'N-Stereogenic Quaternary Ammonium Salts' from L-Amino Acids: Synthesis, Separation, and Absolute Configuration

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Diastereoisomeric linear and cyclic 'N-chiral quaternary ammonium salts' (QASs) were efficiently synthesized from corresponding L-amino acids in high yields. The diastereoisomers of each pair of 'N-chiral QASs' were successfully separated. The absolute configurations of these QASs were determined predominately by X-ray single-crystal analysis. The ^{1}H-NMR data of 'N-chiral QASs' provided characteristic information on the configuration of the N-chiral center. 'N-Chiral QASs' exemplified by [*N*(*R*)]-**2a** and [*N*(*S*)]-**2a** are stable in protic and aprotic solvents within a broad pH and temperature range.

Introduction. – Chiral quaternary ammonium salts (QASs) are of great potential in asymmetric phase-transfer-catalyzed reactions [1]. Among them cinchona-alkaloid-derived QASs give more impressive enantioselectivity for various reactions than other phase-transfer catalysts (PTCs) do, with only few notable exceptions [2]. However, the major drawback of those QASs is the difficulty in modifying the structure for a better selectivity or reactivity. Furthermore, the role of the N-atom in those chiral QASs was neglected by organic chemists, whereas chiral C- [3], P- [4], and S-centered [5] molecules have been studied intensively. In addition, there are few reports dealing with an intentional construction of 'N-chiral QAS' [6]. Investigations on their properties and applications were hampered by their separations which are much more difficult than the separations of other chiral compounds. Only two methods, repeated fractional crystallization and resolution by chiral materials, were reported as convenient and successful separations of 'N-chiral QASs'. However, the two methods bear insurmountable disadvantages: *i*) Repeated fractional crystallization gave only one single diastereoisomer[1]); *ii*) separation of 'N-chiral QASs' by chiral materials is difficult to operate, not applicable universally, and the method gave unsatisfactory optical purities [7][8]. Recently, *Tayama* and *Tanaka* resolved a N-centered tetraalkylammonium salts with (*R*)-binol as chiral complexing agent and obtained two pure enantiomers from each enantiomer mixture [9] (binol = [1,1′-binaphthalene]-2,2′-diol).

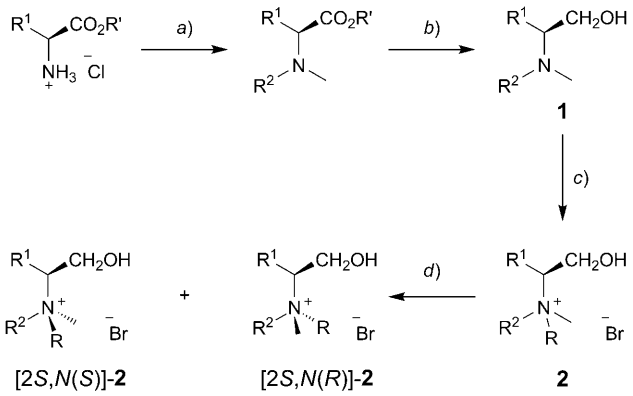
[1]) When the introduction order of the two substituents at the N-atom was reversed, the ratio of the two diastereoisomers was also reversed. So the other diastereoisomer was obtained by repeated fractional crystallization. See [6b–d].

Chiral amino acids and their derivatives have been widely used in asymmetric synthesis. Recently, proline derivatives were employed as starting materials to prepare 'N-chiral QASs' [6a–d]. Other amino acids with various functional groups provide the possibility to diversify the structures of 'N-chiral QASs'. Furthermore, the 'N-chirality' in 'N-chiral QASs' may be induced by the 'C-chirality' of tertiary amines formed from L-amino acids. Therefore, synthesis of 'N-chiral QASs' from well-available compounds with convenient separation procedures is of great practical value. Herein, we describe the successful synthesis, separation, absolute-configuration determination, and stability of 'N-chiral QASs' from L-amino acids.

Results and Discussion. – L-Amino acids with different side chains were used as starting materials to prepare tertiary amines by a modified 'one-pot' method in high yields[2]). Allylation of the obtained tertiary amines afforded linear 'N-chiral QASs' **2a**–**2f** (*Scheme* and *Table 1*). Alkylations of the cyclic tertiary amine (3*S*)-1,2,3,4-tetrahydro-2-methylisoquinoline-3-methanol prepared from L-phenylalanine [11] gave the cyclic 'N-chiral QASs' **2g**–**2i** (*Scheme* and *Table 1*).

The ^{1}H-NMR data of the prepared 'N-chiral QASs' **2** suggested that they are mixtures of diastereoisomers with a ratio of 1.1 : 1 to 1.5 : 1, indicating that the induction of the 'N-chirality' by 'C-chirality' was only modest.

Scheme



R' = Me, except for **2e**, where R' = Et; for R^1, R^2, and R, see *Table 1*

a) 1. $NaHCO_3$ (1.2 equiv.), MeOH, 0°, 15 min; 2. PhCHO (1.05 equiv.), r.t., 2.0–3.5 h; 3. KBH_4 (0.4 equiv.), 0° to r.t., 0.5–1 h; 4. 37% HCHO soln. (1.8 equiv.), r.t., 2.5–4.5 h; 5. KBH_4 (2.0 equiv.), 0° to r.t., 5–11 h; total yield 78–91%. *b*) $LiAlH_4$ (1.0 equiv.), 0.5–1 h, Et_2O, 0°; 87–97%. *c*) RX (2.0 equiv.), MeCN, reflux 5–48 h; 84–95%. *d*) Separation.

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[2]) The tertiary amines were prepared by reduction of the corresponding L-amino acid esters by $LiAlH_4$, and the esters were prepared according to [10]. The neutralization of L-amino acid ester hydrochlorides and imine (iminium) formation/reduction was carried out in the same flask without isolation.

Table 1. *Synthesis of N-Chiral QASs* **2** *from* L*-Amino Acid Derivatives*[a])

	R^1	R^2	RX	Yield [%]
2a	Me	Bn	$H_2C{=}CHCH_2Br$	95
2b	i-Bu	Bn	$H_2C{=}CHCH_2Br$	90
2c	Ph	Bn	$H_2C{=}CHCH_2Br$	91
2d	Bn	Bn	$H_2C{=}CHCH_2Br$	92
2e	$PhCH_2CH_2$	Bn	$H_2C{=}CHCH_2Br$	89
2f	4-OH−Bn	Bn	$H_2C{=}CHCH_2Br$	90
2g	$H_2C-C_6H_4-CH_2$[b])		$H_2C{=}CHCH_2Br$	95
2h	$H_2C-C_6H_4-CH_2$[b])		$Me_2C{=}CHCH_2Br$	92
2i	$H_2C-C_6H_4-CH_2$[b])		9-(chloromethyl)anthracene	84

[a]) The d.e. of these N-chiral QASs is 1.1 : 1 to 1.5 : 1. [b]) Resulting in an isoquinolinium structure.

Separation of enantiomeric or diastereoisomeric 'N-chiral QASs' is a difficult problem in the research of 'N-chiral QAS'-catalyzed reactions. Based on the methods previously used for the separation of 'N-chiral QASs', we attempted to separate the diastereoisomers **2**. However, only three pairs of 'N-chiral QASs' were separated successfully, *i.e.*, the diastereoisomers of 'N-chiral QASs' **2f** and **2i** by recrystallization, and the diastereoisomers of **2a** by the method of *Tayama* and *Tanaka* with (*R*)-binol and (*S*)-binol.

Precipitation and column chromatography were introduced to separate the 'N-chiral QASs'. In view of the different solubility of the diastereoisomeric 'N-chiral QASs', we attempted to separate the 'N-chiral QASs' by precipitation, and to our surprise, the diastereoisomers of **2b**, **2d**, and **2e** were separated efficiently. The diastereoisomers of **2c** were separated by classical column chromatography, and those of **2g** and **2h** by the combination of column chromatography and the method of *Tayama* and *Tanaka*. Thus, nine pairs of diastereoisomeric 'N-chiral QASs' were successfully separated, and eighteen pure 'N-chiral QASs' were obtained.

The absolute configuration of these QASs was determined predominately by X-ray single-crystal analysis. The two diastereoisomers of **2d** were crystallized from EtOH and acetone, respectively, to give suitable single crystals for X-ray analysis of [*N*(*S*)]-**2d** and [*N*(*R*)]-**2d**, respectively (*Fig.*)[3]).

Only one of the diastereoisomer **2b**, **2e**, **2f**, and **2i** could be crystallized for X-ray crystallographic analysis, and they were successively determined as [*N*(*S*)]-**2b**, [*N*(*R*)]-**2e**, [*N*(*S*)]-**2f**, and [*N*(*R*)]-**2i**[3]). One of the diastereoisomers of **2a**, **2g**, and **2h** was crystallized as a 1:1 complex with (*S*)-binol; X-ray crystallographic analysis of these complexes revealed that they were [*N*(*R*)]-**2a**, [*N*(*R*)]-**2g**, and [*N*(*R*)]-**2h**[3]). The absolute configurations of their corresponding diastereoisomers could be thus assigned as [*N*(*S*)]-**2a**, [*N*(*R*)]-**2b**, [*N*(*S*)]-**2e**, [*N*(*R*)]-**2f**, [*N*(*S*)]-**2g**, [*N*(*S*)]-**2h**, and [*N*(*S*)]-**2i**.

