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Double-coupling of dibromo arenes with aryltriolborates for synthesis of diaryl-substituted planar frameworks

Gao-Qiang Li, Yasunori Yamamoto *, Norio Miyaura

Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

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ABSTRACT

A new method for simple and practical synthesis of diaryl-substituted arenes using potassium aryltriolborates was developed. Double-cross-coupling of dibromo arenes with aryltriolborates was carried out in the presence of a palladium catalyst, such as $Pd(OAc)_2$, $Pd(PPh_3)_4$ or $Pd(OAc)_2$/BIPHEP. The use of CuCl (40 mol %) with a palladium catalyst was found to be highly effective to give diaryl-substituted aromatic compounds in good yields.

1. Introduction

Over the past 3 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] Diiodo arenes were the best choice for the double couplings, and dibromo arenes mainly yielded single coupling products.[5] In addition, although many excellent ligands have been developed for different substrates,[5] these procedures suffer from lack of generality.

Diaryl-substituted planar frameworks, such as naphthalene,[9–13] biphenylene,[14,15] dibenzothiophene,[16] dibenzofuran,[15] and xanthene[15,17] 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.[14] 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-coupling,[22,23] copper-catalyzed *N*-arylation of amines[24] 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).

2. Results and discussion

Most of the Pd-catalyzed reactions described for the synthesis of diaryl-substituted planar frameworks involved the use of a phosphine ligand and base, with a strong base being used to obtain satisfactory yields, which sometimes caused serious problems, such as functional group compatibility and contamination. In our

* Corresponding author. Tel./fax: +81 11 706 6560; e-mail address: yasuyama@eng.hokudai.ac.jp (Y. Yamamoto).

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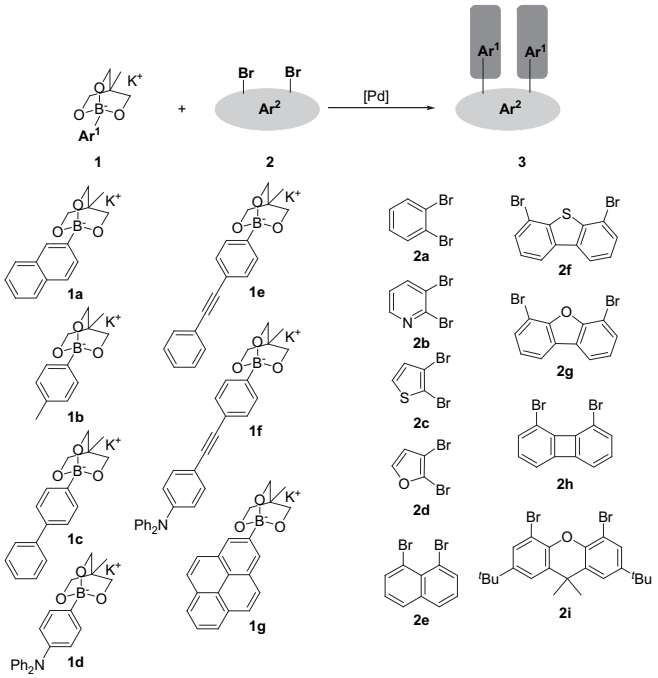


Scheme 1. Double-coupling of dibromo arenes with potassium aryltriolborates.

previous work, when aryltriolborates were used for palladium-catalyzed cross-coupling reactions,[22] 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,[22d] 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.[22a] When 2.4 equiv 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).

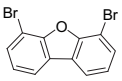
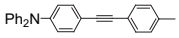
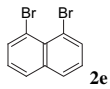
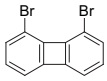
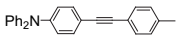
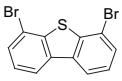
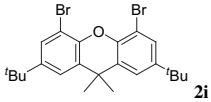
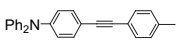
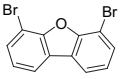
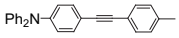
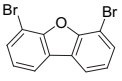
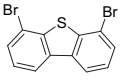
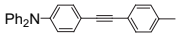
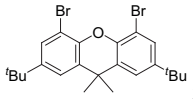
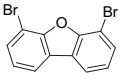
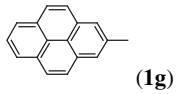
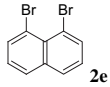
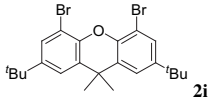
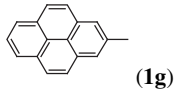
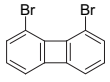
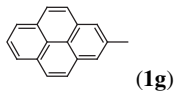
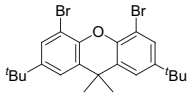
We next synthesized biphenyltriolborate (**1c**) to prepare different diaryl-substituted frameworks. Compounds **3ce** and **3cf**

