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Intramolecular trapping of amides by 1-lithio-1-bromocyclopropanes

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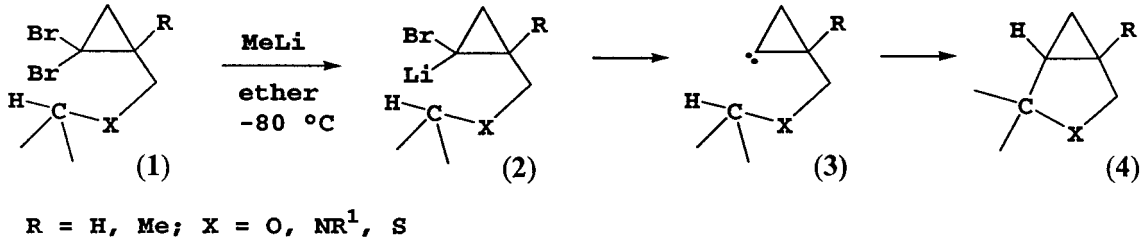
Abstract—Reaction of 2-acylaminomethyl-1,1-dibromocyclopropanes with methyllithium at −90°C leads to selective bromine-lithium exchange and cyclisation to give a 1-bromo-3-azabicyclo[3.1.0]hexan-2-ol.

The reaction of 1,1-dibromocyclopropanes with methyllithium is known to lead to a very rapid lithium-halogen exchange, followed in most cases by formal elimination of lithium bromide to produce a cyclopropylidene (or a related carbenoid).[1] If the reaction is carried out at low temperature or, in some cases, if there is a co-ordinating group present in the molecule, the organolithium may be trapped in intermolecular processes by reaction with electrophiles.[1] There are many examples of intramolecular trapping of the cyclopropylidene; thus insertion into CH bonds is a characteristic reaction of carbenes and is of considerable synthetic potential,[2,3] e.g., in the presence of monocyclic ethers,[4] amines[5] and sulfides[6] of the general structure (**1**) insertion occurs exclusively at the CH bond adjacent to the heteroatom and 5,6-related to the carbenic carbon (1,5-insertion) to give (**4**) (Scheme 1). This type of insertion was the key step in a total synthesis of the natural product 3,4-methanoproline.[7]

There are fewer cases of similar intramolecular reactions of the lithiobromides acting as nucleophiles; one such is the 1,3-elimination of BrCl from 1,1-dibromo-2-chloromethylcyclopropanes on reaction with methyllithium.[8] In another type of process, the reaction of the tetrabromide (**5**) with methyllithium leads to the tetracyclic diketone (**6**) apparently by a double intramolecular trapping of the derived lithiobromides by the ester group in the adjacent cyclopropane ring.[9] In a rather simpler system, methyl 3-(2,2-dibromocycloprop-1-yl)propanoate is converted into 1-bromobicyclo[3.1.0]hexan-2-one by reaction with methyllithium.[10] We have recently reported that reaction of esters of type (**7**) with MeLi leads to hemiacetals (**9**), apparently derived by cyclisation of an intermediate lithiobromide (**8**).[11]

We now report that reaction of the amide (**11**), and related compounds with methyllithium also leads to the intramolecular trapping of a lithiobromocyclopropane with the formation of a five-membered ring.[12]

The amide (**11**) was obtained as shown in Scheme 3. Reaction of the (*S*)-bromide (**10**)[7] with (*R*)-α-phenylethylamine gave the corresponding secondary amine; this was treated with trifluoroacetic anhydride to give amide (**11**). This compound showed the signals for two rotamers about the amide bond by ^{1}H and ^{13}C NMR spectroscopy. The amide



Scheme 1.

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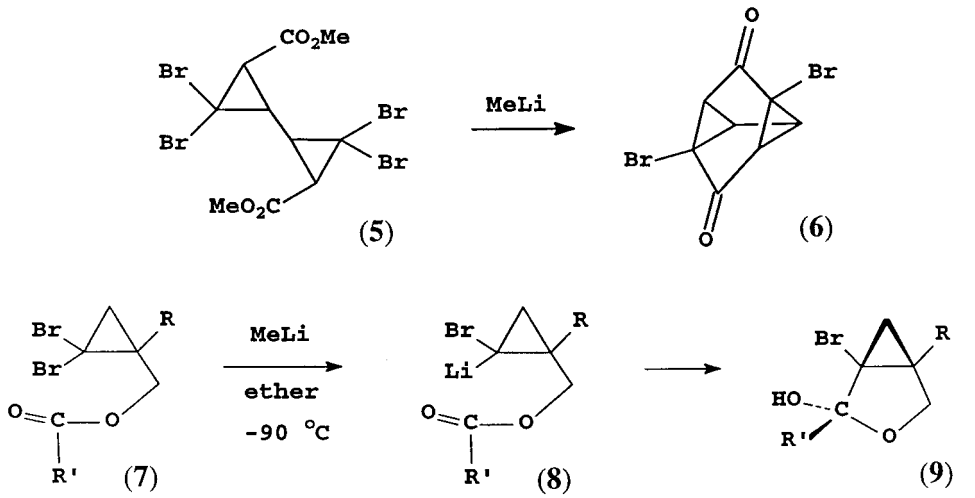


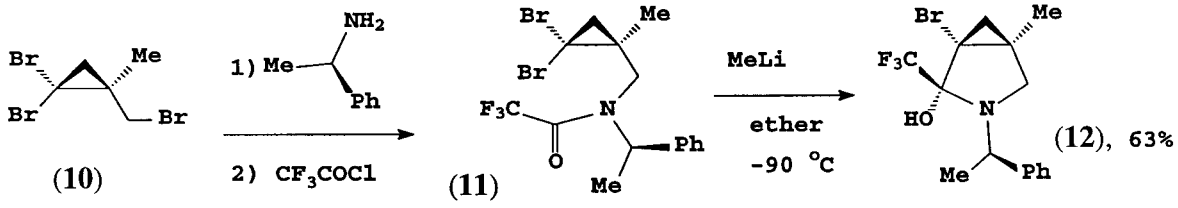
Scheme 2.

(**11**) gave a single product, hemiaminal (**12**), on reaction with methyllithium (Scheme 3).

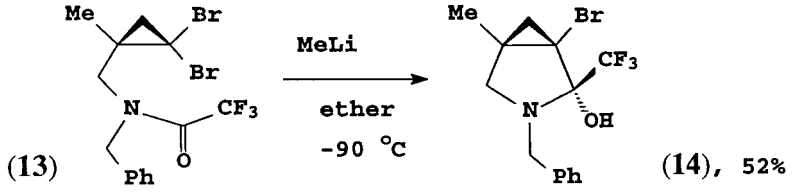
The stereochemistry at C-2 was assigned by analogy with (**9**) and with that of a related azabicycle discussed later.

Amide (**13**), derived from *N*-benzyl-*N*-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)amine, behaved in a similar manner (Scheme 4).

