Carbene Reactions of α-Oxacyclo- and α-Azacyclo-*N*-aziridinylimines: Effect of Heteroatom and Ring Size in the Ring Expansion Reaction

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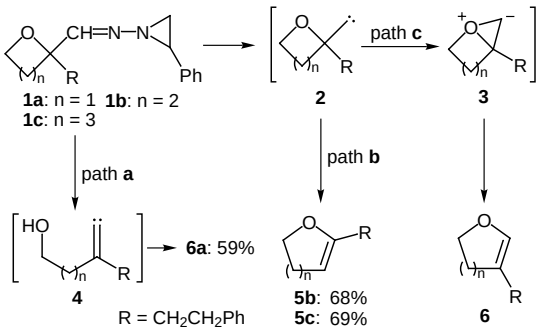
Abstract: Carbenes, generated from thermolysis of α-oxacyclo- and α-azacyclo-*N*-aziridinylimines in refluxing toluene, underwent ring expansions via insertion of alkyl carbenes into carbon−carbon bonds and intramolecular ammonium ylide formations, respectively. Ring expansion reaction of α-oxetanyl-*N*-aziridinylimines occurred via alkylidenecarbene intermediates, whereas thermal reaction of α-azetidinyl-*N*-aziridinylimines afforded α-aminoacetylene compounds via 1,2-H migration of alkylidenecarbene intermediates.

Key words: carbenes, heterocycles, hydrazones, ring expansions, ylides

Singlet carbenes, in particular, can function as Lewis acids by interacting with a pair of non-bonding electrons contributed by a Lewis base.[1] If the Lewis base is an uncharged species, the outcome of such an acid-base reaction is an ylide. Nucleophilic species that are known to trap carbenes include ethers, thioethers, amines, and halides. Compounds containing heteroatoms in the sp^2 or in the sp state of hybridization interact similarly with carbenes. Examples of such functional groups include aldehydes, esters, ketones, imines, thiocarbonyl compounds, and nitriles. [2]

Among these ylides, the chemistry of sulfur ylides has been the subject of extensive research, largely because of their easy preparation and the interesting rearrangements which they often undergo.[3] A large variety of sulfur compounds, including cyclic and acyclic alkyl and aryl sulfides, are known to trap carbenes to form sulfur ylides. These ylides become increasingly useful in organic synthesis and evidence also exists for their involvement in biochemical processes.[4] In contrast to sulfur ylides, oxonium ylides have been postulated as intermediates when diazo compounds decompose in the presence of 1,3-dioxolanes,[5] styrene oxide,[6] allylic ethers[7] and oxetanes.[8] Carbenoids react with the oxygen of epoxides[9] and sulfoxides[10] effecting transfer of oxygen to the carbene center to form oxonium ylides. Oxonium ylides have also been generated by deprotonation and desilylation of oxonium ions.[11]

Since Eschenmoser reported that *N*-aziridinylimines of α,β-epoxy ketones underwent thermal fragmentation,[12] *N*-aziridinylimines have been utilized as precursors of both diazoalkanes[13] and carbenes.[14] In connection with our interest in the synthetic utility of *N*-aziridinylimines,[15] we found that thermal reaction of α,β-epoxy-*N*-aziridinylimines in refluxing toluene generated β-hydroxyalkylidene carbenes, which underwent 1,5-C−H insertion[16] and 1,5-O−Si insertion[17] to afford cyclopentenols and dihydrofurans, respectively. As an extension of this work, we also reported that the thermolysis of α-thia-*N*-aziridinylimines proceeded via sulfur ylide intermediates.[18] Our next attention was given to α-oxacyclo and α-azacyclo-*N*-aziridinylimines to examine the effect of oxygen and nitrogen along with ring size of α-heterocycles in the ring expansion reactions.

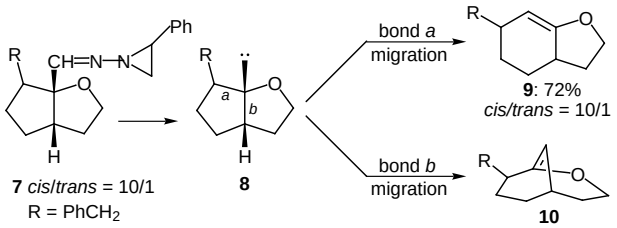


Scheme 1

The reaction of oxetanes with alkoxycarbonyl carbenes has been previously studied and the reaction was known to proceed via competitive oxonium ylide formation and C−H insertion.[19] However, with tetrahydrofuran, carbenes reacted to give only C−H insertion products.[20] In thermal reaction of α-oxacyclo-*N*-aziridinyl imines, we were interested in whether (i) the reaction would involve carbene **2** or alkylidenecarbene **4** (path **a**) and (ii) carbene **2** would undergo insertion into carbon−carbon bond to afford **5** (path **b**) or oxonium ylide formation to afford **6** (path **c**) as shown in Scheme 1.[21]

Thermal reaction of α-oxetanyl-*N*-aziridinylimine **1a** in refluxing toluene for 5 hours gave dihydrofuran **6a** in 59% yield, indicating that the reaction must involve alkylidenecarbene **4** and the subsequent 1,5-O−H insertion probably because of the relief of an oxetane ring strain and the difficulty of the formation of a highly strained oxonium ylide intermediate **3a**. However, when the thermal reaction of α-tetrahydrofuranyl derivative **1b** was carried out in refluxing toluene for 5 hours, **5b** was isolated in 68% yield. This result is in contrast with the previous

result obtained with **1a**. Apparently, the ring expansion occurred via insertion of carbene **2b** into carbon−carbon bond. A similar result was also obtained with α-tetrahydropyranyl-*N*-aziridinylimines. Thus, it is evident that the thermal reaction of α-oxacyclo-*N*-aziridinylimines proceeds through two different pathways and depends on the ring size of the oxacycles. The thermal reaction of highly strained epoxy and oxetanyl derivatives proceeds via alkylidenecarbene intermediates **4** due to relief of ring strain, whereas relatively stable tetrahydrofuranyl and tetrahydropyranyl derivatives undergo ring expansion via carbene intermediates **2**. Several experimental results are summarized in Table 1. In the case of α-oxetanyl-*N*-aziridinylimines, the oxetane ring underwent ring expansion (Entries 1, 2, and 3), whereas the carbocyclic ring underwent ring expansion in α-tetrahydrofuranyl (Entries 4 and 6) and α-tetrahydropyranyl derivatives (Entries 5 and 7). For the thermal reaction of bicyclic ether **7**, in the carbene intermediate **8**, migration of bond *a* would be expected to afford **9** because migration of bond *b* is unlikely due to the formation of the strained bridged bicyclic product **10**. Thus, the thermal reaction of **7** in refluxing toluene for 7 hours afforded **9** in 72% yield (Scheme 2).



