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Synthesis of Chiral 1,2-Diamines from α-Pinene and Their Use in Asymmetric Nitroaldol Reaction

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Abstract—Chiral diamines with C_1 and C_2 symmetry have been synthesized from 2-hydroxypinan-3-one and tested as ligands in Cu-catalyzed asymmetric nitroaldol reaction of nitromethane with 4-nitrobenzaldehyde.

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Compounds possessing a 1,2-diamine fragment exhibit a broad spectrum of biological activity and are used in organic synthesis as intermediate products for the preparation of heterocyclic systems and as chelating ligands in medicinal chemistry [1–3]. Enantiomerically pure 1,2-diamines are known as efficient chiral ligands in various asymmetric syntheses [4–6]. Therefore, development of methods for stereoselective synthesis of new diamines is a topical problem. For this purpose, appropriate chiral building blocks are bicyclic monoterpenes available as pure enantiomers. In recent time, α-pinene derivatives have been used as substrates in the synthesis of enantiomerically pure compounds [7, 8], chiral auxiliaries [9, 10], and ligands for asymmetric synthesis [11–14].

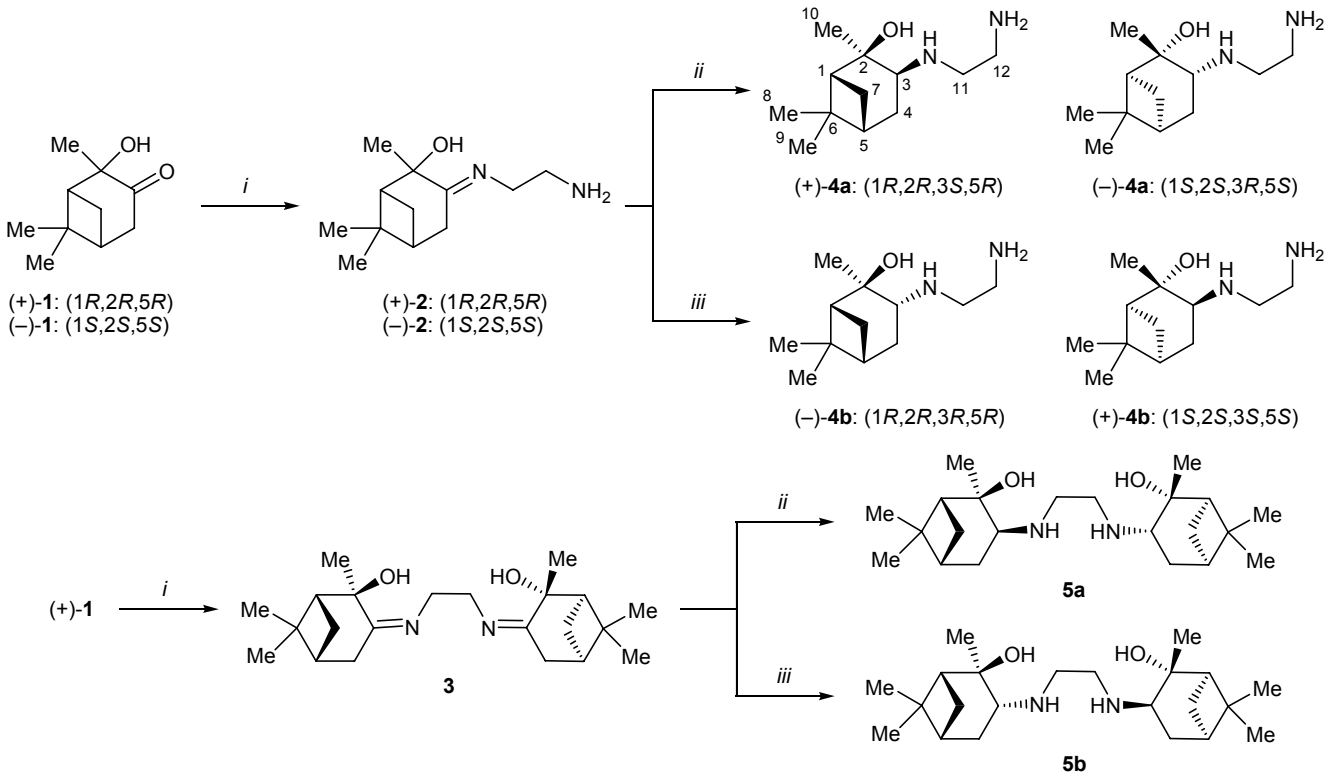
In this article we report the synthesis of new chiral 1,2-diamines based on α-pinene and their use as ligands in catalytic asymmetric nitroaldol reaction. 1,2-Diamines having a chiral terpene fragment (Scheme 1) were synthesized from α-hydroxy ketone **1** which was prepared by oxidation of α-pinene with potassium permanganate [15]. Compounds **2**, **3**, and **5a** were obtained according to the procedures reported previously [16].

Imines (–)-**2** and (+)-**2** were reduced in two ways. The reduction with $LiAlH_4$ in diethyl ether gave *cis*-amino alcohols (+)-**4a** and (–)-**4a**, whereas the reduction with $NaBH(AcO)_3$ in propan-2-ol afforded *trans* isomers (–)-**4b** and (+)-**4b**. Compounds **4a** and **4b** were isolated in 67–82% yield by silica gel column chromatography.

The structure of newly synthesized compounds **4a** and **4b** was determined on the basis of spectral data. The presence of a signal from 3-H in the ^{1}H NMR spectra of **4** indicated reduction of the imino group in **2** to amino. The 3-H signal in the spectrum of (+)-**4a** is overlapped by signals from the methylene protons of the ethylenediamine fragment (δ 2.60–2.79 ppm), while the corresponding signal of (–)-**4b** appears as a broadened triplet at δ 3.06 ppm (J = 5.6 Hz). In the spectrum of (+)-**4a**, the 7β-H signal is overlapped by those belonging to the methyl protons, and the 7β-H proton of (–)-**4b** resonated as a doublet at δ 1.55 ppm (J = 10.2 Hz). The C^2 signal in the ^{13}C NMR spectra of the *cis* and *trans* isomers was located at δ_C 71.38 and 77.60 ppm, respectively.

The reduction of diimine **3** with sodium triacetoxyhydridoborate in propan-2-ol gave 78% of *trans*-amino alcohol **5b** whose NMR spectra confirmed the assumed structure. The structure of **5a** and **5b** was unambiguously determined by X-ray analysis. Both compounds crystallized in the chiral $P2_12_12_1$ space group with one molecule in the independent part of the unit cell (see figure). On the basis of the Flack parameter, *cis* isomer **5a** was assigned (1*R*,2*R*,3*S*,5*R*) configuration of the chiral centers, and *trans* isomer **5b**, (1*R*,2*R*,3*R*,5*R*) configuration. However, despite CuK_α radiation, the error in the determination of the Flack

Scheme 1.

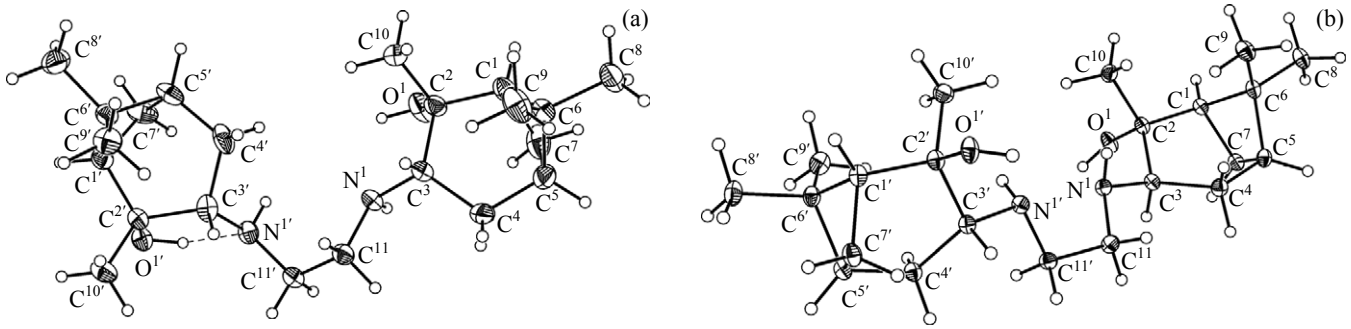


Reagents and conditions: *i*: $H_2N(CH_2)_2NH_2$, PhH, $BF_3 \cdot OEt_2$, 4-Å molecular sieves, 80°C; *ii*: $LiAlH_4$, Et_2O; *iii*: $NaBH(AcO)_3$, *i*-PrOH, 20°C.

parameter was fairly high. Nevertheless, these results are consistent with the relative configuration following from the known (1*R*,2*R*,5*R*) configuration of the pinane fragment; therefore, the assigned configurations of **5a** and **5b** may be regarded as absolute.

The structures of molecules **5a** and **5b** are appreciably different due to different configurations of C^3. Presumably, the different structures of their molecules are also determined by the formation of different inter- and intramolecular bond systems involving the OH and NH groups due to conformational mobility of the bridge connecting the pinane fragments.

The torsion angle $N^1C^3C^2O^1$ characterizing mutual orientation of the NH and OH groups in molecule **5b** is –93.41(11)° [$N^{1'}C^{3'}C^{2'}O^{1'}$ –95.37(10)°], which hampers intramolecular hydrogen bonding. On the other hand, all acidic protons are involved in intermolecular hydrogen bonds. The O–H···N bonds are fairly strong (Table 1), whereas N–H···O bonds are very weak, which is likely to be determined by steric factors.



