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\[
2 \text{Ar}_1^1 \text{Ar}_1^2 + \text{Br}_2 \text{Ar}_2^2 \text{Br} \xrightarrow{[\text{Pd}]} \text{Ar}_1^1 \text{Ar}_2^2 \text{Ar}_1^1
\]

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1. Introduction

Over the past three decades, it has become increasingly clear that organoboronic acids are valuable reagents capable of undergoing many catalytic C-C bond formations in organic synthesis.1 Much interest has recently been shown in hindered cross-coupling reactions due to the presence of ortho-substituted biaryls in natural products, biologically active compounds, and valuable materials.2 On the other hand, there has been a large number of reports of selective couplings with di- or trihalo aromatic compounds, because of the steric hindrance of second and third couplings.3-8 Diodo arenes were the best choice for the double couplings, and dibromo arenes mainly yielded single coupling products. In addition, although many excellent ligands have been developed for different substrates, these procedures suffer from lack of generality.

Diaryl-substituted planar frameworks such as naphthalene,9-13 biphenylene,14,15 dibenzothiophene,10 dibenzofuran15 and xanthene15,17 have fascinating scaffolds with unusual geometry in organic molecules. The two aryl units bonded to planar frameworks in sufficiently close positions provide a parallel face-to-face arrangement, thus indicating π-π interactions that play an important role in a variety of chemical properties such as molecular recognition,18 stereocontrolled reactions,19 protein and nucleic acid structures,20 and crystal packing.21 Some applications have taken advantage of the difficult or impossible rotations of aryl rings along the naphthalene axis. For example, 1,8-diacridyl-, 1,8-diquinolyl-, and 1,8-dipyridyl-naphthalenes have been developed for new photoluminescent or chiral sensors.11 Results of some studies on diaryl biphenylene have also been.21 However, the incorporation of bulky aryl rings into the peri position of naphthalene, biphenylene, and their analogues is still synthetically challenging due to severe steric hindrance to carbon-carbon bond formation and often unsuccessful reactions or reactions resulting in low yields.6-8,14,15

We recently reported that aryltriolborates, which have good stability in air- and water, undergo very smooth and fast transmetalation to various transition metal complexes. The utility of these tetra-coordinated arylboron compounds has already been demonstrated in palladium-catalyzed cross-couplings,22,23 copper-catalyzed N-arylation of amines24 and rhodium-catalyzed 1,4-addition to enones.25 For the synthesis of biaryls, we have used DMF and water as a solvent, 3 mol% Pd(OAc)2 as a catalyst, without a ligand and base, to give biaryls in very high yields.22a

Herein, we report the utilization of aryltriolborates to provide efficient and facile synthesis of highly congested diaryl-substituted planar frameworks (Scheme 1).
Tetrahedron

To further show the advantage of aryltriolborates, we compared the reactivities of boronic acid and aryltriolborate (1d) in the coupling reaction of congested 1,8-dibromonaphtalene. As shown in Table 2, when 3 equivalents of boronic acid was used to furnish the coupling with 1,8-dibromonaphtalene, the Pd(OAc)₂/CuCl system did not give the desired product; when 10 mol% Pd(PPh₃)₄ and 2 equivalents of K₂CO₃ were used, 33% isolated yield was achieved. However, without the use of a base, no desired product was obtained. In contrast, when 3 equivalents of aryltriolborates was used for the coupling, the Pd(OAc)₂/CuCl system gave 88% yield (entry 6); without a base, when 10 mol% Pd(PPh₃)₄ was used, 77% isolated yield was also observed (entry 4), and when 2 equivalents of K₂CO₃ was used, the yield was slightly improved to 84% (entry 5). From the results, we conclude that aryltriolborates undergo very fast and smooth transmetallation compared with boronic acids.

