMMOENG 120™ were purchased from Solvent Innovations. Non commercially available aldehydes **16,21–27** were synthesised following known procedures.[6–910] Solvents were dried and distilled under argon following general laboratory methods.

General procedure for the sulfamidation of α,α-disubstituted aldehydes (GP 1)

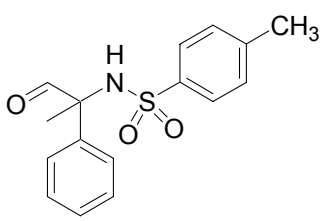
Method A: A solution or suspension of the catalyst (1 equiv.) in the solvent (10 to 20 ml/mmol aldehyde) was treated successively with the sulfonyl azide (1 to 1.2 equiv.) and the aldehyde (1 equiv.) at room temperature until TLC monitoring indicated complete consumption of the aldehyde. The solvent was then removed by evaporation under reduced pressure and the product isolated by flash chromatography. When ionic liquids were used as solvent, the ionic liquid phase was extracted excessively with ethyl acetate and THF after completion of the reaction, until TLC-control of the separated non-ionic phase indicated there was no more product (about 5 times). The non-ionic phases were collected and the solvent removed by evaporation. The product was then isolated by flash chromatography of the residue.

Method B: A solution of 1 equiv. of the catalyst in ethanol (20 – 30 ml of ethanol/mmol aldehyde) was treated successively with sodium azide (1.4 equiv.), aldehyde (1 equiv.), and sulfonyl chloride (1.2 equiv.) at room temperature. After TLC monitoring indicated complete consumption of the aldehyde, the solvent was removed under reduced pressure and the product isolated by flash chromatography.

General procedure for the determination of enantiomeric excess of α-sulfamidated α,α-disubstituted aldehydes as Mosher's-Ester (GP 2)[11]

An analytic sample (approx. 10 – 20 mg) of the product obtained from GP 1 was stirred with a slight excess of sodium borohydride in ethanol (2 – 3 ml) for 1 h. The reaction was then quenched by addition of half-saturated ammonium chloride solution (approx. 5 ml). The resulting alcohol was extracted twice with dichloromethane (10 ml each), the combined organic phases dried over sodium sulfate, the solvent removed by evaporation and the residue dried under high vacuum for several hours. The crude product was then dissolved in pyridine or pyridine/carbontetrachloride (0.2 ml) and treated under argon atmosphere with a slight excess of (*S*)-(+)-2-methoxy-2-trifluoromethyl-2-phenylacetyl chloride (*Mosher's chloride*). The reaction mixture was left over night, followed by addition of water (2 ml). After extraction with diethylether (15 ml) the organic phase was washed with diluted hydrochloric acid, saturated aqueous potassium carbonate solution, and saturated aqueous sodium chloride solution. After drying over sodium sulfate and removing the solvent by evaporation, a crude product was obtained, which was analysed by NMR without further purification. The enantiomeric excess was determined by comparison of the integrals of the diastereomeric fluorine signals in the ^{19}F NMR spectrum. If the fluorine signals could not be properly resolved, the diastereomers were resolved by HPLC with chiral stationary phase.

Synthesis of the products



(+)-2-Phenyl-2-(4'-toluene)sulfonylaminopropionaldehyde **4a**: The product was synthesised using **1**, tosyl azide (**2a**) and the catalyst. Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered the product as a colourless solid. For reaction conditions and yields, *see* Tables 1–4. – mp = 113 °C. – R_f = 0.22 (*n*-pentane/Et_2O 2:1). – HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/isopropanol 64 :36, 0.8 ml/min) : R_t(min) = 15.4 min, R_t(maj) = 27.7 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.82 (s, 3 H, CR_3CH_3), 2.28 (s, 3 H, $C^{4'}{}_{Ts}CH_3$), 5.85 (bs, 1 H, NH), 6.99 (d, *J* = 8.0 Hz, 2 H, $C^{3'}H_{Ts}$), 7.03 – 7.09 (m, 2 H, CH_{Ph}), 7.09 – 7.21 (m, 3 H, CH_{Ph}), 7.29 (d, *J* = 8.3 Hz, 2 H, $C^{2'}H_{Ts}$), 9.06 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (+, $CR_3\underline{C}H_3$), 21.5 (+, $C^{4'}{}_{Ts}\underline{C}H_3$), 66.9 (q, CR_4), 126.8 (+, CH_{ar}), 127.6 (+, CH_{ar}), 128.7 (+, $C^{4''}H_{Ph}$), 129.0 (+, CH_{ar}), 129.3 (+, CH_{ar}), 134.3 (q, $C^{1'}{}_{Ts}SO_2$), 139.3 (q, $\underline{C^{1''}}_{Ph}CR_3$), 142.9 (q, $\underline{C^{4'}}_{Ts}CH_3$), 194.4 (+, CHO) ppm. – MS (FAB): *m/z* (%) = 304 (19) [M^++1], 274 (100) [M^+–CHO], 172 (49) [$C_7H_{10}NSO_2^+$]. – MS (EI, I, 70 eV): *m/z* (%) = 274 (100) [M^+–CHO], 155 (34) [$C_7H_7SO_2^+$], 149 (16) [M^+–$C_7H_7SO_2$], 104 (6) [$C_8H_8^+$], 91 (50) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$]. – HRMS (I):

calcd.: 274.0902 [M^+–CHO], found: 274.0900. – $C_{16}H_{17}NO_3S$ (303.38 g/mol), calcd.: C 63.35, H 5.65, N 4.62, S 10.57, found: C 63.71, H 5.68, N 4.64, S 10.60. – IR (KBr): 3252.1 (m, υ[NH]), 3092.7 (w), 3068.6 (w, υ[CH_{ar}]), 3028.7 (w, υ[CH_{ar}]), 2923.7 (m, υ[CH_3]), 2850.4 (m, υ[CH_3]), 1743.9 (m, δ[NH]), 1733.0 (m, υ(C=O)), 1598.8 (w, υ[C–C_{ar}]), 1583.0 (w, υ[C–C_{ar}]), 1495.5 (m, υ[C–C_{ar}]), 1442.9 (m, δ_{as}[CH_3]), 1365.5 (m, δ_{sy}[CH_3]), 1327.4 (m, υ_{as}[$SO_2$1156.2 (m, υ_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +59.7° (c = 0.330, $CHCl_3$; for 56% *ee*).

Screening of reaction conditions and catalysts in the synthesis of 4a:

Table 1. Screening of different solvents and temperatures.

solvent	catalyst loading[a]	temperature	time	%yield[b]	%*ee*[c]
THF[d]	0.4 equiv.	–5 °C (2 d), then rt (4 d)	6 d	11	53 ± 3
THF[d,e]	0.4 equiv.	rt	7 d	21	rac
CH_2Cl_2[d]	0.4 equiv.	–5 °C (2 d), then rt (4 d)	6 d	-	-
CH_3CN[d]	0.4 equiv.	–5 °C (2 d), then rt (4 d)	6 d	14	54 ± 3
THF[d,e]	0.4 equiv.	50° C	4 h	4	rac
toluene	0.4 equiv.	rt	9 d	-	-
MeOH	1 equiv.	0 °C	5 d	<10	n. d.[f]
MeOH	2 equiv.	rt	1 d	32	59 ± 3
tech. EtOH[d,g]	0.4 equiv.	rt	9 d	13	n. d.[f]
tech. EtOH[g]	1 equiv.	0 °C	5 d	<10	n. d.[f]
tech. EtOH[g]	1 equiv.	rt	1 d	38	56 ± 3
tech. EtOH[g]	2 equiv.	50 °C	4 h	34	59 ± 3
abs. EtOH[h]	1 equiv.	rt	1 d	35	59 ± 3
abs. EtOH[i,j]	1 equiv.	rt	1 d	31	62 ± 3
abs. EtOH[i,j,k]	1 equiv.	rt	1 d	27	n. d.[f]
tech. EtOH[g,l]	2 equiv.	rt	1 d	32	45 ± 3
tech. EtOH[g,m]	1 equiv.	rt	1 d	<10	n. d.[f]
*i*PrOH	1 equiv.	rt	1 d	21	53 ± 3
*n*PrOH	1 equiv.	rt	1 d	33	60 ± 3
*n*BuOH	1 equiv.	rt	1 d	27	57 ± 3
*t*BuOH	1 equiv.	rt	1 d	25	54 ± 3
n-pentanol	1 equiv.	rt	1 d	25	52 ± 3

CH_2Cl_2/H_2O	1 equiv.	rt	7 d	-	-
toluene/H_2O	1 equiv.	rt	7 d	-	-
DMSO[d]	1 equiv.	rt	2 h	28	60 ± 3
DMSO/EtOH	1 equiv.	0 °C	1 d	32	58 ± 3
EtOH/hν	1 equiv.	~50° C	16 h	-[n]	-

[a] With respect to the aldehyde. [b] Isolated yields after flash chromatography. [c] *ee*'s were determined by HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/*i*PrOH 64:36, 0.85 ml/min). [d] After reaction the reaction mixture was diluted with water or half saturated aqueous ammonium chloride solution and the product extracted with ethyl acetate. [e] The reaction was carried out with DL-proline. [f] Not determined. [g] Technical ethanol, denatured with 1% petrol ether. [h] Absolute ethanol, dried over potassium hydroxida and distilled over sodium/diethylphthalate. [i] Absolute ethanol as purchased (>99.9%). [j] The reaction was carried out in a *one-pot* procedure, following GP 1, Method B. [k] A tenfold excess of the aldehyde was used with respect to the sulfonyl chloride. [l] Slow addition of azide in EtOH. [m] Slow addition of aldehyde in EtOH. [n] Decomposition.

Table 2. Screening of different additives in the synthesis of **4a**.[a]

solvent	additive	additive amount	time	%yield[b]	%*ee*[c]
THF + AcOH[d]	AcOH.	1 drop	>7 d	-	-
THF + NEt_3[d]	NEt_3	1 drop	>7 d	-	-
CH_2Cl_2	TFA	20 Vol%	1 d	-[e]	-
tech. EtOH	Bu_4NI	0.84 equiv.	1 d	36	59 ± 3
THF	Bu_4NI	0.84 equiv.	4 d	26	55 ± 3
tech. EtOH	18-crown-6	1 equiv	1 d	27	49 ±3
tech. EtOH	18-crown-6/KCl	1 equiv. each	1 d	27	50 ± 3
tech. EtOH	NaOAc/AcOH[f]	pH = 6.3	>7 d	-	-
tech. EtOH	NaOAc/AcOH[g]	pH = 4.76	>7 d	-	-
tech. EtOH	AcOH	0.1 mol/l	>7 d	-	-

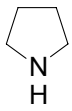
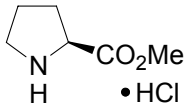
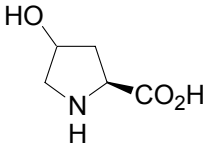
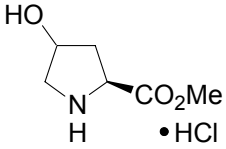
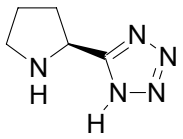
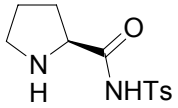
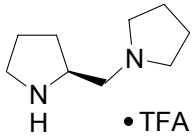
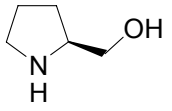
[a] Unless stated differently, 1 equiv. of L-proline with respect to the aldehyde was used. All experiments were carried out at room temperature. [b] Isolated yields after flash chromatography. [c] *ee*'s were determined by HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/*i*PrOH 64:36, 0.85 ml/min). [d] 0.4 equiv. of L-proline were used. [e] Decomposition. [f] Calcd. pH 6.3; NaOAc 0.10 mol/l, AcOH 0.021 mol/l. [g] Calcd. pH 4.76; NaOAc 0.1 mol/l, AcOH 0.1 mol/l.

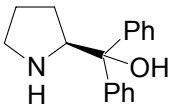
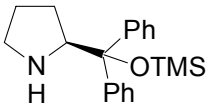
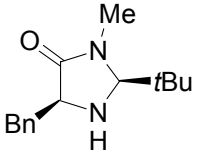
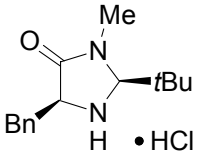
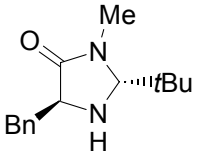
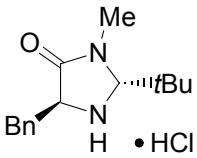
Table 3. Synthesis of **4a** in ionic liquids.

solvent	catalyst loading[a]	temperature	time	%yield[b]	%*ee*[c]
[bmim][BF_4]	1 equiv.	rt	1 d	38	72 ± 2
[bmim][BF_4]	0.2 equiv.	rt	1 d	17	53 ± 3
[bmim][BF_4]	1 equiv.	80 °C	1 d[d]	29	n. d.[e]
[capemim][BF_4]	1 equiv.	rt	1 d	53	20 ± 4
[C_3OHmim][BF_4]	1 equiv.	rt	1 d	-[f]	-

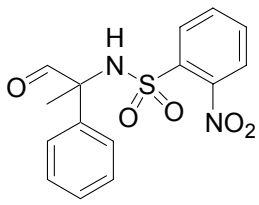
[a] With respect to the aldehyde. [b] Isolated yields after flash chromatography. [c] *ee*'s were determined by HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/*i*PrOH 64:36, 0.85 ml/min). [d] TLC indicated complete reaction after 3 h. [e] Not determined. [f] The reaction resulted in a different product which could not be identified.

Table 4. Screening of different catalysts in the synthesis of **4a**.[a]

solvent	catalyst	structure	time	%yield[b]	%*ee*[c]
EtOH	**5**		1 d	36	rac
tech. EtOH[d]			4 d	-	-
DMSO			1 d	27	59 ± 3
tech. EtOH[d]			4 d	-	-
EtOH	**6**		1d	24	66 ± 2
DMSO	**7**		1d	25	66 ± 2
tech. EtOH[d]	**8**		70 min	23	45 ± 3
tech. EtOH[d]	**9**		4 d	<10	n. d.

tech. EtOH[d]	**10**		1 d	-[e]	-
abs. EtOH[f]	**11**		1 d	40	n. d.
tech. EtOH[d]		 (20 mol%)	2 d	-	-
tech. EtOH[d]		 (20 mol%)	>7 d	-	-
tech. EtOH[d]		 (20 mol%)	2 d	-	-
tech. EtOH[d]		 (20 mol%)	>7 d	-	-

[a] Unless stated differently, 1 equiv. of the catalyst was used. All experiments were carried out at room temperature. [b] Isolated yields after flash chromatography. [c] *ee*'s were determined by HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/*i*PrOH 64:36, 0.85 ml/min). [d] Technical ethanol, denatured with 1% petrol ether. [e] A different product was isolated which could not be identified. [f] Absolute ethanol as purchased (>99.9%).

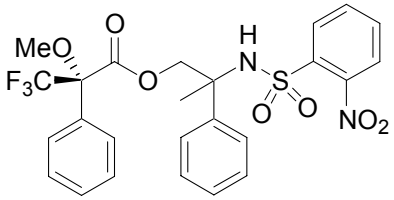


2-(2'-Nitrobenzene)sulfonylamino-2-phenylpropionaldehyde **4b**:

The compound was synthesised following GP 1, Method A, using **1**, 2-nitrobenzenesulfonyl azide (**2b**) and the catalyst. The product was purified by flash chromatography on silica with *n*-pentane/diethylether 3:2. For reaction conditions and yields, *see* Tables 5–8. – mp = 173 °C. – R_f = 0.15 (*n*-pentane/Et_2O 2:1). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (s, 3 H, CH_3), 6.99 – 7.22 (m, 9 H, CH_{ar}), 7.44 (ddd, *J* = 7.7, 7.6, 1.7 Hz, 1 H, CH_{Ns}), 7.68 (dd, *J* = 7.9, 1.1 Hz, 1 H, CH_{Ns}), 9.07 (s, 1 H, CHO) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 (+, CH_3), 67.3 (q, CR_4), 124.9 (+,$C^{4''}{}_{Ph}H$), 127.9 (+, $C^{2''}{}_{Ph}H$), 128.9 (+, $C^{3''}{}_{Ph}H$), 129.2 (+, $C_{Ns}H$), 130.2 (+, $C_{Ns}H$), 132.4 (+, $C_{Ns}H$), 132.7 (+, $C_{Ns}H$), 133.6 (q, $C^{1'}{}_{Ns}SO_2$), 135.4 (q, $\underline{C^{1''}}_{Ph}CR_3$), 147.4 (q, $C^{2'}{}_{Ns}NO_2$), 193.4 (+, CHO) ppm. – MS (FAB): *m/z* (%) = 335 (22) [M^++1], 307 (100), 289 (70) [M^++1–NO_2], 274 (52), 186 (26) [$C_6H_5NO_4S^+$], 165 (34). – MS (EI, II, 70 eV): *m/z* (%) = 305 (96) [M^+–CHO], 186 (100) [$C_6H_4NSO_4^+$], 149 (16) [M^+–$C_6H_4NSO_4$], 121

(44), 112 (21), 104 (17) [$C_8H_8^+$], 91 (14) [$C_7H_7^+$], 77 (18) [$C_6H_5^+$], 57 (16). – HRMS (I): calcd.: 305.0596 [M^+–CHO], found: 305.0596. – $C_{15}H_{14}N_2O_5S$ (334.35 g/mol), calcd.: C 53.88, H 4.22, N 8.38, S 9.59; found: C 54.12, H 4.40, N 8.12, S 9.85. – IR (KBr): 3321.8 (m, υ[NH]), 3094.7 (w, υ[CH_{ar}]), 3024.0 (w, υ[CH_{ar}]), 2953.4 (w, υ[CH]), 2887.5 (w, [υ[CH]), 1717.1 (m, υ[C=O]), 1593.5 (w, υ[C-C_{ar}]), 1541.4 (m, υ_{as}[NO_2]), 1443.8 (w, δ_{as}[CH_3]), 1394.0 (m, δ_{sy}[CH_3]), 1367.0 (m, υ_{as}[SO_2]), 1337.0 (m, υ_{sy}[NO_2]), 1157.4 (m, υ_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +226.3° (c = 0.175, $CHCl_3$; for 61% *ee*).

Determination of enantiomeric excess of 4b as Mosher's-Ester:



*(2*S*)-2'-Phenyl-2'-(2'''-nitrobenzene)sulfonylaminopropyl 2-methoxy-2-trifluoromethylphenylacetate*: The reaction was carried out following GP 2. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.64, **1.70** (2 × s, 3 H, $NHCR_2C\underline{H}_3$), 3.41 (m, 3 H, OCH_3), 4.54, **4.54** (2 × d, *J* = 11.3 and 11.1 Hz, 1 H, C<u>H</u>HOR), **4.74**, 4.80 (2 × d, *J* = 11.1 and 11.3 Hz, 1 H, CH<u>H</u>OR), 5.88, **5.93** (2 × s, 1 H, NH), 6.95 – 7.49 (m, 14 H, CH_{ar}) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = δ = **24.6**, 25.1 ($NHCR_2\underline{C}H_3$), 55.6, 55.6 (OCH_3), 60.8, **60.9** (CR_3NH), 71.6, **71.8** (CH_2OR), 77.4 ($\underline{C}R_3CF_3$), 125.0, **125.0** ($C_{ar}H$), 126.2, **126.3** (2 $C_{ar}H$), 127.5, **127.5** ($C_{ar}H$), **127.5**, 127.5 ($C_{ar}H$), 128.3, 128.3 ($C_{ar}H$), 128.5 (2 $C_{ar}H$), **128.6**, 128.7 (2 $C_{ar}H$), **129.8**, 129.9 ($C_{ar}H$), 130.3 ($C_{ar}H$), 131.9 ($\underline{C}_{ar}CR_2NHR$), 132.6, **132.6** ($C_{ar}H$), 132.9, **133.0** ($C_{ar}H$), 135.6, **135.7** ($C_{ar}SO_2$), 139.4, 139.4 ($\underline{C}_{ar}CR_2OCH_3$), 147.5, 147.5 ($C_{ar}NO_2$), 166.4, 166.4 ($CO_2$) ppm. – ^{19}F NMR (300 MHz, $CDCl_3$): δ = **–71.98**, –71.89 ppm.

