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Rapid Access to Halohydrofurans via Brønsted Acid-Catalyzed Hydroxylation/Halocyclization of Cyclopropyl Methanols with Water and Electrophilic Halides

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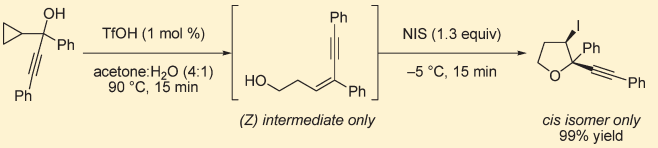
Supporting Information

ABSTRACT: A one-pot, two-step method to prepare 3-halohydrofurans efficiently by TfOH-catalyzed hydroxylation/halocyclization of cyclopropyl methanols with H_2O and *N*-halosuccinimide (NXS, X = I, Br, Cl) or Selectfluor is described. The reactions proceed rapidly under mild and operationally straightforward conditions with a catalyst loading as low as 1 mol % and afford the 3-halohydrofuran products in moderate to excellent yields and, in most cases, with preferential *cis* diastereoselectivity. The method was shown to be applicable to cyclopropyl methanols containing electron-withdrawing, electron-donating, and sterically demanding functional groups and electrophilic halide sources. The mechanism is suggested to involve protonation of the alcohol substrate by the Brønsted acid catalyst and ionization of the starting material. This results in ring-opening of the cyclopropane moiety and in situ formation of a homoallylic alcohol intermediate, which undergoes subsequent intramolecular halocyclization on treating with the electrophilic halide source to give the halohydrofuran. The observed *cis* product selectivity is thought to be determined by the reaction proceeding through an in situ generated unsaturated alcohol intermediate that contains a (*Z*)-alkene moiety under the kinetically controlled conditions.



INTRODUCTION

Furans are an important member of the heterocyclic family of compounds due to their presence in a myriad of bioactive natural products[1−5] such as azaspiracid,[2] kadlongirin A,[3] okadaic acid,[4] and xyloketal J[5] (Figure 1). Because of this and their ability to serve as a versatile building block in organic synthesis, an immense number of efficient and convenient methods for the construction of furans have been developed over the years.[1,6,7] This has hitherto included the halocyclization of homoallylic alcohols in the presence of an electrophilic halide source, such as NXS and Selectfluor, that provided the corresponding 3-halohydrofuran derivatives.[7] While this synthetic approach was shown to be a powerful and reliable route to the oxygen heterocycle, the reactions were reported to rely on the use of preformed unsaturated alcoholic substrates, which can often require several nontrivial and time-consuming steps. In this regard, the establishing of mild and efficient synthetic strategies to this class of furans from inexpensive and commercially available substrates or ones that can be accessed in one step is desirable.

As part of an ongoing program exploring the utility of alcohol pro-electrophiles in organic synthesis,[8−12] we recently described a regioselective route to conjugated enynes based on TfOH-catalyzed ring-opening of 1-cyclopropyl-2-propyn-1-ols with alcohols.[9c] On the basis of these earlier studies, we reasoned that a synthetic approach to 3-halohydrofurans could be achieved through NXS or Selectfluor-mediated cyclization of a homoallylic alcohol formed in situ from Brønsted acid-catalyzed hydroxylative ring-opening of cyclopropyl methanols. While Brønsted acid-mediated reactions of alcohol pro-electrophiles have come under increasing scrutiny,[9−12] to our knowledge those that make use of cyclopropyl methanols have thus far been limited to works describing the synthesis of conjugated enynes mentioned above[9c] and homoallylic halides as well as ring expansion and fission reactions.[12] Herein, we report a one-pot, two-step TfOH-catalyzed hydroxylation/halocyclization of cyclopropyl methanols with H_2O and NXS or Selectfluor (Scheme 1). The 3-halohydrofuran products were obtained in moderate to excellent yields and, in most cases, with preferential *cis* diastereoselectivity.

RESULTS AND DISCUSSION

We chose 1-cyclopropyl-1,3-diphenylprop-2-yn-1-ol (**1a**) as the probe substrate to establish the reaction conditions (Table 1). Initially, this revealed treating a solution of **1a** in 4:1 acetone and H_2O with 5 mol % of TfOH at 90 °C for 15 min followed by 1.3 equiv of NIS at −5 °C for 15 min gave the best result (entry 1). Under these conditions, *cis*-3-iodo-2-phenyl-2-(phenylethynyl)tetrahydrofuran (**2a**) was obtained in near quantitative yield. The product structure and stereochemistry was determined on the basis of ^{1}H NMR measurements and ^{1}H−^{1}H NOESY correlations observed between the H-3 and

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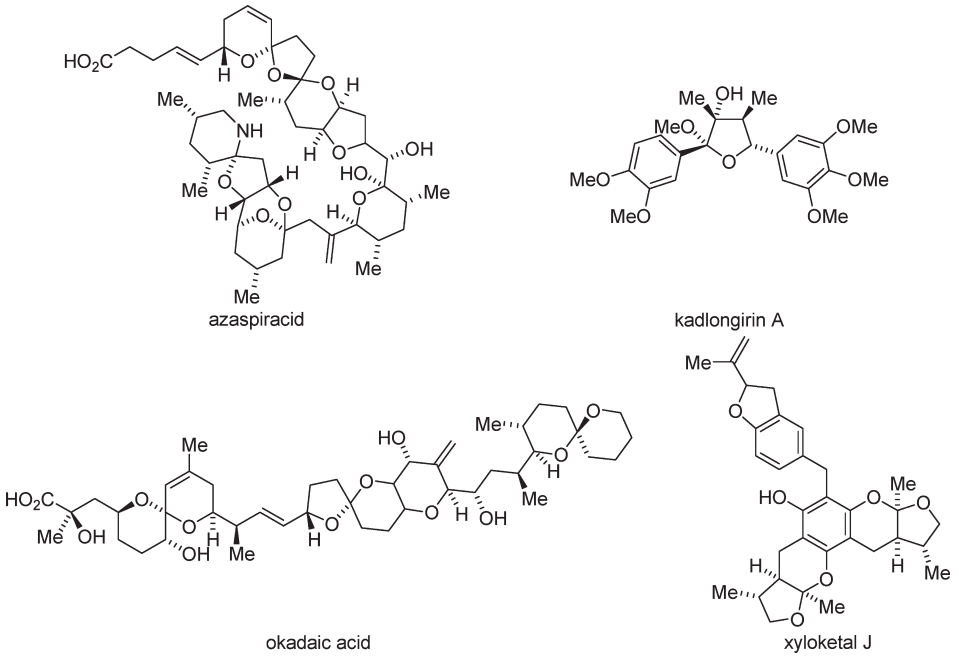
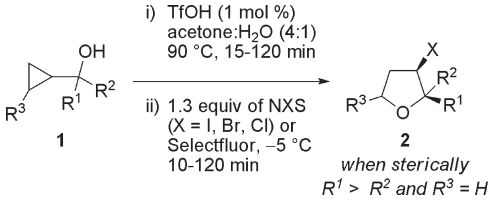


Figure 1. Examples of bioactive compounds containing a furan moiety.

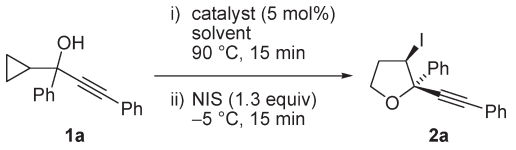
Scheme 1. One-Pot, Two-Step Halohydrofuran Synthesis from Ring-Opening of Cyclopropyl Methanols with H_2O followed by Halocyclization with an Electrophilic Halide Source



ortho protons of the phenyl group that implied a *cis* orientation between the I and alkyne moieties in the adduct (see Figure 2 and the Supporting Information). The relative *cis* diastereoselectivity of the 3-iodohydrofuran adduct was also confirmed by X-ray crystallography (see Figure S64 in the Supporting Information).[13]

As shown in entry 2, a comparable product yield was found on decreasing the catalyst loading from 5 to 1 mol %. However, a marked decrease in product yield was observed on further reducing the catalyst loading from 1 to 0.5 mol % or carrying out the reaction in one step at 90 °C for 15 min (entries 3−4). A similar effect on product yields was observed on lowering the amount of NIS from 1.3 to 1.1 equiv or changing the iodide source from NIS to I_2 (entries 5−6). Likewise, changing the organic component of the solvent system from acetone to THF or CH_2Cl_2 was found to lead to lower product yields (entries 7−8). Markedly lower product yields of 25−55% were also obtained on repeating the reaction with other Brønsted acids such as Tf_2NH, TFA, HCl, and *p*-TsOH·H_2O in place of TfOH (entries 9−12). On the basis of these results, reaction of **1a** in the presence of 1 mol % of TfOH in a 4:1 acetone:H_2O solvent system at 90 °C for 15 min followed by 1.3 equiv of NIS at −5 °C for 15 min was deemed to provide the optimal conditions.

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	yield (%)
1	TfOH	acetone:H_2O	99
2	TfOH[b]	acetone:H_2O	99
3	TfOH[c]	acetone:H_2O	55
4	TfOH[d]	acetone:H_2O	42
5[e]	TfOH	acetone:H_2O	85
6[f]	TfOH	acetone:H_2O	52
7	TfOH	THF:H_2O	62
8	TfOH	CH_2Cl_2:H_2O	48
9	Tf_2NH	acetone:H_2O	40
10	TFA	acetone:H_2O	55
11	HCl	acetone:H_2O	25
12	*p*-TsOH·H_2O	acetone:H_2O	45

[a] All reactions were performed with 5 mol % of catalyst in 4:1 solvent:H_2O at 90 °C for 15 min followed by addition of 1.3 equiv of NIS at −5 °C for 15 min. [b] Reaction conducted with 1 mol % of TfOH. [c] Reaction conducted with 0.5 mol % of TfOH. [d] Reaction conducted with 5 mol % of TfOH and 1.3 equiv of NIS in 4:1 of solvent:H_2O at 90 °C for 15 min. [e] Reaction conducted with 1.1 equiv of NIS. [f] Reaction conducted with 3 equiv of I_2.

