

Efficient Synthesis of Substituted 3-Iodofurans by Electrophilic Cyclization of Propargylic Oxirane Derivatives

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The electrophilic cyclization of various propargylic oxirane compounds and I₂ offers an efficient and straightforward route to highly substituted iodofurans under mild reaction conditions. Further functionalization has demonstrated that

the iodo derivatives obtained are potential synthetic intermediates for the amplification of molecular complexity. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

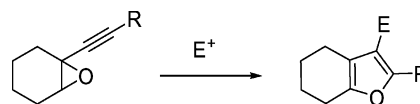
Introduction

Furans are an important class of heterocyclic compounds which are extensively used as an important reaction intermediate in organic synthesis.^[1] It is also a significant component of a number of natural products and synthetic materials, including industrial intermediates and pharmaceuticals.^[2] Of these, halofurans are important derivatives that provide an opportunity for further functionalization. For example, iodofurans are frequently employed as substrates in a variety of C–C, C–N, or C–S bond-forming reactions and also serve as building blocks in combinatorial chemistry.^[3–6] Therefore, iodofurans have received much attention because of their potential usefulness in the synthesis of complex furan derivatives. In general, substituted furans are accessed by ring derivatization or cyclization of acyclic precursors. Several interesting approaches to the synthesis of functionalized furans by the electrophilic cyclization of 3-alkyne-1,2-diols,^[7] 2,4-dialkenyl-1,3-dicarbonyls,^[8] and 2-alkynylcarbonyl compounds have been reported.^[9] Very recently, similar cyclization reactions were also achieved by using 2-(1-alkynyl)alk-2-en-1-ones^[10] and 1,4-disubstituted but-3-yn-1-ones.^[11]

However, of the above oxygen-containing compounds that can be subjected to cyclization, unsaturated alcohols or ketones are the substrates of major interest. The analogous chemistry of alkynes has been far less studied although it would appear to be a very promising route to an extraordi-

nary range of useful, functionally substituted heterocycles and carbocycles. Therefore the development of synthetic routes that allow the facile assembly of substituted furans or iodofurans under mild conditions from simple readily available alkynes still remains an important objective.

Electrophile-promoted cyclization has proven to be an elegant synthetic route to a wide range of halogenated heterocyclic compounds.^[12,13] Recently, we reported some important methods for the synthesis of polysubstituted furans by ammonium ylide and Pd-catalyzed routes.^[14,15] On the basis of this work we considered that propargylic oxiranes could serve as potential substrates for the synthesis of polysubstituted furans. An extensive review of the literature revealed that only a limited number of propargylic oxiranes had been employed as possible halofuran precursors.^[16] Because propargylic oxirane compounds are more readily available than the reported unsaturated alcohols or ketones we envisioned that the utilization of propargylic oxiranes for electrophilic cyclization could significantly expand the range of starting materials suitable for the synthesis of functionally substituted furans. Herein, we report an efficient method for the synthesis of highly substituted furans by electrophilic cyclization of propargylic oxiranes (Scheme 1).



Scheme 1.

Results and Discussion

Our initial study began with the reaction of propargylic oxirane **1a** and I₂ in THF at room temp. in the absence of base; the desired furan product **2a** was isolated in only 37% yield (Table 1, entry 1). Encouraged by this positive result,

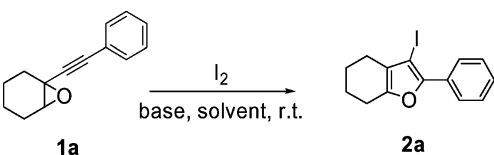
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we optimized the reaction condition by experimenting with various bases and solvents. The addition of inorganic bases such as Na_2CO_3 and K_2CO_3 increased the yield of **2a** to 45 and 55%, respectively (entries 2 and 3). Interestingly, with NaHCO_3 as the base, product **2a** was isolated in 72% yield in a shorter reaction time (entry 4). When the reaction was performed with the strong bases $t\text{BuOK}$ and NaOMe , no product was obtained although the starting material did decompose. The organic base Et_3N was also evaluated; only a moderate yield of the product was obtained (entry 7). On the other hand, the effect of solvent was also very important in the electrophilic cyclization. THF proved to be the optimal medium. Solvents such as CH_2Cl_2 , CH_3CN , or CH_3OH did not improve the yield (entries 8–10).

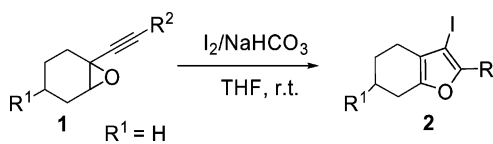
Table 1. Electrophile-induced cyclization of propargylic oxirane **1a**.^[a]

				
Entry	Base	Solvent	Time [h]	% Yield ^[b]
1	–	THF	3	37
2	Na_2CO_3	THF	3	45
3	K_2CO_3	THF	3	55
4	NaHCO_3	THF	2	72
5	$t\text{BuOK}$	THF	3	0
6	NaOMe	THF	3	0
7	Et_3N	THF	5	46
8	NaHCO_3	CH_2Cl_2	3	58
9	NaHCO_3	CH_3CN	3	61
10	NaHCO_3	CH_3OH	3	35

[a] Conditions: 0.25 mmol of **1a**, 2 equiv. of I_2 and 2 equiv. of NaHCO_3 in 3 mL of THF at room temp. [b] Isolated yield.