**Table 2. Reaction conditions for synthesis of 1,8-Bis[4-(diphenylamino)phenyl] naphthalene (3de)**

<table>
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<tr>
<th>entry</th>
<th>1</th>
<th>[Pd]</th>
<th>ligand (equiv.)</th>
<th>additive (equiv.)</th>
<th>Yield (%)</th>
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<tr>
<td>1</td>
<td>Pd(PPh₃)₄</td>
<td>none</td>
<td>none</td>
<td>trace</td>
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<td>2</td>
<td>Pd(PPh₃)₄</td>
<td>none</td>
<td>K₂CO₃ (2.0)</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>Pd(OAc)₂</td>
<td>BIPHEP</td>
<td>CuCl (0.4)</td>
<td>trace</td>
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<td>4</td>
<td>Pd(PPh₃)₄</td>
<td>none</td>
<td>K₂CO₃ (2.0)</td>
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<tr>
<td>5</td>
<td>Pd(PPh₃)₄</td>
<td>none</td>
<td>CuCl (0.4)</td>
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</tr>
<tr>
<td>6</td>
<td>Pd(OAc)₂</td>
<td>BIPHEP</td>
<td></td>
<td>88</td>
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</table>

A mixture of 1,8-dibromonaphtalene (2c, 0.2 mmol), 4-(diphenylamino)phenyl boronic acid (3 equiv.) or 4-(diphenylamino)phenyl triolborate (3 equiv.) was stirred at 80 °C for 14 h in the presence of Pd catalyst (10 mol%).

*Isolated yields.

'11 mol% of BIPHEP was used.

Next, we synthesized aryltriolborates (1d-g) used for electronic materials. We used triolborate (1d) to synthesize planar frameworks by the Pd(OAc)₂/CuCl system. Bis(4-(diphenylamino)phenyl)arenes (3de-i) were obtained in 88%, 84%, 79%, 82% and 80% yields, respectively (Table 1, entries 16-20).

When 4-(phenylethynyl)phenyltriolborate (1e) was used to synthesize diaryl-substituted arenes, neither the Pd(OAc)₂/DMF-H₂O reaction system nor the Pd(OAc)₂/CuCl reaction system gave the desired product. The reasons for this are not known. To achieve coupling, we next tried using a Pd(PPh₃)₄/K₂CO₃ reaction system (Table 2, entry 5). The corresponding diaryl arenes (3ee, 3ef, 3eg and 3ei) were isolated in 76%, 88%, 90% and 97% yields, respectively (Table 1, entries 21-24). This reaction system was also used for aryltriolborate (1f) and pyrenyltriolborate (1g).

Under condition B, the reaction of 1f with 2g gave the desired product in moderate yield (54%, Table 1, entry 27). Using condition C, however, the desired products (3fe, 3ff, 3fg and 3fi) were obtained in 82%, 83%, 74% and 90% yields, respectively.

**Scheme 1. Double coupling of dibromo arenes with potassium aryltriolborates**

used for palladium-catalyzed cross-coupling reactions, the use of a phosphine ligand and base could sometimes be avoided.

To further show the efficiency of this methodology, we first tried to synthesize ortho-disubstituted benzene, pyridine, thiophene, and furan (Table 1, entries 1-6). Ortho-disubstituted benzene was obtained in excellent yields, 92% yield being obtained even for highly congested di(2-naphthyl)substituted benzene. However, only moderate yield (60%) was observed for ortho-disubstituted heteroaromatics, such as ortho-diaryl-substituted pyridine. To compensate this deficiency, we tried another reaction system described for the synthesis of tetra-ortho-substituted biaryls, which could avoid the use of a base and greatly improve the functional group tolerance. As expected, ortho-disubstituted pyridine, thiophene and furan were obtained in high yields (Table 1, entries 4-6). The yield of ortho-diaryl-substituted pyridine was greatly improved from 60% to 91% (Table 1, entries 3 and 4).

Next, we designed five kinds of aryl dibromides (2e-i) with different distances and angles between two carbon-bromide bonds, and then we used 4-tolyltriolborate (1b) to synthesize diaryl-substituted planar frameworks according to the procedure described in our previous report. When 2.4 equivalents of aryltriolborate (1b) was used, diaryl arenes (3be-i) were obtained in excellent yields without the use of a ligand and base at room temperature (Table 1, entries 7-11).

