## **Efficient Synthesis of Oxygenated Terphenyls and Other Oligomers:** Sequential Arylation Reactions Through Phenol Oxidation-Rearomatization

## Toshifumi Dohi, Tohru Kamitanaka, Shohei Watanabe, Yinjun Hu, Naohiko Washimi, and Yasuyuki Kita\*<sup>[a]</sup>

Oxygenated terphenyls and their derivatives are naturally-occurring compounds of particular interest in many scientific fields in which they have been applied following synthetic modification.<sup>[1]</sup> Typically, their preparation mostly relies on elegant metal-catalyzed coupling reactions using substrates prefunctionalized with metal and halogen atoms.<sup>[2]</sup> Recently, direct arylation of carbon-hydrogen bonds in reactions of phenols with aryl halides have been investigated to find an improved synthetic route to oxygenated terphenyls, that is, one that has less steps and avoids bottlenecks caused by the preparation and use of functionalized substrates, a problem that features in conventional methods.<sup>[3]</sup> However, these reactions involving direct arylations of carbon-hydrogen bonds have several problems regarding reaction control, such as undesired multiple arylation reactions of a single substrate and the difficulty in introducing two different aryl groups; these problems are due to the aromatic products being reactive and sensitive under the reaction conditions. Therefore, a more concise and promising route to terphenyls is still in demand, especially a route that allows control of the reactions and access to diverse products.

In this communication, we report a concise and expeditious route toward well-defined oxygenated terphenyls and other longer oligomers using a new strategy involving controlled sequential arylation reactions of phenols under mild reaction conditions [Eq. (1)]. Our developed approach involves two important steps: 1) the oxidation of phenols to the quinone monoacetal<sup>[4]</sup> and 2) a bond-forming rearomatization reaction of the quinone monoacetal.<sup>[5,6]</sup>

The quinone monoacetal 1a' was first synthesized by treatment of a solution of phenol 1a in methanol with an oxidant, specifically, the hypervalent iodine reagent, PhI-(OAc)<sub>2</sub> (Scheme 1).<sup>[7,8]</sup> The obtained quinone **1a'** was then subjected to a controlled coupling reaction with an oxygenated aromatic nucleophile (Ar<sup>1</sup>H) in the presence of a solid

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Scheme 1. New synthetic strategy for the preparation of oxygenated terphenyls based on aryl coupling reactions involving sequential oxidation/ HFIP = 1,1,1,3,3,3-hexafluoroisopropanol. rearomatization. PIDA = phenyliodine(III) diacetate.

acid promoter in the form of montmorillonite (MT) clay;<sup>[5a]</sup> the aryl-aryl bond was formed successfully when the reaction was carried out in a solvent mixture containing a fluoroalcohol,<sup>[9]</sup> thus giving biaryl **2aa**, that is, the monoarylated intermediate.<sup>[10]</sup> Notably, this rearomatization reaction should occur with regeneration of the initial phenol functionality.<sup>[11]</sup> Therefore, repetition of the net arylation reaction should be possible using the biaryl phenol 2aa with a second nucleophile (Ar<sup>2</sup>H). Based on this consideration, we examined the further transformation of product 2aa to terphenyl 3aaa (the second nucleophile being the same as the first nucleophile, 1,3-dimethoxybenzene). To our delight, the reaction worked well, thus suggesting that the presence of the bulky aryl group (Ar<sup>1</sup>) in the corresponding biaryl-derived quinone acetal does not affect the activation mode of the MT clay. This arylation reaction of biaryl 2aa proceeded

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in good yield via the corresponding quinone intermediate; the target terphenyl **3aaa** is a rather strained molecule with more restricted conformational flexibility compared to biaryl **2aa**. All the steps starting from phenol **1a** worked well under ambient reaction conditions and were not affected by the presence of moisture.

With this success, we explored the scope of the second arylation step by subjecting aryl quinone monoacetal 2aa', which was formed from biaryl 2aa, to the reaction conditions (MT K-10 as the clay catalyst)<sup>[12]</sup> in the presence of a variety of oxygenated aromatic nucleophiles with substituents and functional groups (Ar<sup>2</sup>H) attached to the most sterically demanding positions (Table 1). A series of oxygenated terphenyls 3aab-aad were obtained in good to excellent yields (Table 1, entries 1-3). In addition, when using an allyl-protected oxygenated aryl nucleophile, the terphenyl 3aae was formed in preference to a potential side reaction involving the alkene moiety of the allyl groups (Table 1, entry 4).<sup>[5c]</sup> The oxygenated phenol, anilide, and naphthalene were all found to be suitable coupling partners, giving terphenyls 3aaf-aah (Table 1, entries 5-7). The pyrrole-containing terphenyl 3aai was also obtained by this method (Table 1, entry 8).<sup>[13]</sup> These reactions clearly demonstrate that our synthetic method is both flexible and chemoselective regarding the introduction of aromatic nucleophiles in both the biaryl and terphenyl-forming steps.<sup>[14]</sup> Interestingly, the use of a boron-containing aromatic nucleophile gave cyclic-boronate-containing terphenyl 3aaj, the protection of the phenolic oxygen atom occurring after workup (Scheme 2).<sup>[15]</sup> Obviously, the halogen and boron-functional-



