DOI: 10.1002/ejoc.201000111

Reductive Ring-Opening of Phthalan and Isochroman: Application to the Stereoselective Synthesis of Tetrahydroisoquinolines and Tetrahydrobenzazepines

Daniel García,[a] Francisco Foubelo,*[a] and Miguel Yus*[a]

Dedicated to Professor Saverio Florio on the occasion of his 70th birthday

Keywords: Lithium / Lithiation / Zincates / Diastereoselectivity / Hydrolysis / Nitrogen heterocycles / Sulfinylimines

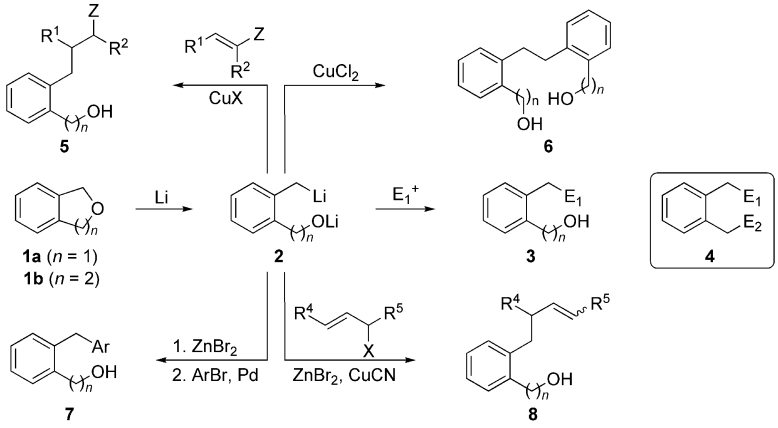
The reaction of the dianionic intermediates **2a**,**b** resulting from the lithiation of phthalan (**1a**) and isochroman (**1b**) with chiral *N*-*tert*-butylsulfinyl aldimines **9** in the presence of $ZnMe_2$ gave, after hydrolysis, *N*-*tert*-butylsulfinyl amino alcohols **10** and **13**, respectively, with high diastereoselectivity. Successive treatment of compounds **10** and **13** with hydrogen chloride in methanol, thionyl chloride in chloroform and sodium hydroxide led to the formation of tetrahydroisoquinolines **19** and tetrahydrobenzazepines **20**. Depending on the structure of the starting chiral imine **9**, benzoindolizidine **21**, benzoquinolizidine **22** and benzopyrroloazepine **23** are also accessible through this methodology.

Introduction

Functionalised organolithium compounds[1] are of interest in organic synthesis because their reactions with electrophiles yield polyfunctionalised molecules in a single process. Organolithium compounds can be prepared through a wide range of methodologies,[2] including by the reductive ring-opening of some heterocycles[3] such as strained heterocycles (three- and four-membered-ring heterocycles) and those bearing activated bonds (cyclic compounds with allylic and benzylic carbon–heteroatom bonds[4] as well as aryl ethers and thioethers). Lithium metal is the lithiating reagent in these electron-transfer processes,[5] either alone or in the presence of an arene in a stoichiometric or catalytic amount.[6] Phthalan (**1a**)[7] and isochroman (**1b**)[8] can be regarded as special kinds of cyclic benzyl ethers. These heterocycles are opened reductively with lithium and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB) at 0 °C to afford dianions **2** which have found widespread use in organic synthesis. Thus, the reactions of these intermediates with different electrophiles lead after hydrolysis to functionalised alcohols **3**.[9] In the case of phthalan (**1a**), it is possible to introduce two different electrophiles at both benzylic positions in a sequential manner by performing a double lithiation to give compounds of type **4**.[7a] The reactivity of organolithium intermediates **2** can be modulated by exchanging lithium by another metal. For instance, conjugate addition products **5** are obtained upon reaction of electrophilic olefins with dianions **2** in the presence of copper(I) salts and dimerisation leading to compounds **6** occurs with copper(II) chloride.[10] Also, compounds **7**[11] have been prepared by the palladium-catalysed Negishi cross-coupling reaction of aryl bromides and the in situ generated organozinc reagents resulting from a lithium–zinc transmetallation of intermediates **2** with zinc bromide. Another synthetically useful finding is the reaction of intermediates **2** with an equimolecular amount of zinc bromide and copper cyanide followed by treatment with different allylic chlorides or bromides to give almost exclusively the corresponding alcohols **8**[12] resulting from an S_N2' displacement in a highly regioselective manner (Scheme 1).

We considered it of interest to study the reactivity of the anionic intermediates **2** [resulting from the reductive ring-opening of phthalan (**1a**) and isochroman (**1b**)] with chiral *N*-*tert*-butylsulfinylimines as electrophiles in order to apply this methodology to the synthesis of substituted nitrogen-containingheterocyclessuchastetrahydroisoquinolines[13]and -benzazepines. These electrophilic reagents have found many applications in synthesis[14] due to the possibility of preparing both their enantiomers[15] and also because the chiral auxiliary can be easily removed under acidic conditions.[16] In addition, practical processes for recycling the *tert*-butylsulfinyl group upon deprotection of *N*-*tert*-butylsulfinylamines have been reported recently, making this chiral auxiliary of interest for large-scale industrial processes.[17] Tetrahydroisoquinolines are present in many natural products[18] that display antitumour and antimicrobial

[a] Departamento de Química Orgánica, Facultad de Ciencias and Instituto de Síntesis Orgánica (ISO), Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain
Fax: +34-965-903-549
E-mail: foubelo@ua.es; yus@ua.es



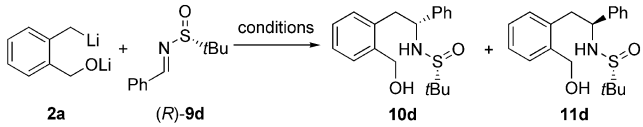
Scheme 1. Synthetic applications of the dianionic species **2** resulting from the reductive ring-opening lithiation of phthalan (**1a**) and isochroman (**1b**).

activities. For this reason the asymmetric synthesis of substituted tetrahydroisoquinolines[19] is of great interest for synthetic organic chemists. With regard to tetrahydrobenzazepines, 1- and 4-substituted 2,3,4,5-tetrahydro-1*H*-benzazepines[20] are dopamine receptor agonists and antagonists[21] and also promising candidates for combating neurological disorders such as Parkinson's[22] and Alzheimer's disease.[23]

Results and Discussion

Dianionic intermediate **2a** was prepared by the treatment of phthalan (**1a**) with an excess of lithium (1:10 molar ratio) and a catalytic amount of DTBB (5 mol-%) in THF at 0 °C for 40 min. After removing the excess lithium by filtration at room temperature, a THF solution of the chiral aldimine (*R*)-**9d** [easily prepared from benzaldehyde and (*R*)-*tert*-butylsulfinamide][24] was added to the resulting solution of the functionalised organolithium compound **2a** at –78 °C and the reaction mixture was allowed to warm to room temperature over 12 h. Final hydrolysis led to a mixture of the diastereomeric *N*-*tert*-butylsulfinylamino alcohols **10d** and **11d** in a 78:22 ratio, the major diastereoisomer **10d** being isolated in a yield of 47% (Table 1, entry 1). Different additives and reaction conditions were applied to improve both the diastereoselectivity and yield of the reaction. It has previously been reported that the yields and diastereoselectivities of the reactions of organolithium compounds with ketimines are improved in the presence of $AlMe_3$.[16] For this reason, $AlMe_3$ was added to a THF solution of intermediate **2a** and the mixture was stirred for 15 min at room temperature prior to the addition of aldimine (*R*)-**9d** at –65 °C. Under these reaction conditions, amino alcohol derivatives **10d** and **11d** were obtained with a higher diastereoselectivity (95:5 *dr*) but in a very low yield due to a poor conversion (Table 1, entry 2). The yield increased to 42% when the reaction was performed with the same additive at –55 °C and the organolithium intermediate **2a** was added to a solution of aldimine (*R*)-**3** and $AlMe_3$ (an inverse addition), however, the diastereomeric ratio was in this case 69:31 (Table 1, entry 3). We recently found that dialkylzincs do not react with *N*-*tert*-butylsulfinylimines, but the reaction with triorganozincates gave the expected α-branched sulfinamides in good-to-excellent yields with diastereomeric

Table 1. Screening and optimisation of the reaction conditions for the reaction of oranolithium **2a** and aldimine (*R*)-**9d**.[a]



Entry	Additive (1.1 equiv.)	Conditions *T* [°C] (time [h])	Hydrolysis temp. [°C]	Product Yield [%][b]	**10d/11d**[c]
1	–	–78 to 20 (12)	–78 to 20	47	78:22
2	$AlMe_3$	–65 (12)	–65 to 20	25	95:5
3	$AlMe_3$	–55 (12)	–55 to 20	42	69:31
4	$ZnMe_2$	–65 (12)	–65 to 20	78	86:14
5	$ZnMe_2$	–30 (12)	–30 to 20	69	83:17
6	$ZnMe_2$	–5 (12)	–5 to 20	61	67:33
7	$ZnEt_2$	–65 (12)	–65 to 20	27[d]	63:37

[a] Intermediate **2a** was prepared from phthalan (**1a**; 3 equiv.). [b] Yield of the major reaction product **10d** based on the starting aldimine (*R*)-**9d**. [c] The diastereomeric mixture was determined by ^1H NMR analysis of the crude reaction mixture. [d] Sulfinamide **12** was obtained in 37% yield.

ratios of up to 98:2.[25] Thus, when $ZnMe_2$ was used as an additive, the reaction of the resulting mixed organozincate with aldimine (*R*)-**9d** at –65 °C for 12 h gave, after hydrolysis, the expected mixture of amino alcohols **10d** and **11d** in 78% yield and 86:14 ratio (Table 1, entry 4). The yields and stereoselectivities were lower when the process was performed with the same additive at –30 and –5 °C (Table 1, entries 5 and 6). A mixture of the expected compounds **10d** and **11d** and the sulfinamide **12** (Figure 1) was also obtained when $ZnEt_2$ was used instead of $ZnMe_2$. Compound **12** results from the addition of the ethyl group to the imine (Table 1, entry 7). For the resulting mixed zincate, in this case there is competition between the benzyl and ethyl groups to be transferred because both are transferable. However, in the case of $ZnMe_2$, and due to the slow transfer rate of the methyl group, it can be used as a non-transferable group in these processes. The stereochemistry of the major isomer **10d** was unambiguously determined by single-crystal X-ray analysis and the structure obtained showed that the configuration of the new stereogenic centre was *R* (Figure 1). This result is consistent with an approach of the nucleophile to the less hindered *re* face of C=N in a s-*cis*-like conformation. Theoretical calculations[26] support the view that it is the most stable conformation of the two-fold Lewis acid (there is a large excess of lithium cations and organozinc compounds) coordinated (*R*)-sulfinyl aldimine (Figure 1).

