Synthesis of Hexahydro-1*H*-benzo[*c*]chromen-1-amines via the Intramolecular Ring-Opening Reactions of Aziridines by π-Nucleophiles

Aravinda B. Pulipaka, Stephen C. Bergmeier*

Department of Chemistry & Biochemistry, Clippinger Laboratory, Ohio University, Athens, OH 45701, USA
E-mail: bergmeis@ohio.edu

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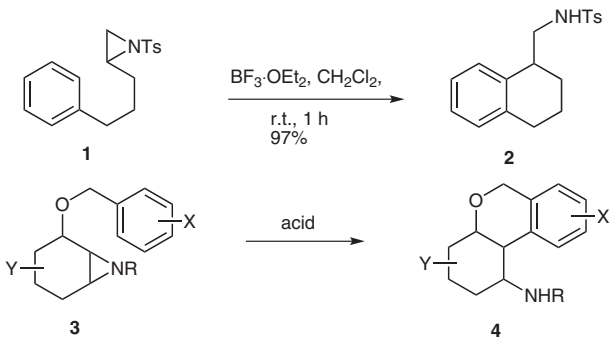
Abstract: The intramolecular cyclization of aziridines with π-nucleophiles can be a useful route to a number of heterocyclic and carbocyclic systems. This methodology has been applied to the synthesis of hexahydro-1*H*-benzo[*c*]chromen-1-amines, the basic skeleton of many *amaryllidaceae* alkaloids. The success of the aziridine cyclization is largely dependent on the N-substitution of aziridine, with activated aziridines not undergoing the cyclization reaction. Only *N*-H-, *N*-alkyl- and *N*-arylaziridines underwent the cyclization reaction. The ring opening of an unactivated aziridines with a π-nucleophile is one of the first examples of such a reaction.

Key words: heterocycles, electrophilic additions, ring opening, ethers, amines

Aziridines are versatile building blocks for the synthesis of biologically active natural and synthetic compounds. These are well-known electrophiles and capable of reacting with a variety of nucleophiles including heteroatom nucleophiles (amines, azides, alcohols, etc.) and carbon nucleophiles (aryl groups, enolates, etc.).[1,2]

We, and others have reported on the use of π-nucleophiles such as allylsilanes,[3] olefins[4] and aromatic rings[5] to open aziridine rings. Recently we reported on the intramolecular cyclization of aziridines with simple π-nucleophiles such as aromatic rings, and substituted olefins (Scheme 1).[4d]

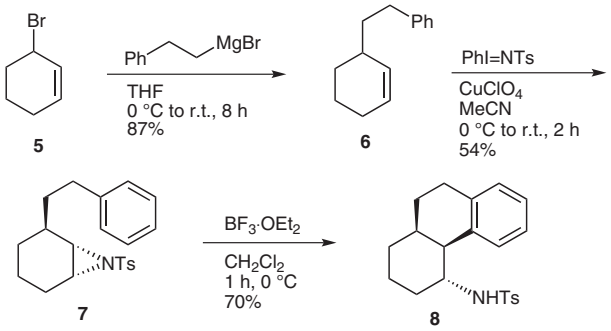
The reaction is believed to proceed via an initial acid-catalyzed nucleophilic attack of the π-bond on the more substituted carbon of the aziridine. All of the reported examples of such an aziridine ring opening via a π-nucleophile have used an electron-stabilizing group on the nitrogen of the aziridine ring.



Scheme 1 Previously reported example of an aziridine/π-nucleophile cyclization and proposed possible oxygen-linked cyclization

We were interested in using this methodology for the synthesis of more complex polycyclic molecules such as the *amaryllidaceae* alkaloid homolycorane.[6] Such structures could come from an acid-catalyzed cyclization of an aziridine such as **3**. This reaction could also provide a route for the synthesis of pancratistatin and related alkaloids.[7] For example, Keck has reported on the synthesis of pancratistatin via benzochromenes such as **4**.[8]

Since there were no reports of a fused-ring aziridine/π-nucleophile cyclization, we first prepared and attempted the cyclization of aziridine **7** (Scheme 2). Treatment of 3-bromocyclohexene with phenethylmagnesium bromide provided **6** in excellent yield.[9] The olefin was then aziridinated in 54% yield using PhI=NTs and $CuClO_4$.[10] Cyclization of **7** was then carried out using standard conditions and was complete in less than one hour to provide the octahydrophenanthrene **8** in 70% yield.



Scheme 2 Intramolecular cyclization of a carbon-linked fused-ring aziridine

Confident that the use of a fused-ring aziridine was not detrimental to the cyclization we proceeded to prepare the appropriate ether linked aziridine **11** (Scheme 3). The use of PhI=NTs as an aziridination reagent provided very low yields of the desired aziridine **11**. Significant amounts of the debenzylated alcohol were also obtained. The chloramine-T with NBS system provided moderately better yields of **11**. The use of our standard cyclization conditions (100 mol% $BF_3{\cdot}OEt_2$, 0 °C, CH_2Cl_2)[4d] with **11** gave only the starting material. Increasing the temperature and increasing the amount of $BF_3{\cdot}OEt_2$ only led to the formation of **12** and **13**, presumably via the reaction of ad-

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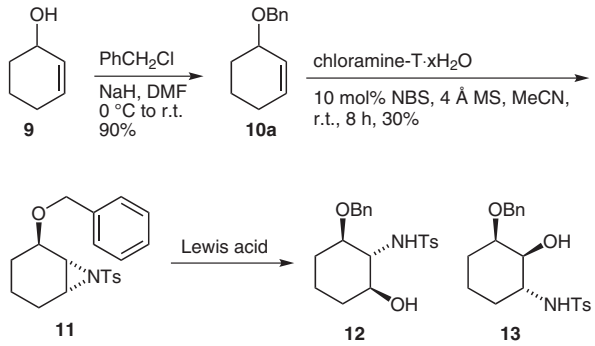
ventitious water with the aziridine ring. None of the expected product **4** was isolated. An examination of other acids [e.g., $B(C_6F_5)_3$, silica gel], heating, or the presence of electron-donating groups on the benzene ring (e.g., OMe) did not provide any of the required product.



Scheme 3 Synthesis and attempted cyclization of an oxygen-linked *N*-tosylaziridine

Given the facile nature of the carbon-linked aziridine (Scheme 2), we were puzzled as to why a simple modification of the substrate inhibited the cyclization reaction. We wished to find out where the Lewis acid was complexed in both the all-carbon system as well as the ether-linked system. This complexation should be measurable via NMR spectroscopy.[11] Tosylaziridine **14** was chosen as our test aziridine as it had no π-nucleophile that could open the aziridine under Lewis acid catalysis. Aziridine **14** was readily prepared via tosylation of the commercially available 2-methylaziridine and treated with 100 mol% of $BF_3{\cdot}OEt_2$ in $CDCl_3$. Although the ^1H NMR spectrum showed some Lewis acid induced changes, there was sufficient overlap so as to make any type of quantification difficult. We thus examined the ^{13}C NMR spectrum and were able to cleanly determine the Δδ (relative to the uncomplexed aziridine) as shown in Figure 1.[12]

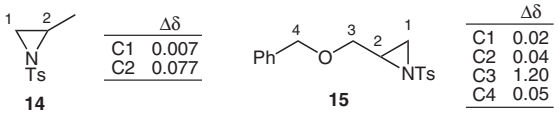
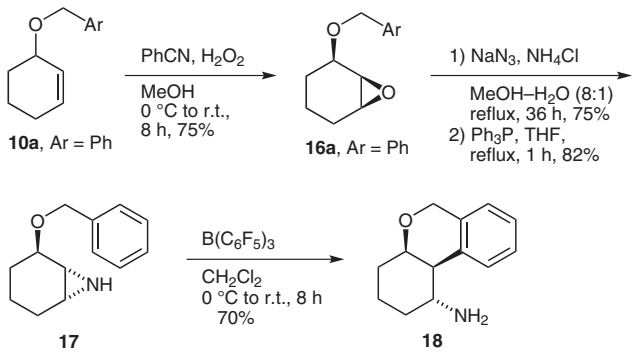


Figure 1 Δδ values of aziridines in CH_2Cl_2 with 100 mol% $BF_3{\cdot}OEt_2$

Based upon these results, we next examined the simple aziridine **15** containing an ether linkage.[11a] This compound was readily prepared via the aziridination of allyl benzyl ether with Chloramine-T and NBS.[13] Again a solution of **15** was treated with 100 mol% of $BF_3{\cdot}OEt_2$ and the ^{13}C NMR spectrum was recorded. This experiment showed clear differences when compared to the all-carbon aziridine **14**. The C2 showed a negligible Δδ and C3, adjacent to the ether oxygen showed a large Δδ of >1 ppm. Clearly the primary site of Lewis acid complexation in this system is the ether oxygen, and not the NTs of the aziridine.

