Intramolecular Aryl-Aryl Coupling via C-F Bond Activation Tolerant towards C-I Functionality

Ann-Kristin Steiner[a] , Mikhail Feofanov[b] and Konstantin Amsharov *[a,b,c]

[a]Institute of Organic Chemistry II, University Erlangen-Nuremberg, Nikolaus-Fiebiger-Str. 10, 91058 Erlangen, Germany.

[b] Institute of Chemistry - Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt-Mothes-Str. 2, 06120 Halle

[c] South Ural State University, pr. Lenina 76, 454080 Chelyabinsk, Russia

Table of Content

OVERVIEW OF COMPOUNDS SYNTHESIZED 4

1 EXPERIMENTAL SECTION 8

2 REFERENCES 41

3 SPECTROSCOPIC ANALYSIS AND CHARACTERIZATION 42

3.1 Building Blocks 1–12 and Precursors P1–19 42

2-Bromo-2’-fluoro-1,1’-biphenyl (1) 42

(2’-Fluoro-[1,1’-biphenyl]2-yl)boronic acid (2) 44

2-Fluoro-4''-methyl-1,1':2',1''-terphenyl (P1) 47

4''-(*Tert*-butyl)-2-fluoro-1,1':2',1''-terphenyl (P2) 50

2-Fluoro-4''-methoxy-1,1':2',1''-terphenyl (P3) 52

Methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (P4) 55

2''-Fluoro-*N,N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (P5) 58

4-(2'-Fluoro-[1,1'-biphenyl]-2-yl)pyridine (P6) 60

4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (P7). 63

4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (P8). 65

2-(2'-Fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (P9) 67

4''-Chloro-2-fluoro-1,1':2',1''-terphenyl (P10) 69

4''-Bromo-2-fluoro-1,1':2',1''-terphenyl (P11) 72

2-Fluoro-4''-nitro-1,1':2',1''-terphenyl (3) 74

2''-Fluoro-[1,1':2',1''-terphenyl]-4-amine (4) 77

2-Fluoro-4’’-iodo-1,1’:2’,1’’-terphenyl (P12) 79

2-fluoro-3''-iodo-1,1':2',1''-terphenyl (P13). 82

2-fluoro-2''-iodo-1,1':2',1''-terphenyl (P14). 84

2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (P15). 86

2-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5). 88

2-fluoro-4-nitro-1,1':2',1''-terphenyl (6). 89

2-fluoro-[1,1':2',1''-terphenyl]-4-amine (7). 91

2-fluoro-4-iodo-1,1':2',1''-terphenyl (P16). 92

2-fluoro-5-nitro-1,1':2',1''-terphenyl (8). 94

6-fluoro-[1,1':2',1''-terphenyl]-3-amine (9). 96

2-fluoro-5-iodo-1,1':2',1''-terphenyl (P17). 97

6-fluoro-[1,1':2',1''-terphenyl]-2-amine (10). 99

2-fluoro-6-iodo-1,1':2',1''-terphenyl (P18). 101

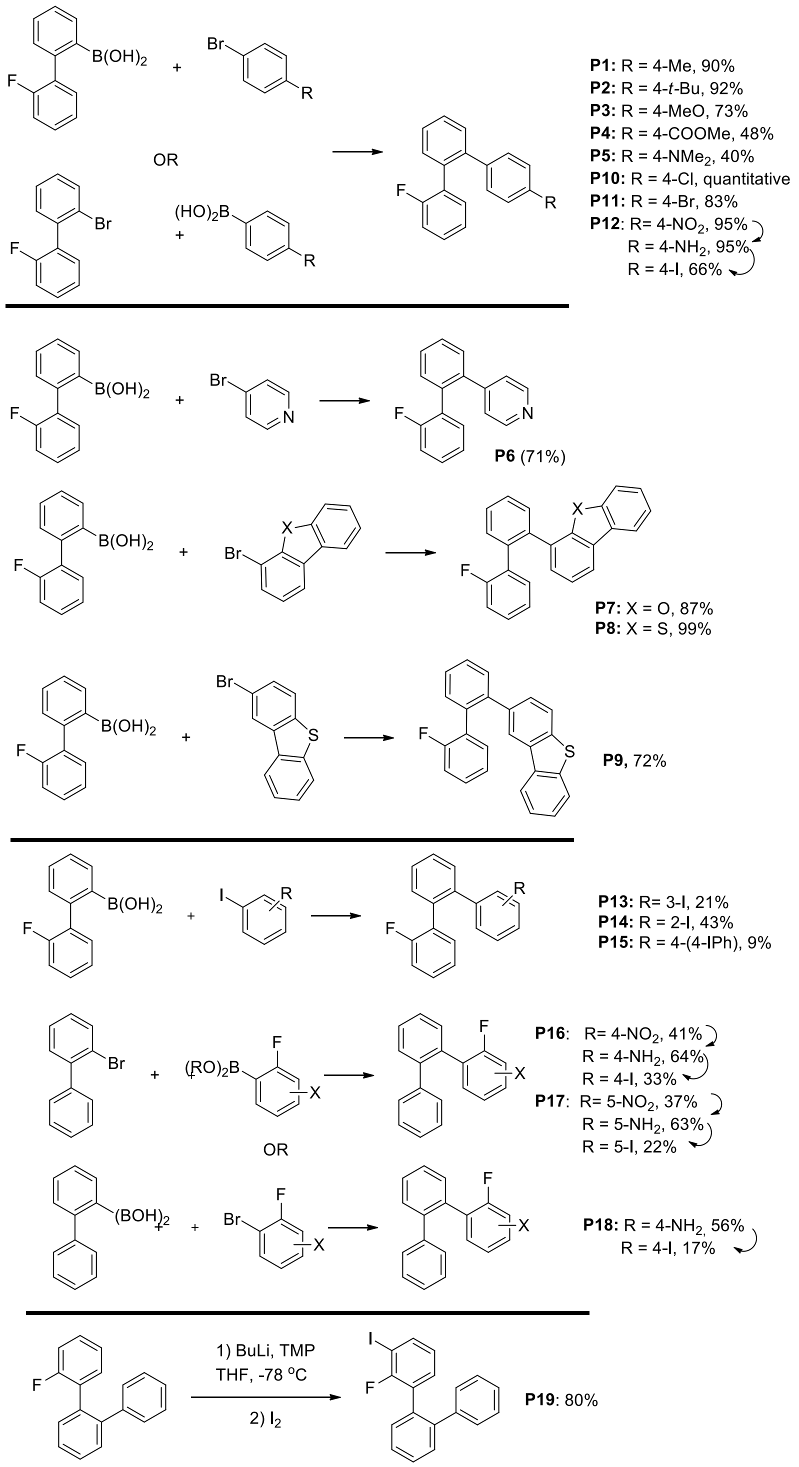
2-fluoro-3-iodo-1,1':2',1''-terphenyl (P19). 103

1-Fluoro-4-iodobenzo[*c*]phenanthrene (P20). 105

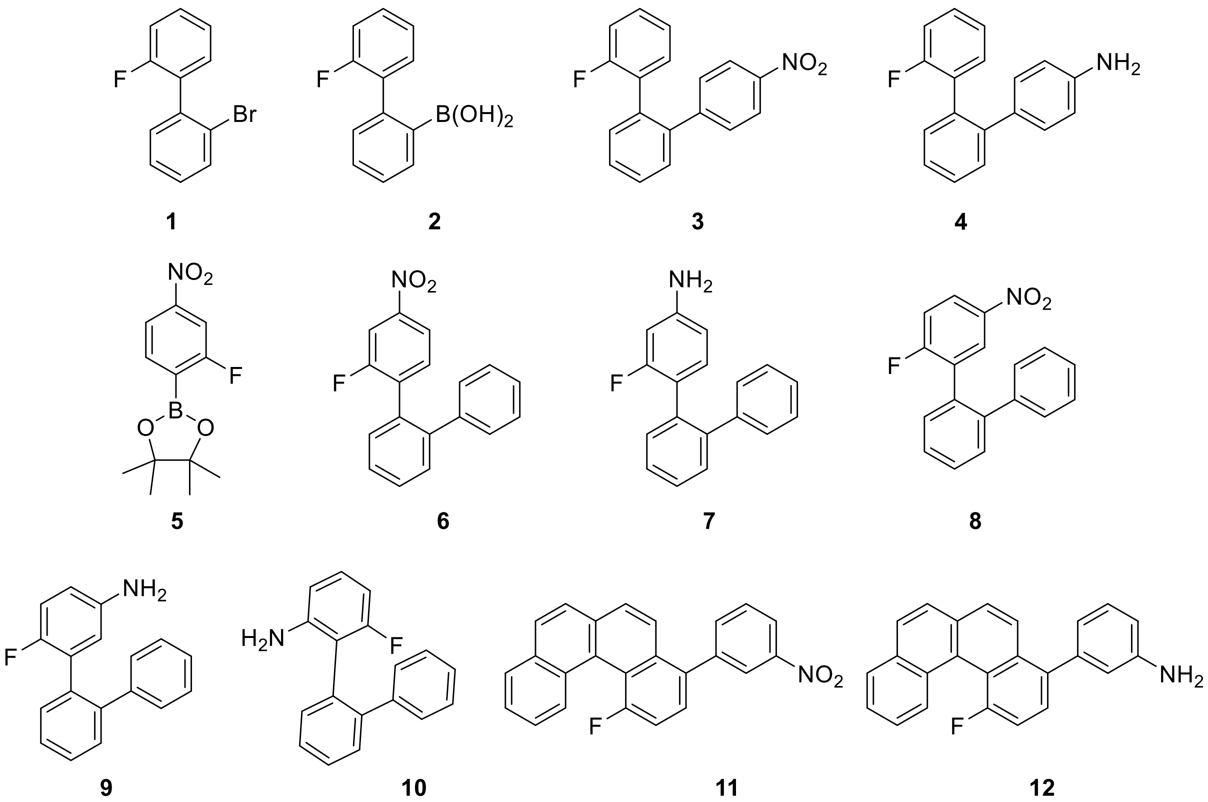
1-Fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (11) 108
3-(1-Fluorobenzo[*c*]phenanthren-4-yl)aniline (12) 111
1-Fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (P21) 113

3.2 Carbon-Based Nanographenes T1-T12 116
2-Methyltriphenylene (T1) 116
2-(*Tert*-butyl)triphenylene (T2) 118
Condensation of 2-Fluoro-4''-methoxy-1,1':2',1''-terphenyl (P3) 121
Condensation of Methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (P4) 122
Condensation of 2''-Fluoro-*N,N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (P5) 122
Condensation of 4-(2'-Fluoro-[1,1'-biphenyl]-2-yl)pyridine (P6) 126
Triphenyleno[1,2-b]benzofuran (T3). 128
Benzo[b]triphenyleno[2,1-d]thiophene (T4). 130
Benzo[*b*]triphenyleno[1,2-*d*]thiophene (T5) and Benzo[b]triphenyleno[2,3-d]thiophene (T6)... 132
2-Chlorotriphenylene (T7) 140
2-Bromotriphenylene (T8) 143
2-Iodotriphenylene (T9)... 146
Condensation of 2-fluoro-3''-iodo-1,1':2',1''-terphenyl (P13). 149
Condensation of 2-fluoro-2''-iodo-1,1':2',1''-terphenyl (P14). 149
2-(4-iodophenyl)triphenylene (T10). 150
Condensation of 2-fluoro-4-iodo-1,1':2',1''-terphenyl (P16). 151
Condensation of 2-fluoro-5-iodo-1,1':2',1''-terphenyl (P17). 152
Condensation of 2-fluoro-6-iodo-1,1':2',1''-terphenyl (P18). 152
Condensation of 2-fluoro-3-iodo-1,1':2',1''-terphenyl (P19) 153
3-Iodobenzo[*ghi*]fluoranthene (T11) 153
3-(3-Iodophenyl)benzo[*ghi*]fluoranthene (T12) 156

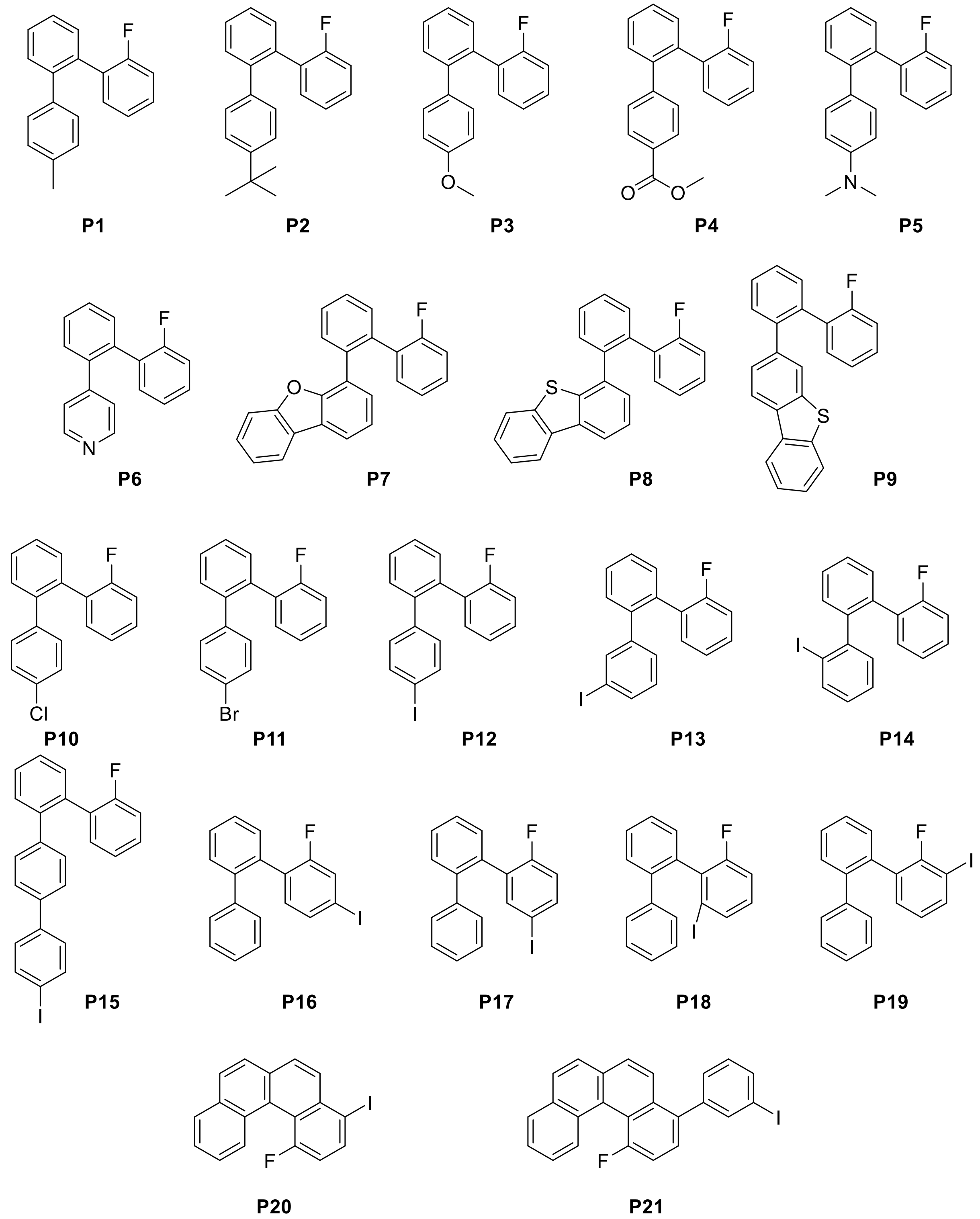
Overview of Compounds Synthesized



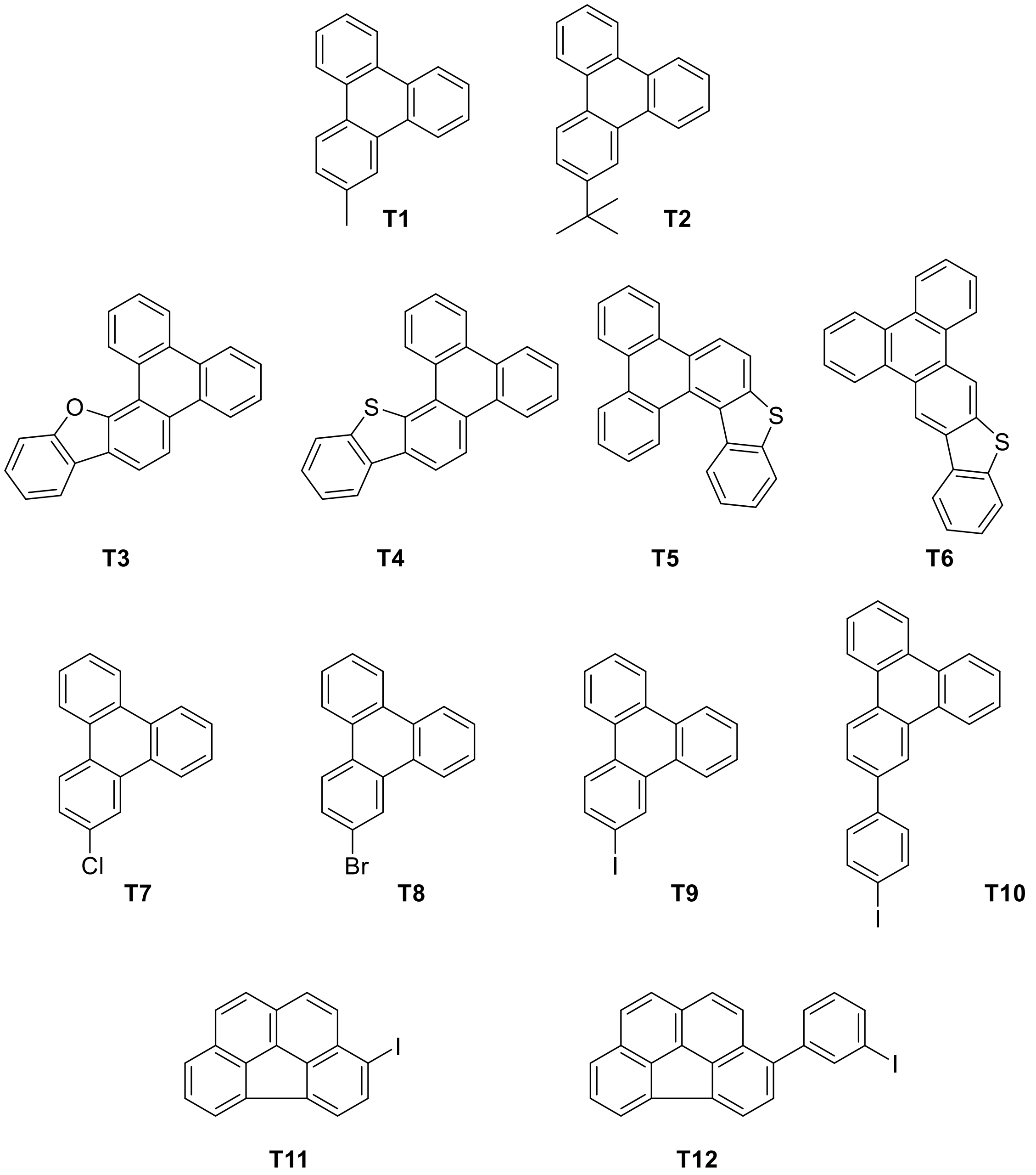
Scheme S1: Synthesis of precursor terphenyls **P1-18** via Suzuki cross-coupling reaction. All reaction conditions used can be found in the Experimental Section. **P10, P16, P17** were obtained in a three-step procedure: after Suzuki reaction, the NO_2-substituent was reduced to NH_2, which was reacted in a Sandmeyer reaction to obtain iodinated terphenyl **P10, P16, P17**. **P18** was obtained in two-step procedure: after Suzuki reaction, NH_2-substituent was converted into iodine group yielding **P18**. **P19** was synthesized via ortho-iodination after lithiation of 2-fluoro-1,1':2',1"-terphenyl. The yields of isolated products are given.



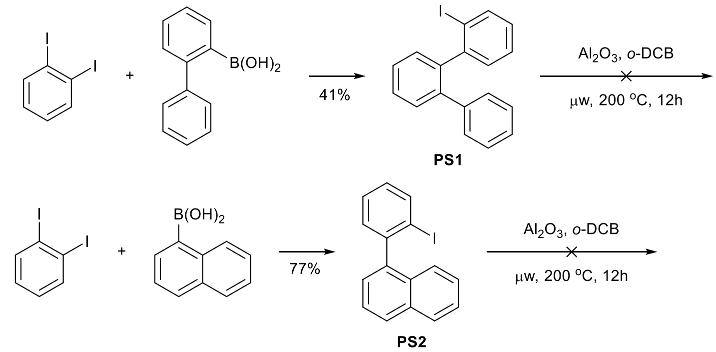
Scheme S2. Building Blocks



Scheme S3. Precursors



Scheme S4. Carbon-Based Nanostructures.



Scheme S5. Synthesis of 2-iodo-1,1':2',1''-terphenyl and 1-(2-iodophenyl)naphthalene and their dehydroiodination on activated alumina (no reaction was observed).

1 EXPERIMENTAL SECTION

All chemicals and solvents were purchased in reagent grade from commercial suppliers (Acros®, Sigma-Aldrich® or Fluka®, Fluorochem®, Merck®, chemPur®) and used as received, unless otherwise specified. Solvents in HPLC grade were purchased from Fisher Chemicals®. γ-Al_2O_3 (neutral, Brockmann I, 50–200 mm, 60A) was purchased from Acros$^{®}$. **Flash column chromatography** was performed on a Interchim PuriFlash 430 using flash grade silica gel from (Machery-Nagel 60 M (40–63 mm, deactivated)). **NMR spectra** were recorded on a Bruker Avance 400, a Bruker Avance Neo 400 or a Joel JNM EX-400, all operating at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 377 MHz (^{19}F NMR) and on a Bruker Avance 300 operating at 282 MHz (^{19}F NMR) at room temperature. The signals were referenced to residual solvent peaks (in parts per million (ppm) ^{1}H: $CDCl_3$, 7.24 ppm; CD_2Cl_2, 5.32 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; CD_2Cl_2, 53.8 ppm). Coupling constants were assigned as observed. The obtained spectra were evaluated with the program MestReNova 11.0.4. **LDI-MS spectra** were recorded on a Shimadzu Biotech AXIMA Confidence MALDI-TOF instrument. **High resolution APPI spectra** were recorded on a Bruker ESI TOF maXis 4G instrument. The data was evaluated with the program Bruker Compass DataAnalysis 4.2. **Analytical HPLC measurements** were performed on a Shimadzu Prominence Liquid Chromatograph LC-20AT with communication bus module CBM-20A, diode array detector SPD-M20A, and column oven CTO-20AC. **Preparative HPLC separations** were performed on a Shimadzu Prominence Liquid Chromatograph LC-20AT with communication bus module CBM-20A, diode array detector SPDM20A, degassing unit DGU-20A 5R, column oven CTO-20A, auto sampler SIL-20A HT and fraction collector FRC-10A. For analysis a Buckyprep column (4.6ID x 250 mm) and a Cosmosil PBr column (4.6ID x 250 mm), both from Nacalai Tesque, were used. For separation a Cosmosil PBr column (10ID x 250 mm) and a Cosmosil Buckyprep column (10 x 250 mm) were used. As eluent a DCM/MeOH mixture was used (UV-vis detection). The data (HPLC chromatograms and UV/vis spectra) were evaluated with the programs Shimadzu LCsolution and Shimadzu LabSolutions, respectively. **Microwave-assisted reactions** were performed using a *Discover SP Microwave Synthesizer*, CEM or a *Biotage® Initiator+*. The reaction temperature was monitored by using external surface sensors. **TLC analysis** was carried out with TLC sheets coated with silica gel with fluorescent indicator 254 nm from Machery-Nagel (ALUGRAM® SIL G/UV254) and visualized via UV-light of 254nm or 366 nm.

General Procedure for Suzuki Cross-Coupling Reaction:

A single neck round-bottom flask equipped with a magnetic stirring bar was charged with aryl halide (1 mmol, 1 equiv), boronic acid/ester (1.1–2 mmol, 1.1–2 equiv), K_2CO_3 or Cs_2CO_3 or K_3PO_4 (2 mmol, 2 equiv) and a mixture of toluene/MeOH 2:1 (13–15 mL), toluene/MeOH/H_2O 2.5:1:0.3 (20 mL), THF/H_2O 5:1 (18 mL) or DME/H_2O 3:1 (15 mL). The mixture was degassed under dynamic vacuum for 15 minutes under ultrasonification. Under nitrogen atmosphere $Pd(PPh_3)_4$/$Pd(PPh_3)_2Cl_2$ (0.02–0.05 mmol, 2–5 mol%, 0.02–0.05 equiv) was added as catalyst and the suspension degassed for 10 minutes under stirring. The reaction mixture was stirred at reflux for 7–20 h under nitrogen atmosphere. After cooling to room temperature water was added, phases were separated and the aqueous layer extracted with CH_2Cl_2 three times. The combined organic fractions were dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude material was filtered through silica gel with CH_2Cl_2/hexanes 1:1 and after removal of the solvent it was purified by flash column chromatography on silica gel which yielded the pure cross-coupled product.

General Procedure: Al_2O_3-Mediated HF Elimination in Microwave

Typically, a Schlenk ampule was charged with γ-Al_2O_3 (30 g, 0.29 mol) which was activated by annealing at 250 °C overnight in air. Afterwards, it was activated by annealing at 590°C under vacuum (3 x 10^{-2} mbar) for 4 h. A flame-dried and argon flushed microwave vial (2-5 mL) was charged with the respective fluoroarene (~10 mg, 23.0–40.9 µmol, 1 equiv.) and *o*-

DCB (4 mL). Under Ar atmosphere previously activated γ-Al_2O_3 was added (1.5 – 3 g, 14.7–29.4 mmol, 514–1079 equiv.) and the vial closed. The condensation was carried out at 180–260 °C for the indicated time in the microwave. Afterwards Al_2O_3 was extracted with toluene or *o*-DCB. Pure product was obtained either after simple solvent evaporation or by HPLC separation of the crude product mixture.

2-Bromo-2'-fluoro-1,1'-biphenyl (1)[1]**.** 1-Bromo-2-iodo-benzene (10.0 g, 4.54 mL, 35.4 mmol, 1 equiv), 2-fluorophenylboronic acid (5.44 g, 38.9 mmol, 1.1 eq), Cs_2CO_3 (23.0 g, 70.7 mmol, 2 equiv), and Pd(dppf)Cl_2 (517 mg, 707 µmol, 0.02 equiv) in THF/H_2O 5:1 (100 mL/20 mL) were reacted according to the general procedure (reflux, 18 h). The product was isolated by flash column chromatography on silica gel (hexanes) as colorless oil which crystallized as hard white solid by scratching (7.63 g, 86 %): R_f = 0.47 (SiO_2, hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.41–7.34 (m, 2H), 7.32–7.18 (m, 4H), 7.17–7.12 (ddd, *J* = 9.5, 8.3, 1.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, *J* = 247.3 Hz), 137.3, 133.0, 131.8, 131.7 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 7.9 Hz), 129.6, 129.0 (d, *J* = 15.9 Hz), 127.4, 124.0 (d, *J* = 3.7 Hz), 115.8 (d, *J* = 22.1 Hz) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.76 – -114.84 (m, 1F) ppm. HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1) t_R = 4.36 min. UV/vis (DCM/MeOH) λ_{max} 267 (sh), 226 nm.

(2'-Fluoro-[1,1'-biphenyl]2-yl)boronic acid (2). A two-necked round-bottom flask equipped with a magnetic stirring bar and a rubber septum was charged with 2-bromo-2'-fluoro-1,1'-biphenyl (1.50 g, 6.97 mmol, 1 equiv) and THF (10 mL) and the clear solution was cooled to -78 °C. *n*-BuLi (765 mg, 5.97 mL, 2.5 M in hexanes, 14.9 mmol, 2.5 equiv) was added dropwise via a syringe and the yellow solution stirred for 30 minutes at -78 °C. Trimethyl borate (3.10 g, 3.39 mL, 29.9 mmol, 5 equiv) was added in one portion via a syringe and the mixture allowed to reach room temperature over a period of 3 h. A 1 M aqueous solution of HCl (5 mL) was added to quench the reaction and stirring at room temperature was continued for further 30 minutes. Water (10 mL) and CH_2Cl_2 (10 mL) were added, layers were separated and the aqueous phase extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, filtered and the solvent evaporated to dryness. After short column chromatography over silica gel using a solvent gradient (hexanes/CH_2Cl_2 5:1 $\rightarrow$ CH_2Cl_2 $\rightarrow$ CH_2Cl_2/MeOH 20:1) and precipitation with hexanes product **2** was obtained as white solid (722 mg, 56 %): R_f = 0.28 (SiO_2, CH_2Cl_2/EtOAc 20:1). ^1H NMR (500 MHz, 30 °C, DMSO-*d_6*) δ 7.73 (s, 2H, -$B(OH)_2$), 7.57 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.41 (td, *J* = 7.6, 1.6 Hz, 1H), 7.36–7.32 (m, 3H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.22–7.15 (m, 2H) ppm. ^{13}C\{1H, 19F\} NMR (125 MHz, 30 °C, DMSO-*d_6*) δ 159.5, 139.1, 133.3, 131.7, 131.0, 129.78, 129.2, 129.0, 127.0, 124.4, 115.6 ppm (signal of C-B not observed). ^{19}F\{1H\} NMR (470 MHz, 30 °C, DMSO-*d_6*) δ -116.72 (s, 1F) ppm. HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1) t_R = 4.17 min. UV/vis (DCM/MeOH) λ_{max} 275 (sh), 240, (219) nm. HR MS (APPI) calcd. for $C_{12}H_{10}BFO_2$ ($M^{+\bullet}$, 100) *m/z* 216.0754, found 216.0754.

2-Fluoro-4''-methyl-1,1':2',1''-terphenyl (P1). 2-Bromo-2'-fluoro-1,1'-biphenyl (**1**, 250 mg, 996 µmol, 1 equiv), 4-tolylphenylboronic acid (176 mg, 1.29 mmol, 1.3 equiv), K_3PO_4 (423 mg, 1.99 mmol, 2 equiv), and $Pd(PPh_3)_2Cl_2$ (35.0 mg, 49.8 µmol, 0.05 equiv) in THF/H_2O 5:1 (15 mL/3 mL) were reacted according to the general procedure (reflux, 20 h). The product was isolated by flash column chromatography on silica gel (hexanes $\rightarrow$ hexanes/CH_2Cl_2 9:1) as colorless oil (236 mg, 90 %): R_f = 0.60 (SiO_2, hexanes/CH_2Cl_2 5:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.50 – 7.36 (m, 4H), 7.27 – 7.22 (m, 1H), 7.18 (td, *J* = 7.6, 1.9 Hz, 1H), 7.11 – 7.01 (m, 5H), 6.95 (ddd, *J* = 9.6, 8.3, 1.1 Hz, 1H), 2.30 (s, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.0 (d, *J* = 245.4 Hz), 142.1, 138.8, 136.8, 134.8, 132.6 (d, *J* = 3.6 Hz), 131.4, 130.6, 129.8 (d, *J* = 16.0 Hz), 129.4, 129.3 (d, *J* = 8.0 Hz), 128.9, 128.6, 127.4, 124.2 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 22.4 Hz). 21.2. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -114.64 – -114.72 (m). HPLC (PBr column, 1.0 mL/min, 35 °C, CH_2Cl_2/MeOH 3:7) t_R = 4.34 min.

UV/vis (CH_2Cl_2/MeOH) λ_{max} 254 (sh), 233, 218 (sh) nm. HR MS (APPI) calcd. for $C_{19}H_{15}F$ ($M^{+\bullet}$, 100) *m/z* 262.1152, found 262.1147.

4''-(*Tert*-butyl)-2-fluoro-1,1':2',1''-terphenyl (P2). 2-Bromo-2'-fluoro-1,1'-biphenyl (**1**, 100 mg, 398 µmol, 1 equiv), 4-*tert*-butylphenylboronic acid (85.1 mg, 478 µmol, 1.2 equiv), K_3PO_4 (169 mg, 797 µmol, 2 equiv), and $Pd(PPh_3)_4$ (23.0 mg, 19.9 µmol, 0.05 equiv) in THF/H_2O 5:1 (10 mL/2 mL) were reacted according to the general procedure (reflux, 20 h). The product was isolated by flash column chromatography on silica gel (hexanes) and obtained as white solid after precipitation with MeOH under ultrasonification (111 mg, 92 %): R_f = 0.19 (SiO_2, hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 4H), 7.23 – 7.17 (m, 3H), 7.12 (vis td, *J* = 7.6, 1.9 Hz, 1H), 7.10 – 7.05 (m, 2H), 7.01 (vis td, *J* = 7.5, 1.2 Hz, 1H), 6.94 (ddd, *J* = 9.7, 8.2, 1.1 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, *J* = 246.2 Hz), 149.5, 141.7, 138.3, 134.4, 132.3 (d, *J* = 3.5 Hz), 131.1, 130.3, 129.4 (d, *J* = 15.8 Hz), 128.9, 128.8 (d, *J* = 8.1 Hz), 128.2, 126.9, 124.7, 123.6 (d, *J* = 3.6 Hz), 115.4 (d, *J* = 22.6 Hz)., 34.5, 31.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.22– -115.64 (m). HPLC (PBr column, 1.0 mL/min, 35 °C, CH_2Cl_2/MeOH 1:1) t_R = 3.82 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 257 (sh), 234, 222 (sh) nm. HR MS (APPI) calcd. for $C_{22}H_{21}F$ ($M^{+\bullet}$, 100) *m/z* 304.1622, found 304.1619.

2-Fluoro-4''-methoxy-1,1':2',1''-terphenyl (P3). 2-Bromo-2'-fluoro-1,1'-biphenyl (**1**, 1.65 g, 6.58 mmol, 1 equiv), (4-methoxyphenyl)boronic acid (1.00 g, 6.58 mmol, 1 equiv), Cs_2CO_3 (4.29 g, 13.2 mmol, 2 equiv), and $Pd(PPh_3)_4$ (380 mg, 329 µmol, 0.05 equiv) in toluene/MeOH 2:1 (40 mL/20 mL) were reacted according to the general procedure (reflux, overnight). The product **P3** was isolated by flash column chromatography on silica gel and obtained as colorless oil (1.33 g, 73 %): R_f = 0.42 (SiO_2, hexanes/CH_2Cl_2 2:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.49 – 7.36 (m, 4H), 7.32 – 7.22 (m, 1H), 7.19 (vis td, *J* = 7.6, 1.9 Hz, 1H), 7.12 – 7.05 (m, 3H), 6.96 (ddd, *J* = 9.6, 7.4, 1.1 Hz, 1H), 6.78 – 6.73 (m, 2H), 3.75 (s, 3H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.1 (d, *J* = 245.3 Hz), 159.1, 141.8, 134.9, 134.2, 132.7 (d, *J* = 3.4 Hz), 131.4, 130.7, 130.6, 129.9 (d, *J* = 6.0 Hz), 129.3 (d, *J* = 8.2 Hz), 128.7, 127.3, 124.3 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 22.3 Hz), 113.7, 55.5. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -114.71 – -115.63 (m). HPLC (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 3:7) t_R = 4.38 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 260 (sh), 237 nm. HR MS (APPI) calcd. for $C_{19}H_{15}FO$ ($M^{+\bullet}$, 100) *m/z* 278.1101, found 278.1100.

Methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (P4). 2-Bromo-2'-fluoro-1,1'-biphenyl (**1**, 1.40 mg, 5.56 mmol, 1 equiv), 4-(methoxycarbonyl)phenyl)boronic acid (1.00 g, 5.56 mmol, 1 equiv), Cs_2CO_3 (3.62 g, 11.1 mmol, 2 equiv), and $Pd(PPh_3)_4$ (320 mg, 278 µmol, 0.05 equiv) in toluene/MeOH 2:1 (40 mL/20 mL) were reacted according to the general procedure (reflux, overnight). The product was isolated by flash column chromatography on silica gel and obtained as colorless oil which crystallized after a few days in air as white solid (0.81 g, 48 %): R_f = 0.19 (SiO_2, hexanes/CH_2Cl_2 2:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.88 – 7.84 (m, 2H), 7.54 – 7.42 (m, 4H), 7.29 – 7.21 (m, 3H), 7.18 (td, *J* = 7.6, 1.9 Hz, 1H), 7.08 (td, *J* = 7.5, 1.2 Hz, 1H), 6.97 – 6.90 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.1, 159.8 (d, *J* = 245.8 Hz), 146.5, 141.1, 134.9, 132.5 (d, *J* = 3.2 Hz), 131.5, 130.3, 129.7, 129.6, 129.4, 129.1, 128.9, 128.7, 128.3, 124.4 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.2 Hz), 52.3. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -114.72 – -115.64 (m). HPLC (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 3:7) t_R = 4.46 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 266, 238 nm. HR MS (APPI) calcd. for $C_{20}H_{16}FO_2$ ($M^{+\bullet}$, 100) *m/z* 307.1129, found 307.1123.

2''-Fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (P5). (4-(Dimethylamino)phenyl)boronic acid (1.00 g, 6.06 mmol, 1 equiv), 2-bromo-2'-fluoro-1,1'-biphenyl (**1**, 1.52 g, 6.06 mmol, 1 equiv), Cs_2CO_3 (3.95 g, 12.1 mmol, 2 equiv), and $Pd(PPh_3)_4$ (350 mg, 303 µmol, 0.05 equiv) in toluene/MeOH 2:1 (60 mL/30 mL) were reacted according to the general procedure (reflux, 19 h). Product **P5** was isolated by flash column chromatography on silica gel (hexanes/CH_2Cl_2 2:1) as light yellow solid (715 mg, 40 %): R_f = 0.23 (SiO_2, hexanes/CH_2Cl_2 2:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.46 – 7.42 (m, 2H), 7.37 – 7.35 (m, 2H), 7.29 – 7.18 (m, 2H), 7.10 (vis td, *J* = 7.5, 1.1 Hz, 1H), 7.06 – 6.95 (m, 3H), 6.62 – 6.55 (m, 2H), 2.91 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.17 (d, *J* = 245.3 Hz), 149.9, 142.3, 134.6, 132.7 (d, *J* = 3.5 Hz), 131.5, 130.5, 130.4, 130.3, 129.6, 129.2 (d, *J* = 8.1 Hz), 128.7, 126.7, 124.3 (d, *J* = 3.3 Hz), 115.8 (d, *J* = 22.3 Hz), 112.2, 40.6. ^{19}F NMR (282 MHz, CD_2Cl_2) δ -114.81 – -115.73 (m). HPLC (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 3:7) t_R = 4.61 min. UV/vis (DCM/MeOH) λ_{max} 296, 230 nm. HR MS (APPI) calcd. for $C_{20}H_{18}FN$ ($M^{+\bullet}$, 100) *m/z* 291.1418, found 291.1424.

4-(2'-Fluoro-[1,1'-biphenyl]-2-yl)pyridine (P6). 2-Bromo-2'-fluoro-1,1'-biphenyl (**1**, 500 mg, 1.99 mmol, 1 equiv), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (470 mg, 2.29 mmol, 1.15 equiv), Cs_2CO_3 (1.30 g, 3.98 mmol, 2 equiv), and $Pd(PPh_3)_4$ (92.0 mg, 79.7 µmol, 0.04 equiv) in toluene/MeOH 2:1 (60 mL/30 mL) were reacted according to the general procedure (reflux, 20 h). The product was isolated by flash column chromatography on silica gel (hexanes/EtOAc 5:1) and obtained as light yellow solid after drying in vacuum (350 mg, 71 %): R_f = 0.13 (SiO_2, hexanes/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 7.50 – 7.39 (m, 4H), 7.26 – 7.21 (m, 1H), 7.15 (td, *J* = 7.5, 1.8 Hz, 1H), 7.08 – 7.04 (m, 3H), 6.91 (ddd, *J* = 9.7, 8.3, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, *J* = 246.8 Hz), 149.3, 138.9, 134.4, 131.8 (d, *J* = 3.3 Hz), 131.2 (d, *J* = 0.9 Hz), 129.6, 129.4 (d, *J* = 8.1 Hz), 128.5 (d, *J* = 1.9 Hz), 128.3 (d, *J* = 15.7 Hz), 124.0 (d, *J* = 3.9 Hz), 115.6 (d, *J* = 22.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.76 – -114.82 (m, 1F). HPLC (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:9) t_R = 4.98 min. UV/vis (DCM/MeOH) λ_{max} 229, 256 (sh) nm. HR MS (APPI) calcd. for $C_{17}H_{13}FN$ ($M^{+\bullet}$, 100) *m/z* 250.1027, found 250.1034.

4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (P7). A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 4-bromodibenzo[b,d]furan (84 mg, 0.34 mmol), (2’-fluoro-[1,1’-biphenyl]2-yl)boronic acid (**2**, 73 mg, 0.34 mmol), K_2CO_3 (185 mg, 1.34 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 μmol). The solids were suspended in 12:5:1.5 toluene/MeOH/H_2O (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (**P7**) in 87% yield (100 mg). R_f = 0.18 (SiO_2, hexanes)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.73 – 7.64 (m, 1H), 7.61 – 7.52 (m, 3H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.30 (td, *J* = 7.6, 1.1 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.11 (td, *J* = 7.5, 1.9 Hz, 1H), 7.09 – 6.98 (m, 1H), 6.85 (td, *J* = 8.3, 0.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7 (d, *J* = 246.6 Hz), 156.0, 153.5, 136.2, 135.7, 131.7 (d, *J* = 3.4 Hz), 131.0, 130.9, 129.0 (d, *J* = 15.6 Hz), 128.8, 128.7, 128.5, 128.0, 127.9, 127.0), 125.7, 124.1 (d, *J* = 7.1 Hz), 123.3 (d, *J* = 3.6 Hz), 122.5, 122.4, 120.5, 119.5, 115.1 (d, *J* = 22.5 Hz), 111.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.39 (ddd, *J* = 9.9, 7.6, 5.5 Hz, 1F). HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 40°C, DCM/MeOH 4:6, t_R 3.95min). UV/vis (DCM/MeOH) λ 289, 320 (sh) nm. HR MS (APPI; Toluene): Chemical Formula: $C_{24}H_{15}FO$, calc. 338.1102, found 338.1107**.**

4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (P8). A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 4-bromodibenzo[b,d]thiophene (90 mg, 0.34 mmol), (2’-fluoro-[1,1’-biphenyl]2-yl)boronic acid (**2**, 73 mg, 0.34 mmol), K_2CO_3 (185 mg, 1.34 mmol) and $Pd(PPh_3)_4$ (14 mg, 12 μmol). The solids were suspended in 12:5:1.5 toluene/MeOH/H_2O (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (**P8**) in 99%

yield (120 mg). R_f = 0.13 (SiO_2, hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.07 (m, 1H), 8.01 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.74 – 7.66 (m, 1H), 7.57 – 7.51 (m, 3H), 7.49 – 7.40 (m, 2H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.16 – 7.02 (m, 3H), 6.96 – 6.77 (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.1 (d, *J* = 245.9 Hz), 140.3, 140.3, 140.0, 136.7, 136.2, 136.0, 135.5, 132.2 (d, *J* = 3.3 Hz), 131.7, 130.3, 130.3, 129.4 (d, *J* = 8.1 Hz), 128.9 (d, *J* = 15.6 Hz), 128.6, 128.5, 127.2, 124.9, 124.6, 123.9 (d, *J* = 3.6 Hz), 123.1, 122.1, 120.6, 115.6 (d, *J* = 22.5 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2) δ -115.37 (s, 1F). HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 40°C, DCM/MeOH 4:6, t_R 7.86 min). UV/vis (DCM/MeOH) λ 280, 295, 338, 359, 379 nm HRMS (APPI; Toluene): Chemical Formula: $C_{24}H_{15}FS$, calc. 354.0878, found 354.0879.

2-(2'-Fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (P9). 2-Bromodibenzothiophene (80.0 mg, 370 µmol, 1 equiv), (2'-fluoro-[1,1'-biphenyl]-2-yl)boronic acid (**2**, 195 mg, 741 µmol, 2 equiv), Cs_2CO_3 (241 mg, 741 µmol, 2 equiv), and $Pd(PPh_3)_2Cl_2$ (13.0 mg, 18.5 µmol, 0.05 equiv) in toluene/MeOH/H_2O 2.5:1:0.3 (7.6 mL) were reacted according to the general procedure (reflux, 18 h). The product was isolated by flash column chromatography on silica gel (hexanes) and obtained as white solid after drying *in vacuo* (95 mg, 72 %). R_f = 0.15 (SiO_2, hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.84 – 7.79 (m, 1H), 7.64 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.57 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.54 – 7.38 (m, 5H), 7.254 – 7.14 (m, 3H), 7.01 (td, *J* = 7.5, 1.2 Hz, 1H), 6.90 (ddd, *J* = 9.5, 8.1, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, *J* = 246.4 Hz), 141.4, 139.7, 137.8, 137.8, 135.6, 135.3, 134.6, 132.1 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 1.3 Hz), 130.4, 129.1 (d, *J* = 15.7 Hz), 128.9 (d, *J* = 8.0 Hz), 128.3, 128.1, 127.3, 126.6, 124.3, 123.8 (d, *J* = 3.6 Hz), 122.8, 122.2, 122.0, 121.4, 115.5 (d, *J* = 22.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.74 – -114.80 (m, 1F). HPLC (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:1) t_R = 4.93 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 330, 317, 280 (sh), 264 (sh), 240 nm. HR MS (APPI) calcd. for $C_{24}H_{15}FS$ ($M^{+\bullet}$, 100) *m/z* 354.0873, found 354.0881.

4''-Chloro-2-fluoro-1,1':2',1''-terphenyl (P10). 2-Bromo-2'-fluoro-1,1'-biphenyl (**1**, 200 mg, 797 µmol, 1 equiv), 4-chlorophenylboronic acid (249 mg, 1.59 mmol, 2 equiv), K_2CO_3 (220 mg, 1.59 mmol, 2 equiv), and $Pd(PPh_3)_2Cl_2$ (28.0 mg, 39.8 µmol, 0.05 equiv) in DME/H_2O 3:1 (12 mL) were reacted according to the general procedure (80 °C, 18 h). The product was isolated by flash column chromatography on silica gel (hexanes) and obtained as white solid after drying in vacuum (224 mg, quantitative): R_f = 0.46 (SiO_2, hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 4H), 7.24 – 7.19 (m, 1H), 7.17 – 7.10 (m, 3H), 7.07 – 7.02 (m, 3H), 6.92 (ddd, *J* = 9.6, 8.2, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, *J* = 246.6 Hz), 140.5, 139.8, 134.4, 132.7, 132.0 (d, *J* = 3.6 Hz), 131.1, 130.5, 129.9, 129.1 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 16.0 Hz), 128.3, 128.0, 127.5, 123.9 (d, *J* = 3.7 Hz), 115.5 (d, *J* = 22.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.78 – -114.84 (m, 1F). HPLC (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 2:8) t_R = 4.80 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 259 (sh), 251 (sh), 231 nm. HR MS (APPI) calcd. for $C_{18}H_{12}ClF$ ($M^{+\bullet}$, 100) *m/z* 282.0606, found 282.0599.

4''-Bromo-2-fluoro-1,1':2',1''-terphenyl (P11). 1-Bromo-4-iodobenzene (250 mg, 884 µmol, 1 equiv), 7,6(2'-fluoro-[1,1'-biphenyl]-2-yl)boronic acid (**2**, 191 mg, 884 µmol, 1 equiv), Cs_2CO_3 (576 mg, 1.77 mmol, 2 equiv), and $Pd(PPh_3)_4$ (51.1 mg, 44.2 µmol, 0.05 equiv) in THF/H_2O 5:1 (12 mL) were reacted according to the general procedure (reflux, 18 h). Product **P9** was isolated by flash column chromatography on silica gel (hexanes) and obtained as light yellow solid after drying in vacuum (241 mg, 83 %): R_f = 0.33 (SiO_2, hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.32 – 7.29 (m, 2H), 7.24 – 7.19 (m, 1H), 7.12 (td, *J* = 7.5, 1.9 Hz, 1H), 7.04 (td, *J* = 7.4, 1.2 Hz, 1H), 7.02 – 6.98 (m, 2H), 6.92 (ddd, *J* = 9.6, 8.3, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, *J* = 246.6 Hz), 140.4, 140.3, 134.3, 132.0 (d, *J* = 3.5 Hz), 131.1, 131.0, 130.8, 129.9, 129.1 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 15.7 Hz), 128.3, 127.5, 123.9 (d, *J* = 3.7 Hz), 120.9, 115.6 (d, *J* = 22.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.78 – -114.84 (m, 1F). HPLC (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 2:8) t_R = 5.08 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 260 (sh), 251 (sh), 232 nm. HR MS (APPI) calcd. for $C_{18}H_{12}BrF$ ($M^{+\bullet}$, 100) *m/z* 326.0101, found 326.0107.

2-Fluoro-4''-nitro-1,1':2,1''-terphenyl (3). 1-Bromo-4-nitrobenzene (200 mg, 803 µmol, 1 equiv), (2'-fluoro-[1,1'-biphenyl]-2-yl)boronic acid (**2**, 174 mg, 803 µmol, 1 equiv), Cs_2CO_3 (523 mg, 1.61 mmol, 2 equiv), and $Pd(PPh_3)_4$ (46.4 mg, 40.2 µmol, 0.05 equiv) in THF/H_2O 5:1 (20 mL/4 mL) were reacted according to the general procedure (100 °C, 16 h). Product **3** was isolated by flash column chromatography on silica gel (hexanes/CH_2Cl_2 5:1) and obtained as light yellow solid (223 mg, 95 %): R_f = 0.37 (SiO_2, hexanes/DCM 2:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.41 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.21 (m, 1H), 7.16 (td, *J* = 7.5, 1.9 Hz, 1H), 7.07 (td, *J* = 7.4, 1.2 Hz, 1H), 6.90 (ddd, *J* = 9.6, 8.2, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, *J* = 246.8 Hz), 148.3, 146.6, 139.4, 134.5, 131.8 (d, *J* = 3.3 Hz), 131.3, 130.0, 129.8, 129.5 (d, *J* = 8.1 Hz), 128.5, 128.5, 128.3 (d, *J* = 15.7 Hz), 124.1 (d, *J* = 3.6 Hz), 123.1, 115.7 (d, *J* = 22.2 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.70 – -114.77 (m, 1F). HPLC (PBr column, 1.0 mL/min, 40 °C, DCM/MeOH 3:7) t_R = 4.56 min. UV/vis (DCM/MeOH) λ_{max} 297 nm. HR MS (APPI) calcd. for $C_{18}H_{12}FNO_2$ ($M^{+\bullet}$, 100) *m/z* 293.0847, found 293.0845.

2-Fluoro-[1,1':2',1''-terphenyl]-4-amine (4). 2-Fluoro-4''-nitro-1,1':2',1''-terphenyl (**3**, 200 mg, 682 µmol, 1 equiv) was dissolved in EtOAc (7 mL) and under N_2 atmosphere $SnCl_2$ x $2H_2O$ (769 mg, 3.41 mmol, 5 equiv) was added. The mixture was heated at reflux overnight. After cooling to room temperature a sat. aq. $NaHCO_3$ solution (7 mL) was added, phases were separated and the aqueous fraction extracted with EtOAc (3 x 10 mL). After evaporation of the solvent the resulting red oil was purified by flash column chromatography on silica gel (hexanes/EtOAc 5:1) and product **4** was isolated as red-orange oil (170 mg, 95%). R_f = 0.39 (SiO_2, hexanes/EtOAc 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 4H), 7.22 – 7.11 (m, 1H), 7.13 (td, *J* = 7.6, 1.6 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.96 – 6.92 (m, 3H), 6.53 – 6.49

(m, 1H), 3.56 (broad s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (d, *J* = 246.4 Hz), 145.0, 141.7, 134.2, 132.2 (d, *J* = 3.6 Hz), 131.7, 130.9 (d, *J* = 1.4 Hz), 130.1, 130.0, 129.6 (d, *J* = 15.8 Hz), 128.6 (d, *J* = 8.0 Hz), 128.1, 126.4, 123.6 (d, *J* = 3.7 Hz), 115.4 (d, *J* = 22.5 Hz), 114.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.96 – -115.02 (m, 1F). HPLC (Buckyprep column, 1.0 mL/min, 35 °C, MeOH/DCM 8:2) t_R = 4.04 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 271, 237 nm. HR MS (APPI) calcd. for $C_{18}H_{14}FN$ ($M^{+\bullet}$, 100) *m/z* 263.1105, found 263.1107.

2-Fluoro-4''-iodo-1,1':2',1''-terphenyl (P12). A 50 mL round-bottom flask was charged with crude 2-fluoro-[1,1':2',1"-terphenyl]-4-amine (**4**, 200 mg, 682 µmol, 1 equiv), MeCN (8 mL) and conc. HCl (0.2 mL). The mixture was cooled to −13 °C in an ice-salt bath. A solution of sodium nitrite (105 mg, 1.52 mmol, 2 equiv) in water (0.5 mL) was added dropwise to the reaction mixture. The solution was stirred at −13 °C for 30 min, and a solution of KI (252 mg, 1.52 mmol, 2 equiv) in water (0.3 mL) was added. The reaction mixture was stirred for 15 min at −13 °C and another 1 h at room temperature. A sat. aq. $Na_2S_2O_3$-solution (15 mL) was added, phases were separated and the aqueous layer extracted with DCM (3 x 10 mL). The combined organic fractions were dried over $NaSO_4$, filtered, and the solvent evaporated *in vacuo*. The oily residue was dissolved in hexanes/DCM 2:1 and short column chromatography on silica gel rinsed with hexanes/DCM 2:1 afforded 2-fluoro-4"-iodo-1,1':2',1"-terphenyl (**P10**) as white solid (188 mg, 66 %). R_f = 0.85 (SiO_2, hexanes/DCM 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.46 – 7.36 (m, 4H), 7.25 – 7.19 (m, 1H), 7.12 (td, *J* = 7.5, 1.9 Hz, 1H), 7.04 (td, *J* = 7.5, 1.2 Hz, 1H), 6.93 (ddd, *J* = 9.6, 8.2, 1.2 Hz, 1H), 6.89 – 6.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, *J* = 245.9 Hz), 141.5, 141.0, 137.4, 134.8, 132.6 (d, *J* = 3.5 Hz), 131.6, 131.6, 130.4, 129.7 (d, *J* = 8.1 Hz), 129.3 (d, *J* = 15.7 Hz), 128.8, 128.1, 124.5 (d, *J* = 3.4 Hz), 115.9 (d, *J* = 22.4 Hz), 92.8. ^{19}F NMR (377 MHz, CD_2Cl_2) δ -114.78 – -114.84 (m, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 35 °C, MeOH/DCM 8:2) t_R = 5.50 min. UV/vis (CH_2Cl_2/MeOH) λ_{max}

258 (sh), 236 nm. HR MS (APPI) calcd. for $C_{18}H_{12}FI$ ($M^{+\bullet}$, 100) *m/z* 373.9962, found 373.9968.

2-fluoro-3''-iodo-1,1':2',1''-terphenyl (P13). A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1, 3-diiodobenzene (660 mg, 2 mmol), (2'-fluoro-[1,1'-biphenyl]-2-yl)boronic acid (**2**, 210 mg, 1 mmol), K_2CO_3 (414 mg, 3 mmol) and $Pd(PPh_3)_4$ (51 mg, 44 μmol). The solids were suspended in 2:1 dioxane/H_2O (30 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 24 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 2-fluoro-3''-iodo-1,1':2',1''-terphenyl (**P13**) as white oil in 21% yield (80 mg). R_f = 0.45 (SiO_2, hexanes). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.56 (dt, *J* = 12.0, 1.6 Hz, 2H), 7.52 – 7.37 (m, 4H), 7.33 – 7.25 (m, 1H), 7.19 (td, *J* = 7.5, 1.9 Hz, 1H), 7.15 – 7.08 (m, 2H), 7.03 – 6.91 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.9 (d, *J* = 245.7 Hz), 140.5, 138.5, 136.0, 134.9, 132.5 (d, *J* = 3.4 Hz), 131.4, 130.3, 129.8, 129.6 (d, *J* = 8.0 Hz), 129.1 (d, *J* = 16.0 Hz), 129.0, 128.7, 128.2, 124.4 (d, *J* = 3.7 Hz), 115.8 (d, *J* = 22.4 Hz), 93.9. ^{19}F NMR (376 MHz, CD_2Cl_2) δ -115.60 (ddd, *J* = 10.0, 7.5, 5.1 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 4.78 min. UV/vis (CH_2Cl_2/MeOH) λ 273 (sh). HR MS (APPI) calcd. for $C_{18}H_{12}FI$ ($M^{+\bullet}$, 100) *m/z* 373.9962, found 373.9974.

2-fluoro-2''-iodo-1,1':2',1''-terphenyl (P14). A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1, 2-diiodobenzene (330 mg, 1 mmol), (2'-fluoro-[1,1'-biphenyl]-2-yl)boronic acid (210 mg, 1 mmol), K_2CO_3 (280 mg, 2 mmol) and $Pd(PPh_3)_4$ (40 mg, 35 μmol). The solids were suspended in 8:2 dioxane/H_2O (10 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 96 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 2-fluoro-2''-iodo-1,1':2',1''-terphenyl as white oil in 43% yield (160 mg). R$_f$ = 0.48 (SiO_2, hexanes). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 – 7.42 (m, 3H), 7.39 – 7.32 (m, 1H), 7.26 – 7.14 (m, 4H), 7.00 (dt, *J* = 8.6, 1.2 Hz, 2H), 6.96 – 6.88 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.0 (d, *J* = 246.0 Hz), 146.1, 144.1, 139.2, 135.1, 132.5 (d, *J* = 3.4 Hz), 131.2 (d, *J* = 1.2 Hz), 131.2 (d, *J* = 1.6 Hz), 131.1, 129.4 (d, *J* = 8.1 Hz), 129.0, 128.8 (d, *J* = 15.6 Hz), 128.2, 128.1, 127.8, 123.8 (d, *J* = 3.7 Hz), 115.6 (d, *J* = 22.5 Hz), 100.2 ^{19}F NMR (376 MHz, CD_2Cl_2) δ -114.44 (dd, *J* = 13.6, 8.2 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 4.56 min. UV/vis (CH_2Cl_2/MeOH) λ 274 (sh). HR MS (APPI) calcd. for $C_{18}H_{12}FI$ ($M^{+\bullet}$, 100) *m/z* 373.9962, found 373.9958.

2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (P15). A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 4,4'-diiodobiphenyl (820 mg, 2 mmol), (2'-fluoro-[1,1'-biphenyl]-2-yl)boronic acid (210 mg, 1 mmol), K_2CO_3 (414 mg, 3 mmol) and $Pd(PPh_3)_4$ (51 mg, 44 μmol). The solids were suspended in 2:1 dioxane/H_2O (30 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 24 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (**P15**) as white solid in 9% yield (41 mg). R$_f$ = 0.20 (SiO_2, hexanes). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.79 – 7.73 (m, 2H), 7.53 – 7.39 (m, 6H), 7.37 – 7.31 (m, 2H), 7.30 – 7.18 (m, 4H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 6.96 (ddd, *J* = 9.5, 8.2, 1.0 Hz, 1H).^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.9 (d, *J* = 245.5 Hz), 141.5, 141.4, 141.3, 140.5, 134.8, 132.6 (d, *J* = 3.5 Hz), 131.5 (d, *J* = 1.0 Hz), 130.5, 130.2, 129.5 (d, *J* = 8.1 Hz), 129.1, 128.7, 127.8, 127.2, 126.8, 126.6, 124.3 (d, *J* = 3.7 Hz), 115.8 (d, *J* = 22.5 Hz), 93.2. ^{19}F NMR (376 MHz, CD_2Cl_2) δ -115.58 (ddd, *J* = 10.1, 7.5, 5.2 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 6.23 min. UV/vis (CH_2Cl_2/MeOH) λ 297 (sh). HR MS (APPI) calcd. for $C_{24}H_{16}FI$ ($M^{+\bullet}$, 100) *m/z* 450.0275, found 450.0282.

2-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)[2]. A 250 mL round bottom flask, equipped with a magnetic stir bar was charged with 1-bromo-2-fluoro-4-nitrobenzene (11.88 g, 8.56 mmol), bis(pinacolato)diboron (2.24 g, 8.82 mmol), KOAc (2.71 g, 27.6 mmol) Pd(dppf)Cl2 (150 mg, 0.18 mmol) and dissolved in 1,4-dioxane (65 mL). The mixture was degassed and stirred at 80 °C for 24 h under N_2 atmosphere. After the completion of the reaction, the mixture was diluted with CH_2Cl_2 (100 mL) and washed with water (30 mL). The organic layer was dried over $MgSO_4$ and purified by silica gel column chromatography, eluting with hexane- hexane:EtOAc (5:1), yielding 2-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as yellow oil which slowly solidifies to an yellow solid in 70 % (1.6g). R_f = 0.36 (SiO_2, hexanes-EtOAc 4:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 1H), 7.91 (t, J = 6.9 Hz, 1H), 7.88 – 7.83 (m, 1H), 1.37 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6 (d, J = 255.7 Hz), 150.9 (d, J = 9.2 Hz), 137.7 (d, J = 8.6 Hz), 118.6 (d, J=3.0 Hz), 110.8 (d, J = 31.4 Hz), 84.7, 24.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.67 – -98.74 (m, 1F).

2-fluoro-4-nitro-1,1':2',1''-terphenyl (6). A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-bromobiphenyl (233 mg, 1 mmol), 2-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, (**5**, 267 mg, 1 mmol), K_2CO_3 (555 mg, 4 mmol) and $Pd(PPh_3)_4$ (42 mg, 36 μmol). The solids were suspended in 12/5/1.5 Tol/MeOH/H_2O (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with hexane-hexane:EtOAc (95:5) yielding 2-fluoro-4-nitro-1,1':2',1"-terphenyl as yellow solid in 41% yield (120 mg). In the case, when side product (3-fluoronitrobenzene) remains after chromatography, it can be evaporated under reduced pressure. R_f = 0.42 (SiO_2, hexanes/EtOAC 9:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.97 – 7.92 (m, 1H), 7.86 – 7.78 (m, 1H), 7.60 – 7.47 (m, 3H), 7.43 (d, J = 6.9 Hz, 1H), 7.37 (dd, J = 8.4, 7.3 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.15 (d, J = 4.1 Hz, 2H).^{13}C

NMR (101 MHz, CD_2Cl_2) δ 159.4 (d, *J* = 250.7 Hz), 148.2 (d, *J* = 8.5 Hz), 142.2, 141.0 (d, *J* = 1.1 Hz), 137.0 (d, *J* = 16.2 Hz), 133.3 (d, *J* = 3.9 Hz), 132.8 (d, *J* = 1.1 Hz), 130.9 (d, *J* = 1.3 Hz), 130.8, 129.7, 129.6, 128.5, 127.9, 127.5, 119.3 (d, *J* = 3.7 Hz), 111.7 (d, *J* = 28.1 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -110.70 – -110.81 (m, 1F). HR MS (APPI) calcd. for $C_{18}H_{12}FNO_2$ ($M^{+\bullet}$, 100) *m/z* 293.0847, found 293.0851.

2-fluoro-[1,1':2',1''-terphenyl]-4-amine (7). 2-fluoro-4-nitro-1,1':2',1''-terphenyl (**6,** 120 mg, 409 µmol, 1 equiv) was dissolved in EtOAc (7 mL) and under N_2 atmosphere $SnCl_2$ x $2H_2O$ (461 mg, 2.04 mmol, 5 equiv) was added. The mixture was heated at reflux overnight. After cooling to room temperature a sat. aq. $NaHCO_3$ solution (7 mL) was added, phases were separated and the aqueous fraction extracted with EtOAc (3 x 10 mL). After evaporation of the solvent the resulting red oil was purified by flash column chromatography on silica gel (hexanes/EtOAc 5:1) and product 2-fluoro-[1,1':2',1''-terphenyl]-4-amine was isolated as yellow oil (82 mg, 64%). R_f = 0.34 (SiO_2, hexanes/EtOAc 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.45 – 7.36 (m, 4H), 7.30 – 7.17 (m, 5H), 6.89 (t, *J* = 8.4 Hz, 1H), 6.37 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.26 (dd, *J* = 11.8, 2.3 Hz, 1H), 3.79 (brs, 2H).^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.6 (d, *J* = 243.7 Hz), 148.2 (d, *J* = 10.8 Hz), 142.3 (d, *J* = 1.1 Hz), 142.4, 135.2, 133.0 (d, *J* = 5.6 Hz), 131.7 (d, *J* = 1.1 Hz), 130.5, 129.6, 128.2, 128.0, 127.5, 126.8, 119.0 (d, *J* = 16.3 Hz), 110.8 (d, *J* = 2.7 Hz), 101.9 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -115.42 (dd, *J* = 11.8, 8.5 Hz, 1F).HR MS (APPI) calcd. for $C_{18}H_{14}FN$ ($M^{+\bullet}$, 100) *m/z* 263.1105, found 263.1110.

2-fluoro-4-iodo-1,1':2',1''-terphenyl (P16). A 100 mL round-bottom flask was charged with 2-fluoro-[1,1':2',1''-terphenyl]-4-amine (**7**, 80 mg, 317 µmol), and conc H_2SO_4 (3 ml). The mixture was cooled to 0 °C in an ice- bath. Sodium nitrite (80 mg, 1.19 mmol) was added to the reaction mixture. The solution was stirred at −0 °C for 3h, and NaI (225 mg, 1.5 mmol) with 5-10 g of ice was added. The reaction mixture was stirred for 30 min at 0 °C. A sat. aq.

$Na_2S_2O_3$-solution (15 mL) was added, phases were separated and the aqueous layer extracted with DCM (3 x 30 mL). The combined organic fractions were dried over $NaSO_4$, filtered, and the solvent evaporated *in vacuo*. After evaporation of the solvent the resulting red oil was purified by flash column chromatography on silica gel (Hexane) and product **2-**fluoro-4-iodo-1,1':2',1''-terphenyl was isolated as white oil (40 mg, 33%). R_f = 0.41 (SiO_2, hexanes). ^1H NMR (500 MHz, CD_2Cl_2) δ 7.51 – 7.39 (m, 4H), 7.38 – 7.35 (m, 1H), 7.31 (dd, *J* = 9.1, 1.7 Hz, 1H), 7.27 – 7.20 (m, 3H), 7.14 (dd, *J* = 7.1, 2.5 Hz, 2H), 6.90 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 159.5 (d, *J* = 251.5 Hz), 142.1, 141.5, 133.9 (d, *J* = 3.8 Hz), 133.5 (d, *J* = 3.8 Hz), 131.2, 131.0, 130.7, 129.6, 129.0, 128.4, 128.3, 127.7, 127.2, 125.1 (d, *J* = 25.2 Hz), 92.2 (d, *J* = 8.0 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2) δ -112.79 (t, *J* = 8.5 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 4.66 min. UV/vis (CH_2Cl_2/MeOH) λ 282 (sh). HR MS (APPI) calcd. for $C_{18}H_{12}FI$ ($M^{+\bullet}$, 100) *m/z* 373.9962, found 373.9968

2-fluoro-5-nitro-1,1':2',1''-terphenyl (8). A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-bromobiphenyl (466 mg, 2 mmol), (2-fluoro-5-nitrophenyl)boronic acid, (370 mg, 2 mmol), K_2CO_3 (1.1 mg, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 12/5/1.5 Tol/MeOH/H_2O (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with hexane-hexane:EtOAc (95:5) yielding 2-fluoro-4-nitro-1,1':2',1''-terphenyl as yellow-orange solid in 37% yield (221 mg). In the case, when side product (4-fluoronitrobenzene) remains after chromatography, it can be evaporated under reduced pressure. R_f = 0.39 (SiO_2, hexanes/EtOAc 9:1). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.16 – 8.06 (m, 2H), 7.59 – 7.46 (m, 3H), 7.46 – 7.39 (m, 1H), 7.27 – 7.19 (m, 3H), 7.19 – 7.12 (m, 2H), 7.11 – 7.03 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 163.5 (d, *J* = 257.4 Hz), 142.3, 141.0 (d, *J* = 1.2 Hz), 132.5, 131.3, 131.1, 131.1, 130.8, 129.6, 129.6, 128.5, 128.4 (d, *J* = 5.7

Hz), 128.0, 127.5, 125.2 (d, J = 10.1 Hz), 116.9 (d, J = 25.5 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -104.01 – -104.11 (m, 1F). HRMS (APPI) calcd. for $C_{18}H_{12}FNO_2$ ($M^{+\bullet}$, 100) *m/z* 293.0847, found 293.0854.

6-fluoro-[1,1':2',1''-terphenyl]-3-amine (9). 6-fluoro-[1,1':2',1''-terphenyl]-3-amine (**8**, 200 mg, 682 µmol, 1 equiv) was dissolved in EtOAc (7 mL) and under N_2 atmosphere $SnCl_2$ x $2H_2O$ (769 mg, 3.41 mmol, 5 equiv) was added. The mixture was heated at reflux overnight. After cooling to room temperature a sat. aq. $NaHCO_3$ solution (7 mL) was added, phases were separated and the aqueous fraction extracted with EtOAc (3 x 10 mL). After evaporation of the solvent the resulting red oil was purified by flash column chromatography on silica gel (hexanes/EtOAc 5:1) and product was isolated as red-orange oil (115 mg, 63%). R_f = 0.29 (SiO_2, hexanes/EtOAc 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.53 – 7.37 (m, 4H), 7.33 – 7.18 (m, 5H), 6.78 – 6.69 (m, 1H), 6.58 – 6.48 (m, 2H), 3.72 (brs, 2H). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 153.4 (d, J = 235.7 Hz), 143.0 (d, J = 2.3 Hz), 142.0, 141.9 (d, J = 1.1 Hz), 135.2, 131.3 (d, J = 1.0 Hz), 130.5, 129.6, 128.5, 128.2, 127.5, 127.0, 118.3 (d, J = 3.0 Hz), 116.1, 115.9, 115.44 (d, J = 7.6 Hz). ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -129.46 (ddd, J = 9.9, 6.1, 4.1 Hz, 1F). HR MS (APPI) calcd. for $C_{18}H_{14}FN$ ($M^{+\bullet}$, 100) *m/z* 263.1105, found 263.1100.

2-fluoro-5-iodo-1,1':2',1''-terphenyl (P17). A 100 mL round-bottom flask was charged with 6-fluoro-[1,1':2',1''-terphenyl]-3-amine (110 mg, 418 µmol), and conc H_2SO_4 (3 ml). The mixture was cooled to 0 °C in an ice- bath. Sodium nitrite (80 mg, 1.19 mmol) was added to the reaction mixture. The solution was stirred at −0 °C for 3h, and NaI (225 mg, 1.5 mmol) with 5-10 g of ice was added. The reaction mixture was stirred for 30 min at 0 °C. A sat. aq. $Na_2S_2O_3$-solution (15 mL) was added, phases were separated and the aqueous layer extracted with DCM (3 x 30 mL). The combined organic fractions were dried over $NaSO_4$, filtered, and the solvent evaporated *in vacuo*. After evaporation of the solvent the resulting red oil was purified by flash column chromatography on silica gel (Hexane) and product **2-**fluoro-4-iodo-1,1':2',1''-terphenyl was isolated as white oil (35 mg, 22%). R_f = 0.37 (SiO_2, hexanes). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.58 – 7.51 (m, 2H), 7.51 – 7.41 (m, 5H), 7.40 – 7.32 (m, 1H), 7.29 – 7.18 (m, 4H), 7.19 – 7.10 (m, 3H), 6.75 – 6.66 (m, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.9 (d, *J* = 247.5 Hz), 142.2, 141.4, 141.1 (d, *J* = 3.5 Hz), 138.2 (d, *J* = 7.9 Hz), 133.4 (d, *J* = 0.7 Hz), 132.3 (d, *J* = 17.1 Hz), 131.2 (d, *J* = 1.1 Hz), 130.6, 129.6, 129.1, 128.3, 127.3, 127.3, 127.3, 117.9 (d, *J* = 23.7 Hz), 87.0 (d, *J* = 3.8 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -116.43 (ddd, *J* = 9.6, 6.7, 5.0 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 5.03 min. UV/vis (CH_2Cl_2/MeOH) λ 286 (sh). HR MS (APPI) calcd. for $C_{18}H_{12}FI$ ($M^{+\bullet}$, 100) *m/z* 373.9962, found 373.9957

6-fluoro-[1,1':2',1''-terphenyl]-2-amine (10). A 250 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-bromo-3-fluoroaniline (475 mg, 2.5 mmol), 2-biphenylboronic acid, (495 mg, 2.5 mmol), K_2CO_3 (1.35 g, 10 mmol) and $Pd(PPh_3)_4$ (105 mg, 90 μmol). The solids were suspended in 30/12.5/4Tol/MeOH/H_2O (46.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with hexane-hexane:EtOAc (4:1) yielding 6-fluoro-[1,1':2',1''-terphenyl]-2-amine as yellow oil in 56% yield (408 mg). R_f = 0.25 (SiO_2, hexanes/EtOAc 5:1)

^1H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 3H), 7.42 – 7.35 (m, 1H), 7.32 – 7.16 (m, 5H), 7.06 – 6.89 (m, 1H), 6.40 (dt, *J* = 9.0, 4.6 Hz, 2H), 3.54 (brs, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.6 (d, *J* = 241.8 Hz), 145.7 (d, *J* = 6.1 Hz), 142.6, 140.9, 131.3, 130.7 (d, *J* = 0.8 Hz), 130.5, 129.0 (d, *J* = 10.4 Hz), 128.6, 128.5, 127.8, 127.7, 126.9, 115.1 (d, *J* = 20.5 Hz), 110.3 (d, *J* = 2.7 Hz), 104.6 (d, *J* = 23.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.90 (dd, *J* = 9.2, 6.4 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 4.11 min. UV/vis (CH_2Cl_2/MeOH) λ 292 (sh). HR MS (APPI) calcd. for $C_{18}H_{14}FN$ ($M^{+\bullet}$, 100) *m/z* 263.1105, found 263.1112.

2-fluoro-6-iodo-1,1':2',1''-terphenyl (P18). A 100 mL round-bottom flask was charged with 6-fluoro-[1,1':2',1''-terphenyl]-2-amine (340 mg, 1.36 µmol), and conc H_2SO_4 (6 ml). The mixture was cooled to 0 °C in an ice- bath. Sodium nitrite (152 mg, 2.26 mmol) was added to the reaction mixture. The solution was stirred at −0 °C for 3h, and NaI (450 mg, 3 mmol) with 5-10 g of ice was added. The reaction mixture was stirred for 30 min at 0 °C. A sat. aq. $Na_2S_2O_3$-solution (15 mL) was added, phases were separated and the aqueous layer extracted with DCM (3 x 30 mL). The combined organic fractions were dried over $NaSO_4$, filtered, and the solvent evaporated *in vacuo*. After evaporation of the solvent the resulting red oil was purified by flash column chromatography on silica gel (Hexane) and product **2**-fluoro-6-iodo-1,1':2',1''-terphenyl was isolated as white oil (86 mg, 17%). R_f = 0.44 (SiO_2, hexanes). ^1H NMR (500 MHz, CD_2Cl_2) δ 7.68 – 7.63 (m, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.47 (m, 2H), 7.31 – 7.21 (m, 6H), 7.05 – 6.96 (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 159.5 (d, *J* = 248.2 Hz), 142.2, 141.1, 137.0, 135.0 (d, *J* = 3.5 Hz), 134.7 (d, *J* = 18.9 Hz), 131.2, 130.7 (d, *J* = 8.6 Hz), 130.5, 129.4, 129.3, 128.1, 127.7, 127.3, 115.5 (d, *J* = 23.3 Hz), 102.0 (d, *J* = 1.5 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2) δ -106.55 (t, *J* = 7.3 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 4.22 min. UV/vis (CH_2Cl_2/MeOH) λ 280 (sh). HR MS (APPI) calcd. for $C_{18}H_{12}FI$ ($M^{+\bullet}$, 100) *m/z* 373.9962, found 373.9957

2-fluoro-3-iodo-1,1':2',1''-terphenyl (P19). A 250 mL flame-dried two-necked round-bottom flask was charged with TMEDA (1 ml, 6 mmol) and dry THF (50 mL) under argon. The solution was cooled to -78 °C and n-BuLi (2.5 ml, 6 mmol,) was added dropwise. The yellow solution was stirred for 30 min and solution of 2-fluoro-1,1':2',1''-terphenyl (1.2 g, 5 mmol) in THF (5 ml) was added dropwise and stirred for atother 30 minutes. I_2 (2.5 g, 10 mmol) was dissolved in THF (20 mL) and added dropwise to the reaction mixture. The red-brown reaction mixture was allowed to reach room temperature overnight. A sat. aq. $Na_2S_2O_3$-solution (100 mL) was added, phases were separated and the aqueous layer extracted with DCM (3 x 50 mL). The organic fractions were combined and the solvent evaporated in vacuo. Residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 2-fluoro-3-iodo-1,1':2',1''-terphenyl as orange oil in 80% yield (1.5 g). R_f = 0.48 (SiO_2, hexanes). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.65 (dd, *J* = 5.9, 1.7 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 12.3, 6.5 Hz, 3H), 7.17 – 7.07 (m, 3H), 6.80 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 158.78 (d, *J* = 244.6 Hz), 142.1, 141.4, 138.7, 138.7, 132.99, 132.96, 131.17, 131.16, 130.6, 130.4, 130.3, 129.6, 127.0, 128.3, 127.6, 127.2, 125.7, 125.7, 81.73 (d, *J* = 26.8 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2) δ -94.78 (t, *J* = 6.3 Hz, 1F). HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, MeOH/DCM 6:4) t_R = 4.62 min. UV/vis (CH_2Cl_2/MeOH) λ 281 (sh). HR MS (APPI) calcd. for $C_{18}H_{12}FI$ ($M^{+\bullet}$, 100) *m/z* 373.9962, found 373.9966.

1-Fluoro-4-iodobenzo[*c*]phenanthrene (P20). A 25 mL flame-dried two-necked round-bottom flask was charged with 4-bromo-1-fluorobenzo[*c*]phenanthrene[3] (170 mg, 523 µmol, 1 equiv) and dry THF (5 mL) under argon. The solution was cooled to -78 °C and *t*-BuLi (330 µl, 627 µmol, 1.2 equiv) was added dropwise. The greenish suspension was stirred for 30 min at -78 °C. I_2 (239 mg, 941 µmol, 1.8 equiv) was dissolved in THF (2 mL) and added dropwise to the reaction mixture. The red-brown reaction mixture was allowed to reach room temperature overnight. A sat. aq. $Na_2S_2O_3$-solution (10 mL) was added, phases were separated and the aqueous layer extracted with DCM (3 x 10 mL). The combined organic fractions were dried over $NaSO_4$, filtered, and the solvent evaporated *in vacuo*. The crude product was purified by HPLC separation (Buckyprep column, 5.0 mL/min 40 °C, DCM/MeOH 3:7) which afforded precursor **P20** as light yellow solid (105 mg, 46 %). R_f = 0.66 (SiO_2, hexanes/DCM 5:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.27 – 8.17 (m, 3H), 8.05 – 7.99 (m, 2H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.17 (dd, *J* = 12.3, 8.3

Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (d, *J* = 254.6 Hz), 137.9 (d, *J* = 8.8 Hz), 136.2 (d, *J* = 4.3 Hz), 133.4 (d, *J* = 1.4 Hz), 132.4, 131.5 (d, *J* = 2.4 Hz), 130.1 (d, *J* = 3.4 Hz), 129.9 (d, *J* = 16.7 Hz), 129.8 (d, *J* = 2.9 Hz), 129.6, 127.9 (d, J = 2.0 Hz), 126.7, 126.0, 125.6 (d, *J* = 2.9 Hz), 124.7 (d, *J* = 3.2 Hz), 120.4 (d, *J* = 13.3 Hz), 113.9 (d, *J* = 25.0 Hz), 93.0 (d, *J* = 3.5 Hz).. ^{19}F NMR (377 MHz, $CDCl_3$) δ -99.28 – -99.36 (m, 1F). HPLC (Buckyprep column, 1.0 mL/min, 35 °C, MeOH/DCM 6:4) t_R = 5.67 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 365 (sh), 337, 324, 306, 291, 281, 247 (sh), 228 nm. LDI MS *m/z* 372 (M^+, 100). HR MS (APPI) calcd. for $C_{18}H_{10}FI$ ($M^{+\bullet}$, 100) *m/z* 371.9806, found 371.9813.

1-Fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (11). 4-Bromo-1-fluorobenzo[*c*]phenanthrene[3] (100 mg, 308 µmol, 1 equiv), 3-nitrophenylboronic acid (77.0 mg, 461 µmol, 1.5 equiv), Cs_2CO_3 (200 mg, 615 µmol, 2 equiv), and $Pd(PPh_3)_2Cl_2$ (10.8 mg, 15.4 µmol, 0.05 equiv) in toluene/MeOH/H_2O 2.5:1:0.3 (7.6 mL) were reacted according to the general procedure (reflux, 18 h). Product **11** was isolated by flash column chromatography on silica gel (hexanes/DCM 2:1) and obtained as yellow solid after drying in vacuum (quantitative): R_f = 0.46 (SiO_2, hexanes/DCM 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (t, *J* = 2.0 Hz, 1H), 8.37 – 8.30 (m, 2H), 8.02 – 7.98 (m, 2H), 7.87 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.85 – 7.57 (m, 7H), 7.46 – 7.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, *J* = 255.6 Hz), 148.5, 142.1, 136.6, 133.6 (d, *J* = 3.6 Hz), 132.9 (d, *J* = 4.5 Hz), 132.9 (s), 131.5, 130.0, 129.7, 129.5, 129.4, 129.0, 128.3, 127.7 (d, *J* = 9.1 Hz), 127.5, 126.3, 125.4 (d, *J* = 24.6 Hz), 125.2, 124.5 (d, *J* = 3.4 Hz), 124.2 (d, J = 2.0 Hz), 122.5, 119.2 (d, *J* = 13.0 Hz), 111.9 (d, *J* = 24.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -97.97 – -98.05 (m, 1F). HPLC (Buckyprep column, 1.0 mL/min, 35 °C, MeOH/DCM 6:4) t_R = 6.01 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 384 (sh), 366 (sh), 336 (sh), 322 (sh), 287, 280 (sh), 227 nm. HR MS (APPI) calcd. for $C_{24}H_{14}FNO_2$ ($M^{+\bullet}$, 100) *m/z* 367.1003, found 367.1009.

3-(1-Fluorobenzo[c]phenanthren-4-yl)aniline (12). 1-Fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (**5**, 113 mg, 308 µmol, 1 equiv) was suspended in EtOAc (10 mL) and the suspension degassed for 2 min under dynamic vacuum. Under nitrogen atmosphere $SnCl_2$ x $2H_2O$ (347 mg, 1.54 mmol, 5 equiv) was added and the mixture stirred under reflux overnight (18 h). After cooling to room temperature a sat. aq. $NaHCO_3$ solution (10 mL) was added. The resulting white solid was filtered off by suction filtration through a Büchner funnel and washed thoroughly with H_2O and DCM (20 mL each). Phases were separated and the aqueous fraction extracted with DCM (3 x 10 mL). The combined organic fractions were dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexanes/EtOAc 9:1 – 75:25) and obtained as white fluffy solid after drying in vacuum (103 mg, 99%). Compound **12** contained residual solvent according to NMR (EtOAc), but was used without further purification: R_f = 0.29 (SiO_2, hexanes/EtOAc 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.27 (m, 1H), 8.02 – 7.97 (m, 2H), 7.95 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.57 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.39 (dd, *J* = 12.4, 8.0 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.88 – 6.83 (m, 1H), 6.80 (dd, *J* = 4.9, 4.0 Hz, 1H), 3.79 (s, 2H).. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (d, *J* = 253.5 Hz), 146.4, 141.6, 136.6 (d, *J* = 3.5 Hz), 133.3 (d, *J* = 4.3 Hz), 132.8, 131.4, 130.2 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 16.8 Hz), 129.3, 128.6, 127.4, 127.3, 127.2 (d, *J* = 9.0 Hz), 125.9, 125.6, 125.6 (d, *J* = 2.5 Hz), 125.0 (d, *J* = 2.7 Hz), 124.4, 121.1, 118.9 (d, *J* = 12.7 Hz), 117.2, 114.2, 111.7 (d, *J* = 24.2 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -100.06 – -100.15 (m, 1F). HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/DCM 6:4) t_R = 5.03 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 383, 337 (sh), 323 (sh), 301 (sh), 287, 281, 228 nm. HR MS (APPI) calcd. for $C_{24}H_{16}FN$ ($M^{+\bullet}$, 100) *m/z* 337.1261, found 337.1266.

1-Fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (P21). A 25 mL round-bottom flask was charged with 3-(1-fluorobenzo[*c*]phenanthren-4-yl)aniline (**6**, 150 mg, 445 µmol, 1 equiv), MeCN (5 mL) and conc. HCl (0.1 mL). The mixture was cooled to −13 °C in an ice-salt bath. A solution of sodium nitrite (61.4 mg, 889 µmol, 2 equiv) in water (0.5 mL) was added dropwise to the reaction mixture. The yellow solution was stirred at −13 °C for 30 min, and a solution of KI (148 mg, 889 µmol, 2 equiv) in water (0.5 mL) was added. The red-brown reaction mixture was stirred for 15 min at −13 °C and another 1 h at room temperature. A sat. aq. $Na_2S_2O_3$-solution (10 mL) was added, phases were separated and the aqueous layer extracted with DCM (3 x 10 mL). The combined organic fractions were dried over $NaSO_4$, filtered, and the solvent evaporated *in vacuo*. The oily residue was purified by flash column chromatography on silica gel (hexanes/DCM 5:1) which afforded precursor **P21** as white solid (132 mg, 66 %): R_f = 0.41 (SiO_2, hexanes/DCM 2:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.37 – 8.29 (m, 1H), 8.04 – 8.01 (m, 2H), 7.93 (t, *J* = 1.8 Hz, 1H), 7.86 – 7.78 (m, 4H), 7.66 – 7.62 (m, 2H), 7.58 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.43 (dd, *J* = 12.4, 8.0 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 159.5 (d, *J* = 253.5 Hz), 143.0, 139.7, 137.0, 135.2 (d, *J* = 3.6 Hz), 133.5 (d, *J* = 4.6 Hz), 133.3, 131.9, 130.5, 130.4 (d, *J* = 3.1 Hz), 130.3, 129.9 (d, *J* = 16.6 Hz), 129.1, 128.2, 128.0 (d, *J* = 9.2 Hz), 127.9, 126.5, 126.0, 125.5 (d, *J* = 2.8 Hz), 125.3 (d, *J* = 2.4 Hz), 124.7 (d, *J* = 3.3 Hz), 119.3 (d, *J* = 12.7 Hz), 112.2 (d, *J* = 24.4 Hz), 94.6. ^{19}F NMR (377 MHz, $CDCl_2$) δ -99.74 – -99.81 (t, 1F). HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/DCM 1:1) t_R = 5.96 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 337 (sh), 323 (sh), 289, 281, 229 nm. HR MS (APPI) calcd. for $C_{24}H_{14}FI$ ($M^{+\bullet}$, 100) *m/z* 448.0119, found 448.0128.

2-iodo-1,1':2',1''-terphenyl (PS1)[4]**.** A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1,2-diiodobenzene (660 mg, 2 mmol), [1,1'-biphenyl]-2-yl)boronic acid (400 mg, 2 mmol), K_2CO_3 (560 mg, 4 mmol) and $Pd(PPh_3)_4$ (80 mg, 69 µmol). The solids were suspended in 4:1 dioxane/H_2O (20 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 2-iodo-1,1':2',1''-terphenyl **(PS1)** as white oil in 41% yield (290 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.50 – 7.44 (m, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.19 (m, 6H), 7.14 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.94 (td, *J* = 7.6, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 142.7, 140.8, 140.6, 138.9, 131.1, 130.8, 130.1, 129.6, 128.3, 128.1, 127.6, 127.5, 126.8, 126.5, 100.4.

1-(2-iodophenyl)naphthalene (PS2)[5]. A 100 ml round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1,2-diiodobenzene (660 mg, 2 mmol), naphthalene-1-boronic acid (370 mg, 2 mmol), K_2CO_3 (560 mg, 4 mmol) and $Pd(PPh_3)_4$ (80 mg, 69 μmol). The solids were suspended in 4:1 dioxane/H_2O (20 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the residue was purified by silica gel column chromatography, eluting with (Hexane) yielding 1-(2-iodophenyl)naphthalene **(PS2)** as white solid in 77% yield (510 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.07 (m, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.60 – 7.46 (m, 4H), 7.46 – 7.37 (m, 2H), 7.20 (td, *J* = 7.7, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.1, 139.0, 133.4, 131.3, 130.8, 129.0, 128.2, 128.1, 127.8, 126.94, 126.1, 125.9, 125.8, 125.1, 100.6. HR MS (APPI) calcd. for $C_{16}H_{11}I$ ($M^{+\bullet}$, 100) *m/z* 329.9900, found 329.9918.

2-Methyltriphenylene (T1)[6,7]. 2-Fluoro-4''-metyl-1,1':2',1''-terphenyl (**P1**) (10.0 mg, 38.1 µmol) activated aluminium oxide (2.0 g, 19.6 mmol) were reacted according to the general procedure. The condensation was carried out at 250 °C for 4 h. After extraction of Al_2O_3 with hot toluene (10 mL) and solvent evaporation pure 2-methyltriphenylene (**T1**) was obtained as white solid (8.8 mg, 95 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.59 (m, 4H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.43 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.66 – 7.59 (m, 4H), 7.47 (dd, *J* = 8.4, 1.7 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 129.9, 129.8, 129.7, 129.4, 128.7, 127.5, 127.1, 127.1, 127.1, 126.8, 123.3, 123.3, 123.2, 123.1, 21.8 (three signals coincident or not observed). HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/CH_2Cl_2 8:2) t_R = 12.52 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 345, 337, 329, 322, 315, 305 (sh), 286, 275, 258, 250, 221 nm. LDI MS *m/z* 242 (M^+, 100 %).

9-(*Tert*-butyl)triphenylene (T2)[8,9]**.** 4''-(*Tert*-butyl)-2-fluoro-1,1':2',1''-terphenyl (**P2**) (10.0 mg, 33.5 µmol) and activated aluminium oxide (3.0 g, 29.4 mmol) were reacted according to the general procedure. The condensation was carried out at 250°C for 4 h. After Soxhlet extraction of Al_2O_3 with toluene (50 mL) overnight and solvent evaporation, the crude product was purified by HPLC separation (PBr column, 5.0 mL/min, 40 °C, DCM/MeOH 1:1). Pure 2-(*tert*-butyl)triphenylene (**T2**) was obtained as white solid (6.4 mg, 69 %): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.76–8.70 (m, 1H), 8.70–8.63 (m, 4H), 8.61 (d, *J* = 8.7 Hz, 1H), 7.76 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.73–7.62 (m, 4H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 150.7, 130.5, 130.4, 130.2, 129.9, 129.8, 127.9, 127.7, 127.6, 127.6, 127.4, 125.9, 123.8, 123.7, 123.7, 123.6, 123.6, 119.8, 35.4, 31.6 (two signals coincident or not observed). HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/CH_2Cl_2 6:4) t_R = 4.66 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 345, 336, 329, 322, 287, 276, 260, 252 nm. LDI MS *m/z* 284 (M^+, 100). HR MS (APPI) calcd. for $C_{22}H_{20}$ ($M^{+\bullet}$, 100) *m/z* 284.1560, found 284.1557.

Condensation of 2-Fluoro-4''-methoxy-1,1':2',1''-terphenyl (P3). 2-Fluoro-4''-methoxy-1,1':2',1''-terphenyl (**P3**) (10.2 mg, 37.7 µmol) and activated aluminium oxide (2.5 g, 24.5 mmol) were reacted according to the general procedure. The condensation was carried out at 200 °C for 5 h. HPLC analysis of the reaction mixture (PBr column (analyt.), 1.0 mL/min, 35°C, DCM/MeOH 3:7) did not indicate the formation of desired product 2-methoxytriphenylene.

Condensation of Methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (P4). Methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (**P4**) (10.3 mg, 33.6 µmol) and activated aluminium oxide (3.0 g, 29.4 mmol) were reacted according to the general procedure. The condensation was carried out at 200 °C for 5 h. HPLC analysis of the reaction mixture (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 3:7) did not indicate the formation of desired product methyl triphenylene-2-carboxylate.

Condensation of 2''-Fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (P5). 2''-Fluoro-N,N-dimethyl-[1,1':2',1''-terphenyl]-4-amine (**P5**) (10.3 mg, 35.4 µmol) and activated aluminium oxide (2.6 g, 25.5 mmol) were reacted according to the general procedure. The condensation was carried out at 200 °C for 5 h. HPLC analysis of the reaction mixture (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9) indicated the formation of a complex mixture of several products. However, the formation of desired product *N*,*N*-dimethyltriphenylen-2-amine was not observed.

Condensation of 4-(2'-Fluoro-[1,1'-biphenyl]-2-yl)pyridine (P6). 4-(2'-Fluoro-[1,1'-biphenyl]-2-yl)pyridine (**P6**) (10.2 mg, 40.9 µmol) and activated aluminium oxide (2.6 g, 25.5 mmol) was reacted according to the general procedure. The condensation was carried out at 200 °C for 5 h. HPLC analysis of the reaction mixture (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9) indicated the formation of a complex mixture of several products. However, the formation of desired product *N*,*N*-dimethyltriphenylen-2-amine was not observed.

Triphenyleno[1,2-b]benzofuran (T3). 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (15 mg, 44 µmol) was reacted according to the general procedure using 2 g of activated aluminium oxide. The condensation was carried out at 240 °C for 12 h. After extraction of Al_2O_3 with hot toluene (10 mL) and solvent evaporation the crude product was purified by HPLC separation (PBr column, 5.0 mL/min, 40 °C, DCM/MeOH 1:1). Pure triphenyleno[1,2-b]benzofuran was obtained as white solid (5.5 mg, 39 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.95 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.86 – 8.67 (m, 4H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.14 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.79 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.59 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.48 (td, J = 7.6, 0.9 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.6, 154.3, 130.5, 130.4, 130.31, 130.29, 128.9, 128.6, 128.0, 127.9, 127.84, 127.82, 127.5, 124.4, 124.2, 123.9, 123.7, 123.6, 123.4, 120.9, 119.8, 119.0, 117.8, 112.2. HPLC (PBr column, 1.0 mL/min, 40 °C, MeOH/CH_2Cl_2 1:1) t_R = 8.46 min). UV/Vis (DCM-MeOH 1:1, 293 K): λ [nm]) = 360, 343, 321, 308, 297, 288. LDI MS *m/z* 318 (M^+, 100). HRMS (APPI; Toluene): Chemical Formula: $C_{24}H_{14}S$, calc. 318.1045, found 318.1046.

Benzo[b]triphenyleno[2,1-d]thiophene (T4)[10]. 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (15 mg, 42 µmol) was reacted according to the general procedure using 2 g of activated aluminium oxide. The condensation was carried out at 240 °C for 12 h. After extraction of Al_2O_3 with hot toluene (10 mL) and solvent evaporation the crude product was purified by HPLC separation (PBr column, 5.0 mL/min, 40 °C, DCM/MeOH 1:1). Pure benzo[b]triphenyleno[2,1-d]thiophene was obtained as white solid (8 mg, 57 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.36 (dd, J = 8.3, 0.9 Hz, 1H), 8.90 (d, J = 9.0 Hz, 1H), 8.84 (dd, J = 8.2, 1.4 Hz, 1H), 8.82 – 8.78 (m, 1H), 8.77 – 8.72 (m, 1H), 8.54 (d, J = 8.7 Hz, 1H), 8.41 – 8.32 (m, 1H), 8.13 – 8.02 (m, 1H), 7.89 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.81 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.64 – 7.54 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 139.8, 136.1, 136.0, 135.3, 131.1, 130.6, 130.4, 130.0, 128.0, 128.0, 127.6, 127.6, 127.3, 127.0, 125.3, 124.5, 123.9, 123.7, 122.5, 122.0, 121.2, 121.1. HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/CH_2Cl_2 1:1) t_R = 11.13 min). UV/Vis (DCM-MeOH 1:1, 293 K): λ [nm]) = 368, 351, 329, 318. HRMS (APPI; Toluene): Chemical Formula: $C_{24}H_{14}S$, calc. 334.0816, found 334.0817.

Benzo[*b*]triphenyleno[1,2-*d*]thiophene (T5) and Benzo[*b*]triphenyleno[2,3-*d*]thiophene (T6). 2-(2'-Fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (**P**)9 (10.3 mg, 29.1 µmol) and activated aluminium oxide (3.2 g, 31.4 mmol) were reacted according to the general procedure. The condensation was carried out at 240 °C for 4 h. After extraction of Al_2O_3 with *o*-DCB (10 mL) and evaporation of the solvent, the two isomers were separated by HPLC chromatography (PBr column (semiprep), 5.0 mL/min, 40 °C, DCM/MeOH 7:3). Both isomers were isolated as white solids (**T5**: 5.1 mg, 52%, **T6**: 2.3 mg, 24%). **Benzo[*b*]triphenyleno[1,2-*d*]thiophene (T5)**[10]: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.87 (dd, *J* = 8.2, 1.0 Hz, 2H), 8.71 – 8.58 (m, 4H), 8.56 – 8.53 (m, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.96 (ddd, *J* = 8.0, 1.2, 0.6 Hz, 1H), 7.73 – 7.67 (m, 3H), 7.50 – 7.43 (m, 2H), 7.31 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 140.8, 140.3, 137.2, 131.4, 130.9, 130.4, 130.2, 129.4, 129.0, 128.9, 128.7, 128.3, 128.0, 127.4, 126.6, 125.9, 125.5, 124.0, 123.6, 123.5, 123.4, 122.2, 121.8. HPLC (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) t_R = 7.51 min. UV/vis (DCM/MeOH) λ_{max} 377, 360, 339, 324 (sh), 308 (sh), 295, 279, 270, 260, 250 nm. LDI MS *m/z* 334 (M^+, 100). HR MS (APPI) calcd. for $C_{24}H_{14}S$ ($M^{+\bullet}$, 100) *m/z* 334.0811, found 334.0819. **Benzo[*b*]triphenyleno[2,3-*d*]thiophene (T6):** ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.44 (s, 1H), 9.12 (s, 1H), 8.89 – 8.87 (m, 1H), 8.75 – 8.66 (m, 3H), 8.46 – 8.42 (m, 1H), 7.96 – 7.91 (m, 1H), 7.77 – 7.68 (m, 4H), 7.60 – 7.53 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2) □ δ 140.7, 139.5, 135.8, 135.6, 130.4, 130.4, 130.0, 129.8, 129.6, 128.0, 127.9, 127.9, 127.8, 127.6, 125.2, 123.9, 123.9 123.9, 123.6, 123.4, 122.3, 117.4, 116.3. HPLC (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) t_R = 11.55 min. UV/vis (DCM/MeOH) λ_{max} 372, 353, 332, 318, 286, 273, 263 (sh), 251 nm. LDI MS *m/z* 334 (M^+, 100). HR MS (APPI) calcd. for $C_{24}H_{14}S$ ($M^{+\bullet}$, 100) *m/z* 334.0811, found 334.0812.

2-Chlorotriphenylene (T7)[7,9]**.** 4''-Chloro-2-fluoro-1,1':2',1''-terphenyl (**P10**) (10.1 mg, 35.7 µmol) and activated aluminium oxide (3.0 g, 29.4 mmol) were reacted according to the general procedure. The condensation was carried out at 260 °C for 12 h. After Soxhlet extraction of Al_2O_3 with toluene (50 mL) overnight and solvent evaporation the crude product was purified by HPLC separation (PBr column, 5.0 mL/min, 40 °C, DCM/MeOH 1:1). Pure 2-chlorotriphenylene (**T7**) was obtained as white solid (6.4 mg, 68 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.60 – 8.55 (m, 2H), 8.54 – 8.46 (m, 4H), 7.65 – 7.57 (m, 4H), 7.54 (dd, *J* = 8.8, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 133.7, 131.6, 130.5, 130.0, 129.5, 129.0, 128.6, 128.4, 128.0, 127.9, 127.9, 127.8, 125.5, 123.8, 123.8, 123.8, 123.7, 123.4. HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/CH_2Cl_2 1:1) t_R = 6.92 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 346, 338, 331, 323, 317 (sh), 307 (sh), 286, 276, 260, 252 nm. LDI MS *m/z* 262 (M^+, 100 %).

2-Bromotriphenylene (T8)[11]**.** 4''-Bromo-2-fluoro-1,1':2',1''-terphenyl (**P11**) (10.2 mg, 31.2 µmol) and activated aluminium oxide (3.0 g, 29.4 mmol) were reacted according to the general procedure. The condensation was carried out at 250 °C for 12 h. After Soxhlet extraction of Al_2O_3 with toluene (50 mL) overnight and solvent evaporation the crude product was purified by HPLC separation (PBr column, 5.0 mL/min, 40 °C, DCM/MeOH 1:1). Pure 2-bromotriphenylene (**T8**) was obtained as white solid (6.5 mg, 68 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.78 (d, *J* = 2.1 Hz, 1H), 8.68 – 8.63 (m, 2H), 8.62 – 8.54 (m, 2H), 8.51 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.73 – 7.65 (m, 4H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 131.9, 130.6, 130.5, 130.1, 129.5, 129.0, 128.9, 128.4, 128.1, 127.9, 127.9, 126.6, 125.6, 123.8, 123.8, 123.7, 123.6, 122.0. HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/CH_2Cl_2 1:1) t_R = 7.36 min. UV/vis (CH_2Cl_2/MeOH) λ_{max} 347, 338, 331, 323, 307 (sh), 286, 276, 261, 253, 223 (sh) nm. HR MS (APPI) calcd. for $C_{18}H_{11}Br$ ($M^{+\bullet}$, 100) *m/z* 306.0039, found 306.0046.

2-Iodotriphenylene (T9)[12]**.** 2-Fluoro-4''-iodo-1,1':2',1''-terphenyl (**P12**) (10.0 mg, 26.7 µmol) and activated aluminium oxide (1.5 g, 14.7 mmol) were reacted according to the general procedure. The condensation was carried out at 240 °C for 12 h. After Soxhlet extraction of Al_2O_3 with toluene (50 mL) overnight and solvent evaporation the crude product was purified by HPLC separation (PBr column, 5.0 mL/min, 40 °C, DCM/MeOH 7:3). Pure 2-iodotriphenylene (**T9**) was obtained as white solid (6.9 mg, 73 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.00 (d, *J* = 1.8 Hz, 1H), 8.71–8.55 (m, 4H), 8.39 (d, *J* = 8.7 Hz, 1H), 7.96 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.74–7.65 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 136.3, 132.9, 132.1, 130.4, 130.2, 129.5, 129.5, 128.7, 128.3, 128.2, 127.9, 127.9, 125.5, 123.8, 123.7, 123.5, 93.7 (one signal coincident or not observed). HPLC (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) t_R = 7.97 min. UV/vis (DCM/MeOH) λ_{max} 348, 339, 332, 323, 309 (sh), 299 (sh) 287 (sh), 279 (sh), 262, 256 nm. LDI MS *m/z* 354 (M^+, 100). HR MS (APPI) calcd. for $C_{18}H_{11}I$ ($M^{+\bullet}$, 100) *m/z* 353.9900, found 353.9895.

The same method was used for the CDHF of **P13**, **P16**, **P17**. Yields of **T9** are given in the figure 3.

Condensation of P14. P14 (10.0 mg, 26.7 µmol) and activated aluminium oxide (2.6 g, 25.5 mmol) were reacted according to the general procedure. The condensation was carried out at 190 °C for 12 h. HPLC analysis of the reaction mixture (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) indicated the formation of a triphenylene. However, the formation of desired product 1-iodotriphenylene was not observed.

Condensation of P18. P18 (10.0 mg, 26.7 µmol) and activated aluminium oxide (2.6 g, 25.5 mmol) were reacted according to the general procedure. The condensation was carried out at 190 °C for 12 h. HPLC analysis of the reaction mixture (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) indicated the formation of a triphenylene. However, the formation of desired product 1-iodotriphenylene was not observed.

Condensation of P19. P19 (10.0 mg, 26.7 µmol) and activated aluminium oxide (2.6 g, 25.5 mmol) were reacted according to the general procedure. The condensation was carried out at 240 °C for 24 h. HPLC analysis of the reaction mixture (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) indicated no reaction.

2-(4-iodophenyl)triphenylene (T10). 2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (10.0 mg, 22.2 µmol) and activated aluminium oxide (3.0 g, 29.4 mmol) were reacted according to the general procedure. The condensation was carried out at 190°C for 60 h. After Soxhlet extraction of Al_2O_3 with toluene (50 mL) overnight and solvent evaporation, the crude product was purified by HPLC separation (PBr column, 5.0 mL/min, 40 °C, DCM/MeOH 4:6). Pure 2-(4-iodophenyl)triphenylene was obtained as white solid (8.1 mg, 85 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 1.9 Hz, 1H), 8.76 – 8.71 (m, 2H), 8.70 - 8.7 (m, 3H), 7.88-7.85 (m 3H), 7.72-7.67 (m, 4H), 7.60 – 7.53 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 138.7, 138.0, 130.2, 130.1, 129.9, 129.6, 129.5, 129.2, 129.2, 127.5, 127.4, 127.4, 127.3, 126.0, 124.1, 123.4, 123.4, 123.3, 121.6, 93.3. HPLC (PBr column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6) t_R = 13.86 min. UV/vis (DCM/MeOH) λ_{max} 305, 278, 262 nm. HRMS (APPI) calcd. for $C_{24}H_{15}I$ ($M^{+\bullet}$, 100) *m/z* 430.0213, found 430.0218.

3-Iodobenzo[*ghi*]fluoranthene (T11). 1-Fluoro-4-iodobenzo[*c*]phenanthrene (**P20**) (10.2 mg, 27.4 µmol) and activated aluminium oxide (2.5 g, 24.5 mmol) were reacted according to the general procedure. The condensation was carried out at 180 °C for 12 h. After extraction of Al_2O_3 with toluene (10 mL) and solvent evaporation pure 3-iodobenzo[ghi]fluoranthene (**T8**) was obtained as yellow solid (9.6 mg, 99 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 8.06 (d, *J* = 7.0 Hz, 1H), 7.98 – 7.89 (m, 4H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.66 (dd, *J* = 8.0, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.8, 136.7, 133.9, 132.9, 132.8, 131.0, 129.3, 128.6, 127.8, 127.3, 127.0, 126.9, 126.6, 124.9, 124.7, 123.7, 96.6. HPLC (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) t_R = 9.22 min. UV/vis (DCM/MeOH) λ_{max} 403 (sh), 384 (sh), 360, 342, 326, 294, 283, 248, 234 nm. LDI MS *m/z* 352 (M^+, 100). HR MS (APPI) calcd. for $C_{18}H_9I$ ($M^{+\bullet}$, 100) *m/z* 351.9743, found 351.9738.

3-(3-Iodophenyl)benzo[*ghi*]fluoranthene (T12). 1-Fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (**P21**) (10.3 mg, 23.0 µmol) and activated aluminium oxide (2.2 g, 21.6 mmol) were reacted according to the general procedure. The condensation was carried out at 180 °C for 12 h. After extraction of Al_2O_3 with toluene (10 mL) and solvent evaporation pure 3-(3-iodophenyl)benzo[*ghi*]fluoranthene (**T9**) was obtained as yellow solid (9.5 mg, 97 %): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.21 (d, *J* = 7.2 Hz, 1H), 8.18 (d, *J* = 7.0 Hz, 1H), 8.11 (t, *J* = 1.7 Hz, 1H), 8.06 – 7.96 (m, 5H), 7.84 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 141.8, 138.7, 138.6, 137.0, 136.8, 136.5, 133.6, 133.4, 132.9, 130.2, 129.4, 128.9, 128.5, 127.7, 126.9, 126.7, 126.5, 125.6, 125.5, 125.1, 124.9, 123.6, 123.5, 94.3. HPLC (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1) t_R = 9.36 min. UV/vis (DCM/MeOH) λ_{max} 404 (sh), 359, 344, 296, 285, 265, 259, 249 nm. LDI MS *m/z* 428 (M^+, 100 %). HR MS (APPI) calcd. for $C_{24}H_{13}I$ ($M^{+\bullet}$, 100) *m/z* 428.0056, found 428.0049.