With the optimal conditions established, the generality of the present procedure was next examined and the results are summarized in Table 2. Reactions of cyclopropyl methanols with a pendant aryl group at both positions on the carbinol carbon and NIS gave the corresponding 3-iodohydrofurans in

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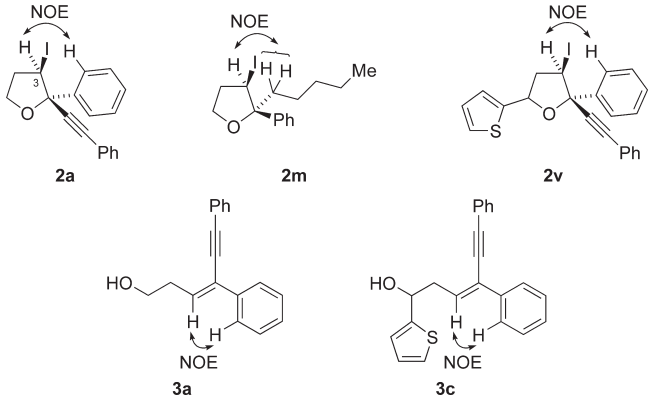


Figure 2. ^{1}H−^{1}H NOESY analysis of **2a**, **2m**, **2v**, **3a**, and **3c**.

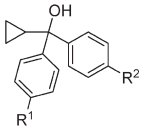
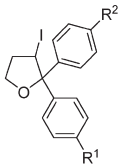
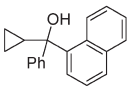
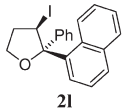
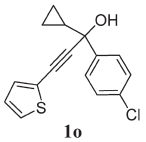
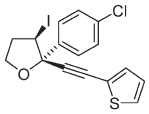
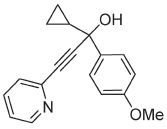
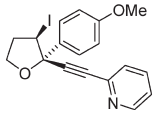
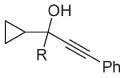
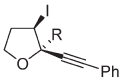
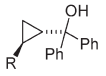
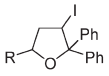
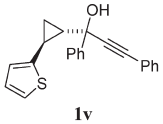
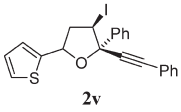
excellent yields although a catalyst loading of 5 mol % was required for those containing two electron-deficient aryl substituents (entries 1−11). The analogous reactions involving starting alcohols containing alkyl and aryl substituents on the carbinol carbon and/or cyclopropane ring were also found to afford the corresponding 3-iodohydrofuran products in comparable yields of 83−98% (entries 12−13 and 19−20). Similarly, the present procedure was shown to work well for substituted cyclopropyl methanols containing other bioactively important heteroaryl ring structures[14] and acetylenic groups (entries 14−17 and 21). In these reactions, the corresponding 3-iodohydrofuran adducts **2o**−**r** and **2v** were furnished in yields of 80−96%. However, we found reaction of the tertiary cyclopropyl methanol **1s** bearing a methyl and terminal alkyne unit to be less effective, affording a mixture of decomposition products that could not be identified by ^{1}H NMR analysis of the crude mixture (entry 18). Similarly, reaction of the secondary cyclopropyl methanol **1x** with a pentyl side chain on the carbinol carbon was found to result in the near quantitative recovery of the starting alcohol (entry 23). On the other hand, the analogous reaction with the phenyl-substituted secondary alcohol **1w** was found to proceed well and afford **2w** in 60% yield albeit at a catalyst loading of 5 mol % (entry 22). This is notable given that the closely related TfOH-catalyzed ring-opening of the same substrate with EtOH was previously reported by us not to be possible, and instead, chemoselectively gave the propargylation product.[9c]

In this work, TfOH-catalyzed hydroxylative ring-opening of **1a** and **1m** followed by halocyclization with other *N*-halosuccinimides and Selectfluor were also examined (Table 3). Under the standard conditions, reactions of **1a** and **1m** with NBS gave the corresponding 3-bromohalofurans **2y** and **2*β*** in excellent yields (entries 1 and 4). In contrast, the analogous reactions of **1a** and **1m** with less electrophilic halide sources such as NCS or Selectfluor were found to lead to moderate product yields (entries 2−3 and 5−6). In the case of the fluorocyclizations, the product yields obtained were found to be comparable to one example reported in a seminal work by Gouverneur and co-workers in an analogous reaction with a homoallylic alcohol and Selectfluor.[7a] The structure of **2*α*** was also confirmed by X-ray crystallographic analysis (see Figure S65 in the Supporting Information).[13]

At this juncture, we would like to highlight the diastereoselective nature of the present reaction. In reactions involving substrates in which one of the substituents on the carbinol carbon was significantly more sterically demanding than the other and R^3 = H, the corresponding 3-halohydrofuran derivative was furnished with exclusive *cis* diastereoselectivity (entries 11−17 and 22 in Table 2 and Table 3). In addition to our earlier spectroscopic and crystallographic measurements for **2a** and **2*α***, the relative *cis* configurations of **2*l*−r**, **2w**, **2y**,**z**, and **2*β*−*δ*** were determined on the basis of ^{1}H−^{1}H NOESY analysis of **2m**. This revealed ^{1}H−^{1}H NOESY correlations could be found between the H-3 and CH_2 of the pentyl group that established a *cis* orientation between the I and Ph substituents of the product (see Figure 2 and the Supporting Information). However, no or close to no diastereoselectivity was observed for hydroxylative ring-opening/iodocyclization of starting alcohols containing two slightly different para-substituted aryl groups on the carbinol carbon (entries 7−10 in Table 2). A similar diastereoselective outcome was found for reactions in which the cyclopropane ring of the substrate contained a substituent (entries 19−21 in Table 2). On the other hand, only two out of the four possible product diastereomers were afforded in one of these latter reactions involving a starting alcohol containing two different functional groups on the carbinol carbon (entry 21 in Table 2). Although furnished as an inseparable mixture of isomers, the *cis* relationship between the I and alkyne moieties for one of the diastereomers of **2v** was confirmed on the basis of ^{1}H−^{1}H NOESY analysis showing correlations between the H-3 and ortho protons of the phenyl group of the product (see Figure 2 and the Supporting Information).

It is evident from the above-mentioned observations that steric effects play an important role in determining the product diastereoselectivities in these reactions. Moreover, the preferential *cis* product selectivities also suggest that the halohydrofuran forming process could follow an anti addition pathway previously reported for *endo* iodocyclizations of homoallylic alcohols with I_2 or NIS.[16] If this is the case, a reaction mechanism that involves in situ formation of a (*Z*)-homoallylic alcohol intermediate with the hydroxylative ring-opening and halocyclization steps proceeding under kinetic control might be anticipated. To support this hypothesis and gain a better understanding of the reaction mechanism, we conducted the following experiments. First is the TfOH-catalyzed hydroxylative ring-opening of **1a**, which was found to give (*Z*)-**3a** as the sole product in 99% yield under the conditions shown in Scheme 2. Similarly, the analogous reaction of **1v** in the presence of 1 mol % of TfOH under the same conditions was found to furnish **3c** as a single (*Z*)-stereo- and regioisomer in 86% yield. In both the homoallylic alcohols obtained, the stereochemistry of the C=C bond was confirmed by ^{1}H−^{1}H NOESY measurements showing correlations between the alkenyl proton with those at the ortho position of the phenyl group in these adducts (Figure 2 and the Supporting Information).[17] Further treating **3a** and **3c** with 1.3 equiv of NIS at −5 °C gave the expected iodohydrofurans **2a** exclusively as the *cis* isomer and **2v** as an inseparable 5:3 *cis*/*trans* ratio of diastereomers in 99% and 83% yield, respectively. Repeating this sequential stepwise process with **1j** was shown to give **3b** as an inseparable 7:5 mixture of (*Z*)/(*E*) isomers in 98% yield. Subsequent iodocyclization with NIS then provided **2j** as an inseparable 3:2 mixture of *cis*/*trans* diastereomers in 98% yield. In all three cases, the product diastereoselectivities and yields obtained were comparable to the analogous reactions described in entry 2 in Table 1 and entries 9 and 21 in Table 2. The premise that both the hydroxylative ring-opening and halocyclization steps proceed under kinetic control would be consistent with our findings showing a linear increase in product yields was observed with increasing temperature for the TfOH-mediated reaction of **1a** under the conditions described in Figure 3. Indeed, this is

Table 2. TfOH-Catalyzed Hydroxylation/Iodocyclization of Cyclopropyl Methanols 1b−x[a]

entry	substrate	product	yield (%)
1[b]	 **1b-k**	 **2b**, $R^1 = R^2 = F$	95
2[b]		**2c**, $R^1 = R^2 = Cl$	93
3[b]		**2d**, $R^1 = R^2 = Br$	88
4		**2e**, $R^1 = R^2 = H$	79
5		**2f**, $R^1 = R^2 = Me$	99
6		**2g**, $R^1 = R^2 = OMe$	97
7		**2h**, $R^1 = Cl$, $R^2 = Me$	96[c]
8		**2i**, $R^1 = Cl$, $R^2 = OMe$	98[d]
9		**2j**, $R^1 = Me$, $R^2 = H$	98[e]
10		**2k**, $R^1 = Ph$, $R^2 = H$	94[f]
11	 **1l**	 **2l**	80
12	 **1m-n**	 **2m**, R = $(CH_2)_4CH_3$	88
13		**2n**, R = $C(CH_3)_3$	83
14	 **1o**	 **2o**	96
15	 **1p**	 **2p**	92
16	 **1q-r**	 **2q**, R = C≡CPh	86
17		**2r**, R = 1-methylcyclohexyl	90
18	 **1s**	 **2s**	-[g]
19	 **1t-u**	 **2t**, R = Ph	98[h]
20		**2u**, R = $(CH_2)_4CH_3$	94[h]
21	 **1v**	 **2v**	80[h]
22[b]	 **1w-x**	 **2w**, R = Ph	60
23		**2x**, R = $(CH_2)_4CH_3$	-[i]