Clearly the nitrogen of the aziridine must be made more basic for the reaction to proceed as planned. As the use of other electron-stabilizing groups on the nitrogen was not expected to significantly change the basicity of the aziridine, we decided to examine an unsubstituted aziridine. While the nucleophilic ring-opening reactions of aziridines which lack an electron-stabilizing group are well known,[14] there have been no reports on the use of weaker π-nucleophiles reacting with such a nonactivated aziridine.

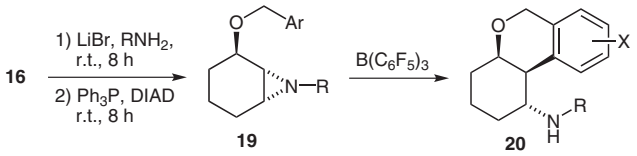
The requisite aziridine is readily prepared from alkene **10a** (Scheme 4).[15] Epoxidation of **10a** with perbenzimidic acid, generated in situ from PhCN and H_2O_2, provided *cis*-epoxide **16a** in 75% yield after purification.[16] Reaction of **16a** with sodium azide provides a mixture of regioisomeric azido alcohols. This mixture was then directly cyclized to unsubstituted aziridine **17**. Treatment of **17** with 100 mol% of $B(C_6F_5)_3$ cleanly provided cyclization product **18** in 70% isolated yield.



Scheme 4 First successful ring opening of an unactivated aziridine with a π-nucleophile

This ring-opening of an unactivated aziridine with a π-nucleophile is one of the first examples of such a reaction. This reaction enhances the utility as no deprotection of the resulting amine is required for further transformations.

Given the ease of the cyclization with the unsubstituted aziridine, we wished to examine the scope of this cyclization reaction. To this end, a series of *N*-alkyl- and *O*-arylmethyl-substituted aziridines were prepared by the general route shown in Scheme 5. The results of these reactions are summarized in Table 1.



Scheme 5 General method for the synthesis of 1-aminochromenes

Table 1 Hexahydro-1*H*-benzo[*c*]chromen-1-amines **20**

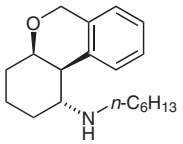
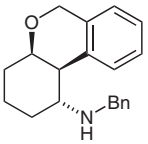
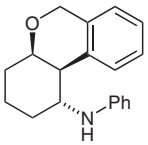
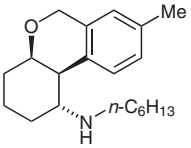
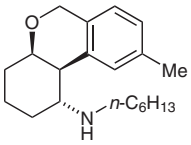
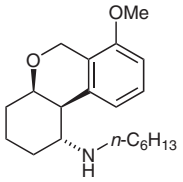
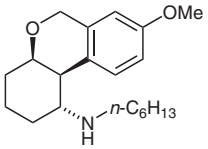
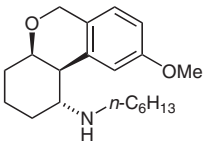
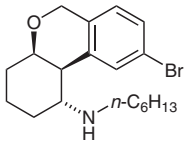
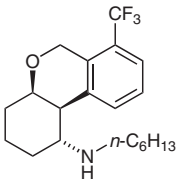
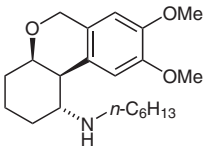
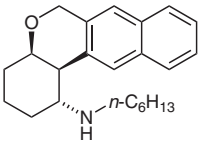
Entry	$ArCH_2X$	Alkene **10**, yield (%)	Epoxide **16**, yield (%)	RNH_2	Aziridine **19**, yield (%)	Product		Yield (%)
1	$PhCH_2Cl$	**10a** 90	**16a** 75	*n*-C_6H_{13}	**19a** 49		**20a**	80
2	$PhCH_2Cl$	**10a** 90	**16a** 75	$PhCH_2$	**19b** 44		**20b**	90
3	$PhCH_2Cl$	**10a** 90	**16a** 75	Ph	**19c** 51		**20c**	70
4	3-$MeC_6H_4CH_2Cl$	**10b** 65	**16b** 84	*n*-C_6H_{13}	**19d** 55		**20d**	72
5	4-$MeC_6H_4CH_2Cl$	**10c** 92	**16c** 81	*n*-C_6H_{13}	**19e** 65		**20e**	60
6	2-$MeOC_6H_4CH_2Cl$	**10d** 89	**16d** 84	*n*-C_6H_{13}	**19f** 61		**20f**	64
7	3-$MeOC_6H_4CH_2Cl$	**10e** 84	**16e** 72	*n*-C_6H_{13}	**19g** 63		**20g**	75
8	4-$MeOC_6H_4CH_2Cl$	**10f** 88	**16f** 75	*n*-C_6H_{13}	**19h** 57		**20h**	25
9	4-$BrC_6H_4CH_2Br$	**10g** 64	**16g** 48	*n*-C_6H_{13}	**19i** 53		**20i**	45

Table 1 Hexahydro-1*H*-benzo[*c*]chromen-1-amines **20** (continued)

Entry	$ArCH_2X$	Alkene **10**, yield (%)	Epoxide **16**, yield (%)	RNH_2	Aziridine **19**, yield (%)	Product		Yield (%)
10	2-$CF_3C_6H_4CH_2Cl$	**10h** 81	**16h** 37	*n*-C_6H_{13}	**19j** 25		**20j**	0
11	3,4-$(MeO)_2C_6H_3CH_2Br$	**10i** 60	**16i** 61	*n*-C_6H_{13}	**19k** 66		**20k**	40
12	$C_{10}H_7CH_2Br$	**10j** 80	**16j** 58	*n*-C_6H_{13}	**19l** 66		**20l**	46

Cyclohexenol (**9**) was alkylated with a series of substituted benzyl halides to provide ethers **10b–j**. As before (Scheme 4) the olefin was epoxidized with perbenzimidic acid to generate the *cis*-epoxides **16b–j**. The epoxides were then opened using a primary amine and LiBr. This provided a mixture of regioisomeric amino alcohols. This mixture was directly cyclized to form aziridines **19a–l**.

We first examined the cyclizations of aziridines **19a–c** carrying a small substituent on the aziridine nitrogen. The *n*-hexylaziridine **19a** smoothly cyclized to chromene **20a** in 80% yield. The benzylaziridine provided product **20b** in an excellent 90% isolated yield. We were concerned that two possible π-nucleophiles were present in this molecule: one, the expected nucleophile of the benzyl ether, and the other, the benzyl on the aziridine ring. Only the benzyl ether nucleophile opened the aziridine. This is likely due to the unfavorable 5-*endo-tet* transition state that would be required for the *N*-benzyl group to open the aziridine ring. We next converted aziridine **19c** into **20c** in excellent yield. We were pleased to note that the reduced basicity of the *N*-phenylaziridine relative to the *N*-H- or *N*-alkylaziridines was not detrimental to the cyclization.

Satisfied that the range of substitution on the aziridine nitrogen was acceptably broad, we turned our attention to substitution on the aromatic ring. We chose to use only the *n*-hexyl substitution on the aziridine ring due to the lack of interfering peaks in the aromatic region of the ^1H NMR spectra. We then examined a variety of substitution patterns and electron-donating and electron-withdrawing substitution on the aromatic ring.

Cyclization of a symmetrical 4-substituted aromatic ring was relatively uneventful with the 4-Me and 4-OMe (Table 1, entries 5 and 8) providing the expected products **20e** and **20h**. We were disappointed to see that the 4-OMe provided the product **20h** in only 25% yield. A problem with this system was the loss of the 4-methoxybenzyl group under the acidic reaction conditions. We were quite pleased to note that the 4-bromobenzyl (entry 9) provided the expected product in a low (but acceptable) yield of 45%. The 2-OMe benzyl substrate **19f**, also provided the expected product **20f** in 64% yield.

A key question in these cyclizations was the regioselectivity of the cyclization reaction when an unsymmetrical substrate was used. In a simpler cyclization system, (i.e., compound **1** with a 3-OMe group on the aromatic ring, Scheme 1) we observed a roughly 3:1 mixture of regioisomeric cyclization products.[4d]

In this study, we examined three compounds with 3-substituted benzyl ethers. Two possible regioisomeric products can be formed (para or ortho to the 3-substituent). We were quite pleased to observe a single product being formed in all cases (entries 4, 7 and 11). The regiochemistries of these products were determined by ^1H NMR spectra. These compounds show a clear singlet in the aromatic region, which is possible only for regioisomers **20d**, **20g**, and **20k**. If the other regioisomer were to be formed, none of the aromatic protons would be singlets. In addition to the methyl- and methoxy-substituted aromatic ring, a polycyclic aromatic (2-naphthalene) was examined. Again, a single regioisomer was isolated. Although the yields for these cyclizations were not as high compared to others, none of the regioisomeric products were found. Only starting material and decomposition products were observed. Clearly, the greater steric bulk of the fused-ring aziridine has improved the regioselectivity of the cyclization reaction.

