3-Azabicyclo[3.1.0]hex-1-ylamines by Ti-Mediated Intramolecular Reductive Cyclopropanation of α-(*N*-Allylamino)-Substituted *N*,*N*-Dialkylcarboxamides and Carbonitriles

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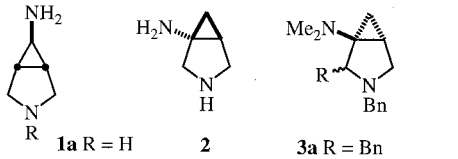
Dedicated to Professor Ekkehard Winterfeldt on the occasion of his 70th birthday

Keywords: Amides / Cyclopropanations / Lewis acids / Nitriles / Titanium

A variety of tris- and monoprotected derivatives with the 1-amino-3-azabicyclo[3.1.0]hexane and 1-amino-3-azabicyclo[4.1.0]heptane skeleton **10** have been synthesized by intramolecular reductive cyclopropanation of α-(*N*-allylamino)-substituted *N*,*N*-dialkylcarboxamides **6**, **8**, and **9**. Starting from derivatives of the naturally occurring amino acid serine (**4a**, **4b**), the enantiomerically pure compounds **10a** and **10b** were obtained with *endo*/*exo* ratios of 2.5:1 (**a**) and 2:1 (**b**), in 26 and 30% overall yields, respectively. The unprotected bicyclic amines **11aa**, **11ab**, **11ba**, and **11ad** have been prepared by palladium-catalyzed hydrogenative deprotection of **10aa**, **10ab**, **10ba** and **10ad**, respectively, under acidic conditions, in 91, 95, 96, and 99% yields, respectively. X-ray crystal structure analyses of **10aa** and **10ad** in each case found an equatorial position of the *N*-benzyl group on the heterocycle and a common boat conformation for the 3-azabicyclo[3.1.0]hexane and 3-azabicyclo[4.1.0]heptane skeletons as a whole. One-step preparations of the bicyclic diamines **11ac** (41% yield) and **14a** (48% yield) have been performed by application of the Kulinkovich–de Meijere procedure to the nitriles **12a** and **12b**.

The transformations of carboxylic acid esters and *N*,*N*-dialkylcarboxamides into cyclopropanols and cyclopropylamines, respectively, by the action of low-valent titanium reagents produced in situ from titanium alkoxides and organomagnesium halides (the so-called Kulinkovich reaction and its de Meijere variant) developed over the last 12 years have demonstrated their wide applicability in the syntheses of natural products and other compounds with potentially useful properties.[1] One of the most recent examples is the elegant synthesis of the enantiomerically pure amino acid (*S*)-cleonin, elaborated by Taddei et al.[2] Another biologically interesting cyclopropylamine, the 3-azabicyclo[3.1.0]hexylamine **1**, a key constituent of the highly active antibiotic trovafloxacin,[3] has also been successfully prepared by this approach.[4] This bicyclic diamine is also interesting as a rigid scaffold with two nitrogen atoms held at a well defined distance, as is the isomeric 1-amino-3-azabicyclo[3.1.0]hexane (**2**), some derivatives of which (**3a**, **3b**) have been prepared as 2:1 mixtures of *exo* and *endo* diastereomers by intramolecular reductive cyclopropanation of *N*-allyl-α-aminocarboxylic acid *N*,*N*-dimethylamides.[5]



1a R = H **1b** R = Boc **2** **3a** R = Bn **3b** R = *p*-TBSOBn

In order to be able to utilize these scaffolds in combinatorial approaches to libraries of compounds containing at least two different aromatic or heteroaromatic substituents on the two nitrogen atoms, these nitrogen atoms would have to be chemically addressable individually and selectively. For the diamine **1a**, this problem has recently been solved by a high-yield preparation of the Boc-protected derivative **1b**.[4] For the isomer **2**, we embarked on a project to prepare a variety of tris- and monoprotected derivatives incorporating the 1-amino-3-azabicyclo[3.1.0]hexane and the homologous 3-azabicyclo[4.1.0]heptane skeletons through intra-

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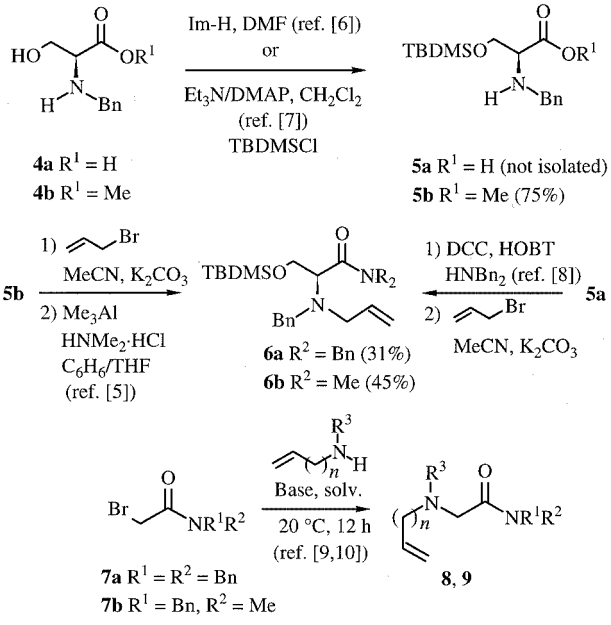
molecular cyclopropanation of *N*-allyl and *N*-homoallyl benzylmethyl- and dibenzylamides of types **8** and **9**.

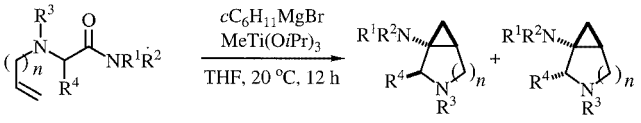
The starting *N*-allylserine amides **6a** and **6b** were prepared from *N*-benzylserine **4a** or its methyl ester **4b** by application of an established set of procedures, as shown in Scheme 1. The *N*-allylglycine *N*,*N*-dialkylamides **8** and **9aa** were prepared in good yields from 2-bromoacetamides **7a** and **7b** by nucleophilic substitution[9,10] with the appropriately *N*-substituted allyl- or homoallylamine (Scheme 1). Compound **8ac** ($R^1 = R^2 = Bn$, $R^3 = Boc$, not shown in Scheme 1) was obtained by treatment of 2-bromoacetamide **7a** with allylamine in THF, followed by Boc-protection of the nitrogen moiety.[11]



R^1	R^2	R^3	Product	*n*	Base	Solv.	Yield (%)
Bn	Bn	Bn	**8aa**	1	Et_3N	THF	93
Bn	Me	Bn	**8ba**	1	Et_3N	THF	85
Bn	Bn	Me	**8ab**	1	Et_3N	THF	98
Bn	Bn	Bn	**9aa**	2	NaH	DMF	76

Scheme 1. Preparations of the starting α-(*N*-allylamino)-substituted *N*,*N*-dialkylcarboxamides **6a**, **6b**, **8**, and **9aa**

Under the conditions previously published [*c*PentMgCl, $ClTi(OiPr)_3$, THF, room temp.] for the reductive intramolecular cyclopropanation of α-substituted *N*-allylglycine *N*,*N*-dialkylamides to yield compounds **3a** and **3b**,[5] the serine and glycine *N*,*N*-dibenzyl-, *N*,*N*-dimethyl-, and *N*-benzyl-*N*-methylamides of types **6**, **8**, and **9** did not cyclize to the bicyclic diamines. However, the target 1-amino-3-azabicyclo[3.1.0]hexane and 3-azabicyclo[4.1.0]heptane derivatives **10** were obtained from **6a**, **6b**, **8**, and **9aa** in moderate to good yields by use of a slightly different procedure (methyltitanium triisopropoxide[12] in place of chlorotitanium triisopropoxide and cyclohexylmagnesium bromide[13] instead of cyclopentylmagnesium chloride) (Scheme 2).



Starting Material	R^1	R^2	R^3	R^4	*n*	Product	Yield (%)	*endo*/*exo*
6a	Bn	Bn	Bn	$TBDMSOCH_2$	1	**10a**	83	2.5 : 1
6b	Me	Me	Bn	$TBDMSOCH_2$	1	**10b**	89	2 : 1
8aa	Bn	Bn	Bn	H	1	**10aa**	58	–
8ba	Bn	Me	Bn	H	1	**10ba**	56	–
8ab	Bn	Bn	Me	H	1	**10ab**	66	–
8ac	Bn	Bn	Boc [a]	H	1	**10ac**	43	–
9aa	Bn	Bn	Bn	H	2	**10ad**	59	–

[a] Boc = *tert*-butoxycarbonyl

Scheme 2. Intramolecular reductive cyclopropanation of α-(*N*-allylamino)-substituted *N*,*N*-dialkylcarboxamides **6a**, **6b**, **8**, and **9aa**

The structural features of the homologous *N*,*N*,3-tribenzyl-3-azabicyclo[3.1.0]hex-1-ylamine (**10aa**) and *N*,*N*,3-tribenzyl-3-azabicyclo[4.1.0]hept-1-ylamine (**10ad**) were established by X-ray crystal structure analyses (Figure 1). Their crystal parameters are very similar,[14] and in both cases the two phenyl rings of the dibenzylamino fragment are orthogonal with respect to each other. The *N*-benzyl group on the heterocycle adopts an equatorial position in both cases, bending the envelope of the azacyclopentane moiety in **10aa** and the chair of the azacyclohexane in **10ad** in such a way that the azabicyclo[3.1.0]hexane and azabicyclo[4.1.0]heptane systems adopt overall boat conformations.

Both compounds were racemates and therefore crystallized in a centrosymmetric space group. The geometries of the molecules and their packing in the crystals are quite similar, but the conformations of the molecules are different, as demonstrated by superposition of the molecules with their three-membered ring carbon and the nitrogen atoms of their dibenzylamino groups held in the same place (Figure 1). Molecule **10aa** has an *ap* orientation (with respect to the heterobicycle) of the quasiequatorial N2−C20 bond [dihedral angle C2−N2−C20−C21 = −163.0(1)°] and an *sc* orientation of the quasiaxial N2−C13 bond [angle C2−N2−C13−C14 = 69.7(1)°]. In contrast, molecule **10ad** has an *ap* orientation of the quasiaxial bond N2−C14 and an *sc* orientation of the quasiequatorial bond N2−C7 [dihedral angles C1−N2−C14−C15 = −169.9(1)° and C1−N2−C7−C8 = 66.0(1)°, respectively].

