Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Photocyclization of diarylethylenes with boronate moiety: a useful synthetic tool to soluble PAH building blocks

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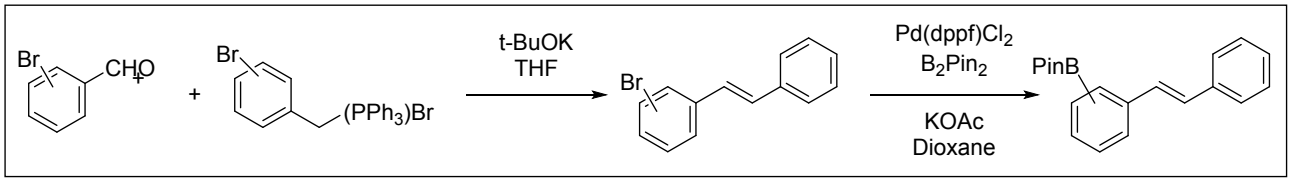
General Information

All chemicals and solvents were purchased in reagent grade from commercial suppliers (Acros®, SigmaAldrich® or Fluka®, Fluorochem®, Merck®, ChemPur®) and used as received unless otherwise specified. Flash column chromatography was performed on Interchim PuriFlash 430 using flash grade silica gel from MacheryNagel 60 M (40-63 mm, deactivated). NMR spectra were recorded on a Bruker Avance Neo 300 operating at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR) or on a Bruker Avance Neo 400 operating at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR). The signals were referenced to residual solvent peaks (in parts per million (ppm) ^{1}H: CD_2Cl_2, 5.32 ppm; $CDCl_3$, 7.27 ppm ^{13}C: CD_2Cl_2, 53.84 ppm; $CDCl_3$ 77.00 ppm). Coupling constants were assigned as observed. The obtained spectra were evaluated with the program MestReNova. APPI MS spectra were recorded on a Bruker ESI TOF maXis4G instrument. The data was evaluated with the program Bruker Compass DataAnalysis 4.2. TLC analyses were carried out with TLC sheets coated with silica gel with fluorescent indicator254 nm from Machery-Nagel (ALUGRAM® SIL G/UV254) and visualized via UV-light of 254nm or 366 nm.

Experimental procedures

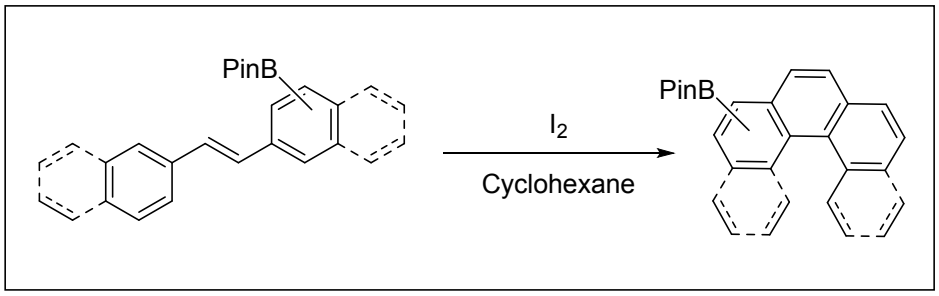
Synthesis of BPin *ortho*-fused PAH derivatives

General procedure for Wittig/Miyaura reaction



Bromotriphenyl- λ 5 -phosphane (1.25 mmol) was dissolved in 10 ml of dry THF in a two-neck flask. The mixture was degassed and the flask was filled with argon. After stirring at r.t. for 5 min t-BuOK (2 mmol) was added in portions and a solution of aldehyde (1 mmol) in 5 ml of THF was added dropwise. The obtained orange suspension was refluxed under argon atmosphere overnight, cooled down and quenched with 1M HCl to pH=5.5. The mixture was concentrated under reduced pressure, extracted with dichloromethane and organic layer was dried over anhydrous $MgSO_4$. Filtration through a short silica plug gave the mixture of (Z/E) bromostylbenes. The obtained stilbenes, potassium acetate (2.5 mmol), bis(pinacolato)diboron (1.25 mmol) and Pd(dppf)Cl2 (4 mmol) were dissolved in 75 ml of dioxane and refluxed under argon atmosphere for 10 hours. After full conversion the mixture was extracted with dichloromethane and washed with brine, organic layer was dried over anhydrous $MgSO_4$ and filtered through a short silica plug to give a mixture of (Z/E)- BPin-diarylethenes.

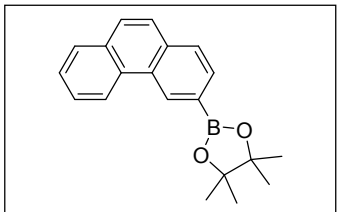
General procedure for photocyclization



The obtained mixture of diarylethenes was dissolved in 600 ml of cyclohexane (as obtained from Acros, solvent was not degassed). Iodine (1 mmol) was added to the solution before it was irradiated using 400 W high-pressure mercury-vapor lamp under ambient conditions and air. After full conversion the mixture was concentrated under reduced pressure, quenched with $Na_2S_2O_3$ solution and extracted with dichloromethane. Combined organic layer was dried over anhydrous MgSO4. The final product was isolated by flash chromatography (Hexane:Ethylacetate=90:10) .

5 g scale synthesis was carried out in 1l of cyclohexane with 4g of iodine. Reaction time:12 h.

4,4,5,5-tetramethyl-2-(phenanthren-3-yl)-1,3,2-dioxaborolane.



Chemical Formula: $C_{20}H_{21}BO_2$
Molecular Weight: 304,1960

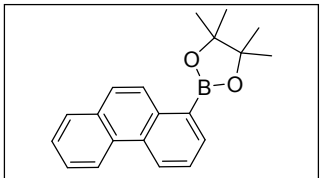
Yellow semi-solid. Yield 99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.87 (d, *J* = 8.6 Hz, 1H), 8.02 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.90 (dd, *J* = 7.8, 2.1 Hz, 2H), 7.78 (q, *J* = 8.9 Hz, 2H), 7.69 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 1.44 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.0, 132.0, 131.8, 130.6, 130.2, 129.5, 128.5, 128.1, 127.7, 126.8, 126.6, 126.5, 123.0, 84.0, 25.0.

HRMS (APPI; Toluene): Chemical Formula: $C_{20}H_{21}BO_2$, calc. 304.1635, found 304.1636

4,4,5,5-tetramethyl-2-(phenanthren-1-yl)-1,3,2-dioxaborolane



Chemical Formula: $C_{20}H_{21}BO_2$
Molecular Weight: 304,1960

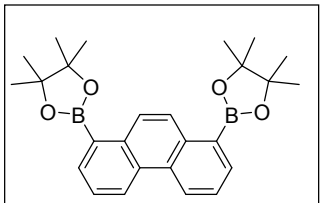
Orange semi-solid. Yield 93%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8.3 Hz, 1H), 8.74 (m, 2H), 8.21 (d, *J* = 7.0 Hz, 1H), 7.92 (t, *J* = 6.4 Hz, 1H), 7.86 – 7.79 (m, 1H), 7.70-7.60 (m, 3H), 1.46 (d, *J* = 9.7 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 135.7, 131.7, 130.5, 129.9, 128.3, 127.2, 127.1, 126.4, 126.3, 125.8, 125.6, 122.6, 83.9, 25.0.

HRMS (APPI; Toluene): Chemical Formula: $C_{20}H_{21}BO_2$, calc. 304.1635, found 304.1637

1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene



Chemical Formula: $C_{26}H_{32}B_2O_4$
Molecular Weight: 430,1580

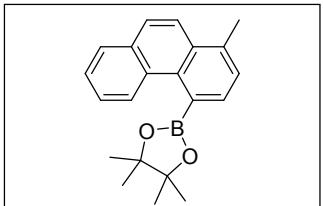
Brown semi-solid. Yield 80%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (d, *J* = 9.3 Hz, 2H), 8.80 (s, 2H), 8.21 (d, *J* = 7.8 Hz, 2H), 7.71 – 7.60 (m, 2H), 1.48 (s, 24H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 135.8, 135.6, 130.2, 127.4, 125.8, 125.3, 83.8, 25.0.

HRMS (APPI; Toluene): Chemical Formula: $C_{26}H_{32}B_2O_4$, calc. 430.2487, found 430.2488.

4,4,5,5-tetramethyl-2-(1-methylphenanthren-4-yl)-1,3,2-dioxaborolane.



Chemical Formula: $C_{21}H_{23}BO_2$
Molecular Weight: 318,2230

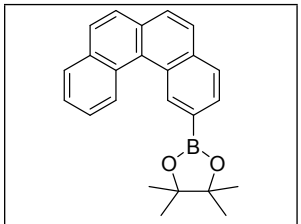
Orange semi-solid. Yield 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.97 (d, *J* = 9.1 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.78 (dd, *J* = 11.8, 8.1 Hz, 2H), 7.58 (dtd, *J* = 14.9, 7.0, 1.4 Hz, 2H), 7.45 (dd, *J* = 7.1, 0.7 Hz, 1H), .2.77 (s, 3H) 1.49 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 134.0, 132.6, 132.4, 131.2, 131.2, 128.1, 127.1, 127.0, 126.7, 126.4, 125.0, 123.0, 84.1, 24.7, 20.2.

HRMS (APPI; Toluene): Chemical Formula: $C_{21}H_{23}BO_2$, calc. 318,1791, found 318,1792.

