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Synthesis of bis(alk-3-en-1-ynyl)benzene with either *E*- or *Z*-configuration via a one-pot three-component coupling reaction and its optical properties

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Abstract—A convenient, efficient and stereoselective synthesis of a range of bis(alk-3-en-1-ynyl)benzenes with *E*- and *Z*-configuration is described. The protocol involves Cu-mediated cross-coupling reaction of (*E*)- and (*Z*)-alk-1-enyldisiamylboranes with (trimethylsilyl)ethynyl bromide and Pd/Cu-catalyzed cross-coupling reaction with diiodobenzene. The sequential cross-coupling reaction proceeds readily under extremely mild conditions in a one-pot manner to afford bis(alk-3-en-1-ynyl)benzenes in good to excellent yields. The optical properties of the products are also described.

The development of molecular wire-like architectures has attracted much attention due to their stimulating potential in the field of molecular electronics.[1] For example, 1,4-bis(phenylethynyl)benzene derivatives display interesting properties such as molecular switch[2] and liquid-crystalline.[3] There has been lately a growing interest in highly conjugated systems based on phenylacetylene scaffolding.[4] Conjugated systems containing 1,2-, 1,3- and 1,4-diethynylphenyl units have been used in the preparation of aromatic oligomers bearing multiple ethynyl groups with electroluminescence properties.[4c] Bunz and co-workers[5] and Beeby et al.[6] independently have reported photophysical properties of the parent species 1,4-bis(phenylethynyl)benzene. On the other hand, the photochemistry of (*E*,*E*)-1,2- and (*E*,*E*)-1,4-bis(phenylethenyl)benzene, whose benzene rings are linked by ethenyl groups, has been investigated as well.[7] To our knowledge, there is no report on the synthesis and the optical properties of bis-(4-phenylbut-3-en-1-ynyl)benzene in which the internal benzene ring is connected to two ethynyl moieties of butenynyl groups and the terminal benzene rings are each connected to an ethenyl moiety. We have previously reported the stereoselective synthesis of (*E*)- and (*Z*)-alk-3-en-1-ynes (**3** and **4**) from (*E*)- and (*Z*)-alk-1-enyldisiamylboranes (**1** and **2**) and (trimethylsilyl)ethynyl bromide via Cu-mediated cross-coupling reaction.[8] In continuation of our interest in one-pot synthesis of conjugated compounds from **3** and **4**,[9] here we wish to report the first stereoselective synthesis of bis(alk-3-en-1-ynyl)benzenes[10] with *E*- and *Z*-configuration through a sequential one-pot, two-step process involving Cu-mediated cross-coupling of **1** and **2** with (trimethylsilyl)ethynyl bromide and Pd/Cu-catalyzed cross-coupling of **3** and **4** with diiodobenzene.

The cross-coupling of (*E*)-2-phenylethenyldisiamylborane (**1a**)[11] with (trimethylsilyl)ethynyl bromide followed by 1,4-diiodobenzene was chosen as the initial model reaction in order to optimize the reaction conditions. The reaction of **1a** with (trimethylsilyl)ethynyl bromide (0.67 equiv) was carried out in the presence of Cu(acac)$_2$ (0.05 equiv) as the catalyst and 1 M NaOMe (0.75 equiv) as the base in THF at −15 °C to room temperature overnight: conditions similar to those in our previous work.[8] The cross-coupling product, (*E*)-4-phenylbut-3-en-1-yne (**3a**), was formed in 75% GC yield based on (trimethylsilyl)ethynyl bromide employed, that

