Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

for

Fluorine on Fluorenes

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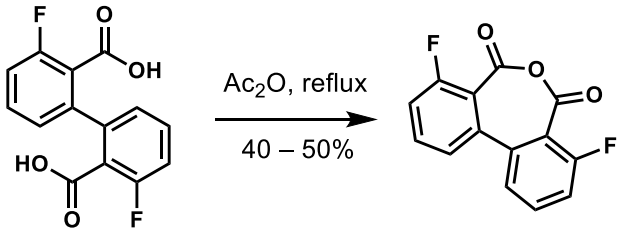
Contents

1. General Methods

All moisture and air sensitive reactions were performed under an argon atmosphere in oven-dried or flame-dried glassware. Tetrahydrofuran (THF), dichloromethane (DCM), and diethyl ether (Et_2O) were dried using a Glass Contour solvent purification system. Toluene (PhMe) was purchased from Fisher (ACS Grade) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured on a Varian Mecury-300 (300 MHz/75 MHz), Varian INOVA-500 (500 MHz/125 MHz), or Agilent 600 DD2 (600 MHz/150 MHz) spectrometers at ambient temperature. Chemical shifts are reported in parts per million (ppm) and are referenced to the solvent (*e.g.,* δ 7.26 for $CHCl_3$; δ 77.0 for $CDCl_3$). ^{19}F NMR spectra were measured on a Varian Mercury-300 (282 MHz), Varian INOVA-500 (470 MHz), or an Agilent 600 DD2 (564 MHz) spectrometer and reported in ppm relative to TFA (−76.5 ppm). Multiplicities are indicated as follows: br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), sext (sextet), sept (septet), etc. or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Shimadzu IRAffinity-1 Fourier transform or a ThermoFisher Nicolet Summit FTIR spectrophotometer. High-resolution mass spectra (HRMS) were obtained with an Agilent 1100 quaternary LC system. Compounds requiring electron impact (EI^+) ionization were obtained at the University of Illinois Mass Spectrometry Laboratory. Melting points (m.p.) were recorded on a DigiMelt MPA160 instrument and are uncorrected. Thin layer chromatography (TLC) was performed on glass plates, 250 μm, particle size 5–17 μm, pore size 60 Å. All reactions were monitored by TLC and analyzed under UV (254 and/or 365 nm) light and visualized using either PAA, $KMnO_4$, PMA, DNP, or $AgNO_3$ stains. Flash column chromatography was performed on silica gel, 200–400 mesh or premium silica gel, 60 Å, 40–75 μm. Purity and homogeneity of all materials was determined by TLC, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and LCMS. Dibromodimethylhydantoin (DBDMH) was purchased from AK Scientific (98%) and used without purification. Triflic acid was purchased from Oakwood Chemical and distilled prior to use.

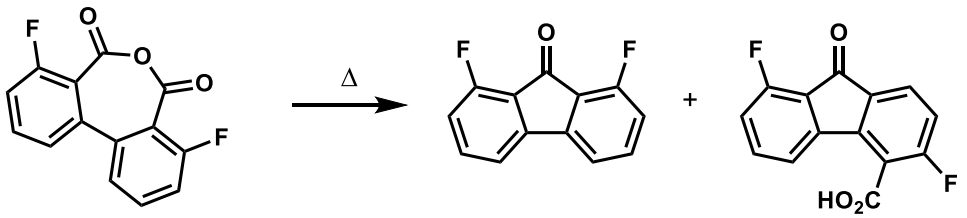
*2. Pyrolysis of Anhydride **3***



D1 **3**

3,3'-Difluoro-[1,1'-biphenyl]-2,2'-dicarboxylic acid (**D1**) was prepared according to a protocol found in the literature.[1]

4,8-Difluorodibenzo[*c*,*e*]oxepine-5,7-dione (**3**) was prepared in 40–50% yield by refluxing a mixture of 3,3'-difluoro-[1,1'-biphenyl]-2,2'-dicarboxylic acid in acetic anhydride.[2] The anhydride crystallizes from the reaction mixture when cooled. The anhydride was analyzed by ^{1}H for confirmation, but was not characterized completely. ^{1}H NMR (300 MHz, d_4-methanol) 7.83 (td, *J* = 8.2, 5.6 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 9.0 Hz, 1H).



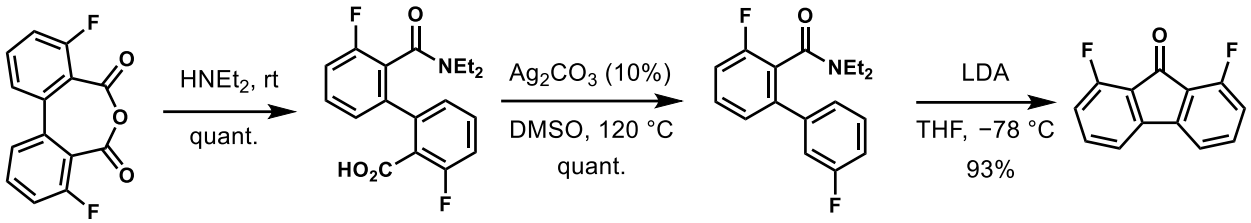
3 **6** **7**

A typical procedure for pyrolysis of 4,8-difluorodibenzo[*c*,*e*]oxepine-5,7-dione (**3**) is as follows: A test tube charged with 4,8-difluorodibenzo[*c*,*e*]oxepine-5,7-dione **3** was heated in a tube furnace (200–220 °C external temperature) open to air for one hour. After cooling to room temperature, the reaction mixture was assayed by ^{19}F NMR (d_4-MeOH). The ratio of products varied somewhat between run to run. In one case the ratio was 1.0:6.7 of 1,8-difluorofluorenone **6** to 3,8-difluoro-9-oxo-9*H*-fluorene-4-carboxylic acid **7** as determined by ^{19}F NMR analysis of the crude reaction mixture.

Pyrolyzing the anhydride in a similar manner between 300–330 °C (external temperature) for 30 min resulted in reaction that gave a 1:2 mixture of 1,8-difluorofluorenone **6** and 1,6-difluorofluorenone, respectively, as assigned based on ^{19}F NMR analysis of the crude reaction mixture.

3,8-difluoro-9-oxo-9*H*-fluorene-4-carboxylic acid (**7**) was assigned on the basis of the crude reaction mixture's ^{1}H and ^{19}F NMR spectra as: ^{1}H NMR (300 MHz, d_4-methanol) 7.24 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.60 (td, *J* = 8.1 Hz, 5.0 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.22 (dd, *J*= 9.6, 8.3 Hz, 1H), 7.12 (ddd, *J* = 9.2, 8.2, 0.9 Hz, 1H); ^{19}F NMR (272 MHz, d_4-methanol) −108.75 (dd, *J* = 9.6, 5.0 Hz), −115.60 (dd, *J* = 9.2, 5.0 Hz).

*3. Synthesis of 1,8-difluorofluorenone (**6**)*



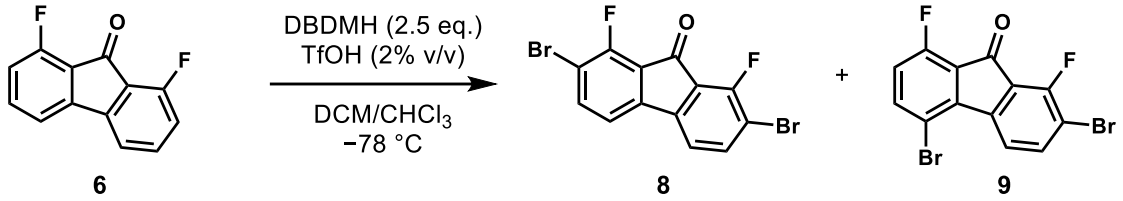
3 **4** **5** **6**

Anhydride **3** (188 mg, 0.72 mmol, 1.0 equiv) was vigorously stirred in 7 mL of diethylamine overnight. A white solid precipitated from the reaction mixture. After evaporation of diethylamine, the crude solid was diluted with diethyl ether and acidified with 1M HCl. The aqueous layer was extracted with diethyl ether (x2) and the combined organic extracts washed with 1M HCl and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and afforded compound **4** as a white, crude solid (240 mg, quantitative) that was used in the next step without purification. Compound **4** was not characterized completely. ^{1}H NMR (300 MHz, $CDCl_3$) 7.46 (ddd, *J* = 8.5, 7.6, 5.6 Hz, 1H), 7.35 (ddd, *J* = 8.5, 7.6, 5.4 Hz, 1H), 7.23–7.13 (m, 3H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.59–3.19 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (254 MHz, $CDCl_3$) −113.24 – −113.29 (m, 1H), −113.27 – −113.92 (m, 1H).

