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Synthesis and reactions of partially reduced biisoquinolines

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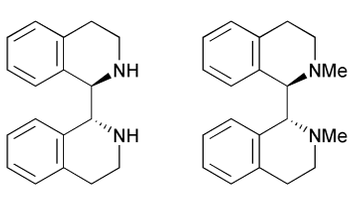
An improved synthesis of the 1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline ring system is described. The reactivity of this system has been investigated, including the unusually high basicity of the parent compound and its *N,N′*-dimethyl derivative. The resolution of the parent compound has been achieved for the first time, along with the development of a straightforward method for assaying its enantiomeric purity.

Introduction

Chiral diamines have seen numerous applications in asymmetric synthesis.[1] Simple diamines have been used as the chiral backbone of a wide range of chiral ligands, with the diamine sometimes,[2] but not always,[3] coordinating to a metal. Chiral bases and modifiers have received much attention, most notably sparteine and proline derivatives.[4] The cinchona alkaloids have seen success as phase-transfer catalysts and chiral modifiers for metal-catalysed hydrogenation.[5] However, the number and structural variety of chiral diamines used is relatively limited. In particular in the case of C_2-symmetric diamines 1,2-diphenylethane-1,2-diamine and cyclohexane-1,2-diamine are almost invariably used. Since the rigidity of chiral ligands can have a profound effect on the extent of asymmetric induction, these compounds are of significant interest. Recently we initiated research into the synthesis and applications of geometrically-constrained chiral 1,2-diamines. Our first target was 1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline **1**, and during the course of these studies we found that the basicity of the *N*,*N*-dimethyl derivative **2** was unusually high.[6] Two main approaches to the octahydrobiisoquinoline ring system have been described. Double Bischler–Napieralski cyclisation followed by reduction of the resulting bis-imine is effective for isoquinoline derivatives with electron-rich aromatic rings,[7] while imine coupling has been used for substituted and unsubstituted rings.[8] Both of these approaches give mixtures of *dl* and *meso* diastereoisomers. The most definitive structural study to date used the latter approach, and assigned the stereochemistry of the diastereoisomers of the parent compound **1**.[9] There is also a single report of the oxidative coupling of a 2-lithiotetrahydroisoquinoline derivative.[10] Since our preliminary communication, Read *et al.* have used the Bischler–Napieralski route to prepare a range of macrocycles with a biisoquinoline backbone, and have also described enantiocontrol in the reduction of the bis-imine intermediate.[11] We now report the results of a detailed study into the chemistry of compound **1**, including the highly efficient resolution of this compound.

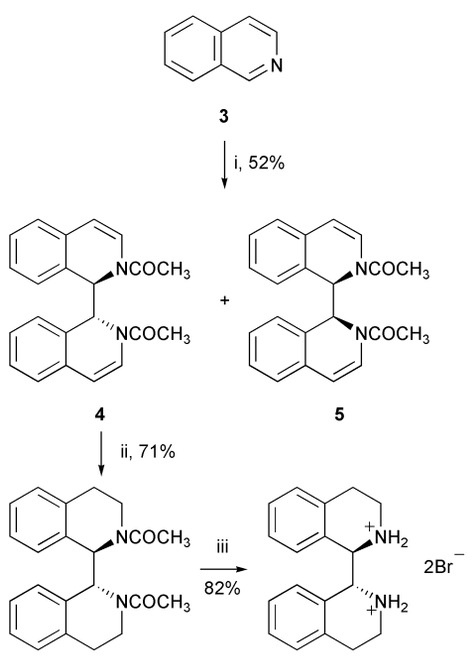


1 **2**

Results and discussion

Efficient preparation of 1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline

The synthesis of compound **1** and its *meso* diastereoisomer were first reported in 1970.[9] Reductive coupling of isoquinoline **3** gave, in our hands, 52% of a 1 : 1 mixture of diastereoisomers of **4** and **5**. The hydrogenation of **4** was reported to proceed smoothly at 25–55 psi over Rh–C in a Parr apparatus. We found that almost no hydrogenation occurred under these conditions, and, after much experimentation, found that complete hydrogenation could be accomplished at 150 psi for 1 week over Pd–C, but only if the starting material was ground to a fine powder and suspended in water prior to the addition of acetic acid as hydrogenation solvent. In this way, compound **6** was formed in 71% yield. The synthesis was completed as previously reported by vigorous hydrolysis using hydrobromic acid, acetic acid and water to provide the desired compound as the hydrobromide salt **7** (**Scheme 1**).



Scheme 1 *Reagents and conditions:* i, Zn, Ac_2O; ii, H_2, Pd–C, 150 psi; iii, HBr, H_2O, AcOH.

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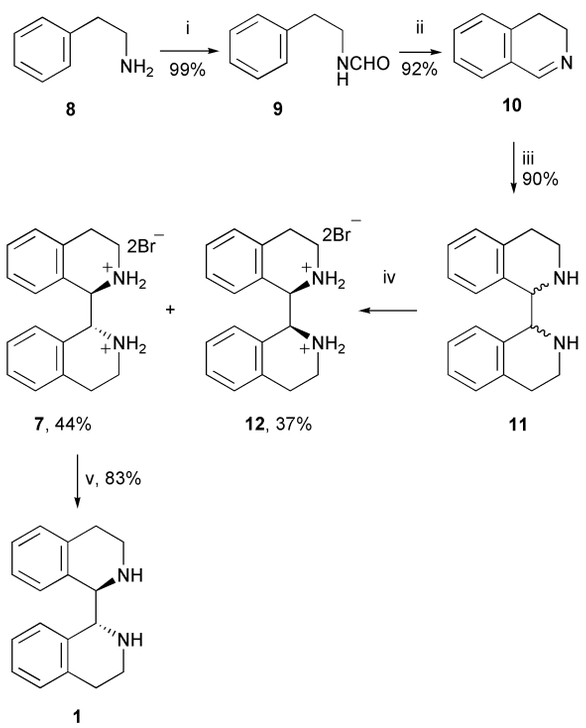
The difficulties encountered during the hydrogenation step and the low yield obtained in the first step prompted us to search for an alternative synthesis. We elected to avoid the hydrogenation step by carrying out the reductive coupling at a lower oxidation level. Reaction of phenylethylamine **8** with ethyl formate, followed by cyclisation with polyphosphoric acid gave dihydroisoquinoline **10** cleanly. Dimerisation of **10** using zinc with 1,2-dibromoethane and chlorotrimethylsilane[12] gave a 1 : 1 mixture of diastereoisomers **11**, from which the *dl* isomer was easily separated and characterised as the double hydrobromide salt **7**, the free base of which was liberated with sodium hydroxide (**Scheme 2**).



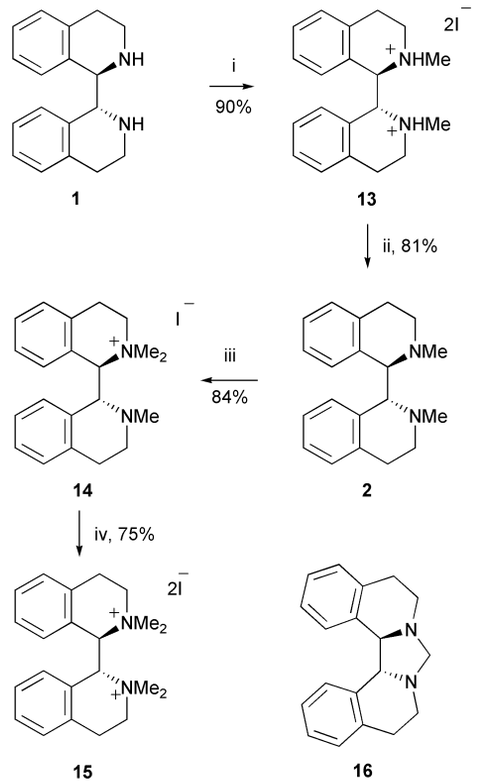
Scheme 2 *Reagents and conditions:* i, EtOCHO, reflux, 12 h; ii, PPA, 160 °C, 12 h; iii, Zn, $BrCH_2CH_2Br$, Me_3SiCl, CH_3CN; iv, HBr; v, NaOH, H_2O, CH_2Cl_2.

Alkylation of 1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline

We were interested in forming simple *N*-alkyl derivatives of **1**, and investigated the reactions of this compound with iodomethane. We were slightly surprised to find that reaction of **1** in neat iodomethane produced only the double salt **13** (Scheme 3), with no evidence of further alkylation. The free base **2** was liberated with sodium hydroxide and allowed to react with iodomethane, again as solvent, to give the triply alkylated derivative **14** as a yellow precipitate. Dissolution of this in chloroform allowed the final methyl group to be introduced, giving **15**. Similar compounds have been previously reported, and not surprisingly found to be prone to rapid elimination.[13] However, a sample of **15** proved to be stable in the solid state for over 6 months, while solutions of this compound showed no appreciable decomposition.

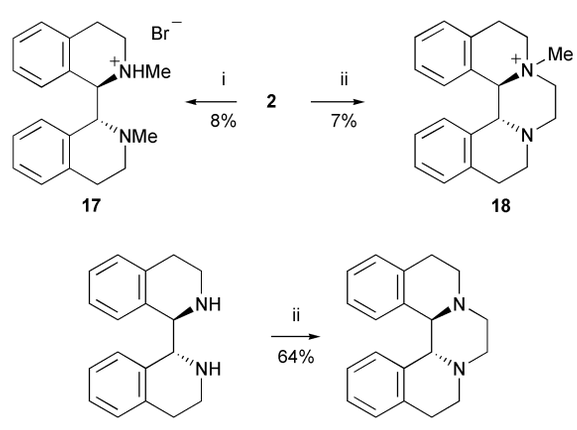
The stereochemistry of **1** was previously determined by the formation of formaldehyde adduct **16**. We initially repeated the synthesis of this compound, and confirmed the stereochemical assignments of Nielsen, although we were eventually fortunate enough to obtain crystals of **2** suitable for single crystal X-ray diffraction.[14]

While further alkylation of **2** with iodomethane proceeded cleanly and in high yield, reaction with 1,2-dibromoethane was much less effective. At 60 °C we were only able to isolate the single salt **17**. Despite the difference in counter ion, we are confident of this assignment based on the greatly increased



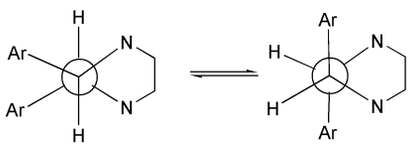
Scheme 3 *Reagents and conditions:* i, CH_3I, 6 h; ii, NaOH, H_2O, CH_2Cl_2; iii, CH_3I, 6 h; iv, CH_3I, $CHCl_3$, reflux, 24 h.

solubility of **17** in organic solvents compared to double salt **13**. Salt **17** was clearly symmetrical, indicating rapid proton transfer between the two hydrogen atoms. At room temperature little reaction occurred, but rather than simply bridging the nitrogen atoms to give a double salt analogous to **15**, single salt **18** was obtained in low yield as a single stereoisomer (unknown stereochemistry) at nitrogen (**Scheme 4**). Presumably in the putative bridged double salt intermediate the close proximity of the two positive charges aids the demethylation. In both cases the balance of material was recovered **2**. In contrast to these results, bridging compound **1** with 1,2-dibromoethane occurred smoothly to give compound **19** in moderate yield. The hydrogen atoms at the 8 and 8′ positions show significant broadening in the room temperature 400 MHz ^{1}H NMR spectrum of compound **19**. The effect is not noticeable with other hydrogen atoms, although broadening was observed in a number of signals in the ^{13}C NMR spectrum as previously observed by Read and co-workers for an analogous compound.[11] This is presumably due to rapid interconversion between the two



Scheme 4 *Reagents and conditions:* i, $BrCH_2CH_2Br$, 60 °C; ii, $BrCH_2CH_2Br$, 25 °C, 48 h.

