Electronic Supplementary Material (ESI) for ChemComm.


# Solid-state construction of zig-zag periphery via intramolecular C-H insertion induced by alumina-mediated C-F activation.

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# Instrumental Parameters

**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.

**Flash column chromatography** was performed on a Interchim PuriFlash XS420 using flash grade silica gel from (Machery-Nagel 60 M (40–63 mm, deactivated)).

**NMR spectra** were recorded on a Bruker Avance 400 at 400 MHz ($^{1}$H NMR), 376 MHz ($^{19}$F NMR), 101 MHz ($^{13}$C NMR) and a Bruker Avance Neo 500, operating at 500 MHz ($^{1}$H NMR), 470 MHz ($^{19}$F NMR) and 126 MHz ($^{13}$C NMR). The signals were referenced to residual solvent peaks (in parts per million (ppm) $^{1}$H: $CDCl_3$, 7.27 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.

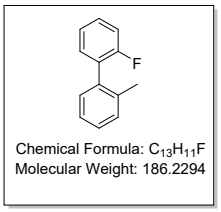
**High resolution APPI spectra** were recorded on a Bruker ESI TOF maXis 4G instrument. The data was evaluated with the program Bruker Compass DataAnalysis 4.2.

# Experimental.

**Synthesis of precursors**.

1-benzyl-2-fluorobenzene (**1c**) was purchased from Chempur®.

**2-fluoro-2'-methyl-1,1'-biphenyl (1a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-bromotoluene (610 mg, 3.57 mmol), 2-fluorophenylboronic acid (500 mg, 3.57 mmol), $K_2CO_3$ (2.96g, 21.4 mmol) and $Pd(PPh_3)_4$ (107 mg, 92 µmol). The solids were suspended in 6:4/1 toluene/MeOH/$H_2O$ (55 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-fluoro-2'-methyl-1,1'-biphenyl as colorless oil in 68% yield (450 mg, 2.42 mmol).

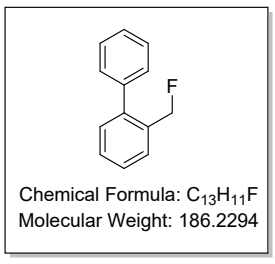
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.09 (m, 6H), 7.06 (td, *J* = 7.4, 1.2 Hz, 1H), 7.01 (ddd, *J* = 9.5, 8.2, 1.1 Hz, 1H), 2.10 (d, *J* = 1.2 Hz, 3H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -114.67 (s, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.6 (d, *J* = 245.7 Hz), 136.6, 135.7, 131.5 (d, *J* = 3.7 Hz), 130.0, 129.9, 129.3 (d, *J* = 16.7 Hz), 129.0 (d, *J* = 8.0 Hz), 127.9, 125.6, 123.9 (d, *J* = 3.6 Hz), 115.5 (d, *J* = 22.5 Hz), 19.9 (d, *J* = 2.8 Hz).

The spectroscopic data were consistent with previously reported[1].

**2-(fluoromethyl)-1,1'-biphenyl (1b).**




To a stirred solution of the 2-(bromomethyl)-1,1'-biphenyl (160 mg, 0.64 mmol.) in anhydrous $CH_3CN$ (5 ml) was added tetrabutylammonium trifluoride trihydrate (330 mg,, 1.28 mmol). The reaction mixture was stirred 18 h at 85 °C. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane-cyclohexane:DCM 9:1 yielding 2-(fluoromethyl)-1,1'-biphenyl as colorless oil in 92% yield (110 mg, 0.59 mmol)..

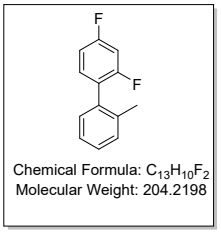
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 1H), 7.37 – 7.18 (m, 8H), 5.18 (d, *J* = 48.1 Hz, 2H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -199.69 (t, *J* = 48.2 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.2 (d, *J* = 4.4 Hz), 140.0 (d, *J* = 1.0 Hz), 133.3 (d, *J* = 16.0 Hz), 130.1 (d, *J* = 1.3 Hz), 129.7 (d, *J* = 6.6 Hz), 129.2 (d, *J* = 1.4 Hz), 128.9 (d, *J* = 3.6 Hz), 128.2, 127.6 (d, *J* = 1.8 Hz), 127.4, 82.7 (d, *J* = 164.8 Hz).

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

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



Chemical Formula: $C_{13}H_{10}F_2$
Molecular Weight: 204.2198

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-methyliodobenzene (450 mg, 2 mmol), 2,4-difluorophenylboronic acid (310 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2,4-difluoro-2'-methyl-1,1'-biphenyl as colorless oil in 49% yield (200 mg, 0.98 mmol).