Screening of reaction conditions and catalysts in the synthesis of 4b:

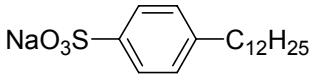
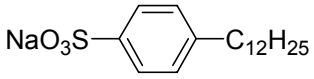
Table 5. Screening of different solvents in the synthesis of **4b**.

solvent	catalyst loading[a]	temperature	time	%yield[b]	%*ee*[c]
tech. EtOH[d]	1 equiv.	rt	1 d	46	67 ± 2
abs. EtOH[e]	1 equiv.	rt	1 d	44	56 ± 3
abs. EtOH[f]	1 equiv.	rt	1 d	44	55 ± 3
abs. EtOH[e,g]	1 equiv.	rt	2 d	41	56 ± 3
abs. EtOH[e]	0.1 equiv.	rt	1 d	18	51 ± 3
ethylene glycol	1 equiv.	rt	18 d	12	n. d.[h]

*i*PrOH	1 equiv.	rt	1 d	38	68 ± 2
DMSO/THF 1:1[i]	1 equiv.	0 °C	1 d	30	61 ± 2
DMPU	1.1 equiv.	rt	2 d	-	-
Stroh-Rum™ [j]	1 equiv.	rt	14 d	19	41 ± 3

[a] With respect to the aldehyde. [b] Isolated yields after flash chromatography. [c] *ee*'s were obtained by determination of the diastereomeric excess of Mosher's Ester of **4b** by ^{19}F NMR spectroscopy. [d] Technical ethanol, denatured with 1% petrol ether. [e] As purchased (>99.9%). [f] Dried over potassium hydroxide, distilled over sodium/diethylphthalate. [g] Tenfold dilution. [h] Not determined. [i] After reaction the reaction mixture was diluted with water or half saturated aqueous ammonium chloride solution and the product extracted with ethyl acetate. [j] Ethanol content 80 Vol%.

Table 6. Screening of different additives in the synthesis of **4b**.[a]

solvent	additive	additive amount	time	%yield[b]	%*ee*[c]
abs. EtOH[d]	none	-	1 d	44	56 ± 3
abs. EtOH[e]	none	-	1 d	44	55 ± 3
abs. EtOH[d]	water	4 Vol%	9 d	37	59 ± 2
tech. EtOH[e]	(petrol ether)	(1 Vol%)	1 d	46	67 ± 2
abs. EtOH[e]	*n*-pentane	1 Vol%	1 d	42	65 ± 2
abs. EtOH[e]	*n*-hexane	1 Vol%	1 d	>39	64 ± 2
abs. EtOH[e]	*n*-hexane	1 Vol%	11 d	41	65 ± 2
	water	4 Vol%			
abs. EtOH[e]	cyclohexane	1 Vol%	1 d	41	62 ± 2
abs. EtOH[e]	*n*-heptane	1 Vol%	1 d	35	55 ± 3
abs. EtOH[e]	*n*-octane	1 Vol%	1 d	43	60 ± 2
abs. EtOH[e]	*n*-octane	2 Vol%	1 d	44	62 ± 2
abs. EtOH[e]	*n*-octane	5 Vol%	1 d	45	66 ± 2
abs. EtOH[e]	*n*-octane	10 Vol%	1 d	40	64 ± 2
abs. EtOH[e]	*n*-octane	25 Vol%	1 d	41	61 ± 2
abs. EtOH[e]	*n*-octane	50 Vol%	1 d	40	62 ± 2
abs. EtOH[e]	*n*-decane	1 Vol%	1 d	45	57 ± 3
abs. EtOH[e]		1 equiv.	1 d	38	58 ± 2
abs. EtOH[e]		10 wt% of solvent	5 d	33	43 ± 3

[a] Unless stated differently, 1 equiv. of L-proline was used with respect to **1**. All experiments were carried out at room temperature. [b] Isolated yields after flash chromatography. [c] *ee*'s

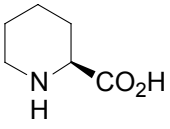
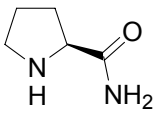
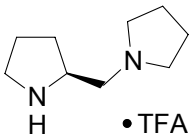
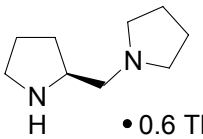
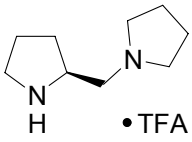
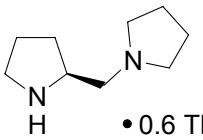
were obtained by determination of the diastereomeric excess of Mosher's Ester of **4b** by ^{19}F NMR spectroscopy. [d] Absolute ethanol as purchased (>99.9%). [e] Absolute ethanol, dried over potassium hydroxide, distilled over sodium/diethylphthalate. [f] Technical ethanol, denatured with 1% petrol ether.

Table 7. Synthesis of **4b** in ionic liquids.[a]

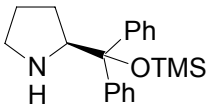
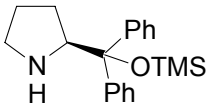
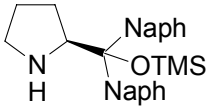
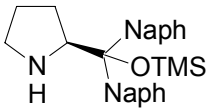
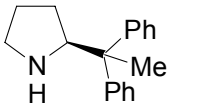
solvent	temperature	time	%yield[b]	%*ee*[c]
[bmim][BF_4]	rt	1 d	55	66 ± 2
ECOENG 212™	rt	1 d	36	56 ± 3
ECOENG 1111P™	rt	2 d	21	59 ± 2
AMMOENG 100™	rt	3 d	38	28 ± 3
AMMOENG 102™	rt	3 d	-	-
AMMOENG 120™	rt	3 d	-	-

[a] Reactions were carried out following GP 1, Method A, using 1 equiv. of catalyst with respect to the aldehyde. [b] Isolated yields after flash chromatography. [c] *ee*'s were obtained by determination of the diastereomeric excess of Mosher's Ester of **4b** by ^{19}F NMR spectroscopy.

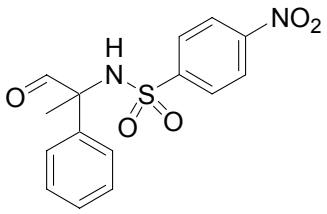
Table 8. Screening of different catalysts in the synthesis of **4b**.[a]

solvent	catalyst	structure	time	%yield[b]	%*ee*[c]
abs. EtOH[d]			1 d	37	n. d.[e]
abs. EtOH[d]			1 d	7	31 ± 3
DMSO	**8**		1 d[f]	26	57 ± 2
DMSO	**8**		1 d	22	47 ± 3
DMSO	**8**	 (20 mol%)	1 d	10	55 ± 3
EtOH	**8**		1 d	20	60 ± 2

[g]

abs. EtOH[d]	**11**		1 d	26[h]	n. d.[e]
abs. EtOH[d]	**11**		1 d	30[i]	n. d.[e]
abs. EtOH[d]	**12**		1 d	38[h]	n. d.[e]
abs. EtOH[d]	**12**		1 d	29[i]	64 ± 2
abs. EtOH[d]	**13**		1 d	52	55 ± 3

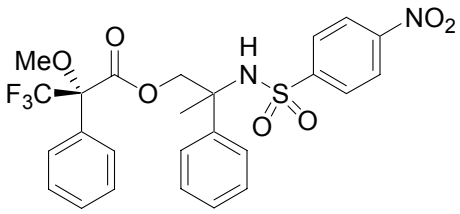
[a] Unless stated differently, 1 equiv. of the catalyst was used. All experiments were carried out at room temperature unless stated differently. [b] Isolated yields after flash chromatography. [c] *ee*'s were obtained by determination of the diastereomeric excess of Mosher's Ester of **4b** by ^{19}F NMR spectroscopy. [d] Absolute ethanol as purchased (>99.9%). [e] Not determined. [f] TLC indicated complete reaction after 70 min. [g] The reaction was carried out at 0 °C and 1.3 equiv. of the catalyst were used. [h] After complete reaction the product was reduced *in situ* with sodium borohydride to yield the corresponding alcohol. [i] According to NMR spectroscopy the product contained significant amounts of catalyst. Corrected yield is given.



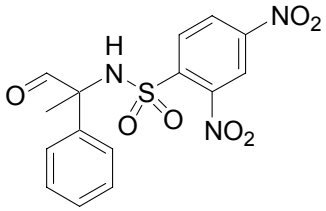
*(*S*)-(+)-2-(4'-Nitrobenzene)sulfonylamino-2-phenylpropion-aldehyde* **4c**: The compound was synthesised following GP 1, Method A, using **1** (67.1 mg, 0.50 mmol), 4-nitrobenzenesulfonyl azide (**2c**, 136.9 mg, 0.60 mmol), and **3** (57.6 mg, 0.5 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 5:1 delivered a colourless solid (86.8 mg, 0.260 mmol) in 52% yield. – When carried out in technical ethanol under otherwise unchanged conditions the reaction delivered **4c** (76.3 mg, 0.228 mmol) in 46% yield. – mp = 183 – 187 °C. – R_f = 0.17 (cyclohexane/ethyl acetate 5:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 3 H, CH_3), 6.28 (bs, 1 H, NH), 6.99 – 7.05 (m, 2 H, $C^{2'}H_{ar}$), 7.10 – 7.17 (m, 2 H, $C^{3'}H_{ar}$), 7.23 (dddd, *J* = 8.0, 6.7, 1.1, 1.1 Hz, 1 H, $C^{4'}H_{ar}$), 7.48 (ddd, *J* = 9.2, 2.2, 2.2 Hz, 2 H, $C^{2''}H_{Ns}$), 8.01 (ddd, *J* = 9.2, 2.2, 2.2 Hz, 2 H, $C^{3''}H_{Ns}$), 9.07 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (+, CH_3), 66.8 (q, CR_4), 123.8 (+, $C_{ar}H$), 127.9 (+, $C_{ar}H$), 128.1 (+, $C_{ar}H$), 129.0 (+, $C_{ar}H$), 129.3 (+, $C^{4'}{}_{ar}H$), 132.8 (q, $\underline{C}^{1'}CR_4$), 147.4 (q, $C^{1''}SO_2$), 149.4 (q, $C^{2''}NO_2$), 193.6 (+, CHO) ppm. – MS (EI, KA, 70 eV): *m/z* (%) = 305 (100) [M^+–CHO], 186 (10) [$C_6H_4NO_4S^+$], 104 (7) [$C_8H_8^+$], 77 (27) [$C_6H_5^+$]. – HRMS (KA): calcd.: 305.0596 [M^+–CHO], found: 305.0598. – IR (KBr): 3295.2 (m, ν[NH]), 3068.8 (w, ν[CH_{ar}]), 3041.0 (w, ν[CH_{ar}]), 2953.1

(m, ν[CH_3]), 2923.9 (m, ν[CH_3]), 2853.3 (m, ν[CHO]), 2716.8 (w, ν[CHO]), 1722.0 (m, ν[C=O]), 1608.1 (w, ν[C-C_{ar}]), 1524.4 (m, ν_{as}[NO_2]), 1492.8 (w, ν[C-C_{ar}]), 1446.5 (m, δ_{as}[CH_3]), 1383.6 (m, δ_{sy}[CH_3]), 1350.6 (m, ν_{as}[SO_2]), 1314.6 (m, ν_{sy}[NO_2]), 1170.9 (m, ν_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +18.6° (c = 0.370, $CHCl_3$).

Determination of enantiomeric excess of 4c as Mosher's-Ester:

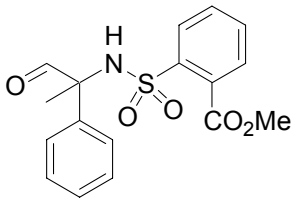


*(2*S*)-2'-Phenyl-2'-(4'''-nitrobenzene)sulfonylamino-propyl 2-methoxy-2-trifluoromethylphenylacetate*: The reaction was carried out following GP 2. – ^{1}H NMR (300 MHz, C_6D_6): δ = 1.14, **1.25** (2 × s, 3 H, $NHCR_2C\underline{H}_3$), **3.33**, 3.38 (2 × q, *J* = 1.1 and 0.8 Hz, 3 H, OCH_3), 4.17, **4.22** (2 × d, *J* = 11.1 and 11.1 Hz, 1 H, C<u>H</u>HOR), **4.50**, 4.70 (2 × d, *J* = 10.8 and 11.1 Hz, 1 H, CH<u>H</u>OR), 6.62, **6.68** (2 × d, *J* = 4.3 and 4.3 Hz, 4 H, CH_{ar}), 6.71 – 7.48 (m, 8 H, CH_{ar}), **7.54**, 7.62 (2 × d, *J* = 7.4 and 7.6 Hz, 2 H, CH_{ar}) ppm. – ^{19}F NMR (300 MHz, $CDCl_3$): δ = **–73.75**, –73.71 ppm. – When absolute ethanol was used in the synthesis of **4c** the diastereomeric excess was 82 ± 1% *de*. – When technical ethanol was used in the synthesis of **4c** the diastereomeric excess was 83 ± 1% *de*.

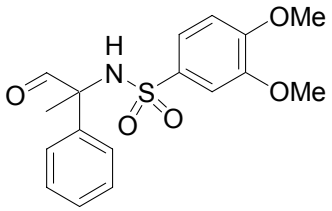


(+)-2-(2',4'-Dinitrobenzene)sulfonylamino-2-phenylpropion-aldehyde **4d**: The compound was synthesised following GP 1, Method A, using **1** (67.1 mg, 0.50 mmol), 2,4-dinitrobenzene-sulfonyl azide (**2d**, 150.3 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 5:1 to 3:2 delivered a yellow solid (51.1 mg, 0.135 mmol) in 27% yield and 45 ± 1% *ee*. – mp = 128 °C (decomp.). – R_f = 0.48 (cyclohexane/ethyl acetate 3:2). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 50:50, 0.5 ml/min): R_t(maj) = 22.2 min, R_t(min) = 46.1 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, CH_3), 6.44 (d, *J* = 9.6 Hz, 1 H, $C^{6'}H_{ar}$), 7.37 – 7.51 (m, 5 H, CH_{Ph}), 7.97 (dd, *J* = 9.5, 2.4 Hz, 1 H, $C^{5'}H_{ar}$), 9.15 (d, *J* = 2.8 Hz, 1 H, $C^{3'}H_{ar}$), 9.22 (s, 1 H, CHO), 10.12 (bs, 1 H, NH) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (+, CH_3), 67.4 (q, CR_4), 116.8 (+, $C_{ar}H$), 124.3 (+, $C_{ar}H$), 126.9 (+, $C^{2''}{}_{Ph}H$), 129.4 (+, $C_{ar}H$), 129.6 (+, $C_{ar}H$), 130.3 (+, $C^{3''}{}_{Ph}H$), 132.1 (q, $C^{2'}{}_{ar}NO_2$), 134.5 (q, $\underline{C}^{1'}{}_{Ph}CR_4$), 136.7 (q, $C^{4'}{}_{ar}NO_2$), 145.8 (q, $C^{1'}{}_{ar}SO_2$), 192.7 (+, CHO) ppm. – IR (KBr): 3295.7 (m, ν[NH]), 3107.2 (w, ν[CH_{ar}]), 2983.4 (w, ν[CH_3]), 2852.3 (w,

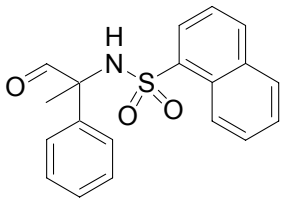
ν[CHO]), 1725.4 (m, ν[C=O]), 1617.5 (m, ν[C-C_{ar}]), 1586.4 (m, ν[C-C_{ar}]), 1523.2 (m, ν_{as}[NO_2]), 1425.7 (m, δ_{as}[CH_3]), 1334.8 (m, ν_{as}[NO_2]), 1157.2 (m, ν_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +14.4° (c = 0.655, $CHCl_3$). – Due to fast decomposition (within days) no further analytical data could be obtained.



(+)-2-(2'-Methoxycarbonylbenzene)sulfonylamino-2-phenylpropion-aldehyde **4e**: The compound was synthesised following GP 1, Method A, using **1** (67.1 mg, 0.50 mmol), 2-methoxycarbonyl-benzenesulfonyl azide (**2e**, 144.7 mg, 0.60 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered a colourless solid (67.1 mg, 0.193 mmol) in 39% yield and 8% *ee*. – mp = 134 – 137 °C. – R_f = 0.16 (*n*-pentane/diethylether 2:1). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 80:20, 0.7 ml/min): R_t(maj) = 24.0 min, R_t(min) = 31.4 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3 H, $CR_3C\underline{H}_3$), 4.04 (s, 3 H, CO_2CH_3), 7.08 – 7.20 (m, 5 H, CH_{Ph}), 7.22 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1 H, $C^{5'}H_{ar}$), 7.31 (dd, *J* = 8.0, 1.1 Hz, 1 H, $C^{6'}H_{ar}$), 7.44 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1 H, $C^{4'}H_{ar}$), 7.57 (bs, 1 H, NH), 7.72 (dd, *J* = 7.7, 1.1 Hz, 1 H, $C^{3'}H_{ar}$), 9.21 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4 (+, $CR_3\underline{C}H_3$), 53.5 (+, $CO_2\underline{C}H_3$), 67.4 (q, CR_4), 127.6 (+, $C^{2''}{}_{Ph}H$), 128.5 (+, $C_{ar}H$), 128.7 (+, $C^{3''}{}_{Ph}H$), 128.7 (+, $C_{ar}H$), 129.7 (q, $\underline{C^{2'}}{}_{ar}CO_2$), 130.4 (+, $C_{ar}H$), 131.5 (+, CarH), 131.6 (+, $C_{ar}H$), 134.2 (q, $C^{1'}{}_{ar}SO_2$), 141.3 (q, $\underline{C^{1''}}{}_{Ph}CR_4$), 168.1 (q, CO_2), 194.2 (+, CHO) ppm. – MS (FAB), *m/z* (%) = 348 (49) [M^++1], 318 (31) [M^+–CHO], 289 (28) [M^++1–CO_2CH_3], 259 (10) [M^+–CHO–CO_2CH_3], 216 (36) [$C_8H_8NO_4S^+$], 199 (100) [$C_8H_7O_4S^+$]. – MS (EI, II, 70 eV), *m/z* (%) = 318 (36) [M^+–CHO], 286 (67) [M^+–CHO–C_2H_5OH], 199 (100) [$C_7H_6NO_4S^+$], 184 (6) [$C_8H_9NO_2S^+$], 135 (13) [$C_8H_7O_2^+$], 103 (11) [$C_8H_7^+$], 77 (14) [$C_6H_5^+$]. – HRMS (I): calcd.: 318.0800 (M^+–CHO), found: 318.0807. – $C_{17}H_{17}NO_5S$ (347.39 g/mol), calcd.: C 58.78, H 4.93, N 4.03, S 9.23; found: C 58.82, H 4.86, 3.93, S 8.74. – IR (KBr): 3256.9 (m, ν[NH]), 3088.4 (m, ν[CH_{ar}]), 3044.3 (m, ν[CH_{ar}]), 3011.7 (m, ν[CH_{ar}]), 2990.2 (m, ν[CH_3]), 2960.9 (m, ν[CH_3]), 1716.0 (m, ν[C=O]), 1590.2 (m, ν[C-C_{ar}]), 1495.0 (m, ν[C-C_{ar}]), 1435.3 (m, δ_{as}[CH_3]), 1389.8 (m, δ_{sy}[CH_3]), 1334.0 (m, ν_{as}[SO_2]), 1161.0 (m, ν_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +78.7° (c = 0.385, $CHCl_3$).



