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Supplementary Information

Development of novel synthetic routes to bis(perfluoroalkyl)-substituted anthracene derivatives

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General: ^1H, ^{13}C and ^{19}F NMR spectra were measured with a JEOL JNM-AL300 (300.40 MHz for ^1H, 75.45 MHz for ^{13}C and 282.65 MHz for ^{19}F) spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane (Me_4Si) and hexafluorobenzene (C_6F_6: δ -163.00 ppm for ^{19}F) as an internal reference. Infrared spectra (IR) were determined in a liquid film or KBr disk method with an FT/IR-4100 (JASCO). High resolution mass spectra were taken with a JEOL JMS-700 MS spectrometer. Elemental analyses were conducted with a PerkinElmer 2400 Series II CHNS/O System. Melting points were recorded on a Yamato Scientific MP-21 type instrument at atmospheric pressure. Column chromatography was carried out on silica gel (Kanto Chemical Co.,Inc., Silica gel 60) and TLC analysis was performed on silica gel TLC plates (Merck, Silica gel 60 F_{254}).

Materials: All reactions were carried out under an atmosphere of argon in dried glassware with magnetic stir bar. Anhydrous tetrahydrofuran (THF), diethyl ether and dichloromethane were purchased from Kanto Chemical Co., Inc. and used as received. CF_3SiMe_3 was commercially available from Central Glass Co., Ltd. *n*-Butyllithium was also commercially available from Kanto Chemical Co., Inc. Methyllithium-lithium bromide complex was purchased from Sigma-Aldrich®. The concentration of both *n*-Butyllithium and methyllithium-lithium bromide complex was determined by titration using 1,10-phenanthroline and *sec*-Butanol prior to use. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use.

Preparation of bromo-substituted anthraquinones 1b and 1d

2-Bromo-9,10-anthraquinone were prepared from the corresponding amino-counterparts according to reported procedure.[1] In a 100 mL round-bottomed flask with a magnetic stirrer bar was placed $CuBr_2$ (2.390 g, 10.7 mmol), *tert*-butyl nitrite (*tert*-BuONO, 1.103 g, 10.7 mmol), and MeCN (15 mL). To the suspension was added slowly a solution of 2-amino-9,10-anthraquinone (0.959 g, 4.30 mmol) in THF (35 mL), followed by stirring at room temperature for 20 h. After 20 h, the solvent was removed using rotary evaporator and the residue was filtered with rinsing by H_2O. The filter-cake was purified by silica-gel column chromatography using hexane/CH_2Cl_2 (1/1) as an eluent, giving pure 2-bromo-9,10-anthraquinone (0.984 g, 3.44 mmol, 80%) as a yellow solid.

2,6-Dibromo-9,10-anthraquinone (**1d**) was obtained in 52% yield by the reaction of 2,6-diamino-9,10-anthraquinone (2.380 g, 10 mmol) with $CuBr_2$ (4.470 g, 20 mmol) in the presence of tert-BuONO (2.4 mL, 20 mmol) in MeCN (40 mL) at 65 °C for 2 h, followed by the addition of *6N* HCl aq. The obtained **1b** and **1d** are known compounds and were accordant with reported NMR data.

2-Bromo-9,10-anthraquinone (1b)

^{1}H NMR ($CDCl_3$) δ 7.83 (dd, J = 5.9, 3.3 Hz, 2H), 7.93 (dd, J = 8.4, 2.1 Hz, 2H), 8.18 (d, J = 8.4 Hz, 1H), 8.32 (m, 2H), 8.44 (d, J = 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 127.3, 127.4, 129.0, 129.7, 130.2, 132.1, 133.2, 133.3, 134.3, 134.4, 134.5, 137.1, 182.0, 182.3.

2,6-Dibromo-9,10-anthraquinone (1d)

^{1}H NMR ($CDCl_3$) δ 7.95 (dd, J = 8.1, 2.1 Hz, 2H), 8.17 (d, J = 8.1 Hz, 2H), 8.44 (d, J = 2.1 Hz, 2H).

Preparation of iodo-substituted anthraquinones 1c and 1e

2-Iodo-9,10-anthraquinone (**1c**) were prepared from the corresponding amino-counterparts according to reported procedure.[2] In a 100 mL round-bottomed flask with a stirrer bar was placed 2-amino-9,10-anthraquinone (1.780 g, 8 mmol) and 10 mL of concentrated HCl aq. (*c*-HCl.). After cooling with ice-water bath, an aqueous solution of $NaNO_2$ (0.828 g, 12 mmol) in H_2O (7.0 mL) was added dropwise, followed by being stirred below 0 °C for 1 h. To the whole was added slowly an aqueous solution of NaI (4.940 g, 33 mmol) in H_2O (40 mL) *via* a syringe. After the addition, the reaction mixture was stirred at room temperature for 2 h, then continuously at 50 °C for overnight (approx. 15 h). To the reaction mixture was added aqueous sodium sulfite (Na_2SO_3)

solution, followed by the extraction with CH_2Cl_2 (40 mL, 3 times). The organic layer was washed with aqueous NaOH solution, dried over Na_2SO_4, and concentrated by using rotary evaporator. The residue was column chromatographed by using hexane/CH_2Cl_2 (1/1) as an eluent to obtain pure 2-iodo-9,10-anthraquinone (2.107 g, 6.30 mmol, 79%) as a reddish solid.

2,6-Diiodo-9,10-anthraquinone (**1e**) was obtained in 81% yield by the reaction of 2,6-diamino-9,10-anthraquinone (4.760 g, 20 mmol) with $NaNO_2$ (3.360 g, 44 mmol) in 105 mL of mixed solvent (MeCN/*c*-HCl aq. = 2/1) at 0 °C for 0.5 h, followed by adding KI (8.300 g, 50 mmol), was carried out at 60 °C for 13 h.[3] The obtained **1b** and **1d** are known compounds and were accordant with reported NMR data.

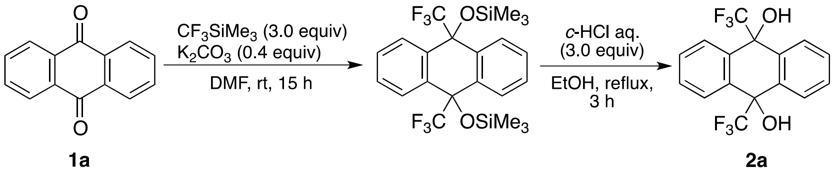
2-Iodo-9,10-anthraquinone (1c)

^{1}H NMR ($CDCl_3$) δ 7.82 (dd, *J* = 5.7, 2.7 Hz, 2H), 8.00 (d, *J* = 8.1 Hz, 1H), 8.15 (dd, *J* = 8.1, 1.8 Hz, 2H), 8.30 (m, 2H), 8.49 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 127.2, 127.3, 128.5, 132.4, 132.9, 133.1, 133.8, 134.0, 134.3, 134.4, 136.1, 143.0, 181.8, 182.5.

2,6-Diiodo-9,10-anthraquinone (1e)

^{1}H NMR ($CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 8.18 (dd, *J* = 8.4, 1.8 Hz, 2H), 8.49 (d, *J* = 1.8 Hz, 2H).

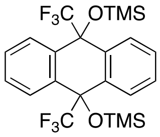
Typical Procedure for the preparation of 9,10-bis(trifluoromethyl)-9,10-dihydroanthracen-9,10-diol (2a)[4]



A 50 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum and an inlet tube for argon was charged with a 9,10-anthraquinone (2.082 g, 10 mmol) and K_2CO_3 (0.553 g, 4.0 mmol) in DMF (20 mL). To the solution was added CF_3SiMe_3 (3.30 mL, 22 mmol) via a syringe at 0 °C, followed by continuous stirring at room temperature for 15 h. After being stirred for 15 h, the whole was poured into mixed solution of sat. NH_4Cl (20 mL) and 1N HCl solution (5.0 mL), followed by extraction with Et_2O (40 mL, 3 times). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as an eluent yielded pure

9,10-bis(trifluoromethyl)-9,10-bis(trimethylsiloxy)-9,10-dihydroanthracene (4.039 g, 8.2 mmol, 82%) as a white solid.

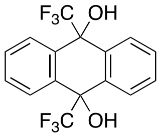
9,10-bis(trifluoromethyl)-9,10-bis(trimethylsiloxy)-9,10-dihydroanthracene



Yield: 82% (white solid). M.P. 118 – 120 °C. ^{1}H NMR (CDCl$_3$) δ −0.10 (s, 18H), 7.48 – 7.55 (m, 4H), 7.93 – 7.99 (m, 4H). ^{19}F NMR (CDCl$_3$) δ −79.29 (s). ^{13}C NMR (CDCl$_3$) δ 1.7, 75.9 (q, J = 27.9 Hz), 125.7 (q, J = 289.0 Hz), 130.0, 130.7 (q, J = 3.1 Hz), 134.1. IR (KBr) ν 3073, 2968, 1487, 1447, 1411, 1237, 1175, 1075, 944, 930, 876, 846 cm^{-1}. Anal. Calcd for: C, 53.64; H, 5.32. Found: C, 53.54; H, 5.38.