Condensation of PS1. PS1 (47 mg, 130 µmol) and activated aluminium oxide (2.6 g, 25.5 mmol) were reacted according to the general procedure. The condensation was carried out at 200 °C for 12 h. ^{1}H NMR of the reaction mixture indicated no reaction.

Condensation of PS2. PS2 (40 mg, 120 µmol) and activated aluminium oxide (2.6 g, 25.5 mmol) were reacted according to the general procedure. The condensation was carried out at 200 °C for 12 h. ^{1}H NMR of the reaction mixture indicated no reaction.

2 References.

1 T. H. Jepsen, M. Larsen, M. Jørgensen, K. A. Solanko, A. D. Bond, A. Kadziola and M. B. Nielsen, *European J. Org. Chem.*, 2011, 53–57.

2 A. G. Cairns, H. M. Senn, M. P. Murphy and R. C. Hartley, *Chem. - A Eur. J.*, 2014, **20**, 3742–3751.

3 K. Y. Amsharov, M. A. Kabdulov and M. Jansen, *European J. Org. Chem.*, 2009, 6328–6335.

4 S. Karmakar, T. Mandal and J. Dash, *European J. Org. Chem.*, 2019, **2019**, 5916–5924.

5 W. A. Henderson, R. Lopresti and A. Zweig, *J. Am. Chem. Soc.*, 1969, **91**, 6049–6057.

6 Z. Liu, X. Zhang and R. C. Larock, *J. Am. Chem. Soc.*, 2005, **127**, 15716–15717.

7 Y. Zhang, S. Pan, H. Jiang, Y. Zhang and D. Chen, *Org. Lett.*, 2016, **18**, 5192–5195.

8 S. Yang, F. Wang, Y. Wu, W. Hua and F. Zhang, *Org. Lett.*, 2018, **20**, 1491–1495.

9 W. Mao and C. Zhu, *J. Org. Chem.*, 2017, **82**, 9133–9143.

10 L. J. Baldwin, M. L. Tedjamulia, J. G. Stuart, R. N. Castle and M. L. Lee, *J. Heterocycl. Chem.*, 1984, **21**, 1775–1779.

11 I. S. Kovalev, D. S. Kopchuk, A. F. Khasanov, G. V. Zyryanov, V. L. Rusinov and O. N. Chupakhin, *Mendeleev Commun.*, 2014, **24**, 117–118.

12 R. Nandy and S. Sankararaman, *Org. Biomol. Chem.*, 2010, **8**, 2260–2266.

3 Spectroscopic Analysis and Characterization

3.1 Building Blocks 1–12 and Precursors P1–19

2-Bromo-2’-fluoro-1,1’-biphenyl (1)

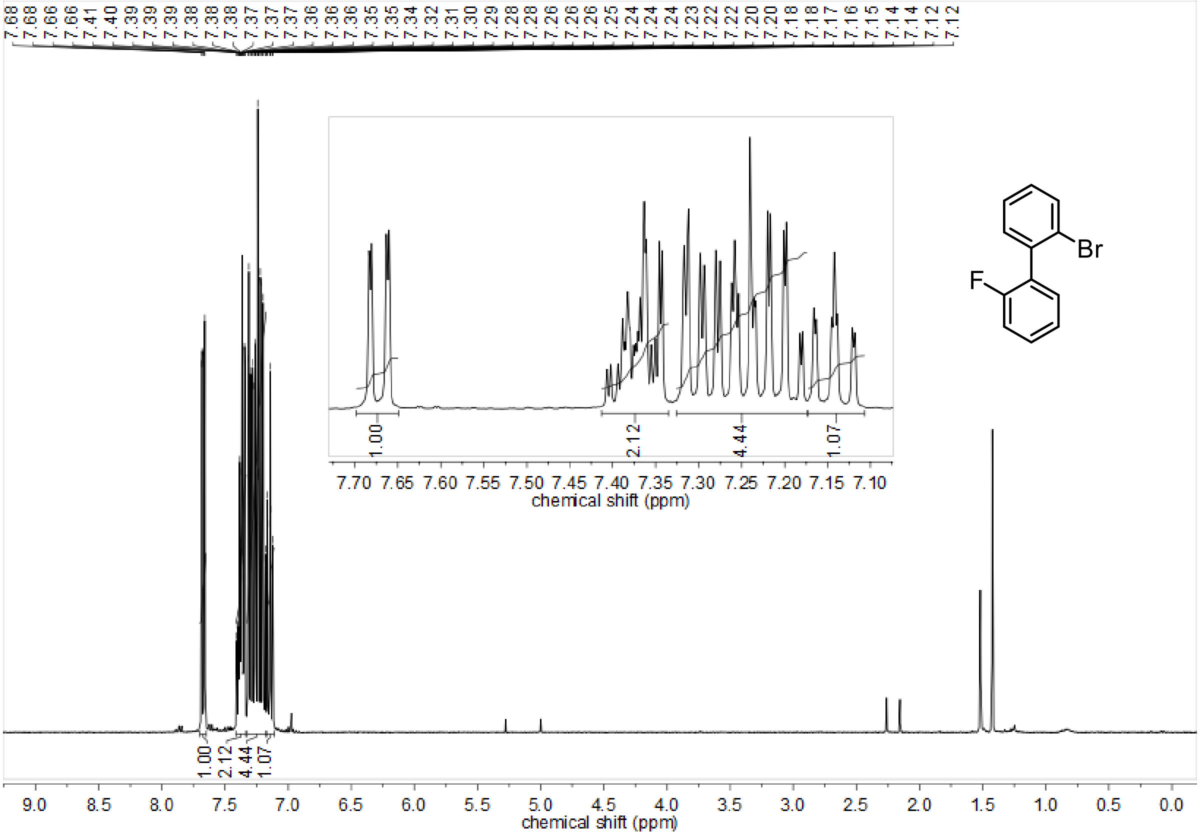


Figure S1: ^{1}H NMR spectrum of 2-bromo-2’-fluoro-1,1’-biphenyl (**1**) (in $CDCl_3$).

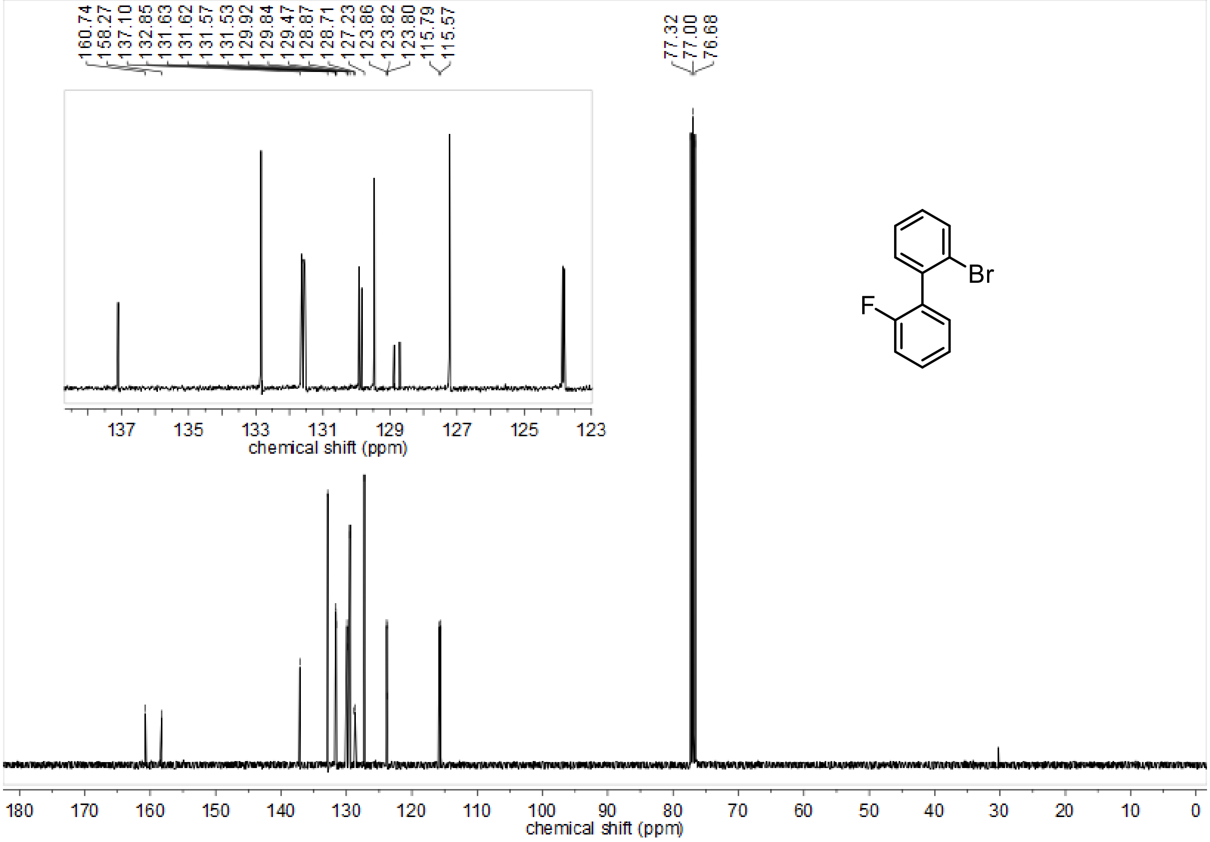


Figure S2: ^{13}C NMR spectrum of 2-bromo-2’-fluoro-1,1’-biphenyl (**1**) (in CDCl$_3$).

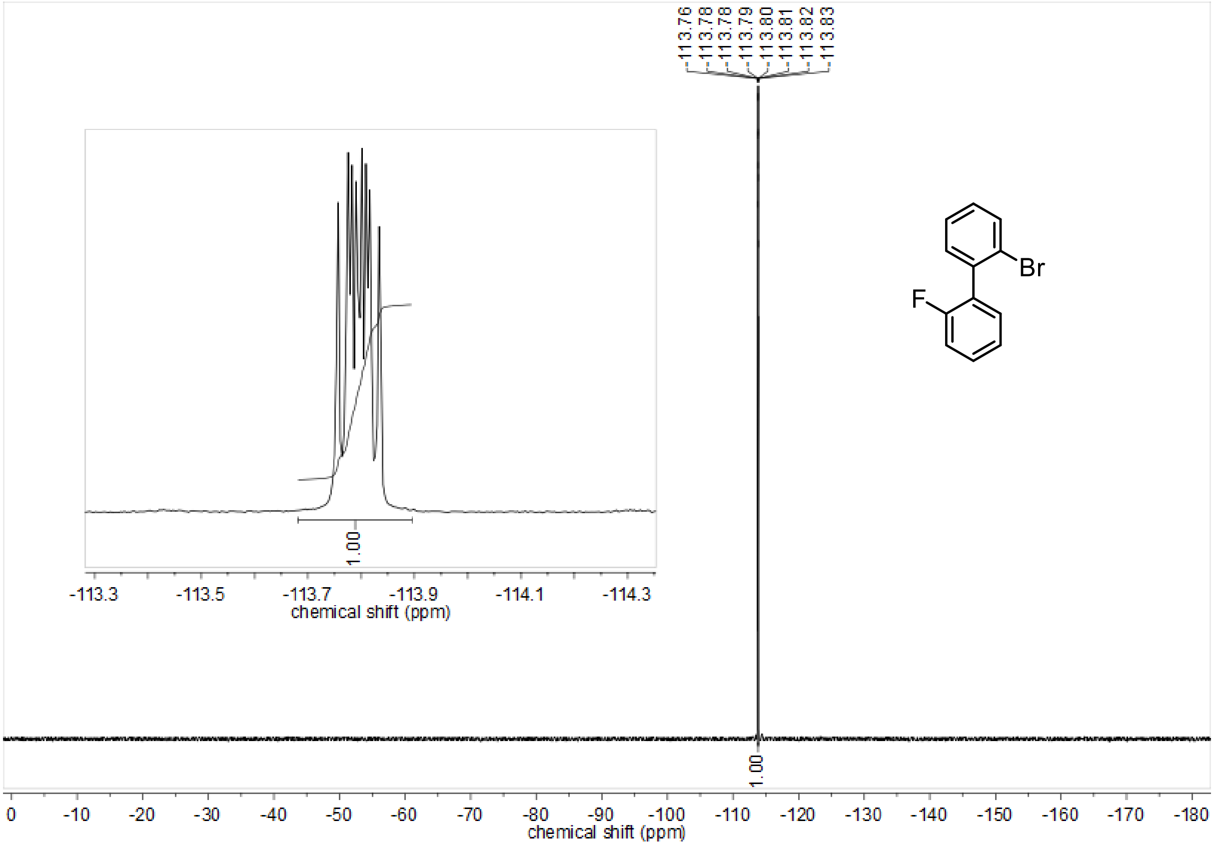


Figure S3: ^{19}F NMR spectrum of 2-bromo-2’-fluoro-1,1’-biphenyl (**1**) (in CDCl$_3$).[redacted]

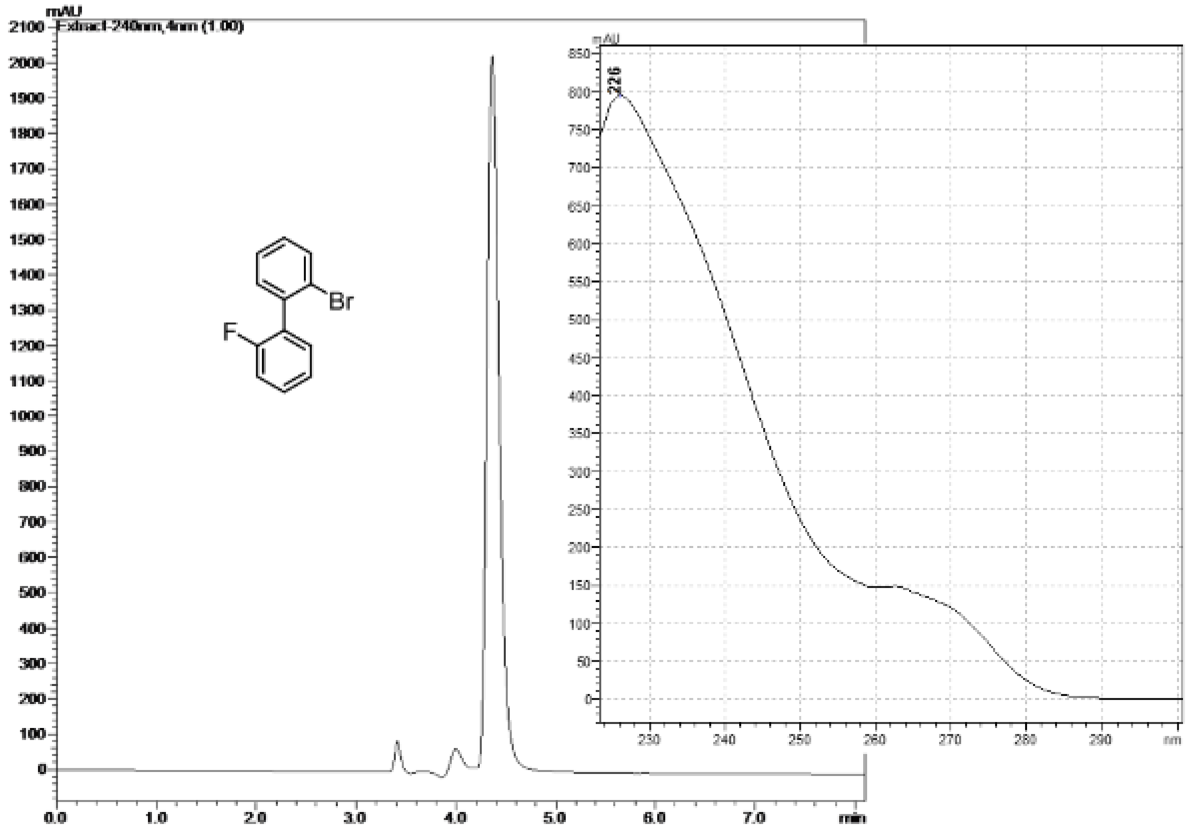


Figure S4: HPLC chromatogram of 2-bromo-2’-fluoro-1,1’-biphenyl **(1)** (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1), t_R = 4.36 min, (inset) UV/vis spectrum.

(2’-Fluoro-[1,1’-biphenyl]2-yl)boronic acid (2)

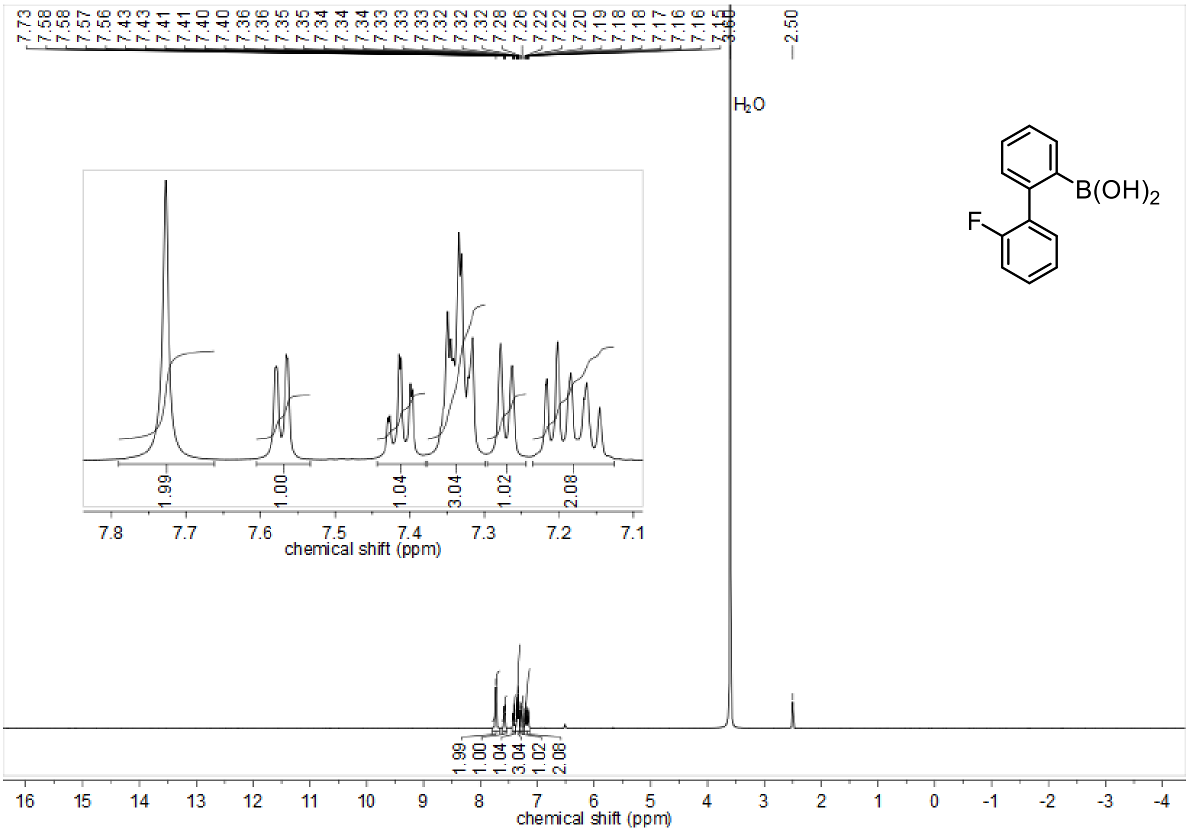


Figure S5: ^{1}H NMR spectrum of (2’-fluoro-[1,1’-biphenyl]2-yl)boronic acid (**2**) (in DMSO-d_6, 30 °C).

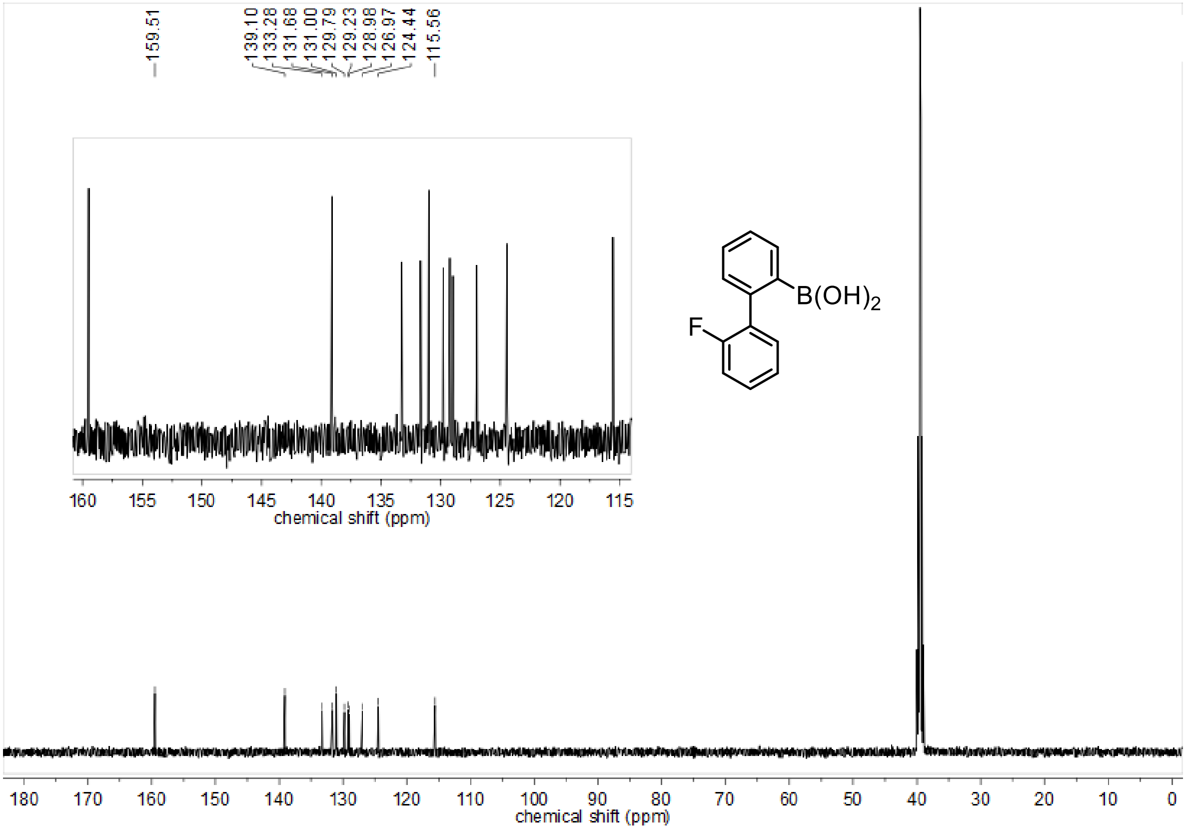


Figure S6: ^{13}C NMR spectrum (fluorine decoupled.) of (2’-fluoro-[1,1’-biphenyl]2-yl)boronic acid (**2**) (in DMSO-d_6, 30 °C).

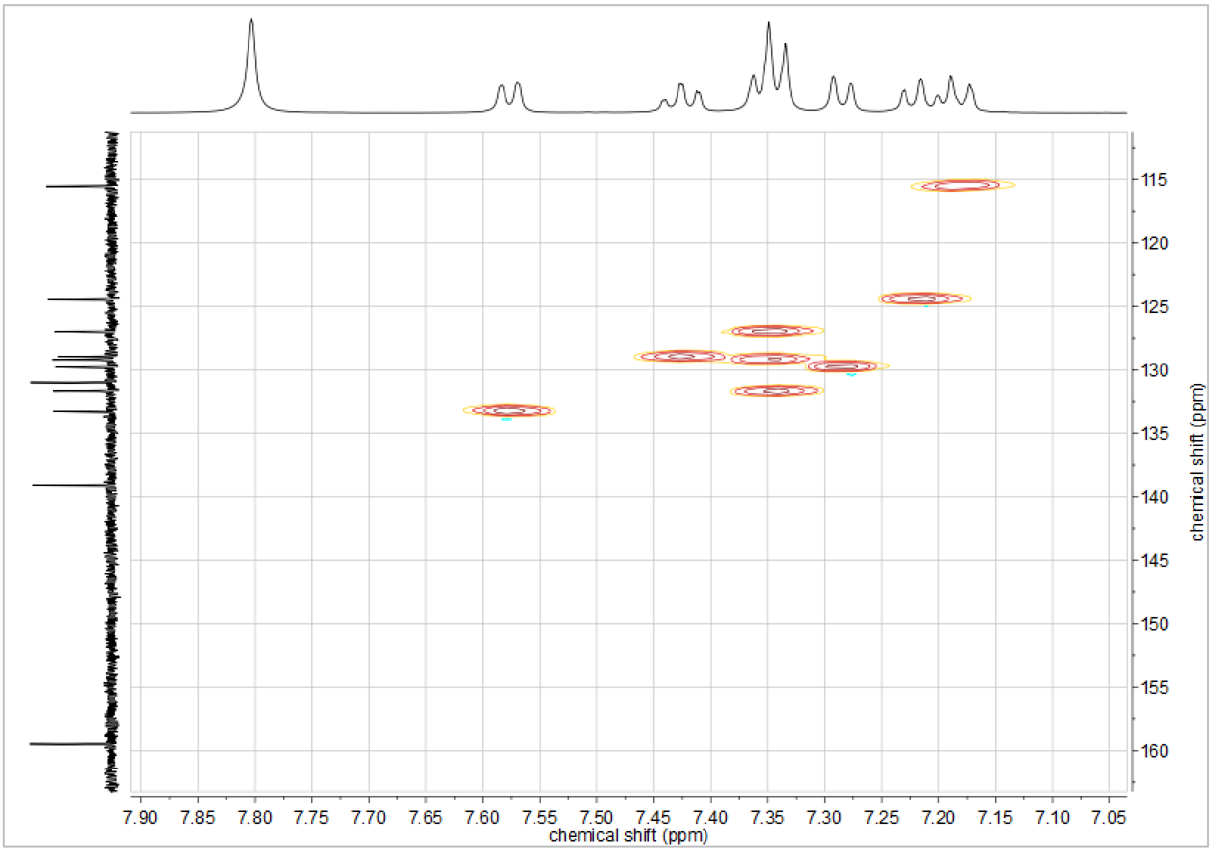


Figure S7: HSQC of (2’-fluoro-[1,1’-biphenyl]2-yl)boronic acid (**2**) (in DMSO-d_6, 30 °C).

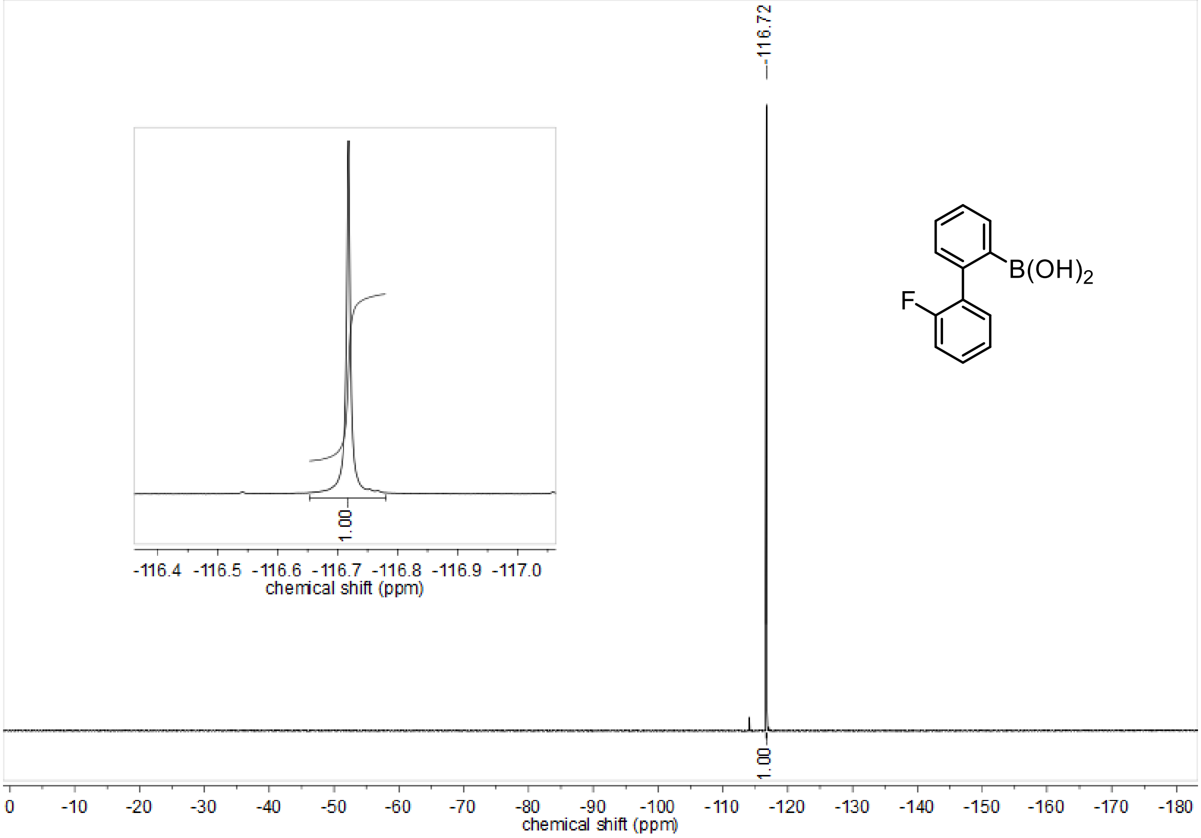


Figure S8: ^{19}F NMR spectrum (proton decoupled) of (2'-fluoro-[1,1'-biphenyl]2-yl)boronic acid (**2**) (in DMSO-d_6, 30 °C).

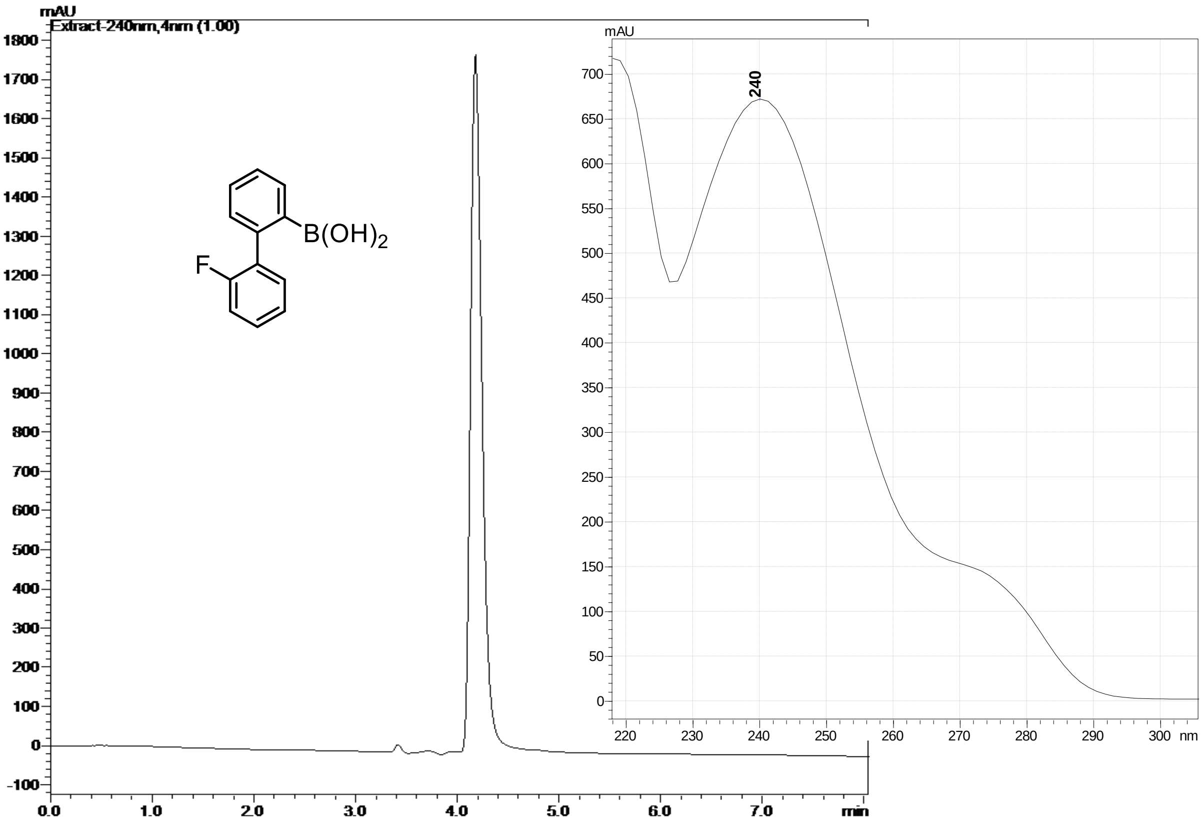
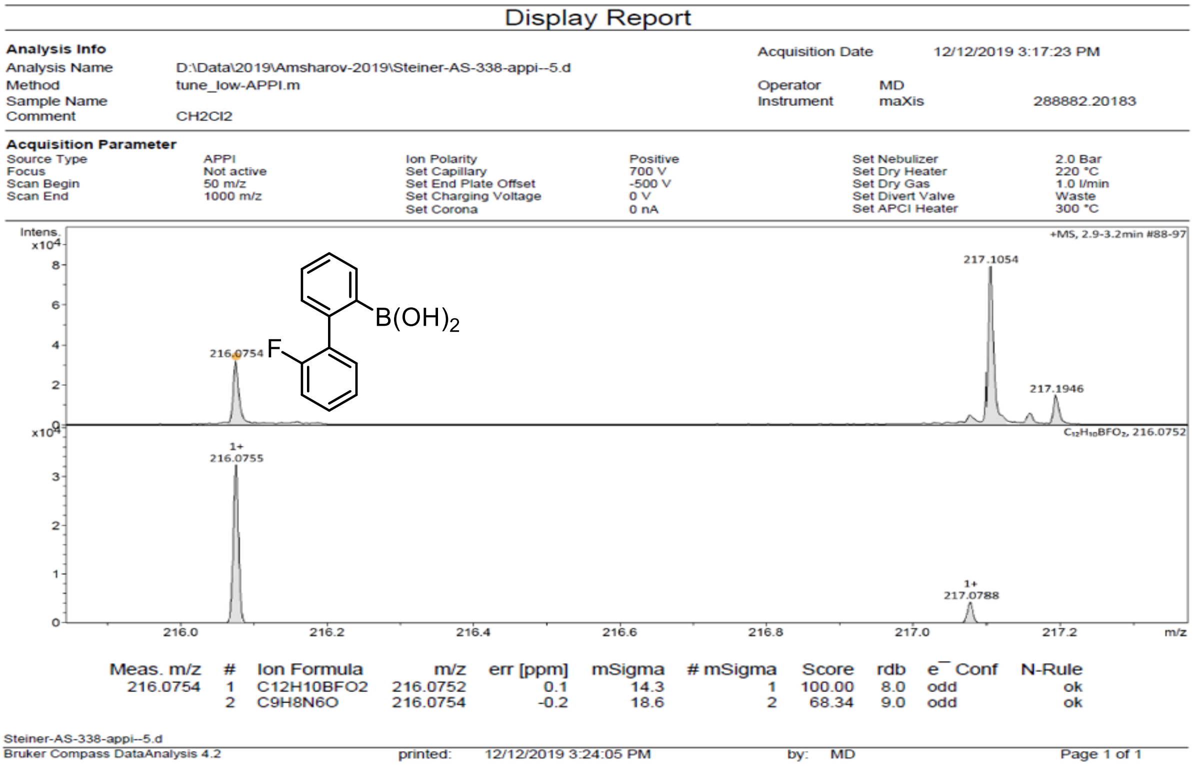


Figure S9: HPLC chromatogram of (2'-fluoro-[1,1'-biphenyl]2-yl)boronic acid (**2**) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1), t_R = 4.17 min, (inset) UV/vis spectrum.



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-338-appi--5.d	Acquisition Date	12/12/2019 3:17:23 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	300 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
216.0754	1	C12H10BFO2	216.0752	0.1	14.3	1	100.00	8.0	odd	ok
	2	C9H8N6O	216.0754	-0.2	18.6	2	68.34	9.0	odd	ok

Steiner-AS-338-appi--5.d

Bruker Compass DataAnalysis 4.2 printed: 12/12/2019 3:24:05 PM by: MD Page 1 of 1

Figure S10: HR MS (APPI) spectrum of (2’-fluoro-[1,1’-biphenyl]2-yl)boronic acid (**2**), *m/z* 216.0754 (M^+, 100 %).

2-Fluoro-4''-methyl-1,1':2',1''-terphenyl (P1)

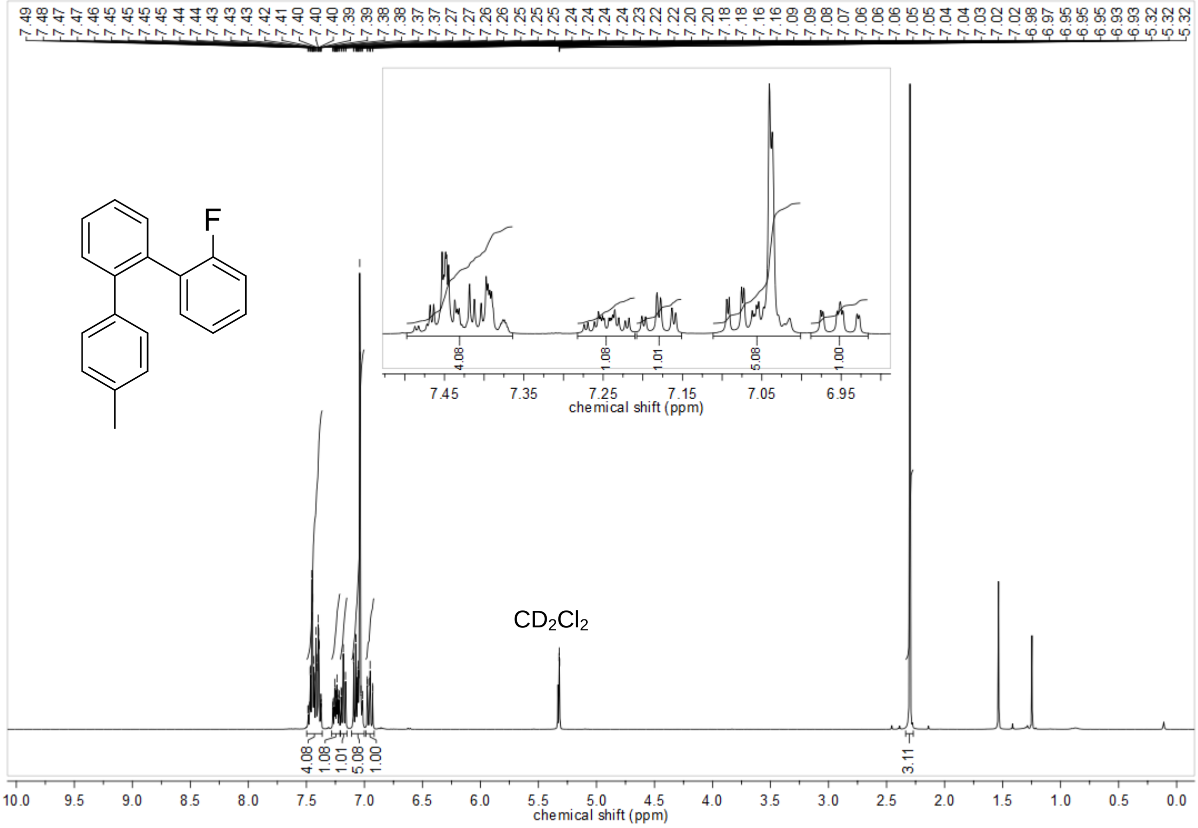


Figure S11: ^{1}H NMR spectrum of 2-fluoro-4''-methyl-1,1':2',1''-terphenyl (**P1**) (in CD_2Cl_2).

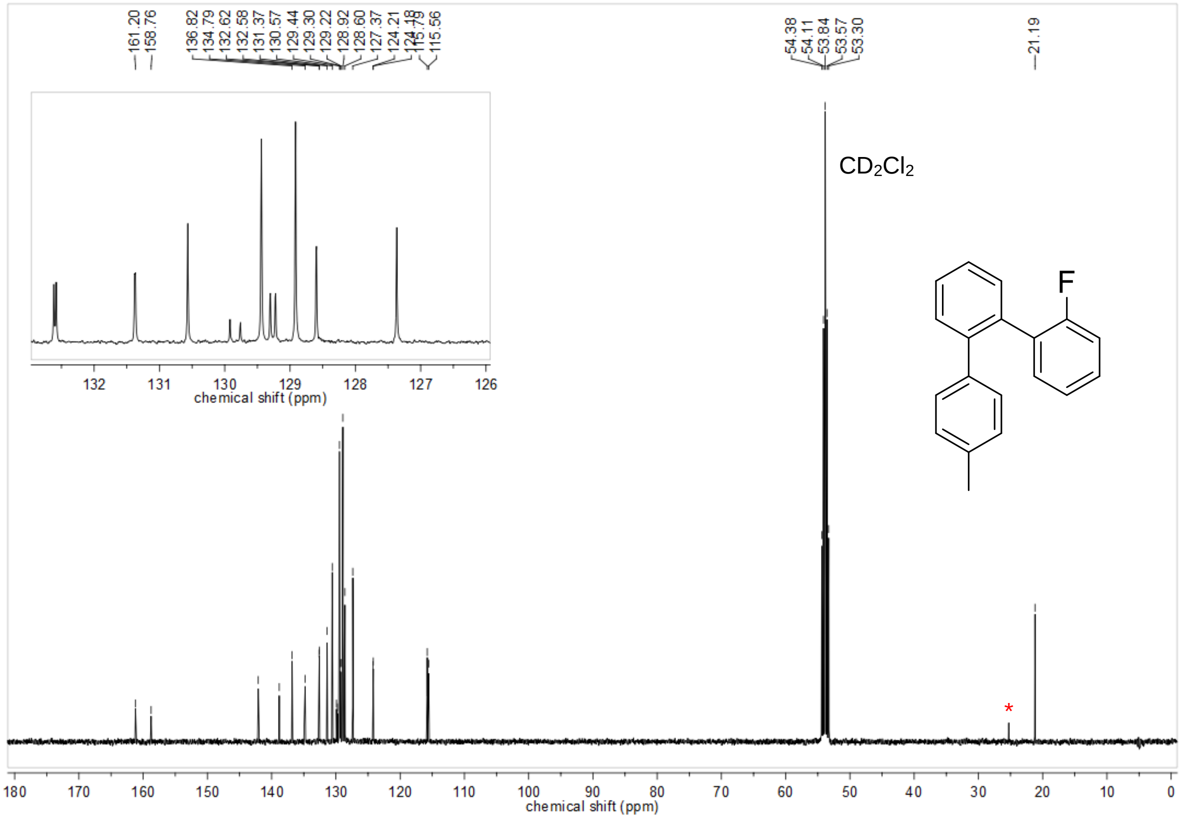


Figure S12: ^{13}C NMR spectrum of 2-fluoro-4''-methyl-1,1':2',1''-terphenyl (**P1**) (in CD_2Cl_2).

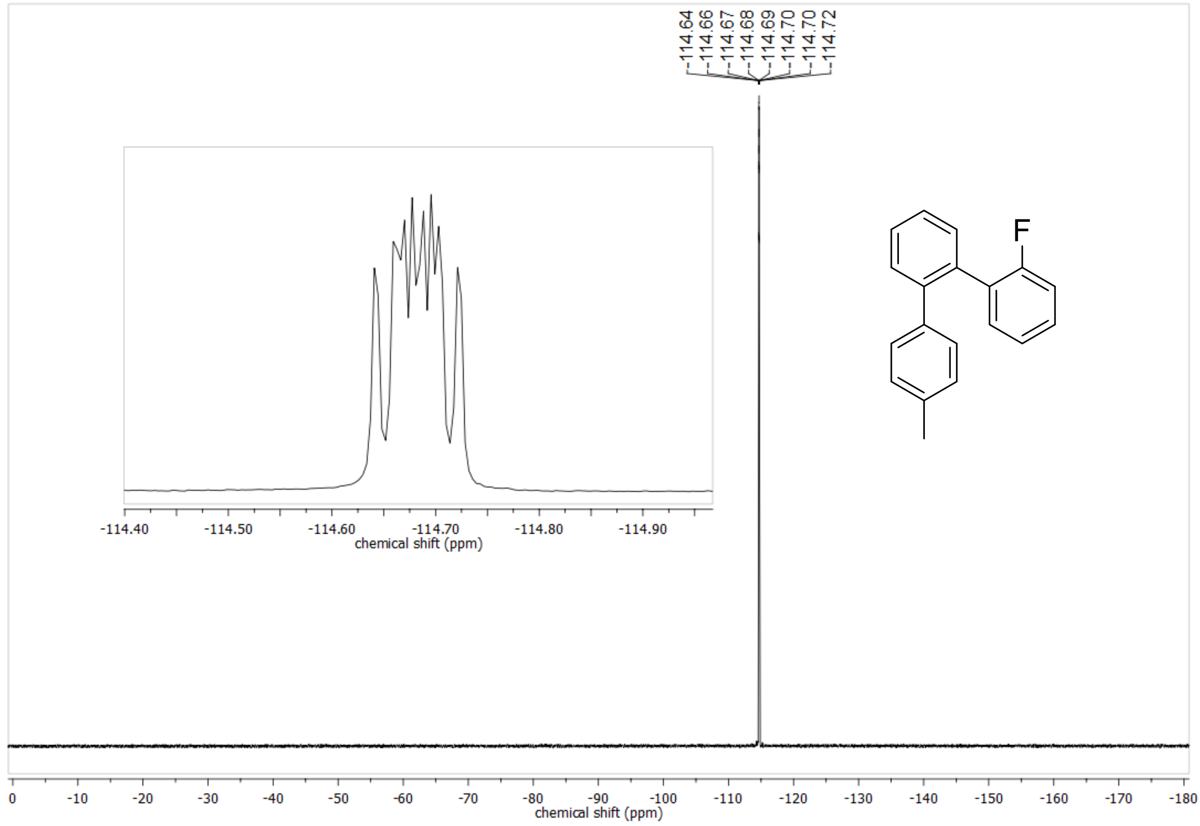


Figure S13: ^{19}F NMR spectrum of 2-fluoro-4''-methyl-1,1':2',1''-terphenyl (**P1**) (in CD_2Cl_2).

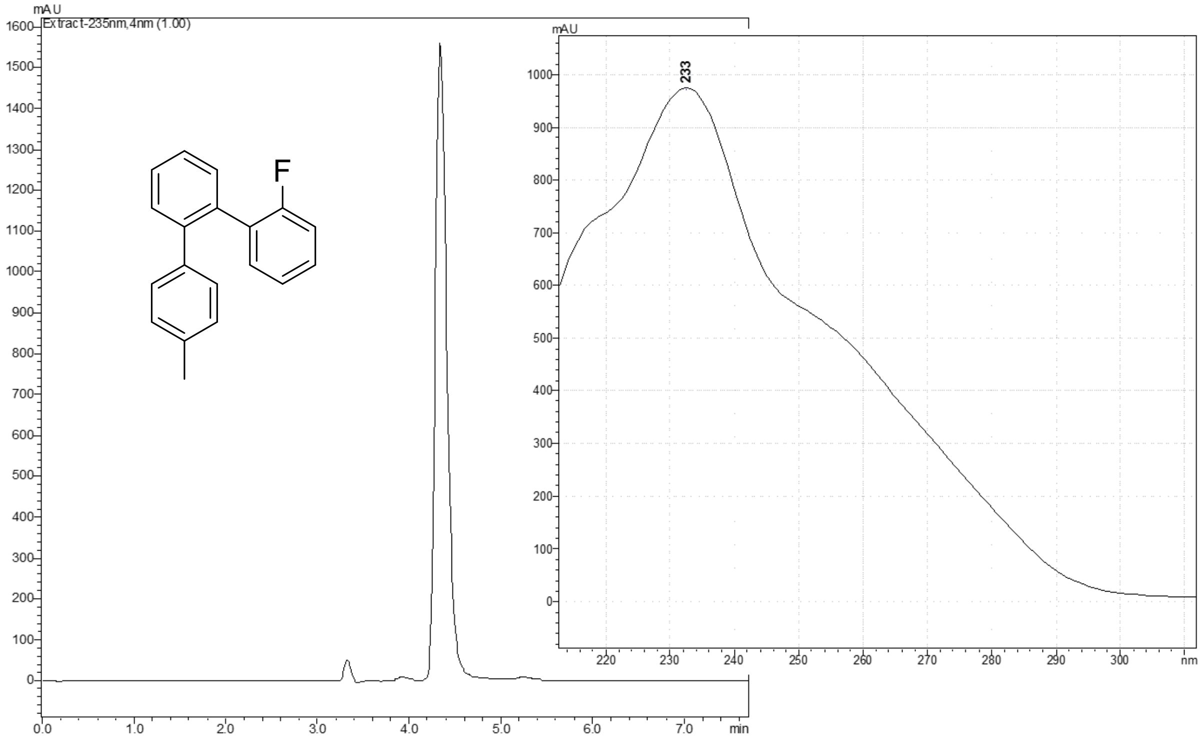
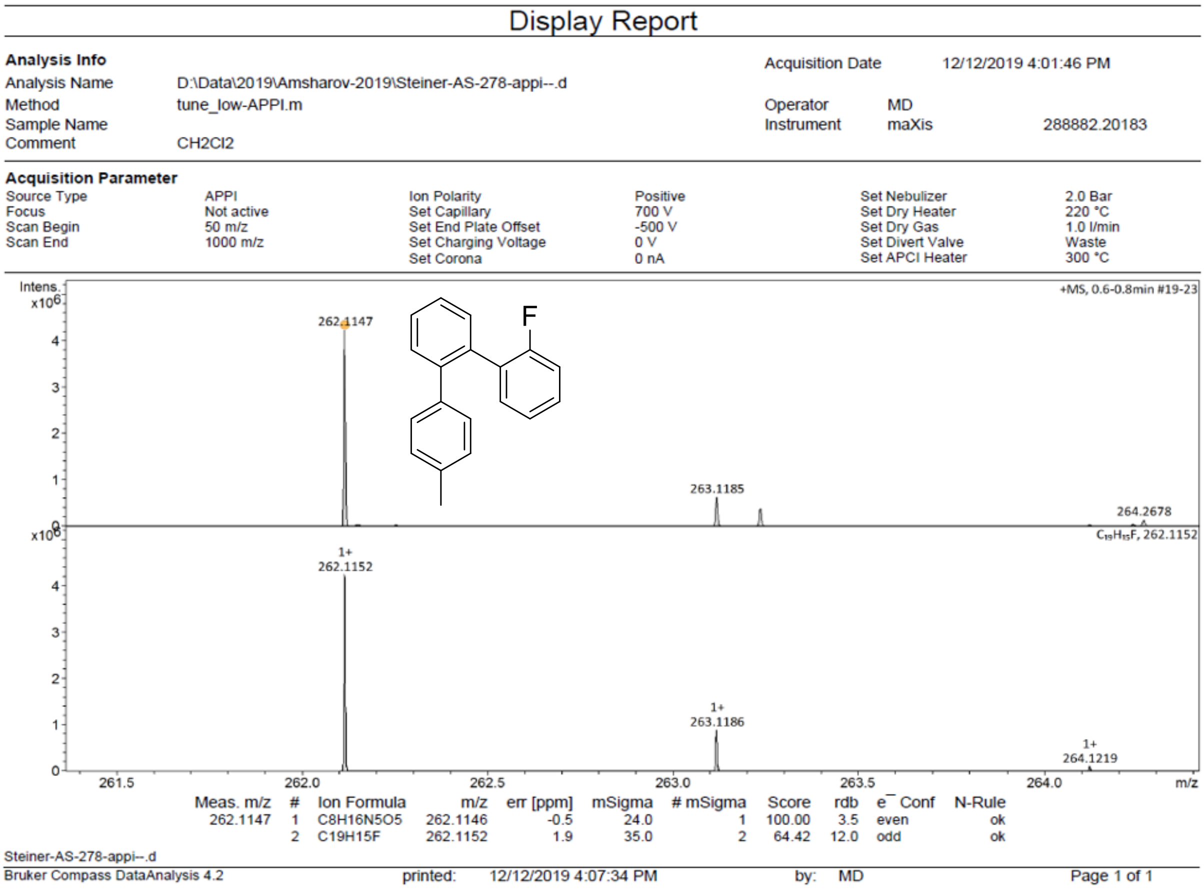


Figure S14: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, CH_2Cl_2/MeOH 3:7, t_R = 4.34 min) and UV/vis spectrum (inset) of 2-fluoro-4''-methyl-1,1':2',1''-terphenyl (**P1**).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-AS-278-appi--.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2
Acquisition Date 12/12/2019 4:01:46 PM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	300 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
262.1147	1	C8H16N5O5	262.1146	-0.5	24.0	1	100.00	3.5	even	ok
	2	C19H15F	262.1152	1.9	35.0	2	64.42	12.0	odd	ok

Steiner-AS-278-appi--.d

Bruker Compass DataAnalysis 4.2 printed: 12/12/2019 4:07:34 PM by: MD Page 1 of 1

Figure S15: HR MS (APPI) spectrum of 2-fluoro-4''-methyl-1,1':2',1''-terphenyl (**P1**), *m/z* 262.1147 (M^+, 100 %).

4''-(*Tert*-butyl)-2-fluoro-1,1':2',1''-terphenyl (P2)

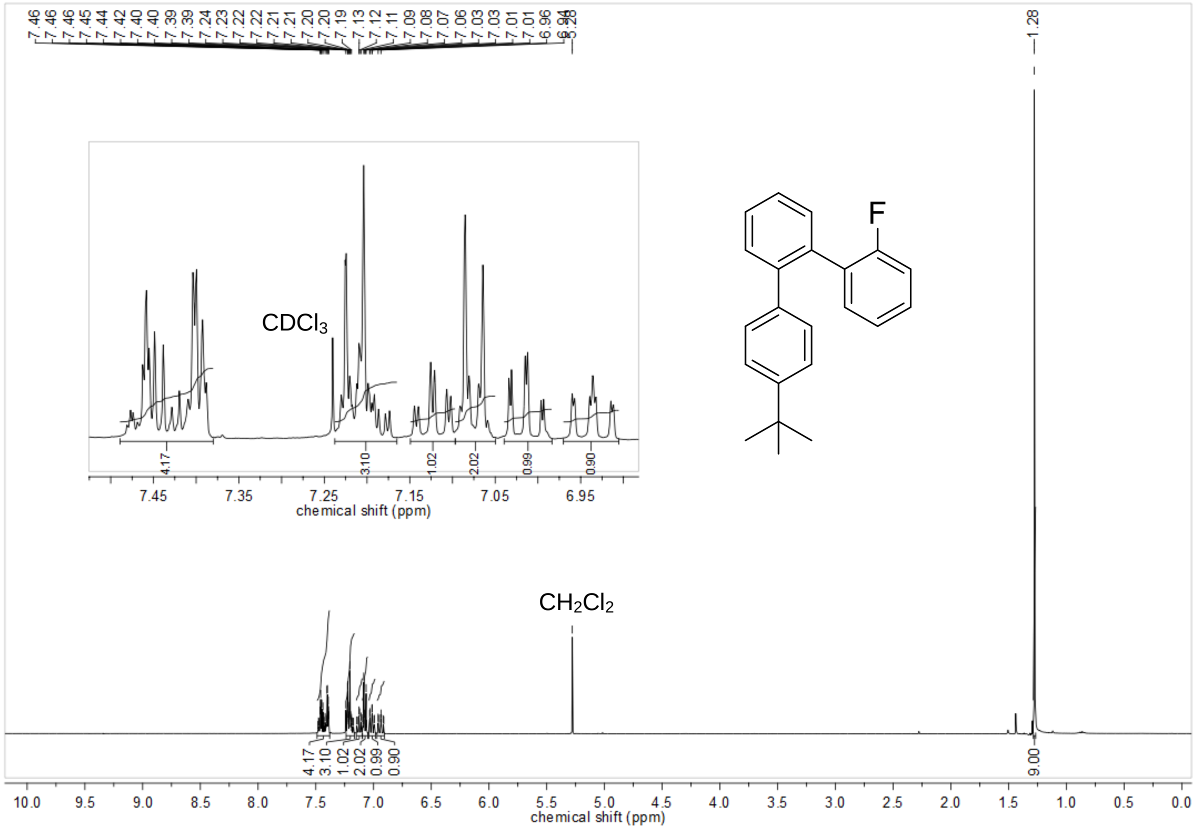


Figure S16: ^{1}H NMR spectrum of 4"-(*tert*-butyl)-2-fluoro-1,1':2',1"-terphenyl (**P2**) (in $CDCl_3$).

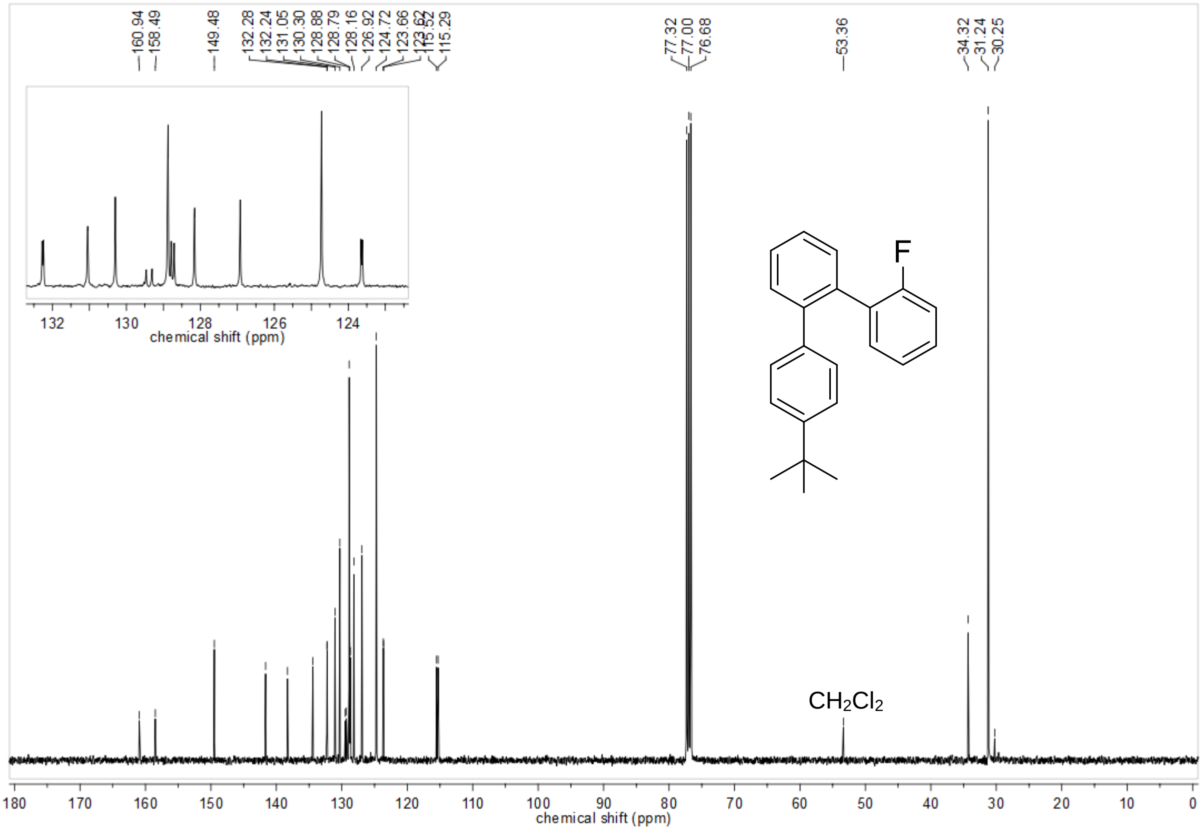


Figure S17: ^{13}C NMR spectrum of 4"-(*tert*-butyl)-2-fluoro-1,1':2',1"-terphenyl (**P2**) (in $CDCl_3$).

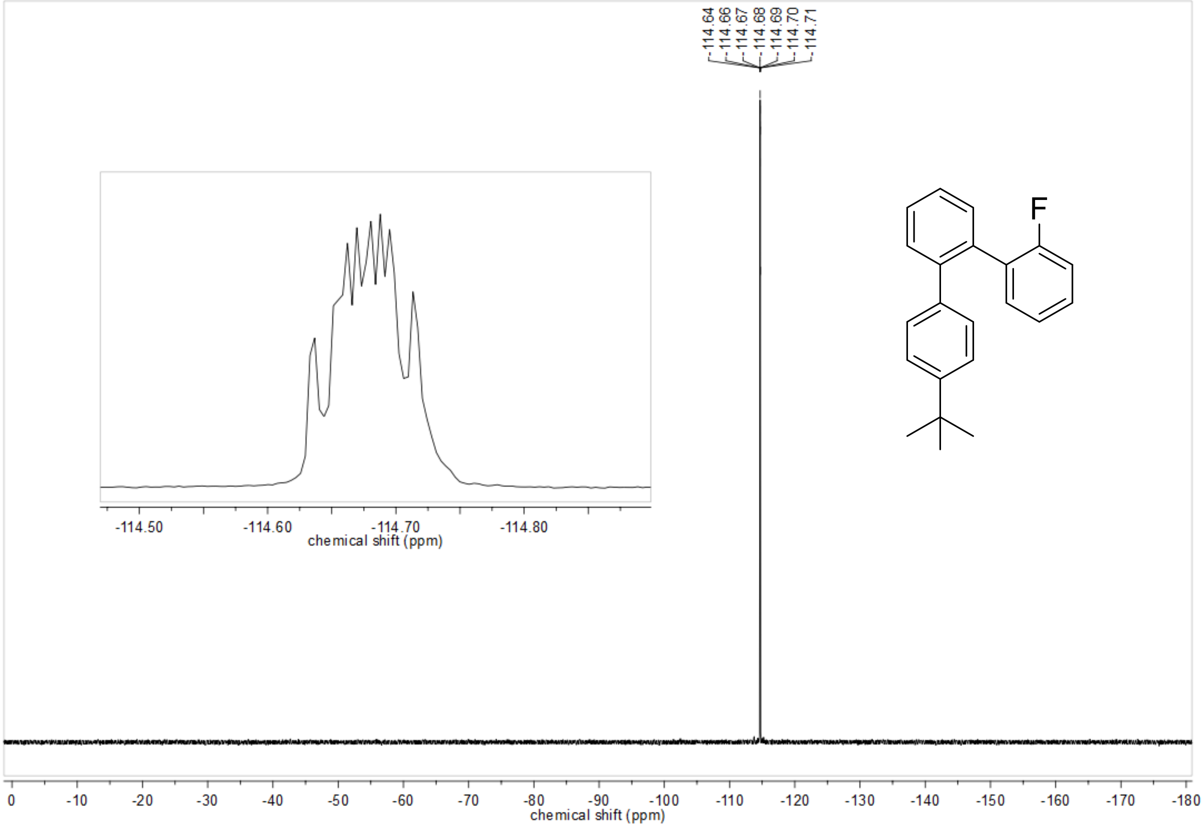


Figure S18: ^{19}F NMR spectrum of 4''-(*tert*-butyl)-2-fluoro-1,1':2',1''-terphenyl (**P2**) (in CDCl$_3$).

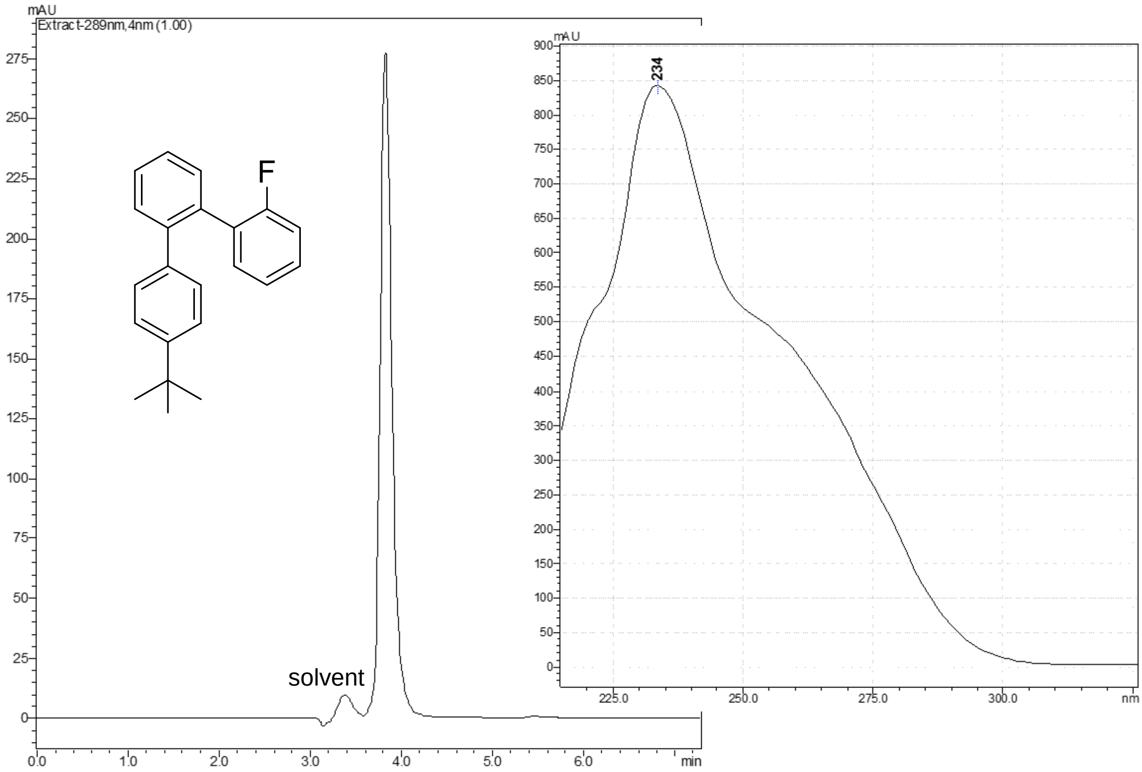
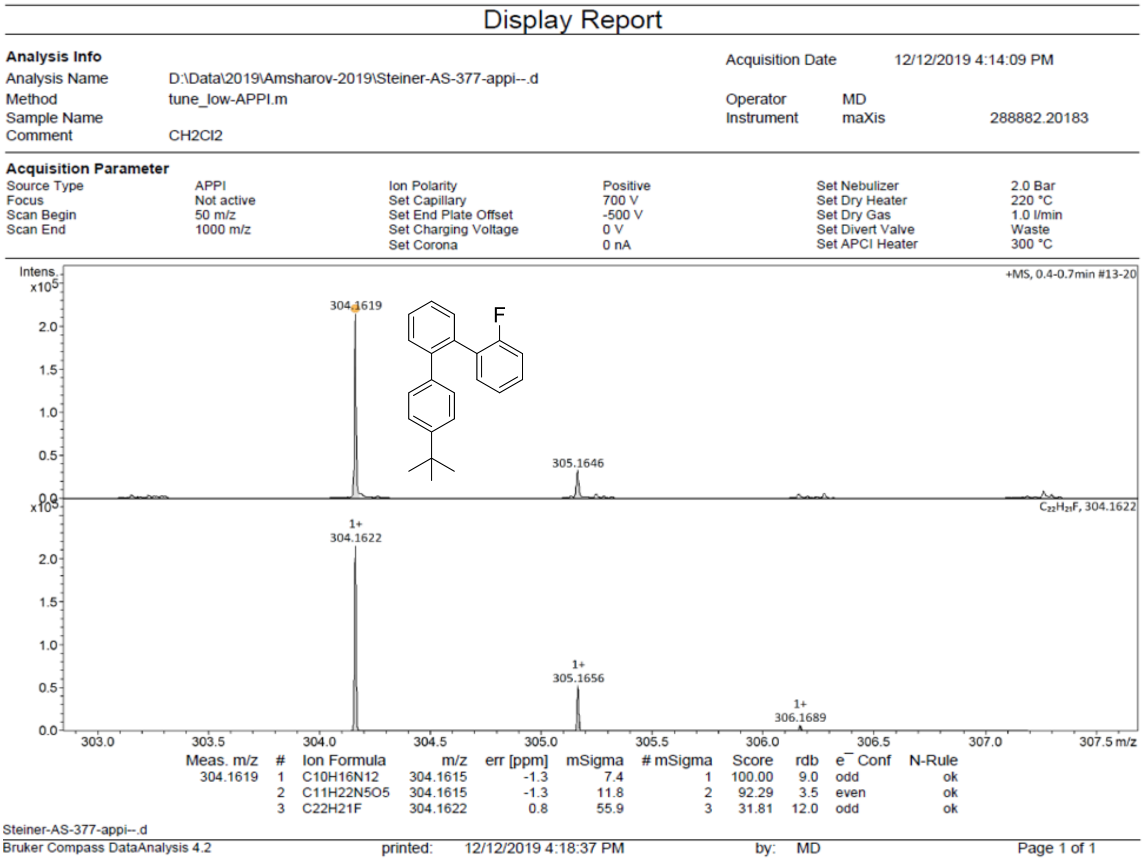


Figure S19: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:1, t$_R$ 3.82 min) and UV/vis spectrum (inset) of 4''-(*tert*-butyl)-2-fluoro-1,1':2',1''-terphenyl (**P2**).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-AS-377-appi--.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2

Acquisition Date 12/12/2019 4:14:09 PM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	300 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
304.1619	1	C10H16N12	304.1615	-1.3	7.4	1	100.00	9.0	odd	ok
	2	C11H22N5O5	304.1615	-1.3	11.8	2	92.29	3.5	even	ok
	3	C22H21F	304.1622	0.8	55.9	3	31.81	12.0	odd	ok

Steiner-AS-377-appi--.d
Bruker Compass DataAnalysis 4.2 printed: 12/12/2019 4:18:37 PM by: MD Page 1 of 1

Figure S20: HR MS (APPI) spectrum of 4''-(*tert*-butyl)-2-fluoro-1,1':2',1''-terphenyl (**P2**), *m/z* 304.1619 (M^+, 100 %).

2-Fluoro-4''-methoxy-1,1':2',1''-terphenyl (P3)

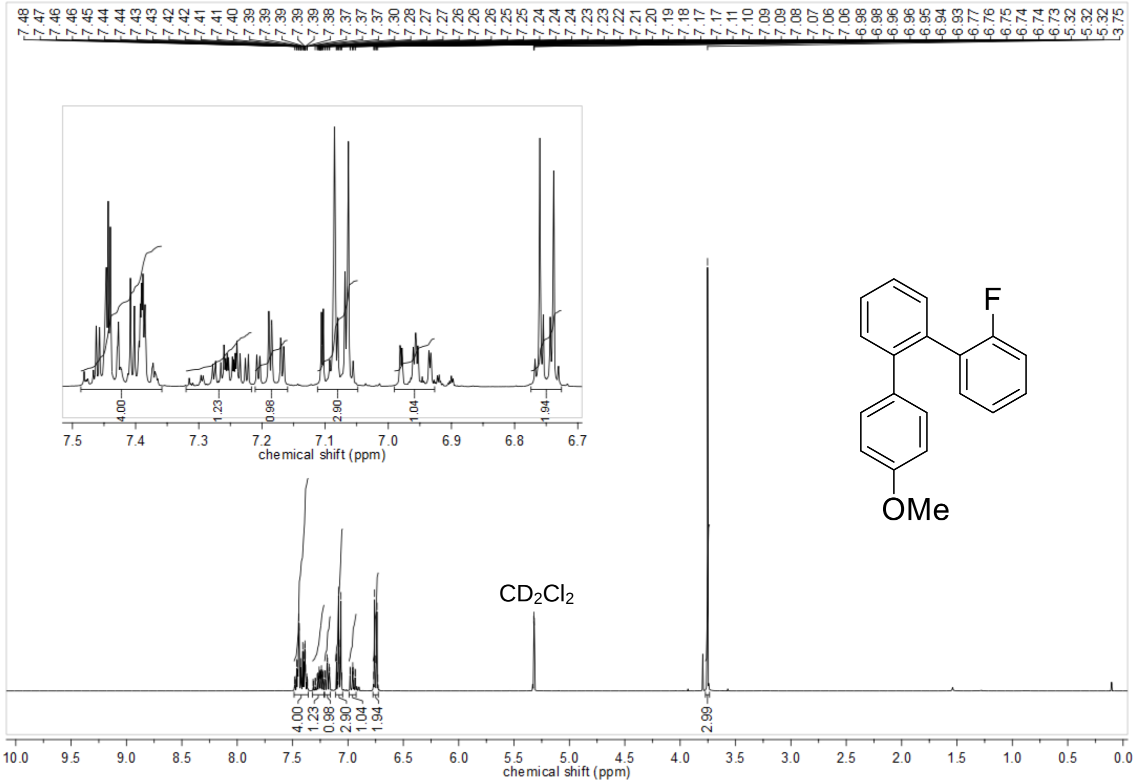


Figure S21: ^{1}H NMR spectrum of 2-fluoro-4''-methoxy-1,1':2',1''-terphenyl (**P3**) (in CD_2Cl_2).

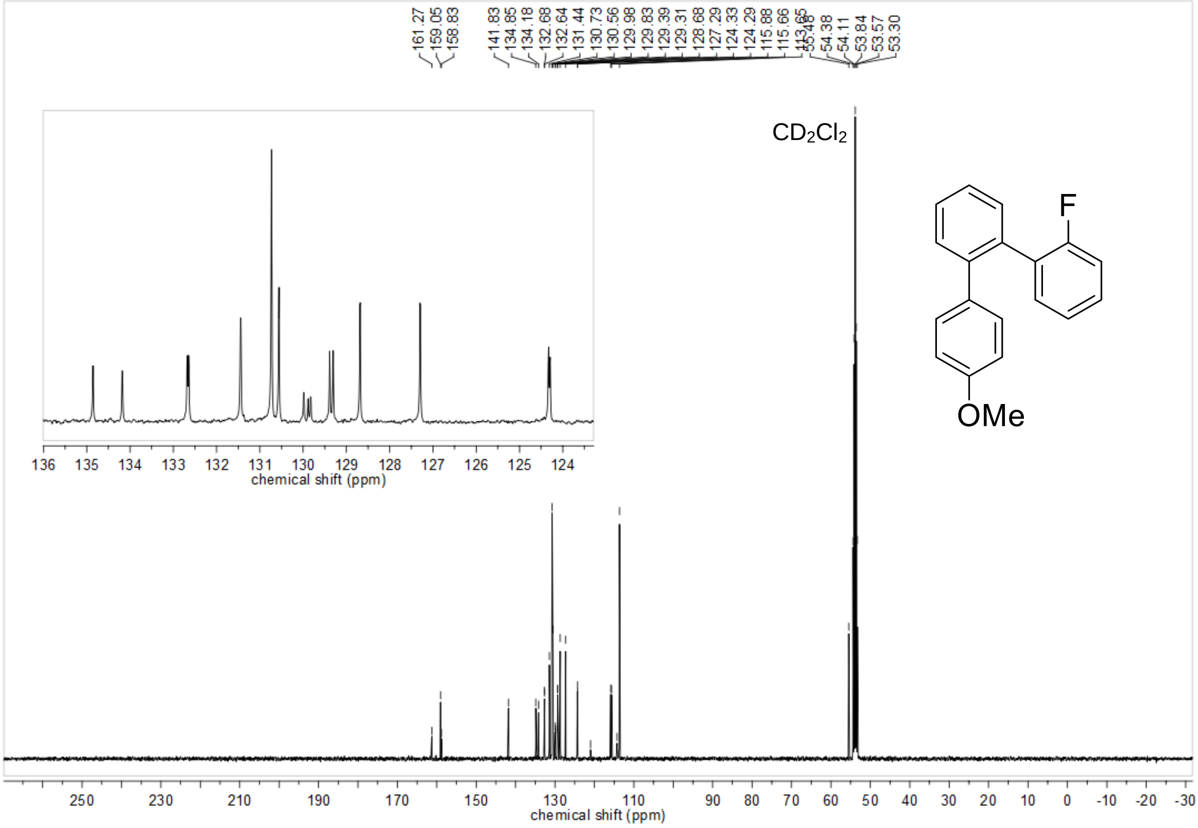


Figure S22: ^{13}C NMR spectrum of 2-fluoro-4''-methoxy-1,1':2',1''-terphenyl (**P3**) (in CD_2Cl_2).

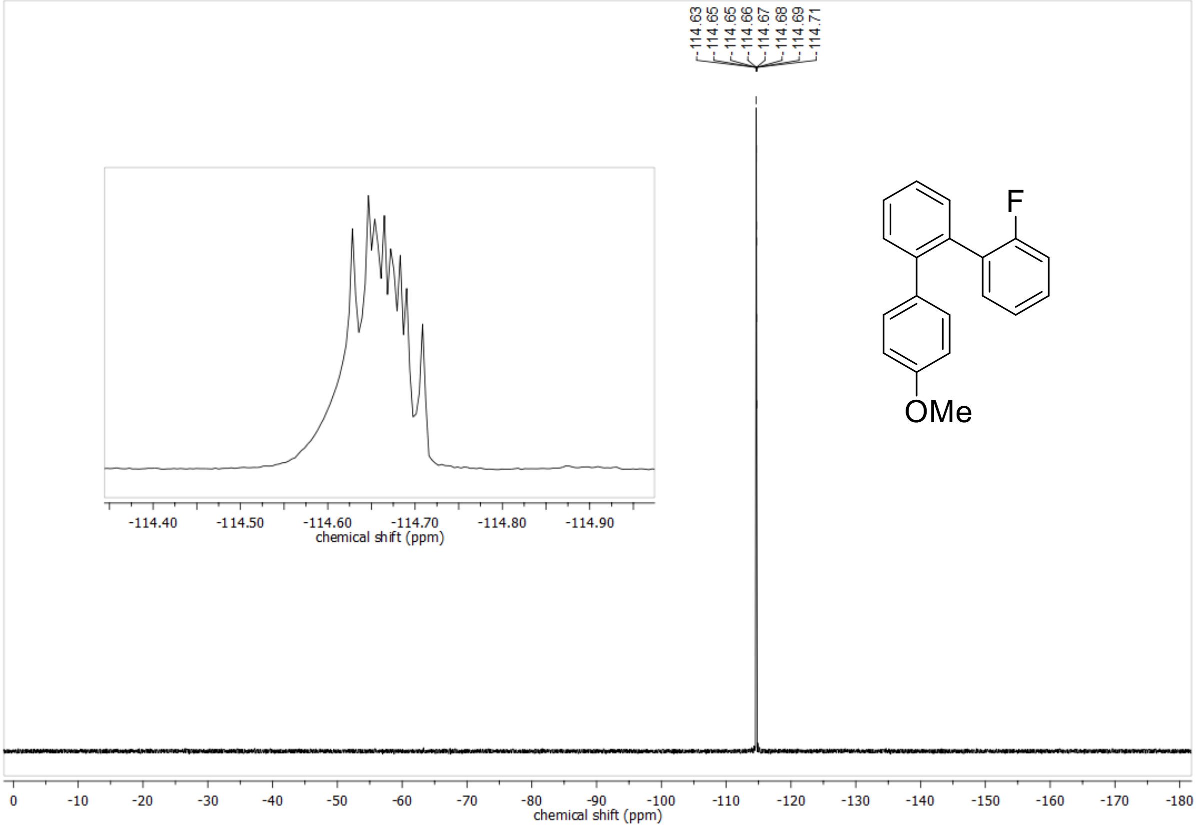


Figure S23*:* ^{19}F NMR spectrum of 2-fluoro-4''-methoxy-1,1':2',1''-terphenyl (**P3**) (in CD_2Cl_2).

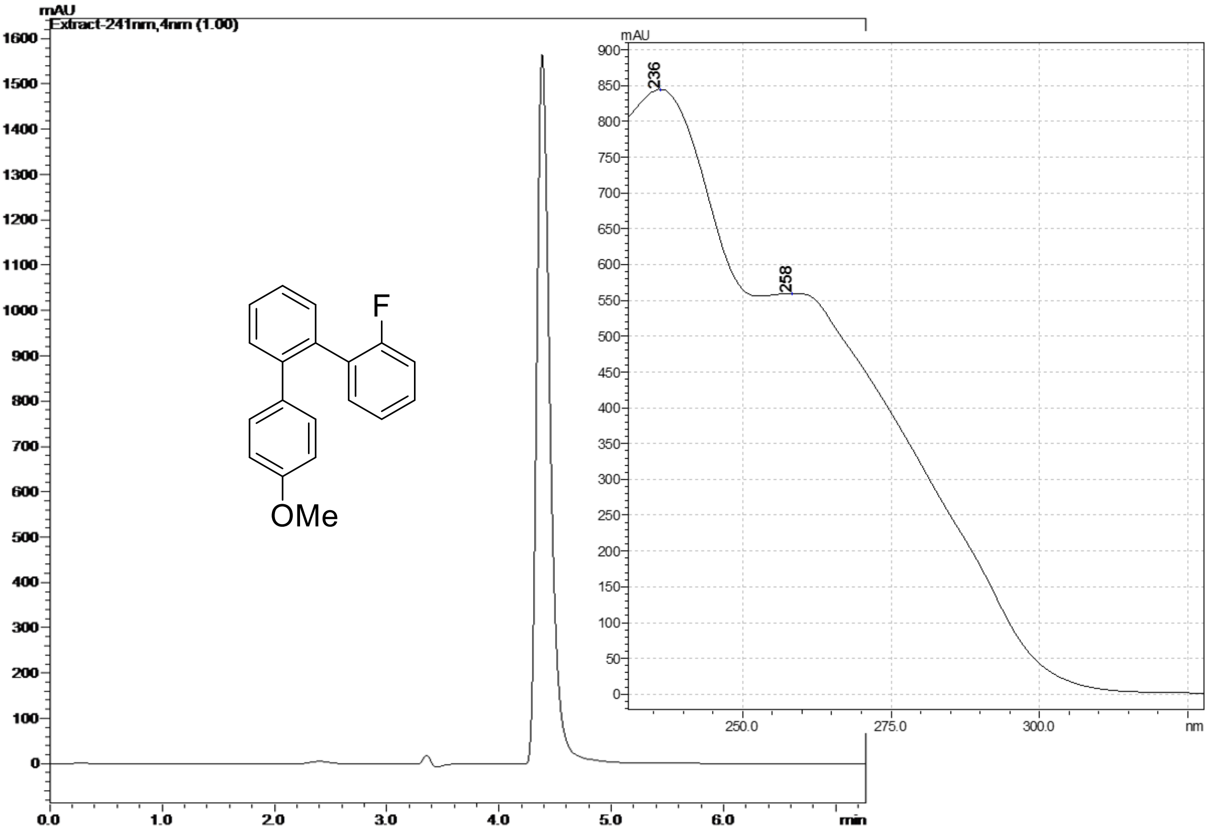
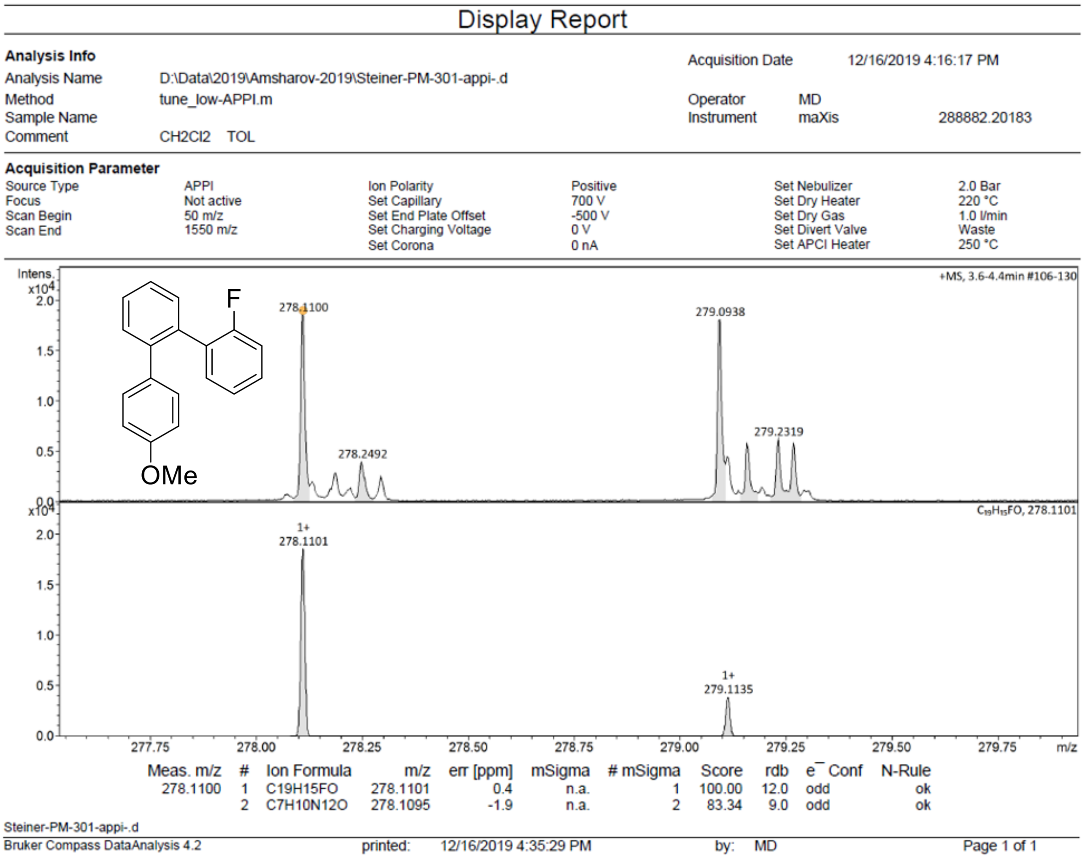


Figure S24: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 3:7), t_R = 4.38 min and UV/vis spectrum (inset) of 2-fluoro-4"-methoxy-1,1':2',1"-terphenyl (**P3**).


Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-PM-301-appi-.d	Acquisition Date	12/16/2019 4:16:17 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2 TOL			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
278.1100	1	C19H15FO	278.1101	0.4	n.a.	1	100.00	12.0	odd	ok
	2	C7H10N12O	278.1095	-1.9	n.a.	2	83.34	9.0	odd	ok

Steiner-PM-301-appi-.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 4:35:29 PM by: MD Page 1 of 1

Figure S25: HR MS (APPI) spectrum of 2-fluoro-4"-methoxy-1,1':2',1"-terphenyl (**P3**), *m/z* 278.1100 (M^+, 100 %).

Methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (P4)

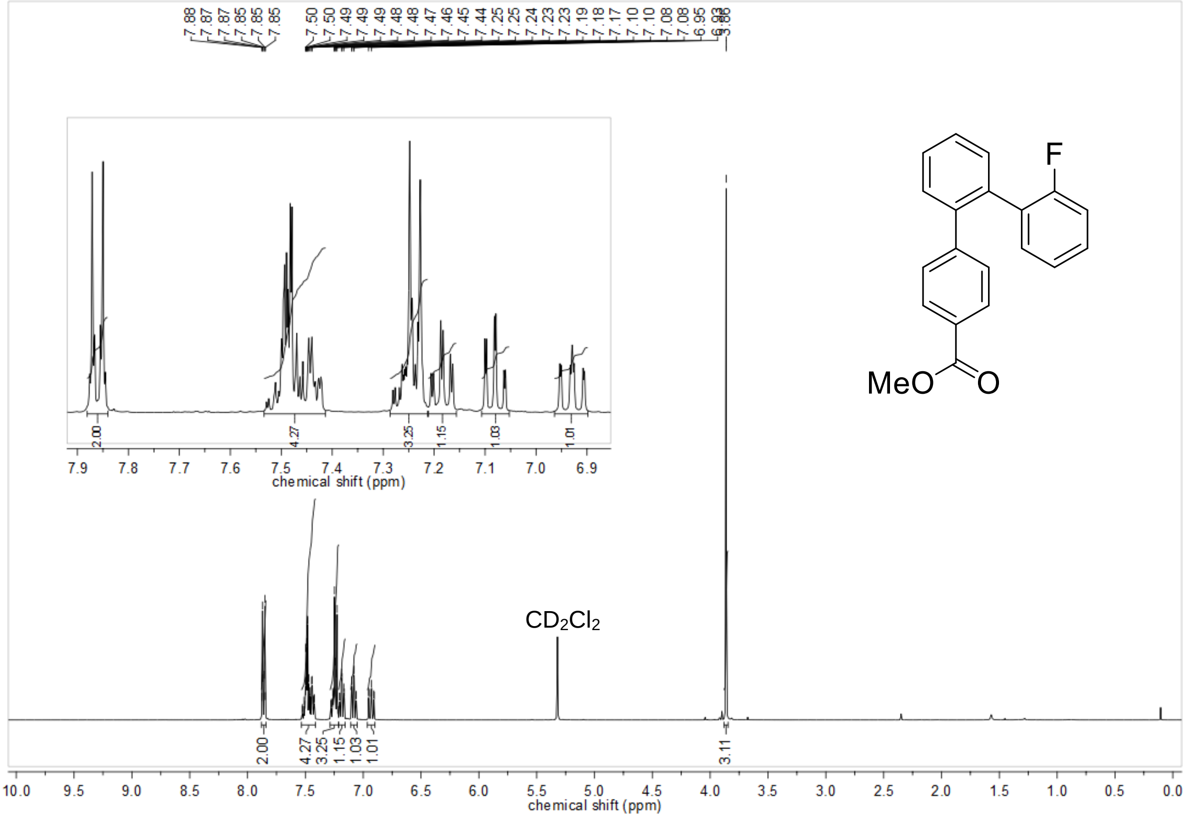


Figure S26: ^{1}H NMR spectrum of methyl 2"-fluoro-[1,1':2',1"-terphenyl]-4-carboxylate (**P4**) (in CD_2Cl_2).

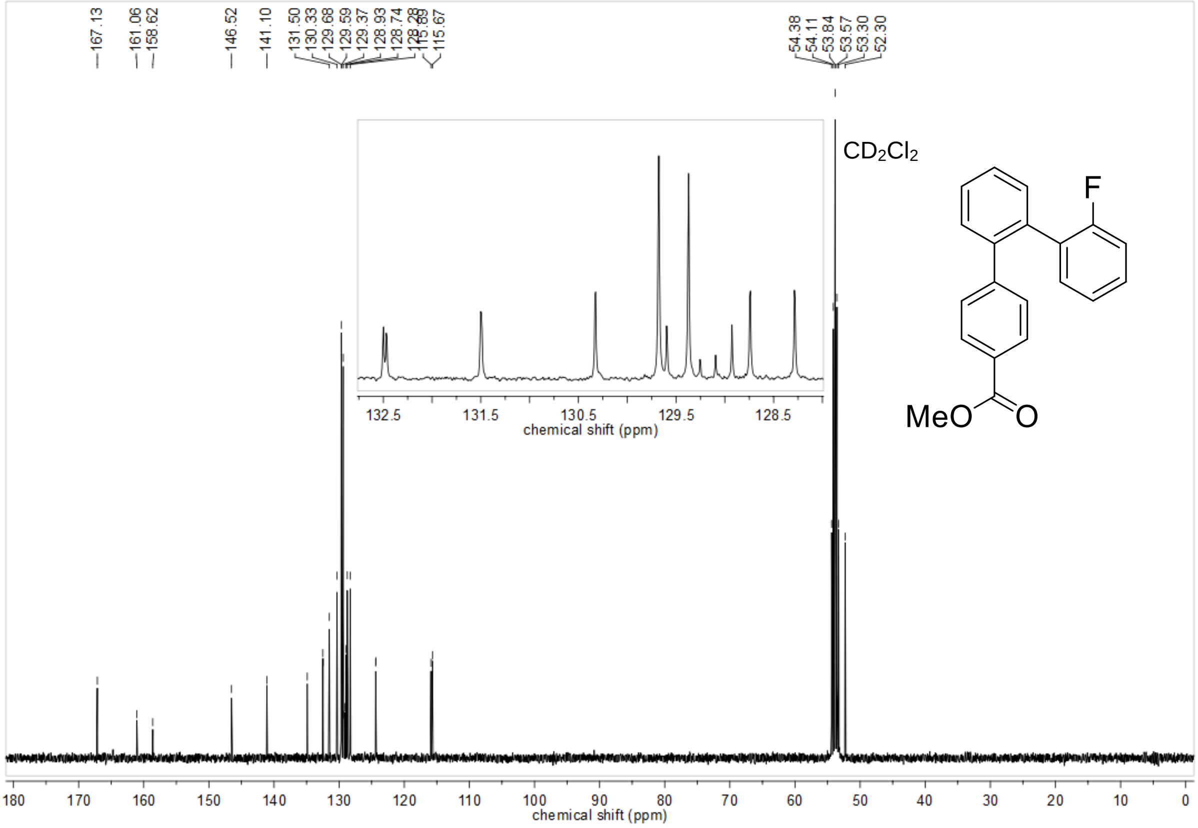


Figure S27: ^{13}C NMR spectrum of methyl 2"-fluoro-[1,1':2',1"-terphenyl]-4-carboxylate (**P4**) (in CD_2Cl_2).

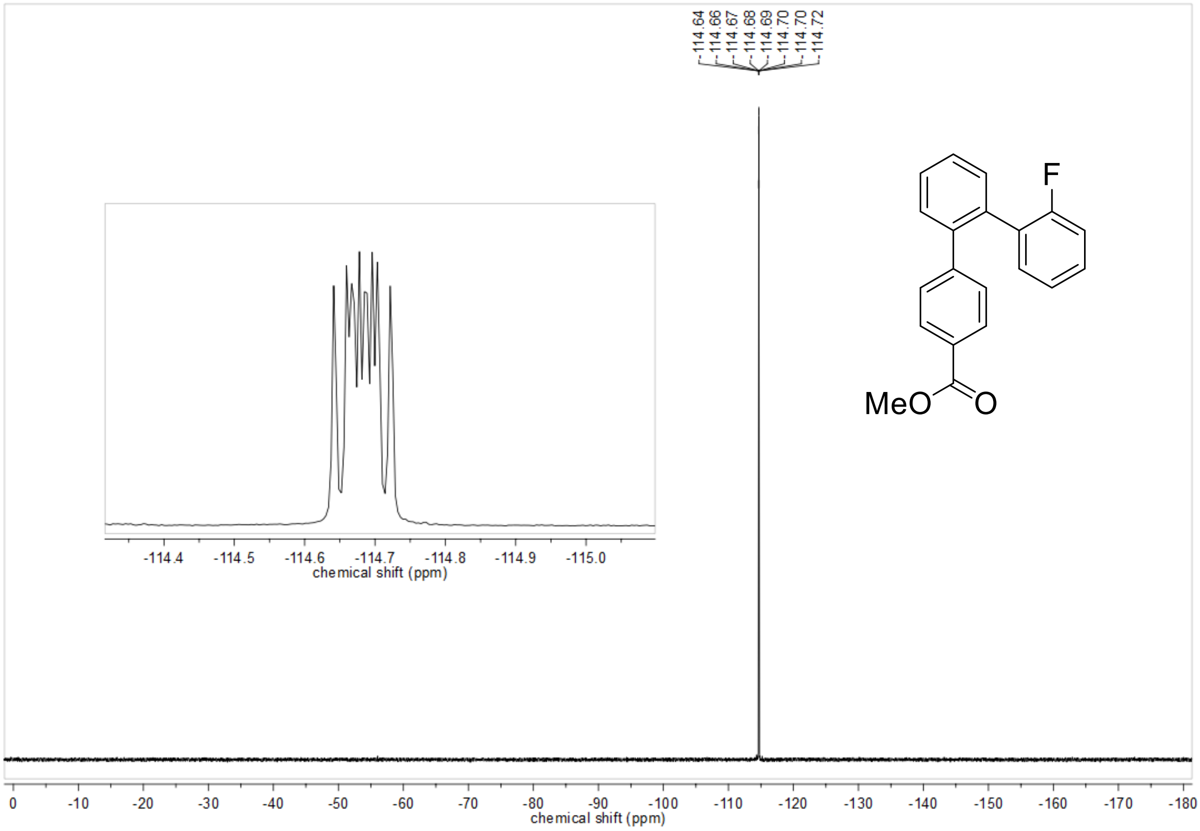


Figure S28: ^{19}F NMR spectrum of methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (**P4**) (in CD_2Cl_2).

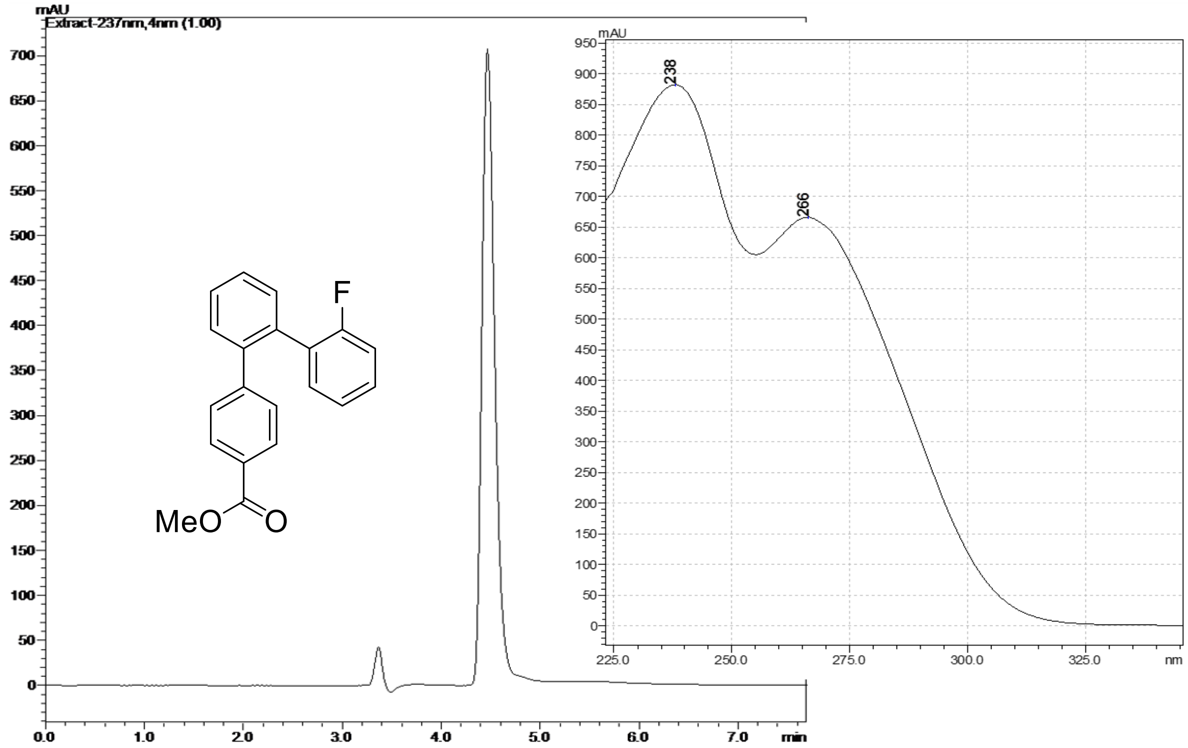
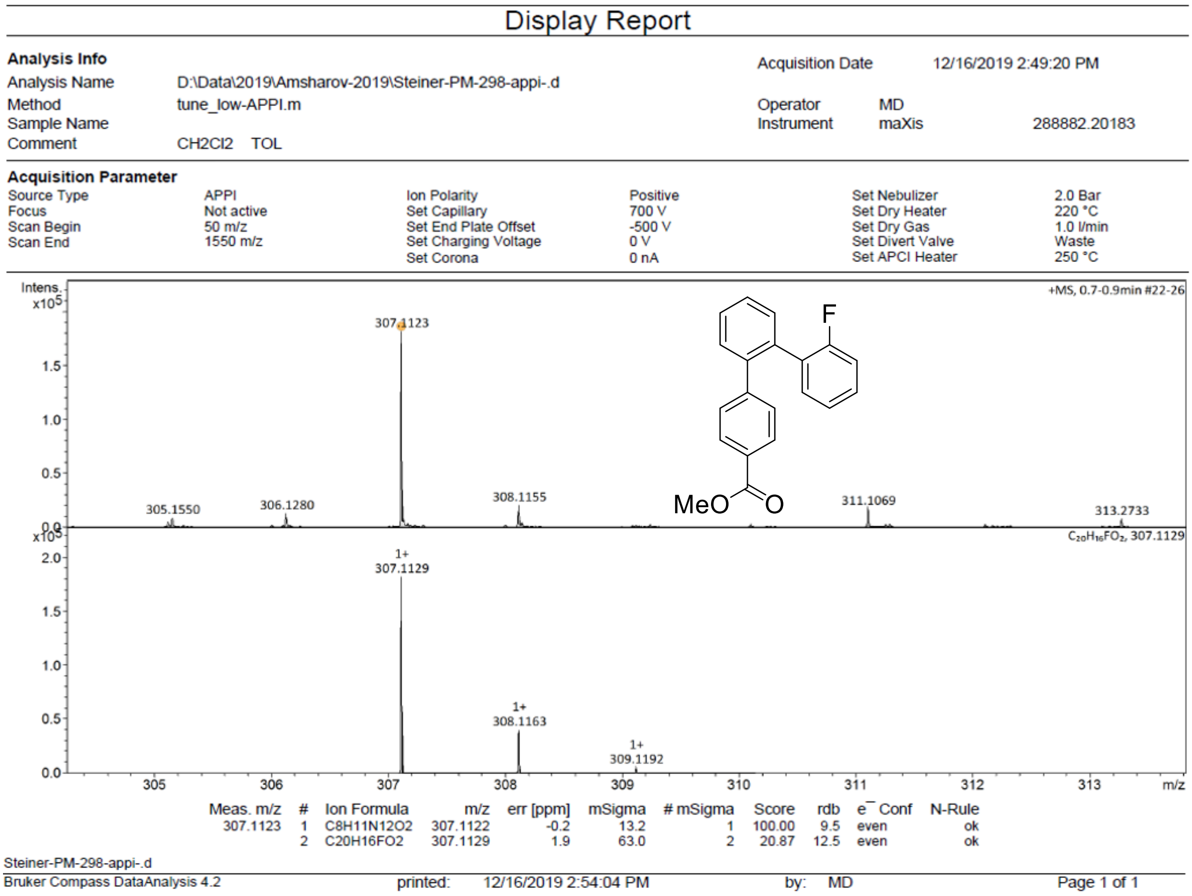


Figure S29: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 3:7), t_R = 4.46 min and UV/vis spectrum (inset) of methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (**P4**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-PM-298-appi-.d	Acquisition Date	12/16/2019 2:49:20 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2 TOL			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
307.1123	1	C8H11N12O2	307.1122	-0.2	13.2	1	100.00	9.5	even	ok
	2	C20H16FO2	307.1129	1.9	63.0	2	20.87	12.5	even	ok

Steiner-PM-298-appi-.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 2:54:04 PM by: MD Page 1 of 1

Figure S30: HR MS (APPI) spectrum of 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (**P4**), *m/z* 307.1123 (M^+, 100 %).

2''-Fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (P5)

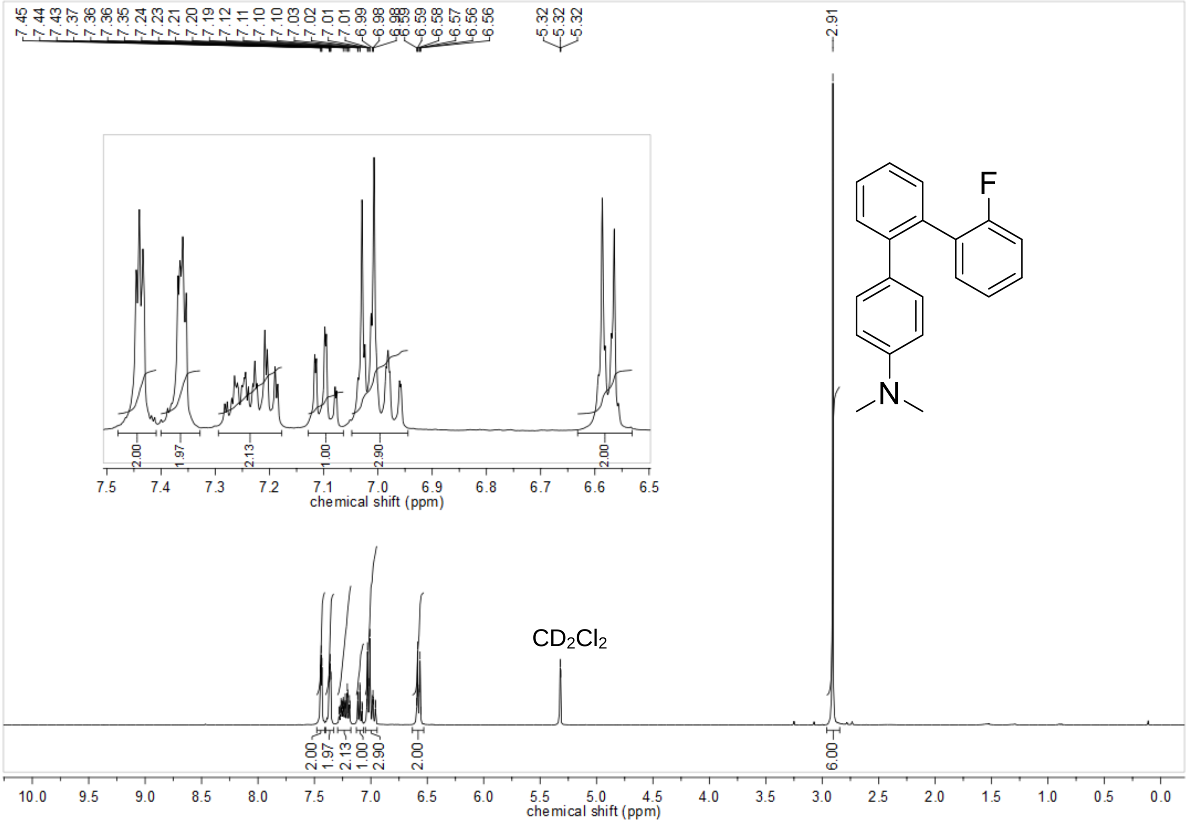


Figure S31: ^{1}H NMR spectrum of 2''-fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (**P5**) (in CD_2Cl_2).

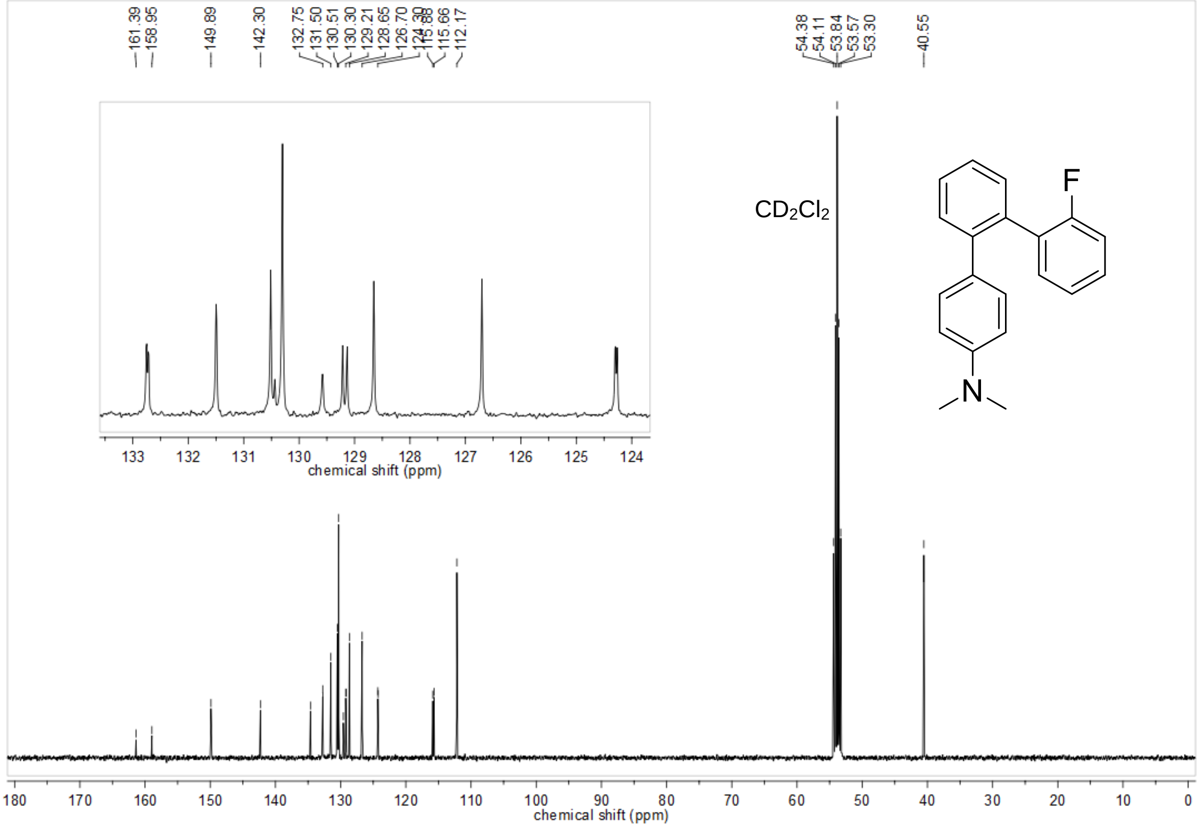


Figure S32: ^{13}C NMR spectrum of 2''-fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (**P5**) (in CD_2Cl_2).