The unprotected diamines **11aa** and **11ad** and the partially unprotected diamines **11ba**, **11ab**, and **11ac** were obtained by catalytic hydrogenation under appropriate conditions (Scheme 3).

However, these derivatives still did not allow the potential aryl substituents on the primary amino group to be fully controlled. The best way to solve this problem would be by way of a one-step preparation of the bicyclic diamines with a protected secondary amino group and an unprotected primary amino group. By the logic of the titanium-mediated transformation, this might be achievable by the use of

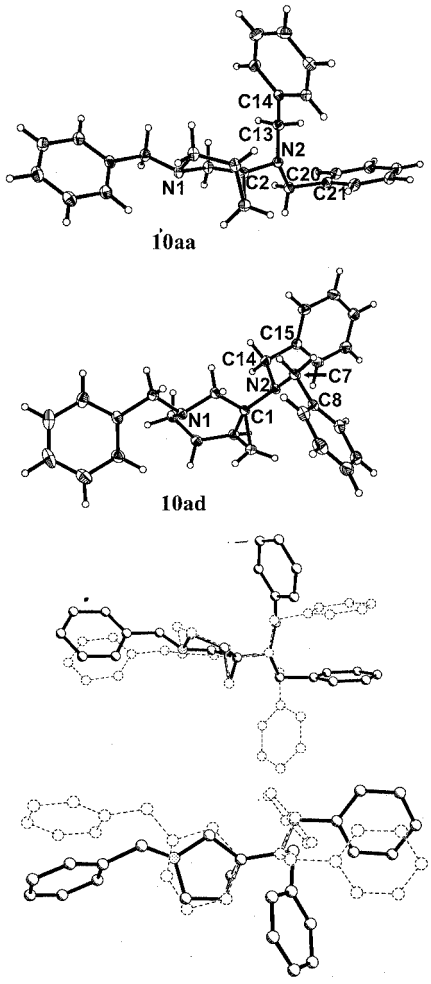
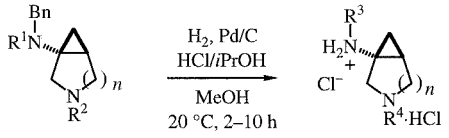


Figure 1. Molecular structures of *N*,*N*,3-tribenzyl-3-azabicyclo[3.1.0]hex-1-ylamine (**10aa**) and *N*,*N*,3-tribenzyl-3-azabicyclo[4.1.0]hept-1-ylamine (**10ad**) in the crystal (top, displacement ellipsoids are shown at the 50% probability level) and their superposition (bottom)[14]



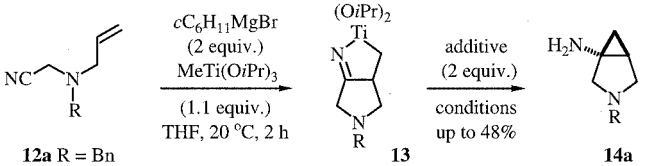
Starting Material	R^1	R^2	*n*	Product	R^3	R^4	Yield (%)
10aa	Bn	Bn	1	**11aa**	H	H	91
10ba	Me	Bn	1	**11ba**	Me	H	96
10ab	Bn	Me	1	**11ab**[a]	H	Me	95
10ac	Bn	Boc	1	**11ac**	H	Boc	76
10ad	Bn	Bn	2	**11ad**	H	H	99

[a] Compound **11ac** was obtained as a free base.

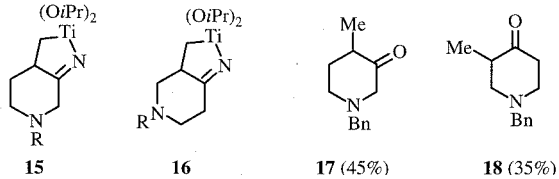
Scheme 3. Deprotection of the benzyl-protected 3-azabicyclo[3.1.0]hex-1-ylamines **10** and *N*,*N*,3-tribenzyl-3-azabicyclo[4.1.0]hept-1-ylamine (**10ad**)

nitriles as starting materials. Early attempts to convert aliphatic nitriles into primary cyclopropylamines by use of Grignard reagents and $Ti(OiPr)_4$, however, met with only very moderate success.[15] Szymoniak et al., though, found out that nitriles did react with titanacyclopropane intermediates generated in situ to form remarkably stable azatitanacyclopentane intermediates, which − on activation with an added Lewis acid (LA) such as boron trifluoride−diethyl ether − eventually underwent ring-contraction to give Lewis acid complexed primary cyclopropylamines. Aqueous workup under basic conditions then furnished the primary cyclopropylamines in moderate to good yields.[16] In an independent development, it was found that aromatic nitriles in particular could be converted into primary cyclopropylamines by treatment with dialkylzinc reagents in the presence of $Ti(OiPr)_4$ and addition of lithium isopropoxide or lithium iodide.[17]

The appropriate starting nitrile for an intramolecular application of this approach − compound **12a** − was prepared by a published procedure.[18] Treatment of chloroacetonitrile with allylamine, Et_3N, and K_2CO_3 in DMF, followed by protection with Boc_2O and Et_3N in MeOH, afforded compound **12b** in 35% overall yield.[19] Intramolecular reductive cyclopropanation of nitriles **12a** and **12b** upon treatment with methyltitanium triisopropoxide and cyclohexylmagnesium bromide with subsequent addition of a Lewis acid did indeed provide the 3-benzyl-3-azabicyclo[3.1.0]hex-1-ylamine (**14a**) and 3-*tert*-butoxycarbonyl-3-azabicyclo[3.1.0]hex-1-ylamine (**11ac**), albeit in moderate yields (Scheme 4).



Product	R	Additive	*T* [°C]	*t* [h]	Yield (%)
14a	Bn	$BF_3·Et_2O$	20	1	trace
14a	Bn	$BF_3·Et_2O$	70	2	46
14a	Bn	LiI	70	3	48
14a	Bn	LiI	70	16	43
14a	Bn	NaI	70	3	28
11ac	Boc	LiI	70	14	trace
11ac	Boc	LiI	70	3	41



Scheme 4. Intramolecular reductive cyclopropanation of *N*-allylaminocarbonitriles **12a** and **12b**

While only traces of the product **14a** were detected under the conditions developed by Szymoniak et al. to accelerate the ring-contraction of the intermediate azatitanacyclopen-

tene (i.e., addition of $BF_3{\cdot}OEt_2$ as a Lewis acid at ambient temperature), compound **14a** could be obtained by heating the reaction mixture at 70 °C for 2 h. The reaction, however, proceeded more cleanly, to give the bicyclic diamine **14a** in 48% yield, when the reaction mixture was heated at 70 °C for 3 h after addition of 2 equivalents of lithium iodide. No by-products could be isolated; only unidentified oligomeric materials were detected. The structure of the diamine **14a** was confirmed by X-ray crystal structure analysis of its hemihydrochloride **14a**·0.5 HCl (Figure 2). In contrast to the behavior of **12a** and **12b**, the homologous *N*-allyl-*N*-benzyl-3-aminopropionitrile and 2-amino-*N*-benzyl-*N*-homoallylacetonitrile predominantly gave the 1-benzyl-4-methylpiperidin-3-one (**17**,[20] 45%) and 1-benzyl-3-methylpiperidin-4-one (**18**,[21] 35%) resulting from hydrolysis of the intermediate azatitanacyclopentenes **15** and **16**, respectively, these compounds apparently being particularly stable in these cases, with only traces of the corresponding azabicyclo[4.1.0]heptane derivatives.

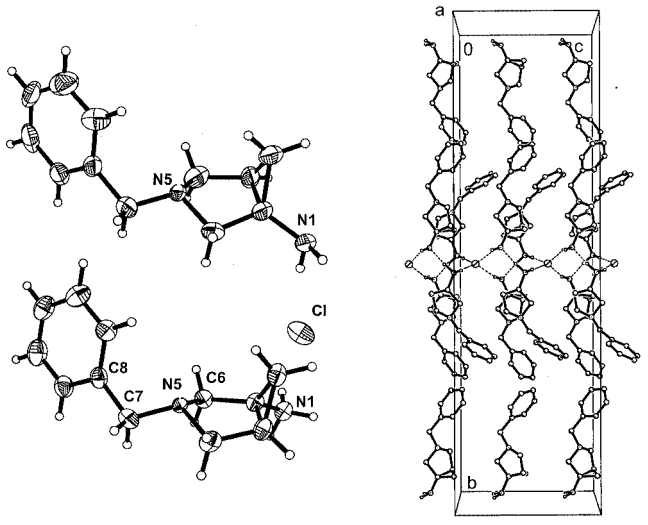


Figure 2. Molecular structure (left) and crystal packing (right) of 3-benzyl-3-azabicyclo[3.1.0]hex-1-ylamine hemihydrochloride (**14a**·0.5 HCl) in the crystal (displacement ellipsoids are shown at the 50% probability level)[14]

The structure of **14a**·0.5HCl is another example of the conformational flexibility of this class of compounds. The unit cell contains two independent molecules, both partially disordered. The independent molecules are different conformers. The dihedral angle C6−N5−C7−C8, describing the conformation of the benzyl group relative to the bicyclic system, is 172.5(2)° in one independent molecule and −72.8(2)° in the second. Molecules in crystals of **14a**·0.5 HCl are linked together by a network of hydrogen bonds of N−H···Cl and N−H···N types, forming a layered structure.