Compound **5** (45 mg, 0.15 mmol, quantitative) was prepared from compound **4** (50 mg, 0.15 mmol) using a protocol described in the literature.[3] The ^{1}H and ^{19}F NMR matched the previously reported spectral data.[4] ^{1}H NMR (500 MHz, $CDCl_3$) 7.37 (td, J = 8.1, 5.8 Hz, 1H), 7.31 (td, J = 8.0, 5.9 Hz, 1H), 7.24 (dt, J = 7.8, 1.3 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.09 (td, J = 8.6, 1.0 Hz, 1H), 7.01 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H), 3.74 (dq, J = 14.0, 7.1 Hz, 1H), 3.03 (dq, J = 14.0, 7.1 Hz, 1H), 2.98 (dq, J = 14.3, 7.1 Hz, 1H), 2.77 (dq, J = 14.3, 7.1 Hz, 1H), 0.90 (t, J = 7.1 Hz, 3H), 0.83 (t, J = 7.1 Hz, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) −113.47 (ddd, J = 9.9, 8.6, 5.9 Hz, 1F), −116.49 (dd, J = 8.9, 5.8 Hz, 1F).

Compound **6** was prepared from compound **5** according to a protocol described in the literature.[4]

*4. Synthesis of 2,7-dibromo-1,8-difluoro-9H-fluoren-9-one (**8**)*



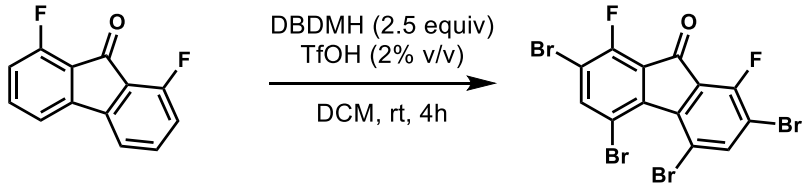
6 **8** **9**

To a mechanically stirred solution of DBDMH (2.15 g, 7.50 mmol, 2.5 equiv) in DCM/$CHCl_3$ (7:1) containing 2% v/v triflic acid at −78 °C was slowly added a solution of 1,8-difluorofluorenone **6** (648 mg, 3.0 mmol, 1.0 equiv). Upon completion as determined by TLC, the reaction mixture was quenched by the addition of $NaHCO_3$ (sat. aq.) and allowed to warm to room temperature. The phases were separated and the aqueous extracted with DCM (x3). The combined organic extracts were washed with Na_2SO_3 (aq. soln) and 1.0 M NaOH, and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed in vacuo to afford a crude solid (1.10 g) that contained **8** and **9** in a 2:1 ratio, respectively, as determined by ^{19}F NMR. Compound **8** was isolated as yellow needles (473 mg, 42%; 40% PhMe/Hex, 3.5 mg/mL) by recrystallization from the crude mixture as follows: the crude solid was dissolved in a mixture of hot toluene and hexane, and the solution was allowed to cool to room temperature overnight.

Compound **8** did not melt below 260 °C; ^1H NMR (300 MHz, $CDCl_3$) 7.72 (dd, J = 7.8, 6.0 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150, MHz) 155.7 (d, J_{CF} = 266.4 Hz), 184.2, 143.6, 140.0, 120.4 (d, J_{CF} = 13.5 Hz), 117.7 (d, J_{CF} = 4.1 Hz), 111.8 (d, J_{CF} = 20.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) −106.78 (d, J = 6.0 Hz); IR (neat, cm^{-1}) 1716; HRMS (ESI^+) calcd for $C_{13}H_4Br_2F_2NaO$ $[M+Na]^+$ 394.8489; found 394.8478.

The inseparable mixture of **8** and **9** (7.75 g, 20.6 mmol) from the combined mother liquor of numerous bromination reactions could be recycled back to 1,8-difluorofluorenone **6** by treatment of a degassed toluene solution (0.05 M) of **8** and **9** with triethylsilane (16.0 mL, 100 mmol, 5.0 eq) and $PdCl_2$ (10 mol%) at room temperature for 2 h. After filtration over Celite, the reaction mixture was washed with $NaHCO_3$ (sat. aq.), water, and brine. After drying over anhydrous Na_2SO_4, the extracts were filtered and concentrated. The crude solid was purified by silica gel chromatography (PhMe) to afford compound **6** (3.35 g) in 75% yield.[5]

*5. Synthesis of 2,4,5,7-tetrabromo-1,8-difluoro-9H-fluoren-9-one (**14**)*



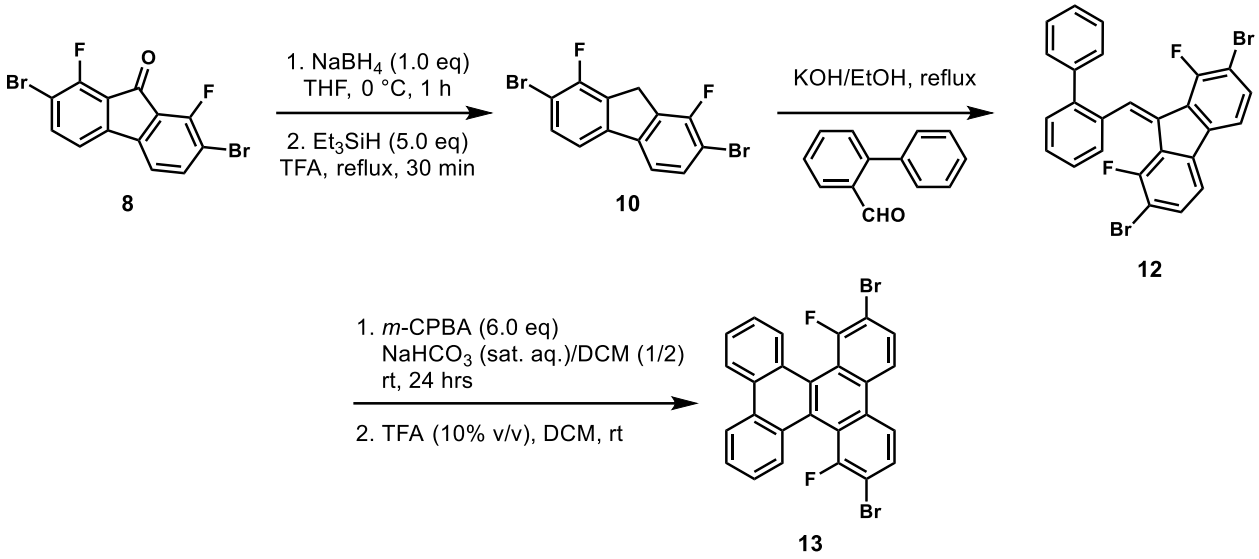
6 **14**

2,4,5,7-tetrabromo-1,8-difluoro-9*H*-fluoren-9-one (**14**)

To a stirred solution of 1,8-difluorofluoreneone **6** (216 mg, 1.0 mmol, 1.0 equiv), DBDMH (715 mg, 2.5 mmol, 2.5 equiv) in DCM (25 mL) was added triflic acid (0.5 mL) at room temperature. The reaction mixture was stirred for four hours before being quenched by the addition of $NaHCO_3$ (sat. aq.) The phases were separated and the aqueous phase extracted with DCM (x3). The combined organic extracts were washed with $NaHCO_3$ (sat. aq.) and Na_2SO_3 (aq.) solutions, and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed in vacuo to afford a crude solid that contained compound **14** with ~95% purity (89% yield)**.** The primary impurity is a pentabrominated fluorenone byproduct that cannot be removed chromatographically (this is seen as an impurity in the ^{19}F NMR). Further purification could be achieved by recrystallization from a solution of **14** dissolved in a minimal amount of hot ethyl acetate layered with three times the volume of hexane.

m.p. 216–218 °C; ^{1}H NMR (600 MHz, $CDCl_3$) 7.97 (d, J = 6.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) 181.4, 155.5 (d, J_{CF} = 267.2 Hz), 145.5, 142.8 (dd, J_{CF} = 3.0, 2.0 Hz), 123.7 (d, J_{CF} = 13.6 Hz), 113.5 (d, J_{CF} = 21.2 Hz), 112.0 (d, J_{CF} = 3.5 Hz), ^{19}F NMR (564 MHz, $CDCl_3$) −110.59 (d, J = 6.0 Hz); IR (neat, cm^{-1}) 1718; HRMS (EI^+) calcd for $C_{13}H_2Br_4F_2O$ [M^+] 527.6802; found: 527.6807.