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[3]) CCDC-689671 (complex of [*N*(*R*)]-**2h** and (*S*)-binol), CCDC-689672 (complex of [*N*(*R*)]-**2a** and (*S*)-binol), CCDC-689673 ([*N*(*R*)]-**2d**), CCDC-689674 ([*N*(*S*)]-**2b**), CCDC-689675 ([*N*(*R*)]-**2i**), CCDC-689788 (complex of [*N*(*R*)]-**2g** and (*S*)-binol), CCDC-689789 ([*N*(*R*)]-**2e**), CCDC-689790 ([*N*(*S*)]-**2d**), and CCDC-689791 ([*N*(*S*)]-**2f**) contain the supplementary crystallographic data for this work. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

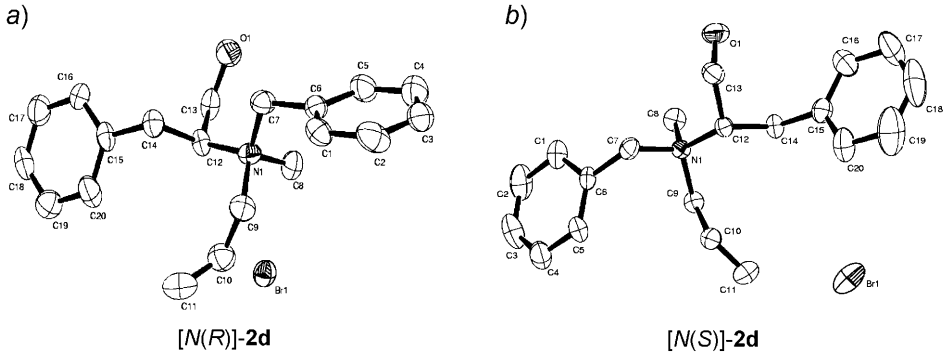

Figure. *ORTEP Diagrams of the two diastereoisomers of N-chiral QASs* **2d**: a) *[*N(R)*]-***2d** *and* b) *[*N(S)*]-***2d**. H-Atoms and solvent molecules are omitted for clarity.

The absolute configurations of the two diastereoisomers of **2c** had to be determined by other methods since none of them afforded crystals suitable for X-ray crystal analysis. We investigated the ^{1}H-NMR spectra of the 'N-chiral QASs' with known absolute configuration determined by X-ray crystallography in detail. The differences of the chemical shifts of the two H-atoms of PhCH_2N in '[$N(R)$]-QASs' and those of '[$N(S)$]-QASs' were determined (*Table 2*). It was found that the differences of the chemical shifts $\Delta\delta$ (0.34 to 0.80 ppm) of the two H-atoms in '[$N(R)$]-QASs' were much larger than those (0.00 to 0.50 ppm) in the '[$N(S)$]-QASs' (*Table 2*). The corresponding $\Delta\delta$ of the two diastereoisomers of **2c** were 0.74 and 0.91, respectively. Therefore, the former diastereoisomer was deduced as [$N(S)$]-**2c** and the latter as [$N(R)$]-**2c**.

Table 2. *Differences Δδ of the Chemical Shifts of the Two H-Atoms in PhC*H_2*N of Linear [*N(R)*]- and [*N(S)*]-QASs* **2** *and the Differences* $\Delta\Delta\delta$ *between* $\Delta\delta_R$ *and* $\Delta\delta_S$[a])

	Configuration at N-atom	$\Delta\delta$ [ppm]	$\Delta\Delta\delta = \Delta\delta_R - \Delta\delta_S$ [ppm]
2a	*R*	0.60	0.55
	S	0.05	
2b	*R*	0.80	0.30
	S	0.50	
2c	*R*	0.91	0.17
	S	0.74	
2d	*R*	0.65	0.43
	S	0.22	
2e	*R*	0.34	0.28
	S	0.06	
2f	*R*	0.35	0.35
	S	0.00	

[a]) ^{1}H-NMR in $CDCl_3$, except for **2e** and **2f** whose ^{1}H-NMR were recorded in (D_6)DMSO.

As potential PTCs, the stability of 'N-chiral QASs' is the first concern for their application. We investigated the stability of the 'N-chiral QASs' as exemplified by the 'N-chiral QASs' [$N(R)$]-**2a** and [$N(S)$]-**2a** at various pH values (1.0, 4.0, 7.0, 11.0, and

14.0), temperatures (0, 25, and 50°), and intervals (10, 24, and 48 h) by means of ^{1}H-NMR (D_2O) spectra to monitor possible changes. No detectable changes were observed, indicating that the QASs are stable under these conditions. Additionally, no racemization of [*N*(*R*)]-**2a** and [*N*(*S*)]-**2a** was found in DMSO, MeOH, or $CHCl_3$ even after two weeks. These results suggest that these '*N*-chiral QASs' have potential in an asymmetric phase-transfer-catalyzed reaction, and they are being investigated in our lab.

Conclusions. – We have successfully synthesized and separated a series of linear and cyclic 'N-chiral QASs' from the corresponding L-amino acid derivatives. The absolute configurations of these QASs were determined by X-ray single-crystal analysis. In the linear 'N-chiral QASs', the differences of the chemical shifts of the two H-atoms of the PhCH_2N moiety in '[*N*(*R*)]-QASs' are much larger than those in the diastereoisomeric '[*N*(*S*)]-QASs'. No racemization of 'N-chiral QASs' was found in protic and aprotic solvents, and they were stable in broad pH and temperature ranges, suggesting that these 'N-chiral QASs' have potential in phase-transfer-catalyzed reactions.

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Experimental Part

1. *General.* Commercial reagents were used without purification. All solvents including petroleum ether (60–90°) were distilled prior to use. Anh. MeCN was freshly distilled from CaH_2. The hydrochloride salts of amino esters were synthesized *via* reported procedures. Column chromatography (CC): Silica gel (SiO_2; 200–300 mesh). TLC: SiO_2 GF_{254} plates. M.p.: *X-6* melting-point apparatus; uncorrected. Optical rotations: *Perkin-Elmer 341* automatic polarimeter. IR Spectra: *Perkin-Elmer FT-IR* spectrometer. NMR Spectra: *Bruker Advance-600* spectrometer, with $SiMe_4$ as internal standard. Electrospray-ionization mass spectra (ESI-MS) and HR-ESI-MS: *Bruker Daltonics-Bio-TOF-Q* mass spectrometer. X-Ray measurement: *Enraf-Nonius-CAD4* or *Rigaku-Raxis-Rapid* diffractometer; programs used: *Siemens* SHELXTL plus/SHELXL-97.

2. N-*Benzyl*-N-*methyl-Substituted Amino Acid Esters: General Procedure.* $NaHCO_3$ (101 mg, 1.2 mmol) was added to a soln. of L-amino acid ester hydrochloride (1.0 mmol) in MeOH (5 ml) with stirring. After 15 min, benzaldehyde (0.11 ml, 1.05 mmol) was added. The resulting soln. was stirred for 2.0–3.5 h at r.t. The mixture was cooled to 0°, then KBH_4 (22 mg, 0.4 mmol) was added, and the mixture stirred for 0.5–1 h at r.t. to give the corresponding benzylamino derivative. The latter was treated with 37% HCHO soln. (0.14 ml, 1.8 mmol) and stirred for 2.5–4.5 h. The resulting soln. was again treated with KBH_4 (108 mg, 2 mmol) below 0° and then stirred for 5–11 h at r.t. The org. solvents were evaporated to afford a slurry syrup, which was diluted with H_2O (5 ml) and extracted with AcOEt (3 × 8 ml). The org. layer was washed with brine, dried, and concentrated, and the residue separated by CC (SiO_2) to give one of the title compounds with yields between 78% and 91%.

3. N-*Benzyl*-N-*methyl-Substituted Amino Alcohols* **1a**–**1f**: *General Procedure.* To the *N*-benzyl-*N*-methyl-substituted amino acid ester (1 mmol) in anh. Et_2O (5 ml), $LiAlH_4$ (38 mg, 1 mmol) was added at 0°. After 0.5–1 h, the soln. was quenched by the sequential addition of H_2O (0.04 ml), 10% NaOH soln. (0.04 ml), and H_2O (0.12 ml). The resulting slurry was filtered through *Celite*, and the filtrate was dried. Then the solvent was evaporated to give one of the title compounds with yields between 87% and 97%. These materials can be used directly for the next step.

4. *'N-Chiral QASs'* **2**: *General Procedure.* A mixture of the tertiary amine **1** (1 mmol) and allyl bromide (0.17 ml, 2 mmol) in anh. MeCN (5 ml) was refluxed for 5–48 h. After being cooled to r.t., the excess allyl bromide and MeCN were evaporated. The residue was purified by flash CC (SiO_2, AcOEt/

MeOH 10:1) to afford the diastereoisomer mixtures **2** of the 'N-chiral QASs' with yields between 84% and 95%.