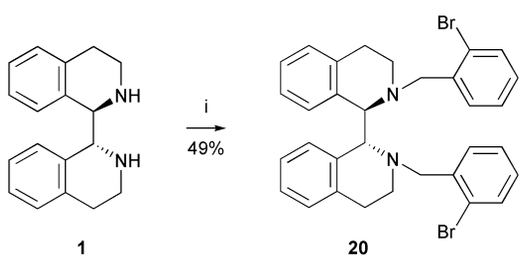
conformers **19a** and **19b** (**Scheme 5**; ethylene bridge of the isoquinoline ring omitted for clarity). A variable temperature proton NMR study (300 MHz) established the coalescence temperature to be −20 °C, exactly as reported for the 6,6′,7,7′-tetramethoxy analogue.[7] However, while in this case the conformer corresponding to **19a** was favoured (5 : 4), we have observed a 2 : 1 preference for **19b**. The conformational assignments were based on the upfield chemical shifts of H7 (6.75 ppm) and H8 (5.85 ppm) in **19a** due to shielding by the other aromatic ring (observed to varying extents for most derivatives of compound **1**). Since the two conformers are of different energy, the barrier to inversion cannot be determined without a detailed lineshape analysis.



19a **19b**

Scheme 5

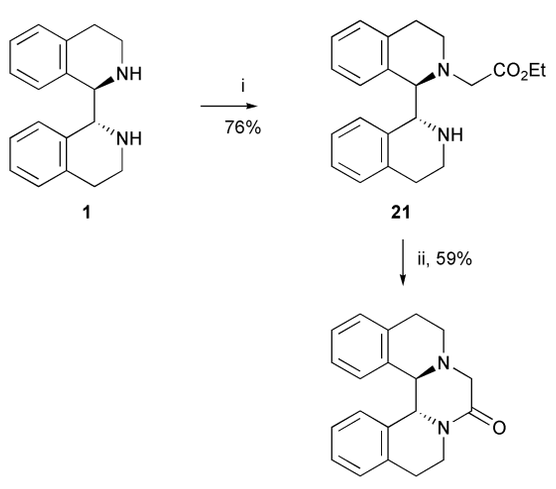
During reaction with 2-bromobenzyl bromide, although 1,2-elimination cannot compete, a significant amount of salt **7** was obtained, presumably by 1,1-elimination although trapping experiments to assess carbene formation were not carried out. The expected product **20** was therefore formed in only modest yield (**Scheme 6**).



1 **20**

Scheme 6 *Reagents and conditions:* i, 2-bromobenzyl bromide, THF, 25 °C, 12 h.

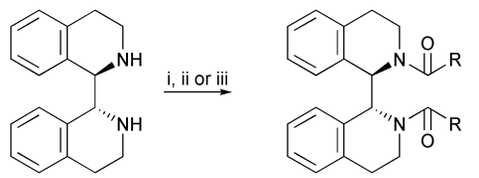
Ethyl 2-bromoacetate is an ambident electrophile which also possesses acidic hydrogen atoms. Reaction of **1** in neat ethyl 2-bromoacetate gave a complex mixture from which no products could be isolated. However, a 1 : 1 mixture in dichloromethane gave single alkylation product **21** cleanly and in high yield, although once again some formation of salt **7** was observed. Cyclisation of **21** to the amide **22** was accomplished with sodium hydride in toluene (**Scheme 7**).



1 **21** **22**

Scheme 7 *Reagents and conditions:* i, ethyl 2-bromoacetate, CH_2Cl_2, 25 °C, 12 h; ii, NaH, toluene, 110 °C, 4.5 h.

As noted by Read *et al.*,[11] biisoquinoline amides are straightforward to prepare. We prepared three representative amides, **23**–**25** from either the acid chlorides or carboxylic acid–water-soluble carbodiimide (**Scheme 8**).



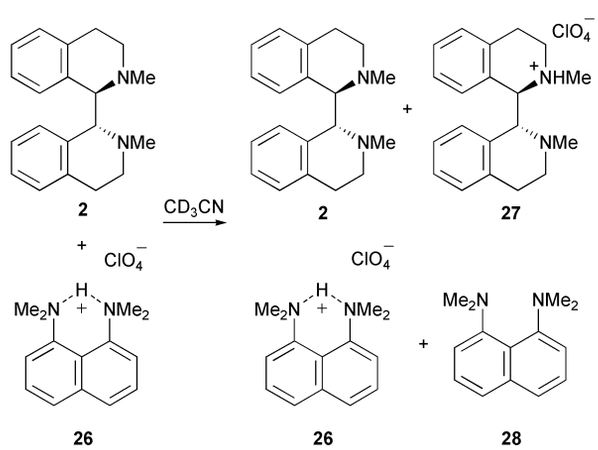
1

23, R = Et 92%
24, R = CH_2Ph 90%
25, R = Ph 50%

Scheme 8 *Reagents and conditions:* i, EtCOCl, Et_3N, CH_2Cl_2, DMAP (R = Et); ii, $PhCH_2COCl$, Et_3N, CH_2Cl_2, DMAP (R = $PhCH_2$); iii, $PhCO_2H$, $Me_2N(CH_2)_3C{=}N{=}CEt{\cdot}HCl$, 25 °C, 12 h (R = Ph).

The unusually high basicity of compound 2

The reluctance of compound **1** to undergo exhaustive methylation, even upon heating in neat iodomethane, prompted us to investigate the basicity of compound **2**. A theoretical study of this compound showed a particularly high proton affinity,[6] leading us to classify this compound as a proton sponge.[15,16] This was confirmed by NMR experiments comparing this compound with known proton sponge **28**. A 1 : 1 mixture of **2** and the perchlorate salt **26** in deuterated acetonitrile showed clearly that **26** was approximately 50% deprotonated under these conditions, leading to the conclusion that **2** and **28** have essentially identical pK_a values (18.2)[17] in acetonitrile (**Scheme 9**). While **26** and **28** exchange protons relatively slowly at room temperature, the corresponding exchange in **2** is rapid on the NMR timescale, so that only a single set of signals was observed for this compound. The pK_a of **28** in water is 12.1, whereas that of TMEDA is 9.1.[18] Therefore, while we have not directly measured the basicity of **2** in water, we extrapolate that it is almost 3 orders of magnitude more basic than the simplest tertiary diamine with a two-carbon bridge. Although compound **2** lacks the kinetic properties normally associated with proton sponges, applications of organic superbases are beginning to emerge,[19,20] so that the unusually high basicity of compound **2** is of interest. Similar competition experiments showed that **1** has a pK_a of 17.85 in acetonitrile, slightly less basic than the tertiary diamine as expected.

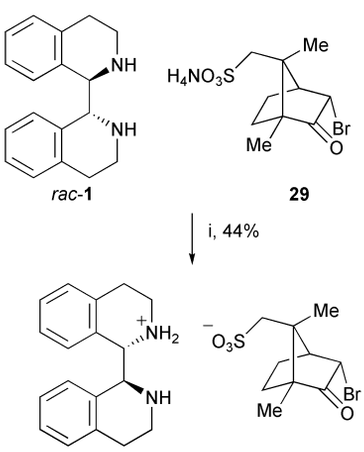


Scheme 9

Resolution of 1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline

Having undertaken a preliminary study of biisoquinoline derivative **1**, we required access to the individual enantiomers of this compound for further study. Salts of **1** with camphor-

sulfonic acid did not crystallise well from organic solvents, while those with tartaric acid were relatively insoluble. After much experimentation we found that the salt of **1** with D-(+)-α-bromocamphor-π-sulfonic acid **29** (used as the ammonium salt) crystallises as the single (*S*,*S*)-diamine enantiomer in high yield (**Scheme 10**). This method produced crystals suitable for X-ray diffraction (**Fig. 1**),[14] so that the absolute stereochemistry of the liberated parent diamine has been established. The enantiomeric diamine was accessible either from the mother liquors, or by use of the enantiomeric resolving agent. The enantiomeric purity of **1** could be readily assessed by proton NMR spectroscopy of the corresponding camphorsulfonate salt (but not the D-(+)-α-bromocamphor-π-sulfonate salt, for which no separation of peaks was observed). The proton NMR spectra of racemic **1** and both enantiomers of **1** in the presence of camphorsulfonic acid are shown in **Fig. 2**, showing clearly the diastereomeric salts in the former. Based on this data we estimate the enantiomeric purity of resolved **1** to be better than 95%. Both one and two equivalents of camphorsulfonic acid were suitable for this purpose, although the latter gave better separation of the benzylic CH peaks which were most convenient for the assessment of enantiomeric purity.



Scheme 10 *Reagents and conditions:* i, recrystallise from ethanol.