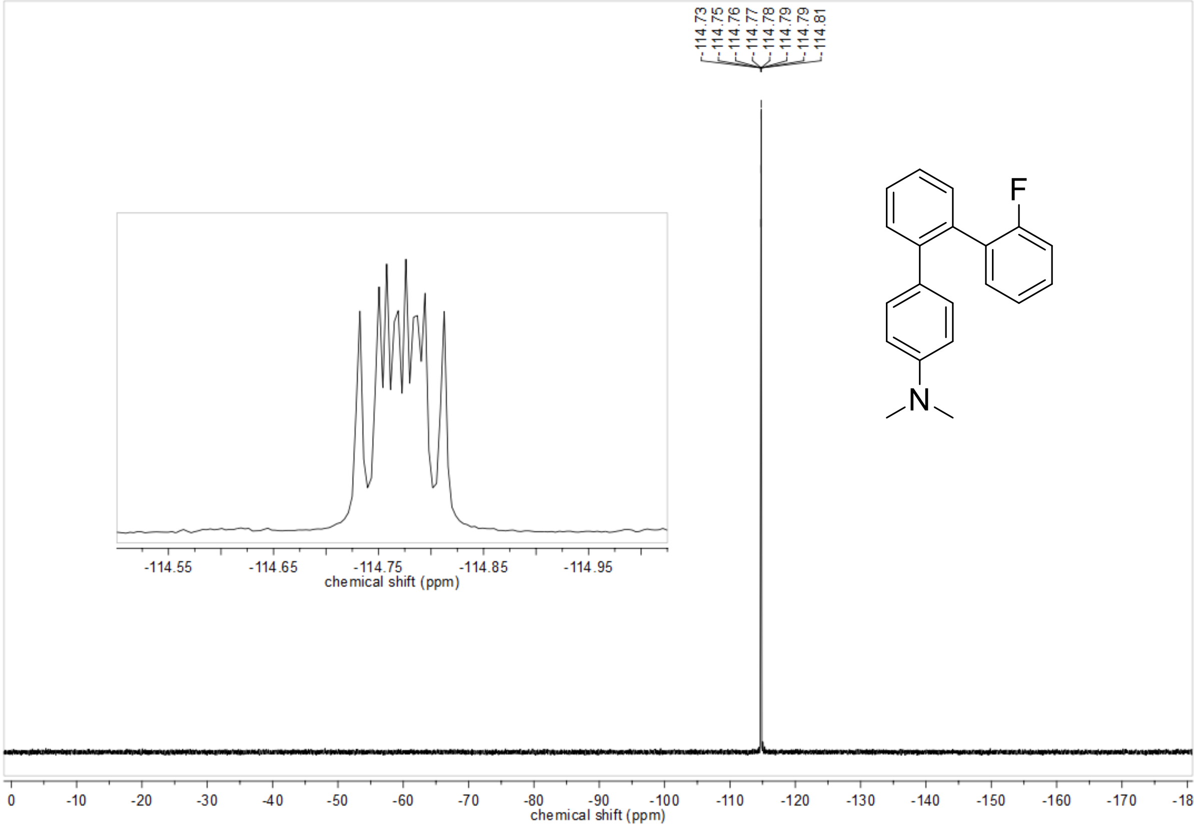


Figure S33: ^{19}F NMR spectrum of 2''-fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (**P5**) (in CD_2Cl_2).

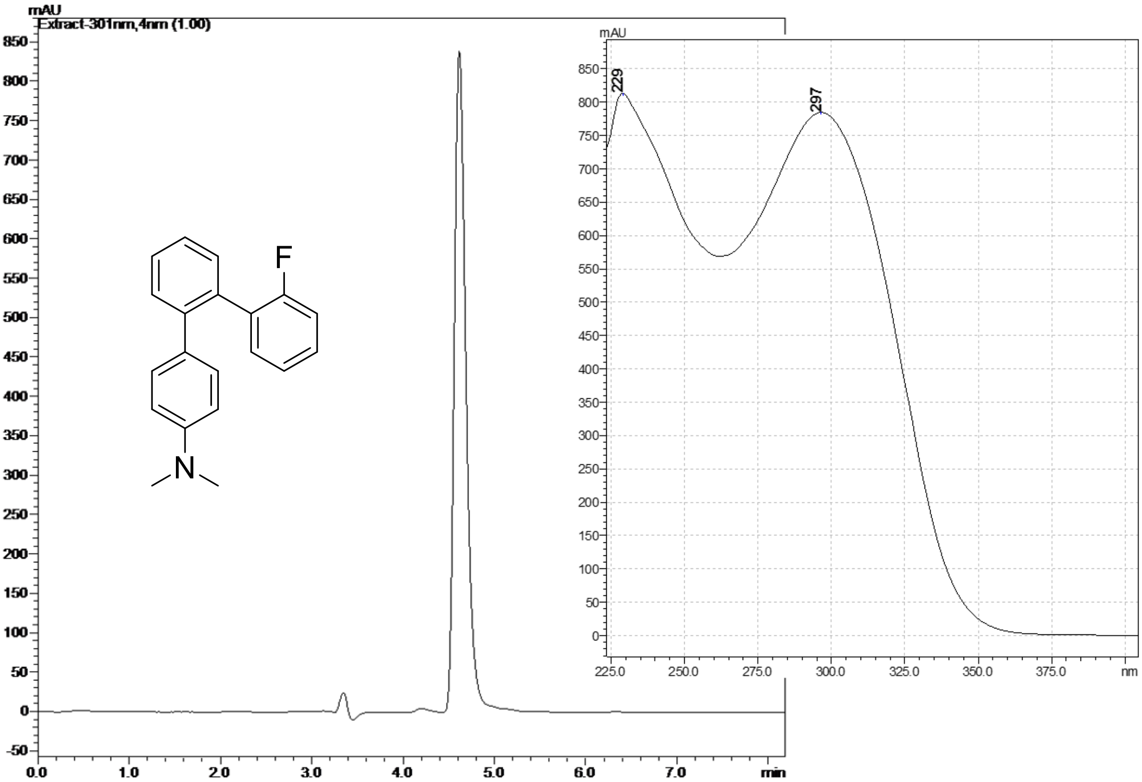
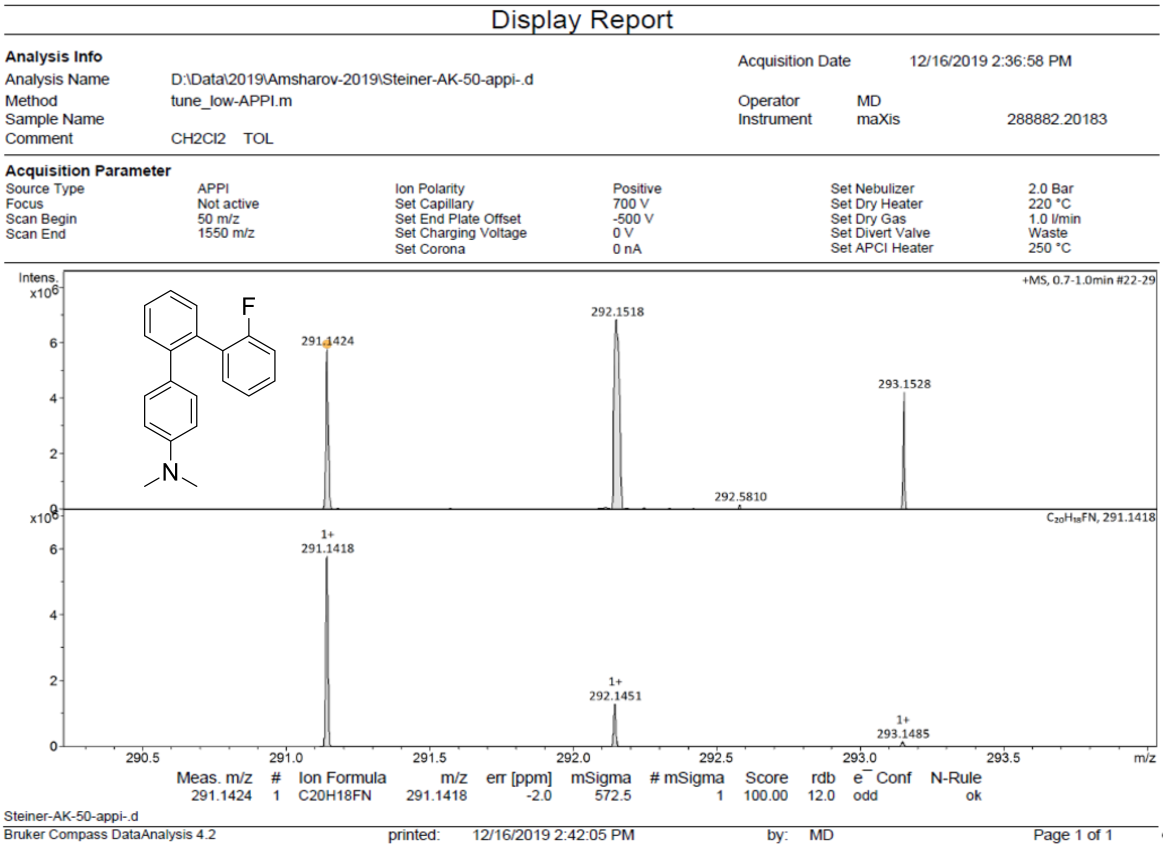


Figure S34: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 3:7), t_R = 4.61 min and UV/vis spectrum (inset) of 2''-fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (**P5**).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-AK-50-appi-.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2 TOL

Acquisition Date 12/16/2019 2:36:58 PM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
291.1424	1	C20H18FN	291.1418	-2.0	572.5	1	100.00	12.0	odd	ok

Steiner-AK-50-appi-.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 2:42:05 PM by: MD Page 1 of 1

Figure S35: HR MS (APPI) spectrum of 2''-fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (**P5**), *m/z* 291.1424 (M^+, 100 %).

4-(2'-Fluoro-[1,1'-biphenyl]-2-yl)pyridine (P6)

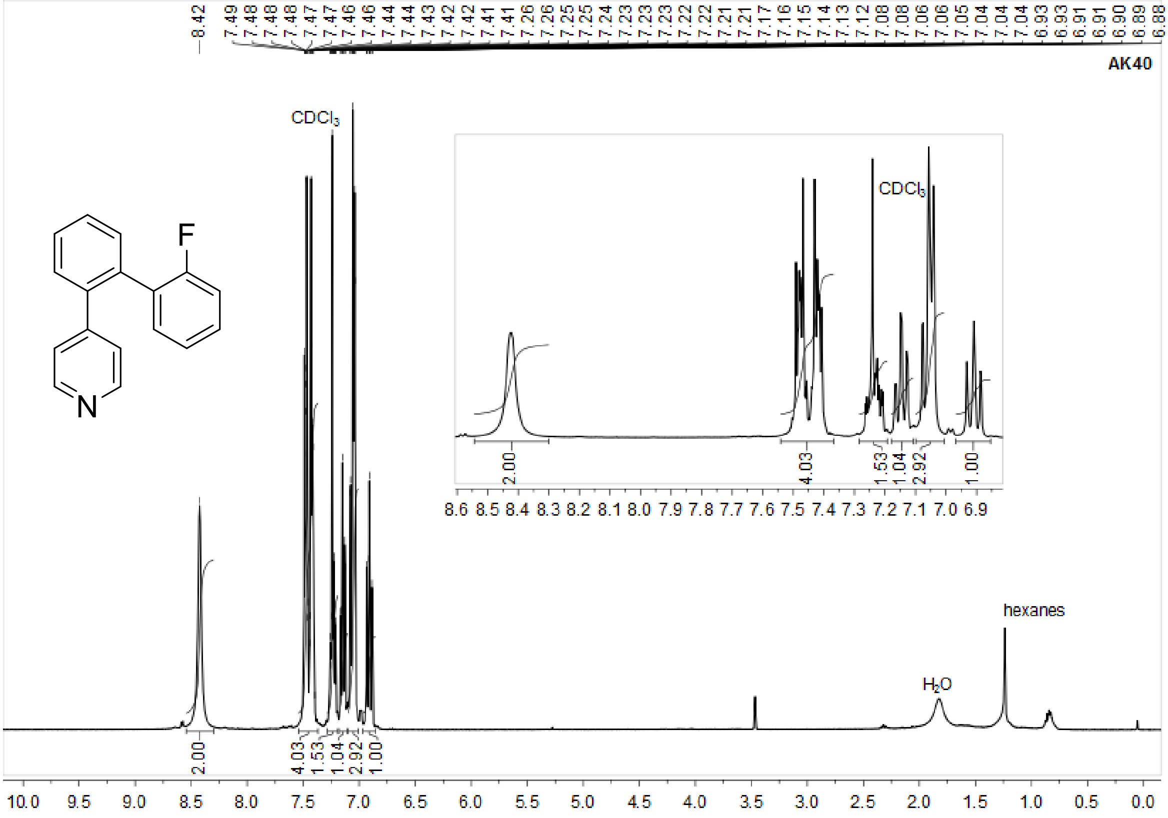


Figure S36: ^{1}H NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)pyridine (**P6**) (in $CDCl_3$).

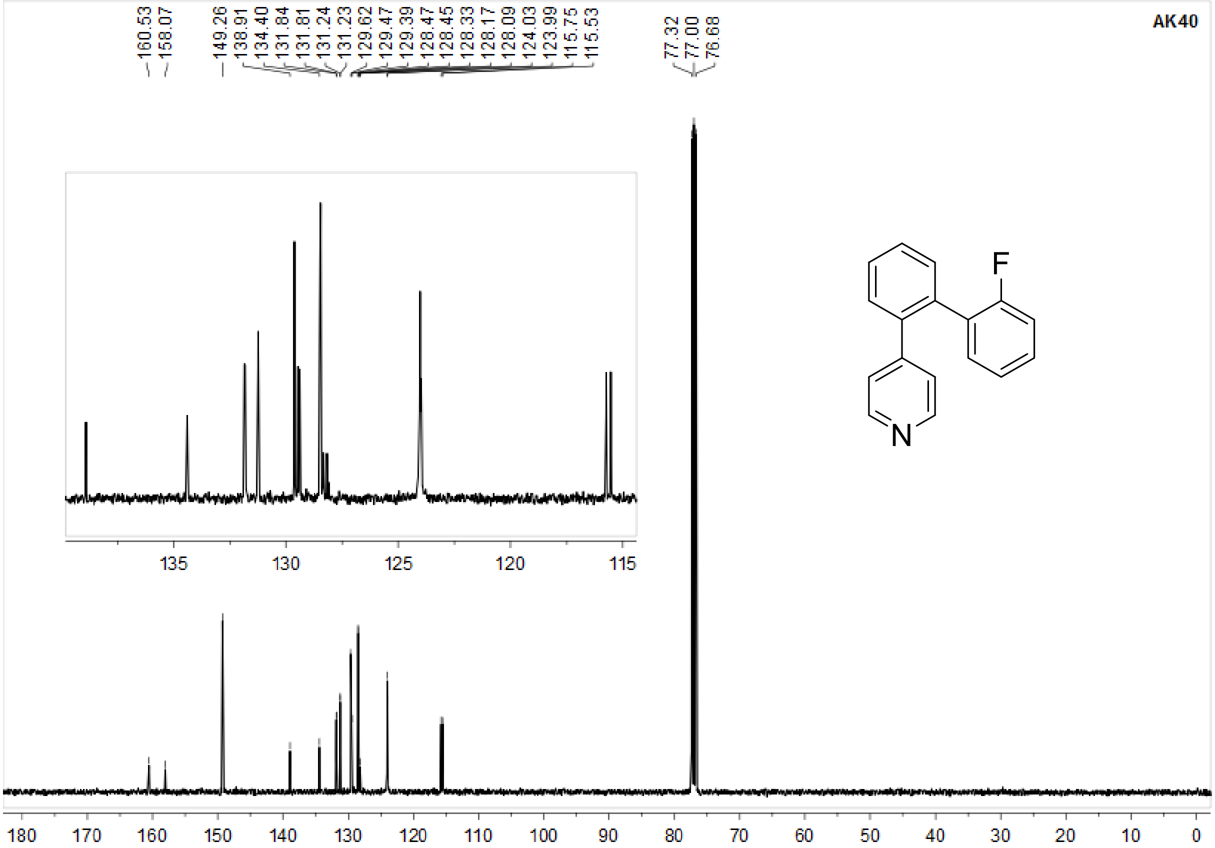


Figure S37: ^{13}C NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)pyridine (**P6**) (in CDCl$_3$).

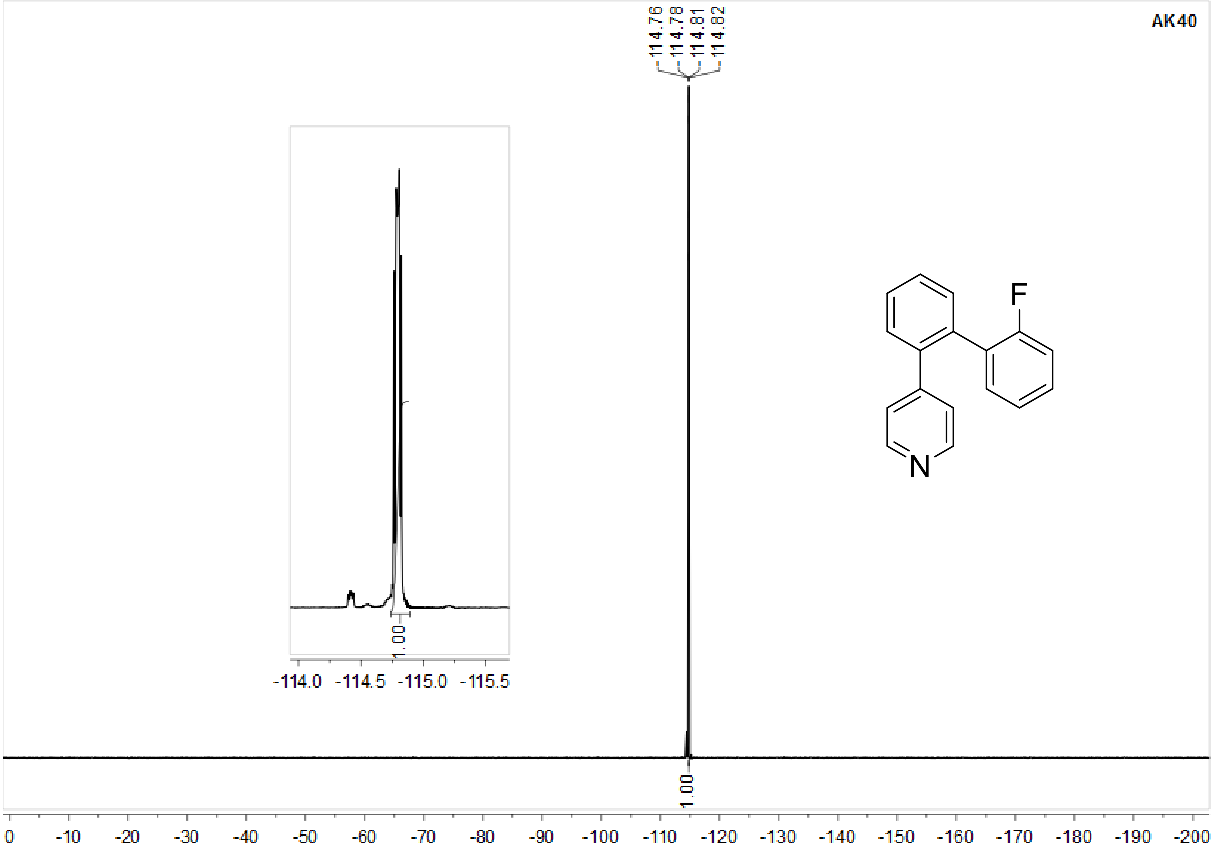


Figure S38: ^{19}F NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)pyridine (**P6**) (in CDCl$_3$).

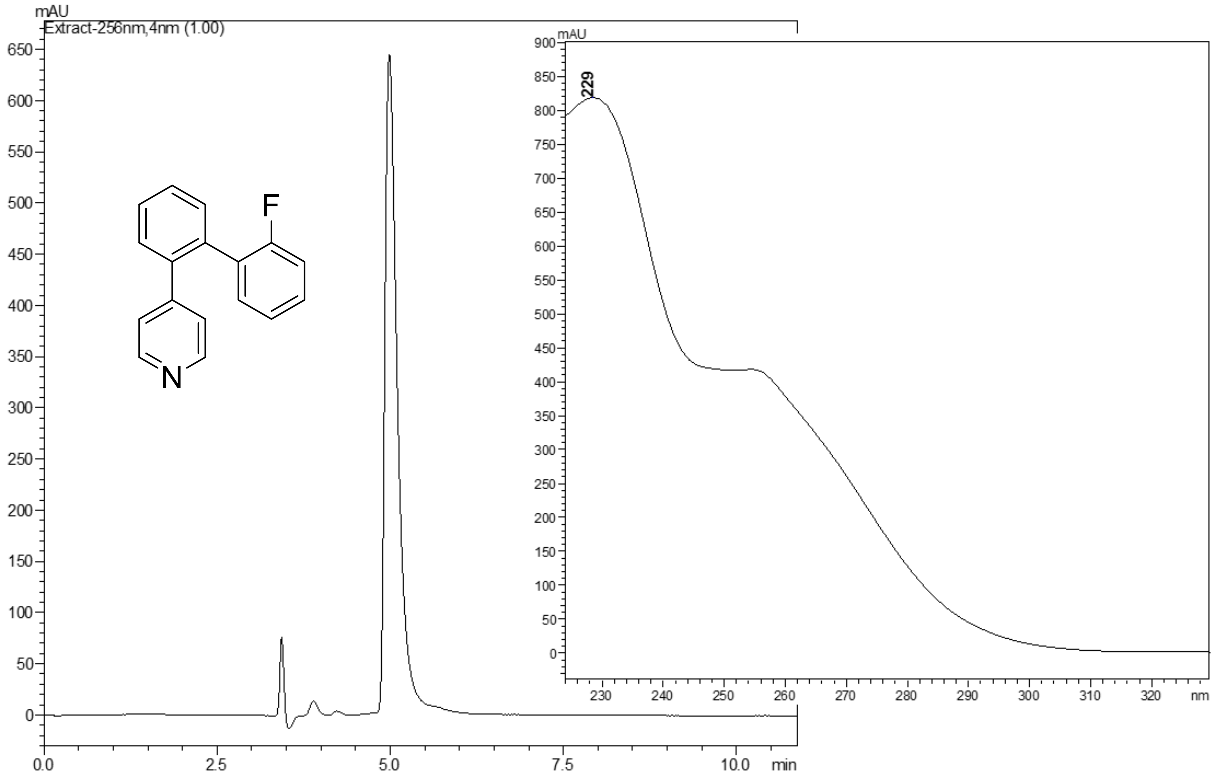
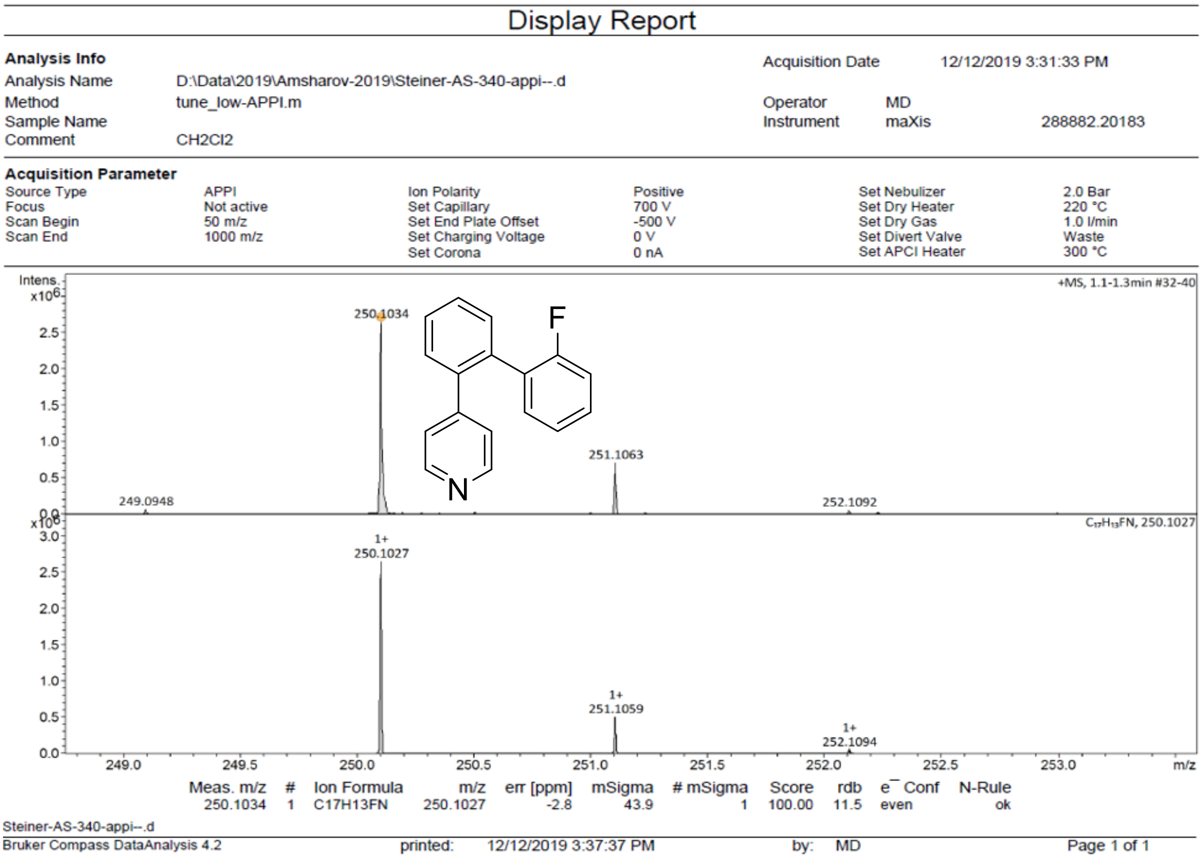


Figure S39: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9, t_R 4.98 min) and UV/vis spectrum (inset) of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)pyridine (**P6**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-340-appi--.d	Acquisition Date	12/12/2019 3:31:33 PM
Method	tune_low-APPI.m	Operator	MD
Sample Name		Instrument	maXis 288882.20183
Comment	CH2Cl2		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	300 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
250.1034	1	C17H13FN	250.1027	-2.8	43.9	1	100.00	11.5	even	ok

Steiner-AS-340-appi--.d

Bruker Compass DataAnalysis 4.2 printed: 12/12/2019 3:37:37 PM by: MD Page 1 of 1

Figure S40: HR MS (APPI) spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)pyridine (**P6**), *m/z* 250.1034 (M^+, 100 %).

4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (P7).

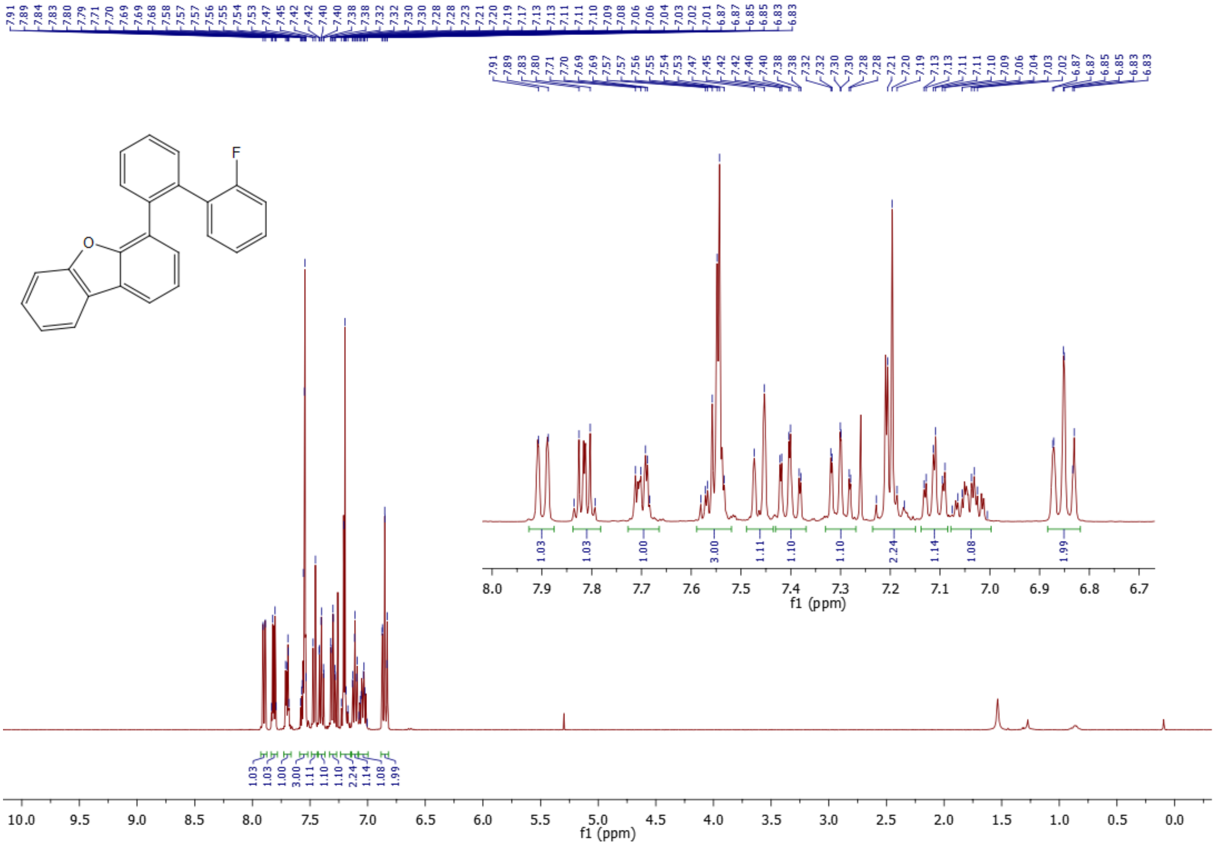


Figure S41: ^{1}H NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (**P7**) (in $CDCl_3$).

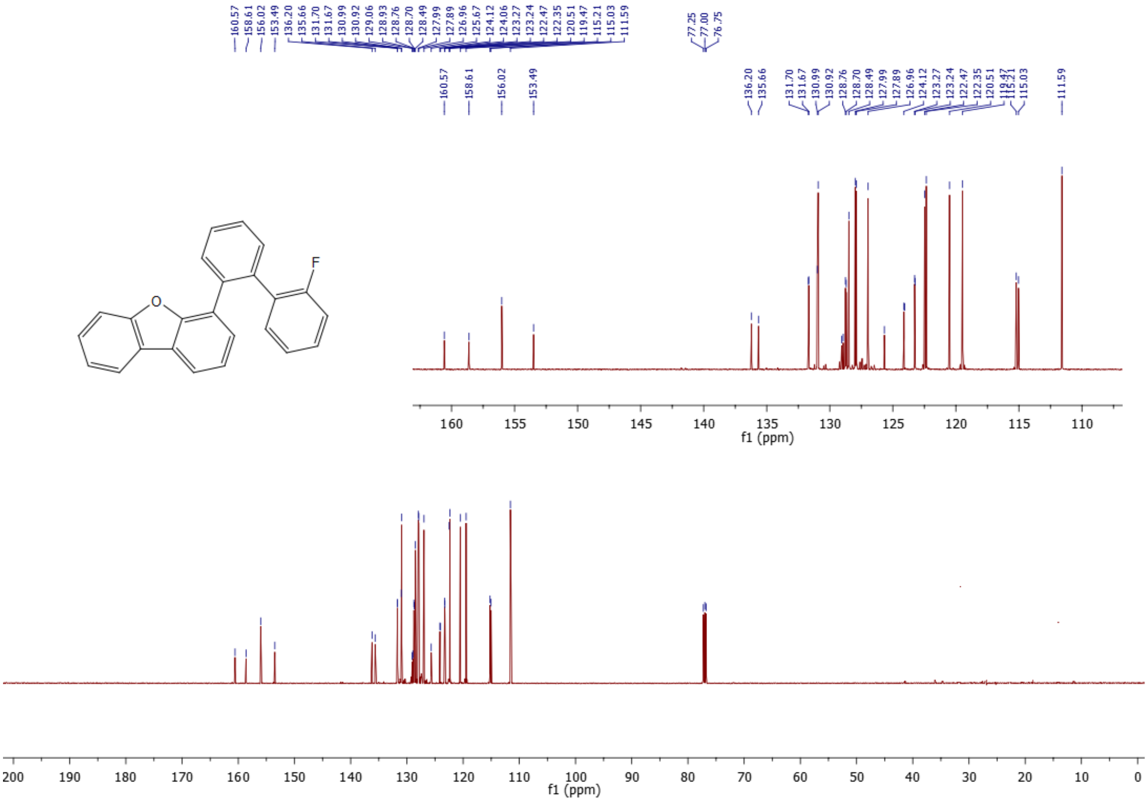


Figure S42: ^{13}C NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (**P7**) (in CD_2Cl_2).

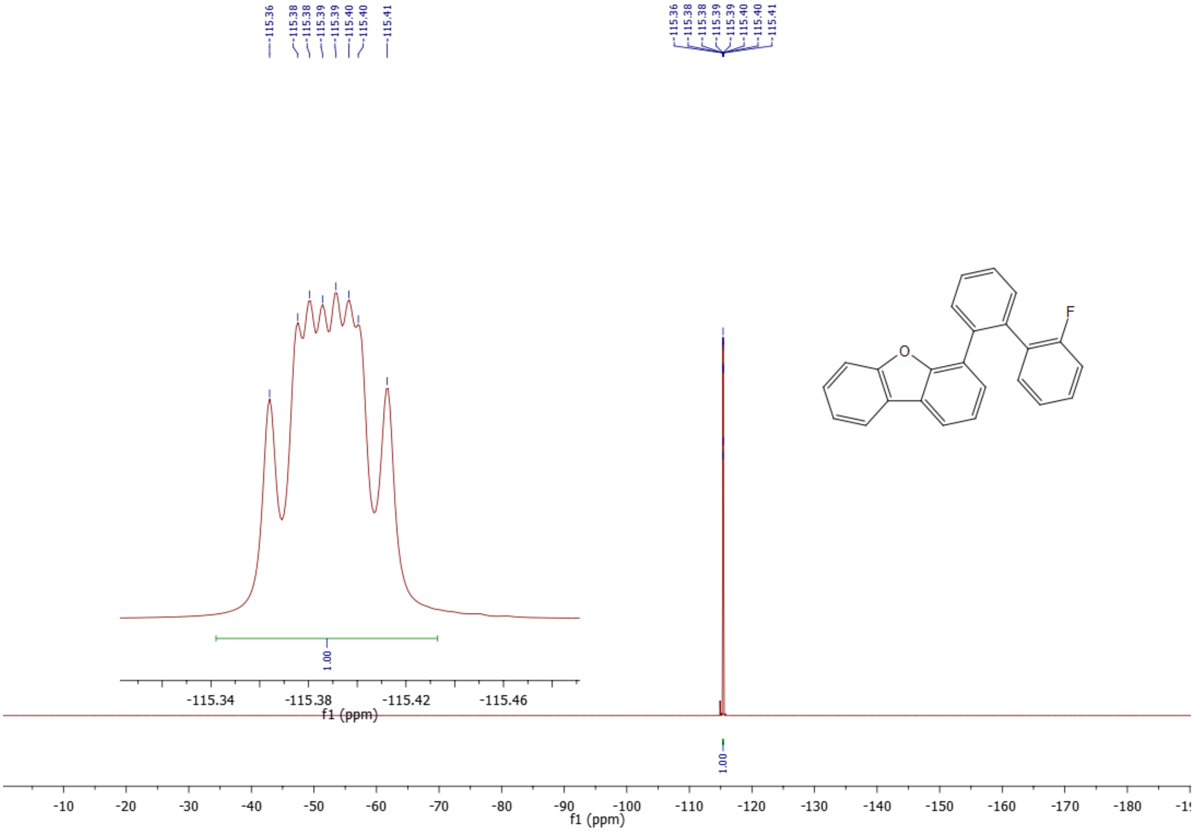


Figure S43: ^{19}F NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (**P7**) (in CD_2Cl_2).

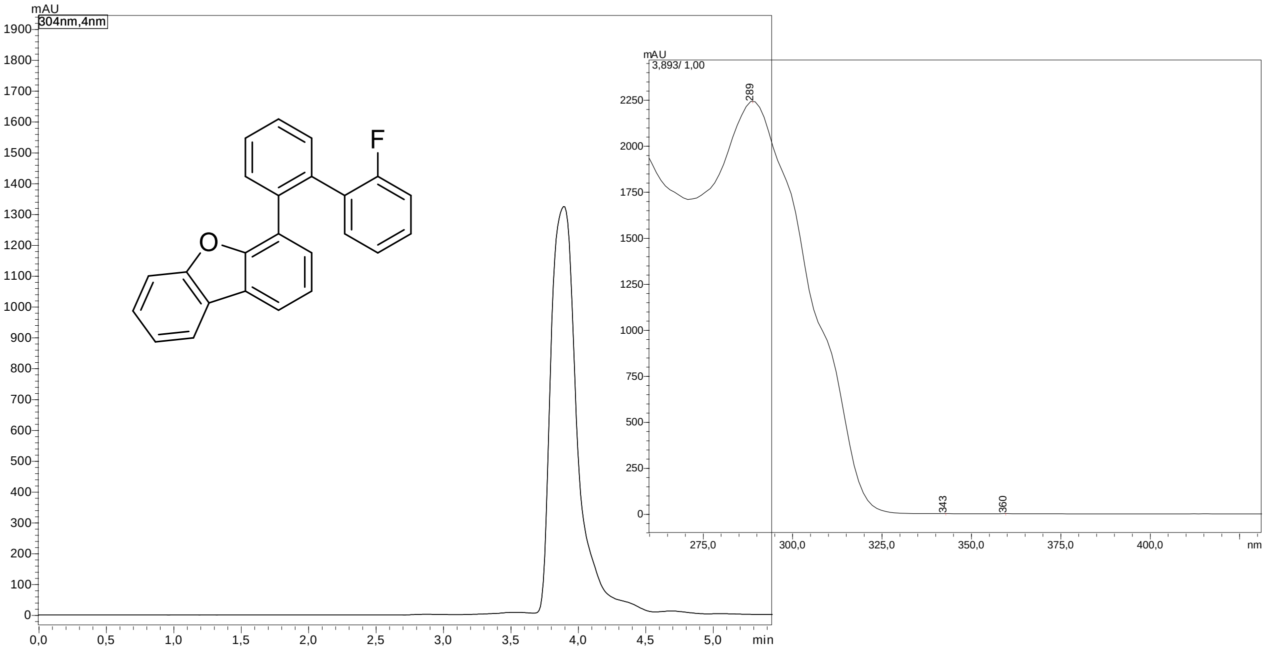


Figure S44: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 40°C, DCM/MeOH 4:6, t_R 3.95min) and UV/vis spectrum (inset) of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]furan (**P7**).

4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (P8).

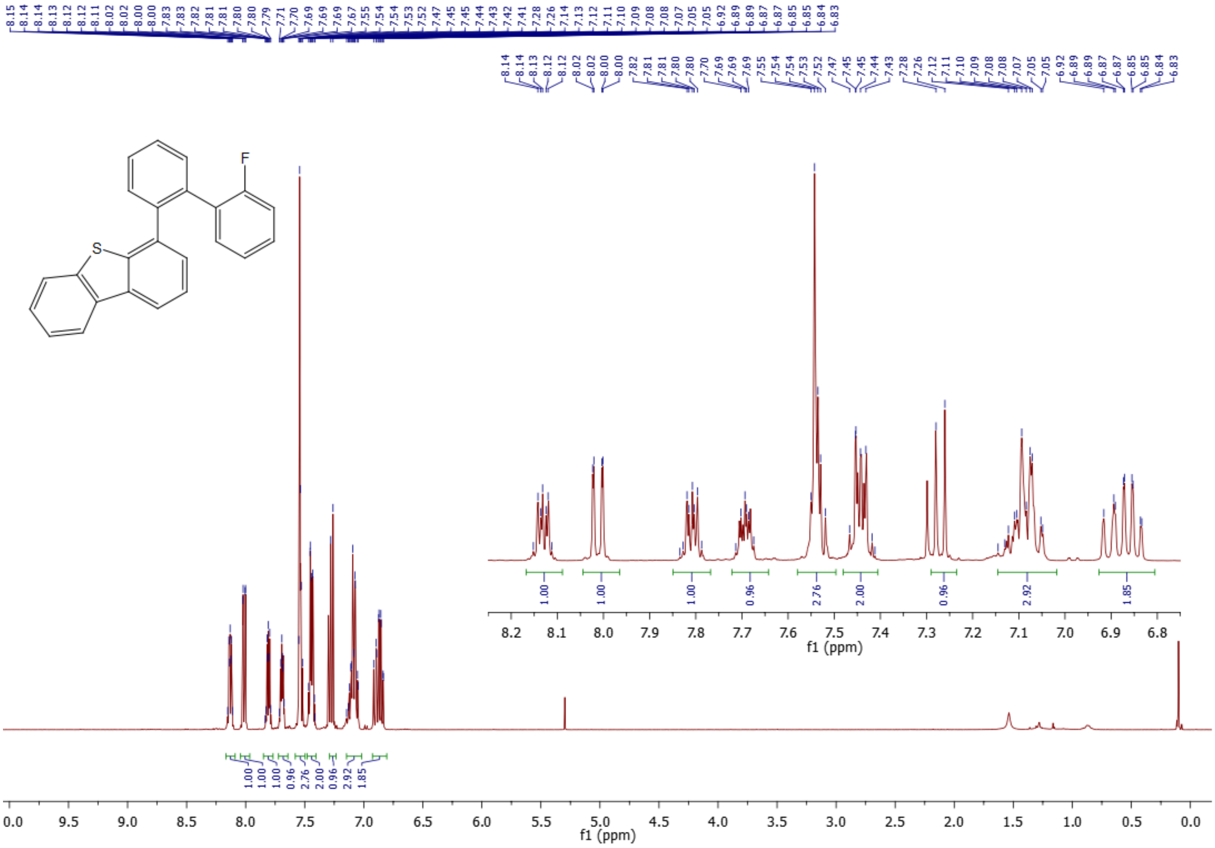


Figure S45: ^{1}H NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (**P8**) (in $CDCl_3$).

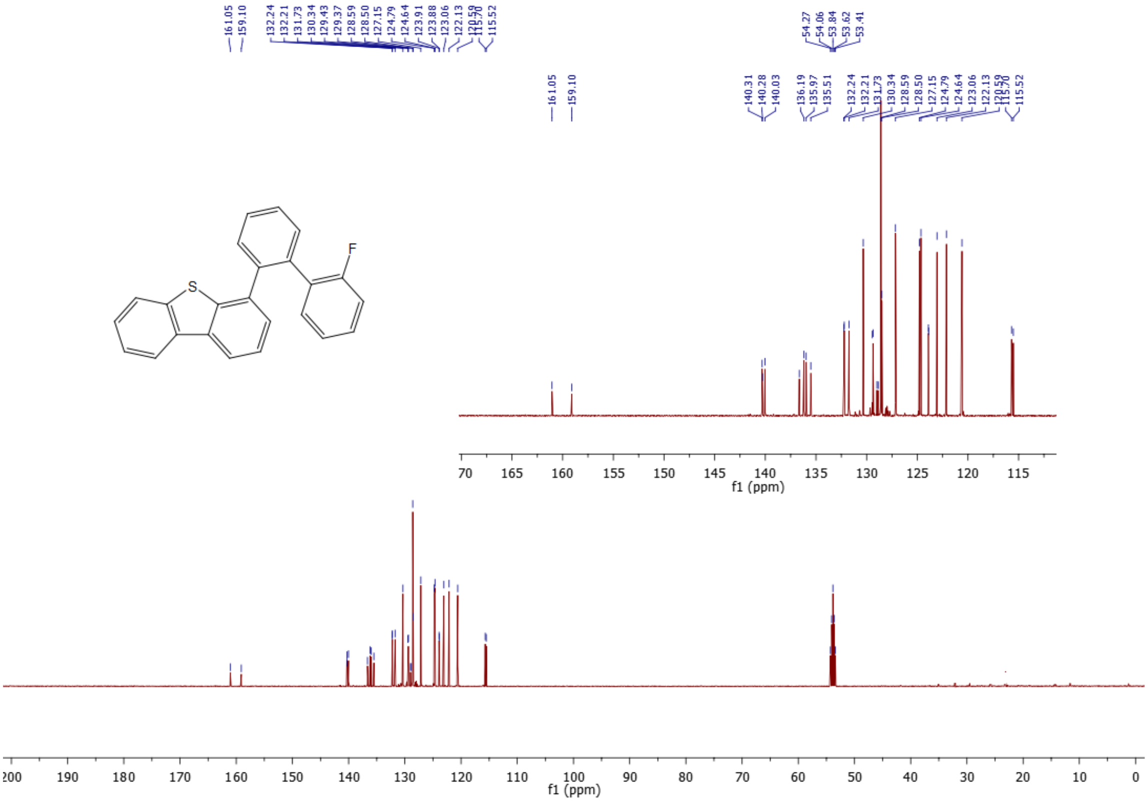


Figure S46: ^{13}C NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (**P8**) (in CD_2Cl_2).

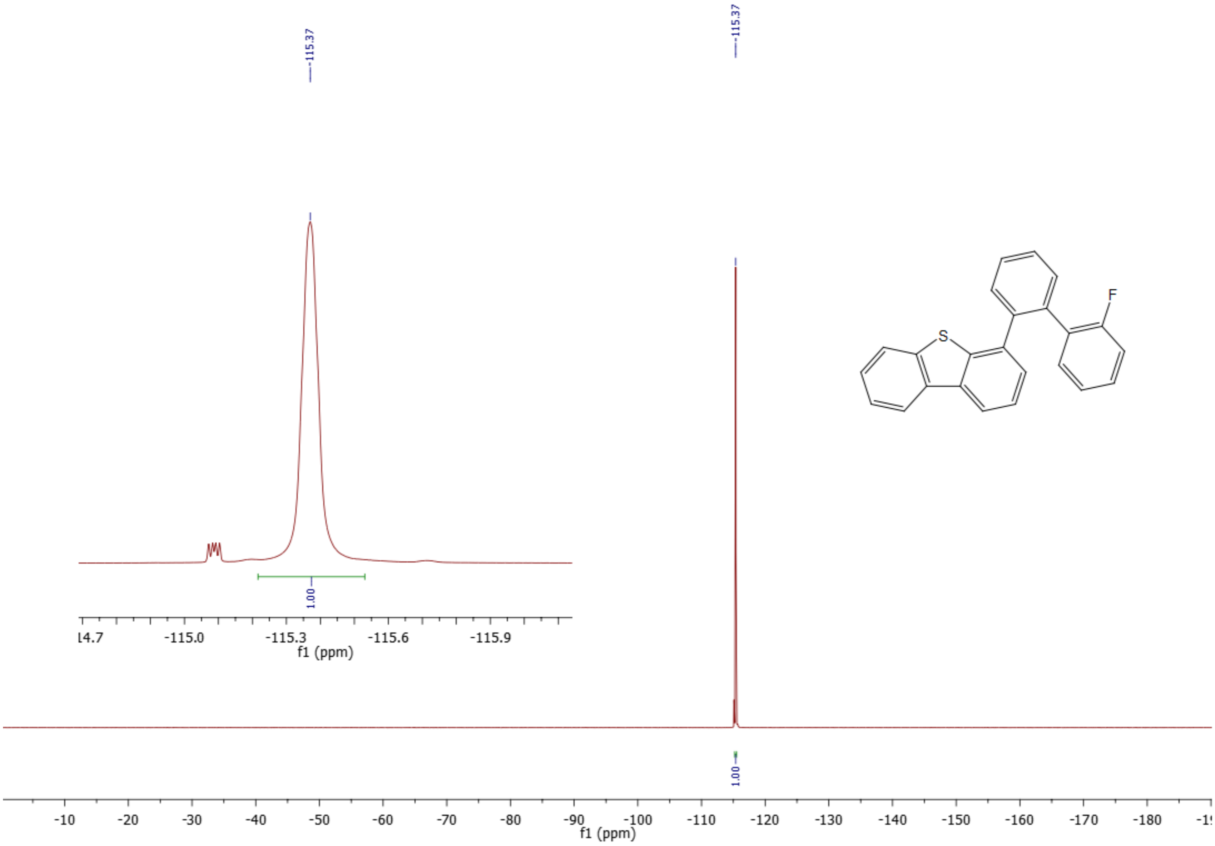


Figure S47: ^{19}F NMR spectrum of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (**P8**) (in CD_2Cl_2).

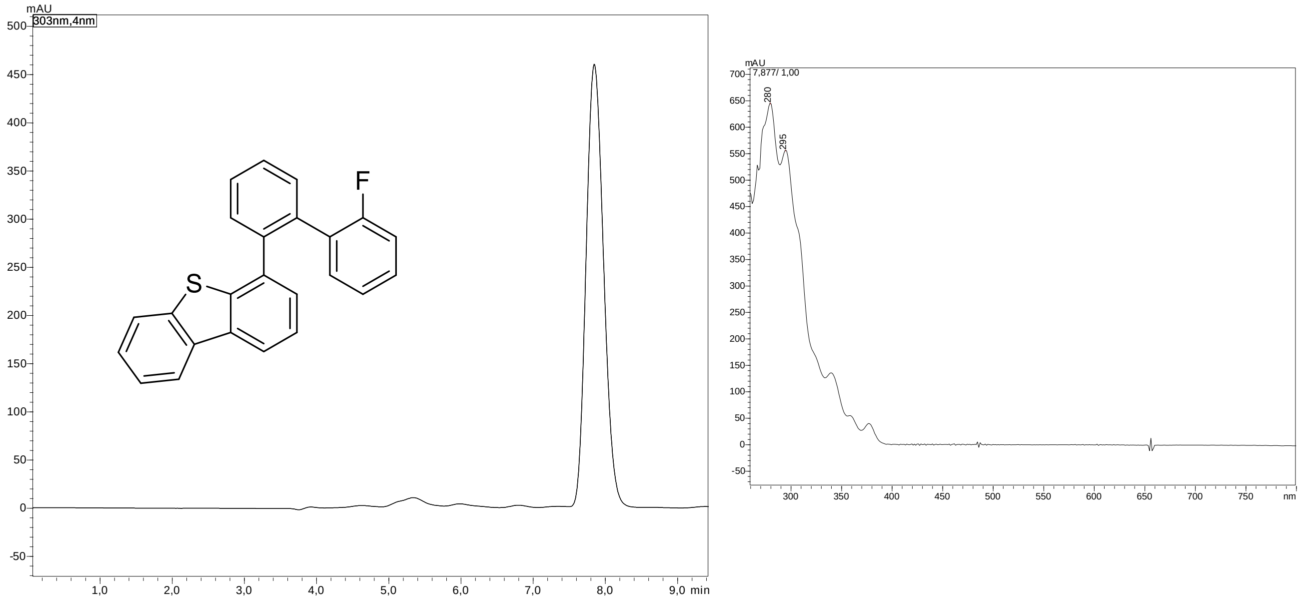


Figure S48: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 40°C, DCM/MeOH 4:6, t_R 7.86 min) and UV/vis spectrum (inset) of 4-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[b,d]thiophene (**P8**).

2-(2'-Fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (P9)

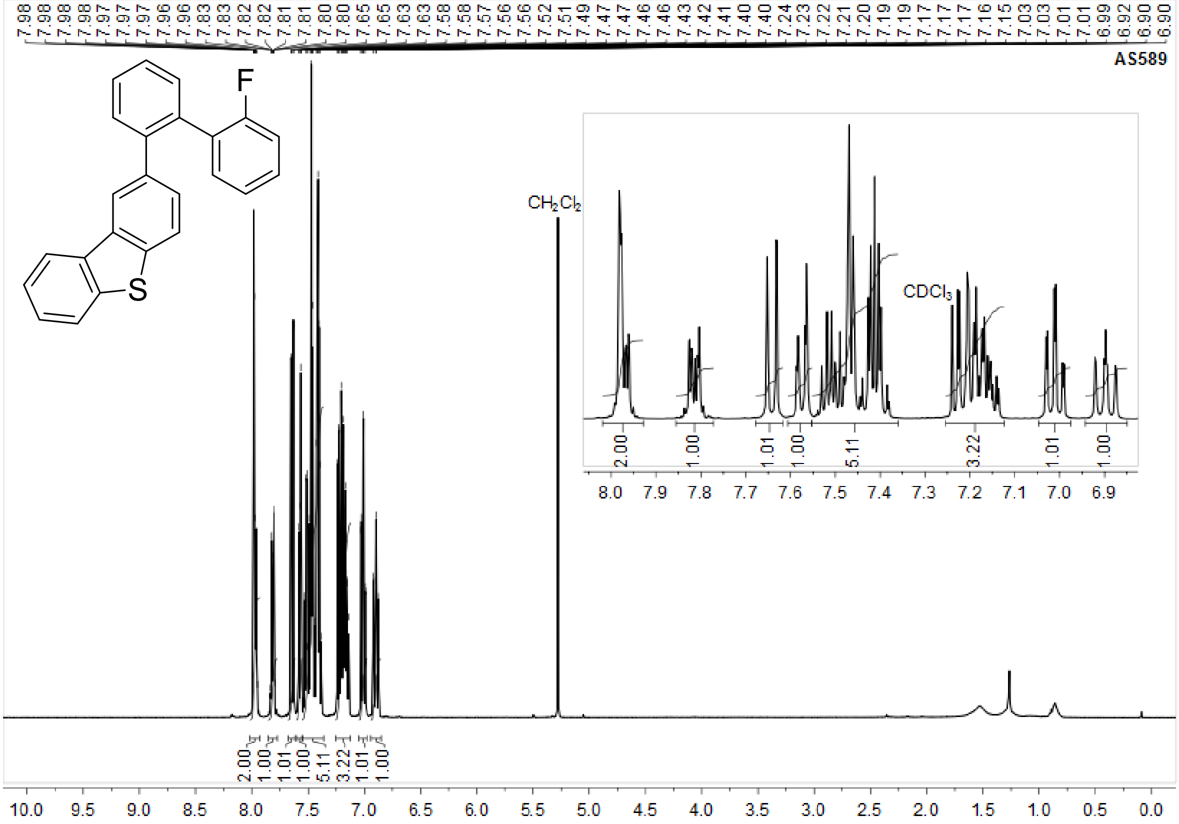


Figure S49: ^{1}H NMR spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (**P9**) (in CDCl$_3$).

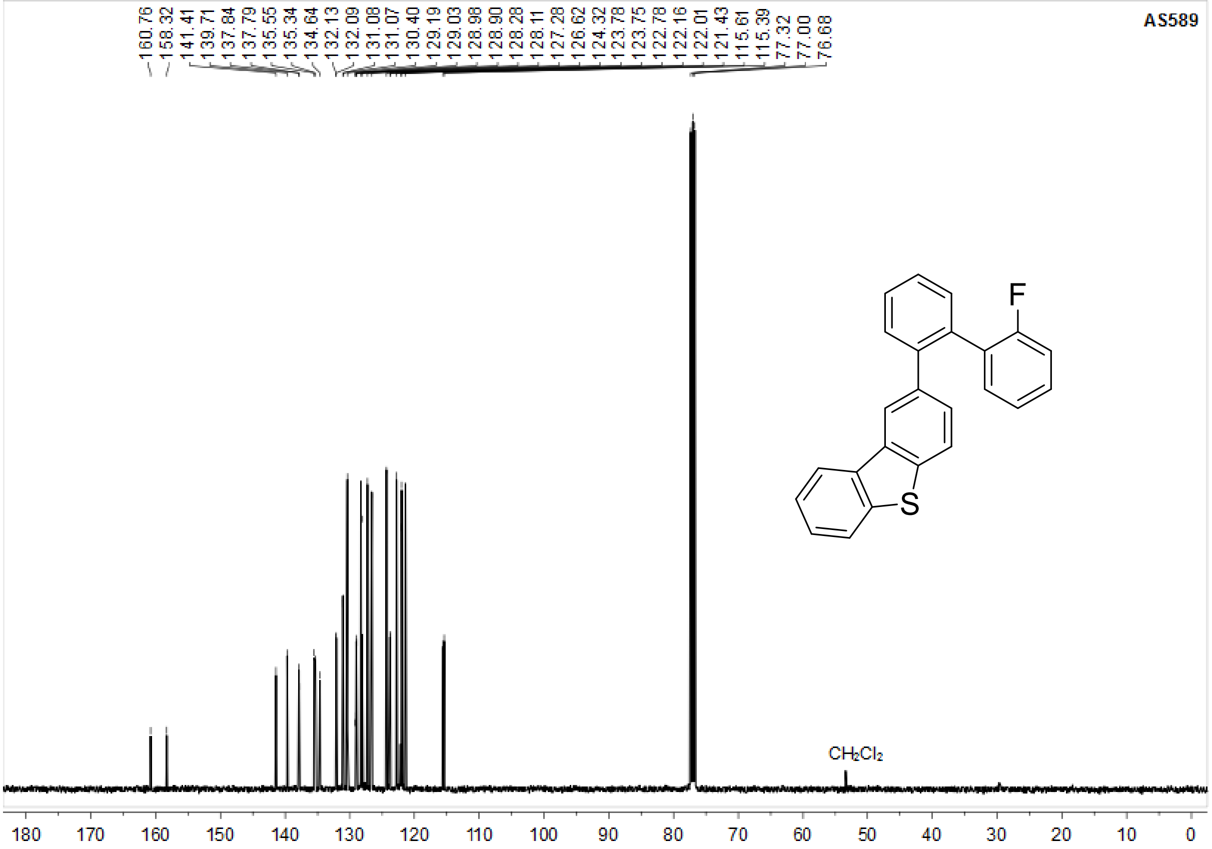


Figure S50: ^{13}C NMR spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (**P9**) (in CDCl$_3$).

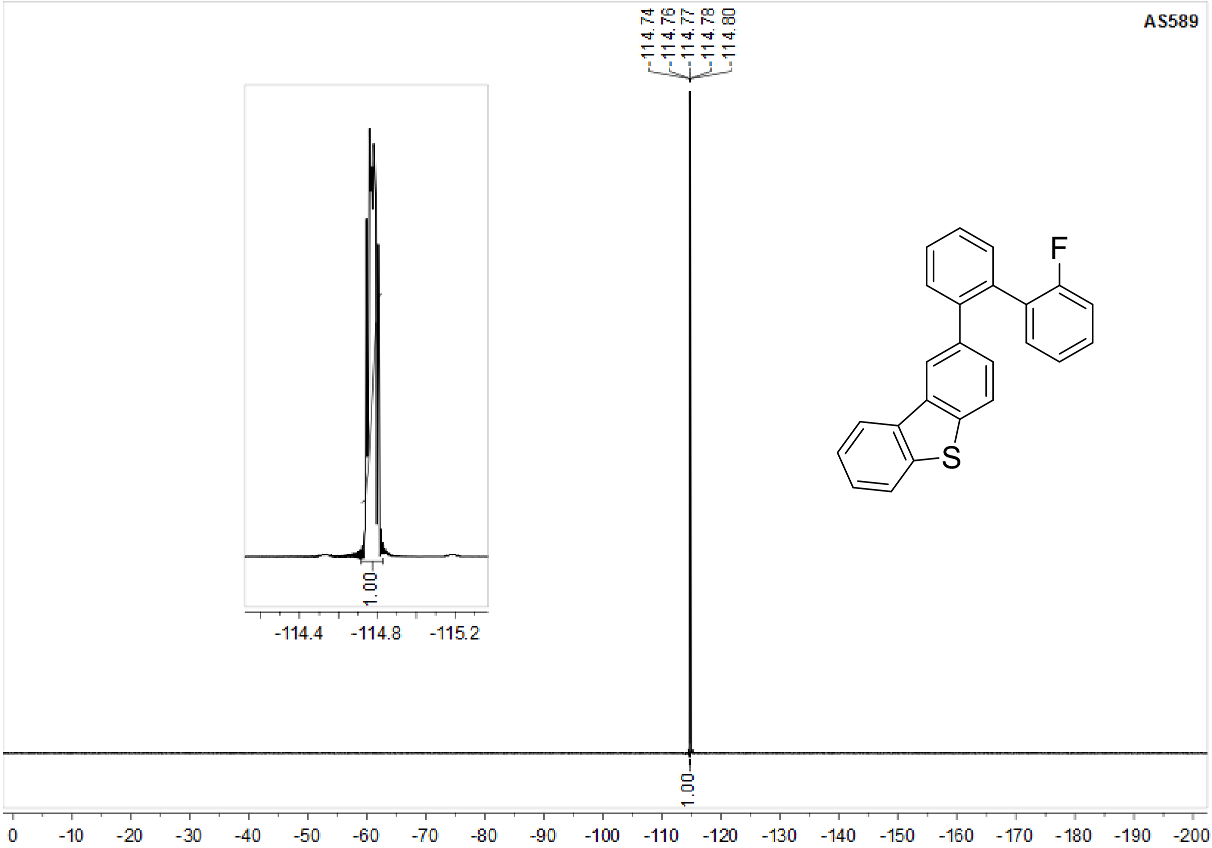


Figure S51: ^{19}F NMR spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (**P9**) (in $CDCl_3$).

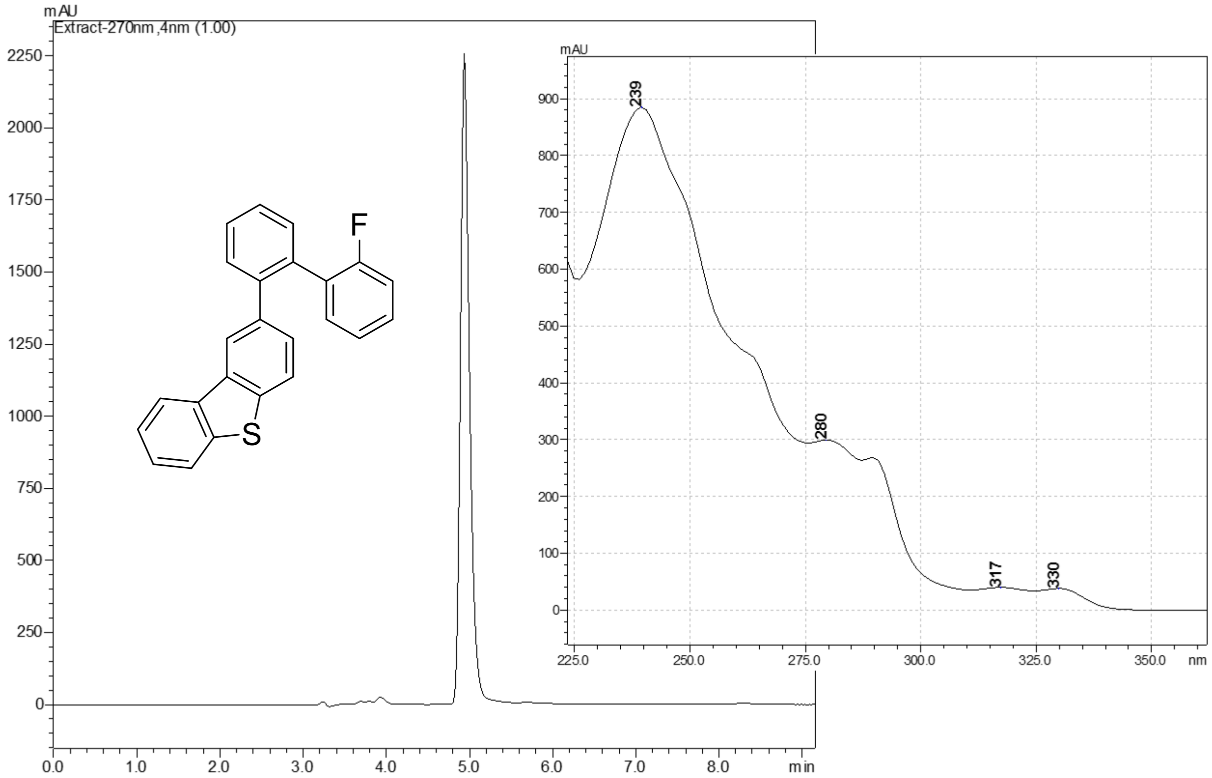
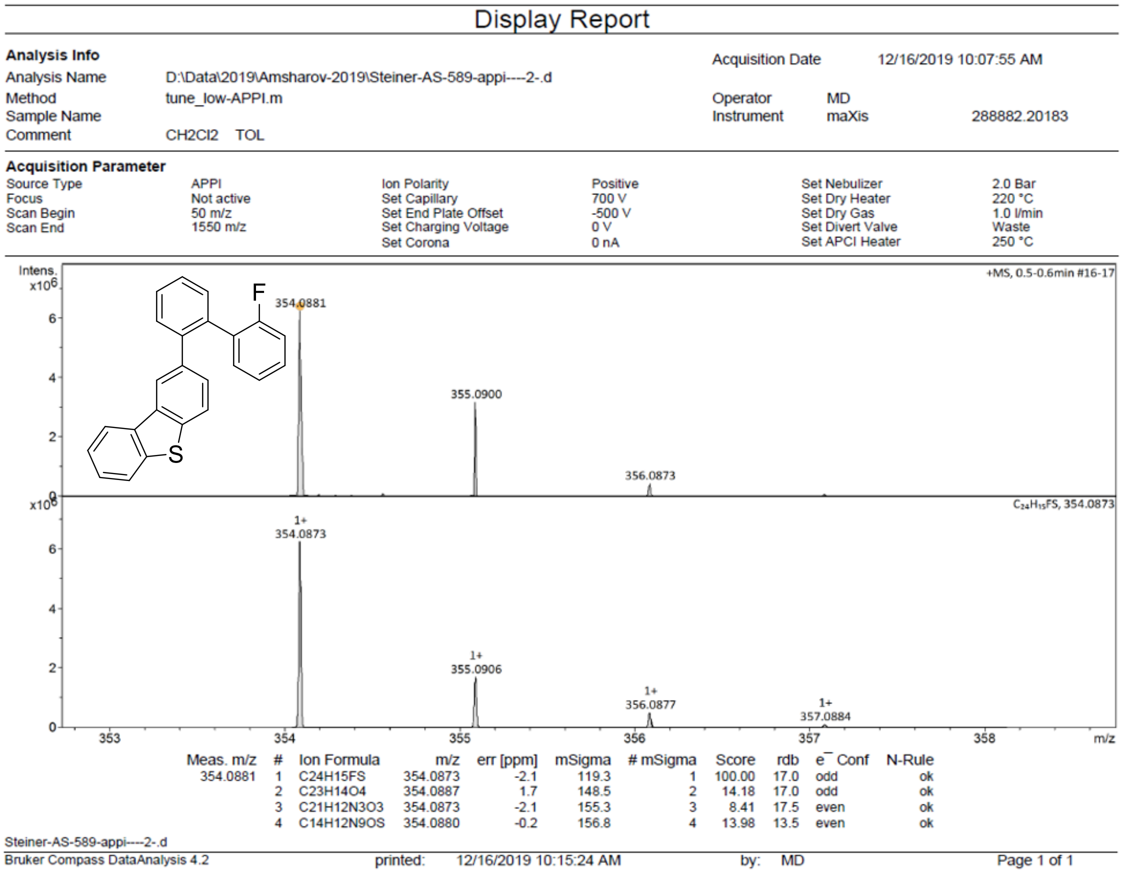


Figure S52: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:1), t_R = 4.93 min and UV/vis spectrum (inset) of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (**P9**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-589-appi----2-.d	Acquisition Date	12/16/2019 10:07:55 AM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2 TOL			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
354.0881	1	C24H15FS	354.0873	-2.1	119.3	1	100.00	17.0	odd	ok
	2	C23H14O4	354.0887	1.7	148.5	2	14.18	17.0	odd	ok
	3	C21H12N3O3	354.0873	-2.1	155.3	3	8.41	17.5	even	ok
	4	C14H12N9OS	354.0880	-0.2	156.8	4	13.98	13.5	even	ok

Steiner-AS-589-appi----2-.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 10:15:24 AM by: MD Page 1 of 1

Figure S53: HR MS (APPI) spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)dibenzo[*b*,*d*]thiophene (**P9**),.*m/z* 354.0881 (M^+, 100 %).

4''-Chloro-2-fluoro-1,1':2',1''-terphenyl (P10)

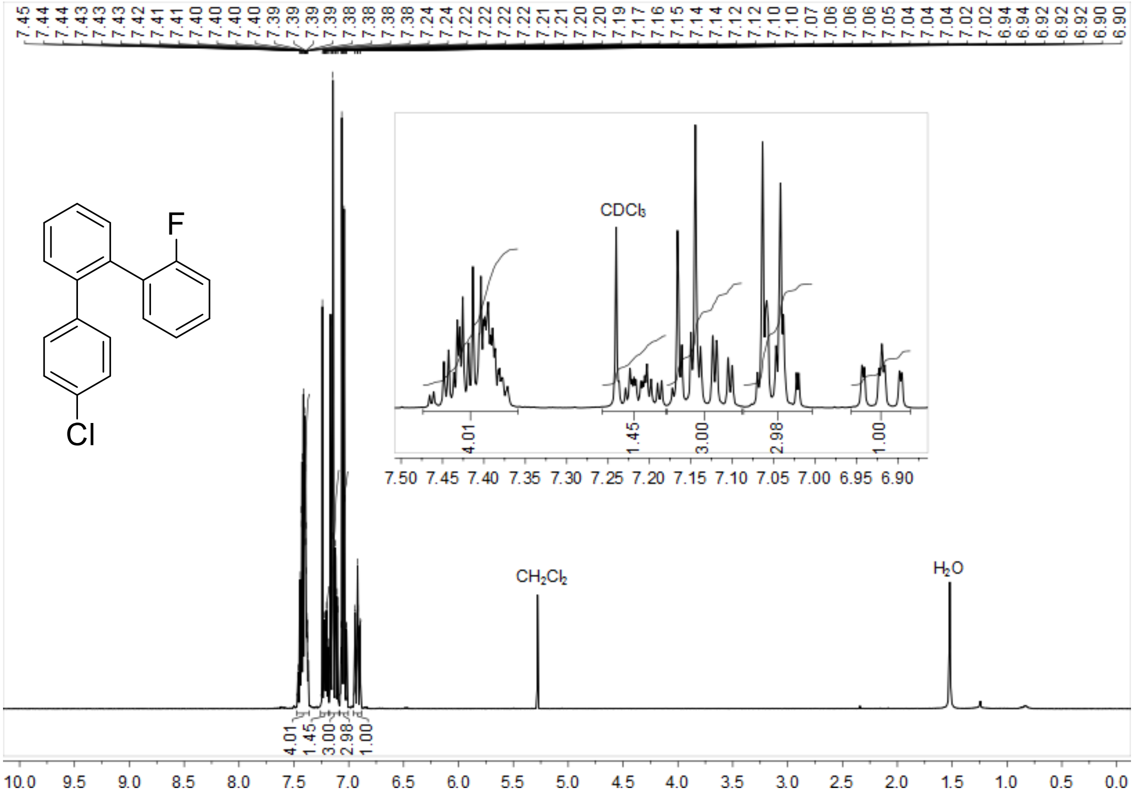


Figure S54: ^{1}H NMR spectrum of 4"-chloro-2-fluoro-1,1':2',1"-terphenyl (**P10**) (in $CDCl_3$).

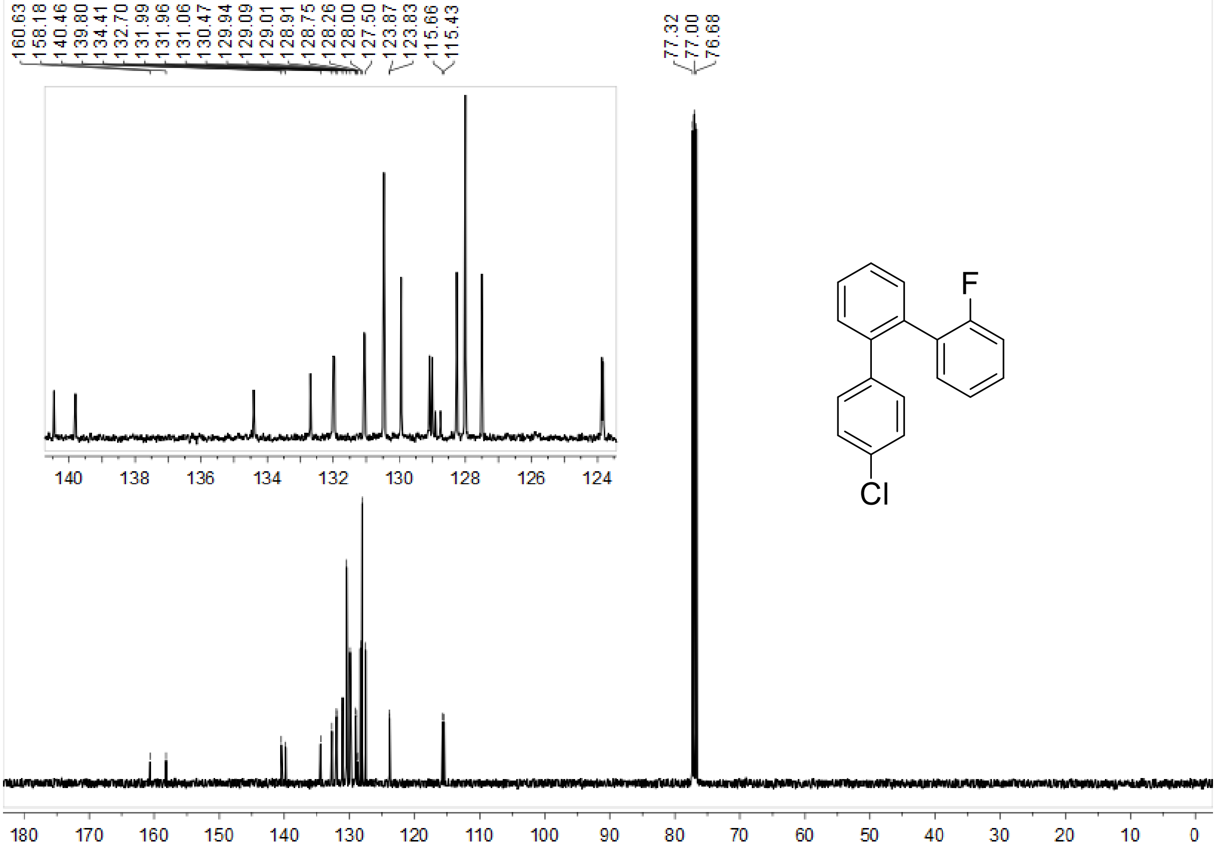


Figure S55: ^{13}C NMR spectrum of 4''-chloro-2-fluoro-1,1':2',1''-terphenyl (**P10**) (in $CDCl_3$).

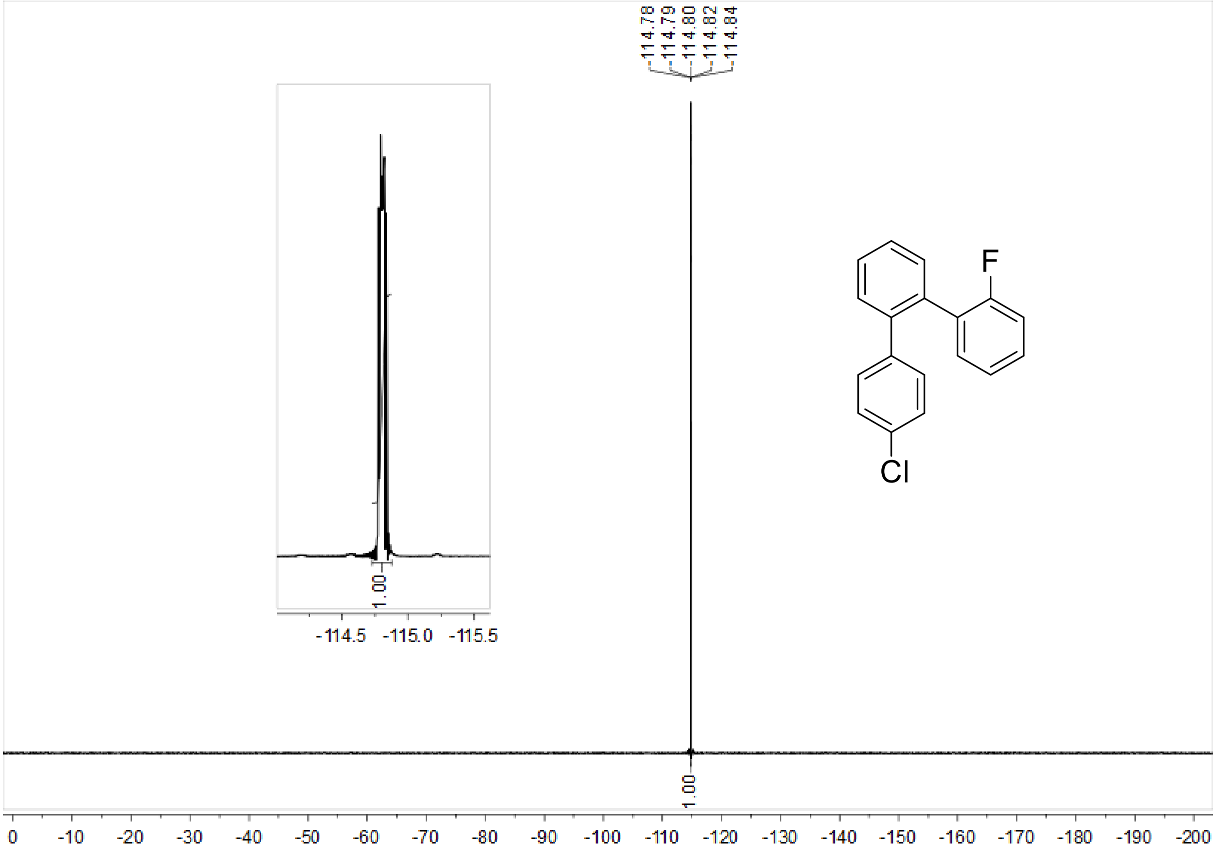


Figure S56: ^{19}F NMR spectrum of 4''-chloro-2-fluoro-1,1':2',1''-terphenyl (**P10**) (in $CDCl_3$).

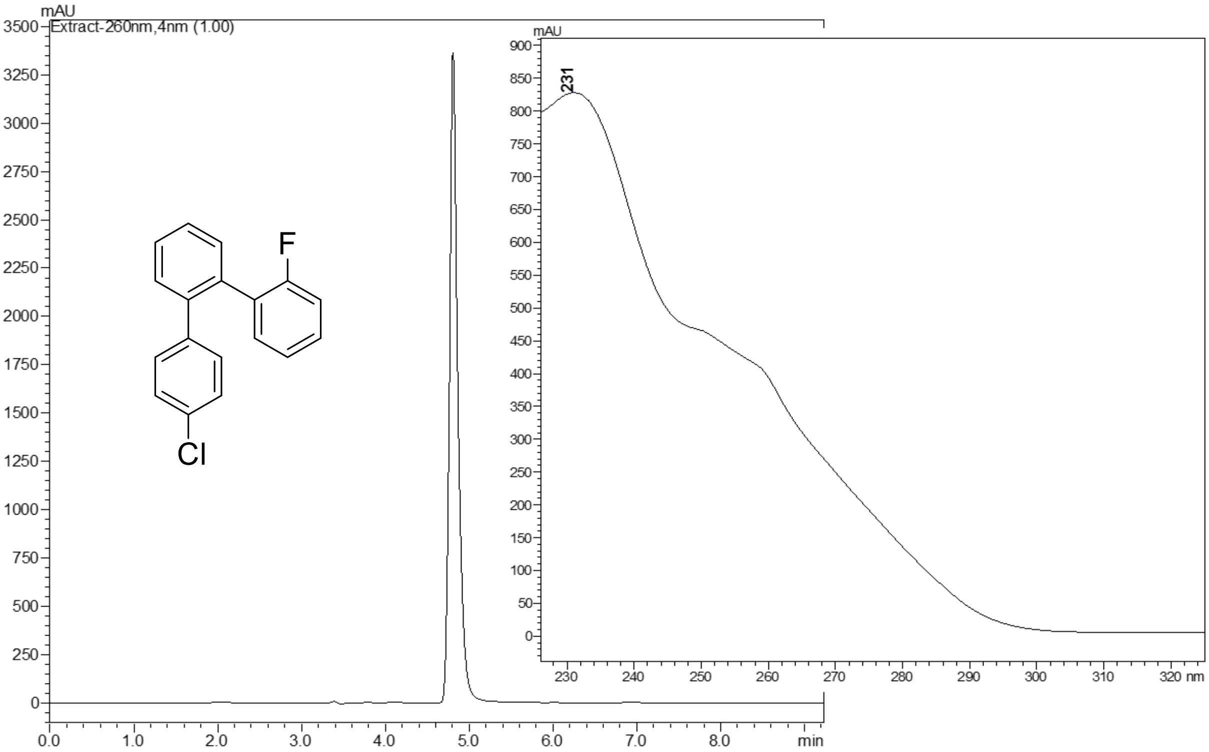
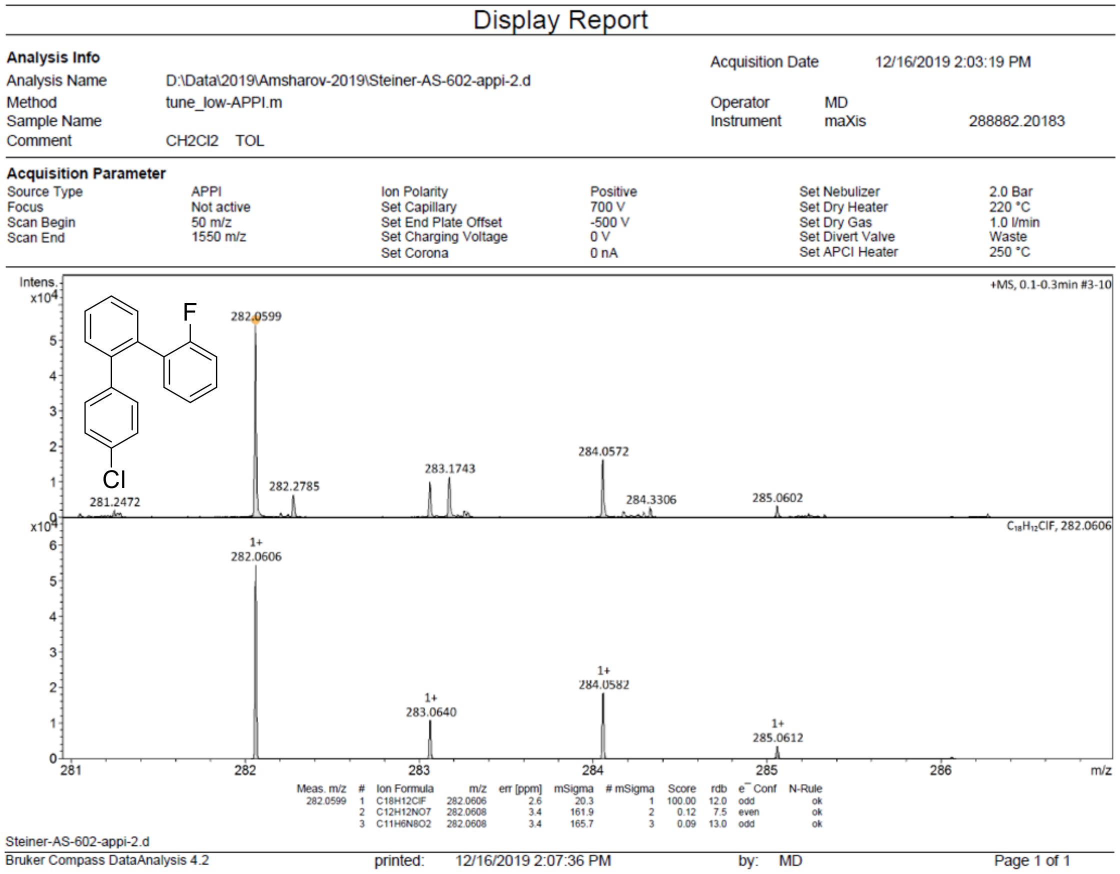


Figure S57: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 2:8, t_R = 4.80 min) and UV/vis spectrum (inset) of 4''-chloro-2-fluoro-1,1':2',1''-terphenyl (**P10**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-602-appi-2.d	Acquisition Date	12/16/2019 2:03:19 PM
Method	tune_low-APPI.m	Operator	MD
Sample Name		Instrument	maXis 288882.20183
Comment	CH2Cl2 TOL		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
282.0599	1	C18H12ClF	282.0606	2.6	20.3	1	100.00	12.0	odd	ok
	2	C12H12NO7	282.0608	3.4	161.9	2	0.12	7.5	even	ok
	3	C11H6N8O2	282.0608	3.4	165.7	3	0.09	13.0	odd	ok

Steiner-AS-602-appi-2.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 2:07:36 PM by: MD Page 1 of 1

Figure S58: HR MS (APPI) spectrum of 4''-chloro-2-fluoro-1,1':2',1''-terphenyl (**P10**), *m/z* 282.0599 (M^+, 100 %).

4''-Bromo-2-fluoro-1,1':2',1''-terphenyl (P11)

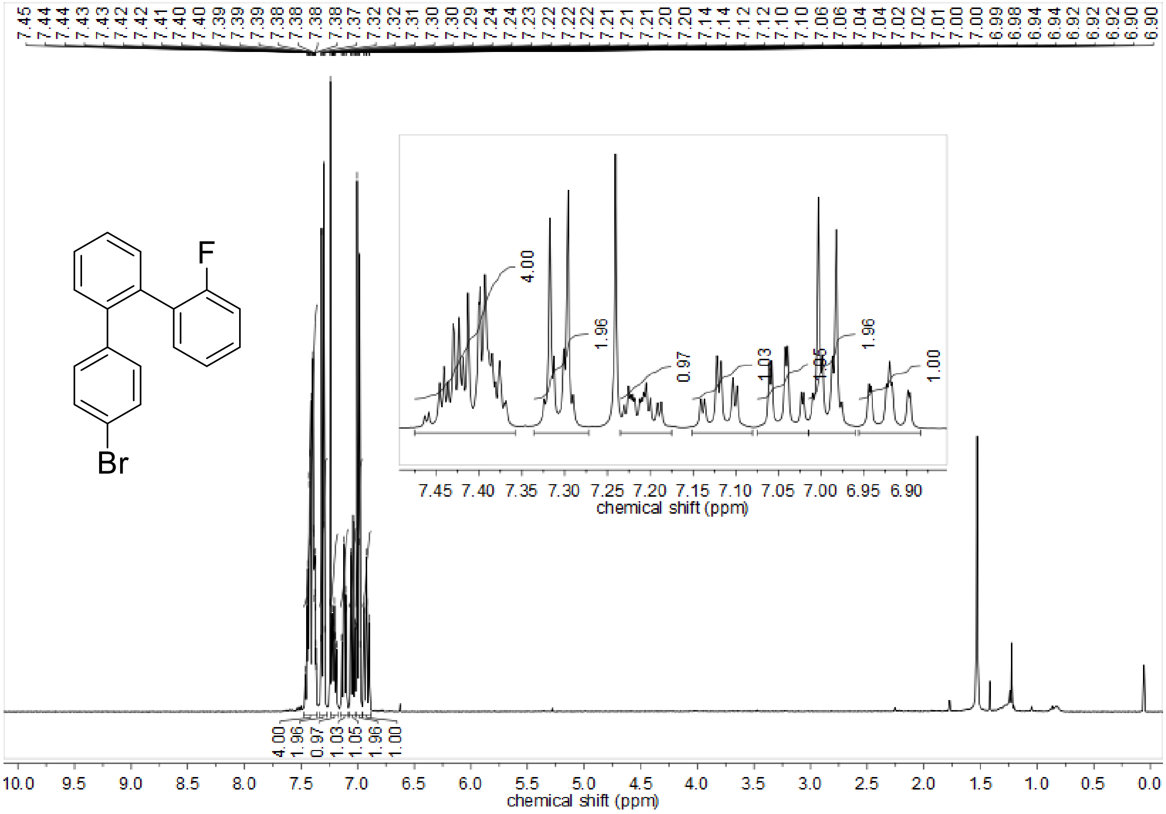


Figure S59: ^{1}H NMR spectrum of 4"-bromo-2-fluoro-1,1':2',1"-terphenyl (**P11**) (in CDCl$_3$).

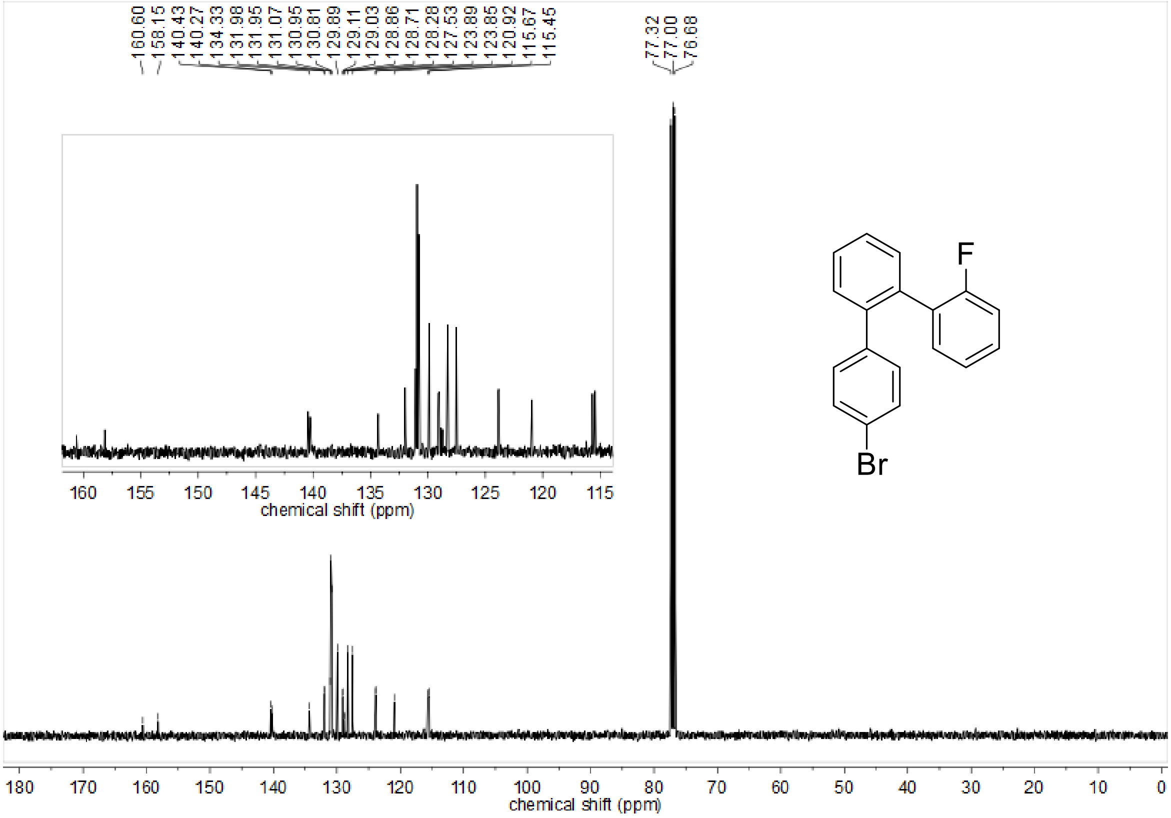


Figure S60: ^{13}C NMR spectrum of 4"-bromo-2-fluoro-1,1':2',1"-terphenyl (**P11**) (in CDCl$_3$).

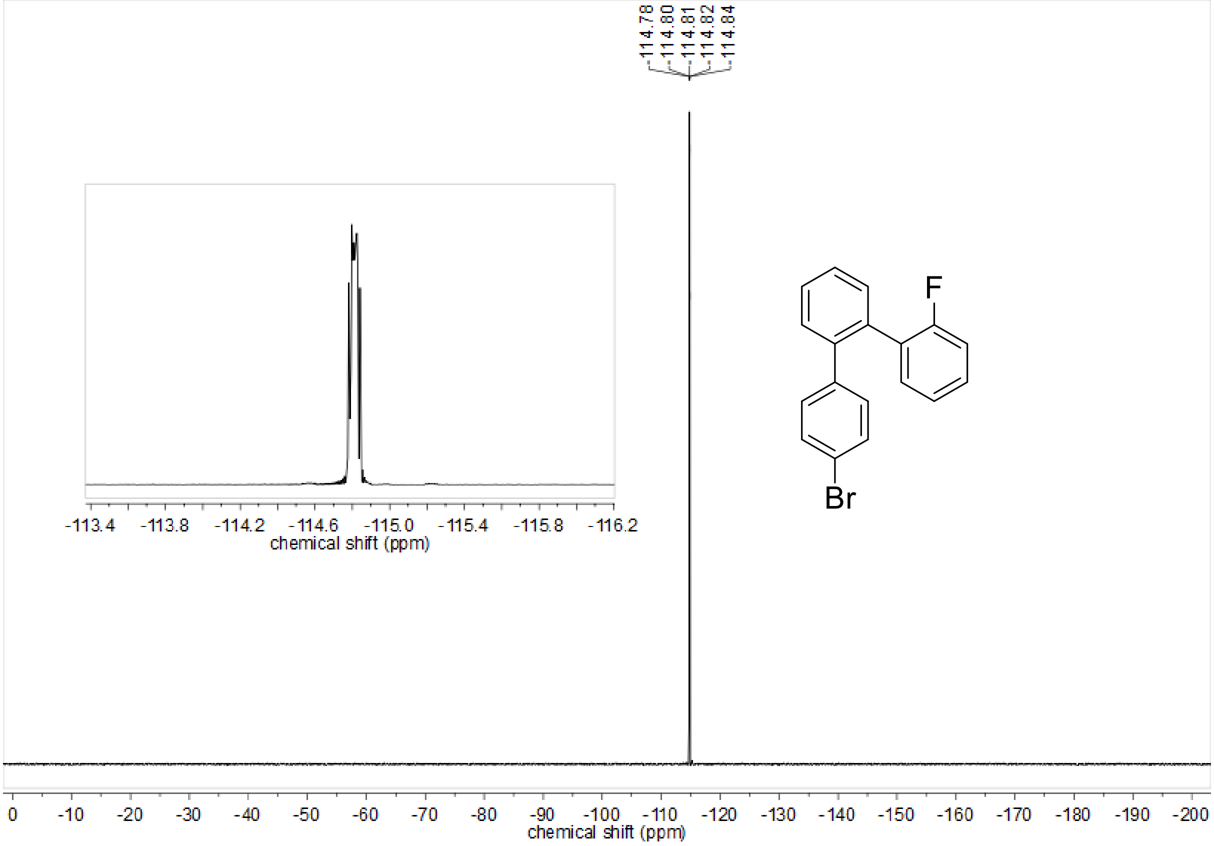


Figure S61: ^{19}F NMR spectrum of 4''-bromo-2-fluoro-1,1':2',1''-terphenyl (**P11**) (in CDCl$_3$).

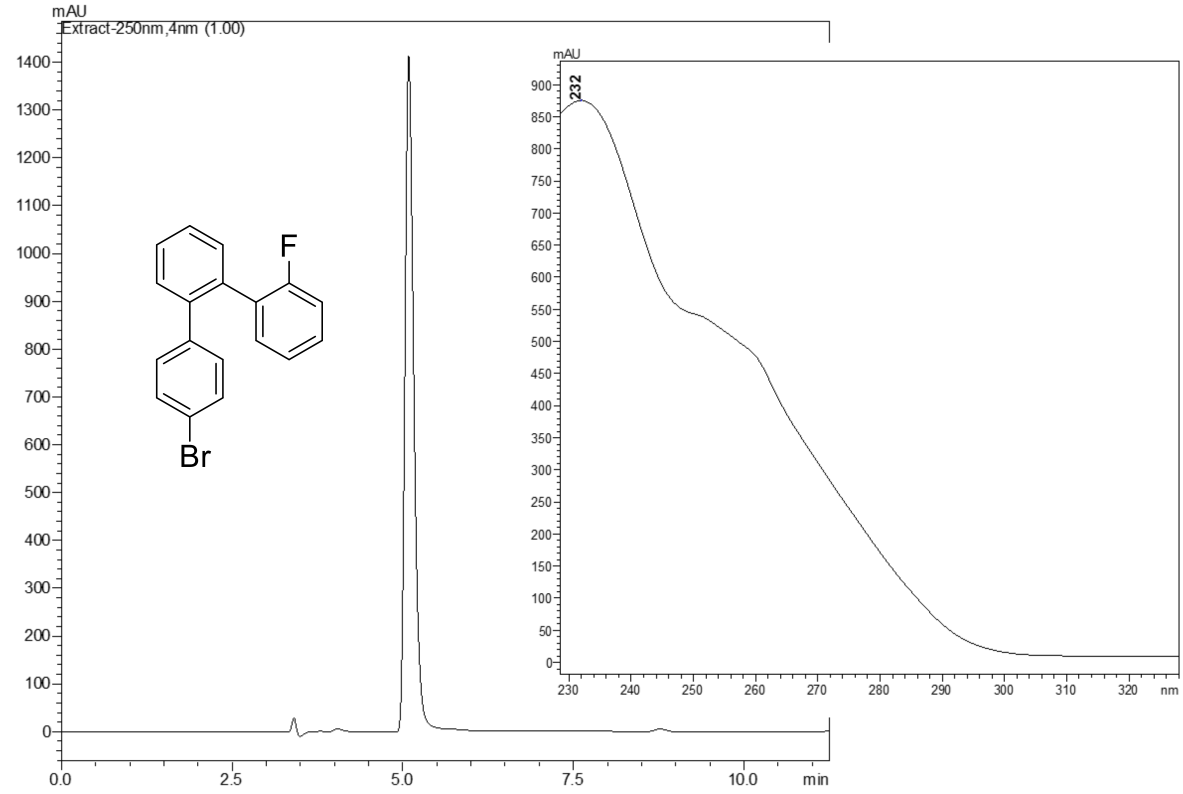
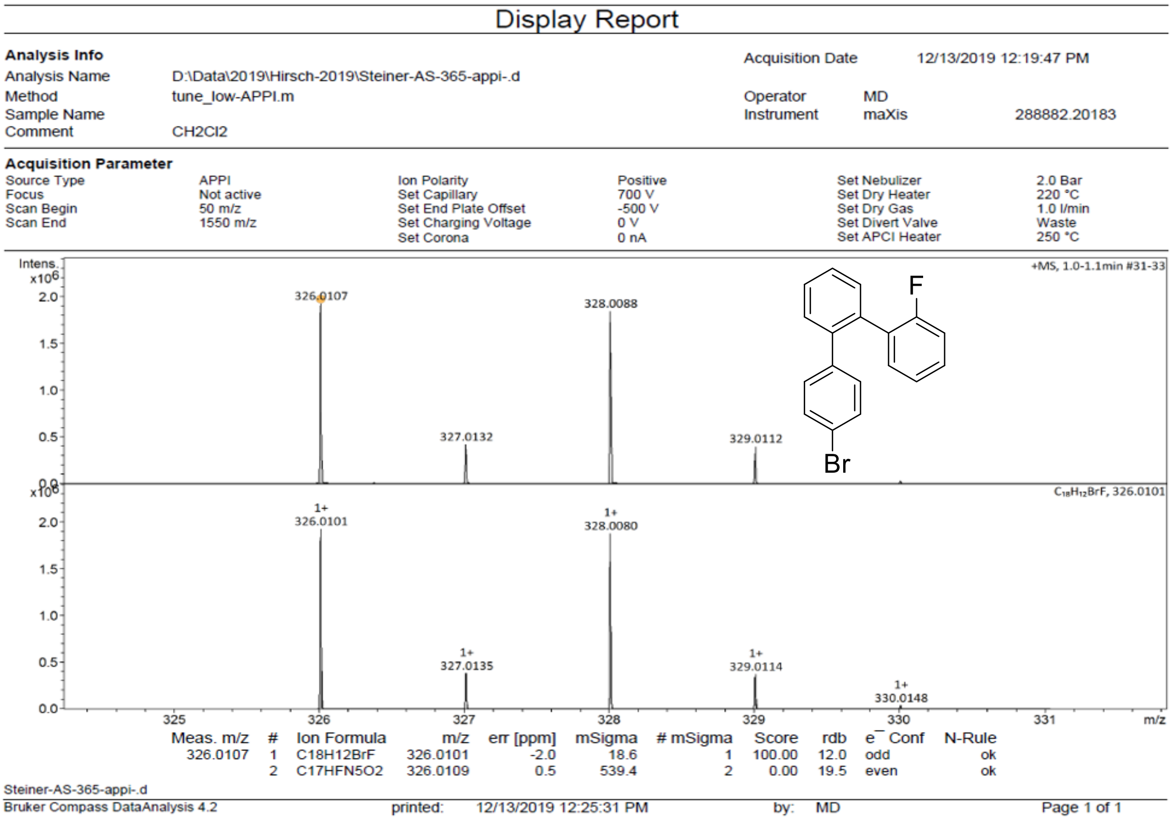


Figure S62: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 2:8, t_R = 5.08 min) and UV/vis spectrum (inset) of 4''-bromo-2-fluoro-1,1':2',1''-terphenyl (**P11**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Hirsch-2019\Steiner-AS-365-appi-.d	Acquisition Date	12/13/2019 12:19:47 PM
Method	tune_low-APPI.m	Operator	MD
Sample Name		Instrument	maXis 288882.20183
Comment	CH2Cl2		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
326.0107	1	C18H12BrF	326.0101	-2.0	18.6	1	100.00	12.0	odd	ok
	2	C17HFN5O2	326.0109	0.5	539.4	2	0.00	19.5	even	ok

Steiner-AS-365-appi-.d
Bruker Compass DataAnalysis 4.2 printed: 12/13/2019 12:25:31 PM by: MD Page 1 of 1

Figure S63: HR MS (APPI) spectrum of 4''-bromo-2-fluoro-1,1':2',1''-terphenyl (**P11**), *m/z* 326.0107 (M^+, 100 %).

2-Fluoro-4''-nitro-1,1':2',1''-terphenyl (3)

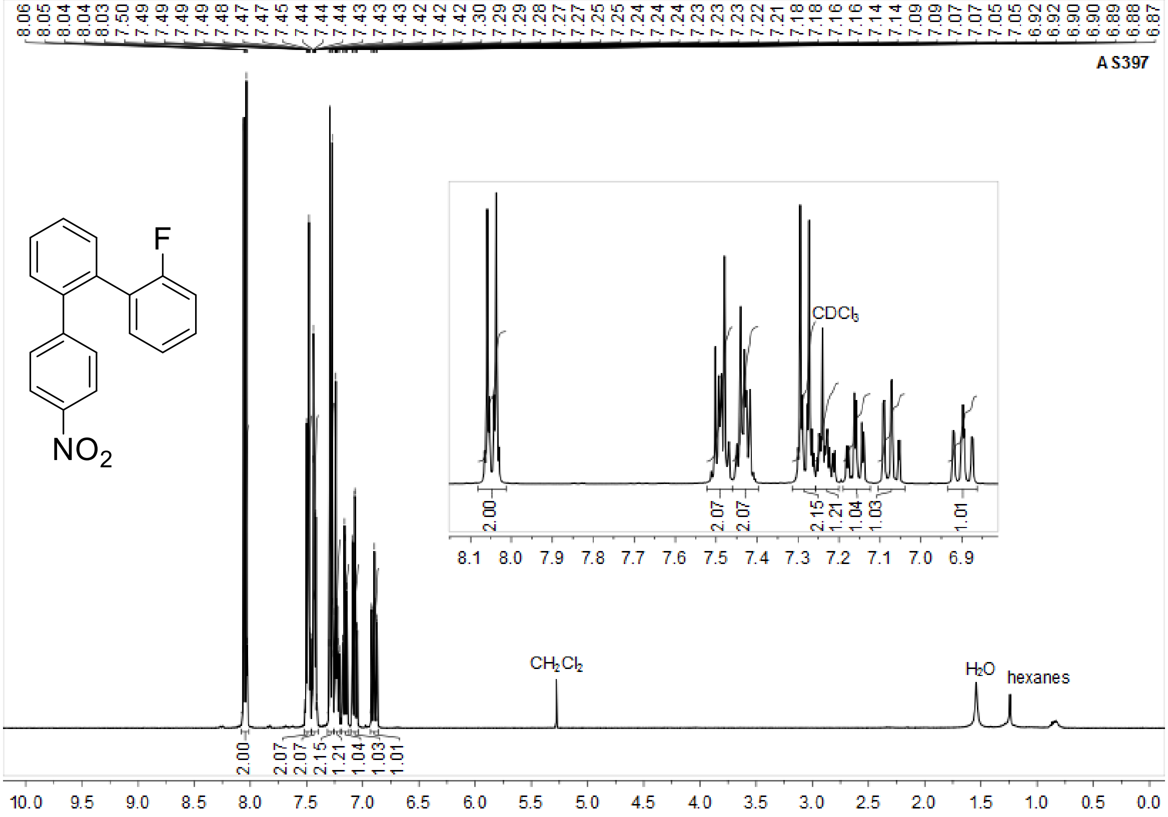


Figure S64: ^{1}H NMR spectrum of 2-fluoro-4''-nitro-1,1':2',1''-terphenyl (**3**) (in $CDCl_3$).

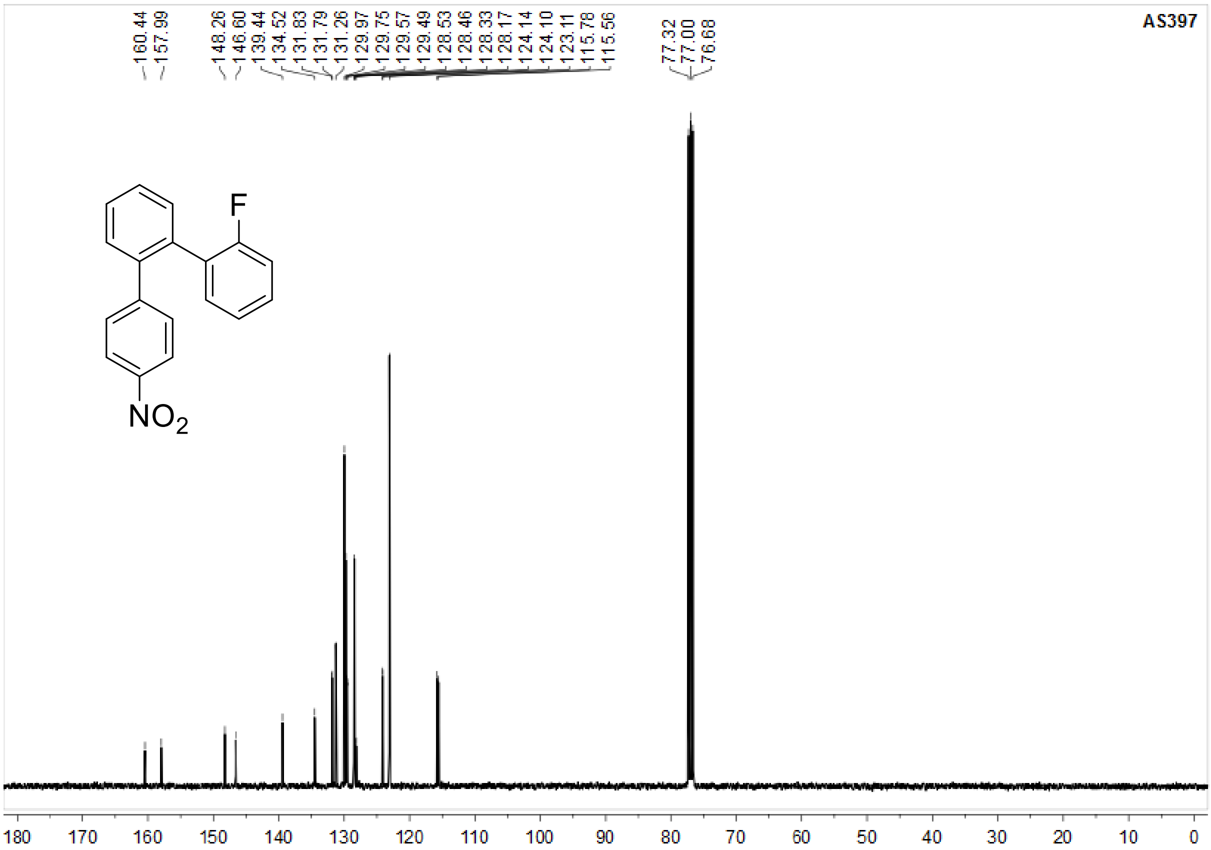


Figure S65: ^{13}C NMR spectrum of 2-fluoro-4''-nitro-1,1':2',1''-terphenyl (**3**) (in $CDCl_3$).