Scheme 2. Synthesis of cyclic-boronate terphenyl **3aaj**. The use of the corresponding boronic-acid nucleophile gave the same cyclic product **3aaj** in comparable yield. pin = pinacolate.

ized terphenyls **3aad** and **3aaj** are valuable for preparing more elaborate terphenyl derivatives, which are difficult to access using conventional strategies involving metal-catalyzed reactions.<sup>[2,3]</sup>

To show that various starting phenols 1 could be used for providing diverse oxygenated terphenyl compounds 3 by this method, we subjected several substituted phenols 1 to a sequence of arylation reactions (Table 2). Using the standard reaction conditions (Scheme 1), phenols 1b-h having alkyl, aryl, halogen, oxygen, and cyclic substituents were transformed into the corresponding aryl phenols 2ba-ha, the aryl group (Ar<sup>1</sup>) being incorporated at the less-hindered position of the phenol ring with perfect levels of regioselec-





[a] Aryl quinone monoacetal **2aa'** was formed from aryl phenol **2aa**. All reactions were performed using 2 equiv of the aryl nucleophile (Ar<sup>2</sup>H), the isolated quinone acetal **2aa'**, and montmorillonite clay in an open flask at room temperature unless otherwise noted. [b] Yield based on quinone **2aa'**. [c] Overall yield from the starting phenol **1a** is shown in parenthesis. [d] 3 equiv of  $Ar^2H$  was used.



tivity (Table 2, entries 2–7). Therefore, the formation of the aryl-aryl bonds is very sensitive to the steric hindrance of

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![](_page_2_Figure_2.jpeg)

 Table 2. Terphenyls 3 from different phenols 1.<sup>[a]</sup>

[a] Intermediate quinone monoacetals were prepared by the reactions of either phenols 1 or aryl phenols 2 with PIDA in methanol (see Scheme 1). The following arylation reactions involving the obtained quinone acetals were all conducted using 2 equiv of the aryl nucleophiles ( $Ar^{1}H=1,3$ -dimethoxybenzene,  $Ar^{2}H=1,3,5$ -trimethoxybenzene). Detailed data for each step can be found in the Supporting Information. [b] Two-step yield from phenols 1. [c] Two-step yield from aryl phenols 2. Phenols 1: 4-methoxyphenol (1a, entry 1); 4-methoxy-3-methylphenol (1b, entry 2); 2-methoxy-(1,1'-biphenyl)-5-ol (1c, entry 3); 3-chloro-4-methoxy-1,3-benzenediol-3-benzoate (1f, entry 6); 2,3-dihydro-5-benzofuranol (1g, entry 7); 4-methoxy-3,5-dimethylphenol (1h, entry 8).

the substrates,<sup>[5a]</sup> while the second arylation step could occur at the sterically hindered positions to form the congested terphenyls **3** in the reactions of the obtained aryl phenols **2**. In most cases, the terphenyls **3** were obtained in high yields, however, the aryl phenol **2ea** failed to react with the aryl nucleophile ( $Ar^2H=1,3,5$ -trimethoxybenzene) probably because the reaction site of the corresponding intermediate quinone acetal is less electrophilic owing to the strong resonance effect of the *ortho*-methoxy substituent (Table 2, entry 5). However, when using a substrate with an *ortho*benzoyloxy substituent, the corresponding intermediate quinone acetal was sufficiently electrophilic to react with the second nucleophile (Table 2, entry 6).

The above results show that our method represents a mild and efficient route to fully *meta*-linked terphenyls **3** from phenols **1** with different aromatic nucleophiles, Ar<sup>1</sup>H and Ar<sup>2</sup>H. In addition, the method provides access to other structurally important isomers,<sup>[1]</sup> such as the *para*-linked terphenyl, by using simple synthetic techniques in combination with the unique recognition of the acetal group by the MT clay catalyst. The linear terphenyl isomer *para*-**3aaa** was obtained using the same starting material (**1a**) as that for *meta*-**3aaa**; the acetal part was desymmetrized by replacing methanol with a secondary alcohol in the first oxidation step of phenol **1a** (Scheme 3). In the resulting quinone inter-

![](_page_2_Figure_8.jpeg)

Scheme 3. Synthetic route to linear oxygenated terphenyls. Reaction conditions: a) iodomethane, potassium carbonate, acetone, reflux; b) aluminium chloride, dichloromethane, room temperature (73% for the two-step conversion).  $Ar^{1}H = Ar^{2}H = 1,3$ -dimethoxybenzene. PIFA = phenyl iodine(III) bis(trifluoroacetate).

mediate, the smaller group of the mixed acetal can preferentially interact with the interlayer protons within the sandwich sheets of the clay catalyst,<sup>[16]</sup> thus causing selective elimination of methanol during the arylation step. To transfer the phenol functionality to the *para* position, the phenol group of the intermediate *ortho*-aryl phenol was first protected as a methoxy group and then the isopropyl group was chemoselectively removed using aluminum chloride in  $CH_2Cl_2$ . Finally, the resulting *meta*-aryl phenol was transformed into terphenyl *para*-**3 aaa** using the developed reaction conditions.