Table 1
Double-cross-coupling of dibromo arenes with aryltriolborates

Entry	**1** (Ar^1=)	**2**	Conditions	**3**	Yield (%)	Entry	**1** (Ar^1=)	**2**	Conditions	**3**	Yield (%)
1	2-Naphthyl (**1a**)	**2a**	A[a]	**3aa**	92	17	4-$Ph_2NC_6H_4$ (**1d**)	**2f**	B	**3df**	84
2	4-Tolyl (**1b**)[b]	**2a**	A[a]	**3ba**	86	18	4-$Ph_2NC_6H_4$ (**1d**)	**2g**	B	**3dg**	79
3	4-Tolyl (**1b**)[b]	**2b**	A[a]	**3bb**	60	19	4-$Ph_2NC_6H_4$ (**1d**)	**2h**	B	**3dh**	82
4	4-Tolyl (**1b**)	**2b**	B	**3bb**	91	20	4-$Ph_2NC_6H_4$ (**1d**)	**2i**	B	**3di**	80
5	4-Tolyl (**1b**)[c]	**2c**	B	**3bc**	87	21	4-PhC≡CC_6H_4 (**1e**)	**2e**	C	**3ee**	76
6	4-Tolyl (**1b**)	**2d**	B	**3bd**	81	22	4-PhC≡CC_6H_4 (**1e**)	**2f**	C	**3ef**	88
7	4-Tolyl (**1b**)[d]	**2e**	A	**3be**	86	23	4-PhC≡CC_6H_4 (**1e**)	**2g**	C	**3eg**	90
8	4-Tolyl (**1b**)[d]	**2f**	A	**3bf**	90	24	4-PhC≡CC_6H_4 (**1e**)	**2i**	C[e]	**3ei**	97

(*continued on next page*)

Table 1 (*continued*)

Entry	**1** (Ar^1=)	**2**	Conditions	**3**	Yield (%)	Entry	**1** (Ar^1=)	**2**	Conditions	**3**	Yield (%)
9	4-Tolyl (**1b**)[d]	 **2g**	A	**3bg**	83	25	 (**1f**)	 **2e**	C	**3fe**	82
10	4-Tolyl (**1b**)[d]	 **2h**	A	**3bh**	91	26	 (**1f**)	 **2f**	C	**3ff**	83
11	4-Tolyl (**1b**)[d]	 **2i**	A	**3bi**	98	27	 (**1f**)	 **2g**	B	**3fg**	54
12	4-Biphenyl (**1c**)	 **2e**	A	**3ce**	87	28	 (**1f**)	 **2g**	C	**3fg**	74
13	4-Biphenyl (**1c**)	 **2f**	A	**3cf**	98	29	 (**1f**)	 **2i**	C	**3fi**	90
14	4-Biphenyl (**1c**)	 **2g**	B	**3cg**	84	30	 (**1g**)	 **2e**	C	**3ge**	81
15	4-Biphenyl (**1c**)	 **2i**	B	**3ci**	90	31	 (**1g**)	 **2h**	C	**3gh**	71
16	4-$Ph_2NC_6H_4$ (**1d**)	 **2e**	B	**3de**	88	32	 (**1g**)	 **2i**	C	**3gi**	89

Condition A: triolborate (**1**, 3.0 equiv), $Pd(OAc)_2$ (10 mol %), DMF/H_2O (4/1, 10 mL), rt, 16 h.
Condition B: triolborate (**1**, 3.0 equiv), $Pd(OAc)_2$ (10 mol %)/BIPHEP (2,2′-bis(diphenylphosphino)biphenyl, 11 mol %), CuCl (0.4 equiv), DMF (15 mL), 80 °C, 14 h.
Condition C: triolborate (**1**, 3.0 equiv), $Pd(PPh_3)_4$ (10 mol %), K_2CO_3 (2 equiv), DMF (15 mL), 80 °C, 14 h.
[a] $Pd(OAc)_2$ (6 mol %) was used.
[b] Triolborate (**1**, 2.2 equiv) was used.
[c] Triolborate (**1**, 4.0 equiv) was used.
[d] Triolborate (**1**, 2.4 equiv) was used.
[e] Toluene was used.

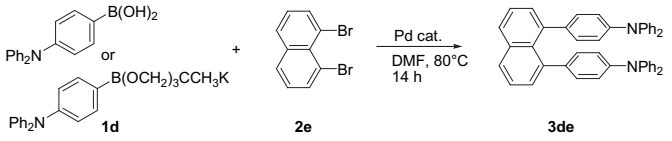
were obtained successfully in 87% and 98% yields, respectively, by the same procedure with 3 equiv of biphenyl triolborate (**1c**) (Table 1, entries 12 and 13). Unfortunately, when biphenyl triolborate (**1c**) was used for reaction with dibromides **2g** and **2i**, no desired products were obtained. 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)biphenyl) as a ligand without the use of a base to synthesize tetra-*ortho*-substituted biaryls in high yields.[22d] When this method was used, **3cg** and **3ci** were obtained smoothly in 84% and 90% yields, respectively (Table 1, entries 14 and 15).

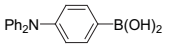
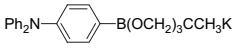
To further show the advantage of aryltriolborates, we compared the reactivities of boronic acid and aryltriolborate (**1d**) in the coupling reaction of congested 1,8-dibromonaphthalene. As shown in Table 2, when 3 equiv of boronic acid was used to furnish the coupling with 1,8-dibromonaphtalene, the $Pd(OAc)_2$/CuCl system did not give the desired product; when 10 mol % $Pd(PPh_3)_4$ and 2 equiv of K_2CO_3 were used, 33% isolated yield was achieved. However, without the use of a base, no desired product was obtained. In contrast, when 3 equiv of aryltriolborates was used for the coupling, the $Pd(OAc)_2$/CuCl system gave 88% yield (entry 6); without a base, when 10 mol % $Pd(PPh_3)_4$ was used, 77% isolated yield was also observed (entry 4), and when 2 equiv of K_2CO_3 was used, the yield was slightly improved to 84% (entry 5). From the results, we conclude that aryltriolborates undergo very fast and smooth transmetalation compared with boronic acids.

