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Gold-Catalyzed Intermolecular Hydrophenoxylation of Unactivated Internal Alkynes

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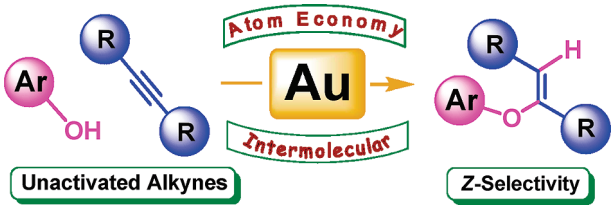

A general and simple strategy for the synthesis of functionally diverse arylvinyl ethers is reported through gold-catalyzed intermolecular addition of electronically and sterically substituted phenols with unactivated alkynes. Addition of phenols to unsymmetrical alkynes provides the corresponding mixture of regioisomers with appreciable selectivity. Multiple hydrophenoxylations of polyphenols with diphenylacetylene are demonstrated successfully.

Introduction

Development of new methods for the direct formation of the O−C(sp^2) bond is of fundamental interest in synthetic organic chemistry.[1] Addition of an alcoholic O−H bond across alkynes through either inter- or intramolecular fashion provides general access to enol ethers or cyclic ethers with 100% atom efficiency.[2] Generally, the precursors for the intramolecular reactions are obtained through specialized protocols involving multiple synthetic steps, whereas simple starting materials are adequate for the intermolecular reactions.[3] Although entropically unfavorable due to the decrease of disorder in the system, the intermolecular mode of reaction is often advantageous over its intramolecular variant. While transition-metal-catalyzed intramolecular hydroalkoxylations to alkynes are relatively well-known,[4] the intermolecular version is little explored.[5] The challenge lies in effecting the nucleophilic attack of the hard alkoxides obtained from the corresponding alcohols, on soft electron-rich alkynes. A solution would be to use soft and alkynophilic cationic gold complexes that are known to

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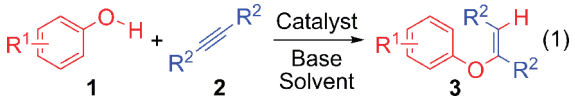
accomplish complicated transformations with ease.[6] For example, gold catalysts promote cyclization through the reaction of phenolic/alcoholic−OH group with tethered alkynes and provide complex oxygen-functionalized heterocycles efficiently.[7] A recent report for the synthesis of isoflavanone involves gold(I)-catalyzed annulation of salicylaldehydes and aryl acetylenes without direct formation of the O−C bond.[8] Intermolecular hydration and hydroalkoxylations of terminal and internal alkynes using water and 1°- or 2°-alcohols have been achieved with gold catalysis;[9] however, 3°-alcohol and phenols were found to be unreactive.[9k] The interesting disclosure of the Yamamoto group describes the success in effecting phenol addition to specific diyne precursors; the reaction proceeds either involving the η^2-coordinated Pd(0) complex or via the active σ-cumulenyl palladium intermediate.[10] A regioselective addition of activated 4-chlorophenol to the specific case of ruthenocene-bearing alkyne was demonstrated by Sato and co-workers.[11] The transannular addition of 4-chlorophenol to 1,1′-dialkynylferrocene was reported recently.[12] The reactivity of internal unactivated alkynes with oxygen-bearing nucleophiles is poor compared to that of terminal alkynes.[9g,j] Considering the above shortcomings, we envisioned that the simple intermolecular addition of phenols to unactivated alkynes is a challenging problem (eq 1).[13] It would provide a novel synthetic strategy for creating a range of arylvinyl ether skeletons exclusively with *Z*-olefin stereochemistry in one step. Furthermore, this new transformation would find wide application in the synthesis of benzofuran, benzoxathiin, and flavonoid frameworks of medicinally useful targets.[14] Herein we report an operationally simple strategy for the synthesis of functionally diverse vinyl(1,2-disubstituted)aryl ethers involving gold-catalyzed addition of phenols to aryl- and alkyl-substituted alkynes (eq 1).



Results and Discussion

Our research plan is to find a simple synthetic protocol for the preparation of benzofurans through metal-catalyzed intermolecular annulation of phenols and alkynes involving C−H bond functionalization. To start with, reaction of a simple and activated nucleophilic substrate 3-nitrophenol (**1a**) with diphenylacetylene (**2a**) under different catalytic conditions was explored (Table 1). During the optimization process, a negligible amount of byproduct showing a molecular ion peak at 318 was noticed in the GC−MS analysis. Formation of a small amount of the byproduct was observed when a combination of gold(III) chloride ($AuCl_3$), **4a**/**4b**, and Ag_2CO_3 in nitromethane was employed at 100 °C (Table 1, entries 1 and 2). To our surprise, the byproduct was found to be the hydrophenoxylation product **3aa** exclusively with *Z*-olefin stereochemistry (entry 2; see the Supporting Information for X-ray structure of **3aa**).[15] Other silver salts, such as AgOTf, AgOAc, $AgBF_4$, and $AgNO_3$, were found to be ineffective. Not even a trace of **3aa** was detected in the absence of ligands or by the use of other phosphines such as PPh_3 and PCy_3 (entries 3−5). Explorations of various combinations of ligands with gold catalysts such as AuCl, PPh_3AuCl, PPh_3AuOTf, PPh_3AuSbF_6, and $AuBr_3$ also led to poor yields of **3aa**. $AuCl_3$ turned out to be superior in comparison among other gold catalysts screened. With a selective base and catalyst in hand, solvents and other Buchwald ligands were then surveyed. 1,2-Dichloroethane, THF, and 1,4-dioxane provided lower amounts of **3aa**, as detected in GC, whereas CH_2Cl_2 appeared to be effective. Among other Buchwald ligands screened (entries 6−9), **4b** (JohnPhos) with Ag_2CO_3 in CH_2Cl_2 was found to be the best, and the yield of **3aa** was 98% by GC (entry 7). In general, the sterically encumbered ligand **4d** is more active than **4b** in the cross-coupling reactions; however, the reverse trend of ligand activity (**4b** > **4d**) was observed in the current study.[16] Optimizations using mixture of various gold catalysts, bases, and solvents with **4b** resulted in poor yield of the product

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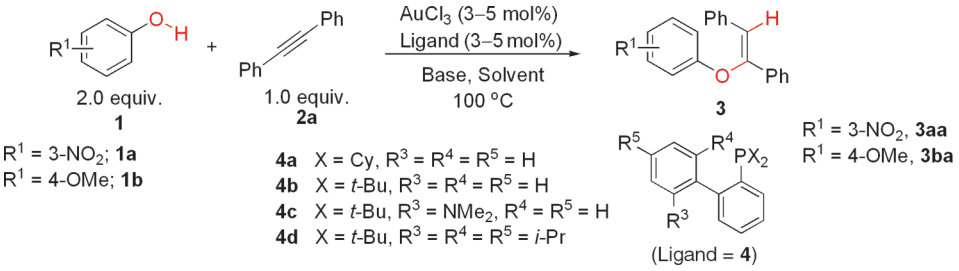
TABLE 1. Optimization of Reaction Conditions[a]



entry	1	gold	ligand	base	solvent	time (h)	product (3)	yield (%)[d]
1[b]	**1a**	$AuCl_3$	**4a**	Ag_2CO_3	CH_3NO_2	36	**3aa**	4
2[b]	**1a**	$AuCl_3$	**4b**	Ag_2CO_3	CH_3NO_2	36	**3aa**	16
3[b]	**1a**	$AuCl_3$	Nil	Ag_2CO_3	CH_3NO_2	48	**3aa**	0
4[b]	**1a**	$AuCl_3$	PPh_3	Ag_2CO_3	CH_3NO_2	48	**3aa**	0
5[b]	**1a**	$AuCl_3$	PCy_3	Ag_2CO_3	CH_3NO_2	48	**3aa**	0
6[b]	**1a**	$AuCl_3$	**4a**	Ag_2CO_3	CH_2Cl_2	36	**3aa**	11
7[b]	**1a**	$AuCl_3$	**4b**	Ag_2CO_3	CH_2Cl_2	24	**3aa**	98
8[b]	**1a**	$AuCl_3$	**4c**	Ag_2CO_3	CH_2Cl_2	36	**3aa**	39
9[b]	**1a**	$AuCl_3$	**4d**	Ag_2CO_3	CH_2Cl_2	36	**3aa**	52
10[b]	**1a**	Ph_3PAuCl	**4b**	Ag_2CO_3	CH_2Cl_2	48	**3aa**	trace
11[b]	**1a**	AuCl	**4b**	Ag_2CO_3	CH_2Cl_2	48	**3aa**	trace
12[b]	**1a**	$AuBr_3$	**4b**	Ag_2CO_3	CH_2Cl_2	36	**3aa**	13
13[b]	**1a**	$AuCl_3$	**4b**	AgOTf	CH_2Cl_2	36	**3aa**	28
14[b]	**1a**	$AuCl_3$	**4b**	AgOAc	CH_2Cl_2	48	**3aa**	trace
15[b]	**1a**	$AuCl_3$	**4b**	$AgSbF_6$	CH_2Cl_2	36	**3aa**	35
16[b]	**1a**	$AuCl_3$	**4b**	K_2CO_3	CH_2Cl_2	48	**3aa**	< 5
17[b]	**1a**	$AuCl_3$	**4b**	K_2CO_3	THF	36	**3aa**	15
18[c]	**1b**	$AuCl_3$	**4b**	Ag_2CO_3	CH_2Cl_2	24	**3ba**	7
19[c]	**1b**	$AuCl_3$	**4b**	K_2CO_3	CH_2Cl_2	36	**3ba**	< 1
20[c]	**1b**	$AuCl_3$	**4b**	K_3PO_4	THF	48	**3ba**	84
21[c]	**1b**	$AuCl_3$	**4b**	K_2CO_3	THF	48	**3ba**	95
22[c]	**1b**	$AuCl_3$	**4b**	Cs_2CO_3	THF	48	**3ba**	51

[a]Reactions were carried out using **1** (0.5 mmol), **2a** (0.25 mmol), and base (0.5 mmol) in solvent (0.3 mL) at 100 °C. [b]$AuCl_3$ and ligand (3 mol % each) were used for 24 h. [c]$AuCl_3$ and ligand (5 mol % each) were used for 48 h. [d]GC yields based on alkynes using dodecane as standard.