Structures of the molecules of (a) 3,3′-(ethane-1,2-diyldiimino)bis{(1*R*,2*R*,3*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol} (**5a**) and (b) 3,3′-(ethane-1,2-diyldiimino)bis{(1*R*,2*R*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol} (**5b**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

Table 1. Hydrogen bond parameters in the crystal structures of compounds **5a** and **5b**

5a				5b			
D–H···A	H···A, Å	D···A, Å	∠DHA, deg	D–H···A	H···A, Å	D···A, Å	∠DHA, deg
O^1–H^1···$O^{1'a}$	2.11(2)	2.974(2)	152(2)	N^1–H^2···O^{1b}	2.41(2)	3.2146(13)	146.2(11)
$O^{1'}$–$H^{1'}$···$N^{1'}$	1.75(2)	2.528(2)	139(2)	$N^{1'}$–$H^{2'}$···$O^{1'c}$	2.40(2)	3.1617(13)	146.1(12)
$N^{1'}$–$H^{2'}$···$O^{1'a}$	2.37(2)	3.246(2)	172.4(13)	$O^{1'}$–$H^{1'}$···N^{1b}	2.13(2)	2.8704(13)	157(2)
				O^1–H^1···$N^{1'c}$	2.06(2)	2.8574(12)	154(2)

Symmetry operations: [a] $x - 0.5, -y + 0.5, -z$; [b] $x - 1, y, z$; [c] $x + 1, y, z$.

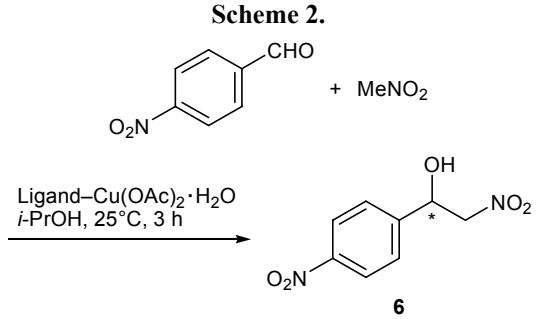
These four hydrogen bonds give rise to chains formed by translationally related molecules **5b** along the *a* crystallographic axis. The amino and hydroxy groups in molecule **5a** are oriented *syn* [torsion angles $N^1C^3C^2O^1$ –30.7(2) and $N^{1'}C^{3'}C^{2'}O^{1'}$ –8.8°]. There is only one intramolecular hydrogen bond $O^{1'}$–$H^{1'}$···$N^{1'}$, and the amino group $N^{1'}H^{2'}$ is not involved in other hydrogen bonds. By contrast, no intramolecular hydrogen bond is formed by the amino and hydroxy groups of the other aminopinane moiety, but both these participate in intermolecular hydrogen bonding. Presumably, this is responsible for the different torsion angles $N^1C^3C^2O^1$ and $N^{1'}C^{3'}C^{2'}O^{1'}$. Molecules **5a** in crystal are related to each other through a symmetry axis, and they form chains along the *a* crystallographic axis.

Compounds **2**–**5** were tested as catalysts in nitroaldol reaction which underlies one of the most convenient procedures for the synthesis of β-nitro alcohols as intermediate products for the preparation of biologically active compounds [17–19]. Asymmetric nitroaldol reactions are often catalyzed by chiral copper complexes with nitrogen-containing ligands [20–27]. These catalysts are advantageous due to low toxicity of copper salts, strong chelating ability of ligands, and mild reaction conditions (no organic base is necessary) [28–30].

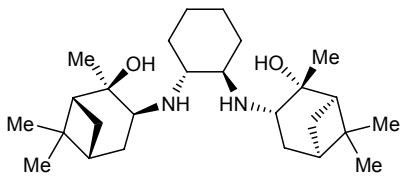
The reaction of nitromethane with 4-nitrobenzaldehyde was carried out using 12 mol % of the chiral ligand and 10 mol % of $Cu(OAc)_2 \cdot H_2O$ in propan-2-ol at 25°C (3 h; Scheme 2). Initially, asymmetric induction in the presence of isomeric amines **4a** and **4b** was studied. As follows from the data in Table 2, the enantiomeric purity of nitro alcohol **6** strongly depends on the ligand steric structure. Amines (–)-**4b** and (+)-**4b** with *trans*-oriented OH and NH groups ensured considerably higher enantioselectivity (*ee* 50%) than did *cis* isomers (+)-**4a** and (–)-**4a** (*ee* 4–8%). Ligands (+)-**4a** and (–)-**4b** with (1*R*,2*R*,5*R*)-configuration of the chiral centers favored formation of (*S*)-nitro alcohol **6**, whereas the reaction catalyzed by compounds (–)-**4a** and (+)-**4b** with (1*S*,2*S*,5*S*)-configuration gave (*R*)-**6** as the major enantiomer. The best result (yield 93%, *ee* 50%) was obtained in the presence of (1*R*,2*R*,3*R*,5*R*)-(–)-**4b**. Replacement of the solvent (propan-2-ol) by ethanol or aprotic THF did not improve the enantioselectivity (Table 2; run nos. 5, 6). In going from primary amine (–)-**4b** to secondary diamine **5b**, the *ee* value decreased from 50 to 38% (Table 2; run nos. 3, 10). Imines (–)-**2** and **3** turned out to be less efficient than the corresponding reduction products. In the reaction with ligand **3**, 30% of racemic nitro alcohol **6** was obtained (Table 2, run no. 8). The use of ligand (–)-**2** having a primary amino group slightly increased the yield (54%) and optical purity (8%) of compound **6** (Table 2, run no. 7).

The catalytic efficiency was not improved when previously synthesized amines **7a** and **7b** possessing

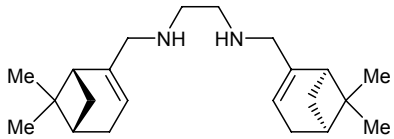
Scheme 2.



6



7a



7b

Table 2. Asymmetric nitroaldol reaction of nitromethane with 4-nitrobenzaldehyde in the presence of ligands **2**–**5** and **7**[a]

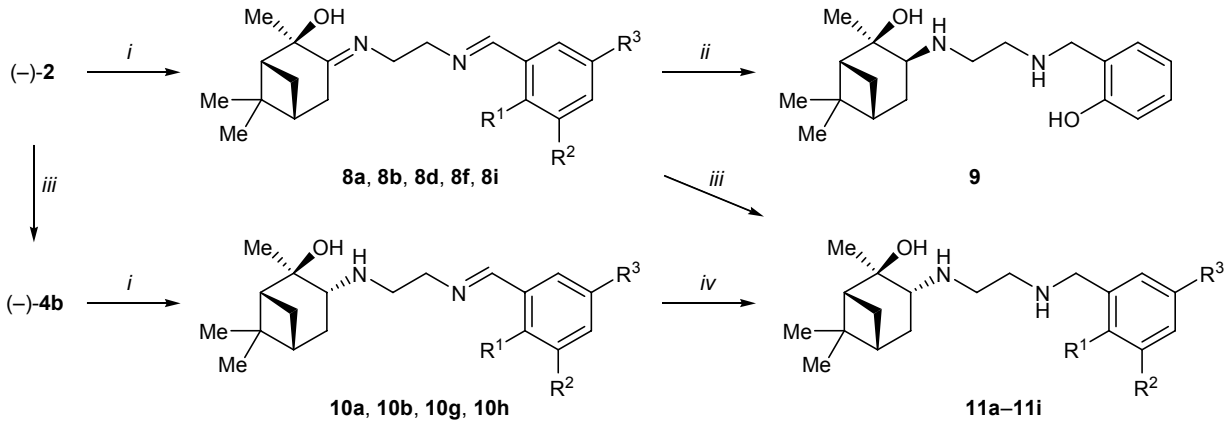
Run no.	Ligand	Solvent	Yield of **6**,[b] %	*ee*, % (configuration)[c]
1	(+)-**4a**	*i*-PrOH	91	8 (*S*)
2	(–)-**4a**	*i*-PrOH	90	4 (*R*)
3	(–)-**4b**	*i*-PrOH	93	50 (*S*)
4	(+)-**4b**	*i*-PrOH	86	50 (*R*)
5	(–)-**4b**	EtOH	90	50 (*S*)
6	(–)-**4b**	THF	80	50 (*S*)
7	(–)-**2**	*i*-PrOH	54	8 (*S*)
8	**3**	*i*-PrOH	30	1 (*S*)
9	**5a**	*i*-PrOH	87	6 (*S*)
10	**5b**	*i*-PrOH	95	38 (*S*)
11	**7a**	*i*-PrOH	88	6 (*S*)
12	**7b**	*i*-PrOH	89	7 (*S*)

[a] All reactions were carried out using 0.5 mmol of 4-nitrobenzaldehyde, 5 mmol of nitromethane, 12 mol % of chiral diamine, and 10 mol % of $Cu(OAc)_2 \cdot H_2O$; 25°C, 3 h.
[b] Yield of **6** isolated by column chromatography.
[c] Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column. The absolute configuration was determined by comparing the retention times with published data [29].

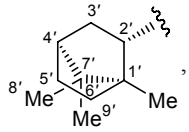
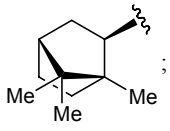
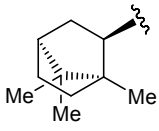
cyclohexyl and myrtenyl fragments were used as ligands. The nitroaldol reactions in the presence of ligands **5a**, **7a**, and **7b** were characterized by almost the same yield and enantioselectivity (Table 2, run nos. 9, 11, 12).

