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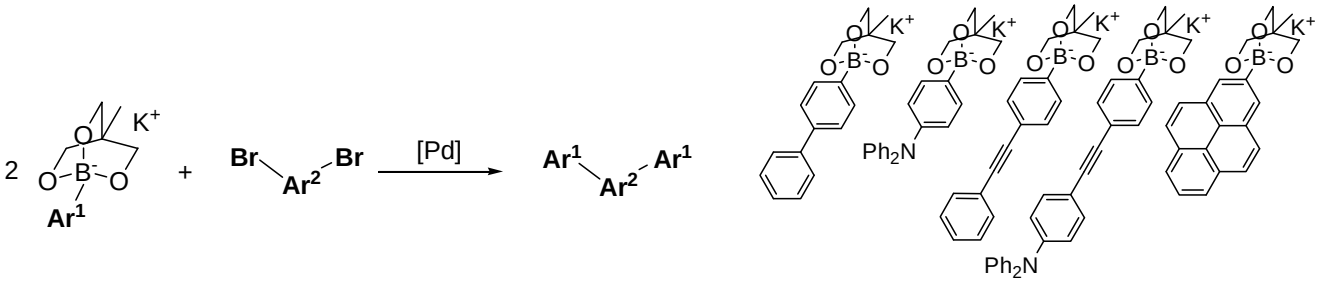
Gao-Qiang Li, Yasunori Yamamoto* and Norio Miyaura

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



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Double-Coupling of Dibromo Arenes with Aryltriolborates for Synthesis of Diaryl-Substituted Planar Frameworks.

Gao-Qiang Li[a], Yasunori Yamamoto[a,*] and Norio Miyaura[a]

[a] *Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
aryltriolborates
palladium catalyst
cross-coupling reaction
dibromo arenes
double arylation

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 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] 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.

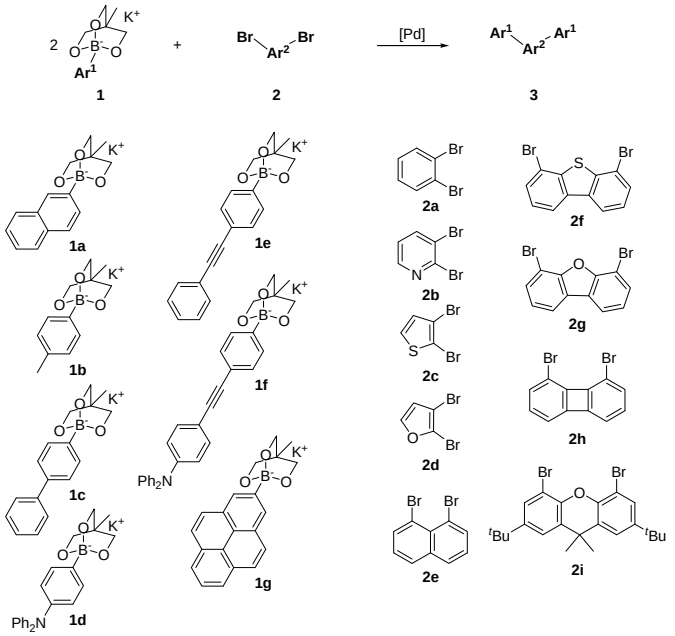
Diaryl-substituted planar frameworks such as naphthalene,[9-13] biphenylene,[14,15] dibenzothiophene,[16] dibenzofuran[15] and xanthene[15,17] have fascinating scaffolds with unusual geometry in organic molecules. The two aryl units bonded to planar frameworks in sufficiently close positions provide 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 previous work, when aryltriolborates were

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



Scheme 1. Double coupling of dibromo arenes with potassium aryltriolborates

used for palladium-catalyzed cross-coupling reactions,[22] the use of a phosphine ligand and base could sometimes be avoided.

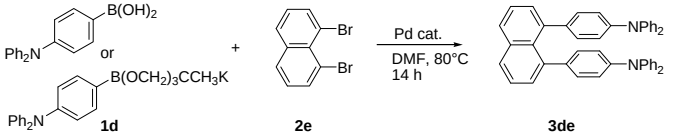
To further show the efficiency of this methodology, we first tried to synthesize *ortho*-disubstituted benzene, pyridine, thiophene, and furan (Table 1, entries 1-6). *Ortho*-disubstituted benzene was obtained in excellent yields, 92% yield being obtained even for highly congested di(2-naphthyl)substituted 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 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 (**1c**) 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 (**1c**) (Table 1, entries 12 and 13). Unfortunately, when biphenyl triolborate (**1c**) 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)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, **2g** and **2i** 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 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% $Pd(PPh_3)_4$ and 2 equivalents 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 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% $Pd(PPh_3)_4$ was used, 77% isolated yield was also observed (entry 4), and when 2 equivalents 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.