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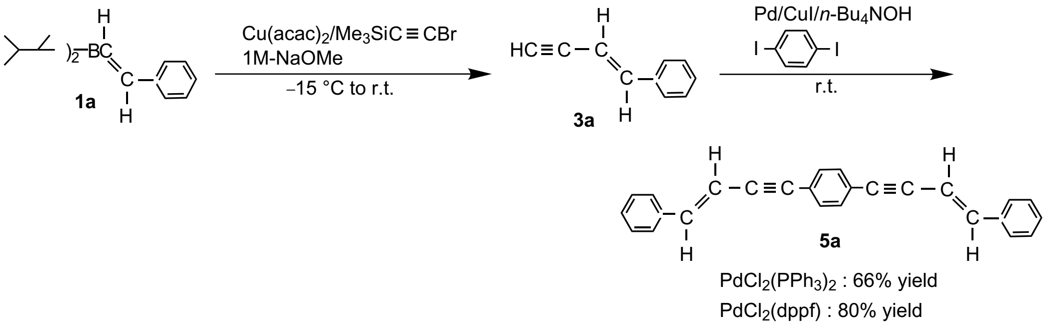
is, the amount of **3a** corresponds closely to 0.5 equiv towards **1a**. Intermediate **3a** was subsequently subjected to the reaction with 1,4-diiodobenzene (0.25 equiv) under the same conditions that we reported earlier[9]—that is, $PdCl_2(PPh_3)_2$ (0.01 equiv) and CuI (0.02 equiv) as the catalyst system and *n*-Bu_4NOH (1 equiv) as the base in THF at room temperature for 4 h. The desired product, 1,4-bis[(*E*)-4-phenylbut-3-en-1-ynyl]benzene (**5a**), was obtained in 66% isolated yield, based on 1,4-diiodobenzene employed, as shown in Scheme 1.

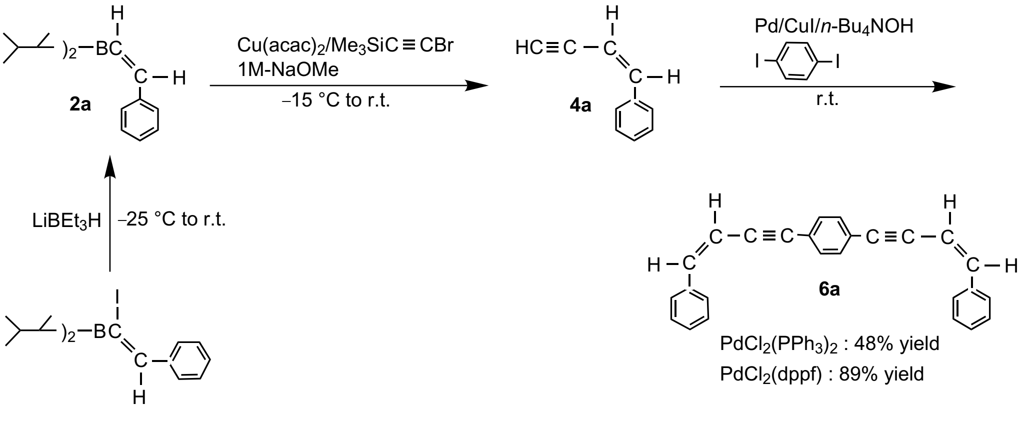
Using $PdCl_2(dppf)$ as the palladium catalyst in place of $PdCl_2(PPh_3)_2$, we observed a significant improvement in the yield of product **5a**, 80% isolated yield.[12] We next examined the cross-coupling reaction of (*Z*)-4-phenylbut-3-en-1-yne (**4a**) with 1,4-diiodobenzene. (*Z*)-2-Phenylethenyldisiamylborane (**2a**) was generated by treatment of (*Z*)-1-iodo-2-phenylethenyldisiamylborane[11] with $LiBEt_3H$ (1 equiv),[13] followed by cross-coupling reaction with (trimethylsilyl)ethynyl bromide (0.67 equiv) as illustrated in Scheme 2, giving **4a** in 73% GC yield based on (trimethylsilyl)ethynyl bromide employed. Thus, about a half amount of **2a** was converted into **4a**. Subsequent reaction of **4a** with 1,4-diiodobenzene (0.25 equiv) was conducted in the same manner as $PdCl_2(dppf)$ was used, affording the desired product, 1,4-bis[(*Z*)-4-phenylbut-3-en-1-ynyl]benzene (**6a**),[14] in 89% isolated yield based on 1,4-diiodobenzene employed. Use of $PdCl_2(PPh_3)_2$ as the palladium catalyst gave **6a** in much lower yield (48%). It is noteworthy that both **5a** and **6a** were synthesized stereoselectively in high yields without isolation of terminal conjugated enynes (**3a** and **4a**).