Unsymmetrical ligands in which the substituents on the nitrogen atoms exhibit different electronic and steric properties could strongly affect both catalytic efficiency and enantioselectivity [31]. In this work we have synthesized C_1-symmetric diamines containing terpene and aromatic fragments (Scheme 3). Diamines **11a**–**11f** with a substituted 2-hydroxybenzyl group on one nitrogen atom were synthesized with a view to elucidating the effect of the size and steric and electronic properties of substituents in the aromatic ring on the catalytic activity in the nitroaldol condensation. Introduction of a chiral terpene fragment into an aromatic substituent could enhance the catalytic effi-

Scheme 3.



R^1 = OH, R^2 = R^3 = H (**a**); R^2 = H, R^3 = Me (**c**); R^2 = H, R^3 = Br (**d**); R^2 = R^3 = *t*-Bu (**e**); R^2 = *t*-Bu, R^3 = Me (**f**);

R^2 =  , R^3 = Me (**g**); R^2 =  ; R^3 = Me (**h**); R^2 =  ; R^3 = Me (**i**); R^1 = R^2 = R^3 = H (**b**).

Reagents and conditions: *i*: aldehyde **12**, MeOH, 20°C; *ii*: $LiAlH_4$, Et_2O; *iii*: $NaBH(OAc)_3$, *i*-PrOH, 20°C; *iv*: $NaBH_4$, MeOH, 20°C.

ciency [32]. Therefore, the aromatic fragment in unsymmetrical diamino alcohols **11g**–**11i** contained an isobornyl or bornyl substituent (Scheme 3).

Diamino alcohols **11a**–**11i** were synthesized from compound (–)-**2** or (–)-**4b** whose condensation with the corresponding aldehydes afforded intermediate diimines **8a**, **8c**–**8f**, and **8i** or imino amines **10a**, **10b**, **10g**, and **10h**. The condensation was monitored by IR and NMR spectroscopy. The IR spectra of **8** and **10** contained a strong C=N stretching vibration band in the region 1631–1645 cm^{-1}, and the N=CH proton resonated in their ^1H NMR spectra as a singlet at δ 8.27–8.39 ppm. Compounds **8** and **10** were then subjected to hydride reduction without additional purification.

The reduction of the C=N bond in **8** with sodium triacetoxyhydridoborate in propan-2-ol and in **10** with sodium tetrahydridoborate in ethanol afforded *trans*-amino alcohols **11a**–**11i**, which were isolated in 49–83% yield by column chromatography. The structure of the newly synthesized compounds was determined on the basis of their spectral data. In the IR spectra of the reduction products we observed absorption bands in the region 3273–3441 cm^{-1} due to stretching vibrations of the O–H and N–H bonds. Signals from both terpene and aromatic fragments were present in their ^1H and ^{13}C NMR spectra. The ^1H NMR spectra contained signals at δ 3.06–3.32 (3-H) and 3.81–4.01 ppm (NC$\mathbf{H}_2$Ar).

Table 3. Asymmetric nitroaldol reaction of nitromethane with 4-nitrobenzaldehyde in the presence of ligands **8a**, **9**, and **11a**–**11i**[a]

Run no.	Ligand	Yield of **6**,[b] %	*ee*, % (configuration)[c]
1	**8a**	55	1 (*S*)
2	**9**	89	32 (*S*)
3	**11a**	83	56 (*S*)
4[d]	**11a**	48	56 (*S*)
5[e]	**11a**	5	–
6[f]	**11a**	49	1 (*S*)
7	**11b**	88	23 (*S*)
8	**11c**	79	54 (*S*)
9	**11d**	40	57 (*S*)
10	**11e**	76	2 (*S*)
11	**11f**	75	11 (*S*)
12	**11g**	80	20 (*S*)
13	**11h**	84	5 (*S*)
14	**11i**	54	8 (*R*)

[a] All reactions were carried out using 0.5 mmol of 4-nitrobenzaldehyde, 5 mmol of nitromethane, 12 mol % of chiral diamine, and 10 mol % of $Cu(OAc)_2 \cdot H_2O$; 25°C, 3 h.

[b] Yield of **6** isolated by column chromatography.

[c] Enantiomeric excess was determined by HPLC using a Chiralcel OD-H column. The absolute configuration was determined by comparing the retention times with published data [29].

[d] In the presence of 5 mol % of the catalyst.

[e] In the presence of 10 mol % of $Cu(CF_3SO_3)_2$; 48 h.

[f] In the absence of copper(II) acetate.

The results of the copper-catalyzed asymmetric reaction of nitromethane with 4-nitrobenzaldehyde in the presence of diamino alcohols **11a**–**11i**, other conditions being equal, are collected in Table 3.

As with ligands **2**–**5**, the amines were more efficient ligands than the corresponding imines. Unsymmetrical diimine **8a** showed a moderate catalytic activity, and the product was racemic nitro alcohol **6** (Table 3, run no. 1). Diamine **9** with *cis* orientation of the OH and NH groups in the terpene fragment was less efficient than its *trans* isomer **11a** (*ee* 32 and 56%, respectively; Table 3, run nos. 2, 3). Among unsymmetrical diamines **11a–11i**, the best result (yield of **6** 83%, *ee* 56%) was obtained using ligand **11a** containing 2-hydroxybenzyl fragment. Reduction of the amount of the catalyst [**11a**–$Cu(OAc)_2 \cdot H_2O$] to 5 mol % did not improve the optical purity of the product, but the yield decreased to 48% (Table 3, run no. 4). When $Cu(OAc)_2$ was replaced by $Cu(CF_3SO_3)_2$, no compound **6** was formed even after 48 h (Table 3, run no. 5), while 49% of racemic alcohol **6** was obtained in the presence of chiral ligand **11a** taken alone (no copper acetate was added; Table 3, run no. 6).

In the reaction with ligand **11b** having no hydroxy group in the aromatic ring, the optical purity of the product was considerably lower (*ee* 23%; Table 3, run no. 7). Presumably, the presence of a phenolic hydroxy group is necessary to ensure catalytic activity of such ligands in the nitroaldol reaction. The reaction stereoselectivity almost did not change in going to ligands **11c** and **11d** with a methyl group or bromine atom in the *para* position with respect to the phenolic hydroxy group (Table 3; run nos. 8, 9); however, the catalytic efficiency in the reaction with **11d** was appreciably lower. Introduction of *tert*-butyl groups into the *ortho* and *para* positions with respect to the hydroxy group (ligand **11e**) sharply reduced the stereoselectivity, and the product was almost racemic (Table 3, run no. 10). The optical purity of **6** increased to 11% in going to less sterically hindered ligand **11f** (Table 3, run no. 11).

Replacement of the *tert*-butyl group neighboring to OH in **11e** by a bulkier (1*R*,2*S*,4*S*)-isobornyl substituent (**11g**) improved the *ee* value from 6 to 20% (Table 3, run no. 12). On the other hand, lower enantioselectivity (compared to **11g**) was observed in the presence of stereoisomeric ligands **11h** and **11i** with (1*S*,2*R*,4*R*)- and (1*R*,2*R*,4*S*)-configurations of the terpene fragment. The catalytic system containing bornyl ligand **11i** was less efficient, the catalytic activities being comparable (Table 3; run nos. 13, 14). Moreover, ligand **11i** favored formation of (*R*)-2-nitro-1-(4-nitrophenyl)ethanol (**6**), whereas all other ligands gave rise to excess (*S*)-enantiomer of **6**.

In summary, we have synthesized a number of new α-pinene-based chiral 1,2-diamino alcohols and shown that these compounds can be used as ligands in copper-catalyzed enantioselective nitroaldol reaction. Complexes generated *in situ* from the diamines and $Cu(OAc)_2 \cdot H_2O$ catalyze the reaction of nitromethane with 4-nitrobenzaldehyde, so that it occurs under mild conditions with a high yield and moderate enantioselectivity. The best result (*ee* 56%) was obtained with diamine **11a** which was synthesized from amine (1*R*,2*R*,3*R*,5*R*)-(–)-**4b** and salicylaldehyde.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II spectrometer at 300.17 and 75.48 MHz, respectively, from solutions in $CDCl_3$. Signals were assigned using *J*-modulation and two-dimensional heteronuclear correlation (HSQC) techniques. The IR spectra were measured on a Shimadzu IR Prestige 21 spectrometer with Fourier transform. The melting points were determined on a Kofler hot stage. The optical rotations were measured at 23°C on a PolAAr 3001 polarimeter (λ 589 nm). The elemental analyses were obtained using a Vario MicroCube automated CHNS analyzer.

Single crystals of compounds **5a** and **5b** for X-ray analysis were obtained by slow evaporation of their solutions in hexane. The X-ray diffraction data were acquired on a Smart Apex2 CCD diffractometer (graphite monochromator, CuK_α radiation, λ 1.54178 Å; ω-scanning). The initial data arrays were processed using SAINT and SADABS programs included into APEX2 suite [33]. The structures were solved by the direct method and were refined against F^2_{hkl} by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms using SHELXTL [34]. The coordinates of atoms and their temperature factors for structures **5a** and **5b** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 1036992 and 1036991, respectively).

The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates. Silica gel (Alfa Aesar, 70–230 mesh) was used for column chromatography. All solvents were dried and purified according to standard procedures.

(1*R*,2*R*,5*R*)-2-Hydroxypinan-3-one (+)-**1**, $[\alpha]_D$ = +38.8° (*c* = 1.8, $CHCl_3$), and (1*S*,2*S*,5*S*)-2-hydroxypinan-3-one (–)-**1**, $[\alpha]_D$ = –40.0° (*c* = 1.0, $CHCl_3$), were synthesized by oxidation of (–)- and (+)-α-pinenes, respectively, according to the procedure described in [15].

