Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Folding of Fluorinated Oligoarylenes into Non-alternant PAHs with Various Topological Shapes

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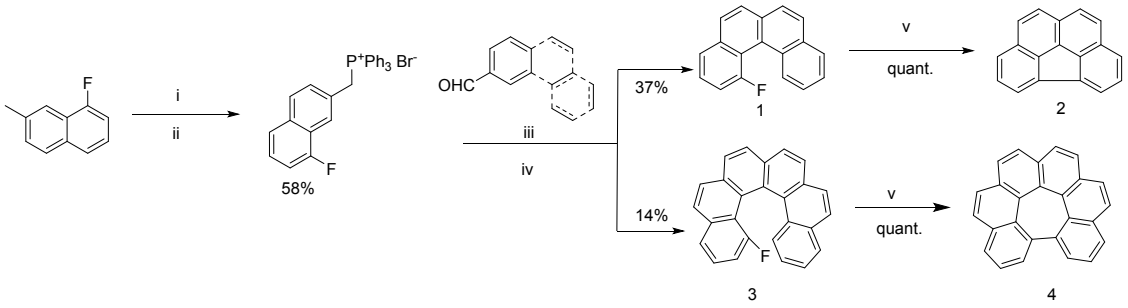
General Information

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. Microwave assisted experiments were carried out using Discover SP Microwave Synthesizer, CEM. Solvents in HPLC (High Performance Liquid Chromatography) grade were purchased from VWR® and SigmaAldrich®.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) and 282 (^{19}F NMR), on a Bruker Avance Neo 400 operating at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 377 (^{19}F NMR), on a Bruker Avance Neo 500, operating at 500 MHz (^{1}H NMR), 125 MHz (^{13}C NMR) and 470 MHz (^{19}F NMR) and on a Bruker Avance Neo 600, operating at 600 MHz (^{1}H NMR), 150 MHz (^{13}C NMR) and 564(^{19}F NMR) at room temperature. The signals were referenced to residual solvent peaks (in parts per million (ppm) ^{1}H: CD_2Cl_2, 5.32 ppm, ^{13}C: CD_2Cl_2, 53.84 ppm). Coupling constants were assigned as observed. The obtained spectra were evaluated with the program MestReNova. X-RAY High resolution APPI MS spectra were recorded on a Bruker ESI TOF maXis4G instrument. The data was evaluated with the program Bruker Compass DataAnalysis 4.2. HPLC measurements were performed on a Shimadzu Prominence Liquid Chromatograph LC-20AT with communication bus module CBM-20A, diode array detector SPDM20A, the degassing unit DGU-20A5 R, column oven CTO-20AC or CTO-20A, respectively and with auto sampler SIL-20A HT. For separation a Cosmosil 5-PYE column (4.6 mm x 250mm) from Nacalai Tesque was used. As eluent a DCM (dichloromethane)/MeOH or toluene/MeOH mixture was used (UV-Vis detection). The data was evaluated with the programs Shimadzu LCsolution and Shimadzu LabSolutions. TLC (thin-layer chromatography) 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.

Synthesis of Precursors.

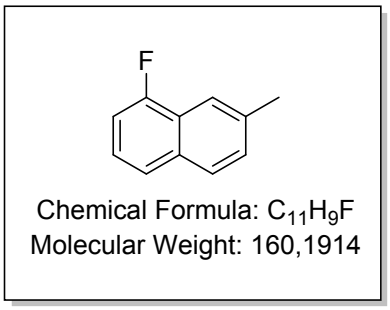


Scheme S1. Synthesis of helicenes with fluorine in cavity and AmCFA i. *N*-Bromosuccinimide, fluorobenzene. ii. PPh_3, toluene. iii. KOH, $CHCl_3/H_2O$ 50/50. iv. hv, I_2, propyleneoxide, cyclohexane. v. Al_2O_3, 180 °C.

General Procedure A.

The corresponding bromo- or iodoarene (1-10 mmol, 1 equiv.) and boronic acid (1 equiv.) were dissolved in 50-100 ml of toluene:methanol (2:1) mixture containing potassium carbonate (6 equiv.) and 2.5% mol of tetrakis(triphenylphosphine)palladium(0) as catalyst. The reaction mixture was stirred under reflux and argon atmosphere for 15 hours. Then the reaction mixture was extracted with dichloromethane and washed with water, organic layer was dried over Na_2SO_4, filtrated through a short silica plague. Solvent evaporation under reduced pressure was followed by flash chromatography purification of product (Hexane:Dichloromethane=10:1).

1-fluoro-7-methylnaphthalene



Three neck flask (100 ml) equipped with condenser, magnetic stirrer and two dropping funnels was charged with 2.15 g (0.089mol) of Mg and 15 ml of diethyl ether under the atmosphere of Ar/N_2. Then around 1ml of solution of 1-(chloromethyl)-2-fluorobenzene 9.65 (0.067mol) in 25 ml of diethyl ether was added was added in one portion in order to initiate boiling (if it was not the case then place the flask into a warm water +50C). The remaining solution was added dropwise within 45 minutes to sustain the boiling. The obtained suspension was stirred at reflux (36 °C) for 30 minutes and then solution of 8.7 g (0.067mol) 4,4-dimethoxybutan-2-one in 15 ml of diethyl ether was added dropwise. The mixture was stirred for another 2 hours at 36 °C and cooled to 0 °C. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl (75ml) and organic layer was washed with brine (3x50ml). The combined organic layers were dried over Na_2SO_4. After filtration and

concentration under reduced pressure 17.0 g of crude 1-(2-fluorophenyl)-4,4-dimethoxy-2-methylbutan-2-ol was obtained as an orange oil which was used further without additional purification.

Two neck flask equipped with condenser, magnetic stirrer and dropping funnel was charged with 300 ml of conc. Acetic acid and 30 ml of conc. sulfuric acid. The mixture of acids was heated at reflux and obtained 1-(4,4-dimethoxy-2-methylbutyl)-2-fluorobenzene was added in portions within 4-5 hours. After cooling down to r.t. the obtained black suspension was extracted with petroleum ether and washed with brine. The combined organic layers were dried over Na_2SO_4. The organic layer was filtered through a short silica plug which was washed with petroleum ether 200ml (this step may be omitted, thus only filtration in order to get rid of Na_2SO_4). The solvent was removed under reduced pressure and the obtained oil was distilled under vacuum (155 C; 5mbar) (kugelrohr may be used). The product was obtained as colorless oil 6.1 g (56%).

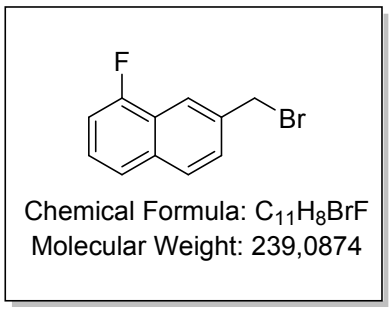
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.88 (s, 1H), 7.79 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.35 (td, *J* = 8.0, 5.4 Hz, 1H), 7.17 – 7.10 (m, 1H), 2.55 (s, 3H).

^{19}F NMR (282 MHz, CD_2Cl_2) δ -123.10 – -125.88 (m, 1F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.8 (d, *J* = 250.1 Hz), 136.8, 133.7 (d, *J* = 5.0 Hz), 129.6, 127.8 (d, *J* = 3.1 Hz), 125.0 (d, *J* = 8.2 Hz), 124.2 (d, *J* = 16.1 Hz), 123.9 (d, *J* = 4.1 Hz), 119.5 (d, *J* = 5.0 Hz), 109.8 (d, *J* = 19.8 Hz), 22.0.

HRMS (APPI; Toluene): Chemical Formula: $C_{11}H_9F$, calc. 160.0688, found 160.0690.

7-(bromomethyl)-1-fluoronaphthalene



1.6 g of 1-fluoro-7-methylnaphthalene (10 mmol) and 1.78 g NBS (*N*-Bromosuccinimide) (10 mmol) were dissolved in 25 g of fluorobenzene and catalytic amount of DBPO (dibenzoylperoxide) was added. Mixture was refluxed under nitrogen atmosphere for 4 h. After cooling down to r.t. the mixture was filtered through SiO_2. Solvent was evaporated under reduced pressure and resulted colorless solid was directly used in the next reaction

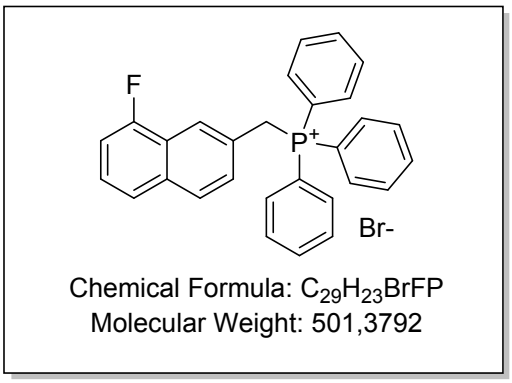
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.09 (s, 1H), 7.89 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.19 (ddd, *J* = 10.8, 7.7, 0.7 Hz, 1H), 4.71 (s, 2H).

^{19}F NMR (282 MHz, CD_2Cl_2) δ -123.20 – -123.30 (m, 1F).

^{13}C NMR (101 MHz, CD_2CL) δ 159.3 (d, *J* = 251.6 Hz), 136.5, 135.0 (d, *J* = 4.3 Hz), 128.9 (d, *J* = 3.1 Hz), 128.4, 127.0 (d, *J* = 8.5 Hz), 124.1 (d, *J* = 3.9 Hz), 123.8 (d, *J* = 16.4 Hz), 120.8 (d, *J* = 5.0 Hz), 110.6 (d, *J* = 19.9 Hz), 34.2.

HRMS (APPI; Toluene): Chemical Formula: $C_{11}H_8BrF$, calc. 237.9793, found 237.9794.

((8-fluoronaphthalen-2-yl)methyl)triphenylphosphonium bromide



Chemical Formula: $C_{29}H_{23}BrFP$
Molecular Weight: 501,3792

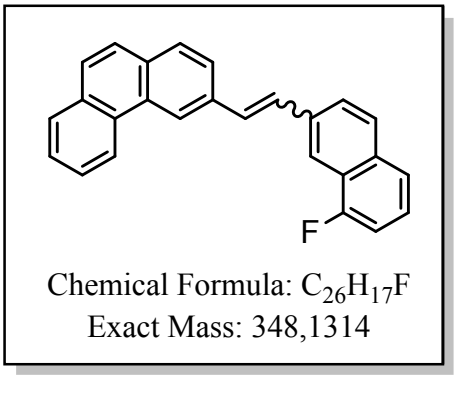
7-(bromomethyl)-1-fluoronaphthalene and triphenylphosphine (2.9 g, 11 mmol) were mixed with 100 ml of toluene and refluxed for 12 h. After cooling down solid was filtered and washed with cold toluene. Yield 2.85 g (58% for two steps).

^{1}H NMR (300 MH, CD_2Cl_2) δ 7.90 – 7.70 (m, 10H), 7.70 – 7.55 (m, 9H), 7.49 – 7.35 (m, 2H), 7.10 (dd, *J* = 10.6, 7.7 Hz, 1H), 5.54 (d, *J* = 14.8 Hz, 1H).

^{19}F NMR (282 MHz, CD_2Cl_2) δ -123.40 (dd, *J* = 10.4, 5.3 Hz).

^{13}C NMR (101 MHz, CD_2CL) δ 158.8 (d, *J* = 251.8 Hz), 135.7 (d, *J* = 2.8 Hz), 134.9 (d, *J* = 9.7 Hz), 130.6 (d, *J* = 12.6 Hz), 130.3 (d, *J* = 4.4 Hz), 128.9 (t, *J* = 2.5 Hz), 127.1 (d, *J* = 8.2 Hz), 126.1 (d, *J* = 8.3 Hz), 124.03 , 123.7 (d, *J* = 6.7 Hz), 123.6 (d, *J* = 5.7 Hz), 123.5 , 118.1 (d, *J* = 85.9 Hz), 110.5 (d, *J* = 19.9 Hz), 31.6 (d, *J* = 47.3 Hz).

3-(2-(8-fluoronaphthalen-2-yl)vinyl)phenanthrene.



Chemical Formula: $C_{26}H_{17}F$
Exact Mass: 348,1314

To solution of phenanthrene-3-carbaldehyde (100 mg, 0.485 mmol, 1 equiv.) and [(8-fluoro-2-naphthalenyl)methyl]triphenylphosphonium bromide (267 mg, 0.533 mmol, 1.1 equiv.) in $CHCl_3$ (4 mL) aqueous solution of KOH (50 %, 1.6 mL) was added dropwise under inert atmosphere. The mixture was heated to 80 °C and stirred 18 h . After the end of the

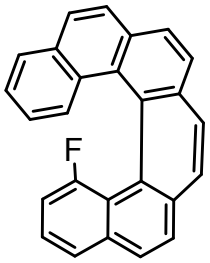
reaction mixture was cooled to room temperature, water was added, phases were separated , and the aqueous layer was extracted with DCM. The combine organic frictions were dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes→hexanes: DCM 9:1) yielding 3-(2-(8-fluoronaphthalen-2-yl)vinyl)phenanthrene as white solid (130 mg, 77 %).

^{1}H NMR (400 MHz, $CDCl_3$) d 8.63 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.09 (s, 1H), 7.89 – 7.83 (m, 1H), 7.75 – 7.66 (m, 3H), 7.63 – 7.43 (m, 6H), 7.36 (td, J = 8.0, 5.4 Hz, 1H), 7.11 (dd, J = 10.7, 7.7 Hz, 1H), 7.03 – 6.89 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -123.15 (m, 1F)

HRMS (APPI; Toluene): Chemical Formula: $C_{26}H_{17}F$, calc. 348.1314, found 348.1315.

12-fluorohexahelicene (3).



Chemical Formula: $C_{26}H_{15}F$
Exact Mass: 346,1158

Solution of 3-(2-(8-fluoronaphthalen-2-yl)vinyl)phenanthrene (133 mg, 0.382 mmol) in 800 ml of cyclohexane was irradiated in the presence of I_2 (104 mg, 0.41 mmol) and methylpropyleneoxide (0.26 ml) for 3 h. After completion of reaction ½ of cyclohexane was evaporated under reduced pressure, washed with $Na_2S_2O_3$ solution, dried over Na_2SO_4. Cyclohexane was evaporated under reduced pressure and residue was purified by column chromatography (Hexane) and HPLC (DCM/MeOH 1:1) yielding 12-fluorohexahelicene as yellow solid in 18% (24 mg).

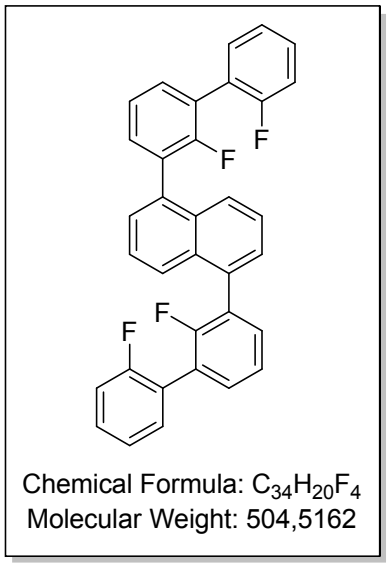
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.15 (d, *J* = 8.1 Hz, 1H), 8.07 – 8.03 (m, 3H), 8.02 – 7.99 (m, 2H), 7.98 – 7.93 (m, 2H), 7.86 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.75 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.26 (td, *J* = 7.8, 4.9 Hz, 1H), 7.22 – 7.16 (m, 2H), 6.59 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 6.40 (ddd, *J* = 13.0, 7.8, 1.2 Hz, 1H).

^{19}F NMR (377 MHz, CD_2Cl_2) δ -101.95 (dd, *J* = 13.0, 4.7 Hz, 1F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.2 (d, *J* = 253.9 Hz), 134.3 (d, *J* = 4.2 Hz), 132.8, 132.5, 132.2, 130.4 (d, *J* = 1.7 Hz), 130.0 (d, *J* = 8.8 Hz), 129.1 (d, *J* = 7.6 Hz), 128.2, 128.0, 127.89, 127.7 (d, *J* = 1.0 Hz), 127.6 (d, *J* = 3.1 Hz), 126.80, 126.76 , 126.7, 126.6, 126.5 , 126.4, 125.6, 124.2, 123.9 (d, *J* = 3.2 Hz), 123.5 (d, *J* = 3.3 Hz), 121.3 (d, 24 Hz), 111.68 (d, *J* = 24.4 Hz).

HRMS (APPI; Toluene): Chemical Formula: $C_{26}H_{15}F$, calc. 346.1158, found 346.1160.

1,5-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene (9).



Chemical Formula: $C_{34}H_{20}F_4$
Molecular Weight: 504,5162

The compound was obtained according to the General Procedure A using 1,5-dibromonaphtalene (114 mg) and (2,2'-difluoro-[1,1'-biphenyl]-3-yl)boronic acid (200 mg). Yield 100 mg (50%).

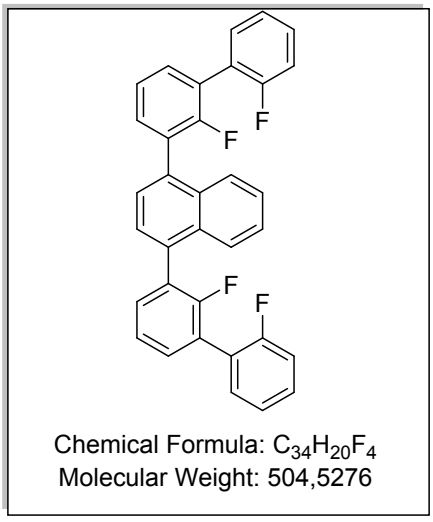
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.82 (dd, *J* = 7.1, 2.0 Hz, 2H), 7.62 – 7.47 (m, 10H), 7.46 – 7.37 (m, 4H), 7.33 – 7.25 (m, 2H), 7.25 – 7.17 (m, 2H).

^{19}F NMR (377 MHz, CD_2Cl_2) δ -115.01 – -115.27 (m, 2F), -115.95 – -115.98 (m. 1F), -116.19 – -116.42 (m, 1F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.4 (d, *J* = 247.9 Hz), 157.5 (d, *J* = 248.3 Hz), 134.6, 132.7 (dd, *J* = 6.8, 3.7 Hz), 132.3, 132.1 (dd, *J* = 2.5, 1.3 Hz), 131.7 (d, *J* = 1.6 Hz), 130.4 (d, *J* = 8.2 Hz), 128.9 (d, *J* = 17.7 Hz), 128.3, 126.7, 126.1, 124.63 (d, *J* = 3.8 Hz), 124.6, 124.5, 124.40 – 124.16 (m), 124.16 – 123.82 (m), 116.1 (d, *J* = 22.2 Hz).

HRMS (APPI; Toluene): Chemical Formula: $C_{34}H_{20}F_4$, calc. 504.1501, found 504.1501.

1,4-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene (10).



Chemical Formula: $C_{34}H_{20}F_4$
Molecular Weight: 504,5276

The compound was obtained according to the General Procedure A using 1,4-dibromonaphtalene (86 mg) and (2,2'-difluoro-[1,1'-biphenyl]-3-yl)boronic acid[1] (150 mg). Yield 80 mg (52%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.81 (dt, *J* = 6.2, 2.8 Hz, 2H), 7.61 (s, 2H), 7.58 – 7.48 (m, 8H), 7.46 – 7.39 (m, 4H), 7.32 – 7.25 (m, 2H), 7.24 – 7.18 (m, 2H).

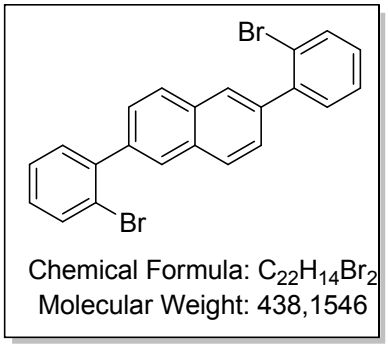
^{19}F NMR (377 MHz, CD_2Cl_2) δ -115.05 – -115.34 (m, 2F), -115.71 – -115.94 (m, 1F), -116.18 – -116.38 (m, 1F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.0 (d, *J* = 247.6 Hz), 157.1 (d, *J* = 247.9 Hz), 134.3 (d, *J* = 3.0 Hz), 132.39 – 132.24 (m), 131.88, 131.78 – 131.65 (m), 131.44 – 131.24 (m), 130.0 (d,

J = 8.1 Hz), 128.46 – 128.01 (m), 127.24, 126.2 (d, *J* = 17.8 Hz), 124.2 (t, *J* = 3.5 Hz), 123.9 (dd, *J* = 16.8, 7.1 Hz), 123.6 (dd, *J* = 15.7, 2.2 Hz), 115.7 (d, *J* = 22.4 Hz).

HRMS (APPI; Toluene): Chemical Formula: $C_{34}H_{20}F_4$, calc. 504.1501, found 504.1503.

2,6-bis(2-bromophenyl)naphthalene (8).



Chemical Formula: $C_{22}H_{14}Br_2$
Molecular Weight: 438,1546

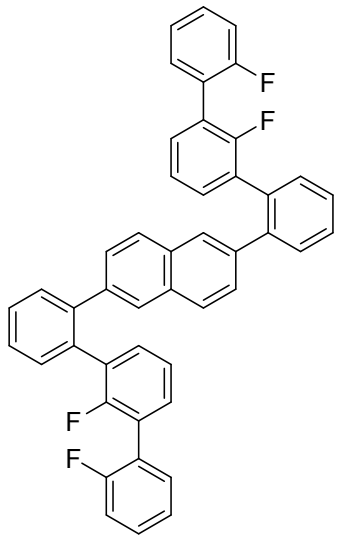
The compound was obtained according to the General Procedure A using 1-bromo-2-iodobenzene (160 mg) and(2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene[2] (200 mg). Yield 175 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.62 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.51 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.335-7.28 (m, 2H), 7.19 – 7.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 139.1, 133.2, 132.2, 131.5, 128.9, 128.07, 128.04, 127.7, 127.5, 122.8.

HRMS (APPI; Toluene): Chemical Formula: $C_{22}H_{14}Br_2$, calc. 435.9462 found 435.9463.

2,6-bis(2',2''-difluoro-[1,1':3',1''-terphenyl]-2-yl)naphthalene (11).



Chemical Formula: $C_{46}H_{28}F_4$
Molecular Weight: 656,7081

The compound was obtained according to the General Procedure A using 2,6-bis(2-bromophenyl) naphthalene (75 mg) and (2,2'-Difluoro-[1,1'-biphenyl]-3-yl)boronic acid (160 mg). Yield 52 mg (46%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 1.7 Hz, 2H), 7.60 – 7.55 (m, 4H), 7.50 (dtd, *J* = 10.4, 7.5, 2.7 Hz, 6H), 7.32 (tt, *J* = 8.3, 2.6 Hz, 2H), 7.27 – 7.20 (m, 4H), 7.14 (dd, *J* = 7.0, 1.8 Hz, 2H), 7.09 (dd, *J* = 7.7, 3.5 Hz, 6H), 7.05 (t, *J* = 7.6 Hz, 2H).

^{19}F NMR (376 MHz, CD_2Cl_2) δ -115.32 – -115.58 (m, 2F), -117.18 (dt, *J* = 16.3, 6.8 Hz, 2F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.2 (d, *J*=239 Hz), 142.0, 139.3, 134.9, 132.46 (d, *J* = 3.5 Hz), 132.4, 132.07 – 131.85 (m), 131.4 (d, *J* = 1.3 Hz), 131.0 (dd, *J* = 3.0, 1.4 Hz), 130.8,

130.2, 130.1, 128.8, 128.1, 127.7, 124.4 (d, J = 3.7 Hz), 124.04 – 123.93 (m), 116.0 (d, J = 22.3 Hz).

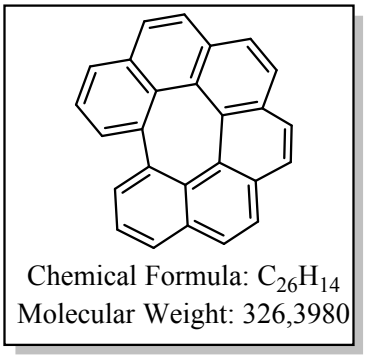
HRMS (APPI; Toluene): Chemical Formula: $C_{46}H_{28}F_4$, calc. 656.2127 found 656.2127.

Synthesis of Non-alternant PAHs

General Procedure B.

A glass tube was charged with 2-5 g of γ-Al_2O_3 (neutral, 50-200 micron) and preactivated at 450 C for 3-4 hours. Then it was connected to a Schlenk line and heated at 590 C under vacuum (10^{-3} mbar) for another 2 hours. The vessel was cooled down to r.t. and 1-10 mmol of fluoroarene was added under argon atmosphere. The tube containing the obtained mixture was sealed under vacuum and heated at 180-220°C for 2-96 h. After cooling to room temperature, products were extracted with toluene. Separation and final purification of the products were carried out by flash chromatography or HPLC of the respective toluene/*o*-DCB (*ortho*-dichlorobenzene) extract.

1,16-dehydrohexahelicene (4).



Chemical Formula: $C_{26}H_{14}$
Molecular Weight: 326,3980

The compound was obtained according to the General Procedure B using 12-fluorohexahelicene (15 mg). Yield 14 mg (99%)

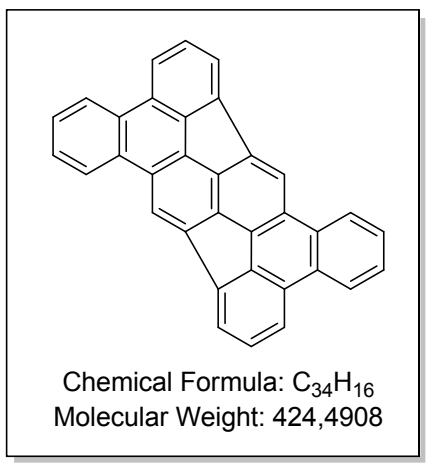
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.84 – 7.79 (m, 4H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.24 (dd, *J* = 7.3, 1.5 Hz, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 141.6, 136.3, 135.2, 133.7, 133,0, 132.3, 131.2, 130.9, 129.1, 128.7, 128.5, 128.0, 127.7, 126.7.

