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–(Csp³) 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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achieve complicated transformations with ease. For example, gold catalysts promote cyclization through the reaction of phenolic/alcoholic–OH group with tethered alkynes and provide complex oxygen-functionalized heterocycles efficiently. A recent report for the synthesis of iso-flavanone involves gold(I)-catalyzed annulation of salicylalddehydes and acryl aldehydes without direct formation of the O–C bond. Intermolecular hydration and hydroalkoxylation of terminal and internal alkynes using water and 1° or 2°-alkyls have been achieved with gold catalysis, however, 3°-alcohol and phenols were found to be unreactive. The interesting disclosure of the Yamamoto group describes the success in effecting phenol addition to specific diyne precursors; the reaction proceeds either involving the η2-coordinated Pd(0) complex or via the active α-cumulenyl palladium intermediate. A regioselective addition of activated 4-chlorophenol to the specific case of ruthenocene-bearing alkyn e was demonstrated by Sato and co-workers. The transannular addition of 4-chlorophenol to 1,1-dialkynylenefurocene was reported recently. The reactivity of internal unactivated alkynes with oxygen-bearing nucleophiles is poor compared to that of terminal alkynes. Considering the above shortcomings, we envisioned that the simple intermolecular addition of phenols to unactivated alkynes is a challenging problem (eq 1). It would provide a novel synthetic strategy for creating a range of vinyl ether skeletons exclusively with Z-olefin stereochemistry in one step. Furthermore, this new transformation would find wide application in the synthesis of benzofuran, benzoazathiin, and flavonoid frameworks of medicinally useful targets. 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 annihilation of phenols and alkynes involving C–H bond functionalization. To start with, reaction of a simple and activated nucleophile 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 (AuCl3), 4a/4b, and Ag2CO3 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). Other silver salts, such as AgOTf, AgOAac, AgBF4, and AgNO3, 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 PPh3 and PCy3 (entries 3–5). Explorations of various combinations of ligands with gold catalysts such as AuCl, PPh3AuCl, PPh2AuOTf, PPh2AuBF4, and AuBr3 also led to poor yields of 3aa. AuCl3 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 CH2Cl2 appeared to be effective. Among other Buchwald ligands screened (entries 6–9), 4b (JohnPhos) with Ag2CO3 in CH2Cl2 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.
were used for 24 h.

Dai, L.-Z.; Shi, Y.-L.; Zhao, G.-L.; Shi, M. J. Org. Lett. 967. (e) Zhao, G.-L.; Shi, Y.-L.; Shi, M.

Y.-L.; Shi, M. condition B [AuCl₃ (5 mol %), ligand such as Ag₂CO₃, is sufficient for activated phenols with lower electronic affinity. Bases and solvents (entries 19-22) revealed that relatively strong bases, such as K₂CO₃, are required in the case of electron-rich phenols having higher pKₐ, and a milder base, such as Ag₂CO₃, is sufficient for activated phenols with lower electronic affinity.

To investigate the generality of the addition of various phenols with symmetrical and unsymmetrical alkynes, condition A [AuCl₃ (3 mol %), ligand 4b (3 mol %), Ag₂CO₃ base in CH₂Cl₂ at 100 °C] is employed for nonactivated phenols. The effect of substitution on the phenols in the hydrophenoxylation of diphenylacetylene was surveyed 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 K₂CO₃ 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 K₂CO₃, are required in the case of electron-rich phenols having higher pKₐ, and a milder base, such as Ag₂CO₃, is sufficient for activated phenols with lower pKₐ.

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prolonged reaction time, justifying the moderate yield encountered in this reaction. Activated phenols bearing F, Cl, or CF₃ groups at the 4- and/or 3-positions gave the desired hydrophenoxyl 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.²⁹ 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 hydrophenoxyl 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 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, hydrophenoxyl 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 hydrophenoxyl 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 hydrophenoxyl 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.²⁹

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

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(²⁰) For the details of spectral data, see Supporting Information.
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.\(^2\) 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.\(^2\)

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 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 2) were 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) with 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.