5. *Separation of Diastereoisomers of 'N-Chiral QASs'.* 5.1. *Precipitation.* The two diastereoisomers of the QASs **2b**, **2d**, and **2e** were separated by precipitation. Taken the separation of the diastereoisomers of **2e** as an example, a white solid appeared immediately when acetone was added to the slurry of **2e** obtained above. Acetone was added till no more white solid appeared. The mixture was stirred at r.t. for 0.5–1 h. The solid collected by filtration was [*N*(*R*)]-**2e**. The filtrate was concentrated to give [*N*(*S*)]-**2e**. Also the two diastereoisomers of **2b** and **2d** were separated by this procedure.

5.2. *Column Chromatography.* The two diastereoisomers of **2c** (1 mmol) were separated by CC (SiO_2, AcOEt/MeOH 60:1 (800 ml), 40:1 (500 ml), 20:1 (400 ml), and 10:1 (200 ml)): [*N*(*R*)]-**2c** (65 mg, 0.18 mmol) and [*N*(*S*)]-**2c** (101 mg, 0.28 mmol).

After the separation of [*N*(*R*)]-**2g** (1 mmol) and [*N*(*R*)]-**2h** (1 mmol) by *Tayama* and *Tanaka*'s method (chiral binol complexes with 'N-chiral QASs'), the rest of the mixtures of **2g** and **2h** were subjected to CC (SiO_2, AcOEt/MeOH 60:1 (500 ml), 30:1 (300 ml), and 10:1 (200 ml)): [*N*(*S*)]-**2g** (104 mg, 0.35 mmol) and [*N*(*S*)]-**2h** (107 mg, 0.33 mmol).

5.3. *Recrystallization.* [*N*(*S*)]-**2f** and [*N*(*S*)]-**2i** were recrystallized from the EtOH soln. of **2f** and the MeOH soln. of **2i**, resp. After removal of [*N*(*S*)]-**2f** and [*N*(*S*)]-**2i** from their mother liquor, [*N*(*R*)]-**2f** and [*N*(*R*)]-**2i** were crystallized from the mother liquor.

5.4. Tayama *and* Tanaka*'s Method: Chiral binol Complexes with 'N-Chiral QASs'.* To a soln. of **2a** (299 mg, 1.00 mmol) in CH_2Cl_2 (3.0 ml) was added (*S*)-binol (126 mg, 0.44 mmol) at r.t., and the mixture was stirred for 24 h. The precipitate was isolated by filtration and crystallized in EtOH to give the corresponding 1:1 complex as colorless crystals. The complex was extracted with H_2O and Et_2O to dissociate the complex. From the H_2O layer, we obtained the single diastereoisomer of [*N*(*R*)]-**2a** (110 mg, 0.37 mmol). The same procedure, but with (*R*)-binol (160 mg, 0.37 mmol), afforded [*N*(*S*)]-**2a** (143 mg, 0.48 mmol).

With 0.55 equiv. of (*S*)-binol, [*N*(*R*)]-**2g** and [*N*(*R*)]-**2h** were separated according to the above procedure.

6. *Data of Synthesized Compounds.* N-*Benzyl*-N-*methyl*-L-*alanine Methyl Ester.* CC (SiO_2, petroleum ether/AcOEt 25:1). Yield 85%. Colorless oil. $[\alpha]_D^{25} = -71$ ($c = 0.10$, MeOH). IR (film): 3027, 2983, 2950, 2845, 1737, 1453, 1193, 736. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.29–7.34 (*m*, 4 H); 7.23–7.26 (*m*, 1 H); 3.73 (*s*, 3 H); 3.71 (*d*, $J = 13.4$, 1 H); 3.61 (*d*, $J = 13.4$, 1 H); 3.48 (*q*, $J = 7.1$, 1 H); 2.28 (*s*, 3 H); 1.34 (*d*, $J = 7.1$, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 173.9; 139.4; 128.8; 128.2; 127.0; 60.7; 58.4; 51.2; 37.9; 14.8. ESI-MS: 208.0 ($[M+H]^+$).

N-*Benzyl*-N-*methyl*-L-*alaninol* (**1a**). CC (SiO_2, petroleum ether/AcOEt 10:1). Yield 97%. Colorless oil. $[\alpha]_D^{25} = +44$ ($c = 0.10$, MeOH). IR (film): 3433, 3027, 2965, 1493, 1452, 1042, 734. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.29–7.33 (*m*, 4 H); 7.24–7.26 (*m*, 1 H); 3.67 (*d*, $J = 13.1$, 1 H); 3.45 (*d*, $J = 13.1$, 1 H); 3.36–3.43 (*m*, 2 H); 2.94–3.00 (*m*, 1 H); 2.14 (*s*, 3 H); 0.92 (*d*, $J = 6.7$, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 139.2; 128.8; 128.4; 127.1; 62.9; 58.7; 57.8; 35.4; 8.5. ESI-MS: 180.1 ($[M+H]^+$), 202.1 ($[M+Na]^+$).

N-*Benzyl*-N-*methyl*-L-*leucine Methyl Ester.* CC (SiO_2, petroleum ether/AcOEt 30:1). Yield 87%. Off-yellow liquid. $[\alpha]_D^{25} = -70$ ($c = 0.10$, MeOH). IR (film): 3029, 2954, 2870, 1732, 1454, 1156, 736. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.29–7.32 (*m*, 4 H); 7.21–7.24 (*m*, 1 H); 3.78 (*d*, $J = 13.6$, 1 H); 3.72 (*s*, 3 H); 3.58 (*d*, $J = 13.6$, 1 H); 3.40 (*dd*, $J = 8.2$, 7.1, 1 H); 2.25 (*s*, 3 H); 1.73–1.78 (*m*, 1 H); 1.63–1.68 (*m*, 1 H); 1.53–1.58 (*m*, 1 H); 0.92 (*d*, $J = 6.7$, 3 H); 0.87 (*d*, $J = 6.5$, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 173.5; 139.7; 128.7; 128.2; 126.9; 63.7; 58.5; 50.9; 38.7; 37.7; 24.7; 23.0; 22.0. ESI-MS: 250.1 ($[M+H]^+$), 272.1 ($[M+Na]^+$).

N-*Benzyl*-N-*methyl*-L-*leucinol* (**1b**). CC (SiO_2, petroleum ether/AcOEt 15:1). Yield 95%. Pale yellow liquid. $[\alpha]_D^{25} = +22$ ($c = 0.10$, MeOH). IR (film): 3431, 3029, 2955, 2868, 1454, 1366, 1020, 735. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.28–7.32 (*m*, 4 H); 7.23–7.26 (*m*, 1 H); 3.69 (*d*, $J = 13.2$, 1 H); 3.53 (*dd*, $J = 10.4$, 4.9, 1 H); 3.47 (*d*, $J = 13.2$, 1 H); 3.33 (*t*, $J = 10.4$, 1 H); 2.83–2.87 (*m*, 1 H); 2.15 (*s*, 3 H); 1.51–1.57 (*m*, 1 H); 1.40–1.44 (*m*, 1 H); 1.05–1.09 (*m*, 1 H); 0.94 (*d*, $J = 7.1$, 3 H); 0.89 (*d*, $J = 7.1$, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 139.3; 128.8; 128.4; 127.1; 61.6; 61.3; 57.9; 35.7; 33.8; 25.4; 23.8; 22.2. ESI-MS: 222.0 ($[M+H]^+$).

(2S)-N-*Benzyl*-N-*methyl-2-phenylglycine Methyl Ester.* CC (SiO_2, petroleum/AcOEt 35:1). Yield 89%. Colorless liquid. $[\alpha]_D^{25} = +79$ ($c = 0.10$, MeOH). IR (film): 3028, 2949, 2842, 1735, 1601, 1493, 1452, 1340, 1204, 1165, 737. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.46 (*d*, *J* = 6.9, 2 H); 7.28–7.37 (*m*, 7 H); 7.22–7.25 (*m*, 1 H); 4.34 (*s*, 1 H); 3.73 (*s*, 3 H); 3.65 (*d*, *J* = 13.4, 1 H); 3.51 (*d*, *J* = 13.4, 1 H); 2.21 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 172.4; 138.9; 136.6; 128.9; 128.8; 128.5; 128.2; 128.1; 127.0; 72.1; 58.6; 51.7; 39.1. ESI-MS: 270.1 ($[M+H]^+$), 292.1 ($[M+Na]^+$).

(2S)-N-*Benzyl*-N-*methyl-2-phenylglycinol* (**1c**). CC (SiO_2, petroleum ether/AcOEt 10:1). Yield 92%. Colorless liquid. $[\alpha]_D^{25} = +39$ ($c = 0.10$, MeOH). IR (film): 3425, 3028, 2932, 2880, 1601, 1493, 1452, 1031, 737. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.38 (*t*, *J* = 6.8, 2 H); 7.29–7.35 (*m*, 5 H); 7.24 (*d*, *J* = 6.8, 3 H); 4.05 (*t*, *J* = 10.6, 1 H); 3.86 (*dd*, *J* = 9.8, 5.1, 1 H); 3.68 (*dd*, *J* = 10.6, 5.1, 1 H); 3.62 (*d*, *J* = 13.1, 1 H); 3.36 (*d*, *J* = 13.1, 1 H); 2.14 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 138.9; 135.5; 129.1; 128.9; 128.4; 128.3; 127.9; 127.2; 68.2; 60.8; 58.5; 36.9. ESI-MS: 242.2 ($[M+H]^+$).

