# Alumina-Promoted Oxodefluorination

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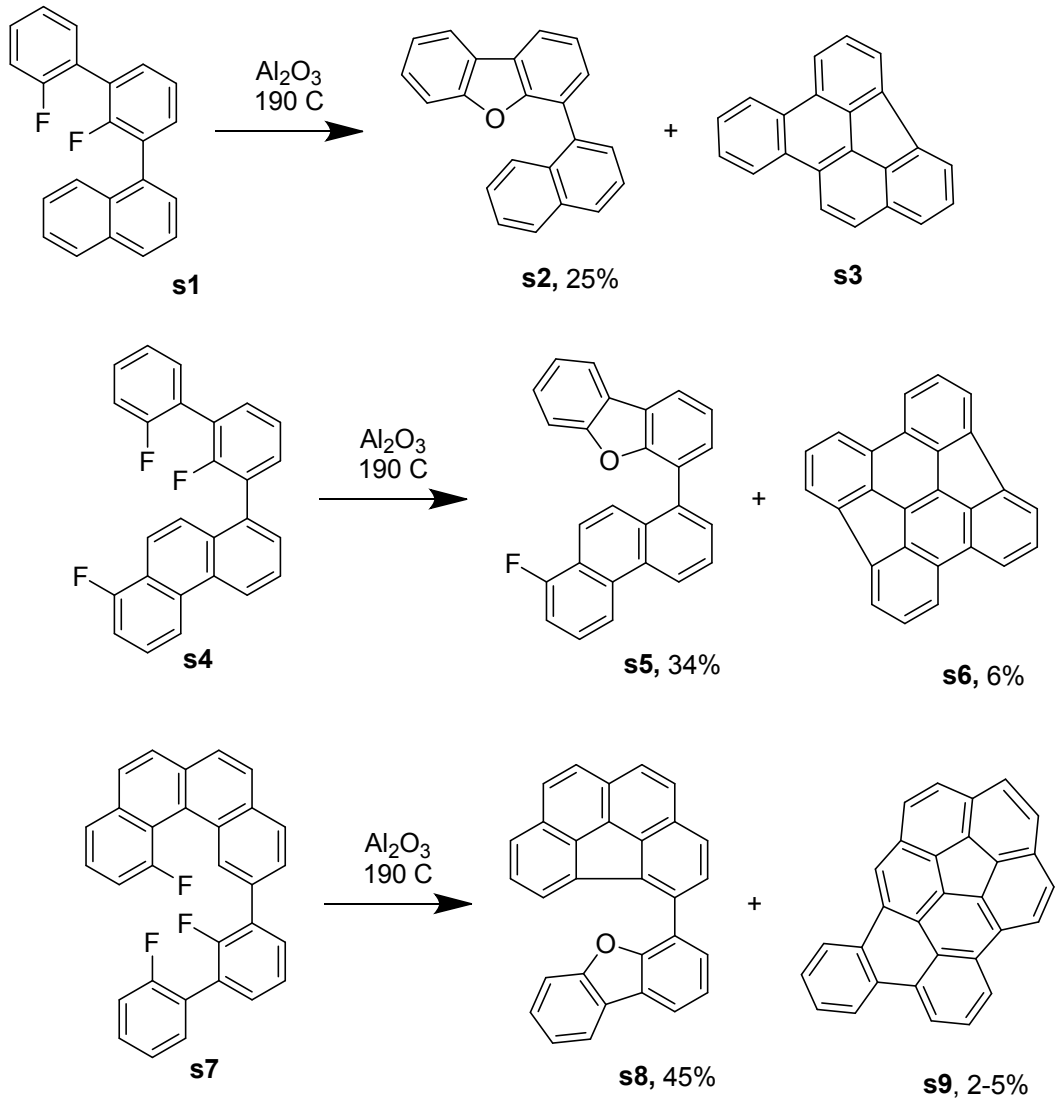
## Table of contents

## 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 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/MeOH or toluene/MeOH mixture was used (UV-vis detection). The data was evaluated with the programs Shimadzu LCsolution and Shimadzu LabSolutions. 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. Electrochemical data were obtained in o-dichlorobenzene solution of $Bu_4NPF_6$ (0.1 M). Cyclic voltammagrams were obtained using a glassy carbon working electrode, a Pt counter electrode, and a non-aqueous silver (0.01M AgNO3, 0.1 TBAP in acetonitrile) reference electrode. The data were evaluated with the programs Gamry Echem Analyst v.7.07.

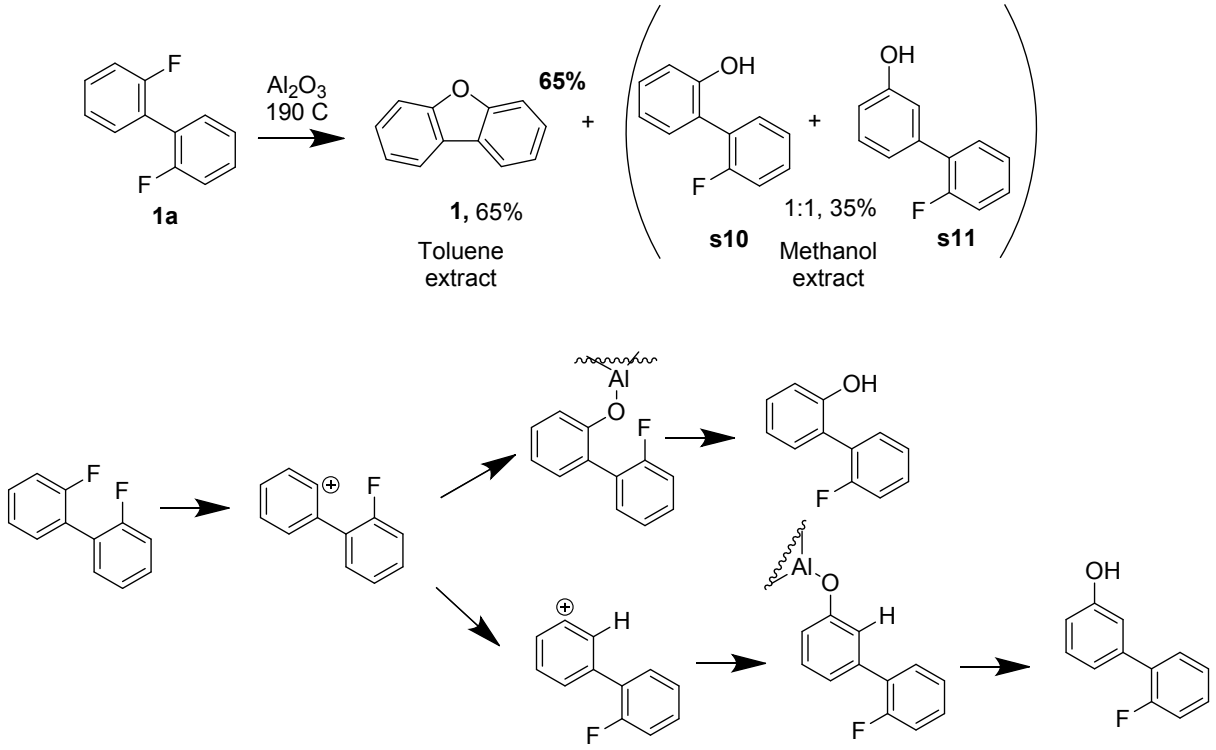
## Competition between C-C and C-O couplings




**Scheme 1.** Competition between C-C and C-O couplings

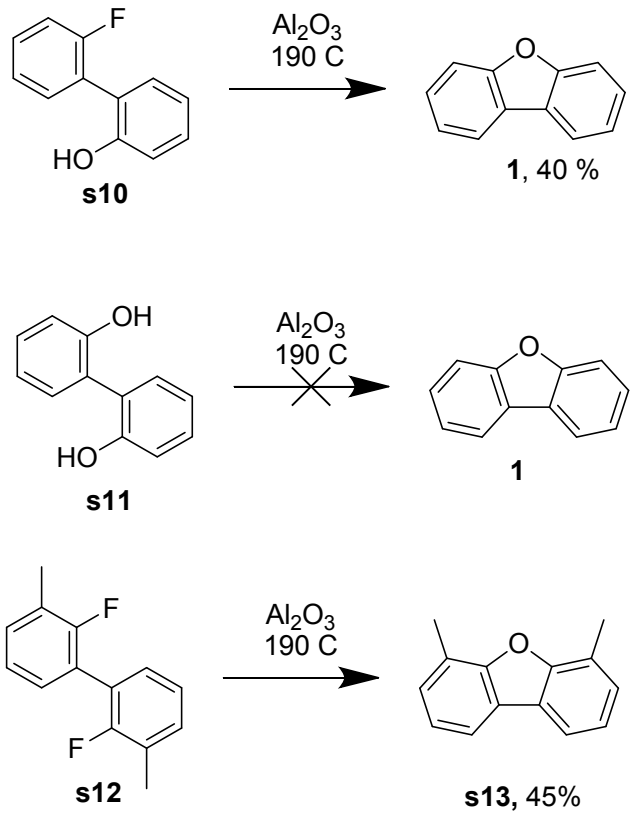
The corresponding fluorinated precursors clearly demonstrate the competition between C-O and C-C coupling.

## Mechanistic considerations




**Scheme 2**. Possible mechanism of alumina-promoted oxodefluorination.

As it has been indicated, extraction with toluene yields pure product **1**, whereas methanol extract contains intermediate product **s10** and side product **s11**. While **s10** confirms the suggested mechanism, the exact route of formation of **s11** remains questionable, however 1,2 H-shift in the first "incipient phenyl-cation" appears to be the most probable pathway.



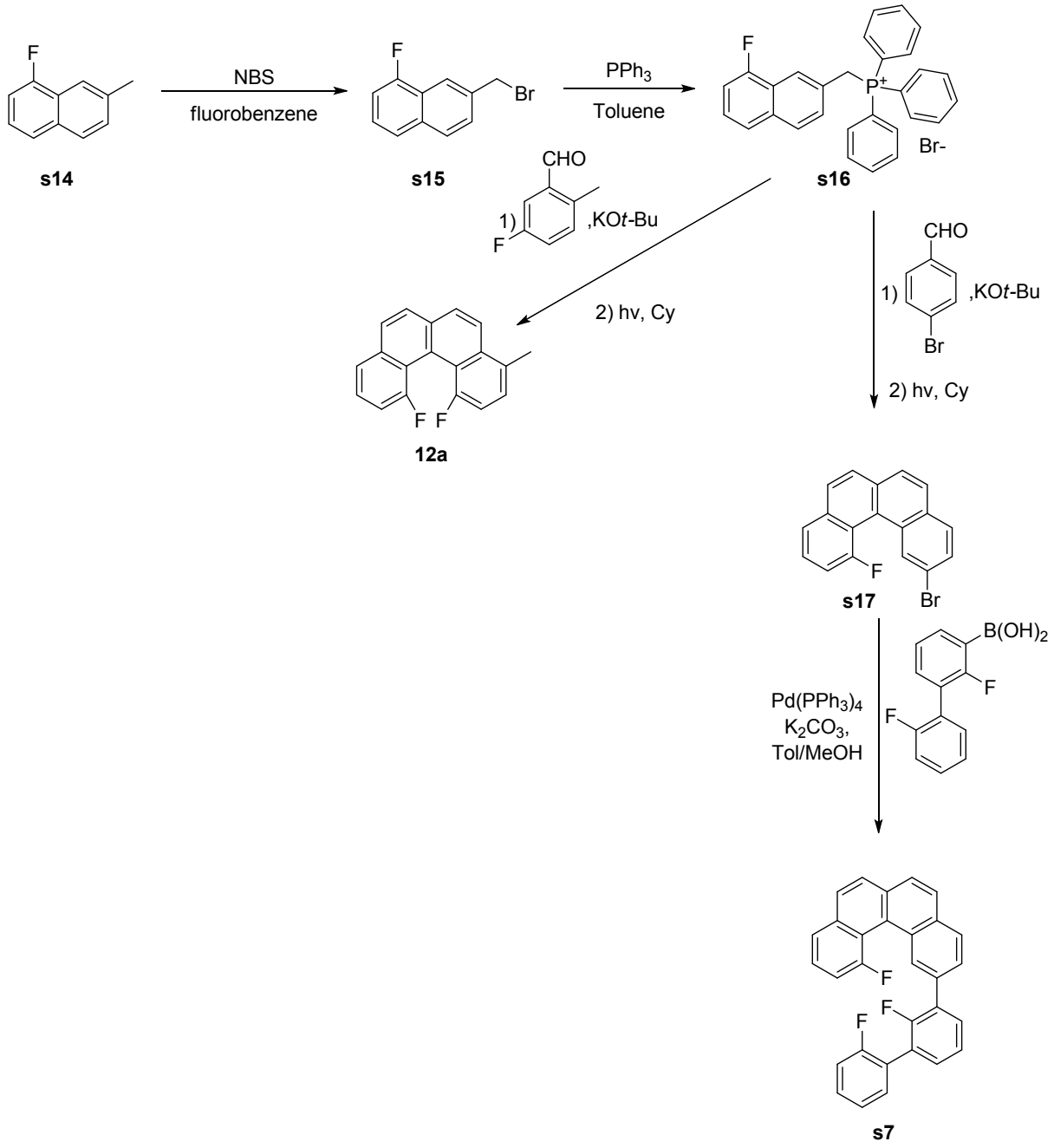

**Scheme 3.** Studying of mechanism of alumina-promoted oxodefluorination,

**s10**, indeed transforms into **1**, although in lower yields, which might be connected to the fact that hydroxo-group interacts not only with active sites of alumina.

The fact that **s11** does not undergo the transformation to **1** proves that the reaction cannot be considered as double hydrolysis-dehydration.

Meanwhile, aryne-mechanism should be excluded as well, as **s12** transforms into s**13**. Although full conversion is hardly achieved even at longer reaction times of 30-48 h.

## Synthesis of benzofluoranthrene precursors.



## Experimental procedures

Fluorobenzene, *para*-fluorotoluene, 1-bromo-4-fluorobenzene, 1-fluoro-4-iodobenzene, 1,4-difluorobenzene, 1-fluoro-4-(trifluoromethyl)benzene, 1-fluoro-4-methoxybenzene were purchased from Sigma Aldrich. 2,3-difluoro-1,4-diiodobenzene, 1,4-dibromo-2,5-difluorobenzene and 1,5-dibromo-2,4-difluorobenzene were purchased from Chempur.

**General Procedure A.**

The corresponding bromo- or iodoarene (1-10 mmol, 1eq) and boronic acid (1eq) were dissolved in 50-100 ml of toluene:methanol (2:1) mixture containing potassium carbonate (6eq) 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).

**General Procedure B.**

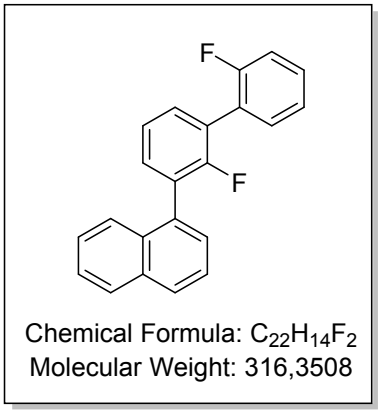
To a solution of 2,2,6,6-Tetramethylpiperidine (2.42 g, 2.92 mL, 17.1 mmol, 1.5 equiv) in THF (30 ml) at -78 °C was added *n*-BuLi (1.02 g, 6.40 mL, 2.5 M in hexanes, 16.0 mmol, 1.4 equiv) dropwise via a syringe and the orange suspension stirred for 30 minutes at -78 °C. Corresponding fluorobenzene (11.4 mmol, 1 equiv) dissolved in THF (5 mL) was added dropwise and the suspension stirred for further 30 minutes at -78 °C. $CuBr_2$ (2.55 g, 11.4 mmol, 1 equiv) was added under vigorous stirring and the resulting blue suspension stirred for additional 45 minutes at -78 °C. Nitrobenzene (1.41 g, 1.17 mL, 11.4 mmol, 1 equiv) was added in one portion and the dark green mixture was allowed to reach room temperature over a period of 3 h. A sat. aq. $NH_4Cl$-solution was added, layers were separated and the aqueous phase extracted with $CH_2Cl_2$. The combined organic phases were washed with a sat. aq. $NH_4Cl$-solution and dried over $Na_2SO_4$, filtered and the solvent evaporated to dryness. Solvent evaporation under reduced pressure was followed by flash chromatography purification of product (Hexane:Dichloromethane=10:1).

**General Procedure C.**

A glass tube was charged with 2-5 g of $\gamma$-$Al_2O_3$ (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 0.1-0.5 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 6-48 h. After cooling to room temperature, products were extracted with toluene. If needed, separation and final purification of the products were carried out by flash chromatography or HPLC of the respective toluene extract.

**1-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene (s1).**



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

The compound was obtained according to the General Procedure A using 1-bromonaphtalene (200 mg) and (2,2'-difluoro-[1,1'-biphenyl]-3-yl)boronic acid[1] (215 mg). Yield 170 mg (58%).

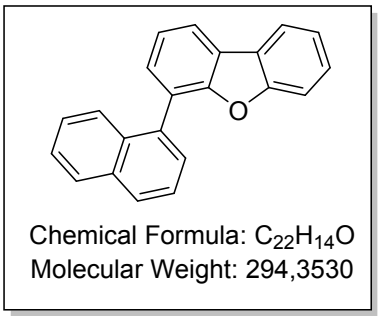
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.98 – 7.90 (m, 2H), 7.78 – 7.70 (m, 1H), 7.63 – 7.56 (m, 1H), 7.56 – 7.36 (m, 8H), 7.28 (td, *J* = 7.5, 1.2 Hz, 1H), 7.25 – 7.16 (m, 1H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -115.18 (dd, *J* = 23.1, 11.7 Hz, 1F), -116.17 – -116.33 (m, 1F).

**$^{13}$C NMR (**101 MHz, $CD_2Cl_2$) δ 160.4 (d, *J* = 247.8 Hz), 157.5 (d, *J* = 248.3 Hz), 134.3, 134.0, 132.7 (d, *J* = 3.7 Hz), 132.2, 132.1 (dd, *J* = 3.2, 1.5 Hz), 131.65 – 131.51 (m), 130.4 (d, *J* = 8.2 Hz), 128.9, 128.7, 128.2, 126.7, 126.4, 126.1 (d, *J* = 1.1 Hz), 125.8, 124.6 (dd, *J* = 11.8, 4.0 Hz), 124.2 (d, *J* = 16.8 Hz), 124.0 (d, *J* = 15.8 Hz), 116.1 (d, *J* = 22.4 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{22}H_{14}F_2$, calc. 316.1064 found 316.1065.

**4-(naphthalen-1-yl)dibenzo[b,d]furan (s2).**



Chemical Formula: $C_{22}H_{14}O$
Molecular Weight: 294,3530

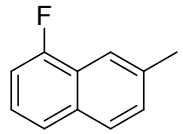
The compound was obtained according to the General Procedure C using 1-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene (40 mg). Yield 16 mg (10%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.05 (ddd, *J* = 7.5, 4.7, 1.4 Hz, 1H), 8.01 – 7.96 (m, 1H), 7.75 – 7.69 (m, 1H), 7.69 – 7.61 (m, 1H), 7.59 – 7.47 (m, 2H), 7.48 – 7.34 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.3, 154.2, 134.6, 133.8, 131.8, 129.2, 128.5, 128.3, 127.9, 127.2, 126.2, 126.1, 125.9, 125.4, 125.0, 124.5, 124.3, 122.8, 122.7, 120.7, 112.0, 112.0.

The spectroscopic data were consistent with previously reported[2].

**1-fluoro-7-methylnaphthalene (s14).**




Chemical Formula: $C_{11}H_9F$
Molecular Weight: 160,1914

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 reactionary 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-(4,4-dimethoxy-2-methylbutyl)-2-fluorobenzene 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%).

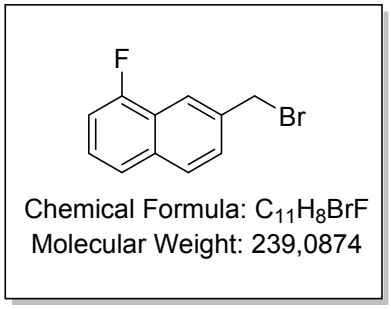
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.88 (s, 1H), 7.79 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.35 (td, *J* = 8.0, 5.4 Hz, 1H), 7.17 – 7.10 (m, 1H), 2.55 (s, 3H).

**$^{19}$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 (s15).**



Chemical Formula: $C_{11}H_8BrF$
Molecular Weight: 239,0874

1.6 g of 1-fluoro-7-methylnaphthalene (10 mmol) and 1.78 g NBS (10 mmol) were dissolved in 25 g of fluorobenzene and catalytic amount of DBPO 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

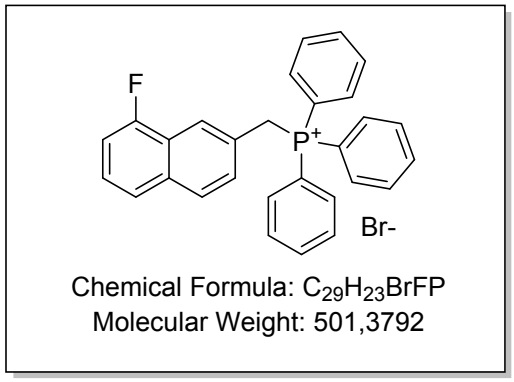
**$^{1}$H NMR** (300 MHz, $CD_2Cl_2$) δ 8.09 (s, 1H), 7.89 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.19 (ddd, *J* = 10.8, 7.7, 0.7 Hz, 1H), 4.71 (s, 2H).

**$^{19}$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 (s16).**



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

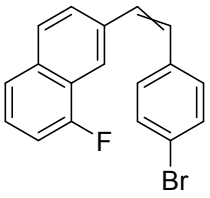
7-(bromomethyl)-1-fluoronaphthalene and triphenylphosphine (2.9 g, 11 mmol) were mixed with 100 ml of toluene and refluxed for 12 h. After cooling down solid was filtered and washed wiyh cold toluene. Yield 2.85 g (58% for two steps).

**$^{1}$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 (s), 123.7 (d, *J* = 6.7 Hz), 123.6 (d, *J* = 5.7 Hz), 123.5 (s), 118.1 (d, *J* = 85.9 Hz), 110.5 (d, *J* = 19.9 Hz), 31.6 (d, *J* = 47.3 Hz).

**7-(4-bromostyryl)-1-fluoronaphthalene.**



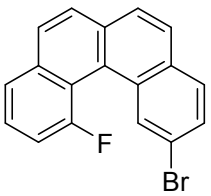
Chemical Formula: $C_{18}H_{12}BrF$
Molecular Weight: 327,1964

The ((8-fluoronaphthalen-2-yl)methyl)triphenyl phosphonium bromide (2.8 g, 5.6 mmol) and 4-bromobenzaldehyde (1.03 g, 5.6 mmol) were dissolved in 50 mL of absolute ethanol. The mixture was stirred while KOtBu (0.71 g, 6.4 mmol) in ethanol was added dropwise for 5-10 min. The solution obtained was refluxed for 10-20 h (TLC monitoring). The reaction mixture was cooled to room temperature and neutralized by addition of 1M HCl. After concentration by evaporation under reduced pressure, the mixture was diluted with water and the product was extracted with DCM. The DCM solution was dried over $MgSO_4$ and filtered through a short silica gel plug using DCM:PE mixture as eluent. After evaporation the 7-(4-bromostyryl)-1-fluoronaphthalene was obtained as an oil with yield of 88% (1.6 g) as mixture of cis/trans isomers. The resulting product was used in the next step without additional purification.

**$^{1}$H NMR** (300 MHz, $CD_2Cl_2$) δ 8.12 (s, 0.65 H), 7.98 (s, 0.75H), 7.94 – 7.76 (m, 1.46 H), 7.75 – 7.31 (m, 10.6H), 7.27 (d, *J* = 12.1 Hz, 1.2 H), 7.17 (dt, *J* = 10.6, 2.2 Hz, 3.2 H), 6.84 (d, *J* = 12.2 Hz, 1H), 6.66 (d, *J* = 12.2 Hz, 1H).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{18}H_{10}BrF$, calc. 326.0106, found 326.0108.

**11-bromo-1-fluorobenzo[c]phenanthrene (s17).**



Chemical Formula: $C_{18}H_{10}BrF$
Molecular Weight: 325,1804

Solution of 7-(4-bromostyryl)-1-fluoronaphthalene (1.6 g, 4.9 mmol) in 300 ml of cyclohexane was irradiated in the presence of $I_2$ (1.57 g, 6.16 mmol) and methylpropyleneoxide (1.5 ml) for 25 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 (Hex:DCM 95:5) yielding 11-bromo-1-fluorobenzo[c]phenanthrene as white solid in 30% (450 mg).

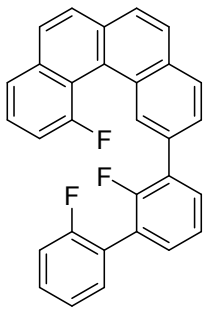
**$^1$H NMR** (300 MHz, $CD_2Cl_2$) δ 8.47 (dd, *J* = 14.1, 1.8 Hz, 1H), 8.03 – 7.92 (m, 2H), 7.93 – 7.81 (m, 4H), 7.68 (ddd, *J* = 12.8, 6.1, 3.4 Hz, 2H), 7.51 – 7.39 (m, 1H).

**$^{19}$F NMR** (282 MHz, $CD_2Cl_2$) δ -99.72 (ddd, *J* = 13.6, 5.3, 3.9 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 159.6 (d, *J* = 252.4 Hz), 136.1 (d, *J* = 4.4 Hz), 132.7, 132.3, 132.2, 129.5, 129.4 (d, *J* = 0.8 Hz), 128.4, 128.1 (d, *J* = 3.0 Hz), 127.80, 127.44, 127.35, 126.9, 124.7 (d, *J* = 3.2 Hz), 123.8 (d, *J* = 3.2 Hz), 119.6 (d, *J* = 3.1 Hz), 118.7 (d, *J* = 12.9 Hz), 113.43 (d, *J* = 24.4 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{18}H_{10}BrF$, calc. 323.9950, found 323.9951.

**11-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1-fluorobenzo[c]phenanthrene (s7).**




Chemical Formula: $C_{30}H_{17}F_3$
Molecular Weight: 434,4612

The compound was obtained according to the General Procedure A using 11-bromo-1-fluorobenzo[c]phenanthrene (63 mg) and (2,2'-difluoro-[1,1'-biphenyl]-3-yl)boronic acid (50 mg). Yield 80 mg (95%).

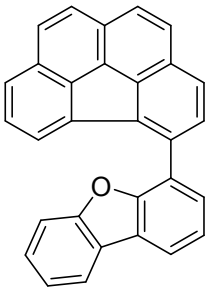
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 15.2 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.81 (m, 5H), 7.76 (td, *J* = 7.3, 2.0 Hz, 1H), 7.62 (td, *J* = 7.8, 4.8 Hz, 1H), 7.53 – 7.35 (m, 5H), 7.31 – 7.16 (m, 2H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -99.00 (t, *J* = 13.4 Hz, 1F), -114.35 (t, *J* = 12.3 Hz, 1F), -119.43 (d, *J* = 15.2 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.9 (d, *J*=247 Hz), 159.4 (d. *J*=240 Hz), 156.9 (d, *J*=237 Hz), 135.6 (d, *J* = 4.4 Hz), 132.6 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 21.7 Hz), 131.7 (d, *J* = 1.8 Hz), 131.4 (d, *J* = 3.6 Hz), 130.8 (d, *J* = 1.4 Hz), 130.30 – 129.86 (m), 129.6 (d, *J* = 8.2 Hz), 128.1, 127.5, 127.3 (d, *J* = 4.7 Hz), 127. (d, *J* = 2.8 Hz), 126.6 (d, *J* = 9.4 Hz), 126.3, 124.7, 124.30 – 123.97 (m), 123.7 (d, *J* = 15.4 Hz), 118.6 (d, *J* = 12.9 Hz), 115.8 (d, *J* = 22.4 Hz), 112.7 (d, *J* = 24.4 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{30}H_{17}F_3$, calc. 434.1282, found 434.1286.

**4-(benzo[ghi]fluoranthen-5-yl)dibenzo[b,d]furan (s8).**




Chemical Formula: $C_{30}H_{16}O$
Molecular Weight: 392,4570

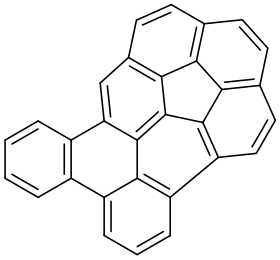
The compound was obtained according to the General Procedure C using 11-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1-fluorobenzo[c]phenanthrene (40 mg). Yield 16 mg (45%).

**$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.18 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.16 – 8.07 (m, 3H), 8.06 – 7.97 (m, 5H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.0 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.47 – 7.40 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 156.7, 154.1, 137.4, 135.5, 135.0, 134.6, 134.4, 133.6, 133.2, 131.2, 129.1, 128.8, 128.2, 127.9, 127.7, 127.5, 127.3, 127.3, 127.2, 127.0, 126.9, 125.7, 125.5, 125.4, 125.3, 125.1, 124.7, 123.6, 123.4, 121.3, 121.1, 112.2.

**HRMS** (APPI; Toluene): Chemical Formula: $C_{30}H_{16}O$, calc. 392.1201 found 392.1203.

**Benzo[fg]benzo[4,5]fluoreno[2,1,9,8-opqra]tetracene (s9).**



Chemical Formula: $C_{30}H_{14}$
Molecular Weight: 374,4420

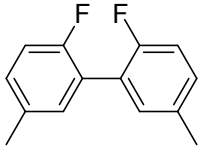
The compound was obtained according to the General Procedure C using 11-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1-fluorobenzo[c]phenanthrene (40 mg). Yield 1 mg (3%).

**$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.82 (dd, *J* = 7.9, 0.8 Hz, 1H), 8.80 – 8.71 (m, 4H), 8.34 (d, *J* = 8.7 Hz, 1H), 8.05 (t, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.85 – 7.76 (m, 3H), 7.75 – 7.66 (m, 2H).

**UV/Vis** (DCM-MeOH, 1-1, 293 K): λ [nm]) = 275, 288, 306, 319, 352, 410.

**HRMS** (APPI; Toluene): Chemical Formula: $C_{30}H_{14}$, calc. 374,1096, found 374,1096.

**2,2'-difluoro-5,5'-dimethyl-1,1'-biphenyl (2a).**




Chemical Formula: $C_{14}H_{12}F_2$
Molecular Weight: 218,2468

The compound was obtained according to the General Procedure B using p-fluorotoluene (1.25 g). Yield 530 mg (43%).

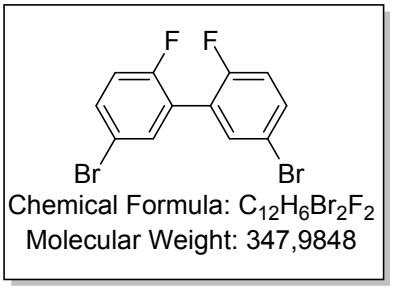
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.16 (tt, *J* = 4.0, 2.3 Hz, 1H), 7.10 – 6.99 (m, 1H), 2.37 (s, 2H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -120.28 (s, 2F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.1 (dd, *J* = 246.8, 1.5 Hz), 133.4 (t, *J* = 1.7 Hz), 131.9 (t, *J* = 2.2 Hz), 130.18 – 129.90 (m), 123.23 (dd, *J* = 10.4, 4.8 Hz), 115.60 – 115.14 (m), 20.64.

**HRMS** (APPI; Toluene): Chemical Formula: $C_{14}H_{12}F_2$, calc. 218.0907, found 218.0910.

**2,2'-difluoro-5,5'-dibromo-1,1'-biphenyl (3a).**




The compound was obtained according to the General Procedure B using 1-bromo-4-fluorobenzene (2 g). Yield 692 mg (35%)

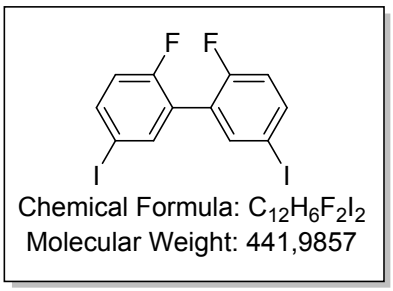
**$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.57 – 7.50 (m, 4H), 7.09 (ddd, *J* = 7.3, 6.0, 2.9 Hz, 2H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -117.01 (brs, 2F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 159.3 (dd, *J* = 251.0, 1.8 Hz), 134.4 (t, *J* = 2.3 Hz), 133.75 – 133.57 (m), 124.6 (dd, *J* = 11.0, 5.4 Hz), 118.48 – 117.79 (m), 117.0 (d, *J* = 1.3 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{12}H_6Br_2F_2$, calc. 345.8804, found 345.8807.

**2,2'-difluoro-5,5'-diiodo-1,1'-biphenyl (4a).**




The compound was obtained according to the General Procedure B using 1-fluoro-4-iodobenzene (2.5 g). Yield 870 mg (34%)

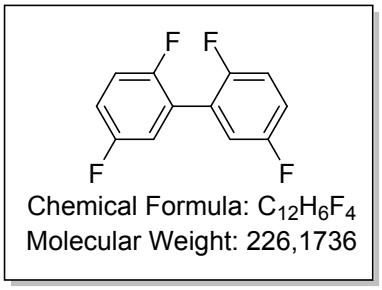
**$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.86 – 7.57 (m, 4H), 7.09 – 6.82 (m, 2H).

**$^{19}$F NMR** (283 MHz, $CDCl_3$) δ -115.48 (s, 2F).

**$^{13}$C NMR** (76 MHz, $CDCl_3$) δ 159.7 (dd, *J* = 252.3, 1.7 Hz), 139.8 (t, *J* = 2.2 Hz), 139.1 (t, *J* = 4.1 Hz), 124.5 (dd, *J* = 9.9, 6.0 Hz), 118.65 – 117.53 (m), 86.9 (t, *J* = 1.8 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{12}H_6I_2F_2$, calc. 441.8527, found 441.8528.

**2,2',5,5'-tetrafluoro-1,1'-biphenyl (5a).**




The compound was obtained according to the General Procedure B using 1,4-difluorobenzene (1.3 g). Yield 515 mg (40%)

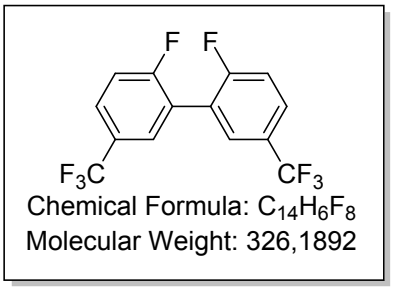
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.28 – 6.95 (m, 1H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -119.52 (dt, *J* = 15.3, 7.8 Hz, 2F), -121.41 (s, 2F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.4 (dd, *J* = 243.4, 1.6 Hz), 157.13 – 154.05 (m), 124.10 – 123.34 (m), 117.8 (dt, *J* = 24.8, 2.8 Hz), 117.34 – 116.80 (m), 116.80 – 116.44 (m).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{12}H_6F_4$, calc. 226.0406, found 226.0406.

**2,2'-difluoro-5,5'-bis(trifluoromethyl)-1,1'-biphenyl (6a).**




The compound was obtained according to the General Procedure B using 1-fluoro-4-(trifluoromethyl)benzene (1.8 g). Yield 880 mg (49%)

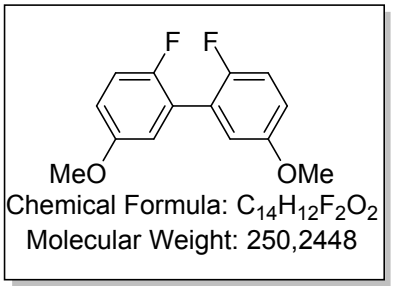
**$^1$H NMR** (300 MHz, $CD_2Cl_2$) δ 7.87 – 7.64 (m, 4H), 7.52 – 7.24 (m, 2H).

**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$) δ -62.42 (s, 6F), -109.46 (s, 2F).

**$^{13}$C NMR** (76 MHz, $CD_2Cl_2$) δ 164.19 – 160.06 (m), 129.89 – 129.14 (m), 128.5 (dq, *J* = 7.8, 3.8 Hz), 128.32 – 126.62 (m), 123.83 – 123.01 (m), 117.66 – 116.71 (m).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{14}H_6F_8$, calc. 326.0342, found 326.0343.

**2,2'-difluoro-5,5'-dimethoxy-1,1'-biphenyl (7a)**.




The compound was obtained according to the General Procedure B using 1-fluoro-4-methoxybenzene (1.5g). Yield 700 mg (47%)

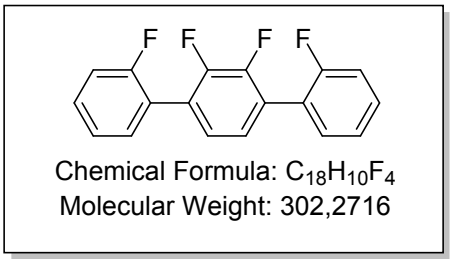
**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.13 – 7.03 (m, 2H), 6.94 – 6.85 (m, 4H).

**$^{19}$F NMR** (283 MHz, $CDCl_3$) δ -125.72 (s).

**$^{13}$C NMR** (76 MHz, $CDCl_3$) δ 155.5, 154.2 (dd, J=320, 2Hz), 124.28 – 123.62 (m), 116.78 – 115.88 (m), 115.04 – 114.72 (m), 55.8.

**HRMS** (APPI; Toluene): Chemical Formula: $C_{14}H_{12}F_2O_2$, calc. 250.0805, found 250.0806.

**2,2',2'',3'-tetrafluoro-1,1':4',1''-terphenyl (9a).**




Chemical Formula: $C_{18}H_{10}F_4$
Molecular Weight: 302,2716

The compound was obtained according to the General Procedure A using 2,3-difluoro-1,4-diiodobenzene (250 mg) and 2-fluorophenylboronic acid (190 mg). Yield 160 mg (80%)

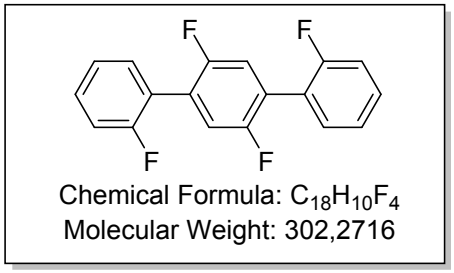
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.50 – 7.42 (m, 4H), 7.33 – 7.27 (m, 2H), 7.24 (ddd, *J* = 9.9, 6.7, 1.8 Hz, 4H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -115.18 (m, 2F), -136.25 – -143.23 (m, 2F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.2 (d, *J* = 248.6 Hz), 148.7 (dd, *J* = 251.8, 15.5 Hz), 131.9 (d, *J* = 2.0 Hz), 131.0 (d, *J* = 8.1 Hz), 126.2 (dt, *J* = 4.9, 2.5 Hz), 125.6 (dd, *J* = 7.9, 5.6 Hz), 124.8 (d, *J* = 3.6 Hz), 122.5 (d, *J* = 1.6 Hz), 116.3 (d, *J* = 22.3 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{18}H_{10}F_4$, calc. 302.0719, found 302.0716.

**2,2',2'',5'-tetrafluoro-1,1':4',1''-terphenyl (8a).**




Chemical Formula: $C_{18}H_{10}F_4$
Molecular Weight: 302,2716

The compound was obtained according to the General Procedure A using 1,4-dibromo-2,5-difluorobenzene (500 mg) and 2-fluorophenylboronic acid (514 mg). Yield 510 mg (92%)

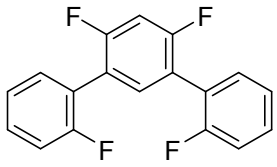
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.45 (ddd, *J* = 9.1, 6.5, 4.1 Hz, 1H), 7.29 (dt, *J* = 7.3, 3.9 Hz, 1H), 7.22 (ddd, *J* = 9.9, 9.4, 4.8 Hz, 1H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -115.27 (dd, *J* = 22.3, 11.6 Hz, 2F), -121.21 (brs, 1F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.2 (d, *J* = 248.7 Hz), 156.0 (dd, *J* = 245.7, 4.4 Hz), 131.9 (d, *J* = 2.5 Hz), 131.0 (d, *J* = 8.2 Hz), 124.8, 124.8, 122.6 (d, *J* = 15.1 Hz), 118.96 – 118.22 (m), 116.3 (d, *J* = 22.0 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{18}H_{10}F_4$, calc. 302.0719, found 302.0717.

**2,2'',4',6'-tetrafluoro-1,1':3',1''-terphenyl (10a).**


Chemical Formula: $C_{18}H_{10}F_4$
Molecular Weight: 302,2716

The compound was obtained according to the General Procedure A using 1,5-dibromo-2,4-difluorobenzene (500 mg) and 2-fluorophenylboronic acid (470 mg). Yield 500 mg (84%)

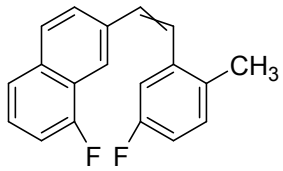
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.50 – 7.39 (m, 5H), 7.29 – 7.23 (m, 2H), 7.23 – 7.17 (m, 2H), 7.07 (t, *J* = 9.8 Hz, 1H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -111.23 – -111.76 (m, 2F), -115.47 (s, 2F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.3 (d, *J*=247 Hz), 160.1 (dd, *J*=251.0, 12.2 Hz), 134.3 (t, *J* = 4.7 Hz), 132.0 (d, *J* = 2.6 Hz), 130.7, 130.6, 124.8 (d, *J* = 3.7 Hz), 122.8 (d, *J* = 15.6 Hz), 120.63 – 120.00 (m), 116.2 (d, *J* = 22.4 Hz), 104.7 (t, *J* = 26.7 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{18}H_{10}F_4$, calc. 302.0719, found 302.0718.

**1-fluoro-7-(5-fluoro-2-methylstyryl)naphthalene.**


Chemical Formula: $C_{19}H_{14}F_2$
Molecular Weight: 280,3178

The ((8-fluoronaphthalen-2-yl)methyl)triphenyl phosphonium bromide (750 mg, 1.5 mmol) and 2-methyl-4-fluorobenzaldehyde (206 g, 1.5 mmol) were dissolved in 50 mL of absolute ethanol. The mixture was stirred while KOtBu (0.19 g, 1.7 mmol) in ethanol was added dropwise for 5-10 min. The solution obtained was refluxed for 10-20 h (TLC monitoring). The reaction mixture was cooled to room temperature and neutralized by addition of 1M HCl. After concentration by evaporation under reduced pressure, the mixture was diluted with water and the product was extracted with DCM. The DCM solution was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (Hexane: cyclohexane-10:1). Yield 340 mg (81%).

*Z*-isomer:

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.60 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.24 – 7.16 (m, 2H), 7.15 – 7.05 (m, 1H), 6.89 (d, *J* = 2.8 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.71 (d, *J* = 12.2 Hz, 1H), 2.26 (s, 3H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -117.91 (dd, *J* = 14.9, 7.4 Hz, 1F), -123.34 (d, *J* = 14.1 Hz, 1F).

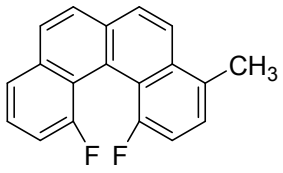
*E*-isomer:

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.86 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.79 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.33 (m, 3H), 7.22 – 7.14 (m, 3H), 6.92 (td, *J* = 8.3, 2.7 Hz, 1H), 2.45 (s, 3H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -117.15 – -117.60 (m, 1F), -122.95 (d, *J* = 12.0 Hz, 1F).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{19}H_{14}F_2$, calc. 280.1064, found 280.1066.