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	Ph_2N–C$_6$H$_4$–$B(OH)_2$	$Pd(PPh_3)_4$	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	Ph_2N–C$_6$H$_4$–$B(OCH_2)_3CCH_3K$	$Pd(PPh_3)_4$	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%).

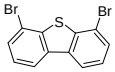
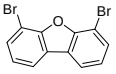
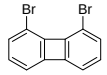
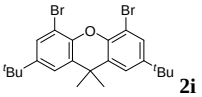
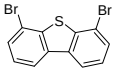
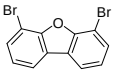
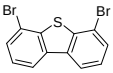
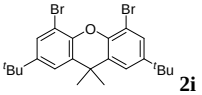
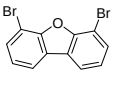
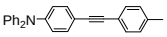
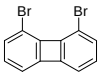
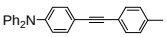
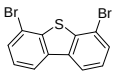
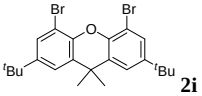
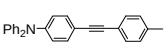
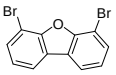
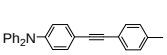
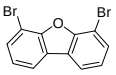
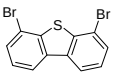
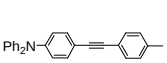
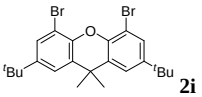
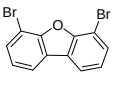
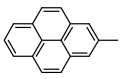
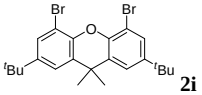
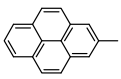
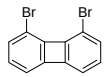
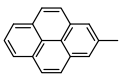
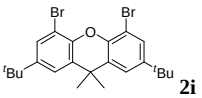
[b]Isolated yields.

[c]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-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, 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

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
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 eq.), $Pd(OAc)_2$ (10 mol%), DMF/H_2O (4/1, 10 mL), r.t., 16 h.

Condition B: triolborate (**1**, 3.0 eq.), $Pd(OAc)_2$ (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.), $Pd(PPh_3)_4$ (10 mol%), K_2CO_3 (2 eq.), DMF (15 mL), 80 °C, 14 h.

[a] $Pd(OAc)_2$ (6 mol%) was used.

[b] triolborate (**1**, 2.2 eq.) was used.

[c] triolborate (**1**, 4.0 eq.) was used.

[d] triolborate (**1**, 2.4 eq.) was used.

[e] toluene was used.

(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-naphthyltriolborate (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-tolyl triolborate **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 biphenyltriolborate (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 2h 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 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 pyrenyl triolborate (**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$_2$O 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 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 $MgSO_4$, and then purified by chromatography on silica gel.

4.2.3. Pd(PPh$_3$)$_4$/K$_2$CO$_3$ system

The triolborate, dibromides (0.2 mmol), $Pd(PPh_3)_4$ (10 mol%) and K_2CO_3 (2 eq) were placed in 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 $MgSO_4$, 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**,[6o,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 (38550), 303 (12028); ^{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 (53217), 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 (42156), 294 (sh) (16375), 313 (sh) (10104), 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 (34237), 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 (24632), 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)[6o,7a]

UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 242 (41088), 304 (23788); ^{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 (30782), 292 (21498), 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 (36863); ^1H 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 (40122), 304 (sh) (16926); ^1H 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 (13526), 337 (12296); ^1H 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 (24152), 312 (24152), 344 (sh) (20127); ^1H 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 (28156), 346 (19644); ^1H 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 (20442), 308 (25552), 347 (20442); ^1H 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 (27509); ^1H 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 (15860), 314 (17302); ^1H 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 (33275), 303 (39716); ^1H 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 (84377); ^1H 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 (40494); ^1H 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): 30323, 2358, 1586, 1510, 1487, 1268, 820 cm^{-1}; UV: λ_{max} ($CHCl_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 306 (44825), 352 (63570); ^1H 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 (43555), 299 (47039), 361 (67075); ^1H 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 (63270), 362 (74385); ^1H 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 (39363), 351 (63586); ^1H 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 (49688), 278 (24844), 315 (21144), 328 (27487), 344 (sh) (11629); ^1H 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 (73509), 328 (28740), 344 (22661), 382 (sh) (4974); ^1H 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 (36037), 313 (33258), 325 (36873), 342 (25305); ^1H 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.

Acknowledgments

This work was supported in part by the Global COE Program (Project No. B01, Catalysis as the Basis for Innovation in Materials Science) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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