[a] All reactions were performed with 1 mol % of TfOH in 4:1 acetone:H_2O at 90 °C followed by 1.3 equiv of NIS at −5 °C.[15] [b] Reaction conducted with 5 mol % of TfOH. [c] Obtained as an inseparable 5:4 mixture of *cis*/*trans* isomers. [d] Obtained as an inseparable 7:4 mixture of *cis*/*trans* isomers. [e] Obtained as an inseparable 3:2 mixture of *cis*/*trans* isomers. [f] Obtained as an inseparable 1:1 mixture of *cis*/*trans* isomers. [g] Mixture of unknown side products afforded based on ^{1}H NMR analysis of the crude mixture. [h] Obtained as an inseparable 5:3 mixture of *cis*/*trans* isomers. [i] No reaction based on TLC and ^{1}H NMR analysis and recovery of the starting alcohol in near quantitative yield.

further supported by the fact that when the respective solutions of 4:1 acetone:H_2O containing **2a** and **3a** were subjected to 1 mol % of TfOH at 90 °C for 24 h, this resulted in both cases in only the recovery of these compounds along with a small amount

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Scheme 2. TfOH-Catalyzed Hydroxylation/Halocyclization of 1a, 1j, and 1v with H_2O and NIS

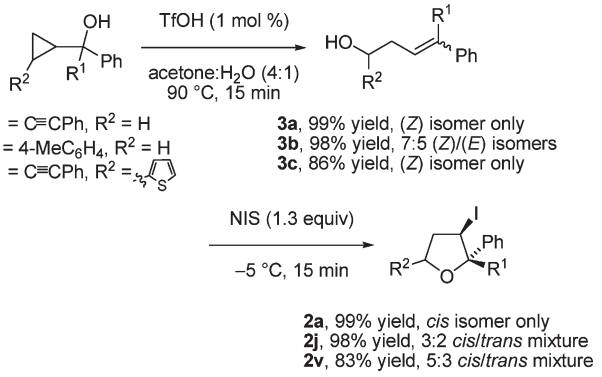


Table 3. TfOH-Catalyzed Hydroxylation/Halocyclization of Cyclopropyl Methanols 1a and 1m[a]

entry	substrates	product	yield (%)
1	**1a** + NBS	**2y**, X = Br	85
2	**1a** + NCS[b]	**2z**, X = Cl	35
3	**1a** + Selectfluor	**2α**, X = F	55
4	**1m** + NBS	**2β**, X = Br	82
5	**1m** + NCS[b]	**2γ**, X = Cl	30
6	**1m** + Selectfluor	**2δ**, X = F	45

[a] All reactions were performed with 1 mol % of TfOH in 4:1 acetone: H_2O at 90 °C followed by 1.3 equiv of the electrophilic halide source at −5 °C.[15] [b] Reaction conducted at reflux.

of unknown side products based on ^{1}H NMR analysis of the crude reaction mixtures.

On the basis of the above results, we tentatively propose the first step of the present reaction to proceed by the mechanism illustrated in Scheme 3 for the hydroxylative ring-opening of **1v** and iodocyclization with NIS. In a manner similar to that described for the analogous TfOH-catalyzed ring-opening of

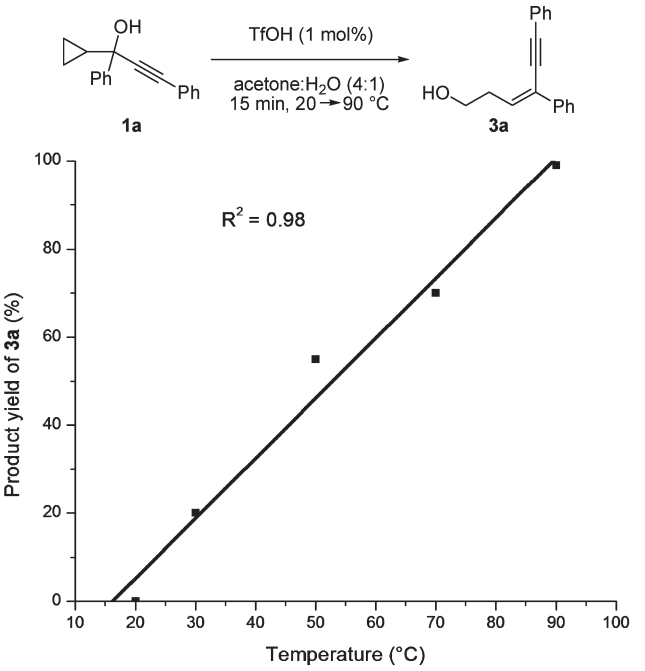
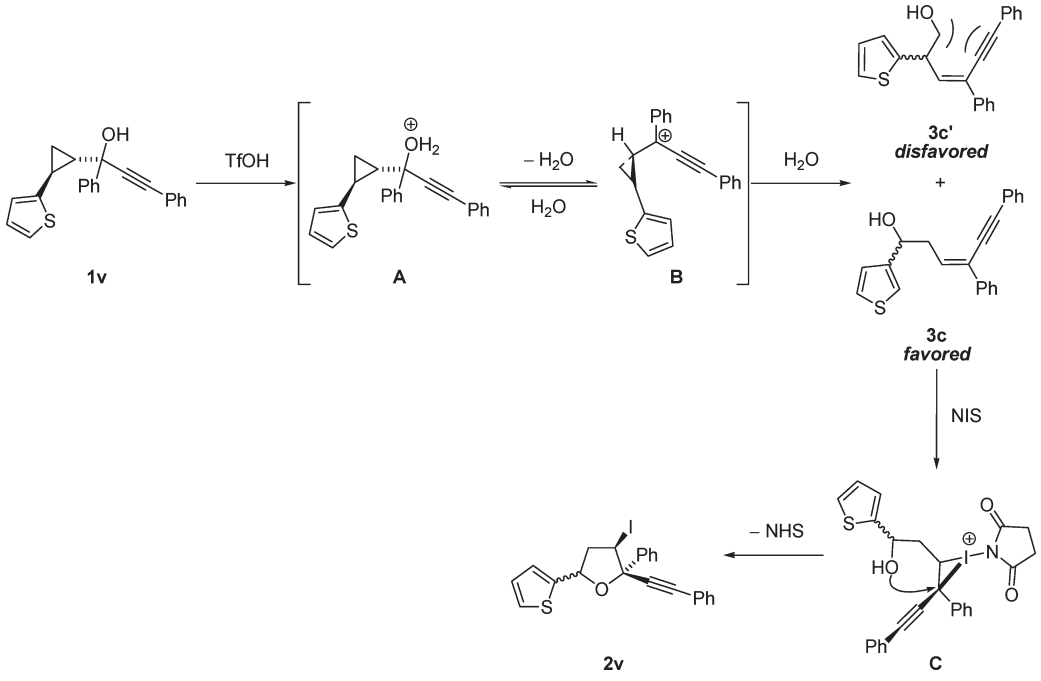


Figure 3. TfOH-Catalyzed Hydroxylative Ring-Opening of **1a** to **3a** at Different Temperatures

Scheme 3. Tentative Mechanism for TfOH-Catalyzed Hydroxylation/Halocyclization of 1v with H_2O and NIS



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cyclopropyl methanols with alcohols,[9c] this could involve dehydration of the substrate by the Brønsted acid to give the putative carbocationic species **B**.[18] While it is possible that this step is reversible given that the reaction is carried out in the presence of H_2O, subsequent cyclopropylcarbinol−homoallylic rearrangement of this newly formed cationic species and trapping by H_2O would provide the (*Z*)-homoallylic alcohol **3c**. The second step then involves rapid cyclization of this unsaturated alcohol intermediate from the opposite face of the cationic iodonium moiety in **C** formed on treating with NIS to furnish the 3-halohydrofuran **2v**.[16] The possible involvement of a carbocationic intermediate would be consistent with our earlier findings showing a marked decrease in product yields as the polarity of the organic component or acidity of the solvent system decreases in control experiments with **1a** (entries 1−3 and 7−8 in Table 1). It would also account for the contrasting activities found for the reactions of the respective tertiary and secondary alcohols **1s** and **1x** depicted in entries 18 and 23 in Table 2 since it appears that they cannot efficiently stabilize the resulting cationic charge. We postulate that the *E*/*Z* selectivities observed on forming the homoallylic alcohol intermediate **3c** could be due to **B** adopting the conformer depicted in Scheme 3.[19] This would provide a carbocationic species with the least amount of unfavorable steric interactions between the functional groups and the cyclopropane ring prior to the hydroxylative ring-opening process. For reactions where $R^3 \neq H$ and provided the trisubstituted furan adduct, we surmise that a possible reason for preferential S_N1' attack at the carbon center bearing the substituent is so that formation of the more sterically demanding primary homoallylic alcohol **3c′** can be avoided.[19]

CONCLUSION

In summary, we have described an efficient one-pot, two-step synthetic route to 3-halohydrofurans based on TfOH-catalyzed hydroxylation followed by *N*-halosuccinamide or Selectfluor-mediated halocyclization of cyclopropyl methanols. The reaction was shown to be applicable to a wide variety of substrates bearing electronic and sterically demanding substituent combinations. The efficiency of the present mild and operationally straightforward method was demonstrated by the moderate to excellent product yields and, in most cases, with exclusive *cis* selectivity achieved at a low catalyst loading of 1 mol %. Additionally, the present procedure was shown to benefit from reagents and a catalyst that are low cost and commercially available.