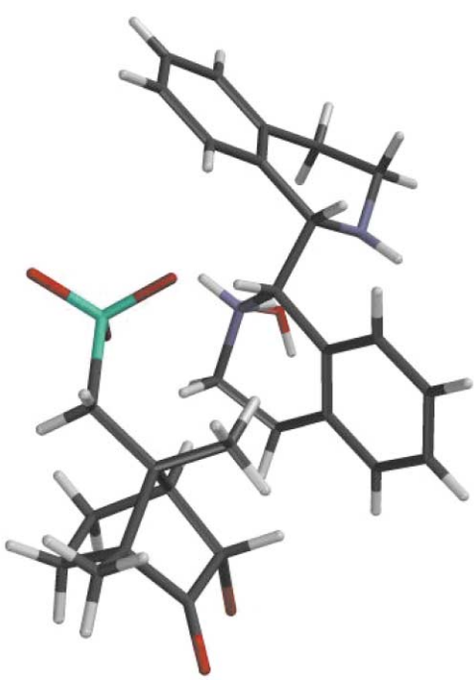


Fig. 1 Structure of the salt of (*S*,*S*)-**1** with D-(+)-α-bromocamphor-π-sulfonic acid from single crystal X-ray diffraction data.[14]

Conclusions

A new synthesis of geometrically-constrained diamine **1** has been developed. A preliminary investigation of the chemistry of this compound has been undertaken, providing a range of alkylated derivatives. The stability of compound **15** is unexpected, and we anticipate applications of this compound as a chiral phase-transfer catalyst. This chemistry, along with applications of compounds **1** and **2** as chiral superbases is under investigation and will be reported in due course.

Experimental

General experimental points

All melting points were determined on a Gallenkamp melting point apparatus, and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer. Mass spectra were recorded on a Fisons VG Platform II spectrometer. High-resolution mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre in Swansea. Elemental analyses were recorded using a Perkin Elmer 240 C elemental analyser. NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 400 MHz for ^{1}H and at 100 MHz for ^{13}C at 25 °C. All chemical shifts are reported in ppm downfield from TMS. Flash chromatography was performed unless otherwise stated on Matrex silica 60 35–70 micron.

(1*RS*,1′*RS*)-2,2′-Diacetyl-1,1′,2,2′-tetrahydro-1,1′-biisoquinoline 4 and *meso*-2,2′-diacetyl-1,1′,2,2′-tetrahydro-1,1′-biisoquinoline 5

Isoquinoline **3** (25 g, 0.194 mol) was dissolved in acetic anhydride (150 ml). Zinc dust (25 g, 0.388 mol) was added in small portions over a 3 h period; the temperature of the reaction mixture was maintained between 25–35 °C with external cooling (ice bath). Vigorous stirring was continued at rt for a further 15 h under an atmosphere of nitrogen. The mixture was poured into ice water (500 ml), stirred for 2 h and filtered to give an orange granular solid. The solid was heated to reflux in methanol (250 ml) for 2 h and filtered hot to give the filtrate containing **4**, and a solid containing zinc and **5**. The filtrate was concentrated to 100 ml, cooled to 0 °C and filtered to give compound **4** (8.0 g, 24%) as colourless crystals, mp 203–205 °C (Lit. mp 205–208 °C)[9]; ν_{max} (Nujol)/cm^{-1} 1670 and 1620; δ_H (400 MHz; $CDCl_3$) 7.24 (4H, m, 4 × aromatic C*H*), 6.82 (2H, apparent dt, *J* 1.9, 7.0, 2 × aromatic C*H*), 6.72 (2H, d, *J* 7.6, 2 × CHC*H*N), 6.26 (2H, d, *J* 7.6, 2 × C*H*CHN), 6.01 (2H, d, *J* 7.5, 2 × aromatic C*H*), 5.87 (2H, s, 2 × C*H*N) and 2.23 (6H, s, 2 × CH_3); δ_C (100 MHz; $CDCl_3$) 169.4 (2 × CO), 131.1 (2 × aromatic C), 129.3 (2 × aromatic C), 129.2 (2 × aromatic CH), 128.4 (2 × aromatic CH), 126.2 (2 × aromatic CH), 126.1 (2 × aromatic CH), 124.6 (2 × CH*C*HN), 111.5 (2 × *C*HCHN), 53.0 (2 × CHN) and 22.0 (2 × CH_3); *m*/*z* (APCI) 345 (MH^+, 100%). The solid was continuously extracted with CH_2Cl_2 using a Soxhlet apparatus for 8 h. The solvent was removed under reduced pressure to give colourless crystals (9.2 g, 28%). The product was found to contain a mixture of compounds and although compound **5** was the major product we were unable to isolate it from the mixture, mp 255–257 °C (Lit. mp 250–255 °C)[9]; ν_{max} (Nujol)/cm^{-1} 1660 and 1620; δ_H (400 MHz; $CDCl_3$) 7.24 (2H, apparent t, *J* 7.5, 2 × aromatic C*H*), 7.09 (2H, apparent t, *J* 7.5, 2 × aromatic C*H*), 6.92 (2H, d, *J* 7.5, 2 × aromatic C*H*), 6.75 (2H, d, *J* 7.5, 2 × aromatic CH), 6.44 (2H, d, *J* 7.7, 2 × CHC*H*N), 5.87 (2H, s, 2 × C*H*N), 5.66 (2H, d, *J* 7.7, 2 × C*H*CHN) and 2.11 (2 × CH_3); δ_C (100 MHz; $CDCl_3$) 169.5 (2 × CO), 131.7 (2 × aromatic C), 129.4 (2 × aromatic C), 128.6 (2 × aromatic CH), 127.8 (2 × aromatic CH), 127.0 (2 × aromatic CH), 126.2 (2 × aromatic CH), 124.7 (2 × CH*C*HN), 110.4 (2 × *C*HCHN), 55.8 (2 × CHN) and 21.8 (2 × CH_3); *m*/*z* (APCI) 345 (MH^+, 100%).

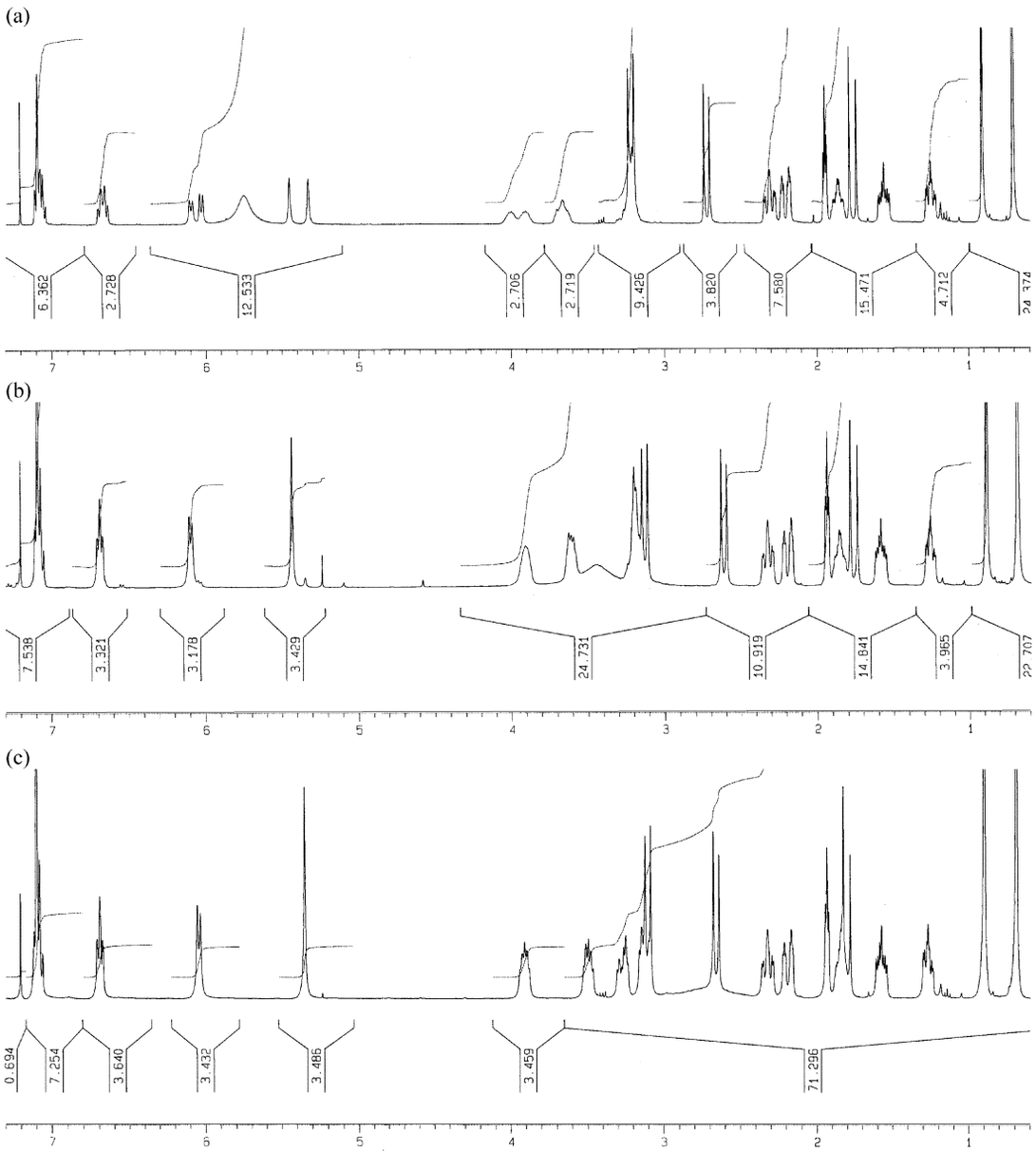


Fig. 2 Proton NMR spectra of double salts of (a) racemic (b) (*S*,*S*)- and (c) (*R*,*R*)-**1** with camphorsulfonic acid.

