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Supporting Information

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Palladium-catalyzed Annulation of *vic*-Bis(pinacolatoboryl)alkenes and -phenanthrenes with 2,2-Dibromobiaryls: Facile Synthesis of Functionalized Phenanthrenes and Dibenzo[*g*,*p*]chrysenes

Masaki Shimizu,* Ikuhiro Nagao, Yosuke Tomioka, and Tamejiro Hiyama

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: m.shimizu@hs2.ecs.kyoto-u.ac.jp

General Information

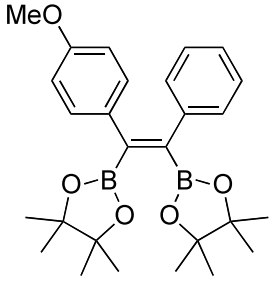
Melting points were determined using a Yanagimoto Micro Point Apparatus. ^{1}H NMR spectra measured on a Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet. ^{13}C NMR spectra were measured on a Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard (δ = 0 ppm) or chloroform (δ = 77.0 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with $CFCl_3$ as an internal standard (δ = 0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization 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.

Preparation of *vic*-diborylalkenes 1

vic-Diborylalkenes **1** were prepared according to the procedure of platinum-catalyzed diborylation of alkynes with bis(pinacolato)diboron, reported by Ishiyama, Miyaura, Suzuki, and coworkers [Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A., *J. Am. Chem. Soc.* **1993**, 115, 11018–11019; Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N., *Organometallics* **1996**, 15, 713–720].

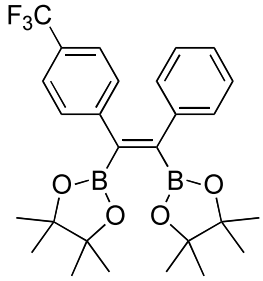
CAS No.
1a: 151416-94-3, **1b**: 178106-74-6, **1f**: 179117-39-6, **1g**: 151416-93-2.

(*Z*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)1-(4-methoxyphenyl)-2-phenylethene (1c)



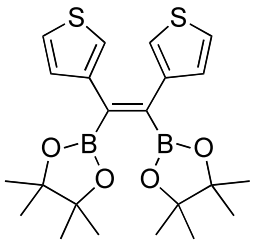
Purification: recrystallization from hexane. Yield: 47%, colorless solid. Mp: 151.9–152.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 12H), 1.34 (s, 12H), 3.71 (s, 3H), 6.61 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 6.8 Hz, 2H), 7.01–7.09 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.97, 25.02, 45.0, 83.9, 84.0, 112.8, 125.5, 127.3, 129.2, 130.4, 133.3, 141.3, 157.4. IR (KBr): ν = 2991, 2977, 1606, 1508, 1389, 1250, 1173, 1149, 1027, 970, 853, 847, 777, 706, 548 cm^{-1}. MS (EI) *m/z*: 464 (0.4, M^+ + 2), 463 (2, M^+ + 1), 462 (6, M^+), 461 (4, M^+ – 1), 460 (4, M^+ – 2), 459 (2, M^+ – 3), 404 (2), 321 (7), 262 (37), 208 (100). HRMS Calcd for $C_{27}H_{36}B_2O_5$: M^+, 462.2749. Found: 462.2760. Anal. Calcd for: $C_{27}H_{36}B_2O_5$: C, 70.16; H, 7.85. Found: C, 70.13; H, 7.59.

(*Z*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-2-(4-(trifluoromethyl)-phenyl)ethene (1d)



Purification: recrystallization from hexane. Yield: 55%, colorless solid. Mp: 188.9–190.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 12H), 1.34 (s, 12H), 6.93 (dd, J = 6.0, 2.0 Hz, 2H), 7.04–7.09 (m, 5H), 7.32 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.96, 25.00, 84.2, 84.3, 124.3 (q, J = 3.8 Hz), 126.1, 127.0 (q, J = 272.2 Hz), 127.5 (q, J = 32.0 Hz), 127.6, 128.9, 129.5, 140.4, 145.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.83 (s, 3F). IR (KBr): ν = 2984, 1612, 1469, 1442, 1391, 1380, 1372, 1358, 1325, 1310, 1270, 1189, 1163, 1149, 1138, 1118, 1109, 1066, 1022, 969, 851, 716, 704 cm^{-1}. MS (EI) *m/z*: 502 (0.1, M^+ + 2), 501 (0.3, M^+ + 1), 500 (1, M^+), 499 (1, M^+ – 1), 498 (0.1, M^+ – 2), 443 (3), 359 (19), 246 (20), 84 (100). HRMS Calcd for $C_{27}H_{33}B_2F_3O_4$: M^+, 500.2517. Found: 500.2523. Anal. Calcd for: $C_{27}H_{33}B_2F_3O_4$: C, 68.84; H, 6.65. Found: C, 64.74; H, 6.72.

(*Z*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di(thiophen-3-yl)ethene (1e)



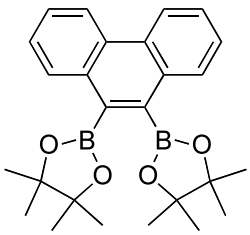
Purification: recrystallization from hexane. Yield: 60%, colorless solid. Mp: 139.3–142.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 24H), 6.60 (dd, *J* = 5.2, 1.6 Hz, 2H), 6.98 (dd, *J* = 3.2, 1.6 Hz, 2H), 7.03 (dd, *J* = 5.2, 3.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 84.0, 122.9, 123.5, 128.7, 141.4. IR (KBr): ν = 2976, 1583, 1390, 1379, 1371, 1338, 1313, 1139, 853, 794, 682, 580 cm^{-1}. MS (EI) *m/z*: 446 (2, M^+ + 2), 445 (5, M^+ + 1), 444 (18, M^+), 443 (9, M^+ – 1), 442 (2, M^+ – 2), 386 (4), 303 (14), 190 (100), 84 (63). HRMS Calcd for $C_{22}H_{30}B_2O_4S_2$: M^+, 444.1772. Found: 444.1774.

Typical procedures for preparation of 9,10-diborylphenanthrenes 2

Method A: A stirred toluene (1 L) solution of **1a** (1.73 g, 4 mmol) and I_2 (1.02 g, 4 mmol) was purged with argon for 30 min. The resulting solution was irradiated with a 400 W high-pressure mercury lamp at room temperature for 12 h. The organic layer was washed with saturated aqueous $Na_2S_2O_3$ solution and saturated aqueous NaCl solution, and then dried over anhydrous $MgSO_4$. Removal of organic solvent by rotary evaporator followed by recrystallization from hexane gave **2a** (1.27 g, 74% yield) as a colorless solid.

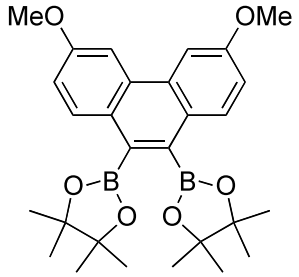
Method B: A stirred toluene (500 mL) solution of **1b** (0.98 g, 2.0 mmol) and I_2 (0.51 g, 2.0 mmol) was purged with argon for 30 min before the addition of propylene oxide (1.40 mL, 20 mmol). The solution was irradiated with a 400 W high-pressure mercury lamp at room temperature for 6 h. The organic layer was washed with an aqueous $Na_2S_2O_3$ solution and saturated aqueous NaCl solution, and then dried over anhydrous $MgSO_4$. Removal of organic solvent by rotary evaporator followed by recrystallization from diethyl ether gave **2b** (0.95 g, 97% yield) as a colorless solid.