With our optimized reaction conditions in hand, we then carried out the sequential cross-coupling reaction using combinations of typical alk-1-enyldisiamylboranes (**1** and **2**) and diiodobenzenes (1,2-, 1,3- and 1,4-), and the results are summarized in Table 1. Most of the reactions proceeded smoothly to furnish bis[(*E*)-alk-3-en-1-ynyl]benzene (**5**) and bis[(*Z*)-alk-3-en-1-ynyl]benzene (**6**) in good to excellent yields. The reaction of **1a** with 1,2-diiodobenzene gave 1,2-bis[(*E*)-4-phenylbut-3-en-1-ynyl]benzene (**5c**)[15] in only 39% isolated yield. Unfortunately, in the reaction of **2a** with 1,2-diiodobenzene the desired product could not be obtained, though other palladium catalysts were employed under similar reaction conditions. There appears to be steric repulsion between phenyl groups. It should be noted that the whole transformation can be performed sequentially in one-pot manner.

The UV–vis absorption and fluorescence emission spectra of the bis(alk-3-en-1-ynyl)benzenes (**5a–f**, **6a**, **6b**, **6d–f**) thus prepared were recorded as dilute THF solutions and are summarized in Table 2. The UV–vis spectra of selected compounds are shown in Figure 1. In THF solution, the UV–vis spectrum of **5a** showed a continuous absorption from 250 to 400 nm. The absorption maximum was observed at 355 nm ($\varepsilon = 151{,}300$), whose

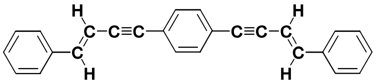
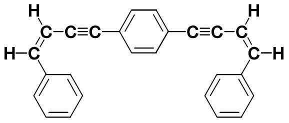
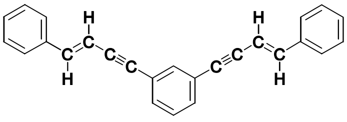
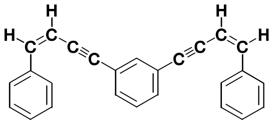
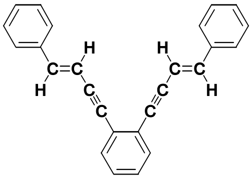
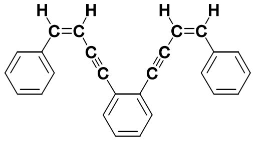
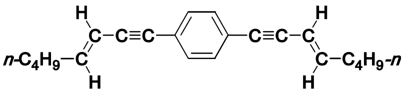
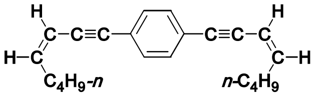
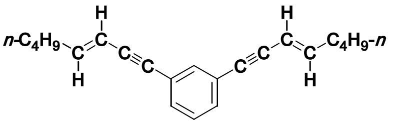
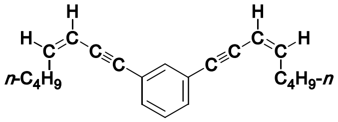
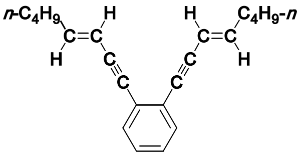
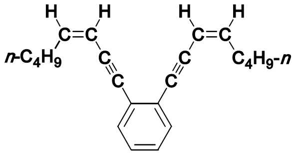


Scheme 1.



Scheme 2.