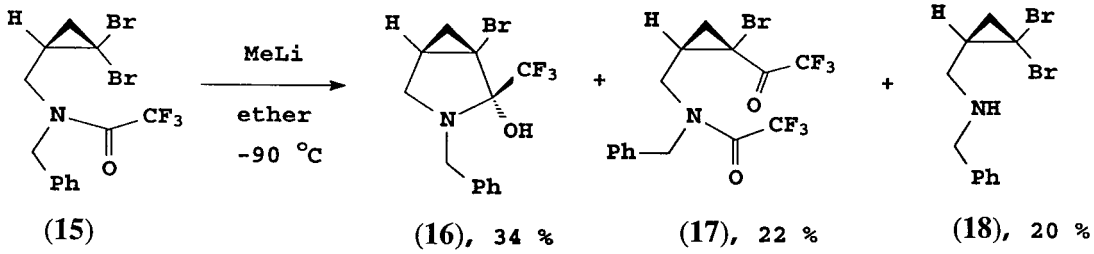
The corresponding racemic amide (**15**), without a methyl group at the cyclopropane C-1 position showed a more complex reaction when treated with methyllithium under the same conditions. A mixture of three compounds was obtained. The expected hemiaminal (**16**) was formed only in 34% yield (Scheme 5). In the ^{1}H NMR spectrum, this exhibited a similar coupling behaviour to that with the analogous hemiacetals. The vicinal coupling constant of H_{endo}-4 was zero, thus the signal, which appeared at 2.94 ppm, showed only the geminal coupling constant (9.0 Hz) from coupling with H_{exo}-4. In the ^{13}C NMR spectrum, the carbon at the hemiaminal centre (C-2) appeared as a quartet (J=30.5 Hz) at 90.3 ppm due to CF coupling. The trifluoromethyl group also gave a quartet (J=289.0 Hz) at



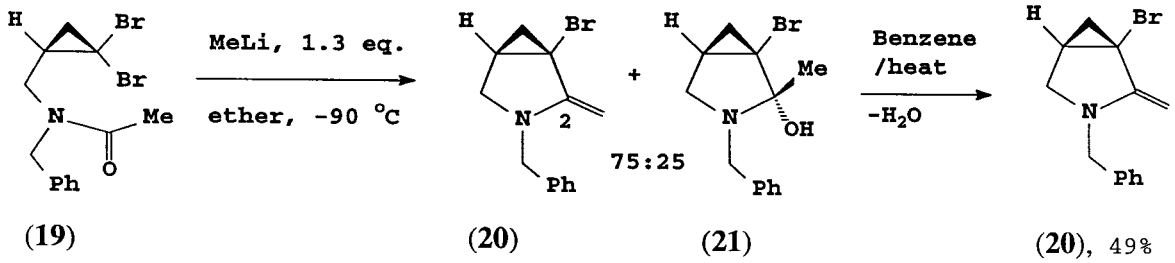
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

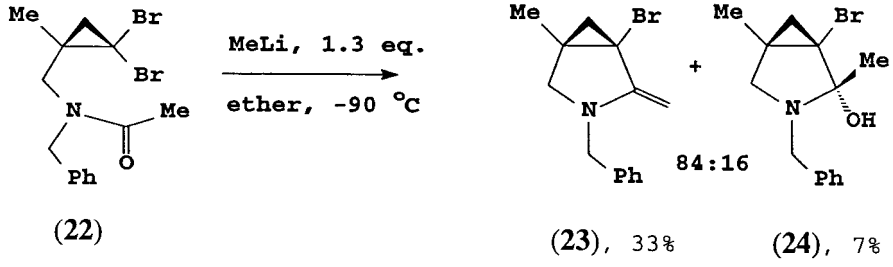
124.1 ppm. Two other products were identified as the keto-amide (**17**) (22%) and hydrolysed amine (**18**) (20%). These compounds are presumably derived from an intermolecular reaction of the lithiocyclopropane derived from (**15**) with another molecule of (**15**). It is not clear whether the ring trifluoroacetyl group in (**17**) is *cis* or *trans* with regard to the amide function. Compound (**17**) was again present as a mixture of two rotamers about the amide bond by ^{1}H and ^{13}C NMR. In the ^{13}C NMR the two carbonyl groups appeared as quartets (J=39 Hz each); the major rotamer of (**17**) gave a signal for the amide carbonyl at 157.8 ppm and for the ketone at 184.7 ppm.

When the amide (**19**) was treated at low temperature (−90°C) with 1.3 mol.equiv. of methyllithium for 30 min, two products were isolated in moderate yield (Scheme 6), the enamine (**20**) and the aminal (**21**). The methylene group of the enamine showed two singlets in the ^{1}H NMR spectrum at 3.82 ppm and 4.02 ppm and two ^{13}C signals at 75.5 ($C{=}CH_2$) and 154.1 (C-2); these values are very close to those reported for *N*-alkyl-2-methylenetetrahydropyrrole.[13] If the mixture of (**20**) and (**21**) was heated in benzene and water was removed by azeotropic distillation, the product was (**20**). When (**20**) was dissolved in deuterochloroform and the proton NMR spectrum run immediately, only the signals corresponding to the enamine were detected. However, if the solution was allowed to stand for some hours, the signals corresponding to (**21**) were again observed in addition to those for (**20**), suggesting an acid catalysed equilibrium was being established involving traces of water in the solvent. The enamine decomposed over several days at room temperature in $CDCl_3$ to give unidentified products.

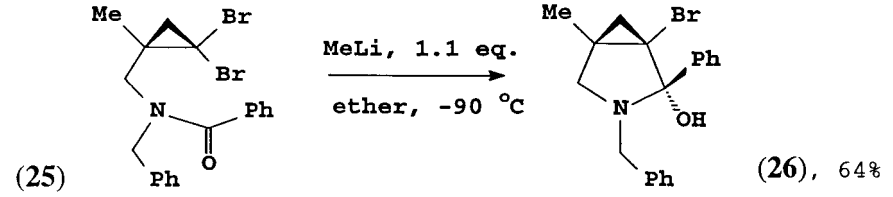
In the same way, the methyl-substituted analogue (**22**) gave (**23**) and (**24**) (Scheme 7) and the corresponding benzoyl derivative (**25**) led to (**26**) (Scheme 8).

The stereochemistry of (**26**) was established by n.O.e. experiments which showed that irradiation of the *o*-hydrogens of the 2-phenyl group caused a 4.5% enhancement in the signal for the *endo*-cyclopropane proton. Indeed, in the calculated *endo*-(**26**) structure (by HyperChem 5.0 with AM1 method, until gradient became less then 0.1 kcal/(Åmol)), these hydrogens are very close each to other—just 0.24 nm apart. Calculations on *exo*-(**26**) gave a structure with these hydrogens far from each other (Fig. 1). The other n.O.e. enhancements were consistent with the calculated preferred conformation shown for *endo*-(**26**).

The ester (**27**, X=O, R=H) has been shown to react with methyllithium to produce compound (**28**) by initial hemiacetal formation, followed by ring-opening and addition of the resulting alcohol to the β-position of the enone (Scheme 9).[11] However, in the case of compound (**27**, X=NCH_2Ph, R=Me), the product was a white powder with a broad NMR spectrum which was thought to be a polymer. Microanalysis showed a carbon percentage slightly lower then that in the



Scheme 7.



Scheme 8.