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene (2a)



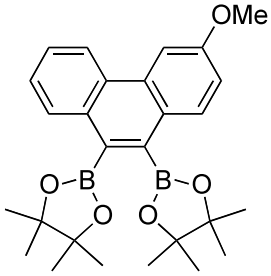
Preparation: method A, purification: recrystallization from hexane. Yield: 72%, colorless solid. Mp: 248.3–249.8 °C. TLC: R_f 0.50 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 24H), 7.52–7.64 (m, 4H), 8.42 (d, *J* = 7.6 Hz, 2H), 8.66 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.3, 84.3, 116.3, 122.3, 126.1, 126.5, 128.7, 130.2, 133.3. IR (KBr): ν = 2980, 2940, 1632, 1456, 1382, 1376, 1352, 1324, 1282, 1264, 1250, 1190, 1170, 1148, 1112, 976, 878, 844, 762, 730, 690, 674, 530 cm^{-1}. MS (EI) *m/z*: 432 (7, M^+ + 2), 431 (41, M^+ + 1), 430 (100, M^+), 415 (1), 373 (49), 289 (88), 288 (70). HRMS Calcd for $C_{26}H_{32}B_2O_4$: M^+ 430.2487. Found: 430.2475.

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethoxyphenanthrene (2b)



Preparation: method B, purification: recrystallization from Et_2O. Yield: 97%, colorless solid. Mp: 234.7–241.7 °C. TLC: R_f 0.33 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 24H), 4.01 (s, 6H), 7.20 (dd, J = 9.2, 2.4 Hz, 2H), 7.93 (s, 2H), 8.38 (d, J = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4, 55.4, 84.2, 104.1, 115.8, 128.7, 130.5, 131.4, 157.8. IR (KBr): ν = 2978, 2936, 1616, 1519, 1507, 1469, 1456, 1445, 1430, 1390, 1378, 1340, 1313, 1286, 1268, 1259, 1215, 1187, 1273, 1145, 1113, 1054, 1041, 1009, 969, 868, 846, 835, 804, 795 cm^{-1}. MS (EI) *m/z*: 492 (7, M^+ + 2), 491 (35, M^+ + 1), 490 (100, M^+), 475 (2), 432 (5), 349 (26), 290 (17). Anal. Calcd for: $C_{28}H_{36}B_2O_6$: C, 68.60; H, 7.40. Found: C, 68.43; H, 7.43.

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-methoxyphenanthrene (2c)



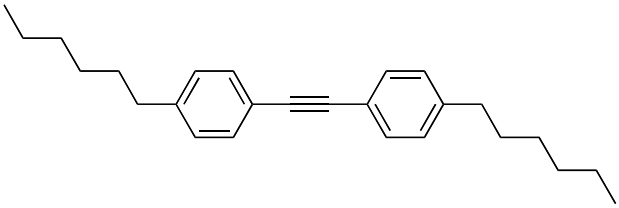
Preparation: method B, purification: recrystallization from Et_2O. Yield: 65%, colorless solid. Mp: 182.6–186.6 °C. TLC: R_f 0.44 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 12H), 1.52 (s, 12H), 4.01 (s, 3H), 7.21 (dd, J = 9.2, 2.8 Hz, 1H), 7.53–7.62 (m, 2H), 8.03 (d, J = 2.8 Hz, 1H), 8.37 (d, J = 9.2 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.40, 25.45, 55.4, 84.2, 84.3, 103.7, 116.1, 122.4, 126.1, 126.2, 128.3, 128.9, 129.9, 130.4, 132.0, 133.9, 158.1. IR (KBr): ν = 3443, 2979, 1615, 1523, 1501, 1450, 1419, 1391, 1379, 1370, 1346, 1317, 1285, 1267, 1256, 1243, 1222, 1185, 1166, 1135, 1106, 1038, 968, 858, 848, 842, 763 cm^{-1}. MS (EI) *m/z*: 462 (17, M^+ + 2), 461 (56, M^+ + 1), 460 (100, M^+), 459 (74, M^+ – 1), 458 (19, M^+ – 2), 403 (28), 402 (24), 320 (30), 319 (82), 318 (54). HRMS Calcd for $C_{27}H_{34}B_2O_5$: M^+, 460.2592. Found: 460.2585. Anal. Calcd for: $C_{27}H_{34}B_2O_5$: C, 70.47; H, 7.45. Found: C, 70.42; H, 7.45.

1,2-Bis(4-hexylphenyl)ethyne

Preparation of 1,2-bis(4-hexylphenyl)ethyne was achieved according to the procedure described in the following literature: A. Orita, K. Miyamoto, M. Nakashima, F. Ye, J. Otera, *Adv. Synth. Catal.* **2004**, *346*, 767–776.

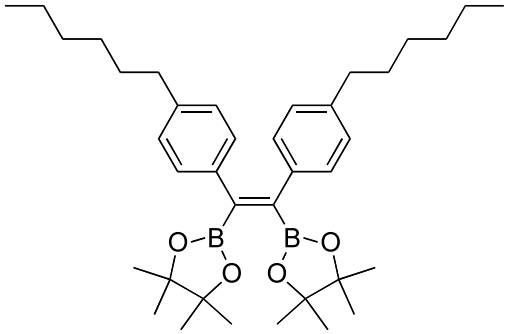
A solution of 1-bromo-4-hexylbenzene (2.68 g, 11.1 mmol), 1-ethynyl-4-hexylbenzene (2.07 g, 11.1 mmol), $Pd(PPh_3)_4$ (0.64 g, 0.6 mmol), CuI (0.11 g, 0.6 mmol), and diisopropylamine (22 mL) in toluene (67 mL) was stirred at room temperature for 12 h. After filtration, the filtrate was washed with saturated aqueous NH_4Cl solution (60 mL). The aqueous solution was extracted with AcOEt (60 mL x 3). The combined organic layer was washed with saturated aqueous NaCl

solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 10:3) to give 1,2-bis(4-hexylphenyl)ethyne (1.30 g, 81% yield) as colorless solid.



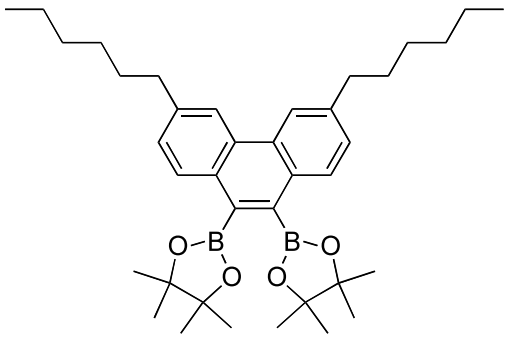
Mp: 30.0–32.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 6.4 Hz, 6H), 1.30–1.42 (m, 12H), 1.61–1.70 (m, 4H), 2.64 (t, J = 7.8 Hz, 4H), 7.18 (d, J = 8.4 Hz, 4H), 7.47 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 29.0, 31.3, 31.8, 36.0, 88.9, 120.5, 128.3, 131.3, 143.0. IR (KBr): ν = 2956, 2928, 2855, 1519, 1466, 1457, 829, 818 cm^{-1}. MS (EI) *m/z*: 348 (4, M^+ + 2), 347 (28, M^+ + 1), 346 (100, M^+), 275 (76), 204 (27). HRMS Calcd for $C_{26}H_{34}$: M^+, 346.2661. Found: 346.2653.