(1*RS*,1′*RS*)-2,2′-Diacetyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline 6

(1*RS*,1′*RS*)-2,2′-Diacetyl-1,1′,2,2′-tetrahydro-1,1′-biisoquinoline **4** (5 g, 15 mmol) was ground into a fine powder and stirred in water (10 ml) for 1 h. Acetic acid (100 ml) was added and the mixture was allowed to stir until most of the starting material had dissolved, after which the undissolved material was removed by filtration. 5% Palladium on carbon (0.5 g) was added and the reaction mixture was stirred under hydrogen (150 psi) at room temperature for 1 week. The catalyst was removed by filtration and washed with water (50 ml) and methanol (50 ml). The filtrate and washings were combined and concentrated under reduced pressure to give a white solid. Recrystallisation from toluene gave the *title compound* (3.6 g, 71%) as colourless crystals, mp 229–231 °C (Lit. mp 211–213 °C)[9] (Found: MH^+, 349.1909. $C_{22}H_{25}N_2O_2$ requires M, 349.1916); ν_{max} (Nujol)/cm^{-1} 1645; δ_H (400 MHz; $CDCl_3$) 7.22 (4H, m, 4 × aromatic C*H*), 6.97 (2H, apparent t, *J* 7.3, 2 × aromatic C*H*), 6.16 (2H, d, *J* 7.6, 2 × aromatic C*H*), 5.62 (2H, s, 2 × C*H*N), 4.13 (2H, ddd, *J* 10.7, 6.4, 4.2, 2 × CH*H*N), 3.79 (2H, ddd, *J* 15.6, 10.7, 6.4, 2 × CH*H*CH_2N), 3.56 (2H, apparent td, *J* 10.7, 5.4, 2 × C*H*HN), 3.03 (2H, ddd, *J* 15.6, 5.4, 4.2, 2 × C*H*HCH_2N) and 2.21 (6H, s, 2 × CH_3); δ_C (100 MHz; $CDCl_3$) 171.3 (2 × CO), 135.8 (2 × aromatic C), 134.6 (2 × aromatic C), 130.1 (2 × aromatic CH), 128.0 (2 × aromatic CH), 127.9 (2 × aromatic CH), 125.8 (2 × aromatic CH), 57.4 (2 × CHN), 44.6 (2 × CH_2N), 28.4 (2 × *C*$H_2$$CH_2$N) and 22.8 (2 × CH_3); *m*/*z* (APCI) 349 (MH^+, 100%).

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline bishydrobromide 7

A mixture of (1*RS*,1′*RS*)-2,2′-diacetyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline **6** (1.7 g, 4.9 mmol), conc. hydrobromic acid (20 ml), acetic acid (20 ml) and water (20 ml) were heated to reflux for 48 h. The solution was concentrated and the resulting residue was washed with water, triturated with toluene and filtered to give a pale brown solid. Recrystallisation form 10% aqueous hydrobromic acid gave the *title compound* (1.7 g, 82%) as a white powder, mp 270–273 °C (Lit. mp 290–292 °C)[9] (Found: C, 50.69; H, 5.14; N, 6.40. $C_{18}H_{22}N_2Br_2$ requires C, 50.73; H, 5.20; N, 6.57%); ν_{max} (Nujol)/cm^{-1} 2927, 2790, 1382 and 771; δ_H (400 MHz; D_2O) 7.27 (4H, m, 4 × aromatic C*H*), 7.11 (2H, apparent t, *J* 8.0, 2 × aromatic C*H*), 6.73 (2H, d, *J* 8.0, 2 × aromatic C*H*), 5.55 (2H, s, 2 × C*H*N), 3.63 (2H, apparent dt, *J* 13.0, 5.8, 2 × CH*H*N), 3.44 (2H, ddd, *J* 13.0, 8.2, 5.4, 2 × C*H*HN), 3.17 (2H, ddd, *J* 17.8, 8.2, 5.5, 2 × CH*H*-CH_2N) and 3.05 (2H, apparent dt, *J* 17.8, 5.8, 2 × C*H*HCH_2N);

δ_C (100 MHz; D_2O) 133.2 (2 × aromatic C), 130.0 (2 × aromatic CH), 129.7 (2 × aromatic CH), 127.8 (2 × aromatic CH), 127.5 (2 × aromatic CH), 125.7 (2 × aromatic C), 57.0 (2 × CHN), 41.0 (2 × CH_2N) and 24.8 (2 × CH_2CH_2N); *m/z* (APCI) 265 (cation $[M - H]^+$, 100%).

2-Phenylethylformamide 9

2-Phenylethylamine (100 g, 0.83 mol) and ethyl formate (182 g, 2.07 mol) were heated to reflux for 12 h. Removal of excess ethyl formate under reduced pressure gave the *title compound* (123 g, 99%) as a colourless oil (Found: C, 72.33; H, 7.73; N, 9.12. $C_9H_{11}NO$ requires C, 72.46; N, 7.43; H, 9.39%); ν_{max} (film)/cm^{-1} 3277, 3029, 1670, 1537, 1184 and 745; δ_H (400 MHz; $CDCl_3$) 8.1 (1H, s, CHO), 7.29 (2H, apparent t, *J* 7.2, 2 × aromatic CH), 7.19 (3H, m, 3 × aromatic CH), 6.2–6.7 (1H, broad s, NH), 3.50 (2H, t, *J* 7.0, CH_2N) and 2.81 (2H, t, *J* 7.0, CH_2CH_2N); δ_C (100 MHz; $CDCl_3$) 161.4 (CHO) 138.6 (aromatic C), 128.8 (aromatic CH), 128.7 (aromatic CH), 126.6 (aromatic CH), 39.2 (CH_2N) and 35.5 (CH_2CH_2N); *m/z* (APCI) 150 (MH^+, 100%).

3,4-Dihydroisoquinoline 10

2-Phenylethylformamide **9** (12 g, 92 mmol) and polyphosphoric acid (70 g) were heated to 160 °C for 12 h. The mixture was poured into ice water and stirred for 2 h. The mixture was made basic with 5 M NaOH and the product was extracted into diethyl ether (3 × 50 ml). The combined ether extracts were dried over sodium sulfate, filtered and concentrated *in vacuo* to yield the *title compound* (9.7 g, 92%) as a pale yellow oil; ν_{max} (film)/cm^{-1} 2935, 1626, 1209 and 756; δ_H (400 MHz; $CDCl_3$) 8.34 (1H, broad s, CHN), 7.25 (1H, apparent td, *J* 7.3, 1.7, aromatic CH), 7.18 (2H, m, 2 × aromatic CH), 7.05 (1H, d, *J* 7.3, aromatic CH), 3.66 (2H, apparent td, *J* 7.7, 2.0, CH_2N) and 2.64 (2H, t, *J* 7.7, CH_2CH_2N); δ_C (100 MHz; $CDCl_3$) 160.7 (CHN), 136.7 (aromatic C), 131.7 (aromatic C), 128.9 (aromatic CH), 127.8 (aromatic CH), 127.6 (aromatic CH), 127.5 (aromatic CH), 47.8 (CH_2N) and 25.4 (CH_2CH_2N); *m/z* (APCI) 132 (MH^+, 100%).

1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline 11

Zinc (15 g, 0.23 mol) and 1,2-dibromoethane (0.2 ml, 2.3 mmol) were heated to reflux in acetonitrile (30 ml) for 1 h. The mixture was allowed to cool to rt, chlorotrimethylsilane (0.2 ml) was added and stirred for a further 45 min. 3,4-Dihydroisoquinoline **10** (15 g, 0.115 mol) was added in one portion and chlorotrimethylsilane (29 ml, 0.23 mol) was added dropwise to maintain a temperature between 35 and 40 °C. The reaction mixture was stirred for a further 12 h after which NH_4OH (40% aqueous solution, 50 ml) and saturated aqueous NH_4Cl solution (50 ml) were added with external cooling (ice bath). The zinc was removed by filtration and the organic phase was separated. The remaining aqueous phase was extracted with CH_2Cl_2 (3 × 30 ml) and all the organic phases were combined, dried over sodium sulfate, filtered and concentrated under reduced pressure to give the *title compound* (13.56 g, 90%) as a viscous yellow oil (1:1 mixture of diastereoisomers); ν_{max} ($CHCl_3$)/cm^{-1} 3300, 2964, 1660, 1274, 1126 and 788; δ_H (400 MHz; $CDCl_3$) 7.27 (2H, d, *J* 7.7, aromatic CH), 7.13 (2H, apparent t, *J* 7.5, 2 × aromatic CH), 7.06 (2H, apparent t, *J* 7.3, 2 × aromatic CH), 6.99 (6H, m, 6 × aromatic CH), 6.92 (2H, m, 2 × aromatic CH), 6.76 (2H, d, *J* 7.8, 2 × aromatic CH), 4.58 (2H, s, 2 × CHN), 4.56 (2H, s, 2 × CHN), 3.11–2.99 (4H, m, 4 × CHHN), 2.84–2.60 (8H, m, 4 × $CHHCH_2N$, 4 × CHHN) and 2.55–2.48 (4H, m, 4 × $CHHCH_2N$); *m/z* (APCI) 265 (MH^+, 100%).

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline bishydrobromide 7 and *meso*-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline bishydrobromide 12

1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **11** (13 g, 49 mmol) was stirred in conc. hydrobromic acid at rt for 8 h. The resulting precipitate was filtered to give a mixture of the (1*RS*,1′*RS*) and *meso* bishydrobromide salts as a white powder. The white powder was heated to boiling point in 10% aqueous hydrobromic acid and filtered hot to give **7** (9.2 g, 44%) as a white powder, mp 270–273 °C, other data as previously reported. The remaining filtrate was allowed to cool and filtered to give **12** (7.8 g, 37%) as an off-white solid, mp 268–270 °C (Lit. mp 264–269 °C)[9]; δ_H (400 MHz; D_2O) 7.32 (2H, apparent t, *J* 7.4, 2 × aromatic CH), 7.26 (2H, d, *J* 7.4, 2 × aromatic CH), 7.18 (2H, apparent t, *J* 7.6, 2 × aromatic CH), 6.99 (2H, d, *J* 8.0, 2 × aromatic CH), 5.51 (2H, s, 2 × CHN), 3.58 (2H, apparent dt, *J* 12.9, 5.2, 2 × CHHN), 3.43 (2H, ddd, *J* 12.9, 9.5, 5.5, 2 × CHHN), 3.07 (2H, ddd, *J* 17.7, 9.5, 5.8, 2 × $CHHCH_2N$) and 2.99 (2H, apparent dt, *J* 17.7, 5.2, 2 × $CHHCH_2N$); δ_C (100 MHz; D_2O) 133.4 (2 × aromatic C), 130.6 (2 × aromatic CH), 130.0 (2 × aromatic CH), 128.5 (2 × aromatic CH), 126.6 (2 × aromatic CH), 126.4 (2 × aromatic C), 57.9 (2 × CHN), 41.6 (2 × CH_2N) and 24.8 (2 × CH_2CH_2N); *m/z* (APCI) 265 (cation $[M - H]^+$, 100%).