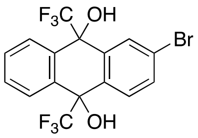
The bis(trimethylsilyl) ether obtained (3.541 g, 7.2 mmol) were mixed with concentrated hydrochloric acid (2.0 mL, 24 mmol) in EtOH (15 mL) and the whole was stirred at reflux temperature for 3 h. The reaction mixture was poured into aqueous saturated NH$_4$Cl solution (20 mL), followed by extraction with AcOEt (20 mL, 3 times). The organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/AcOEt (2/1) as an eluent yielded pure 9,10-bis(trifluoromethyl)-9,10-dihydroanthracen-9,10-diol (**2a**, 2.198 g, 6.3 mmol, 88%) as a white solid. In the preparation of **2b**–**e** were conducted hydrolysis without any purification of bis(trimethylsilyl) ether intermediates because the mixture of silyl ether and desilylated compounds were obtained in the first step.

9,10-Bis(trifluoromethyl)-9,10-dihydroanthracen-9,10-diol (2a)



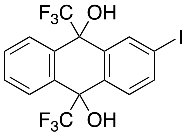
Yield: 88% (white solid). M.P. 197 – 199 °C. ^{1}H NMR (Acetone-d_6) δ 6.52 – 6.54 (m, 2H), 7.55 – 7.63 (m, 4H), 8.02-8.16 (m, 4H). ^{19}F NMR (Acetone-d_6) δ −76.98 (s). ^{13}C NMR (Acetone-d_6) δ 73.7 (q, J =27.3 Hz), 125.7 (q, J = 287.8 Hz), 129.4 (q, J = 3.1 Hz), 129.7, 135.0. IR (KBr) ν 3534, 3078, 1658, 1488, 1450, 1333, 1212, 1176, 1042, 912 cm^{-1}. Anal. Calcd for: C, 53.64; H, 5.32. Found: C, 53.54; H, 5.38.

2-Bromo-9,10-bis(trifluroomethyl)-9,10-dihydroanthracen-9,10-diol (2b)



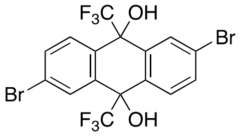
Yield: Quant (white solid). M.P. 165.0 – 166.1 °C. ^{1}H NMR (CDCl$_3$) δ □□□□ (dd, J = 6.0, 3.3 Hz, 2H), 7.71 (dd, J = 2.1 Hz, 1H), 7.91 (qd, J = 8.7, 2.3 Hz, 1H), 8.04 – 8.01 (m, 2H), 8.19 (t, J = 2.1 Hz, 1H). ^{19}F NMR (CDCl$_3$) δ□−79.34 (s, 3F), −79.40 (s, 3F). ^{13}C NMR (CDCl$_3$) δ 72.9 (q, J = 28.0 Hz), 73.0 (q, J = 28.0 Hz), 123.7 (q, *J* = 285.7 Hz), 123.8 (q, *J* = 285.7 Hz), 124.3, 128.3 (q, *J* = 2.9 Hz), 129.8, 129.9, 130.2 (q, *J* = 2.9 Hz), 131.5 (q, *J* = 3.1 Hz), 132.2, 132.7, 133.0, 135.2. IR (KBr) ν 3516, 3302, 3175, 1754, 1622, 1591, 1481, 1335, 1284, 1185, 940, 753 cm^{-1}. HRMS (APCI–) Calcd for (M+) $C_{16}H_{9}{}^{79}BrF_{6}O_{2}$: 425.9690, Found 425.9667.

2-Iodo-9,10-bis(trifluoromethyl)-9,10-dihydroanthracen-9,10-diol (2c)



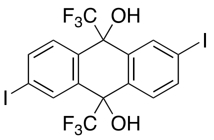
Yield: 91% (white solid). M.P. 177.0 – 178.0 °C. ^{1}H NMR ($CDCl_3$) δ□7.56 (dd, *J* = 1.8, 6.0 Hz, 2H), 7.75 (dq, *J*=2.2, 8.5 Hz, 1H), 7.91 (dd, *J*=1.8, 8.4 Hz, 1H), 8.04-8.00 (m, 2H), 8.39 (t, *J* = 2.1 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ□–79.34 (s, 3F), –79.42 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 73.5 (q, *J* = 27.8 Hz), 73.6 (q, *J* = 34.0 Hz), 123.9 (q, *J* = 279.5 Hz), 129.3 (q, *J* = 2.3 Hz), 129.3, 129.4, 129.4, 130.1 (q, *J* = 2.9 Hz), 131,5 (q, *J* = 290.0), 133.0, 133.2, 135.4, 137.4 (q, *J* = 3.1 Hz), 138.3, 138.4. IR (KBr) ν 3514, 3317, 3193, 3083, 2821, 1709, 1621, 1585, 1478, 1219, 934, 714, cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{16}H_{9}F_{6}O_{2}I$: 473.9551, Found 473.9540.

2,6-Dibromo-9,10-bis(trifluoromethyl)-9,10-dihydroanthracen-9,10-diol (2d)



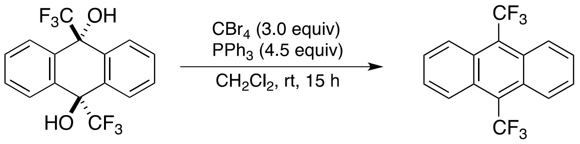
Yield: 85% (white solid). M.P. 275.0 – 276.0 °C. ^{1}H NMR (MeOH-*d*4) δ 7.73 (dq, *J* = 8.4, 2.2 Hz, 2H), 7.93 (dd, *J* = 1.8, 8.7 Hz, 2H), 8.12 (dq, *J* = 2.1, 2.1 Hz, 2H). ^{19}F NMR (MeOH-*d*4) δ□–77.55 (s). ^{13}C NMR (MeOH-*d*4) δ 73.7 (q, *J* = 27.5 Hz), 125.6 (q, *J* = 285.7 Hz), 131.6 (q, *J* = 2.7 Hz), 132.5 (q, *J* = 2.9 Hz), 133.3, 134.4, 137.6. IR (KBr) ν 3548, 3356, 3109, 3083, 2979, 1800, 1666, 1563, 1482, 1343, 1189, 1048, 898, 780 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{16}H_{8}Br_{2}F_{6}O_{2}$: 503.8795, Found 503.8838.

2,6-Diiodo-9,10-bis(trifluoromethyl)-9,10-dihydroanthracen-9,10-diol (2e)



Yield: 74% (white solid). M.P. 284.0 – 285.5 °C. ^{1}H NMR (MeOH-*d*4) δ 2.96 (s, 2H), 7.72 (dq, *J* = 8.4, 2.2 Hz, 2H), 7.91 (dd, *J* = 2.1, 8.7 Hz, 2H), 8.31 (dq, *J* = 2.1, 2.1 Hz, 2H). ^{19}F NMR (MeOH-*d*4) δ□–79.56 (s). ^{13}C NMR (MeOH-*d*4) δ 73.6 (q, *J* = 27.3 Hz), 95.9, 125.2 (q, *J* = 286.1 Hz), 131.4 (q, *J* = 2.5 Hz), 134.9, 137.3, 138.7 (q, *J* = 2.8 Hz), 139.2. IR (KBr) ν 3514, 3097, 2982, 2880, 1825, 1658, 1557, 1478, 1389, 1280, 1046, 718 cm^{-1}.

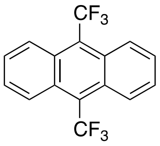
Typical procedure for the preparation of 9,10-bis(trifluoromethyl)anthracene (3a)



2a **3a**

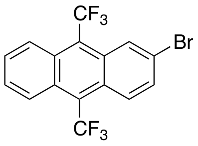
A 30 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a 9,10-bis(trifluoromethyl)anthracen-9,10-diol (**2a**, 0.104 g, 0.3 mmol) and CBr_4 (0.298 g, 0.9 mmol) in CH_2Cl_2 (2.0 mL). To the solution was slowly added PPh_3 (0.367 g, 1.4 mmol) in CH_2Cl_2 (2.0 mL) via a syringe at 0 °C, followed by continuous stirring at room temperature for 15 h. After being stirred for 15 h, the whole was poured into saturated aqueous NH_4Cl solution (20 mL), followed by extraction with CH_2Cl_2 (20 mL, 3 times). The organic layers were dried overanhydrous Na_2SO_4, filetered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as an eluent yielded pure 9,10-bis(trifluoromethyl)anthracene (**3a**, 0.062 g, 66%) as a yellow powder.