(Z)-1,2-Bis(4-hexylphenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene



Purification: GPC. Yield: 48%, colorless solid. Mp: 82.7–83.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 6.8 Hz, 6H), 1.22–1.32 (m, 12H), 1.33 (s, 24H), 1.48–1.57 (m, 4H), 2.47 (t, J = 7.6 Hz, 4H), 6.83 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 25.0, 29.0, 31.2, 31.8, 35.7, 83.9, 125.3, 129.0, 138.4, 139.9. IR (KBr): ν = 2979, 2956, 2928, 2856, 1506, 1466, 1390, 1378, 1339, 1308, 1272, 1228, 1214, 1178, 1167, 1140, 1109, 1027, 969, 850, 825, 695 cm^{-1}. MS (EI) *m/z*: 602 (1, M^+ + 2), 601 (2, M^+ + 1), 600 (5, M^+), 599 (2, M^+ – 1), 598 (2, M^+ – 2), 371 (6), 346 (100). HRMS Calcd for $C_{38}H_{58}B_2O_4$: M^+, 600.4521. Found: *m/z* 600.4537. Anal. Calcd for: $C_{38}H_{58}B_2O_4$: C, 76.01; H, 9.74. Found: C, 75.95; H, 9.97.

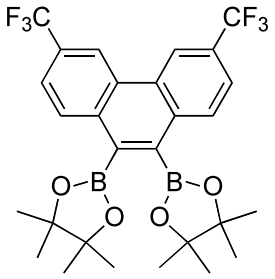
9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dihexylphenanthrene (2d)



Preparation: method A, purification: GPC. Yield: 66%, yellow solid. Mp: 79.3–83.4 °C. TLC: R_f 0.63 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J = 7.2 Hz, 6H), 1.30–1.46

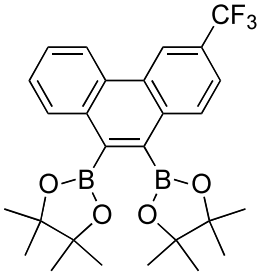
(m, 12H), 1.51 (s, 24H), 1.70–1.80 (m, 4H), 2.85 (t, J = 8.0 Hz, 4H), 7.40 (d, J = 8.4 Hz, 2H), 8.33 (d, J = 8.4 Hz, 2H), 8.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.8, 25.4, 29.2, 31.8, 31.9, 36.6, 84.1, 121.5, 127.0, 128.6, 130.2, 131.8, 140.9. IR (KBr): ν = 3393, 2927, 2856, 1616, 1516, 1444, 1433, 1390, 1370, 1340, 1313, 1283, 1266, 1255, 1213, 1182, 1166, 1146, 1116, 968, 850, 841, 834, 820, 808, 704, 669 cm^{-1}. MS (FAB) *m/z*: 600 (24, M^+ + 2), 599 (47, M^+ + 1), 598 (100, M^+), 597 (72, M^+ – 1), 596 (30, M^+ – 2), 583 (6), 527 (32), 499 (35), 457 (13), 417 (17), 415 (15). Anal. Calcd for: $C_{38}H_{56}B_2O_4$: C, 76.26; H, 9.43. Found: C, 76.08; H, 9.63.

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-bis(trifluoromethyl)phenanthrene (2e)



Preparation: method A, purification: recrystallization from hexane. Yield: 62%, colorless solid. Mp: 202.2–203.7°C. TLC: R_f 0.35 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 24H), 7.83 (d, J = 8.8 Hz, 2H), 8.62 (d, J = 8.8 Hz, 2H), 8.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4, 84.9, 119.8 (q, J = 4.5 Hz), 123.0 (q, J = 3.0 Hz), 124.3 (q, J = 270.9 Hz), 128.8 (q, J = 32.0 Hz), 129.6, 130.0, 135.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.5(s). IR (KBr): ν = 2994, 1521, 1473, 1436, 1394, 1381, 1373, 1362, 1348, 1303, 1281, 1265, 1255, 1226, 1210, 1181, 1122, 1085, 1035, 1012, 969, 926, 895, 849, 863, 831, 819, 749, 730, 702, 686, 643, 637 cm^{-1}. MS (EI) *m/z*: 568 (1, M^+ + 2), 567 (6, M^+ + 1), 566 (20, M^+), 548 (2), 547 (5), 510 (3), 509 (10), 427 (5), 426 (21), 425 (100), 409 (8). Anal. Calcd for: $C_{28}H_{30}B_2F_6O_4$: C, 59.40; H, 5.34. Found: C, 5.92; H, 5.37.

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)phenanthrene (2f)

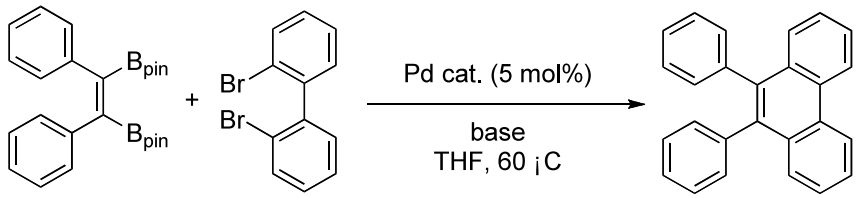


Preparation: method A, purification: recrystallization from hexane. Yield: 74%, colorless solid. Mp: 183.6–185.2 °C. TLC: R_f 0.53 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (s, 12H), 1.52 (s, 12H), 7.60–7.71 (m, 2H), 7.76 (d, J = 8.8 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.64 (d, J = 8.8 Hz, 1H), 8.68 (d, J = 8.8 Hz, 1H), 8.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.2, 25.5, 84.6 (2C), 119.8 (q, J = 3.8 Hz), 122.1 (q, J = 3.8 Hz), 122.4, 124.5 (q, J = 269.9 Hz), 127.0, 127.3, 127.9 (q, J = 31.2 Hz), 129.0, 129.7, 129.8, 130.1, 133.6, 135.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.4 (s). IR (KBr): ν = 2978, 2933, 1525, 1472, 1454, 1392, 1352, 1303, 1285, 1265, 1254, 1232, 1215, 1191, 1178, 1119, 1080, 1020, 1012, 996, 968, 918, 896, 855, 843, 831, 763, 698, 687, 673, 652 cm^{-1}. MS (EI) *m/z*: 500 (4, M^+ + 2), 499 (25, M^+ + 1), 498 (87, M^+), 479 (7), 441 (37), 358 (41), 357 (100), 356 (80). Anal. Calcd for: $C_{27}H_{31}B_2F_3O_4$: C, 65.10; H, 6.27. Found: C, 65.06; H, 6.20.

Cross-coupling reaction of 1,2-bis(pinacolatoboryl)stilbene (1a) with 2,2′-dibromobiphyl (3a)

Representative results on screening of the conditions for the reaction of **1a** with **3a** were summarized in the following Table.

