Fragmentation Reactions of Quaternized γ-Amino Alcohols − Diastereoselective Synthesis of Highly Functionalized Oxetanes and Unsaturated Aldehydes and Ketones with a (*Z*)-C−C Double Bond

Detlef Mölm, Ulrich Flörke, and Nikolaus Risch*

Fachbereich Chemie und Chemietechnik, Universität − GH Paderborn,
Warburger Strasse 100, D-33098 Paderborn, Germany
Fax: (internat.) + 49(0)5251/603245
E-mail: nr@chemie.uni-paderborn.de

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Quaternized γ-amino alcohols **5** derived from ternary iminium salts **2** are stereospecifically converted into both unsaturated aldehydes/ketones **6** with a (*Z*)-C−C double bond in a Grob-type fragmentation and highly functionalized oxetanes **7** by intramolecular substitution.

Typical methods used for the preparation of the synthetically very useful unsaturated carbonyl compounds include the base-induced fragmentation of monotosylated 1,3-diols[1][2][3][4][5][6], flash thermolysis of γ-hydroxyammonium compounds[7] and the selective C−C bond cleavage of quaternized β-amino aldehydes and β-amino ketones[8]. In most cases, the generated C−C double bond is an *exo*-methylene group. Only a few examples are known in which fragmentation reactions lead specifically to unsaturated compounds with either (*E*)- or (*Z*)-C−C double bonds[9][10][11].

We now wish to report a method for obtaining not only aldehydes and ketones **6** with a (*Z*)-C−C double bond by a Grob-type fragmentation but also highly functionalized oxetanes by the intramolecular substitution of readily available quaternized γ-amino alcohols **5**.

Functionalized oxetanes have attracted much interest, since they can undergo preparatively valuable ring-opening reactions[12][13][14][15][16].

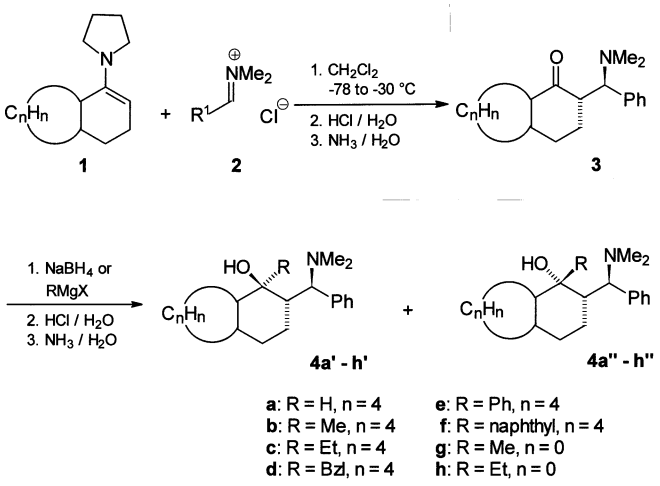
Results and Discussion

The efficient C−C bond formation of enamines **1** with preformed ternary iminium salts **2** is the basis of our synthetic strategy. This type of Mannich reaction is easy to perform and guarantees good yields, an excellent *anti* diastereoselectivity and a great diversity of β-amino ketones **3**[17]. This high diastereoselectivity is essential for the ensuing fragmentation and intramolecular substitution reaction, respectively.

The reduction of **3** was carried out with $NaBH_4$ and yielded the amino alcohols **4** (R = H)[18][19]. The addition of Grignard reagents gave **4** (R = Me, Et, Bzl, Ph and naphthyl)[20][21][22]. The diastereoselectivities of these reactions are shown in Table 1.

The mixture of isomers of **4b** was separated chromatographically into the diastereoisomers **4b′** and **4b′′**. The configuration of **4b′′** was determined by a single-crystal X-ray structure analysis (Figure 1). Using these data we assigned the relative configuration of **4′** and **4′′** to all entries **a**−**h**[20][21][22] (Table 1).

Scheme 1



The excellent diastereoselectivities for formation of the tertiary amino alcohols **4d**−**h** are remarkable. The subsequent quaternization of **4** to the ammonium iodides **5** by refluxing with methyl iodide transforms the amino group into a suitable leaving group which is necessary for the reactions that follow[8].

In the course of our previous research on bond cleavage reactions of 1-azaadamantane derivatives, quaternized β-amino ketones and β-amino aldehydes, NaH in THF was found to be very effective for inducing fragmentation reactions[8][23]. Under similar reaction conditions we observed, that the isomers **5′** and **5′′** react in a different manner. **5′** was converted exclusively to the expected compounds **6** by C−C bond cleavage. However, **5′′** was transformed to the

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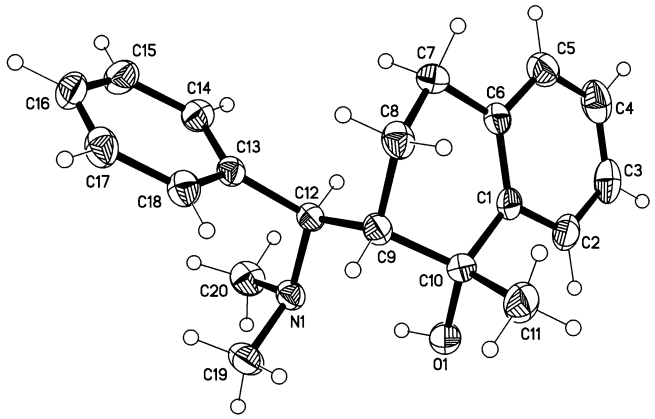
Table 1. Ratios of the isomers **4′** and **4′′** and the results of the reaction of the ammonium iodides **5′** and **5′′** with NaH/THF

Entry	*n*	R	Amino alcohols **4** [%]	ratio **4′/4′′** (**5′/5′′**)	(*Z*)-Alkene **6** [%]	Oxetane **7** [%]	Ratio **6/7**
a	4	H	86	> 99:< 1	72	—[c]	> 99:< 1
b	4	Me	95	> 39:61	89[a]	71[d]	> 40:60[e]
c	4	Et	90	> 27:73	—[b]	76	> 25:75[e]
d	4	Bzl	86	< 1:> 99	—[c]	87	< 1:>99[e]
e	4	Ph	84	< 1:> 99	—[b]	59	> 28:72[e]
f	4	naphthyl	54	< 1:> 99	—[b]	62	> 17:83[e]
g	0	Me	81	< 1:> 99	81	—[c]	> 99:< 1
h	0	Bzl	79	< 1:> 99	92	—[c]	> 99:< 1

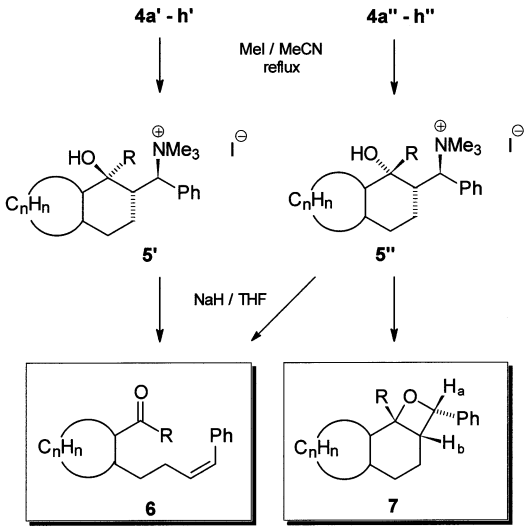
[a] Isolated yield from **5b′** (R = Me). – [b] Only detected in the crude product, not isolated. – [c] Not found. – [d] Isolated yield from **5b′′** (R = Me). – [e] Ratio detected by ^{1}H NMR of the mixture of isomers of **5**.