(entries 10−17). Under the optimized condition shown in entry 7, addition of unactivated 4-methoxyphenol (**1b**) with **2a** produced **3ba** in only 7% yield (entry 18). Further screening of bases and solvents (entries 19−22) revealed that K_2CO_3 in THF improved the yield of **3ba** to 95% (entry 21). The effective addition of respective phenols to alkynes solely depends on the nature of bases and solvents used. Such divergence in the behavior of bases is interesting; however, the origin of this effect is unclear. It appears that relatively strong bases, such as K_2CO_3, are required in the case of electron-rich phenols having higher pK_a, and a milder base, such as Ag_2CO_3, is sufficient for activated phenols with lower pK_a.[17,18]

To investigate the generality of the addition of various phenols with symmetrical and unsymmetrical alkynes, condition A [$AuCl_3$ (3 mol %), ligand **4b** (3 mol %), Ag_2CO_3 base in CH_2Cl_2 at 100 °C] is used for activated phenols and condition B [$AuCl_3$ (5 mol %), ligand **4b** (5 mol %), K_2CO_3 base in THF at 100 °C] is employed for nonactivated phenols. The effect of substitution on the phenols in the hydrophenoxylations with diphenylacetylene was surveyed at first (Table 2). Electron-donating substituent at the 4-position on phenols reacted effectively with **2a** in good yields (**3ba**, **3ca**, and **3da**). The *Z*-selectivity of **3ba** is established based on the NOESY studies; intramolecular NOEs between vinyl-H (δ = 6.62 ppm) and the *ortho*-hydrogens (δ = 7.60, 7.68 ppm) of the phenyl groups of **3ba** are clearly seen, whereas the NOEs between vinyl-H and *ortho*-hydrogens (δ = 6.78 ppm) of the 4-methoxyphenyl moiety of **3ba** are not observed.[19] However, addition of 3-methoxyphenol to **2a** afforded the corresponding product **3ka** in 51% yield; incomplete conversion of **2a** was noticed even with

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(19) NOESY studies confirmed the *Z*-olefin stereochemistry of compounds **3ba**, **3fa**, **3ma**, **3oa**, **3ab**, **3cc**, **3hd**, **6b**, **6b′**, and **8b**. See Supporting Information.

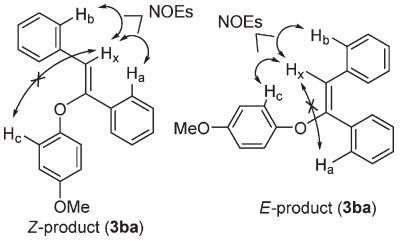
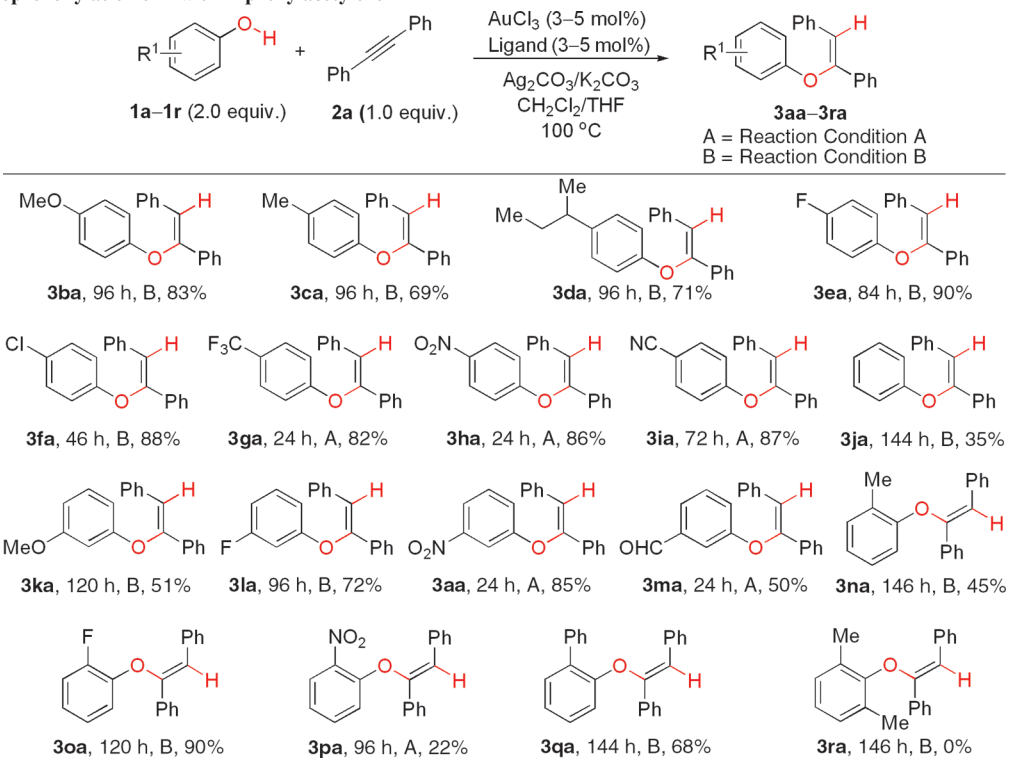


TABLE 2. Hydrophenoxylation of 1 with Diphenylacetylene[a,b]



[a]Reactions were performed employing **1** (2.0 mmol) and **2** (1.0 mmol) at 100 °C. Condition A: Ag_2CO_3 (2.0 mmol), $AuCl_3$, and **4b** (3 mol % each) in CH_2Cl_2 (1.0 mL) were used. Condition B: K_2CO_3 (2.0 mmol), $AuCl_3$, and **4b** (5 mol % each) in THF (1.0 mL) were used. [b]Isolated yields based on alkynes; average of two runs.

prolonged reaction time, justifying the moderate yield encountered in this reaction. Activated phenols bearing F, Cl, or CF_3 groups at the 4- and/or 3-positions gave the desired hydrophenoxylation products in good to excellent yields (**3ea**, **3fa**, and **3ga**); the required product **3la** was prepared in 72% yield from 3-fluorophenol (**1l**) and **2a**. The presence of common functional groups such as nitro, cyano, and formyl on phenols was well-tolerated, and the respective products were obtained in excellent yields (**3ha**, **3ia**, **3aa**, and **3ma**). However, *meta*-directing groups on the phenol (3-formylphenol, **1m**) impart moderate reactivity, and the synthesis of **3ma** resulted in 50% isolated yield. NOESY studies confirmed the *Z*-olefin stereochemistry of **3fa** and **3ma**.[19] Poor yield, sluggish reaction profile, and incomplete conversion of **2a** was observed in the addition of electronically neutral phenol (**1j**) to **2a** even with the extended reaction time. Our experimental results reveal that the para-directing group on phenol leads to better yield, while *meta*- and unsubstituted phenols are less effective in the hydrophenoxylations of alkynes. Presumably, the electronic effect of the functional group in the *para*-position decides the rate and stability of the phenolate and therefore influences the attack on alkynes.

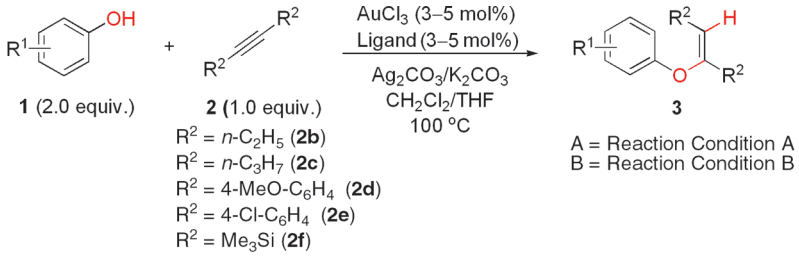
The effect of *ortho*-substitution on phenols was next examined to assess the steric effect in the hydrophenoxylation reaction, and the results are summarized in Table 2. The presence of a compact electron-poor *o*-substituent, such as a F group, did not affect the reaction efficiency, and the product **3oa** was obtained in 90% yield under the optimized condition B. However, bulky the *ortho*-moiety on phenols inhibits the effective addition to **2a**. Reaction of **2a** with sterically demanding substrates such as 2-methyl- and 2-nitrophenols proceeded in low to moderate yields (**3na** and **3pa**). Similarly, hydrophenoxylation of 2-phenylphenol (**1q**) with **2a** gave **3qa** in 68% yield. Unfortunately, the reaction failed completely when the sterically encumbered substrate 2,6-dimethylphenol was run with **2a**. Hydrophenoxylations of phenols with terminal alkyne were then explored; a reaction of 4-nitrophenol (**1h**) with phenylacetylene under the optimized catalytic condition A was performed, and the corresponding Markovnikov's addition product was obtained in poor yield.[20]

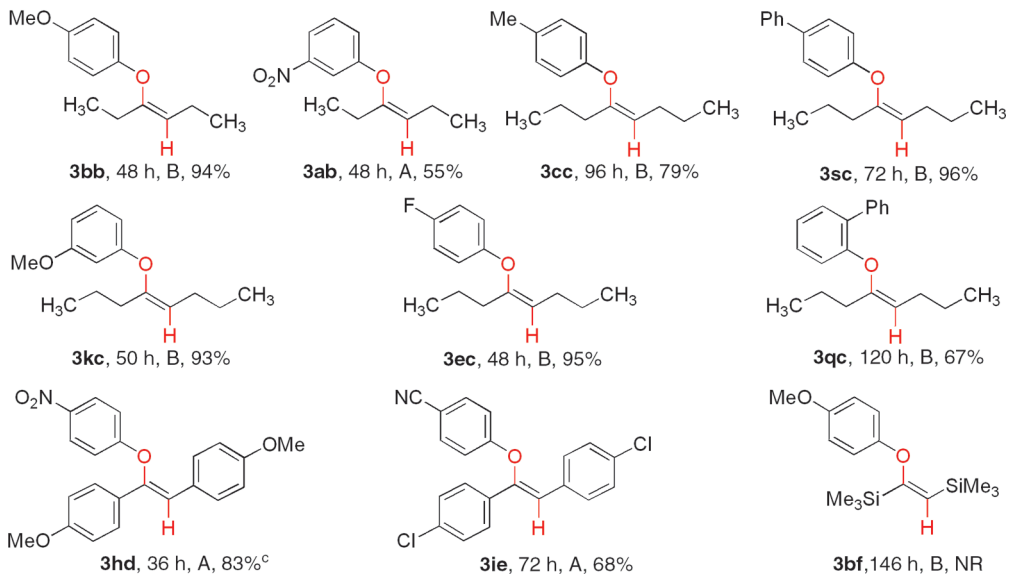
Next, we turned our attention to evaluate the effect of substitution on symmetrical alkynes (Table 3). At first, we tested the addition of phenols to the alkyl-substituted alkynes. Excellent yields of the desired hydrophenoxylation products were attained in the reaction of 3-hexyne (**2b**) or 4-octyne (**2c**) with electron-rich phenols having a methoxy or methyl group at the 4- and/or 3-position (**3bb**, **3cc**, and **3kc**). Phenols bearing an electron-withdrawing group at the *para*-position underwent hydrophenoxylation with **2c** efficiently, providing yields over 95% (**3sc** and **3ec**). Product **3ab** was obtained from the addition of 3-nitrophenol (**1a**) and **2b**, albeit in moderate yield, a consequence of the *meta*-substitution on phenols. Similarly, addition of sterically demanding 2-phenylphenol (**1q**) with **2c** afforded **3qc** in 67% yield. Once again, the *Z*-selectivity of **3ab** and **3cc** was established based on the NOESY studies.[19]

These results suggest that the addition of phenols to alkyl-substituted alkynes is more effective than to aryl-substituted

(20) For the details of spectral data, see Supporting Information.

