Supporting information of

Straightforward and regiospecific synthesis of 1,3,5,7-tetra-arylated acene bearing different aryl groups

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This supplementary information file replaces that originally published on 16 May 2023, in which the legend for Fig. S5 was incorrect. This does not affect the results or conclusions reported in the article.

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General, Measurement, and Materials.

^{1}H, ^{19}F, and $^{13}C\{^{1}H\}$ NMR spectra were recorded using Bruker AVANCE-400 NMR spectrometer and AVANCE-600 NMR spectrometer. APCI TOF/Mass spectra were recorded on Bruker micrOTOF2−kp. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN elemental analyzer and Yanaco CHN coder MT-6 or MT-5. Crystal Structure Determination Intensity data were collected on a Bruker SMART APEX II ULTRA with Mo Kα radiation.

UV−vis absorption and PL spectra for solution, crystal, and ground powder samples were recorded on a Hitachi U-3900H and Hitachi F-2700 fluorescence spectrophotometer, respectively. Evaluation of emission lifetime was carried out with a HORIBA FluoroCube. The PL quantum yields of the emission were measured using a Hamamatsu Photonics C9920-02 absolute PL quantum yield spectrometer.

UV−vis absorption and PL spectra for a vacuum-deposited film were recorded on a Hitachi U-3010 and JASCO FP-6500 spectrophotometers, respectively. The HOMO energy level was estimated by photoelectron yield spectroscopy (PYS) using a Riken Keiki AC-3 spectrometer. Out-of-plane XRD measurements were performed using MiniFlex600 (Rigaku). The atomic force microscopy (AFM) measurement of the surface morphology of the samples was conducted on AFM5100N and AFM5000II (Hitachi High-Tech Corporation). Differential scanning calorimetry (DSC) measurements were carried out on a DSC-60 (Shimadzu Co.) at 10 °C min^{-1} under a N_2 atmosphere.

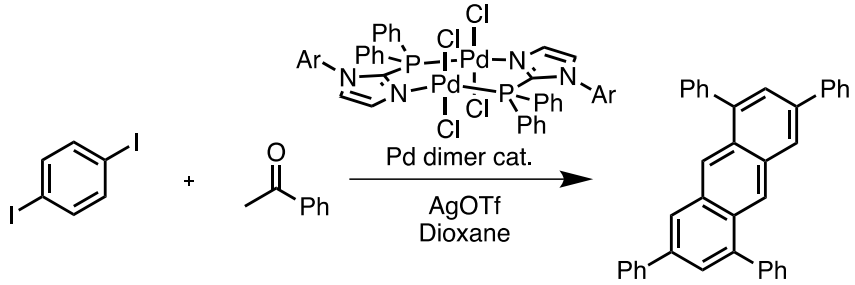
Anhydrous toluene, THF, 1,4-dioxane, CPME, DMF, and DMAc were purchased from Kanto Chemical and used as dry solvents. PVK (Poly(9-vinylcarbazole) and TPBi (2,2′,2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) were purchased from Tokyo Chemical Industry.

Fabrication and characterization of OLEDs

OLEDs were fabricated in the following configuration: ITO/PEDOT:PSS/PVK/**TAAnt 1**/TPBi/LiF/Al. The patterned indium tin oxide (ITO) glass (conductivity: 10 Ω/square) was pre-cleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 rpm and air-dried at 110 °C for 10 min on a hot plate. The substrate was then transferred to a N_2-filled glove box where it was re-dried at 110 °C for 10 min on a hot plate. Subsequently, a thin layer (34 nm) of PVK ($CHCl_3$ solution) was spin-coated onto the PEDOT:PSS surface at 800 rpm and dried at 150 °C for 10 min on a hot plate. **TAAnt 1** (30 nm) was deposited onto the PVK layer with conventional thermal evaporation at a chamber pressure lower than 2×10^{-4} Pa. TPBi (40 nm), LiF (1 nm) and Al (100 nm) were then deposited onto the active

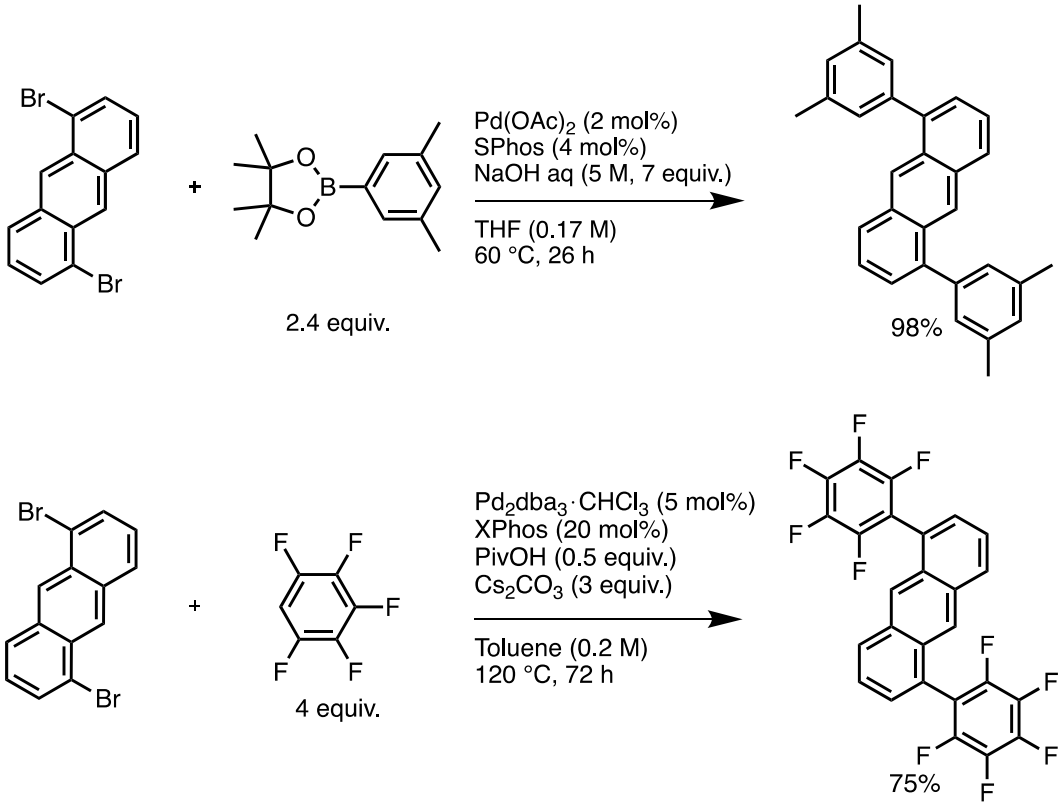
layer with conventional thermal evaporation, which provided the devices with an active area of 2 × 2 mm^2. Current-voltage characteristics and luminance of the OLED were simultaneously measured using an ADCMT 6245 DC voltage current source/monitor (ADC CORPORATION) and an LS-100 luminance meter (KONICA MINOLTA, INC.), respectively. The EL spectra were measured using an array spectrometer (MCPD-9800-311C, Otsuka Electronics Co, Ltd.).

Example of synthesis of 1,3,5,7-tetra-arylated anthracene



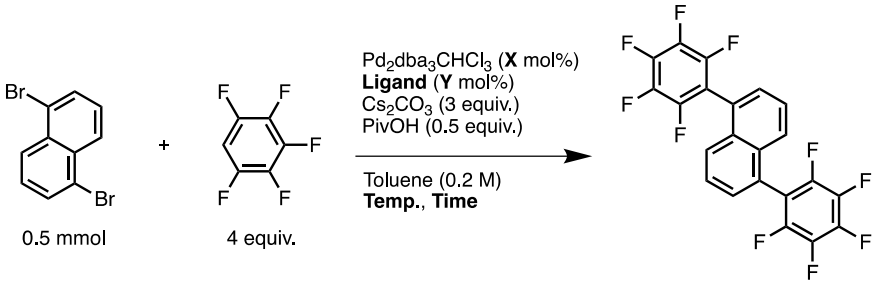
Scheme S1. Synthesis of 1,3,5,7-tetraphenylanthracene by Michaels's method.[1]

Additional data for synthetic parts



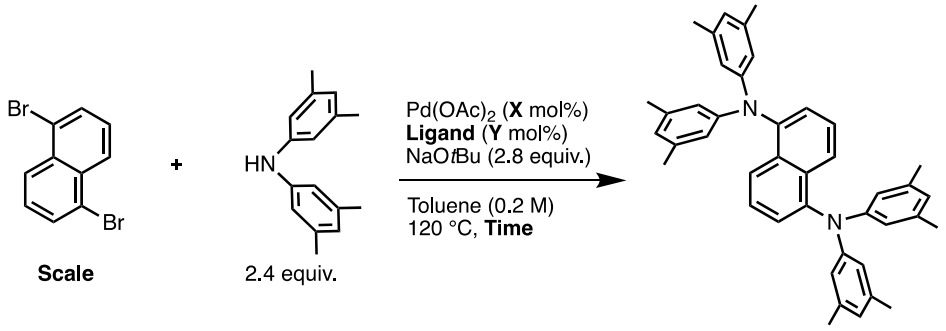
Scheme S2. Synthesis of 1,5-diarylanthracenes.

Table S1. Optimisation of reaction conditions for direct C–H arylation reaction.



Entry	X	Ligand	Y	Temp. [°C]	Time [h]	Isolated yield [%]
1	1	P(*o*-MeOPh)$_3$	4	100	96	18
2	1	SPhos	4	100	24	36
3	2.5	SPhos	10	120	46	86

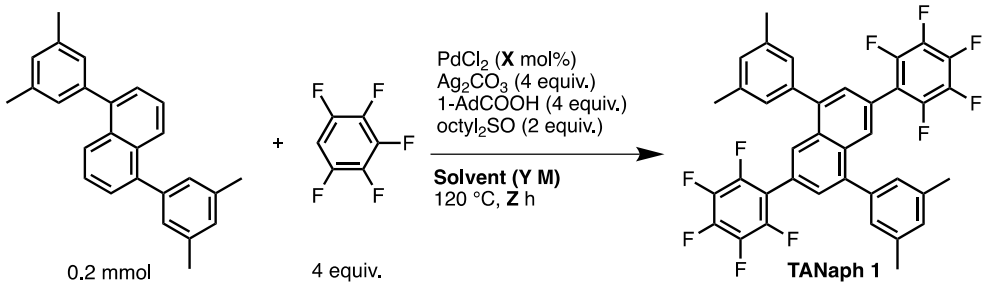
Table S2. Optimisation of reaction condition for Buchwald-Hartwig amination reaction.



Entry	Scale [mmol]	X	Ligand	Y	Time	Conversion [%][a]	Isolated yield [%]
1	0.5	4	P*t*Bu$_3$HBF$_4$	8	24	-[b]	26
2	0.5	10	P*t*Bu$_3$HBF$_4$	20	48	-[b]	25
3	0.1	10	SPhos	20	20	86	-[c]
4	0.1	10	XPhos	20	20	98	-[c]
5	0.2	5	XPhos	10	24	89	-[c]
6	0.4	10	XPhos	20	24	-[b]	81

[a] The conversion was determined by ^{1}H NMR analyses of a crude product with ferrocene as an internal standard. [b] Not measured. [c] Not isolated.

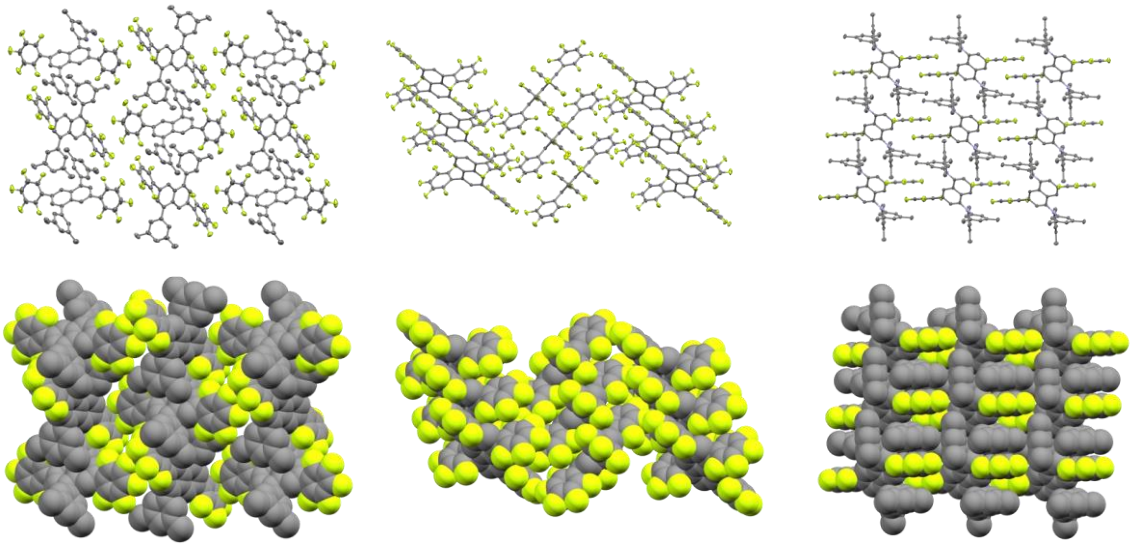
Table S3. Optimisation of reaction condition for CDC reaction.



Entry	X	Solvent	Y	Z	NMR yield [%][a]	Isolated yield [%]
1	10	CPME	0.25	48	-	21
2	10	DMAc	0.25	48	3.6	-
3	10	DMF	0.25	48	4.4	-
4	20	CPME	0.25	72	48	-
5	20	CPME	0.4	72	59	-
6	20	CPME : DMF (4:1)	0.4	72	81	66

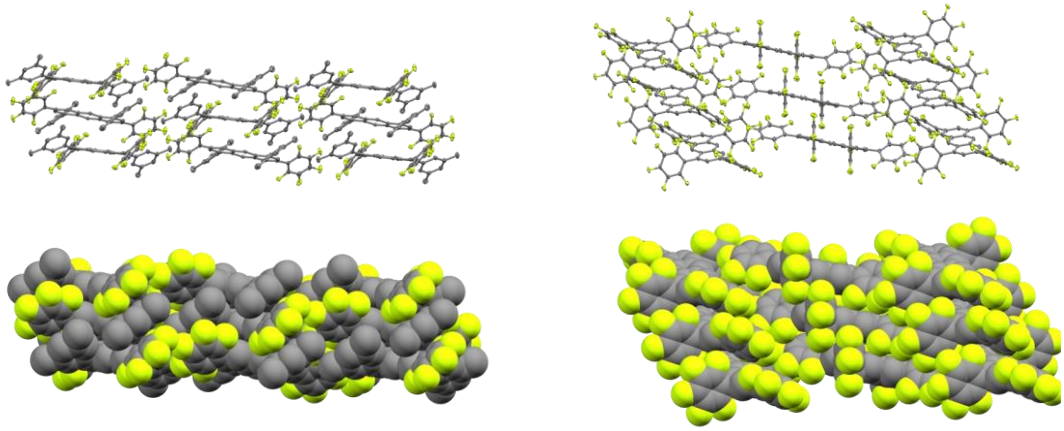
[a] The yield was determined by ^{19}F NMR analyses of a crude product with hexafluorobenzene as an Internal standard.

Packing structure of tetra-arylated acenes



TANaph 1 **TANaph 2** **TANaph 3**

Figure S1. Packing structures of TANaphs from single X-ray structural analysis.



TAAnt 1 **TAAnt 2**

Figure S2. Packing structures of TAAnts from single X-ray structural analysis.

HOMO-LUMO distributions and optical properties of the partial structure compounds of tetra-arylated acenes

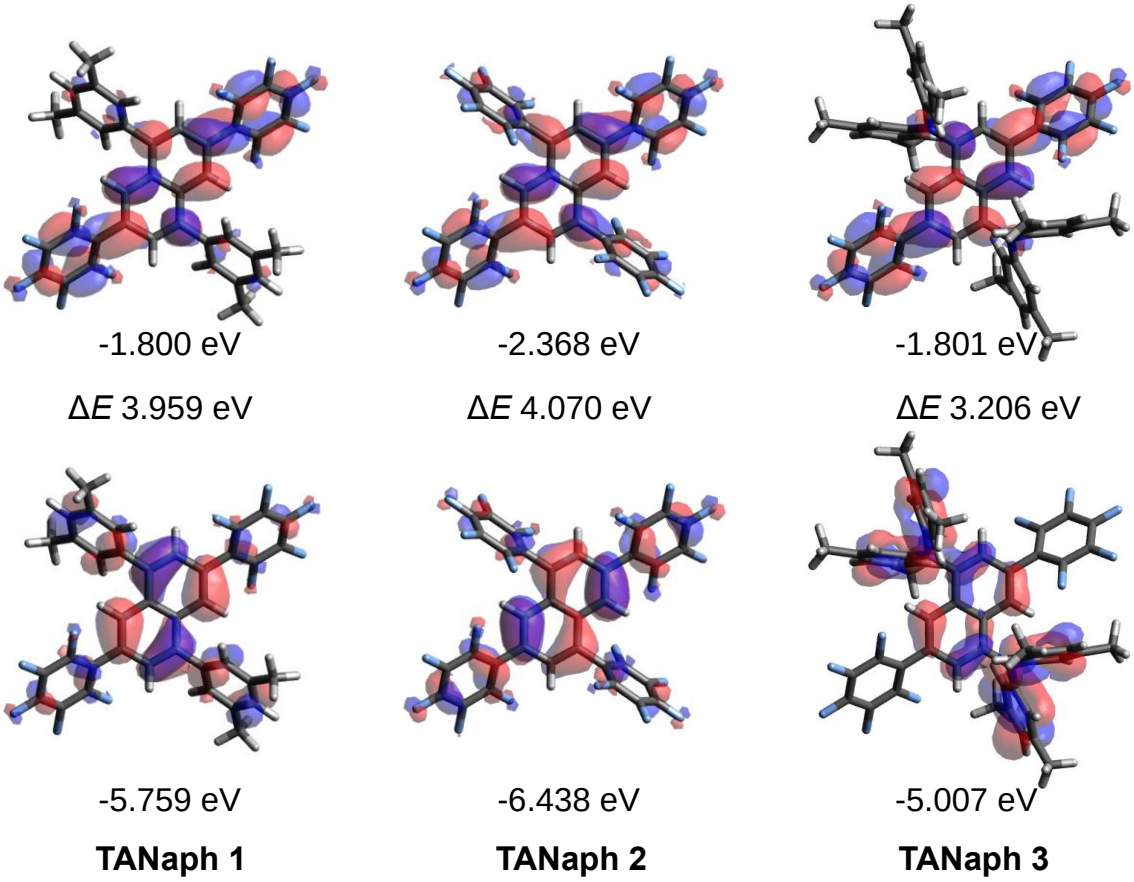


Figure S3. Calculated HOMO distribution (bottom), LUMO distribution (top), and the bandgap of TANaphs (DFT: B3LYP/6-31(G)).