We next synthesized biphenyltriolborate (1e) to prepare different diaryl-substituted frameworks. 3ce and 3cf were obtained successfully in 87% and 98% yields, respectively, by the same procedure with 3 equivalents of biphenyl triolborate (1e) (Table 1, entries 12 and 13). Unfortunately, when biphenyl triolborate (1e) was used for reaction with dibromides 3cg and 3ci, no desired products were obtained. In our previous work, we found that aryltriolborate could be used for hindered coupling by using Pd(OAc)₂ and CuCl as co-catalysts, and BIPHEP (2,2'-bis(diphenylphosphino)biapenyl) as a ligand without the use of a base to synthesize tetra-ortho-substituted biaryls in high yields. When this method was used, 2g and 2i were obtained smoothly in 84% and 90% yields, respectively (Table 1, entries 14 and 15).
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<th>entry</th>
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<th>2</th>
<th>conditions</th>
<th>Yield (%)</th>
<th>entry</th>
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<th>2</th>
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<th>Yield (%)</th>
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<td>A&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>17</td>
<td>4-PhN=C=CH&lt;sub&gt;2&lt;/sub&gt; (1d)</td>
<td>2f</td>
<td>B</td>
</tr>
<tr>
<td>2</td>
<td>4-tolyl (1b)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>A&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3ba</td>
<td>86</td>
<td>18</td>
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<td>B</td>
</tr>
<tr>
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<td>4-tolyl (1b)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2b</td>
<td>A&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>B</td>
<td>3bb</td>
<td>91</td>
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<td>3bc</td>
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<td>2e</td>
<td>C</td>
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<td>2d</td>
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<td>3bd</td>
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<td>2e</td>
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<td>C</td>
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<td>2f</td>
<td>A</td>
<td>3bf</td>
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<td>C&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>4-biphenyl (1c)</td>
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<td>3eg</td>
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<td>2e</td>
<td>B</td>
<td>3de</td>
<td>88</td>
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<td>2p</td>
<td>C</td>
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Condition A: triolborate (1, 3.0 eq.), Pd(OAc)<sub>2</sub> (10 mol%), DMF/H<sub>2</sub>O (4/1, 10 mL), r.t., 16 h.

Condition B: triolborate (1, 3.0 eq.), Pd(OAc)<sub>2</sub> (10 mol%) / BIPHEP (2,2'-bis(diphenylphosphino)biphenyl, 11 mol%), CuCl (0.4 eq.), DMF (15 mL), 80 °C, 14 h.

Condition C: triolborate (1, 3.0 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol%), K<sub>2</sub>CO<sub>3</sub> (2 eq.), DMF (15 mL), 80 °C, 14 h.

<sup>a</sup>Pd(OAc)<sub>2</sub> (6 mol%) was used.

<sup>b</sup>Triolborate (1, 2.2 eq.) was used.

<sup>c</sup>Triolborate (1, 4.0 eq.) was used.

<sup>d</sup>Triolborate (1, 2.4 eq.) was used.

<sup>e</sup>Toluene was used.
Tetrahedron

(Table 1, entries 25, 26, 28 and 29). Similarly bis(pyridyl) arenes (3ge, 3gh and 3gi) were obtained in 81%, 71% and 89% yields, respectively (Table 1, entries 30-32).

3. Conclusions

We have demonstrated the efficiency of potassium triolborates for double-coupling reaction of dibromo arenes such as naphthalene, biphenylene, dibenzothiophene, dibenzofuran and xanthene. Triolborates showed several advantages over boronic acids, including high nucleophilicity of aryl groups for smooth transmetalation to a palladium catalyst and high solubility in organic solvents, allowing the use of water-free solvents for preventing hydrolytic B-C bond cleavage. We have developed a general method for double-coupling reaction of dibromo arenes.

