141.78, 109.30, 73.90 (down), 41.10. Anal. Calcd for ($C_{16}H_{22}N_4P_2F_{12}$·H_2O): C, 33.23; H, 4.18; N, 9.69. Found: C, 32.80; H, 4.00; N, 9.54.

Preparation of DMAP·HCl. To a solution of 150 mg (1.23 mmol) of DMAP in 5 mL of H_2O at 0 °C was added 3 mL of 6 M HCl. The excess HCl and water were removed via vacuum transfer: UV (H_2O) λ_{max} 280 nm; ^1H NMR (D_2O, CH_3CN standard) 7.86 (2 H, d, J = 7.7), 6.71 (2 H, d, J = 7.7), 3.04 (6 H, s (CD_3OD)), 8.02 (2 H, d, J = 7.3), 6.90 (2 H, d, J = 7.3), 3.13 (6 H, s ($CD_3)_2CO$)), 8.19 (2 H, d, J = 7.5), 7.04 (2 H, d, J = 7.6), 3.32 (6 H, s); ^{13}C NMR (CD_3OD) 158.6, 139.6, 108.2, 40.7.

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Registry No. 1·2Cl^-, 130146-51-9; 1·2PF_6^-, 130146-54-2; 2·4Cl^-, 90432-32-9; 2·4PF_6^-, 114692-31-8; 3·2Cl^-, 106538-37-8; 4, 130146-52-0; DMAP·HPF_6, 130146-53-1; DMAP·HCl, 71561-71-2; DMAP, 1122-58-3.

Reductive Radical Cyclizations of Haloalkenes Promoted by Samarium Diiodide. Sequential Cyclization/Intermolecular Carbonyl Addition Reactions

Gary A. Molander*[,1] and Lori S. Harring

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

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A sequential radical cyclization/intermolecular carbonyl addition process promoted by samarium(II) iodide (SmI_2) is reported. Treatment of appropriate haloalkenes with SmI_2 in the presence of a variety of ketones leads to products resulting from cyclization followed by intermolecular addition of the resultant anion to the carbonyl electrophiles. Although several mechanisms can be envisioned, this process is most likely initiated by SmI_2-induced formation of a hexenyl radical. Intramolecular addition of this radical to the tethered alkene leads to generation of a new alkyl radical, which can be reduced in situ to the corresponding organosamarium species. This organosamarium adds to the carbonyl electrophile, completing the tandem process. In this study, 2-(allyloxy)ethyl iodide and 2-(allyloxy)-1-iodobenzene were the most thoroughly examined radical precursors. The anion intermediates ultimately derived from these starting materials were trapped with a range of ketones to yield the corresponding heterocyclic derivatives.

Intramolecular radical cyclization reactions have proven to be an efficient means for the generation of heterocyclic compounds. Although such radical cyclization processes have found widespread use in recent years,[2] the currently available methods are not without some drawbacks and limitations. We have recently developed an efficient and mild route to a variety of heterocyclic compounds which complements these more traditional protocols. The method involves a sequential radical cyclization/intermolecular carbonyl addition reaction which leads to functionalized heterocycles.

Perhaps the most commonly utilized means of radical generation involves treatment of a halide with R_3SnH. Generally, the radicals produced in the R_3SnH-mediated cyclization process are terminated by hydrogen abstraction, usually from the R_3SnH present in the reaction mixture. This process, however, results in a net loss of functionality in proceeding from the starting material to the products of the reaction. In addition, the removal of tin-containing byproducts from the reaction mixture is not always a trivial matter.[3] Alternative methods for radical cyclization/termination, including atom-transfer reactions,[4] electrochemical processes,[5] oxidative free-radical cyclization processes,[6] and other miscellaneous reactions,[7] have been developed which involve entrapment or further reaction of intermediate radical species. These processes tend to provide products with greater or at least comparable functionality in the products as compared to that found in the starting material. Although reaction sequences have also been developed in which radical cyclization precedes a second (radical) carbon–carbon bond-forming reaction, care must be taken in these transformations to tune each substrate in order to avoid polymerization and other undesirable side reactions.[8]

Other reductive processes provide useful alternatives to the aforementioned reactions for further elaboration of the cyclized radical intermediates.[9] Previously, Kagan dem-

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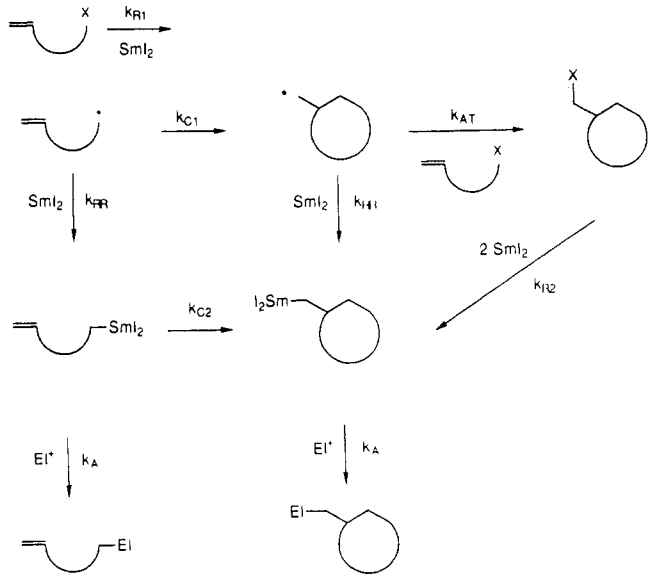
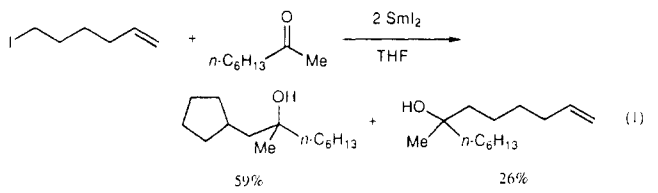
Scheme I

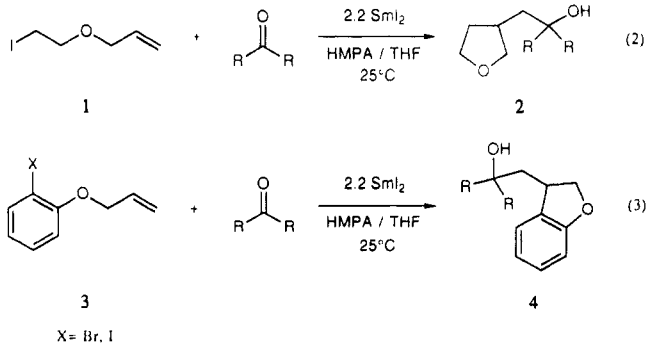


onstrated the SmI_2-promoted reductive cyclization of 5-bromo-1-hexene, in which a cyclized intermediate could be coupled with 2-octanone in a respectable yield (eq 1).[10] In addition to this cyclized product, the product resulting from addition of a hexenylsamarium species to 2-octanone was isolated.