N-*Benzyl*-N-*methyl*-L-*phenylalanine Methyl Ester.* CC (SiO_2, petroleum ether/AcOEt 35:1). Yield 87%. Colorless liquid. $[\alpha]_D^{25} = -80$ ($c = 0.10$, MeOH) ([12]: $[\alpha]_D^{23} = -81.6$ ($c = 0.5$, $CDCl_3$)). IR (film): 3028, 2930, 2848, 2801, 1732, 1604, 1495, 1454, 1165, 1025, 737. ^{1}H- and ^{13}C-NMR and MS: identical with those reported [12].

N-*Benzyl*-N-*methyl*-L-*phenylalaninol* (**1d**). CC (SiO_2, petroleum ether/AcOEt 10:1). Yield 96%. Colorless liquid. $[\alpha]_D^{25} = -35$ ($c = 0.10$, MeOH). IR (film): 3437, 3027, 2938, 2857, 1602, 1494, 1454, 1032, 730. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.24–7.36 (*m*, 7 H); 7.19 (*t*, *J* = 7.0, 1 H); 7.13 (*d*, *J* = 7.0, 2 H); 3.76 (*d*, *J* = 13.0, 1 H); 3.56 (*d*, *J* = 13.0, 1 H); 3.38–3.45 (*m*, 2 H); 3.04–3.09 (*m*, 1 H); 3.00 (*dd*, *J* = 13.4, 4.4, 1 H); 2.39 (*dd*, *J* = 13.4, 9.8, 1 H); 2.28 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 139.2; 139.0; 129.0; 128.9; 128.6; 128.5; 127.3; 126.2; 65.6; 60.6; 58.2; 35.9; 31.4. ESI-MS: 256.1 ($[M+H]^+$).

N-*Benzyl*-N-*methyl*-L-*homophenylalanine Ethyl Ester.* CC (SiO_2, petroleum ether/AcOEt 40:1). Yield 91%. Colorless liquid. $[\alpha]_D^{25} = -75$ ($c = 0.10$, MeOH). IR (film): 3026, 2940, 1728, 1603, 1495, 1454, 1369, 1155, 1028, 699. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.30–7.35 (*m*, 4 H); 7.23–7.28 (*m*, 3 H); 7.18 (*d*, *J* = 7.3, 3 H); 4.15–4.21 (*m*, 2 H); 3.82 (*d*, *J* = 13.6, 1 H); 3.61 (*d*, *J* = 13.6, 1 H); 3.31 (*t*, *J* = 7.1, 1 H); 2.76–2.81 (*m*, 1 H); 2.64–2.69 (*m*, 1 H); 2.30 (*s*, 3 H); 2.02–2.09 (*m*, 2 H); 1.31 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 172.5; 141.8; 139.6; 128.7; 128.5; 128.4; 128.2; 126.9; 125.9; 65.0; 60.0; 58.4; 37.7; 32.4; 31.5; 14.6. ESI-MS: 312.2 ($[M+H]^+$).

N-*Benzyl*-N-*methyl*-L-*homophenylalaninol* (**1e**). CC (SiO_2, petroleum ether/AcOEt 10:1). Yield 94%. Colorless liquid. $[\alpha]_D^{25} = +20$ ($c = 0.10$, MeOH). IR (film): 3424, 3025, 2932, 2857, 1602, 1494, 1453, 1362, 1126, 1037, 699. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.29–7.31 (*m*, 4 H); 7.18–7.25 (*m*, 6 H); 3.70 (*d*, *J* = 13.1, 1 H); 3.62 (*dd*, *J* = 10.4, 5.0, 1 H); 3.47 (*d*, *J* = 13.1, 1 H); 3.41 (*t*, *J* = 10.4, 1 H); 2.81–2.85 (*m*, 1 H); 2.64–2.68 (*m*, 1 H); 2.53–2.58 (*m*, 1 H); 2.18 (*s*, 3 H); 1.93–1.99 (*m*, 1 H); 1.47–1.53 (*m*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 141.8; 139.1; 128.8; 128.5; 128.4; 128.2; 127.2; 126.1; 63.1; 60.9; 58.2; 35.7; 33.3; 26.9. ESI-MS: 270.2 ($[M+H]^+$).

N-*Benzyl*-N-*methyl*-L-*tyrosine Methyl Ester.* CC (SiO_2, petroleum ether/AcOEt 15:1). Yield 81%. Colorless liquid. $[\alpha]_D^{25} = -43$ ($c = 0.10$, MeOH) ([12]: $[\alpha]_D^{23} = -39.2$ ($c = 0.011$, MeOH)). ^{1}H- and ^{13}C-NMR and MS: identical with those reported in [12].

N-*Benzyl*-N-*methyl*-L-*tyrosinol* (**1f**). CC (SiO_2, petroleum ether/AcOEt 5:1). Yield 87%. Colorless liquid. $[\alpha]_D^{25} = -20$ ($c = 0.10$, MeOH). IR (film): 3452, 3028, 2941, 1614, 1495, 1360, 1231, 1036, 734. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.24–7.34 (*m*, 5 H); 6.90 (*d*, *J* = 8.2, 2 H); 6.66 (*d*, *J* = 8.2, 2 H); 3.76 (*d*, *J* = 12.9, 1 H); 3.56 (*d*, *J* = 12.9, 1 H); 3.39 (br. *d*, *J* = 8.0, 2 H); 2.99–3.03 (*m*, 1 H); 2.91 (*dd*, *J* = 13.5, 4.2, 1 H); 2.30 (*dd*, *J* = 13.5, 3.4, 1 H); 2.27 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 154.8; 138.8; 130.1; 129.9; 128.9; 128.6; 127.4; 115.6; 65.2; 60.3; 58.2; 35.9; 30.3. ESI-MS: 272.0 ($[M+H]^+$), 294.0 ($[M+Na]^+$).

(3S)-1,2,3,4-Tetrahydro-2-methylisoquinoline-3-methanol (**1g**). Yield 75%. Colorless crystals (CH_2Cl_2/hexane). M.p. 103–105° ([12]: m.p. 104–106°). $[\alpha]_D^{25} = -69$ ($c = 1.0$, $CHCl_3$) ([12]: $[\alpha]_D^{23} = -64$ ($c = 1.0$, $CHCl_3$)). ^{1}H- and ^{13}C-NMR and MS: identical with those reported in [12].

[N(R)]-N-*Allyl*-N-*benzyl*-N-*[(1S)-2-hydroxy-1-methylethyl]*-N-*methylammonium Bromide* (= *[N(R)]*-N-*[(1S)-2-Hydroxy-1-methylethyl]*-N-*methyl*-N-*prop-2-en-1-ylbenzenemethanaminium Bromide*; [*N*(*R*)]-**2a**). Yield 37%. Pale yellow liquid. $[\alpha]_D^{25} = +6.4$ ($c = 0.60$, MeOH). IR (KBr): 3400, 3017, 2986, 1457, 1072, 759. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.69 (*d*, *J* = 6.7, 2 H); 7.43–7.48 (*m*, 3 H); 5.96–6.03 (*m*, 1 H); 5.73 (*d*, *J* = 16.8, 1 H); 5.68 (*d*, *J* = 10.1, 1 H); 5.43 (*t*, *J* = 5.7, 1 H); 5.17 (*d*, *J* = 12.9, 1 H); 4.57

(*d*, *J* = 12.9, 1 H); 4.35–4.38 (*m*, 1 H); 4.26 (*dd*, *J* = 13.5, 7.3, 1 H); 4.05–4.07 (*m*, 1 H); 3.91 (*dd*, *J* = 13.5, 7.2, 1 H); 3.78–3.81 (*m*, 1 H); 3.14 (*s*, 3 H); 1.60 (*d*, *J* = 6.9, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 133.6; 130.7; 129.3; 128.9; 127.1; 124.7; 68.0; 63.8; 62.8; 60.6; 47.1; 12.7. HR-ESI-MS: 220.1689 ($[M-Br]^+$, $C_{14}H_{22}NO^+$; calc. 220.1696).

*X-Ray Analysis of the 1:1 Complex of [*N(R)*]-***2a*** and (*S*)-binol* [12]. Slow evaporation of a soln. of the complex in EtOH gave a single crystal suitable for X-ray analysis (0.42 × 0.40 × 0.38 mm; colorless). $C_{34}H_{36}BrNO_3$ (586.55): Orthorhombic $P2_12_12_1$; $a = 10.660(4)$, $b = 13.834(4)$, $c = 20.015(2)$ Å, $\beta = 90°$, $V = 2951.8$ (13) Å^3; $Z = 4$, $D_{calc} = 1.427$ Mg/m^3. Intensities were measured on a *CAD4* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 1.79–25.45$, $\mu = 1.427$ mm^{-1}) at 292 K. Of the total 4778 reflections, 4394 were independent, and 2717 were observed. $R = 0.0391$, $R_w = 0.0926$.