UV/Vis (DCM, 293 K): λ [nm]) 245, 260, 304, 323.

HRMS (APPI; Toluene): Chemical Formula: $C_{26}H_{14}$, calc. 326.1096, found 326.1098.

Benzo[*c*]diindeno[1,2,3,4-*ghij*:1',2',3',4'-*tuva*]picene (12).



Chemical Formula: $C_{34}H_{16}$
Molecular Weight: 424,4908

The compound was obtained according to the General Procedure B using 1,5-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene (40 mg). Yield 4 mg (12%).

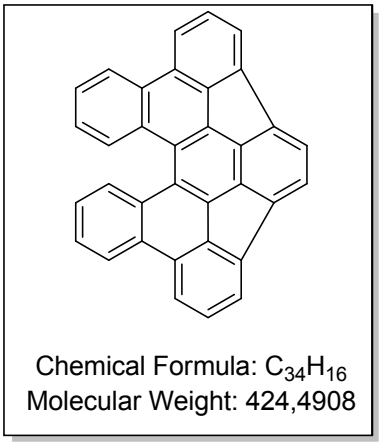
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.64 (dd, *J* = 7.5, 1.9 Hz, 3H), 8.46 (s, 2H), 8.15 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.81 – 7.70 (m, 5H), 7.56 (dd, *J* = 8.1, 7.2 Hz, H).

^{13}C NMR was not recorded due to low solubility of benzo[*c*]diindeno[1,2,3,4-*ghij*:1',2',3',4'-*tuva*]picene.

UV/Vis (DCM-MeOH, 1-1, 293 K): λ [nm]) = 299, 417, 433.

HRMS (APPI; Toluene): Chemical Formula: $C_{34}H_{16}$, calc. 424.1252, found 424.1253.

***as*-indaceno[3,2,1,8,7,6-*pqrstuv*]dibenzo[*f,j*]picene (13).**



The compound was obtained according to the General Procedure B using 1,4-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene (40 mg). Yield 5 mg (15%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.39 – 9.25 (m, 2H), 8.76 (dd, *J* = 7.9, 1.6 Hz, 2H), 8.24 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 7.1 Hz, 4H), 7.81 – 7.68 (m, 4H), 7.59 (dd, *J* = 8.1, 7.1 Hz, 2H).

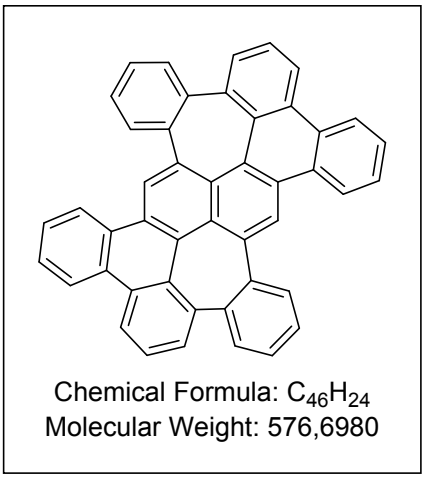
^{13}C NMR (151 MHz, CD_2Cl_2) δ 139.79, 138.98, 137.62, 137.03, 135.28, 133.89, 129.71, 129.32, 128.95, 128.02, 126.99, 126.42, 125.96, 125.50, 124.04, 123.19.

UV/Vis (DCM-MeOH, 1-1, 293 K): λ [nm]) = 298, 360, 390, 412.

HRMS (APPI; Toluene): Chemical Formula: $C_{34}H_{16}$, calc. 424.1252, found 424.1252.

Dibenzo[e,gh]dibenzo[4,5:6,7]pleiadeno[2,1,12-pqa]pleiadene (14).

The compound was obtained according to the General Procedure B using 2,6-bis(2',2''-difluoro-[1,1';3',1''-terphenyl]-2-yl)naphthalene (40 mg). Yield 5 mg (15%).



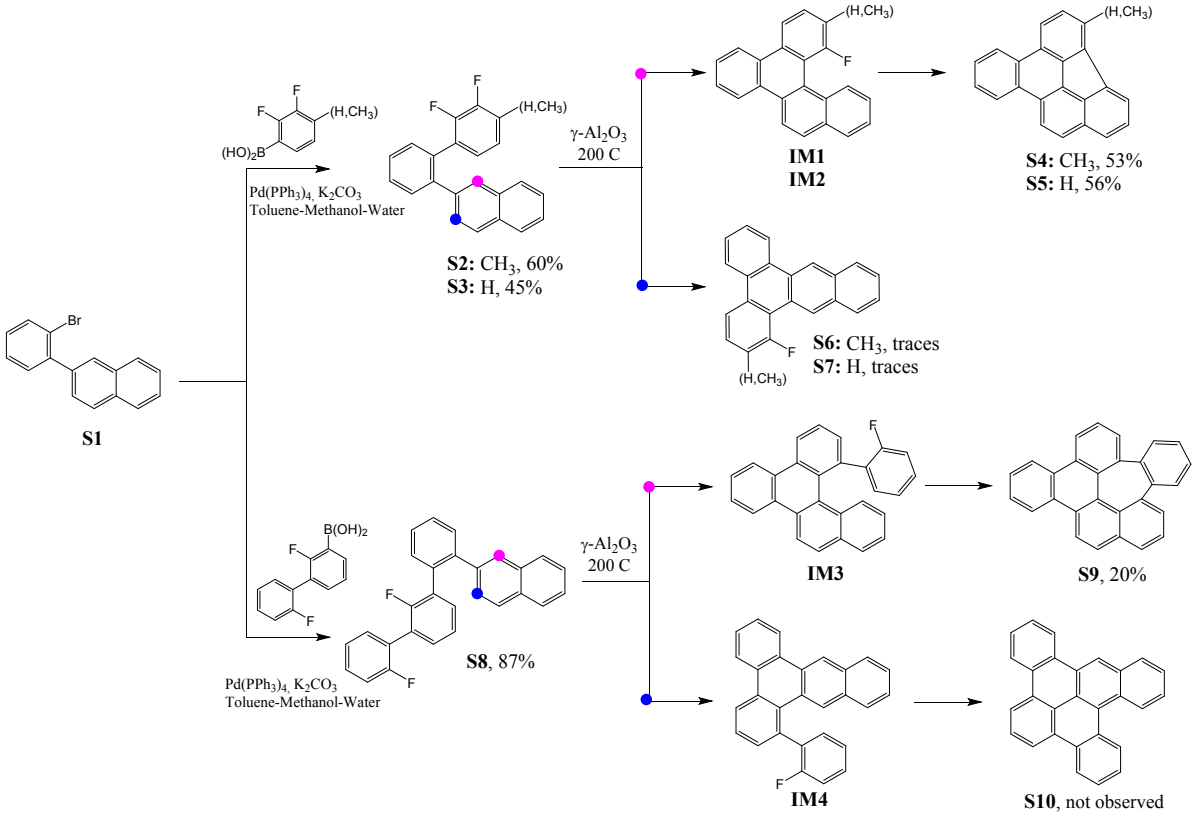
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.58 (m, 2H), 8.56 (s, 2H), 8.45 – 8.35 (m, 4H), 7.64 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.58 – 7.52 (m, 6H), 7.40 (ddd, *J* = 11.9, 9.1, 5.4 Hz, 4H), 7.24 (dd, *J* = 7.4, 1.6 Hz, 2H), 7.15 (dd, *J* = 7.6, 1.5 Hz, 2H).

^{13}C NMR was not recorded due to low solubility of dibenzo[e,gh]dibenzo[4,5:6,7]pleiadeno[2,1,12-pqa]pleiadene

UV/Vis (DCM-MeOH, 1-1, 293 K): λ [nm]) = 266, 298, 356.

HRMS (APPI; Toluene): Chemical Formula: $C_{46}H_{24}$, calc. 576.1878, found 576.1879.

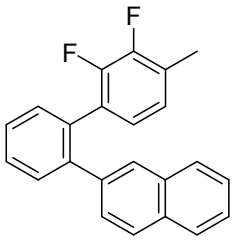
Comments on the Regioselectivity of the Reaction.



Scheme S2. Synthesis of the model compounds revealing the regioselectivity.

To study the regioselectivity of the reaction, we have obtained precursors S2, S3, and S8. All of them have two possible directions of the folding, which is defined by the first HF elimination. Considering the electrophilic nature of the reaction[3], it comes as no surprise that alpha-positions (marked pink) tend to be more reactive in comparison to beta-positions (marked blue). Thus, S2 and S3 transform into S4 and S5 in 50% and 55% yield, respectively, whereas only traces of S6 and S7 could be found. Similarly, S9 is the major product obtained after the exposure of S8 to activated alumina.

2-(2',3'-difluoro-4'-methyl-[1,1'-biphenyl]-2-yl)naphthalene (S2).



Chemical Formula: $C_{23}H_{16}F_2$
Molecular Weight: 330,3778

The compound was obtained according to the General Procedure A using 1-bromo-2-(2-naphthyl)benzene (500 mg) and (2,3-difluoro-4-methylphenyl)boronic acid (307 mg). Yield 350 mg (60%).

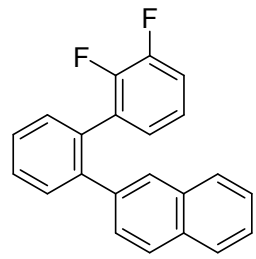
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.80 (ddd, *J* = 11.7, 6.1, 3.7 Hz, 2H), 7.74 (s, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.54 (td, *J* = 7.3, 1.9 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.26 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.86-6.80 (m, 2H), 2.24 (d, *J* = 2.1 Hz, 3H).

^{19}F NMR (377 MHz, CD_2Cl_2) δ -141.92 (d, *J* = 21.4 Hz, 1F), -143.37 (d, *J* = 19.1 Hz, 1F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.65 (dd, *J*=253, 14 Hz), 148.12 (dd, *J*=245, 13 Hz), 142.0, 134.0, 133.6, 132.6, 131.45, 131.0, 128.9, 128.4, 127.9, 127.8, 127.6, 126.4, 126.3, 125.59 (t, *J* = 4.0 Hz), 14.62 – 14.15 (m).

HRMS (APPI; Toluene): Chemical Formula: $C_{23}H_{16}F_2$, calc. 330,1220, found 330.1221.

2-(2',3'-difluoro-[1,1'-biphenyl]-2-yl)naphthalene (S3).



Chemical Formula: $C_{22}H_{14}F_2$
Molecular Weight: 316,3508

The compound was obtained according to the General Procedure A using 1-bromo-2-(2-naphthyl)benzene[4] (400 mg) and 2,3-difluorophenylboronic acid (223 mg). Yield 200 mg (45%).

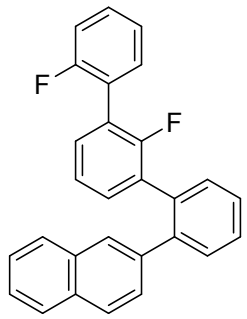
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.81 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.72 (brs, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.59 – 7.53 (m, 1H), 7.53 – 7.43 (m, 4H), 7.25 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.09 – 7.00 (m, 1H), 6.99 – 6.94 (m, 2H).

^{19}F NMR (377 MHz, CD_2Cl_2) δ -139.15 (dd, *J* = 21.6, 10.5 Hz, 1F), -140.96 – -141.18 (m, 1F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 151.03 (dd, *J* = 247.2, 13.3 Hz), 148.17 (dd, *J* = 247.0, 12.8 Hz), 142.03, 139.00, 133.77 (d, *J* = 2.3 Hz), 133.65, 132.62, 131.93 (d, *J* = 12.5 Hz), 131.37, 131.02, 129.15, 128.45, 128.36, 127.92, 127.84, 127.70, 127.63 – 127.26 (m), 126.46 (d, *J* = 10.9 Hz), 124.15 (dd, *J* = 7.1, 4.9 Hz), 116.35 (d, *J* = 17.1 Hz).

HRMS (APPI; Toluene): Chemical Formula: $C_{22}H_{14}F_2$, calc. 316.1064, found 316.1066.

2-(2',2''-difluoro-[1,1':3',1''-terphenyl]-2-yl)naphthalene (S8).



Chemical Formula: $C_{28}H_{18}F_2$
Molecular Weight: 392,4393

The compound was obtained according to the General Procedure A using 1-bromo-2-(2-naphthyl)benzene (111 mg) and and (2,2'-difluoro-[1,1'-biphenyl]-3-yl)boronic acid (92 mg). Yield 134 mg (87%).

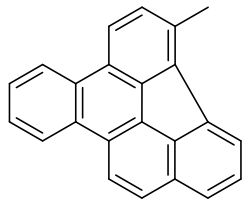
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.82 – 7.77 (m, 1H), 7.74 (dd, *J* = 5.8, 3.8 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.60 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.47 – 7.40 (m, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.18 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.13 – 7.02 (m, 4H).

^{19}F NMR (376 MHz, CD_2Cl_2) δ -115.42 – -115.58 (m, 1F), -116.96 – -117.10 (m, 1F).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.1 (d, *J* = 248.2 Hz), 157.1 (d, *J* = 248.0 Hz), 142.1, 139.2, 135.0, 133.7, 132.6, 132.5 (d, *J* = 3.7 Hz), 131.9 (dd, *J* = 3.2, 1.8 Hz), 131.4 (d, *J* = 1.2 Hz), 131.0 (dd, *J* = 3.2, 1.6 Hz), 130.8, 130.4 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 8.1 Hz), 13.0, 128.8, 128.5, 128.3, 128.0, 127.8, 127.7, 127.6, 126.3 (d, *J* = 13.0 Hz), 124.4 (d, *J* = 3.6 Hz), 124.0 (d, *J* = 4.4 Hz), 123.9 (d, *J* = 2.0 Hz), 123.8, 116.0 (d, *J* = 22.3 Hz).

HRMS (APPI; Toluene): Chemical Formula: $C_{28}H_{18}F_2$, calc. 392.1377, found 330.137.

4-methylindeno[1,2,3,4-*defg*]chrysene (S4).



Chemical Formula: $C_{23}H_{14}$
Molecular Weight: 290,3573

The compound was obtained according to the General Procedure B using 2-(2',3'-difluoro-4'-methyl-[1,1'-biphenyl]-2-yl)naphthalene (9) (45 mg). Yield 17 mg (53%).

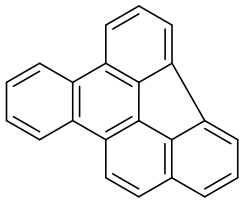
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.77 (dd, *J* = 6.0, 3.4 Hz, 1H), 8.72 (dd, *J* = 6.0, 3.3 Hz, 1H), 8.48 (d, *J* = 8.7 Hz, 1H), 8.36 (d, *J* = 8.1 Hz, 1H), 8.20 (d, *J* = 7.0 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.74 (m, 3H), 7.60 (d, *J* = 8.2 Hz, 1H), 2.99 (s, 3H).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 138.78, 136.24, 135.26, 135.23, 133.42, 133.40, 132.67, 132.56, 132.50, 131.72, 131.52, 131.19, 129.82, 129.57, 129.16, 128.82, 128.54, 128.33,

128.10, 127.92, 127.23, 127.19, 127.00, 126.37, 125.66, 125.27, 125.17, 125.01, 124.85, 122.83, 122.44, 14.28.

HRMS (APPI; Toluene): Chemical Formula: $C_{23}H_{14}$, calc. 290.1096, found 290.1096.

Indeno[1,2,3,4-*defg*]chrysene (S5).


Chemical Formula: $C_{22}H_{12}$
Molecular Weight: 276,3307

The compound was obtained according to the General Procedure B using 2-(2',3'-difluoro-[1,1'-biphenyl]-2-yl)naphthalene (40 mg). Yield 16 mg (56%).

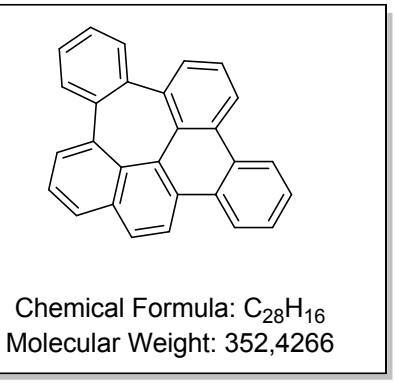
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.82 – 8.76 (m, 1H), 8.72-8.70 (m, 1H), 8.44 (dd, *J* = 8.3, 7.2 Hz, 2H), 8.20 – 8.15 (m, 2H), 8.12 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.72 (m, 4H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 138.41, 137.47, 133.61, 132.70, 132.53, 131.94, 131.63, 129.21, 128.90, 128.85, 127.44, 127.33, 127.28, 126.87, 125.68, 125.43, 125.08, 123.85, 123.30, 122.58, 122.42.

UV/Vis (DCM-MeOH, 1-1, 293 K): λ [nm]) = 279, 299, 312, 352, 365, 390.

HRMS (APPI; Toluene): Chemical Formula: $C_{22}H_{12}$, calc. 276.0939, found 276.0940.

Tribenzo[b,gh,pq]pleiadene(S9).


Chemical Formula: $C_{28}H_{16}$
Molecular Weight: 352,4266

The compound was obtained according to the General Procedure B using 2-(2',2''-difluoro-[1,1':3',1''-terphenyl]-2-yl)naphthalene (40 mg). Yield 7 mg (20%)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.55 (dd, *J* = 6.1, 3.3 Hz, 1H), 8.46-8.42 (ddd, *J* = 8.8, 5.7, 3.4 Hz, 3H), 7.83 (dd, *J* = 11.5, 5.1 Hz, 2H), 7.79 – 7.73 (m, 2H), 7.72 – 7.60 (m, 4H), 7.44 – 7.34 (m, 2H), 7.14 (dd, *J* = 6.5, 2.6 Hz, 1H), 7.10 – 7.06 (m, 1H).

UV/Vis (DCM, 293 K): λ [nm]) 246, 264, 283, 352

HRMS (APPI; Toluene): Chemical Formula: $C_{28}H_{16}$, calc. 352.1252, found 326.1252.

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

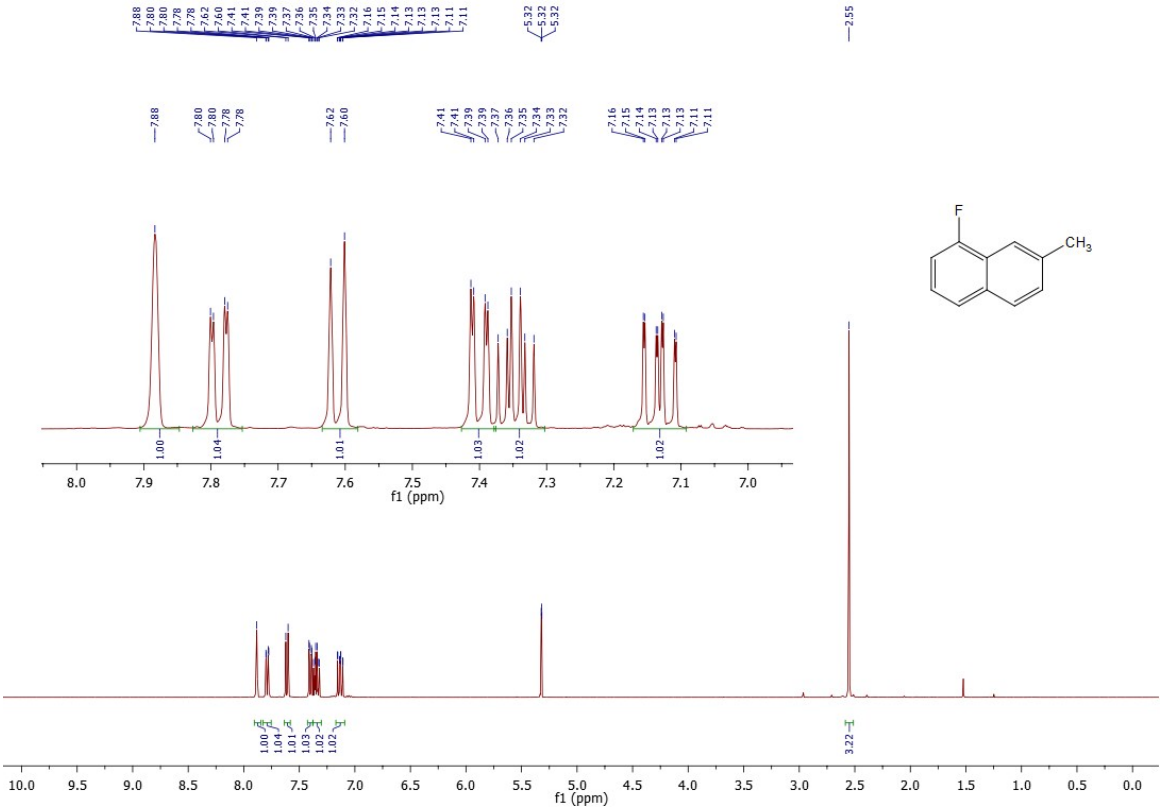


Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of 1-fluoro-7-methylnaphthalene.

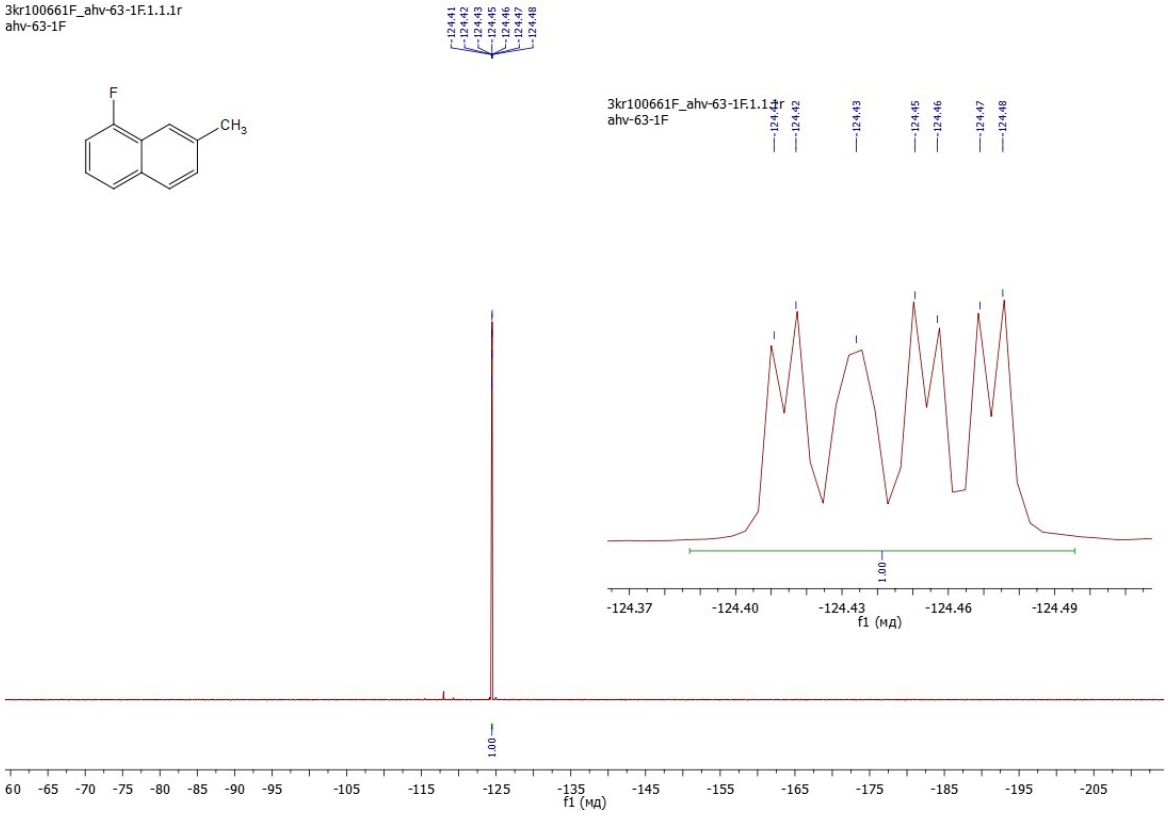


Figure S2. ^{19}F NMR (377 MHz, CD_2Cl_2) spectrum of 1-fluoro-7-methylnaphthalene.

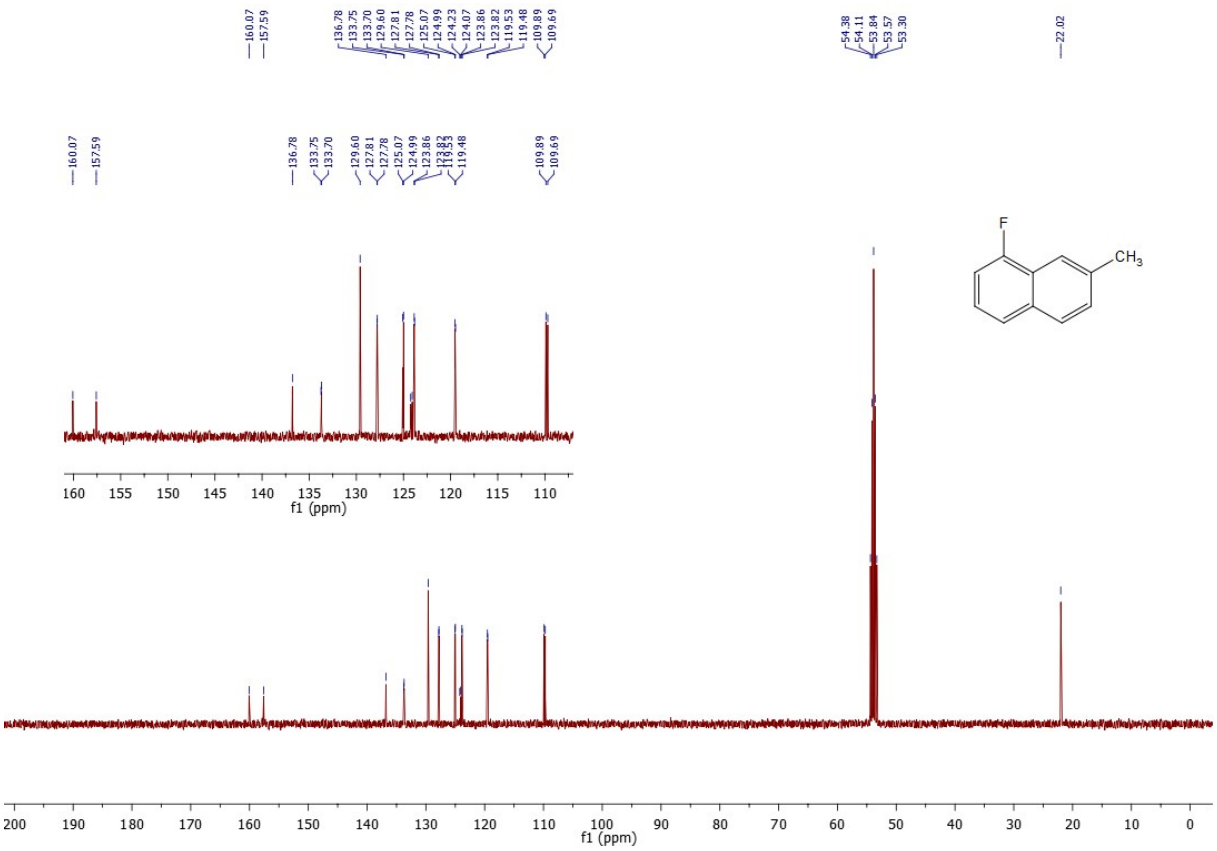


Figure S3. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of 1-fluoro-7-methylnaphthalene.

