# Monodeazacinchona Alkaloid Derivatives: Synthesis and Preliminary Applications as Phase-Transfer Catalysts[‡]

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Four analogues of cinchona alkaloids (**5**–**8**) lacking the quinoline nitrogen atom have been prepared. Quaternization afforded the phase-transfer catalysts **10a**, **10b**, **11a**, and **12d**. Other optically active catalyst salts were prepared from the cinchona alkaloids themselves (compounds **13**, **14**, **15**). The performances of these PT catalysts and of some others were compared in three test reactions. The deazacinchona derivatives exhibited selectivities similar to or sometimes even better than those of the natural product-derived compounds.



Cinchona alkaloids are of increasing interest as reagents,[1] ligands, and catalysts[2] [including phase-transfer catalysis[3] (PTC)] for enantioselective reactions. Conformational studies have been used to interpret the exceptional performance of these compounds.[4] For PTC applications, common interpretations focus mainly on the "binding pocket forming" and sandwiching interaction between the catalysts' large flat aromatic partial structures and the substrate, which are reinforced by polar effects. It is unknown whether the polarity of the quinoline nucleus contributes to this. Modification of the fundamental structure of these alkaloids might aid understanding of which features of the skeletons are essential for the PT catalytic action; our first results in this area were published recently.[5] In this context we now became interested in the synthesis of deazacinchona alkaloids, transformation of these into phase transfer catalysts, and comparison of their performance with that of other enantioselective PT catalysts.

## Deaza($N^{aryl}$)cinchona Alkaloids

Recent work by H. M. R. Hoffmann showed that quinine and quinidine can be degraded relatively easily[6] into the optically active 2-(hydroxymethyl)-5-vinylquinuclidine isomers **1** and **2**, and these have now become commercially available (Scheme 1).[7] Swern oxidation transformed these compounds into the aldehydes **3** and **4**, respectively. A mixture of epimers **3** and **4** was also prepared earlier by Uskokovic' et al. in the course of their cinchona alkaloid synthesis.[8] Organometallic couplings with 1-lithionaphthalene and compound **3** generated a mixture of diastereomers **5** (13% yield) and **6** (29%), which could be separated by chromatography. The purity of the isomers could be determined most easily by reference to the NMR signals of the vinylic protons on C(1′′), which gave rise to characteristic triplets of doublets centered 0.26 ppm apart at δ = 6.09 (**5**) and 5.83 ppm (**6**). In addition, comparison with the equivalently positioned C(10) hydrogen atoms in cinchonine and quinidine (conventional alkaloid numbering) permitted the assignments of absolute configurations: the chemical shift of the C(1′′)H signal of **6** was practically identical to those of its counterparts in the two natural alkaloids. This meant that **5** had to have (1*R*,2′*R*,4′*S*,5′*R*) stereochemistry and **6** (1*S*,2′*R*,4′*S*,5′*R*). This result was corroborated further by an X-ray structure determination of **6**[9] (see Figure 1). Thus, **6** was deaza($N^{aryl}$)cinchonine. It had a positive sign of optical rotation, just like quinidine and cinchonine. In contrast, compound **5** exhibited negative rotation. The formation of **6** as the major product was in line with preferential attack from the less hindered side of **3**. An analogous observation was made by the Uskokovic' group: they obtained the natural alkaloids as main products from the coupling of the **3/4** mixture with quinoline derivatives.[8]

When **4** was treated with lithionaphthalene analogously to the preparation of **5** and **6** from **3**, compounds **7** and **8** were obtained in 4.4 and 9% yields, respectively. Again, the chemical shifts of the C(1′′) protons were centered at δ = 5.83 (**7**) or 6.10 ppm (**8**), matching the shifts of the equivalently positioned protons in quinine and cinchonidine (δ ≈ 5.86 ppm) in the case of **7**. Thus, this product had to have the (1*R*,2′*S*,4′*S*,5′*R*) configuration, and so was monodeaza($N^{aryl}$)cinchonidine. It had a negative sign of optical rota-

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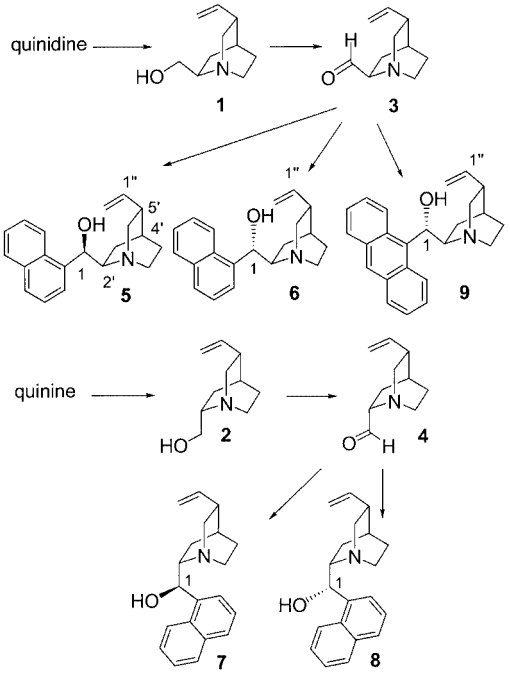



Scheme 1

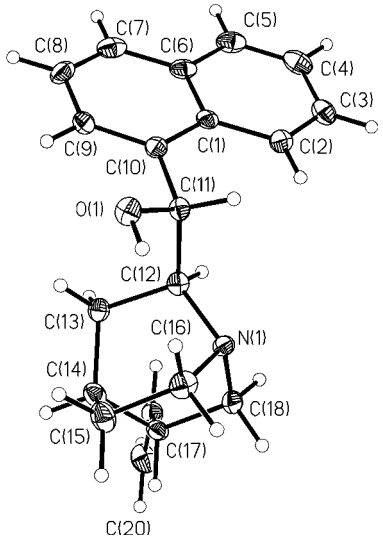


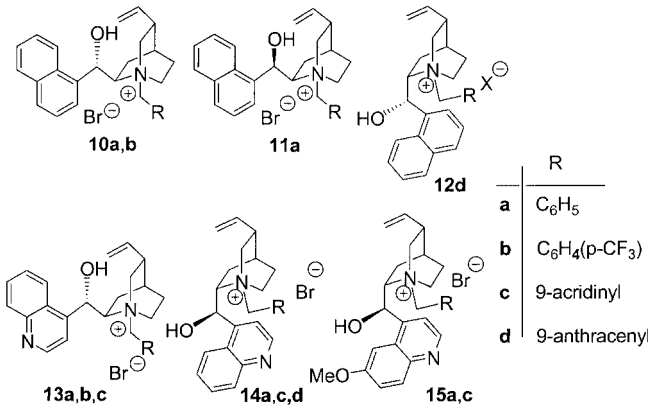

Figure 1. ORTEP drawing of (2*R*,4*S*,5*R*,1′*S*)-2-[1′-hydroxy-1′-(naphth-1-yl)methyl]-5-vinyl-1-azabicyclo[2.2.2]octane (**6**);[9,19,20] numbering not in accordance with chemical nomenclature

tion, as expected. The absolute configuration of **8** − with a positive rotation − then had to be (1*S*,2′*S*,4′*S*,5′*R*).