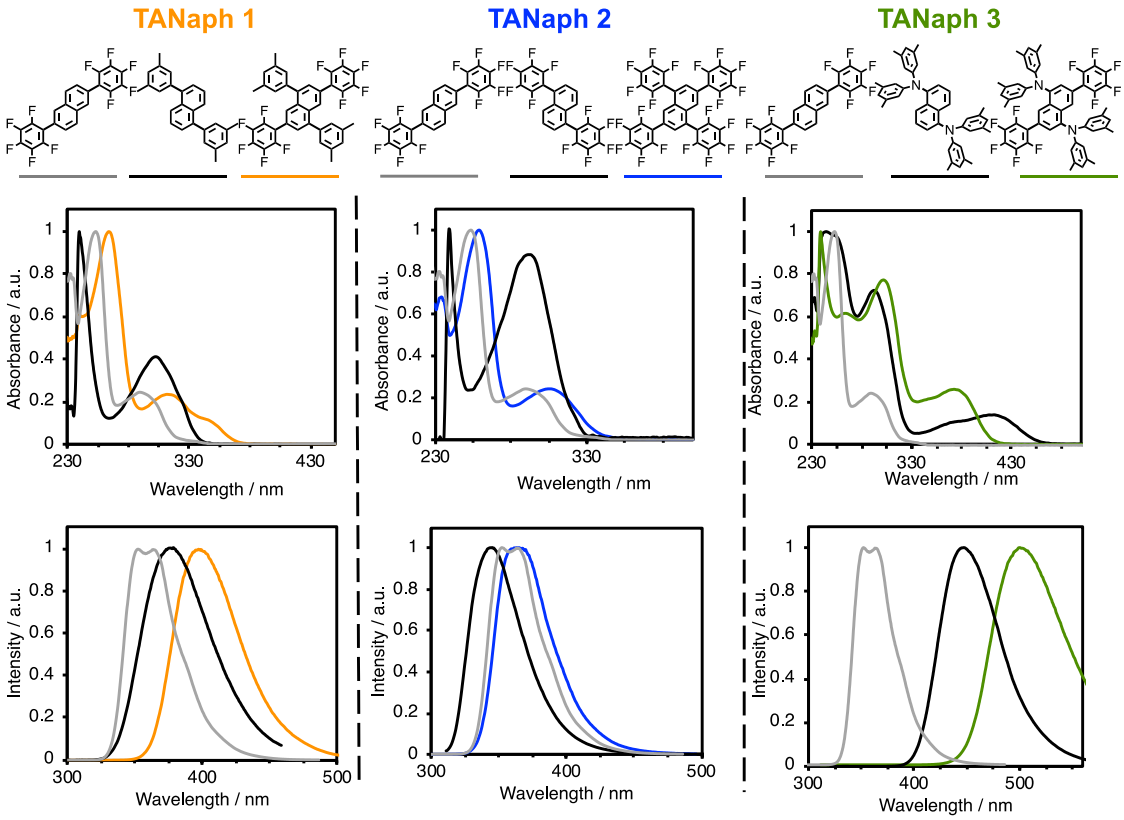


Figure S4. Comparison UV–vis absorption (top) and emission spectra (bottom) of TANaphs and the partial structure compounds in chloroform solution (1.0×10^{-5} M).[2]

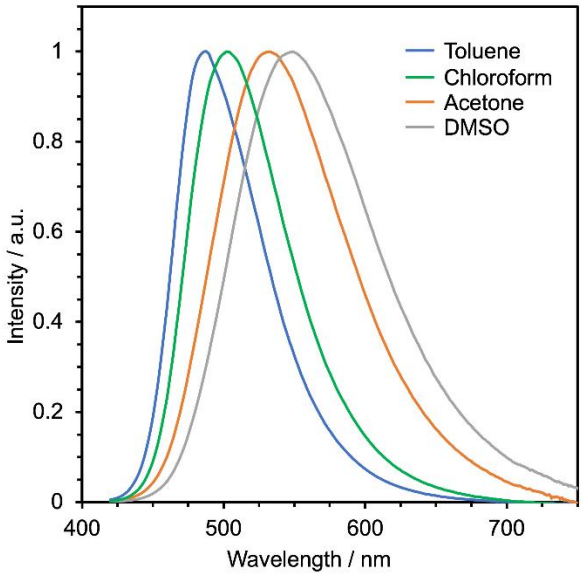


Figure S5. Emission spectra of **TANaph 3** in various solvents (1.0×10^{-5} M).

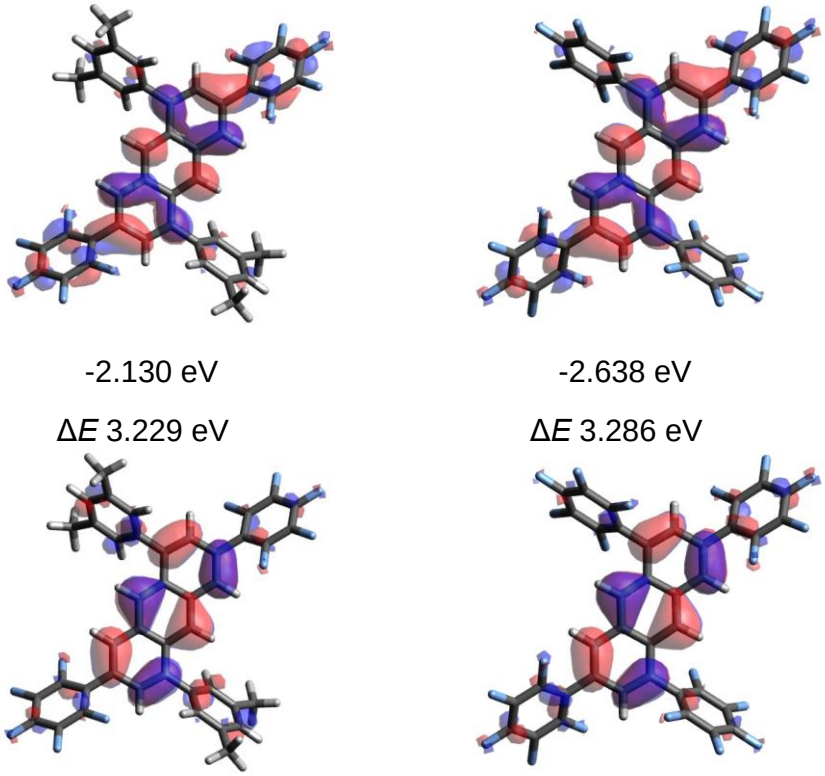


Figure S6. Calculated HOMO distribution (bottom), LUMO distribution (top), and the bandgap of TAAnts (DFT: B3LYP/6-31(G)).

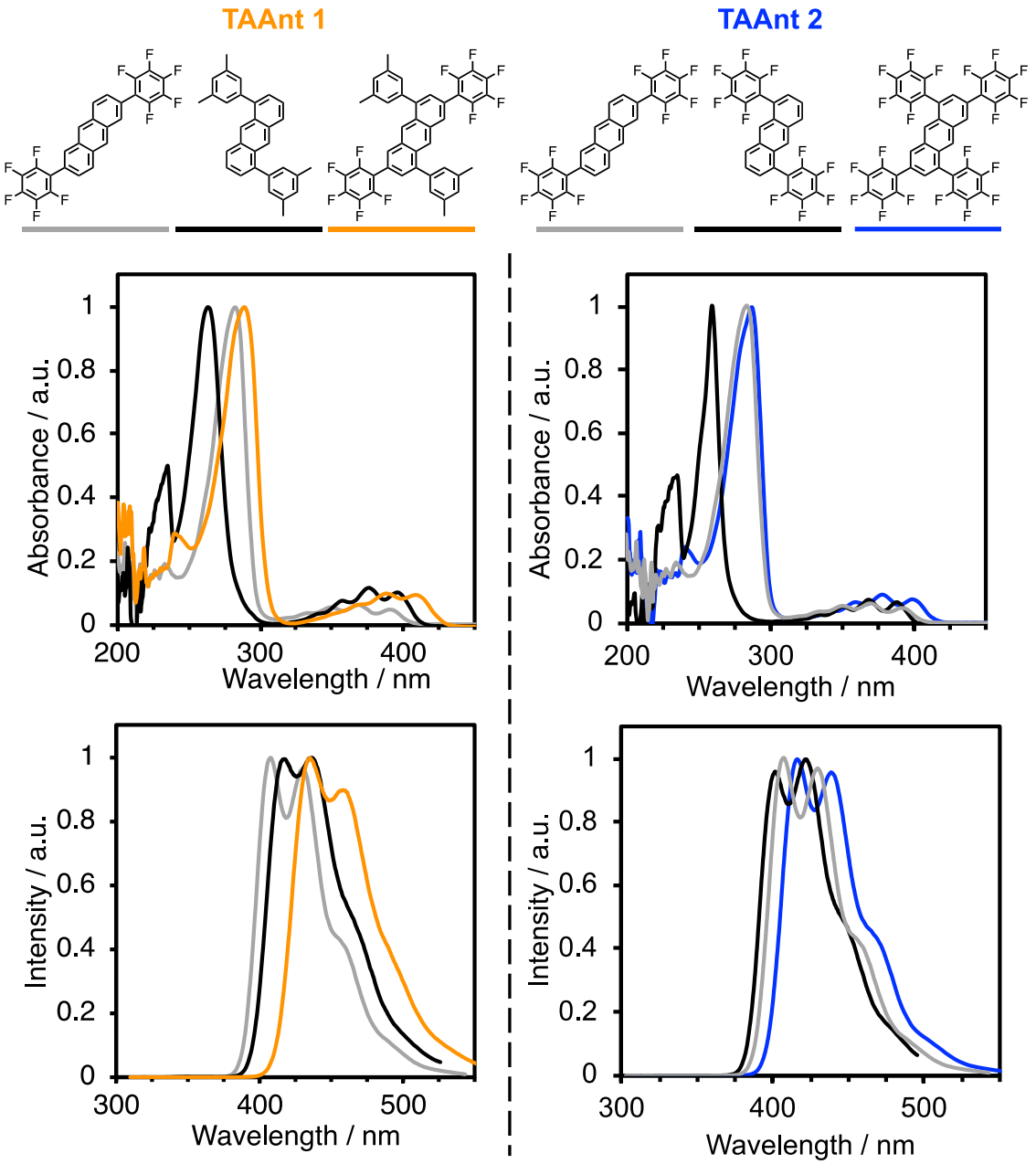


Figure S7. Comparison UV–vis absorption (top) and emission spectra (bottom) of TAAnts and the partial structure compounds in chloroform solution (1.0×10^{-5} M).[2,3]

Additional data for evaluation of organic light-emitting diode of TAAnt 1

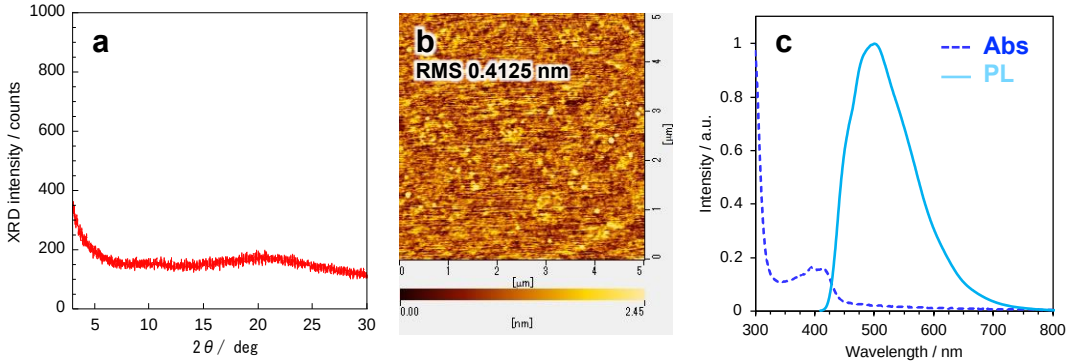


Figure S8. (a) XRD spectrum, (b) AFM image, and (c) UV−vis absorption (dotted line) and emission spectra (solid line) of **TAAnt 1** in the film state.

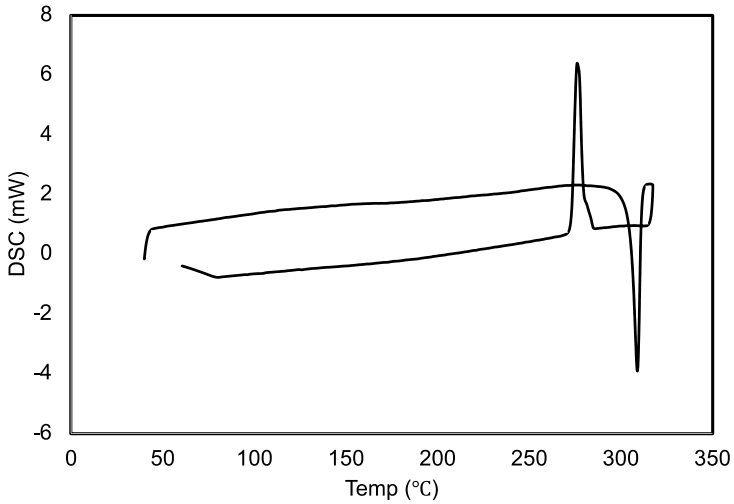


Figure S9. DSC second scan of **TAAnt 1** at rate of 10 °C min^{-1}.

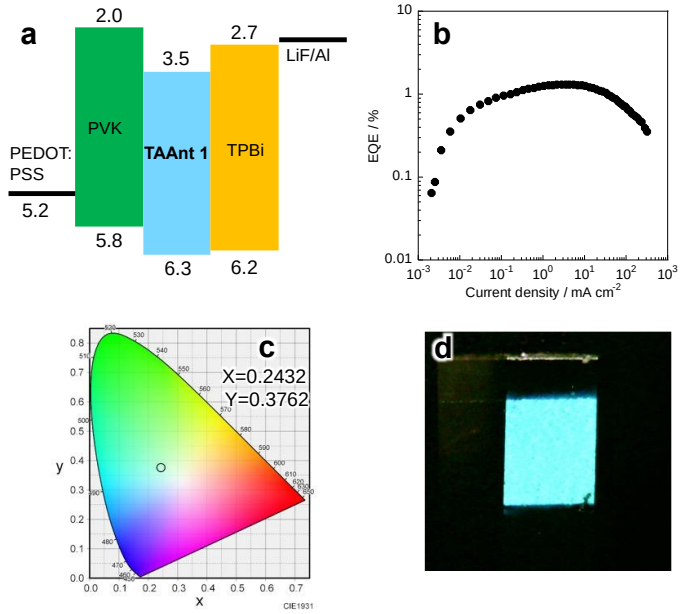


Figure S10. (a) The OLED structure, (b) EQE–current density characteristics, (c) CIE chromaticity coordinates, and (d) Photograph of OLED luminescence.

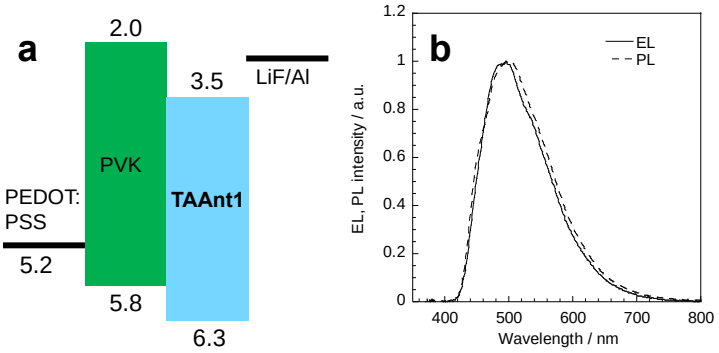
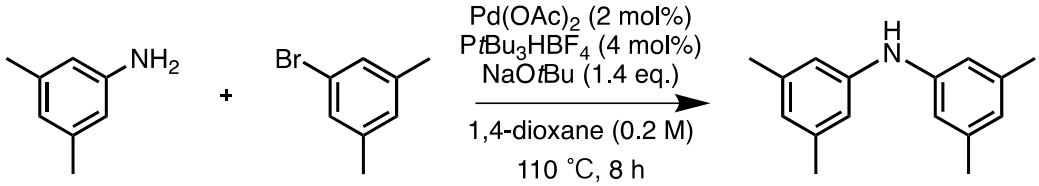


Figure S11. (a) The OLED structure and (b) EL and PL spectra.

Synthetic method

Synthesis of N,N-bis(m-xylyl)amine

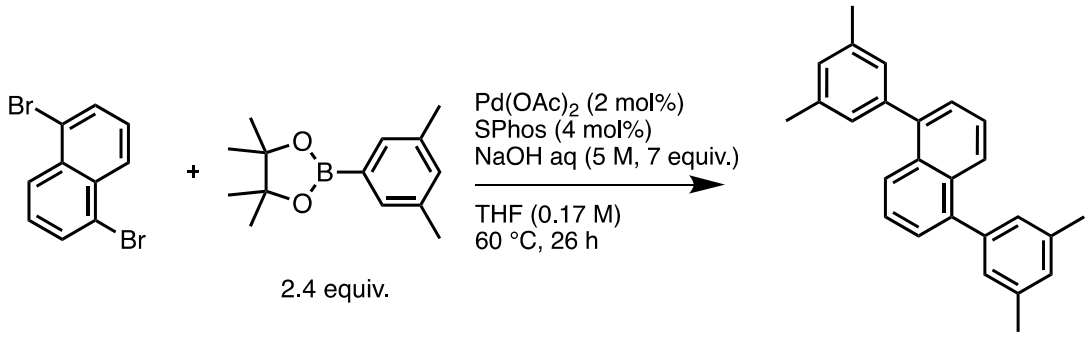


1.2 equiv.

A mixture of $Pd(OAc)_2$ (22 mg, 0.10 mmol), P*t*Bu_3HBF_4 (58 mg, 0.20 mmol), NaO*t*Bu (673 mg, 7.0 mmol), 1-bromo-3,5-dimethylbenzene (685 µL, 5.0 mmol), and 3,5-dimethylaniline (750 µL, 6.0 mmol) was stirred in 1,4-dioxane (25 mL) for 8 h at 110 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with dichloromethane (30 mL). The organic phase was washed with water, and the aqueous layer was extracted with dichloromethane (30 mL x 3). The combined organic solution was dried over Mg_2SO_4. After filtration and removal of the solvent, the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 97:3) to give *N,N*-bis(*m*-xylyl)amine (1.04 g, 92%).[4]

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 6.69 (s, 4 H), 6.57 (s, 2 H), 5.52 (s, 1 H), 2.27 (s, 12 H).

Synthesis of 1,5-bis(m-xylyl)naphthalene



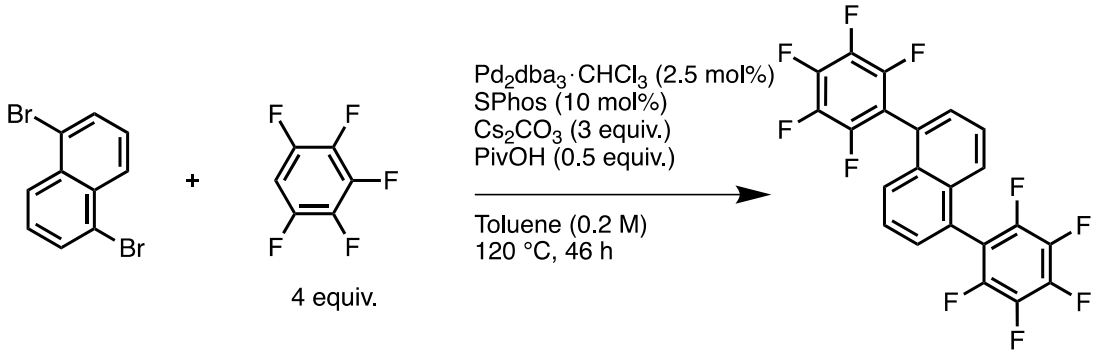
2.4 equiv.

A mixture of $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) and SPhos (41 mg, 0.10 mmol) was stirred in THF (1.2 mL) for 30 minutes at room temperature. The catalyst solution was added to a mixture of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*m*-xylene (556 mg, 2.4 mmol), 5 M NaOH aqueous solution (1.4 mL, 7.0 mmol) and THF (4.8 mL). Then, 1,5-dibromonaphthalene (286 mg, 1.0 mmol) was added to the solution. The reaction mixture was stirred for 26 h at 60 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$ (10 mL). The organic phase was washed with

water, and the aqueous layer was extracted with $CHCl_3$ (30 mL x 3). The combined organic solution was dried over Mg_2SO_4. After filtration and removal of the solvent, the product was isolated by column chromatography on silica gel using a hexane as an eluent to give 1,5-bis(*m*-xylyl)naphthalene (312 mg, 93%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.90 (d, 2 H, *J* = 8.0 Hz), 7.43 (t, 2 H, *J* = 7.8 Hz), 7.39 (d, 2 H, *J* = 6.5 Hz), 7.13 (s, 4 H), 7.08 (s, 2 H), 2.41 (s, 12 H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, room temperature): δ 141.0, 140.7, 137.7, 132.0, 128.8, 128.0, 126.6, 125.7, 125.2, 21.4. APCI-TOF MS: *m/z* Calcd. for $C_{26}H_{24}$ ($M+H^+$) 337.1951, Found 337.1953.