Scheme 2

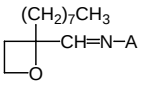
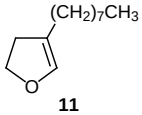
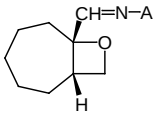
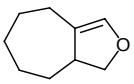
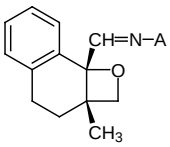
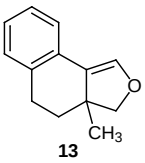
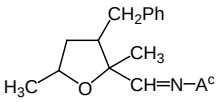
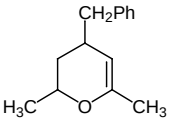
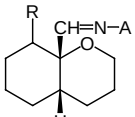
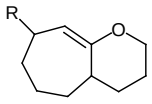
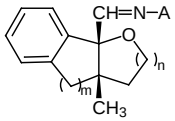
To study the efficiency of ring expansion process of α-oxacyclo-*N*-aziridinylimines, competition experiments were carried out with α-oxetanyl derivative **18** and α-tetrahydropyranyl derivative **21** (Scheme 3). To examine the competition between 1,5-O−H insertion and 1,2-H migration, when the thermal reaction of **18** was carried out in refluxing toluene for 8 hours, **20** was isolated in 55% yield, indicating that 1,5-O−H insertion of an alkylidenecarbene is favored over 1,2-H migration. However, in competition of 1,2-H migration with insertion of the alkyl carbene into the carbon-carbon bond, selective 1,2-H migration occurred. Thus, the thermal reaction of **21** under the same

Biographical Sketches

Sunggak Kim was born on March 17, 1946 in Kyungbuk province, Korea. He studied chemistry at Seoul National University, where he obtained his B.S. in 1969. After he had served in Korean Army for two and half years, he went to Canada in 1972 to receive his graduate training at McGill University in Montreal, where he did his Ph.D degree with Professor George Just. He moved to Harvard in 1976, where he spent three years on postdoctoral studies with Professor E. J. Corey. In 1979, he returned to Korea to join the chemistry faculty at the Korea Advanced Institute of Science. He was promoted to Professor of Chemistry at Korea Advanced Institute of Science and Technology (KAIST) in 1986 and he is currently the director of Center for Molecular Design and Synthesis (CMDS). His research interests focus on the design and the development of new reactions and strategies with general utility in organic synthesis. He developed several synthetically useful reagents including reducing, oxidizing, and coupling reagents. Although he continues his interest in new synthetic methodologies utilizing carbenes, cations, and anions, his major research emphasis in recent years has been on the development of new free radical-mediated methodologies. He is the author of 170 publications and two books. His major scientific awards include the Korean Chemical Society Award for Young Chemists (1985), the Korean Federation of Science and Technology Societies Award (1991), and the Korea Science Prize in Chemistry (1994).

Joo-Yong Yoon was born in Seoul, Korea, in 1971. He graduated from the College of Engineering of Hanyang University in 1994 and got his Ph.D degree under the guidance of Professor Sunggak Kim at the KAIST (Korea Advanced Institute of Science and Technology) in 1999. From 1999 to 2000 he has worked on non-stannane based radical chemistry at Center for Molecular Design and Synthesis, KAIST as a postdoctoral fellow. At present he is doing postdoctorate research in Prof. P. A. Wender's laboratory at the Stanford University.

Table 1 Ring Expansion of α-Oxacyclo-*N*-aziridinylimines

Entry	Substrate[a]	Time (h)	Product	Yield (%)[b]
1		5	 **11**	59
2		8	 **12**	58
3		5	 **13**	69
4	 *cis*/*trans* = 1/2	5	 **14** *cis*/*trans* = 1/2	60
5	 *cis*/*trans* = 1/8 R = $PhCH_2$	8	 **15** *cis*/*trans* = 1/8	62
6	 n = 1, m = 2	5	**16**: n = 1, m = 2	91
7	n = 2, m = 1	5	**17**: n = 2, m = 1	85

[a] All substrates are mixture of *syn*- and *anti*- isomers.

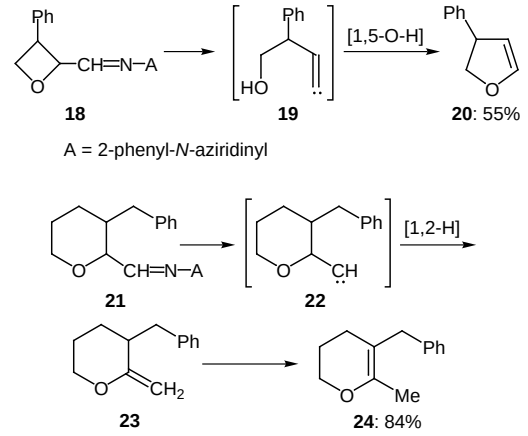
[b] Isolated yield.

[c] A = 2-Phenyl-*N*-aziridinyl.

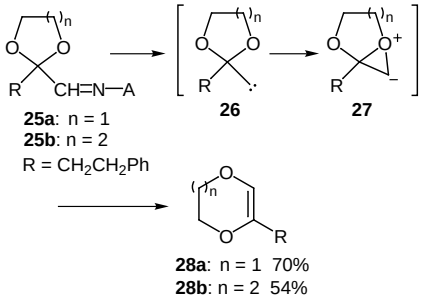
conditions furnished only dehydropyran **24** in 84% yield as a result of selective 1,2-H migration in the carbene **22** and the following isomerization of the double bond.