TABLE 3. Hydrophenoxylation of 1 with Symmetrical Alkynes[a,b]





[a]Reactions were performed employing **1** (2.0 mmol) and **2** (1.0 mmol) at 100 °C. Condition A: Ag_2CO_3 (2.0 mmol), $AuCl_3$, and **4b** (3 mol % each) in CH_2Cl_2 (1.0 mL) were used. Condition B: K_2CO_3 (2.0 mmol), $AuCl_3$, and **4b** (5 mol % each) in THF (1.0 mL) were used. [b]Isolated yields based on alkynes; average of two runs. [c]**2d** (0.5 mmol) was used.

alkynes. We also believe that the efficiency of the reaction depends primarily on the facile attack of the phenol nucleophile on the activated electrophilic Au-alkyne-π intermediate. Moreover, carbophilic gold preferably activates the electron-rich alkynes over the electron-deficient alkynes.[21,22b] The inductively donating alkyl group would enhance the electron density on alkynes, thereby promoting activation by cationic gold. However, the electron density migration is reversed by a neutral or electron-deficient aryl group, diminishing the effective activation by cationic gold. Therefore, we conclude that electron-rich alkynes would show better reactivity in this transformation.[22b]

To further expand the scope of the reaction, we have explored the utility of electron-rich and -deficient aryl-substituted internal alkynes. Addition of 4-nitrophenol (**1h**) to the electron-rich 4-methoxyphenyl-substituted alkyne (**2d**) was performed, and **3hd** was isolated in 83% yield (Table 3).[19] However, moderate yield of **3ie** was produced when electron-deficient 4-chlorophenyl-substituted alkyne (**2e**) reacted with 4-cyanophenol (**1i**) under the optimized condition A. Unfortunately, the attempt to obtain the expected product from the addition of 4-methoxyphenol (**1b**) to the electronically and sterically demanding substrate bis(trimethylsilyl)acetylene (**2f**) turned out to be futile (Table 3, **3bf**).

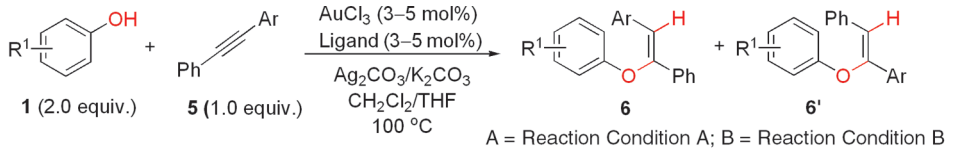
Addition of nucleophile to unactivated unsymmetrical alkynes is very important; first, it would provide two new molecular entities corresponding to the regioisomeric products, and second, better regioselectivity through preferential attack of oxygen nucleophile to alkynes would be realized. Our experience with hydrophenoxylation of symmetrical alkynes revealed that the gold catalyst activates electron-rich-substituted alkynes efficiently. Therefore, we decided to evaluate the reactivity of unsymmetrical alkynes toward the addition of phenols. Table 4 summarizes the scope of the hydrophenoxylation of substituted phenols with unsymmetrical alkynes.

Reaction of 4-nitrophenol (**1h**) with electron-rich unsymmetrical alkyne **5a** afforded the corresponding mixture of products in 94% yield with moderate regioselectivity (Table 4, entry 1). Excellent yields of the desired regioisomeric products were isolated in the hydrophenoxylation of **1h** with phenyl alkyl acetylenes (**5b** and **5c**) (Table 4, entries 2 and 3); this observation clearly demonstrates the effective reactivity of unsymmetrical alkyl-substituted alkynes in the addition to phenols. Pure products **6b** and **6b′** (Table 4, entry

(21) A competitive experiment was performed reacting 4-nitrophenol (**1h**, 30 mg, 0.2 mmol) with 1,2-bis(4-methoxyphenyl)ethyne (**2d**, 50 mg, 0.2 mmol) and 1,2-bis(3-(trifluoromethyl)phenyl)ethyne (**2g**, 65 mg, 0.2 mmol) in the presence of $AuCl_3$ (1.9 mg, 3 mol%), ligand **4b** (1.8 mg, 3 mol %), and Ag_2CO_3 (115 mg, 0.4 mmol) at 100 °C for 72 h. The respective vinyl-H integration in the crude ^{1}H NMR spectrum showed the formation of the corresponding products **3hd** and **3hg** in a 2:1 ratio. This signifies that the reaction of 4-nitrophenol with electron-rich alkyne **2d** is preferred over the electron-deficient alkyne **2g**. See Supporting Information.

(22) (a) Fürstner, A.; Davis, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (b) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485.

TABLE 4. Hydrophenoxylation of 1 with Unsymmetrical Alkynes (5)



entry	phenol	alkyne	products[c]
1[a]	**1h**	**5a**	**6a** + **6a'** (Ar[1] = 4-MeO-C$_6$H$_4$) 96 h; 94% [6a/6a' = 37/63][d]
2[a]	**1h**	**5b**	**6b** + **6b'** 72 h; 93% [6b:6b' = 32:68][d,e]
3[a]	**1h**	**5c**	**6c** + **6c'** 72 h; 81% [6c/6c' = 38/62][d]
4[b]	**1k**	**5a**	**6d** + **6d'** 120 h; 63% [6d/6d' = 91/9][d]
5[b]	**1r**	**5d**	**6e** + **6e'** (Ar[2] = 3-F$_3$C-C$_6$H$_4$) 120 h; 35% [6e/6e' = 30/70][d]

[a]Reactions were carried out using condition A. [b]Reactions were performed employing condition B. [c]Isolated yields of the mixture of regioisomers. [d]Ratios of regioisomers were determined by HPLC analysis. [e]Regioisomers are purified.

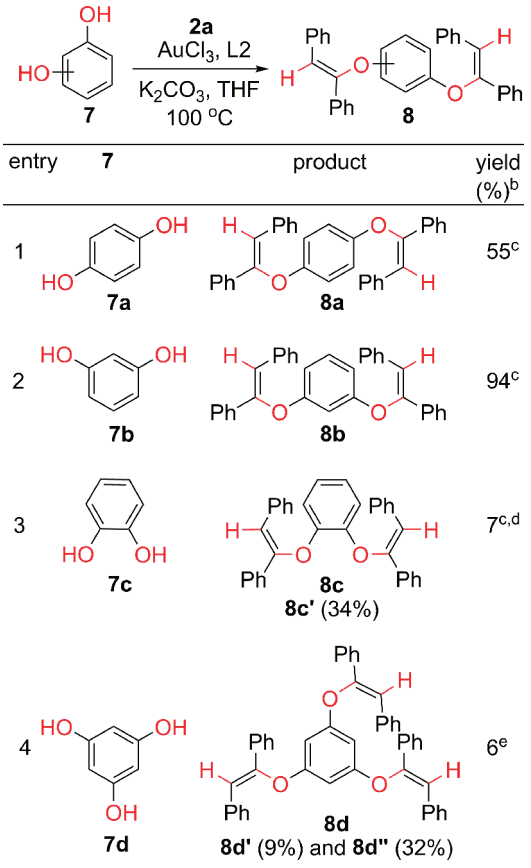
2) could be successfully isolated by column chromatography. The *Z*-olefin stereochemistry of **6b** and **6b′** is again established based on the NOESY studies.[19] When the reaction was run for *meta*-substituted 3-methoxyphenol (**1k**) and electron-rich unsymmetrical alkyne **5a**, the product was obtained in modest yield with better regioselectivity (91:9; Table 4, entry 4). This again demonstrates the reduction in reactivity with *meta*-substituted phenols. The regioselectivity observed in these reactions warrants further investigations of the mode of addition of phenols to unsymmetrical alkynes. It is likely that electronic effects of unsymmetrical alkynes and phenols contribute to the moderate regioselectivity. Gold and other catalytic systems used in the hydration and hydroalkoxylations of unsymmetrical alkynes have led to moderate regioselectivity in the product,[9a,11,22] and our current observations are consistent with this. However, electron-deficient alkyne **5d** reacted sluggishly with **1r**, and an inseparable mixture of regioisomers **6e** and **6e′** was produced in poor yield (Table 4, entry 5); a substantial amount of precursor **5d** was recovered even after continuing the reaction for 4 days. This indicates poor reactivity of phenolic−OH to electron-poor alkynes under the optimized gold-catalyzed reaction condition.

In order to enlarge the molecular diversity based on extended conjugation through the incorporation of more arylvinyl ether moieties in the molecule, multiple hydrophenoxylation of polyphenols with symmetrical alkynes was envisaged. Previous experimental results prompted us to use the optimized condition B in evaluating the addition of a series of electron-rich polyphenols with diphenylacetylene, and the results are shown in Table 5. At first, the reaction of hydroquinone (**7a**) with **2a** was performed, and the corresponding di-*O*-vinylated product was isolated in 55% yield along with trace amount of monoadduct (Table 5, entry 1). The reaction could not be completed even after 4 days; we infer that the addition of the potential intermediate, benzene-1,4-bis(olate),[23] to the electrophilic Au-alkyne-π complex is inefficient, thereby limiting the yield of the product. X-ray crystallographic analysis unambiguously elucidated the structure of **8a** having *Z*-olefin stereochemistry (see the Supporting Information).[15]

Resorcinol (**7b**) underwent efficient addition with **2a** under the optimized condition to furnish the desired di-*O*-vinylated product in 94% yield (Table 5, entry 2). NOESY studies confirm the *Z*-selectivity of **8b**.[19] Further, we were interested in examining the possibility of hydrophenoxylations of sterically encumbered catechol (**7c**) with **2a**. The bond formation

(23) (a) Gao, C.; Gao, L.; Ding, M. U. S. Patent 0272957, **2005**. (b) Forsyth, T. P.; Williams, D. B. G.; Montalban, A. G.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **1998**, *63*, 331.