Experimental Section

General: ^{1}H and ^{13}C NMR: spectra were recorded at 250, 300, 600 (^{1}H), and 62.9, 75.5 [^{13}C, additional DEPT (Distortionless Enhancement by Polarization Transfer)] MHz on Bruker AM 250, AMX 300 and Inova 600 instruments in $CDCl_3$ solution if not otherwise specified, with $CHCl_3/CDCl_3$ as internal reference; δ in ppm, *J* in Hz. IR: Bruker IFS 66 (FT-IR) spectrophotometer, measured as KBr pellets or oils between KBr plates. MS (EI): Finnigan MAT 95 spectrometer. Optical rotations: Perkin−Elmer 241 digital polarimeter, 1 dm cell. M.p.: Büchi 510 capillary melting point apparatus, uncorrected values. TLC: Macherey−Nagel precoated sheets, 0.25 mm Sil G/UV_{254}. Column chromatography: Merck silica gel, grade 60, 230−400 mesh. Starting materials: Anhydrous diethyl ether and THF were obtained by distillation from sodium benzophenone ketyl, CH_2Cl_2 and DMF from CaH_2, and acetonitrile from P_4O_{10}. Compounds **4a** and **4b**,[18] **5b**,[7a] **7a** and **7b**,[9a] alkylallylamines,[9b] alkylhomoallylamines,[10a] and **12a**[18] were prepared by published procedures. Cyclohexylmagnesium bromide was prepared from *c*HexBr and Mg in Et_2O, $MeTi(OiPr)_3$ from MeLi and $ClTi(OiPr)_3$ in Et_2O, $ClTi(OiPr)_3$ from $TiCl_4$ and $Ti(OiPr)_4$ in Et_2O. All other chemicals were used as commercially available (Merck, Acrõs, BASF, Bayer, Hoechst, Degussa AG, and Hüls AG). All reactions were performed under an Ar atmosphere. Organic extracts were dried over $MgSO_4$.

(*S*)-2-Benzylamino-*N*,*N*-dibenzyl-3-(*tert*-butyldimethylsilyloxy)-propionamide: *tert*-Butyldimethylsilyl chloride (1.1 mmol, 300 mg of a 55% solution in toluene) was added dropwise at 0 °C to a suspension of (*S*)-2-benzylamino-3-hydroxypropionic acid (**4a**, 390 mg, 2.00 mmol) and imidazole (150 mg, 2.20 mmol) in anhydrous DMF (10 mL). After the addition was complete, the mixture was stirred for 2 days at room temperature to give crude (*S*)-2-benzylamino-3-(*tert*-butyldimethylsilyloxy)propionic acid (**5a**). Dicyclohexylcarbodiimide (DCC, 310 mg, 1.5 mmol), hydroxybenzotriazole (HOBT, 150 mg, 1.1 mmol), and dibenzylamine (1.5 mmol, 0.3 mL) were then added, and stirring was continued for an additional 16 h. EtOAc (10 mL) was added, the mixture was filtered through Celite, and the solvent was removed under reduced pressure. EtOAc (10 mL) was again added, and the organic phase was washed with $NaHCO_3$, H_2O, and brine, dried, and concentrated under reduced pressure. Column chromatography of the residue (R_f = 0.60, Et_2O/hexane, 1:1) gave (*S*)-2-benzylamino-*N*,*N*-dibenzyl-3-(*tert*-butyldimethylsilyloxy)propionamide (236 mg, 48%) as a colorless oil. $[\alpha]_D^{20}$ = −12.0 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (250 MHz): δ = 0.05 (s, 3 H), 0.09 (s, 3 H), 0.90 (s, 9 H), 2.52 (s, 1 H, NH), 3.50 (d, *J* = 12.5 Hz, 1 H), 3.75−3.97 (m, 4 H), 4.15 (d, *J* = 14.7 Hz, 1 H), 4.26 (d, *J* = 17.4 Hz, 1 H), 5.00 (d, *J* = 17.4 Hz, 1 H), 5.33 (d, *J* = 14.7 Hz, 1 H), 7.19−7.41 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = −5.5 (2 CH_3), 18.3 (C), 25.9 (3 CH_3), 48.9 (CH_2), 49.4 (CH_2), 51.9 (CH_2), 59.0 (CH), 66.0 (CH_2), 126.6 (CH_{ar}), 127.0 (CH_{ar}), 127.4 (CH_{ar}), 127.6 (CH_{ar}), 128.1 (CH_{ar}), 128.3 (CH_{ar}), 128.4 (3 CH_{ar}), 128.6 (2 CH_{ar}), 128.9 (2 CH_{ar}), 129.1 (2 CH_{ar}), 136.9 (C_{ar}), 137.1 (C_{ar}), 139.9 (C_{ar}), 174.7 (C=O) ppm. IR: $\tilde{\nu}$ = 3032 cm^{-1}, 2929, 2856, 1656, 1453, 1115, 785. MS (EI): *m*/*z* (%) = 488 (26) [M^+], 473 (71), 343 (18), 264 (100), 91 (44). $C_{30}H_{40}N_2O_2Si$ (488.75): calcd. C 73.72, H 8.25, N 5.73; found C 73.58, H 8.33, N 5.54.

Preparation of Allylbenzylamino Propionic Acid Derivatives. General Procedure 1 (GP1):[22] Allyl bromide (0.57 mmol) was added dropwise at 0 °C to a suspension of the corresponding benzylamino propionic acid derivative (0.41 mmol) and K_2CO_3 (0.82 mmol) in anhydrous MeCN (8 mL). After the addition was complete, the reaction mixture was stirred for 16 h at 60 °C. EtOAc (5 mL) and $NaHCO_3$ (5 mL) were added, and the organic phase was washed with brine and dried. Evaporation of the solvent under reduced pressure gave the crude products, which were purified by column chromatography on silica gel.

(*S*)-2-(Allylbenzylamino)-*N*,*N*-dibenzyl-3-(*tert*-butyldimethylsilyloxy)propionamide (6a): Derivative **6a** (139 mg, 64%) was obtained from (*S*)-*N*,*N*-dibenzyl-2-benzylamino-3-(*tert*-butyldimethylsilyloxy)propionamide (200 mg, 0.41 mmol), K_2CO_3 (113 mg, 0.82 mmol), and allyl bromide (0.57 mmol, 0.05 mL) according to GP1, as a colorless oil, R_f (Et_2O/hexane, 1:5) = 0.60, $[\alpha]_D^{20} = -2.0$ (c = 0.94, $CHCl_3$). ^1H NMR (250 MHz): δ = 0.10 (s, 3 H), 0.12 (s, 3 H), 0.94 (s, 9 H), 3.25 (dd, J = 7.7, 14.0 Hz, 1 H), 3.44 (dd, J = 5.2, 14.0 Hz, 1 H), 3.71 (d, J = 13.8 Hz, 1 H), 3.87 (dd, J = 5.4, 7.2 Hz, 1 H), 3.95 (d, J = 14.8 Hz, 1 H), 4.02−4.24 (m, 4 H), 4.66 (d, J = 17.2 Hz, 1 H), 5.03−5.21 (m, 3 H), 5.70−5.86 (m, 1 H), 7.08−7.39 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = −5.4 (2 CH_3), 18.3 (C), 25.9 (3 CH_3), 47.8 (CH_2), 49.0 (CH_2), 53.9 (CH_2), 54.5 (CH_2), 59.7 (CH_2), 60.1 (CH), 117.8 (CH_2, CH=*C*H_2), 126.6 (2 CH_{ar}), 126.9 (CH_{ar}), 127.2 (CH_{ar}), 128.1 (5 CH_{ar}), 128.5 (2 CH_{ar}), 128.6 (2 CH_{ar}), 128.9 (2 CH_{ar}), 136.2 (C_{ar}), 136.9 (CH, *C*H=CH_2), 137.4 (C_{ar}), 139.6 (C_{ar}), 171.8 (C=O) ppm. IR: $\tilde{\nu}$ = 3028 cm^{-1}, 2927, 2855, 1652, 1452, 1256, 1099. MS (EI): *m*/*z* (%) = 528 (15) [M^+], 513 (35), 437 (33), 383 (12), 304 (100), 91 (25). $C_{33}H_{44}N_2O_2Si$ (528.81): calcd. C 74.95, H 8.39, N 5.30; found C 75.08, H 8.22, N 5.21.

Methyl (*S*)-2-(Allylbenzylamino)-3-(*tert*-butyldimethylsilyloxy)propionate:[23] This compound (1.14 g, 82%) was obtained from methyl (*S*)-2-benzylamino-3-(*tert*-butyldimethylsilyloxy)propionate (**5b**, 1.11 g, 3.71 mmol), K_2CO_3 (1.03 g, 7.42 mmol), and allyl bromide (5.4 mmol, 0.5 mL) according to GP1, as a colorless oil, R_f (Et_2O/hexane, 1:10) = 0.50. ^1H NMR: δ = 0.01 (s, 6 H), 0.85 (s, 9 H), 3.16 (dd, J = 7.3, 14.5 Hz, 1 H), 3.33−3.35 (m, 1 H), 3.60−3.68 (m, 2 H), 3.72 (s, 3H), 3.81−3.99 (m, 3 H), 5.09−5.25 (m, 2 H), 5.79−5.81 (m, 1 H), 7.22−7.38 (m, 5 H) ppm. ^{13}C NMR: δ = −5.2 (2 CH_3), 18.1 (C), 25.7 (3 CH_3), 51.1 (CH_3), 54.5 (CH_2), 55.1 (CH_2), 62.7 (CH_2), 63.6 (CH), 117.1 (CH_2, CH=*C*H_2), 126.8 (CH_{ar}), 128.1 (2 CH_{ar}), 128.5 (2 CH_{ar}), 136.6 (CH, *C*H=CH_2), 140.1 (C_{ar}), 172.2 (C=O) ppm. IR: $\tilde{\nu}$ = 3064 cm^{-1}, 2953, 2884, 1739, 1472, 1257, 1106.