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline 1

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline bishydrobromide **7** (10 g, 23.5 mmol) was stirred in CH_2Cl_2 (50 ml) and 5 M NaOH (50 ml) at rt for 1 h. The organic layer was separated and dried over NaOH (pellets). Removal of drying agent and solvent gave an orange solid. Recrystallisation from ethanol–water (4 : 1) gave the *title compound* (5.15 g, 83%) as large colourless crystals, mp 127–128 °C (Lit. mp 135–137 °C)[9] (Found: C, 81.90; H, 8.08; N, 10.55. $C_{18}H_{20}N_2$ requires C, 81.78; H, 7.63; N, 10.60%); ν_{max} (Nujol)/cm^{-1} 3300, 2927, 1126 and 783; δ_H (400 MHz; $CDCl_3$) 7.28 (2H, d, *J* 7.7, 2 × aromatic CH), 7.13 (2H, apparent t, *J* 7.5, 2 × aromatic CH), 7.07 (2H, apparent t, *J* 7.4, 2 × aromatic CH), 7.02 (2H, d, *J* 7.3, 2 × aromatic CH), 4.62 (2H, s, 2 × CHN), 3.06 (2H, ddd, *J* 11.6, 4.8, 2.1, 2 × CHHN), 2.83 (2H, ddd, *J* 15.8, 11.2, 4.8, 2 × $CHHCH_2N$), 2.71 (2H, apparent td, *J* 11.6, 3.0, 2 × CHHN) and 2.54 (2H, apparent dt, *J* 15.8, 2.5, 2 × $CHHCH_2N$); δ_C (100 MHz; $CDCl_3$) 136.6 (2 × aromatic C), 135.2 (2 × aromatic C), 128.4 (2 × aromatic CH), 125.3 (2 × aromatic CH), 125.2 (2 × aromatic CH), 124.2 (2 × aromatic CH) 59.1 (2 × CHN), 41.8 (2 × CH_2N) and 29.4 (2 × CH_2CH_2N); *m/z* (APCI) 265 (MH^+, 100%).

(1*RS*,1′*RS*)-2,2′-Dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline bishydroiodide 13

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (2.26 g, 8.6 mmol) was stirred in iodomethane (10 ml) at room temperature for 6 h. Excess iodomethane was removed under reduced pressure to give the *title compound* (4.2 g, 90%) as a pale yellow powder, mp 210–213 °C (Found: C, 43.56; H, 4.96; N, 4.98. $C_{20}H_{26}N_2I_2$ requires C, 43.82; H, 4.78; N, 5.11%); ν_{max} (Nujol)/cm^{-1} 2612, 1052 and 755; δ_H (400 MHz; D_2O) 7.17 (2H, d, *J* 7.5, 2 × aromatic CH), 7.11 (2H, apparent t, *J* 7.5, 2 × aromatic CH), 6.73 (2H, apparent t, *J* 7.5, 2 × aromatic CH), 6.20 (2H, d, *J* 7.8, 2 × aromatic CH), 4.87 (2H, s, 2 × CHN), 3.94 (2H, ddd, *J* 13.5, 12.0, 6.7, 2 × CHHN), 3.53 (2H, m, 2 × CHHN), 3.20 (4H, m, 2 × CH_2CH_2N) and 2.92 (6H, s, 2 × CH_3); δ_C (100 MHz; D_2O) 129.6 (2 × aromatic CH), 129.0 (2 × aromatic CH), 128.8 (2 × aromatic C), 128.6 (2 × aromatic C), 127.3 (2 × aromatic CH), 127.0 (2 × aromatic CH), 65.2 (2 × CHN), 57.0 (2 × CH_2N), 40.7 (2 × CH_3) and 24.8 (2 × CH_2CH_2N); *m/z* (APCI) 293 (cation $[M - H]^+$, 100%).

(1*RS*,1′*RS*)-2,2′-Dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline 2

(1*RS*,1′*RS*)-2,2′-Dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline bishydroiodide **13** (3 g, 5.5 mmol) was stirred in CH_2Cl_2 (50 ml) and 5 M NaOH (50 ml) at rt for 2 h. The

organic phase was separated, dried over NaOH (pellets), filtered and the solvent was removed under reduced pressure to give a yellow solid. Recrystallisation from ethanol gave the *title compound* (1.3 g, 81%) as colourless crystals, mp 126–128 °C (Found: C, 82.28; H, 8.59; N, 9.89. $C_{20}H_{24}N_2$ requires C, 82.15; H, 8.27; N, 9.58%); ν_{max} (Nujol)/cm^{-1} 2790, 1217 and 758; δ_H (400 MHz; $CDCl_3$) 7.30 (2H, d, *J* 7.0, 2 × aromatic CH), 6.85 (6H, m, 6 × aromatic CH), 3.77 (2H, s, 2 × C*H*N), 3.10 (2H, m, 2 × CH*H*N), 2.83 (2H, m, 2 × CH*H*CH_2N), 2.51 (4H, m, 2 × C*H*HCH_2N and 2 × C*H*HN) and 2.42 (6H, s, 2 × CH_3); δ_C(100 MHz; $CDCl_3$) 137.3 (2 × aromatic C), 136.0 (2 × aromatic C), 128.6 (2 × aromatic CH), 128.0 (2 × aromatic CH), 125.8 (2 × aromatic CH), 124.9 (2 × aromatic CH), 69.1 (2 × CHN), 51.4 (2 × CH_2N), 44.5 (2 × CH_3) and 28.9 (2 × *C*H_2CH_2N); *m*/*z* (APCI) 293 (MH$^+$, 100%).

(1*RS*,1′*RS*)-2,2,2′-Trimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinolinyl-2-ium iodide 14

(1*RS*,1′*RS*)-2,2′-Dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline **2** (0.5 g, 1.7 mmol) was dissolved in iodomethane (5 ml) and stirred at room temperature for 6 h. The *title compound* was removed by filtration (0.62 g, 84%) as a pale yellow powder, mp 200–203 °C (Found: M$^+$, 307.2177. $C_{21}H_{27}N_2$ requires M, 307.2174); ν_{max} (Nujol)/cm^{-1} 1100 and 779; δ_H (400 MHz; $CDCl_3$) 7.10 (1H, d, *J* 7.5, aromatic C*H*), 7.05 (1H, apparent t, *J* 7.5, aromatic C*H*), 6.92 (2H, m, 2 × aromatic C*H*), 6.72 (1H, apparent t, *J* 7.4, aromatic C*H*), 6.60 (1H, apparent t, *J* 7.4, aromatic C*H*), 6.28 (1H, d, *J* 7.8, aromatic C*H*), 6.08 (1H, d, *J* 7.7, aromatic C*H*), 4.64 (1H, d, *J* 5.5, C*H*N$^+$), 4.47 (1H, apparent dd, *J* 13.2, 7.9, CH*H*N$^+$), 4.31 (1H, apparent td, *J* 12.6, 6.7, C*H*HN$^+$), 4.13 (1H, d, *J* 5.5, C*H*N), 3.59 (3H, s, N$^+$CH_3), 3.54 (1H, m, CH*H*N), 3.42 (3H, s, N$^+$CH_3), 3.36 (1H, ddd, *J* 18.7, 12.0, 7.9, CH*H*CH_2N$^+$), 3.24 (1H, apparent dd, *J* 18.7, 6.2, C*H*HCH_2N$^+$), 3.01–2.89 (2H, m, CH*H*CH_2N and C*H*HN), 2.61 (1H, m, C*H*HCH_2N) and 2.30 (3H, s, NCH_3); δ_C (100 MHz; $CDCl_3$) 151.9 (aromatic C), 136.1 (aromatic C), 134.3 (aromatic C), 131.3 (aromatic C), 129.8 (aromatic CH), 129.6 (aromatic CH), 129.1 (aromatic CH), 128.7 (aromatic CH), 127.1 (aromatic CH), 126.8 (aromatic CH), 125.9 (aromatic CH), 125.8 (aromatic CH), 77.0 (CHN$^+$), 65.1 (CHN), 55.8 (CH_2N$^+$), 54.8 (N$^+$$CH_3$), 53.0 (N$^+$$CH_3$), 45.8 ($CH_2$N), 41.3 (N$CH_3$), 24.2 (*C*$H_2CH_2N^+$) and 22.1 (*C*$H_2CH_2$N); *m*/*z* (APCI) 293 (cation [MH − CH_3]$^+$, 100%).

(1*RS*,1′*RS*)-2,2,2′,2′-Tetramethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinolinyl-2,2′-diium bisiodide 15

(1*RS*,1′*RS*)-2,2,2′-Trimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinolinyl-2-ium iodide **14** (50 mg, 0.115 mmol) was dissolved in $CHCl_3$ (10 ml). Iodomethane (2 ml) was added and the mixture was heated to reflux for 24 h. Filtration gave the *title compound* (66 mg, 75%) as a white powder, mp 227–229 °C (Found C, 45.78; H, 5.37; N, 4.68. $C_{22}H_{30}N_2$ requires C, 45.85; H, 5.25; N, 4.86%); ν_{max} (Nujol)/cm^{-1} 1150 and 785; δ_H (400 MHz; D_2O) 7.21–7.13 (6H, m, 6 × aromatic C*H*), 6.95 (2H, m, 2 × aromatic C*H*), 5.68 (2H, s, 2 × C*H*N$^+$), 4.22 (2H, m, 2 × CH*H*N$^+$), 3.92 (2H, apparent dd, *J* 14.3, 8.4, 2 × C*H*HN$^+$), 3.79 (6H, s, 2 × N$^+$CH_3), 3.23 (6H, s, 2 × N$^+$CH_3) and 3.19 (4H, m, 2 × *C*H_2CH_2N$^+$); δ_C (100 MHz; D_2O) 127.8 (2 × aromatic CH), 127.4 (2 × aromatic C), 127.2 (2 × aromatic CH), 125.3 (2 × aromatic CH), 125.2 (2 × aromatic C), 125.0 (2 × aromatic CH), 68.7 (2 × CHN$^+$), 53.5 (2 × CH_2N$^+$), 50.9 (2 × N$^+$$CH_3$), 50.7 (2 × N$^+$$CH_3$) and 20.8 (2 × *C*$H_2CH_2N^+$); *m*/*z* (ESI) 321 (cation [M − H]$^+$, 60%), 307 (cation [M − CH_3]$^+$, 100), 162 (65), 146 (60).