EXPERIMENTAL SECTION

General Remarks. All reactions were performed under an argon atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Cyclopropyldiphenyl methanol (**1e**) was purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using precoated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (*n*-hexane:EtOAc as eluent). ^{1}H and ^{13}C NMR spectra were measured on 300, 400, and 500 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as follows: s (singlet), bs (broad singlet), d (doublet), dt (doublet of triplet), t (triplet), bt (broad triplet), q (quartet), aq (apparent quartet), dd (doublet of doublets), dddd (doublet of doublets of doublets of doublets), aquin (apparent quintet), or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. Infrared spectra were recorded on a FTIR spectrometer. Solid samples were examined as a thin film between NaCl salt plates. Low-resolution mass spectra were determined on a mass spectrometer and reported in units of mass to charge (*m*/*z*). High-resolution mass spectra (HRMS) were obtained on a LC/HRMS mass spectrometer.

Experimental Procedure for the Preparation of Substituted 1-Cyclopropyl-2-propyn-1-ols or Cyclopropyl Methanols (1a and 1o−v).[9c] To a solution of the alkyne (3.3 mmol) in THF (10 mL) was added LDA (2.0 M in THF, 1.8 mL) at −78 °C. The resulting solution was stirred for 1 h prior to slow addition of cyclopropyl ketone (3 mmol) in THF (2 mL) at −78 °C. For **1s**−**v**: To a solution of phenylmagnesium chloride or ethynylmagnesium chloride (2.0 M THF solution, 0.58 mL, 1.0 mmol) in THF (5 mL) at 0 °C was added dropwise a solution of cyclopropyl ketone (0.9 mmol) in THF (3 mL). The resulting mixture was slowly warmed to room temperature and stirred for a further 10 h. On completion, the reaction mixture was quenched by adding saturated NH_4Cl (50 mL) and extracted with Et_2O (2 × 25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane:EtOAc = 9:1) gave the title compound.

Experimental Procedure for the Preparation of Substituted Cyclopropyl Methanols (1b−n and 1w, x).[9c,11c,11d] To a solution of cyclopropylmagnesium bromide (0.5 M THF solution; 3.3 mL, 1.6 mmol) in THF (5 mL) at 0 °C was added dropwise a solution of ketone or aldehyde (1.3 mmol) in THF (3 mL). The resulting mixture was stirred at room temperature for 15 h. The mixture was treated with saturated NH_4Cl aq (50 mL). The organic layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane:EtOAc = 9:1) gave the title compound.

Cyclopropyl-1,3-diphenylprop-2-yn-1-ol (1a):[9c] yield 65%; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76−7.74 (m, 2H), 7.46−7.25 (m, 8H), 2.54 (s, 1H), 1.49−1.44 (m, 1H), 0.90−0.85 (m, 1H), 0.75−0.60 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.9, 131.9, 128.6, 128.4, 128.3, 127.8, 125.59, 122.5, 89.1, 86.1, 75.0, 23.9, 3.4, 2.6.

Cyclopropylbis(4-fluorophenyl)methanol (1b): yield 80%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42−7.37 (m, 4H), 7.02−6.96 (m, 4H), 1.88 (s, 1H), 1.60−1.53 (m, 1H), 0.63−0.58 (m, 2H), 0.47−0.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.1, 160.6, 142.8 (d, 1C, J_{C-F} = 12.4 Hz), 128.59 (d, 1C, J_{C-F} = 31.8 Hz), 114.8 (d, 1C, J_{C-F} = 84.1 Hz), 21.8, 1.8; IR (neat, cm^{-1}) 3334, 3018, 1604, 1506, 1215, 1159, 837, 752, 669, 518; HRMS (ESI) calcd for $C_{16}H_{15}OF_2$ 261.1091, found 261.1086.

Bis(4-chlorophenyl)(cyclopropyl)methanol (1c): yield 85%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36−7.27 (m, 8H), 1.87 (s, 1H), 1.58−1.51 (m, 1H), 0.63−0.58 (m, 2H), 0.46−0.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 133.1, 128.2, 128.1, 76.5, 21.5, 1.8; IR (neat, cm^{-1}) 3431, 1635, 1215, 821, 752, 669, 526; HRMS (ESI) calcd for $C_{16}H_{15}OCl_2$ 293.0500, found 293.0493.

Bis(4-bromophenyl)(cyclopropyl)methanol (1d): yield 78%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.27 (m, 8H), 1.91 (s, 1H), 1.59−1.49 (m, 1H), 0.63−0.57 (m, 2H), 0.47−0.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.7, 131.1, 128.6, 121.3, 21.4, 1.8; IR (neat, cm^{-1}) 3587, 3442, 3018, 1485, 1215, 1010, 761, 669, 522; HRMS (ESI) calcd for $C_{16}H_{15}OBr_2$ 380.9490, found 380.9502.

Cyclopropyldi-*p*-tolylmethanol (1f): yield 82%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (d, 4H, *J* = 8.1 Hz), 7.14 (d, 4H, *J* = 7.9 Hz), 2.34 (s, 6H), 1.84 (s, 1H), 1.65−1.33 (m, 1H), 0.61−0.53 (m, 2H), 0.50−0.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.5, 136.5, 128.6, 126.7, 76.8, 21.6, 21.0, 1.7; IR (neat, cm^{-1}) 3585, 3442, 3018,

2399, 1508, 1215, 1022, 815, 752, 669, 572, 499; HRMS (ESI) calcd for $C_{18}H_{21}O$ 253.1592, found 253.1586.

Cyclopropylbis(4-methoxyphenyl)methanol (1g): yield 87%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38−7.33 (m, 4H), 6.86−6.81 (m, 4H), 3.79 (s, 6H), 1.94 (s, 1H), 1.64−1.44 (m, 1H), 0.64−0.46 (m, 2H), 0.42−0.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.4, 139.7, 128.0, 113.1, 76.6, 55.2, 21.8, 1.7; IR (neat, cm^{-1}) 3541, 3431, 3018, 1635, 1508, 1215, 1035, 779, 671, 522; HRMS (ESI) calcd for $C_{18}H_{21}O_3$ 285.1491, found 285.1494.

(4-Chlorophenyl)(cyclopropyl)(*p*-tolyl)methanol (1h): yield 76%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.10 (m, 8H), 2.32 (s, 3H), 1.85 (s, 1H), 1.58−1.51 (m, 1H), 0.63−0.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.0, 143.9, 137.0, 132.7, 128.8, 128.2, 127.9, 126.8, 76.7, 21.5, 21.0, 2.0, 1.5; IR (neat, cm^{-1}) 3008, 1489, 1215, 1091, 1014, 819, 756, 667, 509; HRMS (ESI) calcd for $C_{17}H_{18}OCl$ 273.1046, found 273.1041.

(4-Chlorophenyl)(cyclopropyl)(4-methoxyphenyl)methanol (1i): yield 84%; light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27−7.15 (m, 6H), 6.7 (d, 2H, J = 8.5 Hz), 3.6 (s, 3H), 2.13 (s, 1H), 1.49−1.42 (m, 1H), 0.55−0.34 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.7, 146.1, 139.1, 132.6, 128.2, 127.9, 113.3, 76.5, 55.2, 21.7, 2.1, 1.4; IR (neat, cm^{-1}) 3585, 3446, 1608, 1510, 1249, 1176, 831, 586, 499; HRMS (ESI) calcd for $C_{17}H_{18}O_2Cl$ 289.0995, found 289.0989.

Cyclopropyl(phenyl)(*p*-tolyl)methanol (1j): yield 84%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (d, 2H, J = 7.8 Hz), 7.22−7.09 (m, 5H), 7.00 (d, 2H, J = 7.8 Hz), 2.21 (s, 3H), 1.83 (s, 1H), 1.51−1.44 (m, 1H), 0.49−0.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.5, 144.4, 136.6, 128.7, 127.9, 126.98, 126.92, 126.8, 77.0, 21.7, 21.1, 1.9, 1.7; IR (neat, cm^{-1}) 3356, 3010, 1647, 1510, 1446, 1215, 981, 815, 752, 667, 514; HRMS (ESI) calcd for $C_{17}H_{19}O$ 239.1436, found 239.1430.

Cyclopropyl(phenyl)(4-biphenyl)methanol (1k): yield 68%; white solid; mp 92−94 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−7.24 (m, 14H), 1.93 (s, 1H), 1.71−1.62 (m, 1H), 0.65−0.58 (m, 2H), 0.54−0.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.2, 146.3, 140.8, 139.8, 128.7, 128.0, 127.3, 127.2, 127.0, 126.8, 126.6, 21.6, 1.85, 1.83; IR (neat, cm^{-1}) 3392, 3018, 1645, 1487, 1446, 1215, 1031, 839, 748, 700, 667, 628, 622, 514, 499; HRMS (ESI) calcd for $C_{22}H_{20}ONa$ 323.1412, found 323.1404.

Cyclopropyl(naphthalen-1-yl)(phenyl)methanol (1l): yield 70%; white solid; mp 111−113 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, 1H, J = 7.0 Hz), 8.01 (d, 1H, J = 8.6 Hz), 7.89 (t, 2H, J = 8.9 Hz), 7.61−7.23 (m, 8H), 2.23 (s, 1H), 1.80−1.77 (m, 1H), 0.80−0.50 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.9, 142.1, 135.0, 131.0, 129.1, 128.8, 128.0, 127.4, 126.7, 126.1, 125.4, 125.3, 125.2, 124.7, 77.7, 23.2, 2.3, 2.2; IR (neat, cm^{-1}) 3435, 3018, 1639, 1215, 758, 669, 499; HRMS (ESI) calcd for $C_{20}H_{19}O$ 275.1436, found 275.1435.

