Functionalized Organolithium Compounds by DTBB-Catalyzed Sulfur–Lithium Exchange

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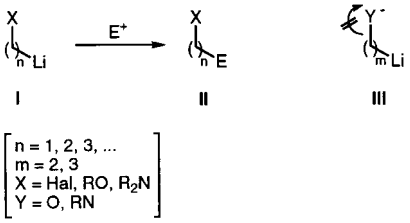
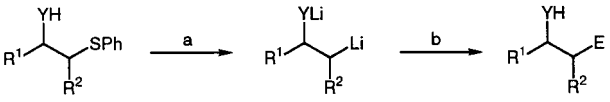
Abstract: The successive reaction of β- or γ-hydroxy or amino phenyl thioethers (**1**, **4**) with butyllithium and an excess of lithium powder in the presence of a catalytic amount of DTBB in THF at –78 °C leads to the formation of the corresponding β- or γ-functionalized organolithium compounds **2** or **5**, respectively, which by treatment with different electrophiles [D_2O, *t*-BuCHO, PhCHO, Me_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$] at temperatures ranging between –78 °C and room temperature yields, after hydrolysis with water, the expected functionalized alcohols or amines **3** or **6**, respectively, in a completely regioselective manner.

Key words: lithiation, arene-catalysis, functionalization, organolithium

Functionalized organolithium compounds (**I**)[1] are interesting intermediates in synthetic organic chemistry because they are able to transfer their functionality to electrophilic reagents, thus in only one reaction step polyfunctionalized molecules (**II**) can be directly prepared. The stability of these intermediates depends strongly on the separation between the functional group and the carbon–lithium bond: β- or γ-functionalized derivatives (**I**, n = 2, 3) are especially unstable undergoing β- or γ-elimination, respectively, even at very low temperatures giving alkenes[2] and cyclopropanes,[3] respectively, as the reaction products. One way to decrease the ability of the heteroatom X to act as a leaving group is to transform this neutral group into a negative one locating a negative charge on it, so intermediates of type **III** are far more stable than **I** as they are able to survive at low temperatures. These sp^3-hybridized β-functionalized organolithium compounds (**III**, m = 2), also called d^2 reagents,[4] have been prepared by (a) mercury–lithium exchange from the corresponding hydroxy or amino mercurials;[5] (b) chlorine–lithium exchange from β-chloro alcohols[6] or amines[7] using a lithium arene;[8] (c) reductive opening of oxiranes[9] or aziridines[10] using the last lithiation mixture[8] or an excess of lithium and a catalytic amount of an arene,[11] naphthalene and 4,4'-di-*tert*-butylbiphenyl (DTBB) being the most commonly used;[12] and (d) to the best of our knowledge, only one example has been described in the literature[6f,g] of using a tin–lithium transmetallation reaction. Concerning sp^3-hybridized γ-functionalized organolithium compounds (**III**, m = 3), also called d^3 reagents,[4] they have been prepared following the former routes (b),[13] (c) (from the corresponding four-membered saturated heterocycles),[14] and (d),[15] as well as by addition of an alkyllithium to allylic derivatives,[16] and in some very special cases by direct deprotonation.[17,18] To the best of our knowledge, very few examples of functionalized organolithium compounds (mainly having the lithium atom at a benzylic position) have been described by sulfur/lithium exchange using a lithium–arene reagent in the lithiation step.[19] In this article we describe the application of an arene-catalyzed lithiation, a methodology developed in our laboratory in the last few years,[11,12] to the general preparation of β- and γ-functionalized organolithium intermediates by a sulfur/lithium exchange.[20,21]



The reaction of different β-hydroxy or β-phenylamino phenyl thioethers **1a–f** with butyllithium (1:1 molar ratio) in THF at –78 °C for 10 min followed by treatment with a dark green suspension of an excess of lithium powder (ca. 1:14 molar ratio) and a catalytic amount of DTBB (1:0.1 molar ratio; 5 mol%) in THF at the same temperature for 1–3 h (see experimental part; after this time the dark green colour appeared again) gave a solution of the corresponding dilithiated intermediate **2a–f**, which by reaction with different electrophiles [D_2O, *t*-BuCHO, PhCHO, Me_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$] at temperatures ranging between –78 °C and room temperature afforded, after hydrolysis with water, the expected functionalized alcohols or amines **3aa–fe** (Scheme 1 and Table 1). In all cases a variable amount (<20%) of the corresponding "reduced" products (**3** with E = H) was detected in the reaction mix-



1a R^1 = Ph, R^2 = H, Y= O
1b R^1 = *n*-C_6H_{13}, R^2 = H, Y= O
1c R^1-R^2 = $(CH_2)_4$, Y= O
1d R^1 = R^2 = H, Y= PhN
1e R^1 = Ph, R^2 = H, Y= PhN
1f R^1 = R^2 = H, Y= *i*-PrN

2a-f **3aa-fe**

(a) i. BuLi, THF, –78 °C, 2 min., ii. Li, DTBB cat. (5 mol %), THF, –78 °C, 1–5 h (see experimental); (b) i. E^+ = D_2O, *t*-BuCHO, PhCHO, Me_2CO, Et_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$, –78 °C → r.t., overnight, ii. H_2O

Scheme 1

ture, which could be easily separated by column chromatography, except when deuterium oxide was used as electrophile (Table 1, entries 1, 6, 12 and 17); the formation of these byproducts is due to the partial decomposition of very reactive intermediates of type **2** by abstracting a proton from the reaction medium.[10b]

Concerning the stereochemical stability of intermediates of type **2**, we prepared the starting material **1c** as the pure *trans*-diastereoisomer and submitted it to the reaction shown in Scheme 1. After isolation different ratios of a *trans/cis* diastereoisomeric mixture were obtained (1.3–5:1; Table 1, entries 10 and 11), so we conclude that intermediates **2** are configurationally unstable.

From the results shown in Table 1 it can be seen that this methodology allows us to prepare for the first time β-functionalized organolithium compounds **2f** derived from an aliphatic amine. These dianionic species are not accessible by any route mentioned above, so even reacting with electrophiles in poor yields (Table 1, entries 21–23) their preparation results in an intrinsic novelty.

Starting materials **1** were prepared following classical methodologies. Thus, hydroxy thioethers **1a–c** were obtained by reaction of the corresponding epoxides with potassium thiophenolate. Successive reaction of 1-bromo-2-chloroethane with potassium thiophenolate and aniline or isopropylamine yielded aminated thioethers **1d** or **1f**, respectively. Finally, compound **1e** was prepared by treatment of benzylidene aniline with lithiomethyl phenyl thioether. In all cases the final hydrolysis with water afforded the corresponding products **1a–f**.

In the second part of this study we report on the application of the methodology shown in Scheme 1 to the prepa-

Biographical Sketches

Francisco Foubelo was born in Carreña-Cabrales (Asturias) in 1961, and received his BSc (1984), MSc (1986) and PhD (1989) degrees in chemistry from the University of Oviedo. After a postdoctoral stay (1989–1991) at Princeton University, he joined the research group of Professot Miguel Yus at the University of Alicante where he became Associate Professor in 1995. He has published more than 40 papers. His current research interests include the preparation of new chiral polyfunctionalized anionic synthons and the development of new methodologies for preparing organolithium compounds.

Ana Gutiérrez was born in Alicante in 1972. She studied chemistry at the University of Alicante and earned her BSc and MSc degrees in 1995. Currently she is carrying out her PhD studies within the research group of Miguel Yus on the preparation of functionalized organolithium compounds from phenyl thioethers.

Miguel Yus was born in Zaragoza in 1947. He received BSc (1969), MSc (1971) and PhD (1973) degrees from the University of Zaragoza. After spending two years as a postdoc in the Max Planck Institut für Kohlenforschung in Mülheim a. d. Ruhr, he returned to the University of Oviedo where he became Associate Professor in 1977, being promoted to full professor in 1987 at the same university. In 1988, he moved to a chair in organic chemistry at the University of Alicante where he is currently head of the Organic Chemistry Department. Professor Yus has been a visiting professor at different institutions such as ETH-Zürich and the universities of Oxford, Harvard, Uppsala, Marseille and Tucson. He is a member or fellow of the chemical societies of Argentina. England, Germany, Japan, Spain, Switzerland and United States. He is co-author of more than 200 papers mainly in the field of development of new methodologies involving organometallic intermediates. His current research interest is focused on the preparation of very reactive functionalized organolithium compounds and their use in synthetic organic chemistry.

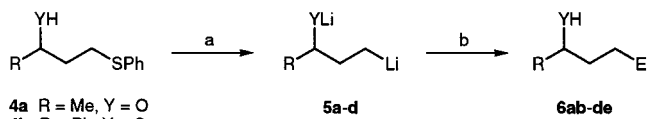
Table 1 Compounds **3** Prepared

Entry	Product	Electrophile	Y	R^1	R^2	E	Yield (%)[a]
1	**3aa**	D_2O	O	Ph	H	D	(90)[b]
2	**3ab**	*t*-BuCHO	O	Ph	H	*t*-BuCHOH	21 (47)[c]
3	**3ac**	PhCHO	O	Ph	H	PhCHOH	48 (69)[d]
4	**3ad**	Me_2CO	O	Ph	H	Me_2COH	62 (93)
5	**3ae**	$(CH_2)_5CO$	O	Ph	H	$(CH_2)_5COH$	32 (42)
6	**3ba**	D_2O	O	*n*-C_6H_{13}	H	D	65 (88)[b]
7	**3bb**	*t*-BuCHO	O	*n*-C_6H_{13}	H	*t*-BuCHOH	49 (59)[e]
8	**3bd**	Me_2CO	O	*n*-C_6H_{13}	H	Me_2COH	50
9	**3be**	$(CH_2)_5CO$	O	*n*-C_6H_{13}	H	$(CH_2)_5COH$	24 (32)
10	**3cd**	Me_2CO	O	$-(CH_2)_4-$		Me_2COH	21[f]
11	**3ce**	$(CH_2)_5CO$	O	$-(CH_2)_4-$		$(CH_2)_5COH$	20 (40)[g]
12	**3da**	D_2O	PhN	H	H	D	43 (99)[b]
13	**3db**	*t*-BuCHO	PhN	H	H	*t*-BuCHOH	21 (32)
14	**3dc**	PhCHO	PhN	H	H	PhCHOH	61
15	**3dd**	Me_2CO	PhN	H	H	Me_2COH	39 (94)
16	**3de**	$(CH_2)_5CO$	PhN	H	H	$(CH_2)_5COH$	25 (38)
17	**3ea**	D_2O	PhN	Ph	H	D	99[b]
18	**3eb**	*t*-BuCHO	PhN	Ph	H	*t*-BuCHOH	(78)[h]
19	**3ec**	PhCHO	PhN	Ph	H	PhCHOH	52 (61)[h]
20	**3ee**	$(CH_2)_5CO$	PhN	Ph	H	$(CH_2)_5COH$	28
21	**3fc**	PhCHO	*i*-PrN	H	H	PhCHOH	10 (14)
22	**3fd**	Me_2CO	*i*-PrN	H	H	Me_2COH	17
23	**3fe**	$(CH_2)_5CO$	*i*-PrN	H	H	$(CH_2)_5COH$	10 (10)

