Synthesis of Enantiopure 3-Quinuclidinone Analogues with Three Stereogenic Centers: *(1S,2R,4S)*- and *(1S,2S,4S)*-2-(Hydroxymethyl)-1-azabicyclo[2.2.2]octan-5-one and Stereocontrol of Nucleophilic Addition to the Carbonyl Group

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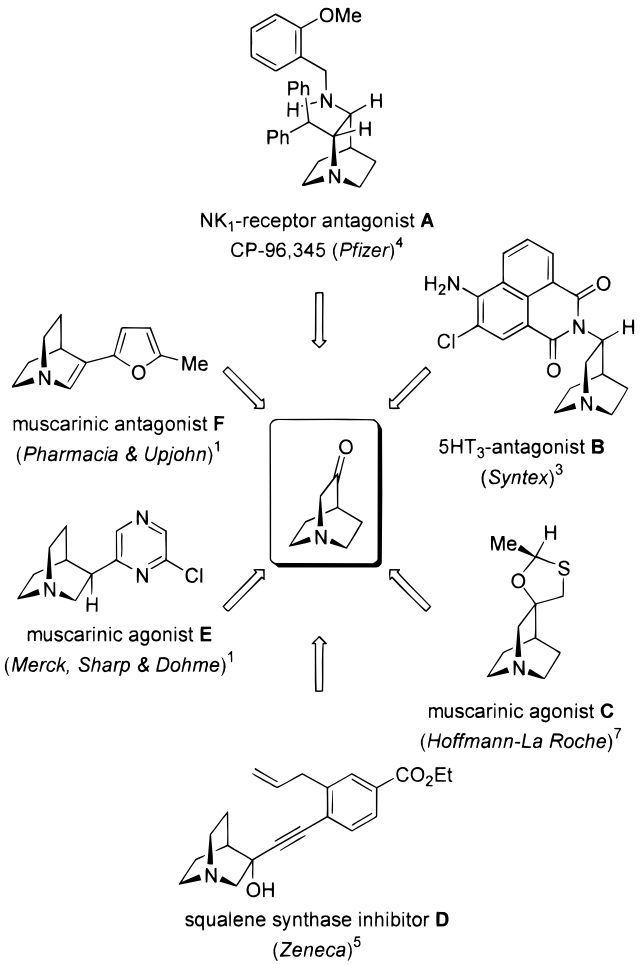
The pseudoenantiomeric title compounds have been prepared from quincorine (QCI) and quincoridine (QCD), respectively, in enantiopure form following an efficient six-step pathway. Nucleophilic attack at the carbonyl group proceeds preferentially from the supposedly more hindered *endo* π-face, giving quinuclidinols with natural configuration at C5 (up to 97%). π-Face selectivity is highest in the QCD series with bulky O-protecting groups, involving an unprecedented 1,7-stereoinduction.

Introduction

Substituted quinuclidines possess interesting and diverse pharmacological activities (Scheme 1). Recent examples include 3-substituted quinuclidines **C**, **E**, and **F** which are among the most potent muscarinic agonists and antagonists.[1] The 1-azabicyclo[2.2.2]octane nucleus has been found to be a good mimic for the quaternary nitrogen in acetylcholine but, unlike acetylcholine, the unprotonated form is able to cross the blood−brain barrier.[2] Selective muscarinic M1-type antagonists capable of penetrating the blood-brain barrier have therapeutic potential for the treatment of Alzheimer's disease.

Quinuclidine derivatives with substituents in the 3-position are able to block 5-HT_3 (**B**) and NK_1-receptors (**A**).[3,4] Substance **P** is a peptide neurotransmitter that binds to the neurokinin-1 receptor and is involved in pain transmission and neurogenic inflammation. CP-96 345 **A** is the first nonpeptide substance **P** antagonist and has shown to be effective in animal models of pain and inflammation.[4] Quinuclidinol **D** is a squalene synthase inhibitor.[5] Protonated quinuclidine squalene synthase inhibitors are carbocation mimics for key steps of the farnesyl pyrophosphate (FPP) to squalene conversion. The 3-phenylethynyl substituent in **D** is supposed to interact with a lipophilic pocket on the enzyme in a manner similar to isoprenyl subunits in a farnesyl chain.[6]

Scheme 1. Selected Medicinally Relevant Compounds Derived from Quinuclidin-3-one



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Tricyclic spiro derivatives of quinuclidine are also potent selective muscarinic agonists.[7] The various pharmacologically active quinuclidines have generally been patented in racemic form although contrasting bioactivity of single isomers and enantiomers is, of course, well-known.

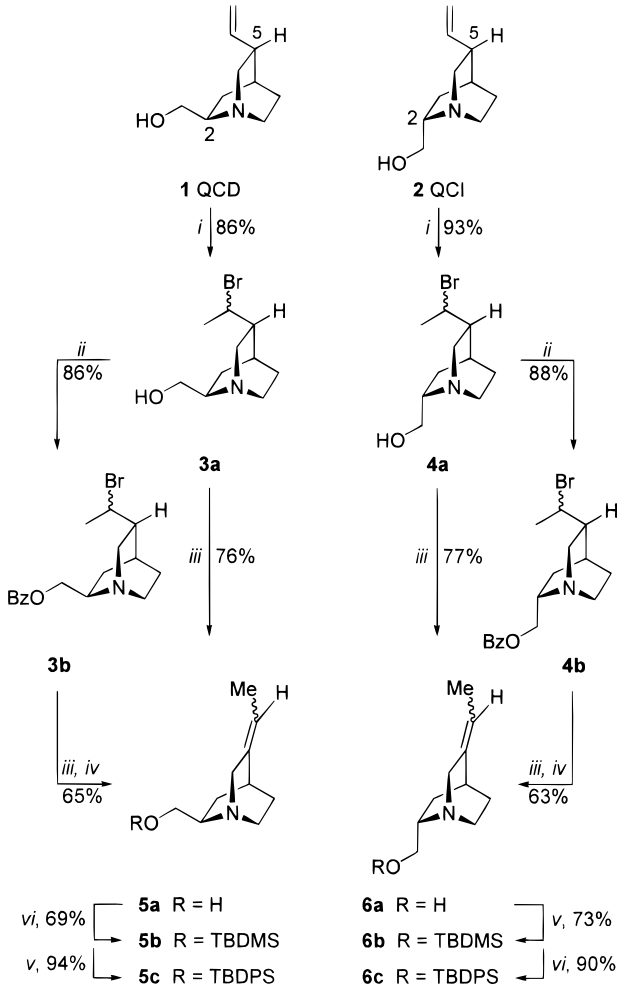
The synthetic methods most frequently used for the preparation of 3-substituted quinuclidines have started from 3-methoxy-carbonylquinuclidine[8] and nucleophilic additions to 3-quinuclidinone.

Results and Discussion

We here report the convenient preparation of enantiopure 2-hydroxymethyl-substituted quinuclidin-3-one analogues from quincoridine, **1** (QCI) and quincorine, **2**[9] (QCD). Oxidative degradation of the vinyl side chain was carried out by (i) double bond shift and (ii) 1,2-dihydroxylation and subsequent 1,2-diol cleavage.

Specifically, hydrobromination of the vinyl group of unprotected β-amino alcohols **1** and **2** in HBr (62%) afforded the alkyl bromides **3a** and **4a** in high yield (86−96%), but the use of fuming HBr was essential. In contrast to the hydrobromination of quinidine,[10] the formation of tricyclic ring ethers was not observed. Selective formation of the trisubstituted Saytzeff olefins **5a** and **6a** under E1-like conditions proceeded via dropwise addition of a DMF solution of alkyl bromides **3a** and **4a** into a preheated mixture of DBU and DMF (100−110 °C). Although acyl protection of the C9−OH group by benzoylation improved the yield of the base-mediated elimination (87% instead of 76%), reaction sequence **1** → **5a** and **2** → **6a** was generally carried out without protecting group, since the additional steps gave no overall improvement (Scheme 2). Bishydroxylation of silylated trisubstituted Saytzeff olefins with catalytic amounts of OsO_4 under two-phase conditions[11] furnished the corresponding diols **7** and **8** as mixtures of four diastereomers, respectively. Olefins **5** and **6** were protected with TBDMS and TBDPS protecting groups in order to maintain sufficient solubility of the intermediate diols in organic solvents and to ease handling. Because of unsatisfactory yields on silylations of C9−OH groups of various QCI and QCD derivatives, protection of trisubstituted olefins **5a** and **6a** was optimized. While the TBDPS group was superior concerning yield (90−94%),

Scheme 2. Preparation of Key Intermediates[a]



[a] Reagents and conditions: (i) 1. HBr (62%), 2. KOH, $NaHCO_3$, 4 d; (ii) 1.5 equiv BzCl, 1.8 equiv Et_3N, CH_2Cl_2, 0 °C → rt, 16 h; (iii) 1.3 equiv DBU, DMF, 110 °C, 3 h; (iv) 8 equiv K_2CO_3, MeOH, r.t., 20 min; (v) 2.0 equiv Et_3N, 0.1 equiv DMAP, 1.5 equiv TBDMSCl, CH_2Cl_2, 0 °C → rt, 10 h; (vi) 2.0 equiv Et_3N, 0.1 equiv DMAP, 1.5 equiv TBDPSCl, CH_2Cl_2, 0 °C → rt, 10 h.

the TBDMS derivatives **5b** and **6b** were more stable, but were formed in lower yield (69−73%). Cleavage of vicinal diols **7** and **8** with $NaIO_4$ in *tert*-BuOH/H_2O provided the protected C-5-ketones **9a**,**b** and **10a**,**b** in high yield (87−93%)[12] and desilylation with TBAF furnished parent hydroxy amino ketones **9d** and **10d**. Unlike quinuclidin-3-one, which contains a plane of symmetry and is achiral, the two title azabicyclics **9d** and **10d** are nonracemic and homochiral, with three stereogenic centers. The transformation of QCI and QCD into their corresponding keto analogues was carried out on a gram scale in 30−35% overall yield. Separation of diastereomers is not required (Scheme 3).

π-Facial Selectivity in Nucleophilic Additions to Carbonyl Group. As evident from Scheme 1, the new azabicyclic hydroxy ketones **9d** and **10d** are promising candidates and precursors for the synthesis of a wide variety of simplified quinine and quinidine analogues. Addition of vinylmagnesium bromide to the C3 carbonyl group of quinidine-based rubanone provides the known and major quinidine metabolite **M** directly.[13] For the

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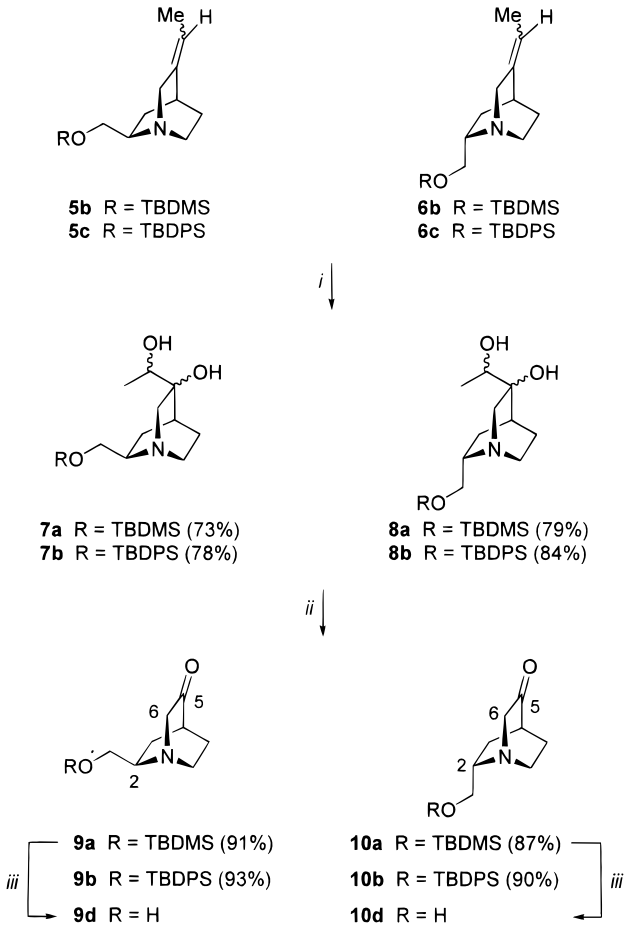
Scheme 3. Preparation of Enantiopure Quinuclidin-3-one Analogs[a]

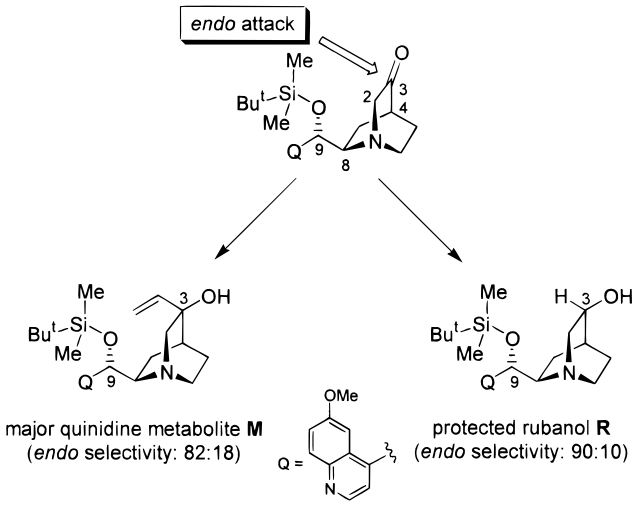


[a] Reagents and conditions: (i) 3 equiv K_2CO_3, 3 equiv $K_3[Fe(CN)_6]$, 0.01 equiv OsO_4 (solid), *t*-BuOH/ H_2O (1:1), 6 h, rt; (ii) 1.3 equiv $NaIO_4$, *t*-BuOH/H_2O, 2 h, rt; (iii) 1.3 equiv TBAF, THF, 0 °C → rt, 12 h.

preparation of naturally configurated analogues of this key metabolite, reaction of TBDMS-protected rubanone with Grignard reagents is the method of choice. Interestingly, the bulky silyl group on the C9 alcohol function of *Cinchona* alkaloids does not block attack at the *endo* face, but appears to actually pull in the nucleophile toward the sterically more hindered carbonyl π-face leading to diastereoselectivities up to 9:1 in rubanol **R** (Scheme 4; see also O-trityl derivative **11d**, Scheme 5, Table 1).[13]

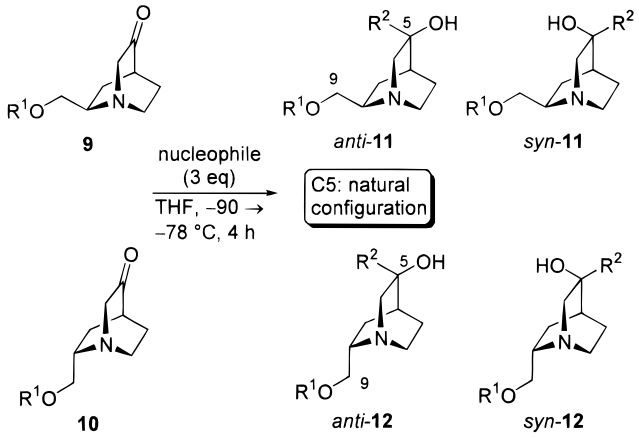
In the case of enantiopure quinuclidin-3-one analogues **9** and **10**, face selectivity of nucleophilic attack at carbon C5 is crucial for obtaining enantiopure analogues of squalene synthase inhibitor **D** (Scheme 1). Addition of L-Selectride to the C5 carbonyl group of **9** and **10** can, in principle, afford two diastereomeric secondary alcohols: *anti*-**11** and *anti*-**12** (natural configuration at carbon C5, corresponding to quinidine metabolite **M** in Scheme 4; *endo* attack of nucleophile) and alcohols *syn*-**11** and *syn*-**12** (nonnatural configuration at C5, *exo* attack of nucleophile). Reaction of unprotected azabicyclic ketone **9d** with bulky L-Selectride gave an inseparable mixture of diastereomeric alcohols *anti*-**11e** and *syn*-**11e** (51:49). In striking contrast, reaction of L-Selectride ($LiBHBu^s_3$) with C9-protected ketones **9a**−**c**,**e** showed diastereoselectivity in favor of the naturally configurated *anti* alcohols with up to 95% de (Scheme 5, entries 1−4, Table 1).

Scheme 4. Establishing the Natural Configuration at Carbon C3 in Quinidine[a]



[a] Note that the azabicyclic core of the natural cinchona alkaloids is numbered according to Rabe, whereas QCI and QCD derivatives are numbered systematically according to IUPAC.

Scheme 5. Synthesis of Substituted 2-Hydroxymethyl Quinuclidin-5-ols



Increasing the size of silyl protecting group furnished de's up to 71%. Trityl protected azabicyclic ketone **9e**, however, provided almost diastereoselectively pure quinuclidinol *anti*-**11d** (de > 95%, entry 4). A similar trend was observed for nucleophilic attack by lithiated phenylacetylene. Whereas unprotected ketone **9d** gave a nearly 1:1 mixture of alcohols *anti*-**11k** and *syn*-**11k** (4% de, entry 16), silylated ketones **9a** (TBDMS) and **9c** (TIPS) furnished *anti*-**11l** in 40% de and *anti*-**11m** in 70% de, respectively (entries 17, 18). Again, trityl protected ketone **9e** reacted with high *endo* selectivity providing *anti*-**11n** (86% de, entry 19). Although the sterically demanding TBDPS protecting group induced high diastereoselectivity, TBDMS- or TIPS-protected azabicyclic ketones **9a** and **9c** were used mainly, because they were more stable toward lithium nucleophiles.[14] For example, the TBDPS ether in protected ketone **9b** was cleaved with 5-methylfuranyl-2-lithium, giving unprotected quinuclidin-5,9-diol **11i** with poor diastereoselectivity (16% de, entry 13). Addition of other organolithium nucleophiles

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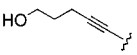
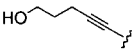
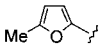
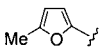
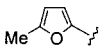
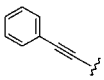
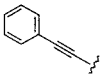
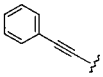
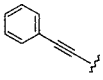
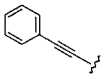
Table 1. Reaction of C5-Ketones with Nucleophiles

entry	ketone	Quinuclidinol	R^1	R^2	nucleophile	yield [%]	de[a] (dr)[a] [%]
1	**9a**	**11a**	TBDMS	H	L-Selectride©	87	62 (81:19)
2	**9b**	**11b**[b]	TBDPS	H	L-Selectride©	82	68 (84:16)
3	**9c**	**11c**	TIPS	H	L-Selectride©	79	72 (86:14)
4	**9e**	**11d**	Trityl	H	L-Selectride©	91	>95 (98:02)
5	**9d**	**11e**	H	H	L-Selectride©	85	02 (51:49)
6	**10a**	**12a**	TBDMS	H	L-Selectride©	84	48 (74:26)
7	**10b**	**12b**	TBDPS	H	L-Selectride©	80	56 (78:22)
8	**9a**	**11f**	TBDMS		R^2Li	69	64 (82:18)
9	**10a**	**12c**	TBDMS		R^2Li	66	34 (67:33)
10	**9a**	**11g**	TBDMS		PhMgBr	77	46 (73:27)
11	**10a**	**12d**	TBDMS		PhMgBr	73	22 (61:39)
12	**9a**	**11h**	TBDMS		R^2Li	76	42 (71:29)
13	**9b**	**11i**[c]	H		R^2Li	65	16 (58:42)
14	**10a**	**12e**	TBDMS		R^2Li	72	18 (59:41)
15	**9a**	**11j**	TBDMS		R^2MgBr	84	16 (58:42)
16	**9b**	**11k**	H		R^2Li	67	04 (52:48)
17	**9a**	**11l**	TBDMS		R^2Li	71	40 (70:30)
18	**9c**	**11m**	TIPS		R^2Li	65	70 (85:15)
19	**9e**	**11n**	Trityl		R^2Li	79	86 (93:07)
20	**10a**	**12f**	TBDMS		R^2Li	75	16 (58:42)

[a] de and dr determined by NMR and GC; de and dr refer to the excess of *anti*-**11** and *anti*-**12**, respectively. [b] *anti*-**11b** and *syn*-**11b** could be separated after mesylation. [c] TBDPS-protected ketone **9** was deprotected upon treatment with lithiated 2-methylfuran.