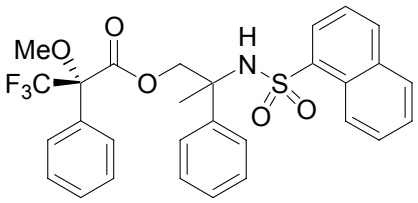
(+)-2-(3',4'-Dimethoxybenzene)sulfonylamino-2-phenylpropionaldehyde **4f**: The compound was synthesised following GP 1, Method A, using **1** (67.1 mg, 0.50 mmol), 3,4-dimethoxybenzenesulfonyl azide (**2f**, 133.8 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 4:1 delivered a colourless oil (75.1 mg, 0.215 mmol) in 43% yield and 67 ± 1% *ee*. – R_f = 0.29 (cyclohexane/ethyl acetate 3:1). – HPLC (Chiracel OD, *n*-heptane/isopropanol 92:8, 1.0 ml/min): R_t(maj) = 34.4 min, R_t(min) = 37.7 min. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3 H, $CR_3C\underline{H}_3$), 3.76 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 5.99 (bs, 1 H, NH), 6.70 (d, *J* = 8.7 Hz, 1 H, $C^{5'}{}_{ar}H$), 6.85 (d, *J* = 2.1 Hz, 1 H, $C^{2'}{}_{ar}H$), 7.06 – 7.14 (m, 3 H, CH_{ar}), 7.15 – 7.25 (m, 3 H, CH_{ar}), 9.11 (s, 1 H, CHO) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1 (+, $CR_3\underline{C}H_3$), 56.1 (+, OCH_3), 56.1 (+, OCH_3), 66.8 (q, CR_4), 109.4 (+, $C_{ar}H$), 110.4 (+, $C_{ar}H$), 120.6 (+, $C_{ar}H$), 127.8 (+, $C^{2''}{}_{Ph}H$), 128.8 (+, $C_{ar}H$), 128.8 (+, $C^{3''}{}_{ar}H$), 133.9 (q, $C_{q,ar}$), 134.0 (q, $C_{q,ar}$), 148.6 (q, $C^{3'}{}_{ar}O$), 152.2 (q, $C^{4''}{}_{ar}H$), 194.3 (+, CHO) ppm. – MS (FAB), *m/z* (%) = 350 (30) [M^++1], 320 (100) [M^+–CHO], 289 (36) [M^+–CHO–OCH_3], 273 (16), 242 (12), 218 (51) [$C_8H_{12}NO_4S^+$], 201 (88) [$C_8H_9O_4S^+$], 165 (26). – MS (EI, II, 70 eV), *m/z* (%) = 349 (1) [M^+], 320 (100) [M^+–CHO], 244 (14), 217 (18) [$C_8H_{11}NO_4S^+$], 201 (82) [$C_8H_9O_4S^+$], 137 (85) [$C_8H_9O_2^+$], 120 (9) [$C_8H_{10}N^+$], 105 (22), 77 (28) [$C_6H_5^+$] – HRMS (I): calcd.: 349.0984, found: 349.0983. – IR (KBr): 3274.3 (m, ν[NH]), 3085.9 (m, ν[CH_{ar}]), 3060.7 (m, ν[CH_{ar}]), 3007.5 (m, ν[CH_{ar}]), 2937.2 (m, ν[CH_3]), 2839.3 (m, ν[OCH_3]), 1731.2 (m, ν[C=O]), 1589.1 (m, ν[C-C_{ar}]), 1509.2 (s, ν[C-C_{ar}]), 1446.2 (m, δ_{as}[CH_3]), 1324.6 (m, ν_{as}[SO_2]), 1262.5 (s, ν_{as}[C-O-C]), 1182.2 (m, ν_{sy}[SO_2]), 1021.1 (m, ν_{sy}[C-O-C] cm^{-1}. – $[\alpha]_D^{20}$ = +269.2° (c = 0.189, $CHCl_3$).



(–)-2-(1'-Naphthalene)sulfonylamino-2-phenylpropionaldehyde **4g**: The reaction was carried out at room temperature following GP 1, Method A, using **1** (67.1 mg, 0.50 mmol), L-proline (**3**, 57.6 mg, 0.50 mmol), and 1-naphthalenesulfonyl azide (**2g**, 140.0 mg, 0.60 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography over silica with *n*-pentane/diethylether 2:1 delivered colourless solid (61.2 mg, 0.180 mmol) in 36% yield. – mp = 168 – 170 °C. – R_f = 0.34 (*n*-pentane/diethylether 2:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (s, 3 H, CH_3), 6.28 (bs, 1 H, NH), 6.82 (dd, *J* = 8.4, 1.2 Hz, 2 H, $C^{2''}H_{Ph}$), 6.90 (dd, *J* = 8.1, 7.6 Hz, 2 H, $C^{3''}H_{Ph}$),

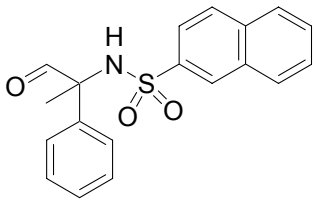
7.04 (dddd, J = 7.3, 7.3, 1.0, 1.0 Hz, 1 H, $C^{4''}H_{Ph}$), 7.13 (dd, J = 7.8, 7.8 Hz, 1 H $C^{3'}H_{Naph}$), 7.58 (ddd, J = 8.1, 7.0, 1.0 Hz, 1 H, $C^{7'}H_{Naph}$), 7.62 (dd, J = 7.5, 1.1 Hz, 1 H, $C^{2'}H_{Naph}$), 7.69 (ddd, J = 8.5, 7.0, 1.5 Hz, 1 H, $C^{8'}H_{Naph}$), 7.85 (d, J = 8.1 Hz, 1 H, $C^{4'}H_{Naph}$), 7.86 (d, J = 8.1 Hz, 1 H, $C^{6'}H_{Naph}$), 8.56 (d, J = 8.6 Hz, 1 H, $C^{9'}H_{Naph}$), 9.04 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (+, CH_3), 66.9 (q, CR_4), 124.1 (+, $C_{ar}H$), 124.2 (+, $C_{ar}H$), 126.7 (+, $C_{ar}H$), 127.4 (+, $C^{2''}{}_{Ph}H$), 127.7 (q, $C^{5'}{}_{Naph}$), 128.5 (+, $C^{3''}{}_{Ph}H$), 128.5 (+, $C_{ar}H$), 128.7 (+, $C_{ar}H$), 129.1 (+, $C_{ar}H$), 129.1 (+, $C_{ar}H$), 133.1 (q, $C^{10'}{}_{Naph}$), 133.7 (+, $C_{ar}H$), 134.0 (q, $C^{1'}{}_{Naph}SO_2$), 136.5 (q, $C^{1''}{}_{Ph}CR_3$), 194.2 (+, CHO) ppm. – MS (EI, II, 70 eV), *m/z* (%) = 310 (100) [M^+–CHO], 191 (18) [$C_{10}H_7O_2S^+$], 127 (75) [$C_{19}H_7^+$], 77 (6) [$C_6H_5^+$]. – HRMS (II): calcd.: 310.0902 (M^+–CHO), found: 310.0902. – IR (KBr): 3330.0 (m, ν[NH]), 3063.1 (w, ν[CH_{ar}]), 3036.4 (w, ν[CH_{ar}]), 2940.6 (w, ν[CH_3]), 1716.6 (m, ν[C=O]), 1508.4 (w, ν[C-C_{ar}]), 1495.0 (w, ν[C-C_{ar}]), 1446.9 (w, δ_{as}[CH_3]), 1376.7 (m, δ_{sy}[CH_3]), 1360.0 (m, ν_{as}[SO_2]), 1128.0 (m, ν_{sy}[SO_2] cm^{-1}. – $[\alpha]_D^{20}$ = –14.2 ° (c = 0.120, $CHCl_3$).

Determination of enantiomeric excess of 4g as Mosher's-Ester:



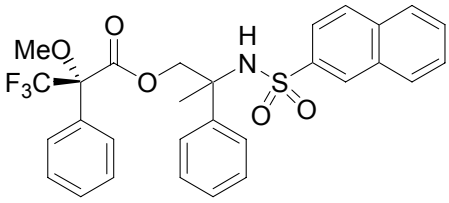
*(*2S*)-2'-(1''-naphthalene)sulfonylamino-2'-phenylpropyl 2-methoxy-2-trifluoromethylphenylacetate*: The compound was synthesised following GP 2.[b] – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52, **1.57** (2 × s, 3 H, $NHCR_2C\underline{H}_3$), 3.42, **3.44** (2 × q, J = 0.9 and 0.8 Hz, 3 H, OCH_3), 4.44, **4.50** (2 × d, J = 11.0 and 11.1 Hz, 1 H, $NHCR_2C\underline{H}HOR$), **4.74**, 4.83 (2 × d, J = 11.1 and 11.0 Hz, 1 H, $NHCR_2CH\underline{H}OR$), **5.40**, 5.40 (2 × bs, 1 H, NH), 6.92 – 7.21 (m, 5 H, CH_{ar}), 7.29 – 7.45 (m, 2 H, CH_{ar}), 7.50 – 7.56 (m, 2 H, CH_{ar}), 7.57 – 7.75 (m, 2 H, CH_{ar}), 7.79, **7.85** (2 × dd, J = 7.4, 1.3 and 7.4, 1.1 Hz, 2 H, CH_{ar}), 7.89 – 8.06 (m, 3 H, CH_{ar}), 8.54, **8.56** (2 × d, J = 6.0 and 7.0 Hz, 1 H, CH_{ar}) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 24.3 (+, $NHCR_2\underline{C}H_3$), 55.5, 55.6 (+, OCH_3), 60.5, 60.6 (q, $NHCR_3$), 72.0, 72.1 (–, CH_2OR), 77.4 (q, $\underline{C}R_3OCH_3$), 124.3, 124.4 (+, $C_{ar}H$), 124.5, 124.5 (+, $C_{ar}H$), 126.0, 126.1 (+, $C_{ar}H$), 126.9 ($C_{ar}H$), 127.4 (+, $C_{ar}H$), 127.9, 128.0 (q, $C_{ar,q}$), 128.2 (+, $C_{ar}H$), 128.4 (+, $C_{ar}H$), 128.5 (+, $C_{ar}H$), 128.6, 128.7 (+, $C_{ar}H$), 129.5 (+, $C_{ar}H$), 129.7 (+, $C_{ar}H$), 129.8, 129.9 (+, $C_{ar}H$), 134.1 (+, $C_{ar}H$), 134.2, 134.2 (q, $C_{ar,q}$), 136.7, 136.8 (q, $C_{ar,q}$), 138.6 (q, $C_{ar,q}$), 139.3, 139.4 (q, $C_{ar,q}$), 166.2 (q, CO_2) ppm. – ^{19}F NMR ($CDCl_3$, 300 MHz): δ = **–71.90**, –71.79 ppm. – The diastereomeric excess was 65 ± 3% *de*.

[b] According to NMR spectra the product mainly consists of unreacted alcohol (ratio alcohol/ester approx. 8:1).



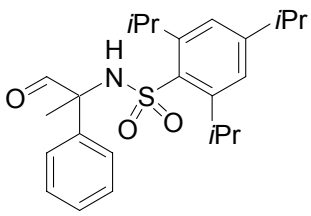
(+)-2-(2'-Naphthalene)sulfonylamino-2-phenylpropionaldehyde **4h**: The reaction was carried out at room temperature following GP 1, Method A, using **1** (67.1 mg, 0.50 mmol), L-proline (**3**, 57.6 mg, 0.50 mmol), and 2-naphthalenesulfonyl azide (**2h**, 140.0 mg, 0.60 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography over silica with *n*-pentane/diethylether 3:1 to 2:1 delivered colourless solid (69.7 mg, 0.205 mmol) in 42% yield. – R_f = 0.29 (*n*-pentane/diethylether 2:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 6.16 (bs, 1 H, NH), 6.95 – 7.02 (m, 3 H, $C^{3''}H_{Ph}/C^{4''}H_{Ph}$), 7.04 – 7.10 (m, 2 H, $C^{2''}H_{Ph}$), 7.52 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1 H, $C^{8'}H_{Naph}$), 7.55 – 7.61 (m, 2 H, $C^{3'}H_{Naph}/C^{5'}H_{Naph}$), 7.68 (d, *J* = 8.1 Hz, 1 H $C^{9'}H_{Naph}$), 7.76 (d, *J* = 8.7 Hz, 1 H, $C^{6'}H_{Naph}$), 7.81 (d, *J* = 9.9 Hz, 1 H, $C^{4'}H_{Naph}$), 7.83 (s, 1 H, $C^{1'}H_{Naph}$), 9.13 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (+, CH_3), 66.9 (q, CR_4), 122.0 (+, $C_{ar}H$), 127.3 (+, $C_{ar}H$), 127.6 (+, $C^{2''}{}_{Ph}H$), 127.8 (+, $C_{ar}H$), 128.1 (+, $C_{ar}H$), 128.6 (+, $C_{ar}H$), 128.7 (+, $C^{3''}{}_{Ph}H$), 128.8 (+, $C_{ar}H$), 129.0 (+, $C_{ar}H$), 129.3 (+, $C_{ar}H$), 131.9 (q, $C_{q,ar}$), 133.4 (q, $C_{q,ar}$), 134.5 (q, $C_{q,ar}$), 138.6 (q, $C_{q,ar}$), 194.3 (+, CHO) ppm. – MS (FAB), *m/z* (%) = 340 (42) [M^++1], 310 (99) [M^+–CHO], 219 (100), 191 (42) [$C_{10}H_7O_2S^+$], 165 (32) [$C_{19}H_7^+$]. – IR (KBr): 3259.8 (m, ν[NH]), 3057.4 (w, ν[CH_{ar}]), 3023.1 (w, ν[CH_{ar}]), 2931.1 (w, ν[CH_3]), 2851.9 (w, ν[CH_3]), 1733.7 (m, ν[C=O]), 1495.3 (w, ν[C-C_{ar}]), 1441.9 (w, δ_{as}[CH_3]), 1386.2 (m, δ_{sy}[CH_3]), 1334.9 (m, ν_{as}[SO_2]), 1152.7 (m, ν_{sy}[SO_2] cm^{-1}. – $[\alpha]_D^{20}$ = +68.5 ° (c = 0.305, $CHCl_3$).

Determination of enantiomeric excess of 4h as Mosher's-Ester:



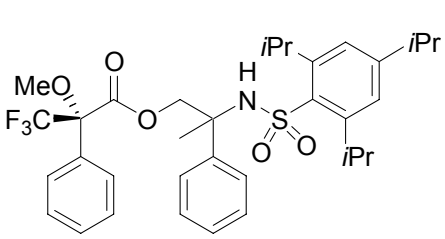
(2S)-2'-(2''-naphthalene)sulfonylamino-2'-phenylpropyl 2-methoxy-2-trifluoromethylphenylacetate: The compound was synthesised following GP 2. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60, **1.63** (2 × s, 3 H, CR_3CH_3), 3.41, **3.43**, (2 × q, *J* = 0.8 and 0.8 Hz, 3 H, OCH_3), 4.46, **4.53** (2 × d, *J* = 11.1 and 11.1 Hz, 1 H, C<u>H</u>HO), **4.77**, 4.82 (2 × d, *J* = 11.1 and 11.1 Hz, 1 H, CH<u>H</u>O), 5.29, 5.30 (2 × bs, 1 H, NH), 6.94 – 7.08 (m, 3 H, CH_{ar}), 7.09 – 7.06 (m, 2 H, CH_{ar}), 7.19 – 7.37 (m, 3 H, CH_{ar}), 7.42 – 7.60 (m, 4 H, CH_{ar}), 7.65 – 7.85 (m, 4 H, CH_{ar}), 8.03, **8.09** (2 × d, *J* = 1.5 Hz, 1 H, CH_{ar}) ppm. – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 29.8, 30.4 (+, $CNR_3\underline{C}H_3$), 55.5, 55.6 (+, OCH_3), 60.4, 60.5 (q, CNR_3), 71.83, 71.86 (–, CH_2OR), 77.4 (q, $\underline{C}R_3OCH_3$), 122.3, 122.3 (+, $C^{3''}{}_{Naph}H$), 126.1, 126.1 (+, $C_{ar}H$), 127.5, 127.5 (+, $C_{ar}H$), 127.6

(+, $C_{ar}H$), 127.9 (+, $C_{ar}H$), 128.0, 128.1 (+, $C_{ar}H$), 128.4, 128.4 (+, $C_{ar}H$), 128.7, 128.7 (+, $C_{ar}H$), 128.9, 128.9 (+, $C_{ar}H$), 129.3, 129.3 (+, $C_{ar}H$), 129.4 (+, $C_{ar}H$), 129.7 (+, $C_{ar}H$), 129.8, 129.9 (+, $C_{ar}H$), 131.3, 131.9 (q, $C_{ar,q}$), 132.0, 132.1 (q, $C_{ar,q}$), 134.7, 134.7 (q, $C_{ar,q}$), 138.9, 139.0 (q, $C_{ar,q}$), 139.7, 139.8 (q, $C_{ar,q}$), 166.2 (q, CO_2) ppm. – ^{19}F NMR ($CDCl_3$, 300 MHz): δ = **–71.89**, –71.78 ppm. – The diastereomeric excess was 64 ± 2% *de*.

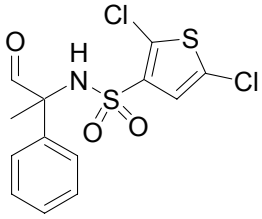


(+)-2-(2',4',6'-Triisopropylbenzene)sulfonylamino-2-phenyl-propionaldehyde **4i**: The compound was synthesised following GP 1, Method A, using **3** (67.1 mg, 0.50 mmol), 2,4,6-triisopropylbenzenesulfonyl azide (**2i**, 185.7 mg, 0.60 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography on silica with *n*-pentane/diethylether 4:1 delivered colourless oil (68.0 mg, 0.164 mmol) in 33% yield. – R_f = 0.22 (*n*-pentane/diethylether 4:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (d, *J* = 6.7 Hz, 6 H, $C^{4'}{}_{ar}CH(C\underline{H}_3)_2$), 1.16 (d, *J* = 6.7 Hz, 12 H, $C^{2'}{}_{ar}CH(C\underline{H}_3)_2$), 1.76 (s, 3 H, $CR_3C\underline{H}_3$), 2.79 (sept, *J* = 6.9 Hz, 1 H, $C^{4'}{}_{ar}C\underline{H}(CH_3)_2$), 3.85 (sept, *J* = 6.7 Hz, 2 H, $C^{2'}{}_{ar}C\underline{H}(CH_3)_2$), 5.89 (bs, 1 H, NH), 6.97 (s, 2 H, $C^{3'}H_{ar}$), 7.03 – 7.36 (m, 5 H, CH_{Ph}), 9.06 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (+, $CR_3\underline{C}H_3$), 23.7, 23.8 (+, $C^{4'}{}_{ar}CH(\underline{C}H_3)_2$), 24.7, 24.9 (+, $C^{2'}{}_{ar}CH(\underline{C}H_3)_2$), 29.8 (+, $C^{2'}{}_{ar}\underline{C}H(CH_3)_2$), 34.3 (+, $C^{4'}{}_{ar}\underline{C}H(CH_3)_2$), 67.7 (q, CR_4), 123.6 (+, $C^{3'}{}_{ar}H$), 127.3 (+, $C^{2''}{}_{Ph}H$), 128.7 (+, $C^{4''}{}_{Ph}H$), 128.9 (+, $C^{3''}{}_{Ph}H$), 135.2 (q, $\underline{C^{1''}}{}_{Ph}CR_4$), 136.1 (q, $C^{1'}{}_{ar}SO_2$), 148.9 (q, $\underline{C^{2'}}{}_{ar}CHR_2$), 152.6 (q, $\underline{C^{4'}}{}_{ar}CHR_2$), 194.7 (+, CHO) ppm. – MS (FAB), *m/z* (%) = 416 (14) [M^++1], 398 (20), 386 (67) [M^+–CHO], 284 (14), 267 (100) [$C_{15}H_{23}O_2S^+$], 251 (10), 203 (20) [$C_{15}H_{23}^+$], 175 (22). – MS (EI, II, 70 eV), *m/z* (%) = 386 (100) [M^+–CHO], 267 (86) [$C_{15}H_{23}O_2S^+$], 251 (27) [$C_{15}H_{23}OS^+$], 218 (22), 203 (27) [$C_{15}H_{23}^+$], 187 (54) [$C_{14}H_{19}^+$], 159 (18) [$C_{12}H_{15}^+$], 120 (27) [$C_8H_{10}N^+$], 105 (24), 91 (13) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$]. – HRMS (I): calcd.: 386.2154, found: 386.2148. – $C_{15}H_{13}N_3O_7S$ (379.35 g/mol), calcd.: C 69.36, H 8.00, N 3.37, S 7.72; found: C 69.14, H 7.81, N 3.13, S 7.03. – IR (KBr): 3295.7 (m, ν[NH]), 3060.1 (w, ν[CH_{ar}]), 2960.9 (m, ν[CH_3]), 2870.7 (m, ν[CH]), 1726.1 (m, ν[C=O]), 1600.2 (m, ν[C-C_{ar}]), 1494.4 (m, ν[C-C_{ar}]), 1462.2 (m, δ_{as}[CH_3]), 1383.9 (m, δ_{sy}[CH_3]), 1363.6 (m, δ_{sy}[CH_3]), 1322.7 (m, ν_{as}[SO_2]), 1150.9 (m, ν_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +22.1° (c = 1.510, $CHCl_3$).