As shown in Scheme 4, we also briefly studied the thermal reaction of α-cyclic acetal substituted *N*- aziridinylimines **25**, in which insertion into carbon−carbon bond can not occur. The thermal reaction of **25a** in refluxing toluene for 5 h afforded **28a** in 70% yield, suggesting that the reaction would proceed via oxonium ylide intermediate **27a**. A similar result was also obtained with **25b**.

In the case of ammonium ylides,[22] unlike sulfur ylides, stable and isolable ammonium ylides have not been yet reported in the literature. This difference in stability is probably due to the absence of $p_\pi-d_\pi$ orbital interaction which contributes to the stabilization of the charge on the sulfur atom. However, ammonium ylides are reactive species which readily undergo the Stevens rearrangement[23] and

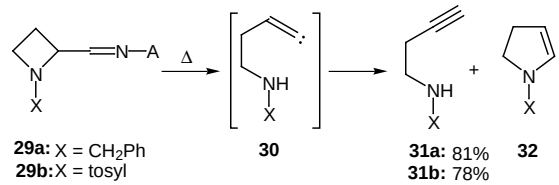


Scheme 3



Scheme 4

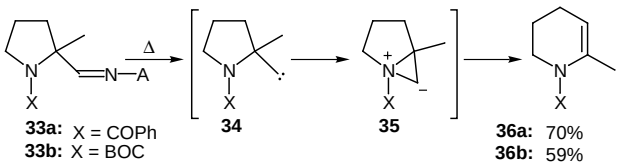
[2,3]-sigmatropic reorganization.[24] In thermal reaction of α-azacyclo-*N*-aziridinylimines, we were interested in whether there were any differences in chemical reactivities between α-oxacyclo- and α-azacyclo-*N*-aziridinylimines. The effect of the ring size was first examined. The thermal reaction of α-azetidinyl-*N*-aziridinylimine **29a** in refluxing toluene for 6 hours did not give dihydropyrrole **32a** but β-aminoacetylene compound **31a** in 81% yield, indicating that the reaction proceeded through the formation of alkylidenecarbene intermediate **30a** and subsequent 1,2-H migration as shown in Scheme 5.



Scheme 5

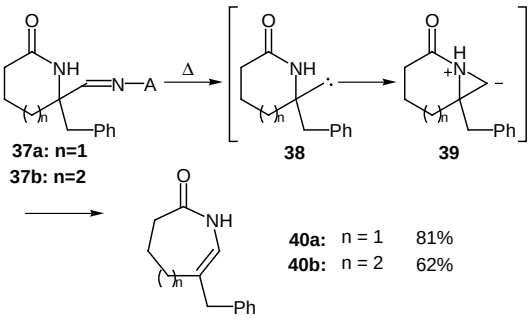
Similarly, the thermolysis of **29b** gave **31b** in 78% yield. It is interesting that 1,2-H migration is favored over ammonium ylide formation or 1,5-N−H insertion with elec-

tron-rich azetidine **29a**. This result is in sharp contrast with the result obtained with compound **18**, in which 1,5-O−H insertion was favored over 1,2-H migration. In order to examine the feasibility of the formation of the ammonium ylides, we began our studies with α-alkyl substituted-α-pyrrolidinyl-*N*-aziridinylimines **33** from which 1,2-H migration could not take place. When pyrrolidine derivative **33a** was refluxed in toluene 6 hours, piperidinyl derivative **36a** was isolated in 70% yield. The possible rationale for this observation is outlined in Scheme 6.



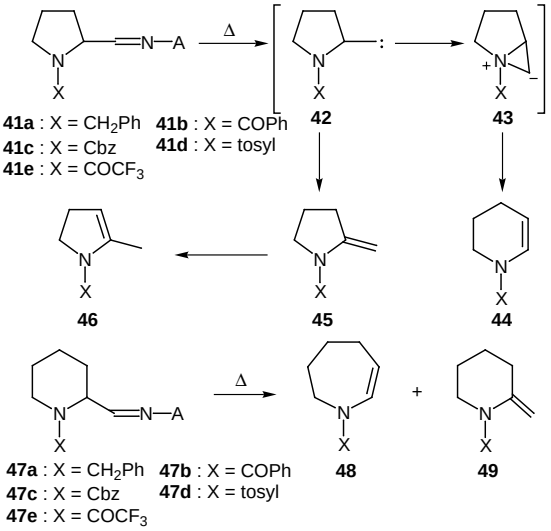
Scheme 6

The thermal reaction of **33a** in refluxing toluene would generate carbene intermediate **34** via aziridine ring opening and subsequent loss of styrene and nitrogen gas. Carbene **34** would be captured by a nitrogen atom to produce the transient ammonium ylide **35** from which **36a** is obtained via rearrangement. Furthermore, this ring expansion reaction could be similarly applied to the lactam derivatives (Scheme 7). Thermal reaction of **37a** in refluxing toluene for 5 hours afforded **40a** in 81% yield via ammonium ylide intermediate **39**. A similar result was also obtained with **37b**.



Scheme 7

To study the relative ease of 1,2-H migration and ring expansion via ammonium ylide intermediates in carbenes, we examined the thermal reaction of α-pyrrolidinyl-*N*-aziridinylimine **41** (Scheme 8). We anticipated that the reaction would give a mixture of two products **44** and **45** resulting from 1,2-H migration and ring expansion via an ammonium ylide intermediate **43** and the ratio of **44** and **45** would depend very much on the electron density at the nitrogen atom, suggesting that the ratio would be controlled by introducing different substituents. According to our reasoning, the higher electron density at the nitrogen atom would increase the formation of the ammonium ylide relative to 1,2-H migration by electrostatic interaction of an electron-deficient alkyl carbene with lone-pair electrons on the nitrogen atom. Thus, the electron densities at various nitrogen atoms were calculated by MOPAC[25] using PM3 method[26] as shown in the Figure. According to the computational data, the order of increasing the electron density at the nitrogen atom is trifluoroacetyl, *p*-toluenesulfonyl, benzyloxycarbonyl, benzoyl, and benzyl group. Since the trifluoroacetyl protected **41e** has the lowest electron density at the nitrogen atom, **46e** from 1,2-H migration would be formed the most. Similarly, it is expected that the most **44a** would be produced with benzyl protected **41a**.



