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Synthesis of Arylnaphthalene Lignan Scaffold by Gold-Catalyzed Intramolecular Sequential Electrophilic Addition and Benzannulation

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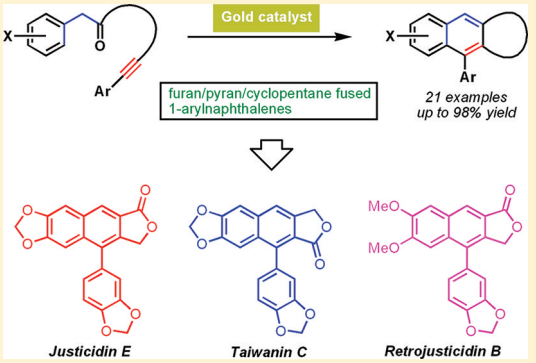
Supporting Information

ABSTRACT: An intramolecular approach to generate compounds containing an arylnaphthalene lignan scaffold in high yields is presented. It involves a sequential intramolecular electrophilic attack of carbonyl on arylalkyne followed by benzannulation catalyzed by gold salt. $AuCl_3$ in combination with $AgSbF_6$ works better to effect this transformation. Selected products have been converted into arylnaphthalene lactone natural products such as justicidin E, taiwanin C, and retrojusticidin B.



INTRODUCTION

Natural product derived compounds and compounds containing natural product scaffolds contribute significantly as sources for new drugs.[1] Hence there has been considerable interest in developing efficient strategies to access natural product inspired compound collections for testing in biochemical screening.[2] In this manuscript, we describe a facile synthesis of a 1-arylnaphthalene lignan scaffold by gold-catalyzed intramolecular cyclization. 1-Arylnaphthalene lactone lignans (for selected examples, see Figure 1) are plant derived natural products[3] having a wide range of bioactivities,[4] such as phosphodiesterase inhibition;[5] 5-lipooxygenase inhibition;[6] antitumor,[7] antiviral,[8] and antibacterial properties;[9] HIV reverse transcriptase inhibition;[10] and cytotoxicity.[11] Importantly, there has been decent activity in making collections of 1-arylnaphthalene lactone lignans to screen them for their biological activities.[5a,8d] In this regard, efforts have been made to develop strategies to access 1-arylnaphthalenes[12] and 1-arylnaphthalene lactone lignans.[13] In the context of developing reactions utilizing the oxo- and alkynophilic characters of gold catalysts,[14] we recently described the gold-catalyzed synthesis of 1-arylnaphthalenes involving intermolecular electrophilic addition followed by benzannulation.[14a] It was found that the catalytic system $AuCl_3/3AgSbF_6$ is the best among the catalysts screened. Herein we describe the intramolecular version of the reaction to generate the 1-arylnaphthalene lignan scaffold. The intramolecular version is more efficient than the intermolecular version in terms of yield, reaction time, and conditions.

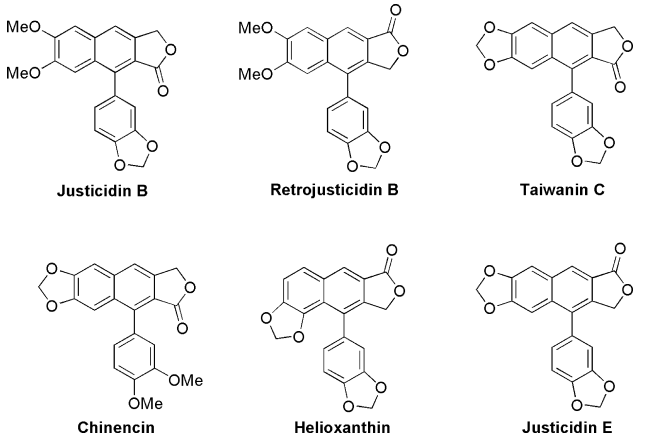


Figure 1. Representative examples of bioactive 1-arylnaphthalene lignans.

RESULTS AND DISCUSSION

Gold-Catalyzed Intramolecular Cyclization Approach to 1-Arylnaphthalenes. At the outset, $AuCl_3/3AgSbF_6$-catalyzed intramolecular cyclization was studied with the substrate **1a** under the condition that was established for the intermolecular reaction.[14a] The reaction proceeded nicely and furnished the cyclized product **2a** in very good yield at room temperature (Table 1). It is worth mentioning that the earlier reported intermolecular reactions required heating and longer reaction times. The substrate **1a** could easily be prepared from

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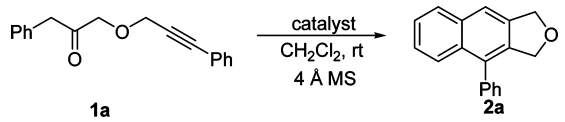
Table 1. Results of Arylnaphthalene 2a Formation with Different Catalysts



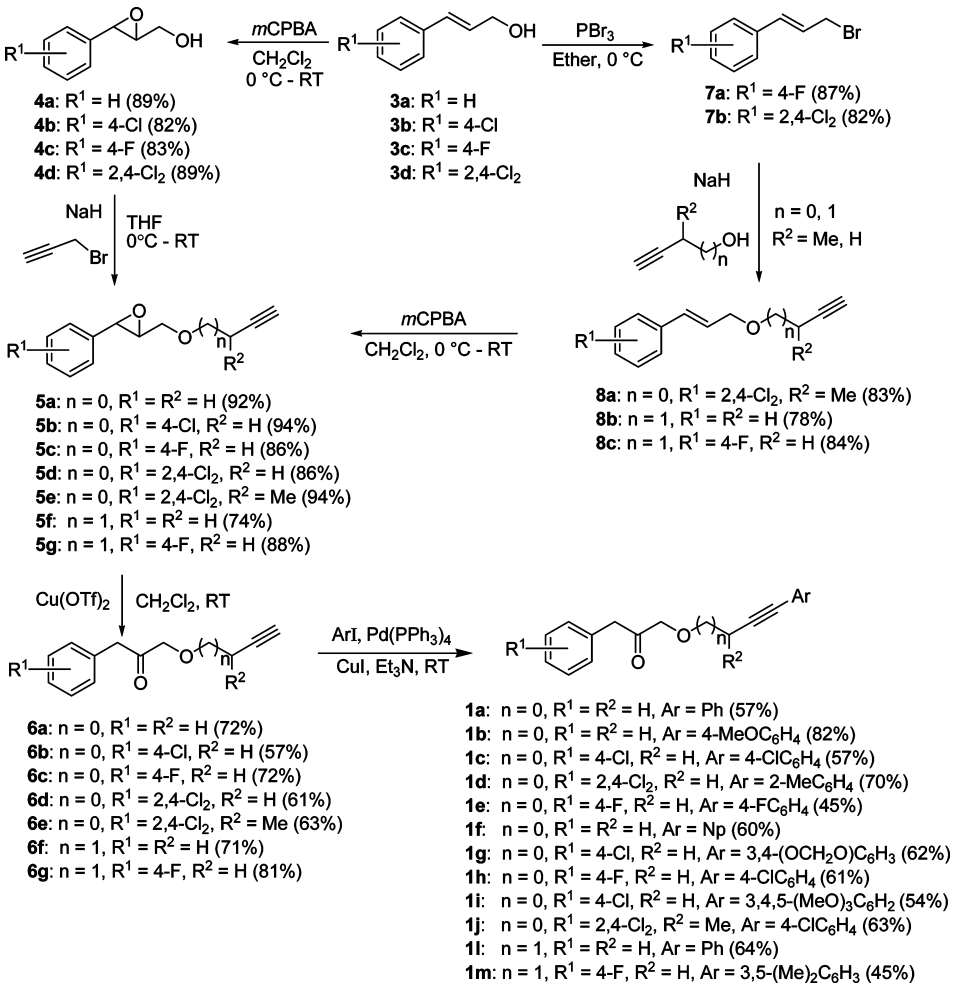
entry	catalyst	time	yield[a] of **2a** (%)
1	$AuCl_3/3AgSbF_6$ (2 mol %)	1 h 45 min	88 (trace)
2	$CuCl_2/2AgSbF_6$ (2 mol %)	24 h	49 (22)
3	$FeCl_3/3AgSbF_6$ (2 mol %)	24 h	54 (20)
4	$AgSbF_6$ (6 mol %)	24 h	trace (>96)
5	$HCl/AgSbF_6$ (2 mol %)	1 h 45 min	41 (42)
6	HOTf (2 mol %)	24 h	61 (17)

[a]Isolated yield. Values within parentheses represent the percentage of recovered starting material **1a**.

cinnamyl alcohol in a few steps as detailed in the following section. Just for comparison, the intramolecular cyclization of **1a** was attempted with oxophilic catalysts such as $CuCl_2$ and $FeCl_3$ in combination with $AgSbF_6$ (entries 2 and 3). As noticed in the intermolecular reactions,[14a] these catalysts were not as effective as $AuCl_3/3AgSbF_6$ for the intramolecular version as well. In order to evaluate the possible role of Brønsted acid catalysis, which has played a reasonable role in gold-catalyzed reactions,[15] substrate **1a** was reacted with HCl pretreated $AgSbF_6$ (2 mol %) for 1 h and 45 min (entry 5). The reaction resulted the product **2a** in only 41% yield, which is significantly less than that obtained in the reaction catalyzed by $AuCl_3/3AgSbF_6$. For a straightforward comparison, Brønsted acid catalyzed intramolecular cyclization of **1a** using 2 mol % of HOTf was studied. It was found that **2a** was obtained in moderate yield after 24 h (entry 6). These reactions reveal that the gold catalyst is superior than the other catalysts studied, perhaps for the reason of extending its coordination to the C≡C bond to bring it closer to the activated carbonyl to effect the required electrophilic addition.

Preparation of Starting Materials. The substrates **1a**–**1j**, **1l**, and **1m** were synthesized following the strategy depicted in the Scheme 1. Readily available *trans*-cinnamyl alcohol derivatives **3a**–**3d** were treated with *m*CPBA to obtain the corresponding epoxyalcohol **4a**–**4d**, which on propargylation using NaH and propargyl bromide afforded epoxyalkynes **5a**–**5d**. Epoxide to ketone rearrangement (Meinwald rearrangement) was achieved using $Cu(OTf)_2$ as the catalyst to obtain **6a**–**6d**. From these compounds, the starting materials **1a**–**1i** containing requisite arylmethyl ketone tethered aryl acetylene were prepared by Sonogashira coupling with corresponding aryl iodides. The synthesis of compounds **1j**, **1l**, and **1m** was accomplished in a slightly modified protocol. Cinnamyl alcohol derivatives **3c** and **3d** were converted into their corresponding bromo derivatives **7a** and **7b**. These cinnamyl bromide

Scheme 1. Synthesis of Substrates 1a–1j, 1l, and 1m



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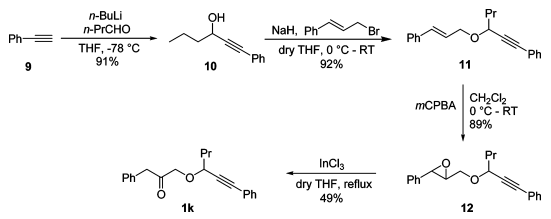
derivatives and cinnamyl bromide coupled with commercially available 3-butyn-2-ol and 3-butyn-1-ol to make enynes **8a**−**8c**, which on epoxidation gave epoxyalkynes **5e**−**5g**. Usual Meinwald rearrangement followed by Sonogashira coupling with respective aryl iodides afforded substrates **1j**, **1l**, and **1m**. It is important to note that this strategy provides ample opportunity to introduce diversity at different stages of the starting substrate making. Hence split and mix technique could be used when a bigger library of compounds is required.

The synthesis of the substrate **1k** was achieved in four steps (Scheme 2). Lithiated phenylacetylene was treated with

Scheme 2. Synthesis of Substrate 1k

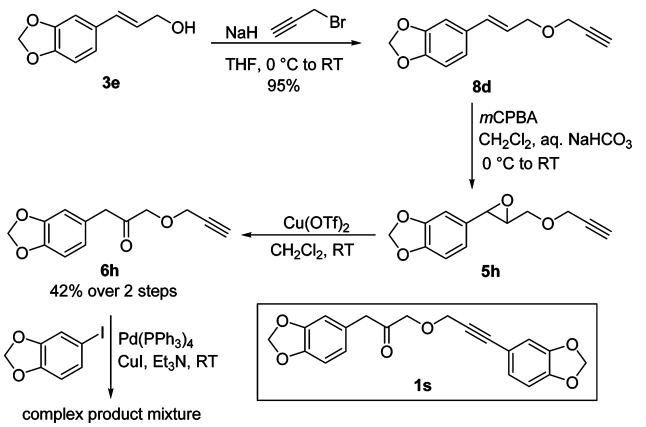


butyraldehyde to obtain propargyl alcohol derivative **10** in good yield. Reaction of sodium salt of **10** with cinnamyl bromide afforded the compound **11**, which on subsequent epoxidation resulted in the epoxyalkyne **12**. $Cu(OTf)_2$ was ineffective to promote epoxide to ketone rearrangement in substrate **12**. It was found that $InCl_3$[27] was moderately successful in effecting the rearrangement of **12** into **1k**.

Model substarates with carbon chain tether **1n** and **1o** were synthesized following the reaction sequence outlined in Scheme 3. 5-Hexyn-1-ol **13** was coupled with 2-iodoanisole under Sonogashira coupling conditions to make compound **14**. This underwent smooth Swern oxidation to give the aldehyde **15**. Reaction of **15** with benzyl and 4-chlorophenylmethyl Grignard reagents gave compounds **16a** and **16b**, respectively. These compounds were converted separately into the desired substrates **1n** and **1o** using Swern oxidation conditions.

In order to make the starting material **1s**, which is required for the synthesis of natural products justicidin E and taiwanin B, the strategy depicted in Scheme 4 was attempted. Propargylation of the cinnamyl alcohol derivative **3e** yielded **8d** in 95% yield. Reaction of **8d** using *m*CPBA in dichloromethane did not result in the expected epoxide. However, in biphasic medium involving dichloromethane and aqueous $NaHCO_3$ solution, the reaction did work, yielding the epoxide **5h**. Since the purification of **5h** was found difficult, the crude material was

Scheme 4. Attempted Preparation of 1s

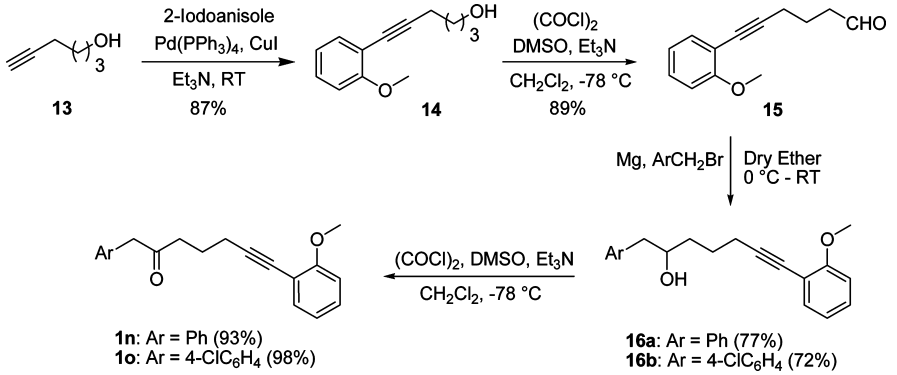


subjected to epoxide-ketone rearrangement using $Cu(OTf)_2$ to obtain **6h** in 42% yield over two steps. However, the Sonogashira reaction of this material to make **1s** resulted in complex reaction mixture.

Hence a different strategy as shown in Scheme 5 was adopted to make starting materials **1p**− **1u**, which bear electron-releasing groups on both aryl rings. This strategy is very effective as the overall yield of the sbustrates prepared (**1p**−**1u**) were excellent. The key reaction is the $BF_3{\cdot}OEt_2$-assisted epoxide opening by aryl lithium to obtain secondary alcohols **20a**−**20f**, which were converted into the corresponding ketones **1p**−**1u** by Swern oxidation.