When **3** was treated with 9-lithioanthracene, a diastereomer mixture was again formed. This time, however, the overall yield was much lower (ca. 5%) and only the major isomer **9** could be isolated in pure form. Its cinchonine-like configuration (1*S*,2′*R*,4′*S*,5′*R*) was again assigned from the facts that the position of the C(1′′) proton signal matched that of cinchonine and that preferential front side attack of the organometallic reagent should produce **9**. Unexpectedly, however, this compound had a negative sign of optical rotation.

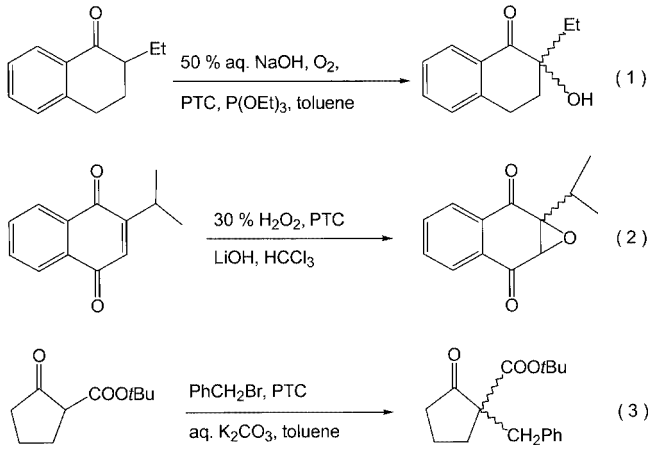
## Phase-Transfer Catalysts

The new compounds and other amines were quaternized to give PT catalysts. As only limited amounts of the deazacinchona alkaloids were available, only representative examples of new PT catalysts (and not all possibly desirable combinations of skeletons and residues) could be prepared. Structural formulae of the catalysts used are given in Scheme 2.




Scheme 2. Phase-transfer catalysts used

The substituents used most widely in previous work with the alkaloid-derived catalysts were *N*-benzyl and *N*-(*p*-trifluoromethyl)benzyl. These were used here too, giving compounds **10a**, **10b** and **11a**. Pioneering studies by Lygo et al.[3c] and by Corey et al.,[3i] later verified by others,[3] had established that catalysts bearing an *N*-(9-anthracenylmethyl) group were among the most enantioselective ones. Consequently, this residue was introduced into **8**, resulting in **12d**. The known derivatives of cinchonine (**13a** = "BCNC" and **13b**), cinchonidine (**14a** = "BCDC" and **14d**) and quinine (**15a** = "QUIBEC") were used for comparison.




Scheme 3

Table 1. Results of reactions (1), (2), and (3)

| Catalyst | Reaction (1) Yield (%) | *ee* (%) | Config. | Reaction (2) Yield (%) | *ee* (%) | Rotation | Reaction (3) Yield (%) | *ee* (%) | Config. |
|---|---|---|---|---|---|---|---|---|---|
| **10a** | 60 | 50 | (*S*) | 62 | 50 | (−) | 21 | 52 | (*S*) |
| **10b** | 71 | 43 | (*S*) | 58 | 66 | (−) | 56 | 37 | (*S*) |
| **11a** | | | | 71 | 32 | (+) | | | |
| **12d** | | | | 75 | 84 | (−) | | | |
| **13a** = BCNC | 98 | 59 | (*S*) | 80 | 42 | (−) | 97 | 46 | (*S*) |
| **13b** | 70 | 66 | (*S*) | 92 | 55 | (−) | 96 | 31 | (*S*) |
| **13c** | 58 | 9.9 | (*S*) | 65 | 52 | (−) | 48 | 39 | (*S*) |
| **14a** = BCDC | | | | 97 | 46 | (+) | 99 | 33 | (*R*) |
| **14c** | 53 | 9.6 | (*R*) | 55 | 71 | (+) | 72 | 16 | (*R*) |
| **14d** | | | | 97 | 74 | (+) | 59 | 35 | (*R*) |
| **15a** = QUIBEC | | | | 69 | 39 | (+) | 99 | 6.9 | (*R*) |
| **15c** | 70 | 7.7 | (*R*) | 41 | 76 | (+) | 36 | 30 | (*R*) |

In addition, the three natural alkaloids were also quaternized with 9-(bromomethyl)acridine as a more polar analogue of the anthracenyl group. This afforded compounds **13c**, **14c** and **15c**.

## Test Reactions

The catalysts in Scheme 2 were evaluated in the three preliminary test reactions shown in Scheme 3: (1) peroxidative hydroxylation of 2-ethyl-1-tetralone, (2) alkaline hydrogen peroxide epoxidation of 2-isopropyl-1,4-naphthoquinone, and (3) benzylation of 2-(*tert*-butoxycarbonyl)cyclopentanone.

All experiments were performed under standardized conditions in order to compare the various enantioselectivities; no attempts at optimization by variation of solvent, temperature, etc. were made. Table 1 gives our results.

Reaction (1) was introduced into PTC practice by Shioiri et al.[11] The initially formed hydroperoxide is reduced in situ by triethyl phosphite. This conversion has repeatedly been used to test potential enantioselective catalysts by us[5,12] and by others.[13] Shioiri's original *ee* of 72% (achieved with catalyst **13b**) has never been surpassed. Results with the present catalysts are given in Table 1. Again, the *ee* value obtained with **13b** was the best in our hands, under conditions somewhat different from Shioiri's. Although our new deaza alkaloid derivatives **10a** and **10b** performed noticeably less well than **13a** and **13b** [50 and 43% *ee* compared to 59 and 66%], they were far better than many other chiral catalysts.[20]

The enantioselective epoxidation of naphthoquinones under PTC was first performed by Wynberg et al.[14] and later improved by Shioiri and co-workers.[15] For reaction (2) specifically, *ee* values of 31% (with QUIBEC, **15a**[14]) and 69% [with *N*-(1-methylnaphthyl)quinidinium chloride[15]] were observed.[16] In this reaction, several of our new catalysts performed better than the derivatives of natural cinchona alkaloids (Table 1). Thus, the deazacinchonine derivatives **10a** and **10b** gave higher *ee* values (50 and 66%) than the related compounds **13a** (= BCNC) and **13b** (42 and 55% *ee*), while **12d** gave the best *ee* of all catalysts. This compound had a 9-anthracenylmethyl residue and did not have an alkaloid-derived analogue. The configuration of the epoxide formed with catalyst type **12** was the opposite of that generated with the "pseudoenantiomeric" catalyst type **11**, as was to be expected. It can furthermore be seen that the 9-acridinylmethyl group in compounds **13c**, **14c**, and **15c** (which are all derivatives of the natural alkaloids) gave rise to high enantiomer ratios of up to 76%, similar to the effects resulting from the anthracenylmethyl residue in **14d** (cf. also refs.[3c,3i]).