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/H_2O 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 $Pd(PPh_3)_4/K_2CO_3$ reaction system

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



Entry	1	[Pd]	Ligand	Additive (equiv)	Yield[b] (%)
1		$Pd(PPh_3)_4$	None	None	Trace
2		$Pd(PPh_3)_4$	None	K_2CO_3 (2.0)	33
3		$Pd(OAc)_2$	BIPHEP[c]	CuCl (0.4)	Trace
4		$Pd(PPh_3)_4$	None	None	77
5		$Pd(PPh_3)_4$	None	K_2CO_3 (2.0)	84
6		$Pd(OAc)_2$	BIPHEP[c]	CuCl (0.4)	88

[a] A mixture of 1,8-dibromonaphthalene (2e, 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 %).
[b] Isolated yields.
[c] BIPHEP (11 mol %) was used.

(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 4-((4-(diphenylamino)phenyl)ethynyl)phenyltriolborate (**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 (Table 1, entries 25, 26, 28, and 29). Similarly bis(pyrenyl) 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-cross-coupling reaction of dibromo arenes.

4. Experimental section

4.1. Synthesis of cyclic potassium aryltriolborates

*4.1.1. Potassium 2-naphthyl triolborate (**1a**).* 2-Naphthyl boronic acid[26] (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. The potassium 2-naphthyl triolborate (**1a**) was precipitated. After cooling to room temperature, the desired triolborate **1a** (95%) was collected by filtration, washed with diethyl ether, and dried under reduced pressure. ^{1}H NMR (400 MHz, DMSO-d_6): δ=0.53 (s, 3H), 3.62 (s, 6H), 7.25–7.31 (m, 2H), 7.51–7.58 (m, 2H), 7.68–7.70 (m, 2H), 7.81 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=16.9, 35.2, 73.5, 124.2, 124.7, 124.8, 127.6, 128.1, 131.2, 132.3, 132.5, 133.4 (C–B is not observed); ^{11}B NMR (128 MHz, DMSO-d_6): δ=4.80; MS (m/z): 122 (8), 152 (10), 255 (M^-, 100); HRMS (FAB^-): m/z calcd for $C_{15}H_{16}BO_3^-$: 255.1198; found: 255.1193.

*4.1.2. Potassium 4-tolyltriolborate (**1b**)[22a].* The synthesis of potassium 4-tolyltriolborate **1b** (96%) using 4-tolyl boronic acid was the same as the synthesis of 2-naphthyl triolborate. ^{1}H NMR (400 MHz, DMSO-d_6): 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); ^{13}C NMR (100 MHz, DMSO-d_6): δ=16.5, 21.2, 34.6, 73.8, 126.5, 132.2, 132.3 (C–B is not observed); ^{11}B NMR (128 MHz, DMSO-d_6): δ=4.62; HRMS (FAB^-): m/z calcd for $C_{17}H_{18}BO_3^-$: 219.1198; found: 219.1197.

*4.1.3. Potassium biphenyl triolborate (**1c**).* The synthesis of potassium biphenyl triolborate **1c** (89%) using biphenyl boronic acid[27] was the same as the synthesis of 2-naphthyl triolborate. ^{1}H NMR (400 MHz, DMSO-d_6): δ=0.48 (s, 3H, CCH_3), 3.59 (s, 6H), 7.25–7.30 (m, 3H), 7.37–7.41 (m, 4H), 7.57–7.59 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): 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); ^{11}B NMR (128 MHz, DMSO-d_6): δ=1.92; MS (m/z): 122 (9), 153 (42), 199 (11), 281 (M^-, 100); HRMS (FAB^-): m/z calcd for $C_{17}H_{18}BO_3^-$: 281.1354; found: 281.1350; elemental analysis: calcd (%) for $C_{17}H_{18}BKO_3$: C, 63.76; H, 5.67; found: C, 62.75; H, 5.62.

*4.1.4. Potassium 4-(diphenylamino)phenyltriolborate (**1d**).* The synthesis of potassium 4-(diphenylamino)phenyl triolborate (**1d**) (89%) using 4-(diphenylamino)phenylboronic acid[28] was the same as the synthesis of 2-naphthyl triolborate. ^{1}H NMR (400 MHz, DMSO-d_6): 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); ^{13}C NMR (100 MHz, DMSO-d_6): δ=16.3, 34.5, 73.7, 121.3, 122.2, 123.7, 129.1, 133.4, 143.2, 148.0 (C–B is not observed); ^{11}B NMR (128 MHz, DMSO-d_6): δ=3.05; MS (m/z): 122 (14), 153 (100), 199 (38), 306 (70), 372 (M^-, 65); HRMS (FAB^-): m/z calcd for $C_{23}H_{23}BNO_3^-$: 372.1776; found: 372.1776; elemental analysis: calcd (%) for $C_{23}H_{23}BKNO_3$: C, 67.16; H, 5.64; N, 3.41; found: C, 62.82; H, 5.56; N, 2.96.

*4.1.5. Potassium 4-(phenylethynyl)phenyltriolborate (**1e**).* The synthesis of potassium 4-(phenylethynyl)phenyl triolborate (**1e**) (85%) using 4-(phenylethynyl)phenyl boronic acid[29] was the same as the synthesis of 2-naphthyl triolborate. ^{1}H NMR (400 MHz, DMSO-d_6): δ=0.50 (s, 3H), 3.60 (s, 6H), 7.19 (d, J=8.4 Hz, 2H), 7.39 (q, J=8.4, 10.8 Hz, 5H), 7.52 (d, J=5.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=16.2, 34.5, 73.7, 87.3, 91.5, 117.4, 123.2, 128.1, 128.7, 128.8, 131.1, 132.4 (C–B is not observed); ^{11}B NMR (128 MHz, DMSO-d_6): δ=1.30; MS (m/z): 148 (100), 297 (36), 305 (M^-, 25); HRMS (FAB^-): m/z calcd for $C_{19}H_{18}BO_3^-$: 305.1354; found: 305.1357; elemental analysis: calcd (%) for $C_{19}H_{18}BKO_3$: C, 66.29; H, 5.27; found: C, 55.63; H,4.53.