Scope of Gold-Catalyzed Intramolecular Annulation. The scope of the gold-catalyzed intramolecular annulation was evaluated with a variety of substrates **1a**−**1u** that were prepared using Schemes 1−3 and 5. The results of intramolecular cascade cyclization are given in Table 2. All the reactions, that were studied, occurred smoothly and completed in less than two hours at room temperature resulting in the arylnaphthalene derivatives **2a**-**2u** in very good yields. This methodology has a wide scope in making 1-arylnaphthalenes fused with tetrahydrofuran, tetrahydropyran and cyclopentane efficiently. The yields of all the products except that of **2l** were very good. Substituents such as Cl, F, OMe and acetal could tolerate the reaction condition. Arylnaphthalene derivatives having electron releasing groups like OMe on both aryl rings could be synthesized efficiently. These compounds resemble more like the naturally occurring arylnaphthanene lignans. Although there are possibilities for the formation of two products from each of **1r**−**1u** *via* electrophilic attack at two different carbons of the aryl ring, compounds **1r** and **1s** resulted in single arylnaph-

Scheme 3. Preparation of Substrates 1n and 1o



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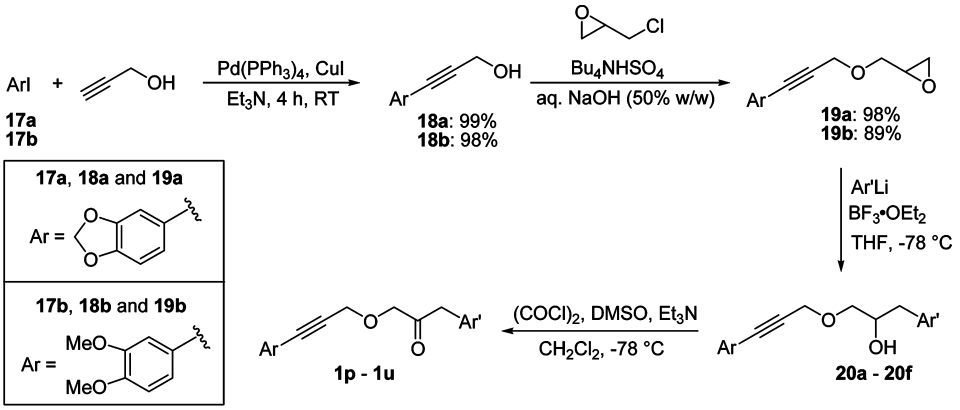
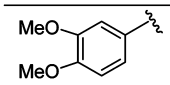
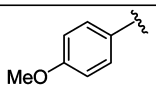
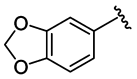
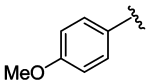
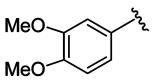
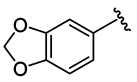
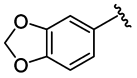
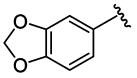
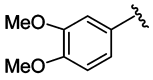
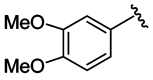
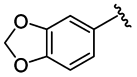
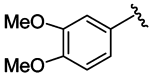
Scheme 5. Synthesis of Substrates 1p−1u



Ar	Ar′	**20** (yield)	**1** (yield)
		**20a** (98)	**1p** (93)
		**20b** (85)	**1q** (83)
		**20c** (76)	**1r** (87)
		**20d** (81)	**1s** (94)
		**20e** (72)	**1t** (91)
		**20f** (73)	**1u** (86)

thalene derivatives **2r** and **2s** respectively. However the compounds **1t** and **1u** which bear dimethoxy substituents on the aryl ring resulted in a mixture of products **2t**+**2t′** and **2u** +**2u′** respectively as expected.

A plausible mechanism for the formation of the products **2a**−**2u** involving cascade electrophilc addition followed by electrophilic benzannulation catalyzed by gold salt is shown in the scheme 6. Gold salt can bind with carbonyl and alkyne to facilitate the reaction by bringing them close to each other.

Arylnaphthalenes fused with furan are nice precursors for the preparation of arylnaphthalene lactone lignan natural products and analogues. Benzylic oxidation on **2a** has already been reported using Jones reagent, which resulted in both possible arylnaphthalene lactones.[16] However, we used $CrO_3/H_5IO_6/CH_3CN$ system, which effects smooth benzylic oxidation at room temperature.[17] Using this reagent system, benzylic oxidation was carried out on **2s**−**2u** to obtain arylnaphthalene lactones **21**−**24** in good yields (scheme 7). The products include justcidin E, taiwanin C, and retrojusticidin B. Benzylic oxidation occurred preferentially at the less hindered methylene site of the two available sites. Over oxidation to result in cyclic anhydride was not observed. Substrate **2s** which contain fused dioxalane in the naphthalene ring resulted in a mixture of lactones, justicidin E (**21**) and taiwanin C (**22**), the former being major. These two products can be easily separated by column chromatography.

In conclusion, intramolecular cyclization of arylmethyl ketone tethered with arylalkyne results in 1-arylnaphthalene lignan scaffold under gold catalysis. Using this method, it has been shown that 1-arylnaphthalenes fused with furan, pyran and cyclopentane could be made in good yields. The worth of this annulation reaction was demonstrated by converting some of the products into naturally occurring arylnaphthalene lactone lignans.

■ EXPERIMENTAL SECTION

General Information. Dichloromethane was distilled freshly over CaH_2. THF was dried over sodium and freshly distilled before use. Triethylamine was dried over potassium hydroxide. For TLC, aluminum plates coated with silica gel containing F254 indicator were used, and the spots were visualized by UV light and/or by heating the plates sprayed with Seebach solution (phosphomolybdic acid (2.5 g), $Ce(SO_4)_2$ (1.0 g), conc H_2SO_4 (6 mL), and H_2O (94 mL)). Column chromatography was performed on silica gel 100−200 mesh, using ethyl acetate and hexanes mixture as eluent. The ^1H and ^{13}C NMR spectra of the synthesized compounds were recorded in a

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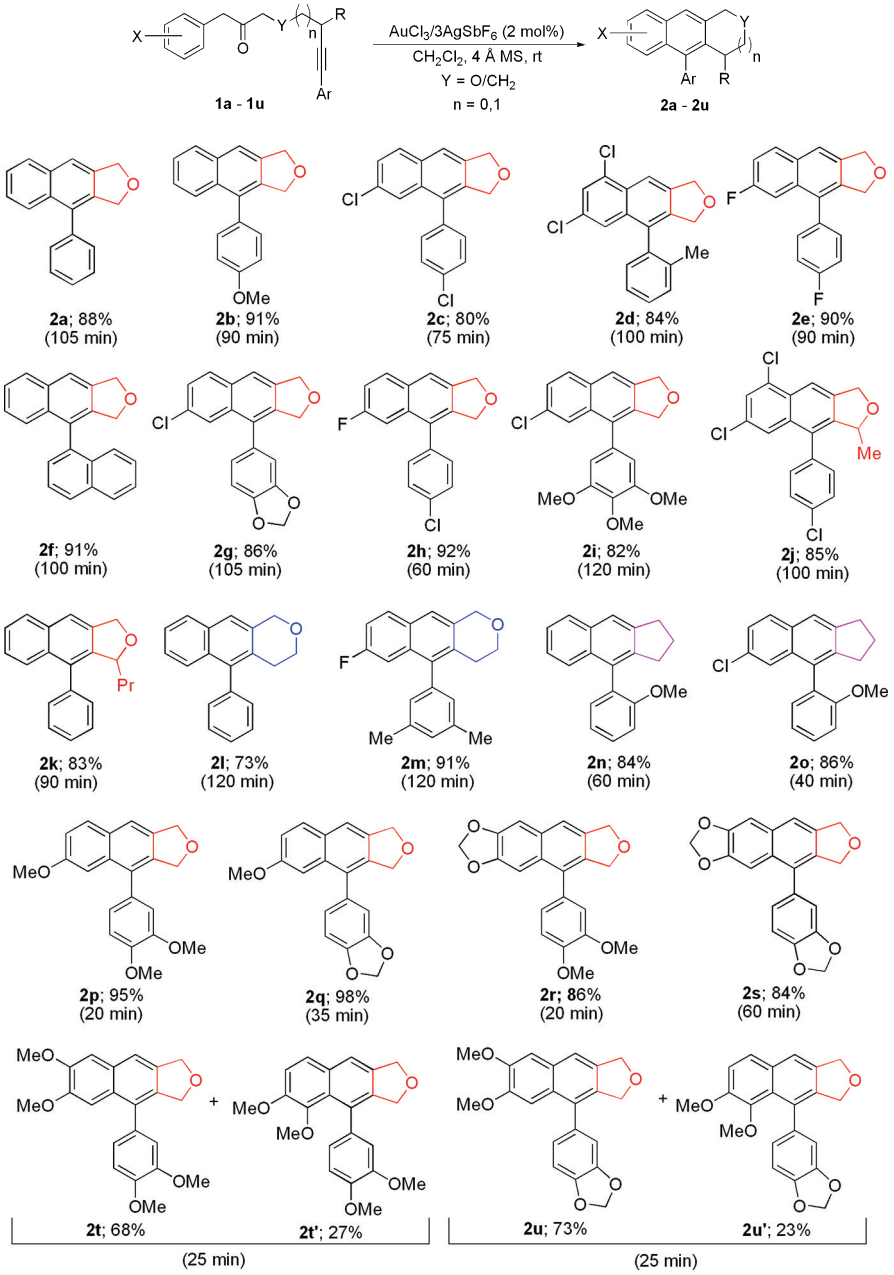
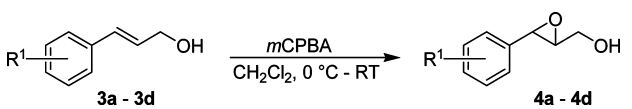
Table 2. Scope of Gold-Catalyzed Intramolecular 1-Arylnaphthalene Synthesis



400 MHz NMR machine using their solutions in $CDCl_3$. IR spectra were recorded using a FT/IR spectrometer. Elemental (C, H, N) analysis was done using a FLASH EA analyzer. High resolution mass spectra (HRMS) were recorded using electrospray ionization. Melting points were determined by using a hot-stage melting point apparatus and are uncorrected.

General Procedure for the Epoxidation of Cinnamyl Alcohol Derivatives 3a–3d.



m-Chloroperoxybenzoic acid (75%, 1.5 equiv) was added to a stirred solution of the substituted cinnamyl alcohol **3** (1.0 equiv) in dichloromethane (5 mL/mmol of **3**) at 0 °C. The reaction was allowed to stir at rt and monitored by TLC. It was found from TLC that the reaction completed in 2 h. A saturated aqueous solution of Na_2SO_3 was added to quench excess *m*CPBA. Dichloromethane was added to the reaction mixture, washed with saturated sodium bicarbonate solution and brine solution, and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude epoxyalcohol **4**, which was purified by column chromatography using silica gel as stationary phase and EtOAc/hexanes (15:85) as eluent to obtain the pure material.

*(3-Phenyloxiran-2-yl)methanol (**4a**).* Obtained in 89% yield as a colorless liquid. R_f = 0.49 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[18] δ 2.16 (t, J = 6.4 Hz, 1H), 3.22–3.23 (m, 1H), 3.77–3.82 (m, 1H), 3.93 (s, 1H), 4.05 (dd, J = 12.4 Hz, 2.4 Hz, 1H), 7.27–7.35 (m, 5H).

*(3-(4-Chlorophenyl)oxiran-2-yl)methanol (**4b**).* Obtained in 82% yield as a colorless liquid. R_f = 0.45 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[19] δ 2.20 (br s, 1H), 3.17–3.19 (m, 1H), 3.80 (d, J = 12.4 Hz, 1H), 3.91 (d, J = 1.6 Hz, 1H), 4.04 (d, J = 12.8 Hz, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H).

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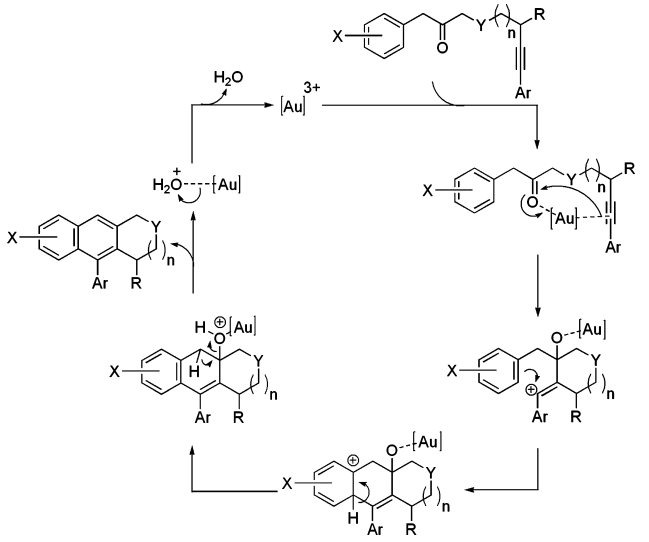
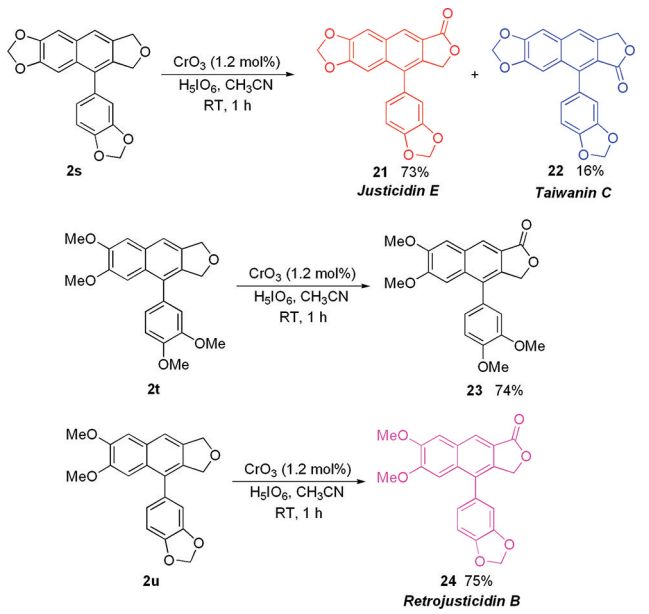
Scheme 6. Plausible Mechanism for the Cyclization



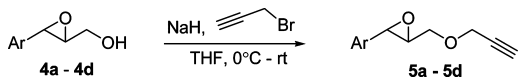
Scheme 7. Synthesis of Arylnaphthalene Lactones



*(3-(4-Fluorophenyl)oxiran-2-yl)methanol (**4c**).* Obtained in 83% yield as a colorless liquid. R_f = 0.48 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[20] δ 2.44 (br s, 1H), 3.20 (s, 1H), 3.79 (d, J = 12.8 Hz, 1H), 3.92 (s, 1H), 4.04 (d, J = 12.8 Hz, 1H), 7.03 (t, J = 8.4 Hz, 2H), 7.24 (dd, J = 7.2 Hz, 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 61.1, 62.5, 115.5 (d, J = 21.6 Hz), 127.4 (d, J = 8.2 Hz), 132.4, 162.8 (d, J = 245.0 Hz).

*(3-(2,4-Dichlorophenyl)oxiran-2-yl)methanol (**4d**).* Obtained in 89% yield as a colorless solid, mp 65–67 °C. R_f = 0.49 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.08 (t, J = 2.0 Hz, 1H), 3.61 (br s, 1H), 3.81 (dd, J = 12.8 Hz, 3.2 Hz, 1H), 4.10 (d, J = 12.4 Hz, 1H), 4.12 (s, 1H), 7.13 (dd, J = 8.4 Hz, 3.2 Hz, 1H), 7.17–7.18 (m, 1H), 7.30–7.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.6, 61.1, 62.1, 126.6, 127.1, 128.6, 133.2, 133.8. IR (KBr, cm^{-1}): 3275, 3148, 2930, 1105, 1070, 1014. Anal. Calcd for $C_9H_8Cl_2O_2$: C, 49.34; H, 3.68. Found: C, 49.22; H, 3.72.