2-(benzo[c]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Chemical Formula: $C_{24}H_{23}BO_2$
Molecular Weight: 354,2560

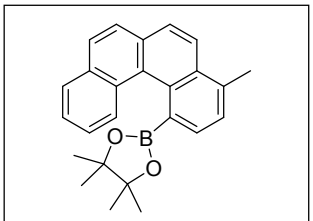
Yellow semi-solid. Yield 78%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.56 (s, 1H), 9.15 (d, *J* = 8.5 Hz, 1H), 8.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.93 (dd, *J* = 8.5, 4.8 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.76 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.71 – 7.64 (m, 1H), 1.41 (s, 12H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 135.8, 135.7, 134.1, 131.4, 131.3, 130.7, 130.0, 129.0, 128.5, 128.3, 128.1, 128.0, 127.9, 127.7, 127.1, 126.7, 126.4, 84.4, 25.2.

HRMS (APPI; Toluene): Chemical Formula: $C_{24}H_{23}BO_2$, calc. 354,1791, found 354,1793.

4,4,5,5-tetramethyl-2-(4-methylbenzo[c]phenanthren-1-yl)-1,3,2-dioxaborolane.



Chemical Formula: $C_{25}H_{25}BO_2$
Molecular Weight: 368,2830

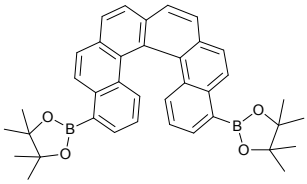
Orange semi-solid. Yield 67%.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.76 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.88 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.75 (dd, *J* = 8.6, 2.2 Hz, 3H), 7.54 – 7.42 (m, 2H), 7.42 – 7.37 (m, 1H), 2.72 (s, 3H), 0.97 (s, 6H), 0.66 (s, 6H).

^{13}C NMR (76 MHz, CD_2Cl_2) δ 136.9, 133.2, 133.2, 133.0, 132.9, 132.7, 130.5, 129.4, 128.5, 128.2, 127.8, 127.4, 127.1, 126.7, 126.2, 126.1, 123.4, 83.6, 25.4, 24.7, 20.2.

HRMS (APPI; Toluene): Chemical Formula: $C_{25}H_{25}BO_2$, calc. 354,1948, found 354,1948.

9,16-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahelicene.



Chemical Formula: $C_{38}H_{38}B_2O_4$
Molecular Weight: 580,3380

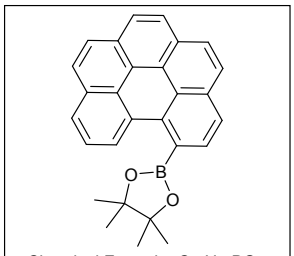
Brown semi-solid. Yield 70%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 8.9, 0.6 Hz, 2H), 8.05 – 7.91 (m, 6H), 7.78 (dd, *J* = 6.9, 1.3 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 8.5, 6.9 Hz, 2H), 1.58 – 1.34 (m, 24H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 135.7, 135.0, 133.0, 131.0, 130.8, 129.4, 128.4, 127.9, 127.0, 126.8, 126.5, 123.9, 83.8, 26.9.

HRMS (APPI; Toluene): Chemical Formula: $C_{38}H_{38}BO_2$, calc. 580.2956, found 580.2956.

2-(benzo[ghi]perylen-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



Chemical Formula: $C_{28}H_{23}BO_2$
Molecular Weight: 402,3000

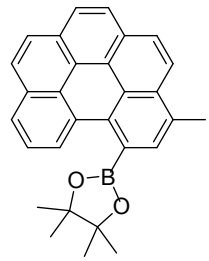
Green semi-solid. Yield 74%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 – 8.76 (m, 1H), 8.40 (s, 2H), 8.28-8.12 (m, 7H), 7.99 (t, *J* = 7.8 Hz, 1H), 1.57 (s, 12H).

^{13}C NMR (76 MHz, $CDCl_3$) δ 135.0, 133.0, 131.8, 131.4, 130.9, 129.3, 129.1, 127.9, 127.3, 127.2, 127.2, 126.9, 126.1, 126.0, 125.8, 125.7, 125.5, 125.1, 124.0, 123.8, 84.3,24.8.

HRMS (APPI; Toluene): Chemical Formula: $C_{28}H_{23}BO_2$, calc. 402.1791, found 402.1792.

4,4,5,5-tetramethyl-2-(5-methylbenzo[ghi]perylen-7-yl)-1,3,2-dioxaborolane.



Chemical Formula: $C_{29}H_{25}BO_2$
Molecular Weight: 416.3270

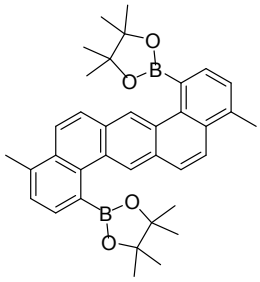
Green semi-solid. Yield 45%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.7 Hz, 1H), 8.40 – 8.34 (m, 2H), 8.29 (d, *J* = 9.0 Hz, 1H), 8.23 – 8.21 (m, 2H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 8.05 (s, 1H), 7.96 (t, *J* = 7.7 Hz, 1H), 3.00 (s, 3H), 1.58 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3, 132.8, 132.3, 131.7, 131.3, 131.1, 129.2, 128.8, 127.6, 127.2, 127.1, 126.4, 126.1, 125.8, 125.8, 125.5, 125.4, 125.1, 124.2, 123.9, 123.3, 84.3, 24.8, 19.9.

HRMS (APPI; Toluene): Chemical Formula: $C_{29}H_{25}BO_2$, calc. 416.1948, found 416.1949.

2,2'-(4,11-dimethylbenzo[k]tetraphene-1,8-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)



Chemical Formula: $C_{36}H_{40}B_2O_4$
Molecular Weight: 558.3320

Brown semi-solid. Yield 60%.

^{1}H NMR (80 MHz, $C_2D_2Cl_4$) δ 8.99 (s, 2H), 8.02 (m, 6H), 7.61 (d, *J* = 7.2 Hz, 2H), 2.90 (s, 6H), 1.62 (s, 24H).

^{13}C NMR (20 MHz, $C_2D_2Cl_4$) δ 137.4, 134.3, 133.5, 131.1, 130.4, 130.1, 127.9, 127.2, 126.4, 123.4, 84.4, 25.1, 20.4.

HRMS (APPI; Toluene): Chemical Formula: $C_{36}H_{40}B_2O_4$, calc. 558.3113, found 558.3113.

Spectral appendix (^{1}H ,^{13}C NMR).

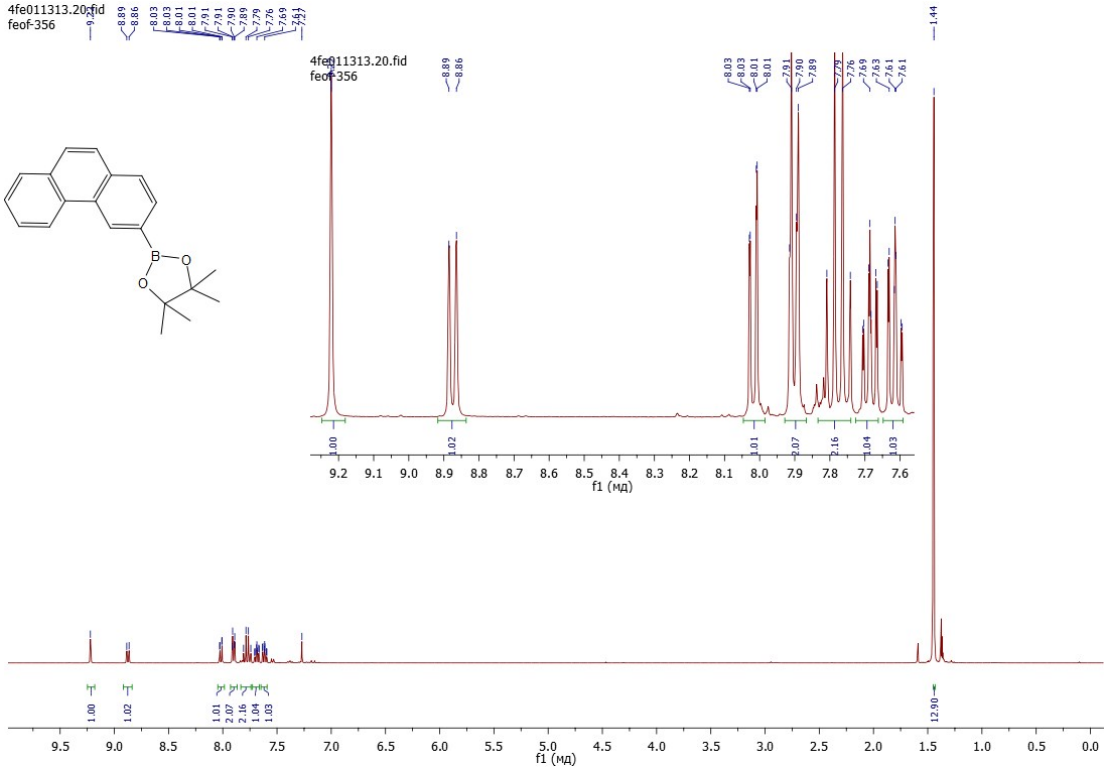


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(phenanthren-3-yl)-1,3,2-dioxaborolane.