(1)

In an effort to delineate the full synthetic potential of SmI_2 in such a process and to clarify the mechanism of this transformation, we have undertaken a more thorough investigation. In this initial study, the two precursors chosen for investigation were 2-(allyloxy)ethyl iodide (**1**)[11] (eq 2) and 2-(allyloxy)-1-iodobenzene (**3**)[12] (eq 3). We chose to examine these systems because the radicals derived from these precursors were known to cyclize rapidly. These substrates were also of interest as the resulting heterocycles bear functionality found in several naturally occuring heterocycles.[13]



(2)

(3)

X = Br, I

Table I. Radical Cyclization/Carbanion Carbonyl Addition of 1

ketone	product	% isolated yield[a]
3-pentanone	**2a**	57
4-heptanone	**2b**	38
cyclopentanone	**2c**	53
cyclohexanone	**2d**	52
2-methylcyclohexanone	**2e**	74[b]
4-*tert*-butylcyclohexanone	**2f**	55[c]

[a] Refers to yields of purified material. All the compounds reported have been fully characterized spectroscopically (^1H NMR, ^{13}C NMR, IR) as well as by high resolution mass spectrometry. [b] A diastereomeric ratio of 1.3:1 was observed in the crude reaction mixture as determined by GC and ^1H NMR and ^{13}C NMR analyses. [c] A diastereomeric ratio of 5:1 was observed in the crude reaction mixture as determined by ^1H NMR and ^{13}C NMR analysis.

The choice of substrate **1** in this study allowed us to resolve the nature of the species undergoing cyclization. Scheme I illustrates possible mechanistic pathways for this type of sequential cyclization/intermolecular coupling of haloalkene substrates. At first glance, the possibility of intramolecular olefin insertion into a carbon–samarium bond (k_{C2}) cannot be ruled out as a plausible mechanism for the production of the cyclized anion. Although direct analogies are not available, kinetic studies performed on olefin insertion reactions of organolanthanides[14] seem to suggest that β-elimination of the straight-chain organosamarium derived from **1** (which would generate ethylene and the alkoxide of allyl alcohol)[10] would occur at a rate at least comparable to that of olefin insertion. This would lead to reduced yields of the desired cyclized/intermolecularly trapped material. As shown in Table I, reasonable yields of the cyclized/coupled products are obtained. We therefore believe that a radical process is involved in the key cyclization step of the tandem process.

Based on this data alone, the interjection of an atom-transfer process (k_{AT}) cannot be ruled out. There is substantial precedent for the exchange of iodide between alkyl iodides and alkyl radicals, and the rate of this atom transfer process has been estimated at 10^5 M^{-1} s^{-1}.[15] Subsequent reduction (k_{RR}) of the cyclized iodide generated by this process would produce an organosamarium species, which could react with the carbonyl electrophile. Further study will be necessary to determine the significance of atom transfer in this overall process.

As is evident from Scheme I, optimization of the desired tandem process requires efficient partitioning between radical cyclization (k_{C1}) and reduction of the first intermediate radical by SmI_2 (k_{RR}). Because k_{RR} is a second-order process which depends on the concentration of SmI_2, it is clear that the desired process would benefit by high-dilution conditions and rapid cyclization rates. Consequently, reactions were carried out at quite low concentrations of SmI_2 (0.005–0.016 M). Besides the fact that important mechanistic information could be gained by use of **1** and **2** as haloalkene precursors, they also were expected to be excellent synthetic substrates. Radicals generated from both **1** and **3** have been shown to cyclize more rapidly than the 1-hexenyl radical ($k_C = 10^5$ s^{-1}), with $k_C = 10^6$ s^{-1} and 4×10^9 s^{-1}, respectively. In addition, efficient cyclization followed by trapping of the various electrophiles employed in this reaction would provide in-

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Table II. Radical Cyclization/Carbanion Carbonyl Addition of 3 (X = I)

ketone	product	% isolated yield[a]
3-pentanone	**4a**	69 (60)[b]
4-heptanone	**4b**	81
cyclopentanone	**4c**	68
cyclohexanone	**4d**	65
2-methylcyclohexanone	**4e**	70[c]
4-*tert*-butylcyclohexanone	**4f**	67[d]

[a] Refers to yields of purified material. All the compounds reported have been fully characterized spectroscopically (^{1}H NMR, ^{13}C NMR, IR) as well as by high-resolution mass spectrometry. [b] Refers to yield of reaction with 2-(allyloxy)-1-bromobenzene (X = Br). [c] A diastereomeric ratio of 1.3:1 was observed in the crude reaction mixture as determined by ^{1}H NMR and ^{13}C NMR analyses. [d] A diastereomeric ratio of 2:1 was observed in the crude reaction mixture as determined by ^{1}H NMR and ^{13}C NMR analyses.

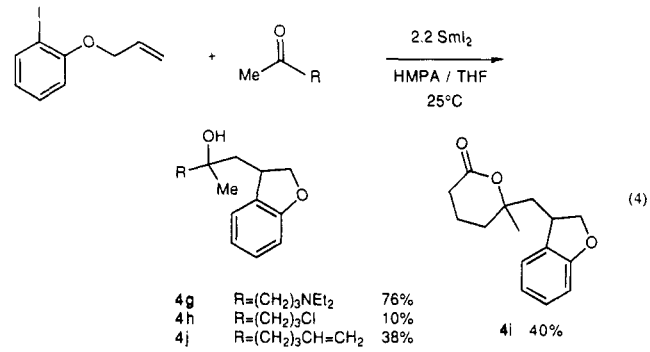
terestingly functionalized heterocyclic derivatives. As expected, good yields of the cyclized, intermolecularly trapped products were isolated from the reaction mixtures (Tables I and II). The major byproduct in most cases was the cyclized, protonated material, with a small amount of the reduced starting material also present.

The intermediacy of an organosamarium species in this tandem process was further supported by running the reaction in the presence of MeOD. At least 75% of the cyclized material was deuterated at the exocyclic methyl position, as determined by GC–MS analysis and ^{13}C NMR. The interception of the initially formed benzofuranylmethyl radical by hydrogen atom abstraction from THF no doubt competes with anion formation, thereby accounting for some of the protonated material. However, it is apparent that a significant amount of the cyclized radical species is reduced by a second equivalent of SmI_2 to generate an anionic species which can subsequently be trapped by a proton source or a carbonyl electrophile.