Table 1. Synthesis of bis(alk-3-en-1-ynyl)benzenes from (*E*)- or (*Z*)-alk-1-enyldisiamylborane, (trimethylsilyl)ethynyl bromide and diiodobenzene through sequential two cross-coupling reactions[a]

Product	Yield[b] (%)	Product	Yield[b] (%)
 **5a**	80 (66)[c]	 **6a**	89 (48)[c]
 **5b**	90	 **6b**	80
 **5c**	39	 **6c**	0
 **5d**	91 (77)[c]	 **6d**	92 (81)[c]
 **5e**	94	 **6e**	95
 **5f**	90	 **6f**	95

[a] Reaction conditions: (i) alk-1-enyldisiamylborane (4 mmol), $Cu(acac)_2$ (0.2 mmol), (trimethylsilyl)ethynyl bromide (2.68 mmol), 1 M NaOMe (3 mmol), and THF (12 mL) at −15 °C to room temperature overnight. (ii) $PdCl_2(dppf)$ (0.04 mmol), CuI (0.08 mmol), n-Bu_4NOH (4 mmol), and diiodobenzene (2 mmol) at room temperature for 4 h.

[b] Isolated yield based on diiodobenzene employed.

[c] $PdCl_2(PPh_3)_2$ was used in place of $PdCl_2(dppf)$.

high extinction coefficient is noteworthy. Similar spectra were observed in toluene and chloroform solutions. Compound **5a** was spectroscopically similar to (*E*,*E*)-1,4-bis(phenylethenyl)benzene[7] rather than 1,4-bis(phenylethynyl)benzene[5,6] which exhibited an absorption band between 250 and 350 nm. Geometrical difference in 1,4-bis-(4-phenylbut-3-en-1-ynyl)benzene showed no effect on the wavelength of maximum UV–vis absorptions, while **5a** had a higher extinction coefficient, compared with **6a** ($\varepsilon = 95{,}600$). The UV–vis spectra of 1,3-bis(phenylethynyl)benzenes with *E*- and *Z*-configuration (**5b** and **6b**)[16] showed absorption bands from 250 to 360 nm with similar patterns and much the same absorption maxima at ca. 320 nm. However, the absorption intensity of **5b** was much higher than that of **6b**. On the other hand, the UV–vis spectrum of **5c** displayed the absorption maximum at 311 nm and the low extinction coefficient. Compounds **5a** and **6a**, in which two phenylbutenynyl groups were substituted at *para*-position, had the longest wavelength absorption, whereas **5c** with *ortho*-substituted phenylbutenynyl groups had the shortest wavelength absorption. These results indicated that **5a**–**c** or **6a** and **6b** were different in the π-conjugation contribution of the phenylbutenynyl groups through the conjugated bond to the central phenyl ring. It appears that the relatively red shifts of **5a** and **6a** are mostly due to the linear conjugated pathway.

The emission spectrum of **5a** obtained by irradiation at excitation wavelength from 220 to 400 nm exhibited two maxima at 388 and 410 nm, respectively. The emission maxima were independent of the selected emission wavelength and the excitation spectrum of the emission closely resembled the UV–vis absorption spectrum. The emission spectra of **5a** and **6a** were also similar to that of (*E*,*E*)-1,4-bis(phenylethenyl)benzene, indicating that

Table 2. UV–vis absorption and fluorescence emission data of bis(alk-3-en-1-ynyl)benzenes[a]

Entry	Compound	Absorption λ_{max} (nm) (ε [M^{-1} cm^{-1}])	Emission λ_{max} (nm)
1	**5a**	355 (151,300)	388, 410
2	**6a**	355 (95,600)	389, 410
3	**5b**	320 (140,500), 341 (11,000)	349
4	**6b**	319 (62,500), 339 (43,900)	349
5	**5c**	311 (43,000)	405
6	**5d**	312 (55,900), 331 (41,200)	336, 352
7	**6d**	297 (47,100), 315 (55,000), 332 (31,300)	336, 353
8	**5e**	276 (69,700), 292 (62,800)	335
9	**6e**	277 (83,000), 293 (72,800),	336
10	**5f**	254 (45,700), 268 (67,800), 304 (25,700)	350
11	**6f**	254 (38,200), 268 (53,100), 304 (23,900)	352

[a] All spectra were recorded at room temperature in THF.