Determination of enantiomeric excess of 4i as Mosher's-Ester:

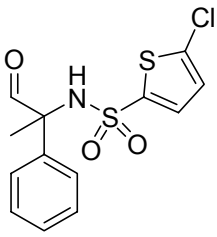


*(*2S*)-2'-(2'',4'',6''-triisopropylbenzene)sulfonylamino-2'-phenylpropyl 2-methoxy-2-trifluoromethylphenyl-acetate*: The compound was synthesised following GP 2. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 – 1.32 (m, 18 H, $CH(C\underline{H}_3)_2$), 1.85 (s, 1 H, $NHCR_2C\underline{H}_3$), 2.83 (qq, *J* = 6.5, 6.4 Hz, 1 H, $C^{4''}{}_{ar}C\underline{H}(CH_3)_2$), 3.38 – 3.43 (m, 3 H, OCH_3), 4.02 (qq, *J* = 6.7, 6.7 Hz, 2 H, $C^{2''}{}_{ar}CH(C\underline{H}_3)_2$), 4.46, 4.48 (2 × d, *J* = 11.0 and 11.0 Hz, 1 H, C<u>H</u>HOR), 4.63, 4.70 (2 × d, *J* = 11.0 and 11.0 Hz, 1 H, CH<u>H</u>OR), 5.23 (bs, 1 H, NH), 7.03 – 7.46 (m, 12 H, CH_{ar}) ppm. – ^{19}F NMR ($CDCl_3$, 300 MHz): δ = **–71.85**, –71.81 ppm. – The diastereomeric excess was 49% *de*.

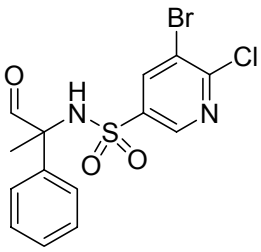


(*S*)-2-*(2',5'-Dichlorothien-3'-yl)sulfonylamino-2-phenylpropion-aldehyde* **4j**: GP 1, Method A: The product was prepared using **1** (134.2 mg, 1.00 mmol), 2,5-dichlorothien-3-ylsulfonyl azide (**2j**, 309.7 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in 10 ml of ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered a colourless solid (98.3 mg, 0.27 mmol) in 27% yield and 47 ± 4% *ee*. – GP 1, Method B: The product was prepared using **1** (134.2 mg, 1.00 mmol), 2,5-dichlorothien-3-ylsulfonyl chloride (301.8 mg, 1.20 mmol), sodium azide (91.0 mg, 1.40 mmol), and L-proline (115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered a colourless solid (138.4 mg, 0.38 mmol) in 38% yield and 47 ± 4% *ee*. – mp = 134 °C. – R_f = 0.57 (*n*-pentane/Et_2O 2:1). – HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/isopropanol 64:36, 0.85 ml/min): R_t(min) = 10.2 min, R_t(maj) = 12.1 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, CH_3), 6.25 (s, 1 H, thiophen-CH_{ar}), 6.50 (bs, 1 H, NH), 7.13 (d, *J* = 7.9 Hz, 2 H, CH_{Ph}), 7.25 – 7.33 (m, *J* = 7.9 Hz, 3 H, CH_{Ph}), 9.13 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (+, CH_3), 66.5 (q, CR_4), 126.2 (+, $C_{ar}H$), 126.4 (+, $C_{ar}H$), 127.6 (+,$C^{4''}{}_{Ph}H$), 128.4 (+, $C_{ar}H$), 128.8 (+, $C_{ar}H$), 129.3 (q, $\underline{C}_{ar}$), 132.1 (q, $C_{ar}SO_2$), 138.1 (q, $\underline{C^{1''}}_{Ph}CR_3$), 193.5 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 334 (100)/336 (88)/338 (16) [M^+–CHO], 214(39)/216 (19)/218 (5) [$C_4HS_2O_2Cl_2^+$], 150 (15) [M^+–$C_4HS_2O_2Cl_2$], 104 (17) [$C_8H_8^+$], 91 (1) [$C_7H_7^+$], 77 (8) [$C_6H_5^+$]. – HRMS (I): calcd.: 362.9557 [M^+], found: 362.9561. – $C_{13}H_{11}NCl_2O_3S_2$ (364.26 g/mol), calcd.: C 42.87, H 3.04, N 3.85, S 17.60, found: C 43.15, H 3.46, N 3.94,

S 17.43. – IR (KBr): 3267.5 (m, υ[NH]), 3063.5 (w, υ[CH_{ar}]), 3028.2 (w, υ[CH_{ar}]), 2984.6 (w, υ[CH_{ar}]), 2942.1 (w, υ[CH_3]), 2865.4 (w, υ[CH_3]), 2521.2 (w, comb[CHO]), 1722.4 (m, δ[NH]), 1720.3 (m, υ(C=O)), 1599.3 (w, υ[C–C_{ar}]), 1494.1 (w, υ[C–C_{ar}]), 1445.8 (m, δ_{as}[CH_3]), 1367.4 (m, δ_{sy}[CH_3]), 1337.5 (m, υ_{as}[SO_2]), 1173.6 (m, υ_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +12.0° (c = 0.510, $CHCl_3$).

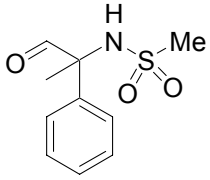


2-(5'-Chlorothien-2'-yl)sulfonylamino-2-phenylpropionaldehyde **4k**: GP 1, Method A: The product was prepared using **1** (134.2 mg, 1.00 mmol), 5-chlorothien-2-ylsulfonyl azide (**2k**, 268.4 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered a colourless solid (119.0 mg, 0.36 mmol) in 36% yield and 54 ± 2% *ee*. – GP 1, Method B: The product was prepared using **1** (134.2 mg, 1.00 mmol), 5-chlorothien-2-ylsulfonyl chloride (260.5 mg, 1.20 mmol), sodium azide (91.0 mg, 1.40 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered a colourless solid (115.3 mg, 0.35 mmol) in 35% yield and 54 ± 2% *ee*. – mp = 123 °C. – R_f = 0.44 (*n*-pentane/Et_2O 2:1). – HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/isopropanol 64 :36, 0.85 ml/min): R_t(min) = 11.0 min, R_t(maj) = 14.0 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, CH_3), 6.19 (bs, 1 H, NH), 6.50 (d, *J* = 4.0 Hz, 1 H, thiophen-CH_{ar}), 6.66 (d, *J* = 4.0 Hz, 1 H, thiophen-CH_{ar}), 7.08 (dd, *J* = 8.2, 1.5 Hz, 2 H, CH_{Ph}), 7.17 – 7.23 (m, *J* = 8.2 Hz, 3 H, CH_{Ph}), 9.03 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8 (+, CH_3), 66.9 (q, CR_4), 126.1 (+, $C_{ar}H$), 127.7 (+, $C_{ar}H$), 128.9 (+, $C^{4''}{}_{Ph}H$), 129.0 (+, $C_{ar}H$), 131.2 (+, $C_{ar}H$), 133.2 (q, $\underline{C^{1''}}_{Ph}CR_3$), 136.9 (q, $C_{ar}SO_2$), 140.9 (q, $C_{ar}Cl$), 193.8 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 300 (100)/302 (41) [M^+–CHO], 180 (66)/182 (22) [$C_4H_2S_2O_2Cl^+$], 133 (10) [M^+–$C_4H_3NS_2O_2Cl$], 104 (13) [$C_8H_8^+$], 91 (1) [$C_7H_7^+$], 77 (7) [$C_6H_5^+$]. – HRMS (I): calcd.: 328.9947 [M^+], found: 328.9940. – $C_{13}H_{12}NClO_3S_2$ (329.82 g/mol), calcd.: C 47.34, H 3.67, N 4.25, S 19.44, found: C 47.55, H 3.79, N 4.16, S 19.64. – IR (KBr): 3255.8 (m, υ[NH]), 3061.1 (w, υ[CH_{ar}]), 2984.0 (w, υ[CH_{ar}]), 2942.4 (m, υ[CH_3]), 2859.4 (w, υ[CH_3]), 2720.7 (w, comb[CHO]), 1738.5 (m, δ[NH]), 1729.3 (m, υ(C=O)), 1599.9 (w, υ[C–C_{ar}]), 1494.2 (w, υ[C–C_{ar}]), 1446.6 (m, δ_{as}[CH_3]), 1379.4 (m, δ_{sy}[CH_3]), 1333.5 (m, υ_{as}[SO_2]), 1154.5 (m, υ_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +26.3° (c = 0.505, $CHCl_3$).



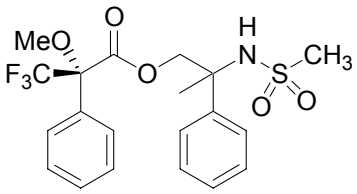
2-(2'-Chloro-3'-bromopyridin-5'-yl)sulfonylamino-2-phenylpropion-aldehyde **4l**: GP 1, Method A: The product was prepared using **1** (134.2 mg, 1.00 mmol), 2-chloro-3-bromopyridin-5-ylsulfonyl azide (**2l**, 357.0 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered a colourless solid (97.1 mg, 0.24 mmol) in 24% yield and 46 ± 8% *ee*. – GP 1, Method B: The product was prepared using **1** (134.2 mg, 1.00 mmol), 2-chloro-3-bromopyridin-5-ylsulfonyl chloride (349.1 mg, 1.20 mmol), sodium azide (91.0 mg, 1.40 mmol) and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 2:1 delivered a colourless solid (125.0 mg, 0.31 mmol) in 31% yield and 60 ± 7% *ee*. – mp = 148 °C. – R_f = 0.28 (*n*-pentane/Et_2O 2:1). – HPLC (Chiralpak AS, 0.8% diethylamine in *n*-heptane/isopropanol 64:36, 0.85 ml/min): R_t(min) = 10.5 min, R_t(maj) = 12.8 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 3 H, CR_3CH_3), 6.43 (bs, 1 H, NH), 7.08 (d, *J* = 7.5 Hz, 2 H, CH_{Ph}), 7.24 – 7.38 (m, 3 H, CH_{Ph}), 7.57 (s, 1 H, CH_{Pyr}), 8.35 (s, 1 H, CH_{Pyr}), 9.14 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (+, $CR_3\underline{C}H_3$), 66.7 (q, CR_4), 120.1 (q, $C^{5'}{}_{Pyr}SO_2$), 128.2 (+, $C_{ar}H$), 129.1 (+, $C_{ar}H$), 130.0 (+, $C^{4''}{}_{Ph}H$), 131.8 (q, $\underline{C}^{1''}{}_{Ph}CR_3$), 137.8 (q, $C_{ar}SO_2$), 140.0 (+, $C_{Pyr}H$), 145.8 (+, $C_{Pyr}H$), 153.9 (q, $C^{5'}{}_{Pyr}SO_2$), 193.5 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 372 (74)/374 (100)/376 (27) [M^+–CHO], 253 (7)/255 (9)/257 (2) [$C_5H_2BrClNSO_2^+$], 189 (21)/191 (28)/193 (6) [$C_5H_2BrClN^+$], 104 (41) [$C_8H_8^+$], 91 (2) [$C_7H_7^+$], 77 (20) [$C_6H_5^+$]. – HRMS (I): calcd.: 401.9441 [M^+], found: 401.9470. – IR (KBr): 3252.7 (m, υ[NH]), 3066.4 (w, υ[CH_{ar}]), 2847.7 (w, υ[CH_3]), 2731.3 (w, comb[CHO]), 1737.5 (m, δ[NH]), 1732.0 (m, υ(C=O)), 1619.0 (w, υ[C–C_{ar}]), 1582.1 (w, υ[C–C_{ar}]), 1493.7 (w, υ[C–C_{ar}]), 1445.4 (w, δ_{as}[CH_3]), 1363.3 (m, δ_{sy}[CH_3]), 1343.1 (m, υ_{as}[SO_2]), 1147.1 (m, υ_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +28.4° (c = 0.575, $CHCl_3$).

(+)-2-Methanesulfonylamino-2-phenylpropionaldehyde **4m**:

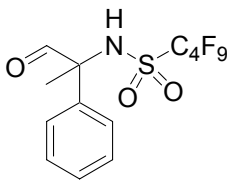


The reaction was carried out following GP 1, Method B, using **1** (134.2 mg, 1.00 mmol), L-proline (**3**, 115.1 mg, 1.00 mmol), methanesulfonyl chloride (137.5 mg, 1.20 mmol), and sodium azide (91.0 mg, 1.40 mmol) within 1 d. Flash chromatography over silica with *n*-pentane/diethylether 1:3 delivered a colourless solid (74.4 mg, 0.327 mmol) in 33% yield. – mp = 85 – 88 °C. – R_f = 0.12 (*n*-pentane/diethylether 1:2). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, CR_3CH_3), 2.51 (s, 3 H, SO_2CH_3), 5.76 (bs, 1 H, NH), 7.28 – 7.53 (m, 5 H, CH_{ar}), 9.22 (s, 1 H, CHO) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.2 ($CR_3\underline{C}H_3$), 47.9 (SO_2CH_3), 66.9 (CR_4), 126.9 ($C^{4'}{}_{ar}H$), 127.8 ($C^{2'}{}_{ar}H$), 129.5 ($C^{3'}{}_{ar}H$), 135.0 ($\underline{C}^{1'}{}_{ar}CR_3$), 194.4 (CHO) ppm. – MS (EI, II, 70 eV), *m/z* (%) = 198 (100) [M^+–CHO], 148 (20) [M^+–SO_2CH_3], 120 (59) [M^+–CO–SO_2CH_3], 104 (20) [M^+–CHO–SO_2CH_3–CH_3], 77 (16) [$C_6H_5^+$]. – HRMS (KA): calcd.: 198.0589 (M^+–CHO), found: 198.0587. – IR (KBr): 3259.6 (m, ν[NH]), 3059.5 (w, ν[CH_{ar}]), 3018.5 (w, ν[CH_{ar}]), 2940.9 (w, ν[CH_3]), 2844.8 (w, ν[CH_3]), 1731.7 (m, ν[C=O]), 1494.6 (w, ν[C-C_{ar}]), 1447.0 (w, δ_{as}[CH_3]), 1384.6 (w, δ_{sy}[CH_3]), 1317.5 (m, ν_{as}[SO_2]), 1076.7 (m, ν_{sy}[SO_2] cm^{-1}. – $[\alpha]_D^{20}$ = +45.6° (c = 0.620, $CHCl_3$).

Determination of enantiomeric excess of 4m as Mosher's-Ester:

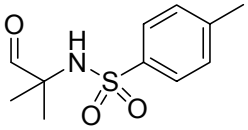


*(*2S*)-2'-methanesulfonylamino-2'-phenylpropyl 2-methoxy-2-trifluoromethylphenylacetate*: The compound was synthesised following GP 2. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74, **1.81** (s, 3 H, CR_3CH_3), 2.66, **2.73** (2 × s, 3 H, SO_2CH_3), 3.44, **3.47**, (2 × q, *J* = 0.8 and 0.8 Hz, 3 H, OCH_3), **4.58**, 4.62 (2 × d, *J* = 11.0 and 11.0 Hz, 1 H, C<u>H</u>HO), 4.73, **4.75** (2 × bs, 1 H, NH), **4.78**, 4.80 (2 × d, *J* = 11.3 and 11.1 Hz, 1 H, CH<u>H</u>O), 7.29 – 7.49 (m, 10 H, CH_{ar}) ppm. – ^{19}F NMR ($CDCl_3$, 300 MHz): δ = **–71.83**, –71.80 ppm. – The diastereomeric excess was 71% *de*.

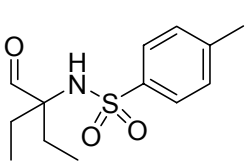


(+)-2-Perfluorobutylsulfonylamino-2-phenylpropionaldehyde **4n**: The reaction was carried out following GP 1, Method B, using **1** (134.2 mg, 1.00 mmol), L-proline (**3**, 115.1 mg, 1.00 mmol), perfluorobutanesulfonyl fluoride (362.5 mg, 1.20 mmol), and sodium azide (91.0 mg, 1.40 mmol) at room temperature within 1 h. Flash chromatography over silica with cyclohexane/ethyl acetate 5:1 delivered a colourless solid (104.9 mg, 0.243 mmol) in 24% yield and 29 ± 1% *ee*.

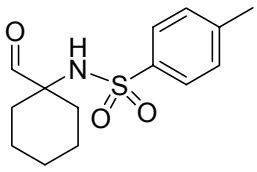
– When carried out at 0 °C the reaction delivered **4n** (61.1 mg, 0.142 mmol) in 14% yield and 32 ± 1% *ee* within 8 h. – mp = 68 – 74 °C. – R_f = 0.21 (cyclohexane/ethyl acetate 5:1). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 90:10, 0.7 ml/min): R_t(min) = 8.1 min, R_t(maj) = 10.5 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (s, 3 H, CR_3CH_3), 6.58 (bs, 1 H, NH), 7.35 – 7.50 (m, 5 H, CH_{ar}), 9.14 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5 ($CR_3\underline{C}H_3$), 68.7 (CR_4), 127.2 ($C^{2'}{}_{ar}H$), 129.6 ($C^{3'}{}_{ar}H$), 129.7 ($C^{4'}{}_{ar}H$), 135.0 ($\underline{C}^{1'}{}_{ar}CR_3$), 192.8 (CHO) ppm. – ^{19}F NMR (300 MHz, $CDCl_3$): δ = –126.5 to –126.3 (m, 2 F, $SO_2CF_2C\underline{F}_2$), –121.6 to –121.3 (m, 2 F, $C\underline{F}_2CF_3$), –112.4 (t, *J* = 13.5 Hz, 2 F, SO_2CF_2), –81.3 (t, *J* = 9.5 Hz, 3 F, CF_3) ppm. – MS (EI, II, 70 eV), *m/z* (%) = 402 (100) [M^+–CHO], 260 (3), 133 (5) [M^+–$NHSO_2C_4F_9$], 119 (11) [M^+–CHO–$SO_2C_4F_9$], 104 (17) [M^+–CHO–$NHSO_2C_4F_9$], 77 (6) [$C_6H_5^+$]. – HRMS (II): calcd.: 402.0210 (M^+–CHO), found: 402.0217. – $C_{13}H_{10}F_9NO_3S$ (431.28 g/mol), calcd.: C 36.20, H 2.34, N 3.25; found: C 36.70, H 2.85, N 3.02. – IR (KBr): 3252.3 (m, ν[NH]), 3065.1 (w, ν[CH_{ar}]), 2846.2 (w, ν[CH_3]), 1735.9 (m, ν[C=O]), 1494.0 (w, ν[C-C_{ar}]), 1448.6 (w, δ_{as}[CH_3]), 1387.1 (m, δ_{sy}[CH_3]), 1358.5 (m, ν_{as}[SO_2]), 1139.5 (m, ν_{sy}[SO_2] cm^{-1}. – $[\alpha]_D^{20}$ = +58.6 ° (c = 0.370, $CHCl_3$).