Stereochemical aspects of the reaction were not investigated in great detail; however, two examples involving ketones which could lead to diastereomeric products (**2e,f** and **4e,f**) were examined. When 2-methylcyclohexanone was used as the carbonyl electrophile, a nearly 1:1 mixture of the two diastereomeric alcohols was obtained for both substrates **1** and **3**. However, in the case of 4-*tert*-butylcyclohexanone, a 5:1 ratio of the two alcohols was observed in the crude reaction mixture involving substrate **1**, and a 2:1 ratio of the two alcohols was observed in the crude reaction mixture of **3**.

The reaction conditions employed in this study were not conducive to the traping of aldehydes in high yields because of the high propensity of aldehydes to undergo reduction in the presence of SmI_2 and HMPA at room temperature. Although both hexanal and nonanal were trapped using this methodology, products resulting from the trapping were isolated only in the range of 30%. However, ketones bearing a wide range of functionality, including remote ester, olefin, and amine appendages, were found to undergo cyclization and trapping quite efficiently. The only exception was in the case of a ketone bearing a γ-chlorine atom, in which case only a 10% yield of the desired product was isolated (eq 4). In all cases, two diastereomeric products were obtained because of the unsymmetrical nature of the ketones. In the case of **4i**, the product isolated was the lactone corresponding to cyclization of the initially formed γ-hydroxy ester.

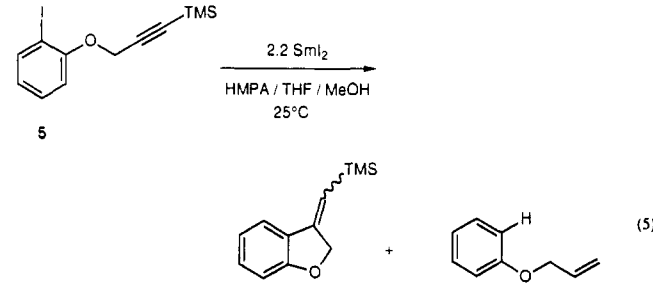
In addition to the carbonyl electrophiles discussed above, several other electrophiles were examined. Among those employed, TMSCl, cyclohexene oxide, and methyl iodide provided none of the desired cyclized trapped products. In all cases, the product resulting from cyclization and



(4)

protonation of the substrate was the predominant product in the reaction mixture.

We were also interested in exploring the scope of the reaction in regard to the range of side chains that could be incorporated into the radical precursor. It was important to determine the effects of chain length, the type of unsaturation in the side chain, and the effect of other heteroatoms on overall reactivity. In this light, substrate **5** was subjected to the reaction conditions in the presence of methanol. In fact, an inseparable mixture of three products was formed. The mixture included the two geometrical olefinic isomers resulting from cyclization onto the alkyne followed by hydrogen atom abstraction, as well as the product resulting from simple reduction of the starting material. Further attempts to trap the cyclized intermediate with an electrophile other than methanol were unsuccessful. These results imply that the alkenyl radical formed from radical cyclization onto the alkyne abstracts a hydrogen from the solvent faster than it is reduced to the anion by SmI_2. Similar results have been observed previously in related processes.[16]



(5)

The use of 2-(3-butenyloxy)iodobenzene was also examined as a radical precursor in this reaction. In fact, it was possible to achieve a 57% isolated yield of the cyclized material which had been trapped in the presence of cyclohexanone. The success of this reaction was somewhat surprising, as the rate of exo cyclization of the radical derived from reduction of 2-(3-butenyloxy)iodobenzene is known to be 60 times slower than the exo cyclization of the corresponding radical derived from 2-(2-propenyloxy)iodobenzene.[3] There was no evidence of the product resulting from formation of the seven-membered ring radical followed by subsequent reduction and electrophile trapping (eq 6). This appears to represent an efficient route into derivatives of the 2*H*,3*H*-benzopyran ring system.

Finally, we had hoped to expand the scope of this reaction further by replacing the oxygen in the side chain by nitrogen. It was necessary to replace the hydrogen on

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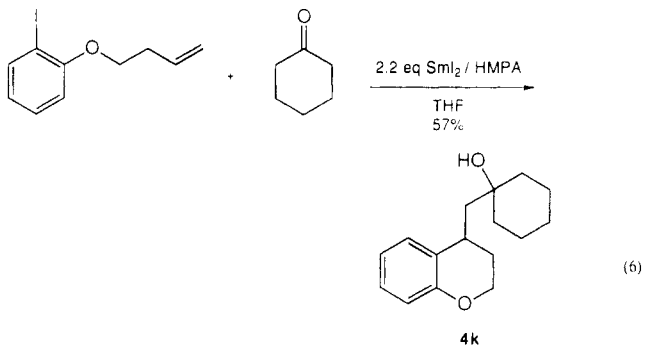
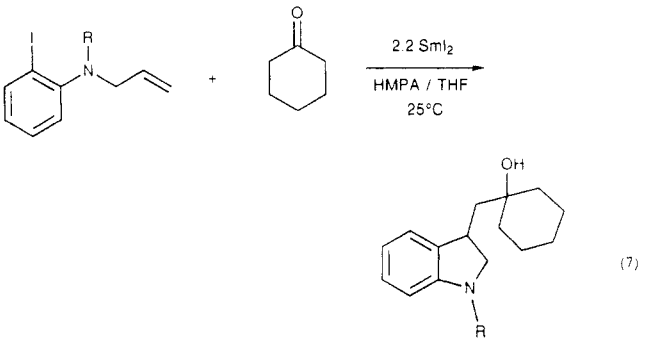


(6)

4k

the nitrogen of the allylamino side chain with a protecting group in order to avoid complications because of the presence of an acidic hydrogen. Some of the protecting groups examined include benzyl, benzoyl, and allyl. In fact, the substrate bearing the diallylamino appendage proved to be the most successful (eq 7). In general, the side products identified in the reaction mixture were starting material, reduced uncyclized material, and the cyclized protonated product. Although yields of the cyclized trapped products were modest, this protocol still represents an efficient route into a variety of substituted 2*H*,3*H*-indole derivatives.



(7)

4l	R=COPh	0%
4m	R=CH_2Ph	27%
4n	R=$CH_2CH{=}CH_2$	38%

The ability of SmI_2 to promote the sequential reductive radical cyclization/carbonyl addition reaction of the substrates discussed above represents a useful advancement in the arena of carbon–carbon bond forming reactions. The reaction conditions appear to be among the mildest available for radical generation and likewise provide reaction mixtures free of tin species which are often difficult to remove. The selective formation of two new carbon–carbon bonds through this sequential process to provide highly functionalized heterocycles demonstrates the synthetic potential of this methodology.