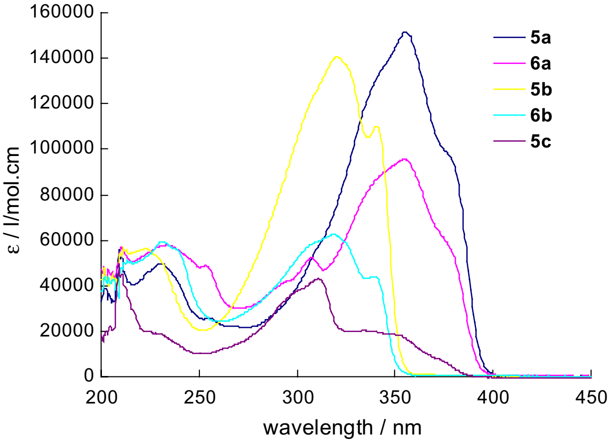


Figure 1.

geometrical difference in 1,4-bis-(4-phenylbut-3-en-1-ynyl)benzene did not affect the emission maxima and bands, although **5a** had lower fluorescence intensity than **6a**.[17] The fluorescence bands of **5a** and **6a** overlapped with their strong absorption bands in the area of 360–400 nm, while **5c** had large Stokes shift (94 nm), albeit its fluorescence was of very low intensity.[18] Bis(oct-3-en-1-ynyl)benzenes (**5d–f**, **6d–f**) displayed UV–vis absorption and emission spectra dependent on substituted positions on phenyl ring in analogy with bis-(4-phenylbut-3-en-1-ynyl)benzenes.

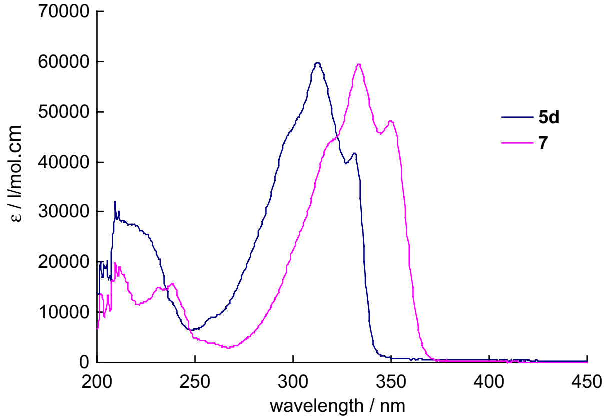


Figure 2.

It is interesting to compare the optical properties of bis(alk-3-en-1-ynyl)benzene and bis(alk-1-en-3-ynyl)benzene in which the carbon–carbon triple and double bonds are interchanged. We could synthesize 1,4-bis[(*E*)-oct-1-en-3-ynyl]benzene (**7**) as an example in the following way (Scheme 3). The cross-coupling reaction of 1,4-bis[(*E*)-ethenyldisiamylboryl]benzene, prepared by hydroboration of 1,4-diethynylbenzene with disiamylborane (2 equiv), with 1-iodohex-1-yne was carried out in the presence of $Cu(acac)_2$ (0.1 equiv) and 2 M NaOH (2 equiv) at −15 °C to room temperature overnight.[19] After usual work-up, the crude product was purified by column chromatography on silica-gel to give product **7** in 70% yield.[20] The UV–vis spectra of **7** and **5d**[21] in THF are shown in Figure 2. The absorption pattern of **7** was like that of **5d**, whereas the absorption maxima of **7** showed red shift (ca. 20 nm) relative to those of **5d**. It may be attributed in part to the better conjugation pathway than **5d**. The fluorescence band of **7** also exhibited red shift compared with **5d**, although the fluorescence intensity was a fourth of that of **5d**.