Commercial salicylaldehyde (**12a**), 2-hydroxy-5-methylbenzaldehyde (**12c**), and 5-bromo-2-hydroxybenzaldehyde (**12d**) (Alfa Aesar) were used without additional purification. Benzaldehyde (**12b**) was distilled prior to use. 3-*tert*-Butyl-2-hydroxy-5-methylbenzaldehyde (**12f**), mp 56–58°C, was prepared as described in [35]; 2-hydroxy-5-methyl-3-{(1*R*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}benzaldehyde (**12g**), *ee* 99%, $[\alpha]_D$ = –39.0° (*c* = 0.3, $CHCl_3$), and 2-hydroxy-5-methyl-3-{(1*S*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}benzaldehyde (**12h**), *ee* 96.4%, $[\alpha]_D$ = +39.6 (*c* = 0.3, $CHCl_3$), were prepared according to [36].

2-Hydroxy-5-methyl-3-{(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}benzaldehyde (12i) was synthesized from 4-methyl-2-{(1*R*,2*R*,4*S*)-(1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}phenol {*ee* >95%, $[\alpha]_D$ = +27.2° (*c* = 0.3, $CHCl_3$)}, according to the procedure described in [36]. The product was purified by repeated column chromatography on silica gel. Yield 40%, yellow thick material, $[\alpha]_D$ = +99.0° (*c* = 0.31, $CHCl_3$). IR spectrum (film), ν, cm^{-1}: 2949, 2878, 2839, 1451, 1379, 2737, 1653, 1616, 745. ^1H NMR spectrum, δ, ppm: 0.74 s (3H, $C^{10}H_3$), 0.94 s and 1.09 s (3H each, C^8H_3, C^9H_3); 1.14–1.27 m (1H), 1.29–1.66 m (4H), and 1.71–1.93 m (2H) (3-H, 4-H, 5-H, 6-H); 2.08–2.25 m (1H, 3-H), 2.37 s (1H, 17-H), 3.78 d.d.d (1H, 2-H, *J* = 2.1, 5.7, 11.7 Hz), 7.19 s and 7.33 s (1H each, 14-H, 16-H), 9.83 s (1H, CHO), 11.21 s (OH). ^{13}C NMR spectrum, δ_C, ppm: 14.68 (C^{10}), 18.73 and 19.82 (C^8, C^9), 20.69 (C^{17}), 28.50 (C^5), 28.88 (C^3), 34.77 (C^6), 39.96 (C^4), 45.59 (C^2), 50.40 and 50.62 (C^1, C^7); 119.79, 127.84, 131.51 (C^{11}, C^{13}, C^{15}); 131.24 and 138.17 (C^{14}, ^{16}), 158.74 (C^{12}), 196.76 (C^{18}). Found, %: C 79.30; H 9.14. $C_{18}H_{24}O_2$. Calculated, %: C 79.37; H 8.88.

Compounds **2**, **3**, **5a**, **7a**, **7b**, **8a**, **8e**, and **9** were described previously [16, 37].

(1*R*,2*R*,3*S*,5*R*)-3-(2-Aminoethylamino)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (+)-(4a). A solution of 1.64 g (7.80 mmol) of imine **2** in 15 mL of anhydrous diethyl ether was added dropwise under vigorous stirring to a suspension of 1.18 g (31.19 mmol) of $LiAlH_4$ in 60 mL of anhydrous diethyl ether. The mixture was stirred for 6 h at room temperature, 1.2 mL of ethyl acetate, 1.2 mL of 10% aqueous sodium hydroxide, and 3.6 mL of water were added dropwise, and the mixture was stirred for 4 h at room temperature. The precipitate was filtered off and washed with diethyl ether, the organic phase was dried over K_2CO_3, the solvent was removed under reduced pressure, and the product was isolated by silica gel column chromatography (gradient elution with $CHCl_3$–MeOH, 5:0 to 5:4). Yield 1.1 g (67%), light yellow oily material, $[\alpha]_D$ = +37.0° (*c* = 1.2, $CHCl_3$). IR spectrum (film), ν, cm^{-1}: 3300, 2908, 1583, 1471, 1369, 1323, 1122, 902. ^{1}H NMR spectrum, δ, ppm: 0.88 s (3H, C^9H_3), 1.16–1.26 m (2H, 7β-H, 4β-H), 1.16 s (6H, C^8H_3, $C^{10}H_3$), 1.75–1.81 m (1H, 5-H), 1.88 br.t (1H, 1-H), 1.99–2.07 m (1H, 7α-H), 2.35–2.46 m (1H, 4α-H), 2.60–2.79 m (5H, 3-H, 11-H, 12-H). ^{13}C NMR spectrum, δ_C, ppm: 23.85 (C^9), 27.76 (C^8), 27.91 (C^7), 31.17 (C^{10}), 37.71 (C^4), 38.10 (C^6), 40.25 (C^5), 41.68 (C^{12}), 52.69 (C^{11}), 53.97 (C^1), 57.35 (C^3), 71.38 (C^2). Found, %: C 67.68; H 11.30; N 13.12. $C_{12}H_{24}N_2O$. Calculated, %: C 67.88; H 11.39; N 13.19.

(1*S*,2*S*,3*R*,5*S*)-3-(2-Aminoethylamino)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (–)-(4a) was synthesized in a similar way. Yield 67%, light yellow oily material, $[\alpha]_D$ = –37.6° (*c* = 1.4, $CHCl_3$). Found, %: C 67.76; H 11.68; N 13.07. $C_{12}H_{24}N_2O$. Calculated, %: C 67.88; H 11.39; N 13.19. The spectral parameters of (–)-**4a** coincided with those given above for (+)-**4a**.

(1*R*,2*R*,3*R*,5*R*)-3-(2-Aminoethylamino)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (–)-(4b). Sodium triacetoxyhydridoborate, 2.24 g (10.55 mmol), was added in portions to a solution of 1.48 g (7.04 mmol) of imine **2** in 75 mL of propan-2-ol, the mixture was stirred for 3 h at 20°C, 2.24 g of $Na(OAc)_3BH$ was added in one portion, and the mixture was stirred for 3 h. The mixture was treated with 10% aqueous sodium hydroxide and brine and extracted with ethyl acetate. The extract was washed with brine and dried over K_2CO_3, the solvent was removed under reduced pressure, and the residue was subjected to silica gel column chromatography (gradient elution with $CHCl_3$–MeOH, 5:0 to 5:4). Yield 1.22 g (82%), light yellow oily material, $[\alpha]_D$ = –45.9° (*c* = 0.8, $CHCl_3$). IR spectrum (film), ν, cm^{-1}: 3350, 3292, 2910, 1570, 1460, 1384, 1070, 1033, 925, 894. ^{1}H NMR spectrum, δ, ppm: 0.86 s (3H, C^9H_3), 1.21 s (3H, C^8H_3), 1.32 s (3H, $C^{10}H_3$), 1.32–1.42 m (1H, 4β-H), 1.55 d (1H, 7β-H, *J* = 10.2 Hz), 1.66 br.s (4H), 1.84 br.t (1H, 1-H, *J* = 5.6 Hz), 1.87–1.93 m (1H, 5-H), 2.05–2.12 m (1H, 7α-H), 2.22–2.31 m (1H, 4α-H), 2.65–2.87 m (4H, 11-H, 12-H), 3.06 br.t (1H, 3-H, *J* = 9.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.07 (C^9), 24.71 (C^7), 24.84 (C^8), 27.66 (C^{10}), 33.24 (C^4), 39.05 (C^6), 40.23 (C^5), 42.11 (C^{12}), 51.30 (C^{11}), 55.62 (C^1), 60.70 (C^3), 77.60 (C^2). Found, %: C 67.70; H 11.48; N 13.10. $C_{12}H_{24}N_2O$. Calculated, %: C 67.88; H 11.39; N 13.19.

(1*S*,2*S*,3*S*,5*S*)-3-(2-Aminoethylamino)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (+)-(4b) was synthesized in a similar way. Yield 69%, yellow oily material, $[\alpha]_D$ = +46.9° (*c* = 1.5, $CHCl_3$). Found, %: C 67.40; H 11.28; N 13.00. $C_{12}H_{24}N_2O$. Calculated, %: C 67.88; H 11.39; N 13.19. The spectral parameters of (+)-**4b** coincided with those given above for (–)-**4b**.

3,3′-(Ethane-1,2-diyldiimino)bis{(1*R*,2*R*,3*S*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol} (5a) was synthesized as described in [16]. Colorless crystals, mp 108–110°C (from hexane), $[\alpha]_D$ = +49.5° (*c* = 0.5, $CHCl_3$). X-Ray diffraction data: $C_{22}H_{40}N_2O_2$. Orthorhombic crystals; unit cell parameters (100 K): *a* = 8.3850(2), *b* = 12.0230(3), *c* = 21.1157(5) Å; *V* = 2128.73(9) $Å^3$; *Z* = 4; space group $P2_12_12_1$; d_{calc} = 1.138 g/cm^3; μ = 0.556 mm^{-1}. Total of 31750 reflection intensities (θ_{max} = 67.33°) were measured from a 0.26×0.18×0.18-mm single crystal of **5a**. The structure was refined from 3787 independent reflections (R_{int} = 0.0429). Divergence factors wR_2 = 0.0915 (all independent reflections), R_1 = 0.0346 [3783 reflections with $I > 2\sigma(I)$]; goodness of fit 1.041; Flack parameter 0.03(19).