6. *Synthesis of 3,14-dibromo-4,13-difluorodibenzo[g,p]chrysene (**13**)*



2,7-dibromo-1,8-difluoro-9*H*-fluorene (**10**):

To a stirred solution of fluorenone **8** (748 mg, 2.0 mmol, 1.0 equiv) in THF (50 mL) at 0 °C was added sodium borohydride (76 mg, 2.0 mmol, 1.0 equiv) in portions. The reaction mixture was quenched by the addition of 1 M HCl and extracted with DCM (x3). The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and afforded the crude fluorenol as a white solid (753 mg) that was used in the next step without purification.

To a stirred solution of crude fluorenol (753 mg) in TFA (100 mL) at room temperature was added triethylsilane (1.6 mL, 10 mmol, 5.0 equiv). The reaction mixture was refluxed for 30 min before diluting with water and DCM at room temperature. The phases were separated and the aqueous layer was extracted with DCM (x2). The combined organic extracts were washed with water and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed in vacuo to afford a crude solid. The crude solid was purified by silica gel chromatography (dry load, hexanes as eluent) affording fluorene **10** as a white solid (608 mg, 84% yield).

m.p. 160–162 °C; ^{1}H NMR (600 MHz, $CDCl_3$) 7.58 (dd, J = 8.1, 6.2 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 4.00 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 155.9 (d, J_{CF} = 249.1 Hz), 142.7, 133.0, 129.4 (d, J_{CF} = 19.4 Hz), 117.1 (d, J_{CF} = 3.9 Hz), 108.0 (d, J_{CF} = 20.2 Hz), 30.9; ^{19}F NMR (564 MHz, $CDCl_3$) −111.4 (d, J = 6.2 Hz); IR (neat, cm^{-1}) 2853, 2903, 2922, 2951, 1570, 1473, 1442, 1425, 1220, 996; HRMS (EI^{+}) calcd for $C_{13}H_6Br_2F_2$ [M^{+}] 357.8799; found: 357.8813.

9-([1,1'-biphenyl]-2-ylmethylene)-2,7-dibromo-1,8-difluoro-9*H*-fluorene (**12**):

To a stirred suspension of 2,7-dibromo-1,8-difluoro-9*H*-fluorene **10** (486 mg, 1.35 mmol, 1.0 equiv) and [1,1'-biphenyl]-2-carbaldehyde (369 mg, 2.0 mol, 1.5 equiv) in degassed absolute ethanol (14 mL) was added KOH (151 mg, 2.7 mol, 2.0 equiv). The reaction mixture was heated to reflux for 6 h. The reaction mixture was cooled to room temperature and quenched with NH_4Cl (sat. aq.) and diluted with DCM. The phases were separated and the aqueous layer was extracted with DCM (x2). The combined organic extracts were washed with water and brine, and dried over

anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo to afford a crude solid. The crude mixture was purified by silica gel chromatography (dry load, gradient of 5, 10, 15, 20, 25% DCM in hexane) to afford compound **12** as a yellow solid (672 mg, 95% yield).

m.p. 215–217 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 8.03 (d, J = 4.3 Hz, 1H), 7.60 – 7.31 (m, 13H); ^{13}C NMR (150 MHz, $CDCl_3$) 155.3 (d, J_{CF} = 253.2 Hz), 154.4 (d, J_{CF} = 258.4 Hz), 141.7 (m), 141.5, 140.5, 139.3 (m), 138.7 (d, J_{CF} = 1.9 Hz), 138.6 (d, J_{CF} = 2.1 Hz), 136.3 (d, J_{CF} = 4.7 Hz), 133.4, 132.3, 131.1 (d, J_{CF} = 7.8 Hz), 129.8, 129.1, 129.0, 128.2, 127.5, 126.9 (d, J_{CF} = 12.0 Hz), 126.6, 123.9 (d, J_{CF} = 16.1 Hz), 116.7 (d, J_{CF} = 3.5 Hz), 116.6 (d, J_{CF} = 4.0 Hz), 109.2 (d, J_{CF} = 22.5 Hz), 108.8 (d, J_{CF} = 21.0 Hz); ^{19}F NMR (272 MHz, $CDCl_3$) −91.12 (d, J = 5.3 Hz, 1F), −112.46 (t, J = 5.3 Hz, 1F); IR (neat, cm^{-1}) 2976, 2959, 2951, 2920, 2868, 2850, 1457, 1413, 1411; HRMS (EI^{+}) calcd for $C_{26}H_{14}Br_2F_2$ [M^{+}]: 521.9424; found: 521.9419.

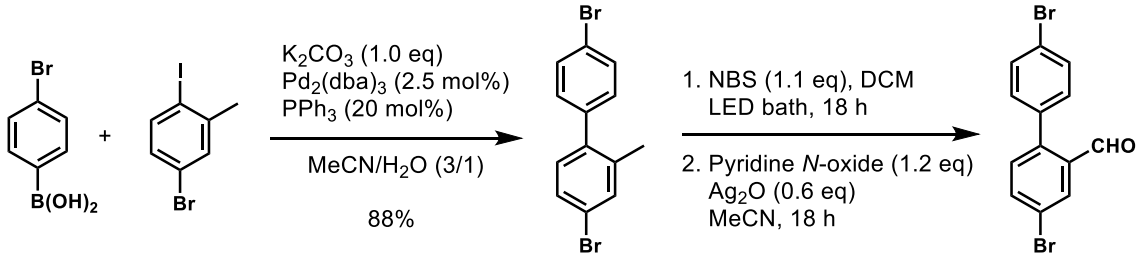
3,14-dibromo-4,13-difluorodibenzo[*g*,*p*]chrysene (**13**):

To a vigorously stirred solution of 9-([1,1'-biphenyl]-2-ylmethylene)-2,7-dibromo-1,8-difluoro-9*H*-fluorene **13** (783 mg, 1.5 mmol, 1.0 equiv) in DCM (75 mL) and $NaHCO_3$ (sat. aq., 35 mL) at room temperature was added *m*-CPBA (1.50 g, 9.0 mmol, 6.0 equiv) in 2 equiv portions every 4 h. The reaction mixture turned reddish-orange in color. Upon completion of the reaction, the phases were separated and the aqueous layer was extracted with DCM (x3). The combined organic extracts were washed with Na_2SO_3 (aq.) and $NaHCO_3$ (sat. aq.), and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo to afford a crude solid (860 mg) that was used in the next step without purification.

To a solution of crude epoxide in DCM (68 mL) at room temperature was added TFA (7.5 mL) all at once. The reaction mixture was allowed to stir at room temperature overnight before dilution with water. The phases were separated and the aqueous layer extracted with DCM (x2). The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. After filtration the solvent was removed in vacuo to afford a crude solid. The crude solid was purified by silica gel chromatography **13** (dry load, gradient of 5, 10, 15, 20, 25% DCM in hexane) to afford compound as an off-white solid (393 mg, 50% yield).

m.p. 243–245 °C; ^{1}H NMR (600 MHz, $CDCl_3$) 8.60 (d, J = 8.1 Hz, 2H), 8.36 (d, J = 8.8 Hz, 2H), 7.95 (dd, J = 13.5, 8.2 Hz, 2H), 7.86 (dd, J = 8.8, 6.5 Hz, 2H), 7.70 (t, J = 7.5 Hz, 2H), 7.62 (t, J = 7.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 154.8 (d, J_{CF} = 255.4 Hz), 131.2, 131.1 (t, J_{CF} = 2.8 Hz), 130.1 (d, J_{CF} = 1.4 Hz), 129.4 (d, J_{CF} = 4.1 Hz), 129.2 (d, J_{CF} = 13.9 Hz), 127.2, 126.8 (d, J_{CF} = 2.8 Hz), 126.0 (d, J_{CF} = 2.2 Hz), 122.9, 120.6 (d, J_{CF} = 2.2 Hz), 119.3 (d, J_{CF} = 12.2 Hz), 109.0 (d, J_{CF} = 23.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) −91.36 (dd, J = 13.5, 6.5 Hz); IR (neat, cm^{-1}) 3072, 2923, 1595, 1533, 1451, 1370, 1308; HRMS (ESI^{+}) calcd for $C_{26}H_{12}Br_2F_2$ [M]$^{+}$ 519.9268; found: 519.9251.

