

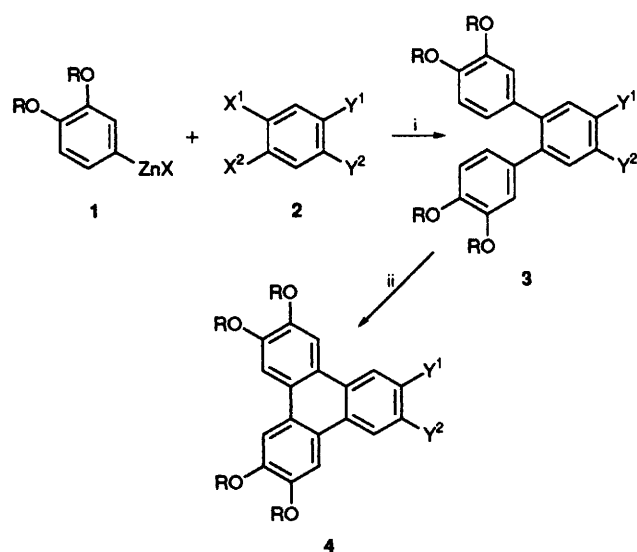
## A Flexible and Rational Synthesis of Substituted Triphenylenes by Palladium-catalysed Cross-coupling of Arylzinc Halides

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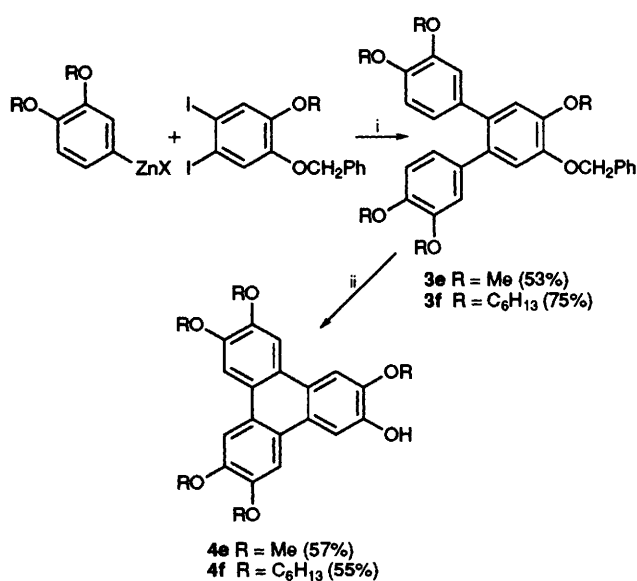
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A new, flexible route to substituted triphenylenes has been developed which involves the preparation of terphenyls using a palladium-catalysed cross-coupling of arylzinc halides with 1,2-dihalogenobenzenes, followed by oxidative cyclisation of these terphenyls using ferric chloride.

While symmetrically substituted hexaalkoxytriphenylenes have been the subject of much study due to their ability to form discotic liquid crystals,<sup>1</sup> the properties of unsymmetrically substituted triphenylenes have been much less explored, principally due to the paucity of methods for their synthesis. The only existing rational route involves the iodine-promoted



**Scheme 1** Reagents and conditions: i, Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%), PPh<sub>3</sub> (5 mol%), THF, reflux, 4.5 h; ii, FeCl<sub>3</sub> (3 equiv.), conc. H<sub>2</sub>SO<sub>4</sub> (trace), CH<sub>2</sub>Cl<sub>2</sub>, room temp., 1 h, then MeOH quench



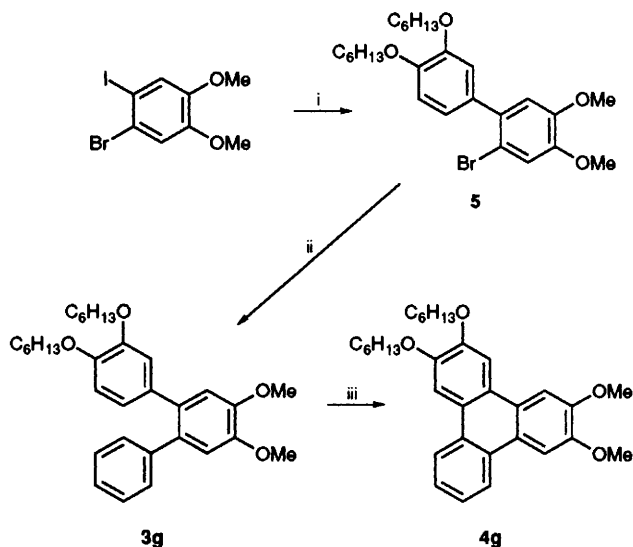
**Scheme 2** Reagents and conditions: i, Pd<sub>2</sub>(dba)<sub>3</sub> (1.25 mol%), PPh<sub>3</sub> (5 mol%), THF, reflux, 4.5 h; ii, FeCl<sub>3</sub> (3 equiv.), conc. H<sub>2</sub>SO<sub>4</sub> (trace), CH<sub>2</sub>Cl<sub>2</sub>, room temp., 1 h, then MeOH quench

photocyclisation of *ortho*-terphenyls,<sup>2</sup> which were themselves prepared by Ullman coupling reactions under rather vigorous conditions. The main drawback to this process is the generally poor yields obtained in the Ullman reaction. Very recently, iron(III) chloride has been shown to promote the cyclotrimerisation of 1,2-dialkoxybenzene derivatives,<sup>3</sup> and also to allow a selective coupling of a 3,3',4,4'-tetraalkoxybiphenyl and a 1,2-dialkoxybenzene.<sup>4</sup> It is of some note that dimerisation of the biphenyl appears not to compete.