Table. Double cross-coupling reaction of **1a** with **3a**.[a]



1a (1.2 equiv) **3a** **4aa**

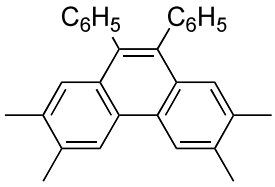
Entry	Pd cat.	Base (equiv)	Yield (%)[b]
1[c]	$PdCl_2$(dppf)	3 M KOH (6)	(13)
2	$PdCl_2$(dppf)	KOAc (6)	0
3	$PdCl_2$(dppf)	CsF (6)	4
4	$PdCl_2$(dppf)	K_2CO_3 (6)	10
5	$PdCl_2$(dppf)	K_2CO_3 (6)/H_2O (6)	19
6	$PdCl_2$(dppf)	K_2CO_3 (6)/H_2O (50)	40
7	$PdCl_2$(dppf)	K_2CO_3 (6)/H_2O (100)	31
8	$Pd(P^tBu_3)_2$	K_2CO_3 (6)/H_2O (50)	42
9	$Pd(OAc)_2/PCy_3$	K_2CO_3 (6)/H_2O (50)	40
10	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	72 (80)
11[d]	$Pd(PPh_3)_4$	K_2CO_3 (6)/H_2O (50)	(82)

[a] A THF solution (1 mL) of **1a** (0.06 mmol), **3a** (0.05 mmol), Pd cat. (2.5 mmol), and base (0.3 mmol) was heated at 60 °C for 24 h. [b] Yield calculated from GC analysis using *n*-dodecane as an internal standard. The value in parentheses is isolated yield. [c] The reaction was effected at room temperature. [d] The coupling was effected in gram-scale. Reaction conditions: **1a** (2.16 g, 6 mmol), **3a** (1.56 g, 5 mmol), $Pd(PPh_3)_4$ (0.30 g, 0.25 mmol), and K_2CO_3 (4.10 g, 30 mmol), H_2O (4.5 mL, 250 mmol), THF (100 mL), 60 °C, 48 h; **4aa** (1.35 g, 82% yield).

General procedure for double cross-coupling reaction of 1 with 2,2′-dibromobiaryls

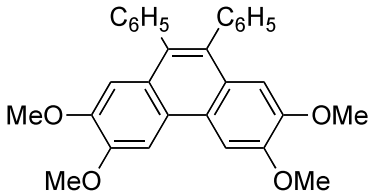
To a Schlenk tube (80 mL) were added $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), **1a** (0.52 g, 1.2 mmol), and **3a** (0.31 g, 1.0 mmol) and K_2CO_3 (0.83 g, 6.0 mmol). The tube was then capped with a rubber septum, evacuated, and purged with argon. The evacuation–purge operation was repeated twice. THF (20 mL) and H_2O (0.90 mL, 50 mmol) was added to the mixture at room temperature. After stirred at room temperature for 5 min, the solution was heated at 60 °C for 48 h. The mixture was allowed to cool to room temperature, and diluted with EtOAc (20 mL). The resulting solution was washed with saturated aqueous NH_4Cl solution (20 mL) and the aqueous layer was extracted with EtOAc (40 mL x 3). The combined organic layer was washed with saturated aqueous NaCl solution (20 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. Recrystallization of the crude product from MeOH gave **4aa** (0.26 g, 80% yield, CAS No. 602-15-3) as a colorless solid.

2,3,6,7-Tetramethyl-9,10-diphenylphenanthrene (4ab)



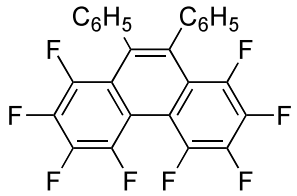
Purification: recrystallization from MeOH. Yield: 85%, colorless solid. Mp: 224.8–226.1 °C. TLC: R_f 0.18 (hexane/EtOAc 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 6H), 2.55 (s, 6H), 7.12–7.26 (m, 12H), 8.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 20.6, 122.5, 126.0, 127.3, 127.6, 127.9, 129.9, 131.0, 135.1, 135.2, 135.7, 139.9. IR (KBr): ν = 3046, 2914, 2850, 1488, 1448, 1438, 1023, 865, 759, 722, 700, 635, 622, 436 cm^{-1}. MS (EI) *m/z*: 388 (6, M^+ + 2), 387 (33, M^+ + 1), 386 (100, M^+), 371 (6), 356 (11). Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.01; H, 6.72.

2,3,6,7-Tetramethoxy-9,10-diphenylphenanthrene (4ac)



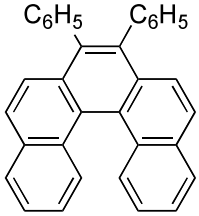
Purification: silica gel column chromatography (hexane/AcOEt 2:1). Yield: 82%, colorless solid. Mp: 229.6–230.5 °C. TLC: R_f 0.17 (hexane/AcOEt 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 6H), 4.16 (s, 6H), 6.91 (s, 2H), 7.14–7.26 (m, 10H), 7.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 56.2, 102.7, 107.9, 124.0, 126.1, 126.2, 127.4, 130.9, 134.8, 139.8, 148.3, 148.9. IR (KBr): ν = 1618, 1529, 1506, 1494, 1474, 1463, 1440, 1418, 1259, 1197, 1168, 1104, 1047, 1031, 1005, 998, 854, 725, 703, 627, 592 cm^{-1}. MS (EI) *m/z*: 452 (6, M^+ + 2), 451 (32, M^+ + 1), 450 (100, M^+), 348 (1), 436 (6), 403 (6). HRMS Calcd for $C_{30}H_{26}O_4$: M^+, 450.1831. Found: 450.1839.

1,2,3,4,5,6,7,8-Octafluoro-9,10-diphenylphenanthrene (4ad)



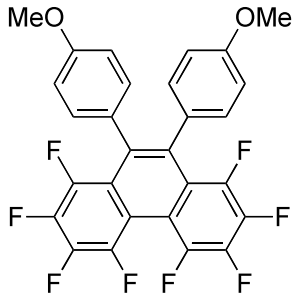
Purification: silica gel column chromatography (hexane/AcOEt 40:1). Yield: 65%, colorless solid. Mp: 175.2–176.3 °C. TLC: R_f 0.22 (hexane/AcOEt 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.0 (dd, J = 6.4, 3.2 Hz, 4H), 7.1 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.5, 118.1, 126.8, 127.1, 129.28, 129.31, 134.9, 138.04, 138.08, 140.0 (dm, J = 251.7 Hz), 140.6 (dt, J = 253.2, 15.3 Hz), 143.7 (dd, J = 254.6, 10.7 Hz), 144.1 (dm, J = 256.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –155.3 ~ –155.7 (m, 2F), –154.2 ~ –154.6 (m, 2F), –134.2 ~ –134.6 (m, 2F), –129.9 (s, 2F). IR (KBr): ν =2831, 1639, 1611, 1512, 1483, 1468, 1348, 1290, 1279, 1242, 1178, 1112, 1087, 1056, 1036, 1013, 967, 845, 836, 845, 808, 780, 737, 716, 653, 562, 552 cm^{-1}. MS (EI) *m/z*: 476 (4, M^+ + 2), 475 (28, M^+ + 1), 474 (100, M^+), 454 (22), 434 (25), 397 (32), 277 (16). Anal. Calcd for $C_{26}H_{10}F_8$: C, 65.83; H, 2.12. Found: C, 65.94; H, 2.08.