3,3′-(Ethane-1,2-diyldiimino)bis{(1*R*,2*R*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol} (5b). Sodium triacetoxyhydridoborate, 1.02 g (4.83 mmol), was added in portions to a solution of 0.58 g (1.61 mmol) of diimine **3** in 35 mL of propan-2-ol, the mixture was stirred for 3 h at 20°C, an additional 1.02 g of $Na(OAc)_3BH$ was added in one portion, and the mixture was stirred for 3 h. The mixture was treated with 10% aqueous sodium hydroxide and brine and extracted with ethyl acetate. The extract was washed with brine and dried over K_2CO_3, the solvent was removed under reduced pressure, and the residue

(0.58 g) was recrystallized from petroleum ether. Yield 0.46 g (78%), colorless crystalline powder, mp 112–114°C, $[\alpha]_D$ = –58.9° (*c* = 0.5, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3292, 3253, 2906, 1473, 1454, 1381, 1359, 1217, 1153, 1120, 1095, 1028, 883, 854. ^1H NMR spectrum, δ, ppm: 0.86 s (6H, C^9H_3), 1.22 s (6H, C^8H_3), 1.32 s (6H, $C^{10}H_3$), 1.36–1.43 m (2H, 4β-H), 1.57 d (2H, 7β-H, *J* = 10.2 Hz), 1.83–1.94 m (4H, 1-H, 5-H), 2.09 m (2H, 7α-H), 2.24–2.33 m (2H, 4α-H), 2.77 m and 2.89 m (2H each, 11-H), 3.10 br.t (2H, 3α-H). ^{13}C NMR spectrum, δ_C, ppm: 23.09 (C^9), 24.74 (C^7), 24.90 (C^8), 27.70 (C^{10}), 33.19 (C^4), 39.07 (C^6), 40.27 (C^5), 48.66 (C^{11}), 55.57 (C^1), 60.69 (C^3), 77.62 (C^2). Found, %: C 72.30; H 11.07; N 7.50. $C_{22}H_{40}N_2O_2$. Calculated, %: C 72.48; H 11.06; N 7.68.

X-Ray diffraction data: $C_{22}H_{40}N_2O_2$; orthorhombic crystals; unit cell parameters (100 K): *a* = 5.92870(10), *b* = 12.2569(2), *c* = 28.2763(4) Å; *V* = 2054.77(6) $Å^3$; *Z* = 4; space group $P2_12_12_1$; d_{calc} = 1.178 g/cm^3; μ = 0.576 mm^{-1}. Total of 28861 reflection intensities (θ_{max} = 67.73°) were measured from a 0.28×0.24×0.16-mm single crystal of **5b**. The structure was refined from 3693 independent reflections (R_{int} = 0.0316). Divergence factors wR_2 = 0.0732 (all independent reflections), R_1 = 0.0279 [3673 reflections with $I > 2\sigma(I)$]; goodness of fit 1.078; Flack parameter 0.03(16).

Diimines **8c**, **8d**, and **8f** were synthesized according to the procedure reported in [16]. The reaction mixtures were analyzed by NMR, and the products were used in further syntheses without additional purification.

(1*R*,2*R*,5*R*)-3-({2-[(2-Hydroxy-5-methylbenzylidene)amino]ethyl}imino)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (8c). Yellow thick oily material. IR spectrum (film), ν, cm^{-1}: 3404 (OH), 1635 (C=N). ^1H NMR spectrum, δ, ppm: 0.67 s (3H, CH_3), 1.26 s (3H, CH_3), 1.40 s (3H, CH_3), 1.44 d (1H, 7β-H, *J* = 10.6 Hz), 1.99 m (2H, 1-H, 5-H), 2.19–2.33 m (1H, 7α-H), 2.27 s (3H, 5′-CH_3), 2.49 m (2H, 4-H), 3.53–3.71 m (2H, 11-H), 3.83–4.01 m (2H, 12-H), 6.82 d (1H, H_{arom}, *J* = 8.3 Hz), 7.01 s (1H, H_{arom}), 7.09 d.d (1H, H_{arom}, *J* = 8.3, 1.7 Hz), 8.29 s (1H, N=CH), 13.21 br.s (1H, 2′-OH). ^{13}C NMR spectrum, δ_C, ppm: 20.27 (5′-CH_3), 22.62 (C^9), 27.24 (C^8), 28.01 (C^7), 28.32 (C^{10}), 33.73 (C^4), 38.30 (C^5, C^6), 50.26 (C^1), 50.63 (C^{11}), 59.84 (C^{12}), 76.43 (C^2), 116.68 (CH_{arom}), 118.30 (C_{arom}), 127.48 ($C^{5'}$), 131.19, 133.00 (CH_{arom}), 158.99 ($C^{2'}$), 166.02 (N=CH), 177.42 (C^3).

(1*R*,2*R*,5*R*)-3-({2-[(5-Bromo-2-hydroxybenzylidene)amino]ethyl}imino)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (8d). Yellow thick material. IR spectrum (film), ν, cm^{-1}: 3421 (OH), 1633 (C=N). ^1H NMR spectrum, δ, ppm: 0.68 s (3H, CH_3), 1.27 s (3H, CH_3), 1.39 s (3H, CH_3), 1.45 d (1H, 7β-H, *J* = 10.6 Hz), 2.00 m (2H, 1-H, 5-H), 2.28 m (1H, 7α-H), 2.48 m (2H, 4-H), 3.53–3.70 m (2H, 11-H), 3.85–4.04 m (2H, 12-H), 6.82 d (1H, H_{arom}, *J* = 8.3 Hz), 7.33 s (1H, H_{arom}), 7.30–7.37 m (1H, H_{arom}), 8.27 s (1H, N=CH), 13.56 br.s (1H, 2′-OH). ^{13}C NMR spectrum, δ_C, ppm: 22.64 (C^9), 27.24 (C^8), 28.03 (C^7), 28.35 (C^{10}), 33.76 (C^4), 38.30 (C^5), 38.34 (C^6), 50.22 (C^1), 50.39 (C^{11}), 59.67 (C^{12}), 76.44 (C^2), 109.80 (C_{arom}), 119.09 (CH_{arom}), 119.97 (C_{arom}), 133.26, 134.90 (CH_{arom}), 160.57 ($C^{2'}$), 164.75 (N=CH), 177.53 (C^3).

(1*R*,2*R*,5*R*)-3-({2-[(3-*tert*-Butyl-2-hydroxy-5-methylbenzylidene)amino]ethyl}imino)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (8f). Yellow thick material. IR spectrum (KBr), ν, cm^{-1}: 3415 (OH), 1631 (C=N). ^1H NMR spectrum, δ, ppm: 0.69 s (3H, CH_3), 1.26 s (3H, CH_3), 1.40 s (9H, *t*-Bu), 1.41 s (3H, CH_3), 1.43 d (1H, 7β-H, *J* = 10.5 Hz), 1.99 m (2H, 1-H, 5-H), 2.23–2.30 m (1H, 7α-H), 2.27 s (3H, 5′-CH_3), 2.52 m (2H, 4-H), 2.59 br.s (1H, 2-OH), 3.57–3.74 m (2H, 11-H), 3.84–4.00 m (2H, 12-H), 6.88 br.s (1H, H_{arom}), 7.10 br.s (1H, H_{arom}), 8.30 s (1H, N=CH), 13.81 br.s (1H, 2′-OH). ^{13}C NMR spectrum, δ_C, ppm: 20.63 (2′-CH_3), 22.67 (C^9), 27.30 (C^8), 28.03 (C^7), 28.36 (C^{10}), 29.35 [C(**C**$H_3)_3$], 33.72 (C^4), 34.66 [**C**$(CH_3)_3$], 38.34 (C^5), 38.38 (C^6), 50.29 (C^1), 50.72 (C^{11}), 59.68 (C^{12}), 76.47 (C^2), 118.22, 126.42 (C_{arom}), 129.41, 130.42 (CH_{arom}), 137.06 (C_{arom}), 158.27 ($C^{2'}$), 166.72 (N=CH), 177.56 (C^3).

(1*R*,2*R*,5*R*)-3-[2-(2-Hydroxy-5-methyl-3-{(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}-benzylideneamino)ethylimino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (8i). A solution of 0.27 g (1.28 mmol) of amine (–)-**2** and 0.35 g (1.28 mmol) of aldehyde **12i** in 20 mL of anhydrous benzene containing 0.8 g of 4-Å molecular sieves was heated for 4 h under reflux. The mixture was filtered, and the filtrate was evaporated under reduced pressure to obtain a bright yellow powder. IR spectrum (film), ν, cm^{-1}: 3420 (OH), 1631 (C=N). ^1H NMR spectrum, δ, ppm: 0.70 s (3H, CH_3), 0.74 s (3H, CH_3), 0.93 s (3H, CH_3), 0.93–1.60 m (5H, 3′-H, 5′-H, 6′-H, 7β-H), 1.09 s (3H, CH_3), 1.27 s (3H, CH_3), 1.43 s (3H, CH_3), 1.74 m (1H, 4′-H), 1.79–1.88 m (1H, 5′-H), 1.95–2.03 m (2H, 1-H, 5-H), 2.09–2.20 m (1H, 3′-H), 2.24–2.36 m (1H, 7α-H), 2.31 s (3H, 5″-H), 2.49 m (2H, 4-H), 2.55 br.s (1H, 2-OH), 2.52–3.71 m (2H, 11-H), 3.79 m (1H, 2′-H), 3.85–3.98 m (2H, 12-H), 6.89 s (1H, H_{arom}),

7.11 s (1H, H_{arom}), 8.31 s (1H, N=CH), 13.55 br.s (1H, 2″-OH). ^{13}C NMR spectrum, δ_C, ppm: 14.83, 18.76, 19.85 (CH_3); 20.79 (5″-CH_3); 22.73, 27.30 (CH_3); 28.07 (C^7), 28.36 (CH_3), 28.51 ($C^{5'}$), 28.98 ($C^{6'}$), 33.65 (C^4), 34.84 ($C^{3'}$), 38.27 (C^5), 38.33 (C^6), 40.17 ($C^{2'}$), 45.64 ($C^{4'}$), 50.19 (C^1), 50.32 ($C^{1'}$), 50.50 ($C^{7'}$), 50.81 (C^{11}), 59.64 (C^{12}), 76.46 (C^2), 117.64, 126.22 (C_{arom}), 129.06 (CH_{arom}), 130.41 (C_{arom}), 133.33 (CH_{arom}), 158.04 (ArOH), 166.35 (N=CH), 177.63 (C^3).