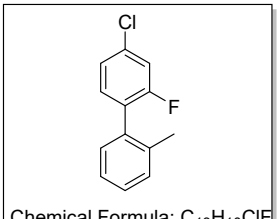
**$^{1}$H NMR** (500 MHz, $CD_2Cl_2$) δ 7.35 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.99 (tdd, *J* = 8.5, 2.5, 0.9 Hz, 1H), 6.97 – 6.91 (m, 1H), 2.20 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CD_2Cl_2$) δ -111.28 (q, *J* = 8.2 Hz, 1F), -112.34 – -112.48 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CD_2Cl_2$) δ 162.9 (dd, *J* = 247.5, 11.8 Hz), 160.1 (dd, *J* = 247.4, 12.0 Hz), 137.2, 135.3, 132.7 (dd, *J* = 9.5, 5.3 Hz), 130.5, 130.4, 128.6, 126.1, 125.8 (dd, *J* = 17.1, 3.8 Hz), 111.6 (dd, *J* = 21.0, 3.8 Hz), 104.1 (dd, *J* = 26.7, 25.4 Hz), 20.0 (d, *J* = 2.6 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}F_2$, 204.0746; found, 204.0768.

**4-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (3a).**



Chemical Formula: $C_{13}H_{10}ClF$
Molecular Weight: 220.6714

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-methyliodobenzene (450 mg, 2 mmol), (4-chloro-2-fluorophenyl)boronic acid (350 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was stirred at 80 °C for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 4-chloro-2-fluoro-2'-methyl-1,1'-biphenyl as white oil in 77% yield (340 mg, 1.45 mmol).

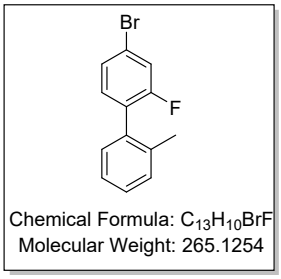
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 3H), 7.23 – 7.17 (m, 4H), 2.22 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -111.89 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.4 (d, $J$ = 249.5 Hz), 136.6, 134.6, 133.9 (d, $J$ = 10.0 Hz), 132.2 (d, $J$ = 4.7 Hz), 130.1, 130.0, 128.3, 127.9 (d, $J$ = 17.1 Hz), 125.7, 124.4 (d, $J$ = 3.7 Hz), 116.3 (d, $J$ = 26.2 Hz), 19.8 (d, $J$ = 2.8 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}ClF$, 220.6709; found, 220.6713

**4-bromo-2-fluoro-2'-methyl-1,1'-biphenyl (4a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-methyliodobenzene (450 mg, 2 mmol), (4-bromo-2-fluorophenyl)boronic acid (440 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was stirred at 70 °C for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 4-bromo-2-fluoro-2'-methyl-1,1'-biphenyl as white solid in 89% yield (470 mg, 1.70 mmol).

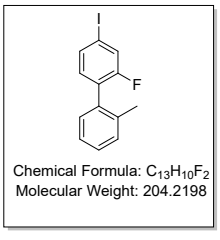
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 7.21 (d, $J$ = 7.5 Hz, 1H), 7.15 (t, $J$ = 8.0 Hz, 1H), 2.22 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -111.63 (t, $J$ = 8.4 Hz, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.4 (d, $J$ = 250.7 Hz), 136.5, 134.6, 132.6 (d, $J$ = 4.4 Hz), 130.1, 129.9, 128.4 (d, $J$ = 17.0 Hz), 128.3, 127.3 (d, $J$ = 3.7 Hz), 125.7, 121.3 (d, $J$ = 9.2 Hz), 119.2 (d, $J$ = 26.0 Hz), 19.8 (d, $J$ = 2.9 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}BrF$, 263.9945; found, 263.9966.

**2-fluoro-4-iodo-2'-methyl-1,1'-biphenyl (5a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 4-bromo-3-fluoroaniline (665 mg, 3.49 mmol), 2-methylphenylboronic acid (703 mg, 5.17 mmol), $K_2CO_3$ (1.45 g, 10.5 mmol) and $Pd(dppf)Cl_2$ (120 mg, 0.16 mmol). The solids were suspended in Dioxane/$H_2O$ 3/1 (20 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux °C for 16 h. The solvent was

evaporated and the product was purified by silica gel column chromatography, eluting with Hexane-Hexane:EtOAc 1:1 yielding 2-fluoro-2'-methyl-[1,1'-biphenyl]-4-amine as yellow oil in 72% yield (503 mg, 2.5 mmol).

A 100 mL round-bottom flask was charged with 2-fluoro-2'-methyl-[1,1'-biphenyl]-4-amine (503 mg, 2.5 mmol), and conc $H_2SO_4$ (8.3 ml). The mixture was cooled to 0 °C in an ice-bath. Sodium nitrite (300 mg, 4.34 mmol) was added to the reaction mixture. The solution was stirred at 0 °C for 3h, and NaI (850 mg, 5.53 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 $Na_2SO_4$, 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-5-iodo-2-methyl-1,1'-biphenyl was isolated as white oil in 55% yield (430 mg, 1.38 mmol).