Figure 1. Molecular structure of **4b′′**



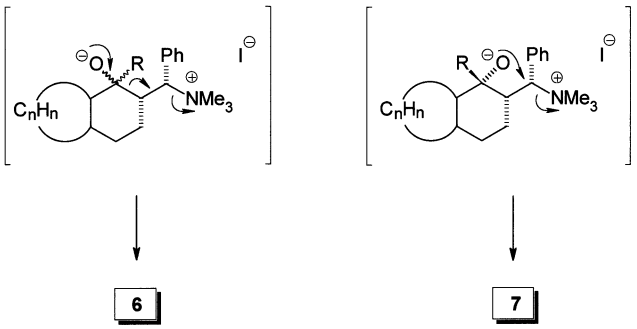
oxetane **7** by intramolecular substitution and to **6** in a competitive reaction[24][25][26] (Schemes 2 and 3, Table 1).

Scheme 2



As mentioned before, the *anti* configuration in **3** is responsible for the observed stereochemistry in the products **6** and **7**. The base-mediated, selective Grob-type C–C bond cleavage of **5′** proceeds stereospecifically to the aldehydes and ketones **6** with a (*Z*)-C–C double bond. The ^{1}H-NMR

Scheme 3. Fragmentation of the anions of **5′** and **5′′** and intramolecular substitution of the anion **5′′**



data show characteristic coupling constants of J = 11.6 Hz for the olefinic protons[27][28]. We did not investigate the kinetic parameters of this reaction but the mild reaction conditions (room temp.) and the stereoselectivity are in accordance with a concerted bond cleavage[29].

On the other hand, intramolecular substitution of **5′′** (R = Me, Et, Bzl, Ph, Naphthyl) leads to the highly functionalized oxetanes **7**. The ^{1}H-NMR coupling constants of H_a and H_b are in accordance with those of oxetanes with *cis* configuration (Scheme 2)[30][31].

In conclusion, Grob-type transformation of quaternized γ-amino alcohols **5′** with NaH in THF gives access to unsaturated aldehydes and ketones **6** with a (*Z*)-C–C double bond. In a competitive reaction, an intramolecular substitution leads to highly functionalized oxetanes **7**. In comparison with other methods (e.g. fragmentation of tosylates[11], Paterno-Büchi reaction[12]), our procedure considerably extends the synthetic potential of these types of reaction since the aminoalkylation of carbonyl compounds gives an easy access to numerous of Mannich bases.

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Experimental Section

General: IR: Nicolet 510 P FT IR spectrometer. – GC/MS: Finnigan MAT Magnum System 240. – ^{1}H and ^{13}C NMR: Bruker ARX 200 (200 MHz and 50 MHz, for ^{1}H and $^{13\,C,}$ respectively). Chemical shifts are reported relative to TMS as an internal refer-

ence. $CDCl_3$ was used as solvent. Signals of minor diastereoisomers are markeded with *. − Elemental analyses: Perkin-Elmer 240. − Column chromatography: Merck silica gel 60 (70−230 mesh).

X-ray Crystallographic Study of **4b**′′: Crystal data: $C_{20}H_{25}NO$, M_r = 295.41, monoclinic, space group $P2_1/n$, a = 7.864(2), b = 10.370(4), c = 20.524(6) Å, β = 98.03(2)°, V = 1657.3(9) Å^3, Z = 4, D_c = 1.184 Mg/m^3. Data collection: AXS Bruker P4 diffractometer, Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, crystal size 0.35 × 0.48 × 0.53 mm, T = 190(2) K, ω-scan, 2.2 ≤ Θ ≤ 27.5°, −10 ≤ h ≤ 10, −2 ≤ k ≤ 13, 0 ≤ l ≤ 26, 4651 reflections collected, 3826 independent reflections (R_{int} = 0.016), μ = 0.072 mm^{-1}. Structure solution by direct methods, full-matrix least-squares refinement based on 3826 F^2 and 204 parameters, hydrogen atoms located from difference map and refined with "riding model", all but hydrogen atoms refined anisotropically, max(Δ/σ) < 0.001, Goof = 1.010, $R1$ [$I > 2\sigma(I)$] = 0.043, $wR2$ (all data) = 0.111, min/max height in final ΔF map −0.191/0.296 e/Å^3. Programs used: SHELXTL V5[32]. Crystallographic data (excluding structure factors) for **4b**′′ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101984. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for the Preparation of β-Amino Ketones **3**[17]: To a solution of 1-cyclohept-1-enylpyrrolidine (n = 0) and 1-(8,9-dihydro-7*H*-benzocyclohepten-5-yl)pyrrolidine, respectively (10 mmol) in CH_2Cl_2 (20 ml) at −80°C benzylidenedimethylammonium chloride (1.83 g, 11 mmol) was added under argon in one portion. After stirring for an additional 3 h at this temperature, the reaction was quenched with HCl solution (20 ml 37% HCl/H_2O = 1:1) and then the mixture was extracted with Et_2O (4 × 50 ml). While stirring the acidic phase, NH_3 solution (100 ml, 25% NH_3/H_2O = 1:4) was added and then the aqueous solution was extracted with CH_2Cl_2 (4 × 50 ml). The combined organic phases were dried with Na_2SO_4 and the solvent was then removed in vacuo (room temp.) leading to the Mannich bases **3**.

(1′RS,2SR)-2-[Dimethylamino(phenyl)methyl]cyclohexanone (**3**, n = 0): Yield: 2.24 g (94%), m.p. 55°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.43−1.85 (m, 5 H), 2.01−2.09 (m, 1 H), 2.07 [s, 6 H, $N(CH_3)_2$], 2.31−2.46 (m, 1 H, 2.61−2.76 (m, 1 H), 3.11−3.18 (m, COCH), 4.05 (d, J = 11.5 Hz, CHN), 7.16−7.21 (m, 2 H, aromatic H), 7.29−7.44 (m, 3 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.51, 28.60, 29.92, 39.90 (t, CH_2), 41.37 [q, $N(CH_3)_2$], 52.67 (d, CO*C*H), 68.85 (d, CHN), 128.00, 128.43, 129.89 (d, $C_{ar.}H$), 134.01 (s, $C_{ar.}$), 213.66 (s, CO). − IR (KBr): $\tilde{\nu}$ = 3031 cm^{-1}, 2944, 2857, 2830, 2787, 1705, 1495, 1456, 1306, 1198, 1111, 1034, 860. − $C_{15}H_{21}NO$ (231.33): calcd. C 77.88, H 9.15, N6.05; found C 77.99, H 8.95, N 6.40.