[a] Yield of isolated pure product (> 95% from GC and 300 MHz ^{1}H NMR) after column chromatography (silica gel, hexane/ethyl acetate) and recrystallization based on the starting materials **1**; in parenthesis isolated crude yield (purity > 90% from 300 MHz ^{1}H NMR).
[b] > 90% deuterium incorporation measured by mass spectrometry.
[c] 1.7:1 Diastereoisomeric ratio (from 75 MHz ^{13}C NMR).
[d] 1.2:1 Diastereoisomeric ratio (from 75 MHz ^{13}C NMR).
[e] 1.3:1 Diastereoisomeric ratio (from 75 MHz ^{13}C NMR).
[f] 5:1 *trans*:*cis* ratio (from 75 MHz ^{13}C NMR).
[g] 1.3:1 *trans*:*cis* ratio (from 75 MHz ^{13}C NMR).
[h] 1:1 Diastereoisomeric ratio (from 75 MHz ^{13}C NMR).

ration of γ-functionalized organolithium compounds of type **III** with m = 3. Thus, when γ–oxygenated or γ-aminated thioethers **4a–d** were submitted to the same protocol as for starting materials **1**, and using different electrophiles [D_2O, *t*-BuCHO, PhCHO, Me_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$], the expected products **6ab–de** were isolated after hydrolysis, dianionic intermediates **5a–d** being presumably involved in the reaction (Scheme 2 and Table 2).

One important remark has to be noted concerning the results shown in Scheme 2. Not only aliphatic amine derivatives (**5c**) can be prepared for the first time (which are also not accessible by other methodologies) but also we were able to generate an intermediate in which the anionic



4a R = Me, Y = O
4b R = Ph, Y = O
4c R = H, Y = *i*-PrN
4d R = Me, Y = NH

5a-d

6ab-de

(a) and (b) as shown in Scheme 1

Scheme 2

Table 2 Compounds **6** Prepared

Entry	Product	Electrophile	Y	R	E	Yield (%)[a]
1	**6ab**	*t*-BuCHO	O	Me	*t*-BuCHOH	55[b]
2	**6ac**	PhCHO	O	Me	PhCHOH	64[c]
3	**6ad**	Me_2CO	O	Me	Me_2COH	33(73)
4	**6ae**	$(CH_2)_5CO$	O	Me	$(CH_2)_5COH$	53
5	**6bc**	PhCHO	O	Ph	PhCHOH	33(68)[d]
6	**6be**	$(CH_2)_5CO$	O	Ph	$(CH_2)_5COH$	53
7	(*S*)-**6bd**	Me_2CO	O	Ph	Me_2COH	43
8	(*S*,*S*/*R*)-**6bc**	PhCHO	O	Ph	PhCHOH	60[c]
9	**6cc**	PhCHO	*i*-PrN	H	PhCHOH	16
10	**6ce**	$(CH_2)_5CO$	*i*-PrN	H	$(CH_2)_5COH$	30
11	**6cf**	Et_2CO	*i*-PrN	H	Et_2COH	11
12	**6cg**	$(CH_2)_4CO$	*i*-PrN	H	$(CH_2)_4COH$	18
13	**6db**	*t*-BuCHO	NH	Me	*t*-BuCHOH	28(36)[c]
14	**6dc**	PhCHO	NH	Me	PhCHOH	23(24)[c]
15	**6dd**	Me_2CO	NH	Me	Me_2COH	52
16	**6de**	$(CH_2)_5CO$	NH	Me	$(CH_2)_5COH$	34

[a] Yield of isolated product (>95% from GC and 300 MHz ^{1}H NMR) after column chromatography (silica gel, hexane/ethyl acetate) and recrystallization based on the starting materials **7**; in parenthesis isolated crude yield (purity >90% from 300 MHz ^{1}H NMR).
[b] 1:0.7 Diastereoisomeric ratio (from 75 MHz ^{13}C NMR).
[c] 1:1 Diastereoisomeric ratio (from 75 MHz ^{13}C NMR).
[d] 1:1.5–2.2 Diastereoisomeric ratio (from 75 MHz ^{13}C NMR).

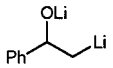
nitrogen has no substitution (**5d**), i.e., a primary amine derivative, and from this, although with modest yields, functionalized primary amines **6db–de** could be directly prepared (Table 2, entries 13–16).

In this case, and in order to study the possibility of preparing enantiomerically pure compounds, we prepared the chiral derivative (*S*)-**4b** and reacted it under the reaction conditions shown in Scheme 2; when acetone was used as electrophile enantiomerically pure product (*S*)-**6bd** was isolated (Table 2, entry 7). However, using a prochiral electrophile such as benzaldehyde, a ca. 1:1 diastereomeric mixture was obtained. This result, which has been already observed in other cases,[6c,9e,14h] shows that the asymmetric induction is practically nonexistent; an explanation for this behaviour can be found by considering the high reactivity of intermediates of type **5**.

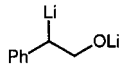
Concerning starting materials **4**, oxygenated derivatives **4a**,**b** [or (*S*)-**4b**] were prepared by treatment of the corresponding epoxides with lithiomethyl phenyl thioether and final hydrolysis. Compound **4c** was prepared following the same procedure as for **1f** but using 1-bromo-3-chloropropane instead of 1-bromo-2-chloroethane. Finally Michael-type addition of thiophenol to methyl vinyl ketone followed by reductive amination (H_4NOAc/$NaBH_3CN$) afforded compound **4d**, after hydrolysis.

In conclusion, we have shown in this paper that the DTBB-catalyzed lithiation of oxygen- or nitrogen-containing phenyl thioethers is an adequate methodology to

prepare β- and γ-functionalized organolithium intermediates, which are rather stable at low temperature and react with different electrophiles (mainly carbonyl compounds) to give functionalized alcohols or amines. In some cases (aliphatic amine derivatives) the mentioned derivatives are only accesible by the way described in this paper. Finally, the results of this methodology compare well with other methodologies used : as an example, either the reductive opening of styrene oxide or the lithiation of its chlorohydrin (2-chloro-2-phenylethanol) afford the benzylic derivative **2'a**. However, the successive thiophenolate opening of the same epoxide followed by DTBB-catalyzed lithiation afforded the corresponding regioisomer **2a** (Table 1, entry 1).



2a



2'a

Melting points are uncorrected. IR were recorded on a Nicolet 510 P-FT and only the structurally most important peaks are listed. NMR spectra were determined on a Bruker AC-300 using TMS as internal standard; coupling constants (*J*) are given in Hz. Optical rotations were measured on a Jasco DIP-1000 polarimeter. Low resolution electron impact (EI) mass spectra were obtained at 70 eV on a Shimadzu QP-5000. HRMS (EI) were recorded on VG-Micromass ZAB-ZF, Kratos MS 80 RFA, and Finnigan MAT 95 S. Microanalysis were performed by the Microanalyses Service of the University of Alicante and the University of Zaragoza. All reagents were commercially available and of the best grade. Reaction solvents were dried and distilled under N_2 using standard procedures. Analytical TLC was performed on Schleicher & Schuell F1400/LS silica gel plates andthe spots visualized with UV light at 254 nm. GLC analysis were performed on a HP 5890.

Preparation of Compounds 1a–c; General Procedure

Thiophenol (1.10 g, 1.02 mL, 10 mmol) was added dropwise to KOH (0.68g, 12 mmol) in MeOH (30 mL) at r.t. After 10 min, the corresponding epoxide (10 mmol) was added dropwise. The mixture was heated at 50 °C for 2 h. After that, the solvent was removed on a rotary evaporator and the residue was hydrolyzed with H_2O (20 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue, which was purified by column chromatography (silica gel, hexane/EtOAc) to give title compounds **1a–c**.

1-Phenyl-2-phenylsulfanylethanol (1a)

Pale yellow oil, R_f 0.33 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 230 (M^+, 7), 212 (11), 124 (100), 107 (29), 91 (15), 79 (45), 78 (17), 77 (41), 65 (10), 51 (32), 45 (37).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.99 (br s, OH, 1H), 3.07 (dd, *J* = 9.5 Hz, 13.7, C*H*H, 1H), 3.28 (dd, *J* = 3.7 Hz, 13.7, CH*H*, 1H), 4.68 (dd, *J* = 3.7 Hz, 9.5, C*H*OH, 1H), 7.20–7.40 (m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.78 (CH_2), 71.61 (CHOH), 125.77, 126.62, 127.87, 128.44, 129.02, 130.02, 134.91, 142.10 (ArC).

IR (neat): ν = 3600–3100 (OH) cm^{-1}.

HRMS: calcd for $C_{14}H_{14}OS$: 230.0765; found: 230.0768.

1-Phenylsulfanyloctan-2-ol (1b)

Pale yellow oil, R_f 0.51 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 238 (M^+, 12), 124 (100), 110 (26), 109 (17), 91 (14), 78 (13), 69 (24), 65 (11), 55 (52), 51 (11), 45 (34), 44 (43), 43 (44).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.7 Hz, CH_3, 3H), 1.24–1.58 [m, $CH_3(CH_2)_5$, 10H], 2.50 br s, OH, 1H), 2.84 (dd, *J* = 8.5 Hz, 13.7, C*H*HSPh, 1H), 3.14 (dd, *J* = 3.5, 13.7 Hz, CH*H*SPh, 1H), 3.60–3.70 (m, C*H*OH, 1H), 7.14–7.40 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.01 (CH_3), 22.52, 25.56, 29.19, 31.68, 36.08 [$(CH_3CH_2)_5$],42.13 (CH_2S), 69.33 (CHOH), 126.47, 128.98, 129.92, 135.35 (ArC).

IR (film): ν = 3683–3131 (OH) cm^{-1}.