The new epimers **10a** and **11a** permitted the influence of the stereochemistry of the 1-hydroxy group on enantioselection to be investigated. This cannot easily be done in the natural products series, as the *epi* compounds are not readily available. Compounds **10a** and **11a** produced opposite configurations, although to different extents (50 vs. 32% *ee*). Similarly, the reversed hydroxy group configurations in the cinchonidinium compound **14d** and the deaza derivative **12d** gave rise to products with opposite configurations.

The PTC alkylation reaction (3) was introduced originally by Manabe,[17] with *ee* values of a maximum of 50% being obtained when a very unusual, special phosphonium salt catalyst was applied. Our comparisons with various catalysts of type **13**, **14**, and **15** yielded enantiomeric excesses of between 7% (**15a** = QUIBEC) and 46% (**13a** = BCNC) (Table 1). The deaza analogues of **13a** and **13b**, compounds **10a** and **10b**, were both somewhat more selective agents. With compounds **10** and **13**, substitution of more polar *p*-(trifluoromethyl)benzyl for benzyl as *N*-substituent was not advantageous. This result is contrary to findings with other types of reactions.

It may be mentioned in passing that simple quinuclidinium salts prepared by quaternization of **1** and **2**[5] gave very low *ee* values in these reactions, whereas lupininium salts[10] performed somewhat better, with *ee* values of up to 41%.[20]

## Conclusions

Although this investigation was of limited scope, some conclusions can be drawn, particularly in the context of published facts including our previous results.

(1) The enantioselectivities exhibited by PT catalysts are fairly sensitive to the type of reaction. Catalysts may interchange their efficacy rankings in different conversions.

(2) Exchange of the quinoline residue for a naphthalene group in such cinchona-related catalysts seems to have some effect on the achievable asymmetric induction. In two cases higher enantiomeric excesses were found with these less polar side arms, while in the third case the optical induction was lower. If, however, no large aromatic group was present on the side arm, the enantioselective action of the catalyst was very low.

(3) The presence of bulky 9-anthracenylmethyl groups on the quinuclidine nitrogen atom of the catalysts increased the *ee* values in this study, as in the literature.[3] A similar effect was observed with the more polar 9-acridinylmethyl group in most cases.

(4) The hydroxy group configuration at C(1) of the catalysts had a determining influence on product configuration.

## Experimental Section

**General:** X-ray measurement: Nonius Kappa CCD; programs used: Siemens SHELXTL plus/SHELXL-97.[9,18,19] NMR spectra in $CDCl_3$ with TMS as internal standard; AC 250-P (Bruker: $^1H$: 250 MHz; $^{13}C$: 62.89 MHz) or DRX 500 (Bruker: $^1H$: 500 MHz; $^{13}C$:125.78 MHz). Polarimetry: Jasco DIP-360. IR: Genesis FT Instrument (Mattson). HPLC determination of enantiomer ratios: apparatus from Therma Separation Products, pump P 4000, detector UV 6000 LP; chiral columns Chirasep DNBPG from Merck A.G. [(*R*)-*N*-(3,5-dinitrobenzoylphenyl)glycine on aminopropyl-silica gel] or Chiralcel OD from Daicel Chemical Ind. Ltd. (cellulose carbamate on silica gel). MS: VG AutoSpec from Fisons Instruments. Melting points: Büchi apparatus (Dr. Tottoli). Boiling points of kugelrohr distillations refer to air bath temperatures.

**(2*R*,4*S*,5*R*)-5-Vinyl-1-azabicyclo[2.2.2]octane-2-carbaldehyde (3):** DMSO (13.2 g, 169 mmol) in dry $CH_2Cl_2$ (19.0 mL) was cooled to −45 °C, and oxalyl chloride (3.36 g, 26.3 mmol) in $CH_2Cl_2$ (36.0 mL) was added slowly whilst stirring, over 50 min. After a further 30 min at −45 °C, (2*R*,4*S*,5*R*)-2-(hydroxymethyl)-5-vinylquinuclidine[4,5] (**1**, 8.0 g, 48.3 mmol) in dry $CH_2Cl_2$ (80.0 mL) was added dropwise over 1.0 h at −45 °C. The mixture was stirred for an additional 1 h at this temperature, and then treated with triethylamine (43.2 mL). Warming to room temp. was followed by stirring for 30 min. $H_2O$ (80.0 mL) was added, the mixture was kept overnight, and the phases were separated. The organic layer was washed thrice with 30.0 mL of $H_2O$, dried with $Na_2SO_4$, and filtered. Solvents were removed, and the residue was distilled in a kugelrohr apparatus. Yield: 5.74 g (72.0%); b.p. 140 °C/0.26 Torr. IR (KBr): $\tilde{\nu}$ = 3230, 3075, 2933, 2869, 2802, 1729, 1685, 1637, 1560, 1456, 1375, 1203, 1054, 993, 910, 823, 757 $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): δ = 1.40−1.84 (m, 4 H, 2 × 7-H, 2 × 3-H), 2.12−3.48 (m, 7 H, 2-H, 4-H, 5-H, 2 × 6-H, 2 × 8-H), 4.93−5.11 (m, 2 H, 2 × 2′-H), 5.66−5.97 (m, 1 H, 1′-H), 9.81 (d, $^3J$ = 4.40 Hz, 1 H, CHO) ppm. $^{13}C$ NMR (62 MHz, $CDCl_3$): δ = 23.9, 27.1 (C-3, C-7), 27.5 (C-4), 39.9 (C-5), 46.5, 49.0 (C-8, C-6), 57.3 (C-2), 114.6 (C-2′), 140.3 (C-1′), 203.6 (CHO). The sensitive compound must be used immediately.