Compounds 10a, **10b**, **10g**, **and 10h (***general procedure***).** A solution of 4.00 mmol of amine (–)-**4b** and 4.00 mmol of the corresponding aldehyde in 10 mL of methanol was stirred for 4 h at 20°C. The solvent was removed under reduced pressure, and the residue was analyzed by IR and NMR spectroscopy. The crude products were used in further syntheses without additional purification.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(2-Hydroxybenzylideneamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (10a). Orange oily material. IR spectrum (film), ν, cm^{-1}: 3392 (OH), 1633 (C=N). ^1H NMR spectrum, δ, ppm: 0.85 s (3H, CH_3), 1.21 s (3H, CH_3), 1.31 s (3H, CH_3), 1.35–1.42 m (1H, 4β-H), 1.56 d (1H, 7β-H, J = 10.3 Hz), 1.84 t (1H, 1-H, J = 5.6 Hz), 1.91 m (1H, 5-H), 2.06–2.14 m (1H, 7α-H), 2.22–2.32 m (1H, 4α-H), 2.96–3.08 m (2H, 11-H), 3.12 br.t (1H, 3-H, J = 8.9 Hz), 3.73 m (2H, 12-H), 6.86 t.d (1H, H_{arom}, J = 7.4, 0.8 Hz), 6.95 d (1H, H_{arom}, J = 8.3 Hz), 7.28 m (2H, H_{arom}), 8.39 s (1H, N=CH). ^{13}C NMR spectrum, δ_C, ppm: 23.05 (C^9), 24.68 (C^7), 24.70 (C^8), 27.62 (C^{10}), 33.09 (C^4), 39.12 (C^6), 40.25 (C^5), 48.88 (C^{11}), 55.84 (C^1), 59.56 (C^{12}), 60.32 (C^3), 77.78 (C^2), 117.04, 118.47 (CH_{arom}), 118.75 (C_{arom}), 131.24, 132.19 (CH_{arom}), 161.28 ($C^{2'}$), 165.89 (N=CH).

(1*R*,2*R*,3*R*,4*R*)-3-[2-(Benzylideneamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (10b). IR spectrum (film), ν, cm^{-1}: 3396 (OH), 1645 (C=N). According to the ^1H NMR data, the fraction of compound **10b** in the reaction mixture was ~55%.

(1*R*,2*R*,5*R*)-3-[2-(2-Hydroxy-5-methyl-3-{(1*R*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}-benzylideneamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (10g). Bright yellow vitreous solid. IR spectrum (KBr), ν, cm^{-1}: 3421 (OH), 1631 (C=N). ^1H NMR spectrum, δ, ppm: 0.77 s (3H, CH_3), 0.84 s (3H, CH_3), 0.86 s (3H, CH_3), 0.90 s (3H, CH_3), 1.23 s (3H, CH_3), 1.35 s (3H, CH_3), 1.31–1.65 m (6H, 3′-H, 4-H, 5′-H, 6′-H, 7β-H), 1.83–1.98 m (4H, 1-H, 4′-H, 5-H, 5′-H), 2.08–2.34 m (3H, 3′-H, 4-H, 7α-H), 2.28 s (3H, 5-CH_3), 3.08 m (2H, 11-H), 3.19 t (1H, 3-H, J = 9.1 Hz), 3.34 t (1H, 2′-H, J = 9.0 Hz), 3.77 m (2H, 12-H), 6.88 s (1H, H_{arom}), 7.17 s (1H, H_{arom}), 8.36 s (1H, N=CH). ^{13}C NMR spectrum, δ_C, ppm: 12.23, 20.36 (CH_3); 20.79 (5″-CH_3); 21.44, 23.10, 24.67 (CH_3); 24.70 (C^7), 27.51 ($C^{5'}$), 27.67 (CH_3), 32.52 (C^4), 33.91 ($C^{3'}$), 39.17 (C^6), 39.64 ($C^{6'}$), 40.24 (C^5), 44.52 ($C^{2'}$), 45.75 ($C^{4'}$), 47.97 ($C^{1'}$), 48.58 (C^{11}), 49.89 ($C^{7'}$), 55.77 (C^1), 59.05 (C^{12}), 60.52 (C^3), 77.56 (C^2), 117.47, 126.24 (C_{arom}), 128.74 (CH_{arom}), 131.64 (C_{arom}), 131.83 (CH_{arom}), 158.48 ($C^{2''}$), 166.56 (N=CH).

(1*R*,2*R*,5*R*)-3-[2-(2-Hydroxy-5-methyl-3-{(1*S*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}-benzylideneamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (10h). Bright yellow vitreous solid. IR spectrum (KBr), ν, cm^{-1}: 3419 (OH), 1631 (C=N). ^1H NMR spectrum, δ, ppm: 0.77 s (3H, CH_3), 0.84 s (3H, CH_3), 0.87 s (3H, CH_3), 0.90 s (3H, CH_3), 1.23 s (3H, CH_3), 1.34 s (3H, CH_3), 1.31–1.65 m (6H, 3′-H, 4-H, 5′-H, 6′-H, 7β-H), 1.83–1.99 m (4H, 1-H, 4′-H, 5-H, 5′-H), 2.09–2.34 m (3H, 3′-H, 4-H, 7α-H), 2.28 s (3H, 5″-CH_3), 2.99–3.13 m (2H, 11-H), 3.19 t (1H, 3-H, J = 9.1 Hz), 3.34 t (1H, 2′-H, J = 9.1 Hz), 3.77 d (2H, 12-H, J = 5.9 Hz), 6.88 s (1H, H_{arom}), 7.17 s (1H, H_{arom}), 8.35 s (1H, N=CH). ^{13}C NMR spectrum, δ_C, ppm: 12.24, 20.37 (CH_3); 20.79 (5″-CH_3); 21.43, 23.08, 24.66 (CH_3); 24.70 (C^7), 27.51 ($C^{5'}$), 27.66 (CH_3), 32.56 (C^4), 33.93 ($C^{3'}$), 39.15 (C^6), 39.64 ($C^{6'}$), 40.23 (C^5), 44.51 ($C^{2'}$), 45.74 ($C^{4'}$), 47.96 ($C^{1'}$), 48.62 (C^{11}), 49.86 ($C^{7'}$), 55.74 (C^1), 59.07 (C^{12}), 60.48 (C^3), 77.56 (C^2), 117.47, 126.24 (C_{arom}), 128.72 (CH_{arom}), 131.63 (C_{arom}), 131.82 (CH_{arom}), 158.43 ($C^{2''}$), 166.54 (N=CH).

Unsymmetrical diamino alcohols 11a–11i (*general procedure***).** *a*. Sodium triacetoxyhydridoborate, 8.40 mmol, was added in portions to a solution of 2.80 mmol of diimino alcohol **8c**–**8f** or **8i** in 50 mL of propan-2-ol, and the mixture was stirred for 3 h at 20°C. An additional 2.80 mmol of $Na(OAc)_3BH$ was then added in one portion, the mixture was stirred for 3 h, 10% aqueous sodium hydroxide and brine were added, and the mixture was extracted with ethyl acetate. The extract was washed with brine and dried over K_2CO_3, the solvent was removed under reduced pressure, and the residue was subjected to silica gel column chromatography (gradient elution with $CHCl_3$–MeOH, 5:0 to 5:0.7).

b. Sodium tetrahydridoborate, 9.25 mmol, was added in portions to a solution of 3.70 mmol of compound **10a**, **10b**, **10g**, or **10h** in 20 mL of anhydrous

methanol, and the mixture was stirred for 6 h at room temperature. The mixture was treated with 25 mL of water and extracted with methylene chloride. The extract was dried over K_2CO_3, the solvent was removed under reduced pressure, and the residue was subjected to silica gel column chromatography (gradient elution with $CHCl_3$–MeOH, 5:0 to 5:0.7).