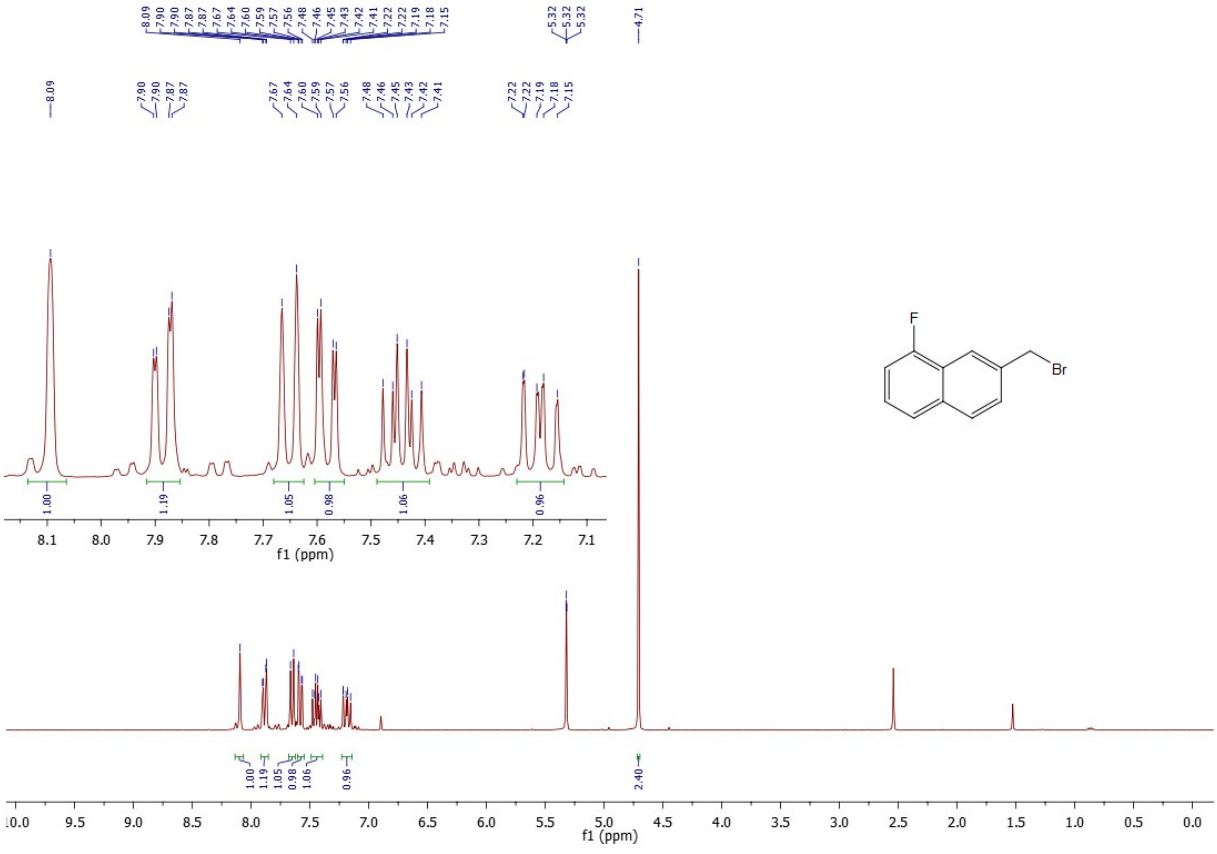


Figure S4. ^{1}H NMR (300 MHz, CD_2Cl_2) spectrum of 7-(bromomethyl)-1-fluoronaphthalene.

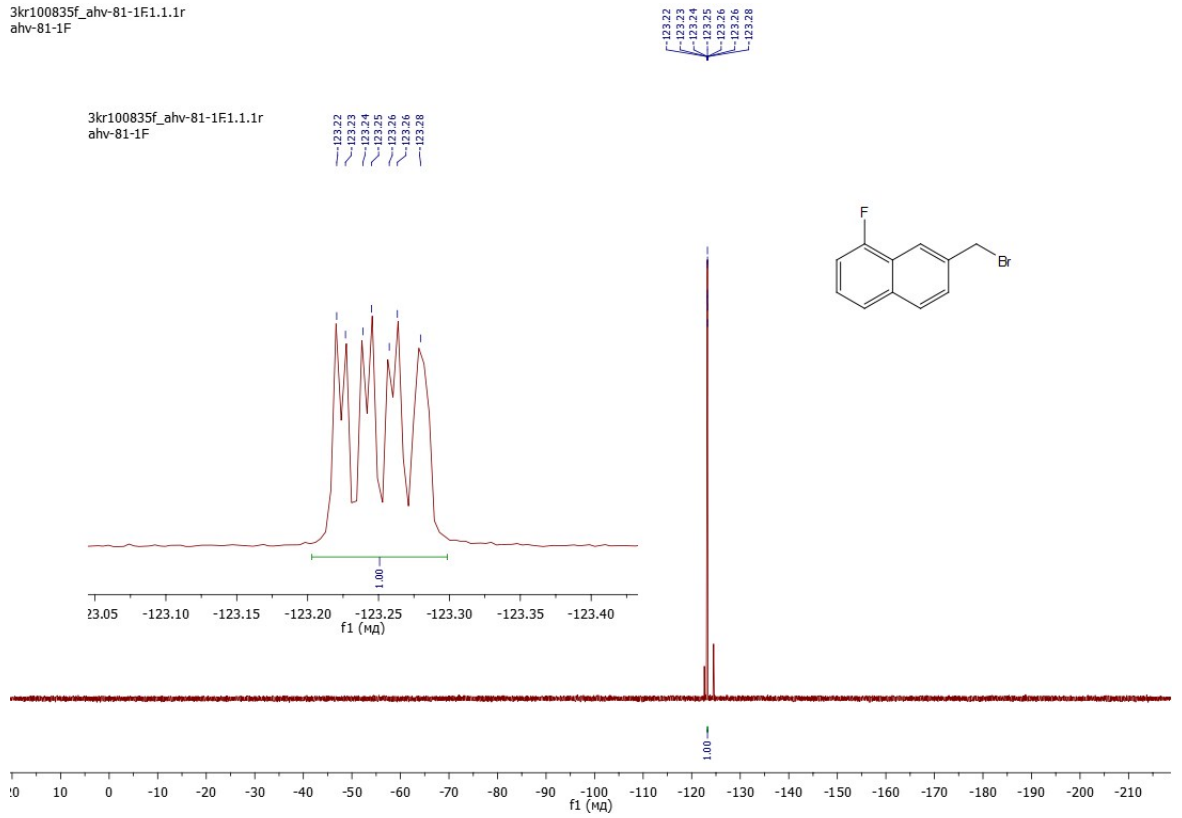


Figure S5. ^{19}F NMR (282 MHz, CD_2Cl_2) spectrum of 7-(bromomethyl)-1-fluoronaphthalene.

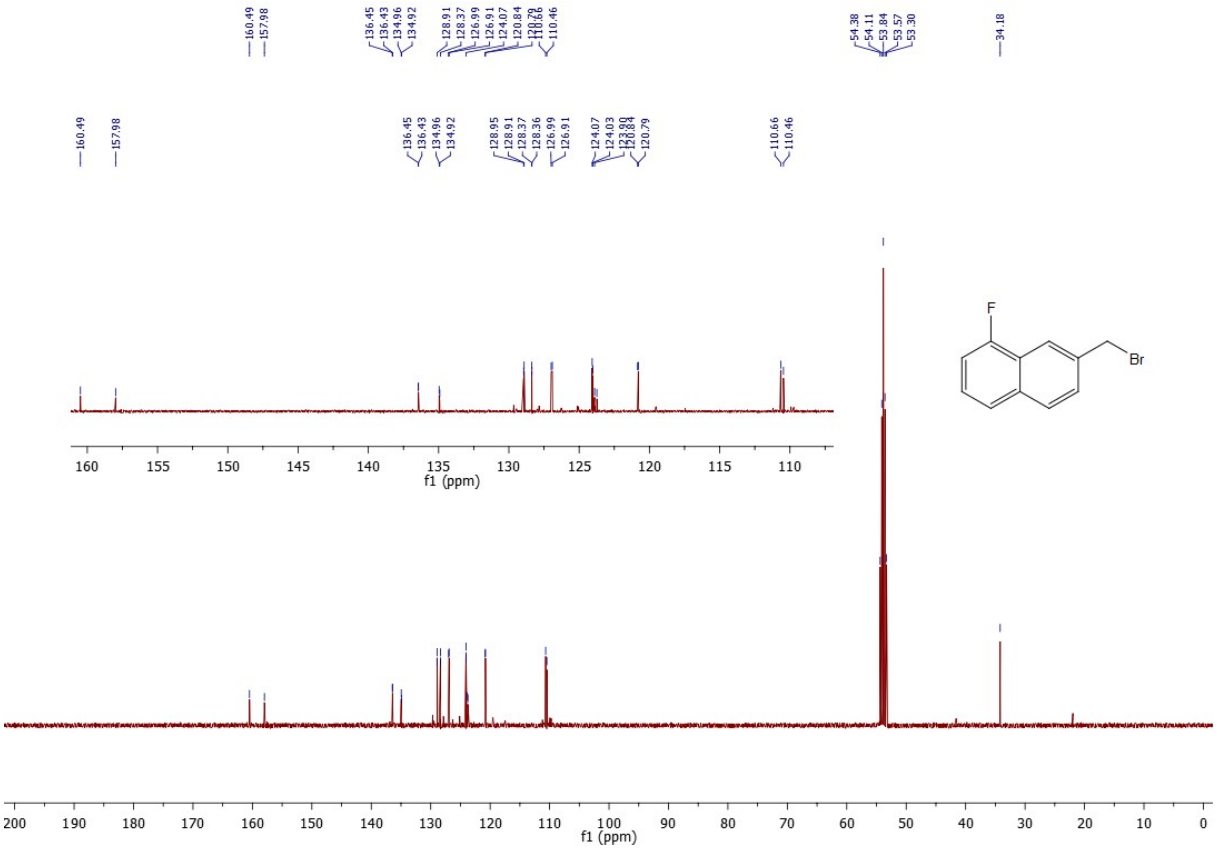


Figure S6. ^{13}C NMR (77 MHz, CD_2Cl_2) spectrum of 7-(bromomethyl)-1-fluoronaphthalene.

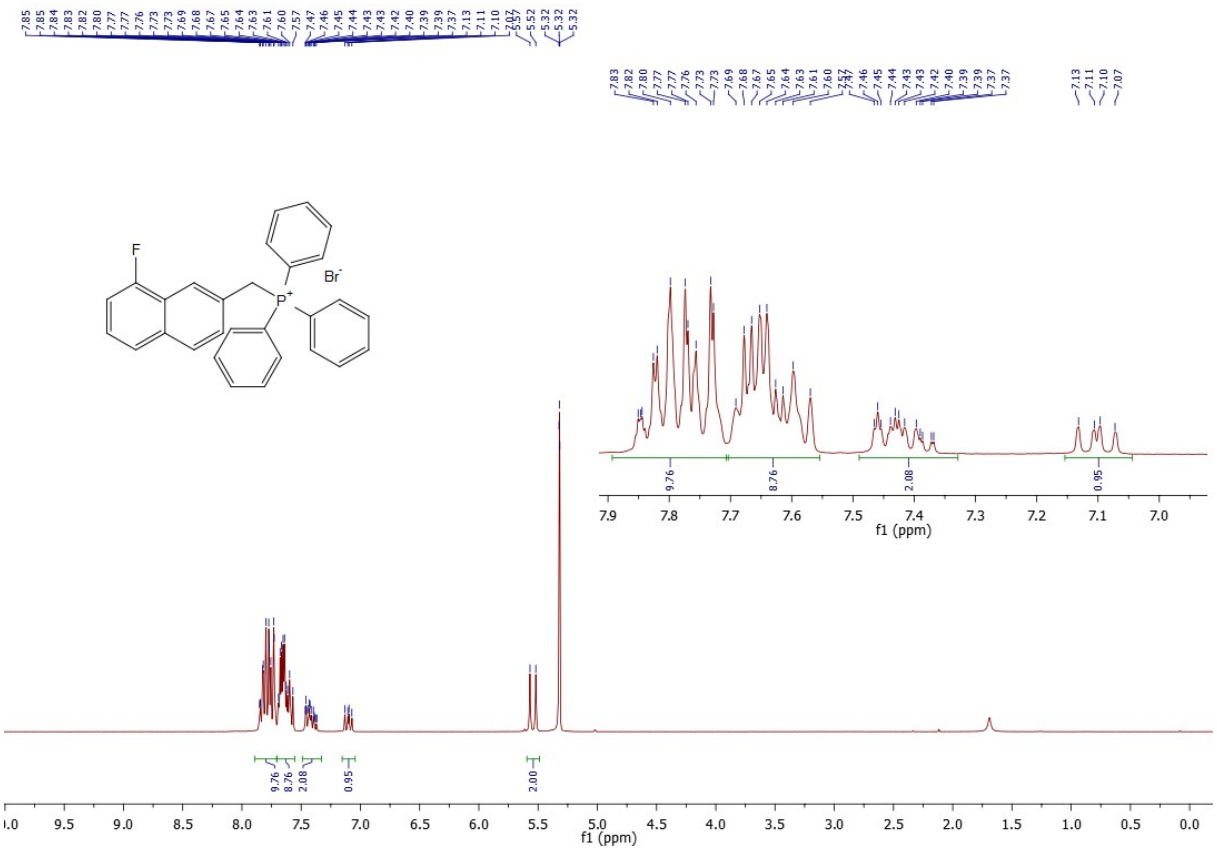


Figure S7. ^{1}H NMR (300 MHz, CD_2Cl_2) spectrum of ((8-fluoronaphthalen-2-yl)methyl) triphenylphosphonium bromide.

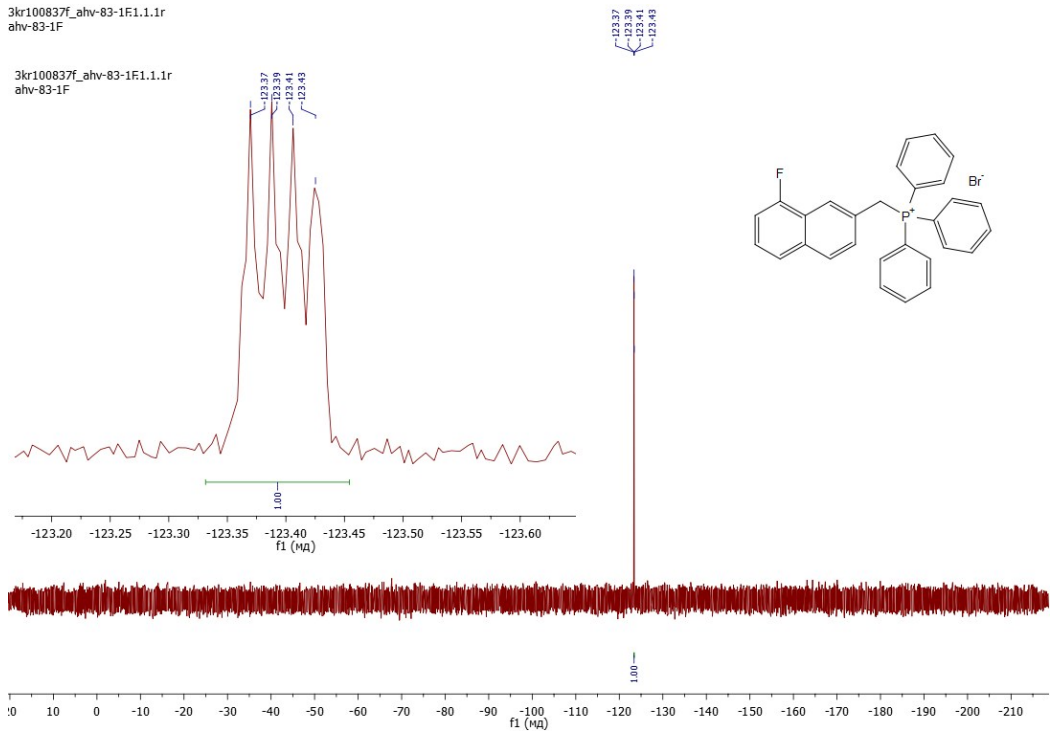


Figure S8. ^{19}F NMR (282 MHz, CD_2Cl_2) spectrum of ((8-fluoronaphthalen-2-yl)methyl) triphenylphosphonium bromide.

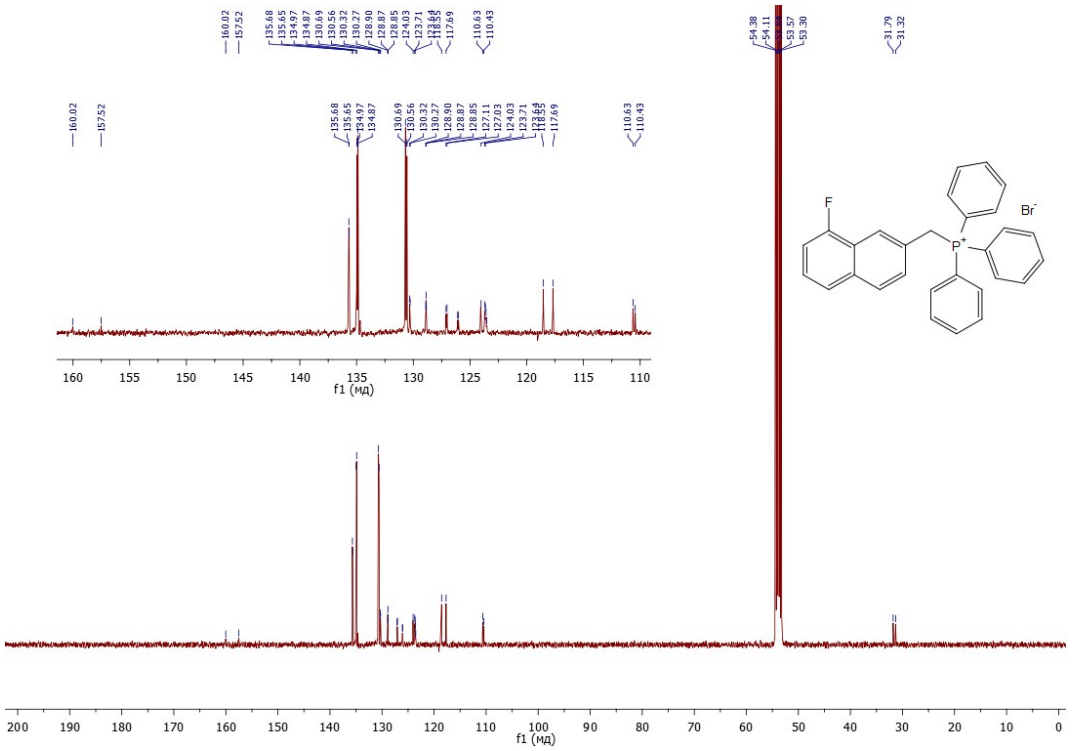


Figure S9. ^{13}C NMR (77 MHz, CD_2Cl_2) spectrum of ((8-fluoronaphthalen-2-yl)methyl) triphenylphosphonium bromide.

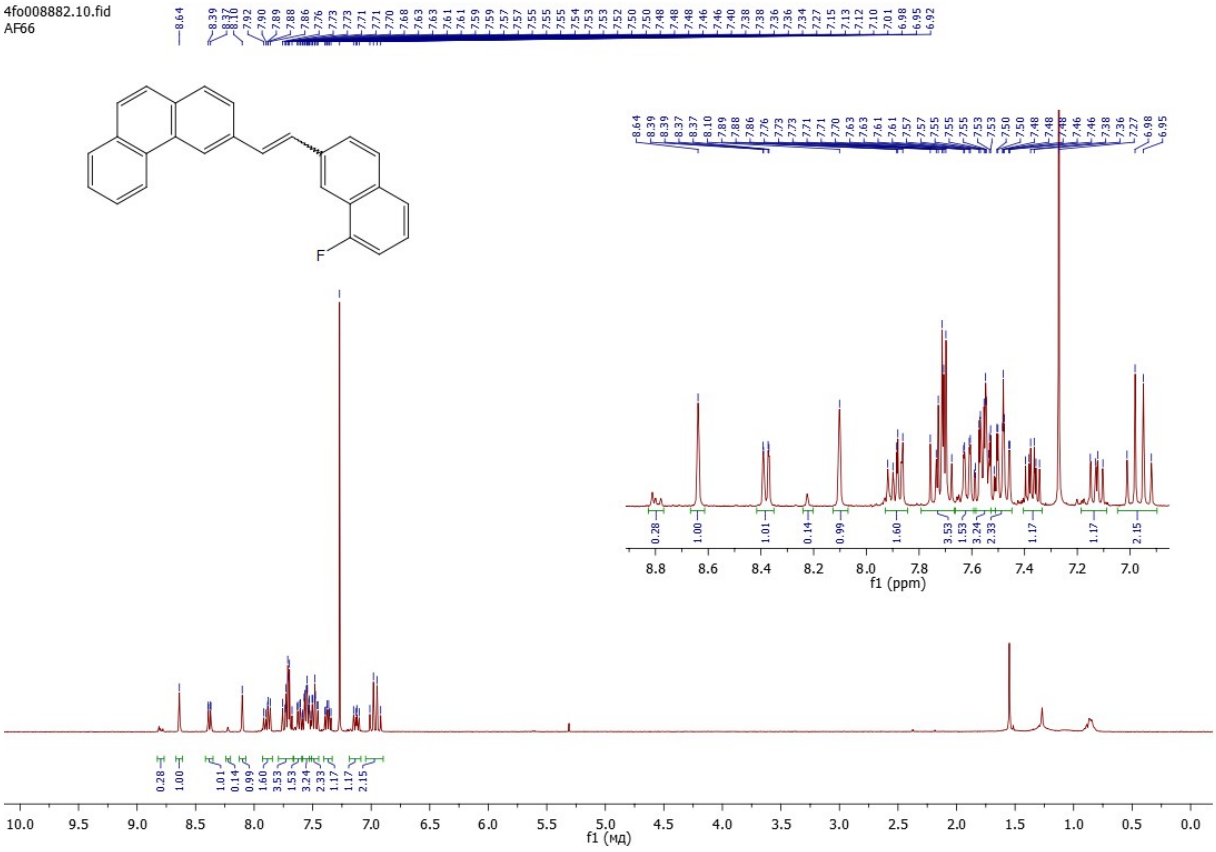


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(2-(8-fluoronaphthalen-2-yl)vinyl)phenanthrene

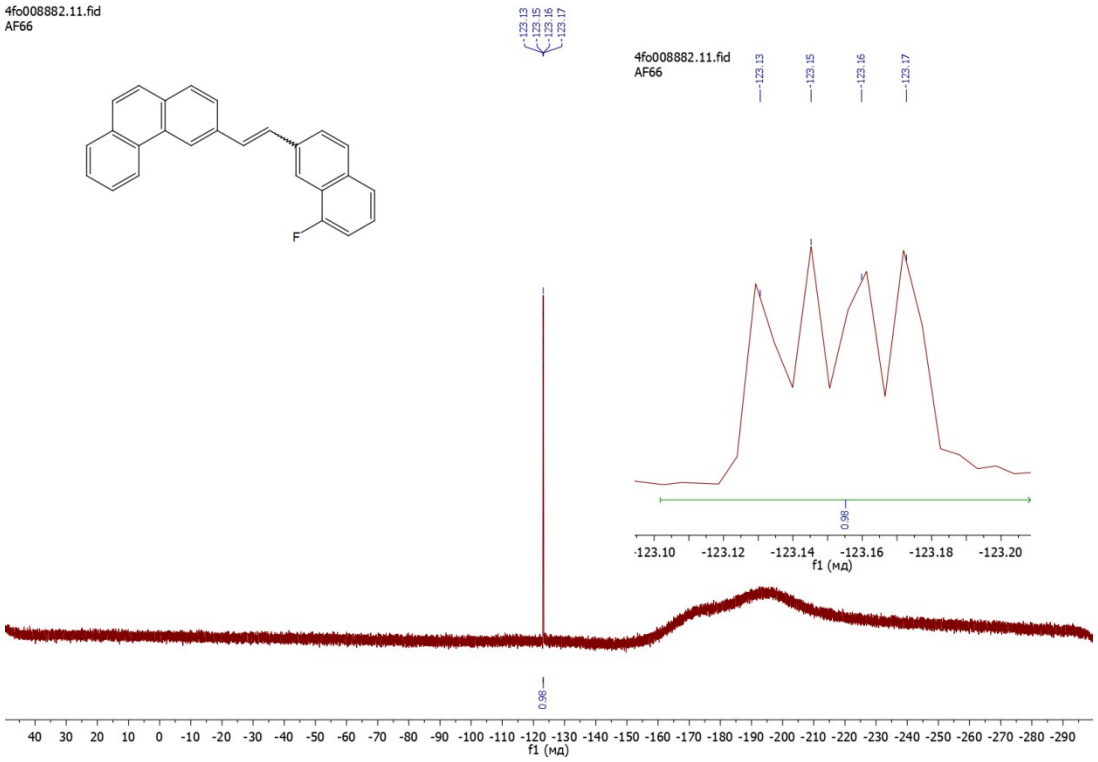


Figure S11. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of 3-(2-(8-fluoronaphthalen-2-yl)vinyl)phenanthrene

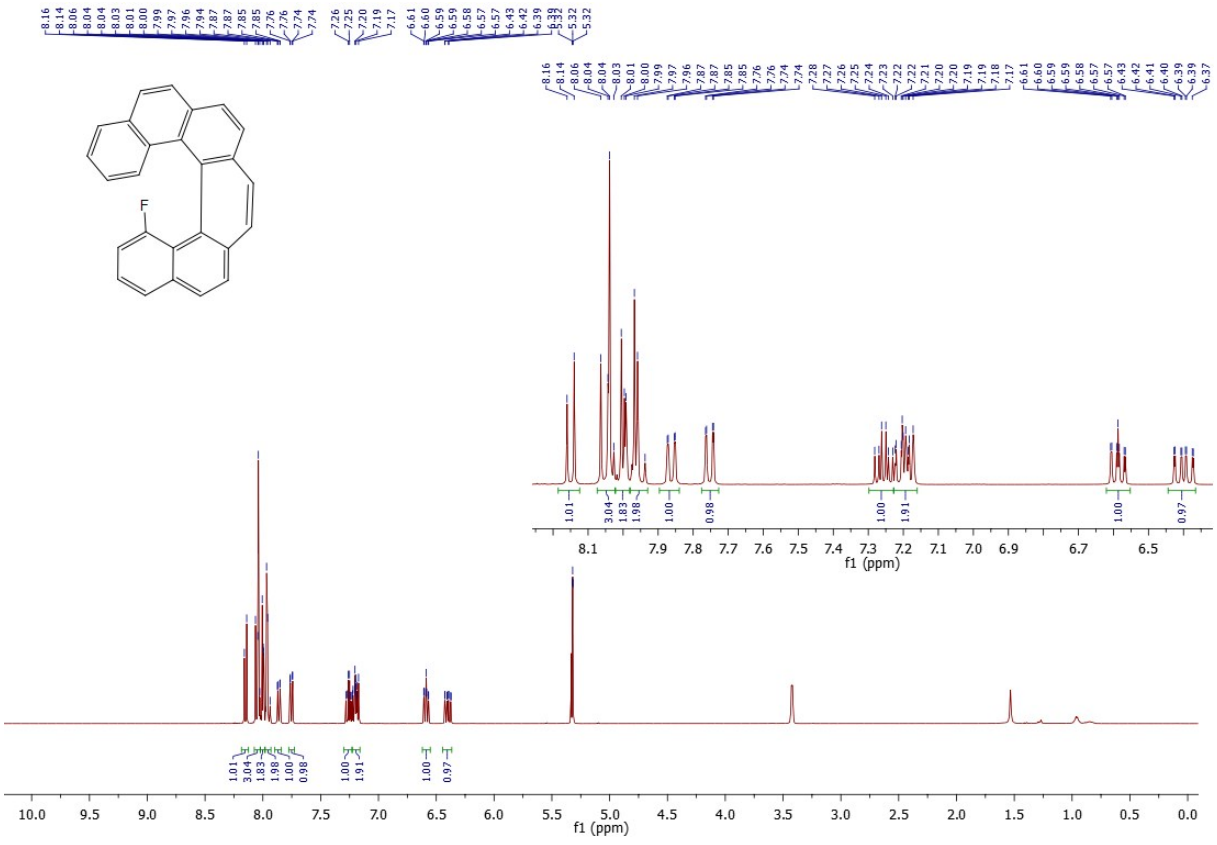


Figure S12. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **3**.