Experimental Section

Preparation of 2-(Allyloxy)ethyl Iodide (1). According to the method of Bergman,[11] 2-(allyloxy)ethanol was prepared in 44% yield. The alcohol was converted to the corresponding tosylate (TsCl, Et_3N, CH_2Cl_2), followed by conversion to the iodide under standard Finkelstein conditions (NaI, acetone heated to reflux) to yield the desired product. ^1H NMR ($CDCl_3$): δ 6.01–5.82 (m, 1 H), 5.35–5.18 (m, 2 H), 4.07–4.02 (m, 2 H), 3.74–3.67 (m, 2 H), 3.30–3.22 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 134.54, 117.79, 71.99, 70.92, 3.24. IR ($CDCl_3$): 2857, 1084, 906, 706 cm^{-1}.

Preparation of 2-(Allyloxy)-1-iodobenzene (3). According to the procedure of Goering,[12] 2-iodophenol (13.6 mmol) was treated with K_2CO_3 (15 mmol) and allyl bromide (15 mmol) in refluxing acetone (5 mL) overnight. The reaction mixture was poured into ether and washed with 10% NaOH followed by water. The organic layer was dried over Na_2SO_4, filtered, and concentrated to yield a crude yellow oil. The crude product was distilled under reduced pressure to provide the desired product in 88% yield. ^1H NMR ($CDCl_3$): δ 7.35–7.30 (m, 1 H), 6.86–6.77 (m, 1 H), 6.36–6.21 (m, 2 H), 5.67–5.51 (m, 1 H), 5.13–4.85 (m, 2 H), 4.15–4.13 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 156.94, 139.40, 132.47, 129.29, 122.58, 117.52, 112.37, 86.58, 69.53. IR ($CDCl_3$): 3062, 2921, 2864, 1648, 1580, 1422, 1276, 1247, 1123, 996, 928, 747 cm^{-1}.

Preparation of 2-(3-Butenyloxy)-1-iodobenzene. The preparation of 3 was followed, with allyl bromide being replaced with 1-bromo-4-butene. The product was isolated by flash chromatography on silica gel using 10:1 hexanes–EtOAc. ^1H NMR ($CDCl_3$): δ 7.73–7.70 (m, 1 H), 7.25–7.20 (m, 1 H), 6.76–6.62 (m, 2 H), 6.00–5.86 (m, 1 H), 5.19–5.07 (m, 2 H), 4.02–3.98 (t, J = 6.6 Hz, 2 H), 2.58–2.52 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 157.37, 139.41, 134.29, 129.36, 122.45, 117.26, 112.09, 86.67, 33.50. IR ($CDCl_3$): 3070, 2931, 2869, 1584, 1464, 1437, 1379, 1275, 1247 cm^{-1}.

Preparation of 2-(2-Propynyloxy)-1-iodobenzene. The preparation of 3 was followed, with allyl bromide being replaced with propargyl bromide (80% solution in toluene). The crude material was Kugelrohr distilled to yield the desired product in 86% yield as a white crystalline solid (mp 40–41 °C). ^1H NMR ($CDCl_3$): δ 7.72–6.63 (m, 4 H), 4.68 (s, 2 H), 2.44 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 136.65, 129.32, 123.41, 112.95, 87.63, 86.53, 76.37, 56.83. IR ($CDCl_3$): 3286, 3061, 2920, 2866, 1583, 1472, 1449, 1369, 1292, 1224 cm^{-1}.

Preparation of 2-((3-(Trimethylsilyl)-2-propynyl)oxy)-1-iodobenzene. To a 0 °C solution of diisopropylamine (2 mmol) in THF (10 mL) was added 2 mmol of nBuLi. After 20 min at 0 °C, the solution was cooled to −78 °C, and the 2-(propynyloxy)-1-iodobenzene (1.94 mmol) was added all at once as a solution in 3 mL of THF. After 1 h at −78 °C, 2 mmol of TMSCl was added to the mixture, which was then allowed to warm to room temperature. The reaction was quenched with saturated NH_4Cl, followed by normal extractive workup in ether. The organic phase was dried over $MgSO_4$, filtered, and concentrated. The product was isolated in 51% yield by flash chromatography on silica gel using 20:1 hexanes–EtOAc. ^1H NMR ($CDCl_3$): δ 7.60–6.50 (m, 4 H), 4.54 (s, 2 H), −0.01 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 156.37, 139.39, 129.11, 123.18, 113.34, 99.51, 93.22, 86.64, 57.72, −0.47.

Preparation of 2-Iodo-*N*-allylaniline. To a room temperature solution of 2-iodoaniline (9.1 mmol) in 20 mL of DMF was added K_2CO_3 (9.1 mmol), followed by 10 mmol of freshly distilled allyl bromide. The solution was stirred at room temperature for 16 h and was quenched with water. A normal extractive workup with ether followed. The organic layer was dried over K_2CO_3 and concentrated, and the product was isolated in 70% yield (86% pure by GC) by using flash chromatography on silica gel, eluting with 20:1 hexanes–EtOAc. ^1H NMR ($CDCl_3$): δ 7.71–7.68 (m, 1 H), 7.26–7.06 (m, 1 H), 6.60–6.45 (m, 2 H), 6.05–5.92 (m, 1 H), 5.34–5.13 (m, 2 H), 4.36 (br s, 1 H), 3.87–3.83 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 146.98, 138.98, 134.59, 129.34, 118.72, 116.41, 110.89, 85.37, 46.48.

Preparation of 2-Iodo-*N*-allyl-*N*-benzylaniline. To a 0 °C solution of oil-free NaH (1.4 mmol) in 5 mL of DMF was added the 2-iodo-*N*-allylaniline (1.37 mmol) as a solution in 5 mL of DMF. This was stirred at 0 °C for 1 h, followed by quenching with benzyl bromide (1.4 mmol). The cloudy, off-white mixture was stirred for several hours as it warmed to room temperature. The reaction mixture was quenched with saturated NH_4Cl and extracted with ether. The organic layer was dried over K_2CO_3 and concentrated, and the crude material was flash chromatographed on silica gel using 100% hexane to yield the desired product in 35% yield as a clear, colorless oil. ^1H NMR ($CDCl_3$): δ 7.90–6.76 (m, 9 H), 5.94–5.81 (m, 1 H), 5.20–5.03 (m, 2 H), 4.29–4.11 (m, 2 H), 3.68–3.50 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 151.69, 139.96, 138.04, 134.38, 128.76, 128.47, 128.11, 126.93, 125.66, 124.27, 118.05, 100.09, 56.85, 56.09. IR ($CDCl_3$): 3061, 3026, 2921, 2814, 1578, 1494, 1468, 1267, 1013 cm^{-1}.

