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Pd(0)-Catalyzed Cross-Coupling of 1,1-Diboronates with 2,2′-Dibromobiphenyls: Synthesis of 9*H*-Fluorenes

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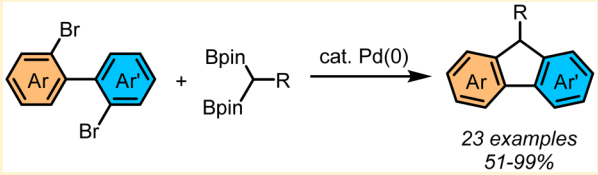
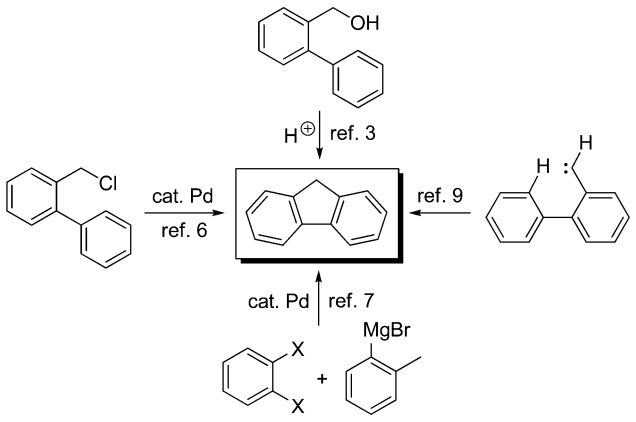
Supporting Information

ABSTRACT: An efficient and mild synthesis of 9*H*-fluorene derivatives through a Pd(0)-catalyzed cross-coupling reaction of 1,1-diboronates with 2,2′-dibromobiphenyls has been developed. This reaction features high yields, operational simplicity, and mild reaction conditions, thus providing an excellent alternative to published methods for 9*H*-fluorene synthesis.



Fluorene and its derivatives are important structural motifs found in many advanced materials, and they have also been extensively used as dyes and optical brightening agents.[1] Moreover, they have been widely used as ligands in organometallic chemistry because of their high donor ability and diverse coordination modes.[2] Due to the importance of fluorene derivatives, many viable methods for their synthesis have been developed. The classical method for the synthesis of fluorenes is intramolecular Friedel−Crafts alkylation promoted by Brønsted or Lewis acids.[3] Recently, some transition-metal-catalyzed or -mediated reactions to construct fluorenes have been reported.[4] These reactions include Pd-catalyzed rearrangement reactions,[5] Pd-catalyzed C−H bond activations,[6] Pd-catalyzed annulative tandem reaction of dihalobenzenes with Grignard reagents,[7] activation of C−F/C−H bonds of ortho-arylated *α*,*α*,*α*-trifluorotoluene derivatives,[8] and formal intramolecular carbene C−H insertions (Scheme 1).[9] However, most of these reactions suffer drawbacks, which include poor availability of the starting materials, harsh reaction conditions, and low efficiency. Thus, further development of new methods for the efficient synthesis of substituted fluorene derivatives is highly desirable.

Scheme 1. Construction of Fluorene Skeletons



It is apparent that the key to accessing fluorene derivatives is the construction of carbon−carbon bonds. In this context, organoboron compounds have been widely applied in carbon−carbon bond construction, as represented by Suzuki−Miyaura cross-coupling reactions.[10] Among the various organoboron compounds, alkylboron compounds have not been extensively explored in transition-metal-catalyzed coupling reactions because of their low reactivity.[10c,11] However, recent studies revealed that 1,1-diboron compounds can effectively take part in transition-metal-catalyzed coupling reactions to construct $C(sp^3)-C(sp^2)$ bonds.[12] The high reactivity of 1,1-diboron compounds is attributed to the fact that the adjacent boron activates the other boron group to facilitate the transmetalation process in the cross-coupling reaction. However, because of the low reactivity of the produced monoboron compounds, further coupling under the same reaction conditions does not occur in most cases.[12h]

In contrast to intermolecular reactions, intramolecular reactions normally occur much more easily. We have thus conceived that, by suitably designing an intramolecular process, two boron groups may be explored in the construction of a ring system through Pd-catalyzed tandem cross-coupling reactions (Scheme 2). Shibata et al. have recently explored this strategy in the synthesis of cyclopentadithiophene.[12i] Herein, we report further investigation based on this design. We demonstrate that a general method can be established for the synthesis of 9*H*-fluorene derivatives based on a Pd(0)-catalyzed tandem coupling reaction.

We initially investigated the cross-coupling reaction of 2,2′-dibromo-1,1′-biphenyl (**1a**) and 1,1-diboronate (**2a**) using $Pd(PtBu_3)_2$ as the catalyst and KOH as the base. Gratifyingly, the desired product could be detected by GC-MS (eq 1).

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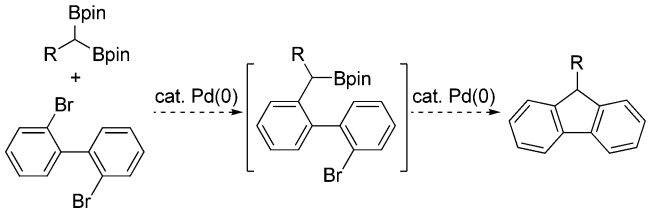
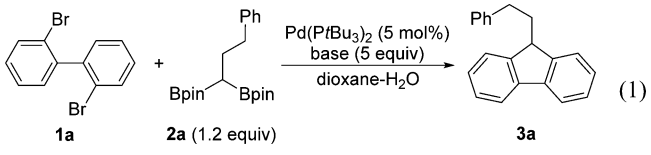
Scheme 2. Construction of Fluorenes through Pd(0)-Catalyzed Tandem Cross-Coupling