Scheme 8

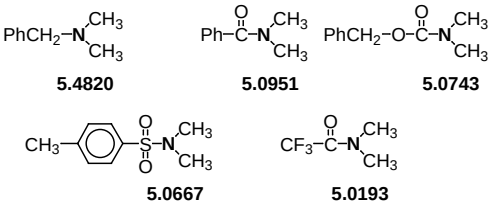
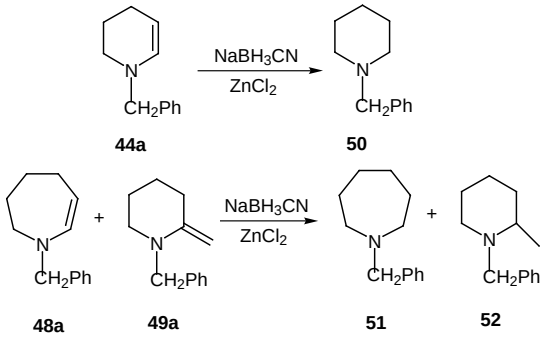


Figure Electron density of various nitrogen atoms.

Some experimental results for the thermal reaction of **41** and **47** are summarized in Table 2. Among piperidine derivatives **44**, *N*-benzyl protected derivative **44a** was labile and was reduced into *N*-benzylpiperidine with sodium cyanoborohydride and zinc chloride in methanol.[27] Similarly, **48a** and **49a** were also unstable and were reduced into *N*-benzylazepane and *N*-benzyl-2-methylpiperidine, respectively (Scheme 9). The experimental results obtained with pyrrolidine derivative **41** are in good agreement with the computational data. The thermal reaction of **41b** in refluxing toluene for 2 h afforded the ring expanded product **44b** in 59% yield along with 1,2-H migration product **46b**

in 12% yield. When slightly more electron-poor carbamate **41c** was used, a 50:26 mixture of **44c** and **46c** was obtained as we anticipated. As shown in Table 2, it is gratifying that the reaction of **41a** in refluxing toluene gave **44a** exclusively, whereas 1,2-H migration product **46e** was a sole product with **41e** under the same condition. However, as compared with pyrrolidine derivatives **41**, piperidine derivatives **47** gave much lower selectivities. Somewhat surprisingly, the thermal reaction of **47** in refluxing toluene provided 1,2-H migration products consistently as a major product. For instance, the reaction of **47a** under the same conditions afforded 1,2-H migration product **49a** as a major product along with the ring expansion product **48a** in 19% yield. This result is in sharp contrast with the result obtained with **41a**, where the ring expansion product was obtained as a sole product. Similarly, 1,2-H migration products **49b** and **49c** were obtained as major products with **47b** and **47c**. In the case of **47e**, only 1,2-H migration product **49e** was obtained. Although we have no clear answer for this observation, the results may be due to higher strain energy of pyrrolidine derivatives **41** relative to piperidine derivatives **47**, thereby promoting the ring expansion of **41**.[28] Spectral data of compounds **44**, **46**, **48** and **49** are assembled in Table 3.



Scheme 9

Table 2 Thermal Reaction of **41** and **47**

substrate	product 44	yield 46	substrate	product 48	yield 49
41a	71%	0%	**47a**	19%	54%
41b	59%	12%	**47b**	6%	64%
41c	50%	26%	**47c**	3%	86%
41d	17%	47%	**47d**	3%	81%
41e	0%	60%	**47e**	0%	72%

In conclusion, it has been found that carbene reactions of α-heterocyclo-*N*-aziridinylimines depend very much on the nature of heteroatoms and ring sizes. Ring expansion of α-oxacyclo-*N*-aziridinylimines occurred via two different pathways (i) 1,5-O−H insertion of alkylidenecarbene intermediates for oxetane derivatives and (ii) insertion of alkyl carbenes into carbon−carbon bonds for tetrahydrofuran and tetrahydropyran derivatives. Similarly, thermal reaction of α-azetidinyl-*N*-aziridinylimines proceeded via alkylidene carbene intermediates. However, the thermal reaction of α-pyrrolidinyl- and α-piperidinyl-*N*-aziridinylimines proceeded via the formation of ammonium ylides and/or 1,2-H migration and the ratio of two processes would depend on the electron density of the nitrogen atom and the ring size.

All reagents used were of commercial quality. All dry solvents were freshly distilled under N_2 from the appropriate drying agent before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC-200 and AC-300 spectrometers. The chemical shifts in $CDCl_3$ or benzene-d_6 reported in δ (ppm) relative to $CDCl_3$ or Me_4Si as an internal reference. IR spectra were measured on a Bomen MB-100 Fourier Transform spectrometer. HRMS were obtained on a VG Autospec Ultma GC/MS system using direct insertion probe (DIP) and electron impact (EI) (70 eV) method. Flash chromatography was carried out on Merck silica 60, 230-400 mesh ASTM; eluents are given in parentheses. Analytical TLC was performed on E. Merck precoated silica gel 60 F_{254} plates.

Thermal Reaction of α-Oxetanyl-*N*-aziridinylimine 1a; 4-Phenethyl-2,3-dihydrofuran (6a); Typical Procedure

In a flask equipped with a reflux condenser, α-oxetanyl-*N*-aziridinylimine **1a** (120 mg, 0.39 mmol) was dissolved in degassed toluene (3 mL) under N_2. The reaction flask was immersed into a preheated oil bath which was maintained at 120 °C. The reaction mixture was heated at reflux for 5 h and the evolution of N_2 gas observed. The mixture was allowed to cool to r.t. and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc, 30:1) to afford the dihydrofuran derivative **6a** (40 mg) in 59% yield.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.36 (t, 2 H, *J* = 8.0 Hz), 2.54 (t, 2 H, *J* = 9.4 Hz), 2.74 (t, 2 H, *J* = 8.0 Hz), 4.29 (t, 2 H, *J* = 9.4 Hz), 6.06 (s, 1 H), 7.16−7.27 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.2, 32.4, 34.6, 69.7, 113.9, 125.8, 128.3, 140.0, 141.9.

IR (film): ν = 2905, 1663, 1496, 1452 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{12}H_{14}O$ (M^+): 174.1045, found 174.1040.