*7. 3,14-dibromo-5,12-difluorodibenzo[g,p]chrysene (**19**)*

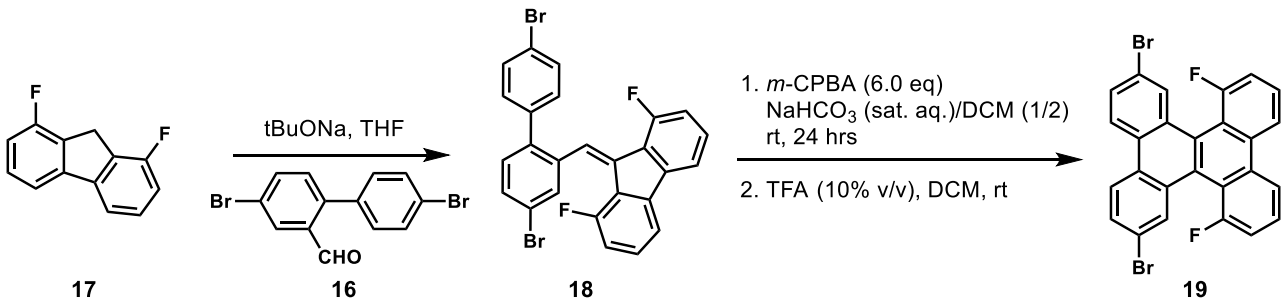


15 **16**

The synthesis of 4,4'-dibromo-[1,1'-biphenyl]-2-carbaldehyde was carried out in three steps as shown above. Suzuki cross coupling of commercially available 4-bromophenylboronic acid and 4-bromo-1-iodo-2-methylbenzene to give 4,4'-dibromo-2-methyl-1,1'-biphenyl (**15**, 6.83 g, 88% yield) was carried out according to protocol found in the literature.[6]

A stirred solution of 4,4'-dibromo-2-methyl-1,1'-biphenyl (**15**, 6.83 g, 20.95 mmol) and NBS (4.10 g, 23.0 mmol, 1.1 equiv) in DCM (0.2 M) was irradiated with white LED strip light bath overnight. The reaction mixture was quenched by the addition of $NaHCO_3$ (sat. aq.) and $NaSO_3$ (aq. soln). The phases were separated and the organic was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo and afforded the crude benzylic bromide (8.32 g, 98% yield) which was used in the next step without purification.

The benzylic bromide was converted to carbaldehyde **16** (3.6 g, 51% yield, white solid) according to a protocol found in the literature.[7] Carbaldehyde **16** was characterized by ^{1}H NMR and used immediately in the next step. ^{1}H NMR (300 MHz, $CDCl_3$) 9.89 (s, 1H), 8.14 (d, *J* = 2.2 Hz, 1H), 7.76 (ddd, *J* = 8.2, 2.2, 0.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H).



17 **16** **18** **19**

9-((4,4'-dibromo-[1,1'-biphenyl]-2-yl)methylene)-1,8-difluoro-9*H*-fluorene (**18**)

To a solution of 1,8-difluorofluorene (893 mg, 4.42 mmol, 1.0 equiv) in THF (0.1 M) was added *t*BuONa (425 mg, 4,42 mmol, 1.0 equiv) at room temperature. After stirring for 5 minutes, carbaldehyde **16** (2.25 g, 6.63 mmol, 1.5 equiv) was added and the reaction mixture stirred overnight. The reaction was incomplete and made no further progress.* The reaction mixture was quenched by the addition of NH_4Cl (sat. aq.). The phases were separated and the aqueous extracted with diethyl ether (x2). The combined organic extracts were washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo to afford a crude solid. The crude solid was purified by silica gel chromatography (dry load, hexane

as eluent to recover unreacted fluorene, then a gradient of 2, 5% ethyl acetate in hexane) affording compound **18** as a yellow solid (1.71 g, 92% yield BRSM).

m.p. 172 – 175 °C; ^{1}H NMR (600 MHz, $CDCl_3$) 7.82 (d, *J* = 4.4 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.50 (brt, *J* = 2.7 Hz, 1H), 7.49 – 7.47 (d, *J* = 8.6 Hz, 2H), 7.39 (td, *J* = 7.9, 4.6 Hz, 1H), 7.34 – 7.28 (m, 4H), 7.00 (dd, *J* = 11.1, 8.1 Hz, 1H), 6.95 (dd, *J* = 10.7, 8.1 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) 159.4 (d, J_{CF} = 252.6 Hz), 158.4 (d, J_{CF} = 256.6 Hz), 143.6 (dd, J_{CF} = 5.1, 2.2 Hz), 141.1 (dd, J_{CF} = 5.0, 2.4 Hz), 138.8 (d, J_{CF} = 5.2 Hz), 138.6 (d, J_{CF} = 5.4 Hz), 133.6 (d, J_{CF} = 7.6 Hz), 133.5 (d, J_{CF} = 2.3 Hz), 133.4 (d, J_{CF} = 2.4 Hz), 133.1 (t, J_{CF} = 5.3 Hz), 131.4, 131.2, 131.1, 130.6 (d, J_{CF} = 8.2 Hz), 130.2, 129.4 (d, J_{CF} = 8.1 Hz), 125.4 (d, J_{CF} = 11.0 Hz), 122.2 (d, J_{CF} = 15.0 Hz), 122.0, 120.7, 116.2 (d, J_{CF} = 3.1 Hz), 116.0 (d, J_{CF} = 2.9 Hz), 115.5 (d, J_{CF} = 23.1 Hz), 115.3 (d, J_{CF} = 21.7 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) –98.97 (ddd, *J* = 10.9, 4.7, 2.6 Hz, 1F), –118.22 (dt, *J* = 10.6, 4.6 Hz, 1F); IR (neat, cm^{-1}) 3070, 1914, 1620, 1582, 1482, 1425, 1350, 1235; HRMS (EI^+) calcd for $C_{26}H_{14}Br_2F_2$ [M^+]: 521.9424; found: 521.9430.

*Disproportionation byproducts of the carbaldehyde (Cannizzaro reaction) were identified in the reaction mixture.

3,14-dibromo-5,12-difluorodibenzo[*g*,*p*]chrysene (**19**)

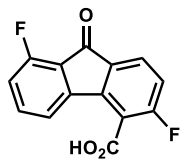
Compound **19** was prepared in an analogous way to compound **13**. Compound **19** was isolated as an off-white solid (206 mg, 53% yield).

m.p. 259 – 260 °C; ^{1}H NMR (600 MHz, $CDCl_3$) 8.53 (d, *J* = 8.4 Hz, 2H), 8.38 (d, *J* = 8.7 Hz, 2H), 8.12 (d, *J* = 12.9 Hz, 2H), 7.75 – 7.70 (m, 4H), 7.43 (dd, *J* = 12.2, 7.9 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) 158.6 (d, J_{CF} = 254.0 Hz), 132.8 (t, J_{CF} = 3.4 Hz), 131.8 (d, J_{CF} = 14.4 Hz), 131.2 (d, J_{CF} = 4.0 Hz), 129.9, 128.3 (d, J_{CF} = 9.7 Hz), 128.0, 126.3, 124.3, 120.2 (d, J_{CF} = 3.5 Hz), 120.1, 117.8 (d, J_{CF} = 10.8 Hz), 115.0 (d, J_{CF} = 23.9 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) −99.00 – −99.08 (m); IR (neat, cm^{-1}) 3072, 2922, 1611, 1592, 1571, 1471, 1451, 1307, 1239; HRMS (EI^+) calcd for $C_{26}H_{12}Br_2F_2$ [M^+]: 519.9268; found 519.9274.