(*S*)-2-(Allylbenzylamino)-3-(*tert*-butyldimethylsilyloxy)-*N*,*N*-dimethylpropionamide (6b): Me_3Al (12.2 mL of a 2 M solution in hexane) was added at 5 °C over a period of 1 h to a solution of $Me_2NH{\cdot}HCl$ (2.00 g, 24.5 mmol) in anhydrous benzene (10 mL). The solution was stirred for 2 h at 20 °C and transferred to a solution (precooled to 5 °C) of methyl (*S*)-2-(allylbenzylamino)-3-(*tert*-butyldimethylsilyloxy)propionate (1.11 g, 3.06 mmol) in a mixture of anhydrous benzene (50 mL) and THF (15 mL). After the addition was complete, the reaction mixture was stirred for 2 days at 70 °C, and then cooled in an ice bath and carefully quenched with aq. 10% NaOH solution (50 mL). EtOAc (10 mL) was added, and the organic phase was washed with brine (50 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue gave **6b** (587 mg, 51%) as a colorless oil, R_f (Et_2O/hexane, 1:1) = 0.58, $[\alpha]_D^{20} = -11.4$ (c = 1, $CHCl_3$). ^1H NMR (250 MHz): δ = 0.04 (s, 3 H), 0.07 (s, 3 H), 0.88 (s, 9 H), 2.88 (s, 3 H), 2.90 (s, 3 H), 3.23−3.33 (m, 2 H), 3.75−4.02 (m, 5 H), 5.06−5.21 (m, 2 H), 5.73−5.86 (m, 1 H), 7.17−7.34 (m, 5 H) ppm. ^{13}C NMR (62.9 MHz): δ = −5.4 (2 CH_3), 18.1 (C), 25.8 (3 CH_3), 35.4 (CH_3), 37.2 (CH_3), 54.2 (CH_2), 54.6 (CH_2), 59.4 (CH), 62.1 (CH_2), 116.9 (CH_2, CH=*C*H_2), 126.6 (CH_{ar}), 128.0 (2 CH_{ar}), 128.6 (2 CH_{ar}), 136.9 (CH, *C*H=CH_2), 140.2 (C_{ar}), 172.1 (C=O) ppm. IR: $\tilde{\nu}$ = 3063 cm^{-1}, 2928, 1699, 1494, 1361, 1257, 1102. MS (CI): *m*/*z* (%) = 377 (100%) [M + H^+], 337 (3), 287 (5), 232 (3). HRMS (EI) calcd. for $C_{21}H_{36}N_2O_2Si$ [M^+] 376.2546, found 376.2546.

Preparation of *N*-Alkyl-2-allylalkylamino-*N*-benzylacetamides 8. General Procedure 2 (GP2): Et_3N (24 mmol, 3.3 mL) and alkylbenzylamine (13.2 mmol) were added dropwise at 0 °C to a solution of *N*-alkyl,*N*-benzyl-bromoacetamide (**7**, 12 mmol) in anhydrous THF (25 mL). After the addition was complete, the reaction mixture was stirred for an additional 20 h at ambient temperature. Water (10 mL) and EtOAc (10 mL) were added, and the organic phase was washed with saturated aq. $NaHCO_3$ solution (20 mL), brine (30 mL), and dried. Evaporation of the solvent under reduced pressure gave compounds **8** as yellow oils, which were purified by column chromatography on silica gel.

2-(Allylbenzylamino)-*N*,*N*-dibenzylacetamide (8aa): Compound **8aa** (37.9 g, 93%) was obtained from the bromoacetamide **7a** (33.7 g, 0.106 mol), Et_3N (0.202 mol, 28 mL), and allylbenzylamine (17.27 g, 0.117 mol) according to GP2, as a colorless oil, R_f (hexane/Et_2O, 2:1) = 0.33. ^1H NMR (250 MHz): δ = 3.27 (d, J = 6.5 Hz, 2 H), 3.40 (s, 2 H), 3.77 (s, 2 H), 4.49 (s, 2 H), 4.60 (s, 2 H), 5.13−5.26 (m, 2 H), 5.88 (ddt, J = 6.6, 10.2, 17.1 Hz, 1 H), 7.06−7.38 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = 47.6 (CH_2), 49.3 (CH_2), 55.7 (CH_2), 57.0 (CH_2), 58.1 (CH_2), 118.7 (CH_2, CH=*C*H_2), 126.5 (2 CH_{ar}), 127.0 (CH_{ar}), 127.3 (2 CH_{ar}), 128.1 (4 CH_{ar}), 128.5 (2 CH_{ar}), 128.6 (2 CH_{ar}), 129.1 (2 CH_{ar}), 135.0 (CH, *C*H=CH_2), 136.6 (C_{ar}), 137.2 (C_{ar}), 138.3 (C_{ar}), 171.0 (C=O) ppm. IR: $\tilde{\nu}$ = 3028 cm^{-1}, 2922, 1650, 1494, 1451, 1213, 1076, 734. MS (EI): *m*/*z* (%) = 384 (6) [M^+], 343 (14), 293 (48), 160 (78), 91 (100). $C_{26}H_{28}N_2O$ (384.52): calcd. C 81.21, H 7.34, N 7.28; found C 81.04, H 7.11, N 7.09.

2-(Allylmethylamino)-*N*,*N*-dibenzylacetamide (8ab): Compound **8ab** (19 g, 98%) was obtained from the bromoacetamide **7a** (20 g, 63 mmol), Et_3N (126 mmol, 17.5 mL), and allylmethylamine (6.57 mL, 69 mmol) according to GP2, as a colorless oil, R_f (hexane/Et_2O, 1:2) = 0. 28. ^1H NMR (250 MHz): δ = 2.36 (s, 3 H), 3.10 (d, J = 6.6 Hz, 2 H), 3.29 (s, 2 H), 4.57 (s, 2 H), 4.60 (s, 2 H), 5.08−5.20 (m, 2 H), 5.82 (ddt, J = 6.5, 10.3, 17.0 Hz, 1 H), 7.15−7.39 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz): δ = 42.6 (CH_3), 47.8 (CH_2), 49.5 (CH_2), 59.7 (CH_2), 60.8 (CH_2), 118.3 (CH_2, CH=*C*H_2), 126.7 (2 CH_{ar}), 127.4 (CH_{ar}), 127.5 (CH_{ar}), 128.3 (2 CH_{ar}), 128.6 (2 CH_{ar}), 128.9 (2 CH_{ar}), 135.0 (CH, *C*H=CH_2), 136.8 (C_{ar}), 137.3 (C_{ar}), 170.7 (C=O) ppm. IR: $\tilde{\nu}$ = 3029 cm^{-1}, 2919, 2788, 1649, 1451, 1233, 699. MS (EI): *m*/*z* (%) = 308 (7) [M^+], 279 (11), 217 (3), 91 (26), 84 (100). $C_{20}H_{24}N_2O$ (308.43): calcd. C 77.88, H 7.84, N 9.08; found C 77.59, H 7.61, N 8.97.

2-(Allylbenzylamino)-*N*-benzyl-*N*-methylacetamide (8ba): Compound **8ba** (3.15 g, 85%) was obtained from the bromoacetamide **7b** (2.9 g, 12 mmol) and allylbenzylamine (1.95 g, 13.2 mmol) according to GP2, as a colorless oil, R_f (hexane/Et_2O, 1:1) = 0.39. ^1H NMR (250 MHz): δ = 2.86 (s, 3 H, minor rotamer), 2.88 (s, 3 H, major rotamer), 3.20−3.23 (m, 2 H), 3.33 (s, 2 H), 3.69 (s, 2 H), minor), 3.74 (s, 2 H, major), 4.54 (s, 2 H, minor), 4.56 (s, 2 H, major), 5.12−5.26 (m, 2 H), 5.77−5.95 (m, 1 H), 7.05−7.38 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz): δ = 33.6 (CH_3, minor), 34.6 (CH_3, major), 50.8 (CH_2, major), 52.8 (CH_2, minor), 55.8 (CH_2, major), 56.0 (CH_2 minor), 57.1 (CH_2, major), 57.3 (CH_2, minor), 58.1 (CH_2, major), 58.2 (CH_2, minor), 118.3 (CH_2, minor, CH=*C*H_2), 118.4 (CH_2, major, CH=*C*H_2), 126.5 (CH_{ar}), 127.0 (CH_{ar}), 127.2 (CH_{ar}), 128.2 (2 CH_{ar}), 128.5 (2 CH_{ar}), 128.7 (CH_{ar}), 129.2 (2 CH_{ar}), 135.2 (CH, minor, *C*H=CH_2), 135.3 (CH, major, *C*H=CH_2), 136.9 (C_{ar}, minor), 137.3 (C_{ar}, major), 138.5 (C_{ar}, minor), 138.7 (C_{ar}, major), 170.7 (C=O) ppm. IR: $\tilde{\nu}$ = 3028 cm^{-1}, 2920, 2836, 1646, 1452, 1261, 1103, 699. MS (EI): *m*/*z* (%) = 308 (7) [M^+], 267 (14), 217 (48), 160 (88), 91 (100). $C_{20}H_{24}N_2O$ (308.43): calcd. C 77.88, H 7.84, N 9.08; found C 77.99, H 7.97, N 8.89.

2-[(Allyl)(*tert*-butoxycarbonyl)amino]-*N*,*N*-dibenzylacetamide (8ac): Et_3N (9.1 mmol, 1.26 mL) and allylamine (286 mg, 5.01 mmol)

were added dropwise at 0 °C to a solution of *N*,*N*-dibenzyl(bromoacetyl)amide (**7a**, 1.45 g, 4.56 mmol) in anhydrous THF (15 mL). After the addition was complete, the reaction mixture was stirred for an additional 12 h at ambient temperature. Saturated aq. $NaHCO_3$ solution (10 mL) and EtOAc (10 mL) were added, and the organic phase was washed with brine (20 mL), dried, and concentrated under reduced pressure to give an oil, which was used without further purification. This oil was taken up in a mixture of H_2O (7 mL) and dioxane (15 mL), and to this solution were added a solution of NaOH (160 mg, 4.0 mmol) in H_2O (7 mL) and di-*tert*-butyl pyrocarbonate (Boc_2O, 1.09 g, 5 mmol). The mixture was stirred for an additional 2 days, concentrated to about 50% of its original volume, and extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with brine (20 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue gave **8ac** (1.02 g, 57%) as a colorless oil, R_f (Et_2O/hexane 2:1) = 0.59. ^1H NMR (250 MHz): δ = 1.40 (s, 9 H), 3.64−3.70 (m, 2 H), 3.88 (s, 2 H), 4.47 (s, 2 H), 4.58 (s, 2 H), 5.04−5.19 (m, 2 H), 6.85 (m, 1 H), 7.05−7.32 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz): δ = 28.3 (3 CH_3), 43.0 (CH_2), 48.4 (CH_2), 50.7 (CH_2), 60.3 (CH_2), 79.1 (C), 115.5 (CH_2, CH=*C*H_2), 126.4 (2 CH_{ar}), 127.6 (CH_{ar}), 127.9 (CH_{ar}), 128.0 (2 CH_{ar}), 128.6 (2 CH_{ar}), 129.0 (2 CH_{ar}), 135.0 (CH, *C*H=CH_2), 135.7 (C_{ar}), 136.4 (C_{ar}), 155.8 (C=O), 167.4 (C=O) ppm. IR: $\tilde{\nu}$ = 3031 cm^{-1}, 2978, 1700, 1652, 1448, 1172.