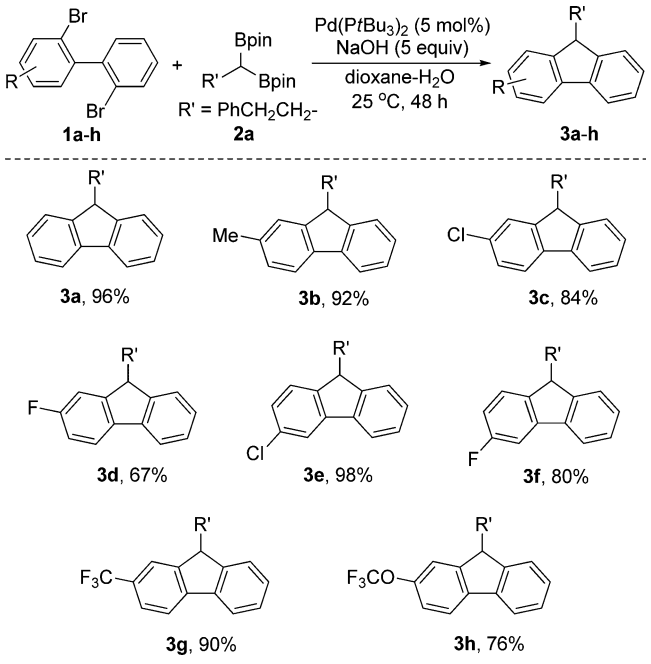
KOH (10M), 90 °C, 3 h; detected by GC-MS
KOH (10M), 25 °C, 48 h; 89% isolated yield
NaOH (5M), 25 °C, 48 h; 96% isolated yield

Switching the catalyst from $Pd(PtBu_3)_2$ to $Pd(PPh_3)_4$ gave none of the desired product, **2a**. Considering the fact that 1,1-diboronates are prone to hydrolysis, we further examined the reaction at lower temperature with various bases. With some experimentation, we found that 1,1-diboronates could react with 2,2′-dibromobiphenyls under ambient temperature with aqueous NaOH (5 M) as the base to afford 9*H*-fluorene derivative **3a**.[13]

With the optimized reaction conditions, the scope of 2,2′-dibromobiphenyls was studied using 1,1-diboronate (**2a**) as the nucleophile (Scheme 3). The reaction was found not to be significantly affected by the electronic nature of the substituents. The reaction worked well with both electron-donating substituents, such as a methyl group (**3b**), and electron-withdrawing groups, such as chloro, fluoro, and trifluoromethyl groups (**3c**–**g**). The transformation also worked with a substrate that bears an OCF_3 substituent (**3h**).

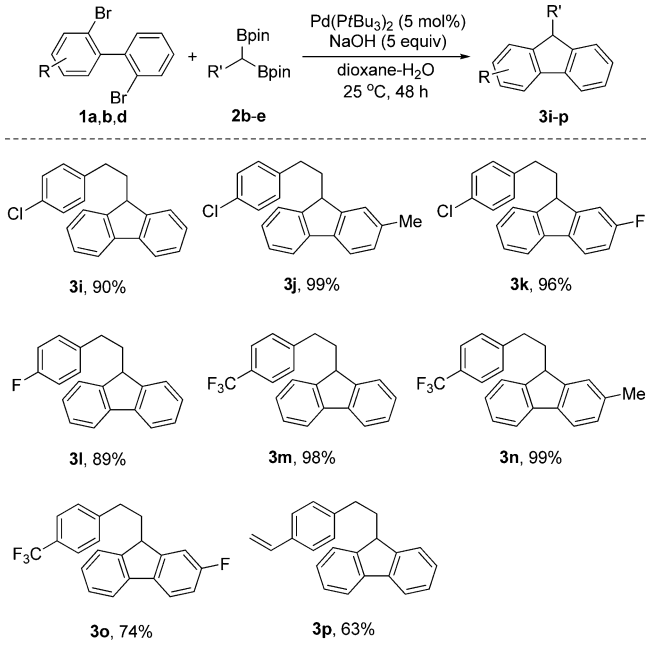
Next, the scope of the 1,1-diboronates was investigated (Scheme 4). First, the substituent groups on the aromatic ring

Scheme 3. Substrate Scope of 2,2′-Dibromobiphenyls[a]



[a]Reaction conditions: **1a**–**h** (0.3 mmol), **2a** (1.3 equiv), $Pd(PtBu_3)_2$ (5 mol %), NaOH (5 M, 5 equiv), 1,4-dioxane (1.5 mL).

Scheme 4. Substrate Scope of 2,2′-Dibromobiphenyls and 1,1-Diboronates[a]



[a]Reaction conditions: **1a**,**b**,**d** (0.3 mmol), **2b**–**e** (1.3 equiv), $Pd(PtBu_3)_2$ (5 mol %), NaOH (5 M, 5 equiv), 1,4-dioxane (1.5 mL).

of the 1,1-diboronate were varied. Halogen substituents and a trifluoromethyl group were found to tolerate the reaction conditions, affording the corresponding fluorene products in good to excellent yields (**3i**–**o**). Gratifyingly, the vinyl substituent also tolerates the reaction, affording the corresponding product **3p** in 63% yield. The structure of **3i** was confirmed by single-crystal X-ray diffraction (see Supporting Information).

To further demonstrate the scope of the reaction, bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methane **4** was then applied in this reaction. It was observed that the transformation with **4** was less efficient under the same reaction conditions as those used above. With some experimentation, it was concluded that the poor efficiency of the reaction was attributed to the low stability of 1,1-diboronate **4** under the optimized reaction conditions. Gratifyingly, the reaction could be improved through slow addition of 2 equiv of 1,1-diboronate **4** with a syringe pump. With such modification, the reaction afforded the desired products in moderate to good yields. The transformation, too, was not markedly affected by electronic effects of the substituents (Scheme 5).

In summary, a concise and efficient Pd(0)-catalyzed cross-coupling reaction of 1,1-diboronates with 2,2′-dibromobiphenyls has been reported. Various fluorene derivatives can be synthesized in a straightforward manner through this method. The high reactivity of the 1,1-diboronates and the ease of intramolecular reaction are the two key factors that contribute to the success of this Pd(0)-catalyzed tandem coupling reaction.

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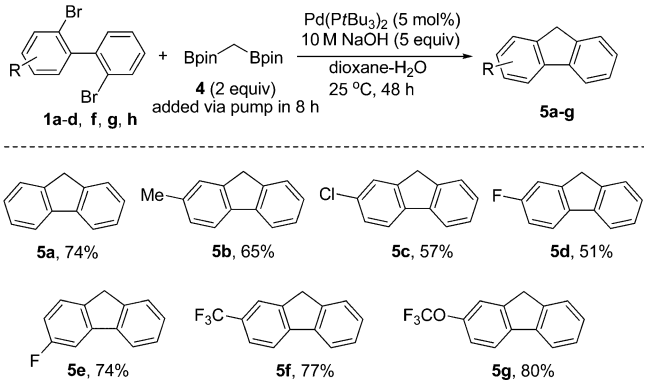
Scheme 5. Reaction with 1,1-Diboronate 4[a]



[a]Reaction conditions: **1a−d,g,h** (0.3 mmol), **4** (2.0 equiv), $Pd(PtBu_3)_2$ (5 mol %), NaOH (10 M, 5 equiv), 1,4-dioxane (1.5 mL). 1,1-Diboronate **4** is added by a syringe pump in 8 h.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were performed under a nitrogen atmosphere in oven-dried reaction flasks. All solvents were freshly distilled. The boiling point of petroleum ether was between 60 and 90 °C. Commercially available reagents were used as received. For chromatography, 200−300 mesh silica gel was used. Chemical shifts for ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra are reported relative to the chemical shift of tetramethylsilane (TMS): chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. EA, ethyl acetate. 2,2′-Dibromo-1,1′-biphenyl (**1a**) was commercially available.