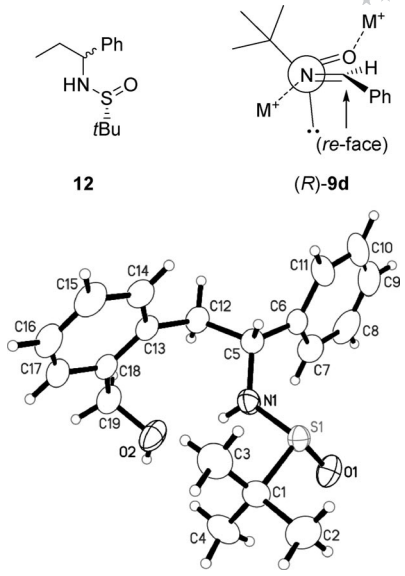
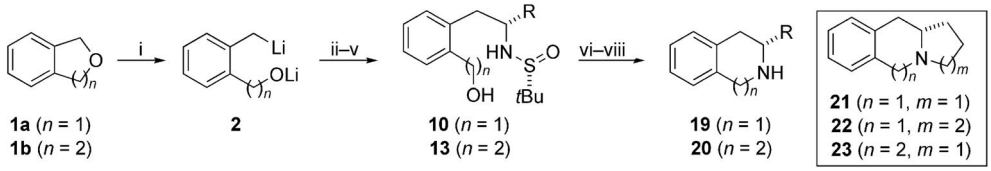


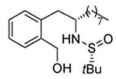
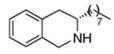
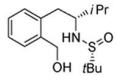
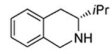
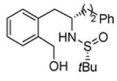
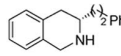
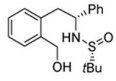
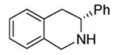
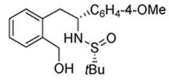
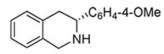
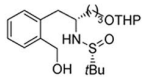
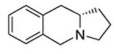
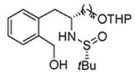
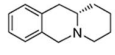
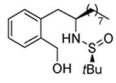
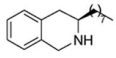
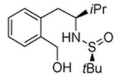
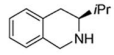
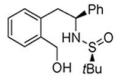
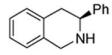
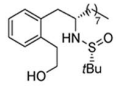
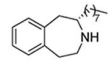
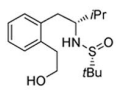
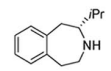
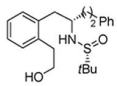
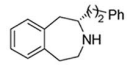
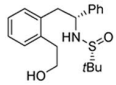
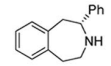
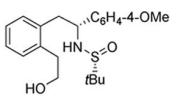
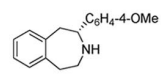
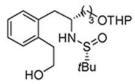
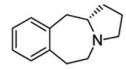
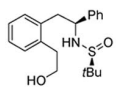
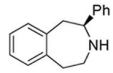
Figure 1. Structure of compound **12**, the most stable conformation of (*R*)-**9d** and X-ray crystal structure of **10d**.

The dianionic intermediate **2a** was then treated with different chiral *N*-sulfinyl aldimines **9** under the optimised conditions (Table 1, entry 4). Compounds **10** were obtained in good-to-moderate yields (Scheme 2, Table 2, entries 1–10) and diastereomeric ratios ranging between 71:29 and 87:13 (Table 2, entries 9 and 3, respectively). The major diastereomers were easily isolated after column chromatography and fully characterised in all cases. Aiming to broaden the scope of this tandem reductive ring-opening lithiation–transmetallation reaction with chiral *N*-*tert*-butylsulfinyl aldimines **9**, we studied the process with isochroman (**1b**). Under the same reaction conditions, the expected *N*-*tert*-butylsulfinylamino alcohol derivatives **13** were generally obtained in fairly good yields (Scheme 2, Table 2, entries 11–17). In all cases we assume that the nucleophilic attack occurs predominantly on the *re* face of the imine unit with R_S isomers (Table 2, entries 1–7 and 11–16) and on the *si* face in the case of S_S derivatives (Table 2, entries 8–10 and 17), which are the less hindered faces of the imines according to the most stable proposed *s*-*cis* conformation (Figure 1). The *tert*-butylsulfinyl group was easily removed from compounds **10** and **13** after treatment with a 4 M HCl/dioxane solution in methanol to give amino alcohols of general structure **14** and **15** (Figure 2) in almost quantitative yields for the phthalan (**1a**) and isochroman (**1b**) derivatives, respectively. Under these acidic reaction conditions, the tetrahydropyranyl group was also removed and amino diols **16**, **17** and **18** (Figure 2) were obtained from compounds **10f**, **10g** and **13f**, respectively (Table 2, entries 6, 7 and 16, respectively). The successive treatment of amino alcohols **14**–**18** with thionyl chloride in chloroform at 50 °C and then with a 5 M aqueous solution of sodium hydroxide in THF at room temperature led to nitrogen-containing heterocycles through an intramolecular dehydration process (Scheme 2 and Table 2).[27] In this way, tetrahydroisoquinolines **19** were prepared in situ from amino alcohols **14** (Table 2, entries 1–5 and 8–10), whereas the homologous amino alcohols **15** led to tetrahydrobenzazepines **20** (Table 2, entries 11–15 and 17). Interestingly, amino diols **16**–**18** underwent a double dehydration reaction leading to benzoindolizidine **21**, benzoquinolizidine **22** and benzopyrroloazepine **23**, respectively (Table 2, entries 6, 7, and 16, respectively). The *ee* values of the heterocycles **19**–**23** were determined by chiral HPLC analysis and in all cases were obtained with a purity in excess of 95%.



Scheme 2. Reagents and conditions: (i) Li, DTBB (5 mol-%), THF, 0 °C, 40 min; (ii) filtration; (iii) $ZnMe_2$, 20 °C, 15 min; (iv) RCH=NS(O)*t*Bu (**9**), –65 °C, 12 h; (v) H_2O, –65 to 20 °C; (vi) 4 M HCl/dioxane, MeOH, 20 °C; (vii) Cl_2SO, $CHCl_3$, 50 °C; (viii) 5 M $NaOH/H_2O$, THF, 20 °C.

Table 2. Preparation of nitrogen-containing heterocycles **19**–**23**.

Entry	Starting heterocycle	Aldimine **9**	R	Compounds **10** and **13**[a]		Yield (%)[c]	*dr*[d]	Heterocyclic compounds **19**–**23**[a,b]		Yield (%)[e]
1	**1a**	(*R*)-**9a**	$CH_3(CH_2)_7$	**10a**		79	85:15	**19a**		80
2	**1a**	(*R*)-**9b**	*i*Pr	**10b**		69	77:23	**19b**		78
3	**1a**	(*R*)-**9c**	$Ph(CH_2)_2$	**10c**		71	87:13	**19c**		79
4	**1a**	(*R*)-**9d**	Ph	**10d**		78	86:14	**19d**		72
5	**1a**	(*R*)-**9e**	4-$OMeC_6H_4$	**10e**		92	95:5	**19e**		95
6	**1a**	(*R*)-**9f**	$THPO(CH_2)_3$	**10f**		80	83:17	**21**		60
7	**1a**	(*R*)-**9g**	$THPO(CH_2)_4$	**10g**		72	82:18	**22**		55
8	**1a**	(*S*)-**9a**	$CH_3(CH_2)_7$	*ent*-**10a**		55	85:15	*ent*-**19a**		76
9	**1a**	(*S*)-**9b**	*i*Pr	*ent*-**10b**		57	71:29	*ent*-**19b**		68
10[f]	**1a**	(*S*)-**9d**	Ph	*ent*-**10d**		54	77:23	*ent*-**19d**		62
11	**1b**	(*R*)-**9a**	$CH_3(CH_2)_7$	**13a**		77	86:14	**20a**		70
12	**1b**	(*R*)-**9b**	*i*Pr	**13b**		80	95:5	**20b**		61
13	**1b**	(*R*)-**9c**	$Ph(CH_2)_2$	**13c**		79	91:9	**20c**		81
14	**1b**	(*R*)-**9d**	Ph	**13d**		90	95:5	**20d**		82
15	**1b**	(*R*)-**9e**	4-$OMeC_6H_4$	**13e**		92	95:5	**20e**		60
16	**1b**	(*R*)-**9f**	$THPO(CH_2)_3$	**13f**		54	91:9	**23**		51
17	**1b**	(*S*)-**9d**	Ph	*ent*-**13d**		54	77:23	*ent*-**20d**		60

[a] Products **10**, **13** and **19**–**23** were ≥95% pure (GLC and 300 MHz ^{1}H NMR). [b] *ee* ≥ 95%, as determined by HPLC using a ChiralCel OJ column. [c] Isolated yield of the major diastereoisomer based on the starting aldimine **9**. [d] Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. [e] Isolated yield from compounds **10** and **13**. [f] The reaction was performed in the absence of $ZnMe_2$ as additive.

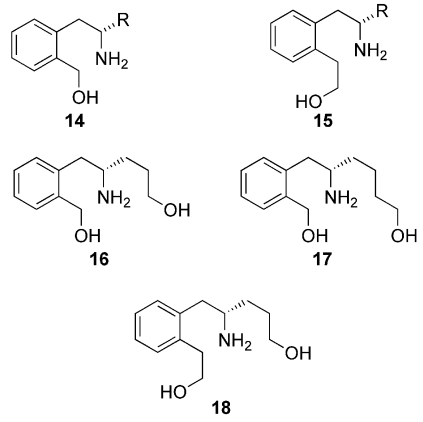


Figure 2. Structures of amino alcohols **14**–**18**.

Conclusions

We have reported herein a straightforward synthesis of substituted tetrahydroisoquinolines **19**, tetrahydrobenzazepines **20**, benzoindolizidine **21**, benzoquinolizidine **22** and benzopyrroloazepine **23** with high enantiomeric purity starting from phthalan (**1a**) or isochroman (**1b**) and chiral *N*-*tert*-butylsulfinyl aldimines **9** by a strategy of two one-pot processes: 1) reaction of the dianionic intermediate **2** (resulting from reductive ring-opening of the corresponding heterocycle **1**) with chiral aldimines **9** in the presence of $ZnMe_2$ and 2) cyclisation of the amino alcohol resulting from the removal of the *tert*-butylsulfinyl unit. The configurations of the chiral heterocycles were determined from those of the starting chiral aldimines **9** and thus both enantiomeric heterocycles are accessible through this methodology by choosing the appropriate starting chiral aldimine **9**.

Experimental Section

General: All reactions requiring anhydrous conditions were performed in oven-dried glassware under argon. Unless otherwise indicated, all commercially available chemicals were purchased from Acros or Aldrich and used without purification. *N*-*tert*-Butanesulfinamides (S_S and R_S) were a gift from Medalchemy (>99% *ee* by chiral HPLC on a Chiracel AS column, 90:10 *n*-hexane/*i*PrOH, 1.2 mL/min, λ = 222 nm). *N*-*tert*-Butanesulfinylimines were prepared from freshly distilled aldehydes and *N*-*tert*-butanesulfinamides (S_S and R_S, >99% *ee*) following a previously reported procedure with $CuSO_4$.[28] TLC was performed on Merck silica gel 60 F_{254} using aluminium plates and visualised with phosphomolybdic acid (PMA) stain. Chromatographic purification was performed by flash chromatography using Merck silica gel 60 (0.040–0.063 mm) and *n*-hexane/EtOAc as eluent.

IR spectra were recorded (film) with a Nicolet Impact 510 P-FT spectrometer. Melting points were measured with an OptiMelt (Stanford Research Systems) apparatus using open-glass capillaries. HPLC analyses were performed on a JASCO 200-series instrument equipped with a Chiralcel-OJ column. Gas chromatographic analyses (GLC) were determined with a Hewlett–Packard HP-5890 instrument equipped with a flame-ionisation detector (FID) and a 12 m capillary column (0.2 mm diameter, 0.33 μm film thickness) using nitrogen (2 mL/min) as a carrier gas with $T_{injector}$ = 275 °C, $T_{detector}$ = 300 °C, T_{column} = 60 °C (3 min) and 60–270 °C (15 °C/min), and P = 40 kPa as routine working conditions. ^{1}H NMR spectra were recorded with a Bruker AC-300 spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. The data is reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br. s = broad signal, coupling constant(s) in Hz, integration. ^{13}C NMR spectra were recorded with proton-decoupling with a Bruker 75 MHz spectrometer and DEPT-135 experiments were performed to assign CH, CH_2 and CH_3. Optical rotations were measured with a Perkin–Elmer 341 polarimeter (concentration is given in g/100 mL, solvent). HRMS (EI) were recorded with a Finnigan MAT 95S spectrometer.

Typical Procedure for the Diastereoselective Synthesis of Compounds 10 and 13: A solution of phthalan (**1a**, 360 mg, 3.0 mmol) or isochroman (**1b**, 402 mg, 3.0 mmol) was added dropwise to a blue suspension of lithium powder (140 mg, 20.0 mmol) and a catalytic amount of DTBB (80.0 mg, 0.3 mmol) in THF (5 mL) under argon and the mixture was stirred at 0 °C for 45 min. Then the excess lithium was filtered off (by cannula under argon and used a filter plate) and a solution of $ZnMe_2$ (3.0 mL, 1.0 M in hexane) was added dropwise. Stirring was continued for 15 min at room temperature. After that, the reaction mixture was cooled to –65 °C and a solution of the corresponding aldimine **9** (1.0 mmol) in THF (0.4 mL) was added dropwise. After 12 h at the same temperature, the reaction mixture was finally hydrolysed with water (5 mL), extracted with ethyl acetate (3×15 mL) once at room temp., dried with anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to yield pure products **10** and **13**.