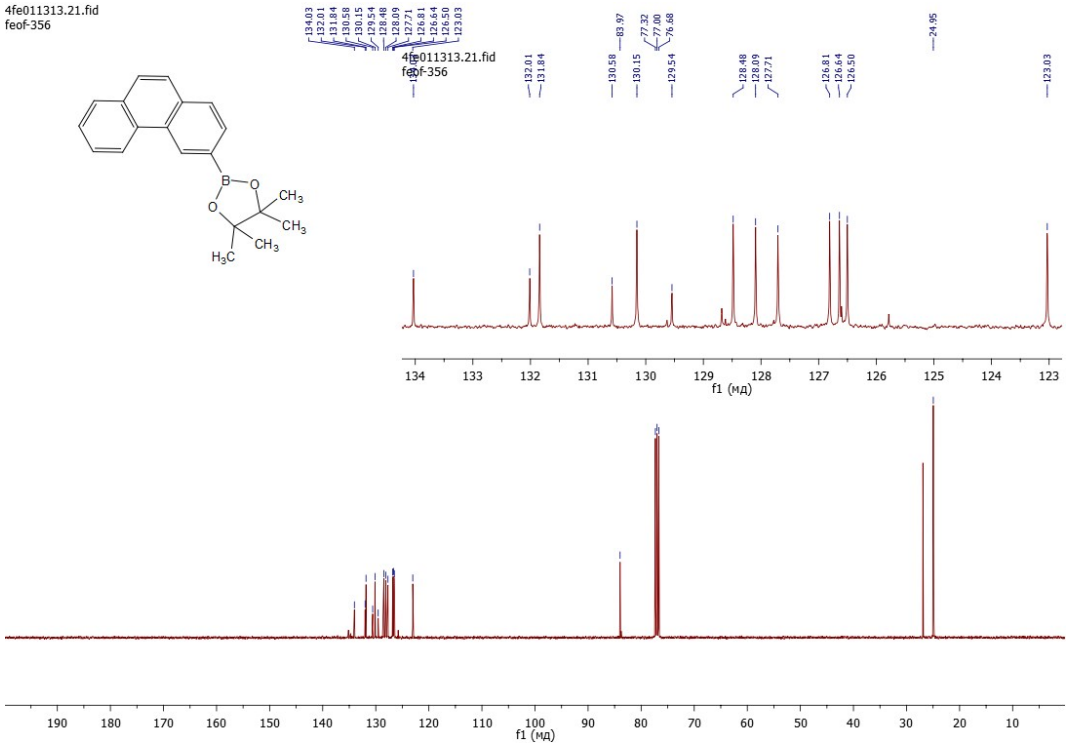


Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(phenanthren-3-yl)-1,3,2-dioxaborolane.

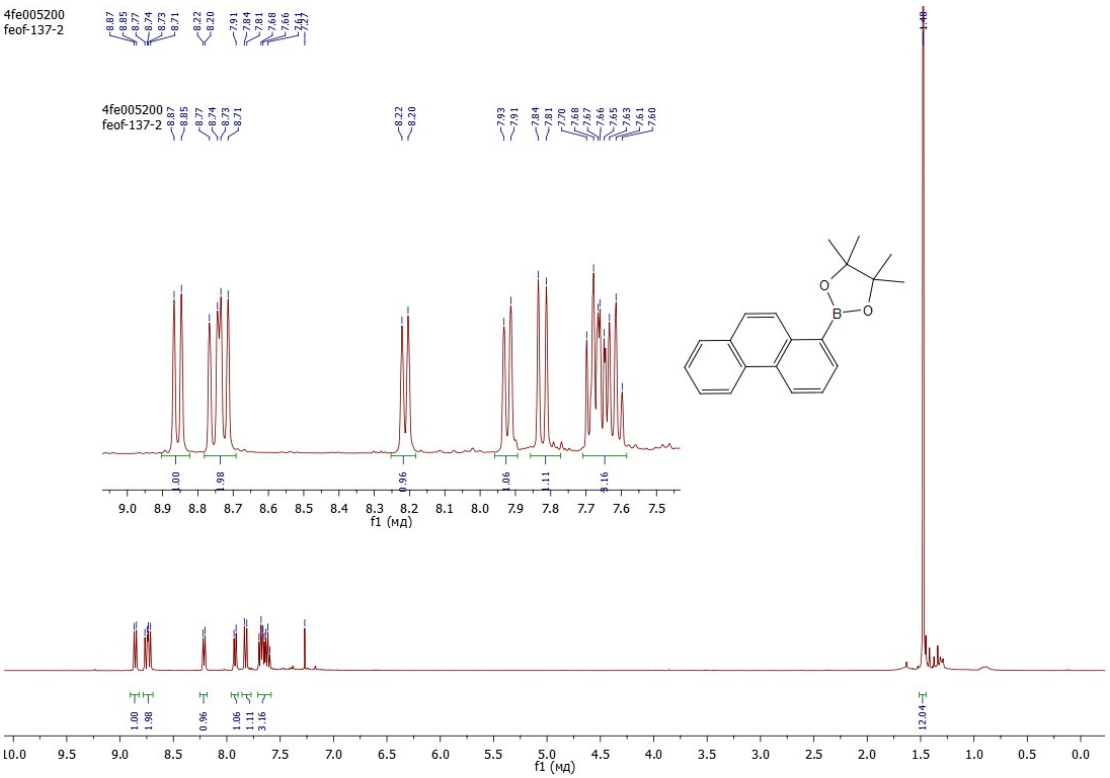


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(phenanthren-1-yl)-1,3,2-dioxaborolane.

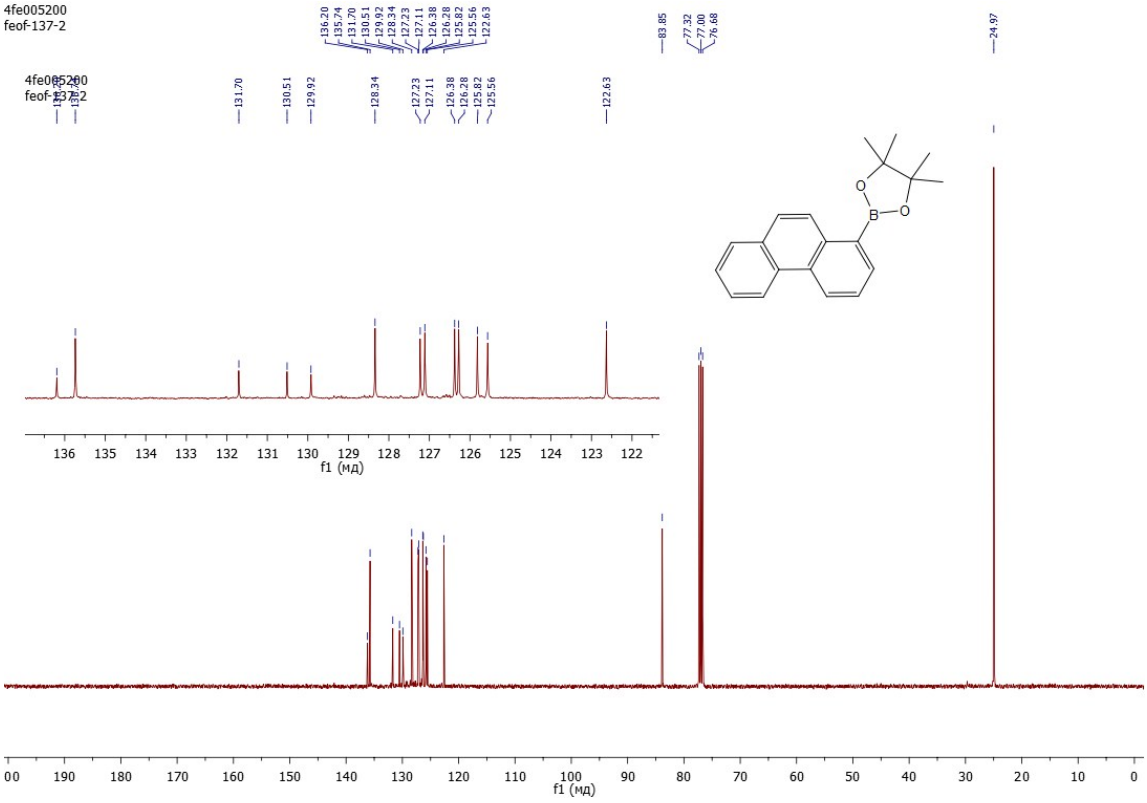


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(phenanthren-1-yl)-1,3,2-dioxaborolane