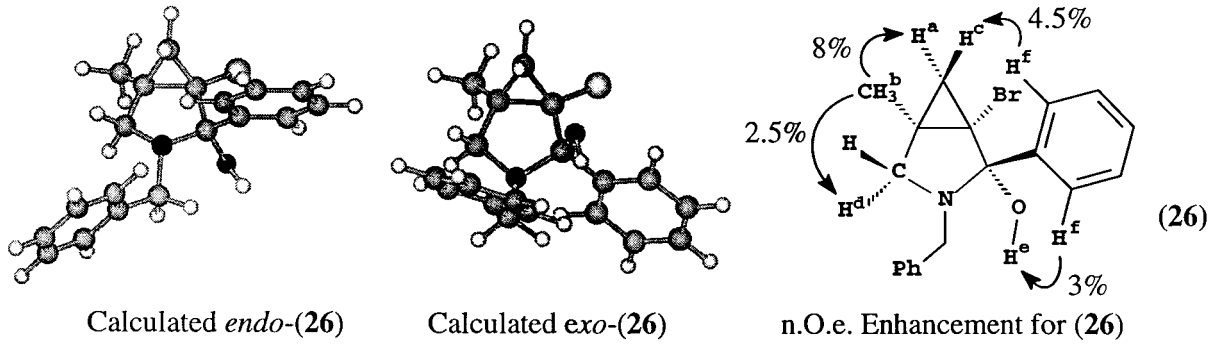
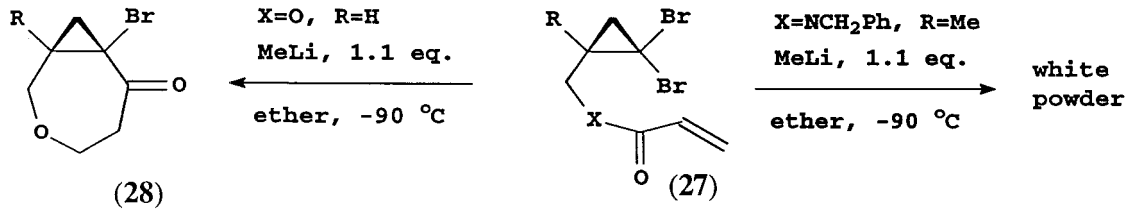


Figure 1.



Scheme 9.

starting material suggesting a reaction at the acylamide group rather than the dibromide.

The potential applications of the enantiomerically pure 3-azabicyclo[3.1.0]hexane derivatives described in this paper in the synthesis of natural products containing this skeleton such as CC-1065 and adozelesin[14] are currently being examined.

1. Experimental

1.1. General

Reagents were obtained from commercial suppliers (Aldrich, Lancaster) and were used without further purification unless otherwise stated. Solvents were purified when necessary using the methods suggested by Perrin et al.[15] Dichloromethane was distilled over calcium hydride, diethyl ether over sodium wire. Petroleum ether was of boiling point 40–60°C unless otherwise stated. Reactions were performed using oven dried glassware (160°C) cooled under a stream of dry nitrogen or argon; the experiments were conducted under a positive atmosphere of one of these gases. Organic solutions were dried over anhydrous magnesium sulfate, and, unless stated, were evaporated at 14 mmHg. Yields quoted are for purified compounds unless otherwise stated. Any ratios given are calculated by comparing integrals of protons in the ^{1}H NMR spectra unless otherwise stated.

All new compounds were homogenous by TLC or by GLC. GLC was conducted using a Carlo Erba HRGC 5300 (F.I.D., on a capillary column). TLC was performed using Aldrich silica plates coated with silica gel 60 (F254). Compounds were visualised by examination under an ultraviolet source, by exposure to iodine vapour or by contact with phosphomolybdic acid hydrate (2% solution in ethanol) followed by heating to 180°C. Column chromatography was conducted with Fisher Scientific silica gel 60 under medium pressure.

Melting points are uncorrected. Infrared spectra were obtained as KBr discs or as liquid films on a Perkin–Elmer 1600 FTIR spectrometer. Low resolution mass spectra were obtained on a Finnigan 8430 spectrometer. Accurate mass measurements refer to ^{79}Br for monobromides and to ^{79}Br^{81}Br for dibromides unless stated and were obtained from the EPSRC Mass Spectrometry Service in Swansea. Microanalyses were performed on a Carlo Erba Model 1106 CHN analyser.

NMR spectra were recorded in $CDCl_3$ unless otherwise stated on a Bruker AC250 at 250 MHz for protons and 62.9 MHz for carbon and in the latter case were broad-band decoupled; DEPT spectra were also run and the signs of signals (+ for CH, CH_3; − for CH_2) are indicated on the data for the broad-band decoupled spectrum. Those signals with no sign in such a spectrum are quaternary. When a n.O.e difference spectrum was obtained conditions were as follows: recorded on a Bruker 250 MHz spectrometer, a total of 576 scans per FID, interleaved in blocks of 24 each with 4 'dummy scans', using Bruker program N.O.EDIFF.AU; irradiation period: 8 s; 90 degree pulse, FID acquisition time: 2 s; sample stationary. Data were processed with 1 Hz line broadening.

1.1.1. *N*-(*R*)-α-Phenylethyl-*N*-(2,2-dibromo-1(*S*)-methylcyclopropylmethyl)-2,2,2-trifluoroacetamide (11). (a) A solution of (*R*)-α-phenylethylamine (1.21 ml, 10 mmol) and 1,1-dibromo-2(*S*)-bromomethyl-2-methylcyclopropane[7] (1.53 g, 5.00 mmol) in dimethysulfoxide (5 ml) was stirred at 60°C over 4 h. Water (15 ml) and 5% sodium hydroxide solution (5 ml, 6.5 mmol) were added and the product was extracted with ether (2×15 ml). Chromatography on silica

(petrol–ether, 3:1) gave N-(R)-α-*phenylethyl*-N-*(2,2-dibromo-1*(S)-*methylcyclopropylmethyl)amine* as a colourless oil (1.59 g, 92%) (Found C 44.91, H 5.07, N 4.08. Calculated for $C_{13}H_{17}Br_2N$: C 44.99, H 4.94, N 4.04) which showed $[\alpha]_D^{20}$ +12.8° (c 1.396, $CHCl_3$); δ_H: 1.37 (3H, d, *J*=6.5 Hz), 1.38 (1H, d, *J*=7.5 Hz), 1.44 (1H, d, *J*=7.5 Hz), 1.48 (3H, s), 1.55 (1H, s), 2.53 (1H, d, *J*=12.5 Hz), 2.71 (1H, d, *J*=12.5 Hz), 3.73 (1H, q, *J*=6.5 Hz), 7.18–7.32 (5H, m); δ_C: 21.9+, 24.3+, 30.1, 33.5−, 36.4, 55.9−, 58.5+, 126.6+, 126.9+, 128.4+, 145.5; ν_{max}: 3321 w, 3082 m, 3061 m, 3024 m, 2964 s, 2926 s, 2893 m, 2858 s, 1492 m, 1452 s, 1369 s, 1323 m, 1305 m, 1268 m, 1198 m, 1124 s, 1073 s, 1026 s, 760 s, 700 s cm^{-1}.