8. References

1. H. Gong, H. Zeng, F. Zhou and C.-J. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 5718–5721.
2. E. H. Huntress, I. S. Cliff, *J. Am. Chem. Soc.*, 1933, **55**, 2559–2567.
3. J. Cornelia, C. Sanchez, D. Banawa and I. Larrosa, *Chem. Commun.* 2009, 7176–7178.
4. C. F. Dickinson, J. K. Yang, G. P. A. Yap, M. A. Tius, *Org. Lett.*, 2022, **24**, 5095–5098.
5. R. Boukherroub, C. Chatgilialoglu, G. Manuel, *Organometallics*, 1996, **15**, 1508–1510.
6. S. Zhou, Y. Zhou, H. Tian, Y. Zhu, Y. Pan, F. Zhou, Q. Zhang, Z. Shen, X. Fan, *J. Polym. Sci. A1*, 2014, **52**, 1519–1524.
7. D. X. Chen, C. M. Ho, Q. Y. Rudy, P. R. Wu, F. M. Wong, W. Wu, *Tetrahedron Lett.* 2008, **49**, 4147–4148.

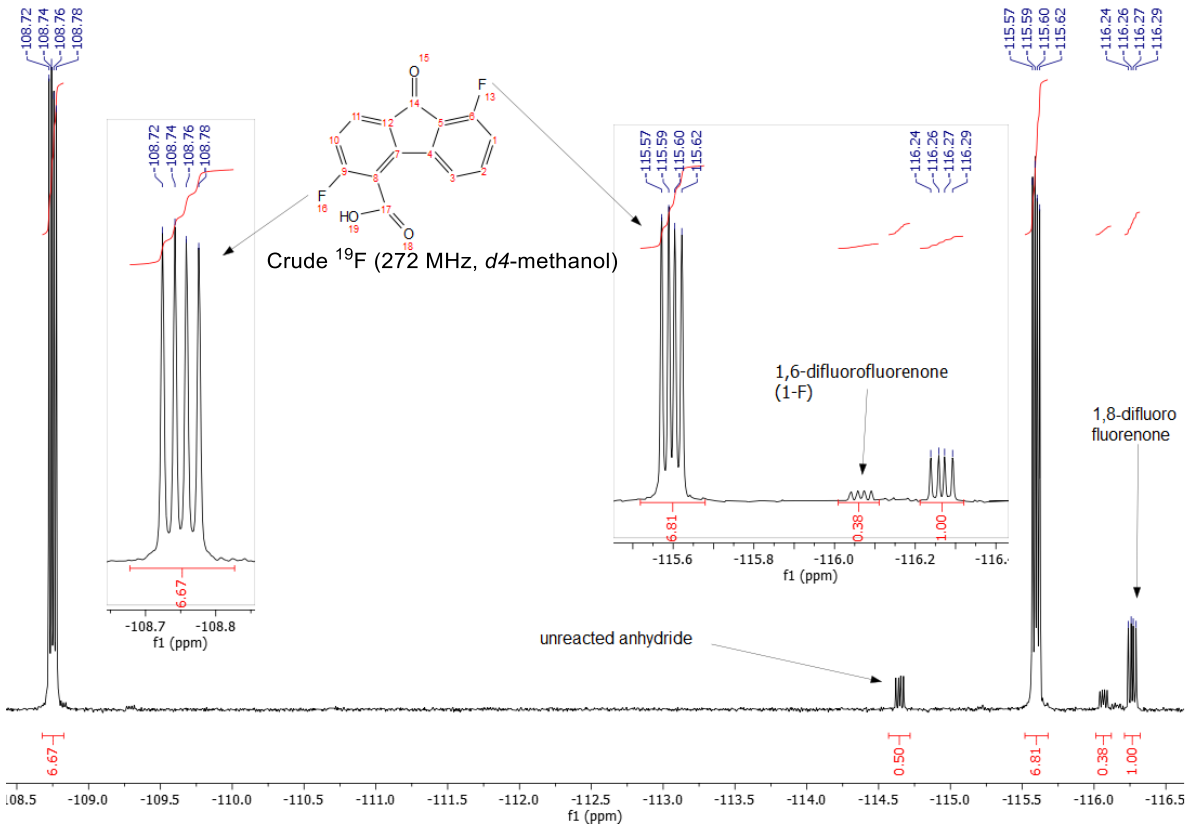
9. NMR Spectra

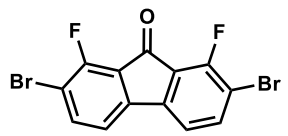


7

Crude ^{1}H (300 MHz, *d4*-methanol)

Crude ^{19}F (272 MHz, *d4*-methanol)





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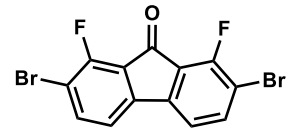
^{1}H NMR (600 MHz, $CDCl_3$)



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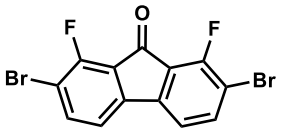
^{13}C NMR (150 MHz, $CDCl_3$)



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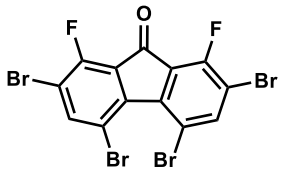
^{19}F NMR (564 MHz, $CDCl_3$)



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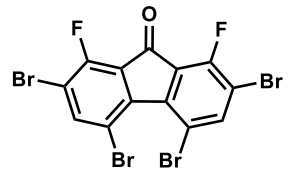

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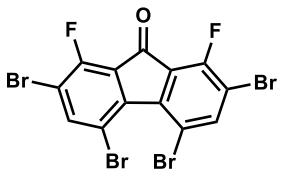

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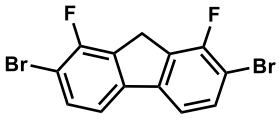

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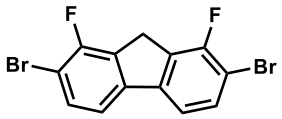

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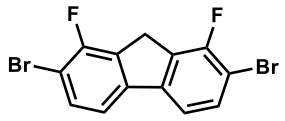

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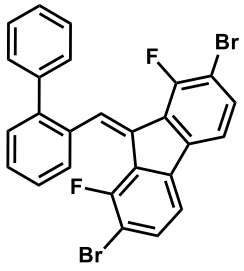

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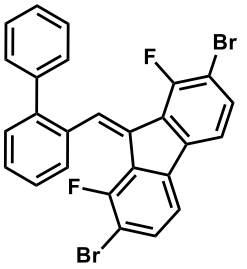