### Table 3. Hydrophenoxylation of 1 with Symmetrical Alkynes\(^a,b\)

<table>
<thead>
<tr>
<th>Alkynes</th>
<th>Products</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexyl-3-phenylacetylene (2a)</td>
<td>3ab, 48 h, B, 55%</td>
<td></td>
</tr>
<tr>
<td>1-methyl-4-phenyl-2-pentecenyne (2b)</td>
<td>3bb, 48 h, B, 94%</td>
<td></td>
</tr>
<tr>
<td>1-methyl-4-phenyl-2-pentecenyne (2c)</td>
<td>3cc, 96 h, B, 79%</td>
<td></td>
</tr>
<tr>
<td>1-methyl-4-phenyl-2-pentecenyne (2d)</td>
<td>3bc, 72 h, B, 96%</td>
<td></td>
</tr>
<tr>
<td>1-methyl-4-phenyl-2-pentecenyne (2e)</td>
<td>3cd, 120 h, B, 67%</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Reactions were performed employing \(1\) (2.0 mmol) and \(2\) (1.0 mmol) at 100 °C. Condition A: \(\text{Ag}_2\text{CO}_3\) (2.0 mmol), \(\text{AuCl}_3\), and \(4b\) (3 mol % each) in \(\text{CH}_2\text{Cl}_2\) (1.0 mL) were used. Condition B: \(\text{K}_2\text{CO}_3\) (2.0 mmol), \(\text{AuCl}_3\), and \(4b\) (5 mol % each) in \(\text{THF}\) (1.0 mL) were used. \(^{b}\) Isolated yields based on alkynes; average of two runs. \(^{2d}\) (0.5 mmol) was used.

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\(^{(21)}\) A competitive experiment was performed reacting 4-nitrophenol (\(1b\), 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 \(\text{AuCl}_3\) (1.9 mg, 3 mol%), ligand \(4b\) (1.8 mg, 3 mol %), and \(\text{Ag}_2\text{CO}_3\) (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.

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 hydrophenoxylations of polyphenols with symmetrical alkynes were 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


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**TABLE 4. Hydrophenoxylations of 1 with Unsymmetrical Alkynes (5)**

<table>
<thead>
<tr>
<th>entry</th>
<th>phenol</th>
<th>alkyne</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^a)</td>
<td>1h</td>
<td>5a</td>
<td>6a, 6a'</td>
</tr>
<tr>
<td>2(^a)</td>
<td>1h</td>
<td>5b</td>
<td>6b, 6b'</td>
</tr>
<tr>
<td>3(^a)</td>
<td>1h</td>
<td>5c</td>
<td>6c, 6c'</td>
</tr>
<tr>
<td>4(^b)</td>
<td>1k</td>
<td>5a</td>
<td>6d, 6d'</td>
</tr>
<tr>
<td>5(^b)</td>
<td>1r</td>
<td>5d</td>
<td>6e, 6e'</td>
</tr>
</tbody>
</table>

\(^a\)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.

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 carbo-philic 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 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 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$_2$CO$_3$, AuCl$_3$, and 4b in THF-$d_6$ 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

### Table 5. Hydrophenoxylation of Polyphenols (7) with 2a$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>product</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7a</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>7b</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>7c</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>7d</td>
<td>6</td>
</tr>
</tbody>
</table>

$^a$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$_2$CO$_3$ (4.0 mmol each), AuCl$_3$ and 4b (10 mol % each), and continued for 96 h. $^d$Reaction was continued for 168 h; di- (8d) and mono-O-vinylated phloroglucinols (8d*) were obtained.

### Scheme 1. Proposed Catalytic Cycle

[Diagram showing the catalytic cycle]

AuCl₃ and 4b in THF-d₆ at room temperature shows identical results in the ³¹P NMR spectrum to that observed in the previous reaction. Similarly, the ³¹P NMR spectrum of the sample of AuCl₃ and 4b in CDCl₃ at room temperature shows three peaks at δ = 106.2, 59.9, and 18.0 ppm; the signal at δ = 18.0 ppm corresponds to 4b in CDCl₃, and the peaks at δ = 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 AuCl₃ and Ph₃P=AuCl with 4b (entries 10 and 11, Table 1). However, the ³¹P NMR spectrum of a mixture of AuCl₃ and 4b in CDCl₃ shows two signals at δ = 60.0 and 17.9 ppm in a 1:4 ratio corresponding to 15 and 4b, respectively, and the sample of Ph₃P=AuCl and 4b in CDCl₃ shows no formation of 15; the latter shows signals at δ = 18.2 (for 4b) and 29.0 ppm. 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 hydrophenoxylations 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. 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 K₂CO₃ (2.0 mmol) were taken. The tube was evacuated and backfilled with argon three times. In a separate Schlenk flask, a heterogeneous solution of AuCl₃ (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.