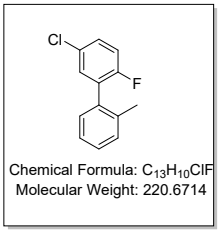
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.53 (dd, *J* = 8.9, 1.6 Hz, 1H), 7.36 – 7.23 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 2.21 (s, 3H).

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -111.88 (t, *J* = 8.1 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.2 (d, *J* = 251.7 Hz), 136.5, 134.7, 133.3 (d, *J* = 3.7 Hz), 132.8 (d, *J* = 4.1 Hz), 130.1, 129.8, 129.1 (d, *J* = 16.8 Hz), 128.3, 125.7, 124.9 (d, *J* = 25.2 Hz), 92.0 (d, *J* = 8.0 Hz), 19.9 (d, *J* = 3.0 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}IF$, 311.9811; found, 311.9816.

**5-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (6a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-methyliodobenzene (450 mg, 2 mmol), (5-chloro-2-fluorophenyl)boronic acid (350 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was stirred at 80 °C for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 5-chloro-2-fluoro-2'-methyl-1,1'-biphenyl as white oil in 91% yield (400 mg, 1.82 mmol).

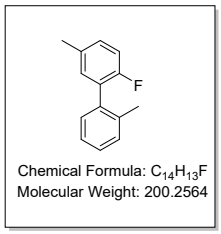
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 7.27 (dt, *J* = 6.4, 3.2 Hz, 3H), 7.21 (d, *J* = 6.8 Hz, 1H), 7.09 (t, *J* = 8.9 Hz, 1H), 2.23 (s, 4H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -117.36 – -117.48 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 158.2 (d, *J* = 246.0 Hz), 136.5, 134.4, 131.3 (d, *J* = 4.0 Hz), 130.9 (d, *J* = 18.7 Hz), 130.0, 129.9, 128.9 (d, *J* = 3.4 Hz), 128.8 (d, *J* = 8.2 Hz), 128.41, 125.8, 116.8 (d, *J* = 24.7 Hz), 19.8 (d, *J* = 2.9 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}ClF$, 220.6709; found, 220.6721.

**2-fluoro-2',5-dimethyl-1,1'-biphenyl (7a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-methyliodobenzene (450 mg, 2 mmol), (2-fluoro-5-methylphenyl)boronic acid (310 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-fluoro-2',5-dimethyl-1,1'-biphenyl as white oil in74% yield (297 mg, 1.49 mmol).

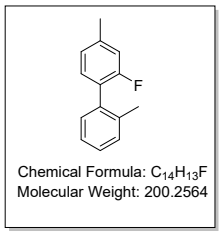
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 4H), 7.18 – 7.11 (m, 1H), 7.09 – 7.00 (m, 2H), 2.38 (s, 3H), 2.24 (d, *J* = 2.1 Hz, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -120.18 – -120.31 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.8 (d, *J* = 243.1 Hz), 136.6, 136.0, 133.3 (d, *J* = 3.7 Hz), 131.9 (d, *J* = 3.6 Hz), 130.0, 129.9, 129.4 (d, *J* = 7.8 Hz), 128.8 (d, *J* = 17.2 Hz), 127.8, 125.6, 115.1 (d, *J* = 22.6 Hz), 20.6, 19.9 (d, *J* = 2.9 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{14}H_{13}F$, 200.0996; found, 200.1006.

**2-fluoro-2',4-dimethyl-1,1'-biphenyl (8a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-methyliodobenzene (450 mg, 2 mmol), (2-fluoro-4-methylphenyl)boronic acid (310 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-fluoro-2',3-dimethyl-1,1'-biphenyl as white oil in 82% yield (328 mg, 1.64 mmol).

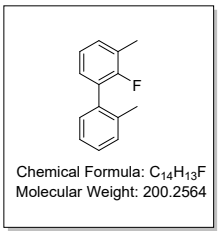
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 4H), 7.17 (td, *J* = 7.7, 3.7 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 10.7 Hz, 1H), 2.44 (s, 3H), 2.26 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -115.72 (d, *J* = 8.3 Hz, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.5 (d, *J* = 245.4 Hz), 139.4 (d, *J* = 7.8 Hz), 136.7, 135.8, 131.2 (d, *J* = 4.4 Hz), 130.2, 129.9, 127.8, 126.2 (d, *J* = 16.9 Hz), 125.6, 124.7 (d, *J* = 3.0 Hz), 116.0 (d, *J* = 22.4 Hz), 21.0 (d, *J* = 1.6 Hz), 19.9 (d, *J* = 2.9 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{14}H_{13}F$, 200.0996; found, 200.1016.