Most of the aromatic substituents examined have been electron-donating groups. The CF_3 substituted benzyl substrate **19j**, provided no cyclized product. Even after extended reaction times (>24 h), heating (reflux), or the

addition of more acid (300 mol%) only starting material and some decomposition products were isolated. This is in contrast to our previous results using a simpler carbon-linked system in which the CF_3 substituted arene provided cyclized product in good yield.[4d]

In conclusion, we have demonstrated the first example of an unactivated aziridine/π-nucleophile cyclization. The scope of the reaction in terms of the N-substitution appears very good, with *N*-H-, *N*-alkyl- and *N*-arylaziridines undergoing the reaction. The allowed substitution on the arene is reasonably broad with a variety of electron-donating groups. As might be expected for an electrophilic aromatic substitution reaction, substitution of the aromatic ring with a strongly electron-withdrawing group is not tolerated. The regioselectivity of the cyclization when using an unsymmetrical arene is excellent with a single regioisomer being isolated. This method should be an excellent route to *amaryllidaceae* alkaloids and other bioactive nitrogen-containing molecules.

All chemicals were purchased from the usual commercial suppliers and used without further purification, unless otherwise noted. THF and CH_2Cl_2 were dried using a column purification system. IR spectra were obtained neat. R_f values were obtained by TLC on aluminum backed, silica coated, TLC plates containing a fluorescent (254 nm) indicator. Spots were identified via UV or staining with an ethanolic solution of ninhydrin, followed by heating. Compounds were purified by either an automated flash purification system utilizing silica gel or by flash chromatography using 32-63D 60Å silica gel according to the method of Still.[17] NMR spectra were obtained at 300 (^{1}H) or 75 MHz (^{13}C).

2-(Benzyloxy)-7-tosyl-7-azabicyclo[4.1.0]heptane (11)
To a solution of **10a** (0.2 g, 1.06 mmol), NBS (38 mg, 0.213 mmol), and chloramine-T (0.24 g, 1.06 mmol) in anhyd MeCN (3 mL) was added molecular sieves (4 Å, 200 mg) and the mixture was stirred at r.t. for 8 h. The mixture was filtered, concentrated, and chromatographed (EtOAc–hexanes, 8:92) to provide 114 mg (30%) of aziridine **11** as a colorless oil; R_f = 0.5 (EtOAc–hexanes, 20:80).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.0 Hz, 2 H), 7.20 (m, 7 H), 4.50 (d, *J* = 11.5 Hz, 1 H), 4.39 (d, *J* = 11.5 Hz, 1 H), 3.52 (m, 1 H), 3.06 (m, 1 H), 2.98 (d, *J* = 6.5 Hz, 1 H), 2.43 (s, 3 H), 1.8 (m, 1 H), 1.68 (m, 2 H), 1.42 (m, 1 H), 1.17 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5, 144.3, 142, 140.7, 138.8, 128.3, 127.6, 127.4, 72.6, 69.1, 42, 40.4, 26.6, 22.6, 21.6, 15.1.

1-[2-(Cyclohex-2-enyl)ethyl]benzene (6)
To a suspension of Mg turnings (0.12 g, 4.96 mmol) in anhyd THF (5 mL) was slowly added a solution of phenethyl bromide (0.861 g, 4.65 mmol) in THF (5 mL). The mixture was stirred at r.t. for 30 min and then added dropwise to a solution of **5** (0.5 g, 3.1 mmol) in THF (1 mL) and the mixture stirred for 8 h. The mixture was quenched with sat. aq NH_4Cl (5 mL) and extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), concentrated, and chromatographed (hexanes) to provide 0.5 g (87%) of **6** as colorless oil which matched the reported spectra.[3]

2-Phenethyl-7-tosyl-7-azabicyclo[4.1.0]heptane (7)
PhINTs (1.2 g, 3.2 mmol) was added slowly to a 0 °C solution of $CuClO_4$ (35 mg, 0.32 mmol) and olefin **6** (0.4 g, 2.15 mmol) in MeCN (10 mL), and the mixture was stirred for 2 h at 0 °C and 45 min at r.t. The mixture was filtered through a plug of silica gel, concentrated, and chromatographed (EtOAc–hexanes, 10:90) to provide 0.41 g (54%) of **7** as a colorless oil; R_f = 0.5 (EtOAc–hexanes, 15:85).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.6 (m, 4 H), 7.3 (m, 3 H), 7.0 (m, 2 H), 3.0 (m, 1 H), 2.75 (m, 1 H), 2.4 (m, 4 H), 2.3 (m, 2 H), 2.0 (m, 2 H), 1.85 (m, 6 H), 1.3 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 137.7, 136.5, 129.4, 128.5, 128.2, 127, 42, 41.7, 33.7, 33.2, 33, 32.6, 28.5, 24.7, 20.5.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{25}NO_2S$ + Na $[M + Na]^+$: 375.1504; found: 378.1501.

1,2,3,4,4a,9,10,10a-Octahydro-*N*-tosylphenanthren-4-amine (8)
$BF_3{\cdot}OEt_2$ (18 μL, 0.140 mmol) was added to a 0 °C solution of aziridine **7** (50 mg, 0.14 mmol) in CH_2Cl_2 (1 mL), and the mixture was warmed to r.t. After 1 h, the mixture was diluted with CH_2Cl_2 (5 mL) and washed with sat. aq $NaHCO_3$ (5 mL), brine (5 mL), and H_2O (5 mL), concentrated, and chromatographed (EtOAc–hexanes, 15:85) to provide 35 mg (70%) of **8** as a colorless oil; R_f = 0.2 (EtOAc–hexanes, 15:85).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4 (d, *J* = 7.7 Hz, 2 H), 7.3 (m, 1 H), 7.1 (d, *J* = 7.4 Hz, 1 H), 7.0 (d, *J* = 8.3 Hz, 2 H), 7.05 (d, *J* = 7.6 Hz, 2 H), 4.6 (d, *J* = 11.5 Hz, 1 H), 3.4 (m, 1 H), 2.7 (t, *J* = 9.5 Hz, 2 H), 2.55 (m, 1 H), 2.5 (s, 3 H), 2.2 (m, 1 H), 2.0 (m, 1 H), 1.95 (m 1 H), 1.52 (m, 4 H), 1.4 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.6, 137.1, 136.5, 129.3, 128.2, 127.1, 126.6, 126.5, 125.3, 53.3, 45.7, 32.7, 29.2, 27.1, 24.0, 20.2.

HRMS-(ESI): *m*/*z* calcd for $C_{21}H_{25}NO_2S$ $[M + H]^+$: 356.1684; found: 356.1690.

Arylmethyl Cyclohexenyl Ethers 10; General Procedure
Cyclohexenol (**9**; 5.08 mmol, 100 mol%) in DMF (10 mL, 0.5 M) was added to suspension of NaH (15.3 mmol, 300 mol%, previously washed with hexanes (20 mL)] in DMF (20 mL) and the mixture was stirred at 0 °C for 10 min. The desired benzyl halide (5.08 mmol, 100 mol%) in DMF (10 mL) was slowly added to the alkoxide solution. The mixture was warmed to r.t. and stirred 16 h. The mixture was quenched by the addition H_2O (100 mL) and the aqueous layer extracted with Et_2O (3 × 50 mL). The organic layers were combined, washed with brine (50 mL), dried ($MgSO_4$), concentrated, and chromatographed (EtOAc in hexanes) to provide the desired ether.

1-[(Cyclohex-2-enyloxy)methyl]benzene (10a)
Benzyl chloride provided 0.86 g (90%) of **10a**; R_f = 0.8 (EtOAc–hexanes, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8 (m, 5 H), 5.94 (m, 2 H), 4.71 (dd, *J* = 13.3, 12.0 Hz, 2 H), 4.0 (m, 1 H), 2.2 (m, 5 H), 1.7 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2, 130.8, 128.4, 128.3, 127.9, 127.8, 127.6, 127.3, 72.3, 70.0, 28.5, 25.3, 19.3.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O$ $[M^+]$: 188.1201; found: 188.1203.