General Procedure for the Propargylation of 4a– 4d.



NaH (60% dispersion in mineral oil, 1.5 equiv) was taken in a dry two neck RB flask, and dry THF was added to this. The reaction flask was cooled in an ice bath. To this a solution of epoxycinnamylalcohol **4** (1.0 equiv) in THF was added slowly. The reaction mixture was allowed to stir for 0.5 h at 0 °C, and then propargyl bromide (80 wt % solution in toluene, 1.2 equiv) in THF was added dropwise. The reaction mixture was brought to room temperature. The reaction completed in 2 h. Excess NaH was quenched by adding few drops of ethyl acetate. THF was removed from the reaction mixture by evaporation, and the residue was taken in EtOAc, which was washed with water and finally with saturated brine solution. The EtOAc fraction was dried over anhydrous Na_2SO_4, and the solvents were evaporated to obtain the crude product. Pure product **5** was obtained by column chromatography using silica gel as stationary phase and EtOAc/hexanes (1:20) as eluent.

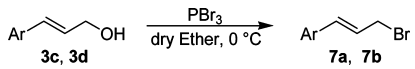
*2-Phenyl-3-((prop-2-ynyloxy)methyl)oxirane (**5a**).* Obtained in 92% yield as a colorless liquid. R_f = 0.41 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (d, J = 0.8 Hz, 1H), 3.24 (quint, J = 2.4 Hz, 1H), 3.70 (dd, J = 11.2 Hz, 5.2 Hz, 1H), 3.83 (s, 1H), 3.92 (dd, J = 11.2 Hz, 2.8 Hz, 1H), 4.27 (s, 2H), 7.26–7.29 (m, 2H), 7.31–7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 58.1, 60.3, 69.0, 74.9, 79.0, 125.4, 127.9, 128.1, 136.4. IR (neat, cm^{-1}): 3274, 2853, 2116, 1246, 1103. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.65; H, 6.48.

*2-(4-Chlorophenyl)-3-((prop-2-ynyloxy)methyl)oxirane (**5b**).* Obtained in 94% yield as a colorless liquid. R_f = 0.38 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (t, J = 2.2 Hz, 1H), 3.19 (quint, J = 2.2 Hz, 1H), 3.70 (dd, J = 11.4 Hz, 5.1 Hz, 1H), 3.80 (d, J = 1.2 Hz, 1H), 3.89 (dd, J = 11.4 Hz, 3.1 Hz, 1H), 4.25 (d, J = 2.3 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 58.6, 60.7, 69.1, 75.0, 79.1, 127.0, 128.7, 134.0, 135.3. IR (neat, cm^{-1}): 3297, 2909, 2118, 1495, 1227, 1092, 1015, 826. Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98; Found: C, 64.85; H, 4.91.

*2-(4-Fluorophenyl)-3-((prop-2-ynyloxy)methyl)oxirane (**5c**).* Obtained in 86% yield as a colorless liquid. R_f = 0.47 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (td, J = 2.4 Hz, 0.8 Hz, 1H), 3.20 (quint, J = 2.4 Hz, 1H), 3.69 (dd, J = 11.2 Hz, 4.8 Hz, 1H), 3.81 (d, J = 1.6 Hz, 1H), 3.90 (dd, J = 11.2 Hz, 3.2 Hz, 1H), 4.25 (d, J = 2.4 Hz, 2H), 7.00–7.05 (m, 2H), 7.21–7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 58.5, 60.6, 69.1, 75.0, 79.1, 115.4 (d, J = 21.6 Hz), 127.3 (d, J = 8.2 Hz), 132.4, 162.6 (d, J = 244.9 Hz). IR (neat, cm^{-1}): 3298, 2909, 2118, 1495, 1227, 1087, 1015, 826. Anal. Calcd for $C_{12}H_{11}FO_2$: C, 69.89; H, 5.38. Found: C, 69.75; H, 5.32.

*2-(2,4-Dichlorophenyl)-3-((prop-2-ynyloxy)methyl)oxirane (**5d**).* Obtained in 86% yield as a colorless liquid. R_f = 0.39 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 1H), 3.06 (t, J = 2.4 Hz, 1H), 3.69 (dd, J = 11.6 Hz, 5.6 Hz, 1H), 3.98 (dd, J = 11.6 Hz, 2.4 Hz, 1H), 4.09 (s, 1H), 4.27 (s, 2H), 7.17 (d, J = 8.4 Hz, 1H), 7.24 (td, J = 8.4 Hz, 1.6 Hz, 1H), 7.36 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.9, 58.5, 60.3, 69.0, 75.0, 79.1, 126.9, 127.4, 128.9, 133.4, 133.5, 134.1. IR (neat, cm^{-1}): 3300, 3082, 3009, 2926, 2118, 1267, 1103, 1047, 885, 829. Anal. Calcd for $C_{12}H_{10}Cl_2O_2$: C, 56.06; H, 3.92. Found: C, 56.15; H, 3.86.

Preparation of (*E*)-Cinnamyl Bromide Derivatives 7a and 7b.



To an ice-cold solution of PBr_3 (1.2 equiv) in dry ether was added slowly dropwise a solution of (*E*)-cinnamyl alcohol

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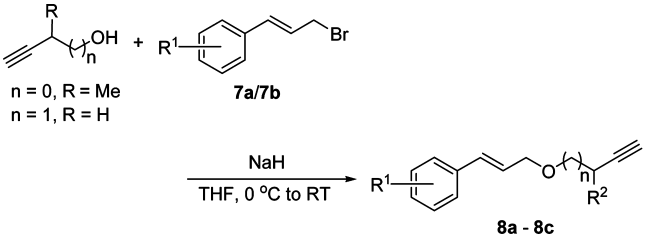
derivative (**3c**/**3d**, 1.0 equiv) in dry ether. It was then allowed to stir at 0 °C for 30 min. Reaction mixture was poured onto ice-cold water and was extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and dried over anhydrous $MgSO_4$. Ether was evaporated, and the product obtained was used for the next step without further purification.

*(E)-1-(3-Bromoprop-1-enyl)-4-fluorobenzene (**7a**).* Obtained in 87% yield as a colorless solid, mp 39−41 °C. R_f = 0.71 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.14 (d, J = 8.0 Hz, 2H), 6.30 (dt, J = 15.6 Hz, 8.0 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 7.10−7.03 (m, 2H), 7.33−7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.3, 115.6 (d, J = 21.6 Hz), 124.9, 128.3 (d, J = 8.0 Hz), 131.9, 133.3, 162.7 (d, J = 246.6 Hz). IR (KBr, cm^{-1}): 2924, 2857, 1643, 1601, 1235, 1202, 583. Anal. Calcd for C_9H_8BrF: C, 50.26; H, 3.75. Found: C, 50.15; H, 3.71.

*(E)-1-(3-Bromoprop-1-enyl)-2,4-dichlorobenzene (**7b**).* Obtained as a colorless liquid in 82% yield. R_f = 0.76 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (d, J = 7.7 Hz, 2H), 6.37 (dt, J = 15.6 Hz, 7.7 Hz, 1H), 6.96 (d, J = 15.6 Hz, 1H), 7.22 (dd, J = 8.4 Hz, 1.7 Hz, 1H), 7.38 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.5, 127.3, 127.7, 128.3, 129.2, 129.5, 132.4, 133.8, 134.3. IR (neat, cm^{-1}): 3080, 1694, 1588, 1101, 599. Anal. Calcd for $C_9H_7BrCl_2$: C, 40.64; H, 2.65. Found: C, 40.55; H, 2.61.

*(E)-1-(3-(But-3-yn-2-yloxy)prop-1-enyl)-2,4-dichlorobenzene (**8a**).*

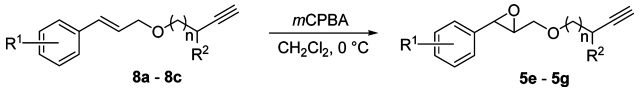


NaH (60% dispersion in mineral oil, 226 mg, 5.64 mmol) was taken in a dry two necked RB flask. To this was added dry THF (10 mL), and the contents of the reaction flask was stirred gently in an ice bath. To this was added 3-butyn-2-ol (0.32 mL, 4.14 mmol) in anhydrous THF (5 mL) dropwise, and the mixture was allowed to stir at the same temperature for 30 min. To this was added slowly a solution of 2,4-dichlorocinnamyl bromide **7b** (1.0 g, 3.76 mmol) in THF (5 mL). The reaction was brought to room temperature and monitored by TLC. It was found that it completed in 2 h. Excess NaH was quenched by adding few drops of water slowly. THF was evaporated, and the residue was taken in ethyl acetate. It was washed with water and saturated brine solution. The organic layer was dried over Na_2SO_4 and concentrated. The crude mixture was purified by column chromatography using silica gel as stationary phase and EtOAc/hexanes (1:50) as eluent to obtain pure **8a** (796 mg, 83%) as a colorless liquid. R_f = 0.39 in 1:20 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (d, J = 6.4 Hz, 3H), 2.48 (d, J = 1.6 Hz, 1H), 4.18 (dd, J = 12.0 Hz, 6.4 Hz, 1H), 4.28 (qd, J = 6.4 Hz, 1.6 Hz, 1H), 4.44 (dd, J = 12.0 Hz, 4.2 Hz, 1H), 6.27 (dt, J = 16.0 Hz, 6.0 Hz, 1H), 6.96 (d, J = 16.0 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 1.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 64.6, 68.9, 73.2, 83.5, 127.2, 127.60, 127.64, 129.1, 133.4, 133.56, 133.62. IR (neat, cm^{-1}): 3304, 2990, 2938, 1647, 1103. Anal. Calcd for $C_{13}H_{12}Cl_2O$: C, 61.20; H, 4.74; Found: C, 61.35; H, 4.69.

*(E)-(3-(But-3-ynyloxy)prop-1-enyl)benzene (**8b**).* Obtained in 78% yield as a colorless liquid following the above procedure using homopropargyl alcohol and cinnamyl bromide. R_f = 0.58 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (t, J = 2.4 Hz, 1H), 2.55 (td, J = 6.8 Hz, 2.4 Hz, 2H), 3.65 (t, J = 6.8 Hz, 2H), 4.21 (d, J = 6.0 Hz, 2H), 6.33 (dt, J = 16.0 Hz, 6.0 Hz, 1H), 6.66 (d, J = 16.0 Hz, 1H), 7.21−7.44 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 63.9, 69.3, 71.4, 81.2, 125.6, 126.3, 127.6, 128.4, 132.4, 136.4. IR (neat, cm^{-1}): 3297, 2919, 2120, 1728, 1452, 1113, 750, 698. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.75; H, 7.62.

*(E)-1-(3-(But-3-ynyloxy)prop-1-enyl)-4-fluorobenzene (**8c**).* Obtained in 84% yield as a light yellow colored liquid following the above procedure using homoporpargyl alcohol and 4-fluorocinnamyl bromide **7a**. R_f = 0.60 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00 (t, J = 2.8 Hz, 1H), 2.51 (td, J = 6.8 Hz, 2.8 Hz, 2H), 3.62 (t, J = 6.8 Hz, 2H), 4.18 (d, J = 6.0 Hz, 2H), 6.20 (dt, J = 15.6 Hz, 6.0 Hz, 1H), 6.58 (d, J = 15.6 Hz, 1H), 6.99−7.03 (m, 2H), 7.34−7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 68.2, 69.3, 71.4, 81.2, 115.4 (d, J = 21.5 Hz), 125.5, 127.8 (d, J = 7.9 Hz), 131.4, 132.8, 162.3 (d, J = 245.4 Hz). IR (neat, cm^{-1}): 3434, 3302, 3073, 1603, 1227, 1159, 1117. Anal. Calcd for $C_{13}H_{13}FO$: C, 76.45; H, 6.42; Found: C, 76.32; H, 6.38.

Epoxidation of 8a−8c.



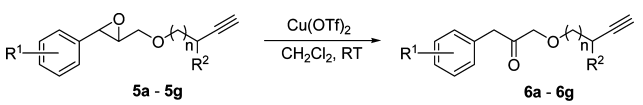
The procedure employed for the epoxidation of compounds **3a−3d** was used to make **5e−5g** from **8a−8c**.

*2-((But-3-yn-2-yloxy)methyl)-3-(2,4-dichlorophenyl)oxirane (**5e**).* Obtained in 94% yield as a colorless liquid. R_f = 0.54 in 1:10 EtOAc/hexanes. Mixture of two diastereomers (1.4:1.0). ^{1}H NMR (400 MHz, $CDCl_3$) of major diastereomer: δ 1.47 (d, J = 6.4 Hz, 3H), 2.46−2.47 (m, 1H), 3.05−3.09 (m, 1H), 3.83 (dd, J = 11.6 Hz, 3.6 Hz, 1H), 3.90 (dd, J = 11.6 Hz, 4.8 Hz, 1H), 4.12 (d, J = 1.6 Hz, 1H), 4.28−4.33 (m, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.22 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.35 (d, J = 1.6 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$) of minor diastereomer: δ 1.49 (d, J = 6.4 Hz, 3H), 2.46−2.47 (m, 1H), 3.05−3.09 (m, 1H), 3.54 (dd, J = 11.6 Hz, 6.4 Hz, 1H), 4.05 (d, J = 2.0 Hz, 1H), 4.16 (dd, J = 11.6 Hz, 2.4 Hz, 1H), 4.28−4.33 (m, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.22 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.35 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) of mixture of diastereomers: δ 21.8, 21.9, 52.8, 53.2, 60.4, 60.7, 65.6, 67.5, 68.4, 73.51, 73.54, 83.0, 126.9, 127.4, 128.9, 133.5, 133.56, 133.61, 134.0. IR (neat, cm^{-1}): 3300, 3082, 3009, 2926, 2118, 1267, 1103, 1087, 1047, 885, 829. Anal. Calcd for $C_{13}H_{12}Cl_2O_2$: C, 57.59; H, 4.46. Found: C, 57.45; H, 4.51.

*2-((But-3-ynyloxy)methyl)-3-phenyloxirane (**5f**).* Obtained in 74% yield as a light yellow colored liquid. R_f = 0.37 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00 (s, 1H), 2.50−2.54 (m, 2H), 3.23 (br s, 1H), 3.61−3.74 (m, 3H), 3.80 (s, 1H), 3.89 (dd, J = 11.6 Hz, 2.4 Hz, 1H), 7.27−7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 55.3, 60.7, 69.1, 69.4, 70.3, 80.9, 125.4, 127.9, 128.2, 136.6. IR (neat, cm^{-1}): 3276, 2857, 2116, 1246, 1105, 882. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.31; H, 6.92.

*2-((But-3-ynyloxy)methyl)-3-(4-fluorophenyl)oxirane (**5g**).* Obtained in 88% yield as a colorless liquid. R_f = 0.48 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 1H), 2.49−2.52 (m, 2H), 3.18 (s, 1H), 3.60−3.72 (m, 3H), 3.79 (s, 1H), 3.87 (dd, J = 11.6 Hz, 1.2 Hz, 1H), 7.01−7.05 (m, 2H), 7.22−7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 55.2, 61.0, 69.4, 69.5, 70.5, 81.0, 115.4 (d, J = 21.7 Hz), 127.3 (d, J = 8.2 Hz), 132.5, 162.7 (d, J = 245.0 Hz). IR (neat, cm^{-1}): 3297, 2917, 2114, 1229, 1117. Anal. Calcd for $C_{13}H_{13}FO_2$: C, 70.90; H, 5.95. Found: C, 70.81; H, 6.02.

General Procedure for the Rearrangement of Epoxialkynes 5a−5g Using Copper Triflate.