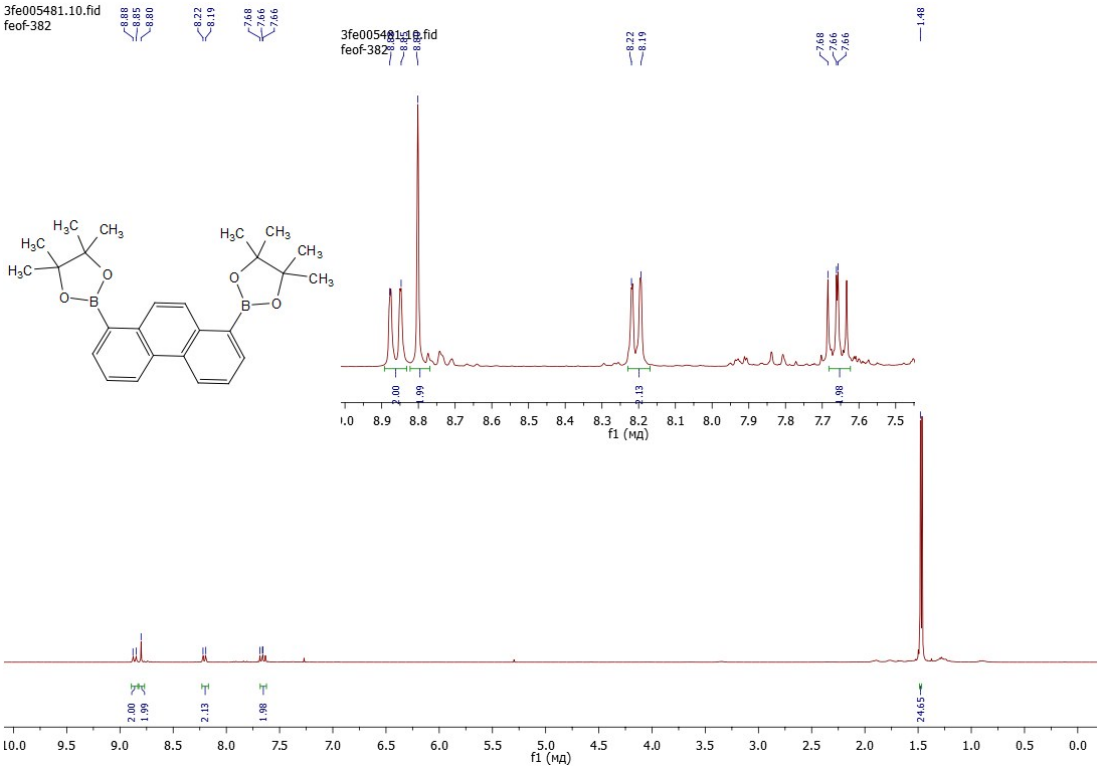


Figure S5. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene.

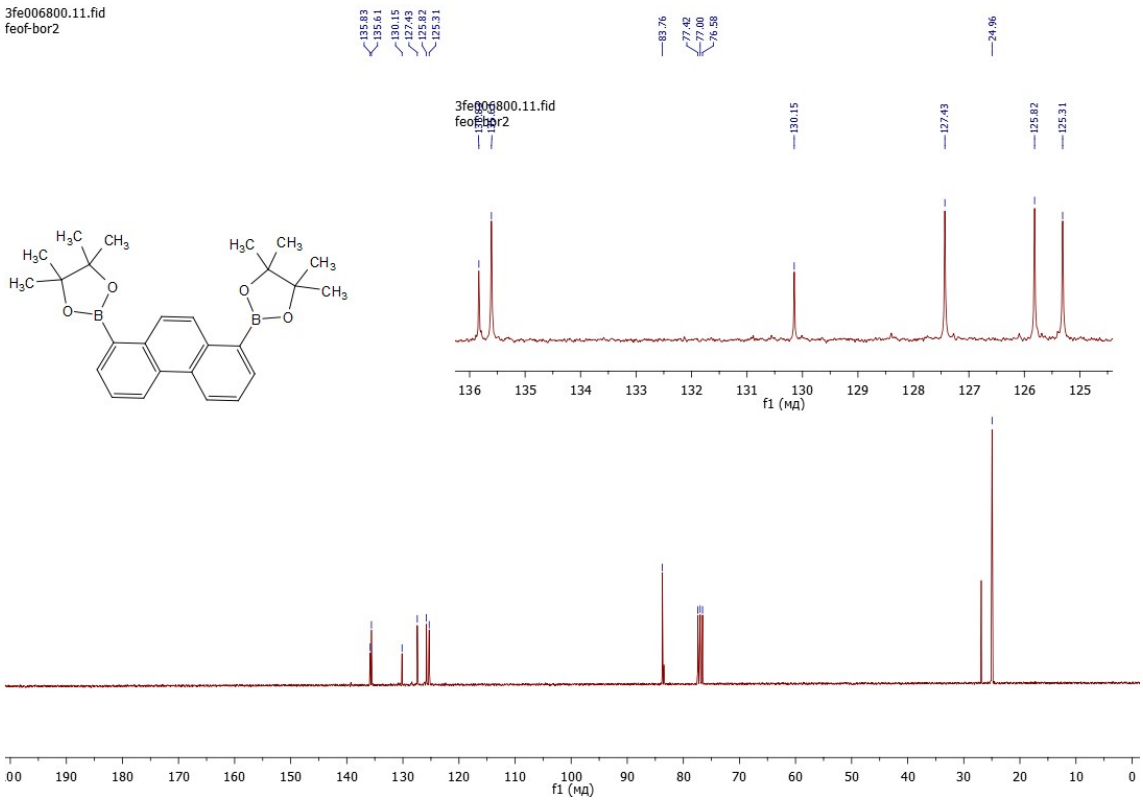


Figure S6. ^{13}C NMR (76 MHz, $CDCl_3$) spectrum of 1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenanthrene.

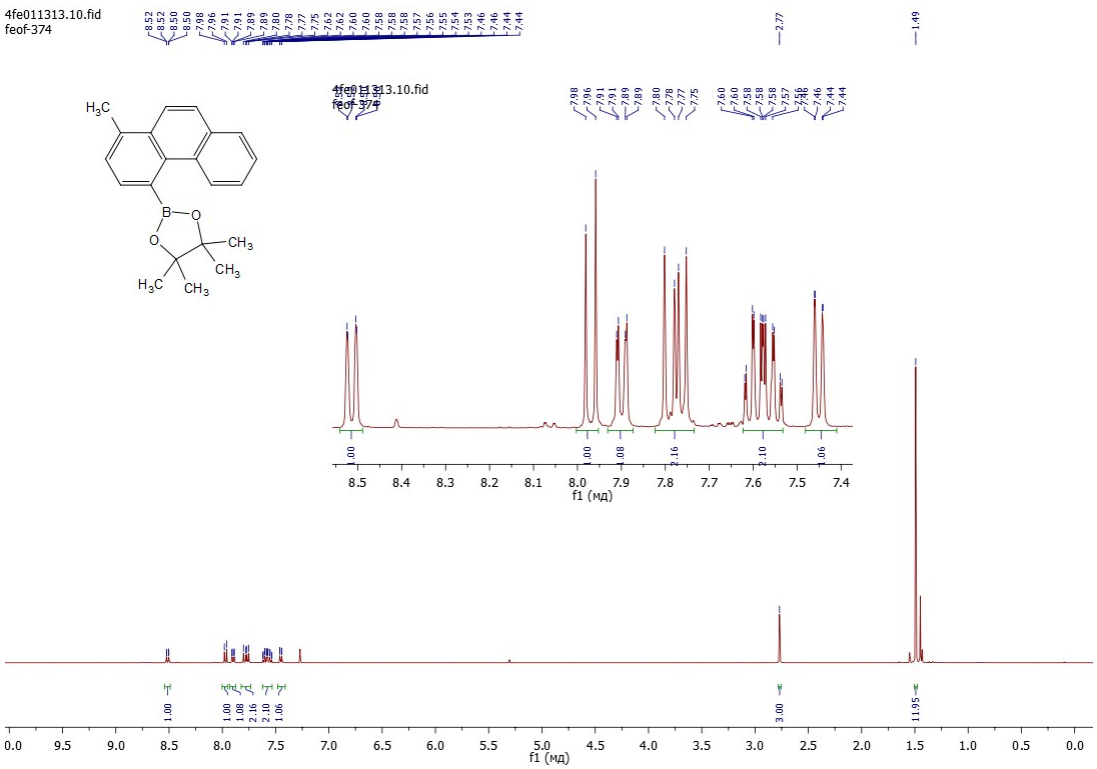


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-methylphenanthren-4-yl)-1,3,2-dioxaborolane.

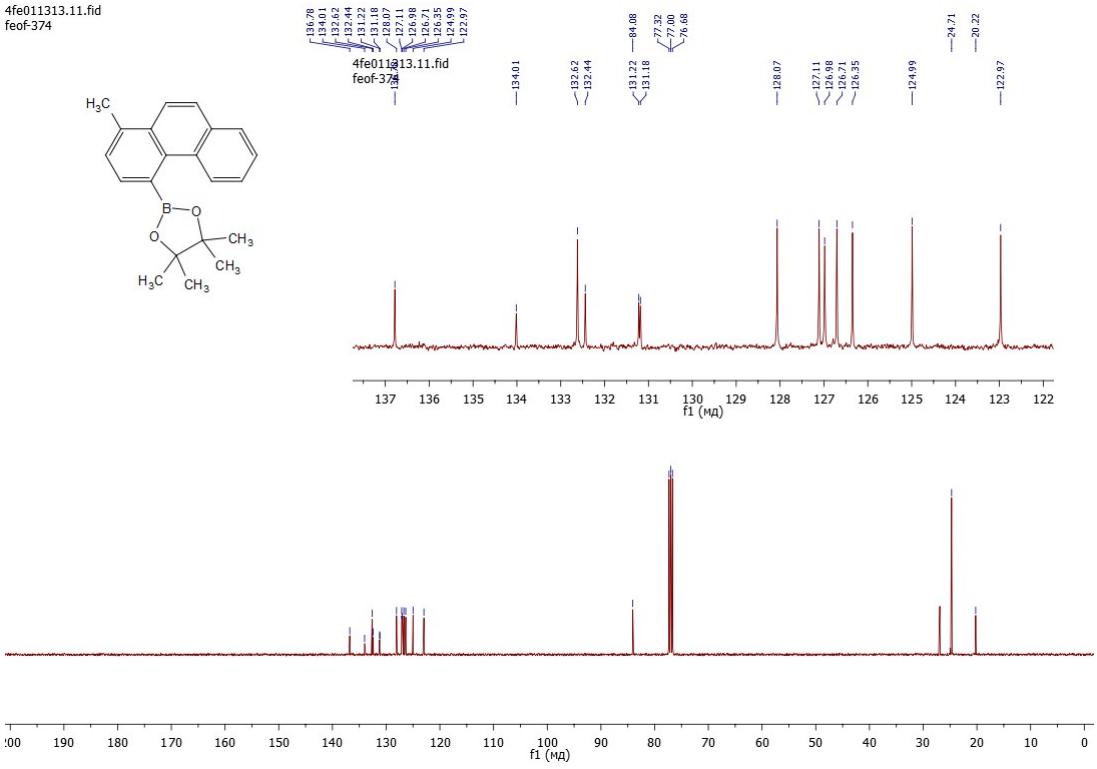


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4,4,5,5-tetramethyl-2-(1-methylphenanthren-4-yl)-1,3,2-dioxaborolane.