(b) Trifluoroacetic anhydride (1 ml, 5 mmol) was added to *N*-(*R*)-α-phenylethyl-*N*-(2,2-dibromo-1(*S*)-methylcyclopropylmethyl)amine (294 mg, 0.85 mmol) in dichloromethane (5 ml). After 2 h the volatiles were removed and the residue was dissolved in chloroform (5 ml). The organic layer was washed with sat.aq. $NaHCO_3$ (2×5 ml) and water (5 ml), dried and the solvent was removed to give a colourless oil, N-(R)-α-*phenylethyl*-N-*(2,2-dibromo-1*(S)-*methylcyclopropylmethyl)-2,2,2-trifluoroacetamide* (**11**) (357 mg, 95%) (Found C 40.79, H 3.80, N 3.08. Calculated for $C_{15}H_{16}Br_2F_3NO$: C 40.66, H 3.64, N 3.16) which showed $[\alpha]_D^{20}$ +16.0° (c 0.918, $CHCl_3$); δ_H: 1.07 (1H, d, *J*=8.5 Hz), 1.18 (1H, d, *J*=8.5 Hz), 1.22 (3H, s), 1.75 (3H, d, *J*=7.0 Hz), 3.08 (1H, d, *J*=14.5 Hz), 3.61 (1H, d, *J*=14.5 Hz), 5.40 (1H, q, *J*=7.0 Hz), 7.27–7.40 (5H, m); δ_C: 17.2+, 21.0+, 27.0, 36.1−, 37.1, 50.2−, 55.3+, 116.9 (q, J_{CF} 288.0 Hz), 127.4+, 128.5+, 128.9+, 138.0, 158.0 (q, J_{CF} 35.5 Hz); ν_{max}: 3372 br.w, 2986 w, 2940 w, 1694 s, 1450 m, 1219 s, 1192 s, 1143 s, 1087 m, 1027 m, 764 m, 745 m, 698 m cm^{-1}.

1.1.2. (1*R*,2*R*,5*S*)-1-Bromo-2-trifluoromethyl-5-methyl-*N*-(*R*)-α-methylbenzyl-3-azabicyclo[3.1.0]hexan-2-ol (12). 1.5 M Methyllithium in ether (0.44 ml, 0.66 mmol) was added to *N*-(*R*)-α-phenylethyl-*N*-(2,2-dibromo-1(*S*)-methylcyclopropylmethyl)-2,2,2-trifluoroacetamide (**11**) (267 mg, 0.603 mmol) in ether (15 ml) at −90°C for 5 min. The solution was stirred for 30 min at −90°C then warmed to 0°C for 30 min and sat.aq. NH_4Cl (5 ml) was added. The water layer was extracted with ether (10 ml). The combined organic layers were evaporated to give crude (>85% pure by NMR) product, half of which was columned on silica to yield *(1*R*,2*R*,5*S*)-1-bromo-2-trifluoromethyl-5-methyl*-N-(R)-α-*methylbenzyl-3-azabicyclo[3.1.0]hexan-2-ol* (**12**) (69 mg, 63%) (Found M^+: 363.0446. $C_{15}H_{17}BrF_3NO$ requires: 363.0446) which showed $[\alpha]_D^{25}$+34.0° (c 1.00, $CHCl_3$); δ_H: 0.95 (1H, d, *J*=6.0 Hz), 1.20 (3H, s), 1.36 (3H, d, *J*=7.0 Hz), 1.63 (1H, d, *J*=6.0 Hz), 2.60 (1H, d, *J*=8.5 Hz), 2.83 (1H, s), 2.99 (1H, d, *J*=8.5 Hz), 4.60 (1H, q, *J*=7.0 Hz), 7.22–7.38 (5H, m); δ_C: 17.52+, 19.33+, 24.71−, 25.52, 46.08, 50.81−, 52.65+, 91.51 (q, J_{CF} 29.55 Hz), 124.15 (q, J_{CF} 289.5 Hz), 127.3+, 128.3+, 128.6+, 141.1; ν_{max}: 3548 m, 3350 br. w, 3031 m, 2977 s, 2931 s, 2850 m, 1693 m, 1495 m, 1454 s, 1388 m, 1166 br. s, 1068 s, 969 m, 762 m, 746 m, 700 s cm^{-1}; m/z,%: 365, 3; 363, 3 (M^+); 350, 17; 348, 22; 296, 18; 294, 18; 260, 10; 258, 10; 192, 12; 194, 12; 106, 17; 105, 100.

1.1.3. *N*-Benzyl-*N*-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)-2,2,2-trifluoroacetamide (13). Trifluoroacetic anhydride (1 ml, 5 mmol) was added to *N*-benzyl-*N*-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)-amine[7] (1.20 g, 3.60 mmol) in dichloromethane (10 ml). After 2 h the volatiles were removed and the residue was dissolved in chloroform (20 ml). The organic layer was washed with sat.aq. $NaHCO_3$ (2×10 ml) and water (10 ml), dried and the solvent was removed to give a colourless oil, N-*benzyl*-N-*(2,2-dibromo-1*(R)-*methylcyclopropylmethyl)-2,2,2-trifluoroacetamide* (**13**) (1.55 g, 100%) as two rotamers (67:33) (Found C 39.10, H 3.53, N 3.46. Calculated for $C_{14}H_{14}Br_2F_3NO$: C 39.19, H 3.29, N 3.26) which showed $[\alpha]_D^{20}$−9.4° (c 1.138, $CHCl_3$); ν_{max}: 3371 w, 3066 m, 3032 m, 2935 m, 1693 br s, 1497 m, 1454 br s, 1367 s, 1292 s, 1250 s, 1210 s, 1142 s, 1090 s, 1029 s, 997 s, 960 s, 894 w, 844 w, 736 s, 698 s cm^{-1}. The major rotamer showed δ_H: 1.36 (1H, d, *J*=8.0 Hz), 1.39 (3H, s), 1.56 (1H, d, *J*8.0 Hz), 3.69 (1H, d, *J*14.5 Hz), 3.78 (1H, d, *J*14.5 Hz), 4.74 (1H, d, *J*16.5 Hz), 4.83 (1H, d, *J*16.5 Hz), 7.16–7.43 (5H, m); δ_C: 20.42+, 27.51, 33.55−, 35.10, 50.07− (q, J_{CF} 4.0 Hz), 51.14−, 116.40 (q, J_{CF} 288.0 Hz), 126.28+, 127.89+, 128.80+, 134.41, 157.91 (q, J_{CF} 35.5 Hz). The minor rotamer showed δ_H: 1.46 (1H, d, *J*8.0 Hz), 1.54 (3H, s), 1.64 (1H, d, *J*8.0 Hz), 3.50 (1H, d, *J*15.0 Hz), 3.91 (1H, d, *J*15.0 Hz), 4.57 (1H, d, *J*15.0 Hz), 4.94 (1H, d, *J*15.0 Hz), 7.16–7.43 (5H, m); δ_C: 19.98+, 26.35, 33.82−, 34.20, 47.85−, 52.32− (q, J_{CF} 4.0 Hz), 116.36 (q, J_{CF} 288.0 Hz), 127.19+, 127.69+, 128.68+, 134.46, 157.50 (q, J_{CF} 35.5 Hz).