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 K₂CO₃ (2.0 mmol) were taken. The flask was evacuated and backfilled with argon three times. A solution of AuCl₃ (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.
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(3a): 270 mg, 85% yield; pale yellow solid; mp 112–114 °C; Rf = 0.53 (49:1 hexane/EtOAc); 1H NMR (400 MHz, CDCl3) 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); 13C NMR (101 MHz, CDCl3) δ 156.9, 149.3, 148.7, 134.8, 134.0, 130.3, 129.0, 128.9, 128.8, 128.6, 128.5, 127.8, 127.2, 127.1, 125.8, 117.2, 116.2; MS (EI) m/z (%) = 318 (M+ 1, 68), 302 (2), 288 (18), 211 (100), 197 (4). Anal. calecd for C32H21NO4: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.68; H, 4.81; N, 4.46.

(3b): 151 mg, 50% yield; yellow solid; mp 78–81 °C; Rf = 0.43 (49:1 hexane/EtOAc); 1H NMR (400 MHz, CDCl3) 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 (dd, 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); 13C NMR (101 MHz, CDCl3) 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) vmax 3059, 2924, 2845, 1697, 1591, 1456, 1471, 682, 692 cm−1; MS (EI) m/z (%) = 301 (M+ 1, 77), 211 (100), 179 (4). Anal. calecd for C14H11NO3: C, 83.98; H, 5.37. Found: C, 84.12; H, 5.33.

(3c): 129 mg, 45% yield; colorless solid; mp 72–73 °C; Rf = 0.37 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.09 (d, J = 8.0 Hz, 1H), 7.08–7.05 (m, 1H), 7.00–6.92 (m, 1H), 6.94 (t, J = 4.8 Hz, 1H), 6.87 (dt, J = 8.4, 4.8 Hz, 1H), 6.61 (s, 1H); 13C NMR (101 MHz, CDCl3) δ 153.5, 149.6, 149.0, 139.0, 135.6, 128.5, 128.3, 127.6, 127.4, 127.1, 126.8, 125.0, 124.9, 123.9, 119.0, 118.0, 116.3, 115.0, 114.7, 113.7, 111.7, 110.5, 107.8, 107.6; MS (KBr) vmax 3045, 2226, 1605, 1502, 1331, 918, 777 cm−1; MS (EI) m/z (%) = 298 (M+ 1, 100), 211 (97), 179 (5), 165 (2). Anal. calecd for C14H11NO3: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.62; H, 4.98; N, 4.76.

(3d): 262 mg, 90% yield; colorless solid; mp 100–101 °C; Rf = 0.62 (49:1 hexane/EtOAc); 1H NMR (400 MHz, CDCl3) δ 7.41–7.38 (m, 4H), 7.38–7.28 (m, 7H), 7.27–7.10 (m, 1H), 7.13 (t, J = 8.4 Hz, 1H), 6.67 (s, 1H), 6.66–6.50 (m, 2H), 6.56–6.50 (m, 1H), 3.75 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 152.5, 149.6, 143.0, 130.7, 128.8, 128.5, 128.4, 127.4, 126.1, 122.0, 113.7, 116.3; IR (KBr) vmax 3055, 3022, 1591, 1487, 1222, 1167, 1020, 763 cm−1; MS (EI) m/z (%) = 273 (M+ 1, 100), 179 (4), 165 (3). Anal. calecd for C14H11NO3: O, 88.20; H, 5.92; N, 5.81. Found: C, 88.21; H, 6.29.

(3e): 70 mg, 22% yield; pale yellow thick liquid; mp 78–84 °C; Rf = 0.50 (hexane); 1H NMR (400 MHz, CDCl3) 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); 13C NMR (101 MHz, CDCl3) δ 149.5, 143.9, 134.3, 132.8, 129.1, 128.9, 128.7, 125.9, 125.8, 121.8, 116.7, 111.7; IR (KBr) vmax 3059, 2920, 1645, 1549, 1480, 1386, 1370, 1261, 1219, 1202, 767 cm−1; MS (EI) m/z (%) = 214 (M+ 1, 68), 192 (2), 188 (18), 178 (100), 197 (4). Anal. calecd for C14H10NO3: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.62; H, 4.81; N, 4.51.