***N*,*N*-Dibenzyl-2-[(benzyl)(but-3-enyl)amino]acetamide (9aa):** A solution of *N*-benzylbut-3-enylamine (322 mg, 2 mmol) in DMF (3 mL) was added at 0 °C to a suspension of NaH (104 mg of a 60% suspension in mineral oil, 2.6 mmol) in DMF (4 mL). The reaction mixture was stirred for 10 min at 0 °C, *N*,*N*-dibenzylbromoacetamide (**7a**, 732 mg, 2.3 mmol) was then added in one portion, and stirring was continued for an additional 2 h at ambient temperature. The reaction mixture was cooled with an ice bath, and a 2:1 mixture of sat. aq. NH_4Cl solution and 25% aq. NH_4OH solution (6 mL) was added. The aqueous layer was extracted with Et_2O, and the combined organic phases were washed with brine and dried. After evaporation of the solvent, the residue was purified by column chromatography on silica gel to give **9aa** (605 mg, 76%) as a yellow oil, R_f (hexane/Et_2O, 2:1) = 0.37. ^1H NMR (250 MHz): δ = 2.20−2.29 (m, 2 H), 2.71 (ps t, *J* = 7.2 Hz, 2 H), 3.37 (s, 2 H), 3.72 (s, 2 H), 4.50 (s, 2 H), 4.56 (s, 2 H), 4.92−5.02 (m, 2 H), 5.82 (ddt, *J* = 6.7, 10.2, 17.1 Hz, 1 H), 7.05−7.39 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = 31.4 (CH_2), 47.8 (CH_2), 49.3 (CH_2), 53.6 (CH_2), 56.8 (CH_2), 58.4 (CH_2), 115.8 (CH_2, CH=*C*H_2), 126.4 (2 CH_{ar}), 127.2 (CH_{ar}), 127.3 (CH_{ar}), 127.4 (CH_{ar}), 128.2 (2 CH_{ar}), 128.3 (2 CH_{ar}), 128.6 (2 CH_{ar}), 128.8 (2 CH_{ar}), 129.2 (2 CH_{ar}), 136.5 (C_{ar}), 136.7 (CH, *C*H=CH_2), 137.2 (C_{ar}), 138.4 (C_{ar}), 171.1 (C=O) ppm. IR: $\tilde{\nu}$ = 3062 cm^{-1}, 3028, 2921, 1650, 1451, 1211, 698. MS (EI): *m*/*z* (%) = 398 (3) [M^+], 357 (37), 174 (82), 91 (100). HRMS (EI) calcd. for $C_{27}H_{30}N_2O$ [M^+] 398.2358, found 398.2358.

Preparation of 3-Azabicyclo[3.1.0]hex-1-ylamine and 3-Azabicyclo[4.1.0]hept-1-ylamine 10. General Procedure 3 (GP3): Cyclohexylmagnesium bromide (5 mmol, 5 mL of a 1 M solution in Et_2O) was added dropwise at room temperature to a well stirred solution of *N*,*N*-dialkylpropionamide **6**, **8**, or **9** (1 mmol) and methyltitanium triisopropoxide (351 mg, 1.46 mmol) in anhydrous THF (30 mL). After addition was complete, the mixture was stirred for 12 h, and then poured into ice-cold water (10 mL) and stirred for an additional 1 h. The mixture was filtered through Celite, the aqueous phase was extracted with Et_2O (3 × 50 mL), and the combined ethereal phases were washed with sat. aq. $NaHCO_3$ solution (100 mL) and brine (100 mL) and dried. Evaporation of the solvent under reduced pressure gave compounds **10**, which were purified by column chromatography on silica gel.

***endo*- and *exo*-(1*R*,2*R*,5*S*)-*N*,*N*,3-Tribenzyl-2-(*tert*-butyldimethylsilyloxymethyl)-3-azabicyclo[3.1.0]hex-1-ylamine (10a):** 3-Azabicyclo[3.1.0]hex-1-ylamine **10a** (265 mg, 83%) was obtained from compound **6a** (330 mg, 0.62 mmol), methyltitanium triisopropoxide (206 mg, 0.858 mmol), and cyclohexylmagnesium bromide (2.87 mmol, 3.5 mL of a 0.82 M solution in Et_2O) according to GP3, in an *endo*/*exo* ratio of 2.5:1. ***endo*-10a:** Colorless oil, R_f (hexane/Et_2O, 10:1) = 0.20. $[\alpha]_D^{20}$ = +3.6 (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz): δ = 0.15 (s, 3 H), 0.17 (s, 3 H), 0.53 (dd, *J* = 4.0, 8.5 Hz, 1 H, CH_2 *c*Pr), 0.85−0.91 (m, 2 H, CH and CH_2 *c*Pr), 1.02 (s, 9 H), 1.86 (dd, *J* = 3.5, 8.5 Hz, 1 H, CH_2N), 2.46 (d, *J* = 8.5 Hz, 1 H, CH_2N), 3.25 (t, *J* = 5.0 Hz, 1 H, CHN), 3.37 (d, *J* = 13.5 Hz, 1 H, CH_2Ph), 3.75 (dd, *J* = 4.5, 10.5 Hz, 1 H, CH_2O), 3.84 (s, 2 H), 3.85 (s, 2 H), 3.92 (dd, *J* = 5.0, 10.5 Hz, 1 H, CH_2O), 4.06 (d, *J* = 13.5 Hz, 1 H, CH_2Ph), 7.18−7.32 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = −5.2 (2 CH_3), 13.9 (CH_2, CH_2 *c*Pr), 18.4 (C), 25.4 (CH, CH *c*Pr), 26.1 (3 CH_3), 53.1 (CH_2, CH_2N), 53.2 (C), 56.8 (2 CH_2), 58.1 (CH_2, CH_2Ph), 62.5 (CH, CHN), 64.8 (CH_2, CH_2O), 126.6 (CH_{ar}), 126.7 (2 CH_{ar}), 127.9 (5 CH_{ar}), 128.0 (2 CH_{ar}), 128.9 (5 CH_{ar}), 131.8 (C_{ar}), 139.1 (C_{ar}), 140.6 (C_{ar}) ppm. IR: $\tilde{\nu}$ = 3027 cm^{-1}, 2927, 1453, 1256, 873, 698. MS (EI): *m*/*z* (%) = 512 (6) [M^+], 421 (40), 381 (100), 367 (39), 316 (25), 276 (19), 91 (44). $C_{33}H_{44}N_2OSi$ (512.81): calcd. C 77.29, H 8.65, N 5.46; found C 77.12, H 8.55, N 5.51.

***exo*-10a:** Colorless solid, R_f (hexane/Et_2O, 10:1) = 0.32, m.p. 54−56 °C, $[\alpha]_D^{20}$= +17.0 (*c* = 0.5, $CHCl_3$). ^1H NMR (250 MHz): δ = 0.06 (s, 3 H), 0.12 (s, 3 H), 0.78−0.84 (m, 3 H), 0.89 (s, 9 H), 1.60−1.66 (m, 1 H), 2.50 (d, *J* = 8.1 Hz, 1 H), 2.81 (t, *J* = 3.4 Hz, 1 H), 2.86 (dd, *J* = 3.4, 8.1 Hz, 1 H), 3.60−3.84 (m, 5 H), 3.90−3.97 (m, 2 H), 7.15−7.37 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = −5.3 (2 CH_3), 14.6 (CH_2), 18.0 (C), 24.3 (CH), 26.1 (3 CH_3), 26.9 (CH_2), 30.2 (CH_2), 51.7 (C), 52.1 (CH_2), 54.6 (CH_2), 61.7 (CH_2), 65.9 (CH), 126.3 (2 CH_{ar}), 126.7 (CH_{ar}), 127.9 (6 CH_{ar}), 128.1 (5 CH_{ar}), 129.5 (CH_{ar}), 138.1 (C_{ar}), 140.9 (2 C_{ar}) ppm. IR: $\tilde{\nu}$ = 3027 cm^{-1}, 2926, 1452, 1255, 1099, 697. MS (EI): *m*/*z* (%) = 512 (3) [M^+], 421 (50), 381 (100), 367 (51), 316 (27), 276 (33), 91 (9). $C_{33}H_{44}N_2OSi$ (512.81): calcd. C 77.29, H 8.65, N 5.46; found C 77.07, H 8.42, N 5.55.

***endo*- and *exo*-(1*R*,2*R*,5*S*)-3-Benzyl-2-(*tert*-butyldimethylsilyloxymethyl)-*N*,*N*-dimethyl-3-azabicyclo[3.1.0]hex-1-ylamine (10b):** Compound **10b** (1.83 g, 89%) was obtained from the *N*,*N*-dialkylpropionamide **6b** (2.15 g, 5.7 mmol), methyltitanium triisopropoxide (2.06 g, 8.6 mmol), and cyclohexylmagnesium bromide (34 mmol, 35 mL of a 0.98 M solution in Et_2O) according to GP3, in an *endo*/*exo* ratio of 2:1. ***endo*-10b:** Colorless oil, R_f (hexane/Et_2O, 2:1) = 0.29, $[\alpha]_D^{20}$ = +13.8 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz): δ = 0.07 (s, 6 H, 2 CH_3), 0.61 (dd, *J* = 4.3, 8.6 Hz, 1 H, CH_2 *c*Pr), 0.91 (s, 9 H, 3 CH_3), 1.04 (t, *J* = 4.0 Hz, 1 H, CH_2 *c*Pr), 1.26−1.33 (m, 1 H, CH *c*Pr), 2.35 (dd, *J* = 4.0, 9.0 Hz, 1 H, CH_2N), 2.47 (s, 6 H, 2 CH_3), 2.71 (d, *J* = 9.0 Hz, 1 H, CH_2N), 3.02 (t, *J* = 4.5 Hz, 1 H, CHN), 3.30 (d, *J* = 13.5 Hz, 1 H, CH_2Ph), 3.70 (dd, *J* = 4.5, 10.5 Hz, 1 H, CH_2O), 3.89 (dd, *J* = 4.5, 10.5 Hz, 1 H, CH_2O), 4.21 (d, *J* = 13.5 Hz, 1 H, CH_2Ph), 7.18−7.28 (m, 5 H) ppm. ^{13}C NMR (75.5 MHz): δ = −5.4 (2 CH_3), 14.7 (CH_2), 18.3 (C), 23.3 (CH), 26.0 (3 CH_3), 42.0 (2 CH_3), 54.2 (CH_3), 54.3 (C), 58.7 (CH_2), 62.5 (CH), 65.3 (CH_2), 128.0 (CH_{ar}), 128.5 (2 CH_{ar}), 128.5 (2 CH_{ar}), 139.8 (C) ppm. IR: $\tilde{\nu}$ = 2927 cm^{-1}, 2855, 1453, 1257, 1100. MS (EI): *m*/*z* (%) = 360 (12) [M^+], 316 (66), 229 (79), 215 (100), 123 (11), 91 (21). HRMS (EI) calcd. for $C_{21}H_{36}N_2OSi$ [M^+] 360.2597, found 360.2597.