TABLE 5. Hydrophenoxylation of Polyphenols (7) with 2a[a]

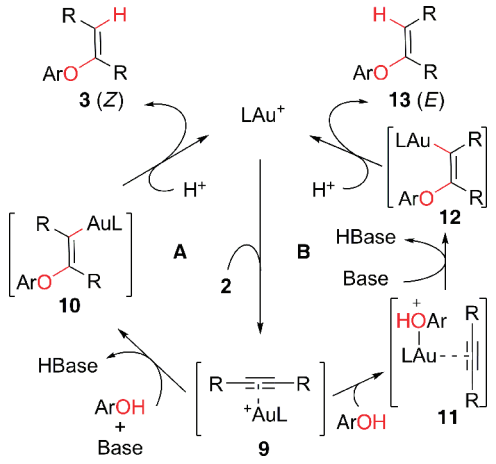


[a]Reactions were performed using **7** (1.0 mmol) and THF (2.0 mL) in condition B. [b]Isolated yields based on **7**. [c]Reaction was carried out employing **2a** and K_2CO_3 (4.0 mmol each), $AuCl_3$ and **4b** (10 mol % each), and continued for 96 h. [d]Reaction was continued for 168 h; monoadduct (**8c′**) was also obtained. [e]Reaction was performed using **2a** and K_2CO_3 (6.0 mmol each), $AuCl_3$ and **4b** (15 mol % each), and continued for 168 h; di- (**8d′**) and mono-*O*-vinylated phloroglucinols (**8d″**) were obtained.

between **7c** and **2a** would be difficult, in view of the close proximity of the −OH groups in the catechol. It is worth noting that di-*O*-vinylated catechol (**8c**) was isolated in only 7% yield after continuing the reaction for 7 days (Table 5, entry 3). Moderate yield of the corresponding mono-*O*-vinylated catechol (**8c′**) was also produced along with unreacted **7c**. Finally, we have explored the challenging hydrophenoxylation of phloroglucinol (**7d**) with **2a**. Tri-*O*-vinylated phloroglucinol (**8d**) was obtained, although in poor yield, when the reaction between **7d** and **2a** was executed under the optimized condition for 7 days; the corresponding di- and mono-*O*-vinylated phloroglucinols were also produced in 9 and 32%, respectively. To the best of our knowledge, these new molecular entities are prepared for the first time via simultaneous addition of phenols to the alkynes catalyzed by gold.

Even though the detailed mechanism of this reaction is not yet established, it is likely to proceed through the following catalytic cycle, as shown in Scheme 1. The soft and carbophilic JohnPhos ligated Au complex activates the alkyne to provide gold-alkyne-π complex **9**.[16,22] This ligand is found to be very crucial for the present reaction, suggesting that its

SCHEME 1. Proposed Catalytic Cycle



bulkiness enhances the reactivity of the gold complex and triggers the subsequent nucleophilic addition of phenols.[24] The phenolate attack from the opposite side of **9** to yield *O*-vinyl-Au species **10**.[18,25] Protodemetalation furnishes arylvinyl ethers with *Z*-olefins **3** and regenerates the active gold catalyst, as depicted in cycle A. An alternate pathway B would involve coordination of phenols to gold complex **9**[9k,25b] followed by base-induced deprotonation and C−O bond formation leading to the *O*-vinyl-Au species **12** with *Z*-configuration. Protodemetalation would generate (*E*)-arylvinyl ethers **13**. Even though the transformation of **11** to **12** should be possible with any mild base, our observation for the hydrophenoxylation reaction is that it requires specific choices of base and solvent. Further, exclusive formation of *Z*-olefins is observed in the reaction. On the basis of this evidence, route B appears unlikely.

Experimental results reveal that the gold(III) chloride and ligand **4b** mixture allows the intermolecular addition of phenols to alkynes at 100 °C without losing its activity for at least 4−6 days. In order to understand the plausible reactive species involved in the catalytic system, NMR experiment is performed by reacting 4-methoxyphenol (**1b**), diphenylacetylene (**2a**), K_2CO_3, $AuCl_3$, and **4b** in THF-d_8 solvent at room temperature. In the ^{31}P NMR, three new signals at $\delta = 106.8$, 59.6, and 55.0 ppm appear and the signal at $\delta = 17.4$ ppm corresponding to the ligand **4b** is absent. At about 30 min, the signal at $\delta = 106.8$ ppm disappears. The peaks at $\delta = 55.0$ and 59.6 ppm can be assigned to the phosphineoxide (**14**) and phosphine−Au(I) complex (**15**), respectively (Figure 1).[24a,26,27] However, efforts to isolate the species with a signal at $\delta = 106.8$ ppm failed; therefore, the structure of this species cannot be established. The sample of

(24) (a) Nieto-Oberhuber, C.; Lopez, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178. (b) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066.

(25) (a) For gold-catalyzed carboxylate addition to alkynes, see: Harkat, H.; Weibel, J.-M.; Pale, P. *Tetrahedron Lett.* **2006**, *47*, 6273. (b) For gold-catalyzed intermolecular hydroamination of alkynes, see: Mizushima, E.; Hayashi, T.; Tanaka, M. *Org. Lett.* **2003**, *5*, 3349.

(26) (a) Baillie, C.; Xiao, J. *Tetrahedron* **2004**, *60*, 4159. (b) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.

(27) It is likely that a part of phosphine is involved for the conversion of Au(III) to Au(I) species in the redox process with simultaneous formation of phosphine oxide using a trace amount of adventitious water present in the system.

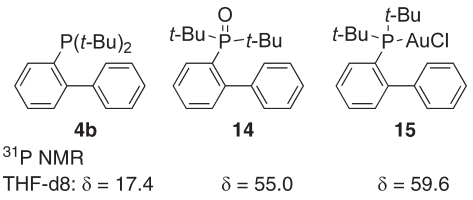


FIGURE 1. ^{31}P NMR chemical shifts of the mixture of JohnPhos and $AuCl_3$.

$AuCl_3$ and **4b** in THF-d_8 at room temperature shows identical results in the ^{31}P NMR spectrum to that observed in the previous reaction. Similarly, the ^{31}P NMR spectrum of the sample of $AuCl_3$ and **4b** in $CDCl_3$ at room temperature shows three peaks at $\delta = 106.2$, 59.9, and 18.0 ppm; the signal at $\delta = 18.0$ ppm corresponds to **4b** in $CDCl_3$, and the peaks at $\delta = 106.2$ and 59.9 ppm resemble those from the previous reaction. We believe that **15** may be responsible for the hydrophenoxylations to alkynes at the elevated temperature. The formation of **15** can also be expected in the reactions of AuCl and Ph_3PAuCl with **4b** (entries 10 and 11, Table 1). However, the ^{31}P NMR spectrum of a mixture of AuCl and **4b** in $CDCl_3$ shows two signals at $\delta = 60.0$ and 17.9 ppm in a 1:4 ratio corresponding to **15** and **4b**, respectively, and the sample of Ph_3PAuCl and **4b** in $CDCl_3$ shows no formation of **15**; the latter shows signals at $\delta = 18.2$ (for **4b**) and 29.0 ppm.[28] These observations account for the trace formation of **3aa** in these reactions (entries 10 and 11 in Table 1).

Conclusion

In summary, we have demonstrated an efficient and atom-economical gold-catalyzed intermolecular hydrophenoxylation of alkynes. The present methodology provides a new one-step protocol for the synthesis of a wide array of vinyl-(1,2-disubstituted)aryl ethers. We believe that the current strategy would trigger synthetic explorations of oxygen-containing heterocycles of pharmaceutical interest.[7] Efforts are underway to optimize milder reaction conditions, unravel mechanistic details, and investigate novel synthetic applications.

Experimental Section

General Procedure for the Reaction of Unactivated Phenols to Alkynes (GP-1, Condition A): In an oven-dried pressure tube, phenol (2.0 mmol), alkyne (1.0 mmol), and Ag_2CO_3 (2.0 mmol) were taken. The tube was evacuated and backfilled with argon three times. In a separate Schlenk flask, a heterogeneous solution of $AuCl_3$ (0.03 mmol) and ligand [**4b** (JohnPhos), 2-(di-*tert*-butylphosphino)biphenyl, 0.03 mmol] in DCM (1.0 mL) was freshly prepared and introduced to the parent reaction mixture under an argon atmosphere. The resulting reaction mixture was heated at 100 °C. Progress of the reaction was monitored by GC analysis while noticing complete consumption of alkynes employed. Reaction was continued for the time shown in the respective tables and brought to room temperature. The reaction mixture was diluted with dichloromethane (5 mL) and filtered over a small pad of Celite. Solvent was evaporated under reduced pressure, and the crude reaction mixture was purified using silica gel column chromatography.

(28) Duan, H.; Sengupta, S.; Petersen, J. L.; Akhmedov, N. G.; Shi, X. *J. Am. Chem. Soc.* **2009**, *131*, 12100.

General Procedure for the Reaction of Unactivated Phenols to Alkynes (GP-2, Condition B): In an oven-dried Schlenk flask, phenol (2.0 mmol), alkyne (1.0 mmol), and K_2CO_3 (2.0 mmol) were taken. The flask was evacuated and backfilled with argon three times. A solution of $AuCl_3$ (0.05 mmol) and **4b** (JohnPhos, 0.05 mmol) in THF (1.0 mL) was freshly prepared in a separate Schlenk flask and introduced to the parent mixture under an argon atmosphere. The resulting reaction mixture was heated at 100 °C. Progress of the reaction was monitored by GC analysis while noticing complete consumption of alkynes employed. Reaction was continued for the time shown in the respective tables and allowed to cool to room temperature. The reaction mixture was diluted with dichloromethane (5 mL) and filtered over a small pad of Celite. Solvent was evaporated under reduced pressure, and the crude reaction mixture was purified using silica gel column chromatography.

(*Z*)-(1-(4-Methoxyphenoxy)ethene-1,2-diyl)dibenzene (3ba): 251 mg, 83% yield; colorless solid; mp 102−104 °C; $R_f = 0.56$ (49:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71−7.66 (m, 2H), 7.63−7.58 (m, 2H), 7.38−7.28 (m, 5H), 7.27−7.21 (m, 1H), 7.01−6.93 (m, 2H), 6.82−6.75 (m, 2H), 6.62 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 150.2, 150.1, 136.1, 134.9, 128.9, 128.5, 128.3, 127.3, 126.2, 117.1, 116.5, 114.7, 55.5; IR (KBr) ν_{max} 3074, 2928, 1630, 1502, 1444, 1205, 1103, 1037, 759 cm^{-1}; MS (EI) *m*/*z* (%) 303 ($M^+ + 1$, 100), 211 (73), 197 (3). Anal. calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.56; H, 5.95.

(*Z*)-(1-(4-Methylphenoxy)ethene-1,2-diyl)dibenzene (3ca): 198 mg, 69% yield; colorless solid; mp 90−92 °C; $R_f = 0.43$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 7.6$ Hz, 2H), 7.39−7.19 (m, 6H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.66 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 149.9, 136.1, 134.8, 131.2, 130.1, 128.9, 128.5, 128.4, 128.3, 127.3, 126.1, 116.6, 116.1, 20.5; IR (KBr) ν_{max} 3030, 2916, 2860, 1608, 1506, 1448, 1219, 1168, 806, 688, 569 cm^{-1}; MS (EI) *m*/*z* (%) 287 ($M^+ + 1$, 100), 211 (54), 179 (3). Anal. calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.16; H, 6.28.