(1′RS,2SR)-2-[Dimethylamino(phenyl)methyl]-3,4-dihydro-2H-naphthalen-1-one (**3**, n = 4): Yield: 2.33 g (83%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71−1.96 (m, 1 H, $ArCH_2CHH$), 2.10−2.27 (m, 1 H, $ArCH_2CHH$), 2.23 (s, 6 H, $N(CH_3)_2$), 2.74−3.07 (m, 2 H, $ArCH_2$), 3.24−3.34 (m, 1 H, COCH), 4.08 (d, J = 7.8 Hz, 1 H, CHN), 7.17−7.48 (m, 8 H, aromatic H), 8.02−8.06 (m, 1 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.41 (t, $C_{ar.}CH_2CH_2$), 27.37 (t, $C_{ar.}CH_2$), 43.13 [q, $N(CH_3)_2$], 49.51 (d, CO*C*H), 68.78 (s, CHN), 126.93, 127.56, 128.10, 128.22, 129.04, 130.02 ($C_{ar.}H$), 133.27 ($C_{ar.}$), 133.30 ($C_{ar.}H$), 137.12, 143.50 (s, $C_{ar.}$), 199.23 (CO). − IR (Film): $\tilde{\nu}$ = 3027 cm^{-1}, 2942, 2863, 2824, 2780, 1686, 1642, 1599, 1491, 1455, 1319, 1301, 1291, 1223, 1204, 1038, 1024, 928. − $C_{19}H_{21}NO$ (279.38): calcd. C 81.68, H 7.58, N 5.01; found C 81.44, H 7.29, N 5.21.

General Procedure for the Preparation of the Secondary γ-Amino Alcohol **4a**′: To a solution of $NaBH_4$ (0.189 g, 10 mmol) in ethanol (150 ml) at 0°C a solution of the Mannich base (5 mmol) in ethanol (25 ml) was added. The mixture was stirred at room temp. for an additional 15 h. Then the reaction was quenched with HCl solution (50 ml 37% HCl/H_2O = 1:2). Ethanol was removed in vacuo carefully and the remaining aqueous solution was extracted with Et_2O (3 × 50 ml). To the acidic solution was added NH_3 solution (100 ml, 25% NH_3/H_2O = 1:2) and then the basified solution was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic phases were dried with Na_2SO_4. The solvent was then removed in vacuo leading to the amino alcohol **4a**′ (R = H).

(1RS,1′RS,2SR)-[Dimethylamino(phenyl)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol (**4a**′): Yield: 1.21 g (86%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24−1.34 (m, 1 H, $ArCH_2CHH$), 1.50−1.60 (m, 1 H, $ArCH_2CHH$), 2.28 (s, 6 H, $N(CH_3)_2$), 2.39−2.89 (m, 3 H, $ArCH_2$, *C*HCHN), 3.74 (d, J = 11.1 Hz, CHN), 4.96 (d, J = 9.2 Hz, *C*HOH), 7.08−7.47 (m, 8 H, aromatic H), 7.76 (d, J = 7.5 Hz, 1 H, aromatic H), 8.14 (br. s, 1 H, OH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.44 (t, $C_{ar.}CH_2CH_2$), 29.43 (t, $C_{ar.}CH_2CH_2$), 40.33 (d, C*H*CHN), 41.24 [br. q, $N(CH_3)_2$], 76.34, 76.43 (d, CHN, COH), 126.46, 126.64, 127.06, 127.24, 128.10, 128.30, 128.47, 129.03, 130.26 (d, $C_{ar.}H$), 133.10, 135.96, 140.28 (s, $C_{ar.}$). − IR (film): $\tilde{\nu}$ = 2940 cm^{-1}, 2915, 2890, 1452, 1489, 1047, 754, 743. − $C_{19}H_{23}NO$ (281.39): calcd. C 81.10, H 8.24, N 4.98; found C 81.02, H 8.02, N 5.12.

General Procedure for the Preparation of the Amino Alcohols with Grignard Reagents: Grignard reagents were prepared according to literature procedures. A solution of the Mannich base (5 mmol) in Et_2O (20 ml) was added dropwise to the prepared Grignard reagent (10 mmol). The mixture was stirred at room temp. for additional 15 h and then quenched with HCl solution (30 ml, 37% HCl/H_2O = 1:2). The organic phase was removed and the aqueous solution extracted with Et_2O (3 × 20 ml). Then NH_3 solution was added (50 ml, 25% NH_3/H_2O = 1:1) and the basified solution extracted with CH_2Cl_2. The combined organic phases were dried with Na_2SO_4 and the solvent removed in vacuo. In the case of **4b** the diastereoisomers were separated by column chromatography on silica gel leading to **4b**′ as minor and **4b**′′ as major diastereoisomer with CH_2Cl_2/MeOH (98:2).

(1RS,1′RS,2SR)-2-[Dimethylamino(phenyl)methyl]-1-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (**4b**′′): Yield: 0.5 g (23%), m.p. 114°C . − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40−1.50 (m, 1 H, $ArCH_2CHH$), 1.60 (s, 3 H, CCH_3), 2.10 (s, 6 H, $NCH_3)_2$), 2.00−2.23 (m, 1 H, $ArCH_2CHH$), 2.47−2.53 (m, 2 H, $ArCH_2CH_2$), 2.61−2.71 (m, 1 H, CCH), 3.75 (d, J = 11.7 Hz, CHN), 7.03−7.42 (m, 8 H, aromatic H), 7.87−7.92 (m, 1 H, aromatic H), 9.50 (br. s, 1 H, OH). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.09 (t, $C_{ar.}CH_2CH_2$), 24.31 (t, $C_{ar.}CH_2CH_2$), 35.50 (q, C*C*H$_3$), 40.39 (d, C*C*H), 40.45 (br. q, $N(CH_3)_2$), 69.84 (d, CHN), 74.41 (s, COH), 126.55, 127.23, 128.02, 128.21, 128.37, 128.48 (d, $C_{ar.}H$), 132.66, 134.31, 145.68 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 2989, 2793, 1475, 1470, 1451, 1148, 1002, 965, 856, 641. − GC MS (80 eV); *m/z* (%): 296 [M$^+$ + 1] (2), 134 (100), 91 (10). − $C_{20}H_{25}NO$ (295.43): calcd. C 81.31, H 8.53, N 4.74; found C 81.11, H 8.70, N 4.81.

(1RS,1′SR,2RS)-2-[Dimethylamino(phenyl)methyl]-1-methyl-1,2,3,4-tetrahydronaphthalen-1-ol (**4b**′): Yield: 0.30 g (14%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.40−1.50 (m, 1 H, $ArCH_2CHH$), 1.65 (s, 3 H, CCH_3), 2.25 [s, 6 H, $N(CH_3)_2$], 2.00−2.23 (m, 1 H,

ArCH$_2$CH*H*), 2.60−2.91 (m, 3 H, ArC*H*$_2$CH$_2$C*H*), 3.90 (d, *J* = 11.8 Hz, CHN), 7.03−7.50 (m, 8 H, aromatic H), 7.75−7.78 (m, 1 H, aromatic H). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 24.56 (t, C$_{ar.}$CH$_2$*C*H$_2$), 28.05 (q, C*C*H$_3$), 29.42 (t, C$_{ar.}$*C*H$_2$CH$_2$),41.34 (br. q, N(CH$_3$)$_2$), 42.63 (d, C*C*H), 71.73 (d, CHN), 74.76 (s, COH), 126.20, 126.26, 126.75, 126.94, 128.17, 128.53, 128.61 (d, C$_{ar.}$H), 133.06, 134.74, 145.51 (s, C$_{ar.}$). − GC-MS (80 eV); *m/z* (%): 295 [M$^+$] (2), 134 (100), 91 (9). − C$_{20}$H$_{25}$NO (295): calcd. C 81.31, H 8.53, N 4.74; found C 81.22, H 8.41, N 4.77.