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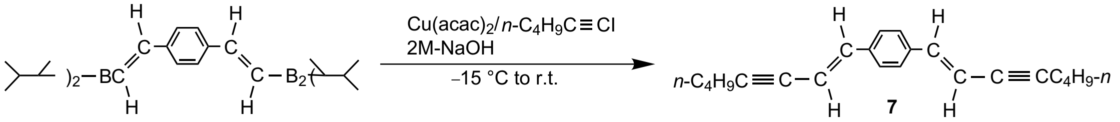

Scheme 3.

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11. (a) Brown, H. C. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975; (b) Matteson, D. S. *Stereodirected Synthesis with Organoboranes*; Springer: Berlin, 1995.
12. *General procedure for the preparation of* **5**: To a stirred solution of **1a** (4 mmol) in THF (12 mL) at −15 °C, Cu(acac)$_2$ (0.052 g, 0.2 mmol) was added under an argon flow, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) and 1 M NaOMe (3 mL, 3 mmol), and the resulting mixture was allowed to warm gradually to room temperature and stirred overnight. The mixture was cooled to 0 °C, and PdCl$_2$(dppf)·CH$_2$Cl$_2$ (0.033 g, 0.04 mmol) and CuI (0.015 g, 0.08 mmol) were added to the cooled mixture under an argon flow followed by dropwise addition of *n*-Bu$_4$NOH (40 wt% solution in H$_2$O) (2.66 mL, 4 mmol) and diiodobenzene (0.66 g, 2 mmol). After stirring for 4 h at room temperature, the reaction mixture was treated with 3 M NaOH (4 mL) and H$_2$O$_2$ (30 wt% solution in H$_2$O) (2 mL) at 0 °C and stirred for 1 h at the same temperature to decompose the residual organoboron compound. The resultant mixture was extracted with ether, washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated under vacuo. Purification by column chromatography on aluminum oxide (Merck aluminum oxide 60 active basic) provided product **5**. Compound **5a** [eluent: hexane/CH$_2$Cl$_2$ (9/1)]: mp 193–196 °C. IR (KBr): 956, 840, 748, 690 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.39 (d, 2H, $J = 16.1$ Hz), 7.05 (d, 2H, $J = 16.1$ Hz), 7.26–7.37 (m, 6H), 7.42–7.45 (m, 8H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 90.9 ($\equiv$C × 2), 91.5 ($\equiv$C × 2), 107.9 (=CH × 2), 123.1 (=C × 2), 126.4 (=CH × 4), 128.8 (=CH × 6), 131.4 (=CH × 4), 136.2 (=C × 2), 141.7 (=CH × 2). EIMS: *m/z* (%) = 330 (M$^+$, 100), 329 (15), 328 (20), 327 (24), 326 (22), 313 (10), 202 (13). HRMS (EI) Calcd for C$_{26}$H$_{18}$ (M$^+$): 330.1409. Found: 330.1417.
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14. *General procedure for the preparation of* **6**: To a solution of disiamylborane (4 mmol) in THF (12 mL) was added 1-iodo-2-phenylethyne (0.912 g, 4 mmol) dropwise at −15 °C under argon, and the reaction mixture was stirred for 2 h at 0 °C. A solution of 1 M LiBEt$_3$H (4 mL, 4 mmol) in THF was added dropwise to a stirred solution of (*Z*)-1-iodo-2-phenylethenyldisiamylborane, thus prepared, in THF at −25 °C, and the mixture was allowed to warm gradually to room temperature over 1 h. Et$_3$B, liberated from LiBEt$_3$H, was removed under reduced pressure, accompanied by the solvent. After the addition of THF (12 mL) to the residue under argon, the resulting solution of **2a** in THF was subjected to the reaction process as described in the general procedure