2-Methyl-2-(4'-toluene)sulfonylaminopropionaldehyde **28**: The compound was prepared following GP 1, Method A, using 2-methylpropionaldehyde (**14**, 72.1 mg, 1.00 mmol), 4-toluenesulfonyl azide (**2a**, 236.7 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 1:1 delivered a colourless oil (101.2 mg, 0.42 mmol) in 42% yield. – R_f = 0.27 (*n*-pentane/Et_2O 1:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (s, 6 H, $C\underline{H}_3CR_2C\underline{H}_3$), 2.35 (s, 3 H, Ts-$CH_3$), 5.44 (bs, 1 H, NH), 7.22 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 7.70 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 9.37 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (+, Ts-CH_3), 22.5 (+, 2 CH_3), 62.4 (q, CR_4), 126.8 (+, $C_{ar}H$), 129.7 (+, $C_{ar}H$), 139.6 (q, $C_{ar}SO_2$), 143.5 (q, $\underline{C}_{ar}CH_3$), 199.5 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 212 (100) [M^+–CHO], 155 (65) [$C_7H_7SO_2^+$], 91 (50) [$C_7H_7^+$]. – HRMS (FAB): calcd.: 242.0850 [M^+], found: 242.0857. – $C_{11}H_{16}NO_3S$ (241.30 g/mol), calcd.: C 54.75, H 6.27, N 5.80, S 13.29, found: C 54.65, H 6.42, N 5.63, S 13.41. – IR (KBr): 3246.4 (m, υ[NH]), 3064.1 (vw, υ[CH_{ar}]), 2990.0 (w, υ[CH_{ar}]), 2935.8 (w, υ[CH_3]), 2817.2 (m, υ[CH_3]), 2712.6 (w, comb[CHO]), 1740.0 (m, υ(C=O)), 1738.9 (m, δ[NH]), 1598.0 (w, υ[C–C_{ar}]), 1496.6 (w, υ[C–C_{ar}]), 1433.1 (m, δ_{as}[CH_3]), 1388.7 (m, δ_{sy}[CH_3]), 1324.0 (m, υ_{as}[SO_2]), 1146.1 (m, υ_{sy}[SO_2]) cm^{-1}.

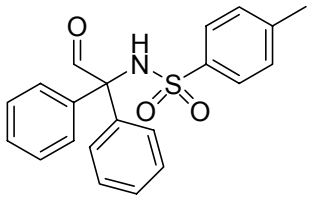


2-Ethyl-2-(4'-toluene)sulfonylaminobutyraldehyde **29**: The compound was prepared following GP 1, Method A, using 2-ethylbutyraldehyde (**15**, 100.2 mg, 1.00 mmol), 4-toluenesulfonyl azide (**2a**, 236.7 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 1:1 delivered a colourless oil (126.6 mg, 0.47 mmol) in 47% yield. – R_f = 0.63 (*n*-pentane/Et_2O 1:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.51 (t, *J* = 7.5 Hz, 6 H, $CR_2(CH_2C\underline{H}_3)_2$) , 1.62 (qd, *J* = 14.9, 7.5 Hz, 2 H, CH_2), 1.96 (qd, *J* = 14.9, 7.5 Hz, 2 H, CH_2), 2.35 (s, 3 H, Ts-CH_3), 5.26 (bs, 1 H, NH), 7.21 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 7.71 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 9.14 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.5 (+,$CR_2(CH_2\underline{C}H_3)_2$), 21.5 (+, Ts-$CH_3$), 26.2 (-, $CR_2\underline{C}H_2CH_3)_2$), 65.9 (q, CR_4), 126.8 (+, $C_{ar}H$), 129.6 (+, $C_{ar}H$), 139.7 (q, $C_{ar}SO_2$), 143.3 (q, $\underline{C}_{Ts}CH_3$), 199.6 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 240 (100) [M^+–CHO], 155 (52) [$C_7H_7SO_2^+$], 91 (71) [$C_7H_7^+$]. – HRMS (I): calcd.: 240.1058 [M^+–CHO], found: 240.1054. – $C_{13}H_{19}NO_3S$ (269.36 g/mol), calcd.: C 57.97, H 7.11, N 5.20, S 11.90, found: C 57.99, H 7.15, N 5.18, S 11.99. – IR (KBr): 3308.0 (m, υ[NH]), 2978.5 (w, υ[CH_{ar}]), 2952.4 (w, υ[CH_3]), 2882.1 (w, υ[CH_3]), 2741.6 (w, comb[CHO]), 1728.3 (m, δ[NH]), 1724.7 (m, υ[C=O]), 1598.7 (w, υ[C–C_{ar}]), 1494.9 (w, υ[C–C_{ar}]), 1456.6 (m, δ_{as}[CH_3]), 1426.1 (m, δ_{as}[CH_3]), 1380.9 (m, δ_{sy}[CH_3]), 1334.2 (m, υ_{as}[SO_2]), 1157.2 (m, υ_{sy}[SO_2]) cm^{-1}.



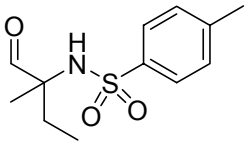
2-(4'-Toluene)sulfonylaminocyclohexanecarbaldehyde **30**: The compound was prepared following GP 1, Method A, using cyclohexanecarbaldehyde (**16**, 112.2 mg, 1.00 mmol), 4-toluenesulfonyl azide (**2a**, 236.7 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 1:1 delivered a colourless solid (146.2 mg, 0.52 mmol) in 52% yield. – mp = 93 °C. – R_f = 0.34 (*n*-pentane/Et_2O 1:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (m, 3 H, cyclohexyl), 1.36 (m, 3 H, cyclohexyl), 1.58 (m, 4 H, cyclohexyl), 2.36 (s, 3 H, Ts-CH_3), 5.22 (bs, 1 H, NH), 7.23 (d, *J* = 8.0 Hz, 2 H, CH_{Ts}), 7.72 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 9.53 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (–, 2 CH_2), 21.6 (+, Ts-CH_3), 24.7 (–, CH_2), 30.2 (–, 2 CH_2), 65.2 (q, CR_4), 127.0 (+, $C_{ar}H$), 129.7 (+, $C_{ar}H$), 139.1 (q, $C_{Ts}SO_2$), 143.7 (q, $\underline{C}_{Ts}CH_3$), 201.0 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 252 (100) [M^+–CHO], 155 (19)

[$C_7H_7SO_2^+$], 91 (24) [$C_7H_7^+$], 43 (9). – HRMS (I): calcd.: 252.1058 [M^+–CHO], found: 252.1054. – $C_{14}H_{19}NO_3S$ (281.37 g/mol), calcd.: C 59.76, H 6.81, N 4.98, S 11.40, found: C 59.80, H 6.76, N 5.01, S 11.45. – IR (KBr): 3297.0 (m, υ[NH]), 3061.7 (w, υ[CH_{ar}]), 3041.3 (w, υ[CH_{ar}]), 2945.9 (m, υ[CH_3]), 2867.8 (w, υ[CH_3]), 2731.8 (vw, comb[CHO]), 1724.4 (m, δ[NH], υ[C=O]), 1596.9 (w, υ[C–C_{ar}]), 1495.1 (w, υ[C–C_{ar}]), 1471.6 (w, δ_{as}[CH_3]), 1446.7 (m, δ_{as}[CH_3]), 1388.5 (m, δ_{sy}[CH_3]), 1328.2 (m, υ_{as}[SO_2]), 1154.4 (m, υ_{sy}[SO_2]) cm^{-1}.

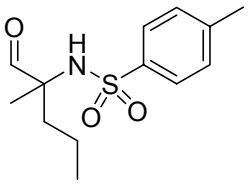


2,2-Diphenyl-2-(4'-toluene)sulfonylaminoacetaldehyde **31**:

The compound was prepared following GP 1, Method A, using 2,2-diphenylacetaldehyde (**17**, 196.2 mg, 1.00 mmol), 4-toluenesulfonyl azide (**2a**, 236.7 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml) within 2 d reaction time. Flash chromatography on silica with *n*-pentane/diethylether 1:1 delivered a colourless solid (131.4 mg, 0.36 mmol) in 36% yield. – mp = 118 °C. – R_f = 0.48 (*n*-pentane/Et_2O 2:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, Ts-CH_3), 6.32 (bs, 1 H, NH), 6.82 (d, *J* = 8.0 Hz, 2 H, CH_{Ts}), 6.92 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 7.19 – 7.24 (m, 10 H, CH_{Ph}), 9.29 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (+, Ts-CH_3), 74.2 (q, CR_4), 126.2 (+, $C^{4''}{}_{ar}H$), 128.6 (+, $C_{ar}H$), 128.7 (+, $C_{ar}H$), 128.9 (+, $C_{ar}H$), 129.7 (+, $C_{ar}H$), 134.3 (q, $\underline{C}^{1''}{}_{Ph}CR_3$), 139.0 (q, $C_{ar}SO_2$), 142.1 (q, $\underline{C}_{Ts}CH_3$), 190.7 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 336 (97) [M^+–CHO], 180 (12), 155 (22) [$C_7H_7SO_2^+$], 104 (11) [$C_8H_8^+$], 91 (53) [$C_7H_7^+$], 77 (9) [$C_6H_5^+$], 58 (23), 43 (100). – HRMS (I): calcd.: 336.1058 [M^+–CHO], found: 336.1056. – $C_{21}H_{19}NO_3S$ (365.45 g/mol), calcd.: C 69.02, H 5.24, N 3.83, S 8.77, found: C 69.08, H 5.19, N 3.88, S 8.81. – IR (KBr): 3299.1 (m, υ[NH]), 3057.7 (w, υ[CH_{ar}]), 3034.8 (w, υ[CH_{ar}]), 2920.6 (w, υ[CH_3]), 2895.5 (w, υ[CH_3]), 2732.2 (vw, comb[CHO]), 1733.9 (m, δ[NH]), 1725.7 (m, υ[C=O]), 1598.1 (w, υ[C–C_{ar}]), 1492.7 (m, υ[C–C_{ar}]), 1447.6 (m, δ_{as}[CH_3]), 1333.6 (m, υ_{as}[SO_2]), 1164.2 (m, υ_{sy}[SO_2]) cm^{-1}.

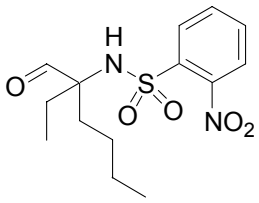


2-Methyl-2-(4'-toluene)sulfonylaminobutyraldehyde **32**: The compound was prepared following GP 1, Method A, using 2-methylbutyraldehyde (**18**, 86.1 mg, 1.00 mmol), 4-toluenesulfonyl azide (**2a**, 236.7 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 1:1 delivered a colourless oil (125.2 mg, 0.49 mmol) in 49% yield and 5% *ee*. – R_f = 0.47 (*n*-pentane/Et_2O 1:1). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 98:2, 1.0 ml/min): R_t(min) = 42.9 min, R_t(maj) = 47.9 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.69 (t, *J* = 7.5 Hz, 3 H, $CH_2C\underline{H}_3$), 1.18 (s, 3 H, CR_3CH_3), 1.61 (q, *J* = 7.4 Hz, 1 H, $CR_3C\underline{H}HCH_3$), 1.83 (q, *J* = 7.4 Hz, 1 H, $CR_3CH\underline{H}CH_3$), 2.35 (s, 3 H, Ts-CH_3), 5.37 (bs, 1 H, NH), 7.22 (d, *J* = 8.0 Hz, 2 H, CH_{Ts}), 7.70 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 9.26 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.5 (+, $CH_2\underline{C}H_3$), 19.6 (+, $CR_3\underline{C}H_3$), 21.5 (+, Ts-CH_3), 28.8 (–, CH_2), 65.9 (q, CR_4), 126.8 (+, $C_{ar}H$), 129.7 (+, $C_{ar}H$), 139.7 (q, $C_{ar}SO_2$), 143.4 (q, $\underline{C}_{ar}CH_3$), 199.7 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 226 (100) [M^+–CHO], 155 (65) [$C_7H_7SO_2^+$], 91 (95) [$C_7H_7^+$]. – HRMS (I): calcd.: 226.0902 [M^+–CHO], found: 226.0899. – $C_{12}H_{17}NO_3S$ (255.33 g/mol), calcd.: C 56.45, H 6.71, N 5.49, S 12.56, found: C 56.54, H 6.83, N 5.37, S 12.68. – IR (KBr): 3242.0 (s, υ[NH]), 3065.6 (vw, υ[CH_{ar}]), 3030.1 (vw, υ[CH_{ar}]), 2982.9 (m, υ[CH_3]), 2888.4 (w, υ[CH_3]), 2735.1 (w, comb[CHO]), 1715.6 (s, υ[C=O]), 1704.9 (w, δ[NH]), 1597.4 (w, υ[C–C_{ar}]), 1497.0 (w, υ[C–C_{ar}]), 1434.9 (m, δ_{as}[CH_3]), 1388.7 (m, δ_{sy}[CH_3]), 1336.1 (m, υ_{as}[SO_2]), 1165.9 (m, υ_{sy}[SO_2]) cm^{-1}.



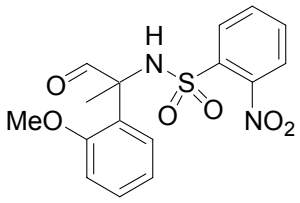
2-Methyl-2-(4'-toluene)sulfonylaminopentanal **33**: The compound was prepared following GP 1, Method A, using 2-methylpentanal (**19**, 100.2 mg, 1.00 mmol), 4-toluenesulfonyl azide (**2a**, 236.7 mg, 1.20 mmol), and L-proline (**3**, 115.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with *n*-pentane/diethylether 1:1 delivered a colourless oil (137.1 mg, 0.51 mmol) in 51% yield and 12% *ee*. – R_f = 0.55 (*n*-pentane/Et_2O 1:1). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 98:2, 1.0 ml/min): R_t(min) = 32.5 min, R_t(maj) = 37.3 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.70 (t, *J* = 7.3 Hz, 3 H, $CH_2C\underline{H}_3$), 0.94 (m, 1 H, CH_2), 1.17 (m, 1 H, CH_2), 1.18 (s, 3 H, CR_3CH_3), 1.50 (ddd, *J* = 14.3, 12.3, 4.6 Hz, 1 H, CH_2), 1.74 (ddd, *J* = 14.3, 12.3, 4.6 Hz , 1 H, CH_2), 2.35 (s, 3 H, Ts-CH_3), 5.43 (bs, 1 H, NH), 7.22 (d, *J* = 7.9 Hz, 2 H, CH_{Ts}), 7.69 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 9.28 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (+, $CH_2\underline{C}H_3$), 16.6 (–, CH_2), 20.1 (+, $CR_3\underline{C}H_3$), 21.5

(+, Ts-CH_3), 37.8 (–, CH_2), 65.6 (q, CR_4), 126.8 (+, $C_{ar}H$), 129.6 (+, $C_{ar}H$), 139.7 (q, $C_{ar}SO_2$), 143.1 (q, $\underline{C}_{ar}CH_3$), 199.6 (+, CHO) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 240 (100) [M^+–CHO], 155 (48) [$C_7H_7SO_2^+$], 91 (65) [$C_7H_7^+$]. – HRMS (I): calcd.: 240.1058 [M^+–CHO], found: 240.1053. – $C_{13}H_{19}NO_3S$ (269.36 g/mol), calcd.: C 57.97, H 7.11, N 5.20, S 11.90, found: C 58.02, H 7.13, N 5.15, S 11.97. – IR (KBr): 3263.2 (s, υ[NH]), 3062.2 (vw, υ[CH_{ar}]), 3028.4 (vw, υ[CH_{ar}]), 2984.1 (m, υ[CH_3]), 2885.7 (w, υ[CH_3]), 2729.1 (w, comb[CHO]), 1727.4 (s, υ[C=O]), 1721.9 (w, δ[NH]), 1599.2 (w, υ[C–C_{ar}]), 1492.7 (w, υ[C–C_{ar}]), 1428.4 (m, δ_{as}[CH_3]), 1381.5 (m, δ_{sy}[CH_3]), 1325.5 (m, υ_{as}[SO_2]), 1157.3 (m, υ_{sy}[SO_2]) cm^{-1}.



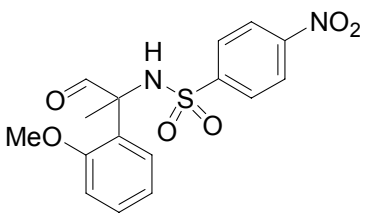
(+)-*2-Ethyl-2-(2'-nitrobenzene)sulfonylaminohexanal* **34**: The product was synthesised following GP 1, Method A, using 2-ethylhexanal (**20**, 64.1 mg, 0.5 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 136.9 mg, 0.6 mmol), and L-proline (**3**, 57.6 mg, 0.5 mmol) in technical ethanol (10 ml). After 3 d TLC monitoring indicated complete consumption of the aldehyde, and the solvent was removed by evaporation under reduced pressure. Flash chromatography on silica with *n*-pentane/diethylether 3:2 delivered a colourless solid (89.9 mg, 0.27 mmol) in 54% yield 28 ± 1% *ee*. – mp = 86 °C. – R_f = 0.12 (*n*-pentane/Et_2O 3:2). – HPLC (Chiralpak AS, n-heptane/isopropanol 98:2, 1.0 ml/min): R_t(min) = 52.0 min, R_t(maj) = 57.7 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (dd, *J* = 7.5, 7.5 Hz, 3 H, $CR_3CH_2C\underline{H}_3$), 0.70 (t, *J* = 7.4 Hz, 3 H, $CH_2CH_2C\underline{H}_3$), 0.81 – 0.96 (m, 1 H, $C\underline{H}HCH_2CH_3$), 0.98 – 1.12 (m, 3 H, $CH\underline{H}C\underline{H}_2CH_3$), 1.69 (ddd, *J* = 14.7, 11.7, 4.5 Hz, 1 H, $CR_3C\underline{H}HCH_2$), 1.77 (dq, *J* = 14.7, 7.3 Hz, 1 H, $CR_3C\underline{H}HCH_3$), 2.02 (ddd, *J* = 14.6, 12.73, 3.76 Hz, 1 H, $CR_3CH\underline{H}CH_2$), 2.10 (dq, *J* = 15.0, 7.6 Hz, 1 H, $CR_3CH\underline{H}CH_3$), 6.18 (s, 1 H, NH), 7.69 – 7.77 (m, 2 H, CH_{ar}), 7.87 – 7.94 (m, 1 H, CH_{ar}), 8.10 – 8.17 (m, 1 H, CH_{ar}), 9.29 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.6 (+, $CR_3CH_2\underline{C}H_3$), 13.8 (+, $CH_2CH_2CH_3$), 22.6 (–, $CH_2\underline{C}H_2CH_3$), 25.4 (–, $\underline{C}H_2CH_2CH_3$), 26.9 (–, $CR_3\underline{C}H_2CH_3$), 33.3 (–, $CR_3\underline{C}H_2CH_2$), 71.0 (q, CR_4), 125.6 (+, $C^{3'}{}_{ar}H$), 129.9 ($C^{6'}{}_{ar}H$), 133.2 (+, $C^{4'}{}_{ar}H$), 133.6 (+, $C^{5'}{}_{ar}H$), 136.6 (q, $C^{1'}{}_{ar}SO_2$), 147.8 (q, $C^{2'}{}_{ar}NO_2$), 198.7 (q, CHO) ppm. – MS (FAB): *m/z* (%) = 329 (100) [M^++1], 307 (60), 299 (43) [M^+–CHO], 289 (37), 282 (13) [M^+–NO_2], 186 (49) [$C_6H_4NO_4S^+$]. – MS (EI, II, 70 eV): *m/z* (%) = 299 (100) [M^+–CHO], 186 (98) [$C_6H_4NO_4S^+$]. – HRMS (I): calcd.: 299.1066 [M^+–CHO], found: 299.1071. – $C_{14}H_{20}N_2O_5S$ (328.39 g/mol), calcd.: C 51.21, H 6.14, N 8.53, S 9.76, found: C 51.14, H 6.02, N 8.55, S 9.69. – IR (KBr): 3331.1

(m, υ[NH]), 3094.9 (m, υ[CH_{ar}]), 2957.9 (m, υ[CH]), 2872.1 (m, υ[CH]), 1742.3 (m, υ[C=O]), 1593.2 (w, υ[C-C_{ar}]), 1539.8 (m, υ_{as}[NO_2]), 1467.5 (m, δ_{as}[CH_3]), 1445.7 (m, δ[CH_2]), 1364.1 (m, υ_{as}[SO_2]), 1339.6 (m, υ_{sy}[NO_2]), 1166.9 (m, υ_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +0.93° (c = 0.325, $CHCl_3$).