**(2*S*,4*S*,5*R*)-5-Vinyl-1-azabicyclo[2.2.2]octane-2-carbaldehyde (4):** This compound was prepared from **2**[4,5] analogously to the preparation of **3** from **1**. Yield: 75.0%, b.p. 80 °C/0.01 Torr. IR (KBr): $\tilde{\nu}$ = 3264, 3073, 2946, 2871, 2812, 1725, 1637, 1456, 1421, 1317, 1089, 1070, 910, 823, 757 $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): δ = 1.43−1.84 (m, 4 H, 2 × 3-H, 2 × 7-H), 2.23−3.34 (m, 7 H, 2-H, 2 × 6-H, 2 × 8-H, 5-H, 4-H), 4.94−5.12 (m, 2 H, 2 × 2′-H), 5.71−5.96 (m, 1 H, 1′-H), 9.81 (d, $^3J$ = 4.16 Hz, 1 H, CHO) ppm. $^{13}C$ NMR (62 MHz, $CDCl_3$): δ = 20.9, 27.2 (C-3, C-7), 30.9, 39.6 (C-5, C-4), 48.65, 50.8 (C-6, C-8), 65.0 (C-2), 114.7 (C-2′), 139.9 (C-1′), 203.4 (CHO) ppm. The sensitive compound must be used immediately.

**(1*R*,2*R*,4*S*,5*R*)-(1-Naphthyl)(5-vinyl-1-azabicyclo[2.2.2]oct-2-yl)-methanol (5) and (1*S*,2*R*,4*S*,5*R*)-(1-Naphthyl)(5-vinyl-1-azabicyclo-[2.2.2]oct-2-yl)methanol (6):** Abs. ether (230 mL) and a solution of butyllithium in hexane (1.62 M, 11.0 mL, 16.8 mmol) were combined and cooled to −68 °C. 1-Bromonaphthalene (4.17 g, 17.4 mmol) in abs. THF (115 mL) was added slowly at this temperature. Stirring was then continued for another 30 min, and **3** (2.87 g, 17.4 mmol) in abs. ether (115 mL) was slowly added dropwise. The reaction was allowed to proceed for 1.5 h at −68 °C, and was then quenched by the addition of $H_2O$ (107 mL) at −68 °C and allowed to warm to room temp. overnight. The phases were separated, and the aqueous one was extracted twice with 70 mL of ether. The combined organic solutions were dried ($Na_2SO_4$), and the solvent was removed. The residue was chromatographed on silica gel with ethyl acetate/triethylamine (9:1) to give the diastereomerically pure products **6** ($R_f$ = 0.21) and **5** ($R_f$ = 0.15), which were crystallized from EtOH.

**Compound 6:** Yield: 1.46 g (28.6%), m.p. 212−217 °C. $[\alpha]_D^{23}$ = +122.95 (*c* = 0.40, MeOH). IR (KBr): $\tilde{\nu}$ = 3388, 3067, 3050, 2923, 2862, 1637, 1590, 1445, 1345, 1320, 1093, 795 $cm^{-1}$. $^1H$ NMR (500 MHz, [$D_6$]DMSO): δ = 1.34−1.66 (m, 4 H, 2 × 3-H, 2 × 7-H), 1.89−1.93 (m, 1 H, 4-H), 2.14−2.16 (m, 1 H, 8-H), 2.51−2.65 (m, 3 H, 5-H, 6-H, 8-H), 2.98−3.03 (m, 2 H, 2-H, 6-H), 5.03−5.08 (m, 2 H, 2 × 2′′-H), 5.30 (br. s, 1 H, OH), 5.41 (d, $^3J$ = 4.70 Hz, 1 H, 1′-H), 6.09 (ddd, *J* = 17.6, 10.5 and 7.6, 1 H, 1′′-H), 7.43−7.52 (m, 3 H, 3-$H^{Naph}$, 6-$H^{Naph}$, 7-$H^{Naph}$), 7.57 (d, $^3J$ = 7.02 Hz, 1 H, 4-$H^{Naph}$), 7.78 (d, $^3J$ = 8.09 Hz, 1 H, 5-$H^{Naph}$), 7.90 (d, $^3J$ = 8.52 Hz, 1 H, 8-$H^{Naph}$), 8.17 (d, $^3J$ = 8.36 Hz, 1 H, 2-$H^{Naph}$) ppm. $^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 21.15, 26.2 (C-3, C-7), 28.3, 39.9 (C-5, C-4), 49.4, 49.9 (C-6, C-8), 60.0 (C-2), 72.3 (C-1′), 114.6 (C-1′′),123.0, 123.5, 125.3, 125.4, 126.2, 128.0, 128.9, 130.3, 133.7, 138.8, 140.4 (10 $C^{Naph}$, C-2′′) ppm. $C_{20}H_{23}NO$ (293.4): calcd. C 81.87, H 7.90, N 4.77; found C 81.66, H 7.73, N 4.75.

**Compound 5:** Yield: 677 mg (13.2%), $[\alpha]_D^{23}$ = −47.2 (*c* = 0.42, MeOH). IR (KBr): $\tilde{\nu}$ = 3412, 3065, 2945, 2867, 1633, 1454, 1378, 1261, 1110, 1023, 788 $cm^{-1}$. $^1H$ NMR (500 MHz, [$D_6$]DMSO): δ = 1.62−1.70 (m, 4 H, 2 × 3-H, 2 × 7-H), 2.17 (br. s, 1 H, OH), 2.35−2.40 (m, 2 H, 8-H, 5-H), 2.82−2.84 (m, 1 H, 5-H), 2.85−2.87 (m, 1 H, 8-H), 3.05−3.07 (m, 1 H, 6-H), 3.33−3.31 (m, 2 H, 2-H,

6-H), 4.90−4.98 (m, 2 H, 2 × 2′′-H), 5.26 (d, $^3J$ = 6.63 Hz, 1 H, 1-H), 5.83 (ddd, $J$ = 17.4, 10.3, 7.6, 1 H, 1′′-H), 7.43−7.52 (m, 3 H, 3-H$^{Naph3}$, 6-H$^{Naph}$, 7-H$^{Naph}$), 7.57 (d, $^3J$ = 6.77 Hz, 1 H, 4-H$^{Naph}$), 7.78 (d, $^3J$ = 8.10 Hz, 1 H, 5-H$^{Naph}$), 7.91 (d, $^3J$ = 8.90 Hz, 8-H$^{Naph}$), 8.21 (d, $^3J$ = 8.30 Hz, 1 H, 2-H$^{Naph}$) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO): δ = 23.35, 26.4 (C-3, C-7), 27.85, 48.4 (C-5, C-4), 49.2, 52.3 (C-6, C-8), 60.5 (C-2), 71.8 (C-1′), 114.1 (C-2′′),123.6, 123.9, 125.0, 125.2, 125.5, 126.8, 128.5, 130.6, 133.25, 141.1, 141.4 (10 C$^{Naph}$, C-1′′) ppm. $C_{20}H_{23}NO$ (293.4): calcd. C 81.87, H 7.90, N 4.77; found C 81.80, H 7.69, N 4.72.