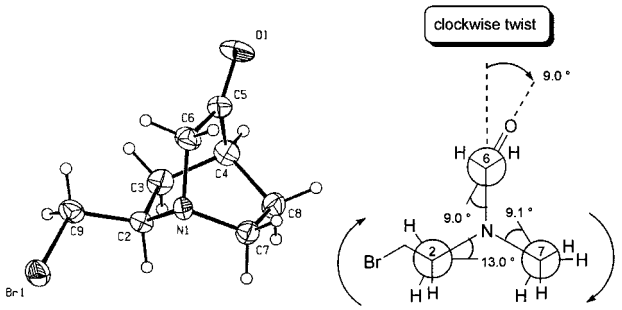
and Grignard reagents showed similar diastereoselectivities except for vinylmagnesium bromide giving only 16% de in the reaction with TBDMS-protected ketone **9a** (entry 15). TBDMS-protected ketone **10a**, with the more remote side chain, showed lower diastereoselectivity compared with QCD-derived ketone **9a**. Reaction of TBDMS-protected ketone **10a** with phenylmagnesium bromide furnished quinuclidin-5-ol **12d** with only 22% de (entry 11), whereas the corresponding reaction with parent QCD-derived ketone **9a** showed 46% de (entry 10). Likewise, reactions with lithiated alkynes (QCI-derived ketone, 34% de; QCD-derived ketone, 64% de), lithiated furan derivatives (QCI, 18% de; QCD, 42% de) and L-Selectride (QCI, 48% de; QCD, 62% de) showed the general trend toward lower diastereoselectivities with QCI-derived ketones **10a**,**b**. Thus, diastereoselectivity of

nucleophilic attack at C5 is not limited to QCD-derived ketones, but appears in QCI-derived ketones, although less so.

The study of electronic effects in various sterically unbiased trigonal carbon centers continues to attract considerable theoretical and experimental attention and has been treated in detail in a recent thematic issue of *Chemical Reviews*.[15] Among the many models, transition-state hyperconjugation[15−17] and electrostatic field interaction[18,19] are two popular explanations for face selectivity. Extended studies of reactions of 5-substituted adamantan-2-ones and their derivatives suggest that the reagent prefers to attack the face antiperiplanar to the more electron-rich vicinal bonds.[20] π-Facial selectivities of sterically unbiased systems have also been observed in substituted carbocyclic bicyclo[2.2.2]octanones, which are rigid models of our title ketones **9** and **10**.[21] A more hindered approach was preferred in the lithium aluminum hydride reduction of substituted bicyclo[2.2.2]octan-2-ones since an isopropyl group at the position adjacent to the keto group seemed to attract the hydride attack from the sterically more demanding *endo* face.[22] This is analogous to the predominance of the more hindered approach in the $LiAlH_4$ reduction of 4-*tert*-butylcyclohexanone. Mehta et al. studied the facial selectivities of 5,6-*endo*,*syn*-disubstituted bicyclo[2.2.2]octan-2-ones.[23] *anti*-Substituents have an effect on face selectivity in nucleophilic additions to these ketones (*syn*:*anti* = 50:50 to 70:30). Addition of organometallic reagents to benzobicyclo[2.2.2]octan-2-one also exhibited *syn* preference.[24] In the case of our ketones **9** and **10**, however, electronic effects cannot exclusively explain the diastereoselectivity of nucleophilic attack, because one π-face of the C5 carbonyl group is affected by hydroxymethyl substitution at C2 and, in particular, by C9-hydroxy protecting groups.

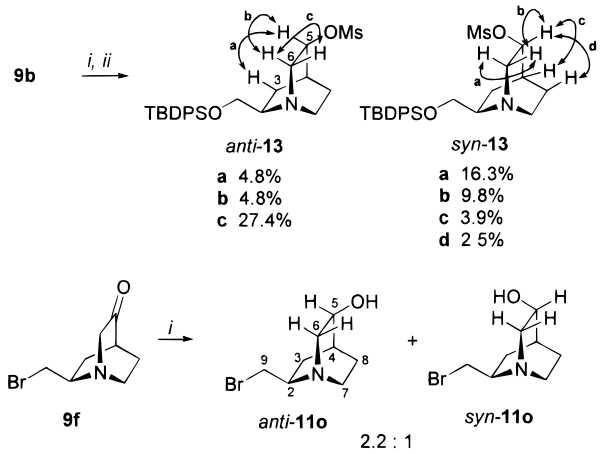
Chelation by α- and β-alkoxy substituents is well-known to control nucleophilic attack at the carbonyl group.[25] A priori, high face selectivities in nucleophilic attack at the C5 carbonyl group of QCD-derived ketones **9a**−**e** may also be considered to be caused partially by interaction of the boron hydride, organolithium and Grignard reagent with the lone-pair electrons of the remote and protected C9 oxygen. Chelation was indeed considered as a simple explanation in our earlier work on the preparation of *Cinchona* alkaloid derivatives by reduction and alkylation of rubanone.[13] Test experiments with parent unprotected quinuclidinone **9d** did not provide significant face selectivities. However, diastereoselectivity is strongly influenced by *the size of protecting groups at C9-oxygen*. Even sterically less demanding δ-bromo ketone **9f** (Scheme 6) provides a moderate diastereomeric excess of 36% (68:32) in favor of *endo*-attack (Scheme 7).

Scheme 6. X-ray Diffraction of δ-bromo Ketone 9f and Torsion of the Azabicyclic Cage[a]



[a] Torsion angles not drawn to scale.

Scheme 7. Structural Assignment of Functionalized *anti*- and *syn*-Quinuclidinols[a]



[a] Reagents and conditions: (i) 3 equiv $LiBHBu^s_3$, THF, −90 °C → −78 °C, 4 h, 82%; (ii) MsCl, 2.0 equiv Et_3N, DCM, 0 °C → rt, 12 h, 94%.

Twisting of the azabicyclic moiety, rather than chelation of the reagent, is an important factor requiring consideration. First of all, X-ray analyses of δ-bromo ketone **9f** and alcohols *anti*-**11o** and *syn*-**11o** support our configurational assignments at carbon C5. Twisting of the azabicyclic core is demonstrated in Scheme 6.[26] Torsion angles α(N1−C6−C5−C4) = 9.0°, α(N1−C7−C8−C4) = 9.1°, and α(N1−C2−C3−C4) = 13.0° indicate clockwise torsion of the azabicyclic cage favoring nucleo-

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Scheme 8. X-ray Structure of δ-Bromo Quinuclidinols *anti*-11o and *syn*-11o

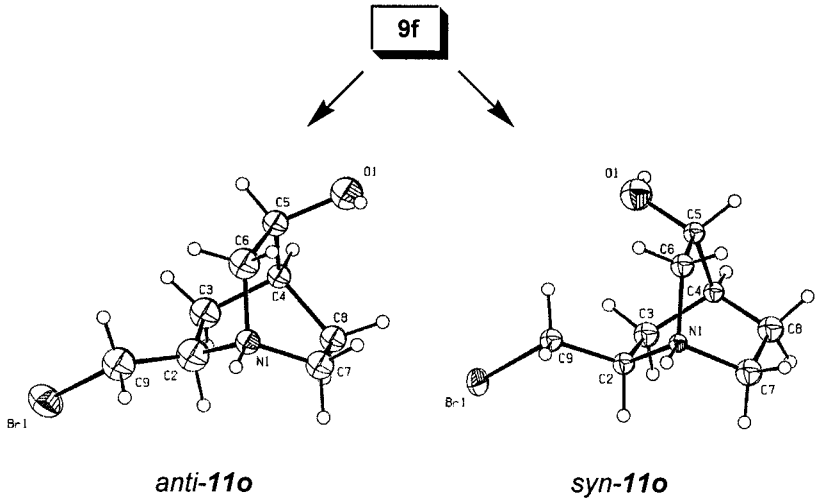

Table 2. Torsion Angles (in degrees) of C9-Brominated Quinuclidine Derivatives

torsion angles	bromoketone **9f**	*anti*-quinuclidin-5-ol, *anti*-**11o**	*syn*-quinuclidinol, *syn*-**11o**
N1−C2−C3−C4	13	12	−2
N1−C6−C5−C4	9	17	−11
N1−C7−C8−C4	9	18	−18
Σ (twisting)	31	47	−31

philic attack from the *endo* face. Clockwise torsion of the azabicyclo[2.2.2]octanone core is also observed in parent *Cinchona* alkaloid ketones which as we have shown previously exhibit fair *endo* diastereoselectivities.[13,27] In fact, we have now observed that clockwise twist dominates nearly all crystal structures of quincorine and quincoridine derivatives.[26,27] Introduction of the bridgehead nitrogen softens and distorts an otherwise rigid bicyclic ketone, which in turn appears to affect the stereochemical outcome of nucleophilic additions.[28] While the *endo*-preference (up to 78:22) of nucleophilic attack to QCI-based ketone **10** (Scheme 5) finds a parallel in the work of Mehta,[23] the *endo*-preference to QCD-based ketone **9** is unprecedented (Schemes 5 and 7). Moreover, clockwise twist in the QCD-series is more developed than in the QCI-series (X-ray evidence[26]).

Assignment of *anti*- and *syn*-Configuration of Functionalized 5-Hydroxy Quinuclidines. Because of signal overlap NOE-measurements on quinuclidin-5-ol **11b** were not informative, and assignment of *anti*- and *syn*-diastereomers was not straightforward initially. However, the derived mesylates *anti*-**13** and *syn*-**13** were readily separated by column chromatography. The configuration of either diastereomer was assigned by NOE and COSY measurements (Scheme 7). In the case of *anti*-**13**, H-5 shows characteristic NOEs with H_{3endo} (**a** 4.8%) and H_{6endo} (**b** 4.8%), whereas H-5 in *syn*-**13** shows NOEs with H_{6exo} (**b** 9.8%) and H_{8exo} (**d** 2.5%). Moreover, diastereomeric quinuclidinols *anti*-**13** and *syn*-**13** can be easily distinguished by the H_{6endo} and H_{6exo} signals, since the H_{6endo} signal of *anti*-**13** is shifted downfield (δ 3.51) relative to the corresponding signal of the *exo* epimer (δ 3.16). In contrast, the H_{6exo} signal of the *endo* diastereomer *anti*-**13** (δ 2.78) is shifted to higher field compared with H_{6exo} in *syn*-**13** (δ 3.09). These effects were previously observed in spectroscopic work on parent *Cinchona* alkaloid derivatives.[13]

Although brominated quinuclidin-5-ols *anti*-**11o** and *syn*-**11o** were obtained as a chromatographically inseparable mixture, we were able to separate *syn*-**11o** and *anti*-**11o** via fractional crystallization and fully characterized both diastereomers by X-ray structure analysis.[26] Thus, the NMR work is corroborated further. Like its parent ketone **9f**, the azabicyclic core of major diastereomer *anti*-**11o** is twisted clockwise (Scheme 8, Table 2), whereas *syn*-**11o** is twisted anticlockwise. A change of twist-sense necessitates two full eclipsing interactions in the C2−C3 and the C7−C8 bridge en route from starting bromo ketone **9f** to the minor product *syn*-**11o**. We suggest that unfavorable eclipsing in the bridges is engendered by nucleophilic attack from the *exo*-face. Hence, *endo* attack is favored (Scheme 9) with formation of naturally configured *anti*-alcohols.

Chromatographically separable mesylated quinuclidin-5-ols *anti*-**13** and *syn*-**13** afford 1,2,4-triazole derivatives, such as **14**, without epimerization, upon treatment with sodium 1,2,4-triazolate in DMF (Scheme 10). These reactions are considered to be S_N2-like, proceeding with clean inversion of configuration (*anti*-**13** → **14**). Parent triazole- and tetrazole-substituted quinuclidines derived from quinuclidin-3-one are potent and selective muscarinic ligands. In some cases, high diastereomeric excess of quinuclidin-5-ols is not decisive, since the stereogenic center at carbon C5 is lost. The reaction of methylfuranyl-substituted quinuclidin-5-ol **11i** (16% de) with formic acid provided the first enantiomerically pure analogue of antimuscarinic quinuclidin-5-ene **F** (Scheme 1) containing three stereogenic centers and a hydroxymethyl group. Phenylacetylene-substituted quinuclidinols **11m**,**n** not only exhibit considerable structural similarity to squalene synthase inhibitor **D**, but in contrast to lead structure **D**, they contain four stereocenters centers and are obtained in high diastereomeric excess.

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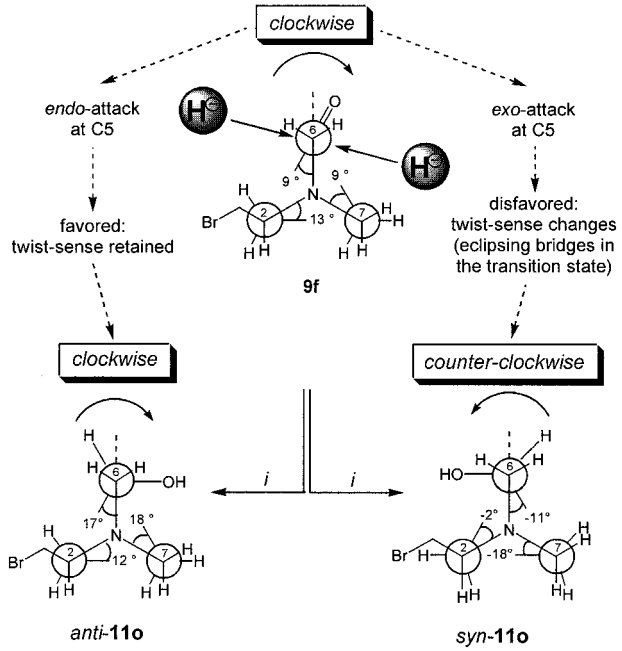
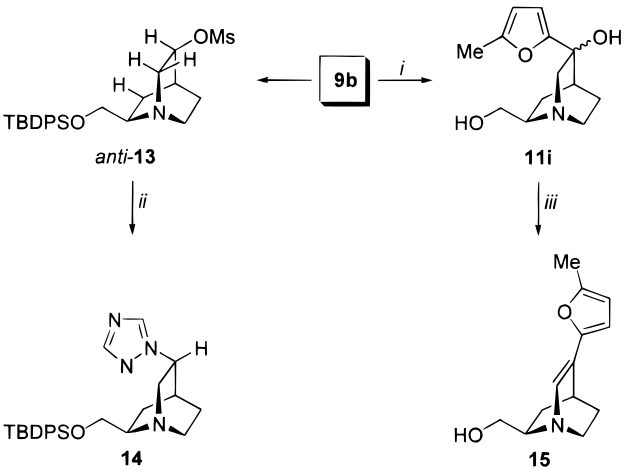
Scheme 9. Newman-Projection of δ-Bromo Quinuclidinols *anti*-11o (Clockwise Twist) and *syn*-11o (Counterclockwise Twist)[a]



[a] Bond angles and bond lengths not drawn to scale. Reagents and conditions: (i) 3 equiv LiBHBu^s$_3$, THF, −90 °C → −78 °C, 4 h, 85%.

Scheme 10. Synthesis of Potential Lead Structures[a]



[a] Reagents and conditions: (i) 3 equiv 5-methyl-2-furanyllithium, THF, −90 °C → −78 °C, 4 h; (ii) 1,2,4-sodium triazolate, DMF, 100 °C, 8 h, 74%; (iii) HCOOH (99%), 2 h, 96%.

Conclusion

We have prepared new 1-azabicyclic ketones **9** and **10** derived from quinidine and quinine. Our ketones are single-isomer 1,2-amino alcohols containing three stereogenic centers each, including the *N*-chiral 1*S*-configurated bridgehead. Because of their low molecular weight and their compact bicyclic structure, both **9** and **10** are attractive homochiral building blocks for asymmetric synthesis, pharmacology and combinatorial chemistry.[9,29−31] Substrate control of stereochemistry in reactions of the simple QCI and QCD derivatives is a challenge greater than substrate control with the sterically more demanding parent *Cinchona* alkaloids. Nonetheless, nucleophilic attack is preferentially directed toward the supposedly more hindered *endo* π-face of the carbonyl group, giving functionalized quinuclidinols with natural configuration at carbon C5 in diastereomeric excess up to 97%. π-Face selectivity, especially in the QCD series, is unprecedented and depends on the size of the remote O-protecting group (1,7-induction). The origin of π-facial selectivity is suggested to be due to torsional strain (*exo*-attack leading to *syn*-product, Scheme 9) rather than electronic.

Experimental Section

^{13}C NMR assignments for each signal were established by DEPT measurements; multiplicities are indicated by CH_3 (primary), CH_2 (secondary), CH (tertiary) or C (quaternary). THF was distilled over sodium and benzophenone before use. Dichloromethane (DCM) was distilled over CaH_2 before use. *N*,*N*-Dimethylformamide was dried and distilled over BaO and stored over molecular sieves (4 Å). Ethyl acetate (EA), CCl_4, $CHCl_3$, DBU, and methyl *tert*-butyl ether (MTBE) were distilled before use.

Short procedure for the synthesis of azabicyclic ketones **9d** *and* **10d**. QCD, **1**, or QCI, **2** (1 equiv), was added to concentrated hydrobromic acid (62%) at 0 °C. The reaction mixture was stirred for 4 days at room temperature (rt). After neutralization with aq KOH (pH 9), the solution was extracted with $CHCl_3$. The combined organic layer was dried (over $MgSO_4$) and the solvent removed. Purification by column chromatography (EA/MeOH 4:1) afforded the alkyl bromides **3a** and **4a**. DBU (1.2 equiv) was added dropwise to the alkyl bromide **3a** or **4a** (1 equiv) in DMF at 100 °C under argon. The mixture was stirred for 4 h at 110 °C. Solvent and base were removed (Kugelrohr apparatus) and the residue dissolved in $CHCl_3$. After extraction (saturated aqueous $NaHCO_3$), the combined organic layer was dried (over $MgSO_4$), evaporated, and purified by chromatography (EA/MeOH 4:1) to furnish the desired trisubstituted alkenes **5a** and **6a**. Et_3N (1.3 equiv) was added to **5a** or **6a** (1 equiv) in abs. CH_2Cl_2 at rt. After the solution was stirred under argon for 15 min, DMAP (0.1 equiv) and TBDMSCl (1.1 equiv) were added at 0 °C, and the mixture was stirred for 16 h at rt, followed by extraction with saturated aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$), evaporated and purified by chromatography (EA/MeOH 20:1) to yield silyl ethers **5b** and **6b**, respectively. Silylated *iso*-QCD, **5b**, or *iso*-QCI, **6b**,**c,** was added to a two-phase system of K_2CO_3 (3 equiv) and $K_3[Fe(CN)_6]$ (3 equiv) in *tert*-BuOH/H_2O (1:1). After 45 min elapsed, solid OsO_4 (0.01 equiv) was added. The reaction mixture was stirred for 5 h at rt, followed by extraction (saturated aqueous $NaHCO_3$, aq $NaHSO_3$). The organic layer was dried ($MgSO_4$), evaporated, and purified by chromatography (EA/MeOH 4:1) to yield diols **7a** and **8a**. A saturated solution of $NaIO_4$ (1.3 equiv) in H_2O was added to the silylated diol (1 equiv) in *tert*-butanol. The mixture was stirred vigorously for 2 h at rt, treated with saturated aqueous $NaHCO_3$, and extracted with $CHCl_3$. After the mixture was dried (over $MgSO_4$), the crude product was purified by column chromatography (EA/MeOH 20:1) to afford the silylated C5-ketones **9a** and **10a**. A 1.0 M solution of TBAF in abs THF (1.3 equiv) was added to C5 ketone **9a** or **10a** (1 equiv) in abs THF at 0 °C. The reaction mixture was stirred for 10 h at rt, followed by addition of $CHCl_3$ and extraction (saturated aqueous $NaHCO_3$, saturated aqueous NaCl). The combined organic layer was dried ($MgSO_4$), evaporated and purified by chromatography (EA/MeOH 6:1) to yield the title compounds **9d** and **10d**.