Copper triflate (2 mol %) was added to a solution of the epoxyalkyne **5a−5g** in dichloromethane under anhydrous conditions. The reaction mixture was stirred at room

temperature. Reaction was found to complete in 0.5 h. Dichloromethane was evaporated, and the crude product was directly loaded onto a silica gel column. It was eluted with EtOAc/hexanes (1:10) to obtain pure rearranged products **6a**−**6g**.

*1-Phenyl-3-(prop-2-ynyloxy)propan-2-one (**6a**).* Obtained in 72% yield as a yellow colored liquid. R_f = 0.29 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (t, J = 1.2 Hz, 1H), 3.80 (s, 2H), 4.25 (s, 2H), 4.24 (t, J = 2.4 Hz, 2H), 7.22−7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.3, 58.4, 73.4, 75.7, 78.5, 127.2, 128.8, 129.5, 133.3, 205.4. IR (neat, cm^{-1}): 3285, 2924, 2120, 1728, 1497, 1454, 700. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.45; H, 6.51.

*1-(4-Chlorophenyl)-3-(prop-2-ynyloxy)propan-2-one (**6b**).* Obtained in 57% yield as a yellow colored liquid. R_f = 0.14 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (t, J = 2.4 Hz, 1H), 3.76 (s, 2H), 4.19 (s, 2H), 4.23 (d, J = 2.4 Hz, 2H), 7.13−7.15 (m, 2H), 7.27−7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.2, 58.3, 73.6, 75.7, 78.4, 128.7, 130.8, 131.6, 132.9, 204.8. IR (neat, cm^{-1}): 3437, 3295, 3054, 2901, 1730, 1092, 1015. Anal. Calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98. Found: C, 64.85; H, 4.91.

*1-(4-Fluorophenyl)-3-(prop-2-ynyloxy)propan-2-one (**6c**).* Obtained in 72% yield as a light yellow colored liquid. R_f = 0.21 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (m, 1H), 3.77 (s, 2H), 4.21 (s, 2H), 4.24 (d, J = 2.4 Hz, 2H), 6.99−7.03 (m, 2H), 7.16−7.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.1, 58.4, 73.5, 75.7, 78.4, 115.5 (d, J = 21.3 Hz), 128.8, 131.0 (d, J = 8.0 Hz), 161.9 (d, J = 243.9 Hz), 205.1. IR (neat, cm^{-1}): 3301, 3073, 2961, 1728, 1109, 1052. Anal. Calcd for $C_{12}H_{11}FO_2$: C, 69.89; H, 5.38. Found: C, 69.75; H, 5.31.

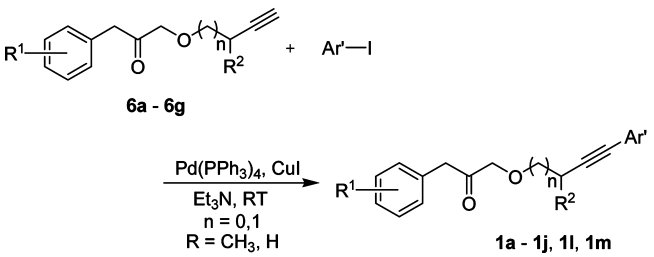
*1-(2,4-Dichlorophenyl)-3-(prop-2-ynyloxy)propan-2-one (**6d**).* Obtained in 61% yield as a light yellow colored liquid. R_f = 0.23 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 1H), 3.91 (s, 2H), 4.28 (s, 2H), 4.30 (s, 2H), 7.14−7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.4, 58.5, 74.0, 75.8, 78.4, 127.3, 129.3, 130.5, 132.5, 133.8, 135.0, 203.7. IR (neat, cm^{-1}): 3439, 3294, 3054, 2901, 1730, 1092, 1055, 1015. Anal. Calcd for $C_{12}H_{10}Cl_2O_2$: C, 56.06; H, 3.92. Found: C, 55.85; H, 4.01.

*1-(But-3-yn-2-yloxy)-3-(2,4-dichlorophenyl)propan-2-one (**6e**).* Obtained in 63% yield as a colorless liquid. R_f = 0.50 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52 (d, J = 6.4 Hz, 3H), 2.48 (d, J = 2.0 Hz, 1H), 3.93 (s, 2H), 4.20 (d, J = 17.2 Hz, 1H), 4.32 (qd, J = 6.4 Hz, 2.0 Hz, 1H), 4.37 (d, J = 17.2 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.21 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 43.4, 65.8, 73.3, 74.2, 82.4, 127.2, 129.2, 130.7, 132.5, 133.7, 135.0, 204.2. IR (neat, cm^{-1}): 3438, 3295, 3054, 2901, 1730, 1092, 1056, 1015. Anal. Calcd for $C_{13}H_{12}Cl_2O_2$: C, 57.59; H, 4.46. Found: C, 57.65; H, 4.41.

*1-(But-3-ynyloxy)-3-phenylpropan-2-one (**6f**).* Obtained in 71% yield as a light yellow colored liquid. R_f = 0.18 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (t, J = 2.8 Hz, 1H), 2.51 (td, J = 6.8 Hz, 2.8 Hz, 2H), 3.60 (t, J = 6.8 Hz, 2H), 3.79 (s, 2H), 4.15 (s, 2H), 7.23−7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 46.1, 69.6, 75.4, 80.9, 127.1, 128.7, 129.4, 133.3, 205.9. IR (neat, cm^{-1}): 3279, 2924, 2120, 1729, 1499, 1454, 700. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.32; H, 6.88.

*1-(But-3-ynyloxy)-3-(4-fluorophenyl)propan-2-one (**6g**).* Obtained in 81% as a light yellow colored liquid. R_f = 0.26 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.02 (br s, 1H), 2.50−2.54 (m, 2H), 3.61 (t, J = 6.4 Hz, 2H), 3.78 (s, 2H), 4.14 (s, 2H), 6.99−7.03 (m, 2H), 7.17−7.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 45.1, 69.60, 69.65, 75.5, 80.9, 115.5 (d, J = 21.2 Hz), 129.0, 131.0 (d, J = 8.0 Hz), 162.0 (d, J = 244.7 Hz), 205.9. IR (neat, cm^{-1}): 3301, 3073, 2961, 1728, 1716, 1107, 1048. Anal. Calcd for $C_{13}H_{13}FO_2$: C, 70.90; H, 5.95. Found: C, 70.79; H, 5.88.

General Procedure for the Sonogashira Coupling of 6a−6g.



To a solution of aryl iodide (1.2 equiv) in triethylamine (3 mL/mmol of **6a**−**6g**) were added $Pd(PPh_3)_4$ (2 mol %) and CuI (4 mol %), and the mixture was stirred for 30 min. To this was added alkyne **6a**−**6g** (1.0 equiv), and the mixture was allowed to stir overnight at room temperature. The reaction mixture was filtered, and triethylamine was evaporated. The crude was loaded on silica gel column and eluted with EtOAc/hexanes to obtain pure coupled product **1a**−**1j**, **1l**, and **1m**.

*1-Phenyl-3-(3-phenylprop-2-ynyloxy)propan-2-one (**1a**).* Obtained by the coupling of **6a** with iodobenzene in 57% yield as a light yellow colored solid, mp 40−42 °C. R_f = 0.33 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 2H), 4.28 (s, 2H), 4.47 (s, 2H), 7.22−7.26 (m, 3H), 7.29−7.34 (m, 5H), 7.40−742 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.2, 59.1, 73.5, 83.8, 87.3, 122.1, 127.0, 128.2, 128.6, 129.4, 131.6, 133.2, 205.5. IR (KBr, cm^{-1}): 3436, 3061, 3030, 2239, 1734, 1067, 756. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10; Found: C, 81.65; H, 6.17.

*1-(3-(4-Methoxyphenyl)prop-2-ynyloxy)-3-phenylpropan-2-one (**1b**).* Obtained by the coupling of **6a** with 4-iodoanisole in 82% yield as a light yellow colored liquid. R_f = 0.30 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H), 3.80 (s, 2H), 4.28 (s, 2H), 4.45 (s, 2H), 6.85 (d, J = 8.4 Hz, 2H), 7.22−7.34 (m, 5H), 7.37 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.0, 55.0, 59.1, 73.4, 82.4, 87.1, 113.7, 114.0, 126.8, 133.1, 133.2, 159.7, 205.4. IR (neat, cm^{-1}): 3421, 3060, 3027, 2239, 1734, 1093, 1062, 756. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16; Found: C, 77.45; H, 6.20.

*1-(4-Chlorophenyl)-3-(3-(4-chlorophenyl)prop-2-ynyloxy)-propan-2-one (**1c**).* Obtained by the coupling of **6b** and 1-chloro-4-iodobenzene in 57% yield as a colorless liquid. R_f = 0.18 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 2H), 4.24 (s, 2H), 4.45 (s, 2H), 7.13−7.15 (m, 2H), 7.26−7.31(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.3, 59.1, 73.7, 84.7, 86.3, 120.5, 128.6, 128.7, 130.8, 131.6, 132.9, 133.0, 134.7, 205.0. IR (neat, cm^{-1}): 3297, 3056, 2907, 1736, 1094, 1019. Anal. Calcd for $C_{18}H_{14}Cl_2O_2$: C, 64.88; H, 4.23. Found: C, 64.75; H, 4.37.

*1-(2,4-Dichlorophenyl)-3-(3-o-tolylprop-2-ynyloxy)propan-2-one (**1d**).* Obtained by the coupling of **6d** and 2-iodotoluene in 70% yield as a light yellow colored liquid. R_f = 0.73 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.96 (s, 2H), 4.36 (s, 2H), 4.57 (s, 2H), 7.13- 7.18 (m, 2H), 7.19−7.26 (m, 3H), 7.40−7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 43.5, 59.4, 74.0, 86.4, 87.4, 121.9, 125.6, 127.2, 128.7, 129.3, 129.5, 130.6, 132.1, 132.5, 133.8, 135.0, 140.3, 204.0. IR (neat, cm^{-1}): 3298, 3056, 2907, 1740, 1101, 1092, 1090, 1019. Anal. Calcd for $C_{19}H_{16}Cl_2O_2$: C, 65.72; H, 4.64. Found: C, 65.82; H, 4.59.

*1-(4-Fluorophenyl)-3-(3-(4-fluorophenyl)prop-2-ynyloxy)propan-2-one (**1e**).* Obtained by the coupling of **6c** and 4-fluoro-1-iodobenzene in 45% yield as a light yellow colored liquid. R_f = 0.28 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 2H), 4.26 (s, 2H), 4.46 (s, 2H), 6.97−7.01 (m, 4H), 7.16−7.20 (m, 2H), 7.37−7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.2, 59.2, 73.7, 83.4, 86.4, 115.5 (d, J = 21.2 Hz), 115.6 (d, J = 21.9 Hz), 118.2, 128.3, 131.0 (d, J = 7.7 Hz), 133.7 (d, J = 7.3 Hz), 162.0 (d, J = 244.0 Hz), 162.7 (d, J = 248.7 Hz), 205.5. IR (neat, cm^{-1}): 3201, 3073, 2961, 1728, 1716, 1136, 1109. Anal. Calcd for $C_{18}H_{14}F_2O_2$: C, 71.99; H, 4.70. Found: C, 71.85; H, 4.76.

*1-(3-(Naphthalen-1-yl)prop-2-ynyloxy)-3-phenylpropan-2-one (**1f**).* Obtained by the coupling of **6a** and 1-iodonaphthalene in 60% yield as a light yellow colored liquid. R_f = 0.26 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 2H), 4.36 (s, 2H), 4.61 (s, 2H), 7.23−7.83 (m, 11H), 8.24 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.4, 59.4, 73.6, 85.4, 88.6, 119.8, 125.1, 125.9, 126.4, 126.9, 127.1, 128.3, 128.7, 129.2, 129.4, 130.8, 133.2, 133.3, 205.5. IR (neat, cm^{-1}): 3057, 2922, 2224, 1728, 1103. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.19; H, 5.65.

*1-(3-(Benzo[d][1,3]dioxol-5-yl)prop-2-ynyloxy)-3-(4-chlorophenyl)propan-2-one (**1g**).* Obtained by the coupling of **6b** and 1-iodo-3,4-(methylenedioxy)benzene in 62% yield as a colorless liquid. R_f = 0.45 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 2H), 4.24 (s, 2H), 4.44 (s, 2H), 5.97 (s, 2H), 6.75 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 1.0 Hz, 1H), 6.92 (dd, J = 8.0 Hz, 1.3 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.3, 59.2, 73.7, 82.0, 87.3, 101.3, 108.4, 111.6, 115.2, 126.5, 128.7, 130.8, 131.7, 132.9, 147.3, 148.2, 205.2. IR (neat, cm^{-1}): 3294, 3057, 2908, 1728, 1092, 1041. Anal. Calcd for $C_{19}H_{15}ClO_4$: C, 66.58; H, 4.41. Found: C, 66.48; H, 4.51.

*1-(3-(4-Chlorophenyl)prop-2-ynyloxy)-3-(4-fluorophenyl)propan-2-one (**1h**).* Obtained by the coupling of **6c** and 1-chloro-4-iodobenzene in 61% yield as a light yellow colored liquid. R_f = 0.38 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 2H), 4.25 (d, J = 8.3 Hz, 2H), 4.45 (d, J = 8.2 Hz, 2H), 6.98−7.02 (m, 2H), 7.17−7.20 (m, 2H), 7.27−7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.2, 59.2, 73.8, 84.7, 86.3, 115.5 (d, J = 21.3 Hz), 120.6, 128.7, 128.9, 131.0 (d, J = 7.9 Hz), 132.9, 134.8, 162.0 (d, J = 244.2 Hz), 205.4. IR (neat, cm^{-1}): 3201, 3073, 2961, 1728, 1716, 1109, 1089. Anal. Calcd for $C_{18}H_{14}ClFO_2$: C, 68.25; H, 4.45. Found: C, 68.49; H, 4.61.

*1-(4-Chlorophenyl)-3-(3-(3,4,5-trimethoxyphenyl)prop-2-ynyloxy)propan-2-one (**1i**).* Obtained by the coupling of **6b** and 3,4,5-(trimethoxy)iodobenzene in 54% yield as a yellow colored liquid. R_f = 0.26 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 2H), 3.81 (s, 6H), 3.83 (s, 3H), 4.23 (s, 2H), 4.43 (s, 2H), 6.63 (s, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.2, 55.9, 59.1, 60.8, 73.8, 82.7, 87.3, 108.8, 116.9, 128.6, 130.8, 131.6, 132.8, 139.0, 152.9, 205.1. IR (neat, cm^{-1}): 3390, 2948, 1726, 1578, 1117, 1009, 658. Anal. Calcd for $C_{21}H_{21}ClO_5$: C, 64.87; H, 5.44. Found: C, 64.75; H, 5.51.

*1-(4-(4-Chlorophenyl)but-3-yn-2-yloxy)-3-(2,4-dichlorophenyl)-propan-2-one (**1j**).* Obtained by the coupling of **6e** and 1-chloro-4-iodobenzene in 63% yield as a light yellow colored solid, mp 45−47 °C. R_f = 0.29 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (d, J = 6.8 Hz, 3H), 3.96 (s, 2H), 4.26 (d, J = 16.8 Hz, 1H), 4.41 (d, J = 16.8 Hz, 1H), 4.53 (q, J = 6.8 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.19 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.28−7.34 (m, 4H), 7.38 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 43.5, 66.6, 73.5, 85.0, 88.6, 120.6, 127.2, 128.7, 129.3, 130.7, 132.5, 132.9, 133.8, 134.7, 135.0, 204.5. IR (KBr, cm^{-1}): 3296, 3056, 2907, 1738, 1101, 1096, 1094, 1019. Anal. Calcd for $C_{19}H_{15}Cl_3O_2$: C, 59.79; H, 3.96. Found: C, 59.65; H, 4.02.