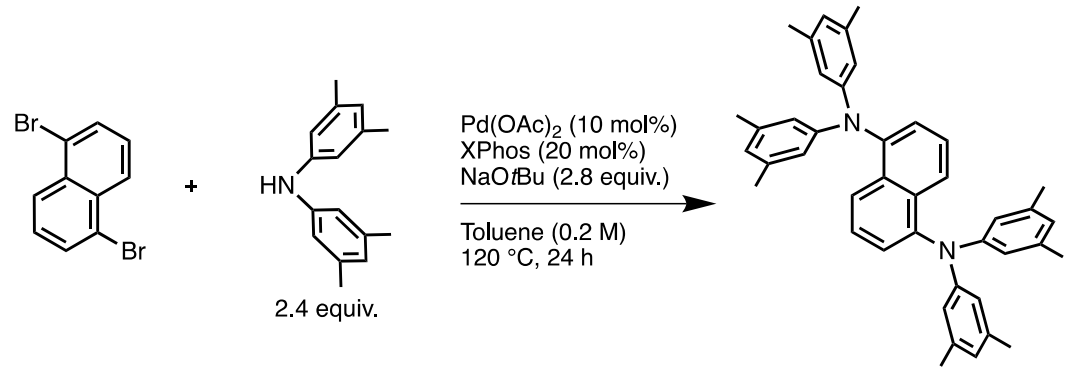
Synthesis of 1,5-bis(pentafluorophenyl)naphthalene



A mixture of $Pd_2dba_3 \cdot CHCl_3$ (13.3 mg, 0.0125 mmol), SPhos (20.5 mg, 0.050 mmol), pivalic acid (30 μL, 0.25 mmol), cesium carbonate (490 mg, 1.5 mmol), 1,5-dibromonaphthalene (143 mg, 0.50 mmol), and pentafluorobenzene (220 μL, 2.0 mmol) was stirred in toluene (2.5 mL) for 46 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$ (10 mL). The organic phase was washed with water, and the aqueous layer was extracted with $CHCl_3$ (10 mL x 3). The combined organic solution was dried over Na_2SO_4. After filtration and removal of the solvent, the product was isolated by column chromatography on silica gel using a hexane as an eluent to give 1,5-bis(pentafluorophenyl)naphthalene (197 mg, 86%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.65 (d, 2 H, *J* = 8.5 Hz), 7.61 (dd, 2 H, *J* = 8.5, 6.5 Hz), 7.52 (d, 2 H, *J* = 7.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -142.3 (dd, 4 F, J_F = 22.8, 8.8 Hz), -157.1 (t, 2 F, J_F = 20.2 Hz), -164.6 (td, 4 F, J_F = 21.9, 8.2 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, room temperature): δ 144.6 (dm, J_F = 248.0 Hz), 141.1 (dm, J_F = 258.0 Hz), 137.8 (dm, J_F = 249.0 Hz), 131.8, 129.6, 126.7, 126.4, 124.6, 114.0. APCI-TOF MS: *m/z* Calcd. for $C_{22}H_6F_{10}$ ($M+H^+$) 461.0383, Found 461.0383.

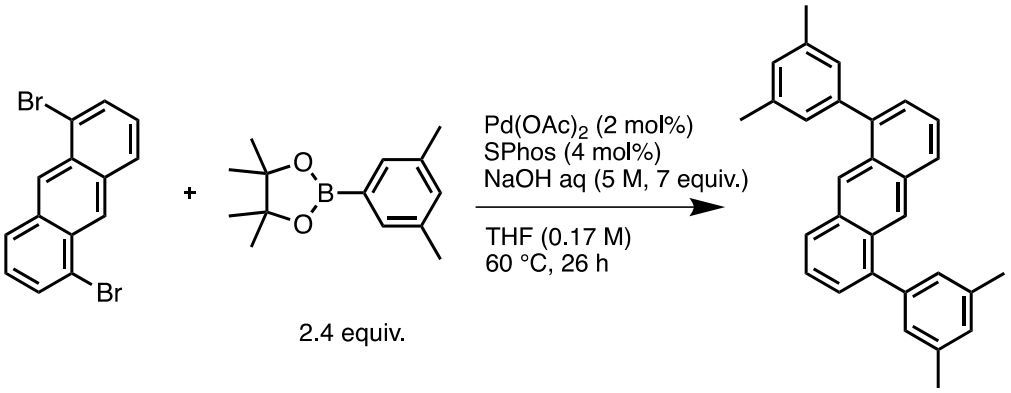
Synthesis of 1,5-bis[N,N-bis(m-xylyl)amino]naphthalene



A mixture of $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), XPhos (38 mg, 0.080 mmol), NaO*t*Bu (108 mg, 1.1 mmol), 1,5-dibromonaphthalene (114 mg, 0.40 mmol), and *N,N*-bis(*m*-xylyl)amine (234 µL, 0.96 mmol) was stirred in toluene (25 mL) for 24 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The mixture was extracted by Soxhlet extraction with MeOH, hexane and $CHCl_3$. A solvent of the $CHCl_3$-soluble fraction was removed in vacuo to give 1,5-bis[*N,N*-di(*m*-xylyl)amino]naphthalene (186 mg, 81%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.90 (d, 2 H, *J* = 8.6 Hz), 7.32 (dd, 2 H, *J* = 8.3, 7.4 Hz), 7.24 (d, 2 H, *J* = 7.3 Hz), 6.64 (s, 8 H), 6.59 (s, 4 H), 2.18 (s, 24 H). ^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K): δ 148.7, 144.3, 138.2, 133.4, 126.8, 126.1, 123.3, 122.5, 120.0, 21.1. APCI-TOF MS: *m/z* Calcd. for $C_{42}H_{42}N_2$ ($M+H^+$) 575.3421, Found 575.3441.

Synthesis of 1,5-bis(m-xylyl)anthracene

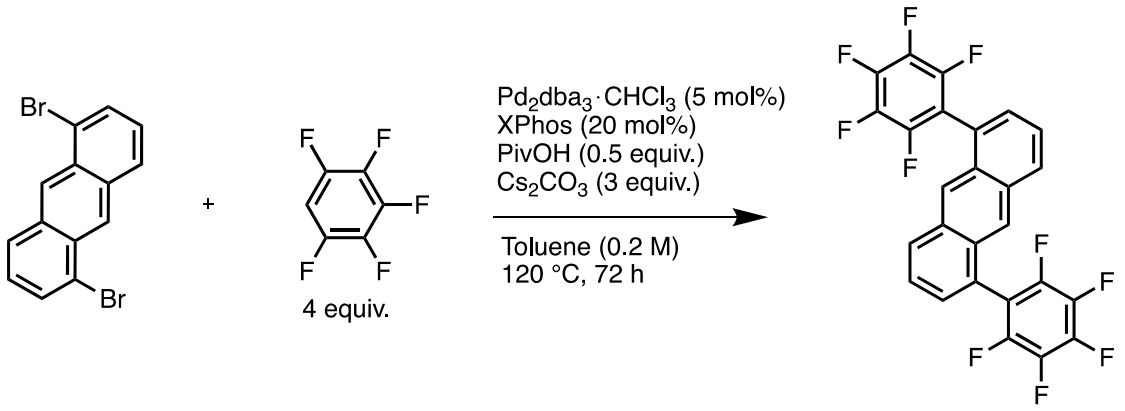


A mixture of $Pd(OAc)_2$ (11.2 mg, 0.050 mmol) and SPhos (41 mg, 0.10 mmol) was stirred in THF (1.2 mL) for 30 minutes at room temperature. The catalyst solution was added to a mixture of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*m*-xylene (556 mg, 2.4 mmol), 5 M

NaOH aqueous solution (1.4 mL, 7.0 mmol) and THF (4.8 mL). Then, 1,5-dibromoanthracene (366 mg, 1.0 mmol) was added to the solution. The reaction mixture was stirred for 26 h at 60 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$ (10 mL). The organic phase was washed with water, and the aqueous layer was extracted with $CHCl_3$ (10 mL x 3). The combined organic solution was dried over Mg_2SO_4. After filtration and removal of the solvent, the product was isolated by column chromatography on silica gel using a hexane as an eluent to give 1,5-bis(*m*-xylyl)anthracene (380 mg, 98%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.52 (s, 2 H), 7.90 (dd, 2 H, *J* = 8.5, 1.0 Hz), 7.45 (dd, 2 H, *J* = 8.5, 7.0 Hz), 7.37 (dd, 2 H, *J* = 6.8, 1.3 Hz), 7.22 (s, 4 H), 7.14 (s, 2 H), 2.45 (s, 12 H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, room temperature): δ 140.8, 140.2, 137.9, 132.0, 130.1, 129.0, 128.2, 127.9, 126.1, 125.3,124.8, 21.5. APCI-TOF MS: *m/z* Calcd. for $C_{30}H_{26}$ ($M+H^+$) 387.2108, Found 387.2104.

Synthesis of 1,5-bis(pentafluorophenyl)anthracene[3]

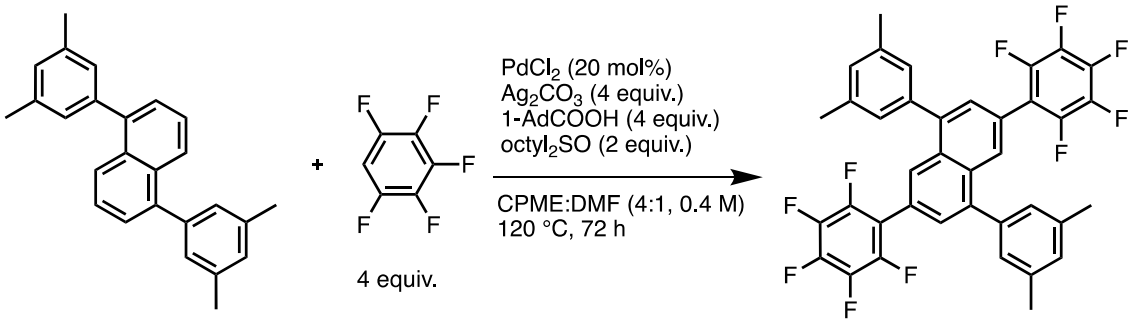


A mixture of Pd_2dba_3·$CHCl_3$ (53.2 mg, 0.050 mmol), XPhos (95.0 mg, 0.20 mmol), pivalic acid (60 µL, 0.5 mmol), cesium carbonate (980 mg, 3.0 mmol), 1,5-dibromoanthracene (336 mg, 1.0 mmol), and pentafluorobenzene (440 µL, 4.0 mmol) was stirred in toluene (5.0 mL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. The organic phase was washed with water, and the solvent was removed in vacuo. The resulting solid was washed with hexane (50 mL) and $CHCl_3$ (20 mL). The remained solid was dissolved in toluene (100 mL, 100 °C). Following filtration of the hot solution, the solvent was removed in vacuo and washed with hexane. After drying the solid to give 1,5-bis(pentafluorophenyl)anthracene (380 mg, 75%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.12 (s, 2 H), 8.07 (d, 2 H, *J* = 8.5 Hz), 7.58 (dd, 2 H, *J* = 8.5, 7.0 Hz), 7.48 (dd, 2 H, *J* = 6.5, 1.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$, room

temperature): δ -142.4 (dd, 4 F, J_F = 23.6, 9.1 Hz), -157.2 (t, 2 F, J_F = 20.0 Hz), -164.6 (td, 4 F, J_F = 21.8, 7.3 Hz).

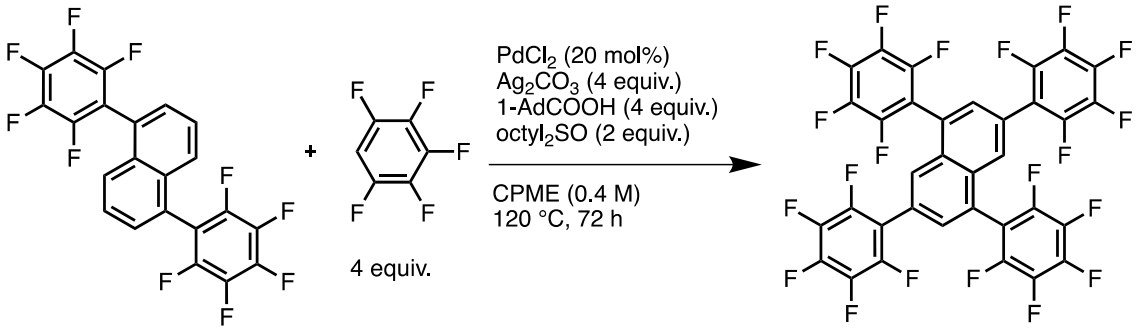
Synthesis of 1,5-bis(m-xylyl)-3,7-bis(pentafluorophenyl)naphthalene



A mixture of $PdCl_2$ (7.2 mg, 0.040 mmol), di-*n*-octylsulfoxide (110 mg, 0.40 mmol), 1-adamantanecarboxylic acid (144 mg, 0.80 mmol), silver(I) carbonate (180 mg, 0.80 mmol), 1,5-di(*m*-xylyl)naphthalene (67.3 mg, 0.20 mmol), and pentafluorobenzene (88 µL, 0.80 mmol) was stirred in cyclopentylmethylether (0.40 mL) and *N,N*-dimethylformamide (0.10 mL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using a hexane as an eluent and HPLC. The solvent was removed in vacuo to give 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)naphthalene (87.9 mg, 66%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.04 (s, 2 H), 7.51 (s, 2 H), 7.18 (s, 2 H), 7.11 (s, 2 H), 2.42 (s, 12 H). ^{19}F NMR (376 MHz, 1,1,2,2-tetrachloroethane-d_2, room temperature): δ -146.3 (dd, 4 F, J_F = 23.7, 7.9 Hz), -158.3 (t, 2 F, J_F = 21.0 Hz), -165.1 (dt, 4 F, J_F = 22.4, 7.0 Hz). ^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K): δ 144.3 (dm, J_F = 244.4 Hz), 141.9, 139.3, 137.9, 137.9 (dm, J_F = 265.4 Hz), 131.9, 129.3, 128.1, 127.8, 127.7, 124.2, 115.9, 21.0. Elemental analysis: Calcd.: C 68.27%, H 3.32%; Found: C 68.59%, H 3.27%. APCI-TOF MS: *m/z* Calcd. for $C_{30}H_{22}F_{10}$ ($M+H^+$) 669.1635, Found 669.1639.

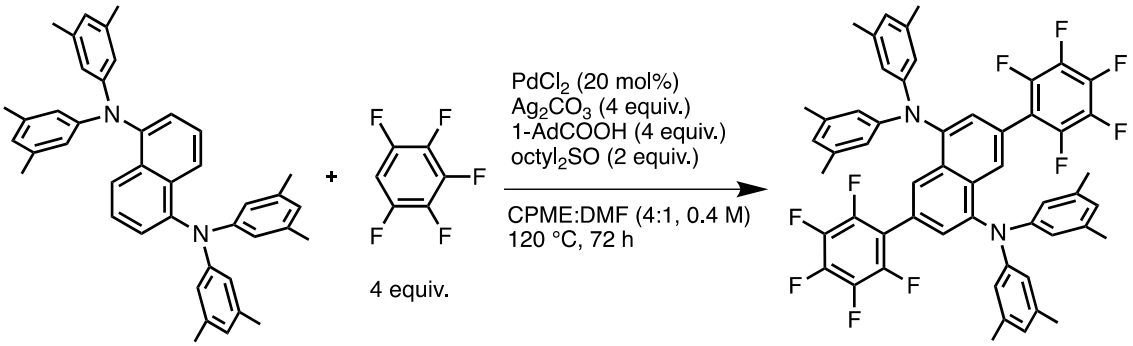
Synthesis of 1,3,5,7-tetrakis(pentafluorophenyl)naphthalene



A mixture of $PdCl_2$ (7.2 mg, 0.040 mmol), di-*n*-octylsulfoxide (110 mg, 0.40 mmol), 1-adamantanecarboxylic acid (144 mg, 0.80 mmol), silver(I) carbonate (180 mg, 0.80 mmol), 1,5-bis(pentafluorophenyl)naphthalene (67.3 mg, 0.20 mmol), and pentafluorobenzene (88 µL, 0.80 mmol) was stirred in cyclopentylmethylether (0.40 mL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using a hexane as an eluent. The solvent was removed in vacuo to give 1,3,5,7-tetrakis(pentafluorophenyl)naphthalene (30.0 mg, 19%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.78 (s, 2 H), 7.66 (s, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -141.9 (dd, 4 F, J_F = 21.9, 7.9 Hz), -145.9 (dd, 4 F, J_F = 22.8, 8.8 Hz), -155.2 (t, 2 F, J_F = 21.0 Hz), -156.2 (t, 2 F, J_F = 21.0 Hz), -163.5 (td, 4 F, J_F = 21.0, 7.0 Hz), -164.0 (td, 4 F, J_F = 21.9, 7.0 Hz). ^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K): δ 144.6 (dm, J_F = 242.2 Hz), 144.3 (dm, J_F = 253.2 Hz), 141.6 (dm, J_F = 266.5 Hz), 138.0 (dm, J_F = 254.3 Hz) 131.5, 131.4, 128.4, 125.9, 114.2, 112.6. As the solubility of this compound was low, a few signal of quaternary carbons could not be observed even by high temperature NMR with 24 h integration. An analytically pure sample was obtained by recrystallization from toluene solution. Elemental analysis: Calcd. for $C_{34}H_4F_{20}\cdot[C_7H_8]_{0.5}$: C 53.72%, H 0.96%; Found: C 54.10%, H 0.63%. APCI-TOF MS: *m/z* Calcd. for $C_{34}H_4F_{20}$ M 791.9994, Found 791.9972.

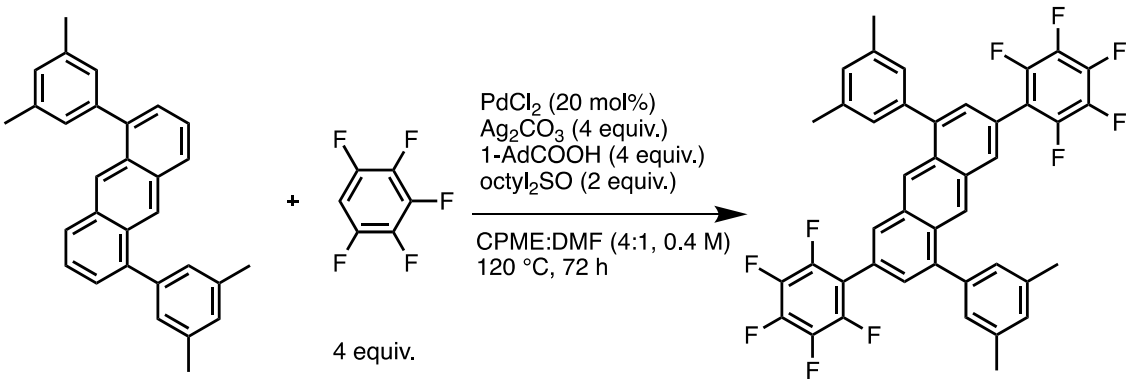
Synthesis of 1,5-bis[N,N-bis(m-xylyl)amino]-3,7-bis(pentafluorophenyl)naphthalene



A mixture of $PdCl_2$ (7.2 mg, 0.040 mmol), di-*n*-octylsulfoxide (110 mg, 0.40 mmol), 1-adamantanecarboxylic acid (144 mg, 0.80 mmol), silver(I) carbonate (180 mg, 0.80 mmol), 1,5- bis[*N,N*-di(*m*-xylyl)amino]naphthalene (67.3 mg, 0.20 mmol), and pentafluorobenzene (88 µL, 0.80 mmol) was stirred in cyclopentylmethylether (0.40 mL) and *N,N*-dimethylformamide (0.10 mL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel (hexane/$CHCl_3$ = 4:1) and HPLC. The solvent was removed in vacuo to give 1,5-bis[*N,N*-bis(*m*-xylyl)amino]-3,7-bis(pentafluorophenyl)naphthalene (10.0 mg, 5.5%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.05 (s, 2 H), 7.34 (s, 2 H), 6.69 (s, 8 H), 6.67 (s, 4 H), 2.23 (s, 24 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.1 (dd, 4 F, J_F = 22.8, 7.0 Hz), -158.4 (t, 2 F, J_F = 21.0 Hz), -165.5 (td, 4 F, J_F = 21.5, 7.6 Hz). APCI-TOF MS: *m/z* Calcd. for $C_{54}H_{40}F_{10}N_2$ ($M+H^+$) 907.3105, Found 907.3088.