(*Z*)-(1-(4-*sec*-Butylphenoxy)ethene-1,2-diyl)dibenzene (3da): 233 mg, 71% yield; colorless solid; mp 78−79 °C; $R_f = 0.75$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, $J = 6.4$ Hz, 2H), 7.62 (d, $J = 6.4$ Hz, 2H), 7.37−7.26 (m, 5H), 7.23 (t, $J = 6.0$ Hz, 1H), 7.03 (d, $J = 6.8$ Hz, 2H), 6.95 (d, $J = 6.8$ Hz, 2H), 6.65 (s, 1H), 2.63−2.45 (m, 1H), 1.61−1.47 (m, 2H), 1.19 (d, $J = 5.6$ Hz, 3H), 0.81 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 150.0, 141.2, 136.3, 134.9, 129.0, 128.5, 128.3, 128.1, 127.3, 126.2, 116.6, 116.0, 40.8, 31.3, 21.7, 12.2; IR (KBr) ν_{max} 3028, 2957, 2918, 1604, 1504, 1221, 1020, 821, 767 cm^{-1}; MS (EI) *m*/*z* (%) 329 ($M^+ + 1$, 100), 211 (86), 197 (7). Anal. calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.58; H, 7.41.

(*Z*)-(1-(4-Fluorophenoxy)ethene-1,2-diyl)dibenzene (3ea): 262 mg, 90% yield; colorless solid; mp 62−65 °C; $R_f = 0.71$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71−7.64 (m, 2H), 7.62−7.58 (m, 2H), 7.39−7.31 (m, 5H), 7.30−7.22 (m, 1H), 7.03−6.89 (m, 4H), 6.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.7, 152.2, 149.8, 135.7, 134.6, 128.9, 128.6, 128.59, 128.54, 127.5, 126.1, 117.3, 117.2, 116.8, 116.2, 116.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.2; IR (KBr) ν_{max} 3043, 1633, 1502, 1446, 1195, 1093, 516 cm^{-1}; MS (EI) *m*/*z* (%) 291 ($M^+ + 1$, 100), 211 (79), 197 (3), 179 (5). Anal. calcd for $C_{20}H_{15}FO$: C, 82.74; H, 5.21. Found: C, 82.57; H, 5.26.

(*Z*)-(1-(4-Chlorophenoxy)ethene-1,2-diyl)dibenzene (3fa): 270 mg, 88% yield; colorless solid; mp 88−90 °C; $R_f = 0.75$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $J = 7.2$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.39−7.28 (m, 5H), 7.27−7.14 (m, 3H), 6.95 (d, $J = 8.8$ Hz, 2H), 6.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 149.4, 135.6, 134.5, 129.7, 128.9, 128.7, 128.6, 127.6, 127.0, 126.0, 117.5, 116.9; IR (KBr) ν_{max} 3072, 3020, 1591,

1485, 1446, 1221, 1093, 815 cm^{-1}; MS (EI) m/z (%) 305 ($M^+ - 1$, 44), 283 (82), 255 (84), 127 (100). Anal. calcd for $C_{20}H_{15}ClO$: C, 78.30; H, 4.93. Found: C, 78.41; H, 4.88.

(*Z*)-(1-(4-(Trifluoromethyl)phenoxy)ethene-1,2-diyl)dibenzene (3ga): 279 mg, 82% yield; colorless solid; mp 58−60 °C; R_f = 0.78 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.57 (m, 4H), 7.51 (d, J = 8.4 Hz, 2H), 7.41−7.31 (m, 5H), 7.29−7.22 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 6.76 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 148.9, 135.2, 134.2, 129.0, 128.8, 128.7, 128.6, 127.7, 127.2, 127.1, 125.8, 117.2, 116.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.7; IR (KBr) ν_{max} 3061, 1612, 1512, 1325, 1232, 1066, 839, 692 cm^{-1}; MS (EI) m/z (%) = 341 ($M^+ + 1$, 100), 211 (82), 197 (2), 179 (8). Anal. calcd for $C_{21}H_{15}F_3O$: C, 74.11; H, 4.44. Found: C, 74.23; H, 4.48.

(*Z*)-(1-(4-Nitrophenoxy)ethene-1,2-diyl)dibenzene (3ha): 273 mg, 86% yield; pale yellow thick liquid; R_f = 0.43 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.60−7.53 (br d, J = 7.6 Hz, 4H), 7.40−7.29 (m, 5H), 7.28−7.20 (m, 1H), 7.11 (d, J = 8.8 Hz, 2H), 6.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 148.5, 142.6, 134.8, 133.8, 129.0, 128.9, 128.7, 128.0, 126.1, 125.7, 117.4, 116.3; IR (neat) ν_{max} 3059, 2924, 1647, 1518, 1489, 1340, 750 cm^{-1}; MS (EI) m/z (%) 318 ($M^+ + 1$, 98), 302 (7), 288 (30), 211 (100), 197 (8), 178 (8). Anal. calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.62; H, 4.81; N, 4.48.

(*Z*)-4-(1,2-Diphenylvinyloxy)benzonitrile (3ia): 259 mg, 87% yield; colorless solid; mp 88−89 °C, R_f = 0.37 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.65 (m, 2H), 7.64−7.58 (m, 2H), 7.38−7.27 (m, 5H), 7.26−7.18 (m, 3H), 6.95 (dt, J = 8.8, 2.0 Hz, 2H), 6.74 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 148.5, 134.9, 134.3, 133.9, 129.0, 128.9, 128.88, 128.7, 127.9, 125.7, 118.8, 117.3, 116.9, 105.6; IR (KBr) ν_{max} 3045, 2226, 1601, 1502, 1331, 918, 777 cm^{-1}; MS (EI) m/z (%) 298 ($M^+ + 1$, 88), 211 (100), 197 (2), 179 (5), 165 (2). Anal. calcd for $C_{21}H_{15}NO$: C, 84.82; H, 5.08; N, 4.71. Found: C, 84.75; H, 5.12; N, 4.76.

(*Z*)-(1-Phenoxyethene-1,2-diyl)dibenzene (3ja): 96 mg, 35% yield; colorless solid; mp 58−61 °C; R_f = 0.27 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dt, J = 7.6, 1.6 Hz, 2H), 7.62 (dt, J = 8.4, 1.6 Hz, 2H), 7.38−7.19 (m, 8H), 7.08−7.01 (m, 2H), 6.99−6.93 (m, 1H), 6.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 149.6, 136.0, 134.7, 129.6, 128.9, 128.6, 128.5, 128.4, 127.4, 126.1, 122.0, 116.7, 116.3; IR (KBr) ν_{max} 3055, 3022, 1591, 1487, 1222, 1167, 1020, 763 cm^{-1}; MS (EI) m/z (%) 273 ($M^+ + 1$, 100), 211 (33), 179 (4). Anal. calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.31; H, 5.86.

(*Z*)-(1-(3-Methoxyphenoxy)ethene-1,2-diyl)dibenzene (3ka): 155 mg, 51% yield; colorless solid; mp 98−100 °C; R_f = 0.62 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.58 (m, 4H), 7.38−7.27 (m, 5H), 7.26−7.20 (m, 1H), 7.13 (t, J = 8.4 Hz, 1H), 6.67 (s, 1H), 6.66−6.60 (m, 2H), 6.56−6.50 (m, 1H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 157.5, 149.5, 136.0, 134.7, 130.0, 128.9, 128.6, 128.5, 128.4, 127.4, 125.9, 116.8, 108.7, 107.5, 102.7, 55.2; IR (KBr) ν_{max} 2959, 1591, 1491, 1446, 1259, 1020, 758 cm^{-1}; MS (EI) m/z (%) 303 ($M^+ + 1$, 100), 211 (26), 179 (5). Anal. calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.35; H, 5.97.

(*Z*)-(1-(3-Fluorophenoxy)ethene-1,2-diyl)dibenzene (3la): 209 mg, 72% yield; colorless solid; mp 80−82 °C; R_f = 0.75 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.57 (m, 4H), 7.41−7.28 (m, 5H), 7.28−7.21 (m, 1H), 7.21−7.13 (m, 1H), 6.83 (br d, J = 8.2 Hz, 1H), 6.81−6.73 (m, 1H), 6.71 (s, 1H), 6.70−6.62 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 162.7, 157.8, 157.7, 149.3, 135.6, 134.4, 130.5, 130.4, 129.0, 128.7, 128.61, 128.59, 127.6, 125.9, 117.0, 112.03, 112.01, 109.1, 108.9, 104.2, 104.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.2; IR (KBr) ν_{max} 3080, 1608, 1485, 1446, 1338, 1263, 1126, 1020, 835, 688 cm^{-1}; MS (EI) m/z (%) 291 ($M^+ + 1$, 100), 211 (65), 197 (2), 179 (8). Anal. calcd for $C_{20}H_{15}FO$: C, 82.74; H, 5.21. Found: C, 82.65; H, 5.26.

(*Z*)-(1-(3-Nitrophenoxy)ethene-1,2-diyl)dibenzene (3aa): 270 mg, 85% yield; pale yellow solid; mp 112−114 °C; R_f = 0.53 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.58 (m, 4H), 7.51 (d, J = 8.8 Hz, 2H), 7.41−7.30 (m, 5H), 7.29−7.22 (m, 1H), 7.12 (d, J = 8.8 Hz, 2H), 6.75 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 149.3, 148.7, 134.8, 134.0, 130.3, 129.0, 128.9, 128.8, 128.6, 127.8, 125.8, 122.3, 117.4, 117.1, 111.3; IR (KBr) ν_{max} 3080, 2932, 1645, 1521, 1446, 1350, 1269, 1022, 767 cm^{-1}; MS (EI) m/z (%) 318 ($M^+ + 1$, 68), 302 (2), 288 (18), 211 (100), 197 (4). Anal. calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.68; H, 4.81; N, 4.46.

(*Z*)-3-(1,2-Diphenylvinyloxy)benzaldehyde (3ma): 151 mg, 50% yield; yellow solid; mp 78−81 °C; R_f = 0.43 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.69−7.59 (m, 4H), 7.55−7.46 (m, 2H), 7.45−7.20 (m, 8H), 6.75 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 157.0, 149.1, 138.0, 135.3, 134.3, 130.3, 129.0, 128.7, 128.6, 128.5, 127.6, 125.9, 124.0, 122.4, 117.1, 116.2; IR (KBr) ν_{max} 3059, 2924, 2845, 1697, 1591, 1446, 1244, 761, 692 cm^{-1}; MS (EI) m/z (%) 301 ($M^+ + 1$, 77), 211 (100), 179 (4). Anal. calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.12; H, 5.33.

(*Z*)-(1-(*o*-Tolyloxy)ethene-1,2-diyl)dibenzene (3na): 129 mg, 45% yield; colorless solid; mp 72−73 °C; R_f = 0.37 (hexane): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.65−7.58 (m, 2H), 7.42−7.31 (m, 5H), 7.31−7.22 (m, 2H), 6.99 (td, J = 8.0, 4.0 Hz, 1H), 6.92 (td, J = 8.0, 4.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.73 (s, 1H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 150.0, 136.1, 135.0, 131.1, 128.9, 128.6, 128.5, 128.4, 127.4, 126.9, 126.6, 125.9, 121.8, 116.7, 114.3, 16.6; IR (KBr) ν_{max} 3057, 2924, 1639, 1489, 1448, 1180, 1116, 1076, 754, 692 cm^{-1}; MS (EI) m/z (%) 287 ($M^+ + 1$, 100), 211 (73), 197 (4), 179 (8), 165 (3). Anal. calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.21; H, 6.29.