**2-fluoro-2',3-dimethyl-1,1'-biphenyl (9a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-methyliodobenzene (450 mg, 2 mmol), (2-fluoro-3-methylphenyl)boronic acid (310 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-fluoro-2',3-dimethyl-1,1'-biphenyl as white oil in 80% yield (320 mg, 1.60 mmol).

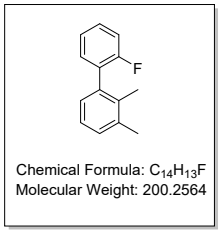
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.28 – 7.16 (m, 3H), 7.12 – 7.03 (m, 2H), 2.35 (d, *J* = 2.2 Hz, 3H), 2.22 (q, *J* = 1.3 Hz, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -119.44 (s, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 158.1 (d, *J* = 244.6 Hz), 136.6, 136.1, 130.5 (d, *J* = 5.0 Hz), 130.0, 129.9, 128.9 (d, *J* = 3.7 Hz), 128.8, 127.8, 125.5, 124.9 (d, *J* = 18.2 Hz), 123.4 (d, *J* = 4.3 Hz), 19.9 (d, *J* = 2.8 Hz), 14.7 (d, *J* = 4.4 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{14}H_{13}F$, 200.0996; found, 200.1011.

**2'-fluoro-2,3-dimethyl-1,1'-biphenyl (9b).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-bromo-2,3-dimethylbenzene (365 mg, 2 mmol), 2-fluorophenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2'-fluoro-2,3-dimethyl-1,1'-biphenyl as white oil in 85% yield (340 mg, 1.70 mmol).

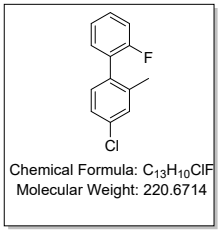
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.39 (ddt, *J* = 7.1, 5.4, 2.6 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.28 – 7.12 (m, 5H), 2.41 (s, 3H), 2.17 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -114.58 (dt, *J* = 13.2, 6.6 Hz, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.7 (d, *J* = 245.5 Hz), 136.9, 135.8, 135.2, 131.6 (d, *J* = 3.7 Hz), 129.9 (d, *J* = 16.8 Hz), 129.5, 128.9 (d, *J* = 8.0 Hz), 127.8, 125.3, 123.9 (d, *J* = 3.7 Hz), 115.4 (d, *J* = 22.6 Hz), 20.5, 16.7 (d, *J* = 2.3 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{14}H_{13}F$, 200.0996; found, 200.1026.

**4-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (3b).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-fluoro-2-iodobenzene (444 mg, 2 mmol), (4-chloro-2-methylphenyl)boronic acid (340 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 4-chloro-2'-fluoro-2-methyl-1,1'-biphenyl as white oil in 91% yield (400 mg, 1.81 mmol).

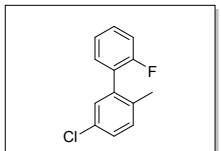
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.28 – 7.11 (m, 5H), 2.21 (s, 3H).

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.55 – -114.78 (m, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.6 (d, *J* = 246.1 Hz), 138.6, 134.2, 133.7, 131.4 (d, *J* = 3.6 Hz), 131.3 (d, *J* = 0.7 Hz), 129.9, 129.4 (d, *J* = 8.0 Hz), 128.1 (d, *J* = 16.7 Hz), 125.8, 124.1 (d, *J* = 3.7 Hz), 115.6 (d, *J* = 22.3 Hz), 19.8 (d, *J* = 2.9 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}ClF$, 220.6709; found, 220.6726.

**5-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (7b).**



Chemical Formula: $C_{13}H_{10}ClF$
Molecular Weight: 220.6714

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-fluoro-2-iodobenzene (444 mg, 2 mmol), (5-chloro-2-methylphenyl)boronic acid (340 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 5-chloro-2'-fluoro-2-methyl-1,1'-biphenyl as white oil in 98% yield (430 mg, 1.95 mmol).

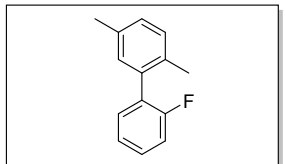
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 1H), 7.31 – 7.19 (m, 5H), 7.19 – 7.12 (m, 1H), 2.18 (s, 3H).

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.67 (dt, *J* = 10.4, 6.0 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.5 (d, *J* = 246.5 Hz), 137.3, 135.2, 131.3 (d, *J* = 3.5 Hz), 131.2, 131.1, 129.9 (d, *J* = 1.1 Hz), 129.5 (d, *J* = 8.0 Hz), 128.0 (d, *J* = 16.4 Hz), 127.9, 124.1 (d, *J* = 3.7 Hz), 115.6 (d, *J* = 22.4 Hz), 19.3 (d, *J* = 3.0 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{10}ClF$, 220.6709; found, 220.6716.