Synthesis of 1,5-bis(m-xylyl)-3,7-bis(pentafluorophenyl)anthracene

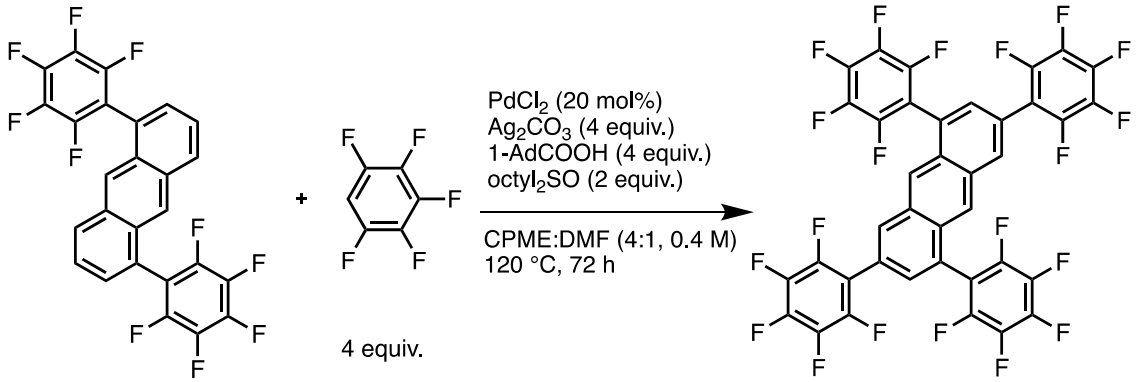


A mixture of $PdCl_2$ (7.2 mg, 0.040 mmol), di-*n*-octylsulfoxide (110 mg, 0.40 mmol), 1-adamantanecarboxylic acid (144 mg, 0.80 mmol), silver(I) carbonate (180 mg, 0.80 mmol),

1,5-di(*m*-xylyl)anthracene (77.3 mg, 0.20 mmol), and pentafluorobenzene (88 μL, 0.80 mmol) was stirred in cyclopentylmethylether (0.40 mL) and *N,N*-dimethylformamide (0.10 mL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using a hexane as an eluent. The solvent was removed in vacuo to give 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)anthracene (106 mg, 74%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.61 (s, 2 H), 8.03 (s, 2 H), 7.43 (s, 2 H), 7.24 (s, 4 H), 7.16 (s, 2 H), 2.45 (s, 12 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -145.7 (dd, 4 F, J_F = 23.7, 7.9 Hz), -158.2 (t, 2 F, J_F = 21.0 Hz), -165.1 (td, 4 F, J_F = 21.9, 8.2 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, room temperature): δ 144.4 (dm, J_F = 244.9 Hz), 141.2, 139.6, 138.1, 137.9 (dm, J_F = 249.3 Hz), 132.2, 130.5, 130.1, 129.5, 127.8, 127.4, 126.5, 123.4, 115.9, 21.4. As the solubility of this compound was low, a few signal of quaternary carbons could not be observed even by NMR with 24 h integration. Elemental analysis: Calcd.: C 70.20%, H 3.37%; Found: C 70.38%, H 3.41%. APCI-TOF MS: *m/z* Calcd. for $C_{42}H_{24}F_{10}$ ($M+H^+$) 719.1791, Found 719.1790.

Synthesis of 1,3,5,7-tetrakis(pentafluorophenyl)anthracene



A mixture of $PdCl_2$ (3.6 mg, 0.020 mmol), di-*n*-octylsulfoxide (55 mg, 0.20 mmol), 1-adamantanecarboxylic acid (72 mg, 0.40 mmol), silver(I) carbonate (90 mg, 0.40 mmol), 1,5-bis(pentafluorophenyl)anthracene (51 mg, 0.10 mmol), and pentafluorobenzene (44 μL, 0.40 mmol) was stirred in cyclopentylmethylether (0.20 mL) and *N,N*-dimethylformamide (50 μL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using a hexane as an eluent and HPLC. The solvent was removed in vacuo to give 1,3,5,7-tetrakis(pentafluorophenyl)anthracene (12.4 mg, 15%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.26 (s, 4 H), 7.58 (s, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -142.0 (dd, 4 F, J_F = 22.8, 7.0 Hz), -145.7 (dd, 4 F, J_F = 22.8, 8.8 Hz), -156.0 (t, 2 F, J_F = 21.0 Hz), -156.6 (t, 2 F, J_F = 21.0 Hz), -163.8 (td, 4 F, J_F = 21.0, 7.0 Hz), -164.4 (td, 4 F, J_F = 21.9, 7.0 Hz). ^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K): δ 144.7 (dm, J_F = 242.2 Hz), 144.3 (dm, J_F = 253.2 Hz), 138.0 (dm, J_F = 255.4 Hz), 132.7, 132.3, 130.7, 129.7, 125.3, 124.9, 124.0, 114.5, 113.1. As the solubility of this compound was low, a few signal of quaternary carbons could not be observed even by high temperature NMR with 24 h integration. Elemental analysis: Calcd.: C 54.18%, H 0.72%; Found: C 54.15%, H 0.78%. APCI-TOF MS: *m/z* Calcd. for $C_{38}H_6F_{20}$ ($M+H^+$) 843.0223, Found 843.0220.

NMR spectra

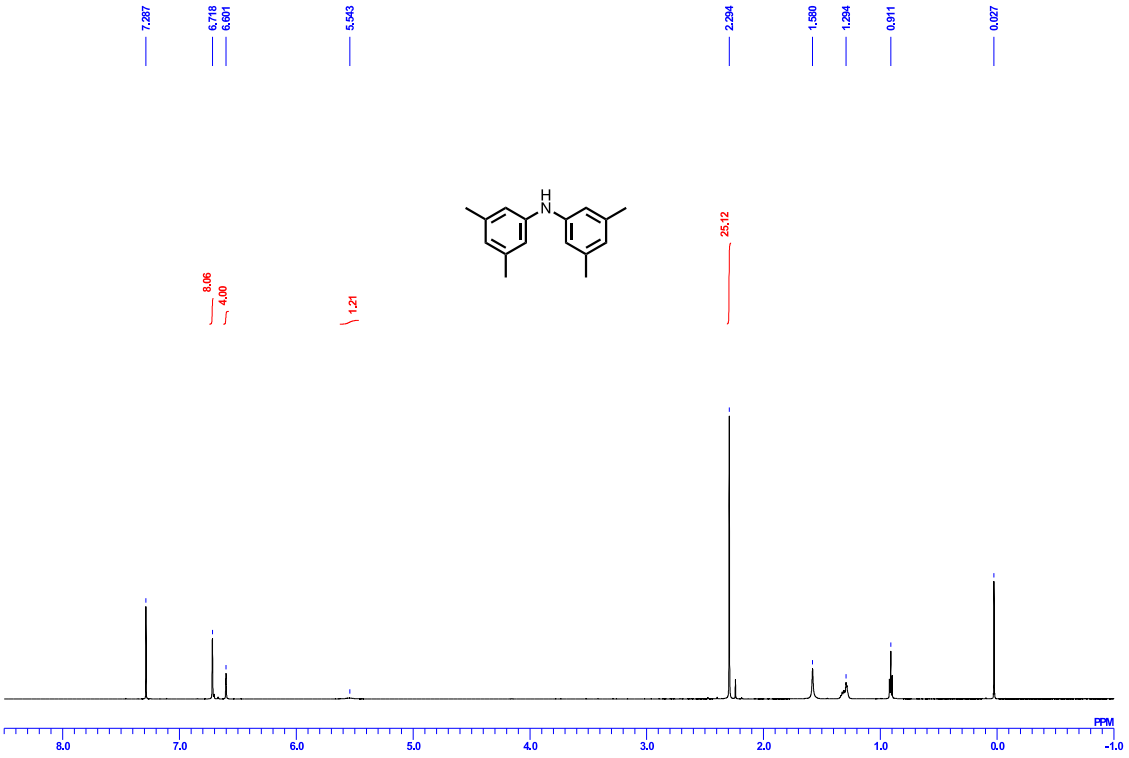


Figure S12. ^{1}H NMR spectrum of *N,N*-bis(*m*-xylyl)amine (600 MHz, $CDCl_3$, r.t.).

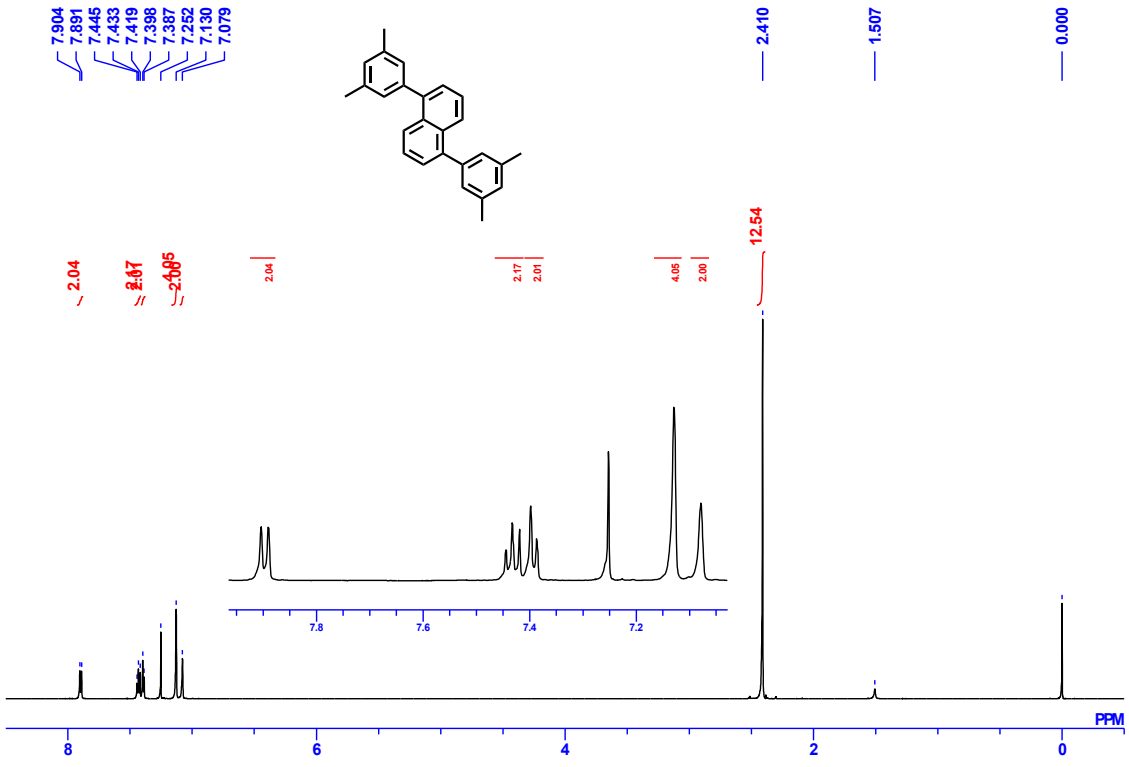


Figure S13. ^{1}H NMR spectrum of 1,5-bis(*m*-xylyl)naphthalene (600 MHz, $CDCl_3$, r.t.).

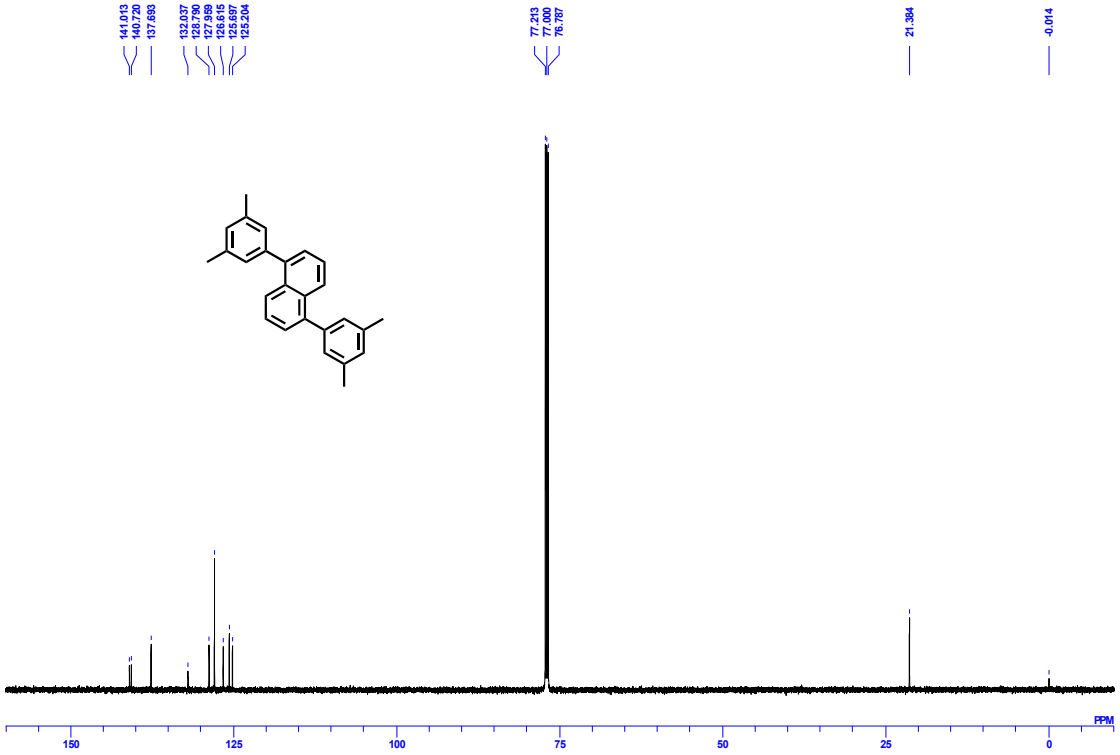


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of 1,5-bis(*m*-xylyl)naphthalene (150 MHz, $CDCl_3$, r.t.).

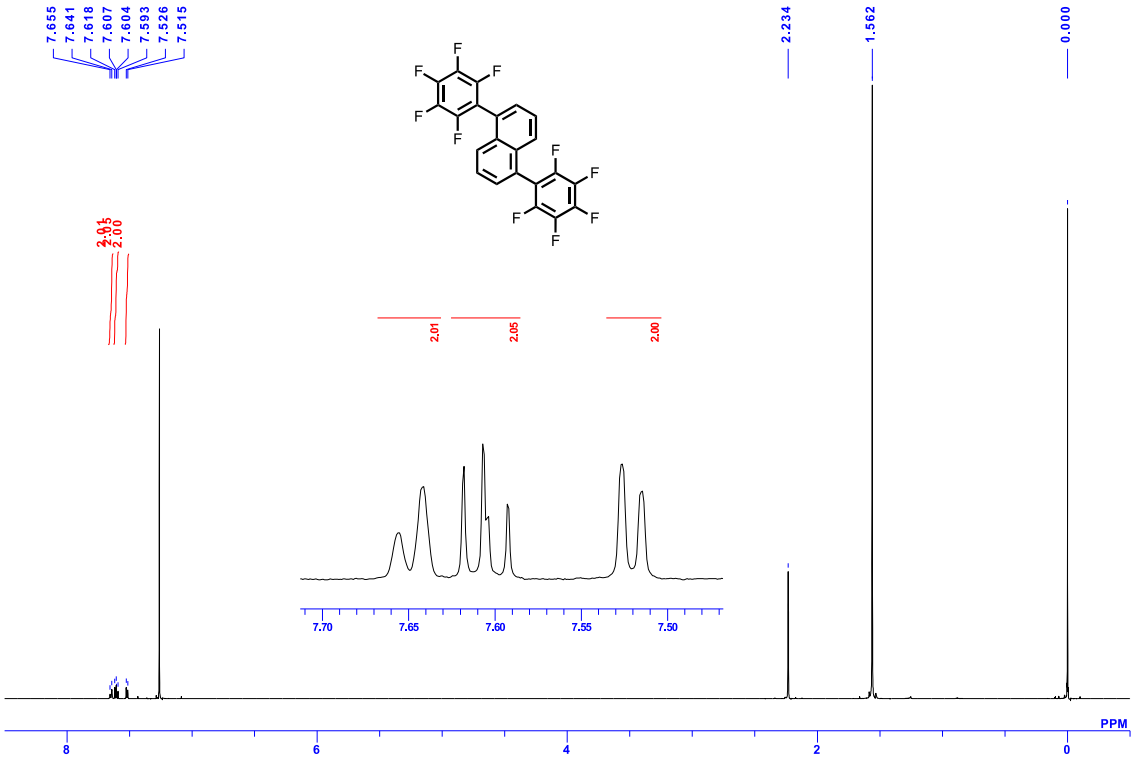


Figure S15. ^{1}H NMR spectrum of 1,5-bis(pentafluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.).

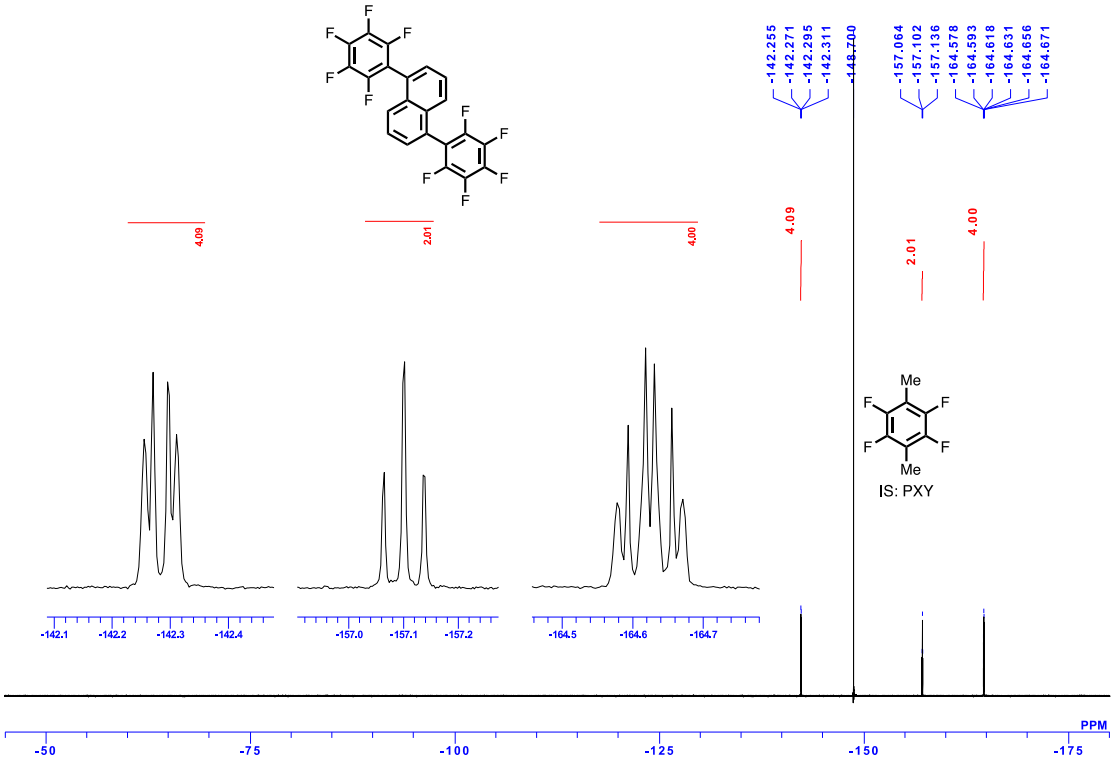


Figure S16. ^{19}F NMR spectrum of 1,5-bis(pentafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.).