**(1*S*,2*S*,4*S*,5*R*)-(1-Naphthyl)(5-vinyl-1-azabicyclo[2.2.2]oct-2-yl)-methanol (7) and (1*R*,2*S*,4*S*,5*R*)-(1-Naphthyl)(5-vinyl-1-azabicyclo-[2.2.2]oct-2-yl)methanol (8):** These compounds were prepared from **4** and 1-bromonaphthalene, similarly to the production of **5** and **6** from **3**. The crude mixture was separated by column chromatography on silica gel with ethyl acetate/triethylamine (9:1). Compound **7** was eluted first ($R_f$ = 0.20), and **8** ($R_f$ = 0.16) second. The compounds were recrystallized from ethyl acetate.

**Compound 7:** Yield 9%, m.p. 94−95 °C, $[\alpha]_D^{25}$ = +221.0 ($c$ = 0.55, MeOH). IR (KBr): ṽ = 3473, 3411, 3070, 2948, 2875, 1635, 1500, 1457, 1388, 1353, 1322, 1248, 1106, 1027, 784 cm$^{-1}$. $^1$H NMR (250 MHz, [D$_6$]DMSO): δ = 1.31−1.97 (m, 5 H, 4-H, 2 × 3-H, 2 × 7-H), 2.12−2.22 (m, 1 H, 8-H), 2.47−2.70 (m, 3 H, 6-H, 5-H, 8-H), 2.96−3.07 (m, 2 H, 2-H, 6-H), 3.31 (br. s, 1 H, OH), 5.04−5.18 (m, 2 H, 2 × 2′′-H),5.32 (d, $^3J$ = 6.64 Hz, 1 H, 1′-H), 6.10 (ddd, $^3J$ = 17.3, $^3J$ = 10.4, $^3J$ = 7.57 Hz, 1′′-H),7.43−7.52 (m, 3 H, 3-H$^{Naph}$, 6-H$^{Naph}$, 7-H$^{Naph}$), 7.57 (d, $^3J$ = 7.02 Hz, 1 H, 5-H$^{Naph}$), 7.78 (d, $^3J$ = 8.09 Hz, 1 H, 4-H$^{Naph}$), 7.90 (d, $^3J$ = 8.37 Hz, 1 H, 8-H$^{Naph}$), 8.17 (d, $^3J$ = 8.13 Hz, 1 H, 2-H$^{Naph}$) ppm. $^{13}$C NMR (62 MHz, [D$_6$]DMSO): δ = 23.5, 26.6 (C-3, C-7), 27.8, 48.45 (C-5, C-4), 49.2, 52.4 (C-6, C-8), 60.5 (C-2), 71.9 (C-1′), 114.3 (C-2′′),123.5, 124.0, 125.0, 125.1, 125.4, 126.4, 128.65, 130.9, 134.0, 141.2, 141.8 (10 C$^{Naph}$, C-1′′) ppm. $C_{20}H_{23}NO$ (293.4): calcd. C 81.87, H 7.90, N 4.77; found C 81.62, H 7.77, N 4.85.

**Compound 8:** Yield 4.4%, m.p. 94−95 °C, $[\alpha]_D^{25}$ = −72.9 ($c$ = 0.40, MeOH). IR (KBr): ṽ = 3392, 3075, 3046, 2917, 2863, 1637, 1594, 1448, 1376, 1376, 1322, 1294, 1097, 995, 914, 792 cm$^{-1}$. $^1$H NMR (250 MHz, [D$_6$]DMSO): δ = 1.42−1.88 (m, 6 H, 8-H, 4-H, 2 × 3-H, 2 × 7-H), 2.18−3.19 (m, 5 H, 2-H, 2 × 6-H, 5-H, 8-H), 4.90−5.00 (m, 2 H, 2 × 2′′-H), 5.28 (d, $^3J$ = 6.63 Hz, 1 H, 1′-H), 5.85 (ddd, $^3J$ = 17.5, $^3J$ = 10.3, $^3J$ = 7.56 Hz, 1 H, 1′′-H),7.59 (d, $^3J$ = 6.25 Hz, 1 H, 5-H$^{Naph}$), 7.79 (d, $^3J$ = 8.02 Hz, 1 H, 4-H$^{Naph}$), 7.92 (d, $^3J$ = 9.47 Hz, 1 H, 8-H$^{Naph}$), 8.22 (d, $^3J$ = 7.42 Hz, 1 H, 2-H$^{Naph}$) ppm. $^{13}$C NMR (62 MHz, [D$_6$]DMSO): δ = 21.5, 26.1 (C-3, C-7), 29.0, 39.3 (C-5, C-4), 38.5, 50.0 (C-6, C-8), 60.3 (C-2), 72.0 (C-1′), 114.5 (C-2′′), 123.0, 123.4, 125.3, 125.8, 126.2, 128.0, 128.9, 130.2, 133.8, 138.1, 140.6 (10 C$^{Naph}$, C-1′′) ppm. $C_{20}H_{23}NO$ (293.4): calcd. C 81.87, H 7.90, N 4.77; found C 81.91, H 7.95, N 4.75.