*1-Phenyl-3-(4-phenylbut-3-ynyloxy)propan-2-one (**1l**).* Obtained by the coupling of **6f** and iodobenzene in 64% yield as a light yellow colored liquid. R_f = 0.18 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (t, J = 6.8 Hz, 2H), 3.70 (t, J = 6.8 Hz, 2H), 3.82 (s, 2H), 4.18 (s, 2H), 7.24−7.25 (m, 2H), 7.26−7.35 (m, 6H), 7.41−7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 46.1, 69.8, 75.4, 81.7, 86.3, 123.4, 127.0, 127.8, 128.2, 128.6, 129.4, 131.5, 133.3, 206.0. IR (neat, cm^{-1}): 3437, 3059, 3028, 2238, 1733, 1067, 756. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.10; H, 6.48.

*1-(4-(3,5-Dimethylphenyl)but-3-ynyloxy)-3-(4-fluorophenyl)-propan-2-one (**1m**).* Obtained by the coupling of **6g** and 3,5-dimethyliodobenzene in 45% yield as a light yellow colored liquid. R_f = 0.36 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 6H), 2.75 (t, J = 6.8 Hz, 2H), 3.70 (t, J = 6.8 Hz, 2H), 3.82 (s, 2H), 4.18 (s, 2H), 6.94 (s, 1H), 6.98−7.04 (m, 4H), 7.18−7.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 21.0, 45.0, 69.9, 75.5, 82.0, 85.5, 115.4 (d, J = 21.3 Hz), 122.9, 129.0, 129.2, 129.7, 131.0 (d, J = 7.8 Hz), 137.7, 161.9 (d, J = 243.9 Hz), 206.3. IR (neat, cm^{-1}): 3310, 2917, 1730, 1601, 1107. Anal. Calcd for $C_{21}H_{21}FO_2$: C, 77.75; H, 6.53. Found: C, 77.65; H, 6.59.

*1-Phenylhex-1-yn-3-ol (**10**).* To a stirred solution of phenylacetylene (2.0 mL, 18.2 mmol) in dry THF (50 mL) was added dropwise a 1.6 M solution of *n*-BuLi in hexanes (13.7 mL, 21.8 mmol) at −78 °C. The mixture was stirred for 15 min, and then a solution of *n*-butaraldehyde (1.96 mL, 21.8 mmol) in anhydrous THF (30 mL) was added. The reaction mixture was then warmed to room temperature. A few drops of methanol were added to quench the excess *n*-BuLi. THF was evaporated, and the residue was taken in EtOAc, which was washed with saturated ammonium chloride solution. Solvents from the organic fraction were removed in a rotovap to obtain the crude product. Pure 1-phenylhex-1-yn-3-ol **10** (2.9 g, 91%) was obtained by column chromatography using silica gel as stationary phase and EtOAc/hexanes (1:10) as eluent. R_f = 0.26 in 1:30 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[21] δ 0.99 (t, J = 7.6 Hz, 3H), 1.52−1.60 (m, 2H), 1.76−1.82 (m, 2H), 1.98 (br s, 1H), 4.61 (s, 1H), 7.30−7.31 (m, 3H), 7.42−7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 18.5, 39.9, 62.7, 84.7, 90.2, 122.6, 128.2, 128.3, 131.6.

*(E)-1-(3-(1-Phenylhex-1-yn-3-yloxy)prop-1-enyl)benzene (**11**).* NaH (60% dispersion in mineral oil, 0.34 g, 8.6 mmol) was taken in a dry two necked RB flask and dry THF (25 mL). The reaction flask was cooled in an ice bath. Propargyl alcohol derivative **10** (1.0 g, 5.74 mmol) was added slowly dropwise, and the mixture was allowed to stir at 0 °C for 30 min. Then a solution of cinnamyl bromide (1.24 g, 6.31 mmol) in dry THF (5 mL) was added slowly. Reaction was monitored by TLC and found to complete in 2 h. Excess NaH was quenched by adding few drops of water slowly. THF was evaporated, and the residue was taken in ethyl acetate (50 mL) and washed with water (40 mL) and then brine solution (50 mL). Organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude mixture was purified by column chromatography using silica gel as stationary phase and EtOAc/hexanes (1:50) as eluent to obtain pure compound **11** (1.54 g, 92%) as a colorless liquid. R_f = 0.65 in 1:30 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, J = 7.2 Hz, 3H), 1.55−1.62 (m, 2H), 1.77−1.87 (m, 2H), 4.22 (dd, J = 12.5 Hz, 6.7 Hz, 1H), 4.37 (t, J = 6.4 Hz, 1H), 4.49 (dd, J = 12.5 Hz, 5.5 Hz, 1H), 6.30−6.37 (m, 1H), 6.66 (d, J = 15.9 Hz, 1H), 7.22−7.46 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 18.7, 37.9, 69.1, 69.3, 85.8, 88.4, 122.8, 125.9, 126.5, 127.6, 128.2, 128.5, 131.7, 132.7, 136.7. IR (neat, cm^{-1}): 3028, 2959, 2868, 1599, 1113, 1068. Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.79; H, 7.68.

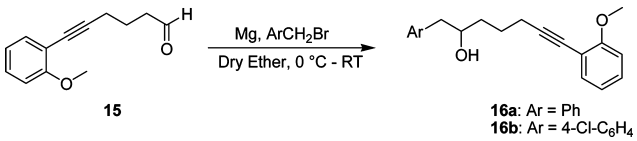
*2-Phenyl-3-((1-phenylhex-1-yn-3-yloxy)methyl)oxirane (**12**).* *m*-Chloroperoxybenzoic acid (75%, 0.89 g, 5.16 mmol) was added to a stirred solution of **11** (1.00 g, 3.44 mmol) in dichloromethane (10 mL) at 0 °C. The reaction was brought to room temperature and monitored by TLC. It was found to complete in 2 h. Saturated aqueous solution of Na_2SO_3 (3 mL) was added to quench excess *m*CPBA. The reaction mixture was diluted by adding dichloromethane (20 mL) and washed two times with saturated sodium bicarbonate solution (2 × 30 mL). It was washed with brine solution (30 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude epoxide product, which was purified by column chromatography using silica gel as stationary phase and EtOAc/hexanes (1:20) as eluent to obtain pure **12** as a yellow colored liquid (0.94 g, 89%). R_f = 0.39 in 1:10 EtOAc/hexanes. Mixture of isomers (1.3: 1). ^{1}H NMR (400 MHz, $CDCl_3$) of major diastereomer: δ 0.96−1.00 (m, 3H), 1.53−1.88 (m, 4H), 3.24−3.27 (m, 1H), 3.85 (dd, J = 11.6 Hz, 3.2 Hz, 1H), 3.88 (br s, 1H), 3.99 (dd, J = 11.6 Hz, 4.4 Hz, 1H), 4.38−4.41 (m, 1H), 7.30−7.44 (m, 10H). ^{1}H NMR (400 MHz, $CDCl_3$) of minor diastereomer: δ 0.96−1.00 (m, 3H), 1.53−1.88 (m, 4H), 3.29−3.30 (m, 1H), 3.61 (dd, J = 11.2 Hz, 6.0 Hz, 1H), 3.78 (br s, 1H), 4.15 (dd, J = 11.2 Hz, 2.4 Hz, 1H), 4.38−4.41 (m, 2H), 7.30−7.44 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) of mixture of diastereomers: δ 13.8, 18.5, 37.7, 37.8, 56.0, 56.1, 60.8, 61.1, 67.9, 69.0, 70.5, 86.1, 88.1, 122.6, 125.7, 128.2, 128.4, 130.1, 131.7, 137.0. IR (neat, cm^{-1}): 3063, 3028, 2961, 2870, 2203, 1098. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.19; H, 7.28.

*1-Phenyl-3-(1-phenylhex-1-yn-3-yloxy)propan-2-one (**1k**).* A solution of epoxide **12** (200.0 mg, 0.65 mmol) in dry THF (1 mL) was added to a stirred suspension of $InCl_3$ (86.7 mg, 0.39 mmol) in dry THF (3 mL) at room temperature under nitrogen. The reaction was heated at reflux for 4 h. After completion of the reaction, THF was evaporated, and the reaction mixture was quenched with brine and extracted with ether. The ether extract was dried over $MgSO_4$ and evaporated to leave a crude product, which was purified by column chromatography over silica gel to obtain pure **1k** (99.0 mg, 49%) as a colorless liquid. R_f = 0.30 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, J = 7.6 Hz, 3H), 1.55−1.60 (m, 2H), 1.81−1.89 (m, 2H), 3.84 (s, 2H), 4.22 (d, J = 16.8 Hz, 1H), 4.37−4.41 (m, 2H), 7.21−7.40 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 18.5, 37.7, 46.3, 70.6, 73.0, 86.8, 87.1, 122.3, 127.0, 128.2, 128.5, 128.6, 129.5, 131.7, 133.5, 206.4. IR (neat, cm^{-1}): 3307, 3150, 2965, 1730, 1094. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.19; H, 7.16.

*6-(2-Methoxyphenyl)hex-5-yn-1-ol (**14**).* $Pd(PPh_3)_4$ (0.160 g, 0.14 mmol) and CuI (0.053 g, 0.28 mmol) were taken in triethylamine (40 mL) under nitrogen atmosphere. 2-Iodoanisole (1.98 mL, 15.21 mmol) was added at room temperature and allowed to stir for 45 min. Then 5-hexyn-1-ol (1.5 mL, 13.83 mmol) was added, and the reaction was allowed to stir overnight. The reaction mixture was filtered to remove quaternary ammonium salt formed in the reaction. Triethylamine was evaporated, and the crude was loaded on a silica gel column. Column was eluted with mixture of EtOAc/hexanes (1:5) to obtain pure coupled product **14** (2.47 g, 87%) as a yellow colored liquid. R_f = 0.10 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[22] δ 1.70- 1.74 (m, 4H), 1.99 (br s, 1H), 2.50 (t, J = 6.4 Hz, 2H), 3.70 (t, J = 6.0 Hz, 2H), 3.86 (s, 3H), 6.84 (d, J = 8.4 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 7.24 (m, 1H), 7.36 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.4, 24.8, 31.8, 55.6, 62.1, 76.9, 94.2, 110.4, 112.8, 120.3, 128.9, 133.4, 159.6.

*6-(2-Methoxyphenyl)hex-5-ynal (**15**).* Oxalyl chloride (0.68 mL, 8.08 mmol) was dissolved in dry dichloromethane (15 mL) and cooled to −78 °C. To this solution was added dry DMSO (1.1 mL, 16.2 mmol), and the mixture was stirred for 10 min. Then a solution of 6-(2-methoxyphenyl)-5-hexyn-1-ol **14** (1.50 g, 7.34 mmol) in dichloromethane (10 mL) was added. The reaction mixture was stirred for additional 15 min, and then triethylamine (5.1 mL, 36.7 mmol) was added slowly dropwise. The reaction mixture was warmed to 0 °C and then to rt. It was diluted with dichloromethane (40 mL), washed with water and brine solution, and dried over anhydrous Na_2SO_4. Evaporation of dichloromethane gave the crude product, which was purified by column chromatography using silica gel as stationary phase and EtOAc/hexanes (1:20) as eluent to obtain pure **15** (1.33 g, 89%) as pale brown colored liquid. R_f = 0.32 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (m, 2H), 2.55 (t, J = 6.8 Hz, 2H), 2.67 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 6.84−6.90 (m, 2H), 7.25 (td, J = 7.6 Hz, 1.4 Hz, 1H), 7.36 (dd, J = 7.6 Hz, 1.4 Hz, 1H), 9.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 21.1, 42.7, 55.6, 77.8, 92.8, 110.4, 112.6, 120.3, 129.1, 133.4, 159.8, 202.0. IR (neat, cm^{-1}): 3401, 3059, 2934, 2724, 1726, 1117. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.35; H, 6.93.

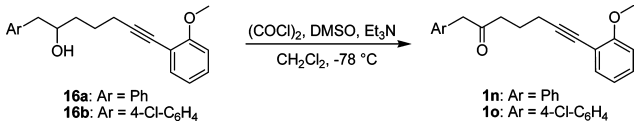
*7-(2-Methoxyphenyl)-1-phenylhept-6-yn-2-ol (**16a**).*



A solution of benzyl bromide (1.16 mL, 9.90 mmol) in dry ether (10 mL) was added slowly to a suspension of magnesium (241 mg, 9.90 mmol) in ether (5 mL) contained in a dry 50 mL two necked RB flask fitted with a reflux condenser. The reaction mixture was stirred at room temperature for 1 h, during which almost all the magnesium was consumed. The reaction flask was kept in an ice bath, and a solution of **15** (0.5 g, 2.47 mmol) in anhydrous ether (10 mL) was added dropwise over a period of 30 min. Then the reaction mixture was allowed to stir at room temperature for 7 h. It was treated with drops of methanol to quench the excess benzylmegnesium bromide. Then the reaction mixture was poured into a separatory funnel containing 50 mL of water. The two layers were separated, and the aqueous layer was extracted with ether (2 × 30 mL). The combined organic layers were washed with saturated brine solution and dried over anhydrous $MgSO_4$. Ether was evaporated to obtain crude product, which was purified by column chromatography using EtOAc/hexanes (1:9) as eluent to obtain pure **16a** (0.563 g, 77%) as a colorless solid, mp 56−58 °C. R_f = 0.30 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60−1.89 (m, 5H), 2.51−2.54 (m, 2H), 2.71 (dd, J = 13.2 Hz, 8.4 Hz, 1H), 2.87 (dd, J = 13.2 Hz, 4.4 Hz, 1H), 3.85 (s, 3H), 3.94 (br s, 1H), 6.84−6.91 (m, 2H), 7.23−7.37 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 25.0, 36.0, 44.2, 55.7, 72.2, 76.9, 94.4, 110.6, 113.0, 120.4, 126.4, 128.6, 129.0, 129.5, 133.6, 138.7, 159.9. IR (KBr, cm^{-1}): 3543, 2930, 2843, 1024, 704. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.45; H, 7.58.

*1-(4-Chlorophenyl)-7-(2-methoxyphenyl)hept-6-yn-2-ol (**16b**).* Prepared in 72% yield as a light yellow liquid following the procedure employed for the preparation of **15a** using 4-chlorobenzyl Grignard in the place of benzyl Grignard. R_f = 0.23 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63−1.74 (m, 4H), 2.15 (br s, 1H), 2.44- 2.51 (m, 2H), 2.64 (dd, J = 13.6 Hz, 8.0 Hz, 1H), 2.74 (dd, J = 13.6 Hz, 4.4 Hz, 1H), 3.82 (s, 3H), 3.82−3.91 (m, 1H), 6.83−6.91 (m, 2H), 7.12−7.35 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 24.6, 35.7, 43.2, 55.5, 71.7, 77.0, 94.1, 110.4, 112.7, 120.3, 127.8, 128.0, 128.9, 130.6, 133.4, 137.0, 159.6. IR (neat, cm^{-1}): 3366, 2942, 2829, 1090, 1026, 752. Anal. Calcd for $C_{20}H_{21}ClO_2$: C, 73.05; H, 6.44. Found: C, 73.12; H, 6.39.

*7-(2-Methoxyphenyl)-1-phenylhept-6-yn-2-one (**1n**).*



Prepared in 93% yield as a light yellow colored solid by the oxidation of **16a** following the Swern oxidation procedure used for the oxidation of compound **14**. Mp 117−119 °C. R_f = 0.41 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86−1.90 (m, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H), 3.74 (s, 2H), 3.87 (s, 3H), 6.85−6.91 (m, 2H), 7.21−7.35 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 22.6, 40.6, 50.2, 55.7, 77.5, 93.2, 110.5, 112.7, 120.3, 126.9, 128.6, 129.0, 129.4, 133.5, 134.2, 159.8, 207.9. IR (KBr, cm^{-1}): 3432, 3057, 3005, 2915, 1719, 1088, 710. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.23; H, 6.85.