3,4-Diphenyldibenzo[*c*,*g*]phenanthrene (4ae)



Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1.5). Yield: 32%, colorless solid. Mp: 318.0–318.9 °C. TLC: R_f 0.33 (hexane/AcOEt/CH_2Cl_2 40:1:1.5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12–7.16 (m, 2H), 7.21–7.32 (m, 10H), 7.52 (dd, J = 6.8, 6.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 6.8 Hz, 2H), 8.47 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.5, 124.6, 126.2, 126.4, 126.5, 127.0, 127.4, 127.5 (2C), 129.4, 130.5, 130.6, 130.9, 131.5, 131.9, 137.7, 139.2. IR (KBr): ν = 3053, 3018, 1601, 1559, 1500, 1440, 1387, 1262, 1154, 1069, 1026, 861, 836, 817, 753, 733, 704, 666, 620, 528 cm^{-1}. MS (EI) *m/z*: 432 (7, M^+ + 2), 431 (37, M^+ + 1), 430 (100, M^+), 353 (60), 276 (7). HRMS Calcd for $C_{34}H_{22}$: M^+, 430.1722. Found: 430.1714.

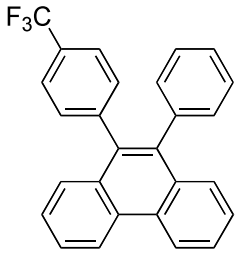
9,10-Bis(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octafluorophenanthrene (4bd)



Purification: recrystallization from MeOH. Yield: 85%, colorless solid. Mp: 150.7–151.8 °C. TLC: R_f 0.54 (hexane/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 6H), 6.70 (d, J = 8.4 Hz, 4H), 6.88 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 111.4, 112.7, 118.6, 130.28,

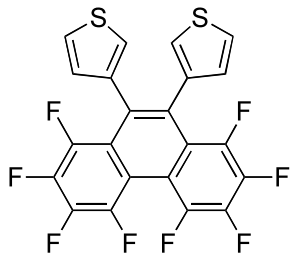
130.32, 130.4, 130.5, 135.1, 139.9 (d, J = 260.8 Hz), 140.6 (d, J = 250.9 Hz), 143.8 (d, J = 254.6 Hz), 144.1 (d, J = 246.3 Hz), 158.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ –155.9 ~ –155.7 (m, 2F), –154.7 ~ –154.5 (m, 2F), –134.7 ~ –134.6 (m, 2F), –130.2 ~ –130.1 (m, 2F). IR (KBr): ν = 2831, 1639, 1611, 1511, 1463, 1348, 1290, 1246, 1178, 1112, 1086, 1036, 966, 845, 835, 807, 780, 737, 716, 653, 562 cm^{-1}. MS (EI) *m/z*: 536 (5, M^+ + 2), 535 (30, M^+ + 1), 534 (100, M^+), 514 (8), 428 (7), 267 (6). Anal. Calcd for $C_{24}H_{14}F_8O_2$: C, 62.93; H, 2.64. Found: C, 62.63; H, 2.64.

9-Phenyl-10-[4-(trifluoromethyl)phenyl]phenanthrene (4da)



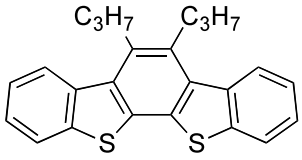
Purification: recrystallization from MeOH. Yield: 77%, colorless solid. Mp: 116.3–116.9 °C. TLC: R_f 0.31 (hexane/EtOAc 40:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.15 (m, 2H), 7.22–7.34 (m, 5H), 7.46 (d, J = 8.2 Hz, 1H), 7.49–7.56 (m, 4H), 7.58 (d, J = 8.2 Hz, 1H), 7.69 (dd, J = 7.0, 1.3 Hz, 1H), 7.71 (dd, J = 7.0, 1.3 Hz, 1H), 8.83 (d, J = 8.2 Hz, 1H), 8.84 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.4, 122.5, 124.1 (q, J = 269.9 Hz), 124.5 (q, J = 3.1 Hz), 126.5, 126.65, 126.68, 126.7 (2C), 127.2, 127.7, 127.8, 128.5 (q, J = 32.8 Hz), 129.9, 130.0, 130.7, 131.1, 131.3, 131.5, 135.5, 137.3, 138.8, 143.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.9 (s, 3F). IR (KBr): ν = 1617, 1488, 1448, 1420, 1406, 1322, 1162, 1119, 1107, 1067, 1020, 859, 824, 766, 744, 727, 704, 632 cm^{-1}. MS (EI) *m/z*: 400 (4, M^+ + 2), 399 (29, M^+ + 1), 398 (100, M^+), 326 (13), 252 (21). HRMS Calcd for $C_{27}H_{17}F_3$: M^+, 398.1282. Found: 398.1282. Anal. Calcd for $C_{27}H_{17}F_3$: C, 81.39; H, 4.30. Found: C, 81.31; H, 4.55.

1,2,3,4,5,6,7,8-Octafluoro-9,10-di(thiophen-3-yl)phenanthrene (4ed)



Purification: silica gel column chromatography (hexane/EtOAc/CH_2Cl_2 30:1:1). Yield: 90%, colorless solid. Mp: 162.8–163.0 °C. TLC: R_f 0.28 (hexane/EtOAc/CH_2Cl_2 30:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (d, J = 4.8 Hz, 2H), 6.84 (d, J = 2.8 Hz, 2H), 7.19 (dd, J = 4.8, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.5, 118.2, 123.4, 124.2, 128.8, 131.2, 137.3, 140.1 (dm, J = 253.2 Hz), 140.6 (dt, J = 252.4, 15.2 Hz), 143.6 (d, J = 154.6, 10.6 Hz), 144.1 (dd, J = 153.9, 8.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –155.2 ~ –155.3 (m, 2F), –154.4 ~ –154.2 (m, 2F), –136.34 ~ –136.27 (m, 2F), –129.95 ~ –129.87 (m, 2F). IR (KBr): ν = 1639, 1594, 1513, 1469, 1444, 1401, 1341, 1279, 1189, 1108, 1085, 1056, 987, 951, 853, 825, 799, 786, 751, 673 cm^{-1}. MS (EI) *m/z*: 489 (3, M^+ + 3), 488 (13, M^+ + 2), 487 (27, M^+ + 1), 486 (100, M^+), 453 (18), 421 (19), 403 (6). Anal. Calcd for $C_{22}H_6F_8S_2$: C, 54.32; H, 1.24. Found: C, 54.05; H, 1.38.

5,6-Diphenylbenzo[2,1-*b*:3,4-*b*']bis[1]benzothiophene (4gg)



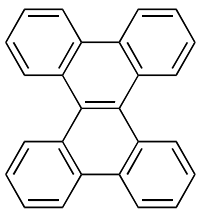
Purification: silica gel column chromatography (hexane/EtOAc/CH_2Cl_2 30:1:1). Yield: 57%, colorless solid. Mp: 177.4–179.0 °C. TLC: R_f 0.33 (hexane/EtOAc/CH_2Cl_2 30:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (t, *J* = 7.2 Hz, 6H), 1.87 (dq, *J* = 8.4, 7.2 Hz, 4H), 3.39 (t, *J* = 8.4 Hz, 4H), 7.44–7.56 (m, 4H), 7.94 (d, *J* = 7.6 Hz, 2H), 8.32 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 23.6, 31.7, 123.1, 124.6, 124.9, 125.6, 131.5, 132.4, 134.6, 136.3, 139.6. IR (KBr): ν = 3101, 3064, 2952, 2927, 2896, 2867, 1526, 1467, 1429, 1395, 1289, 1232, 1221, 1083, 977, 761, 727, 663 cm^{-1}. MS (EI) *m/z*: 377 (4, M^+ + 3), 376 (17, M^+ + 2), 375 (36, M^+ + 1), 374 (100, M^+), 373 (2, M^+ – 1), 372 (3, M^+ – 2), 345 (65). HRMS Calcd for $C_{24}H_{22}S_2$: M^+, 374.1163. Found: 374.1158.