*[*N*(*S*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-2-hydroxy-1-methylethyl]*-N-*methylammonium Bromide* (= *[*N*(*S*)]*-N-*[(1*S*)-2-Hydroxy-1-methylethyl]*-N-*methyl*-N-*prop-2-en-1-ylbenzenemethanaminium Bromide*; [*N*(*S*)]-**2a**). Yield 48%. Pale yellow liquid. $[\alpha]_D^{25} = -23.5$ ($c = 0.70$, MeOH). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.61 (*d*, *J* = 6.9, 2 H); 7.38–7.41 (*m*, 3 H); 6.04–6.11 (*m*, 1 H); 5.64 (*d*, *J* = 17.9, 1 H); 5.61 (*d*, *J* = 9.6, 1 H); 5.51 (br. *s*, 1 H); 4.79–4.85 (*m*, 2 H); 4.47–4.51 (*m*, 1 H); 4.25 (br. *d*, *J* = 12.4, 1 H); 3.92 (br. *d*, *J* = 12.8, 1 H); 3.69–3.74 (overlap, 2 H); 3.00 (*s*, 3 H); 1.58 (*d*, *J* = 5.2, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 133.4; 130.7; 129.3; 128.6; 127.2; 125.0; 68.0; 63.2; 62.9; 60.5; 46.5; 12.6. HR-ESI-MS: 220.1693 ($[M-Br]^+$, $C_{14}H_{22}NO^+$; calc. 220.1696).

*[*N*(*S*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-3-methylbutyl]*-N-*methylammonium Bromide* (= *[*N*(*S*)]*-N-*[(1*S*)-1-(Hydroxymethyl)-3-methylbutyl]*-N-*methyl*-N-*prop-2-en-1-ylbenzenemethanaminium Bromide*; [*N*(*S*)]-**2b**). Yield 42%. Colorless crystals (acetone). M.p. 143–144°. $[\alpha]_D^{25} = -23$ ($c = 1.50$, MeOH). IR (KBr): 3423, 3021, 2949, 1632, 1458, 1053, 760. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.70 (*d*, *J* = 6.8, 2 H); 7.44–7.49 (*m*, 3 H); 5.99–6.04 (*m*, 1 H); 5.67 (*d*, *J* = 9.8, 1 H); 5.66 (*d*, *J* = 17.6, 1 H); 5.46 (*t*, *J* = 6.8, 1 H); 5.17 (*d*, *J* = 12.9, 1 H); 4.91 (*dd*, *J* = 13.6, 6.5, 1 H); 4.67 (*d*, *J* = 12.9, 1 H); 4.53 (*dd*, *J* = 14.5, 5.7, 1 H); 4.04 (*d*, *J* = 14.5, 1 H); 3.62 (*dd*, *J* = 13.6, 7.6, 1 H); 3.47 (*dd*, *J* = 8.9, 2.1, 1 H); 2.97 (*s*, 3 H); 2.16 (*td*, *J* = 12.0, 3.7, 1 H); 1.82–1.86 (*m*, 1 H); 1.53 (*t*, *J* = 12.0, 1 H); 1.07 (*d*, *J* = 6.7, 3 H); 0.97 (*d*, *J* = 6.5, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 133.5; 130.8; 129.3; 128.8; 127.1; 124.8; 71.7; 63.4; 63.2; 57.2; 46.7; 33.5; 26.0; 24.0; 21.4. HR-ESI-MS: 262.2159 ($[M-Br]^+$, $C_{14}H_{22}NO^+$; calc. 262.2165).

*X-Ray Analysis of [*N*(*S*)]-***2b*** [12]. Slow evaporation of a soln. of [*N*(*S*)]-**2b** in acetone gave a single crystal suitable for X-ray analysis (0.48 × 0.42 × 0.40 mm; colorless). $C_{17}H_{28}BrNO$ (342.31): Orthorhombic $P2_12_12_1$; $a = 8.083(4)$, $b = 11.977(5)$, $c = 18.029(12)$ Å, $\beta = 90°$, $V = 1745.5(17)$ Å^3; $Z = 4$, $D_{calc} = 1.303$ Mg/m^3. Intensities were measured on a *CAD4* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 2.04–25.52$, $\mu = 2.352$ mm^{-1}) at 292 K. Of the total 2002 reflections, 1842 were independent, and 1187 were observed. $R = 0.0637$, $R_w = 0.1835$.

*[*N*(*R*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-3-methylbutyl]*-N-*methylammonium Bromide* (= *[*N*(*R*)]*-N-*[(1*S*)-1-(Hydroxymethyl)-3-methylbutyl]*-N-*methyl*-N-*prop-2-en-1-ylbenzenemethanaminium Bromide*; [*N*(*R*)]-**2b**). Yield 30%. Pale yellow liquid. $[\alpha]_D^{25} = +26.7$ ($c = 2.40$, MeOH). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.70 (*d*, *J* = 6.7, 2 H); 7.44–7.48 (*m*, 3 H); 5.94–5.97 (*m*, 1 H); 5.69 (*d*, *J* = 17.3, 1 H); 5.67 (*d*, *J* = 10.3, 1 H); 5.31 (*d*, *J* = 12.6, 1 H); 4.51 (*d*, *J* = 12.6, 1 H); 4.49 (*d*, *J* = 11.8, 1 H); 4.24–4.26 (*m*, 1 H); 4.06 (*d*, *J* = 13.4, 1 H); 3.92–3.96 (*m*, 1 H); 3.51 (*d*, *J* = 10.0, 1 H); 3.16 (*s*, 3 H); 2.17 (*m*, 1 H); 1.85 (br. *s*, 2 H); 1.59 (*t*, *J* = 11.0, 1 H); 1.05 (*d*, *J* = 6.4, 3 H); 0.91 (*d*, *J* = 6.3, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 133.7; 130.7; 129.3; 128.9; 127.2; 124.7; 71.1; 64.4; 62.9; 57.3; 47.4; 33.6; 26.0; 24.0; 21.3. HR-ESI-MS: 262.2175 ($[M-Br]^+$, $C_{14}H_{22}NO^+$; calc. 262.2165).

*[*N*(*R*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-2-hydroxy-1-phenylethyl]*-N-*methylammonium Bromide* (= *[*N*(*R*),*α*S]*-*α*-*(Hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzenemethanaminium Bromide*; [*N*(*R*)]-**2c**). [*N*(*R*)]-**2c** was eluted after [*N*(*S*)]-**2c**. Yield 18%. Colorless oil. $[\alpha]_D^{25} = +65$ ($c = 0.11$, MeOH). IR (KBr): 3421, 2920, 1627, 1458, 1054, 752. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.55–7.62 (*m*, 3 H); 7.44–7.49 (*m*, 7 H); 6.12–6.19 (*m*, 1 H), 5.93 (br. *s*, 1 H); 5.76 (*d*, *J* = 16.9, 1 H); 5.73 (*d*, *J* = 10.4, 1 H); 5.25 (*d*, *J* = 13.0, 1 H); 5.02–5.04 (*m*, 1 H); 4.80–4.85 (*m*, 1 H); 4.59 (*dd*, *J* = 13.4, 7.5, 1 H); 4.51 (*d*, *J* = 13.0, 1 H); 4.39 (br. *d*, *J* = 13.6, 1 H); 3.92 (*dd*, *J* = 13.4, 6.3, 1 H); 3.00 (*s*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 133.7; 130.9; 130.8; 130.7; 129.6; 129.4; 129.2; 127.1; 125.0; 75.3; 64.9; 62.1; 60.8; 47.3. HR-ESI-MS: 282.1856 ($[M-Br]^+$, $C_{14}H_{22}NO^+$; calc. 282.1852).

*[*N*(*S*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-2-hydroxy-1-phenylethyl]*-N-*methylammonium Bromide* (= *[*N*(*S*),*α*S]-α-(Hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzenemethanaminium Bromide*; [*N*(*S*)]-**2c**). [*N*(*S*)]-**2c** was eluted before [*N*(*R*)]-**2c**. Yield 28%. Colorless oil. $[\alpha]_D^{25} = +32$ ($c = 0.18$, MeOH). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.61 (br. *d*, *J* = 6.9, 4 H); 7.41 – 7.52 (*m*, 6 H); 6.07 – 6.14 (*m*, 1 H); 5.95 (br. *s*, 1 H); 5.65 (*d*, *J* = 10.2, 1 H); 5.61 (*d*, *J* = 12.5, 1 H); 5.56 (*d*, *J* = 16.9, 1 H); 5.02 (*dd*, *J* = 7.9, 2.3, 1 H), 4.95 (*dd*, *J* = 13.4, 6.9, 1 H); 4.88 (*dd*, *J* = 14.0, 8.1, 1 H); 4.70 (*d*, *J* = 12.5, 1 H); 4.37 (*d*, *J* = 14.0, 1 H); 3.59 (*dd*, *J* = 13.4, 7.1, 1 H); 2.77 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 133.8; 131.0; 130.7; 129.6; 129.3; 129.0; 127.0; 125.6; 75.8; 63.7; 63.4; 60.7; 47.0. HR-ESI-MS: 282.1853 ($[M - Br]^+$, $C_{14}H_{22}NO^+$; calc. 282.1852).