9,10-Bis(trifluoromethyl)anthracene (3a)



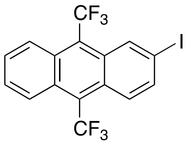
Yield: 66% (yellow powder). M.P. 152 – 154 °C. ^{1}H NMR ($CDCl_3$) δ 7.56 – 7.64 (m, 4H), 8.45 – 8.56 (m, 4H). ^{19}F NMR ($CDCl_3$) δ –49.81 (s). ^{13}C NMR ($CDCl_3$) δ 124.6 (q, J = 6.2 Hz), 125.6 (q, J = 276.6 Hz), 127.1, 128.9 (q, J = 42.2 Hz). IR (KBr) ν 3153, 3097, 3047, 1535, 1450, 1379, 1289, 1210, 1184, 1126, 1105, 956, 765, 675 cm^{-1}. HRMS (APCI) Calcd for (M+) $C_{16}H_8F_6$: 314.0530, Found 314.0504.

2-Bromo-9,10-bis(trifluoromethyl)anthracene (3b)



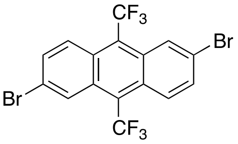
Yield: 94% (yellow powder). M.P. 79 – 80 °C. ^{1}H NMR ($CDCl_3$) δ□7.64 (dd, J = 6.9, 3.3 Hz, 2H), 7.69 (d, J = 1.8 Hz, 1H), 8.38 (dd, J = 9.8, 2.0 Hz, 1H), 8.49 (m, 2H), 8.69 (t, J = 1.7 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ –49.82 (s, 3F), –49.98 (s, 3F). IR (KBr) ν 3168, 3088, 3044, 2923, 1921, 1741, 1607, 1280, 1115, 957, 813, 702 cm^{-1}. Anal. Calcd for $C_{24}H_{12}F_6$: C, 48.88; H, 1.79. Found: C, 48.48; H, 1.80.

2-Iodo-9,10-bis(trifluoromethyl)anthracene (3c)



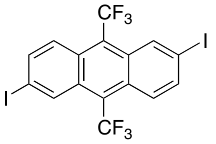
Yield: 52% (yellow powder). M.P. 100 – 101 °C. ^{1}H NMR ($CDCl_3$) δ□7.63 (dd, J = 6.9, 3.3 Hz, 2H), 7.81 (dd, J = 9.8, 1.4 Hz, 1H), 8.21 (dd, J = 9.6, 1.8 Hz, 1H), 8.49 (dd, J = 5.4, 2.1 Hz, 2H), 8.90 (s, 1H). ^{19}F NMR ($CDCl_3$) δ −49.83 (s, 3F), −49.84 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 119.7, 123.4, 124.6 (q, J = 6.0 Hz), 124.6 (q, J = 5.8 Hz), 126.2 (q, J = 28.7 Hz), 127.1, 127.5, 127.7, 129.1 (q, J = 234.9 Hz), 129.1 (q, J = 233.7 Hz), 129.3, 129.6, 130.0, 133.3(q, J = 6.2 Hz), 133.3(q, J = 6.4 Hz), 135.5. IR (KBr) ν 3164, 3087, 3064, 3033, 1925, 1523, 1492, 1342, 1281, 1120, 1051, 955, 764 cm^{-1}. Anal. Calcd for $C_{16}H_7F_6I$: C, 43.66; H, 1.60. Found: C, 43.80; H, 1.58.

2,6-Dibromo-9,10-bis(trifluoromethyl)anthracene (3d)



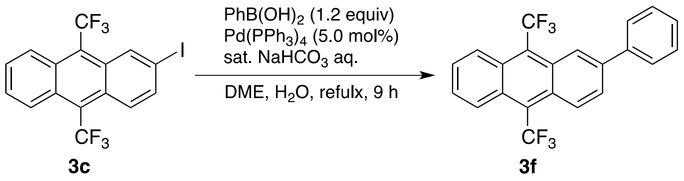
Yield: 73% (yellow powder). M.P. 206 – 207 °C. ^{1}H NMR ($CDCl_3$) δ 7.69 (dd, J = 9.8, 1.7 Hz, 2H), 8.36 (dd, J = 9.6, 1.1 Hz, 2H), 8.66 (brs, 2H). ^{19}F NMR ($CDCl_3$) δ −50.00 (s). ^{13}C NMR ($CDCl_3$) δ 122.9, 124.4 (q, J = 161.6 Hz), 126.2 (q, J = 3.7 Hz), 126.7 (q, J = 4.9 Hz), 128.1, 129.8, 131.4. IR (KBr) ν 3452, 3171, 3068, 2997, 1925, 1768, 1614, 1520, 1412, 1345, 1270, 868, 806, 775, 714 cm^{-1}. Anal. Calcd for $C_{16}H_6Br_2F_6$: C, 40.71; H, 1.28. Found: C, 40.70; H, 1.26.

2,6-Diiodo-9,10-bis(trifluoromethyl)anthracene (3e)



Yield: 84% (yellow powder). M.P. 234 – 235 °C. ^{1}H NMR ($CDCl_3$) δ 7.85 (dd, J = 9.8, 1.7 Hz, 2H), 8.02 (dd, J = 9.9, 1.5 Hz, 2H), 8.88 (brs, 2H). ^{19}F NMR ($CDCl_3$) δ −49.90 (s). ^{13}C NMR ($CDCl_3$) δ 124.8 (q, J = 283.6 Hz), 124.9, 125.8 (q, J = 6.0 Hz), 128.0, 130.1, 133.3 (q, J = 6.4 Hz), 136.2. IR (KBr) ν 3442, 3166, 3153, 1929, 1774, 1601, 1515, 1210, 1124, 955, 806, 769 cm^{-1}. Anal. Calcd for $C_{16}H_6F_6I_2$: C, 33.95; H, 1.07. Found: C, 33.91; H, 1.00.

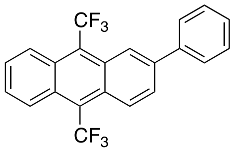
Typical procedure for Suzuki-Miyaura cross-coupling reaction of 2-iodo-9,10-bis(trifluoromethyl)anthracene (3c) with aromatic boronic acid[5]



A 50 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a 2-iodo-9,10-bis(trifluoromethyl)anthracene (**3c**, 0.868 g, 1.97 mmol), $Pd(PPh_3)_4$ (0.161 g, 0.1 mmol) in DME (10 mL). After stirring at room temperature for 20 min, to the resulting solution was added aqueous saturated NaHCO3 solution

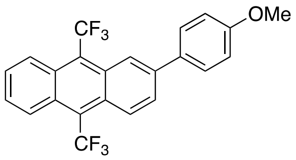
(6.0 mL), phenylboronic acid (0.268 g, 2.2 mmol), and the whole was refluxed for 9 h. After being stirred for 9 h, the resulting mixture was poured into H_2O (20 mL), followed by extraction with CH_2Cl_2 (20 mL, 3 times). The organic layers were washed with 1*N* NaOH aq. (20 mL) and dried overanhydrous Na_2SO_4, filetered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as an eluent yielded pure 2-phenyl-9,10-bis(trifluoromethyl)anthracene (**3f**, 0.568 g, 1.46 mmol, 74%) as a yellow powder.

2-Phenyl-9,10-bis(trifluoromethyl)anthracene (3f)



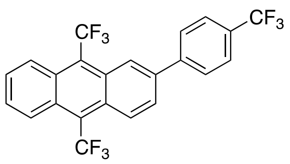
Yield: 74% (yellow powder). M.P. 105 – 106 °C. ^{1}H NMR ($CDCl_3$) δ 7.43 – 7.46 (m, 1H), 7.55 (dd, *J* = 9.5, 1.7 Hz, 1H), 7.62 (dd, *J* = 6.6, 3.6 Hz, 2H), 7.78 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.90 (dd, *J* = 9.5, 1.7 Hz, 1H), 8.51 (m, 2H), 8.60 (dd, *J* = 9.6, 2.1 Hz, 1H), 8.69 (t, *J* = 2.0 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ –49.70 (s, 3F), -49.83 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 121.9 (q, *J* = 5.6 Hz), 124.5 (q, *J* = 6.0 Hz), 124.6 (q, *J* = 5.8 Hz), 125.2 (q, *J* = 5.6 Hz), 125.5 (q, *J* = 29.0 Hz), 125.6 (q, *J* = 28.8 Hz), 125.6 (q, *J* = 28.0 Hz), 125.7 (q, *J* = 276.0 Hz), 125.7 (q, *J* = 275.4 Hz), 127.0, 127.0, 127.2 (q, *J* = 1.2 Hz), 127.4, 128.3, 128.4, 128.4, 129.1, 129.6 (q, *J* = 1.6 Hz), 139.3, 139.3, 139.8, 139.9. IR (KBr) ν 3447, 3065, 2957, 2852, 2352, 1920, 1631, 1581, 1493, 1290, 1186961, 884 cm^{-1}. Anal Calcd for $C_{22}H_{12}F_6$: C, 67.70; H, 3.10. Found: C, 67.83; H, 2.80.