CAS No.
4ac: 96970-13-7, **4ae**: 138092-94-1, **4af**: 182346-90-3, **4ca**: 938082-96-3, **4fa**: 68684-64-0, **4ga**: 19793-67-0.

General procedure for double cross-coupling reaction of 2 with 2,2′-dibromobiaryls

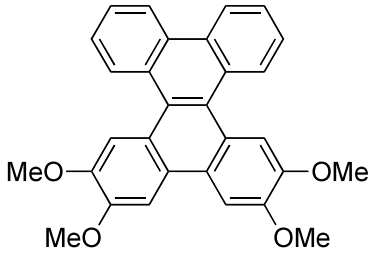
To a vial tube (5 mL) were added $Pd(PPh_3)_4$ (2.9 mg, 2.5 μmol), **2a** (26 mg, 0.060 mmol), **3a** (16 mg, 0.050 mmol). The tube was then capped with a rubber septum, evacuated for 5 min and purged with argon. The evacuation–purge operation was repeated twice. THF (1 mL) and 3 M aq. K_3PO_4 (0.10 mL, 0.30 mmol) was added to the mixture at room temperature. After stirred at room temperature for 5 min, the solution was heated at 60 °C for 48 h. The reaction mixture was diluted with dichloromethane (10 mL) and filtered through a pad of Celite. The filtrate was concentrated with rotary evaporator. The crude product was purified by column chromatography on silica gel (eluent: hexane/EtOAc/CH_2Cl_2 40:1:1) followed by preparative GPC to give **5aa** (16 mg, >99% yield) as a colorless solid.

Dibenzo[*g*,*p*]chrysene (5aa)



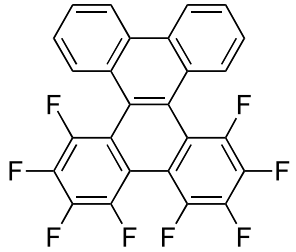
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: >99%, colorless solid. Mp: 216.8–219.3 °C. TLC: R_f 0.25 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.72 (m, 8H), 8.68–8.74 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.5, 126.4 (2C), 127.3, 128.7, 129.1, 130.7. IR (KBr): ν = 3025, 2852, 2501, 1485, 1449, 1426, 761, 749, 743, 724 cm^{-1}. MS (EI) *m/z*: 329 (36, M^+ + 1), 328 (100, M^+), 300 (5), 162 (14). Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 95.21; H, 5.20.

2,3,6,7-Tetramethoxydibenzo[*g*,*p*]chrysene (5ac)



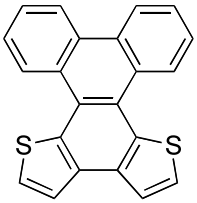
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 30:15:1). Yield: 54%, colorless solid. Mp: 117.4–122.4 °C. TLC: R_f 0.20 (hexane/AcOEt/CH_2Cl_2 30:15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (s, 6H), 4.19 (s, 6H), 7.60–7.70 (m, 4H), 7.89 (s, 2H), 8.20 (s, 2H), 8.70 (d, J = 7.6 Hz, 2H), 8.75 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.1, 56.2, 104.1, 110.1, 123.1, 123.7, 125.0, 126.1, 126.2, 126.3, 127.8, 129.4, 130.3, 148.1, 148.8. IR (KBr): ν = 3420, 2997, 2933, 2904, 2831, 1616, 1511, 1489, 1465, 1456, 1439, 1429, 1411, 1386, 1256, 1212, 1198, 1170, 1117, 1093, 1047, 794, 755, 730 cm^{-1}. MS (EI) *m/z*: 450 (11, M^+ + 2), 449 (60, M^+ + 1), 448 (100, M^+), 418 (3), 402 (10), 374 (10). HRMS Calcd for $C_{30}H_{24}O_4$: M^+, 448.1675. Found: 448.1671.

1,2,3,4,5,6,7,8-Octafluorodibenzo[*g*,*p*]chrysene (5ad)



Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 76%, colorless solid. Mp: 302.4–310.6 °C. TLC: R_f 0.33 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.68 (m, 2H), 7.72–7.78 (m, 2H), 7.90–7.98 (m, 2H), 8.61 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.5–110.8 (m), 116.2 (d, J = 13.8 Hz), 122.9, 126.11, 126.14, 126.6, 127.8, 128.2 (d, J = 3.8 Hz), 128.6, 128.7, 130.4, 139.7 (dm, J = 262.3 Hz), 141.0 (dm, J = 250.8 Hz), 142.7 (dm, J = 255.5 Hz), 145.0 (dm, J = 258.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –155.6 ~ –155.4 (m, 2F), –152.9 ~ –152.6 (m, 2F), –129.8 (bs, 2F), –127.5 ~ –127.3 (m, 2F). IR (KBr): ν = 1638, 1516, 1490, 1473, 1408, 1357, 1120, 1095, 1074, 966, 8002, 765, 758, 745, 734, 722, 699 cm^{-1}. MS (EI) *m/z*: 474 (6, M^+ + 2), 473 (411, M^+ + 1), 472 (100, M^+), 452 (52), 432 (20). HRMS Calcd for $C_{26}H_8F_8$: M^+, 472.0498. Found: 472.0493.

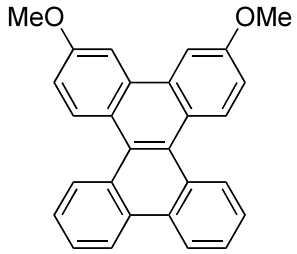
Dithieno[2,3-*a*:3',2'-*c*]triphenylene (5af)



Purification: GPC. Yield: 88%, colorless solid. Mp: 266.3–269.8 °C. TLC: R_f 0.30 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.84 (m, 6H), 7.79 (d, J =

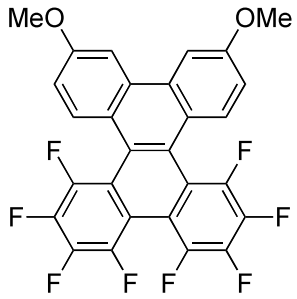
5.6 Hz, 2H), 8.81 (d, *J* = 8.0 Hz, 2H), 9.42 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.2, 123.2, 124.8, 126.4, 126.9, 127.0, 127.1, 129.6, 129.8, 135.1. IR (KBr): ν = 1498, 1441, 1214, 1104, 848, 755, 722, 555 cm^{-1}. MS (EI) *m/z*: 342 (12, $M^+ + 2$), 341 (26, $M^+ + 1$), 340 (100, M^+), 295 (12). Anal. Calcd for: $C_{22}H_{12}S_2$: C, 77.61; H, 3.55. Found: C, 77.74; H, 3.53.