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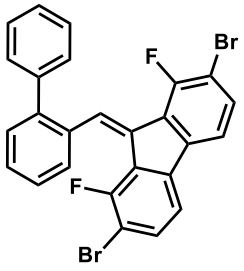
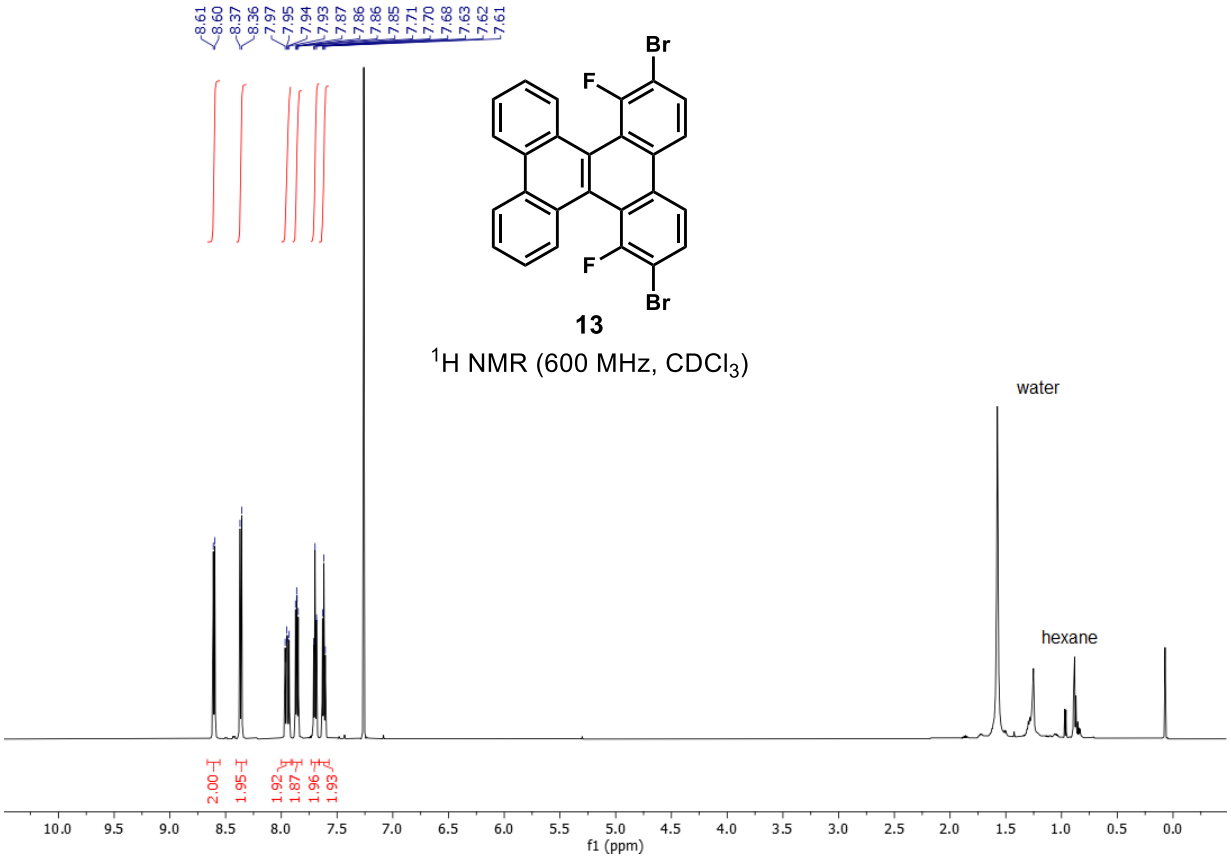


12

^{19}F NMR (272 MHz, $CDCl_3$)



13

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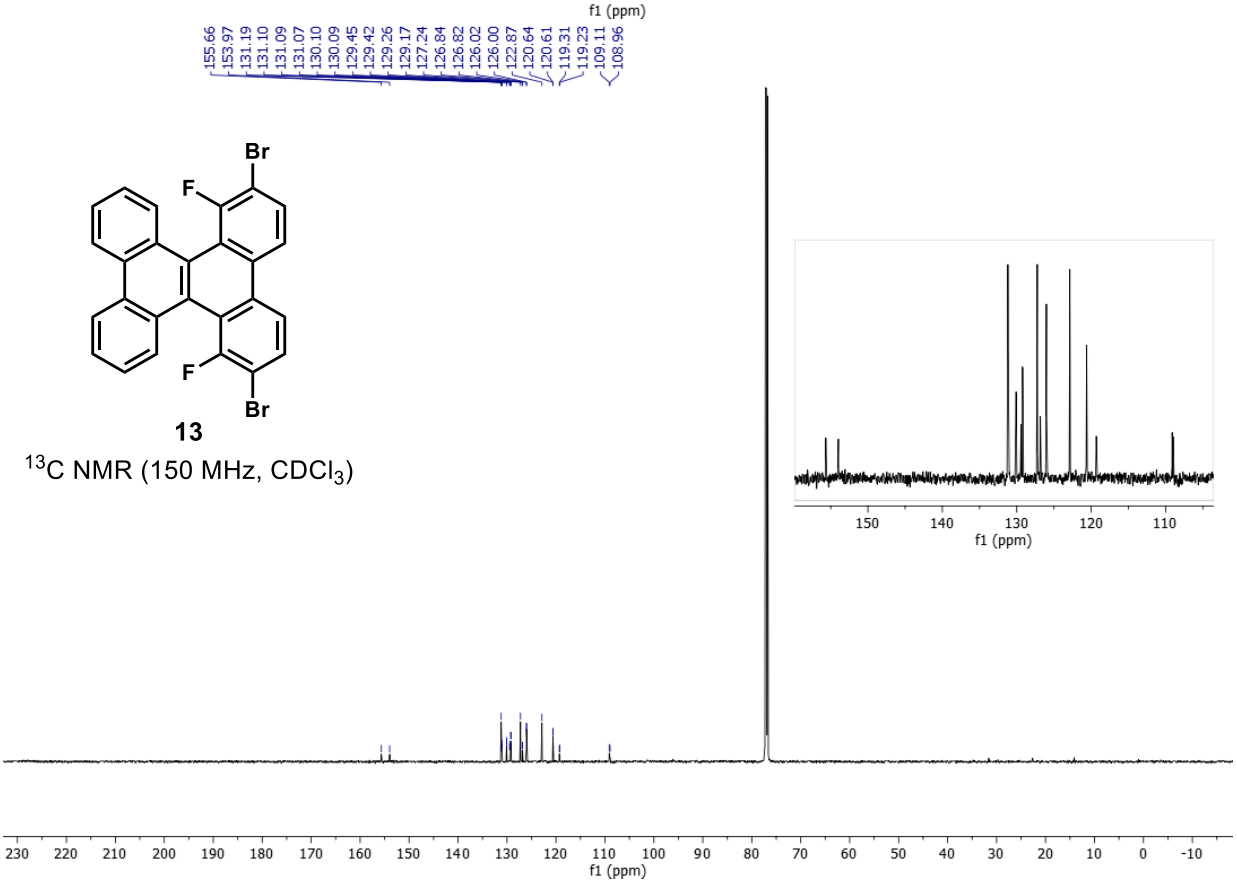

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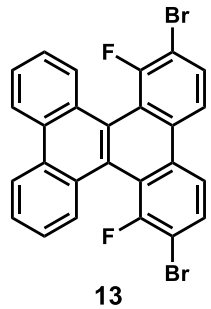
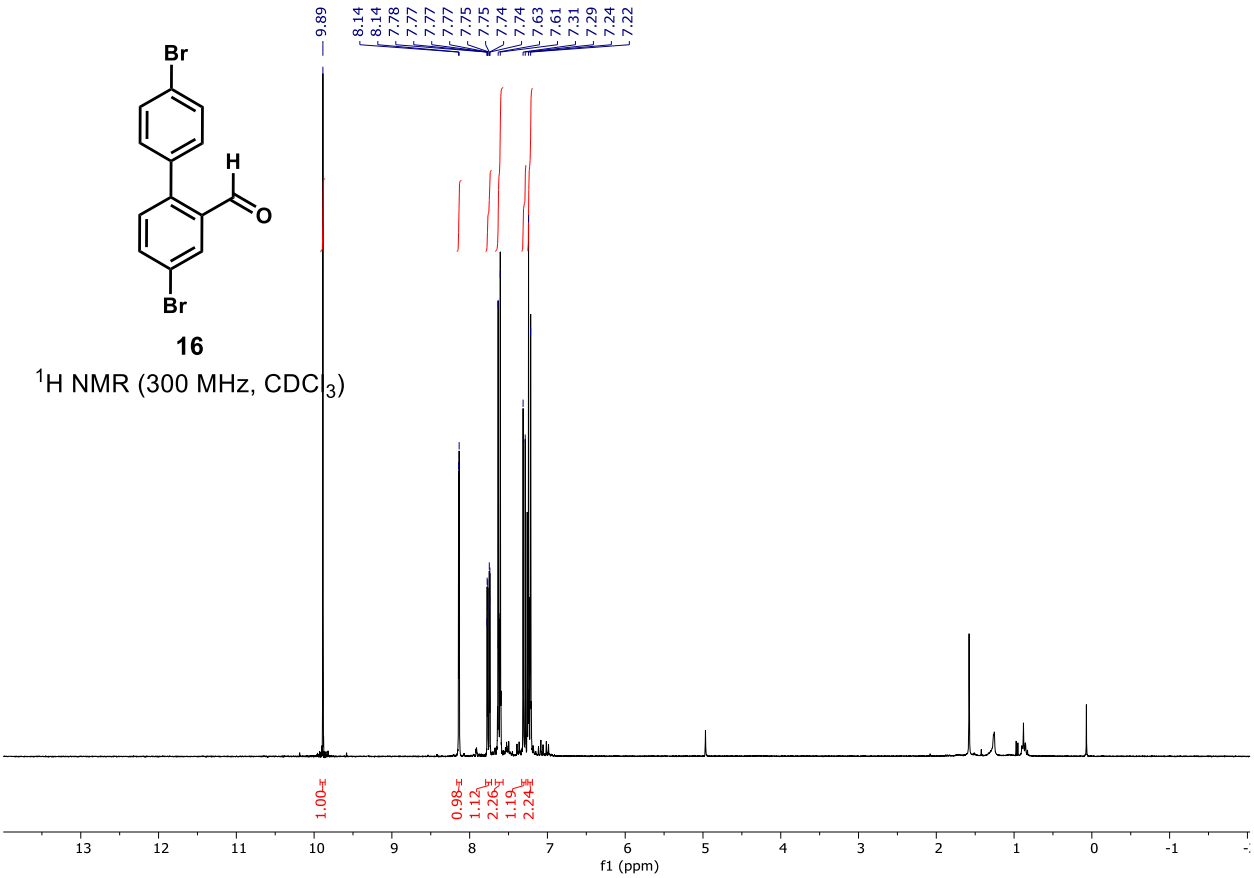