Preparation of 2-Iodo-*N*-allyl-*N*-benzoylaniline. To a 0 °C solution of 2-iodo-*N*-allylaniline (4.2 mmol) in 5 mL of 10% NaOH was added the benzoyl chloride. After 1 h at room temperature, the mixture was neutralized with 10% HCl to pH 7 and was extracted with ethyl acetate. The organic layer was dried over K_2CO_3, filtered, and concentrated. The crude material was flash chromatographed on silica gel using 10:1 hexanes–EtOAc to yield the desired product as a white crystalline solid (mp 99–101 °C) in 68% yield. ^1H NMR ($CDCl_3$): δ 7.67–6.72 (m, 9 H),

6.00–5.90 (m, 1 H), 5.07–5.00 (m, 2 H), 4.96–4.90 (dd, J = 4.8, 14.6 Hz, 1 H), 3.85–3.78 (dd, J = 7.5, 14.5 Hz). ^{13}C NMR ($CDCl_3$): δ 169.48, 144.16, 139.50, 135.27, 131.87, 131.23, 129.29, 128.68, 128.39, 127.77, 127.07, 118.48, 99.69, 51.79. IR ($CDCl_3$): 3065, 2928, 2964, 1638, 1470, 1383, 1305 cm^{-1}.

Preparation of 2-Iodo-*N*,*N*-diallylaniline. The preparation follows that of 2-iodo-*N*-benzyl-*N*-allylaniline, with allyl bromide used in place of benzyl bromide. The crude material was flash chromatographed on silica gel using 100% hexanes to yield the desired product as a clear, colorless oil in 48% yield. ^{1}H NMR ($CDCl_3$): δ 7.91–6.79 (m, 4 H), 5.94–5.81 (m, 2 H), 5.24–5.13 (m, 4 H), 3.68–3.66 (d, J = 6.1 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ 151.76, 139.89, 134.78, 128.39, 125.53, 124.12, 117.68, 100.63, 56.01. IR ($CDCl_3$): 3075, 2978, 2921, 2810, 1578, 1434, 1273, 1214 cm^{-1}.

General Procedure for the Cyclization and Trapping of Haloalkene Substrates 1 and 3. To an oven-dried flask equipped with stirbar was added Sm metal (1.1 mmol, 0.165 g). The flask was flamed while being flushed with argon. The flask was cooled to 0 °C, and 20 mL of THF was added, followed by CH_2I_2 (1.0 mmol, 0.267 g). The solution remained at 0 °C for 15 min and then was warmed to room temperature and stirred for an additional hour. At this time, 1.0 mL of HMPA was added, and the initially blue solution turned deep purple. A solution of the substrate (0.40 mmol) and the electrophile (0.48 mmol) in 5 mL of THF was added to the SmI_2/HMPA solution over a period of approximately 1 min. In the case of 2-(allyloxy)ethyl iodide (1), an additional 50 mL of THF was added to the SmI_2/HMPA solution prior to introduction of the substrate/electrophile solution which was in 10 mL of THF. The substrate/electrophile solution was added over a period of approximately 45 min, via syringe pump. After being stirred for 1 h, the reaction mixture was quenched with saturated K_2CO_3, followed by extraction with ether. The organic layer was washed two times with water, dried over $MgSO_4$, filtered, and concentrated. The crude reaction product was purified by flash chromatography on silica gel to yield the desired product.

3-(2-Ethyl-2-hydroxybutyl)tetrahydrofuran (2a) was isolated in 57% yield as a clear, colorless oil by flash chromatography on silica gel (4:1 hexanes–EtOAc). Product purity was >95% as indicated by ^{13}C NMR analysis. ^{1}H NMR ($CDCl_3$): δ 3.99–3.94 (m, 1 H), 3.82–3.71 (m, 1 H), 3.69–3.66 (m, 1 H), 3.27–3.21 (m, 1 H), 2.30–2.19 (m, 1 H), 2.10–2.00 (m, 1 H), 1.60–1.12 (m, 8 H), 0.83–0.78 (t, J = 7.6 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ 74.54, 74.11, 67.50, 41.30, 34.71, 33.92, 31.34, 30.78, 7.82, 7.64. IR ($CDCl_3$): 3610, 2970, 2880, 1459, 1382, 1096, 1045 cm^{-1}. Exact mass calcd for $C_{10}H_{19}O_2$ (M – 1) 171.1385, found 171.1386.

3-(2-Hydroxy-2-propylpentyl)tetrahydrofuran (2b) was isolated in 38% yield as a clear, colorless oil by flash chromatography on silica gel (4:1 hexanes–EtOAc). The product was >95% pure as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 3.95–3.89 (t, J = 7.8 Hz, 1 H), 3.67–3.60 (m, 1 H), 3.22–3.16 (t, J = 8.6 Hz, 1 H), 2.25–2.15 (m, 1 H), 2.06–1.96 (m, 1 H), 1.56–1.13 (m, 12 H), 0.85–0.80 (t, J = 7.1 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ 74.44, 74.18, 67.59, 42.33, 42.20, 41.58, 34.87, 34.00, 16.91, 16.75, 14.57. IR ($CDCl_3$): 3606, 3418, 2958, 2872, 1455 cm^{-1}. Exact mass calcd for $C_{12}H_{21}O_2$ (M – 1) 199.1698, found 199.1694.

3-((1-Hydroxycyclopentyl)methyl)tetrahydrofuran (2c) was isolated in 53% as a clear, colorless oil by flash chromatography on silica gel (4:1 hexanes–EtOAc). The product was >95% pure as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 3.99–3.94 (t, J = 7.8 Hz, 1 H), 3.82–3.71 (m, 1 H), 3.69–3.63 (m, 1 H), 3.29–3.24 (t, J = 8.6 Hz, H), 2.39–2.28 (m, 1 H), 2.11–2.01 (m, 1 H), 1.77–1.44 (m, 11 H), 1.36 (br s, 1 H). ^{13}C NMR ($CDCl_3$): δ 82.26, 74.13, 67.65, 44.24, 40.42, 39.86, 36.14, 33.91, 23.47, 23.41. IR ($CDCl_3$): 3420, 2960, 2871, 909, 702 cm^{-1}. Exact mass calcd for $C_{10}H_{17}O$ 169.1229, found 169.1238.

3-((1-Hydroxycyclohexyl)methyl)tetrahydrofuran (2d) was isolated in 52% yield as a clear colorless oil by flash chromatography on silica gel (4:1 hexanes–EtOAc). The product was >95% pure as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 4.01–3.93 (t, J = 7.6 Hz, 1 H), 3.82–3.62 (m, 2 H), 3.29–3.21 (t, J = 8.2 Hz, 1 H), 2.45–2.05 (m, 2 H), 1.66–1.35 (m, 14 H). ^{13}C NMR ($CDCl_3$): δ 74.39, 71.46, 67.72, 45.71, 38.31, 37.65, 34.60, 34.28, 25.79, 22.27. IR ($CDCl_3$): 3602, 3414, 2933, 2860, 1717, 1448 cm^{-1}. Exact mass calcd for $C_{11}H_{19}O_2$ (M – 1) 183.1385, found 183.1394.