1-Cyclopropyl-1-phenylhexan-1-ol (1m): yield 76%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38−7.12 (m, 5H), 1.89−1.63 (m, 2H), 1.44 (s, 1H), 1.21−1.03 (m, 7H), 0.76−0.73 (m, 3H), 0.39 (q, 2H, J = 7.0 Hz), 0.30−0.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5, 128.1, 127.9, 126.5, 125.5, 75.0, 42.3, 32.3, 23.3, 22.5, 21.8, 14.0, 1.4, 0.7; IR (neat, cm^{-1}) 3369, 3012, 2933, 2870, 2399, 1645, 1446, 1215, 1029, 914, 752, 702, 667, 518; HRMS (ESI) calcd for $C_{15}H_{23}O$ 219.1749, found 219.1753.

1-Cyclopropyl-2,2-dimethyl-1-phenylpropan-1-ol (1n): yield 72%; light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51−7.20 (m, 5H), 1.71−1.67 (m, 1H), 1.25 (s, 1H), 0.98 (s, 9H), 0.82−0.72 (m, 1H), 0.65−0.58 (m, 1H), 0.38−0.31 (m, 1H), 0.11−−0.04 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.0, 127.5, 126.8, 126.2, 78.2, 39.3, 26.0, 16.4, 4.1, 0.3; IR (neat, cm^{-1}) 2976, 1481, 1215, 1145, 773, 704, 667, 470; HRMS (ESI) calcd for $C_{14}H_{21}O$ 205.1592, found 205.1600.

1-(4-Chlorophenyl)-1-cyclopropyl-3-(thiophen-2-yl)prop-2-yn-1-ol (1o):[9c] yield 65%; pale yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.66−7.63 (m, 2H), 7.459−7.451 (m, 1H), 7.35−7.26 (m, 3H), 7.10−7.09 (m, 1H), 2.49 (s, 1H), 1.43−1.37 (m, 1H), 0.85−0.81 (m, 1H), 0.71−0.67 (m, 1H), 0.63−0.57 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.4, 133.5, 129.9, 129.3, 128.3, 127.0, 125.5, 121.1, 88.2, 81.4, 74.4, 23.8, 3.3, 2.5.

1-Cyclopropyl-1-(4-methoxyphenyl)-3-(pyridin-2-yl)prop-2-yn-1-ol (1p):[9c] yield 69%; light brown solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.53−8.52 (m, 1H), 7.68−7.66 (m, 2H), 7.63−7.59 (m, 1H), 7.39 (d, 1H, J = 7.8 Hz), 7.25−7.19 (m, 1H), 6.90−6.87 (m, 2H), 6.90−6.87 (m, 2H), 3.79 (s, 3H), 3.41 (s, 1H), 1.50−1.44 (m, 1H), 0.86−0.82 (m, 1H), 0.74−0.71 (m, 1H), 0.61−0.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.0, 149.8, 142.7, 136.8, 136.2, 127.2, 126.9, 123.0, 113.4, 90.4, 84.6, 73.7, 55.2, 23.6, 3.0, 2.4.

3-Cyclopropyl-1,5-diphenylpenta-1,4-diyn-3-ol (1q):[9c] yield 86%; colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49−7.25 (m, 10H), 2.71 (s, 1H), 1.71−1.62 (m, 1H), 0.85−0.82 (m, 2H), 0.70−0.66 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 131.9, 128.7, 128.2, 122.0, 87.6, 83.6, 66.4, 22.5, 2.7.

1-Cyclopropyl-1-(1-methylcyclohexyl)-3-phenylprop-2-yn-1-ol (1r):[9c] yield 78%; light yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40−7.25 (m, 5H), 1.91 (s, 1H), 1.77−1.60 (m, 7H), 1.58−1.39 (m, 2H), 1.33−1.25 (m, 1H), 1.16 (s, 3H), 1.14−1.09 (m, 1H), 0.68−0.56 (m, 3H), 0.47−0.41 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 131.6, 128.2, 128.1, 122.9, 88.8, 85.8, 80.3, 42.4, 32.4, 31.5, 26.3, 22.1, 22.0, 17.9, 15.7, 4.6, 0.5.

2-Cyclopropylbut-3-yn-2-ol (1s): yield 72%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 1H), 2.28 (bs, 1H), 1.57 (s, 3H), 1.19−1.07 (m, 1H), 0.64−0.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 84.9, 71.6, 69.8, 29.6, 21.6, 2.4, 1.5: IR (neat, cm^{-1}) 3369, 1446, 1215, 921, 756, 702, 669, 518; HRMS (ESI) calcd for $C_7H_{11}O$ 111.0810, found 111.0809

Diphenyl(2-phenylcyclopropyl)methanol (1t): yield 82%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29−7.00 (m, 13H), 6.93 (d, 2H, J = 7.7 Hz), 1.97−1.92 (m, 2H), 1.76−1.71 (m, 1H), 1.11−1.06 (m, 1H), 0.90−0.86 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.4, 147.0, 142.6, 128.5, 128.27, 128.20, 127.4, 127.2, 126.7, 126.2, 125.7, 77.4, 33.5, 20.4, 12.0; IR (neat, cm^{-1}) 3437, 3018, 1643, 1215, 772, 700, 636; HRMS (ESI) calcd for $C_{22}H_{21}O$ 301.1592, found 301.1601.

(2-Pentylcyclopropyl)diphenylmethanol (1u): yield 78%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44−7.39 (m, 4H), 7.31−7.21 (m, 6H), 1.86 (s, 1H), 1.40−1.20 (m, 9H), 0.85−0.81 (m, 4H), 0.66−0.62 (m, 1H), 0.40−0.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.5, 147.3, 127.9, 127.8, 127.0, 126.9, 126.8, 126.6, 77.2, 33.7, 31.6, 29.4, 29.0, 22.6, 15.2, 14.0, 9.1; IR (neat, cm^{-1}) 3437, 3018, 2399, 1639, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{21}H_{27}O$ 295.2062, found 295.2061.

1,3-Diphenyl-1-(2-(thiophen-2-yl)cyclopropyl)prop-2-yn-1-ol (1v):[9c] yield 83%; light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80−7.78 (m, 2H), 7.51−7.33 (m, 8H), 7.05−6.71 (m, 3H), 2.66 (s, 1H), 2.52−2.48 (m, 1H), 1.83−1.78 (m, 1H), 1.62−1.57 (m, 1H), 1.16−1.09 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 144.3, 131.9, 128.8, 128.46, 128.43, 128.0, 126.8, 125.4, 123.3, 122.7, 122.2, 89.1, 86.6, 73.7, 35.0, 16.6, 13.2.

Cyclopropyl(phenyl)methanol (1w): yield 83%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42−7.27 (m, 5H), 3.97 (d, 1H, J = 8.2 Hz), 2.77 (s, 1H), 1.23−1.15 (m, 1H), 0.65−0.48 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 128.3, 127.4, 126.1, 78.4, 19.1, 3.7, 2.8; IR (neat, cm^{-1}) 3435, 3014,1633, 1492, 1452, 1215, 1026, 921, 769, 669; HRMS (ESI) calcd for $C_{10}H_{13}O$ 149.0966, found 149.0968.

1-Cyclopropylhexan-1-ol (1x): yield 79%; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.86−2.81 (m, 1H), 1.61−1.55 (m, 3H), 1.46−1.24 (m, 6H), 0.91−0.85 (m, 4H), 0.52−0.45 (m, 2H), 0.27−0.18 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 76.9, 37.2, 31.9, 25.4, 22.6, 18.0, 14.0, 2.7, 2.4; IR (neat, cm^{-1}) 3352, 1449, 1215, 914, 757, 667, 519; HRMS (ESI) calcd for $C_9H_{19}O$ 143.1436, found 143.1442.

Representative Procedure for TfOH-Catalyzed, *N*-Halosuccinimide or Selectfluor-Mediated Synthesis of 3-Halohydrofurans 2. To a round-bottomed flask containing **1** (0.2 mmol) in acetone:H_2O (4:1, 4 mL) was added TfOH (2 μmol) under a nitrogen atmosphere at room temperature. The reaction mixture was stirred at 90 °C and monitored to completion by TLC analysis. The reaction mixture was brought to −5 °C and a solution of NXS or Selectfluor (0.26 mmol) in acetone (2 mL) was added. The resulting reaction mixture was then stirred at the same temperature and monitored to completion by TLC analysis. The reaction mixture was quenched with a 10% aq solution of $Na_2S_2O_3$ (10 mL), extracted with EtOAc (3 × 10 mL), and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 19:1) gave the title compound.

***cis*-Tetrahydro-3-iodo-2-phenyl-2-(2-phenylethynyl)furan (2a):** white solid; mp 117−119 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77−7.55 (m, 4H), 7.41−7.34 (m, 6H), 4.33−4.29 (m, 1H), 4.20 (aq, 1H, J = 7.4 Hz), 4.11 (t, 1H, J = 8.7 Hz), 2.70−2.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.2, 131.9, 128.7, 128.5, 128.33, 128.31, 126.0, 122.3, 88.7, 88.3, 85.5, 67.1, 37.8, 33.1; IR (neat, cm^{-1}) 3464, 3431, 3016, 1635, 1490, 1215, 1026, 752, 667, 532; HRMS (ESI) calcd for $C_{18}H_{16}OI$ 375.0246, found 375.0258.

2,2-Bis(4-fluorophenyl)tetrahydro-3-iodofuran (2b): reaction time (min), step 1/2 (90/15); white solid; mp 91−93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51−7.35 (m, 4H), 7.02−6.94 (m, 4H), 5.23 (dd, 1H, J_1 = 3.0 Hz, J_2 = 4.7 Hz), 4.43 (aq, 1H, J = 7.9 Hz), 4.05−4.00 (m, 1H), 2.55−2.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.1, 162.9, 160.7, 160.4, 142.1, 138.4, 127.6 (d, 1C, J_{C-F} = 32.2 Hz), 127.0 (d, 1C, J_{C-F} = 31.8 Hz), 115.7, 115.5, 114.7, 114.5, 90.4, 65.9, 38.3, 35.2; IR (neat, cm^{-1}) 3018, 1600, 1506, 1215, 1159, 1047, 833, 744, 669, 559, 513; HRMS (ESI) calcd for $C_{16}H_{14}OIF_2$ 387.0057, found 387.0076.