3,6-Dimethoxydibenzo[*g*,*p*]chrysene (5ba)



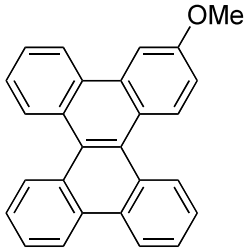
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 4:1:1). Yield: 64%, colorless solid. Mp: 105.8–108.8°C. TLC: R_f 0.50 (hexane/AcOEt/CH_2Cl_2 4:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (s, 6H), 7.27 (dd, *J* = 9.8, 2.4 Hz, 2H), 7.58–7.68 (m, 4H), 8.02 (d, *J* = 2.8 Hz, 2H), 8.61–8.72 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 106.0, 114.9, 123.3, 123.7, 125.7, 125.8, 126.2, 128.4, 129.0, 130.2, 130.3, 131.7, 157.8. IR (KBr): ν = 2904, 2832, 1613, 1575, 1541, 1508, 1488, 1462, 1427, 1384, 1286, 1266, 1230, 1207, 1177, 1145, 1113, 1197, 1042, 1025, 940, 840, 815, 791, 760, 731, 583, 567 cm^{-1}. MS (EI) *m/z*: 390 (9, $M^+ + 2$), 389 (57, $M^+ + 1$), 388 (100, M^+), 373 (32), 345 (18), 302 (25). HRMS Calcd for $C_{28}H_{20}O_2$: M^+, 388.1463. Found: 388.1464.

1,2,3,4,5,6,7,8-Octafluoro-11,14-dimethoxydibenzo[*g*,*p*]chrysene (5bd)



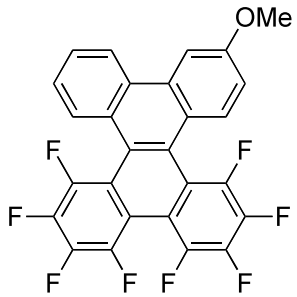
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 8:1:1). Yield: 94%, colorless solid. Mp: 301.1–301.5°C. TLC: R_f 0.50 (hexane/AcOEt/CH_2Cl_2 4:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.07 (s, 6H), 7.24–7.28 (m, 2H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.895 (s, 1H), 7.901 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.0, 105.5, 110.6, 115.40, 115.42, 116.4 (d, *J* = 8.4 Hz), 123.3 (d, *J* = 3.9 Hz), 124.9, 130.7, 130.8, 131.9, 139.5 (dm, *J* = 251.6 Hz), 141.1 (dm, *J* = 246.3 Hz), 142.8 (dm, *J* = 246.3 Hz), 145.0 (dm, *J* = 226.0 Hz), 159.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ –156.6 (quintet, *J* = 11.3 Hz, 2F), –153.2 (t, *J* = 22.6 Hz, 2F), –130.1 (bs, 2F), –128.9 ~ –128.6 (m, 2F). IR (KBr): ν = 3443, 1638, 1616, 1562, 1515, 1488, 1471, 1430, 1406, 1358, 1293, 1278, 1240, 1204, 1183, 1177, 1074, 1054, 1032, 1025, 968, 877, 821, 720, 694 cm^{-1}. MS (EI) *m/z*: 534 (6, $M^+ + 2$), 533 (36, $M^+ + 1$), 532 (100, M^+), 517 (18), 489 (16), 446 (16), 426 (15). HRMS Calcd for $C_{28}H_{12}F_8O_2$: M^+, 532.0710. Found: 532.0714. Anal. Calcd for: $C_{28}H_{12}F_8O_2$: C, 63.17; H, 2.27. Found: C, 63.00; H, 2.55.

3-Methoxydibenzo[*g*,*p*]chrysene (5ca)



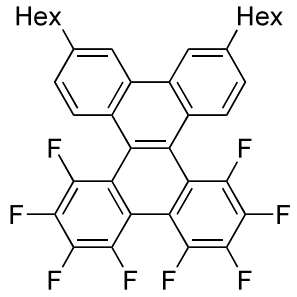
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:5:1). Yield: 61%, colorless solid. Mp: 108.6–112.6 °C. TLC: R_f 0.35 (hexane/AcOEt/CH_2Cl_2 40:5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (s, 3H), 7.27 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.60–7.70 (m, 6H), 8.10 (d, *J* = 2.8 Hz, 1H), 8.60–8.72 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 105.7, 115.4, 123.4, 123.5, 125.7, 126.0, 126.2, 126.3, 126.4, 126.5, 127.5, 128.5, 128.8, 129.0, 129.2, 129.4, 130.27, 131.31, 130.4, 130.7, 132.3, 158.1. IR (KBr): ν = 2831, 1613, 1540, 1502, 1486, 1448, 1426, 1384, 1353, 1286, 1262, 1232, 1206, 1176, 1145, 1097, 1046, 1018, 909, 859, 822, 792, 761, 729, 713, 664, 617, 568 cm^{-1}. MS (EI) *m/z*: 359 (30, M^+ + 1), 358 (100, M^+), 313 (28). HRMS Calcd for $C_{27}H_{18}O$: M^+, 358.1358. Found: 358.1353.

1,2,3,4,5,6,7,8-Octafluoro-11-methoxydibenzo[*g*,*p*]chrysene (5cd)



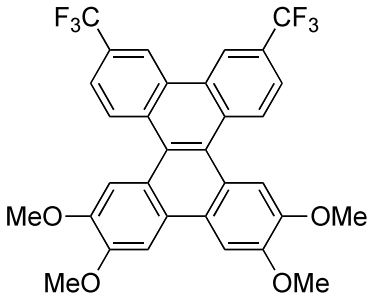
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 4:1:1). Yield: 80 %, colorless solid. Mp: 259.0–259.7 °C. TLC: R_f 0.40 (hexane/AcOEt/CH_2Cl_2 4:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (s, 3H), 7.26 (m, 1H), 7.61–7.66 (m, 1H), 7.69–7.75 (m, 1H), 7.82–7.96 (m, 2H), 7.98 (d, *J* = 2.4 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 104.9, 110.3, 110.7, 115.4, 116.0 (d, *J* = 8.4 Hz), 116.2 (d, *J* = 8.4 Hz), 122.7 (d, *J* = 4.6 Hz), 122.9, 124.5, 126.10, 126.11, 126.6, 127.5, 128.5 (d, *J* = 3.8 Hz), 128.7, 128.8, 129.9, 130.3, 130.4, 132.1, 139.5 (dm, *J* = 251.6 Hz), 140.8 (dm, *J* = 251.6 Hz), 142.6 (dm, *J* = 251.6 Hz), 144.9 (dm, *J* = 251.6 Hz), 159.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ –156.6 ~ –156.3 (m, 1F), –155.8 ~ –155.6 (m, 1F), –153.1 ~ –152.8 (m, 2F), –130.0 (bs, 2F), –128.4 ~ –128.2 (m, 1F), –128.0 ~ –128.8 (m, 1F). IR (KBr): ν = 1638, 1615, 1514, 1469, 1438, 1406, 1358, 1340, 1293, 1276, 1266, 1240, 1210, 1178, 1162, 1122, 1099, 1075, 1047, 1031, 1017, 966, 870, 826, 796, 779, 763, 752, 734, 721, 696 cm^{-1}. MS (EI) *m/z*: 504 (6, M^+ + 2), 503 (38, M^+ + 1), 502 (100, M^+), 471 (3), 459 (14), 440 (18), 439 (50). HRMS Calcd for $C_{27}H_{10}F_8O$: M^+, 502.0604. Found: 502.0609. Anal. Calcd for: $C_{27}H_{10}F_8O$: C, 64.55; H, 2.01. Found: C, 64.26; H, 2.26.