2-[Dimethylamino(phenyl)methyl]-1-ethyl-1,2,3,4-tetrahydronaphthalen-1-ol (**4c**): Yield: 1.39 g (90%). − Major diastereoisomer: *(1RS,1′RS,2SR)* (**4c**′′) (only distinct signals are quoted): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.06 (t, *J* = 7.3 Hz, 3 H, CH$_2$C*H*$_3$), 2.18 [s, 3 H, N(CH$_3$)$_2$], 3.95 (d, *J* = 11.7 Hz, CHN). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 8.28 (q, CH$_2$*C*H$_3$), 23.09 (t, C$_{ar.}$CH$_2$*C*H$_2$), 27.31 (t, C$_{ar.}$*C*H$_2$CH$_2$), 29.27 (t, *C*H$_2$CH$_3$), 31.26 (d, C*C*H), 40.56 [br. q, N(CH$_3$)$_2$], 71.11 (d, CHN), 75.43 (s, COH), 124.81−129.69 (d, C$_{ar.}$H), 132.66, 134.28, 142.82 (s, C$_{ar.}$). − GC MS (80 eV); *m/z* (%): 309 [M$^+$] (6), 134 (100).

Minor diastereoisomer: *(1RS,1′SR,2RS)* (**4c**′) (only distinct signals are quoted): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.42 (q, CH$_2$*C*H$_3$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.50 (t, C$_{ar.}$CH$_2$*C*H$_2$), 23.61 (t, C$_{ar.}$*C*H$_2$CH$_2$), 35.59 (CCH), 37.83 (t, *C*H$_2$CH$_3$), 40.56 [br. q, N(CH$_3$)$_2$], 69.07 (d, CHN), 75.55 (s, COH), 124.81−129.69 (d, C$_{ar.}$H), 132.28 , 133.98, 145.04 (s, C$_{ar.}$). − GC MS (80 eV); *m/z* (%): 309 [M$^+$] (7), 134 (100). − IR (film): ṽ = 3059 cm^{-1}, 2945, 2874, 2834, 2791, 1466, 1453, 1440, 991, 734. − C$_{21}$H$_{27}$NO (309.45): calcd. C 81.51, H 8.79, N 4.53; found C 81.72, H 8.50, N 4.38.

(1RS,1′RS,2SR)-1-Benzyl-2-dimethylamino(phenyl)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol (**4d**′′): Yield: 1.60 g (86%), m.p. 161°C. − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.30−1.41 (m, 1 H, ArCH$_2$C*H*H), 1.85 (s, 6 H, N(CH$_3$)$_2$), 1.99−2.18 (m, 1 H, ArCH$_2$CH*H*), 2.44−2.50 (m, 3 H, CC*H*, ArC*H*$_2$CH$_2$), 2.95, 3.07 (AB, *J* = 13.9 Hz, 2 H, PhCH$_2$), 3.72 (d, *J* = 11.7 Hz, CHN), 6.92−7.45 (m, 13 H, aromatic H), 7.76−7.81 (m, 1 H, aromatic H), 9.32 (s, 1 H, OH). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 22.60 (t, C$_{ar.}$CH$_2$*C*H$_2$), 24.49 (t, C$_{ar.}$*C*H$_2$CH$_2$), 35.01 (d, C*C*H), 51.74 (t, PhCH$_2$), 69.29 (d, CHN), 76.86 (s, COH), 126.52, 126.61, 126.78, 128.01, 128.17, 128.21, 128.37, 131.37 (d, C$_{ar.}$H), 132.50, 134.49, 139.09, 145.60 (s, C$_{ar.}$). − IR (KBr): ṽ = 3420 cm^{-1}, 3059, 3025, 2868, 2792, 1493, 1452. − GC MS (80 eV); *m/z* (%): 371 [M$^+$] (2), 280 (28), 134 (100), 91 (74). − C$_{26}$H$_{29}$NO (371.52): calcd. C 83.99, H 7.87, N 3.77; found C 83.70, H 7.65, N 3.98.

(1RS,1′RS,2SR)-2-[Dimethylamino(phenyl)methyl]-1-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (**4e**′′): Yield: 1.50 g (84%), m.p. 75°C. − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.17−1.37 (m, 2 H, ArCH$_2$C*H*$_2$), 2.16 [s, 6 H, N(CH$_3$)$_2$], 2.43−2.56 (m, 2 H, ArCH$_2$), 2.73−2.82 (m, 1 H, CCH), 3.87 (d, *J* = 11.6 Hz,1 H, CHN), 7.07−7.38 (m, 13 H, aromatic H), 7.72−7.77 (m, 1 H, aromatic H), 10.1 (br. s, 1 H, OH). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 22.20 (t, C$_{ar.}$CH$_2$*C*H$_2$), 24.47 (t, C$_{ar.}$*C*H$_2$), 40.86 [br. q, N(CH$_3$)$_2$], 41.15 (d, C*C*H), 70.20 (d, CHN), 79.55 (s, COH), 126.89, 126.96, 127.18, 127.65, 127.95, 128.01, 128.11, 128.23, 128.87, 129.54, 130.27 (d, C$_{ar.}$H), 132.61, 136.17, 142.78, 151.65 (s, C$_{ar.}$). − IR (KBr): ṽ = 3431 cm^{-1}, 3056, 2943, 2831, 2789, 1499, 1452, 1444, 1049, 1005, 755, 501. − C$_{25}$H$_{27}$NO (357.49): calcd. C 84.00, H 7.61, N 3.92; found C 83.66, H 7.51, N 3.80.

(1RS,1′RS,2SR)-2-[Dimethylamino(phenyl)methyl]-3,4-dihydro-2H-[1,1′]binaphthalyl-1-ol (**4f**′′): Yield: 1.10 g (54%), m.p. 96°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.16−1.25 (m, 2 H, ArCH$_2$C*H*H), 1.34−1.46 (m, 2 H, ArCH$_2$CH*H*), 2.27 [s, 3 H, N(CH$_3$)$_2$], 2.45−2.48 (m, 2 H, ArCH$_2$), 3.54−3.60 (m, 1 H, CCH), 3.98 (d, *J* = 11.6 Hz, 1 H, CHN), 6.44 (d, *J* = 7.4 Hz, 1 H, aromatic H), 7.11−7.98 (m, 14 H, aromatic H), 9.50 (d, *J* = 8.7 Hz, 1 H, aromatic H), 9.81 (br. s, 1 H, OH). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 22.07 (t, C$_{ar.}$CH$_2$*C*H$_2$), 23.45 (t, C$_{ar.}$*C*H$_2$CH$_2$), 37.41 (d, *C*CH), 40.64 [br. q, N(CH$_3$)$_2$], 70.19 (d, CHN), 81.74 (s, 1 H, COH), 124.01, 124.71, 124.78, 126.36, 126.63, 127.30, 127.35, 127.47, 127.54, 128.15, 128.46, 129.01, 129.16 (d, C$_{ar.}$H), 131.32, 132.13, 135.00, 135.82, 143.39, 144.06 (s, C$_{ar.}$). − IR (KBr): ṽ = 3435 cm^{-1}, 3054, 2945, 2832, 1482, 1452, 1154, 1002, 800, 708. − C$_{29}$H$_{29}$NO (407.55): calcd. C 85.47, H 7.17, N 3.44; found C 85.35, H 6.98, N 3.52.