**2'-fluoro-2,5-dimethyl-1,1'-biphenyl (8b).**



Chemical Formula: $C_{14}H_{13}F$
Molecular Weight: 200.2564

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-bromo-2,4-dimethylbenzene (370 mg, 2 mmol), 2-fluorophenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the

atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2'-fluoro-2,5-dimethyl-1,1'-biphenyl as colorless oil in 88% yield (350 mg, 1.76 mmol).

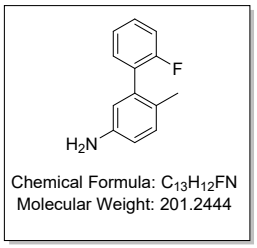
**$^{1}$H NMR** (500 MHz, $CD_2Cl_2$) δ 7.45 – 7.36 (m, 1H), 7.34 – 7.14 (m, 5H), 7.10 (s, 1H), 2.41 (s, 3H), 2.21 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CD_2Cl_2$) δ -115.58 – -115.87 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CD_2Cl_2$) δ 160.1 (d, *J* = 244.6 Hz), 136.0, 135.6, 133.9, 132.0 (d, *J* = 3.8 Hz), 131.1, 130.3, 129.9 (d, *J* = 16.8 Hz), 129.4 (d, *J* = 8.1 Hz), 129.1, 124.5 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 22.7 Hz), 21.1, 19.6 (d, *J* = 2.7 Hz).

The spectroscopic data were consistent with previously reported[3].

**2'-fluoro-6-methyl-[1,1'-biphenyl]-3-amine (10a).**



Chemical Formula: $C_{13}H_{12}FN$
Molecular Weight: 201.2444

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 3-bromo-4-methylaniline (650 mg, 3.49 mmol), 2-fluorophenylboronic acid (718 mg, 5.17 mmol), $K_2CO_3$ (1.45 g, 10.5 mmol) and $Pd(dppf)Cl_2$ (120 mg, 0.16 mmol). The solids were suspended in Dioxane/$H_2O$ 3/1 (20 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux °C for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with Hexane-Hexane:EtOAc 1:1 yielding 2-fluoro-2'-methyl-[1,1'-biphenyl]-4-amine as yellow oil in 66% yield (462 mg, 2.3 mmol).

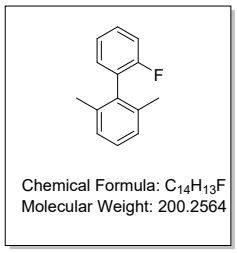
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (dddd, *J* = 8.2, 7.2, 5.2, 1.9 Hz, 1H), 7.25 (td, *J* = 7.5, 1.9 Hz, 1H), 7.19 (td, *J* = 7.4, 1.1 Hz, 1H), 7.13 (ddd, *J* = 9.5, 8.3, 1.0 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.66 (dd, *J* = 8.1, 2.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 3.59 (brs, 2H), 2.10 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -114.83 – -114.92 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.6 (d, *J* = 245.8 Hz), 143.9, 136.4, 131.4 (d, *J* = 3.9 Hz), 130.7, 129.4 (d, *J* = 16.8 Hz), 128.8 (d, *J* = 7.9 Hz), 126.5, 123.8 (d, *J* = 3.7 Hz), 116.9, 115.4 (d, *J* = 22.6 Hz), 115.0, 18.8 (d, *J* = 2.9 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{13}H_{12}FN$, 201.0949; found, 201.0961.

**2'-fluoro-2,6-dimethyl-1,1'-biphenyl (11a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-fluoro-2-iodobenzene (444 mg, 2 mmol), (2,6-dimethylphenyl)boronic acid (300 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2'-fluoro-2,6-dimethyl-1,1'-biphenyl as white oil in 25% yield (100 mg, 0.50 mmol).

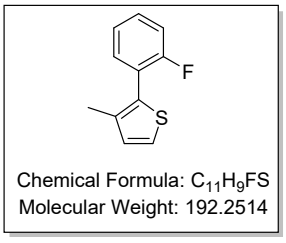
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 1H), 7.24 (td, *J* = 7.6, 1.3 Hz, 2H), 7.18 (dt, *J* = 11.0, 7.4 Hz, 4H), 2.10 (s, 6H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -115.05 – -115.15 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.5 (d, *J* = 244.3 Hz), 136.7, 135.3, 131.4 (d, *J* = 3.9 Hz), 129.0 (d, *J* = 7.9 Hz), 128.0 (d, *J* = 18.0 Hz), 127.7, 127.3, 124.1 (d, *J* = 3.7 Hz), 115.7 (d, *J* = 22.4 Hz), 20.4.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{14}H_{13}F$, 200.0996; found, 200.1014.

**2-(2-fluorophenyl)-3-methylthiophene (12a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-bromo-3-methylthiophene (355 mg, 2 mmol), 2-fluorophenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-(2-fluorophenyl)-3-methylthiophene as brown oil in 83% yield (318 mg, 1.66 mmol).