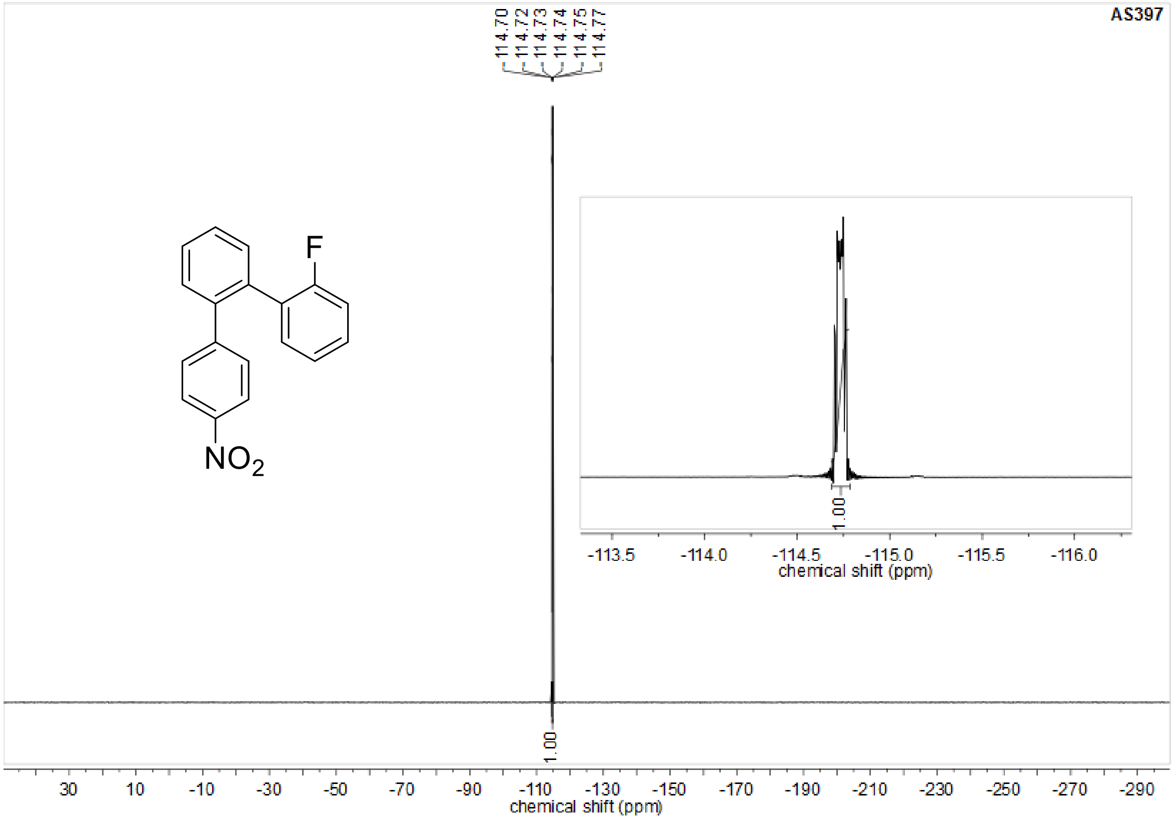


Figure S66: ^{19}F NMR spectrum of 2-fluoro-4''-nitro-1,1':2',1''-terphenyl (**3**) (in $CDCl_3$).

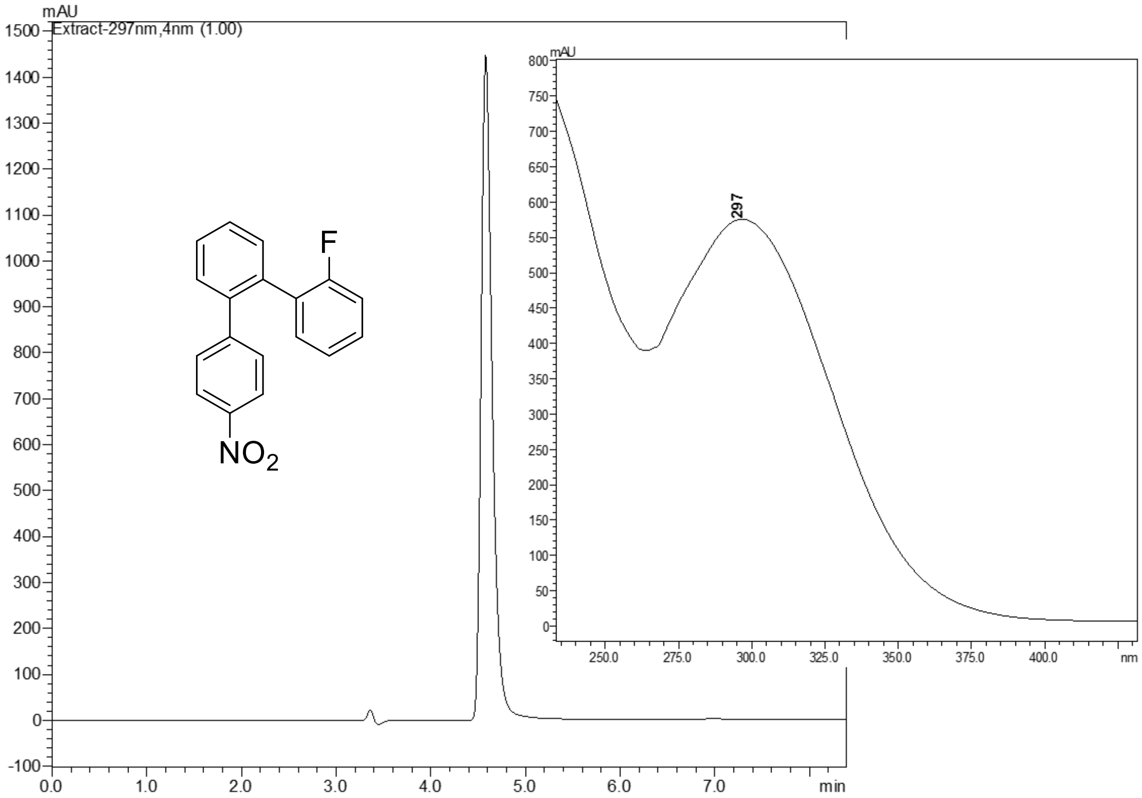
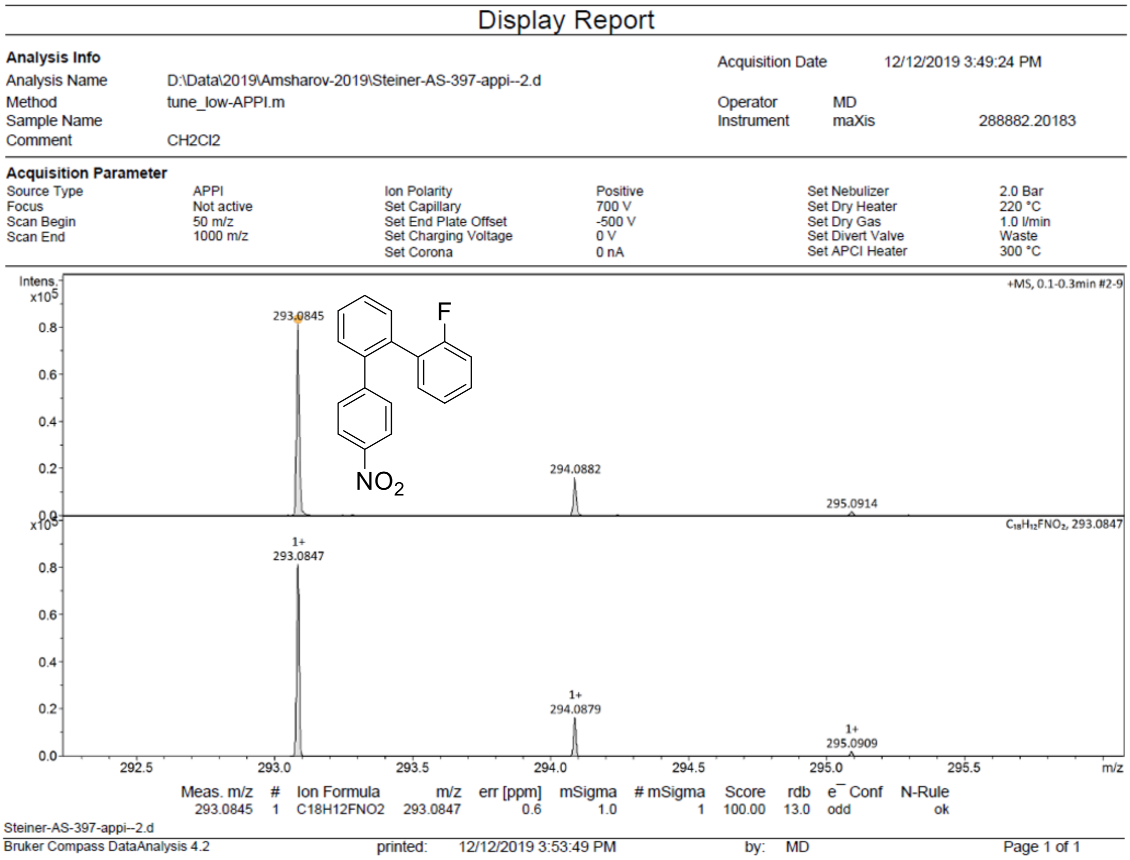


Figure S67: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 3:7, t_R 4.56 min) and UV/vis spectrum (inset) of 2-fluoro-4"-nitro-1,1':2',1"-terphenyl (**3**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-397-appi--2.d	Acquisition Date	12/12/2019 3:49:24 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	300 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
293.0845	1	C18H12FNO2	293.0847	0.6	1.0	1	100.00	13.0	odd	ok

Steiner-AS-397-appi--2.d

Bruker Compass DataAnalysis 4.2 printed: 12/12/2019 3:53:49 PM by: MD Page 1 of 1

Figure S68: HR MS (APPI) spectrum of 2-fluoro-4"-nitro-1,1':2',1"-terphenyl (**3**), *m/z* 293.0845 (M^+, 100 %).

2''-Fluoro-[1,1':2',1''-terphenyl]-4-amine (4)

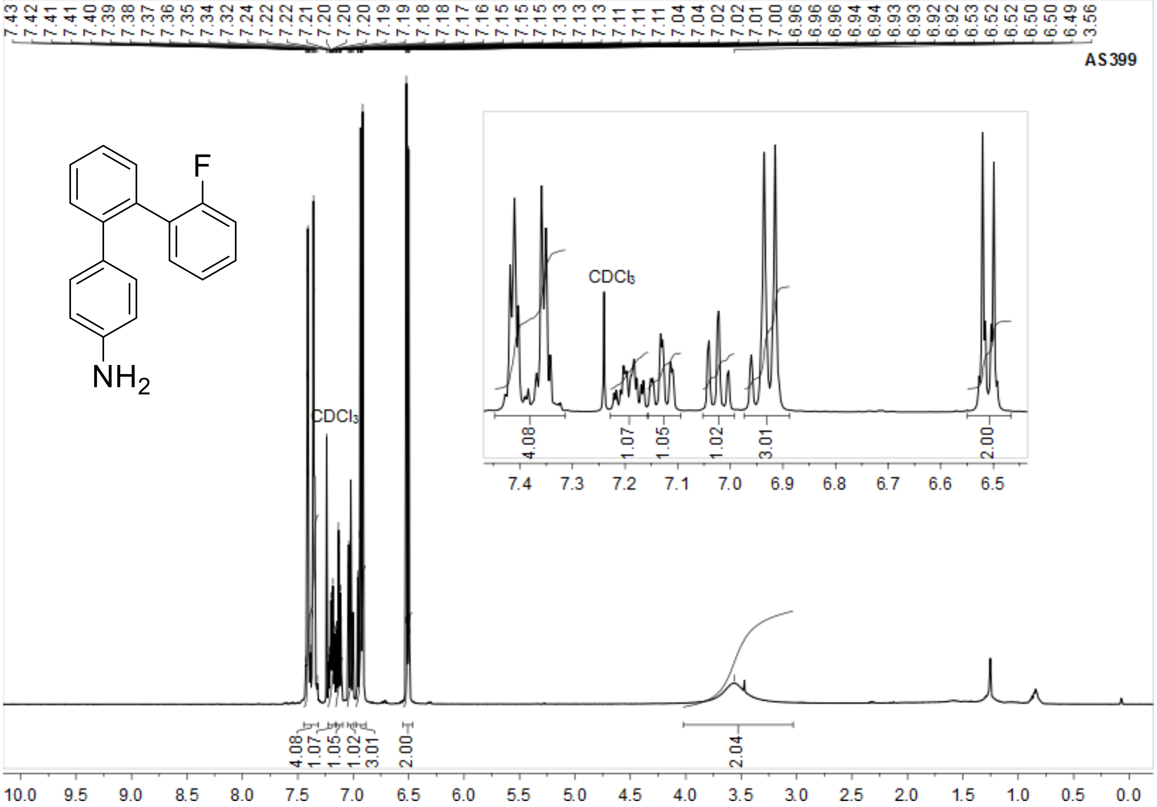


Figure S69: ^{1}H NMR spectrum of 2''-fluoro-[1,1':2',1''-terphenyl]-4-amine (**4**) (in $CDCl_3$).

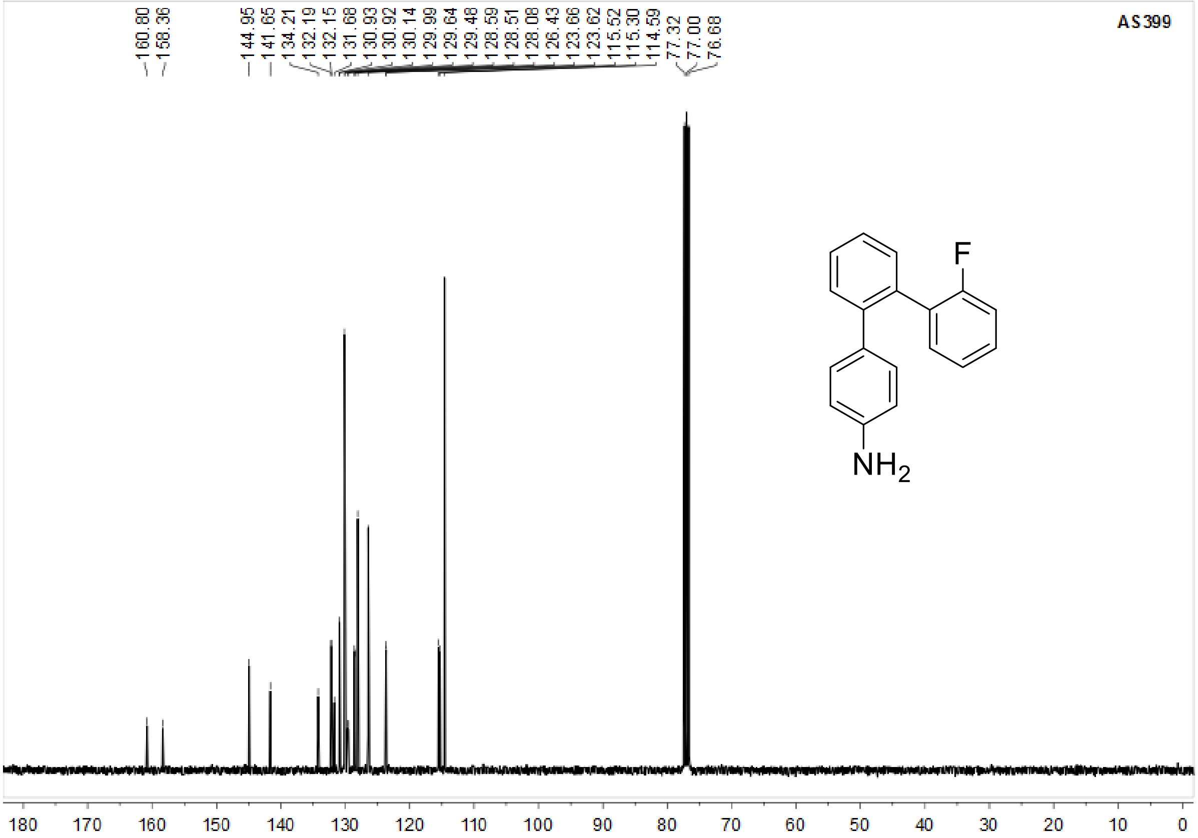


Figure S70: ^{13}C NMR spectrum of 2''-fluoro-[1,1':2',1''-terphenyl]-4-amine (**4**) (in $CDCl_3$).

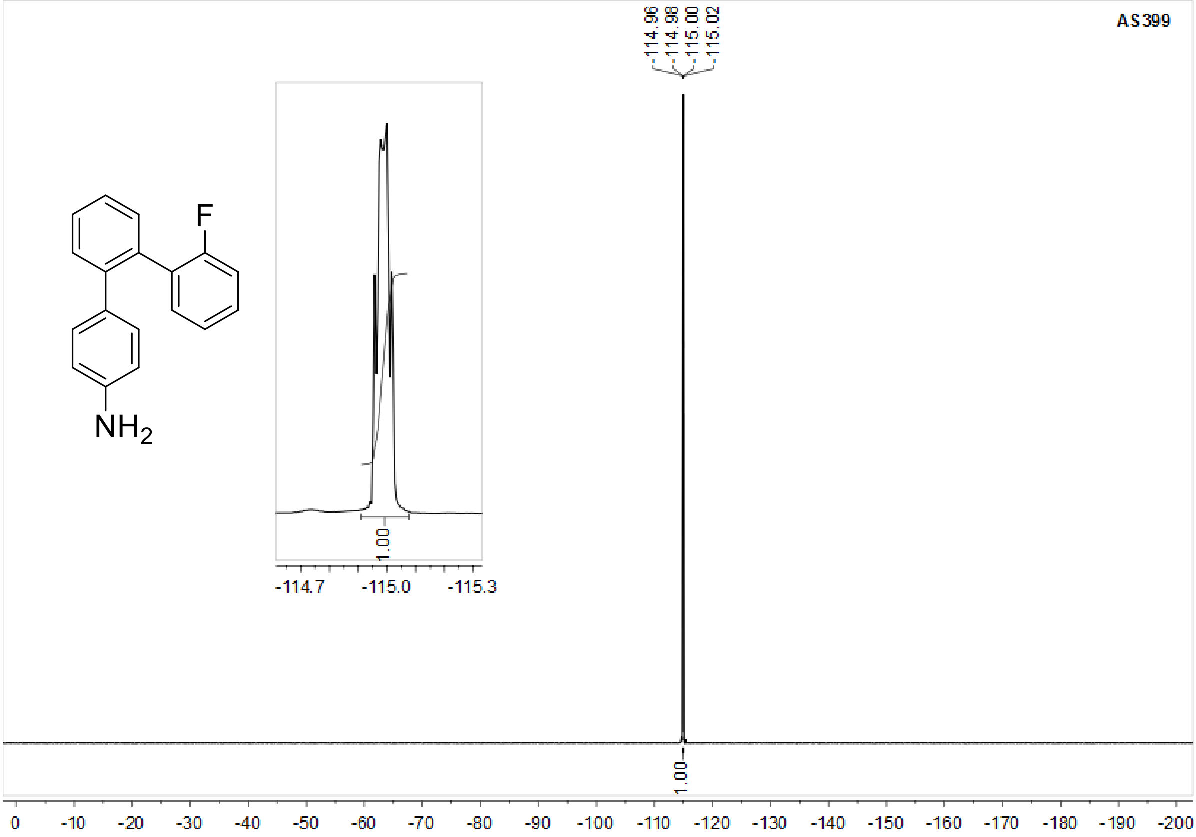


Figure S71: ^{19}F NMR spectrum of 2''-fluoro-[1,1':2',1''-terphenyl]-4-amine (**4**) (in $CDCl_3$).

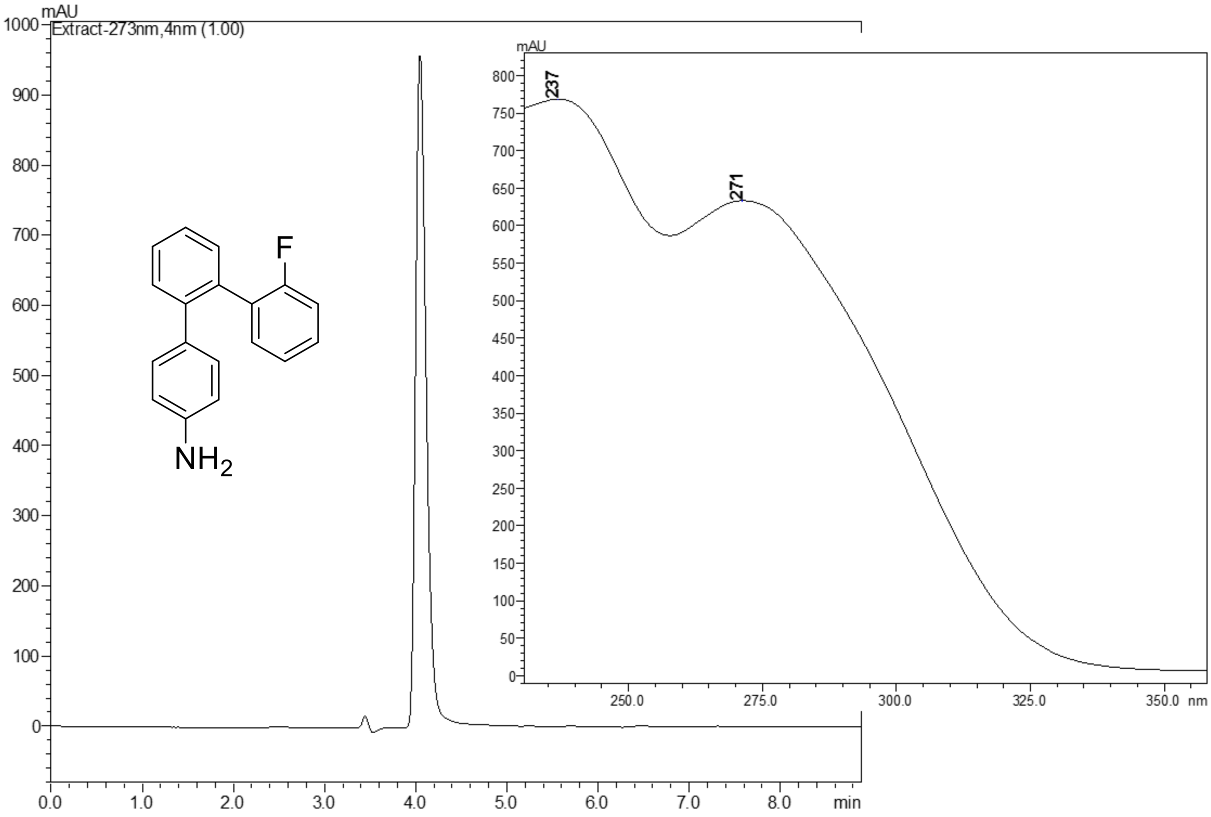
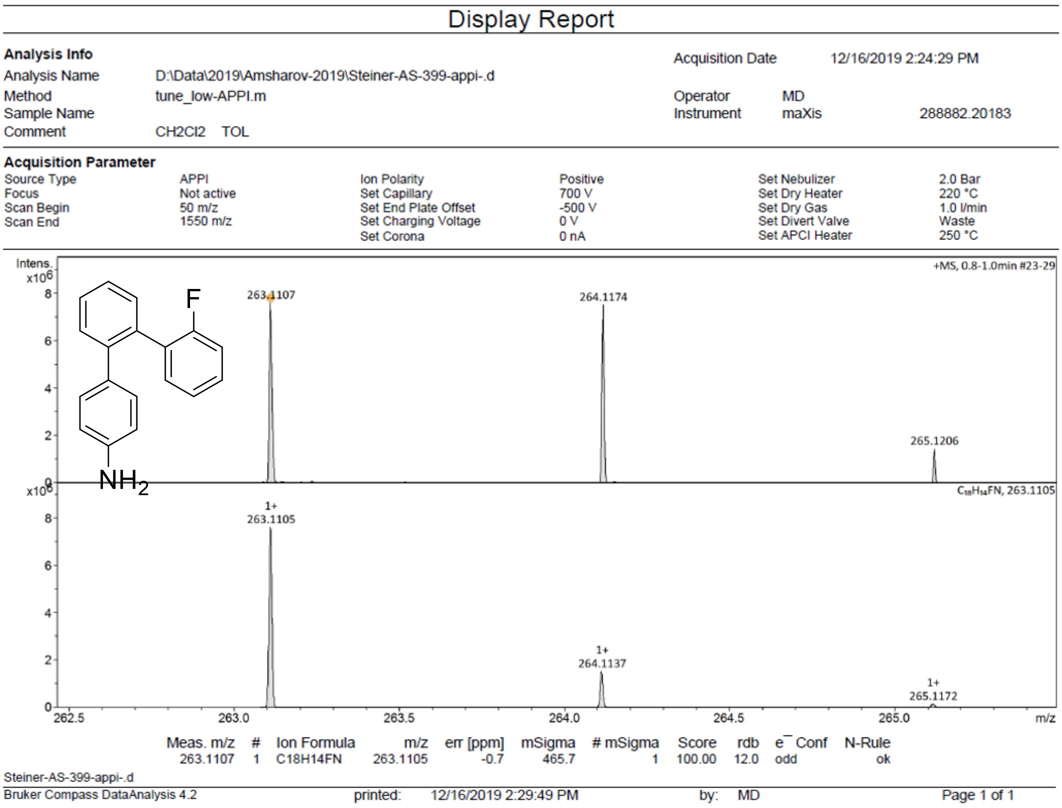


Figure S72: HPLC chromatogram (Buckyprep column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 2:8, t_R 4.04 min) and UV/vis spectrum (inset) of 2''-fluoro-[1,1':2',1''-terphenyl]-4-amine (**4**).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-AS-399-appi-.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2 TOL

Acquisition Date 12/16/2019 2:24:29 PM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
263.1107	1	C18H14FN	263.1105	-0.7	465.7	1	100.00	12.0	odd	ok

Steiner-AS-399-appi-.d
Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 2:29:49 PM by: MD Page 1 of 1

Figure S73: HR MS (APPI) spectrum of 2"-fluoro-[1,1':2',1"-terphenyl]-4-amine (**4**), *m/z* 263.1107 (M^+, 100 %).

2-Fluoro-4’’-iodo-1,1’:2’,1’’-terphenyl (P12)

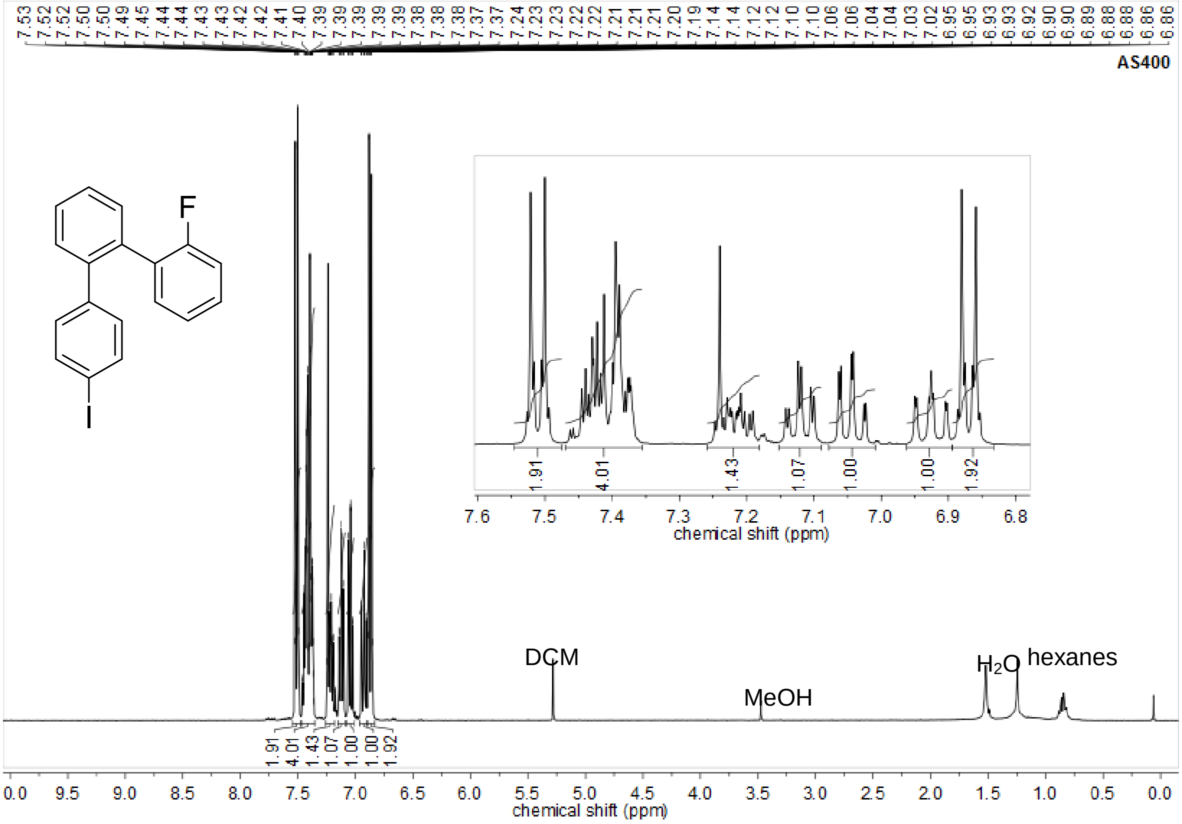


Figure S74: ^{1}H NMR spectrum of 2-fluoro-4’’-iodo-1,1’:2’,1’’-terphenyl (**P12**) (in $CDCl_3$).

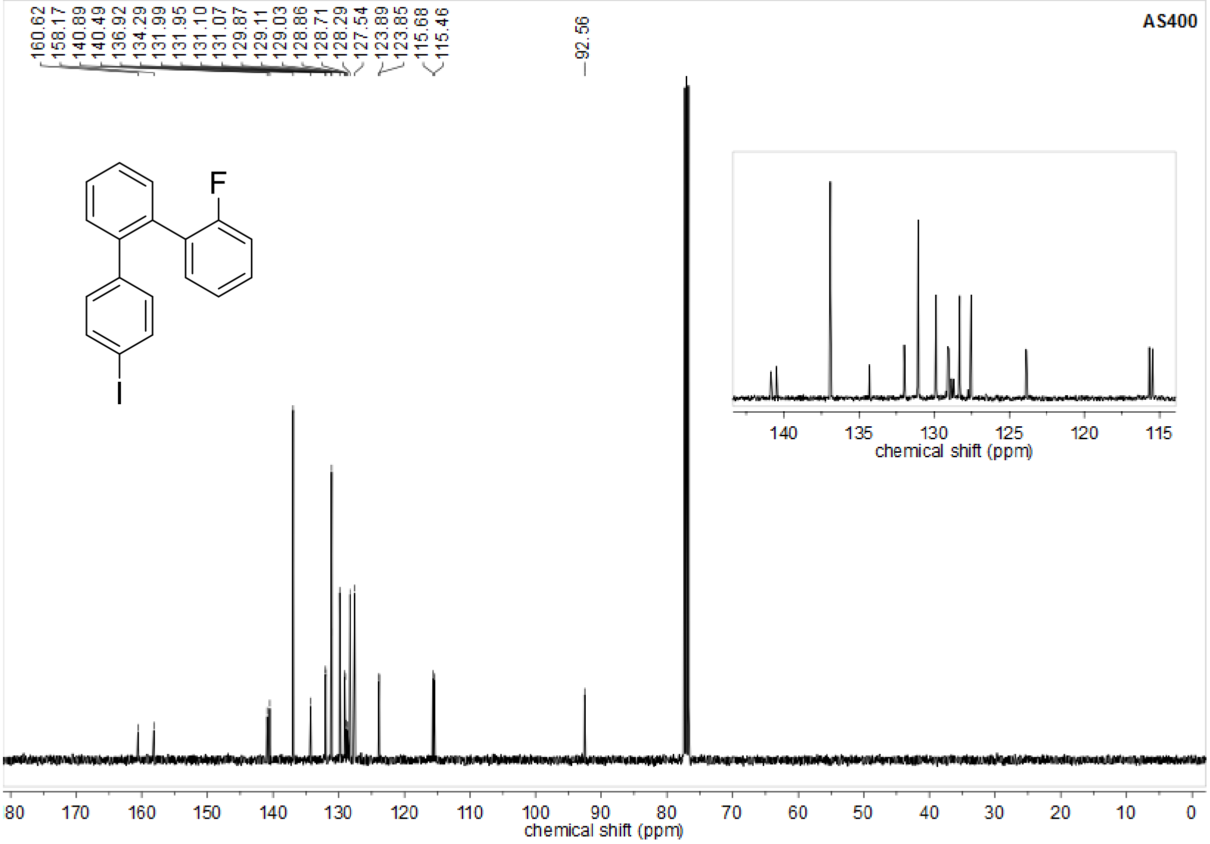


Figure S75: ^{13}C NMR spectrum of 2-fluoro-4’’-iodo-1,1’:2’,1’’-terphenyl (**P12**) (in $CDCl_3$).

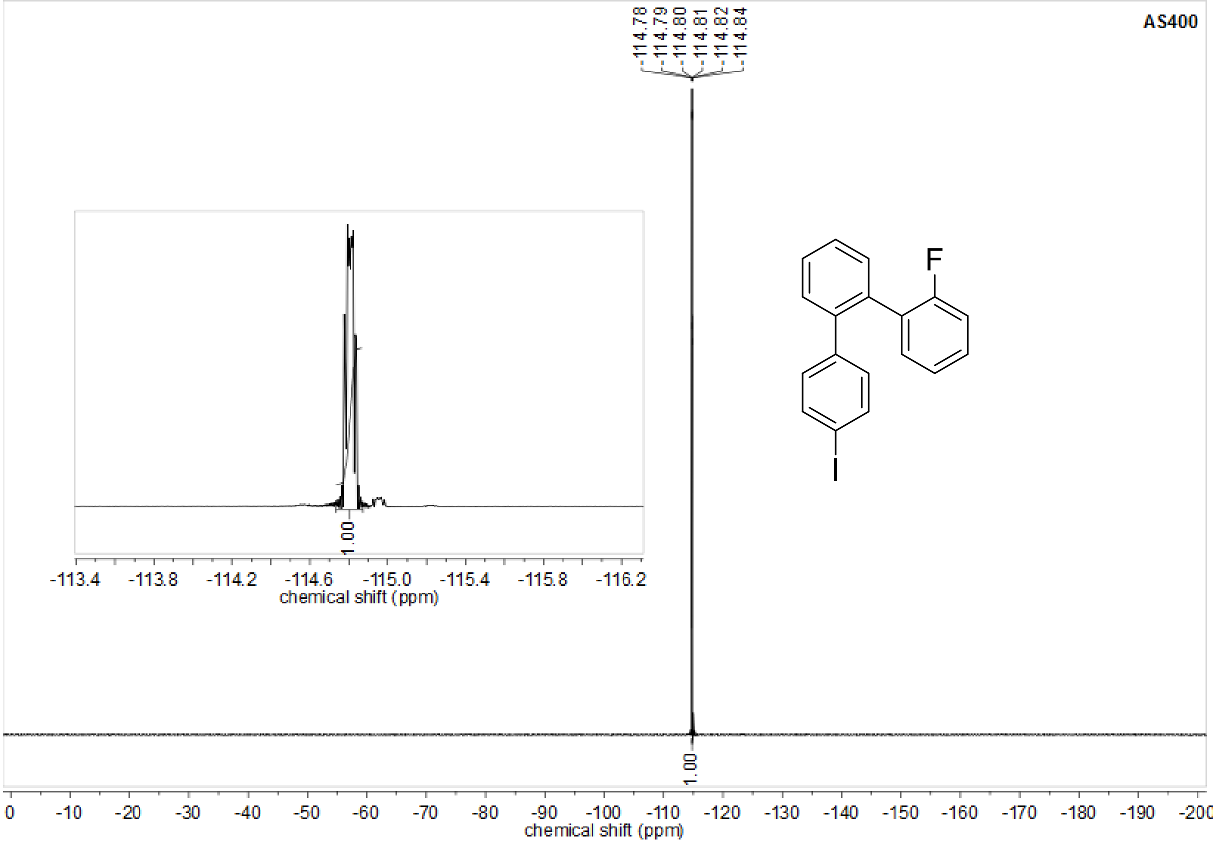


Figure S41: ^{19}F NMR spectrum of 2-fluoro-4’’-iodo-1,1’:2’,1’’-terphenyl (**P12**) (in $CDCl_3$).

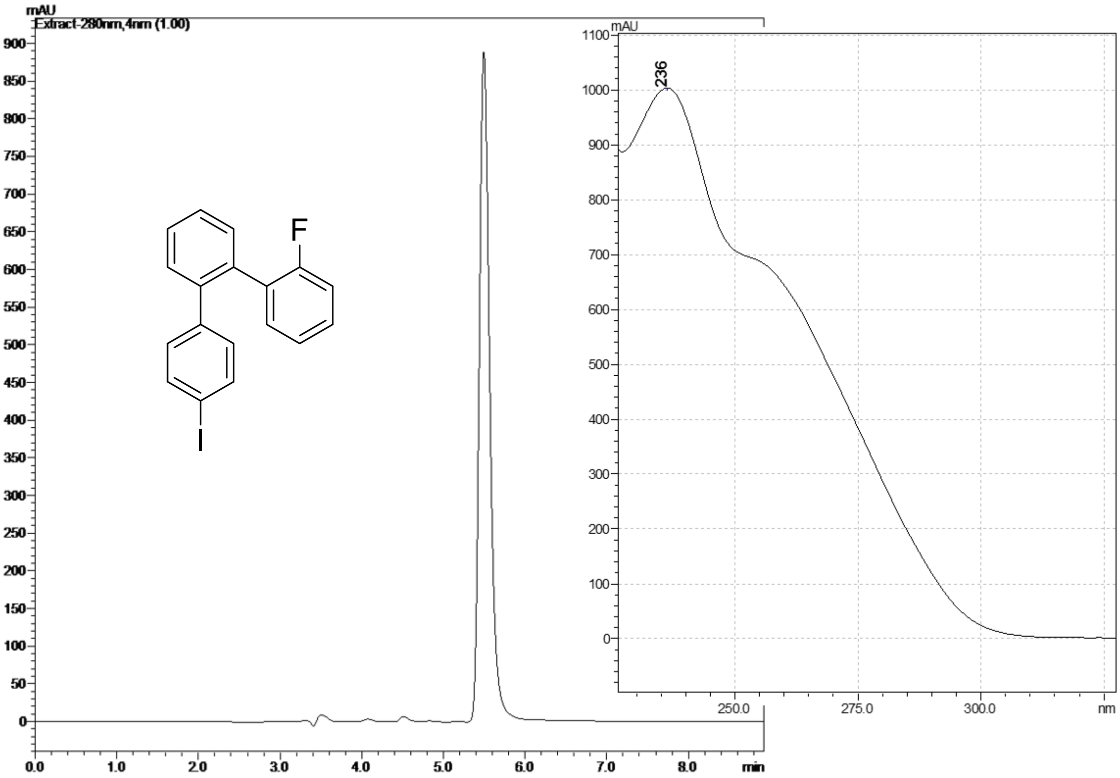
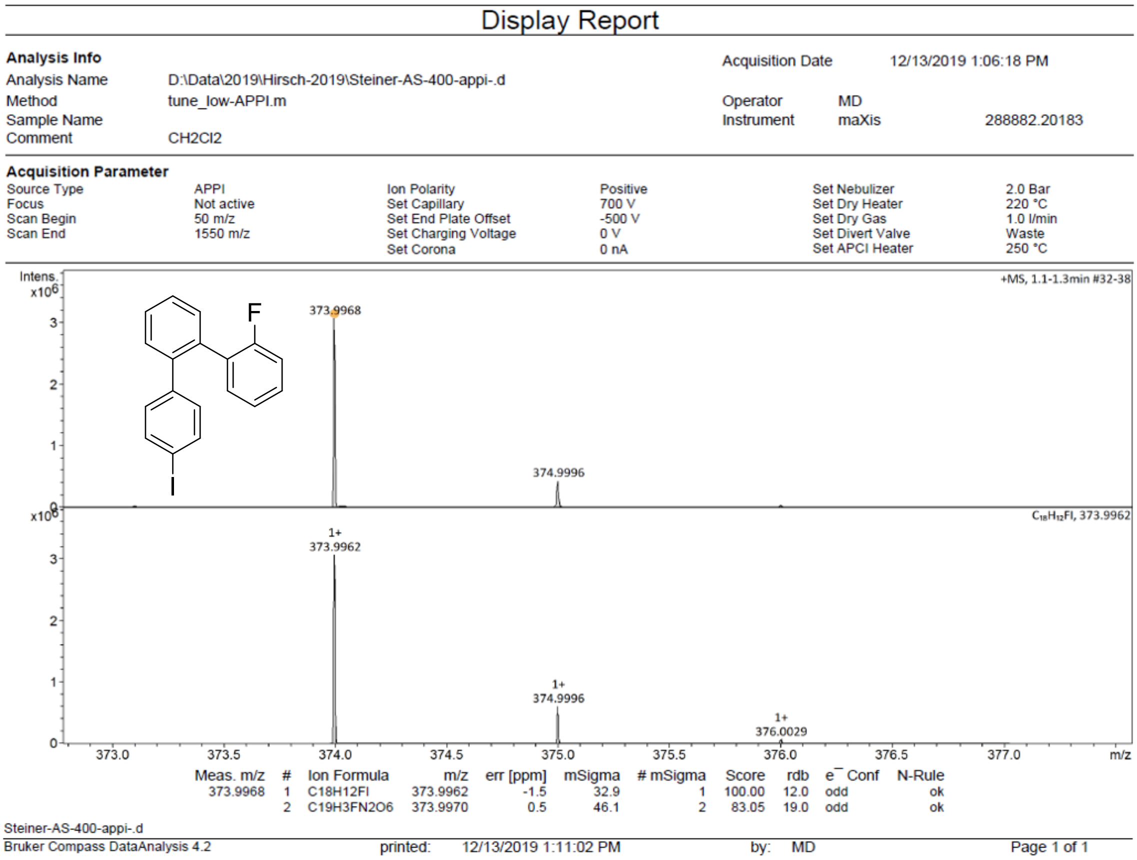


Figure S77: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 2:8, t_R 5.50 min) and UV/vis spectrum (inset) of 2-fluoro-4’’-iodo-1,1’:2’,1’’-terphenyl (**P12**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Hirsch-2019\Steiner-AS-400-appi-.d	Acquisition Date	12/13/2019 1:06:18 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
373.9968	1	C18H12FI	373.9962	-1.5	32.9	1	100.00	12.0	odd	ok
	2	C19H3FN2O6	373.9970	0.5	46.1	2	83.05	19.0	odd	ok

Steiner-AS-400-appi-.d

Bruker Compass DataAnalysis 4.2 printed: 12/13/2019 1:11:02 PM by: MD Page 1 of 1

Figure S78: HR MS (APPI) spectrum of 2-fluoro-4’’-iodo-1,1’:2’,1’’-terphenyl (**P12**),.*m/z* 373.9968 (M^+, 100 %).

2-fluoro-3''-iodo-1,1':2',1''-terphenyl (P13).

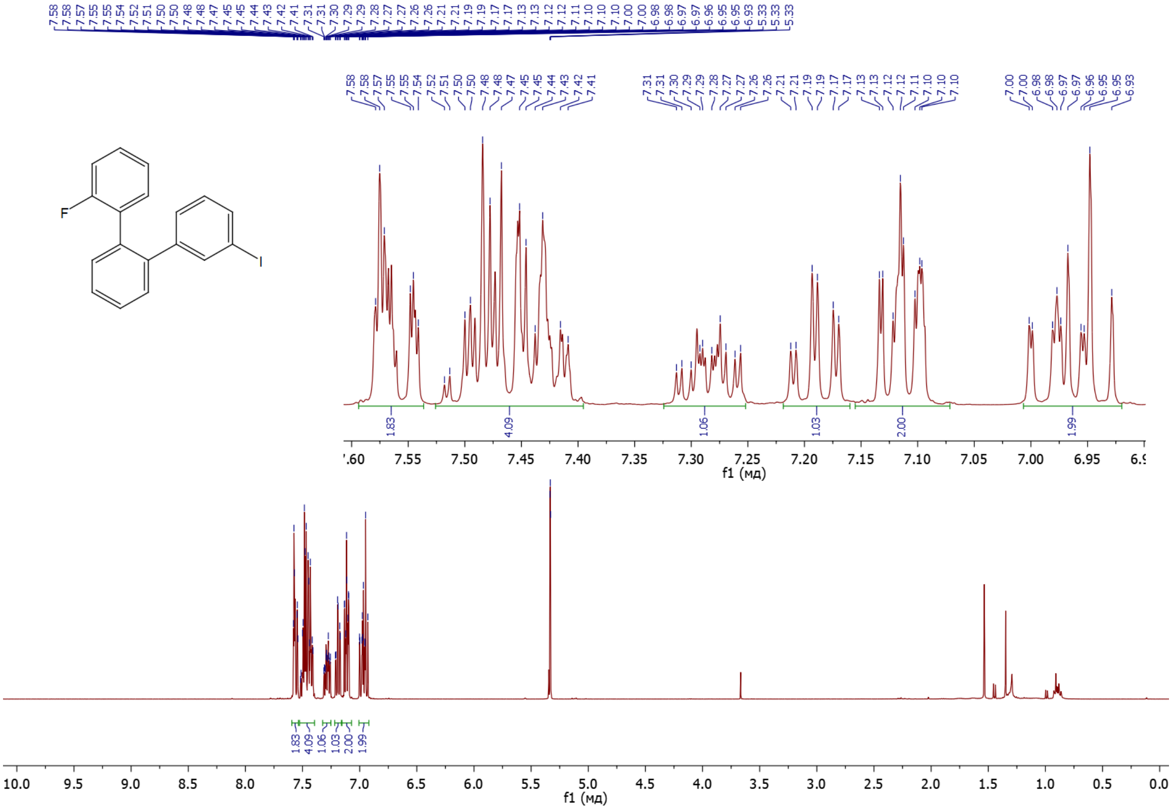


Figure S79: ^{1}H NMR spectrum of 2-fluoro-3''-iodo-1,1':2',1''-terphenyl (**P13**) (in CD_2Cl_2).

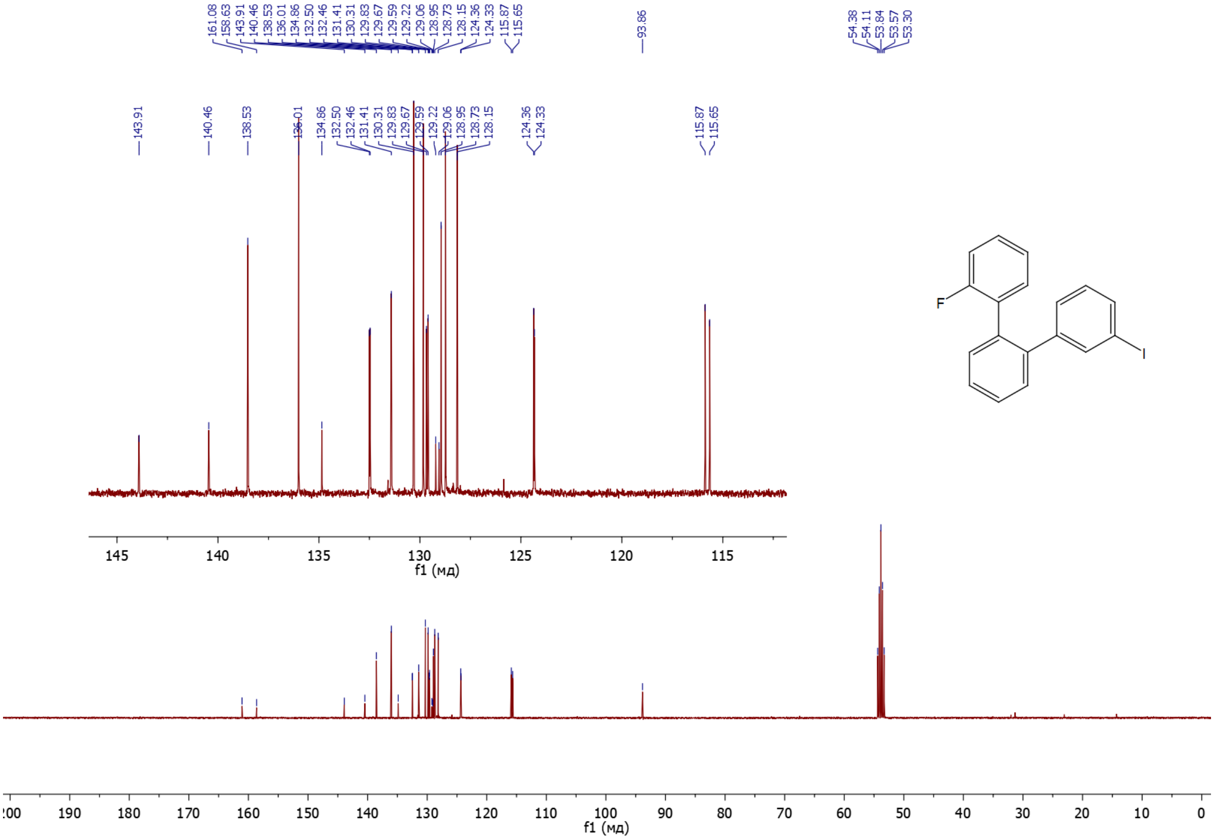


Figure S80: ^{13}C NMR spectrum of 2-fluoro-3''-iodo-1,1':2',1''-terphenyl (**P13**) (in CD_2Cl_2).

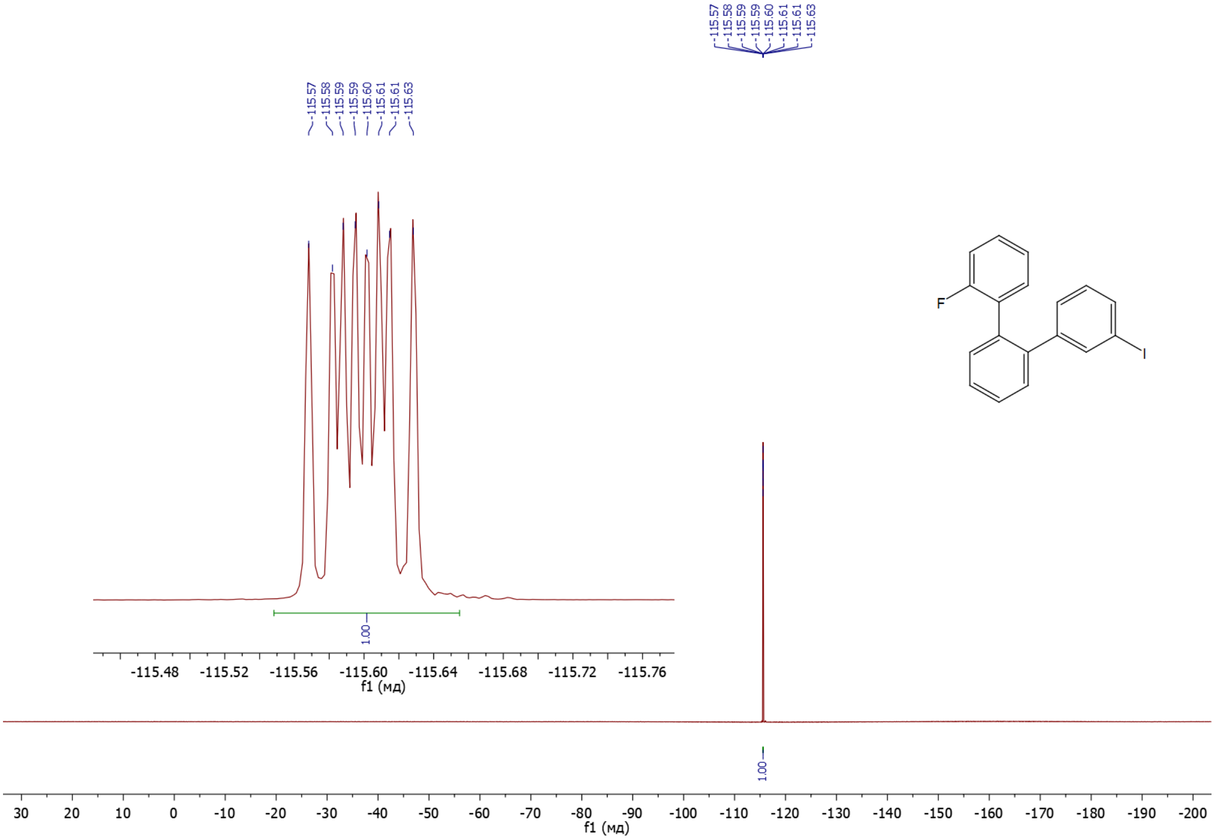


Figure S81: ^{19}F NMR spectrum of 2-fluoro-3"-iodo-1,1':2',1"-terphenyl (**P13**) (in CD_2Cl_2).

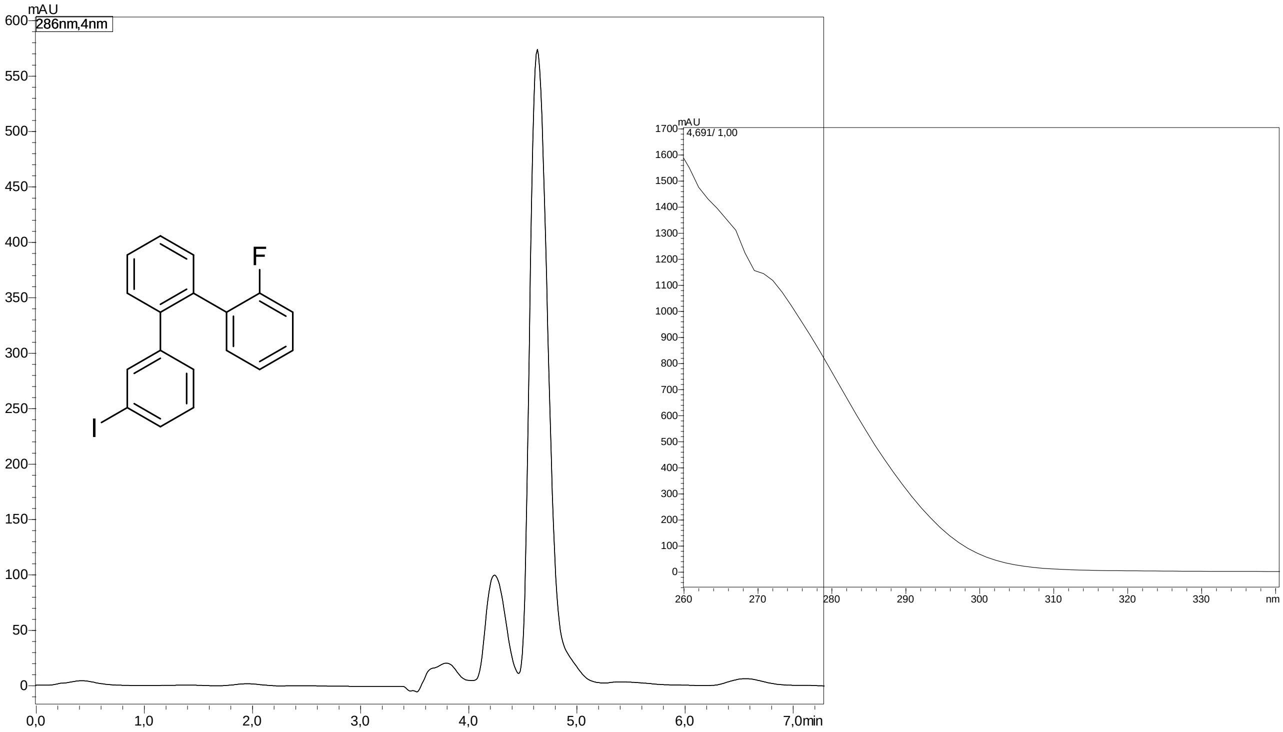


Figure S82: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 4:6, t_R 4.76 min) and UV/vis spectrum (inset) of 2-fluoro-3"-iodo-1,1':2',1"-terphenyl (**P13**).

2-fluoro-2''-iodo-1,1':2',1''-terphenyl (P14).

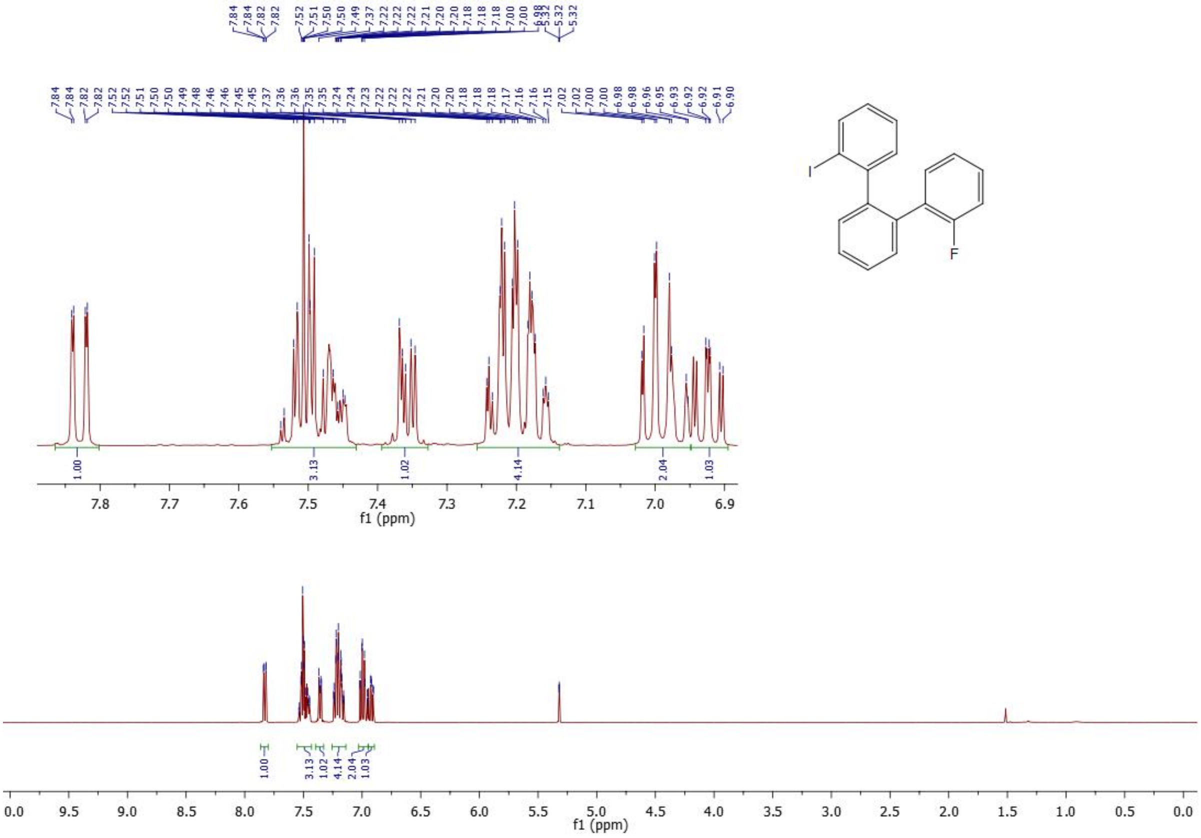


Figure S83: ^{1}H NMR spectrum of 2-fluoro-2''-iodo-1,1':2',1''-terphenyl (**P14**) (in CD_2Cl_2).

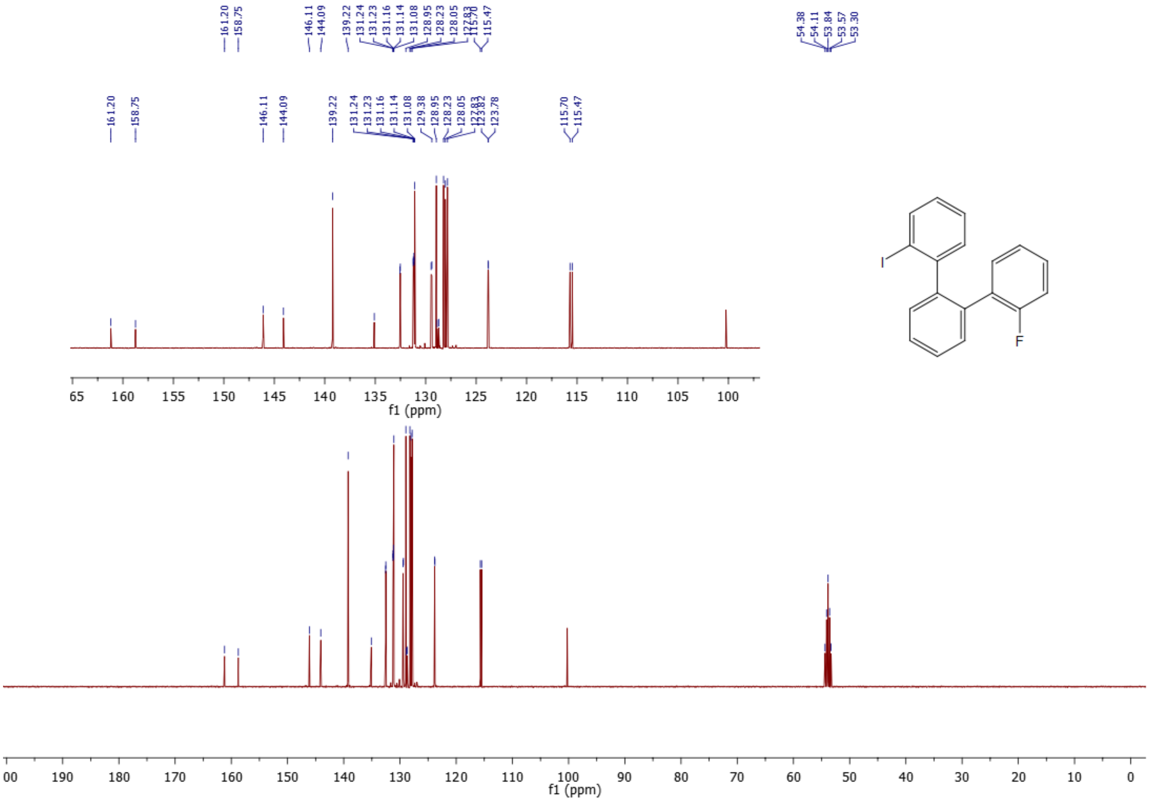


Figure S84: ^{13}C NMR spectrum of 2-fluoro-2''-iodo-1,1':2',1''-terphenyl (**P14**) (in CD_2Cl_2).

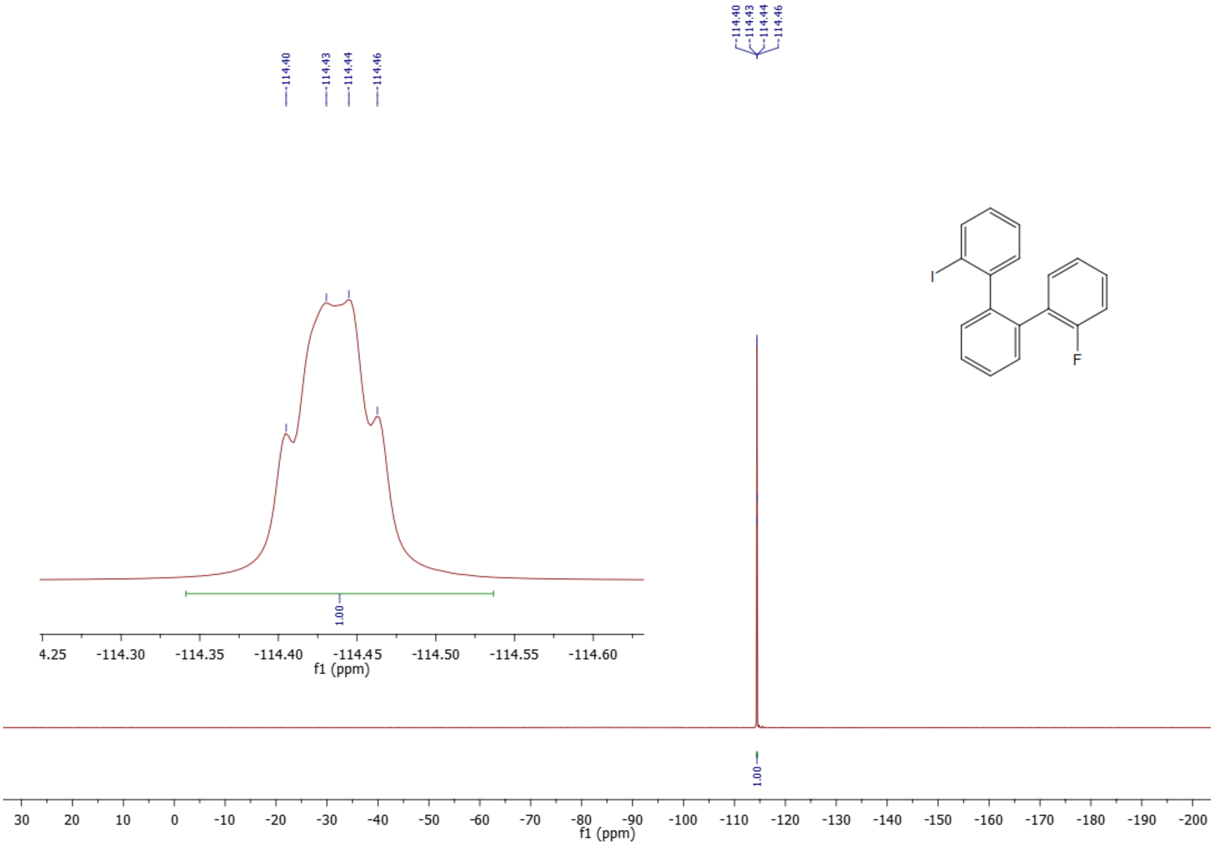


Figure S85: ^{19}F NMR spectrum of 2-fluoro-2''-iodo-1,1':2',1''-terphenyl (**P14**) (in CD_2Cl_2).

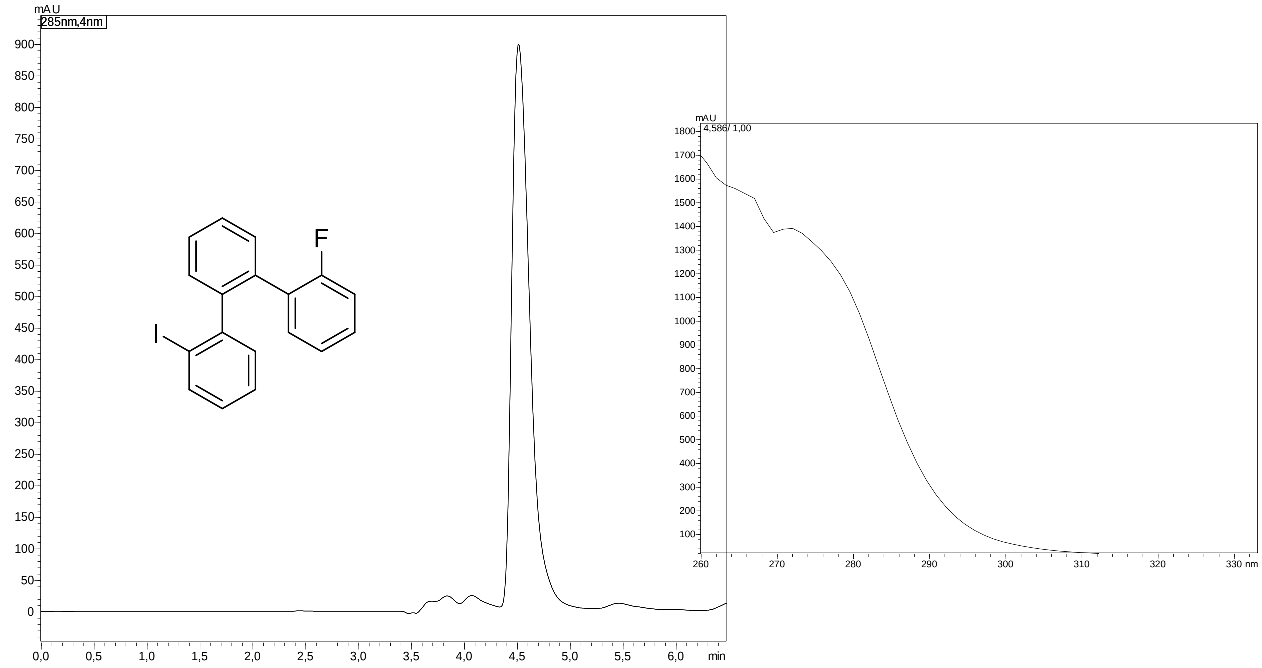


Figure S86: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 4:6, t_R 4.58 min) and UV/vis spectrum (inset) of 2-fluoro-2''-iodo-1,1':2',1''-terphenyl (**P14**).

2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (P15).

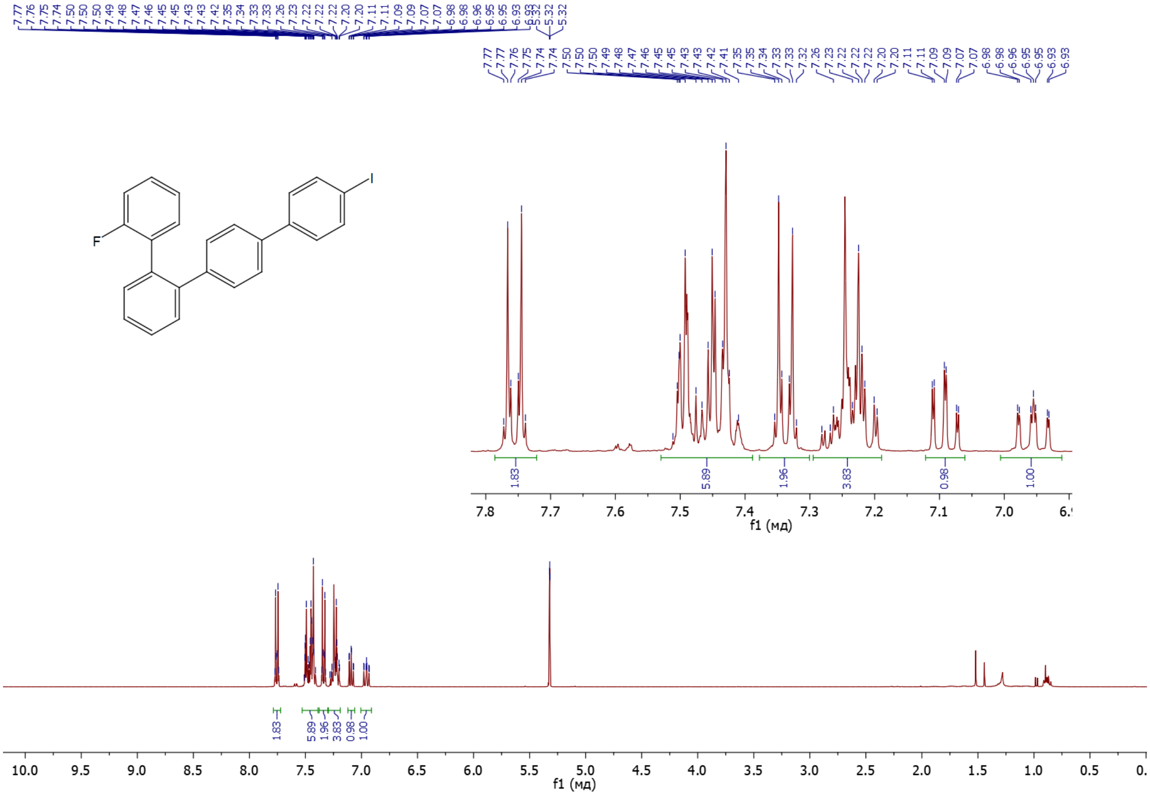


Figure S87: ^{1}H NMR spectrum of 2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (**P15**) (in CD_2Cl_2).

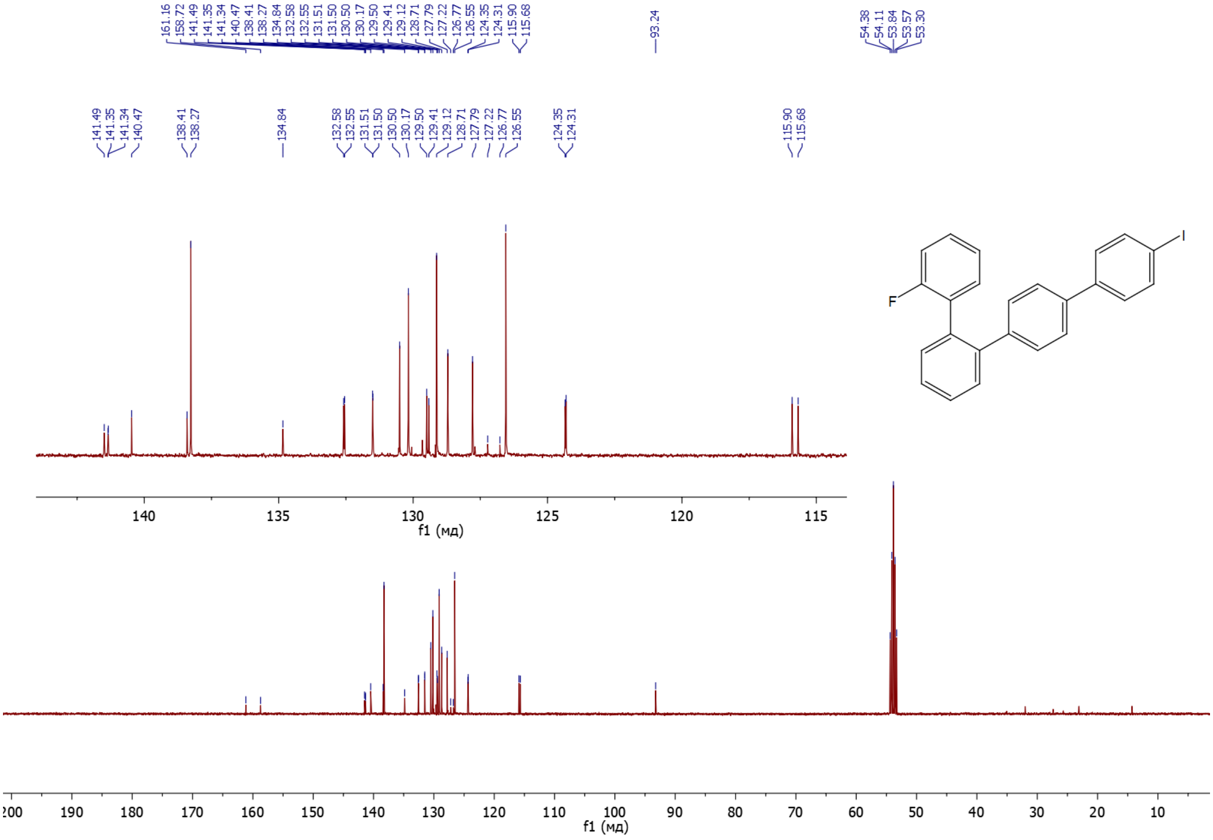


Figure S88: ^{13}C NMR spectrum of 2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (**P15**) (in CD_2Cl_2).

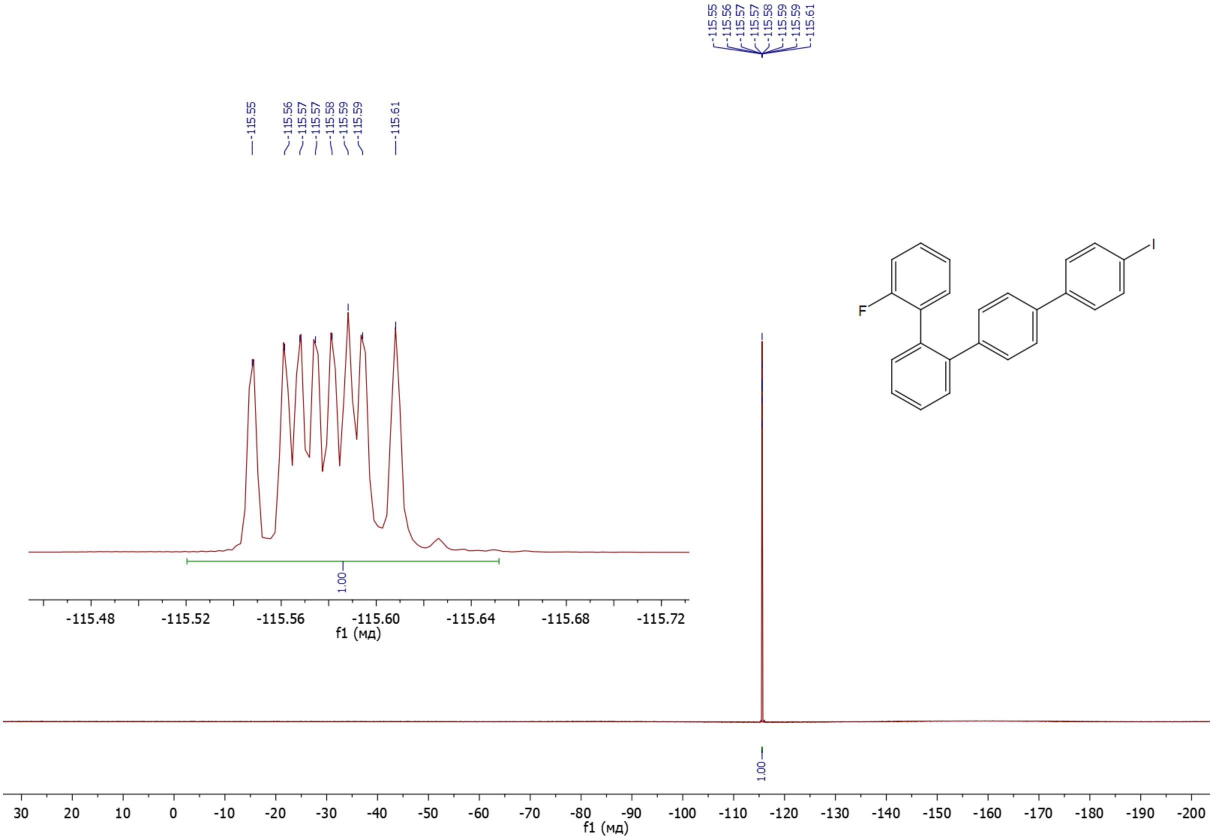


Figure S89: ^{13}C NMR spectrum of 2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (**P15**) (in CD_2Cl_2).

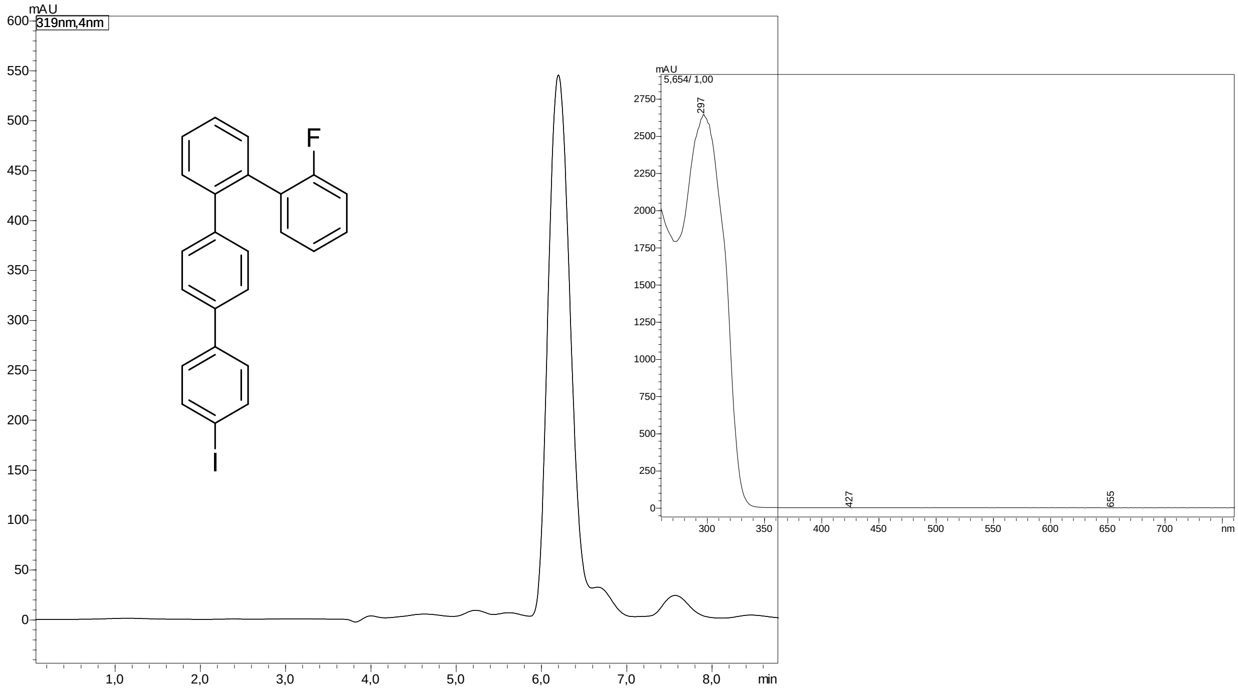


Figure S90: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 4:6, t_R 6.23 min) and UV/vis spectrum (inset) of 2-fluoro-4'''-iodo-1,1':2',1'':4'',1'''-quaterphenyl (**P15**)

2-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5).

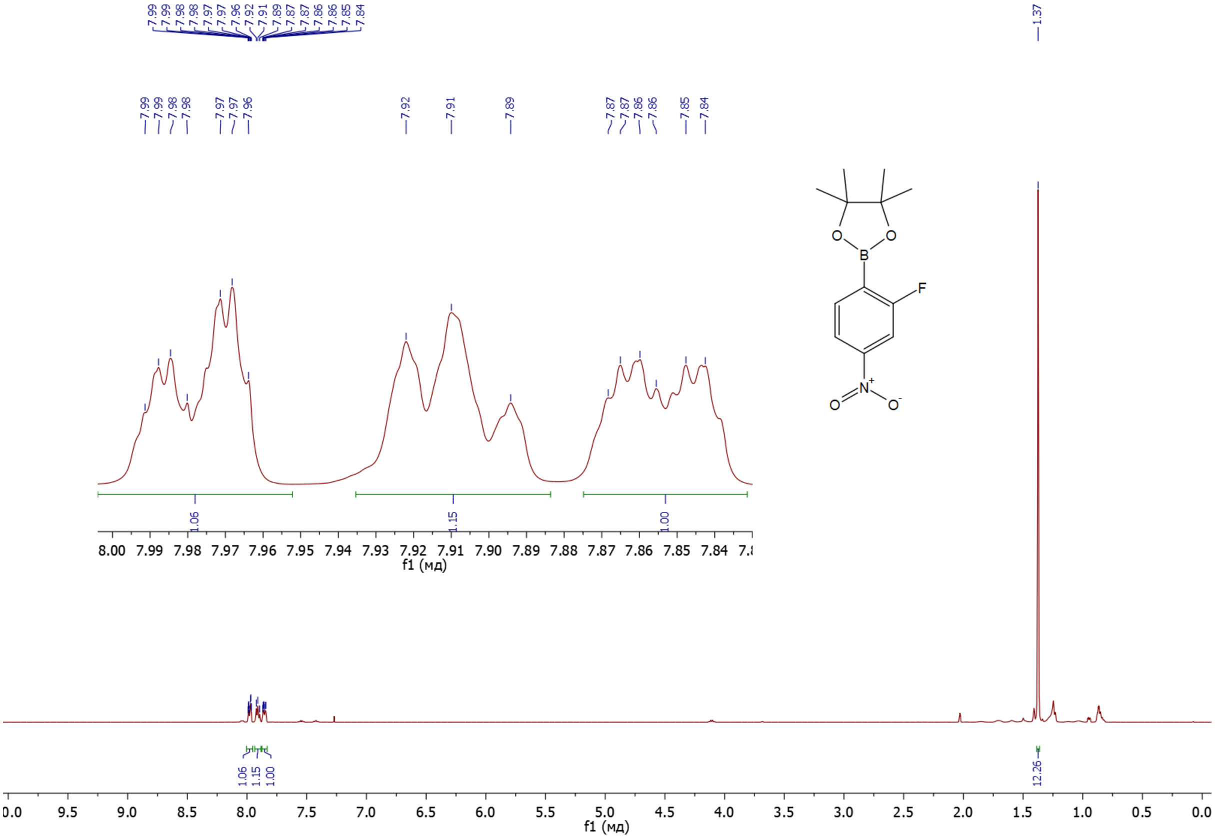


Figure S91: ^{1}H NMR spectrum of **2**-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (in $CDCl_3$).

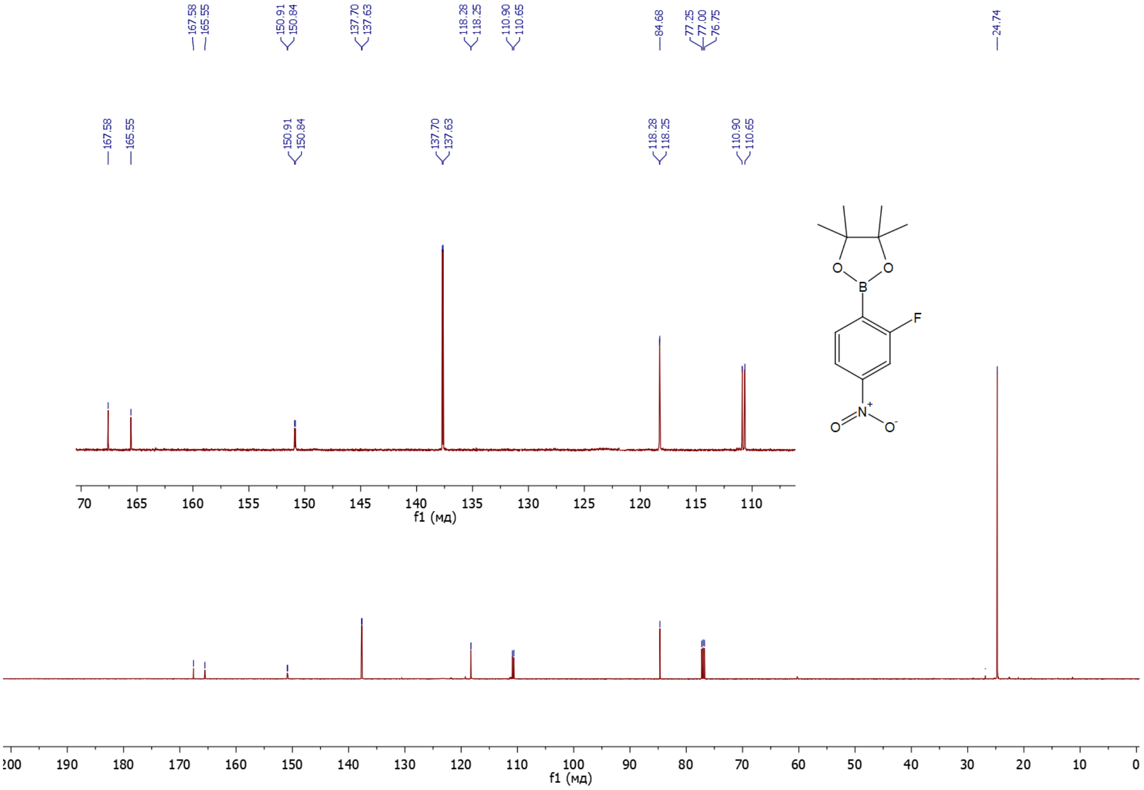


Figure S92: ^{13}C NMR spectrum of **2**-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (in $CDCl_3$).

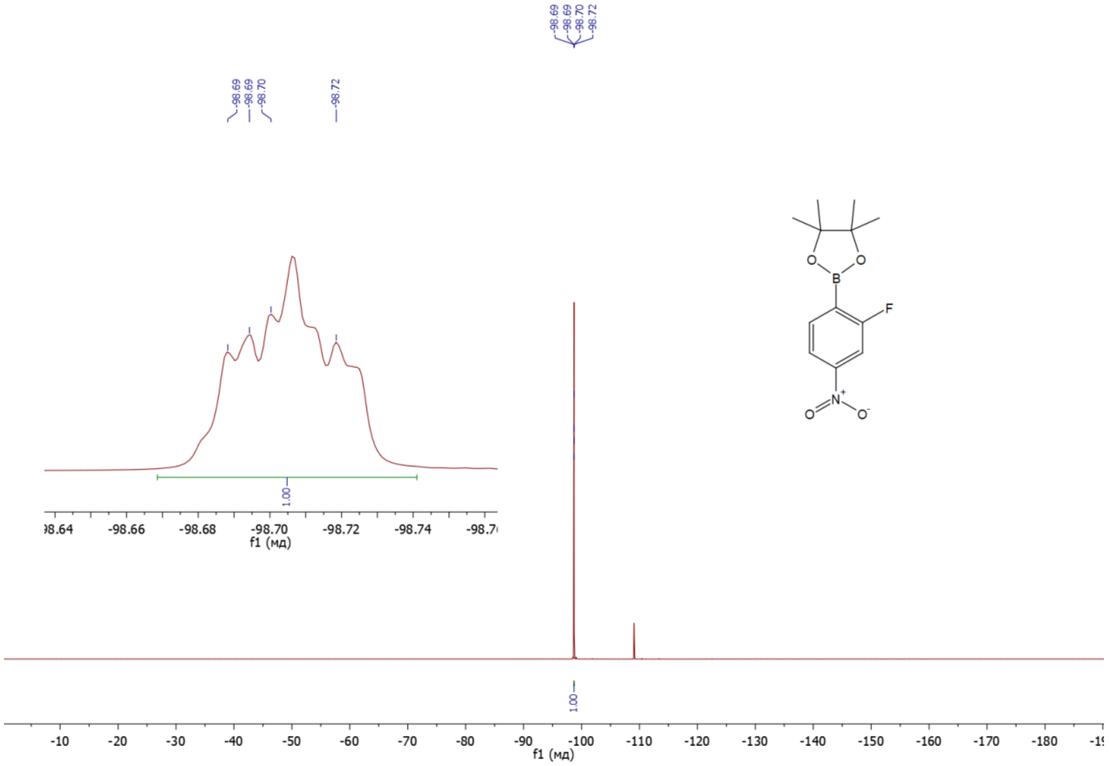


Figure S93: ^{19}F NMR spectrum of **2**-(2-fluoro-4-nitrophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (in CDCl$_3$).

2-fluoro-4-nitro-1,1':2',1''-terphenyl (6).

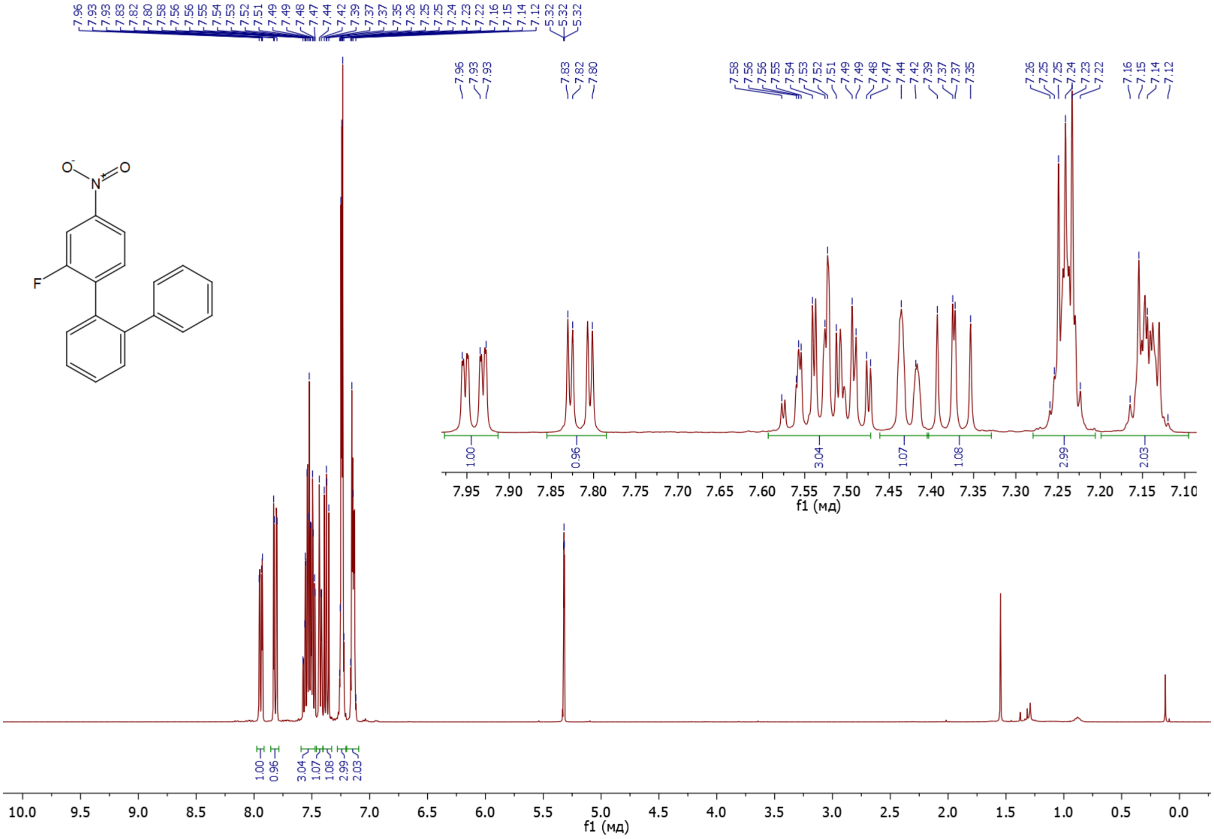


Figure S94: ^{1}H NMR spectrum of 2-fluoro-4-nitro-1,1':2',1"-terphenyl (**6**) (in CD$_2$Cl$_2$).

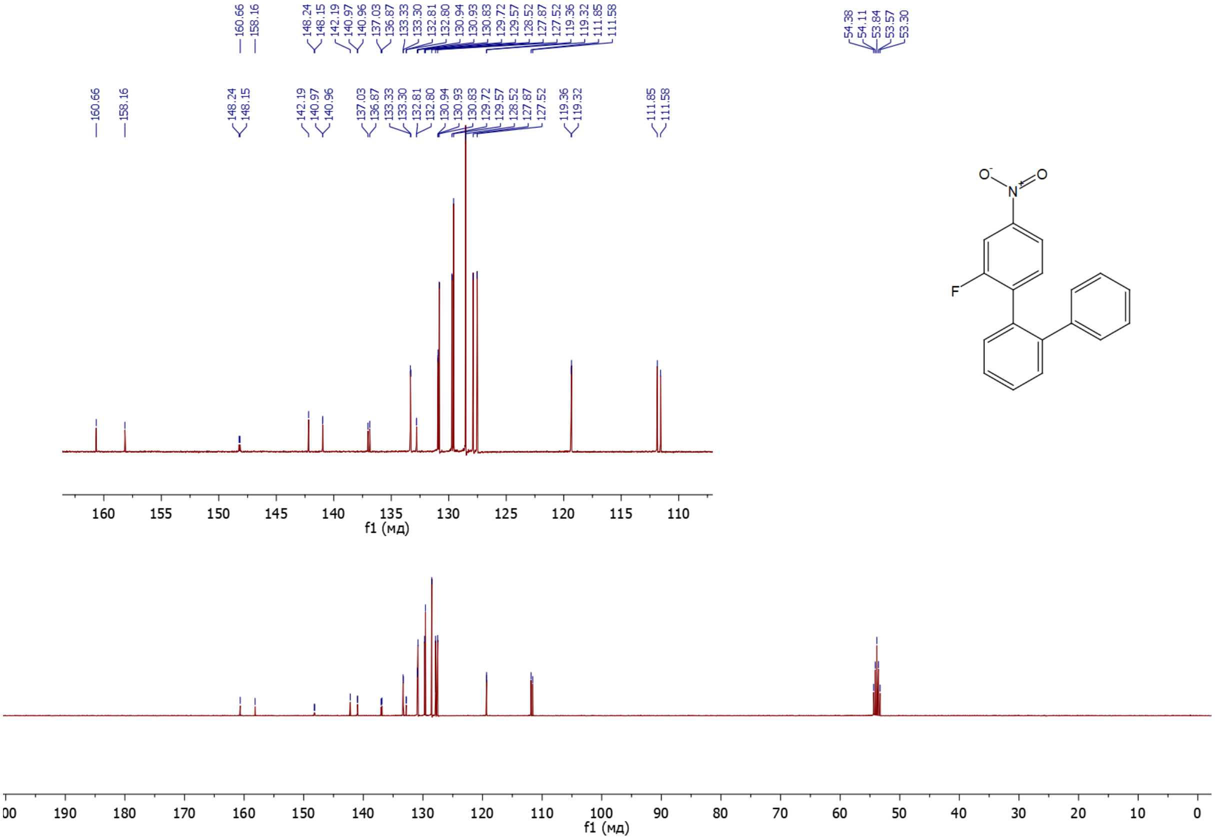


Figure S95: ^{13}C NMR spectrum of 2-fluoro-4-nitro-1,1':2',1''-terphenyl (**6**) (in CD_2Cl_2).

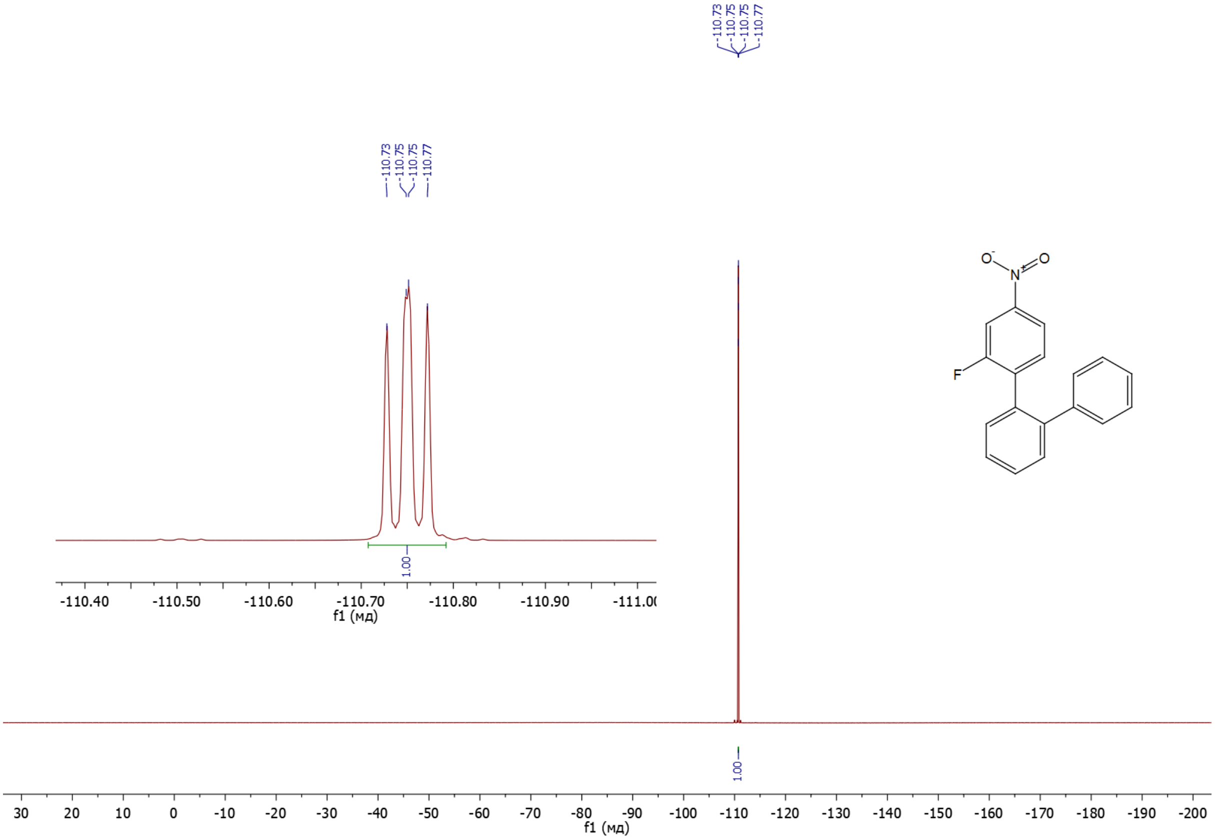


Figure S96: ^{19}F NMR spectrum of 2-fluoro-4-nitro-1,1':2',1''-terphenyl (**6**) (in CD_2Cl_2).

2-fluoro-[1,1':2',1''-terphenyl]-4-amine (7).

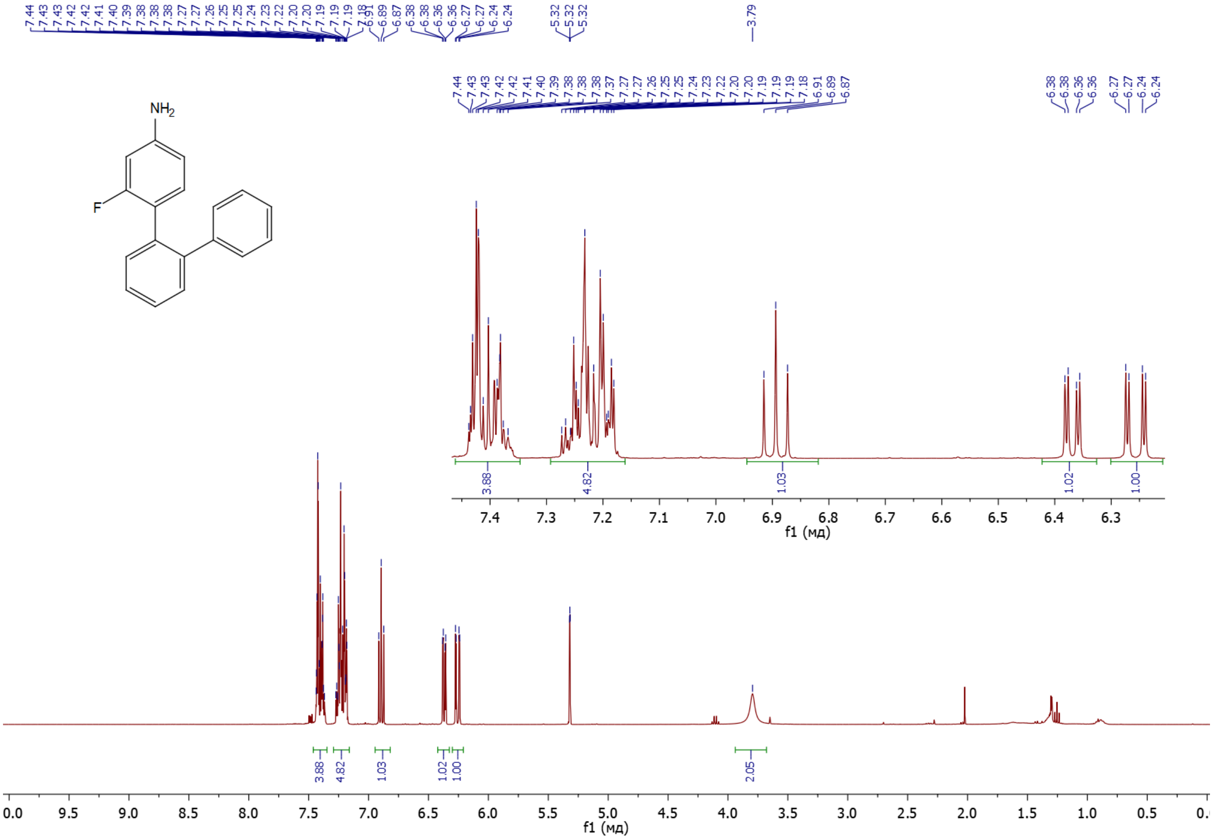


Figure S97: ^{1}H NMR spectrum of 2-fluoro-[1,1':2',1''-terphenyl]-4-amine (7) (in CD_2Cl_2).

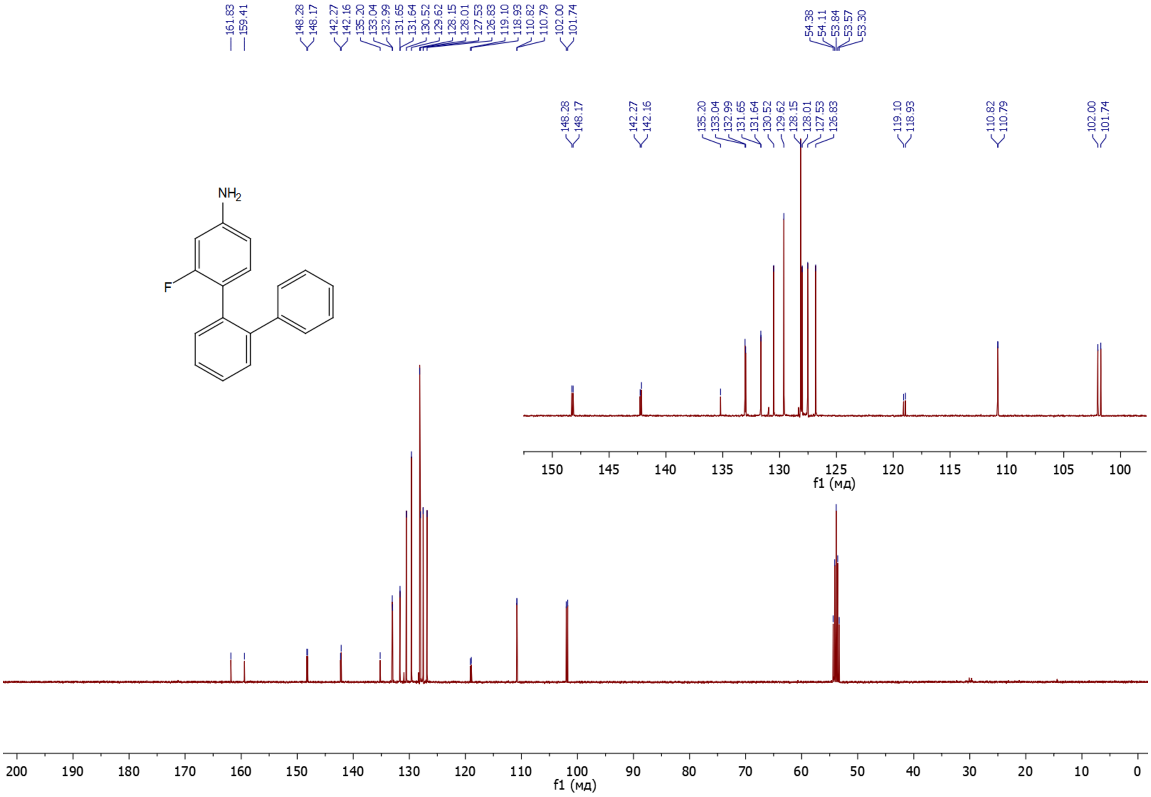


Figure S98: ^{13}C NMR spectrum of 2-fluoro-[1,1':2',1''-terphenyl]-4-amine (7) (in CD_2Cl_2).