(*Z*)-(1-(2-Fluorophenoxy)ethene-1,2-diyl)dibenzene (3oa): 262 mg, 90% yield; colorless thick liquid; R_f = 0.68 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dt, J = 7.2, 1.6 Hz, 2H), 7.63 (dt, J = 7.2, 1.6 Hz, 2H), 7.40−7.27 (m, 5H), 7.25−7.22 (m, 1H), 7.19−7.11 (m, 1H), 6.95−6.83 (m, 3H), 6.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 151.7, 149.7, 144.0, 143.9, 135.5, 134.5, 128.9, 128.7, 127.62, 127.59, 125.9, 124.4, 124.3, 122.7, 122.6, 117.4, 116.8, 116.7, 116.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −134.4; IR (neat) ν_{max} 3059, 3026, 1645, 1610, 1500, 1448, 1199, 1018, 750, 692 cm^{-1}; MS (EI) m/z (%) 291 ($M^+ + 1$, 100), 211 (94), 197 (3), 180 (5). Anal. calcd for $C_{20}H_{15}FO$: C, 82.74; H, 5.21. Found: C, 82.65; H, 5.28.

(*Z*)-(1-(2-Nitrophenoxy)ethene-1,2-diyl)dibenzene (3pa): 70 mg, 22% yield; pale yellow thick liquid; R_f = 0.28 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.4, 1.6 Hz, 1H), 7.65 (br d, J = 8.4 Hz, 4H), 7.39−7.20 (m, 7H), 7.05−6.96 (m, 2H), 6.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 148.3, 139.6, 134.8, 134.2, 133.8, 129.1, 129.0, 128.9, 128.7, 127.9, 125.8, 121.8, 117.6, 117.1; IR (neat) ν_{max} 3059, 2930, 1732, 1602, 1352, 1089, 920 cm^{-1}; MS (EI) m/z (%) 318 ($M^+ + 1$, 47), 286 (13), 225 (9), 211 (100), 197 (54), 186 (7). Anal. calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.62; H, 4.81; N, 4.51.

(*Z*)-(2-(1,2-Diphenylvinyloxy)biphenyl (3qa): 237 mg, 68% yield; colorless solid; mp 84−86 °C; R_f = 0.50 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dt, J = 7.2, 1.2 Hz, 2H), 7.63 (dt, J = 7.2, 1.2 Hz, 2H), 7.54−7.44 (m, 3H), 7.43−7.38 (m, 3H), 7.33−7.18 (m, 6H), 7.10 (ddd, J = 9.6, 7.6, 1.6 Hz, 1H), 7.03 (ddd, J = 9.6, 7.6, 1.6 Hz, 1H), 6.92 (dd, J = 8.0, 1.2 Hz, 1H), 6.64 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 150.1, 138.2, 135.9, 134.9, 131.4, 131.0, 129.7, 128.9, 128.5, 128.48, 128.4, 128.3, 128.1, 127.3, 127.2, 126.0, 122.3, 116.5, 115.5; IR (KBr) ν_{max} 3032, 2922, 1628, 1475, 1446, 1332, 1253, 1022, 746, 690

cm^{-1}; MS (EI) m/z (%) 349 ($M^+ + 1$, 100), 271 (65), 257 (21), 211 (44). Anal. calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.55; H, 5.83.

(*Z*)-1-(Hex-3-en-3-yloxy)-4-methoxybenzene (3bb): 194 mg, 94% yield; colorless liquid; $R_f = 0.43$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 6.94−6.81(m, 4H), 4.99 (br t, $J = 7.2$ Hz, 1H), 3.79 (s, 3H), 2.19−2.05 (m, 4H), 1.07 (t, $J = 7.6$ Hz, 3H), 0.99 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 152.1, 150.5, 116.8, 115.9, 114.5, 55.5, 25.2, 18.4, 14.2, 11.5; IR (neat) ν_{max} 3043, 2966, 2935, 2878, 2835, 1684, 1504, 1462, 1296, 1211, 1101, 1039, 829 cm^{-1}; MS (EI) m/z (%) 207 ($M^+ + 1$, 100), 194 (2), 165 (2), 115 (14). Anal. calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.88; H, 8.75.

(*Z*)-1-(Hex-3-en-3-yloxy)-3-nitrobenzene (3ab): 122 mg, 55% yield; pale yellow liquid; $R_f = 0.32$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.0$ Hz, 1H), 7.72 (s, 1H), 7.43 (t, $J = 8.0$ Hz, 1H), 7.24 (br d, $J = 1.2$ Hz, 1H), 5.12 (t, $J = 6.8$ Hz, 1H), 2.16 (q, $J = 7.2$ Hz, 2H), 1.98 (q, $J = 7.2$ Hz, 2H), 1.06 (t, $J = 7.6$ Hz, 3H), 0.94 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 150.9, 149.3, 130.1, 122.1, 118.0, 116.2, 110.2, 25.4, 18.6, 13.9, 11.4; IR (neat) ν_{max} 3082, 2970, 2937, 2879, 1685, 1614, 1531, 1350, 1277, 1232, 1024, 796 cm^{-1}; MS (EI) m/z (%) 222 ($M^+ + 1$, 100), 206 (53), 192 (54), 156 (53), 115(54). Anal. calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.10; H, 6.88; N, 6.45.

(Z)-1-Methyl-4-(oct-4-en-4-yloxy)benzene (3cc): 172 mg, 79% yield; colorless thick liquid; $R_f = 0.71$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, $J = 8.4$ Hz, 2H), 6.85 (d, $J = 8.4$ Hz, 2H), 5.02 (t, $J = 7.2$ Hz, 1H), 2.32 (s, 3H), 2.11 (t, $J = 7.2$ Hz, 2H), 2.03 (q, $J = 7.2$ Hz, 2H), 1.53−1.43 (m, 2H), 1.43−1.33 (m, 2H), 0.96−0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 150.6, 130.5, 129.9, 115.9, 34.3, 27.2, 22.8, 20.6, 20.1,13.9, 13.6; IR (neat) ν_{max} 3028, 2962, 2868, 1684, 1506, 1222, 1167, 920, 815 cm^{-1}; MS (EI) m/z (%) 219 ($M^+ + 1$, 100), 178 (3), 161 (5), 143 (67), 129 (14). Anal. calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.61; H, 10.10.

(*Z*)-4-(Oct-4-en-4-yloxy)biphenyl (3sc): 268 mg, 96% yield; colorless liquid; $R_f = 0.6$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62−7.50 (m, 4H), 7.44 (t, $J = 7.2$ Hz, 2H), 7.37−7.31 (m, 1H), 7.03 (dt, $J = 6.8$, 2.0 Hz, 2H), 5.08 (t, $J = 7.2$ Hz, 1H), 2.16 (t, $J = 7.2$ Hz, 2H), 2.05 (q, $J = 7.6$ Hz, 2H), 1.58−1.48 (m, 2H), 1.47−1.38 (m, 2H), 0.98−0.89 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 150.5, 140.8, 134.4, 128.7, 128.2, 126.8, 126.7, 116.3, 116.2, 34.4, 27.2, 22.7, 20.1, 13.9, 13.6; IR (neat) ν_{max} 2959, 2928, 2868, 1684, 1606, 1514, 1230, 1167, 835, 761, 696 cm^{-1}; MS (EI) m/z (%) 281 ($M^+ + 1$, 100), 161 (7), 143 (76), 129 (19). Anal. calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.61; H, 8.70.

(*Z*)-1-Methoxy-3-(oct-4-en-4yloxy)benzene (3kc): 217 mg, 93% yield; colorless liquid; $R_f = 0.44$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, $J = 8.4$ Hz, 1H), 6.57−6.48 (m, 3H), 5.01 (t, $J = 6.4$ Hz, 1H), 3.78 (s, 3H), 2.10 (t, $J = 7.2$ Hz, 2H), 1.99 (q, $J = 7.2$ Hz, 2H), 1.54−1.41 (m, 2H), 1.41−1.31 (m, 2H), 0.94−0.84 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 158.0, 150.4, 129.8, 116.3, 108.3, 106.8, 102.1, 55.2, 34.4, 27.2, 22.7, 20.1, 13.9, 13.6; IR (neat) ν_{max} 2959, 2872, 1684, 1602, 1454, 1280, 1143, 962, 850, 688 cm^{-1}; MS (EI) m/z (%) 235 ($M^+ + 1$, 100), 143 (63), 125 (5). Anal. calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.95; H, 9.39.

(*Z*)-1-Fluoro-4-(oct-4-en-4-yloxy)benzene (3ec): 210 mg, 95% yield; colorless liquid; $R_f = 0.55$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 6.99−6.91 (m, 2H), 6.89−6.82 (m, 2H), 4.99 (t, $J = 7.2$ Hz, 1H), 2.06 (t, $J = 7.6$ Hz, 2H), 1.98 (q, $J = 7.2$ Hz, 2H), 1.52−1.41 (m, 2H), 1.41−1.31 (m, 2H), 0.93−0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 156.4, 152.74, 152.72, 150.7, 117.0, 116.9, 116.1, 115.9, 115.7, 34.2, 27.2, 22.7, 20.1, 13.8, 13.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −123.4; IR (neat) ν_{max} 2959, 2928, 1682, 1502, 1201, 922, 829 cm^{-1}; MS (EI) m/z (%) 223 ($M^+ + 1$, 75), 161 (6), 143 (100), 129 (18). Anal. calcd for $C_{14}H_{19}FO$: C, 75.64; H, 8.61. Found: C, 75.59; H, 8.67.

(*Z*)-2-(Oct-4-en-4-yloxy)biphenyl (3qc): 187 mg, 67% yield; colorless thick liquid; $R_f = 0.57$ (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $J = 7.6$ Hz, 2H), 7.47−7.31 (m, 4H), 7.26 (t, $J = 7.2$ Hz, 1H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 8.4$ Hz, 1H), 5.01 (t, $J = 7.2$ Hz, 1H), 2.09 (t, $J = 7.2$ Hz, 2H), 2.02 (q, $J = 7.2$ Hz, 2H), 1.44−1.32 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.84 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 150.7, 138.4, 131.0, 129.5, 128.3, 127.9, 126.8, 121.4, 115.6, 114.7, 34.3, 29.7, 27.3, 22.7, 20.1, 13.9, 13.5; IR (neat) ν_{max} 3061, 2959, 2934, 2872, 1682, 1583, 1477, 1217, 1118, 750, 698 cm^{-1}; MS (EI) m/z (%) 281 ($M^+ + 1$, 100), 161 (5), 143 (46), 129 (11). Anal. calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.74; H, 8.59.