2,2-Bis(4-chlorophenyl)tetrahydro-3-iodofuran (2c): reaction time (min), step 1/2 (120/15); light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, 2H, J = 8.5 Hz), 7.26−7.16 (m, 6H), 5.14−5.12 (m, 1H), 4.35 (aq, 1H, J = 8.0 Hz), 3.97−3.92 (m,1H), 2.45−2.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.5, 140.9, 133.4, 133.0, 128.9, 128.0, 127.2, 126.6, 90.5, 65.9, 38.2, 34.5; IR (neat, cm^{-1}) 3462, 1635, 1215, 752, 669, 522; HRMS (ESI) calcd for $C_{16}H_{14}OCl_2I$ 418.9466, found 418.9478.

2,2-Bis(4-bromophenyl)tetrahydro-3-iodofuran (2d): reaction time (min), step 1/2 (120/15); light brown solid; mp 160−162 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44−7.36 (m, 6H), 7.27 (d, 2H, J = 8.5 Hz), 5.19 (dd, 1H, J_1 = 2.4 Hz, J_2 = 4.8 Hz), 4.42 (aq, 1H, J = 8.0 Hz), 4.04−3.99 (m, 1H), 2.53−2.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.9, 141.4, 131.9, 130.9, 127.5, 127.0, 121.6, 121.2, 90.6, 65.9, 38.2, 34.2; IR (neat, cm^{-1}) 3333, 3018, 1635, 1215, 783, 669, 524; HRMS (ESI) calcd for $C_{16}H_{14}OIBr_2$ 508.8436, found 508.8446.

Tetrahydro-3-iodo-2,2-diphenylfuran (2e): reaction time (min), step 1/2 (30/20); pale yellow solid; mp 83−85 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (d, 2H, J = 7.4 Hz), 7.44 (d, 2H, J = 7.3 Hz), 7.31−7.15 (m, 6H), 5.32−5.30 (m, 1H), 4.43 (aq, 1H, J = 8.0 Hz), 4.07−4.02 (m, 1H), 2.52−2.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5, 142.6, 128.7, 127.7, 127.3, 127.0, 125.8, 125.2, 91.2, 65.6, 38.3, 36.0; IR (neat, cm^{-1}) 3300, 3018, 1489, 1448, 1215, 1029, 752, 669, 518; HRMS (ESI) calcd for $C_{16}H_{16}OI$ 351.0246, found 351.0230.

Tetrahydro-3-iodo-2,2-di-*p*-tolylfuran (2f): reaction time (min), step 1/2 (15/20); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.41 (d, 2H, J = 8.1 Hz), 7.32 (d, 2H, J = 8.1 Hz), 7.10−7.05 (m, 4H), 5.28 (bt, 1H, J = 3.6 Hz), 4.41 (aq, 1H, J = 7.9 Hz), 4.10−3.96 (m, 1H), 2.51−2.44 (m, 2H), 2.279 (s, 3H), 2.271 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.8, 139.9, 136.8, 136.4, 129.3, 128.4, 125.6, 125.1,91.1, 65.5, 38.4, 36.5, 21.1, 20.9; IR (neat, cm^{-1}) 3334, 3018, 1651, 1215, 748, 669, 513; HRMS (ESI) calcd for $C_{18}H_{20}OI$ 379.0559, found 379.0555.

Tetrahydro-3-iodo-2,2-bis(4-methoxyphenyl)furan (2g): reaction time (min), step 1/2 (20/15); brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, 2H, J = 8.7 Hz), 7.34 (d, 2H, J = 8.7 Hz), 6.85−6.79 (m, 4H), 5.26 (bt, 1H, J = 3.8 Hz), 4.41 (aq, 1H, J = 7.8 Hz), 4.04−3.99 (m, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.53−2.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.6, 158.3, 139.3, 134.9, 127.0, 126.4, 113.9, 112.9, 90.6, 65.7, 55.2, 55.1, 38.5, 36.7; IR (neat, cm^{-1}) 3242, 1606, 1508, 1174, 1033, 833, 688, 524; HRMS (ESI) calcd for $C_{18}H_{20}O_3I$ 411.0457, found 411.0461.

2-(4-Chlorophenyl)tetrahydro-3-iodo-2-*p*-tolylfuran (2h): reaction time (min), step 1/2 (60/15); pale yellow oil; dr ratio = 5:4; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, 1H, J = 8.4 Hz), 7.37−7.06 (m, 7H), 5.25−5.23 (m, 1H, *cis* or *trans* isomer), 5.22−5.20 (m, 1H, *cis* or *trans* isomer), 4.43−4.35 (m, 1H), 4.04−3.98 (m, 1H), 2.49−2.40 (m, 2H), 2.279 (s, 1H, *cis* or *trans* isomer), 2.271 (s, 1H, *cis* or *trans* isomer); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 143.2, 141.5, 139.2, 137.2, 136.8, 133.1, 132.6, 129.5, 128.8, 128.5, 127.9, 127.2, 126.7, 125.6, 125.0, 90.8, 65.77 (*cis* or *trans* isomer), 65.71 (*cis* or *trans* isomer), 38.4 (*cis* or *trans* isomer), 38.2 (*cis* or *trans* isomer), 35.5 (*cis* or *trans* isomer), 35.4 (*cis* or *trans* isomer), 21.1 (*cis* or *trans* isomer), 20.9 (*cis* or *trans* isomer); IR (neat, cm^{-1}) 3496, 1635, 1215, 752, 499; HRMS (ESI) calcd for $C_{17}H_{17}OClI$ 399.0013, found 399.0016.

2-(4-Chlorophenyl)tetrahydro-3-iodo-2-(4-methoxyphenyl)furan (2i): reaction time (min), step 1/2 (60/15); brown color oil; dr ratio = 7:4; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46−7.20 (m, 6H), 6.83−677 (m, 2H), 5.23−5.18 (m, 1H), 4.42−4.34 (m, 1H), 4.04−3.96 (m, 1H), 3.75 (s, 3H, *cis* or *trans* isomer), 3.74 (s, 3H, *cis* or *trans* isomer), 2.52−2.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.8, 158.5, 145.3, 134.2, 133.1, 132.6, 128.8, 127.8, 127.2, 127.0, 126.7, 126.4, 114.1, 113.1, 90.6, 65.8 (*cis* or *trans* isomer), 65.7 (*cis* or *trans* isomer), 55.2 (*cis* or *trans* isomer), 55.1 (*cis* or *trans* isomer), 38.4 (*cis* or *trans* isomer), 38.3 (*cis* or *trans* isomer), 35.8 (*cis* or *trans* isomer), 35.4 (*cis* or *trans* isomer); IR (neat, cm^{-1}) 3435, 3018, 1606, 1508, 1251, 1215, 1033, 759, 669; HRMS (ESI) calcd for $C_{17}H_{17}O_2ClI$ 414.9962, found 414.9964.

Tetrahydro-3-iodo-2-phenyl-2-*p*-tolylfuran (2j): reaction time (min), step 1/2 (15/10); colorless oil; dr ratio = 3:2; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44−6.98 (m, 9H), 5.18 (bt, 1H, J = 3.3 Hz), 4.34 (aq, 1H, J = 8.0 Hz), 4.02−3.95 (m, 1H), 2.40−2.32 (m, 2H), 2.20 (s, 3H, *cis* or *trans* isomer), 2.19 (s, 3H, *cis* or *trans* isomer); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.3, 144.1, 141.3, 140.9, 137.0, 136.4, 129.4, 128.7, 128.4, 127.7, 127.2, 126.8, 125.99, 125.96, 125.0, 91.0, 65.1, 57.0 (*cis* or *trans* isomer), 56.9 (*cis* or *trans* isomer), 36.45 (*cis* or *trans* isomer), 36.42 (*cis* or *trans* isomer), 21.0 (*cis* or *trans* isomer), 20.9 (*cis* or *trans* isomer); IR (neat, cm^{-1}) 3400, 3392, 3018, 1647, 1215, 756, 669, 518, 497; HRMS (ESI) calcd for $C_{17}H_{18}OI$ 365.0402, found 365.0389.

2-(4-Biphenyl)tetrahydro-3-iodo-2-phenylfuran (2k): reaction time (min), step 1/2 (60/15); off white solid; mp 134−136 °C; dr ratio = 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60−7.17 (m, 14H), 5.34−5.31 (m, 1H), 4.45 (aq, 1H, J = 7.9 Hz), 4.12−4.04 (m, 1H), 2.54−2.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 145.5, 142.7, 141.7, 140.7, 140.4, 140.1, 139.6, 128.8, 128.7, 128.6, 127.8, 127.45, 127.43, 127.3, 127.2, 127.09, 127.04, 126.4, 126.2, 125.8, 125.7, 125.2, 91.24 (*cis* or *trans* isomer), 91.21 (*cis* or *trans* isomer), 65.7, 38.3, 35.97 (*cis* or *trans* isomer), 35.94 (*cis* or *trans* isomer); IR (neat, cm^{-1}) 3018, 1215, 759, 669, 511; HRMS (ESI) calcd for $C_{22}H_{20}OI$ 427.0559, found 427.0558.

***cis*-Tetrahydro-3-iodo-2-(naphthalen-1-yl)-2-phenylfuran (2l):** reaction time (min), step 1/2 (120/60); brown solid; mp 116−118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17−8.08 (m, 2H), 7.82−7.49 (m, 5H), 7.36−7.12 (m, 5H), 5.77 (d, 1H, J = 5.3 Hz), 4.46 (aq, 1H, J = 8.1 Hz), 4.11−4.06 (m, 1H), 2.89−2.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.4, 134.1, 129.9, 128.9, 128.7, 128.3, 127.2, 126.3, 125.6, 125.2, 125.0, 124.65, 124.61, 92.3, 65.3, 39.2, 35.3; IR (neat, cm^{-1}) 3419, 3018, 1645, 1215, 761, 669, 499; HRMS (ESI) calcd for $C_{20}H_{18}OI$ 401.0402, found 401.0421.