(2*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(hydroxymethyl)phenyl]decan-2-amine (10a): Yellow oil; R_f = 0.21 (hexane/EtOAc, 1:1). $[\alpha]_D^{20}$ = +14 (c = 0.84, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3315, 3063, 3014, 2959, 2924, 2849 cm^{-1}. ^{1}H NMR: δ = 0.88 (t, J = 7.0 Hz, 3 H), 0.92 (s, 9 H), 1.23–1.39 (m, 10 H), 1.41–1.49 (m, 2 H), 1.62–1.72 (m, 1 H), 1.77–1.84 (m, 2 H), 2.85–2.89 (m, 2 H), 3.44 (br. s, 1 H), 4.25–4.46 (br. s, 2 H), 4.49 (d, J = 11.6 Hz, 1 H), 4.72 (d, J = 11.6 Hz, 1 H), 7.17–7.34 (m, 4 H) ppm. ^{13}C NMR: δ = 14.2, 22.5 (CH_3), 22.7, 26.2, 29.4, 29.7, 29.8, 32.0, 37.8, 37.9 (CH_2), 56.3 (C), 59.0 (CH), 63.0 (CH_2), 126.5, 128.0, 129.7, 129.9, 138.3, 139.1 (ArC) ppm. MS: *m*/*z* (%) = 311 (2) [M – C_4H_8]$^+$, 293 (15), 244 (35), 190 (10), 142 (10), 133 (11), 132 (100), 119 (10), 117 (10), 104 (23), 91 (13), 57 (13). HRMS: calcd. $C_{17}H_{29}NSO_2$ [M – C_4H_8]$^+$ 311.1919; found 311.1913.

(2*R*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(hydroxymethyl)phenyl]-3-methylbutan-2-amine (10b): White solid; m.p. 87–88 °C (pentane/dichloromethane); R_f = 0.20 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = +33 (c = 0.57, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3258, 3069, 3020, 2955, 2916, 2872 cm^{-1}. ^{1}H NMR: δ = 0.86 (s, 9 H), 1.09 (t, J = 7.0 Hz, 6 H), 2.12–2.16 (m, 1 H), 2.77–2.90 (m, 2 H), 3.34–3.39 (m, 1 H), 4.54 (d, J = 11.3 Hz, 1 H), 4.71 (d, J = 6.8 Hz, 1 H), 4.78 (d, J = 11.3 Hz, 1 H), 7.14–7.22 (m, 3 H), 7.27–7.30 (m, 1 H) ppm. ^{13}C NMR: δ = 17.4, 18.9, 22.5 (CH_3), 32.7, 33.3 (CH_2), 56.4 (C), 63.1 (CH), 64.1 (CH_2), 126.4, 128.1, 2×129.8, 138.7, 139.0 (ArC) ppm. MS: *m*/*z* (%) = 241 (6) [M – C_4H_8]$^+$, 223 (29), 174 (47), 133 (18), 132 (100), 120 (14), 117 (18), 105 (10), 104 (16), 91 (15), 57 (20). HRMS: calcd. for $C_{12}H_{19}NO_2S$ [M – C_4H_8]$^+$ 241.1136; found 241.1137.

(2*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(hydroxymethyl)phenyl]-4-phenylbutan-2-amine (10c): White solid; m.p. 85–86 °C (pentane/dichloromethane); R_f = 0.19 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –8 (c = 0.61, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3261, 3060, 3025, 2925, 2865 cm^{-1}. ^{1}H NMR: δ = 0.97 (s, 9 H), 2.00–2.10 (m, 2 H), 2.12–2.22 (m, 2 H), 2.79–2.96 (m, 3 H), 2.99–3.04 (m, 1 H), 3.50–3.57 (m, 1 H), 3.92

(br. s, 1 H), 4.27 (d, J = 6.1 Hz, 1 H), 4.51 (d, J = 11.6 Hz, 1 H), 4.75 (d, J = 11.6 Hz, 1 H), 7.17–7.32 (m, 9 H) ppm. ^{13}C NMR: δ = 22.5 (CH_3), 32.0, 37.6, 39.1 (CH_2), 56.3 (C), 58.4 (CH), 63.0 (CH_2), 126.0, 126.4, 128.0, 128.5, 128.6, 129.6, 129.8, 138.1, 139.0, 141.7 (ArC) ppm. MS: m/z (%) = 303 (8) $[M - C_4H_8]^+$, 286 (10), 285 (51), 238 (12), 237 (25), 236 (74), 164 (10), 133 (20), 132 (100), 131 (10), 117 (35), 105 (14), 104 (13), 91 (79), 77 (12), 57 (22). HRMS: calcd. for $C_{21}H_{29}NO_2S$ 359.1919 $[M]^+$; found 359.1909.

(1*R*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-2-[2-(hydroxymethyl)phenyl]-1-phenylethanamine (10d): White solid; m.p. 129–130 °C (pentane/dichloromethane); R_f = 0.20 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –40 (c = 0.16, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3450–3310, 2920 cm^{-1}. ^{1}H NMR: δ = 1.00 (s, 9 H), 3.02 (dd, J = 13.6, 6.3 Hz, 1 H), 3.43 (dd, J = 13.6, 8.7 Hz, 1 H), 4.22 (br. s, 1 H), 4.48 (d, J = 11.5 Hz, 1 H), 4.59–4.65 (m, 1 H), 4.72 (d, J = 11.5 Hz, 1 H), 5.11 (br. s, 1 H), 7.10–7.15 (m, 1 H), 7.16–7.24 (m, 2 H), 7.23–7.32 (m, 4 H), 7.41 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR: δ = 22.5 (CH_3), 40.2 (CH_2), 56.3 (C), 60.9 (CH_2), 63.0 (CH), 126.8, 127.2, 127.8, 127.9, 128.5, 129.6, 130.3, 136.7, 139.0, 142.5 (ArC) ppm. MS (MALDI-TOF): m/z = 332 $[M + H]^+$. HRMS: calcd. for $C_{19}H_{23}NOS$ $[M - H_2O]^+$ 313.1500; found 313.1487.

Crystal Data of 10d: $C_{19}H_{25}NO_2S$, M = 331.46, monoclinic, a = 10.3893(9), b = 18.4104(16), c = 10.3906(9) Å, β = 106.513(2)°, V = 1905.5(3) Å^3, space group $P2(1)$, Z = 4, D_c = 1.155 Mg/m^3; λ = 0.71073 Å, μ = 0.179 mm^{-1}, $F(000)$ = 712, T = 23 ± 1 °C. Data collection was performed with a Bruker Smart CCD diffractometer based on three ω scans (starting = –34°) at ϕ = 0, 120 and 240° with the detector at 2θ = –32°. For each of these runs, 606 frames were collected at 0.3° intervals and 30 s per frame. An additional run at ϕ = 0° of 100 frames was collected to improve redundancy. The diffraction frames were integrated by using the program SAINT[29] and the integrated intensities were corrected for Lorentz/polarisation effects with SADABS.[30] The structure was solved by direct methods[31] and refined to all 7474 unique F_o by full-matrix least-squares.[31] All the hydrogen atoms were placed at idealised positions and refined as rigid atoms. Final $wR2$ = 0.1176 for all data and 429 parameters, $R1$ = 0.0454 for 6318 $F_o > 4\sigma(F_o)$.

CCDC-727086 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(1*R*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-2-[2-(hydroxymethyl)phenyl]-1-(4-methoxyphenyl)ethanamine (10e): Yellow oil; R_f = 0.14 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –36 (c = 0.90, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3316, 3057, 2965, 2861, 2834 cm^{-1}. ^{1}H NMR: δ = 1.00 (s, 9 H), 2.99 (dd, J = 7.3, 6.3 Hz, 1 H), 3.42 (dd, J = 8.6, 5.0 Hz, 1 H), 3.74 (s, 3 H), 4.47 (br. s, 1 H), 4.49 (d, J = 11.4 Hz, 1 H), 4.51–4.58 (m, 1 H), 4.78 (d, J = 11.4 Hz, 1 H), 5.08 (br. s, 1 H), 6.83 (d, J = 8.8 Hz, 1 H), 7.10–7.20 (m, 3 H), 7.26–7.35 (m, 3 H) ppm. ^{13}C NMR: δ = 22.6 (CH_3), 40.5 (CH_2), 55.3 (CH_3), 56.4 (C), 61.0 (CH), 63.1 (CH_2), 113.9, 126.8, 128.0, 128.4, 129.8, 130.2, 135.1, 137.3, 139.1, 159.1 (ArC) ppm. MS: m/z (%)= 343 (3) $[M - H_2O]^+$, 241 (27), 240 (34), 224 (21), 223 (100), 184 (44), 166 (10), 136 (18), 135 (23), 134 (20), 121 (16), 115 (10), 57 (12). HRMS: calcd. for $C_{16}H_{17}O_2$ $[M - C_4H_9SONH]^+$ 241.1223; found 241.1216.

(2*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(hydroxymethyl)phenyl]-5-(tetrahydro-2*H*-pyran-2-yloxy)pentan-2-amine (10f): Colourless oil; R_f = 0.10 (hexane/EtOAc, 1:5). $[\alpha]_D^{20}$ = –1.5 (c = 1.21, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3359, 3238, 3039, 2950, 2868, 1034 cm^{-1}. ^{1}H NMR: δ = 0.97 (s, 9 H), 1.50–1.59 (m, 4 H), 1.70–1.86 (m, 6 H), 2.84–3.03 (m, 2 H), 3.41–3.57 (m, 3 H), 3.79–3.87 (m, 2 H), 4.26 (br. s, 1 H), 4.54–4.58 (m, 2 H), 4.78 (d, J = 11.6 Hz, 1 H), 7.17–7.23 (m, 3 H), 7.29–7.33 (m, 1 H) ppm. ^{13}C NMR: δ = 19.7, 19.8 (CH_2), 22.5 (CH_3), 26.2, 26.3, 30.7, 30.8, 33.6, 33.7 (CH_2), 38.2, 38.3 (CH_2), 56.2 (C), 58.4, 58.5 (CH), 62.4, 62.5, 63.0, 67.3, 67.4 (CH_2), 99.0 (CH), 126.6, 128.0, 129.8, 130.0, 137.8, 139.2 (ArC) ppm. MS: m/z (%) = 341 (1) $[M - C_4H_8]^+$, 257 (28), 239 (16), 192 (16), 191 (16), 190 (19), 172 (15), 132 (29), 122 (11), 118 (14), 85 (100), 57 (24). HRMS: calcd. for $C_{17}H_{27}NSO_4$ $[M - C_4H_8]^+$ 341.1655; found 341.1640.

(2*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(hydroxymethyl)phenyl]-6-(tetrahydro-2*H*-pyran-2-yloxy)hexan-2-amine (10g): Colourless oil; R_f = 0.14 (hexane/EtOAc, 1:6). $[\alpha]_D^{20}$ = +10.5 (c = 0.95, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3400, 3063, 2941, 2866, 1033 cm^{-1}. ^{1}H NMR: δ = 0.94 (s, 9 H), 1.14–1.86 (m, 12 H), 2.88–2.99 (m, 2 H), 3.41–3.50 (m, 3 H), 3.76–3.88 (m, 2 H), 4.39 (br. s, 1 H), 4.52–4.57 (m, 3 H), 4.78 (d, J = 11.4 Hz, 1 H), 7.16–7.23 (m, 3 H), 7.31 (d, J = 7.3 Hz, 1 H) ppm. ^{13}C NMR: δ = 19.7 (CH_2), 22.4 (CH_3), 22.8, 25.4, 29.7, 30.7, 37.9, 38.0 (CH_2), 56.1 (C), 58.6 (CH), 62.4, 62.9, 67.3 (CH_2), 98.9 (CH), 126.4, 127.9, 129.6, 129.8, 137.9, 139.1 (ArC) ppm. MS: m/z (%) = 271 (27) $[M - C_4H_8 - C_5H_8O]^+$, 253 (20), 206 (12), 205 (17), 204 (22), 132 (50), 85 (100), 57 (17). HRMS: calcd. for $C_{13}H_{21}NSO_3$ $[M - C_4H_8 - C_5H_8O]^+$ 271.1242; found 271.1226.