1-[(Cyclohex-2-enyloxy)methyl]-3-methylbenzene (10b)
3-Methylbenzyl chloride provided 0.67 g (65%) of **10b**; R_f = 0.8 (EtOAc–hexanes, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (m, 4 H), 5.8 (m, 2 H), 4.57 (dd, *J* = 11.9, 8.2 Hz, 2 H), 4.02 (m, 1 H), 2.4 (s, 3 H), 1.8 (m, 5 H), 1.62 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.0, 137.9, 130.9, 128.5, 128.4, 128.2, 127.9, 124.8, 72.3, 70.1, 28.5, 25.3, 21.5, 19.4.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O$ + Na $[M + Na]^+$: 225.1255; found: 225.1249.

1-[(Cyclohex-2-enyloxy)methyl]-4-methylbenzene (10c)
4-Methylbenzyl chloride provided 0.95 g (92%) of **10c**; R_f = 0.3 (EtOAc–hexanes, 4:96).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 7.9 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 2 H), 5.84 (m, 2 H), 4.52 (dd, *J* = 11.9, 7.4 Hz, 2 H), 3.99 (m, 1 H), 2.4 (s, 3 H), 1.8 (m, 5 H), 1.62, (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.8, 134.8, 129.6, 127.8, 126.7, 126.5, 70.7, 68.6, 27.2, 24.0, 19.9, 18.1.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O$ + Na [M + Na]$^+$: 225.1255; found: 225.1249.

1-[(Cyclohex-2-enyloxy)methyl]-2-methoxybenzene (10d)
2-Methoxybenzyl chloride provided 0.99 g (89%) of **10d**; R_f = 0.3 (EtOAc–hexanes, 4:96).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.4 Hz, 1 H), 7.28 (t, *J* = 8.0, 7.4 Hz, 1 H), 7.0 (t, *J* = 7.4 Hz, 1 H), 6.89 (d, *J* = 8.2 Hz, 1 H), 5.9 (m, 2 H), 4.65 (dd, *J* = 12.8, 6.5 Hz, 2 H), 4.06 (m, 1 H), 3.87 (s, 3 H), 1.84 (m, 5 H), 1.62 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.7, 128.7, 128.5, 128.3, 128.2, 120.5, 110.1, 72.6, 67.7, 64.8, 55.3, 28.5, 25.4, 19.4.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_2$ + Na [M + Na]$^+$: 241.1204; found: 241.1201.

1-[(Cyclohex-2-enyloxy)methyl]-3-methoxybenzene (10e)
3-Methoxybenzyl chloride provided 0.93 g (84%) of **10e**; R_f = 0.3 (EtOAc–hexanes, 4:96).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (t, *J* = 8.1, 7.98 Hz, 1 H), 6.97 (m, 2 H), 6.83 (d, *J* = 8.3 Hz, 1 H), 5.83 (m, 2 H), 4.54 (dd, *J* = 12.1, 6.8 Hz, 2 H), 3.98 (m, 1 H), 3.84 (s, 3 H), 1.77 (m, 5 H), 1.57 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 140.8, 130.9, 129.3, 127.8, 119.9, 113.1, 112.9, 72.2, 69.9, 55.2, 28.4, 25.3, 19.5.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_2$ + Na [M + Na]$^+$: 241.1204; found: 241.1205.

1-[(Cyclohex-2-enyloxy)methyl]-4-methoxybenzene (10f)
4-Methoxybenzyl chloride provided 0.98 g (88%) of **10f**; R_f = 0.3 (EtOAc–hexanes, 4:96).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.9 Hz, 2 H), 6.90 (d, *J* = 4.7 Hz, 2 H), 5.85 (m, 2 H), 4.5 (dd, *J* = 11.5, 7.9 Hz, 2 H), 3.97 (m, 1 H), 3.82 (s, 3 H), 1.8 (m, 5 H), 1.62 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 130.3, 129.9, 128.4, 127.1, 112.9, 71.1, 68.9, 54.4, 27.6, 24.4, 18.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_2$ + Na [M + Na]$^+$: 241.1204; found: 241.1205.

1-[(Cyclohex-2-enyloxy)methyl]-4-bromobenzene (10g)
4-Bromobenzyl bromide provided 0.87 g (64%) of **10g**; R_f = 0.28 (EtOAc–hexanes, 2:98).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.3 Hz, 2 H), 5.83 (m, 2 H), 4.53 (dd, *J* = 11.5, 6.4 Hz, 2 H), 3.94 (m, 1 H), 2.0 (m, 2 H), 1.77 (m, 3 H), 1.58 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 131.4, 131.2, 129.2, 127.6, 121.2, 72.5, 69.3, 28.4, 25.3, 19.3.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{15}BrO$ [M$^+$]: 266.0306; found: 266.0307.

1-[(Cyclohex-2-enyloxy)methyl]-2-(trifluoromethyl)benzene (10h)
2-(Trifluoromethyl)benzyl chloride provided 1.05 g (81%) of **10h**; R_f = 0.2 (EtOAc–hexanes, 4:96).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (m, 4 H), 5.95 (m, 2 H), 4.65 (m, 2 H), 4.06 (m, 1 H), 1.84 (m, 5 H), 1.62 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.1, 131.9, 131.0, 129.0, 128.3, 127.5, 125.9, 120.2, 72.9, 65.9, 28.3, 24.1, 19.2.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{15}F_3O$ [M$^+$]: 256.1075; found: 256.1081.

4-[(Cyclohex-2-enyloxy)methyl]-3,4-dimethoxybenzene (10i)
3,4-Dimethoxybenzyl bromide[18] provided 0.76 g (60%) of **10i**; R_f = 0.3 (EtOAc–hexanes, 4:96).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.79 (m, 3 H), 5.77 (m, 2 H), 4.45 (dd, *J* = 11.7, 7.5 Hz, 2 H), 3.93 (m, 1 H), 3.88 (s, 3 H), 3.85 (s, 3 H), 1.6 (m, 5 H), 1.4 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.9, 148.4, 131.7, 130.9, 127.8, 120.1, 111.0, 110.9, 71.9, 69.9, 55.9, 55.8, 28.4, 25.2, 19.3.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{20}O_3$ + Na [M + Na]$^+$: 271.1310; found: 271.1307.

2-[(Cyclohex-2-enyloxy)methyl]naphthalene (10j)
2-(Bromomethyl)naphthalene provided 0.97 g (80%) of **10j**; R_f = 0.3 (EtOAc–hexanes, 2:98).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (m, 4 H), 7.51 (m, 3 H), 5.96 (m, 2 H), 4.76 (dd, *J* = 12.2, 7.1 Hz, 2 H), 4.08 (m, 1 H), 1.86 (m, 5 H), 1.6 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.7, 133.4, 133.0, 131.1, 128.1, 127.9, 127.9, 127.8, 126.3, 126.1, 125.9, 125.8, 72.3, 70.2, 28.5, 25.4, 19.4.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{18}O$ + Na [M + Na]$^+$: 261.1255; found: 261.1252.

Epoxides 16, General Procedure
A solution of the olefin **10** (3.95 mmol, 100 mol%) in MeOH (10 mL) was added to a mixture of PhCN (23.7 mmol, 600 mol%), 30% H_2O_2 (23.7 mmol, 600 mol%), and $KHCO_3$ (2.95 mmol, 75 mol%) in MeOH (10 mL) at 0 °C and the mixture was warmed to r.t. and stirred for 18 h. H_2O (100 mL) was added and the mixture was extracted with Et_2O (3 × 50 mL). The organic layers were combined, washed with brine (50 mL), dried ($MgSO_4$), concentrated and chromatographed (EtOAc in hexanes) to provide the desired epoxide.

2-(Benzyloxy)-7-oxabicyclo[4.1.0]heptane (16a)
Olefin **10a** (1 g, 5.31 mmol) provided 0.81 g (75%) of **16a**; R_f = 0.5 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (m, 5 H), 4.70 (s, 2 H), 3.84 (m, 1 H), 3.32 (m, 2 H), 1.84 (m, 2 H), 1.64 (m, 3 H), 1.31 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8, 128.3, 127.5, 74.7, 70.2, 53.9, 53.4, 24.9, 23.1, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}O_2$ + Na [M + Na]$^+$: 227.1048; found: 227.1045.

2-(3-Methylbenzyloxy)-7-oxabicyclo[4.1.0]heptane (16b)
Olefin **10b** (0.5 g, 2.47 mmol) provided 0.45 g (84%) of **16b**; R_f = 0.5 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (m, 3 H), 7.1 (m, 1 H), 4.70 (s, 2 H), 3.84 (m, 1 H), 3.32 (m, 1 H), 3.3 (m, 1 H), 2.4 (s, 3 H), 1.8 (m, 2 H), 1.54 (m, 3 H), 1.31 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8, 128.3, 127.5, 74.7, 70.2, 53.9, 53.4, 24.9, 23.1, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_2$ + Na [M + Na]$^+$: 241.1204; found: 241.1206.