(1*S*,2*R*,4*S*,5*R*,10*R*/*S*)-2-Hydroxymethyl-5-(10-bromoethyl)-1-azabicyclo[2.2.2]octane (3a) and (1*S*,2*S*,4*S*,5R,-

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(31) Schrake, O.; Rahn, V. S.; Frackenpohl, J.; Braje, W. M.; Hoffmann, H. M. R. *Org. Lett.* **1999**, *1*, 1607.

10*/R/S*)-2-Hydroxymethyl-5-(10-bromoethyl)-1-azabicyclo-[2.2.2]octane (4a). QCD, **1**, (10.40 g, 62.28 mmol) and QCI, **2**, respectively, (11.50 g, 68.26 mmol) were carefully added within 15 min to concentrated hydrobromic acid (62%) at 0 °C. The homogeneous reaction mixture was stirred for 4 days at ambient temperature. After neutralization with aq KOH (pH 9), the solution was diluted with H_2O and extracted with $CHCl_3$. The combined organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. Purification by column chromatography (EA-MeOH 4:1) afforded the alkyl bromides **3a** (86%, 13.23 g, 53.56 mmol) and **4a** (93%, 15.68 g, 63.48 mmol) as slightly yellow waxy solids and diastereomeric mixtures (**3a** 2.2:1, **4a** 1.9:1). Data for **3a**. IR ($CHCl_3$) (ν): 3416, 2944, 1452, 1412, 1260, 1228, 1024 cm^{-1}. ^1H NMR (400 MHz) (δ): 4.11 (m, 1 H, H-10), 4.05 (m, 1 H, OH), 3.51 (m, 1 H, H-9), 3.42 (dd, 1 H, *J* 11, 5 Hz, H-9), 2.97−2.75 (4 H, H-7, H-6, H-2), 2.70/2.49 (ddd, 1 H, *J* 14.2, 7.7, 2.1 Hz, H-6), 1.92−1.81 (m, 2 H, H-5, H-4), 1.71/1.67 (d, 3 H, *J* 6.5 Hz, H-11), 1.68−1.40 (m, 3 H, H-8, H-3), 1.00−0.95 (m, 1 H, H-3). ^{13}C NMR (100 MHz) (δ): 62.01 (CH_2, C-9), 57.24 (CH, C-2), 55.18 (CH, C-10), 48.98 (CH_2, C-6), 48.54 (CH_2, C-7), 45.34 (CH, C-5), 27.12 (CH_2, C-8), 25.21 (CH, C-4), 25.12 (CH_3, C-11), 23.03 (CH_2, C-3). MS *m/z*: 249 (M^+, 1), 247 (M^+, 1), 168 (100). HRMS calcd for $C_{10}H_{18}NO^{81}Br$: 249.2583; found: 249.2584. Data for **4a**. IR ($CHCl_3$) (ν): 3444, 2948, 1452, 1412, 1260, 1236, 1032 cm^{-1}. ^1H NMR (400 MHz) (δ): 4.15 (m, 1 H, H-10), 3.85 (s, 1 H, OH), 3.49−3.42 (m, 2 H, H-9), 3.24−3.16 (dd, 1 H, *J* 14.1, 9.4 Hz, H-2), 3.02−2.89 (m, 2 H, H-7), 2.72−2.70 (m, 1 H, H-6), 2.65−2.58 (m, 1 H, H-6), 1.96−1.93 (m, 2 H, H-5, H-4), 1.75/1.72 (d, 3 H, *J* 6.5 Hz, H-11), 1.67−1.58 (m, 1 H, H-8), 1.56−1.41 (m, 2 H, H-8, H-3), 0.83−0.75 (m, 1 H, H-3). ^{13}C NMR (100 MHz) δ 62.89 (CH_2, C-9), 57.61 (CH_2, C-6), 57.38 (CH, C-2), 56.98 (CH, C-10), 45.59 (CH, C-5), 39.93 (CH_2, C-7), 27.84 (CH_2, C-8), 25.25 (CH, C-4), 25.02 (CH_3, C-11), 23.72 (CH_2, C-3). MS *m/z*: 249 (M^+, 2), 247 (M^+, 1), 168 (100), 138 (5). HRMS calcd for $C_{10}H_{18}NO^{81}Br$: 249.2583; found: 249.2569.

(1*S*,2*R*,4*S*,5*R*,10*R*/*S*)-2-(Benzoyloxymethyl)-5-(10-bromoethyl)-1-azabicyclo[2.2.2]octane (3b) and (1*S*,2*S*,4*S*,-5*R*,10/*R*/*S*)-2-(Benzoyloxymethyl)-5-(10-bromoethyl)-1-azabicyclo[2.2.2]-octane (4b). Benzoyl chloride (6.5 mL, 56 mmol, 1.3 equiv) was added dropwise to a stirred solution of **3a** (10.63 g, 43.03 mmol) or **4a** (10.63 g, 43.03 mmol) and triethylamine (11.9 mL, 86.1 mmol, 2.0 equiv) in abs CH_2Cl_2 (90 mL) at 0 °C. After the mixture was stirred under argon for 14 h at rt, the mixture was diluted with CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$. The combined organic layer was dried ($MgSO_4$), evaporated, and chromatographed (EA/MeOH 10:1) to yield **3b** (86%, 12.99 g, 37.00 mmol) or **4b** (88%, 13.29 g, 37.87 mmol), respectively.

Data for **3b**. IR ($CHCl_3$) (ν): 3008, 2948, 1716, 1600, 1452, 1272, 1224, 1116 cm^{-1}. ^1H NMR (400 MHz) (δ): 8.10−8.04 (m, 2 H, Ar−H), 7.91−7.88 (m, 3 H, Ar−H), 4.58−4.49 (dd, 1 H, *J* 12.2, 8.4 Hz, H-9), 4.39−4.34 (dd, 1 H, *J* 12.2, 4.7 Hz, H-9), 4.13−4.08 (dd, 1 H, *J* 11, 6.5 Hz, H-10), 3.49−3.46 (m, 1 H, H-2), 3.42−3.36 (m, 1 H, H-6), 3.22−3.04 (m, 2 H, H-7), 2.81−2.76 (ddd, 1 H, *J* 14.3, 8.2, 2.5 Hz, H-6), 2.45 (m, 1 H, H-5), 2.02−1.93 (m, 1 H, H-4), 1.83−1.70 (m, 3 H, H-8, H-3), 1.74 (d, 3 H, *J* 6.5 Hz, H-11), 1.49−1.42 (m, 1 H, H-3). ^{13}C NMR (100 MHz) δ 166.63 (C, C-12), 133.05 (C, C-13), 130.94 (CH, Ar−H), 129.04 (CH, Ar−H), 128.80 (CH, Ar−H), 127.60 (CH, Ar−H), 127.15 (CH, Ar−H), 64.63 (CH_2, C-9), 55.72 (CH, C-2), 52.50 (CH, C-10), 48.52 (CH_2, C-6), 46.92 (CH_2, C-7), 45.33 (CH, C-5), 27.21 (CH, C-4), 26.66 (CH_2, C-8), 25.16 (CH_3, C-11), 24.27 (CH_2, C-3). MS *m/z*: 353 (M^+, 1), 351 (M^+, 1), 272 (21), 136 (20), 105 (100). FAB-MS *m/z*: 354 (100), 352 (98), 272 (54). HRMS calcd for $C_{17}H_{22}NO_2{}^{79}Br$: 351.0834; found 351.0837. Data for **4b**. IR ($CHCl_3$) (ν): 2952, 1720, 1620, 1600, 1452, 1272, 1116, 1024 cm^{-1}. ^1H NMR (400 MHz) (δ): 8.12−8.04 (m, 2 H, Ar−H), 7.95−7.87 (m, 1 H, Ar−H), 7.50−7.42 (m, 2 H, Ar−H), 4.56−4.51 (dd, 1 H, *J* 12.3, 8.5 Hz, H-9), 4.47−4.42 (dd, 1 H, *J* 12.3, 5.0 Hz, H-9), 4.16−4.12 (dd, 1 H, *J* 10.7, 6.6 Hz, H-10), 3.73−3.62 (m, 1 H, H-7), 3.58−3.52 (dd, 1 H, *J* 14.1, 9.9 Hz, H-6), 3.39−3.26 (m, 1 H, H-2), 3.18−3.07 (m, 1 H, H-5), 3.06−3.00 (ddd, 1 H, *J* 14.4, 8.3, 2.6 Hz, H-6), 2.57−2.47 (m, 1 H, H-7), 2.23−1.87 (m, 3 H, H-4, H-8, H-3), 1.77/1.75 (d, 3 H, *J* 6.5 Hz, H-11), 1.66−1.55 (m, 1 H, H-8), 1.31−1.23 (m, 1 H, H-3). ^{13}C NMR (100 MHz) δ 166.39 (C, C-12), 133.13 (C, C-13), 131.61 (CH, Ar−H), 129.95 (CH, Ar−H), 129.55 (CH, Ar−H), 128.36 (CH, Ar−H), 127.89 (CH, Ar−H), 64.09 (CH_2, C-9), 55.58 (CH_2, C-6), 54.56 (CH, C-2), 52.10 (CH, C-10), 44.05 (CH, C-5), 40.11 (CH_2, C-7), 26.33 (CH_2, C-8), 25.81 (CH, C-4), 24.88 (CH_3, C-11), 23.16 (CH_2, C-3). MS *m/z*: 353 (M^+, 1), 351 (M^+, 0.4), 272 (6), 136 (5), 105 (100). FAB-MS *m/z*: 354 (56), 352 (64), 272 (100). HRMS calcd for $C_{17}H_{22}NO_2{}^{79}Br$: 351.0834; found 351.0819. Anal. Calcd for $C_{17}H_{22}NO_2Br$: C 57.96, H 6.29, N 3.97; found C 58.19, H 6.14, N 3.82.

General Procedure for the Elimination of 3a,b *and* 4a,b. DBU (1.2 equiv) was added dropwise to a solution of the alkyl bromide **3a**,**b** or **4a**,**b** (1 equiv) in anhydrous DMF at 100 °C under argon, and the mixture was stirred for 4 h at 110 °C. Solvent and base were removed (Kugelrohr apparatus), and the residue was dissolved in $CHCl_3$. After extraction with saturated aqueous $NaHCO_3$, the combined organic layer was dried ($MgSO_4$), evaporated, and purified by chromatography (EA/MeOH 4:1 for **3a** and **4a** and EA/MeOH 10:1 for **3b** and **4b**, respectively) to furnish the desired trisubstituted alkenes **5a**, **5d**, **6a,** and **6d** as inseparable *E*/*Z* mixtures.

(1*S*,2*R*,4*S*)-2-Hydroxymethyl-(*E*/*Z*)-5-ethylidene-1-azabicyclo[2.2.2]octane (5a). 3a (14.21 g, 57.30 mmol) was allowed to react according to the general procedure to afford **5a** (76%, 7.27 g, 43.55 mmol). IR ($CHCl_3$) (ν): 3000, 2940, 1452, 1412, 1236, 1088, 1016 cm^{-1}. ^1H NMR (400 MHz) (δ): 5.19−5.11 (m, 1 H, H-10), 3.71 (bs, 1 H, OH), 3.58−3.54 (d, 1 H, *J* 17.6 Hz, H-6), 3.50−3.38 (m, 2 H, H-9), 3.27−3.23 (d, 1 H, *J* 17.2 Hz, H-6), 3.08−2.98 (m, 1 H, H-7), 2.95−2.86 (m, 2 H, H-7, H-2), 2.29−2.27 (m, 1 H, H-4), 1.82−1.75 (m, 1 H, H-3), 1.71−1.62 (m, 1 H, H-8), 1.58−1.55 (m, 1 H, H-8), 1.50−1.47 (d, 3 H, *J* 6.9 Hz, H-11), 1.05−1.00 (m, 1 H, H-3). ^{13}C NMR (100 MHz) δ 141.14/140.04 (C, C-5), 113.74/113.26 (CH, C-10), 62.84 (CH_2, C-9), 57.61 (CH, C-2), 49.82/49.26 (CH_2, C-6), 46.78 (CH_2, C-7), 32.76 (CH, C-4), 30.62/29.38 (CH_2, C-8), 27.49/26.65 (CH_2, C-3), 12.58/12.27 (CH_3, C-11). MS *m/z* 167 (M^+, 100): 150 (76), 136 (96). HRMS calcd for $C_{10}H_{17}NO$: 167.1310; found 167.1310.

(1*S*,2*S*,4*S*)-2-Hydroxymethyl-(*E*/*Z*)-5-ethylidene-1-azabicyclo[2.2.2]octane (6a). 4a (17.00 g, 68.83 mmol) was allowed to react according to the general procedure to afford **6a** (77%, 8.85 g, 53.0 mmol). IR ($CHCl_3$) (ν): 3000, 2940, 1436, 1412, 1228, 1072, 1028 cm^{-1}. ^1H NMR (400 MHz) (δ): 5.24−5.17 (m, 1 H, H-10), 3.68 (bs, 1 H, OH), 3.59−3.32 (m, 4 H, H-6, H-9, H-6), 3.08−2.98 (m, 1 H, H-7), 2.95−2.86 (m, 1 H, H-7), 2.72−2.61 (m, 1 H, H-2), 2.29−2.26 (m, 1 H, H-4), 1.76−1.68 (m, 1 H, H-3), 1.71−1.62 (m, 2 H, H-8), 1.51−1.48 (m, 3 H, H-11), 1.05−0.99 (m, 1 H, H-3). ^{13}C NMR (100 MHz) (δ): 141.38/140.80 (C, C-5), 114.80/114.28 (CH, C-10), 62.84 (CH_2, C-9), 58.58 (CH, C-2), 57.63/55.96 (CH_2, C-6), 41.78/40.77 (CH_2, C-7), 32.73 (CH, C-4), 31.02/30.11 (CH_2, C-8), 28.05/26.81 (CH_2, C-3), 12.69/12.37 (CH_3, C-11). MS *m/z*: 167 (M^+, 91), 150 (72), 136 (100). HRMS calcd for $C_{10}H_{17}NO$: 167.1310; found 167.1295.

(1*S*,2*R*,4*S*)-2-(Benzoyloxymethyl)-(*E*/*Z*)-5-ethylidene-1-azabicyclo[2.2.2]octane (5d). 3b (3.32 g, 9.46 mmol) was allowed to react according to the general procedure to afford **5d** (87%, 2.23 g, 8.23 mmol; *E*/*Z* ratio: 3.1:1). IR ($CHCl_3$) (ν): 3000, 2940, 1716, 1580, 1452, 1276, 1116, 1024 cm^{-1}. ^1H NMR (400 MHz) (δ): 8.07−8.04 (m, 2 H, Ar−H), 7.56−7.51 (m, 1 H, Ar−H), 7.45−7.39 (m, 2 H, Ar−H), 5.23−5.19 (m, 1 H, H-10), 4.43−4.37 (dd, 1 H, *J* 11.5, 8.0 Hz, H-9), 4.26−4.21 (dd, 1 H, *J* 11.7, 5.5 Hz, H-9), 3.73−3.69 (m, 1 H, H-6), 3.42−3.30 (m, 2 H, H-6, H-7), 3.05−2.79 (m, 2 H, H-7, H-2), 2.37−2.35 (m, 1 H, H-4), 1.96−1.89 (m, 1 H, H-3), 1.75−1.64 (m, 2 H, H-8), 1.60/1.53 (m, 3 H, H-11), 1.40−1.35 (m, 1 H, H-3). ^{13}C NMR (100 MHz) (δ): 166.73 (C, C-12), 141.04/139.91 (C, C-5), 132.94/131.18 (CH, Ar−H), 130.15 (C, C-13), 129.73 (CH, Ar−H), 128.29 (CH, Ar−H), 113.92/113.46 (CH, C-10), 65.98 (CH_2, C-9), 54.62 (CH, C-2), 49.98/49.61 (CH_2, C-6), 48.01 (CH_2, C-7), 32.85 (CH, C-4), 31.17/30.12 (CH_2, C-8), 27.13/26.24 (CH_2, C-3), 12.61/12.34 (CH_3, C-11). MS *m/z*: 271 (M^+, 25), 256 (5), 166 (25), 150 (76), 136 (67), 105 (100). HRMS calcd for $C_{17}H_{21}N_1O_2$: 271.1361; found 271.1401.

(1*S*,2*S*,4*S*)-2-(Benzoyloxymethyl)-(E/Z)-5-ethylidene-1-azabicyclo[2.2.2]octane (6d). 4b (7.40 g, 21.1 mmol) was allowed to react according to the general procedure to afford **6d** (85%, 4.87 g, 18.0 mmol). IR ($CHCl_3$) (ν): 3008, 2944, 1716, 1600, 1448, 1276, 1116, 1024 cm^{-1}. ^1H NMR (400 MHz) (δ): 8.08−8.04 (M, 2 H, Ar−H), 7.55−7.50 (m, 1 H, Ar−H), 7.45−7.37 (m, 2 H, Ar−H), 5.28−5.21 (m, 1 H, H-10), 4.48−4.33/4.47−4.42 (dd, 1 H, *J* 11.5, 8.2 Hz, H-9), 4.32−4.27/4.33−4.28 (dd, 1 H, *J* 11.5, 5.8 Hz, H-9), 3.56−3.53 (m, 1 H, H-7), 3.32−3.23 (m, 1 H, H-6), 3.21−3.11 (m, 1 H, H-6), 2.87−2.78 (m, 2 H, H-7, H-2), 2.37−2.33 (m, 1 H, H-4), 1.94−1.85 (m, 1 H, H-3), 1.69−1.62 (m, 2 H, H-8), 1.61/1.53 (m, 3 H, H-11), 1.41−1.32 (m, 1 H, H-3). ^{13}C NMR (100 MHz) (δ): 166.74 (C, C-12), 140.39/139.34 (C, C-5), 132.96 (CH, Ar−H), 130.13 (C, C-13), 129.51 (CH, Ar−H), 128.32 (CH, Ar−H), 114.94/ 114.49 (CH, C-10), 65.85 (CH_2, C-9), 57.79/55.51 (CH_2, C-6), 55.50/55.21 (CH, C-2), 41.93 (CH_2, C-7), 32.86 (CH, C-4), 31.63/30.75 (CH_2, C-8), 27.97/26.75 (CH_2, C-3), 12.73/12.42 (CH_3, C-11). MS *m*/*z*: 271 (M^+, 37), 256 (5), 166 (20), 150 (62), 136 (45), 105 (100). HRMS calcd for $C_{17}H_{21}N_1O_2$: 271.1572; found 271.1571.