1.1.4. (1*S*,2*S*,5*R*)-1-Bromo-2-trifluoromethyl-5-methyl-*N*-benzyl-3-azabicyclo[3.1.0]hexan-2-ol (14). 1.27 M Methyllithium in ether (0.87 ml, 1.10 mmol) was added to *N*-benzyl-*N*-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)-2,2,2-trifluoroacetamide (**13**) (430 mg, 1.00 mmol) in ether (20 ml) at −90°C for 5 min. The solution was stirred for 30 min at −90°C then warmed to 0°C for 30 min and sat.aq. NH_4Cl (10 ml) was added. The water layer was extracted with ether (20 ml). The combined organic layers were evaporated to give crude product (350 mg) which was columned on silica (petrol:ether=1:4) to yield *(1*S*,2*S*,5*R*)-1-bromo-2-trifluoromethyl-5-methyl*-N-*benzyl-3-azabicyclo[3.1.0]hexan-2-ol* (**14**), (183 mg, 52%), (Found C 48.21, H 4.43, N 3.88. Calculated for $C_{14}H_{15}BrF_3NO$: C 48.02, H 4.32, N 4.00), which showed $[\alpha]_D^{25}$ −41.6° (c 0.972, $CHCl_3$), δ_H: 0.88 (1H, d, *J*6.0 Hz), 1.31 (3H, s), 1.82 (1H, d, *J*6.0 Hz), 2.73 (1H, d, *J*9.0 Hz), 2.99 (1H, d, *J*9.0 Hz), 3.17 (1H, s), 3.51 (1H, d, *J*14.5 Hz), 4.43 (1H, d, *J*14.5 Hz), 7.20–7.36 (5H, m); δ_C: 17.19+, 24.83− (q, J_{CF} 2.0 Hz), 26.20, 46.32, 50.63− (q, J_{CF} 3.0 Hz), 57.25−, 90.98 (q, J_{CF} 29.5 Hz), 123.89 (q, J_{CF} 290.0 Hz), 126.93+, 127.88+, 128.21+, 138.36; ν_{max}: 3541 br m, 3087 w, 3064 w, 3030 m, 2960 m, 2927 m, 2852 m, 1496 m, 1454 s, 1369 s, 1341 s, 1254 s, 1156 br. s, 1064 s, 983 s, 958 s, 743 s, 718 m, 699 s, 674 m cm^{-1}.

1.1.5. *N*-Benzyl-*N*-(2,2-dibromocyclopropylmethyl)-2,2,2-trifluoroacetamide (15). Trifluoroacetic anhydride (0.34 ml, 2.4 mmol) was added to *N*-benzyl-(2,2-dibromocyclopropylmethyl)amine[7] (700 mg, 2.2 mmol) in dichloromethane (30 ml). After 30 min the volatiles were removed and the residue was dissolved in ether (30 ml) and washed with sat. aq. $NaHCO_3$ (2×20 ml) and water (20 ml), dried and evaporated to give a colourless oil, N-*benzyl*-N-*(2,2-*

dibromocyclopropylmethyl)-2,2,2-trifluoroacetamide (**15**) (770 mg, 85%) as two rotamers (67:33) (Found M^+: 414.9217. $C_{13}H_{12}Br_2F_3NO$ requires: 414.9217); ν_{max}: 3032 w, 2936 w, 1694 s, 1452 s, 1386 w, 1362 w, 1205 s, 1144 s, 1001 m, 740 m, 702 m cm^{-1}; m/z,%: 417, 1; 415, 2; 413, 1 (M^+); 229, 2; 202, 5; 91, 100; 65, 4. The major rotamer showed δ_H: 1.25 (1H, t, *J*7.0 Hz), 1.76 (1H, dd, *J*7.0, 10.5 Hz), 1.89 (1H, dddd, *J*5.0, 6.5, 7.0, 10.5 Hz), 3.45 (1H, dd, *J*6.5, 14.5 Hz), 3.62 (1H, dd, *J*5.0, 14.5 Hz), 4.74 (1H, d, *J*16.5 Hz), 4.87 (1H, d, *J*16.5 Hz), 7.22–7.45 (5H, m); δ_C: 25.5, 27.5−, 28.4+, 48.8−, 51.2−, 116.5 (q, J_{CF} 288 Hz), 127.2+, 127.7+, 129.1+, 134.6, 157.5 (q, J_{CF} 39 Hz). The minor rotamer showed δ_H: 1.35 (1H, t, *J*7.0 Hz), 1.76 (1H, dd, *J*7.0, 10.5 Hz), 1.89 (1H, dddd, *J*5.0, 6.5, 7.0, 10.5 Hz), 3.60 (1H, dd, *J*6.5, 14.5 Hz), 3.62 (1H, dd, *J*5.0, 14.5 Hz), 4.71 (1H, d, *J*15.0 Hz), 4.96 (1H, d, *J*15.0 Hz), 7.22–7.45 (5H, m); δ_C: 24.9, 27.3−, 29.6+, 48.7−, 49.5−, 116.5 (q, J_{CF} 288 Hz), 128.1+, 128.4+, 128.9+, 135.0, 157.5 (q, J_{CF} 39 Hz).

1.1.6. 3-Benzyl-1-bromo-2-trifluoromethyl-3-azabicyclo-[3.1.0]hexan-2-ol (16). Methyllithium in ether (0.46 ml, 0.62 mmol, 1.35 M) was added dropwise to *N*-benzyl-*N*-(2,2-dibromocyclopropylmethyl)-2,2,2-trifluoroacetamide (**15**) (200 mg, 0.48 mmol) in ether (10 ml) at −90°C. The solution was stirred for 30 min at −80°C, then quenched with a sat. aq. NH_4Cl (5 ml). The aqueous layer was extracted with ether (2×10 ml). The combined organic layers were dried and evaporated. Chromatography on silica (petrol–ether, 1:1) gave *3-benzyl-1-bromo-2-trifluoromethyl-3-azabicyclo[3.1.0]hexan-2-ol* (**16**) (55 mg, 34%), N-*benzyl*-N-*[2-bromo-2-(2,2,2-trifluoroacetyl)cyclopropylmethyl]-2,2,2-trifluoroacetamide* (**17**) (45 mg, 22%) and N-*benzyl-(2,2-dibromocyclopropylmethyl)amine* (**18**) (30 mg, 20%). Compound (**16**) (Found M^+: 335.0133. $C_{13}H_{13}BrF_3NO$ requires: 335.0133) showed δ_H: 1.38 (1H, dd, *J*6.0, 9.0 Hz), 1.71 (1H, dd, *J*5.0, 6.0 Hz), 1.89 (1H, ddd, *J*4.0, 5.0, 9.0 Hz), 2.94 (1H, d, *J*9.0 Hz), 3.02 (1H, dd, *J*4.0, 9.0 Hz), 3.27 (1H, s), 3.54 (1H, d, *J*14.5 Hz), 4.44 (1H, d, *J*14.5 Hz), 7.24–7.39 (5H, m); δ_C: 19.6−, 24.2+, 38.2, 51.7−, 52.1−, 90.3 (q, J_{CF} 30.5 Hz), 124.1 (q, J_{CF} 289.0 Hz), 127.1+, 128.0+, 128.4+, 138.4; ν_{max}: 3544 br s., 3030 w. 2920 w, 2851 m, 1682 w, 1455 m, 1364 m, 1182 s, 1150 s, 1076 m, 1035 m, 959 m, 742 m, 699 m cm^{-1}; m/z,%: 337, 1; 335, 1 (M^+); 320, 1; 318, 1; 267, 22; 91, 100. Compound (**17**) (Found M^+: 430.9956. $C_{15}H_{12}BrF_6NO_2$ requires: 430.9956) showed a mixture of rotamers (77:23) by NMR The major rotamer showed δ_H: 1.52 (1H, dd, *J*6.5, 9.5 Hz), 1.72 (1H, dd, *J*6.5, 8.5 Hz), 2.22 (1H, dddd, *J*6.5, 7.0, 8.5, 9.5 Hz), 3.05 (1H, dd, *J*6.5, 14.5 Hz), 3.49 (1H, dd, *J*7.0, 14.5 Hz), 4.49 (1H, d, *J*16.0 Hz), 4.68 (1H, d, *J*16.0 Hz), 7.15–7.42 (5H, m); δ_C: 24.6−, 28.4, 34.5+, 44.4−, 51.7−, 115.5 (q, J_{CF} 291 Hz), 116.4 (q, J_{CF} 288 Hz), 127.5+, 128.7+, 129.2+, 134.0, 157.8 (q, J_{CF} 39 Hz), 184.7 (q, J_{CF} 39 Hz). The minor rotamer showed δ_H: 1.66 (1H, dd, *J*6.5, 9.5 Hz), 1.87 (1H, dd, *J*6.5, 8.5 Hz), 2.22 (1H, m), 3.06 (1H, underneath the peak for the major isomer), 3.63 (1H, dd, *J*4.5, 14.5 Hz), 4.66 (2H, s), 7.15–7.42 (5H, m); δ_C: 25.3−, 29.9, 35.1+, 44.1−, 49.8−, 115.5 (q, J_{CF} 291 Hz), 116.4 (q, J_{CF} 288 Hz), 127.8+, 128.4+, 129.1+, 134.8, 157.8 (q, J_{CF} 39 Hz), 184.8 (q, J_{CF} 39 Hz); ν_{max}: 3035 w, 1738 s, 1694 s, 1682 s, 1454 s, 1245 s, 1210 s, 1149 s, 1072 m, 999 m, 743 m, 702 s cm^{-1}; m/z,%: 433, 10; 431, 8 (M^+); 352, 10; 202, 18; 91, 100. The analytical data of (**18**) were identical to those reported.[7]