*4.1.6. Potassium 4-((4-(diphenylamino)phenyl) ethynyl)phenyltriolborate (**1f**).* 4-((4-Bromophenyl)ethynyl)-*N*,*N*-diphenylaniline[30] 4.23 g (100 mmol) was dissolved in 100 mL THF and cooled to −78 °C under nitrogen. ^{n}BuLi (110 mmol) was added dropwise into the reaction system at −78 °C and stirred for 2 h at the same temperature. Trimethyl borate (200 mmol) was added dropwise at −78 °C. After addition, the mixture was allowed to gradually warm to room temperature overnight. Dilute HCl (2 M, 60 mL) was dropped and stirred for 1 h. Dichloromethane was added and the layers separated. The aqueous layer was extracted with dichloromethane and combined organic layers were washed with water, dried over $MgSO_4$, filtered, and the solvent evaporated under reduced pressure. The crude solid was washed with hexane and dried under reduced pressure to give desired boronic acid as a green-yellow solid (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.02–7.15 (m, 8H), 7.29 (t, J=8.0 Hz, 4H),

7.41 (d, J=8.0 Hz, 2H), 7.61 (d, J=8.0 Hz, 2H), 8.16 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=88.9, 92.2, 115.8, 122.2, 123.8, 125.2, 128.0, 129.5, 131.0, 132.8, 135.6, 147.2, 148.3 (C–B is not observed).

The synthesis of triolborate **1f** (81%) was the same as the synthesis of 2-naphthyl triolborate. ^{1}H NMR (400 MHz, DMSO-d_6): δ=0.45 (s, 3H), 3.55 (s, 6H), 6.86 (d, J=8.0 Hz, 2H), 7.02–7.12 (m, 8H), 7.29–7.35 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=16.8, 35.0, 74.2, 88.0, 91.1, 116.5, 118.4, 122.2, 124.4, 125.3, 129.2, 130.3, 132.8, 147.1, 147.6 (C–B and the other C are not observed); ^{11}B NMR (128 MHz, DMSO-d_6): δ=2.98; MS (m/z): 122 (18), 153 (100), 306 (50), 444 (14), 472 (M^-, 50); HRMS (FAB$^-$): m/z calcd for $C_{31}H_{27}BNO_3^-$: 472.2089; found: 472.2087; elemental analysis: calcd (%) for $C_{31}H_{27}BKNO_3$: C, 72.80; H, 5.32; N, 2.74; found: C, 67.27; H, 5.23; N, 2.27.

*4.1.7. Potassium 2-pyrenyltriolborate (**1g**)[23].* 4,4,5,5-Tetramethyl-2-(2-pyrenyl)-1,3,2-dioxaborolane[23,31] (3.28 g, 10 mmol), 1,1,1-tris (hydroxymethyl)ethane (1.08 g, 9 mmol) and KOH (0.504 g, 9 mmol) were dissolve in 70 mL 1,4-dioxane. Water (0.5 mL) was added. The mixture was warmed to 60 °C and stirred for 16 h. After cooling to room temperature the potassium pyrenyltriolborate (**1g**) was collected by filtration, washed with diethyl ether, and dried under reduced pressure (95%). ^{1}H NMR (400 MHz, DMSO-d_6): δ=0.56 (s, 3H), 3.72 (s, 6H), 7.91–8.13 (m, 7H), 8.30 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ=16.3, 34.7, 73.8, 122.4, 123.5, 124.6, 124.8, 125.1, 128.3, 130.4, 130.5 (C–B is not observed); ^{11}B NMR (128 MHz, DMSO-d_6): δ=1.72; MS (m/z): 122 (16), 153 (60), 238 (12), 328 (20), 329 (M^-, 100); HRMS (FAB$^-$): m/z calcd for $C_{21}H_{18}BO_3^-$: 329.1354; found: 329.1353; elemental analysis: calcd (%) for $C_{21}H_{18}BKO_3$: C, 68.49; H, 4.93; found: C, 54.05; H, 4.91.

4.2. General procedures for double-cross-coupling

4.2.1. $Pd(OAc)_2$/DMF/H_2O system[22a]. The triolborate, dibromides (0.2 mmol), and palladium acetate (10 mol %) were placed in a flask under an atmosphere of nitrogen. DMF/H_2O (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 $MgSO_4$, and then purified by chromatography on silica gel.

4.2.2. $Pd(OAc)_2$/CuCl system[22d]. The triolborate, dibromides (0.2 mmol), palladium acetate (10 mol %), BIPHEP (11 mol), and CuCl (0.4 equiv) were placed in a flask under an atmosphere of nitrogen. DMF (15 mL) 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 $MgSO_4$, and then purified by chromatography on silica gel.

4.2.3. $Pd(PPh_3)_4$/K_2CO_3 system. The triolborate, dibromides (0.2 mmol), $Pd(PPh_3)_4$ (10 mol %), and K_2CO_3 (2 equiv) were placed in flask under an atmosphere of nitrogen. DMF (15 mL) 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 $MgSO_4$, and then purified by chromatography on silica gel.

