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Full Paper

New Synthesis of Dibenzofulvenes by Palladium-Catalyzed Double Cross-Coupling Reactions

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Palladium-catalyzed double cross-coupling reactions of 1,1-bis(pinacolato)borylalk-1-enes with 2,2′-dibromobiaryls and of 9-stannafluorenes with 1,1-dibromoalk-1-enes have been demonstrated to serve as new synthetic methods for dibenzofulvenes.

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Introduction

There has been growing interest in cross-conjugated compounds having a 9-(alkylidene)fluorene framework, as organic functional materials.[1] For example, 9-[bis(4-propoxyphenyl) methylidene]fluorene (**1**) shows crystallization-induced emission enhancement with high solid-state quantum yields (Fig. 1).[1a–1c] Fused fulvalene **2** acts as an electron acceptor in a solar cell device with good performances.[1d,1e] Indeno[1,2-*b*] fluorene derivative **3** has been developed for use as an air-stable n-type semiconducting material.[1f–1h] Dibenzofulvene **4** is demonstrated to act as a molecular motor.[1i–1k] Hence, the development of a new synthetic approach to the 9-(diorganomethylidene) fluorene skeleton is important to expand the repertoire of accessible dibenzofulvenes and thereby to contribute to the advancement of optoelectronic organic materials.

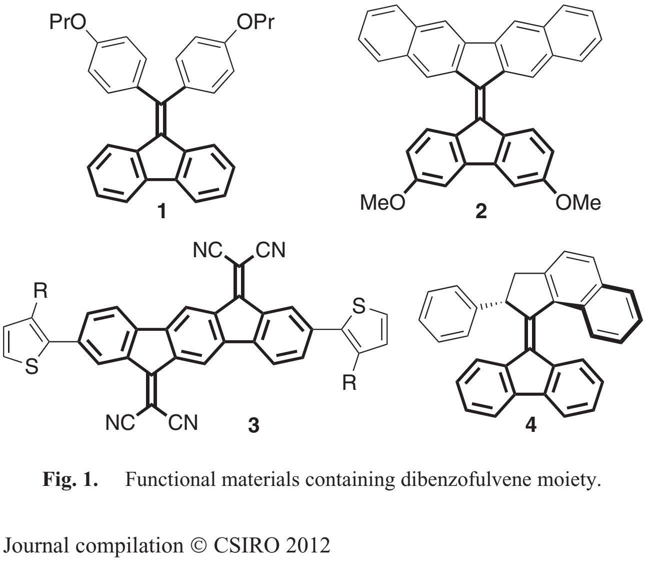
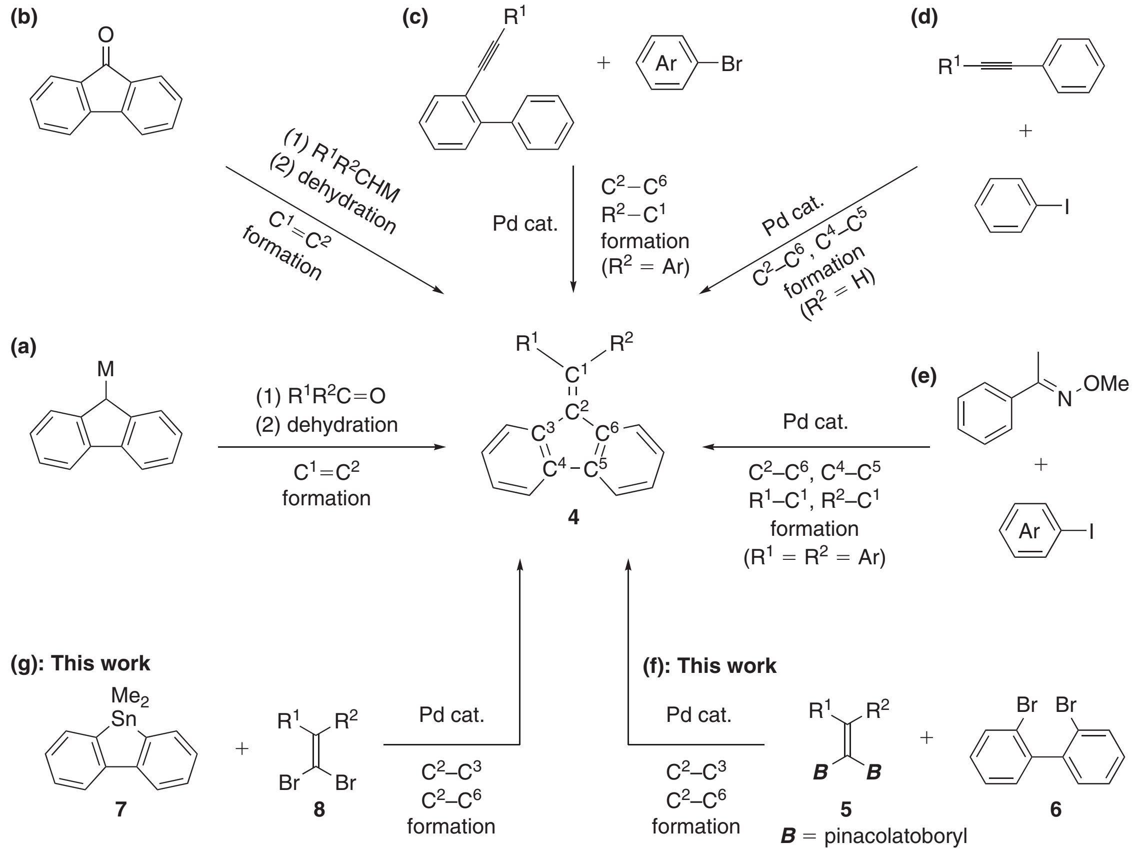


Fig. 1. Functional materials containing dibenzofulvene moiety.