(1*R*,2*R*,3*R*,5*R*)-3-[2-(2-Hydroxybenzylamino)-ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (11a). Yield 71% [calculated on the initial amine (–)-**4b**], yellow–orange oily material, $[\alpha]_D$ = –27.1° (*c* = 1.1, $CHCl_3$). IR spectrum (film), ν, cm^{-1}: 3392, 3313, 2914, 1591, 1440, 1382, 1257, 1107, 756. ^{1}H NMR spectrum, δ, ppm: 0.87 s (3H, CH_3), 1.23 s (3H, CH_3), 1.33 s (3H, CH_3), 1.33–1.42 m (1H, 4β-H), 1.55 d (1H, 7β-H, *J* = 10.3 Hz), 1.86 t (1H, 1-H, *J* = 5.6 Hz), 1.93 m (1H, 5-H), 2.07–2.15 m (1H, 7α-H), 2.23–2.33 m (1H, 4α-H), 2.70–2.97 m (4H, 11-H, 12-H), 3.08 br.t (1H, 3-H, *J* = 8.9 Hz), 4.01 m (2H, NHC**H**$_2$Ar), 6.76 t.d (1H, H_{arom}, *J* = 7.3, 1.0 Hz), 6.82 d (1H, H_{arom}, *J* = 8.0 Hz), 6.99 d (1H, H_{arom}, *J* = 7.4 Hz), 7.15 br.t (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 23.08 (C^9), 24.70 (C^7), 24.76 (C^8), 27.64 (C^{10}), 33.03 (C^4), 39.10 (C^6), 40.23 (C^5), 47.17 and 48.33 (C^{11}, C^{12}), 52.32 (NH**C**H$_2$Ar), 55.62 (C^1), 60.49 (C^3), 77.60 (C^2), 116.41, 118.93 (CH_{arom}), 122.51 (C_{arom}), 128.32, 128.66 (CH_{arom}), 158.20 ($C^{2'}$). Found, %: C 71.52; H 9.38; N 8.86. $C_{19}H_{30}N_2O_2$. Calculated, %: C 71.66; H 9.50; N 8.80.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(Benzylamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (11b). Ratio **10b**–$NaBH_4$ 1:3 (method *b*). Yield 49% [calculated on (–)-**4b**], light yellow oily material, $[\alpha]_D$ = –29.5° (*c* = 0.3, $CHCl_3$). IR spectrum (film), ν, cm^{-1}: 3400, 3313, 2912, 1454, 1381, 1217, 1112, 754, 698. ^{1}H NMR spectrum, δ, ppm: 0.87 s (3H, CH_3), 1.23 s (3H, CH_3), 1.33 s (3H, CH_3), 1.33–1.43 m (1H, 4β-H), 1.56 d (1H, 7β-H, *J* = 10.2 Hz), 1.70 br.s (3H), 1.84–1.95 m (2H, 1-H, 5-H), 2.07–2.12 m (1H, 7α-H), 2.22–2.32 m (1H, 4α-H), 2.77–2.89 m (4H, 11-H, 12-H), 3.06 br.t (1H, 3-H, *J* = 8.9 Hz), 3.81 s (2H, NHC**H**$_2$Ar), 7.24–7.33 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 23.11 (C^9), 24.73 (C^7), 24.88 (C^8), 27.69 (C^{10}), 33.27 (C^4), 39.09 (C^6), 40.29 (C^5), 48.40 and 49.21 (C^{11}, C^{12}), 53.83 (NH**C**H$_2$Ar), 55.70 (C^1), 60.90 (C^3), 77.65 (C^2), 126.87, 128.11, 128.35 (CH_{arom}), 140.45 (C_{arom}). Found, %: C 75.68; H 10.15; N 9.06. $C_{19}H_{30}N_2O$. Calculated, %: C 75.45; H 10.00; N 9.26.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(2-Hydroxy-5-methylbenzylamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]-heptan-2-ol (11c). Yield 78% [calculated on (–)-**2**], yellow oily material, $[\alpha]_D$ = –25.9° (*c* = 0.4, $CHCl_3$). IR spectrum (film), ν, cm^{-1}: 3400, 3309, 2916, 1600, 1498, 1454, 1384, 1350, 1259, 1116, 817, 756. ^{1}H NMR spectrum, δ, ppm: 0.87 s (3H, CH_3), 1.24 s (3H, CH_3), 1.34 s (3H, CH_3), 1.34–1.46 m (1H, 4β-H), 1.56 d (1H, 7β-H, *J* = 10.3 Hz), 1.86 t (1H, 1-H, *J* = 5.6 Hz), 1.93 m (1H, 5-H), 2.08–2.17 m (1H, 7α-H), 2.23 (3H, 5′-CH_3), 2.20–2.32 m (1H, 4α-H), 2.71–2.87 m (3H, 11-H, 12-H), 2.94 m (1H, 11-H), 3.08 t (1H, 3-H, *J* = 9.0 Hz), 3.98 m (2H, NHC**H**$_2$Ar), 6.73 d (1H, H_{arom}, *J* = 8.1 Hz), 6.80 s (1H, H_{arom}), 6.95 d (1H, H_{arom}, *J* = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.41 (5′-CH_3), 23.10 (C^9), 24.71 (C^7), 24.77 (C^8), 27.67 (C^{10}), 32.88 (C^4), 39.12 (C^6), 40.24 (C^5), 47.03 and 48.14 (C^{11}, C^{12}), 52.20 (NH**C**H$_2$Ar), 55.60 (C^1), 60.53 (C^3), 77.55 (C^2), 116.19 (CH_{arom}), 122.08, 128.05 (C_{arom}), 129.05, 129.13 (CH_{arom}), 155.68 ($C^{2'}$). Found, %: C 72.31; H 9.63; N 8.37. $C_{20}H_{32}N_2O_2$. Calculated, %: C 72.25; H 9.70; N 8.43.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(5-Bromo-2-hydroxybenzylamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]-heptan-2-ol (11d). Yield 69% [calculated on (–)-**2**], light brown powder, mp 61–63°C, $[\alpha]_D$ = –24.4° (*c* = 0.5, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3294, 2918, 1579, 1479, 1427, 1386, 1267, 1118, 817, 758, 628. ^{1}H NMR spectrum, δ, ppm: 0.90 s (3H, CH_3), 1.24 s (3H, CH_3), 1.41 s (3H, CH_3), 1.49–1.61 m (1H, 4β-H), 1.55 d (1H, 7β-H, *J* = 10.6 Hz), 1.88 t (1H, 1-H, *J* = 5.4 Hz), 1.94 m (1H, 5-H), 2.09–2.16 m (1H, 7α-H), 2.22–2.31 m (1H, 4α-H), 2.90 m (3H, 11-H, 12-H), 3.08 m (1H, 11-H), 3.19 t (1H, 3-H, *J* = 9.1 Hz), 3.97 m (2H, NHC**H**$_2$Ar), 6.73 d (1H, H_{arom}, *J* = 8.6 Hz), 7.13 s (1H, H_{arom}), 7.23 br.d (1H, H_{arom}, *J* = 10.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.19 (C^9), 24.65 (C^7), 24.79 (C^8), 27.68 (C^{10}), 31.14 (C^4), 39.28 (C^6), 40.05 (C^5), 45.82 and 46.57 (C^{11}, C^{12}), 50.77 (NH**C**H$_2$Ar), 55.35 (C^1), 61.06 (C^3), 77.07 (C^2), 110.82 (C_{arom}), 118.36 (CH_{arom}), 123.66 (C_{arom}), 131.59, 131.87 (CH_{arom}), 156.94 ($C^{2'}$). Found, %: C 57.12; H 7.04; N 6.98. $C_{19}H_{29}BrN_2O_2$. Calculated, %: C 57.43; H 7.36; N 7.05.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(3,5-Di-*tert*-butyl-2-hydroxybenzylamino)ethylamino]-2,6,6-trimethylbicyclo-[3.1.1]heptan-2-ol (11e). Yield 78%, colorless thick oily material, $[\alpha]_D$ = –22.2° (*c* = 0.4, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3425, 3278, 2953, 1604, 1477, 1386, 1361, 1236, 1105, 758. ^{1}H NMR spectrum, δ, ppm: 0.88 s (3H, CH_3), 1.24 s and 1.29 s (12H, CH_3, *t*-Bu), 1.32–1.44 m (1H, 4β-H), 1.35 s and 1.43 s (12H,