4. Experimental section

4.1. Synthesis of cyclic potassium aryltriolborates

4.1.1. Potassium 2-naphthyltriolborate (1a)

2-naphthyl boronic acid26 (100 mmol) and 1, 1, 1-tris(hydroxymethyl)ethane (100 mmol) were dissolved in toluene (200 mL). Water was removed by azeotropic distillation by the Dean-Stark method for 4 h. After cooling to room temperature, KOH (95 mmol) was added and heated at reflux for 4 h by the Dean-Stark method for 4 h. After cooling to room temperature, the mixture was allowed to gradually warm to room temperature overnight. Dilute HCl (2 M, 60 mL) was added and stirred for 1 h. Dichloromethane was added and the layers separated. The aqueous layer was extracted with dichloromethane and combined organic layers washed with water, dried over MgSO4, filtered and the solvent evaporated under reduced pressure. 1H NMR (400 MHz, CDCl3): δ = 0.53 (s, 3H), 3.62 (s, 6H), 6.78 (d, J = 7.3 Hz, 2H), 7.18 (d, J = 7.3 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ = 16.3, 34.5, 73.6, 123.9, 126.2, 126.2, 128.7, 132.8, 135.7, 141.7 (C-B is not observed); 11B NMR (128 MHz, CDCl3): δ = -1.30; MS (m/z): 219.1198; found: 219.1197.

4.1.2. Potassium 4-locyltriolborate (1b)22a

The synthesis of potassium 4-tolyl triolborate 1b (96%) using 4-locyl boronic acid was the same as the synthesis of 2-naphthyl triolborate. 1H NMR (400 MHz, DMSO-d6): δ = 0.46 (s, 3H), 2.16 (s, 3H), 3.55 (s, 6H), 6.79 (d, J = 7.3 Hz, 2H), 7.18 (d, J = 7.3 Hz, 2H); 13C NMR (100 MHz, DMSO-d6): δ = 16.5, 21.2, 34.6, 73.8, 126.3, 132.2, 132.3 (C-B is not observed); 11B NMR (128 MHz, DMSO-d6): δ = -4.48; MS (m/z): 122 (8), 152 (10), 255 (M+, 100); HRMS (FAB+): m/z calcd for C8H10B2O3: 219.1198; found: 219.1197.

4.1.3. Potassium biphenyltriolborate (1c)

The synthesis of potassium biphenyl triolborate 1c (89%) using biphenyl boronic acid29 was the same as the synthesis of 2-naphthyl triolborate. 1H NMR (400 MHz, DMSO-d6): δ = 0.48 (s, 3H), 3.55 (s, 6H), 6.87 (t, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, DMSO-d6): δ = 16.3, 34.5, 73.7, 121.3, 122.7, 123.7, 129.1, 133.4, 143.2, 148.0 (C-B is not observed); 11B NMR (128 MHz, DMSO-d6): δ = 3.05; MS (m/z): 122 (14), 153 (100), 199 (38), 306 (70), 372 (M+, 65); HRMS (FAB+): m/z calcd for C19H18BNO3: 372.1776; found: 372.1776; elemental analysis: calcd (%) for C19H18BNO3: C, 55.67; H, 4.53.