3,4-Dihydro-6-phenethyl-2*H*-pyran (5b)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.62−1.70 (m, 2 H), 1.80−1.85 (m, 2 H), 2.13 (t, 2 H, *J* = 7.8 Hz), 2.64 (t, 2 H, *J* = 7.8 Hz), 3.84 (t, 2 H, *J* = 5.1 Hz), 4.25 (t, 1 H, *J* = 3.6 Hz), 6.97−7.08 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6, 22.9, 33.8, 36.8, 65.9, 95.5, 125.9, 128.4, 128.6, 142.0, 154.0.

IR (film): ν = 2933, 1675 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O$ (M^+): 188.1201, found 188.1208.

3-Phenethylcyclohept-2-ene Ether (5c)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.45−1.70 (m, 4 H), 1.81−1.95 (m, 2 H), 2.11 (t, 2 H, *J* = 7.8 Hz), 2.60 (t, 2 H, *J* = 7.8 Hz), 3.76 (t, 2 H, *J* = 5.1 Hz), 4.44 (t, 1 H, *J* = 5.6 Hz), 6.94−7.09 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6, 23.9, 25.0, 31.6, 32.9, 64.9, 92.5, 126.5, 127.7, 128.4, 139.8, 153.8.

Table 3 Spectral Data of Compounds **44**, **46**, **48**, and **49** (Scheme 8)

Product	^{1}H NMR (200 MHz, $CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR (50 MHz, $CDCl_3$/TMS) δ, *J* (Hz)	IR (film) ν (cm^{-1})	HRMS Calcd	Found
44b	1.77−1.92 (m, 2 H), 2.37−2.58 (m, 2 H), 3.86 (t, 2 H, *J* = 8.1), 5.01 (2 s, 1 H), 6.72 (br s, 1 H), 7.24−7.46 (m, 5 H)	23.1, 30.1, 41.5, 104.5, 126.8, 128.6, 131.4, 134.4, 134.8, 160.2	2924, 1637, 1388, 1263, 1148	187.0997	187.0995
46b	2.15 (s, 3 H), 2.59 (t, 2 H, *J* = 6.5), 3.45 (q, 2 H, *J* = 6.5), 5.04 (m, 1 H), 7.24−7.78 (m, 5 H)	23.1, 30.1, 41.5, 104.5, 126.8, 128.6, 131.4, 134.4, 134.8, 160.2	2930, 1656, 1447, 1270, 1176	187.0997	187.0993
44c	1.69−1.87 (m, 2 H), 1.97−2.06 (m, 2 H), 3.58 (t, 2 H, *J* = 6.1), 4.83 (m, 1 H), 5.07 (2 s, 2 H), 6.79 (d, 1 H, *J* = 8.5), 7.23−7.36 (m, 5 H)	21.9, 29.5, 41.0, 66.4, 108.5, 127.8, 127.9, 128.5, 130.7, 137.1, 151.2	2933, 1701, 1399, 1247, 1192	217.1103	217.1109
46c	2.11 (s, 3 H), 3.18 (q, 2 H, *J* = 6.7), 3.84 (t, 2 H, *J* = 9.2), 4.95 (m, 1 H), 5.12 (2 s, 2 H), 7.24−7.35 (m, 5 H)	18.9, 27.5, 40.9, 66.4, 113.9, 127.8, 127.9, 128.5, 137.0, 138.3, 153.4	2888, 1663, 1454, 1272, 1132	217.1103	217.1105
44d	1.55−1.74 (m, 2 H), 1.84−1.90 (m, 2 H), 2.40 (s, 3 H), 3.31−3.37 (m, 2 H), 4.95 (m, 1 H), 6.61 (d, 1 H, *J* = 8.4), 7.28 (d, 2 H, *J* = 8.3), 7.68 (d, 2 H, *J* = 8.3)	21.6, 22.8, 30.7, 46.9, 123.5, 126.7, 127.1, 129.2, 137.2, 144.8	2945, 1644, 1450, 1339, 1162	237.0823	237.0819
46d	2.11 (s, 3 H), 2.40 (s, 3 H), 2.50 (t, 2 H, *J* = 6.6), 2.92 (t, 2 H, *J* = 6.6), 4.54 (t, 1 H, *J* = 6.1), 7.28 (d, 2 H, *J* = 8.3), 7.68 (d, 2 H, *J* = 8.3)	18.7, 21.6, 27.8, 46.4, 126.9, 127.5, 129.0, 129.1, 137.8, 144.8	2865, 1638, 1595, 1498, 1301, 1094	237.0823	237.0815
46e	2.12 (s, 3 H), 2.42−2.47 (m, 2 H), 2.98−3.27 (m, 2 H), 4.72 (m, 1 H)	17.0, 27.5, 44.5, 113.9, 114.2 (q, *J* = 342.6), 128.9, 154.3 (q, *J* = 37.9)	2938, 1741, 1498, 1268, 1028	179.0558	179.0558
48b	1.68−1.84 (m, 4 H), 2.00−2.11 (m, 2 H), 3.61 (t, 2 H, *J* = 5.2), 5.02 (t, 1 H, *J* = 5.0), 6.23 (s, 1 H), 7.23−7.51 (m, 5 H)	24.3, 24.8, 28.0, 43.2, 109.0, 127.1, 127.5, 129.0, 130.6, 133.4, 169.1	2944, 1631, 1378, 1273, 1149	201.1154	201.1142
48c	1.64−1.81 (m, 4 H), 1.97− 2.06 (m, 2 H), 3.69 (t, 2 H, *J* = 5.9), 5.14 (s, 2 H), 5.17 (t, 1 H, *J* = 4.8), 6.18 (s, 1 H), 7.28−7.35 (m, 5 H)	23.9, 25.3, 29.2, 40.7, 66.4, 109.0, 127.8, 127.9, 128.5, 131.2, 137.1, 151.1	2841,1661, 1498,1136, 1028	231.1259	231.1247
49c	1.59−1.75 (m, 4 H), 2.18 (t, 2 H, *J* = 5.5), 3.57 (m, 2 H), 4.89 (d, 2 H, *J* = 3.5), 5.15 (s, 2 H), 7.28−7.32 (m, 5 H)	22.7, 25.7, 32.6, 44.6, 66.9, 111.5, 127.5, 127.9, 128.5, 138.5, 143.9, 154.3	2931, 1705, 1397, 1340, 1250, 1190	231.1259	231.1239
48d	1.42−1.53 (m, 4 H), 1.73−1.85 (m, 2 H), 2.32 (s, 3 H), 3.41 (t, 2 H, *J* = 5.0), 4.97 (m, 1 H), 6.38 (d, 1 H, *J* = 2.3), 7.18 (d, 2 H, *J* = 8.4), 7.62 (d, 2 H, *J* = 8.3)	21.4, 23.1, 27.6, 29.7, 48.4, 120.9, 126.2, 128.0, 132.3, 140.2, 143.9	2863, 1598, 1495, 1402, 1250, 1032	251.0980	251.0975
49d	1.40−1.58 (m, 4 H), 1.92 (t, 2 H, *J* = 5.5), 2.35 (s, 3 H), 3.55 (t, 2 H, *J* = 5.0), 4.72 (s, 1 H), 4.96 (s, 1 H), 7.22 (d, 2 H, *J* = 8.3), 7.66 (d, 2 H, *J* = 8.2)	21.3, 24.1, 24.6, 31.7, 47.7, 108.0, 126.7, 127.1, 129.4, 137.8, 142.9	2942, 1645, 1447, 1340, 1159, 1092	251.0980	251.0972
49e	1.63−1.87 (m, 4 H), 2.27 (t, 2 H, *J* = 5.2), 3.68 (t, 2 H, *J* = 5.4), 4.58 (d, 2 H, *J* = 3.2)	24.2, 25.7, 30.7, 46.5, 98.5, 114.2 (q, *J* = 338.4), 17.0, 27.5, 44.5, 113.9, 114.2 (q, *J* = 338.3), 137.7, 154.3 (q, *J* = 37.4)	2948, 1738, 1455, 1272, 1014	193.0714	193.0717