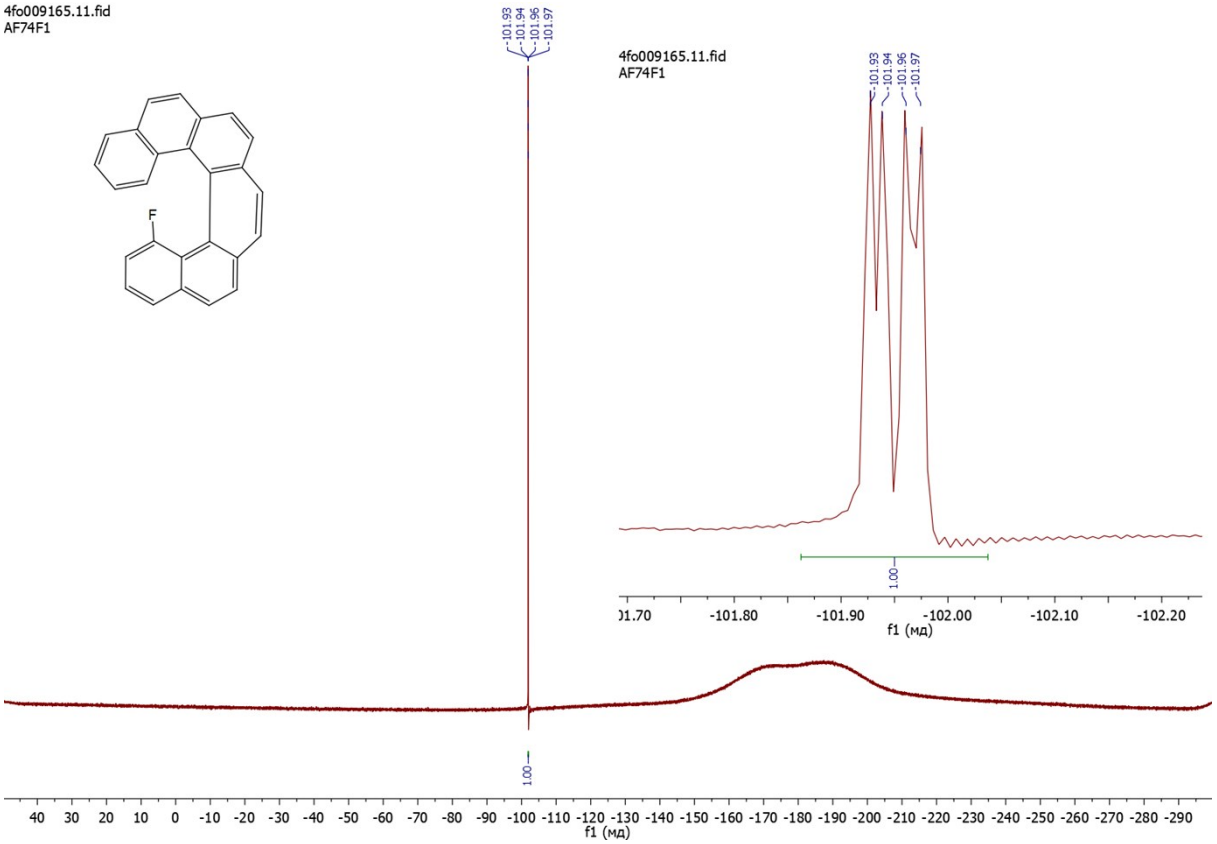


Figure S13. ^{19}F NMR (377 MHz, CD_2Cl_2) spectrum of **3**.

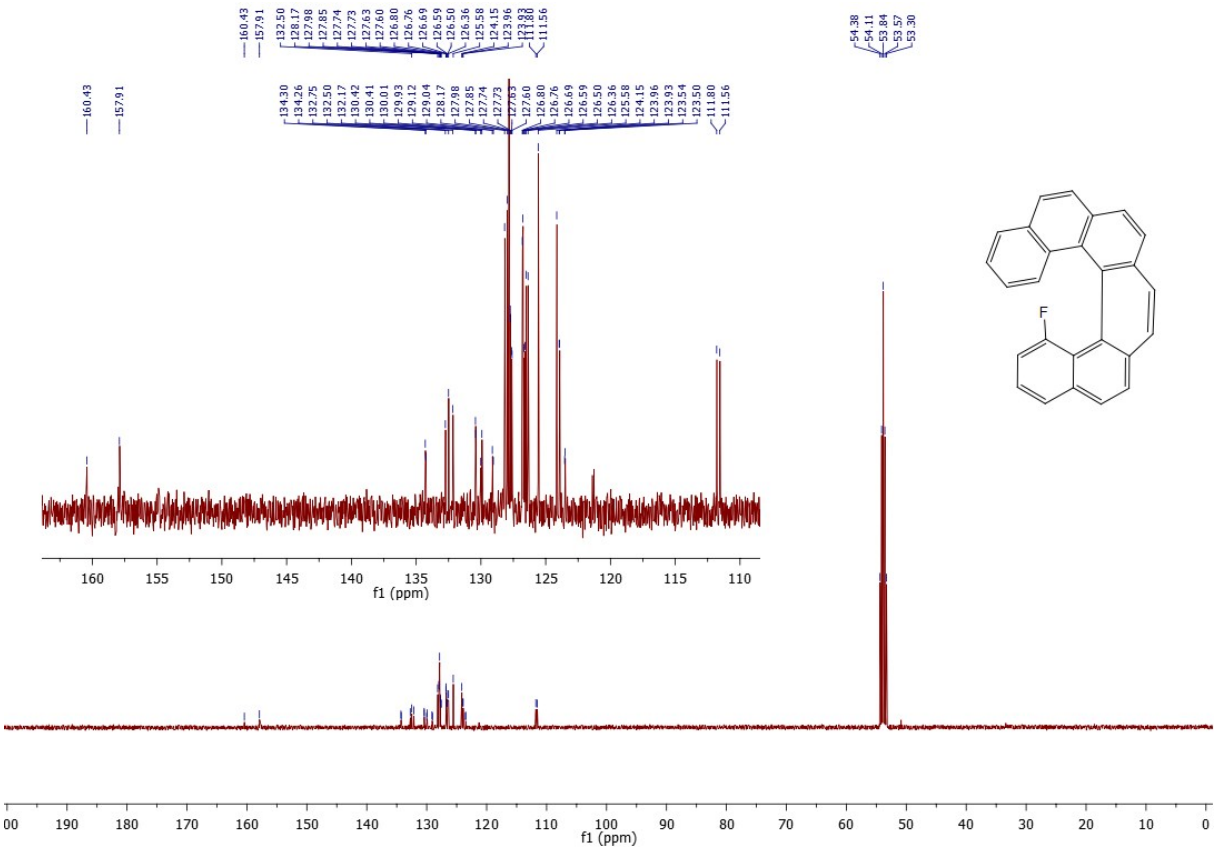


Figure S14. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **3**.

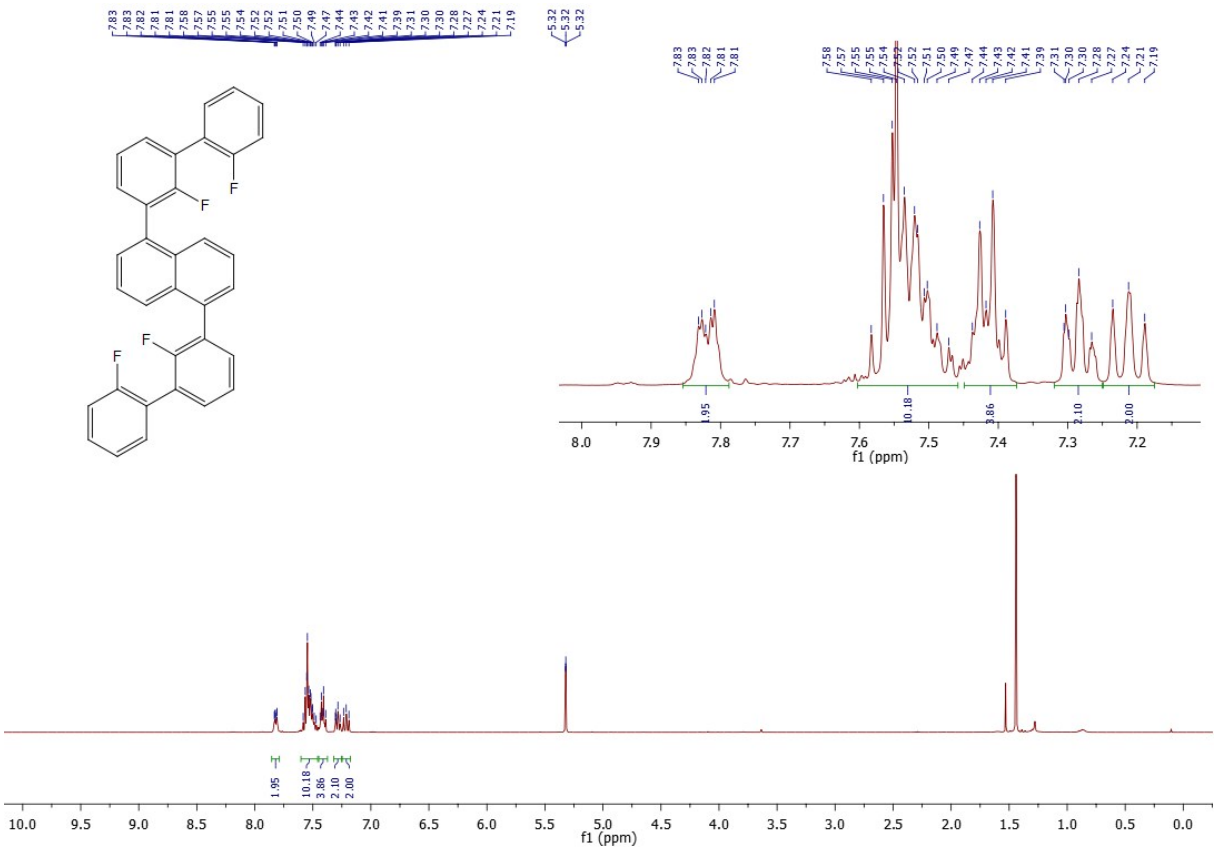


Figure S15. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **9**.

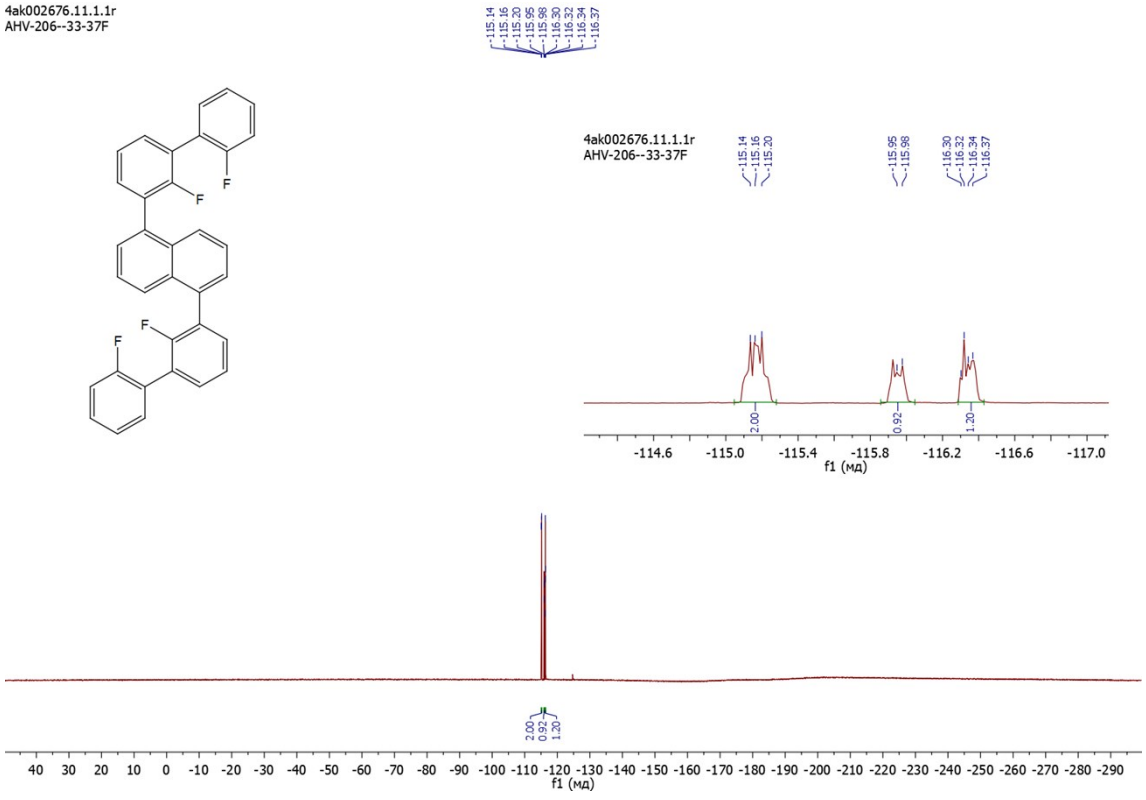


Figure S16. ^{19}F NMR (377 MHz, CD_2Cl_2) spectrum of **9**.

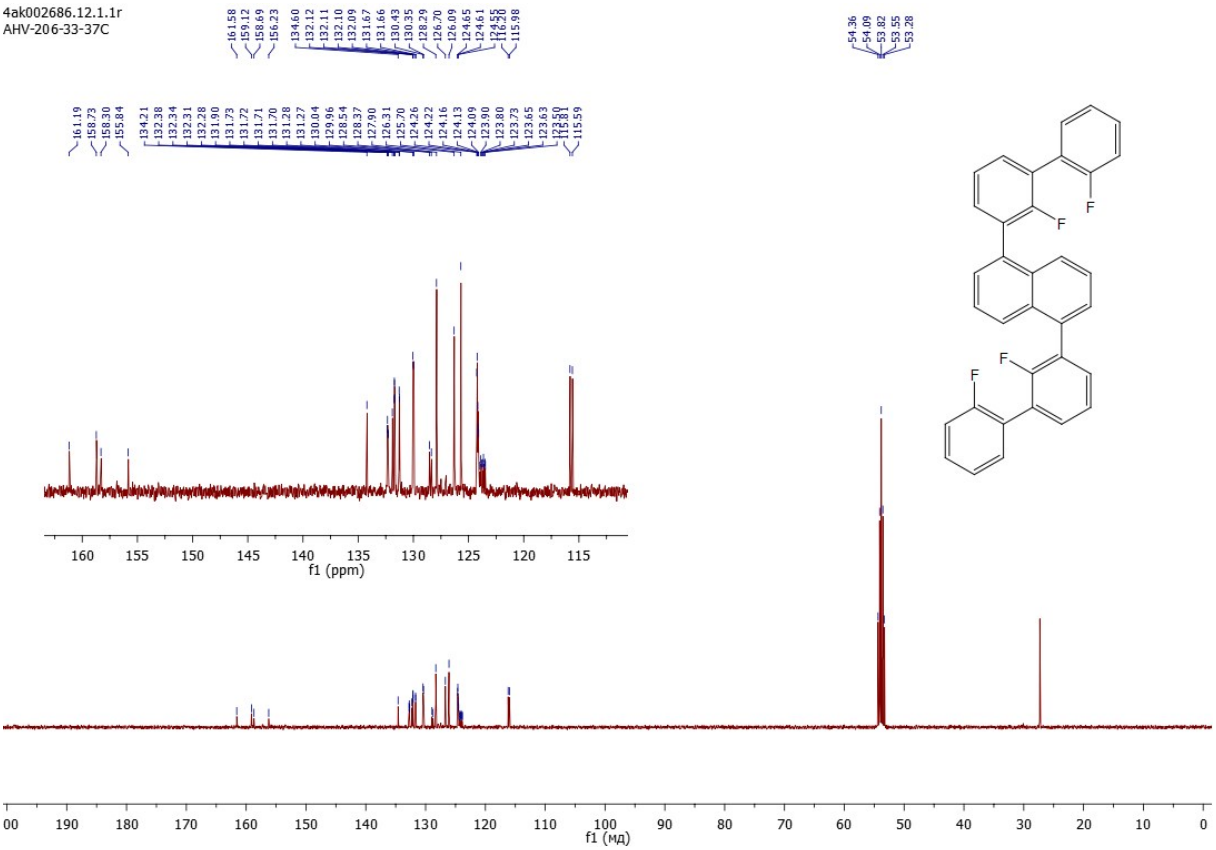


Figure S17. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **9**.

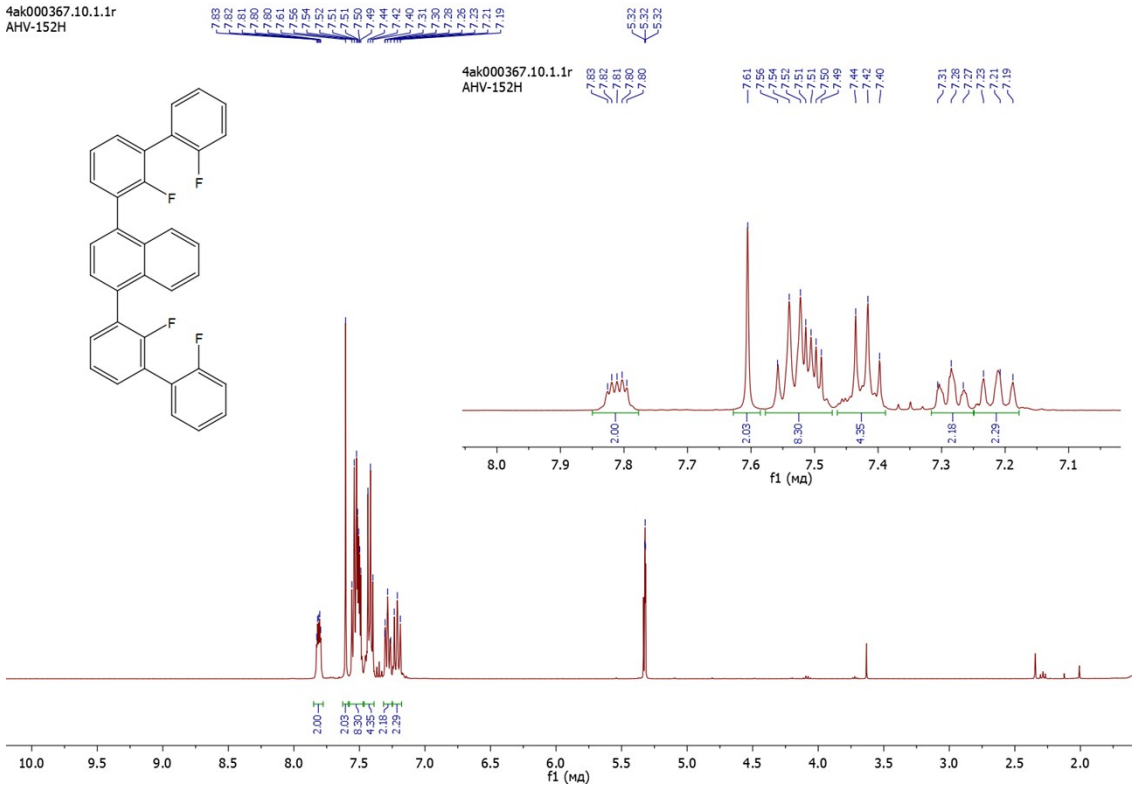


Figure S18. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **10**.