HRMS: calcd for $C_{14}H_{22}OS$: 238.1391; found: 238.1382.

trans-2-Phenylsulfanylcyclohexanol (1c)

Pale yellow oil, R_f 0.38 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 208 (M^+, 23), 110 (100), 98 (14), 81 (29), 79 (11), 55 (16), 45 (14), 43 (11).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18–1.39 (m, CH_2CH_2, 4H), 1.64–1.72 (m, CH_2CHS, 2H), 2.03–2.14 (m, CH_2CHOH, 2H), 2.79 (td, *J* = 4.0 Hz, 10.1, CHSPh, 1H), 3.13 (br s, OH, 1H), 3.34 (td, *J* = 4.4 Hz, 10.1, C*H*OH, 1H), 7.26–7.32, 7.45–7.48 (2m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1, 25.9, 32.5, 33.7 [$(CH_2)_4$], 56.2 (CHS), 71.9 (CHOH), 127.5, 128.7, 132.6, 133.5 (ArC).

IR (neat): ν = 3657–3118 (OH) cm^{-1}.

HRMS: calcd for $C_{14}H_{22}OS$: 208.0922; found: 208.0916.

2-Chloroethyl Phenyl Thioether[22]

Thiophenol (1.65 g, 1.54 mL, 15 mmol) was added dropwise to KOH (1.00 g, 18 mmol) in MeOH (40 mL) at r.t. After 10 min, 1-bromo-2-chloroethane (2.14 g, 1.24 mL, 15 mmol) was added dropwise and stirring was continued for 1 h at the same temperature. Then, the solvent was removed on a rotary evaporator and the residue was hydrolyzed with H_2O (25 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue which was purified by column chromatography (silica gel, hexane) to give the title compound as a pale yellow oil, R_f 0.35 (hexane).

MS (EI): *m/z* (%) = 172 (M^+, 19), 123 (68), 110 (13), 109 (18), 77 (14), 69 (16), 66 (11), 65 (34), 63 (10), 51 (27), 50 (12), 45 (100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.17–3.24 (m, CH_2SPh, 2H), 3.57–3.63 (m, $ClCH_2$, 2H), 7.23–7.40 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.1 (CH_2S), 42.2 (CH_2Cl), 127.0, 129.15, 130.4, 134.2 (ArC).

IR (neat): ν = 3075–3060, 3020 (ArH) cm^{-1}.

***N*-Phenyl-2-phenylsulfanylethylamine (1d)**

To 2-chloroethyl phenyl thioether (1.73 g, 10 mmol) in MeOH (30 mL) was added $NaHCO_3$ (2.52 g, 30 mmol) and aniline (0.93 g, 0.91 mL, 10 mmol). The mixture was heated at 50 °C for 2 h. After that, the solvent was removed on a rotary evaporator and the residue was hydrolyzed with H_2O (25 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue, which was purified by column chromatography (silica gel, hexane/EtOAc) to give the title compound as a white solid, mp 39 °C, R_f 0.29 (hexane/EtOAc: 20/1).

MS (EI): *m/z* (%) = 229 (M^+, 10), 124 (26), 106 (100), 77 (25), 65 (12), 51 (16), 45 (12).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.13 (t, *J* = 6.4 Hz, CH_2SPh, 2H), 3.35 (t, *J* = 6.4 Hz, PhNHCH_2, 2H), 4.01 (br s, NH, 1H), 6.55–6.74, 7.13–7.40 (2m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.7 (CH_2S), 42.55 (CH_2NH), 113.0, 117.75, 126.6, 129.0, 129.3, 130.2, 135.1, 147.45 (ArC).

IR (neat): ν = 3400 (NH) cm^{-1}.

HRMS: calcd for $C_{14}H_{15}NS$: 229.0925; found: 229.0926.

1-Phenyl-*N*-phenyl-2-phenylsulfanylethylamine (1e)
To a cooled (0°C) solution of thioanisole (1.24 g, 1.17 mL, 10 mmol) and tetramethylethylenediamine (1.16 g, 1.51 mL, 10 mmol) in THF was added a 1.6 M BuLi hexane solution (6.89 mL, 11 mmol) under Ar and stirring was continued at the same temperature for 1 h. After that, the mixture was cooled to –78°C and a THF solution (2 mL) of *N*-benzylideneaniline (1.81 g, 10 mmol) was added via syringe. The system was allowed to reach r.t. after 3 h and was hydrolyzed with H_2O (30 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue, which was purified by column chromatography (silica gel, hexane/EtOAc) to give the title compound as a white solid mp 56–57°C; R_f 0.18 (hexane/EtOAc: 20/1).

MS (EI): *m/z* (%) = 213 (M^+ – PhNH, 2), 212 (16), 183 (14), 182 (100), 104 (28), 93 (20), 78 (13), 77 (54), 66 (15), 65 (16), 51 (32), 45 (13), 44 (20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.14 (dd, *J* = 9.16, 13.43 Hz, C*H*H, 1H), 3.36 (dd, *J* = 4.27, 13.43 Hz,CH*H*, 1H), 4.39 (dd, *J* = 4.58, 9.15 Hz, CH, 1H), 4.51 (br s, NH, 1H), 6.44–6.68, 7.02–7.38 (2m, ArH, 15H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 34.7 (CH_2), 57.2 (CH), 113.8, 117.8, 126.3, 126.9, 127.55, 128.8, 129.0, 129.1, 130.6, 135.0, 142.4, 147.1 (ArC).

IR ($CHCl_3$) ν = 3400 (NH) cm^{-1}.

Anal. calcd for $C_{20}H_{19}NS$: C, 78.66; H, 6.28; N, 4.59; S, 10.48; found: C, 78.23; H, 6.34; N, 4.57; S, 10.73.

***N*-Isopropyl-2-phenylsulfanylethylamine (1f)**
A solution of 2-chloroethyl phenyl thioether (1.73 g, 10 mmol) in isopropylamine (8 mL) was heated at 50°C in a sealed tube for 20 h. After that, the solvent was removed on a rotary evaporator and the residue was hydrolyzed with H_2O (25 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was extracted with 1 M HCl (2 × 20 mL) and this acidic aqueous layer was basified with NaOH and extracted again with EtOAc (3 × 25 mL). This new organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue which was the title compound (>90% pure) as a yellow oil, R_f 0.41 (hexane/EtOAc: 1/1).

MS (EI): *m/z* (%) = 195 (M^+, 1), 124 (21), 72 (100), 44 (11), 43 (17), 42 (14).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 [2d, *J* = 6.4 Hz, $(CH_3)_2CH$, 6H], 2.14 (br s, NH, 1H), 2.76–2.85 (m, C*H*NHCH$_2$CH_2, 3H), 3.05–3.10 (m, CH_2NH, 2H), 7.16–7.38 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8 [$(CH_3)_2$CH], 34.2 (CH_2SPh), 45.6 [$(CH_3)_2CH$], 48.25 (CH_2NH), 126.2, 128.9, 129.6, 135.6 (ArC).

IR (neat): ν = 3300 (NH) cm^{-1}.

HRMS: calcd for $C_{11}H_{17}NS$: 195.1082; found: 195.1050.

Preparation of Compounds 4a,b. General Procedure
To a cooled (0°C) solution of thioanisole (1.24 g, 1.17 mL, 10 mmol) and tetramethylethylenediamine (1.16 g, 1.51 mL, 10 mmol) in THF was added a 1.6 M BuLi hexane solution (6.87 mL, 11 mmol) under Ar and stirring was continued at the same temperature for 1 h. After that, the mixture was cooled down to –78°C and the corresponding epoxide [propylene oxide, styrene oxide or (*S*)-styrene oxide] was added dropwise. The system was allowed to reach r.t. after 3 h and was hydrolyzed with H_2O (30 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue, which was purified by column chromatography (silica gel, hexane/EtOAc) to give the title compounds.

4-Phenylsulfanylbutan-2-ol (4a):[23]
Pale yellow oil, R_f 0.33 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 182 (M^+, 6), 110 (25), 77 (11), 72 (42), 66 (11), 65 (18), 57 (47), 55 (22), 51 (17), 45 (68), 43 (100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.4 Hz, CH_3, 3H), 1.71–1.80 (m, PhSCH$_2$CH_2, O*H*, 3H), 2.95–3.11 (m, PhSCH_2, 2H), 3.96 (sextet, *J* = 6.1 Hz, C*H*OH, 1H), 7.14–7.36 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.5 (CH_3), 30.1 (*C*H$_2$CH$_2$S), 38.1 (CH_2S), 66.9 (CHOH), 125.9, 128.9, 129.1, 136.3 (ArC).

IR (neat): ν = 3715–3110 (OH) cm^{-1}.

1-Phenyl-3-phenylsulfanylpropanol (4b)
White solid, mp 44°C, R_f 0.39 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 244 (M^+, 5), 135 (11), 134 (44), 133 (66), 124 (18), 117 (34), 115 (16), 110 (30), 109 (28), 107 (18), 105 (42), 91 (29), 79 (78), 78 (29), 77 (100), 69 (17), 66 (19), 65 (43), 59 (10), 57 (22), 56 (16), 55 (27), 52 (12), 51 (64), 50 (20), 45 (62), 44 (40), 43 (48), 41 (25).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93–2.15 (m, CHOHCH_2, 2H), 2.21 (br s, OH, 1H), 2.98 (t, *J* = 7.0 Hz, PhSCH_2, 2H), 4.83 (dd, *J* = 4.9 Hz, 7.9, C*H*OH, 1H), 7.15–7.35 (m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.9 (CH_2S), 38.0 (*C*H$_2$CH$_2$S), 72.0 (CHOH), 125.7, 125.9, 127.7, 128.5, 128.9, 129.1, 136.1, 143.9 (ArC).

IR ($CHCl_3$): ν = 3725–3120 (OH) cm^{-1}.

Anal. calcd for $C_{15}H_{16}OS$: C, 73.74; H, 6.61; S, 13.10; found: C, 73.53; H, 7.01; S, 12.84.

(*S*)-1-Phenyl-3-phenylsulfanylpropanol [(*S*)-4b]
White solid, mp 61°C, R_f 0.42 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 244 (M^+, 5), 135 (11), 134 (44), 133 (66), 124 (18), 117 (34), 115 (16), 110(30), 109 (28), 107 (18), 105 (42), 91 (29), 79 (78), 78 (29), 77 (100), 69 (17), 66 (19), 65 (43), 59 (10), 57 (22), 56 (16), 55 (27), 52 (12), 51 (64), 50 (20), 45 (62), 44 (40), 43 (48), 41 (25).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93–2.15 (m, CHOHCH_2, 2H), 2.21 (br s, OH, 1H), 2.98 (t, *J* = 7.0 Hz, PhSCH_2, 2H), 4.83 (dd, *J* = 4.9 Hz, 7.9, C*H*OH, 1H), 7.15–7.35 (m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.9 (CH_2S), 38.0 (*C*H$_2$CH$_2$S), 73.0 (CHOH), 125.7, 125.9, 127.7, 128.5, 128.9, 129.1, 136.1, 143.9 (ArC).