6-Benzyl-2,3,3a,4,5,6-hexahydrobenzofuran (9) (Scheme 2)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.60−1.67 (m, 6 H), 1.92−1.98 (m, 1 H), 2.31−2.37 (m, 1 H), 2.55 (d, 2 H, *J* = 7.5 Hz), 3.96 (t, 2 H, *J* = 5.0 Hz), 4.52 (d, 1 H, *J* = 3.8 Hz), 7.08−7.21 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.3, 28.0, 30.6, 34.9, 39.9, 49.3, 66.2, 95.3, 126.3, 127.8, 128.1, 138.2, 160.2.

IR (film): ν = 2921, 1653, 1440, 1264, 1003 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{18}O$ (M^+): 214.1358, found 214.1347.

4-Heptyl-2,3-dihydrofuran (11) (Table 1)
^1H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, 3 H, *J* = 6.7 Hz), 1.23−1.44 (m, 10 H), 2.01 (t, 2 H, *J* = 6.8 Hz), 2.50 (tt, 2 H, *J* = 9.3, 1.0 Hz), 4.27 (t, 2 H, *J* = 9.3 Hz), 6.03 (t, 1 H, *J* = 1.0 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.2, 28.0, 29.3, 29.6, 31.9, 32.4, 69.7, 114.8, 139.4.

IR (film): ν = 2926, 2855, 1462, 1094 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{11}H_{20}O$ (M^+): 168.1514, found 168.1518.

4,5,6,7,8,8a-Hexahydro-1*H*-cyclohepta[*c*]furan (12) (Table 1)
^1H NMR (200 MHz, $CDCl_3$): δ = 1.23−1.63 (m, 8 H), 2.00−2.36 (m, 2 H), 2.71−2.80 (m, 1 H), 3.59 (t, 1 H, *J* = 8.5 Hz), 4.15 (t, 1 H, *J* = 8.5 Hz), 5.83 (t, 1 H, *J* = 1.6 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.4, 28.2, 28.8, 30.4, 34.8, 45.5, 76.5, 118.7, 140.9.

IR (film): ν = 2955, 2918, 1472, 1079 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_9H_{14}O$ (M^+): 138.1045, found 138.1051.

3a-Methyl-3,3a,4,5-tetrahydronaphtho[1,2-*c*]furan (13) (Table 1)
^1H NMR (200 MHz, $CDCl_3$): δ = 1.21 (s, 3 H), 1.65−1.98 (m, 2 H), 2.78−3.11 (m, 2 H), 3.98 (d, 1 H, *J* = 8.4 Hz), 4.33 (d, 1 H, *J* = 8.4 Hz), 6.73 (s, 1 H), 7.07−7.38 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.4, 26.5, 33.2, 42.9, 84.1, 121.1, 123.9, 125.6, 126.0, 129.0, 129.1, 133.3, 138.4.

IR (film): ν = 2923, 1691, 1483, 1453, 1147, 1087 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{14}O$ (M^+): 186.1045, found 186.1046.

4-Benzyl-2,6-dimethyl-3,4-dihydro-2*H*-pyran (14) (Table 1)
^1H NMR (200 MHz, 7 wt % benzene-d_6 in CCl_4): δ = 1.12 (d, 3 H, *J* = 6.3 Hz), 1.32, 1.36 (2 s, 3 H), 1.38−1.50 (m, 2 H), 1.71−1.80 (dd, 1 H, *J* = 6.9, 12.3 Hz), 2.40−2.52 (m, 1 H), 2.75 (dd, 1 H, *J* = 5.0, 13.8 Hz), 3.90−4.16 (m, 1 H), 4.46 (m, 1 H), 6.98−7.18 (m, 5 H).

^{13}C NMR (50 MHz, 7 wt % benzene-d_6 in CCl_4): δ = 12.2, 21.4, 38.1, 39.2, 41.5, 74.8, 89.7, 126.5, 128.8, 129.4, 140.3, 159.4.

IR (film): ν = 2970, 1693, 1495, 1451, 1168 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{18}O$ (M^+): 202.1358, found 202.1340.