As shown in Scheme 1, the conventional methods of synthesizing 9-(diorganomethylidene)fluorenes **4** involve aldehyde/ketone addition of fluorenylmetal reagents, followed by dehydration[2] and Wittig-type olefination/Knoevenagel condensation of fluorenone (routes a and b).[3] These approaches involve the formation of a carbon–carbon double bond ($C^1{=}C^2$) from the tricyclic starting materials. Recently, several types of palladium-catalyzed syntheses of **4** from acyclic starting compounds have been developed, as shown in routes c–e.[4–7] In these methods, the molecular skeleton of the fluorene moiety is constructed by the formation of a bond between benzylic and aromatic carbons (C^2–C^6) or the concomitant formation of a biaryl bond (C^4–C^5) and a C^2–C^6 bond. These methods involve the use of non-tricyclic substrates and afford numerous structurally diverse fluorene moieties and hence are more attractive than the conventional syntheses. Recently, we demonstrated that palladium-catalyzed double cross-coupling reactions of organodiboron compounds and 9-stannafluorenes with organic dihalides is a versatile method for the synthesis of polycyclic aromatic hydrocarbons such as fused fluorenes, phenanthrenes, triphenylenes, and dibenzo[*g*,*p*]chrysenes.[8] We then planned double cross-coupling reactions of 1,1-diborylalk-1-enes **5**[9] with 2,2′-dibromobiaryls **6** (route f) and that of 9-stannafluorene **7** with 1,1-dibromoalk-1-enes **8** (route *g*), with the aim of developing a new synthetic route to **4** and increasing the synthetic utility of the double cross-coupling strategy of dimetallic reagents and their equivalents. The proposed reactions involve the construction of a five-membered ring through simultaneous C^2–C^3 and C^2–C^6 bond formation. We report the palladium-catalyzed [4 + 1] type annulations.[10]

Results and Discussion

At the outset, we screened the conditions for the double cross-coupling reaction of 1,1-diborylalk-1-enes with 2,2′-dihalobiaryls

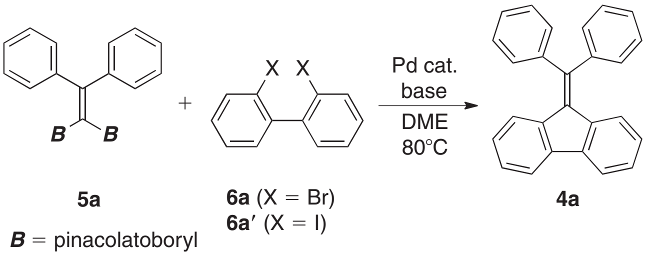


Scheme 1.

using 2,2-diphenyl-1,1-bis(pinacolatoboryl)ethene (**5a**) and 2,2′-dibromo- and 2,2′-diiodobiaryls (**6a** and **6a′**). The results are summarized in Table 1. The reaction of **5a** (1.0 equiv.) with **6a** (1.3 equiv.) in dimethoxyethane (DME) at 80°C in the presence of PdCl$_2$(dppf) catalyst and 3 M aq. KOH afforded the expected product **4a** in only 13 % gas chromatographic (GC) yield (entry 1). The use of other bases such as K$_2$CO$_3$, K$_3$PO$_4$, and Cs$_2$CO$_3$ instead of KOH did not affect the yield of **4a** (entries 2–4). When diiodide **6a′** is used in place of **6a**, the yields of **4a** were lower than those obtained using **6a** (entries 5–7). In all cases, the major product was 1,1-diphenylethene, suggesting that protodeborylation of **5a** was much faster than transmetalation to a palladium complex generated from PdCl$_2$(dppf) in the presence of **6a** or **6a′**. We then examined a palladium catalyst using **6a** as the dihalide and K$_3$PO$_4$ as the base. As shown in entries 9 and 10, the yield of **4a** largely increased when using Pd(OAc)$_2$/2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl and Pd(P^{t}Bu$_3$)$_2$, although 1,1-diphenylethene was still observed to be the major by-product. Finally, the best result (77 % GC yield; 74 % isolated yield) was obtained when the **5a**/**6a** molar ratio was reversed to 1.3/1.0 and highly concentrated aq. K$_3$PO$_4$ (6 M) was used as the base (entry 11).

The scope of the annulation of **5** and **6** is shown in Table 2. Annulation of **5a** with substituted dibromobiphenyls **6b** and **6c** proceeded under the optimized conditions to give **4b** and **4c**, respectively, in moderate yields. Dibromobithiophene **6d** and dibromobinaphthyl **6e** could also be used for the annulation, although the isolated yields of the corresponding products, **4e** and **4d**, respectively, were low.[11] Substituted diboryldiphenylethenes **5b** and **5c** reacted with **6a** and **6b** to give **4f**–**4i** in

Table 1. Screening of reaction conditions[A]



Entry	6	Catalyst	Base	Yield [%][B]
1	**6a**	PdCl$_2$(dppf)	3 M aq. KOH	13
2	**6a**	PdCl$_2$(dppf)	3 M aq. K$_2$CO$_3$	11
3	**6a**	PdCl$_2$(dppf)	3 M aq. K$_3$PO$_4$	13
4	**6a**	PdCl$_2$(dppf)	3 M aq. Cs$_2$CO$_3$	13
5	**6a′**	PdCl$_2$(dppf)	3 M aq. KOH	6
6	**6a′**	PdCl$_2$(dppf)	3 M aq. K$_3$PO$_4$	5
7	**6a′**	PdCl$_2$(dppf)	3 M aq. Cs$_2$CO$_3$	9
8	**6a**	Pd(PPh$_3$)$_4$	3 M aq. K$_3$PO$_4$	11
9[C]	**6a**	Pd(OAc)$_2$/L	3 M aq. K$_3$PO$_4$	64
10	**6a**	Pd(P^{t}Bu$_3$)$_2$	3 M aq. K$_3$PO$_4$	67
11[D]	**6a**	Pd(P^{t}Bu$_3$)$_2$	6 M aq. K$_3$PO$_4$	77 (74)

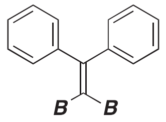
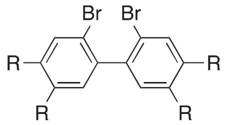
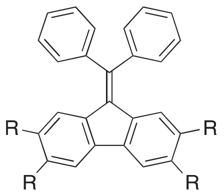
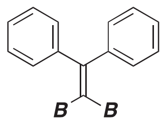
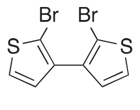
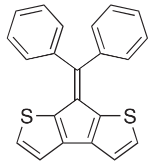
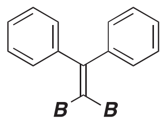
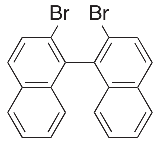
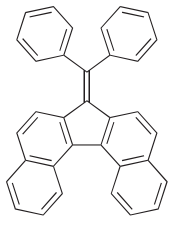
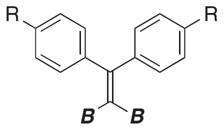
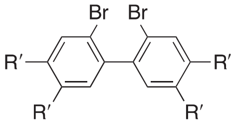
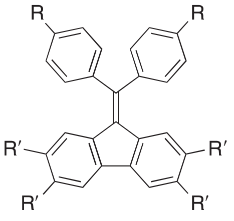
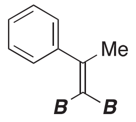
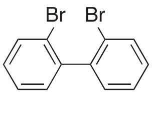
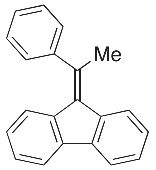
[A] **5a** (1.0 equiv.), **6** (1.3 equiv.), Pd catalyst (10 mol %), base (6 equiv.), 1,2-dimethoxyethane (DME), 80°C.