General Procedure for the Silylation of 5a and 6a. Triethylamine (1.3 equiv) was added to a solution of **5a** or **6a** (1 equiv) in abs CH_2Cl_2 at rt. After the mixture was stirred under argon for 15 min, DMAP (0.1 equiv) and the corresponding silyl chloride (1.1 equiv) were added at 0 °C, and the homogeneous mixture was stirred for 16 h at rt, followed by extraction with saturated aqueous $NaHCO_3$. The combined organic layer was dried ($MgSO_4$), evaporated, and purified by chromatography (EA/MeOH 20:1) to yield silyl ethers **5b**,**c** and **6b**,**c**, respectively, as inseparable *E*/*Z* mixtures.

(1*S*,2*R*,4*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-(*E*/*Z*)-5-ethylidene-1-azabicyclo[2.2.2]-octane (5b). 5a (6.58 g, 39.4 mmol) and TBDMSCl (6.50 g, 43.3 mmol) were allowed to react according to the general procedure to afford **5b** (69%, 7.64 g, 27.2 mmol, *E*/*Z* ratio 2.65:1). IR ($CHCl_3$) (ν): 2952, 2928, 1464, 1256, 1104, 1028 cm^{-1}. ^1H NMR (400 MHz) (δ): 5.18−5.12/5.11−5.06 (m, 1 H, H-10), 3.73−3.69/3.72−3.68 (dd, 1 H, *J* 10.1, 5.8 Hz, H-9), 3.60−3.52 (m, 2 H, H-9, OH), 3.29−3.24/3.21−3.16 (d, 1 H, *J* 17.5 Hz, H-6), 2.95−2.74 (m, 4 H, H-6, H-7, H-2), 2.33−2.28 (m, 1 H, H-4), 1.82−1.76 (m, 1 H, H-3), 1.69−1.60 (m, 2 H, H-8), 1.59−1.56/1.49−1.46 (m, 3 H, H-11), 1.46−1.39 (m, 1 H, H-3), 0.92−0.88 (s, 9 H, SiC(CH_3)$_3$), 0.08−0.04 (m, 6 H, SiCH_3). ^{13}C NMR (100 MHz) (δ): 142.35/141.21 (C, C-5), 112.81/112.39 (CH, C-10), 65.91 (CH_2, C-9), 57.35 (CH, C-2), 51.26/50.46 (CH_2, C-6), 50.16/48.85 (CH_2, C-7), 33.26 (CH, C-4), 31.48/30.49 (CH_2, C-8), 27.54/26.66 (CH_2, C-3), 25.98 (CH_3, SiC(CH_3)$_3$), 25.81 (CH_3, SiC(CH_3)$_3$), 25.78 (CH_3, SiC(CH_3)$_3$), 18.39/18.08 (C, SiC(CH_3)$_3$), 12.56/12.23 (CH_3, C-11), −3.42 (CH_3, SiCH_3), −5.33 (CH_3, SiCH_3). MS *m*/*z*: 281 (M^+, 23), 266 (17), 224 (100), 149 (16), 136 (31). HRMS calcd for $C_{16}H_{31}NOSi$: 281.2174; found 281.2169.

(1*S*,2*S*,4*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-(*E*/*Z*)-5-ethylidene-1-azabicyclo[2.2.2]-octane (6b). 6a (8.80 g, 52.7 mmol) and TBDMSCl (8.69 g, 58.0 mmol) were allowed to react according to the general procedure to afford **6b** (73%, 10.81 g, 38.47 mmol, *E*/*Z* ratio 5:1). IR ($CHCl_3$) (ν): 2952, 2928, 1472, 1256, 1108, 1004 cm^{-1}. ^1H NMR (400 MHz) (δ): 5.34−5.25 (m, 1 H, H-10), 4.01−3.96 (dd, 1 H, *J* 11.0, 5.0 Hz, H-9), 3.76−3.72 (dd, 1 H, *J* 11.0, 5.2 Hz, H-9), 3.67−3.62 (d, 1 H, *J* 18.7 Hz, H-6), 3.62−3.57 (m, 1 H, H-7), 3.42−3.33 (m, 1 H, H-6), 3.12−3.03 (m, 1 H, H-2), 2.92−2.83 (m, 1 H, H-7), 2.45−2.41 (m, 1 H, H-4), 1.81−1.60 (m, 4 H, H-3, H-8, H-3), 1.53−1.51 (d, 3 H, *J* 6.9 Hz, H-11), 0.91−0.86 (s, 9 H, SiC(CH_3)$_3$), 0.09−0.05 (m, 6 H, SiCH_3). ^{13}C NMR (100 MHz) (δ): 144.23/143.16 (C, C-5), 116.41/115.96 (CH, C-10), 64.18 (CH_2, C-9), 58.64/58.33 (CH, C-2), 55.72 (CH_2, C-6), 43.39 (CH_2, C-7), 32.53 (CH, C-4), 29.53/28.73 (CH_2, C-8), 26.66/25.13 (CH_2, C-3), 25.93 (CH_3, SiC(CH_3)$_3$), 25.74 (CH_3, SiC(CH_3)$_3$), 25.59 (CH_3, SiC(CH_3)$_3$), 18.29/18.04 (C, SiC(CH_3)$_3$), 12.76/12.55 (CH_3, C-11), −3.48 (CH_3, SiCH_3), −5.33 (CH_3, SiCH_3). MS *m*/*z*: 282 (M^++1, 18), 281 (M^+, 6), 266 (14), 224 (100), 149 (12), 136 (23). HRMS calcd for $C_{16}H_{31}NOSi$: 281.2174; found 281.2175.

(1*S*,2*R*,4*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-(*E*/*Z*)-5-ethylidene-1-azabicyclo[2.2.2]-octane (5c). 5a (4.50 g, 27.0 mmol) and TBDPSCl (7.71 mL, 29.6 mmol) were allowed to react according to the general procedure to afford **5c** (94%, 10.26 g, 25.33 mmol). IR ($CHCl_3$) (ν): 3000, 2932, 1600, 1572, 1428, 1260, 1112, 1024 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.72−7.68 (m, 4 H, Ar−H), 7.46−7.37 (m, 6 H, Ar−H), 5.25−5.18/5.14−5.06 (m, 1 H, H-10), 3.85−3.74 (m, 2 H, H-9), 3.71 (bs, 1 H, OH), 3.37−3.32 (d, 1 H, *J* 17.4 Hz, H-6), 3.09−2.95 (m, 2 H, H-7, H-6), 2.94−2.80 (m, 2 H, H-7, H-2), 2.40−2.36 (m, 1 H, H-4), 1.89−1.83 (m, 1 H, H-3), 1.79−1.63 (m, 3 H, H-8, H-3), 1.62−1.58/1.49−1.46 (m, 3 H, H-11), 1.09−1.05 (s, 9 H, SiC(CH_3)$_3$). ^{13}C NMR (100 MHz) (δ): 141.00/140.36 (C, C-5), 135.70 (CH, Ar−H), 133.49 (C, Ph−Si), 129.60 (CH, Ar−H), 127.67 (CH, Ar−H), 113.51/113.06 (CH, C-10), 66.28/65.97 (CH_2, C-9), 57.37/57.20 (CH, C-2), 50.00/50.18 (CH_2, C-6), 49.34/48.72 (CH_2, C-7), 33.08 (CH, C-4), 30.80/29.97 (CH_2, C-8), 27.70/26.29 (CH_2, C-3), 26.91 (CH_3, SiC(CH_3)$_3$), 19.26 (C, SiC(CH_3)$_3$), 12.59/12.29 (CH_3, C-11). MS *m*/*z*: 405 (M^+, 8), 348 (100), 266 (7), 199 (29), 136 (7). HRMS calcd for $C_{26}H_{35}NOSi$: 405.2488; found 405.2489.

(1*S*,2*S*,4*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-(E/Z)-5-ethylidene-1-azabicyclo[2.2.2]-octane (6c). 6a (5.00 g, 29.9 mmol) and TBDPSCl (8.57 mL, 32.9 mmol) were allowed to react according to the general procedure to afford **6c** (90%, 10.91 g, 26.95 mmol). IR ($CHCl_3$) (ν): 3000, 2932, 1600, 1472, 1428, 1260, 1112 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.74−7.68 (m, 4 H, Ar−H), 7.47−7.34 (m, 6 H, Ar−H), 5.29−5.19 (m, 1 H, H-10), 3.84−3.77 (m, 2 H, H-9), 3.53−3.47 (d, 1 H, *J* 18.3 Hz, H-6), 3.43−3.37 (d, 1 H, *J* 18.3 Hz, H-6), 3.18−3.03 (m, 1 H, H-7), 2.99−2.91 (m, 1 H, H-7), 2.74−2.62 (m, 1 H, H-2), 2.37−2.33 (m, 1 H, H-4), 1.92−1.79 (m, 2 H, H-3, H-8), 1.69−1.57 (m, 2 H, H-8, H-3), 1.53−1.49 (d, 3 H, *J* 6.7 Hz, H-11), 1.10/1.06 (s, 9 H, SiC(CH_3)$_3$). ^{13}C NMR (100 MHz) (δ): 141.59 (C, C-5), 135.90 (CH, Ar−H), 134.92 (CH, Ar−H), 133.47 (C, Ph−Si), 129.64 (CH, Ar−H), 127.56 (CH, Ar−H), 114.66/114.45 (CH, C-10), 66.39 (CH_2, C-9), 58.17/57.34 (CH, C-2), 55.59 (CH_2, C-6), 43.12/42.37 (CH_2, C-7), 33.01 (CH, C-4), 31.31 (CH_2, C-8), 27.69/27.35 (CH_2, C-3), 26.67 (CH_3, SiC(CH_3)$_3$), 19.27 (C, SiC(CH_3)$_3$), 12.71/12.39 (CH_3, C-11). MS *m*/*z*: 405 (M^+, 3), 349 (5), 199 (100). HRMS calcd for $C_{26}H_{35}NOSi$: 405.2488; found 405.2476.

General Procedure for the Bishydroxylation of Silylated *iso*-quincoridines 5b−c and silylated iso-quincorines 6b,c. Silylated *iso*-QCD **5b**,**c** or silylated *iso*-QCI **6b**,**c**, respectively, was added to a vigorously stirred two-phase system of K_2CO_3 (3 equiv) and $K_3[Fe(CN)_6]$ (3 equiv) in *tert*-butyl alcohol/H_2O (1:1, 5 mL per mmol alkaloid). After 45 min solid osmium(VIII)oxide (0.01 equiv) was added in small portions, and the reaction mixture was stirred for 5 h under argon at rt, followed by extraction with saturated aqueous $NaHCO_3$ and aq $NaHSO_3$ (10%). The combined organic layer was dried ($MgSO_4$), evaporated, and purified by chromatography (EA/MeOH 4:1) to yield the desired C10−C3 diols **7a**,**b** and **8a**,**b** as inseparable mixtures of four possible diastereomers. In most cases, only the one or two most intensive NMR signals are given.

(1*S*,2*R*,4*S*,5*R*/*S*,10*R*/*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-(5,10-dihydroxyethyl)-1-azabicyclo[2.2.2]octane (7a). 5b (3.00 g, 10.7 mmol) was allowed to react according to the general procedure to afford **7a** (73%, 2.45 g, 7.79 mmol). IR ($CHCl_3$) (ν): 3436, 2952, 2932, 1460, 1256, 1120, 1000 cm^{-1}. ^1H NMR (400 MHz) (δ): 3.98−3.94 (dd, 1 H, *J* 12.4, 6.2 Hz, H-9), 3.89−3.84 (dd, 1 H, *J* 10.7, 4.4 Hz, H-9), 3.77−3.74 (m, 1 H, H-10), 3.64−3.62 (m, 1 H, H-2), 2.97−2.93/2.88−2.85 (d, 1 H, *J* 14.3 Hz, H-6), 2.90−2.69 (m, 2 H, H-7), 2.48−2.43/2.44−2.41 (d, *J* 14.6 Hz, H-6), 2.18−2.12 (m, 1 H, H-4), 2.01−1.93/1.83−1.81 (m, 1 H, H-3), 1.62−1.33 (m, 3 H, H-8, H-3), 1.16−1.13/1.09−1.08 (m/d, 3 H, *J* 6.3 Hz, H-11), 0.90/0.89 (s, 9 H, SiC(CH_3)$_3$), 0.11−0.10/0.07−0.04 (m, 6 H, SiCH_3). ^{13}C NMR (100 MHz) (δ): 73.70 (C, C-5), 69.64/67.54 (CH, C-10), 66.74/65.83 (CH_2, C-9), 56.32/55.72 (CH, C-2), 55.53/54.29 (CH_2, C-6), 49.82/49.13 (CH_2, C-7), 29.68/28.35 (CH, C-4), 25.36 (CH_3, SiC(CH_3)$_3$), 25.27/24.75 (CH_2, C-8), 21.79/20.55 (CH_2, C-3), 17.85 (C, SiC(CH_3)$_3$), 15.66/15.57 (CH_3, C-11), −6.03 (CH_3, SiCH_3). MS *m*/*z*: 315 (M^+, 10), 300 (11), 258 (89), 170 (100); FAB-MS 316 (M^++1, 100). HRMS calcd for $C_{16}H_{33}NO_3Si$: 315.2229; found 315.2228.

(1*S*,2*S*,4*S*,5*R*/*S*,10*R*/*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-(5,10-dihydroxyethyl)-1-azabicyclo[2.2.2]octane (8a). 6b (6.00 g, 21.4 mmol) was allowed to react according to the general procedure to afford **8a** (79%, 5.31 g, 16.9 mmol). IR ($CHCl_3$) (ν): 3420, 2956, 2928, 1472, 1256, 1120, 1092, 1052 cm^{-1}. ^1H NMR (400 MHz) (δ): 3.92−3.83 (m, 1 H, H-9), 3.73−3.61 (m, 2 H, H-9, H-10), 3.11−2.96 (m, 2 H, H-7, H-2), 2.75−2.71 (d, 1 H, *J* 14.3 Hz, H-6), 2.57−2.45 (d, *J* 14.6 Hz, H-6), 2.49−2.43 (m, 1 H, H-7), 2.15−2.11 (m, 1 H, H-4), 1.99−1.95 (m, 1 H, H-3), 1.84−1.72 (m, 1 H, H-8), 1.55−1.40 (m, 1 H, H-8), 1.38−1.27 (m, 1 H, H-3), 1.19−1.14 (m, 3 H, H-11), 0.89 (s, 9 H, SiC(CH_3)$_3$), 0.07−0.04 (m, 6 H, SiCH_3). ^{13}C NMR (100 MHz) (δ): 73.39/73.14 (C, C-5), 69.38/68.52 (CH, C-10), 65.90/65.59 (CH_2, C-9), 61.56/61.41 (CH_2, C-6), 57.18/56.38 (CH, C-2), 41.97/41.84 (CH_2, C-7), 29.54/29.16 (CH, C-4), 26.58/25.28 (CH_2, C-8), 25.98 (CH_3, SiC(CH_3)$_3$), 23.09/21.63 (CH_2, C-3), 18.38 (C, Si*C*(CH_3)$_3$), 16.32/16.12 (CH_3, C-11), −5.33 (CH_3, SiCH_3). MS *m*/*z*: 315 (M^+, 10), 298 (16), 58 (100), 170 (73); FAB-MS 316 (M^++1, 100), 298 (17). HRMS calcd for $C_{16}H_{33}NO_3Si$: 315.2229; found 315.2230.

(1*S*,2*R*,4*S*,5*R*/*S*,10*R*/*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-5-(5,10-dihydroxyethyl)-1-azabicyclo[2.2.2]octane (7b). 5c (10.00 g, 24.69 mmol) was allowed to react according to the general procedure to afford **7b** (78%, 8.45 g, 19.3 mmol). IR ($CHCl_3$) (ν): 3568, 2934, 1589, 1471, 1251, 1113, 997 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.70−7.63 (m, 4 H, Ar−H), 7.43−7.34 (m, 6 H, Ar−H), 3.84−3.70 (m, 2 H, H-9, H-10), 3.60−3.55 (m, 1 H, H-9), 2.90−2.75 (m, 3 H, H-2, H-7), 2.65−2.61 (d, 1 H, *J* 14.7 Hz, H-6), 2.43−2.39 (d, 1 H, *J* 14.7 Hz, H-6), 2.11−2.05 (m, 1 H, H-4), 1.96−1.88 (m, 1 H, H-3), 1.69−1.59 (m, 1 H, H-8), 1.57−1.43 (m, 1 H, H-8), 1.39−1.29 (m, 1 H, H-3), 1.13−1.11/0.98−0.97 (d, 3 H, *J* 6.2 Hz, H-11), 1.07/1.05 (s, 9 H, SiC(CH_3)$_3$). ^{13}C NMR (100 MHz) (δ): 135.71 (CH, Ar−H), 133.49 (C, Ar−Si), 129.67 (CH, Ar−H), 127.66 (CH, Ar−H), 73.27/72.68 (C, C-5), 69.53/67.56 (CH, C-10), 66.87/66.23 (CH_2, C-9), 56.56/55.68 (CH, C-2), 55.00/54.13 (CH_2, C-6), 49.61/49.05 (CH_2, C-7), 29.67/28.90 (CH, C-4), 26.92 (CH_3, SiC(CH_3)$_3$), 26.02/24.22 (CH_2, C-8), 22.54/21.21 (CH_2, C-3), 19.24 (C, Si*C*(CH_3)$_3$), 16.26/16.19 (CH_3, C-11). MS *m*/*z*: 439 (M^+, 4), 421 (3), 382 (100), 364 (8), 170 (28). HRMS calcd for $C_{26}H_{37}NO_3Si$: 439.2542; found 439.2535.

(1*S*,2*S*,4*S*,5*R*/*S*,10*R*/*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-5-(5,10-dihydroxyethyl)-1-azabicyclo[2.2.2]octane (8b). 6c (10.00 g, 24.69 mmol) was allowed to react according to the general procedure to afford **8b** (84%, 9.11 g, 20.7 mmol). IR ($CHCl_3$) (ν): 3568, 2932, 1589, 1472, 1427, 1265, 1112, 998 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.69−7.64 (m, 4 H, Ar−H), 7.42−7.34 (m, 6 H, Ar−H), 3.85−3.66 (m, 3 H, H-9, H-10), 3.13−3.05 (m, 1 H, H-7), 3.02−2.93 (m, 1 H, H-2), 2.73−2.66 (m, 1 H, H-6), 2.52−2.48 (d, 1 H, *J* 14.3 Hz, H-6), 2.46−2.38 (m, 1 H, H-7), 2.12−2.07 (m, 1 H, H-4), 1.93−1.78 (m, 1 H, H-3), 1.54−1.35 (m, 2 H, H-8), 1.29−1.22 (m, 1 H, H-3), 1.16−1.10 (m, 3 H, H-11), 1.05 (s, 9 H, SiC(CH_3)$_3$). ^{13}C NMR (100 MHz) (δ): 135.65 (CH, Ar−H), 133.75 (C, Ar−Si), 129.67 (CH, Ar−H), 127.68 (CH, Ar−H), 73.39/73.10 (C, C-5), 69.34/68.36 (CH, C-10), 66.69/66.48 (CH_2, C-9), 61.56/61.42 (CH_2, C-6), 57.02/56.28 (CH, C-2), 42.05/41.99 (CH_2, C-7), 29.59/29.15 (CH, C-4), 26.90 (CH_3, SiC(CH_3)$_3$), 26.84/25.52 (CH_2, C-8), 23.13/21.59 (CH_2, C-3), 19.27 (C, Si*C*(CH_3)$_3$), 16.29/16.09 (CH_3, C-11). MS *m*/*z*: 439 (M^+, 2), 408 (8), 383 (36), 351 (100), 199 (14). HRMS calcd for $C_{26}H_{37}NO_3Si$: 439.2542; found 439.2539.