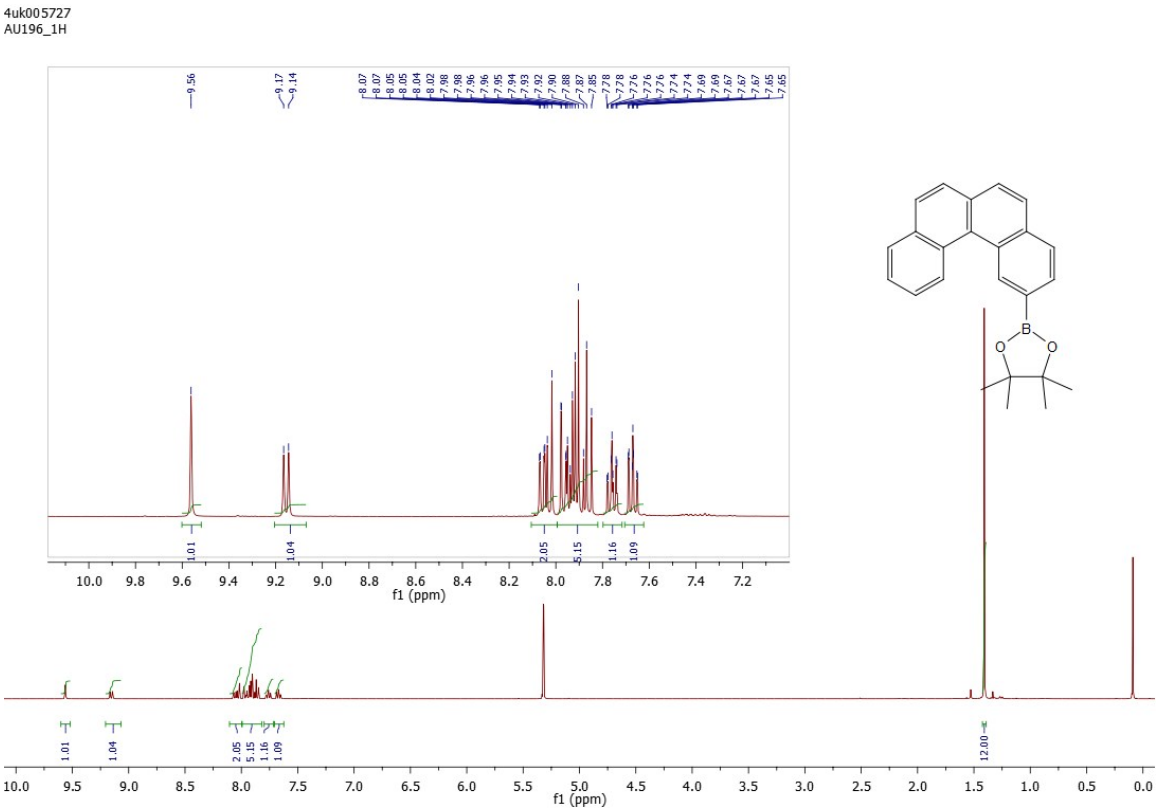


Figure S9. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of 2-(benzo[c]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

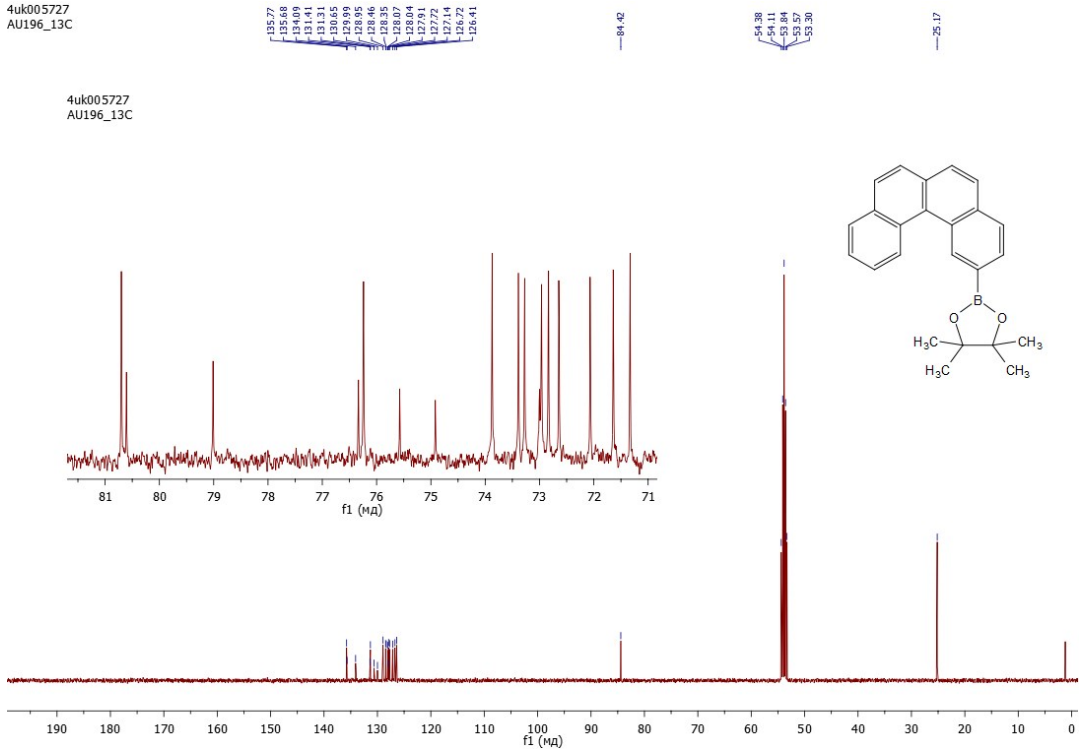


Figure S10. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of 2-(benzo[c]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

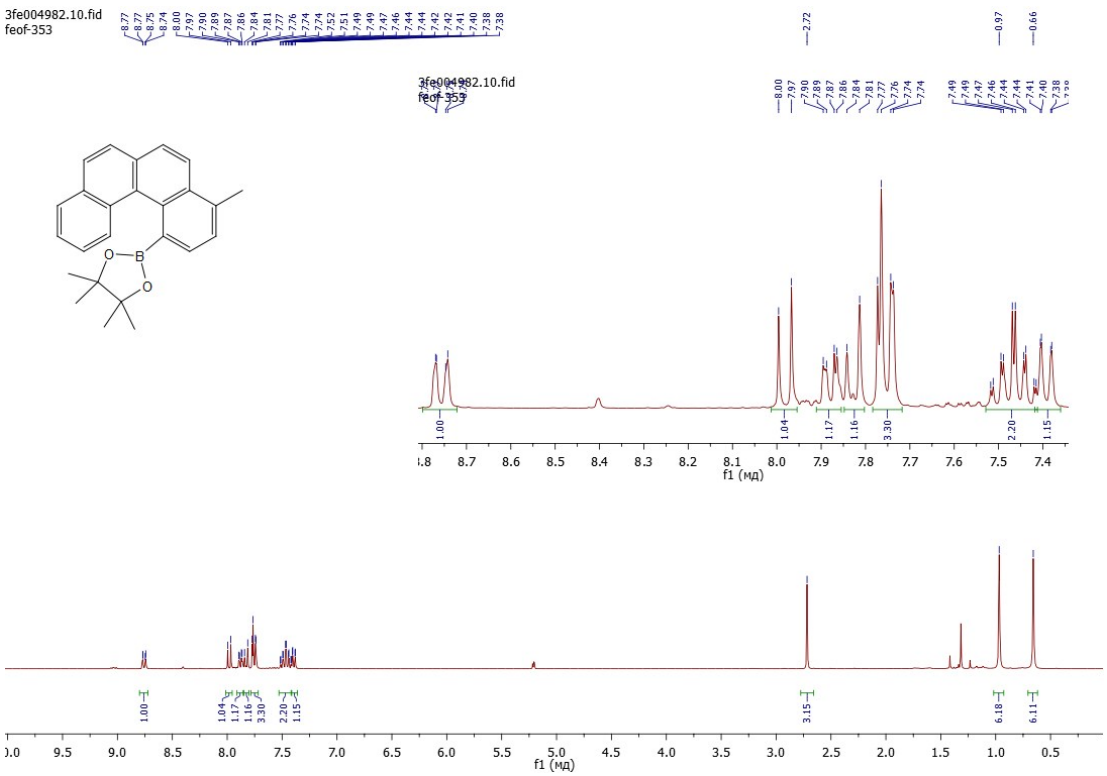


Figure S11. ^{1}H NMR (300 MHz, CD_2Cl_2) spectrum of 4,4,5,5-tetramethyl-2-(4-methylbenzo[c]phenanthren-1-yl)-1,3,2-dioxaborolane.