[B] Gas chromatographic yield. The value in parentheses is isolated yield.

[C] L: 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl.

[D] **5a** (1.3 equiv.), **6** (1.0 equiv.), Pd catalyst (10 mol %), base (6 equiv.), DME, 80°C.

Table 2. Palladium-catalyzed double cross-coupling reaction of 5 with 6[A]

Entry	5		6		4		Yield [%][B]
1		**5a**		**6b** (R = Me)		**4b**	50
2[C]		**5a**		**6c** (R = OMe)		**4c**	58
3[C]		**5a**		**6d**		**4d**	37
4		**5a**		**6e**		**4e**	30
5		**5b** (R = Me)		**6a** (R′ = H)		**4f**	42
6[C]		**5b** (R = Me)		**6b** (R′ = Me)		**4g**	48
7		**5c** (R = F)		**6a** (R′ = H)		**4h**	36
8[C]		**5c** (R = F)		**6b** (R′ = Me)		**4i**	42
9[D]		**5d**		**6a**		**4j**	57

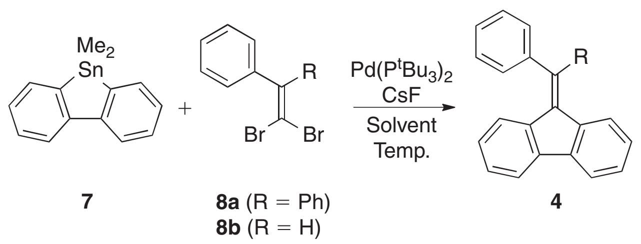
[A] **5** (1.3 equiv.), **6** (1.0 equiv.), Pd(P^{t}Bu$_3$)$_2$ (10 mol %), 6 M aq. K$_3$PO$_4$ (6 equiv.), 1,2-dimethoxyethane (DME), 80°C, 6 h.
[B] Isolated yields.
[C] **5** (1.5 equiv.), **6** (1.0 equiv.), Pd(P^{t}Bu$_3$)$_2$ (20 mol %), 6 M aq. K$_3$PO$_4$ (6 equiv.), DME, 80°C, 6 h.
[D] **5** (1.5 equiv.), **6** (1.0 equiv.), Pd(P^{t}Bu$_3$)$_2$ (20 mol %), 6 M aq. KOH (6 equiv.), DME, 80°C, 6 h.

36–48 % yields. In addition, methyl- and phenyl-substituted 1,1-diborylethene **5d** underwent annulation to afford **4j** in acceptable yield. The low-to-moderate isolated yields of **4** were ascribed to the competing protodeborylation of **5** under the reaction conditions adopted.

We then focussed on the double cross-coupling reaction of 9-stannafluorene **7** with 1,1-dibromoalk-1-enes **8**; this reaction can be regarded as an umpolung variant of the annulation using **5** and **6**. The representative results for the screening of the reaction conditions using **7** and **8a**/**8b** are summarized in Table 3. Under the optimized conditions (Pd(P^{t}Bu$_3$)$_2$, THF, 60°C) for the annulation between **7** and 1,2-dibromoarenes,[8d] the reaction of **7** with **8a** did not proceed at all, and **7** and **8a** were quantitatively recovered (entry 1). However, when CsF (5 equiv.) was added under the same conditions, the desired product (**4a**) was formed in a moderate yield (entry 2). The yield of **4a** largely increased upon heating the reaction mixture to 130°C in 1,4-dioxane (entry 3). When using the less hindered **8b**, annulation proceeded smoothly even at 60°C in the presence of CsF to give **4k** in good to high yields (entry 4). As shown in entry 5, the reaction carried out at 130°C resulted in a slightly lower yield (75 %).

The scope of application of **8** to the double cross-coupling reaction of **7** is summarized in Table 4. Dibromostyrene derivatives **8c**–**8h** underwent the annulation smoothly at 60°C to give **4c**–**4h** in good-to-excellent yields (entries 1–6). Thus, functional groups such as MeO, CF$_3$, CO$_2$Me, CN, Cl, and F groups/atoms were tolerated under the reaction conditions. The coupling of (dibromoethenyl)thiophene **8i** gave **4r** in 96 % yield (entry 7). Ethyl- and phenyl-substituted dibenzofulvene **4s** was produced in a moderate yield from **8j** (entry 8). The annulation of 2,2-diaryl-1,1-dibromoethenes **8k**–**8m** proceeded

Table 3. Screening of reaction conditions[A]



Entry	8	Solvent/temp [°C]	Time [h]	4	Yield [%][B]
1[C]	**8a**	THF/60	48	**4a**	0
2	**8a**	THF/60	48	**4a**	62
3	**8a**	Dioxane/130	12	**4a**	86 (90)
4[D]	**8b**	Dioxane/60	24	**4k**	88 (80)
5	**8b**	Dioxane/130	24	**4k**	75

[A] **7** (0.05 mmol), **8** (0.05 mmol), Pd(P^{t}Bu$_3$)$_2$ (2.5 μmol), CsF (5 equiv.), solvent (1 mL).

[B] Yield was estimated by ^{1}H NMR spectroscopy using 1,3,5-(MeO)$_3$-C$_6$H$_3$ as an internal standard. The values in parentheses are isolated yields.

[C] **7** (0.05 mmol), **8a** (0.05 mmol), Pd(P^{t}Bu$_3$)$_2$ (2.5 μmol), THF (1 mL).

[D] **7** (0.50 mmol), **8b** (0.50 mmol), Pd(P^{t}Bu$_3$)$_2$ (25 μmol), CsF (2.5 mmol), 1,4-dioxane (10 mL).

upon heating the reaction mixture at 130°C, to afford **4f**, **4t**, and **4u**, respectively, in good yields (entries 9–11). Bifluorenylidene **4v** was obtained in an excellent yield from the reaction of **7** with (dibromomethylene)fluorene **8n** (entry 12). Double annulation of **7** with tetrabromides **8o** and **8p** was also feasible, and **4w** and **4x** were obtained in high-to-excellent yields (entries 13 and 14). Thus, palladium-catalyzed annulation of 9-stannafluorenes with 1,1-dibromoalk-1-enes is a powerful tool for the synthesis of dibenzofulvenes.