(9b*RS*,9c*RS*)-1,2,4,5,9b,9c-Hexahydro-2a,3a-diaza-benzo[*c*,*g*]-fluorene 16

A mixture of (1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline **1** (1 g, 3.8 mmol), 37% formalin (0.29 ml) and acetonitrile (5 ml) was heated to 60 °C for 3 h. The mixture stirred for a further 15 h at rt. Concentration under reduced pressure gave a brown solid which on recrystallisation from ethanol yielded the *title compound* (0.98 g, 94%) as colourless crystals, mp 119–121 °C (Lit mp 110–125 °C)[9] (Found: MH$^+$, 277.1703. $C_{19}H_{21}N_2$ requires M, 277.1704); ν_{max} (Nujol)/cm^{-1} 2928, 1137 and 785; δ_H (400 MHz; $CDCl_3$) 7.16 (4H, m, 4 × aromatic C*H*), 7.06 (2H, m, 2 × aromatic C*H*), 6.68 (2H, d, *J* 7.6, 2 × aromatic C*H*), 4.09 (2H, s, NCH_2N), 3.92 (2H, s, 2 × C*H*N), 3.12 (2H, m, 2 × CH_2CH*H*N), 2.97–2.86 (4H, m, 2 × CH*H*CH_2N and 2 × CH_2C*H*HN) and 2.76 (2H, m, 2 × C*H*H-CH_2N); δ_C (100 MHz; $CDCl_3$) 136.3 (2 × aromatic C), 134.9 (2 × aromatic C), 129.5 (2 × aromatic CH), 129.0 (2 × aromatic CH), 127.1 (2 × aromatic CH), 125.7 (2 × aromatic CH), 76.2 (NCH_2N), 66.7 (2 × CHN), 47.1 (2 × CH_2N) and 28.0 (2 × *C*H_2CH_2N); *m*/*z* (APCI) 277 (MH$^+$, 100%).

(1*RS*,1′*RS*)-2,2′-Dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline hydrobromide salt 17

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline **1** (0.4 g, 1.37 mmol) was dissolved in 1,2-dibromoethane (10 ml) and stirred at 60 °C for 48 h. The reaction mixture was allowed to cool to room temperature and the 1,2-dibromoethane removed under reduced pressure. Acetone (10 ml) was added to the resulting solid, and the undissolved solid collected by filtration to give the *title compound* (42 mg, 8%) as a white powder, mp 194–196 °C; δ_H (400 MHz; $CDCl_3$) 7.15 (2H, apparent t, *J* 7.4, 2 × aromatic CH), 7.10 (2H, d, *J* 7.1, 2 × aromatic CH), 6.95 (2H, apparent t, *J* 7.2, 2 × aromatic CH), 6.45 (2H, d, *J* 7.8, 2 × aromatic CH), 3.90 (2H, s, 2 × CHN), 3.75–3.65 (2H, m, 2 × CH*H*N), 3.15–2.85 (6H, m, 2 × C*H*HN, 2 × CH_2CH_2N) and 2.65 (6H, s, 2 × CH_3); δ_C (100 MHz; $CDCl_3$) 133.6 (2 × aromatic C), 130.5 (2 × aromatic CH), 130.0 (2 × aromatic C), 129.4 (2 × aromatic CH), 128.8 (2 × aromatic CH), 126.3 (2 × aromatic CH), 67.9 (2 × CHN), 47.8 (2 × CH_2N), 43.4 (2 × CH_3) and 31.3 (2 × *C*H_2CH_2N).

(10b*RS*,10c*RS*)-2a-Methyl-1,2,3,4,5,6,10b,10c-octahydro-4a-aza-2a-azonia-dibenzo[*c*,*g*]phenanthrene bromide 18

(1*RS*,1′*RS*)-2,2′-Dimethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline **2** (0.83 g, 2.8 mmol) was dissolved in 1,2-dibromoethane (10 ml) and stirred at 25 °C for 48 h. The reaction mixture was concentrated under reduced pressure to give an orange solid. The white precipitate which formed on addition of acetone (10 ml), was removed by filtration to give the *title compound* (75 mg, 7%) as a white powder, mp 227–229 °C; ν_{max} (Nujol)/cm^{-1} 1144 and 756; δ_H (400 MHz; $CDCl_3$) 7.29 (1H, apparent t, *J* 7.4, aromatic C*H*), 7.22 (1H, d, *J* 7.6, aromatic C*H*), 7.07 (2H, m, 2 × aromatic C*H*), 6.90 (1H, apparent t, *J* 7.4, aromatic C*H*), 6.60 (1H, m, aromatic C*H*), 6.11 (1H, d, *J* 7.6, aromatic C*H*), 5.40 (1H, d, *J* 7.8, aromatic C*H*), 4.67 (1H, d, *J* 9.5, C*H*N$^+$), 4.50 (1H, m, CH*H*N$^+$), 4.32 (1H, m, C*H*HN$^+$), 4.28 (2H, m, N$^+$CH_2CH_2N), 4.23 (1H, d, *J* 9.5, C*H*N), 3.82 (1H, apparent d, *J* 15.1, N$^+$$CH_2$CH*H*N), 3.79 (1H, m, CH*H*N), 3.47 (3H, s, CH_3), 3.38 (2H, m, *C*H_2CH_2N$^+$), 3.17 (1H, apparent d, *J* 15.1, N$^+$$CH_2$C*H*HN), 2.97 (2H, m, CH*H*CH_2N and CH*H*N) and 2.90 (1H, m, C*H*HCH_2N); δ_C (100 MHz; $CDCl_3$) 135.2 (aromatic C), 132.3 (aromatic CH), 130.7 (aromatic CH), 129.7 (aromatic CH), 129.3 (aromatic C), 129.0 (aromatic CH), 128.6 (aromatic CH), 128.5 (aromatic CH), 128.1 (aromatic CH), 126.7 (aromatic C), 126.2 (aromatic CH), 124.1 (aromatic C), 67.5 (CHN$^+$), 60.7 (CHN), 57.7 (CH_2N$^+$), 52.1 (N$^+$$CH_3$), 49.7 (N$^+$*C*$H_2CH_2$N), 47.6 (N$^+$*C*$H_2$*C*$H_2$N), 44.6 ($CH_2$N), 28.7 (*C*$H_2CH_2N^+$) and 23.3 (*C*$H_2CH_2$N); *m*/*z* (ES) 305 (cation M$^+$, 100%), 81 (100), 79 (97).

(10b*RS*,10c*RS*)-1,2,3,4,5,6,10b,10c-Octahydro-2a,4a-diazadibenzo[*c*,*g*]phenanthrene 19

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (0.34 g, 1.29 mmol) was dissolved in 1,2-dibromoethane (10 ml) and stirred at 25 °C for 48 h. The reaction mixture was concentrated under reduced pressure to give a pale yellow crystalline solid. Recrystallisation from ethanol–water (4 : 1) gave the *title compound* (0.37 g, 64%) as colourless crystals, mp 134–135 °C (Found: MH^+, 291.1859. $C_{20}H_{23}N_2$ requires M, 291.1861); ν_{max} (Nujol)/cm^{-1} 1155 and 735; δ_H (400 MHz; $CDCl_3$) 7.06 (4H, m, 4 × aromatic C*H*), 6.93 (2H, apparent t, *J* 6.8, 2 × aromatic C*H*), 6.62 (2H, broad s, 2 × aromatic C*H*), 4.54 (2H, s, 2 × C*H*N), 3.40 (2H, m, 2 × CH*H*N), 3.07–2.99 (6H, m, 2 × C*H*HN, 2 × CH*H*CH_2N and NC*H*HC*H*HN), 2.82 (2H, apparent broad d, *J* 8.4, NCH*H*CH*H*N) and 2.73 (2H, m, 2 × C*H*HCH_2N); δ_C (100 MHz; $CDCl_3$) 135.5 (2 × aromatic C), 135.5 (2 × aromatic C), 129.5 (2 × aromatic CH), 128.3 (broad, 2 × aromatic CH), 126.9 (2 × aromatic CH), 125.8 (broad, 2 × aromatic CH), 58.7 (2 × CHN), 48.5 (broad, 2 × CH_2N), 47.8 (broad, NCH_2CH_2N) and 26.6 (broad, 2 × *C*H_2CH_2N); *m*/*z* (APCI) 291 (MH^+, 100%).

(1*RS*,1′*RS*)-2,2′-(2-Bromobenzyl)-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline 20

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (0.1 g, 0.38 mmol) and 2-bromobenzyl bromide (0.19 g, 0.76 mmol), were stirred at 25 °C in THF (30 ml) for 12 h. A white precipitate of the hydrobromide salt **7** was removed by filtration. The remaining filtrate was concentrated under reduced pressure and recrystallised from ethanol to give the *title compound* (0.112 g, 49%) as colourless crystals, mp 135–137 °C (Found: C, 64.02; H, 5.09; N, 4.46. $C_{32}H_{30}N_2$ requires C, 63.80; H, 5.02; N, 4.65%); ν_{max} (Nujol)/cm^{-1} 2916, 2814 and 744; δ_H (400 MHz; $CDCl_3$) 7.48–7.40 (4H, m, 4 × aromatic C*H*), 7.20–7.14 (4H, m, 4 × aromatic C*H*), 7.02 (2H, apparent td, *J* 7.6, 1.6, 2 × aromatic C*H*), 6.90 (2H, apparent td, *J* 7.3, 1.2, 2 × aromatic C*H*), 6.86–6.79 (4H, m, 4 × aromatic C*H*), 4.13 (2H, s, 2 × C*H*N), 3.89 (2H, d, *J* 14.2, 2 × NC*H*H), 3.75 (2H, d, *J* 14.2, 2 × NCH*H*), 3.25 (2H, ddd, *J* 10.7, 6.1, 4.1, 2 × CH*H*N) and 2.62–2.52 (6H, m, 2 × C*H*$_2$CH$_2$N and 2 × C*H*HN); δ_C (100 MHz; $CDCl_3$) 139.1 (2 × aromatic C), 136.6 (2 × aromatic C), 133.1 (2 × aromatic CH), 131.4 (2 × aromatic CH), 129.1 (2 × aromatic CH), 128.7 (2 × aromatic CH), 128.5 (2 × aromatic C), 128.2 (2 × aromatic CH), 128.0 (2 × aromatic CBr), 127.6 (2 × aromatic CH), 126.1 (2 × aromatic CH), 125.1 (2 × aromatic CH), 67.7 (2 × CHN), 59.6 (2 × NCH_2Ar), 46.8 (2 × CH_2N) and 27.5 (2 × *C*H_2CH_2N); *m*/*z* (APCI) 605 (MH^+ {2 × ^{81}Br}, 39%), 603 (MH^+ {^{79}Br^{81}Br}, 100), 601 (MH^+ {2 × ^{79}Br}, 43).