**(1*S*,2*R*,4*S*,5*R*)-(1-Anthracenyl)(5-vinyl-1-azabicyclo[2.2.2]oct-2-yl)-methanol (9) [and Its (1*R*,2*R*,4*S*,5*R*) Diastereomer]:** These were prepared from **3** and 9-bromoanthracene, analogously to the formation of **5** and **6** from **3**. Although the presence of the diastereomer was apparent by TLC, only **9** could be isolated by preparative HPLC (LiChrospher Si; ethyl acetate/triethylamine, 9:1; flow 10 mL/min); $R_f$ = 0.19 on TLC plates. Yield 5%, $[\alpha]_D^{23}$ = −19.0 ($c$ = 0.10, MeOH). IR (KBr): ṽ = 3422, 3056, 2955, 2868, 1631, 1454, 1378, 1267, 1110, 1023, 783 cm$^{-1}$. $^1$H NMR (250 MHz, CDCl$_3$): δ = 1.43−1.96 (m, 4 H, 2 × 3-H, 2 × 7-H), 2.48−2.55 (m, 2 H, 8-H, 5-H), 2.62−2.67 (m, 1 H, 5-H), 2.89−2.94 (m, 1 H, 8-H), 3.11−3.20 (m, 1 H, 6-H), 3.28 (br. s, 1 H, OH), 3.51−3.68 (m, 2 H, 2-H, 6-H), 5.18−5.32 (m, 3 H, 1-H, 2 × 2′′-H), 5.99−6.12 (ddd, $J$ = 17.1, 9.64, 7.11 Hz, 1 H, 1′′-H),7.44−7.48 (m, 4 H, H$^{Anth}$), 8.03−8.05 (m, 4 H, H$^{Anth}$), 8.46 (s, 1 H, H$^{Anth}$) ppm. $^{13}$C NMR (62 MHz, CDCl$_3$): δ = 21.7, 24.2 (C-3, C-7) 27.9, 48.6 (C-5, C-4), 49.2, 58.8 (C-6, C-8), 62.2 (C-2), 71.2 (C-1), 116.6 (C-2′′),122.3, 124.7, 125.0, 125.8, 126.1, 127.2, 128.5, 129.2, 130.45, 131.55, 131.8, 133.5, 133.9, 134.1, 137.7 (14 C$^{Anth}$, C-1′′). $C_{24}H_{25}NO$ (343.5): calcd. C 83.92, H 7.34, N 4.08; found C 84.02, H 7.51, N 4.13.

**Preparation of the Catalysts:** This was performed by stirring the bases with the appropriate halides in MeCN/CHCl$_3$ at room temp. for 24−72 h (compounds **10a**, **10b**, **11a**), by stirring in that mixture for 24 h and then heating at 45 °C for 5−8 h (compounds **13c**, **14c**, **15c**), by heating under reflux for 2 h in toluene (compound **12d**), or by boiling for 2−24 h in MeCN (compounds **18**).

**(1*S*,2*R*,4*S*,5*R*)-1-Benzyl-2-[(hydroxy)(1-naphthyl)methyl]-5-vinyl-quinuclidinium Bromide (10a):** M.p. 262−264 °C, $[\alpha]_D^{25}$ = +114.7 ($c$ = 0.86, MeOH). IR (KBr): ṽ = 3410, 3200, 2945, 1632, 1454, 1405, 1212, 1165, 1058, 1001, 783, 766 cm$^{-1}$. $^1$H NMR (500 MHz, [D$_6$]DMSO): δ = 1.05−1.78 (m, 4 H, 2 × 3-H, 2 × 7-H),), 2.26−2.36 (m, 1 H, 4-H), 2.63−2.66 (m, 1 H, 5-H), 2.90−3.01 (m, 1 H, 8-H), 3.43−3.50 (m, 1 H, 8-H), 3.81−3.95 (m, 2 H, 6-H, 2-H), 4.18−4.32 (m, 1 H, 2-H), 4.90 (d, 1 H, CH$_2$), 5.06 (d, 1 H, CH$_2$), 5.20−5.23 (m, 2 H, 2′′-H), 5.99 (ddd, 1 H, 1′′-H), 6.47 (br. s, 1 H, OH), 6.59 (d, 1 H, 1′-H), 7.56−7.62 (m, 5 H, 3-H$^{Naph}$, 6-H$^{Naph}$, 7-H$^{Naph}$, 2 × H$^{Bz}$), 7.66 (t, 1 H, H$^{Bz}$), 7.71−7.73 (m, 2 H, 2 × H$^{Bz}$), 7.87 (d, 1 H, 5-H$^{Naph}$), 7.95 (d, 1 H, 4-H$^{Naph}$), 8.01 (d, 1 H, 8-H$^{Naph}$), 8.24 (d, 1 H, 2-H$^{Naph}$) ppm. $^{13}$C NMR (62 MHz, [D$_6$]DMSO): δ = 21.3, 23.0 (C-3, C-7), 26.2, 36.5 (C-5, C-4), 53.9, 55.8 (C-6, C-8), 61.1 (CH$_2$), 65.1, 67.9 (C-1′, C-2), 116.9 (C-2′′), 122.55, 123.0, 123.1, 123.8, 124.7, 125.2, 125.3, 125.6, 126.7, 128.4, 128.7, 129.0, 130.5, 133.0, 133.1, 134.7, 134.8 (16 C$^{arom}$, C-1′′) ppm. $C_{27}H_{30}BrNO{\cdot}1H_2O$ (372.5): calcd. C 67.22, H 6.69, N 2.90; found C 67.19, H 6.60, N 2.88.

**(1*S*,2*R*,4*S*,5*R*)-2-[(Hydroxy)(1-naphthyl)methyl]-1-(4-trifluoromethylbenzyl)-5-vinylquinuclidinium Bromide (10b):** M.p. 265−267 °C, $[\alpha]_D^{25}$ = +80.0 ($c$ = 0.10, MeOH). $C_{28}H_{29}BrNOF_3$ (532.4): calcd. C 63.16, H 5.49, N 2.63; C 62.83, H 5.66, N 2.73.

**(1*R*,2*R*,4*S*,5*R*)-1-Benzyl-2-[(hydroxy)(1-naphthyl)methyl]-5-vinyl-quinuclidinium Bromide (11a):** M.p. 173−176 °C, $[\alpha]_D^{25}$ =-43.3 ($c$ = 0.24, MeOH). IR (KBr): ṽ = 3411, 3272, 3204, 2937, 1637, 1457, 1407, 1311, 1214, 1160, 1118, 1058, 1035, 1002, 921, 784, 765, 703 cm$^{-1}$. $^1$H NMR (250 MHz, [D$_6$]DMSO): δ = 1.26−2.69 (m, 7 H, 8-H, 5-H, 4-H, 2 × 3-H, 2 × 7-H), 3.35−3.91 (m, 3 H, 6-H, 2-H, 8-H), 4.09−4.29 (m, 1 H, 6-H), 4.97 (d, $^2J$ = 11.9 Hz, 1 H, CH$_2$), 5.15 (d, $^2J$ = 12.0 Hz, 1 H, CH$_2$), 5.17−5.26 (m, 2 H, 2 × 2′′-H), 5.67 (ddd, $^3J$ = 17.1, $^3J$ = 10.5, $^3J$ = 6.44 Hz, 1 H, 1′′-H), 6.50 (br. s, 1 H, 1′-H), 7.57−7.85 (m, 8 H, 5 × H$^{Bz}$, 3 × H$^{Naph}$), 7.87 (d, $^3J$ = 6.97 Hz, 1 H, 5-H$^{Naph}$), 7.96 (d, $^3J$ = 8.11 Hz, 1 H, 4-H$^{Naph}$), 8.03 (d, $^3J$ = 7.87 Hz, 1 H, 8-H$^{Naph}$), 8.23 (d, $^3J$ = 8.24 Hz, 1 H, 2-H$^{Naph}$) ppm. $^{13}$C NMR (62 MHz, [D$_6$]DMSO): δ = 20.8, 23.4 (C-3, C-7), 26.1, 36.5 (C-5, C-4), 55.8, 53.9, 54.5 (CH$_2$, C-6, C-8), 66.0, 67.4 (C-1′, C-2), 116.7 (C-2′′), 120.0, 123.6, 124.1, 124.5, 124.8, 125.3, 125.9, 126.2, 126.7, 127.6, 128.4, 129.6, 132.9, 131.0, 133.55, 134.2, 136.4 (16 C$^{arom}$, C-1′′) ppm. $C_{27}H_{30}BrNO$ (464.4): calcd. C 69.82, H 6.51, C 3.02; found C 70.12, H 6.37, N 3.00.