Thus, we chose the following optimal reaction conditions for all subsequent experiments: 0.25 mmol of propargylic oxirane, 2 equiv. of I_2 , 2 equiv. of NaHCO_3 in 5 mL of THF stirred under argon at room temperature for an appropriate amount of time (Table 2). First, the effect of a variety of alkyne substituents R^2 on the electrophilic cyclization was examined. On the whole, both electron-rich and electron-poor C-aryl-substituted alkynes reacted to form the corresponding products in moderate-to-good yields. The cyclization of both 2-bromophenyl- **1b** and 3-bromophenyl-substituted propargylic epoxides **1c** using I_2 generated the corresponding 3-iodofuran in 73 and 83% yields, respectively (entries 2 and 3). Good results were also obtained with 4-bromophenyl **1d** and 4-chlorophenyl **1e** as substituents (entries 4 and 5). The reaction of electron-rich 4-methylphenyl propargylic oxirane also proceeded smoothly in good yield (entry 6). Unfortunately, when hept-1-yne group was used, the expected product was not obtained due to its rapid decomposition in air to form complex unknown compounds. However, a single product was observed by TLC under argon.

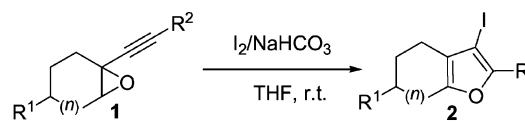
Table 2. Iodocyclization of propargylic oxirane compounds.^[a]

					
Entry	1	R^2	Time [h]	2	% Yield
1	1a	Ph	2	2a	72
2	1b	<i>o</i> -Br- C_6H_4	5	2b	73 ^[b]
3	1c	<i>m</i> -Br- C_6H_4	5	2c	83 ^[b]
4	1d	<i>p</i> -Br- C_6H_4	12	2d	85 ^[b]
5	1e	<i>p</i> -Cl- C_6H_4	10	2e	93 ^[b]
6	1f	<i>p</i> -CH ₃ - C_6H_4	4	2f	90 ^[b]
7	1g	<i>n</i> -C ₅ H ₁₁	2	–	– ^[c]

[a] All reactions were run under the following conditions unless specified: 0.25 mmol of **1**, 2 equiv. of I_2 , 2 equiv. of NaHCO_3 in THF at room temperature. [b] 5 equiv. of I_2 and 5 equiv. of NaHCO_3 were required. [c] The product decomposed as soon as it was exposed to air.

Next we elucidated the scope of the reaction by examining the effect of various R^1 groups on the aliphatic ring. As can be seen in Table 3 (entries 1 and 2), R^1 groups play a negligible role in the electrophilic cyclization. For example, furan **2h** was generated exclusively in 95% yield from substrate **1h** bearing a methyl group (entry 1); the use of 1,3-

Table 3. Iodocyclization of propargylic oxirane compounds.^[a]

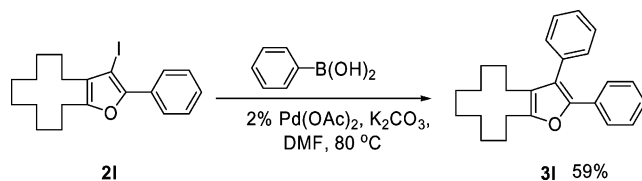
				
Entry	1	Time [h]	2	% Yield
1	1h	2	2h	95
2	1i	2	2i	90
3	1j	2	2j	98
4	1k	2	2k	83
5	1l	2	2l	94
6	1m	2	2m	85
7	1n	5	2n	75 ^[b]
8	1o	7	2o	96 ^[b]

[a] All reactions were performed with 0.25 mmol of **1**, 2 equiv. of I_2 and 2 equiv. of NaHCO_3 in 5 mL of THF at room temp. [b] 5 equiv. of I_2 and 5 equiv. of NaHCO_3 were required.

dioxolane as the R¹ moiety in compound **1i** did not influence the efficiency of this reaction (entry 2) in which the corresponding product **2i** was formed in 90% yield.

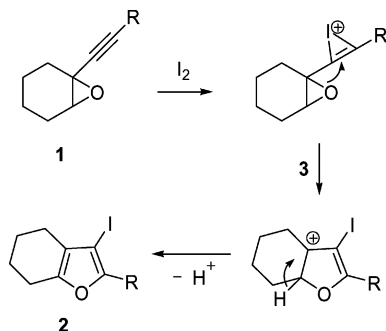
As shown in Table 3, this methodology could also be extended to other propargylic oxiranes bearing various alicyclic substituents, as well as 2-methyl epoxide. The reaction of compound **1j** with I₂ went to completion with quantitative conversion and an excellent yield (entry 3). Changing the substituent R¹ to an 8- or 12-membered ring epoxide gave 83 and 94% (entries 4 and 5) yields, respectively. The cyclization of 2-methyl-substituted epoxides (entries 6–8) also afforded polysubstituted 3-iodofurans in good-to-excellent yields. For example, the cyclization of epoxide **1m** afforded furan **2m** in 85% yield (entry 6). Compared with the reaction of **1o**, epoxide **1n** gave a relatively low yield of 75%, probably due to the steric hindrance of the *o*-bromine atom (entries 7 and 8). In fact, a similar effect is evident in the data reported in Table 2 (entries 2–4).