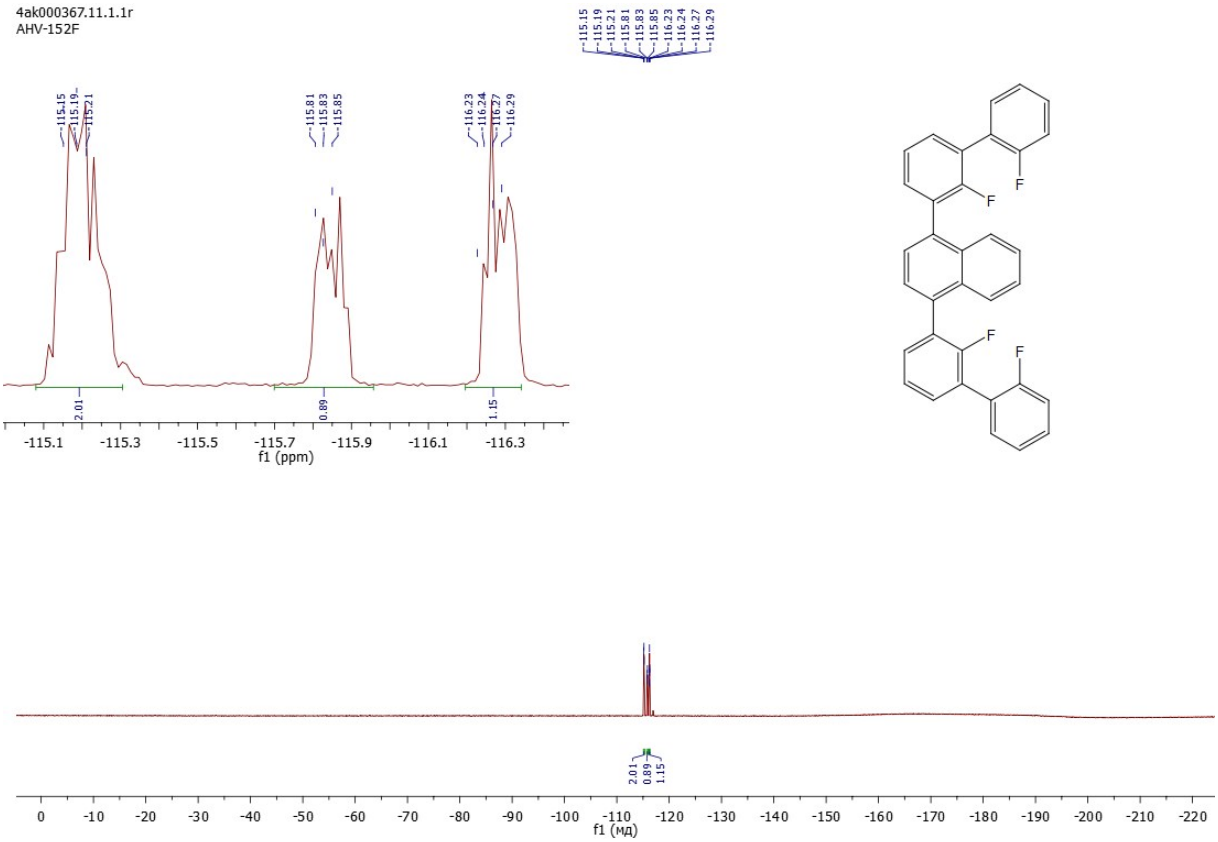


Figure S19. ^{19}F NMR (377 MHz, CD_2Cl_2) spectrum of **10**

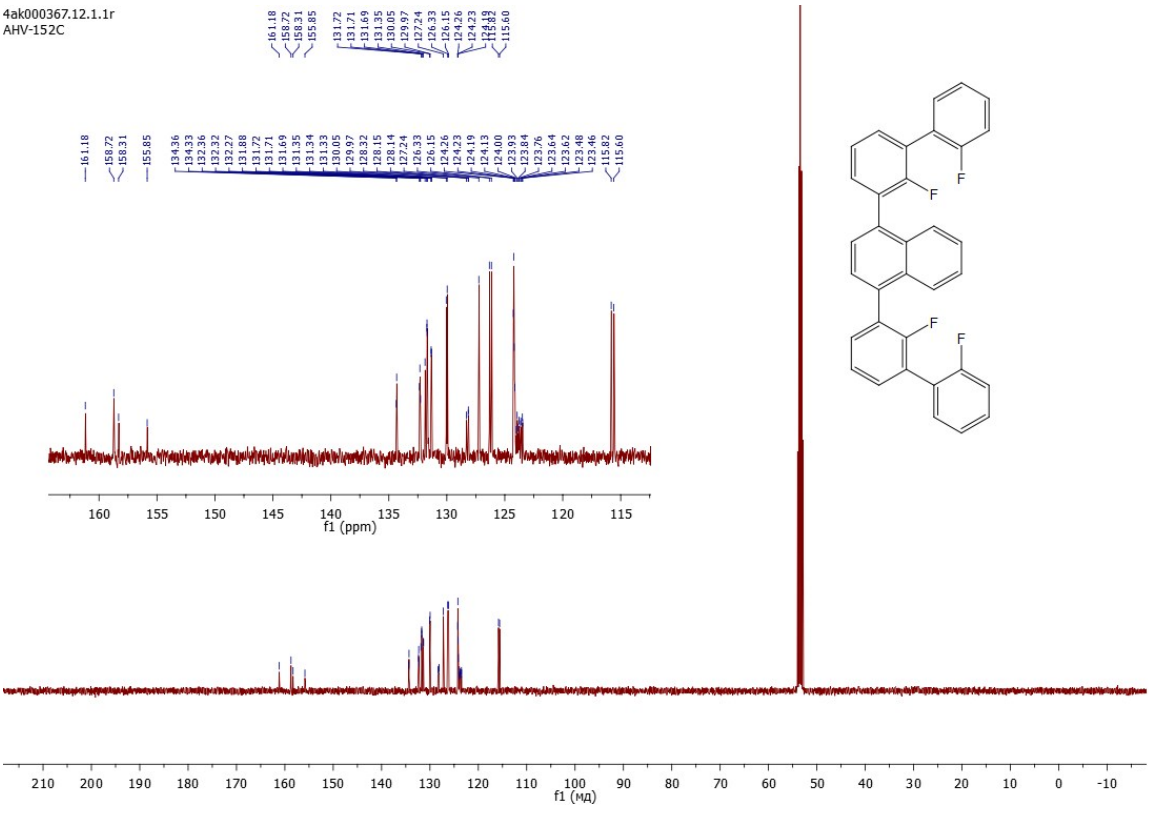


Figure S20. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **10**.

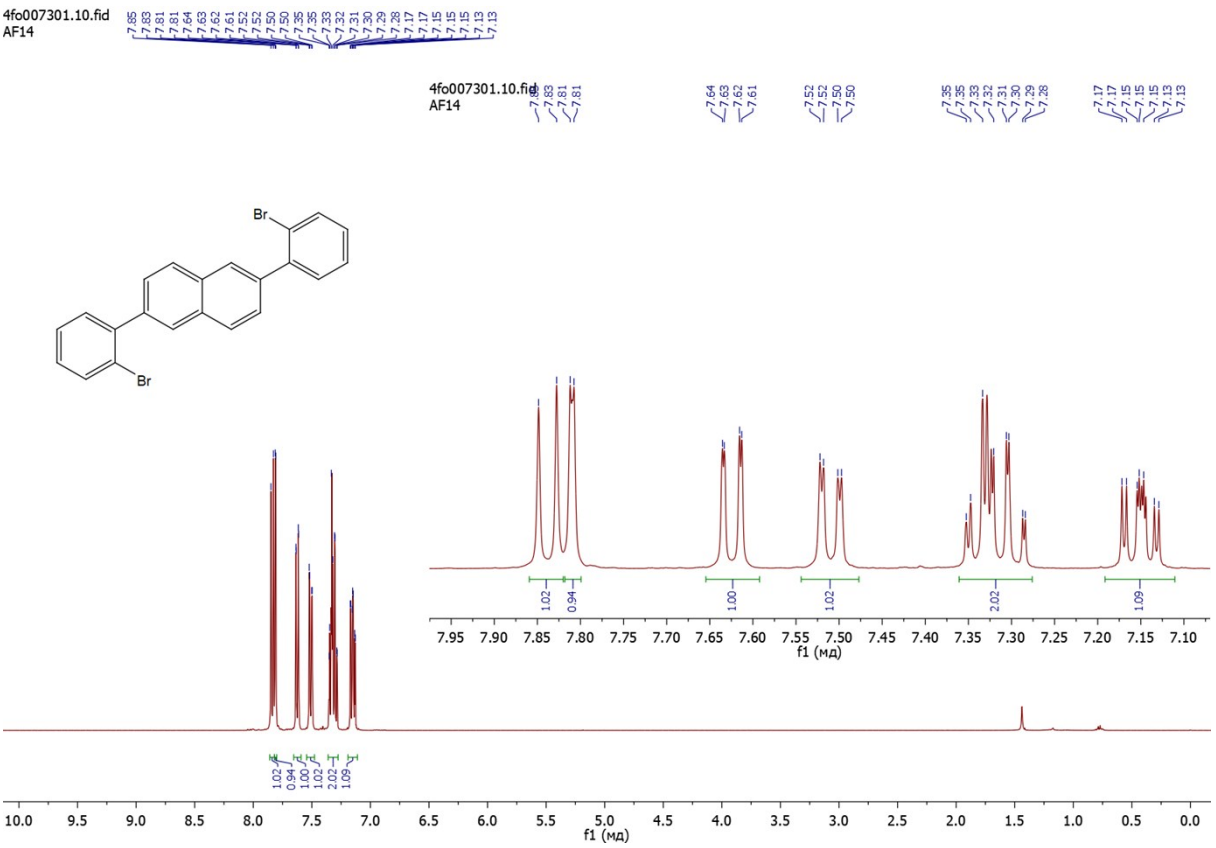


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**.

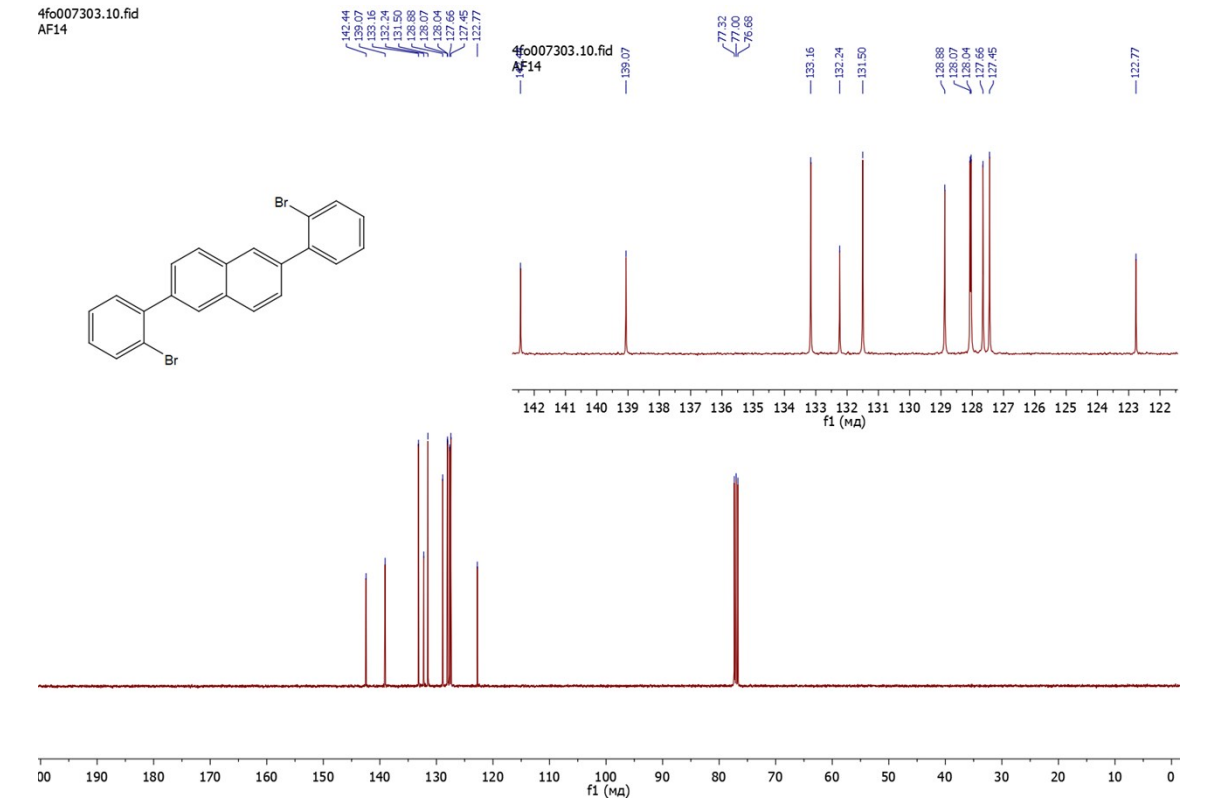


Figure S22. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **8**.

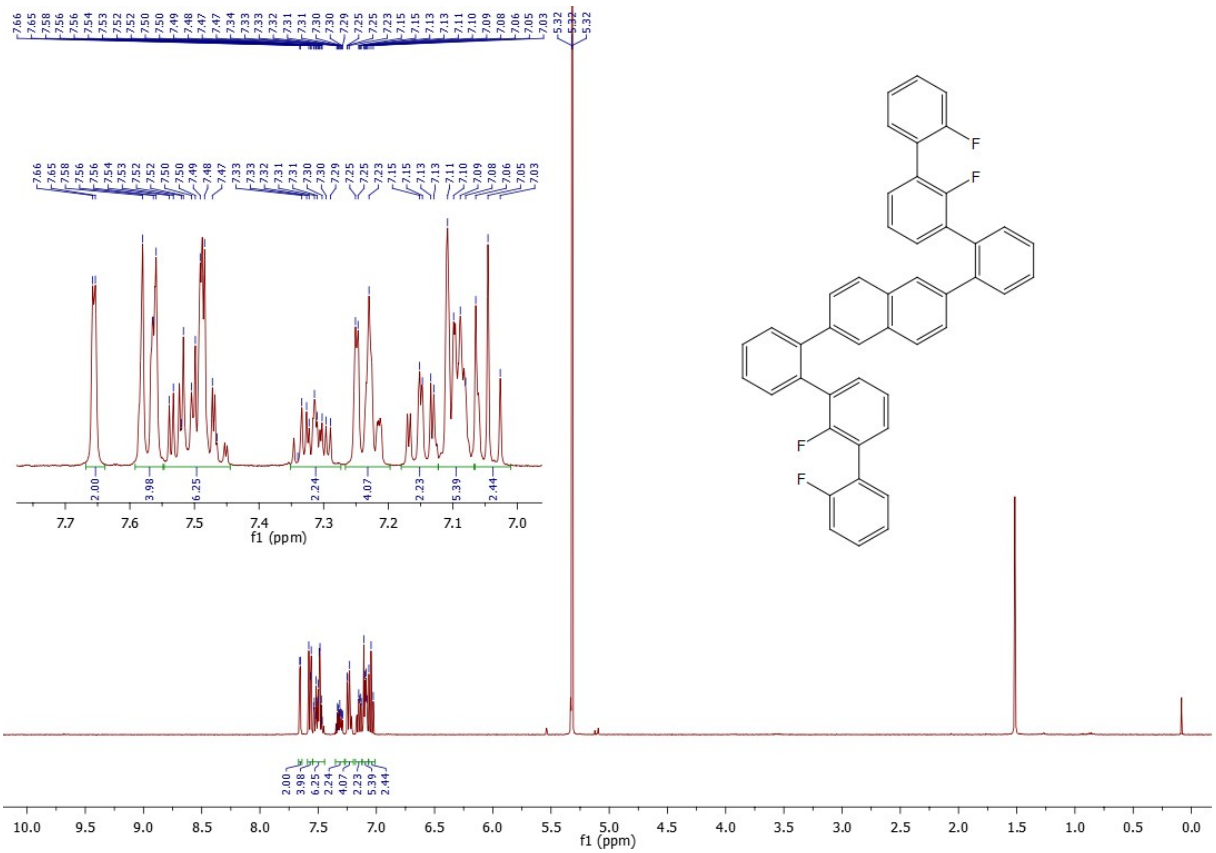


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**.

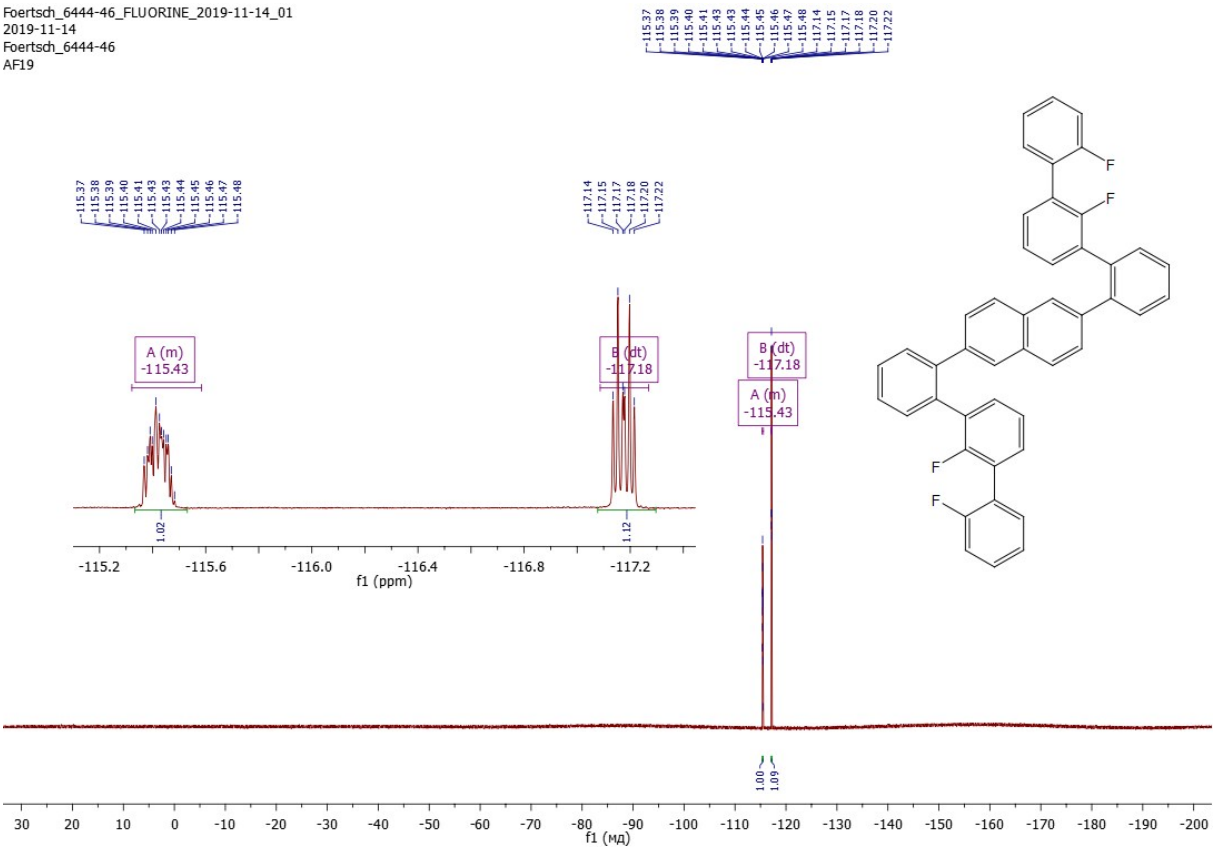


Figure S24. ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **11**.

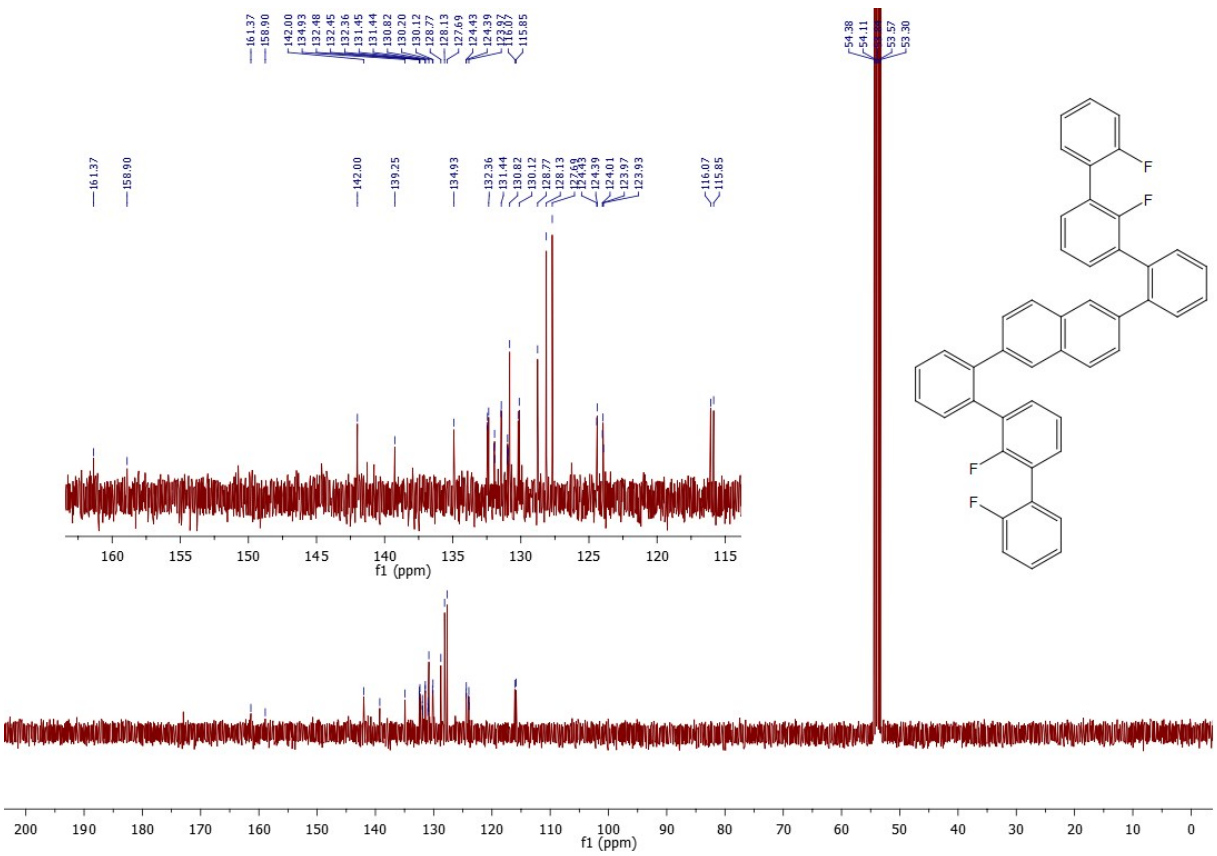


Figure S25. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **11**.

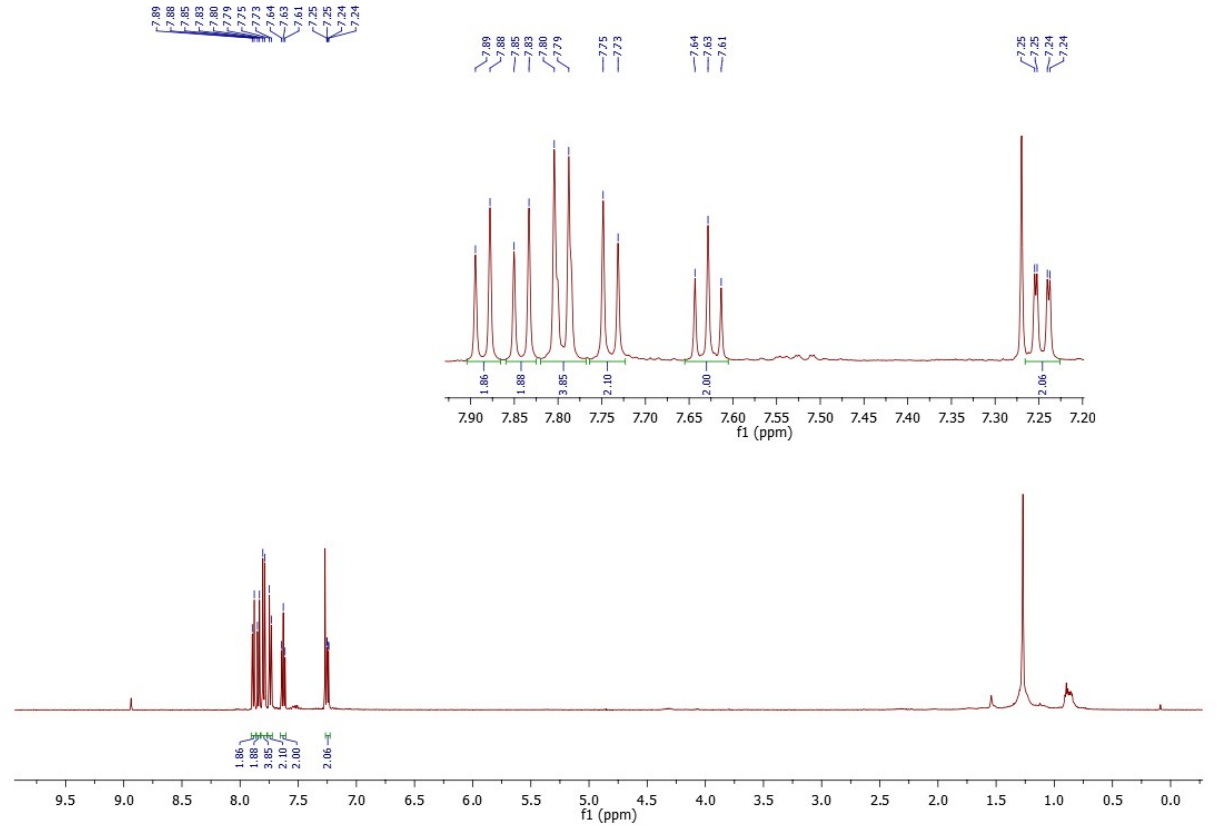


Figure S26. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **4**.

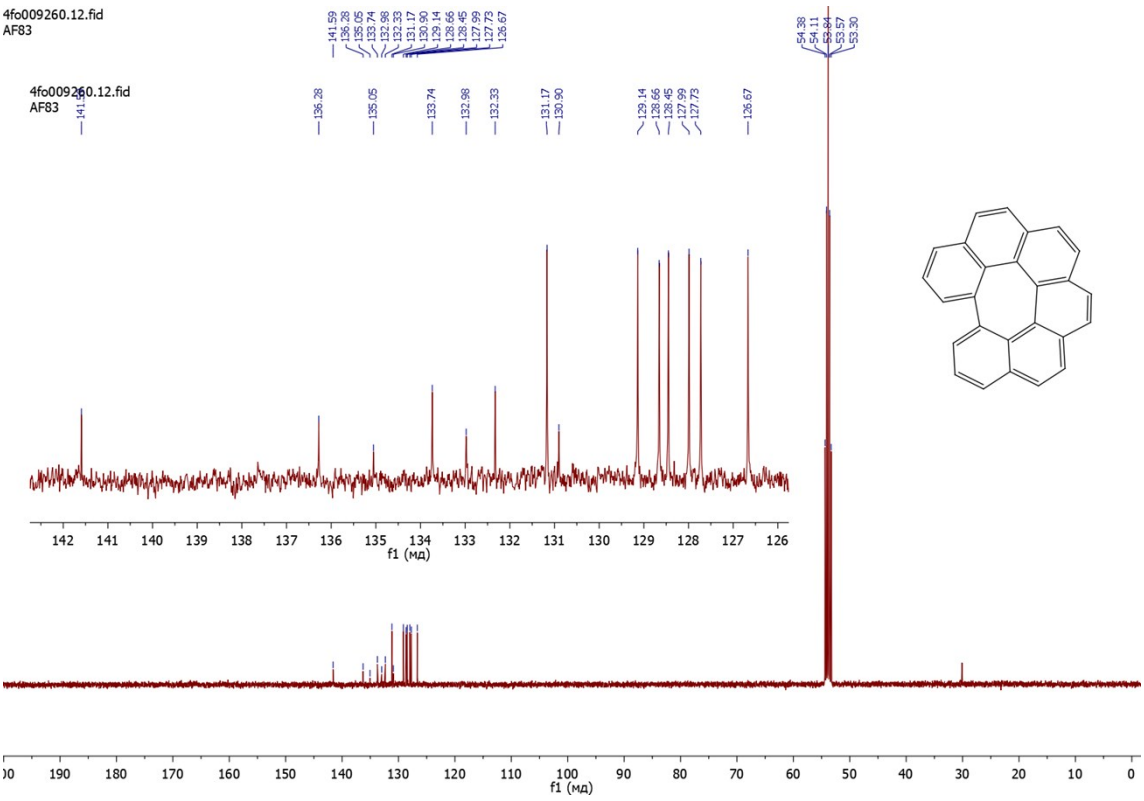


Figure S27. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **4**.