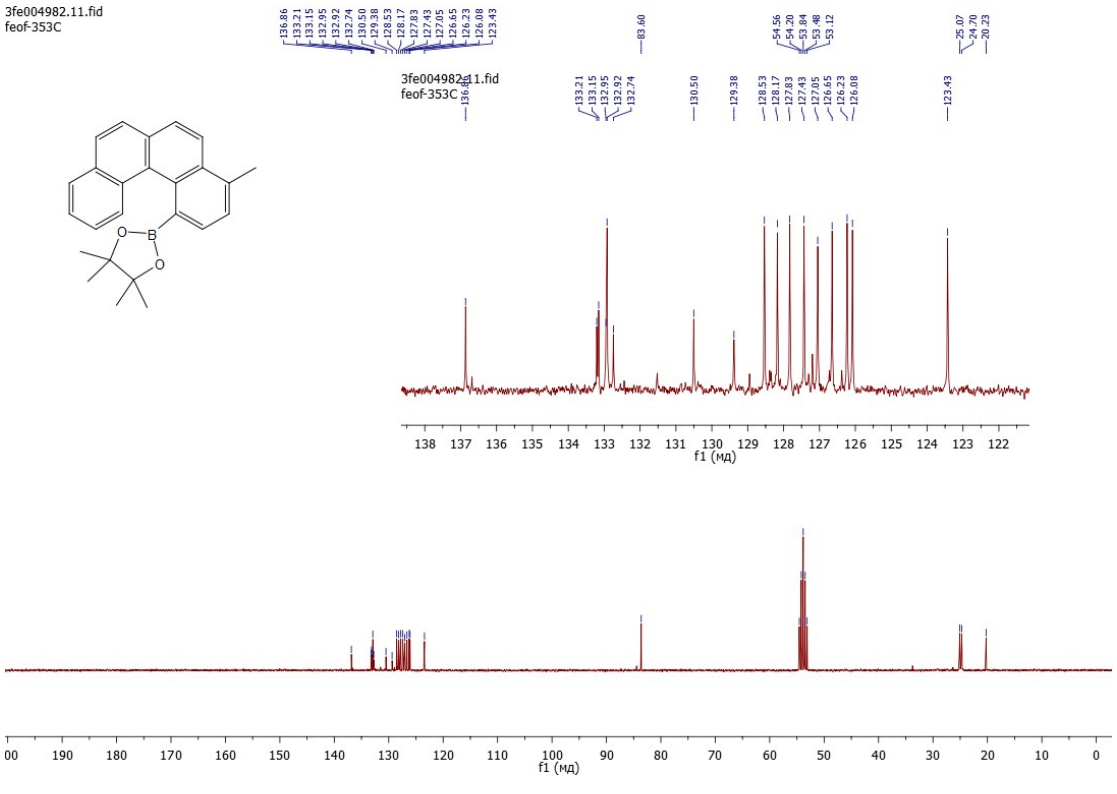


Figure S12. ^{13}C NMR (76 MHz, CD_2Cl_2) spectrum of 4,4,5,5-tetramethyl-2-(4-methylbenzo[c]phenanthren-1-yl)-1,3,2-dioxaborolane.

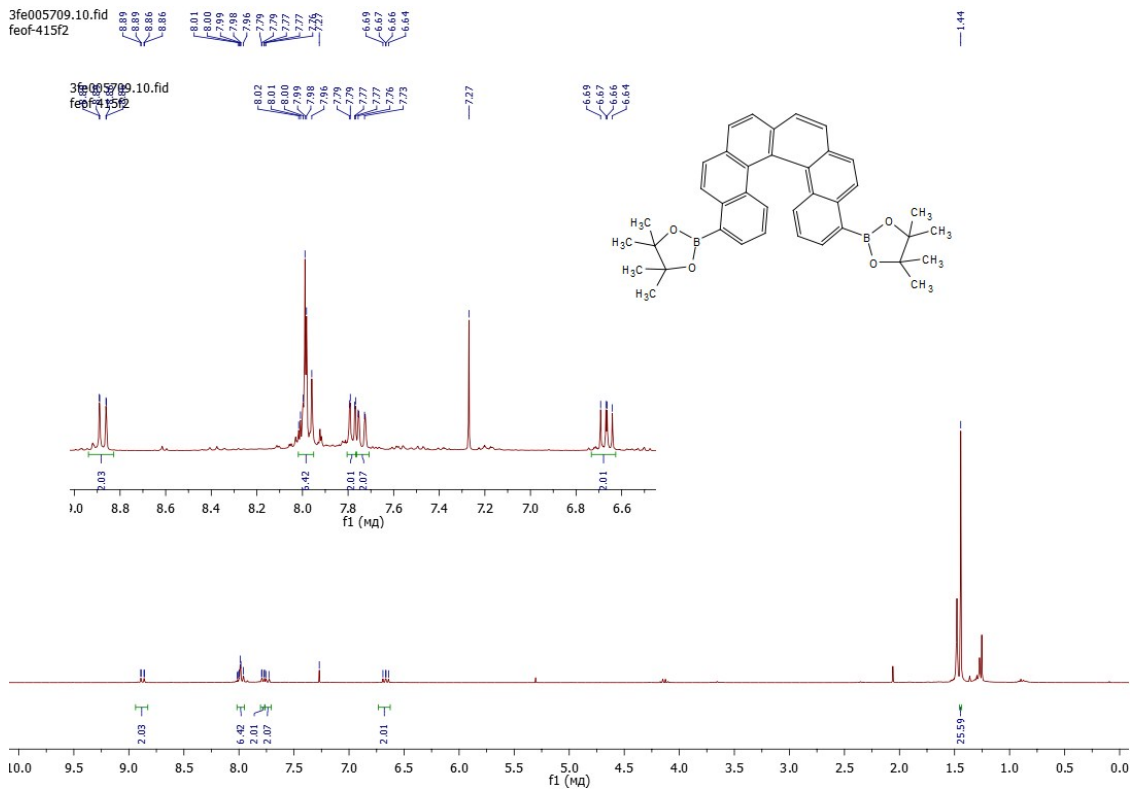


Figure S12. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 9,16-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahelicene.

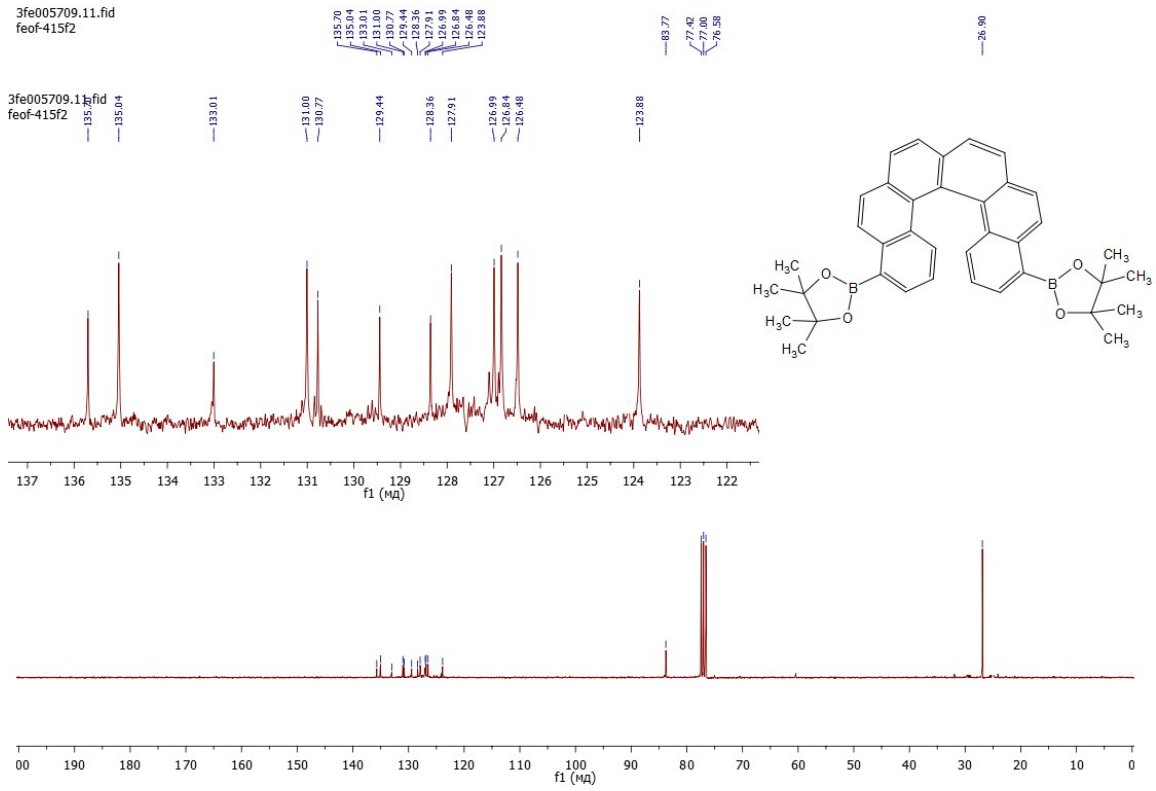


Figure S14. ^{13}C NMR (76 MHz, $CDCl_3$) spectrum of 9,16-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexahelicene.