IR (neat): ν = 3720–3120 (OH) cm^{-1}.

Anal. calcd for $C_{15}H_{16}OS$: C, 73.74; H, 6.61; S, 13.10; found: C, 73.88; H, 6.27; S, 12.90.

3-Chloropropyl Phenyl Thioether[24]
Thiophenol (1.65 g, 1.54 mL, 15 mmol) was added dropwise to KOH (1.00 g, 18 mmol) in MeOH (40 mL) at r.t. After 10 min, 1-bromo-3-chloropropane (2.35 g, 1.48 mL, 15 mmol) was added dropwise and stirring was continued for 1 h at the same temperature. Then, the solvent was removed on a rotary evaporator and the residue was hydrolyzed with H_2O (30 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue, which was purified by column chro-

matography (silica gel, hexane) to give title compound, pale yellow oil, R_f 0.32 (hexane).

MS (EI): *m/z* (%) = 186 (M^+, 17), 122 (51), 110 (51), 109 (14), 77 (18), 69 (15), 66 (20), 65 (34), 51 (37), 50 (12), 45 (100), 41 (35).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (q, *J* = 6.7 Hz, $CH_2CH_2CH_2$, 2H), 3.05 (t, *J* = 7.0 Hz, CH_2S, 2H), 3.64 (t, *J* = 6.1 Hz, $ClCH_2$, 2H), 7.17–7.36 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.7, 31.6 (CH_2CH_2S), 43.3 (CH_2Cl), 126.2, 128.9, 129.5, 135.6 (ArC).

IR (neat): ν = 3075, 3060, 3020, 3000 (ArH) cm^{-1}.

N-Isopropyl-3-phenylsulfanylpropylamine (4c)
Compound **4c** was prepared following the same reaction conditions as that for compound **1f**, using in this case 3-chloropropyl phenyl thioether instead of 2-chloroethyl phenyl thioether resulting in a pale yellow liquid, R_f 0.11 (EtOAc).

MS (EI): *m/z* (%) = 209 (M^+, 10), 84 (14), 72 (100), 58 (41), 56 (21), 45 (12), 44 (12), 43 (34), 42 (25).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 [d, *J* = 6.1 Hz, $(CH_3)_2CH$, 6H], 1.23 (br s, NH, 1H), 1.82 (q, *J* = 7.2 Hz, $CH_2CH_2CH_2$, 2H), 2.71 (t, *J* = 6.7 Hz, CH_2SPh, 2H), 2.69–2.79 [m, $(CH_3)_2CH$, 1H], 2.98 (t, *J* = 7.17, $NHCH_2$, 2H), 7.16–7.19, 7.24–7.35 (2m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9 [$(CH_3)_2CH$], 29.8 (CH_2SPh), 31.6 (CH_2CH_2NH), 46.15 (CH_2NH), 48.6 [$(CH_3)_2CH$], 125.8, 128.8, 129.04, 136.5 (ArC).

IR (neat): ν = 3380 (NH) cm^{-1}.

HRMS: calcd for $C_{14}H_{19}NS$: 209.1238; found: 209.1236.

4-Phenylsulfanyl-2-butanamine (4d)[25]
Sodium cyanoborohydride (0.50 g, 8 mmol) was added to 4-phenylsulfanylbutan-2-one (1.44 g, 8 mmol, easily prepared from thiophenol and methyl vinyl ketone)[23] in MeOH (30 mL), 4Å molecular sieves (1.30 g) and ammonium acetate (6.16 g, 80 mmol) at r.t. under Ar. The mixture was stirred for 48 h at the same temperature and after that it was filtered, the solvent removed on a rotary evaporator and the residue diluted with H_2O (5 mL), basified with 15% NaOH and extracted with EtOAc (3 × 25 mL). The organic layer was extracted with 1 M HCl (2 × 20 mL) and this acidic aqueous layer was basified with NaOH and extracted again with EtOAc (3 × 25 mL). This new organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue, containing the title compound (>90% pure) as a yellow liquid, R_f 0.41 (EtOAc).

MS (EI): *m/z* (%) = 182 (M^+, 4), 44 (100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (d, *J* = 6.7 Hz, CH_3, 3H), 1.19 (br s, NH_2, 2H), 1.41–1.73 (m, $NHCHCH_2$, 2H), 2.90–3.08 (m, CH_2SPh, $CHNH_2$, 3H), 7.13–7.35 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.0 (CH_3), 30.6 (CH_2S), 39.05 (CH_2CH), 46.0 (CHNH), 125.75, 128.8, 128.9, 136.6 (ArC).

IR ($CHCl_3$) ν = 3300 (NH) cm^{-1}.

Lithiation of Functionalized Phenyl Thioethers 1 and 4 and Reaction with Electrophiles. Preparation of Compounds 3 and 6; General Procedure
A 1.6 M BuLi hexane solution (0.69 mL, 1.1 mmol) was added at –78 °C to a functionalized phenyl thioether (**1** or **2**, 1.0 mmol) THF solution (2 mL) under Ar at –78 °C. After 10 min at this temperature, the corresponding alcoholate (compounds **1**) or amide (compounds **4**) solution was added via syringe to a cooled (–78 °C) blue suspension of lithium powder (0.10 g, 14.0 mmol) and a catalytic amount of DTBB (0.03 g, 0.11 mmol) in THF under Ar. The mixture was stirred at the same temperature for 1.5 h in the case of compounds **1a–e** and **4a–b**, 2 h in the case of compound **4c**, 3 h in the case of compound **1f** and 5 h in the case of compound **4d**. Then, the corresponding electrophile (1.1 mmol, 0.5 mL in the case of deuterium oxide) was added at –78 °C and the temperature was allowed to rise to 20 °C overnight. The resulting mixture was hydrolyzed with H_2O (15 mL) and extracted with EtOAc (3 × 20 mL). The organic layer was dried (Na_2SO_4) and evaporated (15 mmHg) to give a residue, which was purified by column chromatography (silica gel, hexane/EtOAc) and/or recrystallized to yield pure products **3** and **6**. Yields are included in Tables 1 and 2. Physical, spectroscopical and analytical data as well as literature references for known compounds follow.

2-Deuterio-1-phenylethanol (3aa)[26]
Colorless liquid, R_f 0.31 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) =124 (M, 18), 107 (64), 105 (18), 104 (11), 79 (100), 78 (31), 77 (57), 53 (21), 52 (17), 51 (46), 50 (19), 44 (58).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44–1.49 (m, CH_2D, 2H), 2.04 (br s, OH, 1H), 4.86 (t, *J* = 6.4 Hz, CHOH, 1H), 7.23–7.37 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.8 (t, *J* = 19.5 Hz, CH_2D), 70.3 (CHOH), 125.3, 127.4, 128.4, 145.8 (ArC).

IR (neat): ν = 3745–3110 (OH) cm^{-1}.

HRMS calcd for C_8H_9DO: 123.0794; found: 123.0794.

***syn*-4,4-Dimethyl-1-phenylpentane-1,3-diol [*syn*-3ab][27]**
White solid mp 99 °C, R_f 0.15 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 208 (M^+, 2), 190 (12), 134 (16), 133 (62), 120 (13), 107 (66), 105 (71), 104 (28), 103 (12), 92 (15), 84 (41), 79 (54), 78 (24), 77 (51), 71 (21), 69 (55), 57 (100), 55 (15), 51 (25), 43 (47).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 [s, $(CH_3)_3C$, 9H], 1.76 (ddd, *J* = 3.4, 10.5, 14.4 Hz, CHH, 1H), 1.88 (ddd, *J* = 2.4, 7.6, 14.4 Hz, CHH, 1H), 3.21 (br s, OH, 2H), 3.49 [dd, *J* = 2.4, 10.5 Hz, $(CH_3)_3CCHOH$, 1H], 5.04 (dd, *J* = 3.4, 7.6 Hz, PhCHOH, 1H), 7.25–7.38 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 [$(CH_3)_3C$], 34.6 [$(CH_3)_3C$], 39.35 ($CCHOHCH_2$), 71.7 (PhCHOH), 76.1 (CCHOH), 125.5, 127.1, 128.4, 144.8 (ArC).

IR ($CHCl_3$): ν = 3600–3150 (OH) cm^{-1}.

***anti*-4,4-Dimethyl-1-phenylpentane-1,3-diol [*anti*-3ab][27]**
White solid mp 93 °C, R_f 0.16 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 208 (M^+, 2), 133 (52), 107 (55), 105 (66), 104 (28), 103 (12), 92 (16), 84 (40), 79 (51), 78 (22), 77 (48), 71 (19), 69 (50), 57 (100), 55 (13), 51 (24), 43 (41).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 [s, $(CH_3)_3C$, 9H], 1.71–1.85 (m, CH_2, 2H), 3.58 [dd, *J* = 2.4 Hz, 9.8, $(CH_3)_3CCHOH$, 1H], 3.73 (br s, OH, 2H), 4.89 (dd, *J* = 3.36, 9.46, PhCHOH, 1H), 7.26–7.39 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 [$(CH_3)_3C$], 34.9 [$(CH_3)_3C$], 39.9 ($CCHOHCH_2$), 75.75 (PhCHOH), 80.85 (CCHOH), 125.7, 127.5, 128.5, 144.7 (ArC).

IR ($CHCl_3$): ν = 3600–3150 (OH) cm^{-1}.

1,3-Diphenylpropane-1,3-diol (3ac) (diastereoisomeric mixture)[28]
White solid mp 123 °C, R_f 0.18 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 211 (M^++1–H_2O, 5), 108 (12), 107 (23), 105 (55), 104 (100), 103 (13), 79 (49), 78 (23), 77 (54), 51 (28).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (t, *J* = 5.8 Hz, CH_2, 2H), 3.28 (br s, OH, 2H), 4.89–4.96 (m, $CHOHCH_2CHOH$, 2H), 7.23–7.33 (m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.4, 47.5 (CH_2), 71.6, 74.9 (CHOH), 125.3, 125.65, 127.4, 127.6, 128.4, 128.4, 144.1 (ArC).