(3f): 237 mg, 68% yield; colorless solid; mp 84–86 °C; Rf = 0.50 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.74–7.67 (m, 4H), 7.51 (d, J = 7.2, 1.2 Hz, 2H), 7.42–7.33 (m, 5H), 7.29–7.20 (m, 1H), 6.93 (dd, J = 7.2, 1.2 Hz, 2H), 6.86–6.78 (m, 1H), 6.71 (s, 1H), 6.64–6.56 (m, 2H); 13C NMR (101 MHz, CDCl3) δ 164.6, 162.7, 157.8, 157.7, 149.3, 135.6, 134.4, 130.5, 130.4, 129.0, 128.7, 128.6, 125.9, 125.9, 117.0, 112.0, 110.8, 109.8, 104.2, 104.1; 19F NMR (376 MHz, CDCl3) δ −111.2; IR (KBr) vmax 3050, 1608, 1485, 1446, 1388, 1263, 1126, 1020, 835, 688 cm−1; MS (EI) m/z (%) = 291 (M+ 1, 100), 211 (65), 197 (2), 179 (8). Anal. calecd for C20H15FO: C, 82.74; H, 4.21. Found: C, 82.65; H, 5.26.
(Z)-1-(Hex-3-en-3-yl)oxy-4-methoxybenzene (3ab): 122 mg, 55% yield; pale yellow liquid; Rf = 0.32 (hexane); 1H NMR (400 MHz, CDCl3) δ 7.68 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 2H), 2.52 (t, J = 7.2 Hz, 3H), 1.54–1.34 (m, 3H), 1.47–1.38 (m, 2H), 0.98–0.89 (m, 6H); 13C NMR (100 MHz, CDCl3) δ 156.5, 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) νmax 2959, 2928, 2928, 1684, 1606, 1543, 1230, 1167, 835, 761, 696 cm−1; MS (EI) m/z (%) 281 (M+ + 1, 100), 178 (3), 165 (5), 143 (67), 129 (14). Anal. calc for C13H11NO: C, 66.9; H, 6.45.

(Z)-1-Methyl-4-(oct-4-en-4-yloxy)benzene (3cc): 268 mg, 96% yield; colorless liquid; Rf = 0.60 (hexane); 1H NMR (400 MHz, CDCl3) 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 = 7.2 Hz, 2H), 1.53–1.43 (m, 2H), 1.43–1.33 (m, 2H), 0.96–0.87 (m, 6H); 13C NMR (100 MHz, CDCl3) δ 154.6, 150.5, 140.5, 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) νmax 2959, 2928, 2928, 1684, 1606, 1543, 1230, 1167, 835, 761, 696 cm−1; MS (EI) m/z (%) 281 (M+ + 1, 100), 178 (3), 165 (5), 143 (67), 129 (19). Anal. calc for C13H11NO: C, 66.9; H, 6.45. Found: C, 65.6; H, 7.80.

(Z)-1-Fluoro-4-(oct-4-en-4-yloxy)benzene (3cc): 210 mg, 95% yield; colorless liquid; Rf = 0.55 (hexane); 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 158.0, 150.4, 129.8, 118.6, 108.3, 106.8, 102.1, 55.2, 34.4, 27.2, 22.7, 20.1, 13.9, 13.6; IR (neat) νmax 2959, 2928, 2928, 1684, 1602, 1545, 1280, 1143, 982, 850, 688 cm−1; MS (EI) m/z (%) 235 (M+ + 1, 100), 143 (63), 125 (5). Anal. calc for C13H11FNO: C, 78.68; H, 9.46. Found: C, 76.95; H, 9.39.

(Z)-1-Fluro-4-(oct-4-en-4-yloxy)benzene (3cc): 210 mg, 95% yield; colorless liquid; Rf = 0.55 (hexane); 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 158.0, 150.4, 129.8, 118.6, 108.3, 106.8, 102.1, 55.2, 34.4, 27.2, 22.7, 20.1, 13.9, 13.6; IR (neat) νmax 2959, 2928, 2928, 1684, 1602, 1545, 1280, 1143, 982, 850, 688 cm−1; MS (EI) m/z (%) 235 (M+ + 1, 100), 143 (63), 125 (5). Anal. calc for C13H11FNO: C, 78.68; H, 9.46. Found: C, 76.95; H, 9.39.

(Z)-1-Fluro-4-(oct-4-en-4-yloxy)benzene (3cc): 210 mg, 95% yield; colorless liquid; Rf = 0.55 (hexane); 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 158.0, 150.4, 129.8, 118.6, 108.3, 106.8, 102.1, 55.2, 34.4, 27.2, 22.7, 20.1, 13.9, 13.6; IR (neat) νmax 2959, 2928, 2928, 1684, 1602, 1545, 1280, 1143, 982, 850, 688 cm−1; MS (EI) m/z (%) 235 (M+ + 1, 100), 143 (63), 125 (5). Anal. calc for C13H11FNO: C, 78.68; H, 9.46. Found: C, 76.95; H, 9.39.
λ = 267 nm) for 6b 6bδ = τ9 (4.33 min, 32%; minor) (4.62 min, 68%; major).