Conclusion

We have presented palladium-catalyzed double cross-coupling reactions of 1,1-diborylalk-1-enes with 2,2′-dibromobiaryls and 9-stannafluorenes with 1,1-dibromoalk-1-enes as new strategies for the synthesis of dibenzofulvenes. While the product yields in the boron-based annulation are largely moderate because of the competing protodeborylation of diboryl reagents used, the proposed stannafluorene-based strategy is highly effective for dibenzofulvene synthesis.

Experimental

Melting points were determined using a Yanagimoto Micro Point Apparatus. ^{1}H NMR spectra were measured on Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ 0) or chloroform (δ 7.26). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C NMR spectra were measured on Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard (δ 0) or chloroform (δ 77.0). ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with CFCl$_3$ as an internal standard (δ 0). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer. Gas chromatography–mass spectrometry (GC-MS) analyses were performed with a JEOL JMS-700 spectrometer by electron ionization (EI) at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F$_{254}$ and column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. Tetrahydrofuran was passed through two packed columns of neutral alumina and copper oxide under a nitrogen atmosphere before use. All reactions were carried out under an argon atmosphere.

Typical Procedure for Preparation of 1,1-Dibromoalkenes

To a toluene (100 mL) solution of CBr$_4$ (19.8 g, 60 mmol) and benzophenone (5.46 g, 30 mmol) was added PPh$_3$ (31.8 g, 120 mmol), and then the resulting mixture was stirred at 120°C for 100 h. The reaction mixture was filtered though a silica gel column and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane) to give 1,1-dibromo-2,2-diphenylethene as a colourless solid (7.7 g, 76 % yield).

1,1-Dibromo-2,2-bis(4-methylphenyl)ethene

Yield: 60 %. Colourless solid. Mp 120.3–121.0°C. R_f 0.50 (hexane/EtOAc 9 : 1). δ_H (400 MHz, CDCl$_3$) 2.34 (s, 6H), 7.13 (d, J 8.4, 4H), 7.18 (d, J 8.4, 4H); δ_C (100 MHz, CDCl$_3$) 21.4, 89.2, 128.6, 128.8, 137.7, 138.5, 147.5. ν_{max} (KBr)/cm^{-1} 2916, 1506, 1445, 1182, 1113, 1022, 955, 833, 814, 754, 739, 577, 534, 486. m/z (FAB) 368 (8 %, [M + 4]$^+$), 367 (4, [M + 3]$^+$), 366 (16, [M + 2]$^+$), 368 (3, [M + 1]$^+$) 364 (8, M$^+$), 206 (11). (Found: C 52.58, H 3.96. Anal. Calc. for C$_{16}$H$_{14}$Br$_2$: C 52.49, H 3.85 %.)

1,1-Dibromo-2,2-bis(4-fluorophenyl)ethene

Yield: 61 %. Colourless solid. Mp 60.3–60.5°C. R_f 0.50 (hexane/EtOAc 9 : 1). δ_H (400 MHz, CDCl$_3$) 7.03 (t, J 8.8, 4H), 7.22−7.29 (m, 4H); δ_C (100 MHz, CDCl$_3$) 90.8, 115.4 (d, J 22.1), 130.6 (d, J 8.4), 136.9 (d, J 3.0), 145.6, 162.0 (d, J 247.1); δ_F (282 MHz, CDCl$_3$) −113.3. ν_{max} (KBr)/cm^{-1} 3043, 1896, 1599, 1501, 1402, 1292, 1217, 1153, 1096, 1017, 955, 833, 750. m/z (FAB) 376 (19 %, [M + 4]$^+$), 375 (8, [M + 3]$^+$), 374 (38, [M + 2]$^+$), 373 (4, [M + 1]$^+$), 372 (21, M$^+$), 214 (52). (Found: C 45.06, H 2.36. Anal. Calc. for C$_{14}$H$_8$Br$_2$F$_2$: C 44.96, H 2.16 %.)

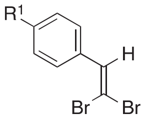
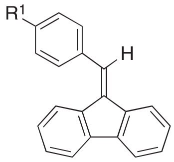
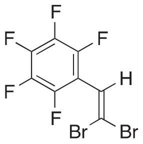
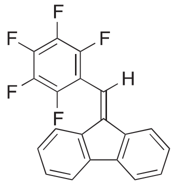
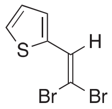
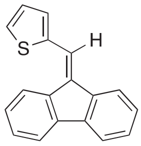
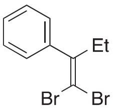
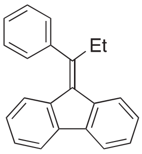
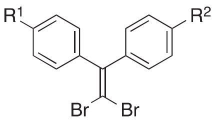
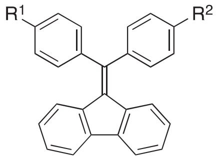
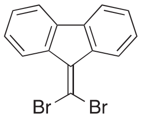
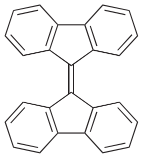
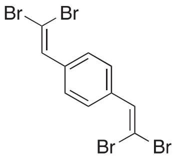
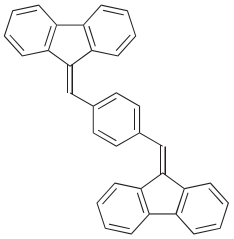
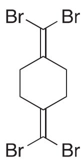
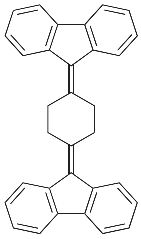
*1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2-bis(4-methylphenyl)ethene (**5b**)*

Prepared according to the reported procedure.[9] Yield: 34 %. Colourless solid. Mp 160.0–160.7°C. R_f 0.68 (hexane/EtOAc 2 : 1). δ_H (400 MHz, CDCl$_3$) 1.16 (s, 24H), 2.33 (s, 6H), 7.04 (d, J 7.6, 4H), 7.12 (d, J 7.6, 4H); δ_C (100 MHz, CDCl$_3$) 21.4, 24.7, 83.1, 128.1, 129.4, 137.3, 141.7, 164.5. ν_{max} (KBr)/cm^{-1} 2980, 1593, 1506, 1465, 1344, 1298, 1269, 1144, 1026, 966, 853, 824. m/z (FAB) 462 (1 %, [M + 2]$^+$), 461 (5, [M + 1]$^+$), 460 (8, M$^+$), 459 (3, [M − 1]$^+$), 458 (1, [M − 2]$^+$). (Found: C 73.14, H 8.17. Anal. Calc. for C$_{28}$H$_{38}$B$_2$O$_4$: C 73.07, H 8.32 %.)