(1′RS,2SR)-2-[Dimethylamino(phenyl)methyl]-1-methylcyclohexanol (**4g**′′): Yield: 1.00 g (81%). − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.06−1.30 (m, 2 H, CH$_2$), 1.37 (s, 3 H, CCH$_3$), 1.40−1.84 (m, 6 H, 3 CH$_2$), 2.13 [s, 6 H, N(CH$_3$)$_2$], 2.24−2.28 (m, 1 H, CCH), 4.09 (d, *J* = 11.8 Hz, 2 H, CHN), 7.11−7.13 (m, 2 H, aromatic H), 7.27−7.38 (m, 3 H, aromatic H), 8.9 (br. s, 1 H, OH). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 19.41 (t, CH$_2$), 24.00 (t, CH$_2$), 25.59 (t, CH$_2$), 28.16 (q, C*C*H$_3$), 36.59 (t, CH$_2$), 40.34 [br. q, N(CH$_3$)$_2$], 40.59 (d, C*C*H), 68.95 (d, CHN), 72.45 (s, COH), 127,21, 127.63, 129.22 (d, C$_{ar.}$H), 132.22 (s, C$_{ar.}$). − IR (Film): ṽ = 3086 cm^{-1}, 2985, 2862, 2834, 2791, 1457, 1452, 1010, 706. − GC MS (80eV); *m/z* (%): 247 [M$^+$] (100), 134 (54), 43 (36). − C$_{16}$H$_{25}$NO (247.38): calcd. C 77.62, H 10.19, N 5.66; found C 77.55, H 10.32, N 5.78.

(1′RS,2SR)-1-Benzyl-2-dimethylamino(phenyl)methyl]-cyclohexanol (**4h**′′): Yield 1.28 g (79%), m.p. 116°C. − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.05−1.85 (m, 8 H, 4 CH$_2$), 2.00 [s, 6 H, N(CH$_3$)$_2$], 2.13−2.17 (m, 1 H, CC*H*CHN), 2.93, 3.06 (AB, *J* = 13.6 Hz, 2 H, ArCH$_2$), 4.11 (d, *J* = 11.9 Hz, CHN), 7.00−7.15 (m, 2 H, aromatic H), 7.22−7.36 (m, 6 H, aromatic H), 7.46−7.49 (m, 2 H, aromatic H), 9.10 (br. s, 1 H, OH). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 19.49, 23.84, 25.19, 36.57 (t, CH$_2$), 36.57 (d, C*C*HCHN), 39.87 [br. q, N(CH$_3$)$_2$], 44.78 (t, ArCH$_2$), 68.77 (d, CHN), 74.39 (s, COH), 125.69, 127.19, 127.58, 127.66, 130.70 (d, C$_{ar.}$H), 132.06, 138.63 (s, C$_{ar.}$). − IR (KBr): ṽ = 3400 cm^{-1}, 3083, 3059, 3025, 3940, 2852, 2833, 2791, 1453, 703. − GC MS (80 eV); *m/z* (%): 247 [M$^+$] (100), 134 (53), 91 (10), 43 (37). − C$_{22}$H$_{29}$NO (323.47): calcd.C 81.69, H 9.04, N 4.33; found C 81.76, H 8.50, N 4.60.

General Procedure for the Quaternization of the γ-Amino Alcohols **4 to 5**: A mixture of the amino alcohol **4** (4 mmol) and a five-fold amount of methyl iodide (20 mmol) was dissolved in anhydrous acetonitrile (30 ml) and refluxed for 24 h. After the solvent had been removed in vacuo, the solid residue was dissolved in a small amount of CH$_2$Cl$_2$ (20 ml). Then petroleum ether (20 ml) was added and the precipitate was filtered off. After the removal of the solvent from the precipitate in vacuo, a quantitative yield of the product was obtained as a colorless powder.

(1RS,1′RS,2SR)-[Phenyl(trimethylammonio)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol Iodide (**5a**′): Yield: 1.59 g (94%), m.p. 121°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.26−1.57 (m, 1 H, ArCH$_2$C*H*$_2$), 2.26−2.32 (m, 1 H, ArC*H*H), 2.79−2.99 (m, 1 H, ArCH*H*), 3.35 [s, 9 H, N(CH$_3$)$_3$], 4.35−4.44 (m, 1 H, C*H*CHN), 5.12 (d, *J* = 7.6 Hz, 1 H, C*H*OH), 5.42 (s, 1 H, CHN), 6.97−7.48 (m, 9 H, aromatic H), 7.96 (br. s, 1 H, OH). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 27.14 (t, C$_{ar.}$CH$_2$*C*H$_2$), 29.55 (t, C$_{ar.}$*C*H$_2$CH$_2$), 43.26 (d, *C*HCHN), 54.09 [q, N(CH$_3$)$_3$], 69.91 (d, CHOH), 79.89 (d, CHN), 126.63, 127.57, 128.40, 129.22, 129.71, 130.23, 130.87 (d, C$_{ar.}$H), 132.74, 136.64, 138.43 (s, C$_{ar.}$). − IR (KBr): ṽ = 3375 cm^{-1},

2927, 1484, 1453, 1437, 1029, 951, 757, 745. − $C_{20}H_{25}INO$ (422.33): calcd. C 56.88, H 5.67, N 3.32; C 56.75, H 5.74, N 3.45.

(1RS,1′RS,2SR)-1-Methyl-2-[phenyl(trimethylammonio)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol Iodide (**5b′′**): Yield: 1.71 g (98%), m.p. 159°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.85 (s, 3 H, C*C*H$_3$), 2.41−2.79 (m, 4 H, ArCH$_2$CH$_2$), 3.14 (m, 1 H, C*H*CHN), 3.45 (s, 9 H, N(CH$_3$)$_3$), 4.99 (s, 1 H, C*H*N), 6.44−7.68 (m, 9 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.89 (t, $C_{ar.}$CH$_2$*C*H$_2$), 25.25 (t, $C_{ar.}$*C*H$_2$), 31.89 (q, C*C*H$_3$), 44.65 (d, *C*HCHN), 54.04 [q, N(CH$_3$)$_3$], 73.61 (d, CH*C*HN), 78.14 (s, COH), 125.50, 126.46, 127.28, 128.23, 129.97 (d, $C_{ar.}$H), 132.29, 135.84, 141.65 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3146 cm^{-1}, 2969, 1487, 1464, 781, 741. − $C_{21}H_{28}INO$ (437.36): calcd. C 57.67, H 6.45, N 3.20; found C 57.60, H 6.51, N 3.13.