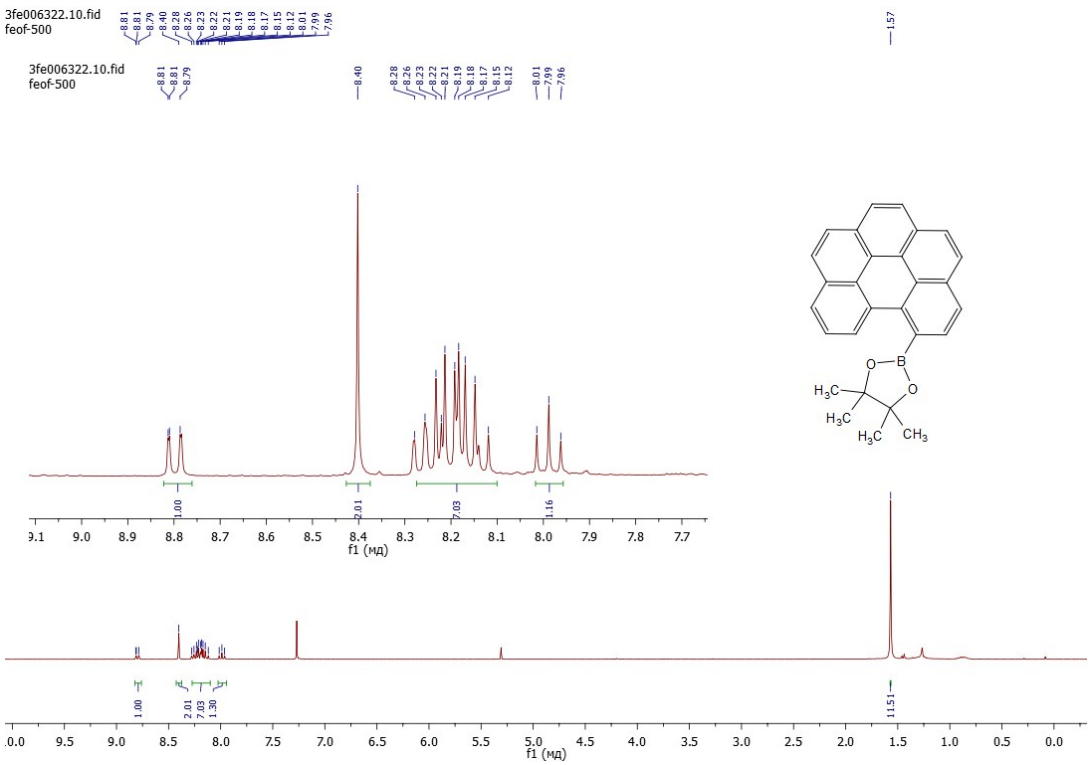


Figure S15. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 2-(benzo[ghi]perylen-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

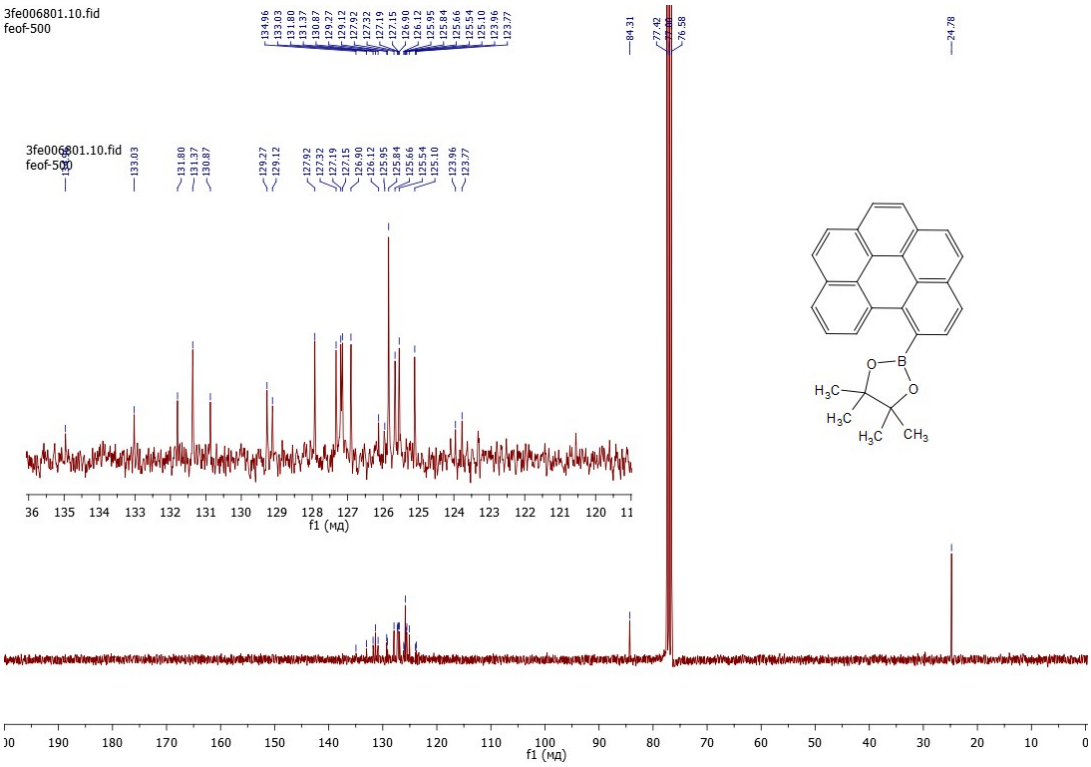
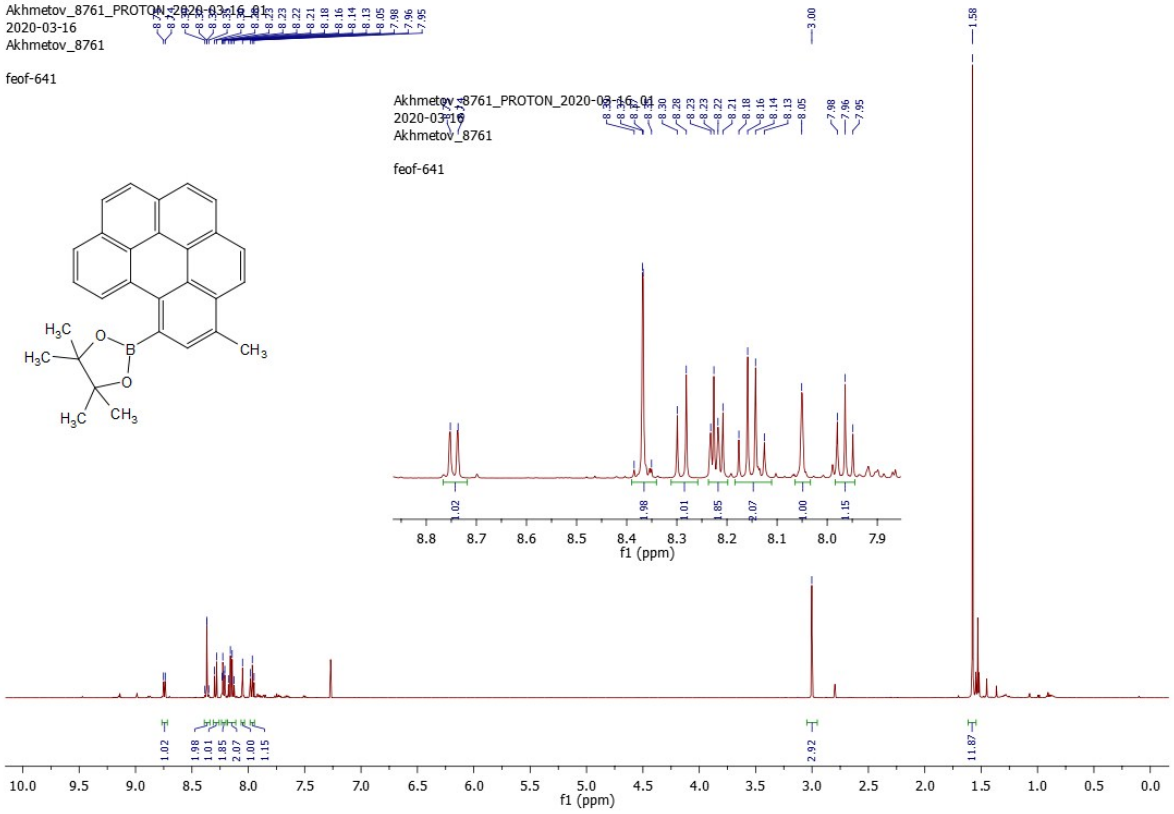
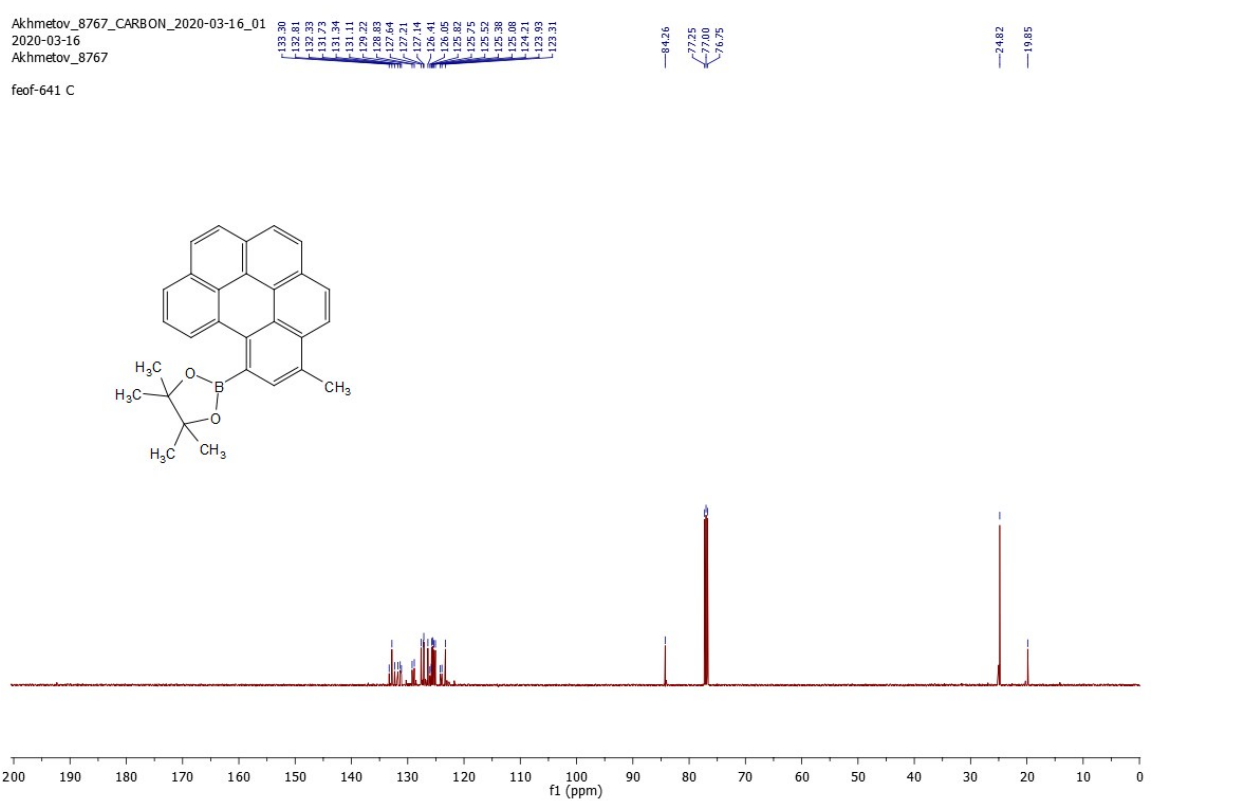