**1,12-difluoro-4-methylbenzo[c]phenanthrene (12a).**



Chemical Formula: $C_{19}H_{12}F_2$
Molecular Weight: 278,3018

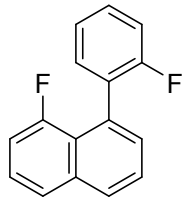
Solution of 1-fluoro-7-(5-fluoro-2-methylstyryl)naphthalene (300 g, 1.07 mmol) in 300 ml of cyclohexane was irradiated in the presence of $I_2$ (270 mg, 1.1 mmol) and methylpropyleneoxide (1.5 ml) for 25 h . After completion of reaction ½ of cyclohexane was evaporated under reduced pressure, washed with $Na_2S_2O_3$ solution, dried over $Na_2SO_4$. Cyclohexane was evaporated under reduced pressure and residue was purified by column chromatography (Hex:DCM 95:5) yielding 11-bromo-1-fluorobenzo[c]phenanthrene as white solid in 97% (290 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.73 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.65 (s, 1H), 7.64 – 7.58 (m, 2H), 7.41 (td, *J* = 7.9, 5.0 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.15 (ddd, *J* = 12.6, 7.7, 1.1 Hz, 1H), 7.05 (dd, *J* = 12.4, 7.9 Hz, 1H), 2.60 (s, 3H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -107.90 (dd, *J* = 45.5, 11.4 Hz, 1F), -110.89 (dd, *J* = 44.4, 11.7 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.6 (dd, *J* = 252, 3.2 Hz), 159.3 (dd, *J* = 250, 3.2 Hz), 134.5 (d, *J* = 4.2 Hz), 132.9 (d, *J* = 3.7 Hz), 131.3 (s), 129.0 (d, *J* = 3.6 Hz), 127.4 (d, *J* = 3.0 Hz), 127.37 – 127.23 (m), 126.6 (d, *J* = 9.6 Hz), 126.5 (s), 126.4 (s), 123.8 (d, *J* = 2.4 Hz), 123.0 (d, *J* = 3.1 Hz), 120.6 (td, *J* = 14.0, 3.1 Hz), 119.8 (s), 111.22 (d, *J* = 23.9 Hz), 110.4 (d, *J* = 23.3 Hz), 19.38 (s).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{19}H_{12}F_2$, calc. 278.0907, found 278.0907.



Chemical Formula: $C_{16}H_{10}F_2$
Molecular Weight: 240,2528

**1-fluoro-8-(2-fluorophenyl)naphthalene (11a).**

The compound was obtained according to the General Procedure A using 1-bromo-8-fluoronaphtalene[3] (225 mg) and 2-fluorophenylboronic acid (150 mg). Yield 180 mg (75%)

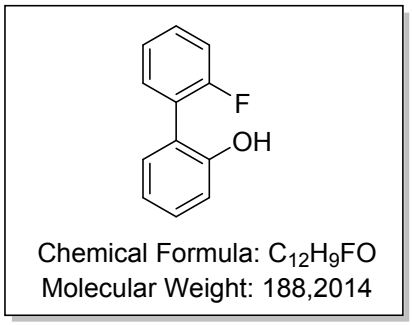
**$^1$H NMR** (300 MHz, $CD_2Cl_2$) δ 7.99 – 7.90 (m, 1H), 7.75 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.59 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.53 – 7.36 (m, 4H), 7.31 – 7.21 (m, 1H), 7.20 – 7.08 (m, 2H).

**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$) δ -113.24 (d, *J* = 13.3 Hz, 1F), -116.27 (dd, *J* = 18.6, 8.3 Hz, 1F).

**$^{13}$C NMR** (76 MHz, $CD_2Cl_2$) δ 160.8 (dd, *J*=324, 5 Hz), 159.6 (d, *J*=336 Hz), 136.12 (d, *J* = 3.8 Hz), 131.40 (dd, *J* = 3.5, 1.9 Hz), 131.01 (dd, *J* = 16.9, 3.4 Hz), 130.80 (s), 130.20 (s), 130.20 (s), 129.49 (d, *J* = 8.0 Hz), 128.69 (d, *J* = 3.4 Hz), 126.54 (d, *J* = 1.6 Hz), 126.36 (d, *J* = 8.9 Hz), 125.00 (d, *J* = 4.2 Hz), 123.96 (d, *J* = 3.5 Hz), 122.59 (d, *J* = 11.1 Hz), 115.01 (d, *J* = 22.2 Hz), 111.70 (d, *J* = 22.3 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{16}H_{10}F_2$, calc. 240.0751, found 240.0753

**2'-fluoro-[1,1'-biphenyl]-2-ol (s10).**



Chemical Formula: $C_{12}H_9FO$
Molecular Weight: 188,2014

The compound was obtained according to the General Procedure A using 2-bromophenol (500 mg) and 2-fluorophenylboronic acid (406 mg). Yield 150 mg (75%)

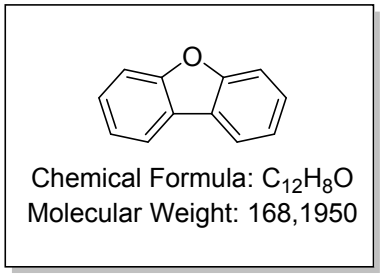
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.45 – 7.36 (m, 2H), 7.34 – 7.24 (m, 3H), 7.24 – 7.18 (m, 1H), 7.02 (td, *J* = 7.5, 1.2 Hz, 1H), 6.98 (dd, *J* = 8.2, 1.0 Hz, 1H), 5.09 (s, 1H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -114.96 (t, *J* = 11.6 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.4 (d, *J* = 246.3 Hz), 153.4, 132.4 (d, *J* = 3.2 Hz), 131.6 (d, *J* = 1.0 Hz), 130.4, 130.3, 130.2, 125.1 (d, *J* = 3.7 Hz), 122.9, 121.1, 116.4 (d, *J*=23 Hz), 116.3.

The spectroscopic data were consistent with previously reported[4]

**Dibenzo[b,d]furan (1).**



Chemical Formula: $C_{12}H_8O$
Molecular Weight: 168,1950

The compound was obtained according to the General Procedure C using 2,2'-difluoro-1,1'-biphenyl[1] (40 mg) or 2'-

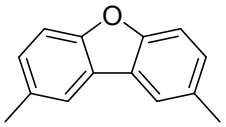
fluoro-[1,1'-biphenyl]-2-ol (40 mg). Yield 23 mg (65%) or 15 mg (40%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.36 (td, *J* = 7.6, 0.9 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.2, 127.1, 124.2, 122.7, 120.6, 111.7.

The spectroscopic data were consistent with previously reported[5].

**2,8-dimethyldibenzo[b,d]furan (2).**



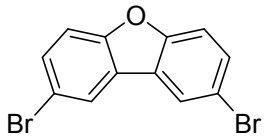
Chemical Formula: $C_{14}H_{12}O$
Molecular Weight: 196,2490

The compound was obtained according to the General Procedure C using 2,2'-difluoro-5,5'-dimethyl-1,1'-biphenyl (40 mg). Yield 22 mg (60%).

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.75 – 7.72 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (dd, *J* = 8.5, 1.7 Hz, 2H), 2.50 (s, 6H).

The spectroscopic data were consistent with previously reported[6]

**2,8-dibromodibenzo[b,d]furan (3)**




Chemical Formula: $C_{12}H_6Br_2O$
Molecular Weight: 325,9870

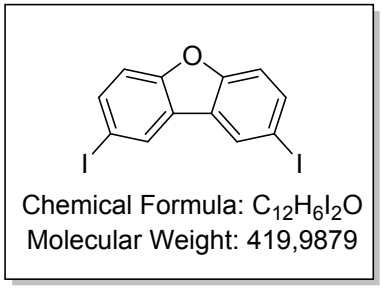
The compound was obtained according to the General Procedure C using 2,2'-difluoro-5,5'-dibromo-1,1'-biphenyl (40 mg). Yield 15 mg (40%).

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.10 – 8.06 (m, 2H), 7.61 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.53 – 7.45 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 155.9, 131.2, 125.6, 124.2, 116.3, 113.8.

The spectroscopic data were consistent with previously reported[7].

**2,8-diiododibenzo[b,d]furan (4).**



Chemical Formula: $C_{12}H_6I_2O$
Molecular Weight: 419,9879

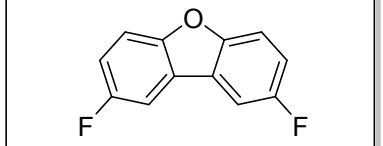
The compound was obtained according to the General Procedure C using 2,2'-difluoro-5,5'-diiodo-1,1'-biphenyl (40 mg). Yield 22 mg (54%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.7 Hz, 2H), 7.76 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.7, 136.4, 129.8, 125.5, 113.9, 86.1.

The spectroscopic data were consistent with previously reported[8]

**2,8-fluorodibenzo[b,d]furan (5).**



Chemical Formula: $C_{12}H_6F_2O$
Molecular Weight: 204,1758

The compound was obtained according to the General Procedure C using 2,2'-difluoro-5,5'-difluoro-1,1'-biphenyl (40 mg). Yield 1 mg (2%).

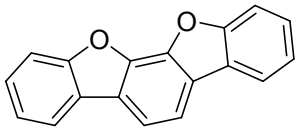
**$^1$H NMR** (300 MHz, $CD_2Cl_2$) δ 7.60 (dd, *J* = 8.2, 2.7 Hz, 2H), 7.52 (dd, *J* = 9.0, 4.0 Hz, 2H), 7.22 (td, *J* = 9.1, 2.7 Hz, 2H).

**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$) δ -120.83 (d, *J* = 9.0 Hz, 2F).

**$^{13}$C NMR** (76 MHz, $CD_2Cl_2$) δ 159.4 (d, *J* = 239.2 Hz), 153.7, 125.2 (dd, *J* = 10.4, 3.8 Hz), 115.6 (d, *J* = 25.9 Hz), 113.1 (d, *J* = 9.3 Hz), 107.2 (d, *J* = 25.4 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{12}H_6F_2O$, calc. 204.0389, found 204.0390.

**Benzo[1,2-*b*:5,4-*b'*]bisbenzofuran (9).**



Chemical Formula: $C_{18}H_{10}O_2$
Molecular Weight: 258,2760

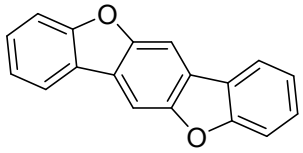
The compound was obtained according to the General Procedure C using 2,2',2'',3'-tetrafluoro-1,1':4',1''-terphenyl (40 mg). Yield 10 mg (30%).

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.10 – 8.05 (m, 2H), 7.98 (s, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.44 (td, *J* = 7.6, 0.9 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 157.0, 139.2, 127.6, 124.99, 124.96, 123.8, 121.1, 115.7, 112.4.

The spectroscopic data were consistent with previously reported[9]

**Benzo[2,1-b:3,4-b']bisbenzofuran (8).**



Chemical Formula: $C_{18}H_{10}O_2$
Molecular Weight: 258,2760

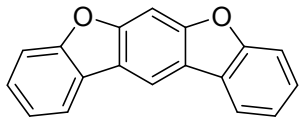
The compound was obtained according to the General Procedure C using 2,2',2",5'-tetrafluoro-1,1':4',1"-terphenyl (40 mg). Yield 14 mg (40%).

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.11 (s, 2H), 8.09 – 8.04 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.47 (m, 2H), 7.40 (dd, *J* = 11.3, 4.6 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 157.7, 153.2, 128.0, 124.9, 124.5, 123.2, 121.2, 112., 103.0.

The spectroscopic data were consistent with previously reported[9]

**Benzo[1,2-b:5,4-b']bisbenzofuran (10).**



Chemical Formula: $C_{18}H_{10}O_2$
Molecular Weight: 258,2760

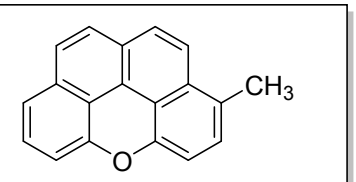
The compound was obtained according to the General Procedure C using 2,2",4',6'-tetrafluoro-1,1':3',1"-terphenyl (40 mg). Yield 6 mg (15%)

**$^1$H NMR** (300 MHz, $CD_2Cl_2$) δ 8.50 (s, 1H), 8.10 – 8.03 (m, 2H), 7.74 (d, *J* = 0.6 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.53 – 7.44 (m, 2H), 7.40 (td, *J* = 7.4, 1.2 Hz, 2H).

**$^{13}$C NMR** (76 MHz, $CD_2Cl_2$) δ 157.3, 156.5, 127.1, 124.6, 123.4, 121.0, 120.8, 111.93, 111.9, 95.7.

The spectroscopic data were consistent with previously[10]

**3-methylnaphtho[2,1,8,7-klmn]xanthene (12).**



Chemical Formula: $C_{19}H_{12}O$
Molecular Weight: 256,3040

The compound was obtained according to the General Procedure C using 1,12-difluoro-4-methylbenzo[c] phenanthrene (40 mg). Yield 26 mg (70%).

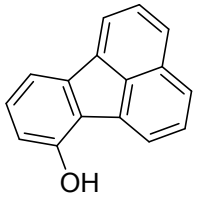
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.07 (dd, *J* = 6.7, 2.1 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 2.60 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.6, 150.9, 132.7, 131.1, 128.4, 128.0, 126.8, 126.4, 126.2, 125.5, 123.9, 122.7, 122.5, 119.9, 119.84, 119.76, 109.4, 109.0, 18.6.

**UV/Vis** (Toluene, 293 K): λ [nm]) = 286, 313, 342, 361, 381. 402.

**HRMS** (APPI; Toluene): Chemical Formula: $C_{19}H_{12}O$, calc. 256.0888, found 278.0889.

**Fluoranthen-7-ol (11c).**




Chemical Formula: $C_{16}H_{10}O$
Molecular Weight: 218,2550

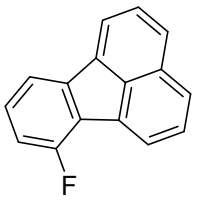
The compound was obtained according to the General Procedure C using 1-fluoro-8-(2-fluorophenyl)naphthalene (40 mg). Yield 4 mg (10%).

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 8.11 (d, *J* = 6.9 Hz, 1H), 7.98 (d, *J* = 7.0 Hz, 1H), 7.86 (dd, *J* = 17.0, 8.2 Hz, 2H), 7.66 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.58 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.35 – 7.23 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.59 – 5.45 (brs, 1H).

**$^{13}$C NMR** (151 MHz, $CD_2Cl_2$) δ 152.8, 141.8, 137.2, 136.0, 132.3, 130.3, 129.2, 128.7, 128.2, 127.3, 126.3, 125.4, 123.5, 120.9, 115.8, 115.0.

**HRMS** (APPI; Toluene): Chemical Formula: $C_{16}H_{10}O$, calc. 218.0732, found 218.0734.

**7-fluorofluoranthene (11b).**




Chemical Formula: $C_{16}H_9F$
Molecular Weight: 220,2464

The compound was obtained according to the General Procedure C using 1-fluoro-8-(2-fluorophenyl)naphthalene (40 mg). Yield 4.5 mg (12%).

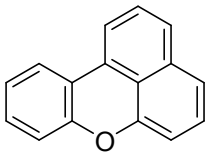
**$^1$H NMR (**400 MHz, $CD_2Cl_2$) δ 8.09 (d, *J* = 6.9 Hz, 1H), 8.03 (d, *J* = 6.9 Hz, 1H), 7.93 (d, *J* = 5.1 Hz, 1H), 7.91 (d, *J* = 5.2 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.73 – 7.66 (m, 2H), 7.43 – 7.35 (m, 1H), 7.12 (dd, *J* = 9.9, 7.6 Hz, 1H).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$) δ -118.95 (brs, 1F).

**$^{13}$C NMR** (151 MHz, $CD_2Cl_2$) δ 159.6 (d, *J* = 249.8 Hz), 142.5 (d, *J* = 6.5 Hz), 136.7, 134.1, 132.3, 130.4, 129.6 (d, *J* = 7.3 Hz), 128.7, 128.4, 127.7, 127.3, 125.9 (d, *J* = 16.0 Hz), 123.9 (d, *J* = 4.0 Hz), 121.5, 118.0 (d, *J* = 2.9 Hz), 115.2 (d, *J* = 20.2 Hz).

**HRMS** (APPI; Toluene): Chemical Formula: $C_{16}H_9F$, calc. 218.0732, found 218.0734.

**Benzo[kl]xanthene (11).**



Chemical Formula: $C_{16}H_{10}O$
Molecular Weight: 218,2550

The compound was obtained according to the General Procedure C using 1-fluoro-8-(2-fluorophenyl)naphthalene (40 mg). Yield 6 mg (17%).

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.87 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.62 (dd, *J* = 10.0, 4.0 Hz, 2H), 7.44 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 7.18 – 7.07 (m, 2H), 6.95 – 6.89 (m, 1H).

The spectroscopic data were consistent with previously reported[11]

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

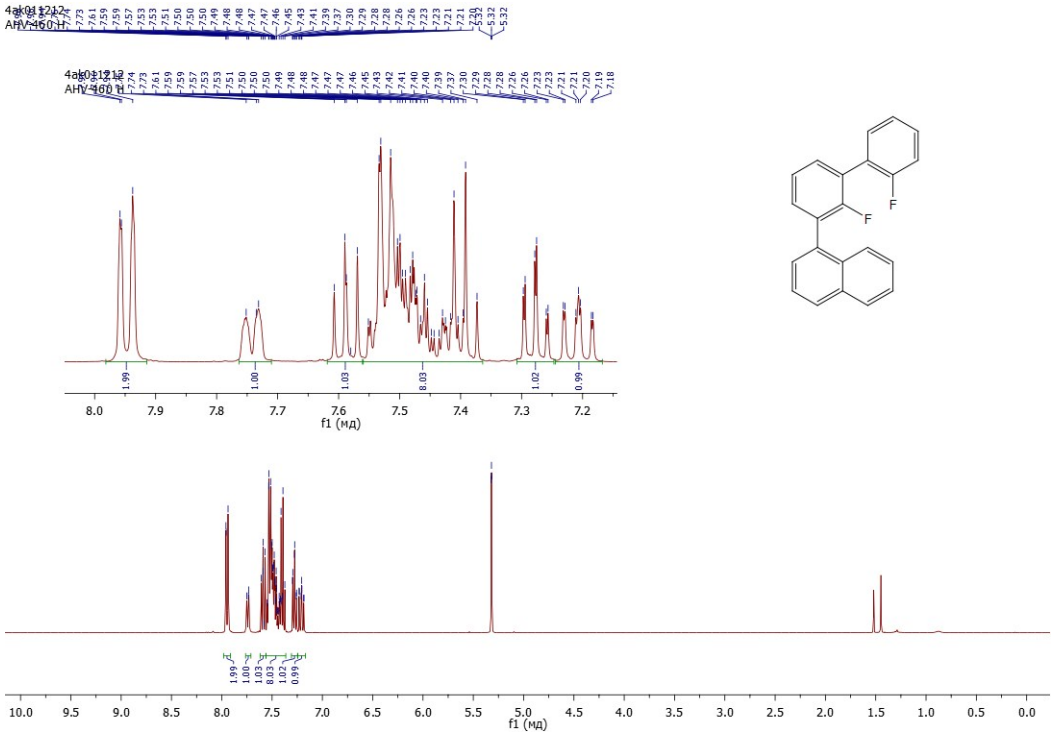


**Figure S1**. $^{1}$H NMR (400 MHz, $CD_2Cl_2$) spectrum of 1-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene.

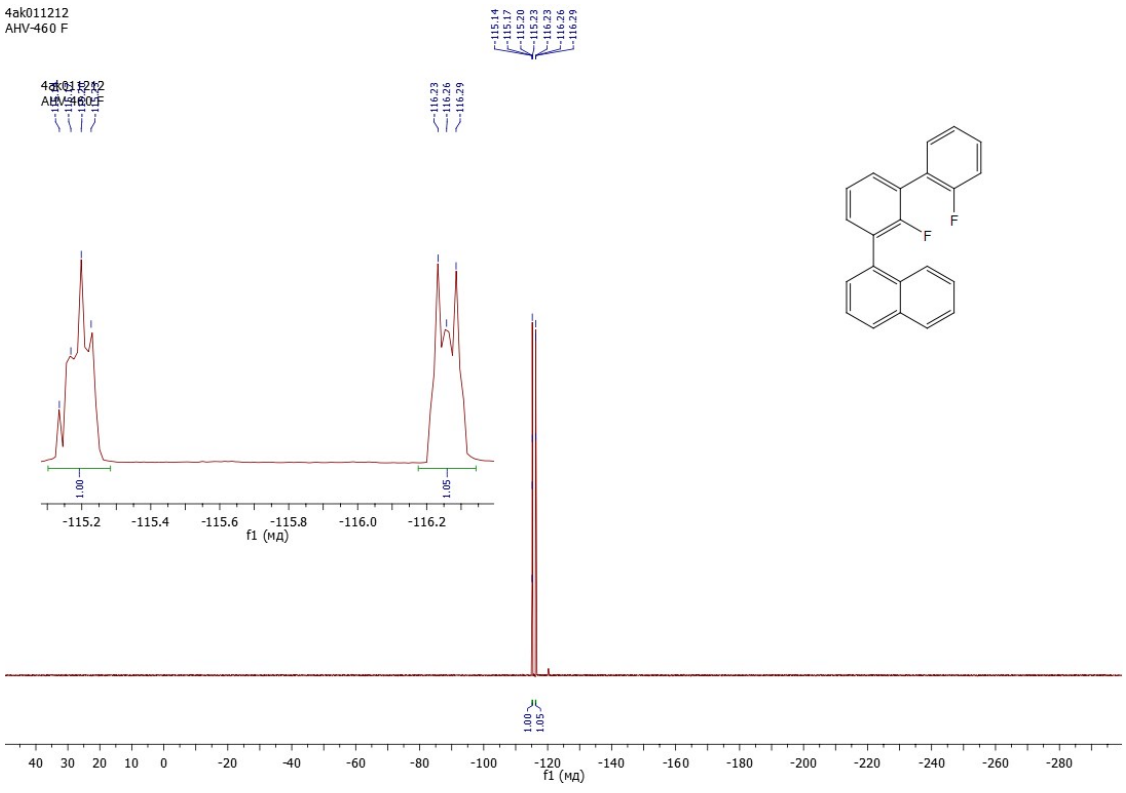


**Figure S2**. $^{19}$F NMR (377 MHz, $CD_2Cl_2$) spectrum of 1-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene.

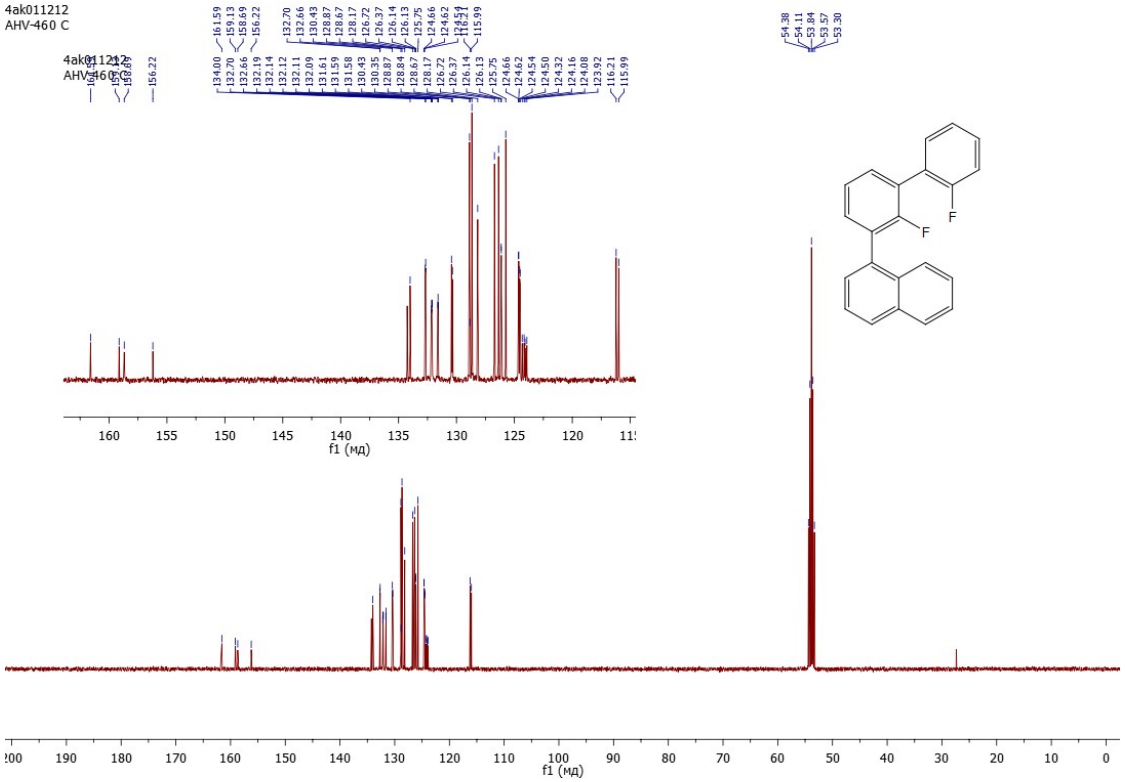


**Figure S3**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) spectrum of 1-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)naphthalene.