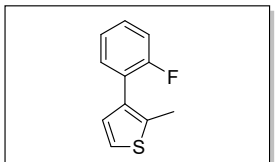
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 3H), 7.23 – 7.13 (m, 2H), 6.97 (d, *J* = 4.2 Hz, 1H), 2.23 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -112.74 – -112.99 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.8 (d, *J* = 248.4 Hz), 135.8, 132.4, 130.6, 130.3, 129.5 (d, *J* = 8.0 Hz), 124.8, 124.0 (d, *J* = 3.6 Hz), 122.3 (d, *J* = 15.4 Hz), 116.0 (d, *J* = 22.4 Hz), 14.7 (d, *J* = 3.6 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{11}H_9FS$, 192.0404; found, 192.0426.

**3-(2-fluorophenyl)-2-methylthiophene (13a).**



Chemical Formula: $C_{11}H_9FS$
Molecular Weight: 192.2514

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 3-bromo-2-methylthiophene (355 mg, 2 mmol), 2-fluorophenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 3-(2-fluorophenyl)-2-methylthiophene as brown oil in 86% yield (330 mg, 1.72 mmol).

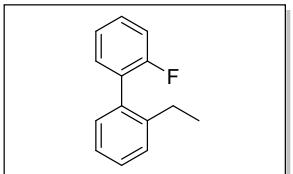
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.37 (m, 2H), 7.25 – 7.13 (m, 3H), 7.05 (d, *J* = 5.1 Hz, 1H), 2.46 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -114.39 – -114.52 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.8 (d, *J* = 246.9 Hz), 136.5, 132.4, 131.5 (d, *J* = 3.7 Hz), 129.5 (d, *J* = 1.5 Hz), 128.9 (d, *J* = 8.1 Hz), 124.4 (d, *J* = 15.7 Hz), 124.0 (d, *J* = 3.6 Hz), 121.6, 115.9 (d, *J* = 22.7 Hz), 14.0 (d, *J* = 3.2 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{11}H_9FS$, 192.0404; found, 192.0426.

**2-ethyl-2'-fluoro-1,1'-biphenyl (14a).**



Chemical Formula: $C_{14}H_{13}F$
Molecular Weight: 200.2564

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-fluoroiodobenzene (444 mg, 2 mmol), 2-ethylphenylboronic acid (320 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-ethyl-2'-fluoro-1,1'-biphenyl as colorless oil in 73% yield (292 mg, 1.46 mmol).

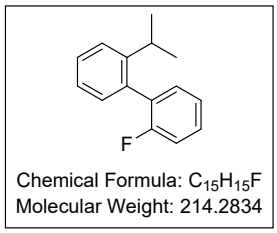
**$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.41 – 7.33 (m, 3H), 7.31 – 7.12 (m, 5H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.08 (t, *J* = 7.6 Hz, 3H).

**$^{19}$F NMR** (376 MHz, $CD_2Cl_2$) δ -115.47 – -115.65 (m, 1F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.1 (d, *J* = 244.1 Hz), 143.1, 135.6, 132.2 (d, *J* = 3.6 Hz), 130.6, 129.7, 129.5 (d, *J* = 8.0 Hz), 128.7 (d, *J* = 8.9 Hz), 126.0, 124.4 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.6 Hz), 26.6, 15.3.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{14}H_{13}F$, 200.0096; found, 200.1015

**2-fluoro-2'-isopropyl-1,1'-biphenyl (15a).**



Chemical Formula: $C_{15}H_{15}F$
Molecular Weight: 214.2834

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-iodo-2-isopropylbenzene (500 mg, 2 mmol), 2-fluorophenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-fluoro-2'-isopropyl-1,1'-biphenyl as orange solid in 16% yield (70 mg, 0.32 mmol).

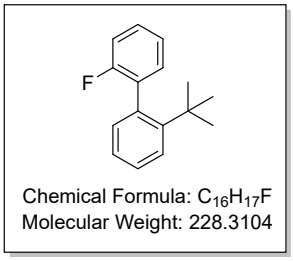
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 3H), 7.29 – 7.09 (m, 5H), 2.89 – 2.82 (m, 1H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.11 (d, *J* = 6.7 Hz, 3H).

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.35 (dt, *J* = 8.3, 6.3 Hz).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 245.0 Hz), 147.3, 134.4, 131.8 (d, *J* = 3.6 Hz), 130.1, 129.3 (d, *J* = 17.1 Hz), 128.9 (d, *J* = 7.9 Hz), 128.3, 125.4, 125.3, 123.8 (d, *J* = 3.8 Hz), 115.5, 30.2, 24.5, 23.4.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{15}H_{15}F$, 214.1153; found, 214.1166.

**2-(tert-butyl)-2'-fluoro-1,1'-biphenyl (16a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-(*tert*-butyl)-2-iodobenzene[4] (444 mg, 2 mmol), 2-fluorophenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2-(tert-butyl)-2'-fluoro-1,1'-biphenyl as white solid in 58% yield (264 mg, 1.16 mmol).