The reaction was repeated on a comparable scale and gave the same three products with yields as follows: (**16**) 37%; (**17**) 18% and (**18**) 28%.

1.1.7. (*R*)-*N*-Benzyl-*N*-(2,2-dibromocyclopropylmethyl)-acetamide (19). Acetic anhydride (0.32 ml, 3.5 mmol) was added to (*R*)-*N*-benzyl-(2,2-dibromocyclopropylmethyl)-amine[7] (1.03 g, 3.2 mmol) in dichloromethane (20 ml). After 2 h the volatiles were removed and the residue was dissolved in ether (30 ml) and washed with sat. aq. $NaHCO_3$ (2×20 ml) and water (20 ml). The organic layer was dried and evaporated to give (R)-N-*benzyl*-N-*(2,2-dibromocyclopropylmethyl)acetamide* (**19**) (1.11 g, 96%) as a colourless viscous oil (Found: C 43.04, H 4.18, N 3.97. $C_{13}H_{15}Br_2NO$ requires: C 43.24, H 4.19, N 3.88) which showed two rotamers (76:24) by NMR, $[\alpha]_D^{20}$ −29.0° (c 1.175, $CHCl_3$); ν_{max}: 3029 w, 2929 w, 1638 s, 1467 s, 1437 s, 1414 s, 1381 s, 1363 s, 1252 s, 1207 s, 1105 m, 980 m, 962 m, 730 s, 684 m cm^{-1}; m/z,%: 363, 2; 361, 5; 359, 2 (M^+); 188, 8; 175, 20; 174, 34; 146, 16; 120, 8; 106, 19; 91, 100, 65, 10.). The major rotamer showed δ_H: 1.32 (1H, t, *J*7.5 Hz), 1.79 (1H, dd, *J*7.5, 10.5 Hz), 1.89–2.04 (1H, m, together with peaks for the minor isomer), 2.22 (3H, s), 3.28 (1H, dd, *J*7.0, 14.5 Hz), 3.93 (1H, dd, *J*5.5, 14.5 Hz), 4.77 (2H, s), 7.23–7.46 (5H, m); δ_C: 21.7+, 27.1, 27.2−, 29.7+, 48.3−, 52.4−, 126.2+, 127.7+, 129.0+, 136.6, 171.5. The minor rotamer showed δ_H: 1.32 (1H, t, *J*7.5 Hz), 1.78–1.85 (1H, m, peaks underneath those of major isomer), 1.89–2.04 (1H, m, together with peaks for the major isomer), 2.31 (3H, s), 3.38 (1H, dd, *J*5.5, 15.5 Hz), 3.63 (1H, dd, *J*5.5, 15.5 Hz), 4.68 (1H, d, *J*15.0 Hz), 4.89 (1H, d, *J*15.0 Hz), 7.23–7.46 (5H, m); δ_C: 21.8+, 25.6, 27.7−, 29.7+, 48.3−, 49.9−, 127.4+, 127.8+, 128.6+, 137.5, 170.6.

1.1.8. (1*S*,5*R*)-3-Benzyl-1-bromo-2-methylene-3-azabicyclo[3.1.0]hexane (20). 1.37 M Methyllithium in ether (0.95 ml, 1.3 mmol) was added dropwise to a solution of (**19**) (361 mg, 1.00 mmol) in dry ether (20 ml) at −90°C. After 15 min at −90°C the reaction mixture was warmed to 0°C for 30 min and then was quenched with sat. aq. NH_4Cl (5 ml). The aqueous layer was extracted with ether (2×10 ml). The combined organic layers were dried and evaporated to yield crude product (254 mg). The ^1H NMR showed that it was a mixture, which contained two main components, which were non-separable by column chromatography, (**20**) and (**21**) in ratio 75:25; *(1*S*,2*S*,5*R*)-3-benzyl-1-bromo-2-methyl-3-azabicyclo[3.1.0]hexan-2-ol* (**21**) showed δ_H: 1.34 (1H, dd, *J*4.5, 5.0 Hz), 1.49 (3H, s), 1.53 (1H, peaks underneath peaks of (**20**)), 1.85 (1H, ddd, *J*3.5, 4.5, 9.0 Hz), 2.76 (1H, d, *J*9.0 Hz), 2.88 (1H, dd, *J*3.5, 9.0 Hz), 3.57 (1H, d, *J*14.5 Hz), 4.17 (1H, d, *J*14.5 Hz), 7.20–7.40 (5H, m); δ_C: 19.4−, 21.1+, 23.4+, 50.4−, 50.5−, 126.8+, 128.0+, 128.2+, quaternary carbons were not detected. To part of this mixture (120 mg), benzene (3 ml) was added and distilled over 5 min at normal pressure. Then more benzene (3 ml) was added and distilled again. Chromatography of the residue on silica (petrol–ether, 2:1, 3 drops of triethylamine per 100 ml of eluant) gave *(1*S*,5*R*)-3-benzyl-1-bromo-2-methylene-3-azabicyclo-*

[3.1.0]hexane (**20**) (61 mg, 49%) (Found M^+: 263.0310. $C_{13}H_{14}BrN$ requires: 263.0310) showed δ_H (benzene-d_6): 0.97 (1H, dd, *J*5.5, 5.0 Hz), 1.27 (1H, dd, *J*9.0, 5.5 Hz), 1.57 (1H, ddd, *J*9.0, 5.0, 5.0 Hz), 2.47 (1H, d, *J*9.5 Hz), 2.78 (1H, dd, *J*9.5, 5.0 Hz), 3.66 (1H, d, *J*15.5 Hz), 3.89 (1H, d, *J*15.5 Hz), 3.99 (1H, broad s), 4.50 (1H, broad s), 7.05–7.30 (5H, m); δ_H: 1.19 (1H, t, *J*5.0 Hz), 1.53 (1H, dd, *J*5.0, 9.0 Hz), 2.03 (1H, td, *J*5.0, 9.0 Hz), 3.04 (1H, d, *J*9.0 Hz), 3.40 (1H, dd, *J*5.0, 9.0 Hz), 3.82 (1H, broad s), 4.06 (1H, d, *J*15.5 Hz), 4.07 (1H, broad s), 4.25 (1H, d, *J*15.5 Hz), 7.20–7.40 (5H, m); δ_C: 23.4−, 24.6+, 34.2, 50.8−, 52.1−, 75.5−, 127.0+, 127.5+, 128.5+, 137.8, 154.1; ν_{max}: 3568 w, 3085 m, 3062 m, 3028 s, 2999 m, 2875 s, 2838 s, 1948 w, 1877 w, 1810 w, 1644 s, 1604 m, 1495 s, 1453 s, 1356 s, 1301 s, 1217 m, 1180 s, 1129 s, 1080 m, 1039 m, 1010 m, 956 m, 912 m, 890 m, 735 s, 699 s cm^{-1}; m/z,%: 265, 14; 264, 39; 263, 19 (M^+); 262, 19; 184, 20; 182, 11; 91, 100; 65, 30.