(2*R*,*S*$_R$)-*N*-(*tert*-Butylsulfinyl)-1-(2-hydroxymethylphenyl)decan-2-amine (*ent*-10a): The physical and spectroscopic data were found to be same as for **10a**. $[\alpha]_D^{20}$ = –15 (c = 0.79, CH_2Cl_2).

(2*S*,*S*$_R$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(hydroxymethyl)phenyl]-3-methylbutan-2-amine (*ent*-10b): The physical and spectroscopic data were found to be same as for **10b**. $[\alpha]_D^{20}$ = –45 (c = 0.57, CH_2Cl_2).

(1*S*,*S*$_R$)-*N*-(*tert*-Butylsulfinyl)-2-[2-(hydroxymethyl)phenyl]-1-phenylethanamine (*ent*-10d): Physical and spectroscopic data were found to be same than for **10d**. $[\alpha]_D^{22}$ = +34 (c = 0.67, CH_2Cl_2).

(1*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-2-[2-(hydroxymethyl)phenyl]-1-phenylethanamine (11d): M.p. 127–128 °C (pentane/dichloromethane); R_f = 0.14 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –38 (c = 0.48, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3430–3300, 2923 cm^{-1}. ^{1}H NMR: δ = 1.10 (s, 9 H), 3.12 (dd, J = 11.8, 5.3 Hz, 1 H), 3.20 (dd, J = 11.8, 6.3 Hz, 1 H), 3.70 (br. s, 1 H), 4.10–4.16 (m, 1 H), 4.62–4.71 (m, 3 H), 7.11–7.16 (m, 1 H), 7.26–7.34 (m, 8 H) ppm. ^{13}C NMR: δ = 22.7 (CH_3), 42.1 (CH_2), 56.0 (C), 60.8 (CH_2), 63.3 (CH), 127.3, 127.5, 127.8, 128.5, 128.7, 130.2, 130.8, 136.2, 139.6, 142.6 (ArC) ppm. MS (MALDI-TOF): m/z = 332 $[M + H]^+$.

(2*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(2-hydroxyethyl)phenyl]decan-2-amine (13a): Colourless oil; R_f = 0.34 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –13 (c = 1.32, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3359, 3069, 3020, 2926, 2854 cm^{-1}. ^{1}H NMR: δ = 0.87 (t, J = 6.9 Hz, 3 H), 1.04 (s, 9 H), 1.23–1.33 (m, 13 H), 1.41–1.45 (m, 1 H), 1.57–1.68 (m, 1 H), 2.87–2.93 (m, 4 H), 3.42 (q, J = 6.5 Hz, 1 H), 3.55 (d, J = 6.0 Hz, 1 H), 3.74–3.81 (m, 2 H), 7.16–7.30 (m, 4 H) ppm. ^{13}C NMR: δ = 14.1 (CH_3), 21.0 (CH_2), 22.5 (CH_3), 25.9, 29.3, 29.4, 29.5, 31.8, 35.2, 35.8, 36.0, 39.1 (CH_2), 55.8 (C), 58.0 (CH), 63.2 (CH_2), 126.3, 126.5, 129.9, 130.6, 138.3, 139.4 (ArC) ppm. HRMS: calcd. for $C_{22}H_{40}NO_2S$ $[M + H]^+$ 382.277; found 382.276.

(2*R*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[2-(2-hydroxyethyl)phenyl]-3-methylbutan-2-amine (13b): Pale-yellow oil; R_f = 0.17 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –10 (c = 1.1, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3346, 3057, 3020, 2957, 2861 cm^{-1}. ^{1}H NMR: δ = 1.00–1.04 (m, 15 H), 2.05–2.07 (m, 1 H), 2.81 (d, J = 7.0 Hz, 2 H), 2.89 (d, J = 7.0 Hz, 2 H), 3.39–3.42 (m, 1 H), 3.76–3.87 (m, 3 H), 7.13–7.27 (m, 4 H) ppm. ^{13}C NMR: δ = 17.9, 18.4, 22.5 (CH_3), 32.0 (CH), 34.8, 36.0 (CH_2), 56.1 (C), 62.9 (CH), 63.4 (CH_2), 126.4, 126.7, 127.2, 130.1, 130.8, 137.2, 137.5 (ArC) ppm. MS: m/z (%) = 255 (68) $[M - C_4H_8]^+$, 176 (17), 147 (16), 173 (100), 166 (12), 151 (14), 135 (37), 133 (54), 131 (16), 120 (81), 119 (27), 118 (16), 117 (57), 115 (22), 105 (28), 104 (15),

104 (15), 103 (12), 91 (26), 77 (11), 72 (43), 57 (37), 56 (13), 41 (13). HRMS: calcd. for $C_{13}H_{21}NO_2S$ [M – C_4H_8]$^+$ 255.1293; found 255.1287.

(2*S*,R_S)-*N*-(*tert*-Butylsulfinyl)-1-[2-(2-hydroxyethyl)phenyl]-4-phenylbutan-2-amine (13c): Colourless oil; R_f = 0.11 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –33 (*c* = 0.54, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3345, 3057, 3010, 2953, 2910, 2855 cm^{-1}. ^{1}H NMR: δ = 1.02 (s, 9 H), 1.95–2.05 (m, 2 H), 2.70–2.85 (m, 5 H), 2.92–2.97 (m, 1 H), 3.44–3.49 (m, 1 H), 3.56 (br. s, 1 H), 3.69–3.81 (m, 2 H), 7.10–7.17 (m, 7 H), 7.23–7.26 (m, 2 H) ppm. ^{13}C NMR: δ = 22.5 (CH_3), 32.0, 36.0, 37.0, 39.2 (CH_2), 55.9 (C), 57.5 (CH), 63.2 (CH_2), 126.0, 126.3, 126.6, 128.4, 130.0, 130.6, 136.9, 137.2, 141.3 (ArC) ppm. MS: *m*/*z* (%) = 317 (57) [M – C_4H_8]$^+$, 238 (12), 235 (22), 182 (19), 167 (13), 166 (11), 164 (31), 157 (11), 151 (24), 149 (17), 135 (14), 134 (37), 133 (89), 132 (16), 131 (50), 129 (14), 119 (17), 118 (23), 117 (96), 106 (13), 105 (58), 104 (12), 103 (15), 91 (100), 79 (11), 77 (15), 57 (31). HRMS: calcd. for $C_{18}H_{23}NO_2S$ [M – C_4H_8]$^+$ 317.1449; found 317.1444.

(1*R*,R_S)-*N*-(*tert*-Butylsulfinyl)-2-[2-(2-hydroxyethyl)phenyl]-1-phenylethanamine (13d): White foam; R_f = 0.14 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –74 (*c* = 0.97, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3331, 3068, 3015, 2925, 2872 cm^{-1}. ^{1}H NMR: δ = 1.12 (s, 9 H), 2.82 (dt, *J* = 7.0, 2.0 Hz, 2 H), 2.91 (dd, *J* = 8.2, 5.5 Hz, 1 H), 3.46 (dd, *J* = 7.3, 6.0 Hz, 1 H), 3.52 (br. s, 1 H), 3.70–3.82 (m, 2 H), 3.94 (br. s, 1 H), 4.52–4.57 (m, 1 H), 6.81 (d, *J* = 7.3 Hz, 1 H), 6.96–6.98 (m, 1 H), 7.10–7.27 (m, 7 H) ppm. ^{13}C NMR: δ = 22.6 (CH_3), 35.8, 40.4 (CH_2), 56.0 (C), 60.2 (CH), 63.4 (CH_2), 126.1, 126.8, 127.3, 127.9, 128.5, 129.8, 130.8, 135.9, 137.4, 141.9 (ArC) ppm. HRMS: calcd. for $C_{20}H_{25}NOS$ [M – H_2O]$^+$ 327.1657; found 327.1660.

(1*R*,R_S)-*N*-(*tert*-Butylsulfinyl)-2-[2-(2-hydroxyethyl)phenyl]-1-(4-methoxyphenyl)ethanamine (13e): Yellow oil; R_f = 0.16 (hexane/EtOAc, 1:2). $[\alpha]_D^{20}$ = –60 (*c* = 0.88, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3354, 3057, 3020, 2957, 2871 cm^{-1}. ^{1}H NMR: δ = 1.12 (s, 9 H), 2.82–2.91 (m, 4 H), 3.45 (dd, *J* = 7.5, 6.0 Hz, 1 H), 3.78 (br. s, 5 H), 3.88 (br. s, 1 H), 4.47–4.52 (m, 1 H), 6.77–6.81 (m, 2 H), 6.98 (t, *J* = 7.3 Hz, 1 H), 7.07–7.16 (m, 4 H) ppm. ^{13}C NMR: δ = 22.5 (CH_3), 35.8, 40.2 (CH_2), 55.2 (CH_3), 55.9 (C), 59.6 (CH), 63.3 (CH_2), 113.8, 126.0, 126.7, 128.4, 129.8, 130.8, 133.9, 136.0, 137.3, 159.1 (ArC) ppm. MS: *m*/*z* (%) = 255 (70) [M – C_4H_9SONH]$^+$, 240 (64), 238 (22), 237 (100), 184 (93), 183 (11), 166 (17), 136 (14), 135 (65), 134 (33), 133 (23), 129 (27), 121 (43), 119 (12), 115 (10), 105 (11), 91 (14), 57 (15). HRMS: calcd. for $C_{21}H_{29}NO_3S$ [M]$^+$ 375.1831; found 375.1831.

(2*S*,R_S)-*N*-(*tert*-Butylsulfinyl)-1-[2-(2-hydroxyethyl)phenyl]-5-(tetrahydro-2*H*-pyran-2-yloxy)pentan-2-amine (13f): Colourless oil; R_f = 0.14 (hexane/EtOAc, 1:5). $[\alpha]_D^{20}$ = –12.5 (*c* = 1.89, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3355, 3235, 3057, 3020, 2943, 2870, 1037 cm^{-1}. ^{1}H NMR: δ = 1.08 (s, 9 H), 1.42–1.58 (m, 4 H), 1.68–1.78 (m, 6 H), 2.79–3.05 (m, 5 H), 3.38–3.52 (m, 4 H), 3.74–3.88 (m, 4 H), 4.54 (m, 1 H), 7.14–7.19 (m, 4 H) ppm. ^{13}C NMR: δ = 19.6, 19.7 (CH_2), 22.6 (CH_3), 25.5, 26.0, 26.1, 30.7, 32.3, 32.4, 36.1, 39.3 (CH_2), 55.8 (C), 57.5, 57.6 (CH), 62.4, 62.5, 63.4, 67.1 (CH_2), 98.9, 99.1 (CH), 126.4, 126.7, 130.0, 130.9, 137.2 (ArC) ppm. MS: *m*/*z* (%) = 355 (1) [M – C_4H_8]$^+$, 272 (17), 271 (100), 192 (27), 189 (15), 136 (10), 133 (10), 118 (44), 117 (19), 85 (100), 70 (14), 57 (24). HRMS: calcd. for $C_{18}H_{28}NSO_4$ [M – C_4H_9]$^+$ 354.1734; found 354.1784.

(1*S*,S_S)-*N*-(*tert*-Butylsulfinyl)-2-[2-(2-hydroxyethyl)phenyl]-1-phenylethanamine (*ent*-13d): The physical and spectroscopic data were found to be same as for **13d**. $[\alpha]_D^{20}$ = +64 (*c* = 0.64, CH_2Cl_2).

Typical Procedure for the Stereoselective Synthesis of Heterocyclic Compounds 19–23 via Intermediate Amino Alcohols 14–18: A 4 M HCl (1 mL) solution in dioxane was added to a stirred solution of the corresponding *N*-*tert*-butylsulfinylamino alcohol derivative **10** or **13** (0.50 mmol) in MeOH (6 mL) at 0 °C. After stirring for 3 h at this temperature, a saturated $NaHCO_3$ solution was added. The reaction mixture was extracted with ethyl acetate (3 × 10 mL), dried with anhydrous $MgSO_4$ and evaporated (15 Torr) to yield the corresponding amino alcohol **14**–**18** which was pure enough for the next step. The residue was taken up in chloroform (5 mL) and thionyl chloride (0.1 mL, 1.7 mmol) was added at 0 °C. The solution was stirred at 50 °C for 4 h. After that, the solvents were evaporated (15 Torr) and the resulting residue was dissolved in THF (5 mL) and a 5 M sodium hydroxide solution (10 mL) was added. The resulting mixture was vigorously stirred for 10 h at 20 °C and then it was extracted with ethyl acetate (3 × 15 mL), dried with anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, chloroform/methanol) to yield pure heterocycles **19**–**23**.