IR ($CHCl_3$): ν = 3650–3090 (OH) cm^{-1}.

3-Methyl-1-phenylbutane-1,3-diol (3ad)[29]
Colorless oil, R_f 0.47 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 162 ($M^+ - H_2O$, 28), 147 (25), 107 (100), 105 (33), 104 (52), 103 (11), 79 (58), 78 (24), 77 (51), 71 (21), 59 (51), 56 (85), 51 (30), 43 (91).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, C*H*$_3$COHCH$_3$, 3H), 1.37 (s, CH$_3$COHC*H*$_3$, 3H), 1.62 (d, *J* = 14.7 Hz, C*H*H, 1H), 1.91 (dd, *J* = 11.3 Hz, 14.7, CH*H*, 1H), 3.85 (br s, OH, 2H), 5.00 (d, *J* = 11.3 Hz, C*H*OH, 1H), 7.21–7.32 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.4, 31.6 [(*C*H$_3$)$_2$COH], 50.2 (CH_2), 71.5 (CH$_3$*C*OHCH$_3$), 72.1 (Ph*C*OH), 125.6, 127.3, 128.3, 144.7 (ArC).

IR ($CHCl_3$): ν = 3700–3100 (OH) cm^{-1}.

1-(2-Hydroxy-2-phenylethyl)cyclohexanol (3ae)
White solid mp 100 °C, R_f 0.25 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 202 ($M^+ - H_2O$, 10), 120 (12), 107 (39), 104 (100), 96 (40), 81 (49), 79 (40), 77 (39), 71 (10), 69 (13), 68 (10), 67 (17), 55 (54), 54 (12), 51 (22), 43 (27), 42 (27).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30–1.80 (m, 6 CH_2, 12H), 3.31 (br s, OH, 2H), 5.01 (dd, *J* = 4.4 Hz, 9.0, C*H*OH, 1H), 7.23–7.33 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3, 25.7, 35.6, 40.0 (CH_2), 71.3 (CH_2*C*OHCH$_2$), 72.5 (PhCHOH), 125.6, 127.2, 128.3, 144.9 (ArC).

IR ($CHCl_3$): ν = 3700–3100 (OH) cm^{-1}.

HRMS: calcd for $C_{14}H_{20}O_2$–H_2O: 202.1358; found: 202.1358.

1-Deuteriooctan-2-ol (3ba)[30]
Colorless liquid, R_f 0.26 (hexane/EtOAc: 10/1).

MS (EI): *m/z* (%) = 202 ($M^+ - CH_3$, 1), 55 (22), 46 (100), 45 (14), 44 (12), 43 (19).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86–0.91 (m, CH_3, 3H), 1.06–1.52 [s, (C*H*$_2$)$_5$CHOHC*H*$_2$D, 12H], 1.52 (br s, OH, 1H), 3.74–3.81 (m, C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH$_3$*C*H$_2$), 23.3 (t, *J* = 19.2 Hz, CH_2D), 25.7,29.3, 31.8, 39.35 [$(CH_2)_4$], 68.1 (CHOH).

IR (neat): ν = 3675–3105 (OH) cm^{-1}.

2,2-Dimethylundecane-3,5-diol (3bb) (diastereoisomeric mixture)[31]
Colorless oil, R_f 0.30 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 159 (M^+ – *t*-Bu, 5),123 (12), 113 (15), 97 (21), 95 (23), 87 (15), 84 (15), 81 (44), 71 (16), 70 (16), 69 (46), 67 (28), 57 (61), 56 (22), 55 (86), 45 (22), 44 (17), 43 (100), 42 (20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 [s, (C*H*$_3$)$_3$C, C*H*$_3$CH$_2$, 12H], 1.4–1.67 [m, (C*H*$_2$)$_5$CHOHC*H*$_2$, 12H], 2.64 (br s, OH, 2H), 3.46–3.61 [m, (CH$_3$)$_3$CC*H*OH, 1H], 3.91–3.98 (m, CH$_2$C*H*OHCH$_2$, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.0 (CH_3), 22.6 (CH_2), 25.3, 25.5, 25.6 [(*C*H$_3$)$_3$C], 25.95, 29.3, 31.8 (CH_2), 34.6, 34.8 [(CH$_3$)$_3$*C*], 36.9, 37.0, 37.1, 38.3 (CH_2), 69.7, 73.4 (CH$_2$*C*HOHCH$_2$), 75.9, 81.2 (C*C*HOH).

IR (neat) ν = 3715–3055 (OH) cm^{-1}.

2-Methyldecane-2,4-diol (3bd)[32]
Colorless oil, R_f 0.25 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 170 ($M^+ - H_2O$, 1), 95 (21), 85 (30), 82 (16), 81 (25), 79 (12), 71 (61), 69 (17), 68 (42), 67 (46), 55 (32), 53 (15), 43 (100), 42 (10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, CH_3, 3H), 1.24–1.67 [m, (C*H*$_3$)$_2$COH, CH$_3$(C*H*$_2$)$_5$, C*H*$_2$COH, 18H], 3.69 (br s, CHO*H*, CO*H*, 2H), 3.98 (m, C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (*C*H$_3$CH$_2$), 22.5, 25.35, 27.6, 29.3 [CH$_3$(*C*H$_2$)$_4$], 31.8, 31.9 [(*C*H$_3$)$_2$COH], 38.3 (CHOH*C*H$_2$), 47.6 [*C*H$_2$COH(CH$_3$)$_2$], 69.7 (CHOH), 71.6 [*C*OH(CH$_3$)$_2$].

IR (neat): ν = 3660–3070 (OH) cm^{-1}.

1-(2-Hydroxyoctyl)cyclohexanol (3be)[31],
Colorless oil, R_f 0.32 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 210 ($M^+ - H_2O$, 1), 192 (22), 135 (17), 125 (19), 121 (18), 112 (16), 108 (12), 107 (21), 97 (11), 95 (14), 93 (49), 91 (15), 83 (48), 80 (14), 79 (100), 77 (13), 67 (58), 53 (13), 43 (13).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.89 (m, CH_3, 3H), 1.06–1.77 [m, CH$_3$(C*H*$_2$)$_5$, CHOHC*H*$_2$COH, COH(C*H*$_2$)$_5$, 22H], 3.66 (br s, OH, 2H), 3.95–4.00 (m, C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 14.05 (CH_3), 22.05, 22.2, 22.5, 22.6, 25.4, 25.8, 29.3, 29.3, 31.7, 31.8, 35.7, 38.3, 38.4, 40.2 [$(CH_2)_5$], 46.2 (CHOH*C*H$_2$COH), 68.7 (CHOH), 72.5 (COH).

IR (neat): ν = 3725–3040 (OH) cm^{-1}.

2-(1-Hydroxy-1-methylethyl)cyclohexanol (3cd) (diastereoisomeric mixture)[31]
Colorless oil, R_f 0.41 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 143 ($M^+ - CH_3$, 5), 101 (100), 83 (20), 69 (18), 59 (19), 58 (17), 57 (29), 56 (19), 55 (60), 45 (92), 43 (71).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80–2.05 [m, (CH$_3$)$_2$CO, (C*H*$_2$)$_5$, 16H], 3.68 (br s, OH, 2H), 4.17–4.24 (m, C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (*C*H$_3$COHCH$_3$), 24.8, 25.9, 27.5 [$(CH_2)_3$], 29.9 (CH$_3$COH*C*H$_3$), 36.0 (CHOH*C*H$_2$), 53.8 (*C*HCHOH), 73.3 (CHOH), 75.1 (COH).

IR (neat): ν = 3750–3025 (OH) cm^{-1}.

1-(2-Hydroxycyclohexyl)cyclohexanol (3ce) (diastereoisomeric mixture)
White solid mp 67 °C, R_f 0.22 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 180 ($M^+ - H_2O$, 11), 162 (49), 147 (12), 137 (50), 134 (13); 133 (47), 124 (11), 120 (21), 119 (35), 115 (11), 109 (27), 106 (10), 105 (31), 95 (27), 94 (57), 93 (30), 92 (21), 91 (78), 81 (66), 80 (42), 79 (100), 78 (23), 77 (48), 67 (47), 66 (15), 65 (21), 55 (83), 53 (45), 52 (12), 51 (28), 44 (15), 43 (33).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–2.06 [m, (CH$_2$)$_4$CH, (C*H*$_2$)$_5$, 19H], 3.72 (td, *J* = 10.1, 4.3 Hz, C*H*OH, 1H), 7.28 (br s, OH, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.05, 21.3, 24.8, 25.9, 26.1, 26.8, 30.3, 36.2, 36.3 (CH_2), 54.3 (CH), 72.4 (CHOH), 75.8 (COH).

IR ($CHCl_3$): ν = 3690–3025 (OH) cm^{-1}.

HRMS: calcd for $C_{12}H_{22}O_2$–H_2O: 180.1514; found: 180.1514.

2-Deuterio-N-phenylethylamine (3da)[26]
Colorless oil, R_f 0.52 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 122 (M^+, 30), 106 (100), 79 (17), 77 (30), 65 (10), 53 (12), 51 (24).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10–1.25 (m, CH_2D, 2H), 3.13 (t, *J* = 7.0 Hz, PhNHC*H*$_2$, 2H), 3.38 (br s, NH, 1H), 6.57–6.71, 7.14–7.21 (2m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.55 (t, *J* = 7.0 Hz, CH_2D), 38.3 (CH_2NH), 112.7, 117.1, 129.2, 148.4 (ArC).

IR (neat): ν = 3400 (NH) cm^{-1}.

4,4-Dimethyl-1-phenylaminopentan-3-ol (3db)[33]
White solid mp 67 °C, R_f 0.48 (hexane/EtOAc: 2/1).

MS (EI): *m/z* (%) = 207 (M^+, 10), 106 (100), 93 (14), 77 (19), 57 (11), 51 (10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 [s, $(CH_3)_3C$, 9H], 1.52–1.63 (m, C*H*HCHOH, 1H), 1.79–1.88 (m, CH*H*CHOH, 1H), 2.95 (br s, OH, NH, 2H), 3.30 (t, *J* = 6.4 Hz, PhNHCH_2, 2H), 3.38 (d, *J* = 10.7 Hz, C*H*OH, 1H), 6.63–6.74, 7.14–7.20 (2m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 [(CH_3)$_3$C], 30.6 (CH_2CHOH), 34.9 [(CH_3)$_3$*C*], 43.0 (CH_2NH), 79.4 (CHOH), 113.3, 117.7, 129.2, 148.3 (ArC).