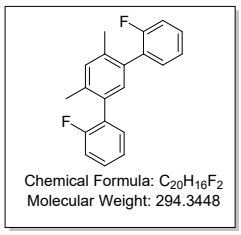
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.60 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 7.18 (td, *J* = 7.5, 1.2 Hz, 1H), 7.12 (ddd, *J* = 9.5, 8.3, 1.1 Hz, 1H), 7.02 (dd, *J* = 7.5, 1.6 Hz, 1H), 1.23 (s, 9H).

**$^{19}$F NMR** (376 MHz, $CD_2Cl_2$) δ -112.23 – -112.36 (m, 1F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.1 (d, *J* = 244.1 Hz), 143.1, 135.6, 132.2 (d, *J* = 3.6 Hz), 130.6 , 129.7, 129.5 (d, *J* = 8.0 Hz), 128.7 (d, *J* = 8.9 Hz), 126.0 (s), 124.4 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.6 Hz), 26.6, 15.3.

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

**2,2''-difluoro-4',6'-dimethyl-1,1':3',1''-terphenyl (17a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1,5-dibromo-2,4-dimethylbenzene (263 mg, 1 mmol), 2-fluorophenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2,2''-difluoro-4',6'-dimethyl-1,1':3',1''-terphenyl as white solid in 54% yield (160 mg, 0.55 mmol).

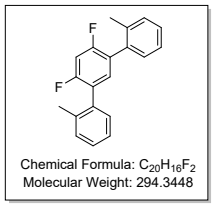
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.27 (d, *J* = 6.3 Hz, 1H), 7.21 (td, *J* = 7.5, 1.2 Hz, 2H), 7.19 – 7.14 (m, 3H), 2.29 (s, 6H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -114.44 (s, 2F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.8 (d, *J* = 245.8 Hz), 136.3, 133.2, 131.8, 131.7 (d, *J* = 5.1 Hz), 129.0 (d, *J* = 8.0 Hz), 128.8 (d, *J* = 16.6 Hz), 123.9 (d, *J* = 3.5 Hz), 115.5 (d, *J* = 22.7 Hz), 19.6.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{16}F_2$, 294.1215; found, 294.1228.

**4',6'-difluoro-2,2''-dimethyl-1,1':3',1''-terphenyl (17b).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1,5-dibromo-2,4-difluorobenzene (271 mg, 1 mmol), 2-methylphenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 4',6'-difluoro-2,2''-dimethyl-1,1':3',1''-terphenyl as white solid in 92% yield (270 mg, 0.92 mmol).

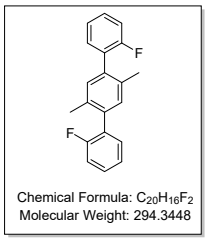
**$^{1}$H NMR** (300 MHz, $CD_2Cl_2$) δ 7.42 – 7.30 (m, 8H), 7.25 (t, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 9.6 Hz, 1H), 2.35 (s, 6H).

**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$) δ -112.75 (t, *J* = 9.1 Hz, 2F).

**$^{13}$C NMR** (76 MHz, $CD_2Cl_2$) δ 159.4 (dd, *J* = 247.9, 12.0 Hz), 137.3, 135.3, 134.2 (t, *J* = 5.1 Hz), 130.7, 130.6, 128.7, 126.3, 125.8 (dd, *J* = 13.5, 7.7 Hz), 104.2 (t, *J* = 26.8 Hz), 20.3 – 20.1 (m).j

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{16}F_2$, 294.1215; found, 294.1210

**2,2''-difluoro-2',5'-dimethyl-1,1':4',1''-terphenyl (18a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1,4-dibromo-2,5-dimethylbenzene (200 mg, 0.76 mmol), 2-fluorophenylboronic acid (234 mg, 1.67 mmol), $Cs_2CO_3$ (987 mg, 3.0 mmol) and $Pd(PPh_3)_2Cl_2$ (24 mg, 38 μmol). The solids were suspended in THF/$H_2O$ (12 mL, 5:1), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 72 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2,2''-difluoro-4',6'-dimethyl-1,1':3',1''-terphenyl as white solid in 78 % yield (174 mg, 0.59 mmol).

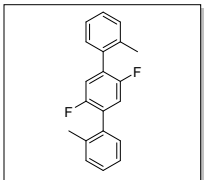
**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.44 – 7.37 (m, 2H), 7.34 (td, *J* = 7.5, 1.9 Hz, 2H), 7.26 (td, *J* = 7.5, 1.0 Hz, 2H), 7.22 – 7.15 (m, 4H), 2.20 (s, 6H).