*1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2-bis(4-fluorophenyl)ethene (**5c**)*

Prepared according to the reported procedure.[9] Yield: 43 %. Colourless solid. Mp 158.5–159.4°C. R_f 0.65 (hexane/EtOAc

Table 4. Palladium-catalyzed double cross-coupling reaction of 7 with 8[A]

Entry	8		4		Yield [%][B]
1		**8c** ($R^1 = \mathrm{OMe}$)		**4l** ($R^1 = \mathrm{OMe}$)	75
2		**8d** ($R^1 = \mathrm{CF_3}$)		**4m** ($R^1 = \mathrm{CF_3}$)	81
3		**8e** ($R^1 = \mathrm{CO_2Me}$)		**4n** ($R^1 = \mathrm{CO_2Me}$)	87
4		**8f** ($R^1 = \mathrm{CN}$)		**4o** ($R^1 = \mathrm{CN}$)	96
5		**8 g** ($R^1 = \mathrm{Cl}$)		**4p** ($R^1 = \mathrm{Cl}$)	58
6		**8h**		**4q**	73
7		**8i**		**4r**	96
8		**8j**		**4s**	55
9[C]		**8k** ($R^1 = R^2 = \mathrm{Me}$)		**4f** ($R^1 = R^2 = \mathrm{Me}$)	69
10[C]		**8l** ($R^1 = R^2 = \mathrm{F}$)		**4t** ($R^1 = R^2 = \mathrm{F}$)	62
11[C]		**8m** ($R^1 = \mathrm{Ph}, R^2 = \mathrm{H}$)		**4u** ($R^1 = \mathrm{Ph}, R^2 = \mathrm{H}$)	72
12		**8n**		**4v**	98
13[D]		**8o**		**4w**	96
14[D]		**8p**		**4x**	87

[A] **7** (0.50 mmol), **8** (0.50 mmol), $\mathrm{Pd(P^tBu_3)_2}$ (25 µmol), CsF (2.5 mmol), 1,4-dioxan, 60°C, 12 h.

[B] Isolated yields.

[C] **7** (1.0 mmol), **8** (1.0 mmol), $\mathrm{Pd(P^tBu_3)_2}$ (50 µmol), CsF (5 mmol), 1,4-dioxan, 130°C, 12 h.

[D] **7** (1.5 mmol), **8** (0.50 mmol), $\mathrm{Pd(P^tBu_3)_2}$ (50 µmol), CsF (50 mmol), 1,4-dioxan, 60°C, 12 h.

2 : 1). δ_H (400 MHz, $CDCl_3$) 1.16 (s, 24H), 6.94 (t, *J* 8.8, 4H), 7.16–7.23 (m, 4H); δ_C (100 MHz, $CDCl_3$) 24.6, 83.3, 114.4 (d, *J* 21.3), 131.0 (d, *J* 9.6), 140.3 (d, *J* 3.0), 162.1, 162.4 (d, *J* 245.5); δ_F (282 MHz, $CDCl_3$) −114.8. ν_{max} (KBr)/cm^{-1} 2982, 1599, 1503, 1381, 1350, 1296, 1217, 1144, 856. *m/z* (FAB) 470 (8 %, $[M+2]^+$), 469 (39, $[M+1]^+$), 468 (48, M^+), 467 (21, $[M-1]^+$), 466 (4, $[M-2]^+$). (Found: C 66.70, H 6.80. Anal. Calc. for $C_{26}H_{32}B_2F_2O_4$: C 66.70, H 6.89 %.)

*1,1-Dibromo-2,2-bis(4-methylphenyl)ethene (**8k**)*

Yield: 60 %. Colourless solid. Mp 120.3–121.0°C. R_f 0.50 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 2.34 (s, 6H), 7.13 (d, *J* 8.4, 4H), 7.18 (d, *J* 8.4, 4H); δ_C (100 MHz, $CDCl_3$) 21.4, 89.2, 128.6, 128.8, 137.7, 138.5, 147.5. ν_{max} (KBr)/cm^{-1} 2916, 1506, 1445, 1182, 1113, 1022, 955, 833, 814, 754, 739, 577, 534, 486. *m/z* (FAB) 368 (8 %, $[M+4]^+$), 367 (4, $[M+3]^+$), 366 (16, $[M+2]^+$), 368 (3, $[M+1]^+$) 364 (8, M^+), 206 (11). (Found: C 52.58, H 3.96. Anal. Calc. for $C_{16}H_{14}Br_2$: C 52.49, H 3.85 %.)

*4,4′-(2,2-Dibromoethene-1,1-diyl)bis(fluorobenzene) (**8l**)*

Yield: 61 %. Colourless solid. Mp 60.3–60.5°C. R_f 0.50 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 7.03 (t, *J* 8.8, 4H), 7.22–7.29 (m, 4H); δ_C (100 MHz, $CDCl_3$) 90.8, 115.4 (d, *J* 22.1), 130.6 (d, *J* 8.4), 136.9 (d, *J* 3.0), 145.6, 162.0 (d, *J* 247.1); δ_F (282 MHz, $CDCl_3$) −113.3. ν_{max} (KBr)/cm^{-1} 3043, 1896, 1599, 1501, 1402, 1292, 1217, 1153, 1096, 1017, 955, 833, 750. *m/z* (FAB) 376 (19 %, $[M+4]^+$), 375 (8, $[M+3]^+$), 374 (38, $[M+2]^+$), 373 (4, $[M+1]^+$), 372 (21, M^+), 214 (52). (Found: C 45.06, H 2.36. Anal. Calc. for $C_{14}H_8Br_2F_2$: C 44.96, H 2.16 %.)

*4-(2,2-Dibromo-1-phenylethenyl)-1,1′-biphenyl (**8m**)*

Yield: 43 %. Colourless solid. R_f 0.20 (hexane/EtOAc/CH_2Cl_2 50 : 1 : 1). δ_H (400 MHz, $CDCl_3$) 7.32–7.46 (m, 10H), 7.55–7.60 (m, 4H); δ_C (100 MHz, $CDCl_3$) 90.2, 126.8, 126.9, 127.4, 127.9, 128.3, 128.66, 128.68, 129.1, 140.0, 140.2, 140.6, 141.3, 147.3. ν_{max} (KBr)/cm^{-1} 1485, 1441, 1400, 1074, 1030, 941, 841, 799, 787, 758, 729, 689, 615, 600. *m/z* (EI) 418 (1 %, $[M+6]^+$), 417 (12, $[M+5]^+$), 416 (57, $[M+4]^+$), 415 (24, $[M+3]^+$), 414 (100, $[M+2]^+$), 413 (12, $[M+1]^+$), 412 (57, M^+). *m/z* (HRMS) Found: 411.9482. Calc. for $C_{20}H_{14}Br_2$ (M^+): 411.9462.