3-((1-Hydroxy-2-methylcyclohexyl)methyl)tetrahydrofuran (2e) was isolated in 74% yield as a 1:1 mixture of diastereomers by flash chromatography on silica gel (4:1 hexanes–EtOAc). The product was a clear, colorless oil isolated with >90% purity as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 4.03–3.22 (m, 8 H), 2.34–2.01 (m, 4 H), 1.74–1.13 (m, 26 H), 0.87–0.85 (d, J = 6.3 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ 74.40, 74.14, 72.82, 72.76, 67.92, 67.29, 43.77, 43.56, 39.23, 39.16, 36.38, 36.11, 34.66, 34.64, 34.24, 34.07, 30.56, 25.44, 25.42, 21.72, 14.97, 14.96. IR ($CDCl_3$): 3610, 3447, 2934, 2842, 1440, 1378, 961, 921, 727 cm^{-1}. Exact mass calcd for $C_{12}H_{22}O_2$ 198.1620, found 198.1620.

3-((4-*tert*-Butyl-1-hydroxycyclohexyl)methyl)tetrahydrofuran (2f) was isolated in 55% yield as a 5:1 mixture of diastereomers by flash chromatography on silica gel (4:1 hexanes–EtOAc). The product was a white solid, mp 59–69 °C, isolated with >95% purity as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 3.96–3.92 (m, 2 H), 3.80–3.63 (m, 4 H), 3.25–3.20 (m, 2 H), 2.37–2.27 (m, 2 H), 2.24–1.99 (m, 2 H), 1.72–1.13 (m, 24 H), 0.80–0.79 (m, 20 H). ^{13}C NMR ($CDCl_3$): δ 74.28, 74.14, 72.12, 70.56, 67.56, 47.72, 47.54, 47.38, 40.01, 39.27, 38.90, 38.07, 37.52, 34.60, 34.55, 34.16, 33.95, 32.29, 32.14, 27.53, 27.44, 24.51, 24.41, 22.29. IR ($CDCl_3$): 3603, 3434, 2941, 2868, 1478, 1445, 1365, 1236, 1083, 1038 cm^{-1}. Exact mass calcd for $C_{15}H_{27}O$ (M – 17) 223.2062, found 223.2079.

2*H*,3*H*-3-(2-Ethyl-2-hydroxybutyl)benzofuran (4a) was isolated as a clear, colorless oil in 69% yield by flash chromatography on silica gel (7:1 hexanes–EtOAc). The product was >95% pure as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 7.19–6.70 (m, 4 H), 4.74–4.67 (t, J = 9.0 Hz, 1 H), 3.61–3.52 (m, 1 H), 2.00–1.16 (m, 7 H), 1.08 (s, 1 H), 0.87–0.81 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 159.67, 131.42, 128.00, 123.80, 120.28, 109.36, 78.66, 43.49, 37.63, 31.99, 30.50, 8.20, 7.64. IR ($CDCl_3$): 3608, 3502, 2970, 2940, 2882, 1597, 1482, 1459, 1233 cm^{-1}. Exact mass calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1465.

2*H*,3*H*-3-(2-Hydroxy-2-propylpentyl)benzofuran (4b) was isolated as a clear, colorless oil in 81% yield by flash chromatography on silica gel (7:1 hexanes–EtOAc). The product was shown to be 91% pure by GLC analysis. ^{1}H NMR ($CDCl_3$): δ 7.06–6.69 (m, 4 H), 4.73–4.67 (t, J = 9.0 Hz, 1 H), 4.21–4.15 (t, J = 8.9 Hz, 1 H), 3.60–3.51 (m, 1 H), 2.00–1.08 (m, 11 H), 0.91–0.85 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 159.72, 131.43, 127.99, 123.79, 120.27, 109.37, 78.32, 74.37, 44.37, 42.73, 41.07, 37.64, 17.14, 16.64, 14.59, 14.54. IR ($CDCl_3$): 3607, 3502, 2960, 2934, 2874, 1597, 1482, 1459, 1232, 1162, 1133, 971, 902 cm^{-1}. Exact mass calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1790.

2*H*,3*H*-3-((1-Hydroxycyclopentyl)methyl)benzofuran (4c) was isolated in 68% yield by flash chromatography on silica gel (5:1 hexanes–EtOAc). The product was >95% pure as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 7.08–6.70 (m, 4 H), 4.75–4.69 (t, J = 9.0 Hz, 1 H), 4.25–4.19 (t, J = 8.5 Hz, 1 H), 3.68–3.58 (m, 1 H), 2.13–1.18 (m, 10 H), 1.07 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 159.69, 131.33, 128.03, 123.89, 120.32, 109.39, 82.30, 78.52, 46.09, 40.84, 39.65, 39.17, 23.56, 23.32. IR ($CDCl_3$): 3602, 2961, 2877, 1597, 1482, 1460, 1230, 910, 740 cm^{-1}. Exact mass calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1295.

2*H*,3*H*-3-((1-Hydroxycyclohexyl)methyl)benzofuran (4d) was isolated as a clear, colorless oil in 65% yield by flash chromatography on silica gel (5:1 hexanes–EtOAc). The product was shown to be >95% pure as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 7.20–6.87 (m, 4 H), 4.81–4.75 (t, J = 9.0 Hz, 1 H), 4.29–4.23 (t, J = 9.0 Hz, 1 H), 3.74–3.65 (q, J = 9.0 Hz, 1 H), 1.77–1.23 (m, 13 H). ^{13}C NMR ($CDCl_3$): δ 159.70, 131.48, 127.96, 123.88, 120.29, 109.32, 78.69, 71.24, 47.57, 38.78, 37.31, 37.05, 25.60, 22.09, 22.02. IR ($CDCl_3$): 3598, 3488, 2933, 2858, 1597, 1482, 1459, 1232, 968 cm^{-1}. Exact mass calcd for $C_{15}H_{19}O_2$ 231.1385, found 231.1376.