4.1.4. Potassium 4-(diphenylamino)phenyltriolborate (1d)

The synthesis of potassium 4-(diphenylamino)phenyl triolborate 1d (89%) using 4-(diphenylamino)phenylboronic acid29 was the same as the synthesis of 2-naphthyl triolborate. 1H NMR (400 MHz, DMSO-d6): δ = 0.45 (s, 3H), 3.55 (s, 6H), 6.71 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 8.0 Hz, 6H), 7.17 (t, J = 8.0 Hz, 4H), 7.28 (t, J = 8.0 Hz, 2H); 13C NMR (100 MHz, DMSO-d6): δ = 16.3, 34.5, 73.7, 121.3, 122.7, 123.7, 129.1, 133.4, 143.2, 148.0 (C-B is not observed); 11B NMR (128 MHz, DMSO-d6): δ = 3.05; MS (m/z): 122 (14), 153 (100), 199 (38), 306 (70), 372 (M+, 65); HRMS (FAB+): m/z calcd for C25H19BNO3: 372.1776; found: 372.1776; elemental analysis: calcd (%) for C25H19BNO3: C, 56.12; H, 3.72; N, 2.96.
The triolborate, dibromides (0.2 mmol), and palladium acetate (10 mol%) were placed in a flask under an atmosphere of nitrogen. DMF/H₂O (4/1; 10 mL) was added, and the reaction mixture was stirred at room temperature for 16 h. The mixture was extracted with dichloromethane, dried over MgSO₄, and then purified by chromatography on silica gel.

4.2. General procedures for double cross-coupling

4.2.1. Pd(OAc)₂/DMF/H₂O system

The triolborate, dibromides (0.2 mmol), palladium acetate (10 mol%), BIPHEP (11 mol), and CuCl (0.4 eq) were placed in a flask under an atmosphere of nitrogen. 15 mL DMF was added, and heated at 80 °C for 14 h. After cooling to room temperature, 15 mL water was added, extracted with dichloromethane, dried over MgSO₄, and then purified by chromatography on silica gel.

4.2.2. Pd(OAc)₂/CuCl₂ system

The triolborate, dibromides (0.2 mmol), palladium acetate (10 mol%), and K₂CO₃ (2 eq) were placed in a flask under an atmosphere of nitrogen. 15 mL DMF was added, and heated at 80 °C for 14 h. After cooling to room temperature, 15 mL water was added, extracted with dichloromethane, dried over MgSO₄, and then purified by chromatography on silica gel.

4.3. Spectral data of diaryl arenes

The spectra of compounds 3ba, 3bb, 3bc, 3ce, 3de, and 3ge are identical to those reported in the literatures.

4.3.1. 1,2-di(2-naphthyl)benzene (3aa)

mp 97-98 °C; IR (neat): 3053, 2925, 1734, 1505, 1489 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.06 (dd, J = 1.7, 8.5 Hz, 2H), 7.31-7.34 (m, 4H), 7.40 (dd, J = 3.6, 5.8 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.49 (dd, J = 3.6, 5.8 Hz, 2H), 7.62-7.67 (m, 4H), 7.73 (d, J = 1.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 125.7, 125.9, 127.2, 127.6, 127.7, 128.0, 128.3, 128.4, 131.1, 132.0, 133.4, 134.9, 140.5; MS (m/z): 150 (10), 163 (12), 215 (6), 252 (2), 313 (6), 315 (16), 330 (M⁺, 100); HRMS (EI): m/z calc d for C₂₉H₂₂₆O: 330.1409; found: 330.1401.

4.3.2. 2,3-diphenylthiophene (3bc)

oil; IR (neat): 3023, 2919, 2862, 812 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.31 (s, 3H), 2.32 (s, 3H), 7.06-7.11 (m, 5H), 7.16-7.20 (m, 4H), 7.25 (d, J = 5.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 21.2, 123.6, 128.9, 129.0, 129.1, 130.5, 131.5, 133.7, 136.3, 137.1, 136.8, 138.3; MS (m/z): 117 (6), 189 (6), 202 (6), 215 (7), 234 (36), 249 (46), 264 (M⁺, 100); HRMS (EI): m/z calc d for C₂₉H₂₂₆O: 264.0973; found: 264.0970.