As mentioned in the Introduction, the presence of the iodide functional group on the furan ring provides an opportunity for further functionalization. By using the general conditions for the Suzuki coupling reaction we investigated the coupling reaction of compound **2l** and phenylboronic acid; the expected tetrasubstituted furan **3l** was obtained in 59% yield (Scheme 2).^[17]



Scheme 2.

Based on previously reported results,^[18] a plausible reaction mechanism is shown in Scheme 3 which involves the cyclic iodonium ion **3** formed by coordination of the propargylic triple bond to an iodine cation. Subsequent *anti* attack by the oxygen on the iodonium ion and elimination of a hydrogen cation led to the formation of 3-iodofuran **2**.



Scheme 3. Plausible reaction mechanism.

Conclusions

In summary, we have developed a new approach to the formation of polysubstituted 3-iodofuran. The process showed considerable synthetic advantages in terms of prod-

uct diversity, mild reaction conditions, the simplicity of the reaction procedure, and good-to-excellent yields. Iodocyclization of propargylic epoxides followed by palladium-catalyzed coupling afforded products with an increased molecular complexity and has provided a powerful tool for the preparation of a wide range of functionalized, polysubstituted furans. Further work to extend this method to the synthesis of complex molecular structures is in progress.

Experimental Section

General Remarks: Column chromatography was carried out on silica gel. ¹H NMR spectra were recorded with a 300 or 400 MHz spectrometer in CDCl₃. ¹³C NMR spectra were recorded with a 75 or 100 MHz spectrometer in CDCl₃ by using TMS as the internal standard. Mass spectra were recorded with a HP5998 MS spectrometer by using the EI method. IR spectra were recorded on a FT-IR spectrometer and only the major peaks are reported. Melting points were determined on a microscopic apparatus and are uncorrected. All new compounds were further characterized by element analysis; copies of their ¹H and ¹³C NMR spectra are provided. Commercially available reagents and solvents were used without further purification. THF was distilled immediately before to use from Na/benzophenone.

Preparation of Propargylic Oxiranes

Synthesis of 1-(2-Phenylethynyl)-7-oxabicyclo[4.1.0]heptane (1a**):**^[19] MCPBA (362 mg, 2.10 mmol) was added to a stirred solution of (cyclohexenylethynyl)benzene (124 mg, 1.0 mmol) (see the electronic supporting information) and Na₂HPO₄ (350 mg, 2.47 mmol) in DCM (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and then allowed to warm to room temp., whereupon it was diluted with diethyl ether and quenched with an aqueous saturated NaHCO₃ solution. The organic layer was washed with 10% NaOH and brine and finally dried with anhydrous MgSO₄. The solvent was evaporated and column chromatography on basic Al₂O₃ with petroleum ether/EtOAc (100:1, v/v) as eluent afforded **1a** as a colorless viscous oil; yield: 178 mg (60%). Compounds **1b–1o** were prepared by the same method.

1-(2-Phenylethynyl)-7-oxabicyclo[4.1.0]heptane (1a**):** Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 1.21–1.43 (m, 2 H), 1.44–1.47 (m, 2 H), 1.91–1.95 (m, 2 H), 2.05–2.12 (m, 1 H), 2.19–2.26 (m, 1 H), 3.42–3.43 (t, *J* = 2.4 Hz, 1 H), 7.25–7.30 (m, 3 H), 7.41–7.44 (m, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 18.8, 19.4, 24.1, 29.6, 50.5, 60.2, 81.8, 89.5, 122.2, 128.1, 128.3, 131.6 ppm. IR (neat): ν̄ = 2939, 1490, 756 cm⁻¹. C₁₄H₁₄O (198.2): calcd. C 84.81, H 7.12; found C 84.77, H 7.15.

1-[2-(2-Bromophenyl)ethynyl]-7-oxabicyclo[4.1.0]heptane (1b**):** Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 1.17–1.46 (m, 4 H), 1.88–1.93 (m, 2 H), 2.01–2.11 (m, 1 H), 2.16–2.25 (m, 1 H), 3.39 (s, 1 H), 7.09–7.14 (t, *J* = 10.4 Hz, 1 H), 7.30–7.33 (d, *J* = 10.8 Hz, 1 H), 7.38–7.41 (m, 1 H), 7.54 (s, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 18.4, 19.0, 23.7, 29.2, 49.9, 59.7, 79.9, 90.8, 121.6, 123.9, 129.3, 129.8, 131.2, 134.0 ppm. IR (neat): ν̄ = 2939, 1555, 1473, 783, 679 cm⁻¹. C₁₄H₁₃BrO (276.0): calcd. C 60.67, H 4.73; found C 60.62, H 4.76.