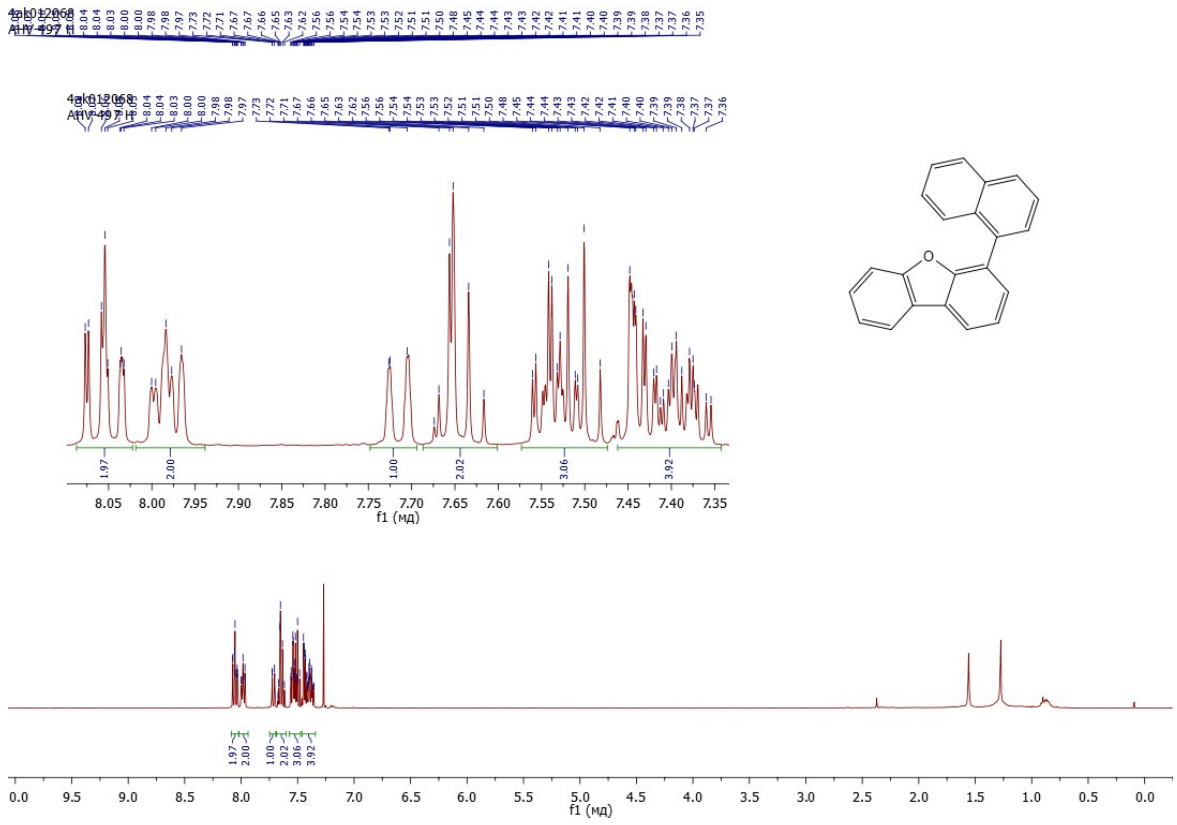


**Figure S4**. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 4-(naphthalen-1-yl)dibenzo[b,d]furan.

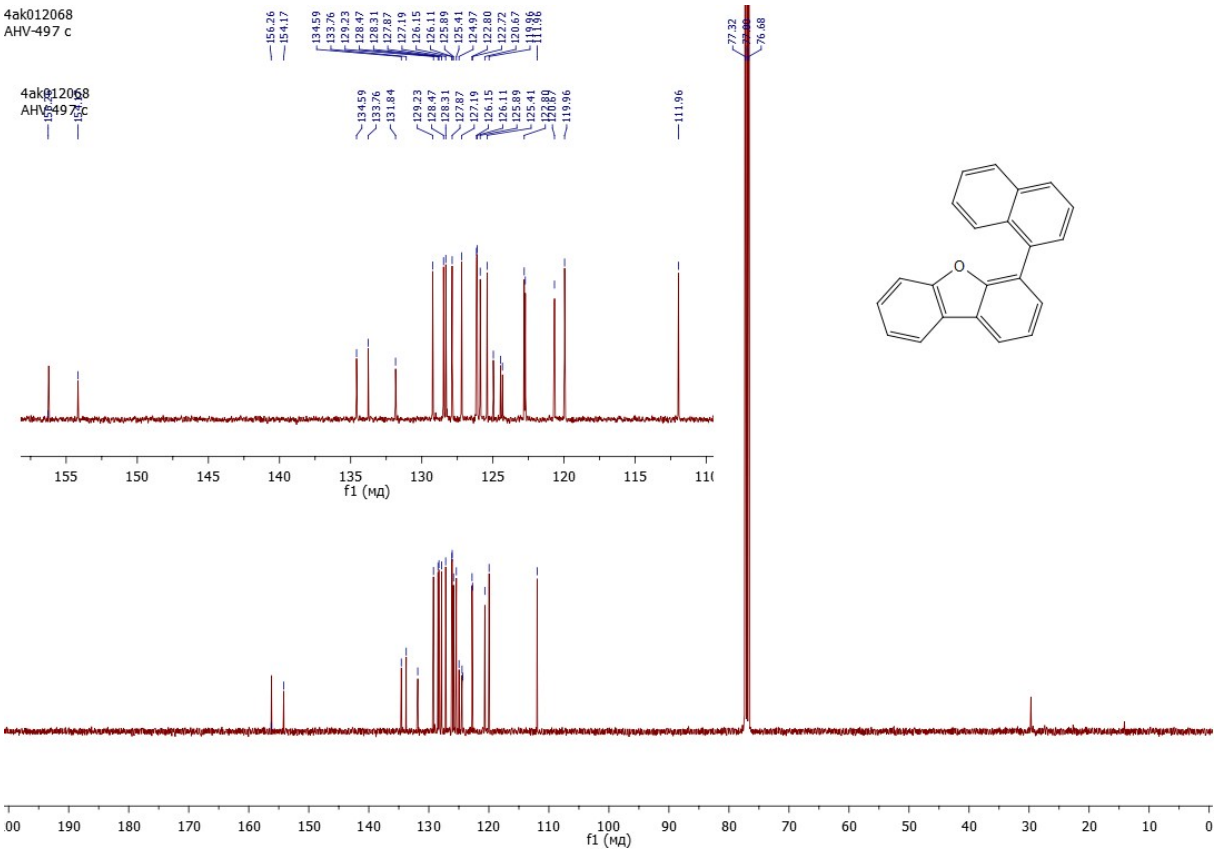


**Figure S5**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) spectrum of 4-(naphthalen-1-yl)dibenzo[b,d]furan.

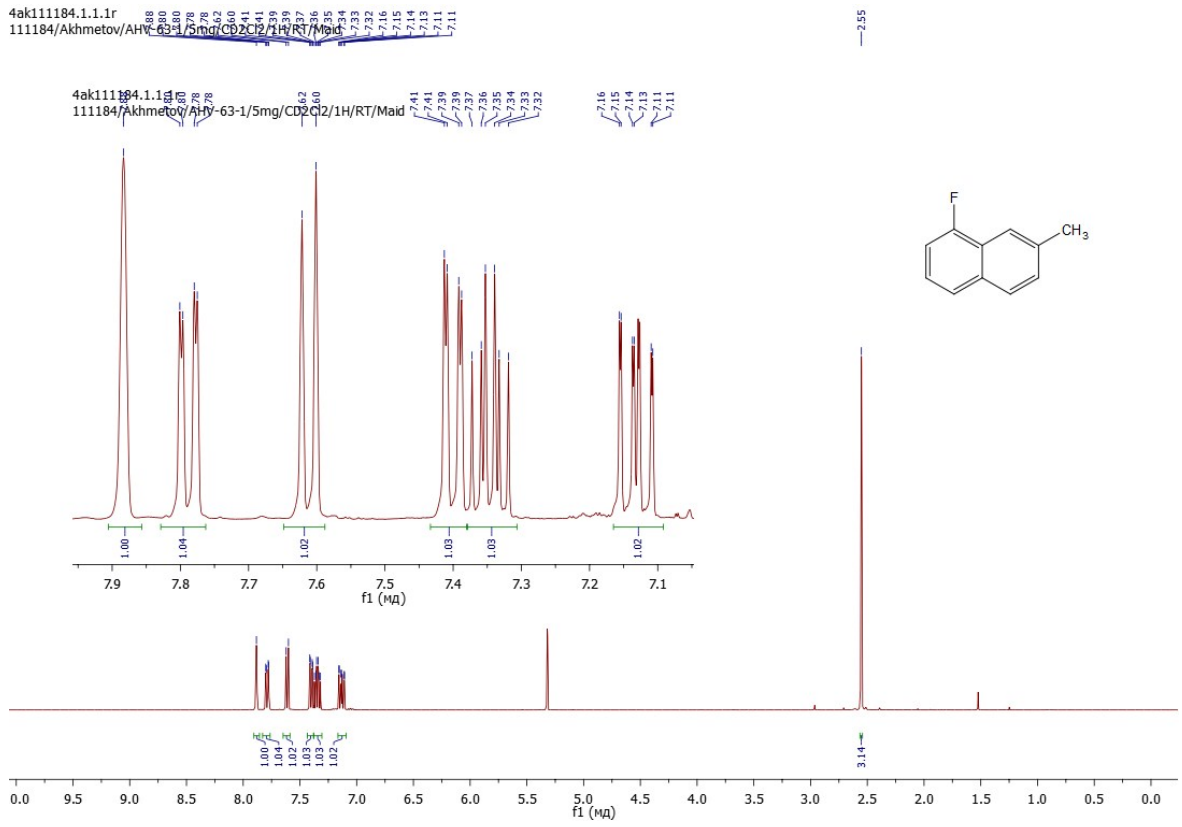


**Figure S6**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) spectrum of 1-fluoro-7-methylnaphthalene.

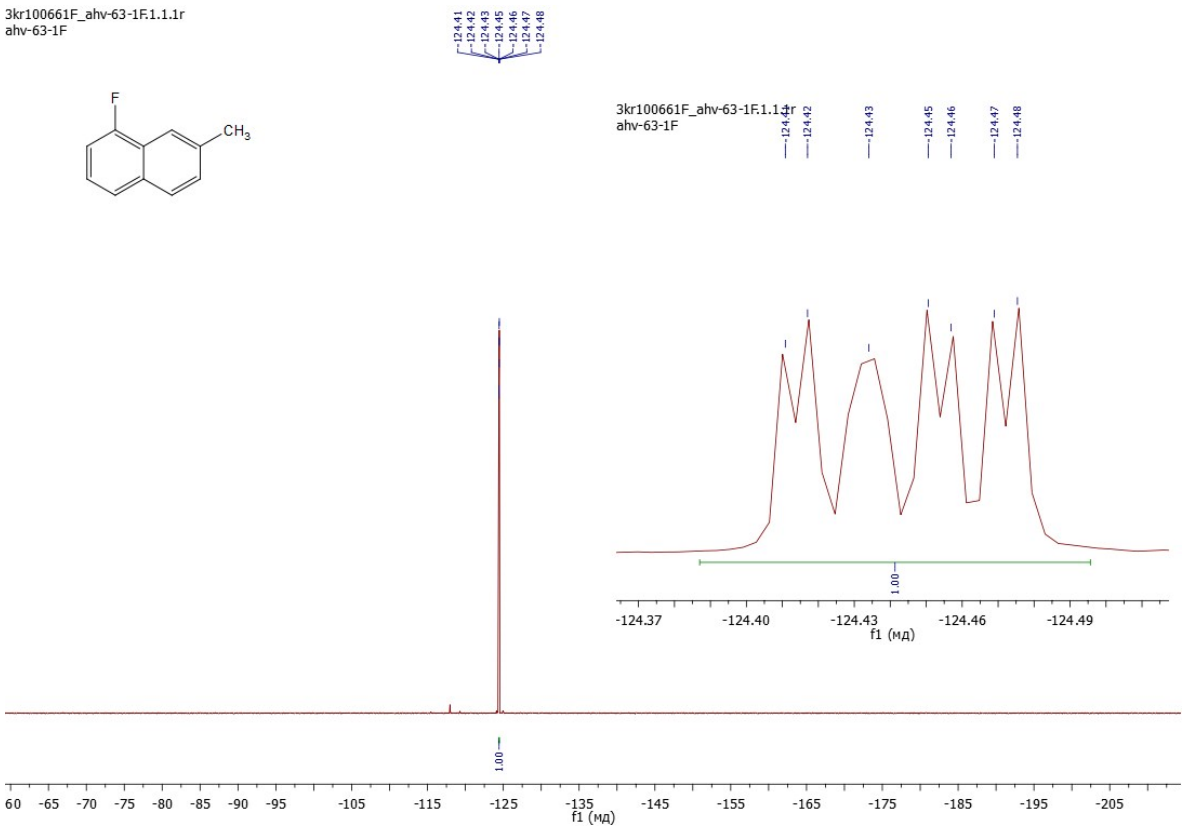


**Figure S7**. $^{19}F$ NMR (377 MHz, $CD_2Cl_2$) spectrum of 1-fluoro-7-methylnaphthalene.

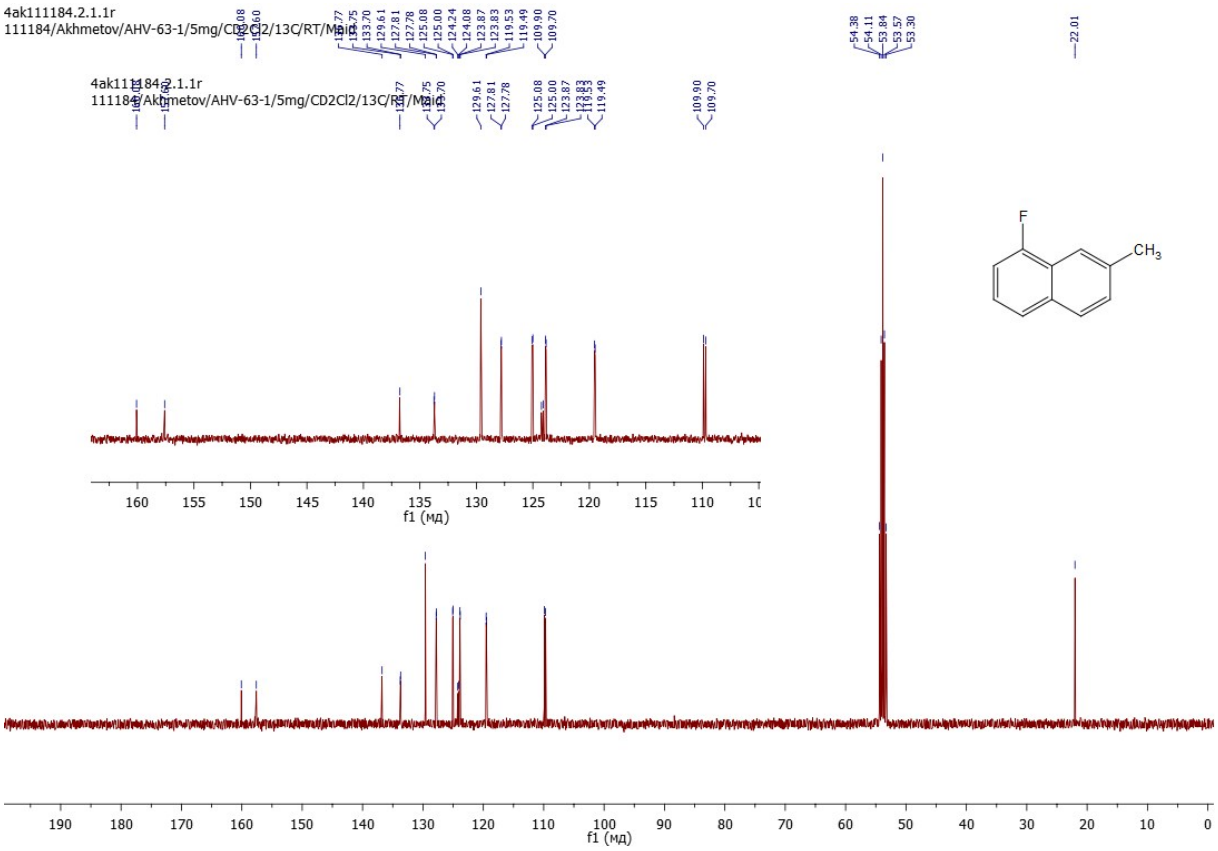


**Figure S8**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) spectrum of 1-fluoro-7-methylnaphthalene.

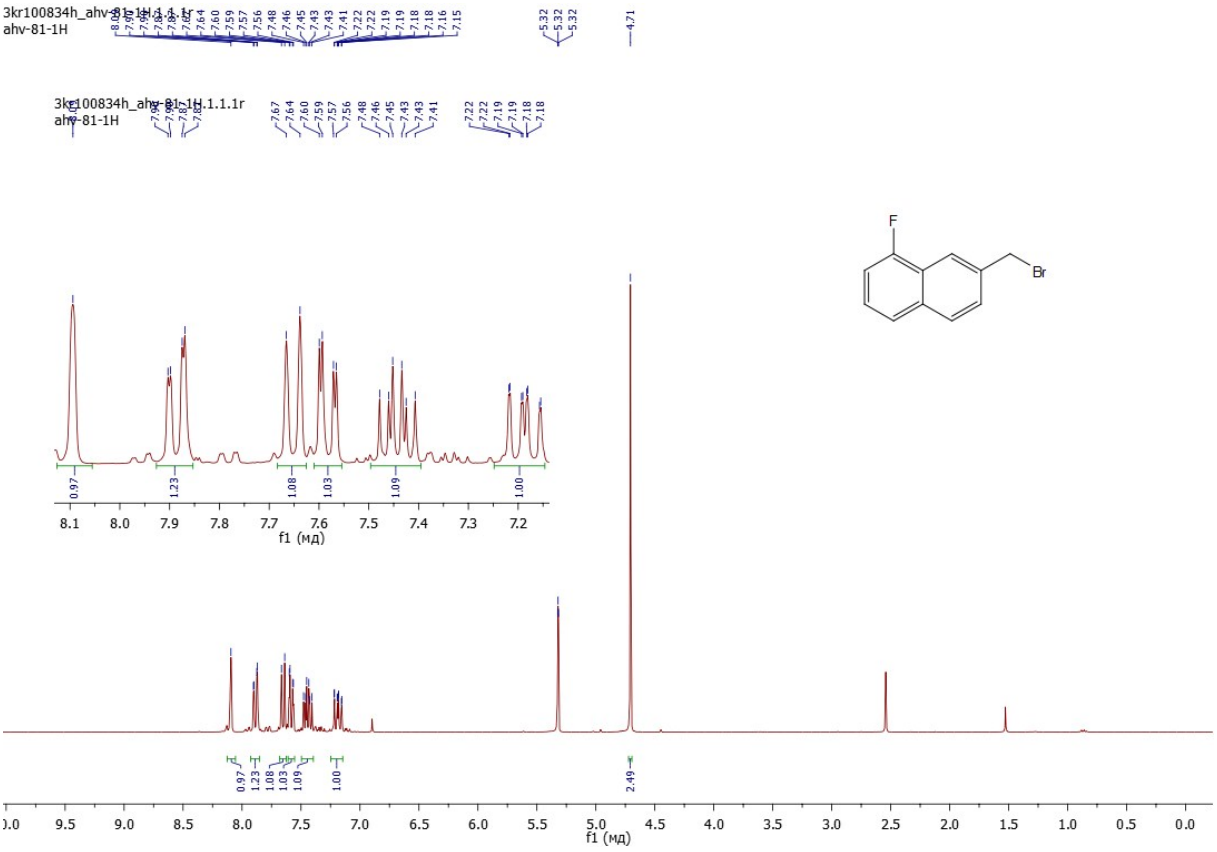


**Figure S9**. $^{1}$H NMR (300 MHz, $CD_2Cl_2$) spectrum of 7-(bromomethyl)-1-fluoronaphthalene.

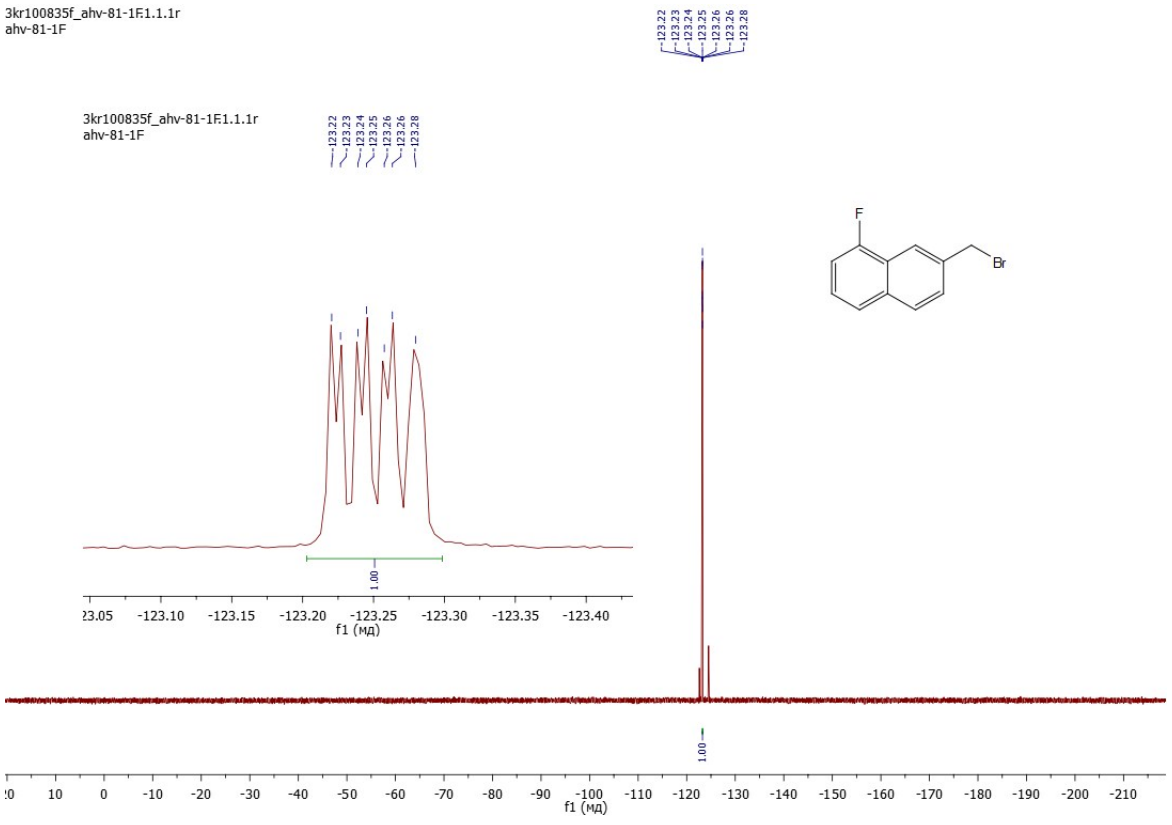


**Figure S10**. $^{19}$F NMR (282 MHz, $CD_2Cl_2$) spectrum of 7-(bromomethyl)-1-fluoronaphthalene.

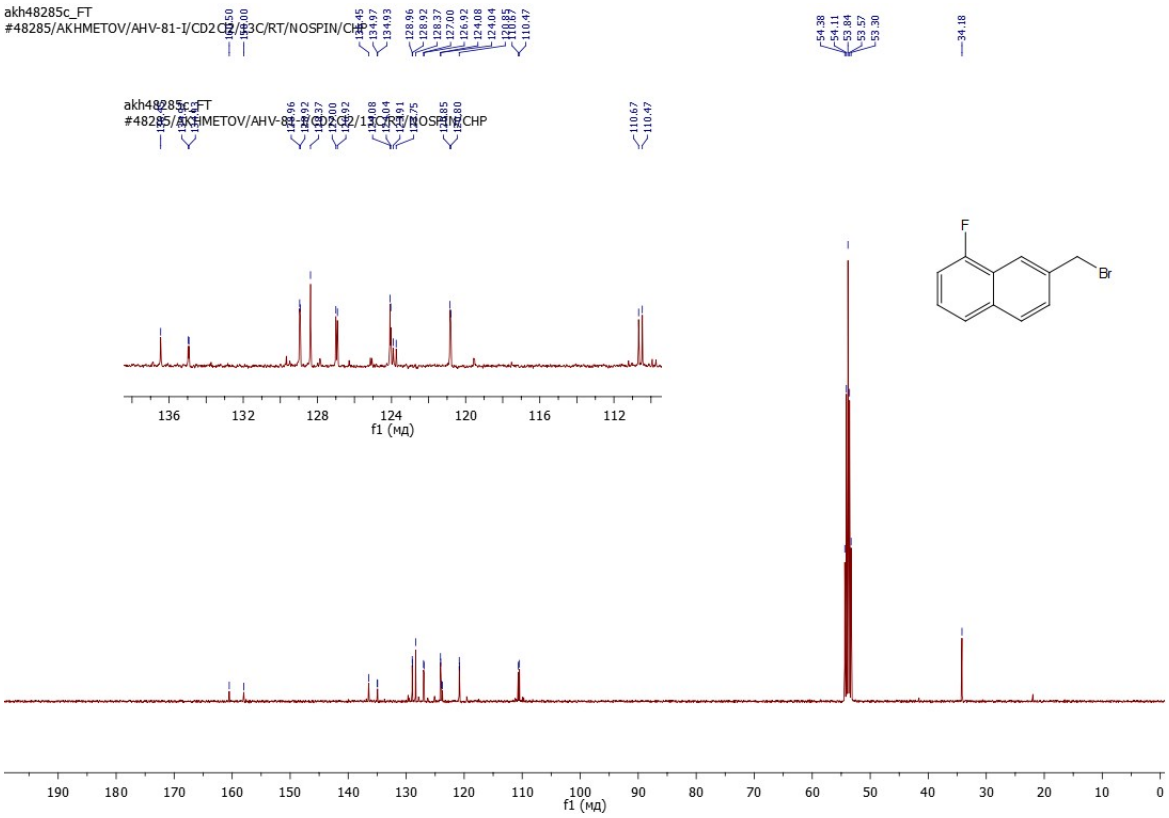


**Figure S11**. $^{13}C$ NMR (77 MHz, $CD_2Cl_2$) spectrum of 7-(bromomethyl)-1-fluoronaphthalene.

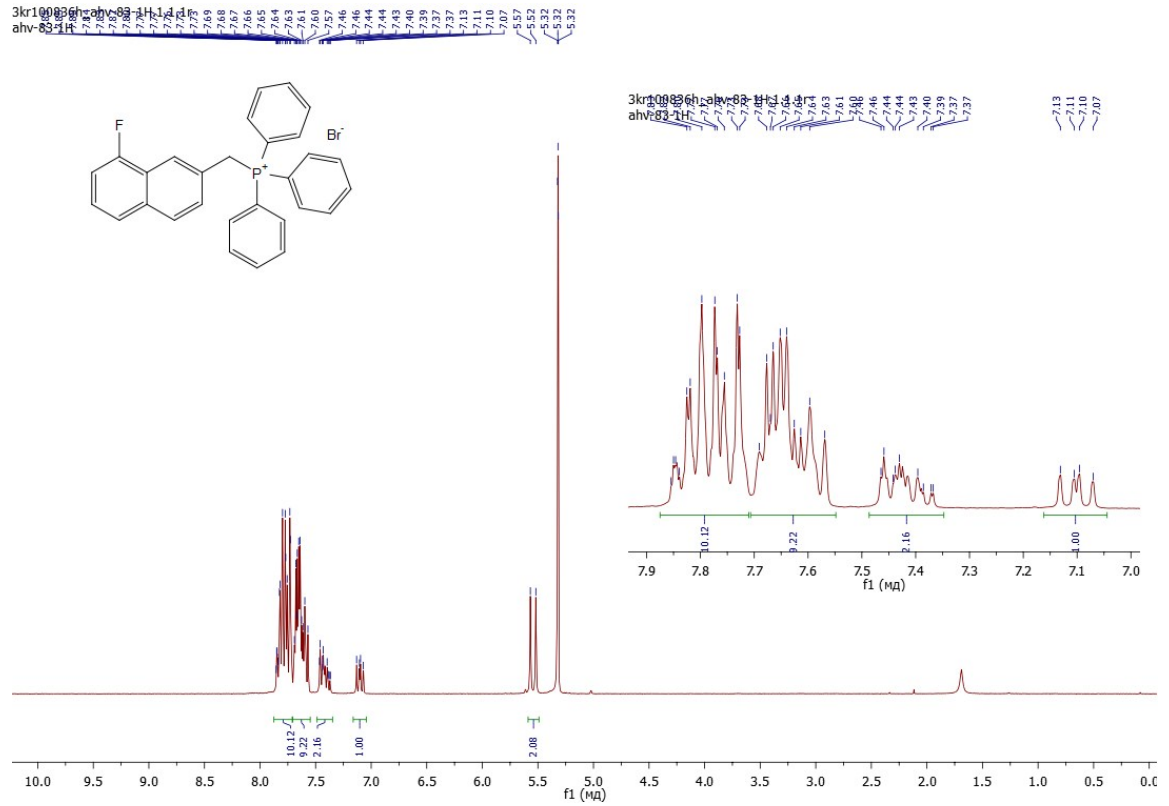


**Figure S12**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$) spectrum of ((8-fluoronaphthalen-2-yl)methyl) triphenylphosphonium bromide.

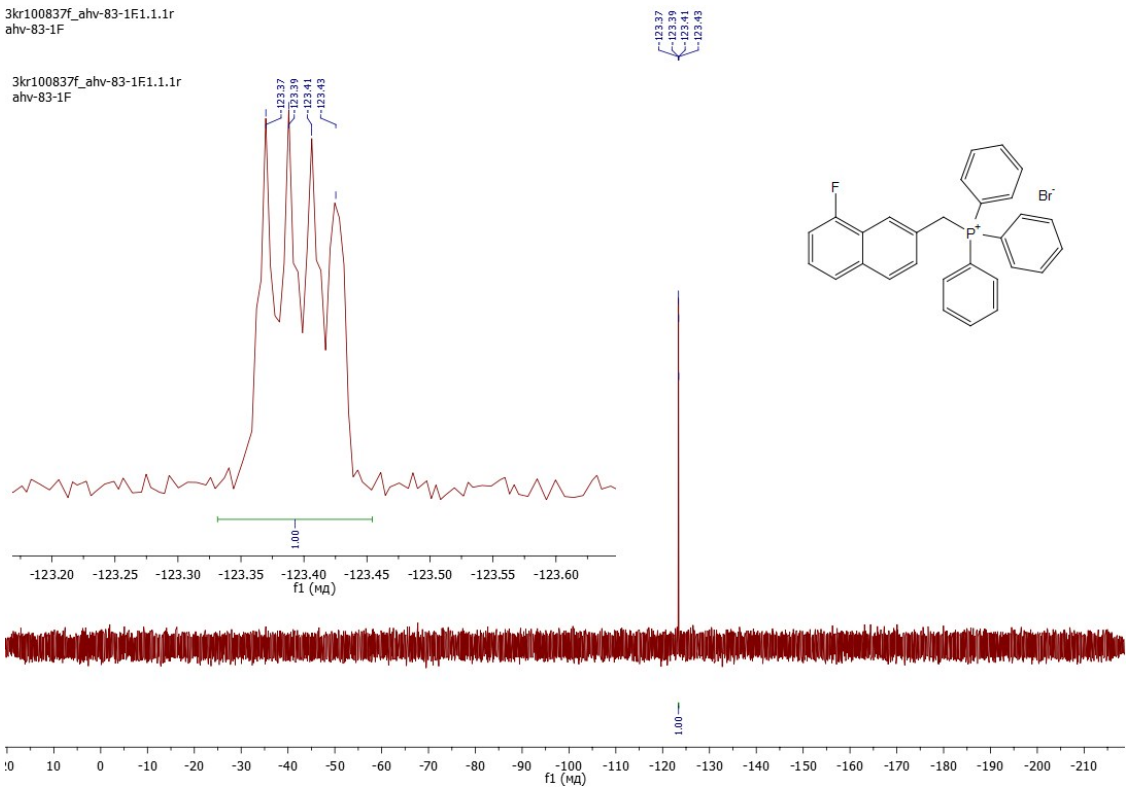


**Figure S13**. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of ((8-fluoronaphthalen-2-yl)methyl) triphenylphosphonium bromide.

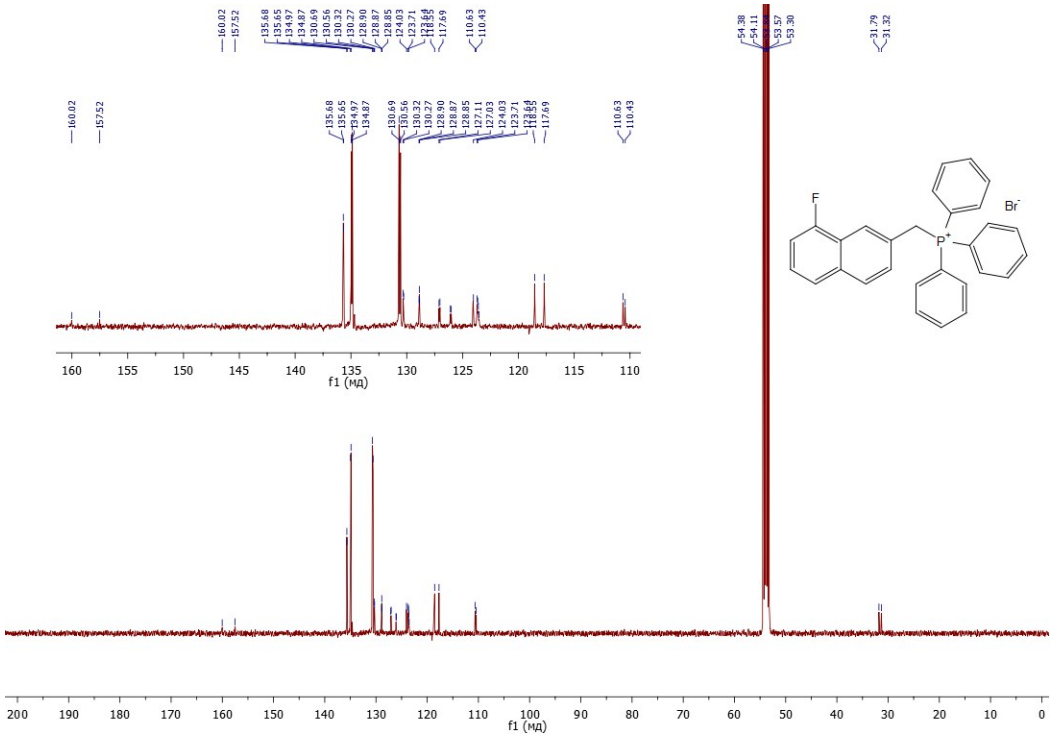


**Figure S14**. $^{13}C$ NMR (77 MHz, $CD_2Cl_2$) spectrum of ((8-fluoronaphthalen-2-yl)methyl) triphenylphosphonium bromide.

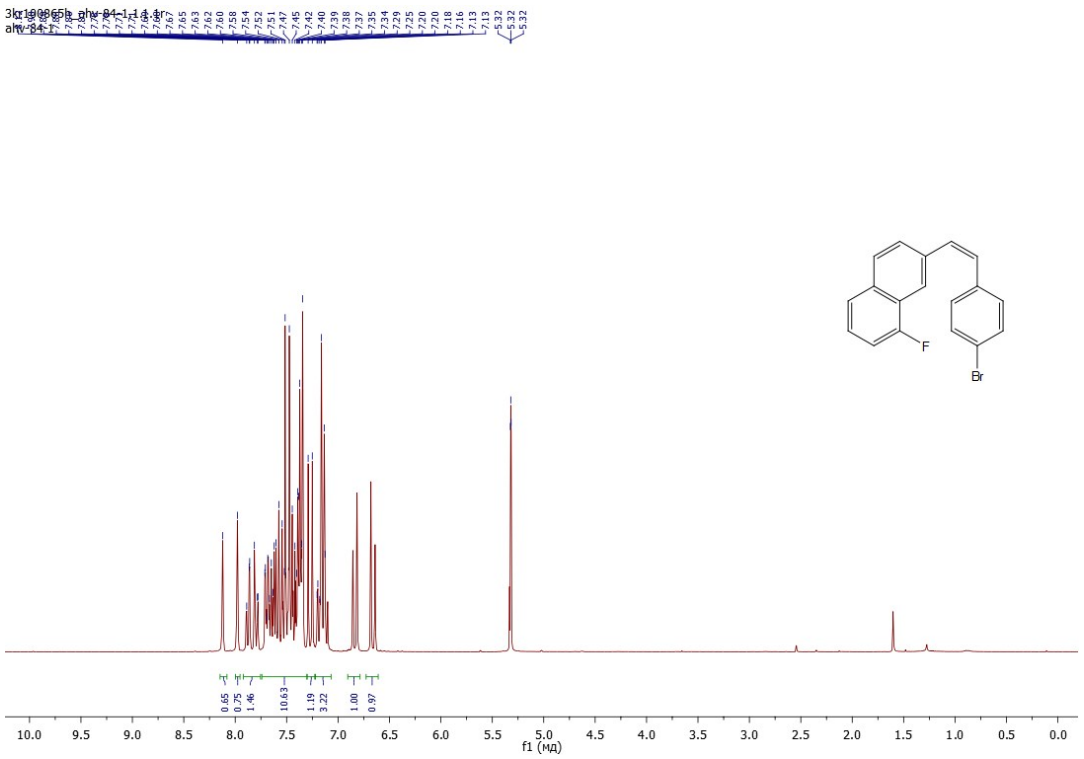


**Figure S15**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$) spectrum of 7-(4-bromostyryl)-1-fluoronaphthalene.

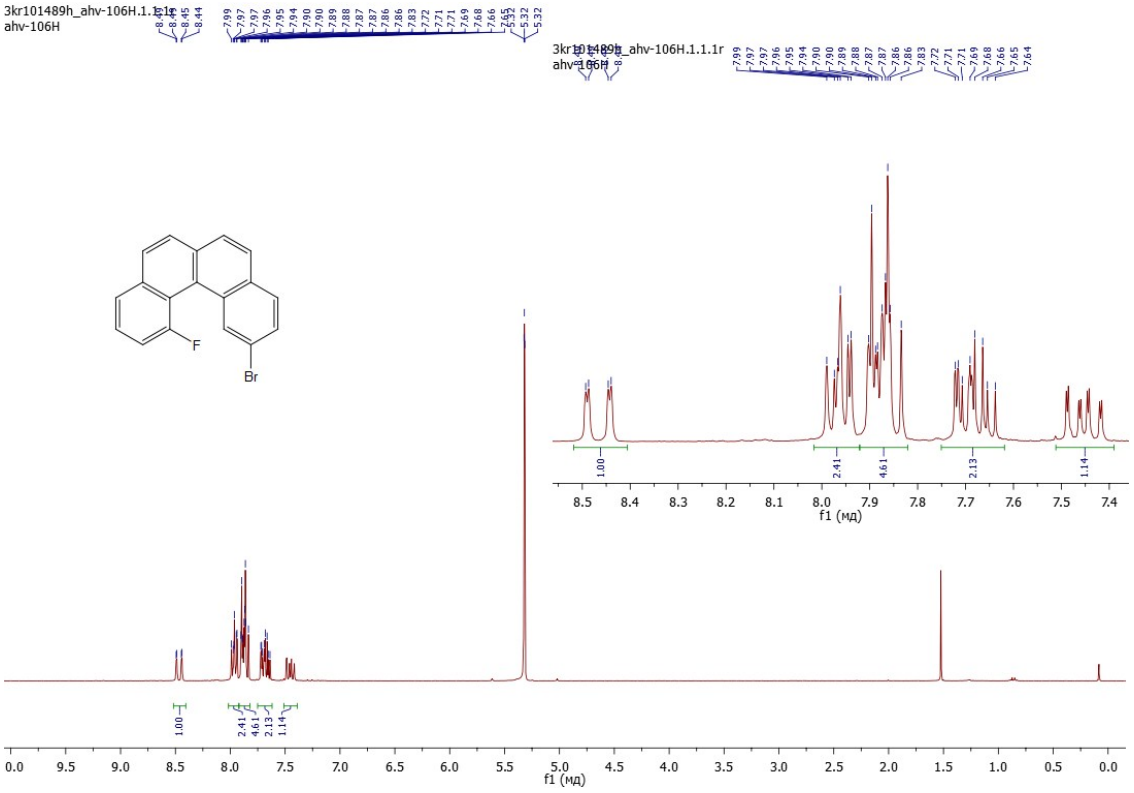


**Figure S16**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$) spectrum of 11-bromo-1-fluorobenzo[c] phenanthrene.

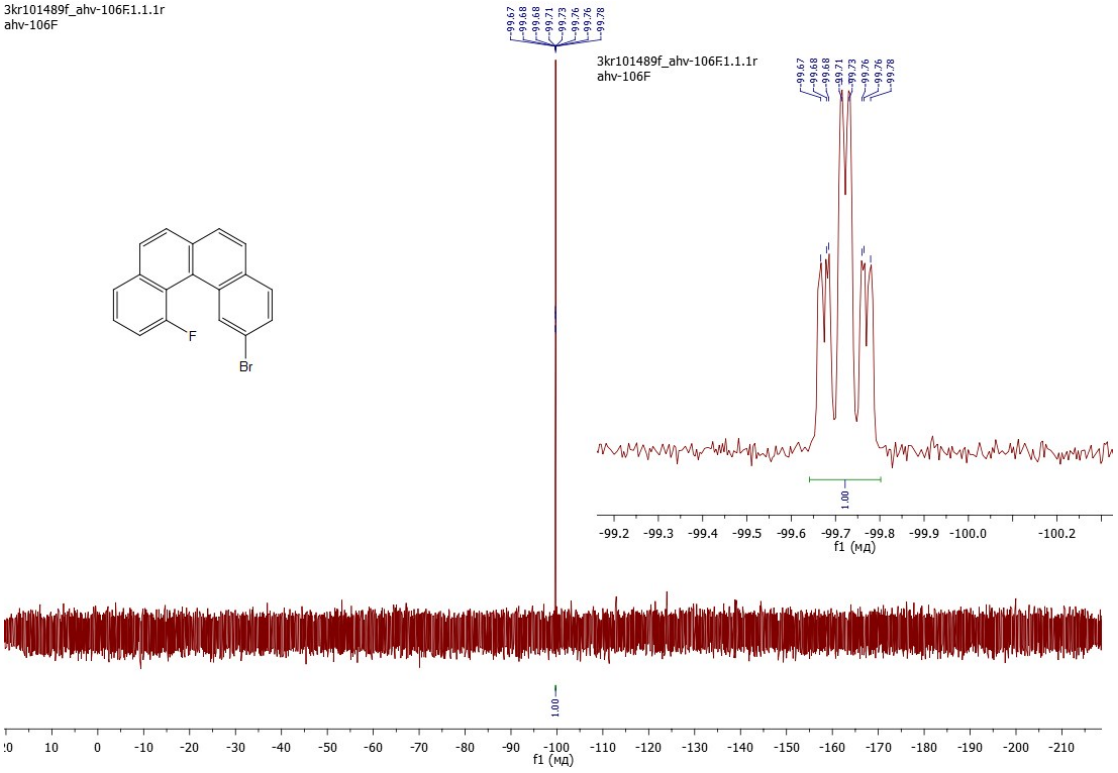


**Figure S17**. $^{19}F$ NMR (282 MHz, $CD_2Cl_2$) spectrum of 11-bromo-1-fluorobenzo[c] phenanthrene.

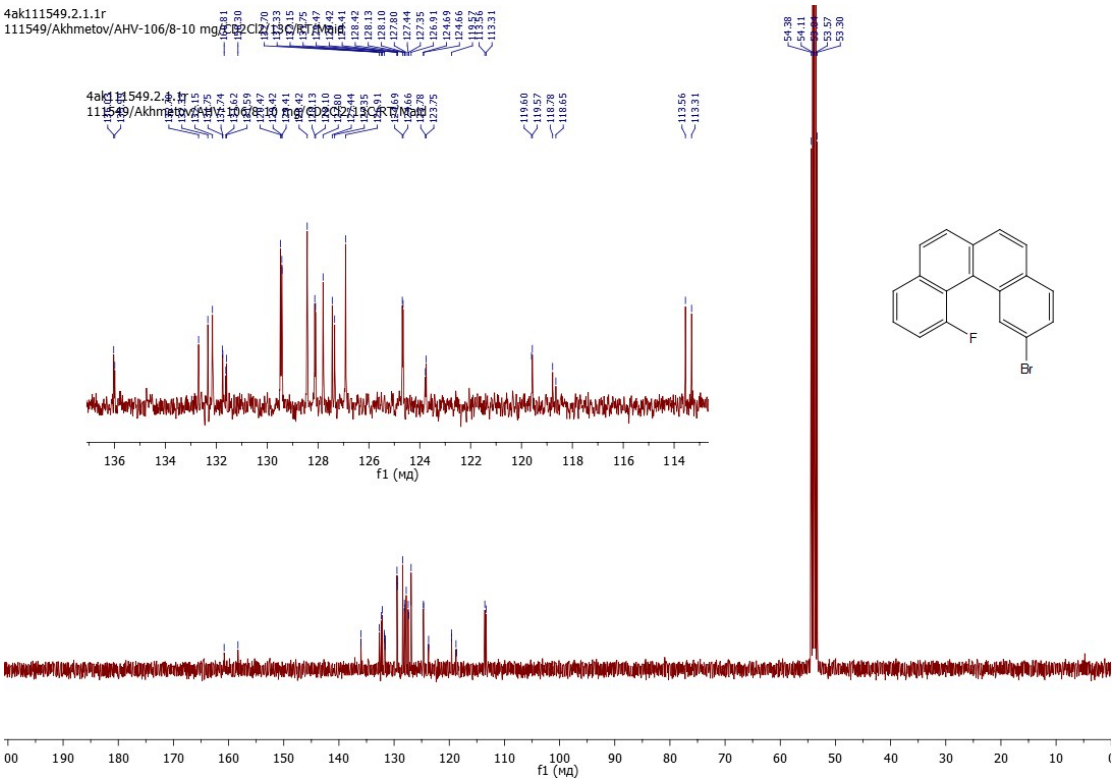


**Figure S18**. $^{13}C$ NMR (77 MHz, $CD_2Cl_2$) spectrum of 11-bromo-1-fluorobenzo[c] phenanthrene.

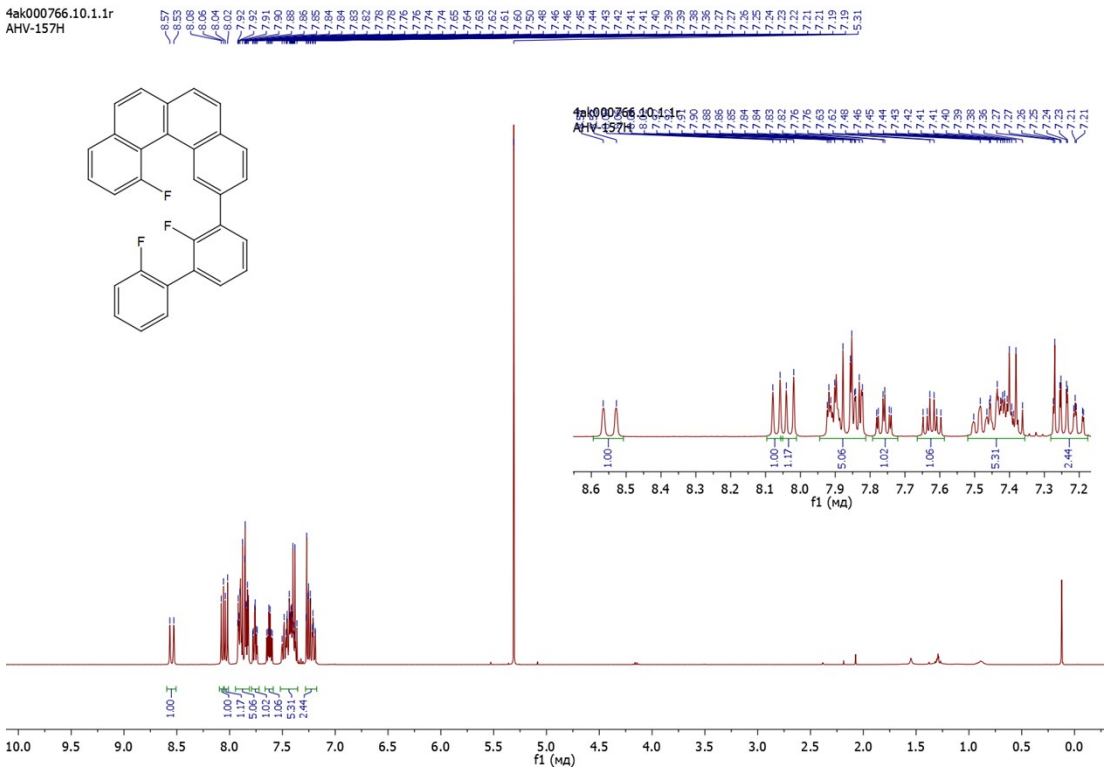


**Figure S19**. $^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of 11-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1-fluorobenzo[c]phenanthrene.

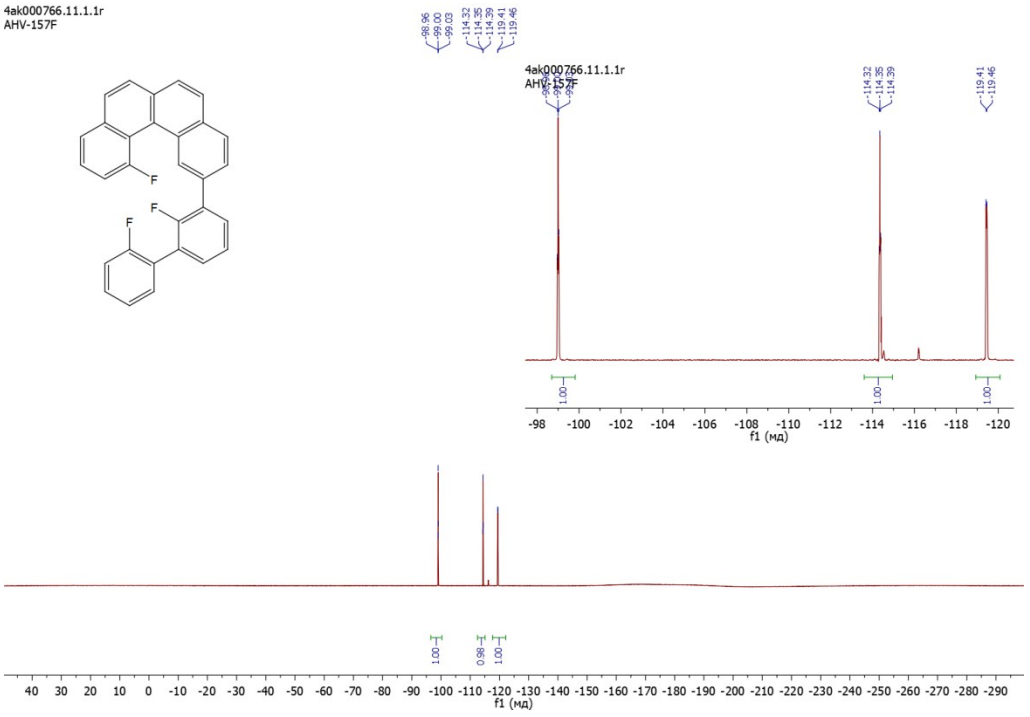


**Figure S20**. $^{19}F$ NMR (377 MHz, $CDCl_3$) spectrum of 11-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1-fluorobenzo[c]phenanthrene.

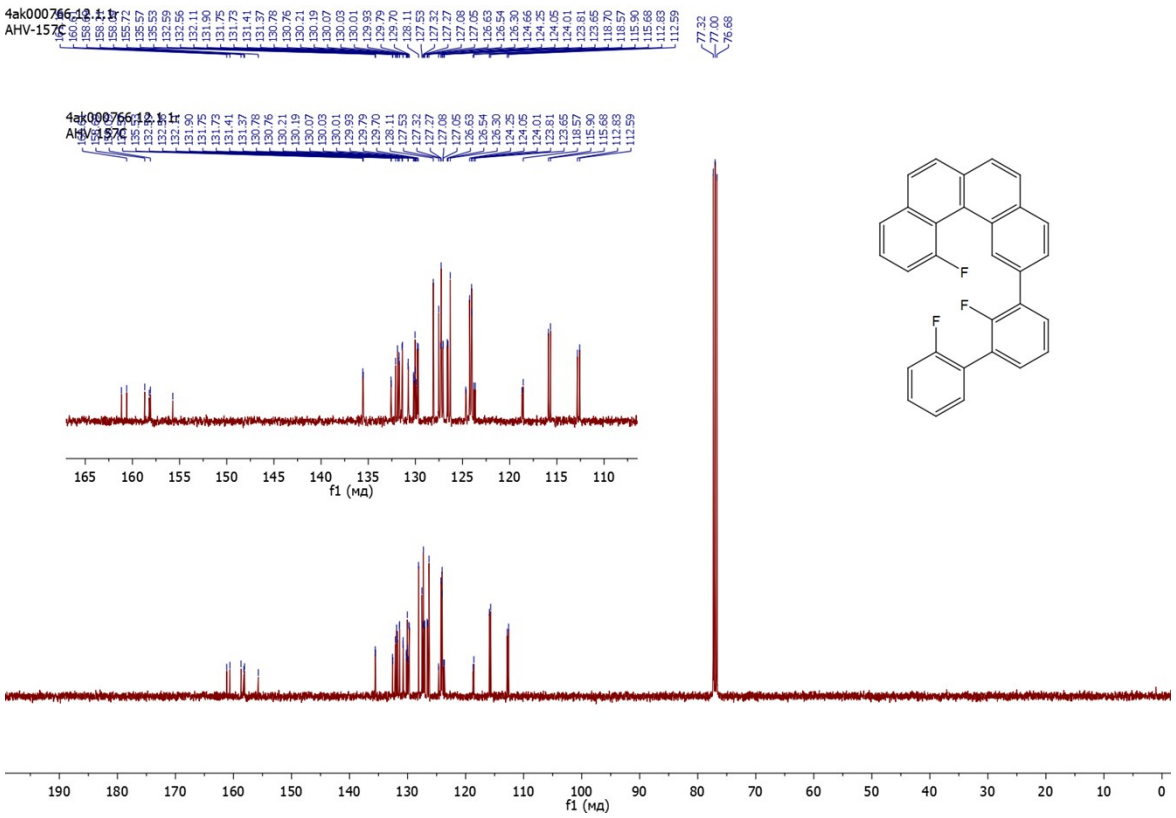


**Figure S21.** $^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of 11-(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1-fluorobenzo[c]phenanthrene.

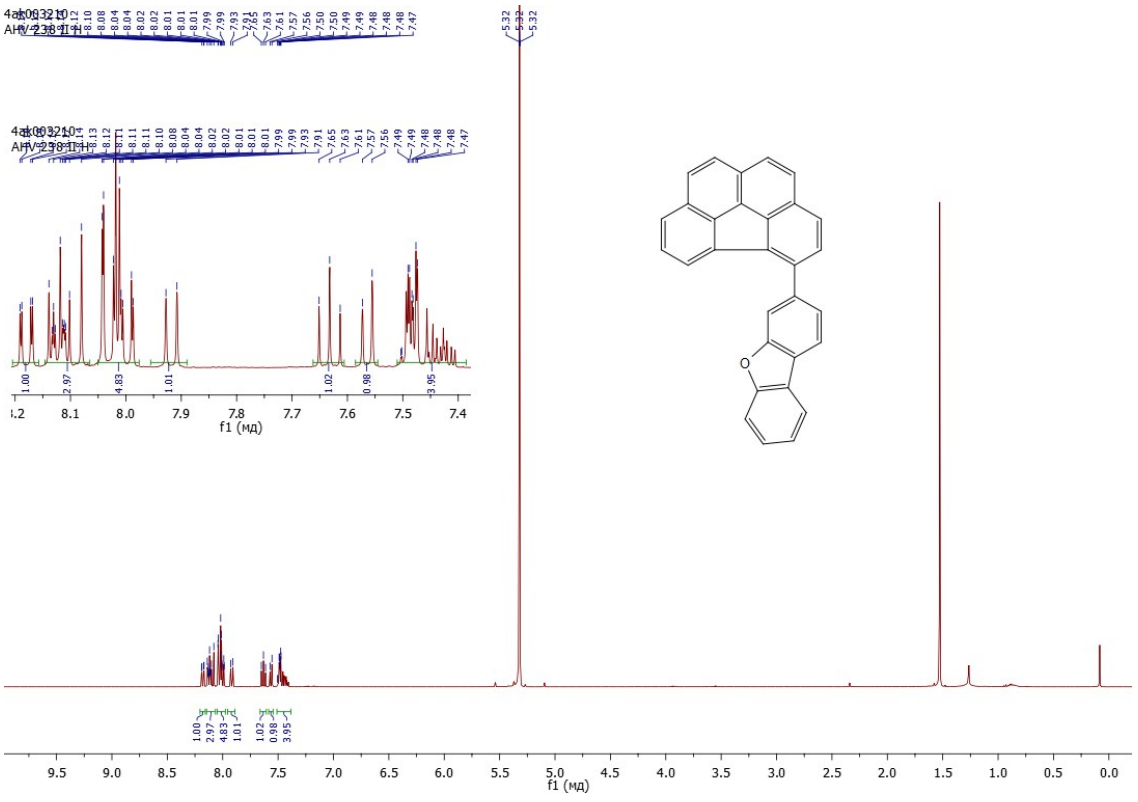


**Figure S22**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) spectrum of 4-(benzo[ghi]fluoranthen-5-yl)dibenzo[b,d]furan.

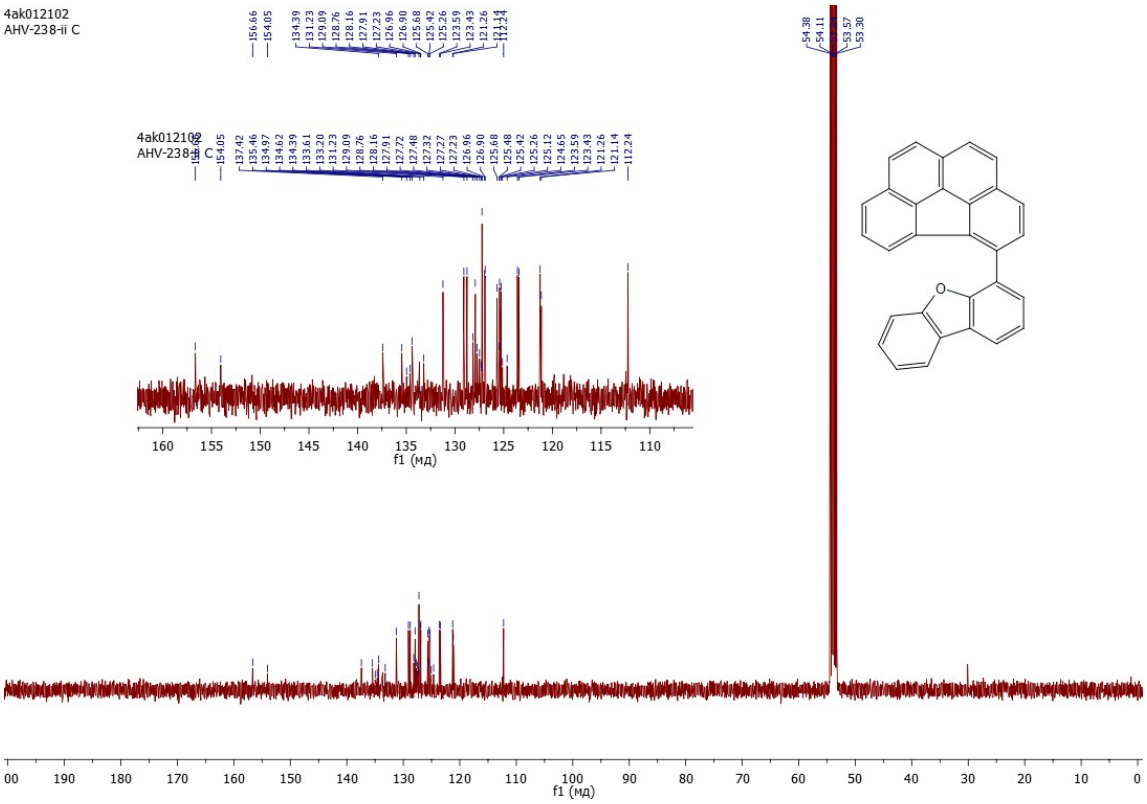


**Figure S23**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) spectrum of 4-(benzo[ghi]fluoranthen-5-yl)dibenzo[b,d]furan.