2*H*,3*H*-3-((1-Hydroxy-2-methylcyclohexyl)methyl)-benzofuran (4e) was isolated as a clear, colorless oil by flash chromatography on silica gel (5:1 hexanes–EtOAc) and was shown to be >90% pure as indicated by ^{13}C NMR. ^{1}H NMR ($CDCl_3$): δ 7.16–6.67 (m, 8 H), 4.69–4.63 (m, 2 H), 4.23–4.05 (m, 2 H), 3.64–3.53 (m, 2 H), 2.19–1.13 (m, 24 H), 0.85–0.83 (d, J = 6.4 Hz, 3 H), 0.82–0.80 (d, J = 6.4 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ 159.74, 159.54, 131.62, 131.46, 127.99, 127.97, 124.21, 123.69, 120.40, 109.38, 109.25, 78.79, 78.47, 72.79, 72.47, 46.86, 45.01, 39.60, 39.44, 37.41, 37.39, 36.74, 35.99, 30.66, 30.52, 25.39, 25.15, 21.80, 21.64, 15.13,

14.87. IR ($CDCl_3$): 3610, 2935, 2856, 1597, 1482, 1460, 1379, 1228, 963, 921, 895, 756, 716, 650 cm^{-1}. Exact mass calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1595.

2*H*,3*H*-3-((4-*tert*-Butyl-1-hydroxycyclohexyl)methyl)benzofuran (4f) was isolated in 71% yield as a 5:1 ratio of diastereomers by flash chromatography on silica gel (4:1 hexanes–EtOAc). The product was a white solid, mp 83–85 °C, and was shown to be >95% pure as indicated by ^{13}C NMR. Spectral data shown are for the major diastereomer. ^1H NMR ($CDCl_3$): δ 7.28–6.78 (m, 4 H), 4.87–4.76 (t, J = 9.0 Hz, 1 H), 4.31–4.22 (t, J = 8.8 Hz, 1 H), 3.80–3.65 (m, 1 H), 2.07–0.79 (m, 12 H), 0.90 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 159.92, 131.73, 128.24, 124.16, 120.57, 109.61, 79.00, 70.90, 49.62, 48.06, 38.88, 37.80, 37.48, 32.70, 27.84, 22.66. IR ($CDCl_3$): 3601, 3481, 2943, 2868, 1597, 1482, 1366, 1232, 909 cm^{-1}. Exact mass calcd for $C_{19}H_{28}O_2$ 288.2089, found 288.2085.

2*H*,3*H*-3-(5-(*N*,*N*-Diethylamino)-2-hydroxy-2-methylpentyl)benzofuran (4g) was isolated in 76% yield as a 1:1 mixture of diastereomers by flash chromatography on silica gel (10:1 hexanes–EtOAc). The product was a clear, colorless oil and was shown to be >95% pure by ^{13}C NMR. ^1H NMR ($CDCl_3$): δ 7.26–6.77 (m, 8 H), 4.84–4.75 (m, 2 H), 4.34–4.22 (m, 2 H), 3.72–3.64 (m, 2 H), 3.43 (s, 2 H), 2.64–1.56 (m, 26 H), 1.22 (s, 3 H), 1.17 (s, 3 H), 1.07–0.99 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 159.72, 159.66, 131.87, 131.82, 127.75, 127.71, 123.82, 120.11, 120.08, 109.16, 109.13, 78.91, 78.87, 69.56, 69.47, 54.04, 53.96, 50.28, 48.33, 47.25, 46.04, 45.83, 43.10, 41.76, 38.17, 37.86, 36.70, 36.64, 28.29, 27.72, 21.56, 21.26, 10.63, 10.40. IR ($CDCl_3$): 3068, 2973, 2821, 1482, 1460, 1374, 1227 cm^{-1}. Exact mass calcd for $C_{18}H_{29}NO_2$ 291.2198, found 291.2187.

2*H*,3*H*-3-(5-Chloro-2-hydroxy-2-methylpentyl)benzofuran (4h) was isolated in 10% yield as a 1:1 mixture of diastereomers by flash chromatography on silica gel (10:1 hexanes–EtOAc). The product was a light yellow, clear oil and was shown to be >95% pure by ^{13}C NMR. ^1H NMR ($CDCl_3$): δ 7.22–6.73 (m, 8 H), 4.77–4.66 (m, 2 H), 4.26–4.18 (m, 2 H), 3.87–3.55 (m, 6 H), 2.14–1.54 (m, 8 H), 1.26 (s, 3 H), 1.19 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 159.80, 159.72, 131.35, 131.25, 128.00, 123.93, 120.27, 120.23, 109.37, 109.33, 82.01, 78.75, 78.35, 77.76, 67.35, 46.04, 45.53, 38.67, 38.62, 38.22, 36.55, 27.15, 26.15, 25.84, 25.42. IR ($CDCl_3$): 3602, 3384, 2948, 1479, 1453, 1229 cm^{-1}. Exact mass calcd for $C_{14}H_{18}O_2$ (M – 36) 218.1307, found 218.1301.

2*H*,3*H*-3-((6-Methyl-2-oxotetrahydropyran-6-yl)methyl)benzofuran (4i) was obtained in 40% yield as a white, crystalline solid, mp 68–100 °C. It was isolated as a 1:1 mixture of diastereomers by flash chromatography on silica gel (10:1 hexanes–EtOAc). The product was shown to be >95% pure by ^{13}C NMR analysis. ^1H NMR ($CDCl_3$): δ 7.26–6.77 (m, 8 H), 4.88–4.28 (t, J = 9 Hz, 2 H), 4.77–4.71 (t, J = 9 Hz, 2 H), 4.27–4.18 (m, 2 H), 3.78–3.69 (m, 2 H), 2.63–1.25 (m, 22 H). ^{13}C NMR ($CDCl_3$): δ 170.59, 170.49, 159.77, 159.22, 130.48, 128.37, 128.35, 123.90, 123.69, 120.50, 120.39, 109.59, 109.51, 83.31, 78.29, 78.15, 47.68, 46.91, 37.71, 37.42, 33.57, 32.12, 31.49, 29.19, 29.16, 26.76, 25.93, 22.56, 16.54, 16.42, 14.02. IR ($CDCl_3$): 3032, 2980, 1724, 1482, 1460, 1140, 1098, 1056 cm^{-1}. Exact mass calcd for $C_{15}H_{18}O_3$ 246.1257, found 246.1257.

2*H*,3*H*-3-(2-Hydroxy-2-methyl-7-octenyl)benzofuran (4j) was isolated in 38% yield as a 1:1 mixture of diastereomers by flash chromatography on silica gel (5:1 hexanes–EtOAc). The product was a clear, colorless oil isolated with >95% purity by ^{13}C NMR analysis. ^1H NMR ($CDCl_3$): δ 7.16–6.68 (m, 8 H), 5.76–5.65 (m, 2 H), 4.95–4.65 (m, 4 H), 4.20–4.13 (m, 2 H), 3.61–3.55 (m, 2 H), 2.01–1.09 (m, 30 H). ^{13}C NMR ($CDCl_3$): δ 159.75, 159.69, 138.71, 138.69, 131.33, 131.30, 128.05, 123.91, 123.82, 120.35, 120.31, 114.62, 114.60, 109.41, 109.38, 78.62, 72.68, 72.60, 46.77, 46.38, 43.69, 41.88, 38.10, 37.83, 33.61, 29.26, 23.57, 23.24. IR ($CDCl_3$): 3606, 3478, 3076, 2933, 2859, 1640, 1597, 1482, 1460, 1227 cm^{-1}. Exact mass calcd for $C_{17}H_{24}O_2$ 260.1776, found 260.1800.