2-(4-Methylbenzyloxy)-7-oxabicyclo[4.1.0]heptane (16c)
Following the general procedure olefin **10c** (0.6 g, 2.96 mmol) provided 0.52 g (81%) of **16c**; R_f = 0.5 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 7.9 Hz, 2 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 4.67 (s, 2 H), 3.79 (s, 2 H), 3.26 (m, 1 H), 3.3 (m, 1 H), 2.36 (s, 3 H), 1.8 (m, 2 H), 1.42 (m, 3 H), 1.22 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 135.6, 129.1, 127.8, 74.4, 70.1, 54.1, 53.5, 24.9, 23.0, 21.2, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_2$ + Na [M + Na]$^+$: 241.1204; found: 241.1206.

2-(2-Methoxybenzyloxy)-7-oxabicyclo[4.1.0]heptane (16d)
Following the general procedure olefin **10d** (0.6 g, 2.74 mmol) provided 0.54 g (84%) of **16d**; R_f = 0.45 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.4 Hz, 1 H), 7.24 (t, *J* = 8.0, 7.6 Hz, 1 H), 6.95 (t, *J* = 7.5, 7.4 Hz, 1 H), 6.8 (d, *J* = 8.2 Hz, 1 H), 4.75 (s, 2 H), 3.84 (s, 3 H), 3.82 (m, 1 H), 3.35 (m, 1 H), 3.27 (m, 1 H), 1.80 (m, 2 H), 1.55 (m, 3 H), 1.23 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6, 126.4, 126.1, 124.8, 118.1, 72.8, 62.6, 52.9, 51.7, 51.2, 22.5, 20.6, 17.5.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_3$ + Na [M + Na]$^+$: 257.1154; found: 257.1146.

2-(3-Methoxybenzyloxy)-7-oxabicyclo[4.1.0]heptane (16e)
Olefin **10e** (0.6 g, 2.74 mmol) provided 0.462 g (72%) of **16e**; R_f = 0.5 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (m, 3 H), 6.9 (s, 1 H), 4.74 (s, 2 H), 3.75 (s, 3 H), 3.73 (m, 1 H), 3.25 (m, 1 H), 3.22 (m, 1 H), 1.80 (m, 2 H), 1.55 (m, 3 H), 1.23 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 140.3, 129.4, 128.6, 119.9, 113.2, 74.6, 70.1, 55.2, 54.1, 53.5, 24.9, 22.9, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_3$ + Na [M + Na]$^+$: 257.1154; found: 257.1144.

2-(4-Methoxybenzyloxy)-7-oxabicyclo[4.1.0]heptane (16f)
Olefin **10f** (0.6 g, 2.74 mmol) provided 0.482 g (75%) of **16f**; R_f = 0.5 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 7.7 Hz, 2 H), 4.62 (s, 2 H), 3.80 (s, 3 H), 3.79 (m, 1 H), 3.28 (m, 1 H), 3.25 (m, 1 H), 1.78 (m, 2 H), 1.51 (m, 3 H), 1.21 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.16, 130.7, 129.3, 113.8, 74.2, 69.8, 55.3, 54.1, 53.5, 24.9, 23.0, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}O_3$ + Na [M + Na]$^+$: 257.1154; found: 257.1149.

2-(4-Bromobenzyloxy)-7-oxabicyclo[4.1.0]heptane (16g)
Olefin **10f** (0.5 g, 1.87 mmol) provided 0.25 g (48%) of **16g**; R_f = 0.5 (EtOAc–hexanes, 25:75).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.5 Hz, 2 H), 4.63 (s, 2 H), 3.77 (m, 1 H), 3.26 (m, 2 H), 1.80 (m, 2 H), 1.59 (m, 3 H), 1.22 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 131.5, 128.4, 121.4, 74.9, 69.4, 54.1, 53.3, 24.9, 22.9, 19.6.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{15}BrO_2$ + Na [M + Na]$^+$: 305.0153; found: 305.0138.

2-[(2-Trifluoromethyl)benzyloxy]-7-oxabicyclo[4.1.0]heptane (16h)
Olefin **10h** (0.3 g, 0.12 mmol) provided 0.12 g (37%) of **16h**; R_f = 0.4 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (m, 2 H), 7.4 (m, 2 H), 4.88 (s, 2 H), 3.83 (m, 1 H), 3.35 (m, 1 H), 3.29 (m, 1 H), 1.80 (m, 2 H), 1.55 (m, 3 H), 1.23 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.9, 129.0, 128.60, 127.4, 127.1, 75.8, 68.3, 54.2, 53.3, 24.8, 22.9, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{15}F_3O_2$ + Na [M + Na]$^+$: 295.0908; found: 295.0922.

2-[(3,4-Dimethoxy)benzyloxy]-7-oxabicyclo[4.1.0]heptane (16i)
Olefin **10i** (1 g, 4.02 mmol) provided 0.65 g (61%) of **16i**; R_f = 0.5 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95 (s, 1 H), 6.88 (d, *J* = 8.1 Hz, 1 H), 6.81 (d, *J* = 8.1 Hz, 1 H), 4.61 (s, 2 H), 3.85 (s, 3 H), 3.82 (s, 3 H), 3.75 (m, 1 H), 3.24 (m, 2 H), 1.77 (m, 2 H), 1.47 (m, 3 H), 1.19 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 148.5, 131.2, 120.2, 111.0, 110.9, 74.3, 70.1, 55.9, 55.9, 54.1, 53.5, 24.9, 22.9, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{20}O_4$ + Na [M + Na]$^+$: 287.1259; found: 287.1259.

2-(2-Napthylmethyloxy)-7-oxabicyclo[4.1.0]heptane (16j)
Olefin **10j** (0.3 g, 1.25 mmol) provided 0.185 g (58%) of **16j**; R_f = 0.4 (EtOAc–hexanes, 20:80).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8 (m, 4 H), 7.54 (d, *J* = 8.7 Hz, 1 H), 7.40 (m, 2 H) 4.85 (s, 2 H), 3.83 (m, 1 H), 3.34 (m, 1 H), 3.28 (m, 1 H), 1.82 (m, 2 H), 1.59 (m, 3 H), 1.22 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.2, 133.3, 133.0, 128.2, 127.9, 127.7, 126.4, 126.1, 125.8, 74.6, 70.3, 54.1, 53.5, 24.9, 23.0, 19.7.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{18}O_2$ [M + Na]$^+$: 277.1204; found: 277.1195.

2-(Benzyloxy)-7-azabicyclo[4.1.0]heptane (17)
A solution of epoxide **16a** (2 g, 9.8 mmol) in MeOH (36 mL) and H_2O (4 mL) was added to a mixture of NaN_3 (6.3 g, 98 mmol) and NH_4Cl (1.04 g, 19.6 mmol) and the mixture was heated to reflux for 36 h. The mixture was diluted with H_2O (50 mL) and the aqueous layer was extracted with EtOAc (3 × 50 mL), dried ($MgSO_4$), and concentrated to give 1.8 g (75%) of a regioisomeric mixture of azido alcohols which were directly carried on to the next step.

R_f = 0.5 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (m, 5 H), 4.68 (dd, *J* = 11.6 Hz, 2 H), 3.87 (m, 1 H), 3.68 (m, 1 H), 3.51 (dd, *J* = 3.1, 5.8 Hz, 1 H), 2.59 (br s, 1 H), 2.2 (m, 2 H), 1.8 (m, 2 H), 1.4 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.5, 127.9, 127.7, 77.1, 74.5, 71.0, 62.8, 29.1, 26.9, 18.4.

Ph_3P (1.91 g, 7.28 mmol) was added to a solution of the above azido alcohol (1.8 g, 7.28 mmol) in MeCN (10 mL) and the mixture was heated to reflux for 1 h. The mixture was concentrated and chromatographed (MeOH–CH_2Cl_2, 10:90) to yield 1.2 g (82%) of aziridine **17** as a colorless oil.

R_f = 0.4 (MeOH–CH_2Cl_2, 10:90).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (m, 5 H), 4.54 (s, 2 H), 3.61 (dd, *J* = 2.3, 5.3 Hz, 1 H), 2.4 (s, 2 H), 1.71 (m, 3 H), 1.39 (m, 1 H), 1.23 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.4, 127.6, 127.5, 74.6, 70.8, 36.8, 33.4, 30.0, 24.2, 15.2.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{17}NO$ [M + H]$^+$: 204.1388; found: 204.1379.