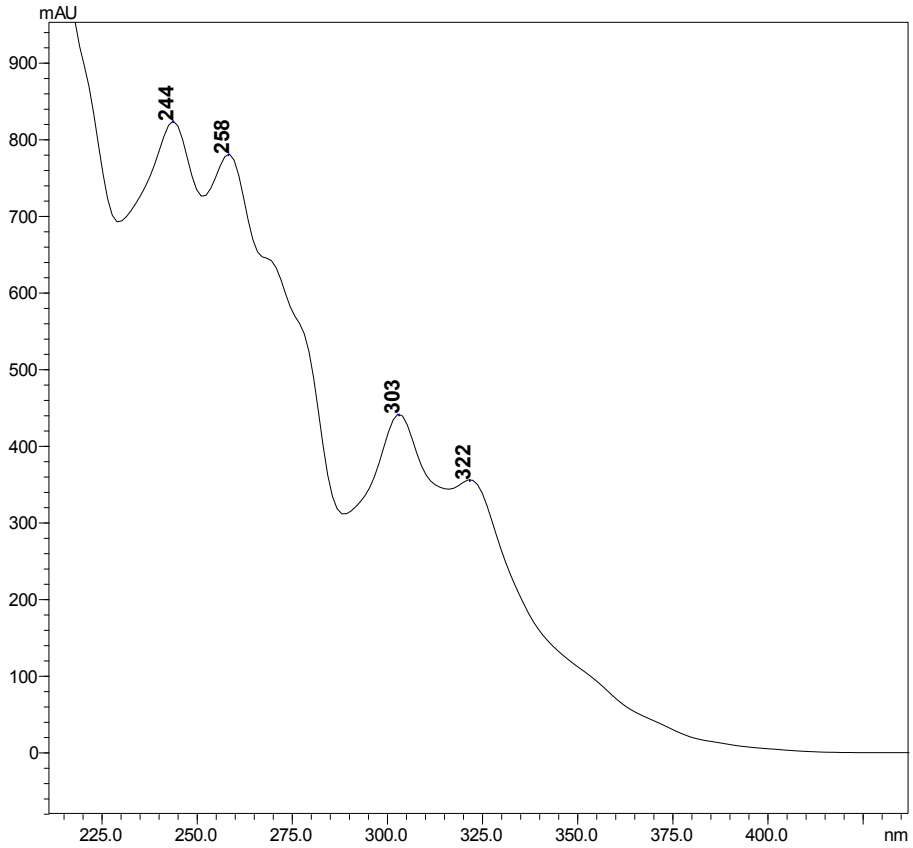


Figure S28. UV-Vis spectrum of **4** (DCM).

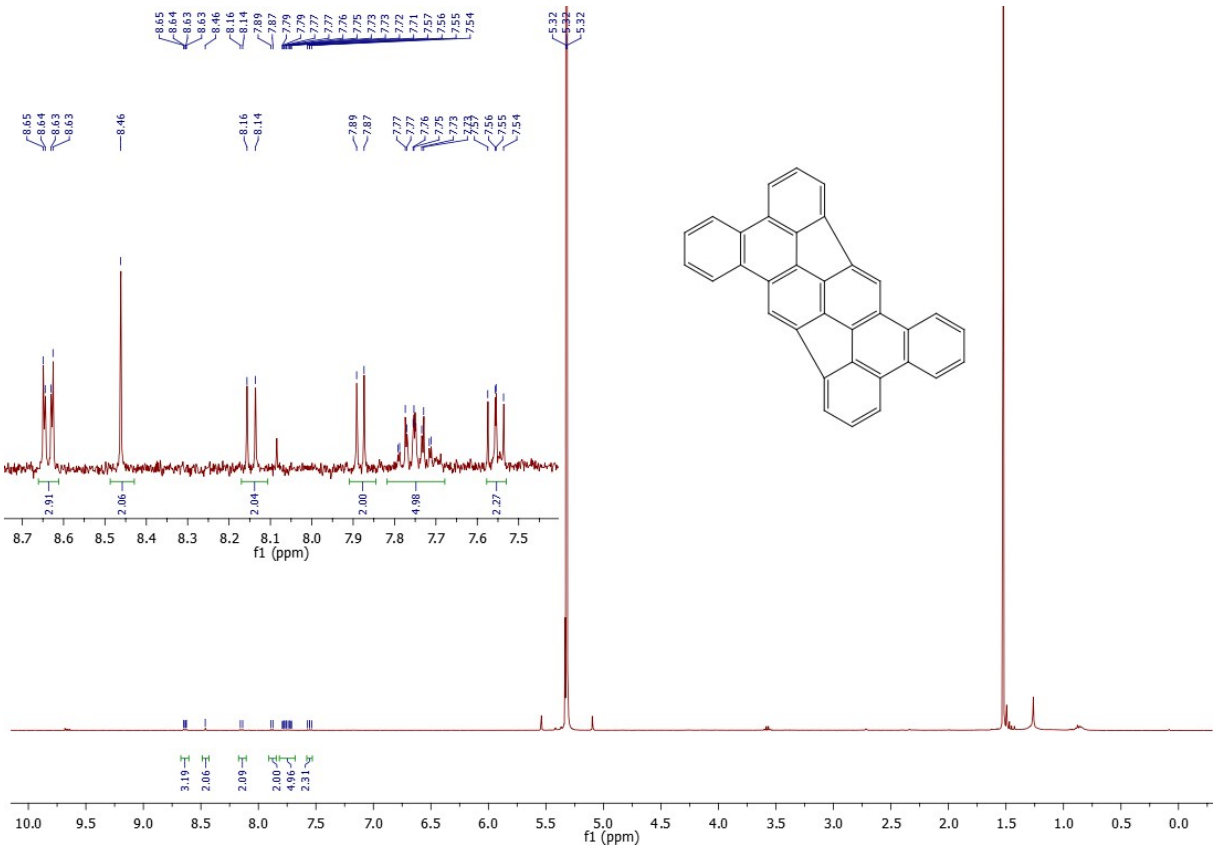


Figure S29. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **12**.

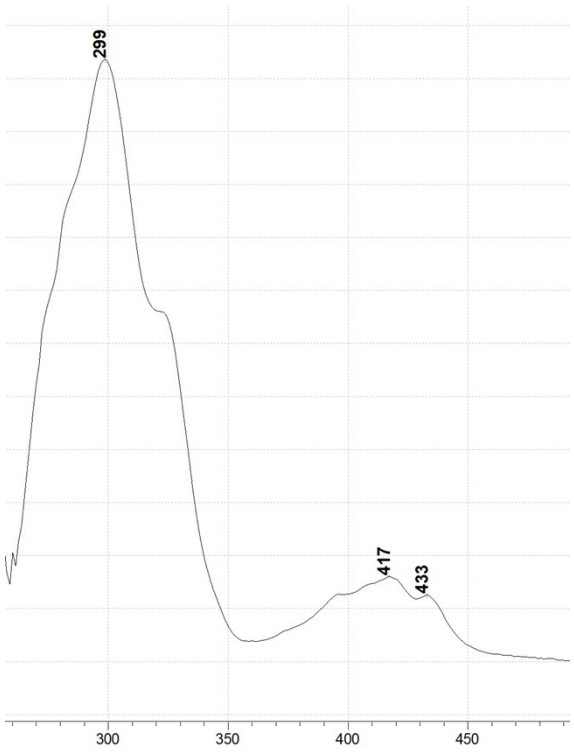


Figure S30. UV-Vis spectrum of **12** (DCM-MeOH 1-1).

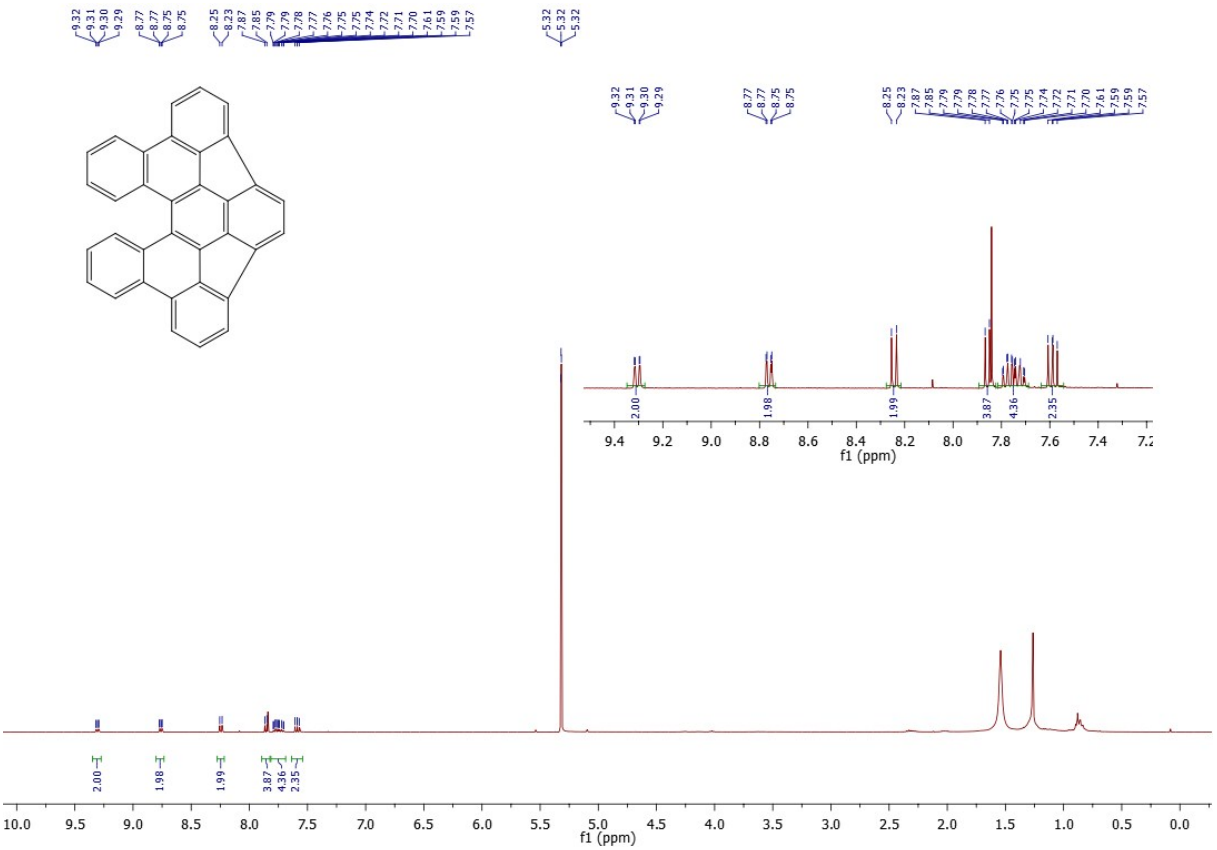


Figure S31. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **13**.

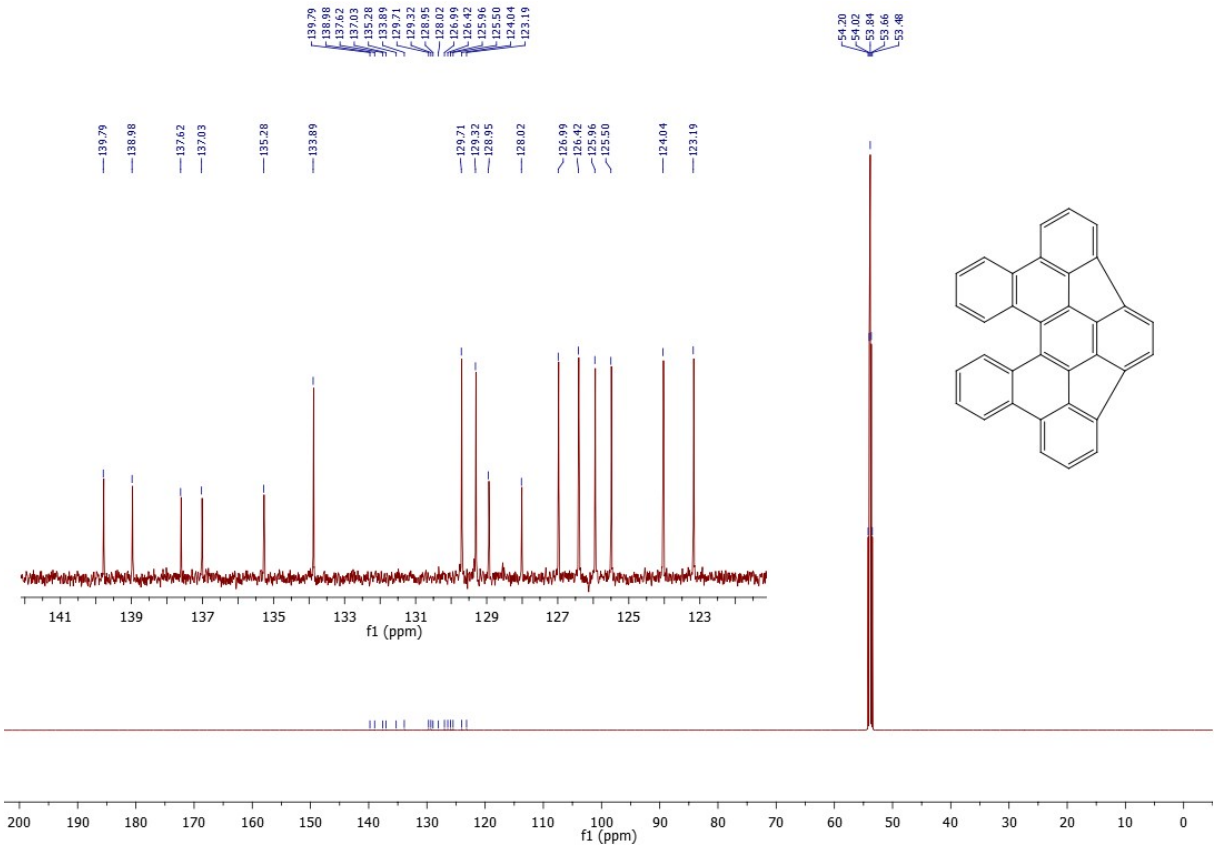


Figure S32. ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of **13**.

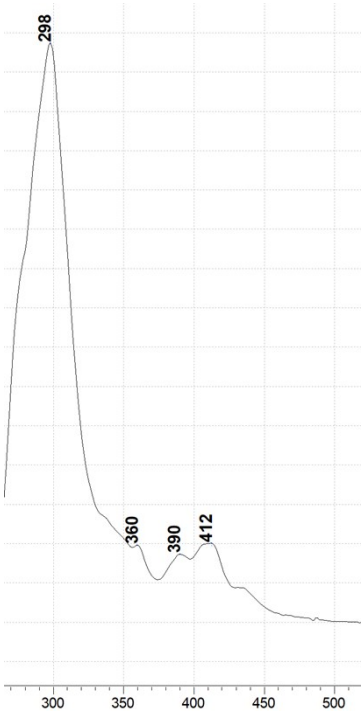


Figure S33. UV-Vis spectrum **13** (DCM-MeOH 1-1).

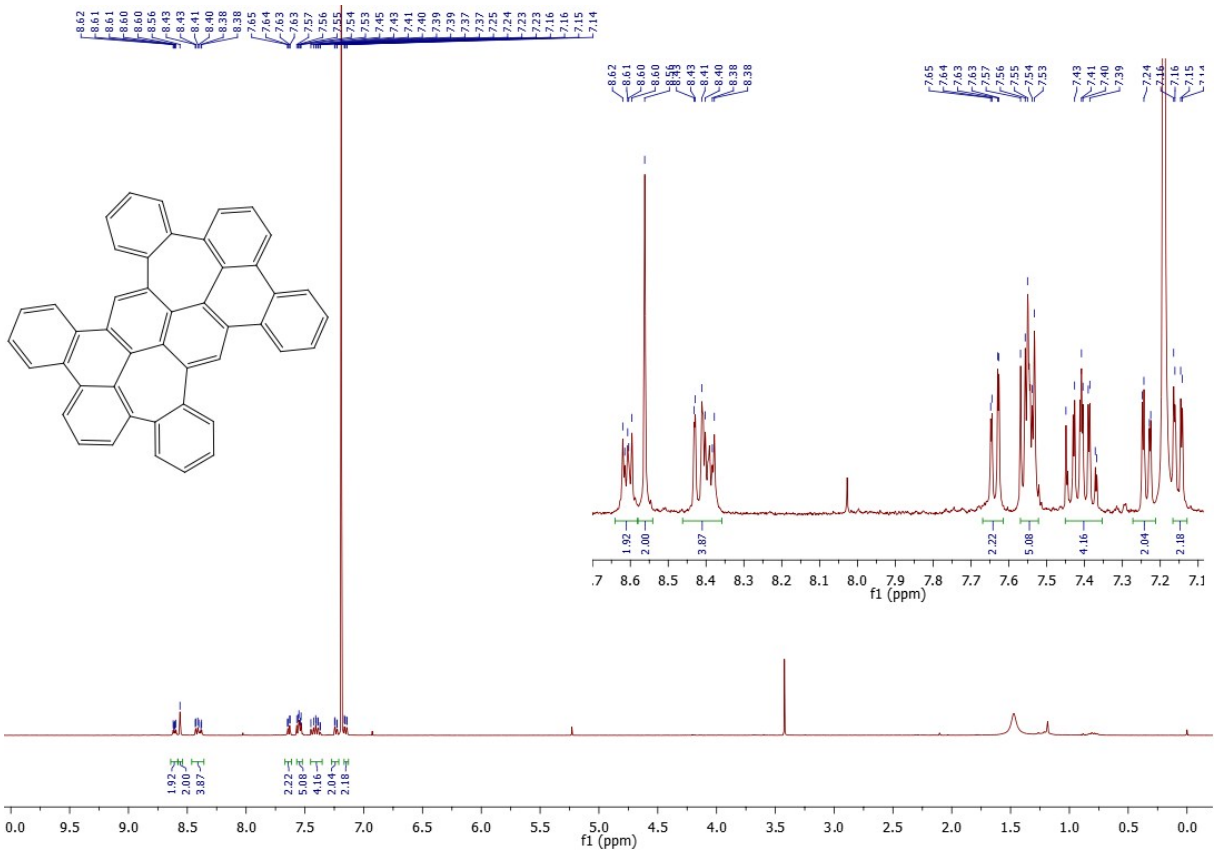


Figure S34. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **14.**

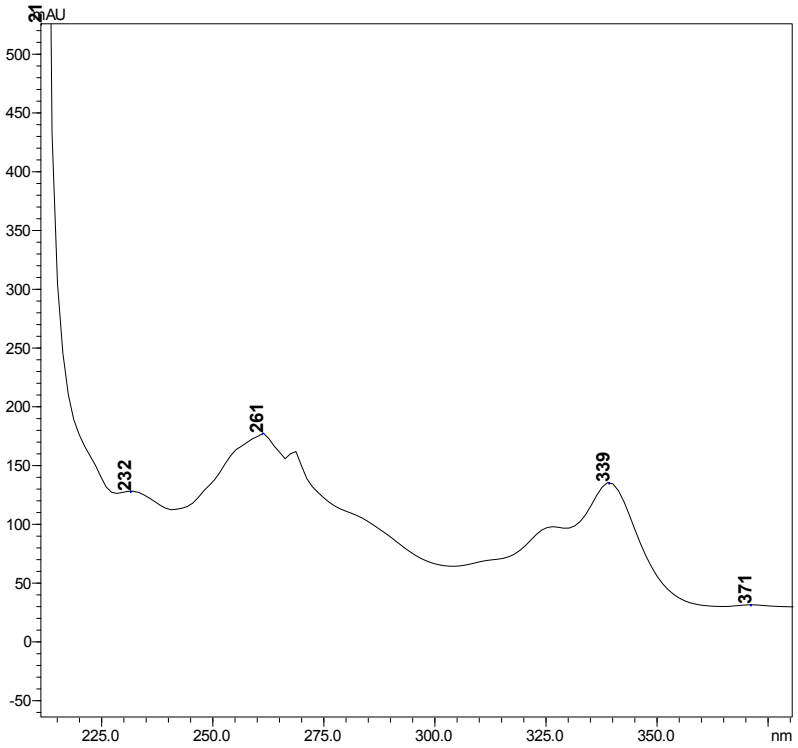


Figure S35. UV-Vis spectrum of **14** (DCM).

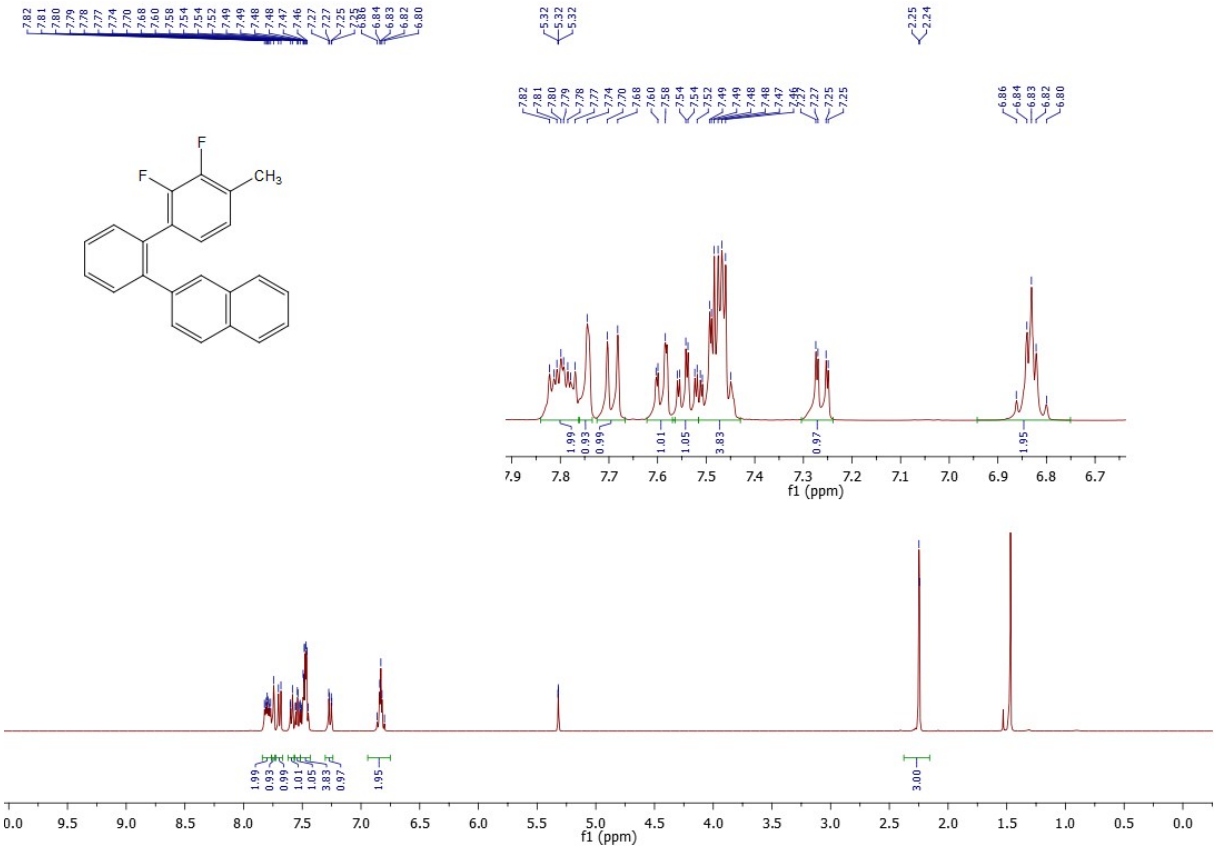


Figure S36. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **S2**.

Figure S37. ^{19}F NMR (377 MHz, CD_2Cl_2) spectrum of **S2**.