***exo*-10b:** Colorless oil, R_f (hexane/Et_2O, 2:1) = 0.77, $[\alpha]_D^{20}$ = +34.9 (c = 1, $CHCl_3$). ^1H NMR (250 MHz): δ = 0.07 (s, 3 H), 0.08 (s, 3 H), 0.66 (dd, J = 3.5, 8.5 Hz, 1 H), 0.85−0.89 (m, 1 H), 0.94 (s, 9 H), 1.57−1.64 (m, 1 H), 2.21 (s, 6 H), 2.61 (d, J = 7.8 Hz, 1 H), 3.01−3.06 (m, 2 H), 3.78 (d, J = 13.9 Hz, 1 H), 3.85−3.88 (m, 2 H), 4.00 (d, J = 13.9 Hz, 1 H), 7.30−7.22 (m, 5 H) ppm. ^{13}C NMR (62.9 MHz): δ = −5.5 (2 CH_3), 14.1 (CH_2), 18.1 (C), 22.9 (CH), 26.9 (3 CH_3), 43.3 (2 CH_3), 52.5 (C), 53.4 (CH_2), 54.4 (CH_2), 61.0 (CH), 64.5 (CH_2), 126.4 (CH_{ar}), 128.0 (3 CH_{ar}), 128.1 (CH_{ar}), 139.6 (C_{ar}) ppm. IR: ṽ = 3027 cm^{-1}, 2925, 1461, 1254, 1042. MS (EI): m/z (%) = 360 (6) [M^+], 316 (25), 229 (53), 215 (100), 123 (26), 110 (29), 91 (21). HRMS (EI) calcd. for $C_{21}H_{36}N_2OSi$ [M^+] 360.2597, found 360.2597.

***N*,N,3-Tribenzyl-3-azabicyclo[3.1.0]hex-1-ylamine (10aa):** The amine **10aa** (32 g, 58%) was obtained from the *N*,*N*-dialkylpropionamide **8aa** (57 g, 0.15 mol), methyltitanium triisopropoxide (54.1 g, 0.225 mol), and cyclohexylmagnesium bromide (0.75 mol, 930 mL of a 0.8 M solution in Et_2O) according to GP3, as a colorless solid, R_f (hexane/Et_2O, 2:1) = 0.56, m.p. 76−79 °C. ^1H NMR (250 MHz): δ = 0.56−0.60 (m, 1 H), 0.97−1.04 (m, 2 H), 2.20 (dd, J = 2.7, 8.5 Hz, 1 H), 2.71 (d, J = 13.1 Hz, 1 H), 2.74 (d, J = 12.7 Hz, 1 H), 2.96 (d, J = 8.2 Hz, 1 H), 3.65 (s, 2 H), 3.75 (d, J = 13.2 Hz, 2 H), 3.85 (d, J = 13.2 Hz, 2 H), 7.23−7.41 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = 16.5 (CH_2), 24.4 (CH), 49.8 (C), 50.8 (CH_2), 54.2 (CH_2), 56.9 (2 CH_2), 59.4 (CH_2), 126.7 (3 CH_{ar}), 127.9 (4 CH_{ar}), 128.1 (2 CH_{ar}), 128.5 (2 CH_{ar}), 128.9 (4 CH_{ar}), 139.2 (C_{ar}), 140.1 (2 C_{ar}) ppm. IR: ṽ = 3022 cm^{-1}, 2929, 2793, 1493, 1454, 1210, 735. MS (EI): m/z (%) = 368 (18) [M^+], 277 (100), 158 (16), 91 (67). $C_{26}H_{28}N_2$ (368.52): calcd. C 84.74, H 7.66, N 7.60; found C 84.70, H 7.51, N 7.50.

***N*,*N*-Dibenzyl-3-methyl-3-azabicyclo[3.1.0.]hex-1-ylamine (10ab):** The amine **10ab** (193 mg, 66%) was obtained from the *N*,*N*-dialkylpropionamide **8ab** (308 mg, 1 mmol), methyltitanium triisopropoxide (351 mg, 1.46 mmol), and cyclohexylmagnesium bromide (5 mmol, 5 mL of a 1 M solution in Et_2O) according to GP3, as a colorless oil, R_f (CH_2Cl_2/MeOH, 15:1, + 1% NH_3) = 0.50. ^1H NMR (250 MHz): δ = 0.53 (dd, J = 4.0, 8.3 Hz, 1 H), 0.88 (ps t, J = 4.3 Hz, 1 H), 1.05−0.98 (m, 1 H), 2.11 (dd, J = 3.5, 8.8 Hz, 1 H), 2.29 (s, 3 H), 2.61 (d, J = 8.4 Hz, 1 H), 2.94 (d, J = 8.4 Hz, 1 H), 2.70 (d, J = 8.8 Hz, 1 H), 3.76 (s, 2 H), 3.78 (s, 2 H), 7.19−7.34 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz): δ = 16.8 (CH_2), 24.8 (CH), 42.0 (CH_3), 50.5 (C), 53.2 (CH_2), 56.7 (CH_2), 56.8 (2 CH_2), 126.8 (2 CH_{ar}), 127.9 (4 CH_{ar}), 128.9 (4 CH_{ar}), 139.9 (2 C_{ar}) ppm. IR: ṽ = 3027 cm^{-1}, 2885, 2776, 1453, 1198, 748. MS (EI): m/z (%) = 292 (13) [M^+], 201 (100), 158 (14), 91 (44). HRMS (EI) calcd. for $C_{20}H_{24}N_2$ [M^+] 292.1939, found 292.1939.

***N*,3-Dibenzyl-*N*-methyl-3-azabicyclo[3.1.0]hex-1-ylamine (10ba):** The amine **10ba** (10.32 g, 56%) was obtained from the *N*,*N*-dialkylpropionamide **8ba** (19.4 g, 63 mmol), methyltitanium triisopropoxide (23 g, 96 mmol), and cyclohexylmagnesium bromide (315 mmol, 308 mL of a 1.02 M solution in Et_2O) according to GP3, as a colorless oil, R_f (hexane/Et_2O, 2:1) = 0.45. ^1H NMR (250 MHz): δ = 0.71 (dd, J = 3.7, 8.5 Hz, 1 H), 1.16 (ps t, J = 3.9 Hz, 1 H), 1.35−1.41 (m, 1 H), 2.30 (s, 3 H), 2.44 (dd, J = 3.5, 8.6 Hz, 1 H), 2.61 (d, J = 8.2 Hz, 1 H), 2.84 (d, J = 8.6 Hz, 1 H), 2.93 (d, J = 8.2 Hz, 1 H), 3.56−3.70 (m, 3 H), 3.80 (d, J = 13.0 Hz, 1 H), 7.21−7.34 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz): δ = 17.0 (CH_2), 24.2 (CH), 39.2 (CH_3), 50.3 (CH_2), 52.1 (C), 54.8 (CH_2), 59.6 (CH_2), 59.8 (CH_2), 126.8 (CH_{ar}), 128.1 (4 CH_{ar}), 128.5 (2 CH_{ar}), 128.8 (3 CH_{ar}), 139.5 (C_{ar}), 139.7 (C_{ar}) ppm. IR: ṽ = 3026 cm^{-1}, 2896, 2787, 1452, 1378, 1027. MS (EI): m/z (%) = 292 (39) [M^+], 201 (40), 173 (46), 158 (43), 91 (100). $C_{20}H_{24}N_2$ (292.43): calcd. C 82.15, H 8.27, N 9.58; found C 81.91, H 8.06, N 9.37.

***N*,*N*-Dibenzyl-(3-*tert*-butoxycarbonyl-3-azabicyclo[3.1.0]hex-1-ylamine (10ac):** The amine **10ac** (262 mg, 43%) was obtained from the *N*,*N*-dialkylpropionamide **8ac** (635 mg, 1.61 mmol), methyltitanium triisopropoxide (581 mg, 2.42 mmol), and cyclohexylmagnesium bromide (8.06 mmol, 10 mL of a 0.8 M solution in Et_2O) according to GP3, as a colorless oil, R_f (hexane/Et_2O, 2:1) = 0.56. ^1H NMR (250 MHz): δ = 0.35 (t, J = 4.7 Hz, 1 H), 0.78−0.83 (m, 1 H), 1.00−1.03 (m, 1 H), 1.45 (s, 9 H, major rotamer), 1.49 (s, 9 H, minor rotamer), 3.08−3.12 (m, 1 H), 3.19 (d, J = 10.6 Hz, 1 H, major), 3.27 (d, J = 10.6 Hz, 1 H, minor), 3.40 (d, J = 10.4 Hz, 1 H, minor), 3.54 (d, J = 10.5 Hz, 1 H, major), 3.58−3.87 (m, 5 H), 7.22−7.32 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz): δ = 18.7 (CH_2 minor), 18.9 (CH_2 major), 24.3 (CH minor), 24.7 (CH major), 28.4 (3 CH_3 major), 28.5 (3 CH_3 minor), 44.6 (CH_2 major), 44.9 (CH_2 minor), 47.6 (CH_2 minor), 48.0 (CH_2 major), 49.3 (CH_2 major), 50.0 (C), 56.8 (CH_2 minor), 56.9 (CH_2 major), 79.3 (C), 127.0 (2 CH_{ar}), 128.1 (4 CH_{ar}), 129.0 (4 CH_{ar}), 139.5 (2 C_{ar}), 155.1 (C=O) ppm. IR: ṽ = 3027 cm^{-1}, 2978, 2862, 1692, 1401, 1116. MS (EI): m/z (%) = 378 (23) [M^+], 287 (38), 231 (100), 187 (23), 91 (59), 57 (62).