(1*RS*,1′*RS*)-2-Ethoxycarbonylmethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline 21

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (0.5 g, 1.89 mmol), ethyl 2-bromoacetate (0.2 ml, 1.89 mmol) and CH_2Cl_2 (30 ml) were stirred at rt for 12 h. The mixture was concentrated under reduced pressure to give a yellow solid. A white precipitate which formed on the addition of $CHCl_3$ (20 ml), was removed by filtration to give the hydrobromide salt **7** (0.1 g, 12%) as a white powder. Concentration of the filtrate and recrystallisation from ethanol–water (4 : 1), gave the *title compound* (0.5 g, 76%) as a white solid, mp 187–189 °C (Found: MH^+, 351.2069. $C_{22}H_{27}N_2O_2$ requires M, 351.2072); ν_{max} (Nujol)/cm^{-1} 3387, 1724, 1222 and 761; δ_H (400 MHz; $CDCl_3$) 9.20 (1H, broad s, N*H*), 7.26 (1H, apparent t, *J* 7.5, aromatic C*H*), 7.19 (1H, d, *J* 7.2, aromatic C*H*), 7.12 (1H, apparent t, *J* 7.2, aromatic C*H*), 7.09 (1H, d, *J* 7.2, aromatic C*H*), 7.00 (1H, apparent t, *J* 7.4, aromatic C*H*), 6.73 (1H, apparent t, *J* 7.4, aromatic C*H*), 6.39 (1H, d, *J* 7.6, aromatic C*H*), 5.56 (1H, d, *J* 7.6, aromatic C*H*), 4.70 (1H, dd, *J* 10.7, 6.5, C*H*NH), 4.23–4.06 (2H, m, C*H*$_2$CH$_3$), 3.83–3.79 (2H, m, CH*H*N and CH*H*NH), 3.43 (2H, apparent s, NC*H*$_2$CO), 3.37 (1H, d, *J* 10.7, C*H*N), 3.11–2.84 (5H, m, CH*H*CH$_2$NH, C*H*HN, C*H*HCH$_2$-NH, C*H*HNH and CH*H*CH$_2$N), 2.74 (1H, apparent dd, *J* 17.2, 4.8, C*H*HCH$_2$N) and 1.20 (3H, t, *J* 7.1, C*H*$_3$); δ_C (100 MHz; $CDCl_3$) 173.5 (CO), 135.0 (aromatic C), 134.6 (aromatic C), 131.9 (aromatic CH), 131.7 (aromatic CH), 129.8 (aromatic CH), 129.4 (aromatic CH), 129.0 (aromatic C), 128.7 (aromatic CH), 128.5 (aromatic C), 128.4 (aromatic CH), 127.0 (aromatic CH), 125.2 (aromatic CH), 63.7 (CHNH), 62.5 (*C*H$_2$CH$_3$), 57.4 (CHN), 54.3 (N*C*H$_2$CO), 44.7 (CH$_2$N), 41.9 (CH$_2$NH), 26.6 (*C*H$_2$CH$_2$NH), 24.1 (*C*H$_2$CH$_2$N) and 14.5 (CH$_3$); *m*/*z* (APCI) 351 (MH^+, 100%).

(10b*RS*,10c*RS*)-1,2,5,6,10b,10c-Hexahydro-2a,4a-diazadibenzo[*c*,*g*]phenanthren-3(4*H*)-one 22

(1*RS*,1′*RS*)-2-Ethoxycarbonylmethyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline **21** (0.15 g, 0.43 mmol) and NaH (60% dispersion in oil, 0.103 g, 4.29 mmol) were heated to reflux in toluene (30 ml) for 4.5 h. The reaction mixture was quenched with water (30 ml) and extracted into ethyl acetate (30 ml). The organic phase was dried over sodium sulfate, filtered and the solvent was removed under reduced pressure to give the *title compound* (76 mg, 59%) as a white solid, 159–160 °C (Found: MH^+, 305.1655. $C_{20}H_{21}N_2O$ requires M, 305.1654); ν_{max} (Nujol)/cm^{-1} 1674, 1144 and 758; δ_H (400 MHz; $CDCl_3$) 7.25–7.10 (5H, m, aromatic C*H*), 7.06 (1H, d, *J* 7.6, aromatic C*H*), 7.00 (1H, apparent t, *J* 7.4, aromatic C*H*), 6.87 (1H, d, *J* 7.6, aromatic C*H*), 4.81 (1H, d, *J* 7.4, C*H*NCO), 4.21 (1H, apparent dt, *J* 12.6, 6.5, CH$_2$CH*H*NCO), 4.11 (1H, d, *J* 7.4, C*H*N), 3.46 (1H, d, *J* 16.2, NC*H*HCO), 3.20–3.14 (4H, m, CH$_2$C*H*HNCO, C*H*$_2$N and NCH*H*CO), 3.01 (1H, apparent dt, *J* 15.6, 6.5, CH*H*CH$_2$NCO) and 2.87–2.76 (3H, m, C*H*HCH$_2$NCO and C*H*$_2$CH$_2$N); δ_C (100 MHz; $CDCl_3$) 167.8 (CO), 137.4 (aromatic C), 137.3 (aromatic C), 135.3 (aromatic C), 134.9 (aromatic C), 129.5 (aromatic CH), 128.8 (aromatic CH), 128.2 (aromatic CH), 127.8 (aromatic CH), 127.4 (aromatic CH), 126.7 (aromatic CH), 126.4 (aromatic CH), 126.1 (aromatic CH), 62.4 (N*C*H$_2$CO), 58.7 (*C*HNCO), 57.7 (CHN), 51.4 (*C*H$_2$NCO), 41.4 (CH$_2$N), 28.5 (*C*H$_2$CH$_2$N) and 28.3 (*C*H$_2$CH$_2$N); *m*/*z* (APCI) 305 (MH^+, 100%).

(1*RS*,1′*RS*)-2,2′-Dipropionyl-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline 23

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (1 g, 3.78 mmol), triethylamine (1.06 ml, 7.6 mmol) and DMAP (0.005 g) were dissolved in CH_2Cl_2 (30 ml) and stirred at rt for 0.5 h. Propionyl chloride (0.66 ml, 7.6 mmol) was added and the solution was stirred for a further 12 h. A white precipitate was removed by filtration and the filtrate was washed with 0.5M HCl (3 × 20 ml), dried over sodium sulfate, filtered and the solvent removed under reduced pressure to give a colourless crystalline solid. Recrystallisation from ethanol/water (4:1) gave the *title compound* (1.31 g, 92%) as colourless crystals, mp 176–177 °C (Found: MH^+, 377.2226. $C_{24}H_{29}N_2O_2$ requires M, 377.2229); ν_{max} (Nujol)/cm^{-1} 1650, 1298 and 771; δ_H (400 MHz; $CDCl_3$) 7.15 (2H, d, *J* 7.2, 2 × aromatic CH), 7.11 (2H, apparent t, *J* 7.3, 2 × aromatic CH), 6.78 (2H, apparent t, *J* 7.2, 2 × aromatic CH), 5.99 (2H, d, *J* 7.5, 2 × aromatic CH), 5.50 (2H, s, 2 × C*H*N), 3.95 (2H, ddd, *J* 11.0, 6.5, 4.0, 2 × CH*H*N), 3.65 (2H, ddd, *J* 15.7, 10.4, 6.5, 2 × CH*H*CH$_2$N), 3.37 (2H, apparent td, *J* 10.8, 5.5, 2 × C*H*HN), 2.86 (2H, ddd, *J* 15.7, 5.5, 4.0, 2 × C*H*HCH$_2$N), 2.18–2.33 (4H, m, 2 × C*H*$_2$CH$_3$) and 1.07 (6H, t, *J* 7.4, 2 × C*H*$_3$); δ_C (100 MHz; $CDCl_3$) 174.4 (2 × CO), 135.9 (2 × aromatic C), 134.9 (2 × aromatic C), 130.1 (2 × aromatic CH), 127.9 (2 × aromatic CH), 127.8 (2 × aromatic CH), 125.7 (2 × aromatic CH), 57.5 (2 × CHN), 43.7 (2 × CH$_2$N), 28.4 (2 × *C*H$_2$CH$_2$N), 27.6 (2 × *C*H$_2$CH$_3$) and 9.6 (2 × CH$_3$); *m*/*z* (APCI) 377 (MH^+, 100%).

(1*RS*,1′*RS*)-2,2′-Bis(phenylacetyl)-1,1′,2,2′,3,3′,4,4′-octahydro-1,1′-biisoquinoline 24

(1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (1.0 g, 3.79 mmol), triethylamine (1.1 ml, 7.58 mmol), DMAP (0.005 g) and phenylacetyl chloride (1.0 ml, 7.58 mmol) were stirred in CH_2Cl_2 (30 ml) at 25 °C, for 12 h. The reaction mixture was washed with water (3 × 30 ml) and 2 M aqueous hydrochloric acid (30 ml), dried over sodium sulfate and filtered. Concentration under reduced pressure and recrystallisation from ethanol–water (4 : 1) gave the *title compound* (1.70 g, 90%) as colourless crystals, mp 123–125 °C (Found: MH^+, 501.2539. $C_{34}H_{33}N_2O_2$ requires M, 501.2537); ν_{max} (Nujol)/cm^{-1} 1646 and 728; δ_H (400 MHz; $CDCl_3$) 7.27–7.07 (14H, m, aromatic C*H*), 6.78 (2H, m, 2 × aromatic C*H*), 5.98 (2H, d, *J* 7.6, aromatic C*H*), 5.54 (2H, s, 2 × C*H*N), 4.05 (2H, m, 2 × CH*H*N), 3.59–3.42 (8H, m, 2 × COCH_2, 2 × C*H*HN and 2 × CH*H*CH_2N) and 2.72 (2H, apparent dt, *J* 14.8, 4.6, 2 × C*H*HCH_2N); δ_C (100 MHz; $CDCl_3$) 171.8 (2 × CO), 135.7 (2 × aromatic C), 135.4 (2 × aromatic C), 134.5 (2 × aromatic C), 130.2 (2 × aromatic CH), 129.7 (4 × aromatic CH), 129.1 (4 × aromatic CH), 128.6 (2 × aromatic CH), 128.0 (2 × aromatic CH), 127.2 (2 × aromatic CH), 125.7 (2 × aromatic CH), 57.5 (2 × CHN), 44.0 (2 × CCH_2), 41.5 (2 × CH_2N) and 28.3 (2 × *C*H_2CH_2N); *m*/*z* (APCI) 501 (MH^+, 100%).