2-(4-Methoxyphenyl)-9,10-bis(trifluoromethyl)anthracene (3g)



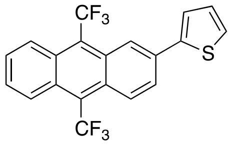
Yield: 80% (yellow powder). M.P. 118 – 119 °C. ^{1}H NMR ($CDCl_3$) δ 3.89 (s, 3H), 7.61 (m, 2H), 7.727 (q, *J* = 5.0 Hz, 1H), 7.728 (ABq, *J* = 8.7 Hz, 2H), 7.89 (dd, *J* = 9.6, 2.1 Hz, 1H), 8.50 (dquint., *J* = 7.5, 2.5 Hz, 2H), 8.57 (dqd, *J* = 9.6, 2.3, 0.6 Hz, 1H), 8.62 (quint., *J* = 2.0 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ –49.82 (s, 3F), –49.88 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 55.3, 114.5, 120.7 (q, *J* = 5.6 Hz), 124.5 (q, *J* = 5.6 Hz), 124.6 (q, *J* = 5.6 Hz), 125.1 (q, *J* = 5.6 Hz), 125.2 (q, *J* = 26.3 Hz), 125.5 (q, *J* = 26.7 Hz), 125.6 (q, *J* = 275.8 Hz), 125.7 (q, *J* = 275.7 Hz), 126.9, 127.07, 127.10, 128.20, 128.22, 128.8, 128.9, 129.6, 129.7, 132.1, 138.7, 159.9. IR (KBr) ν 3434, 3132, 2964, 2898, 2360, 1578, 1496, 1252, 1187, 959, 812 cm^{-1}. Anal. Calcd for $C_{23}H_{14}F_6O$: C, 65.72; H, 3.36. Found: C, 65.46; H, 3.10.

2-[(4-Trifluoromethyl)phenyl]-9,10-bis(trifluoromethyl)anthracene (3h)



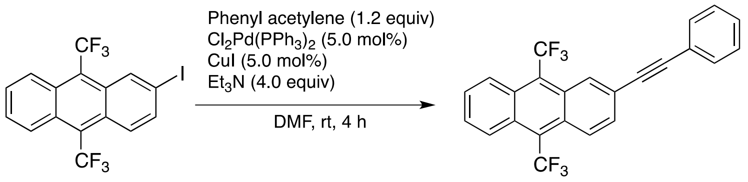
Yield: 90% (yellow powder). M.P. 114 – 116.0 °C. ^{1}H NMR ($CDCl_3$) δ 7.65 (dd, *J* = 7.2, 3.3 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.80 (m, 3H), 8.53 (m, 2H), 8.64 (dqd, *J* = 9.4, 2.0, 0.4 Hz, 1H), 8.70 (quint., *J* = 2.1 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ −49.68 (s, 3F), −49.89 (s, 3F), −63.85 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 124.1 (q, *J* = 270.0 Hz), 124.6 (q, *J* = 5.9 Hz), 124.7 (q, *J* = 5.9 Hz), 125.5 (q, *J* = 275.8 Hz), 125.6 (q, *J* = 275.8 Hz), 125.6 (q, *J* = 5.6 Hz), 126.0 (q, *J* = 4.4 Hz), 126.6, 127.4, 127.5, 127.7, 128.4, 128.5, 129.2, 129.3, 129.36, 129.4, 129.68, 129.71, 130.3 (q, *J* = 32.3 Hz), 137.7, 143.3. IR (KBr) ν 3416, 3139, 2923, 2851, 2360, 11529, 1496, 1383, 1174, 1074, 961, 817 cm^{-1}. Anal. Calcd for $C_{23}H_{11}F_9$: C, 60.27; H, 2.42. Found: C, 60.10; H, 2.36.

2-(2-Thienyl)-9,10-bis(trifluoromethyl)anthracene (3i)



Yield: Quant (yellow powder). M.P. 137 – 138 °C. ^{1}H NMR ($CDCl_3$) δ 7.18 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.43 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.56 (dd, *J* = 3.6, 0.9 Hz, 1H), 7.61 (dd, *J* = 4.1, 2.9 Hz, 1H), 7.61 (dd, *J* = 10.4, 0.8 Hz, 1H), 7.89 (dd, *J* = 9.6, 2.1 Hz, 1H), 8.52 (m, 3H), 8.69 (quint., *J* = 2.1 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ −49.87 (s, 3F), −49.92 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 119.7 (q, *J* = 5.8 Hz), 124.5 (q, *J* = 5.6 Hz), 124.7 (q, *J* = 5.6 Hz), 125.3 (q, *J* = 5.8 Hz), 125.5 (q, *J* = 276.2 Hz), 125.6 (q, *J* = 276.1 Hz), 125.7 (q, *J* = 27.7 Hz), 126.0, 126.6, 127.0, 127.3, 127.4, 128.5, 128.97, 128.99, 128.46, 129.48, 129.8, 132.6, 143.1. IR (KBr) ν 3155, 3048, 2924, 2849, 1742, 1616, 1517, 1474, 1285, 1192, 952, 763 cm^{-1}. Anal. Calcd for $C_{20}H_{10}F_6S$: C, 60.61; H, 2.54. Found: C, 60.22, 2.27.

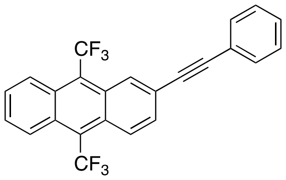
Typical procedure for Sonogashira cross-coupling of 2-iodo-9,10-bis(trifluoromethyl)anthracene (3c) with phenyl acetylene[6]



3c **3j**

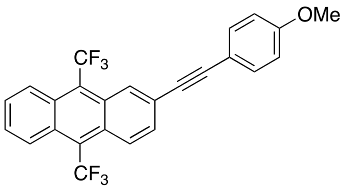
A 50 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a 2-iodo-9,10-bis(trifluoromethyl)anthracene (**3c**, 0.220 g, 0.50 mmol), $Cl_2Pd(PPh_3)_4$ (0.018 g, 0.025 mmol), phenyl acetylene (0.070 mL, 0.60 mmol), CuI (0.005 g, 0.0025 mmol), Et_3N (0.28 mL, 2.0 mmol) in DMF (3.0 mL), and the whole was stirred at room temperature for 4 h. After being stirred for 4 h, the resulting mixture was poured into saturated NH_4Cl aq. (20 mL), followed by extraction with Et_2O (20 mL, 3 times). The organic layers were dried over anhydrous $MgSO_4$, filetered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as an eluent yielded pure 2-phenylethynyl-9,10-bis(trifluoromethyl)anthracene (**3j**, 0.134 g, 0.34 mmol, 65%) as a yellow powder.

2-Phenylethynyl-9,10-bis(trifluoromethyl)anthracene (3j)



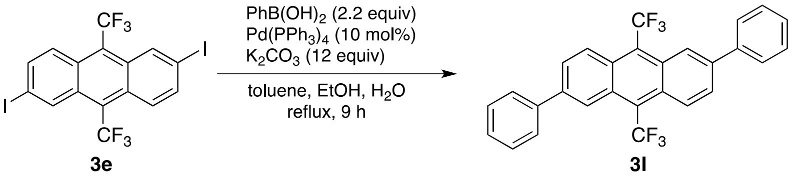
Yield: 65% (yellow powder). M.P. 110 – 112 °C. ^1H NMR ($CDCl_3$) δ 7.38 – 7.42 (m, 3H), 7.61 – 7.69 (m, 5H), 8.45 – 8.52 (m, 3H), 8.69 (t, *J* = 2.1 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ –49.77 (s, 3F), –49.88 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 89.1, 92.4, 122.3, 122.4, 122.6, 124.7 (q, *J* = 5.7 Hz), 124.7 (q, *J* = 5.8 Hz), 125.4 (q, *J* = 275.6 Hz), 125.4 (q, *J* = 275.4 Hz), 127.3, 127.4, 127.7 (q, *J* = 5.7 Hz), 128.4, 128.4, 128.5 (q, *J* = 41.3 Hz), 128.5 (q, *J* = 41.9 Hz), 128.8, 129.1, 129.7, 129.8, 130.90, 130.92, 131.4, 132.5. IR (KBr) ν 3432, 3142, 2925, 2364, 1960, 1615, 1434, 1288, 1027, 921, 852 cm^{-1}. Anal. Calcd for $C_{24}H_{12}F_6$: C, 69.57; H, 2.92. Found: C, 69.48; H, 2.57.