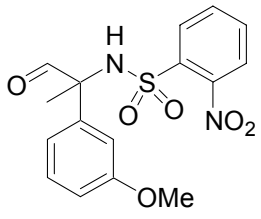
*(*S*)-(+)-2-(2'-Methoxyphenyl)-2-(2''-nitrobenzene)sulfonylamino-propionaldehyde* **35a**: The reaction was carried out following GP 1, Method A, using 2-(2'-methoxyphenyl)propionaldehyde (**21**, 82.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in technical ethanol (10 ml) within 7 d. Flash chromatography on silica with cyclohexane/ethyl acetate 5:2 delivered a colourless solid (37.7 mg, 0.103 mmol) in 21% yield and 72 ± 2% *ee*. – When carried out in absolute ethanol within 4 d under otherwise unchanged reaction conditions, the reaction delivered **35a** (48.5 mg, 0.133 mmol) in 27% yield and 72 ± 2% *ee*. – mp = 185 °C. – R_f = 0.18 (cyclohexane/ethyl acetate 5:2). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 80:20, 0.7 ml/min): R_t(min) = 18.9 min, R_t(maj) = 21.4 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 3 H, CR_3CH_3), 3.22 (s, 3 H, OCH_3), 6.21 (dd, *J* = 8.2, 0.8 Hz, 1 H, $C^{3'}H_{ar}$), 6.95 (dd, *J* = 7.9, 1.3 Hz, 1 H, $C^{6''}H_{Ns}$), 7.03 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1 H, $C^{5''}H_{ar}$), 7.22–7.26 (m, 2 H, $C^{4'}H_{ar}$/$C^{5'}H_{ar}$), 7.48 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1 H, $C^{4''}H_{Ns}$), 7.56 (dd, *J* = 7.7, 1.6 Hz, 1 H, $C^{6'}H_{ar}$), 7.76 (dd, *J* = 8.1, 1.1 Hz, 1 H, $C^{3''}H_{Ns}$), 9.08 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (+, CH_3), 54.5 (+, OCH_3), 65.2 (q, CR_4), 110.0 (+, $C^{3'}{}_{ar}H$), 120.9 (+, $C_{ar}H$), 122.7 (q, $\underline{C^{1'}}_{ar}CR_4$), 124.6 (+, $C_{ar}H$), 129.9 (+, $C_{ar}H$), 130.2 (+, $C_{ar}H$), 131.0 (+, $C_{ar}H$), 132.3 (+, 2x $C_{ar}H$), 134.9 (q, $C^{1''}SO_2$), 147.2 (q, $C^{2''}NO_2$), 156.5 (q, $C^{2'}{}_{ar}O$), 194.2 (q, CHO) ppm. – MS (FAB): *m/z* (%) = 365 (11) [M^++1], 335 (44) [M^+–CHO], 289 (13) [M^+–CHO–NO_2], 186 (31) [$C_6H_4NO_4S^+$], 163 (100) [$C_{10}H_{11}O_2^+$]. – MS (EI, II, 70 eV): *m/z* (%) = 135 (100) [M^+–CHO], 321 (27) [M^+–CO–CH_3], 186 (100) [$C_6H_4NO_4S^+$], 149 (15), 134 (25) [$C_9H_{10}O^+$], 77 (10) [$C_6H_5^+$]. – HRMS (II): calcd.: 335.0702, found: 335.0702. – IR (KBr): 3338.8 (w, ν[NH]), 3023.5 (w, ν[CH_{ar}]), 2952.6 (w, ν[CH_3]), 2924.5 (w, ν[CH_3]), 2853.4 (w, ν[OCH_3]), 1727.8 (w, ν[C=O]), 1592.3 (w, ν[C-C_{ar}]), 1491.5 (w, ν[C-C_{ar}]), 1466.1 (w, δ_{as}[CH_3]), 1387.7 (w, δ_{sy}[CH_3]), 1335.6 (w, ν_{as}[SO_2]), 1254.0 (w, ν_{as}[C-O-C]), 1172.7 (w, ν_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +128.0° (c = 0.210, $CHCl_3$).[c]

[c] determined for 72% *ee*.



(+)-2-(2'-Methoxyphenyl)-2-(4''-nitrobenzene)sulfonylamino-propionaldehyde **35b**:

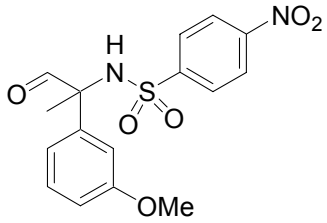
The reaction was carried out following GP 1, Method A, using 2-(2'-methoxyphenyl)propionaldehyde (**21**, 82.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in technical ethanol (10 ml) within 6 d. Flash chromatography on silica with cyclohexane/ethyl acetate 5:2 delivered a colourless solid (37.8 mg, 0.104 mmol) in 21% yield and 59 ± 1% *ee*. – mp = 158 °C. – R_f = 0.22 (cyclohexane/ethyl acetate 5:2). – HPLC (Chiracel OD, *n*-heptane/isopropanol 80:20, 0.7 ml/min): R_t(min) = 21.6 min, R_t(maj) = 24.3 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, CR_3CH_3), 3.35 (s, 3 H, OCH_3), 6.20 (dd, *J* = 8.3, 0.9 Hz, 1 H, $C^{3'}H_{ar}$), 6.37 (bs, 1 H, NH), 7.01 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1 H, $C^{5'}H_{ar}$), 7.18 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1 H, $C^{4'}H_{ar}$), 7.39 (ddd, *J* = 9.2, 2.2, 2.2 Hz, 2 H, $C^{2''}H_{Ns}$), 7.50 (dd, *J* = 7.7, 1.6 Hz, 1 H, $C^{6'}H_{ar}$), 7.93 (dd, *J* = 9.1, 2.2, 2.2 Hz, 2 H, $C^{3''}H_{Ns}$), 9.03 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (+, CH_3), 54.8 (+, OCH_3), 64.3 (q, CR_4), 110.6 (+, $C^{3'}{}_{ar}H$), 121.0 (+, $C_{ar}H$), 122.1 (q, $C^{1'}{}_{ar}CR_4$), 123.0 (+, $C^{3''}{}_{Ns}H$), 127.9 (+, $C^{2''}{}_{Ns}H$), 129.8 (+, $C_{ar}H$), 131.4 (+, $C_{ar}H$), 146.6 (q, $C^{1''}SO_2$), 149.1 (q, $C^{4''}NO_2$), 156.1 (q, $C^{2'}{}_{ar}O$), 194.5 (q, CHO) ppm. – MS (FAB): *m/z* (%) = 365 (15) [M^++1], 335 (56) [M^+–CHO], 289 (52) [M^+–CHO–NO_2], 163 (100) [$C_{10}H_{11}O_2^+$]. – MS (EI, KA, 70 eV): *m/z* (%) = 335 (100) [M^+–CHO], 186 (32) [$C_6H_4NO_4S^+$], 134 (64) [$C_9H_{10}O^+$], 105 (16), 91 (9) [$C_7H_7^+$], 77 (15) [$C_6H_5^+$]. – HRMS (KA): calcd.: 335.0702 [M^+–CHO], found: 335.0705. – IR (KBr): 3301.7 (m, ν[NH]), 3039.5 (w, ν[CH_{ar}]), 2987.2 (w, ν[CH_3]), 2943.7 (w, ν[CH_3]), 2864.8 (w, ν[OCH_3]), 2838.4 (w, ν[OCH_3]), 2728.3 (vw, comb[CHO]), 1726.5 (m, ν[CO]), 1604.8 (m, ν[C-C_{ar}]), 1533.1 (m, ν_{as}[NO_2]), 1490.1 (m, ν[C-C_{ar}]), 1466.2 (m, δ_{as}[CH_3]), 1368.1 (m, δ_{sy}[CH_3]), 1349.8 (m, ν_{as}[SO_2]/ν_{sy}[NO_2]), 1253.5 (m, ν_{as}[C-O-C]), 1173.0 (m, ν_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +39.7° (c = 0.300, $CHCl_3$).[d]



(+)-2-(3'-Methoxyphenyl)-2-(2''-nitrobenzene)sulfonylaminopropion-aldehyde **36a**: The reaction was carried out following GP 1, Method A, using 2-(3'-methoxyphenyl)propionaldehyde (**22**, 82.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in technical ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 5:2 delivered a colourless solid

[d] determined for 72% *ee*.

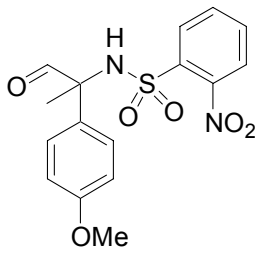
(84.9 mg, 0.233 mmol) in 47% yield and 84% *ee*. – When carried out in absolute ethanol within 3 d under otherwise unchanged reaction conditions, the reaction delivered **36a** (82.5 mg, 0.226 mmol) in 45% yield and 66 ± 1% *ee*. – mp = 148 °C. – R_f = 0.33 (cyclohexane/ethyl acetate 5:2). – HPLC (Chiracel OD, *n*-heptane/isopropanol 90:10, 0.7 ml/min): R_t(maj) = 18.2 min, R_t(min) = 22.8 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, CR_3CH_3), 3.77 (s, 3 H, OCH_3), 6.78 (dd, *J* = 2.1, 2.1 Hz, 1 H, $C^{2'}H_{ar}$), 6.86 (ddd, *J* = 8.2, 2.5, 0.6 Hz, 1 H, $C^{4'}H_{ar}$), 6.97 (ddd, *J* = 7.8, 1.6, 0.7 Hz, 1 H, $C^{6'}H_{ar}$), 7.24 (dd, *J* = 8.1, 8.1 Hz, 1 H, $C^{5'}H_{ar}$), 7.39–7.48 (m, 2 H, $C^{5''}H_{Ns}$/$C^{6''}H_{Ns}$), 7.70 (ddd, *J* = 7.8, 7.4, 1.6 Hz, 1 H, $C^{4''}H_{Ns}$), 7.92 (dd, *J* = 7.9, 1.0 Hz, 1 H, $C^{3'}H_{Ns}$), 9.29 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (+, CH_3), 55.2 (+, OCH_3), 67.2 (q, CR_4), 113.7 (+, $C_{ar}H$), 114.6 (+, $C_{ar}H$), 120.0 (+, $C_{ar}H$), 124.8 (+, $C_{ar}H$), 129.9 (+, $C_{ar}H$), 130.1 (+, $C_{ar}H$), 132.3 (+, $C_{ar}H$), 132.7 (+, CH_{ar}), 134.8 (q, $\underline{C^{1'}}_{ar}CR_4$), 135.2 (q, $C^{1''}SO_2$), 147.3 (q, $C^{2''}NO_2$), 160.0 (q, $C^{3'}{}_{ar}O$), 193.2 (q, CHO) ppm. – MS (FAB): *m/z* (%) = 365 (10) [M^++1], 335 (53) [M^+–CHO], 289 (13) [M^+–CHO–OCH_3], 197 (60), 186 (40) [$C_6H_4NO_4S^+$], 163 (100) [$C_{10}H_{11}O_2^+$]. – HRMS (KA): calcd.: 364.0729, found: 364.0725. – $C_{16}H_{16}N_2O_6S$ (364.37 g/mol), calcd.: C 52.74, H 4.43, N 7.69, S 8.80, found: C 53.01, H 4.56, N 7.62, S 8.46. – IR (KBr): 3319.8 (m, ν[NH]), 2947.6 (m, ν[CH_3]), 1720.3 (m, ν[C=O]), 1600.0 (m), 1539.1 (m, ν_s[NO_2]), 1497.0 (m, ν[C-C_{ar}]), 1467.0 (m, δ_{as}[CH_3]), 1429.6 (m, δ_{as}[OCH_3]), 1391.5 (m, δ_{sy}[CH_3]), 1364.2 (m, ν_{sy}[SO_2]), 1335.1 (m, ν_{sy}[NO_2]), 1259.4 (m, ν_{as}[C-O-C]), 1173.3 (m, ν_{sy}[SO_2]) cm^{-1}. – $[\alpha]_D^{20}$ = +250.7° (c = 0.300, $CHCl_3$).[e]



(+)-2-(3'-Methoxyphenyl)-2-(4''-nitrobenzene)sulfonylamino-propionaldehyde **36b**: The reaction was carried out following GP 1, Method A, using 2-(3'-methoxyphenyl)propionaldehyde (**22**, 82.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in technical ethanol (10 ml) within 4 d.[f] Flash chromatography on silica with cyclohexane/ethyl acetate 5:2 delivered a colourless solid (89.0 mg, 0.244 mmol) in 49% yield and 69% *ee*. – mp = 138 °C. – R_f = 0.27 (cyclohexane/ethyl acetate 5:2). – HPLC (Chiracel OD, *n*-heptane/isopropanol 40:60, 0.5 ml/min): R_t(min) = 28.0 min, R_t(maj) = 36.0 min. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 3 H, CR_3CH_3), 3.59 (s, 3 H, OCH_3), 6.27 (bs, 1 H,

[e] determined for 70% *ee*.
[f] according to TLC analysis the reaction was completed after 2 d.

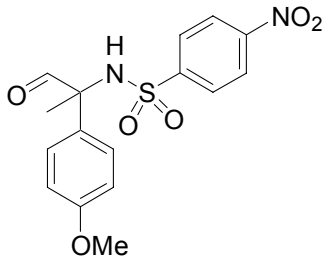
NH), 6.32 (dd, *J* = 2.2, 2.2 Hz, 1 H, $C^{2'}H_{ar}$), 6.67 – 6.77 (m, 2 H, $C^{4'}H_{ar}/C^{6'}H_{ar}$), 7.11 (dd, *J* = 8.0, 8.0 Hz, 1 H, $C^{5'}H_{ar}$), 7.52 (ddd, *J* = 9.2, 2.2, 2.2 Hz, 2 H, $C^{2''}H_{Ns}$), 8.02 (dd, *J* = 9.2, 2.2, 2.2 Hz, 2 H, $C^{3''}H_{Ns}$), 9.04 (s, 1 H, CHO) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1 (+, CH_3), 55.2 (+, OCH_3), 66.7 (q, CR_4), 113.8 (+, $C^{4'}{}_{ar}H$), 114.8 (+, $C^{2'}{}_{ar}H$), 120.2 (+, $C^{6'}{}_{ar}H$), 123.6 (+, $C^{3''}{}_{Ns}H$), 127.9 (+, $C^{2''}{}_{Ns}H$), 130.2 (+, $C^{5'}{}_{ar}H$), 134.1 (q, $\underline{C^{1'}}_{ar}CR_4$), 147.3 (q, $C^{1''}{}_{Ns}SO_2$), 149.4 (q, $C^{4''}{}_{Ns}NO_2$), 159.9 (q, $C^{3'}{}_{ar}O$), 193.4 (CHO) ppm. – MS (FAB): *m/z* (%) = 365 (8) [M^++1], 335 (69) [M^+–CHO], 307 (100) [M^+–CO–NO+1], 289 (86) [M^+–CHO–NO_2], 273 (21), 258 (11), 242 (15), 226 (13), 196 (11), 178 (21) [M^+–Ns], 163 (84) [M^+–NHNs]. – MS (EI, II, 70 eV): *m/z* (%) = 364 (2) [M^+], 335 (100) [M^+–CHO], 148 (23) [$C_9H_{10}NO^+$], 134 (23) [$C_9H_{10}O^+$], 122 (7), 77 (6) [$C_6H_5^+$]. – HRMS (II): calcd.: 335.0702, found: 335.0700. – $C_{16}H_{16}N_2O_6S$ (364.37 g/mol), calcd.: C 52.74, H 4.43, N 7.69, S 8.80, found: C 52.41, H 4.38, N 7.67, S 8.29. – IR (KBr): 3234.2 (s, ν[NH]), 3071.4 (m, ν[CH_{ar}]), 3030.2 (m, ν[CH_{ar}]), 2960.4 (m, ν[CH_3]), 2938.5 (m, ν[CH_3]), 2852.8 (m, ν[OCH_3]), 2711.6 (m, comb[CHO]), 1732.9 (s, ν[C=O]), 1605.5 (s, ν[C-C_{ar}]), 1583.9 (s, ν[C-C_{ar}]), 1528.0 (s, ν_{as}[NO_2]), 1488.8 (s, ν[C-C_{ar}]), 1348.5 (s, ν_{as}[NO_2]/ν_{sy}[SO_2]), 1292.4 (s, ν_{as}[C-O-C], 1174.8 (s, ν_{sy}[SO_2]), 1044.3 (s, ν_{sy}[C-O-C]) cm^{-1}. – $[\alpha]_D^{20}$ = +42.7° (c = 0.295, $CHCl_3$).[g]



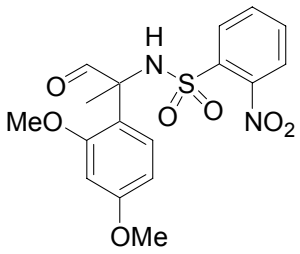
(+)-2-(4'-Methoxyphenyl)-2-(2''-nitrobenzene)sulfonylaminopropionaldehyde **37a**: The reaction was carried out following GP 1, Method A, using 2-(4'-methoxyphenyl)propionaldehyde (**23**, 82.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in technical ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 2:1 delivered a colourless solid (95.9 mg, 0.263 mmol) in 53% yield and 86 ± 1% *ee*. – mp = 145 °C. – R_f = 0.27 (cyclohexane/ethyl acetate 2:1). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 50:50, 0.5 ml/min): R_t(maj) = 30.6 min, R_t(min) = 34.1 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 3.65 (s, 3 H, OCH_3), 6.53 (d, *J* = 9.0 Hz, 2 H, $C^{3'}H_{ar}$), 6.99 (d, *J* = 9.0 Hz, 2 H, $C^{2'}H_{ar}$), 7.13–7.22 (m, 2 H, $C^{5''}H_{Ns}/C^{6''}H_{Ns}$), 7.45 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1 H, $C^{4''}H_{Ns}$), 7.67 (dd, *J* = 8.0, 1.1 Hz, 1 H, $C^{3''}H_{Ns}$), 9.02 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (+, CH_3), 55.5 (+, OCH_3), 66.8 (q, CR_4), 114.2 (+, $C^{3'}H_{ar}$), 124.9 (+, $C^{3''}H_{Ns}$), 125.4 (q, $\underline{C^{1'}}_{ar}CR_3$), 129.3 (+, $C^{2'}H_{ar}$), 130.4 (+, $C^{6''}H_{Ns}$), 132.3 (+, $C^{4''}H_{Ns}$), 132.6 (+, $C^{5''}H_{Ns}$), 135.5 (q, $C^{1''}{}_{Ns}$-SO_2), 147.5 (q, $C^{2''}$-NO_2), 160.3 (q, $C^{4'}{}_{ar}O$), 193.3 (q, CHO) ppm. – MS (FAB): *m/z* (%) = 365 (4) [M^++1], 335 (29) [M^+–CHO], 307 (100) [M^+–CO–NO],

[g] determined for 72% *ee*.

289 (59) [M^+–CHO–NO_2], 163 (50) [M^+–$NHSO_2C_6H_4NO_2$], 305 (29) [M^+–CH_2OH], 289 (61), 203 (31) [$C_6H_7N_2O_4S^+$], 186 (55) [$C_6H_4NO_4S^+$], 165 (25). – $C_{16}H_{16}N_2O_6S$ (364.37 g/mol), calcd.: C 52.74, H 4.43, N 7.69, S 8.80, found: C 52.73, H 4.44, N 7.61, S 8.60. – IR (KBr): 3296.6 (m, ν[NH]), 3020.4 (m, ν[C_{ar}H]), 2962.6 (w, ν[CH_3]), 2941.9 (w, ν[CH_3]), 2842.3 (m, ν[OCH_3]), 1720.6 (m, ν[C=O]), 1582.1 (m, ν[C-C_{ar}]), 1534.1 (s, ν_{as}[NO_2]), 1511.9 (m, ν[C-C_{ar}]), 1468.0 (m, δ_{as}[CH_3]), 1388.2 (m, δ_{sy}[CH_3]), 1361.7 (m, ν_{as}[SO_2]), 1335.3 (m, ν_{sy}[NO_2]), 1258.6 (m, ν_{as}[C-O-C]), 1170.3 (m, ν_{sy}[SO_2]), 1055.6 (m, ν_{sy}[C-O-C]) cm^{-1}. – $[\alpha]_D^{20}$ = +142.6° (c = 0.620, $CHCl_3$).