We now report a new method for the preparation of unsymmetrical triphenylenes, which is in principle applicable to the preparation of a 2,3,6,7,10,11-hexasubstituted triphenylene with complete control of regiochemistry. The possibility of using iron(III) chloride for oxidative cyclisation reactions reduced the synthetic problem to that of preparing substituted *ortho*-terphenyls, and we now report a new, effective approach to the synthesis of these compounds.

Reaction of 2 equiv. of a 3,4-dialkoxyphenylzinc halide **1**, prepared from the corresponding 1-halogeno-3,4-dialkoxybenzene with *n*-butyllithium followed by zinc chloride, with 1,2-dihalogeno-4,5-disubstituted benzene derivatives **2**, occurred in moderate to good yield using the catalyst prepared from tris(dibenzylideneacetone)dipalladium [Pd<sub>2</sub>(dba)<sub>3</sub>] and triphenylphosphine to give the desired terphenyls **3**. The reaction tolerates a variety of substituents Y<sup>1</sup> and Y<sup>2</sup>. Treatment of the terphenyls with iron(III) chloride in dichloromethane with a trace of sulfuric acid then gave the required triphenylene derivatives **4** (Scheme 1). In all cases it proved more effective not to isolate and purify the intermediate *ortho*-terphenyls **3** but to cyclise them directly. Our results are indicated in Table 1.†

Of some note is the observation that benzyl groups appear not to be stable under the cyclisation conditions, which allows



**Scheme 3** Reagents and conditions: i, 3,4-(C<sub>6</sub>H<sub>13</sub>O)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>ZnCl (1.2 equiv.), Pd<sub>2</sub>(dba)<sub>3</sub> (1.25 mol%), PPh<sub>3</sub> (5 mol%), THF, reflux, 4.5 h, 45%; ii, PhZnCl (1.1 equiv.), Pd<sub>2</sub>(dba)<sub>3</sub> (1.25 mol%), PPh<sub>3</sub> (5 mol%), THF, reflux, 4.5 h; iii, FeCl<sub>3</sub> (3 equiv.), conc. H<sub>2</sub>SO<sub>4</sub> (trace), CH<sub>2</sub>Cl<sub>2</sub>, room temp., 1 h, then MeOH quench, 63% overall yield

Table 1 Preparation of unsymmetrical triphenylenes 4

X <sup>1</sup>	X <sup>2</sup>	Y <sup>1</sup>	Y <sup>2</sup>	R	Terphenyl	Triphenylene	Yield, % for 2 steps
I	I	H	H	Me	<b>3a</b>	<b>4a</b>	65
Br	Br	F	F	Me	<b>3b</b>	<b>4b</b>	33
Br	OSO <sub>2</sub> CF <sub>3</sub>	Cl	H	Me	<b>3c</b>	<b>4c</b>	21
I	I	OC <sub>6</sub> H <sub>13</sub>	OC <sub>6</sub> H <sub>13</sub>	C <sub>6</sub> H <sub>13</sub>	<b>3d</b>	<b>4d</b>	70

a direct synthesis of both 2-hydroxy-3,6,7,10,11-pentamethoxytriphenylene **4e** and 2-hydroxy-3,6,7,10,11-pentahexyloxytriphenylene **4f** in good yields (Scheme 2). Such compounds are ideally substituted for further functionalisation, for introduction into polymers for example.

Finally, we have established that this approach is effective for the synthesis of triphenylene derivatives in which each of the original aromatic starting materials is different. Thus, coupling of 3,4-dihexyloxyphenylzinc chloride with 2-bromo-1-iodo-4,5-dimethoxybenzene<sup>‡</sup> occurred selectively at the 1-position to give the biphenyl **5** (45%).<sup>5</sup> Subsequent coupling with phenylzinc chloride, gave the unsymmetrical *ortho*-terphenyl **3g**, which was directly cyclised using FeCl<sub>3</sub> to the triphenylene **4g** (63% for both steps from **5**) (Scheme 3). We have prepared 250 mg of triphenylene **4g** using this route, and the method is certainly amenable to the preparation of gram quantities.

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### Footnotes

<sup>†</sup> Satisfactory spectroscopic and analytical data (either elemental analysis or high-resolution MS) were obtained for all new triphenylenes.

<sup>‡</sup> Prepared from 1-bromo-3,4-dimethoxybenzene by treatment with I<sub>2</sub> and AgO<sub>2</sub>CCF<sub>3</sub>.<sup>6</sup>

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