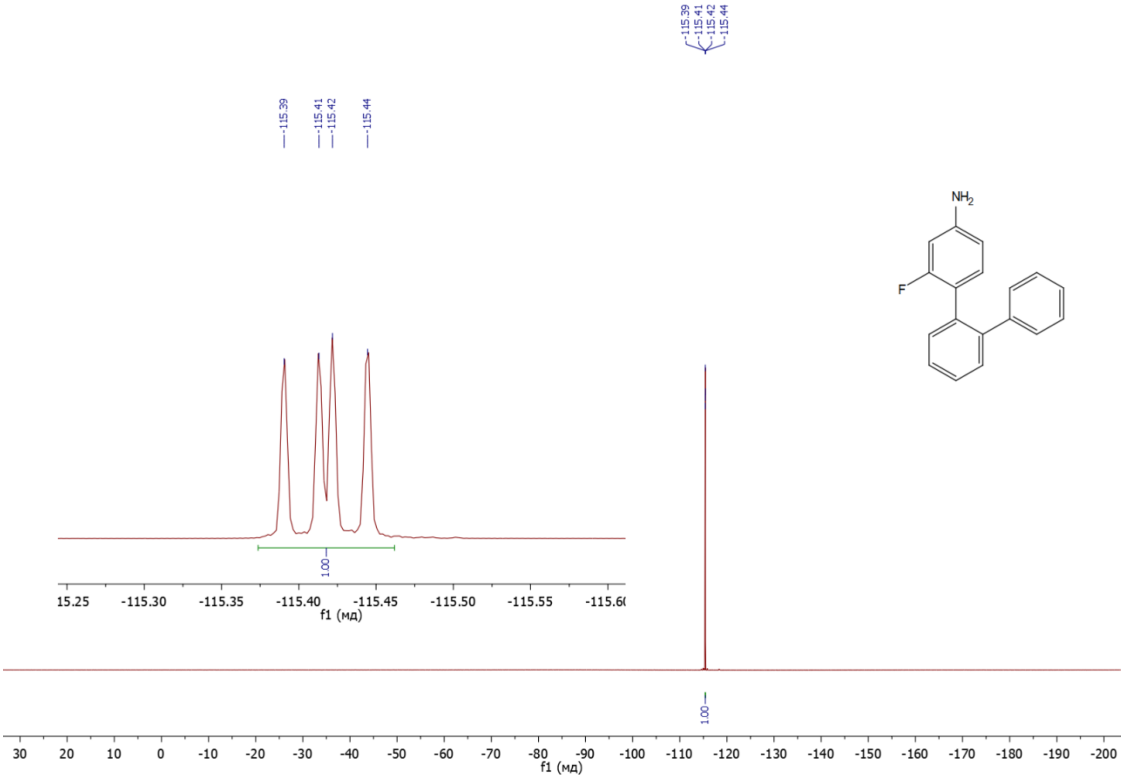


Figure S99: ^{19}F NMR spectrum of 2-fluoro-[1,1':2',1''-terphenyl]-4-amine (**7**) (in CD_2Cl_2).

2-fluoro-4-iodo-1,1':2',1''-terphenyl (P16).

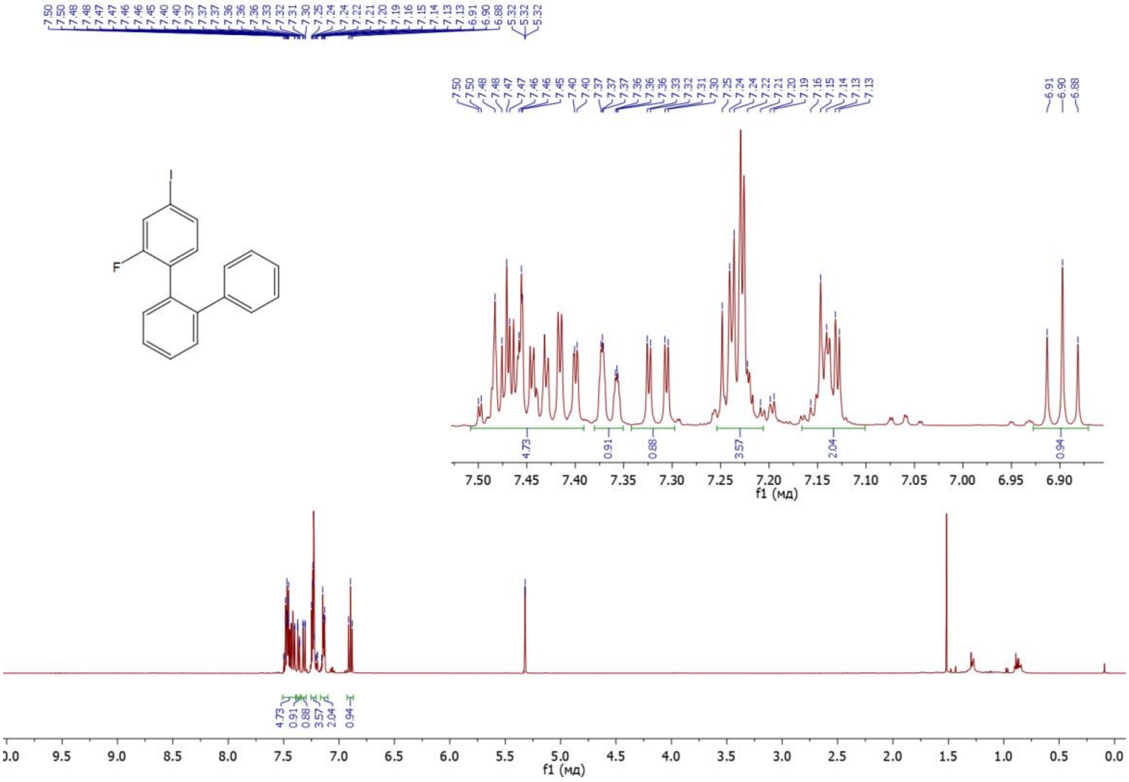


Figure S100: ^{1}H NMR spectrum of 2-fluoro-4-iodo-1,1':2',1''-terphenyl (**P16**) (in CD_2Cl_2).

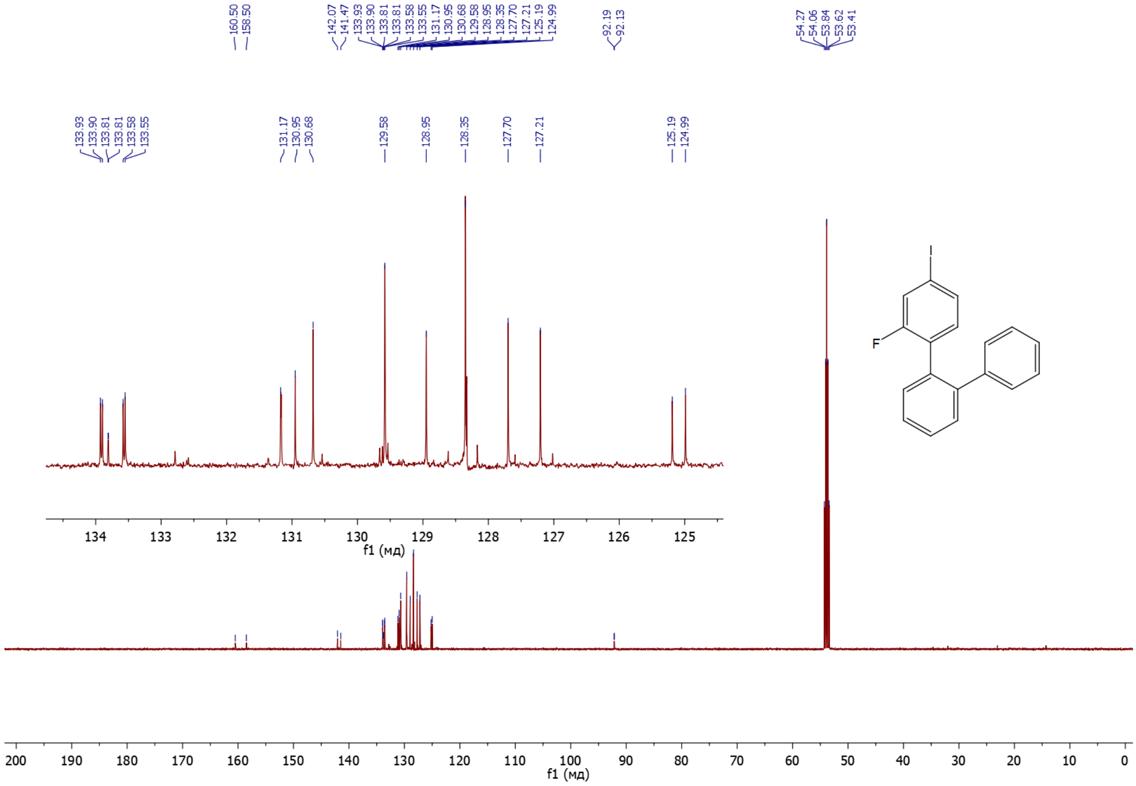


Figure S101: ^{13}C NMR spectrum of 2-fluoro-4-iodo-1,1':2',1''-terphenyl (**P16**) (in CD_2Cl_2).

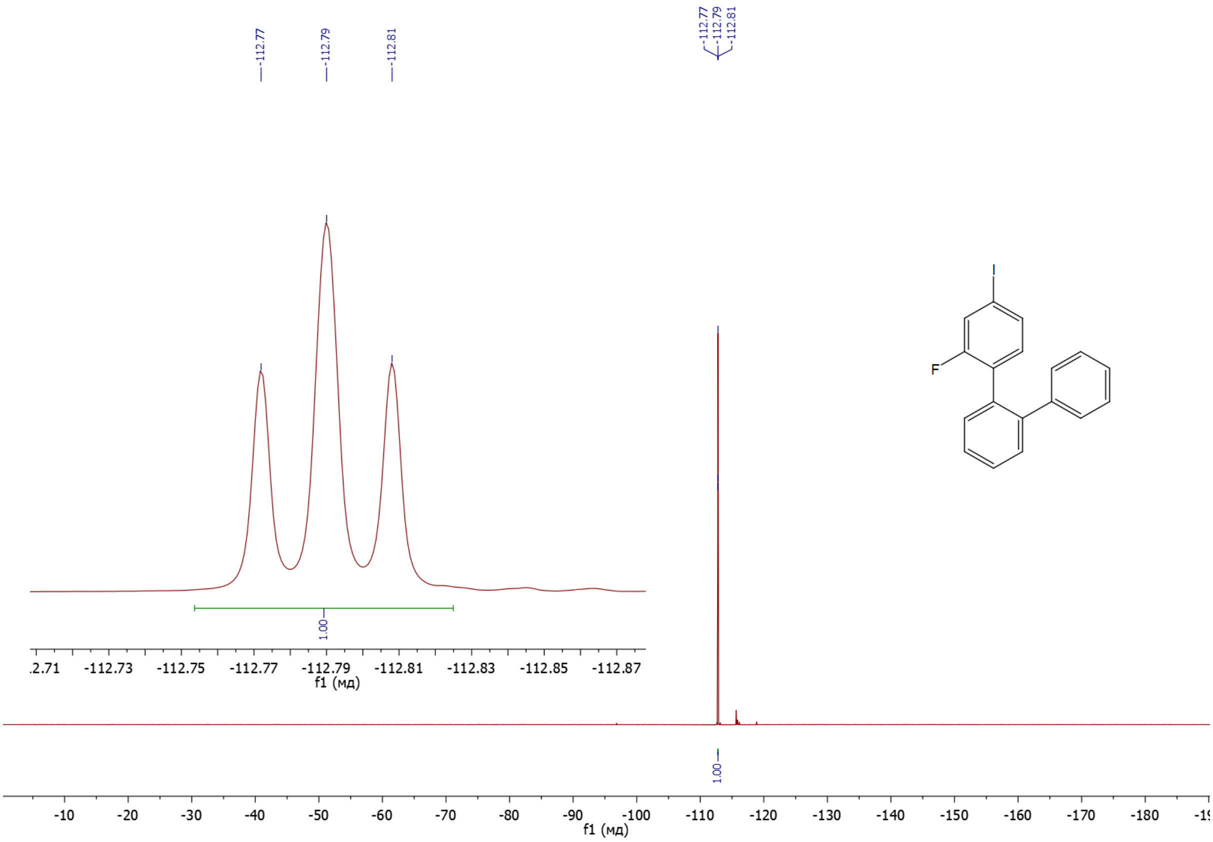


Figure S102: ^{19}F NMR spectrum of 2-fluoro-4-iodo-1,1':2',1''-terphenyl (**P16**) (in CD_2Cl_2).

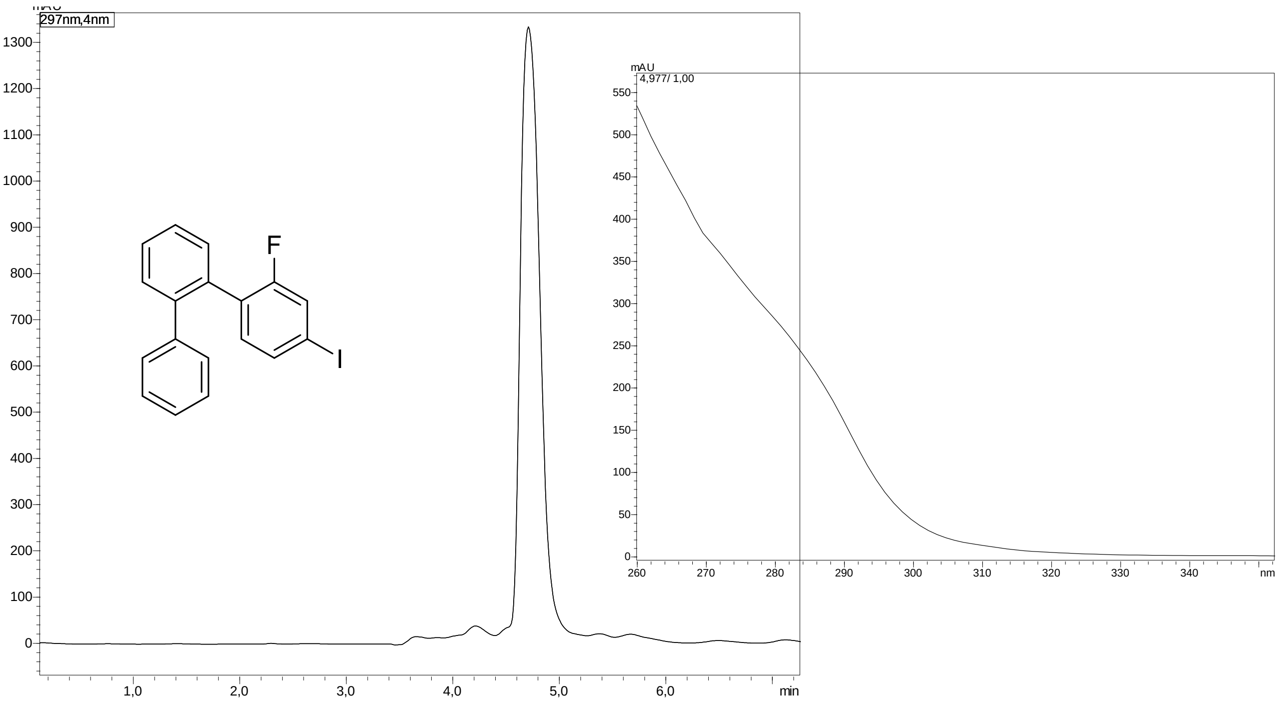


Figure S103: HPLC chromatogram (PBR column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6, t_R 4.66 min) and UV/vis spectrum (inset) of 2-fluoro-4-iodo-1,1':2',1"-terphenyl (**P16**).

2-fluoro-5-nitro-1,1':2',1''-terphenyl (8).

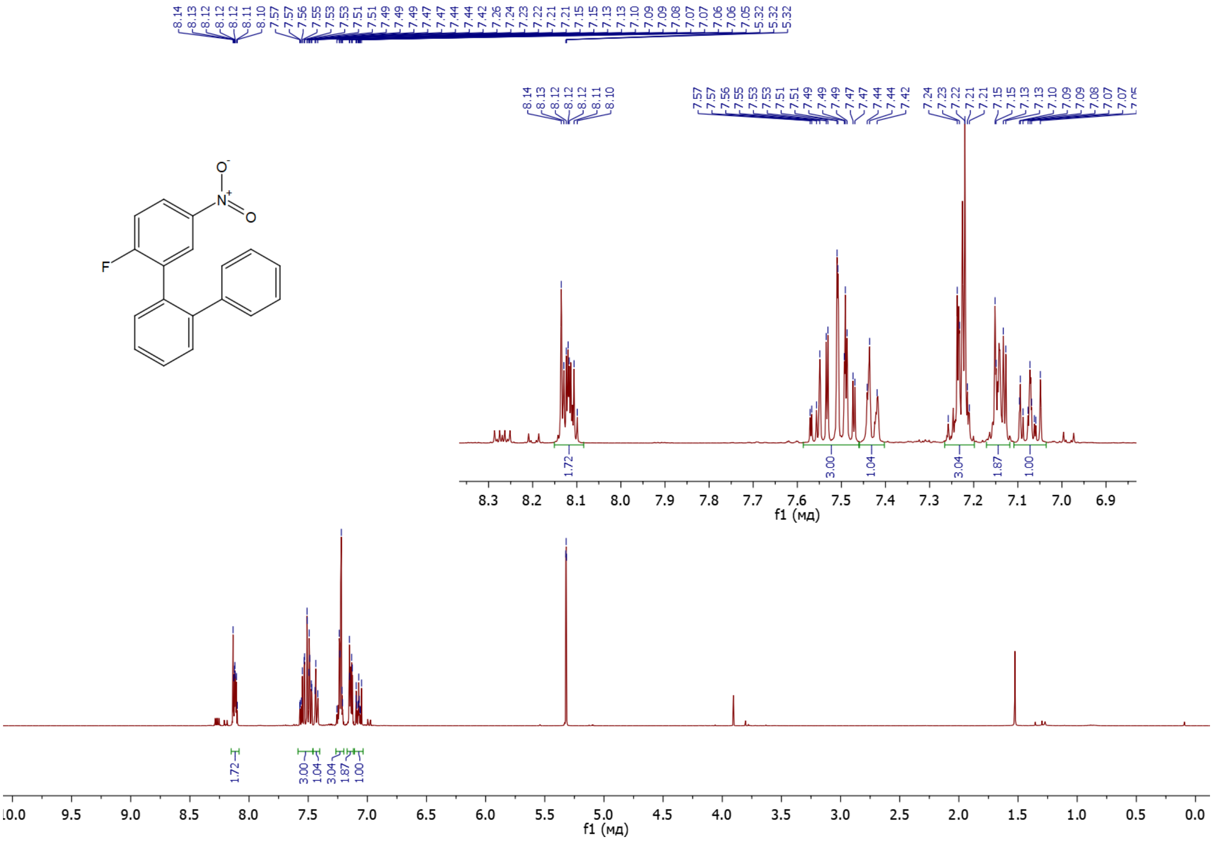


Figure S104: ^{1}H NMR spectrum of 2-fluoro-5-nitro-1,1':2',1"-terphenyl (**8**) (in CD_2Cl_2).

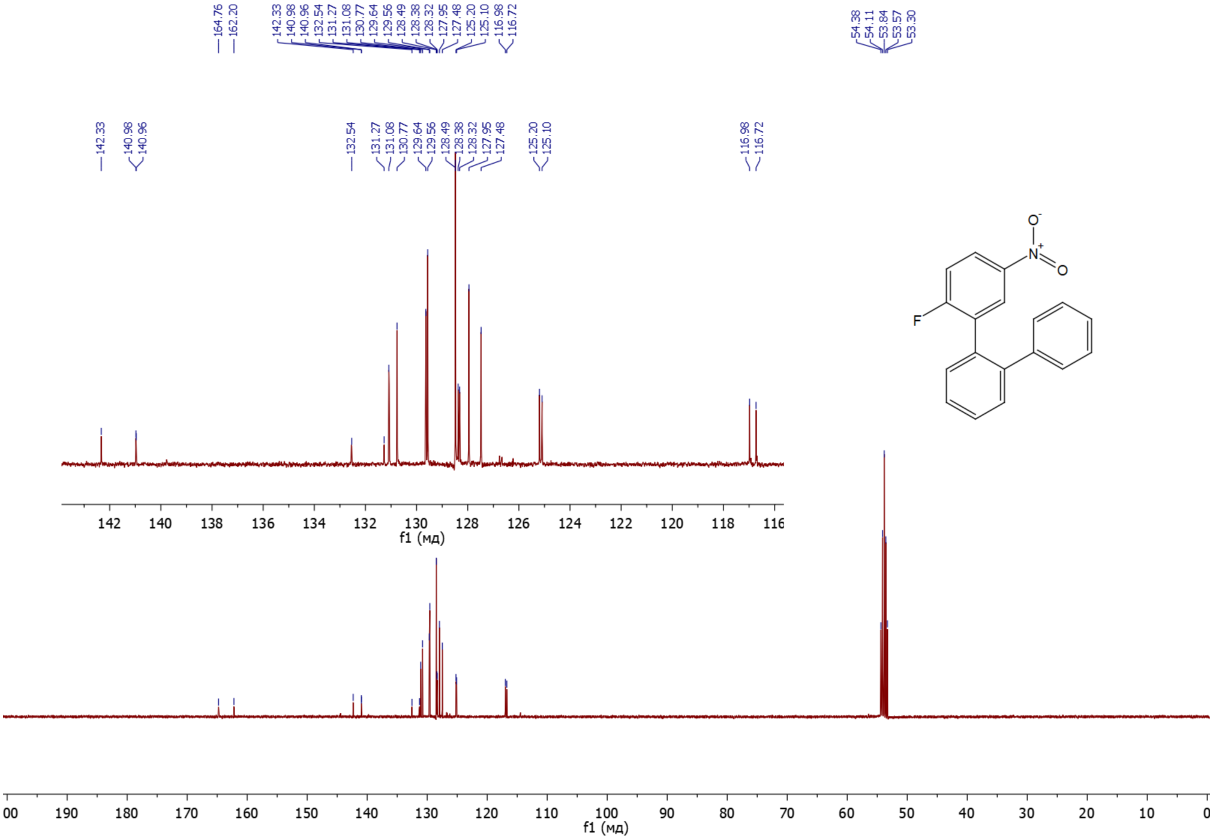


Figure S105: ^{13}C NMR spectrum of 2-fluoro-5-nitro-1,1':2',1''-terphenyl (**8**) (in CD_2Cl_2).

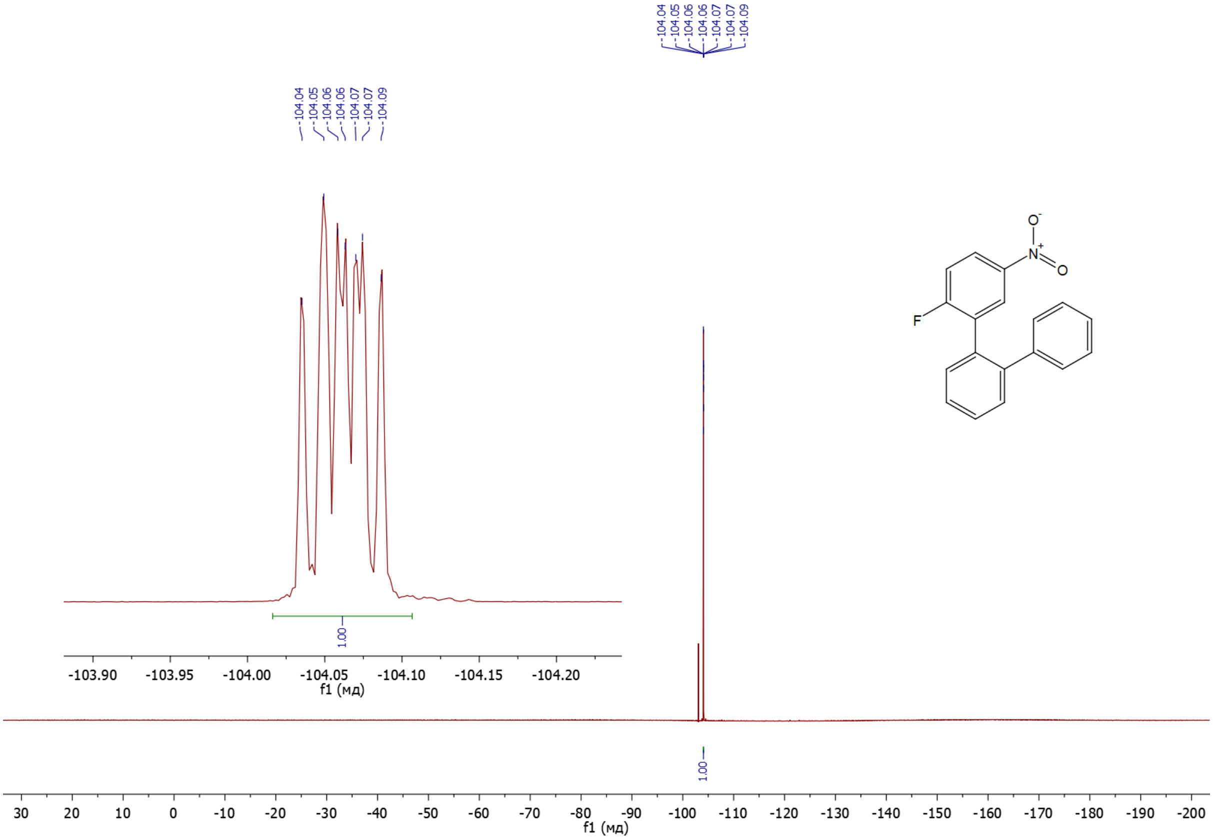


Figure S106: ^{19}F NMR spectrum of 2-fluoro-5-nitro-1,1':2',1''-terphenyl (**8**) (in CD_2Cl_2).

6-fluoro-[1,1':2',1''-terphenyl]-3-amine (9).

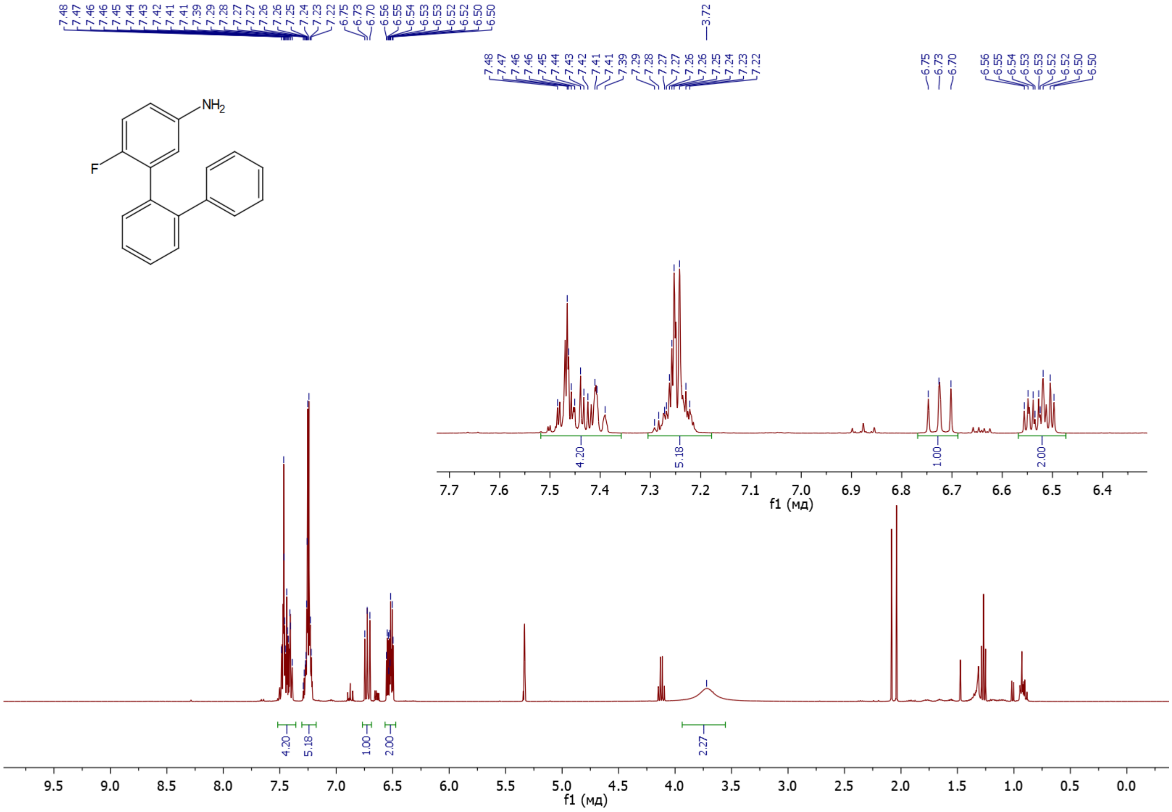


Figure S107: ^{1}H NMR spectrum of **6**-fluoro-[1,1':2',1"-terphenyl]-3-amine (**9**) (in CD_2Cl_2).

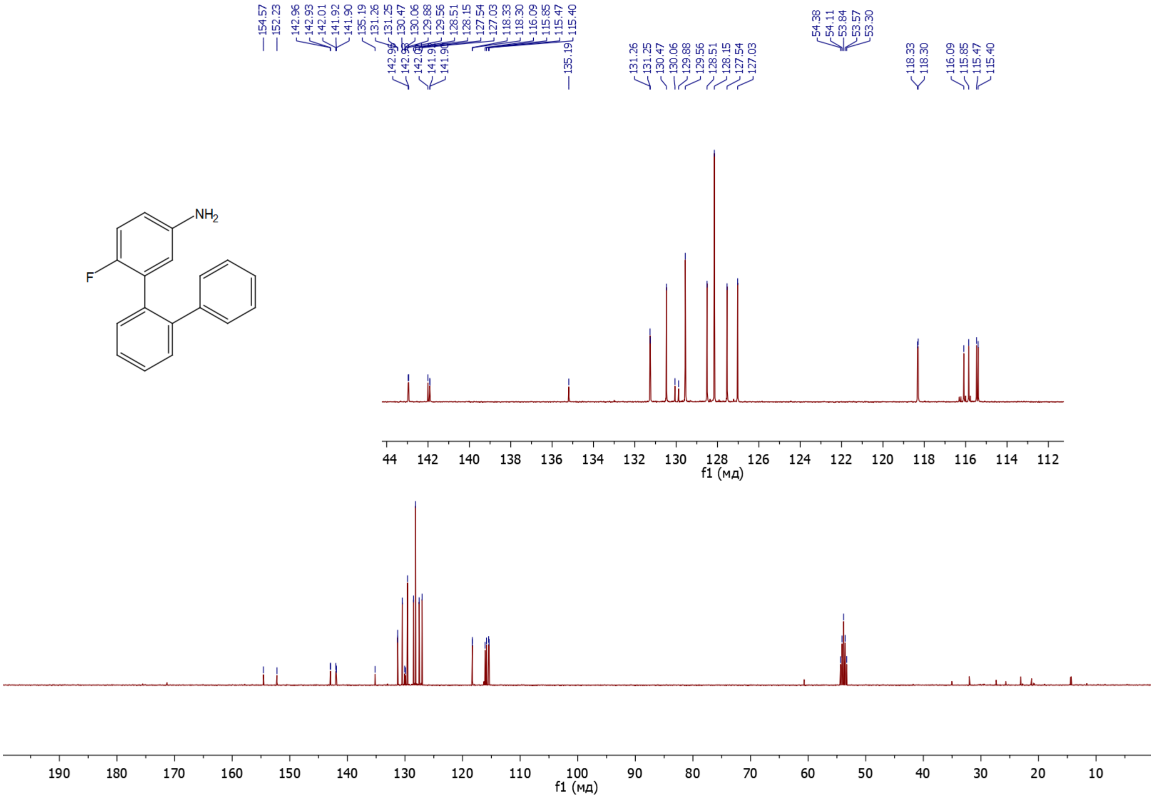


Figure S108: ^{13}C NMR spectrum of **6**-fluoro-[1,1':2',1"-terphenyl]-3-amine (**9**) (in CD_2Cl_2).

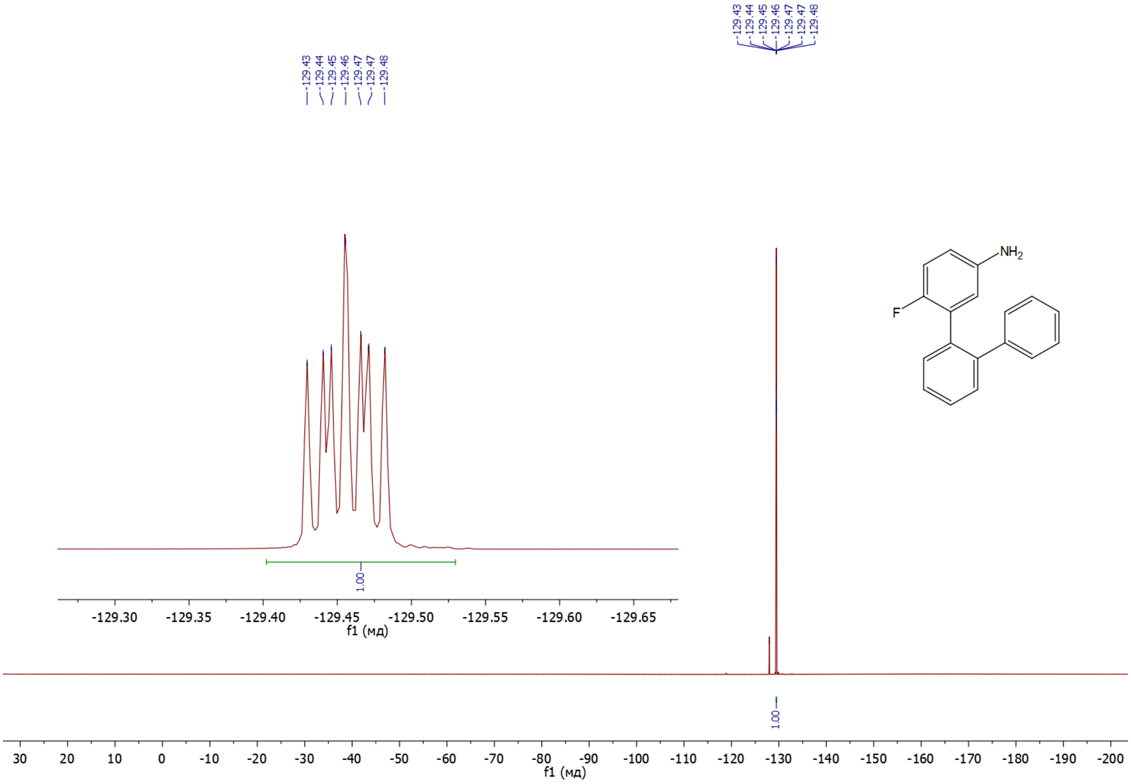


Figure S109: ^{19}F NMR spectrum of **6**-fluoro-[1,1':2',1''-terphenyl]-3-amine (**9**) (in CD_2Cl_2).

2-fluoro-5-iodo-1,1':2',1''-terphenyl (P17).

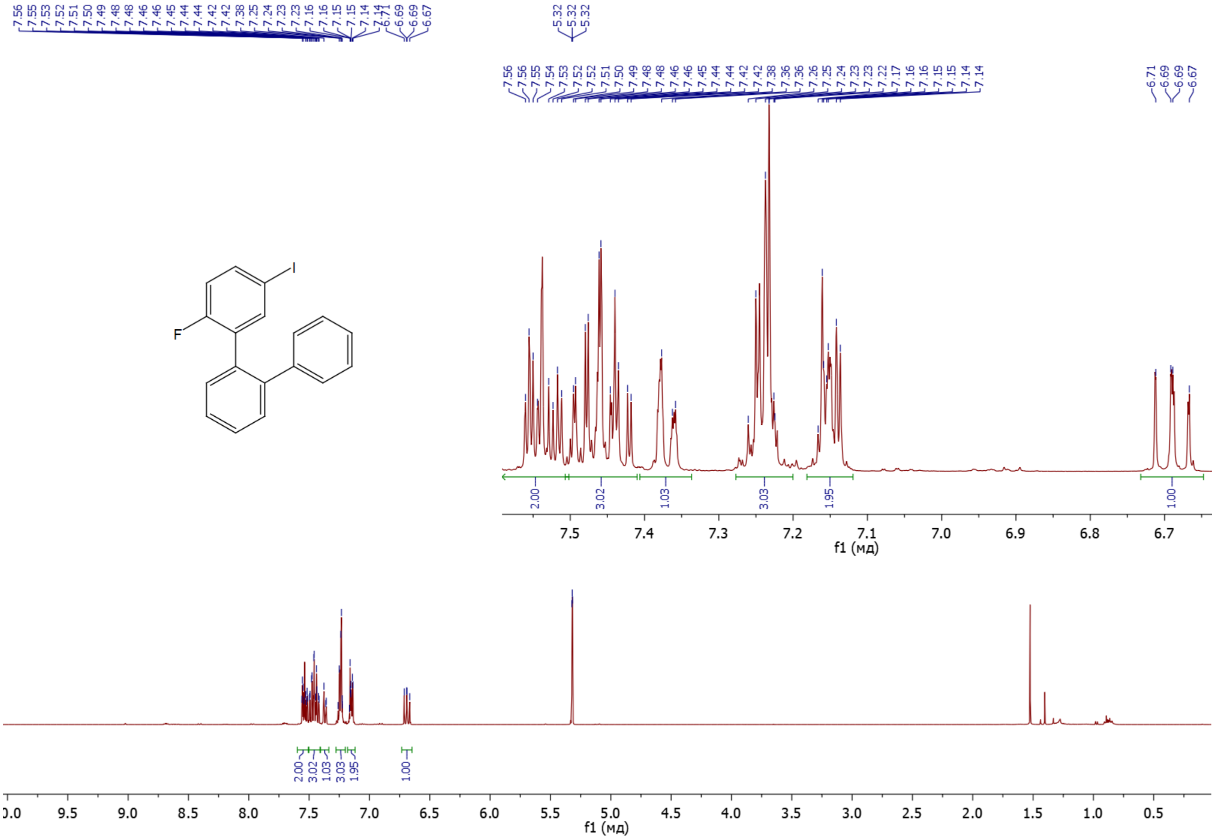


Figure S110: ^{1}H NMR spectrum of 2-fluoro-5-iodo-1,1':2',1''-terphenyl (**P17**) (in CD_2Cl_2).

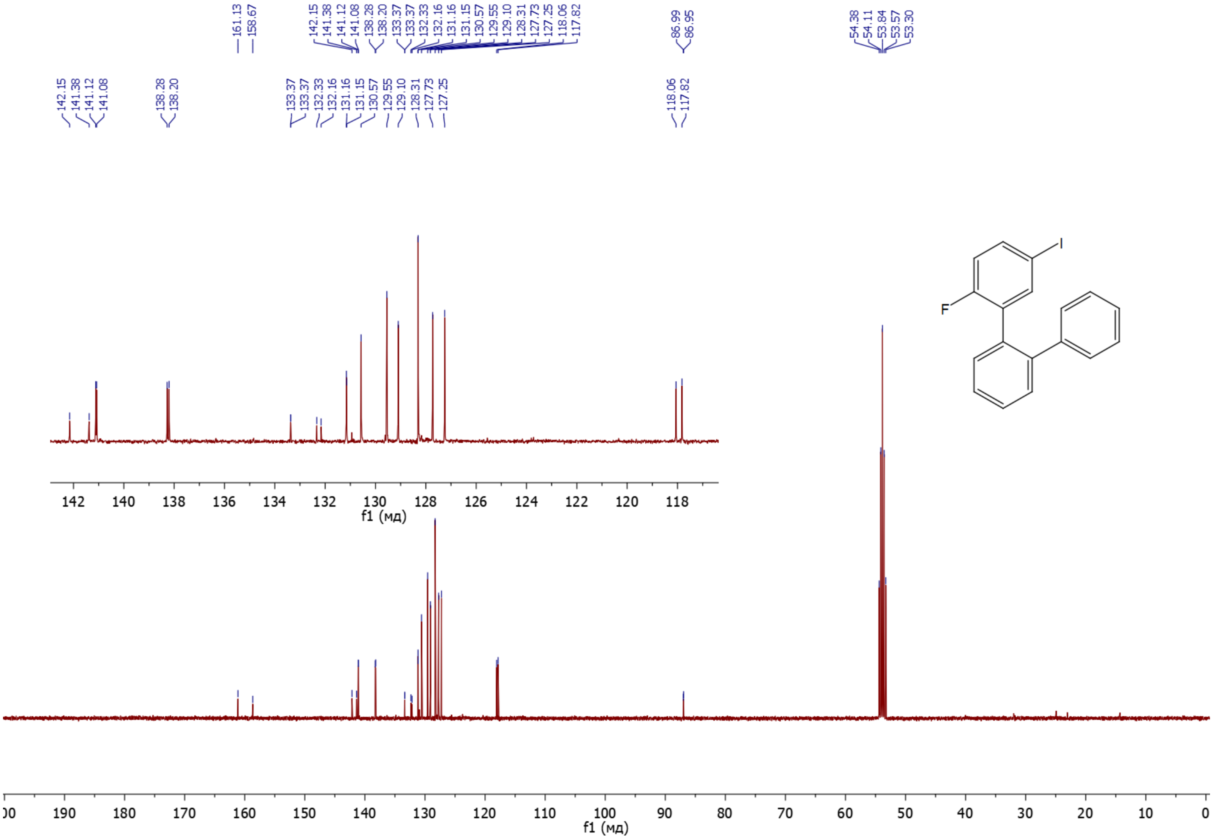


Figure S111: ^{13}C NMR spectrum of 2-fluoro-5-iodo-1,1':2',1''-terphenyl (**P17**) (in CD_2Cl_2).

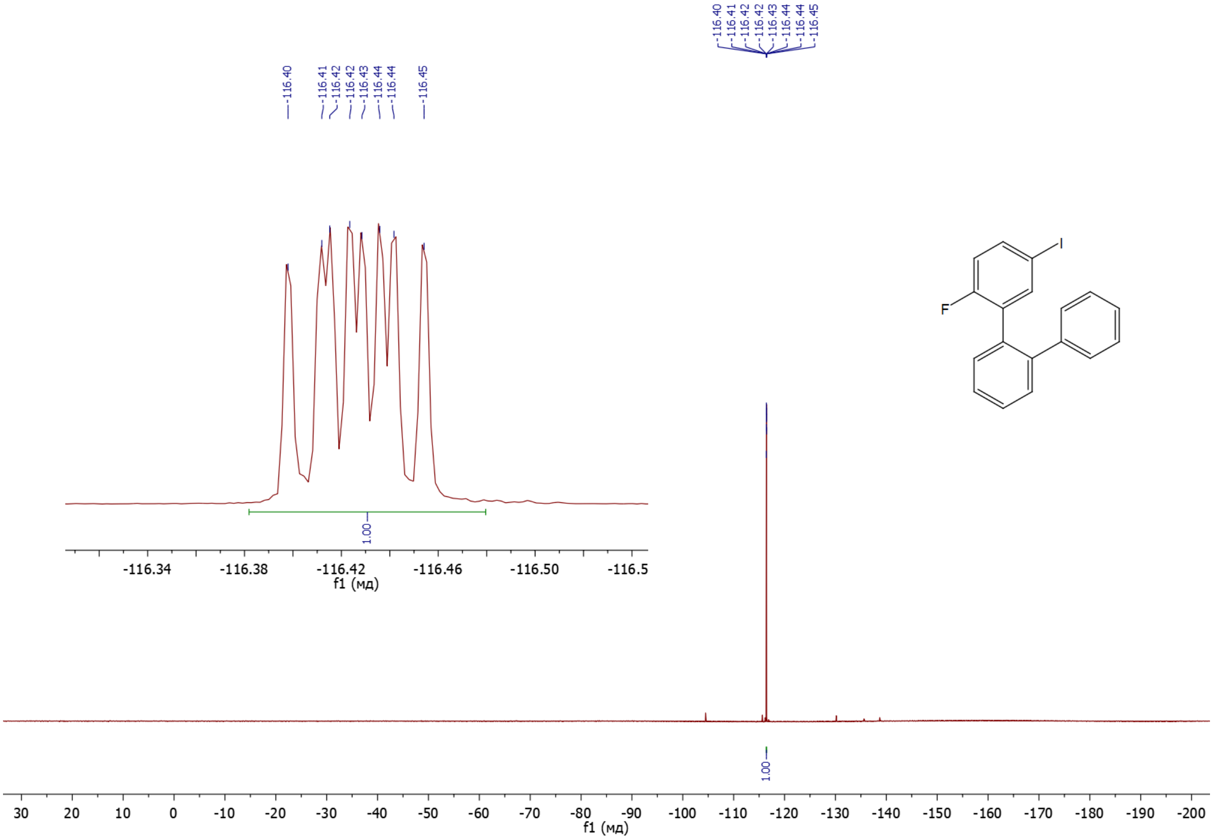


Figure S112: ^{19}F NMR spectrum of 2-fluoro-5-iodo-1,1':2',1''-terphenyl (**P17**) (in CD_2Cl_2).

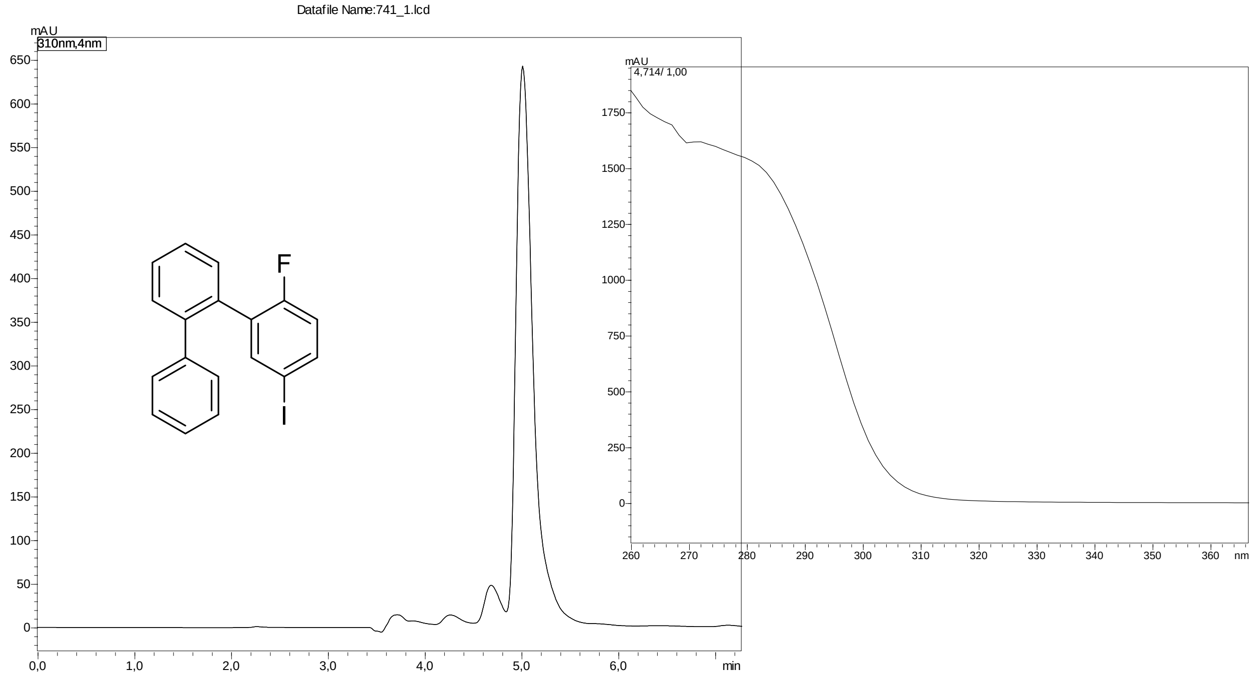


Figure S113: HPLC chromatogram (PBR column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6, t_R 5.03 min) and UV/vis spectrum (inset) of 2-fluoro-5-iodo-1,1':2',1"-terphenyl (**P17**).

6-fluoro-[1,1':2',1''-terphenyl]-2-amine (10).

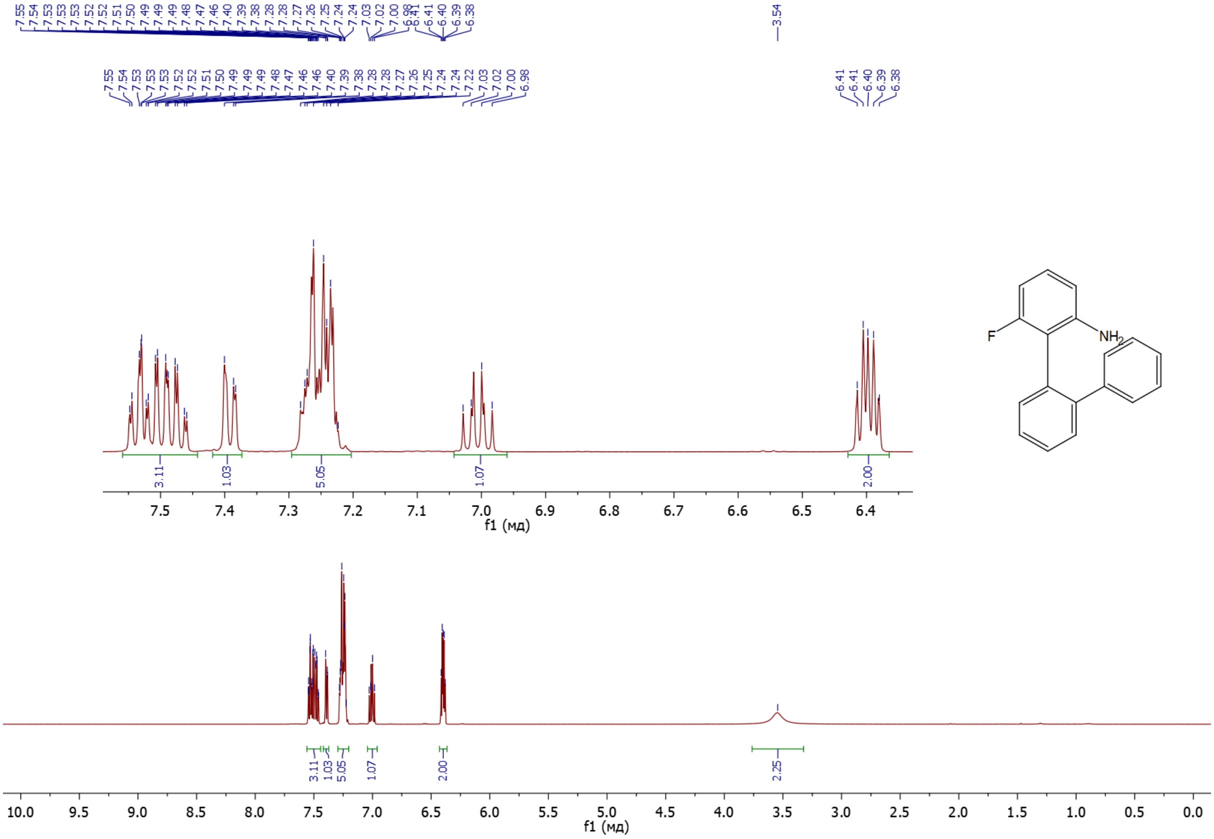


Figure S114: ^{1}H NMR spectrum of 6-fluoro-[1,1':2',1"-terphenyl]-2-amine (**10**) (in $CDCl_3$).

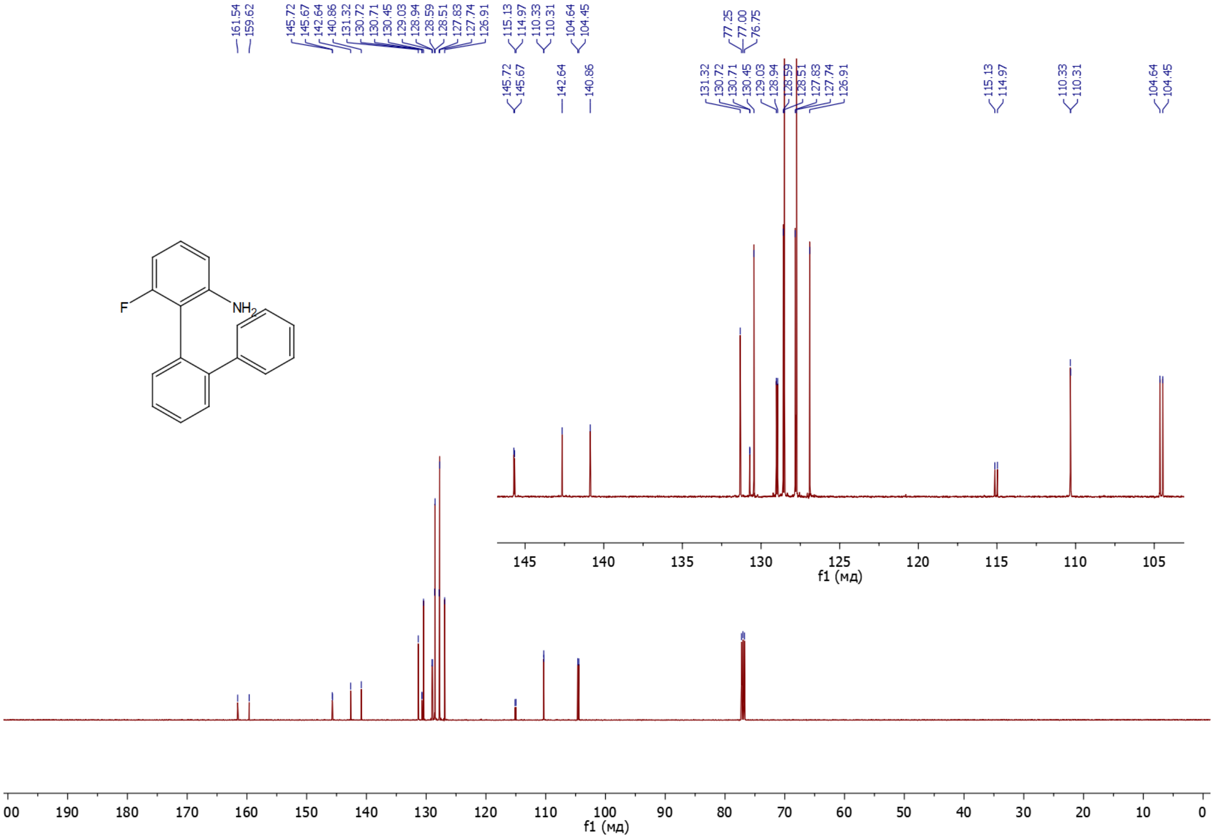


Figure S115: ^{13}C NMR spectrum of 6-fluoro-[1,1':2',1''-terphenyl]-2-amine (**10**) (in CDCl$_3$).

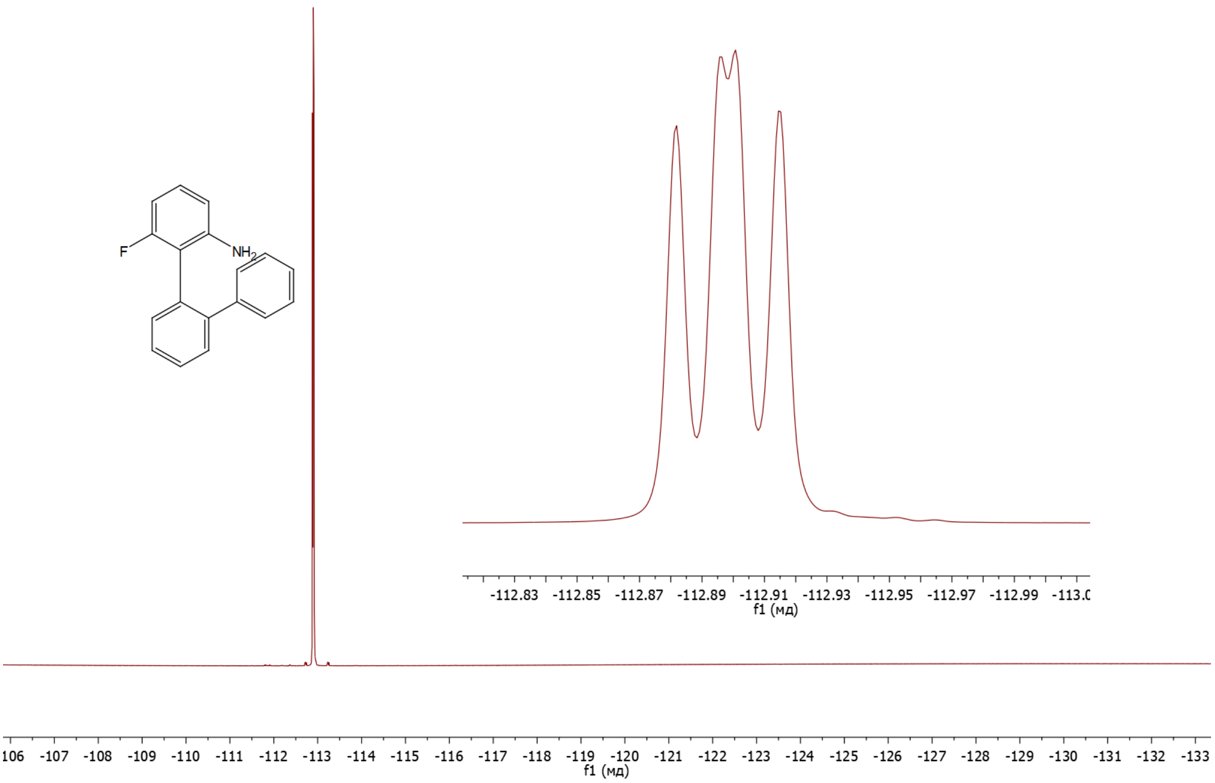


Figure S116: ^{19}F NMR spectrum of 6-fluoro-[1,1':2',1''-terphenyl]-2-amine (**10**) (in CDCl$_3$).

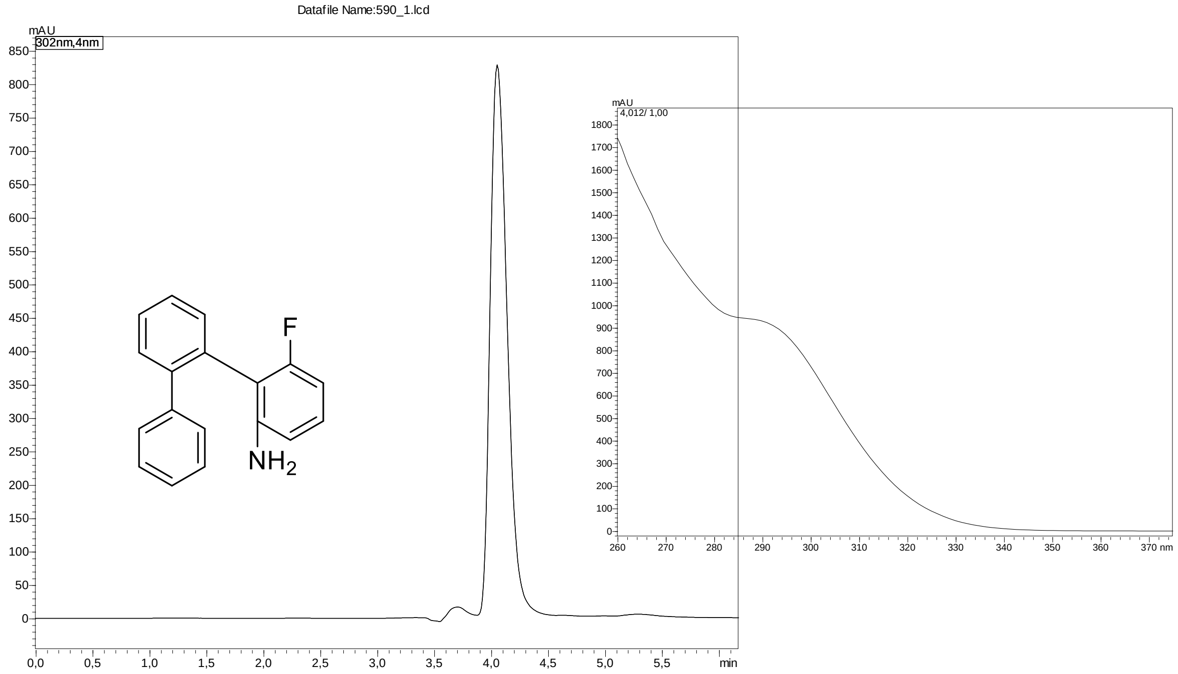


Figure S117: HPLC chromatogram (PBR column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6, t_R 4.11 min) and UV/vis spectrum (inset) of 6-fluoro-[1,1':2',1"-terphenyl]-2-amine (**10**).

2-fluoro-6-iodo-1,1':2',1''-terphenyl (P18).

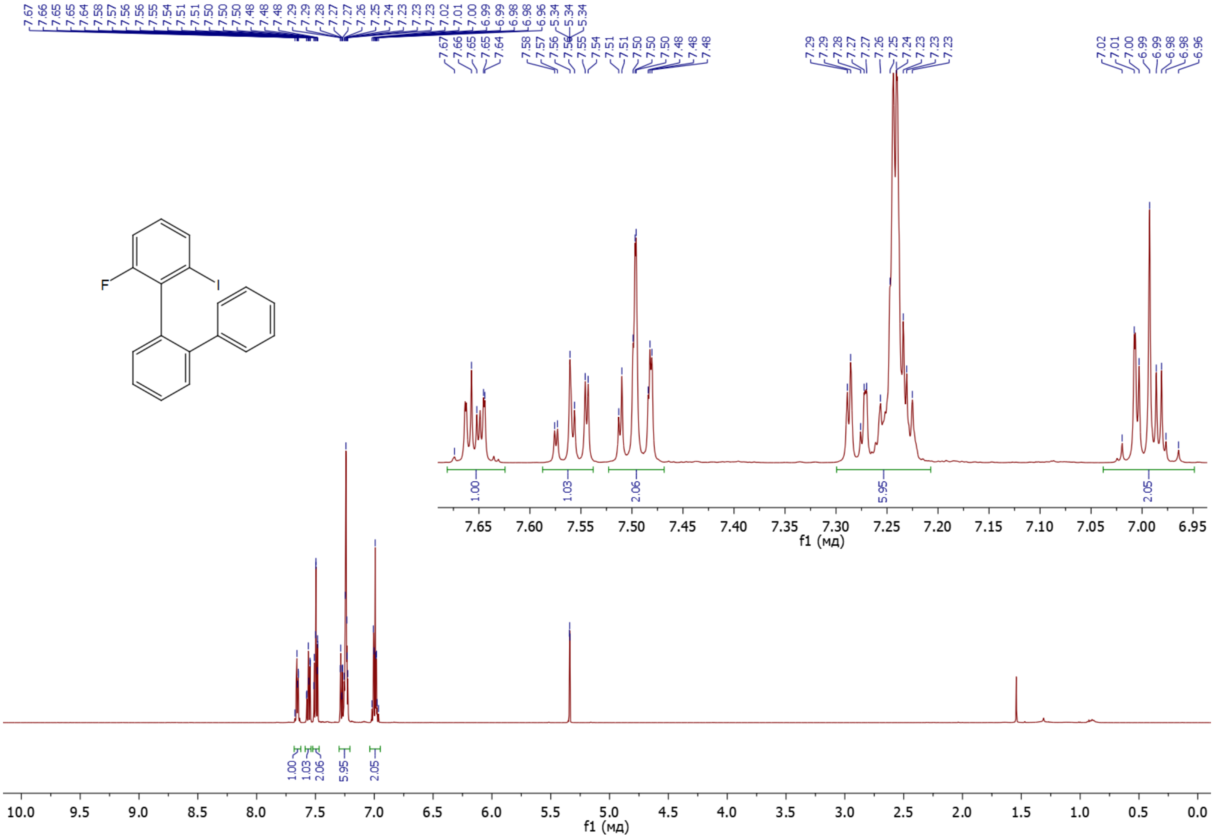


Figure S118: ^{1}H NMR spectrum of 2-fluoro-6-iodo-1,1':2',1"-terphenyl (**P18**) (in CD_2Cl_2).

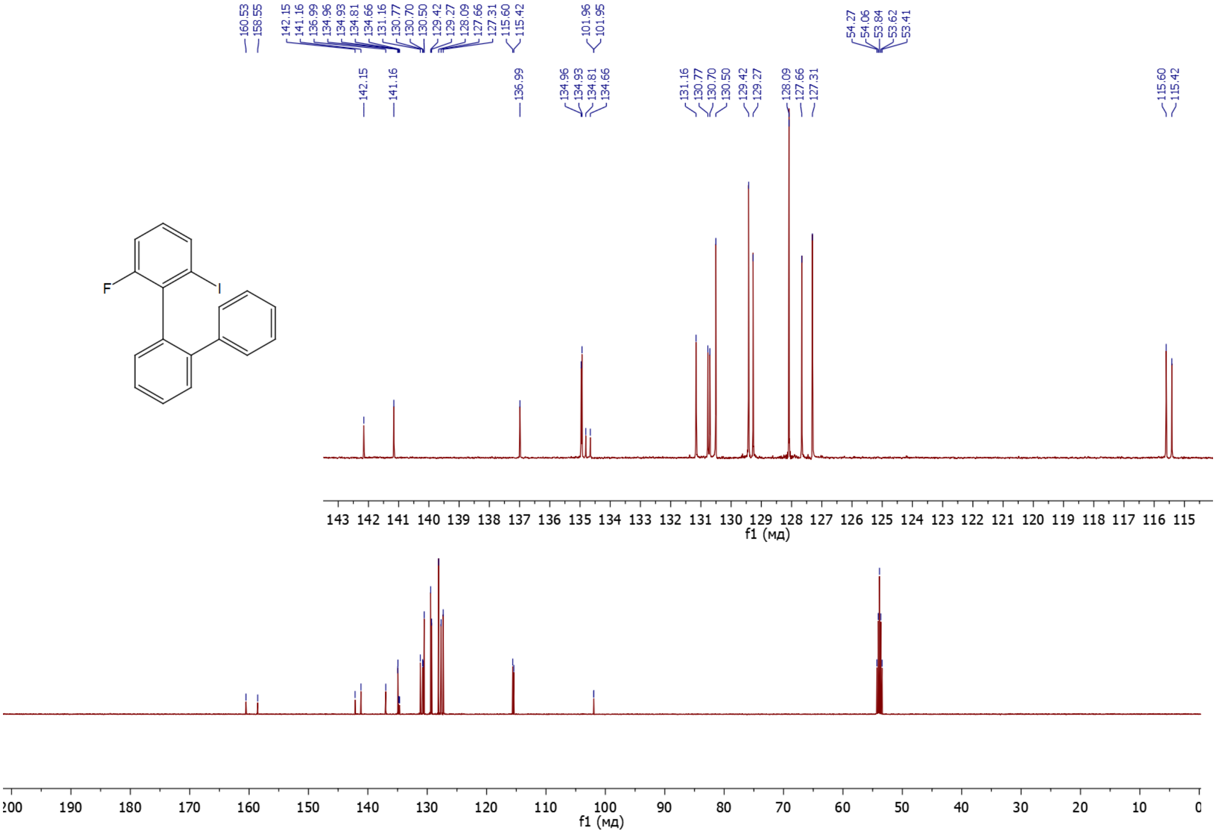


Figure S119: ^{13}C NMR spectrum of 2-fluoro-6-iodo-1,1':2',1''-terphenyl (**P18**) (in CD_2Cl_2).

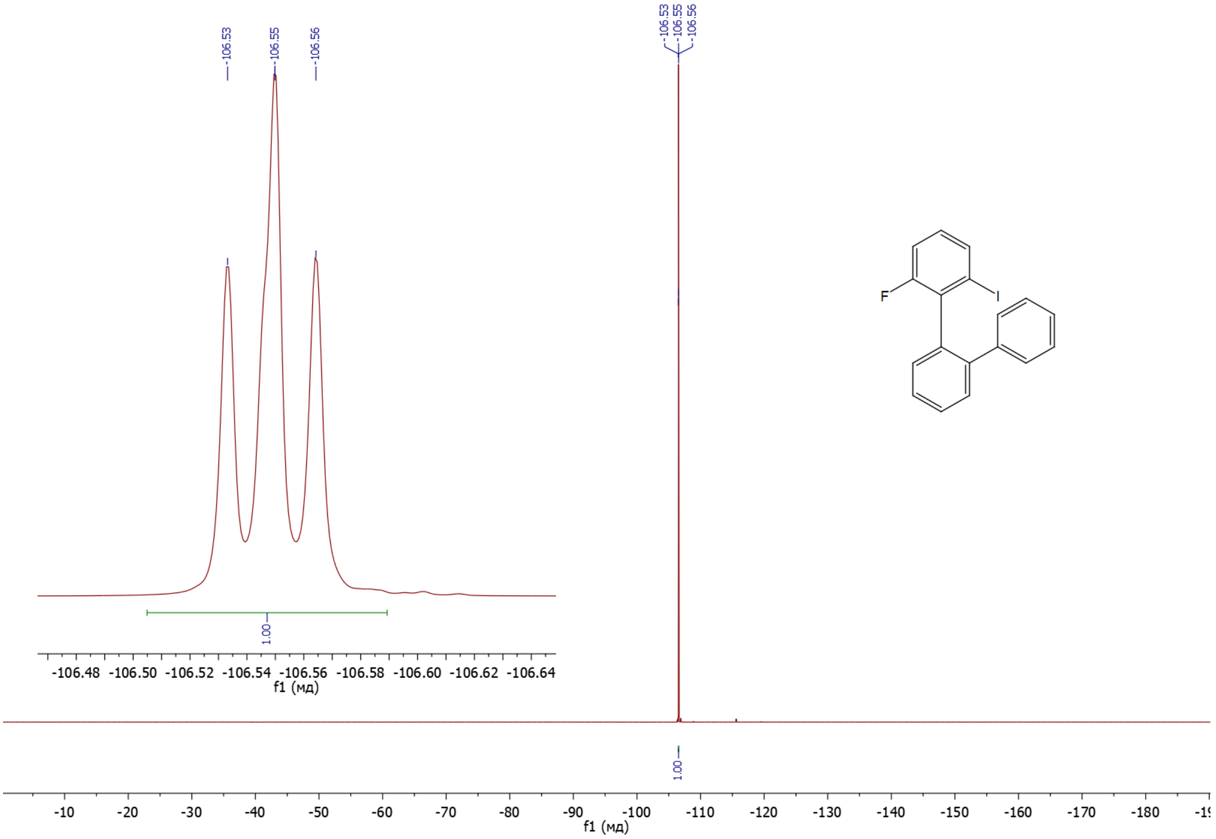


Figure S120: ^{19}F NMR spectrum of 2-fluoro-6-iodo-1,1':2',1''-terphenyl (**P18**) (in CD_2Cl_2).

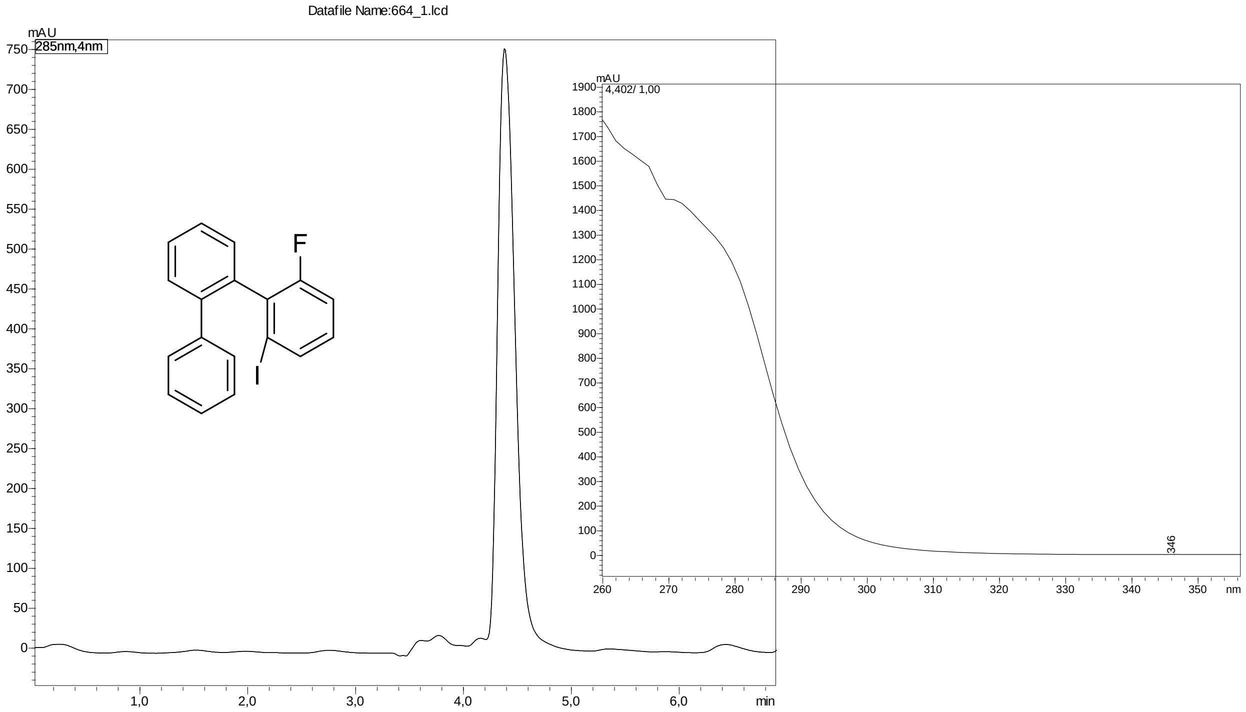


Figure S121: HPLC chromatogram (PBR column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6, t_R 4.22 min) and UV/vis spectrum (inset) of 2-fluoro-6-iodo-1,1':2',1"-terphenyl (**P18**)

2-fluoro-3-iodo-1,1':2',1''-terphenyl (P19).

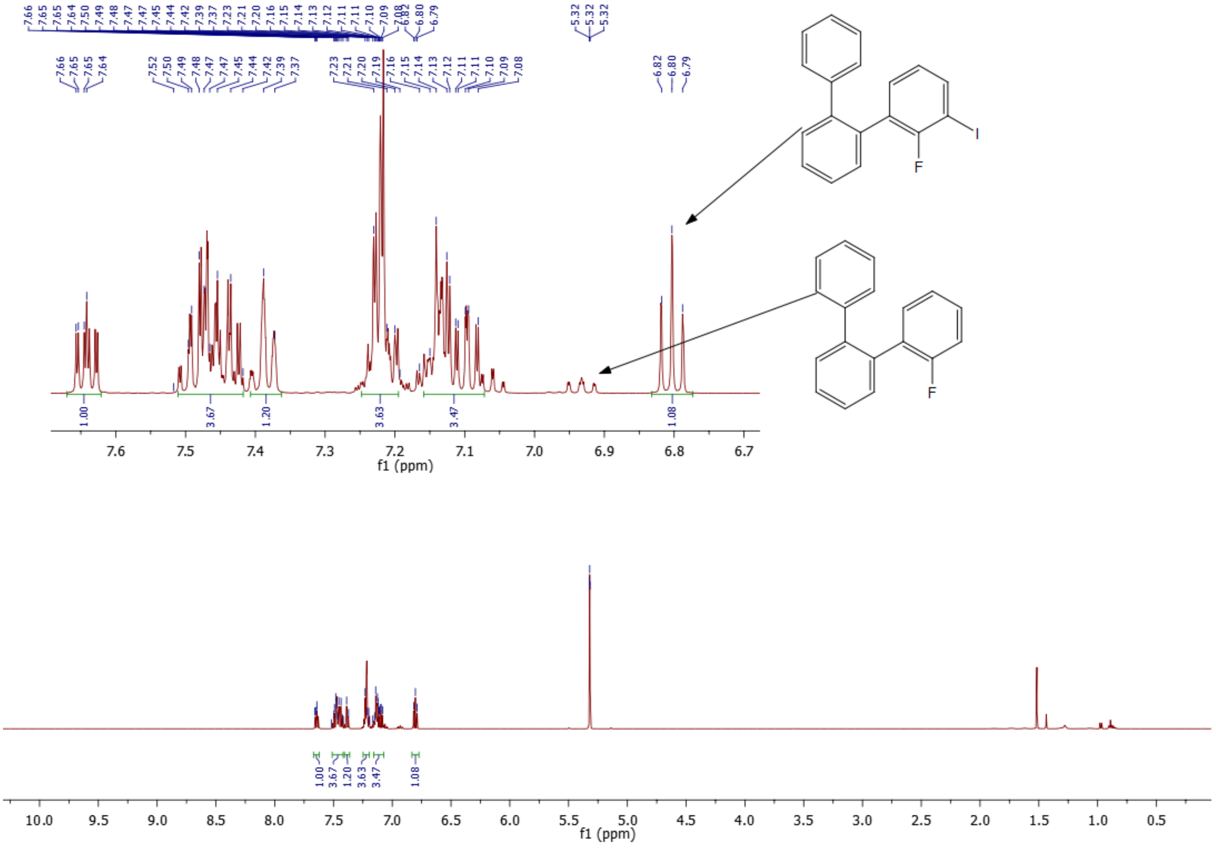


Figure S122: ^{1}H NMR spectrum of 2-fluoro-3-iodo-1,1':2',1"-terphenyl (**P19**) (in CD_2Cl_2).

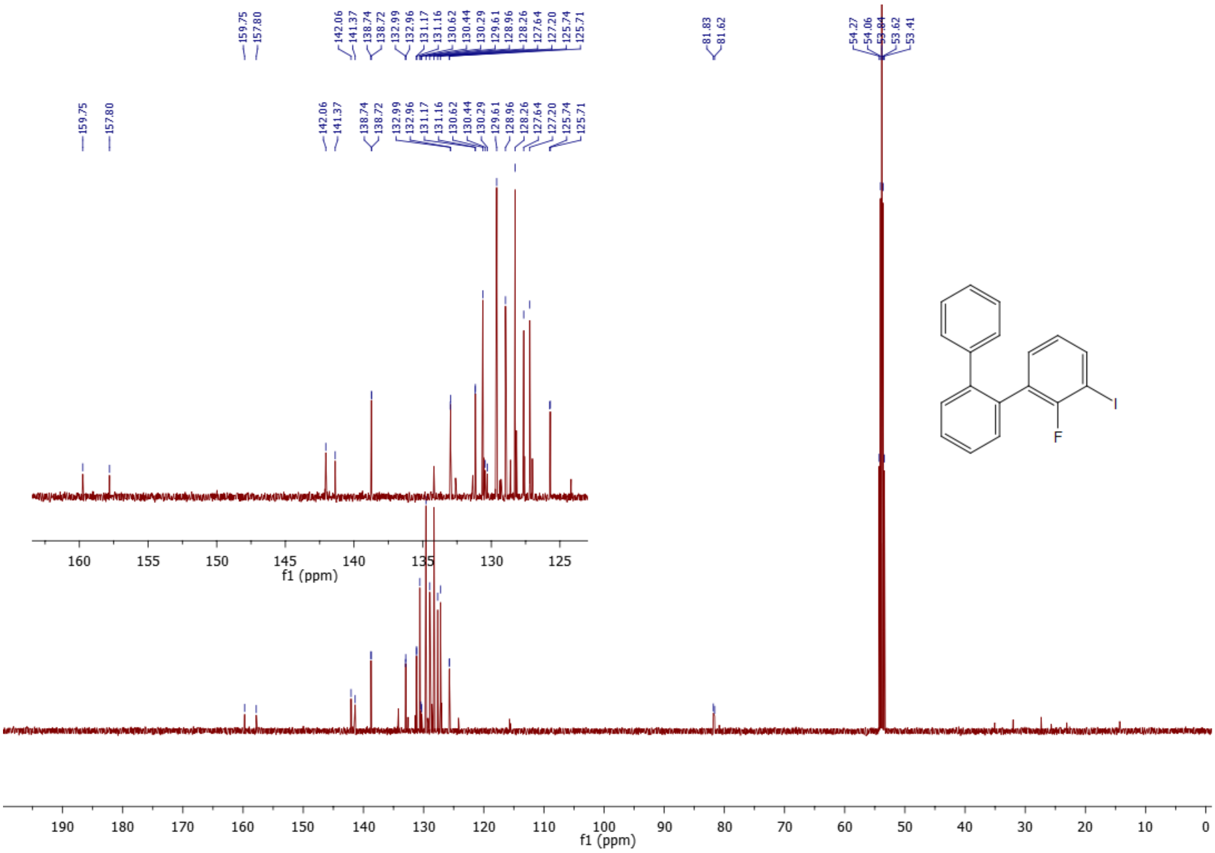


Figure S123: ^{19}F NMR spectrum of 2-fluoro-3-iodo-1,1':2',1"-terphenyl (**P19**) (in CD_2Cl_2).

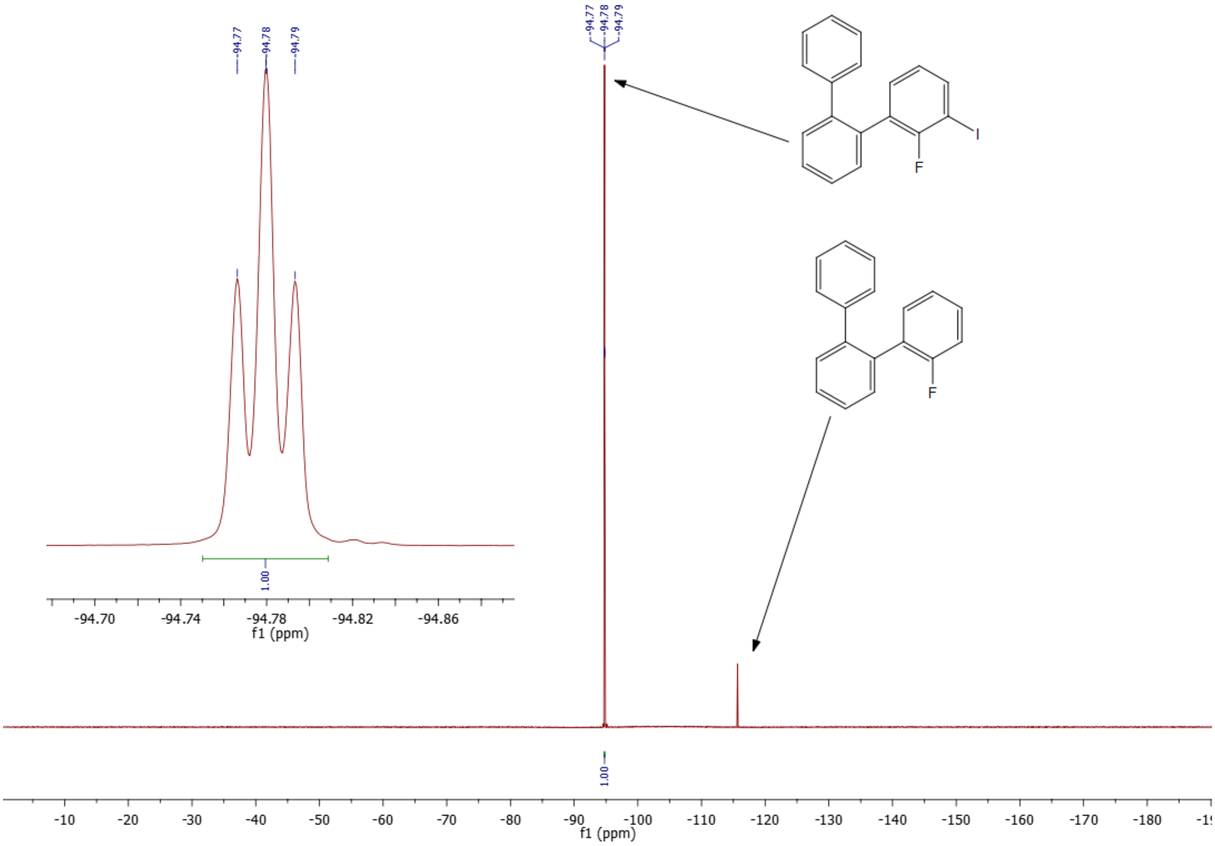


Figure S124: ^{19}F NMR spectrum of 2-fluoro-3-iodo-1,1':2',1"-terphenyl (**P19**) (in CD_2Cl_2).

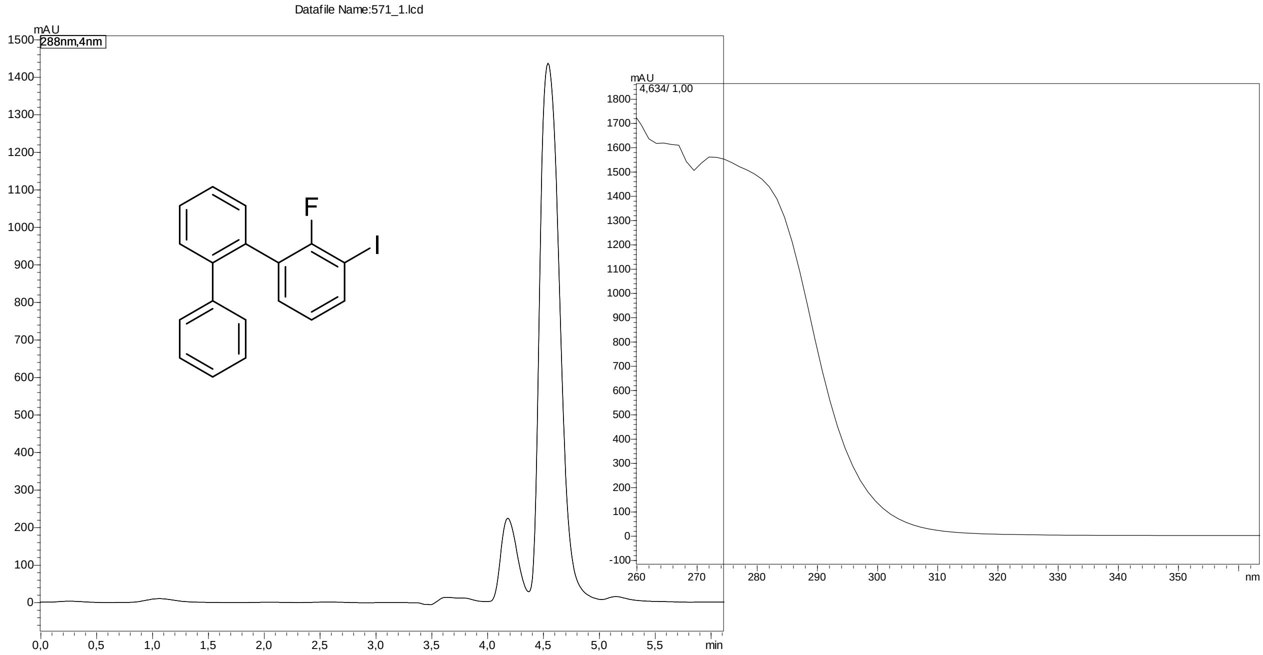


Figure S125: HPLC chromatogram (PBR column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6, t_R 4.62 min) and UV/vis spectrum (inset) of 2-fluoro-3-iodo-1,1':2',1''-terphenyl (**P19**).

1-Fluoro-4-iodobenzo[*c*]phenanthrene (P20)

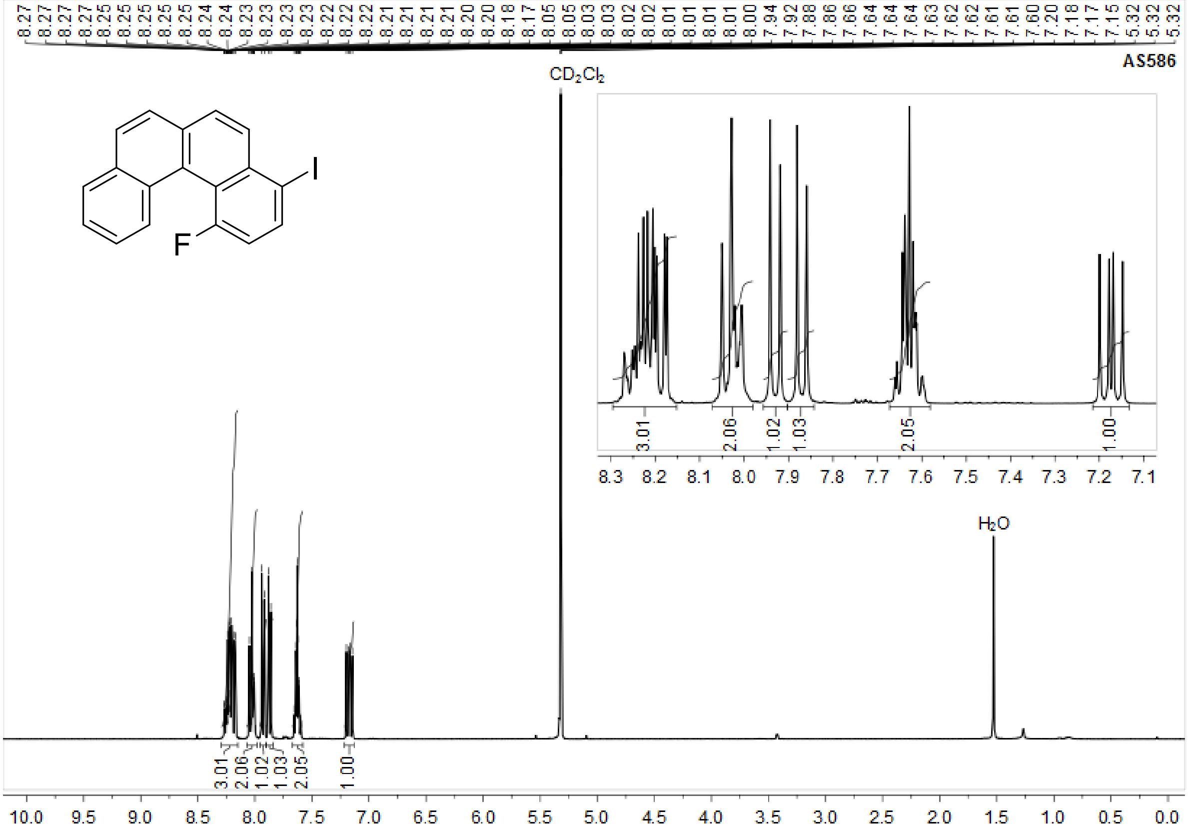


Figure S126: ^{1}H NMR spectrum of 1-fluoro-4-iodobenzo[*c*]phenanthrene (**P20**) (in CD_2Cl_2).

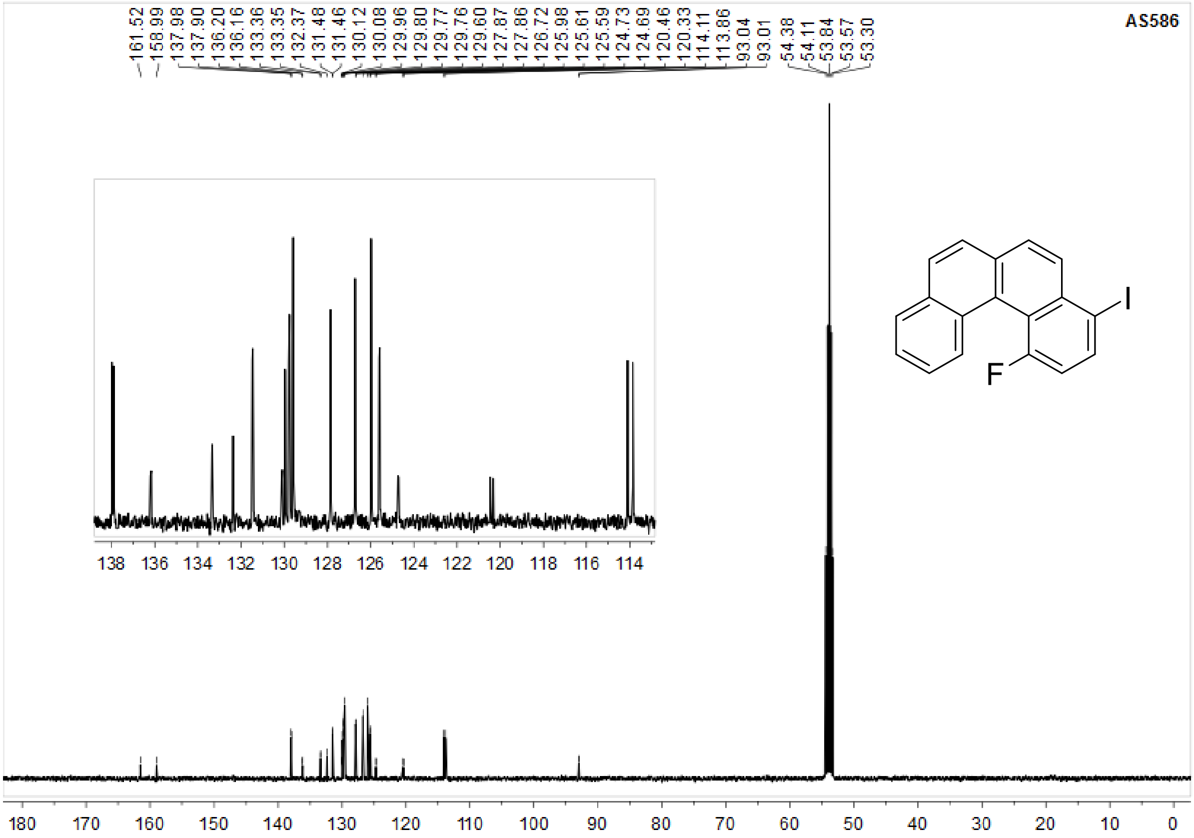


Figure S127: ^{13}C NMR spectrum of 1-fluoro-4-iodobenzo[*c*]phenanthrene (**P20**) (in CD_2Cl_2).

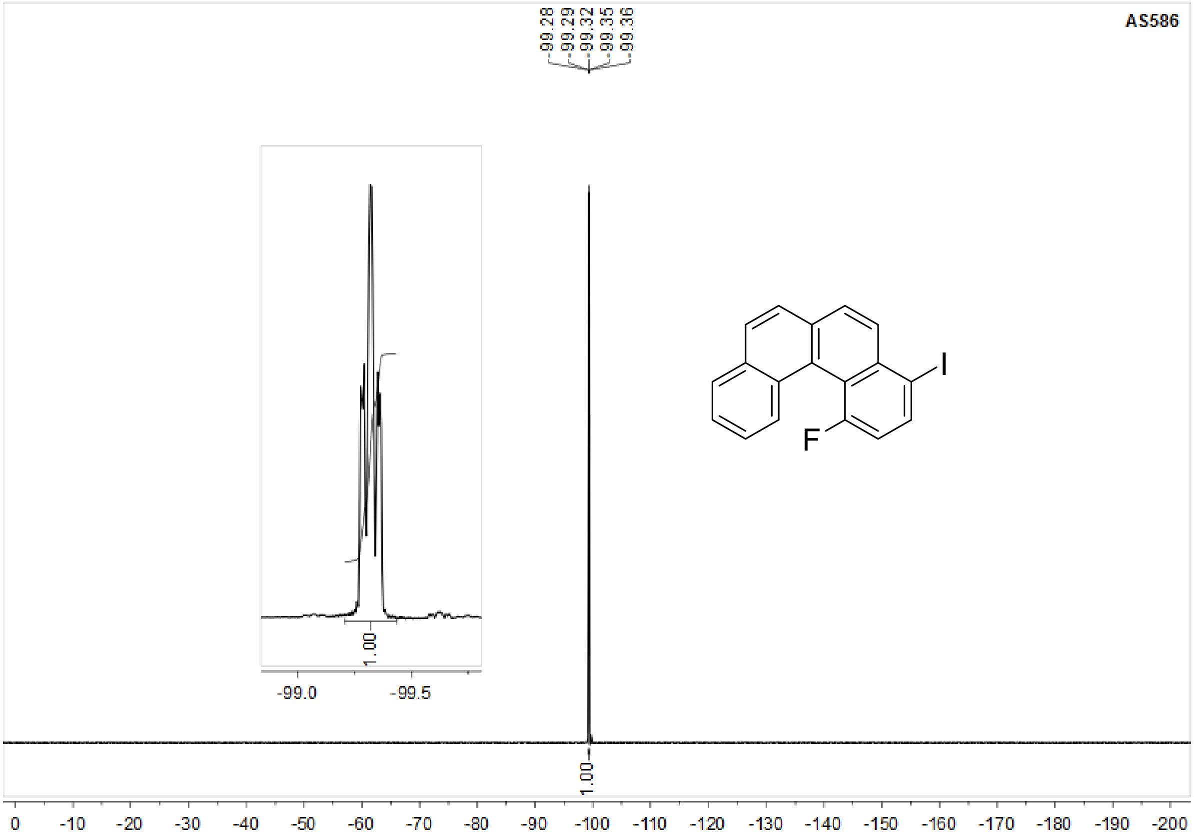


Figure S128: ^{19}F NMR spectrum of 1-fluoro-4-iodobenzo[*c*]phenanthrene (**P20**) (in CD_2Cl_2).

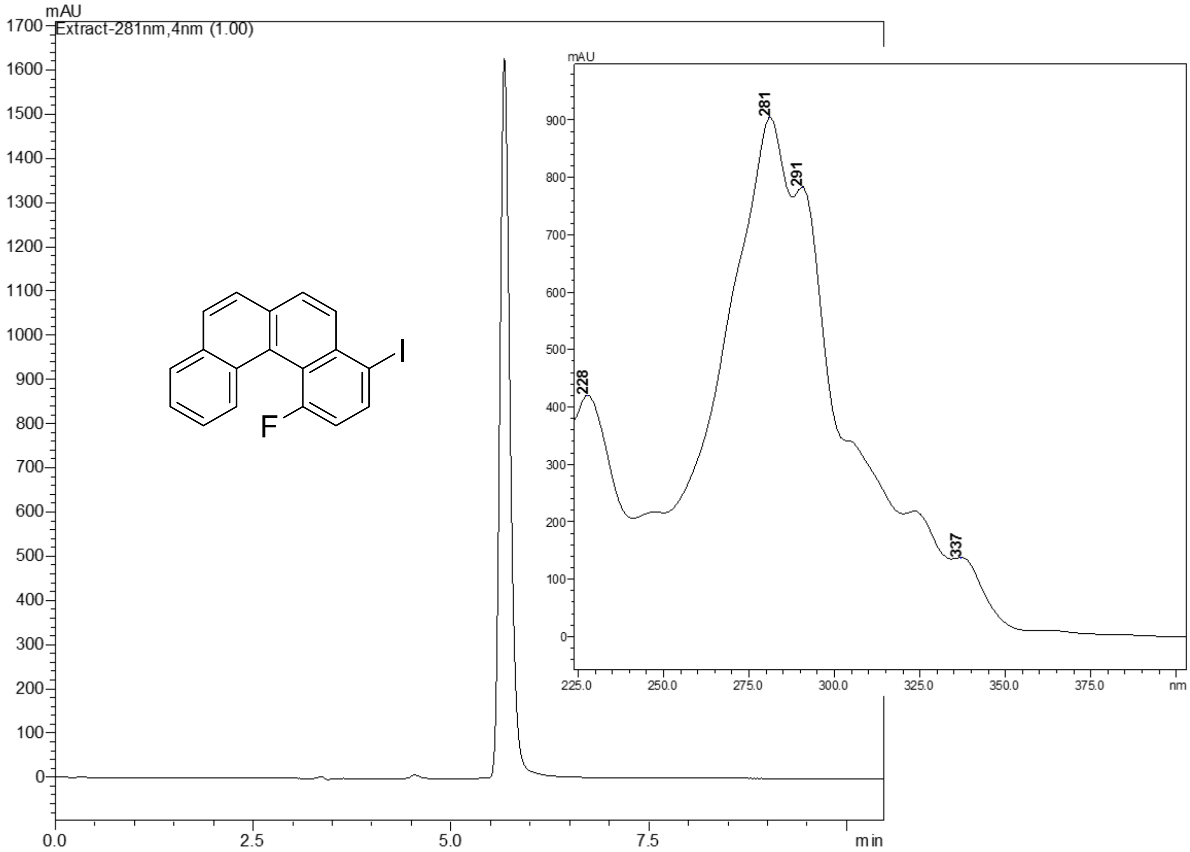


Figure S129: HPLC chromatogram (Buckyprep column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 6:4, t_R 5.67 min) and UV/vis spectrum (inset) of 1-fluoro-4-iodobenzo[*c*]phenanthrene (**P20**).

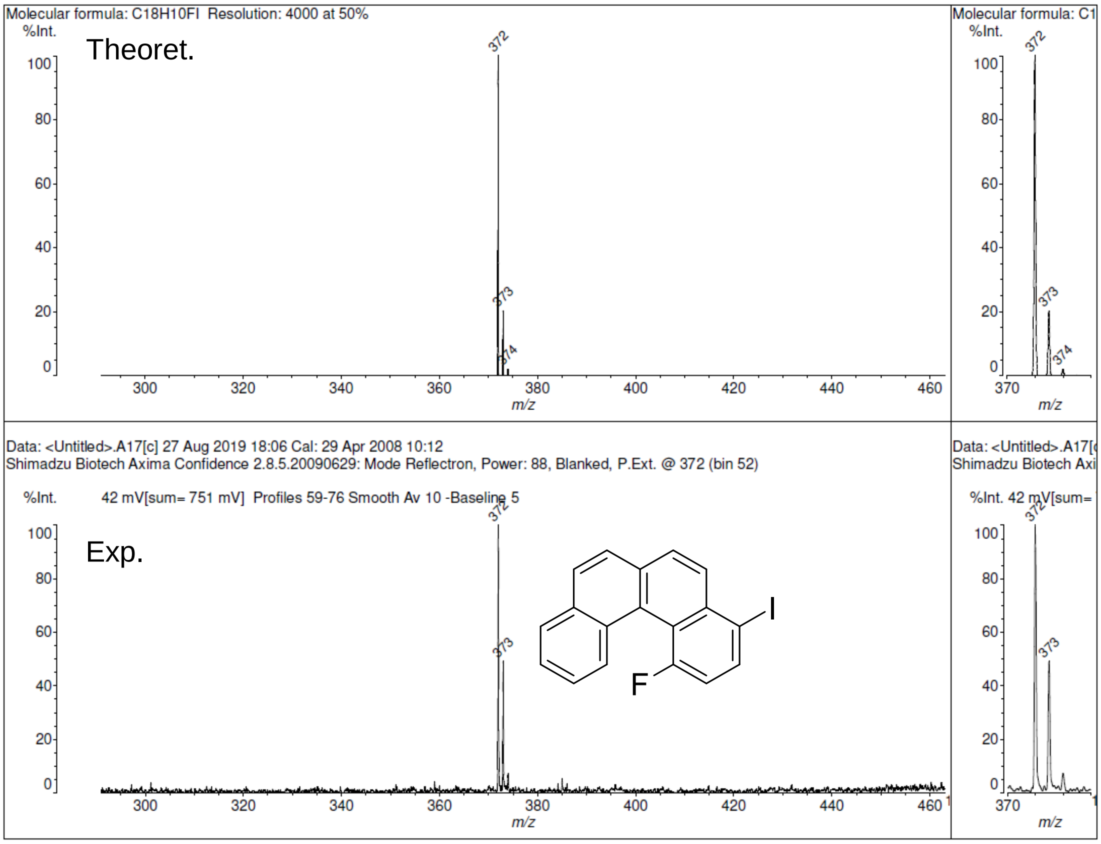
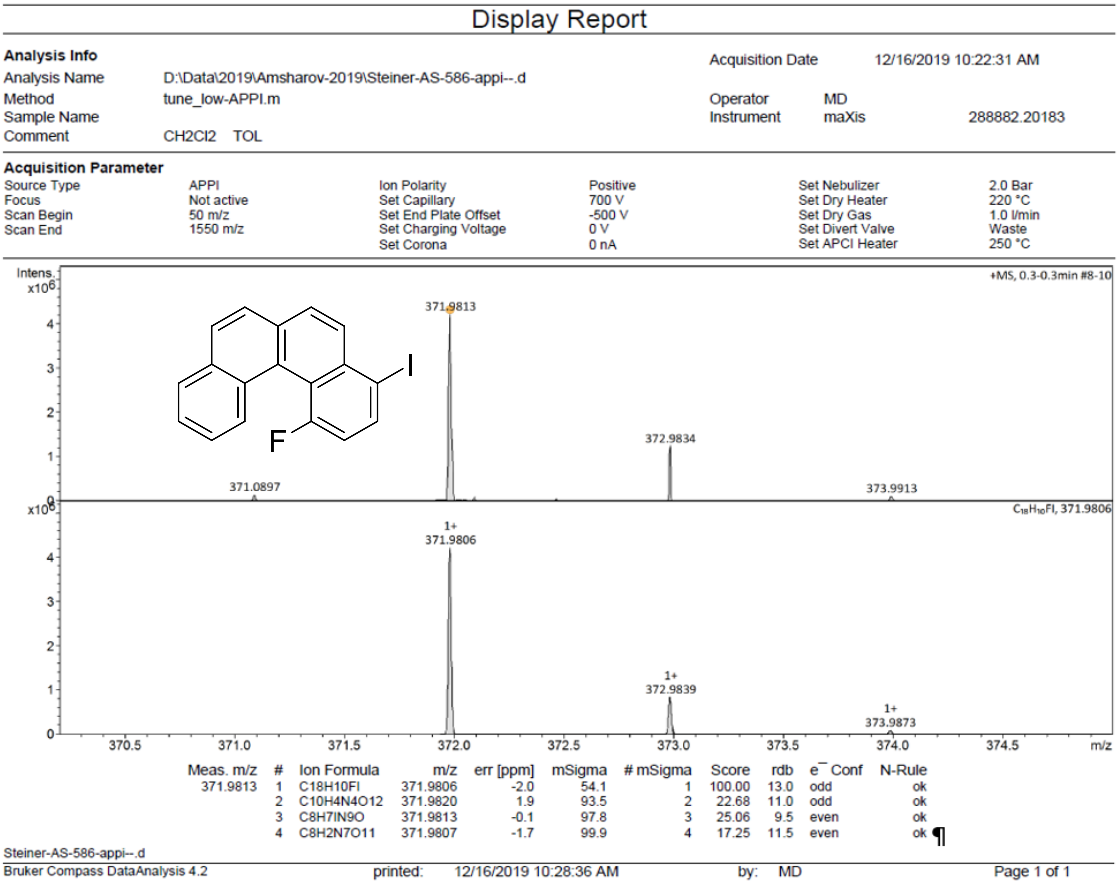


Figure S130: LDI MS spectrum of 1-fluoro-4-iodobenzo[*c*]phenanthrene (**P20**), *m/z* 372 (M^+, 100 %).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-586-appi--.d	Acquisition Date	12/16/2019 10:22:31 AM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2 TOL			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
371.9813	1	C18H10FI	371.9806	-2.0	54.1	1	100.00	13.0	odd	ok
	2	C10H4N4O12	371.9820	1.9	93.5	2	22.68	11.0	odd	ok
	3	C8H7IN9O	371.9813	-0.1	97.8	3	25.06	9.5	even	ok
	4	C8H2N7O11	371.9807	-1.7	99.9	4	17.25	11.5	even	ok ¶

Steiner-AS-586-appi--.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 10:28:36 AM by: MD Page 1 of 1

Figure S42: HR MS (APPI) spectrum of 1-fluoro-4-iodobenzo[*c*]phenanthrene (**P20**), *m/z* 371.9813 (M^+, 100 %).

1-Fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (11)

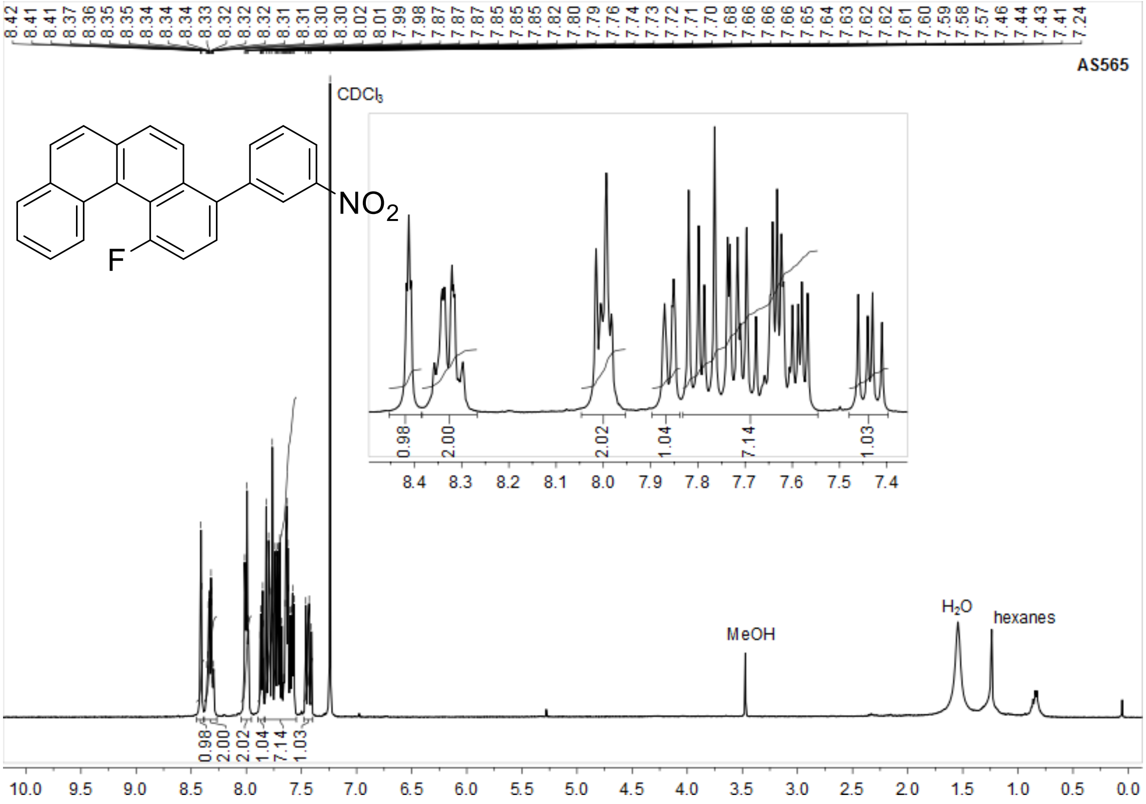


Figure S132: ^{1}H NMR spectrum of 1-fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (**11**) (in $CDCl_3$).