1-[2-(3-Bromophenyl)ethynyl]-7-oxabicyclo[4.1.0]heptane (1c**):** Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 1.36–1.47 (m, 4 H), 1.93–1.97 (m, 2 H), 2.14–2.16 (m, 1 H), 2.25 (s, 1 H), 3.34 (s, 1 H), 7.13–7.17 (m, 1 H), 7.21–7.25 (m, 1 H), 7.43–7.46 (m, 1 H), 7.54–7.57 (m, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 18.7, 19.3,

24.1, 29.4, 50.5, 60.1, 80.4, 94.1, 124.3, 125.6, 126.8, 129.5, 132.2, 133.3 ppm. IR (neat): $\tilde{\nu}$ = 2942, 1468, 1433, 908, 733 cm^{-1} . $\text{C}_{14}\text{H}_{13}\text{BrO}$ (276.0): calcd. C 60.67, H 4.73; found C 60.58, H 4.71.

1-[2-(4-Bromophenyl)ethynyl]-7-oxabicyclo[4.1.0]heptane (1d): Colorless solid; m.p. 92–93 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.23–1.37 (m, 2 H), 1.40–1.48 (m, 2 H), 1.92–1.96 (m, 2 H), 2.04–2.11 (m, 1 H), 2.18–2.24 (m, 1 H), 3.42–3.43 (t, J = 2.4 Hz, 1 H), 7.26–7.29 (m, 2 H), 7.40–7.44 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 18.7, 19.4, 24.1, 29.6, 50.4, 60.2, 90.9, 90.8, 121.2, 122.7, 131.4, 133.1 ppm. IR (KBr): $\tilde{\nu}$ = 3438, 2936, 1483, 836 cm^{-1} . $\text{C}_{14}\text{H}_{13}\text{BrO}$ (276.0): calcd. C 60.67, H 4.73; found C 60.62, H 4.79.

1-[2-(4-Chlorophenyl)ethynyl]-7-oxabicyclo[4.1.0]heptane (1e): Colorless solid; m.p. 72–73 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.24–1.34 (m, 1 H), 1.36–1.39 (m, 1 H), 1.41–1.50 (m, 2 H), 1.94–1.97 (m, 2 H), 2.05–2.12 (m, 1 H), 2.54–2.57 (m, 1 H), 3.43 (s, 1 H), 7.26–7.29 (m, 2 H), 7.34–7.37 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 18.8, 19.4, 24.1, 29.6, 50.5, 60.3, 80.8, 90.6, 120.8, 128.5, 133.0, 134.5 ppm. IR (neat): $\tilde{\nu}$ = 3432, 2938, 1485, 1087, 838, 755 cm^{-1} . $\text{C}_{14}\text{H}_{13}\text{ClO}$ (232.71): calcd. C 75.26, H 5.63; found C 75.21, H 5.65.

1-[2-(*p*-Tolyl)ethynyl]-7-oxabicyclo[4.1.0]heptane (1f): Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.26–1.40 (m, 1 H), 1.42–1.49 (m, 3 H), 1.94–1.96 (d, J = 8.0 Hz, 2 H), 2.08–2.15 (q, J = 8.1, J = 20.1 Hz, 1 H), 2.19–2.27 (m, 1 H), 2.34 (s, 1 H), 2.44 (s, 1 H), 7.08–7.11 (d, J = 7.5 Hz, 2 H), 7.31–7.36 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 18.9, 19.5, 21.5, 24.2, 29.9, 50.8, 60.4, 82.2, 88.9, 119.7, 128.9, 131.7, 138.6 ppm. IR (neat): $\tilde{\nu}$ = 3428, 2918, 2850, 1510, 1435, 910, 732 cm^{-1} . $\text{C}_{15}\text{H}_{16}\text{O}$ (212.1): calcd. C 84.87, H 7.60; found C 84.81, H 7.54.

1-(Hept-1-ynyl)-7-oxabicyclo[4.1.0]heptane (1g): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 0.88–0.91 (m, 3 H), 1.21–1.47 (m, 8 H), 1.48–1.52 (t, J = 7.0 Hz, 2 H), 1.84–1.88 (m, 2 H), 1.89–2.01 (m, 1 H), 2.09–2.16 (m, 1 H), 2.17–2.21 (t, J = 8.0 Hz, 2 H), 3.28 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 13.8, 18.5, 18.9, 19.4, 22.0, 24.1, 28.1, 30.0, 30.9, 50.4, 59.9, 76.7, 77.0, 77.3, 80.5, 82.9 ppm. IR (neat): $\tilde{\nu}$ = 2935, 1460, 844, 759 cm^{-1} . $\text{C}_{13}\text{H}_{20}\text{O}$ (192.2): calcd. C 81.20, H 10.48; found C 81.26, H 10.53.

4-Methyl-1-(2-phenylethynyl)-7-oxabicyclo[4.1.0]heptane (1h, mixture): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 0.86–0.90 (t, J = 7.6 Hz, 3 H), 0.96–1.25 (m, 1 H), 1.32–1.38 (m, 3 H), 1.97–2.02 (m, 2 H), 2.24–2.42 (m, 1 H), 3.40 (s, 0.36 H), 3.46 (s, 0.60 H), 7.25–7.40 (m, 3 H), 7.41–7.45 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.3, 21.9, 23.5, 26.9, 27.2, 28.7, 30.1, 32.3, 33.3, 50.0, 50.9, 59.9, 61.5, 76.5, 77.0, 77.4, 82.0, 89.2, 89.7, 122.2, 128.2, 128.4, 131.7, 131.7 ppm. IR (neat): $\tilde{\nu}$ = 2950, 2926, 1490, 756, 691 cm^{-1} . $\text{C}_{15}\text{H}_{16}\text{O}$ (212.1): calcd. C 84.87, H 7.60; found C 84.91, H 7.63.