***cis*-Tetrahydro-3-iodo-2-pentyl-2-phenylfuran (2m):** reaction time (min), step 1/2 (30/10); colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40−7.25 (m, 5H), 4.63 (dd, 1H, J_1 = 3.8 Hz, J_2 = 5.8 Hz), 4.22 (aq, 1H,

J = 7.9 Hz), 4.02 (dt, 1H, J_1 = 4.0 Hz, J_2 = 8.2 Hz), 2.47−2.31 (m, 2H), 2.01−1.90 (m, 2H), 1.27−1.14 (m, 5H), 0.89−0.80 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.7, 128.3, 126.9, 125.2, 88.1, 66.0, 44.2, 38.3, 37.8, 32.0, 24.6, 22.5, 14.0; IR (neat, cm^{-1}) 3018, 1215, 752, 513; HRMS (ESI) calcd for $C_{15}H_{22}OI$ 345.0715, found 345.0732.

***cis*-2-*tert*-Butyltetrahydro-3-iodo-2-phenylfuran (2n):** reaction time (min), step 1/2 (120/60); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62−7.14 (m, 5H), 4.60 (dd, 1H, J_1 = 6.7 Hz, J_2 = 7.7 Hz), 3.94−3.83 (m, 2H), 2.61−2.43 (m, 1H), 2.17−2.01 (m, 1H), 0.94 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.1, 128.8, 126.8, 126.4.2, 90.4, 66.2, 40.7, 38.9, 27.2, 27.0; IR (neat, cm^{-1}) 3541, 3018, 1635, 1215, 771, 669, 559, 514; HRMS (ESI) calcd for $C_{14}H_{20}OI$ 331.0559, found 331.0565.

***cis*-2-(4-Chlorophenyl)tetrahydro-3-iodo-2-(2-(thiophen-2-yl)ethynyl)furan (2o):** reaction time (min), step 1/2 (20/30); pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, 2H, J = 8.5 Hz), 7.47−7.11 (m, 5H), 4.22−4.06 (m, 2H), 3.93 (t, 1H, J = 8.8 Hz), 2.61−2.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.8, 134.4, 130.0, 129.7, 128.4, 127.5, 125.4, 121.1, 87.3, 85.1, 84.1, 67.1, 37.7, 32.7; IR (neat, cm^{-1}) 3412, 3018, 2399, 1645, 1215, 1031, 927, 744, 669, 624, 522; HRMS (ESI) calcd for $C_{16}H_{13}OSClI$ 414.9420, found 414.9402.

***cis*-2-(2-(Tetrahydro-3-iodo-2-(4-methoxyphenyl)furan-2-yl)ethynyl)pyridine (2p):** reaction time (min), step 1/2 (30/15); light brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.63−8.61 (m, 1H), 7.70−7.52 (m, 4H), 7.27−7.22 (m,1H), 6.92−6.87 (m, 2H), 4.34−4.27 (m, 1H), 4.21−4.05 (m, 2H), 3.81 (s, 3H), 2.73−2.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 150.1, 142.6, 136.1, 130.6, 127.7, 127.4, 123.2, 113.6, 88.2, 87.7, 85.3, 67.1, 55.3, 37.6, 32.5; IR (neat, cm^{-1}) 3367, 3018, 1510, 1465, 1215, 1174, 1029, 752, 667, 511; HRMS (ESI) calcd for $C_{18}H_{17}NO_2I$ 406.0304, found 406.0306.

Tetrahydro-3-iodo-2,2-bis(2-phenylethynyl)furan (2q): reaction time (min), step 1/2 (30/60); light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56−7.49 (m, 4H), 7.34−7.25 (m, 6H), 4.53 (t, 1H, J = 7.3 Hz), 4.26−4.09 (m, 2H), 2.86−2.77 (m, 1H), 2.62−2.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.0, 129.0, 128.9, 128.29, 128.27, 121.8, 121.7, 86.7, 86.6, 84.9, 84.4, 66.9, 37.2, 30.8; IR (neat, cm^{-1}) 3356, 3018, 1490, 1215, 752, 669, 513; HRMS (ESI) calcd for $C_{20}H_{16}OI$ 399.0246, found 399.0257.

***cis*-Tetrahydro-3-iodo-2-(1-methylcyclohexyl)-2-(2-phenylethynyl)furan (2r):** colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54−7.31 (m, 5H), 4.36 (t, 1H, J = 8.3 Hz), 4.03 (aq, 1H, J = 7.6 Hz), 3.80 (aq, 1H, J = 7.4 Hz), 2.59−2.53 (m, 2H), 1.88−1.24 (m, 8H), 1.20 (s, 3H), 0.97−0.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.7, 128.3, 128.2, 122.9, 89.9, 89.7, 88.6, 66.5, 41.8, 40.3, 33.3, 31.9, 26.0, 22.1, 22.0, 21.9, 18.4; IR (neat, cm^{-1}) 3018, 2933, 2399, 1215, 1035, 927, 781, 736, 669, 507; HRMS (ESI) calcd for $C_{19}H_{24}OI$ 395.0872, found 395.0878.

Tetrahydro-3-iodo-2,2,5-triphenylfuran (2t): reaction time (min), step 1/2 (15/15); pale yellow solid; mp 122−124 °C; dr ratio = 1:0.6; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55−7.46 (m, 5H), 7.37−7.09 (m, 19H), 5.67 (dd, 1H, J_1 = 6.1 Hz, J_2 = 8.6 Hz, *cis* or *trans* isomer), 5.42 (bt, 1H, J = 4.1 Hz, *cis* or *trans* isomer), 5.29 (bt, 1H, J = 5.7 Hz, *cis* or *trans* isomer), 4.90 (t, 1H, J = 7.4 Hz, *cis* or *trans* isomer), 3.00 (a quin, 1H, J = 7.1 Hz, *cis* or *trans* isomer), 2.76−2.70 (m, 1H, *cis* or *trans* isomer), 2.67−2.60 (m, 1H, *cis* or *trans* isomer), 2.45−2.38 (m, 1H, *cis* or *trans* isomer); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.4, 146.8, 144.6, 142.6, 141.39, 141.34, 128.7, 128.5, 128.4, 127.76, 127.71, 127.6, 127.4, 127.3, 127.1, 126.6, 126.43, 126.41, 126.3, 126.2, 126.1, 91.8 (*cis* or *trans* isomer), 90.9 (*cis* or *trans* isomer), 81.6 (*cis* or *trans* isomer), 78.3 (*cis* or *trans* isomer), 46.79 (*cis* or *trans* isomer), 46.74 (*cis* or *trans* isomer), 35.1 (*cis* or *trans* isomer), 33.2 (*cis* or *trans* isomer); IR (neat, cm^{-1}) 3417, 3018, 1631, 1448, 1215, 1049, 929, 774, 700, 669; HRMS (ESI) calcd for $C_{22}H_{19}OINa$ 449.0378, found 449.0388.

Tetrahydro-3-iodo-5-pentyl-2,2-diphenylfuran (2u): reaction time (min), step 1/2 (15/30); colorless oil; dr ratio = 1:0.6; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51−7.47 (m, 3H), 7.36−7.08 (m, 13H), 5.38 (dd, 1H, J_1 = 1.7 Hz, J_2 = 4.8 Hz, *cis* or *trans* isomer), 5.20 (dd, 1H, J_1 = 4.5 Hz, J_2 = 6.6 Hz, *cis* or *trans* isomer), 4.67−4.58 (m, 1H, *cis* or *trans* isomer), 3.91 (a quin 1H, J = 6.8 Hz, *cis* or *trans* isomer), 2.65 (vquin, 1H, J = 7.02 Hz, *cis* or *trans* isomer), 2.49 (dddd, 1H, J_1 = 1.9 Hz, J_2 = 5.7 Hz, J_3 = 1.9 Hz, J_4 = 5.7 Hz, *cis* or *trans* isomer), 2.37−2.29 (m, 1H, *cis* or *trans* isomer), 2.07−1.93 (m, 2H), 1.72−1.64 (m, 2H), 1.49−1.45 (m, 2H), 1.39−1.18 (m, 8H), 0.87−0.80 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.5, 146.9, 145.2, 143.0, 128.5, 128.3, 127.6, 127.5, 127.3, 127.1, 127.0, 126.8, 126.2, 125.9, 125.7, 125.4, 91.0 (*cis* or *trans* isomer), 90.1 (*cis* or *trans* isomer), 79.6 (*cis* or *trans* isomer), 77.4 (*cis* or *trans* isomer), 44.5 (*cis* or *trans* isomer), 44.1 (*cis* or *trans* isomer), 37.1, 35.9 (*cis* or *trans* isomer), 35.8 (*cis* or *trans* isomer), 34.0, 31.82 (*cis* or *trans* isomer), 31.80 (*cis* or *trans* isomer), 26.2 (*cis* or *trans* isomer), 26.1 (*cis* or *trans* isomer), 22.65 (*cis* or *trans* isomer), 22.61 (*cis* or *trans* isomer), 14.07 (*cis* or *trans* isomer), 14.02 (*cis* or *trans* isomer), 1.0; IR (neat, cm^{-1}) 3435, 2100, 1633, 1215, 771, 669; HRMS (ESI) calcd for $C_{21}H_{26}OI$ 421.1028, found 421.1016.