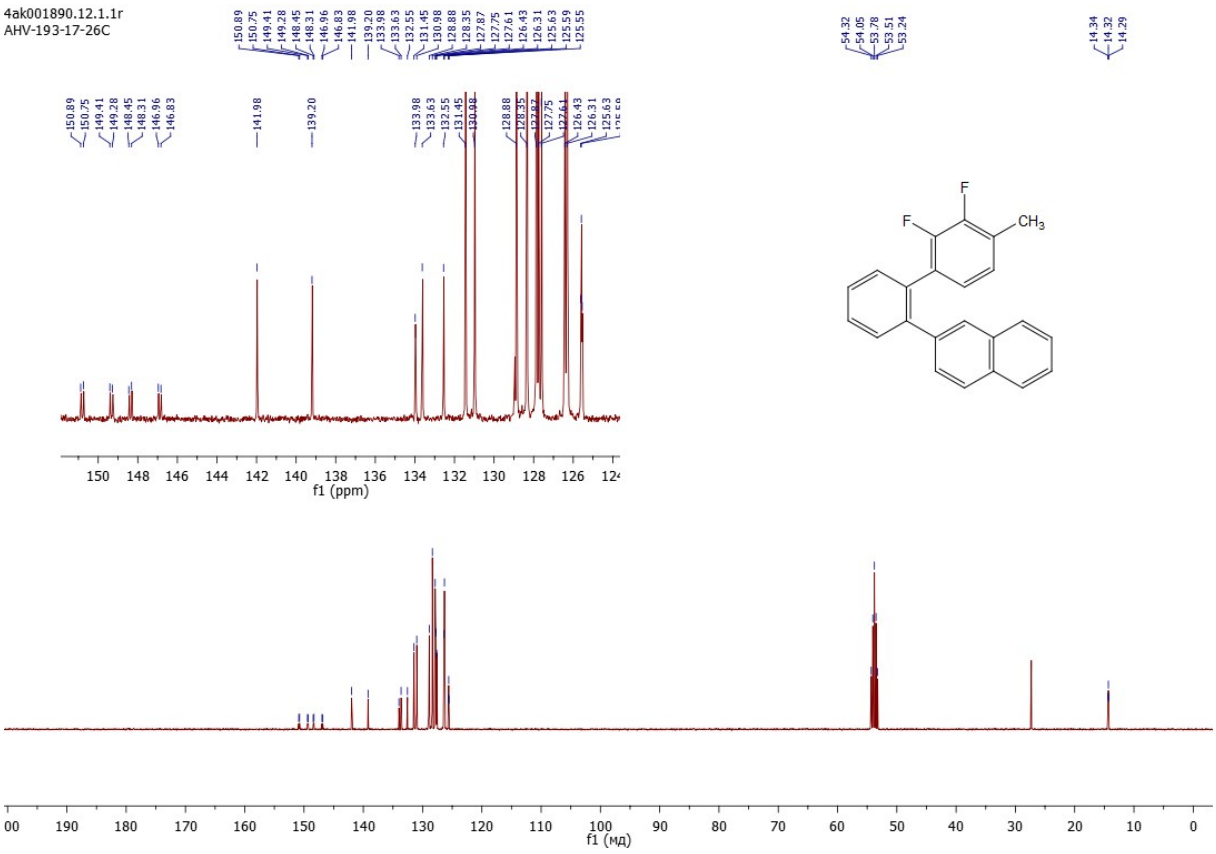


Figure S38. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **S2**

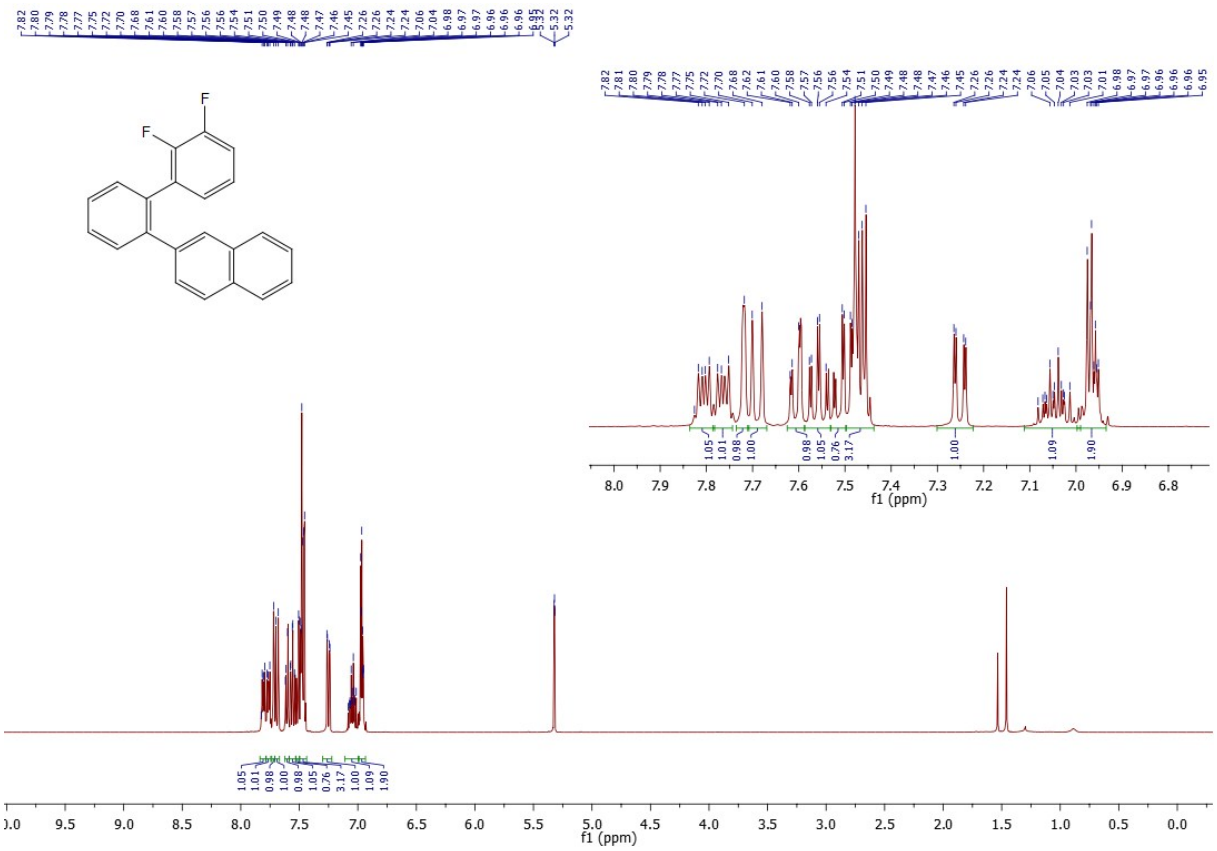


Figure S39. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **S3**.

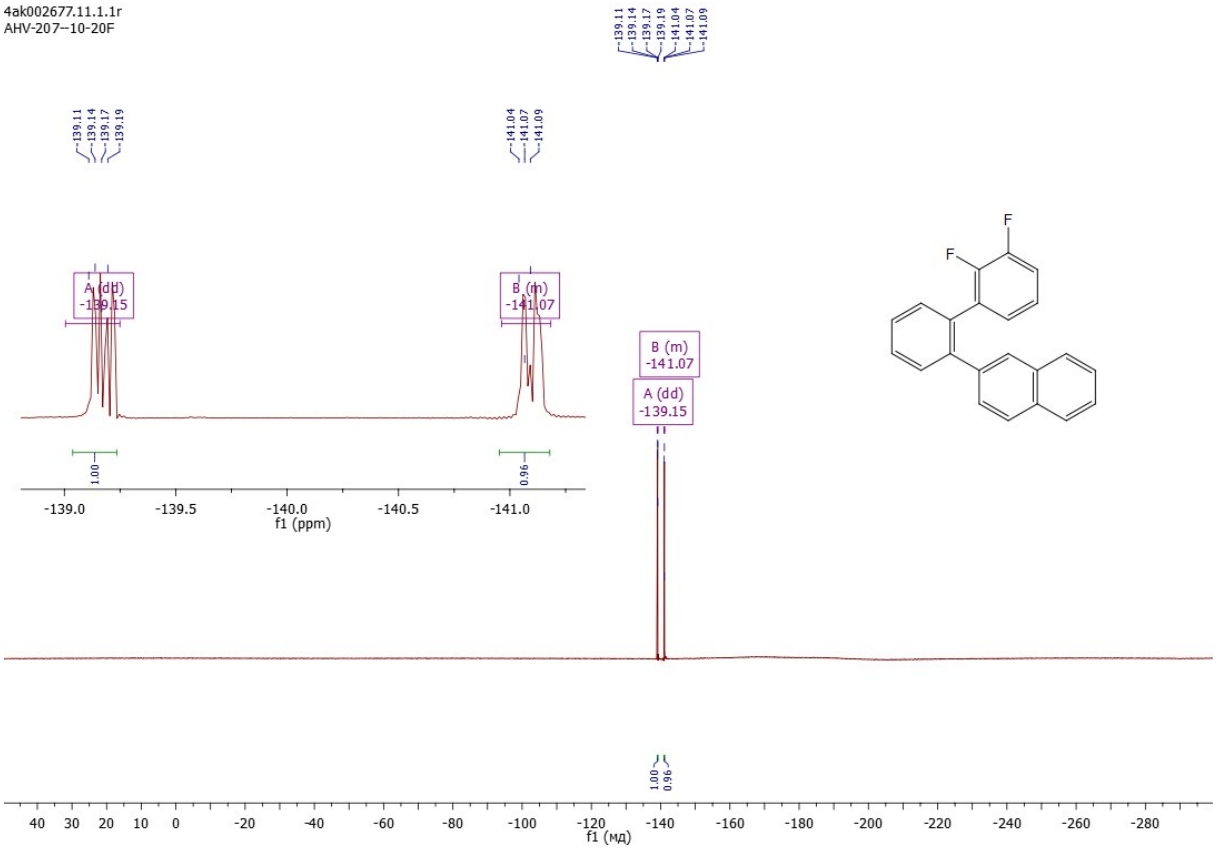


Figure S40. ^{19}F NMR (377 MHz, CD_2Cl_2) spectrum of **S3**.

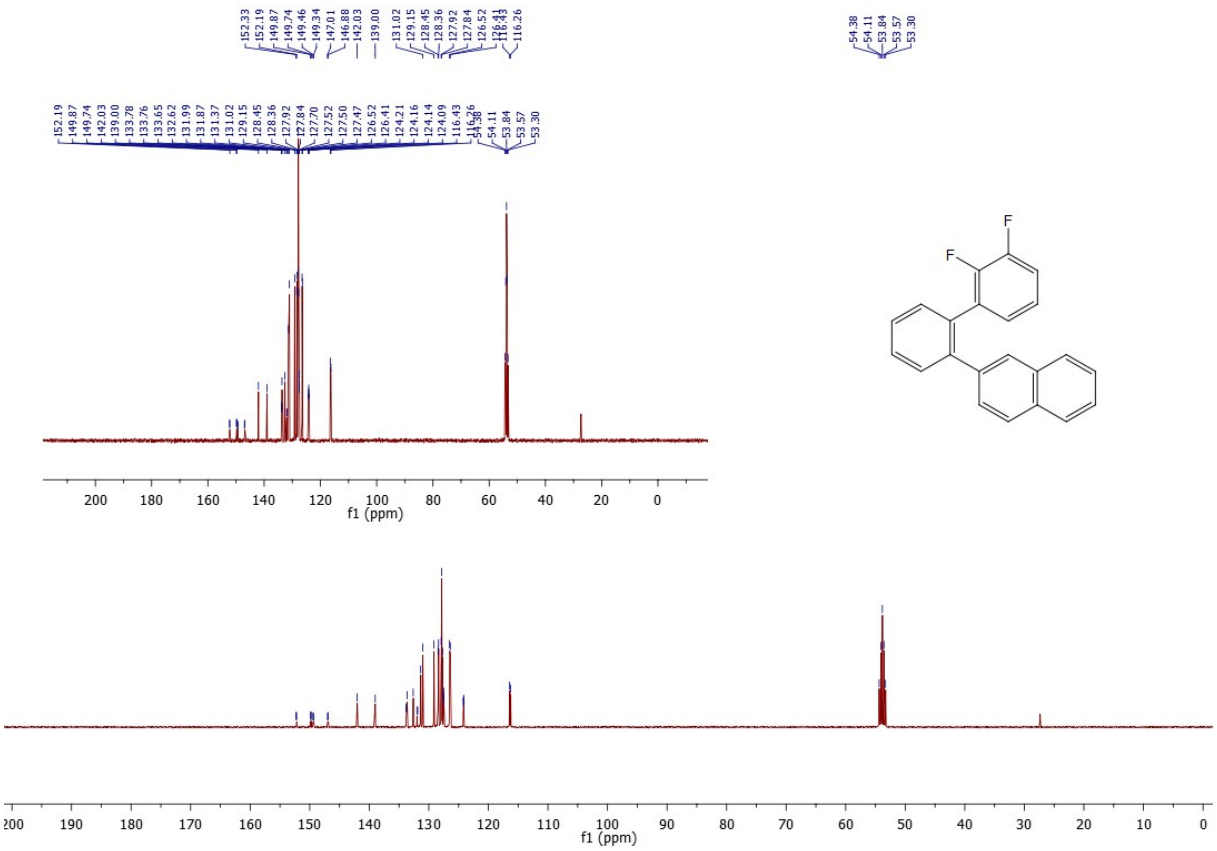


Figure S41. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **S3**.

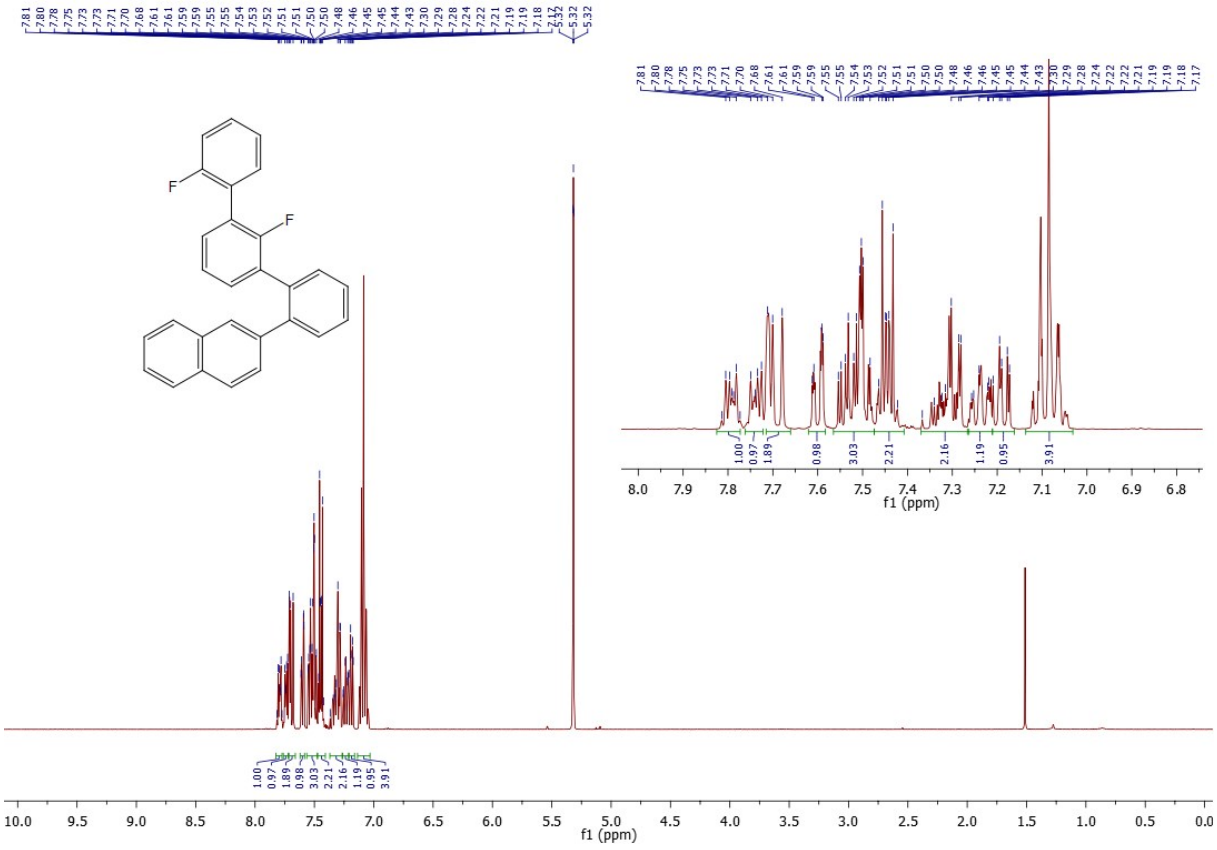


Figure S42. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **S8**.

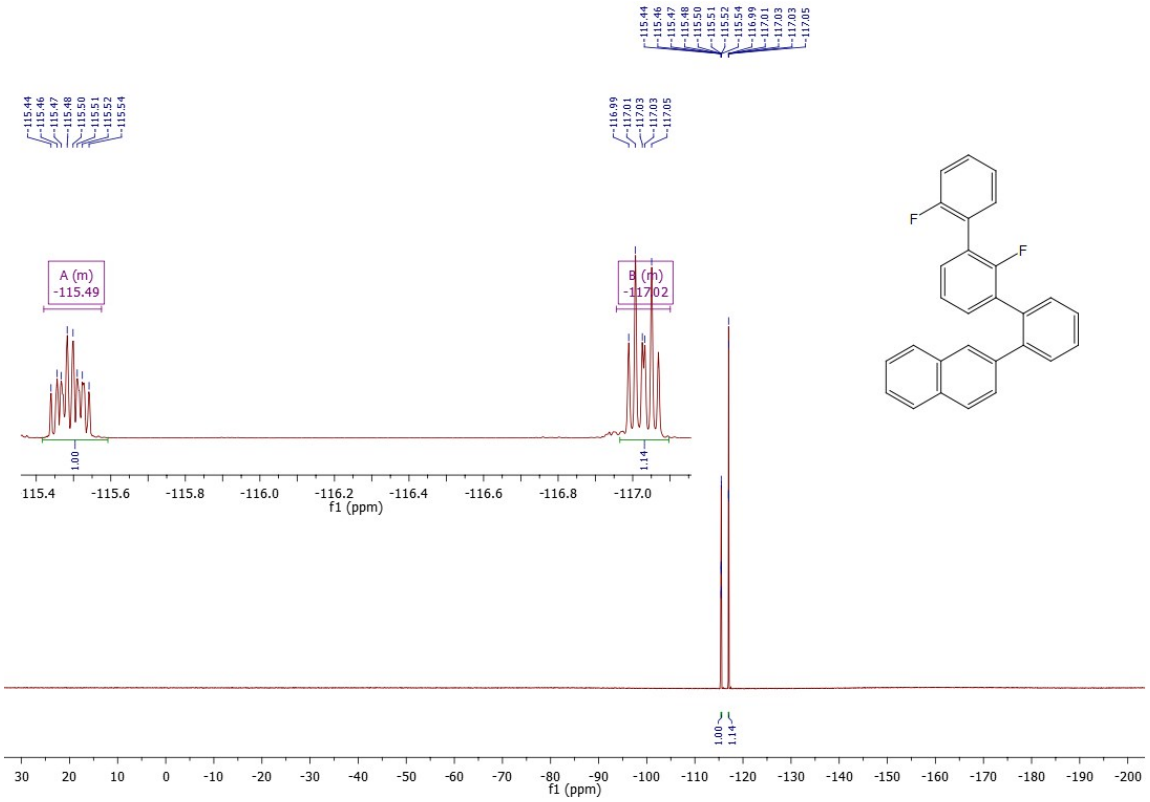


Figure S43. ^{19}F NMR (377 MHz, CD_2Cl_2) spectrum of **S8**.

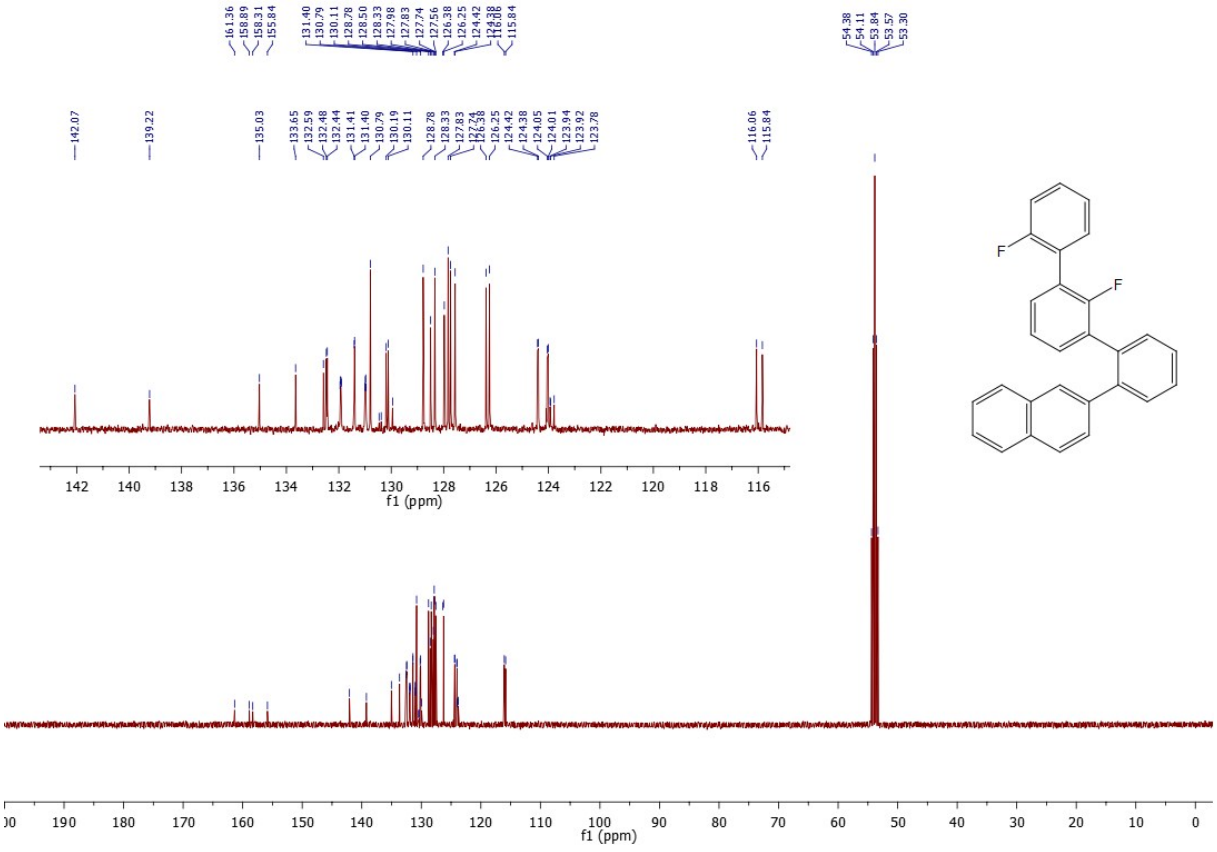


Figure S44. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of **S8**.

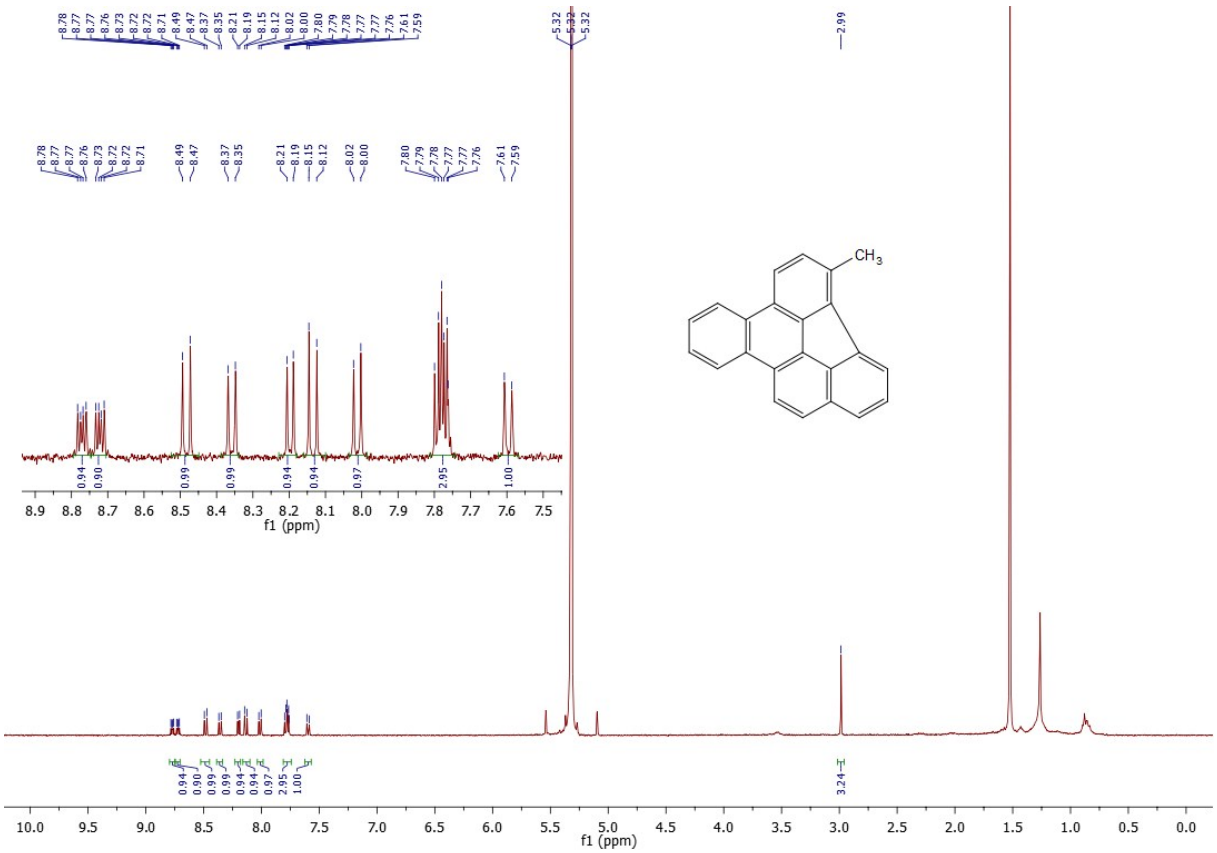


Figure S45. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **S4**.

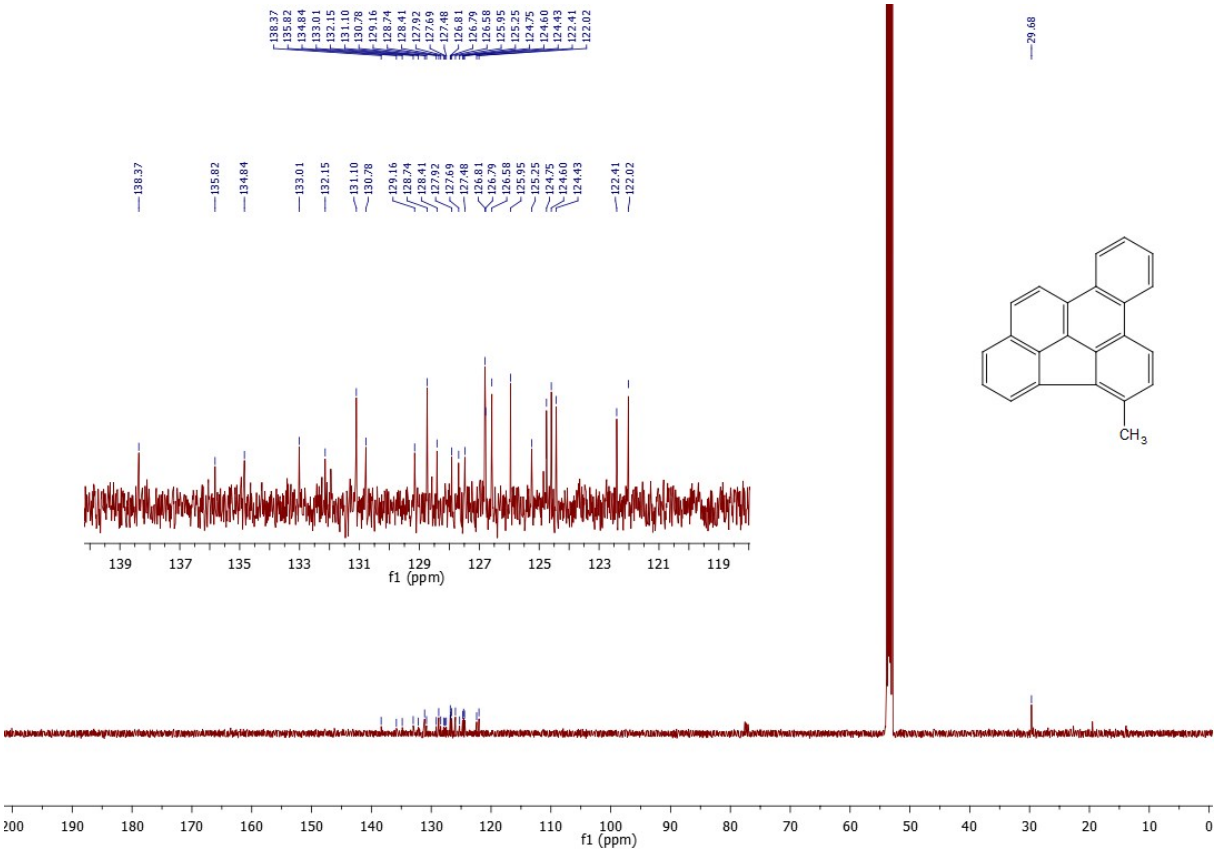


Figure S46. ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of **S4**.