13

^{19}F NMR (564 MHz, $CDCl_3$)


Br
H
O
Br
16
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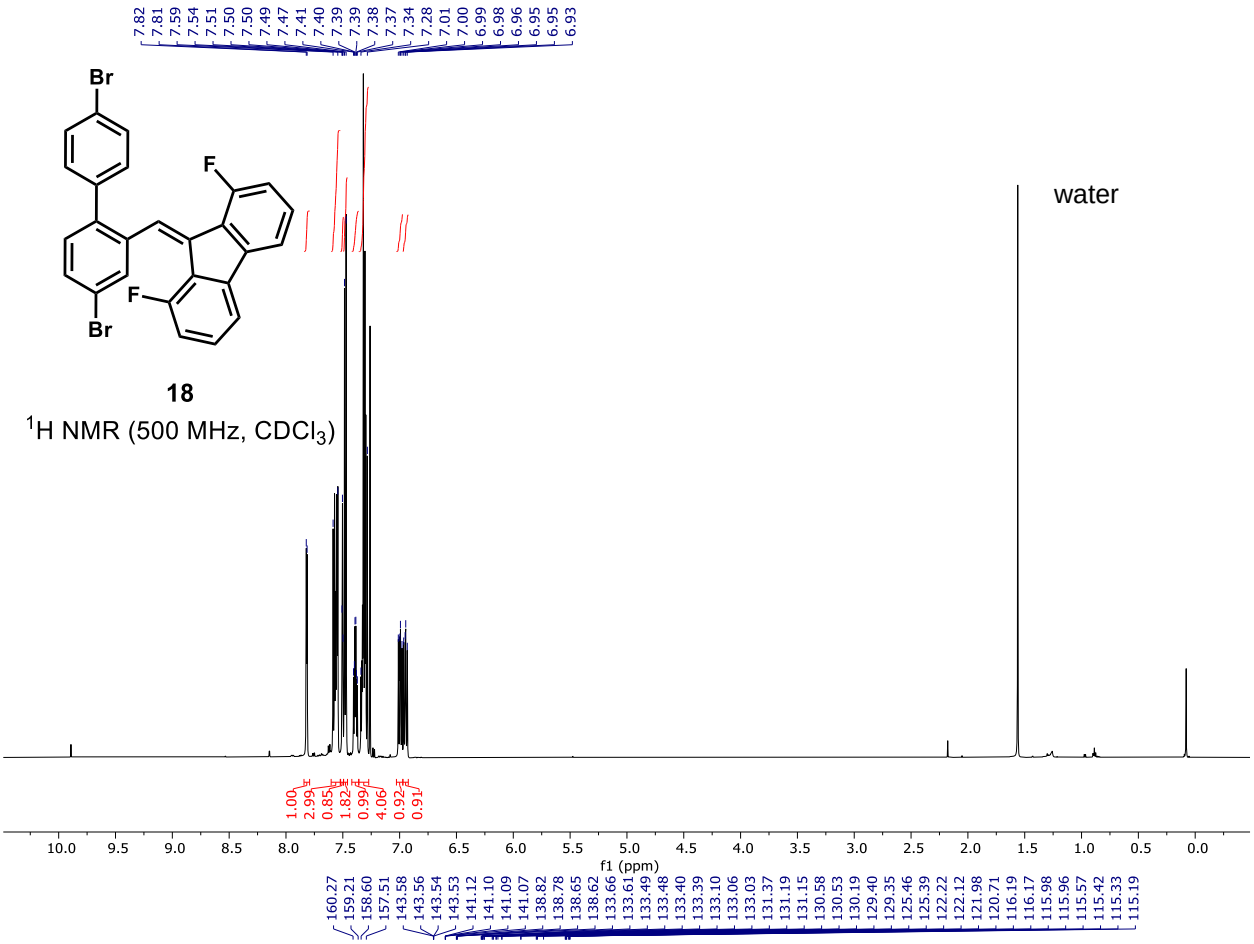
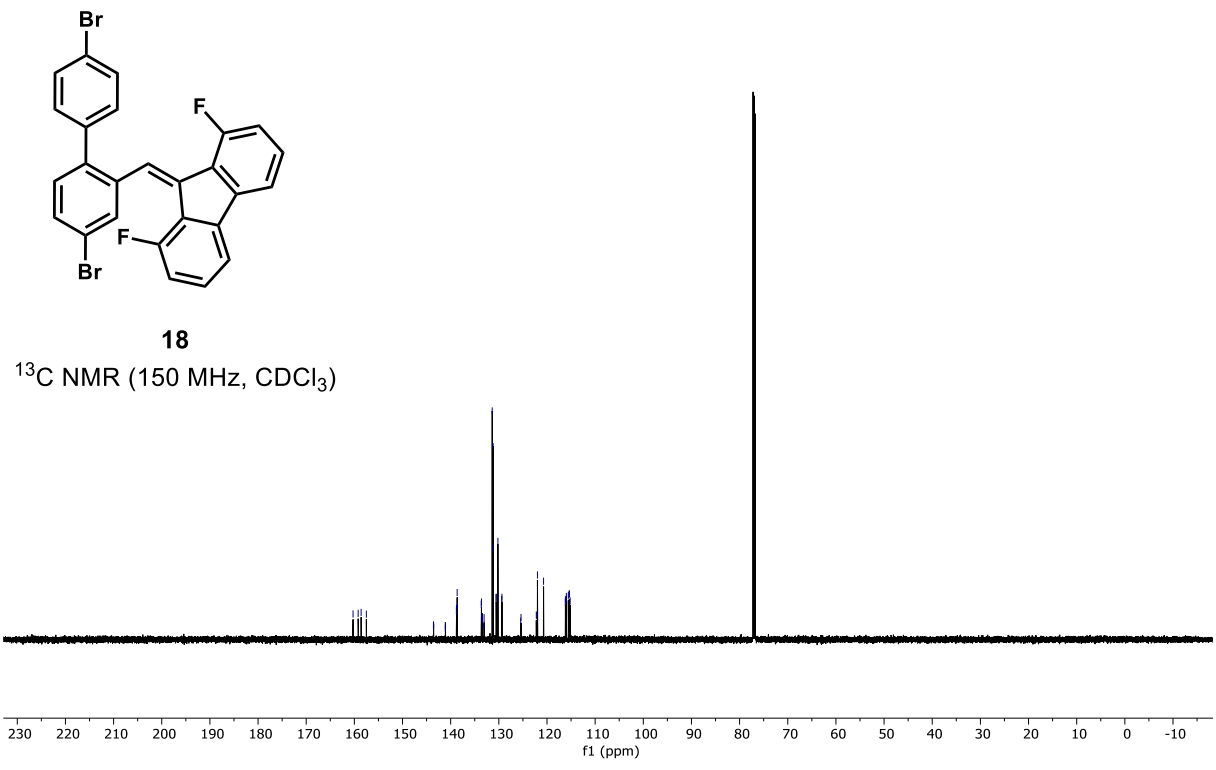
8.14
8.14
7.78
7.77
7.77
7.77
7.75
7.75
7.74
7.74
7.63
7.61
7.31
7.29
7.24
7.22
1.00
0.98
1.12
2.26
1.19
2.24
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)