(1*RS*,1′*RS*)-2,2′-Dibenzoyl-1,1′,2,2′,3,3′4,4′-octahydro-1,1′-biisoquinoline 25

Benzoic acid (0.185 g, 1.52 mmol), 1-[3-(dimethylamino)-propyl]-3-ethylcarbodimide hydrochloride (0.29 g, 1.52 mmol) and CH_2Cl_2 (30 ml) were stirred at 25 °C for 0.5 h. (1*RS*,1′*RS*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (0.2 g, 0.76 mmol) was added and the reaction mixture was stirred at 25 °C for a further 12 h. The reaction mixture was washed with water (3 × 30 ml) and 5% aqueous triethylamine (30 ml), dried over sodium sulfate, filtered and concentrated under reduced pressure. Recrystallisation from ethanol–water (4 : 1) gave the *title compound* (0.18 g, 50%) as colourless crystals, mp 199–201 °C (Found: MH^+, 473.2226. $C_{32}H_{29}N_2O_2$ requires M, 473.2229); ν_{max} (Nujol)/cm^{-1} 1620, 1268, 755 and 705; δ_H (400 MHz; $CDCl_3$) 7.36–7.10 (14H, m, aromatic C*H*), 6.79 (2H, m, 2 × aromatic C*H*), 6.11 (2H, s, C*H*N), 6.04 (2H, d, *J* 7.7, 2 × aromatic C*H*), 4.20 (2H, ddd, *J* 13.4, 8.7, 6.0, 2 × CH*H*N), 3.68 (2H, ddd, *J* 13.4, 6.9, 5.3, 2 × C*H*HN), 3.13 (2H, apparent dt, *J* 16.5, 5.5, 2 × CH*H*CH_2N) and 2.85 (2H, ddd, *J* 16.5, 8.7, 6.9, 2 × C*H*HCH_2N); δ_C (100 MHz; $CDCl_3$) 172.0 (2 × CO), 136.9 (2 × aromatic C), 134.9 (2 × aromatic C), 133.4 (2 × aromatic C), 131.1 (2 × aromatic CH), 129.8 (2 × aromatic CH), 129.0 (4 × aromatic CH), 128.7 (2 × aromatic CH), 128.0 (2 × aromatic CH), 127.1 (4 × aromatic CH), 125.4 (2 × aromatic CH), 55.9 (2 × CHN), 43.5 (2 × CH_2N) and 28.9 (2 × *C*H_2CH_2N); *m*/*z* (APCI) 473 (MH^+, 100%).

(1*S*,1′*S*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline D-(+)-α-bromocamphor-π-sulfonic acid salt

(1*RS*,1′*RS*)-1,1′2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (0.25 g, 0.95 mmol) and D-(+)-α-bromocamphor-π-sulfonic acid ammonium salt (0.31 g, 0.95 mmol) were recrystallised from ethanol (5 ml) to give the *title compound* (0.24 g, 44%) as colourless crystals, mp 183–185 °C; ν_{max} (Nujol)/cm^{-1} 3424, 2964, 1756, 1636, 1210, 1178, 1148, 1038 and 764; δ_H (400 MHz; $CDCl_3$) 7.26–7.15 (6H, m, 6 × aromatic C*H*), 7.07 (2H, d, *J* 7.5, 2 × aromatic C*H*), 4.79 (2H, s, 2 × C*H*N), 4.41 (1H, d, *J* 4.8, C*H*Br), 3.50 (2H, m, 2 × CH*H*N), 3.07 (4H, m, 2 × C*H*HN and 2 × CH*H*CH_2N), 2.86 (1H, d, *J* 14.2, HC*H*SO_3), 2.84–2.78 (3H, m, 2 × C*H*HCH_2N and C*H*CHBr), 2.46 (1H, d, *J* 14.2, *H*CHSO_3), 1.94 (2H, m, CHCH_2), 1.50 (1H, m, CCH*H*), 1.33 (1H, m, CC*H*H), 1.00 (CH_3) and 0.85 (CH_3); δ_C (100 MHz; $CDCl_3$) 212.3 (CO), 135.2 (2 × aromatic C), 130.0 (2 × aromatic C), 129.6 (2 × aromatic CH), 128.3 (2 × aromatic CH), 127.3 (2 × aromatic CH), 127.2 (2 × aromatic CH), 59.6 (*C*CO), 58.9 (2 × CHN), 53.8 (O_3SCH_2), 53.5 (CHBr), 47.2 (C), 46.8 (*C*HCHBr), 40.9 (2 × CH_2N), 30.2 (CH_2), 27.7 (2 × *C*H_2CH_2N), 22.1 (CH_2), 17.6 (CH_3) and 9.9 (CH_3).

(1*S*,1′*S*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline (*S*,*S*)-1

(1*S*,1′*S*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline D-(+)-α-bromocamphor-π-sulfonic acid salt (0.25 g, 0.44 mmol) was stirred in CH_2Cl_2 (20 ml) and 5 M NaOH (20 ml) at rt for 2 h. The organic layer was separated and dried over NaOH (pellets). Removal of drying agent and solvent gave a colourless solid. Recrystallisation from ethanol–water (4 : 1) gave the *title compound* (0.103 g, 90%) as large colourless crystals, mp 127–128 °C; $[\alpha]_D^{298}$ +968 (*c*. 0.05, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 7.32 (2H, d, *J* 7.7, 2 × aromatic C*H*), 7.17 (2H, apparent t, *J* 7.7, 2 × aromatic C*H*), 7.10 (2H, apparent t, *J* 7.7, 2 × aromatic C*H*), 6.98 (2H, d, *J* 7.7, 2 × aromatic C*H*), 4.63 (2H, s, 2 × C*H*N), 3.06 (2H, ddd, *J* 11.6, 4.9, 2.1, 2 × CH*H*N), 2.85 (2H, ddd, *J* 15.5, 11.2, 4.9, 2 × CH*H*CH_2N), 2.76 (2H, apparent td, *J* 11.6, 3.0, 2 × C*H*HN) and 2.55 (2H, apparent dt, *J* 15.5, 2.4, 2 × C*H*HCH_2N); δ_C (100 MHz; $CDCl_3$) 136.8 (2 × aromatic C), 135.3 (2 × aromatic C), 128.4 (2 × aromatic CH), 125.4 (2 × aromatic CH), 125.2 (2 × aromatic CH), 124.4 (2 × aromatic CH) 59.1 (2 × CHN), 41.9 (2 × CH_2N) and 29.5 (2 × *C*H_2CH_2N).

(1*R*,1′*R*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline L-(−)-α-bromocamphor-π-sulfonic acid salt

(1*RS*,1′*RS*)-1,1′2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline **1** (0.25 g, 0.95 mmol) and L-(−)-α-bromocamphor-π-sulfonic acid ammonium salt (0.31 g, 0.95 mmol) were recrystallised from ethanol (5 ml) to give the *title compound* (0.23 g, 42%) as colourless crystals, mp 183–185 °C; ν_{max} (Nujol)/cm^{-1} 3074, 1752, 1202, 1146, 1042 and 759; δ_H (400 MHz; $CDCl_3$) 7.27–7.15 (6H, m, 6 × aromatic C*H*), 7.08 (2H, d, *J* 7.2, 2 × aromatic C*H*), 4.80 (2H, s, 2 × C*H*N), 4.42 (1H, d, *J* 4.8, C*H*Br), 3.49 (2H, m, 2 × CH*H*N), 3.09 (4H, m, 2 × C*H*HN and 2 × CH*H*CH_2N), 2.95 (1H, d, *J* 14.1, CH*H*SO_3), 2.87–2.80 (3H, m, 2 × C*H*HCH_2N and C*H*CHBr), 2.48 (1H, d, *J* 14.1, C*H*HSO_3), 1.98 (2H, m, CHCH_2), 1.54 (1H, m, CCH*H*), 1.35 (1H, m, CC*H*H), 1.04 (CH_3) and 0.86 (CH_3); δ_C (100 MHz; $CDCl_3$) 212.3 (CO), 135.6 (2 × aromatic C), 130.4 (2 × aromatic C), 129.9 (2 × aromatic CH), 128.7 (2 × aromatic CH), 127.6 (2 × aromatic CH), 127.5 (2 × aromatic CH), 59.9 (CCO), 59.3 (2 × CHN), 54.0 (O_3SCH_2), 53.9 (CHBr), 47.4 (C) 47.2 (*C*HCHBr), 41.3 (2 × CH_2N), 30.6 (CH_2), 28.0 (2 × *C*H_2CH_2N), 22.4 (CH_2), 17.9 (CH_3) and 10.3 (CH_3).

(1*R*,1′*R*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline (*R*,*R*)-1

(1*R*,1′*R*)-1,1′,2,2′,3,3′,4,4′-Octahydro-1,1′-biisoquinoline L-(−)-α-bromocamphor-π-sulfonic acid salt (0.6 g, 1.04 mmol) was stirred in CH_2Cl_2 (20 ml) and 5 M NaOH (20 ml) at rt for 2 h. The organic layer was separated and dried over NaOH (pellets). Removal of drying agent and solvent gave a colourless solid. Recrystallisation from ethanol–water (4 : 1) gave the *title compound* (025 g, 91%) as large colourless crystals, mp 127–128 °C; $[\alpha]_D^{298}$ −912 (*c*. 0.05, $CHCl_3$); δ_H (400 MHz; $CDCl_3$ $[\alpha]_D^{298}$) 7.28 (2H, d, *J* 7.7, 2 × aromatic C*H*), 7.13 (2H, apparent t, *J* 7.5, 2 × aromatic C*H*), 7.07 (2H, apparent t, *J* 7.4, 2 × aromatic C*H*), 7.02 (2H, d, *J* 7.3, 2 × aromatic C*H*), 4.62 (2H, s, 2 × C*H*N), 3.06 (2H, ddd, *J* 11.6, 4.9, 2.1, 2 × CH*H*N), 2.83 (2H, ddd, *J* 15.8, 11.2, 4.9, 2 × CH*H*CH_2N), 2.71 (2H, apparent td, *J* 11.6, 3.0, 2 × C*H*HN) and 2.54 (2H, apparent dt, *J* 15.8, 2.6, 2 × C*H*HCH_2N); δ_C (100 MHz; $CDCl_3$) 136.6 (2 × aromatic C), 135.2 (2 × aromatic C), 128.4 (2 × aromatic CH), 125.3 (2 ×

aromatic CH), 125.2 (2 × aromatic CH), 124.2 (2 × aromatic CH) 59.1 (2 × CHN), 41.8 (2 × CH_2N) and 29.4 (2 × CH_2CH_2N).

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