General procedure for the diol cleavage of silylated diols **7a**,**b** *and* **8a**,**b**. A saturated solution of $NaIO_4$ (1.3 equiv) in H_2O was added dropwise to a solution of the silyl-protected diol (1 equiv) in *tert*-butanol. The mixture was stirred vigorously for 2 h at rt under argon, treated with $NaHCO_3$ and extracted with $CHCl_3$. After it was dried (over $MgSO_4$), the organic layer was concentrated, and the crude product was purified by column chromatography (EA/MeOH 20:1) to yield the desired C5-ketones **9a**,**b** and **10a**,**b**, respectively.

(1*S*,2*R*,4*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-one (9a). 7a (630 mg, 2.00 mmol) was allowed to react according to the general procedure to afford **9a** (91%, 489 mg, 1.82 mmol). IR ($CHCl_3$) (ν): 2952, 2928, 1728, 1468, 1404, 1256, 1124, 1096, 1028 cm^{-1}. ^1H NMR (400 MHz) (δ): 3.71−3.66 (dd, 1 H, *J* 19.5, 5.1 Hz, H-6), 3.69−3.68 (d, 1 H, *J* 5.3 Hz, H-9), 3.68−3.67 (d, 1 H, *J* 5.3 Hz, H-9), 3.10−3.04 (d, 1 H, *J* 19.5 Hz, H-6), 3.07−3.02 (m, 1 H, H-7), 3.01−2.95 (m, 1 H, H-2), 2.91−2.83 (ddd, 1 H, *J* 14.7, 10.0, 7.1 Hz, H-7), 2.47−2.45 (m, 1 H, H-4), 2.09−2.00 (m, 1 H, H-3), 1.99−1.91 (m, 2 H, H-8), 1.90−1.84 (m, 1 H, H-3), 0.87 (s, 9 H, SiC(CH_3)$_3$), 0.04 (s, 3 H, SiCH_3), 0.03 (s, 3 H, SiCH_3). ^{13}C NMR (100 MHz) (δ): 219.76 (C, C-5), 65.52 (CH_2, C-9), 58.83 (CH_2, C-6), 56.28 (CH, C-2), 49.77 (CH_2, C-7), 40.72 (CH, C-4), 27.90 (CH_2, C-3), 25.87 (CH_3, SiC(CH_3)$_3$), 25.04 (CH_2, C-8), 18.26 (C, Si*C*(CH_3)$_3$), −5.51 (CH_3, SiCH_3). MS *m*/*z*: 269 (M^+, 5), 254 (13), 241 (33), 212 (69), 184 (100), 156 (10); FAB-MS 270 (M^++1, 100), 184 (25). HRMS calcd for $C_{14}H_{27}NO_2Si$: 269.1811; found 269.1812.

(1*S*,2*S*,4*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-one (10a). 8a (1.00 g, 3.17 mmol) was allowed to react according to the general procedure to afford **10a** (87%, 0.740 g, 2.76 mmol). IR ($CHCl_3$) (ν): 2956, 2928, 1728, 1472, 1408, 1256, 1116, 1048, 1004 cm^{-1}. ^1H NMR (400 MHz) (δ): 3.79−3.76 (dd, 1 H, *J* 10.4, 5.9 Hz, H-9), 3.76−3.72 (dd, 1 H, *J* 10.4, 5.9 Hz, H-9), 3.36−3.31 (d, 1 H, *J* 18.4 Hz, H-6), 3.29−3.24 (d, 1 H, *J* 18.4 Hz, H-6), 3.32−3.25 (m, 1 H, H-7), 2.99−2.90 (m, 1 H, H-2), 2.82−2.73 (m, 1 H, H-7), 2.46−2.42 (m, 1 H, H-4), 2.09−2.02 (m, 1 H, H-3), 1.96−1.87 (m, 2 H, H-8), 1.84−1.78 (ddd, 1 H, *J* 13.5, 7.6, 2.2 Hz, H-3), 0.90 (s, 9 H, SiC(CH_3)$_3$), 0.08 (s, 3 H, SiCH_3), 0.07 (s, 3 H, SiCH_3). ^{13}C NMR (100 MHz) (δ): 219.89 (C, C-5), 65.36 (CH_2, C-9), 64.79 (CH_2, C-6), 57.64 (CH, C-2), 41.79 (CH_2, C-7), 40.45 (CH, C-4), 28.67 (CH_2, C-3), 25.93 (CH_3, SiC(CH_3)$_3$), 25.39 (CH_2, C-8), 18.33 (C, Si*C*(CH_3)$_3$), −5.40 (CH_3, SiCH_3). MS *m*/*z*: 269 (M^+, 5), 254 (13), 241 (38), 212 (60), 184 (100), 156 (11); FAB-MS 270 (M^++1, 100), 184 (24). HRMS calcd for $C_{14}H_{27}NO_2Si$: 269.1811; found 269.1806.

(1*S*,2*R*,4*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-one (9b). 7b (3.45 g, 7.86 mmol) was allowed to react according to the general procedure to afford **9b** (93%, 2.87 g, 7.31 mmol). IR ($CHCl_3$) (ν): 3052, 2956, 1728, 1471, 1427, 1265, 1113, 1026 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.69−7.65 (m, 4 H, Ar−H), 7.47−7.37 (m, 6 H, Ar−H), 3.79−3.75 (dd, 1 H, *J* 10.5, 5.5 Hz, H-9), 3.75−3.70 (dd, 1 H, *J* 10.5, 5.5 Hz, H-9), 3.69−3.63 (dd, 1 H, *J* 19.3, 1.0 Hz, H-6), 3.11−3.06 (d, 1 H, *J* 18.8 Hz, H-6), 3.09−3.02 (m, 2 H, H-7), 2.92−2.84 (m, 1 H, H-2), 2.52−2.48 (m, 1 H, H-4), 2.13−2.07 (m, 1 H, H-3), 2.06−1.92 (m, 3 H, H-8, H-3), 1.07 (s, 9 H, SiC(CH_3)$_3$). ^{13}C NMR (100 MHz) (δ): 219.74 (C, C-5), 135.64 (CH, Ar−H), 133.27 (C, Ar−Si), 129.75 (CH, Ar−H), 127.75 (CH, Ar−H), 66.18 (CH_2, C-9), 58.79 (CH_2, C-6), 56.28 (CH, C-2), 49.77 (CH_2, C-7), 40.71 (CH, C-4), 28.02 (CH_2, C-3), 26.84 (CH_3, SiC(CH_3)$_3$), 25.17 (CH_2, C-8), 19.22 (C, Si*C*(CH_3)$_3$). MS *m*/*z*: 378 (M^+-Me, 1), 365 (15), 336 (100), 308 (92), 199 (16), 183 (12); FAB-MS 394 (M^++1, 65), 336 (100). HRMS calcd for $C_{24}H_{31}NO_2Si$−Me: 378.8189; found 378.8176.

(1*S*,2*S*,4*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-one (10b). 8b (4.00 g, 9.11 mmol) was allowed to react according to the general procedure to afford **10b** (90%, 3.22 g, 8.20 mmol). IR ($CHCl_3$) (ν): 3072, 2958, 1729, 1589, 1472, 1428, 1230, 1113, 1046, 999 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.72−7.68 (m, 4 H, Ar−H), 7.48−7.39 (m, 6 H, Ar−H), 3.85−3.83 (dd, 1 H, *J* 10.5, 6.0 Hz, H-9), 3.84−3.82 (dd, 1 H, *J* 10.5, 5.8 Hz, H-9), 3.40−3.35 (d, 1 H, *J* 18.6 Hz, H-6), 3.33−3.28 (d, 1 H, *J* 18.6 Hz, H-6), 3.32−3.23 (m, 1 H, H-7), 3.09−3.01 (m, 1 H, H-2), 2.87−2.78 (m, 1 H, H-7), 2.51−2.47 (m, 1 H, H-4), 2.15−2.07 (m, 1 H, H-3), 1.93−1.87 (m, 3 H, H-8, H-3), 1.09 (s, 9 H, SiC(CH_3)$_3$). ^{13}C NMR (100 MHz) (δ): 218.57 (C, C-5), 135.62 (CH, Ar−H), 133.26 (C, Ar−Si), 129.81 (CH, Ar−H), 127.77 (CH, Ar−H), 65.70 (CH_2, C-9), 64.38 (CH_2, C-6), 57.63 (CH, C-2), 41.70 (CH_2, C-7), 40.31 (CH, C-4), 28.57 (CH_2, C-3), 26.88 (CH_3, SiC(CH_3)$_3$), 25.07 (CH_2, C-8), 19.24 (C, SiC(CH_3)$_3$). MS *m*/*z*: 378 (M^+−Me, 2), 365 (19), 336 (100), 308 (93), 183 (14); FAB-MS 394 (M^++1, 100), 365 (20), 336 (41). HRMS calcd for $C_{24}H_{31}NO_2Si$−Me: 378.8189; found 378.8180.

(1*S*,2*R*,4*S*)-2-(Hydroxymethyl)-1-azabicyclo[2.2.2]octan-5-one (9d). 9a (137 mg, 0.51 mmol) was allowed to react

according to the general procedure to afford **9d** (97%, 77 mg, 0.49 mmol). IR ($CHCl_3$) (ν): 3360, 2964, 1728, 1456, 1404, 1232, 1148, 1052, 1020 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$ + CD_3OD) (δ): 3.50−3.38 (m, 2 H, H-9), 3.37−3.27 (m, 2 H, H-2, OH), 3.15−2.98 (m, 3 H, H-6, H-7), 2.95−2.87 (m, 1 H, H-7), 2.44−2.40 (m, 1 H, H-4), 2.11−1.95 (m, 2 H, H-3, H-8), 1.66−1.59 (m, 1 H, H-8), 1.44−1.34 (m, 1 H, H-3). ^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD) (δ): 216.41 (C, C-5), 62.60 (CH_2, C-9), 56.65 (CH, C-2), 56.46 (CH_2, C-6), 49.20 (CH_2, C-7), 40.21 (CH, C-4), 27.56 (CH_2, C-3), 25.31 (CH_2, C-8). MS *m*/*z*: 155 (M^+, 21), 127 (100), 110 (43). HRMS calcd for $C_8H_{13}NO_2$: 155.0946; found 155.0944. Anal. Calcd for $C_8H_{13}NO$: C 61.92, H 8.44, N 9.03; found C 62.08, H 8.59, N 9.25.

(1*S*,2*S*,4*S*)-2-(Hydroxymethyl)-1-azabicyclo[2.2.2]octan-5-one (10d). 10b (1.80 g, 4.58 mmol) was allowed to react according to the general procedure to afford **10d** (96%, 682 mg, 4.39 mmol). IR ($CHCl_3$) (ν): 3380, 2964, 1732, 1456, 1408, 1264, 1232, 1080, 1032 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$ + CD_3OD) (δ): 3.64−3.56 (m, 2 H, H-9), 3.39−3.32 (d, 1 H, *J* 17.8 Hz, H-6), 3.25−3.19 (d, 1 H, *J* 18.1 Hz, H-6), 3.18−3.12 (m, 1 H, H-7), 3.07−2.99 (m, 1 H, H-2), 2.79−2.71 (m, 1 H, H-7), 2.42−2.39 (m, 1 H, H-4), 2.09−2.01 (m, 1 H, H-3), 1.90−1.85 (m, 1 H, H-8), 1.68−1.61 (m, 1 H, H-8), 1.47−1.38 (m, 1 H, H-3). ^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD) (δ): 218.60 (C, C-5), 64.17 (CH_2, C-9), 62.48 (CH_2, C-6), 57.72 (CH, C-2), 39.89 (CH, C-4), 39.64 (CH_2, C-7), 28.53 (CH_2, C-3), 25.21 (CH_2, C-8). MS *m*/*z*: 155 (M^+, 17), 127 (100), 110 (42). HRMS calcd for $C_8H_{13}NO_2$: 155.0946; found 155.0947. Anal. Calcd for $C_8H_{13}NO$: C 61.92, H 8.44, N 9.03; found C 62.16, H 8.53, N 9.31.

(1*S*,2*R*,4*S*)-2-(Triisopropylsilyloxymethyl)-1-azabicyclo-[2.2.2]octan-5-one (9c). Triethylamine (0.240 mL, 1.74 mmol, 1.5 equiv) was added to a solution of **9d** (180 mg, 1.16 mmol, 1 equiv) in abs CH_2Cl_2 (5 mL) at rt. After the solution was stirred under argon for 15 min, DMAP (14 mg, 0.12 mmol, 0.1 equiv) and triisopropylsilyl chloride (0.32 mL, 1.5 mmol, 1.3 equiv) were added at 0 °C, and the homogeneous mixture was stirred for 16 h at rt, followed by extraction with saturated aqueous $NaHCO_3$. The combined organic layer was dried (over $MgSO_4$), evaporated, and purified by chromatography (EA/MeOH 20:1) to yield silylated ketone **9c** (91%, 329 mg, 1.06 mmol). IR ($CHCl_3$) (ν): 2946, 1728, 1464, 1404, 1233, 1128, 1068, 1029 cm^{-1}. ^1H NMR (400 MHz) (δ): 3.82−3.80 (d, 1 H, *J* 5.2 Hz, H-9), 3.76−3.74 (d, 1 H, *J* 5.2 Hz, H-9), 3.76−3.70 (d, 1 H, *J* 19.7, H-6), 3.10−3.05 (d, 1 H, *J* 19.4 Hz, H-6), 3.09−3.04 (m, 1 H, H-7), 3.04−2.98 (m, 1 H, H-2), 2.91−2.83 (m, 1 H, H-7), 2.50−2.45 (m, 1 H, H-4), 2.09−1.91 (m, 4 H, H-3, H-8, H-3), 1.14−0.94 (m, 21 H, Si(C*H*(CH_3)$_2$)$_3$). ^{13}C NMR (100 MHz) (δ): 219.85 (C, C-5), 66.10 (CH_2, C-9), 59.09 (CH_2, C-6), 56.46 (CH, C-2), 49.90 (CH_2, C-7), 40.77 (CH, C-4), 27.96 (CH_2, C-3), 25.16 (CH_2, C-8), 17.99 (CH_3, Si(CH(*CH_3*)$_2$)$_3$), 11.88 (CH, Si-(*CH*(CH_3)$_2$)$_3$). MS *m*/*z*: 311 (M^+, 17), 284 (19), 268 (71), 240 (100), 138 (6). HRMS calcd for $C_{17}H_{33}NO_2Si$: 311.2280; found 311.2282.

(1*S*,2*R*,4*S*)-2-(Triphenylmethyloxymethyl)-1-azabicyclo-[2.2.2]octan-5-one (9e). Triethylamine (0.21 mL, 1.5 mmol, 1.5 equiv) was added to a solution of **9d** (155 mg, 1.00 mmol, 1 equiv) in abs CH_2Cl_2 (4 mL) at rt. After the solution was stirred under argon for 15 min, DMAP (12 mg, 0.10 mmol, 0.1 equiv) and triphenylmethyl chloride (363 mg, 1.30 mmol, 1.3 equiv) were added at 0 °C, and the homogeneous mixture was stirred for 16 h at rt, followed by extraction with saturated aqueous $NaHCO_3$. The combined organic layer was dried ($MgSO_4$), evaporated and purified by chromatography (EA/MeOH 20:1) to afford protected ketone **9e** (88%, 349 mg, 0.880 mmol). IR ($CHCl_3$) (ν): 3062, 2999, 2950, 1729, 1597, 1449, 1230, 1080, 1033, 1001 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.45−7.42 (m, 6 H, Ar−H), 7.30−7.26 (m, 6 H, Ar−H), 7.24−7.19 (m, 3 H, Ar−H), 3.45−3.40 (d, 1 H, *J* 19.1, H-6), 3.28−3.23 (dd, 1 H, *J* 9.3, 6.8 Hz, H-9), 3.22−3.14 (m, 1 H, H-2), 3.12−3.03 (m, 1 H, H-7), 3.09−3.04 (d, 1 H, *J* 18.8 Hz, H-6), 3.02−2.97 (dd, 1 H, *J* 9.3, 5.5 Hz, H-9), 2.93−2.85 (m, 1 H, H-7), 2.47−2.42 (m, 1 H, H-4), 2.15−2.08 (m, 1 H, H-3), 2.01−1.92 (m, 2 H, H-8), 1.68−1.61 (m, 1 H, H-3). ^{13}C NMR (100 MHz) (δ): 219.67 (C, C-5), 143.81 (C, Ar−C), 128.65 (CH, Ar−H), 127.81 (CH, Ar−H), 127.02 (CH, Ar−H), 86.71 (C, Ph_3CO), 65.38 (CH_2, C-9), 58.15 (CH_2, C-6), 55.05 (CH, C-2), 49.62 (CH_2, C-7), 40.58 (CH, C-4), 28.72 (CH_2, C-3), 25.27 (CH_2, C-8). MS *m*/*z*: 397 (M^+, 1), 369 (33), 243 (100), 187 (9), 136 (9). HRMS calcd for $C_{27}H_{27}NO_2$: 397.2042; found 397.2044.

(1*S*,2*R*,4*S*)-2-(Bromomethyl)-1-azabicyclo[2.2.2]octan-5-one (9f). Methanesulfonyl chloride (0.39 mL, 5.0 mmol, 1.3 equiv) was added to a solution of unprotected ketone **9d** (600 mg, 3.88 mmol, 1.0 equiv) and Et_3N (1.08 mL, 7.74 mmol, 2.0 equiv) in abs. CH_2Cl_2 (10 mL) at 0 °C. After having been stirred for 10 h at rt, the reaction mixture was diluted with CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$. The organic layer was dried, the solvent evaporated, and the crude product (83%, 748 mg, 3.21 mmol) dissolved in abs dioxan (5 mL). Powdered lithium bromide (838 mg, 9.64 mmol, 3.0 equiv) was added, and the mixture was refluxed for 24 h at 110 °C. After addition of saturated aqueous $NaHCO_3$, the aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were dried ($MgSO_4$) and evaporated. Purification by chromatography (EA/MeOH 20:1) furnished the desired brominated ketone **9f** (81%, 565 mg, 2.60 mmol) as a colorless crystalline solid. IR ($CHCl_3$) (ν): 2963, 1732, 1473, 1457, 1230, 1083, 1032 cm^{-1}. ^1H NMR (400 MHz) (δ): 3.57−3.52 (dd, 1 H, *J* 10.4, 8.2 Hz, H-9), 3.49−3.45 (dd, 1 H, *J* 10.4, 7.2 Hz, H-9), 3.45−3.40 (d, 1 H, *J* 19.7 Hz, H-6), 3.34−3.28 (dd, 1 H, *J* 19.7, 2.3 Hz, H-6), 3.23−3.09 (m, 2 H, H-2, H-7), 2.89−2.81 (m, 1 H, H-7), 2.49−2.45 (m, 1 H, H-4), 2.33−2.25 (m, 1 H, H-3), 1.98−1.92 (m, 2 H, H-8), 1.68−1.61 (ddd, 1 H, *J* 13.7, 7.5, 2.2 Hz, H-3). ^{13}C NMR (100 MHz) (δ): 218.42 (C, C-5), 64.69 (CH_2, C-6), 57.55 (CH, C-2), 40.17 (CH, C-4), 39.76 (CH_2, C-7), 34.15 (CH_2, C-9), 31.81 (CH_2, C-3), 25.37 (CH_2, C-8). MS *m*/*z*: 219 (M^+, 3), 217 (M^+, 3), 191 (10), 189 (10), 110 (100). HRMS calcd for C_8H_{12}-NOBr: 217.0102; found 217.0103.