**(1*S*,2*S*,4*S*,5*R*)-1-(9-Anthracenylmethyl)-2-[(Hydroxy)(1-naphthyl)methyl]-5-vinylquinuclidinium Chloride (12d):** M.p. 217−218 °C, $[\alpha]_D^{25}$ =+56.0 ($c$ = 0.10, MeOH). IR (KBr): ṽ = 3075, 3050, 3006, 2950, 2885, 1625, 1509, 1450, 1419, 1261, 1166, 1124, 995,

917, 821, 784, 734 $cm^{-1}$. $^1H$ NMR (250 MHz, [$D_6$]DMSO): δ = 0.97−1.75 (m, 4 H, 2 × 3-H, 2 × 7-H), 2.30−2.33 (m, 2 H, 8-H, 4-H), 2.70−2.74 (m, 1 H, 5-H), 2.95−3.04 (m, 1 H, 8-H), 8.97 (s, 1 H, 10-$H^{Anth}$), 4.24−4.40 (m, 3 H, 2-H, 2 × 6-H), 4.99−5.17 (m, 2 H, 2 × 2′′-H), 5.87−5.96 (m, 1 H, 1′′-H), 6.05 (d, $^2J$ = 14.1 Hz, 1 H, $CH_2$), 6.37 (d, $^2J$ = 14.1 Hz, 1 H, $CH_2$), 6.93 (br. s, 1 H, 1-H), 7.25−7.84 (m, 7 H, 7 × $H^{arom}$), 7.98−8.06 (m, 3 H, 3 × $H^{arom}$), 8.29 (d, $^3J$ = 7.85 Hz, 2 H, 2 × $H^{arom}$), 8.61 (m, 2 H, 2 × $H^{arom}$), 8.93 (d, $^3J$ = 9.66 Hz, 1 H, $H^{arom}$) ppm. $^{13}C$ NMR (62 MHz, [$D_6$]DMSO): δ = 21.5, 23.5 (C-3, C-7), 25.5, 37.0 (C-5, C-4), 54.1, 54.5, 56.5 ($CH_2$, C-6, C-8), 66.0, 67.3 (C-1′, C-2), 116.7 (C-2′′), 119.2, 123.6, 124.1, 124.5, 124.8, 125.3, 125.5, 125.8, 126.2, 126.7, 127.4, 127.6, 128.4, 128.6, 129.3, 129.5, 129.6, 131.0, 131.1, 131.9, 132.9, 133.15, 133.2, 135.4, 137.2 (24 $C^{arom}$, C-1′′) ppm. $C_{35}H_{34}ClNO$ (520.1): calcd. C 80.83, H 6.59, N 2.69; found C 80.96, H 6.33, N 2.75.

***N*-(9-Acridinylmethyl)cinchoninium Bromide (13c):** M.p.158−160 °C. $[\alpha]_D^{25}$ = +173.2 (*c* = 0.73, MeOH). $C_{33}H_{32}BrN_3O{\cdot}1H_2O$ (584.56): calcd. C 67.81, H 5.86, N 7.19; found C 68.01, H 5.88, N 7.08.

***N*-(9-Acridinylmethyl)cinchonidinium Bromide (14c):** M.p.153−154 °C. $[\alpha]_D^{23}$ = −191.5 (*c* = 0.43, MeOH). $C_{33}H_{32}BrN_3O{\cdot}1H_2O$ (584.56): calcd. C 67.81, H 5.86, N 7.19; found C 67.61, H 5.82, N 7.18.

***N*-(9-Acridinylmethyl)quininium Bromide (15c):** M.p. 144−146 °C, $[\alpha]_D^{23}$ = −333.1 (*c* = 0.50, MeOH). $C_{33}H_{34}BrN_3O_2{\cdot}1H_2O$ (596.6): C 66.45, H 5.90, N 6.84; found C 66.38, H 5.85, N 6.73.

**PTC Oxidation of 2-Ethyl-1-tetralone (Reaction 1):** Aq. NaOH (50%, 2.5 mL), toluene (7.5 mL), triethyl phosphite (239 mg, 0.25 mL, 1.44 mmol), 2-ethyl-1-tetralone (174 mg, 1.00 mmol), and the PT catalyst (5 mol %) were placed in a micro-hydrogenation apparatus connected to a balloon containing oxygen. The mixture was stirred vigorously for 42 h at room temp. $H_2O$ (20.0 mL) and toluene (10.0 mL) were then added, the phases were separated, and the aqueous phase was extracted with toluene (10 mL). The combined organic solutions were washed with HCl (10%, 10.0 mL), $H_2O$ (10 mL), and sat. aq. NaCl (10 mL), and dried with $Na_2SO_4$. The solvent was removed, and the residue was chromatographed on silica gel with petroleum ether (b.p.30−60 °C)/ethyl acetate (10:1). The fraction with $R_f \geq 0.10$, a yellowish oil, contained 2-ethyl-2-hydroxy-1-tetralone and occasionally still some starting material. It was concentrated to dryness and weighed. Relative yields were determined by $^1H$ NMR, enantiomeric excesses by HPLC. $^1H$ NMR (250 MHz, $CDCl_3$): δ = 0.96 (t, $^3J$ = 7.50 Hz, 3 H, $CH_3$), 1.56−1.80 (m, 2 H, $CH_2$), 2.00−2.35 (m, 2 H, 2 × 3-H), 2.92−3.17 (m, 2 H, 2 × 4-H), 3.75 (br. s, 1 H, OH), 7.24 (d, $^3J$ = 8.30 Hz, 1 H, 1 $H^{arom}$), 7.30 (t, $^3J$ = 7.56 Hz, 1 H, 1 $H^{arom}$), 7.56 (dt, $^3J$ = 7.56, $^4J$ = 1.40 Hz, 1 H, 1 $H^{arom}$), 8.00 (dd, $^3J$ = 7.83, $^4J$ = 1.33 Hz, 1 H, 1 $H^{arom}$) ppm. HPLC (Chirasep DNBPG; hexane/2-propanol, 500:1; flow 0.5 mL/min): (*R*)-2-ethyl-2-hydroxy-1-tetralone: 36.8 min.; (*S*) isomer: 38.2 min.