for the preparation of **5**. Compound **6a** [eluent: hexane/CH$_2$Cl$_2$ (9/1)]: mp 119–121 °C. IR (KBr): 833, 788, 688 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.93 (d, 2H, $J = 11.7$ Hz), 6.73 (d, 2H, $J = 11.7$ Hz), 7.25–7.44 (m, 6H), 7.46 (s, 4H), 7.91 (d, 4H, $J = 7.3$ Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 90.3 ($\equiv$C × 2), 95.4 ($\equiv$C × 2), 107.2 (=CH × 2), 123.4 (=C × 2), 128.3 (=CH × 4), 128.7 (=CH × 2), 128.8 (=CH × 4), 131.4 (=CH × 4), 136.5 (=C × 2), 139.2 (=CH × 2). EIMS: *m/z* (%) = 330 (M$^+$, 100), 329 (18), 328 (26), 327 (33), 326 (32), 313 (16), 226 (10), 202 (23), 163 (15).
15. Compound **5c** [eluent: hexane/CH$_2$Cl$_2$ (9/1)]: mp 71–73 °C. IR (KBr): 950, 746, 688 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.47 (d, 2H, $J = 16.1$ Hz), 7.13 (d, 2H, $J = 16.1$ Hz), 7.24–7.35 (m, 8H), 7.42 (d, 4H, $J = 6.8$ Hz), 7.48 (dd, 2H, $J = 5.8$, 3.4 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 90.6 ($\equiv$C × 2), 93.2 ($\equiv$C × 2), 108.2 (=CH × 2), 125.8 (=C × 2), 126.4 (=CH × 4), 127.9 (=CH × 2), 128.7 (=CH × 2), 128.7 (=CH × 4), 131.8 (=CH × 2), 136.3 (=C × 2), 141.8 (=CH × 2). EIMS: *m/z* (%) = 330 (M$^+$, 90), 329 (42), 328 (28), 327 (33), 326 (41), 324 (11), 315 (12), 314 (10), 313 (22), 302 (16), 300 (16), 289 (10), 253 (39), 252 (71), 251 (15), 250 (45), 248 (11), 239 (38), 237 (17), 226 (27), 225 (12), 224 (19), 216 (19), 215 (100), 213 (21), 202 (12), 200 (12), 150 (10), 115 (20), 91 (18), 78 (12), 77 (19).
16. Compound **5b** [eluent: hexane/CH$_2$Cl$_2$ (9/1)]: mp 117–119 °C. IR (KBr): 950, 794, 748, 688 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.38 (d, 2H, $J = 16.1$ Hz), 7.05 (d, 2H, $J = 16.1$ Hz), 7.25–7.37 (m, 7H), 7.39–7.45 (m, 6H), 7.58 (br s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 89.5 ($\equiv$C × 2), 90.9 ($\equiv$C × 2), 107.9 (=CH × 2), 123.8 (=C × 2), 126.4 (=CH × 4), 128.5 (=CH), 128.8 (=CH × 6), 131.1 (=CH × 2), 134.4 (=CH), 136.2 (=C × 2), 141.7 (=CH × 2). EIMS: *m/z* (%) = 330 (M$^+$, 100), 329 (20), 328 (24), 327 (29), 326 (27), 313 (15), 250 (12), 226 (11), 203 (10), 202 (24), 163 (13), 69 (11). Compound **6b** [eluent: hexane/CH$_2$Cl$_2$ (9/1)]: mp 93–95 °C. IR (KBr): 781, 688 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.92 (d, 2H, $J = 11.7$ Hz), 6.73 (d, 2H, $J = 11.7$ Hz), 7.25–7.45 (m, 9H), 7.59 (s, 1H), 7.91 (d, 4H, $J = 7.8$ Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ 88.9 ($\equiv$C × 2), 94.8 ($\equiv$C × 2), 107.1 (=CH × 2), 123.9 (=C × 2), 128.4 (=CH × 4), 128.6 (=CH), 128.6 (=CH × 2), 128.8 (=CH × 4), 131.3 (=CH × 2), 134.1 (=CH), 136.4 (=C × 2), 139.2 (=CH × 2). EIMS: *m/z* (%) = 330 (M$^+$, 100), 329 (21), 328 (24), 327 (30), 326 (30), 313 (16), 250 (11), 202 (21), 163 (10), 69 (17).
17. The fluorescence intensity of **5a** was about 60% of that of **6a**.
18. The fluorescence intensity of **5c** was below 2% of that of **6a**.