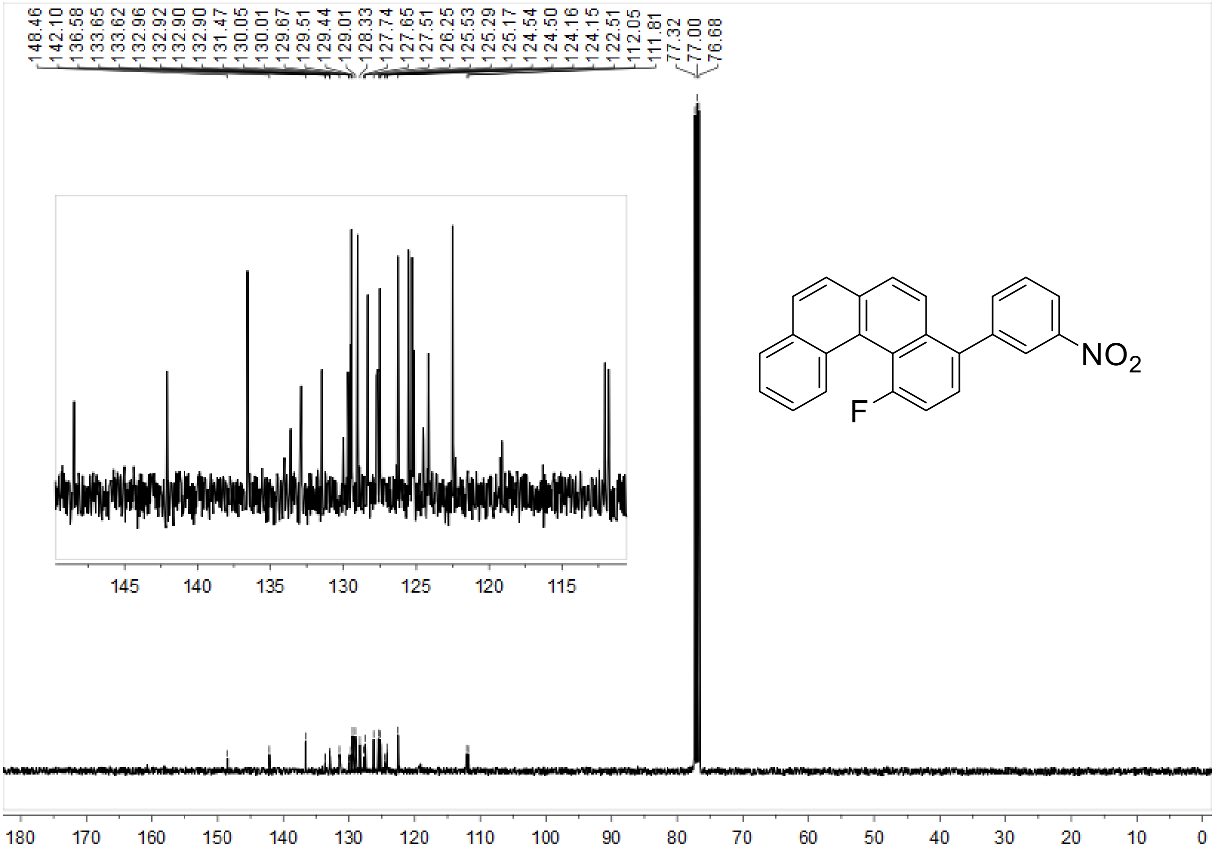


Figure S133: ^{13}C NMR spectrum of 1-fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (**11**) (in $CDCl_3$).

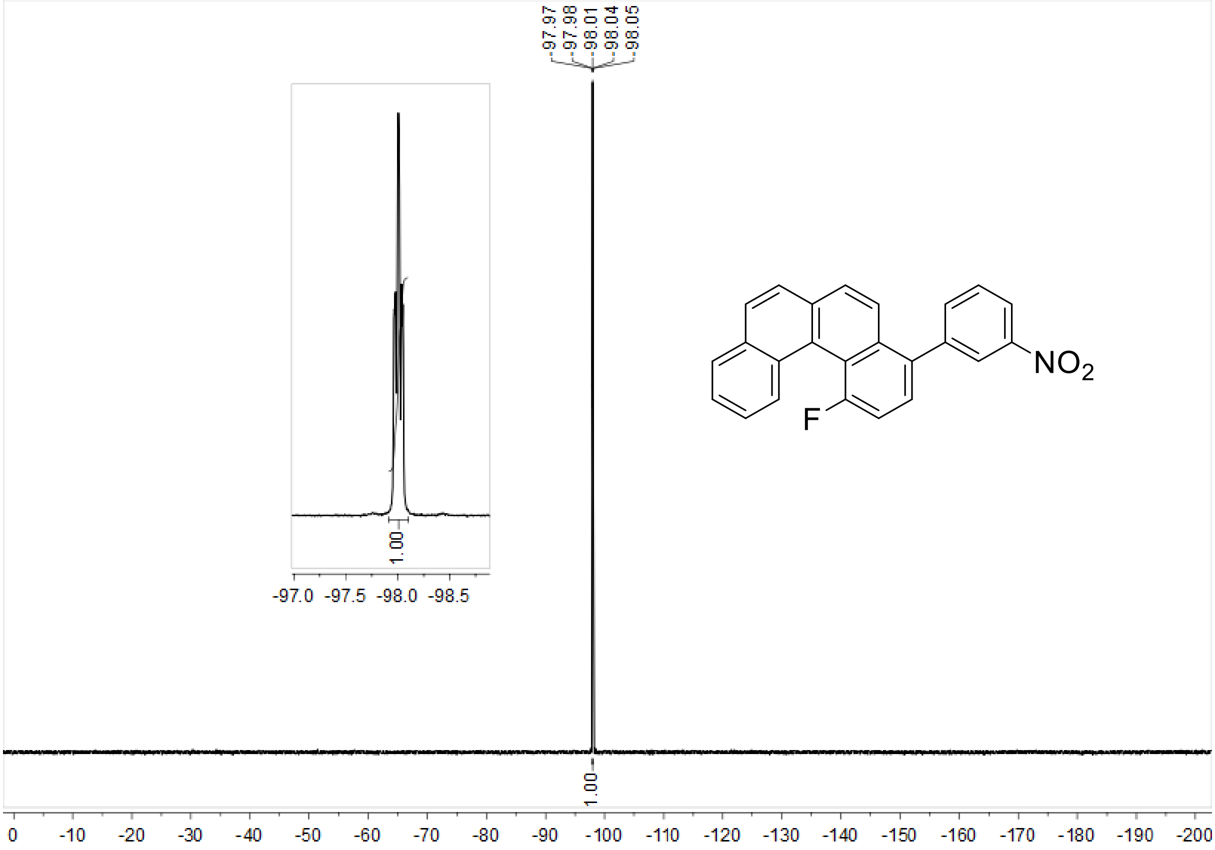


Figure S134: ^{19}F NMR spectrum of 1-fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene) (**11**) (in $CDCl_3$).

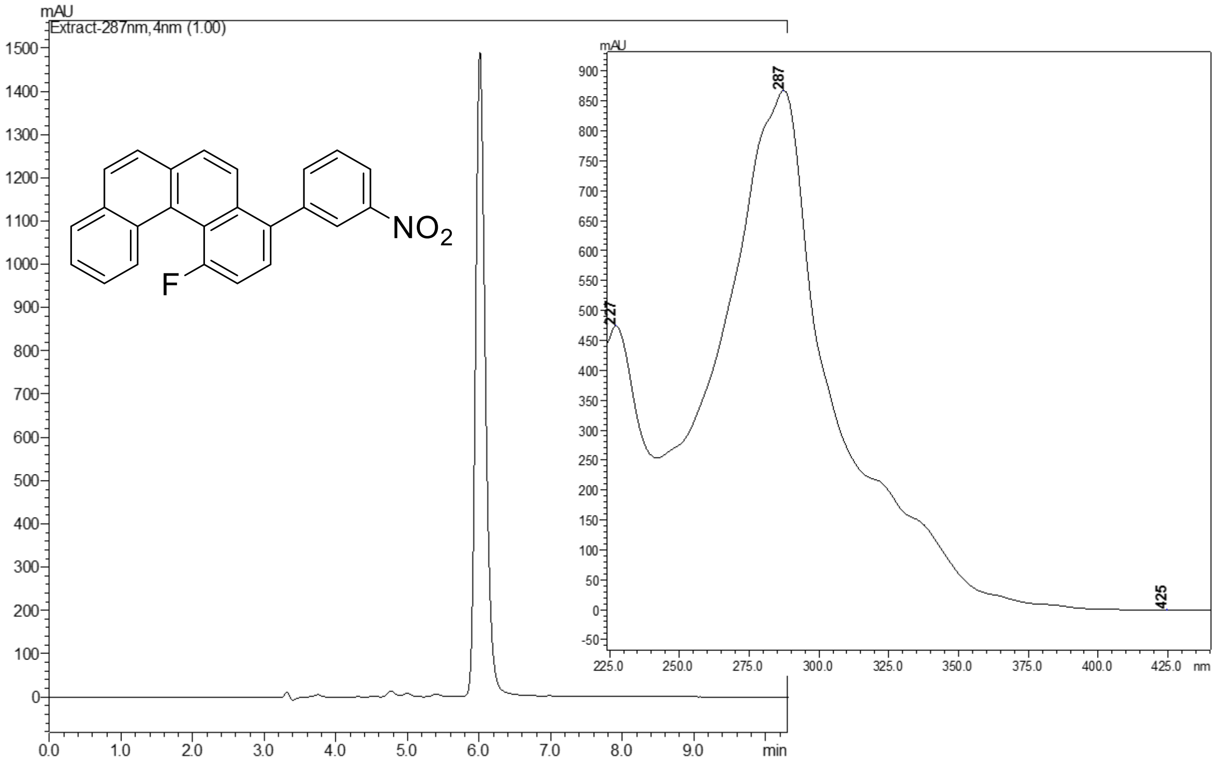
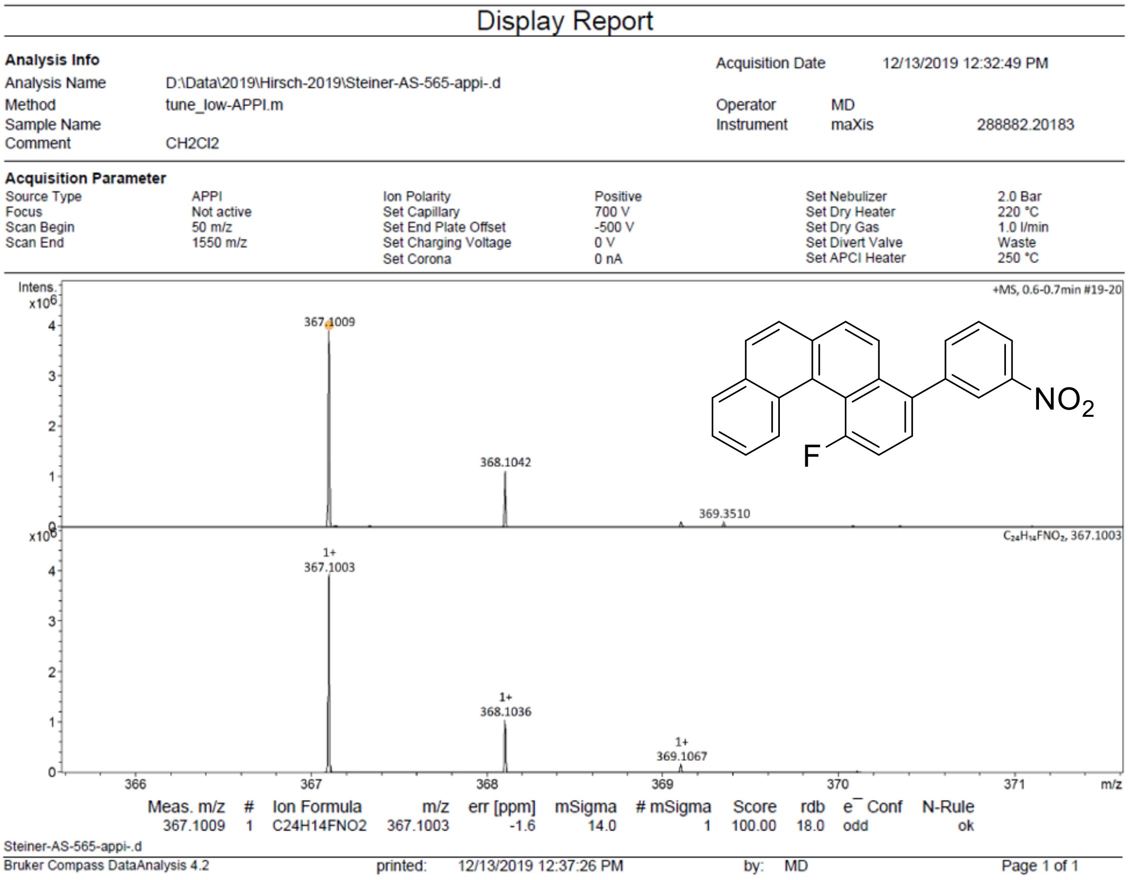


Figure S135: HPLC chromatogram (Buckyprep column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 4:6, t_R 6.01 min) and UV/vis spectrum (inset) of 1-fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (**11**).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Hirsch-2019\Steiner-AS-565-appi-.d	Acquisition Date	12/13/2019 12:32:49 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
367.1009	1	C24H14FNO2	367.1003	-1.6	14.0	1	100.00	18.0	odd	ok

Steiner-AS-565-appi-.d

Bruker Compass DataAnalysis 4.2 printed: 12/13/2019 12:37:26 PM by: MD Page 1 of 1

Figure S136: HR MS (APPI) spectrum of 1-fluoro-4-(3-nitrophenyl)benzo[*c*]phenanthrene (**11**), *m/z* 367.1009 (M^+, 100 %).

3-(1-Fluorobenzo[*c*]phenanthren-4-yl)aniline (12)

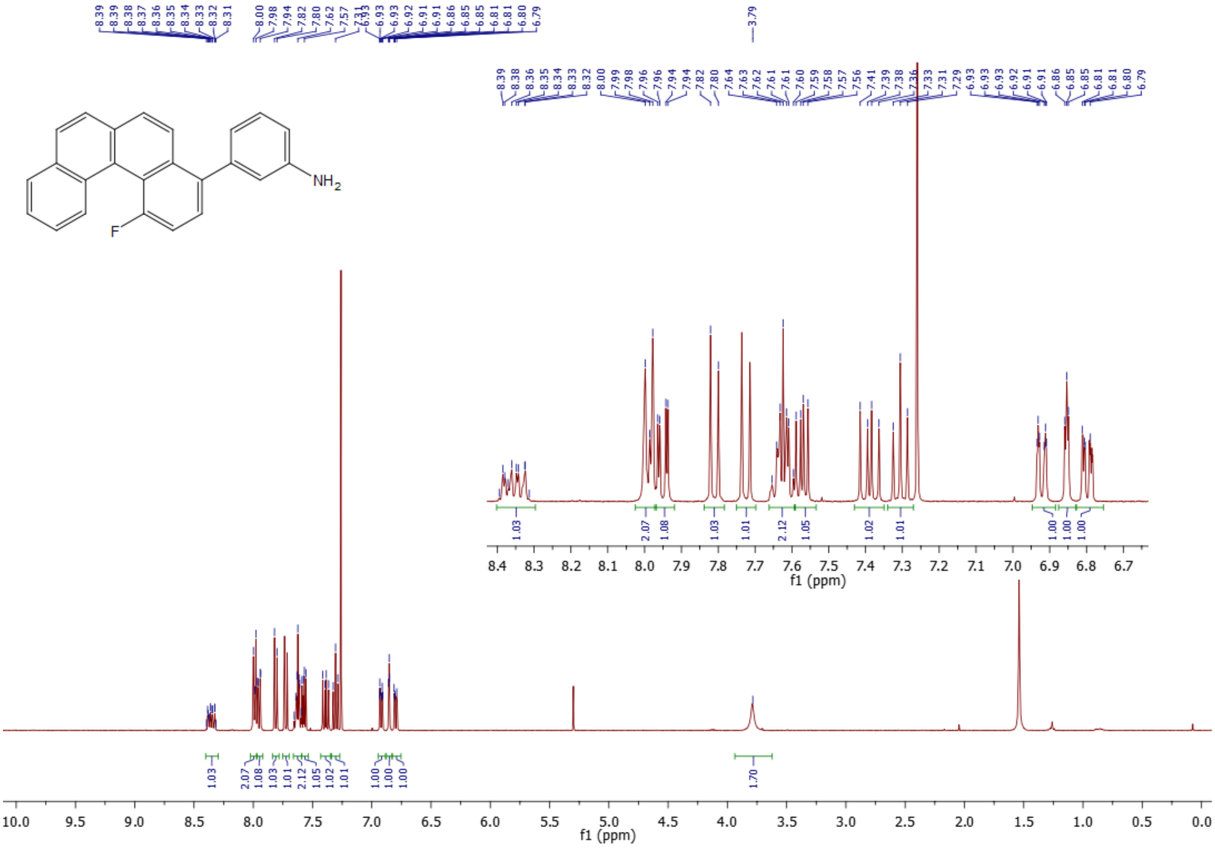


Figure S137: ^{1}H NMR spectrum of 3-(1-fluorobenzo[c]phenanthren-4-yl)aniline (**12**) (in $CDCl_3$).

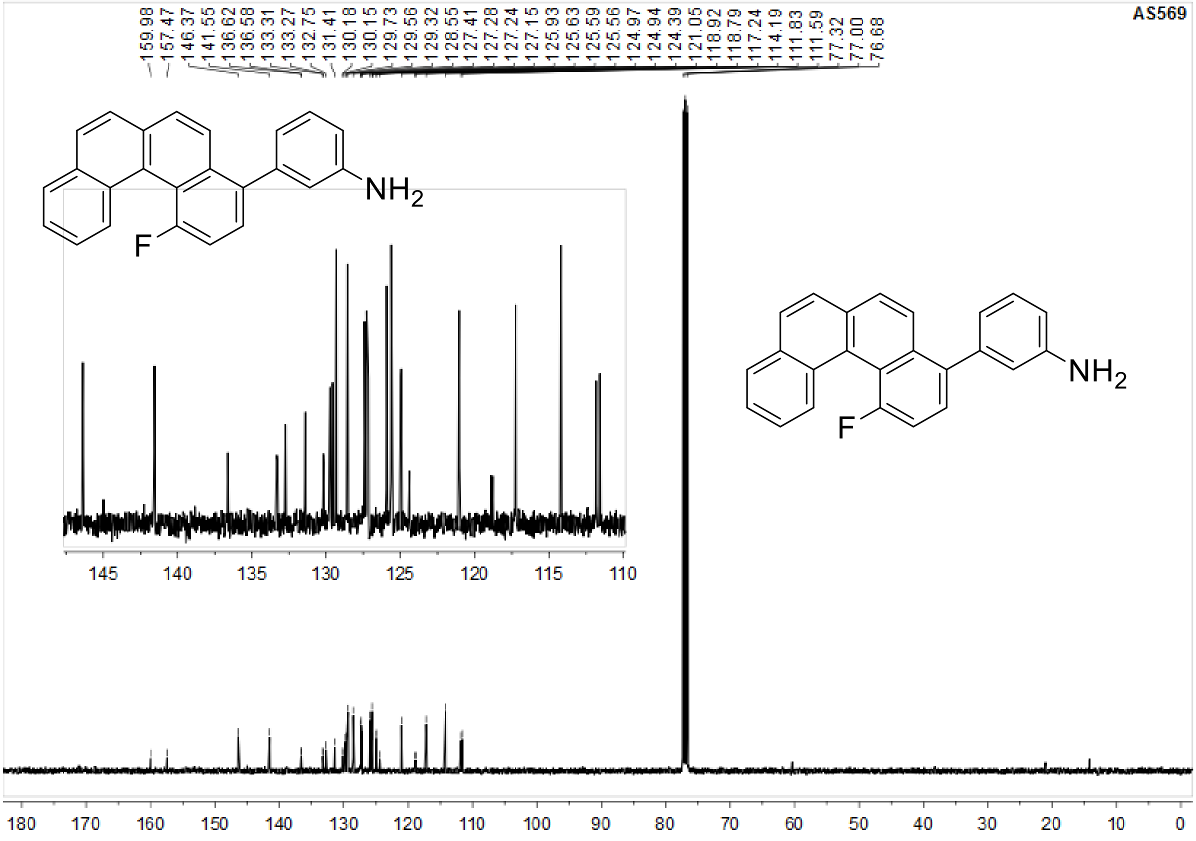


Figure S138: ^{13}C NMR spectrum of 3-(1-fluorobenzo[c]phenanthren-4-yl)aniline (**12**) (in $CDCl_3$).

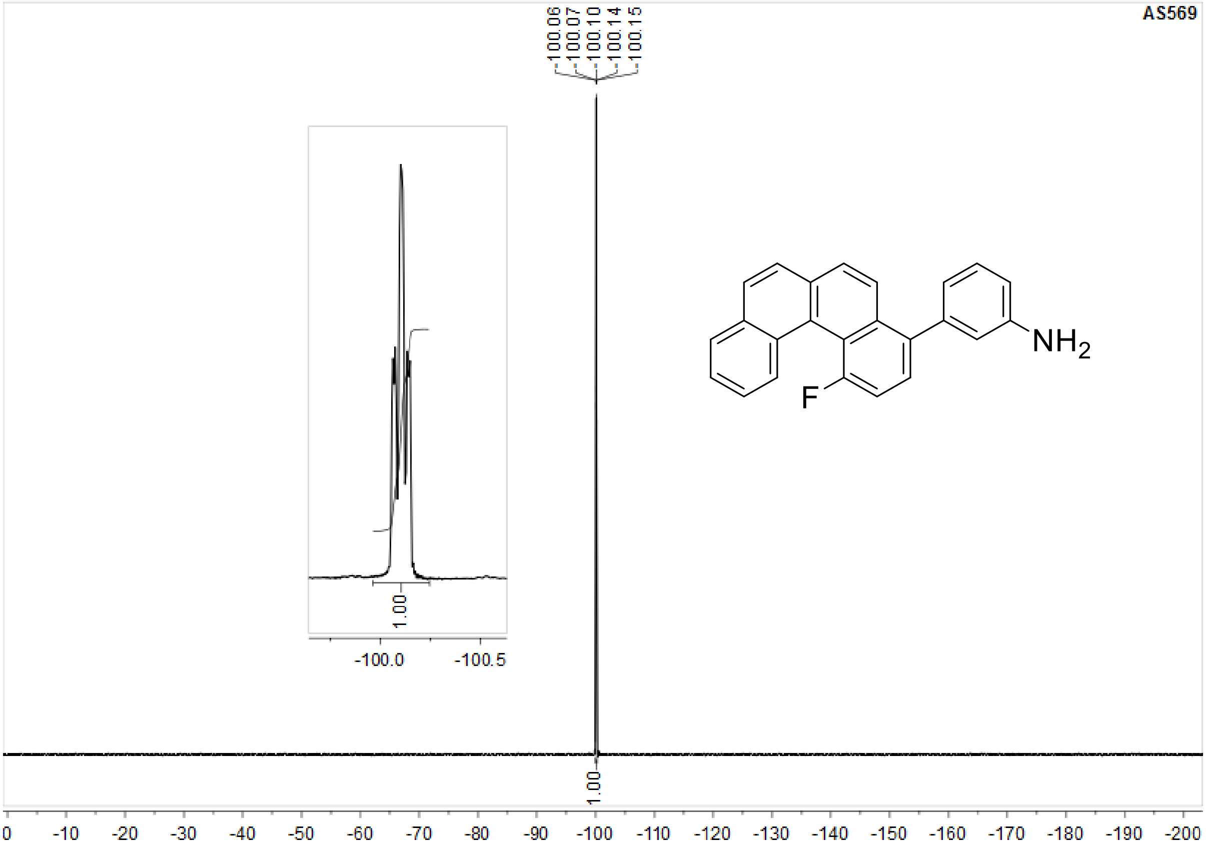


Figure S139: ^{19}F NMR spectrum of 3-(1-fluorobenzo[c]phenanthren-4-yl)aniline (**12**) (in $CDCl_3$).

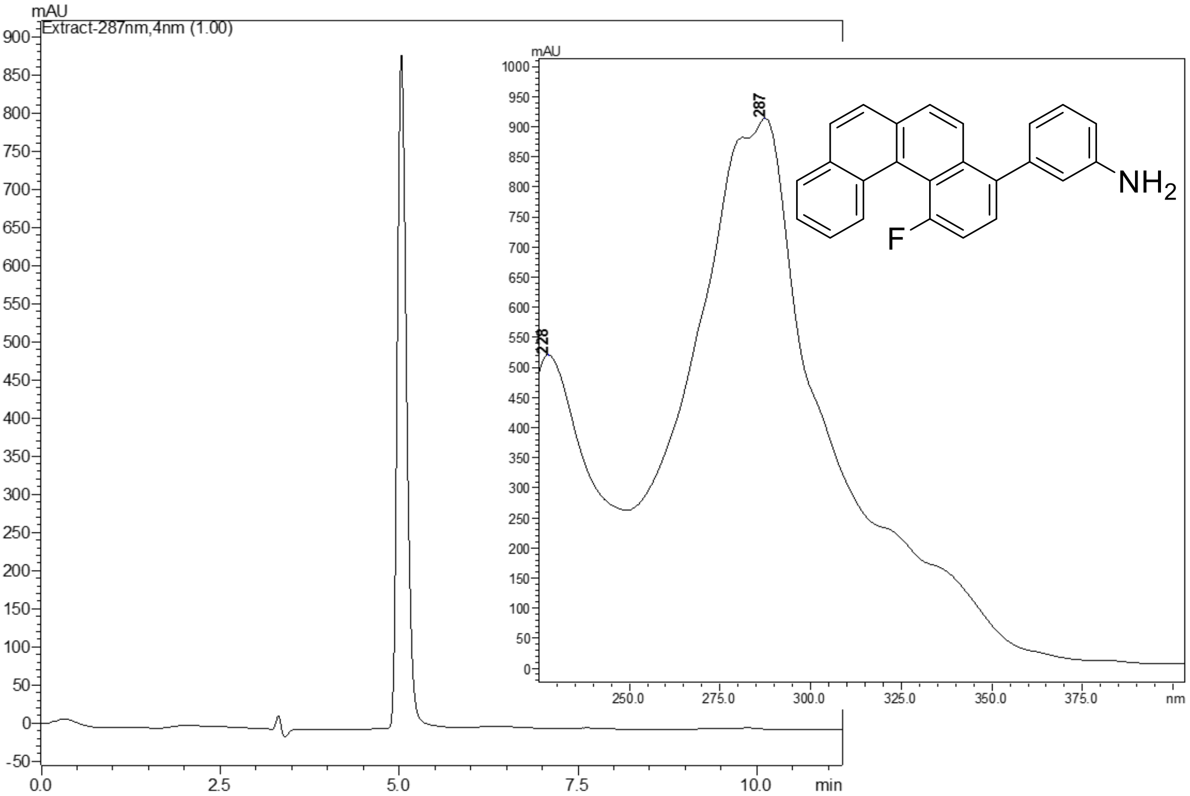
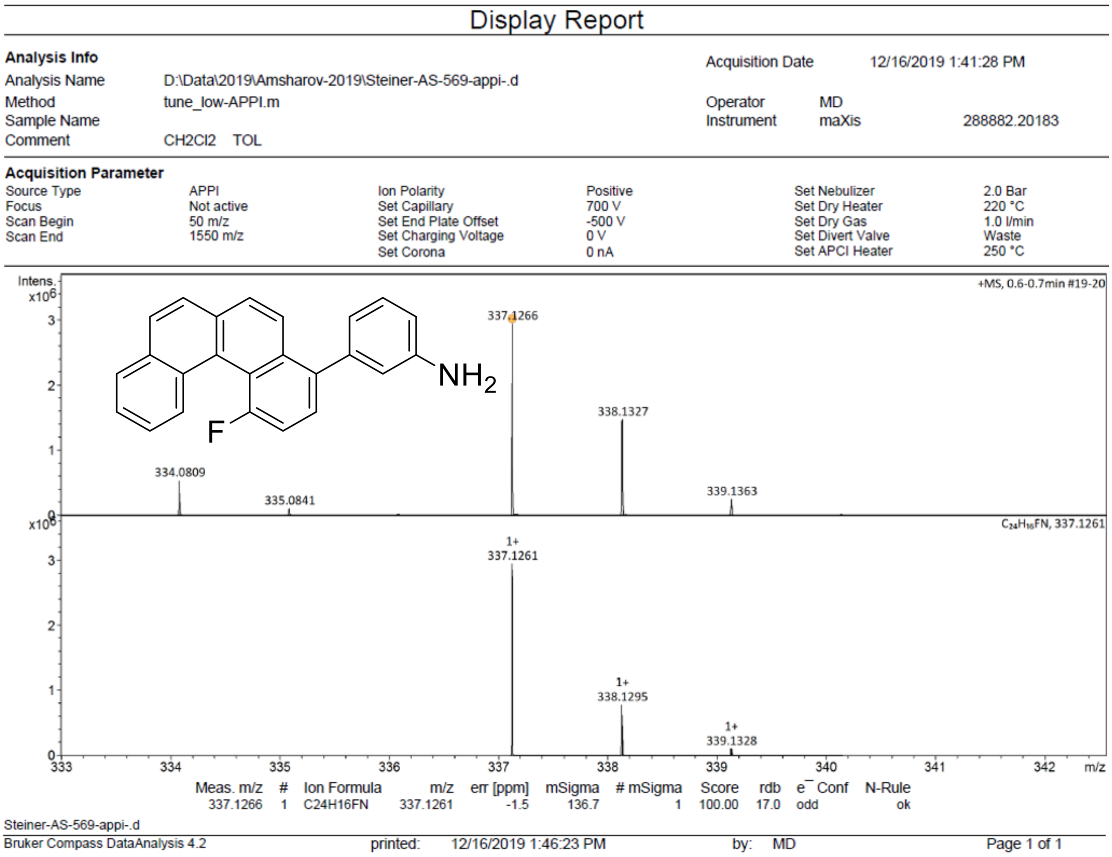


Figure S43: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 4:6, t_R 5.03 min) and UV/vis spectrum (inset) of 3-(1-fluorobenzo[c]phenanthren-4-yl)aniline (**12**).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-AS-569-appi-.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2 TOL

Acquisition Date 12/16/2019 1:41:28 PM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
337.1266	1	C24H16FN	337.1261	-1.5	136.7	1	100.00	17.0	odd	ok

Steiner-AS-569-appi-.d
Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 1:46:23 PM by: MD Page 1 of 1

Figure S141: HR MS (APPI) spectrum of 3-(1-fluorobenzo[c]phenanthren-4-yl)aniline (**12**), *m/z* 337.1266 (M^+, 100 %).

1-Fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (P21)

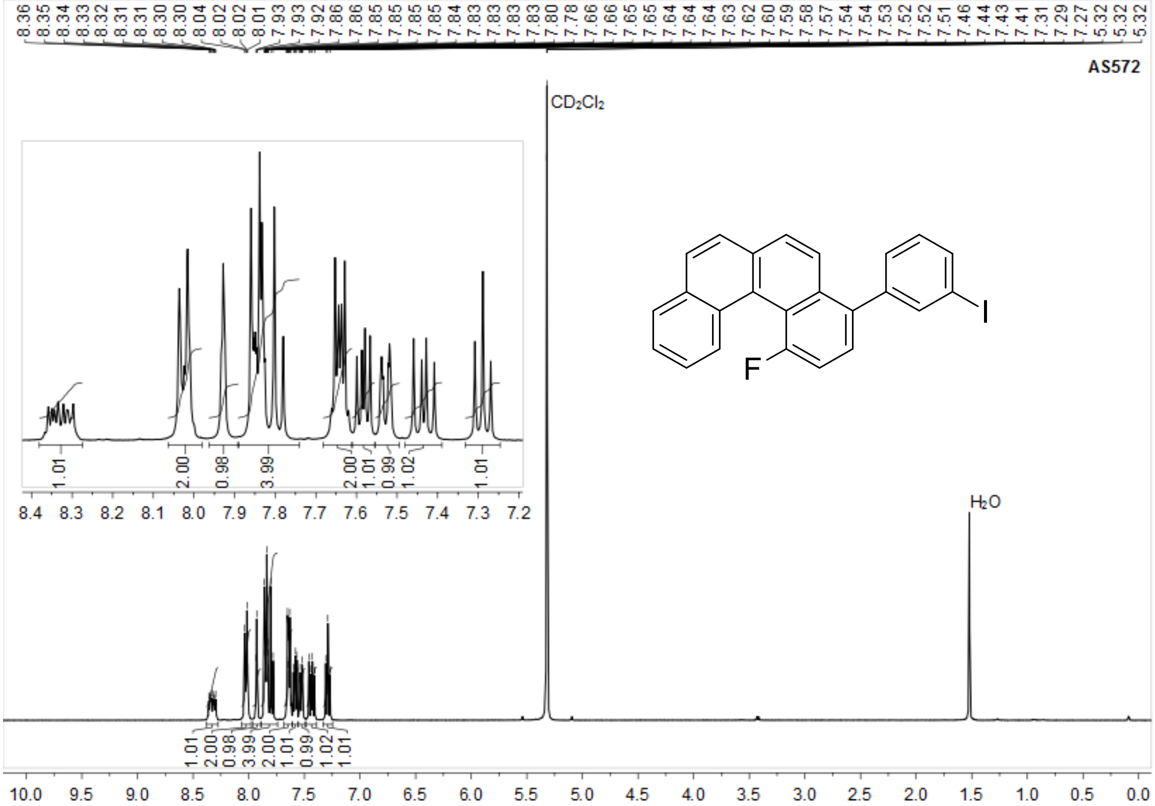


Figure S142: ^{1}H NMR spectrum of 1-fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (**P21**) (in CD_2Cl_2).

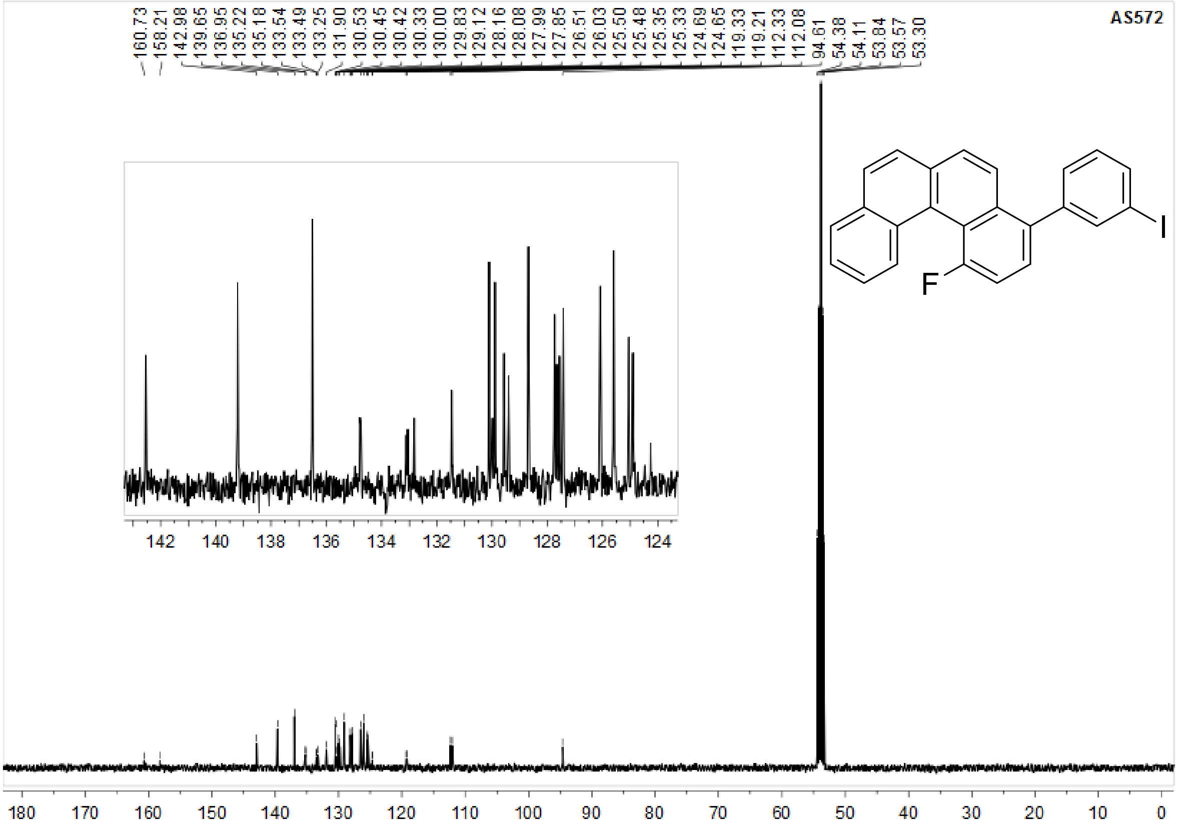


Figure S143: ^{13}C NMR spectrum of 1-fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (**P21**) (in CD_2Cl_2).

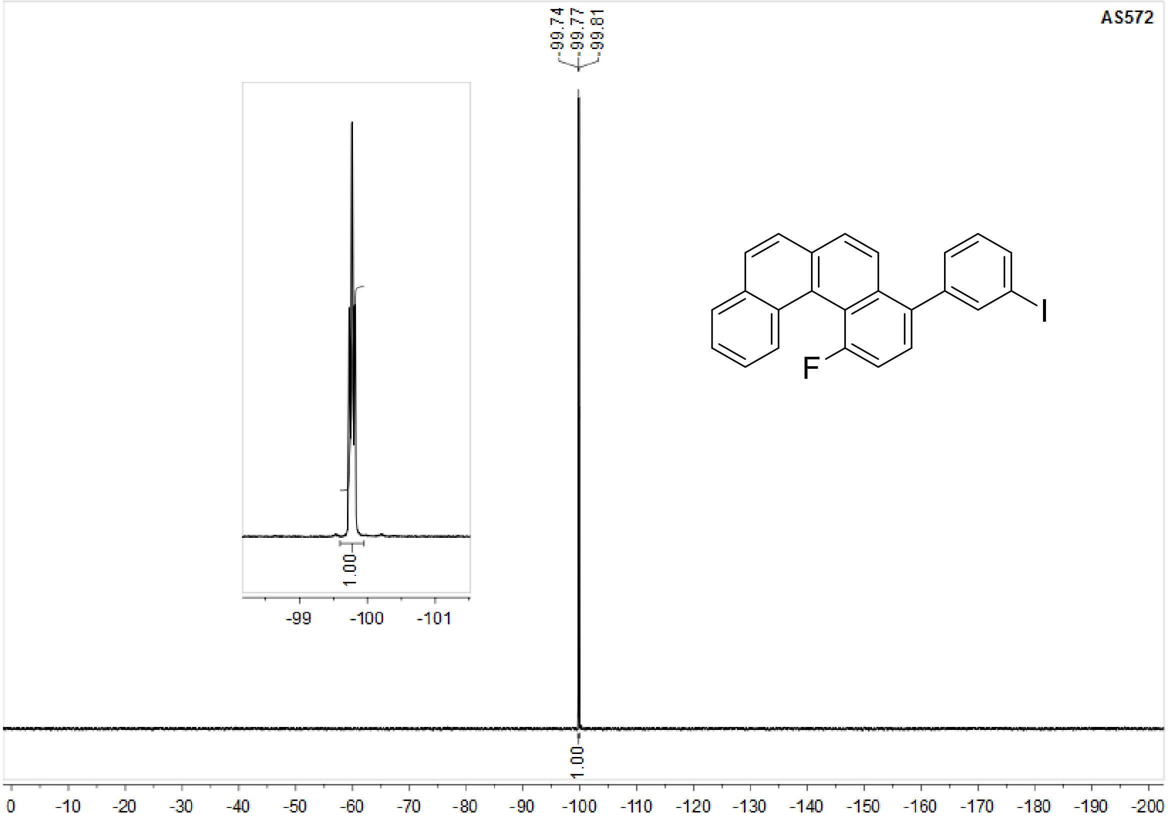


Figure S144: ^{19}F NMR spectrum of 1-fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (**P21**) (in CD_2Cl_2).

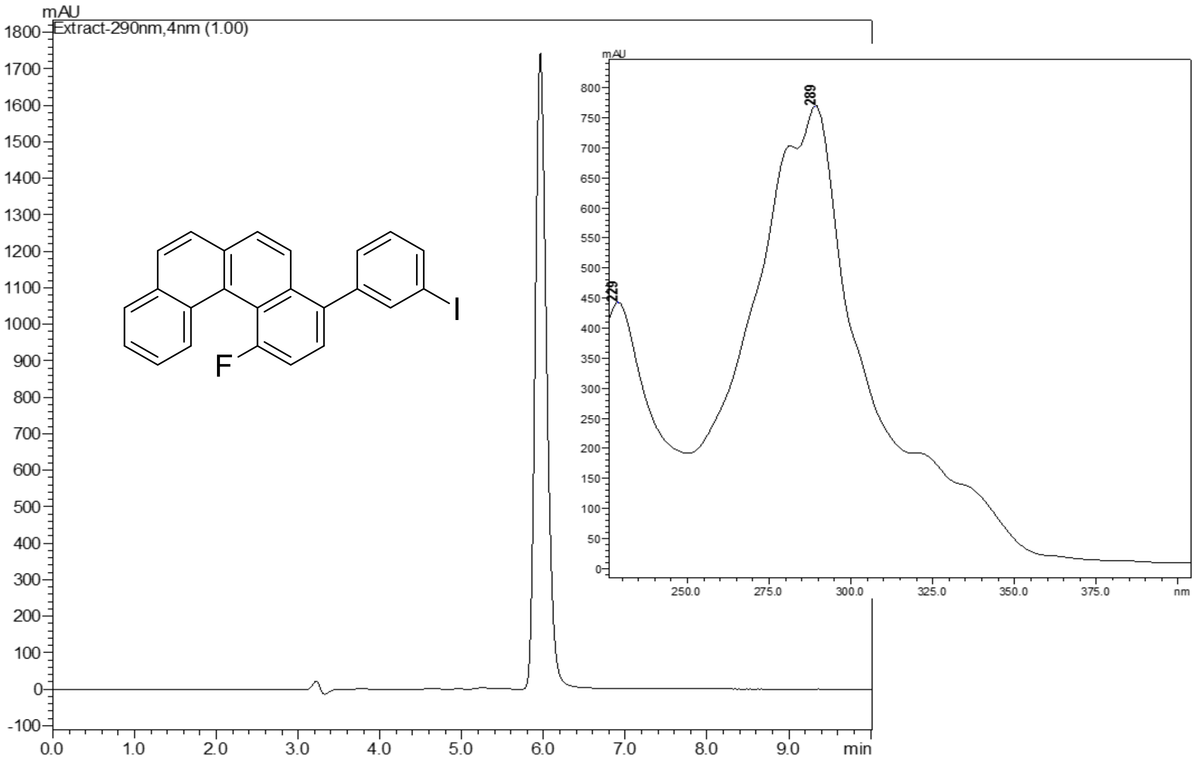
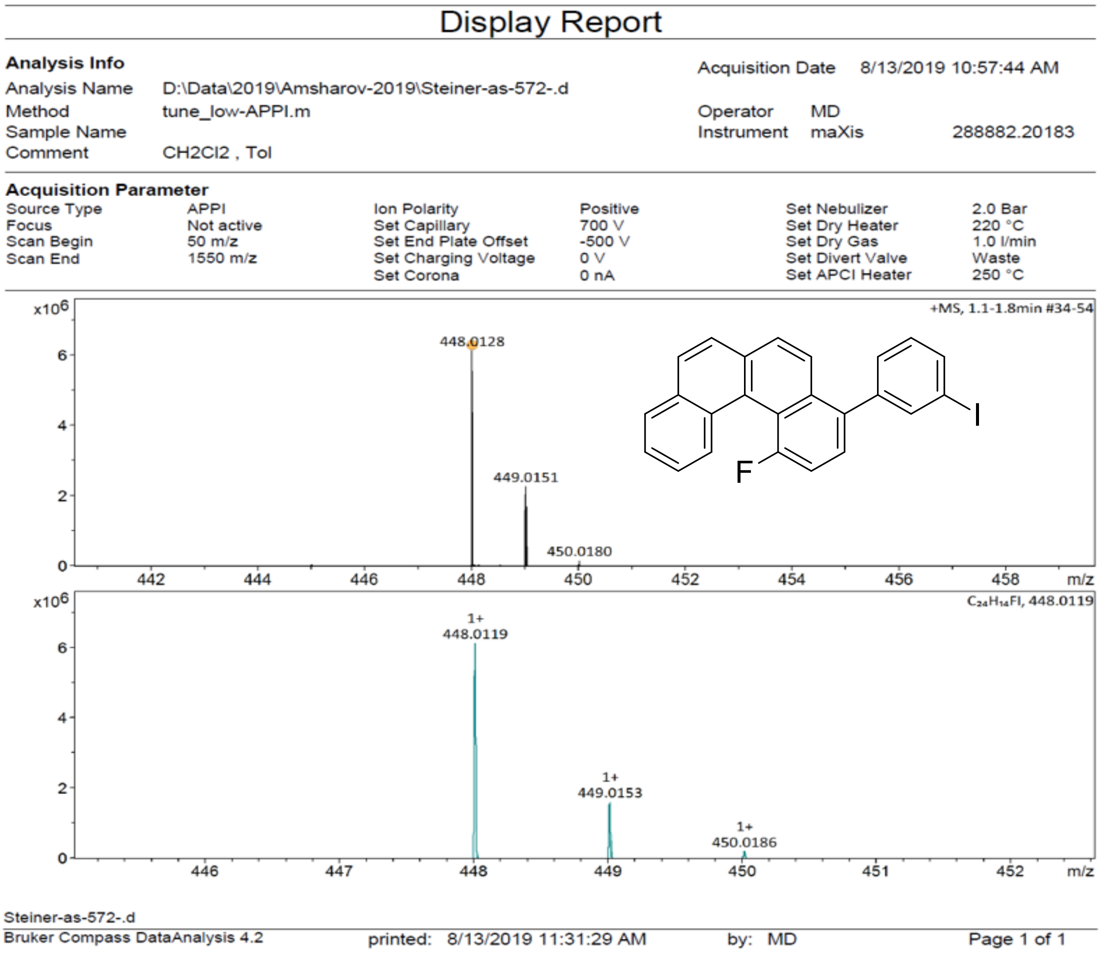


Figure S14544: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1, t_R 5.96 min) and UV/vis spectrum (inset) of 1-fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (**P21**).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-as-572-.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2 , Tol

Acquisition Date 8/13/2019 10:57:44 AM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Steiner-as-572-.d
Bruker Compass DataAnalysis 4.2 printed: 8/13/2019 11:31:29 AM by: MD Page 1 of 1

Figure S146: HR MS (APPI) spectrum of 1-fluoro-4-(3-iodophenyl)benzo[*c*]phenanthrene (**P21**), *m/z* 448.0128 (M^+, 100 %).

3.2 Carbon-Based Nanographenes T1-T12

2-Methyltriphenylene (T1)

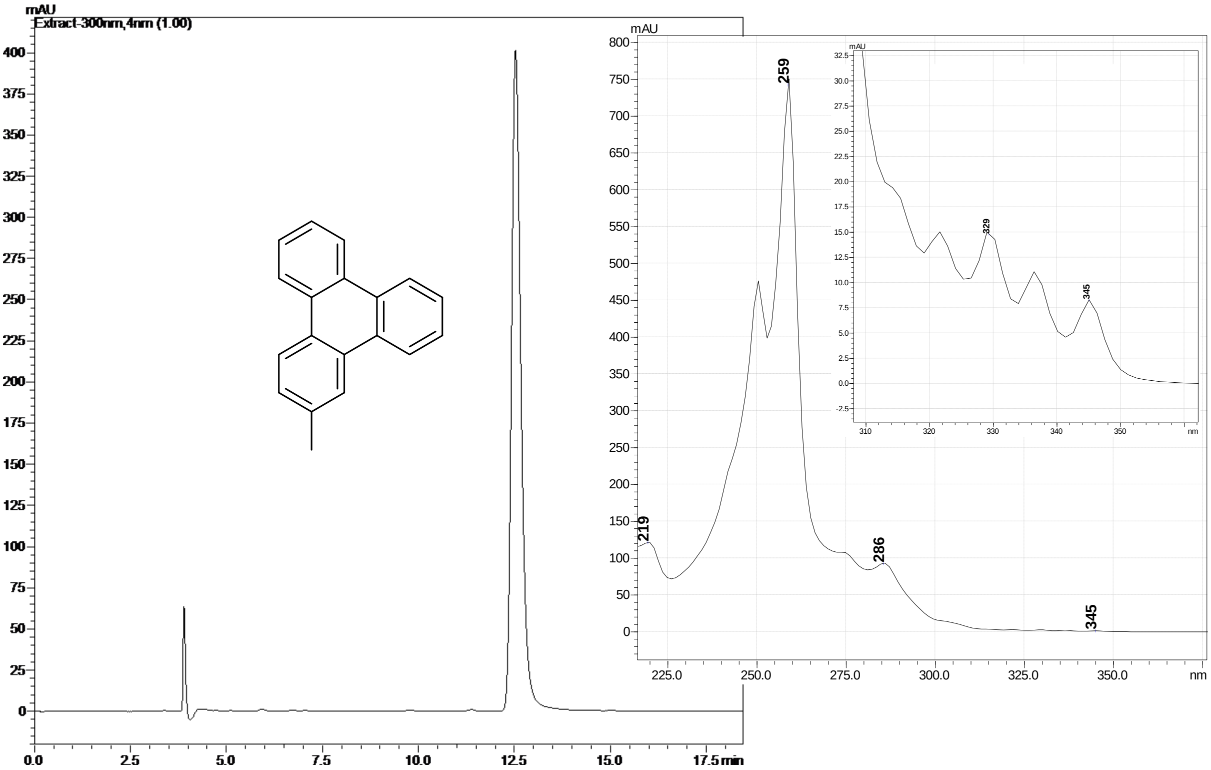


Figure S45: HPLC chromatogram obtained after reaction (250 °C, 4 h) (PBr column (anal.), 1.0 mL/min, 35 °C, DCM/MeOH 2:8), t_R = 12,52 min (**T1**).

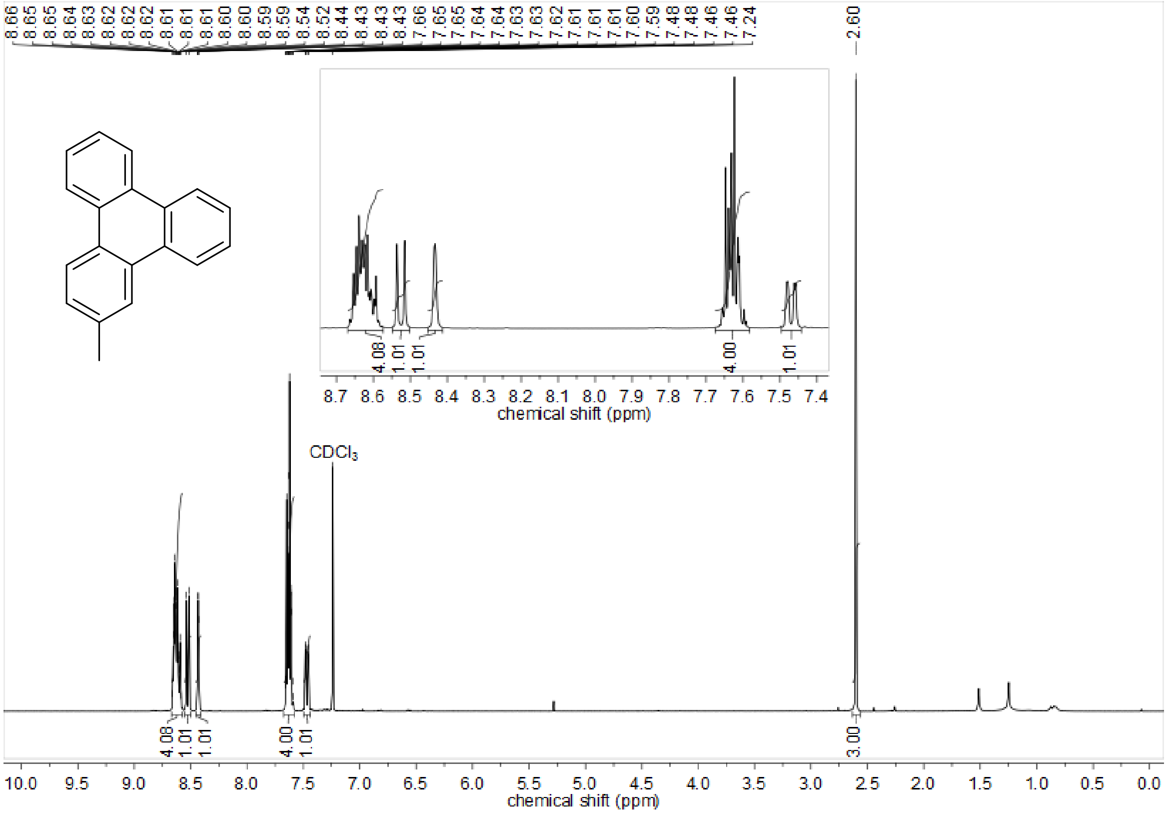


Figure S148: ^{1}H NMR spectrum of 2-methyltriphenylene (**T1**) (from reaction mixture, in $CDCl_3$).

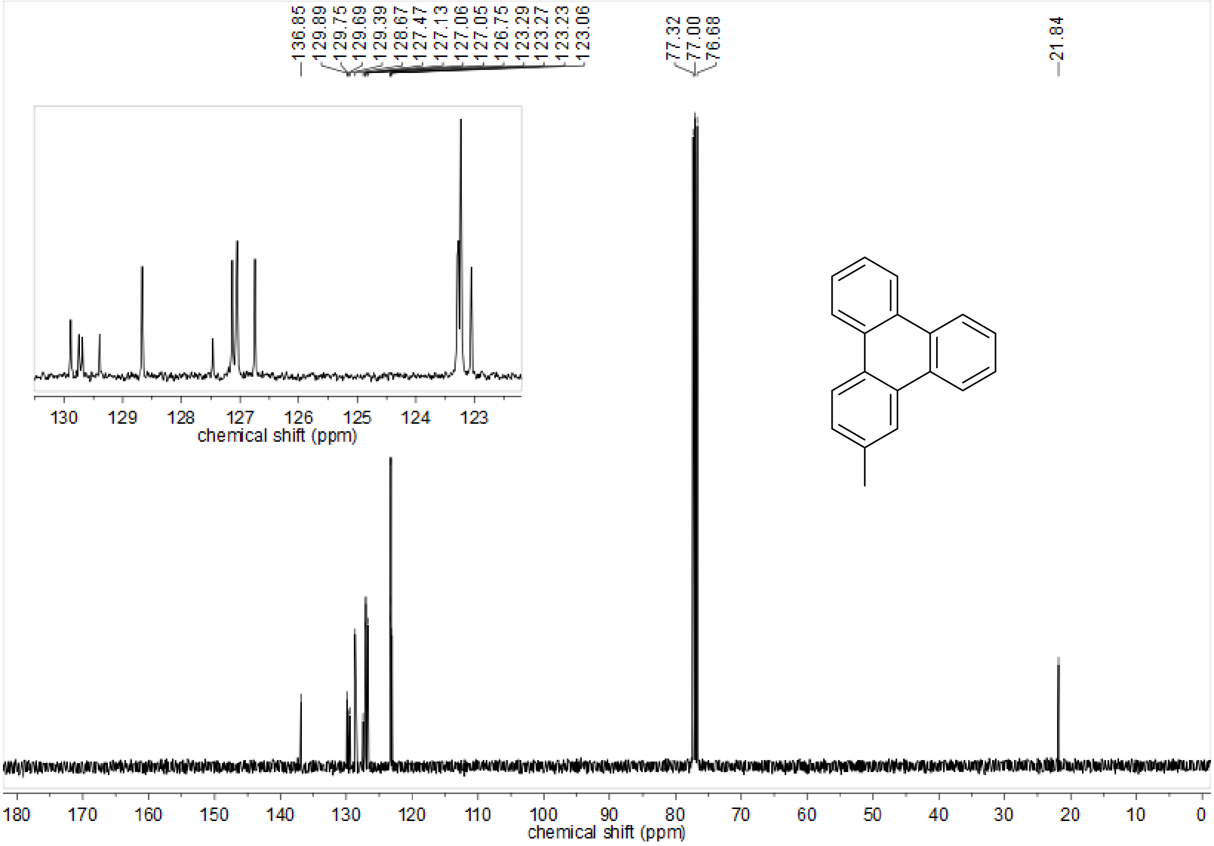
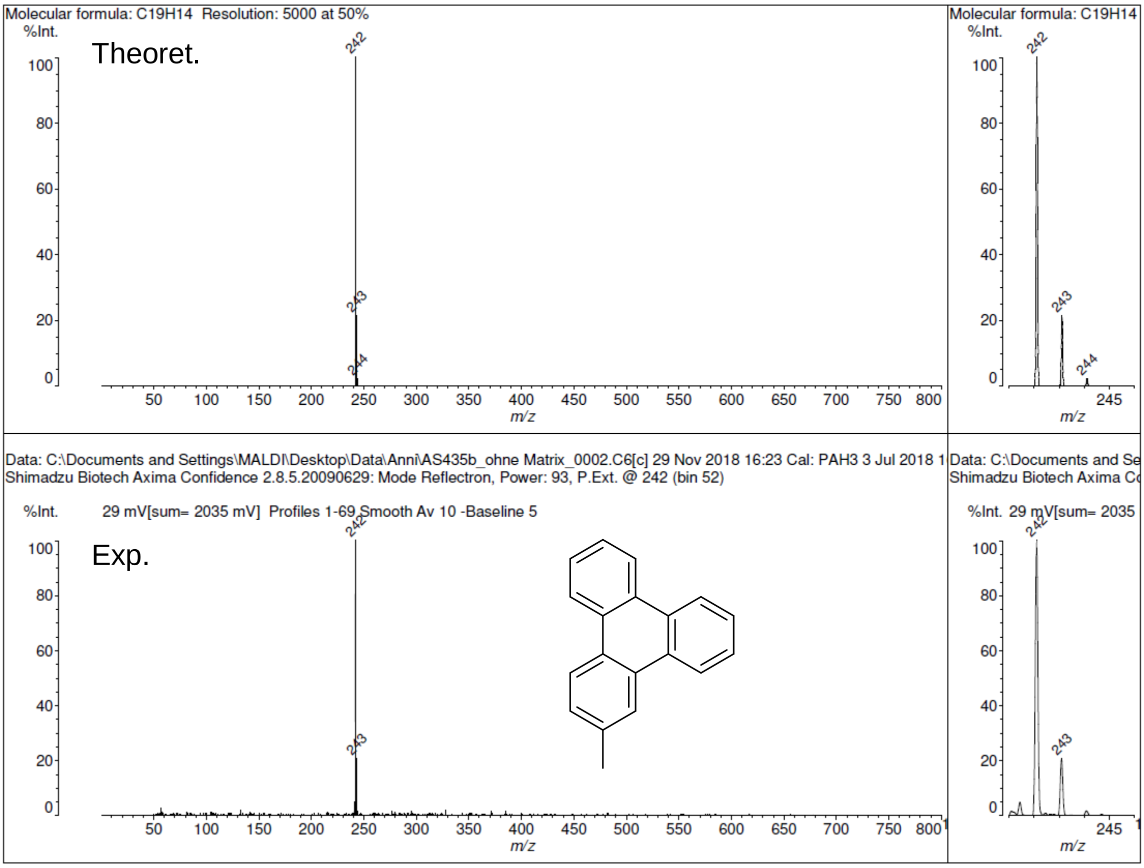


Figure S149: ^{13}C NMR spectrum of 2-methyltriphenylene (**T1**) (from reaction mixture, in $CDCl_3$).


Data: C:\Documents and Settings\MALDI\Desktop\Data\Anni\AS435b_ohne Matrix_0002.C6[c] 29 Nov 2018 16:23 Cal: PAH3 3 Jul 2018 1
Shimadzu Biotech Axima Confidence 2.8.5.20090629: Mode Reflectron, Power: 93, P.Ext. @ 242 (bin 52)

29 mV[sum= 2035 mV] Profiles 1-69 Smooth Av 10 -Baseline 5

Figure S150: LDI MS spectrum of 2-methyltriphenylene (**T1**), *m/z* 242 (M^+, 100 %).

2-(*Tert*-butyl)triphenylene (T2)

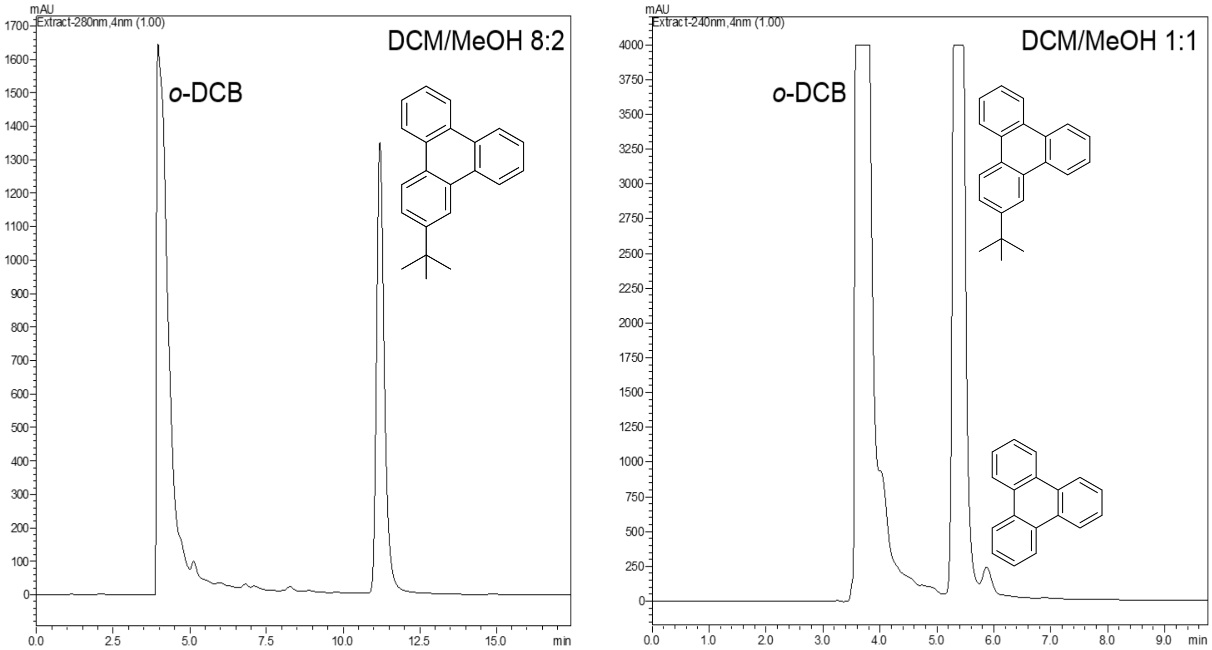


Figure S151: HPLC chromatogram obtained after reaction (250 °C, 4 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 2:8, left and DCM/MeOH 1:1, right).

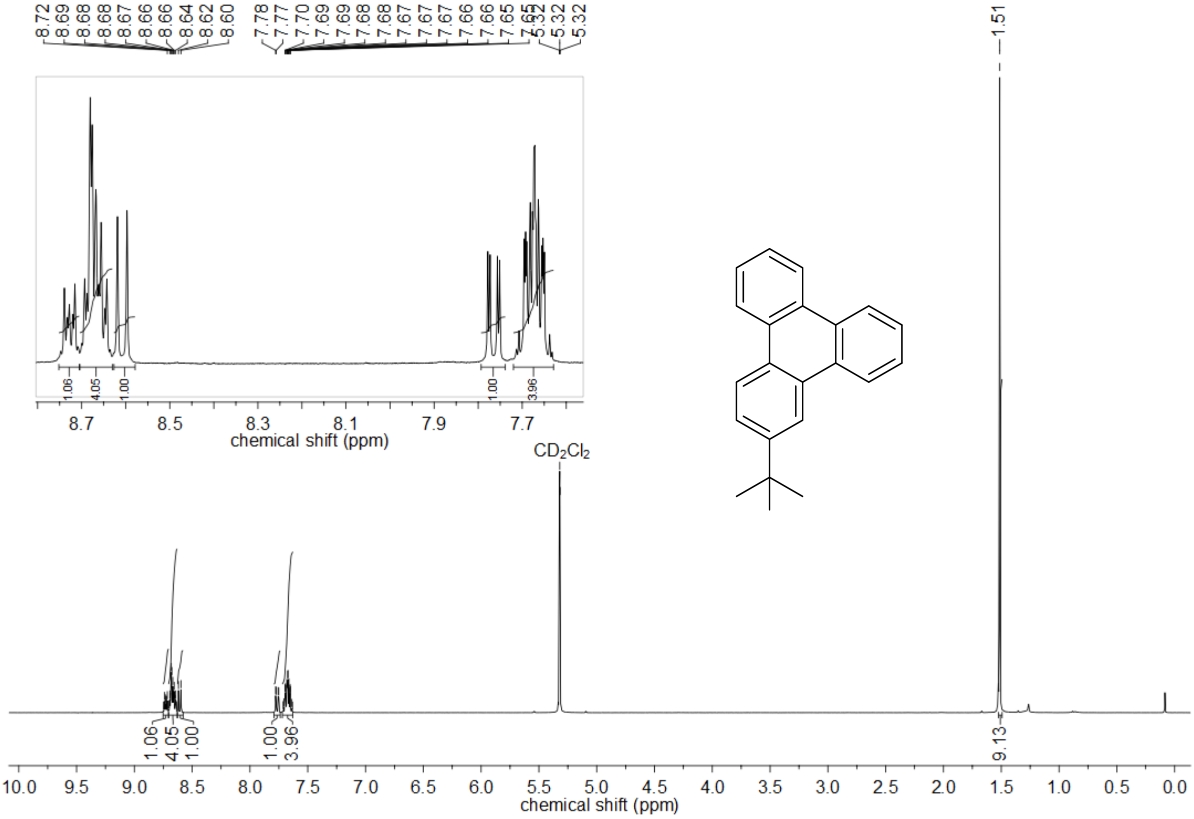


Figure S152: ^{1}H NMR spectrum of 2-(*tert*-butyl)triphenylene (**T2**) (in CD_2Cl_2).

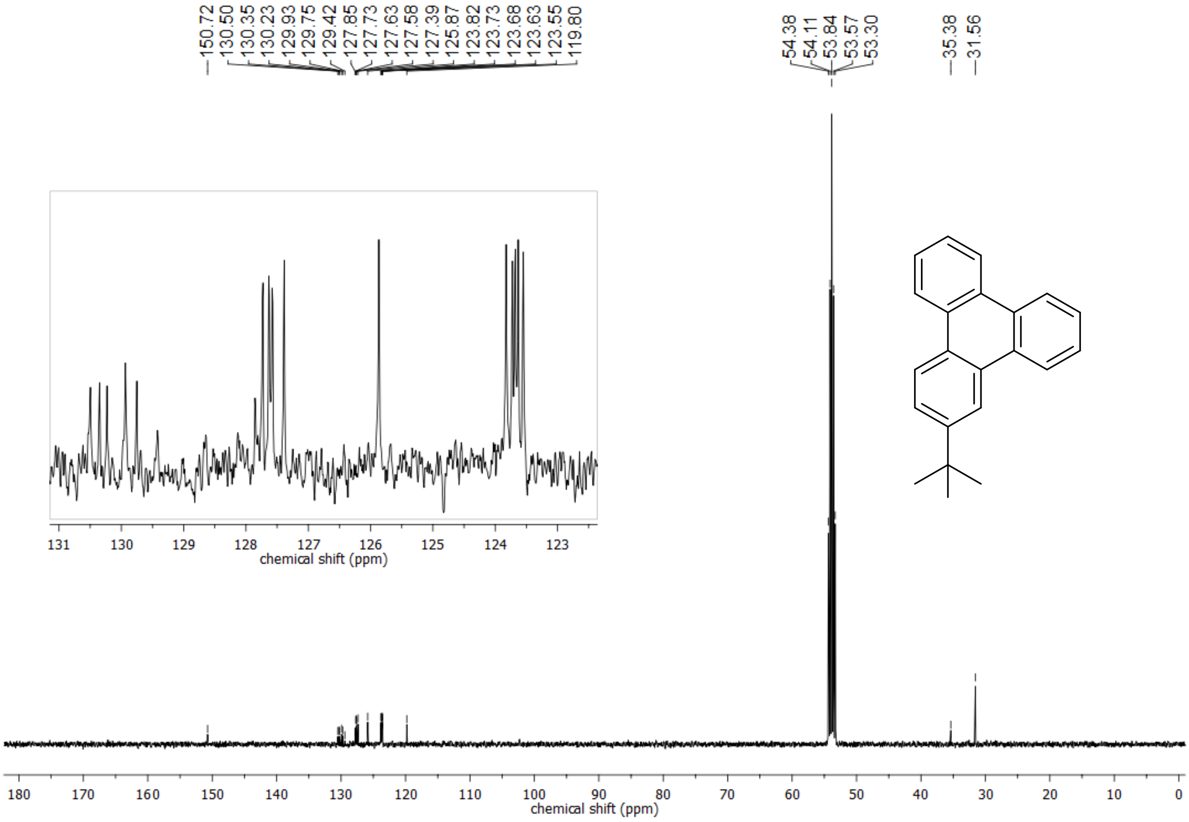


Figure S153: ^{13}C NMR spectrum of 2-(*tert*-butyl)triphenylene (**T2**) (in CD_2Cl_2).

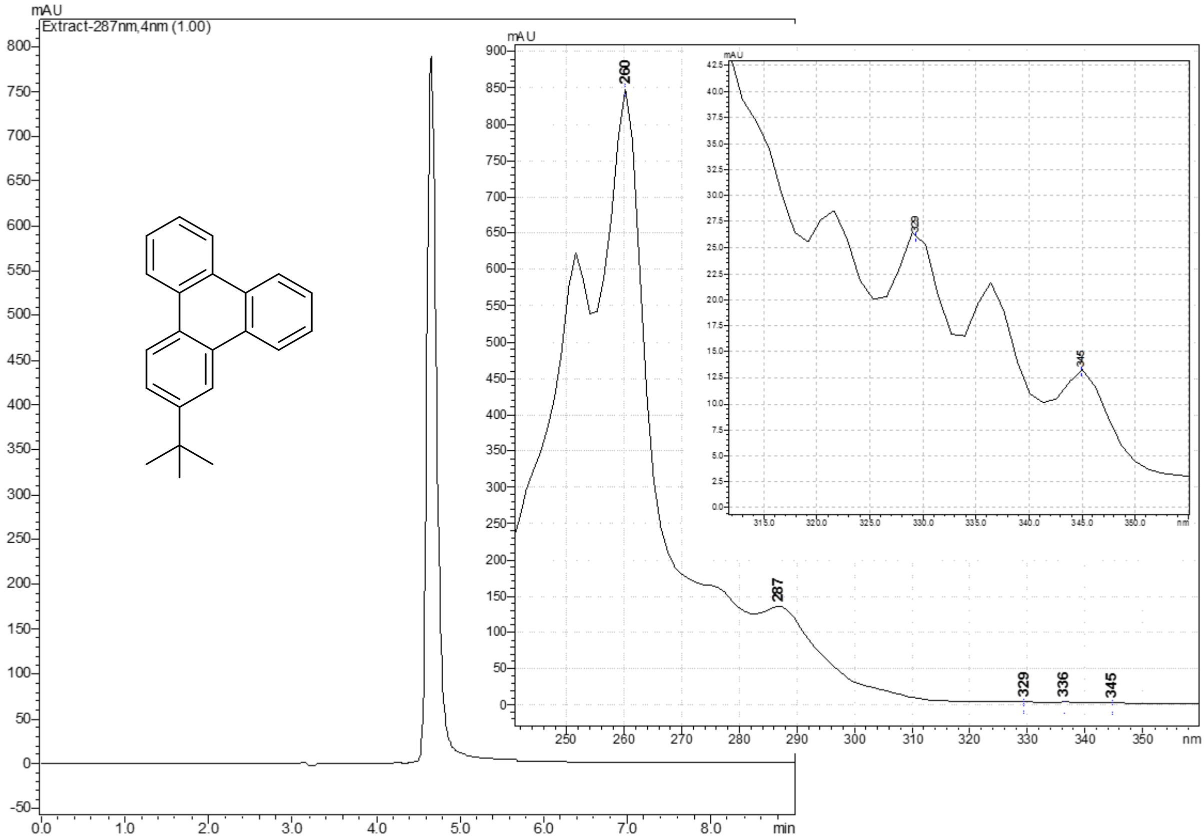
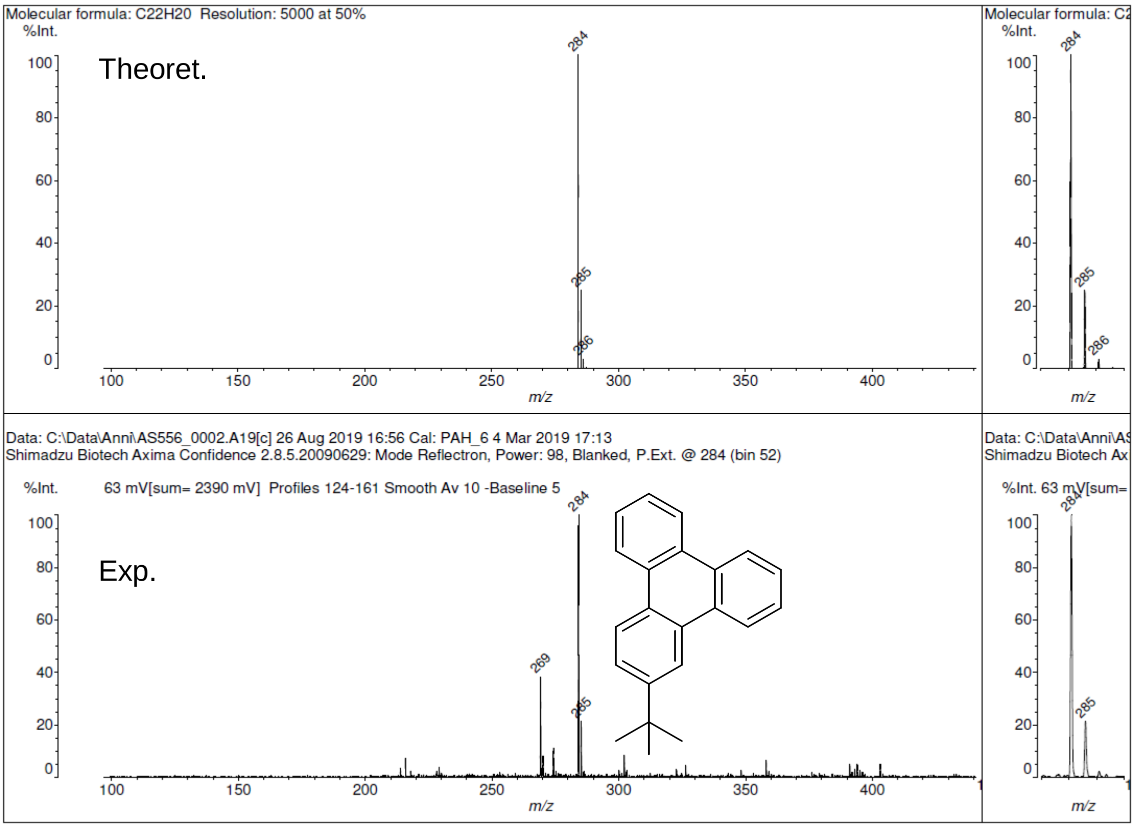


Figure S154: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, CH_2Cl_2/MeOH 6:4, t_R 4.66 min) and UV/vis spectrum (inset) of 2-(*tert*-butyl)triphenylene (**T2**).

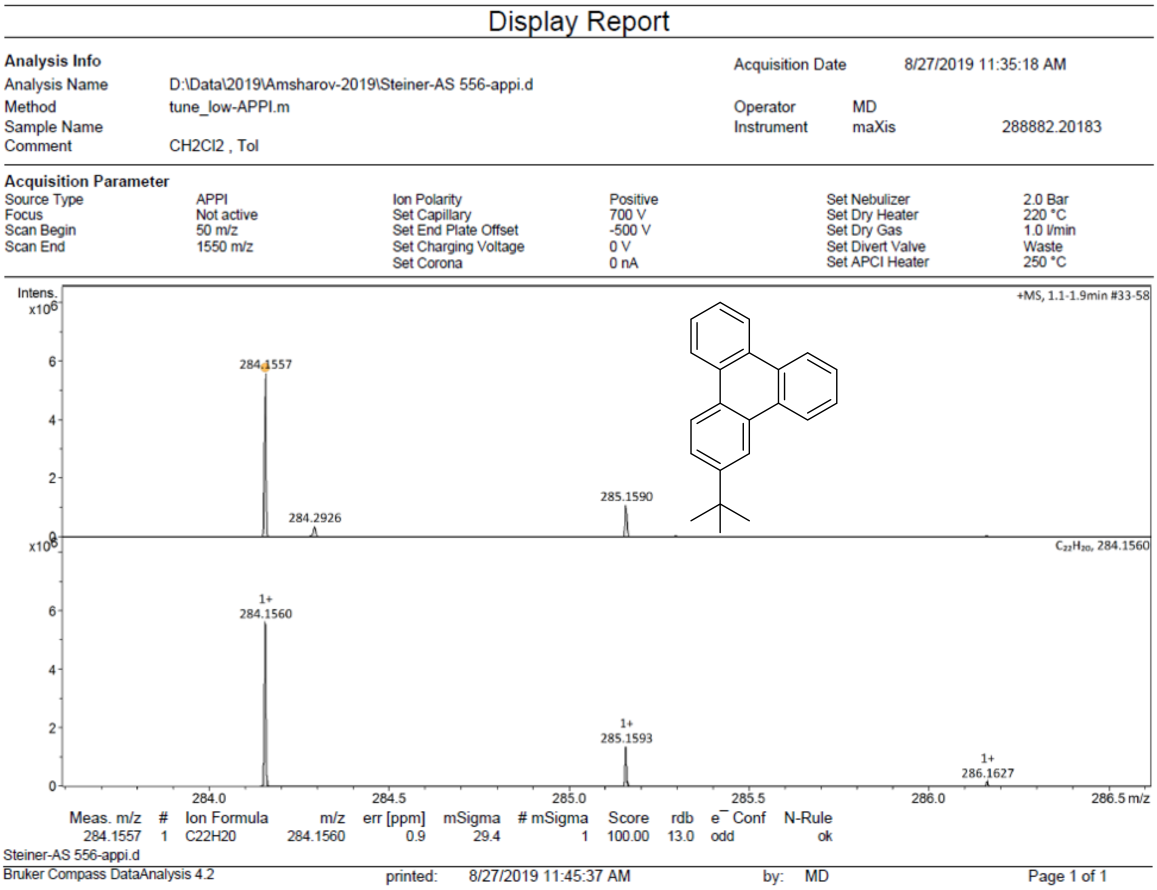


Molecular formula: C22H20 Resolution: 5000 at 50%

Data: C:\Data\Anni\AS556_0002.A19[c] 26 Aug 2019 16:56 Cal: PAH_6 4 Mar 2019 17:13
Shimadzu Biotech Axima Confidence 2.8.5.20090629: Mode Reflectron, Power: 98, Blanked, P.Ext. @ 284 (bin 52)

%Int. 63 mV[sum= 2390 mV] Profiles 124-161 Smooth Av 10 -Baseline 5

Figure S155: LDI MS spectrum of 2-(*tert*-butyl)triphenylene (**T2**), *m/z* 284 (M^+, 100 %).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS 556-appi.d	Acquisition Date	8/27/2019 11:35:18 AM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2 , Tol			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
284.1557	1	C22H20	284.1560	0.9	29.4	1	100.00	13.0	odd	ok

Steiner-AS 556-appi.d

Bruker Compass DataAnalysis 4.2 printed: 8/27/2019 11:45:37 AM by: MD Page 1 of 1

Figure S46: HR MS (APPI) spectrum of 2-(*tert*-butyl)triphenylene (**T2**), *m/z* 284.1557 (M^+, 100 %).

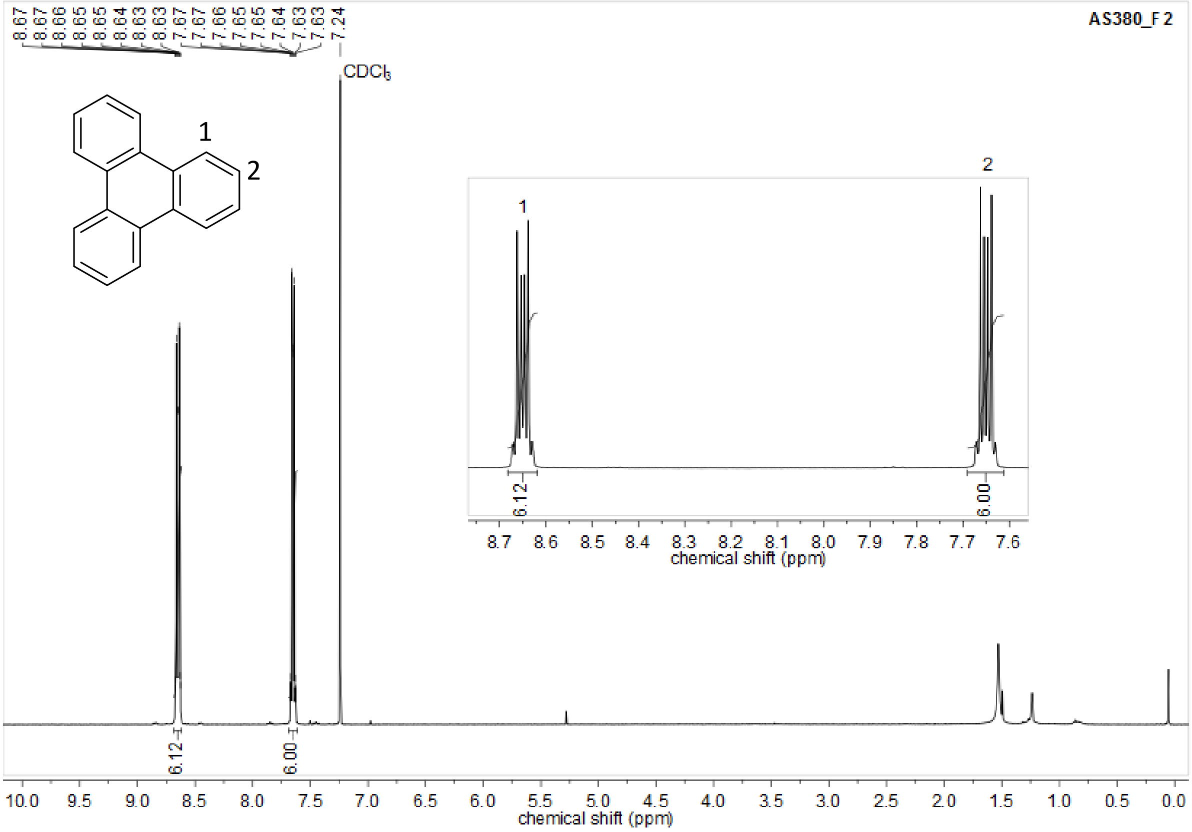


Figure S157: ^{1}H NMR spectrum of triphenylene (F2) (in $CDCl_3$).

Condensation of 2-Fluoro-4''-methoxy-1,1':2',1''-terphenyl (P3)

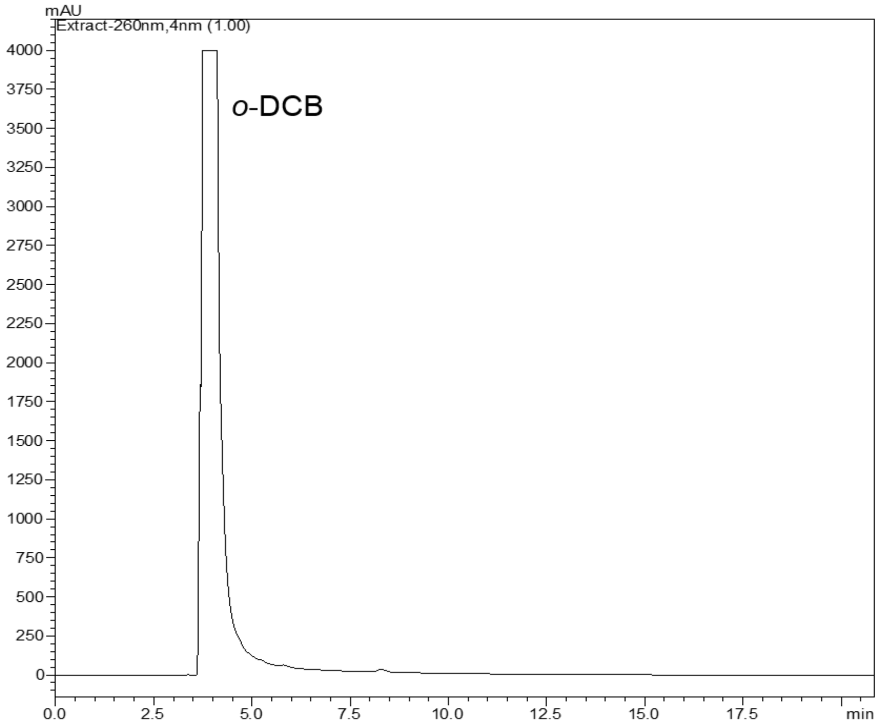


Figure S158: HPLC chromatogram obtained after reaction (200 °C, 5 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 3:7).

Condensation of Methyl 2''-fluoro-[1,1':2',1''-terphenyl]-4-carboxylate (P4)

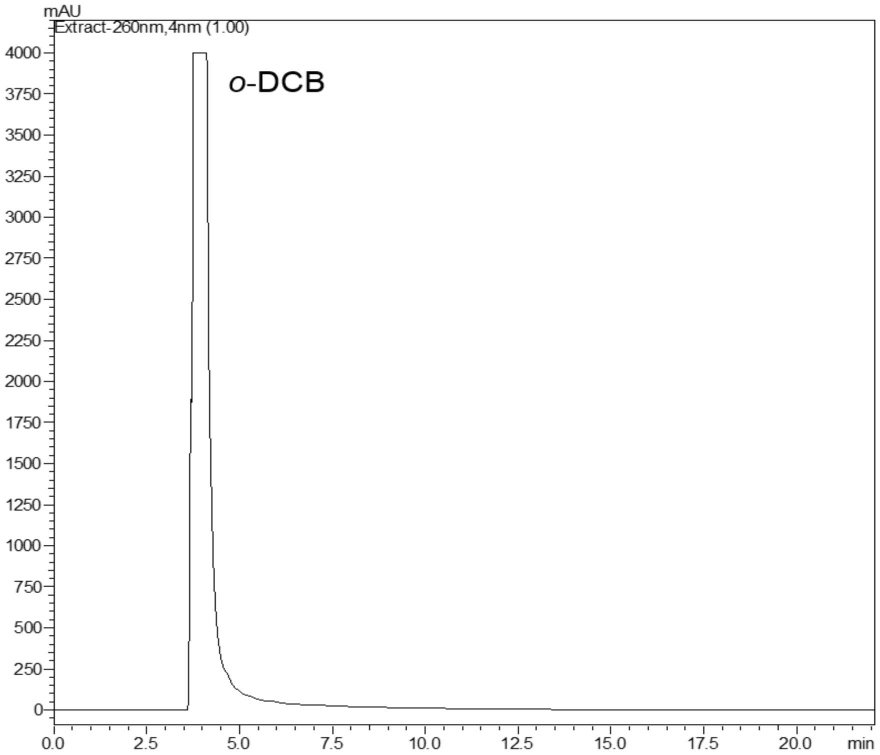


Figure S159: HPLC chromatogram obtained after reaction (200 °C, 5 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 3:7).

Condensation of 2''-Fluoro-*N*,*N*-dimethyl-[1,1':2',1''-terphenyl]-4-amine (P5)

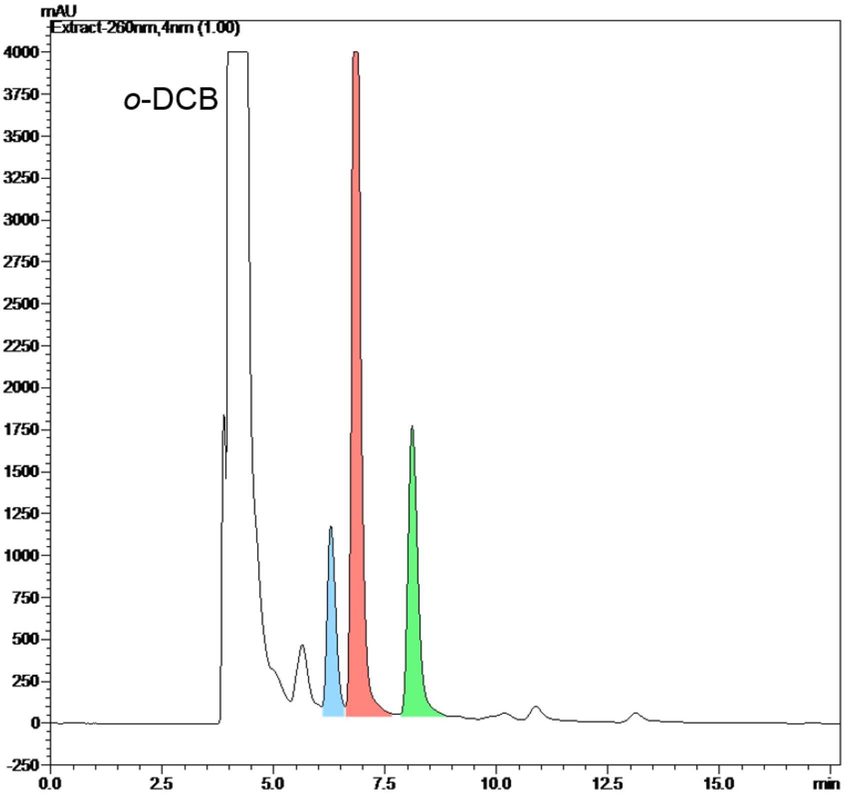


Figure S160: HPLC chromatogram obtained after reaction (200 °C, 5 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9).

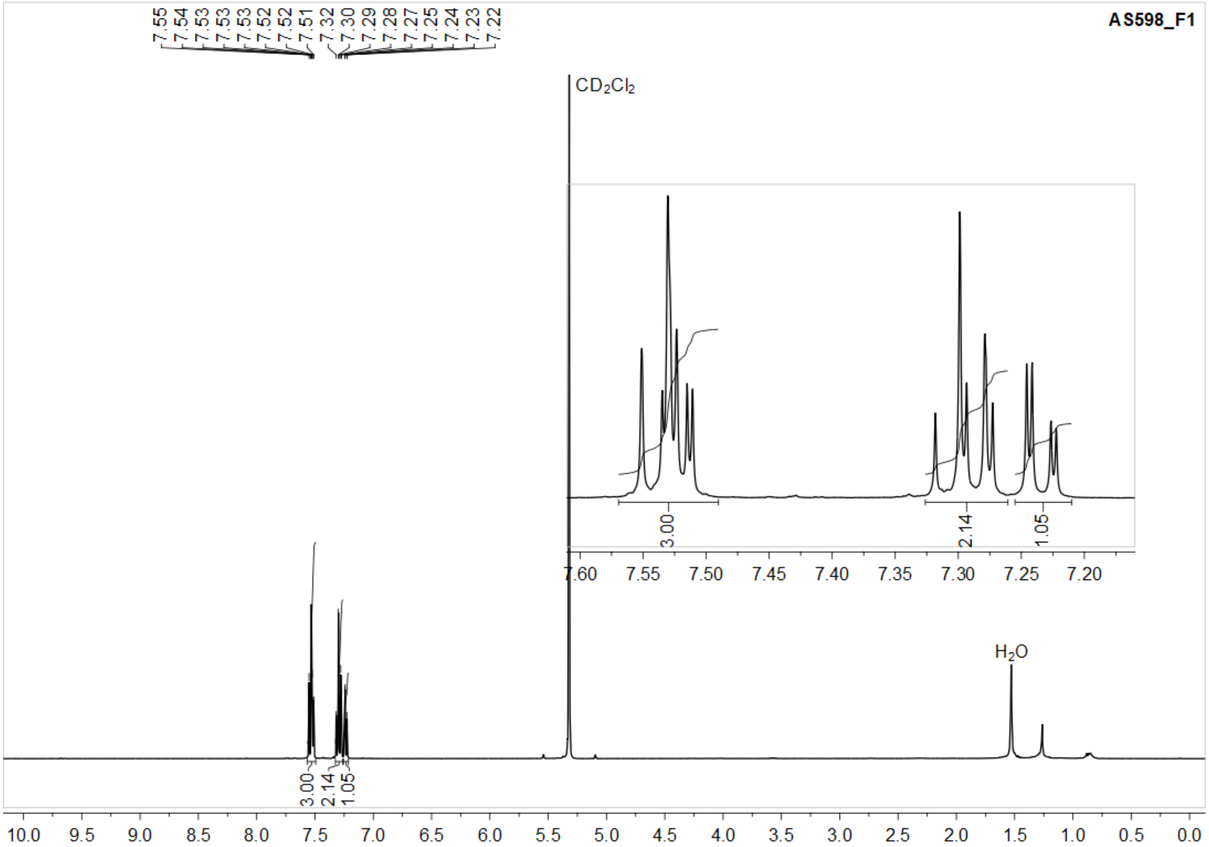


Figure S161: ^{1}H NMR spectrum of F1 (in CD_2Cl_2).

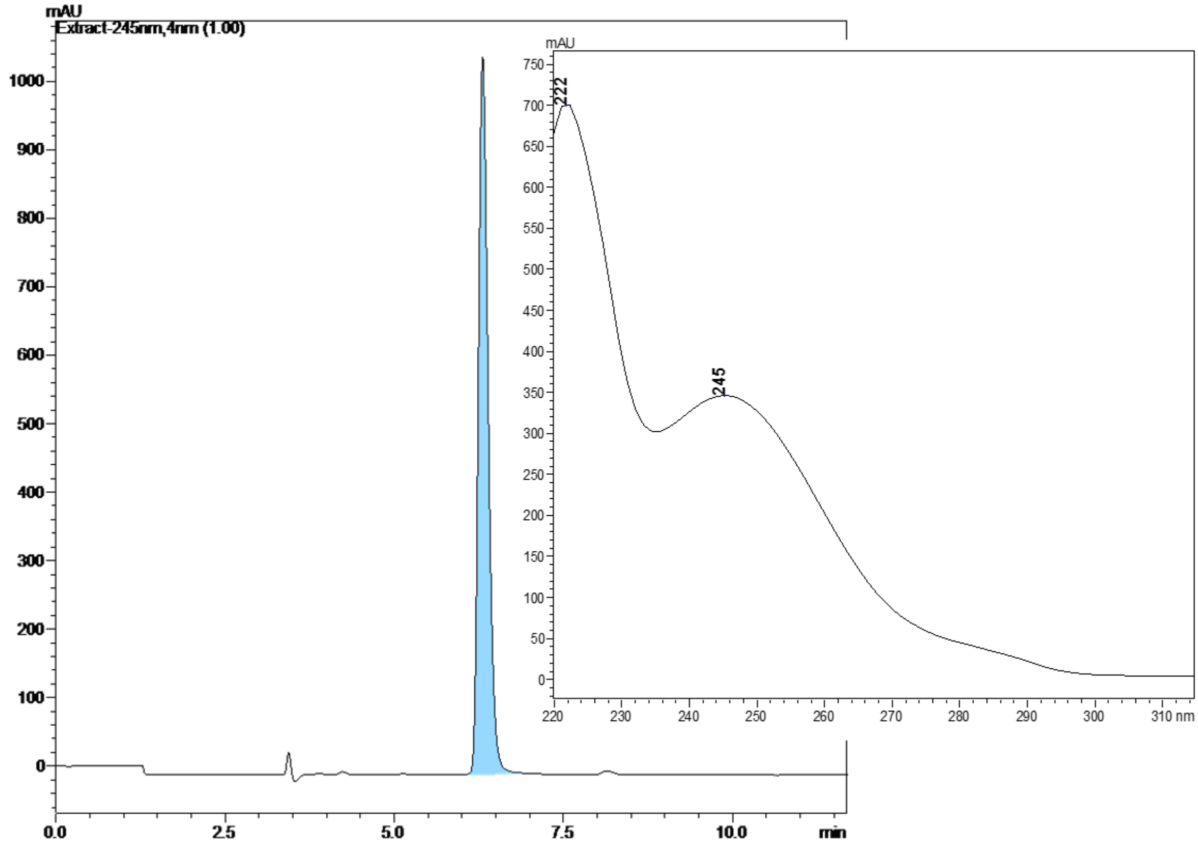


Figure S162: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9) and UV/vis spectrum (inset) of F1 (blue).

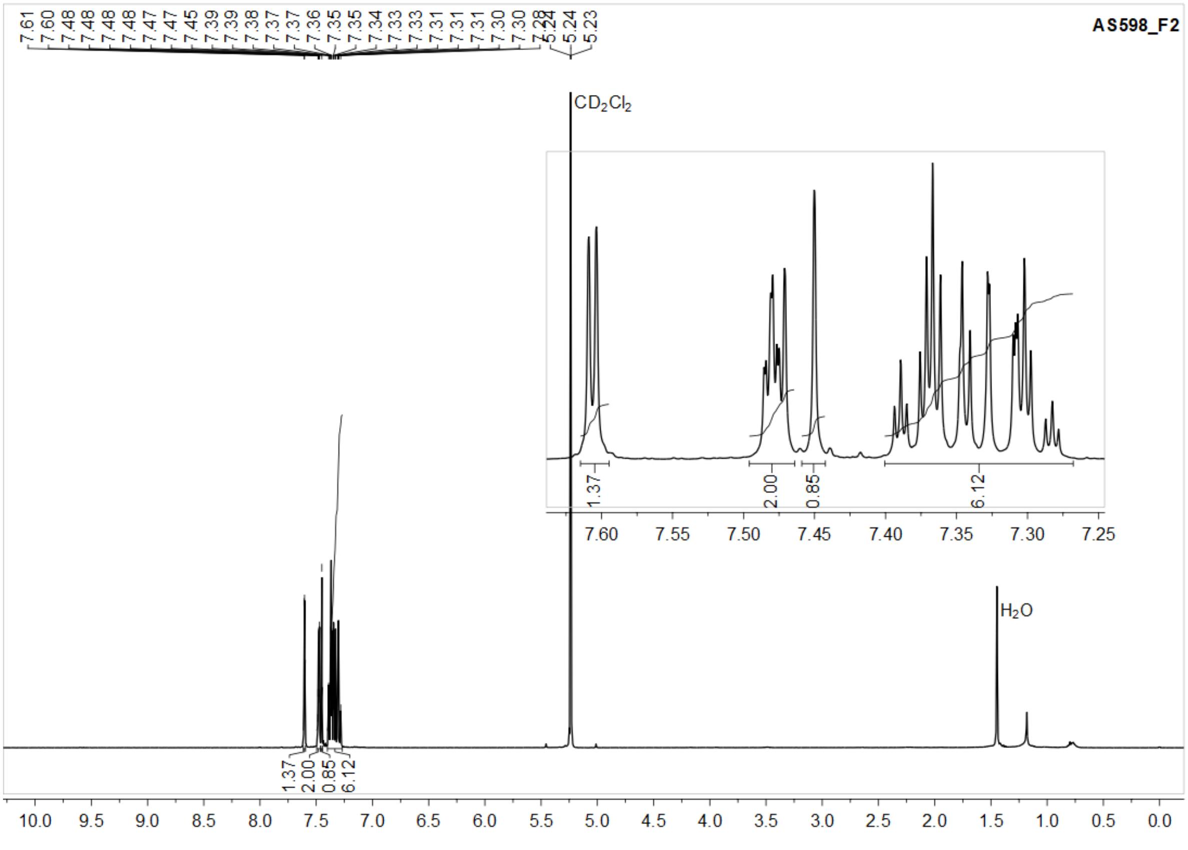


Figure S163: ^{1}H NMR spectrum of F2 (in CD_2Cl_2).

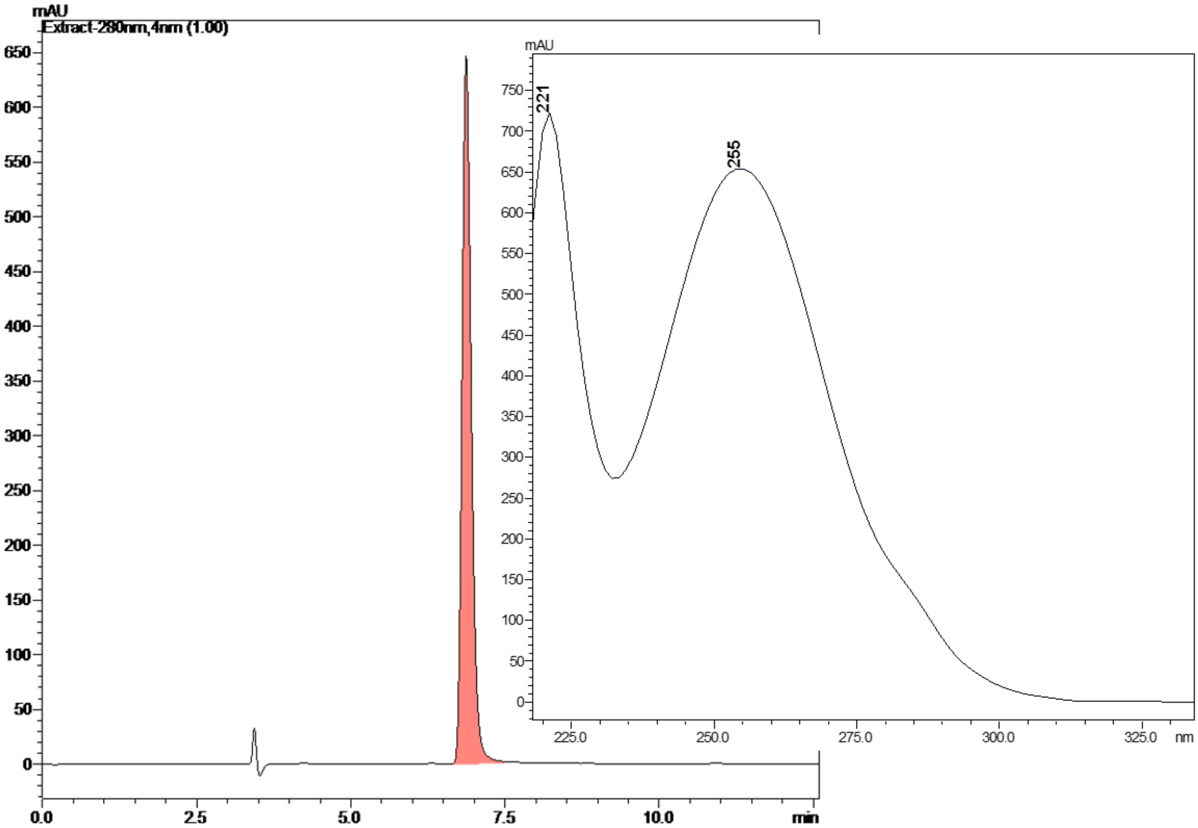


Figure S164: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9) and UV/vis spectrum (inset) of F2 (red).

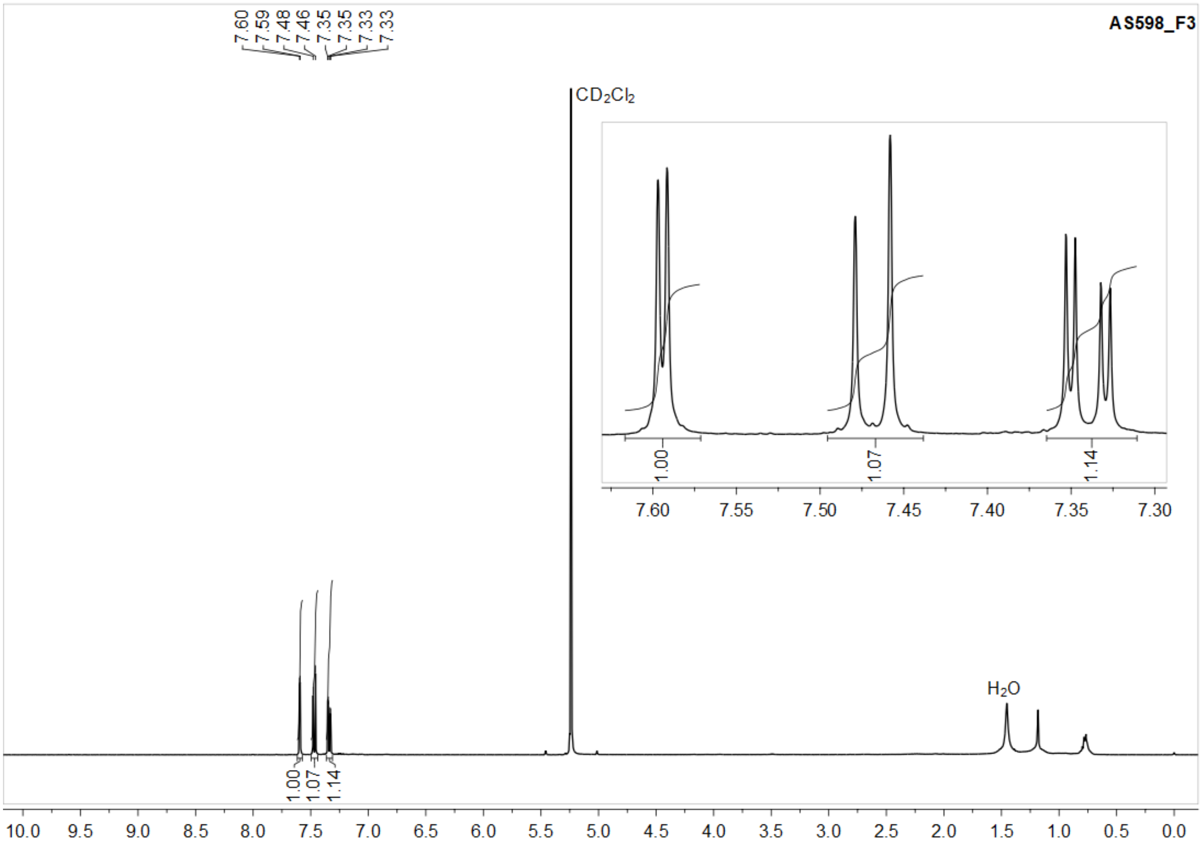


Figure S165: ^{1}H NMR spectrum of F3 (in CD_2Cl_2).