2,3,4,4a,6,10b-Hexahydro-1*H*-benzo[*c*]chromen-1-amine (18)
$B(C_6F_5)_3$ (126 mg, 0.246 mmol) was added to aziridine **17** (50 mg, 0.246 mmol) in CH_2Cl_2 (1 mL) at 0 °C. The mixture was then warmed to r.t. and stirred overnight. The mixture was diluted with CH_2Cl_2 (10 mL) and washed with sat. aq K_2CO_3 (10 mL), brine (10 mL), and H_2O (10 mL). The organic layer was dried ($MgSO_4$), concentrated, and chromatographed (MeOH–CH_2Cl_2, 10:90) to provide 35 mg (70%) of amine **18**; R_f = 0.39 (MeOH–CH_2Cl_2, 10:90).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (m, 5 H), 4.71 (dd, *J* = 11.5, 11.5 Hz, 2 H), 3.29 (m, 1 H), 3.09 (m, 1 H), 2.53 (m, *J* = 9.3 Hz, 1 H), 2.41(br s, 2 H), 2.18 (m, 1 H), 1.99 (m, 1 H), 1.80 (m, 1 H), 1.34 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.4, 127.8, 127.7, 81.9, 73.4, 71.1, 61.9, 32.6, 29.6, 20.1.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{17}NO$ [M + H]$^+$: 204.1388; found: 204.1381.

Conversion of Epoxides 16 into Aziridines 19; General Procedure
A mixture of epoxide **16** (1.47 mmol, 100 mol%), LiBr (0.147 mmol, 10 mol%) and amine (1.47 mmol, 100 mol%) were stirred at r.t. for 5 h. This crude mixture was dissolved in H_2O (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$) and concentrated to provide the amino alcohol as a mixture of regioisomers. This mixture was used directly in the next reaction. To a solution of PPh_3 (1.06 mmol, 106 mol%) in THF (5 mL) was added DIAD (1.06 mmol, 106 mol%) in THF (2 mL) at 0 °C. After 5 min, a solution of the above amino alcohol (1 mmol, 100 mol%) in THF (2 mL) was added, warmed to r.t. and stirred for 8 h. This mixture was concentrated and chromatographed (EtOAc in hexanes) to provide the desired aziridine **19**.

2-(Benzyloxy)-*N*-hexyl-7-azabicyclo[4.1.0]heptane (19a)
Epoxide **16a** (0.3 g, 1.47 mmol) and *n*-hexylamine (0.15 g, 1.47 mmol) provided 0.33 g (75%) of amino alcohol, 0.3 g (0.98 mmol) of which afforded 0.21 g of aziridine **19a** (73%); overall yield: 49%; R_f = 0.65 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 5 H), 4.5 (s, 2 H), 3.54 (m, 1 H), 2.09 (t, *J* = 7.3 Hz, 2 H), 1.2 (m, 18 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8, 128.3, 127.6, 127.4, 74.6, 70.7, 61.2, 53.3, 42.1, 39, 31.8, 298.7, 27.2, 27.1, 24.9, 24.2, 23, 22.6, 19.7, 16.1, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{29}NO$ [M + H]$^+$: 288.2327; found: 288.2314.

***N*-Benzyl-2-(benzyloxy)-7-azabicyclo[4.1.0]heptane (19b)**
Epoxide **16a** (0.3 g, 1.47 mmol) and benzylamine (0.16 g, 1.47 mmol) provided 0.34 g (75%) of amino alcohol, 0.3 g of which (0.96 mmol) afforded 0.189 g of aziridine **19b** (67%); overall yield: 44%; R_f = 0. 65 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (m, 10 H), 4.47 (s, 2H), 3.61 (t, *J* = 7.5 Hz, 1 H), 3.49 (d, *J* = 13.9 Hz, 1 H), 3.33 (d, *J* = 13.9 Hz, 1 H), 1.69 (m, 5 H), 1.37 (m, 1 H), 1.19 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6, 138.7, 128.3, 128.2, 127.6, 127.4, 126.7, 74.3, 70.6, 64.1, 42.1, 39.7, 29.7, 27.4, 24.1, 16.1.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{23}NO$ [M + H]$^+$: 294.1858; found: 294.1845.

2-(Benzyloxy)-*N*-phenyl-7-azabicyclo[4.1.0]heptane (19c)
Epoxide **16a** (0.3 g, 1.47 mmol) and aniline (0.14 g, 1.47 mmol) provided 0.33 g (76%) of amino alcohol, 0.3 g (1 mmol) of which afforded 0.21 g of aziridine **19c** (75%); overall yield: 51%; R_f = 0.65 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (m, 6 H), 7.11 (m, 2 H), 6.8 (t, *J* = 8.4 H, 2 H), 4.65 (s, 2 H), 3.81 (t, *J* = 7.6 Hz, 1 H), 2.37 (s, 2 H), 1.99 (m, 1 H), 1.78 (m, 2 H), 1.30 (m, 1 H), 1.19 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.9, 128.9, 128.7, 128.5, 127.7, 127.6, 122.2, 120.2, 74.4, 71.2, 42.4, 39.6, 29.7, 27.4, 24.4, 15.9.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{21}NO$ [M + H]$^+$: 280.1701; found: 280.1691.

***N*-Hexyl-2-(3-methylbenzyloxy)-7-azabicyclo[4.1.0]heptane (19d)**
Epoxide **16b** (0.4 g, 1.83 mmol) and *n*-hexylamine (0.185 g, 1.83 mmol) provided 0.30 g of aziridine **19d** (55%); R_f = 0.63 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (m, 3 H), 7.1 (d, *J* = 7.3 Hz, 1 H), 4.51 (s, 2 H), 3.57 (dd, *J* = 5.2, 2.7 Hz, 1 H), 2.28 (s, 3 H), 2.14 (t, *J* = 7.1 Hz, 2 H), 1.18 (m, 15 H), 0.79 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.6, 137.9, 128.4, 128.3, 128.2, 124.8, 74.5, 70.8, 61.2, 42.1, 39.1, 31.8, 29.7, 27.3, 27.1, 24.1, 22.6, 21.4, 16.1, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO$ [M + H]$^+$: 302.2484; found: 302.2483.

***N*-Hexyl-2-(4-methylbenzyloxy)-7-azabicyclo[4.1.0]heptane (19e)**
Epoxide **16c** (0.5 g, 2.29 mmol) and *n*-hexylamine (0.23 g, 2.29 mmol) provided 0.45 g of aziridine **19e** (65%); R_f = 0.65 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 7.9 Hz, 2 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 4.6 (s, 2 H), 3.66 (dd, *J* = 5.2, 2.7 Hz, 1 H), 2.36 (s, 3 H), 2.22 (m, 2 H), 1.2 (m, 15 H), 0.89 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.1, 135.7, 129.0, 127.7, 74.3, 61.2, 42.1, 39.0, 31.9, 29.7, 27.3, 27.1, 24.1, 22.6, 21.1, 16.1, 14.1.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO$ [M + H]$^+$: 302.2484; found: 302.2477.

***N*-Hexyl-2-(2-methyloxybenzyloxy)-7-azabicyclo[4.1.0]heptane (19f)**
Epoxide **16d** (0.5 g, 2.13 mmol) and *n*-hexylamine (0.22 g, 2.13 mmol) provided 0.412 g of aziridine **19f** (61%); R_f = 0.65 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.4 Hz, 1 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 6.94 (t, *J* = 7.4 Hz, 1 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 4.68 (s, 2 H), 3.84 (s, 3 H), 3.69 (dd, *J* = 5.2, 2.8 Hz, 1 H), 2.23 (t, *J* = 7.4 Hz, 2 H), 1.29 (m, 15 H), 0.88 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.5, 126.3, 125.9, 124.8, 118.0, 107.6, 72.3, 63.0, 58.8, 52.8, 39.7, 36.7, 29.4, 27.2, 24.9, 24.7, 21.7, 20.1, 13.7, 11.6.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO_2$ [M + H]$^+$: 318.2433; found: 318.2438.

***N*-Hexyl-2-(3-methyloxybenzyloxy)-7-azabicyclo[4.1.0]heptane (19g)**
Epoxide **16e** (0.4 g, 1.7 mmol) and *n*-hexylamine (0.17 g, 1.7 mmol) provided 0.34 g of aziridine **19g** (63%); R_f = 0.65 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (t, *J* = 8.2 Hz, 1 H), 6.85 (d, *J* = 7.2 Hz, 2 H), 6.82 (dd, *J* = 6.9, 1.2 Hz, 1 H), 4.62 (s, 2 H), 3.83 (s, 3 H), 3.66 (dd, *J* = 5.2, 2.6 Hz, 1 H), 2.23 (t, *J* = 7.3 Hz, 2 H), 1.27 (m, 15 H), 0.88 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.3, 119.8, 113.1, 113.0, 74.5, 70.6, 61.2, 55.2, 42.1, 39.1, 31.8, 29.7, 27.3, 27.2, 24.1, 22.6, 16.1, 14.1.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO_2$ [M + H]$^+$: 318.2433; found: 318.2441.