General Procedure for the Reduction of C5-ketones 9a−e *and* 10a,b *with* l-Selectride. A 1.0 M solution of L-Selectride in THF (1.5 equiv) was added dropwise within 5 min to a solution of the C5-ketone (1 equiv) in abs THF at −90 °C. After it was stirred for 2 h at −78 °C, the reaction mixture was warmed to 0 °C within 4 h and then quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with $CHCl_3$, and the organic layer dried ($MgSO_4$) and evaporated. The resulting crude product was purified by column chromatography (EA/MeOH 6:1) to yield the corresponding quinuclidin-5-ols **11a**−**e** and **12a**,**b**.

(1*S*,2*R*,4*S*,5*S*)-2-(tert-Butyldimethylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-ol (11a). 9a (158 mg, 0.590 mmol) was allowed to react according to the general procedure to afford *anti*-**11a** (87%, 138 mg, 0.510 mmol) with 62% de. IR ($CHCl_3$) (ν): 2956, 2932, 1460, 1432, 1256, 1128, 1016 cm^{-1}. ^1H NMR (400 MHz) (δ): 4.19−4.16 (dd, 1 H, *J* 11.8, 3.2 Hz, H-9), 4.15−4.09 (m, 1 H, H-5), 3.85−3.77 (m, 1 H, H-6), 3.72−3.66 (dd, 1 H, *J* 11.8, 4.9 Hz, H-9), 3.40−3.18 (m, 3 H, H-7, H-2), 3.14−3.09 (d, 1 H, *J* 13.7 Hz, H-6), 2.42−2.29 (m, 2 H, H-4, H-3), 1.95−1.88 (m, 1 H, H-8), 1.78−1.62 (m, 2 H, H-8, H-3), 0.86 (s, 9 H, SiC*(*CH_3*)*$_3$), 0.08 (s, 3 H, Si*C*H_3), 0.06 (s, 3 H, Si*C*H_3). ^{13}C NMR (100 MHz) (δ): 63.91 (CH, C-5), 62.02 (CH_2, C-9), 57.35 (CH, C-2), 53.09 (CH_2, C-6), 49.30 (CH_2, C-7), 27.79 (CH, C-4), 25.89 (CH_3, SiC(*CH_3*)$_3$), 23.65 (CH_2, C-8), 18.19 (C, Si*C*(CH_3)$_3$), 16.53 (CH_2, C-3), −5.43 (CH_3, Si*C*H_3), −5.55 (CH_3, Si*C*H_3). MS *m*/*z*: 271 (M^+, 6), 256 (9), 214 (100), 126 (14). HRMS calcd for $C_{14}H_{29}NO_2Si$: 271.1967; found 271.1965.

(1*S*,2*R*,4*S*,5*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-ol (11b). 9b (680 mg, 1.73 mmol) was allowed to react according to the general procedure to afford *anti*-**11b** (82%, 560 mg, 1.42 mmol) with 68% de. The diastereomeric excess given refers to the excess of 5*S*-configurated diastereomer. IR ($CHCl_3$) (ν): 3053, 2933, 1589, 1471, 1428, 1239, 1113, 1019 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.71−7.62 (m, 4 H, Ar−H), 7.43−7.35 (m, 6 H, Ar−H), 4.33−4.19 (br. s, 1 H, OH), 3.95−3.83 (m, 2 H, H-9, H-5), 3.70−3.66 (dd, 1 H, *J* 11.2, 4.9 Hz, H-9), 3.63−3.57 (m, 1 H, H-6), 3.17−2.98 (m, 3 H, H-7, H-2), 2.85−2.80 (d, 1 H, *J* 14.3 Hz, H-6), 2.15−2.06 (m, 2 H, H-4, H-3), 1.87−1.78 (m, 1 H, H-8), 1.58−1.46 (m, 2 H, H-8, H-3), 1.07/1.05 (s, 9H, SiC*(*CH_3*)*$_3$). ^{13}C NMR (100 MHz) (δ): 135.68/134.89 (CH, Ar−H), 132.73 (C, Ar−Si),

129.95 (CH, Ar−H), 127.87/127.58 (CH, Ar−H), 64.84/65.63 (CH, C-5), 64.79/64.35 (CH_2, C-9), 57.68/56.35 (CH, C-2), 53.24/52.22 (CH_2, C-6), 49.17/48.68 (CH_2, C-7), 28.34 (CH, C-4), 26.87 (CH_3, SiC(CH_3)$_3$), 25.86 (CH_2, C-8), 19.20 (C, Si*C*(CH_3)$_3$), 17.23 (CH_2, C-3). MS *m*/*z*: 395 (M^+, 2), 338 (40), 199 (100), 167 (11), 149 (23). HRMS calcd for $C_{24}H_{33}NO_2Si$: 395.2280; found 395.2282.

(1*S*,2*R*,4*S*,5*S*)-2-(Triisopropylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-ol (11c). 9c (103 mg, 0.330 mmol) was allowed to react according to the general procedure to afford *anti*-**11c** (79%, 82 mg, 0.26 mmol) with 71% de. IR ($CHCl_3$) (*ν*): 2944, 1463, 1230, 1114, 1065, 1034 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 3.84−3.79 (m, 1 H, H-5), 3.78−3.74/3.72−3.68 (dd, 1 H, *J* 9.9, 5.1 Hz, H-9), 3.67−3.63/3.61−3.57 (dd, 1 H, *J* 9.9, 6.8 Hz, H-9), 3.38−3.32 (ddd, 1 H, *J* 14.6, 8.1, 1.5 Hz, H-6), 2.99−2.78 (m, 3 H, H-7, H-2), 2.51−2.45 (d, 1 H, *J* 14.6 Hz, H-6), 1.95−1.87 (m, 2 H, H-4, H-3), 1.84−1.77 (m, 1 H, H-8), 1.43−1.34 (m, 2 H, H-8, H-3), 1.09−1.02 (m, 21 H, Si-(C*H*(CH_3)$_2$)$_3$). ^{13}C NMR (100 MHz) (*δ*): 68.16 (CH, C-5), 66.34/66.10 (CH_2, C-9), 56.12/56.10 (CH, C-2), 53.98/53.86 (CH_2, C-6), 49.96 (CH_2, C-7), 29.35 (CH, C-4), 28.15 (CH_2, C-8), 18.33 (CH_2, C-3), 18.05 (CH_3, Si(CH(*C*H_3)$_2$)$_3$), 11.96 (CH, Si(*C*H(CH_3)$_2$)$_3$). MS *m*/*z*: 313 (M^+, 21), 295 (6), 271 (100), 139 (9). HRMS calcd for $C_{17}H_{35}NO_2Si$: 313.2437; found 313.2438.

(1*S*,2*R*,4*S*,5*S*)-2-(Triphenylmethyloxymethyl)-1-azabicyclo[2.2.2]octan-5-ol (11d). 9e (110 mg, 0.28 mmol) was allowed to react according to the general procedure to afford *anti*-**11d** (91%, 101 mg, 0.250 mmol) with 95% de. IR ($CHCl_3$) (*ν*): 3062, 2932, 1599, 1449, 1230, 1153, 1089, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, CD_3OD) (*δ*): 7.45−7.42 (m, 6 H, Ar−H), 7.32−7.28 (m, 6 H, Ar−H), 7.25−7.20 (m, 3 H, Ar−H), 3.83−3.79 (m, 1 H, H-5), 3.65−3.44 (bm, 1 H, OH), 3.41−3.39 (m, 1 H, H-9), 3.34−3.25 (m, 1 H, H-6), 3.24−3.08 (m, 3 H, H-9, H-2, H-7), 3.05−2.96 (m, 1 H, H-7), 2.82−2.78 (d, 1 H, *J* 14.3 Hz, H-6), 2.11−1.99 (m, 2 H, H-4, H-3), 1.89−1.81 (m, 1 H, H-8), 1.52−1.43 (m, 1 H, H-3), 1.29−1.18 (m, 1 H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$, CD_3OD) (*δ*): 143.47 (C, Ar−C), 128.70 (CH, Ar−H), 127.96 (CH, Ar−H), 127.23 (CH, Ar−H), 87.46 (C, Ph_3CO), 65.59 (CH, C-5), 63.96 (CH_2, C-9), 55.35 (CH, C-2), 52.59 (CH_2, C-6), 49.24 (CH_2, C-7), 28.09 (CH, C-4), 26.78 (CH_2, C-8), 17.24 (CH_2, C-3). MS *m*/*z*: 399 (M^+, 4), 338 (9), 271 (5), 243 (100), 165 (31), 156 (91). HRMS calcd for $C_{27}H_{29}NO_2$: 399.2198; found 399.2197.

(1*S*,2*R*,4*S*,5*R*/*S*)-2-(Hydroxymethyl)-1-azabicyclo[2.2.2]-octan-5-ol (11e). 9d (100 mg, 0.65 mmol) was allowed to react according to the general procedure to afford **11e** (85%, 86 mg, 0.55 mmol) with 2% de. IR ($CHCl_3$) (*ν*): 3358, 2932, 1460, 1408, 1232, 1148, 1040, 1018 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, CD_3-OD) (*δ*): 4.15−3.98 (m, 2 H, OH), 3.86−3.82 (m, 1 H, H-5), 3.64−3.43 (m, 2 H, H-9), 3.39−3.26 (m, 2 H, H-2, H-7), 3.21−3.09 (m, 1 H, H-6), 3.01−2.88 (m, 2 H, H-6, H-7), 2.19−2.07 (m, 2 H, H-4, H-3), 1.82−1.68 (m, 1 H, H-8), 1.58−1.44 (m, 1 H, H-8), 1.29−1.24 (m, 1 H, H-3). ^{13}C NMR (100 MHz, $CDCl_3$, CD_3OD) (*δ*): 65.41 (CH, C-5), 62.87 (CH_2, C-9), 53.82 (CH, C-2), 52.10 (CH_2, C-6), 49.78 (CH_2, C-7), 27.83 (CH, C-4), 26.05 (CH_2, C-8), 17.59 (CH_2, C-3). MS *m*/*z*: 157 (M^+, 8), 129 (100), 110 (16). HRMS calcd for $C_8H_{15}NO_2$: 157.1104; found 157.1102. Anal. Calcd for $C_8H_{15}NO_2$: C 61.12, H 9.62, N 8.91; found C 60.73, H 9.86, N 8.72.

(1*S*,2*S*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-ol (12a). 10a (143 mg, 0.530 mmol) was allowed to react according to the general procedure to afford *anti*-**12a** (84%, 121 mg, 0.450 mmol) with 48% de. IR ($CHCl_3$) (*ν*): 2952, 2928, 1472, 1256, 1116, 1032 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 4.10−3.98 (bs, 1 H, OH), 3.85−3.82 (m, 1 H, H-5), 3.69−3.62 (m, 2 H, H-9), 3.23−3.19/3.19−3.10 (dd, 1 H, *J* 14.2, 8.0 Hz, H-6), 3.08−2.97 (m, 2 H, H-7, H-2), 2.74−2.69/2.63−2.58 (m, 1 H, H-6), 2.52−2.45 (m, 1 H, H-7), 2.03−1.95/1.84−1.81 (m, 1 H, H-3), 1.93−1.88 (m, 1 H, H-4), 1.63−1.54 (m, 1 H, H-8), 1.39−1.28 (m, 1 H, H-8), 1.24−1.17 (m, 1 H, H-3), 0.89−0.86 (m, 9 H, SiC(*C*H_3)$_3$), 0.06−0.04 (m, 6 H, Si*C*H_3). ^{13}C NMR (100 MHz) (*δ*): 67.04/66.99 (CH, C-5), 65.44 (CH_2, C-9), 60.55/59.86 (CH_2, C-6), 56.84/56.64 (CH, C-2), 42.47/41.40 (CH_2, C-7), 29.69/28.86 (CH, C-4), 25.96 (CH_3, SiC-(*C*H_3)$_3$), 27.75/24.26 (CH_2, C-8), 22.31/18.85 (CH_2, C-3), 18.35 (C, Si*C*(CH_3)$_3$), −5.37 (CH_3, Si*C*H_3). MS *m*/*z*: 271 (M^+, 7), 256 (8), 214 (100). HRMS calcd for $C_{14}H_{29}NO_2Si$: 271.1967; found 271.1969.

(1*S*,2*S*,4*S*,5*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-1-azabicyclo[2.2.2]octan-5-ol (12b). 10b (770 mg, 1.96 mmol) was allowed to react according to the general procedure to afford *anti*-**12b** (80%, 619 mg, 1.57 mmol) with 55% de. IR ($CHCl_3$) (*ν*): 3317, 3073, 2961, 1589, 1471, 1428, 1240, 1113, 1013 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 7.68−7.62 (m, 4 H, Ar−H), 7.44−7.35 (m, 6 H, Ar−H), 4.27−4.18 (m, 2 H, H-9, H-5), 3.73−3.64 (m, 2 H, H-9, H-7), 3.61−3.52 (m, 2 H, H-6, H-2), 3.32−3.10 (m, 2 H, H-6, H-7), 2.28−2.17 (m, 2 H, H-4, H-3), 1.88−1.65 (m, 3 H, H-8, H-3), 1.07 (s, 9 H, SiC(*C*H_3)$_3$). ^{13}C NMR (100 MHz) (*δ*): 135.65 (CH, Ar−H), 132.08/131.93 (C, Ar−Si), 130.24/130.14 (CH, Ar−H), 128.06 (CH, Ar−H), 63.54/63.33 (CH, C-5), 62.87 (CH_2, C-9), 59.21/58.60 (CH_2, C-6), 58.21/57.62 (CH, C-2), 42.98/42.24 (CH_2, C-7), 27.69/27.24 (CH, C-4), 26.89 (CH_3, SiC(*C*H_3)$_3$), 23.26/20.92 (CH_2, C-8), 19.21/17.19 (CH_2, C-3), 19.18 (C, Si*C*(CH_3)$_3$). MS *m*/*z*: 395 (M^+, 2), 364 (3), 338 (100), 199 (17). HRMS calcd for $C_{24}H_{33}NO_2Si$: 395.2280; found 395.2281.

General procedure for the reaction of C5-ketones **9a**−**e** *and* **10a** *with organolithium or Grignard reagents*. A 1.0 M solution of the Grignard reagent (3 equiv) or the organolithium reagent (3 equiv) in abs. THF was added dropwise within 5 min to a solution of the C5-ketone (1 equiv) in abs THF at −90 °C. After stirring for 2 h at −78 °C the reaction mixture was warmed to 0 °C within 2 h and stirred for 1 h at 0 °C. The reaction mixture was extracted (saturated aqueous $NaHCO_3$ and $CHCl_3$). The combined organic layer was dried ($MgSO_4$), filtered and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography (EA/MeOH 10:1) to yield the corresponding quinuclidin-5-ols **11f**−**n** and **12c**−**f**.

(1*S*,2*R*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-(14-hydroxy-pent-10-ynyl)-1-azabicyclo[2.2.2]octan-5-ol (11f). 9a (100 mg, 0.37 mmol) was allowed to react with bislithiated pent-4-yn-1ol (0.10 mL, 1.1 mmol) according to the general procedure to afford *anti*-**11f** (69%, 91 mg, 0.26 mmol) with 65% de. IR ($CHCl_3$) (*ν*): 3304, 2956, 2932, 1468, 1256, 1120, 1020 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 3.94−3.90 (dd, 1 H, *J* 10.5, 3.8 Hz, H-9), 3.79−3.75 (dd, 1 H, *J* 10.6, 5.1 Hz, H-9), 3.77−3.68 (m, 2 H, H-14, H-14), 3.33−3.29/3.15−3.01 (m, 1 H, H-6), 2.89−2.79 (m, 2 H, H-7, H-2), 2.76−2.70 (m, 1 H, H-7), 2.64−2.60 (d, 1 H, *J* 14.7 Hz, H-6), 2.35−2.31 (m, 1 H, H-4), 2.09−2.04 (m, 1 H, H-3), 1.87−1.84 (m, 1 H, H-8), 1.80−1.61 (m, 2 H, H-8, H-3), 1.59−1.43 (m, 2 H, H-12, H-12), 1.39−1.29 (m, 2 H, H-13, H-13), 0.94−0.89 (m, 9 H, SiC(*C*H_3)$_3$), 0.13−0.10/0.09−0.06 (m, 6 H, Si*C*H_3). ^{13}C NMR (100 MHz) (*δ*): 83.21 (C, C-10), 70.58 (C, C-5), 67.97 (C, C-11), 66.68/65.54 (CH_2, C-9), 59.73/58.89 (CH_2, C-14), 56.28/56.01 (CH, C-2), 49.41/48.62 (CH_2, C-6), 39.91 (CH_2, C-7), 32.65 (CH, C-4), 26.05/25.99 (CH_3, SiC(*C*H_3)$_3$), 25.04 (CH_2, C-8), 23.29 (CH_2, C-12), 23.02 (CH_2, C-3), 18.54/18.43 (C, Si*C*(CH_3)$_3$), 14.13 (CH_2, C-13), −5.37 (CH_3, Si*C*H_3), −5.42 (CH_3, Si*C*H_3). MS *m*/*z*: 327 ($M^+-C_2H_2$, 4), 312 (3), 270 (28), 182 (100); FAB-MS 353 (M^+, 18), 327 ($M^+-C_2H_2$, 100). HRMS calcd for $C_{19}H_{35}NO_3Si$: 353.8404; found 353.8411.

(1*S*,2*S*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-(14-hydroxy-pent-10-ynyl)-1-azabicyclo[2.2.2]octan-5-ol (12c). 10a (100 mg, 0.37 mmol) was allowed to react with bislithiated pent-4-yn-1ol (0.10 mL, 1.1 mmol) according to the general procedure to afford *anti*-**12c** (66%, 87 mg, 0.25 mmol) with 33% de. IR ($CHCl_3$) (*ν*): 3304, 2956, 2928, 1468, 1256, 1116, 1056, 1032 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 3.78−3.58 (m, 4 H, H-9, H-14, H-14), 3.10−2.94 (m, 2 H, H-6, H-7), 2.89−2.72 (m, 3 H, H-7, H-2, H-6), 2.56−2.48 (m, 1 H, H-4), 2.34−2.25/2.11−2.02 (m, 1 H, H-3), 1.85−1.72 (m, 1 H, H-8), 1.64−1.46 (m, 2 H, H-8, H-3), 1.40−1.17 (m, 4 H, H-12, H-12, H-13, H-13), 0.91−0.88 (m, 9 H, SiC(*C*H_3)$_3$), 0.08−0.05 (m, 6 H, Si*C*H_3). ^{13}C NMR (100 MHz) (*δ*): 83.92 (C, C-10), 71.63/71.45 (C, C-5), 67.95 (C, C-11), 66.16/66.12 (CH_2, C-9), 65.81/65.64 (CH_2, C-14), 56.59 (CH, C-2), 42.09/41.71 (CH_2, C-6), 40.64/39.93 (CH_2, C-7), 32.28/32.19 (CH, C-4), 27.12 (CH_2, C-12), 25.98 (CH_3, SiC(*C*H_3)$_3$), 25.13/23.74 (CH_2, C-8), 23.24/21.49

(CH_2, C-3), 18.39 (C, Si*C*(CH_3)$_3$), 14.10 (CH_2, C-13), −5.34 (CH_3, Si*C*H_3), −5.36 (CH_3, Si*C*H_3). MS *m*/*z*: 327 ($M^+-C_2H_2$, 7), 312 (7), 182 (100); FAB-MS 353 (M^+, 20), 327 ($M^+-C_2H_2$, 100). Anal. Calcd for $C_{19}H_{35}NO_3Si$: C 64.49, H 9.97, N 3.96; found C 64.03, H 9.88, N 4.18.