Preparation of 2,2′-Dibromobiphenyls 1b−h. An oven-dried Schlenk flask was charged with (2-bromophenyl)boronic acid (0.42 g, 2.1 mmol) and $Pd(PPh_3)_4$ (3−7 mol %). After being degassed and filled with N_2, 1-bromo-2-iodobenzene (2 mmol), toluene (8 mL), ethanol (4 mL), and 1 M Na_2CO_3 (aq) (4 mL) were added via syringe. The mixture was stirred at 110 °C for 5 h. Upon cooling to room temperature, 10 mL of Et_2O was added. The mixture was then stirred vigorously for 10 min. The organic layer was separated, washed with saturated brine (10 mL), and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by silica gel chromatography (eluted with PE).

*2,2′-Dibromo-4-methyl-1,1′-biphenyl (**1b**).* Yield 94% (613 mg); colorless oil; R_f = 0.40 (PE); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66−7.44 (m, 1H), 7.49 (s, 1H), 7.35 (dt, J = 7.1, 1.2 Hz, 1H), 7.25−7.21 (m, 2H), 7.17 (dd, J = 7.7, 0.9 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 139.6, 139.1, 133.0, 132.5, 131.1, 130.6, 129.2, 127.9, 127.0, 123.7, 123.1, 20.9. EI-MS (m/z, relative intensity): 328 (30), 326 (65), 324 (30), 247 (63), 245 (65), 166 (100), 150 (5), 139 (15), 82 (20); HRMS (ESI) calcd for $C_{13}H_{10}Br_2$ $[M]^+$, 325.9129; found, 325.9128; IR (film): 1463, 1028, 851, 820, 755, 727 cm^{-1}.

*2,2′-Dibromo-4-chloro-1,1′-biphenyl (**1c**).* Yield 88% (612 mg); colorless oil; R_f = 0.65 (PE); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 2.1 Hz, 1H), 7.66 (dd, J = 8.0, 1.1 Hz, 1H), 7.38−7.35 (m, 2H), 7.26 (dt, J = 7.7, 2.1 Hz, 1H), 7.21 (dd, J = 7.5, 1.7 Hz, 1H), 7.18 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.5, 134.4, 132.7, 132.3, 131.7, 130.9, 129.7, 127.4, 127.2, 124.0, 123.4. EI-MS (m/z, relative intensity): 348 (40), 346 (60), 344 (30), 267 (80), 265 (60), 188 (100), 150 (60), 93 (30), 75 (35); HRMS (ESI) calcd for $C_{12}H_7Br_2Cl$ $[M]^+$, 345.8583; found, 345.8577; IR (film): 1581, 1461, 1099, 1003, 799, 762 cm^{-1}.

*2,2′-Dibromo-4-fluoro-1,1′-biphenyl (**1d**).* Yield 88% (581 mg); colorless oil; R_f = 0.60 (PE); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 8.0, 1.0 Hz, 1H), 7.43−7.35 (m, 2H), 7.28−7.20 (m, 3H), 7.09 (dt, J = 8.3, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, J_F = 251.2 Hz), 141.1, 138.2 (d, J_F = 3.7 Hz), 132.6, 131.9 (d, J_F = 8.3 Hz), 131.1, 129.6, 127.2, 123.7 (d, J_F = 9.7 Hz), 123.7, 119.8 (d, J_F = 24.4 Hz), 114.4 (d, J_F = 21.2 Hz). EI-MS (m/z, relative intensity): 332 (40), 330 (60), 328 (40), 251 (50), 249 (50), 170 (100), 144 (15), 85 (15); HRMS (ESI) calcd for $C_{12}H_7Br_2F$ $[M]^+$, 329.8878; found, 329.8886; IR (film): 1601, 1580, 1498, 1463, 1261, 1201, 1005, 876, 756 cm^{-1}.

*2,2′-Dibromo-5-chloro-1,1′-biphenyl (**1e**).* Yield 60% (415 mg); colorless oil; R_f = 0.70 (PE); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.31−7.17 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.9, 133.7, 133.1, 132.7, 131.0, 130.8, 129.8, 129.5, 127.3, 123.2, 121.6. EI-MS (m/z, relative intensity): 348 (50), 346 (70), 344 (40), 267 (90), 265 (70), 188 (100), 150 (50), 93 (30); HRMS (ESI) calcd for $C_{12}H_7Br_2Cl$ $[M]^+$, 345.8583; found, 345.8577; IR (film): 1450, 1380, 1097, 1040, 1030, 1009, 813, 756 cm^{-1}.

*2,2′-Dibromo-5-fluoro-1,1′-biphenyl (**1f**).* Yield 85% (561 mg); colorless oil; R_f = 0.60 (PE); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.0, 1.0 Hz, 1H), 7.63−7.59 (m, 1H), 7.38 (td, J = 7.5, 1.2 Hz, 1H), 7.30−7.21 (m, 2H), 7.02−6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, J_F = 247.9 Hz), 143.6 (d, J_F = 8.1 Hz), 141.0 (d, J_F = 1.3 Hz), 133.8 (d, J_F = 8.1 Hz), 132.7, 130.7, 129.7, 127.2, 123.1, 118.2 (d, J_F = 23.1 Hz), 117.8 (d, J_F = 3.5 Hz), 116.6 (d, J_F = 22.2 Hz). EI-MS (m/z, relative intensity): 332 (25), 330 (35), 328 (25), 251 (50), 249 (50), 170 (100), 144 (15), 85 (20); HRMS (ESI) calcd for $C_{12}H_7Br_2F$ $[M]^+$, 329.8878; found, 329.8882; IR (film): 1575, 1461, 1399, 1189, 1019, 882, 756 cm^{-1}.