18

^{1}H NMR (500 MHz, $CDCl_3$)



18

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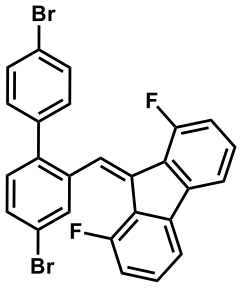

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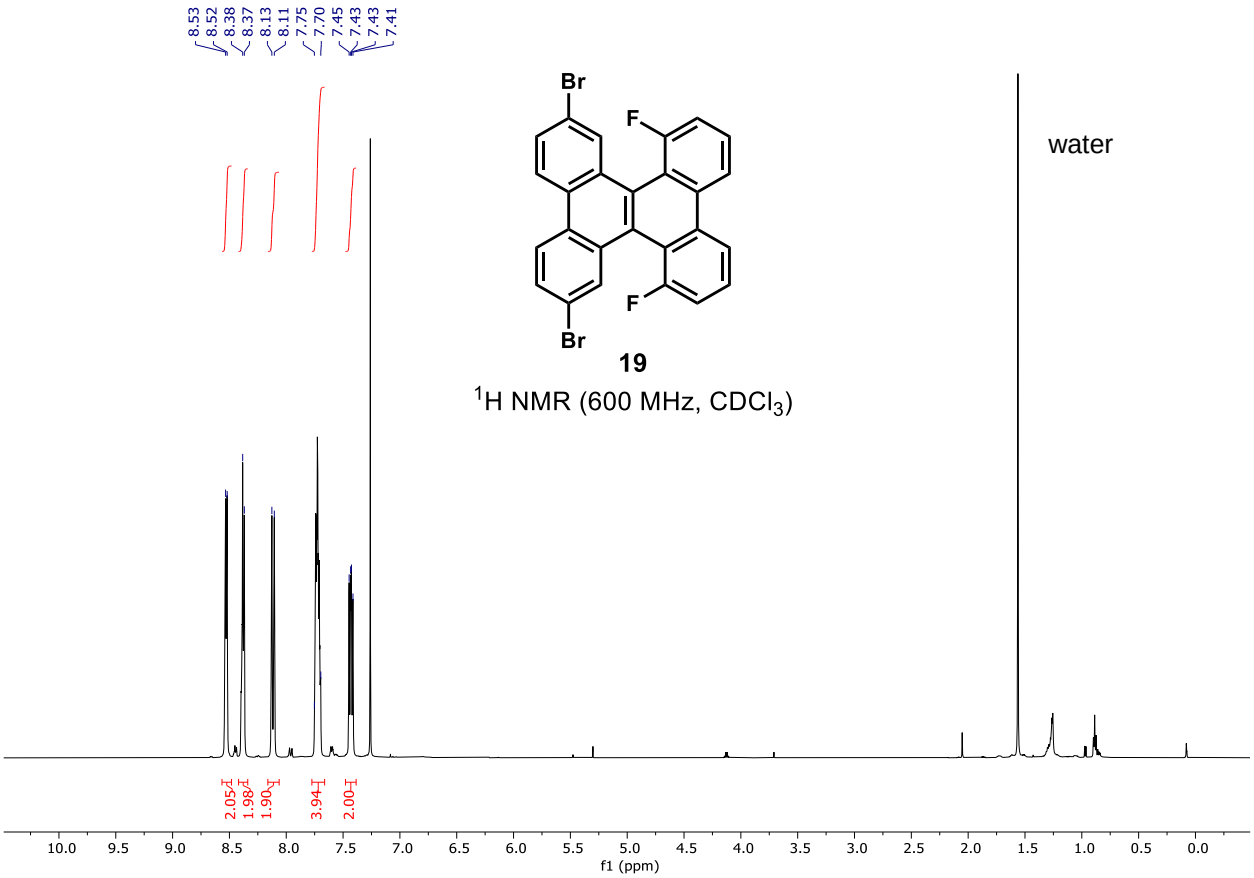

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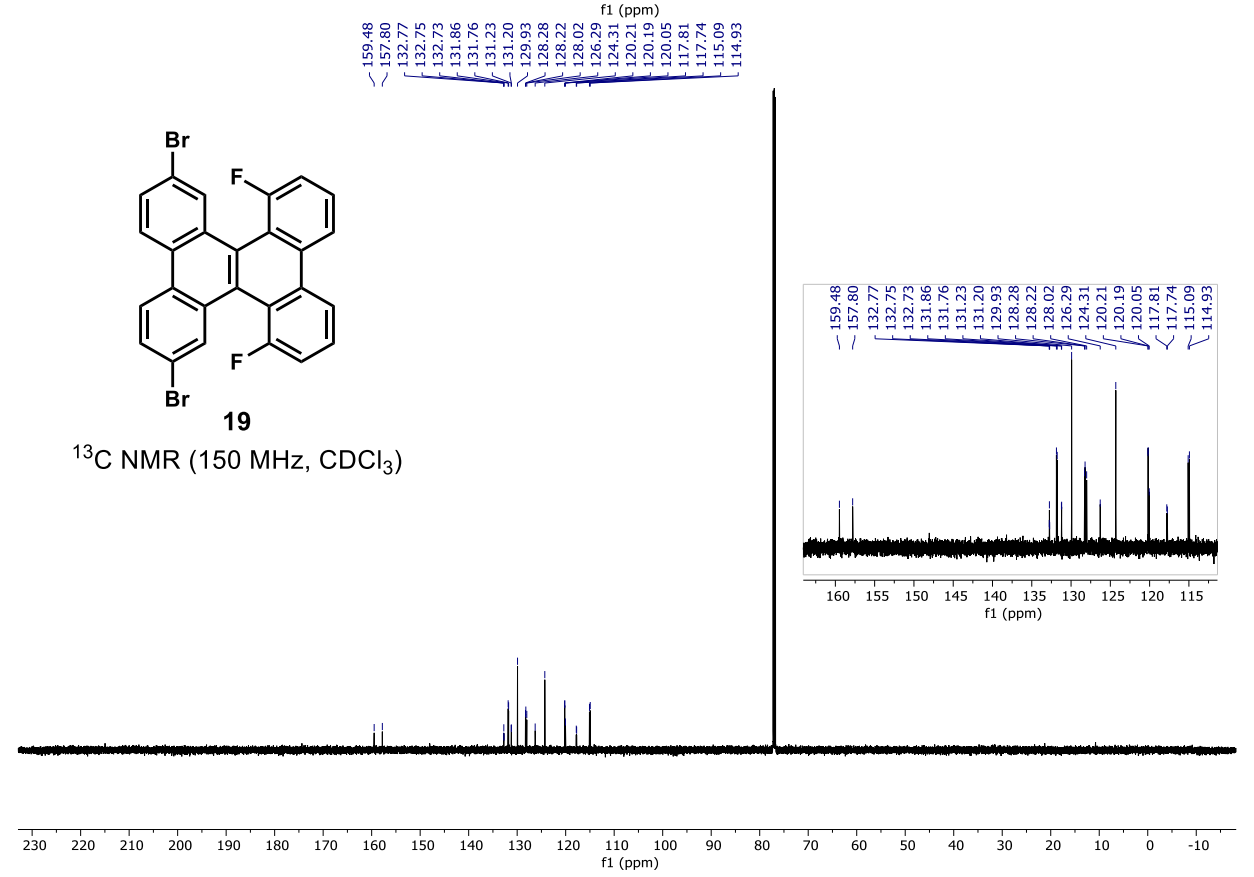

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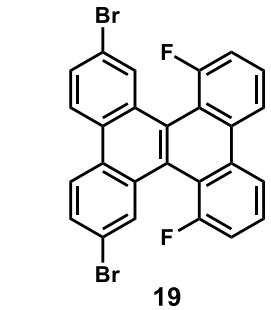

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