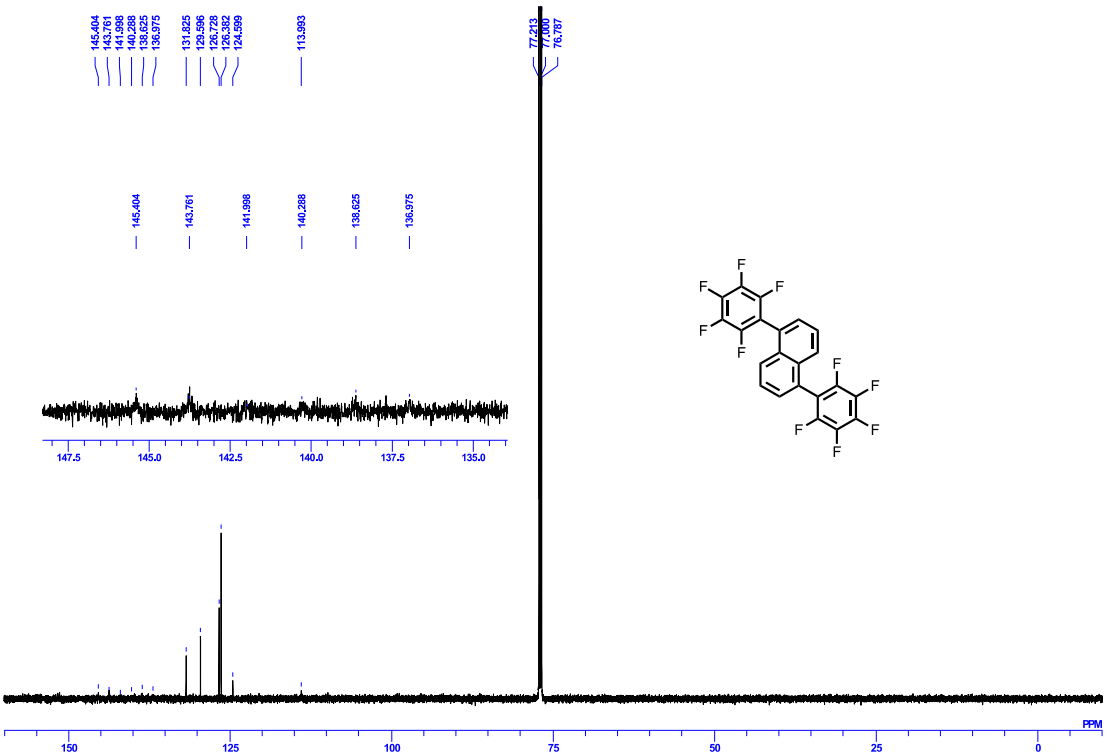


Figure S17. $^{13}C\{^1H\}$ NMR spectrum of 1,5-bis(pentafluorophenyl)naphthalene (150 MHz, $CDCl_3$, r.t.).

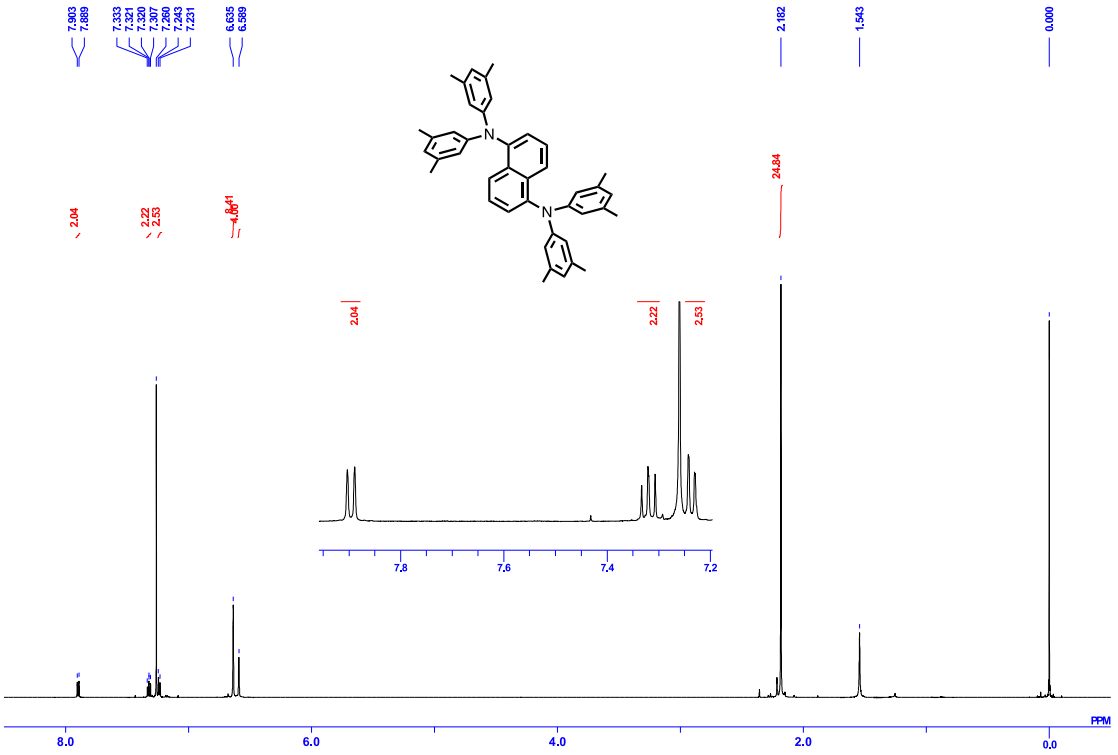


Figure S18. ^{1}H NMR spectrum of 1,5-bis[*N,N*-bis(*m*-xylyl)amino]naphthalene (600 MHz, $CDCl_3$, r.t.).

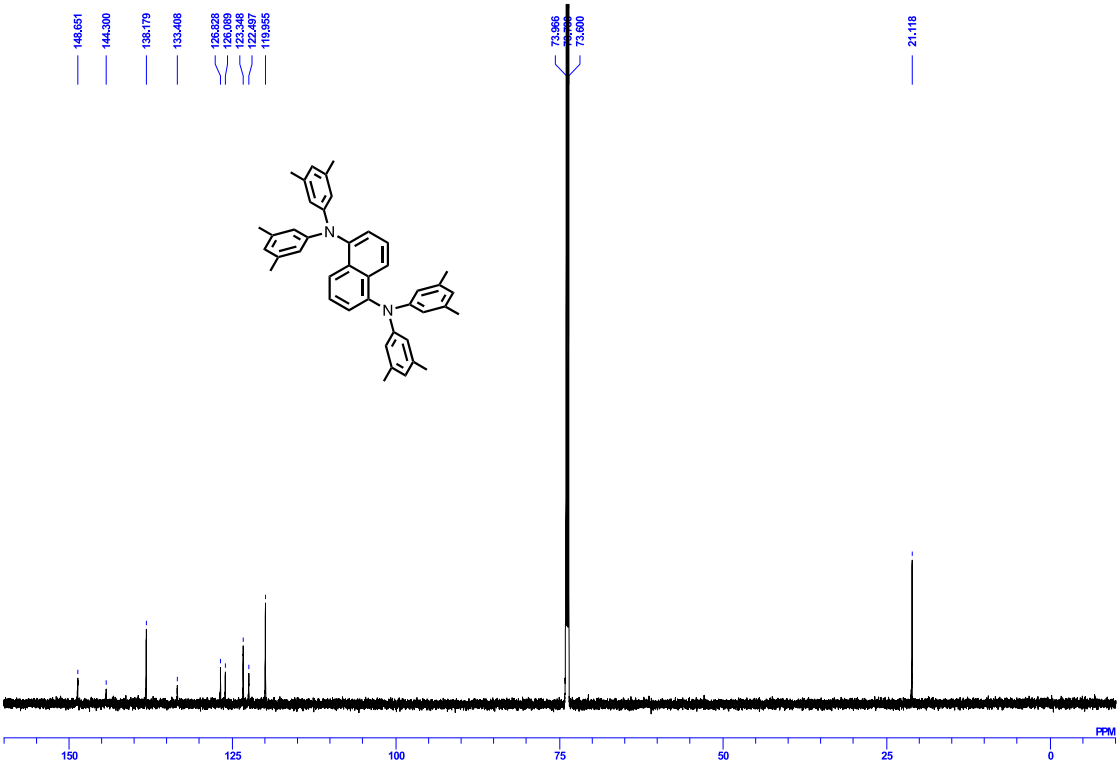


Figure S19. ^{13}C{^{1}H} NMR spectrum of 1,5-bis[*N,N*-bis(*m*-xylyl)amino]naphthalene (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

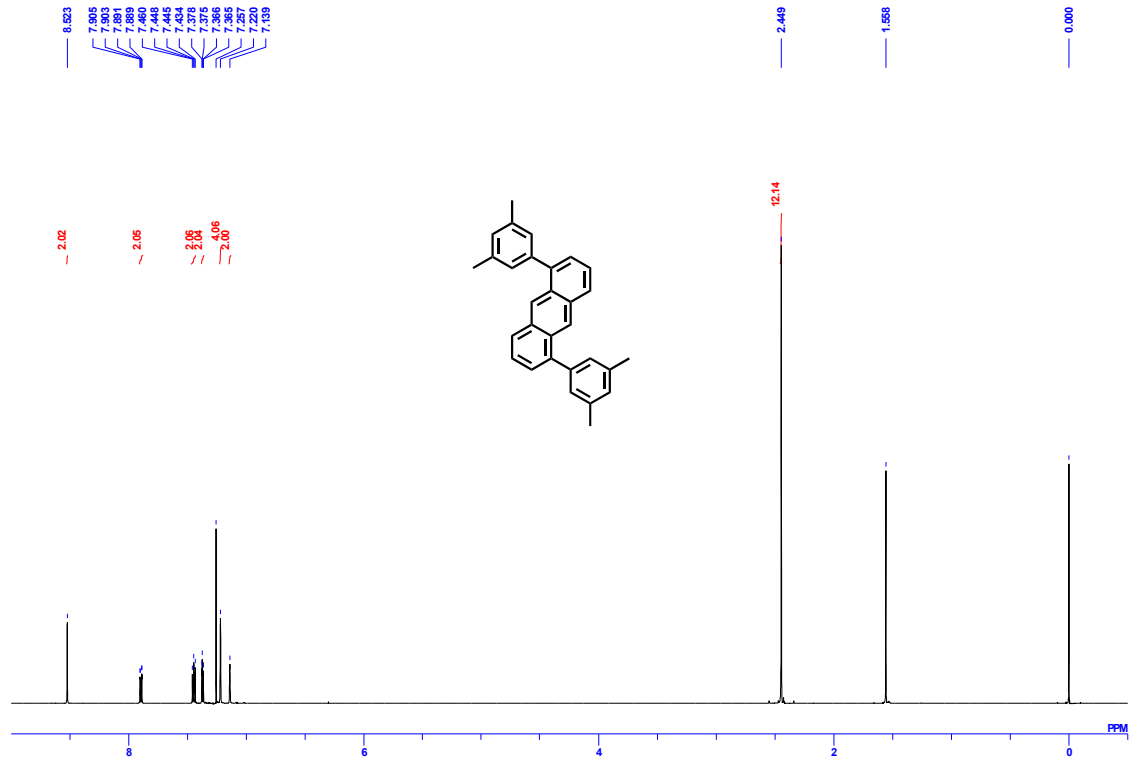


Figure S20. ^{1}H NMR spectrum of 1,5-bis(*m*-xylyl)anthracene (600 MHz, $CDCl_3$, r.t.).

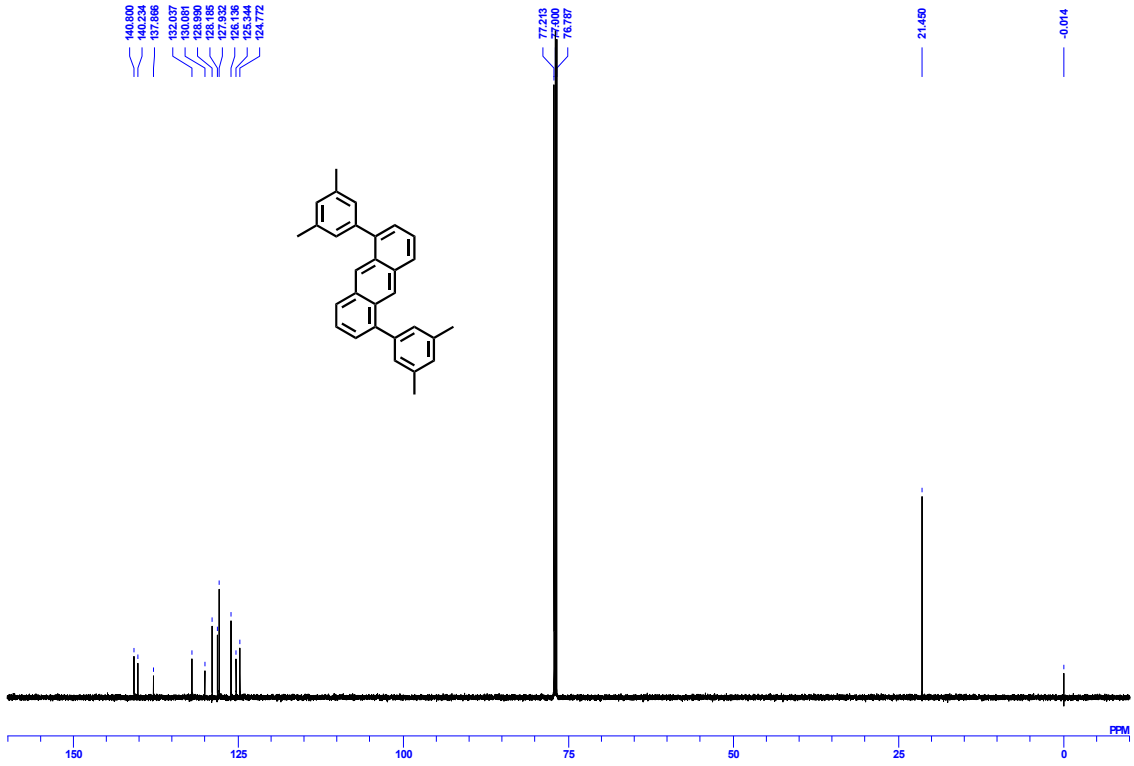


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of 1,5-bis(*m*-xylyl)anthracene (150 MHz, $CDCl_3$, r.t.).

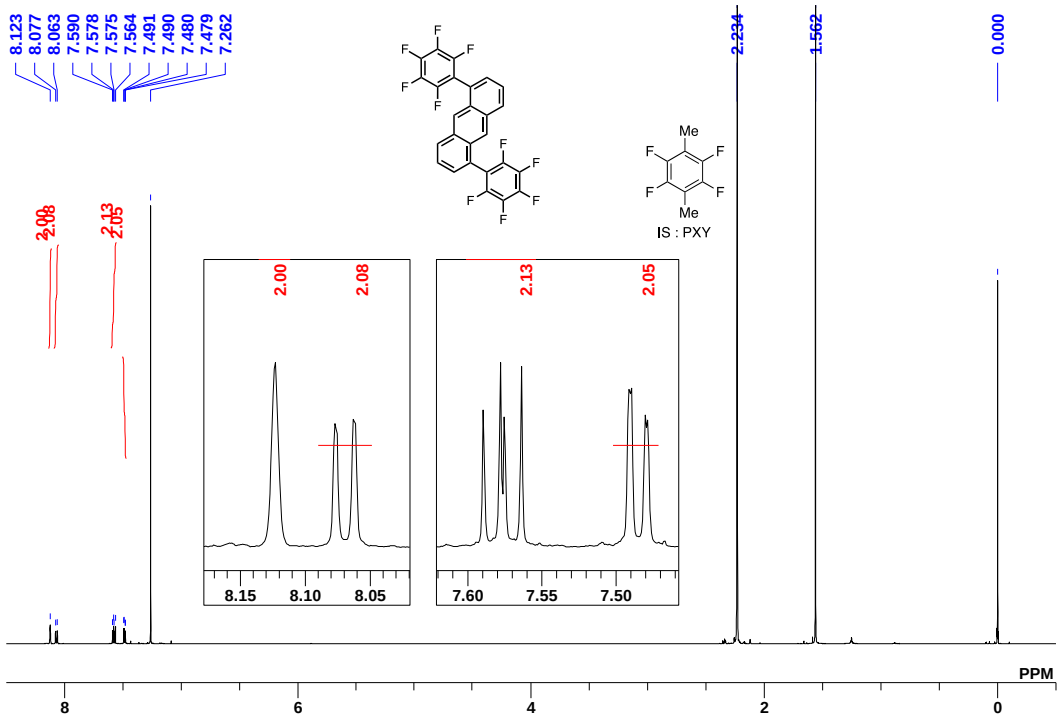


Figure S22. ^{1}H NMR spectrum of 1,5-bis(pentafluorophenyl)anthracene (600 MHz, $CDCl_3$, r.t.).

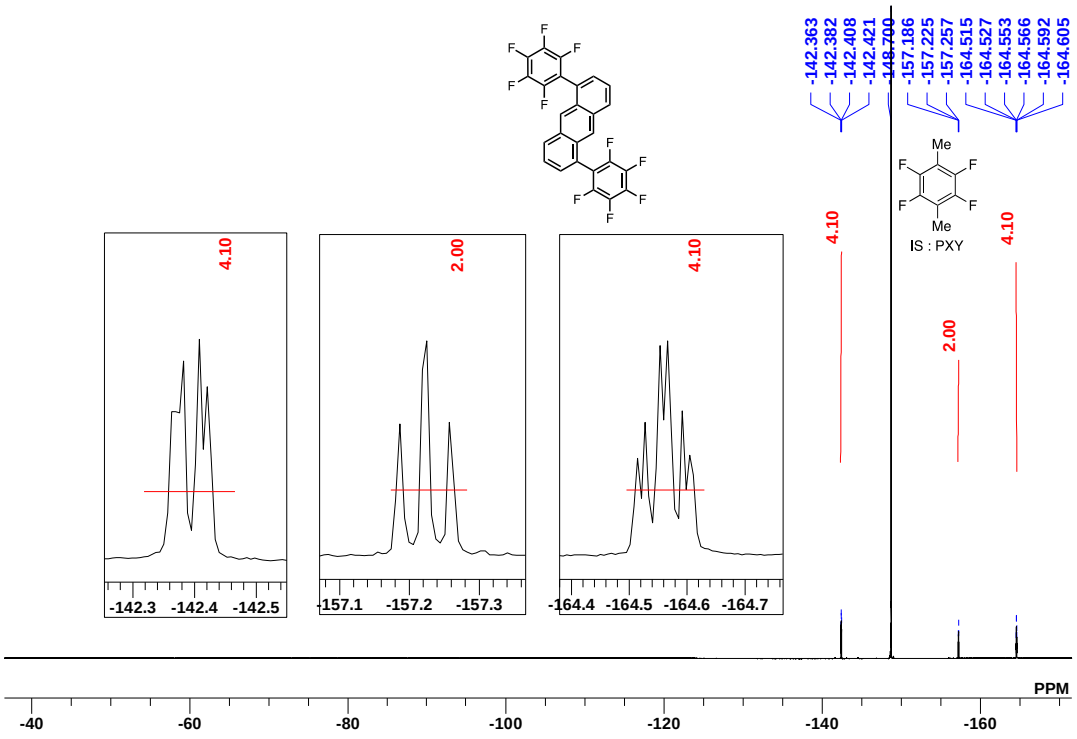


Figure S23. ^{19}F NMR spectrum of 1,5-bis(pentafluorophenyl)anthracene (565 MHz, $CDCl_3$, r.t.).