*1-(4-Chlorophenyl)-7-(2-methoxyphenyl)hept-6-yn-2-one (**1o**).* Prepared in 98% yield as a light yellow colored solid from **16b** following the Swern oxidation procedure used for the oxidation of **14**. Mp 78−80 °C. R_f = 0.45 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86−1.90 (m, 2H), 2.50 (t, J = 6.8 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H), 3.71 (s, 2H), 3.86 (s, 3H), 6.85−6.91 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.24−7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 22.5, 40.7, 49.3, 55.7, 77.7, 93.1, 110.5, 112.7, 120.4, 128.8, 129.1, 130.8, 132.6, 132.9, 133.5, 159.8, 207.3. IR (KBr, cm^{-1}): 3059, 3010, 2915, 1719, 1091, 710. Anal. Calcd for $C_{20}H_{19}ClO_2$: C, 73.50; H, 5.86. Found: C, 73.45; H, 5.91.

*(E)-5-(3-(Prop-2-ynyloxy)prop-1-enyl)benzo[d][1,3]dioxole (**8d**).* NaH (60% dispersion in mineral oil, 0.34 g, 8.42 mmol, 1.5 equiv) was taken in a dry two necked RB flask, and dry THF (15 mL) was added to it. The reaction flask was kept in an ice bath. To this was added dropwise compound **3e** (1.00 g, 5.61 mmol, 1.0 equiv) in anhydrous THF

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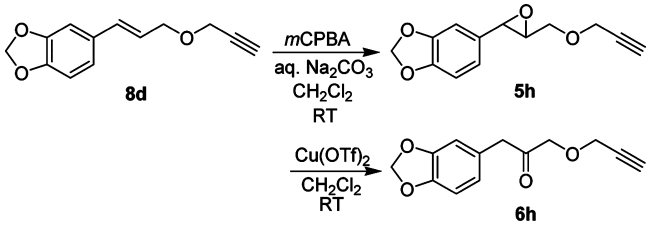
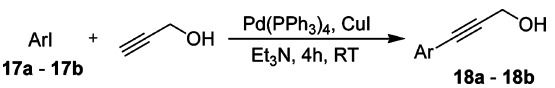
(10 mL), and the mixture was allowed to stir at 0 °C for 30 min. Then propargyl bromide (80 wt % solution in toluene, 0.8 mL, 6.74 mmol, 1.2 equiv) was added slowly. Reaction was monitored by TLC and found to complete in 2 h. Excess NaH was quenched by adding few drops of water slowly. THF was evaporated, and the residue was taken in ethyl acetate and washed with water and brine solution. The organic layer was dried over Na_2SO_4 and concentrated. The crude mixture was purified by column chromatography using silica gel as stationary phase and EtOAc/hexanes (1:10) as eluent to obtain pure **8d** (1.15 g) in 95% as a colorless liquid. R_f = 0.48 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[23] δ 2.47 (t, J = 2.4 Hz, 1H), 4.18−4.21 (m, 4H), 5.93 (s, 2H), 6.10 (dt, J = 15.6 Hz, 6.4 Hz, 1H), 6.54 (d, J = 15.6 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.81 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 6.93 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.8, 70.1, 74.4, 79.7, 101.0, 105.7, 108.1, 121.2, 123.1, 130.9, 133.0, 147.3, 147.9.

*1-(Benzo[d][1,3]dioxol-5-yl)-3-(prop-2-ynyloxy)propan-2-one (**6h**).*



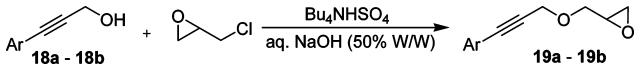
Propargylether derivative **8d** (0.30 g, 1.39 mmol) was disolved in dicloromethane (7 mL). To this solution was added 10% aqueous $NaHCO_3$ solution. Then a solution of *m*-CPBA (75%, 0.54 g, 2.36 mmol) in dichloromethane (3 mL) was added to this biphasic reaction system. The reaction was allowed to stir vigorously. Reaction was monitored by TLC and found to complete in 1 h. Five milliliters of saturated Na_2SO_3 solution was added and stirred vigorously. The two phases were separated, and the organic layer was washed two times with saturated $NaHCO_3$ solution and then once with brine solution. It was dried over anhydrous Na_2SO_4, and dicloromethane was evoporated to obtain crude epoxide **5h**. The crude **5h** was treated with copper triflate (10.0 mg, 0.03 mmol) in dry dicloromethane (6 mL) under anhydrous conditions at room temperature. After 30 min, dicloromethane was evaporated from reaction mixture, and the crude was loaded on a silica gel column. By eluting the column with mixture of EtOAc/hexanes (1:5) pure ketone **6h** (0.14 g, 42% yield over 2 steps) was obtained as a colorless liquid. R_f = 0.40 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (t, J = 2.4 Hz, 1H), 3.68 (s, 2H), 4.20 (s, 2H), 4.23 (d, J = 2.4 Hz, 2H), 5.93 (s, 2H), 6.65 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.70 (d, J = 1.6 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.7, 58.3, 73.4, 75.6, 78.5, 101.0, 108.4, 109.8, 122.5, 126.7, 146.7, 147.8, 205.3. IR (neat, cm^{-1}): υ 3293, 3076, 2893, 2859, 1726, 1252, 1038, 968. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.18; H, 5.27.



To a solution of aryl iodide **17a**/**17b** (1.2 equiv) in triethylamine (3 mL/mmol of propargyl alcohol) were added $Pd(PPh_3)_4$ (2 mol %) and CuI (4 mol %), and the mixture was stirred for 30 min. To this was added propargyl alcohol (1.0 equiv), and the contents of the flask were allowed to stir for 4 h at room temperature. The reaction mixture was filtered, and triethylamine was evaporated. The crude was loaded on a silica gel column and eluted with EtOAc/hexanes to obtain pure coupled product **18a**/**18b**.

*3-(Benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-ol (**18a**).* Obtained in 99% as a colorless solid, mp 74−76 °C (lit.[24] 74−76 °C). R_f = 0.57 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[24] δ 2.17 (br s, 1H), 4.46 (s, 2H), 5.96 (s, 2H), 6.74 (d, J = 8.0 Hz, 1H), 6.88 (s, 1H), 6.96 (dd, J = 8.0 Hz, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.5, 85.5, 85.6, 101.3, 108.4, 111.6, 115.7, 126.3, 147.3, 148.0.

*3-(3,4-Dimethoxyphenyl)prop-2-yn-1-ol (**18b**).* Obtained in 98% as a yellow colored liquid. R_f = 0.48 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[24] δ 2.75 (br s, 1H), 3.80 (s, 3H), 3.82 (s, 3H), 4.45 (s, 2H), 6.73−6.75 (m, 2H), 6.90 (d, J = 1.2 Hz, 1H), 6.97−7.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.3, 55.7, 85.3, 85.8, 110.8, 114.2, 114.6, 124.8, 148.3, 149.3.

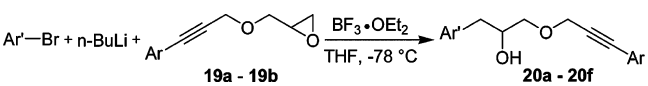


Literature procedure was followed.[28] To a vigorously stirred solution of 50% w/w aq NaOH (1 mL/mmol of **18a**/**18b**) were added epichlorohydrin (5.0 equiv) and tetrabutylammonium hydrogen sulfate (0.1 equiv) at 0 °C. Propargyl alcohol (**18a**/**18b**, 1 equiv) was added slowly. The reaction mixture was allowed to stir at 0 °C for 3 h, and then the aqueous phase was extracted with ether. The organic phase was washed two times with brine solution and dried over $MgSO_4$. After evaporation of ether, the crude mixture was loaded on a silica gel and eluted with mixture of EtOAc/hexanes to obtain pure **19a**/**19b**.

*5-(3-(Oxiran-2-ylmethoxy)prop-1-ynyl)benzo[d][1,3]dioxole (**19a**).* Obtained in 98% as a yellow colored liquid. R_f = 0.67 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 2.80 (t, J = 4.8 Hz, 1H), 3.17−3.22 (m, 1H), 3.53 (dd, J = 11.6 Hz, 6.0 Hz, 1H), 3.86 (dd, J = 11.6 Hz, 3.2 Hz, 1H), 4.38 (d, J = 16.0 Hz, 1H), 4.43 (d, J = 16.0 Hz, 1H), 5.96 (s, 2H), 6.74 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 1.2 Hz, 1H), 6.96 (dd, J =8.0 Hz, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.2, 50.4, 59.1, 70.2, 82.8, 86.3, 101.2, 108.3, 111.6, 115.5, 126.3, 147.3, 148.0. IR (neat, cm^{-1}): υ 3061, 2998, 2901, 2224, 1250, 1213, 1092, 1038, 1034. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.32; H, 5.25.

*2-((3-(3,4-Dimethoxyphenyl)prop-2-ynyloxy)methyl)oxirane (**19b**).* Obtained in 89% as a light yellow colored liquid. R_f = 0.57 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 2.81 (t, J = 4.8 Hz, 1H), 3.18−3.22 (m, 1H), 3.53 (dd, J = 11.2 Hz, 6.0 Hz, 1H), 3.85−3.88 (m, 7H), 4.39 (d, J = 16.0 Hz, 1H), 4.44 (d, J = 16.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 1.6 Hz, 1H), 7.04 (dd, J = 8.0 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.3, 50.5, 55.8, 59.2, 70.3, 83.0, 86.6, 110.8, 114.4, 114.5, 125.0, 148.5, 149.6. IR (neat, cm^{-1}): υ 3057, 2999, 2936, 2839, 2226, 1244, 1209, 1092. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.85; H, 6.47.

General Procedure for the Epoxide Ring Opening of 19a/19b with Aryl Lithium Reagents.[25]



n-BuLi (1.6 M solution in hexanes, 1.2 equiv) was added dropwise to a stirred solution of aryl bromide (1.2 equiv) in dry THF at −78 °C. After 1 h, a solution of the epoxide **19a**/**19b** (1.0 equiv) in dry THF was added slowly to it. Then BF_3·OEt_2 (1.0 equiv) was added rapidly and the reaction was allowed to stir at −78 °C for 30 min. Saturated aq $NaHCO_3$ solution was added at −78 °C to quench the reaction and then warmed to rt. The mixture was extracted with ethyl acetate and washed with saturated brine solution. It was dried over anhydrous Na_2SO_4. Solvents were evaporated from the organic fraction to the get

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crude product, which was purified by column chromatography over silica gel using EtOAc/hexanes as eluent.

*1-(3-(3,4-Dimethoxyphenyl)prop-2-ynyloxy)-3-(4-methoxyphenyl)-propan-2-ol (**20a**).* Prepared from **19b** using 4-bromoanisole as aryl bromide in 98% as a light yellow colored liquid. R_f = 0.34 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (br s, 1H), 2.76 (d, J = 6.4 Hz, 2H), 3.49 (dd, J = 9.6 Hz, 6.8 Hz, 1H), 3.60 (dd, J = 9.6 Hz, 3.2 Hz, 1H), 3.74 (s, 3H), 3.83 (s, 3H), 3.86 (s, 3H), 4.00−4.03 (m, 1H), 4.38 (s, 2H), 6.78 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 1.6 Hz, 1H), 7.03 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.14 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.8, 55.0, 55.7, 59.2, 71.3, 73.0, 83.2, 86.4, 110.8, 113.7, 114.5, 125.0, 125.0, 129.7, 130.2, 148.4, 149.5, 158.1. IR (neat, cm^{-1}): υ 3517, 3070, 2934, 2837, 1601, 1170, 1026. Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.56; H, 6.85.

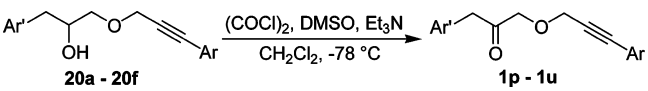
*1-(3-(Benzo[d][1,3]dioxol-5-yl)prop-2-ynyloxy)-3-(4-methoxyphenyl)-propan-2-ol (**20b**).* Prepared from **19a** using 4-bromoanisole as aryl bromide in 85% as a yellow colored liquid. R_f = 0.43 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (br s, 1H), 2.77 (d, J = 6.8 Hz, 2H), 3.48 (dd, J = 9.6 Hz, 7.2 Hz, 1H), 3.61 (dd, J = 9.6 Hz, 3.2 Hz, 1H), 3.78 (s, 3H), 4.0−4.04 (m, 1H), 4.38 (s, 2H), 5.97 (s, 2H), 6.75 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 1.6 Hz, 1H), 6.95 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.9, 55.2, 59.3, 71.4, 73.1, 83.1, 86.4, 101.3, 108.4, 111.7, 113.9, 115.6, 126.4, 129.7, 130.3, 147.3, 148.0, 158.2. IR (neat, cm^{-1}): υ 3468, 3004, 2907, 1248, 1211, 1096. Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.45; H, 5.87.

*1-(Benzo[d][1,3]dioxol-5-yl)-3-(3-(3,4-dimethoxyphenyl)prop-2-ynyloxy)propan-2-ol (**20c**).* Prepared from **19b** using 1-bromo-3,4-(methylenedioxy)benzene as aryl bromide in 76% as a light yellow colored liquid. R_f = 0.39 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (br s, 1H), 2.73−2.75 (m, 2H), 3.49 (dd, J = 9.6 Hz, 6.8 Hz, 1H), 3.61 (dd, J = 9.6 Hz, 3.6 Hz, 1H), 3.86 (s, 3H), 3.87 (s, 3H), 3.99−4.02 (m, 1H), 4.39 (s, 2H), 5.89 (s, 2H), 6.66−6.74 (m, 3H), 6.78 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 1.6 Hz, 1H), 7.04 (dd, J = 8.0 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.4, 55.8, 59.3, 71.3, 73.1, 83.2, 86.5, 100.7, 108.1, 109.6, 110.8, 114.4, 114.5, 122.2, 125.0, 131.4, 146.0, 147.6, 148.5, 149.6. IR (neat, cm^{-1}): υ 3520, 3059, 3003, 2907, 2591, 2206, 1171. Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99. Found: C, 68.25; H, 5.89.

*1-(Benzo[d][1,3]dioxol-5-yl)-3-(3-(benzo[d][1,3]dioxol-5-yl)prop-2-ynyloxy)propan-2-ol (**20d**).* Prepared from **19a** using 1-bromo-3,4-(methylenedioxy)benzene as aryl bromide in 81% as a light yellow colored liquid. R_f = 0.35 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (br s, 1H), 2.74 (d, J = 6.4 Hz, 2H), 3.48 (dd, J = 9.2 Hz, 7.2 Hz, 1H), 3.61 (dd, J = 9.2 Hz, 3.2 Hz, 1H), 3.99−4.02 (m, 1H), 4.38 (s, 2H), 5.92 (s, 2H), 5.97 (s, 2H), 6.67−6.76 (m, 4H), 6.88 (s, 1H), 6.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.3, 59.1, 71.2, 72.9, 83.0, 86.3, 100.7, 101.2, 108.0, 108.2, 109.5, 111.5, 115.4, 122.1, 126.3, 131.4, 145.9, 147.2, 147.4, 147.9. IR (neat, cm^{-1}): υ 3482, 3059, 2920, 1248, 1040, 936. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.82; H, 5.15.

*1-(3,4-Dimethoxyphenyl)-3-(3-(3,4-dimethoxyphenyl)prop-2-ynyloxy)propan-2-ol (**20e**).* Prepared from **19b** using 1-bromo-3,4-dimethoxybenzene as aryl bromide in 72% as a yellow colored liquid. R_f = 0.22 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66−2.72 (m, 2H), 3.43 (dd, J = 9.2 Hz, 6.4 Hz, 1H), 3.53 (dd, J = 9.2 Hz, 3.2 Hz, 1H), 3.73 (s, 3H), 3.747 (s, 3H), 3.753 (s, 3H), 3.76 (s, 3H), 3.95−3.98 (m, 1H), 4.31 (s, 2H), 6.68−6.70 (m, 4H), 6.85 (s, 1H), 6.94 (dd, J = 8.4 Hz, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.0, 55.36, 55.42, 58.9, 71.0, 72.8, 77.2, 83.0, 86.2, 110.6, 110.9, 112.2, 114.0, 114.2, 121.0, 124.7, 130.1, 147.2, 148.2, 148.4, 149.3. IR (neat, cm^{-1}): υ 3513, 3000, 2934, 2838, 1209, 1140, 1096, 1026. Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.25; H, 6.71.