(*Z*)-4,4′-(1-(4-Nitrophenoxy)ethene-1,2-diyl)bismethoxybenzene (3hd): 157 mg, 83% yield; thick yellow liquid; $R_f = 0.43$ (95:5 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (dt, $J = 8.0$, 1.2 Hz, 2H), 7.51−7.45 (m, 4H), 7.10 (dt, $J = 8.0$, 1.2 Hz, 2H), 6.91−6.75 (m, 4H), 6.62 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 159.9, 159.0, 146.8, 142.4, 130.2, 127.4, 126.8, 126.1, 116.2, 115.6, 115.1, 114.3, 114.1, 55.3, 55.2; IR (neat) ν_{max} 2930, 2843, 1608, 1342, 1242, 1176, 1032, 833 cm^{-1}; MS (EI) m/z (%) 378 ($M^+ + 1$, 52), 271 (100), 240 (3). Anal. calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 69.95; H, 5.12; N, 3.76.

(*Z*)-4-(1,2-Bis(4-chlorophenyl)vinyloxy)benzonitrile (3ie): 250 mg, 68% yield; colorless thick liquid; $R_f = 0.40$ (49:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, $J = 6.8$, 2.0 Hz, 2H), 7.51−7.44 (m, 4H), 7.32 (dt, $J = 6.8$, 2.0 Hz, 2H), 7.27 (dt, $J = 6.8$, 2.0 Hz, 2H), 7.05 (dt, $J = 6.8$, 2.0 Hz, 2H), 6.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 147.9, 135.0, 134.4, 133.7, 133.1, 132.1, 130.2, 129.2, 128.9, 126.9, 118.6, 116.8, 116.52, 116.51, 106.1; IR (neat) ν_{max} 3335, 3067, 2926, 2856, 2226, 1901, 1601, 1494, 1091, 831 cm^{-1}; MS (EI) m/z (%) 366 ($M^+ + 1$, 61), 298 (76), 279 (96), 211 (100), 185 (20), 149 (40). Anal. calcd for $C_{21}H_{13}Cl_2NO$: C, 68.87; H, 3.58. Found: C, 68.92; H, 3.91.

(*Z*)-1-Methoxy-4-(1-(4-nitrophenoxy)-2-phenylvinyl)benzene (6a) and (*Z*)-1-Methoxy-4-(2-(4-nitrophenoxy)-2-phenylvinyl)-benzene (6a′): 326 mg, 94% yield; yellow thick liquid; $R_f = 0.40$ (49:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) olefin-H for **6a**/**6a′** δ 6.73 (s, 1H, 31%; minor)/6.64 (s, 1H, 69%; major); HPLC analysis (Daicel Chiralpak AS-H column, hexane/*i*-PrOH = 97:3 for elution, flow rate = 1.0 mL/min; $\lambda = 254$ nm) for **6a**/**6a′** = t_R (7.87 min, 37%; minor)/(8.47 min, 63%; major); ^1H NMR (400 MHz, $CDCl_3$) for **6a** + **6a′** δ 8.12 (br d, $J = 9.2$ Hz, 4H; 2H (for major) + 2H (for minor)), 7.58−7.44 (m, 8H; 4H (for major) + 4H (for minor)), 7.36−7.28 (m, 4H; 2H (for major) + 2H (for minor)), 7.22−7.18 (m, 2H; 1H (for major) + 1H (for minor)), 7.12−7.05 (m, 4H; 2H (for major) + 2H (for minor)), 6.89−6.80 (m, 4H; 2H (for major) + 2H (for minor)), 6.73 (s, 1H, minor), 6.64 (s, 1H, major), 3.78 (s, 3H, major), 3.77 (s, 3H, minor); ^{13}C NMR (101 MHz, $CDCl_3$) for **6a** + **6a′** δ 161.5, 160.1, 148.4, 142.4, 134.0, 130.6, 128.7, 128.5, 127.5, 127.0, 125.9, 125.2, 116.2, 114.2, 55.2 (for major regioisomer); and 159.2, 146.7, 134.8, 130.6, 128.8, 128.5, 127.0, 126.4, 126.0, 125.2, 116.8, 116.0, 115.4, 114.0, 55.1 (for minor regioisomer); IR (neat) for **6a** + **6a′** ν_{max} 3080, 2934, 2837, 1637, 1591, 1342, 1238, 1022, 846 cm^{-1}; MS (EI) m/z (%) for **6a** + **6a′** 348 ($M^+ + 1$, 100), 241 (97), 209 (11), 165 (3). Anal. calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found (as a mixture of **6a** + **6a′**): C, 72.55; H, 4.88; N, 4.07.

(*Z*)-1-Nitro-4-(1-phenylprop-1-en-2-yloxy)benzene (6b) and (*Z*)-1-Nitro-4-(1-phenylprop-1-enyloxy)benzene (6b′): 237 mg, 93% yield; yellow thick liquid; ^1H NMR (400 MHz, $CDCl_3$) olefin-H for **6b** and **6b′** δ 6.06 (s, 1H, 30%; minor) 6.02 (q, $J = 7.2$ Hz, 1H, 70%; major); HPLC analysis (Daicel Chiralcel OD-H column, hexane/*i*-PrOH = 99:1 for elution, flow rate = 1.0 mL/min;

$\lambda = 267$ nm) for **6b**/**6b′** = t_R (4.33 min, 32%; minor)/(4.62 min, 68%; major).

(*Z*)-1-Nitro-4-(1-phenylprop-1-enyloxy)benzene (6b′, major): light yellow thick liquid; R_f = 0.60 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.33−7.24 (m, 3H), 7.03 (d, J = 9.2 Hz, 2H), 6.02 (q, J = 7.2 Hz, 1H), 1.73 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 149.2, 142.2, 134.3, 128.7, 128.4, 126.1, 124.8, 115.5, 113.2, 11.4; IR (neat) ν_{max} 3080, 2989, 2920, 1666, 1591, 1342, 1109, 750 cm^{-1}; MS (EI) m/z (%) 256 (M^+ + 1, 100), 240 (22), 149 (46), 135 (3). Anal. calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.49; H, 5.10; N, 5.55.

(*Z*)-1-Nitro-4-(1-phenylprop-1-en-2-yloxy)benzene (6b, minor): light yellow thick liquid; R_f = 0.58 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.28−7.20 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 8.8 Hz, 2H), 6.06 (s, 1H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 147.5, 142.7, 134.0, 128.5, 128.3, 127.3, 126.1, 117.4, 116.5, 19.7; IR (neat) ν_{max} 3082, 2922, 2849, 1682, 1591, 1340, 1240, 1109, 748 cm^{-1}; MS (EI) m/z (%) 256 (M^+ + 1, 36), 241 (10), 154 (55), 138 (100). Anal. calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.65; H, 5.10; N, 5.43.

(Z)-1-Nitro-4-(1-phenylhex-1-en-2-yloxy)benzene (6c) and (Z)-1-Nitro-4-(1-phenylhex-1-enyloxy)benzene (6c′): 241 mg, 81% yield; yellow thick liquid; R_f = 0. 40 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) olefin-H for **6c**/**6c′** δ 6.08 (s, 1H, 57%; major)/5.95 (s, 1H, 43%; minor); HPLC analysis (Daicel Chiralpak AS-H column, hexane/*i*-PrOH = 97:3 for elution, flow rate = 1.0 mL/min; λ = 254 nm) for **6c**/**6c′** = t_R (6.96 min, 38%; minor)/(7.45 min, 62%; major); ^{1}H NMR (400 MHz, $CDCl_3$) for **6c** + **6c′** δ 8.25−8.15 (m, 4H; 2H (for major) + 2H (for minor)), 7.48−7.38 (m, 4H; 2H (for major) + 2H (for minor)), 7.32−7.20 (m, 4H; 2H (for major) + 2H (for minor)), 7.18−7.12 (m, 2H; 1H (for major) + 1H (for minor)), 7.08−6.99 (m, 4H; 2H (for major) + 2H (for minor)), 6.08 (s, 1H, major), 5.95 (t, J = 7.6 Hz, 1H, minor), 2.33 (t, J = 7.2 Hz, 2H; 1H (for major) + 1H (for minor)), 2.17 (q, J=7.2 Hz, 2H; 1H (for major) + 1H (for minor)), 1.68−1.50 (m, 4H; 2H (for major) + 2H (for minor)), 1.49−1.27 (m, 4H; 2H (for major) + 2H (for minor)), 0.96−0.81 (m, 6H; 3H (for major) + 3H (for minor)); ^{13}C NMR (101 MHz, $CDCl_3$) for **6c** + **6c′** δ 160.9, 151.4, 142.5, 133.9, 128.7, 128.5, 128.4, 126.1, 124.9, 116.3, 33.2, 29.1, 22.1, 13.9 (for major regioisomer); and 162.7, 148.3, 142.1, 134.2, 128.4, 127.3, 119.1, 117.7, 116.7, 115.6, 31.2, 25.6, 22.4, 13.9 (for minor regioisomer); IR (neat) for **6c** + **6c′** ν_{max} 3082, 3026, 2957, 2930, 1668, 1591, 1516, 1342, 1242, 1111, 850, 750 cm^{-1}; MS (EI) m/z (%) for **6c** + **6c′** 296 (M^+ − 1, 86), 278 (11), 154 (17), 138 (100). Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found (as a mixture of **6c** + **6c′**): C, 72.65; H, 6.41; N, 4.76.