(1RS,1′SR,2RS)-1-Methyl-2-[phenyl(trimethylammonio)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol Iodide (**5b′**): Yield: 1.71 g (99%), m.p. 161°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14 (s, 3 H, C*C*H$_3$), 2.41−2.79 (m, 4 H, ArCH$_2$CH$_2$), 3.19 [s, 9 H, N(CH$_3$)$_3$], 5.23 (s, 1 H, C*H*N), 6.44−7.68 (m, 9 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.26 (t, $C_{ar.}$CH$_2$*C*H$_2$), 26.82 (t, $C_{ar.}$*C*H$_2$), 34.50 (q, C*C*H$_3$), 44.65 (d, *C*HCHN), 49.78 [q, N(CH$_3$)$_3$], 73.61 (d, CH*C*HN), 78.14 (s, COH), 125.50, 126.46, 127.28, 128.23, 129.97 (d, $C_{ar.}$H), 132.29, 135.84, 141.65 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3150 cm^{-1}, 2969, 1491, 1464, 776, 741. − $C_{21}H_{28}INO$ (437.36): calcd. C 57.67, H 6.45, N 3.20; found C 57.56, H 6.47, N 3.32.

1-Ethyl-2-[phenyl(trimethylammonio)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol Iodide (**5c**): Yield: 1.72 g (95%), m.p. 119°C. − (only distinct signals are quoted): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.36 [s, je 9 H, N(CH$_3$)$_3$], 4.67* (s, 1 H, CHN), 4.93 (s, 1 H, CHN). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.52 (q, CH$_2$*C*H$_3$), 8.94* (q, CH$_2$*C*H$_3$), 21.85, 23.04, 24.57, 28.78, 31.57, 34.46 (t,CH$_2$), 42.90 (d, C*H*CHN), 45.51* (d, C*H*CHN), 53.37* [q, N(CH$_3$)$_3$], 53.95 [q, N(CH$_3$)$_3$], 75.95 (s, COH), 76.94* (s, COH). − IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1}, 2960, 1459, 148, 160, 710. − $C_{22}H_{30}INO$ (451.39): calcd. C 58.54, H 6.70, N 3.10; found C 58.39, H 6.87, N 3.16.

(1RS,1′RS,2SR)-1-Benzyl-2-[phenyl(trimethylammonio)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol Iodide (**5d′′**): Yield: 2.01 g (98%), m.p. 189°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71−1.82 (m, 1 H, ArCH$_2$C*H*H), 2.36−2.64 (m, 3 H, ArCH$_2$CH*H*), 3.12−3.30 [m, 11 H, ArC*H*$_2$CH$_2$, CC*H*$_2$Ph, N(C*H*$_3$)$_3$], 4.02 (s, 1 H, CCH), 4.91 (s, 1 H, CHN), 6.32 (d, *J* = 7.1 Hz, 2 H, aromatic H), 6.88−7.49 (m, 12 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.11 (t, $C_{ar.}$CH$_2$*C*H$_2$), 23.59 (t, $C_{ar.}$*C*H$_2$CH$_2$), 42.22 (d, C*C*H), 47.85 (t, C*C*H$_2$Ph), 53.94 [q, N(CH$_3$)$_3$], 75.61 (d, CHN), 79.15 (s, COH), 125.64,125.94, 127.18, 127.32, 128.04, 128.33, 128.72, 129.24, 129.75, 131.42 (d, $C_{ar.}$H), 132.15, 135.91, 136.38, 139.44 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3422 cm^{-1}, 3068, 3021, 2950, 1614, 1485, 1467, 760, 705. − $C_{27}H_{32}INO$ (513.43): calcd. C 63.16, H 6.28, N 2.73; found C 63.33, H 6.41, N 2.99.

(1RS,1′RS,2SR)-1-Phenyl-2-[phenyl(trimethylammonio)methyl]-1,2,3,4-tetrahydronaphthalen-1-ol Iodide (**5e′′**): Yield: 1.94 g (97%), m.p. 156°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58−1.66 (m, 1 H, ArCH$_2$C*H*H), 2.43−2.49 (m, 1 H, ArCH$_2$CH*H*), 2.91 [s, 9 H, N(CH$_3$)$_3$], 3.16−3.61 (m, 3 H, ArCH$_2$, CCH), 4.38 (s, 1 H, CHN), 6.70−6.72 (m, 1 H, aromatic H), 6.92−7.67 (m, 14 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.12 (t, $C_{ar.}$CH$_2$*C*H$_2$), 29.60 (t, $C_{ar.}$*C*H$_2$), 46.03 (d, C*C*H), 52.79 [q, N(CH$_3$)$_3$], 77.64 (s, COH), 80.06 (d, CHN), 126.45, 126.79, 127.42, 127.57, 127.63, 127.99, 128.20, 128.30, 128.37, 129.10, 129.81, 129.88 (d,$C_{ar.}$H), 131.66, 135.38 (s, $C_{ar.}$), 135.92 (d, $C_{ar.}$H), 141.32, 145.85 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3415 cm^{-1}, 3050, 2906, 1487, 1447, 759, 700. − $C_{26}H_{30}INO$ (499.41): calcd. C 62.53, H 6.06, N 2.80; found C 62.41, H 6.30, N 2.94.

(1RS,1′RS,2SR)-2-[Phenyl(trimethylammonio)methyl]-3,4-dihydro-2H-[1,1′]binaphthyl-1-ol Iodide (**5f′′**): Yield: 2.03 g (95%,), m.p. 185°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.78−1.83 (m, 1 H, ArCH$_2$C*H*H), 2.56 [s, 9 H, N(CH$_3$)$_3$], 2.65−2.69 (m, 1 H, ArCH$_2$CH*H*), 3.08−3.57 (m, 3 H, ArCH$_2$, CCH), 4.26 (d, 1 H, CHN), 6.71−6.73 (m, 1 H, ArH), 6.84−6.89 (m, 1 H, aromatic H), 7.10−7.18 (m, 2 H, aromatic H), 7.27−7.45 (m, 7 H, aromatic H), 7.67−8.89 (m, 4 H, aromatic H), 8.40−8.42 (m, 1 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.47 (t, $C_{ar.}$CH$_2$*C*H$_2$), 29.79 (t, $C_{ar.}$*C*H$_2$CH$_2$), 43.20 (d, C*C*H), 52.24 [q, N(CH$_3$)$_3$], 77.18 (s, COH), 81.51 (d, CHN), 124.11, 124.78, 125.56, 126.24, 127.24, 127.28, 127.97, 128.05, 128.34, 128.41, 128.64, 129.06, 129.13, 129.52, 129.73 (d, $C_{ar.}$H), 129.93, 131.62, 134.32, 134.66 (s, $C_{ar.}$), 135.44 (d, $C_{ar.}$H), 139.14, 141.28 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3420 cm^{-1}, 3050, 3900, 1556, 1489, 1050, 795. − $C_{30}H_{32}INO$ (535.46): calcd. C 67.29, H 6.02, N 2.62; found C 67.51, H 5.89, N 2.55.