(Z)-1-Nitro-4-(1-phenylprop-1-en-1-yl)benzene (6b, major): light yellow thick liquid; Rf = 0.60 (49:1 hexane/ EtOAc); 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) δ 162.4, 149.2, 142.2, 134.5, 128.7, 128.4, 126.1, 124.8, 115.5, 113.2, 11.4; IR ( neat) vmax 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. calc for C21H16NO: 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-yl)benzene (6b, minor): light yellow thick liquid; Rf = 0.58 (49:1 hexane/ EtOAc); 1H NMR (400 MHz, CDCl3) δ 8.19 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.28–7.20 (m, 2H), 2.17 (d, J = 7.6 Hz, 1H), 0.70 (d, J = 8.8 Hz, 2H), 6.06 (s, 1H), 2.04 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 160.7, 147.5, 147.2, 134.0, 128.5, 128.3, 127.3, 126.1, 117.4, 116.5, 19.7; IR ( neat) vmax 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. calc for C21H16NO: C, 70.28; H, 5.13; N, 5.49. Found: C, 70.65; H, 5.10; N, 5.43.

(Z)-1-Nitro-4-(1-phenylhex-1-en-1-yl)benzene (6c) and (Z)-1-Nitro-4-(1-phenylhex-1-en-1-yl)benzene (6cδ): 81% yield; yellow thick liquid; Rf = 0.40 (49:1 hexane/ EtOAc); 1H NMR (400 MHz, CDCl3) olefin-H for 6cδ 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 6cδ δ = τ9 (6.96 min, 38%; minor) 7.45 (min, 62%; major); 13C NMR (400 MHz, CDCl3) for 6cδ δ = 151.4, 114.0, 101.3, 99.8, 99.5, 97.9, 72.9, 66.9, 29.8, 23.9, 14.3; IR ( neat) νmax 3024, 2957, 2920, 1666, 1591, 1340, 1240, 1109, 748 cm–1; MS (EI) m/z (%) 256 (M+ + 1, 36), 241 (10), 154 (55), 138 (100). Anal. calc for C21H16NO: C, 70.28; H, 5.13; N, 5.49. Found: C, 70.65; H, 5.10; N, 5.43.

(Z)-1-Nitro-4-(2,4-diphenyloxly)benzene (6d) and (Z)-1-Nitro-4-(2,4-diphenyloxly)benzene (6dδ): 101 mg, 63% yield; pale yellow solid; Rf = 0.26 (95:5 hexane/ EtOAc); 1H NMR (400 MHz, CDCl3) olefin-H for 6d δ δ = τ9 (13.9 min, 91%; major) (14.49 min, 9%; minor); 1H NMR (400 MHz, CDCl3) for 6d δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ δ
(Z)-2-(1,2-Diphenylvinloxy)phenol (8c): 97 mg, 34% yield; colorless thick liquid; $R_f = 0.18$ (95:5 hexane/EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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), 6.75 (s, 1H), 6.69 (td, $J = 7.6$, 1.6 Hz, 1H), 6.01 (s, 1H, -OH); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.1, 145.6, 143.0, 135.1, 134.3, 128.7, 128.5, 127.6, 125.6, 123.0, 120.4, 117.2, 115.6, 114.9; IR (neat) $\nu_{\text{max}}$ 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-diphenylvinloxy]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$_3$) $\delta$ 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$_3$) $\delta$ 158.2, 149.6, 135.6, 134.5, 128.9, 128.4, 128.2, 127.2, 125.9, 116.3, 99.7; IR (KBr) $\nu_{\text{max}}$ 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-diphenylvinloxy]phenol (8d): 44 mg, 9% yield; pale-brown thick liquid; $R_f = 0.18$ (90:10 hexane/EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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) $\nu_{\text{max}}$ 3537, 3400 (-OH), 2921, 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$_{14}$H$_{12}$O$_2$: C, 84.62; H, 5.49. Found: C, 84.71; H, 5.39.

(1Z)-5-(1,2-Diphenylvinloxy)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$_3$) $\delta$ 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$_3$) $\delta$ 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) $\nu_{\text{max}}$ 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.