2-(4-methoxyphenyl)ethynyl-9,10-bis(trifluoromethyl)anthracene (3k)



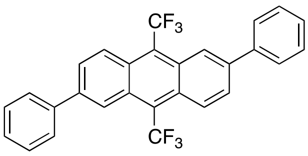
Yield: 80% (yellow powder). M.P. 123 – 124 °C. ^1H NMR ($CDCl_3$) δ 3.86 (s, 3H), 6.93 (m, 2H), 7.61 (m, 5H), 8.48 (m, 3H), 8.65 (t, *J* = 1.8 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ –49.87 (s, 3F), –49.93 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 55.2, 88.1, 92.6, 114.1, 114.6, 122.7, 124.5 (q, *J* = 5.4 Hz), 124.6 (q, *J* = 5.2 Hz), 125.0 (q, *J* = 28.4 Hz), 125.4 (q, *J* = 275.8 Hz), 125.7 (q, *J* = 28.6 Hz), 127.2 (q, *J* = 5.6 Hz), 127.4, 127.42 (q, *J* = 278.1 Hz), 128.09, 128.11, 128.80, 128.82, 129.29, 129.3, 129.4, 129.61, 129.63, 133.4, 160.0. IR (KBr) ν 3124, 3096, 2974, 2217, 1921, 1556, 1435, 1320, 914, 784 cm^{-1}. Anal. Calcd for $C_{25}H_{14}F_6O$: C, 67.57; H, 3.18. Found: C, 67.50; H, 3.35.

Typical procedure for Suzuki-Miyaura cross-coupling of 2,6-diiodo-9,10-bis(trifluoromethyl)anthracene (3e) with phenylboronic acid



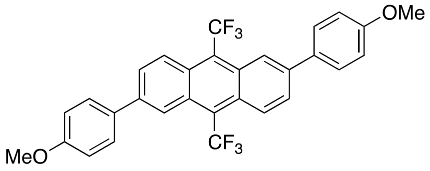
A 50 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a 2,6-diiodo-9,10-bis(trifluoromethyl)anthracene (**3e**, 0.045 g, 0.08 mmol), Pd(PPh$_3$)$_4$ (0.012 g, 0.010 mmol), phenylboronic acid (0.022 g, 0.18 mmol), K_2CO_3 (0.163 g, 1.2 mmol) in H_2O (2.0 mL) and EtOH (1.0 mL) and toluene (4.0 mL), and the whole was refluxed for 12 h. After being stirred for 12 h, the resulting mixture was poured into H_2O (20 mL), followed by extraction with AcOEt (20 mL, 3 times). The organic layers were washed with 1*N* NaOH aq. (20 mL) and dried overanhydrous Na_2SO_4, filetered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as an eluent yielded pure 2,6-diphenyl-9,10-bis(trifluoromethyl)anthracene (**3l**, 0.030 g, 0.064 mmol, 81%) as a yellow powder.

2,6-Diphenyl-9,10-bis(trifluoromethyl)anthracene (3l)



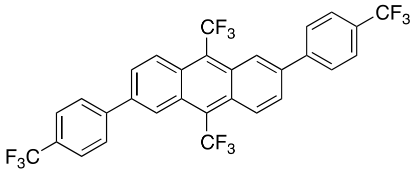
Yield: 81% (yellow powder). M.P. 211 – 213 °C. ^{1}H NMR (CDCl$_3$) δ 7.48 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.56 (dt, *J* = 7.4, 2.3 Hz, 4H), 7.79 (dd, *J* = 7.2, 1.8 Hz, 4H), 7.93 (dt, *J* = 9.7, 1.8 Hz, 2H), 8.61 (d, *J* = 9.7 Hz, 2H), 8.70 (d, *J* = 9.6 Hz, 2H). ^{19}F NMR (CDCl$_3$) δ –49.75 (s). ^{13}C NMR (CDCl$_3$) δ 122.0 (q, *J* = 2.5 Hz), 125.5 (q, *J* = 28.8 Hz), 125.7 (q, *J* = 269.9 Hz), 128.3, 128.8, 129.1, 129.5, 139.2, 139.8. IR (KBr) ν 3426, 3080, 2361, 1632, 1468, 1321, 1279, 1141, 962, 880 cm^{-1}. Anal. Calcd for $C_{28}H_{16}F_6$: C, 72.10; H, 3.46. Found: C, 72.25; H, 3.18.

2,6-Bis(4-methoxyphenyl)-9,10-bis(trifluoromethyl)anthracene (3m)



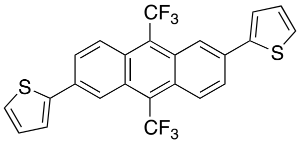
Yield: 66% (yellow powder). M.P. 226 – 228 °C. ^{1}H NMR (CDCl$_3$) δ 3.90 (s, 6H), 7.08 (ABq, *J* = 8.7 Hz, 4H), 7.73 (ABq, *J* = 8.7 Hz, 4H), 7.89 (d, *J* = 9.6 Hz, 2H), 8.57 (d, *J* = 9.6 Hz, 2H), 8.62 (s, 2H). ^{19}F NMR (CDCl$_3$) δ –49.86 (s). ^{13}C NMR (CDCl$_3$) δ 55.4, 114.6, 121.0 (q, *J* = 6.2 Hz), 125.1 (q, *J* = 5.8 Hz), 127.2, 128.6, 132.3, 134.8, 138.6, 141.7, 159.9. IR (KBr) ν 3007, 2960, 2853, 2363, 1918, 1608, 1468, 1248, 1180, 963, 876 cm^{-1}. HRMS (FAB) Calcd for (M+) $C_{30}H_{20}F_6O_2$: 526.1367, Found 526.1336.

2,6-Bis[4-(trifluoromethyl)phenyl]-9,10-bis(trifluoromethyl)anthracene (3n)



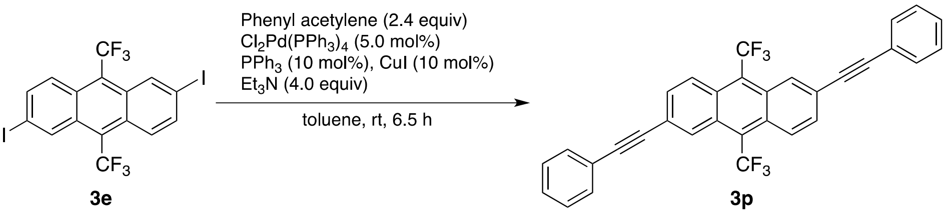
Yield: 90% (yellow powder). M.P. 217 – 218 °C. ^{1}H NMR (CDCl$_3$) δ 7.81 (ABq, *J* = 8.1 Hz, 2H), 7.89 (ABq, *J* = 8.1 Hz, 2H), 7.92 (dd, *J* = 9.1, 1.5 Hz, 2H), 8.68 (d, *J* = 8.4 Hz, 2H), 8.72 (s, 2H). ^{19}F NMR ($CDCl_3$) δ −49.70 (s, 6F), −63.86 (s, 6F). ^{13}C NMR ($CDCl_3$) δ 122.3, 122.8 (q, *J* = 6.2 Hz), 125.5 (q, *J* = 275.6 Hz), 125.7 (q, *J* = 6.0 Hz), 126.1 (q, *J* = 3.7 Hz), 127.1, 129.1, 129.5, 130.4 (q, *J* = 32.3 Hz), 138.1, 143.3. IR (KBr) ν 3428, 3047, 2934, 2850, 1928, 1617, 1209, 1073, 847 cm^{-1}. Anal. Calcd for $C_{30}H_{14}F_{12}$: C, 59.81; H, 2.34. Found: C, 59.51; H, 2.14.

2,6-Dithienyl-9,10-bis(trifluoromethyl)anthracene (3o)



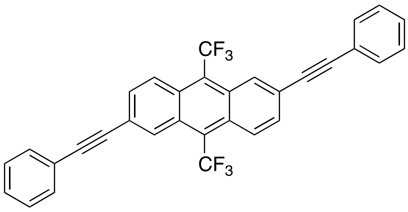
Yield: 82% (yellow powder). M.P. 241.8 – 242.3 °C. 1H NMR ($CDCl_3$) δ 7.19 (dd, *J* = 5.1, 3.6 Hz, 2H), 7.43 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.57 (dd, *J* = 3.6, 0.9 Hz, 2H), 7.90 (dd, *J* = 9.3, 1.8 Hz, 2H), 8.52 (dd, *J* = 9.6, 1.2 Hz, 2H), 8.68 (s, 2H). ^{19}F NMR ($CDCl_3$) δ -49.93 (s, 6F). ^{13}C NMR ($CDCl_3$) δ 119.9 (q, *J* = 5.8 Hz), 124.9, 125.3 (q, *J* = 3.3 Hz), 125.6 (q, *J* = 280.5 Hz), 126.3, 126.6, 128.5, 129.2 (q, *J* = 20.3 Hz), 132.6, 143.2. IR (KBr) ν 3141, 3094, 2329, 1921, 1810, 1735, 1481, 1356, 1281, 1109, 948, 809, 777 cm^{-1}. HRMS (APCI+) Calcd for (M+H) $C_{24}H_{13}F_6S_2$: 479.0363, Found 479.0352.