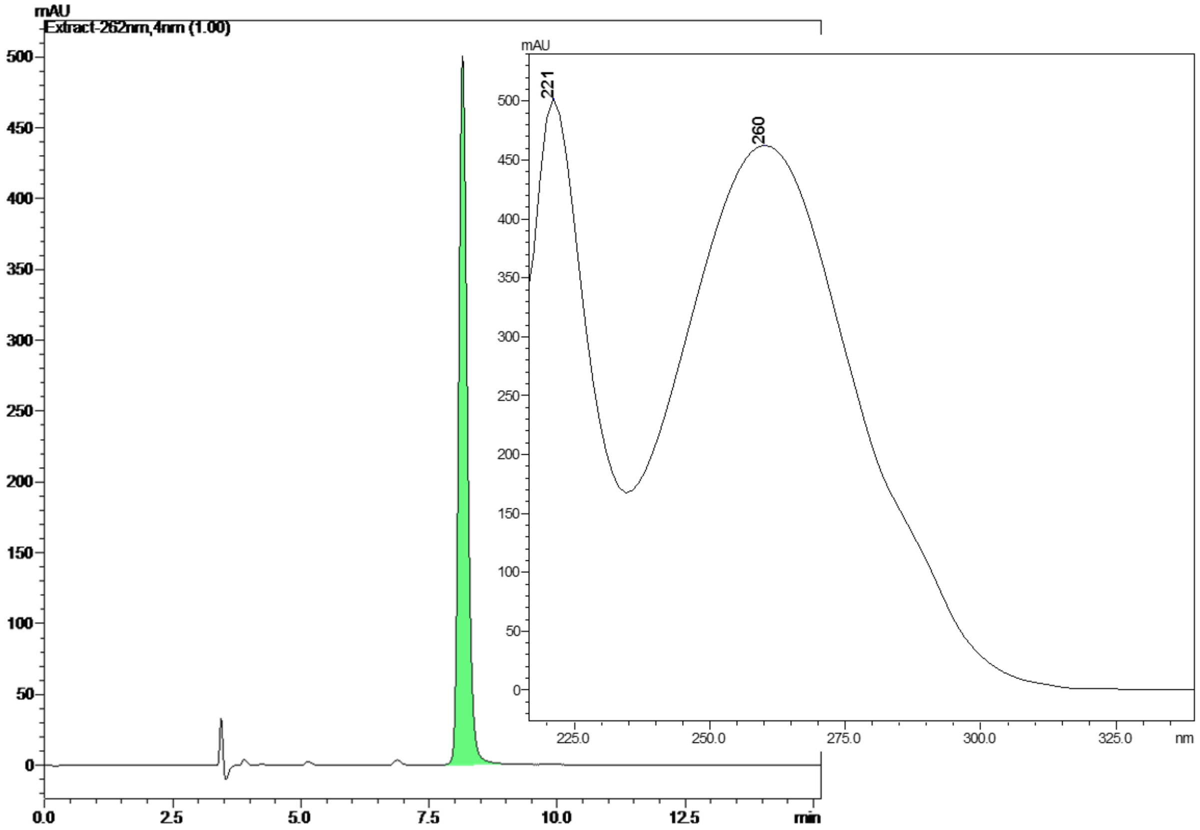


Figure S166: HPLC chromatogram (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9) and UV/vis spectrum (inset) of F3 (green).

Condensation of 4-(2'-Fluoro-[1,1'-biphenyl]-2-yl)pyridine (P6)

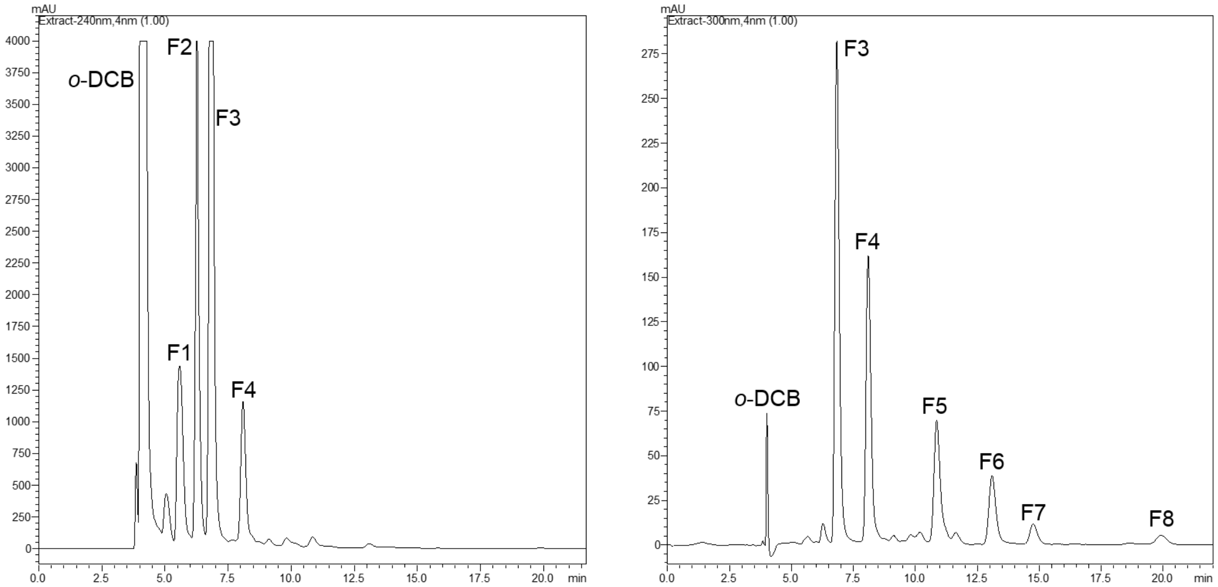


Figure S167: HPLC chromatogram obtained after reaction (200 °C, 5 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:9).

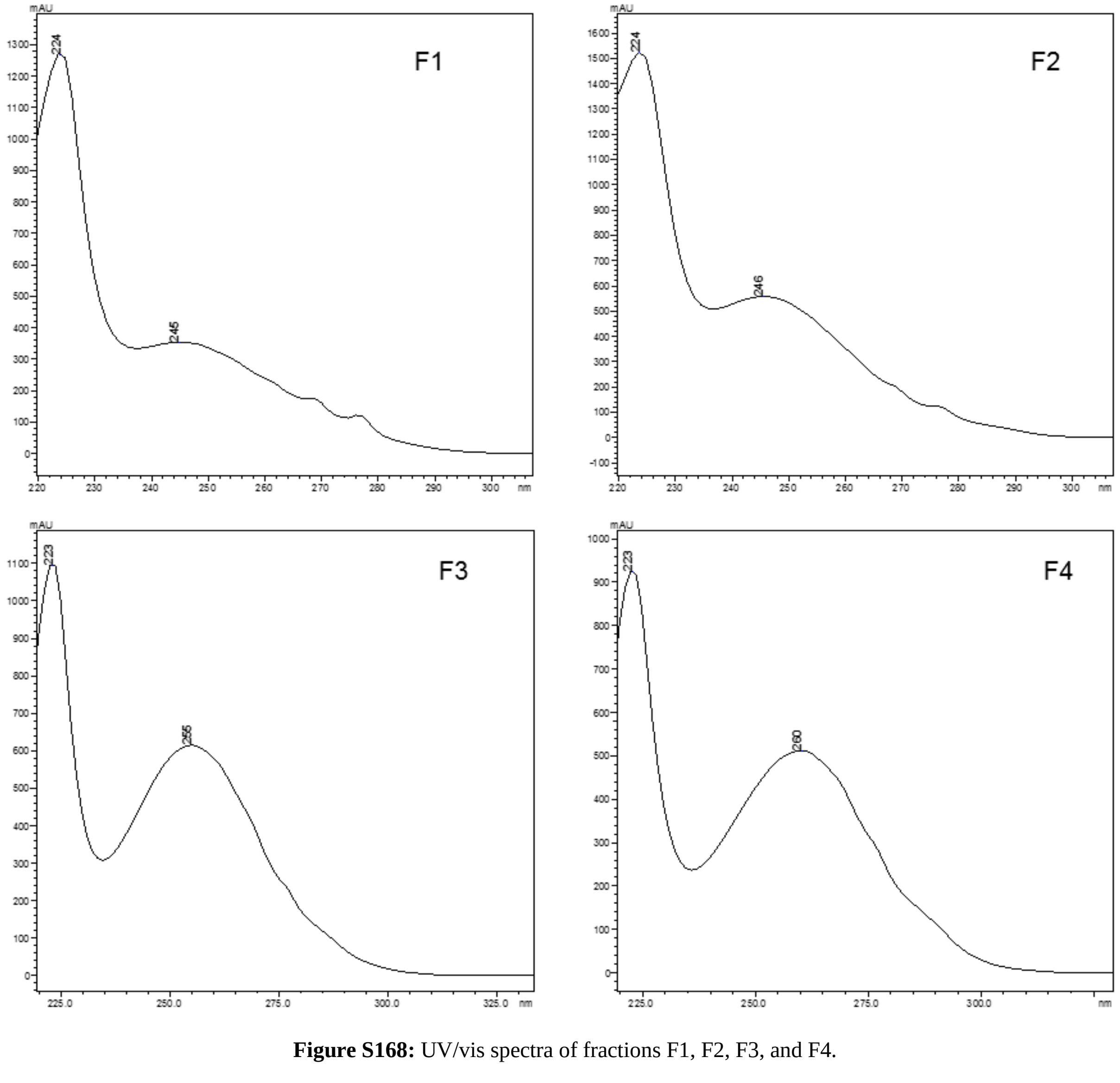


Figure S168: UV/vis spectra of fractions F1, F2, F3, and F4.

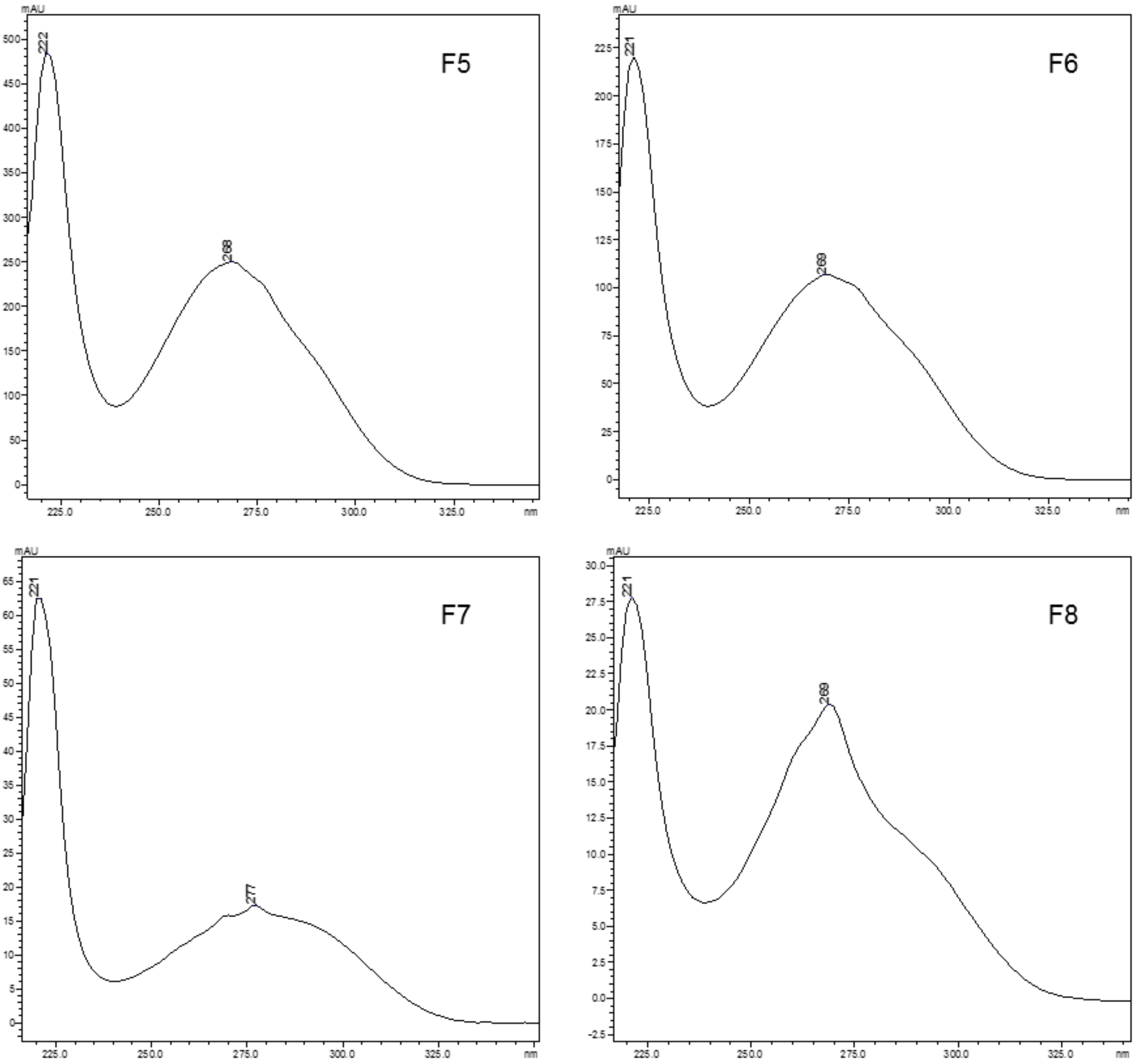


Figure S169: UV/vis spectra of fractions F5, F6, F7, and F8.

Triphenyleno[1,2-b]benzofuran (T3).

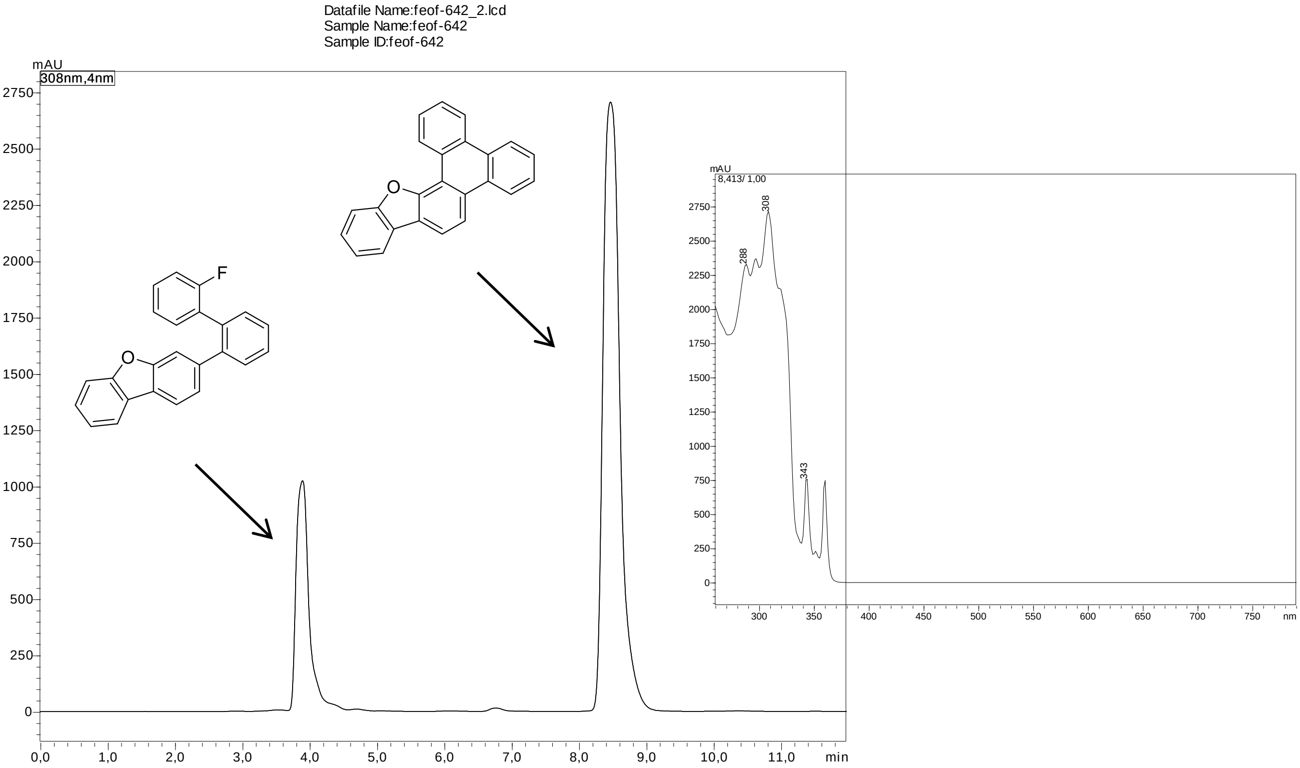


Figure S170: HPLC chromatogram obtained after reaction (240 °C, 12 h) (PBr column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 1:1) and UV/vis spectrum (inset) of triphenyleno[1,2-b]benzofuran (**T3**)

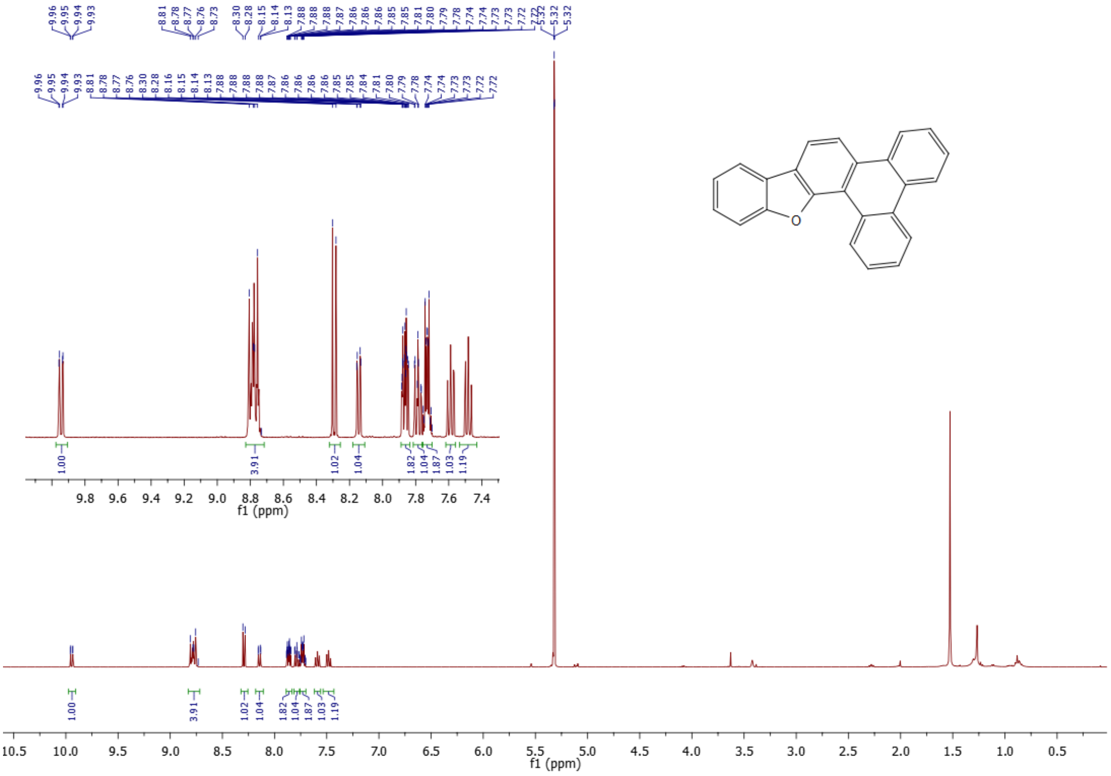


Figure S171: ^{1}H NMR spectrum of triphenyleno[1,2-b]benzofuran (**T3**) (in CD_2Cl_2).

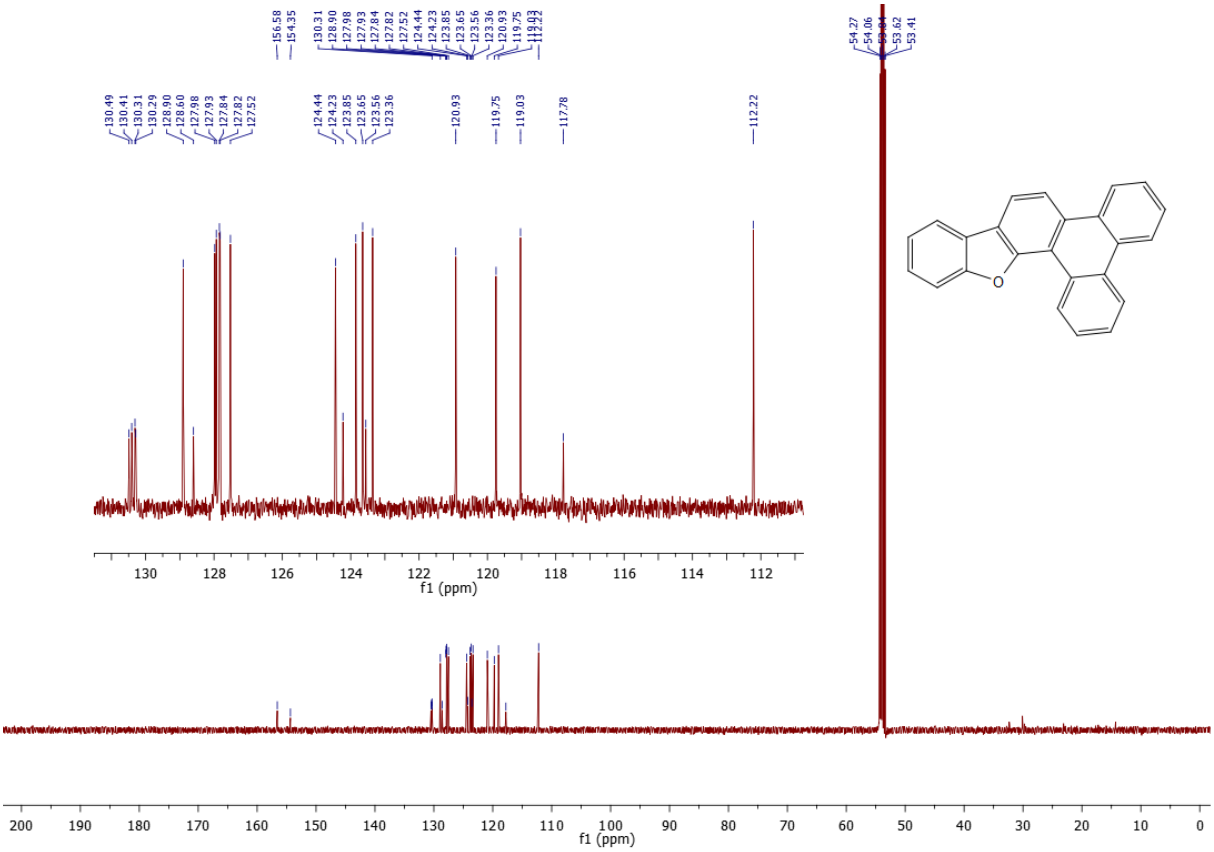
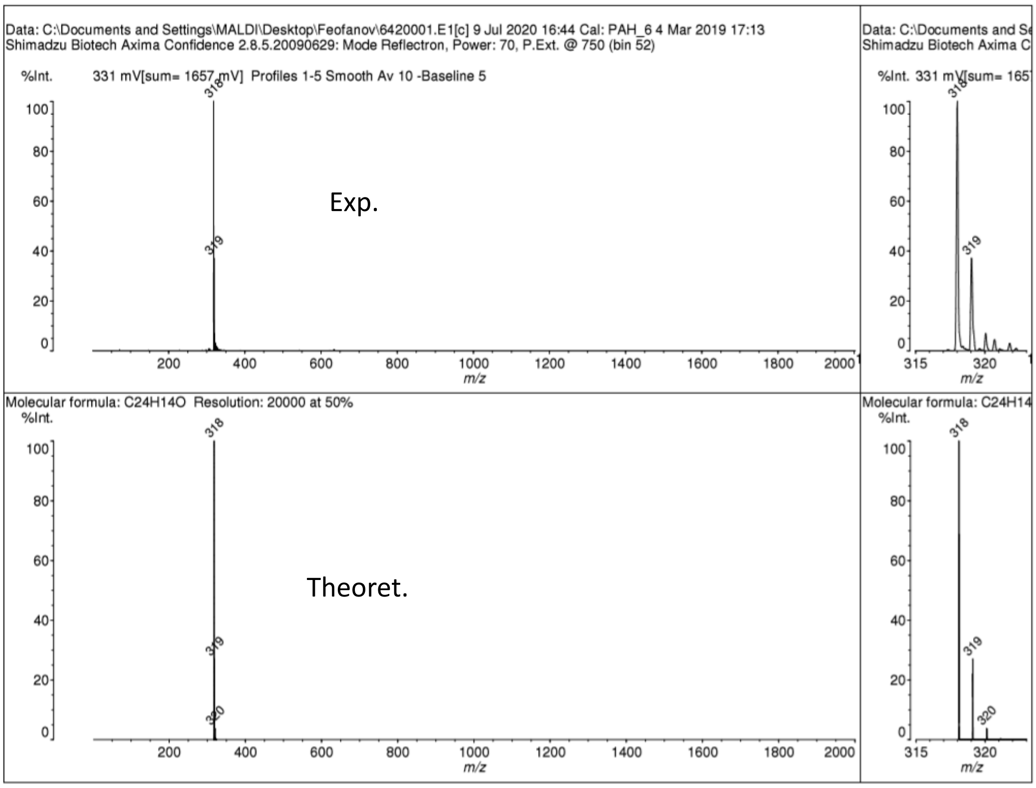


Figure S172: ^{13}C NMR spectrum of triphenyleno[1,2-b]benzofuran (**T3**) (in CD_2Cl_2).


Data: C:\Documents and Settings\MALDI\Desktop\Feofanov\6420001.E1[c] 9 Jul 2020 16:44 Cal: PAH_6 4 Mar 2019 17:13
Shimadzu Biotech Axima Confidence 2.8.5.20090629: Mode Reflectron, Power: 70, P.Ext. @ 750 (bin 52)
%Int. 331 mV[sum= 1657 mV] Profiles 1-5 Smooth Av 10 -Baseline 5

Data: C:\Documents and Se
Shimadzu Biotech Axima C
%Int. 331 mV[sum= 165

Molecular formula: C24H14O Resolution: 20000 at 50%

Molecular formula: C24H14

Figure S173: LDI MS spectrum of triphenyleno[1,2-b]benzofuran (**T3**), *m/z* 318 (M^+, 100 %).

Benzo[b]triphenyleno[2,1-d]thiophene (T4).

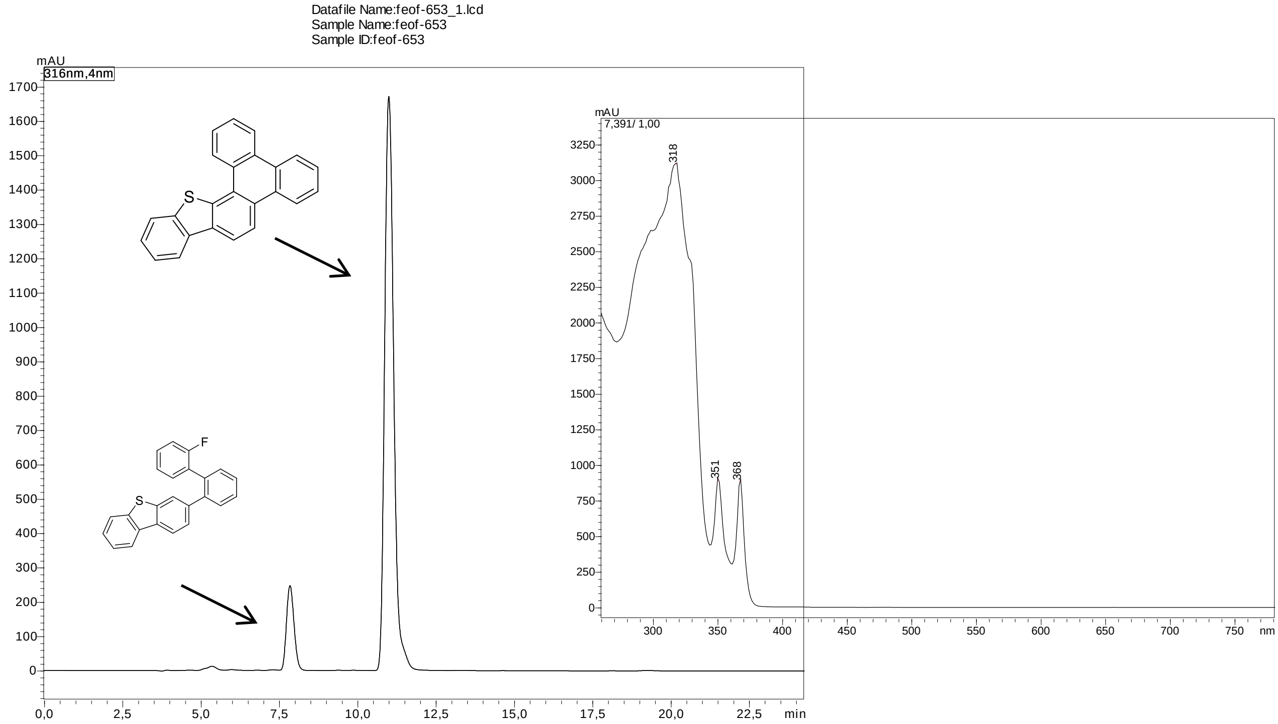


Figure S174: HPLC chromatogram obtained after reaction (240 °C, 12 h) (PBr column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 1:1) and UV/vis spectrum (inset) of benzo[b]triphenyleno[2,1-d]thiophene (**T4**).

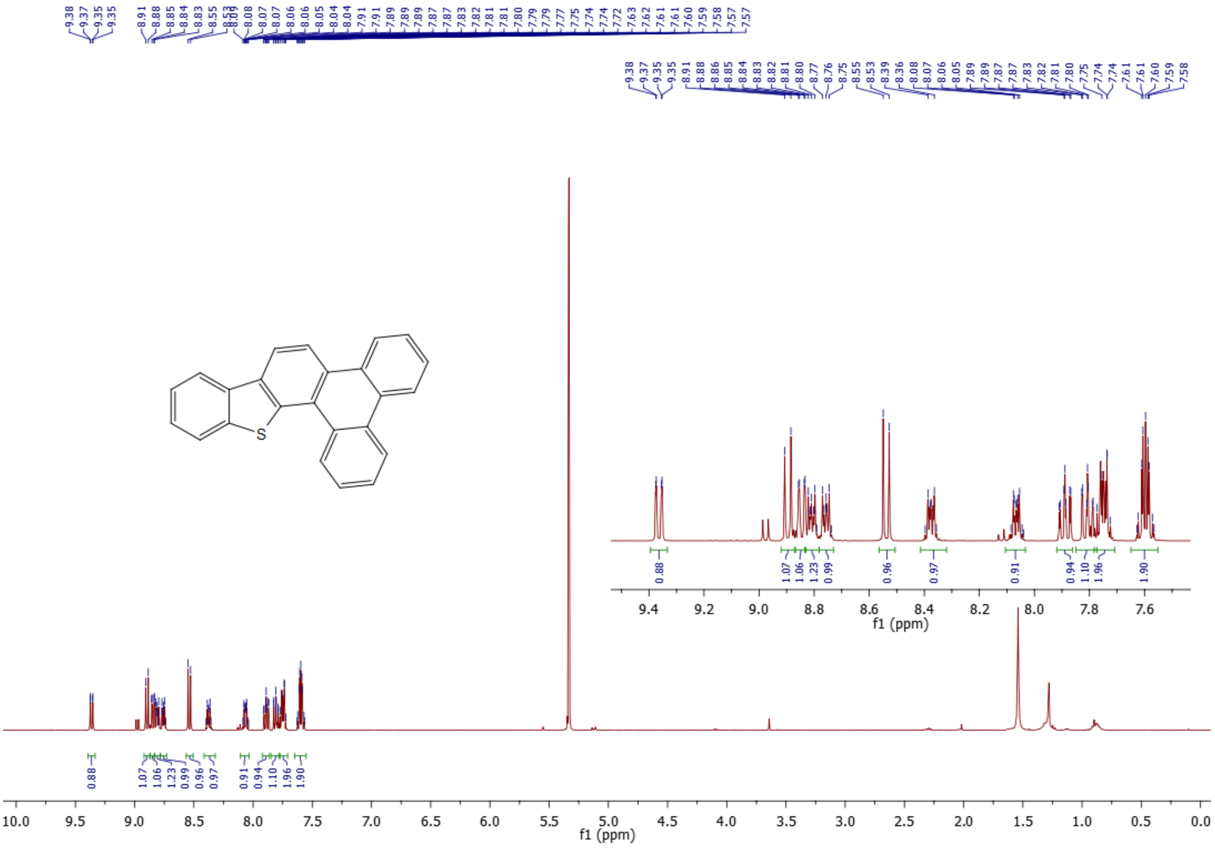


Figure S175: ^{1}H NMR spectrum of benzo[b]triphenyleno[2,1-d]thiophene (**T4**) (in CD_2Cl_2).

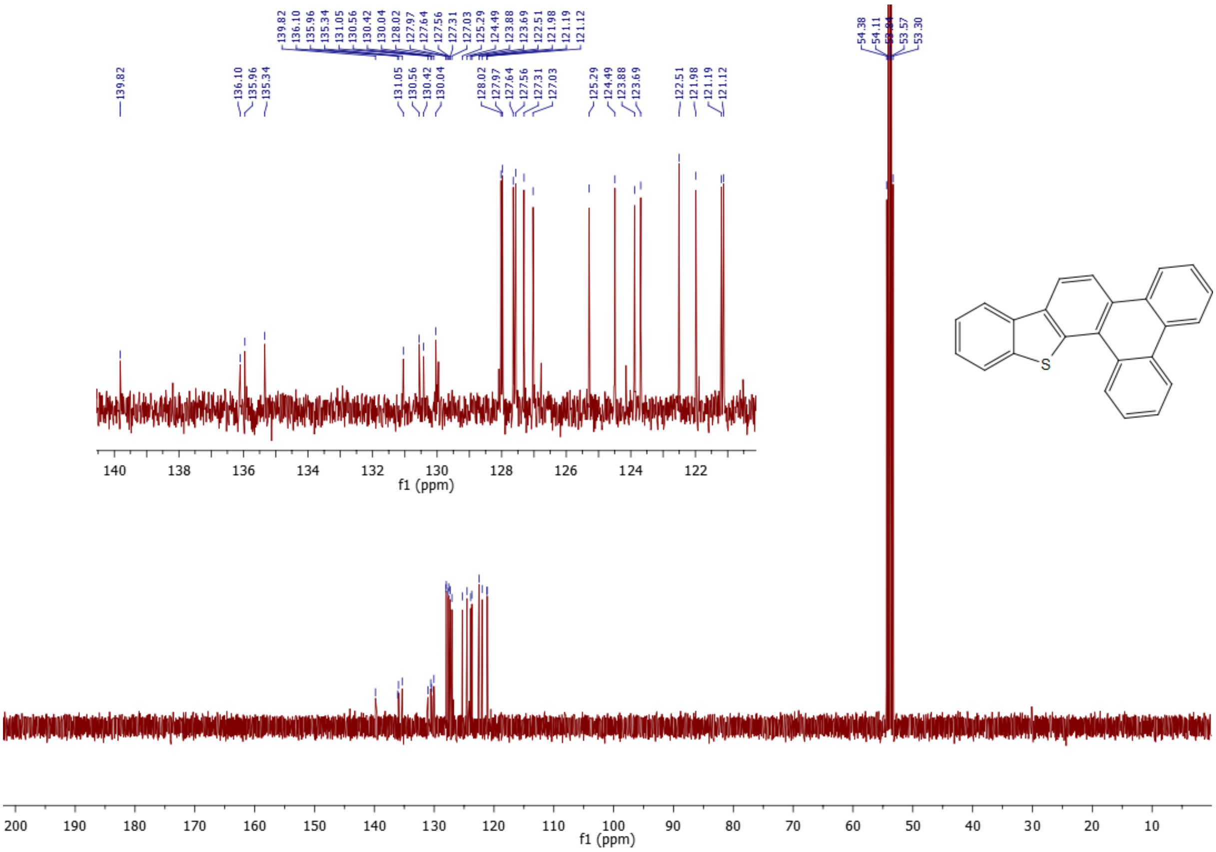
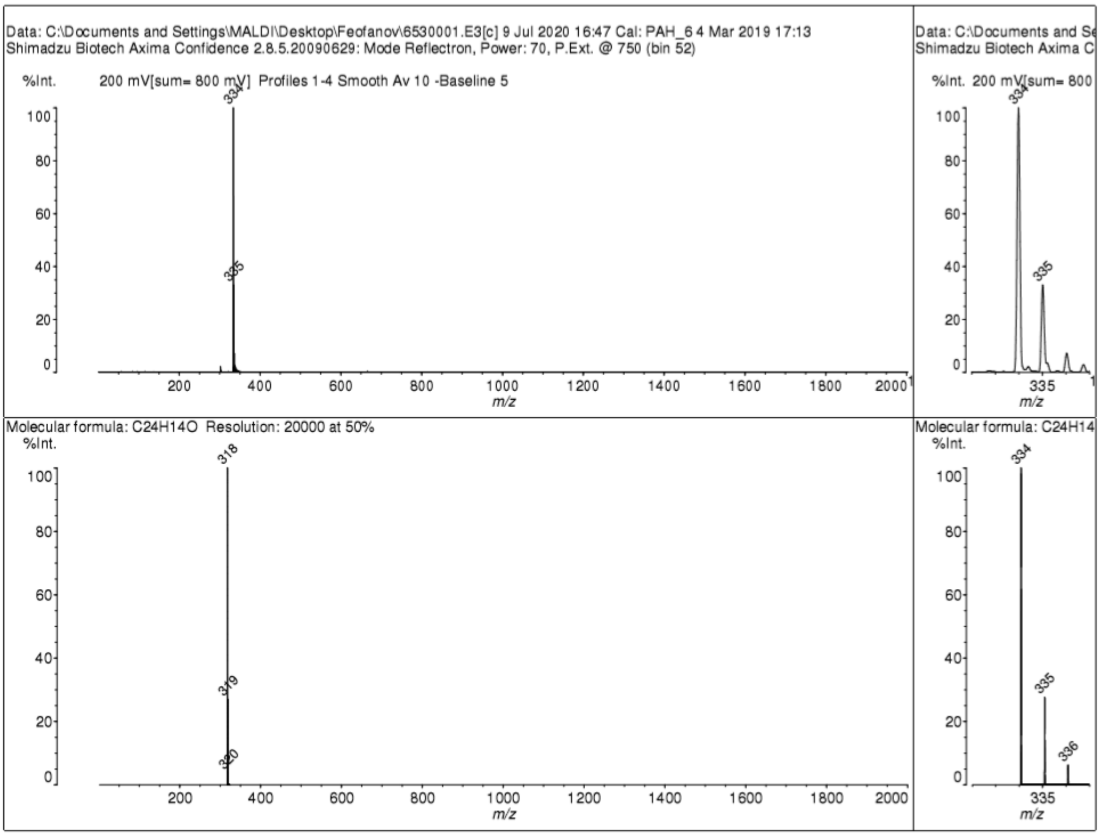


Figure S176: ^{13}C NMR spectrum of benzo[b]triphenyleno[2,1-d]thiophene (**T4**) (in CD_2Cl_2).


Data: C:\Documents and Settings\MALDI\Desktop\Feofanov\6530001.E3[c] 9 Jul 2020 16:47 Cal: PAH_6 4 Mar 2019 17:13
Shimadzu Biotech Axima Confidence 2.8.5.20090629: Mode Reflectron, Power: 70, P.Ext. @ 750 (bin 52)
%Int. 200 mV[sum= 800 mV] Profiles 1-4 Smooth Av 10 -Baseline 5

Data: C:\Documents and S
Shimadzu Biotech Axima C
%Int. 200 mV[sum= 800

Molecular formula: C24H14O Resolution: 20000 at 50%

Molecular formula: C24H14

Figure S177: LDI MS spectrum of benzo[b]triphenyleno[2,1-d]thiophene (**T4**), *m/z* 334 (M^+, 100 %).

Benzo[*b*]triphenyleno[1,2-*d*]thiophene (T5) and Benzo[b]triphenyleno[2,3-d]thiophene (T6)

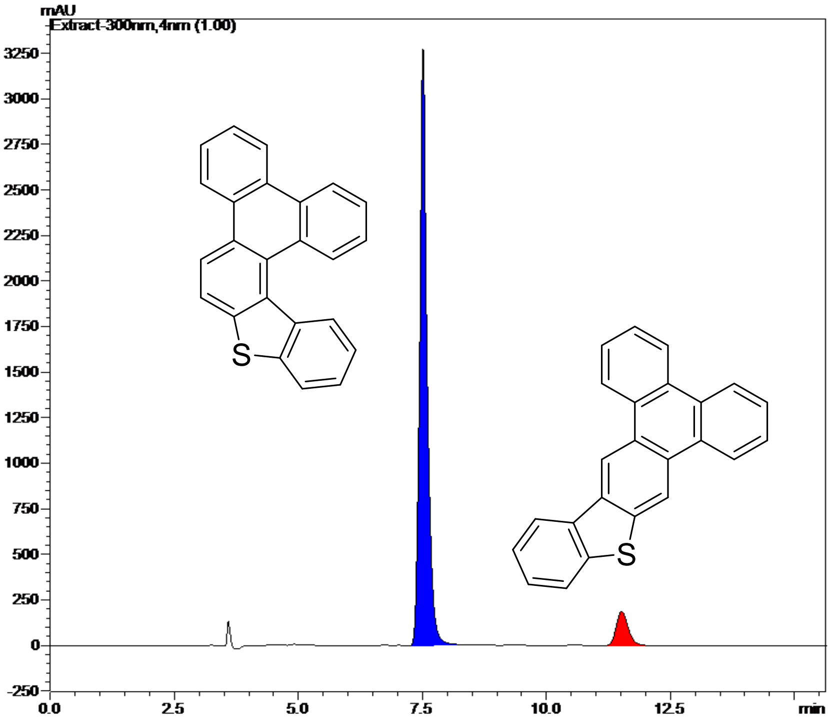


Figure S178: HPLC chromatogram obtained after reaction (250 °C, 4 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1).

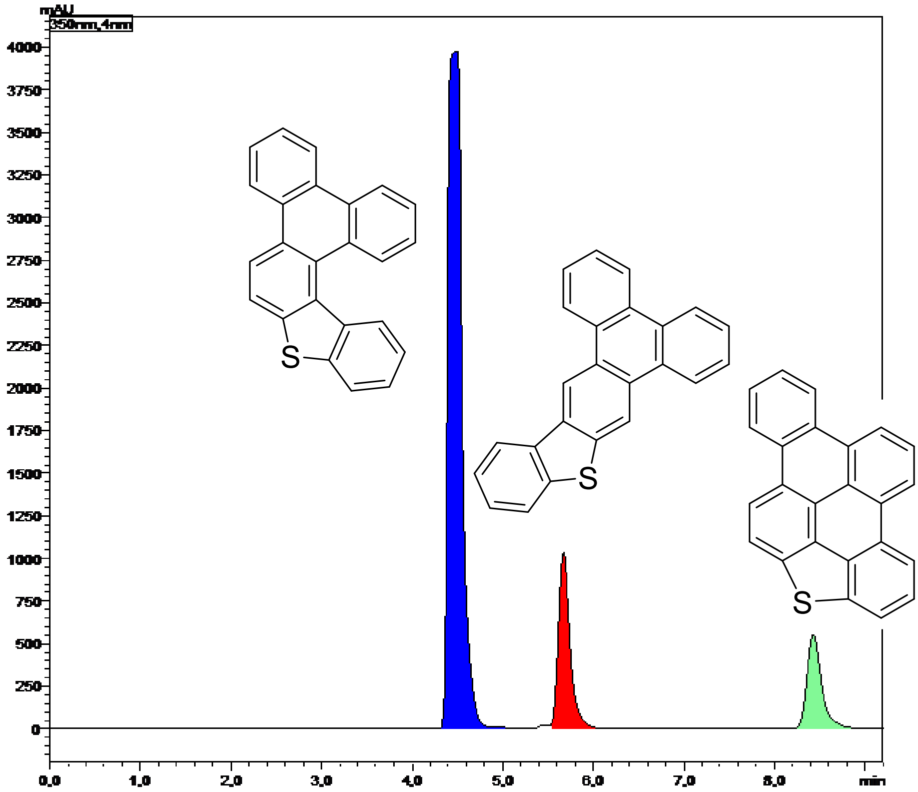


Figure S179: HPLC chromatogram of separation (PBr column (analyt.), 5.0 mL/min, 40 °C, DCM/MeOH 7:3).

Benzo[*b*]triphenyleno[1,2-*d*]thiophene (T5)

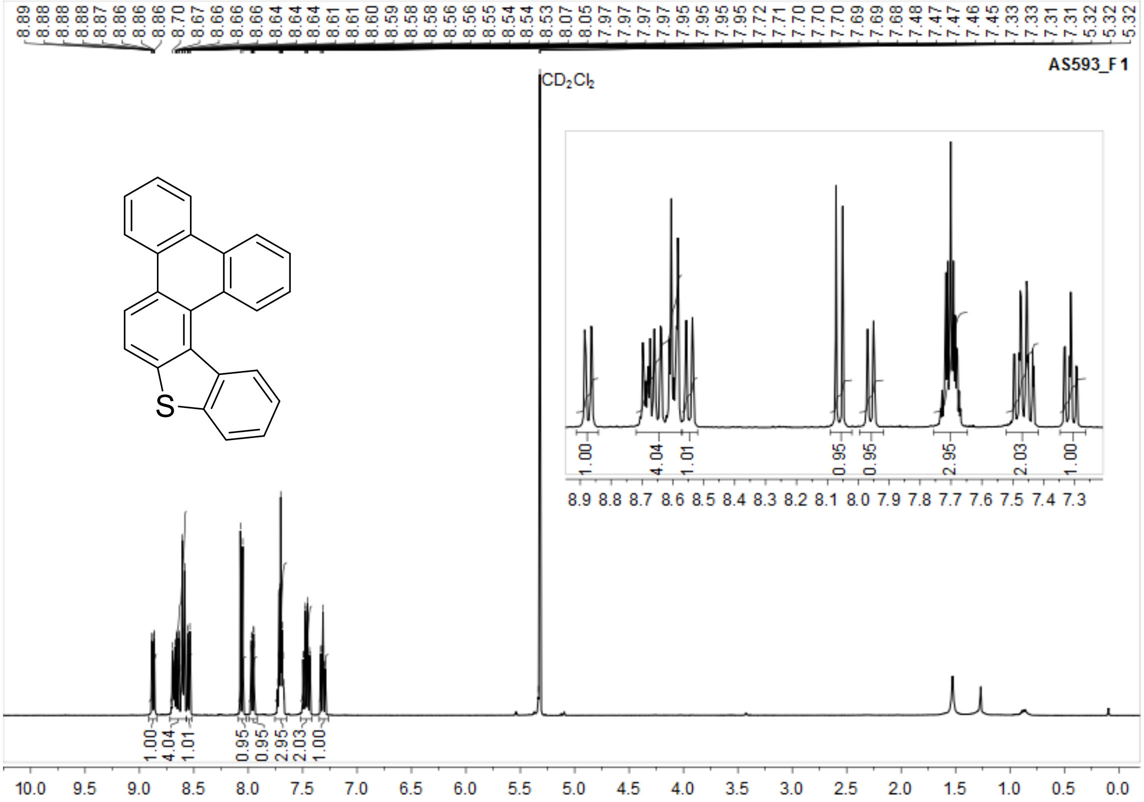


Figure S180: ^{1}H NMR spectrum of benzo[*b*]triphenyleno[1,2-*d*]thiophene (**T5**) (in CD_2Cl_2).

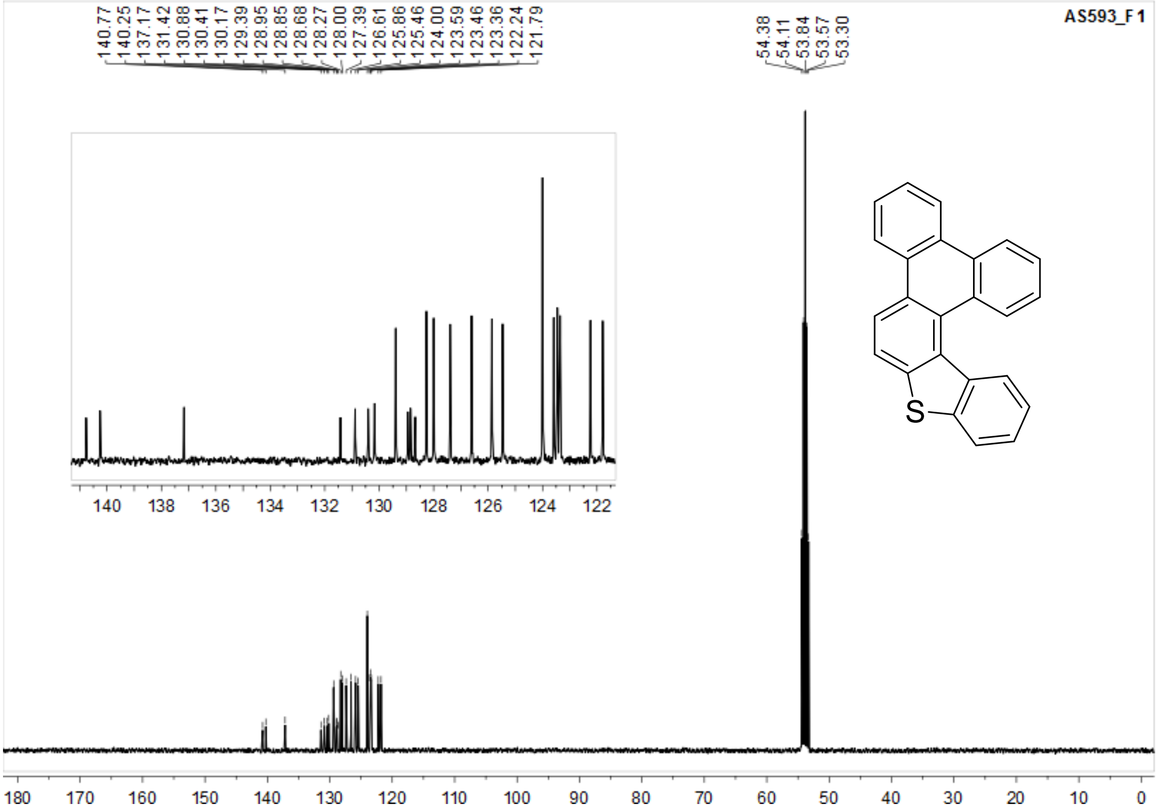


Figure S181: ^{13}C NMR spectrum of benzo[*b*]triphenyleno[1,2-*d*]thiophene (**T5**) (in CD_2Cl_2).

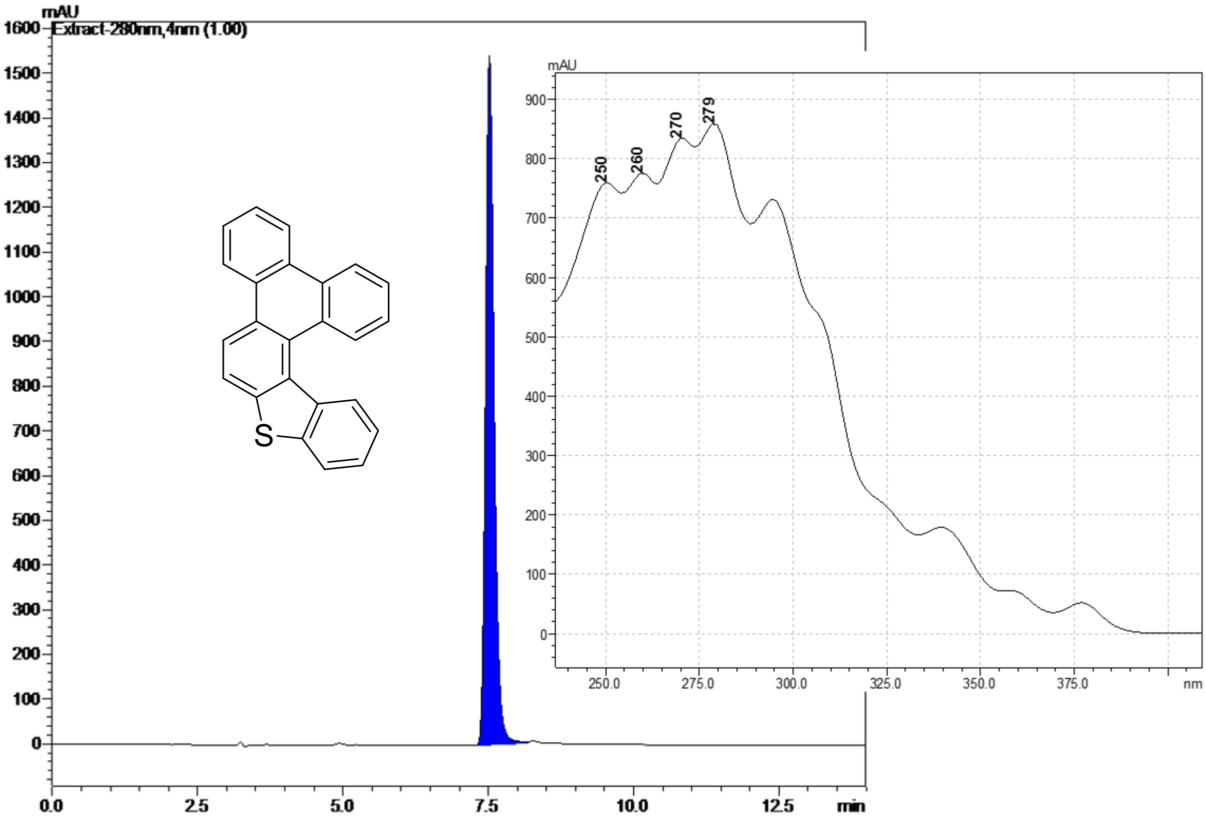


Figure S182: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:1, t_R 7.51 min) and UV/vis spectrum (inset) of benzo[*b*]triphenyleno[1,2-*d*]thiophene (**T5**).

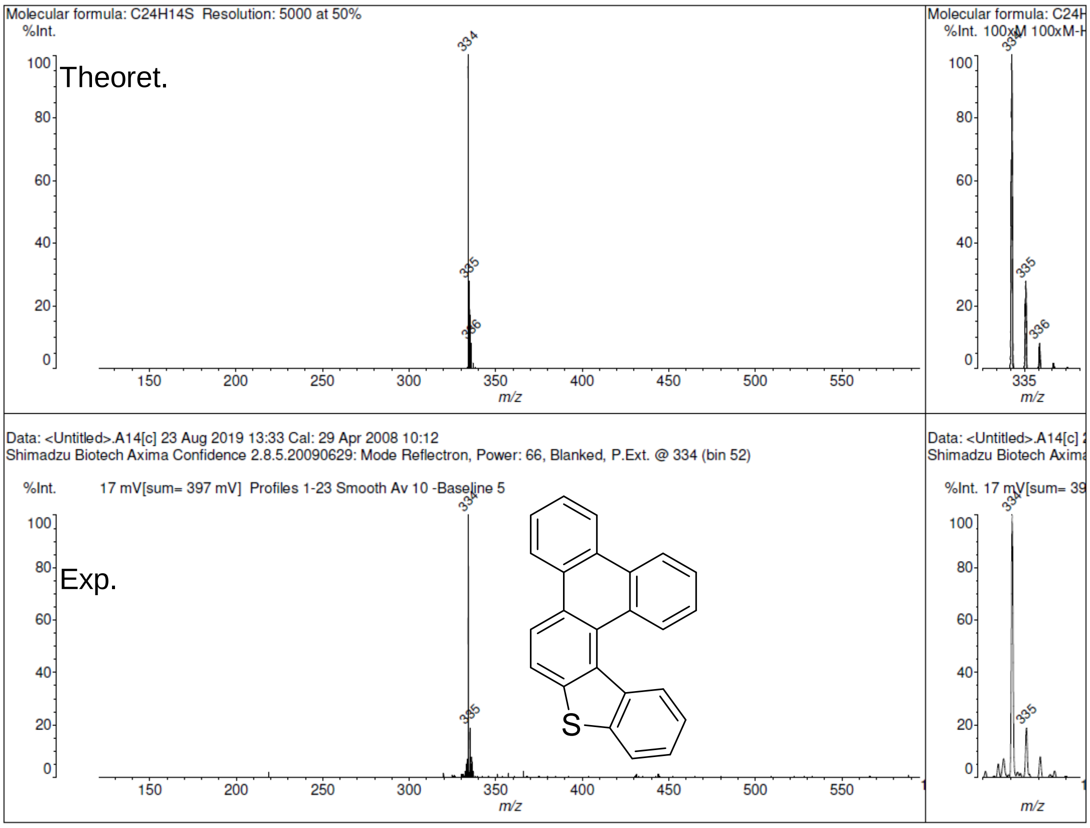
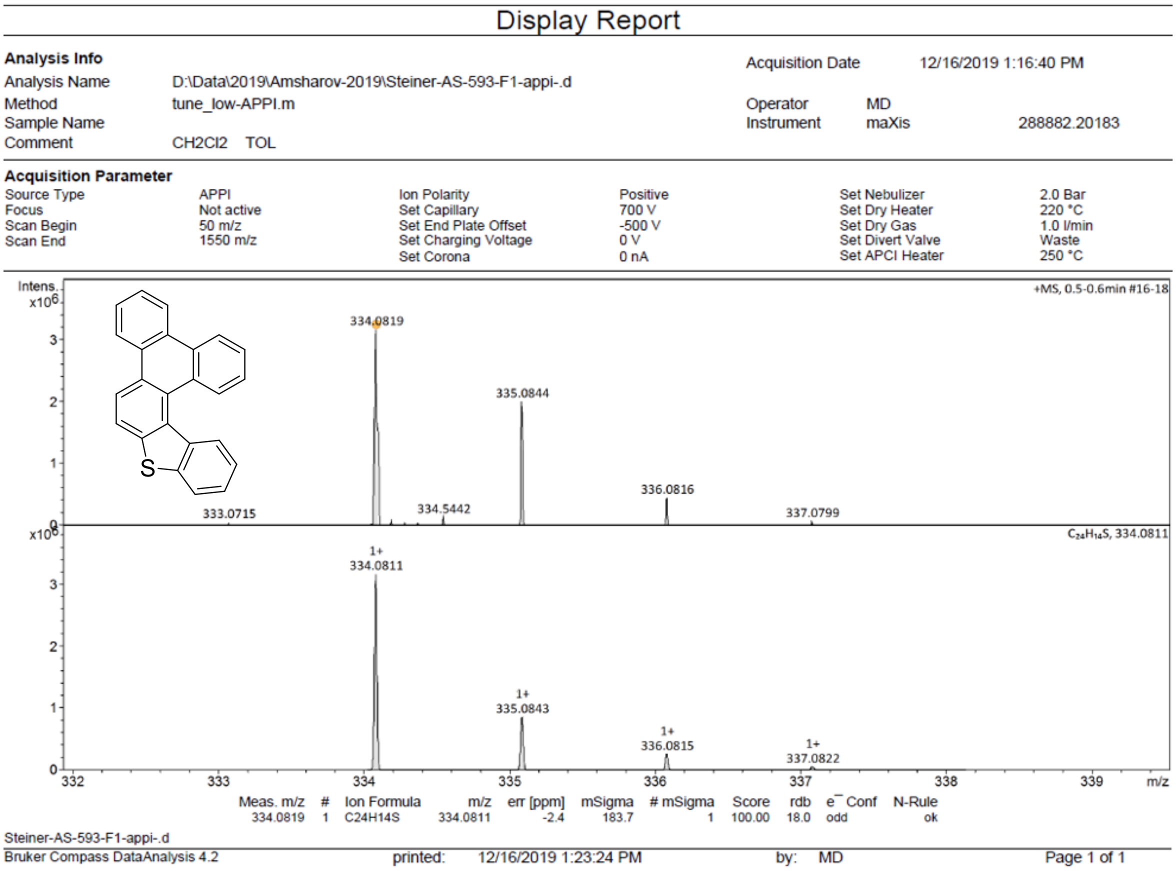


Figure S183: LDI MS spectrum of benzo[*b*]triphenyleno[1,2-*d*]thiophene (**T5**), *m/z* 334 (M^+, 100 %).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-593-F1-appi-.d	Acquisition Date	12/16/2019 1:16:40 PM
Method	tune_low-APPI.m	Operator	MD
Sample Name		Instrument	maXis 288882.20183
Comment	CH2Cl2 TOL		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
334.0819	1	C24H14S	334.0811	-2.4	183.7	1	100.00	18.0	odd	ok

Steiner-AS-593-F1-appi-.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 1:23:24 PM by: MD Page 1 of 1

Figure S18447: HR MS (APPI) spectrum of benzo[*b*]triphenyleno[1,2-*d*]thiophene (**T5**), *m/z* 334.0819 (M^+, 100 %).

Benzo[*b*]triphenyleno[2,3-*d*]thiophene (T4)

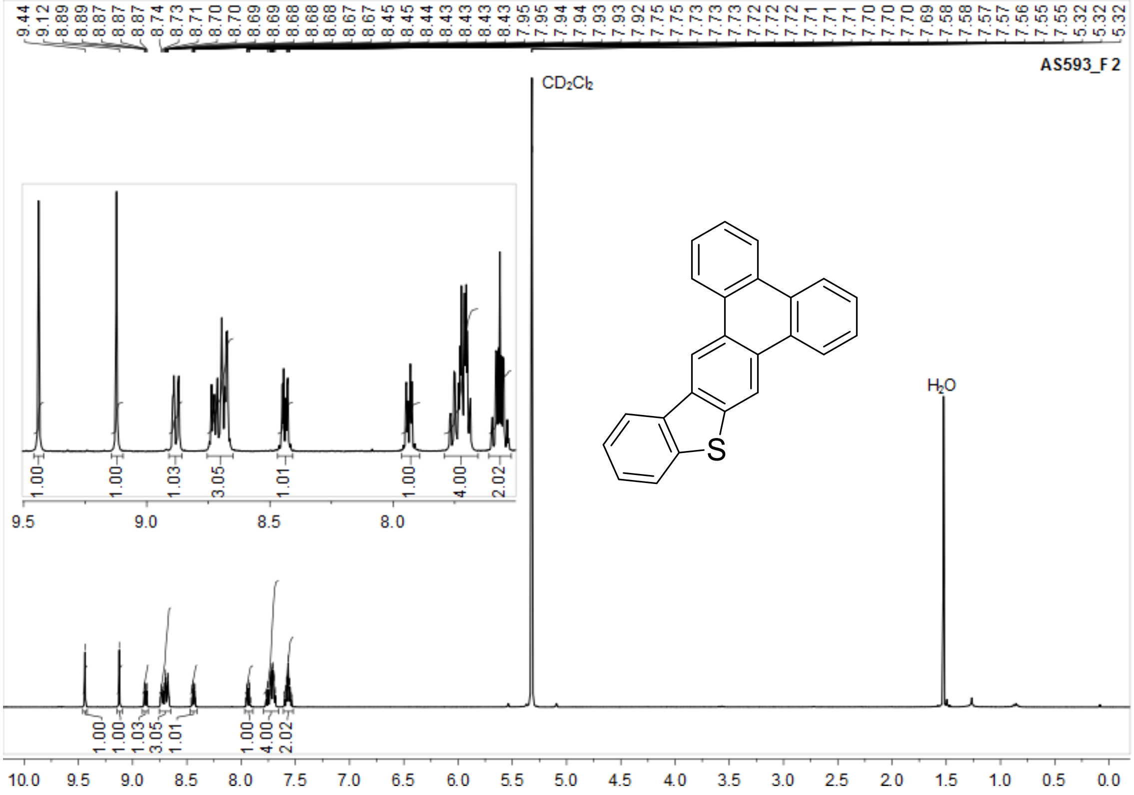


Figure S185: ^{1}H NMR spectrum of benzo[*b*]triphenyleno[2,3-*d*]thiophene (**T6**) (in CD_2Cl_2).

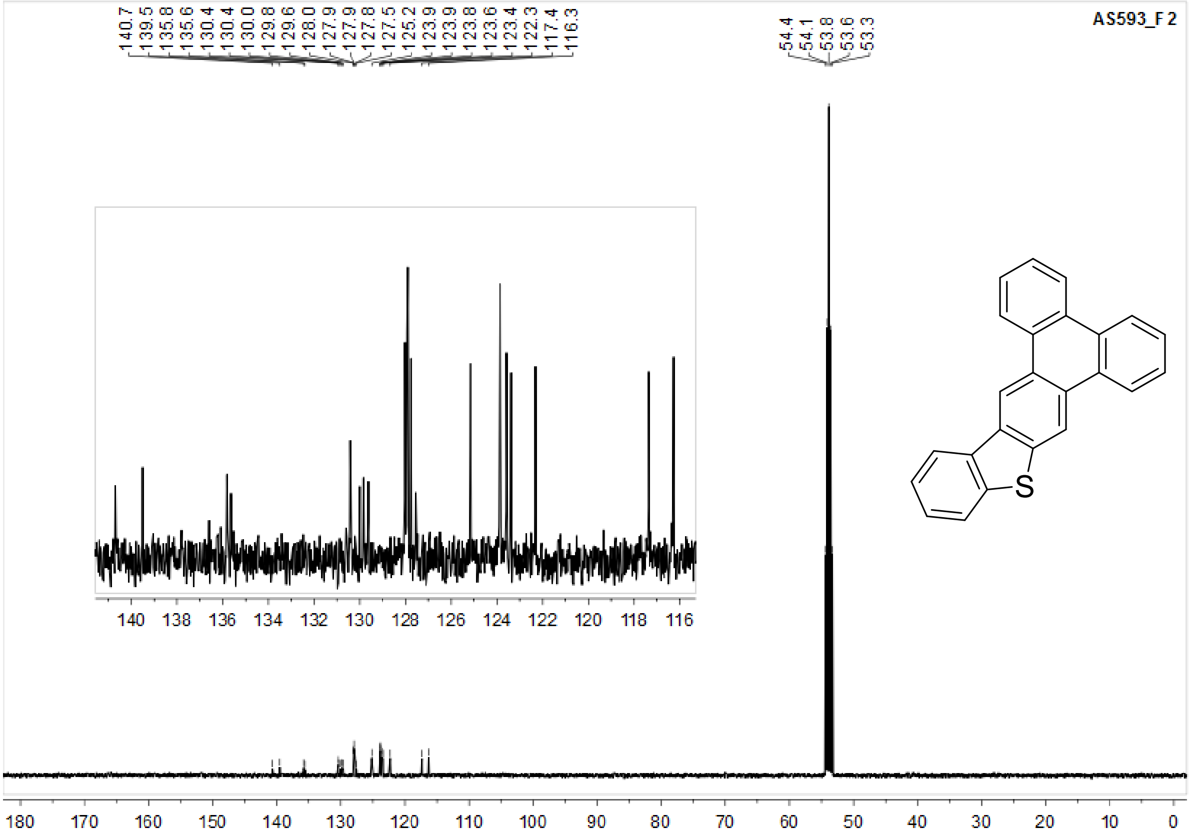


Figure S186: ^{13}C NMR spectrum of benzo[*b*]triphenyleno[2,3-*d*]thiophene (**T6**) (in CD_2Cl_2).

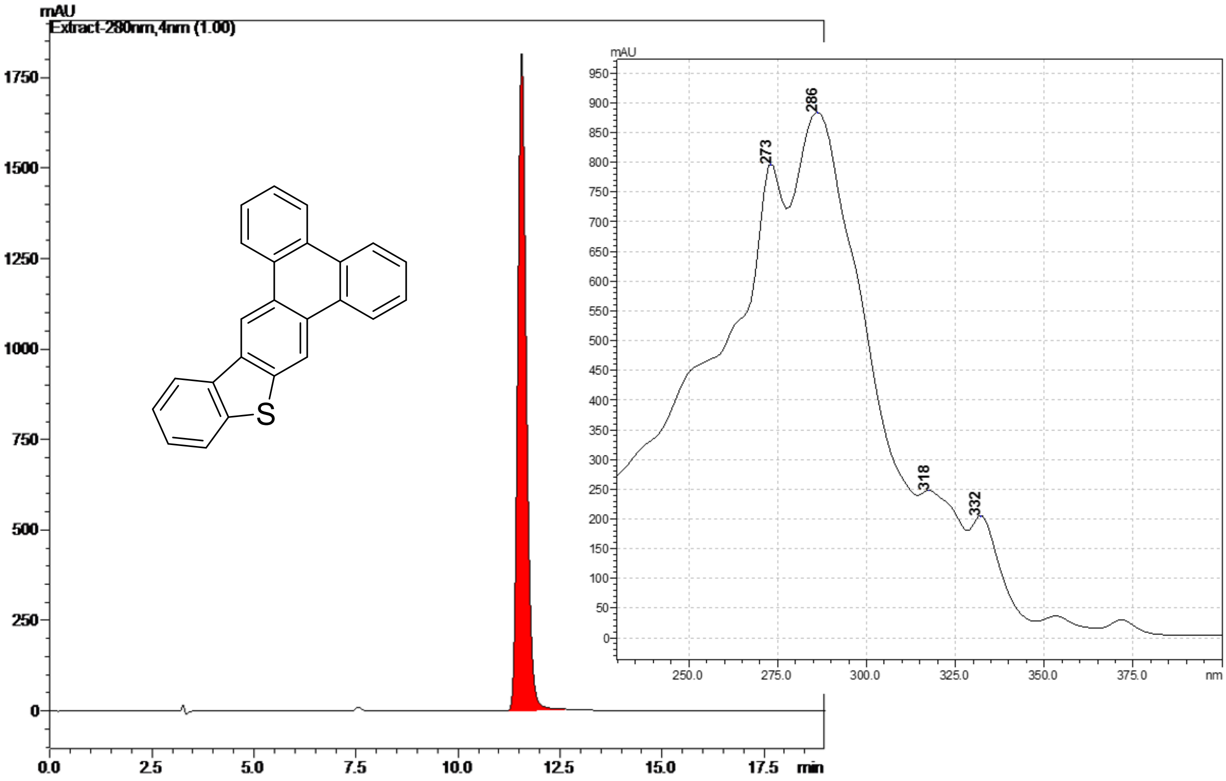


Figure S187: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:1, t_R 11.55 min) and UV/vis spectrum (inset) of benzo[*b*]triphenyleno[2,3-*d*]thiophene (**T6**).

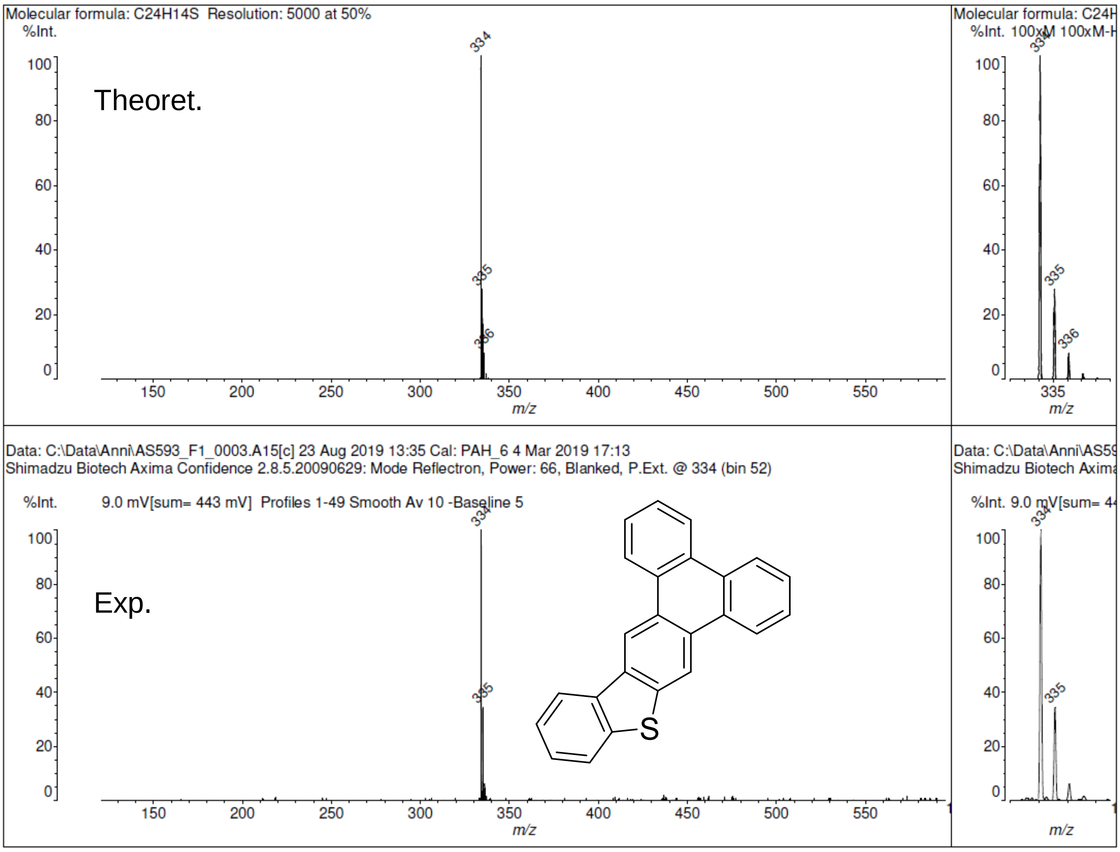
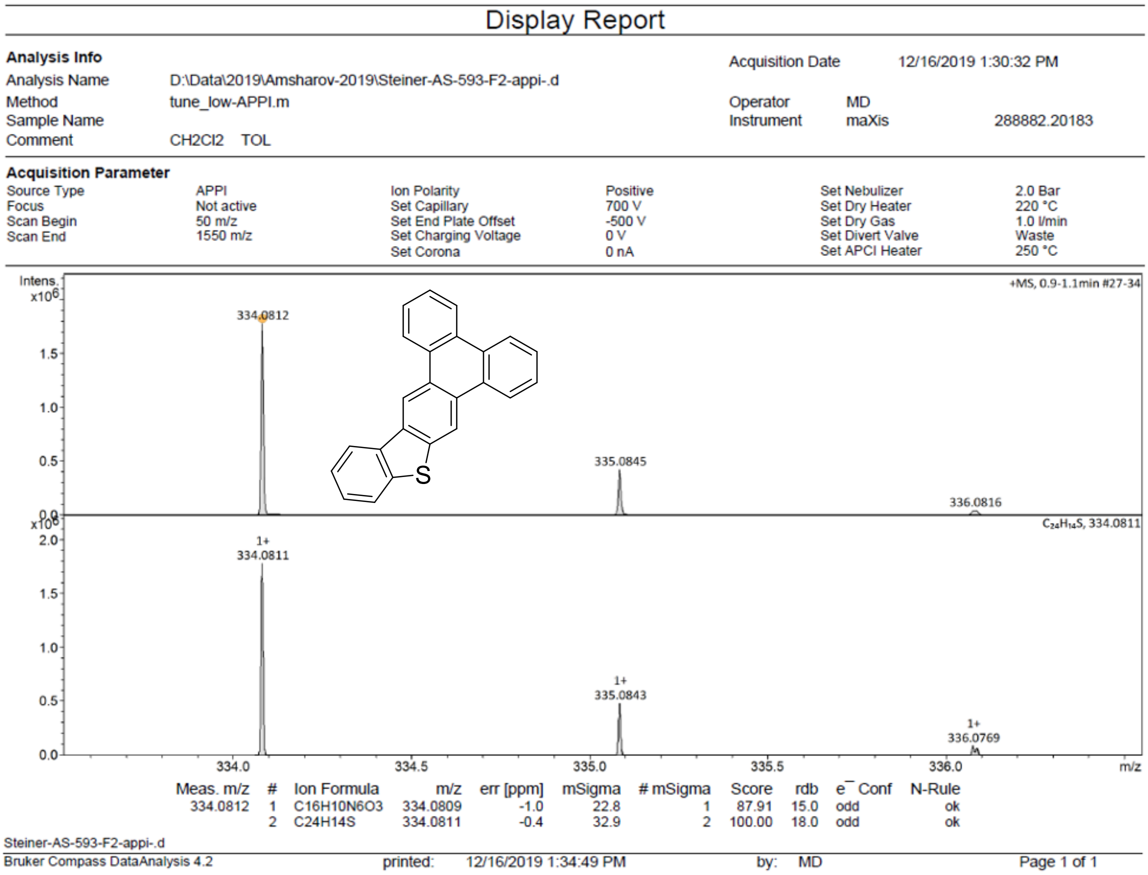


Figure S187: LDI MS spectrum of benzo[*b*]triphenyleno[2,3-*d*]thiophene (**T6**), *m/z* 334 (M$^+$, 100 %).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS-593-F2-appi-.d	Acquisition Date	12/16/2019 1:30:32 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2 TOL			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
334.0812	1	C16H10N6O3	334.0809	-1.0	22.8	1	87.91	15.0	odd	ok
	2	C24H14S	334.0811	-0.4	32.9	2	100.00	18.0	odd	ok

Steiner-AS-593-F2-appi-.d

Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 1:34:49 PM by: MD Page 1 of 1

Figure S188: HR MS (APPI) spectrum of benzo[*b*]triphenyleno[2,3-*d*]thiophene (**T6**), *m/z* 334.0819 (M$^+$, 100 %).

Naphtho[1',2',3',4':4,5]triphenyleno[1,12-*bcd*]thiophene (fraction F3)

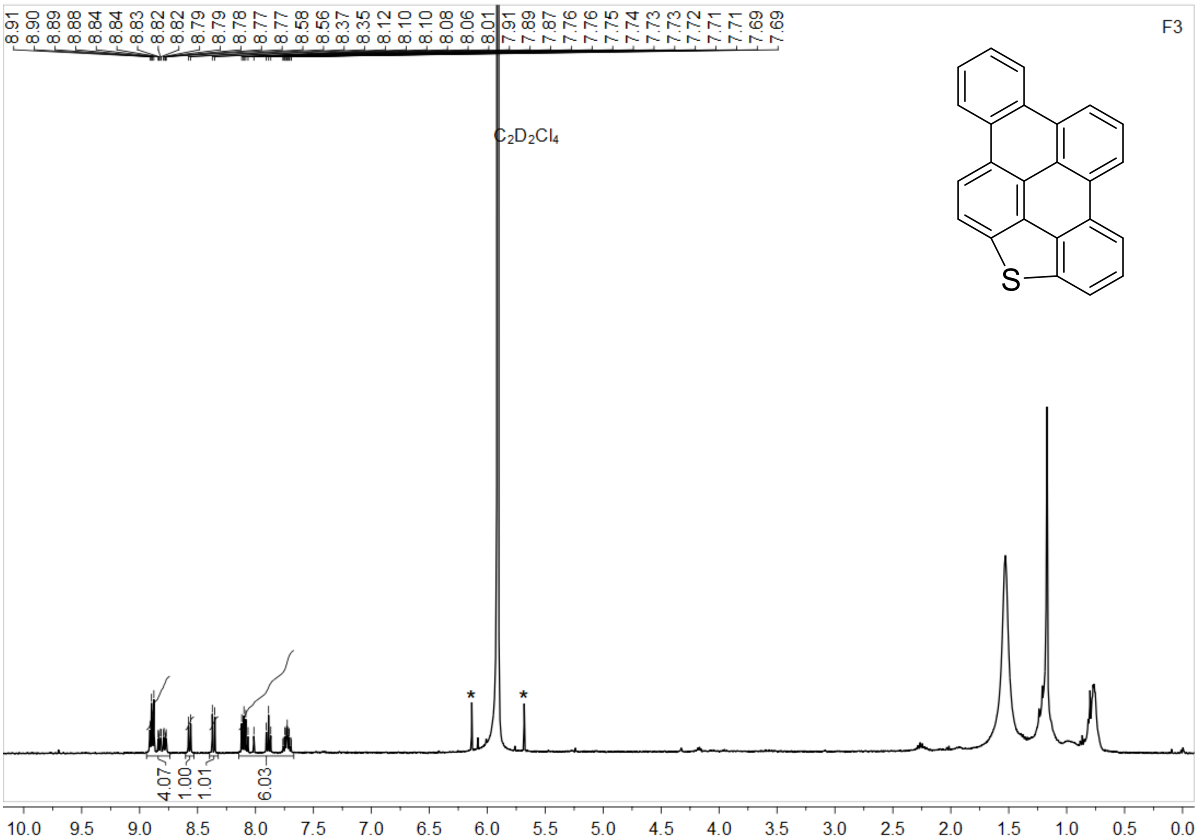


Figure S189: ^{1}H NMR spectrum of naphtho[1',2',3',4':4,5]triphenyleno[1,12-*bcd*]thiophene (fraction F3) (in $C_2D_2Cl_4$).

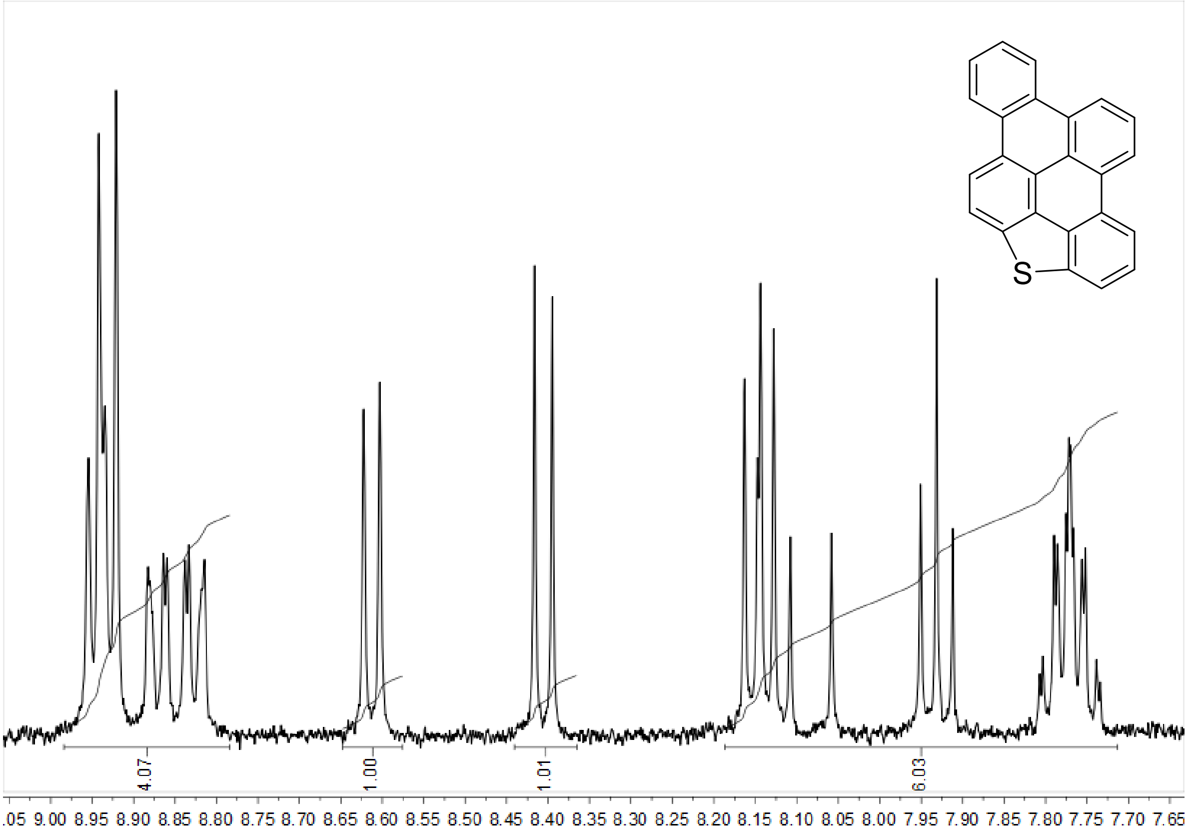


Figure S48: Expansion of ^{1}H NMR spectrum of naphtho[1',2',3',4':4,5]triphenyleno[1,12-*bcd*]thiophene (fraction F3) (in $C_2D_2Cl_4$).

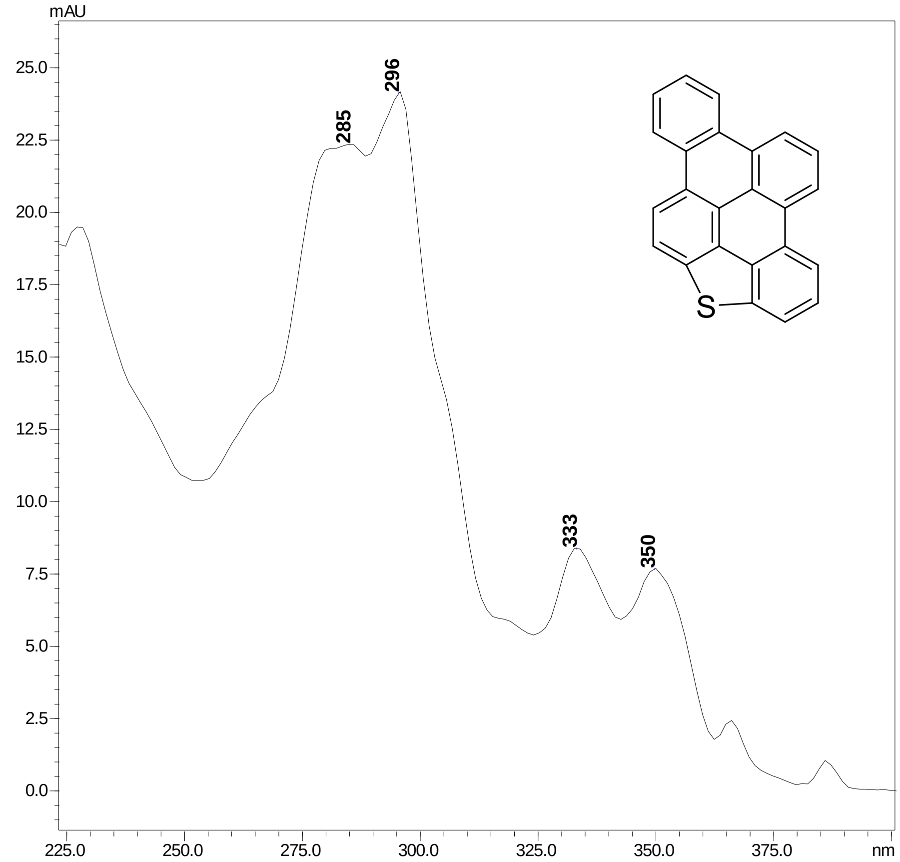


Figure S191: UV/vis spectrum of naphtho[1',2',3',4':4,5]triphenyleno[1,12-*bcd*]thiophene (fraction F3) obtained by HPLC/UV analysis (in DCM/MeOH mixture).

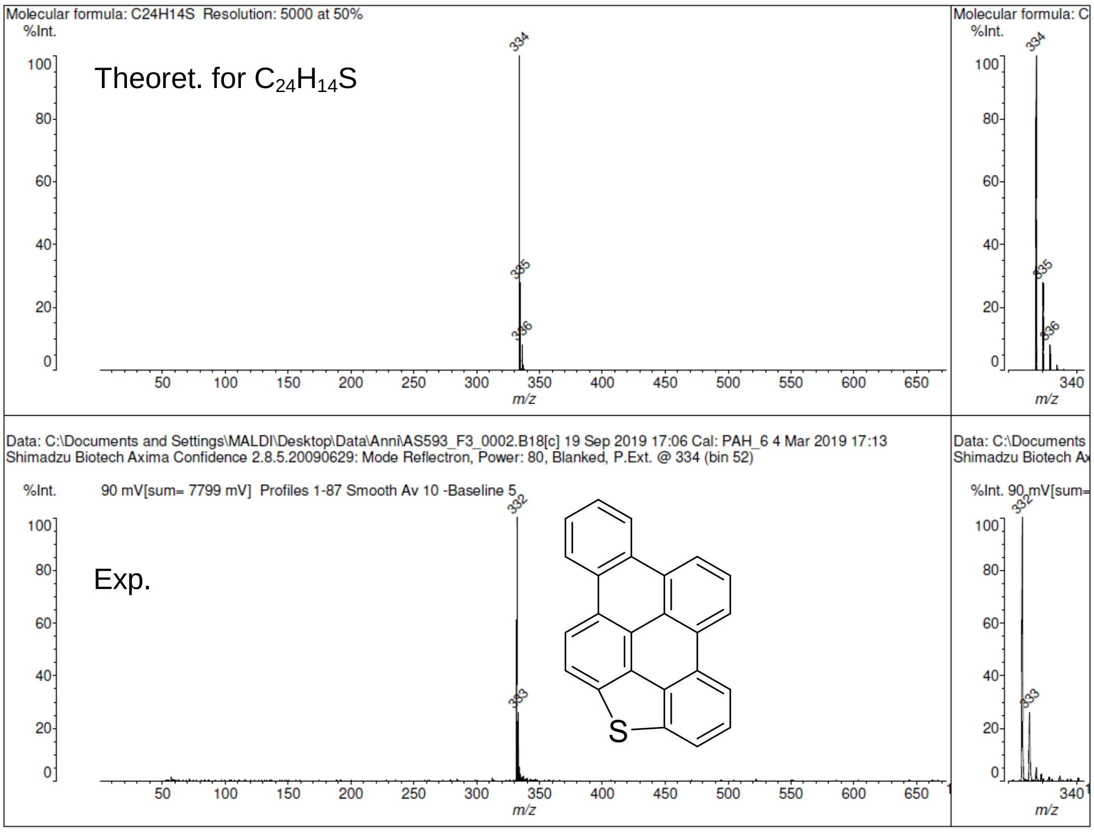


Figure S192: LDI MS spectrum of fraction F3, *m/z* 332 (M^+, 100 %).

2-Chlorotriphenylene (T7)

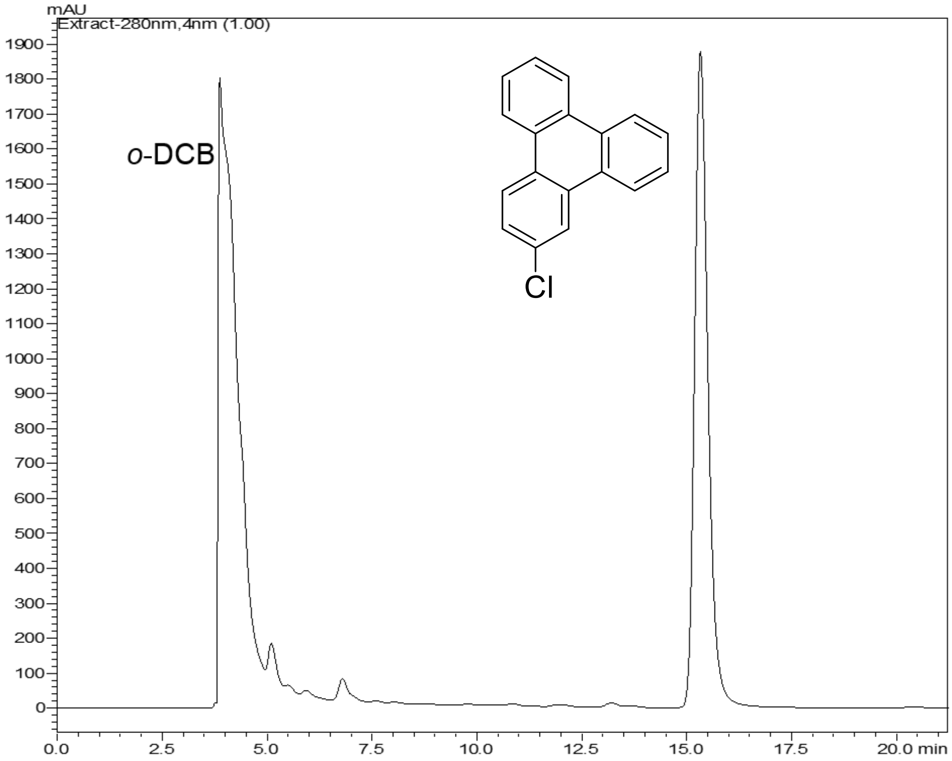


Figure S193: HPLC chromatogram obtained after reaction (260 °C, 12 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 2:8).

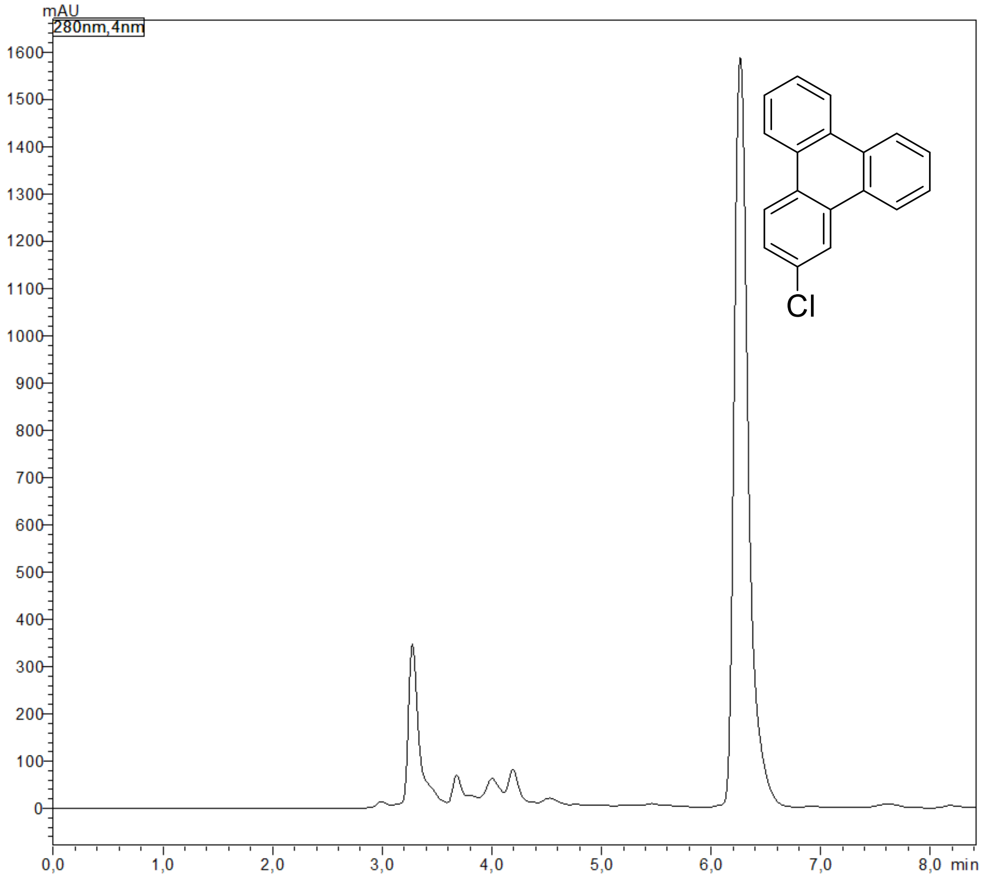


Figure S194: HPLC chromatogram of separation (PBr column (semiprep), 5.0 mL/min, 40 °C, DCM/MeOH 1:1).

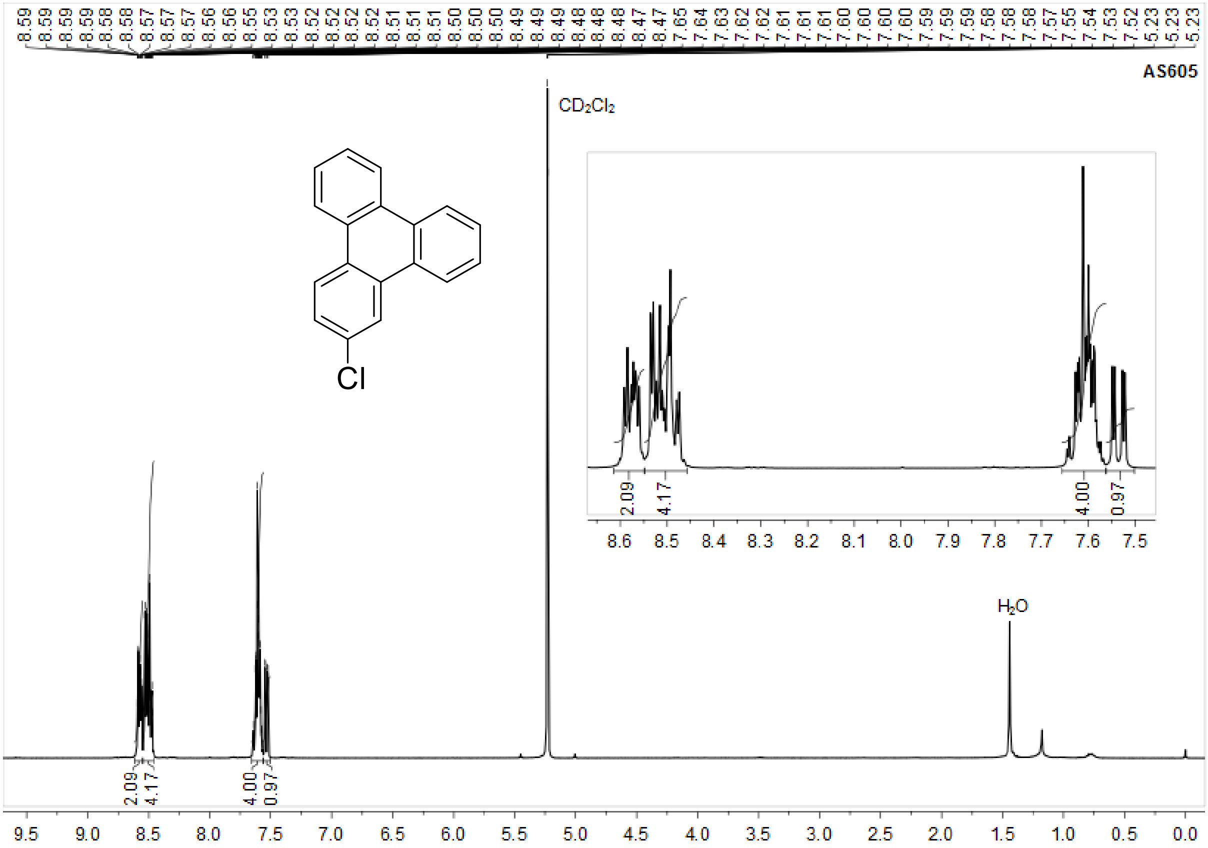


Figure S195: ^{1}H NMR spectrum of 2-chlorotriphenylene (**T7**) (in CD_2Cl_2).

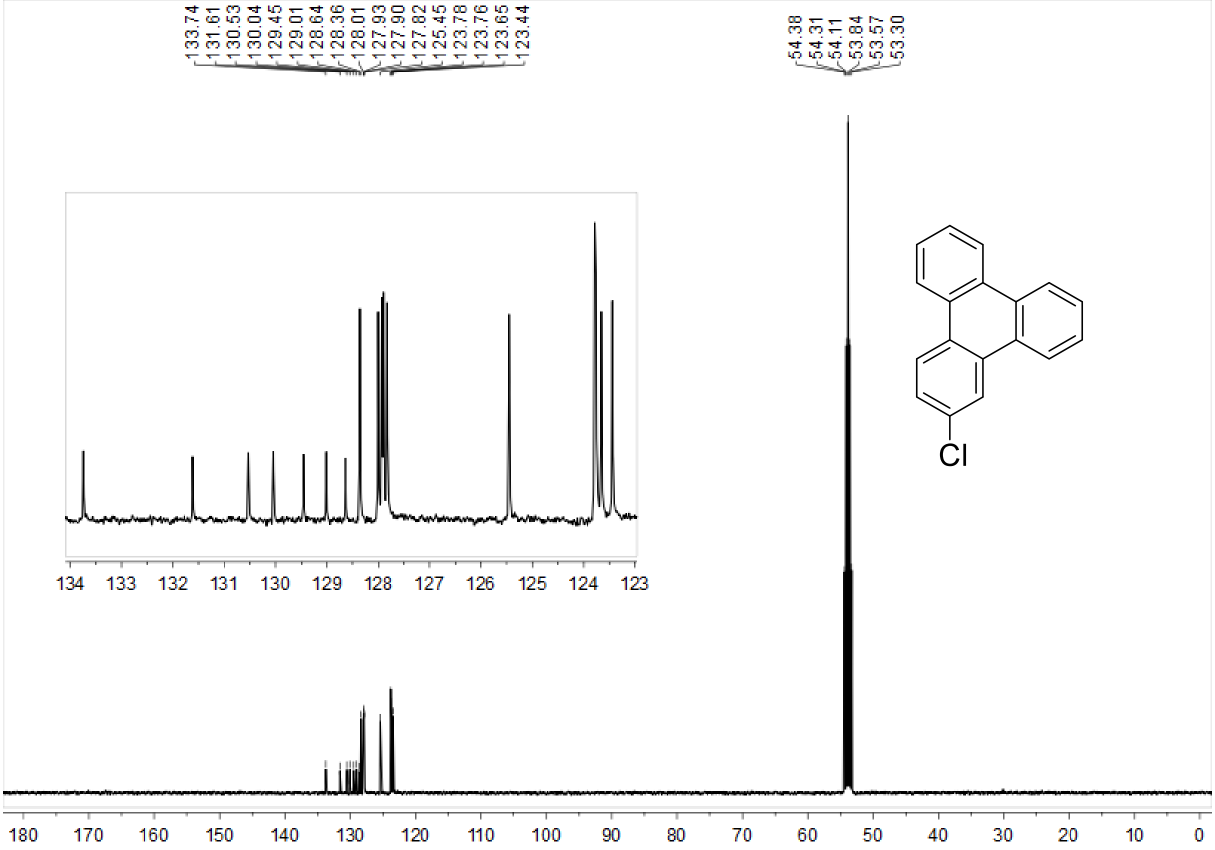


Figure S196: ^{13}C NMR spectrum of 2-chlorotriphenylene (**T7**) (in CD_2Cl_2).

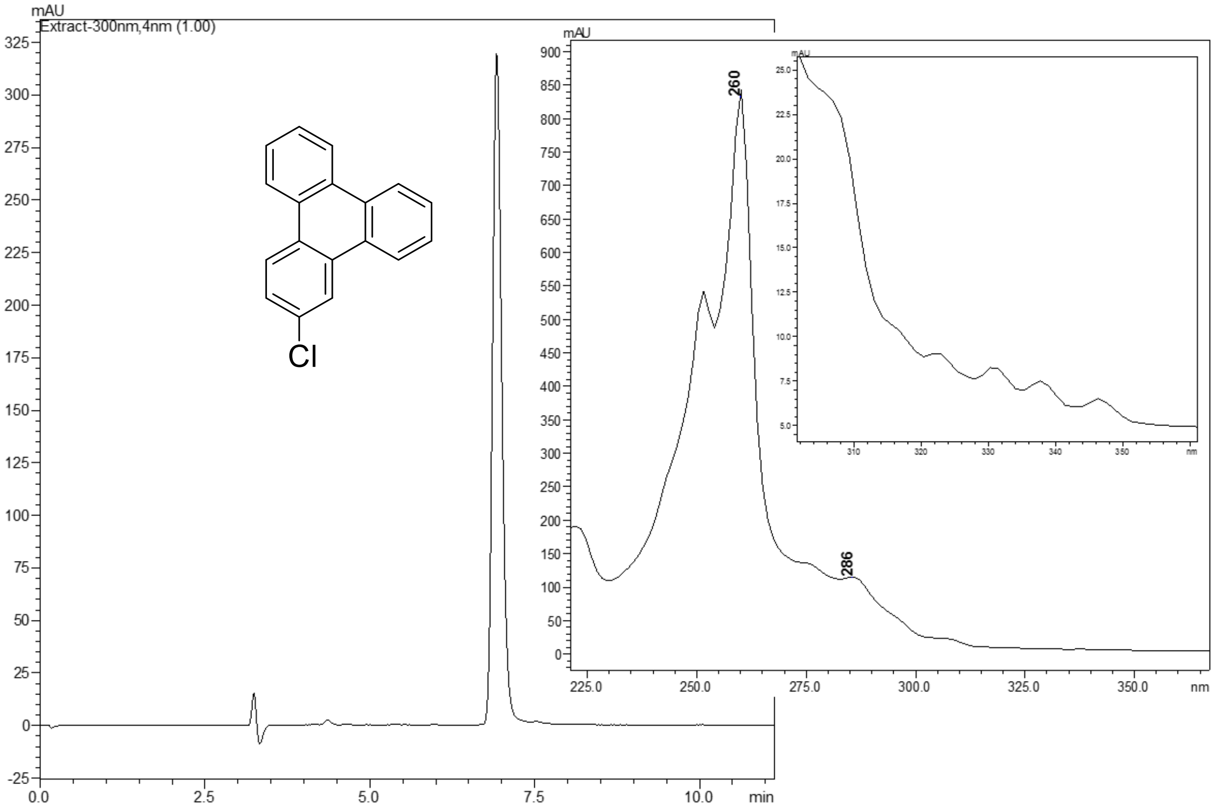


Figure S49: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:1, t_R 6.92 min) and UV/vis spectrum (inset) of 2-chlorotriphenylene (**T7**).

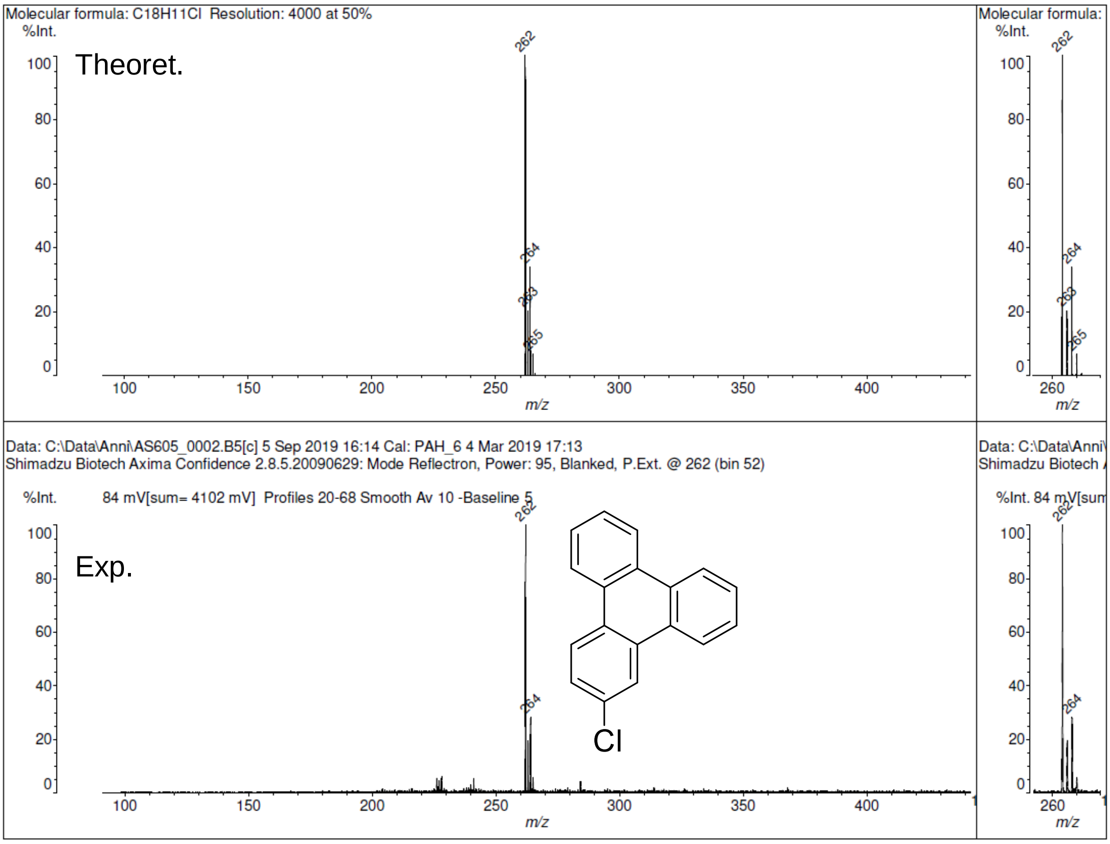


Figure S5098: LDI MS spectrum of 2-chlorotriphenylene (**T7**), *m/z* 262 (M^+, 100 %).