(1*S*,2*R*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-phenyl-1-azabicyclo[2.2.2]octan-5-ol (11g). 9a (64 mg, 0.24 mmol) was allowed to react with phenylmagnesium bromide (0.71 mL, 0.71 mmol) according to the general procedure to afford *anti*-**11g** (77%, 64 mg, 0.18 mmol) with 46% de. IR ($CHCl_3$) (*ν*): 2956, 2928, 1599, 1464, 1256, 1120, 1080, 1020 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 7.54−7.51/7.48−7.46 (m, 2 H, Ar−H), 7.39−7.35/7.31−7.26 (m, 3 H, Ar−H), 4.06−4.02 (dd, 1 H, *J* 10.6, 3.7 Hz, H-9), 3.88−3.84 (dd, 1 H, *J* 10.5, 5.2 Hz, H-9), 3.74−3.67/3.66−3.59 (m, 1 H, H-2), 3.55−3.49/3.16−3.12 (d, 1 H, *J* 15.2, H-6), 3.45−3.41/3.09−3.03 (d, 1 H, *J* 15.1 Hz, H-6), 2.94−2.85 (m, 1 H, H-7), 2.84−2.79 (m, 1 H, H-7), 2.49−2.45 (m, 1 H, H-4), 2.35−2.28 (m, 1 H, H-3), 2.19−2.15/1.88−1.84 (m, 1 H, H-8), 1.75−1.66/1.64−1.57 (m, 1 H, H-8), 1.53−1.46/1.45−1.39 (m, 1 H, H-3), 0.96/0.79 (s, 9 H, SiC(CH_3)$_3$), 0.17/-0.01 (s, 3 H, SiCH_3), 0.16/-0.03 (s, 3 H, SiCH_3). ^{13}C NMR (100 MHz) (*δ*): 145.44/145.37 (C, Ph), 128.56/128.23 (CH, Ph), 127.52/127.11 (CH, Ph), 125.96/125.94 (CH, Ph), 72.67/72.16 (C, C-5), 67.95/66.61 (CH_2, C-9), 58.81/57.82 (CH_2, C-6), 56.41/56.22 (CH, C-2), 49.74/48.91 (CH_2, C-7), 34.98/32.34 (CH, C-4), 26.08/25.86 (CH_3, SiC(*C*H_3)$_3$), 25.03/22.82 (CH_2, C-8), 22.41/20.75 (CH_2, C-3), 18.59/18.30 (C, Si*C*(CH_3)$_3$), −5.37 (CH_3, Si*C*H_3), −5.52 (CH_3, Si*C*H_3). MS *m*/*z*: 347 (M^+, 2), 332 (3), 290 (10), 202 (100), 184 (23). HRMS calcd for $C_{20}H_{33}NO_2Si$: 347.2280; found 347.2281.

(1*S*,2*S*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-phenyl-1-azabicyclo[2.2.2]octan-5-ol (12d). 10a (116 mg, 0.43 mmol) was allowed to react with phenylmagnesium bromide (1.29 mL, 1.29 mmol) according to the general procedure to afford *anti*-**12d** (73%, 109 mg, 0.310 mmol) with 22% de. IR ($CHCl_3$) (*ν*): 3060, 2956, 2928, 1600, 1472, 1256, 1116, 1028 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 7.49−7.44 (m, 2 H, Ar−H), 7.38−7.34 (m, 2 H, Ar−H), 7.29−7.26 (m, 1 H, Ar−H), 3.71−3.69 (d, 1 H, *J* 5.8 Hz, H-9), 3.68−3.65 (dd, 1 H, *J* 6.1, 3.9 Hz, H-9), 3.56−3.52/3.39−3.35 (d, 1 H, *J* 14.3, H-6), 3.23−3.14/3.08−3.00 (m, 1 H, H-2), 3.13−3.08/3.06−3.02 (d, 1 H, *J* 14.1 Hz, H-6), 2.89−2.71 (m, 2 H, H-7), 2.53−2.46 (m, 1 H, H-4), 2.29−2.22 (m, 1 H, H-3), 2.19−2.15 (m, 1 H, H-8), 1.48−1.39 (m, 1 H, H-8), 1.38−1.29 (m, 1 H, H-3), 0.92/0.89 (s, 9 H, SiC(CH_3)$_3$), 0.09 (s, 3 H, SiCH_3), 0.06/0.05 (s, 3 H, SiCH_3). ^{13}C NMR (100 MHz) (*δ*): 146.06/145.95 (C, Ph), 128.36 (CH, Ph), 127.27 (CH, Ph), 126.03/125.98 (CH, Ph), 72.71/72.41 (C, C-5), 65.59/65.32 (CH_2, C-9), 64.74/64.64 (CH_2, C-6), 56.55/56.49 (CH, C-2), 42.14/41.52 (CH_2, C-7), 34.05/33.37 (CH, C-4), 26.06/24.92 (CH_2, C-8), 25.99/25.57 (CH_3, SiC(*C*H_3)$_3$), 23.04/21.29 (CH_2, C-3), 18.35 (C, Si*C*(CH_3)$_3$), −5.34 (CH_3, Si*C*H_3), −5.37 (CH_3, Si*C*H_3). MS *m*/*z*: 347 (M^+, 4), 332 (4), 290 (14), 202 (100), 184 (7). HRMS calcd for $C_{20}H_{33}NO_2Si$: 347.2280; found 347.2284.

(1*S*,2*R*,4*S*,5*S*)-2-*(tert*-Butyldimethylsilyloxymethyl)-5-(13-methylfuranyl)-1-azabicyclo[2.2.2]-octan-5-ol (11h). 9a (100 mg, 0.37 mmol) was allowed to react with 2-methylfuranyllithium (0.60 mmol, 1.6 equiv) according to the general procedure to afford *anti*-**11h** (76%, 99 mg, 0.28 mmol) with 42% de. IR ($CHCl_3$) (*ν*): 2956, 2928, 1472, 1388, 1264, 1112, 1024 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 6.18−6.17/6.12−6.11 (d, 1 H, *J* 3.0 Hz, H-11), 5.93−5.90 (m, 1 H, H-12), 3.82−3.76 (m, 1 H, H-9), 3.70−3.64 (m, 1 H, H-9), 3.51−3.48/3.42−3.39 (d, 1 H, *J* 13.5 Hz, H-6), 3.23−3.14/3.27−3.19 (m, 1 H, H-2), 3.18−3.14/3.11−3.08 (d, 1 H, *J* 13.6 Hz, H-6), 2.95−2.83 (m, 2 H, H-7), 2.69−2.63 (m, 1 H, H-4), 2.33−2.25 (m, 1 H, H-3), 2.29−2.26 (m, 3 H, H-14), 1.87−1.73 (m, 1 H, H-8), 1.56−1.38 (m, 2 H, H-8, H-3), 0.93/0.90 (s, 9 H, SiC(CH_3)$_3$), 0.09/0.08 (s, 3 H, SiCH_3), 0.05/0.02 (s, 3 H, SiCH_3). ^{13}C NMR (100 MHz) (*δ*): 155.64/155.03 (C, C-13), 151.87/151.53 (C, C-10), 106.96/106.51 (CH, C-12), 106.11/106.02 (CH, C-11), 69.72/69.25 (C, C-5), 64.87/64.36 (CH_2, C-9), 62.44/61.89 (CH_2, C-6), 57.01/56.47 (CH, C-2), 47.99/47.32 (CH_2, C-7), 33.09/32.65 (CH, C-4), 25.70/23.28 (CH_2, C-8), 25.84 (CH_3, SiC(*C*H_3)$_3$), 22.81/20.54 (CH_2, C-3), 18.32 (C, Si*C*(CH_3)$_3$), 13.63 (CH_3, C-14), −5.35 (CH_3, Si*C*H_3), −5.42 (CH_3, Si*C*H_3). MS *m*/*z*: 351 (M^+, 4), 335 (M^+-O, 4), 294 (8), 276 (3), 206 (100). HRMS calcd for $C_{19}H_{33}NO_2Si$: 335.2281; found 335.2249. Anal. Calcd for $C_{19}H_{33}NO_3Si$: C 64.97, H 9.47, N 3.99; found C 65.28, H 9.60, N 3.83.

(1*S*,2*R*,4*S*,5*S*)-2-(Hydroxymethyl)-5-(13-methylfuranyl)-1-azabicyclo[2.2.2]octan-5-ol (**11i**). **9b** (200 mg, 0.51 mmol) was allowed to react with 2-methylfuranyllithium (0.76 mmol, 1.5 equiv) according to the general procedure to afford *anti*-**11i** (65%, 78 mg, 0.33 mmol) with 16% de. IR ($CHCl_3$) (*ν*): 2974, 1559, 1413, 1371, 1231, 1145, 1025 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 6.16−6.14/6.11−6.09 (d, 1 H, *J* 3.1 Hz, H-11), 5.90−5.87 (m, 1 H, H-12), 3.79−3.73 (m, 1 H, H-9), 3.52−3.46 (m, 1 H, H-9), 3.43−3.39/3.34−3.16 (m, 1 H, H-6), 3.12−3.07 (m, 1 H, H-2), 2.99−2.89 (m, 1 H, H-7), 2.86−2.81 (d, 1 H, *J* 14.9 Hz, H-6), 2.78−2.72 (m, 1 H, H-7), 2.30−2.20 (m, 1 H, H-4), 2.25−2.24/2.23−2.22 (d, 3 H, *J* 3.1 Hz, H-14), 1.82−1.75 (m, 1 H, H-3), 1.63−1.47 (m, 2 H, H-8, H-3), 0.98−0.87 (m, 1 H, H-8). ^{13}C NMR (100 MHz) (*δ*): 155.80/155.14 (C, C-13), 151.99/151.97 (C, C-10), 106.98/106.83 (CH, C-12), 106.16/106.08 (CH, C-11), 69.69/69.05 (C, C-5), 62.16/62.01 (CH_2, C-9), 61.97/61.82 (CH_2, C-6), 57.68/57.23 (CH, C-2), 48.24/47.83 (CH_2, C-7), 32.93/32.09 (CH, C-4), 25.51/22.50 (CH_2, C-8), 22.38/19.96 (CH_2, C-3), 13.61/13.58 (CH_3, C-14). MS *m*/*z*: 237 (M^+, 1), 226 (4), 206 (100), 199 (14), 137 (16); FAB-MS 238 (M^++1, 100), 206 (52). Anal. Calcd for $C_{13}H_{19}NO_3$: C 65.80, H 8.07, N 5.90; found C 66.07, H 8.02, N 5.68.

(1*S*,2*S*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-(13-methylfuranyl)-1-azabicyclo[2.2.2]-octan-5-ol (12e). 10a (100 mg, 0.37 mmol) was allowed to react with 2-methylfuranyllithium (0.60 mmol, 1.6 equiv) according to the general procedure to afford *anti*-**12e** (72%, 94 mg, 0.27 mmol) with 18% de. IR ($CHCl_3$) (*ν*): 2956, 2928, 1472, 1264, 1112, 1028 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 6.20−6.19/6.17−6.16 (d, 1 H, *J* 3.1 Hz, H-11), 5.92−5.89 (m, 1 H, H-12), 3.85−3.79 (m, 1 H, H-9), 3.74−3.68 (m, 1 H, H-9), 3.56−3.53/3.47−3.43 (d, 1 H, *J* 14.0 Hz, H-6), 3.28−3.19 (m, 1 H, H-7), 3.21−3.17/3.14−3.10 (d, 1 H, *J* 14.2 Hz, H-6), 3.01−2.89 (m, 2 H, H-2, H-7), 2.68−2.64 (m, 1 H, H-4), 2.34−2.24 (m, 1 H, H-3), 2.28 (s, 3 H, H-14), 1.81−1.72 (m, 1 H, H-8), 1.52−1.41 (m, 2 H, H-8, H-3), 0.91/0.89 (s, 9 H, SiC(CH_3)$_3$), 0.09/0.08 (s, 3 H, SiCH_3), 0.07/0.05 (s, 3 H, SiCH_3). ^{13}C NMR (100 MHz) (*δ*): 155.73/155.25 (C, C-13), 152.11 (C, C-10), 106.94/106.90 (CH, C-12), 106.17/106.14 (CH, C-11), 69.88/69.59 (C, C-5), 64.79/64.68 (CH_2, C-9), 62.51/62.46 (CH_2, C-6), 56.84/56.49 (CH, C-2), 42.31/41.70 (CH_2, C-7), 33.17/32.74 (CH, C-4), 25.95 (CH_3, SiC-(*C*H_3)$_3$), 25.72/23.36 (CH_2, C-8), 22.71/20.17 (CH_2, C-3), 18.34 (C, Si*C*(CH_3)$_3$), 13.62 (CH_3, C-14), −5.37 (CH_3, Si*C*H_3), −5.41 (CH_3, Si*C*H_3). MS *m*/*z*: 351 (M^+, 2), 336 (4), 294 (11), 206 (100). HRMS calcd for $C_{19}H_{33}NO_2Si$: 335.2281; found 335.2185. Anal. Calcd for $C_{19}H_{33}NO_3Si$: C 64.97, H 9.47, N 3.99; found C 65.34, H 9.58, N 3.79.

(1*S*,2*R*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-vinyl-1-azabicyclo[2.2.2]octan-5-ol (**11j**). **9a** (190 mg, 0.71 mmol) was allowed to react with vinylmagnesium bromide (2.12 mL, 2.12 mmol) according to the general procedure to afford *anti*-**11j** (84%, 176 mg, 0.590 mmol) with 16% de. IR ($CHCl_3$) (*ν*): 2954, 2930, 1471, 1257, 1120, 1079, 1020 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 6.15−6.08/6.04−5.96 (dd, 1 H, *J* 17.3, 10.8 Hz, H-10), 5.30−5.23 (ddd, 1 H, *J* 17.3, 9.3, 1.5 Hz, H-11), 5.12−5.09 (d, 1 H, *J* 10.8 Hz, H-11), 3.91−3.87 (dd, 1 H, *J* 10.4, 4.4 Hz, H-9), 3.79−3.74 (dd, 1 H, *J* 10.3, 5.3 Hz, H-9), 3.67−3.66 (d, 1 H, *J* 5.6 Hz, H-2), 3.22−3.18/3.10−3.05 (dd, 1 H, *J* 14.8, 1.5 Hz, H-6), 2.99−2.78 (m, 2 H, H-7), 2.88−2.84/2.66−2.62 (d, 1 H, *J* 14.5 Hz, H-6), 2.10−2.04 (m, 1 H, H-4), 1.86−1.82/1.79−1.75 (m, 1 H, H-3), 1.71−1.61 (m, 1 H, H-8), 1.58−1.47 (m, 1 H, H-8), 1.44−1.37 (m, 1 H, H-3), 0.91/0.86 (s, 9 H, SiC(CH_3)$_3$), 0.09/0.08 (s, 3 H, SiCH_3), 0.04 (s, 3 H, SiCH_3). ^{13}C NMR (100 MHz) (*δ*): 142.91/142.79 (CH, C-10), 113.07/112.85 (CH_2, C-11), 71.64/71.03 (C, C-5), 66.42/65.25 (CH_2, C-9), 57.39/57.04 (CH_2, C-6), 56.29/56.07 (CH, C-2), 49.36/49.01 (CH_2, C-7), 34.22/33.43 (CH, C-4), 26.05 (CH_3, SiC-(*C*H_3)$_3$), 25.97/22.85 (CH_2, C-8), 22.62/20.51 (CH_2, C-3), 18.51/18.38 (C, Si*C*(CH_3)$_3$), −5.35 (CH_3, Si*C*H_3), −5.38 (CH_3, Si*C*H_3). MS *m*/*z*: 298 (M^++1, 12), 240 (30), 184 (5), 152 (100). HRMS calcd for $C_{16}H_{31}NO_2Si$: 297.2124; found 297.2124.

(1*S*,2*R*,4*S*,5*S*)-2-(Hydroxymethyl)-5-(10-phenylethynyl)-1-azabicyclo[2.2.2]octan-5-ol (11k). **9b** (100 mg, 0.25 mmol) was allowed to react with lithiated phenyl acetylene (1.12 mmol, 3 equiv) according to the general procedure to afford *anti*-**11k** (67%, 44 mg, 0.17 mmol) with 3% de. IR ($CHCl_3$) (ν): 3421, 2999, 2971, 1599, 1443, 1412, 1236, 1143, 1024 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.41−7.39 (m, 2 H, Ar−H), 7.33−7.26 (m, 3 H, Ar−H), 4.30−4.18 (bs, 1 H, OH), 3.76−3.70/3.64−3.58 (m, 1 H, H-9), 3.53−3.46 (m, 2 H, H-9, H-7), 3.32−3.28/3.02−2.98 (d, 1 H, *J* 14.4 Hz, H-6), 3.23−3.19/2.94−2.89 (d, 1 H, *J* 13.8 Hz, H-6), 3.10−2.85 (m, 2 H, H-7, H-2), 2.18−2.09 (m, 2 H, H-4, H-3), 1.81−1.64 (m, 2 H, H-8), 1.55−1.43 (m, 1 H, H-3). ^{13}C NMR (100 MHz) (δ): 131.65 (CH, Ph), 128.52/128.35 (CH, Ph), 122.46/ 122.34 (C, Ph), 92.65/92.26 (C, C-10), 84.15/84.08 (C, C-11), 67.19/66.73 (C, C-5), 62.05/ 61.99 (CH_2, C-9), 57.65/57.56 (CH_2, C-6), 57.04/56.99 (CH, C-2), 48.09/47.88 (CH_2, C-6), 34.53 (34.33 (CH, C-4), 26.01/22.98 (CH_2, C-8), 21.52/19.05 (CH_2, C-3). FAB-MS *m*/*z*: 258 (M^++1, 100), 240 (8), 226 (18). HRMS calcd for $C_{16}H_{19}NO_2$: 257.3316; found 257.3304. Anal. Calcd for $C_{16}H_{19}NO_2$: C 74.68, H 7.44, N 5.44; found C 74.55, H 7.31, N 5.79.

(1*S*,2*R*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-(10-phenylethynyl)-1-azabicyclo[2.2.2]-octan-5-ol (11l). **9a** (86 mg, 0.32 mmol) was allowed to react with lithiated phenyl acetylene (0.96 mmol, 3 equiv) according to the general procedure to afford *anti*-**11l** (71%, 84 mg, 0.23 mmol) with 39% de. IR ($CHCl_3$) (ν): 3000, 2972, 1464, 1324, 1236, 1144, 1068, 1024 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.42−7.38 (m, 2 H, Ar−H), 7.32−7.27 (m, 3 H, Ar−H), 3.70−3.64/3.60−3.54 (dd, 1 H, *J* 11.6, 10.0 Hz, H-9), 3.49−3.39 (m, 2 H, H-9, H-6), 3.05−2.82 (m, 4 H, H-7, H-2, H-7, H-6), 2.15−2.11 (m, 1 H, H-4), 2.09−2.03 (m, 1 H, H-3), 1.79−1.71/1.68−1.59 (m, 1 H, H-8), 1.53−1.37 (m, 2 H, H-8, H-3), 1.26 (m, 9 H, SiC*(CH*$_3$*)*$_3$), 0.04−0.03 (m, 6 H, Si*CH*$_3$). ^{13}C NMR (100 MHz) (δ): 131.65 (CH, Ph), 128.45/128.25 (CH, Ph), 122.73/122.47 (C, Ph), 93.03/92.67 (C, C-10), 84.06/84.00 (C, C-11), 67.69/67.24 (C, C-5), 62.31/62.23 (CH_2, C-9), 57.91/57.86 (CH_2, C-6), 56.52/56.46 (CH, C-2), 48.31/48.10 (CH_2, C-7), 34.82/34.51 (CH, C-4), 31.22 (CH_3, SiC-*(CH*$_3$*)*$_3$), 26.39/23.53 (CH_2, C-8), 21.72/19.38 (CH_2, C-3), 18.39 (C, Si*C*(CH$_3$)$_3$), −5.36 (CH_3, Si*CH*$_3$), −5.44 (CH_3, Si*CH*$_3$). MS *m*/*z*: 371 (M^+, 4), 343 (3), 314 (11), 226 (100), 198 (37). FAB-MS 371 (M^+, 100): 313 (18), 257 (82). HRMS calcd for $C_{22}H_{33}NO_2Si$: 371.2281; found 371.2271.