2*H*,3*H*-4-((1-Hydroxycyclohexyl)methyl)benzopyran (4k) was isolated as a clear, pale yellow oil in 57% yield by flash chromatography on silica gel (5:1 hexanes–EtOAc). The product was >95% pure by ^{13}C NMR analysis. ^1H NMR ($CDCl_3$): δ 7.06–6.69 (m, 4 H), 4.18–4.06 (m, 2 H), 3.02–3.01 (m, 1 H), 2.13–1.19 (m, 15 H). ^{13}C NMR ($CDCl_3$): δ 154.61, 129.54, 127.84, 127.08, 120.29, 116.77, 72.01, 63.09, 49.60, 39.00, 37.26, 28.85, 25.67, 22.19, 22.17. IR ($CDCl_3$): 3604, 3486, 2933, 2858, 1582, 1489, 1451, 1269, 1224 cm^{-1}. Exact mass calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1618.

***N*-Benzyl-3-((1-hydroxycyclohexyl)methyl)indoline (4m)** was isolated in 27% yield by flash chromatography on silica gel in 10:1 hexanes–EtOAc as a clear, light yellow oil. The product was >90% pure by ^{13}C NMR analysis. ^1H NMR ($CDCl_3$): δ 7.24–6.28 (m, 9 H), 4.32–3.98 (d, J = 15 Hz, 1 H), 3.98–3.93 (d, J = 15 Hz, 1 H), 3.59–3.53 (t, J = 8.6 Hz, 1 H), 3.35–3.26 (m, 1 H), 2.91–2.85 (t, J = 9.0 Hz, 1 H), 2.03–1.97 (dd, J = 2.4, 14.6 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 152.15, 138.52, 134.31, 128.47, 127.83, 127.48, 127.04, 123.25, 117.64, 106.92, 71.46, 62.08, 53.43, 47.02, 47.00, 38.67, 37.13, 35.97, 25.66, 22.10, 22.07. IR ($CDCl_3$): 2933, 2859, 2359, 2253, 1730, 1602, 1488, 1463, 1381, 1272 cm^{-1}. Exact mass calcd for $C_{22}H_{27}NO$: 321.2093, found 321.2112.

***N*-Allyl-3-((1-hydroxycyclohexyl)methyl)indoline (4n)** was isolated in 37% yield by flash chromatography on silica gel in 5:1 hexanes–EtOAc as a clear, colorless oil. The product was >95% pure by ^{13}C NMR analysis. ^1H NMR ($CDCl_3$): δ 7.11–6.39 (m, 4 H), 5.85–5.72 (m, 1 H), 5.19–5.05 (m, 2 H), 3.72–3.44 (m, 3 H), 3.32–3.23 (m, 1 H), 2.92–2.86 (t, J = 9.1 Hz, 1 H), 2.01–1.09 (m, 13 H). ^{13}C NMR ($CDCl_3$): δ 151.77, 134.55, 134.14, 127.41, 123.18, 117.67, 117.13, 107.28, 71.52, 61.58, 51.91, 46.79, 38.72, 37.14, 35.93, 25.68, 22.13, 22.09. IR ($CDCl_3$): 3392, 3075, 2977, 2922, 2814, 1418, 1214, 1101, 922 cm^{-1}. Exact mass calcd for $C_{18}H_{25}NO$ 271.1936, found 271.1951.

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Registry No. **1**, 65805-36-9; **2a**, 130013-24-0; **2b**, 130013-25-1; **2c**, 130013-26-2; **2d**, 130013-27-3; **2e**, 130013-28-4; **2f**, 130013-29-5; **3** (X = Br), 60333-75-7; **3** (X = I), 24892-63-5; **4a**, 130013-30-8; **4b**, 130013-31-9; **4c**, 130013-32-0; **4d**, 130013-33-1; **4e**, 130013-34-2; **4f**, 130013-35-3; **4a** (isomer 1), 130013-36-4; **4a** (isomer 2), 130013-44-4; **4h** (isomer 1), 130013-37-5; **4h** (isomer 2), 130013-45-5; **4i** (isomer 1), 130013-38-6; **4i** (isomer 2), 130013-46-6; **4j** (isomer 1), 130013-39-7; **4j** (isomer 2), 130013-47-7; **4k**, 130013-40-0; **4m**, 130013-41-1; **4n**, 130013-42-2; SmI_2, 32248-43-4; $HO(CH_2)_2OCH_2CH{=}CH_2$, 111-45-5; 2-IC_6H_4OH, 533-58-4; 2-$IC_6H_4O(CH_2)_2CH{=}CH_2$, 57056-88-9; 2-$IC_6H_4OCH_2C{\equiv}CH$, 41876-99-7; 2-$IC_6H_4OCH_2C{\equiv}CTMS$, 130013-21-7; 2-$IC_6H_4NHCH_2CH{=}CH$, 73396-87-9; 2-$IC_6H_4NH_2$, 615-43-0; 2-$IC_6H_4N(CH_2C_6H_5)CH_2CH{=}CH_2$, 130013-22-8; 2-$IC_6H_4N(COC_6H_5)CH_2CH{=}CH_2$, 130013-23-9; 2-$IC_6H_4N(CH_2CH{=}CH_2)_2$, 73396-92-6; $H_3CCH_2COCH_2CH_3$, 96-22-0; $H_3C(CH_2)_2CO(CH_2)_2CH_3$, 123-19-3; $H_3C(CH_2)_4CHO$, 66-25-1; $H_3C(CH_2)_7CHO$, 124-19-6; TMSCl, 75-77-4; MeI, 74-88-4; $H_3CCO(CH_2)_3NEt_2$, 105-14-6; $H_3CCO(CH_2)_3Cl$, 5891-21-4; $H_3CCO(CH_2)_3CH{=}CH_2$, 21889-88-3; $C_6H_5OCH_2CH{=}CH_2$, 1746-13-0; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; cyclohexene oxide, 286-20-4; 2*H*,3*H*-3-((trimethylsilyl)methylene)benzofuran, 130013-43-3.

Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra for compounds **2a–f**, **4a–k**, **4m**, and **4n** (38 pages). Ordering information is given on any current masthead page.