8-Benzyl-2,3,4,4a,5,6,7,8-octahydrocyclohepta[*b*]pyran (15) (Table 1)
^1H NMR (200 MHz, $CDCl_3$): δ = 1.25−1.34 (m, 8 H), 1.62−1.68 (m, 2 H), 2.10−2.22 (m, 1 H), 2.39−2.43 (m, 1 H), 2.52 (d, 2 H, *J* = 7.1 Hz), 3.96 (t, 2 H, *J* = 5.2 Hz), 4.35 (d, 1 H, *J* = 5.4 Hz), 7.05−7.25 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 22.9, 24.6, 25.2, 33.1, 34.6, 38.9, 45.5, 65.4, 98.2, 126.3, 127.5, 128.1, 138.0, 159.2.

IR (film): ν = 2977, 1682, 1451, 1092, 1059 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{22}O$ (M^+): 242.1671, found 242.1690.

10a-Methyl-2,9,10,10a-tetrahydro-1*H*-3-oxabenzo[*f*]azulene (16) (Table 1)
^1H NMR (200 MHz, $CDCl_3$): δ = 1.21 (s, 3 H), 1.86−2.08 (m, 4 H), 2.89−3.06 (m, 2 H), 4.18−4.26 (m, 2 H), 5.80 (s, 1 H), 7.01−7.16 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.6, 31.5, 36.4, 41.2, 43.2, 67.7, 99.0, 124.1, 126.0, 129.7, 130.0, 134.6, 137.3, 166.1.

IR (film): ν = 1670, 1154, 1098, 1013, 754 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{16}O$ (M^+): 200.1201, found 200.1217.

4a-Methyl-3,4,4a,5-tetrahydro-2*H*-benzo[*g*]chromene (17) (Table 1)
^1H NMR (200 MHz, $CDCl_3$): δ = 1.09 (s, 3 H), 1.60−1.73 (m, 2 H), 1.79−1.86 (m, 1 H), 2.03−2.19 (m, 1 H), 2.59 (d, 1 H, *J* = 15.2 Hz), 2.88 (d, 1 H, *J* = 15.2 Hz), 3.72 (dt, 1 H, *J* = 2.3, 8.5 Hz), 4.19−4.28 (m, 1 H), 5.84 (s, 1 H), 6.96−7.16 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.9, 22.3, 34.9, 36.5, 45.3, 68.9, 104.6, 124.6, 124.8, 126.3, 127.3, 131.6, 134.8, 161.5.

IR (film): ν = 1642, 1277, 1142, 1103, 753 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{16}O$ (M^+): 200.1201, found 200.1216.

3-Phenyl-2,3-dihydrofuran (20) (Scheme 3)
^1H NMR (200 MHz, $CDCl_3$): δ = 3.71 (dd, 1 H, *J* = 2.3, 3.6 Hz), 3.75−3.92 (m, 1 H), 4.10 (dd, 1 H, *J* = 2.3, 3.6 Hz), 5.52 (t, 1 H, *J* = 5.2 Hz), 6.08 (d, 1 H, *J* = 5.2 Hz), 7.11−7.29 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 44.8, 73.6, 79.7, 126.1, 128.4, 128.5, 138.9, 165.2.

IR (film): ν = 2918, 1652, 1475, 1455 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{10}H_{10}O$ (M^+): 146.0732, found 146.0737.

5-Phenethyl-6-methyl-3,4-dihydro-2*H*-pyran (24) (Scheme 3)
^1H NMR (200 MHz, $CDCl_3$): δ = 1.63−1.73 (m, 4 H), 1.70 (s, 3 H), 3.15 (s, 2 H), 3.16 (t, 2 H, *J* = 5.1 Hz), 6.96−7.13 (m, 5 H).

^{13}C NMR (50 MHz, 7 wt % benzene-d_6 in CCl_4): δ = 17.0, 23.5, 24.7, 38.8, 65.4, 104.7, 126.0, 128.4, 128.5, 141.0, 172.0.

5-Phenethyl-2,3-dihydro-[1,4]dioxine (28a) (Scheme 4)
^1H NMR (200 MHz, $CDCl_3$): δ = 2.24 (dd, 2 H, *J* = 6.1, 8.2 Hz), 2.77 (t, 2 H, *J* = 7.3 Hz), 3.94−3.98 (m, 2 H), 4.06−4.11 (m, 2 H), 5.76 (s, 1 H), 7.16−7.32 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 32.5, 33.5, 63.8, 64.6, 122.2, 125.8, 128.2, 128.4, 136.6, 141.5.

IR (film): ν = 1684, 1174, 1130, 1093, 701 cm^{-1}.

HRMS (EI): calcd for $C_{12}H_{14}O_2$ (M^+): 190.0994, found 190.1005.

2-Benzyl-6,7-dihydro-5*H*-[1,4]dioxepine (28b) (Scheme 4)
^1H NMR (200 MHz, $CDCl_3$): δ = 2.01 (m, 2 H), 2.18 (t, 2 H, *J* = 8.2 Hz), 2.74 (t, 2 H, *J* = 7.2 Hz), 3.96 (t, 2 H, *J* = 5.7 Hz), 4.06 (t, 2 H, *J* = 5.7 Hz), 5.66 (s, 1 H), 7.13−7.26 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.4, 32.0, 40.3, 60.6, 69.7, 75.9, 126.3, 128.3, 128.6, 140.7, 208.1.

IR (film): ν = 1680, 1188, 1079 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O_2$ (M^+): 204.1150, found 204.1157.

Thermal Reaction of α-Azetidino-*N*-aziridinylimine 29a; *N*-Benzylbut-3-ynylamine (31a); Typical Procedure
In a flask equipped with a reflux condenser, α-azetidinyl-*N*-aziridinylimine **29a** (63 mg, 0.22 mmol) was dissolved in degassed toluene (2 mL) under N_2. After stirring at 120 °C for 6 h, TLC showed the disappearance of the starting material and the generation of a new spot. The mixture was cooled to r.t. and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc, 2:1) to afford **31a** (28 mg, 81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69 (br s, 1 H), 1.98 (t, 1 H, *J* = 2.6 Hz), 2.40 (td, 2 H, *J* = 6.6, 2.6 Hz), 2.79 (t, 2 H, *J* = 6.6 Hz), 3.80 (s, 2 H), 7.18−7.32 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5, 47.3, 53.4, 69.5, 82.5, 127.0, 128.1, 128.4, 140.1.