19. The cross-coupling reaction using Pd catalyst gave a complex mixture of products.
20. Compound **7** (eluent: hexane): IR (neat): 3028, 2956, 2931, 2871, 2860, 1465, 950, 785, 761 cm^{-1}. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 0.93 (t, 6H, $J = 7.3$ Hz), 1.41–1.49 (m, 4H), 1.52–1.59 (m, 4H), 2.37 (dt, 4H, $J = 7.3$, 2.4 Hz), 6.14 (dt, 2H, $J = 16.1$, 2.4 Hz), 6.82 (d, 2H, $J = 16.1$ Hz), 7.29 (s, 4H). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$): δ 13.6 ($\mathrm{CH_3} \times 2$), 19.4 ($\mathrm{CH_2} \times 2$), 22.0 ($\mathrm{CH_2} \times 2$), 30.9 ($\mathrm{CH_2} \times 2$), 79.8 ($\equiv\mathrm{C} \times 2$), 93.6 ($\equiv\mathrm{C} \times 2$), 109.0 ($=\mathrm{CH} \times 2$), 126.3 ($=\mathrm{CH} \times 4$), 136.5 ($=\mathrm{C} \times 2$), 139.4 ($=\mathrm{CH} \times 2$). EIMS: m/z (%) = 290 (M^{+}, 100), 205 (20), 204 (14), 203 (26), 202 (30), 192 (10), 191 (38), 190 (20), 189 (30), 179 (11), 178 (14), 165 (15), 153 (11), 152 (12), 41 (10). HRMS (EI) Calcd for $\mathrm{C_{22}H_{26}}$ (M^{+}): 290.2035. Found: 290.2034.
21. Compound **5d** (eluent: hexane): mp 56–57 °C. IR (KBr): 3020, 2956, 2927, 2871, 2858, 1506, 1463, 1456, 956, 835, 786, 763 cm^{-1}. ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$): δ 0.90 (t, 6H, $J = 7.3$ Hz), 1.30–1.44 (m, 8H), 2.12–2.43 (m, 4H), 5.68 (br d, 2H, $J = 16.1$ Hz), 6.24 (br dt, 2H, $J = 16.1$, 6.8 Hz), 7.32–7.35 (m, 4H). ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$): δ 13.9 ($\mathrm{CH_3} \times 2$), 22.2 ($\mathrm{CH_2} \times 2$), 30.9 ($\mathrm{CH_2} \times 2$), 33.0 ($\mathrm{CH_2} \times 2$), 87.7 ($\equiv\mathrm{C} \times 2$), 90.1 ($\equiv\mathrm{C} \times 2$), 109.4 ($=\mathrm{CH} \times 2$), 123.1 ($=\mathrm{C} \times 2$), 131.2 ($=\mathrm{CH} \times 4$), 145.6 ($=\mathrm{CH} \times 2$). EIMS: m/z (%) = 290 (M^{+}, 100), 261 (12), 248 (16), 247 (67), 234 (10), 205 (17), 204 (20), 203 (18), 202 (30), 191 (25), 190 (11), 189 (17), 179 (10), 178 (23), 176 (10), 165 (18), 152 (17), 139 (14). HRMS (EI) Calcd for $\mathrm{C_{22}H_{26}}$ (M^{+}): 290.2035. Found: 290.2032.