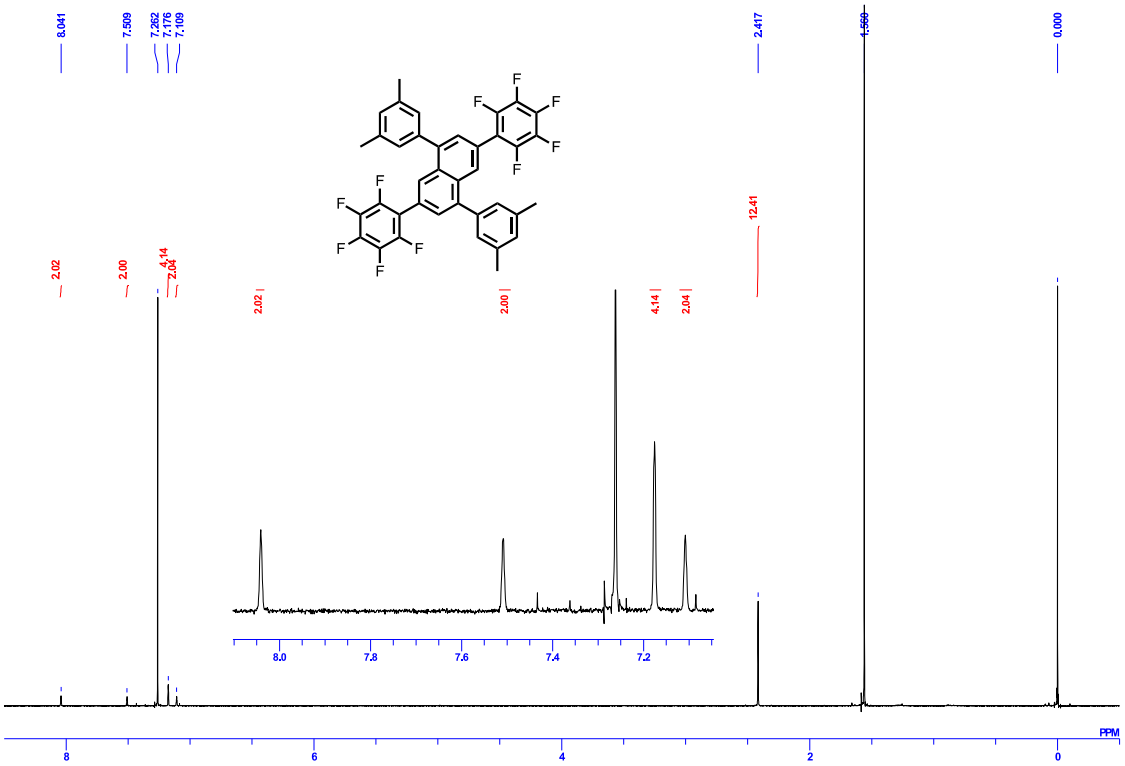


Figure S24. ^{1}H NMR spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.).

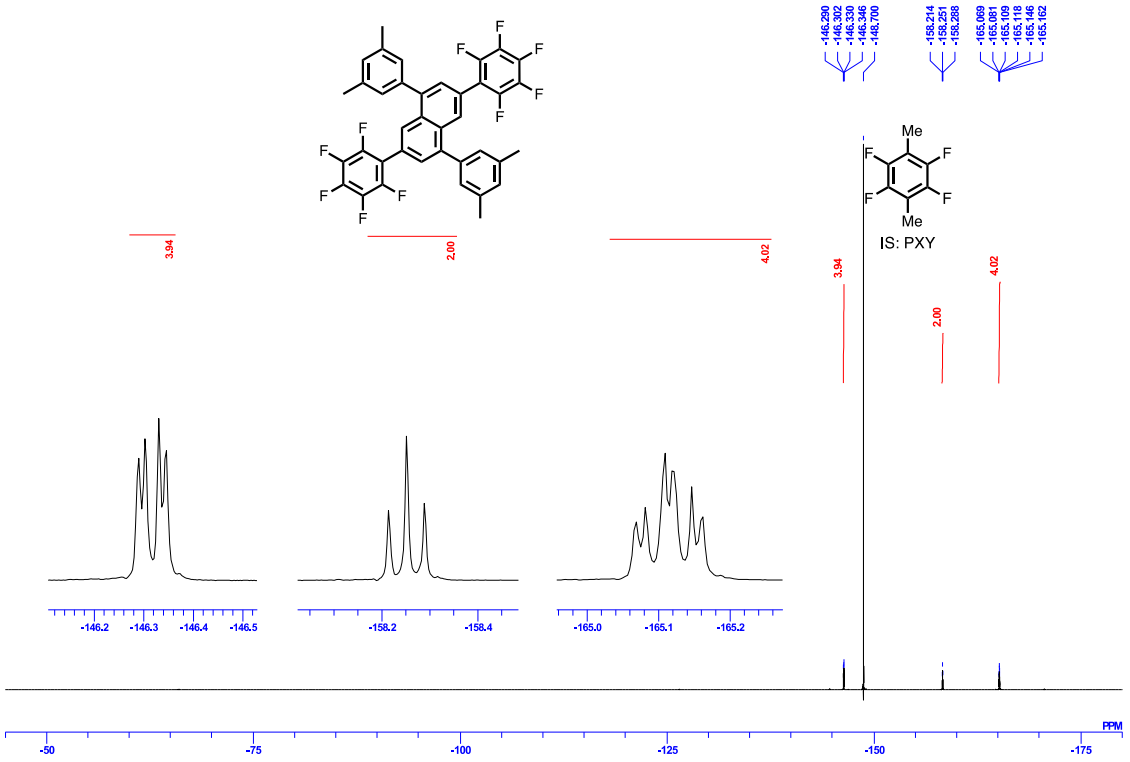


Figure S25. ^{19}F NMR spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.).

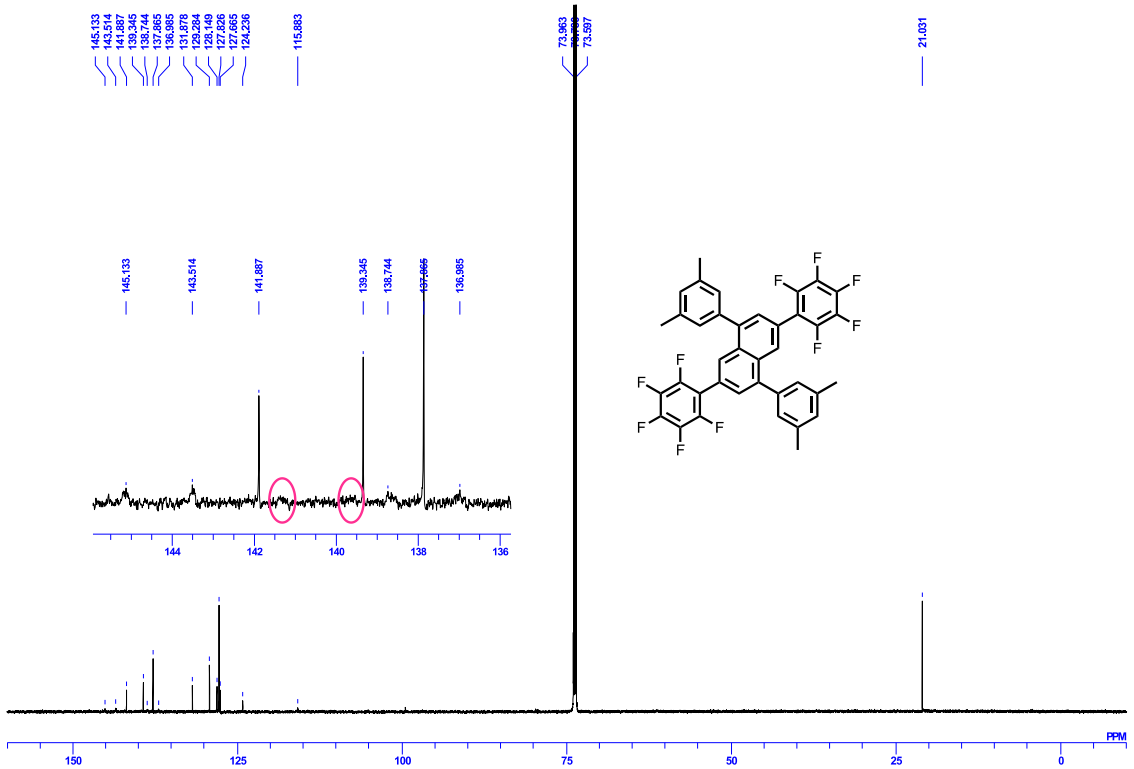


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)naphthalene (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

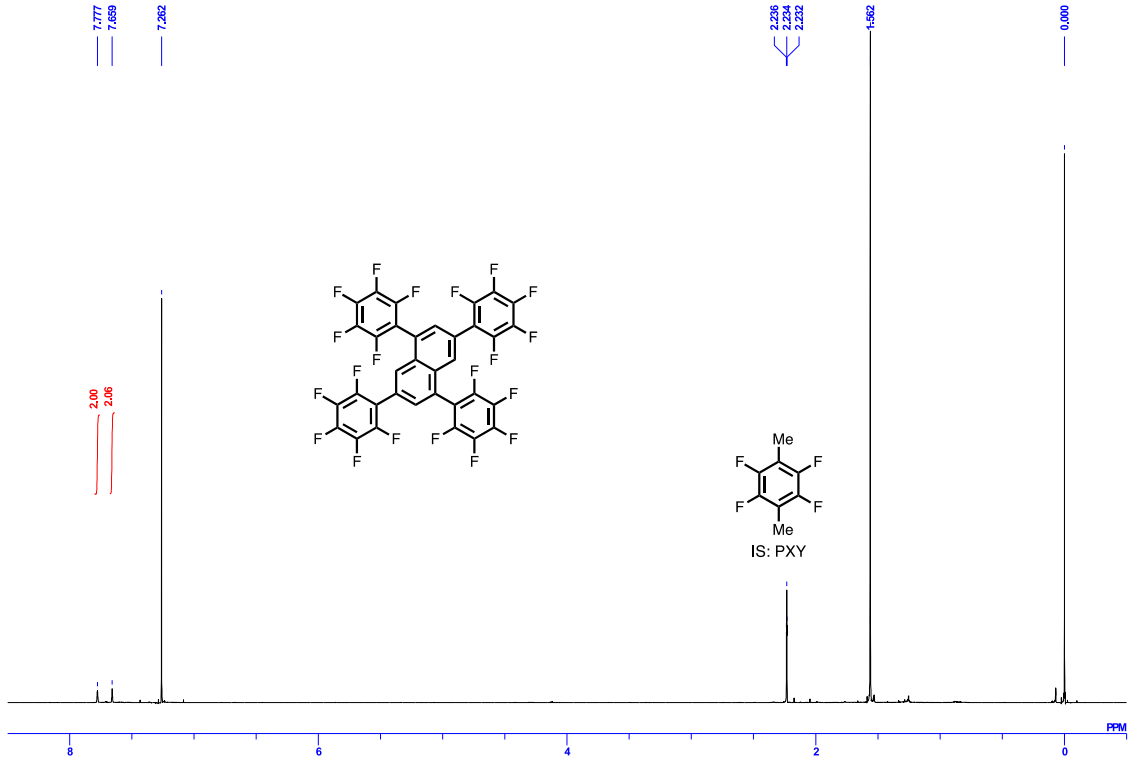


Figure S27. ^{1}H NMR spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.).

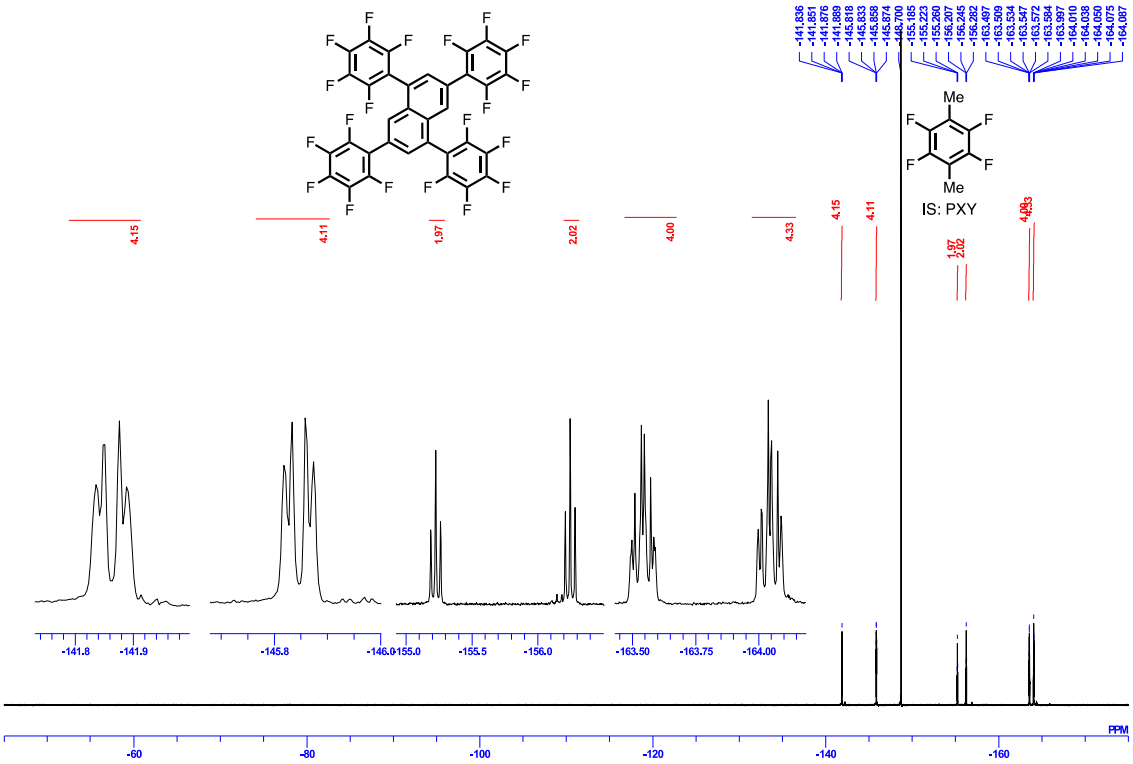


Figure S28. ^{19}F NMR spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.).

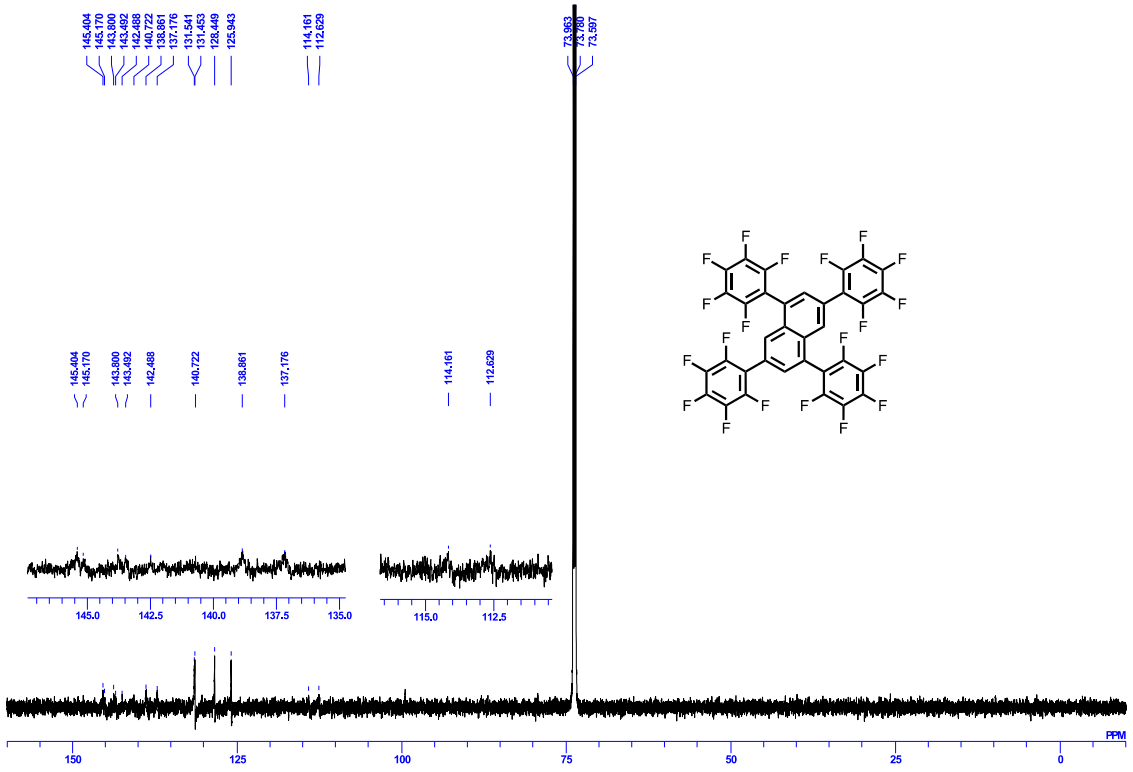


Figure S29. $^{13}C\{^1H\}$ NMR spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)naphthalene (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

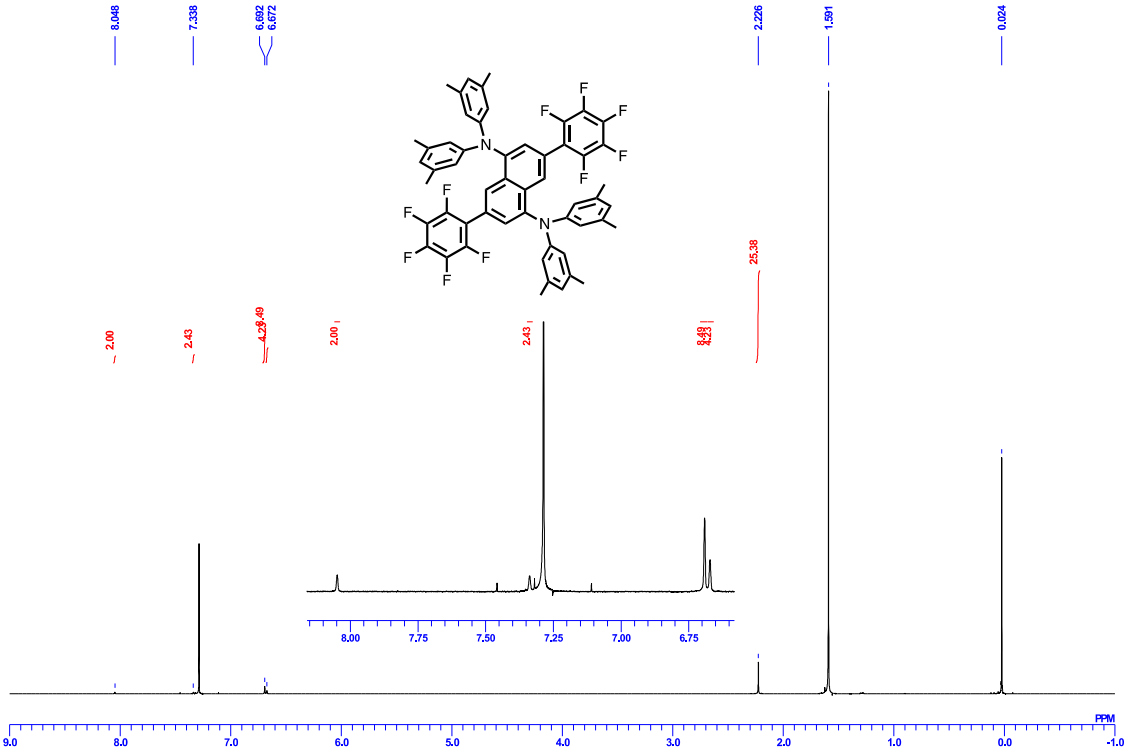


Figure S30. ^{1}H NMR spectrum of 1,5-bis[*N,N*-bis(*m*-xylyl)amino]-3,7-bis(pentafluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.).