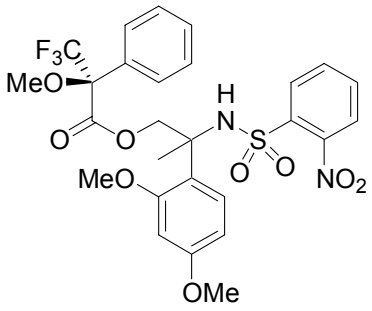


(+)-2-(4'-Methoxyphenyl)-2-(4''-nitrobenzene)sulfonylamino-propionaldehyde **37b**: The reaction was carried out following GP 1, Method A, using 2-(4'-methoxyphenyl)propionaldehyde (**23**, 82.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in technical ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 5:1 to 5:2 delivered a colourless solid (80.7 mg, 0.221 mmol) in 44% yield and 76% *ee*. – mp = 181 °C. – R_f = 0.17 (cyclohexane/ethyl acetate 5:1). – HPLC (Chiracel OD, *n*-heptane/isopropanol 90:10, 1.0 ml/min): R_t(maj) = 50.1 min, R_t(min) = 60.5 min. – ^{1}H NMR (400 MHz, DMF-d^7): δ = 1.69 (s, 3 H, CH_3), 3.76 (s, 3 H, OCH_3), 6.83 (d, *J* = 9.1 Hz, 2 H, $C^{2'}H_{ar}$), 7.27 (d, *J* = 9.1 Hz, 2 H, $C^{3'}H_{ar}$), 7.99 (d, *J* = 8.9 Hz, 2 H, $C^{2''}H_{ar}$), 8.34 (d, *J* = 9.1 Hz, 2 H, $C^{3''}H_{ar}$), 9.62 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, DMF-d^7): δ = 20.8 (+, CH_3), 55.6 (+, OCH_3), 67.5 (q, CR_4), 114.6 (+, $C^{3'}H_{ar}$), 124.8 (+, $C^{3''}H_{ar}$), 128.6 (q, $\underline{C}^{1'}{}_{ar}CR_3$), 128.8 (+, CH_{ar}), 129.4 (+, CH_{ar}), 149.2 (q, $C^{1''}{}_{ar}SO_2$), 150.2 (q, $C^{4''}{}_{ar}NO_2$), 160.4 (q, $C^{4'}{}_{ar}O$), 197.2 (q, CHO) ppm. – MS (EI, II, 70 eV): *m/z* (%) = 335 (100) [M^+–CHO], 186 (10) [$C_6H_4NO_4S^+$], 149 (17) [$C_9H_{11}NO^+$], 134 (24) [$C_8H_8NO^+$]. – HRMS (II): calcd.: 335.0702 (M^+–CHO), found: 335.0697. – $C_{16}H_{16}N_2O_6S$ (364.37 g/mol), calcd.: C 52.74, H 4.43, N 7.69, S 8.80, found: C 52.92, H 4.56, N 7.41, S 8.55. – IR (KBr): 3298.6 (m, ν[NH]), 3039.8 (w, ν[C_{ar}H]), 3020.3 (w, ν[C_{ar}H]), 2964.3 (m, ν[CH_3]), 2938.6 (m, ν[CH_3]), 2839.1 (m, ν[OCH_3]), 1734.9 (m, ν[C=O]), 1607.7 (m, ν[C-C_{ar}]), 1528.8 (m, ν_{as}[NO_2]), 1514.2 (m, ν[C-C_{ar}]), 1464.0 (m, δ_{as}[CH_3]), 1349.7 (m, ν_{as}[SO_2]), 1327.9 (m, ν_{sy}[NO_2]), 1313.3 (m, ν_{sy}[NO_2]), 1259.3 (m, ν_{as}[C-O-C]), 1151.5 (m, ν_{sy}[SO_2]), 1027.8 (m, ν_{sy}[C-O-C]) cm^{-1}. – $[\alpha]_D^{20}$ = +51.7° (c = 0.41, $CHCl_3$).

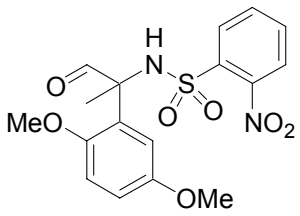


(+)-2-(2',4'-Dimethoxyphenyl)-2-(2''-nitrobenzene)sulfonylamino-propionaldehyde **38**: The reaction was carried out following GP 1, Method A, using 2-(2',4'-dimethoxyphenyl)propionaldehyde (**24**, 97.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in absolute ethanol (10 ml) within 4 d. Flash chromatography on silica with cyclohexane/ethyl acetate 2:1 delivered a bright yellow solid (67.3 mg, 0.171 mmol) in 34% yield. – mp = 177 –179 °C. – R_f = 0.18 (cyclohexane/ethyl acetate 2:1). – ^{1}H NMR (400 MHz, DMF-d^7): δ = 1.82 (s, 3 H, CH_3), 3.24 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 5.93 (d, *J* = 2.4 Hz, 1 H, $C^{3'}H_{ar}$), 6.62 (dd, *J* = 8.6, 2.5 Hz, 1 H, $C^{5'}H_{ar}$), 6.99 (dd, *J* =7.9, 1.3 Hz, 1 H, $C^{6''}H_{Ns}$), 7.22 (bs, 1 H, NH), 7.43 (ddd, *J* = 7.7, 7.7, 1.2 Hz, 1 H, $C^{5''}H_{Ns}$), 7.45 (d, *J* = 8.7 Hz, 1 H, $C^{6'}H_{ar}$), 7.75 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1 H, $C^{4''}H_{Ns}$), 7.99 (dd, *J* = 8.1, 1.0 Hz, 1 H, $C^{3''}H_{Ns}$), 9.24 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, DMF-d^7): δ = 21.7 (+, CH_3), 55.1 (+, OCH_3), 55.9 (+, OCH_3), 66.6 (q, CR_4), 98.1 (+, $C^{3'}{}_{ar}H$), 105.8 (+, $C^{5'}{}_{ar}H$), 115.8 (q, $\underline{C^{1'}}_{ar}CR_4$), 125.7 (+, $C_{ar}H$), 130.4 (+, $C_{ar}H$), 130.9 (+, $C_{ar}H$), 133.3 (+, $C_{ar}H$), 134.1 (+, $C_{ar}H$), 134.4 (q, $C^{1''}{}_{Ns}SO_2$), 147.9 (q, $C^{2''}{}_{Ns}NO_2$), 158.3 (q, $C^{2'}{}_{ar}O/C^{4'}{}_{ar}O$), 197.0 (+, CHO) ppm. – MS (FAB): *m/z* (%) = 395 (5) [M^++1], 365 (38) [M^+–CHO], 307 (78), 289 (43), 193 (100) [$C_{11}H_{13}O_3^+$], 165 (81) [$C_{11}H_{13}O_2^+$]. – MS (EI, II, 70 eV): *m/z* (%) = 365 (10) [M^+–CHO], 351 (8) [M^+–CO–CH_3], 202 (18) [$C_6H_6N_2O_4S^+$], 185.9 (100) [$C_6H_4NO_4S^+$], 164 (5) [$C_{11}H_{12}O_2^+$], 92 (6) [$C_6H_4O^+$]. – HRMS (II): calcd.: 365.0807 (M^+–CHO), found: 365.0808. – $C_{17}H_{18}N_2O_7S$ (394.40 g/mol), calcd.: C 51.77, H 4.60, N 7.10, S 8.13, found: C 51.40, H 4.86, N 7.39, S 8.42. – IR (KBr): 3264.6 (m, ν[NH]), 2950.7 (m, ν[CH_3]), 2840.4 (m, ν[OCH_3]), 1727.6 (m, ν[C=O]), 1584.4 (m, ν[C-C_{ar}]), 1536.3 (m, ν_{as}[NO_2]), 1504.7 (m, ν[C-C_{ar}]), 1466.9 (m, δ_{as}[CH_3]), 1389.6 (m, δ_{sy}[CH_3]), 1362.7 (m, ν_{as}[SO_2]), 1336.3 (m, ν_{sy}[NO_2]), 1266.2 (m, ν_{as}[C-O-C]), 1163.0 (m, ν_{sy}[SO_2]), 1055.5 (m, ν_{sy}[C-O-C]) cm^{-1}. – $[\alpha]_D^{20}$ = +129.5° (c = 0.390, $CHCl_3$).

Determination of enantiomeric excess of 38 as Mosher's-Ester:



*(2*S*)-2'-(2'',4''-Dimethoxyphenyl)-2'-(2'''-nitrobenzene)-sulfonylaminopropyl 2-methoxy-2-trifluoromethylphenyl-acetate*: The reaction was carried out following GP 2.[h] – HPLC (Chiracel OD, *n*-heptane/*i*-PrOH 90:10, 0.7 ml/min): R_t(min) = 32.1 min, R_t(maj) = 40.0 min. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84, **1.87** (2 × s, 3 H, CR_3CH_3), 3.38, **3.40** (2 × s, 3 H, $C_{ar}OCH_3$), **3.46**, 3.48 (2 × d, *J* = 0.82 and 0.94 Hz, 3 H, CR_3OCH_3), 3.74, **3.75** (2 × s, 3 H, $C_{ar}OCH_3$), 4.70, **4.74** (2 × d, *J* = 10.6 and 10.6 Hz, 1 H, CHHO), **4.91**, 5.00 (2 × d, *J* =10.8 and 11.0 Hz, 1 H, CHHO), 5.85, **5.89** (2 × d, *J* = 2.5 and 2.5 Hz, 1 H, $C^{3''}H_{ar}$), 6.52, **6.60** (2 × bs, 1 H, NH), 6.33, **6.37** (2 × dd, *J* = 8.7, 2.6 and 9.0, 2.5 Hz, 1 H, $C^{5''}H_{ar}$), 7.10, **7.16** (2 × d, *J* = 8.7 and 8.7 Hz, 1 H, $C^{6}H_{ar}$), **7.22**, 7.23 (2 × d, *J* = 8.7 and 7.9 Hz, 1 H, CH_{ar}), 7.27 – 7.60 (m, 7 H, CH_{ar}), 7.76 (d, *J* = 8.3 Hz, 1 H, $C^{3'''}H_{Ns}$) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = **23.7**, 23.8 (+, $CR_3\underline{C}H_3$), 54.7, **54.7** (+, OCH_3), 55.5, **55.5** (+, OCH_3), 55.6, **55.6** (+, OCH_3), 60.3, **60.5** (q, CR_3N), **70.6**, 70.7 (–, CH_2), **77.4** (q, $\underline{C}R_3CO_2$), **98.6**, 98.8 (+, $C^{3''}{}_{ar}H$), 103.7, **103.8** (+, $C^{5''}{}_{ar}H$), 118.8, **118.8** (q, $\underline{C^{1''}}_{ar}CR_2N$), 124.6, **124.6** (+, $C_{ar}H$), 127.5, **127.5** (+, $C_{ar}H$), **128.5**, 128.5 (+, $C^{2}{}_{Ph}H$), **128.6** (+, $C^{3}{}_{Ph}H$), **129.7**, 129.7 (+, $C_{ar}H$), **130.5**, 130.5 (+, $C_{ar}H$), **130.7**, 131.0 (q, $\underline{C^{1}}_{Ph}CR_2CO_2$), **132.2**, 132.2 (+, $C_{ar}H$), 132.5, **132.6** (+, $C_{ar}H$), 135.2, **135.3** (q, $C^{1'''}{}_{Ns}SO_2$), 147.6, **147.6** (q, $C^{2'''}{}_{Ns}NO_2$), 158.0, **158.0** (q, $C_{ar}O$), 161.1, **161.1** ($C_{ar}O$) **166.4**, 166.5 (q, CO_2) ppm. – ^{19}F NMR (300 MHz, $CDCl_3$): δ = **–72.12**, –72.10 ppm. – The diastereomeric excess was 45 ± 1% *de*.[i]

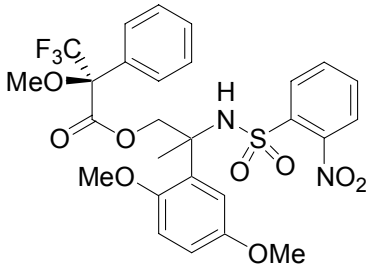


*(*S*)-(+)-2-(2',5'-Dimethoxyphenyl)-2-(2''-nitrobenzene)sulfonyl-aminopropionaldehyde* **39**: The reaction was carried out following GP 1, Method A, using 2-(2',5'-dimethoxyphenyl)propionaldehyde (**25**, 97.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in absolute ethanol (10 ml) within 4 d. Flash chromatography on silica with cyclohexane/ethyl acetate 2:1 delivered a bright yellow solid (62.9 mg, 0.159 mmol) in 32% yield. – mp = 157 – 167 °C. – R_f = 0.15 (cyclohexane/ethyl acetate 2:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91

[h] According to NMR spectroscopy the product contains approx. 44% of unreacted alcohol.
[i] Due to poor resolution of the ^{19}F NMR signals the diastereomeric excess was determined by HPLC.

(s, 3 H, CH_3), 3.21 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 6.15 (d, J = 8.9 Hz, 1 H, $C^{3'}H_{ar}$), 6.69 (dd, J = 8.9, 3.0 Hz, 1 H, $C^{4'}H_{ar}$), 7.10 (d, J = 3.0 Hz, 1 H, $C^{6'}H_{ar}$), 7.12 (dd, J = 8.1, 1.5 Hz, $C^{6''}H_{Ns}$), 7.14 (bs, 1 H, NH), 7.23 (ddd, J = 7.8, 7.7, 1.3 Hz, 1 H, $C^{5''}H_{Ns}$), 7.49 (ddd, J = 7.7, 7.7, 1.4 Hz, 1 H, $C^{4''}H_{Ns}$), 7.78 (dd, J = 7.9, 1.1 Hz, 1 H, $C^{3''}H_{Ns}$), 9.09 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4 (+, CH_3), 54.8 (+, OCH_3), 56.1 (+, OCH_3), 65.2 (q, CR_4), 110.6 (+, $C^{3'}{}_{ar}H$), 114.9 (+, $C^{5'}{}_{ar}H$), 116.4 (+, $C^{6'}{}_{ar}H$), 123.7 (q, $\underline{C}^{1'}{}_{ar}CR_4$), 124.7 (+, $C^{3''}{}_{Ns}H$), 130.4 (+, $C^{6''}{}_{Ns}H$), 132.2 (+, $C_{Ns}H$), 132.4 (+, $C_{Ns}H$), 135.0 (q, $C^{1''}{}_{Ns}SO_2$), 147.2 (q, $C^{2''}{}_{Ns}NO_2$), 150.6 (q, $C_{ar}O$), 153.8 (q, $C_{ar}O$), 194.0 (+, CHO) ppm. – MS (EI, II, 70 eV): *m/z* (%) = 394 (4) [M^+], 365 (100) [M^+–CHO], 179 (7) [$C_{10}H_{13}NO_2^+$], 164 (30) [$C_9H_{12}O_2^+$], 134 (3) [$C_9H_{10}O^+$]. – HRMS (II): calcd.: 394.0835, found: 394.0835. – $C_{17}H_{18}N_2O_7S$ (394.40 g/mol), calcd.: C 51.77, H 4.60, N 7.10, S 8.13, found: C 52.18, H 4.81, N 7.14, S 8.51. – IR (KBr): 3268.4 (w, ν[NH]), 2945.9 (m, ν[CH_3]), 2839.3 (m, ν[OCH_3]), 1731.3 (m, ν[C=O]), 1588.1 (m, ν[C-C_{ar}]), 1532.5 (m, ν_{as}[NO_2]), 1498.7 (m, ν[C-C_{ar}]), 1463.5 (m, δ_{as}[CH_3]), 1385.0 (m, δ_{sy}[CH_3]), 1362.6 (m, ν_{as}[SO_2]), 1332.0 (m, ν_{sy}[NO_2]), 1259.3 (m, ν_{as}[C-O-C]), 1168.1 (m, ν_{sy}[SO_2]), 1050.0 (m, ν_{sy}[C-O-C]) cm^{-1}. – $[\alpha]_D^{20}$ = +131.0° (c = 0.300, $CHCl_3$).

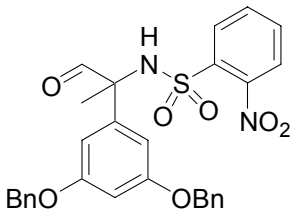
Determination of enantiomeric excess of 39 as Mosher's-Ester:



(2S)-2'-(2'',5''-Dimethoxyphenyl)-2'-(2'''-nitrobenzene)-sulfonylaminopropyl 2-methoxy-2-trifluoromethylphenyl-acetate: The reaction was carried out following GP 2.[j] – HPLC (Chiracel OD, *n*-heptane/*i*-PrOH 90:10, 0.7 ml/min): R_t(min) = 34.8 min, R_t(maj) = 43.0 min. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85, **1.87** (2 × s, 3 H, CR_3CH_3), 3.41, **3.42** (2 × s, 3 H, $C_{ar}OCH_3$), **3.46**, 3.48 (2 × d, J = 1.1 and 0.9 Hz, 3 H, CR_3OCH_3), 3.70, **3.71** (2 × s, 3 H, $C_{ar}OCH_3$), 4.75, **4.79** (2 × d, J = 10.8 and 9.8 Hz, 1 H, C$\underline{H}$HO), **4.90**, 4.97 (2 × d, J = 10.8 and 10.8 Hz, 1 H, CH$\underline{H}$O), 6.27, **6.30** (2 × d, J = 9.1 and 9.1 Hz, 1 H, $C^{3''}H_{ar}$), 6.59 – 6.82 (m, 2 H, CH_{ar}/NH), 6.79, **6.84** (2 × d, J = 3.0 and 3.0 Hz, 1 H, $C^{6''}H_{ar}$), 7.28 – 7.63 (m, 8 H, CH_{ar}), 7.73 – 7.80 (m, 1 H, $C^{6'''}H_{Ns}$) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = **23.3**, 23.4 ($CR_3\underline{C}H_3$), 55.0, **55.0** ($C_{ar}O$), **55.6** (b, $CR_3O\underline{C}H_3$), **56.0**, 56.0 ($C_{ar}OCH_3$), 60.6, **60.8** (CR_3N), **70.4** (CH_2), **77.4** ($\underline{C}R_3CO_2$), **111.3** ($C^{4''}{}_{ar}H$), 113.6, **113.7** ($C^{''}{}_{ar}H$), 115.1, **115.4** ($C''{}_{ar}H$), 124.7, **124.7** ($C_{ar}H$), 127.0, **127.1** ($C_{ar,q}$), 127.5, **127.4** ($C_{ar}H$), **128.5**, 128.6 ($C_{ar}H$), **129.7**, 129.8 ($C_{ar}H$),

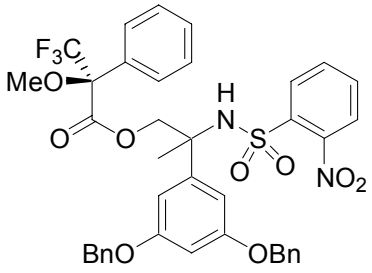
[j] According to NMR spectroscopy the product mainly consists of unreacted alcohol (ratio alcohol/ester approx. 3.2:1).