Typical procedure for Sonogashira cross-coupling of 2,6-diiodo-9,10-bis(trifluoromethyl)anthracene (3e) with phenyl acetylene



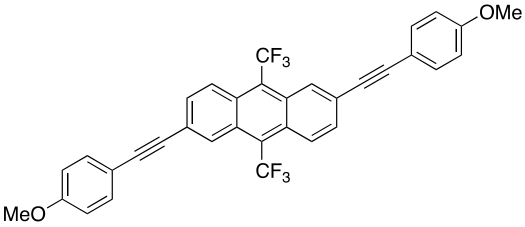
A 50 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a 2,6-diiodo-9,10-bis(trifluoromethyl)anthracene (**3e**, 0.028 g, 0.05 mmol), $Cl_2Pd(PPh_3)_4$ (0.002 g, 0.003 mmol), phenyl acetylene (0.122 g, 0.12 mmol), CuI (0.001 g, 0.005 mmol), PPh3 (0.001 g, 0.004 mmol), and Et_3N (0.28 mL, 2.0 mmol) in toluene (0.3 mL), and the whole was stirred at room temperature for 6.5 h. After being stirred for 4 h, the resulting mixture was poured into saturated NH_4Cl aq. (20 mL), followed by extraction with AcOEt (20 mL, 3 times). The organic layers were dried over anhydrous $MgSO_4$, filetered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as an eluent yielded pure 2,6-bis(phenylethynyl)-9,10-bis(trifluoromethyl)anthracene (**3p**, 0.022 g, 0.043 mmol, 86%) as a yellow powder.

2,6- Bis(phenylethynyl)-9,10-bis(trifluoromethyl)anthracene (3p)



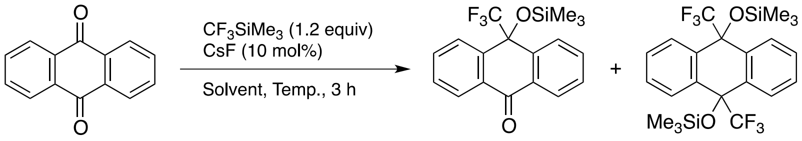
Yield: 86% (yellow powder). M.P. 215 – 216 °C. ^{1}H NMR ($CDCl_3$) δ 7.41 (t, *J* = 3.2 Hz, 6H), 7.64 (q, *J* = 3.2 Hz, 4H), 7.69 (dd, *J* = 9.3, 0.9 Hz, 2H), 8.48 (d, *J* = 8.7 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ –46.20 (s, 6F). ^{13}C NMR ($CDCl_3$) δ 89.1, 92.7, 122.5, 122.7, 124.8 (q, *J* = 5.8 Hz), 125.1, 125.2 (q, *J* = 304.6 Hz), 125.3 (q, *J* = 29.0 Hz), 127.7 (q, *J* = 6.0 Hz), 128.5, 128.7, 128.9, 129.0, 129.7, 131.9. IR (KBr) ν 3437, 3148, 2995, 2210, 1625, 1496, 1326, 1285, 1172, 994, 881, 720 cm^{-1}. Anal. Calcd for $C_{32}H_{16}F_6$: C, 74.71; H, 3.13. Found: C, 74.67; H, 2.96.

2,6-Bis[(4-methoxyphenyl)ethynyl]-9,10-bis(trifluoromethyl)anthracene (3q)



Yield: 57% (reddish crystal). M.P. 215 – 216 °C. ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 6H), 6.93 (ABq, *J* = 8.7 Hz, 4H), 7.57 (ABq, *J* = 8.7 Hz, 4H), 7.67 (m, 2H), 8.45 (m, 2H), 8.63 (m, 2H). ^{19}F NMR ($CDCl_3$) δ -49.00 (s, 6F). IR (KBr) ν 3122, 3076, 2962, 1626, 1514, 1325, 1252, 1171, 1010, 925, 840, 796 cm^{-1}. HRMS (APCI–) Calcd for (M+) $C_{34}H_{20}F_6O_2$: 574.1367, Found 574.1385. Data ^{13}C NMR for this compound **3p** was not obtained due to low solubility in any deuterated solvents.

Optimization of the reaction conditions for the preparation of 9-trifluoromethyl-9-trimethylsiloxy- anthracen-10-one (4a)



1a **mono-adduct** **bis-adduct**

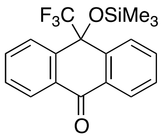
Entry	Solvent	Temp. /°C	Yield[a]/% of **mono-adduct**	Yield[a]/% of **bis-adduct**
1[b]	DMF	25	43	27
2	DME	–25	30	33
3	DME	0	4	42
4	DME	rt	29 [18]	33
5	DME	40	10	28
6[c]	DME	rt	80 [70]	5
7[c]	THF	rt	[90]	-

[a] Determined by ^{19}F NMR. Values in bracket are of isolated yields. [b] Reaction of **1a** with 1.1 equiv of CF_3SiMe_3 in the presence of 0.2 equiv of K_2CO_3 in DMF at room temperature for 4 h was performed according to the reported procedure, see: Ref.[4a]. [c] To the mixture of **1a** and CsF in the solvent was ***added slowly the diluted solution*** of CF_3SiMe_3 in the solvent.

Typical procedure for the preparation of 9-(trifluoromethyl)-9-(trimethylsiloxy)-anthracen-10-one (4a) under the optimized reaction conditions (entry 7)

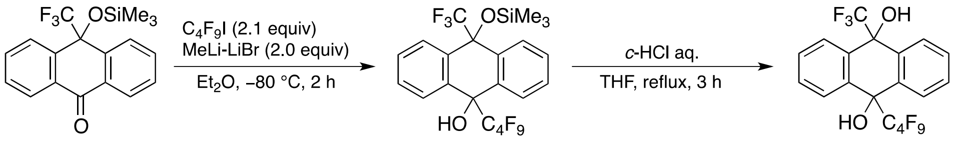
A 300 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, 30 mL of dropping funnel, and an inlet tube for argon was charged with 9,10-anthraquinone (**1a**, 4.164 g, 20 mmol) and CsF (0.304 g, 2.0 mmol) in THF (150 mL). *To the whole was added slowly the diluted solution of* CF_3SiMe_3 *(3.55 mL, 24 mmol) in THF (25 mL)*, followed by stirring at room temperature for 3 h. The resultant was poured into saturated NH_4Cl aq. (30 mL), followed by extraction with AcOEt (30 mL, 3 times). The organic layers were dried over anhydrous Na_2SO_4, filetered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/CH_2Cl_2 (2/1) as an eluent yielded pure 9-(trifluoromethyl)-9-(trimethylsiloxy)anthracen-10-one (**4a**, 6.311 g, 18.0 mmol, 90%) as a white powder.

9-(Trifluoromethyl)-9-(trimethylsiloxy)anthrcen-10-one (4a)



Yield: 90% (white solid). M.P. 84 – 86 °C. ^1H NMR ($CDCl_3$) δ –0.09 (s, 9H), 7.63 (td, J = 7.2, 1.2 Hz, 2H), 7.74 (td, J = 7.2, 1.2 Hz, 2H), 7.99 (t, J = 1.5 Hz, 1H), 8.02 (t, J = 1.5 Hz, 1H), 8.32 (d, J = 1.2 Hz, 1H), 8.35 (d, J = 1.2 Hz, 1H). ^{19}F NMR ($CDCl_3$) δ –80.66 (s, 3F). ^{13}C NMR ($CDCl_3$) δ 1.7, 74.6 (q, J = 29.7 Hz), 123.8 (q, J = 286.5 Hz), 127.4, 129.0 (q, J = 1.8 Hz), 129.9, 131.4, 133.0, 139.0, 182.6. IR (KBr) ν 006, 2971, 2905, 1668, 1599, 1457, 1253, 1082, 956, 818, 712, 679 cm^{-1}. HRMS (APCI+) Calcd for (M+H) $C_{18}H_{18}F_3O_2Si$: 351.1028, Found 351.1008.

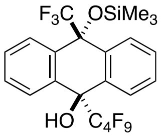
Typical procedure for the preparation of 9-(nonafluorobutyl)-10-(trifluoromethyl)anthracene-9,10-diol (5aA)



4a **5aA**

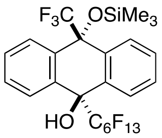
A 30 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, 10 mL of dropping funnel and an inlet tube for argon was charged with a 9-trifluoromethyl-9-trimethylsiloxyanthracen-10-one (**4a**, 0.350 g, 1.0 mmol) and nonafluorobutyl iodide (0.36 mL, 2.1 mmol) in Et_2O (10 mL). To the solution was added MeLi-LiBr in Et_2O (1.5 *M*, 1.33 mL, 2.0 mmol) *via* a syringe at -80 °C, followed by continuous stirring at the same temperature. After being stirred for 2 h, the whole was poured into the aqueous solution of sat. NH_4Cl (10 mL), followed by extraction with Et_2O (10 mL, 3 times). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/CH_2Cl_2 (2/1) as an eluent yielded pure 9-(nonafluorobutyl)-10-(trifluoromethyl)-10-(trimethylsiloxy)anthracen-9-ol (0.449 g, 0.79 mmol, 79%) as a white solid.