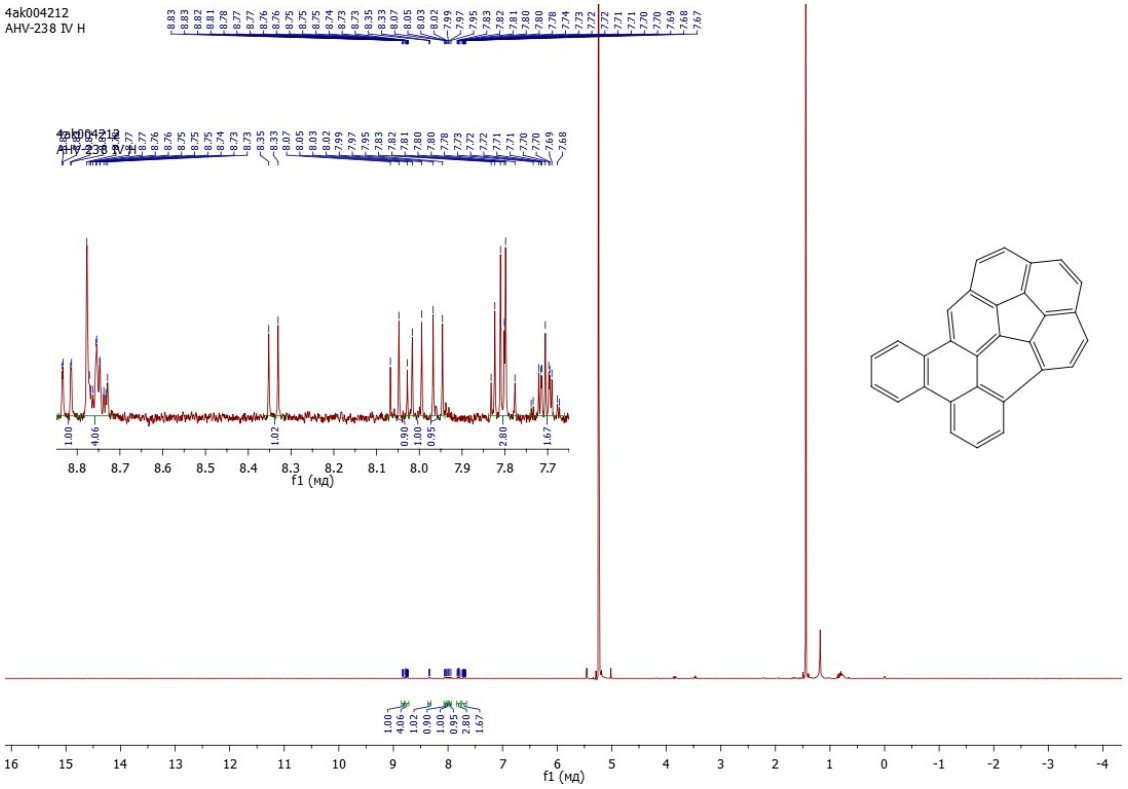


**Figure S24**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) spectrum of Benzo[fg]benzo[4,5]fluoreno[2,1,9,8-opqra]tetracene.