We have shown above that our method provides access to terphenyls **3**, biaryls **2**, and their quinone acetals. We envisaged that the use of these synthetic compounds as substrates for our developed reaction might allow convergent access to a series of additional more-elongated oligomers.<sup>[17]</sup> Indeed, the use of the prepared aryl phenol **2ab** as the nucleophile for the arylation of quinone acetal **2ab**' gave two-plus-two tetrameric oligomer **4** as a single product (Scheme 4). Similarly, terphenyl **3abb** reacted with quinone **2ab**', thus affording the quinquephenyl **5** in 60 % yield. These synthetic oligophenols have recently found new applications in supramolecular chemistry and in the soft material sciences.<sup>[18]</sup> Interestingly, the oxygenated quater- and quinquephenyl compounds, **4** and **5**, respectively, seem to exist in rigid conformations in solution, as determined using NMR spec-

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Scheme 4. Convergent synthesis of more-elongated oligomers.

troscopy; upon heating the NMR sample within the spectrometer probe, coalescence of some of the signals associated with the methoxy groups occurred.<sup>[19]</sup>

In summary, we have established a new sequential arylation method involving the oxidation/rearomatization of phenols. The reaction, which involves guinone monoacetals as key intermediates, can be used for preparing valuable oxygenated terphenyls as well as diverse structurally-defined more-elongated oligomers. The reaction employs hypervalent iodine species as an oxidant and montmorillonite (MT) clay as an acid promoter for the rearomatizing arylation step; the reactions occur under mild reaction conditions and involve simple experimental procedures. The controlled coupling step, in contrast to known aryl-aryl coupling methods, requires neither organometallic compounds nor halogenated substrates, thus leading to fewer synthetic steps and enabling expeditious access to functionalized terphenyls, which can be used for preparing more elaborate terphenyl derivatives. Because oxygenated terphenyls and related oligomers have important applications and are found in nature, the method described herein should prove useful for the synthesis of natural products and analogues thereof, and for the preparation of these compounds for their study in other scientific fields.

#### **Experimental Section**

Typical procedure for the synthesis of terphenyls **3** by the sequential arylation of phenols **1**: To a solution of phenol **1a** (124 mg, 1.0 mmol) in methanol (10 mL) was added phenyliodine(III) diacetate (PIDA, 322 mg, 1.0 mmol) over 5 min at room temperature. The starting material was consumed within 2 h (confirmed by TLC analysis). The solvent was evaporated and the crude reaction mixture was extracted into ethyl acetate. The extract was treated with solid sodium bicarbonate and the suspension was filtered. The resulting filtrate was then concentrated in vacuo to afford a quantitative amount of the crude quinone monoacetal **1a'**, which was used in the next step without purification.

The crude quinone acetal 1a' was dissolved in a mixture of dichloromethane (0.3 mL) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 3 mL) and the resulting solution was treated with 1,3-dimethoxybenzene (Ar<sup>1</sup>H, 276 mg, 2 equiv) and montmorillonite K-10 clay (MT-K10, 100 mg) and the heterogeneous reaction mixture was stirred for 2 h at room temperature. After completion of the reaction, the insoluble clay was filtered through Celite, and then the filtrate was evaporated. The resulting crude residue was purified using column chromatography through silica gel (eluent: n-hexane/AcOEt 4:1) to give the pure product 2aa (234 mg, 90% yield from the phenol 1a) as a colorless powder. The excess 1,3-dimethoxybenzene was recovered during chromatography.

The above procedures were repeated using obtained aryl phenol **2aa** in place of phenol **1a**, the same oxidant, and 1,3-dimethoxybenzene as the second coupling partner ( $Ar^2H$ ) gave the terphenyl product **3aaa** in 78% yield from the aryl phenol **2aa**. MT-K10 could be reused several times without any loss in activity. Experimental procedures as well as characterization data for all terphenyl products **3** and their derivatives are included in the Supporting Information.

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**Keywords:** arylation • biaryls • oxidation • phenols • quinones

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[11] In contrast, the method described in Ref. [6a] only gave biphenols

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- 11] In contrast, the method described in Ref. [6a] only gave biphenols owing to restrictions in the type of aryl nucleophiles that could be used. Selective oxidation of such biphenols to quinone acetals has not been reported previously.
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#### **Arylation Reactions** -

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Efficient Synthesis of Oxygenated Terphenyls and Other Oligomers: Sequential Arylation Reactions Through Phenol Oxidation–Rearomatization

![](_page_5_Figure_6.jpeg)

**One by one**: Starting from simple phenols, a diverse series of oxygenated terphenyl compounds can be prepared in a concise and practical manner using sequential arylation reactions involving phenol oxidation/rearomatization and quinone monoacetal intermediates (see scheme). Many of the terphenyl products can be used for preparing well-defined oligomers and furthermore, contain valuable functional groups that can be transformed for further diversification.