4.3. Spectral data of diaryl arenes

The spectra of compounds **3ba**,[5d,32] **3bb**,[33] **3be**,[34] **3ce**,[6c,7a] and **3ge**[35] 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}; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ=125.7, 125.9, 127.2, 127.6, 127.7, 128.0, 128.3, 128.4, 131.1, 132.0, 133.4, 139.2, 140.5; MS (m/z): 156 (10), 163 (12), 215 (6), 252 (2), 313 (6), 315 (16), 330 (M^+, 100); HRMS (EI): m/z calcd for $C_{26}H_{18}$: 330.1409; found: 330.1401.

*4.3.2. 2,3-Di(p-tolyl)thiophene (**3bc**).* Oil; IR (neat): 3023, 2919, 2862, 812 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.2, 21.2, 123.6, 128.9, 129.0, 129.1, 129.1, 130.5, 131.5, 133.7, 136.4, 137.1, 137.6, 138.3; MS (m/z): 117 (6), 189 (6), 202 (6), 215 (7), 234 (36), 249 (46), 264 (M^+, 100); HRMS (EI): m/z calcd for $C_{18}H_{16}S$: 264.0973; found: 264.0970.

*4.3.3. 2,3-Di(p-tolyl)furan (**3bd**).* Oil; IR (neat): 3029, 2921, 2859, 1803, 1519, 1063, 819 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 (16), 248 (M^+, 100); HRMS (EI): m/z calcd for $C_{18}H_{16}O$: 248.1201; found: 248.1200.

*4.3.4. 1,8-Bis(p-tolyl)naphthalene (**3be**)[34].* UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 241 (38,550), 303 (12,028); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.21 (s, 6H), 6.71 (d, J=7.6 Hz, 4H), 6.81 (d, J=8.0 Hz, 4H), 7.40 (d, J=6.8 Hz, 2H), 7.53 (t, J=7.6 Hz, 2H), 7.92 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.4, 124.6, 127.2, 127.9, 129.1, 129.2, 130.2, 134.6, 134.9, 139.7, 140.1.

*4.3.5. 4,6-Bis(p-tolyl)dibenzo[b,d]thiophene (**3bf**).* Mp 96–97 °C; IR (neat): 1559, 1542, 1509 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 251 (53,217), 326 (4374), 339 (5103); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.40 (s, 6H), 7.26 (d, J=8.1 Hz, 4H), 7.42–7.60 (m, 8H), 8.12–8.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.3, 120.4, 125.0, 126.9, 128.1, 129.5, 136.5, 136.9, 137.6, 137.7, 138.7; MS (m/z): 69 (2), 182 (1), 364 (M^+, 19); HRMS (EI): m/z calcd for $C_{26}H_{20}S$: 364.1286; found: 364.1275.

*4.3.6. 4,6-Bis(p-tolyl)dibenzo[b,d]furan (**3bg**).* Mp 206–207 °C; IR (neat): 3027, 2914, 2853, 1516, 1484, 1395, 1185 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 261 (42,156), 294 (sh) (16,375), 313 (sh) (10,104), 324 (sh) (9058); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.45 (s, 6H), 7.32 (d, J=8.1 Hz, 4H), 7.43 (t, J=8.1 Hz, 2H), 7.65 (dd, J=2.7, 8.1 Hz, 2H), 7.87–7.96 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.3, 119.4, 123.3, 124.9, 125.6, 126.4, 128.5, 129.3, 133.3, 137.5, 153.3; MS (m/z): 174 (5), 303 (2), 332 (2), 348 (M^+, 100); HRMS (EI): m/z calcd for $C_{26}H_{20}O$: 348.1514; found: 348.1506.

*4.3.7. 1,8-Bis(p-tolyl)biphenylene (**3bh**).* Mp 179–180 °C; IR (neat): 1559, 1514 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 263 (34,237), 356 (3938), 377 (3989); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.26 (s, 6H), 6.63–6.68 (m, 5H), 6.75–6.82 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.0, 115.4, 127.3, 128.0, 128.4, 129.2, 132.8, 135.0, 136.4, 148.2, 151.3; MS (m/z): 150 (3), 302 (5), 316 (5), 332 (M^+, 100); HRMS (EI): m/z calcd for $C_{26}H_{20}$: 332.1565; found: 332.1552.

*4.3.8. 4,5-Bis(p-tolyl)-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (**3bi**).* Mp 231–232 °C; IR (neat): 2962, 2359, 1442, 1237, 815 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 250 (24,632), 299 (6032); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.34 (s, 18H), 1.72 (s, 4H), 2.38 (s, 6H), 6.91 (d, J=7.6 Hz, 4H), 7.12–7.19 (m, 6H), 7.41 (d, J=2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.7, 30.8, 31.1, 34.1, 34.8, 120.5, 125.4, 128.0, 128.9, 129.0, 130.1, 134.9, 135.3, 144.8, 145.8; MS (m/z): 222 (6), 236 (8), 397 (6), 471 (8), 487 (100), 502 (M^+, 8); HRMS (EI): m/z calcd for $C_{37}H_{42}O$: 502.3236; found: 502.3222.

*4.3.9. 1,8-Bis(4-biphenyl)naphthalene (**3ce**)[6c,7a].* UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 242 (41,088), 304 (23,788); ^{1}H NMR

(400 MHz, $CDCl_3$): δ=7.03 (d, J=8.1 Hz, 4H), 7.13 (d, J=8.1 Hz, 4H), 7.22–7.32 (m, 10H), 7.48 (dd, J=2.7, 8.1 Hz, 2H), 7.55–7.60 (m, 2H), 7.98 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=125.2, 125.9, 126.8, 127.1, 128.4, 128.7, 129.5, 130.3, 130.9, 135.4, 138.7, 140.1, 141.0, 142.2.