*2,2′-Dibromo-4-(trifluoromethyl)-1,1′-biphenyl (**1g**).* Yield 62% (471 mg); colorless oil; R_f = 0.55 (PE); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 0.58 Hz, 1H), 7.69 (dd, J = 8.0, 1.0 Hz, 1H), 7.64 (dd, J = 8.0, 1.0 Hz, 1H), 7.40 (td, J = 4.7, 14.8, 2H), 7.30 (dt, J = 7.7, 1.7 Hz, 1H), 7.22 (dd, J = 7.5, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 140.9, 132.8, 131.6 (q, J_F = 33.2 Hz), 131.5, 130.6, 130.0, 129.7 (q, J_F = 3.8 Hz), 127.3, 124.1 (q, J_F = 3.6 Hz), 124.0, 123.1 (q, J_F = 272.8 Hz), 122.9. EI-MS (m/z, relative intensity): 382 (30), 380 (60), 378 (30), 361 (10), 301 (70), 299 (70), 220 (100), 201 (20), 170 (15), 150 (15); HRMS (ESI) calcd for $C_{13}H_7Br_2F_3$ $[M]^+$, 379.8846; found, 379.8840; IR (film): 1321, 1172, 1131, 1085, 1072, 757, 689 cm^{-1}.

*2,2′-Dibromo-4-(trifluoromethoxy)-1,1′-biphenyl (**1h**).* Yield 81% (642 mg); colorless oil; R_f = 0.65 (PE); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.0, 1.1 Hz, 1H), 7.56 (d, J = 0.9 Hz, 1H), 7.38 (td, J = 7.5, 1.2 Hz, 1H), 7.30−7.21 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8 (q, J_F = 1.9 Hz), 140.8, 140.7, 132.7, 131.8, 130.9, 129.8, 127.2, 125.0, 124.0, 123.4, 120.4 (q, J_F = 263.6 Hz), 119.5. EI-MS (m/z, relative intensity): 398 (50), 396 (80), 394 (50), 317 (75), 315 (75), 236 (100), 167 (20), 139 (80), 113 (15); HRMS (ESI) calcd for $C_{13}H_7Br_2F_3O$ $[M]^+$, 395.8795; found, 395.8782; IR (film): 1462, 1253, 1216, 1170, 757 cm^{-1}.

General Procedure for Preparation of 1,1-Diboronates 2a−e.[12g] An oven-dried Schlenk tube was charged with *N*-tosylhydrazone (1 mmol) and 60% NaH (1.2 mmol, 48 mg). After being degassed and filled with N_2, the tube was charged with toluene (8 mL). The mixture was stirred at room temperature for 1 h. Then, a solution of B_2pin_2 (1.2 mmol, 305 mg) in toluene (2 mL) was added via syringe. Then, the tube was sealed and heated at 110 °C for 12 h. After cooling to room temperature, 10 mL of Et_2O and 10 mL of H_2O were added. The mixture was stirred vigorously for 10 min. After separation of the organic layer, the aqueous layer was extracted with Et_2O (5 mL × 3). The combined organic solution was washed with saturated brine (10 mL) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by silica gel chromatography (eluted with PE/EA 20:1).

*2,2′-(3-Phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2a**).*[14] Yield 86% (320 mg); white solid; R_f = 0.30 (PE/EA 20:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26−7.13 (m, 5H), 2.61−2.57 (m, 2H), 1.88−1.82 (m, 2H), 1.23 (s, 12H), 1.23 (s, 12H), 0.81 (t, J = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 128.6, 128.1, 125.5, 83.0, 38.7, 28.0, 24.9, 24.5.

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*2,2′-(3-(4-Chlorophenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2b**).* Yield 40% (162 mg); white solid; mp 95−96 °C; R_f = 0.40 (PE/EA 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 2.65−2.32 (m, 2H), 1.84−1.79 (m, 2H), 1.23 (s, 12H), 1.22 (s, 12H), 0.77 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 131.5, 129.9, 128.2, 83.0, 38.0, 27.8, 24.9, 24.5. EI-MS (m/z, relative intensity): 406 (5), 391 (25), 322 (15), 278 (25), 253 (10), 234 (80), 219 (20). 125 (30), 84 (100); HRMS (ESI) calcd for $C_{21}H_{33}B_2ClO_4$ $[M]^+$, 406.2252; found, 406.2252; IR (film): 2979, 2930, 1492, 1379, 1370, 1315, 1263, 1139, 969, 850 cm^{-1}.

*2,2′-(3-(4-Fluorophenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2c**).* Yield 45% (176 mg); white solid; mp 69−70 °C; R_f = 0.40 (PE/EA 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13−7.10 (m, 2H), 6.92 (t, J = 8.0 Hz, 2H), 2.67−2.40 (m, 2H), 1.83−1.81 (m, 2H), 1.23 (s, 24H), 0.78 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J_F = 246.4 Hz), 138.0 (d, J_F = 4.1 Hz), 129.8 (d, J_F = 7.9 Hz), 114.8 (d, J_F = 20.9 Hz), 83.0, 37.8, 28.1, 24.9, 24.5. EI-MS (m/z, relative intensity): 390 (5), 375 (20), 333 (2), 306 (15), 262 (20), 218 (70), 203 (25), 109 (30), 84 (100); HRMS (ESI) calcd for $C_{21}H_{33}B_2FO_4$ $[M]^+$, 390.2549; found, 390.2548; IR (film): 2978, 2929, 1646, 1509, 1379, 1370, 1315, 1220, 1139, 849 cm^{-1}.

*2,2′-(3-(4-(Trifluoromethyl)phenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2d**).* Yield 45% (201 mg); white solid; mp 70−71 °C; R_f = 0.40 (PE/EA 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 2.66−2.63 (m, 2H), 1.89−1.85 (m, 2H), 1.23 (s, 12H), 1.23 (s, 12H), 0.78 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 128.9, 127.9 (q, J_F = 32.3 Hz), 125.0 (q, J_F = 3.7 Hz), 124.5 (q, J_F = 272.0 Hz), 83.1, 38.4, 27.6, 24.9, 24.5. EI-MS (m/z, relative intensity): 440 (5), 425 (60), 356 (15), 312 (20), 268 (100), 253 (40), 101 (35), 84 (80); HRMS (ESI) calcd for $C_{22}H_{33}B_2F_3O_4$ $[M]^+$, 440.2517; found, 440.2517; IR (film): 2979, 1451, 1371, 1325, 1265, 1164, 1139, 1068, 851 cm^{-1}.