IR ($CHCl_3$): ν = 3770–3125 (OH), 3290 (NH) cm^{-1}.

1-Phenyl-3-phenylaminopropanol (3dc)[10b]
White solid mp 44 °C, R_f 0.36 (hexane/EtOAc: 2/1).

MS (EI): *m/z* (%) = 227 (M^+, 22), 209 (23), 133 (12), 130 (15), 107 (14), 106 (100), 105 (70), 104 (54), 103 (15), 94 (20), 93 (26), 91 (15), 79 (21), 78 (26), 77 (75), 65 (14), 52 (15), 51 (47), 50 (15).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01–2.06 (m, CH_2CHOH, 2H), 3.25 (t, *J* = 6.4 Hz, PhNHCH_2, 2H), 3.10–3.70 (br s, OH, NH, 2H), 4.85 (t, *J* = 5.2 Hz, CH, 1H), 6.59–6.75, 7.14–7.35 (2m, ArH,10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.1 (CH_2CHOH), 41.6 (CH_2NH), 73.6 (CHOH), 113.2, 117.7, 125.7, 127.6, 129.2, 144.3, 148.2 (ArC).

IR ($CHCl_3$): ν = 3735–3130 (OH), 3395 (NH) cm^{-1}.

2-Methyl-4-phenylaminobutan-2-ol (3dd)[10b]
White solid mp 60 °C, R_f 0.18 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 179 (M^+, 11), 146 (13), 106 (100), 105 (33), 104 (29), 93 (16), 77 (56), 65 (11), 56 (14), 51 (36), 50 (15).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 [s, $(CH_3)_2$C, 6H], 1.77 (t, *J* = 6.7 Hz, CH_2CHOH, 2H), 3.12 (br s, OH, NH, 2H), 3.25 (t, *J* = 6.7 Hz, PhNHCH_2, 2H), 6.62–6.74, 7.14–7.20 (2m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5 [(CH_3)$_2$COH], 40.4 (CH_2NH), 41.7 (CH_2COH), 70.9 (COH), 113.2, 117.6, 129.1, 148.3 (ArC).

IR ($CHCl_3$): ν = 3670–3100 (OH), 3275 (NH) cm^{-1}.

1-(2-Phenylaminoethyl)cyclohexanol (3de)[10b]
White solid mp 120 °C, R_f 0.32 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 219 (M^+, 5), 106 (100), 105 (14), 104 (13), 81 (12), 79 (12), 77 (31), 67 (13), 55 (11), 51 (18).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.63 [m, $(CH_2)_5$, 10H], 1.79 (t, *J* = 6.7 Hz, CH_2COH, 2H), 2.55–3.50 (br s, OH, NH, 2H), 3.28 (t, *J* = 6.7 Hz, CH_2NH, 2H), 6.62–6.74, 7.15–7.25 (2m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 25.7, 37.7 [$(CH_2)_5$], 39.5 (NHCH_2CH_2), 55.4 (NHCH_2) 71.8 (COH); 113.2, 117.6, 129.2, 148.4 (ArC).

IR ($CHCl_3$): ν = 3600–2990 (OH), 3270 (NH) cm^{-1}.

2-Deuterio-1-phenyl-N-phenylethylamine (3ea)[26]
Colorless oil, R_f 0.46 (hexane/EtOAc: 10/1).

MS (EI): *m/z* (%) = 198 (M^+, 36), 183 (15), 182 (100), 121 (17), 107 (22), 106 (79), 105 (27), 104(32), 99 (11), 94 (21), 93 (60), 90 (12), 80 (23), 79 (23), 78 (36), 77 (78), 57 (20), 52 (11), 51 (53), 50 (14), 43 (41), 42 (10).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (d, *J* = 6.7 Hz, CH_2D, 2H), 1.47–2.00 (br s, NH, 1H), 4.48 (t, *J* = 6.7 Hz, CH, 1H), 6.49–6.67, 7.05–7.38 (2m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.3 (t, *J* = 19.6 Hz, CH_2D), 53.4 (CH), 113.2, 117.2, 125.8, 126.8, 128.61, 129.8, 145.2, 147.3 (ArC).

IR (neat): ν = 3410 (NH) cm^{-1}.

***syn*-4,4-Dimethyl-1-phenyl-1-phenylaminopentan-3-ol (*syn*-3eb):**
White solid mp 148 °C, R_f 0.36 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 283 (M^+, 5), 183 (16), 182 (100), 104 (23), 93 (26), 78 (12), 77 (43), 66 (10), 57 (23), 51 (18), 44 (43).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 [s, $(CH_3)_3$C, 9H], 1.57 (br s, OH, NH, 2H), 1.71–1.96 (m, CH_2, 2H), 3.40 d(d, *J* = 1.9 Hz, 9.8, C*H*OH, 1H), 4.46 (dd, *J* = 5.2 Hz, 8.8, C*H*NH, 1H), 6.42–6.69, 7.05–7.51 (2m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3 [(CH_3)$_3$C], 34.95 [(CH_3)$_3$*C*], 39.85 (CH_2), 59.2 (CHNH), 79.6 (CHOH), 114.2, 117.75, 126.1, 128.6, 128.9, 144.1, 147.2 (ArC).

IR ($CHCl_3$): ν = 3710–3140 (OH), 3395 (NH) cm^{-1}.

Anal. calcd for $C_{19}H_{25}NO$: C, 80.51; H, 8.90; N, 4.94; found: C, 80.01; H, 8.93; N, 4.81.

***anti*-4,4-Dimethyl-1-phenyl-1-phenylaminopentan-3-ol (*anti*-3eb):**
Colorless oil, R_f 0.38 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 183 (15), 182 (100), 104 (26), 93 (30), 78 (10), 77 (47), 57 (22), 51 (16), 44 (38).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 [s, $(CH_3)_3$C, 9H], 1.60 (br s, OH, NH, 2H), 1.79–1.93 (m, CH_2, 2H), 3.44 d(d, *J* = 2.7 Hz, 8.8, C*H*OH, 1H), 4.72 (dd, *J* = 4.3 Hz, 7.3, C*H*NH, 1H), 6.42–6.69, 7.05–7.57 (2m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 [(CH_3)$_3$C], 34.8 [(CH_3)$_3$*C*], 40.1 (CH_2), 55.2 (CHNH), 76.3 (CHOH), 113.2, 117.05, 126.25, 126.8, 128.6, 132.0, 143.85, 148.2 (ArC).

IR ($CHCl_3$): ν = 3650–3100 (OH), 3360 (NH) cm^{-1}.

HRMS: calcd for $C_{19}H_{25}NO$: 283.1936; found: 283.1931.

1,3-Diphenyl-3-phenylaminopropanol (3ec) (diastereoisomeric mixture)[5b]
Colorless oil, R_f 0.39 (hexane/EtOAc: 5/1).

MS (EI): *m/z* (%) = 303 (M^+, 1), 285 (15), 206 (13), 194 (12), 182 (33), 181 (55), 180 (59), 105 (17), 104 (53), 103 (22), 93 (16), 79 (10), 78 (39), 77 (100), 76 (11), 76 (11), 63 (11), 52 (14), 51 (64), 50 (20), 44 (43).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00–2.29 (m, CH_2, 2H), 3.38–3.60 (br s, OH, NH, 2H), 4.50–4.58 (m, C*H*NH, 1H), 4.75–4.79 (m, C*H*OH, 1H), 6.47–6.67, 7.03–7.38 (2m, ArH, 15H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.7, 47.4 (CH_2), 55.3, 57.9 (CHNH), 71.7, 73.6 (CHOH), 113.6, 114.2, 117.4, 117.9, 125.7, 125.7, 126.2, 126.3, 126.9, 126.9, 127.1, 127.5, 127.6, 127.7, 128.5, 128.5, 128.5, 128.6, 128.7, 128.7, 129.0, 143.4, 143.7, 144.3, 144.5, 147.2, 147.2 (ArC).

IR (neat): ν = 3600–3100 (OH), 3300 (NH) cm^{-1}.

1-(2-Phenyl-2-phenylaminoethyl)cyclohexanol (3ee)
Colorless oil, R_f 0.21 (hexane/EtOAc: 10/1).

MS (EI): *m/z* (%) = 295 (M^+, 1), 183 (15), 182 (100), 181 (33), 180 (39); 104 (25), 93 (12), 81 (15), 79 (15), 78 (14), 77 (70), 67 (13), 55 (13), 51 (33).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86–2.03 [m, CHCH_2COH, (CH_2)$_5$, 12H], 3.80 (br s, OH, NH, 2H), 4.57 (dd, *J* = 4.9 Hz, 9.2, C*H*NH, 1H), 6.52–6.68, 7.02–7.42 (2m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 22.3, 25.7, 31.4, 35.8 [(CH_2)$_5$], 40.0 (CHNHCH_2), 55.4 (CHNH), 72.1 (COH); 114.3, 117.8, 125.9, 126.8, 128.65, 128.95, 144.8, 147.3 (ArC).

IR (neat): ν = 3550–3110 (OH), 3370 (NH) cm^{-1}.

HRMS: calcd for $C_{20}H_{25}NO$: 295.1936; found: 295.1931.

3-Isopropylamino-1-phenylpropanol (3fc)
Colorless oil, R_f 0.32 (EtOAc).

MS (EI): *m/z* (%) = 193 (M^+, 3), 117 (15), 105 (17), 104 (19), 91 (18), 79 (12), 78 (15), 77 (33),72 (41), 71 (12), 58 (13), 57 (15), 56 (83), 51 (28), 50 (11), 44 (100), 43 (51), 42 (30).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.1 Hz, CH_3, 3H), 1.16 (d, *J* = 6.7 Hz, CH_3, 3H), 1.7–1.91, 1.92–2.03 (2m, CHOHCH_2, 2H), 2.89–2.99 (m, C*H*NHCH_2, 3H), 4.91 (dd, *J* = 3.1 Hz, 8.5, C*H*OH, 1H), 6.28 (br s, OH, NH, 2H), 7.20–7.37 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 21.0 [(*C*H_3)$_2$CH], 36.2 (*C*H_2CH$_2$NH), 43.9 (CH_2NH), 49.1 (CHNH), 73.45 (CHOH), 125.4, 126.9, 128.15, 144.6 (ArC).

IR (neat): ν = 3550–3100 (OH, NH) cm^{-1}.

HRMS: calcd for $C_{12}H_{19}NO$: 193.1467; found: 193.1455.