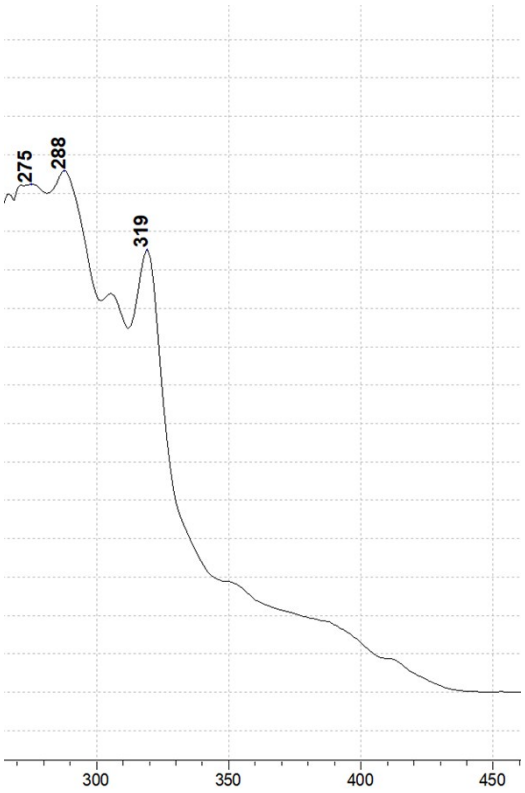


**Figure S25.** UV-Vis spectrum of benzo[*c*]diindeno[1,2,3,4-*ghij*:1',2',3',4'-*tuva*]picene (DCM-MeOH 1-1).

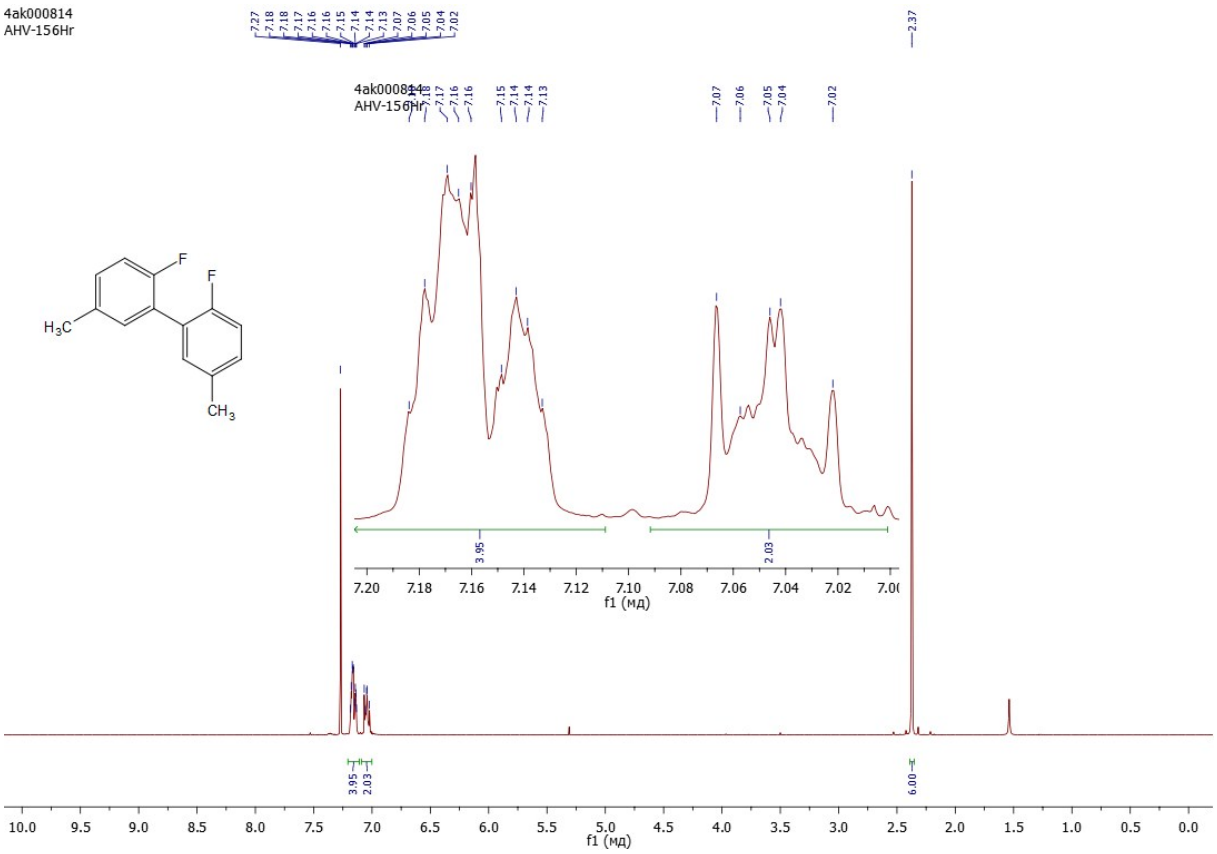


**Figure S26**. $^{1}$H NMR (400 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-dimethyl-1,1'-biphenyl.

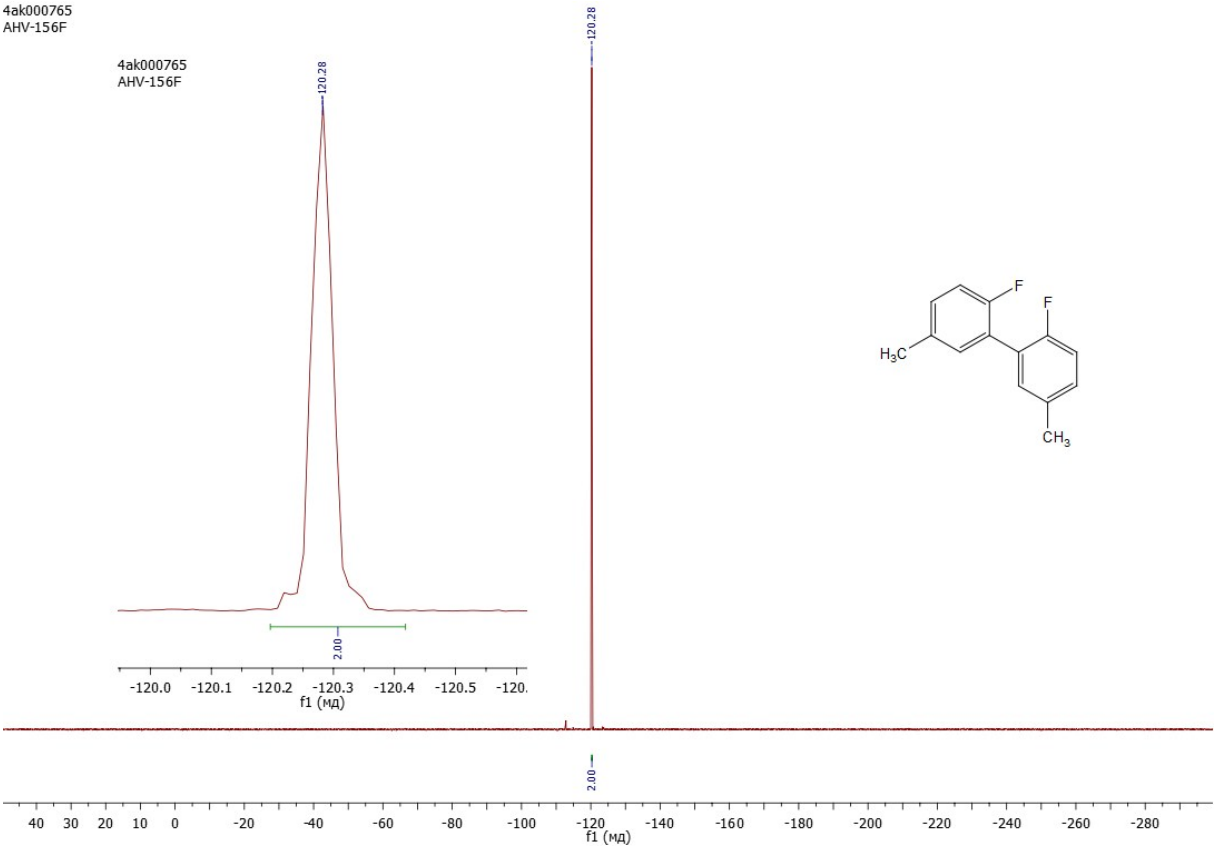


**Figure S27**. $^{19}F$ NMR (377 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-dimethyl-1,1'-biphenyl.

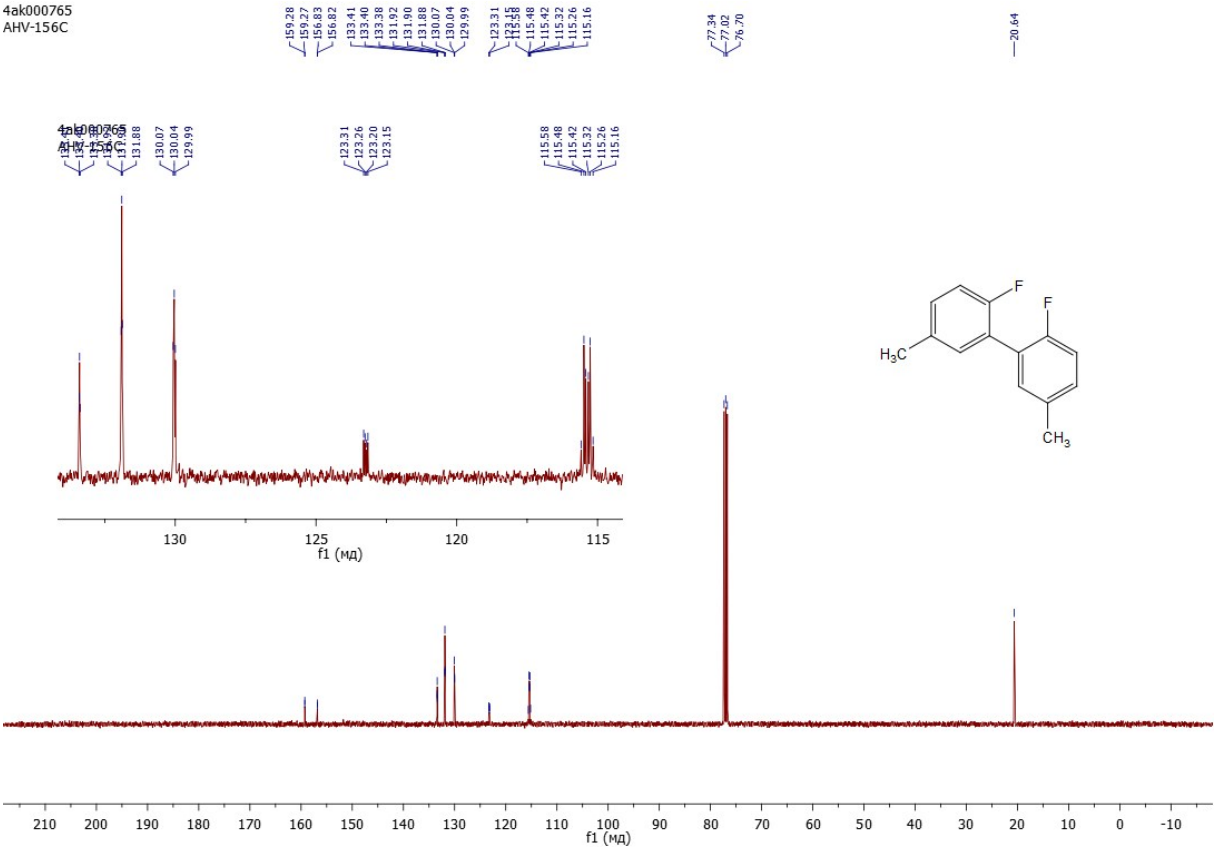


**Figure S28**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-dimethyl-1,1'-biphenyl.

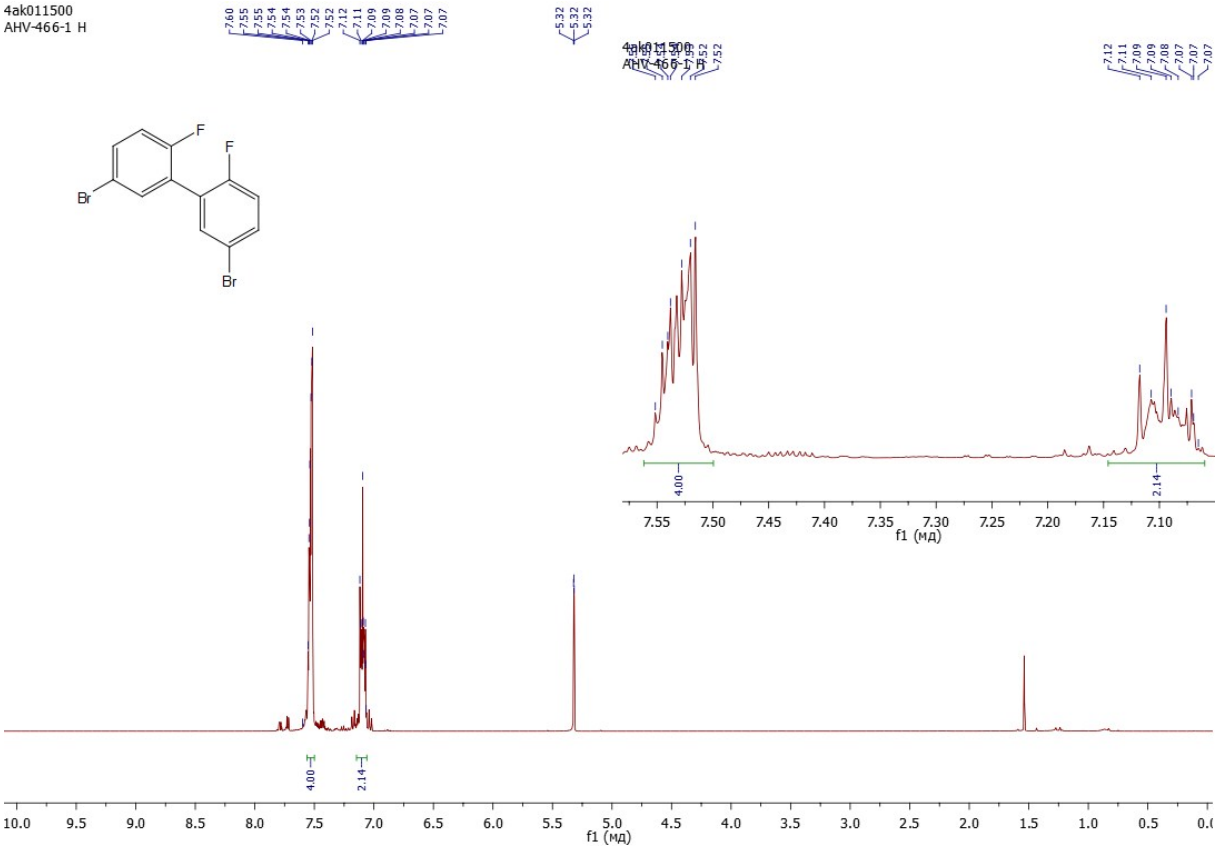


**Figure S29**. $^{1}$H NMR (400 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-dibromo-1,1'-biphenyl.

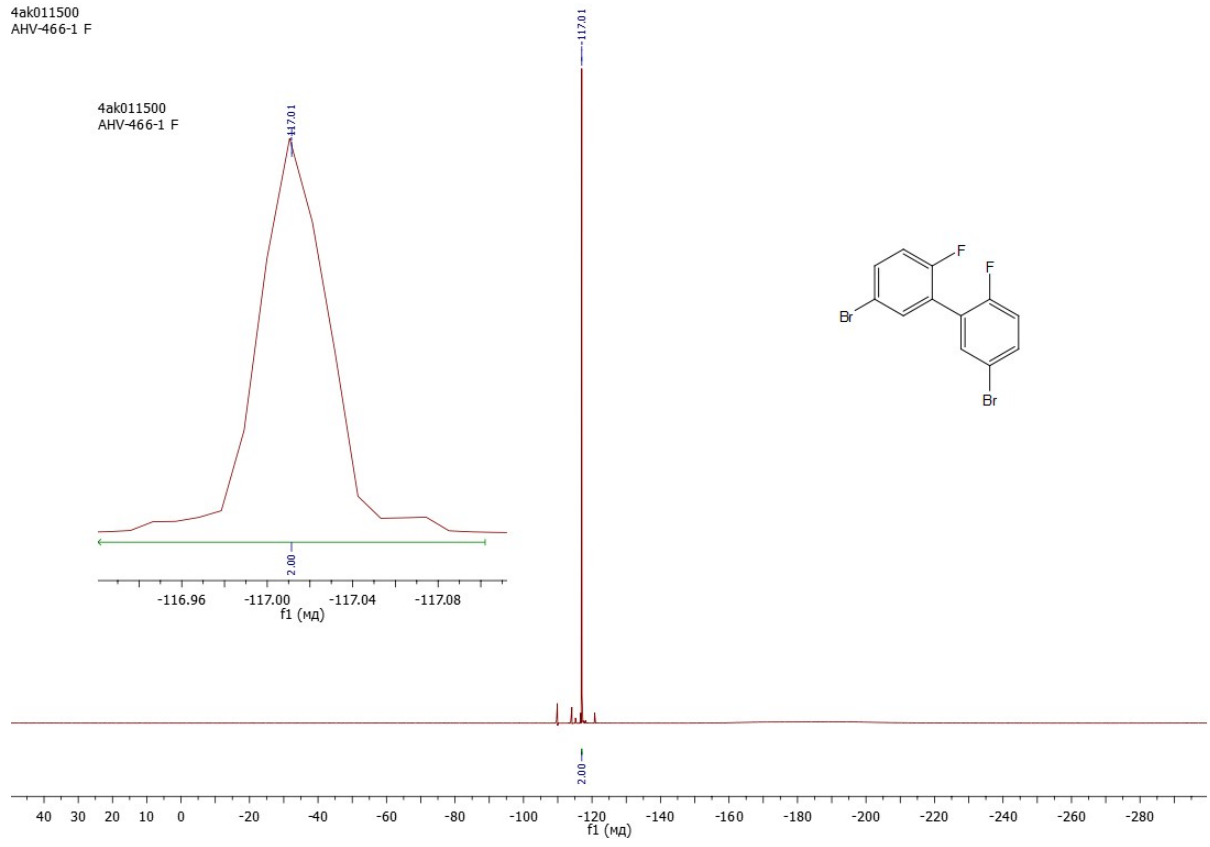


**Figure S30**. $^{19}$F NMR (377 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-dibromo-1,1'-biphenyl.

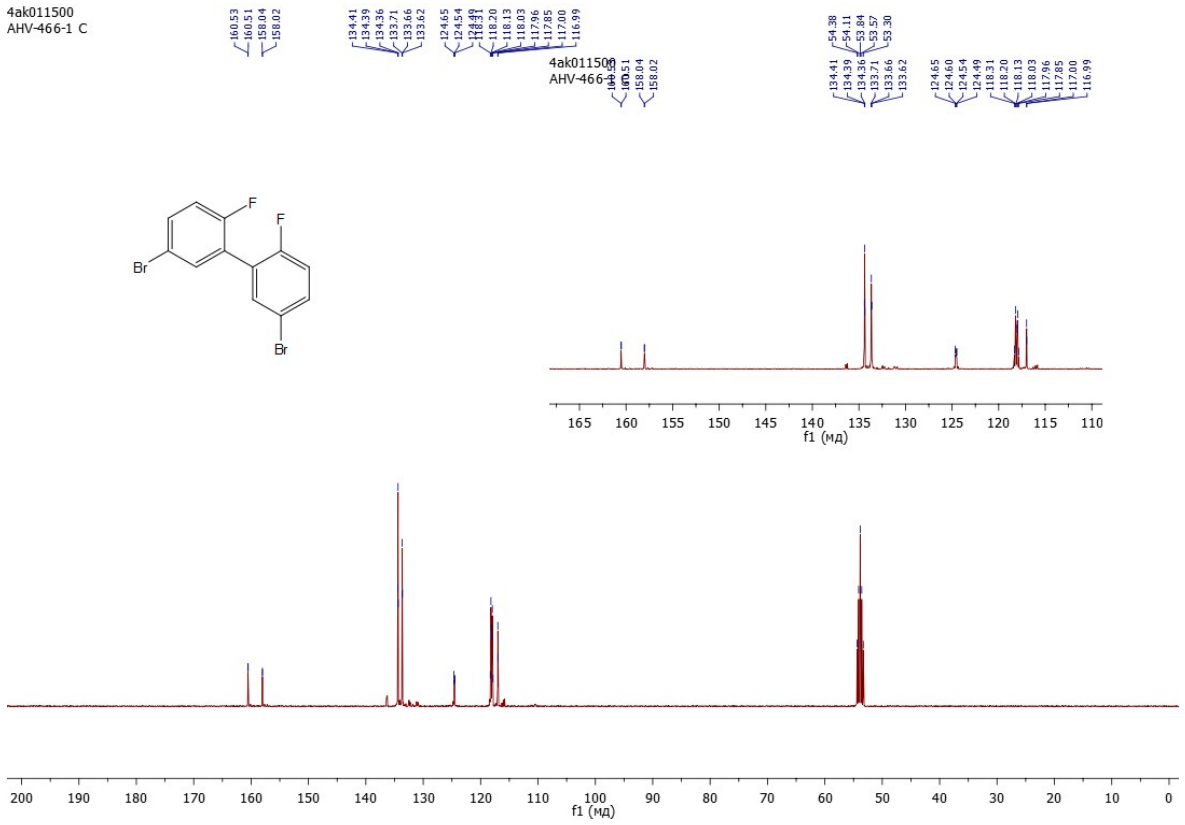


**Figure S31**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-dibromo-1,1'-biphenyl.

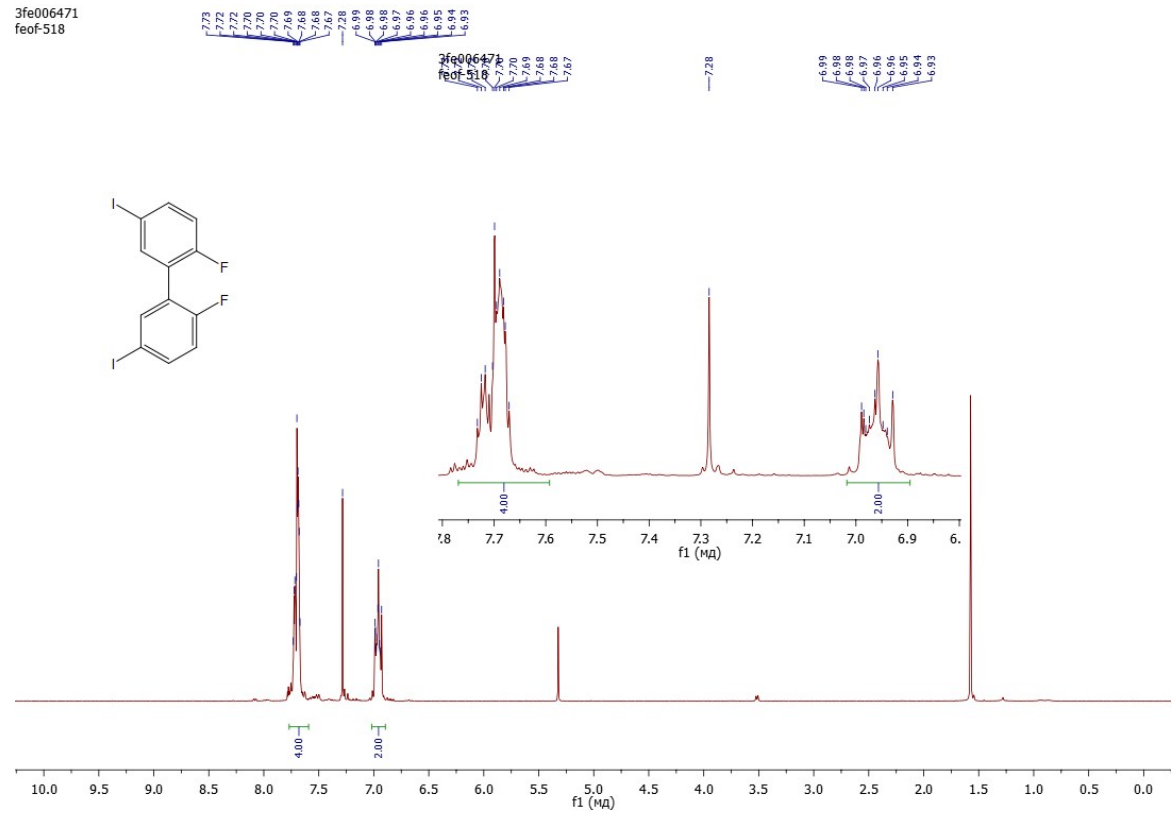


**Figure S32**. $^{1}H$ NMR (300 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-diiododo-1,1'-biphenyl.

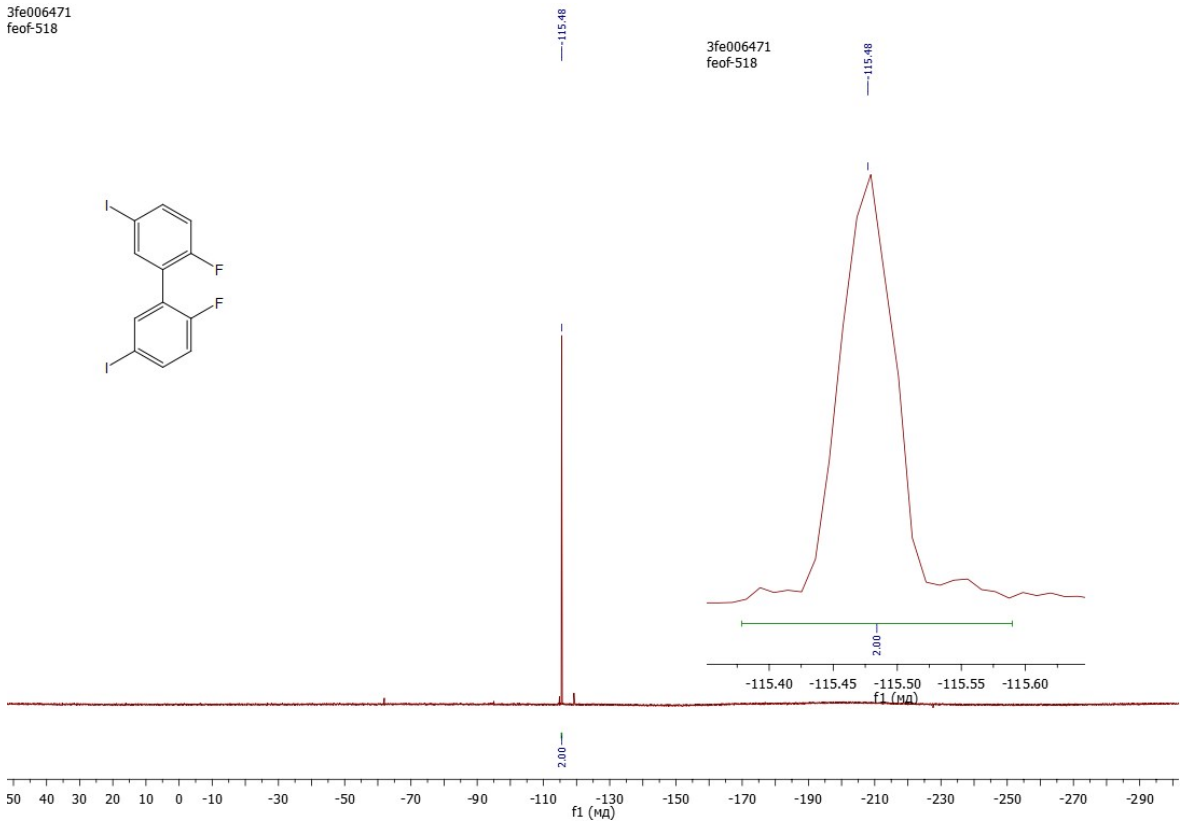


**Figure S33**. $^{19}F$ NMR (283 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-diiododo-1,1'-biphenyl.

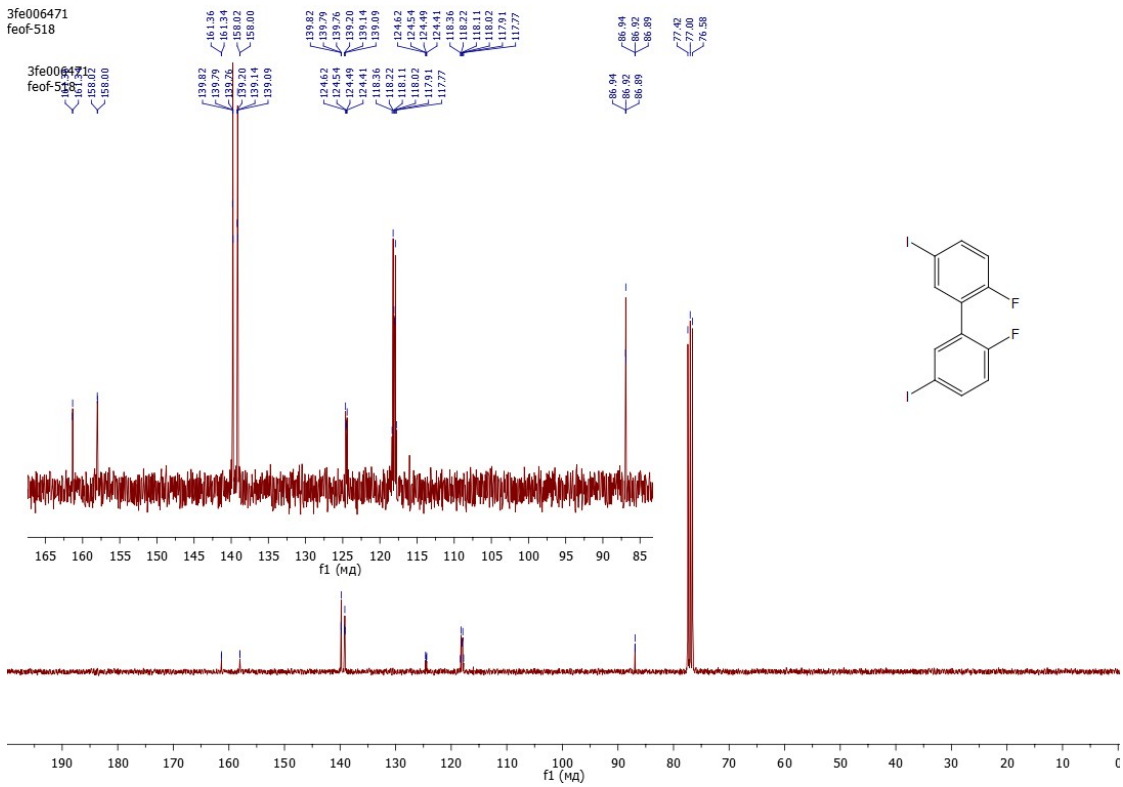


**Figure S34**. $^{13}C$ NMR (76 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-diiododo-1,1'-biphenyl.

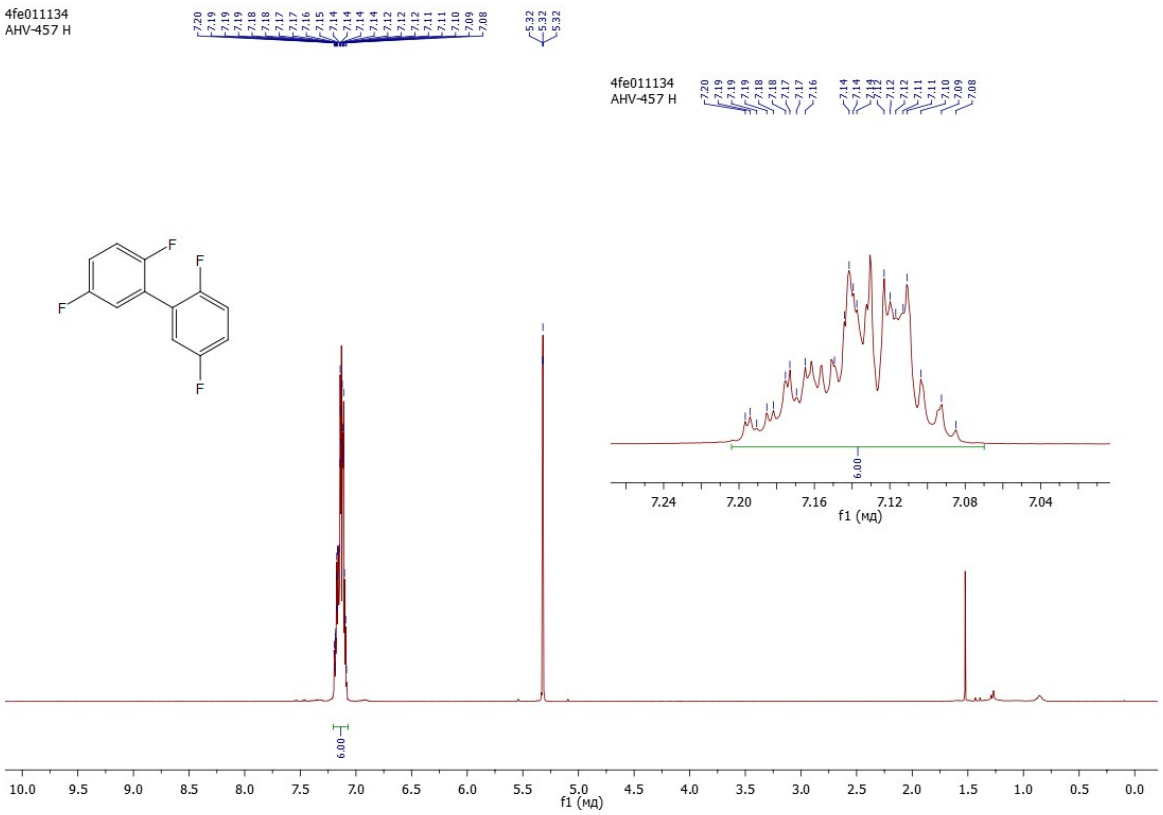


**Figure S35**. $^{1}$H NMR (400 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-difluoro-1,1'-biphenyl.

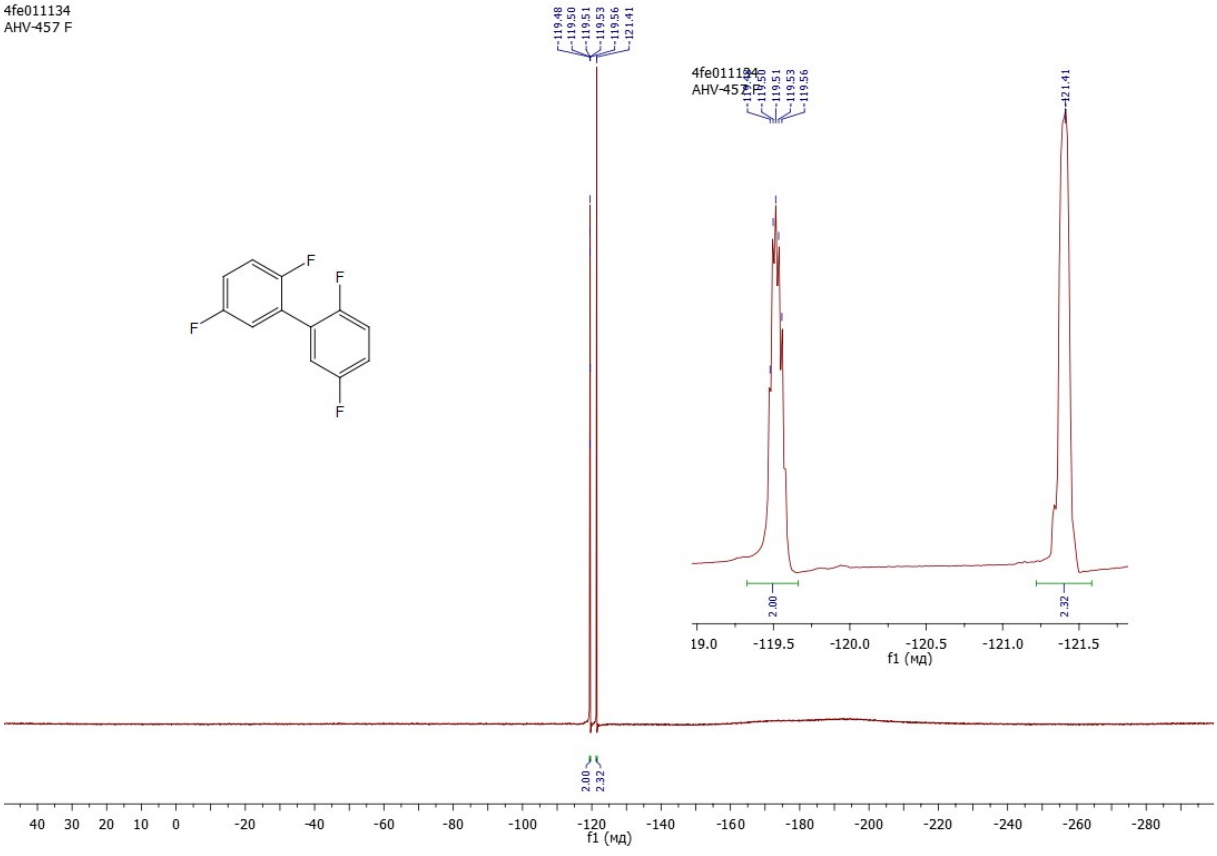


**Figure S36**. $^{19}$F NMR (377 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-difluoro-1,1'-biphenyl.

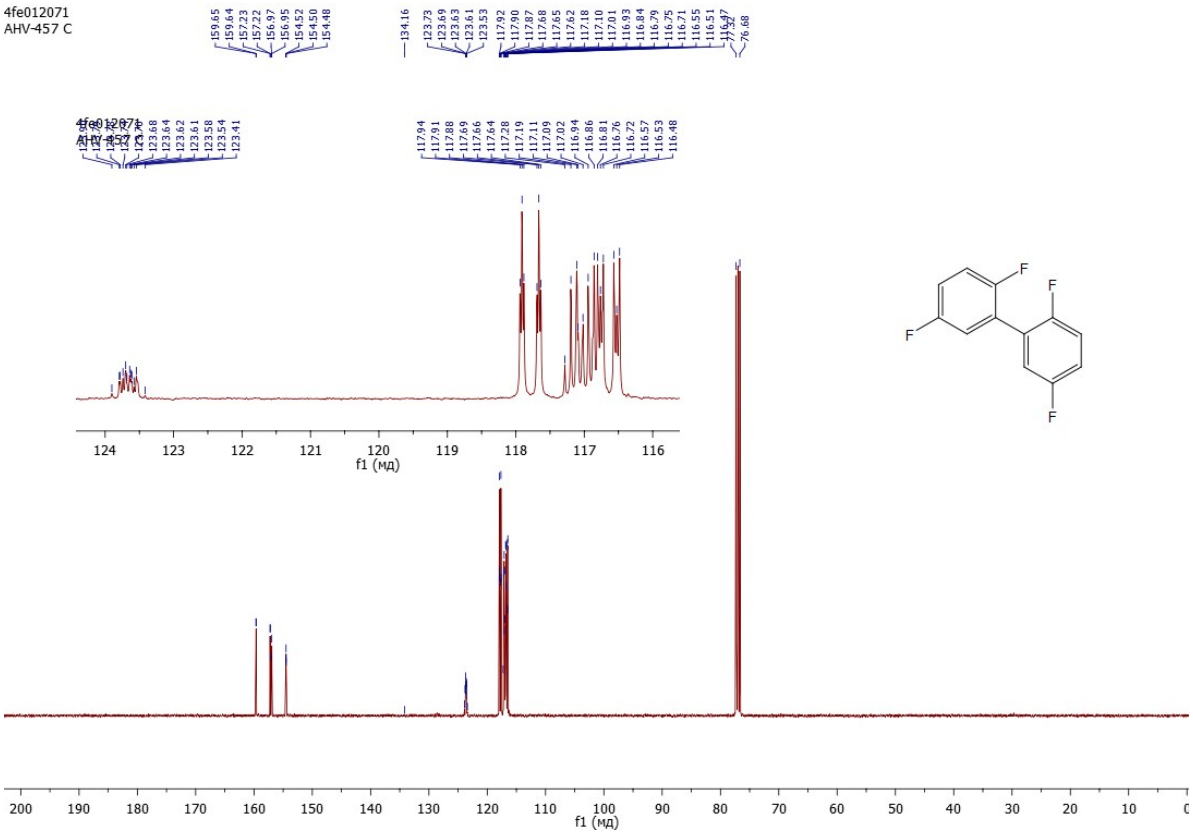


**Figure S37**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2,2'-difluoro-5,5'-difluoro-1,1'-biphenyl.

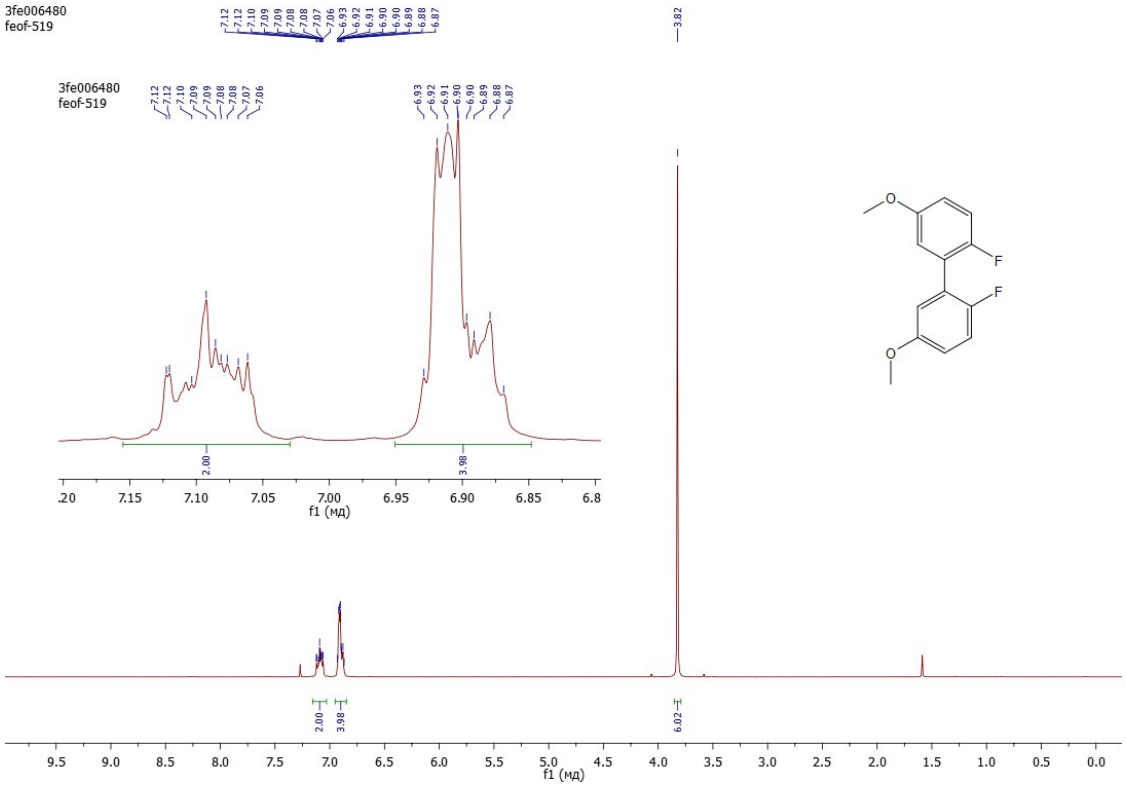


**Figure S38**. $^{1}H$ NMR (300 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-methoxy-1,1'-biphenyl.

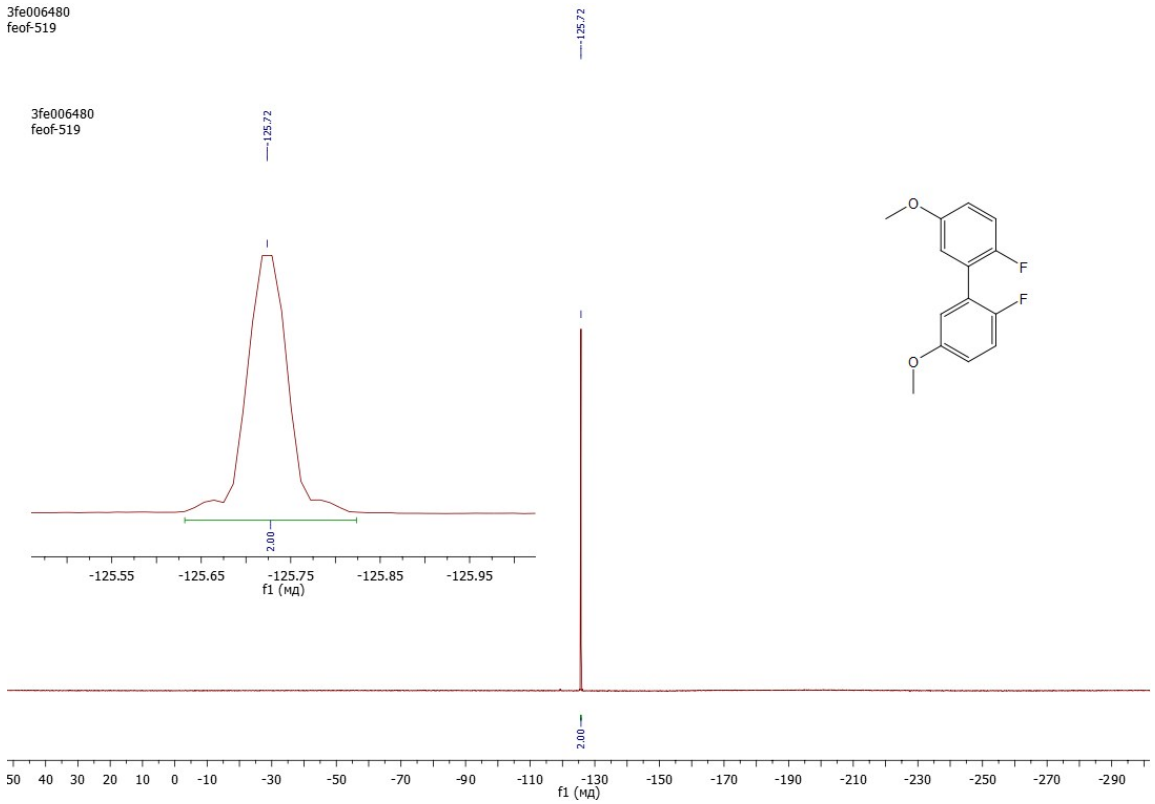


**Figure S39**. $^{19}F$ NMR (283 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-methoxy-1,1'-biphenyl.

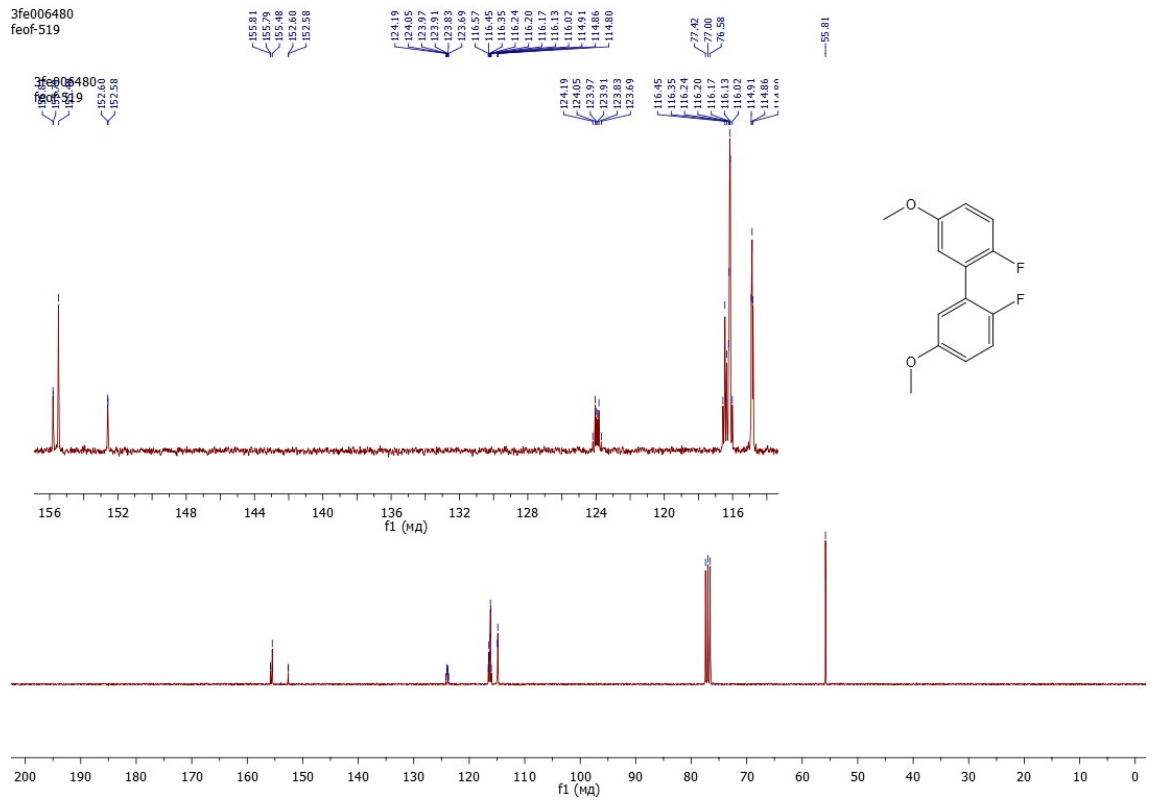


**Figure S40**. $^{13}C$ NMR (76 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-methoxy-1,1'-biphenyl.

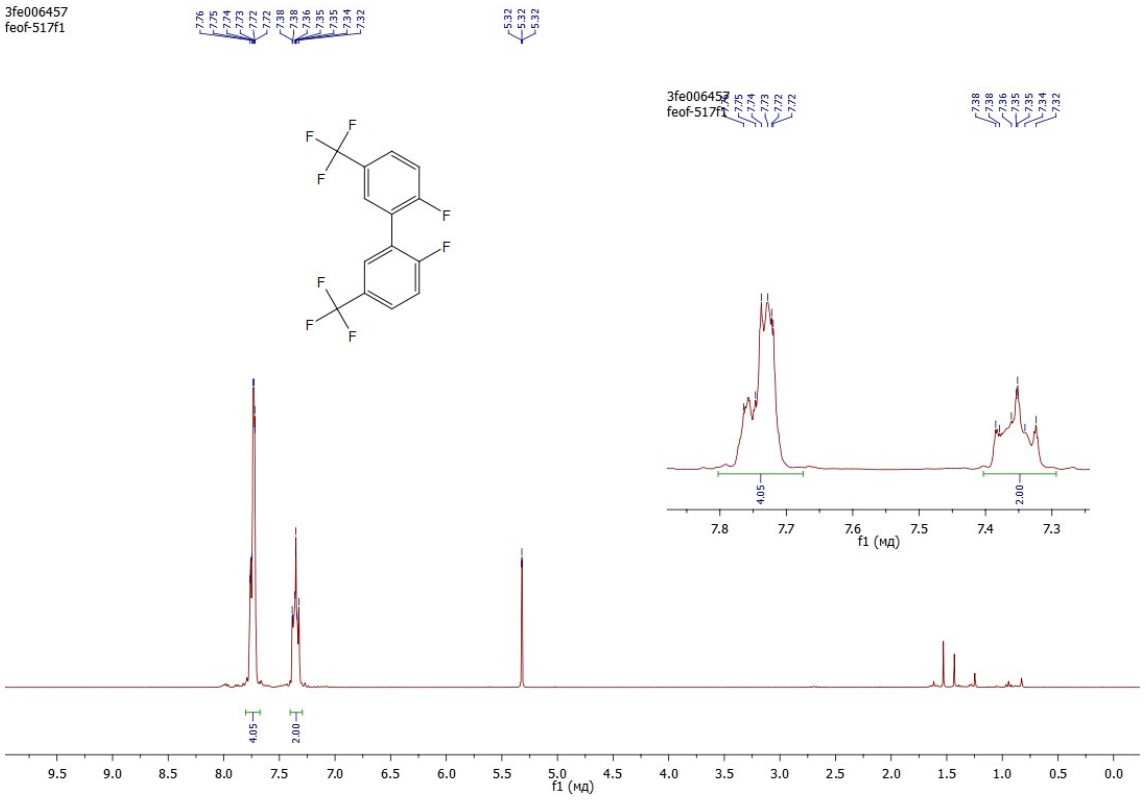


**Figure S41**. $^{1}H$ NMR (300 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-bis(trifluoromethyl)-1,1'-biphenyl

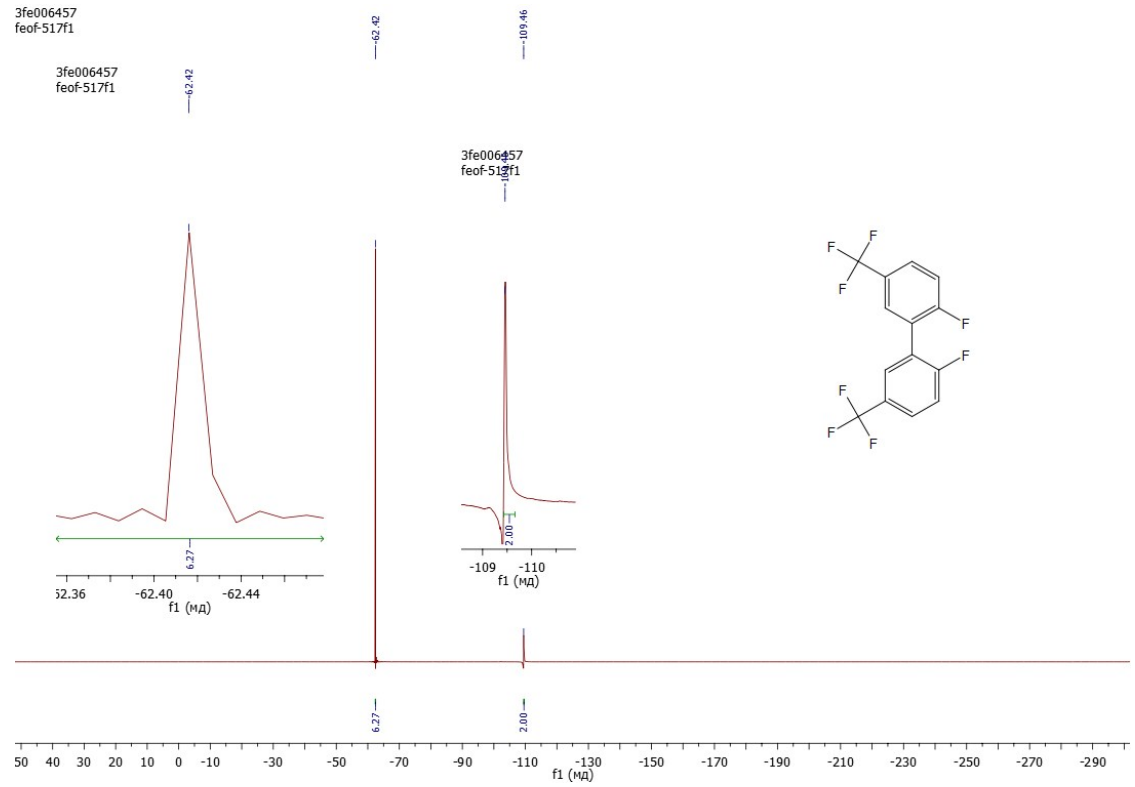


**Figure S42**. $^{19}F$ NMR (283 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-bis(trifluoromethyl)-1,1'-biphenyl

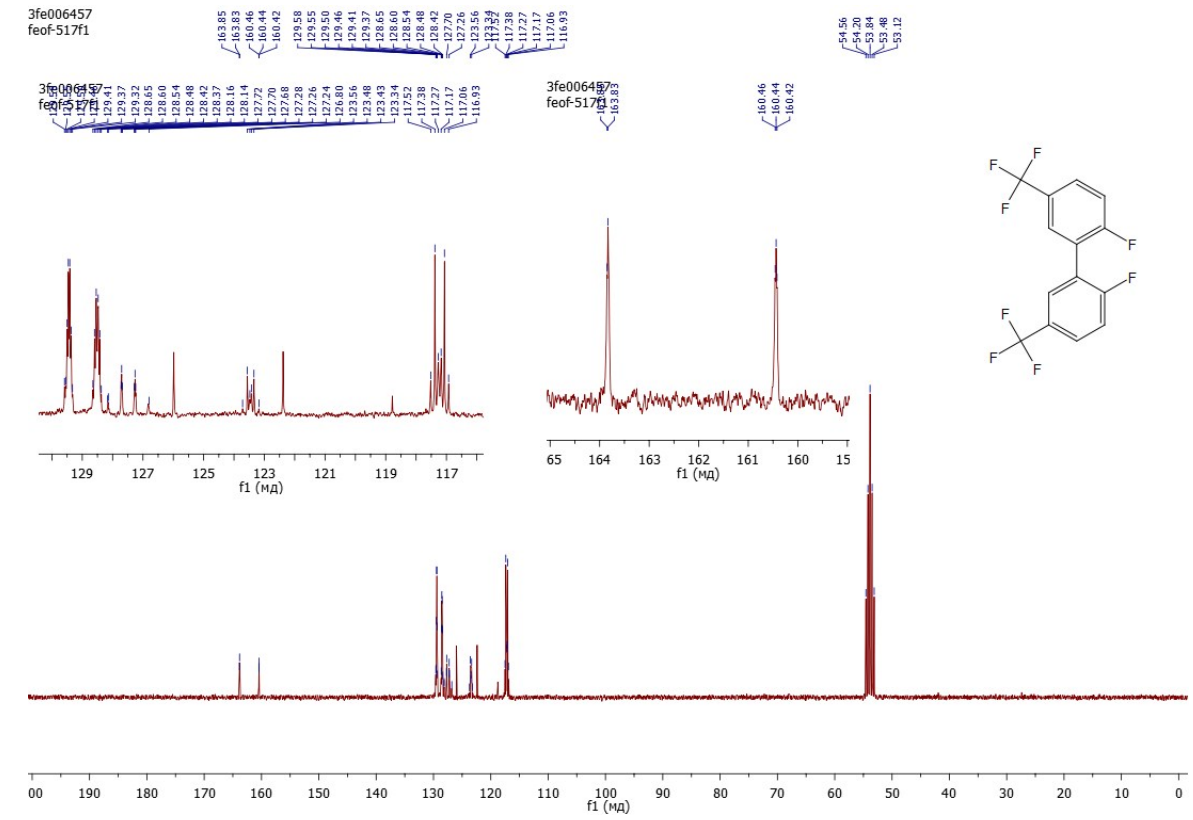


**Figure S43**. $^{13}C$ NMR (76 MHz, $CDCl_3$) of 2,2'-difluoro-5,5'-bis(trifluoromethyl)-1,1'-biphenyl

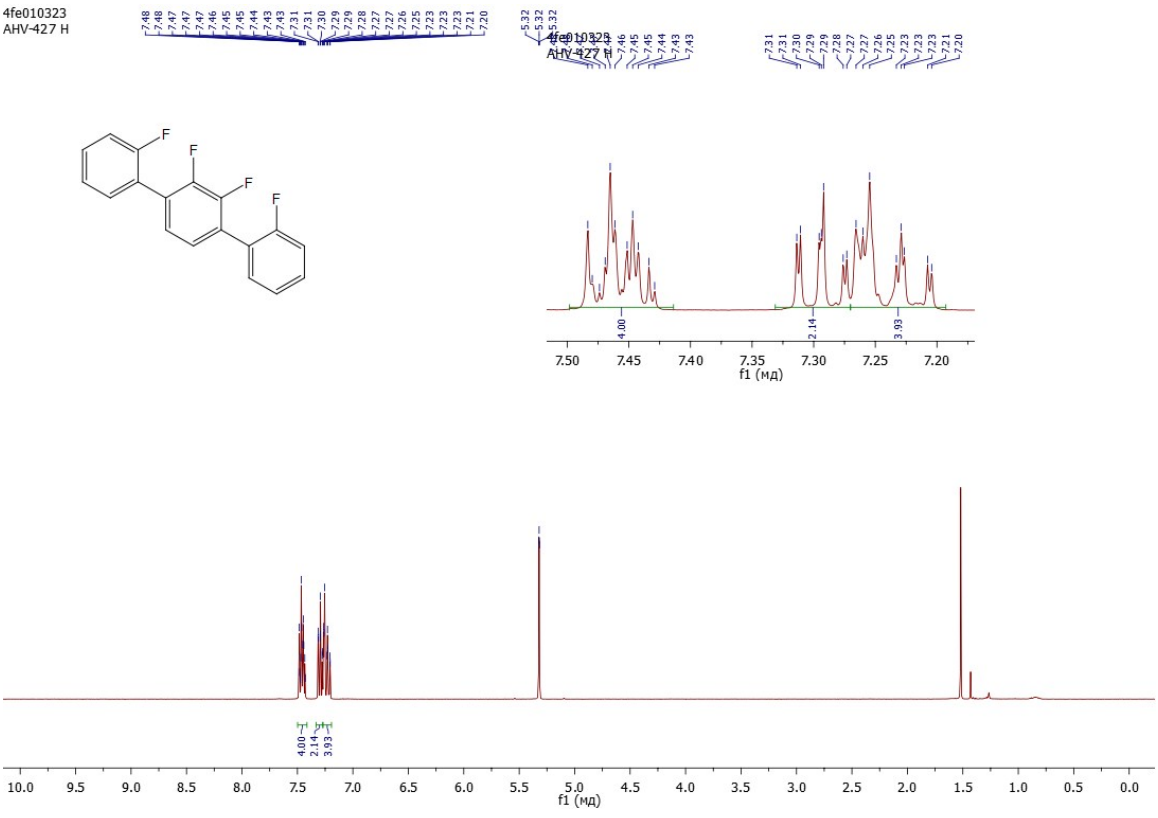


**Figure S44**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of 2,2',2",3'-tetrafluoro-1,1':4',1"-terphenyl.

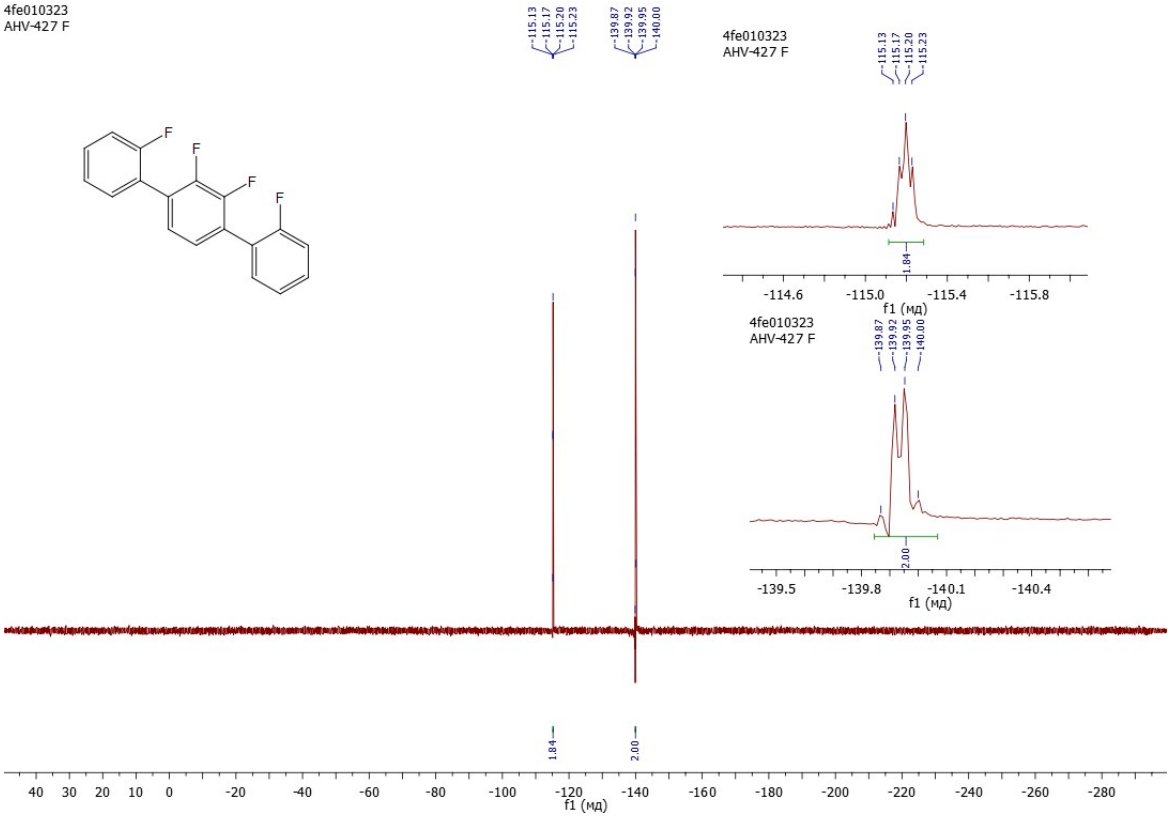


**Figure S45**. $^{19}F$ NMR (377 MHz, $CD_2Cl_2$) of 2,2',2",3'-tetrafluoro-1,1':4',1"-terphenyl.

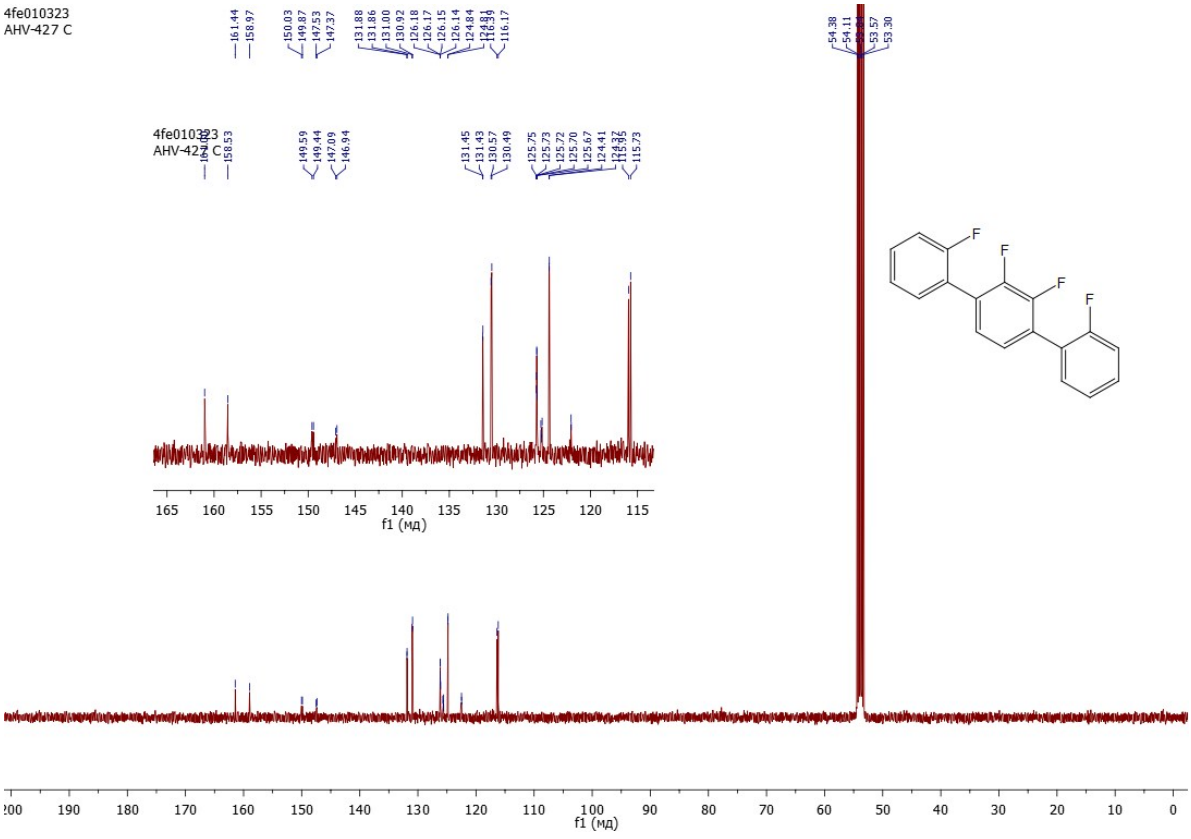


**Figure S46**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2,2',2",3'-tetrafluoro-1,1':4',1"-terphenyl.

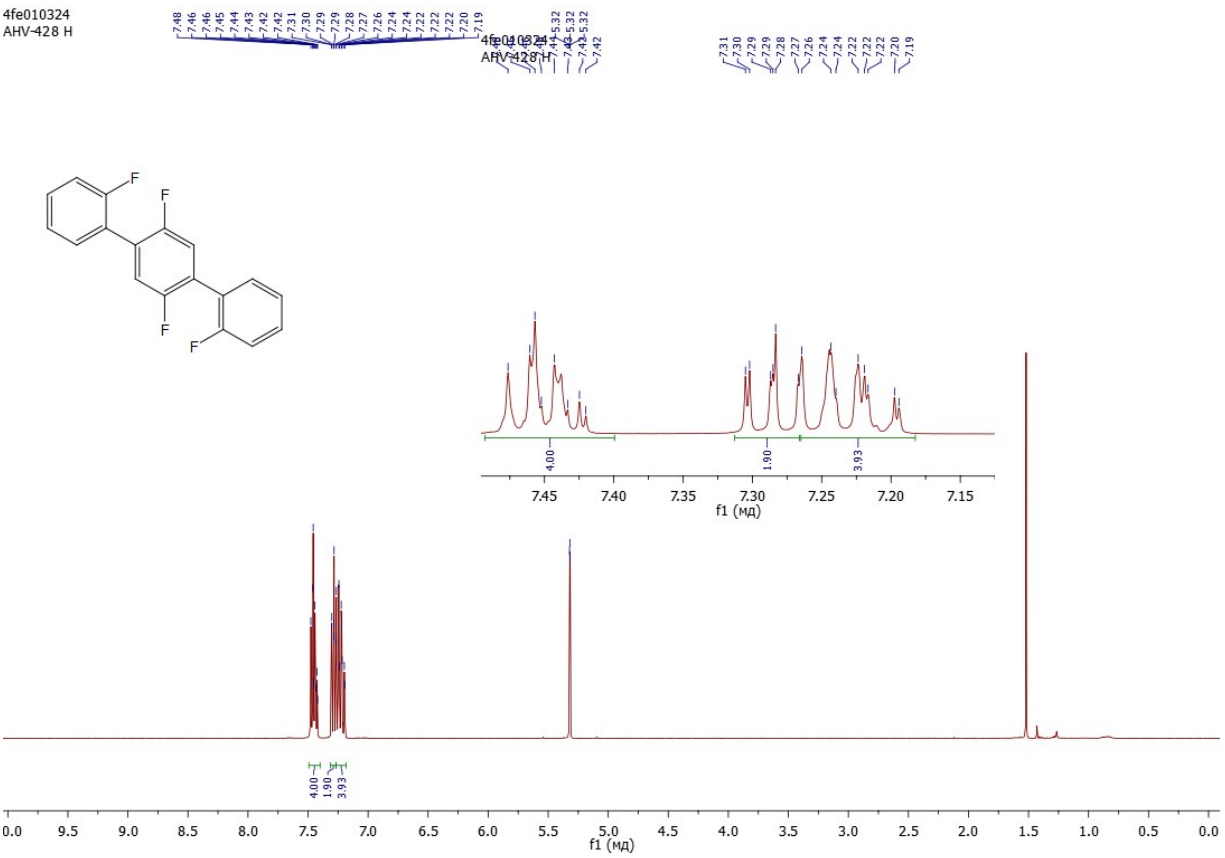


**Figure S47**. $^{1}$H NMR (400 MHz, $CD_2Cl_2$) of 2,2',2",5'-tetrafluoro-1,1':4',1"-terphenyl.

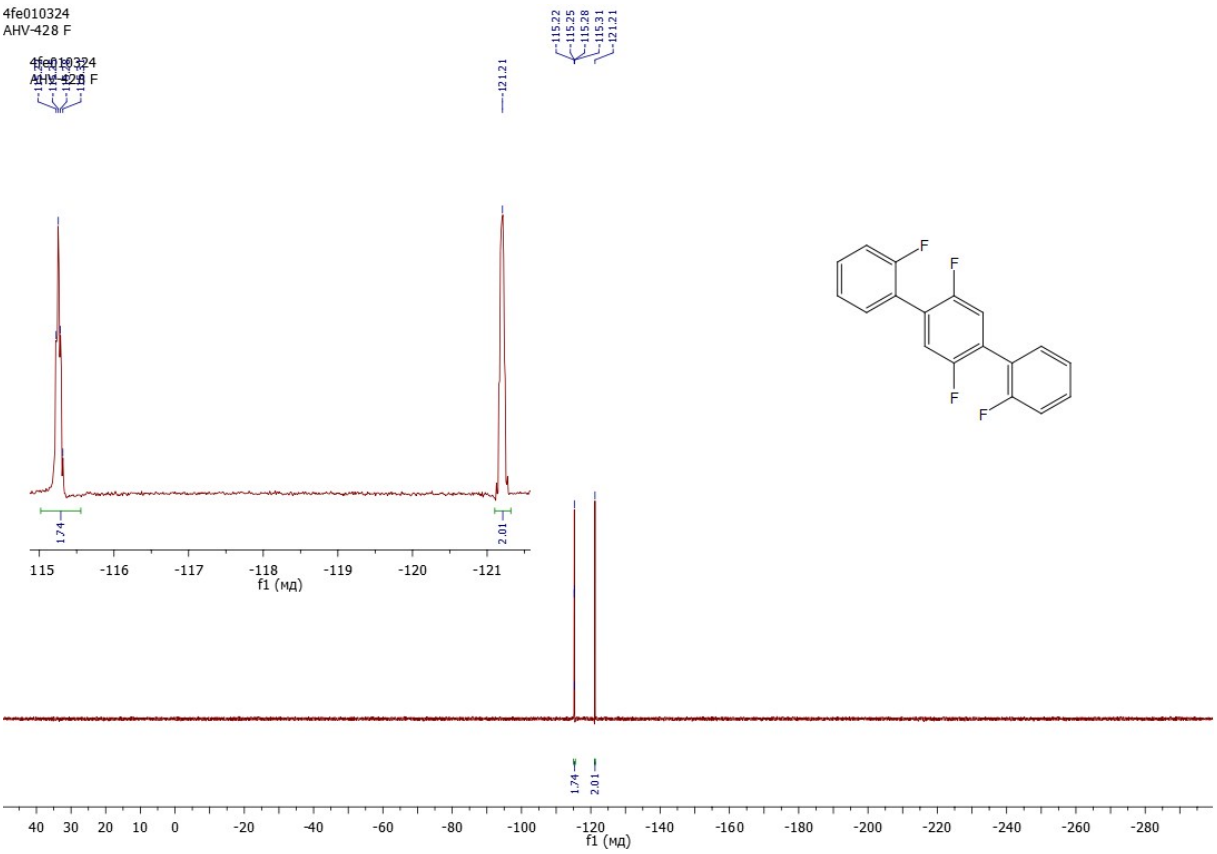


**Figure S48**. $^{19}$F NMR (377 MHz, $CD_2Cl_2$) of 2,2',2",5'-tetrafluoro-1,1':4',1"-terphenyl.

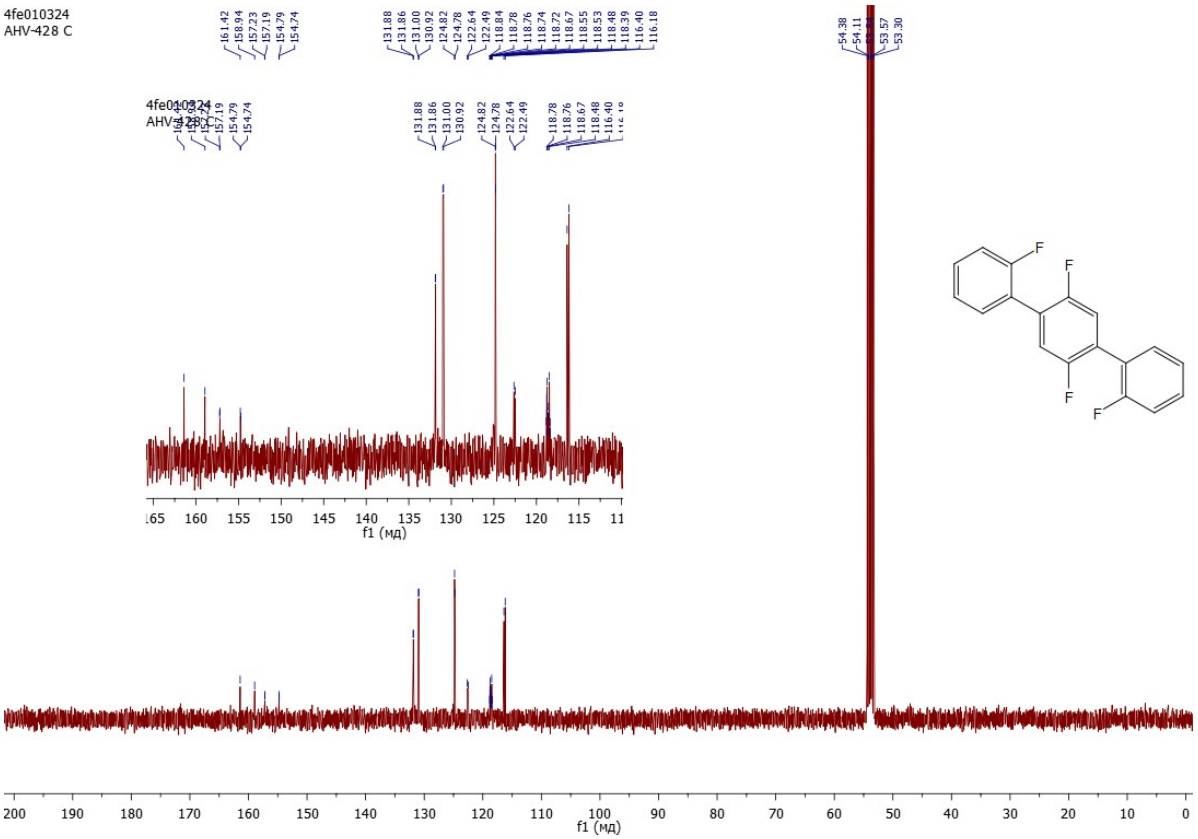


**Figure S49**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2,2',2",5'-tetrafluoro-1,1':4',1"-terphenyl.

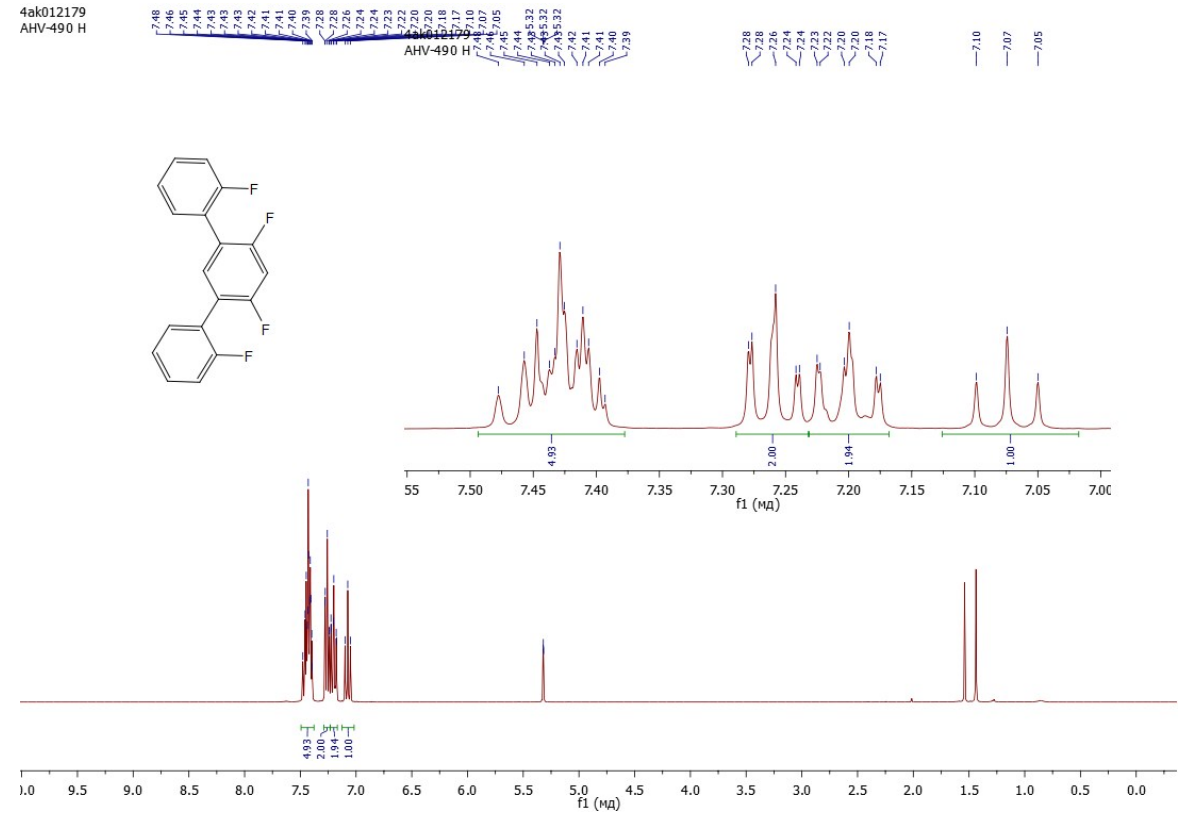


**Figure S50**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of 2,2",4',6'-tetrafluoro-1,1':3',1"-terphenyl.

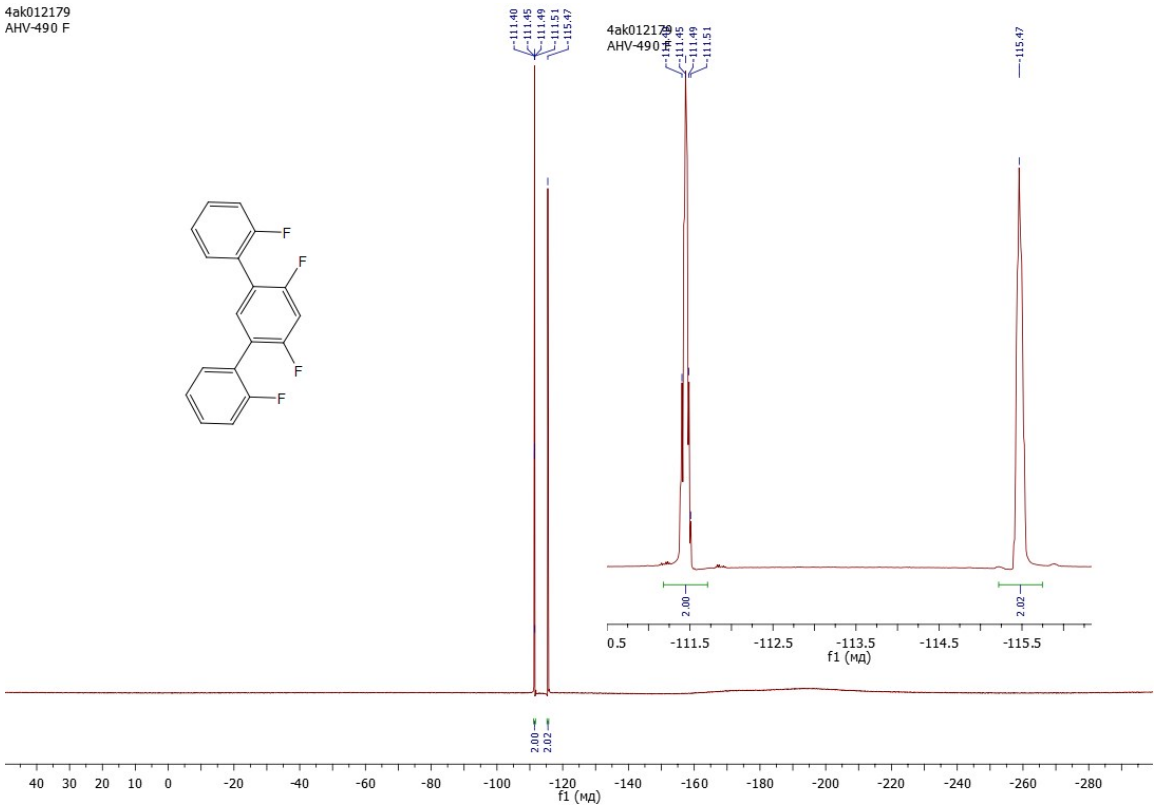


**Figure S51**. $^{19}F$ NMR (377 MHz, $CD_2Cl_2$) of 2,2",4',6'-tetrafluoro-1,1':3',1"-terphenyl.

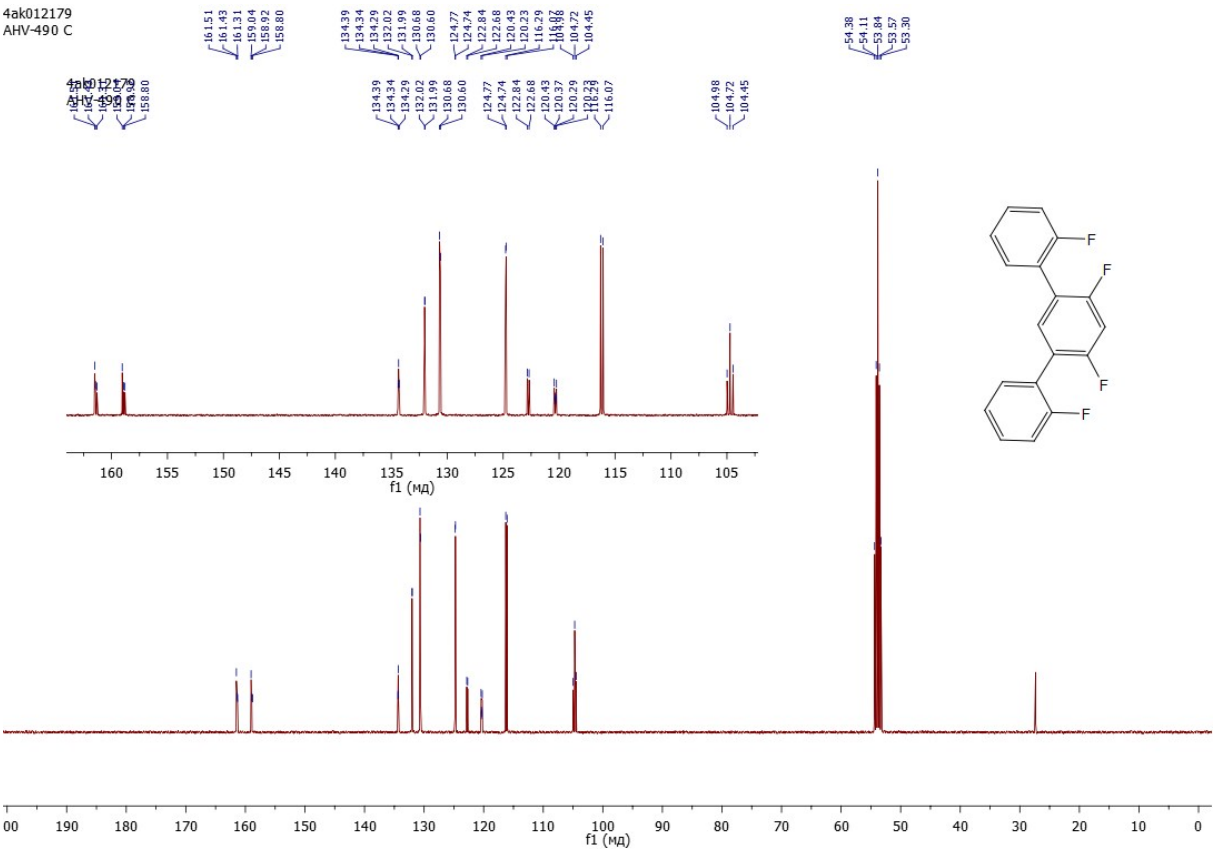


**Figure S52**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2,2",4',6'-tetrafluoro-1,1':3',1"-terphenyl.

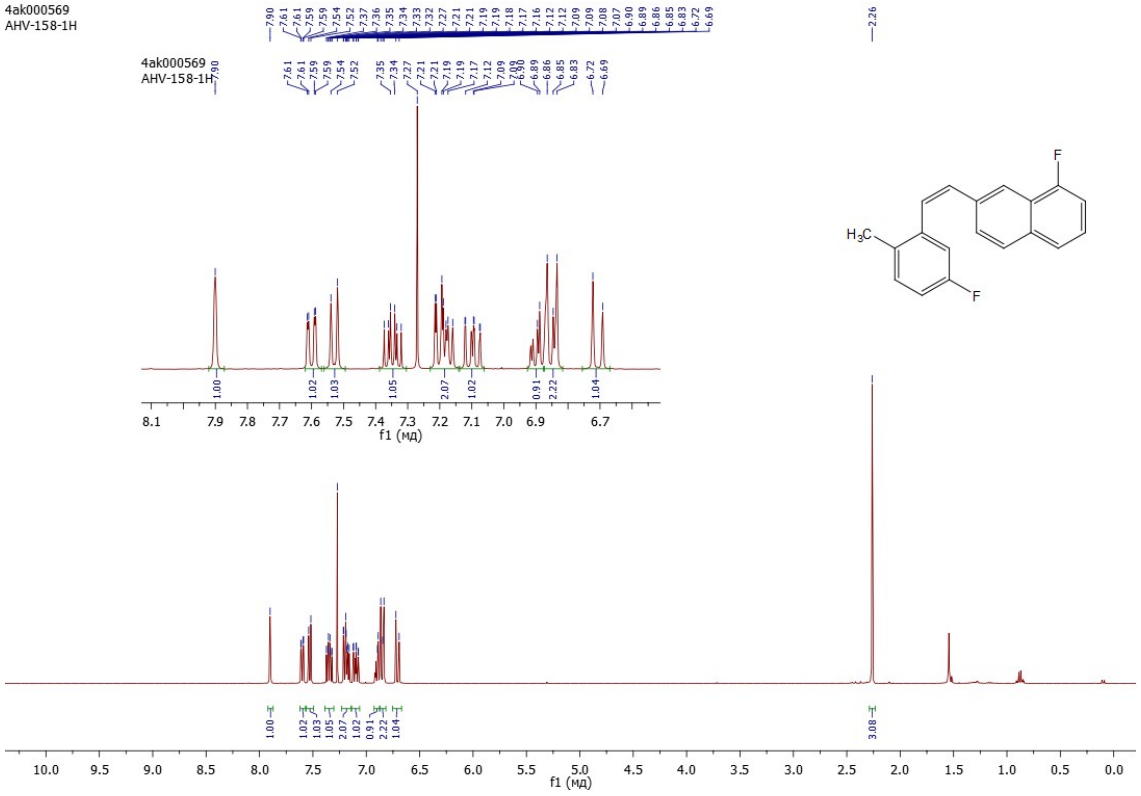


**Figure S53**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of (*Z*)- 1-fluoro-7-(5-fluoro-2-methylstyryl) naphthalene.