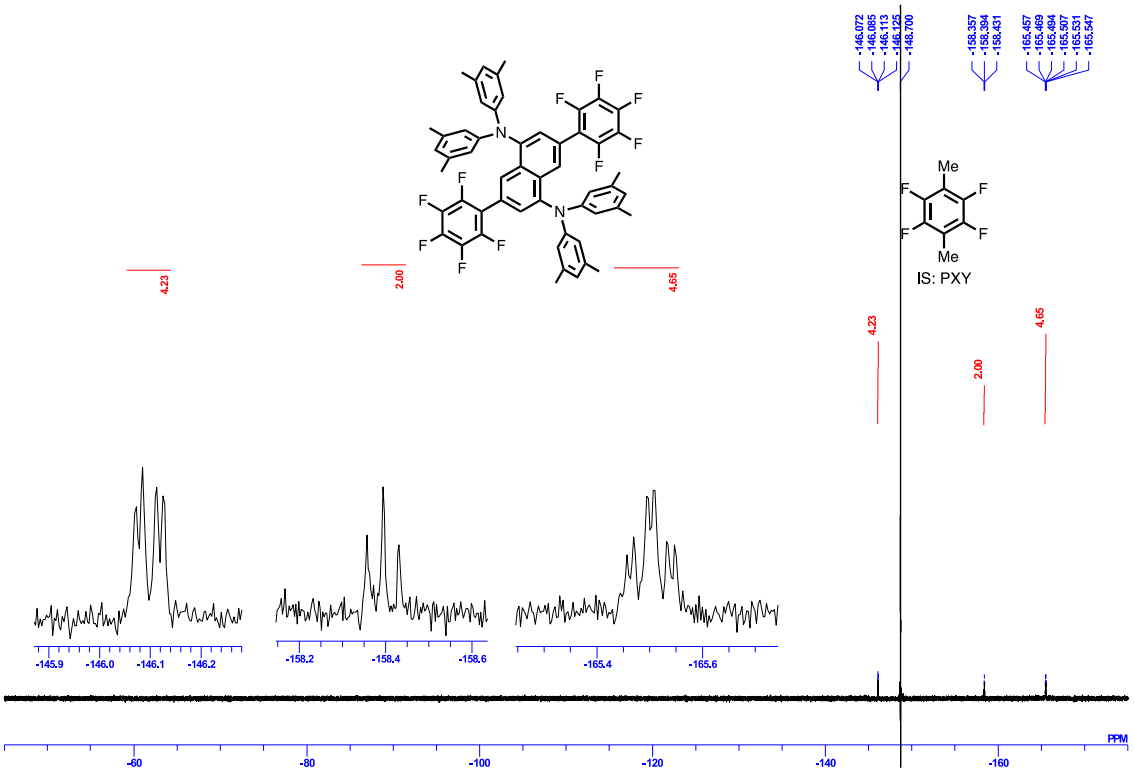


Figure S31. ^{19}F NMR spectrum of 1,5-bis[*N,N*-bis(*m*-xylyl)amino]-3,7-bis(pentafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.).

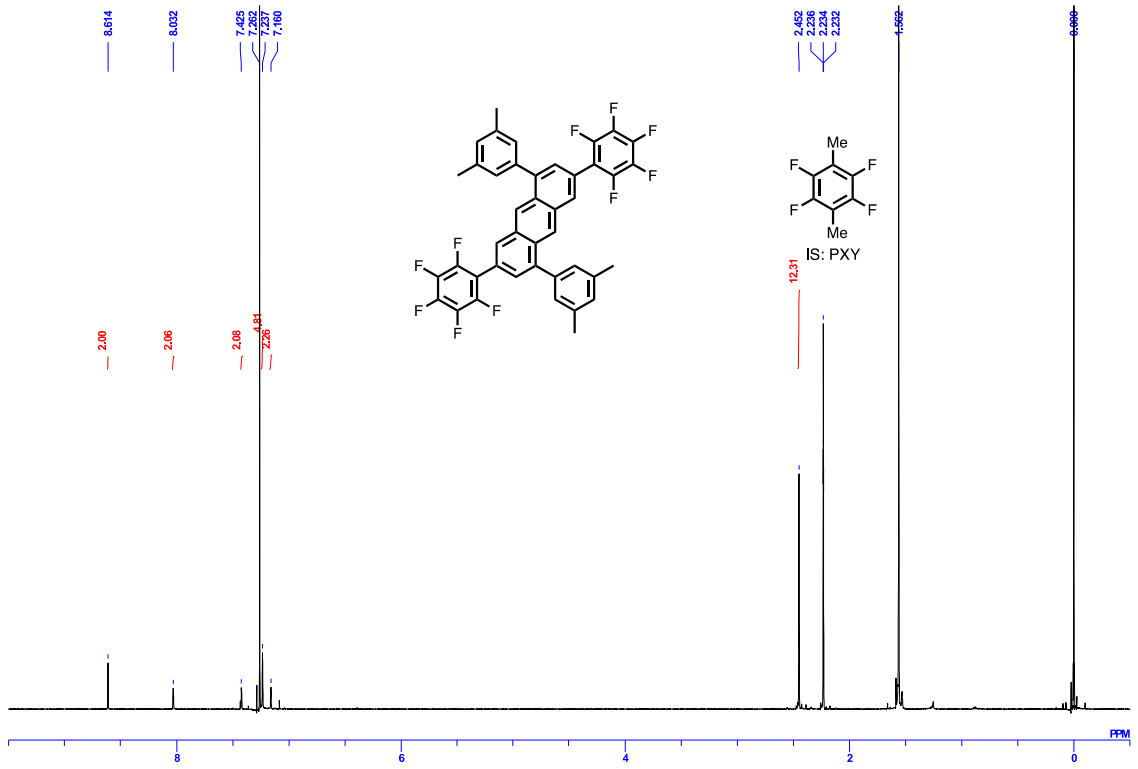


Figure S32. ^{1}H NMR spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)anthracene (600 MHz, $CDCl_3$, r.t.).

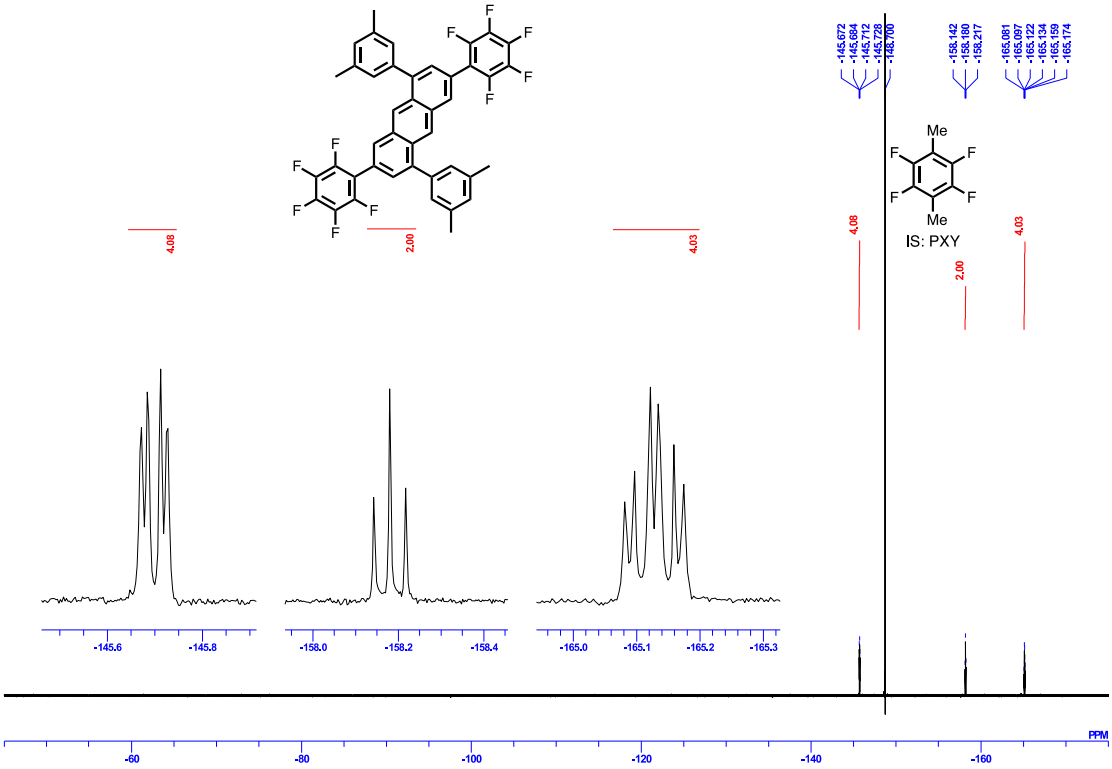


Figure S33. ^{19}F NMR spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)anthracene (565 MHz, $CDCl_3$, r.t.).

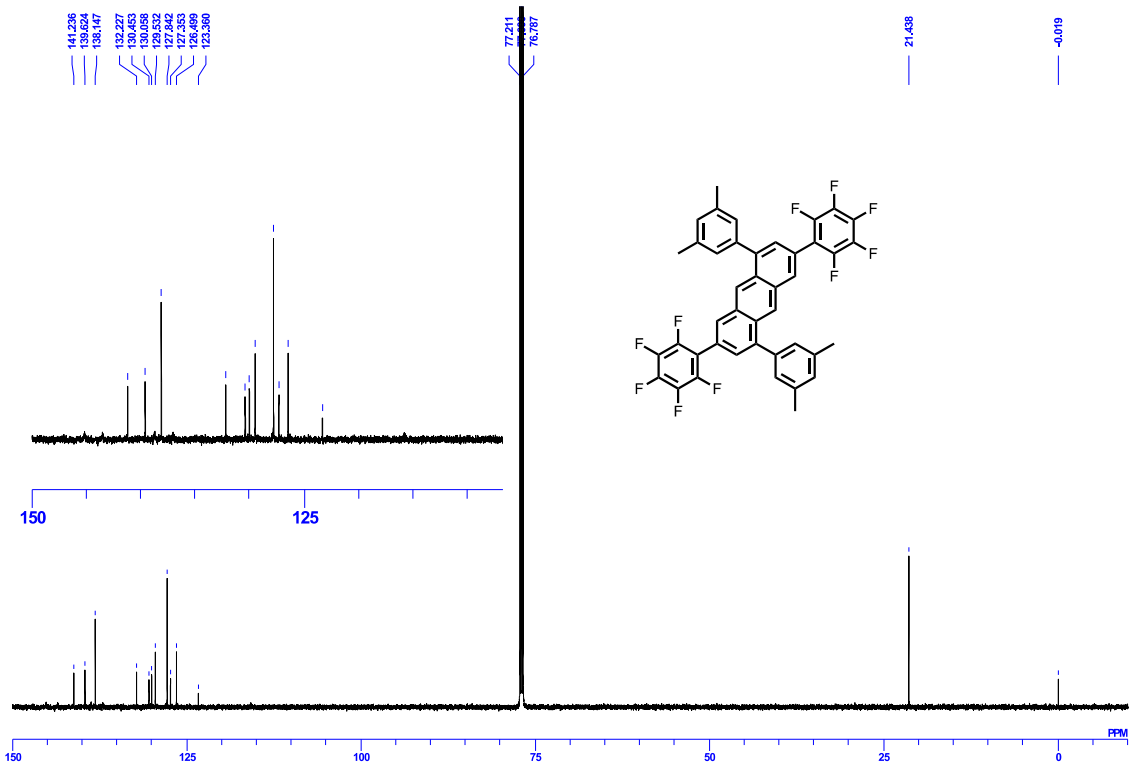


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)anthracene (150 MHz, $CDCl_3$, r.t.).

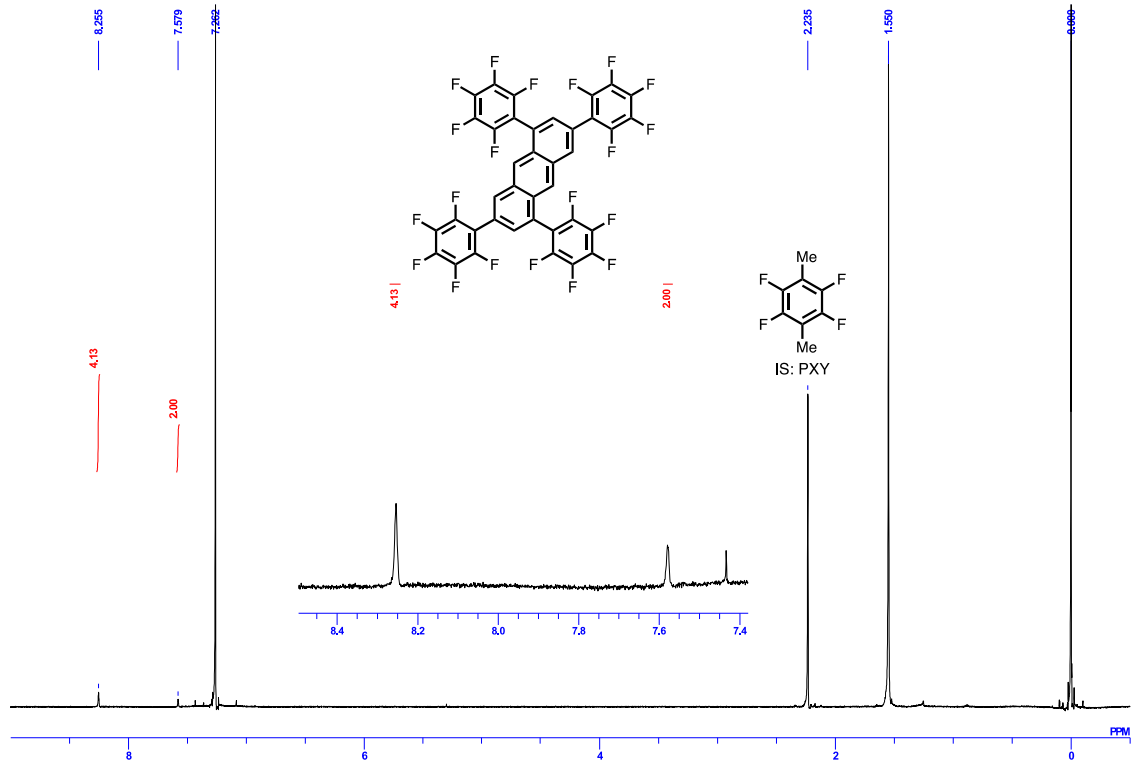


Figure S35. ^{1}H NMR spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)anthracene (600 MHz, $CDCl_3$, r.t.).

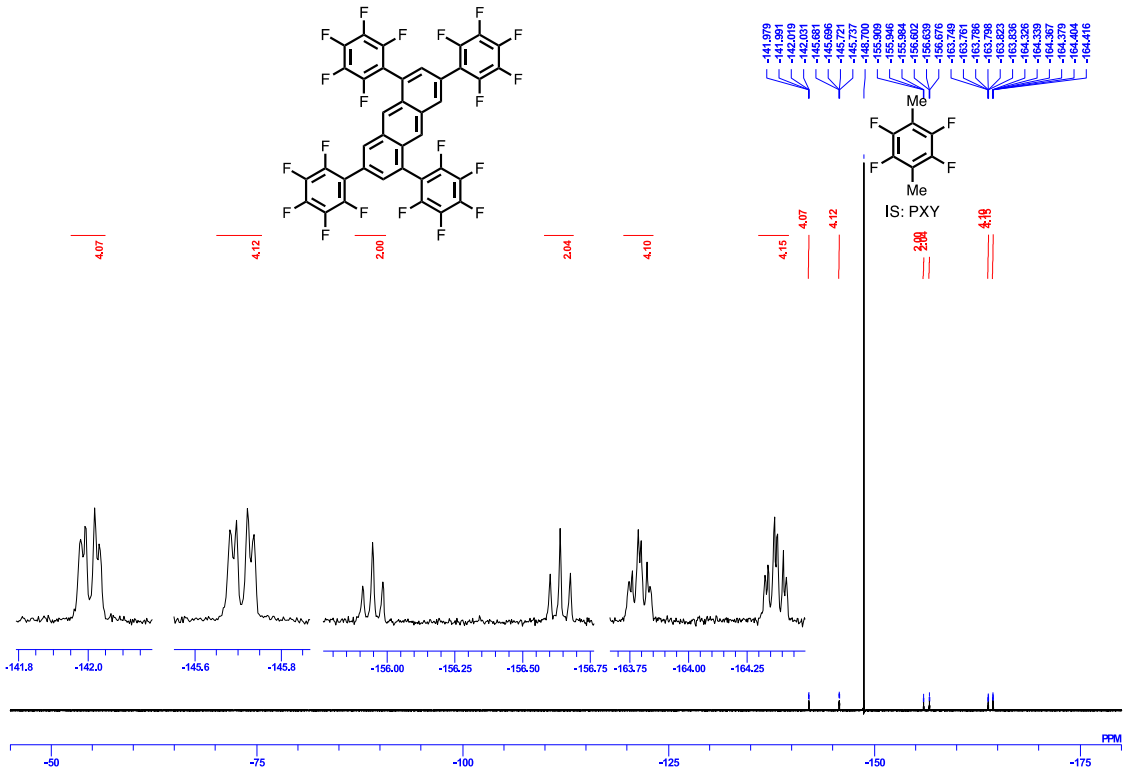


Figure S36. ^{19}F NMR spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)anthracene (565 MHz, $CDCl_3$, r.t.).