CH_3, *t*-Bu), 1.57 d (1H, 7β-H, *J* = 10.3 Hz), 1.87 t (1H, 1-H, *J* = 5.5 Hz), 1.94 m (1H, 5-H), 2.09–2.16 m (1H, 7α-H), 2.26–2.36 m (1H, 4α-H), 2.82–2.98 m (4H, 11-H, 12-H), 3.10 br.t (1H, 3-H), 3.98 m (2H, NHC**H**$_2$Ar), 6.88 m (1H, H_{arom}), 7.24 m (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 23.10 (C^9), 24.72 (C^7), 24.76 (C^8), 27.66 (C^{10}), 29.64 and 31.68 [C(**C**H_3)$_3$], 33.24 (C^4), 34.11 and 34.88 [**C**(CH_3)$_3$], 39.13 (C^6), 40.28 (C^5), 47.58 and 48.72 (C^{11}, C^{12}), 53.29 (NH**C**H_2Ar), 55.72 (C^1), 60.64 (C^3), 77.74 (C^2), 122.20 (C_{arom}), 122.87, 123.06 (CH_{arom}), 135.88, 140.31 (C_{arom}), 154.75 ($C^{2'}$). Found, %: C 75.14; H 10.86; N 6.39. $C_{27}H_{46}N_2O_2$. Calculated, %: C 75.30; H 10.77; N 6.50.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(3-*tert*-Butyl-5-methyl-2-hydroxybenzylamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (11f). Yield 76% [calculated on (–)-**2**], light brown thick oily material, $[\alpha]_D$ = –21.3° (*c* = 0.9, $CHCl_3$). IR spectrum (film), ν, cm^{-1}: 3431, 3307, 2912, 1604, 1465, 1444, 1386, 1359, 1240, 1143, 1111, 862, 758. ^{1}H NMR spectrum, δ, ppm: 0.88 s (3H, CH_3), 1.24 s (3H, CH_3), 1.35 s (3H, CH_3), 1.35–1.48 m (1H, 4β-H), 1.41 s (9H, *t*-Bu), 1.57 d (1H, 7β-H, *J* = 10.3 Hz), 1.87 t (1H, 1-H, *J* = 5.6 Hz), 1.94 m (1H, 5-H), 2.09–2.16 m (1H, 7α-H), 2.24 (3H, 5′-CH_3), 2.24–2.35 m (1H, 4α-H), 2.77–2.98 m (4H, 11-H, 12-H), 3.11 t (1H, 3-H, *J* = 9.0 Hz), 3.95 m (2H, NHC**H**$_2$Ar), 6.70 s (1H, H_{arom}), 6.99 s (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.74 (5′-CH_3), 23.08 (C^9), 24.72 (C^7), 24.77 (C^8), 27.66 (C^{10}), 29.59 [C(**C**H_3)$_3$], 33.08 (C^4), 34.57 [**C**(CH_3)$_3$], 39.15 (C^6), 40.27 (C^5), 47.47 and 48.40 (C^{11}, C^{12}), 52.79 (NH**C**H_2Ar), 55.76 (C^1), 60.68 (C^3), 77.68 (C^2), 122.82 (C_{arom}), 126.52, 126.93 (CH_{arom}), 127.61 (C_{arom}), 136.57 (C_{arom}), 154.84 ($C^{2'}$). Found, %: C 74.02; H 10.47; N 7.10. $C_{24}H_{40}N_2O_2$. Calculated, %: C 74.18; H 10.38; N 7.21.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(2-Hydroxy-5-methyl-3-{(1*R*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}benzylamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (11g). Yield 83% [calculated on (–)-**4b**], colorless vitreous solid, $[\alpha]_D$ = –23.9° (*c* = 1.1, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3441, 3307, 2947, 1606, 1463, 1382, 1369, 1226, 1120, 756. ^{1}H NMR spectrum, δ, ppm: 0.78 s (3H, CH_3), 0.83 s (3H, CH_3), 0.88 s (3H, CH_3), 0.90 s (3H, CH_3), 1.24 s (3H, CH_3), 1.30–1.43 m (2H, 4-H, 5′-H), 1.34 s (3H, CH_3), 1.48–1.63 m (4H, 3′-H, 6′-H, 7β-H), 1.81–1.97 m (4H, 1-H, 4′-H, 5-H, 5′-H), 1.91–1.97 m (2H, 3′-H, 7α-H), 2.24 s (3H, 5″-CH_3), 2.24–2.34 m (1H, 4-H), 2.74–2.97 m (4H, 11-H, 12-H), 3.09 t (1H, 3-H, *J* = 9.0 Hz), 3.29 t (1H, 2′-H, *J* = 9.0 Hz), 3.95 m (2H, NHC**H**$_2$Ar), 6.65 s (1H, H_{arom}), 7.02 s (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 12.22, 20.37 (CH_3); 20.89 (5″-CH_3); 21.47, 23.12 (CH_3); 24.71 (C^7), 24.76 (CH_3), 27.54 ($C^{5'}$), 27.67 (CH_3), 33.09 (C^4), 33.90 ($C^{3'}$), 39.14 (C^6), 39.61 ($C^{6'}$), 40.28 (C^5), 44.71 ($C^{2'}$), 45.78 ($C^{4'}$), 47.88 ($C^{1'}$), 47.39 and 48.32 (C^{11}, C^{12}), 49.78 ($C^{7'}$), 52.48 (NH**C**H_2Ar), 55.67 (C^1), 60.69 (C^3), 76.64 (C^2), 121.55 (C_{arom}), 126.17 (CH_{arom}), 126.54 (C_{arom}), 127.78 (CH_{arom}), 130.68 (C_{arom}), 154.95 ($C^{2''}$). Found, %: C 77.00; H 10.35; N 5.92. $C_{30}H_{48}N_2O_2$. Calculated, %: C 76.87; H 10.32; N 5.98.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(2-Hydroxy-5-methyl-3-{(1*S*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}benzylamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (11h). Yield 69% [calculated on (–)-**4b**], colorless vitreous solid, $[\alpha]_D$ = –19.5° (*c* = 2.0, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3415, 3309, 2947, 1606, 1463, 1381, 1369, 1226, 1116, 864, 756. ^{1}H NMR spectrum, δ, ppm: 0.77 s (3H, CH_3), 0.83 s (3H, CH_3), 0.88 s (3H, CH_3), 0.90 s (3H, CH_3), 1.24 s (3H, CH_3), 1.29–1.48 m (2H, 4-H, 5′-H), 1.36 s (3H, CH_3), 1.49–1.68 m (4H, 7β-H, 3′-H, 6′-H), 1.74–1.97 m (4H, 1-H, 4′-H, 5-H, 5′-H), 2.09–2.18 m (2H, 3′-H, 7α-H), 2.24 s (3H, 5″-CH_3), 2.24–2.34 m (1H, 4-H), 2.72–2.98 m (4H, 11-H, 12-H), 3.11 t (1H, 3-H, *J* = 9.0 Hz), 3.28 t (1H, 2′-H, *J* = 9.0 Hz), 3.91 d and 4.00 d (1H each, 13-H, *J* = 13.6 Hz), 6.65 s (1H, H_{arom}), 7.02 s (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 12.23, 20.24 (CH_3); 20.90 (5″-CH_3); 21.47, 23.11 (CH_3); 24.71 (C^7), 24.79 (CH_3), 27.55 ($C^{5'}$), 27.66 (CH_3), 32.88 (C^4), 33.97 ($C^{3'}$), 39.16 (C^6), 39.64 ($C^{6'}$), 40.24 (C^5), 44.71 ($C^{2'}$), 45.76 ($C^{4'}$), 47.88 ($C^{1'}$), 47.34 and 48.11 (C^{11}, C^{12}), 49.76 ($C^{7'}$), 52.47 (NH**C**H_2Ar), 55.68 (C^1), 60.73 (C^3), 77.60 (C^2), 121.42 (C_{arom}), 126.26 (CH_{arom}), 126.59 (C_{arom}), 127.83 (CH_{arom}), 130.72 (C_{arom}), 154.91 ($C^{2''}$). Found, %: C 76.98; H 10.23; N 5.85. $C_{30}H_{48}N_2O_2$. Calculated, %: C 76.87; H 10.32; N 5.98.

(1*R*,2*R*,3*R*,5*R*)-3-[2-(2-Hydroxy-5-methyl-3-{(1*R*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl}benzylamino)ethylamino]-2,6,6-trimethylbicyclo[3.1.1]heptan-2-ol (11i). Yield 68% [calculated on (–)-**2**], colorless vitreous solid, $[\alpha]_D$ = +28.0° (*c* = 0.4, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 3396, 3273, 2949, 1602, 1560, 1467, 1408, 1390, 1222, 1155, 756. ^{1}H NMR spectrum, δ, ppm: 0.74 s (3H, CH_3), 0.92 s (3H, CH_3), 1.06 s (3H, CH_3), 1.11–1.21 m (1H, 4-H), 1.25 s (3H, CH_3), 1.32–1.41 m (2H, 5′-H, 6′-H), 1.47 s (3H, CH_3), 1.52–1.59 m (1H, 4-H), 1.57 d (1H, 7β-H, *J* = 10.6 Hz), 1.64–2.01 m (5H, 1-H, 3′-H, 4′-H, 5-H,

5′-H), 1.93 s (3H, CH_3), 2.07–2.24 m (3H, 3′-H, 6′-H, 7α-H), 2.27 s (3H, CH_3), 3.02 m (3H) and 3.17 m (1H) (11-H, 12-H), 3.32 t (1H, 3-H, J = 9.3 Hz), 3.72 d.d (1H, 2′-H, J = 11.7, 4.1 Hz), 3.91 d and 4.07 d (1H each, 13-H, J = 13.3 Hz), 6.75 s (1H, H_{arom}), 7.01 s (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.83, 18.79 (CH_3); 19.86 (5″-CH_3), 20.89, 23.07, 24.58 (CH_3); 24.63 (C^7), 24.73 (CH_3), 28.49 ($C^{5'}$), 28.92 (C^4), 29.51 ($C^{3'}$), 34.86 ($C^{6'}$), 39.37 (C^6), 39.95 (C^5), 40.62 ($C^{2'}$), 45.24 and 45.37 (C^{11}, C^{12}), 45.68 ($C^{4'}$), 50.27 ($C^{1'}$), 50.50 ($C^{7'}$), 51.03 (NH**C**H_2Ar), 55.12 (C^1), 62.13 (C^3), 76.16 (C^2), 120.99 (C_{arom}), 127.74, 130.30 (CH_{arom}), 130.93, 131.29 (C_{arom}), 153.72 ($C^{2''}$). Found, %: C 77.02; H 10.28; N 5.82. $C_{30}H_{48}N_2O_2$. Calculated, %: C 76.87; H 10.32; N 5.98.

1-(4-Nitrophenyl)-2-nitroethanol (6) (*general procedure for testing catalytic activity***).** Copper(II) acetate monohydrate, 0.01 g (0.05 mmol, 10 mol %), was added to a solution of 0.06 mmol (12 mol %) of the corresponding ligand in 0.5 mL of propan-2-ol, and the mixture was stirred for 3 h at 25°C. Nitromethane, 0.27 mL (5 mmol), was then added, the mixture was stirred for 0.5 h, 0.075 g (0.5 mmol) of 4-nitrobenzaldehyde was added, and the mixture was stirred for 3 h at 25°C. The solvent was removed under reduced pressure, and the product was isolated from the residue by silica gel column chromatography using petroleum ether–ethyl acetate (4 : 1) as eluent and analyzed by ^1H NMR. The enantiomeric purity of alcohol **6** was determined by HPLC on an Agilent 1100 chromatograph (UV detector, λ 219 nm, 20°C) using a Chiralcel OD-H column (Daicel, 25 cm × 4.6 mm; grain size 5 μm, eluent hexane–*i*-PrOH, 82 : 18, flow rate 1 mL/min); retention times 12.4 min for (*R*)-**6** and 15.0 min for (*S*)-**6**.

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