9-(Nonafluorobutyl)-10-(trifluoromethyl)-10-(trimethylsiloxy)anthracen-9-ol



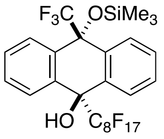
Yield: 79% (white solid). M.P. 99 – 101 °C. ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 2.98 (s, 1H), 7.50 – 7.60 (m, 4H), 7.91 – 7.98 (m, 2H), 8.00 – 8.09 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −81.55 (s, 3F), −82.21 (t, *J* = 9.0 Hz, 3F), −116.49 (m 2F), −120.15 (m, 2F), −127.28 (m, 2F). ^{13}C NMR ($CDCl_3$) δ 1.8, 74.2 (tt, *J* = 19.8, 1.8 Hz), 76.0 (q, *J* = 27.3 Hz), 124.1 (q, *J* = 289.0 Hz), 128.6 (tt, *J* = 5.6, 1.8 Hz), 129.0, 129.5, 129.6, 132.8, 133.4. IR (KBr) ν 3589, 3563, 2963, 1449, 1357, 1235, 1170, 940, 878, 763 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{22}H_{17}F_{12}O_2Si$: 569.0806, Found 569.0824.

9-(Tridecafluorohexyl)-10-(trifluoromethyl)-10-(trimethylsiloxy)anthracen-9-ol



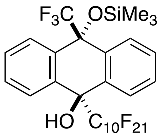
Yield: 68% (white solid). M.P. 58 – 60 °C. ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 3.01 (s, 1H), 7.50 – 7.60 (m, 4H), 7.91 – 8.00 (m, 2H), 8.03 – 8.09 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −81.62 (s, 3F), −82.17 (t, *J* = 9.0 Hz, 3F), −116.45 (m, 2F), −119.28 (m, 2F), −123.11 (brs, 2F), −124.20 (brs, 2F), −127.449 (m, 2F). ^{13}C NMR ($CDCl_3$) δ 2.3, 74.6 (tt, *J* = 19.8, 1.9 Hz), 76.4 (q, *J* = 27.9 Hz), 124.5 (q, *J* = 289.0 Hz), 129.0 (tt, *J* = 5.6, 1.2 Hz), 129.4, 129.9, 130.0, 133.2, 133.8. IR (KBr) ν 3585, 3445, 2966, 1237, 1198, 1151, 1032, 937, 848, 761 cm^{-1}. HRMS (APCI–) Calcd for (M+) $C_{24}H_{18}F_{16}O_2Si$: 670.0821, Found 670.0804.

9-(Heptadecafluorooctyl)-10-(trifluoromethyl)-10-(trimethylsiloxy)anthracen-9-ol



Yield: 70% (white solid). M.P. 84 – 86 °C. ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 2.98 (s, 1H), 7.50 – 7.59 (m, 4H), 7.91 – 7.97 (m, 2H), 8.03 – 8.09 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −81.59 (s, 3F), −82.07 (t, *J* = 9.0 Hz, 3F), −116.40 (m, 2F), −119.18 (brs, 2F), −122.90 (brs, 2F), −123.22 (brs, 4F), −124.08 (brs, 2F), −127.44 (m, 2F). ^{13}C NMR ($CDCl_3$) δ 1.8, 74.3 (tt, *J* = 19.9, 2.4 Hz), 76.0 (q, *J* = 27.9 Hz), 124.2 (q, *J* = 289.0 Hz), 128.6 (t, *J* = 5.6 Hz), 128.9, 129.5, 129.6, 132.8, 133.5. IR (KBr) ν 3586, 3078, 2971, 1371, 1235, 1180, 1155, 1035, 908, 877, 763 cm^{-1}. HRMS (APCI–) Calcd for (M+) $C_{26}H_{18}F_{20}O_2Si$: 770.0757, Found 770.0758.

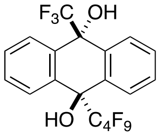
9-(Henicosafluorodecyl)-10-(trifluoromethyl)-10-(trimethylsiloxy)anthracen-9-ol



Yield: 53% (white solid). M.P. 107 – 109 °C. ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 3.01 (s, 1H), 7.50 – 7.59 (m, 4H), 7.92 – 7.97 (m, 2H), 8.03 – 8.09 (m, 2H). ^{19}F NMR ($CDCl_3$) δ −81.60 (s, 3F), −82.05 (t, *J* = 9.3 Hz, 3F), −116.41 (brs, 2F), −119.20 (brs, 2F), −123.13 (brs, 10F), −124.04 (brs, 2F), −127.42 (brs, 2F). ^{13}C NMR ($CDCl_3$) δ 2.1, 74.6 (tt, *J* = 19.8, 1.9 Hz), 76.4 (q, *J* = 27.9 Hz), 124.5 (q, *J* = 289.0 Hz), 129.0 (t, *J* = 5.6 Hz), 129.4, 129.9, 130.0, 133.2, 133.8. IR (KBr) ν 3585, 3076, 2973, 1339, 1224, 1173, 1160, 1037, 940, 879, 763 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{28}H_{18}F_{24}O_2Si$: 870.0693, Found 870.0744.

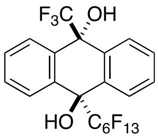
The silyl ether obtained (0.506 g, 0.89 mmol) was mixed with concentrated hydrochloric acid (0.5 mL, 6.0 mmol) in THF (5.0 mL) and the whole was stirred at reflux temperature for 3 h. The reaction mixture was poured into aqueous saturated NH_4Cl solution (10 mL), followed by extraction with AcOEt (10 mL, 3 times). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/CH_2Cl_2 (1/2) as an eluent yielded pure 9-nonafluorobutyl-10-trifluoromethylanthracene-9,10-diol (**5aA**, 0.351 g, 0.71 mmol, 79%) as a white solid.

9-(Nonafluorobutyl)-10-(trifluoromethyl)anthracene-9,10-diol (5aA)



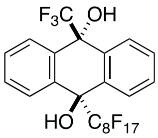
Yield: 79% (white solid). M.P. 118 – 120 °C. ^{1}H NMR ($CDCl_3$) δ 2.88 (s, 1H), 3.15 (d, *J* = 1.2 Hz, 1H), 7.55 – 7.63 (m, 4H), 8.00 – 8.08 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −79.19 (s, 3F), −82.19 (t, *J* = 9.0 Hz, 3F), −119.32 (m, 2F), −121.64 (m, 2F), −127.47 (m, 2F). ^{13}C NMR ($CDCl_3$) δ 73.3 (q, *J* = 27.9 Hz), 73.7 (tt, *J* = 18.6, 2.5 Hz), 124.0 (q, *J* = 287.8 Hz), 128.3 (q, *J* = 3.1 Hz), 128.4 (t, *J* = 5.6 Hz), 129.8, 129.9, 132.6, 132.8. IR (KBr) ν 3610, 3481, 3083, 1450, 1363, 1202, 1185, 1135, 1026, 804, 767 cm^{-1}. HRMS (FAB–) Calcd for (M–H) $C_{19}H_9F_{12}O_2$: 497.0411, Found 497.0401.

9-(Tridecafluorohexyl)-10-(trifluoromethyl)anthracen-9,10-diol (5aB)



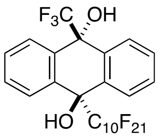
Yield: 77% (white solid). M.P. 91 – 93 °C. ^{1}H NMR ($CDCl_3$) δ 2.88 (d, *J* = 3.0 Hz, 1H), 3.16 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.58 – 7.63 (m, 4H), 8.01 – 8.07 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −79.17 (s, 3F), −82.17 (t, *J* = 9.0 Hz, 3F), −119.15 (m, 2F), −120.06 (m, 2F), −123.28 (brs, 2F), −124.15 (brs, 2F), −127.56 (m, 2F). ^{13}C NMR ($CDCl_3$) δ 73.2 (q, *J* = 27.9 Hz), 73.7 (tt, *J* = 19.2, 1.8 Hz), 124.0 (q, *J* = 287.2 Hz), 128.3 (q, *J* = 2.5 Hz), 128.4 (t, *J* = 5.6 Hz), 129.6, 129.8, 132.7, 132.9. IR (KBr) ν 3489, 3228, 1453, 1360, 1244, 1182, 1025, 924, 768 cm^{-1}. HRMS (FAB–) Calcd for (M–H) $C_{21}H_9F_{16}O_2$: 597.0347, Found 597.0385.