*Representative Procedure for Pd-Catalyzed Double Cross-Coupling Reaction of Diborylalkenes **5** and Dibromides **6***

To a solution of **5** (56 mg, 0.13 mmol), **6** (31 mg, 0.10 mmol), and $Pd(P^tBu_3)_2$ (5.1 mg, 10 µmol) in DME (2 mL) was added 6 M aq. K_3PO_4 (0.1 mL). The solution was stirred at 80°C for 6 h. The resulting mixture was quenched with sat. aq. NH_4Cl (1 mL) and was diluted with Et_2O (3 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated under vacuum. The crude product was purified by preparative TLC (hexane/EtOAc 10 : 1) and then GPC ($CHCl_3$) to give **4a** as a colourless solid (24 mg, 74 % yield).

*9-(Diphenylmethylene)-2,3,6,7-tetramethyl-9*H*-fluorene (**4b**)*

Yield: 50 %. Yellow solid. Mp 225.2–225.6°C. R_f 0.48 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 2.00 (s, 6H), 2.28 (s, 6H), 6.31 (s, 2H), 7.37–7.45 (m, 12H); δ_C (100 MHz, $CDCl_3$) 20.2, 20.4, 119.9, 126.0, 127.7, 128.5, 129.6, 133.8, 134.3, 136.0, 136.7, 138.7, 142.7, 143.1. ν_{max} (KBr)/cm^{-1} 3076, 1622, 1597, 1489, 1443, 1281, 982, 864, 770, 756, 698, 658. *m/z* (EI) 388 (6 %, $[M+2]^+$), 387 (34, $[M+1]^+$), 386 (100, M^+), 149 (51). *m/z* (HRMS) Found: 386.2019. Calc. for $C_{30}H_{26}$ (M^+): 386.2035.

*9-(Diphenylmethylene)-2,3,6,7-tetramethoxy-9*H*-fluorene (**4c**)*

Yield: 58 %. Yellow solid. Mp 239.6–240.0°C. R_f 0.20 (hexane/EtOAc 2 : 1). δ_H (400 MHz, $CDCl_3$) 3.39 (s, 6H), 3.97 (s, 6H), 6.15 (s, 2H), 7.03 (s, 2H), 7.36–7.48 (m, 10H); δ_C (100 MHz, $CDCl_3$) 55.3, 56.1, 101.3, 108.5, 127.8, 128.7, 129.6, 131.1, 134.0, 134.0, 141.5, 142.5, 146.7, 149.1. ν_{max} (KBr)/cm^{-1} 2936, 1601, 1494, 1468, 1439, 1268, 1258, 1217, 1165, 1155, 1080, 866, 833, 756, 704, 561. *m/z* (EI) 452 (10 , $[M+2]^+$), 451 (47, $[M+1]^+$), 450 (100, M^+). (Found: C 80.00, H 5.81. Anal. Calc. for $C_{30}H_{26}O_4$: C 79.98, H 5.82 %.)

*7-(Diphenylmethylene)-7*H*-cyclopenta[1,2-*b*:4,3-*b*′]dithiophene (**4d**)*

Yield: 37 %. Yellow solid. Mp 194.5–195.0°C. R_f 0.40 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 6.98 (d, *J* 4.8, 2H), 7.06 (d, *J* 4.8, 2H), 7.39–7.51 (m, 10H); δ_C (100 MHz, $CDCl_3$) 117.9, 127.9, 128.6, 128.9, 129.3, 129.6, 138.8, 140.5, 142.0, 143.7. ν_{max} (KBr)/cm^{-1} 2918, 1616, 1505, 1442, 878, 853, 772, 754, 727, 700, 685. *m/z* (EI) 344 (14 %, $[M+2]^+$), 343 (31, $[M+1]^+$), 342 (100, M^+), 279 (15). *m/z* (HRMS) Found: 342.0535. Calc. for $C_{22}H_{14}S_2$ (M^+): 342.0537.

*7-(Diphenylmethylene)-7*H*-dibenzo[*c,g*]fluorene (**4e**)*

Yield: 30 %. Orange solid. Mp 244.9–245.6°C. R_f 0.38 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 6.87 (d, *J* 8.8, 2H), 7.43–7.53 (m, 16H), 7.82 (d, *J* 8.0, 2H), 8.55 (d, *J* 8.0, 2H); δ_C (100 MHz, $CDCl_3$) 122.3, 124.6, 125.2, 126.3, 127.1, 128.1, 128.2, 128.5, 128.7, 130.9, 134.0, 135.8, 138.1, 138.4, 142.8, 148.2. ν_{max} (KBr)/cm^{-1} 3045, 1593, 1510, 1443, 820, 781, 696. *m/z* (EI) 432 (9 %, $[M+2]^+$), 431 (40, $[M+1]^+$), 430 (100, M^+). *m/z* (HRMS) Found: 430.1718. Calc. for $C_{34}H_{22}$ (M^+): 430.1722.

*9-[Bis(4-methylphenyl)methylene]-9*H*-fluorene (**4f**)*

Yield: 42 %. Pale yellow solid. Mp 145.0–145.5°C. R_f 0.43 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 2.45 (s, 6H), 6.76 (d, *J* 7.6, 2H), 6.96 (d, *J* 7.6, 2H), 7.20–7.30 (m, 10H), 7.72 (d, *J* 7.6, 2H); δ_C (100 MHz, $CDCl_3$) 21.6, 119.0, 124.6, 126.1, 127.2, 129.3, 129.7, 133.5, 138.0, 138.8, 140.1, 140.1, 145.8. ν_{max} (KBr)/cm^{-1} 3020, 1605, 1506, 1445, 814, 783, 733, 586. *m/z* (EI) 360 (5 %, $[M+2]^+$), 359 (31, $[M+1]^+$), 358 (100, M^+), 343 (16). (Found: C 94.07, H 6.28. Anal. Calc. for $C_{28}H_{22}$: C 93.81, H 6.19 %.)

*9-[Bis(4-methylphenyl)methylene]-2,3,6,7-tetramethyl-9*H*-fluorene (**4g**)*

Yield: 48 %. Yellow solid. Mp 109.5–110.0°C. R_f 0.55 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 2.01 (s, 6H), 2.28 (s, 6H), 2.43 (s, 6H), 6.42 (s, 2H), 7.19 (d, *J* 8.0, 4H), 7.24 (d, *J* 8.0, 4H), 7.40 (s, 2H); δ_C (100 MHz, $CDCl_3$) 20.2, 20.5, 21.5, 119.8, 125.9, 129.1, 129.8, 130.6, 133.7, 135.7, 136.9, 137.5, 138.5, 140.4, 143.2. ν_{max} (KBr)/cm^{-1} 2916, 1510, 1452, 1325, 1233, 899, 880, 804, 764, 714, 598. *m/z* (EI) 416 (20 %, $[M+1]^+$), 415 (55, $[M+1]^+$), 414 (100, M^+), 384 (12). (Found: C 92.47, H 7.56. Anal. Calc. for $C_{32}H_{30}$: C 92.71, H 7.29 %.)