N-Hexyl-2-(4-methyloxybenzyloxy)-7-azabicyclo[4.1.0]heptane (19h)

Epoxide **16f** (0.4 g, 1.7 mmol) and *n*-hexylamine (0.17 g, 1.7 mmol) provided 0.31 g of aziridine **19h** (57%); R_f = 0.63 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.2 (d, *J* = 8.5 Hz, 2 H), 6.78 (d, *J* = 8.5 Hz, 2 H), 4.47 (s, 2 H), 3.72 (s, 3 H), 3.55 (dd, *J* = 5.2, 2.6 Hz, 1 H), 2.12 (t, *J* = 7.4 Hz, 2 H), 1.08 (m, 15 H), 0.78 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 130.8, 129.2, 113.8, 74.2, 61.2, 55.2, 42.1, 39.1, 31.9, 27.4, 27.3, 27.1, 24.1, 22.6, 16.1, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO_2$ + Na [M + Na]$^+$: 340.2252; found: 340.2243.

2-(4-Bromobenzyloxy)-*N*-hexyl-7-azabicyclo[4.1.0]heptane (19i)

Epoxide **16g** (0.2 g, 0.71 mmol) and *n*-hexylamine (71 mg, 0.71 mmol) provided 0.137 g of aziridine **19i** (53%); R_f = 0.6 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.3 Hz, 2 H), 7.25 (d, *J* = 8.6 Hz, 2 H), 3.64 (m, 1 H), 2.22 (t, *J* = 7.4 Hz, 2 H), 1.18 (15 H), 0.88 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 131.4, 129.2, 121.3, 74.8, 70.0, 61.2, 42, 39, 31.9, 29.7, 27.2, 27.1, 24.1, 22.6, 16.1, 14.1.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{28}BrNO$ [M + H]$^+$: 366.1433; found: 366.1443.

2-(2-Trifluoromethylbenzyloxy)-*N*-hexyl-7-azabicyclo[4.1.0]heptane (19j)

Epoxide **16h** (0.1 g, 0.37 mmol) and *n*-hexylamine (37 mg, 0.37 mmol) provided 33 mg of aziridine **19j** (25%); R_f = 0.62 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.8 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 7.27 (t, *J* = 7.7 Hz, 1 H), 4.73 (s, 2 H), 3.60 (dd, *J* = 5.1, 2.7 Hz, 1 H), 2.17 (m, 2 H), 1.14 (m, 15 H), 0.80 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6, 131.9, 129, 127.2, 125.7, 125.6, 75.2, 66.6, 66.5, 61.2, 41.8, 39.1, 31.8, 29.6, 27.2, 27.1, 24.1, 22.5, 16.0, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{28}F_3NO$ [M + H]$^+$: 356.2201; found: 356.2205.

N-Hexyl-2-(3,4-dimethoxybenzyloxy)-7-azabicyclo[4.1.0]heptane (19k)

Epoxide **16i** (0.6 g, 2.26 mmol) and *n*-hexylamine (0.23 g, 2.26 mmol) provided 0.52 g of aziridine **19k** (66%); R_f = 0.62 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90 (d, *J* = 9.1 Hz, 2 H), 6.82 (d, *J* = 7.9 Hz, 1 H), 4.56 (s, 2 H), 3.9 (s, 3 H), 3.88 (s, 3 H), 3.64 (dd, *J* = 5.1, 2.8 Hz, 1 H), 2.21 (t, *J* = 7.4 Hz, 2 H), 1.18 (m, 15 H), 0.86 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 148.5, 131.9, 120.2, 11.0, 110.9, 74.3, 70.7, 61.2, 55.9, 55.8, 42.1, 39.1, 31.87, 29.7, 27.3, 27.1, 24.1, 22.6, 22.3, 21.9, 16.1, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{33}NO_3$ + Na [M + Na]$^+$: 370.2358; found: 370.2366.

N-Hexyl-2-(2-napthylbenzyloxy)-7-azabicyclo[4.1.0]heptane (19l)

Following the general procedure epoxide **16j** (0.15 g, 0.589 mmol) and *n*-hexylamine (60 mg, 0.589 mmol) provided 0.131 g of aziridine **19l** (66%); R_f = 0.68 (EtOAc–hexanes, 30:70).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (m, 2 H), 7.46 (m, 3 H), 7.25 (d, *J* = 8.6 Hz, 2 H), 4.58 (s, 2 H), 3.64 (dd, *J* = 5.2, 2.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8, 136.2, 133.3, 132.9, 128.1, 127.8, 127.6, 126.3, 126.0, 125.8, 125.7, 121.3, 74.7, 70.9, 61.2, 41.9, 39.0, 31.8, 29.7, 27.3, 24.1, 22.6, 16.1, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{31}NO$ + Na [M + Na]$^+$: 360.2303; found: 360.2296.

Cyclization of Aziridines 19 to Chromenes 20; General Procedure

To a solution of aziridine **19** (0.006 mmol, 100 mol%) in CH_2Cl_2 (1 mL) was added $B(C_6F_5)_3$ (0.006 mmol, 100 mol%) at 0 °C. After 10 min, the mixture was warmed to r.t. and stirred for 8 h. The organic layer was diluted with CH_2Cl_2 (10 mL), washed with sat. aq Na_2CO_3 (5 mL), brine (5 mL), dried ($MgSO_4$), concentrated, and chromatographed (MeOH–CH_2Cl_2, 10:90) to provide amine **20**.

N-Hexyl-2,3,4,4a,6,10b-hexahydro-1*H*-benzo[*c*]chromen-1-amine (20a)

Aziridine **19a** (20 mg, 0.0695 mmol) provided 16 mg (80%) of amine **20a**; R_f = 0.25 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (m, 4 H), 4.58 (d, *J* = 11.6 Hz, 1 H), 4.32 (d, *J* = 11.5 Hz, 1 H), 3.18 (m, 1 H), 2.51 (m, 2 H), 2.24 (t, *J* = 9.6 Hz, 1 H), 1.96 (m, 1 H), 1.7 (m, 1 H), 1.67 (m, 1 H), 1.17 (m, 14 H), 0.77 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 128.4, 127.7, 127.6, 78.3, 70.7, 70.2, 67.3, 45.6, 32.2, 31.7, 30.9, 30.2, 29.6, 26.9, 24.6, 22.6, 19.9, 13.9.

Anal. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.00; H, 10.12; N, 4.70.

N-Benzyl-2,3,4,4a,6,10b-hexahydro-1*H*-benzo[*c*]chromen-1-amine (20b)

Aziridine **19b** (20 mg, 0.068 mmol) provided 18 mg (90%) of amine **20b**; R_f = 0.2 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (m, 9 H), 4.63 (d, *J* = 11.5 Hz, 1 H), 4.37 (d, *J* = 11.5 Hz, 1 H), 3.93 (d, *J* = 12.6 Hz, 1 H), 3.69 (d, *J* = 12.5 Hz, 1 H), 3.28 (m, 1 H), 2.38 (t, *J* = 9.5 Hz, 1 H), 2.15 (m, 1 H), 1.94 (m, 1 H), 1.71 (m, 1 H), 1.18 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.2, 127.2, 126.9, 126.52, 126.5125.8, 75.3, 69.3, 66.14, 49.5, 31, 28.9, 28.4, 18.6.

Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.60; H, 7.84; N, 4.63.

N-Phenyl-2,3,4,4a,6,10b-hexahydro-1*H*-benzo[*c*]chromen-1-amine (20c)

Aziridine **19c** (20 mg, 0.071 mmol) provided 14 mg (70%) of amine **20c**; R_f = 0.22 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (m, 3 H), 7.2 (m, 2 H), 7.05 (m, 1 H), 6.8 (m, 2 H), 4.5 (d, *J* = 11.5 Hz, 1 H), 4.35 (d, *J* = 12.6 Hz, 1 H), 3.2 (m, 3 H), 3.0 (s, 1 H), 2.1 (m, 2 H), 1.8 (m, 1 H), 1.2 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 138.2, 129.2, 128.2, 127.6, 127.6, 127.5, 118.3, 114.4, 80.1, 72.9, 70.9, 64, 31.6, 29.8, 19.2.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{21}NO$ [M + H]$^+$: 280.1691; found: 280.1701.