*4.3.10. 4,6-Bis(4-biphenyl)dibenzo[b,d]thiophene (**3cf**).* Mp 145–146 °C; IR (neat): 3030, 1478, 1185 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 263 (30,782), 292 (21,498), 341 (sh) (4397); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.80 (m, 22H), 8.20 (dd, J=2.7, 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=120.7, 125.2, 127.0, 127.1, 127.4, 127.5, 128.7, 128.8, 136.5, 136.6, 138.7, 139.4, 140.6, 140.8; MS (m/z): 244 (23), 488 (M^+, 100); HRMS (EI): m/z calcd for $C_{36}H_{24}S$: 488.1599; found: 488.1581.

*4.3.11. 4,6-Bis(4-biphenyl)dibenzo[b,d]furan (**3cg**).* Mp 284–286 °C; IR (neat): 3028, 2159, 1478, 1394, 1181, 840 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 282 (36,863); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36–7.40 (m, 2H), 7.46–7.50 (m, 6H), 7.68–7.76 (m, 10H), 7.99–8.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=119.3, 123.0, 124.5, 124.7, 126.2, 126.6, 126.7, 126.9, 126.9, 128.4, 128.5, 134.7, 140.3, 152.9; MS (m/z): 236 (30), 289 (8), 306 (40), 320 (55), 400 (10), 472 (M^+, 100); HRMS (EI): m/z calcd for $C_{36}H_{24}O$: 472.1827; found: 472.1815.

*4.3.12. 4,5-Di(4-biphenyl)-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (**3ci**).* Mp 255–256 °C; IR (neat): 2961, 2360, 1437, 1231, 835 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 269 (40,122), 304 (sh) (16,926); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.37 (s, 18H), 1.75 (s, 6H), 7.23–7.28 (m, 8H), 7.34–7.43 (m, 12H), 7.46 (d, J=2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=30.9, 31.1, 34.1, 34.8, 121.0, 125.7, 126.1, 126.5, 128.3, 128.3, 129.7, 130.3, 136.9, 138.8, 140.3, 145.0, 145.8; MS (m/z): 262 (3), 284 (8), 305 (25), 595 (8), 611 (100), 626 (M^+, 8); HRMS (EI): m/z calcd for $C_{47}H_{46}O$: 626.3549; found: 626.3526.

*4.3.13. 1,8-Bis[4-(diphenylamino)phenyl] naphthalene (**3de**).* Mp 278–279 °C; IR (neat): 3027, 1588, 1489, 1271, 815 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 313 (13,526), 337 (12,296); ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.84 (dd, J=8.4, 15.6 Hz, 8H), 7.01 (t, J=6.8 Hz, 4H), 7.17–7.25 (m, 16H), 7.43 (d, J=6.8 Hz, 2H), 7.53 (t, J=7.6 Hz, 2H), 7.91 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=121.0, 122.9, 125.0, 125.1, 128.1, 129.2, 129.4, 130.5, 135.6, 137.1, 140.2, 145.7, 147.7; MS (m/z): 77 (2), 167 (4), 307 (13), 614 (M^+, 100); HRMS (EI): m/z calcd for $C_{46}H_{34}N_2$: 614.2722; found: 614.2717.

*4.3.14. 4,6-Bis[4-(diphenylamino)phenyl]dibenzo[b,d]thiophene (**3df**).* Mp 204–205 °C; IR (neat): 3033, 1585, 1483, 1270, 1179, 746 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 298 (24,152), 312 (24,152), 344 (sh) (20,127); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.04–7.08 (m, 4H), 7.16–7.31 (m, 20H), 7.47–7.61 (m, 8H), 8.13–8.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=119.8, 122.6, 122.7, 124.4, 124.6, 126.4, 128.5, 128.9, 133.6, 136.1, 136.1, 137.9, 147.1, 147.1; MS (m/z): 335 (32), 670 (M^+, 100); HRMS (EI): m/z calcd for $C_{48}H_{34}N_2S$: 670.2443; found: 670.2423.

*4.3.15. 4,6-Bis[4-(diphenylamino)phenyl]dibenzo[b,d]furan (**3dg**).* Mp 255–256 °C; IR (neat): 1589, 1488, 1265 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 302 (28,156), 346 (19,644); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.00–7.03 (m, 4H), 7.16–7.25 (m, 20H), 7.42 (t, J=8.0 Hz, 2H), 7.64 (d, J=7.6 Hz, 2H), 7.86 (d, J=8.8 Hz, 4H), 7.91–7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=118.7, 122.6, 122.8, 124.1, 124.4, 124.7, 125.4, 128.8, 128.8, 129.4, 147.0, 147.1, 152.7; MS (m/z): 411 (4), 488 (6), 654 (M^+, 100); HRMS (EI): m/z calcd for $C_{48}H_{34}N_2O$: 654.2671; found: 654.2660.

*4.3.16. 1,8-Bis[4-(diphenylamino)phenyl]biphenylene (**3dh**).* Mp 298–299 °C; IR (neat): 2360, 2185, 1588, 1489, 1067, 831 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 272 (20,442), 308 (25,552), 347 (20,442); ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.65 (t, J=4 Hz, 2H), 6.74 (d, J=8 Hz, 4H), 6.83–6.89 (m, 8H), 6.97–7.01 (m, 4H), 7.06 (d, J=8.4 Hz, 8H), 7.16 (t, J=8 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=114.7, 121.6, 122.4, 124.4, 128.0, 128.1, 128.6, 128.9, 131.2, 131.8, 146.8, 147.1, 147.2, 150.8; MS (m/z): 319 (22), 638 (M^+, 100); HRMS (EI): m/z calcd for $C_{48}H_{34}N_2$: 638.2722; found: 638.2727.