***N*,*N*,3-Tribenzyl-3-azabicyclo[4.1.0]hept-1-ylamine (10ad):** The amine **10ad** (1.1 g, 59%) was obtained from the *N*,*N*-dialkylpropionamide **9aa** (1.94 g, 4.87 mmol), methyltitanium triisopropoxide (1.76 g, 7.33 mmol), and cyclohexylmagnesium bromide (19.5 mmol, 19.5 mL of a 1 M solution in Et_2O) according to GP3, as a colorless solid, R_f (hexane/Et_2O, 5:1) = 0.52, m.p. 82−84 °C. ^1H NMR (250 MHz): δ = 0.49 (dd, J = 3.9, 6.3 Hz, 1 H), 0.57 (dd, J = 3.8, 9.8 Hz, 1 H), 1.49−1.60 (m, 1 H), 0.73−0.82 (m, 1 H), 1.67−1.80 (m, 1 H), 1.99−2.06 (m, 1 H), 2.15−2.24 (m, 1 H), 2.62 (d, J = 11.1 Hz, 1 H), 3.04 (d, J = 11.2 Hz, 1 H), 3.51 (d, J = 5.7 Hz, 2 H), 3.74 (s, 4 H), 7.16−7.53 (m, 15 H) ppm. ^{13}C NMR (62.9 MHz): δ = 19.8 (CH), 19.9 (CH_2), 24.3 (CH_2), 42.8 (C), 49.5 (CH_2), 52.9 (CH_2), 55.9 (2 CH_2), 63.0 (CH_2), 126.6 (2 CH_{ar}), 126.7 (CH_{ar}), 127.9 (4 CH_{ar}), 128.2 (2 CH_{ar}), 128.7 (2 CH_{ar}), 129.2 (4 CH_{ar}), 139.3 (C_{ar}), 140.4 (2 C_{ar}) ppm. IR: ṽ = 3027 cm^{-1}, 2912, 2770, 1452, 1124, 753. MS (EI): m/z (%) = 382 (15) [M^+], 291 (22), 210 (24), 166 (12), 91 (100).

Preparation of 3-Azabicyclo[3.1.0]hex-1-ylamine Dihydrochlorides 11. General Procedure 4 (GP4): A solution of **10** (1 mmol) in a mixture of MeOH (15 mL) and HCl (1.2 mL of a 5 M solution in *i*PrOH) was hydrogenated for 3 h (if not otherwise specified) at 20 °C under Pd/C catalysis and ambient pressure. The reaction mixture was filtered through Celite and concentrated under reduced pressure. The product was obtained as a colorless solid and purified by recrystallization from MeOH/Et_2O, 2:1.

3-Azabicyclo[3.1.0]hex-1-ylamine Dihydrochloride (11aa): The dihydrochloride **11aa** (156 mg, 91%) was obtained from the 3-azabicyclo[3.1.0]hexane **10aa** (368 mg, 1 mmol) and HCl (1.2 mL of a 5 M solution in *i*PrOH) by use of 5% Pd/C (184 mg) according to GP4, as a colorless solid, m.p. 200−203 °C. ^1H NMR (250 MHz, CD_3OD): δ = 1.20−1.26 (m, 1 H), 1.41 (t, J = 8.2 Hz, 1 H), 2.15−2.22 (m, 1 H), 3.34 (d, J = 11.7 Hz, 1 H), 3.56−3.68 (m, 3 H) ppm. ^{13}C NMR (62.9 MHz, CD_3OD): δ = 14.3 (CH_2), 22.4 (CH), 40.6 (C), 49.6 (2 CH_2) ppm. IR: ṽ = 3441cm^{-1}, 2882, 2534, 1588, 1452, 1217. MS (CI): m/z (%) = 197 (10) [2M + H^+], 116 (33) (M + NH_4^+], 99 (100) [M + H^+]. $C_5H_{10}N_2$·2 HCl (171.07): calcd. C 35.11, H 7.07, N 16.38; found C 35.20, H 6.97, N 16.67.

3-Methyl-3-azabicyclo[3.1.0]hex-1-ylamine Dihydrochloride (11ab): The dihydrochloride **11ab** (2.6 g, 95%) was obtained from the 3-

azabicyclo[3.1.0]hexane **10ab** (4.3 g, 14.7 mmol) and HCl (45.6 mmol, 7.6 mL of a 6 M solution in *i*PrOH) by use of 5% Pd/C (2.16 g) according to GP4 (6 h reaction time), as a colorless solid, m.p. 227−230 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.37 (ps t, *J* = 8.0 Hz, 1 H, CH$_2$ *c*Pr), 1.68 (dd, *J* = 5.3, 6.8 Hz, 1 H, CH$_2$ *c*Pr), 2.13−2.19 (m, 1 H, CH *c*Pr), 2.76 (s, 3 H), 3.28 (br. s, 2 H), 3.38−3.50 (m, 2 H, 4-H), 3.55 (d, *J* = 11.3 Hz, 1 H, 2-H), 3.73 (d, *J* = 11.3 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 11.7 (CH$_2$, CH$_2$ *c*Pr), 19.4 (CH, CH *c*Pr), 38.6 (C), 39.5 (CH$_3$), 55.7 (2 CH$_2$, CH$_2$N) ppm. IR: $\tilde{\nu}$ = 3437 cm^{-1}, 2868, 2654, 1456, 1158. MS (EI): *m*/*z* (%) = 112 (15) [M$^+$], 82 (9), 69 (100), 44 (15). C$_6$H$_{12}$N$_2$·2 HCl (185.09): calcd. C 38.93, H 7.62, N 15.13; found C 38.88, H 7.51, N 15.18.

***N*-Methyl-3-azabicyclo[3.1.0]hex-1-ylamine Dihydrochloride (11ba):** The dihydrochloride **11ba** (3.91 g, 96%) was obtained from the 3-azabicyclo[3.1.0]hexane **10ba** (6.44 g, 22 mmol) and HCl (0.13 mol, 22 mL of a 6 M solution in *i*PrOH) by use of 5% Pd/C (3.22 g) according to GP4, as a colorless solid, m.p. 192−195 °C. ^{1}H NMR (300 MHz, D$_2$O): δ = 1.15 (dd, *J* = 5.0, 8.5 Hz, 1 H, CH$_2$ *c*Pr), 1.55 (dt, *J* = 2.0, 8.9 Hz, 1 H, CH$_2$ *c*Pr), 2.36 (quint, *J* = 4.5 Hz, 1 H, CH *c*Pr), 2.76 (s, 3 H), 3.41 (d, *J* = 11.5 Hz, 1 H, 4-H), 3.63 (dd, *J* = 4.5, 11.5 Hz, 1 H, 4-H), 3.69 (dd, *J* = 2.0, 11.5 Hz, 1 H, 2-H), 3.78 (d, *J* = 11.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (62.9 MHz, D$_2$O): δ = 14.3 (CH$_2$), 22.8 (CH), 34.4 (CH$_3$), 47.7 (C), 48.2 (CH$_2$), 49.6 (CH$_2$) ppm. IR: $\tilde{\nu}$ = 3423 cm^{-1}, 2924, 2680, 2550, 1580, 1411. MS (EI): *m*/*z* (%) = 112 (4) [M$^+$], 97 (2), 83 (100), 68 (21). C$_6$H$_{12}$N$_2$·2 HCl (185.09): calcd. C 38.93, H 7.62, N 15.13; found C 38.74, H 7.51, N 14.96.

3-Azabicyclo[4.1.0]hept-1-ylamine Dihydrochloride (11ad): The dihydrochloride **11ad** (407 mg, 99%) was obtained from the 3-azabicyclo[4.1.0]heptane **10ad** (850 mg, 2.22 mmol) and HCl (15 mmol, 2.5 mL of a 6 M solution in *i*PrOH) by use of 5% Pd/C (425 mg) according to GP4 (14 h reaction time), as a colorless solid, m.p. 175−177 °C. ^{1}H NMR (300 MHz, CD$_3$OD): δ = 1.12−1.21 (m, 1 H, CH$_2$ *c*Pr), 1.37 (dt, *J* = 2.5, 7.0 Hz, 1 H, CH$_2$ *c*Pr), 1.70−1.78 (m, 1 H, CH *c*Pr), 1.95 (dt, *J* = 1.5, 4.5 Hz, 1 H, 5-H), 2.42 (m, 1 H, 5-H), 2.88 (dq, *J* = 1.5, 4.5 Hz, 1 H, 4-H), 3.18−3.24 (m, 1 H, 4-H), 3.32 (s, 2 H, NH$_2$), 3.57 (dd, *J* = 1.5, 19.0 Hz, 1 H, 2-H), 3.72 (d, *J* = 19.0 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75.5 MHz, CD$_3$OD): δ = 15.2 (CH), 15.9 (CH$_2$), 19.7 (CH$_2$), 30.1 (C), 39.7 (CH$_2$), 45.2 (CH$_2$) ppm. IR: $\tilde{\nu}$ = 3430 cm^{-1}, 2956, 1616, 1471, 1046. MS (CI): *m*/*z* (%) = 112 (11) [M$^+$], 95 (19), 82 (100), 71 (43), 42 (38). HRMS (EI) calcd. for C$_6$H$_{12}$N$_2$ [M$^+$] 112.1000, found 112.1000. C$_6$H$_{12}$N$_2$·2 HCl (185.09): calcd. C 38.93, H 7.62; found C 39.04, H 7.40.