(*Z*)-1-Methoxy-3-(1-(4-methoxyphenyl)-2-phenylvinyloxy)-benzene (6d) and (*Z*)-1-Methoxy-3-(2-(4-methoxyphenyl)-1-phenyl-vinyloxy)benzene (6d′): 101 mg, 63% yield; pale yellow solid; R_f= 0.26 (95:5 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) olefin-H for **6d**/**6d′** δ 6.58 (s, 2H; 1H (for major) + 1H (for minor)); HPLC analysis (Daicel Chiralpak AS-H column, hexane/*i*-PrOH = 19:1 for elution, flow rate = 0.3 mL/min; λ = 254 nm) for **6d**/**6d′** = t_R (13.9 min, 91%; major)/(14.49 min, 9%; minor); ^{1}H NMR (400 MHz, $CDCl_3$) for **6d** + **6d′** δ 7.67−7.59 (m, 6H; 3H (for major) + 3H (for minor)), 7.55 (d, J = 8.0 Hz, 2H; 1H (for major) + 1H (for minor)), 7.36−7.25 (m, 4H; 2H (for major) + 2H (for minor)), 7.21 (t, J=8.0 Hz, 2H; 1H (for major) + 1H (for minor)), 7.14 (t, J=8.0 Hz, 2H; 1H (for major) + 1H (for minor)), 6.87 (d, J = 8.0 Hz, 4H; 2H (for major) + 2H (for minor)), 6.65 (br s, 4H; 2H (for major) + 2H (for minor)), 6.58 (s, 2H; 1H (for major) + 1H (for minor)), 6.53 (d, J = 8.0 Hz, 2H; 1H (for major) + 1H (for minor)), 3.80 (s, 6H; 3H (for major) + 3H (for minor)), 3.75 (s, 6H; 3H (for major) + 3H (for minor)); ^{13}C NMR (101 MHz, $CDCl_3$) for **6d** + **6d′** δ 160.9, 159.8, 157.6, 149.4, 134.9, 130.4, 130.1, 130.0, 128.8, 128.6, 127.4, 115.1, 114.0, 108.7, 107.4, 102.7, 55.3, 55.2 (for major regioisomer); and 158.9, 147.8, 136.2, 130.4, 130.1, 128.8, 128.5, 128.0, 127.5, 127.4, 127.1, 125.6, 116.3, 114.0, 108.5, 102.6, 55.3, 55.2 (for minor regioisomer); IR (KBr) for **6d** + **6d′** ν_{max} 2926, 2852, 1604, 1510, 1251, 1141, 835, 692 cm^{-1}; MS (EI) m/z (%) for **6d** + **6d′** 333 (M^+ + 1, 100), 241 (38), 209 (5), 165 (3). Anal. calcd for $C_{22}H_{20}O_3$: C, 79.50; H, 6.06. Found (as a mixture of **6d** + **6d′**): C, 79.44; H, 6.12.

(*Z*)-4-(2-Phenyl-1-(3-(trifluoromethyl)phenyl)vinyloxy)biphenyl (6e) and (*Z*)-4-(1-Phenyl-2-(3-(trifluoromethyl)phenyl)vinyloxy)biphenyl (6e′): 147 mg, 35% yield; pale yellow thick liquid; R_f=0.17 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) olefin-H for **6e**/**6e′** δ 6.79 (s, 1H, 31%; minor)/6.73 (s, 1H, 69%; major); HPLC analysis (Daicel Chiralcel OD-H column, hexane/*i*-PrOH = 19:1 for elution, flow rate = 1.0 mL/min; λ = 254 nm) for **6e**/**6e′** = t_R (5.58 min, 30%; minor)/(5.99 min, 70%; major); ^{1}H NMR (400 MHz, $CDCl_3$) for **6e** + **6e′** δ 7.96 (br s, 2H; 1H (for major) + 1H (for minor)), 7.92 (d, J = 7.6 Hz, 1H; major), 7.80 (d, J = 8.0 Hz, 1H, minor), 7.74 (d, J = 7.6 Hz, 1H, major), 7.68 (d, J = 6.8 Hz, 2H, major), 7.60−7.25 (m, 25H; 11H (for major) + 14H (for minor)), 7.13 (t, J = 8.4 Hz, 4H; 2H (for major) + 2H (for minor)), 6.79 (s, 1H, minor), 6.73 (s, 1H, major); ^{13}C NMR (101 MHz, $CDCl_3$) for **6e** + **6e′** δ = 155.7, 151.4, 140.5, 135.5, 135.4, 131.8, 129.2, 129.0, 128.8, 128.6, 128.5, 128.0, 126.9, 126.8, 126.2, 125.9, 123.9, 118.4, 116.6 (for major regioisomer); and 155.5, 148.2, 137.0, 134.2, 131.4, 131.0, 130.7, 129.0, 128.8, 128.5, 128.0, 126.8, 126.2, 125.1, 122.8, 122.7, 116.6, 115.2 (for minor regioisomer); ^{19}F NMR (376 MHz, $CDCl_3$) for **6e**/**6e′** δ −62.67/−62.75; IR (neat) for **6e** + **6e′** ν_{max} 3061, 3034, 2959, 1892, 1641, 1604, 1514, 1446, 1168, 908, 761, 694 cm^{-1}; MS (EI) m/z (%) for **6e** + **6e′** 417 (M^+ + 1, 89), 315 (7), 279 (100), 265 (9), 247 (2). Anal. calcd for $C_{27}H_{19}F_3O$: C, 77.87; H, 4.60. Found (as a mixture of **6e** + **6e′**): C, 77.92; H, 4.56.

1,4-Bis[(*Z*)-1,2-diphenylvinyloxy]benzene (8a): 256 mg, 55% yield; colorless solid; mp 197−199 °C; R_f = 0.36 (95:5 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J=7.2 Hz, 4H), 7.56 (d, J=7.2 Hz, 4H), 7.34−7.25 (m, 10H), 7.24−7.17 (m, 2H), 6.86 (br s, 4H), 6.58 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 150.0, 136.0, 134.8, 128.9, 128.5, 128.3, 127.3, 126.1, 117.2, 116.5; IR (KBr) ν_{max} 2924, 2849, 1494, 1197, 1020, 758, 690 cm^{-1}; MS (EI) m/z (%) 467 (M^+ + 1, 46), 430 (8), 411 (11), 313 (11), 289 (13), 211 (100), 143 (14). Anal. calcd for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.61; H, 5.58.

1,3-Bis[(*Z*)-1,2-diphenylvinyloxy]benzene (8b): 440 mg, 94% yield; colorless solid; mp 116−117 °C; R_f = 0.45 (95:5 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J=7.2 Hz, 4H), 7.51−7.46 (m, 4H), 7.30−7.18 (m, 12 H), 7.02 (t, J=8.4 Hz, 1H), 6.75 (t, J=2.4 Hz, 1H), 6.61 (br s, 3H), 6.58 (d, J=2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 149.7, 135.9, 134.6, 130.3, 129.0, 128.6, 128.5, 128.4, 127.4, 126.0, 116.6, 110.1, 105.6; IR (KBr) ν_{max} 3057, 2926, 1597, 1483, 1446, 1257, 1132, 690 cm^{-1}; MS (EI) m/z (%) 467 (M^+ + 1, 100), 357 (4), 315 (11), 289 (8), 211 (94), 197 (5). Anal. calcd for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.41; H, 5.66.

1,2-Bis[(*Z*)-1,2-diphenylvinyloxy]benzene (8c): 33 mg, 7% yield; colorless solid; mp 142−143 °C; R_f = 0.39 (95:5 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 7.2, 4.4, Hz, 7H), 7.42−7.32 (m, 10H), 7.31−7.25 (m, 3H), 6.87 (dd, J = 6.0, 2.0 Hz, 2H), 6.76 (s, 2H), 6.68 (dd, J = 6.2, 3.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 145.4, 135.9, 134.9, 129.1, 128.9, 128.7, 128.6, 128.5, 128.0, 127.5, 126.1, 125.6, 122.5, 121.3, 116.9, 116.2, 108.5; IR (KBr) ν_{max} 3024, 1637, 1591, 1493, 1446, 1244, 1111, 1018, 920, 690 cm^{-1}; MS (EI) m/z (%) 467 (M^+ + 1, 6), 303 (22), 289 (69), 211 (59), 197 (100), 167 (4), 65 (13). Anal. calcd for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.45; H, 5.66.

(*Z*)-2-(1,2-Diphenylvinyloxy)phenol (8c′): 97 mg, 34% yield. colorless thick liquid; R_f = 0.18 (95:5, hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 2H), 7.57 (dt, J = 6.8, 1.6 Hz, 2H), 7.41−7.25 (m, 6H), 7.10 (dd, J = 8.0, 1.2 Hz, 1H), 6.92 (td, J = 8.0, 1.6 Hz, 1H), 6.81 (dd, J = 8.0, 1.6 Hz, 1H), 6.75 (s, 1H), 6.69 (td, J = 7.6, 1.6 Hz, 1H), 6.01 (s, 1H, −OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 145.6, 143.0, 135.1, 134.3, 128.7, 128.7, 128.59, 127.6, 125.6, 123.0, 120.4, 117.2, 115.6, 114.9; IR (neat) ν_{max} 3524, 3055, 2976, 1641, 1448, 1203, 1018, 918, 740 cm^{-1}; MS (EI) m/z (%) 289 ($M^+ + 1$, 100), 287 (12), 225 (3), 211 (63), 197 (11), 179 (5). Anal. calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.21; H, 5.56.

1,3,5-Tris[(*Z*)-1,2-diphenylvinyloxy]benzene (8d): 38 mg, 6% yield; colorless solid; mp 194−196 °C; R_f = 0.21 (95:5 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (br s, 6H), 7.33 (d, J = 7.2 Hz, 6H), 7.28−7.16 (m, 18H), 6.52 (s, 3H), 6.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 149.6, 135.6, 134.5, 128.9, 128.4, 128.2, 127.2, 125.9, 116.3, 99.7; IR (KBr) ν_{max} 2922, 2851, 1738, 1601, 1446, 1134, 761, 692 cm^{-1}; MS (EI) m/z (%) 662 ($M^+ + 1$, 100), 483 (47), 412 (35), 369 (16), 313 (24), 211 (51), 178 (14), 149 (9). Anal. calcd for $C_{48}H_{36}O_3$: C, 87.25; H, 5.49. Found: C, 87.16; H, 5.54.

3,5-Bis((*Z*)-1,2-diphenylvinyloxy)phenol (8d′): 44 mg, 9% yield; pale-brown thick liquid; R_f = 0.18 (90:10 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 4H), 7.51 (d, J = 3.4 Hz, 4H), 7.34−7.18 (m, 13H), 6.62 (s, 2H), 6.38 (s, 1H, −OH), 6.14 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 157.6, 149.5, 135.7, 134.5, 129.0, 128.6, 128.5, 128.4, 127.4, 125.8, 116.7, 98.3, 97.9; IR (neat) ν_{max} 3537, 3400 (−O−H), 2924, 1695, 1601, 1448, 1128, 916, 827 cm^{-1}; MS (EI) m/z (%) 483 ($M^+ + 1$, 100), 305 (5), 211 (8), 178 (8), 127 (3). Anal. calcd for $C_{34}H_{26}O_3$: C, 84.62; H, 5.43. Found: C, 84.71; H, 5.39.

(*Z*)-5-(1,2-Diphenylvinyloxy)benzene-1,3-diol (8d″): 99 mg, 32% yield; pale-brown thick liquid; R_f = 0.43 (60:40 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 6.8 Hz, 2H), 7.37−7.17 (m, 6H), 6.64 (s, 1H), 6.14 (s, 2H), 5.85 (s, 1H), 5.65 (br s, 2H, −OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 157.4, 149.2, 135.7, 134.5, 128.9, 128.6, 128.5, 128.4, 127.5, 125.7, 116.8, 97.1, 96.6; IR (neat) ν_{max} 3385 (−O−H), 2930, 1697, 1606, 1132, 1049, 825 cm^{-1}; MS (EI) m/z (%) 305 ($M^+ + 1$, 100), 291 (4), 211 (8), 179 (8), 127 (8). Anal. calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.85; H, 5.26.

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Supporting Information Available: Detailed experimental procedures, spectra, and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.