*1-(Benzo[d][1,3]dioxol-5-yl)-3-(3-(3,4-dimethoxyphenyl)prop-2-ynyloxy)propan-2-ol (**20f**).* Prepared from **19a** using 1-bromo-3,4-dimethoxybenzene as aryl bromide in 73% as a yellow colored liquid. R_f = 0.35 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (br s, 1H), 2.74−2.76 (m, 2H), 3.48 (dd, J = 9.6 Hz, 6.8 Hz, 1H), 3.59 (dd, J = 9.6 Hz, 3.6 Hz, 1H), 3.80 (s, 3H), 3.81 (s, 3H), 3.99−4.07 (m, 1H), 4.36 (s, 2H), 5.93 (s, 2H), 6.71−6.93 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.2, 55.59, 55.65, 59.1, 71.2, 73.0, 83.0, 86.3, 101.1, 108.2, 111.1, 111.5, 112.4, 115.4, 121.1, 126.2, 130.2, 147.2, 147.5, 147.9, 148.7. IR (neat, cm^{-1}): υ 3468, 3073, 2926, 1250, 1090, 1034, 934. Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99. Found: C, 68.25; H, 5.91.



The procedure employed for the preparation of **15** was followed for the Swern oxidation of substartes **20a−20f** into **1p−1u**.

*1-(3-(3,4-Dimethoxyphenyl)prop-2-ynyloxy)-3-(4-methoxyphenyl)propan-2-one (**1p**).* Obtained from **20a** in 93% yield as a yellow colored liquid. R_f = 0.45 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 2H), 3.75 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 4.25 (s, 2H), 4.44 (s, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 1.6 Hz, 1H), 7.01 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.3, 55.1, 55.8, 59.2, 73.5, 82.3, 87.3, 110.8, 114.0, 114.2, 114.3, 125.0, 125.2, 130.4, 148.5, 149.7, 158.6, 205.9. IR (neat, cm^{-1}): υ 3002, 2934, 2838, 1726, 1514, 1138, 1098. Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.32; H, 6.19.

*1-(3-(Benzo[d][1,3]dioxol-5-yl)prop-2-ynyloxy)-3-(4-methoxyphenyl)propan-2-one (**1q**).* Obtained from **20b** in 83% yield as a yellow colored liquid. R_f = 0.27 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 2H), 3.79 (s, 3H), 4.25 (s, 2H), 4.43 (s, 2H), 5.98 (s, 2H), 6.75 (d, J = 8.0 Hz, 1H), 6.83−6.86 (m, 3H), 6.93 (d, J = 8.0 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.4, 55.1, 59.2, 73.4, 82.2, 87.2, 101.3, 108.3, 111.6, 114.1, 115.3, 125.2, 126.5, 130.4, 147.3, 148.1, 158.6, 205.9. IR (neat, cm^{-1}): υ 3468, 2901, 2841, 1726, 1246, 1038. Anal. Calcd for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found: C, 70.86; H, 5.31.

*1-(Benzo[d][1,3]dioxol-5-yl)-3-(3-(3,4-dimethoxyphenyl)prop-2-ynyloxy)propan-2-one (**1r**).* Obtained from **20c** in 87% yield as a yellow colored liquid. R_f = 0.42 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 2H), 3.84 (s, 3H), 3.86 (s, 3H), 4.24 (s, 2H), 4.43 (s, 2H), 5.88 (s, 2H), 6.62−6.64 (m, 1H), 6.68 (d, J = 1.2 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.76−6.79 (m, 1H), 6.90 (d, J = 1.6 Hz, 1H), 7.00 (dd, J = 8.4 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.7, 55.7, 59.2, 73.5, 82.3, 87.3, 100.9, 108.2, 108.5, 109.7, 110.8, 114.1, 114.3, 122.5, 125.0, 126.7, 146.5, 147.7, 148.4, 149.6, 205.7. IR (neat, cm^{-1}): υ 3005, 2940, 2905, 2839, 1728, 1246, 1209, 1171, 1138. Anal. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47. Found: C, 68.39; H, 5.51.

*1-(Benzo[d][1,3]dioxol-5-yl)-3-(3-(benzo[d][1,3]dioxol-5-yl)prop-2-ynyloxy)propan-2-one (**1s**).* Obtained from **20d** in 94% yield as a yellow colored liquid. R_f = 0.62 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 2H), 4.26 (s, 2H), 4.44 (s, 2H), 5.94 (s, 2H), 5.98 (s, 2H), 6.66−6.76 (m, 4H), 6.85 (d, J = 1.6 Hz, 1H), 6.94 (dd, J = 8.0 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.7, 59.1, 73.4, 82.1, 87.2, 100.9, 101.2, 108.3, 109.7, 111.5, 115.2, 122.5, 126.4, 126.7, 146.6, 147.3, 147.7, 148.1, 205.7. IR (neat, cm^{-1}): υ 3075, 2901, 2782, 1726, 1250, 1036, 934. Anal. Calcd for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.31; H, 4.49.

*1-(3,4-Dimethoxyphenyl)-3-(3-(3,4-dimethoxyphenyl)prop-2-ynyloxy)propan-2-one (**1t**).* Obtained from **20e** in 91% as a yellow colored liquid. R_f = 0.37 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 2H), 3.84 (s, 6H), 3.87 (s, 3H), 3.89 (s, 3H), 4.27 (s, 2H), 4.45 (s, 2H), 6.75−6.81 (m, 4H), 6.92 (s, 1H), 7.01 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.5, 55.5, 59.0, 73.3, 82.2, 87.1, 110.7, 111.0, 112.2, 114.0, 114.1, 121.4, 124.8, 125.5, 147.8, 148.3, 148.7, 149.5, 205.6. IR (neat, cm^{-1}): υ 3059, 2936, 2838, 1726, 1265, 1140, 1026, 943. Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29. Found: C, 68.59; H, 6.34.

*1-(3-(Benzo[d][1,3]dioxol-5-yl)prop-2-ynyloxy)-3-(3,4-dimethoxyphenyl)propan-2-one (**1u**).* Obtained from **20f** in 86% as a yellow colored liquid. R_f = 0.52 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 2H), 3.80 (s, 6H), 4.23 (s, 2H), 4.39 (s, 2H), 5.92 (s, 2H), 6.68−6.87 (m, 6H). ^{13}C NMR (100 MHz,

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$CDCl_3$): δ 45.6, 55.6, 58.9, 73.2, 82.0, 87.0, 101.1, 108.2, 111.1, 111.4, 112.3, 115.1, 121.4, 125.5, 126.3, 147.2, 147.96, 148.01, 148.8, 205.7. IR (neat, cm^{-1}): υ 3003, 2932, 1732, 1229, 1022. Anal. Calcd for $C_{21}H_{20}O_6$: C, 68.47; H, 5.47. Found: C, 68.39; H, 5.56.

General Procedure for the Gold-Catalyzed Synthesis of Naphthalene Derivatives. To a solution of the substrate **1a**−**1u** in dry CH_2Cl_2 (5 mL/mmol of **1**) were added activated 4 Å molecular sieves. To this were added $AuCl_3$ (2 mol %) and $AgSbF_6$ (6 mol %), and the reaction mixture was allowed to stir at room temperature. The reaction was monitored by TLC. After completion of the reaction CH_2Cl_2 was evaporated. The residue was directly loaded on a silica gel column and eluted with EtOAc/hexanes mixtures to obtain corresponding pure 1-arylnaphthalene derivative **2a**− **2u**.

*4-Phenyl-1,3-dihydronaphtho[2,3-c]furan (**2a**).* Colorless liquid. R_f = 0.36 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[12h] δ 5.01 (s, 2H), 5.28 (s, 2H), 7.26−7.34 (m, 3H), 7.36−7.47 (m, 4H), 7.66−7.68 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.9, 73.3, 118.8, 125.6, 125.7, 125.7, 127.6, 128.0, 128.6, 129.4, 131.8, 132.5, 133.6, 136.8, 137.6, 138.1.

*4-(4-Methoxyphenyl)-1,3-dihydronaphtho[2,3-c]furan (**2b**).* Colorless liquid. R_f = 0.25 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[12h] δ 3.91 (s, 3H), 5.05 (s, 2H), 5.31 (s, 2H), 7.05 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.69 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 72.9, 73.4, 114.0, 118.5, 118.6, 125.6, 125.7, 128.1, 130.3, 130.6, 132.1, 132.3, 133.8, 137.1, 137.7. 159.1.

*6-Chloro-4-(4-chlorophenyl)-1,3-dihydronaphtho[2,3-c]furan (**2c**).* Colorless liquid. R_f = 0.27 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[12h] δ 4.97 (s, 2H), 5.26 (s, 2H), 7.24−7.28 (m, 2H), 7.40 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.48−7.50 (m, 2H), 7.57 (d, J = 2.0 Hz, 1H), 7.66 (s, 1H), 7.79 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.7, 73.2, 119.0, 119.1, 124.3, 124.4, 126.7, 129.1, 129.6, 130.6, 130.7, 131.9, 132.0, 132.4, 134.1, 135.8, 138.1, 138.2.

*6,8-Dichloro-4-o-tolyl-1,3-dihydronaphtho[2,3-c]furan (**2d**).* Colorless liquid. R_f = 0.86 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (s, 3H), 4.81 (d, J = 13.6 Hz, 1H), 4.96 (d, J = 13.6 Hz, 1H), 5.34 (s, 2H), 7.13 (d, J = 7.2 Hz, 1H), 7.24−7.41 (m, 4H), 7.56 (d, J = 2.0 Hz, 1H), 8.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 72.8, 73.5, 115.5, 123.6, 126.3, 126.6, 128.5, 129.2, 129.4, 130.5, 130.9, 131.9, 133.0, 133.4, 136.1, 136.2, 139.0, 139.3. IR (neat, cm^{-1}): 3387, 3065, 2922, 2855, 1595, 1478, 1334, 1055, 731. Anal. Calcd for $C_{19}H_{14}Cl_2O$: C, 69.32; H, 4.29. Found: C, 69.11; H, 4.35. HRMS-ESI (m/z) $[M + K]^+$ calcd for $C_{19}H_{14}Cl_2KO$ 367.0059, found 367.0061.

*6-Fluoro-4-(4-fluorophenyl)-1,3-dihydronaphtho[2,3-c]furan (**2e**).* Light yellow colored semisolid. R_f = 0.36 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.00 (s, 2H), 5.28 (s, 2H), 7.19−7.34(m, 6H), 7.70 (s, 1H), 7.84−7.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.8, 73.2, 109.0 (d, J = 22.0 Hz), 115.8 (d, J = 21.2 Hz), 116.0 (d, J = 25.3 Hz), 119.0, 130.3 (d, J = 8.9 Hz), 130.6, 131.0 (d, J = 7.7 Hz), 132.8 (d, J = 8.6 Hz), 133.5, 137.1, 138.2, 160.9 (d, 243.9 Hz), 162.4 (d, J = 245.6 Hz). IR (neat, cm^{-1}): 3075, 2932, 2865, 1507, 1447, 1053, 804, 746. Anal. Calcd for $C_{18}H_{12}F_2O$: C, 76.59; H, 4.28. Found: C, 76.45; H, 4.32. HRMS-ESI (m/z) $[M]^+$ calcd for $C_{18}H_{12}F_2O$ 282.0856, found 282.0836.

*4-(Naphthalen-1-yl)-1,3-dihydronaphtho[2,3-c]furan (**2f**).* Colorless liquid. R_f = 0.43 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[26] δ 4.72 (d, J = 13.2 Hz, 1H), 4.92 (d, J = 13.2 Hz, 1H), 5.34 (s, 2H), 7.25−7.34 (m, 4H), 7.42−7.50 (m, 3H), 7.57−7.61 (m, 1H), 7.79 (s, 1H), 7.90−7.78 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.8, 73.4, 119.1, 125.5, 125.7, 125.8, 126.0, 126.4, 127.3, 128.0, 128.3, 128.4, 130.6, 131.8, 132.7, 133.5, 133.8, 135.6, 137.6, 137.9.

*4-(Benzo[d][1,3]dioxol-5-yl)-6-chloro-1,3-dihydronaphtho[2,3-c]furan (**2g**).* Light yellow colored liquid. R_f = 0.50 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.01 (s, 2H), 5.25 (s, 2H), 6.05 (br s, 2H), 6.75−6.78 (m, 2H), 6.94 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.62 (s, 1H), 7.67 (s, 1H), 7.76 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.8, 73.3, 101.3, 108.7, 109.8, 118.6, 122.8, 124.5, 126.5, 129.5, 130.9, 131.5, 131.8, 131.9, 132.8, 138.0, 138.2, 147.3, 147.9. IR (neat, cm^{-1}): 3387, 3055, 2907, 1605, 1040, 737. Anal. Calcd for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 70.15; H, 4.12. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{14}ClO_3$ 325.0631, found 325.0631.

*4-(4-Chlorophenyl)-6-fluoro-1,3-dihydronaphtho[2,3-c]furan (**2h**).* Colorless liquid. R_f = 0.40 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.00 (s, 2H), 5.27 (s, 2H), 7.22−7.30 (m, 4H), 7.50 (d, J = 8.4 Hz, 2H), 7.70 (s, 1H), 7.84−7.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 72.7, 73.3, 109.0 (d, J = 22.1 Hz), 116.1 (d, J = 25.2 Hz), 129.1, 130.3 (d, J = 8.9 Hz), 130.7, 130.8, 132.6 (d, J = 8.5 Hz), 134.0, 136.0, 137.2, 138.1, 160.9 (d, J = 244.3 Hz). IR (neat, cm^{-1}): 3077, 2932, 2865, 1507, 1447, 1092, 1053, 804, 746. Anal. Calcd for $C_{18}H_{12}ClFO$: C, 72.37; H, 4.05. Found: C, 72.15; H, 4.12.

*6-Chloro-4-(3,4,5-trimethoxyphenyl)-1,3-dihydronaphtho[2,3-c]furan (**2i**).* Light yellow colored solid, mp 150−151 °C. R_f = 0.35 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 6H), 3.96 (s, 3H), 5.05 (s, 2H), 5.27 (s, 2H), 6.53 (s, 2H), 7.40−7.43 (m, 1H), 7.65 (s, 1H), 7.71 (s, 1H), 7.77−7.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.1, 60.9, 72.8, 73.2, 106.2, 118.6, 124.5, 126.5, 129.5, 131.8, 131.9, 132.5, 132.8, 137.4, 137.9, 138.0, 153.4. IR (KBr, cm^{-1}): 3003, 2932, 1579, 1460, 1234, 1128, 687. Anal. Calcd for $C_{21}H_{19}ClO_4$: C, 68.02; H, 5.16. Found: C, 68.12; H, 5.09. HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{21}H_{19}ClNaO_4$ 393.0870, found 393.0871.

*5,7-Dichloro-9-(4-chlorophenyl)-1-methyl-1,3-dihydronaphtho-[2,3-c]furan (**2j**).* Yellow colored liquid. R_f = 0.46 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (d, J = 6.4 Hz, 3H), 5.21 (d, J = 13.2 Hz, 1H), 5.32 (d, J = 13.2 Hz, 1H), 5.41 (q, J = 6.4 Hz, 1H), 7.21−7.26 (m, 2H), 7.43 (s, 1H), 7.50−7.54 (m, 3H), 8.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 71.4, 79.6, 116.0, 123.8, 126.6, 128.4, 128.7, 129.4, 130.5, 130.8, 131.4, 131.8, 133.0, 133.7, 134.3, 135.0, 139.5, 142.8. IR (neat, cm^{-1}): 3353, 2976, 2926, 2859, 1593, 1472, 1165, 760. Anal. Calcd for $C_{19}H_{13}Cl_3O$: C, 62.75; H, 3.60. Found: C, 62.88; H, 3.53.