(*S*)-1-(2-Hydroxymethylphenyl)decan-2-amine (14a): Yellow oil; R_f = 0.41 (chloroform/methanol, 5:1). IR (film): $\tilde{\nu}$ = 3413, 3063, 3002, 2924, 2853 cm^{-1}. ^{1}H NMR: δ = 0.89 (t, *J* = 6.7 Hz, 3 H), 1.17–1.48 (m, 13 H), 1.52–1.59 (m, 1 H), 2.64 (dd, *J* = 9.7, 3.5 Hz, 1 H), 2.80 (dd, *J* = 9.7, 3.5 Hz, 1 H), 2.90–3.18 (br. s, 4 H), 4.39 (d, *J* = 11.5 Hz, 1 H), 4.76 (d, *J* = 11.5 Hz, 1 H), 7.17–7.34 (m, 4 H) ppm. ^{13}C NMR: δ = 14.2 (CH_3), 22.7, 26.4, 29.3, 29.6, 29.7, 32.0, 38.4, 40.1 (CH_2), 52.1 (CH), 68.1 (CH_2), 126.6, 128.2, 130.1, 130.3, 138.6, 140.5 (ArC) ppm. MS: *m*/*z* (%) = 245 (2) [M – H_2O]$^+$, 133 (11), 132 (100), 130 (13), 104 (11). HRMS: calcd. for $C_{17}H_{27}N$ [M]$^+$ 245.2143; found 245.2135. $[\alpha]_D^{20}$ = +14.5 (*c* = 1.00, CH_2Cl_2).

(*R*)-1-[2-(hydroxymethyl)phenyl]-3-methylbutan-2-amine (14b): Yellow oil; R_f = 0.27 (chloroform/methanol, 7:1). $[\alpha]_D^{20}$ = +26 (*c* = 0.54, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3372, 3027, 2957, 2930, 2871 cm^{-1}. ^{1}H NMR: δ = 1.02 (t, *J* = 6.5 Hz, 6 H), 1.77–1.81 (m, 1 H), 2.63–2.77 (m, 3 H), 2.90 (br. s, 2 H), 3.71–3.77 (m, 1 H), 4.35 (d, *J* = 11.7 Hz, 1 H), 4.80 (d, *J* = 11.7 Hz, 1 H), 7.10–7.29 (m, 3 H), 7.32 (d, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR: δ = 18.2, 19.0 (CH_3), 34.4 (CH_2), 37.0, 57.9 (CH), 63.1 (CH_2), 126.6, 128.4, 130.0, 130.4, 139.4, 140.5 (ArC) ppm. MS: *m*/*z* (%) = 174 (2) [M – H – H_2O]$^+$, 133 (11), 132 (100), 131 (10), 130 (38), 104 (11). HRMS: calcd. for $C_{12}H_{16}N$ [M – H_2O]$^+$ 174.1288; found 174.1290.

(*S*)-1-[2-(hydroxymethyl)phenyl]-4-phenylbutan-2-amine (14c): Pale-yellow oil; R_f = 0.41 (chloroform/methanol, 5:1). $[\alpha]_D^{20}$ = –2.5 (*c* = 0.75, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3354, 3020, 2919, 2861 cm^{-1}. ^{1}H NMR: δ = 1.73–1.85 (m, 2 H), 1.89–2.01 (m, 2 H), 2.66–3.02 (m, 7 H), 3.59–3.65, 3.72–3.79 (2 m, 1 H), 4.40 (d, *J* = 11.7 Hz, 1 H), 4.76 (d, *J* = 11.7 Hz, 1 H), 7.14–7.34 (m, 9 H) ppm. ^{13}C NMR: δ = 32.8, 39.9, 40.0 (CH_2), 51.6 (CH), 63.2 (CH_2), 126.2, 126.8, 128.3, 128.4, 128.6, 130.1, 130.5, 138.3, 140.5, 141.5 (ArC) ppm. MS: *m*/*z* (%) = 237 (3) [M – H_2O]$^+$, 133 (10), 132 (100), 130 (18), 104 (15), 91 (10). HRMS: calcd. for $C_{17}H_{19}N$ [M – H_2O]$^+$ 237.1517; found 237.1508.

(*R*)-2-[2-(hydroxymethyl)phenyl]-1-phenylethanamine (14d): Pale-yellow oil; R_f = 0.45 (chloroform/methanol, 7:1). $[\alpha]_D^{20}$ = +21 (*c* = 0.43, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3400–3100, 3353, 3288, 3061 cm^{-1}. ^{1}H NMR: δ = 2.92–3.09 (m, 2 H), 3.09 (br. s, 3 H), 4.14 (dd, *J* = 9.2, 4.6 Hz, 1 H), 4.44 (d, *J* = 11.7 Hz, 1 H), 4.84 (d, *J* = 11.7 Hz, 1 H), 7.10–7.41 (m, 9 H) ppm. ^{13}C NMR: δ = 42.2 (CH_2), 56.4 (CH), 63.0 (CH_2), 126.0, 126.8, 127.4, 128.2, 128.6, 129.8, 130.2, 137.6, 140.4, 145.0 (ArC) ppm. MS: *m*/*z* (%) = 209 (39) [M – H_2O]$^+$, 208 (29), 207 (26), 206 (26), 178 (10), 130 (18), 104 (100), 103 (32), 90 (16), 78 (21), 77 (17), 51 (10). HRMS: calcd. for $C_{15}H_{15}N$ [M – H_2O]$^+$ 209.1204; found 209.1215.

(*R*)-2-[2-(hydroxymethyl)phenyl]-1-(4-methoxyphenyl)ethanamine (14e): Orange oil; R_f = 0.45 (chloroform/methanol, 7:1). $[\alpha]_D^{20}$ = +21.5 (*c* = 0.71, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3352, 3063, 2956, 2924, 2855 cm^{-1}. ^1H NMR: δ = 2.92–3.07 (m, 5 H), 3.80 (s, 3 H), 4.12 (dd, *J* = 9.3, 5.0 Hz, 1 H), 4.44 (d, *J* = 11.8 Hz, 1 H), 4.85 (d, *J* = 11.8 Hz, 1 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 7.19–7.37 (m, 6 H) ppm. ^{13}C NMR: δ = 42.5 (CH_2), 55.3 (CH_3), 55.9 (CH), 63.2 (CH_2), 114.1, 127.3, 128.4, 130.0, 130.4, 137.4, 137.9, 140.6, 135.1, 159.0 (ArC) ppm. MS: *m*/*z* (%) = 239 (87) $[M - H_2O]^+$, 238 (62), 224 (17), 222 (10), 208 (12), 134 (26), 132 (10), 131 (13), 130 (18), 121 (23), 105 (19), 104 (100), 103 (27), 78 (23). HRMS: calcd. for $C_{16}H_{17}NO$ $[M - H_2O]^+$ 239.1310; found 239.1318.

(*R*)-1-(2-Hydroxymethylphenyl)decan-2-amine (*ent*-14a): The physical and spectroscopic data were found to be same as for **14a**. $[\alpha]_D^{20}$ = –14 (*c* = 0.84, CH_2Cl_2).

(*S*)-1-[2-(hydroxymethyl)phenyl]-3-methylbutan-2-amine (*ent*-14b): The physical and spectroscopic data were found to be same as for **14b**. $[\alpha]_D^{20}$ = –25.5 (*c* = 1.10, CH_2Cl_2).

(*S*)-[2-(hydroxymethyl)phenyl]-1-phenylethanamine (*ent*-14d): The physical and spectroscopic data were found to be same as for **14d**. $[\alpha]_D^{20}$ = –20 (*c* = 0.54, CH_2Cl_2).

(*S*)-1-[2-(2-Hydroxyethyl)phenyl]decan-2-amine (15a): Yellow oil; R_f = 0.14 (chloroform/methanol, 7:1). $[\alpha]_D^{20}$ = +5.8 (*c* = 1.02, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3356, 3069, 3020, 2925, 2849 cm^{-1}. ^1H NMR: δ = 0.89 (t, *J* = 6.7 Hz, 3 H), 1.18–1.28 (m, 13 H), 1.47–1.51 (m, 1 H), 2.58–3.10 (m, 7 H), 3.68–3.71 (m, 1 H), 3.72–3.85 (m, 2 H), 7.14–7.29 (m, 4 H) ppm. ^{13}C NMR: δ = 14.2 (CH_3), 22.7, 26.4, 29.4, 29.7, 31.9, 35.3, 36.6, 37.7, 39.9 (CH_2), 52.5 (CH), 63.5 (CH_2), 126.5, 126.7, 129.8, 130.4, 138.0, 138.6 (ArC) ppm. MS: *m*/*z* (%) = 258 (5) $[M - H_2O - H]^+$, 257 (30), 145 (12), 144 (100), 143 (10), 115 (10). HRMS: calcd. for $C_{18}H_{27}N$ $[M - H_2O - 2H]^+$ 257.2143; found 257.2143.

(2)-1-[2-(2-Hydroxyethyl)phenyl]-3-methylbutan-2-amine (15b): Yellow oil; R_f = 0.11 (chloroform/methanol, 10:1). $[\alpha]_D^{20}$ = –14.0 (*c* = 0.72, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3357, 2947, 2861 cm^{-1}. ^1H NMR: δ = 0.98 (dd, *J* = 4.6, 2.2 Hz, 6 H), 1.65–1.73 (m, 1 H), 2.76–2.86 (m, 4 H), 3.58–3.79 (m, 2 H), 3.82–3.88 (m, 1 H), 7.13–7.23 (m, 4 H) ppm. ^{13}C NMR: δ = 18.1, 19.2 (CH_3), 34.5 (CH), 36.5, 36.6 (CH_2), 58.0 (CH), 63.6 (CH_2), 126.5, 126.6, 127.2, 129.8, 130.4, 138.4, 138.7 (ArC) ppm. MS: *m*/*z* (%) = 164 (8) $[M - iPr]^+$, 119 (10), 118 (10), 91 (10), 72 (100), 55 (23). HRMS: calcd. for $C_{13}H_{21}N$ $[M]^+$ 164.1070; found 164.1077.

(*S*)-1-[2-(2-Hydroxyethyl)phenyl]-4-phenylbutan-2-amine (15c): Yellow oil; R_f = 0.11 (chloroform/methanol, 7:1). $[\alpha]_D^{20}$ = –13 (*c* = 0.79, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3355, 3023, 2926, 2859 cm^{-1}. ^1H NMR: δ = 1.66–1.92 (m, 2 H), 2.51 (m, 3 H), 2.61–3.00 (m, 6 H), 3.58–3.86 (m, 3 H), 7.11–7.30 (m, 9 H) ppm. ^{13}C NMR: δ = 21.6, 32.7, 36.6, 39.3, 40.0 (CH_2), 52.0 (CH), 63.5 (CH_2), 126.0, 126.6, 128.4, 128.5, 129.9, 130.4, 137.7, 138.6, 141.8 (ArC) ppm. MS: *m*/*z* (%) = 164 (1) $[M - CH_2CH_2Ph]^+$, 135 (11), 134 (100), 117 (26), 115 (10), 104 (11), 91 (75). HRMS: calcd. for $C_{10}H_{14}NO$ $[M - CH_2CH_2Ph]^+$ 164.1070; found 164.1076.