4,4-Ethylenedioxy-1-(2-phenylethynyl)-7-oxabicyclo[4.1.0]heptane (1i): Colorless solid; m.p. 95–96 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.46–1.53 (m, 1 H), 1.65–1.73 (m, 1 H), 2.11–2.17 (m, 2 H), 2.37–2.41 (m, 2 H), 3.46–3.47 (d, J = 4 Hz, 1 H), 3.87–3.99 (m, 4 H), 7.27–7.33 (m, 3 H), 7.42–7.44 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 27.4, 27.7, 50.7, 59.1, 64.1, 64.5, 82.6, 88.2, 105.9, 122.1, 128.2, 128.5, 131.8 ppm. IR (KBr): $\tilde{\nu}$ = 2927, 1365, 1118, 757 cm^{-1} . $\text{C}_{16}\text{H}_{16}\text{O}_3$ (256.1): calcd. C 74.98, H 6.29; found C 74.90, H 6.33.

1-(2-Phenylethynyl)-8-oxabicyclo[5.1.0]octane (1j): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.31–1.42 (m, 1 H), 1.49–1.61 (m, 5 H), 1.64–1.75 (m, 1 H), 1.78–2.12 (m, 2 H), 2.22–2.27 (m, 1 H), 3.36–3.38 (m, J = 7.2 Hz, 1 H), 7.27–7.37 (m, 3 H), 7.42–7.50 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 24.2, 24.7, 29.1, 31.1,

34.5, 54.5, 63.7, 76.8, 77.1, 77.5, 81.4, 90.5, 122.4, 128.2, 128.4, 131.8 ppm. IR (neat): $\tilde{\nu}$ = 2927, 1724, 1449, 909, 753 cm^{-1} . $\text{C}_{15}\text{H}_{16}\text{O}$ (212.29): calcd. C 84.87, H 7.60; found C 84.81, H 7.64.

1-(2-Phenylethynyl)-9-oxabicyclo[6.1.0]nonane (1k): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.24–1.34 (m, 1 H), 1.39–1.48 (m, 4 H), 1.51–1.60 (m, 4 H), 1.77–1.85 (m, 1 H), 2.17–2.26 (m, 2 H), 3.16–3.19 (t, J = 6.0 Hz, 1 H), 7.25–7.30 (m, 3 H), 7.42–7.45 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 25.0, 25.7, 25.9, 26.3, 26.9, 30.5, 53.9, 63.7, 82.4, 88.6, 122.2, 128.1, 128.3, 131.7 ppm. IR (neat): $\tilde{\nu}$ = 2927, 1491, 1446, 926, 756, 691 cm^{-1} . $\text{C}_{16}\text{H}_{18}\text{O}$ (226.1): calcd. C 84.91, H 8.02; found C 84.88, H 7.96.

1-(2-Phenylethynyl)-13-oxabicyclo[10.1.0]tridecane (1l): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.19–1.85 (m, 18 H), 2.16–2.19 (m, 1 H), 2.39–2.42 (m, 1 H), 3.06 (s, 1 H), 7.26–7.31 (m, 3 H), 7.41–7.43 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 23.3, 23.6, 24.2, 24.9, 25.1, 25.6, 26.7, 27.1, 29.6, 35.9, 56.8, 66.2, 85.8, 86.7, 122.5, 128.2, 128.5, 131.7 ppm. IR (neat): $\tilde{\nu}$ = 2931, 1444, 756, 691 cm^{-1} . $\text{C}_{20}\text{H}_{26}\text{O}$ (282.2): calcd. C 85.06, H 9.28; found C 85.10, H 9.32.

2-Methyl-2-(2-phenylethynyl)oxirane (1m): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.64 (s, 3 H), 2.83–2.84 (d, J = 4.2 Hz, 1 H), 3.11–3.12 (d, J = 5.6 Hz, 1 H), 7.27–7.31 (m, 3 H), 7.42–7.44 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 23.3, 47.9, 55.9, 82.3, 88.6, 122.3, 128.5, 128.9, 132.1 ppm. IR (neat): $\tilde{\nu}$ = 3396, 2923, 1491, 756, 691 cm^{-1} . $\text{C}_{11}\text{H}_{10}\text{O}$ (158.1): calcd. C 83.51, H 6.37; found C 83.47, H 6.42.

2-[2-(2-Bromophenyl)ethynyl]-2-methyloxirane (1n): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.62 (m, 3 H), 2.80–2.82 (m, 1 H), 3.07–3.09 (d, J = 5.6 Hz, 1 H), 7.11–7.15 (m, 1 H), 7.31–7.34 (m, 1 H), 7.40–7.43 (m, 1 H), 7.55–7.56 (q, J = 2.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 22.6, 47.1, 55.2, 80.1, 89.6, 121.7, 123.8, 129.5, 130.0, 131.5, 134.2 ppm. IR (neat): $\tilde{\nu}$ = 2984, 1590, 1473, 1069, 829, 681 cm^{-1} . $\text{C}_{11}\text{H}_9\text{BrO}$ (236.0): calcd. C 55.72, H 3.83; found C 55.78, H 3.79.