A solution of (**20**) (5 mg) in $CDCl_3$ (1 ml) showed in 3 h a mixture of (**20**) and (**21**) in ratio 75:25 by ^1H NMR spectroscopy. In 8 h at room temperature it began to decompose and after 3 days it had completely decomposed. Decomposition of (**20**) in chloroform was detected by measuring the rotation angle (c=0.695). It showed $[\alpha]_D^{20}$ +7.9° 5 min after dissolving, $[\alpha]_D^{20}$ +3.5° in 15 min, $[\alpha]_D^{20}$ −6.0° in 1.5 h, and $[\alpha]_D^{20}$ −15.7° in 16 h (became yellow solution). The ^1H NMR spectrum of the final sample showed complete decomposition.

1.1.9. *N*-Benzyl-*N*-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)acetamide (22). Acetic anhydride (0.50 ml, 5 mmol) was added to *N*-benzyl-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)amine[7] (1.00 g, 3.00 mmol) in dichloromethane (10 ml). After 2 h, the volatiles were removed and the residue was dissolved in ether (30 ml) and washed with sat. aq. $NaHCO_3$ (2×10 ml) and water (10 ml), dried and evaporated to give a colourless oil, N-*benzyl*-N-*(2,2-dibromo-1*(R)-*methylcyclopropylmethyl)acetamide* (**22**) (1.09 g, 97%) as two rotamers (3.5:1) (Found C 44.52, H 4.64, N 3.77. Calculated for $C_{14}H_{17}Br_2NO$: C 44.83, H 4.64, N 3.73); $[\alpha]_D^{20}$–20.5° (c 1.010, $CHCl_3$); ν_{max}: 3063 w, 3028 w, 2989 w, 2930 m, 1824 m, 1751 m, 1722 m, 1650 s, 1495 m, 1422 s, 1364 s, 1238 s, 1176 w, 1123 m, 1053 w, 1027 m, 986 m, 962 m, 896 m, 732 s, 695 s cm^{-1}. The major rotamer showed δ_H: 1.39 (3H, s), 1.52 (2H, s), 2.16 (3H, s), 3.47 (1H, d, *J*14.5 Hz), 4.14 (1H, d, *J*14.5 Hz), 4.67 (1H, d, *J*17.5 Hz), 4.70 (1H, d, *J*17.5 Hz), 7.15–7.40 (5H, m); δ_C: 20.97+, 21.56+, 28.52, 33.21−, 37.01, 50.51−, 51.06−, 125.87+, 127.66+, 128.96+, 136.39, 172.05. The minor rotamer showed δ_H: 1.37 (3H, s), 1.53 (1H, d, *J*7.5 Hz), 1.59 (1H, d, *J*7.5 Hz), 2.29 (3H, s), 3.29 (1H, d, *J*15.0 Hz), 3.80 (1H, d, *J*15.0 Hz), 4.44 (1H, d, *J*15.5 Hz), 4.92 (1H, d, *J*15.5 Hz), 7.15–7.40 (5H, m); δ_C: 20.79+, 22.11+, 27.17, 34.47−, 34.68, 47.22−, 54.06−, 127.32+, 127.54+, 128.58+, 136.74, 171.08.

1.1.10. (1*S*,5*R*)-3-Benzyl-1-bromo-5-methyl-2-methylene-3-azabicyclo[3.1.0]hexane (23). 1.27 M Methyllithium in ether (0.87 ml, 1.1 mmol) was added dropwise to a solution of (**22**) (375 mg, 1.00 mmol) in ether (20 ml) at −90°C. After 15 min at −90°C the reaction mixture was warmed to 0°C for 30 min and then quenched with sat. aq. NH_4Cl (5 ml). The aqueous layer was extracted with ether (2×15 ml). The combined organic layers were dried and evaporated to yield crude product (270 mg). Chromatography of 50 mg of the crude material on silica (petrol–ether, 7:3) gave *(1*S,5R*)-3-benzyl-1-bromo-5-methyl-2-methylene-3-azabicyclo[3.1.0]hexane* (**23**) (33%). The compound was not completely pure, the NMR also showing signals of *(1S,2S,5R)-3-benzyl-1-bromo-2,5-dimethyl-3-azabicyclo[3.1.0]hexan-2-ol* (**24**) (7%) [in total 20 mg, ratio (**23**) to (**24**) 84:16]; ν_{max}: 3382 br m, 3062 m, 2954 m, 2924 m, 2833 m, 1646 s, 1452 s, 1356 m, 1057 m, 734 s, 698 s cm^{-1}. Compound (**23**) showed δ_H: 1.19 (1H, d, *J*5.0 Hz), 1.34 (1H, d, *J*5.0 Hz), 1.36 (3H, s), 3.05 (1H, d, *J*9.0 Hz), 3.13 (1H, d, *J*9.0 Hz), 3.80 (1H, broad s), 4.00 (1H, d, *J*15.5 Hz), 4.08 (1H, broad s), 4.27 (1H, d, *J*15.5 Hz), 7.18–7.45 (5H, m); δ_C: 17,71+, 27.13, 28.87−, 42.64, 50.90−, 57.75−, 75.48−, 127.05+, 127.66+, 128.46+, 137.86, 155.18. Compound (**24**) showed δ_H: 0.86 (1H, d, *J*5.0), 1.33 (3H, s), 1.45 (1H, d, *J*5.0), 1.49 (3H, s), 2.14 (1H, br s), 2.64 (1H, d, *J*9.0 Hz), 2.80 (1H, dd, *J*9.0 Hz), 3.46 (1H, d, *J*14.5 Hz), 4.17 (1H, d, *J*14.5 Hz), 7.18–7.45 (5H, m).