1,2,3,4,5,6,7,8-Octafluoro-11,14-dihexyldibenzo[*g*,*p*]chrysene (5dd)



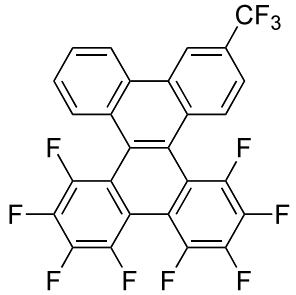
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 82%, yellow solid. Mp: 103.4–107.3 °C. TLC: R_f 0.23 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.2 Hz, 6H), 1.30–1.50 (m, 12H), 1.76–1.86 (m, 4H), 2.92 (t, *J* = 8.0 Hz, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 8.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.8, 29.2, 31.7, 31.9, 36.5, 110.5, 116.3 (d, *J* = 17.7 Hz), 122.2, 125.9, 126.5 (d, *J* = 4.6 Hz), 126.87, 126.88, 128.5, 128.7, 130.4, 139.4 (dm, *J* = 257.0 Hz), 140.8 (dm, *J* = 251.6 Hz), 142.6 (dm, *J* = 252.3 Hz), 142.8, 144.7(dm, *J* = 254.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –156.3 ~ –156.0 (m, 2F), –153.2 ~ –152.9 (m, 2F), –130.0 (bs, 2F), –128.0 ~ –127.7 (m, 2F). IR (KBr): ν = 2925, 2855, 1639, 1616, 1517, 1490, 1470, 1405, 1378, 1360, 1330, 1296, 1262, 1176, 1134, 1095, 1076, 1053, 1032, 966, 955, 934, 893, 877, 835, 824, 805, 799, 750, 734, 722, 693, 647, 615 cm^{-1}. MS (FAB) *m/z*: 641 (24, M^+ + 1), 640 (100, M^+), 639 (15), 638 (3), 569 (34), 496 (44), 425 (8). HRMS Calcd for $C_{38}H_{32}F_8$: M^+, 640.2376. Found: 640.2377.

11,14-Bis(trifluoromethyl)-2,3,6,7-tetramethoxydibenzo[*g*,*p*]chrysene (5ec)



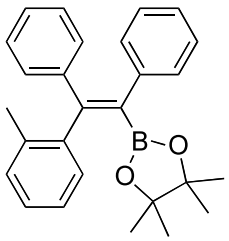
Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 30:15:1). Yield: 40%, yellow solid. Mp: 292.1–296.6 °C. TLC: R_f 0.21 (hexane/AcOEt/CH_2Cl_2 30:15:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (s, 6H), 4.21 (s, 6H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.89 (s, 2H), 8.08 (s, 2H), 8.87 (d, *J* = 8.8 Hz, 2H), 8.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.1, 56.2, 104.1, 109.5, 120.9 (q, *J* = 4.6 Hz), 122.4, 122.9 (q, *J* = 3.3 Hz), 124.2 (q, *J* = 269.9 Hz), 125.5, 126.5, 127.9 (q, *J* = 32.8 Hz), 128.5, 129.1, 131.8, 148.5, 149.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.4 (s). IR (KBr): ν = 2925, 2855, 1639, 1616, 1517, 1490, 1470, 1405, 1378, 1360, 1330, 1296, 1262, 1176, 1134, 1095, 1176, 1053, 1032, 966, 954, 934, 893, 877, 835, 824, 805, 799, 750, 734, 722, 693, 647, 615 cm^{-1}. MS (FAB) *m/z*: 585 (72, M^+ + 1), 584 (100, M^+), 565 (13), 555 (1), 537 (12), 526 (6), 510 (8), 412 (13). HRMS Calcd for $C_{32}H_{22}F_6O_4$: M^+, 584.1422. Found: 584.1432.

1,2,3,4,5,6,7,8-Octafluoro-11-(trifluoromethyl)dibenzo[*g*,*p*]chrysene (5fd)



Purification: silica gel column chromatography (hexane/AcOEt/CH_2Cl_2 40:1:1). Yield: 96%, colorless solid. Mp: 254.6–256.6 °C. TLC: R_f 0.31 (hexane/AcOEt/CH_2Cl_2 40:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.75 (m, 1H), 7.78–7.87 (m, 2H), 7.93–8.08 (m, 2H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.8, 111.1, 115.77, 115.84, 120.4 (q, *J* = 4.6 Hz), 122.1 (q, *J* = 17.3 Hz), 122.9, 124.1 (q, *J* = 269.9 Hz), 125.7, 127.00, 127.02, 128.2, 128.4, 128.56, 128.60, 128.7, 128.9, 129.2 (q, *J* = 30.8 Hz), 129.3, 129.5, 129.9, 130.1, 130.2, 140.2 (dm, *J* = 260.0 Hz), 141.0 (dm, *J* = 254.6 Hz), 142.6 (dm, *J* = 250.9 Hz), 145.0 (dm, *J* = 246.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.6 (s, 3F), –126.9 ~ –126.7 (m, 1F), –127.7 ~ –127.5 (m, 1F), –129.2 (s, 2F), –152.2 ~ –151.7 (m, 2F), –154.3 ~ –153.9 (m, 1F), –154.5 (s, 1F). IR (KBr): ν = 2925, 2855, 1639, 1616, 1517, 1490, 1470, 1405, 1378, 1359, 1330, 1296, 1262, 1176, 1134, 1095, 1076, 1053, 1032, 966, 955, 934, 893, 877, 835, 824, 805, 799, 750, 734, 722, 693, 647, 615 cm^{-1}. MS (FAB) *m/z*: 542 (5, M^+ + 2), 541 (32, M^+ + 1), 540 (100, M^+), 520 (31), 471 (20), 452 (12), 432 (9). Anal. Calcd for: $C_{27}H_7F_{11}$: C, 60.02; H, 1.31. Found: C, 59.80; H, 1.56.

(*E*)-1,2-Diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*o*-tolyl)ethene (6)



Purification: silica gel column chromatography (hexane/EtOAc 14:1). Yield: 71%, colorless solid. Mp: 113.5–114.3 °C. TLC: R_f 0.21 (hexane/EtOAc 14:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 12H), 2.26 (s, 3H), 7.00–7.04 (m, 2H), 7.07–7.11 (m, 3H), 7.12–7.25 (m, 8H), 7.38–7.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 24.4, 83.3, 125.0, 125.8, 126.5, 127.3, 127.4, 127.9, 129.2, 129.8, 130.0, 130.5, 136.8, 140.2, 140.7, 143.3, 149.4. IR (KBr): ν = 2973, 1608, 1598, 1574, 1493, 1443, 1388, 1379, 1371, 1351, 1305, 1271, 1143, 1107, 853, 773, 761, 727, 721, 700, 603, 583 cm^{-1}. MS (EI) *m/z*: 398 (4, M^+ + 2), 397 (28, M^+ + 1), 396 (100, M^+), 395 (23, M^+ – 1), 280 (50), 268 (48). HRMS Calcd for $C_{27}H_{29}BO_2$: M^+, 396.2261. Found: 396.2259. Anal. Calcd for: $C_{27}H_{29}BO_2$: C, 81.82; H, 7.38. Found: C, 81.09; H, 7.23.

(*Z*)-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-diphenylethene (8)
CAS No. [264114-59-4]