4-Isopropylamino-2-methylbutan-2-ol (3fd)
Brown oil, R_f 0.20 (EtOAc).

MS (EI): *m/z* (%) = 145 (M^+, 1), 130 (22), 112 (19), 73 (14), 72 (100), 70 (14), 59 (19), 58 (29), 56 (100), 55 (11), 45 (16), 44 (94), 43 (68), 42 (27).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 [d, *J* = 6.1 Hz, (CH_3)$_2$CH, 6H], 1.22 [s, (CH_3)$_2$COH, 6H], 1.59 (t, *J* = 6.1 Hz, CH_2COH, 2H), 2.73–2.82 (m, C*H*NH, 1H), 2.89 (t, *J* = 5.8 Hz, CH_2NH, 2H), 3.55 (br s, OH, NH, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.6 [(*C*H_3)$_2$CH], 29.6 [(*C*H_3)$_2$COH], 40.65 (*C*H_2COH), 43.3 (CH_2NH), 48.7 (CHNH), 70.8 (COH).

IR (neat): ν = 3750–3020 (OH), 3275 (NH) cm^{-1}.

HRMS: cald for $C_8H_{19}NO$: 145.1467; found: 145.1467.

1-(2-Isopropylaminoethyl)cyclohexanol (3fe)[31]
Colorless oil, R_f 0.24 (MeOH).

MS (EI): *m/z* (%) = 152 (M^+ – 33, 1), 72 (36), 56 (10), 44 (100), 43 (25), 42 (12), 41 (19).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 [d, *J* = 6.7 Hz, (CH_3)$_2$CH, 6H], 1.20–1.70 [m, (CH_2)$_5$, 10H], 1.85 (t, *J* = 6.3 Hz, CH_2COH, 2H), 3.04 (t, *J* = 6.3 Hz, CH_2NH, 2H), 3.08–3.14 (m, C*H*NH, 1H), 6.82 (br s, OH, NH, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.85 (CH_2), 21.9 [(*C*H_3)$_2$CH], 25.8, 36.8, 37.4 (CH_2), 40.9 (CH_2NH), 49.3 (CHNH), 71.0 (COH).

IR (neat): ν = 3690–3100 (OH), 3370 (NH) cm^{-1}.

6,6-Dimethylheptane-2,5-diol (6ab) (diastereoisomeric mixture):
White solid mp 70 °C, R_f 0.31 (hexane/EtOAc: 1/1).

MS (EI): *m/z* (%) = 130 (M^+ – 30, 1), 85 (69), 71 (12), 70 (13), 67 (31), 58 (11), 57 (69), 56 (21), 55 (19), 45 (25), 44 (17), 43 (100), 42 (10), 41 (78).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 [s, (CH_3)$_3$C, 9H], 1.20 (d, *J* = 6.3 Hz, CHCH_3, 3H), 1.25–1.38 (m, CH_2C*H*H, 1H), 1.49–1.74 (m, CH_2CH*H*, 3H), 2.75 (br s, OH, 2H), 3.17–3.22 (m, CC*H*OH, 2H), 3.77–3.81, 3.86–3.91 (2m, CH_3C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.3, 23.9 (*C*H_3CH), 25.7, 25.7 [(*C*H_3)$_3$C], 27.0, 28.4, 35.0, 35.0 [(CH_2)$_2$], 36.5, 37.2 [(CH_3)$_3$*C*], 67.5, 68.5 (CH_3*C*HOH), 80.0, 80.4 (C*C*HOH).

IR ($CHCl_3$): ν = 3715–3010 (OH) cm^{-1}.

Anal. calcd for $C_9H_{20}O_2$: C, 67.44; H, 12.59; found: C, 67.27; H, 12.61.

1-Phenylpentane-1,4-diol (6ac) (diastereoisomeric mixture)[34]
Colorless oil, R_f 0.32 (hexane/EtOAc: 1/2).

MS (EI): *m/z* (%) = 180 (M^+, 1), 120 (33), 117 (13), 107 (79), 106 (79), 105 (27), 91 (15), 79 (100), 78 (21), 77 (66), 71 (14), 57 (10), 56 (55), 55 (14), 51 (28), 45 (32), 43 (51), 41 (36).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14, 1.15 (2d, *J* = 6.1 Hz, CH_3, 3H), 1.25–1.57 (m, CH_2C*H*H, 3H), 1.78–1.84 (m, CH_2CH*H*, 1H), 3.12 (br s, OH, 2H), 3.74–3.84 (m, C*H*OHCH$_3$, 1H), 4.61–4.70 (m, C*H*OHPh, 1H), 7.22–7.33 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.3, 23.6 (CH_3), 34.9, 35.0, 35.9, 36.1 (CH_2CH_2), 67.6, 68.15 (*C*HOHCH$_3$), 74.1, 74.6 (*C*HOHPh), 125.7, 125.8, 127.3, 127.3, 128.3, 144.7, 144.8 (ArC).

IR (neat): ν = 3620–3800 (OH) cm^{-1}.

2-Methylhexane-2,5-diol (6ad)[35]
Colorless oil, R_f 0.22 (hexane/EtOAc: 1/1).

MS (EI): *m/z* (%) = 105 (M^+ – 27, 1), 59 (32), 45 (12), 43 (100), 41 (13).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.1 Hz, CHOHCH_3, 3H), 1.23 [s, (CH_3)$_2$C, 6H], 1.57 (t, *J* = 1.22, COHCH_2, 2H), 1.52–1.64 (m, CHOHCH_2, 2H), 2.70 (br s, OH, 2H), 3.75–3.84 (m,C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (*C*H$_3$CHOH), 29.0, 29.75 [(*C*H$_3$)$_2$COH], 33.7 (CHOH*C*H$_2$), 39.8 (COH*C*H$_2$), 68.3 (*C*HOH), 70.6 (*C*OH).

IR (neat): ν = 3730–3030 (OH) cm^{-1}.

1-(3-Hydroxybutyl)cyclohexanol (6ae)[31]
Colorless oil, R_f 0.46 (EtOAc).

MS (EI): *m/z* (%) = 154 (M^+ – H_2O, 1), 99 (38), 98 (13), 81 (43), 79 (10), 71 (11), 69 (15), 67 (14), 58 (18), 57 (22), 56 (16), 55 (100), 45 (16), 44 (13), 43 (66), 42 (22), 41 (50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.1 Hz, CH_3, 3H), 1.25–1.56 [m, CHOH(CH_2)$_2$, (CH_2)$_5$, 14H], 2.66 (br s, OH, 2H), 3.76–3.80 (m, C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2, 22.3 (CH_2), 23.5 [(*C*H$_3$)$_3$C], 25.8, 32.8, 37.1, 37.9 (CH_2), 68.35 (CHOH), 71.1 (COH).

IR (neat): ν = 3750–3035 (OH) cm^{-1}.

1,4-Diphenylbutane-1,4-diol (6bc) (diastereoisomeric mixture)[36]
White solid mp 88–94 °C, R_f 0.34 (hexane/EtOAc: 1/1).

MS (EI): *m/z* (%) = 224 (M^+ – H_2O, 1), 120 (10), 118 (23), 117 (25), 105 (20), 104 (17), 91 (16), 79 (23), 78 (13), 77 (45), 71 (12), 57 (64), 56 (45), 55 (15), 51 (28), 50 (10), 44 (88), 43 (100), 42 (50), 41 (84).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.73–1.89 (m, CH_2CH_2, 4H), 3.04 (br s, OH, 2H), 4.59–4.65 [m, C*H*OH, 2H], 7.19–7.32 (m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.0, 35.9 (CH_2), 74.0, 74.4 (CHOH), 125.7, 127.35, 128.3, 144.5 (ArC).

IR ($CHCl_3$): ν = 3735–3115 (OH) cm^{-1}.

1-(3-Hydroxy-3-phenylpropyl)cyclohexanol (6be)
White solid mp 83–85 °C, R_f 0.34 (hexane/EtOAc: 1/1).

MS (EI): *m/z* (%) = 216 ($M^+ - H_2O$, 3), 120 (15), 118 (12), 117 (14), 107 (14), 105 (16), 104 (11),91 (25), 82 (10), 81 (40), 79 (39), 78 (14), 77 (39), 69 (12), 67 (24), 65 (11), 57 (26), 56 (18), 55 (100), 53 (16), 51 (22), 44 (71), 43 (66), 42 (30), 41 (80).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22–1.61 [m, CH_2COH, (CH_2)$_5$, 12H], 1.73–1.91 (m, CHOHCH_2, 2H), 2.82 (br s, OH, 2H), 4.64 (dd, *J* = 4.9 Hz, 7.9, C*H*OH, 1H), 7.17–7.33 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 22.2, 25.7, 35.6, 37.1, 37.8 (CH_2), 71.1 (COH), 74.7 (CHOH), 125.8, 127.2, 128.3, 144.95 (ArC).

IR ($CHCl_3$): ν = 3675–3084 (OH) cm^{-1}.

Anal. calcd for $C_{15}H_{22}O_2$: C, 76.87; H, 9.47; found: C, 77.10; H, 9.54.

(1*S*,4*R/S*)-1,4-Diphenylbutane-1,4-diol [(*S*)-6bc] (diastereoisomeric mixture)[36]
White solid mp 90–96 °C, R_f 0.38 (hexane/EtOAc: 1/1), $[\alpha]_D^{25}$ −1.75 (*c* = 1.03, CH_2Cl_2).

MS (EI): *m/z* (%) = 224 ($M^+ - H_2O$, 3), 120 (28), 118 (62), 117 (68), 115 (18), 107 (21), 105 (38), 104 (46), 91 (38), 89 (10), 79 (60), 78 (30), 77 (100), 65 (18), 63 (15), 57 (10), 52 (14), 51 (60), 50 (18), 44 (63), 43 (24), 41 (20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74–1.87 [m, $(CH_2)_2$, 4H], 2.91 (br s, OH, 2H), 4.60–4.68 [m, C*H*OH, 2H], 7.21–7.30 (m, ArH, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.0, 35.9 (CH_2), 74.1, 74.5 (CHOH), 125.8, 127.35, 127.4, 128.3, 144.5, 144.6 (ArC).

IR ($CHCl_3$): ν = 3735–3110 (OH) cm^{-1}.

(S)-4-Methyl-1-phenylpentane-1,4-diol [(*S*)-6bd][37]
White solid mp 87–89 °C, R_f 0.23 (hexane/EtOAc: 1/1), $[\alpha]_D^{25}$ +34.48 (*c* = 1.01, CH_2Cl_2).