1.1.11. *N*-Benzyl-*N*-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)benzamide (25). Benzoyl chloride (0.38 ml, 3.3 mmol) was added to *N*-benzyl-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)amine[7] (1.00 g, 3.00 mmol) and triethylamine (0.82 ml, 6 mmol) in benzene (20 ml) and the mixture was refluxed for 1.5 h, then cooled to room temperature and extracted with 5% HCl (2×30 ml). After drying and evaporating the solvent, the crude product was columned on silica (40 g, ether:petrol=1:1) to yield a colourless oil, N-*benzyl*-N-*(2,2-dibromo-1*(R)-*methylcyclopropylmethyl)benzamide* (**25**) (1.15 g, 88%), which crystallised in three days, m.p. 65–67°C, (Found C 52.43, H 4.66, N 3.16. Calculated for $C_{19}H_{19}Br_2NO$: C 52.20, H 4.38, N 3.20) which showed $[\alpha]_D^{20}$–35.6° (c 1.370, $CHCl_3$); δ_H: 1.30 (1H, br s), 1.53 (4H, br s), 3.74 (1H, d, *J*14.0 Hz), 4.05 (1H, br d, *J*14.0 Hz), 4.68 (2H, br s), 7.15–7.45 (10H, m); δ_C: 13.83+, 21.24, 26.45−, 44.58−, 45.07−, 119.32+ broad, 120.30+, 121.43+, 121.59+, 122.55+, 128.81, 129.46, 165.73; ν_{max} (nujol): 3061 m, 3028 m, 2929 s, 2869 m, 1650 s, 1578 m, 1495 m, 1454 s, 1365 s, 1319 s, 1259 s, 1174 m, 1149 m, 1073 s, 1027 m, 989 m, 960 m, 788 m, 729 s, 697 s, 652 m cm^{-1}.

1.1.12. (1*S*,2*S*,5*R*)-3-Benzyl-1-bromo-5-methyl-2-phenyl-3-azabicyclo[3.1.0]hexan-2-ol (26). 1.27 M Methyllithium in ether (1.15 ml, 1.46 mmol) was added dropwise to a solution of (**25**) (580 mg, 1.33 mmol) in ether (20 ml) at −90°C. After 15 min at −90°C, the reaction mixture was warmed to 0°C for 30 min and then quenched with sat. aq. NH_4Cl (5 ml). The aqueous layer was extracted with ether (2×15 ml). The combined organic layers were dried and evaporated to yield crude product (460 mg). Chromatography of this crude material on silica (petrol–ether, 7:3) gave *(1*S,2S,5R*)-3-benzyl-1-bromo-5-methyl-2-phenyl-3-azabicyclo[3.1.0]hexan-2-ol* (**26**) (305 mg, 64%) (Found C 64.00, H 5.80, N 3.76. Calculated for $C_{19}H_{20}BrNO$: C 63.70, H 5.63, N 3.91), which showed $[\alpha]_D^{20}$–13.3° (c 0.645, $CHCl_3$); δ_H: 0.85 (1H, d, *J*5.5 Hz), 1.39 (3H, s), 1.76 (1H, d, *J*5.5 Hz), 2.76 (1H, d, *J*9.0 Hz), 2.78 (1H, s), 3.02 (1H, d, *J*9.0 Hz), 3.46 (1H, d, *J*14.0 Hz),

3.85 (1H, d, *J*14.0 Hz), 7.20–7.45 (8H, m), 7.76 (2H, dd, *J*7.5, 1.0 Hz); δ_C: 17,61+, 25.22−, 26.90, 51.02−, 54.47, 55.09−, 94.77, 126.88+, 127.23+, 128.16+, 128.19+, 128.25+, 128.29+, 138.92, 139.94; ν_{max}: 3562 s, 3085 w, 3061 m, 3027 m, 2954 s, 2923 s, 2811 s, 1604 w, 1494 s, 1446 s, 1364 s, 1330 s, 1207 s, 1170 s, 1059 s, 1028 s, 1015 s, 975 m, 948 s, 909 m, 866 w, 763 s, 731 s, 700 s, 666 s cm^{-1}.

1.1.13. *N*-Benzyl-*N*-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)acrylamide (27). Acryloyl chloride (0.29 ml, 3.6 mmol) was added to *N*-benzyl-(2,2-dibromo-1(*R*)-methylcyclopropylmethyl)amine[7] (1.00 g, 3.00 mmol) and triethylamine (0.82 ml, 6 mmol) in benzene (20 ml) and the mixture was refluxed for 1.5 h, then cooled to room temperature and extracted with 5% HCl (2×30 ml). The volatiles were removed and the residue was dissolved in ether (30 ml) and washed with sat. aq. $NaHCO_3$ (2×10 ml) and water (10 ml), dried and evaporated to give a colourless oil, N-*benzyl*-N-*(2,2-dibromo-1*(R)-*methylcyclopropylmethyl)acrylamide* (**27**) (1.13 g, 97%), as two rotamers (2.5:1) (Found C 46.30, H 4.65, N 3.48. Calculated for $C_{15}H_{17}Br_2NO$: C 46.54, H 4.43, N 3.62); which showed $[\alpha]_D^{20}$ −33.3° (c 1.015, $CHCl_3$); ν_{max}: 3063 w, 3029 w, 2988 w, 2930 w, 1735 w, 1650 s, 1614 s, 1495 m, 1440 s, 1363 m, 1216 s, 1095 m, 1030 m, 961 m, 794 m, 733 s, 695 s cm^{-1}. The major rotamer showed δ_H: 1.40 (3H, s), 1.55 (2H, s), 3.53 (1H, d, *J*14.5 Hz), 4.19 (1H, d, *J*14.5 Hz), 4.70 (1H, d, *J*17.5 Hz), 4.80 (1H, d, *J*17.5 Hz), 5.72 (1H, dd, *J*10.0, 2.5 Hz), 6.46 (1H, dd, *J*16.5, 2.5 Hz), 6.55 (1H, dd, *J*16.5, 10.0 Hz), 7.15–7.50 (5H, m); δ_C: 21.05+, 28.66, 33.36−, 37.09, 50.39−, 51.16−, 126.08+, 127.34+, 127.60+, 128.90+, 129.33−, 136.59, 167.61. The minor rotamer showed δ_H: 1.34 (2H, br s), 1.54 (3H, s), 3.39 (1H, d, *J*15.5 Hz), 3.89 (1H, d, *J*15.5 Hz), 4.58 (1H, d, *J*15.0 Hz), 4.92 (1H, d, *J*15.0 Hz), 5.82 (1H, br d, *J*10.5 Hz), 6.50 (1H, br d, *J*16.0 Hz), 6.53 (1H, dd, *J*16.0, 10.5 Hz), 7.15–7.50 (5H, m).

1.1.14. Reaction of *N*-benzyl-*N*-(2,2-dibromo-1(*R*)-cyclopropylmethyl)acrylamide (27) with methyllithium. 1.27 M Methyllithium in ether (0.87 ml, 1.10 mmol) was added dropwise to a solution of (**27**) (390 mg, 1.00 mmol) in ether (10 ml) at −90°C. After 15 min at −90°C, the reaction mixture was warmed to 0°C for 30 min (a white precipitate was formed) and then was quenched with sat. aq. NH_4Cl (5 ml) and water (5 ml). The precipitate was filtered, washed with water (2 ml), ether (2 ml) and dried to yield a white powder (250 mg). The aqueous layer was extracted with ether (2×15 ml). The combined organic layers were dried and evaporated to yield 37 mg of a mixture of several compounds (by ^1H NMR). The powder (Found C 44.66, H 6.00, N 3.44. Calculated for $C_{15}H_{17}Br_2NO$ (compound (**27**)): C 46.54, H 4.43, N 3.62), m.p. 187–192°C (decomp.) showed δ_H: 0.8–1.7 (ca. 14H, br s), 4.2–4.7 (ca. 42H, br s), 6.9–7.6 (ca. 44H, br s); ν_{max} (nujol): 3416 br s, 2922 s, 2852 s, 1650 s, 1643 s, 1634 s, 1495 w, 1454 s, 1376 m, 1200 br w, 1076 w, 1028 w, 962 w, 846 w, 730 w, 698 w cm^{-1}.

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