2-[2-(4-Bromophenyl)ethynyl]-2-methyloxirane (1o): Colorless solid; m.p. 70–71 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.64 (s, 3 H), 2.84–2.85 (d, J = 5.6 Hz, 1 H), 3.11–3.12 (d, J = 5.6 Hz, 1 H), 7.28–7.30 (m, 2 H), 7.42–7.45 (m, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 22.9, 47.5, 55.7, 80.9, 89.6, 121.1, 122.9, 131.6, 133.3 ppm. IR (neat): $\tilde{\nu}$ = 2972, 1483, 1067, 821 cm^{-1} . $\text{C}_{11}\text{H}_9\text{BrO}$ (236.0): calcd. C 55.72, H 3.83; found C 55.68, H 3.88.

General Procedure for the Synthesis of Propargylic Oxiranes 2a–2n by Electrophilic Cyclization: Iodine (2.0 equiv.) dissolved in THF (1.5 mL) was gradually added to a solution of propargylic oxirane (0.25 mmol), NaHCO_3 (2.0 equiv.) and THF (1.5 mL). The reaction mixture was flushed with argon and allowed to stir at room temp. for the desired time. The excess I_2 was removed by washing with a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$. The aqueous solution was then extracted with diethyl ether (2 $\times$ 10 mL). The combined ether layers were dried with anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product which was purified by flash chromatography on alkali alumina using pure petroleum as the eluent.

4,5,6,7-Tetrahydro-3-iodo-2-phenylbenzofuran (2a): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.76–1.80 (m, 2 H), 1.83–1.88 (m, 2 H), 2.29–2.33 (m, 2 H), 2.62–2.66 (m, 2 H), 7.24–7.30 (m, 1 H), 7.37–7.41 (m, 2 H), 7.95–7.97 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 22.9, 23.2, 23.3, 23.3, 66.6, 123.2, 125.8, 127.5, 128.3, 130.8, 148.9, 151.2 ppm. IR (neat): $\tilde{\nu}$ = 3335, 2973, 2884, 1452, 1090, 1049 cm^{-1} . $\text{C}_{14}\text{H}_{13}\text{IO}$ (324.0): calcd. C 51.87, H 4.04; found C 51.92, H 3.96.

2-(2-Bromophenyl)-4,5,6,7-tetrahydro-3-iodobenzofuran (2b): Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.75–1.88 (m, 4 H), 2.29–2.32 (t, J = 4.5 Hz, 2 H), 2.61–2.65 (t, J = 6.0 Hz, 2 H), 7.22–7.24 (d, J = 5.7 Hz, 1 H), 7.38–7.40 (t, J = 6.9 Hz, 1 H), 7.92–7.94 (d, J = 5.7 Hz, 1 H), 8.10 (s, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 22.8, 23.1, 23.2, 67.9, 122.5, 123.6, 124.0, 128.3, 129.8, 130.2, 132.7, 147.2, 151.8 ppm. IR (neat): $\tilde{\nu}$ = 2936, 1593, 909, 737 cm^{-1} . $\text{C}_{14}\text{H}_{12}\text{BrIO}$ (401.9): calcd. C 41.72, H 3.00; found C 41.79, H 2.94.

2-(3-Bromophenyl)-4,5,6,7-tetrahydro-3-iodobenzofuran (2c): Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ = 1.76–1.91 (m, 4 H), 2.32–2.36 (m, 2 H), 2.62–2.66 (m, 2 H), 7.21–7.26 (m, 1 H), 7.23–7.37 (m, 1 H), 7.45–7.48 (q, J = 1.8, J = 7.8 Hz, 1 H), 7.64–7.67 (q, J = 0.9, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 22.8, 22.9, 23.2, 23.3, 70.9, 121.8, 123.8, 126.9, 130.3, 131.9, 132.7, 133.2, 150.0, 151.8 ppm. IR (neat): $\tilde{\nu}$ = 3346, 2974, 1452, 1049, 881 cm^{-1} . $\text{C}_{14}\text{H}_{12}\text{BrIO}$ (401.9): calcd. C 41.72, H 3.00; found C 41.77, H 3.03.

2-(4-Bromophenyl)-4,5,6,7-tetrahydro-3-iodobenzofuran (2d): Colorless solid; m.p. 82–83 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.75–1.89 (m, 4 H), 2.29–2.33 (t, J = 7.6 Hz, 2 H), 2.61–2.65 (t, J = 6.8 Hz, 2 H), 7.49–7.52 (d, J = 8.8 Hz, 2 H), 7.84–7.86 (d, J = 11.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 22.8, 23.1, 23.2, 29.7, 67.2, 121.2, 123.5, 127.1, 129.7, 131.4, 147.9, 151.6 ppm. IR (KBr): $\tilde{\nu}$ = 3334, 2973, 1380, 1090, 1049, 881 cm^{-1} . $\text{C}_{14}\text{H}_{12}\text{BrIO}$ (401.9): calcd. C 41.72, H 3.00; found C 41.66, H 3.05.