(1*S*,2*R*,4*S*,5*S*)-2-(Triisopropylsilyloxymethyl)-5-(10-phenylethynyl)-1-azabicyclo[2.2.2]octan-5-ol (11m). **9c** (115 mg, 0.37 mmol) was allowed to react with lithiated phenyl acetylene (1.11 mmol, 3 equiv) according to the general procedure to afford *anti*-**11m** (65%, 99 mg, 0.24 mmol) with 69% de. IR ($CHCl_3$) (ν): 2944, 1490, 1463, 1261, 1120, 1068, 1022 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.43−7.40 (m, 2 H, Ar−H), 7.32−7.29 (m, 3 H, Ar−H), 3.89−3.85/3.84−3.80 (dd, 1 H, *J* 9.5, 5.1 Hz, H-9), 3.77−3.72/3.71−3.67 (dd, 1 H, *J* 9.4, 8.2 Hz, H-9) 3.49−3.44 (dd, *J* 14.7, 1.3 Hz, H-6), 2.99−2.86 (m, 4 H, H-6, H-7, H-2, H-7), 2.18−2.15 (m, 1 H, H-4), 2.08−1.99 (m, 1 H, H-3), 1.91−1.82 (m, 2 H, H-8, H-3), 1.48−1.40 (m, 1 H, H-8), 1.11−0.99 (m, 21 H, Si(C*H*(C*H*$_3$)$_2$)$_3$). ^{13}C NMR (100 MHz) (δ): 131.63 (CH, Ph), 128.24 (CH, Ph), 122.77 (C, Ph), 93.34 (C, C-10), 83.84/83.81 (C, C-11), 68.03 (C, C-5), 65.95/65.74 (CH_2, C-9), 60.04/59.96 (CH_2, C-6), 56.20/56.18 (CH, C-2), 48.74 (CH_2, C-7), 34.91/ 34.88 (CH, C-4), 27.89/27.80 (CH_2, C-8), 19.37/18.69 (CH_2, C-3), 18.00 (CH_3, Si(CH(*CH*$_3$)$_2$)$_3$), 11.88 (CH, Si(*CH*(CH$_3$)$_2$)$_3$). MS *m*/*z*: 413 (M^+, 47), 371 (66), 343 (10), 226 (100). HRMS calcd for $C_{25}H_{39}NO_2Si$: 413.2750; found 413.2752.

(1*S*,2*R*,4*S*,5*S*)-2-(Triphenylmethyloxymethyl)-5-(10-phenylethynyl)-1-azabicyclo[2.2.2]octan-5-ol (11n). **9e** (134 mg, 0.34 mmol) was allowed to react with lithiated phenyl acetylene (1.02 mmol, 3 equiv) according to the general procedure to afford *anti*-**11n** (79%, 133 mg, 0.270 mmol) with 87% de. IR ($CHCl_3$) (ν): 3061, 2999, 2940, 1598, 1491, 1448, 1230, 1070, 1025 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, CD_3OD) (δ): 7.49−7.46 (m, 7 H, Ar−H), 7.34−7.27 (m, 5 H, Ar−H), 7.26−7.22 (m, 6 H, Ar−H), 7.20−7.16 (m, 2 H, Ar−H), 3.31−3.23 (m, 2 H, H-9, H-6), 3.14−3.09 (m, 1 H, H-9), 3.08−3.02 (m, 1 H, H-2), 2.99−2.88 (m, 2 H, H-7), 2.89−2.85 (d, *J* 14.8 Hz, H-6), 2.15−2.11 (m, 1 H, H-4), 2.05−1.97 (m, 1 H, H-3), 1.94−1.87 (m, 1 H, H-8), 1.77−1.71 (m, 1 H, H-8), 1.47−1.39 (m, 1 H, H-3). ^{13}C NMR (100 MHz, $CDCl_3$, CD_3OD) (δ): 144.07 (C, Ph), 131.72 (CH, Ph), 128.74 (CH, Ph), 128.26 (CH, Ph), 127.86 (CH, Ph), 126.88 (CH, Ph), 122.66 (C, Ph), 93.01 (C, C-10), 86.62 (C, Ph$_3$*C*O), 83.64 (C, C-11), 67.71 (C, C-5), 65.56 (CH_2, C-9), 59.50 (CH_2, C-6), 54.59 (CH, C-2), 48.47 (CH_2, C-7), 34.63 (CH, C-4), 28.15 (CH_2, C-8), 19.21 (CH_2, C-3). MS *m*/*z*: 499 (M^+, 3), 370 (9), 256 (18), 243 (100), 212 (40). HRMS calcd for $C_{35}H_{33}NO_2$: 499.2511; found 499.2513. Anal. Calcd for $C_{35}H_{33}NO_2$: C 84.14, H 6.66, N 2.80; found C 83.98, H 6.40, N 2.54.

(1*S*,2*S*,4*S*,5*S*)-2-(*tert*-Butyldimethylsilyloxymethyl)-5-(10-phenylethynyl)-1-azabicyclo[2.2.2]-octan-5-ol (12f). **10a** (100 mg, 0.37 mmol) was allowed to react with lithiated phenyl acetylene (1.11 mmol, 3 equiv) according to the general procedure to afford *anti*-**12f** (75%, 103 mg, 0.280 mmol) with 16% de. IR ($CHCl_3$) (ν): 2972, 2932, 1488, 1264, 1144, 1020 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.49−7.40 (m, 2 H, Ar−H), 7.32−7.28 (m, 3 H, Ar−H), 3.61−3.49 (m, 2 H, H-9), 3.41−3.37 (d, 1 H, *J* 14.0 Hz, H-6), 3.17−3.08 (m, 1 H, H-6), 3.02−2.94 (m, 1 H, H-2), 2.82−2.68 (m, 2 H, H-7), 2.18−2.03 (m, 2 H, H-4, H-3), 1.58−1.51/1.36−1.28 (m, 1 H, H-8), 1.27 (m, 9 H, SiC*(CH*$_3$*)*$_3$), 1.09−1.02 (m, 1 H, H-8), 0.92−0.82 (m, 1 H, H-3), 0.02−0.01 (m, 6 H, Si*CH*$_3$). ^{13}C NMR (100 MHz) (δ): 131.66 (CH, Ph), 128.48/128.34 (CH, Ph), 122.54/122.47 (C, Ph), 92.82/92.77 (C, C-10), 84.27/83.92 (C, C-11), 67.82/67.51 (C, C-5), 66.47/66.31 (CH_2, C-9), 62.72/62.59 (CH_2, C-6), 56.69/56.29 (CH, C-2), 39.51/39.31 (CH_2, C-7), 34.87/34.46 (CH, C-4), 31.23 (CH_3, SiC(*CH*$_3$)$_3$), 27.02/23.74 (CH_2, C-8), 23.29/19.78 (CH_2, C-3), 18.32 (C, Si*C*(CH$_3$)$_3$), −5.31 (CH_3, Si*CH*$_3$), −5.37 (CH_3, Si*CH*$_3$). FAB-MS 372 (M^++1, 23), 282 (27), 258 (100). HRMS calcd for $C_{22}H_{33}NO_2Si$: 371.2281; found 371.2262.

(1*S*,2*R*,4*S*,5*S*)-2-(Bromomethyl)-1-azabicyclo[2.2.2]octan-5-ol (11o). **9f** (102 mg, 0.47 mmol) was allowed to react with L-Selectride (0.71 mL, 0.71 mmol) according to the general procedure to afford diastereomeric alcohols *anti*-**11o** and *syn*-**11o** (85%, 87 mg, 0.40 mmol) in a ratio of 2.2:1 (38% de). IR ($CHCl_3$) (ν): 3385, 2955, 2928, 1453, 1230, 1116, 1028 cm^{-1}. ^1H NMR (400 MHz) (δ): 4.08−4.03 (m, 1 H, H-5), 3.85−3.81/3.61−3.56 (m, 1 H, H-6), 3.74−3.71/3.42−3.35 (m, 2 H, H-7), 3.51−3.44/3.32−3.23 (m, 1 H, H-2), 3.15−3.07/3.04−2.97 (m, 1 H, H-9), 2.91−2.86 (d, 1 H, *J* 13.1 Hz, H-6), 2.14−2.10 (m, 1 H, H-4), 2.00−1.94/1.87−1.79 (m, 1 H, H-3), 1.76−1.67/1.63−1.53 (m, 1 H, H-8), 1.43−1.36 (m, 2 H, H-8, H-3). ^{13}C NMR (100 MHz) (δ): 64.83/64.63 (CH, C-5), 58.02/56.76 (CH, C-2), 51.86/50.95 (CH_2, C-6), 49.26/48.63 (CH_2, C-7), 31.78/30.94 (CH_2, C-9), 29.38/23.77 (CH_2, C-8), 28.67/28.27 (CH, C-4), 21.57/16.72 (CH_2, C-3). MS *m*/*z*: 222 (M^++H, 8), 220 (M^++H, 8), 140 (100), 126 (12). HRMS calcd for $C_8H_{14}NOBr$: 219.0259; found 219.0258. Anal. Calcd for $C_8H_{14}NOBr$: C 43.65, H 6.41, N 6.36; found C 43.86, H 6.58, N 6.09.

(1*S*,2*R*,4*S*,5*S*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-5-(methanesulfonyloxy)-1-azabicyclo-[2.2.2]octane (*anti*-13) and (1*S*,2*R*,4*S*,5*R*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-5-(methane-sulfonyloxy)-1-azabicyclo[2.2.2]octane (*syn*-13). Methanesulfonyl chloride (1.3 equiv) was added to a solution of **11b** (560 mg, 1.42 mmol) and Et_3N (2.0 equiv) in abs CH_2Cl_2 at 0 °C. The reaction mixture was stirred for 8 h at rt, treated with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. After the solution was dried (over $MgSO_4$), the crude product was purified by column chromatography (EA/MeOH 40:1) and mesylates *anti*-**13** (79%, 531 mg, 1.12 mmol) and *syn*-**13** (15%, 100 mg, 0.21 mmol) were separated. Data for *anti*-**13**, IR ($CHCl_3$) (ν): 3051, 2945, 1589, 1471, 1428, 1230, 1174, 1113 cm^{-1}. ^1H NMR (400 MHz) (δ): 7.69−7.66 (m, 4 H, Ar−H), 7.47−7.38 (m, 6 H, Ar−H), 4.77−4.72 (m, 1 H, H-5), 3.72−3.67 (dd, 1 H, *J* 18.1, 15.5 Hz, H-9), 3.69−3.64 (dd, 1 H, *J* 18.2, 15.7 Hz, H-9), 3.53−3.47 (dd, 1 H, *J* 15.4, 8.2 Hz, H-6$_{endo}$), 3.03 (s, 3 H, Me-SO_2), 2.96−2.92 (m, 2 H, H-7), 2.91−2.84 (m, 1 H, H-2), 2.79−2.75 (d, 1 H, *J* 15.3 Hz, H-6$_{exo}$), 2.30−2.25 (m, 1 H, H-4), 1.91−1.83 (m, 2 H, H-8, H-3), 1.52−1.43 (m, 2 H, H-8, H-3), 1.08 (s, 9H, SiC*(CH*$_3$*)*$_3$); NOE H-5 irradiated H-6$_{endo}$ (4.8%), H-3$_{endo}$ (4.8%), H-4 (5.6%), H-6$_{endo}$ irradiated H-5 (4.9%), H-6$_{exo}$ (27.4%). ^{13}C NMR (100 MHz) (δ): 135.61 (CH,

Ar−H), 133.32 (C, Ar−Si), 129.74 (CH, Ar−H), 127.75 (CH, Ar−H), 79.17 (CH, C-5), 66.11 (CH_2, C-9), 55.67 (CH, C-2), 51.02 (CH_2, C-6), 49.58 (CH_2, C-7), 38.51 (CH_3, Me-SO_2), 27.57 (CH, C-4), 27.32 (CH_2, C-8), 26.89 (CH_3, SiC(CH_3)$_3$), 19.24 (C, Si*C*(CH_3)$_3$), 18.09 (CH_2, C-3). MS *m*/*z*: 473 (M^+, 1), 440 (2), 416 (100), 394 (25), 320 (23). HRMS calcd for $C_{25}H_{35}NO_4SSi$: 473.2056; found 473.2054. Data for *syn*-**13**, IR ($CHCl_3$) (*ν*): 3072, 2944, 1589, 1471, 1428, 1231, 1175, 1113 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 7.73−7.69 (m, 4 H, Ar−H), 7.45−7.38 (m, 6 H, Ar−H), 4.79−4.74 (m, 1 H, H-5), 3.79−3.76 (d, 2 H, *J* 6.1 Hz, H-9), 3.16−3.13 (d, 1 H, *J* 14.7 Hz, H-6_{endo}), 3.11−3.05 (m, 1 H, H-6_{exo}), 2.97−2.85 (m, 2 H, H-7, H-2), 2.94 (s, 3 H, Me-SO_2), 2.77−2.69 (m, 1 H, H-7), 2.24−2.21 (m, 1 H, H-4), 1.88−1.81 (m, 1 H, H-3), 1.80−1.72 (m, 1 H, H-8), 1.67−1.56 (m, 2 H, H-8, H-3), 1.09 (s, 9H, SiC*(CH$_3$)*$_3$); NOE H-5 irradiated H-6_{exo} (9.8%), H-8_{exo} (2.5%), H-4 (3.9%), H-6_{endo} irradiated H-5 (9.8%), H-6_{exo} (16.3%), H-7_{exo} (4.1%). ^{13}C NMR (100 MHz) (*δ*): 135.65 (CH, Ar−H), 133.49 (C, Ar−Si), 129.77 (CH, Ar−H), 127.72 (CH, Ar−H), 78.58 (CH, C-5), 65.73 (CH_2, C-9), 56.96 (CH, C-2), 49.90 (CH_2, C-6), 48.92 (CH_2, C-7), 38.55 (CH_3, Me-SO_2), 27.92 (CH, C-4), 26.87 (CH_3, SiC(CH_3)$_3$), 23.96 (CH_2, C-8), 21.68 (CH_2, C-3), 19.27 (C, Si*C*(CH_3)$_3$). MS *m*/*z*: 473 (M^+, 1), 416 (100), 394 (11), 320 (10). HRMS calcd for $C_{25}H_{35}NO_4SSi$: 473.2056; found 473.2057.

(1*S*,2*R*,4*S*,5*R*)-2-(*tert*-Butyldiphenylsilyloxymethyl)-5-(10,11,13-triazolyl)-1-azabicyclo-[2.2.2]octan-5-ol (14). Sodium triazolate (143 mg, 1.57 mmol, 4 equiv) was added to a solution of *anti*-**13** (186 mg, 0.390 mmol) in DMF at rt. The heterogeneous reaction mixture was stirred for 8 h at 110 °C, diluted with CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$. The organic layer was dried (over $MgSO_4$), the solvent evaporated in *vacuo*, and the residue purified by column chromatography (EA/MeOH 20:1) to yield **14** (74%, 129 mg, 0.290 mmol). IR ($CHCl_3$) (*ν*): 3072, 2999, 2952, 1602, 1472, 1427, 1230, 1113, 1011 cm^{-1}. ^1H NMR (400 MHz) (*δ*): 8.04 (s, 1 H, triazol-H), 7.92 (s, 1 H, triazol-H), 7.71−7.66 (m, 4 H, Ar−H), 7.47−7.36 (m, 6 H, Ar−H), 4.34−4.30 (m, 1 H, H-5), 3.84−3.75 (m, 2 H, H-9), 3.46−3.40 (ddd, 1 H, *J* 14.6, 6.9, 2.2 Hz, H-6), 3.28−3.21 (dd, 1 H, *J* 14.6, 9.7 Hz, H-6), 3.06−3.93 (m, 2 H, H-7, H-2), 2.89−2.77 (m, 1 H, H-7), 2.32−2.26 (m, 1 H, H-4), 1.85−1.60 (m, 4 H, H-3, H-8, H-3), 1.04 (s, 9 H, SiC-(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz) (*δ*): 151.41 (CH, triazol-H), 141.93 (CH, triazol-H), 135.68 (CH, Ar−H), 133.55 (C, Ar−Si), 129.65 (CH, Ar−H), 127.63 (CH, Ar−H), 67.40 (C, C-5), 65.75 (CH_2, C-9), 57.13 (CH, C-2), 49.02 (CH_2, C-6), 47.95 (CH_2, C-7), 28.67 (CH, C-4), 26.91 (CH_3, SiC(*C*H$_3$)$_3$), 25.55 (CH_2, C-8), 23.47 (CH_2, C-3), 19.26 (C, Si*C*(CH_3)$_3$). FAB-MS 447 (M^++1, 53): 389 (29), 378 (100), 320 (18), 300 (8), 135 (7). HRMS calcd for $C_{26}H_{34}N_4OSi$: 446.6158; found 446.6152.

(1*S*,2*R*,4*S*)-2-(Hydroxymethyl)-5-(13-methylfuranyl)-1-azabicyclo[2.2.2]oct-5-ene (15). 11i (82 mg, 0.35 mmol) was dissolved in HCOOH (99%, 2 mL), stirred for 4 h at 100 °C, and neutralized with aq KOH. The aqueous layer was extracted with CH_2Cl_2. After it was dried (over $MgSO_4$), the resulting organic layer was concentrated in *vacuo* and the residue purified by column chromatography (EA/MeOH 4:1) to yield **15** (96%, 73 mg, 0.33 mmol). IR ($CHCl_3$) (*ν*): 2999, 2957, 1591, 1412, 1284, 1134, 1023 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, CD_3OD) (*δ*): 6.64 (s, 1 H, H-6), 6.34−6.32 (d, 1 H, *J* 3.3 Hz, H-11), 5.90−5.87 (dd, 1 H, *J* 3.3, 1.0 Hz, H-12), 3.46−3.39 (m, 1 H, H-2), 3.39−3.34 (m, 1 H, H-9), 3.33−3.17 (m, 2 H, H-9, H-7), 3.07−3.04 (bs, 1 H, H-4), 2.94−2.86 (m, 1 H, H-7), 2.31 (s, 3 H, *J* 3.1 Hz, H-14), 2.00−1.93 (m, 1 H, H-3), 1.87−1.79 (m, 1 H, H-8), 1.69−1.61 (m, 1 H, H-8), 0.99−0.95 (m, 1 H, H-3). ^{13}C NMR (100 MHz) (*δ*): 153.82 (C, C-13), 147.17 (C, C-10), 137.18 (C, C-5), 123.66 (CH, C-6), 109.08 (CH, C-12), 107.54 (CH, C-11), 64.19 (CH_2, C-9), 63.67 (CH, C-2), 50.43 (CH_2, C-7), 28.22 (CH, C-4), 29.69 (CH_2, C-3), 24.66 (CH_2, C-8), 13.71 (CH_3, C-14). MS *m*/*z*: 219 (M^+, 87), 202 (15), 190 (25), 161 (100), 146 (27). HRMS calcd for $C_{13}H_{17}NO_2$: 219.1259; found 219.1259.

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Supporting Information Available: X-ray data for compounds **9f**, *anti*-**11o**, and *syn*-**11o** and ^1H and ^{13}C NMR spectra for each new compound. This material is free of charge via the Internet at http://pubs.acs.org.

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