*[*N*(*S*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-2-phenylethyl]*-N-*methylammonium Bromide* (= *[*N*(*S*),*α*S]-α-(Hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzeneethanaminium Bromide*; [*N*(*S*)]-**2d**). Yield 41%. Colorless crystals (EtOH). M.p. 185 – 186°. $[\alpha]_D^{25} = -48$ ($c = 2.00$, MeOH). IR (KBr): 3430, 2970, 1634, 1456, 1115, 741. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.75 (*d*, *J* = 6.8, 2 H); 7.43 – 7.48 (*m*, 3 H); 7.29 – 7.32 (*m*, 4 H); 7.24 – 7.27 (*m*, 1 H); 5.99 – 6.06 (*m*, 1 H); 5.72 (*d*, *J* = 16.9, 1 H); 5.68 (*d*, *J* = 10.4, 1 H); 5.43 (*t*, *J* = 6.1, 1 H); 5.16 (*d*, *J* = 12.9, 1 H); 4.94 (*d*, *J* = 12.9, 1 H); 4.85 (*dd*, *J* = 14.3, 5.8, 1 H); 4.41 (*dd*, *J* = 14.3, 6.1, 1 H); 3.75 (*dd*, *J* = 13.7, 8.0, 2 H); 3.52 (*d*, *J* = 11.0, 1 H); 3.45 (*t*, *J* = 11.0, 1 H); 3.37 (*d*, *J* = 12.1, 1 H); 3.18 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 137.1; 133.7; 130.9; 129.8; 129.5; 129.2; 128.4; 127.6; 127.5; 126.6; 73.5; 63.7; 63.0; 56.6; 47.0; 30.4. HR-ESI-MS: 296.2002 ($[M - Br]^+$, $C_{20}H_{26}NO^+$; calc. 296.2009).

*X-Ray Analysis of [*N*(*S*)]*-**2d** [12]. Slow evaporation of a soln. of [*N*(*S*)]-**2d** in EtOH gave a single crystal suitable for X-ray analysis ($0.42 \times 0.40 \times 0.20$ mm; colorless). $C_{20}H_{26}BrNO$ (376.33): Orthorhombic $P2_12_12_1$; $a = 8.270(5)$, $b = 11.477(6)$, $c = 20.560(9)$ Å, $\beta = 90°$, $V = 1951.3(17)$ Å^3; $Z = 4$, $D_{calc} = 1.281$ Mg/m^3. Intensities were measured on a *CAD4* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 1.98 – 25.49$, $\mu = 2.111$ mm^{-1}) at 292 K. Of the total 3474 reflections, 2985 were independent, and 1534 were observed. $R = 0.0491$, $R_w = 0.1293$.

*[*N*(*R*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-2-phenylethyl]*-N-*methylammonium Bromide* (= *[*N*(*R*),*α*S]-α-(Hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzeneethanaminium Bromide*; [*N*(*R*)]-**2d**). Yield 31%. Colorless crystals (acetone). M.p. 171 – 172°. $[\alpha]_D^{25} = +12$ ($c = 0.08$, MeOH). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.78 (*d*, *J* = 7.0, 2 H); 7.43 (*t*, *J* = 7.3, 1 H); 7.38 (*t*, *J* = 7.3, 2 H); 7.19 – 7.29 (*m*, 5 H); 5.93 – 6.02 (*m*, 1 H); 5.82 (*d*, *J* = 16.8, 1 H); 5.69 (*d*, *J* = 10.0, 1 H); 5.40 (*t*, *J* = 5.4 Hz, 1 H); 5.35 (*d*, *J* = 12.7, 1 H); 4.71 (overlap, 1 H); 4.70 (*d*, *J* = 12.7, 1 H); 4.29 (*dd*, *J* = 14.4, 5.3, 1 H); 3.91 (*dd*, *J* = 13.7, 6.6, 1 H); 3.75 (br. *d*, *J* = 13.7, 1 H); 3.53 – 3.57 (*m*, 2 H); 3.37 – 3.41 (*m*, 1 H); 3.16 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 135.9; 133.8; 130.6; 129.5; 129.2; 129.1; 129.0; 127.4; 127.2; 124.7; 73.3; 64.4; 63.3; 56.1; 47.4; 31.0. HR-ESI-MS: 296.2008 ($[M - Br]^+$, $C_{20}H_{26}NO^+$; calc. 296.2009).

*X-Ray Analysis of [*N*(*R*)]*-**2d** [12]. Slow evaporation of a soln. of [*N*(*R*)]-**2d** in acetone gave a single crystal suitable for X-ray analysis ($0.46 \times 0.36 \times 0.23$ mm; colorless). $C_{20}H_{26}BrNO$ (376.33): Orthorhombic $P2_12_12_1$; $a = 9.6683(18)$, $b = 13.6013(13)$, $c = 14.616(3)$ Å, $\beta = 90°$, $V = 1922.1(6)$ Å^3; $Z = 4$, $D_{calc} = 1.300$ Mg/m^3. Intensities were measured on a *CAD4* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 2.53 – 25.46$, $\mu = 2.143$ mm^{-1}) at 292 K. Of the total 2383 reflections, 2291 were independent, and 1046 were observed. $R = 0.0555$, $R_w = 0.1451$.

*[*N*(*R*)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-3-phenylpropyl]*-N-*methylammonium Bromide* (= *[*N*(*R*),*α*S]-α-(Hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzenepropanaminium Bromide*; [*N*(*R*)]-**2e**). Yield 45%. Colorless crystals (EtOH). M.p. 179 – 180°. $[\alpha]_D^{25} = +51$ ($c = 5.00$, MeOH). IR (KBr): 3429, 3016, 2993, 2786, 1457, 1091, 785. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.60 (*d*, *J* = 6.7, 2 H); 7.46 – 7.52 (*m*, 3 H); 7.28 – 7.33 (*m*, 4 H); 7.20 – 7.23 (*m*, 1 H); 5.87 – 5.91 (*m*, 1 H); 5.61 (*t*, *J* = 5.2, 1 H); 5.53 (*d*, *J* = 18.4, 1 H); 5.52 (*d*, *J* = 9.7, 1 H); 4.76 (*d*, *J* = 13.0, 1 H); 4.42 (*d*, *J* = 13.0, 1 H); 4.24 (*dd*, *J* = 13.6, 7.7, 1 H), 4.13 – 4.16 (*m*, 1 H); 4.01 – 4.03 (*m*, 1 H); 3.64 (*dd*, *J* = 13.6, 6.5, 1 H); 3.33 (overlap with the signal of the H_2O in DMSO, 1 H); 2.94 (*s*, 3 H); 2.77 – 2.82 (*m*, 1 H); 2.48 – 2.55 (*m*, 1 H); 2.23 – 2.31 (*m*, 1 H); 2.18 – 2.22 (*m*, 1 H). ^{13}C-NMR (150 MHz, (D_6)DMSO): 141.0; 133.8; 130.6; 129.3; 129.1; 128.9; 128.4; 127.5; 126.7; 126.5; 71.9; 63.1; 62.7; 57.2; 46.8; 32.5; 26.5. HR-ESI-MS: 310.2150 ($[M - Br]^+$, $C_{21}H_{28}NO^+$; calc. 310.2165).

*X-Ray Analysis of [*N*(*R*)]*-**2e** [12]. Slow evaporation of a soln. of [*N*(*R*)]-**2e** in EtOH gave a single crystal suitable for X-ray analysis ($0.40 \times 0.30 \times 0.18$ mm; colorless). $C_{21}H_{28}BrNO$ (390.35): monoclinic

$P2_1$; $a = 9.128(4)$, $b = 12.148(3)$, $c = 9.773(2)$ Å, $\beta = 114.80(2)^\circ$, $V = 983.8(5)$ Å^3; $Z = 2$, $D_{calc} = 1.318$ Mg/m^3. Intensities were measured on a *CAD4* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 2.30$–25.53, $\mu = 2.096$ mm^{-1}) at 292 K. Of the total 2157 reflections, 2109 are independent, and 1524 were observed. $R = 0.0542$, $R_w = 0.1539$.

*[*N*(S)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-3-phenylpropyl]*-N-*methylammonium Bromide* (= *[*N*(S),*α*S]-*α*-(Hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzenepropanaminium Bromide*; [*N*(*S*)]-**2e**). Yield 35%. Pale yellow viscous liquid. $[\alpha]_D^{25} = +34$ ($c = 1.00$, MeOH). ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.46–7.53 (*m*, 5 H); 7.29–7.35 (*m*, 4 H); 7.22–7.25 (*m*, 1 H); 6.02–6.09 (*m*, 1 H); 5.61 (*d*, $J = 17.0$, 1 H); 5.56 (*d*, $J = 10.2$, 1 H); 5.56 (overlap, 1 H); 4.61 (*d*, $J = 13.2$, 1 H); 4.55 (*d*, $J = 13.2$, 1 H); 4.27 (*dd*, $J = 13.6$, 6.6, 1 H); 4.03–4.08 (*m*, 1 H); 3.93–4.01 (*m*, 1 H); 3.77 (*dd*, $J = 13.6$, 7.5, 1 H); 3.25 (br. *d*, $J = 11.0$, 1 H); 2.94 (*s*, 3 H); 2.76–2.81 (*m*, 1 H); 2.54–2.59 (*m*, 1 H); 2.28–2.38 (*m*, 1 H); 2.13–2.19 (*m*, 1 H). ^{13}C-NMR (150 MHz, (D_6)DMSO): 141.0; 133.6; 130.7; 129.4; 129.1; 128.9; 128.5; 127.6; 126.8; 126.6; 72.1; 63.3; 62.6; 57.2; 46.7; 32.5; 26.6. HR-ESI-MS: 310.2154 ([M – Br]$^+$, $C_{21}H_{28}NO^+$; calc. 310.2165).