9-(Heptadecafluorooctyl)-10-(trifluoromethyl)anthracen-9,10-diol (5aC)



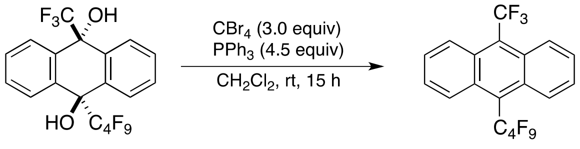
Yield: 82% (white solid). M.P. 117 – 119 °C. ^{1}H NMR ($CDCl_3$) δ 2.87 (s, 1H), 3.15 (d, *J* = 1.2 Hz, 1H), 7.54 – 7.63 (m, 4H), 8.00 – 8.08 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −79.17 (s, 3F), −82.09 (t, *J* = 9.0 Hz, 3F), −119.12 (m, 2F), −120.58 (m, 2F), −123.10 (m, 4F), −123.34 (m, 2F), −124.13 (brs, 2F), −127.47 (m, 2F). ^{13}C NMR ($CDCl_3$) δ 73.2 (q, *J* = 27.9 Hz), 73.9 (tt, *J* = 18.6 1.8 Hz), 124.0 (q, *J* = 287.8 Hz), 128.3 (q, *J* = 3.1 Hz), 128.4 (t, *J* = 5.6 Hz), 129.7, 129.8, 132.7, 132.8. IR (KBr) ν 3596, 3440, 3086, 1450, 1368, 1211, 1151, 1019, 919, 766 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{23}H_{10}F_{20}O_2$: 698.0361, Found 698.0434.

9-(Henicosafluorodecyl)-10-(trifluoromethyl)anthracen-9,10-diol (5aD)



Yield: 80% (white solid). M.P. 132 – 134 °C. ^{1}H NMR ($CDCl_3$) δ 2.86 (s, 1H), 3.14 (d, *J* = 0.6 Hz, 1H), 7.55 – 7.64 (m, 4H), 8.01 – 8.08 (m, 4H). ^{19}F NMR ($CDCl_3$) δ −79.17 (s, 3F), −82.05 (t, *J* = 9.3 Hz, 3F), −119.11 (brs, 2F), −120.57 (brs, 2F), −123.14 (brs, 10F), −124.06 (brs, 2F), −127.45 (brs, 2F). ^{13}C NMR ($CDCl_3$) δ 73.2 (q, *J* = 27.9 Hz), 73.7 (tt, *J* = 14.3, 1.8 Hz), 124.0 (q, *J* = 287.2 Hz), 128.3 (q, *J* = 3.1 Hz), 128.4 (t, *J* = 5.6 Hz), 129.7, 129.8, 132.6, 132.8. IR (KBr) ν 3585, 3077, 2910, 1450, 1338, 1222, 1175, 1037, 939, 879, 763 cm^{-1}. HRMS (APCI–) Calcd for (M–H) $C_{25}H_9F_{24}O_2$: 797.0219, Found 797.0199.

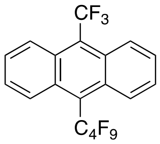
Typical procedure for the preparation of 9-nonafluorobutyl-10-trifluoromethylanthracene (6aA)



5aA **6aA**

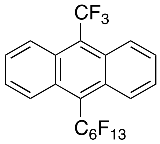
A 30 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a 9-nonafluorobutyl-10-trifluoromethylanthracen-9,10-diol (**5aA**, 0.232 g, 0.47 mmol) and CBr_4 (0.468 g, 1.4 mmol) in CH_2Cl_2 (5.0 mL). To the solution was slowly added PPh_3 (0.551 g, 2.1 mmol) in one portion at 0 °C, followed by continuous stirring at room temperature for 15 h. After being stirred for 15 h, the whole was poured into saturated aqueous NH_4Cl solution (10 mL), followed by extraction with CH_2Cl_2 (5.0 mL, 3 times). The organic layers were dried overanhydrous Na_2SO_4, filetered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as an eluent yielded pure 9-nonafluorobutyl-10-trifluoromethylanthracene (**6aA**, 0.205 g, 0.44 mmol, 93%) as a yellow powder.

9-(Nonafluorobutyl)-10-(trifluoromethyl)anthracene (6aA)



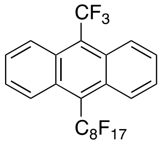
Yield: 93% (yellow powder). M.P. 89 – 91 °C. ^{1}H NMR ($CDCl_3$) δ 7.57 – 7.65 (m, 4H), 8.35 – 8.45 (m, 2H), 8.50 – 8.55 (m, 4H). ^{19}F NMR ($CDCl_3$) δ –49.62 (s, 3F), –81.87 (t, J = 9.0 Hz, 3F), –93.04 (t, J = 16.1 Hz, 2F), –119.39 (q, J = 11.6 Hz, 2F), –126.86 (m, 2F). ^{13}C NMR ($CDCl_3$) δ 124.8 (q, J = 6.3 Hz), 125.4 (tt, J = 9.9, 4.3 Hz), 125.6 (q, J = 277.9 Hz), 126.4, 126.9 (q, J = 1.2 Hz), 127.2 (t, J = 2.3 Hz), 129.4, 131.0 (t, J = 2.5 Hz). IR (KBr) ν 3155, 3100, 3052, 1350, 1290, 1238, 1134, 1032, 932, 829, 765 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{19}H_8F_{12}$: 464.0434, Found 464.0402.

9-(Tridecafluorohexyl)-10-(trifluoromethyl)anthracene (6aB)



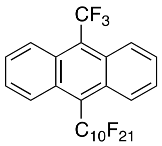
Yield: 64% (yellow powder). M.P. 101 – 103 °C. ^{1}H NMR ($CDCl_3$) δ 7.57 – 7.65 (m, 4H), 8.36 – 8.46 (m, 2H), 8.46 – 8.56 (m, 4H). ^{19}F NMR ($CDCl_3$) δ –49.64 (s, 3F), −81.94 (t, *J* = 9.0 Hz, 3F), −92.92 (t, *J* = 15.8 Hz, 2F), −118.52 (m, 2F), −122.76 (m, 2F), −123.74 (m, 2F), −127.22 (m, 2F). ^{13}C NMR (CDCl$_3$) δ 124.7 (q, *J* = 5.6 Hz), 125.4 (tt, *J* = 9.3, 4.4 Hz), 125.5 (q, *J* = 277.3 Hz), 125.8, 126.4, 126.8, 127.2, 129.4, 131.0. IR (KBr) ν 3165, 3048, 2927, 1364, 1243, 1223, 1146, 1115, 1063, 937, 774 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{21}H_8F_{16}$: 564.0370, Found 564.0394.

9-(Heptadecafluorooctyl)-10-(trifluoromethyl)anthracene (6aC)



Yield: 74% (yellow powder). M.P. 114 – 116 °C. ^{1}H NMR (CDCl$_3$) δ 7.55 – 7.65 (m, 4H), 8.32 – 8.45 (m, 2H), 8.46 – 8.57 (m, 2H). ^{19}F NMR (CDCl$_3$) δ −49.65 (s, 3F), −81.97 (t, *J* = 9.0 Hz, 3F), −92.91 (t, *J* = 16.1 Hz, 2F), −118.46 (m, 2F), −122.52 to −123.04 (m, 6F), −123.88 (brs, 2F), −127.33 (m, 2F). ^{13}C NMR (CDCl$_3$) δ 124.7 (q, *J* = 8.0 Hz), 125.4 (tt, *J* = 9.4, 5.0 Hz), 125.5 (q, *J* = 277.9 Hz), 125.8, 126.3, 126.8, 127.2, 129.3, 131.0. IR (KBr) ν 3156, 3098, 3051, 1446, 1368, 1241, 1148, 990, 766 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{23}H_8F_{20}$: 664.0307, Found 664.0336.

9-(Henicosafluorodecyl)-10-(trifluoromethyl)anthracene (6aD)



Yield: 87% (yellow powder). M.P. 115 – 117 °C. ^{1}H NMR (CDCl$_3$) δ 7.57 – 7.65 (m, 4H), 8.35 – 8.45 (m, 2H), 8.48 – 8.55 (m, 2H). ^{19}F NMR (CDCl$_3$) δ −49.65 (s, 3F), −81.98 (t, *J* = 9.0 Hz, 3F), −92.91 (t, *J* = 15.8 Hz, 2F), −118.46 (m, 2F), −122.25 to −123.22 (m, 10F), −123.94 (m, 2F), −127.34 (m, 2F). ^{13}C NMR (CDCl$_3$) δ 124.7 (q, *J* = 5.6 Hz), 125.4 (tt, *J* = 10.0, 4.4 Hz), 125.5 (q, *J* = 276.7 Hz), 125.8, 126.4, 126.8, 127.2, 129.3, 130.9. IR (KBr) ν 3098, 3075, 3048, 1340, 1215, 1153, 1115, 917, 841, 776 cm^{-1}. HRMS (FAB–) Calcd for (M+) $C_{25}H_8F_{24}$: 764.0243, Found 764.0210.

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