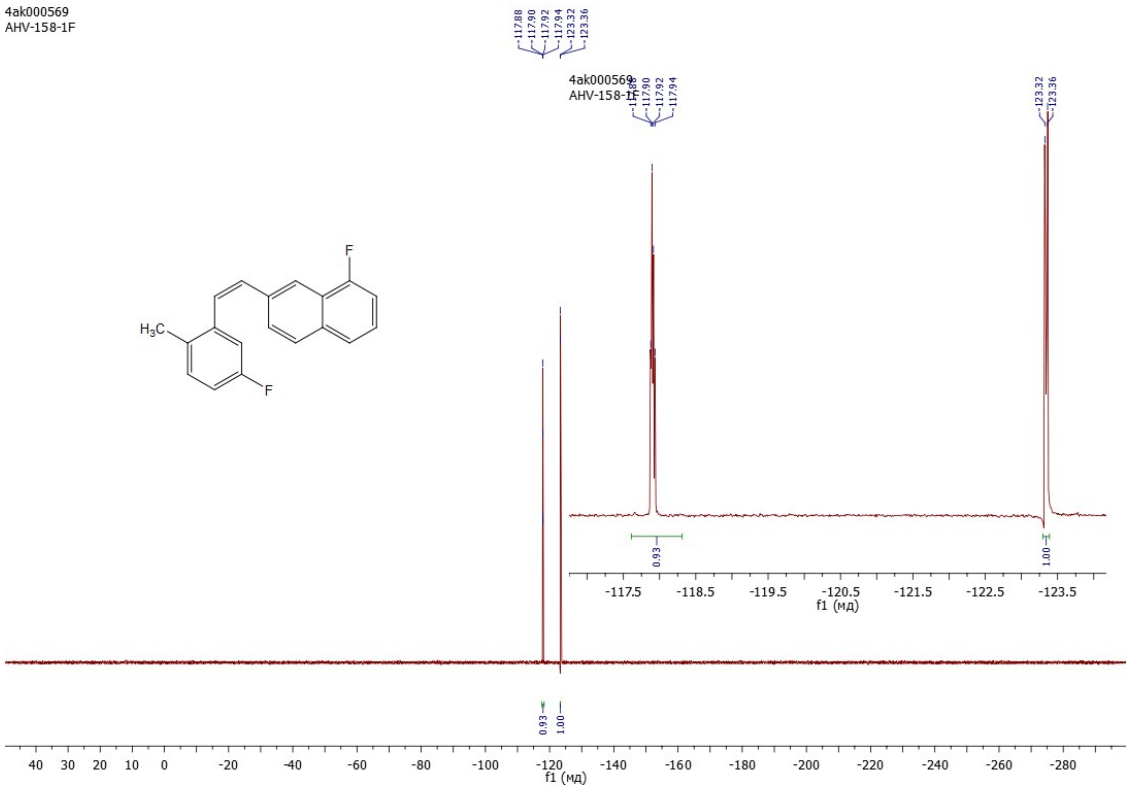


**Figure S54**. $^{19}F$ NMR (377 MHz, $CDCl_3$) of (*Z*)- 1-fluoro-7-(5-fluoro-2-methylstyryl) naphthalene.

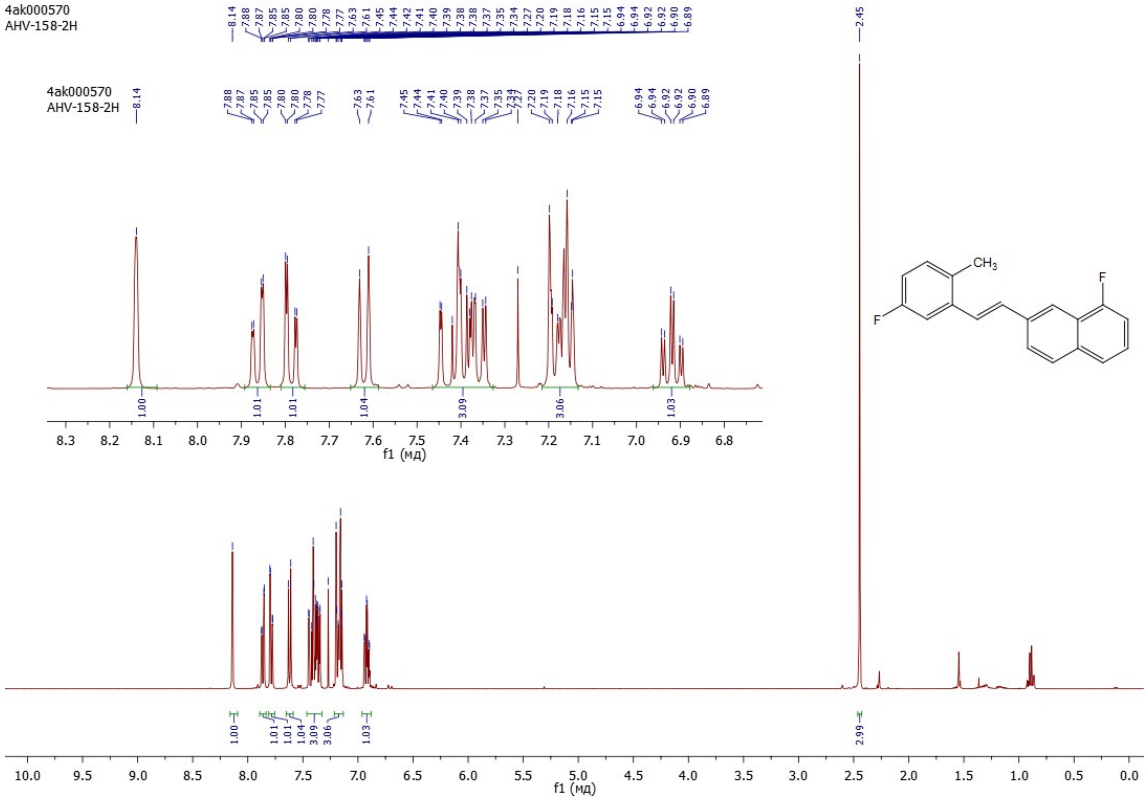


**Figure S55**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of (*E*)- 1-fluoro-7-(5-fluoro-2-methylstyryl) naphthalene.