2-Bromotriphenylene (T8)

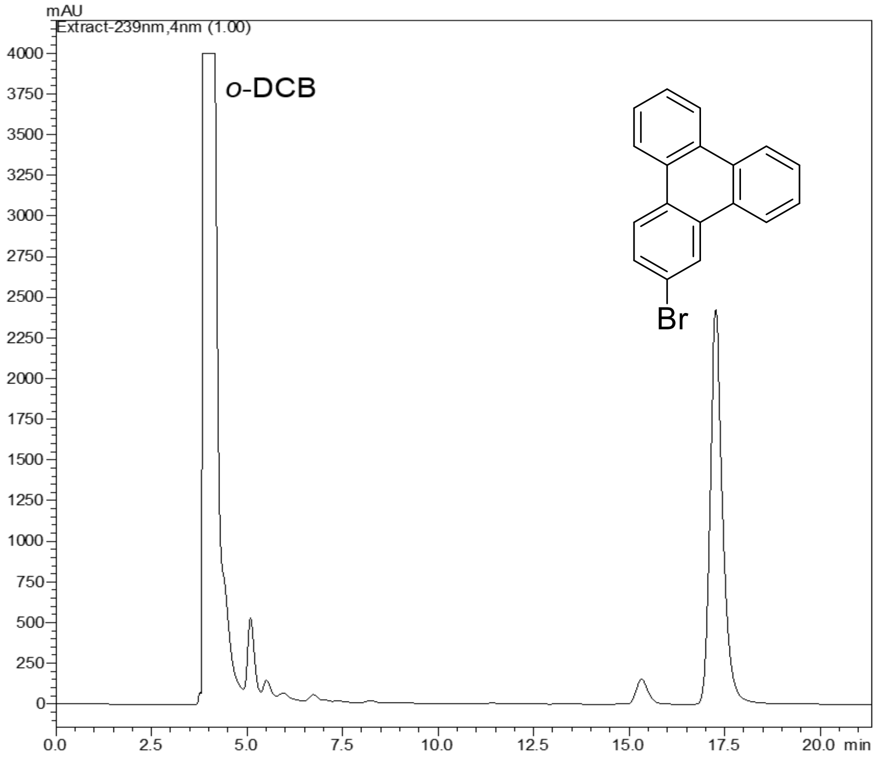


Figure S199: HPLC chromatogram obtained after reaction (250 °C, 12 h) (PBr column (analyt.), 1.0 mL/min, 35 °C, DCM/MeOH 2:8).

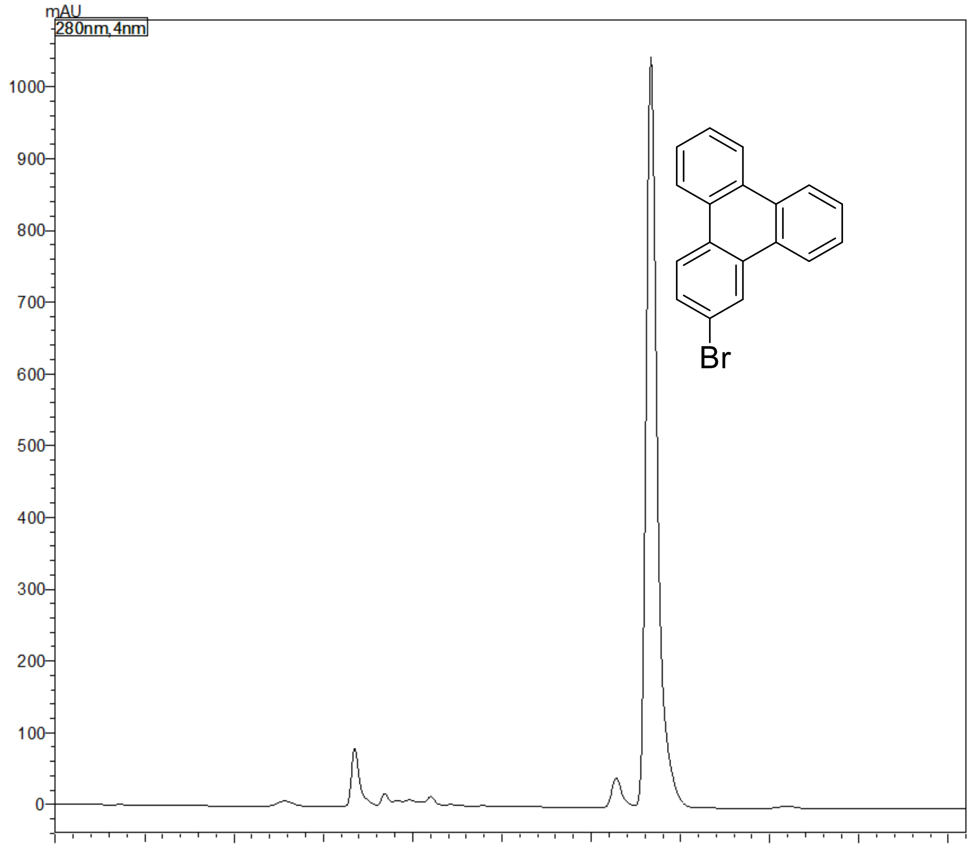


Figure S200: HPLC chromatogram of separation (PBr column (semiprep), 5.0 mL/min, 40 °C, DCM/MeOH 1:1).

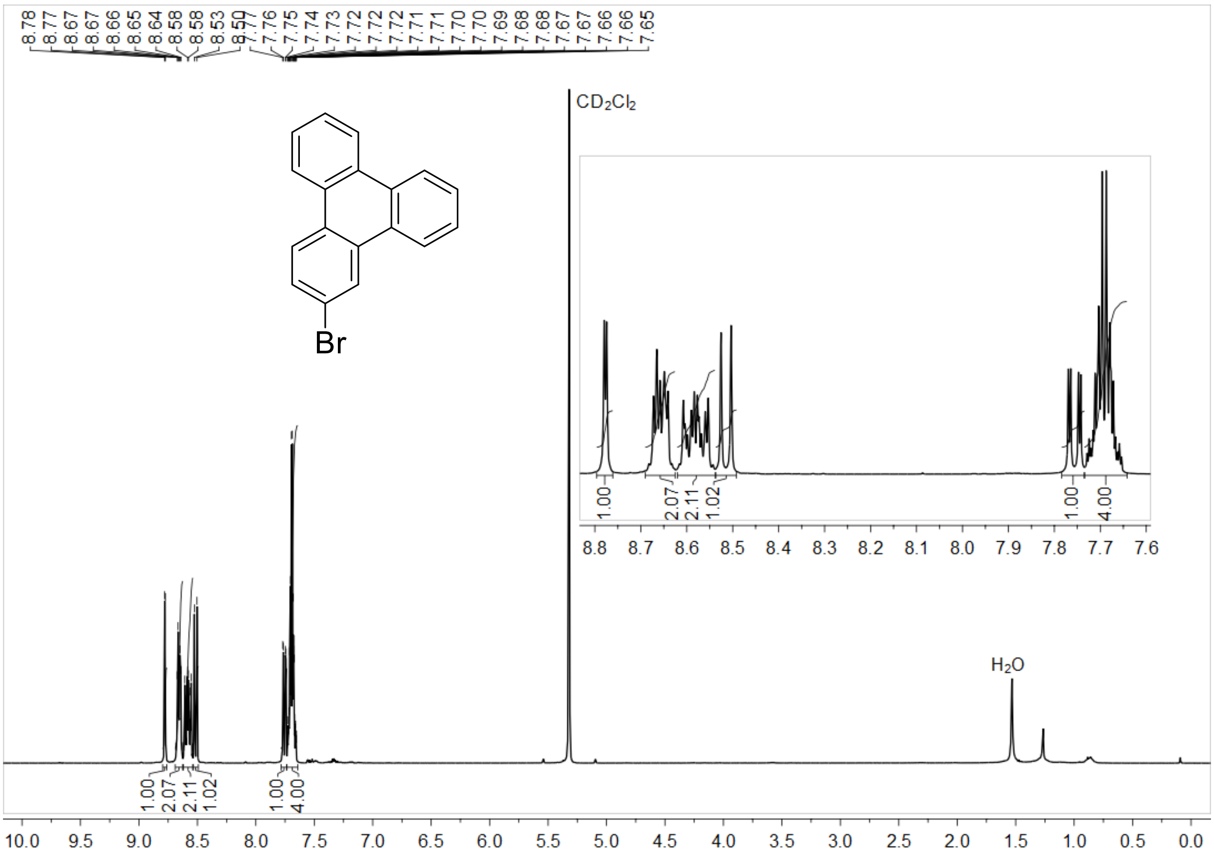


Figure S201: ^{1}H NMR spectrum of 2-bromotriphenylene (**T8**) (in CD_2Cl_2).

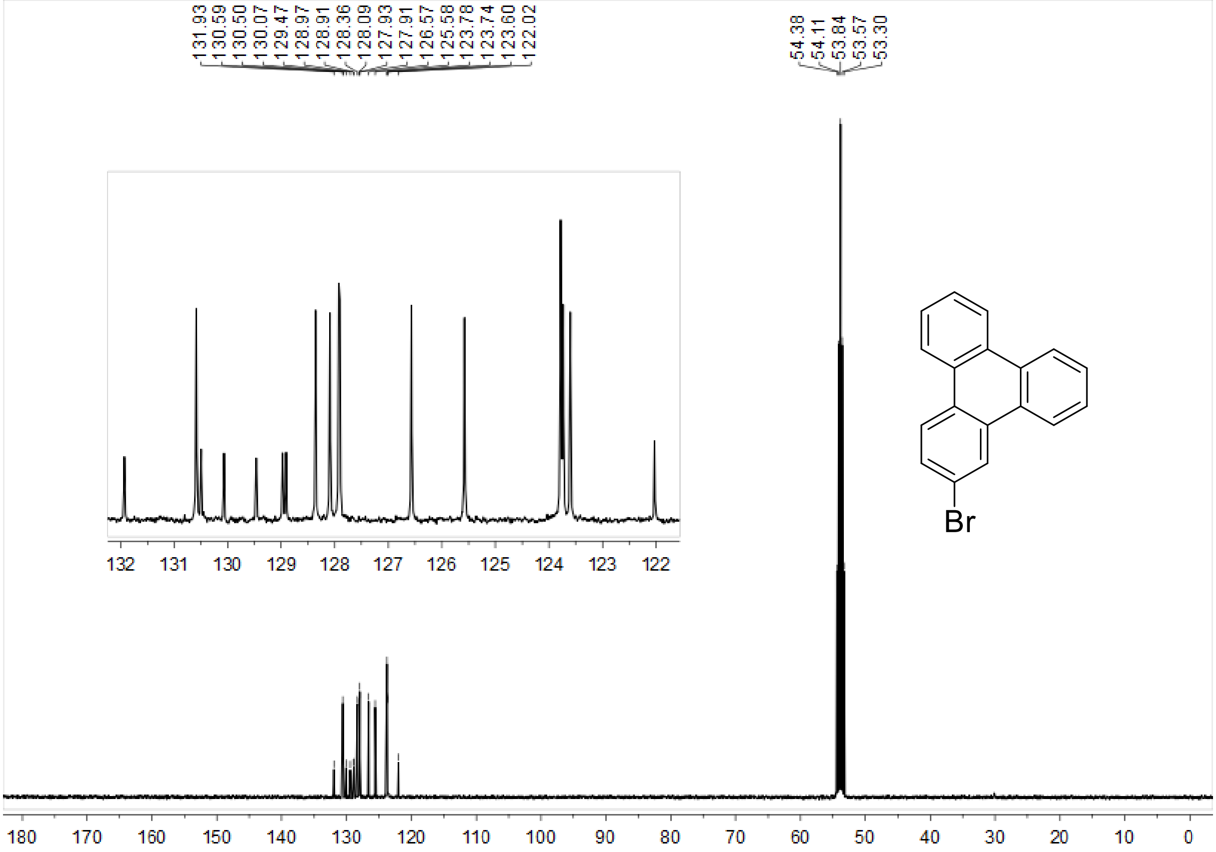


Figure S202: ^{13}C NMR spectrum of 2-bromotriphenylene (**T8**) (in CD_2Cl_2).

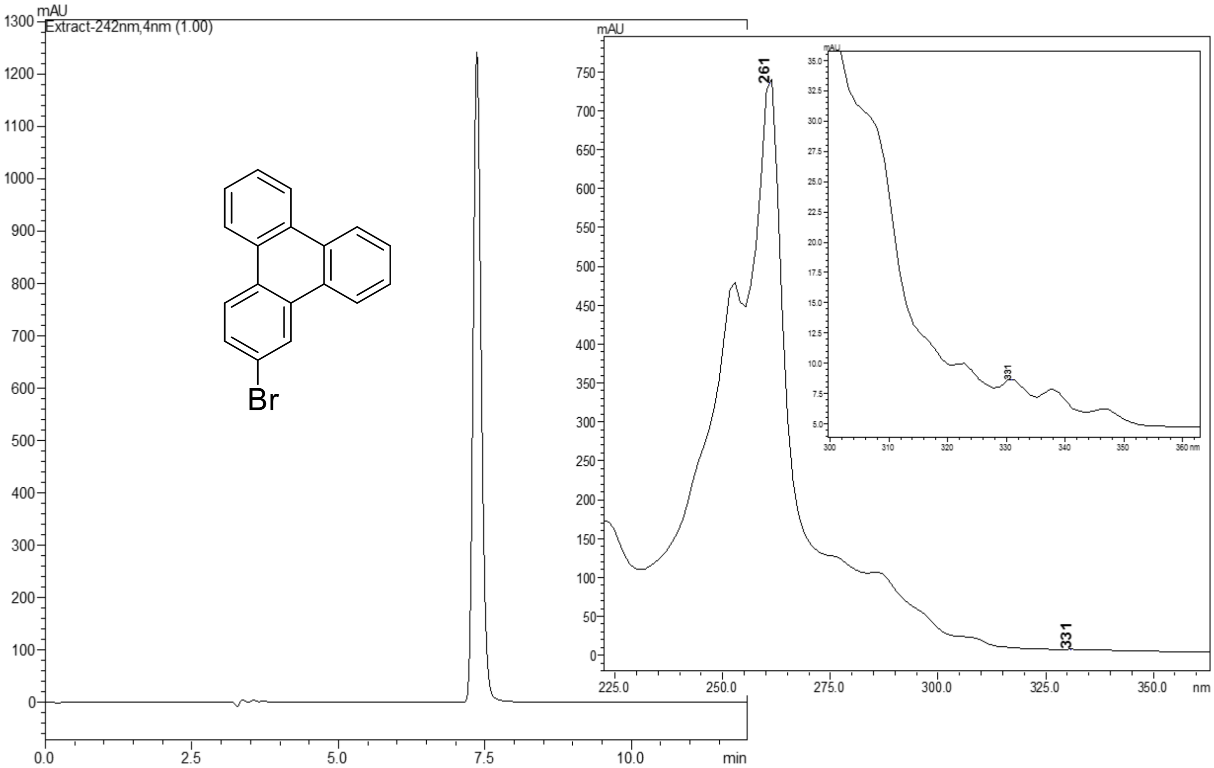
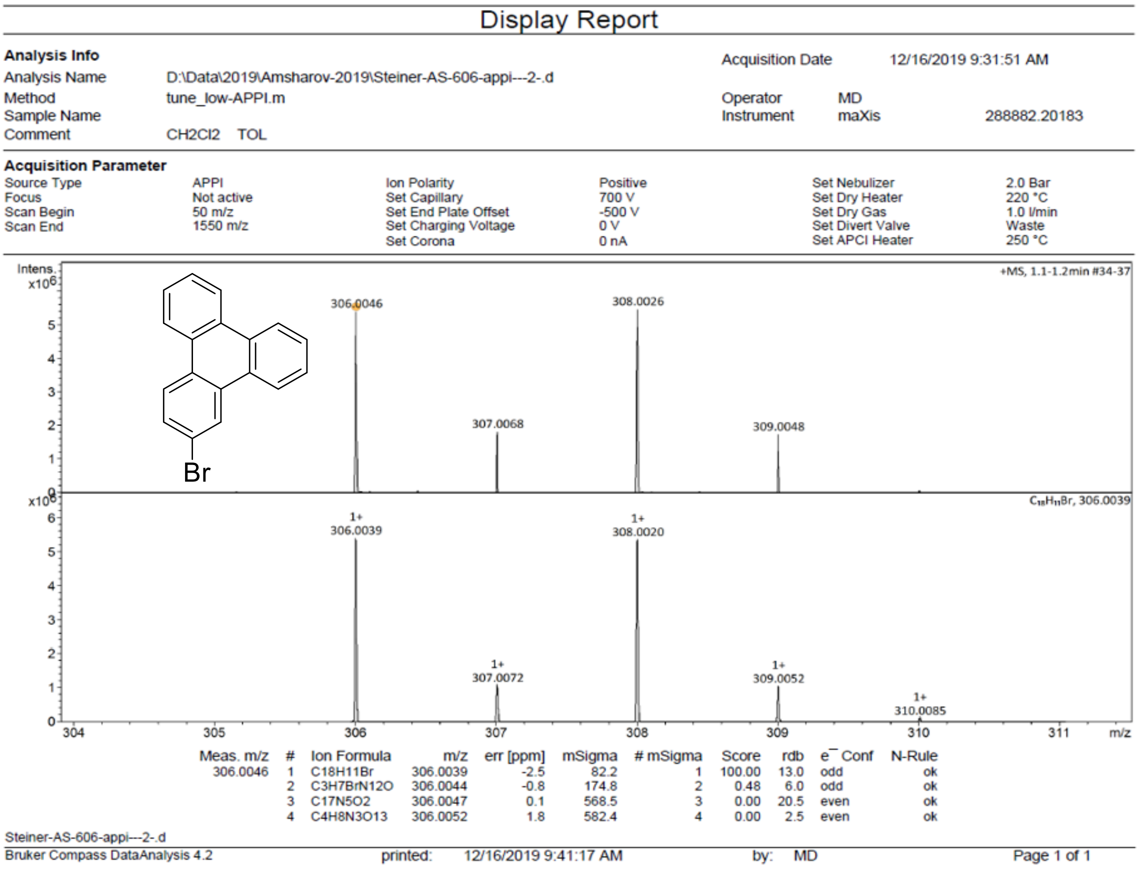


Figure S203: HPLC chromatogram (PBr column, 1.0 mL/min, 35 °C, DCM/MeOH 1:1, t_R 7.36 min) and UV/vis spectrum (inset) of 2-bromotriphenylene (**T8**).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-AS-606-appi---2-.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2 TOL

Acquisition Date 12/16/2019 9:31:51 AM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
306.0046	1	C18H11Br	306.0039	-2.5	82.2	1	100.00	13.0	odd	ok
	2	C3H7BrN12O	306.0044	-0.8	174.8	2	0.48	6.0	odd	ok
	3	C17N5O2	306.0047	0.1	568.5	3	0.00	20.5	even	ok
	4	C4H8N3O13	306.0052	1.8	582.4	4	0.00	2.5	even	ok

Steiner-AS-606-appi---2-.d
Bruker Compass DataAnalysis 4.2 printed: 12/16/2019 9:41:17 AM by: MD Page 1 of 1

Figure S204: HR MS (APPI) spectrum of 2-bromotriphenylene (**T8**), m/z 306.006 (M^+, 100 %).

2-Iodotriphenylene (T9)

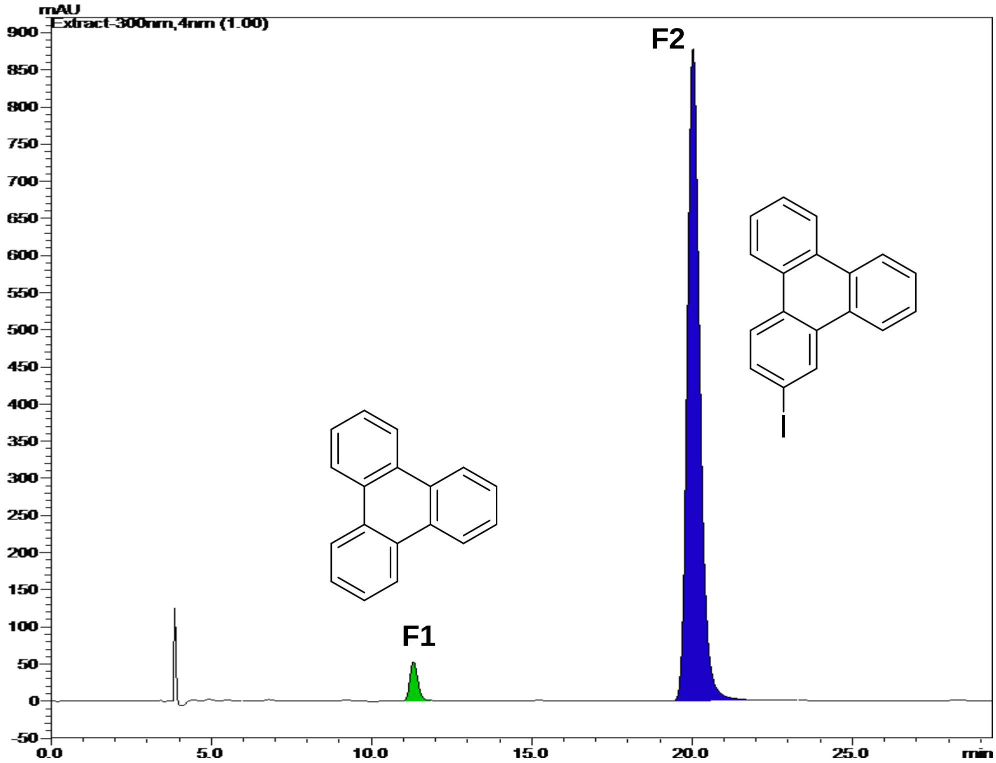


Figure S205: HPLC chromatogram of the reaction mixture (200 °C, 15 h) (PBr column (anal.), 1.0 mL/min, 35 °C, DCM/MeOH 2:8); **F1** (triphenylene): t_R = 11.30 min, **F2** (2-iodotriphenylene): t_R = 20.02 min.

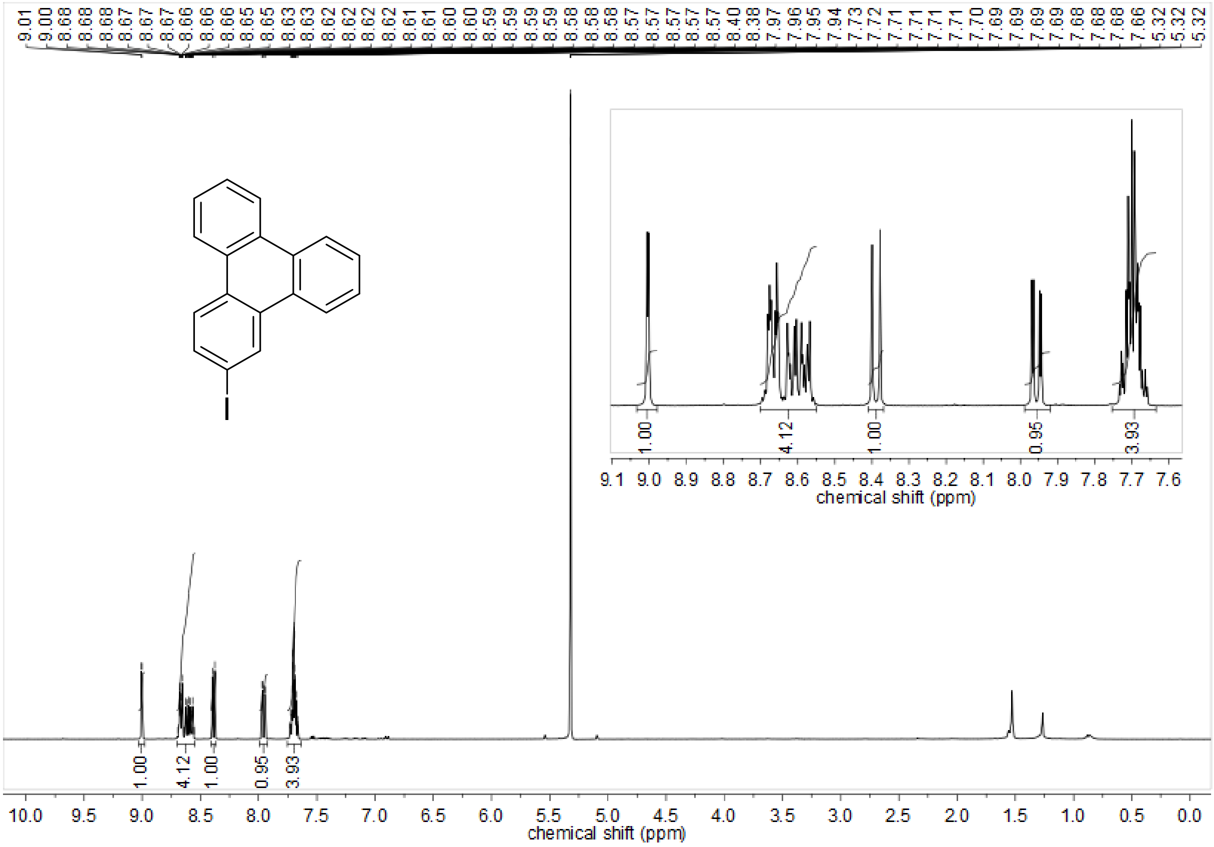


Figure S206: ^{1}H NMR spectrum of 2-iodotriphenylene (**T9**).

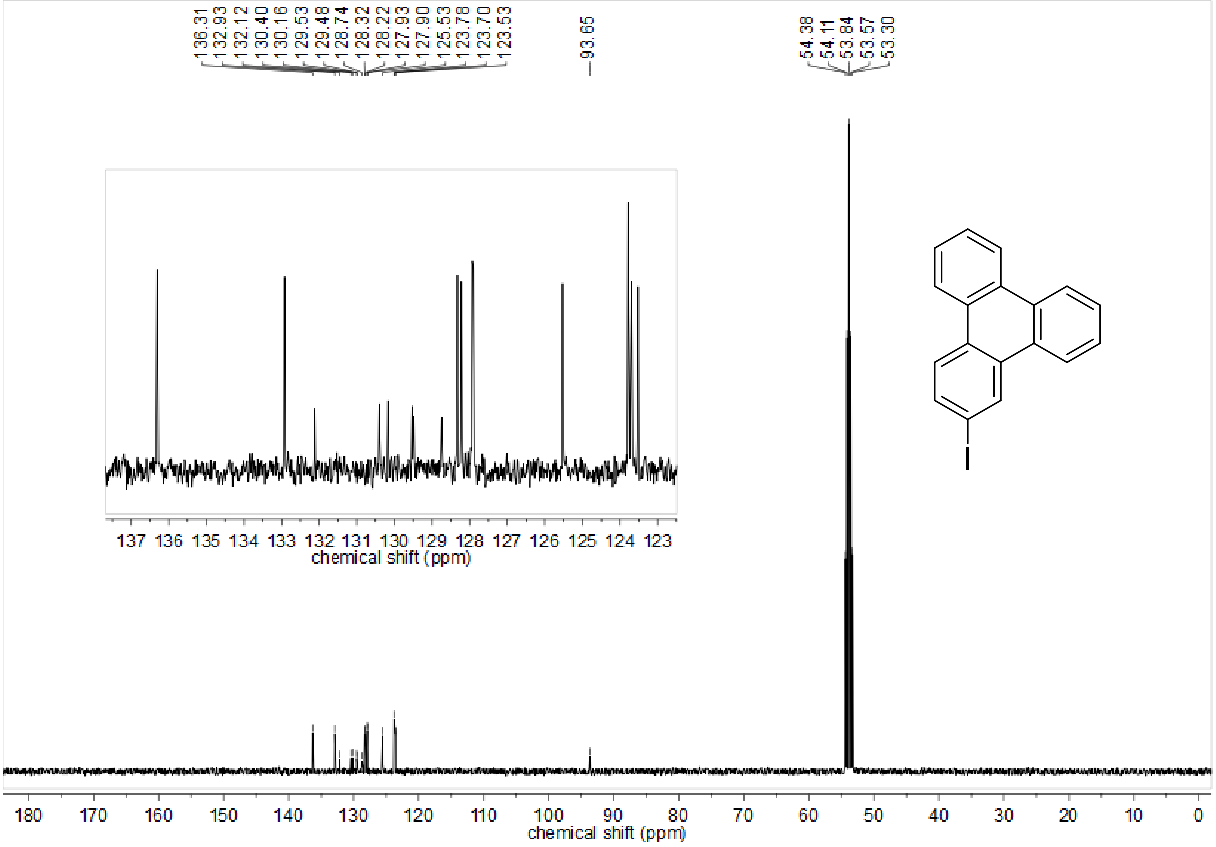


Figure S207: ^{13}C NMR spectrum of 2-iodotriphenylene (**T9**).

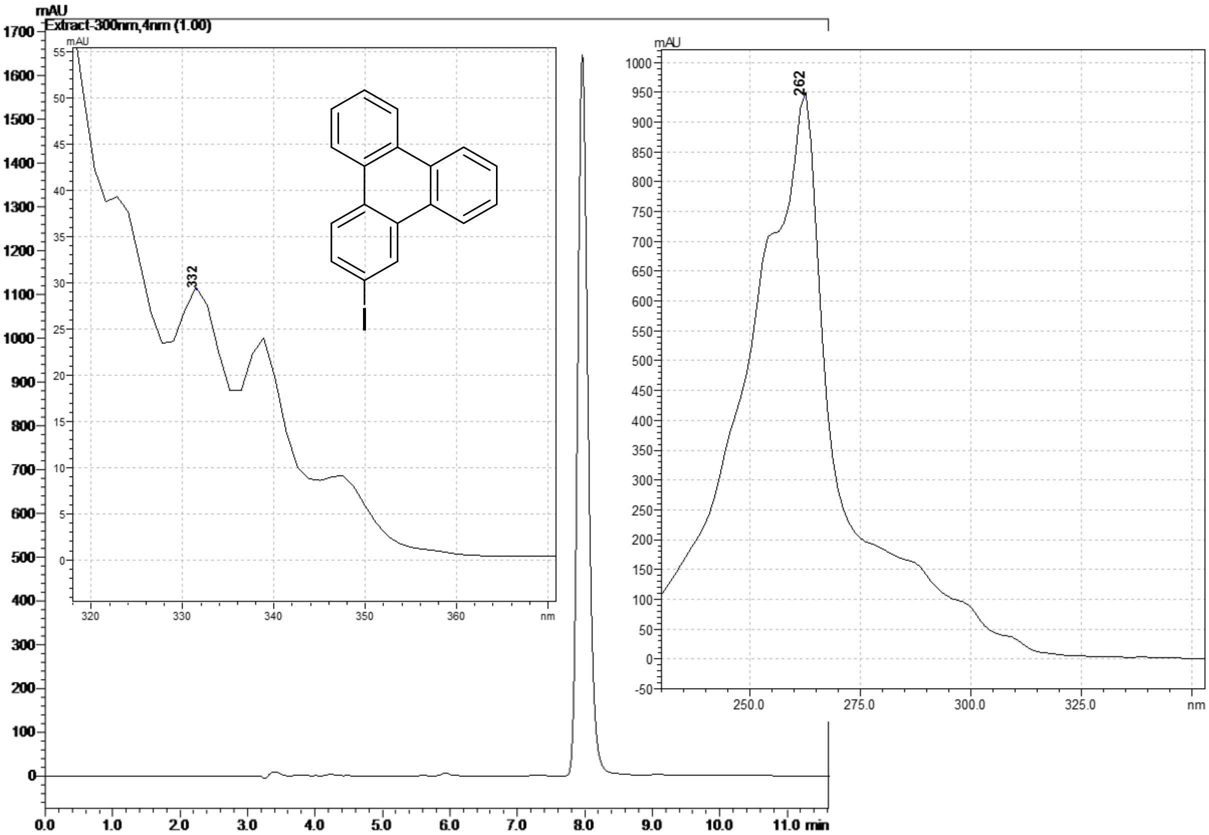
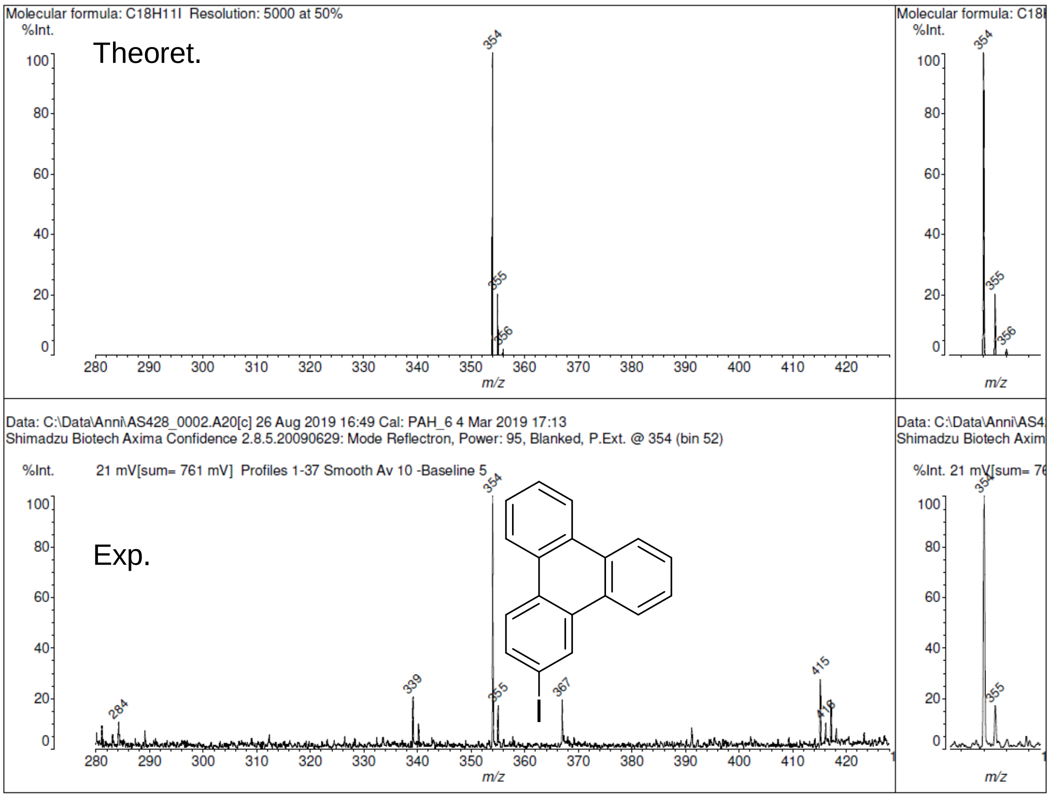


Figure S208: HPLC chromatogram (PBr column (anal.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1), $t_R = 7.97$ min and UV/vis spectrum (inset) of 2-iodotriphenylene (**T9**).

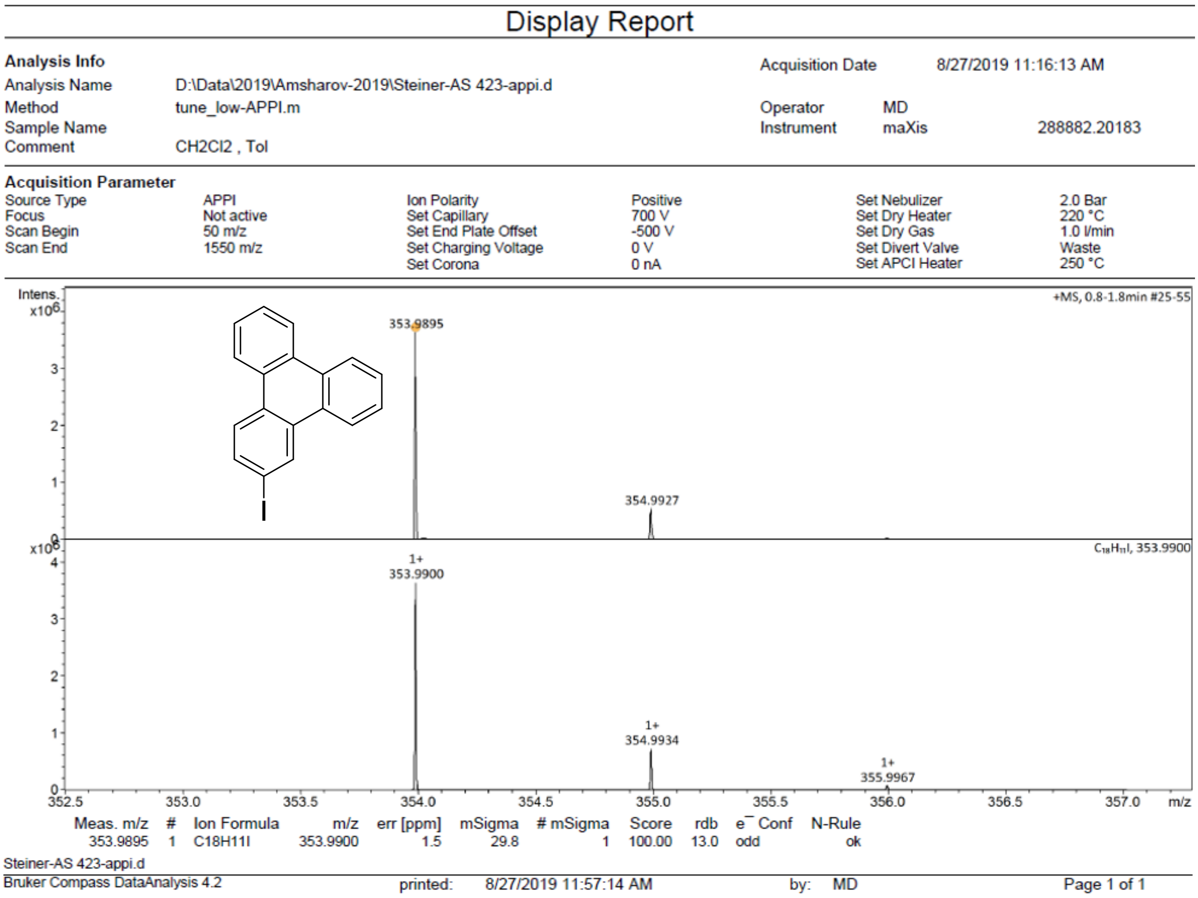


Molecular formula: C18H11I Resolution: 5000 at 50%

Data: C:\Data\Anni\AS428_0002.A20[c] 26 Aug 2019 16:49 Cal: PAH_6 4 Mar 2019 17:13
Shimadzu Biotech Axima Confidence 2.8.5.20090629: Mode Reflectron, Power: 95, Blanked, P.Ext. @ 354 (bin 52)

21 mV[sum= 761 mV] Profiles 1-37 Smooth Av 10 -Baseline 5

Figure S209: LDI MS spectrum of 2-iodotriphenylene (**T9**), *m/z* 354 (M^+, 100 %).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS 423-appi.d	Acquisition Date	8/27/2019 11:16:13 AM
Method	tune_low-APPI.m	Operator	MD
Sample Name		Instrument	maXis 288882.20183
Comment	CH2Cl2 , Tol		

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
353.9895	1	C18H11I	353.9900	1.5	29.8	1	100.00	13.0	odd	ok

Steiner-AS 423-appi.d

Bruker Compass DataAnalysis 4.2 printed: 8/27/2019 11:57:14 AM by: MD Page 1 of 1

Figure S210: HR MS (APPI) spectrum of 2-iodotriphenylene (**T9**), *m/z* 353.9895 (M^+, 100 %).

Condensation of 2-fluoro-3''-iodo-1,1':2',1''-terphenyl (P13).

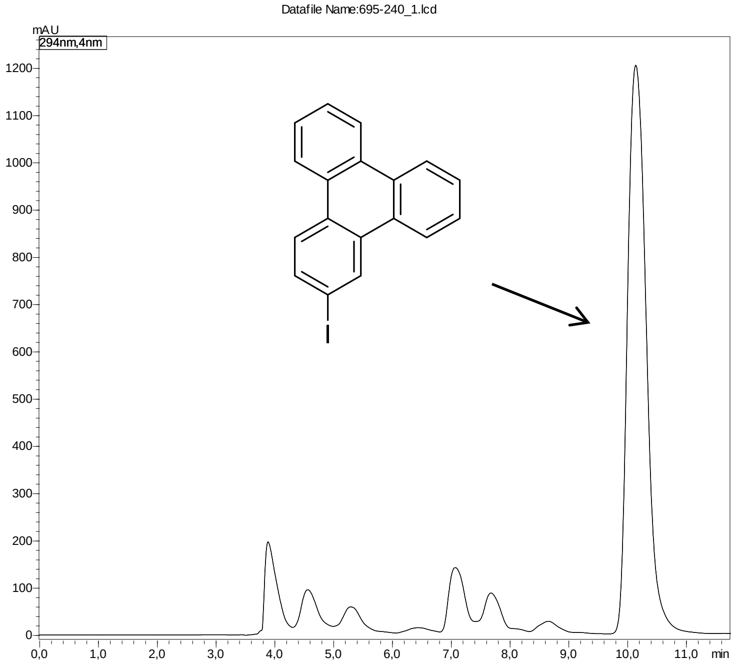


Figure S211: HPLC chromatogram obtained after reaction (240 °C, 16 h) (PBr column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6).

Condensation of 2-fluoro-2''-iodo-1,1':2',1''-terphenyl (P14).

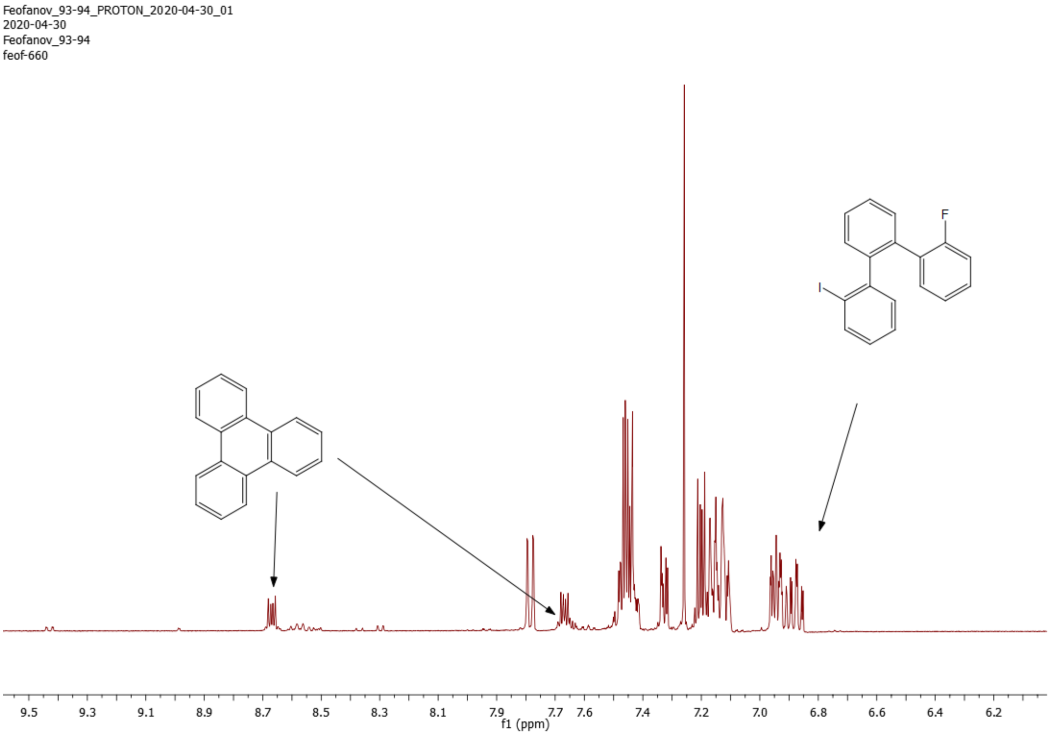


Figure S212: ^{1}H NMR spectrum obtained after reaction (190 ºC, 12h).

2-(4-iodophenyl)triphenylene (T10).

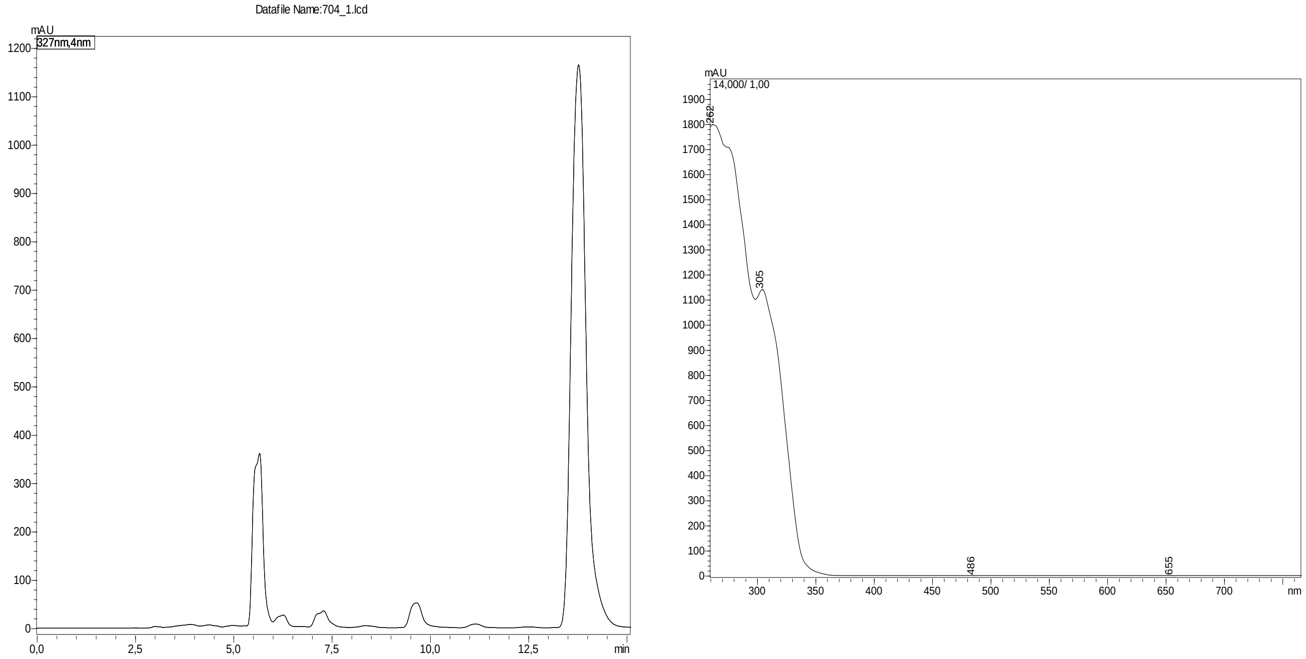


Figure S213: HPLC chromatogram obtained after reaction (190 °C, 60 h) (PBr column (analyt.), 1.0 mL/min, 40 C, DCM/MeOH 4:6) t_R = 13.86 min and UV/vis spectrum (inset) of 2-(4-iodophenyl)triphenylene (**T10**).

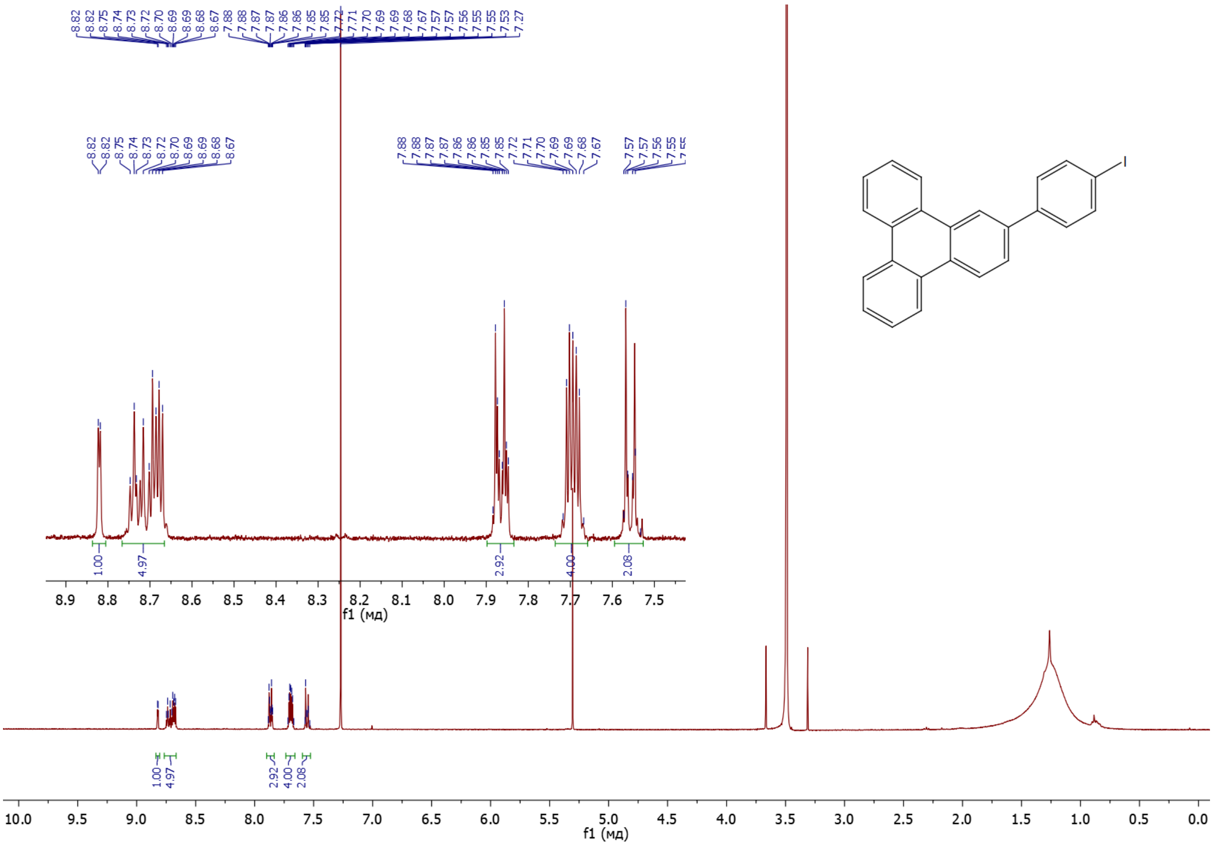


Figure S214: ^{1}H NMR spectrum of 2-(4-iodophenyl)triphenylene (**T10**).

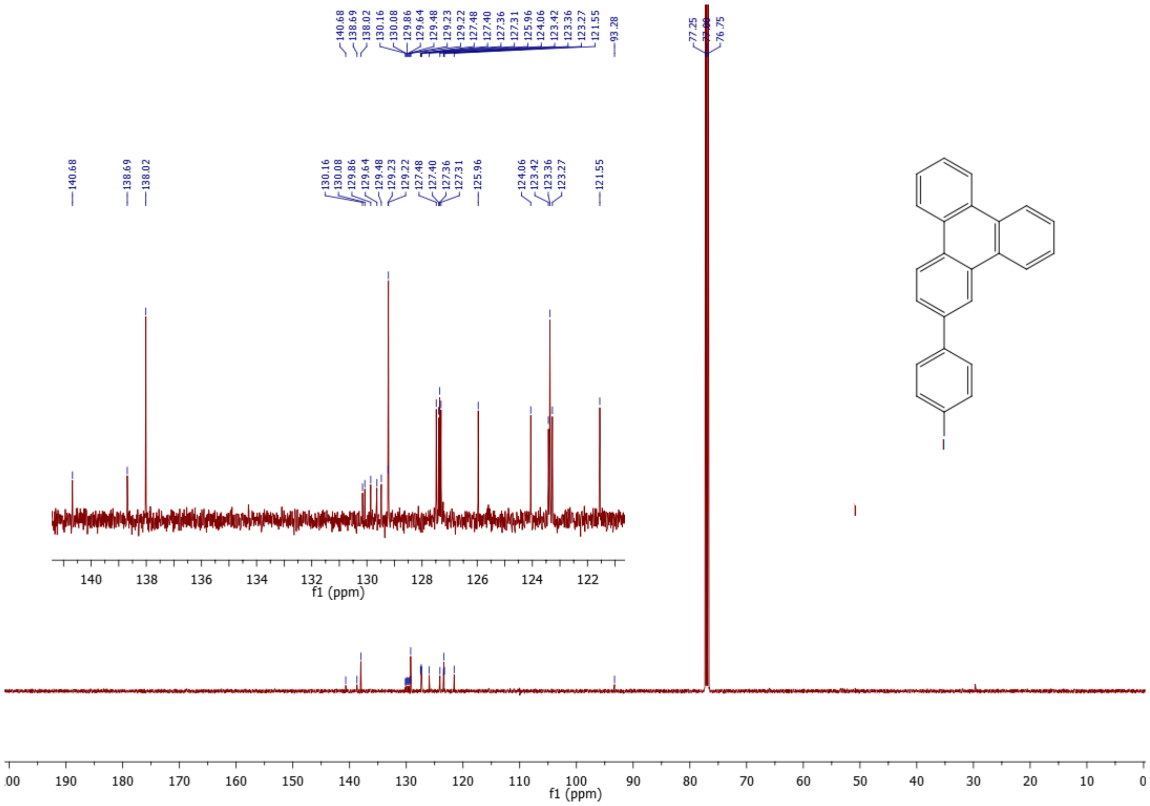


Figure S215: ^{13}C NMR spectrum of 2-(4-iodophenyl)triphenylene (**T10**).

Condensation of 2-fluoro-4-iodo-1,1':2',1''-terphenyl (P16).

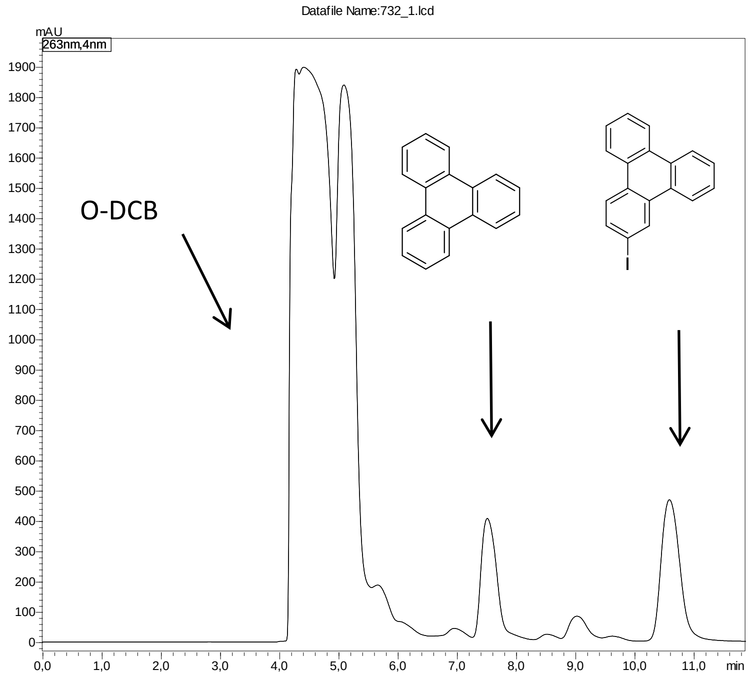


Figure S216: HPLC chromatogram obtained after reaction (240 °C, 12 h) (PBr column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6).

Condensation of 2-fluoro-5-iodo-1,1':2',1''-terphenyl (P17).

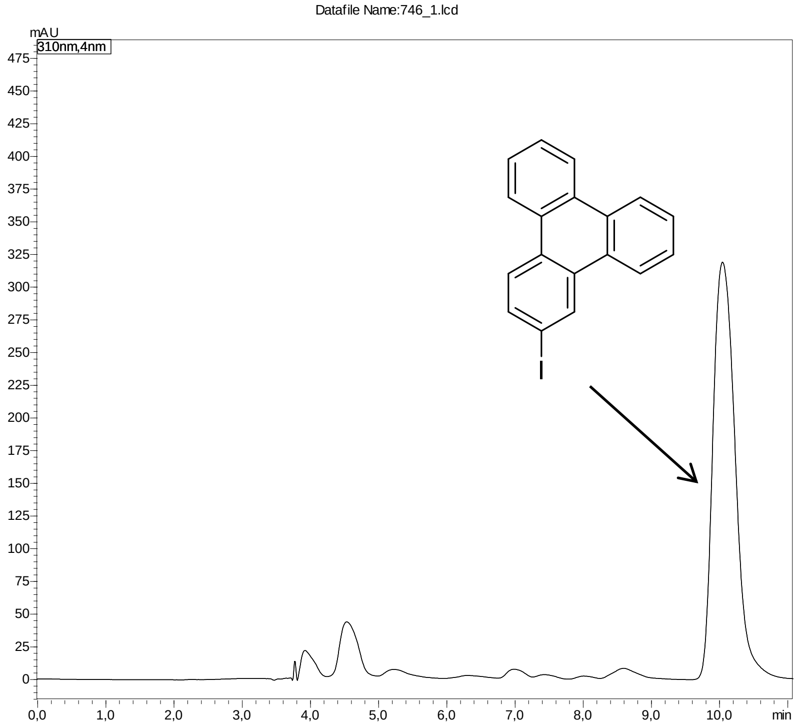


Figure S217: HPLC chromatogram obtained after reaction (240 °C, 12 h) (PBr column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6).

Condensation of 2-fluoro-6-iodo-1,1':2',1''-terphenyl (P18).

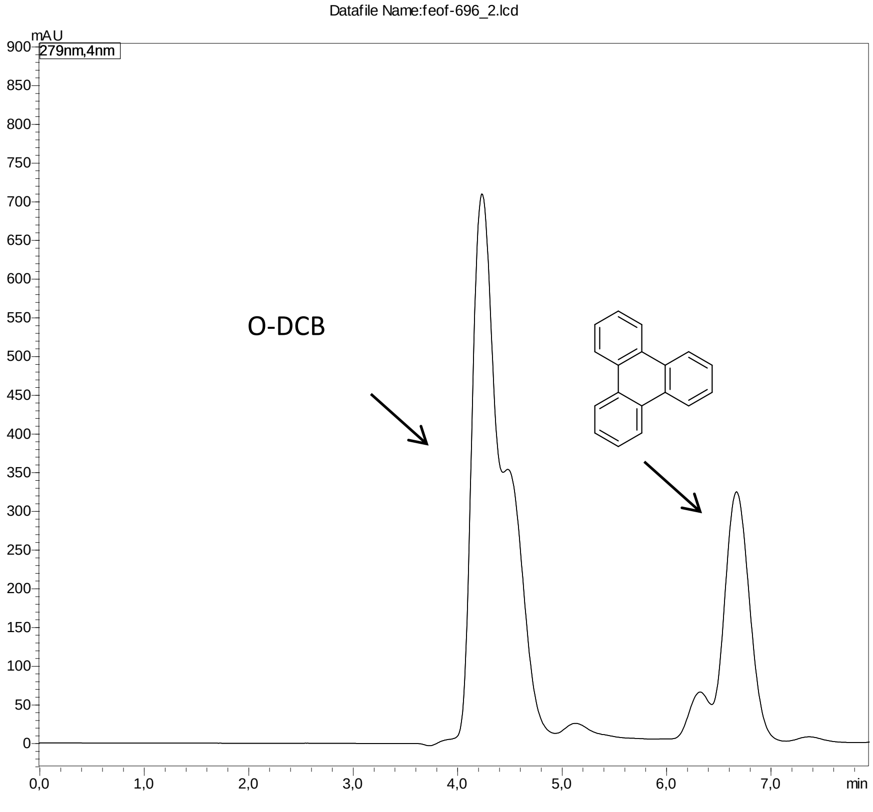


Figure S218: HPLC chromatogram obtained after reaction (190 °C, 12 h) (PBr column (analyt.), 1.0 mL/min, 40 °C, DCM/MeOH 4:6).

Condensation of 2-fluoro-3-iodo-1,1':2',1''-terphenyl (P19)

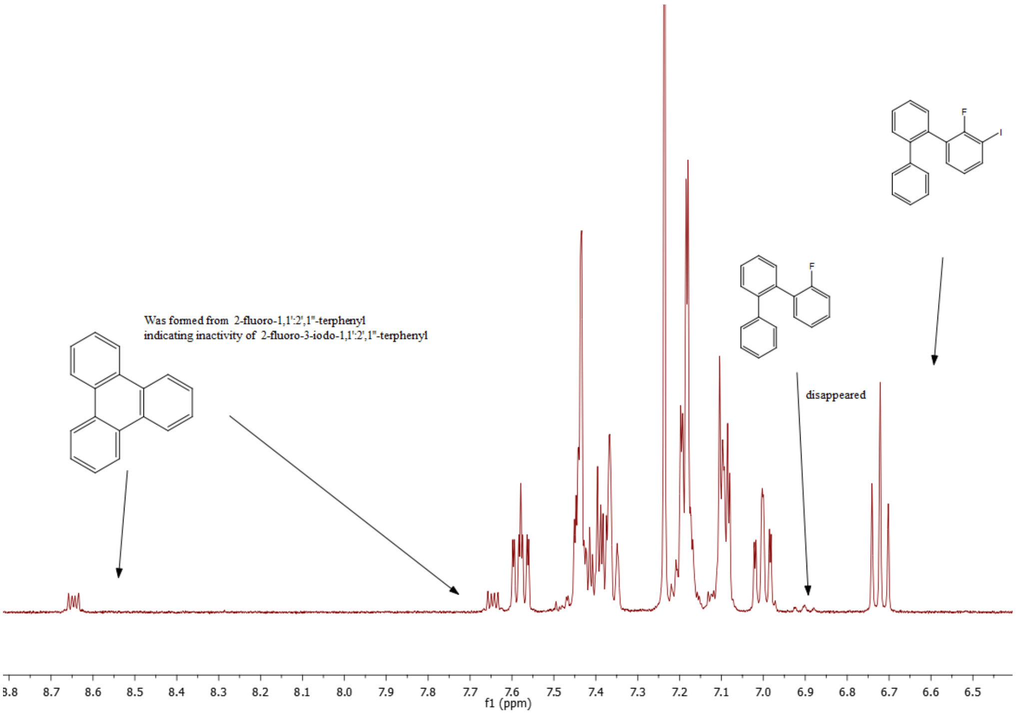


Figure S219: ^{1}H NMR spectrum obtained after reaction (240 ºC, 24h).

3-Iodobenzo[*ghi*]fluoranthene (T11)

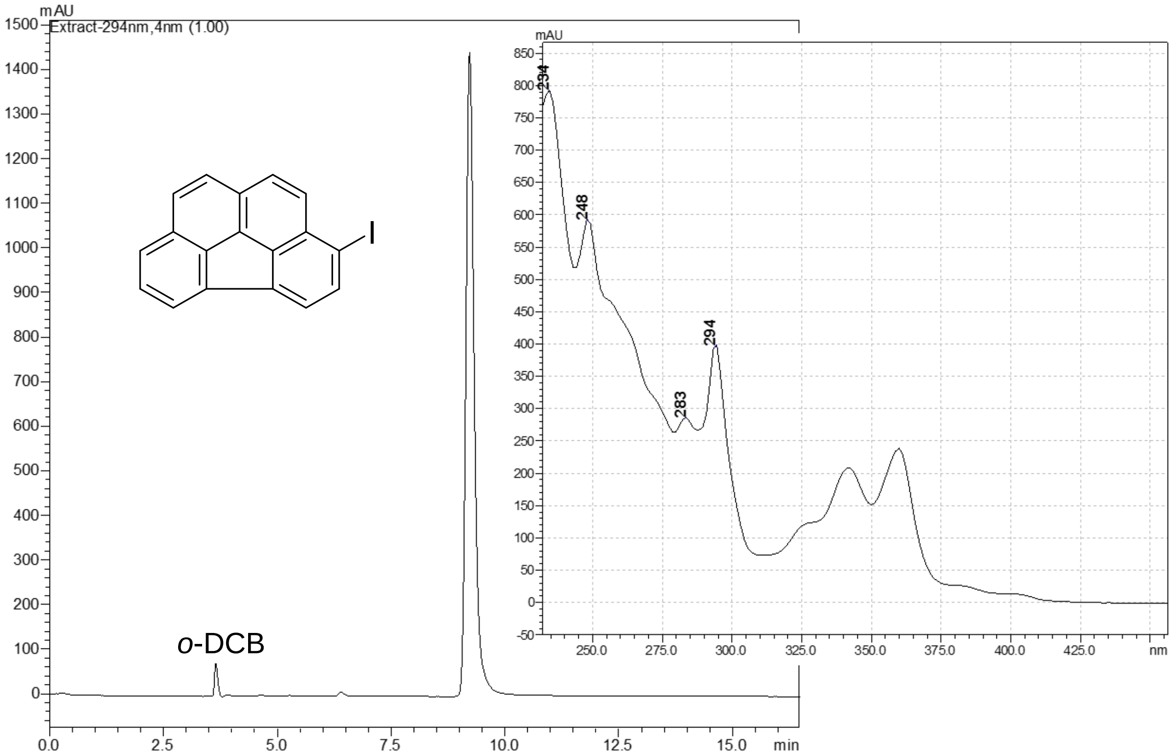


Figure S220: HPLC chromatogram obtained after reaction (180 °C, 12 h) (PBr column (anal.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1); t_R = 9.22 min (**T11**).

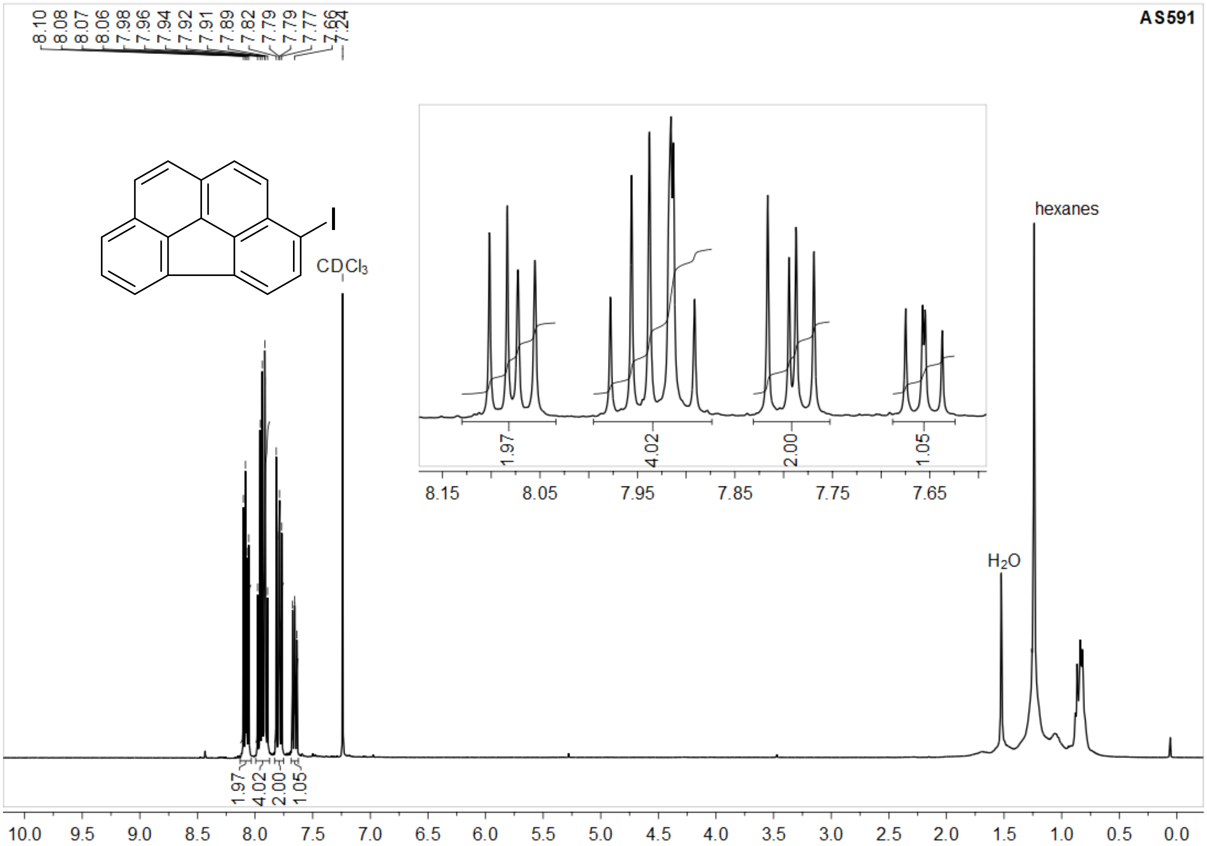


Figure S221: ^{1}H NMR spectrum of 3-iodobenzo[*ghi*]fluoranthene (**T11**) (from reaction mixture, in CDCl$_3$).

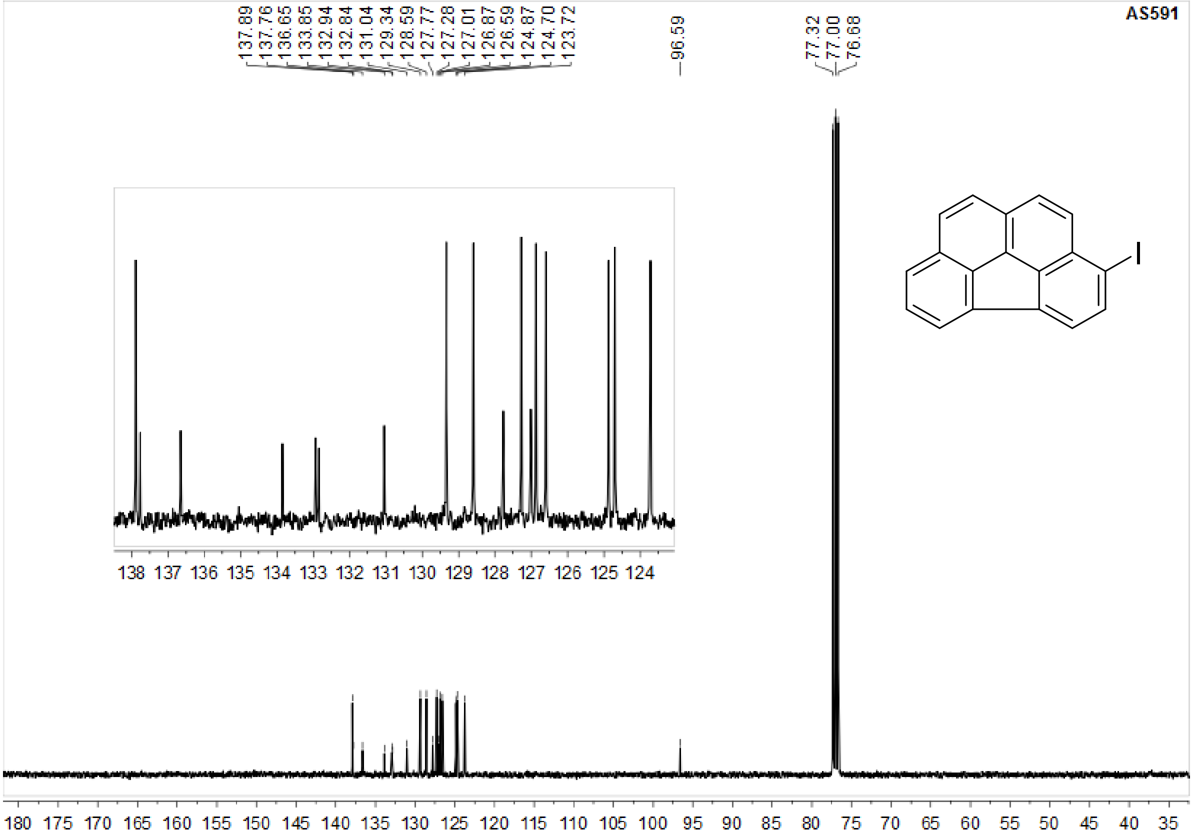


Figure S222: ^{13}C NMR spectrum of 3-iodobenzo[*ghi*]fluoranthene (**T11**) (from reaction mixture, in CDCl$_3$).

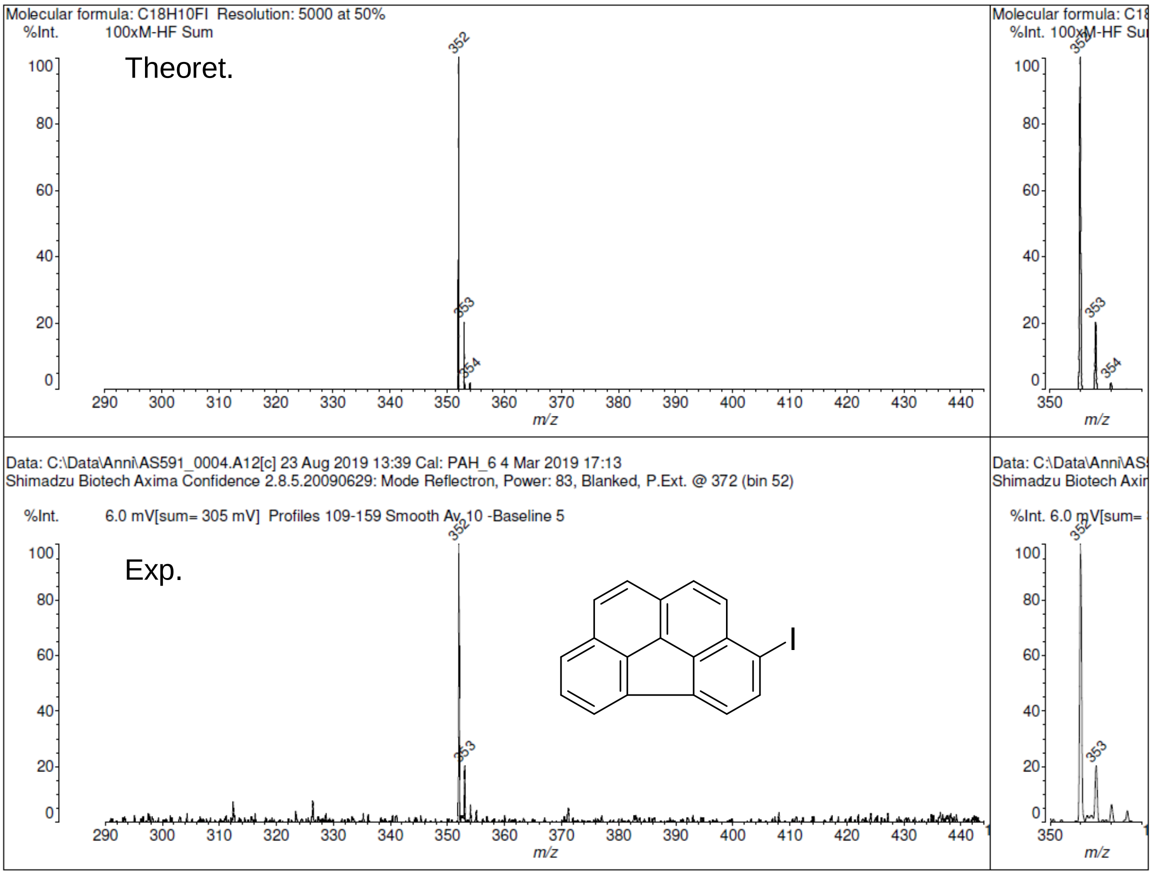
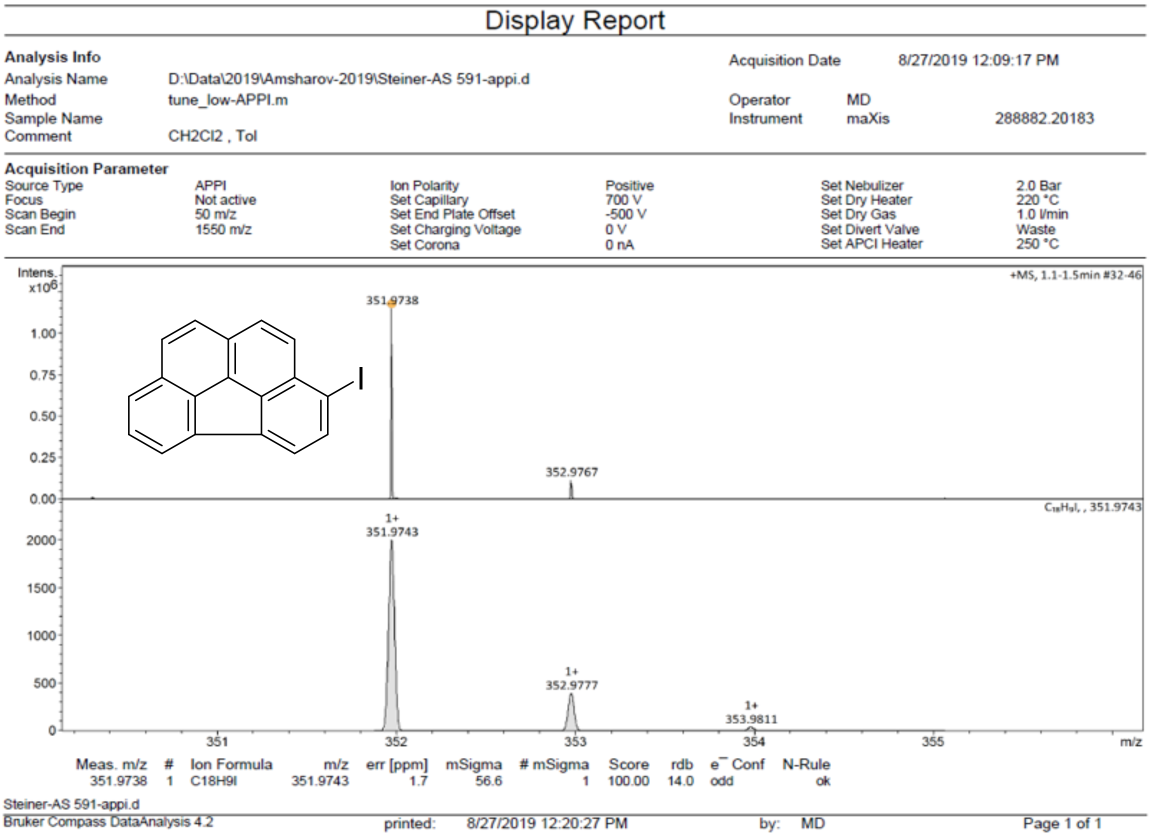


Figure S223: LDI MS spectrum of 3-iodobenzo[*ghi*]fluoranthene (**T11**), *m/z* 352 (M$^+$, 100 %).



Display Report

Analysis Info

Analysis Name	D:\Data\2019\Amsharov-2019\Steiner-AS 591-appi.d	Acquisition Date	8/27/2019 12:09:17 PM	
Method	tune_low-APPI.m	Operator	MD	
Sample Name		Instrument	maXis	288882.20183
Comment	CH2Cl2 , Tol			

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
351.9738	1	C18H9I	351.9743	1.7	56.6	1	100.00	14.0	odd	ok

Steiner-AS 591-appi.d

Bruker Compass DataAnalysis 4.2 printed: 8/27/2019 12:20:27 PM by: MD Page 1 of 1

Figure S224: HR MS (APPI) spectrum of 3-iodobenzo[*ghi*]fluoranthene (**T11**), *m/z* 351.9738 (M$^+$, 100 %).

3-(3-Iodophenyl)benzo[*ghi*]fluoranthene (T12)

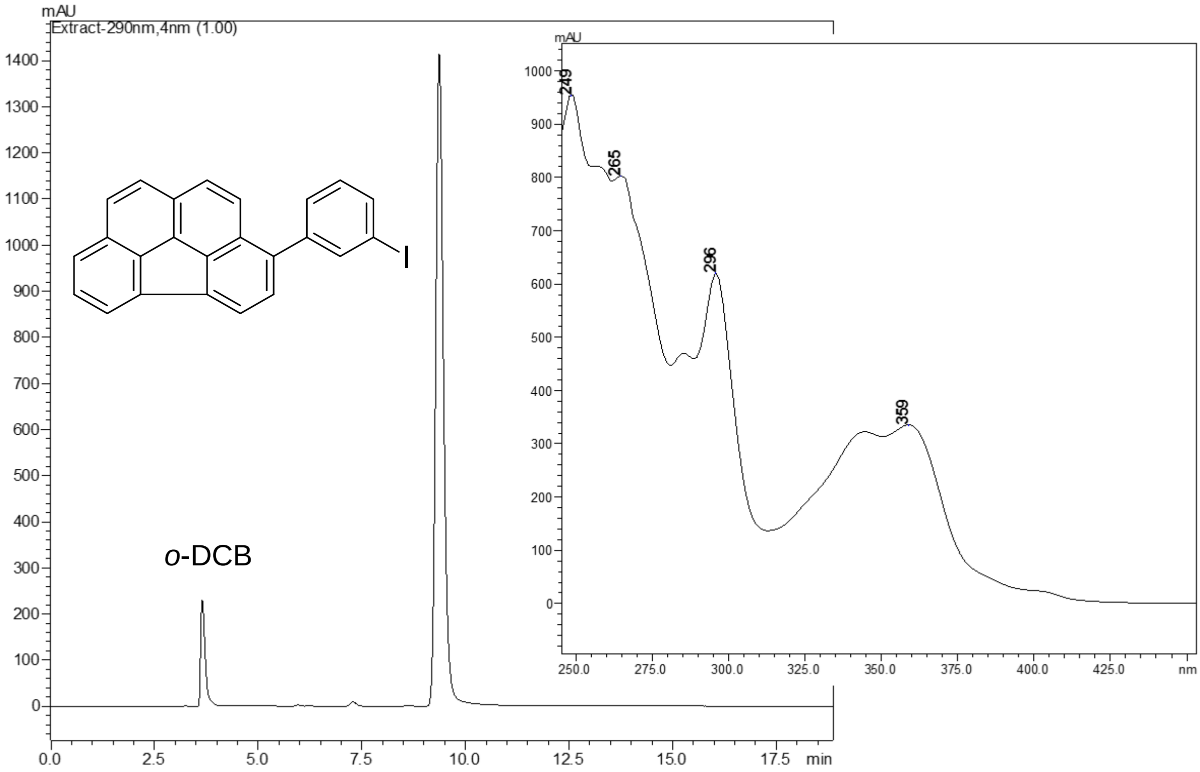


Figure S51: HPLC chromatogram obtained after reaction (180 °C, 12 h) (PBr column (anal.), 1.0 mL/min, 35 °C, DCM/MeOH 1:1); t_R = 9.36 min (**T12**).

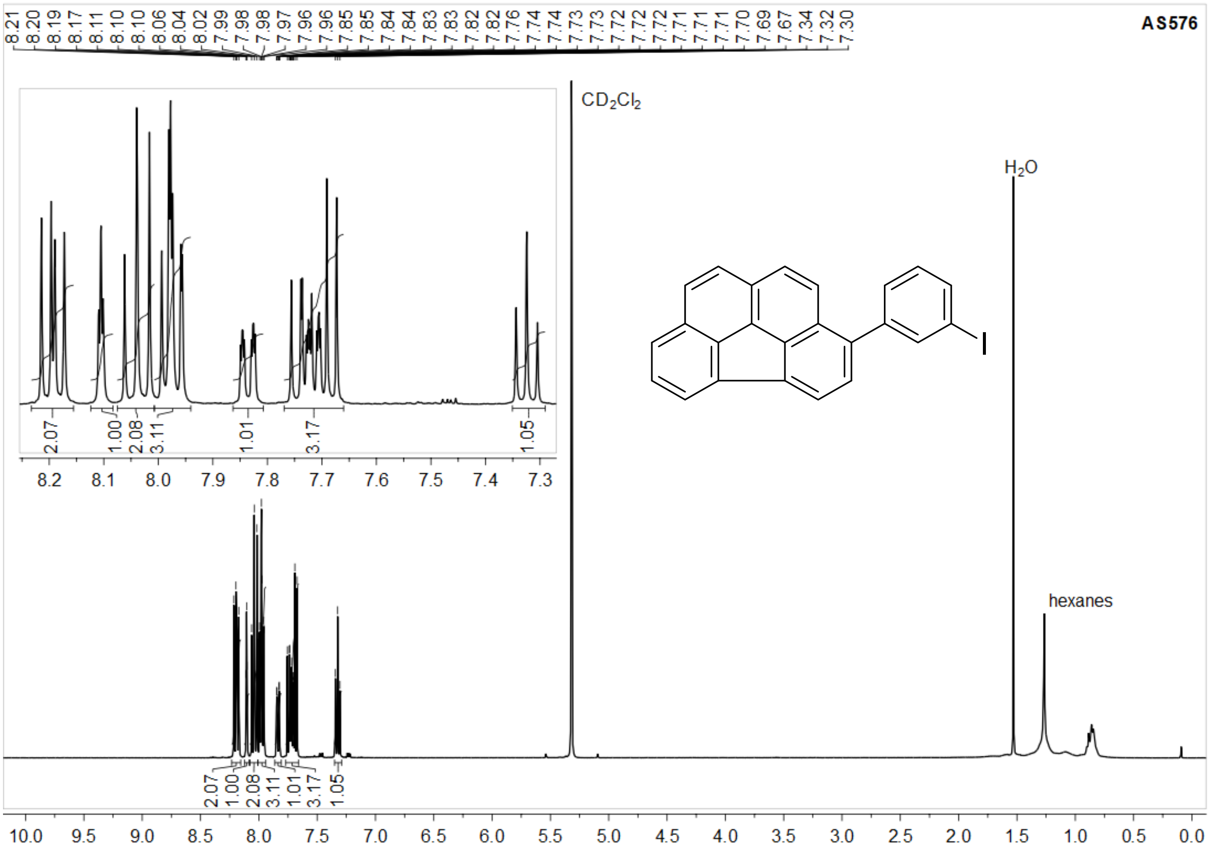


Figure S226: ^{1}H NMR spectrum of 3-(3-iodophenyl)benzo[*ghi*]fluoranthene (**T12**) (from reaction mixture, in CD_2Cl_2).

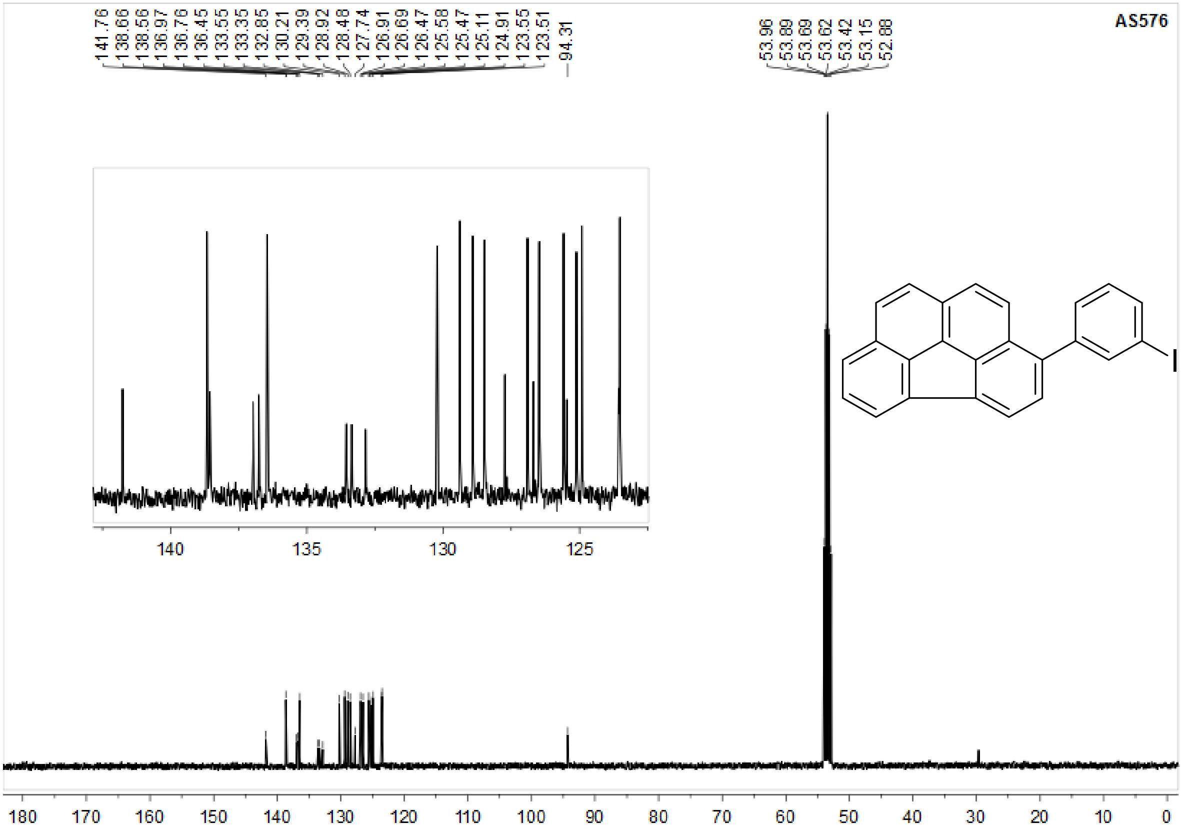
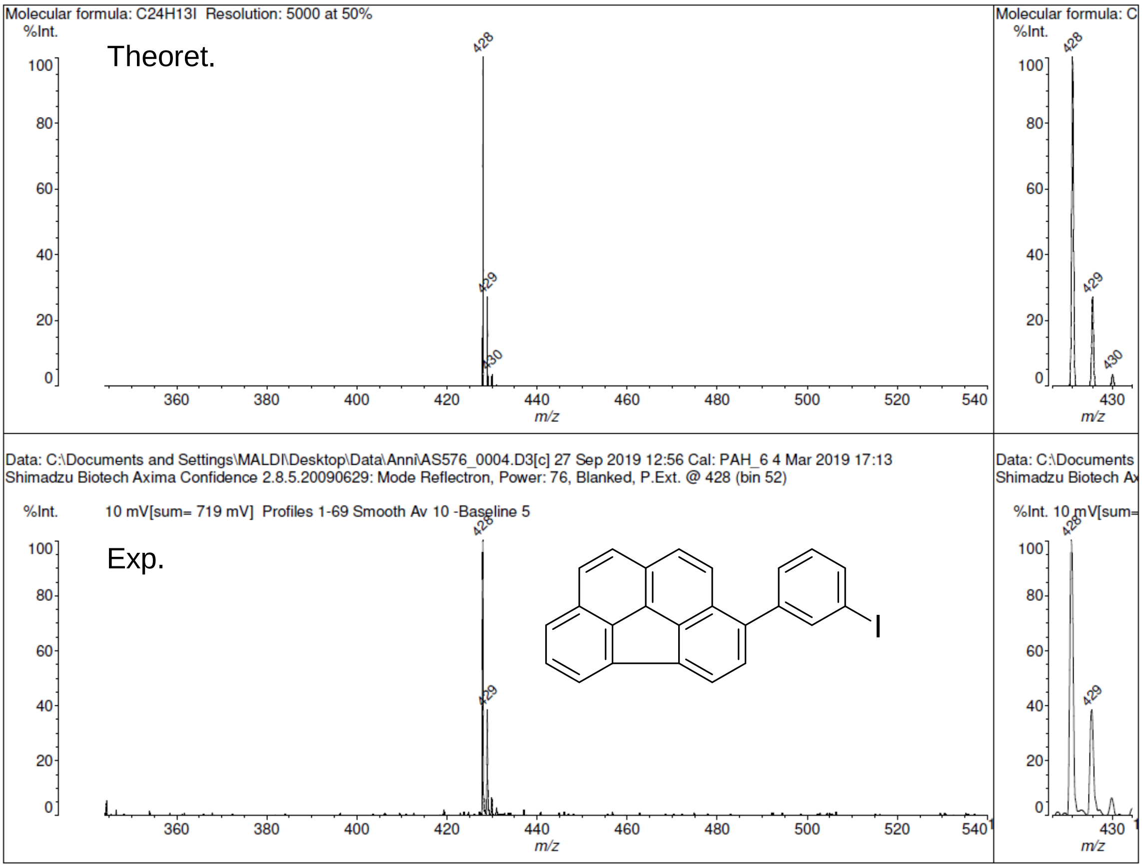


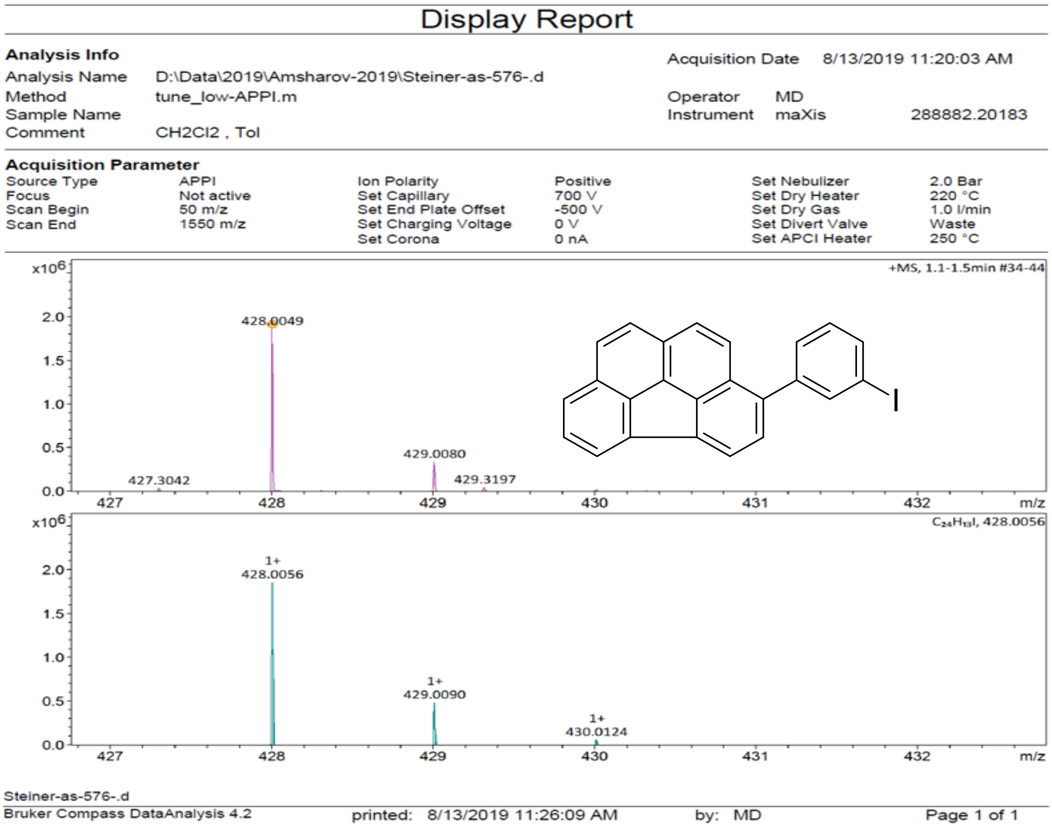
Figure S227: ^{13}C NMR spectrum of 3-(3-iodophenyl)benzo[*ghi*]fluoranthene (**T12**) (from reaction mixture, in CD_2Cl_2).


Molecular formula: C24H13I Resolution: 5000 at 50%

Data: C:\Documents and Settings\MALDI\Desktop\Data\Anni\AS576_0004.D3[c] 27 Sep 2019 12:56 Cal: PAH_6 4 Mar 2019 17:13
Shimadzu Biotech Axima Confidence 2.8.5.20090629: Mode Reflectron, Power: 76, Blanked, P.Ext. @ 428 (bin 52)

%Int.   10 mV[sum= 719 mV] Profiles 1-69 Smooth Av 10 -Baseline 5

Figure S52: LDI MS spectrum of 3-(3-iodophenyl)benzo[*ghi*]fluoranthene (**T12**), *m/z* 428 (M^+, 100 %).



Display Report

Analysis Info

Analysis Name D:\Data\2019\Amsharov-2019\Steiner-as-576-.d
Method tune_low-APPI.m
Sample Name
Comment CH2Cl2 , Tol

Acquisition Date 8/13/2019 11:20:03 AM
Operator MD
Instrument maXis 288882.20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	700 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	1550 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	250 °C

Steiner-as-576-.d
Bruker Compass DataAnalysis 4.2 printed: 8/13/2019 11:26:09 AM by: MD Page 1 of 1

Figure S229: HR MS (APPI) spectrum of 3-(3-iodophenyl)benzo[*ghi*]fluoranthene (**T12**), *m/z* 428.0049 (M^+, 100 %).

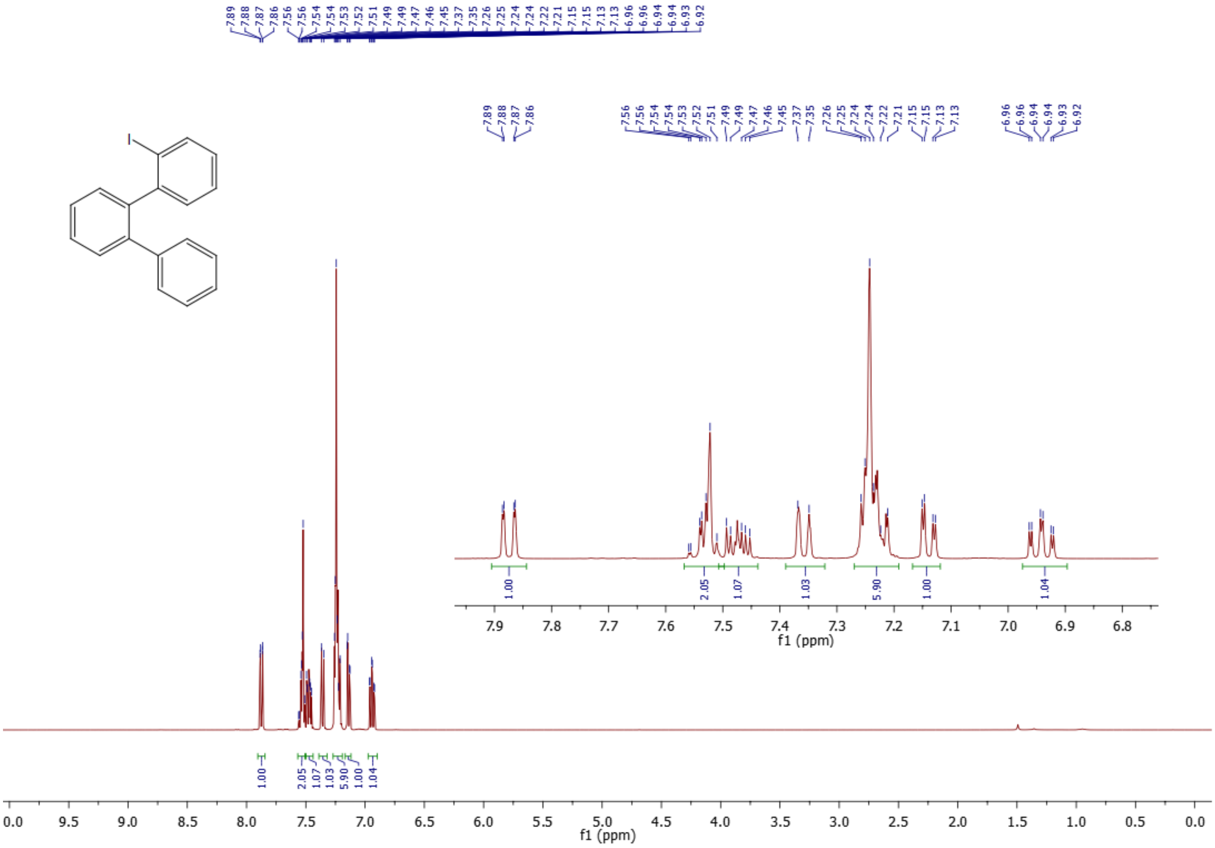


Figure S230: ^{1}H NMR spectrum of 2-iodo-1,1':2',1''-terphenyl (**PS1**) (in $CDCl_3$).

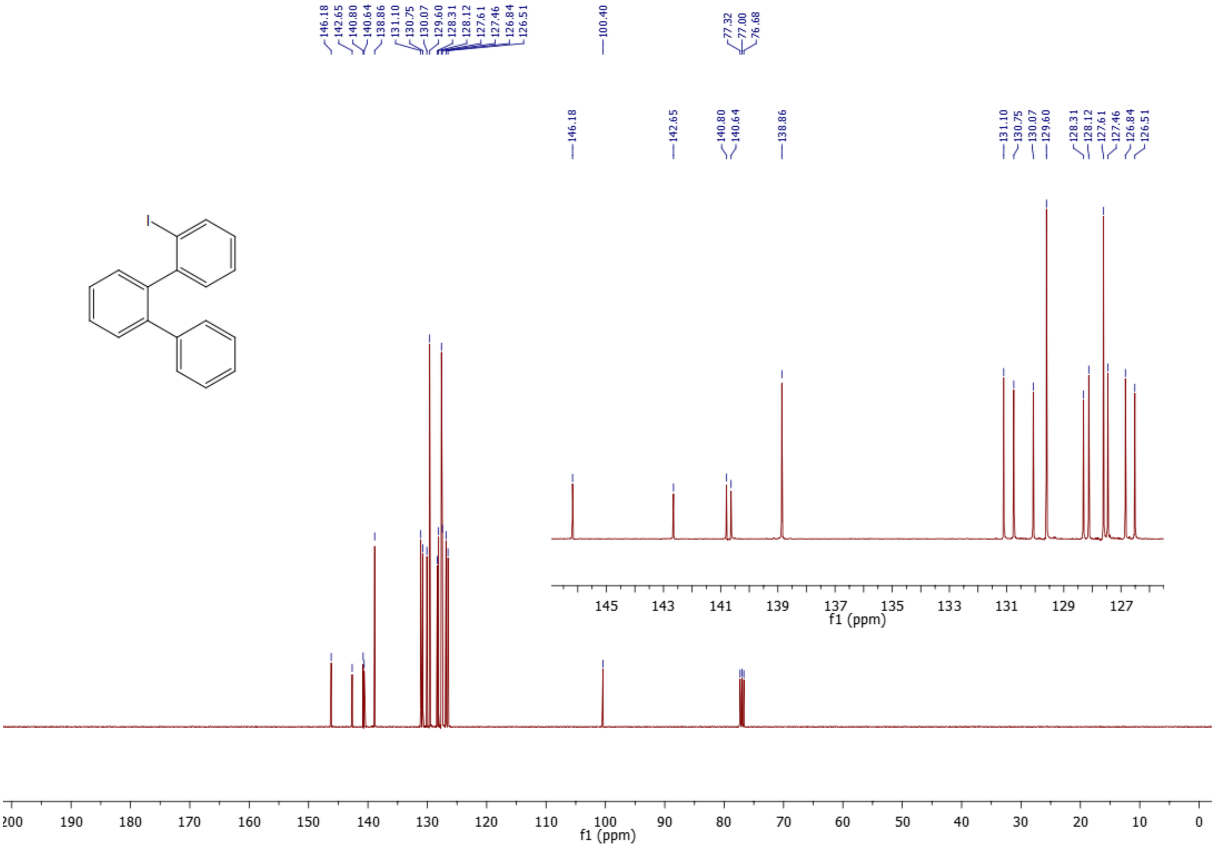


Figure S231: ^{13}C NMR spectrum of 2-iodo-1,1':2',1''-terphenyl (**PS1**) (in $CDCl_3$).

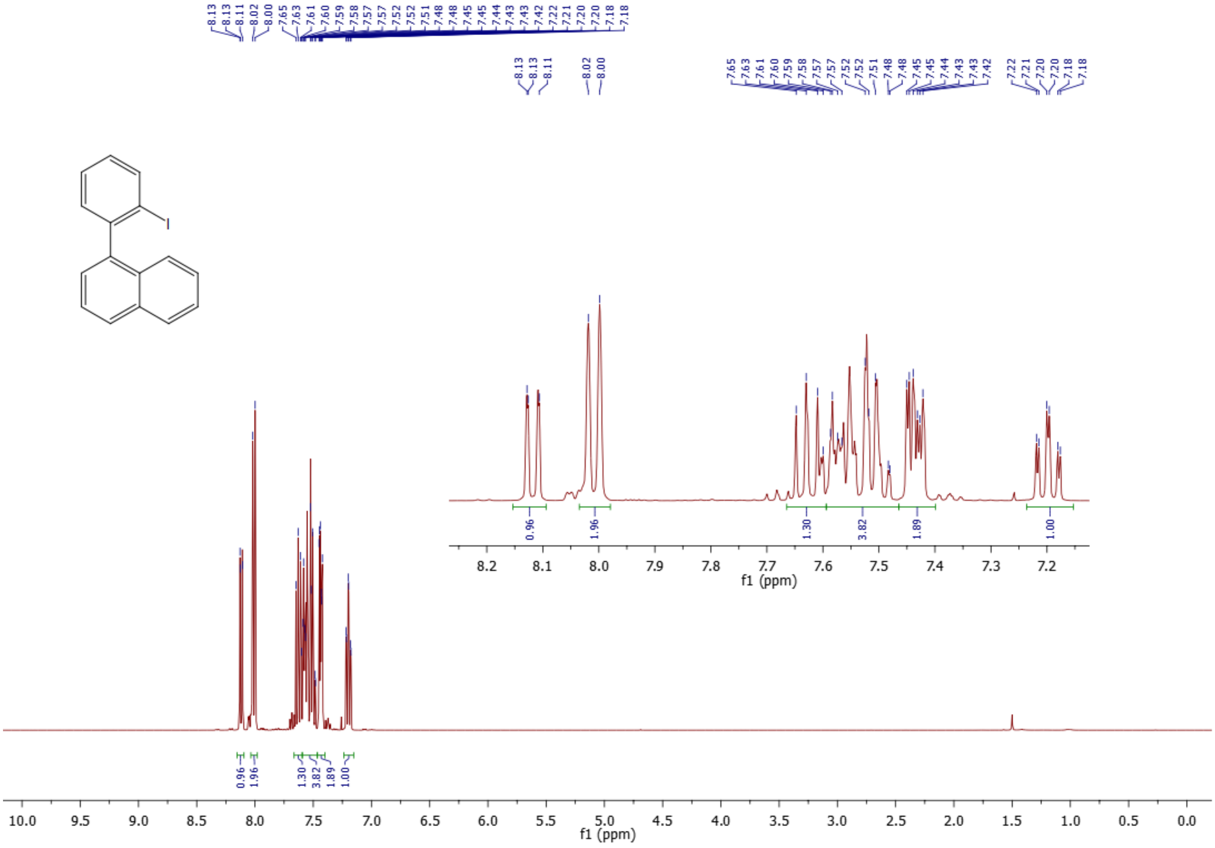


Figure S232: ^{1}H NMR spectrum of 1-(2-iodophenyl)naphthalene (**PS2**) (in $CDCl_3$).

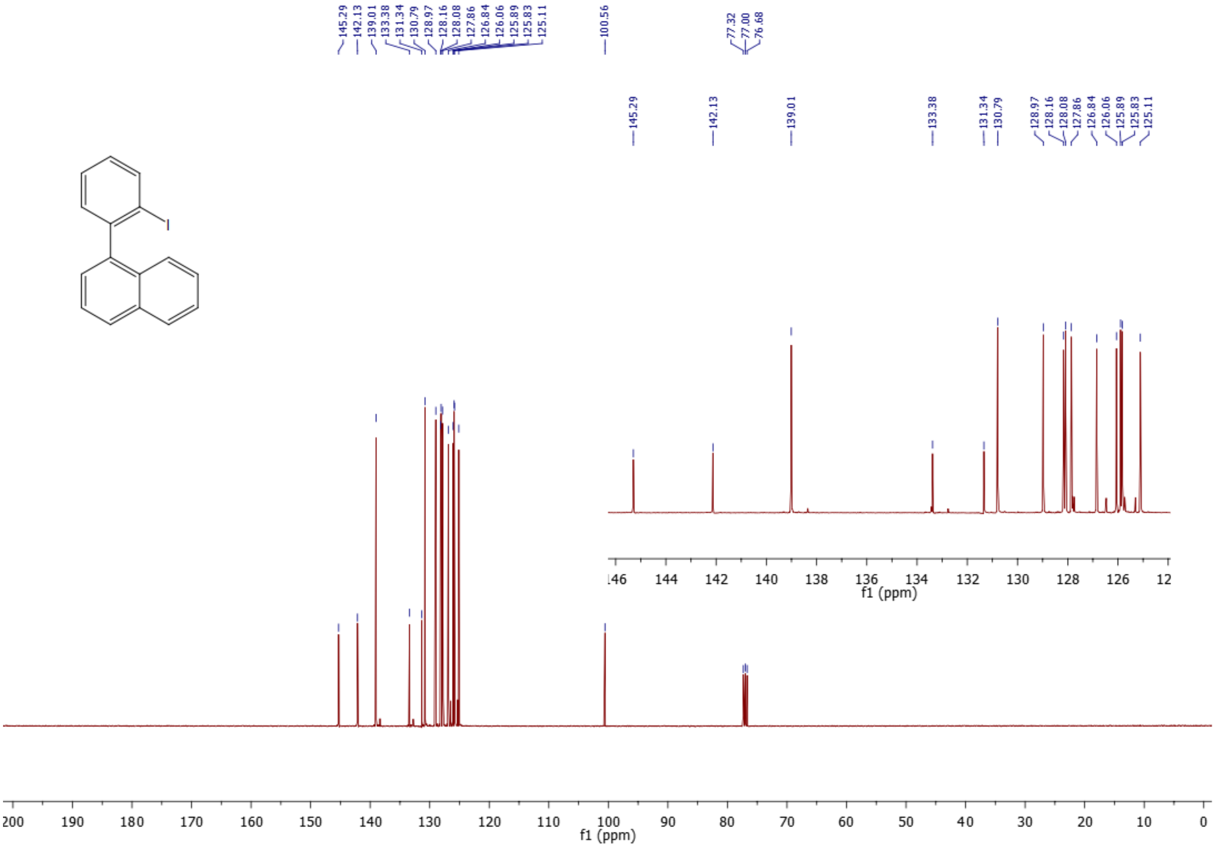


Figure S233: ^{13}C NMR spectrum of 1-(2-iodophenyl)naphthalene (**PS2**) (in $CDCl_3$).