*2,2′-(3-(4-Vinylphenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**2e**).* Yield 50% (199 mg); white solid; mp 77−78 °C; R_f = 0.35 (PE/EA 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.68 (dd, J = 17.6, 10.9 Hz, 1H), 5.67 (dd, J = 17.6, 0.9 Hz, 1H), 5.16 (dd, J = 10.9, 0.8 Hz, 1H), 2.59−2.56 (m, 2H), 1.90−1.75 (m, 2H), 1.23 (s, 12H), 1.22 (s, 12H), 0.80 (t, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 136.9, 135.0, 128.8, 126.0, 112.6, 83.0, 38.4, 27.9, 24.9, 24.5. EI-MS (m/z, relative intensity): 398 (40), 383 (20), 314 (25), 270 (28), 228 (100), 211 (50), 170 (40), 117 (60), 85 (96); HRMS (ESI) calcd for $C_{23}H_{36}B_2O_4$ $[M]^+$, 398.2800; found, 398.2795; IR (film): 2977, 2932, 1379, 1362, 1315, 1264, 1140, 851 cm^{-1}.

Preparation of Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane 4.[15] An oven-dried Schlenk flask was charged with CuI (0.19 g, 1 mmol), B_2pin_2 (5.08 g, 20 mmol), PPh_3 (0.34 g, 1.3 mmol), and LiOMe (1.14 g, 30 mmol). After being degassed and filled with N_2, CH_2Br_2 (1.74 g, 10 mmol) dissolved in DMF (20 mL) was added. The mixture was stirred at room temperature for 24 h. Then, 50 mL of Et_2O was added. The mixture was stirred vigorously for 10 min. The slurry was filtered through a silica gel plug. The organic solution was washed with water (50 mL) and saturated brine (50 mL) and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the crude product was purified by silica gel chromatography (eluted with PE/EA 20:1) (1.65 g, 59%). White solid; R_f = 0.40 (PE/EA 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 24H), 0.35 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.0, 24.7.

General Procedure for Pd(0)-Catalyzed Tandem Coupling Reaction (for Schemes 3 and 4). 2,2′-Dibromobiphenyls (0.30 mmol), 1,1-dibronates (0.39 mmol), $Pd(PtBu_3)_2$ (0.015 mmol), 5 M NaOH (aq) (1.5 mmol, 300 μL), and 1.5 mL of dioxane were mixed in an oven-dried reaction flask. The mixture was stirred at room temperature under a nitrogen atmosphere for 48 h. When the reaction was completed, the crude mixture was cooled to room temperature. Five milliliters of Et_2O was added, and the mixture was filtered through Celite. The solvents were evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel.

*9-Phenethyl-9H-fluorene (**3a**).*[16] Yield 96% (78 mg); white solid; R_f = 0.40 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.3 Hz, 2H), 7.55 (d, J = 7.3 Hz, 2H), 7.38 (t, J = 7.1 Hz, 2H), 7.33 (m, 2H), 7.23 (t, J = 7.4 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.10 (t, J = 6.0 Hz, 2H), 4.07 (t, J = 4.9 Hz, 1H), 2.43−2.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 142.4, 141.3, 128.3, 128.3, 127.0, 126.9, 125.7, 124.3, 119.9, 47.2, 34.8, 31.5.

*2-Methyl-9-phenethyl-9H-fluorene (**3b**).* Yield 92% (78 mg); white solid; mp 49−50 °C; R_f = 0.20 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.35 (m, 2H), 7.28 (t, J = 7.1 Hz, 1H), 7.18 (m, 4H), 7.10 (d, J = 7.4 Hz, 2H), 4.01 (t, J = 5.1 Hz, 1H), 2.43−2.30 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 146.8, 142.4, 141.3, 138.6, 136.8, 128.3, 127.9, 126.9, 126.4, 125.7, 125.0, 124.2, 119.6, 119.5, 47.1, 34.7, 31.5, 21.7; EI-MS (m/z, relative intensity) 284 (M^+, 100), 193 (90), 178 (80), 165 (15), 152 (15), 105 (10), 91 (10); HRMS (ESI) calcd for $C_{22}H_{20}$ $[M]^+$, 284.1564; found, 284.1565; IR (film): 3026, 2921, 2849, 1501, 1455, 821, 768, 740, 700 cm^{-1}.

*2-Chloro-9-phenethyl-9H-fluorene (**3c**).* Yield 84% (77 mg); colorless oil; R_f = 0.25 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.0 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.3 Hz, 1H), 7.48 (s, 1H), 7.33 (m, 3H), 7.21 (q, J = 7.0 Hz, 2H), 7.13 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.1 Hz, 2H), 4.01 (t, J = 5.0 Hz, 1H), 2.40−2.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 146.7, 141.9, 140.2, 139.8, 132.7, 128.3, 128.2, 127.3, 127.2, 125.8, 124.6, 124.3, 120.7, 119.9, 47.1, 34.5, 31.4; EI-MS (m/z, relative intensity) 304 (M^+, 100), 269 (30), 212 (80), 199 (70), 178 (20), 163 (60), 105 (60), 91 (65); HRMS (ESI) calcd for $C_{21}H_{17}Cl$ $[M]^+$, 304.1019; found, 304.1021; IR (film): 3023, 2921, 1606, 1448, 1074, 823, 740, 700 cm^{-1}.

*2-Fluoro-9-phenethyl-9H-fluorene (**3d**).* Yield 67% (58 mg); colorless oil; R_f = 0.24 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.64 (m, 2H), 7.51 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.29 (dt, J = 7.4 Hz, 1.0 Hz, 1H), 7.23−7.20 (m, 3H), 7.13 (t, J = 7.3 Hz, 1H), 7.08−7.03 (m, 3H), 4.01 (t, J = 4.8 Hz, 1H), 2.39−2.28 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J_F = 224.8 Hz), 149.2 (d, J_F = 8.0 Hz), 146.8, 142.0, 137.2, 137.2, 128.3, 128.2, 127.2, 126.6, 125.8, 124.2, 120.8 (d, J_F = 8.8 Hz), 119.5, 114.1 (d, J_F = 23.1 Hz), 111.6 (d, J_F = 22.7 Hz), 47.2 (d, J_F = 2.4 Hz), 34.6, 31.3; EI-MS (m/z, relative intensity) 288 (M^+, 55), 196 (100), 183 (90), 105 (40), 91 (50); HRMS (EI) calcd for $C_{21}H_{17}F$ $[M]^+$, 288.1314; found, 288.1318; IR (film): 3023, 1588, 1251, 827, 768, 737, 700 cm^{-1}.