*4.3.17. 4,5-Bis[4-(diphenylamino)phenyl]-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (**3di**).* Mp >300 °C; IR (neat): 2958, 1592, 1480, 1271 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 314 (27,509); ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.91–6.99 (m, 8H), 7.04–7.06 (m, 8H), 7.12–7.16 (m, 8H), 7.20 (d, J=2.4 Hz, 2H), 7.25–7.28 (m, 4H), 7.40 (d, J=2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=31.1, 31.1, 34.0, 34.7, 120.6, 121.9, 122.2, 124.2, 125.6, 128.4, 128.8, 130.0, 130.1, 131.9, 144.8, 145.6, 145.9, 147.2; MS (m/z): 381 (8), 396 (56), 777 (8), 793 (75), 808 (M^+, 100); HRMS (EI): m/z calcd for $C_{59}H_{56}N_2O$: 808.4393; found: 808.4379.

*4.3.18. 1,8-Bis[4-(phenylethynyl)phenyl] naphthalene (**3ee**).* Mp 229–230 °C; IR (neat): 2360, 2340, 1507, 1180, 821 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 280 (15,860), 314 (17,302); ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.95 (dd, J=1.6 Hz, 6.4 Hz, 4H), 7.15–7.25 (m, 8H), 7.42–7.45 (m, 6H), 7.56–7.61 (m, 4H), 7.97 (dd, J=1.2, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=88.6, 89.1, 120.3, 123.0, 124.8, 127.4, 127.7, 128.5, 128.6, 129.2, 130.0, 131.1, 134.9, 139.1, 142.5; MS (m/z): 480 (M^+, 100); HRMS (EI): m/z calcd for $C_{38}H_{24}$: 480.1878; found: 480.1865.

*4.3.19. 4,6-Bis[4-(phenylethynyl)phenyl]dibenzo[b,d]thiophene (**3ef**).* Mp 238–240 °C; IR (neat): 3033, 2360, 2339, 2159, 1518, 1397, 1179, 1065, 840 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 277 (33,275), 303 (39,716); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.36 (m, 6H), 7.49–7.60 (m, 8H), 7.64–7.72 (m, 8H), 8.19 (dd, J=1.2, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=89.3, 90.3, 121.0, 123.1, 123.3, 125.4, 127.0, 128.4, 128.5, 131.8, 132.2, 136.3, 136.7, 138.6, 140.4; MS (m/z): 268 (21), (M^+, 100); HRMS (EI): m/z calcd for $C_{40}H_{24}S$: 536.1599; found: 536.1589.

*4.3.20. 4,6-Bis[4-(phenylethynyl)phenyl]dibenzo[b,d]furan (**3eg**).* Mp 198–200 °C; IR (neat): 3050, 2159, 1511, 1106, 844 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 299 (84,377); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.35–7.39 (m, 6H), 7.47 (t, J=7.6 Hz, 2H), 7.58–7.61 (m, 4H), 7.69–7.71 (m, 6H), 7.97–7.80 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=89.4, 90.3, 120.1, 122.7, 123.3, 123.5, 124.9, 124.9, 126.6, 128.3, 128.4, 128.5, 131.7, 131.9, 136.0, 153.2; MS (m/z): 260 (19), 442 (4), 520 (M^+, 100); HRMS (EI): m/z calcd for $C_{40}H_{24}O$: 520.1827; found: 520.1804.

*4.3.21. 4,5-Bis[4-(phenylethynyl)phenyl]-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (**3ei**).* Mp 242–243 °C; IR (neat): 3058, 1516, 1179 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 291 (40,494); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.36 (s, 18H), 1.73 (s, 6H), 7.12–7.14 (m, 4H), 7.20–7.23 (m, 6H), 7.25–7.40 (m, 10H), 7.45 (d, J=2.0 Hz, 2H), 7.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=31.3, 31.6, 34.6, 35.2, 89.4, 89.5, 121.6, 121.6, 123.4, 125.8, 126.9, 127.8, 128.1, 128.4, 128.6, 129.6, 130.7, 131.1, 131.6, 131.6, 132.1, 138.1, 145.6, 146.1; MS (m/z): 43 (12), 50 (25), 57 (17), 76 (42), 83 (20), 203 (25), 230 (100), 262 (71), 329 (14), 659 (100), 674 (M^+, 29); HRMS (EI): m/z calcd for $C_{51}H_{46}O$: 674.3549; found: 674.3549.

*4.3.22. 1,8-Bis[4-((4-(diphenylamino)phenyl) ethynyl)phenyl]naphthalene (**3fe**).* Mp 274–275 °C; IR (neat): 30,323, 2358, 1586, 1510, 1487, 1268, 820 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$) 306 (44,825), 352 (63,570); ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.90–7.0 (m, 8H), 7.02–7.07 (m, 12H), 7.12–7.14 (m, 4H), 7.20–7.24 (m, 8H),

7.32 (dd, J=2.0, 6.8 Hz, 4H), 7.42 (dd, J=1.6, 7.2 Hz, 2H), 7.56 (dd, J=7.2, 8.4 Hz, 2H), 7.95 (dd, J=1.6, 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=88.5, 88.9, 116.1, 120.7, 122.0, 122.9, 124.3, 124.8, 128.4, 128.6, 128.9, 129.2, 129.9, 130.4, 132.1, 135.0, 139.2, 142.2, 146.7, 147.1; MS (m/z): 407 (30), 814 (M^+, 100); HRMS (EI): m/z calcd for $C_{62}H_{42}N_2$: 814.3348; found: 814.3547.