4.3.3. 2,3-diphenylfuran (3bd)

oil; IR (neat): 3029, 2921, 2859, 1803, 1519, 1063, 819 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 2.32 (s, 3H), 2.37 (s, 3H), 6.51 (d, J = 2.0 Hz, 1H), 7.09 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.41-7.45 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.8, 20.8, 113.4, 121.1, 125.7, 128.0, 128.1, 128.6, 128.8, 131.0, 136.2, 136.8, 140.7, 148.1; MS (m/z): 91 (24), 119 (36), 189 (9), 219 (38), 233 (24), 248 (M⁺, 100); HRMS (EI): m/z calc d for C₂₉H₂₂₆O: 248.1201; found: 248.1200.
4,6-Bis(4-biphenyl)dibenzo[b,d]furan (3eg)

mp 255-256 °C; IR (neat): 2961, 2360, 1437, 1231, 835 cm⁻¹; UV: λmax (CHCl₃)/nm (ε/dm³ mol⁻¹ cm⁻¹) 314 (23527), 303 (39716); 1H NMR (400 MHz, CDCl₃): δ = 6.95 (dd, J = 1.6 Hz, 6.4 Hz, 4H), 7.15-7.25 (m, 5H), 7.56-7.61 (m, 4H), 7.47 (dd, J = 1.2, 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ = 89.3, 90.3, 121.0, 123.3, 124.7, 127.8, 128.5, 131.1, 131.9, 142.5, MS (m/z): 268 (21), (M⁺, 100); HRMS (EI): m/z calcd for C₃₇H₃₈N₂O: 536.1599; found: 536.1589.

4,6-Bis(4-phenylethynylphenyl)dibenzo[b,d]furan (3ef)

mp 258-260 °C; IR (neat): 2961, 2360, 1437, 1231, 835 cm⁻¹; UV: λmax (CHCl₃)/nm (ε/dm³ mol⁻¹ cm⁻¹) 314 (23527), 303 (39716); 1H NMR (400 MHz, CDCl₃): δ = 6.95 (dd, J = 1.6 Hz, 6.4 Hz, 4H), 7.15-7.25 (m, 5H), 7.56-7.61 (m, 4H), 7.47 (dd, J = 1.2, 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ = 89.3, 90.3, 121.0, 123.3, 124.7, 127.8, 128.5, 131.1, 131.9, 142.5, MS (m/z): 268 (21), (M⁺, 100); HRMS (EI): m/z calcd for C₃₇H₃₈N₂O: 536.1599; found: 536.1589.

4,6-Bis(4-phenylethynylphenyl)dibenzo[b,d]furan (3fg)

mp 255-256 °C; IR (neat): 2961, 2360, 1437, 1231, 835 cm⁻¹; UV: λmax (CHCl₃)/nm (ε/dm³ mol⁻¹ cm⁻¹) 314 (23527), 303 (39716); 1H NMR (400 MHz, CDCl₃): δ = 6.95 (dd, J = 1.6 Hz, 6.4 Hz, 4H), 7.15-7.25 (m, 5H), 7.56-7.61 (m, 4H), 7.47 (dd, J = 1.2, 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ = 89.3, 90.3, 121.0, 123.3, 124.7, 127.8, 128.5, 131.1, 131.9, 142.5, MS (m/z): 268 (21), (M⁺, 100); HRMS (EI): m/z calcd for C₃₇H₃₈N₂O: 536.1599; found: 536.1589.
were not observed); MS (m/z): 264 (13), 326 (23), 528 (M+, 100);
126.9, 129.6, 130.0, 130.7, 131.6, 140.7, 141.4 (three carbons
C75H64N2O: 1008.5019; found: 1008.4974.

EI): m/z calcd for C64H42N2O: 870.3069; found: 870.3074.

m/z calcd for C64H42N2O: 854.3297; found: 854.3294.

CDCl3): (100 MHz, CDCl 3):

6H), 7.46-7.54 (m, 10H); 13C NMR (100 MHz, CDCl 3):

4.3.24. 1,8-Bis(4-(4-(diphenylamino)phenyl)
ethynyl)phenyl)[dimbenzo[d]thiophene (3ff)

1008 (M +, 100); HRMS (EI): m/z calcd for C62H42N2: 814.3547.

814.3348; found: 814.3274.

HRMS (EI): m/z calcd for C55H46O: 807.3069; found: 807.3074.

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References and notes