*3-Chloro-9-phenethyl-9H-fluorene (**3e**).* Yield 98% (60 mg); colorless oil; R_f = 0.30 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.71 (m, 2H), 7.54 (d, J = 7.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.38−7.34 (m, 2H), 7.38−7.20 (m, 3H), 7.16−7.14 (m, 1H), 7.07 (d, J = 7.1 Hz, 2H), 4.02 (t, J = 4.6 Hz, 1H), 2.38−2.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 145.3, 143.1, 142.1, 140.1, 133.1, 128.4, 128.3, 127.7, 127.3, 126.9, 125.9, 125.3, 124.4, 120.2, 46.9, 34.6, 31.4; EI-MS (m/z, relative intensity) 304 (M^+, 100), 269 (30), 213 (90), 199 (95), 178 (80), 163 (70), 105 (75), 92 (75); HRMS (ESI) calcd for $C_{21}H_{17}Cl$ $[M]^+$, 304.1018; found, 304.1020; IR (film): 2921, 2849, 1452, 1080, 774, 740, 700 cm^{-1}.

*3-Fluoro-9-phenethyl-9H-fluorene (**3f**).* Yield 80% (69 mg); colorless oil; R_f = 0.22 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.68 (m, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.45−7.33 (m, 4H), 7.23−7.18 (m, 2H), 7.15−7.11 (m, 1H), 7.08−7.06 (m, 2H), 6.99 (ddd, J = 9.2, 8.4, 2.5 Hz, 1H), 4.00 (t, J = 4.9 Hz, 1H), 2.39−2.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J_F = 243.3 Hz), 161.5, 147.8, 143.2 (d, J_F = 8.8 Hz), 142.2 (d, J_F = 2.2 Hz), 140.4 (d, J_F = 3.2 Hz), 128.3, 128.2, 127.5, 127.1, 125.1 (d, J_F = 8.9 Hz), 124.3, 120.1, 113.7 (d, J_F = 22.9 Hz), 106.8 (d, J_F = 22.8 Hz), 46.6, 34.7, 31.4; ^{19}F NMR (470 MHz, $CDCl_3$) δ −139.3 (m, 2F), −142.8 (m, 2F); EI-MS (m/z, relative intensity) 288 (M^+, 90), 197 (90), 183 (100), 105 (50), 92 (50); HRMS (ESI) calcd for $C_{21}H_{17}F$ $[M]^+$, 288.1314; found, 288.1311; IR (film): 3026, 1619, 1489, 1452, 1179, 774, 746, 697 cm^{-1}.

*9-Phenethyl-2-(trifluoromethyl)-9H-fluorene (**3g**).* Yield 90% (91 mg); colorless oil; R_f = 0.15 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (t, J = 6.5 Hz, 2H), 7.75 (s, 1H), 7.63−7.58 (m, 2H), 7.44−7.40 (m, 2H), 7.25−7.21 (m, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.2 Hz,

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2H), 4.12 (s, 1H), 2.43−2.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.3, 144.6, 141.8, 139.8, 128.8 (q, J_F = 31.8 Hz), 128.4, 128.2, 128.2, 127.4, 126.0, 124.6 (q, J_F = 271.9 Hz), 124.5, 124.4 (q, J_F = 3.9 Hz), 121.1 (q, J_F = 3.7 Hz), 120.6, 119.9, 47.3, 34.4, 31.5; EI-MS (m/z, relative intensity) 338 (M^+, 100), 319 (10), 247 (50), 233 (45), 178 (30), 105 (50), 92 (70); HRMS (ESI) calcd for $C_{22}H_{17}F_3$ $[M]^+$, 338.1282; found, 338.1286; IR (film): 3129, 1328, 1160, 1117, 1065, 743, 700 cm^{-1}.

*9-Phenethyl-2-(trifluoromethoxy)-9H-fluorene (**3h**).* Yield 76% (81 mg); colorless oil; R_f = 0.38 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 7.6, 5.1 Hz, 2H), 7.52 (d, J = 7.3 Hz, 1H), 7.38−7.34 (m, 3H), 7.24−7.21 (m, 3H), 7.14 (q, J = 7.3 Hz, 1H), 7.06 (d, J = 7.1 Hz, 2H), 4.06 (d, J = 5.3 Hz, 1H), 2.40−2.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 148.5 (q, J_F = 1.4 Hz), 147.1, 141.9, 140.1, 140.0, 128.4, 128.3, 127.3, 125.9, 124.4, 120.7 (q, J_F = 256.7 Hz), 120.6, 120.1, 120.1, 117.4, 47.3, 34.6, 31.5; EI-MS (m/z, relative intensity) 354 (M^+, 85), 262 (90), 249 (50), 165 (20), 152 (100), 105 (70), 92 (70); HRMS (EI) calcd for $C_{22}H_{17}F_3O$ $[M]^+$, 354.1231; found, 354.1210; IR (film): 1455, 1257, 1220, 1164, 743, 697 cm^{-1}.

*9-(4-Chlorophenethyl)-9H-fluorene (**3i**).* Yield 90% (82 mg); white solid; mp 80−81 °C; R_f = 0.40 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.4 Hz, 2H), 7.51 (d, J = 7.3 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.33−7.29 (m, 2H), 7.16 (t, J = 8.3 Hz, 2H), 6.97 (t, J = 8.3 Hz, 1H), 7.10 (t, J = 6.0 Hz, 2H), 4.07 (t, J = 4.3 Hz, 1H), 2.43−2.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 141.3, 140.8, 131.5, 129.7, 128.4, 127.2, 127.0, 124.2, 120.0, 47.1, 34.6, 30.7; EI-MS (m/z, relative intensity) 304 (M^+, 50), 179 (100), 165 (70), 139 (20); ^{19}F NMR (470 MHz, $CDCl_3$) δ −139.5 (m, 2F), −143.8 (m, 2F); HRMS (ESI) calcd for $C_{21}H_{17}Cl$ $[M]^+$, 304.1018; found, 304.1020; IR (film): 3063, 1495, 1448, 802, 734 cm^{-1}.