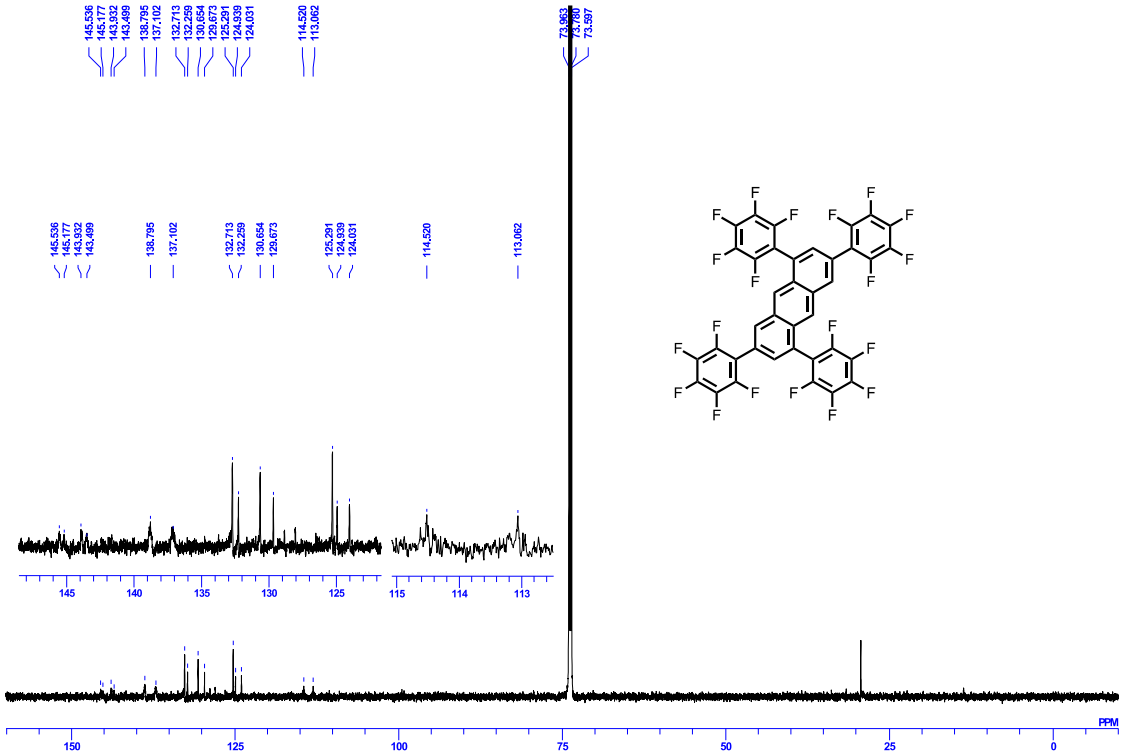


Figure S37. $^{13}C\{^1H\}$ NMR spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)anthracene (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

APCI-TOF MS spectra

[M+H⁺] Calcd. 337.1951 Found. 337.1953

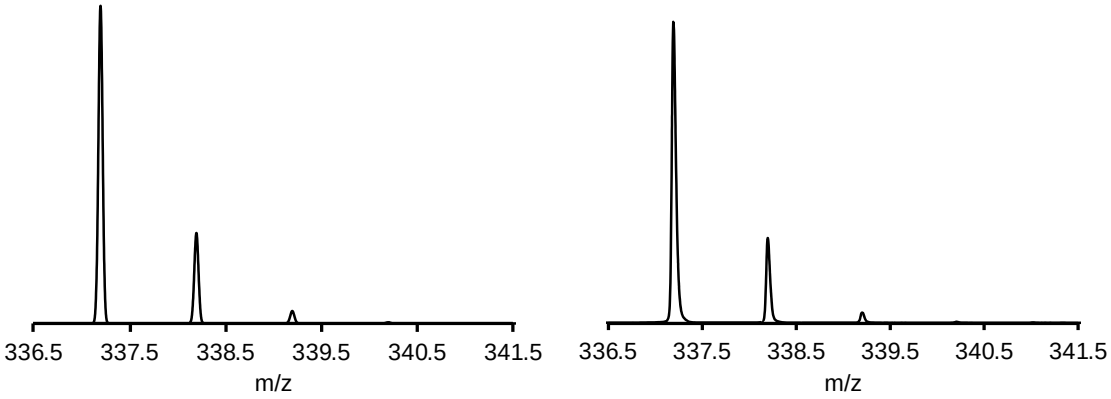


Figure S38. APCI-TOF MS spectrum of 1,5-bis(*m*-xylyl)naphthalene.

[M+H⁺] Calcd. 461.0383 Found. 461.0383

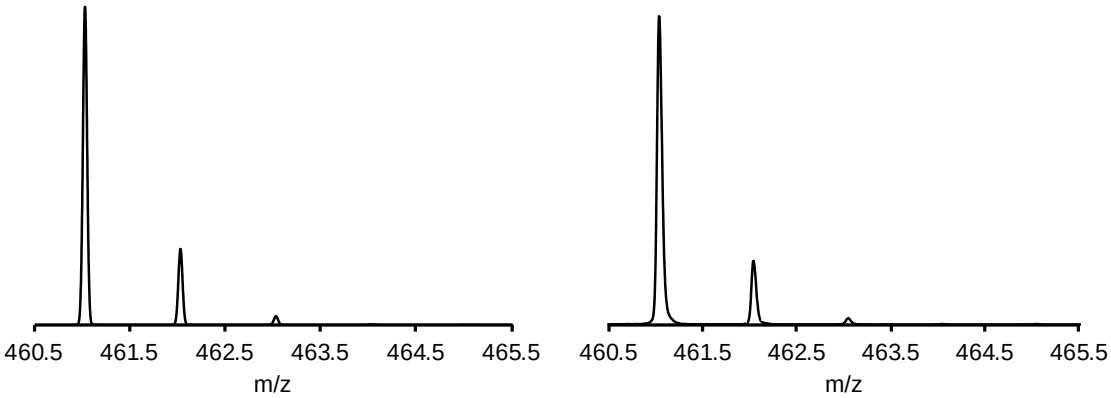


Figure S39. APCI-TOF MS spectrum of 1,5-bis(pentafluorophenyl)naphthalene.

[M+H⁺] Calcd. 575.3421 Found. 575.3441

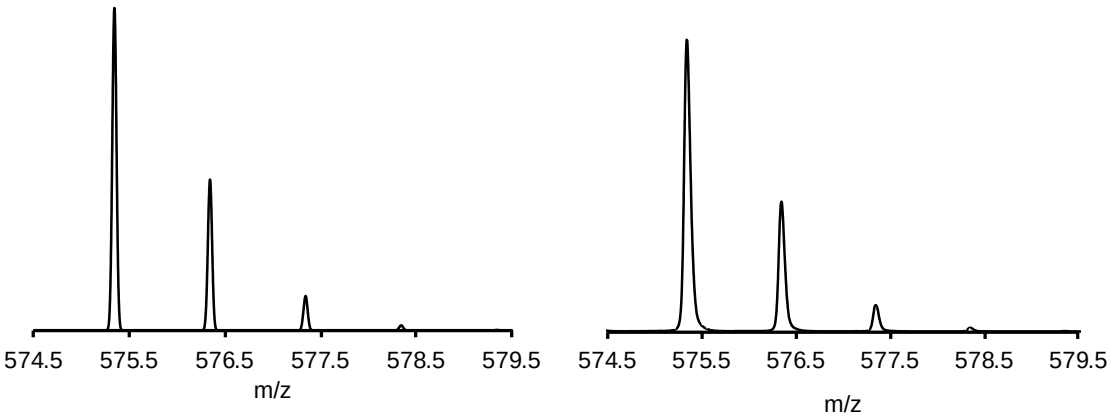


Figure S40. APCI-TOF MS spectrum of 1,5-bis[*N,N*-bis(*m*-xylyl)amino]naphthalene.

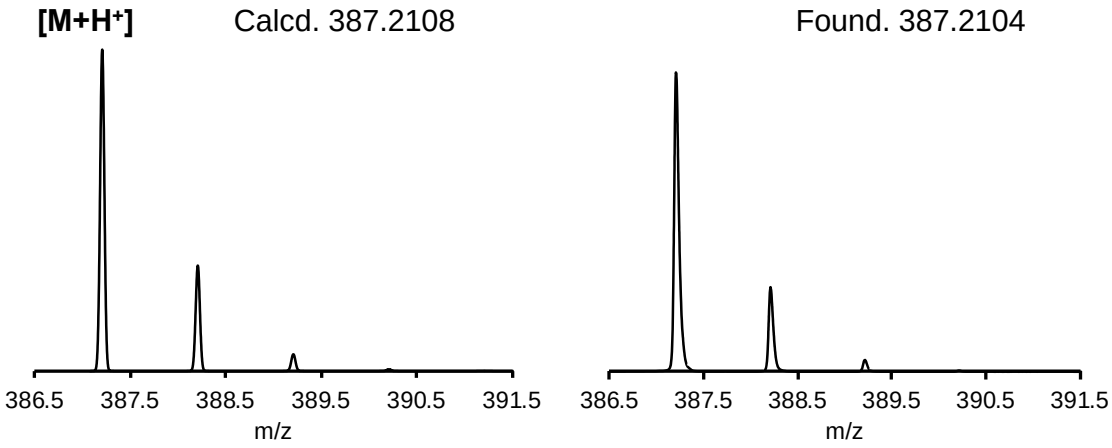


Figure S41. APCI-TOF MS spectrum of 1,5-bis(*m*-xylyl)anthracene.

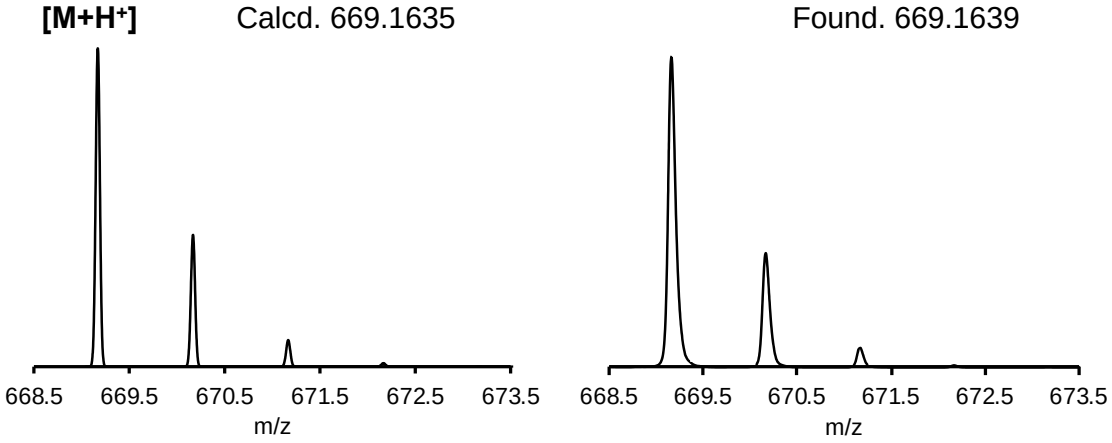


Figure S42. APCI-TOF MS spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)naphthalene.

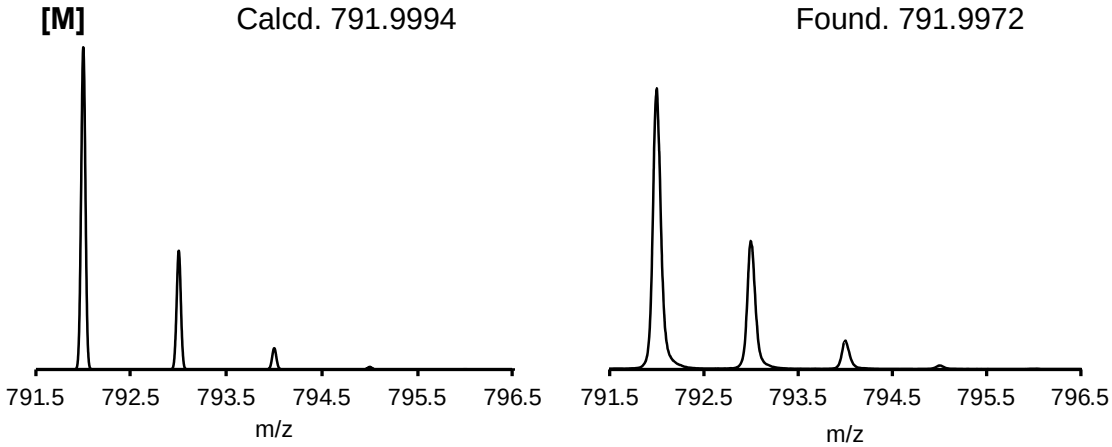


Figure S43. APCI-TOF MS spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)naphthalene.

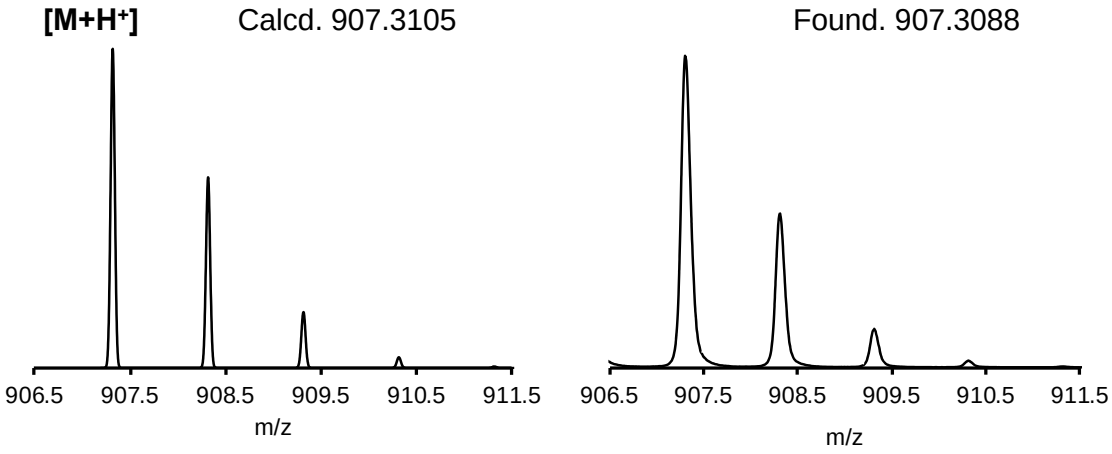


Figure S44. APCI-TOF MS spectrum of 1,5-bis[*N,N*-bis(*m*-xylyl)amino]-3,7-bis(pentafluorophenyl)naphthalene.

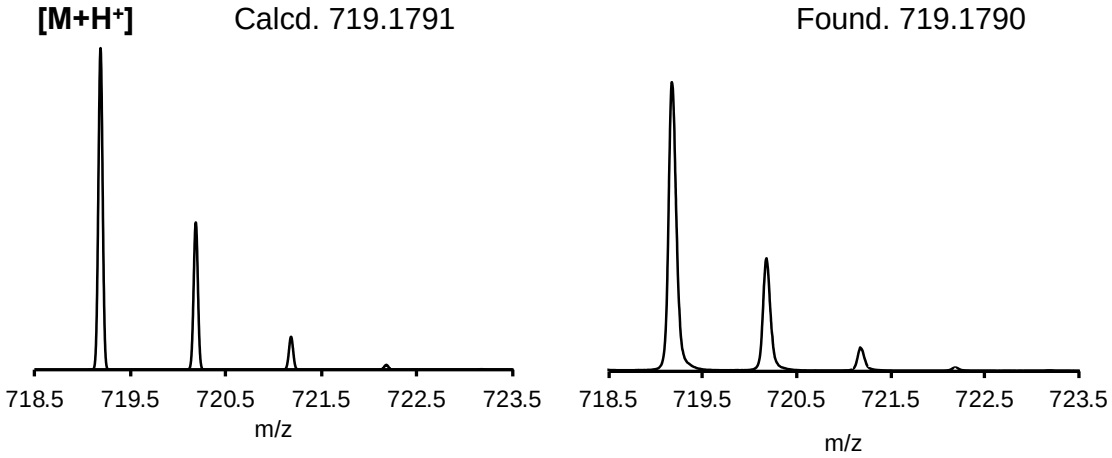


Figure S45. APCI-TOF MS spectrum of 1,5-bis(*m*-xylyl)-3,7-bis(pentafluorophenyl)anthracene.

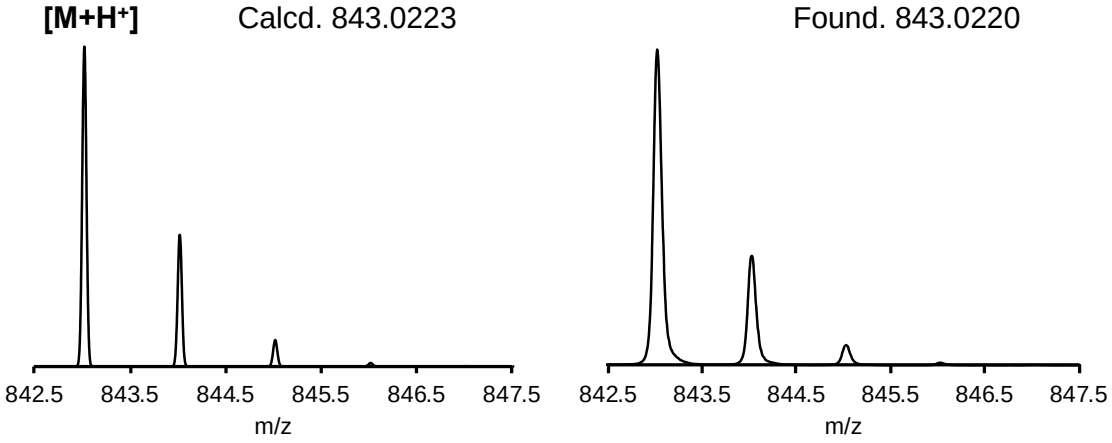


Figure S46. APCI-TOF MS spectrum of 1,3,5,7-tetrakis(pentafluorophenyl)anthracene.

Crystal structure determination

Intensity data were collected on a Bruker SMART APEX II ULTRA with Mo Kα radiation. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters using the SHELXL-97 program. CCDC 2164789, 2234487-2234491 contain the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S4. Crystallographic data 1

	1,5-bis(pentafluorophenyl) naphthalene	TANaph 1	TANaph 2
CCDC number	2164789	2234487	2234488
Empirical Formula	$C_{22}H_6F_{10}$	$C_{38}H_{22}F_{10}$	$C_{34}H_4F_{20}$
Formula Weight	460.27	668.58	792.37
Crystal Color	colorless	colorless	colorless
Crystal Dimensions / mm	0.216 x 0.069 x 0.025	0.550 x 0.115 x 0.024	0.402 x 0.054 x 0.042
Crystal System	monoclinic	monoclinic	monoclinic
Lattice Parameters			
a / Å	13.4090(15)	12.909(8)	6.1719(8)
b / Å	6.5074(7)	8.301(5)	20.881(3)
c / Å	19.584(2)	15.210(9)	11.0462(15)
β / deg.	97.3500(10)	114.905(7)	103.068(2)
V / Å^3	1694.8(3)	1478.3(15)	1386.7(3)
Space Group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
Z	4	2	2
D / gcm^{-3}	1.804	1.502	1.898
*F*000	912.00	680.00	776.00
μ(MoK*α*) / cm^{-1}	1.819	1.305	2.050
Reflection/Parameter Ratio	12.89	13.50	12.08
*R*1 (*I* > 2.00σ(*I*))	0.0337	0.0585	0.0317
R (All reflections)	0.0459	0.1144	0.0396
*wR*2 (All reflections)	0.0926	0.1717	0.0883
Goodness of Fit Indicator	1.004	0.983	1.017

Table S5. Crystallographic data 2

	TANaph 3	TAAnt 1	TAAnt 2
CCDC number	2234491	2234489	2234490
Empirical Formula	$C_{27}H_{20}F_{10}N$	$C_{42}H_{24}F_{10}$	$C_{38}H_{26}F_{20}$
Formula Weight	453.45	718.64	842.43
Crystal Color	yellow	yellow	colorless
Crystal Dimensions / mm	0.647 x 0.040 x 0.030	0.295 x 0.040 x 0.021	0.177 x 0.029 x 0.028
Crystal System	triclinic	triclinic	monoclinic
Lattice Parameters			
a / Å	8.4077(13)	8.02020	11.645(4)
b / Å	11.5245(18)	14.06570	12.590(4)
c / Å	11.9243(19)	14.61500	20.483(7)
α / deg.	73.192(2)	82.42800	
β / deg.	81.887(2)	85.80900	95.087(5)
γ / deg.	85.161(2)	79.95200	
V / Å^3	1093.8(3)	1607.14942	2991.2(17)
Space Group	*P*-1 (#2)	*P*-1 (#2)	$P2_1/c$ (#14)
Z	2	2	4
D / gcm^{-3}	1.377	1.485	1.871
*F*000	468.00	732.00	1656.00
μ(MoK*α*) / cm^{-1}	1.096	1.259	1.964
Reflection/Parameter Ratio	16.07	14.63	12.14
*R*1 (*I* > 2.00σ(*I*))	0.0546	0.0569	0.0569
R (All reflections)	0.0781	0.0965	0.1316
*wR*2 (All reflections)	0.1545	0.1541	0.1439
Goodness of Fit Indicator	1.047	1.049	0.998

Reference

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