(1′RS,2SR)-1-Methyl-2-[Phenyl(trimethylammonio)methyl]cyclohexanol Iodide (**5g′′**): Yield: 1.50 g (96%), m.p. 111°C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31−1.69 (m, 11 H, 4 CH$_2$, CCH$_3$), 1.91−1.96 (m, 1 H, CCH), 3.36 (s, 9 H, N(CH$_3$)$_3$), 5.10 (s, 1 H, CHN), 7.34−7.47 (m, 4 H, aromatic H), 7.73−7.75 (m, 1 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.17, 24.61, 27.48 (t, CH$_2$), 30.08 (q, C*C*H$_3$), 40.73 (t, CH$_2$), 43.94 (d, C*C*H), 53.17 [q, N(CH$_3$)$_3$], 72.32 (s, COH), 79.76 (d, CHN), 128.03, 128.51, 129.46, 129.80, 132.01 (d, $C_{ar.}$H), 135.20 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1}, 2930, 2857, 1485, 1452, 1461, 718, 705. − $C_{17}H_{28}INO$ (389.30): calcd. C 52.45, H 7.25, N 3.60; found C 52.30, H 7.45, N 3.50.

(1′RS,2SR)-1-Benzyl-2-[phenyl(trimethylammonio)methyl]cyclohexanol Iodide (**5h′′**): Yield 1.81 g (96%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04−2.22 (m, 8 H, 4 CH$_2$), 2.55−2.57 (m, 1 H, CCH), 3.04, 3.62 (AB, *J* = 13.0 Hz, 2 H, PhCH$_2$), 3.23 [s, 9 H, N(CH$_3$)$_3$], 5.40 (s, 1 H, CHN), 7.14−7.42 (m, 9 H, aromatic H), 7.90−7.99 (m, 1 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.02, 23.05, 27.31, 36.80, (t, CH$_2$), 42.08 (d, C*C*H), 44.99 (t, PhCH$_2$), 52.81 (q, N(CH$_3$)$_3$), 73.48 (s, COH), 78.68 (d, CHN), 126.36, 127.73, 127.87, 127.97, 128.37, 129.54, 129.72, 130.65, 131.20 (d, $C_{ar.}$H) 132.32, 136.62 (s, $C_{ar.}$). − IR (KBr): $\tilde{\nu}$ = 3404 cm^{-1}, 2935, 2860, 1494, 1487, 1454, 850, 701. − $C_{23}H_{32}INO$ (465.42): calcd. C 59.36, H 6.93, N 3.01; found C 59.20, H 6.80, N 3.26.

General Procedure for the Reactions of **5** *Leading to (Z)-Configurated Carbonyl Compounds* **6** *and/or Oxetanes* **7***:* Under argon, NaH (50 mg, 2 mmol) was added to THF (30 ml) in a 100-ml two-necked, round-bottom flask. Then the quaternized amino alcohol **5** (1 mmol) was added in one portion. After stirring for an additional 15 h at room temp., the mixture was quenched with H_2O (10 ml). THF was removed under reduced pressure and the remaining aqueous phase was acidified with HCl solution (20 ml, 37% HCl/H_2O = 1:2). The acidic aqueous phase was extracted with CH_2Cl_2 (4 × 25 ml) and the combined organic phases were dried with Na_2SO_4. The solvent was then removed in vacuo and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (98:2).

2-[(Z)-4-Phenylbut-3-enyl]benzaldehyde (**6a**): Yield: 171 mg (72%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.69−2.81 (m, 2 H, CH$_2$C*H*$_2$=CH), 3.23−3.31 (m, 2 H, C*H*$_2$CH$_2$=CH), 5.75−5.86 (m, 1 H, C*H*=CHPh) , 6.56 (d, *J* = 11.6 Hz, 1 H, CH=C*H*Ph), 7.27−7.61 (m, 8 H, aromatic H), 7.87−7.91 (m, 1 H, aromatic H), 10.30 (s, 1 H, CHO). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.05

(t, CH_2CH_2=CH) 33.05 (t, CH_2CH_2=CH), 127.15−134.22 (d, 9 $C_{ar.}$H, CH=CHPh), 134.27, 137.84, 144.71 (s, $C_{ar.}$), 192.84 (d, CHO). − IR (film): $\tilde{\nu}$ = 3056 cm^{-1}, 3021, 2929, 2861, 2735, 1689, 1596, 1573, 1492, 1207, 1192, 758, 700. − GC MS (80 eV); *m/z* (%): 236 [M^+] (39), 128 (43), 105 (100), 91 (20), 77 (47). − $C_{17}H_{16}O$ (236.31): calcd. C 86.41, H 6.82; found C 86.50, H 6.75.

1-{2-[(Z)-4-Phenylbut-3-enyl]phenyl}ethanone (**6b**): Yield: 223 mg (89%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.58 (s, 3 H, CH_3), 2.62−2.73 (m, 2 H, CH_2CH=CHPh), 3.05−3.13 (m, 2 H, $ArCH_2$), 5.74−5.83 (m, 1 H, CH=CHPh), 6.48 (d, *J* = 11.7 Hz, 1 H, CH=CHPh), 7.24−7.48 (m, 8 H, aromatic H), 7.59−7.71 (m, 1 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.27 (q, CH_3), 30.90 (t, CH_2CH=CHPh), 34.43 (t, $C_{ar.}CH_2$), 126.48−132.44 (d, 9 $C_{ar.}$H, CH=CHPh), 137.99, 138.31, 142.15 (s, 2 $C_{ar.}$), 202.55 (s, CO). − IR (film): $\tilde{\nu}$ = 3057 cm^{-1}, 3021, 3008, 2926, 1685, 1599, 1446, 1249, 956. − GC MS (80 eV); *m/z* (%): 250 [M^+] (4), 207 (6), 145 (100), 131 (39), 117 (45), 43 (10). − $C_{18}H_{18}O$ (250.34): calcd. C 86.36, H 7.25; found C 86.45, H 7.16.

(Z)-8-Phenyloct-7-en-2-one (**6g**): Yield: 163 mg (81%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44−1.50 (m, 2 H, CH_2), 1.51−1.67 (m, 2 H, CH_2), 2.12 (s, CH_3), 2.34−2.43 (m, 4 H, 2 CH_2), 5.61−5.70 (m, 1 H, CH=CHPh), 6.42−6.46 (d, *J* = 11.6 Hz, 1 H, CH=CHPh), 7.21−7.37 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.19, 28.07, 29.17, 29.66 (t, 4 CH_2), 29.68 (q, CH_3), 43.26 (t, CH_2), 127.90, 129.94, 128.53, 129.00, 132.21 (d, $C_{ar.}$H, CH=CHPh), 137.45 (s, $C_{ar.}$H), 208.74 (s, CO). − IR (Film): $\tilde{\nu}$ = 3022 cm^{-1}, 3008, 2933, 2858, 1716, 1498, 1358, 768. − GC MS (80 eV); *m/z* (%): 202 [M^+] (32), 184 (100), 117 (78), 91 (20), 43 (76). − $C_{14}H_{18}O$ (202.29): calcd. C 83.13, H 8.97; found C 83.06, H 8.85.