*9-(4-Chlorophenethyl)-2-methyl-9H-fluorene (**3j**).* Yield 99% (94 mg); colorless oil; R_f = 0.30 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.39−7.23 (m, 3H), 7.20−7.11 (m, 3H), 6.97 (d, J = 8.4 Hz, 2H), 4.00 (s, 1H), 2.43 (s, 3H), 2.32−2.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 146.6, 141.4, 140.9, 138.7, 136.9, 131.4, 130.0, 128.4, 128.0, 127.1, 126.5, 125.0, 124.2, 119.7, 119.6, 47.0, 34.6, 30.8, 21.8; EI-MS (m/z, relative intensity) 318 (M^+, 50), 207 (20), 193 (100), 178 (60), 165 (15); HRMS (ESI) calcd for $C_{22}H_{19}Cl$ $[M]^+$, 318.1175; found, 318.1176; IR (film): 2918, 1455, 1325, 1164, 1123, 1067, 832, 767 cm^{-1}.

*9-(4-Chlorophenethyl)-2-fluoro-9H-fluorene (**3k**).* Yield 96% (93 mg); colorless oil; R_f = 0.40 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74−7.60 (m, 2H), 7.49 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.3 Hz, 1H), 7.29 (td, J = 7.4, 1.0 Hz, 1H), 7.25−7.13 (m, 3H), 7.07 (td, J = 8.8, 2.3 Hz, 1H), 6.96 (d, J = 8.4 Hz, 2H), 4.02 (t, J = 4.3 Hz, 1H), 2.33−2.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J_F = 245.1 Hz), 149.0 (d, J_F = 8.0 Hz), 146.6, 146.6, 140.5, 137.3, 131.6, 129.6, 128.4, 127.3, 126.7, 124.2, 120.8 (d, J_F = 8 8 Hz), 119.7, 114.3 (d, J_F = 22.9 Hz), 111.6 (d, J_F = 22.7 Hz), 47.2 (d, J_F = 2.2 Hz), 34.5, 30.6; EI-MS (m/z, relative intensity) 322 (M^+, 60), 281 (10), 253 (10), 207 (20), 197 (100), 183 (20); HRMS (ESI) calcd for $C_{21}H_{16}ClF$ $[M]^+$, 322.0924; found, 322.0925; IR (film): 2923, 2853, 1454, 827, 766, 757, 740, 728 cm^{-1}.

*9-(4-Fluorophenethyl)-9H-fluorene (**3l**).* Yield 89% (77 mg); colorless oil; R_f = 0.20 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 7.3 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 7.31 (td, J = 7.4, 1.1 Hz, 2H), 7.05−6.96 (m, 2H), 6.94−6.83 (m, 2H), 4.05 (s, 1H), 2.33−2.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J_F = 243.4 Hz), 146.9, 141.3, 138.0 (d, J_F = 3.0 Hz), 129.6 (d, J_F = 7.9 Hz), 127.1, 127.0, 124.3, 120.0, 115.0 (d, J_F = 21.0 Hz), 47.2, 34.9, 30.6; EI-MS (m/z, relative intensity) 288 (M^+, 70), 179 (100), 165 (70), 123 (15); HRMS (ESI) calcd for $C_{21}H_{17}F[M]^+$, 288.1314; found, 288.1323; IR (film): 2977, 2860, 1509, 1119, 740 cm^{-1}.

*9-(4-(Trifluoromethyl)phenethyl)-9H-fluorene (**3m**).* Yield 98% (99 mg); white solid; mp 78−79 °C; R_f = 0.35 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.4 Hz, 2H), 7.51 (d, J = 7.4 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.31 (td, J = 7.3, 1.1 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 4.07 (d, J = 4.3 Hz, 1H), 2.40−2.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 146.6, 141.4, 128.6, 128.1 (q, J_F = 32.3 Hz), 127.2, 127.1, 125.2 (q, J_F = 3.7 Hz), 124.4 (q, J_F = 271.8 Hz), 124.2, 120.0, 47.1, 34.3, 31.1; EI-MS (m/z, relative intensity) 338 (M^+, 70), 319 (5), 179 (100), 165 (80); HRMS (ESI) calcd for $C_{22}H_{17}F_3$ $[M]^+$, 338.1282; found, 338.1285; IR (film): 2918, 2846, 1455, 1334, 1161, 1121, 1065, 737 cm^{-1}.

*2-Methyl-9-(4-(trifluoromethyl)phenethyl)-9H-fluorene (**3n**).* Yield 99% (104 mg); white solid; mp 72−73 °C; R_f = 0.30 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.30−7.27 (m, 2H), 7.19 (d, J = 7.7 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 4.04 (s, 1H), 2.43 (s, 3H), 2.38−2.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 146.6, 146.4, 141.5, 138.7, 136.9, 128.6, 128.1 (q, J_F = 32.3 Hz), 128.0, 127.2, 126.6, 125.1 (q, J_F = 3.8 Hz), 124.9, 124.4 (q, J_F = 271.7 Hz), 124.2, 119.7, 119.6, 47.0, 34.3, 31.1, 21.7; EI-MS (m/z, relative intensity) 352 (M^+, 70), 333 (10), 281 (10), 253 (10), 207 (30), 193 (100), 179 (80); HRMS (ESI) calcd for $C_{23}H_{19}F_3$ $[M]^+$, 352.1438; found, 352.1438; IR (film): 2921, 1325, 1163, 1121, 1067, 823 cm^{-1}.

*2-Fluoro-9-(4-(trifluoromethyl)phenethyl)-9H-fluorene (**3o**).* Yield 74% (79 mg); white solid; mp 63−64 °C; R_f = 0.30 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.61 (m, 2H), 7.50 (d, J = 7.4 Hz, 1H), 7.45 (d, J = 8.1 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.34−7.21 (m, 1H), 7.20 (dd, J = 8.8, 1.9 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.08 (td, J = 8.8, 2.3 Hz, 1H), 4.06 (d, J = 4.3 Hz, 1H), 2.41−2.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J_F = 245.4 Hz), 148.8 (d, J_F = 8.0 Hz), 146.3, 146.2, 140.5, 137.3 (d, J_F = 2.1 Hz), 128.6, 128.2 (q, J_F = 32.3 Hz), 127.4, 126.8, 125.2 (q, J_F = 3.8 Hz), 124.3 (d, J_F = 271.7 Hz), 124.2, 120.9 (d, J_F = 8.8 Hz), 119.7, 114.4 (d, J_F = 23.0 Hz), 111.6 (d, J_F = 22.8 Hz), 47.2 (d, J_F = 2.1 Hz), 34.2, 30.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ −62.4 (s, 3F), −115.0 (s, 1F); EI-MS (m/z, relative intensity) 356 (M^+, 60), 281 (15), 207 (80), 197 (100), 183 (70), 133 (20); HRMS (ESI) calcd for $C_{22}H_{16}F_4$ $[M]^+$, 356.1188; found, 356.1194; IR (film): 2918, 1455, 1325, 1164, 1123, 1067 cm^{-1}.