*9-Phenyl-1-propyl-1,3-dihydronaphtho[2,3-c]furan (**2k**).* Light yellow colored liquid. R_f = 0.43 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.67 (t, J = 7.2 Hz, 3H), 1.13−1.30 (m, 4H), 5.23 (d, J = 12.8 Hz, 1H), 5.29 (d, J = 12.8 Hz, 1H), 5.41−5.44 (m, 1H), 7.31−7.38 (m, 3H), 7.43−7.52 (m, 4H), 7.63 (d, J = 8.4 HZ, 1H). 7.68 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 18.0, 36.0, 71.8, 83.4, 118.8, 125.5, 125.6, 125.8, 127.6, 127.9, 128.0, 128.9, 129.1, 130.4, 132.1, 133.0, 133.6, 137.9, 138.3, 139.1. IR (neat, cm^{-1}): 3057, 2959, 2874, 1447, 1028, 752, 704. Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.32; H, 6.88.

*5-Phenyl-3,4-dihydro-1H-benzo[g]isochromene (**2l**).* Light yellow colored solid, mp 138−139 °C. R_f = 0.35 in 1:10 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (t, J = 6.0 Hz, 2H), 3.99 (t, J = 6.0 Hz, 2H), 5.05 (s, 2H), 7.27−7.32 (m, 3H), 7.36−7.56 (m, 6H), 7.80 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.0, 65.9, 68.7, 122.4, 125.3, 125.4, 126.0, 127.2, 127.3, 128.5, 129.5, 130.0, 131.7, 131.8, 133.0, 138.5, 138.8. IR (KBr, cm^{-1}): 2930, 2853, 1119, 1086, 993, 756, 702. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.51; H, 6.23. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{17}O$ 261.1279, found 261.1279.

*5-(3,5-Dimethylphenyl)-7-fluoro-3,4-dihydro-1H-benzo[g]-isochromene (**2m**).* Colorless liquid. R_f = 0.59 in 1:5 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 6H), 2.70 (t, J = 6.0 Hz, 2H), 3.96 (t, J = 6.0 Hz, 2H), 5.00 (s, 2H), 6.85 (s, 2H), 7.03 (dd, J = 11.2 Hz, 2.4 Hz, 1H,), 7.08 (s, 1H), 7.19 (td, J = 8.8 Hz, 2.0 Hz, 1H), 7.49 (s, 1H), 7.76 (dd, J = 8.8 Hz, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 28.0, 65.9, 68.6, 109.5 (d, J = 21.7 Hz), 115.7 (d, J = 25.6 Hz), 122.1, 127.5, 128.8, 129.0, 129.6 (d, J = 8.8 Hz), 130.5, 132.3, 132.6 (d, J = 8.5 Hz), 138.1, 138.2, 138.5 (d, J = 5.5 Hz), 160.3 (d, J = 242.6 Hz). IR (neat, cm^{-1}): 3056, 2920, 2853, 1601, 1504, 1180, 876, 779. Anal. Calcd for $C_{21}H_{19}FO$: C, 82.33; H, 6.25. Found: C, 82.21; H, 6.18.

*4-(2-Methoxyphenyl)-2,3-dihydro-1H-cyclopenta[b]naphthalene (**2n**).* Colorless heavy liquid. R_f = 0.61 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01−2.08 (m, 2H), 2.75 (t, J = 7.6 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H), 3.65 (s, 3H), 7.00−7.65 (m, 7H), 7.66 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6, 32.2, 33.1, 55.4, 111.1, 120.5, 121.8, 124.5, 124.6, 125.7, 127.6,

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128.0, 128.7, 131.0, 131.7, 133.1, 142.4, 142.6, 157.2. IR (neat, cm^{-1}): 3059, 2944, 2839, 1599, 1489, 1244, 1026, 750. Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.45; H, 6.68. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{19}O$ 275.1436, found 275.1434.

*6-Chloro-4-(2-methoxyphenyl)-2,3-dihydro-1H-cyclopenta[b]-naphthalene (**2o**).* Colorless heavy liquid. R_f = 0.61 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99−2.05 (m, 2H), 2.70 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.2 Hz, 2H), 3.63 (s, 3H), 6.99 (d, J = 8.4 Hz, 1H), 7.04 (dd, J = 7.6 Hz, 1.0 Hz, 1H), 7.11−7.15 (m, 1H), 7.26 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.34 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.43 (s, 1H), 7.57 (s, 1H), 7.64 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.5, 32.2, 33.0, 55.4, 111.1, 120.6, 121.6, 124.5, 125.3, 127.1, 129.0, 129.1, 130.4, 131.4, 131.5, 132.4, 143.1, 143.7, 157.0. IR (neat, cm^{-1}): 3059, 2953, 2835, 1599, 1489, 1244, 754. Anal. Calcd for $C_{20}H_{17}ClO$: C, 77.79; H, 5.55. Found: C, 77.85; H, 5.51. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{18}ClO$ 309.1046, found 309.1045.

*4-(3,4-Dimethoxyphenyl)-6-methoxy-1,3-dihydronaphtho[2,3-c]furan (**2p**).* Colorless liquid. R_f = 0.46 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (s, 3H), 3.86 (s, 3H), 3.96 (s, 3H), 5.02 (s, 2H), 5.24 (s, 2H), 6.90−6.92 (m, 2H), 6.99 (d, J = 8.8 Hz, 1H), 7.07 (d, J = 2.4 Hz, 1H), 7.13 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.57 (s, 1H), 7.73 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.0, 55.7, 55.8, 72.9, 73.2, 104.2, 111.2, 112.4, 117.8, 118.3, 121.5, 129.0, 129.3, 130.7, 131.0, 132.9, 135.2, 137.3, 148.2, 148.8, 157.5. IR (neat, cm^{-1}): υ 2932, 2838, 2226, 1514, 1213, 1175, 1138, 1028. Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.91; H, 6.05.

*4-(Benzo[d][1,3]dioxol-5-yl)-6-methoxy-1,3-dihydronaphtho[2,3-c]furan (**2q**).* Colorless liquid. R_f = 0.36 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H), 5.03 (s, 2H), 5.26 (s, 2H), 6.05 (d, J = 1.2 Hz, 1H), 6.08 (d, J = 1.2 Hz, 1H), 6.81−6.86 (m, 2H), 6.96 (d, J = 8.0 Hz, 1H), 7.06 (s, 1H), 7.15 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 7.60 (s, 1H), 7.76 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 72.9, 73.3, 101.1, 104.4, 108.6, 109.7, 117.8, 118.5, 122.7, 129.1, 129.4, 130.9, 131.9, 133.1, 135.2, 137.5, 147.0, 147.8, 157.6. IR (neat, cm^{-1}): υ 3063, 3003, 2903, 1236, 1165, 1115, 1038. Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 74.85; H, 5.12.

*5-(3,4-Dimethoxyphenyl)-6,8-dihydro-furo[3′,4′:6,7]naphtho[2,3-d][1,3]dioxole (**2r**).* Colorless liquid. R_f = 0.29 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 3.96 (s, 3H), 4.98 (s, 2H), 5.24 (s, 2H), 6.00 (s, 2H), 6.84 (s, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.01 (s, 1H), 7.13 (s, 1H), 7.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 73.0, 73.4, 101.1, 102.2, 103.9, 111.3, 112.4, 117.8, 121.6, 129.0, 130.7, 130.9, 131.8, 135.5, 136.1, 147.3, 147.7, 148.4, 148.9. IR (neat, cm^{-1}): υ 3057, 2907, 2839, 1236, 1173, 1138, 1105, 1040. Anal. Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 71.83; H, 5.25.

*5-Benzo[1,3]dioxol-5-yl-6,8-dihydro-furo[3′,4′:6,7]naphtho[2,3-d][1,3]dioxole (**2s**).* Colorless liquid. R_f = 0.45 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[13j] δ 4.98 (s, 2H), 5.24 (s, 2H), 6.01 (s, 2H), 6.05 (d, J = 1.6 Hz, 2H), 6.75−6.78 (m, 1H), 6.79 (d, J = 1.2 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 7.00 (s, 1H), 7.13 (s, 1H), 7.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 73.0, 73.5, 101.16, 102.1, 103.9, 108.6, 109.8, 117.9, 122.7, 129.0, 130.8, 131.5, 132.0, 135.6, 136.1, 147.0, 147.4, 147.7, 147.8.

*4-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-1,3-dihydronaphtho-[2,3-c]furan (**2t**).* Colorless liquid. R_f = 0.35 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[13j] δ 3.78 (s, 3H), 3.87 (s, 3H), 3.97 (s, 3H), 4.00 (s, 3H), 5.02 (s, 2H), 5.26 (s, 2H), 6.85−7.12 (m, 4H), 7.15 (s, 1H), 7.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 55.8, 55.9, 73.1, 73.5, 104.5, 106.5, 111.3, 112.4, 117.1, 121.5, 127.4, 129.5, 130.9, 131.1, 135.1, 135.9, 148.3, 148.9, 149.2.

*4-(3,4-Dimethoxyphenyl)-5,6-dimethoxy-1,3-dihydronaphtho-[2,3-c]furan (**2t′**).* Light yellow colored liquid. R_f = 0.44 in 1:3 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[13j] δ 3.25 (s, 3H), 3.85 (s, 3H), 3.94 (s, 6H), 4.84 (d, J = 13.2 Hz, 1H), 4.91 (d, J = 13.2 Hz, 1H), 5.25 (s, 2H), 6.78−6.93 (m, 3H), 7.26−7.30 (m, 1H), 7.60−7.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8, 56.6, 60.5, 73.3, 110.2, 111.9, 114.4, 119.0, 120.1, 124.5, 127.1, 129.9, 130.7, 134.5, 135.4, 139.6, 144.5, 147.5, 147.9, 149.9.

*4-(Benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxy-1,3-dihydronaphtho-[2,3-c]furan (**2u**).* Colorless liquid. R_f = 0.48 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 4.00 (s, 3H), 4.99 (s, 2H), 5.24 (s, 2H), 6.03 (s, 1H), 6.06 (s, 1H), 6.78−6.90 (m, 2H), 6.94 (d, J = 8.0 Hz, 1H), 7.02 (s, 1H), 7.13 (s, 1H), 7.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 55.8, 73.0, 73.4, 101.1, 104.4, 106.4, 108.5, 109.6, 117.2, 122.6, 127.4, 129.4, 130.8, 132.1, 135.2, 135.9, 146.9, 147.8, 149.2. IR (neat, cm^{-1}): υ 3075, 2924, 2855, 1254, 1152, 1038, 930. Anal. Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 71.85; H, 5.23.

*4-(Benzo[d][1,3]dioxol-5-yl)-5,6-dimethoxy-1,3-dihydronaphtho-[2,3-c]furan (**2u′**).* Colorless liquid. R_f = 0.51 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.28 (s, 3H), 3.94 (s, 3H), 4.84 (d, J = 13.2 Hz, 1H), 4.92 (d, J = 13.2 Hz, 1H), 5.24 (d, J = 0.8 Hz, 2H), 6.00 (dd, J = 6.8 Hz, 6.4 Hz, 2H), 6.75 (dd, J = 7.6 Hz, 1,6 Hz, 1H), 6.78 (d, J = 1.2 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 9.2 Hz, 1H), 7.60 (s, 1H), 7.62 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.6, 60.5, 73.3, 73.4, 100.8, 107.3, 109.3, 114.4, 119.1, 120.9, 124.5, 127.2, 129.6, 130.6, 135.4, 135.5, 139.6, 144.4, 146.0, 146.7, 149.9. Anal. Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 72.11; H, 5.09.

Benzylic Oxidation of 2s−2u. A solution of H_5IO_6 (2.0 equiv) in acetonitrile (5 mL/1 mmol of **2s**/**2t**/**2u**) was made by vigorous stirring. To this solution CrO_3 (1.2 mol %) was added, and the mixture was stirred. 1-Arylnaphthalene (2s/2t/2u, 1.0 equiv) was added to the above solution under stirring. An exothermic reaction occurred immediately resulting in the formation of a white precipitate. After 1 h of stirring, acetonitrile was removed by evaporation. The residue was dissolved in H_2O and CH_2Cl_2, and the two phases were separated. Then the aqueous phase was extracted with CH_2Cl_2 two times. The combined organic layers were washed with brine and then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The residue obtained was purified by column chromatography over silica gel by eluting with mixtures of EtOAc/hexanes.

*9-Benzo[1,3]dioxol-5-yl-8H-furo[3′,4′:6,7]naphtho[2,3-d][1,3]-dioxol-6-one (**21**).* Obtained from **2s** in 73% yield as a colorless solid, mp 268−271 °C (lit.[24] 270−271 °C). R_f = 0.43 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[24] δ 5.18 (d, J = 14.8 Hz, 1H), 5.23 (d, J = 14.8 Hz, 1H), 6.08−6.10 (m, 4H), 6.79−6.81 (m, 2H), 6.98 (d, J = 8.4 Hz, 1H), 7.10 (s, 1H), 7.31 (s, 1H), 8.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.4, 101.5, 101.9, 102.0, 105.3, 109.0, 109.7, 121.7, 122.8, 124.7, 129.6, 131.3, 132.7, 133.4, 138.4, 147.7, 148.3, 148.4, 150.5, 171.5.

*5-Benzo[1,3]dioxol-5-yl-8H-furo[3′,4′:6,7]naphtho[2,3-d][1,3]-dioxol-6-one (**22**).* Obtained from **2s** in 16% yield as a colorless solid, mp 273−275 °C (lit.[24] 273−277 °C). R_f = 0.42 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[24] δ 5.38 (s, 2H), 6.06−6.09 (m, 4H), 6.78−6.82 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 7.20 (s, 1H), 7.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 68.0, 101.2, 101.8, 103.67, 103.71, 108.2, 110.6, 119.0, 119.1, 123.5, 128.4, 130.5, 134.7, 139.9, 140.2, 147.5, 147.7, 148.7, 150.0, 169.8.

*4-(3,4-Dimethoxyphenyl)-6,7-dimethoxynaphtho[2,3-c]furan-1(3H)-one (**23**).* Obtained from **2t** in 74% yield as a colorless solid, mp 214−217 °C (lit.[24] 216−217 °C). R_f = 0.38 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[24] δ 3.83 (s, 3H), 3.89 (s, 3H), 3.99 (s, 3H), 4.06 (s, 3H), 5.20 (d, J = 14.4 Hz, 1H), 5.27 (d, J = 14.4 Hz, 1H), 6.90 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 7.31 (s, 1H), 8.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 56.0, 56.1, 69.6, 104.1, 107.7, 111.7, 112.2, 121.4, 121.6, 124.1, 128.6, 129.9, 131.7, 132.2, 137.9, 149.0, 149.3, 150.1, 152.0, 171.7.

*4-(Benzo[d][1,3]dioxol-5-yl)-6,7-dimethoxynaphtho[2,3-c]furan-1(3H)-one (**24**).* Obtained in 75% yield as a yellow colored solid, mp 215−218 °C (lit.[13f] 217−219 °C). R_f = 0.44 in 1:1 EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$):[13f] δ 3.86 (s, 3H), 4.06 (s, 3H), 5.22 (s, 2H), 6.08 (s, 1H), 6.11 (s, 1H), 6.84−6.86 (m, 2H), 6.99 (d, J = 7.6 Hz, 1H), 7.10 (s, 1H), 7.30 (s, 1H), 8.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 56.1, 69.5, 101.4, 104.0, 107.7, 109.0, 109.5, 121.3, 122.7, 124.2, 129.7, 129.9, 131.7, 131.9, 138.0, 147.6, 148.3, 150.1, 152.0, 171.7.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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