*9-[Bis(4-fluorophenyl)methylene]-9*H*-fluorene (**4h**)*

Yield: 36 %. Pale yellow solid. Mp 194.5–195.0°C. R_f 0.44 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 6.68 (d, *J* 8.0, 2H), 6.98 (t, *J* 7.6, 2H), 7.13 (t, *J* 7.6, 4H), 7.27 (t, *J* 7.6, 2H), 7.34 (t, *J* 6.4, 4H), 7.71 (d, *J* 7.6, 2H); δ_C (100 MHz, $CDCl_3$) 115.8 (d, *J* 21.4), 119.3, 124.5, 126.4, 127.8, 131.7 (d, *J* 7.6), 134.7, 138.3, 138.5 (d, *J* 3.0), 140.4, 142.7, 162.6 (d, *J* 246.3); δ_F (282 MHz, $CDCl_3$) −113.3. ν_{max} (KBr)/cm^{-1} 2916, 1890, 1601, 1505, 1445, 1236, 1155, 874, 831, 787, 739, 584, 527. *m/z* (EI) 368 (7 %, $[M+2]^+$), 367 (43, $[M+1]^+$), 366 (100, M^+), 270 (36). (Found: C 85.17, H 4.55. Anal. Calc. for $C_{26}H_{16}F_2$: C 85.23, H 4.40 %.)

*9-[Bis(4-fluorophenyl)methylene]-2,3,6,7-tetramethyl-9*H*-fluorene (**4i**)*

Yield: 42 %. Pale yellow solid. Mp 211.0–211.3°C. R_f 0.50 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 2.03 (s, 6H), 2.29 (s, 6H), 6.37 (s, 2H), 7.29–7.35 (m, 4H), 7.11 (t, *J* 8.4, 4H), 7.41 (s, 2H); δ_C (100 MHz, $CDCl_3$) 20.3, 20.5, 115.6 (d, *J* 21.4), 120.0, 125.7, 131.7 (d, *J* 7.6), 134.0, 135.0, 136.4, 136.4, 138.8, 138.9 (d, *J* 3.0), 140.0, 162.5 (d, *J* 246.3); δ_F (282 MHz, $CDCl_3$) −114.0. ν_{max} (KBr)/cm^{-1} 2920, 1597, 1503, 1452, 1215, 1157, 1091, 876, 835, 592. *m/z* (EI) 424 (13 %, $[M+2]^+$), 423 (76, $[M+1]^+$), 422 (100, M^+), 392 (23). (Found: C 85.00, H 5.96. Anal. Calc. for $C_{30}H_{24}F_2$: C 85.28, H 5.73 %.)

*9-(1-Phenylethylidene)-9*H*-fluorene (**4j**)*

Yield: 57 %. Colourless solid. Mp 111.1–111.8°C. R_f 0.43 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 2.78 (s, 3H), 6.26 (d, *J* 8.0, 1H), 6.86 (t, *J* 7.6, 1H), 7.18 (t, *J* 7.6, 1H), 7.32–7.52 (m, 7H), 7.69 (d, *J* 8.0, 1H), 7.78–7.82 (m, 1H), 7.98–8.02 (m, 1H); δ_C (100 MHz, $CDCl_3$) 26.0, 118.9, 119.4, 124.5, 125.2, 126.3, 126.7, 126.7, 127.1, 127.5, 127.5, 128.9, 132.9, 138.4, 138.8, 139.4, 140.3, 142.7, 145.3. ν_{max} (KBr)/cm^{-1} 3030, 1616, 1593, 1489, 1447, 1341, 1265, 1182, 1072, 1024, 781, 764, 733, 702. *m/z* (EI) 270 (5 %, $[M+2]^+$), 269 (25, $[M+1]^+$), 268 (100, M^+), 253 (86). *m/z* (HRMS) Found: 268.1254. Calc. for $C_{21}H_{16}$ (M^+): 268.1252.

*Representative Procedure for Palladium-Catalyzed Double Cross-Coupling Reaction of 9-Stannafluorenes **7** with 1,1-Dibromoalk-1-enes **8***

A Schlenk tube (80 mL) was charged with **7** (0.30 g, 1.0 mmol), **8a** (0.34 g, 1.0 mmol), $Pd(P^tBu_3)_2$ (26 mg, 50 μmol), CsF (0.76 g, 5.0 mmol), and 1,4-dioxan (20 mL) in a glove box. The vial was taken outside from the glove box and heated at 130°C for 12 h. The reaction mixture was cooled to room temperature, filtered through a pad of Florisil, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane/AcOEt/CH_2Cl_2 50 : 1 : 1) to give **4a** (0.22 g, 65 % yield) as a yellow solid.

*9-[4-(Trifluoromethyl)benzylidene]-9*H*-fluorene (**4m**)*

Yield: 81 %. Colourless solid. Mp 88.7–89.5°C. R_f 0.38 (hexane/$EtOAc_2$ 50 : 1). δ_H (400 MHz, $CDCl_3$) 7.09 (t, *J* 7.2, 1H), 7.33–7.47 (m, 5H), 7.63 (s, 1H), 7.71–7.74 (m, 5H), 7.79 (d, *J* 6.8, 1H); δ_C (100 MHz, $CDCl_3$) 119.7, 119.9, 120.4, 124.3, 125.0, 125.5 ($J_{C\text{–}F}$ 3.9), 126.8, 127.1, 128.7, 129.1, 129.6, 136.1, 137.9, 139.1, 139.4, 140.7, 141.5, 129.5 ($J_{C\text{–}F}$ 50), 130.8 ($J_{C\text{–}F}$ 160); δ_F (282 MHz, $CDCl_3$) −63.10 (s). ν_{max} (KBr)/cm^{-1} 1613, 1449, 1437, 1408, 1325, 1161, 1124, 1105, 1064, 1017, 858, 829, 777, 733. *m/z* (EI) 324 (7 %, $[M+2]^+$), 323 (25, $[M+1]^+$), 322 (100, M^+). *m/z* (HRMS) Found: 322.0962. Calc. for $C_{21}H_{13}F_3$ (M^+): 322.0969.