(*R*)-2-[2-(2-Hydroxyethyl)phenyl]-1-phenylethanamine (15d): Yellow oil; R_f = 0.16 (chloroform/methanol, 10:1). $[\alpha]_D^{20}$ = –6 (*c* = 1.0, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3351, 3060, 3020, 2929, 2867 cm^{-1}. ^1H NMR: δ = 3.01 (br. s, 3 H), 3.01–3.12 (m, 4 H), 3.77–3.92 (m, 1 H), 4.25 (dd, *J* = 9.2, 5.2 Hz, 1 H), 7.16–7.42 (m, 9 H) ppm. ^{13}C NMR: δ = 36.3, 41.9 (CH_2), 57.1 (CH), 63.4 (CH_2), 126.3, 126.4, 126.6, 127.2, 128.4, 129.8, 130.2, 137.1, 138.5, 144.9 (ArC) ppm. MS: *m*/*z* (%) = 223 (2) $[M - H_2O]^+$, 115 (12), 107 (11), 106 (100), 105 (18), 104 (22), 103 (15), 79 (15), 78 (10), 77 (16). HRMS: calcd. for $C_{16}H_{14}$ $[M - H_2O - NH_3]^+$ 206.1095; found 206.1078.

(*R*)-2-[2-(2-Hydroxyethyl)phenyl]-1-(4-methoxyphenyl)ethanamine (15e): Yellow oil; R_f = 0.16 (chloroform/methanol, 7:1). $[\alpha]_D^{20}$ = –6.0 (*c* = 0.73, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3384, 3051, 2929, 2861 cm^{-1}. ^1H NMR: δ = 2.78–3.03 (m, 7 H), 3.66–3.74 (m, 1 H), 3.76 (s, 3 H), 3.80–3.85 (m, 1 H), 4.13–4.17 (m, 1 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 7.11–7.18 (m, 4 H), 7.26 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR: δ = 36.5, 42.1 (CH_2), 55.2 (CH_3), 56.5 (CH), 63.5 (CH_2), 113.9, 126.5, 126.7, 127.5, 129.8, 130.4, 137.1, 137.4, 138.6 (ArC) ppm. MS: *m*/*z* (%) = 165 (1) $[M - PhOMe]^+$, 137 (10), 136 (100), 109 (10), 93 (10). HRMS: calcd. for $C_{10}H_{13}NO$ $[M - PhOMe-H]^+$ 163.0992; found 163.0961.

(*S*)-2-[2-(2-Hydroxyethyl)phenyl]-1-phenylethanamine (*ent*-15d): The physical and spectroscopic data were found to be same as for **15d**. $[\alpha]_D^{20}$ = +9 (*c* = 0.70, CH_2Cl_2).

(*S*)-4-Amino-5-(2-hydroxymethylphenyl)pentan-1-ol (16): Yellow oil; R_f = 0.18 (chloroform/methanol, 2:1). $[\alpha]_D^{20}$ = +13.5 (*c* = 0.52, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3354, 3045, 3008, 2928, 2855 cm^{-1}. ^1H NMR: δ = 1.47–1.53 (m, 1 H), 1.62–1.79 (m, 3 H), 2.65 (dd, *J* = 9.5, 3.8 Hz, 1 H), 2.84 (dd, *J* = 9.5, 3.8 Hz, 1 H), 2.98 (m, 1 H), 3.20 (br. s, 4 H), 3.72–3.77 (m, 2 H), 4.45 (d, *J* = 11.9 Hz, 1 H), 4.72 (d, *J* = 11.9 Hz, 1 H), 7.16–7.24 (m, 2 H), 7.26 (t, *J* = 7.3 Hz, 1 H), 7.33 (d, *J* = 7.9 Hz, 1 H) ppm. ^{13}C NMR: δ = 29.8, 35.2, 40.2 (CH_2), 52.1 (CH), 62.4, 63.0 (CH_2), 126.8, 128.2, 130.1, 130.2, 138.2, 140.1 (ArC) ppm. MS: *m*/*z* (%) = 192 (3) $[M - OH]^+$, 149 (10), 132 (16), 130 (15), 104 (16), 91 (16), 88 (100), 77 (12), 71 (82), 70 (41), 43 (16). HRMS: calcd. for $C_{12}H_{15}N$ $[M - 2H_2O]^+$ 173.1204; found 173.1165.

(*S*)-5-Amino-6-[2-(hydroxymethyl)phenyl]hexan-1-ol (17): Yellow oil; R_f = 0.18 (chloroform/methanol, 10:1). $[\alpha]_D^{20}$ = +12.5 (*c* = 0.75, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3344, 3063, 3020, 2933 cm^{-1}. ^1H NMR: δ = 1.47–1.62 (m, 6 H), 2.66 (dd, *J* = 9.6, 3.7 Hz, 1 H), 2.83 (dd, *J* = 13.4, 3.7 Hz, 1 H), 3.02 (br. s, 5 H), 3.64 (t, *J* = 6.0 Hz, 2 H), 4.41 (d, *J* = 11.8 Hz, 1 H), 4.75 (d, *J* = 11.8 Hz, 1 H), 7.17–7.31 (m, 3 H), 7.33 (d, *J* = 7.1 Hz, 1 H) ppm. ^{13}C NMR: δ = 22.6, 32.6, 37.8, 40.0 (CH_2), 52.1 (CH), 62.3, 63.1 (CH_2), 126.8, 128.3, 130.1, 130.3, 138.4, 140.3 (ArC) ppm. MS: *m*/*z* (%) = 206 (2) $[M - OH]^+$, 132 (16), 130 (10), 104 (16), 103 (11), 102 (100), 91 (12), 85 (72), 84 (15), 67 (14), 57 (11), 56 (12), 44 (16). HRMS: calcd. for $C_{13}H_{17}N$ $[M - 2H_2O]^+$ 187.1361; found 187.1363.

(*S*)-4-Amino-5-[2-(2-hydroxyethyl)phenyl]pentan-1-ol (18): Yellow oil; R_f = 0.18 (chloroform/methanol, 2:1). $[\alpha]_D^{20}$ = +9 (*c* = 0.61, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3354, 3057, 3008, 2929, 2867 cm^{-1}. ^1H NMR: δ = 1.47–1.49 (m, 1 H), 1.65–1.76 (m, 3 H), 2.63–3.07 (m, 8 H), 3.59–3.85 (m, 4 H), 7.14–7.20 (m, 4 H) ppm. ^{13}C NMR: δ = 30.2, 35.5, 36.3, 41.0 (CH_2), 52.4 (CH), 61.7, 62.7 (CH_2), 126.7, 126.8, 130.1, 130.4, 137.7, 137.9 (ArC) ppm. MS: *m*/*z* (%) = 192 (3) $[M - CH_2OH]^+$, 117 (10), 115 (10), 91 (10), 88 (100), 71 (69), 70 (33), 43 (10). HRMS: calcd. for $C_{13}H_{17}N$ $[M - 2H_2O]^+$ 187.1361; found 187.1339.

(*S*)-3-Octyl-1,2,3,4-tetrahydroisoquinoline (19a): Brown oil; R_f = 0.21 (hexane/EtOAc, 1:3); HPLC analysis (0.8 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 9.8 min (95% *ee*). $[\alpha]_D^{20}$ = +60 (*c* = 0.96, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3318, 3020, 2953, 2924, 2852 cm^{-1}. ^1H NMR: δ = 0.89 (t, *J* = 6.8 Hz, 3 H), 1.23–1.30 (m, 10 H), 1.42–1.55 (m, 4 H), 2.25 (br. s, 1 H), 2.52 (dd, *J* = 10.2, 5.8 Hz, 1 H), 2.77–2.88 (m, 2 H), 4.06 (d, *J* = 15.6 Hz, 2 H), 7.00–7.14 (m, 4 H) ppm. ^{13}C NMR: δ = 12.2 (CH_3), 22.8, 26.1, 29.4, 29.7, 29.9, 32.0, 35.5, 36.9 (CH_2), 48.6 (CH), 53.8 (CH_2), 125.8, 126.1, 126.2, 129.4, 135.0, 135.6 (ArC) ppm. MS: *m*/*z* (%) = 245

(3) $[M]^+$, 133 (10), 132 (100), 130 (18), 104 (10). HRMS: calcd. for $C_{17}H_{27}N$ $[M]^+$ 245.2143; found 245.2138.

(*R*)-3-Isopropyl-1,2,3,4-tetrahydroisoquinoline (19b): Pale-brown oil; R_f = 0.25 (chloroform/methanol, 10:1); HPLC analysis (0.8 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 98:2): t_r = 6.0 min (99% *ee*). $[\alpha]_D^{20}$ = –98 (*c* = 0.98, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3400, 3057, 3020, 2957, 2922, 2867 cm^{-1}. ^1H NMR: δ = 1.01 (dt, *J* = 6.8, 3.5 Hz, 6 H), 1.70–1.77 (m, 2 H), 2.58–2.65 (m, 2 H), 2.75 (d, *J* = 12.1 Hz, 1 H), 4.05 (s, 2 H), 7.01 (d, *J* = 8.4 Hz, 1 H), 7.07–7.12 (m, 3 H) ppm. ^{13}C NMR: δ = 18.6, 19.2 (CH_3), 32.2 (CH_2), 33.1, 49.2 (CH), 59.6 (CH_2), 125.7, 126.0, 126.1, 129.5, 135.3, 136.0 (ArC) ppm. MS: *m*/*z* (%) = 174 (2) $[M - H]^+$, 133 (10), 132 (100), 130 (36), 104 (11). HRMS: calcd. for $C_{12}H_{16}N$ $[M]^+$ 174.1288; found 174.1290.

(*S*)-3-(2-Phenylethyl)-1,2,3,4-tetrahydroisoquinoline (19c): Orange oil; R_f = 0.31 (hexane/EtOAc, 1:3); HPLC analysis (0.5 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 70.0 min (98% *ee*). $[\alpha]_D^{20}$ = +56 (*c* = 0.64, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3327, 3063, 3023, 2920, 2853 cm^{-1}. ^1H NMR: δ = 1.82–1.90 (m, 2 H), 2.27 (br. s, 1 H), 2.52–2.61 (m, 1 H), 2.77–2.91 (m, 4 H), 4.05 (s, 2 H), 6.99–7.31 (m, 9 H) ppm. ^{13}C NMR: δ = 32.4, 35.3, 38.4 (CH_2), 48.3 (CH), 53.2 (CH_2), 125.9, 126.0, 126.1, 126.3, 2×128.5, 129.3, 134.6, 135.4, 142.1 (ArC) ppm. MS: *m*/*z* (%) = 237 (2) $[M]^+$, 133 (11), 132 (100), 130 (19), 104 (15), 91 (10). HRMS: calcd. for $C_{17}H_{19}N$ $[M]^+$ 237.1517; found 237.1520.

(*R*)-3-Phenyl-1,2,3,4-tetrahydroisoquinoline (19d):[32] Yellow oil; R_f = 0.34 (chloroform/methanol, 10:1); HPLC analysis (1.0 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 84.2 min (99% *ee*). $[\alpha]_D^{20}$ = +125 (*c* = 0.55, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3420–3385, 3063, 3026, 2923, 2851 cm^{-1}. ^1H NMR: δ = 2.02 (br. s, 1 H), 3.02 (d, *J* = 7.5 Hz, 2 H), 4.05 (t, *J* = 7.5 Hz, 1 H), 4.17 (d, *J* = 15.5 Hz, 1 H), 4.28 (d, *J* = 15.5 Hz, 1 H), 7.07–7.18 (m, 4 H), 7.29–7.40 (m, 3 H), 7.44 (d, *J* = 7.2 Hz, 2 H) ppm. ^{13}C NMR: δ = 37.8 (CH_2), 49.3 (CH), 58.7 (CH_2), 126.1, 126.4, 126.8, 127.6, 128.6, 128.8, 129.2, 134.7, 134.8, 143.9 (ArC) ppm. MS: *m*/*z* (%) = 209 (33) $[M]^+$, 208 (26), 207 (26), 206 (31), 132 (16), 130 (12), 105 (22), 104 (100), 103 (29), 102 (14), 90 (10), 89 (21), 78 (29), 77 (26), 76 (10). HRMS: calcd. for $C_{15}H_{15}N$ $[M]^+$ 209.1204; found 209.1204.