N-Hexyl-2,3,4,4a,6,10b-hexahydro-8-methyl-1H-benzo[c]chromen-1-amine (20d)

Aziridine **19d** (50 mg, 0.165 mmol) provided 36 mg (72%) of amine **20d**; R_f = 0.2 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 7.29 Hz, 2 H), 7.07 (s, 1 H), 4.58 (d, *J* = 11.4 Hz, 1 H), 4.28 (d, *J* = 11.4 Hz, 1 H), 3.18 (m, 2 H), 2.58 (m, 1 H), 2.46 (m, 1 H), 2.28 (s, 3 H), 2.15 (m, 1 H), 2.12 (m, 1 H), 1.92 (m, 1 H), 1.18 (m, 10 H), 0.80 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.4, 128.5, 128.4, 128.3, 125.3, 124.9, 78.0, 70.8, 70.1, 67.2, 45.3, 32.1, 31.8, 31.0, 29.7, 27.0, 22.6, 21.4, 19.9, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO$ [M + H]$^+$: 302.2484; found: 302.2476.

N-Hexyl-9-methyl-2,3,4,4a,6,10b-hexahydro-1H-benzo[c]chromen-1-amine (20e)

Aziridine **19e** (50 mg, 0.165 mmol) provided 30 mg (60%) of amine **20e**; R_f = 0.2 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.07 (m, 3 H), 4.55 (d, *J* = 11.6 Hz, 1 H), 4.17 (d, *J* = 11.6 Hz, 1 H), 3.31 (m, 2 H), 2.58 (m, 1 H), 2.63 (m, 1 H), 2.26 (s, 3 H), 2.19 (m, 1 H), 2.12 (m, 1 H), 1.18 (m, 11 H), 0.80 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.7, 129.6, 129.1, 128.4, 128.3, 127.9, 78.7, 70.3, 70.5, 67.8, 45.4, 32.1, 31.3, 31.1, 29.7, 27.3, 22.6, 21.8, 19.9, 14.0

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO$ [M + H]$^+$: 302.2484; found: 302.2487.

N-Hexyl-7-methoxy-2,3,4,4a,6,10b-hexahydro-1H-benzo[c]chromen-1-amine (20f)

Aziridine **19f** (50 mg, 0.157 mmol) provided 32 mg (64%) of amine **20f**; R_f = 0.18 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (m, 1 H), 6.87 (m, 1 H), 6.79 (d, *J* = 8.2 Hz, 1 H), 4.60 (d, *J* = 11.9 Hz, 1 H), 4.28 (d, *J* = 11.9 Hz, 1 H), 3.76 (s, 3 H), 3.23 (m, 2 H), 2.57 (m, 1 H), 2.48 (m, 1 H), 2.24 (t, *J* = 9.6 Hz, 1 H), 2.12 (m, 1 H), 1.92 (m, 1 H), 1.18 (m, 11 H), 0.80 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.1, 130.8, 129.2, 128.9, 126.9, 120.4, 110.2, 78.3, 70.3, 67.3, 65.8, 55.3, 45.5, 32.2, 31.8, 30.9, 30.3, 27.0, 22.6, 20.0, 14.1.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO_2$ [M + H]$^+$: 318.2433; found: 318.2424.

N-Hexyl-8-methoxy-2,3,4,4a,6,10b-hexahydro-1H-benzo[c]chromen-1-amine (20g)

Aziridine **19g** (50 mg, 0.157 mmol) provided 37.5 mg (75%) of amine **20g**; R_f = 0.18 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (s, 1 H), 6.81 (d, *J* = 8.1 Hz, 1 H), 6.74 (d, *J* = 7.9 Hz, 1 H), 4.56 (d, *J* = 11.7 Hz, 1 H), 4.28 (d, *J* = 11.7 Hz, 1 H), 3.74 (s, 3 H), 3.18 (m, 2 H), 2.60 (m, 1 H), 2.49 (m, 1 H), 2.24 (t, *J* = 9.6 Hz, 1 H), 2.10 (m, 1 H), 1.96 (m, 1 H), 1.18 (m, 11 H), 0.80 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 140.1, 129.4, 119.9, 113.3, 113.0, 78.2, 70.6, 70.1, 67.3, 55.1, 45.5, 32.1, 31.8, 31.0, 27.0, 22.6, 19.9, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO_2$ [M + H]$^+$: 318.2433; found: 318.2429.

N-Hexyl-9-methoxy-2,3,4,4a,6,10b-hexahydro-1H-benzo[c]chromen-1-amine (20h)

Aziridine **19h** (50 mg, 0.157 mmol) provided 12.5 mg (25%) of amine **20h**; R_f = 0.18 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.0 Hz, 1 H), 7.15 (s, 1 H), 6.74 (d, *J* = 7.9 Hz, 1 H), 4.50 (d, *J* = 11.4 Hz, 1 H), 4.13 (d, *J* = 11.3 Hz, 1 H), 3.71 (s, 3 H), 3.57 (m, 2 H), 2.78 (m, 1 H), 2.63 (m, 1 H), 2.15 (t, *J* = 7.6 Hz, 1 H), 2.10 (m, 1 H), 1.43 (m, 1 H), 1.18 (m, 11 H), 0.76 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 143.1, 129.3, 125.5, 114.2, 113.8, 73.6, 70.6, 70.2, 68.2, 55.2, 46.0, 33.7, 31.7, 29.7, 27.0, 22.5, 19.2, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{31}NO_2$ [M + H]$^+$: 318.2433; found: 318.2427.

9-Bromo-N-hexyl-2,3,4,4a,6,10b-hexahydro-1H-benzo[c]chromen-1-amine (20i)

Following the general procedure, aziridine **19i** (50 mg, 0.136 mmol) provided 22.5 mg (45%) of amine **20i**; R_f = 0.22 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.6 Hz, 1 H), 7.19 (s, 1 H), 7.05 (d, *J* = 8.3 Hz, 1 H), 4.52 (d, *J* = 11.3 Hz, 1 H), 4.18 (d, *J* = 11.4 Hz, 1 H), 3.55 (m, 2 H), 3.38 (m, 1 H), 3.17 (m, 1 H), 2.14 (t, *J* = 7.5 Hz, 1 H), 2.10 (m, 1 H), 1.45 (m, 1 H), 1.20 (m, 11 H), 0.76 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.7, 130.6, 129.1, 128.7, 128.5, 127.9, 78.7, 70.8, 70.5, 67.9, 46.4, 33.1, 31.5, 31.3, 29.5, 27.2, 22.8, 20.8, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{28}BrNO$ [M + H]$^+$: 366.1433; found: 366.1433.

8,9-Dimethoxy-N-hexyl-2,3,4,4a,6,10b-hexahydro-1H-benzo[c]chromen-1-amine (20k)

Following the general procedure, aziridine **19k** (50 mg, 0.143 mmol) provided 20 mg (40%) of amine **20k**; R_f = 0.19 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.89 (s, 1 H), 6.80 (s, 1 H), 4.37 (d, *J* = 11.2 Hz, 1 H), 4.25 (d, *J* = 11.4 Hz, 1 H), 3.91 (s, 3 H), 3.86 (s, 3 H), 3.29 (m, 2 H), 3.03 (m, 1 H), 3.17 (m, 1 H), 2.18 (t, *J* = 7.6 Hz, 1 H), 2.10 (m, 1 H), 1.45 (m, 1 H), 1.20 (m, 11 H), 0.76 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.3, 138.1, 127.4, 117.9, 112.3, 111.0, 78.4, 70.6, 70.1, 67.2, 66.4, 54.1, 43.5, 31.1, 30.8, 29.0, 27.4, 21.6, 19.6, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{33}NO_3$ [M + H]$^+$: 348.2539; found: 348.2530.

N-Hexyl-2,3,4,4a,6,12b-hexahydro-1H-naphtho[2,3-c]chromen-1-amine (20l)

Aziridine **19l** (50 mg, 0.148 mmol) provided 23 mg (46%) of amine **20l**; R_f = 0.23 (MeOH–CH_2Cl_2, 5:95).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (s, 1 H), 7.49 (m, 3 H), 7.22 (d, *J* = 8.3 Hz, 2 H), 4.63 (d, *J* = 11.8 Hz, 1 H), 4.25 (d, *J* = 11.8 Hz, 1 H), 3.31 (m, 2 H), 2.72 (m, 1 H), 2.55 (m, 1 H), 2.34 (t, *J* = 9.6 Hz, 1 H), 2.18 (m, 1 H), 2.03 (m, 1 H), 1.81 (m, 1 H), 1.28 (m, 11 H), 0.76 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.2, 128.1, 127.8, 127.6, 126.3, 126.0, 125.8, 125.7, 74.6, 70.0, 61.2, 53.4, 442.1, 39.1, 31.8, 29.7, 27.2, 24.1, 22.6, 16.1, 14.0.

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{31}NO$ [M + H]$^+$: 338.2484; found: 338.2473.

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