MS (EI): *m/z* (%) = 176 ($M^+ - H_2O$, 2), 120 (17), 117 (11), 107 (27), 79 (32), 77 (27), 70 (54), 59 (41), 55 (37), 51 (12), 43 (100), 42 (16), 41 (14).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16, 1.17 [2s, (CH_3)$_2$C, 6H], 1.40–1.50 (m, CHOHC*H*H, 1H), 1.56–1.67 (m, CHOHCH*H*, 1H), 1.71–1.89 (m, COHCH_2, 2H), 3.54 (br s, OH, 2H), 4.61 (dd, *J* = 4.9 Hz, 7.9, C*H*OH, 1H), 7.23–7.32 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.9, 29.6 [(*C*H$_3$)$_2$COH], 33.85, 39.7 [(CH$_2$)$_2$], 70.5 (*C*OH), 74.5 (*C*HOH), 125.8, 127.2, 128.3, 144.85 (ArC).

IR ($CHCl_3$): ν = 3675–3085 (OH) cm^{-1}.

Anal. calcd for $C_{12}H_{18}O_2$: C, 74.18; H, 9.34; found: C, 74.34; H, 9.53.

4-Isopropylamino-1-phenylbutanol (6cc)
Colorless liquid, R_f 0.17 (EtOAc).

MS (EI): *m/z* (%) = 207 (M^+, 7), 174 (34), 131 (43), 91 (20), 77 (17), 72 (100), 58 (22), 56 (15), 44 (41), 43 (25), 42 (15).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 [d, *J* = 6.4 Hz, (CH_3)$_2$CH, 6H], 1.50–1.95 [m, NHCH$_2$(CH_2)$_2$, 4H], 2.53–2.61 [m, (CH$_3$)$_2$C*H*, 1H], 2.73–2.85 (m, NHCH_2, 2H), 3.76 (br s, NH, OH, 2H), 4.66 (dd, *J* = 3.1 Hz, 8.2, C*H*OH, 1H), 7.21–7.38 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3 [(*C*H$_3$)$_2$CH], 22.5 (*C*H$_2$CH$_2$NH), 27.5 (*C*H$_2$CHOH), 46.9 (CH$_2$NH), 48.7 (CHNH), 73.4 (CHOH), 125.7, 126.6, 128.05, 145.8 (ArC).

IR (neat): ν = 3370–3120 (OH), 3380 (NH) cm^{-1}.

HRMS: calcd for $C_{12}H_{19}NS$: 207.1623; found: 207.1619.

1-(3-Isopropylaminopropyl)cyclohexanol (6ce)[31]
Colorless oil, R_f 0.21 (EtOAc),

MS (EI): *m/z* (%) = 182 ($M^+ - H_2O$, 2), 86 (10), 85 (20), 81 (16), 72 (100), 70 (15), 67 (11), 58 (20), 56 (13), 55 (12), 44 (24), 43 (20), 42 (13).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 [d, *J* = 6.4 Hz, (CH_3)$_2$CH, 6H], 1.10–1.97 [m, (CH_2)$_5$, NHCH$_2$(CH_2)$_2$, 14H], 2.63–2.67 (m, NHCH_2, 2H), 2.76–2.85 [m, (CH$_3$)$_2$C*H*, 1H], 3.64 (br s, NH, OH, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3 (CH_2), 22.35 [(*C*H$_3$)$_2$CH], 23.4, 26.0, 37.4, 37.85 (CH_2), 47.4 (CH_2NH), 48.6 (CHNH), 69.6 (COH).

IR (neat): ν = 3450–3100 (OH), 3355 (NH) cm^{-1}.

3-Ethyl-6-isopropylaminohexan-3-ol (6cf)[31]
Colorless oil, R_f 0.16 (MeOH).

MS (EI): *m/z* (%) = 172 ($M^+ - CH_3$, 1), 104 (15), 99 (22), 91 (13), 72 (100), 70 (11), 69 (22), 58 (19), 57 (42), 56 (10), 55 (17), 44 (40), 43 (48).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 [t, *J* = 7.3 Hz, (CH_3CH$_2$)$_2$COH, 6H], 1.07 [d, *J* = 6.1 Hz, (CH_3)$_2$CH, 6H], 1.45 (q, *J* = 7.3 Hz, CH$_3$CH_2COH, 2H), 1.47 (q, *J* = 7.6 Hz, CH$_3$CH_2COH, 2H), 1.41–1.55 [m, COH(CH_2)$_2$, 4H], 1.54 (br s, NH, OH, 2H), 2.61–2.65 (m, NHCH_2, 2H), 2.71–2.85 [m, (CH$_3$)$_2$C*H*, 1H].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.1 [(*C*H$_3$CH$_2$)$_2$COH], 22.6 [(*C*H$_3$)$_2$CH], 24.2, 31.0, 37.7 (CH_2), 47.7 (CH_2NH), 48.7 (CHNH), 72.85 (COH).

IR (neat): ν = 3745–3050 (OH, NH) cm^{-1}.

1-(3-Isopropylaminopropyl)cyclopentanol (6cg)
White solid mp 52 °C, R_f 0.29 (MeOH).

MS (EI): *m/z* (%) = 186 (M^++1, 1), 152 (10), 72 (10), 70 (12), 67 (18), 58 (17), 56 (11), 55 (11), 44 (26), 43 (34), 42 (15).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 [d, *J* = 6.4 Hz, (CH_3)$_2$CH, 6H], 1.50–1.98 [m, (CH_2)$_4$, (CH_2)$_2$CH$_2$N, 12H], 2.63–2.70 (m, NHCH_2, 2H), 2.76–2.84 [m, (CH$_3$)$_2$C*H*, 1H], 3.40 (br s, NH, OH, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5 (CH_2), 24.0 [(*C*H$_3$)$_2$CH], 26.0, 39.7, 40.0 (CH_2), 47.4 (CH_2NH), 48.7 (CHNH), 80.40 (COH).

IR ($CHCl_3$): ν = 3300–3100 (OH), 3255 (NH) cm^{-1}.

HRMS: calcd for $C_{11}H_{23}NO–H_2O–CH_3$: 152.1439; found: 152.1439.

6-Amino-2,2-dimethylheptan-3-ol (6db) (diastereoisomeric mixture)
Colorless oil, R_f 0.29 (MeOH).

MS (EI): *m/z* (%) = 159 (M^+, 1), 85 (18), 57 (19), 56 (11), 44 (100), 43 (26), 42 (12), 41 (26).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 [s, (CH_3)$_3$C, 9H], 1.10, 1.14 2(d, *J* = 6.4 Hz, CHCH_3, 3H), 1.25–1.77 70 (m, CH_2CH_2, 4H), 2.87 (br s, OH, NH_2, 3H), 3.11–3.13 (m, C*H*NH_2, 1H), 3.15 (d, *J* = 1.5 Hz, C*H*OH, 1H), 3.16 (d, *J* = 1.2 Hz, C*H*OH, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.3 (*C*H$_3$CH), 25.8, 25.9 [(*C*H$_3$)$_2$CH], 27.4, 29.9(*C*H$_2$CH$_2$CHNH$_2$), 34.8, 34.9 (*C*H$_2$CHNH$_2$), 36.6, 37.8 [(CH$_3$)$_2$*C*H], 46.1, 48.1 (CHNH$_2$), 79.4, 80.0 (COH).

IR (neat): ν = 3600–3050 (OH), 3350, 3285 (NH_2) cm^{-1}.

HRMS: calcd for $C_9H_{21}NO$: 159.1623; found: 159.1617.

4-Amino-1-phenylpentan-1-ol (6dc) (diastereoisomeric mixture)
Colorless oil, R_f 0.25 (hexane/EtOAc: 3/1).

MS (EI): *m/z* (%) = 179 (M^+, 1), 57 (10), 44 (100).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05, 1.08 (2d, *J* = 6.4 Hz, CH_3, 3H), 1.18–1.53 (m, C*H*$_2$CHNH$_2$, 2H), 1.72–1.88 (m, C*H*$_2$CHOH, 2H), 2.83–2.93 (m, C*H*NH$_2$, 1H), 3.04 (br s, OH, NH_2, 3H), 4.58–4.67 (m, C*H*OH, 1H), 7.21–7.36 (m, ArH, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.8, 25.05 (CH_3), 35.2, 35.9, 36.55, 37.6 (CH_2CH_2), 46.5, 47.4 ($CHNH_2$), 73.3, 74.0 (CHOH), 125.7, 125.7, 126.75, 126.8, 128.1, 145.5, 145.6 (ArC).

IR (neat): ν = 3700–3000 (OH), 3350, 3280 (NH_2) cm^{-1}.

HRMS: calcd for $C_{11}H_{17}NO$: 179.1310; found: 179.1314.

5-Amino-2-methylhexan-2-ol (6dd)[38]
Colorless oil, R_f 0.33 (MeOH).

MS (EI): *m/z* (%) = 202 ($M^+ - H_2O$, 1), 44 (100), 43 (36).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 6.4 Hz, CH_3, 3H), 1.21 [s, (C*H*$_3$)$_2$COH, 6H], 1.22–1.70 [m, $(CH_2)_2$, 4H], 2.54 (br s, OH, NH_2, 3H), 2.87–2.96 (m, C*H*NH$_2$, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7 (*C*H$_3$CH), 22.2, 29.8 [(*C*H$_3$)$_2$COH], 34.1 (*C*H$_2$CHNH$_2$), 40.7 (*C*H$_2$COH), 47.5 ($CHNH_2$), 69.6 (COH).

IR (neat): ν = 3685–3040 (OH, NH) cm^{-1}.

1-(3-Aminobutyl)cyclohexanol (6de)[31]
Colorless oil, R_f 0.36 (MeOH).

MS (EI): *m/z* (%) = 153 ($M^+ - H_2O$, 1), 57 (19), 55 (17), 44 (100), 43 (16), 42 (11), 41 (16).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.4 Hz, CH_3, 3H), 1.12–1.70 [m, (C*H*$_2$)$_2$CH, (C*H*$_2$)$_5$,14H], 2.31 (br s, OH, NH_2, 3H), 2.87–2.92 (m, C*H*NH$_2$, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3, 22.35 (CH_2), 24.8 (CH_3), 25.9, 32.7, 37.45, 38.0, 41.9 (CH_2), 47.6 ($CHNH_2$), 70.1 (COH).

IR (neat): ν = 3690–3075 (OH), 3400, 3370 (NH_2) cm^{-1}.

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