(*R*)-3-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (19e): Brown oil; R_f = 0.21 (EtOAc); HPLC analysis (1.0 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 95:5): t_r = 19.2 min (92% *ee*). $[\alpha]_D^{20}$ = +87 (*c* = 0.85, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3308, 3069, 2953, 2921, 2851, 2833 cm^{-1}. ^1H NMR: δ = 1.95 (br. s, 1 H), 2.95 (d, *J* = 7.1 Hz, 2 H), 3.80 (s, 3 H), 3.96 (t, *J* = 7.2 Hz, 1 H), 4.15 (d, *J* = 15.6 Hz, 1 H), 4.26 (d, *J* = 15.6 Hz, 1 H), 6.90 (d, *J* = 8.7 Hz, 2 H), 7.07–7.16 (m, 4 H), 7.35 (d, *J* = 8.5 Hz, 2 H) ppm. ^{13}C NMR: δ = 37.8 (CH_2), 49.4 (CH), 55.4 (CH_3), 58.1 (CH_2), 114.0, 125.9, 126.2, 126.3, 127.7, 129.2, 135.1, 136.6, 159.0 (ArC) ppm. MS: *m*/*z* (%) = 239 (80) $[M]^+$, 238 (47), 224 (15), 208 (11), 134 (20), 132 (10), 131 (10), 130 (17), 121 (24), 105 (16), 104 (100), 103 (25), 78 (23), 77 (16). HRMS: calcd. for $C_{16}H_{17}NO$ $[M]^+$ 299.1310; found 239.1301.

(*R*)-3-Octyl-1,2,3,4-tetrahydroisoquinoline (*ent*-19a): The physical and spectroscopic data were found to be same as for **19a**. HPLC analysis (0.8 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 7.7 min (96% *ee*). $[\alpha]_D^{20}$ = –58 (*c* = 0.87, CH_2Cl_2).

(*S*)-3-Isopropyl-1,2,3,4-tetrahydroisoquinoline (*ent*-19b): The physical and spectroscopic data were found to be same as for **19b**. HPLC analysis (0.8 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 98:2): t_r = 7.0 min (94% *ee*). $[\alpha]_D^{20}$ = +89 (*c* = 0.77, CH_2Cl_2).

(*S*)-3-Phenyl-1,2,3,4-tetrahydroisoquinoline (*ent*-19d): The physical and spectroscopic data were found to be same as for **19d**. HPLC analysis (1.0 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 79.9 min (99% *ee*). $[\alpha]_D^{22}$ = –99 (*c* = 0.41, CH_2Cl_2).

(*S*)-2-Octyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepine (20a): Yellow oil; R_f = 0.10 (hexane/EtOAc, 1:5); HPLC analysis (0.7 mL/min, λ = 215 nm, *n*-hexane): t_r = 9.2 min (99% *ee*). $[\alpha]_D^{20}$ = +4.5 (*c* = 0.77, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3400–3210, 3069, 3017, 2924, 2852 cm^{-1}. ^1H NMR δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.25–1.39 (m, 11 H), 1.42–1.50 (m, 2 H), 1.52–1.88 (m, 1 H), 2.77–2.86 (m, 3 H), 2.97–3.09 (m, 1 H), 3.09–3.12 (m, 1 H), 3.74–3.80 (m, 1 H), 3.86–3.91 (m, 1 H), 7.11–7.19 (m, 4 H) ppm. ^{13}C NMR: δ = 14.2 (CH_3), 22.8, 26.3, 29.4, 29.7, 29.8, 32.0, 36.6, 37.0, 39.2 (CH_2), 52.8 (CH), 63.7 (CH_2), 126.7, 126.8, 129.9, 130.5, 137.7, 138.9 (ArC) ppm. MS: *m*/*z* (%) = 259 (4) $[M]^+$, 154 (62), 147 (13), 146 (100), 118 (11), 171 (14), 115 (10), 56 (11). HRMS: calcd. for $C_{18}H_{29}N$ $[M]^+$ 259.2300; found 259.2293.

(*R*)-2-Isopropyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepine (20b): Yellow oil; R_f = 0.30 (chloroform/methanol, 10:1); HPLC analysis (0.8 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 98:2): t_r = 6.0 min (96% *ee*). $[\alpha]_D^{20}$ = +7 (*c* = 0.38, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3363, 3066, 3020, 2955, 2867 cm^{-1}. ^1H NMR: δ = 1.01 (dt, *J* = 6.8, 3.5 Hz, 6 H), 1.70–1.77 (m, 2 H), 2.58–2.65 (m, 2 H), 2.75 (d, *J* = 12.1 Hz, 1 H), 4.05 (s, 2 H), 7.01 (d, *J* = 8.4 Hz, 1 H), 7.07–7.12 (m, 3 H) ppm. ^{13}C NMR: δ = 18.5, 18.9 (CH_3), 33.6 (CH), 38.5, 40.8 (CH_2), 57.7 (CH), 61.8 (CH_2), 126.3, 126.4, 129.2, 129.5, 141.0, 141.9 (ArC) ppm. MS: *m*/*z* (%) = 189 (2) $[M]^+$, 147 (10), 146 (100), 129 (11), 117 (15), 115 (11), 81 (20). HRMS: calcd. for $C_{13}H_{19}N$ $[M]^+$ 189.1517; found 189.1508.

(*S*)-2-Phenethyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepine (20c): Orange oil; R_f = 0.27 (chloroform/methanol, 10:1); HPLC analysis (1.0 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 32.3 min (94% *ee*). $[\alpha]_D^{20}$ = –15.5 (*c* = 0.85, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3353, 3057, 3022, 2930 cm^{-1}. ^1H NMR: δ = 1.73–1.89 (m, 2 H), 2.66–2.99 (m, 6 H), 3.01–3.17 (m, 1 H), 3.55 (br. s, 2 H), 3.72–3.84 (m, 1 H), 7.07–7.26 (m, 9 H) ppm. ^{13}C NMR: δ = 21.7, 32.3, 32.5, 36.3, 37.4, 38.6, 39.4, 46.0 (CH_2), 52.1 (CH), 63.3 (CH_2), 125.9, 126.0, 126.5, 126.6, 126.7, 128.3, 128.4, 129.1, 129.7, 129.9, 130.3, 137.4, 138.5, 141.2, 141.4, 141.6 (ArC) ppm. MS: *m*/*z* (%) = 251 (6) $[M]^+$, 160 (25), 147 (10), 146 (100), 117 (20), 115 (15), 105 (12), 91 (36), 77 (11). HRMS: calcd. for $C_{18}H_{21}N$ $[M]^+$ 251.1674; found 251.1663.

(*R*)-2-Phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepine (20d): Yellow oil; R_f = 0.12 (chloroform/methanol, 10:1); HPLC analysis (1.0 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 10.8 min (99% *ee*). $[\alpha]_D^{20}$ = –29 (*c* = 1.20, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3323, 3060 cm^{-1}. ^1H NMR: δ = 2.41 (br. s, 1 H), 2.75–3.01 (m, 3 H), 3.15–3.24 (m, 1 H), 3.31–3.43 (m, 1 H), 3.37 (d, *J* = 9.8 Hz, 1 H), 3.72 (d, *J* = 9.8 Hz, 1 H), 7.05–7.45 (m, 9 H) ppm. ^{13}C NMR: δ = 38.9, 46.9 (CH_2), 48.8 (CH), 63.7 (CH_2), 126.2, 126.4, 126.5, 127.2, 128.6, 129.2, 129.6, 140.8, 142.3, 146.0 (ArC) ppm. MS: *m*/*z* (%) = 223 (48) $[M]^+$, 181 (13), 118 (100), 117 (14), 115 (16), 105 (11), 91 (51), 77 (13). HRMS: calcd. for $C_{16}H_{17}N$ $[M]^+$ 223.1361; found 223.1367.

(*R*)-2-(4-Methoxyphenyl)-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepine (20e): Brown oil; R_f = 0.36 (chloroform/methanol, 10:1). $[\alpha]_D^{20}$ = –23 (*c* = 0.67, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3351, 3069, 3020, 2931, 2837 cm^{-1}. ^1H NMR: δ = 2.75–3.00 (m, 4 H), 3.37 (br. s, 1 H), 3.52–3.64 (m, 2 H), 3.72–3.76 (m, 1 H), 3.78 (d, *J* = 6.0 Hz, 3 H), 6.84–6.89 (m, 2 H), 7.08–7.18 (m, 4 H), 7.24 (d, *J* = 8.5 Hz, 1 H), 7.40 (d, *J* = 8.5 Hz, 1 H) ppm. ^{13}C NMR: δ = 35.9, 36.9, 42.9, 44.5 (CH_2), 55.4 (CH_3), 56.8 (CH), 61.9 (CH_2), 113.9, 114.1, 126.7, 126.8, 126.9, 127.1, 127.6, 128.3, 129.4, 129.9, 130.7 (ArC) ppm. MS: *m*/*z* (%) = 253 (100) $[M]^+$, 252 (16), 238 (11), 209 (10), 149

(11), 148 (82), 147 (11), 135 (23), 134 (23), 121 (56), 118 (23), 117 (22), 116 (14), 115 (21), 91 (16), 78 (13), 77 (13). HRMS: calcd. for $C_{17}H_{19}NO$ $[M]^+$ 253.1467; found 253.1454.

(*S*)-2-Phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepine (*ent*-20d): The physical and spectroscopic data were found to be same as for **20d**. HPLC analysis (1.0 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 17.1 min (98% *ee*). $[\alpha]_D^{20}$ = +25 (*c* = 0.26, CH_2Cl_2).

(*S*)-1,2,3,5,10,10a-Hexahydropyrrolo[1,2-*b*]isoquinoline (21): Brown oil; R_f = 0.28 (chloroform/methanol, 10:1); HPLC analysis (1.0 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 7.0 min (92% *ee*). $[\alpha]_D^{20}$ = +46 (*c* = 0.58, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3063, 3014, 2961, 2904, 2873, 2775, 2718 cm^{-1}. ^1H NMR: δ = 1.49–1.62 (m, 1 H), 1.79–1.96 (m, 2 H), 2.05–2.29 (m, 1 H), 2.32–2.45 (m, 2 H), 2.73 (dd, *J* = 15.8, 10.4 Hz, 1 H), 3.00 (dd, *J* = 15.9, 3.9 Hz, 1 H), 3.26 (dd, *J* = 8.6, 2.7 Hz, 1 H), 3.48 (d, *J* = 14.7 Hz, 1 H), 4.14 (d, *J* = 14.7 Hz, 1 H), 7.05–7.16 (m, 4 H) ppm. ^{13}C NMR: δ = 21.6, 31.1, 36.1, 54.9, 56.0 (CH_2), 60.8 (CH), 125.7, 126.2, 126.7, 129.1, 134.9, 135.1 (ArC) ppm. MS: *m*/*z* (%) = 173 (55) $[M]^+$, 172 (100), 170 (10), 144 (10), 130 (13), 117 (13), 115 (16), 105 (13), 104 (51), 103 (18), 78 (18), 77 (14). HRMS: calcd. for $C_{12}H_{15}N$ $[M]^+$ 173.1204; found 173.1192.

(*S*)-2,3,4,6,11,11a-Hexahydro-1*H*-pyrido[1,2-*b*]isoquinoline (22): Yellow oil; R_f = 0.25 (chloroform/methanol, 10:1); HPLC analysis (0.5 mL/min, λ = 215 nm, *n*-hexane/*i*PrOH, 99:1): t_r = 13.0 min (97% *ee*). $[\alpha]_D^{20}$ = +26 (*c* = 0.50, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3063, 3020, 2930, 2852, 2796, 2756 cm^{-1}. ^1H NMR: δ = 1.25–1.40 (m, 2 H), 1.67–1.86 (m, 4 H), 2.08–2.17 (m, 1 H), 2.24–2.27 (m, 1 H), 2.73–2.77 (m, 2 H), 2.76 (d, *J* = 4.7 Hz, 1 H), 3.40 (d, *J* = 15.2 Hz, 1 H), 3.87 (d, *J* = 15.2 Hz, 1 H), 6.99–7.25 (m, 4 H) ppm. ^{13}C NMR: δ = 24.3, 25.9, 33.6, 36.8, 56.2, 58.3 (CH_2), 58.4 (CH), 125.6, 126.0, 126.3, 128.1, 133.9, 134.2 (ArC) ppm. MS: *m*/*z* (%) = 187 (51) $[M]^+$, 186 (100), 158 (12), 145 (15), 130 (10), 104 (34). HRMS: calcd. for $C_{13}H_{17}N$ $[M]^+$ 187.1361; found 187.1387.