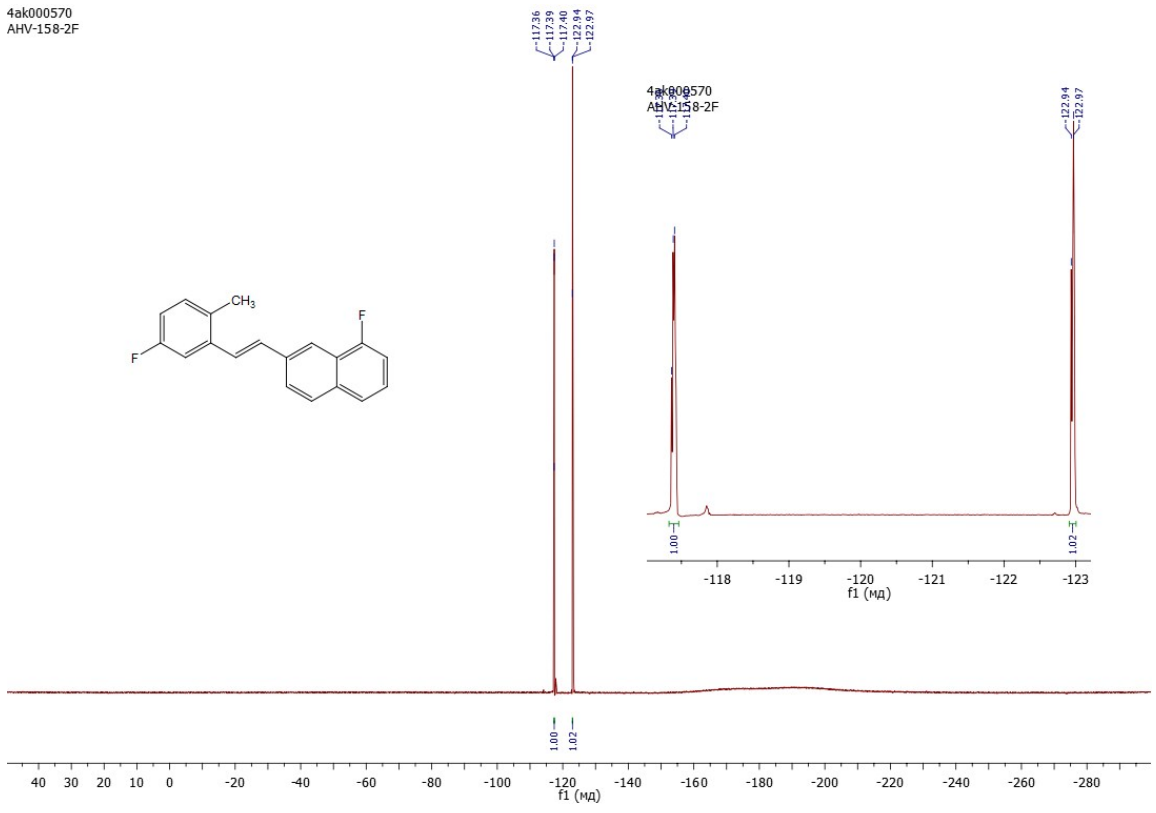


**Figure S56**. $^{19}F$ NMR (377 MHz, $CDCl_3$) of (*E*)- 1-fluoro-7-(5-fluoro-2-methylstyryl) naphthalene.

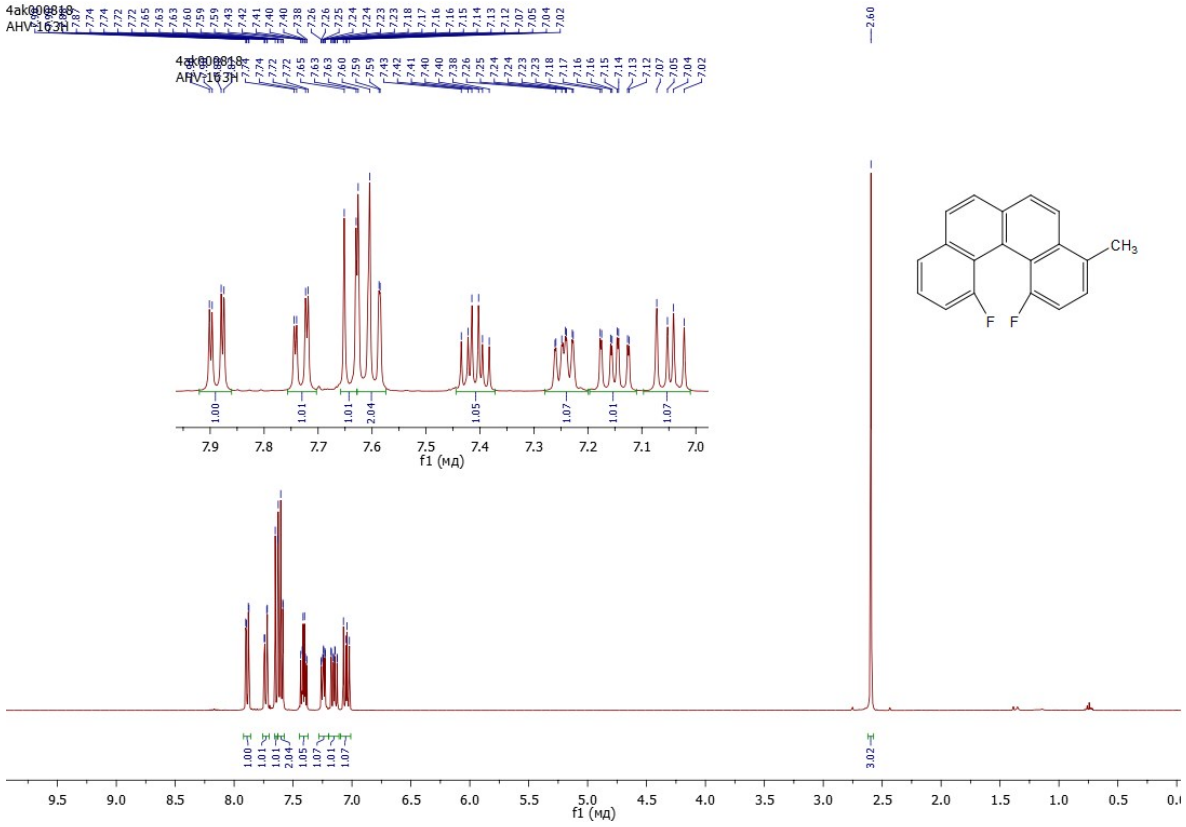


**Figure S57**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of 1,12-difluoro-4-methylbenzo[c]phenanthrene.

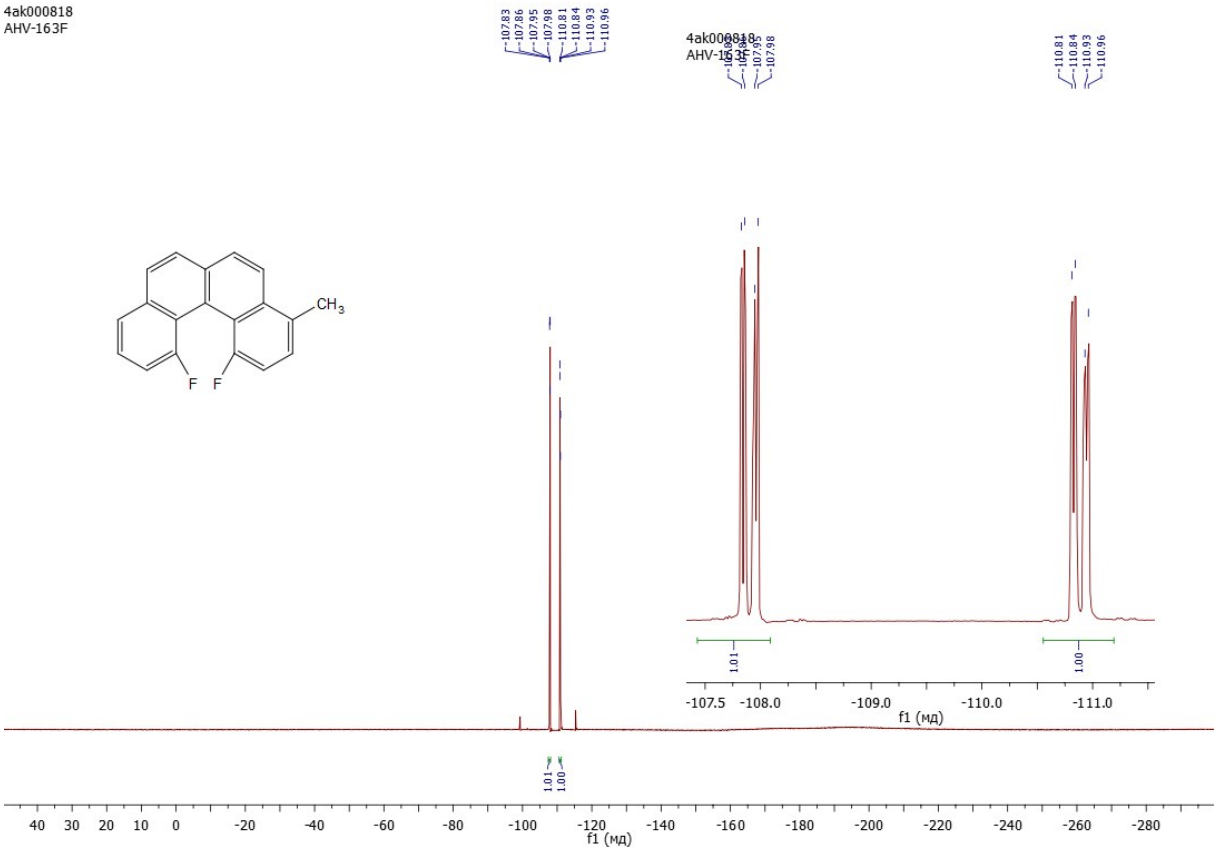


**Figure S58**. $^{19}F$ NMR (377 MHz, $CDCl_3$) of 1,12-difluoro-4-methylbenzo[c]phenanthrene.

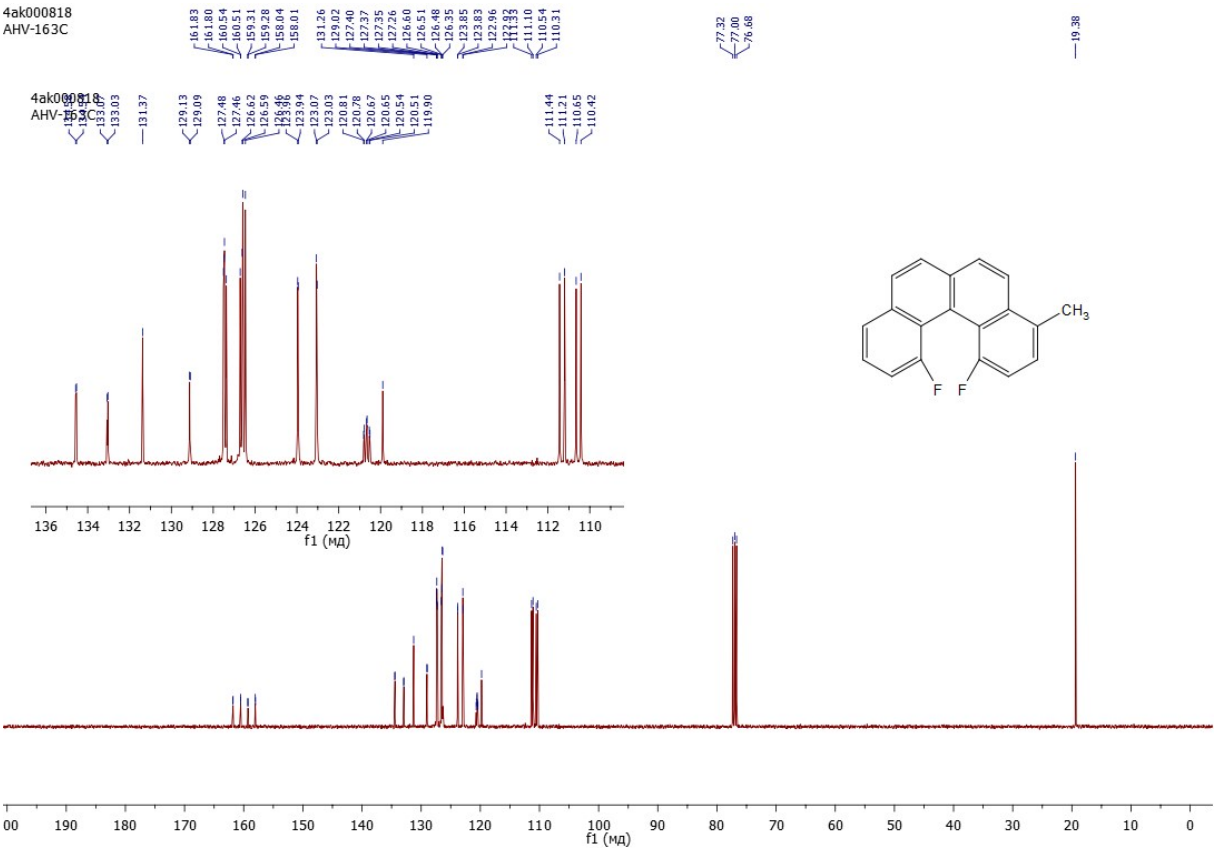


**Figure S59**. $^{13}C$ NMR (101 MHz, $CDCl_3$) of 1,12-difluoro-4-methylbenzo[c]phenanthrene.

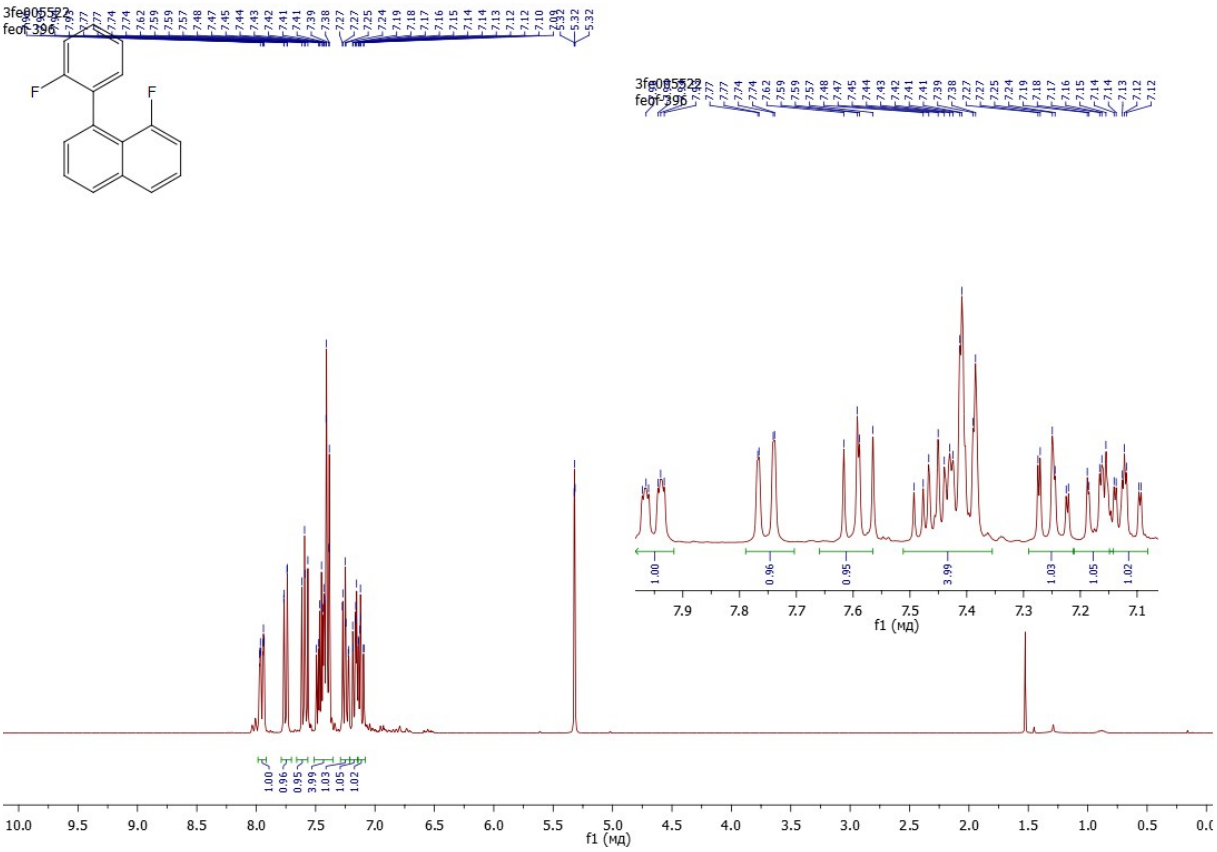


**Figure S60**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$) of 1-fluoro-8-(2-fluorophenyl)naphthalene.

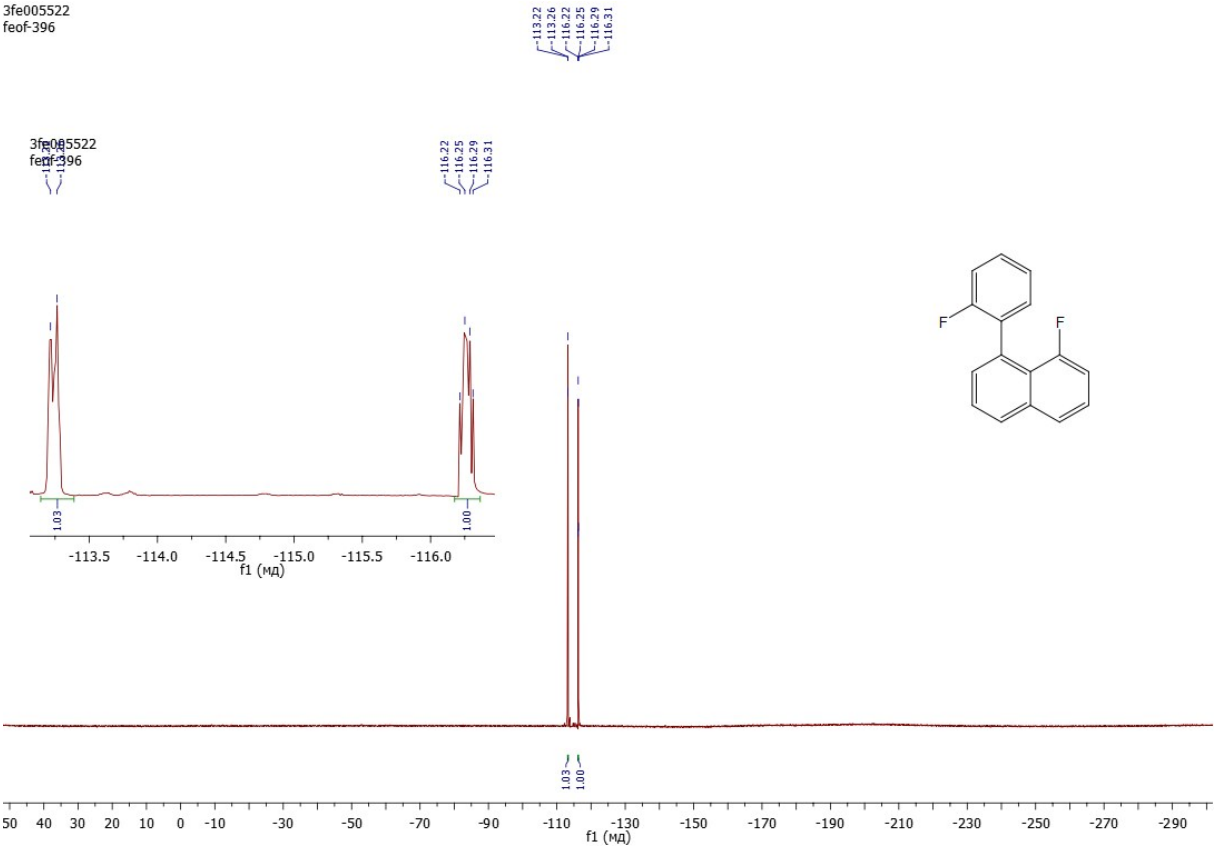


**Figure S61**. $^{19}F$ NMR (288 MHz, $CD_2Cl_2$) of 1-fluoro-8-(2-fluorophenyl)naphthalene.

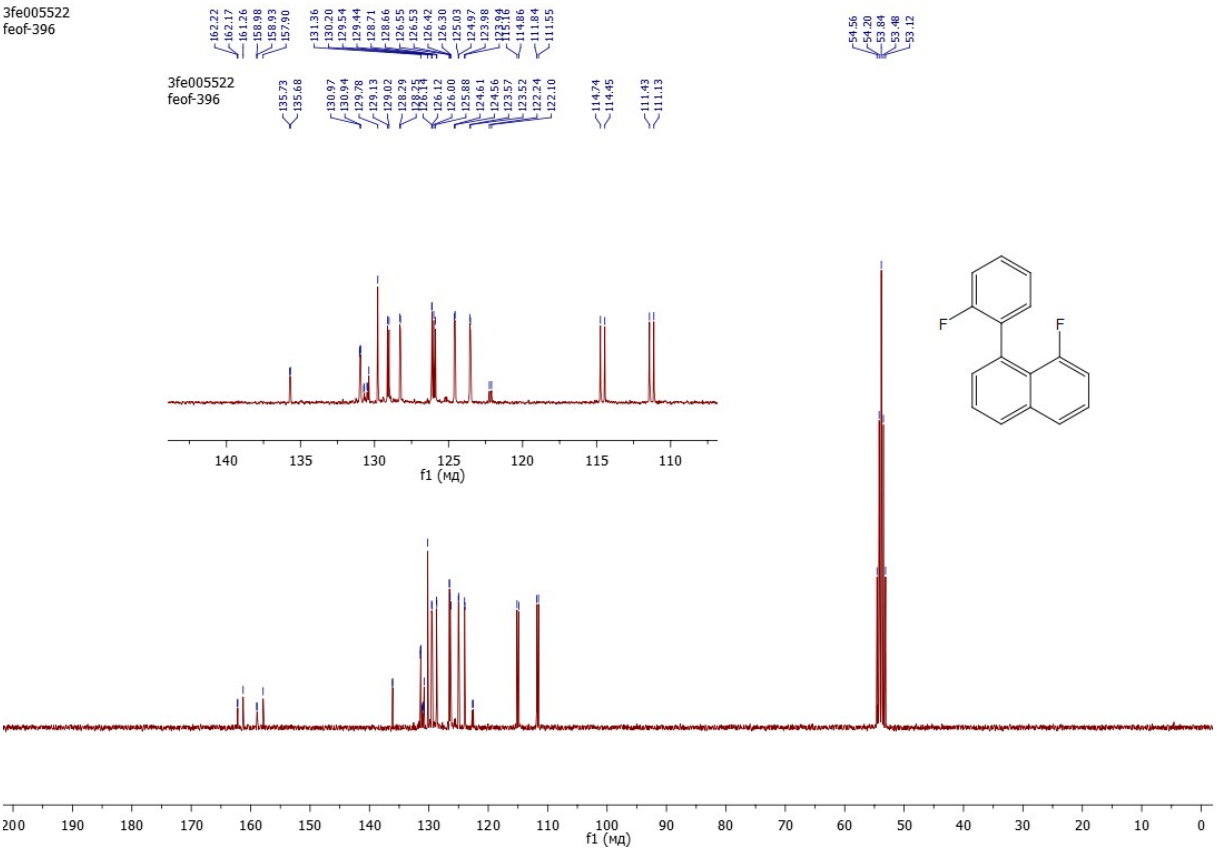


**Figure S62**. $^{1}H$ NMR (75 MHz, $CD_2Cl_2$) of 1-fluoro-8-(2-fluorophenyl)naphthalene.

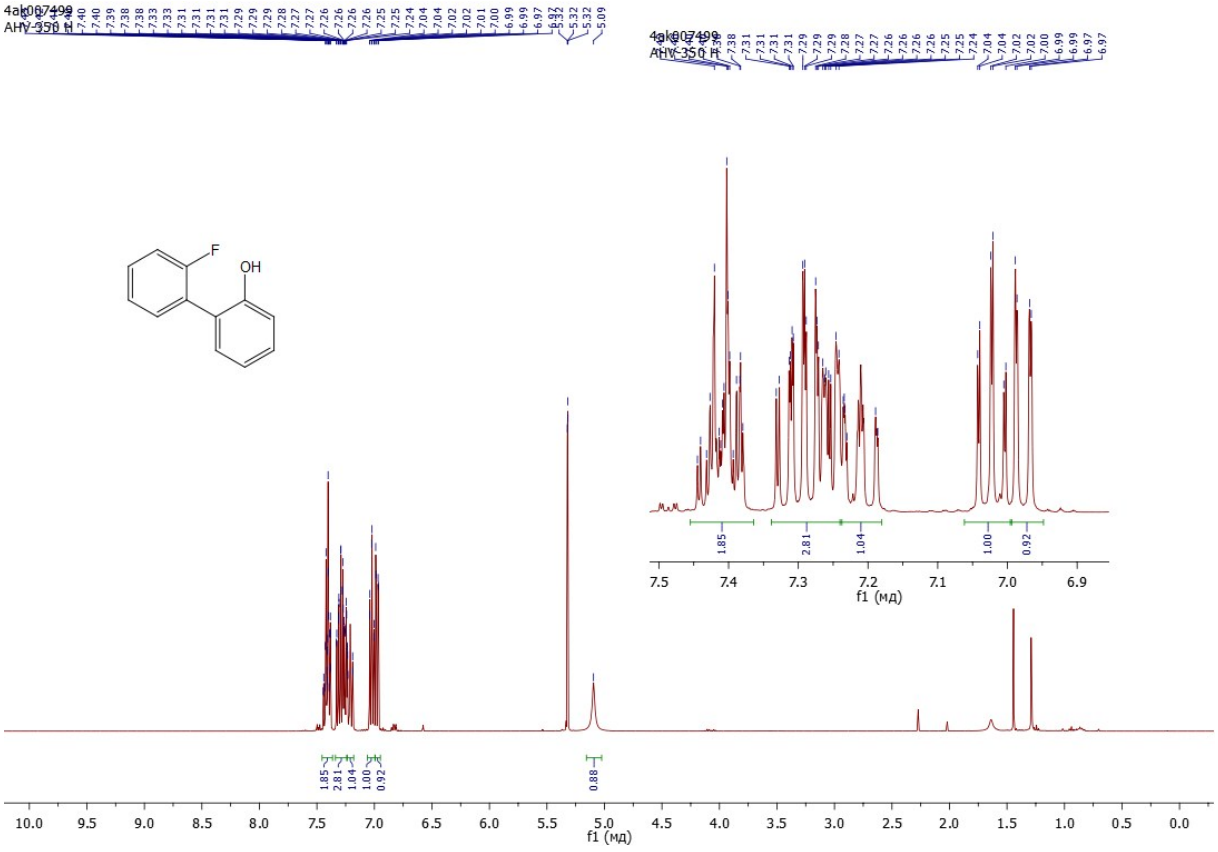


**Figure S63.** $^{1}$H NMR (400 MHz, $CD_2Cl_2$) of 2'-fluoro-[1,1'-biphenyl]-2-ol.

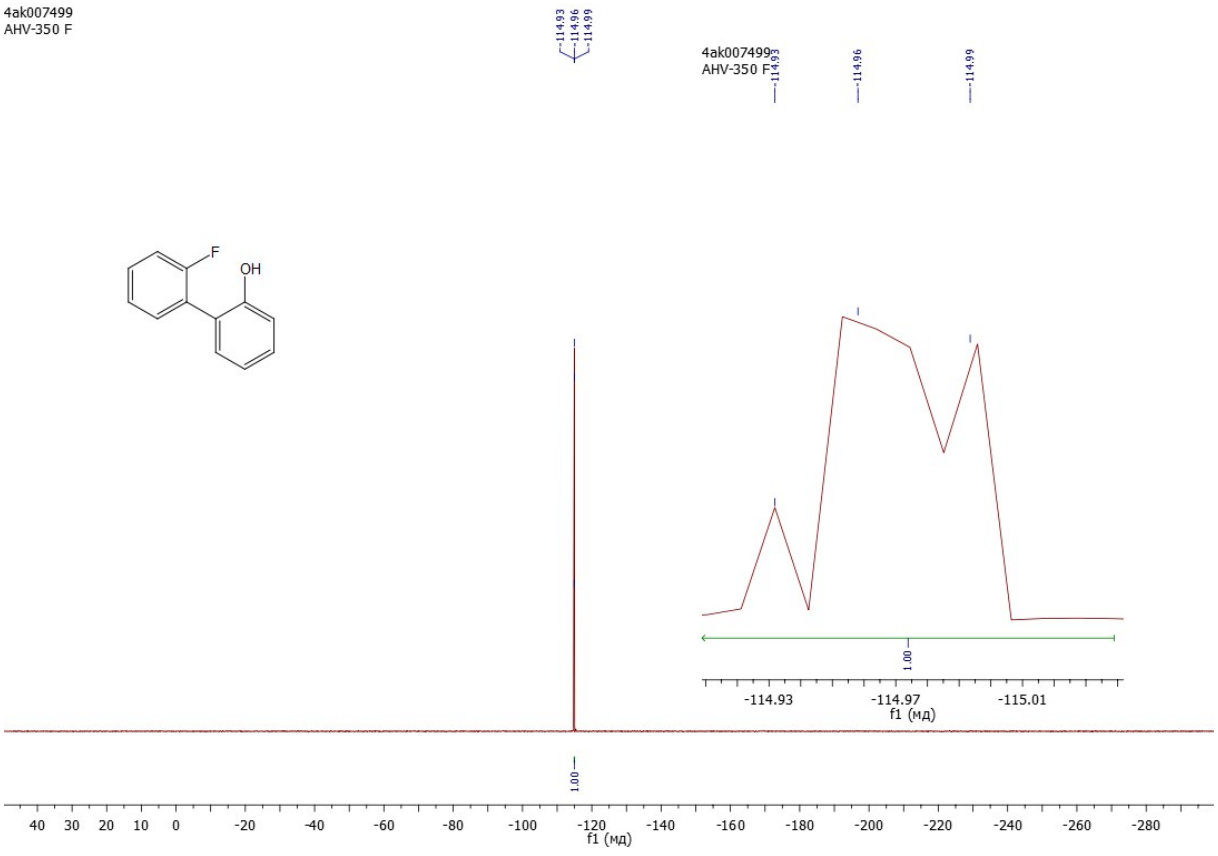


**Figure S64**. $^{19}$F NMR (377 MHz, $CD_2Cl_2$) of 2'-fluoro-[1,1'-biphenyl]-2-ol.

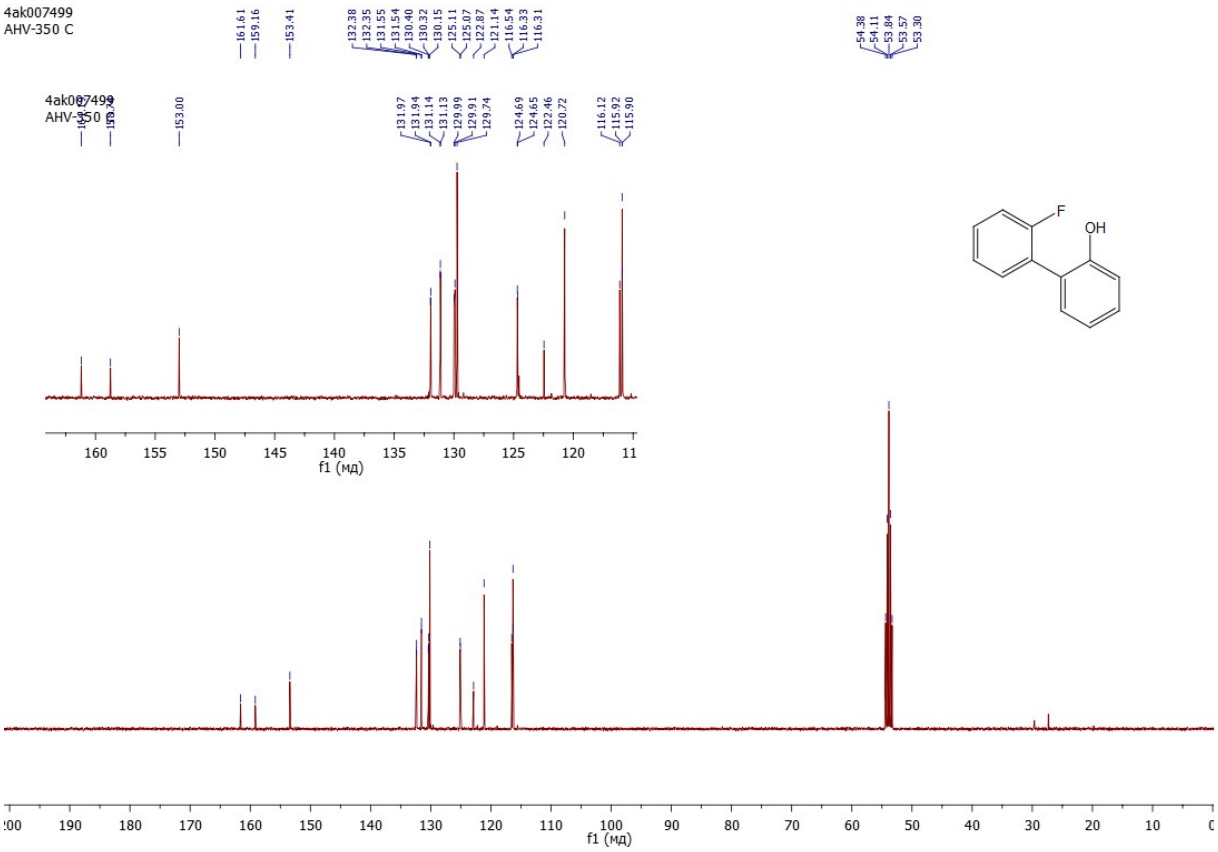


**Figure S65**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2'-fluoro-[1,1'-biphenyl]-2-ol.

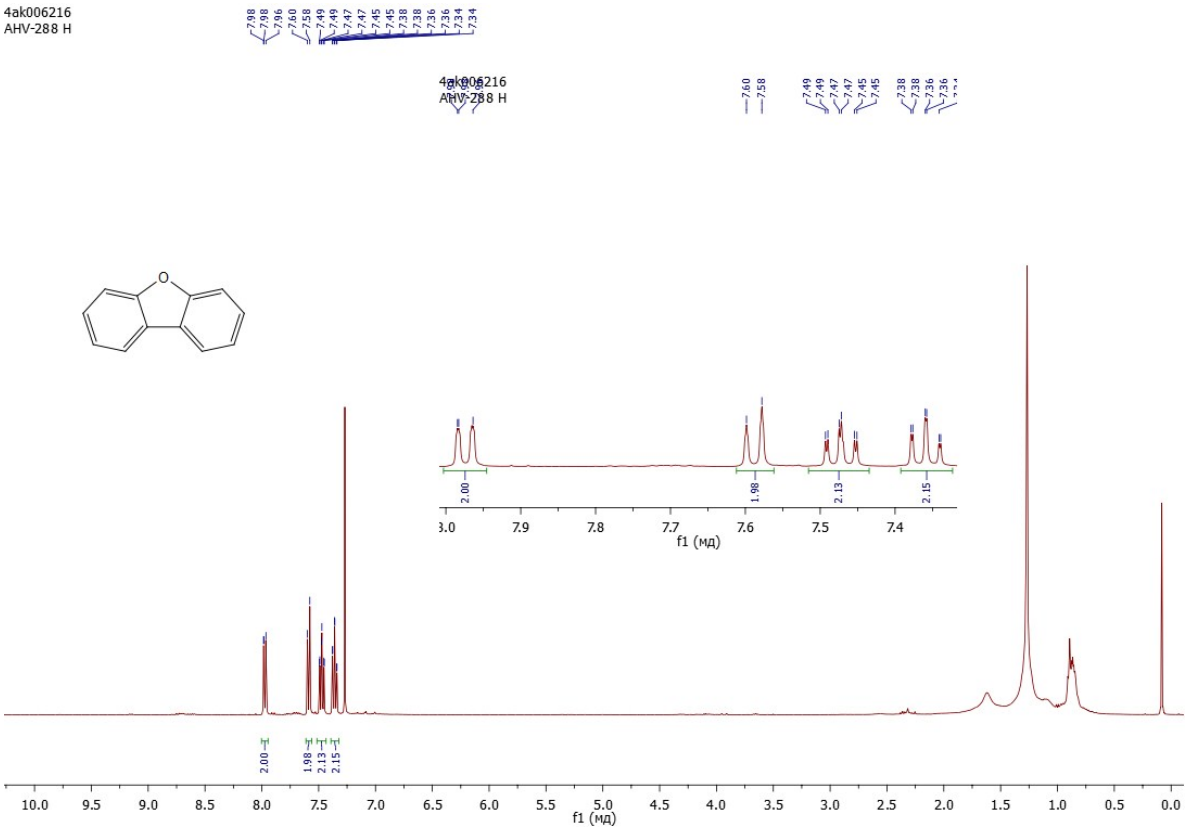


**Figure S66**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of dibenzo[b,d]furan.

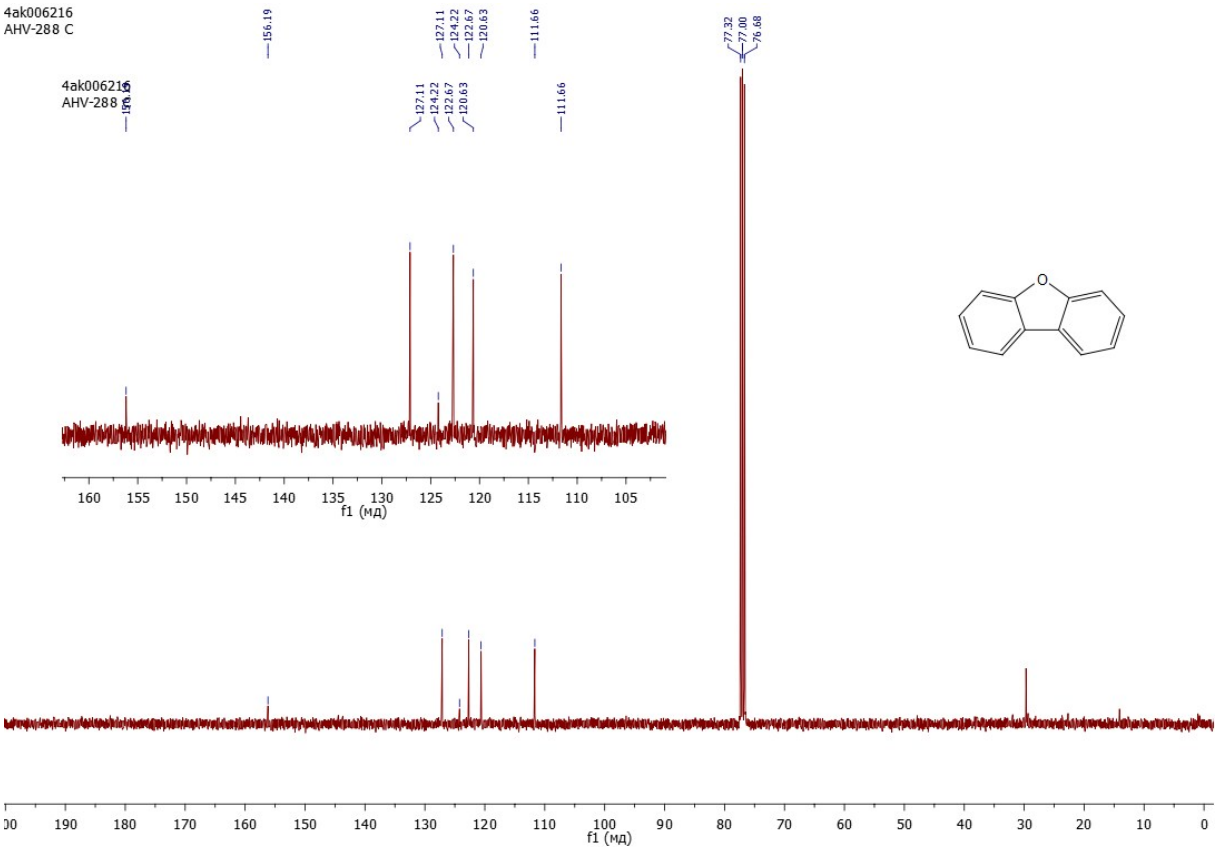


**Figure S67**. $^{13}C$ NMR (101 MHz, $CDCl_3$) of dibenzo[b,d]furan.

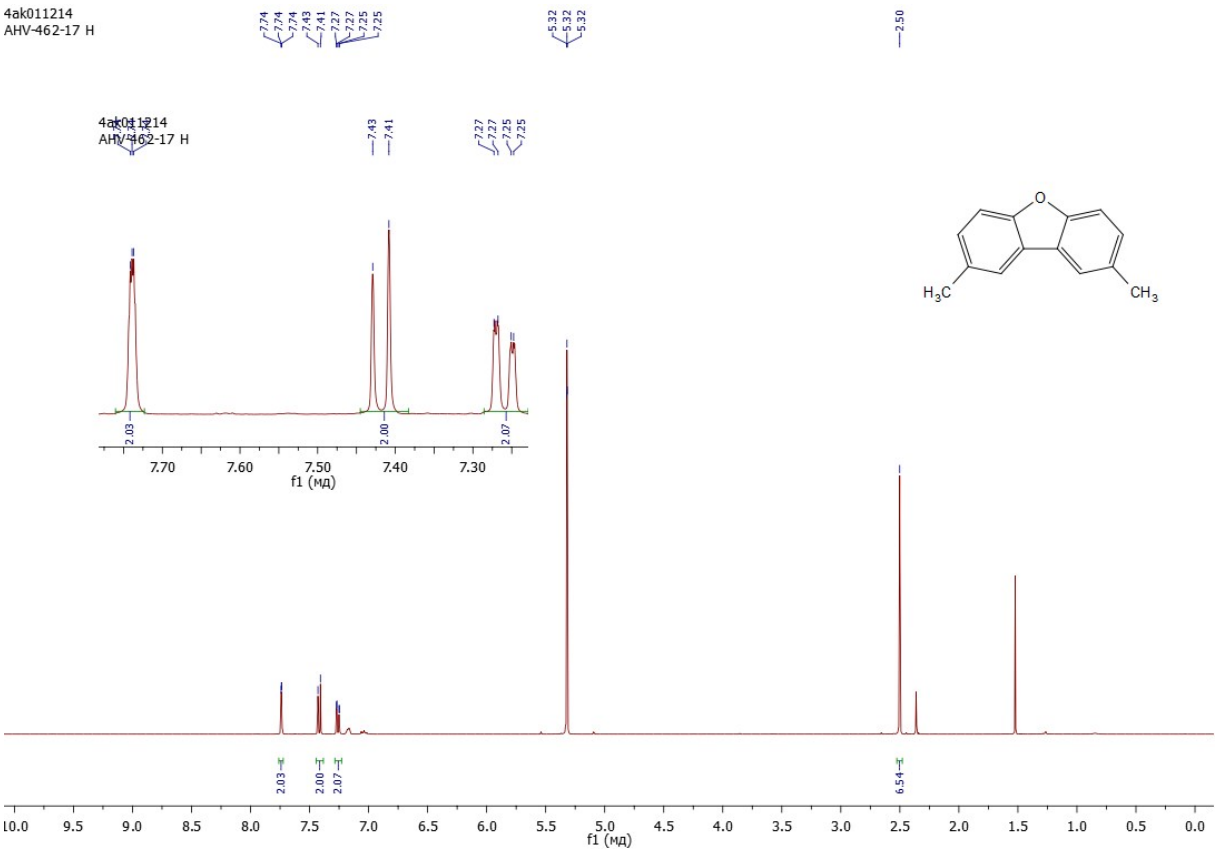


**Figure S68**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of 2,8-dimethyldibenzo[b,d]furan.

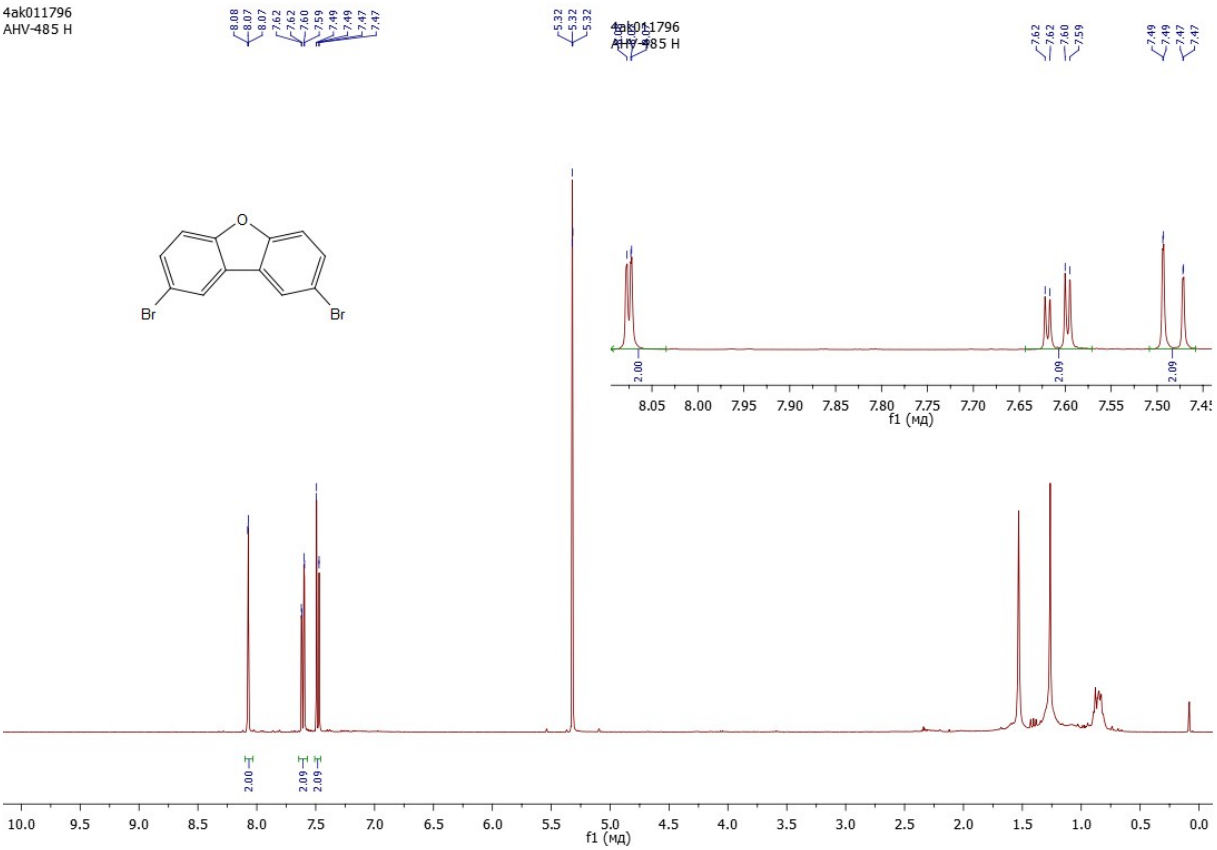


**Figure S69**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of 2,8-dibromodibenzo[b,d]furan.

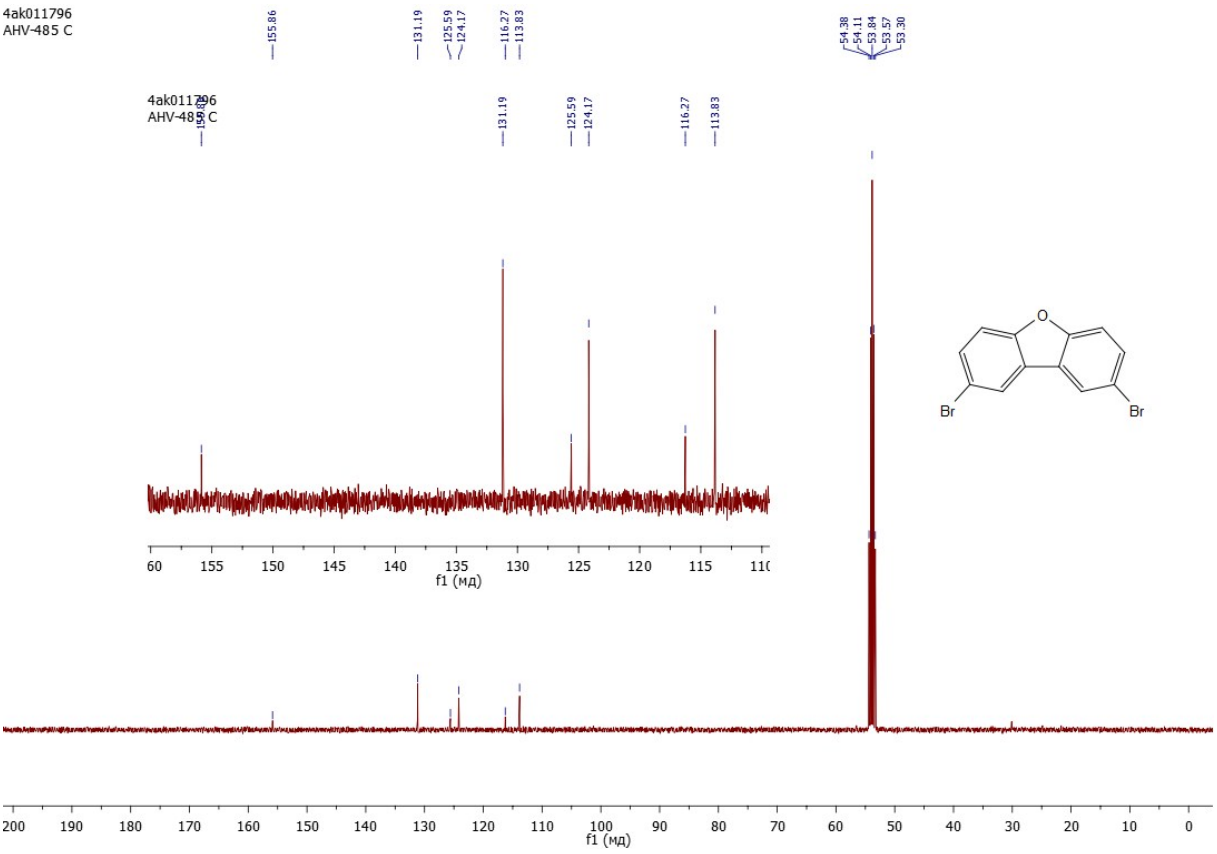


**Figure S70**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of 2,8-dibromodibenzo[b,d]furan.

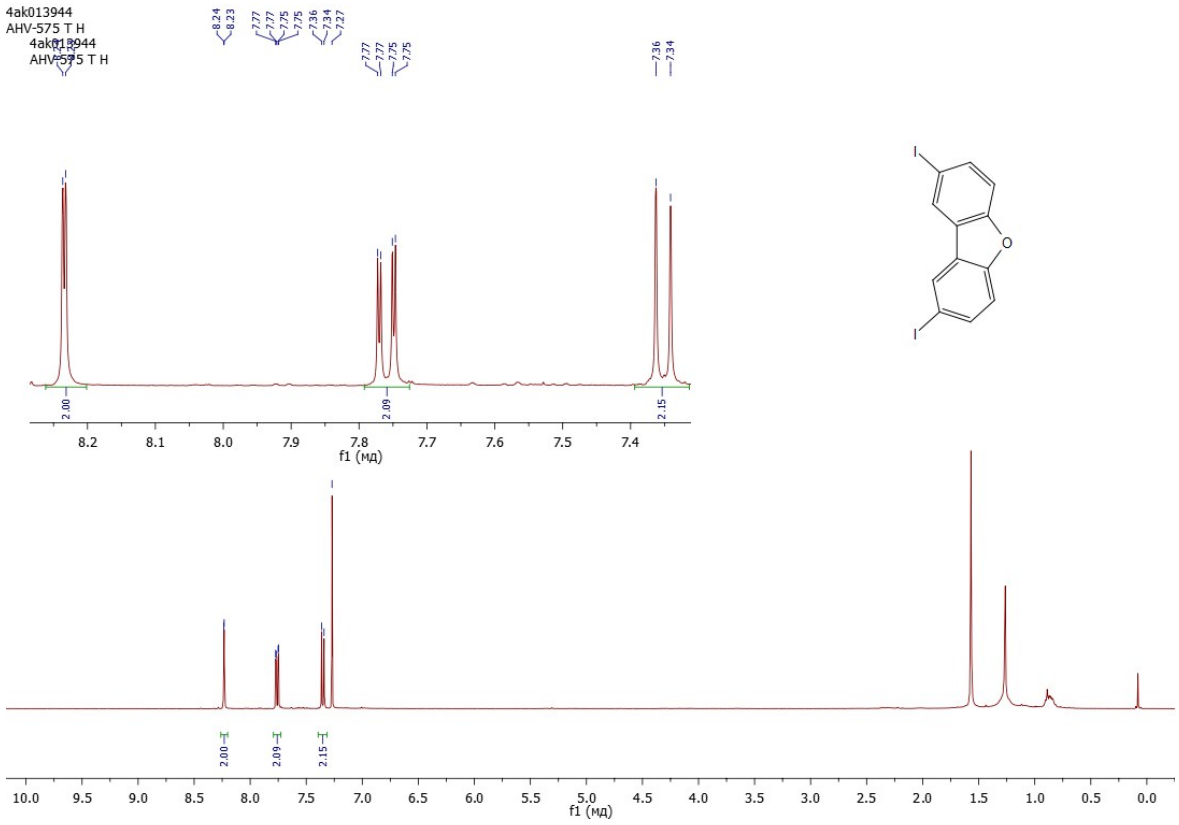


**Figure S71**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of 2,8-diiododibenzo[b,d]furan.

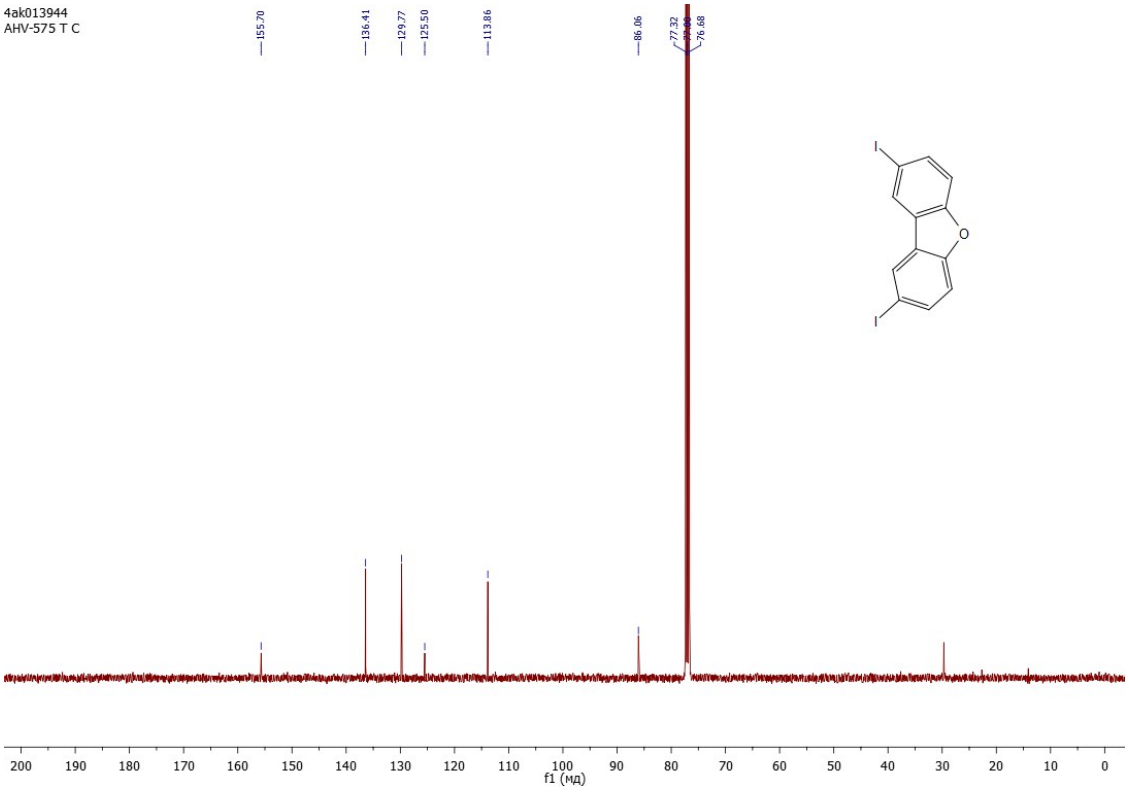


**Figure S72**. $^{13}C$ NMR (101 MHz, $CDCl_3$) of 2,8-diiododibenzo[b,d]furan.

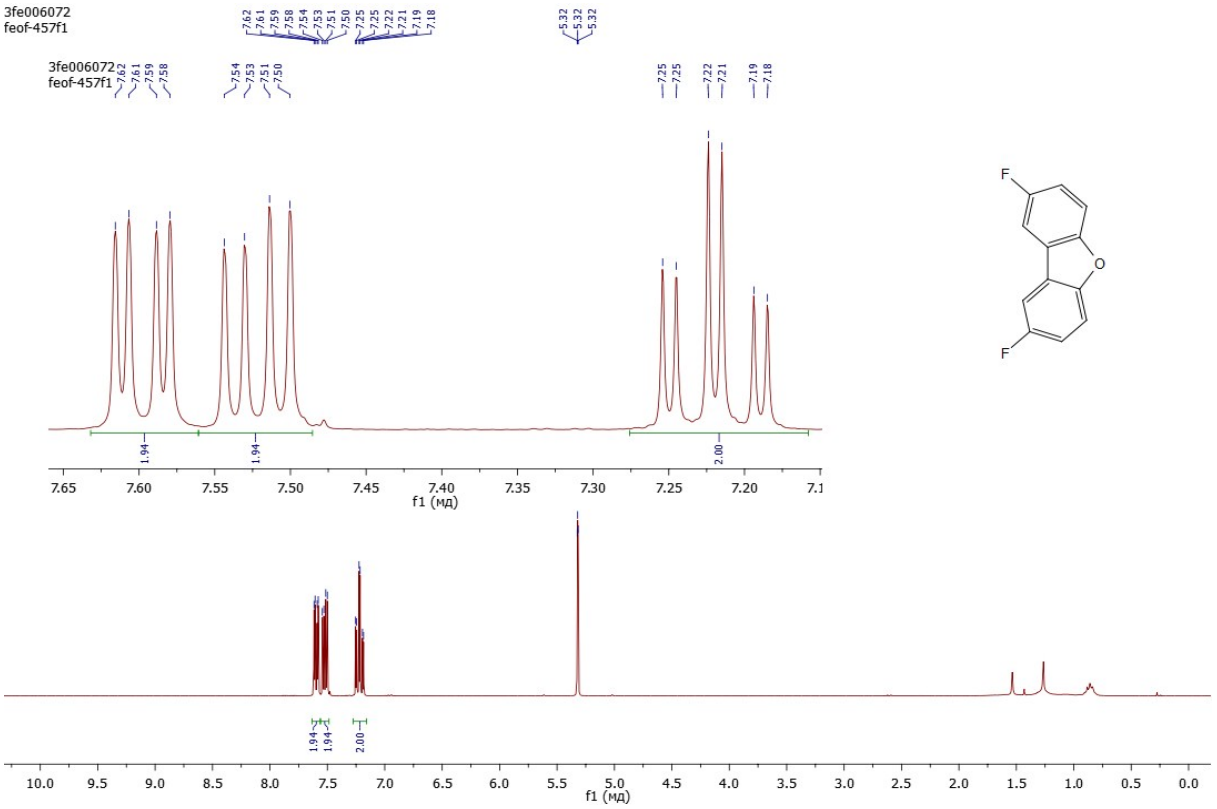


**Figure S73**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$) of 2,8-difluorodibenzo[b,d]furan.

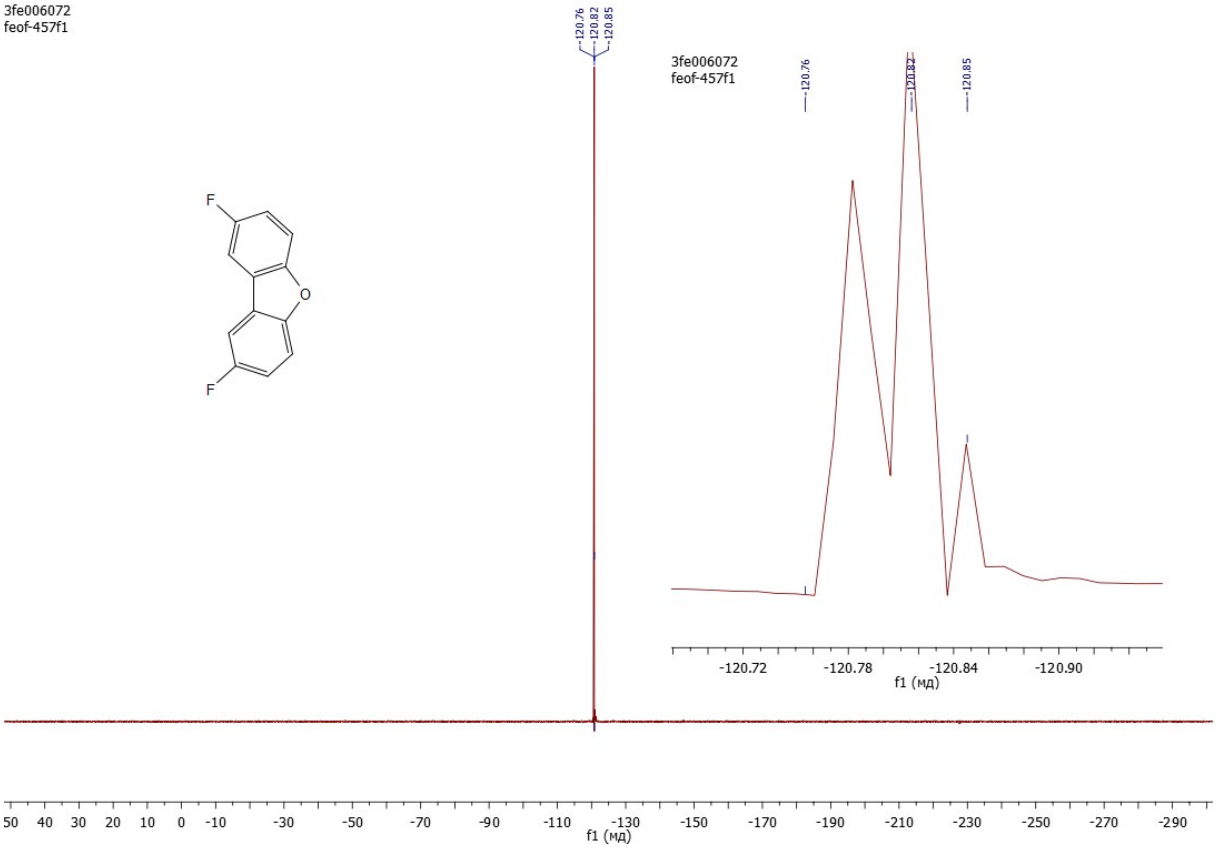