*9-(4-Vinylphenethyl)-9H-fluorene (**3p**).* Yield 63% (56 mg); white solid; mp 49−50 °C; R_f = 0.55 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.3 Hz, 2H), 7.55 (d, J = 7.4 Hz, 2H), 7.37 (d, J = 6.9 Hz, 2H), 7.32 (td, J = 7.4, 1.2 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.66 (dd, J = 17.6, 10.9 Hz, 1H), 5.67 (dd, J = 17.6, 0.7 Hz, 1H), 5.17 (dd, J = 10.9, 0.6 Hz, 1H), 4.07 (t, J = 4.7 Hz, 1H), 2.40−2.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 142.1, 141.3, 136.7, 135.2, 128.5, 127.1, 127.0, 126.2, 124.3, 119.9, 113.0, 47.2, 34.7, 31.2; EI-MS (m/z, relative intensity) 296 (M^+, 80), 192 (20), 179 (100), 165 (80), 131 (50), 118 (60); HRMS (ESI) calcd for $C_{23}H_{20}$ $[M]^+$, 296.1565; found, 296.1567; IR (film): 2976, 2924, 2855, 1449, 1118, 839, 741, 658 cm^{-1}.

General Procedure for Pd(0)-Catalyzed Tandem Coupling Reaction (for Scheme 5). 2,2′-Dibromobiphenyls (0.30 mmol), 1,1-dibronates **4** (0.39 mmol), $Pd(PtBu_3)_2$ (0.015 mmol), and 1.5 mL of dioxane were mixed in an oven-dried reaction flask. Ten molar NaOH (aq) (1.5 mmol, 150 μL) was added using a syringe pump over 8 h. The mixture was stirred at room temperature under a nitrogen atmosphere for 48 h. When the reaction was completed, the crude mixture was cooled to room temperature. Five milliliters of Et_2O was added to the mixture, and the mixture was filtered through Celite. The solvents were evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel.

*9H-Fluorene (**5a**).*[6] Yield 74% (38 mg); white solid; R_f = 0.43 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.30 (td, J = 7.4, 1.1 Hz, 2H), 3.90 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.7, 126.7, 126.7, 125.0, 119.9, 36.9.

*2-Methyl-9H-fluorene (**5b**).*[6] Yield 65% (35 mg); white solid; R_f = 0.41 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 7.29−7.22 (m, 1H), 7.16 (d, J = 7.7 Hz, 1H), 3.83 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.1, 141.8, 139.1, 136.6, 127.6, 126.7, 126.2, 125.8, 125.0, 119.6, 119.5, 36.8, 21.6.

*2-Chloro-9H-fluorene (**5c**).*[6] Yield 57% (30 mg); white solid; R_f = 0.41 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.57−7.46 (m, 2H), 7.44−7.27 (m, 3H), 3.88

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(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.0, 140.7, 140.3, 132.4, 127.1, 127.0, 127.0, 125.4, 125.1, 120.7, 119.9, 36.8.

*2-Fluoro-9H-fluorene (**5d**).*[6] Yield 51% (22 mg); white solid; R_f = 0.45 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.66 (m, 2H), 7.51 (d, J = 7.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.30−7.25 (m, 1H), 7.24−7.19 (m, 1H), 7.06 (td, J = 8.7, 2.2 Hz, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_F = 244.3 Hz), 145.3 (d, J_F = 8.6 Hz), 143.0, 140.9, 137.8, 126.9, 126.4, 125.0, 120.7 (d, J_F = 8.9 Hz), 119.6, 113.9 (d, J_F = 22.9 Hz), 112.3 (d, J_F = 22.9 Hz), 37.0 (d, J_F = 2.2 Hz).

*3-Fluoro-9H-fluorene (**5e**).*[17] Yield 74% (41 mg); white solid; R_f = 0.45 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.4 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.49−7.42 (m, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.33 (td, J = 7.4, 1.2 Hz, 1H), 6.99 (ddd, J = 9.3, 8.3, 2.5 Hz, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J_F = 242.9 Hz), 144.2, 143.6 (d, J_F = 8.8 Hz), 141.0 (d, J_F = 3.1 Hz), 138.4 (d, J_F = 2.3 Hz), 127.3, 126.9, 125.9 (d, J_F = 9.0 Hz), 125.1, 120.1, 113.6 (d, J_F = 23.0 Hz), 106.8 (d, J_F = 22.9 Hz), 36.3.

*2-(Trifluoromethoxy)-9H-fluorene (**5f**).*[6] Yield 77% (54 mg); colorless oil; R_f = 0.45 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.7 Hz, 2H), 7.79 (s, 1H), 7.64 (t, J = 7.9 Hz, 1H), 7.58 (d, J = 7.1 Hz, 1H), 7.39 (ddd, J = 13.3, 10.8, 6.7 Hz, 2H), 3.95 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 143.8, 143.4, 140.3, 128.6 (q, J_F = 31.9 Hz), 127.9, 127.1, 125.2, 124.5 (q, J_F = 272.0 Hz), 124.1 (q, J_F = 3.8 Hz), 121.9 (q, J_F = 3.9 Hz), 120.6, 119.9, 36.9.

*2-(Trifluoromethoxy)-9H-fluorene (**5g**).* Yield 80% (60 mg); white solid; mp 44−45 °C; R_f = 0.45 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.9, 3.3 Hz, 2H), 7.54 (d, J = 7.4 Hz, 1H), 7.38 (dd, J = 11.0, 3.4 Hz, 2H), 7.31 (td, J = 7.4, 1.2 Hz, 1H), 7.24−7.19 (m, 1H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (q, J_F = 1.9 Hz), 144.9, 143.3, 140.5, 127.0, 127.0, 125.1, 120.6 (q, J_F = 256.4 Hz), 120.5, 120.0, 119.9, 118.1, 37.0; EI-MS (m/z, relative intensity) 250 (M^+, 100), 181 (15), 165 (70), 152 (60); HRMS (ESI) calcd for $C_{14}H_9F_3O$ $[M]^+$, 250.0605; found, 250.0605; IR (film): 1456, 1300, 1260, 1219, 1161, 765, 742, 733, 652 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

Optimization of the conditions for the Pd(0)-catalyzed reaction, copies of ^{1}H and ^{13}C spectra for all products, and X-ray structure of **3i**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01100.

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Notes

The authors declare no competing financial interest.

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