*[*N*(S)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-2-(4-hydroxyphenyl)ethyl]*-N-*methylammonium Bromide* (= *[*N*(S),*α*S]-4-Hydroxy-*α*-(hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzeneethanaminium Bromide*; [*N*(*S*)]-**2f**). Yield 41%. Pale yellow crystal (EtOH). M.p. 176–177°. $[\alpha]_D^{25} = -41.6$ ($c = 0.80$, MeOH). IR (KBr): 3297, 3034, 1612, 1515, 1464, 1264, 1058, 850. ^{1}H-NMR (600 MHz, (D_6)DMSO): 9.35 (*s*, 1 H); 7.65 (*d*, $J = 7.5$, 2 H); 7.49–7.53 (*m*, 3 H); 7.09 (*d*, $J = 8.3$, 2 H); 6.72 (*d*, $J = 8.3$, 2 H); 6.11–6.15 (*m*, 1 H); 5.64 (*d*, $J = 16.9$, 1 H); 5.58 (*d*, $J = 10.2$, 1 H); 5.49 (*t*, $J = 4.6$, 1 H); 4.73 (*s*, 2 H); 4.27 (*dd*, $J = 13.8$, 6.1, 1 H); 3.85–3.91 (overlap, 2 H); 3.61 (*d*, $J = 13.8$, 1 H); 3.42 (*d*, $J = 11.5$, 1 H); 3.31 (overlap with the signal of the H_2O in DMSO, 1 H); 3.04 (*s*, 3 H); 3.03 (overlap, 1 H). ^{13}C-NMR (600 MHz, (D_6)DMSO): 156.8; 133.7; 130.8; 129.4; 128.5; 127.4; 126.9; 126.8; 116.0; 73.9; 63.7; 62.9; 56.6; 47.0; 29.6. HR-ESI-MS: 312.1944 ([M – Br]$^+$, $C_{20}H_{26}NO_2^+$; calc. 312.1958).

*X-Ray Analysis of [*N*(S)]*-**2f** [12]. Slow evaporation of a soln. of [*N*(*S*)]-**2f** in EtOH gave a single crystal suitable for X-ray analysis (0.45 × 0.43 × 0.40 mm; pale yellow). $C_{20}H_{26}BrNO_2$ (392.33): Orthorhombic $P2_12_12_1$; $a = 10.3716(10)$, $b = 12.1566(10)$, $c = 15.6790(16)$ Å, $\beta = 90^\circ$, $V = 1976.9(3)$ Å^3; $Z = 4$, $D_{calc} = 1.318$ Mg/m^3. Intensities were measured on a *Rigaku-Raxis-Rapid* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 3.09$–27.47, $\mu = 2.090$ mm^{-1}) at 293 K. Of the total 18872 reflections, 4524 were independent, and 2606 were observed. $R = 0.0540$, $R_w = 0.2107$.

*[*N*(R)]*-N-*Allyl*-N-*benzyl*-N-*[(1*S*)-1-(hydroxymethyl)-2-(4-hydroxyphenyl)ethyl]*-N-*methylammonium Bromide* (= *[*N*(R),*α*S]-4-Hydroxy-*α*-(hydroxymethyl)*-N-*methyl*-N-*(phenylmethyl)*-N-*prop-2-en-1-ylbenzeneethanaminium Bromide*; [*N*(*R*)]-**2f**). Yield 32%. Pale yellow solid. M.p. 171–172°. $[\alpha]_D^{25} = +17$ ($c = 0.08$, MeOH). ^{1}H-NMR (600 MHz, (D_6)DMSO): 9.35 (*s*, 1 H); 7.65 (*d*, $J = 6.7$, 2 H), 7.49–7.54 (*m*, 3 H); 7.07 (*d*, $J = 8.2$, 2 H); 6.73 (*d*, $J = 8.2$, 2 H); 6.05–6.12 (*m*, 1 H); 5.72 (*d*, $J = 16.9$, 1 H); 5.64 (*d*, $J = 10.3$, 1 H); 5.54 (br. *s*, 1 H); 4.91 (*d*, $J = 12.8$, 1 H); 4.56 (*d*, $J = 12.8$, 1 H); 4.42 (*dd*, $J = 13.7$, 8.2, 1 H); 3.95 (br. *d*, $J = 13.7$, 1 H); 3.77 (*dd*, $J = 14.1$, 5.4, 1 H); 3.62 (br. *d*, $J = 13.7$, 1 H); 3.51 (br. *d*, $J = 10.9$, 1 H); 3.35 (overlap with the signal of the H_2O in DMSO, 1 H); 3.07 (*t*, $J = 12.4$, 1 H); 3.03 (*s*, 3 H). ^{13}C-NMR (150 MHz, (D_6)DMSO): 156.8; 133.8; 130.8; 130.7; 129.4; 128.3; 127.3; 127.0; 126.8; 116.0; 73.4; 63.7; 63.0; 56.5; 47.1; 29.4. HR-ESI-MS: 312.1948 ([M – Br]$^+$, $C_{20}H_{26}NO_2^+$; calc. 312.1958).

*[*N*(R),3*S*]-2-Allyl-1,2,3,4-tetrahydro-3-(hydroxymethyl)-2-methylisoquinolinium Bromide* (= *[*N*(R),3*S*]-1,2,3,4-Tetrahydro-3-(hydroxymethyl)-2-methyl-2-prop-2-en-1-ylisoquinolinium Bromide*; [*N*(*R*)]-**2g**). Yield 43%. Pale yellow liquid. $[\alpha]_D^{25} = -5.0$ ($c = 0.50$, MeOH). IR (KBr): 3429, 2976, 1629, 1457, 1054, 756. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.37 (*t*, $J = 7.5$, 1 H); 7.23–7.28 (*m*, 2 H); 7.15 (*d*, $J = 7.5$, 1 H); 6.15–6.19 (*m*, 1 H); 5.98 (*d*, $J = 16.8$, 1 H); 5.77 (*d*, $J = 10.2$, 1 H); 5.27 (br. *s*, 1 H); 4.88 (*d*, $J = 15.2$, 1 H); 4.81 (*dd*, $J = 12.9$, 6.4, 1 H); 4.71 (*dd*, $J = 12.9$, 8.3, 1 H); 4.52 (*d*, $J = 15.2$, 1 H); 4.39 (br. *d*, $J = 13.5$, 1 H); 4.08–4.13 (*m*, 1 H); 4.03 (br. *d*, $J = 13.5$, 1 H); 3.40 (*dd*, $J = 18.3$, 11.0, 1 H); 3.25 (*s*, 3 H); 3.19 (*dd*, $J = 18.3$, 4.6, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 130.5; 129.9; 129.0; 128.7; 127.6; 127.3; 125.9; 124.6; 67.7; 65.9; 62.8; 59.3; 44.0; 27.6. HR-ESI-MS: 218.1531 ([M – Br]$^+$, $C_{14}H_{20}NO^+$; calc. 218.1539).

*X-Ray Analysis of the 1:1 Complex of [*N*(R)]*-**2g** *and (*S*)-binol* [12]. Slow evaporation of a soln. of the complex in EtOH gave a single crystal suitable for X-ray analysis (0.44 × 0.40 × 0.25 mm; colorless). $C_{34}H_{34}BrNO_3$ (584.53): monoclinic $P2_1$; $a = 11.148(4)$, $b = 9.995(4)$, $c = 13.628(3)$ Å, $\beta = 107.93(3)^\circ$, $V = 1444.7(9)$ Å^3; $Z = 2$, $D_{calc} = 1.344$ Mg/m^3. Intensities were measured on a *Enraf-Nonius-CAD4*

diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 1.57 - 25.50$, $\mu = 1.46$ mm^{-1}) at 289 K. Of the total 3339 reflections, 3257 were independent, and 2525 were observed. $R = 0.0403$, $R_w = 0.1082$.

*[*N*(*S*),3*S*]-2-Allyl-1,2,3,4-tetrahydro-3-(hydroxymethyl)-2-methylisoquinolinium Bromide* (= *[*N*(*S*),3*S*]-1,2,3,4-Tetrahydro-3-(hydroxymethyl)-2-methyl-2-prop-2-en-1-ylisoquinolinium Bromide*; [*N*(*S*)]-**2g**). Yield 35%. Primrose yellow liquid. $[\alpha]_D^{25} = +3.0$ ($c = 0.45$, MeOH). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.35 – 7.38 (*m*, 1 H); 7.26 – 7.31 (*m*, 2 H); 7.06 (*d*, *J* = 7.6, 1 H); 5.93 – 5.99 (*m*, 1 H); 5.68 (*d*, *J* = 9.9, 1 H); 5.53 (*d*, *J* = 16.7, 1 H); 4.68 (*dd*, *J* = 13.3, 6.8, 1 H); 4.57 (*d*, *J* = 15.3, 1 H); 4.41 (*d*, *J* = 15.3, 1 H); 4.36 – 4.39 (*m*, 1 H); 4.28 – 4.32 (*m*, 1 H); 4.14 – 4.19 (*m*, 1 H); 3.75 (*dd*, *J* = 13.3, 7.4, 1 H); 3.56 (*s*, 3 H); 3.32 – 3.37 (*m*, 1 H); 3.24 – 3.26 (*m*, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 130.4; 130.0; 129.3; 129.1; 127.8; 126.8; 125.7; 124.1; 71.0; 62.3; 59.7; 58.1; 49.8; 27.5. HR-ESI-MS: 218.1551 ([*M* – Br]$^+$, $C_{14}H_{20}NO^+$; calc. 218.1539).