**Figure S74**. $^{19}F$ NMR (283 MHz, $CD_2Cl_2$) of 2,8-difluorodibenzo[b,d]furan.

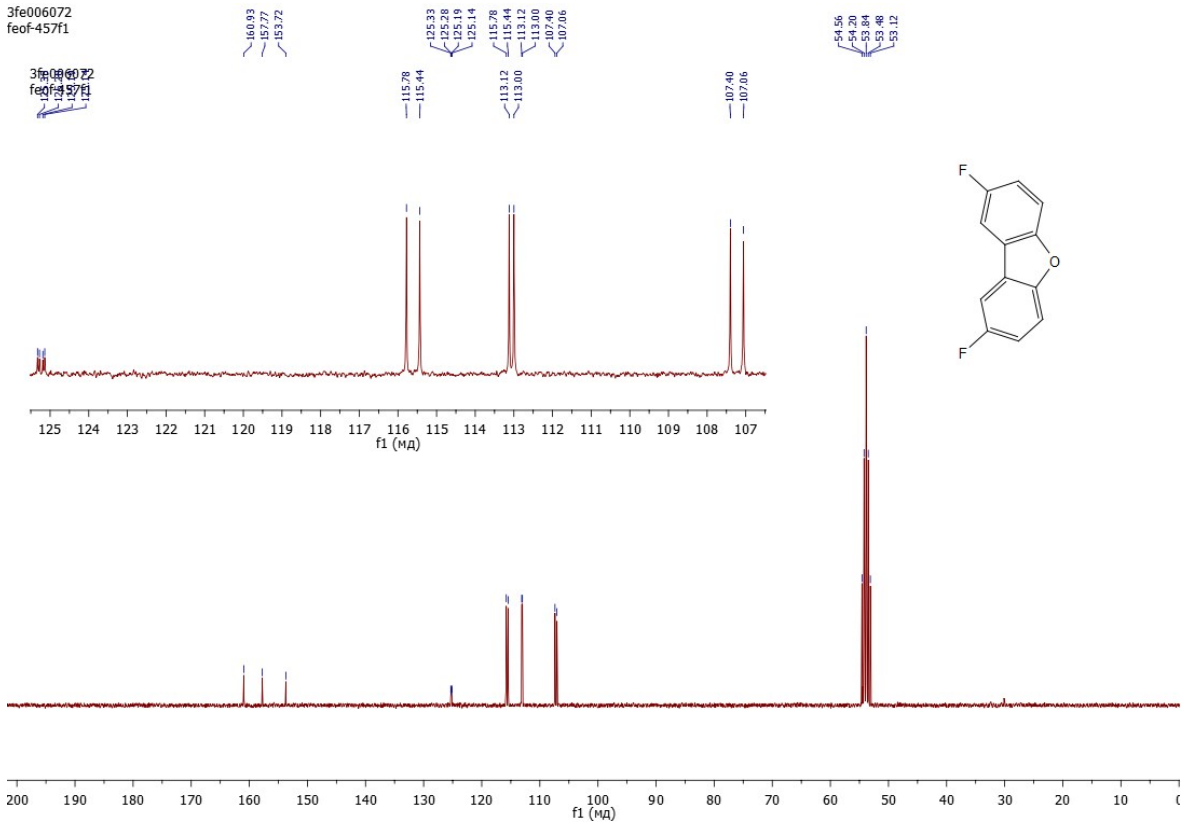


**Figure S75**. $^{13}C$ NMR (76 MHz, $CD_2Cl_2$) of 2,8-difluorobenzo[b,d]furan.

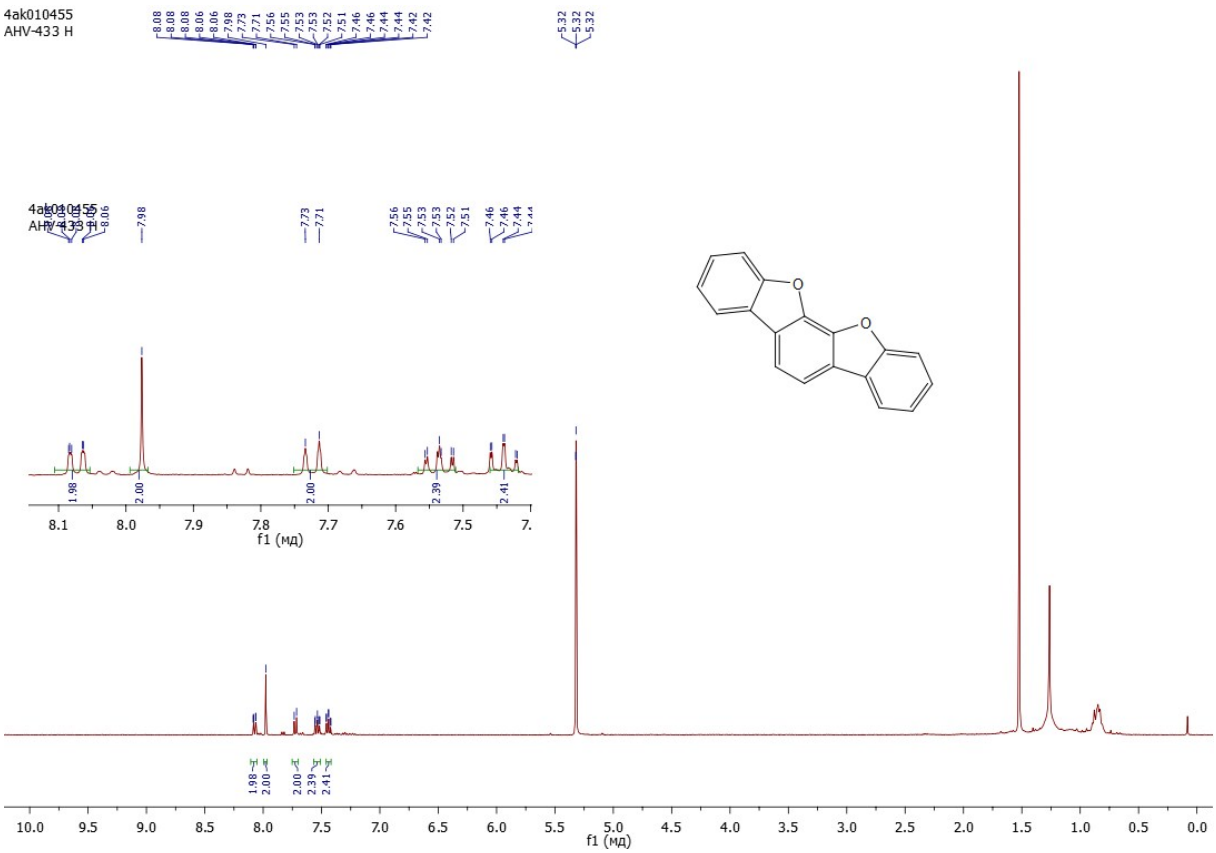


**Figure S76**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of 2,8-difluorodibenzo[b,d]furan.

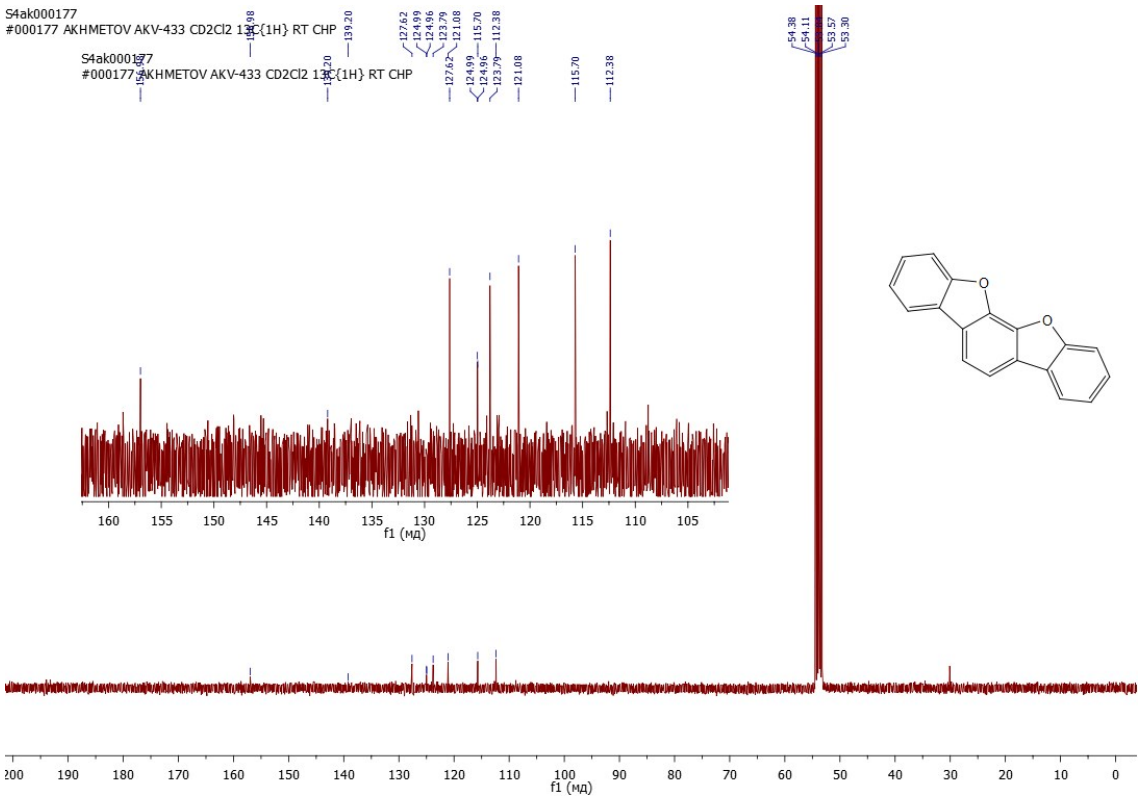


**Figure S77**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$) of benzo[1,2-*b*:5,4-*b'*]bisbenzofuran.

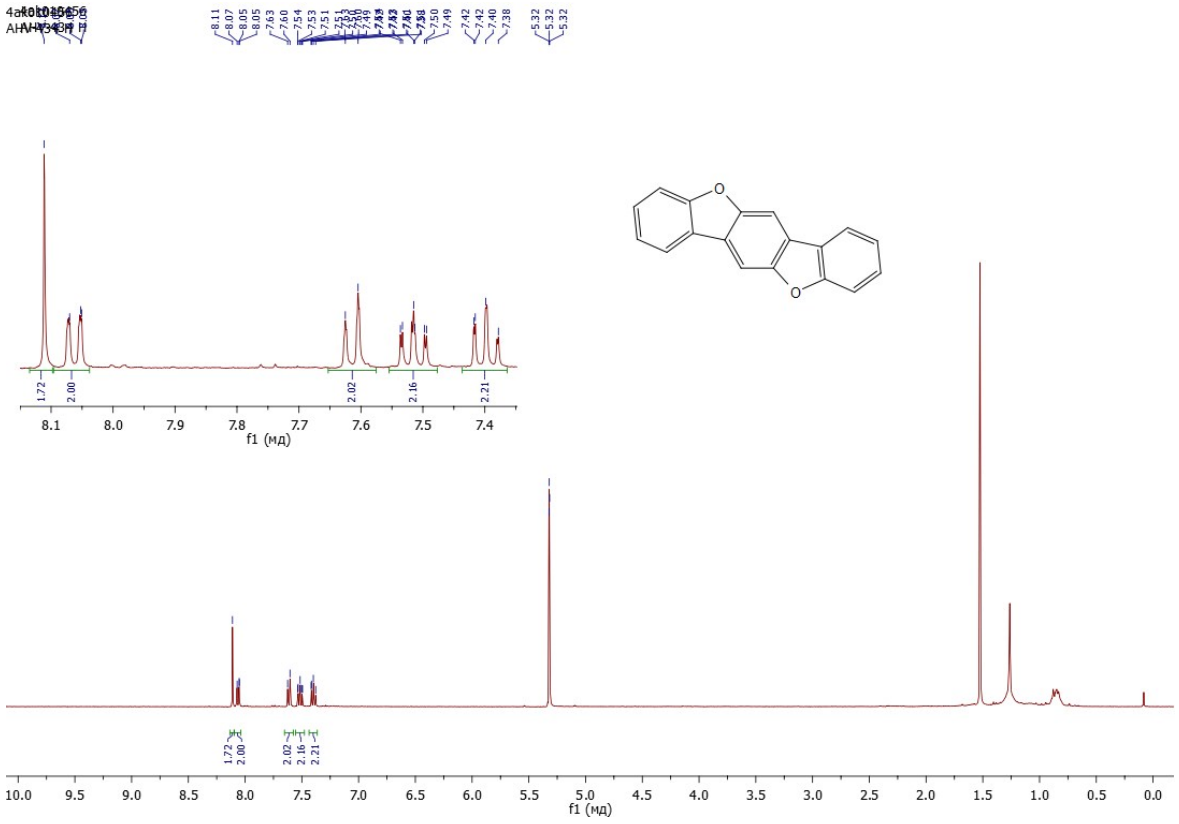


**Figure S78**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of benzo[2,1-b:3,4-b']bisbenzofuran.

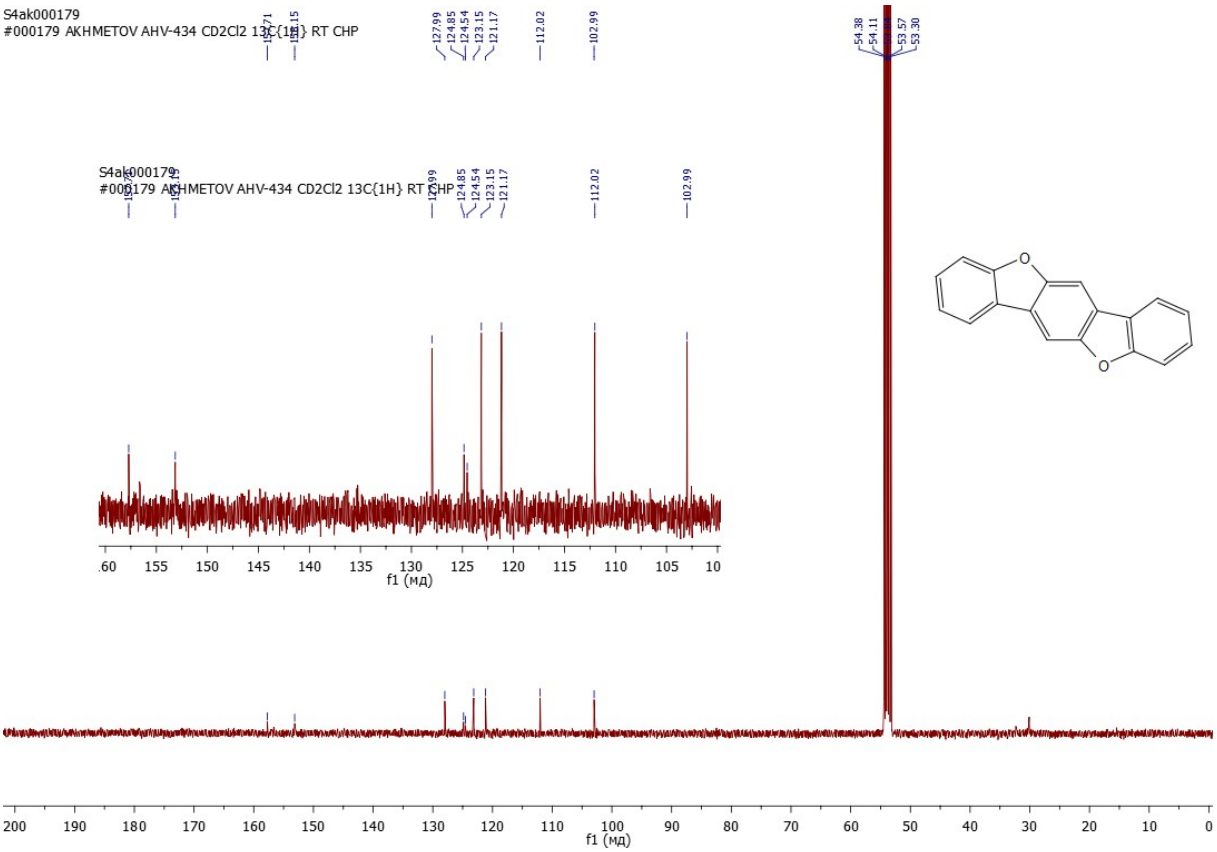


**Figure S79**. $^{13}C$ NMR (400 MHz, $CD_2Cl_2$) of benzo[2,1-b:3,4-b']bisbenzofuran.

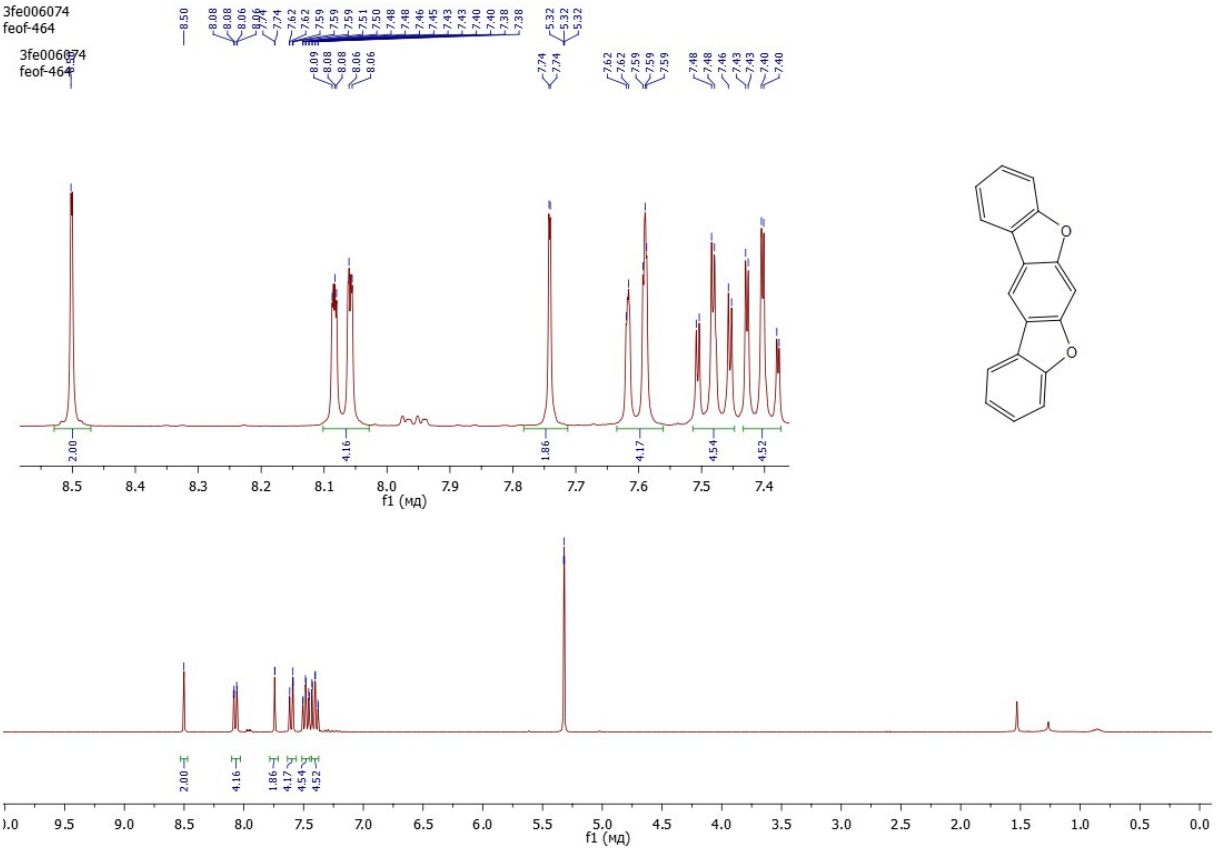


**Figure S80**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$) of benzo[1,2-b:5,4-b']bisbenzofuran.

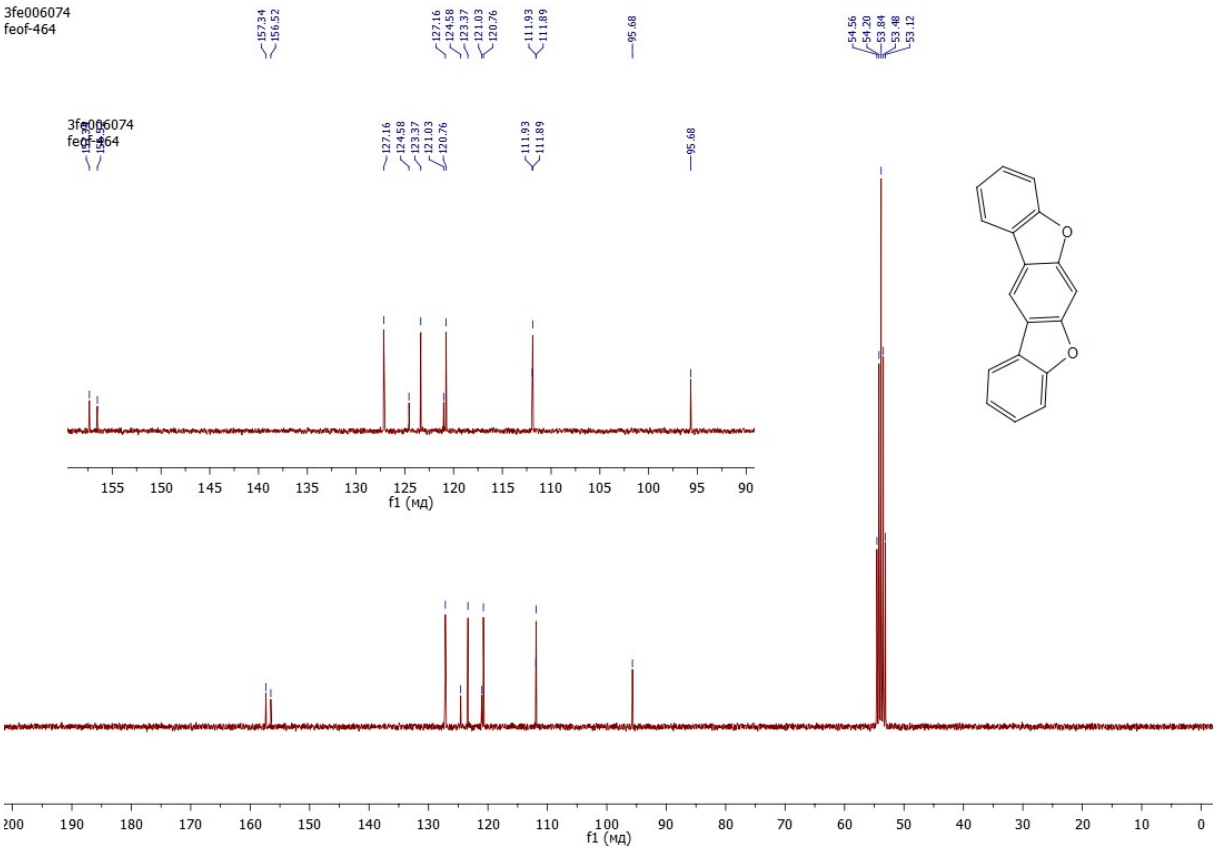


**Figure S81**. $^{13}C$ NMR (76 MHz, $CD_2Cl_2$) of benzo[1,2-b:5,4-b']bisbenzofuran.

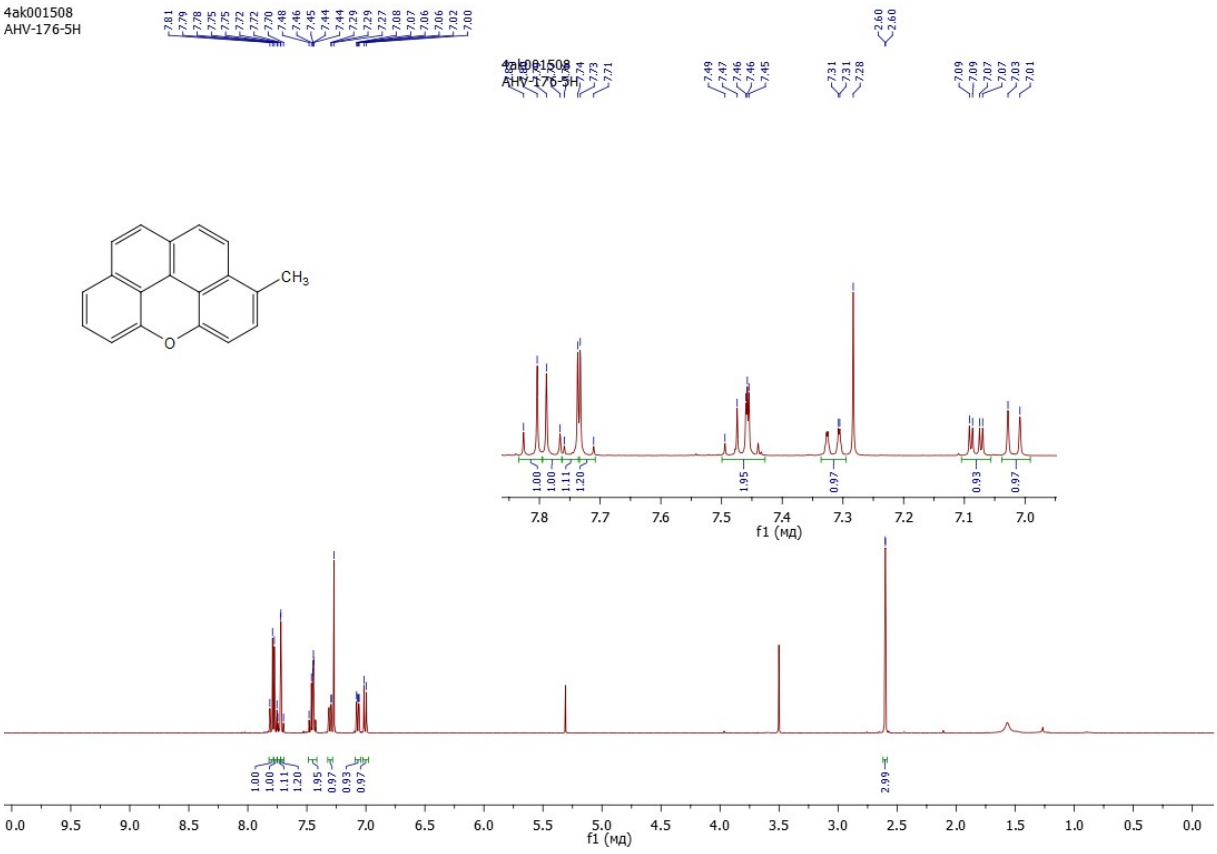


**Figure S82**. $^{1}H$ NMR (400 MHz, $CDCl_3$) of 3-methylnaphtho[2,1,8,7-klmn]xanthene.

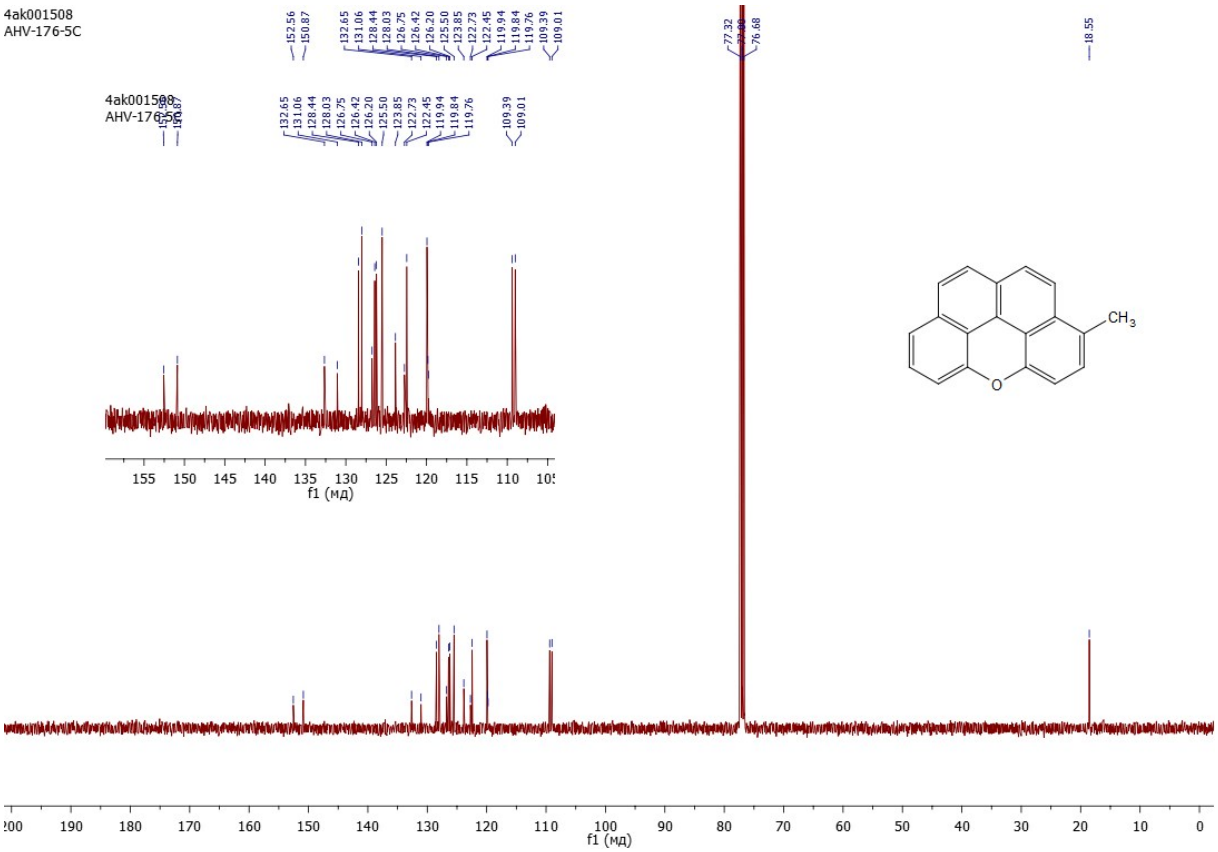


**Figure S83**. $^{13}C$ NMR (101 MHz, $CDCl_3$) of 3-methylnaphtho[2,1,8,7-klmn]xanthene.

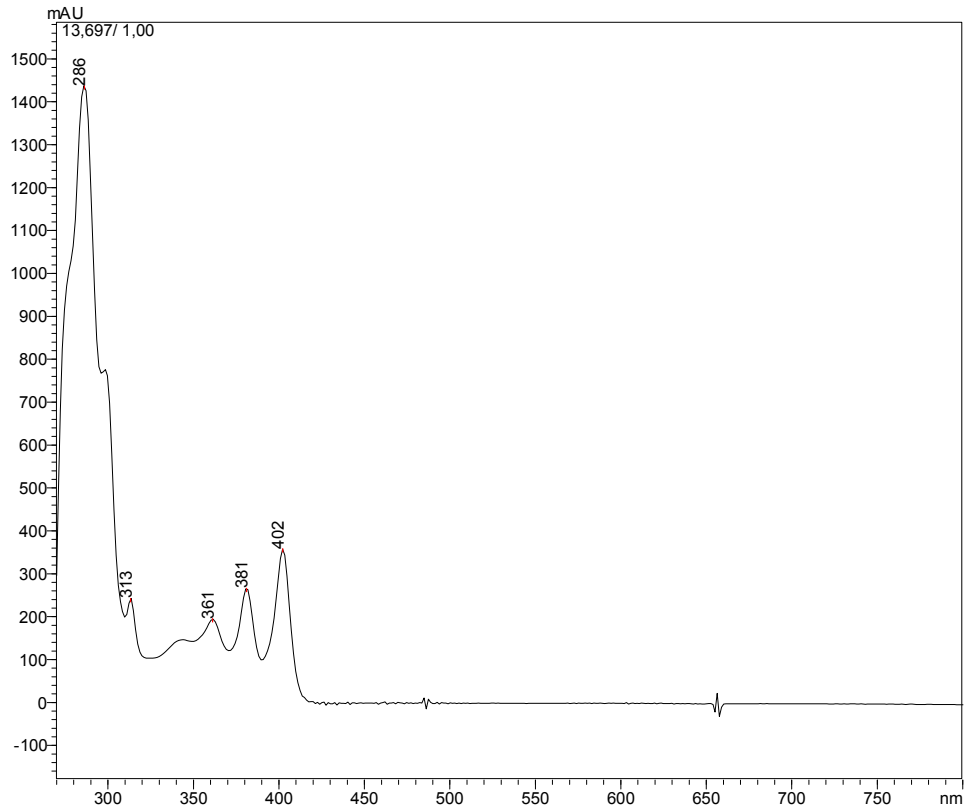


**Figure S84.** UV-Vis spectrum of 3-methylnaphtho[2,1,8,7-klmn]xanthene (DCM-MeOH 7-3) from HPLC.

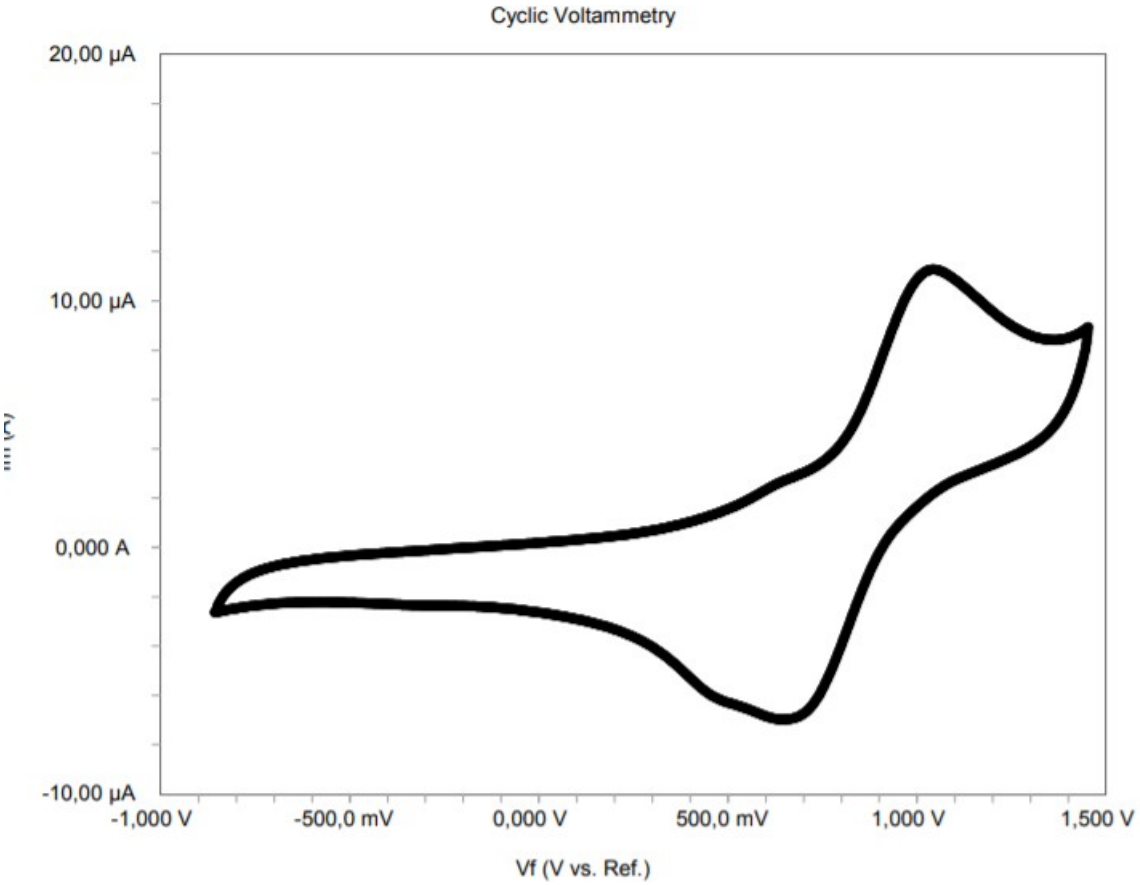


**Figure S85**. Cyclic voltammogram of 3-methylnaphtho[2,1,8,7-klmn]xanthene measured in 0.1 M Bu4NPF6 in 1,2-dichlorobenzene at room temperature with 100 mV/s scan speed.

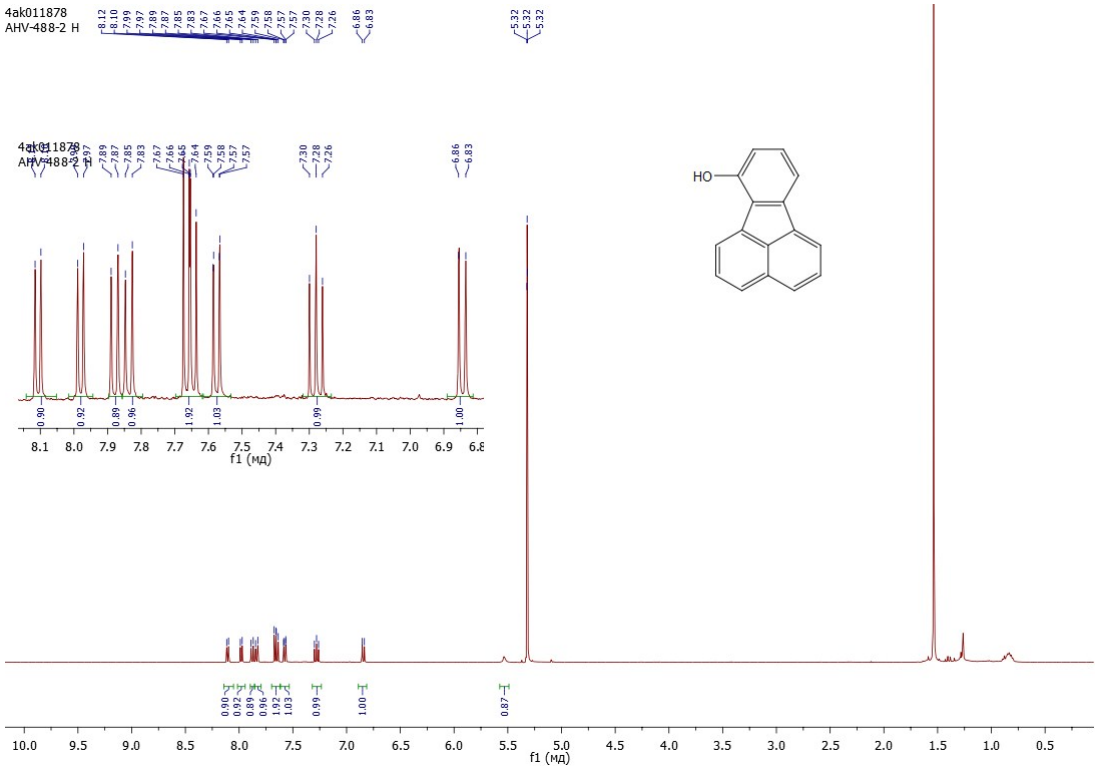


**Figure S86**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of fluoranthen-7-ol.

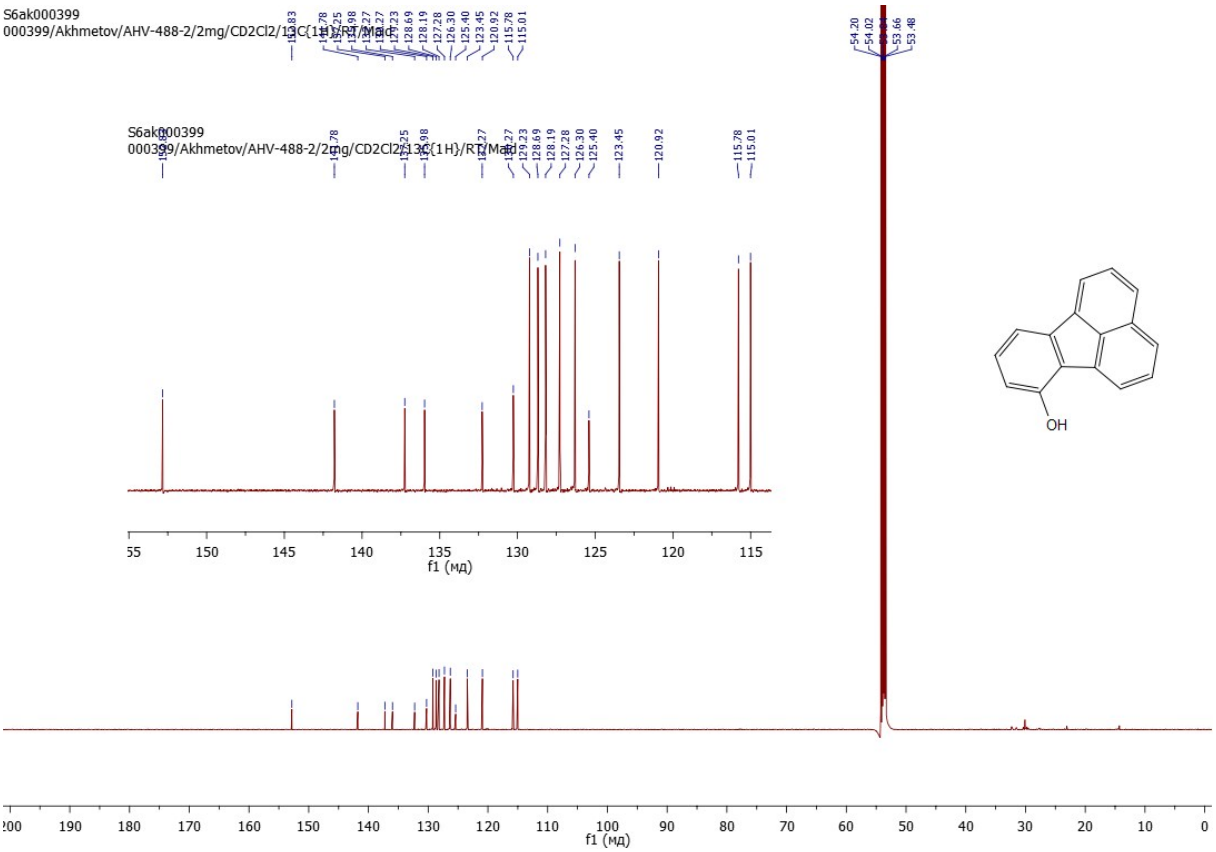


**Figure S87**. $^{13}C$ NMR (151 MHz, $CD_2Cl_2$) of fluoranthen-7-ol.

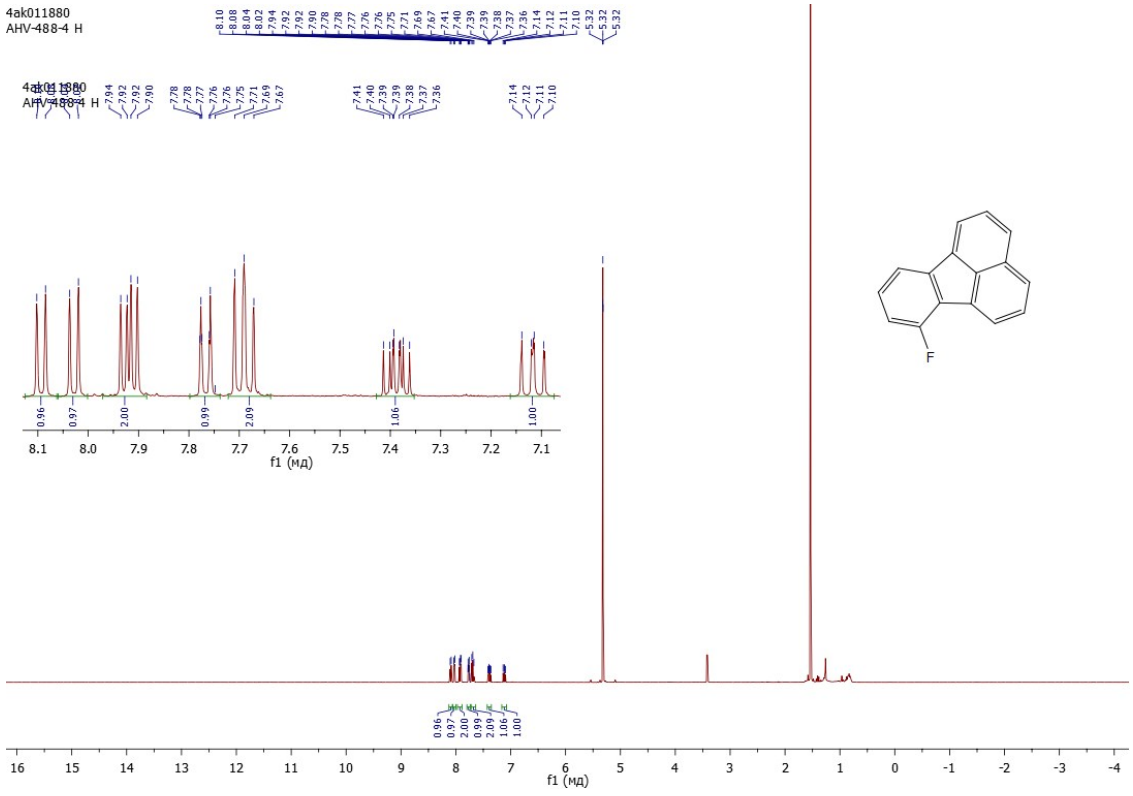


**Figure S88**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of 7-fluorofluoranthrene.

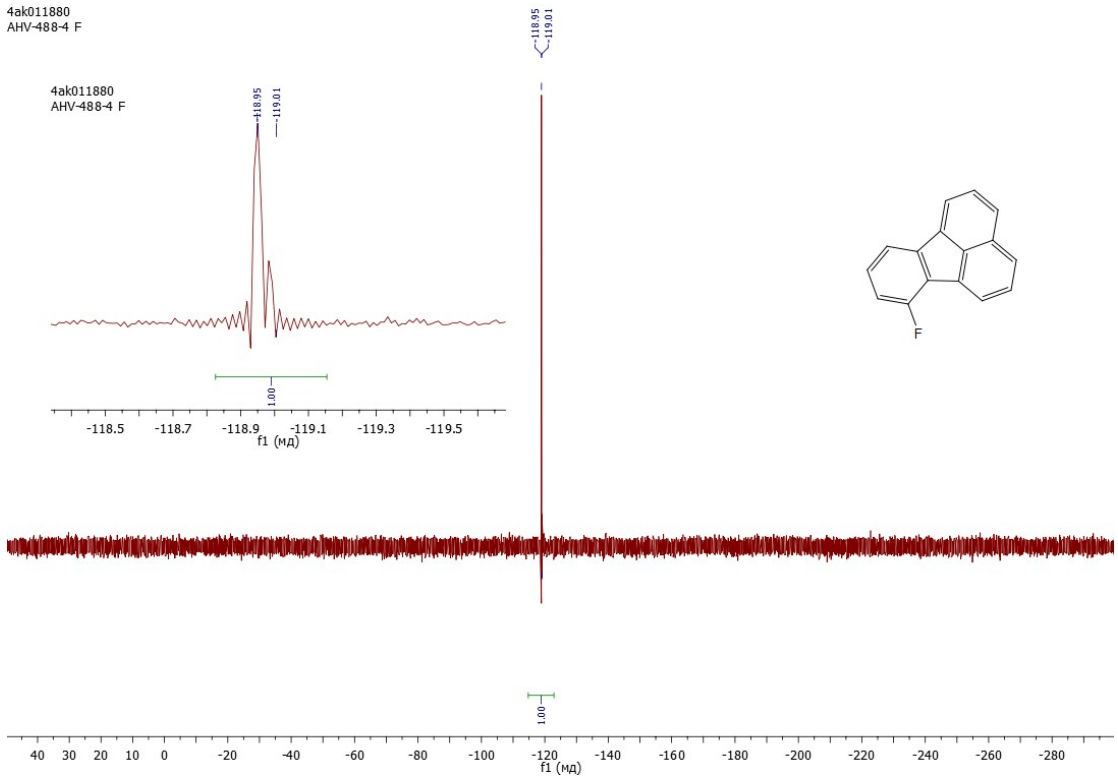


**Figure S89**. $^{19}F$ NMR (377 MHz, $CD_2Cl_2$) of 7-fluorofluoranthrene.

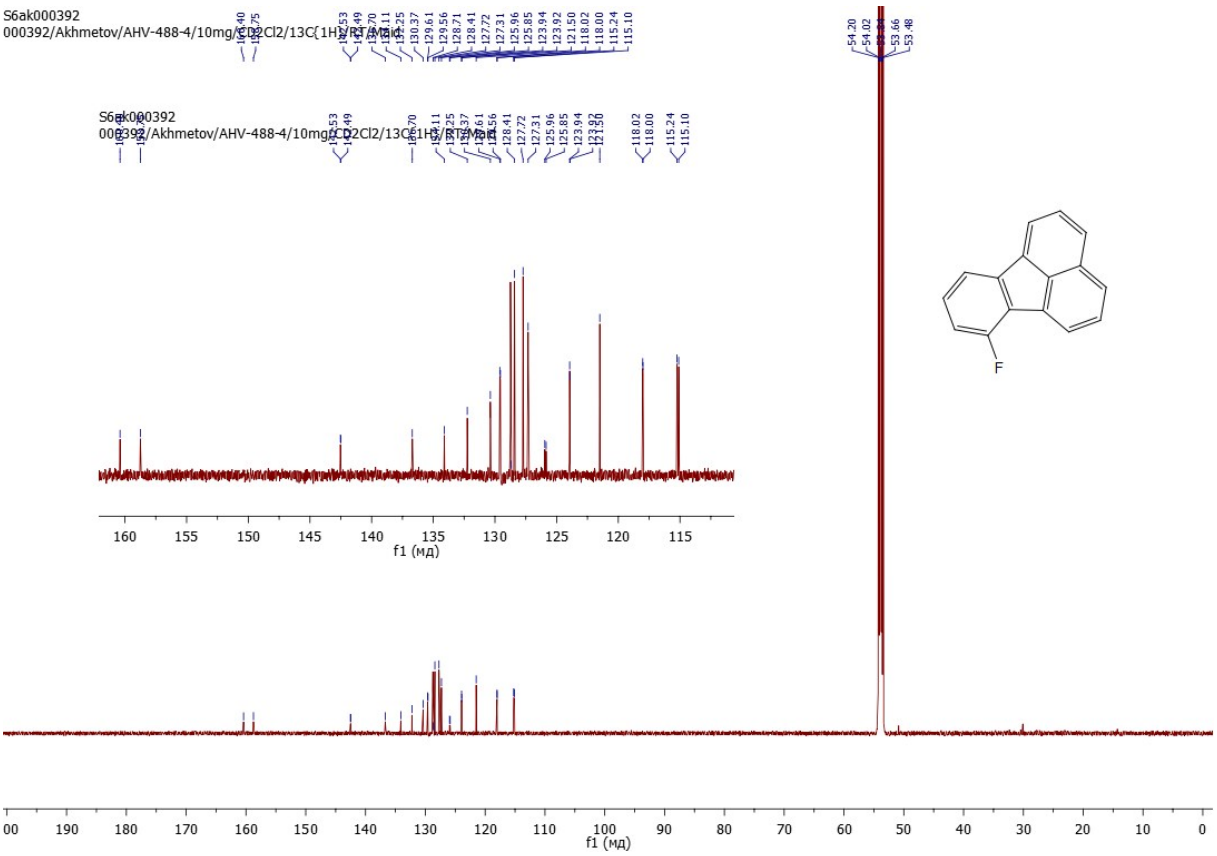


**Figure S90**. $^{13}C$ NMR (151 MHz, $CD_2Cl_2$) of 7-fluorofluoranthrene.

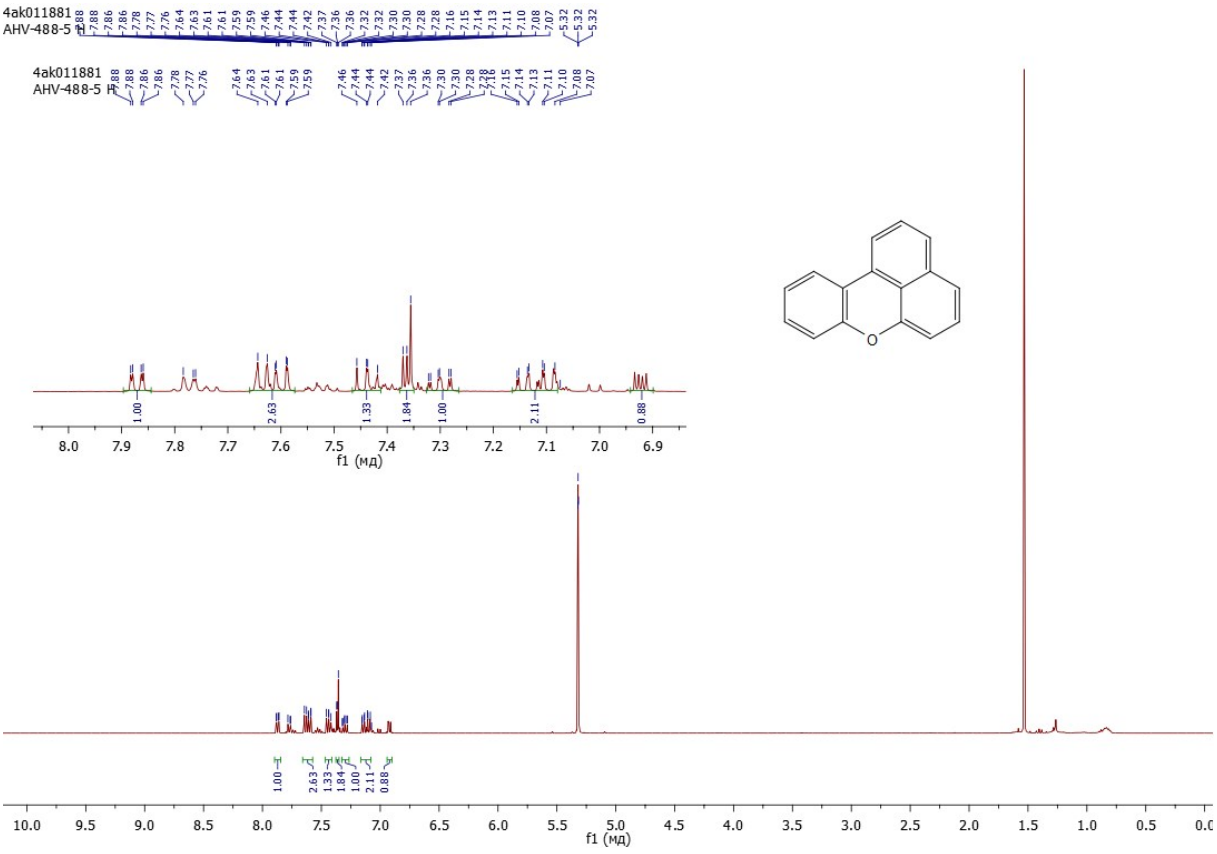


**Figure S91**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) of Benzo[kl]xanthene.