2-(4-Chlorophenyl)-4,5,6,7-tetrahydro-3-iodobenzofuran (2e): Colorless viscous oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.67–1.70 (m, 4 H), 1.77–1.79 (m, 2 H), 2.21–2.24 (m, 2 H), 2.53–2.56 (m, 2 H), 7.26–7.28 (q, J = 1.2, J = 6.4 Hz, 2 H), 7.81–7.83 (q, J = 2, J = 6.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 23.1, 23.4, 23.5, 29.9, 67.4, 123.7, 127.1, 128.7, 129.5, 133.3, 148.2, 151.8 ppm. IR (KBr): $\tilde{\nu}$ = 3334, 2973, 1453, 1090, 881, 667 cm^{-1} . $\text{C}_{14}\text{H}_{12}\text{ClIO}$ (358.0): calcd. C 46.89, H 3.37; found C 46.84, H 3.44.

4,5,6,7-Tetrahydro-3-iodo-2-(*p*-tolyl)benzofuran (2f): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.76–1.88 (m, 4 H), 2.29–2.37 (m, 2 H), 2.41 (s, 1 H), 2.62–2.65 (m, 2 H), 7.19–7.22 (t, J = 8.0 Hz, 2 H), 7.83–7.85 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.3, 22.9, 23.3, 29.7, 65.8, 123.0, 125.8, 128.1, 128.9, 137.4, 149.3, 150.9 ppm. IR (neat): $\tilde{\nu}$ = 3334, 2973, 1452, 1379, 1090, 1049, 881 cm^{-1} . $\text{C}_{15}\text{H}_{15}\text{IO}$ (338.0): calcd. C 53.27, H 4.47; found C 53.33, H 4.41.

4,5,6,7-Tetrahydro-3-iodo-5-methyl-2-phenylbenzofuran (2h): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.06–1.08 (d, J = 8.8 Hz, 3 H), 1.24–1.42 (m, 1 H), 1.81–1.93 (m, 2 H), 2.19–2.32 (m, 3 H), 2.67–2.74 (d, J = 20.8, J = 6.0 Hz, 1 H), 7.23–7.28 (t, J = 10.0 Hz, 1 H), 7.35–7.40 (t, J = 10.0 Hz, 2 H), 7.94–7.96 (d, J = 10.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.3, 22.5, 29.9, 31.1, 31.3, 66.3, 122.8, 125.7, 127.4, 128.2, 130.8, 149.1, 150.9 ppm. IR (neat): $\tilde{\nu}$ = 3374, 2974, 1452, 1088, 1048, 881 cm^{-1} . $\text{C}_{15}\text{H}_{15}\text{IO}$ (338.0): calcd. C 53.27, H 4.47; found C 53.32, H 4.39.

5,5-Ethylenedioxy-4,5,6,7-tetrahydro-3-iodo-2-phenylbenzofuran (2i): Colorless solid; m.p. 79–80 °C. ^1H NMR (400 MHz, CDCl_3): δ = 1.91–1.96 (t, J = 8.8 Hz, 2 H), 2.44–2.48 (t, J = 8.0 Hz, 2 H), 2.93 (s, 1 H), 7.23–7.31 (m, 1 H), 7.36–7.41 (t, J = 9.2 Hz, 2 H), 7.91–7.94 (m, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 20.5, 29.9, 31.9, 34.6, 64.7, 65.7, 109.1, 122.3, 125.8, 127.7, 128.3, 130.6, 147.8, 150.5 ppm. IR (neat): $\tilde{\nu}$ = 3333, 2973, 1452, 1090, 881, 662 cm^{-1} . $\text{C}_{16}\text{H}_{15}\text{IO}_3$ (382.0): calcd. C 50.28, H 3.96; found C 50.33, H 3.92.

5,6,7,8-Tetrahydro-3-iodo-2-phenyl-4*H*-cyclohepta[b]furan (2j): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.70–1.78 (m, 7 H),

2.45–2.47 (t, J = 6.4 Hz, 2 H), 2.82–2.85 (t, J = 5.6 Hz, 1 H), 7.27–7.29 (d, J = 7.2 Hz, 1 H), 7.36–7.40 (m, 2 H), 7.93–7.95 (t, J = 1.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 26.2, 27.3, 27.9, 28.9, 30.3, 70.3, 125.4, 125.9, 127.5, 128.2, 130.8, 148.2, 152.7 ppm. IR (neat): $\tilde{\nu}$ = 2928, 2253, 1480, 908, 734, 650 cm^{-1} . $\text{C}_{15}\text{H}_{15}\text{IO}$ (338.0): calcd. C 53.27, H 4.47; found C 53.31, H 4.54.

4,5,6,7,8,9-Hexahydro-3-iodo-2-phenylcycloocta[b]furan (2k): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.47–1.54 (m, 4 H), 1.65–1.76 (m, 4 H), 2.52–2.55 (t, J = 6.4 Hz, 2 H), 2.83–2.86 (t, J = 6.4 Hz, 2 H), 7.25–7.29 (t, J = 7.2 Hz, 1 H), 7.37–7.41 (m, 2 H), 7.96–7.99 (t, J = 1.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 24.7, 25.4, 25.7, 26.4, 27.7, 27.9, 69.1, 123.3, 125.8, 127.4, 128.2, 130.8, 148.6, 151.4 ppm. IR (neat): $\tilde{\nu}$ = 2926, 1602, 1447, 1072, 908, 733 cm^{-1} . $\text{C}_{16}\text{H}_{17}\text{IO}$ (352.0): calcd. C 54.56, H 4.86; found C 54.58, H 4.82.