*[*N*(*R*),3*S*]-1,2,3,4-Tetrahydro-3-(hydroxymethyl)-2-methyl-2-(3-methylbut-2-en-1-yl)isoquinolinium Bromide* ([*N*(*R*)]-**2h**). Yield 40%. Colorless solid. M.p. 149 – 150°. $[\alpha]_D^{25} = -30$ ($c = 0.45$, MeOH). IR (KBr): 3421, 2976, 2928, 1638, 1454, 1082, 766. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.31 (*t*, *J* = 7.3, 1 H); 7.22 – 7.26 (*m*, 2 H); 7.14 (*d*, *J* = 7.6, 1 H); 5.51 (*t*, *J* = 7.7, 1 H); 5.25 – 5.29 (*m*, 1 H); 4.70 (*d*, *J* = 15.5, 1 H); 4.59 – 4.67 (*m*, 2 H); 4.51 (*d*, *J* = 15.5, 1 H); 4.40 (br. *d*, *J* = 12.3, 1 H); 4.08 – 4.13 (*m*, 1 H); 4.04 – 4.07 (*m*, 1 H); 3.42 (*dd*, *J* = 18.5, 10.5, 1 H); 3.28 (*s*, 3 H); 3.19 (*dd*, *J* = 18.5, 4.8, 1 H); 1.93 (*s*, 3 H); 1.89 (*s*, 3 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 149.2; 130.0; 128.9; 128.7; 127.5; 127.3; 126.1; 110.8; 66.8; 61.8; 59.4; 44.1; 27.6; 26.6; 19.6. HR-ESI-MS: 246.1850 ([*M* – Br]$^+$, $C_{16}H_{24}NO^+$; calc. 246.1852).

*X-Ray Analysis of the 1:1 Complex of [*N*(*R*)]-***2h*** and (*S*)-binol* [12]. Slow evaporation of a soln. of the complex in EtOH gave a single crystal suitable for X-ray analysis (0.42 × 0.31 × 0.18 mm; colorless). $C_{36}H_{35}BrNO_3$ (609.56): monoclinic $P2_1$; $a = 11.3972(5)$, $b = 10.1329(4)$, $c = 13.8151(5)$ Å, $\beta = 107.93(3)°$, $V = 1517.58(11)$ Å^3; $Z = 2$, $D_{calc} = 1.334$ Mg/m^3. Intensities were measured on a *Rigaku-Raxis-Rapid* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 3.09 - 27.48$, $\mu = 1.391$ mm^{-1}) at 153 K. Of the total 15042 reflections, 6319 were independent, and 4162 were observed. $R = 0.0465$, $R_w = 0.1810$.

*[*N*(*S*),3*S*]-1,2,3,4-Tetrahydro-3-(hydroxymethyl)-2-methyl-2-(3-methylbut-2-en-1-yl)isoquinolinium Bromide* ([*N*(*S*)]-**2h**). Yield 33%. Pale yellow liquid. $[\alpha]_D^{25} = +60$ ($c = 0.22$, MeOH). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.35 (*t*, *J* = 7.3, 1 H); 7.26 – 7.28 (*m*, 2 H); 7.06 (*d*, *J* = 7.7, 1 H); 5.26 – 5.37 (*m*, 2 H); 4.63 (*d*, *J* = 15.2, 1 H); 4.51 (*dd*, *J* = 13.2, 7.4, 1 H); 4.45 (br. *d*, *J* = 13.2, 1 H); 4.38 – 4.41 (*m*, 1 H); 4.36 (*d*, *J* = 15.2, 1 H); 4.14 (br. *d*, *J* = 12.0, 1 H); 3.83 (*dd*, *J* = 13.2, 9.7, 1 H); 3.55 (*s*, 3 H); 3.44 (*dd*, *J* = 18.3, 11.2, 1 H); 3.26 (br. *d*, *J* = 17.6, 1 H). ^{13}C-NMR (150 MHz, $CDCl_3$): 148.7; 130.4; 129.3; 129.0; 127.7; 126.9; 126.1; 110.0; 70.6; 62.3; 59.7; 53.7; 49.9; 27.6; 26.5; 18.7. HR-ESI-MS: 246.1844 ([*M* – Br]$^+$, $C_{16}H_{24}NO^+$; calc. 246.1852).

*[*N*(*S*),3*S*]-2-(Anthracen-9-ylmethyl)-1,2,3,4-tetrahydro-3-(hydroxymethyl)-2-methylisoquinolinium Chloride* ([*N*(*S*)]-**2i**). Yield 40%. Yellow solid. M.p. 127 – 128°. $[\alpha]_D^{25} = -113$ ($c = 0.26$, MeOH). IR (KBr): 3413, 3038, 2927, 1626, 1454, 1083, 761. ^{1}H-NMR (600 MHz, CD_3OD): 8.75 (*s*, 1 H); 8.61 (*d*, *J* = 8.7, 1 H); 8.15 (*t*, *J* = 8.7, 2 H); 7.72 (*t*, *J* = 7.5, 1 H); 7.50 – 7.59 (*m*, 5 H); 7.34 – 7.38 (*m*, 2 H); 7.15 (*d*, *J* = 7.5, 1 H); 6.34 (*d*, *J* = 14.6, 1 H); 5.30 (*d*, *J* = 14.6, 1 H); 4.67 (*d*, *J* = 12.7, 1 H); 4.40 (*d*, *J* = 16.0, 1 H); 4.34 (*d*, *J* = 16.0, 1 H); 4.25 (br. *d*, *J* = 13.5, 1 H); 4.03 – 4.11 (*m*, 2 H); 3.39 (br. *d*, *J* = 15.8, 1 H); 2.78 (*s*, 3 H). ^{13}C-NMR (150 MHz, CD_3OD): 133.9; 132.8; 131.9; 131.7; 131.6; 131.4; 129.7; 129.5; 129.1; 128.9; 128.0; 127.5; 127.4; 127.3; 126.8; 125.2; 125.1; 123.8; 123.2; 118.5; 72.1; 64.1; 59.3; 50.0; 26.9. HR-ESI-MS: 368.2017 ([*M* – Cl]$^+$, $C_{14}H_{22}NO^+$; calc. 368.2009).

*[*N*(*R*),3*S*]-2-(Anthracen-9-ylmethyl)-1,2,3,4-tetrahydro-3-(hydroxymethyl)-2-methylisoquinolinium Chloride* ([*N*(*R*)]-**2i**). Yield 33%. Yellow crystals (MeOH). M.p. 122 – 123°. $[\alpha]_D^{25} = -91$ ($c = 0.14$, MeOH). ^{1}H-NMR (600 MHz, CD_3OD): 8.57 (*s*, 1 H); 8.35 (*d*, *J* = 8.9, 1 H); 8.02 – 8.05 (*m*, 2 H); 7.60 – 7.63 (*m*, 1 H); 7.55 – 7.58 (*m*, 2 H); 7.46 – 7.52 (*m*, 3 H); 7.18 – 7.21 (*m*, 1 H); 7.00 – 7.04 (*m*, 2 H); 5.91 (*d*, *J* = 14.7, 1 H); 4.70 (*d*, *J* = 14.7, 1 H); 4.59 (*d*, *J* = 14.3, 1 H); 4.29 (br. *d*, *J* = 15.7, 1 H); 4.09 – 4.17 (*m*, 2 H); 3.95 (*d*, *J* = 12.7, 1 H); 3.87 – 3.92 (*m*, 1 H); 3.32 (*d*, *J* = 15.7, 1 H); 2.62 (*s*, 3 H). ^{13}C-NMR (150 MHz, CD_3OD): 133.6; 132.4; 131.9; 131.5; 131.4; 131.1; 129.6; 129.5; 129.1; 128.8; 128.0; 127.4; 127.3; 127.1; 126.7; 125.2; 125.1; 123.7; 123.0; 118.2; 71.9; 64.1; 59.1; 49.6; 26.8. HR-ESI-MS: 368.2022 ([*M* – Cl]$^+$, $C_{14}H_{22}NO^+$; calc. 368.2009).

*X-Ray Analysis of [*N*(*R*)]-***2i*** [12]. Slow evaporation of a soln. of [*N*(*R*)]-**2i** in MeOH gave a single crystal suitable for X-ray analysis (0.52 × 0.41 × 0.36 mm; yellow). $C_{26}H_{28}ClNO_2$ (421.94): Orthorhombic

$P2_12_12_1$; $a = 10.6986(3)$, $b = 15.9588(5)$, $c = 25.0076(6)$ Å, $\beta = 90°$, $V = 4269.7(2)$ Å^3; $Z = 8$, $D_{calc} = 1.313$ Mg/m^3. Intensities were measured on a *Rigaku-Raxis-Rapid* diffractometer, with MoK_α radiation (λ 0.71073, $\theta = 3.03 - 27.48$, $\mu = 1.46$ mm^{-1}) at 153 K. Of the total 39571 reflections, 9780 were independent, and 6119 were observed. $R = 0.0387$, $R_w = 0.1240$.

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