Tetrahydro-3-iodo-2-phenyl-2-(2-phenylethynyl)-5-(thiophen-2-yl)furan (2v): reaction time (min), step 1/2 (15/30); light brown solid; mp 71−73 °C dr ratio = 1:0.6; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82−7.77 (m, 2H), 7.57−7.54 (m, 2H), 7.41−6.78 (m, 9H), 5.57 (dd, 1H, J_1 = 7.1 Hz, J_2 = 8.8 Hz, *cis* or *trans* isomer), 5.51 (dd, 1H, J_1 = 6.2 Hz, J_2 = 9.5 Hz, *cis* or *trans* isomer), 4.28−4.21 (m, 1H), 3.09−2.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.4, 145.0, 139.3, 139.0, 136.4, 131.88, 131.85, 128.8, 128.7, 128.6, 128.35, 128.31, 126.7, 126.6, 126.25, 126.22, 125.9, 125.5, 122.4, 122.2, 89.8 (*cis* or *trans* isomer), 89.5 (*cis* or *trans* isomer), 89.2, (*cis* or *trans* isomer), 88.9 (*cis* or *trans* isomer), 86.0 (*cis* or *trans* isomer), 85.9 (*cis* or *trans* isomer), 77.9 (*cis* or *trans* isomer), 77.5 (*cis* or *trans* isomer), 47.6 (*cis* or *trans* isomer), 47.2 (*cis* or *trans* isomer), 32.2 (*cis* or *trans* isomer), 31.7 (*cis* or *trans* isomer); IR (neat, cm^{-1}) 3388, 3018, 1647, 1215, 759, 669, 518; HRMS (ESI) calcd for $C_{22}H_{18}OSI$ 457.0123, found 457.0143.

***cis*-Tetrahydro-3-iodo-2-phenylfuran (2w):** reaction time (min), step 1/2 (120/15); yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41−7.25 (m, 5H), 5.15 (d, 1H, J = 6.3 Hz), 4.21−4.09 (m, 2H), 4.03 (aq, 1H, J = 6.5 Hz), 2.60−2.54 (m, 1H), 2.42−2.34 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 128.6, 128.5, 128.1, 126.4, 126.0, 89.8, 68.0, 38.3, 27.0; IR (neat, cm^{-1}) 3415, 3018, 1643, 1215, 756, 669, 497; HRMS (ESI) calcd for $C_{10}H_{12}OI$ 274.9933, found 274.9943.

***cis*-3-Bromotetrahydro-2-phenyl-2-(2-phenylethynyl)furan (2y):** reaction time (min), step 1/2 (15/20); white solid; mp 95−97 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, 2H, J = 6.6 Hz), 7.54−7.25 (m, 8H), 4.41−4.33 (m, 1H), 4.26−4.14 (m, 2H), 2.71−2.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.8, 131.9, 128.6, 128.4, 128.3, 128.2, 125.7, 122.3, 88.6, 87.1, 84.6, 66.2, 55.6, 35.5; IR (neat, cm^{-1}) 3435, 3018, 1645, 1215, 1039, 779, 669, 524, 503; HRMS (ESI) calcd for $C_{18}H_{16}OBr$ 327.0385, found 327.0383.

***cis*-3-Chlorotetrahydro-2-phenyl-2-(2-phenylethynyl)furan (2z):** reaction time (min), step 1/2 (15/120); white solid; mp 70−72 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63−7.42 (m, 4H), 7.34−7.17 (m, 6H), 4.34−4.27 (m, 1H), 4.19−4.07 (m, 2H), 2.56−2.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.1, 131.9, 128.6, 128.4, 128.3, 128.2, 125.5, 122.4, 88.6, 86.4, 84.5, 65.8, 65.1, 34.7; IR (neat, cm^{-1}) 3018, 1215, 756, 669, 514; HRMS (ESI) calcd for $C_{18}H_{16}OCl$ 283.0890, found 283.0882.

***cis*-3-Fluorotetrahydro-2-phenyl-2-(2-phenylethynyl)furan (2*α*):** reaction time (min), step 1/2 (15/120); white solid; mp 80−82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, 2H, J = 7.4 Hz), 7.49−7.26 (m, 8H), 5.15−5.01 (m, 1H), 4.40 (aq, 1H, J = 8.2 Hz), 4.28−4.20 (m, 1H), 2.35−2.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.9, 131.9, 128.5, 128.1, 125.3, 122.4, 99.1, 97.6, 87.5, 86.25 (d, 1C, J_{C-F} = 24.1 Hz), 83.9 (d, 1C, J_{C-F} = 76.1 Hz), 66.7, 31.2 (d, 1C, J_{C-F} = 84.5 Hz), 30.9; IR (neat, cm^{-1}) 3466, 1718, 1280, 1215, 1051, 752, 669; HRMS (ESI) calcd for $C_{18}H_{16}OF$ 267.1185, found 267.1196.

***cis*-3-Bromotetrahydro-2-pentyl-2-phenylfuran (2*β*):** reaction time (min), step 1/2 (30/15); colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz)

δ 7.33−7.20 (m, 5H), 4.63 (dd, 1H, J_1 = 2.8 Hz, J_2 = 5.3 Hz), 4.21 (aq, 1H, J = 8.3 Hz), 4.02 (dt, 1H, J_1 = 3.6 Hz, J_2 = 8.3 Hz), 2.36−2.19 (m, 2H), 2.04−1.81 (m, 2H), 1.26−1.16 (m, 5H), 0.88−0.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.5, 128.3, 127.0, 125.1, 88.8, 65.4, 59.3, 40.4, 36.2, 32.0, 24.2, 22.4, 13.9; IR (neat, cm^{-1}) 3435, 3018, 1645, 1215, 752, 669; HRMS (ESI) calcd for $C_{15}H_{22}OBr$ 297.0854, found 297.0858.

***cis*-3-Chlorotetrahydro-2-pentyl-2-phenylfuran (2γ):** reaction time (min), step 1/2 (30/120); light brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27−7.14 (m, 5H), 4.50 (dd, 1H, J_1 = 2.6 Hz, J_2 = 5.2 Hz), 4.14 (aq, 1H, J = 8.2 Hz), 3.96 (dt, 1H, J_1 = 3.7 Hz, J_2 = 8.4 Hz), 2.30−1.80 (m, 4H), 1.18−1.12 (m, 5H), 0.87−0.69 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.9, 128.3, 127.0, 125.1, 89.3, 67.0, 65.1, 38.2, 35.5, 32.1, 23.9, 22.4, 14.0; IR (neat, cm^{-1}) 3435, 3018, 1635, 1219, 785, 667, 590, 503; HRMS (ESI) calcd for $C_{15}H_{22}OCl$ 253.1359, found 253.1350.

***cis*-3-Fluorotetrahydro-2-pentyl-2-phenylfuran (2δ):** colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34−7.23 (m, 5H), 5.28−5.09 (m, 1H), 4.19 (aq, 1H, J = 8.4 Hz), 4.04−3.86 (m, 1H), 2.42−1.80 (m, 4H), 1.19−1.17 (m, 5H), 0.92−0.76 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.4, 128.2, 127.0, 125.4, 99.6, 97.2, 89.9 (d, 1C, J_{C-F} = 75.1 Hz), 65.4, 35.5 (d, 1C, J_{C-F} = 31.9 Hz), 32.2, 31.8, 31.6, 23.5, 22.4, 13.9; IR (neat, cm^{-1}) 3018, 1215, 759, 665, 524; HRMS (ESI) calcd for $C_{15}H_{22}OF$ 237.1655, found 237.1651.

(*Z*)-4,6-Diphenylhex-3-en-5-yn-1-ol (3a): yield 99%; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (d, 2H, J = 7.2 Hz), 7.58−7.29 (m, 8H), 6.53 (t, 1H, J = 7.4 Hz), 3.86 (t, 2H, J = 6.4 Hz), 2.89 (q, 2H, J = 6.6 Hz), 2.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.9, 134.0, 131.6, 128.46, 128.44, 127.8, 126.1, 125.7, 123.2, 95.7, 86.5, 71.8, 62.0, 34.9; IR (neat, cm^{-1}) 3419, 3018, 2399, 1645, 756, 667; HRMS (ESI) calcd for $C_{18}H_{17}O$ 249.1279, found 249.1288.

4-Phenyl-4-*p*-tolylbut-3-en-1-ol (3b): yield 98%; colorless oil; mixture of *E*/*Z* isomers = 7:5; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29−6.95 (m, 9H), 6.00−5.95 (m, 1H), 3.62−3.57 (m, 2H), 2.34−2.24 (m, 2H), 2.28 (s, 3H, *E* or *Z* regioisomer), 2.22 (s, 3H, *E* or *Z* regioisomer), 1.62 (bs, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 144.2, 144.1, 142.6, 140.0, 139.6, 136.9, 136.7, 129.88, 129.80, 128.9, 128.8, 128.2, 128.1, 127.3, 127.1, 127.08, 127.05, 125.0, 124.3, 62.6, 33.4 (*E* or *Z* regioisomer), 33.3 (*E* or *Z* regioisomer), 21.2 (*E* or *Z* regioisomer), 21.0 (*E* or *Z* regioisomer); IR (neat, cm^{-1}) 3435, 3018, 2325, 1642, 756, 669; HRMS (ESI) calcd for $C_{17}H_{19}O$ 239.1436, found 239.1438.

(*Z*)-4,6-Diphenyl-1-(thiophen-2-yl)hex-3-en-5-yn-1-ol (3c): yield 86%; pale yellow color oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65−7.51 (m, 4H), 7.36−7.23 (m, 7H), 7.04−6.96 (m, 2H), 6.50 (t, 1H, J = 7.4 Hz), 5.19 (t, 1H, J = 6.4 Hz), 3.17−3.13 (m, 2H), 2.15 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.9, 137.8, 132.6, 131.6, 128.48, 128.44, 128.42, 127.9, 126.7, 126.3, 126.1, 124.8, 123.8, 123.1, 96.0, 86.4, 69.9, 41.1; IR (neat, cm^{-1}) 3415, 3018, 2325, 1645, 757, 669; HRMS (ESI) calcd for $C_{22}H_{19}OS$ 331.1157, found 331.1165.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for all starting materials and products, and CIF files of **2a** and **2α**. This material is available free of charge via the Internet at http://pubs.acs.org.

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