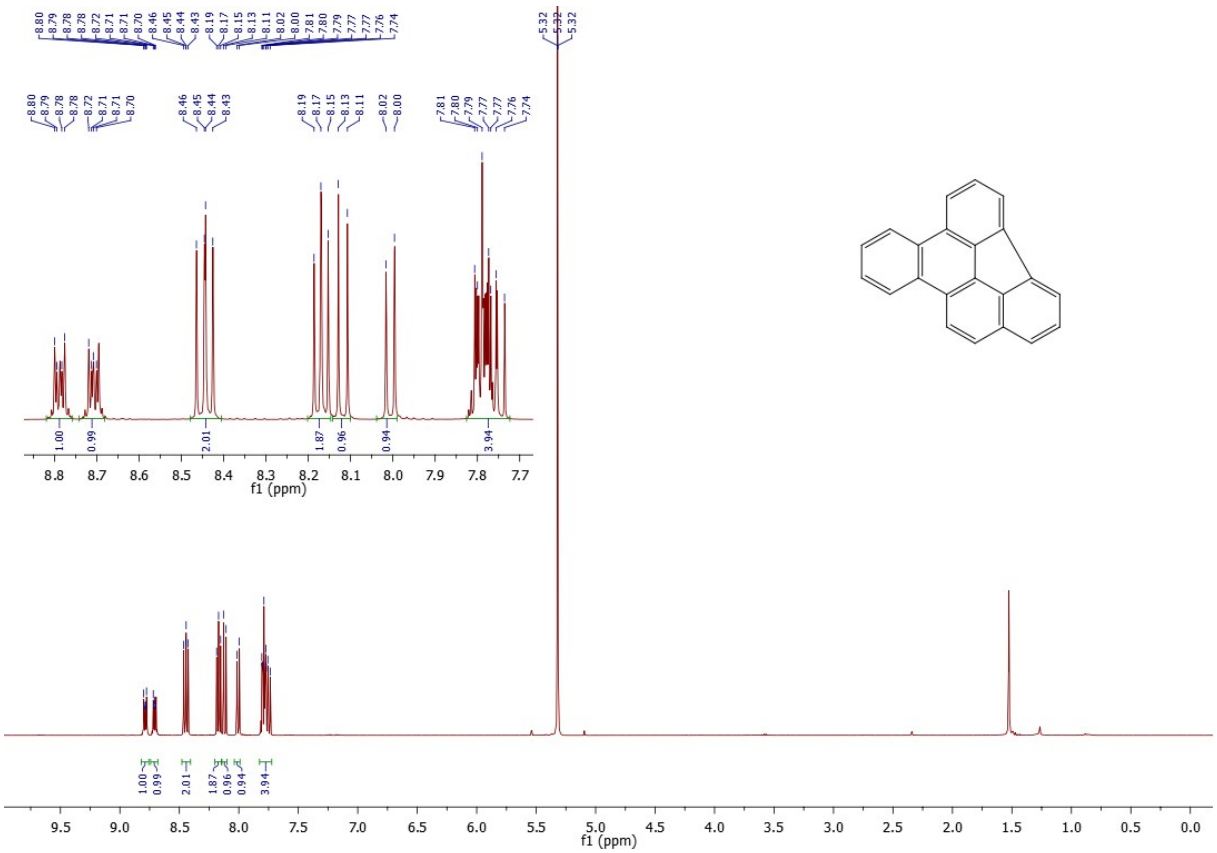


Figure S47. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **S5**.

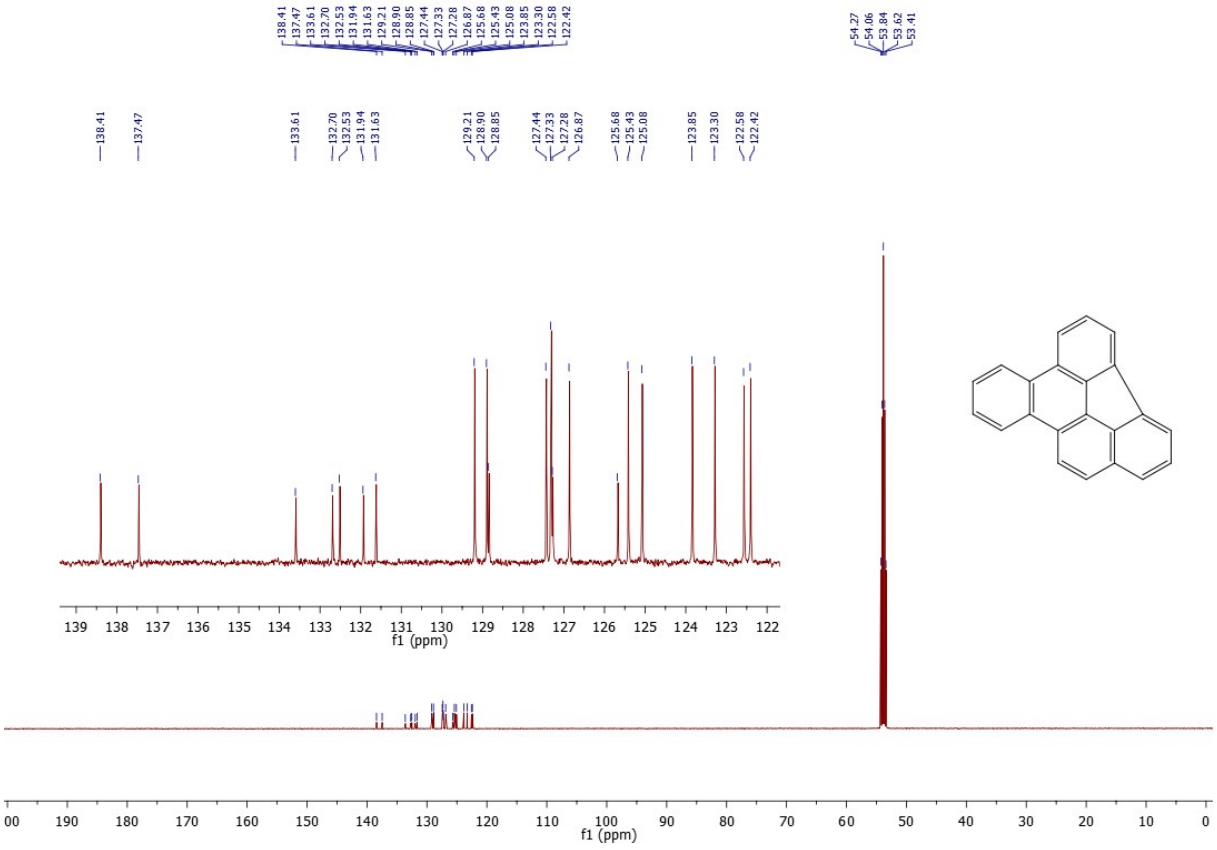


Figure S48. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of **S5**.

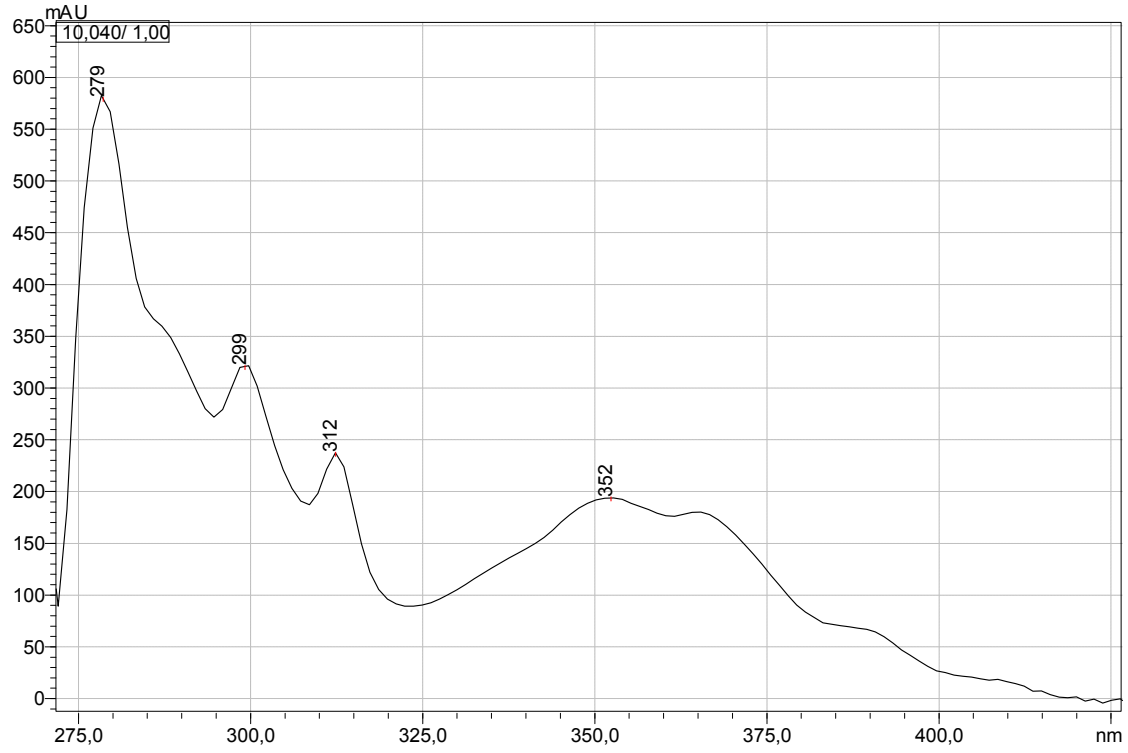


Figure S49. UV-Vis spectrum of **S5**.

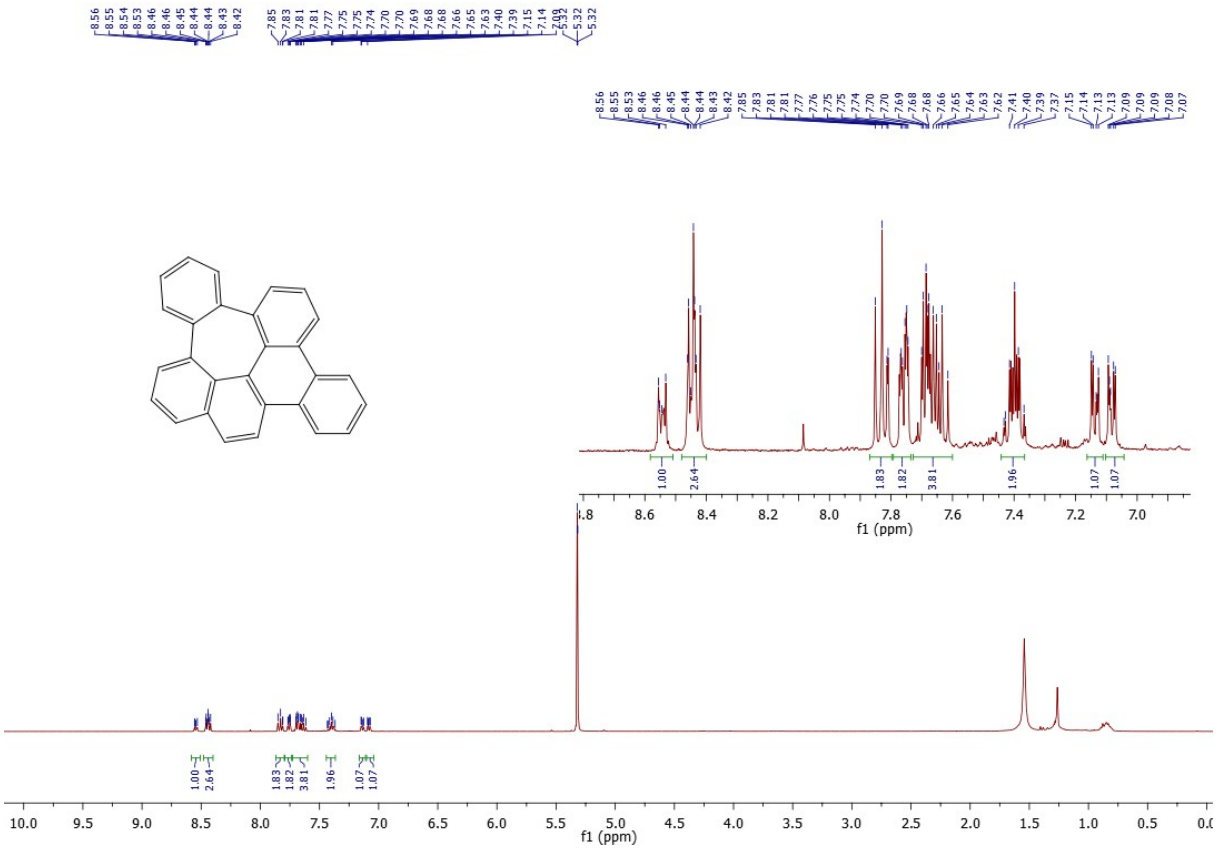


Figure S50. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of **S9**.

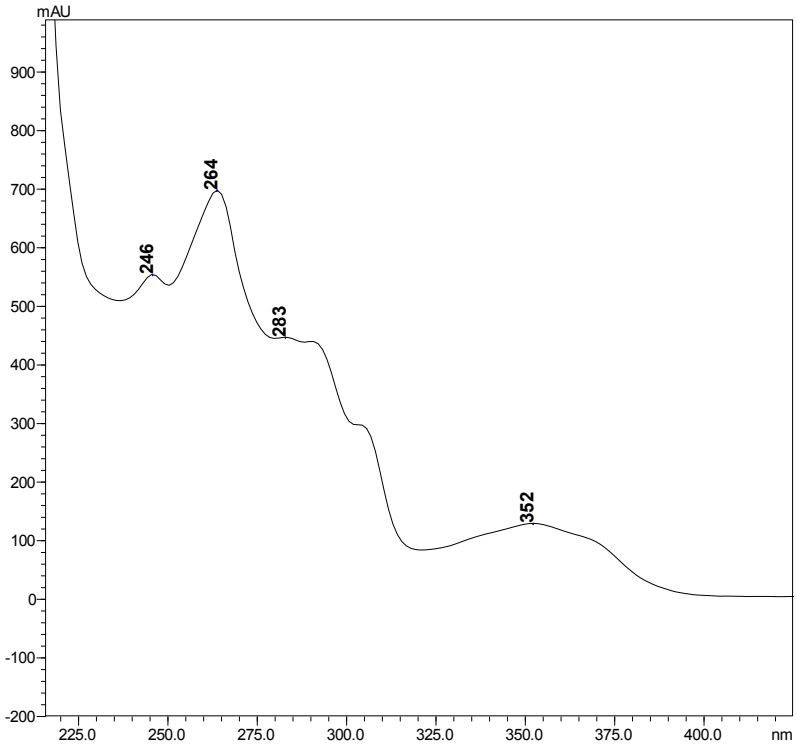


Figure S51. UV-Vis spectrum of **S9** (DCM).

X-ray crystallography

Synchrotron X-ray diffraction data for **14**, 15, and **16** were collected at 100 K on beamline BL14.2 at the BESSY II electron storage ring (Berlin, Germany) using a hybrid pixel detector Pilatus3S 2M (λ = 0.8266 Å). All structures were solved and anisotropically refined using the SHELX package. Selected crystallographic data and CCDC deposition numbers are given in Table S1.

Table S1. Selected crystallographic data and some details of data collection and refinement.

Compound	**13**	**12**	**14**
Formula	$C_{34}H_{16}$	$C_{34}H_{16}$	$C_{46}H_{24}$·0.58 CH_2Cl_2
M_r	424.47	424.47	626.12
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	$P2_1/c$
a [Å]	42.920(4)	26.806(1)	12.746(1)
b [Å]	5.1561(4)	3.7509(3)	24.782(2)
c [Å]	18.3460(6)	20.5591(7)	9.402(1)
α [°]	90	90	90
β [°]	108.246(2)	115.479(3)	91.33(1)
γ [°]	90	90	90
V [Å^3]	3855.8(5)	1866.1(2)	2969.0(5)
Z	8	4	4
D_c [g cm^{-3}]	1.462	1.511	1.401
refls collected/R_{int}	27418/0.028	12174/0.039	28692/0.049
data / parameters	5512 / 371	2552 / 186	8121 / 470
$R_1(I \geq 2\sigma(I))$	0.052 /0.137	0.062/0.167	0.082/0.219
$\Delta\rho_{max\,/\,min}$ [e Å^{-3}]	0.56 /–0.27	0.67 / -0.38	0.59 / -0.51
CCDC	1970883	1970884	1970885

DFT calculations. Inversion of the helicene's fragment.

To estimate the inversion barrier of **13**, we have calculate the geometries and energies of the structures at DFT level (B3LYP/6-31G(d)) with the preoptimization at semi-empirical level of calculations (AM1). Gassuian09 software was exploited[3] . XYZ coordinates are listed below. To estimate the barrier for pristine [5]helicene we have used previously published coordinates, which were used as the preoptimization structures[4].

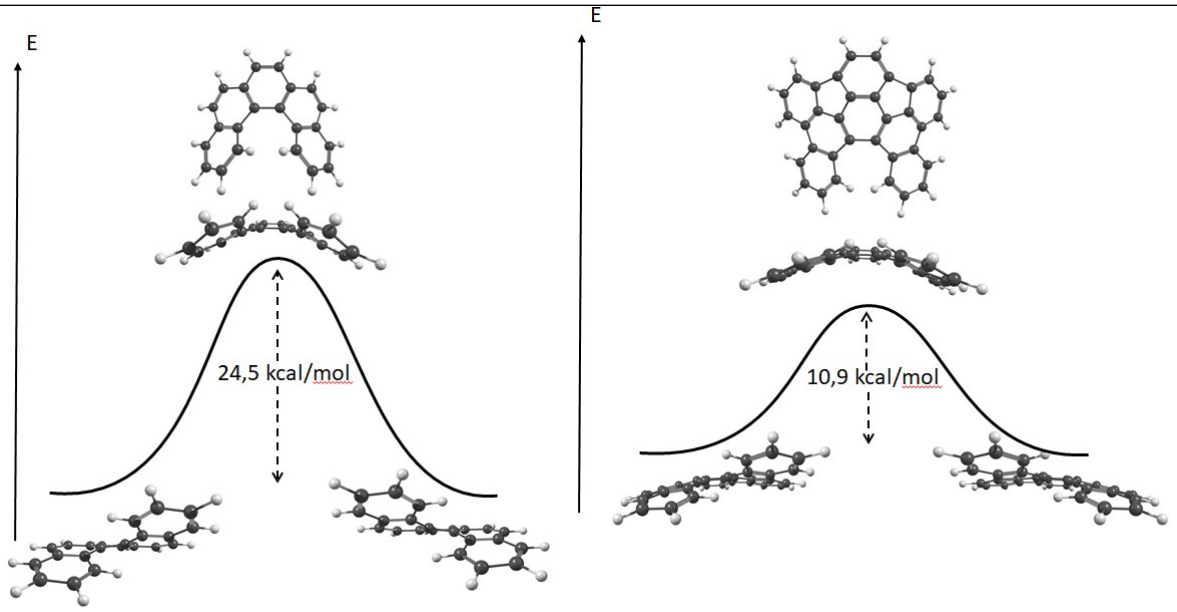


Figure S38. Inversion barriers of the helicene moiety in pristine [5]helicene and **13**.

Table S2. Optimized geometry coordinates of the transition state of **13**.

6	0.656914000	-1.801683000	-0.857171000
6	-0.700892000	-1.784612000	-0.845634000
6	1.349240000	-0.579242000	-0.681353000
6	-1.348663000	-0.543646000	-0.631500000
6	0.772389000	0.692250000	-0.572283000
6	-0.738769000	0.712718000	-0.546179000
6	2.664354000	-0.964872000	-0.252703000
6	3.546867000	-0.048799000	0.302751000
6	3.131937000	1.353416000	0.192500000
6	1.815169000	1.728033000	-0.301692000
6	4.067614000	2.363562000	0.487821000
6	1.640217000	3.097415000	-0.588559000

6	2.589828000	4.068401000	-0.305434000
6	3.805259000	3.706535000	0.276701000
1	5.044329000	2.071049000	0.860661000
1	0.758096000	3.405673000	-1.120480000
1	2.389702000	5.104915000	-0.562904000
1	4.551755000	4.457650000	0.519343000
6	-3.552432000	0.050598000	0.309377000
6	-2.670031000	-0.888326000	-0.192697000
6	-3.078560000	1.435696000	0.243671000
6	-1.748248000	1.773480000	-0.243814000
6	-3.952128000	2.474485000	0.621151000
6	-3.633611000	3.811929000	0.460425000
6	-2.418809000	4.144153000	-0.140856000
6	-1.518529000	3.144888000	-0.480066000
1	-4.923212000	2.212125000	1.029033000
1	-4.334523000	4.584362000	0.764536000
1	-0.626950000	3.435339000	-1.004579000
1	-2.175893000	5.181068000	-0.356294000
6	4.855749000	-1.980450000	1.009125000
6	4.680972000	-0.596079000	0.950137000
6	3.899698000	-2.897174000	0.493585000
6	2.771955000	-2.394420000	-0.143772000
6	1.412567000	-2.948307000	-0.494867000
6	0.662945000	-4.105096000	-0.247337000
1	1.144778000	-5.029557000	0.061450000
6	-0.775181000	-4.085984000	-0.237062000
1	-1.276821000	-5.002429000	0.063541000
6	-1.495755000	-2.912020000	-0.496835000
6	-2.835759000	-2.314348000	-0.122740000
6	-4.783028000	-0.465165000	0.795905000
6	-4.049871000	-2.785219000	0.353691000
1	-4.272073000	-3.846030000	0.433590000
6	-5.016384000	-1.839228000	0.782020000
1	5.407551000	0.048298000	1.436416000

1	5.726470000	-2.377563000	1.522901000
1	4.061738000	-3.964895000	0.616762000
1	-5.547238000	0.188504000	1.203937000
1	-5.969859000	-2.205852000	1.154260000

Table S3. Optimized geometry coordinates of **13**.

6	0.681945000	1.300333000	-0.279365000
6	0.670803000	2.685397000	-0.429274000
6	1.792936000	3.529442000	-0.478691000
6	3.010670000	2.974707000	-0.343091000
6	3.104833000	1.580017000	-0.278674000
6	2.052100000	0.674014000	-0.314042000
6	4.470997000	1.329406000	0.001024000
6	4.938984000	0.041774000	0.190108000
6	3.950299000	-1.017903000	-0.075509000
6	2.555553000	-0.716423000	-0.374644000
6	-0.660087000	0.776681000	0.061559000
6	-1.828292000	1.649697000	0.057980000
6	-1.713027000	3.108089000	-0.102232000
6	-0.424984000	3.575185000	-0.291486000
6	5.193608000	2.559307000	0.170003000
6	6.521075000	2.429501000	0.538830000
6	7.052352000	1.122733000	0.722790000
6	6.306484000	-0.042879000	0.565399000
6	-2.699533000	4.122131000	0.037290000
6	-2.322049000	5.461669000	0.025042000
6	-0.972806000	5.895378000	-0.092416000
6	0.016848000	4.941863000	-0.249025000
6	1.527092000	4.898114000	-0.305607000
6	2.679214000	5.659162000	-0.053550000
6	3.993505000	5.058669000	0.065706000
6	4.191465000	3.674572000	-0.049349000
6	-0.860485000	-0.549187000	0.506513000
6	-2.113979000	-1.057318000	0.807404000

6	-3.247230000	-0.245213000	0.683610000
6	-3.089874000	1.085097000	0.333997000
6	4.369612000	-2.361639000	-0.128130000
6	3.525645000	-3.386859000	-0.523717000
6	2.217720000	-3.085084000	-0.920549000
6	1.756030000	-1.779704000	-0.848018000
1	7.161728000	3.291825000	0.703331000
1	8.095979000	1.032576000	1.012467000
1	6.787905000	-1.000472000	0.741890000
1	-3.747984000	3.876969000	0.178330000
1	-3.094293000	6.217657000	0.140439000
1	-0.748018000	6.957451000	-0.042007000
1	2.618490000	6.730858000	0.119518000
1	4.814844000	5.729966000	0.304141000
1	0.000889000	-1.186607000	0.647783000
1	-2.209109000	-2.085836000	1.144929000
1	-4.236948000	-0.640652000	0.894667000
1	-3.965033000	1.726840000	0.298136000
1	5.402536000	-2.593230000	0.114559000
1	3.891684000	-4.409062000	-0.562562000
1	1.564361000	-3.866667000	-1.298618000
1	0.757543000	-1.558338000	-1.204895000

References.

1 A. K. Steiner and K. Y. Amsharov, *Angew. Chemie - Int. Ed.*, 2017, **56**, 14732–14736.

2 P. Sonar, S. P. Singh, E. L. Williams, Y. Li, M. S. Soh and A. Dodabalapur, *J. Mater. Chem.*, 2012, **22**, 4425–4435.

3 V. Akhmetov, M. Feofanov, O. Papaianina, S. Troyanov and K. Amsharov, *Chem. – A Eur. J.*, 2019, **25**, 11585–11585.

4 H. Y. Harb, K. D. Collins, J. V. G. Altur, S. Bowker, L. Campbell and D. J. Procter, *Org. Lett.*, 2010, **12**, 5446–5449.

5 J. Barroso, J. L. Cabellos, S. Pan, F. Murillo, X. Zarate, M. A. Fernandez-Herrera and G. Merino, *Chem. Commun.*, 2018, **54**, 188–191.