**PTC Epoxidation of 2-Isopropyl-1,4-naphthoquinone (Reaction 2):** A mixture of 2-isopropyl-1,4-naphthoquinone (201 mg, 1.00 mmol), $CHCl_3$ (3.00 mL), and aq. $H_2O_2$ (30%, 1.00 mL) was stirred for 3 min at 0 °C. LiOH (37.0 mg, 2.0 mmol) and the PT catalyst (5 mol %) were then added, and the mixture was stirred for 5 h at 0 °C and for12 h at room temp. Quenching was performed by the addition of HCl (1 N, 10 mL) and the phases were separated. The aqueous layer was extracted thrice with 10 mL of ether. The combined extracts were dried ($Na_2SO_4$), and the solvent was removed. The residue was chromatographed on silica gel with petroleum ether (b.p.30−60 °C)/ether (3:1), and the slightly orange colored fraction of $R_f \approx 0.33$ (containing the product and sometimes a little starting material) was concentrated to dryness and weighed. Relative yields were determined by $^1H$ NMR, *ee*′s by HPLC. $^1H$ NMR (250 MHz, $CDCl_3$): δ =, 1.04 (d, $^3J$ = 6.96 Hz, 3 H, $CH_3$), 1.15 (d, $^3J$ = 6.84 Hz, 3 H, $CH_3$), 2.77 (sept, $^3J$ = 6.90 Hz, 1 H, CH), 3.86 (s, 1 H, CH−O), 7.70−7.78 (m, 2 H, 2 × $H^{arom}$), 7.91−7.99 (m, 1 H, $H^{arom}$), 8.01−8.05 (m, 1 H, $H^{arom}$) ppm. $^{13}C$ NMR (62 MHz, $CDCl_3$): δ = 16.3, 18.8 (2 $CH_3$). 25.7 (CH), 58.0 (CH−O), 67.1 (C−O), 126.7, 127.5, 131.3, 133.0, 134.3, 134.6 (6 $C^{arom}$), 191.5 (CO), 192.3 (CO) ppm. HPLC (Chiralcel OD; hexane/2-propanol, 500:1; flow 0.5 mL/min): (+) enantiomer: 40.5 min; (−) enantiomer: 42.7 min.

**PTC Benzylation of 2-(*tert*-Butoxycarbonyl)cyclopentanone (Reaction 3):** 2-(*tert*-Butoxycarbonyl)cyclopentanone (184 mg, 1.00 mmol) and the PT catalyst (5 mol %) were stirred in toluene (10.0 mL) and sat. aq. $K_2CO_3$ (6.00 mL) for 5 min at room temp. Benzyl bromide (0.18 mL, 1.52 mmol) was added, and the mixture was stirred for 26 h at room temp. The reaction was then quenched by addition of $H_2O$ (40.0 mL) and sat. aq. NaBr (15.0 mL). The phases were separated, and the aqueous one was extracted with $CH_2Cl_2$ (10.0 mL). The combined organic layers were dried ($Na_2SO_4$), and the solvent was removed. The residue was taken up in petroleum ether (b.p. 30−60 °C)/ether (25:1) and chromatographed on silica gel. The fraction with $R_f$ = 0.03 contained 2-benzyl-2-(*tert*-butoxycarbonyl)cyclopentanone and sometimes residual benzyl bromide. The solvent was removed and the residue weighed. Relative yields were determined by $^1H$ NMR spectroscopy, *ee* values by HPLC. $^1H$ NMR (250 MHz, $CDCl_3$): δ = 7.28−7.12 (m, 5 H, 5 $H^{Ar}$), 3.12 (s, 2 H, $CH_2Ph$), 2.41−2.28 (m, 2 H, 2 × 5-H), 2.03−1.82 (m, 3 H, 2 × 4-H, 3-H), 1.59−1.51 (m, 1 H, 3-H), 1.43 (s, 9 H, 3 $CH_3$) ppm. $^{13}C$ NMR (62 MHz, $CDCl_3$): δ = 19.85 (C-4), 28.5 (3 $CH_3$), 32.3 (C-3), 38.4 (C-5), 38.9 ($C_q$), 62.3 ($CH_2$), 82.3 (C−O), 127.3, 129.1, 130.7, 136.9 ($C^{arom}$), 170.7 (COO), 215.6 (CO) ppm. HPLC (Chiralcel OD; hexane/2-propanol, 1000:1; flow 0.5 mL/min): (*S*)-2-benzyl-2-(*tert*-butoxycarbonyl)cyclopentanone: 18.5 min; (*R*) isomer: 20.4 min.

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[16] Epoxidations of (*E*)-enones have been performed with hypochlorite and cinchona alkaloid derived catalysts in up to 90% *ee*, but the opposite enantiomer to that produced in the $H_2O_2$ reactions was obtained.[3e]

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[18] Crystal data and structure refinement parameters: Formula mass: 293.39; crystal size: 0.1 × 0.15 × 0.3 mm; colorless needles; crystal system, space group: trigonal, *P*31; unit cell dimensions: $a$ = 11.8100(8) Å, $b$ = 11.8100(10) Å, $c$ = 9.9270(10) Å; volume: 1199.08(18) Å$^3$; $Z$ = 3; $D_{calcd.}$ = 1.219 Mg/m$^3$; $F(000)$ = 474; absorption coefficient: 0.074 mm$^{-1}$; θ range for data collection: 2.86−27.5°; index ranges: $-15 \le h \le 12$, $-15 \le k \le 15$, $-12 \le l \le 12$; reflections collected/unique: 8113/3205 [$R$(int) = 0.0891]; completeness to θ = 27.49°: 88.8%; absorption correction: none; refinement method: full-matrix, least squares on $F^2$; data/restraints/parameters: 3205/1/199; goodness-of-fit on $F^2$: 1.059; final $R$ indices [$I \ge 2\sigma(I)$]: $R1$ = 0.0577, $wR2$ = 0.1051; $R$ indices (all data): $R1$ = 0.0928, $wR2$ = 0.1212; largest diff. peak and hole: 0.306 and −0.209 e Å$^{-3}$. The absolute configuration could not be determined reliably but follows from the known one of the starting material.

[19] CCDC-172080 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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