130.4 ($C_{ar}H$), 132.0, **132.0** ($C_{ar,q}$), 132.3, **132.3** ($C_{ar}H$), 132.6, **132.7** ($C_{ar}H$), 135.3, **135.3** ($C^{1'''}{}_{Ns}SO_2$), 147.6, **147.6** ($C^{2'''}{}_{Ns}NO_2$), **151.0** ($C_{ar}O$), 153.4, **153.5** ($C_{ar}O$), 166.4, 166.4 (CO_2) ppm. – ^{19}F NMR (300 MHz, $CDCl_3$): δ = **–72.10**, –72.09 ppm. – The diastereomeric excess was 54 ± 2% *de*.[k]



(+)-2-(3',5'-Dibenzyloxyphenyl)-2-(2''-nitrobenzene)sulfonylamino-propionaldehyde **40**: The reaction was carried out following GP 1, Method A, using 2-(3',5'-dibenzyloxyphenyl)propionaldehyde (**26**, 145 mg, 0.42 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 137 mg, 0.60 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in technical ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 4:1 delivered a light yellow oil (72.7 mg, 0.132 mmol) in 31% yield. – R_f = 0.34 (cyclohexane/ethyl acetate 4:1). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97 (s, 3 H, CH_3), 4.68 (d, *J* = 11.7 Hz, 2 H, OC<u>H</u>H), 4.76 (d, *J* = 11.7 Hz, 2 H, OCH<u>H</u>), 6.38 (s, 3 H, $C^{2'}H_{ar}/C^{4'}H_{ar}$), 7.04 (bs, 1 H, NH), 7.12 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1 H, $C^{4''}H_{Ns}$), 7.21 (dd, *J* = 7.9, 1.5 Hz, 1 H, $C^{3''}H_{Ns}$), 7.31 – 7.47 (m, 11 H, $CH_{Ph}/C^{5''}H_{Ns}$), 7.66 (dd, *J* = 8.0, 1.0 Hz, 1 H, $C^{6''}H_{Ns}$), 9.08 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (+, CH_3), 67.1 (q, CR_4), 70.1 (–, OCH_2), 102.6 (+, $C^{4'}{}_{ar}H$), 107.4 (+, $C^{2'}{}_{ar}H$), 124.6 (+, $C^{3''}{}_{Ns}H$), 127.6 (+, Bn-$C^{2'''}{}_{ar}H$), 128.4 (+, Bn-$C^{4'''}{}_{ar}H$), 128.8 (+, Bn-$C^{3'''}{}_{ar}H$), 130.2 (+, $C^{6''}{}_{Ns}H$), 132.1 (+, $C^{4''}{}_{Ns}H$), 132.7 (+, $C^{5''}{}_{Ns}H$), 135.2 (q, $C^{1''}{}_{Ns}SO_2$), 135.6 (q, $\underline{C^{1'}}{}_{ar}CR_3$), 136.3 (q, $\underline{C^{1'''}}{}_{ar}CH_2$), 147.3 (q, $C^{2''}{}_{Ns}NO_2$), 160.2 (q, $C^{3'}{}_{ar}O$), 193.0 (+, CHO) ppm. – MS (EI, II, 70 eV): *m/z* (%) = 517 (69) [M^+–CHO], 317 (33) [M^+–CO–NHNs], 268 (15) [M^+–Bn–Ns], 181 (9), 91 (100) [$C_7H_7^+$]. – HRMS (II): calcd.: 517.1433 (M^+–CHO), found: 517.1427. – $[\alpha]_D^{20}$ = +136.3° (c = 0.27, $CHCl_3$).

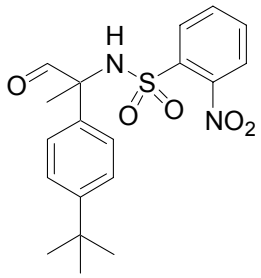
Determination of enantiomeric excess of 40 as Mosher's-Ester:



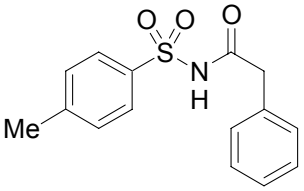
*(2*S*)-2'-(2'',5''-Dimethoxyphenyl)-2'-(2'''-nitrobenzene)-sulfonylaminopropyl 2-methoxy-2-trifluoromethylphenyl-acetate*: The reaction was carried out following GP 2.[l] – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.66, **1.72** (2 × s, 3 H, CR_3CH_3), **3.49**, 3.50 (2 × d, *J* = 1.2 and 0.9 Hz, 3 H, OCH_3), 4.55, **4.59** (2 × d, *J* = 11.5 and 11.3 Hz, 1 H, $CR_3C\underline{H}HO$), **4.78**,

[k] Due to poor resolution of the ^{19}F NMR signals the diastereomeric excess was determined by HPLC.
[l] According to NMR spectroscopy the product mainly consists of unreacted alcohol (ratio alcohol/ester approx. 1.3:1).

4.80 (2 × d, J = 11.3 and 11.7 Hz, 1 H, $CR_3CH\underline{H}O$), **4.81** (s, 4 H, $C_{ar}CH_2O$), 5.90, **5.93** (2 × bs, 1 H, NH), **6.35** (dd, J = 2.1, 2.1 Hz, 1 H, $C^{4''}H_{ar}$), **6.49** (d, J = 2.3 Hz, 2 H, $C^{2''}H_{ar}$), 7.28 – 7.46 (m, 16 H, CH_{ar}), 7.46 – 7.57 (m, 2 H, CH_{ar}), **7.70** (ddd, J = 8.0, 7.3, 0.9 Hz, 1 H, CH_{Ns}) ppm. – ^{19}F NMR (300 MHz, $CDCl_3$): δ = **–71.92**, –71.88 ppm. The diastereomeric excess was 72% *de*.

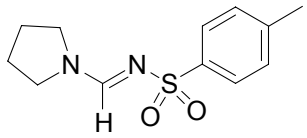


(+)-2-(4'-tert-*butylphenyl)-2-(2''-nitrobenzene)sulfonylaminopropionaldehyde* **41**: The reaction was carried out following GP 1, Method A, using 2-(4'-*tert*-butylphenyl)propionaldehyde (**27**, 95.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 125.5 mg, 0.55 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in absolute ethanol (10 ml) within 1 d. Flash chromatography on silica with cyclohexane/ethyl acetate 5:1 delivered a yellow oil (107.5 mg, 0.275 mmol) in 55% yield and 61 ± 3% *ee*. – mp = 138 – 140 °C. – R_f = 0.37 (cyclohexane/ethyl acetate 5:1). – HPLC (Chiralpak AS, *n*-heptane/isopropanol 80:20, 0.5 ml/min): R_t(maj) = 31.5 min, R_t(min) = 43.5 min. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (s, 9 H, $C(CH_3)_3$), 2.02 (s, 3 H, CH_3), 7.06 (d, J = 8.7 Hz, 2 H, $C^{3'}H_{ar}$), 7.11 (d, J = 8.8 Hz, 2 H, $C^{2'}H_{ar}$), 7.15 – 7.22 (m, 2 H, $C^{5''}H_{Ns}$/$C^{6''}H_{Ns}$), 7.49 (ddd, J = 8.0, 6.5, 2.5 Hz, 1 H, $C^{4''}H_{Ns}$), 7.74 (dd, J = 7.9, 0.6 Hz, 1 H, $C^{3''}H_{Ns}$), 9.10 (s, 1 H, CHO) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (+, CH_3), 31.3 (+, $C(\underline{C}H_3)_3$), 34.6 (q, $\underline{C}(CH_3)_3$), 66.9 (q, CR_4), 124.9 (+, $C^{3''}{}_{Ns}H$), 125.8 (+, $C^{3'}{}_{ar}H$), 127.6 (+, $C^{2'}{}_{ar}H$), 130.1 (q, $\underline{C^{1'}}_{ar}CR_3$), 130.3 (+, $C^{6''}{}_{Ns}H$), 132.3 (+, $C^{4''}{}_{Ns}H$), 132.6 (+, $C^{3''}{}_{Ns}H$), 135.4 (q, $C^{1''}{}_{Ns}SO_2$), 147.4 (q, $\underline{C^{4'}}_{Ar}C(CH_3)_3$), 152.4 (q, $C^{2''}{}_{Ns}NO_2$), 193.4 (+, CHO) ppm. – MS (FAB): *m/z* (%) = 391 (12) [M^++1], 361 (80) [M^+–CHO], 345 (10) [M^++1–NO_2], 189 (47) [$C_{13}H_{17}O^+$], 186 (61) [$C_6H_4NO_4S^+$], 161 (100) [$C_{12}H_{17}^+$]. – $C_{19}H_{22}N_2O_5S$ (390.45 g/mol), calcd.: C 58.45, H 5.68, N 7.17, S 8.21, found: C 58.42, H 5.66, N 6.96, S 8.22. – IR (KBr): 3326.5 (m, ν[NH]), 3054.5 (w, ν[CH_{ar}]), 1718.5 (m, ν[C=O]), 1593.4 (m, ν[C-C_{ar}]), 1540.1 (m, ν_{as}[NO_2]), 1509.1 (m, ν[C-C_{ar}]), 1365.3 (m, ν_{as}[SO_2]), 1340.1 (m, ν_{sy}[NO_2]), 1270.6 (m, ν_{as}[C-O-C]), 1119.6 (m, ν_{sy}[SO_2]), 1058.0 (m, ν_{sy}[C-O-C]) cm^{-1}. – $[\alpha]_D^{20}$ = +198.3° (c = 0.300, $CHCl_3$).



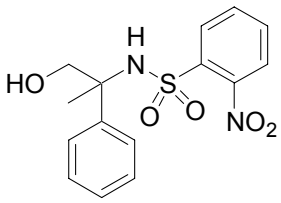
4-Toluene-N-*phenylacetyl sulfonamide* **43**:[12] The reaction was carried out following GP 1, Method A, using phenylacetaldehyde (**42**, 60.1 mg, 0.50 mmol), 4-toluenesulfonyl azide (**2a**, 118.3 mg, 0.60 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) within 1 d. Flash chromatography with *n*-pentane/diethylether 3:1 delivered **43** (38.3 mg, 0.132 mmol) in 26% yield. – R_f = 0.24 (*n*-pentane/diethylether 2:1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 4.46 (d, *J* = 4.5 Hz, 2 H, CH_2), 5.65 (bs, 1 H, NH), 7.28 (d, *J* = 8.1 Hz, 2 H, C^2H_{Ts}), 7.46 (ddd, *J* = 7.9, 7.3, 1.1 Hz, 2 H, $C^{3'}H_{Ph}$), 7.60 (ddd, *J* = 7.6, 7.3, 1.3 Hz, 1 H, $C^{4'}H_{Ph}$), 7.78 (d, *J* = 8.3 Hz, 2 H, C^3H_{Ts}), 7.85 (d, *J* = 7.5 Hz, 2 H, $C^{2'}H_{Ph}$) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (+, CH_3), 48.8 (–, CH_2), 127.3 (+, CH_{ar}), 128.0 (+, CH_{ar}), 129.1 (+, CH_{ar}), 130.0 (+, CH_{ar}), 134.0 (q, $\underline{C}^{1'}{}_{Ph}CH_2$), 134.5 (+, $C^{4'}{}_{Ph}H$), 136.3 (q, $C^1{}_{Ts}SO_2$), 143.8 (q, $\underline{C}^4{}_{Ts}CH_3$), 192.7 (q, CO) ppm.

Isolation of byproduct in the reaction of 2-phenylpropionaldehyde and tosyl azide catalyzed by pyrrolidine:

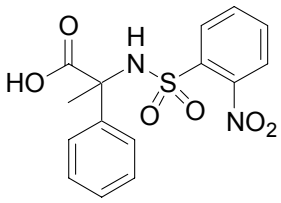


4-Methyl-N-(1-pyrrolidinylmethylene)-benzenesulfonamide **51**: Reaction was carried out following GP 1, Method A, using **1** (134.2 mg, 1.00 mmol), 4-toluenesulfonyl azide (**2a**, 236.7 mg, 1.20 mmol), and pyrrolidine (**5**, 71.1 mg, 1.00 mmol) in ethanol (10 ml). Flash chromatography on silica with ethyl acetate delivered **51** (106 mg, 0.42 mmol) as a colourless solid in 42% yield.[m] – mp = 140 °C. – R_f = 0.29 (ethyl acetate). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.87 (m, 4 H, 2 CH_2), 2.32 (s, 3 H, Ts-CH_3), 3.39 (bt, *J* = 6.5 Hz, 2H, CH_2), 3.51 (bt, *J* = 6.5 Hz, 2H, CH_2), 7.18 (d, *J* = 8.2 Hz, 2 H, CH_{Ts}), 7.71 (d, *J* = 8.3 Hz, 2 H, CH_{Ts}), 8.25 (s, 1 H, CH=N) ppm. – ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.4 (+, Ts-CH_3), 24.2 (–, CH_2), 24.9 (–, CH_2), 46.3 (–, CH_2), 49.8 (–, CH_2), 126.4 (+, $C_{ar}H$), 129.2 (+, $C_{ar}H$), 139.5 (q, $C_{ar}SO_2$), 142.2 (q, $\underline{C}_{ar}CH_3$), 155.7 (+, CH=N) ppm. – MS (EI, I, 70 eV), *m/z* (%) = 252 (42) [M^+], 155 (3) [$C_7H_7SO_2^+$], 97 (52) [M^+–$C_7H_7SO_2$], 91 (28) [$C_7H_7^+$], 77 (18) [$C_6H_5^+$], 70 (64) [$C_4H_8N^+$], 58 (44) [$C_3H_8N^+$], 43 (100) [$C_3H_7^+$]. – HRMS (I): calcd.: 252.0932 [M^+], found: 252.0928. – $C_{12}H_{16}N_2O_2S$ (252.33 g/mol), calcd.: C 57.12, H 6.39, N 11.10, S 12.71, found: C 57.36, H 6.28, N 10.93, S 12.88. – IR (KBr): 3043.0 (w, υ[CH_{ar}]), 2979.6 (m, υ[CH_3]), 2887.4 (w, υ[CH_3]), 1615.9 (m, υ[C=NR]), 1494.0 (vw, υ[C–C_{ar}]), 1456.3 (w, δ_{as}[CH_3]), 1349.0 (w, δ_{sy}[CH_3]), 1315.9 (m, υ_{as}[SO_2]), 1187.6 (w, υ_{sy}[SO_2]) cm^{-1}.

[m] **4a** was obtained in 36% yield.

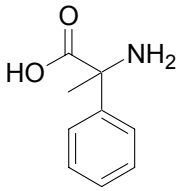


2-(2'-Nitrobenzene)sulfonylamino-2-phenylpropanol **57**: The reaction was carried out following GP 1, Method A, using **1** (67.1 mg, 0.50 mmol), 2-nitrobenzenesulfonyl azide (**2b**, 114.1 mg, 0.50 mmol), and L-proline (**3**, 57.6 mg, 0.50 mmol) in ethanol (10 ml). After the reaction was completed, the reaction mixture was treated with sodium borohydride (26.5 mg, 0.7 mmol) and stirred for 2 h. The solvent was then removed by evaporation under reduced pressure. Flash chromatography on silica with ethyl acetate/cyclohexane 2:3 delivered a colourless solid (45.5 mg, 0.135 mmol) in 27% yield. – mp = 123 °C. – R_f = 0.21 (ethyl acetate/cyclohexane 2:3). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.76 (s, 3 H, CH_3), 2.20 (bs, 1 H, OH), 3.76 (d, *J* = 11.3 Hz, 1 H, CH_2), 3.94 (d, *J* = 11.3 Hz, 1 H, CH_2), 6.24 (s, 1 H, NH), 7.10 – 7.17 (m, 3 H, *m,p*-CH_{Ph}), 7.29 – 7.36 (m, 2 H, *o*-CH_{Ph}), 7.40 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1 H, C^5H_{Ns}), 7.50 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1 H, C^6H_{Ns}), 7.52 (dd, *J* = 8.0, 1.4 Hz, 1 H, C^4H_{Ns}), 7.78 (dd, *J* = 8.0, 1.2 Hz, 1 H, C^3H_{Ns}) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (+, CH_3), 62.8 (q, CR_4), 70.6 (–, CH_2), 125.0 (+. C^3H_{Ns}), 126.4 (+, *m*-CH_{Ph}), 127.9 (+, *p*-CH_{Ph}), 128.4 (+, *o*-CH_{Ph}), 130.5 (+, C^6H_{Ns}), 132.6 (+, C^4H_{Ns}), 132.9 (+, C^5H_{Ns}), 136.0 (q, C-SO_2), 140.9 (*i*-C_{Ph}), 147.6 (C-NO_2) ppm. – MS (FAB): *m/z* (%) = 337 (33) [M^++1], 307 (100), 305 (29) [M^+–CH_2OH], 289 (61), 203 (31) [$C_6H_7N_2O_4S^+$], 186 (55) [$C_6H_5NO_4S^+$], 165 (25). – MS (EI, II, 70 eV): *m/z* (%) = 305 (22) [M^+–CH_2OH], 202 (12) [$C_6H_6N_2O_4S^+$], 186 (100) [$C_6H_4NSO_4^+$], 77 (4) [$C_6H_5^+$]. – HRMS (I): calcd.: 305.0596 [M^+–CH_2OH], found: 305.0603.



2-(2'-Nitrobenzene)sulfonylamino-2-phenylpropionic acid **58**:[13] A solution of potassium dihydrogenphosphate (115.7 mg, 0.85 mmol) in water (1.4 ml) was added to a solution of **4b** (114.2 mg, 0.34 mmol) in acetonitrile (5 ml). Addition of a 35% aqueous hydrogen peroxide solution (32.5µl, 0.38 mmol) to the mixture at 0 °C was followed by dropwise addition of a solution of sodium chlorite (43.4 mg, 0.48 mmol) in water (2 ml). After 1 h of stirring at 0 °C, another 16 µl (0.19 mmol) of hydrogen peroxide solution were added and the mixture stirred in the melting ice bath for 16 h. The reaction was then quenched by addition of sodium sulfite, stirred for 30 min and treated with 0.5N hydrochloric acid (10 ml). The mixture was extracted three times with dichloromethane (15 ml, 5 ml, and 5 ml), the combined organic phases were washed with brine and dried over sodium sulfate. Removal of the solvent by evaporation delivered a colourless solid (109.7 mg, 0.313 mmol) in 92%

yield. – mp = 188 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, CH_3), 7.00 – 7.15 (m, 4 H, *o,p*-CH_{Ph}), 7.24 – 7.35 (m, 3 H, *p*-CH_{Ph}, C^5H_{Ns}, C^6H_{Ns}), 7.60 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1 H, C^4H_{Ns}), 7.80 (dd, *J* = 8.1, 1.1 Hz, 1 H, C^3H_{Ns}) ppm. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (+, CH_3), 65.3 (q, CR_4), 125.9 (+, C^3H_{Ns}), 127.7 (+, *m*-C_{Ph}), 129.2 (+, *o*-C_{Ph}), 129.4 (+, *p*-CH_{Ph}), 130.9 (+, C^6H_{Ns}), 133.6 (+, C^4H_{Ns}), 134.1 (+, C^5H_{Ns}), 136.2 (q, C-SO_2), 139.3 (q, *i*-C_{Ph}), 148.7 (q, C-NO_2), 175.5 (q, COOH) ppm. – MS (FAB): *m/z* (%) = 351 (4) [M^++1], 307 (100), 289 (52), 165 (17). – MS (EI, II, 70 eV): *m/z* (%) = 305 (100) [M^+–CO_2H], 186 (88) [$C_6H_4NSO_4^+$], 104 (10) [$C_8H_8^+$], 77 (9) [$C_6H_5^+$].– HRMS (I): calcd.: 305.0596 (M^+–CO_2H), found: 305.0596.



α-Methylphenylglycine **59**:[14,15] A solution of **58** (104.0 mg, 0.30 mmol) in 5 ml of 1,4-dioxane was treated with a 25–30% methanolic solution of sodium methylate (0.1 ml) and stirred for 2 h. Addition of sodium methylate solution (0.1 ml) was repeated and the reaction mixture stirred for 18 h. The solvent was then removed by evaporation, the residue dissolved in 1M hydrochloric acid and the acidic solution washed three times with dichloromethane. The aqueous phase was dried and the residue taken up in methanol. After filtration, the solvent was removed by evaporation. Purification by ion exchange chromatography using Dowex 50WX8-100 and aqueous 1.4M ammonia solution delivered **59** as a colourless solid in quantitative yield. – ^{1}H NMR (400 MHz, CD_3OD): δ = 1.85 (s, 3 H, CH_3), 7.25 – 7.55 (m, 5 H, CH_{Ph}) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (CH_3), 62.7 (CR_3N), 126.9 ($C_{ar}H$), 130.4 ($C_{ar}H$), 130.7 ($C^4_{ar}H$), 137.5 ($\underline{C}^1_{ar}CR_2N$), 173.1 ($CO_2H$) ppm.

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[1] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *Org. Chem.* **1997**, *62*, 7512–7515.
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