1-(Z)-8-Diphenyloct-6-en-2-one (**6h**): Yield: 259 mg (92%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30−1.45 (m, 2 H, CH_2), 1.47−1.66 (m, 2 H, CH_2), 2.29−2.37 (m, 2 H, CH_2), 2.42−2.47 (m, 2 H, CH_2), 3.67 (s, 2 H, $COCH_2$Ph), 5.59−5.68 (m, 1 H, CH=CHPh), 6.42−6.46 (d, *J* = 11.6 Hz, 1 H, CH=CHPh), 7.19−3.38 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.09, 28.04, 29.09, 41.48, 49.97 (t, 5 CH_2), 126.86, 127.32, 128.48, 129.05, 129.07, 129.50, 129.74, 130.97, 132.78 (d, $C_{ar.}$H, $C_{ar.}$CH=CH), 134.15, 137.46 (s, 2 $C_{ar.}$), 208.08 (s, CO). − IR (Film): $\tilde{\nu}$ = 3059 cm^{-1}, 3026, 2932, 2858, 1712, 1598, 1494, 1453, 1355, 1030, 728. − GC MS (80 eV); *m/z* (%): 278 [M^+] (4), 259 (9), 186 (100), 168 (51), 117 (50), 105 (5), 91 (32). − $C_{20}H_{22}O$ (278.39): calcd. C 86.29, H 7.97; found C 86.20, H 8.09.

(2RS,2aRS,8bSR)-8b-Methyl-2-phenyl-2a,3,4,8b-tetrahydro-2H-1-oxacyclobuta[a]naphthalene (**7b**): Yield: 178 mg (71%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30−1.43 (m, 1 H, $ArCH_2$CHH), 1.61−1.70 (m, 1 H, $ArCH_2$CHH), 1.93 (s, 3 H, CH_3), 2.33−2.48 (m, 1 H, ArCHH), 2.53−2.66 (m, 1 H, ArCHH), 3.20−3.33 (m, 1 H, CCH), 6.06 (d, *J* = 7.6 Hz, 1 H, CHPh), 7.06−7.41 (m, 8 H, aromatic H), 7.52−7.56 (m, 1 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.32 (t, $C_{ar.}CH_2CH_2$), 27.88 (t, $C_{ar.}CH_2CH_2$), 30.09 (q, CH_3), 45.62 (d, CCH), 79.38 (d, OCHPh), 79.52 (s, CCH_3), 125.48, 125.81, 127.68, 128.26, 128.44 (d, $C_{ar.}$H). − $C_{18}H_{18}O$ (250.34): calcd. C 86.36, H 7.25; found C 86.51, H 6.98.

(2RS,2aRS,8bSR)-8b-Ethyl-2-phenyl-2a,3,4,8b-tetrahydro-2H-1-oxacyclobuta[a]naphthalene (**7c**): Yield: 151 mg (76%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.5 Hz, 1.24−1.42 (m, 1 H, $ArCH_2$CHH), 1.56−1.71 (m, 1 H, $ArCH_2$CHH), 2.11−2.25 (m, 1 H, ArCHH), 2.31−2.60 (m, 3 H, ArCHH), 3.29−3.42 (m, 1 H, OCHPh), 6.03 (d, *J* = 7.9 Hz, 1 H, OCHPh) 7.05−7.52 (m, 9 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 8.27 (q, CH_3), 23.44 (t, $ArCH_2CH_2$), 28.04 (t, $ArCH_2CH_2$), 35.96 (t, CH_2CH_3), 42.66 (d, CCH), 80.13 (d, OCHPh), 82.63 (s, CH_3CH_2C), 125.57, 126.00, 126.72, 127.27, 127.34, 127.96, 128.22, 128.44 (d, $C_{ar.}$H), 138.73, 139.76, 140.81 (s, $C_{ar.}$). − $C_{19}H_{20}O$ (264.36): calcd. C 86.33, H 7.63; found C 86.19, H 7.53.

(2RS,2aRS,8bSR)-8b-Benzyl-2-phenyl-2a,3,4,8b-tetrahydro-2H-1-oxacyclobuta[a]naphthalene (**7d**): Yield: 315 mg (87%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.06−1.31 (m, 1 H, $ArCH_2$CHH), 1.44−1.58 (m, 1 H, $ArCH_2$CHH), 1.73−1.89 ($ArCHHCH_2$), 2.29−2.40 ($ArCHHCH_2$), 3.19 (d, *J* = 13.3 Hz, 1 H, PhCHH), 3.39−3.49 (m, 1 H, CCH), 3.55 (d, *J* = 13.3 Hz, 1 H, PhCHH), 5.70 (d, *J* = 8.1 Hz, 1 H, PhCH), 6.96−7.44 (m, 13 H, aromatic H), 7.58−7.62 (m, 1 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.33 (t, $C_{ar.}CH_2CH_2$), 27.70 (t, $C_{ar.}CH_2CH_2$), 41.75 (d, CCH), 49.95 (t, $PhCH_2$), 80.21 (d, OCHPh), 82.20 (s, $PhCH_2C$), 125.81, 126.17, 126.70, 127.27, 127.42, 127.48, 127.70, 128.35, 128.45 (d, $C_{ar.}$H), 136.67, 138.67, 140.38, 140.60 (s, $C_{ar.}$). − $C_{24}H_{22}O$ (326.43): calcd. C 88.31, H 6.79; found C 88.55, H 6.91.

(2RS,2aRS,8bSR)-2,8b-Diphenyl-2a,3,4,8b-tetrahydro-2H-1-oxacyclobuta[a]naphthalene (**7e**): Yield: 184 mg (59%). − ^{1}H NMR (300 MHz, $CDCl_3$): 1.70−1.78 (m, 2 H, $ArCH_2CH_2$), 2.60−2.79 (m, 2 H, $ArCH_2$), 3.41−3.49 (m, 1 H, CCH), 6.07 (d, *J* = 7.4 Hz, 1 H, OCHPh), 7.13−7.56 (m, 14 H, aromatic H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.48 (t, $C_{ar.}CH_2CH_2$), 27.45 (t, $C_{ar.}CH_2CH_2$), 47.44 (d, CCH), 78.91 (d, CHPh), 82.28 (s, CPh), 125.03, 125.07, 125.12, 125.25, 126.65, 126.85, 127.46, 127.62, 127.77, 127.94, 128.16 (d, $C_{ar.}$H), 138.28, 139.38, 139.61, 147.04 (s, $C_{ar.}$). − $C_{23}H_{20}O$ (312.41): calcd. C 88.43, H 6.45; found C 88.60, H 6.33.

(2RS,2aRS,8bRS)-8b-Naphth-1-yl-2-phenyl-2a,3,4,8b-tetrahydro-2H-1-oxacyclobuta[a]naphthalene (**7f**): Yield: 225 mg (62%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.00−2.10 (m, 2 H, $ArCH_2CH_2$), 2.60−2.72 (m, 1 H, ArCHH), 2.92−3.08 (m, 1 H, ArCHH), 3.46−3.54 (m, 1 H, CCH), 5.95 (d, *J* = 7.2 Hz, 1 H, OCHPh), 6.56 (d, *J* = 7.6 Hz, 1 H, aromatic H), 6.85−6.97 (m, 1 H, aromatic H), 7.15−7.49 (m, 10 H, aromatic H), 7.62−7.70 (m, 1 H, aromatic H), 7.84−7.93 (m, 2 H, aromatic H), 8.38−8.42 (m, 1 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.18 (t, $C_{ar.}CH_2CH_2$), 27.53 (t, $C_{ar.}CH_2CH_2$), 45.84 (d, CCH), 78.63 (d, OCHPh), 82.92 (s, COCH), 124.00−140.00 ($C_{ar.}$, $C_{ar.}$H). − $C_{27}H_{22}O$ (362.47): calcd. C 89.47, H 6.12; found C 89.30, H 5.95.

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