IR (film): ν = 3296, 2922, 1456, 1121 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{11}H_{13}N$ (M^+): 159.1048, found 159.1065.

(*N*-But-3-ynyl)-4-methylbenzenesulfonamide (31b) (Scheme 6)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97 (t, 1 H, *J* = 2.6 Hz), 2.32 (tt, 2 H, *J* = 6.6, 2.6 Hz), 2.41 (s, 3 H), 3.08 (td, 2 H, *J* = 6.6, 6.3 Hz), 4.87 (t, 1 H, *J* = 6.3 Hz), 7.29 (d, 2 H, *J* = 8.0 Hz), 7.73 (d, 2 H, *J* = 8.4 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.7, 21.5, 41.2, 70.8, 80.3, 127.0, 129.8, 136.9, 143.6.

IR (film): ν = 3289, 2922, 1599, 1427, 1326, 1160, 1094 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{11}H_{13}NO_2S$ (M^+): 223.0667, found 223.0669.

(6-Methyl-3,4-dihydro-2*H*-pyridin-1-yl)phenylmethanone (36a) (Scheme 6)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.56, 1.62 (2 s, 3 H), 1.90−2.06 (m, 4 H), 3.46, 3.76 (2 t, 2 H, *J* = 5.9 Hz), 6.21, 7.10 (2 s, 1 H), 7.33−7.47 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.7, 27.4, 40.6, 46.1, 116.4, 122.2, 127.4, 128.2, 128.3, 135.4, 168.7.

IR (film): ν = 2927, 1637, 1387, 1269, 1149 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{15}NO$ (M^+): 201.1154, found 201.1154.

6-Methyl-3,4-dihydro-2*H*-pyridine-1-carboxylic Acid *tert*-Butyl Ester (36b) (Scheme 6)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.46 (s, 9 H), 1.64 (s, 3 H), 1.68−1.83 (m, 2 H), 1.92 (t, 2 H, *J* = 5.9 Hz), 3.43−3.54 (m, 2 H), 6.47, 6.62 (2 s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.9, 26.9, 28.3, 40.9, 44.5, 64.3, 111.2, 120.3, 153.2.

IR (film): ν = 1697, 1397, 1360, 1165 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{11}H_{19}NO_2$ (M^+): 197.1416, found 197.1419.

6-Benzyl-1,3,4,5-tetrahydro-2*H*-azepin-2-one (40a) (Scheme 7)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.76−1.89 (m, 2 H), 2.40−2.58 (m, 4 H), 3.34 (d, 2 H, *J* = 7.8 Hz), 4.94 (tt, 1 H, *J* = 7.8, 1.4 Hz), 7.13−7.31 (m, 5 H), 8.37 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.5, 23.0, 32.0, 32.3, 105.2, 126.0, 128.1, 128.4, 134.8, 140.8, 170.8.

IR (film): ν = 3203, 2946, 1671, 1392, 1183 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{15}NO$ (M^+): 201.1154, found 201.1156.

7-Benzyl-3,4,5,6-tetrahydroazocin-2(1*H*)-one (40b) (Scheme 7)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.69−1.78 (m, 2 H), 1.89−2.02 (m, 1 H), 2.10−2.19 (m, 1 H), 2.33 (t, 2 H, *J* = 8.0 Hz), 2.77 (t, 2 H, *J* = 7.4 Hz), 3.33 (d, 2 H, *J* = 7.4 Hz), 5.14 (t, 1 H, *J* = 7.4 Hz), 6.93 (br s, 1 H), 7.12−7.32 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.4, 26.3, 32.6, 34.8, 36.1, 113.0, 126.2, 128.3, 128.5, 135.1, 139.6, 175.7.

IR (film): ν = 2945, 1651, 1454, 1215, 1075 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{17}NO$ (M^+): 215.1310, found 215.1329.

1-Benzylpiperidine (50); Typical Procedure
A solution of **41a** (90 mg, 0.25 mmol) was stirred in refluxing toluene for 4 h and the mixture was concentrated under reduced pressure. After MeOH (3 mL) was added to the crude product, $NaBH_3CN$ (39 mg, 0.50 mmol) and $ZnCl_2$ (42 mg, 0.25 mmol) were added. After stirring for 1 h at r.t., most of the MeOH was evaporated under reduced pressure and the mixture was poured into aq 0.1 N NaOH solution (10 mL). The aqueous layer was extracted with EtOAc (20 mL) and the organic layer was washed with brine (20 mL). The combined organic extracts were dried, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc, 2:1) to afford **50** (31 mg, 71%) as a colorless oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.38−1.47 (m, 2 H), 1.57 (m, 4 H, *J* = 5.9 Hz), 2.28 (t, 4 H, *J* = 4.7 Hz), 3.49 (s, 2 H), 7.22−7.31 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.3, 25.9, 54.4, 63.8, 126.7, 128.0, 129.1, 138.5.

IR (film): ν = 3028, 2935, 2765, 1454, 1347, 1114 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{12}H_{17}N$ (M^+): 175.1361, found 175.1377.

1-Benzylazepane (51) (Scheme 9)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.25−1.39 (m, 4 H), 1.40−1.51 (m, 2 H), 1.58−1.64 (m, 2 H), 2.39 (t, 4 H, *J* = 4.7 Hz), 3.83 (s, 2 H), 7.24−7.38 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.1, 24.2, 53.7, 63.8, 125.9, 127.0, 127.7, 138.5.

IR (film): ν = 3011, 2952, 1603, 1451, 1059 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{19}N$ (M^+): 189.1517, found 189.1523.

1-Benzyl-2-methylpiperidine (52) (Scheme 9)
^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.09 (d, 3 H, *J* = 6.3 Hz), 1.42−1.58 (m, 2 H), 1.60−1.67 (m, 4 H), 2.37 (t, 2 H, *J* = 4.5 Hz), 2.40−2.52 (m, 1 H), 3.49 (s, 2 H), 7.24−7.38 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.3, 24.3, 25.9, 34.6, 54.4, 57.3, 63.7, 126.7, 128.1, 128.7, 142.1.

IR (film): ν = 3030, 2955, 1609, 1454, 1067 cm^{-1}.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{19}N$ (M^+): 189.1517, found 189.1527.

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