Figure S16. ^{13}C NMR (76 MHz, $CDCl_3$) spectrum of 2-(benzo[ghi]perylen-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.


Akhmetov_8761_PROTON_2020-03-16_01
2020-03-16
Akhmetov_8761
feof-641
f1 (ppm)


Akhmetov_8767_CARBON_2020-03-16_01
2020-03-16
Akhmetov_8767
feof-641 C
f1 (ppm)

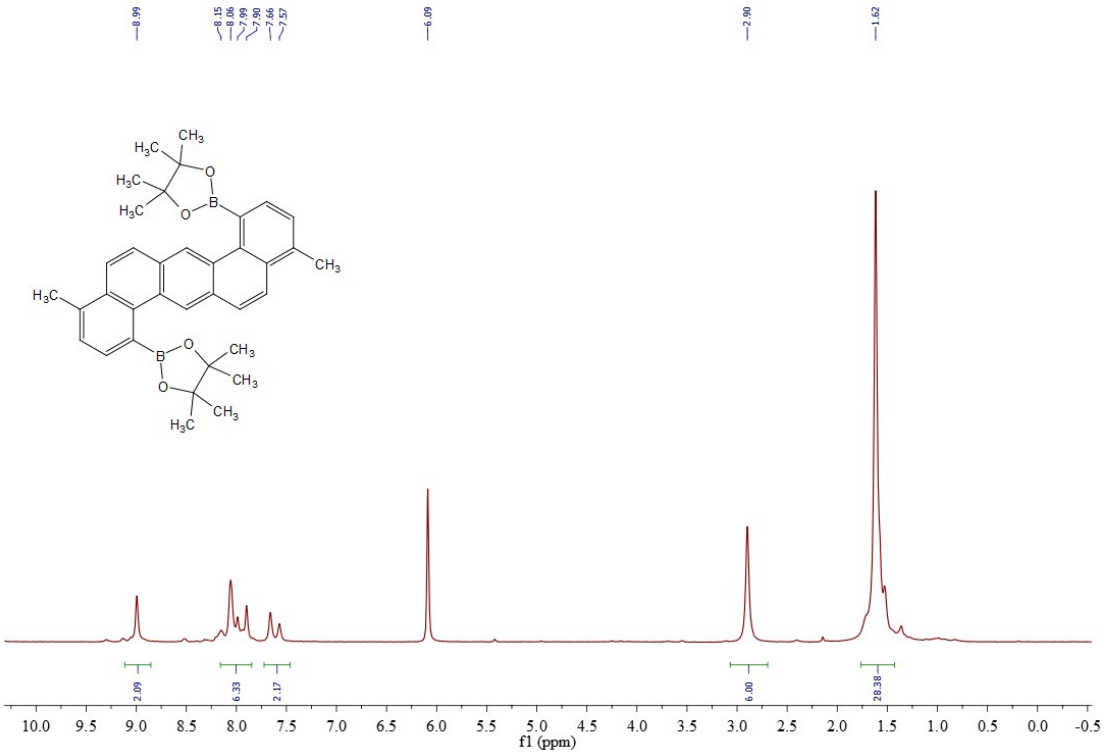


Figure S19. ^{1}H NMR (80 MHz, $C_2D_2Cl_4$) spectrum of 2,2'-(4,11-dimethylbenzo[k]tetraphene-1,8-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)..

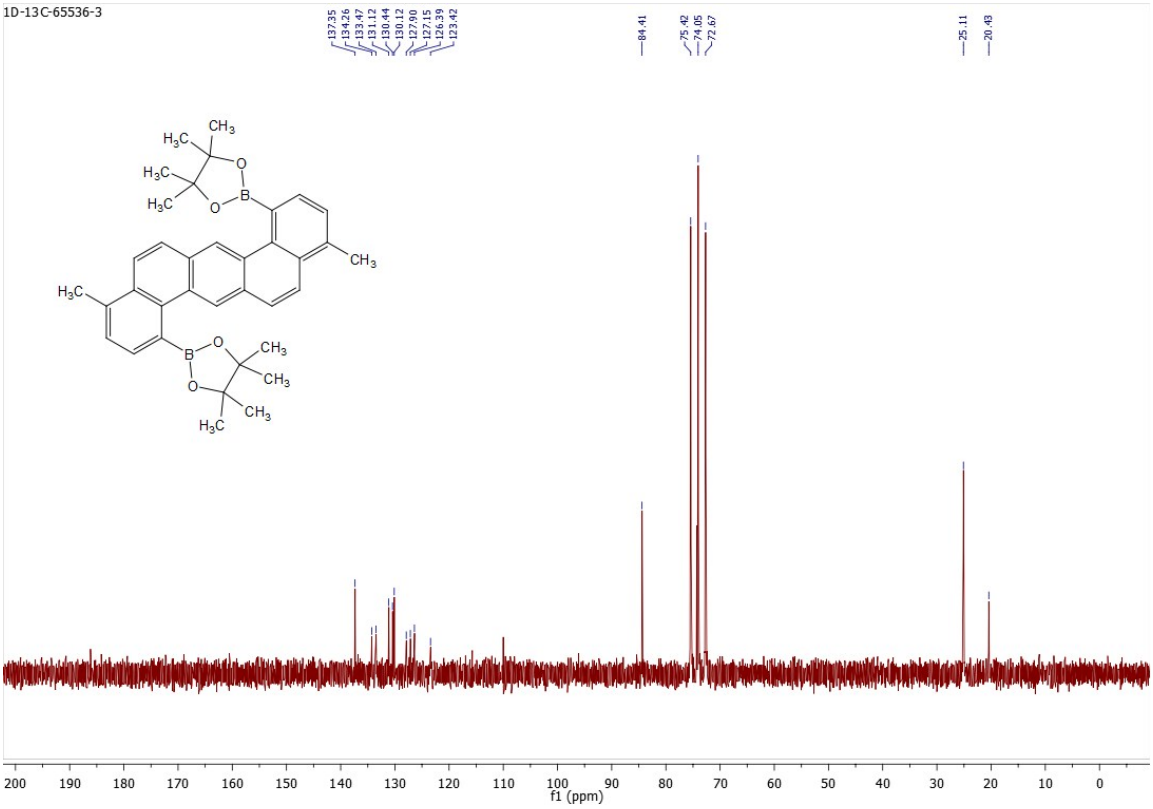


Figure S20. ^{13}C NMR (20 MHz, $C_2D_2Cl_4$) spectrum of 2,2'-(4,11-dimethylbenzo[k]tetraphene-1,8-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).