*4.3.23. 4,6-Bis[4-((4-(diphenylamino)phenyl) ethynyl)phenyl]dibenzo [b,d]thiophene (**3ff**).* Mp 194–196 °C; IR (neat): 3033, 2358, 1585, 1489, 1271, 1181, 836 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 273 (43,555), 299 (47,039), 361 (67,075); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.01–7.08 (m, 8H), 7.11–7.13 (m, 8H), 7.25–7.39 (m, 8H), 7.38–7.40 (m, 4H), 7.49–7.51 (m, 2H), 7.55–7.63 (m, 6H), 7.68–7.70 (m, 4H), 7.18 (dd, J=1.2, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=88.0, 90.1, 115.6, 120.4, 121.8, 122.9, 123.1, 124.5, 124.8, 126.5, 127.8, 128.9, 131.4, 132.1, 135.8, 136.1, 138.0, 139.4, 146.7, 147.5; MS (m/z): 435 (30), 870 (M^+, 100); HRMS (EI): m/z calcd for $C_{64}H_{42}N_2O$: 870.3069; found: 870.3074.

*4.3.24. 4,6-Bis[4-((4-(diphenylamino)phenyl) ethynyl)phenyl]dibenzo [b,d]furan (**3fg**).* Mp 124–125 °C; IR (neat): 3032, 2359, 1586, 1511, 1488, 1271, 834, 693 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 298 (63,270), 362 (74,385); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.01–7.13 (m, 8H), 7.24–7.27 (m, 8H), 7.27–7.29 (m, 8H), 7.41–7.46 (m, 6H), 7.64–7.68 (m, 6H), 7.94–7.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=88.3, 90.2, 115.6, 119.6, 121.9, 122.6, 123.1, 124.5, 124.5, 126.0, 128.0, 131.3, 132.2, 135.2, 146.7, 147.5, 152.7; MS (m/z): 427 (35), 854 (M^+, 100); HRMS (EI): m/z calcd for $C_{64}H_{42}N_2O$: 854.3297; found: 854.3294.

*4.3.25. 4,5-Bis[4-((4-(diphenylamino)phenyl) ethynyl)phenyl]-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (**3fi**).* Mp 243–244 °C; IR (neat): 2956, 2358, 2155, 2024, 1588, 1490, 1441, 1274, 1234, 834 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 282 (39,363), 351 (63,586); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.36 (s, 18H), 1.72 (s, 6H), 6.83 (d, J=6.8 Hz, 4H), 6.84–7.03 (m, 12H), 7.17–7.21 (m, 10H), 7.24–7.26 (m, 4H), 7.30–7.33 (m, 8H), 7.44 (d, J=2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=31.6, 31.6, 34.6, 35.3, 89.0, 89.7, 116.7, 121.5, 121.9, 122.4, 123.3, 124.8, 125.7, 128.7, 129.3, 129.6, 130.7, 131.0, 132.7, 137.8, 145.6, 146.1, 147.2, 147.5; MS (m/z): 412 (7), 496 (27), 993 (67), 1008 (M^+, 100); HRMS (EI): m/z calcd for $C_{75}H_{64}N_2O$: 1008.5019; found: 1008.4974.

*4.3.26. 1,8-Bis(2-pyrenyl)naphthalene (**3ge**)*[35]. UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 245 (49,688), 278 (24,844), 315 (21,144), 328 (27,487), 344 (sh) (11,629); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.28–7.34 (m, 8H), 7.55–7.61 (m, 10H), 7.68–7.70 (m, 4H), 8.14 (dd, J=2.4, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=122.3, 123.6, 124.5, 125.6, 126.4, 126.6, 126.9, 129.6, 130.0, 130.7, 131.6, 140.7, 141.4 (three carbons were not observed); MS (m/z): 264 (13), 326 (23), 528 (M^+, 100); HRMS (EI): m/z calcd for $C_{42}H_{24}$: 528.1870; found: 528.1863.

*4.3.27. 1,8-Bis(2-pyrenyl)biphenylene (**3gh**).* Mp >300 °C; IR (neat): 3037, 2360, 1362, 1257, 876 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 277 (73,509), 328 (28,740), 344 (22,661), 382 (sh) (4974); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=6.84–7.00 (m, 2H), 7.02–7.07 (m, 6H), 7.13–7.25 (m, 6H), 7.46–7.54 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=115.9, 123.2, 123.3, 123.7, 123.9, 125.2, 125.8, 126.1, 128.9, 129.8, 130.1, 133.4, 135.3, 149.2, 151.7 (one carbon was not observed); MS (m/z): 274 (13), 350 (4), 552 (M^+, 100); HRMS (EI): m/z calcd for $C_{44}H_{24}$: 552.1870; found: 552.1866.

*4.3.28. 4,5-Bis(2-pyrenyl)-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (**3gi**).* Mp >300 °C; IR (neat): 2957, 2361, 2163, 1440, 1257, 879, 713 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 263 (36,037), 313 (33,258), 325 (36,873), 342 (25,305); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.43 (s, 18H), 1.88 (s, 6H), 7.11 (s, 8H), 7.40 (d, J=2.4 Hz, 2H), 7.55–7.68 (m, 8H), 7.87 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=31.2, 32.4, 34.2, 34.6, 121.7, 122.6, 123.5, 123.7, 124.7, 125.4, 125.6, 125.7, 126.2, 129.1, 129.2, 129.8, 129.9, 134.9, 144.9, 145.0; MS (m/z): 338 (12), 353 (48), 707 (100), 722 (M^+, 100); HRMS (EI): m/z calcd for $C_{55}H_{46}O$: 722.3549; found: 722.3548.

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