4,5,6,7,8,9,10,11,12,13-Decahydro-3-iodo-2-phenylcyclododeca[b]furan (2l): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.26–1.43 (m, 12 H), 1.72–1.79 (m, 4 H), 2.38–2.42 (t, J = 6.4 Hz, 2 H), 2.63–2.67 (t, J = 6.8 Hz, 2 H), 7.28–7.30 (q, J = 5.2, J = 2.4 Hz, 1 H), 7.37–7.41 (m, 2 H), 7.96–7.98 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 22.2, 22.8, 23.0, 23.5, 24.0, 24.8, 24.9, 26.1, 26.9, 67.9, 123.8, 126.0, 127.5, 128.2, 130.8, 149.5, 151.9 ppm. IR (neat): $\tilde{\nu}$ = 2934, 2253, 1472, 908, 737, 651 cm^{-1} . $\text{C}_{20}\text{H}_{25}\text{IO}$ (408.1): calcd. C 58.83, H 6.17; found C 58.78, H 6.22.

3-Iodo-4-methyl-2-phenylfuran (2m): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.83–1.84 (d, J = 1.0 Hz, 3 H), 7.14–7.16 (t, J = 1.2 Hz, 2 H), 7.24–7.28 (q, J = 6.8, J = 8.4 Hz, 2 H), 7.84–7.86 (t, J = 1.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.8, 68.9, 125.7, 126.0, 127.9, 128.3, 130.4, 138.1, 151.5 ppm. IR (neat): $\tilde{\nu}$ = 2920, 1765, 1481, 1024, 764, 690 cm^{-1} . $\text{C}_{11}\text{H}_9\text{IO}$ (284.0): calcd. C 46.51, H 3.19; found C 46.47, H 3.25.

2-(2-Bromophenyl)-3-iodo-4-methylfuran (2n): Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.98 (s, 3 H), 7.22–7.30 (m, 2 H), 7.40–7.44 (m, 1 H), 7.91–8.10 (m, 1 H), 8.11 (s, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.7, 70.1, 122.5, 124.4, 126.0, 128.7, 129.8, 130.8, 132.3, 138.6, 149.9 ppm. IR (neat): $\tilde{\nu}$ = 2924, 1769, 1467, 908, 733 cm^{-1} . $\text{C}_{11}\text{H}_8\text{BrIO}$ (361.9): calcd. C 36.40, H 2.22; found C 36.45, H 2.27.

2-(4-Bromophenyl)-3-iodo-4-methylfuran (2o): Colorless viscous oil. ^1H NMR (400 MHz, CDCl_3): δ = 1.99–1.20 (d, J = 1.2 Hz, 3 H), 7.31–7.32 (d, J = 1.2 Hz, 1 H), 7.51–7.54 (d, J = 8.8 Hz, 2 H), 7.84–7.86 (t, J = 2.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.7, 69.6, 121.9, 126.0, 127.5, 129.4, 131.5, 138.4, 150.7 ppm. IR (neat): $\tilde{\nu}$ = 3340, 2973, 2885, 1452, 1089, 1049, 881 cm^{-1} . $\text{C}_{11}\text{H}_8\text{BrIO}$ (361.9): calcd. C 36.40, H 2.22; found C 36.37, H 2.18.

4,5,6,7,8,9,10,11,12,13-Decahydro-2,3-diphenylcyclododeca[b]furan (3l): $\text{Pd}(\text{OAc})_2$ (0.92 mg, 2 mol-%) was added to a solution of **2l** (81.60 mg, 0.20 mmol) and K_2CO_3 (55 mg, 0.40 mmol) in DMF (2.0 mL). The mixture was stirred for 5 min and phenylboronic acid (29.3 g, 0.24 mmol) was added. The resulting mixture was then stirred under argon at 80 °C for 6 h and then diluted with aqueous saturated ammonium chloride and extracted with EtOAc. The combined extracts were washed with water four times. The solvent was removed under reduced pressure and the residue upon work-up was purified by chromatography on basic Al_2O_3 with petroleum ether/EtOAc (100:1, v/v) as eluent to give **3l** as a colorless viscous oil (39.1 mg, 59%). ^1H NMR (400 MHz, CDCl_3): δ = 1.16–1.92 (t, J = 5.2 Hz, 4 H), 1.25–1.45 (m, 10 H), 1.86–1.88 (t, J = 4.8 Hz, 2 H), 2.34–2.37 (t, J = 6.8 Hz, 2 H), 2.69–2.72 (t, J = 6.4 Hz, 2 H), 7.10–7.19 (m, 3 H), 7.31–7.41 (m, 7 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 20.7, 22.4, 22.7, 23.3, 24.4, 24.7, 25.2, 26.4, 26.8, 122.1,

123.7, 124.9, 126.3, 127.1, 128.2, 128.7, 129.9, 131.6, 135.2 ppm. IR (neat): $\tilde{\nu}$ = 3409, 2929, 1444, 1026, 763, 696 cm^{-1} . $\text{C}_{26}\text{H}_{30}\text{O}$ (358.2): calcd. C 87.10, H 8.43; found C 87.16, H 8.49.

Supporting Information (see also the footnote on the first page of this article): Experimental characterization for all products.

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