(*S*)-1,2,3,4,5,6,11,11a-Octahydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]azepine (23): Brown oil; R_f = 0.23 (chloroform/methanol, 10:1); HPLC analysis (0.7 mL/min, λ = 215 nm, *n*-hexane): t_r = 8.4 min (99% *ee*). $[\alpha]_D^{20}$ = –18.5 (*c* = 0.71, CH_2Cl_2). IR (film): $\tilde{\nu}$ = 3057, 3018, 2959, 2925, 2792, 2748 cm^{-1}. ^1H NMR: δ = 1.67–1.81 (m, 2 H), 1.87–2.10 (m, 2 H), 2.14–2.26 (m, 2 H), 2.34 (q, *J* = 9.2 Hz, 1 H), 2.78–2.85 (m, 2 H), 3.04–2.10 (m, 1 H), 3.21–3.27 (m, 2 H), 3.34–3.38 (d, *J* = 14.7 Hz, 1 H), 7.09–7.16 (m, 4 H) ppm. ^{13}C NMR: δ = 20.5, 32.5, 36.0, 41.0, 54.0, 56.7 (CH_2), 64.9 (CH), 126.7, 129.3, 129.7, 140.1, 141.3 (ArC) ppm. MS: *m*/*z* (%) = 187 (91) $[M]^+$, 186 (79), 173 (18), 172 (100), 170 (22), 159 (15), 158 (15), 144 (11), 130 (19), 129 (14), 128 (17), 118 (68), 117 (64), 116 (26), 115 (56), 105 (13), 104 (35), 103 (31), 96 (17), 91 (42), 83 (28), 82 (74), 78 (26), 77 (29), 63 (18), 55 (50), 54 (23). HRMS: calcd. for $C_{13}H_{17}N$ $[M]^+$ 187.1361; found 187.1343.

Acknowledgments

This work was generously supported by the Spanish Ministerio de Educación y Ciencia (MEC) (Grant no. CTQ2004–01261, the Consolider Ingenio 2010-CSD2007-00006), and the Generalitat Valenciana (Grant no. PROMETEO/2009/039). D. G. thanks the University of Alicante for a predoctoral fellowship. We also thank Medalchemy S. L. and Chemetall GmbH for a gift of enantiopure *tert*-butylsulfinamides (*S* and *R*) and lithium, respectively.

[1] For recent reviews on functionalised organolithium compounds, see: a) C. Nájera, M. Yus, *Curr. Org. Chem.* **2003**, *7*, 867–926; b) C. Nájera, J. M. Sansano, M. Yus, *Tetrahedron* **2003**, *59*, 9255–9303; c) R. Chinchilla, C. Nájera, M. Yus, *Chem. Rev.* **2004**, *104*, 2667–2722; d) R. Chinchilla, C. Nájera, M. Yus, *Tetrahedron* **2005**, *61*, 3139–3176; e) F. Foubelo, M. Yus, *Chem. Soc. Rev.* **2008**, *37*, 2620–2633.

[2] For a monograph, see: J. Clayden, in: *Organolithiums: Selectivity for Synthesis*, Pergamon Press, Oxford, **2002**.

[3] For recent reviews, see: a) M. Yus, *Pure Appl. Chem.* **2003**, *75*, 1453–1475; b) M. Yus, F. Foubelo, *Adv. Heterocycl. Chem.* **2006**, *91*, 135–158.

[4] For the last papers on this topic from our laboratory, see: a) F. Foubelo, D. García, B. Moreno, M. Yus, *Tetrahedron Lett.* **2007**, *48*, 3379–3383; b) D. García, F. Foubelo, M. Yus, *Heterocycles* **2007**, *74*, 507–519; c) D. García, F. Foubelo, M. Yus, *Tetrahedron* **2008**, *64*, 4275–4286; d) D. García, F. Foubelo, M. Yus, *Heterocycles* **2009**, *77*, 991–1005.

[5] For recent mechanistic studies, see: a) C. Melero, A. Guijarro, M. Yus, *Tetrahedron Lett.* **2006**, *47*, 6267–6271; b) C. Melero, H. Pérez, A. Guijarro, M. Yus, *Tetrahedron Lett.* **2007**, *48*, 4105–4109; c) C. Melero, A. Guijarro, V. Baumann, A. J. Pérez-Jiménez, M. Yus, *Eur. J. Org. Chem.* **2007**, 5514–5526; d) C. Melero, R. P. Herrera, A. Guijarro, M. Yus, *Chem. Eur. J.* **2007**, *13*, 10096–10107; e) H. Pérez, C. Melero, A. Guijarro, M. Yus, *Tetrahedron* **2009**, *65*, 10764–10783.

[6] For a recent review, see: M. Yus in *The Chemistry of Organolithium Compounds* (Eds.: Z. Rappoport, I. Marek), Wiley, Chichester, **2004**, vol. 1, pp. 647–747.

[7] a) J. Almena, F. Foubelo, M. Yus, *Tetrahedron* **1995**, *51*, 3351–3364; b) U. Azzena, S. Demartis, M. G. Fiori, G. Melloni, L. Pisano, *Tetrahedron Lett.* **1995**, *36*, 8213–8216.

[8] J. Almena, F. Foubelo, M. Yus, *Tetrahedron* **1995**, *51*, 3365–3374.

[9] a) T. Soler, A. Bachki, L. R. Falvello, F. Foubelo, M. Yus, *Tetrahedron: Asymmetry* **2000**, *11*, 493–517; b) L. R. Falvello, F. Foubelo, T. Soler, M. Yus, *Tetrahedron: Asymmetry* **2000**, *11*, 2063–2066; c) F. Foubelo, T. Soler, M. Yus, *Tetrahedron: Asymmetry* **2001**, *12*, 801–810.

[10] a) I. Pastor, M. Yus, *Tetrahedron Lett.* **2000**, *41*, 1589–1592; b) I. Pastor, M. Yus, *Tetrahedron* **2001**, *57*, 2371–2378.

[11] a) M. Yus, J. Gomis, *Tetrahedron Lett.* **2001**, *42*, 5721–5724; b) M. Yus, J. Gomis, *Eur. J. Org. Chem.* **2002**, 1989–1995.

[12] M. Yus, J. Gomis, *Eur. J. Org. Chem.* **2003**, 2043–2048.

[13] For a preliminary report, see: D. García, B. Moreno, T. Soler, F. Foubelo, M. Yus, *Tetrahedron Lett.* **2009**, *50*, 4710–4713.

[14] For reviews, see: a) F. A. Davis, P. Zhou, B.-C. Chen, *Chem. Soc. Rev.* **1998**, *27*, 13–18; b) J. A. Ellman, T. D. Owens, T. P. Tang, *Acc. Chem. Res.* **2002**, *35*, 984–995; c) J. A. Ellman, *Pure Appl. Chem.* **2003**, *75*, 39–46; d) P. Zhou, B.-C. Chen, F. A. Davis, *Tetrahedron* **2004**, *60*, 8003–8030; e) D. Morton, R. A. Stockman, *Tetrahedron* **2006**, *62*, 8869–8905; f) G.-Q. Lin, M.-H. Xu, Y.-W. Zhong, X.-W. Sun, *Acc. Chem. Res.* **2008**, *41*, 831–840; g) F. Ferreira, C. Botuha, F. Chemla, A. Pérez-Luna, *Chem. Soc. Rev.* **2009**, *38*, 1162–1186.

[15] a) D. J. Weix, J. A. Ellman, *Org. Lett.* **2003**, *5*, 1317–1320; b) D. J. Weix, J. A. Ellman, *Org. Synth.* **2005**, *82*, 157–165.

[16] D. A. Cogan, G. Liu, J. Ellman, *Tetrahedron* **1999**, *55*, 8883–8904.

[17] a) M. Wakayama, J. A. Ellman, *J. Org. Chem.* **2009**, *74*, 2646–2650; b) V. K. Aggarwal, N. Barbero, E. M. McGarrigle, G. Mickle, R. Navas, J. R. Suárez, M. G. Unthank, M. Yar, *Tetrahedron Lett.* **2009**, *50*, 3482–3484.

[18] For a review, see: J. D. Scott, R. M. Williams, *Chem. Rev.* **2002**, *102*, 1669–1730.

[19] For reviews, see: a) J. L. Vicario, D. Badia, L. Carrillo, J. Etxebarria, *Curr. Org. Chem.* **2003**, *7*, 1775–1792; b) A. B. J. Bracca, T. S. Kaufman, *Tetrahedron* **2004**, *60*, 10575–10610; c) P. Siengalewicz, U. Rinner, J. Mulzer, *Chem. Soc. Rev.* **2008**, *37*, 2676–2690.

[20] For recent syntheses of substituted 2,3,4,5-tetrahydro-1*H*-benzazepines, see: a) J. Crecente-Campo, M. P. Vázquez-Tato,

J. A. Seijas, *Tetrahedron* **2009**, *65*, 2655–2659; b) S. M. Husain, M. T. Heim, D. Schepmann, B. Wünsch, *Tetrahedron: Asymmetry* **2009**, *20*, 1383–1392.

[21] a) J. Weinstock, J. P. Hieble, J. W. Wilson III, *Drug Fut.* **1985**, *10*, 645–697; b) I. Pettersson, T. Liljefors, K. Bogeso, *J. Med. Chem.* **1990**, *33*, 2197–2204; c) W. L. Wu, D. A. Burnett, R. Spring, *J. Med. Chem.* **2005**, *48*, 680–693.

[22] K. K. Gnanalingham, A. J. Hunter, P. Jenner, C. D. Marsden, *Psychopharmacology (Berlin, Ger.)* **1995**, *117*, 403–412.

[23] A. D. Medhurst, A. R. Atkins, I. J. Beresford, K. Brackenborough, M. A. Briggs, A. R. Calver, J. Cilia, J. E. Cluderay, B. Crook, J. B. Davis, R. K. Davis, R. P. Davis, L. A. Dawson, A. G. Foley, J. Gartlon, M. I. Gonzalez, T. Heslop, W. D. Hirst, C. Jennings, D. N. C. Jones, L. P. Lacroix, A. Martyn, S. Ociepka, A. Ray, C. M. Regan, J. C. Roberts, J. Schogger, E. Southam, T. O. Stean, B. K. Trail, N. Upton, G. Wadsworth, J. A. Wald, T. White, J. Witherington, M. L. Woolley, A. Worby, D. M. Wilson, *J. Pharmacol. Exp. Ther.* **2007**, *321*, 1032–1045.

[24] M. Medjahdi, J. C. González-Gómez, F. Foubelo, M. Yus, *Heterocycles* **2008**, *76*, 569–581.

[25] a) R. Almansa, D. Guijarro, M. Yus, *Tetrahedron: Asymmetry* **2008**, *19*, 603–606; b) R. Almansa, D. Guijarro, M. Yus, *Tetrahedron: Asymmetry* **2008**, *19*, 2484–2491.

[26] a) P. V. Bharatam, Amita, D. Kaur, *J. Phys. Org. Chem.* **2002**, *15*, 197–203; b) P. V. Bharatam, P. Uppal, Amita, D. Kaur, *J. Chem. Soc. Perkin Trans. 2* **2000**, 43–50.

[27] F. Foubelo, C. Gómez, A. Gutiérrez, M. Yus, *J. Heterocycl. Chem.* **2000**, *37*, 1061–1064.

[28] G. Liu, D. A. Cogan, T. D. Owens, T. P. Tang, J. A. Ellman, *J. Org. Chem.* **1999**, *64*, 1278–1284.

[29] *SAINT, Area-Detector Integration Software*, version 6.02A, Siemens Industrial Automation, Inc., Madison, WI, **1995**.

[30] G. M. Sheldrick, *SADABS: Area-Detector Absorption Correction*, University of Göttingen, Göttingen, **1996**

[31] G. M. Sheldrick, *SHELX97* [includes *SHELXS97*, *SHELXL97* and *CIFTAB*], Programs for Crystal Structure Analysis (rel. 97-2), University of Göttingen, Göttingen, **1998**.

[32] D. Enders, V. Braig, M. Boudou, G. Raabe, *Synthesis* **2004**, 2980–2990.

Received: January 27, 2010
Published Online: April 8, 2010