[(Allyl)(*tert*-butoxycarbonyl)amino]acetonitrile (12b): Chloroacetonitrile (1.9 g, 25 mmol) and allylamine (25 mmol, 1.87 mL) were added dropwise at 0 °C to a suspension of K$_2$CO$_3$ (7.0 g, 51 mmol), NaI (7.5 g, 50 mmol), and Et$_3$N (0.1 mol, 14 mL) in anhydrous DMF (50 mL). After the addition was complete, the reaction mixture was stirred for 20 h at ambient temperature. Et$_2$O (30 mL) and Celite (1 g) were added, and the solid was filtered off. Ice-cold water (30 mL) was added to the filtrate, and the aqueous layer was separated, cooled to 0 °C, saturated with NaCl, and extracted several times with EtOAc (20 mL each). The combined organic phases were dried, and removal of the solvent gave (*N*-allylamino)acetonitrile as a brown oil pure enough to be used without further purification. To a solution of this in MeOH (50 mL) were added Et$_3$N (36 mmol, 5 mL) and a solution of Boc$_2$O (6.0 g, 27.5 mmol) in MeOH (50 mL) at 0 °C. The resulting mixture was stirred for 2 h at 60 °C and the solvent was removed. Water (30 mL) was added, and the aqueous layer was extracted several times with CH$_2$Cl$_2$. The combined organic phases were washed with brine (30 mL), dried, and concentrated under reduced pressure. Column chromatography of the residue gave **12b** (1.7 g, 35%) as a colorless oil, R_f (Et$_2$O/hexane, 2:1) = 0.33. ^{1}H NMR (250 MHz): δ = 1.40 (s, 9 H), 3.88−4.19 (m, 4 H), 5.23−5.29 (m, 2 H), 6.68−6.85 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz): δ = 28.1 (3 CH$_3$), 33.5 (CH$_2$), 48.7 (CH$_2$), 81.8 (C), 115.9 (CH$_2$, CH=*C*H$_2$), 119.2 (C≡N), 132.1 (CH, *C*H=CH$_2$), 158.5 (C=O) ppm. IR: $\tilde{\nu}$ = 2980 cm^{-1}, 2249, 1699, 1401, 1250, 1168. MS (EI): *m*/*z* (%) = 196 (2) [M$^+$], 140 (25), 123 (12), 57 (100), 41 (46). HRMS (EI) calcd. for C$_{10}$H$_{16}$N$_2$O$_2$ [M$^+$] 196.1212, found 196.1212.

Preparation of 3-Azabicyclo[3.1.0]hex-1-ylamines 14a and 11ac. General Procedure 5 (GP5): Cyclohexylmagnesium bromide (4 mmol, 4 mL of a 1 M solution in Et$_2$O) was added dropwise at ambient temperature to a well stirred solution of allylaminoacetonitrile **12** (2 mmol) and methyltitanium triisopropoxide (529 mg, 2.2 mmol) in anhydrous THF (40 mL). After the addition was complete, the mixture was stirred for 2 h at 20 °C, and LiI (535 mg, 4 mmol) was then added in one portion. The mixture was stirred for an additional 3 h at 70 °C, cooled to 0 °C, quenched with 10% aq. NaOH solution (5 mL), and filtered through Celite. The aqueous phase was extracted with Et$_2$O (3 × 20 mL), and the combined organic phases were washed with brine, dried, and concentrated under reduced pressure. The residue was purified by column chromatography.

3-Benzyl-3-azabicyclo[3.1.0]hex-1-ylamine (14a): The amine **14a** (181 mg, 48%) was obtained from [(allyl)(benzyl)amino]acetonitrile (**12a**, 372 mg, 2 mmol) according to GP5, as a colorless oil, R_f (CH$_2$Cl$_2$/MeOH, 8:1, + 1% NH$_3$) = 0.25. ^{1}H NMR (250 MHz): δ = 0.64 (m, 1 H), 1.09 (ps t, *J* = 4.2 Hz, 1 H), 1.16−1.21 (m, 1 H), 2.28 (br. s, 2 H, NH$_2$), 2.32 (d, *J* = 8.3 Hz, 1 H), 2.49 (dd, *J* = 3.6, 8.6 Hz, 1 H), 2.83 (d, *J* = 8.6 Hz, 1 H), 3.00 (d, *J* = 8.3 Hz, 1 H), 3.58 (s, 2 H), 7.20−7.28 (m, 5 H) ppm. ^{13}C NMR (62.9 MHz): δ = 15.4 (CH$_2$), 23.7 (CH), 40.7 (C), 54.7 (CH$_2$), 59.1 (CH$_2$), 61.2 (CH$_2$), 126.8 (CH$_{ar}$), 128.1 (2 CH$_{ar}$), 128.6 (2 CH$_{ar}$), 139.0 (C$_{ar}$) ppm. IR: $\tilde{\nu}$ = 3278 cm^{-1}, 3061, 2925, 2787, 1452, 1156. MS (EI): *m*/*z* (%) = 188 (24) [M$^+$], 120 (32), 97 (17), 91 (100), 69 (86). HRMS (EI) calcd. for C$_{12}$H$_{16}$N$_2$ [M$^+$] 188.1313, found 188.1302.

3-*tert*-Butoxycarbonyl-3-azabicyclo[3.1.0]hex-1-ylamine (11ac): The amine **11ac** (162 mg, 41%) was obtained from [(allyl)(*tert*-butoxycarbonyl)amino]acetonitrile (**12b**) (393 mg, 2 mmol) according to GP5, as a colorless solid, R_f (CH$_2$Cl$_2$/MeOH, 8:1 + 1% NH$_3$) = 0.33. Alternatively, the compound **11ac** (100 mg, 76%) was prepared from the 3-azabicyclo[3.1.0]hexane **10ac** (250 mg, 0.66 mmol) by use of 5% Pd/C (125 mg) according to GP4. Colorless solid, m.p. 57−59 °C. ^{1}H NMR (250 MHz): δ = 0.46 (t, *J* = 4.7 Hz, 1 H), 0.88−0.94 (m, 1 H), 1.32−1.35 (m, 1 H), 1.40 (s, 9 H), 1.62 (br. s, 2 H, NH$_2$), 3.17−3.21 (m, 1 H), 3.43 (m, 2 H), 3.63−3.76 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz): δ = 17.4 (CH$_2$), 23.4 (CH, minor rotamer), 23.9 (CH, major rotamer), 28.4 (3 CH$_3$), 40.8 (C, major), 41.2 (C, minor), 48.1 (CH$_2$, major), 48.5 (CH$_2$, minor), 54.0 (CH$_2$, minor), 54.4 (CH$_2$, major), 79.2 (C, minor), 79.4 (C, major), 154.6 (C=O) ppm. IR: $\tilde{\nu}$ = 3505 cm^{-1}, 2973, 2881, 1684, 1411, 1172. MS (EI): *m*/*z* (%) = 198 (3) [M$^+$], 142 (30), 125 (14), 69 (100), 57 (48). HRMS (EI) calcd. for C$_{10}$H$_{18}$N$_2$O$_2$ [M$^+$] 198.1368, found 198.1368.

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[13] In our hands, cyclohexylmagnesium bromide consistently gave better yields and purer products than cyclopentylmagnesium halides (bromide and chloride), cf. ref.[4b]. In addition, cyclohexyl halides are significantly less expensive than cyclopentyl halides, a relevant point when the Grignard reagent is prepared on a large scale.

[14] Crystals of the compounds **10aa, 10ad**, and **14a**·0.5 HCl were grown by slow evaporation of their solutions in Et_2O/hexane mixtures. The X-ray single-crystal data were collected on Bruker CCD SMART 1 K (**10aa** and **10ad**) and SMART 6000 (**14a**·0.5 HCl) diffractometers with graphite-monochromated Mo-K_α radiation. The structure solutions and refinements on *F*2 were performed with the Bruker SHELXTL program suite. The hydrogen atoms in structures **10aa** and **10ad** were located by difference Fourier synthesis and refined isotropically. The two independent molecules of **14a** in the crystal are partially disordered. Disordered atoms were refined with fixed site occupation factors of 0.8 and 0.2, the atoms of minor components were refined isotropically. The hydrogen atoms in **14a** were placed in ideal positions and refined in "riding mode" with the 1.2-fold isotropic displacement parameter of the corresponding C atom. **10aa**: $C_{26}H_{28}N_2$, crystal size $0.42 \times 0.30 \times 0.22$ mm^3, triclinic, $a = 5.9783(2)$, $b = 10.6105(4)$, $c = 16.7535(7)$ Å, $\alpha = 84.071(2)$, $\beta = 87.981(2)$, $\gamma = 76.457(2)°$, $V = 1027.58(7)$ Å^3, $Z = 2$, space group $P\bar{1}$, $T = 100.0(2)$ K, $\rho = 1.191$ g cm^{-3}, intensities measured: 12029 ($2\theta_{max} = 60.8°$), independent: 5541 ($R_{int} = 0.0254$), 365 parameters refined, $R_1 = 0.0409$ for 4890 reflections with $I = 4\sigma(I)$, wR_2 (all data) = 0.1177, Goof = 0.993, maximum and minimum residual electron density 0.362 and −0.183 e Å^{-3}. **10ad**: $C_{27}H_{30}N_2$, crystal size $0.42 \times 0.28 \times 0.06$ mm^3, triclinic, $a = 6.0829(4)$, $b = 9.8909(6)$, $c = 18.028(1)$ Å, $\alpha = 96.586(2)$, $\beta = 90.077(2)$, $\gamma = 91.642(2)°$, $V = 1077.0(1)$ Å^3, $Z = 2$, space group $P\bar{1}$, $T = 100.0(2)$ K, $\rho = 1.180$ g cm^{-3}, intensities measured: 12494 ($2\theta_{max} = 59.0°$), independent: 5730 ($R_{int} = 0.0334$), 382 parameters refined, $R_1 = 0.0475$ for 4305 reflections with $I = 4\sigma(I)$, wR_2 (all data) = 0.1271, Goof = 1.021, maximum and minimum residual electron density 0.357 and −0.193 e Å^{-3}. **14a**·0.5 HCl: $C_{12}H_{16}N_2$·0.5HCl, crystal size $0.55 \times 0.54 \times 0.04$ mm^3, orthorhombic, $a = 10.2447(3)$, $b = 39.482(1)$, $c = 11.5005(3)$ Å, $V = 4651.7(2)$ Å^3, $Z = 16$, space group *Aba2*, $T = 120(2)$ K, $\rho = 1.179$ g cm^{-3}, intensities measured: 15492 ($2\theta_{max} = 55.0°$), independent: 5318 ($R_{int} = 0.0653$), 298 parameters refined, $R_1 = 0.0421$ for 3770 reflections with $I = 4\sigma(I)$, wR_2 (all data) = 0.0962, Goof = 0.957, maximum and minimum residual electron density 0.240 and −0.231 e Å^{-3}. CCDC-178102 (**10aa**), CCDC-178103 (**10ad**) and CCDC-178104 (**14a**·0.5 HCl) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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