*Methyl 4-[(9*H*-Fluoren-9-ylidene)methyl]benzoate (**4n**)*

Yield: 87 %. Colourless solid. Mp 116.2–117.0°C. R_f 0.30 (hexane/EtOAc 10 : 1). δ_H (400 MHz, $CDCl_3$) 7.06 (dd, *J* 7.2, 7.2, 1H), 7.31–7.42 (m, 3H), 7.50 (d, *J* 8.0, 1H), 7.64 (s, 1H), 7.66 (d, *J* 8.0, 2H), 7.71 (d, *J* 8.0, 2H), 7.77 (d, *J* 7.2, 1H), 8.13–8.15 (m, 2H), 3.98 (s, 3H), δ_C (100 MHz, $CDCl_3$) 52.2, 119.6, 119.8, 120.3, 124.4, 125.6, 126.7, 127.0, 128.6, 128.9, 129.3, 129.4, 129.7, 136.1, 137.6, 139.1, 139.3, 141.1, 141.7, 166.8. ν_{max} (KBr)/cm^{-1} 1703, 1603, 1450, 1437, 1283, 1113, 1103, 772, 727. *m/z* (EI) 314 (9 %, $[M+2]^+$), 313 (35, $[M+1]^+$), 312 (100, M^+). *m/z* (HRMS) Found: 312.1153. Calc. for $C_{22}H_{16}O_2$ (M^+): 312.1150.

*4-[(9*H*-Fluoren-9-ylidene)methyl]benzonitrile (**4o**)*

Yield: 96 %. Colourless solid. Mp 140.6–141.4°C. R_f 0.22 (hexane/EtOAc 50 : 1). δ_H (400 MHz, $CDCl_3$) 7.07 (dd, *J* 7.6, 7.6, 1H), 7.32–7.43 (m, 4H), 7.57 (s, 1H), 7.67–7.77 (m, 6H); δ_C (100 MHz, $CDCl_3$) 11.4, 118.8, 119.7, 120.0, 120.5, 124.2, 124.3, 126.9, 127.2, 128.9, 129.3, 130.0, 132.3, 135.8, 138.5, 138.9, 139.4, 141.6, 141.9. ν_{max} (KBr)/cm^{-1} 1602, 1501, 1449, 1437, 866, 831, 777, 731, 565. *m/z* (EI) 281 (6 %, $[M+2]^+$), 280 (25, $[M+1]^+$), 279 (100, M^+). *m/z* (HRMS) Found: 278.0967. Calc. for $C_{21}H_{13}N$ (M^+): 279.1048.

*9-(4-Chlorobenzylidene)-9*H*-fluorene (**4p**)*

Yield: 58 %. Colourless solid. Mp 143.6–144.4°C. R_f 0.34 (hexane). δ_H (400 MHz, $CDCl_3$) 7.08 (t, *J* 7.6, 1H), 7.33 (t, *J* 8.0, 2H), 7.39 (t, *J* 7.6, 1H), 7.43 (d, *J* 8.4, 2H); δ_C (100 MHz, $CDCl_3$) 119.6, 119.8, 120.2, 124.3, 125.6, 126.7, 127.0, 128.4, 128.8, 130.6, 132.6, 133.8, 135.3, 136.2, 137.0, 139.19, 139.22, 141.3. ν_{max} (KBr)/cm^{-1} 1487, 1449, 1437, 1397, 1084, 1015, 862, 824, 779, 731. *m/z* (EI) 291 (5 %, $[M+3]^+$), 290 (25, $[M+2]^+$), 289 (19, $[M+1]^+$), 288 (70, M^+), 252 (100). *m/z* (HRMS) Found: 288.0710. Calc. for $C_{20}H_{13}Cl$ (M^+): 288.0706.

*9-(1-Phenylpropylidene)-9*H*-fluorene (**4s**)*

Yield: 55 %. Colourless solid. Mp 132.0–132.7°C. R_f 0.33 (hexane/$EtOAc_2$/CH_2Cl_2 50 : 1 : 1). δ_H (400 MHz, $CDCl_3$) 1.31 (t, *J* 7.6, 3H), 3.12 (q, *J* 7.6, 2H), 6.13 (d, *J* 6.1, 1H), 6.83 (dd, *J* 7.2, 7.2, 1H), 7.31 (dd, *J* 6.4, 2.0, 2H), 7.35–7.51 (m, 5H), 7.67 (d, *J* 7.2, 1H), 7.77–7.79 (m, 1H), 7.95–7.97 (m, 1H); δ_C (100 MHz, $CDCl_3$) 11.8, 31.3, 118.9, 119.4, 124.6, 124.7, 126.3, 126.7, 126.9, 127.2, 127.5, 127.8, 128.8, 132.2, 138.1, 138.5, 139.5, 140.4, 143.8, 149.1. ν_{max} (KBr)/cm^{-1} 1445, 785, 766, 733, 704, 602. *m/z* (EI) 284 (4 %, $[M+2]^+$), 283 (33, $[M+1]^+$), 282 (100, M^+). *m/z* (HRMS) Found: 282.1403. Calc. for $C_{22}H_{18}$ (M^+): 282.1409.

*9-[Bis(4-fluorophenyl)methylene]-9*H*-fluorene (**4t**)*

Yield: 36 %. Pale yellow solid. Mp 194.5–195.0°C. R_f 0.44 (hexane/EtOAc 9 : 1). δ_H (400 MHz, $CDCl_3$) 6.68 (d, *J* 8.0, 2H), 6.98 (t, *J* 7.6, 2H), 7.13 (t, *J* 7.6, 4H), 7.27 (t, *J* 7.6, 2H), 7.34 (t, J 6.4, 4H), 7.71 (d, J 7.6, 2H); δ_C (100 MHz, $CDCl_3$) 115.8 (d, J 21.4), 119.3, 124.5, 126.4, 127.8, 131.7 (d, J 7.6), 134.7, 138.3, 138.5 (d, J 3.0), 140.4, 142.7, 162.6 (d, J 246.3); δ_F (282 MHz, $CDCl_3$) −113.3. ν_{max} (KBr)/cm^{-1} 2916, 1890, 1601, 1505, 1445, 1236, 1155, 874, 831, 787, 739, 584, 527. m/z (EI) 368 (7 %, $[M+2]^+$), 367 (43, $[M+1]^+$), 366 (100, M^+), 270 (36). (Found: C 85.17, H 4.55. Anal. Calc. for $C_{26}H_{16}F_2$: C 85.23, H 4.40 %.)

Supplementary Material

^{1}H and ^{13}C NMR spectra of **8m**, **4b**, **4d**, **4e**, **4j**, **4m**, **4n**, **4o**, **4p**, and **4s** are available on the Journal's website.

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[10] In ref. [8d], two examples of the annulation using **7** and 1,1-dibromoalk-1-enes were preliminarily reported.

[11] To the best of our knowledge, this is the first synthesis of dinaphthofulvenes of type **4e**.