$^{19}$F NMR (376 MHz, $CD_2Cl_2$) δ -115.62 – -115.68 (m, 2F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.1 (d, *J* = 244.6 Hz), 135.9, 134.3, 132.1 (d, *J* = 3.8 Hz), 132.0, 129.6 (d, *J* = 8.0 Hz), 129.3 (d, *J* = 16.8 Hz), 124.5 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.6 Hz), 19.5 (d, *J* = 3.0 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{16}F_2$, 294.1215; found, 294.1227.

**2',5'-difluoro-2,2''-dimethyl-1,1':4',1''-terphenyl (18b).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1,4-dibromo-2,5-difluorobenzene (271 mg, 1 mmol), 2-methylphenylboronic acid (280 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2',5'-difluoro-2,2"-dimethyl-1,1':4',1"-terphenyl as white solid in 75% yield (220 mg, 0.75 mmol).

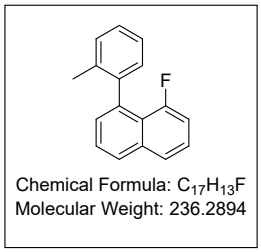
**$^1$H NMR** (300 MHz, $CD_2Cl_2$) δ 7.40 – 7.33 (m, 4H), 7.34 – 7.29 (m, 4H), 7.09 (t, *J* = 7.9 Hz, 2H), 2.32 (s, 6H).

**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$) δ -121.45 – -121.69 (m, 2F).

**$^{13}$C NMR** (76 MHz, $CD_2Cl_2$) δ 155.8 (dd, *J* = 243.4, 3.7 Hz), 137.2, 135.1, 130.6, 130.4, 130.1 (dd, *J* = 15.3, 12.5 Hz), 128.9, 126.2, 118.95 – 117.49 (m), 20.37 – 19.44 (m).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{16}F_2$, 294.1215; found, 294.1223.

**1-fluoro-8-(o-tolyl)naphthalene (19a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-bromo-8-fluoronaphthalene (446 mg, 2 mmol), 2-methylphenylboronic acid (260 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was

evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 1-fluoro-8-(o-tolyl)naphthalene as yellow oil in 53% yield (250 mg, 1.06 mmol).

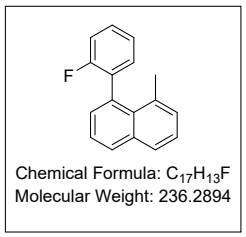
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.43 (td, *J* = 7.9, 4.8 Hz, 1H), 7.38 – 7.22 (m, 5H), 7.07 (dd, *J* = 12.7, 7.6 Hz, 1H), 2.08 (s, 3H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -111.54 – -111.73 (m, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.3 (d, *J* = 255.5 Hz), 142.7 (d, *J* = 3.1 Hz), 136.6, 136.0 (d, *J* = 3.9 Hz), 135.7 (d, *J* = 3.8 Hz), 129.1, 128.9 (d, *J* = 2.6 Hz), 128.7, 127.3 (d, *J* = 3.4 Hz), 127.1, 126.2 (d, *J* = 1.6 Hz), 125.7 (d, *J* = 8.7 Hz), 124.9, 124.5 (d, *J* = 4.3 Hz), 122.3 (d, *J* = 10.7 Hz), 111.0 (d, *J* = 22.0 Hz), 20.0 (d, *J* = 0.9 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{14}H_{13}F$, 236.0996; found, 236.1008.

**1-(2-fluorophenyl)-8-methylnaphthalene (19b).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-bromo-8-methylnaphthalene[6] (520 mg, 2.4 mmol), (2-fluorophenyl)boronic acid (362 mg, 2.6 mmol), $Cs_2CO_3$ (1.53 g, 4.7 mmol) and $Pd(PPh_3)_2Cl_2$ (33 mg, 47.0 μmol). The solids were suspended in THF/$H_2O$ (12 mL, 5:1), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 24 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with hexane yielding 1-(o-tolyl)naphthalene as white solid in 71 % yield (394 mg, 1.7 mmol).

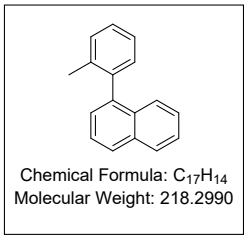
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.50 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.45 – 7.32 (m, 4H), 7.31 – 7.25 (m, 1H), 7.25 – 7.19 (m, 1H), 7.16 (t, *J* = 9.3 Hz, 1H), 2.14 (s, 3H).

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.35 (td, *J* = 8.4, 5.5 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.0 (d, *J* = 244.1 Hz), 134.9 (d, *J* = 6.8 Hz), 133.3, 132.7, 132.5, 131.9 (d, *J* = 3.3 Hz), 131.4, 129.8, 129.7, 129.7, 129.1 (d, *J* = 7.8 Hz), 127.6, 125.5, 124.3, 123.4 (d, *J* = 3.7 Hz), 115.1 (d, *J* = 22.2 Hz), 23.6.

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

**1-(o-tolyl)naphthalene.**



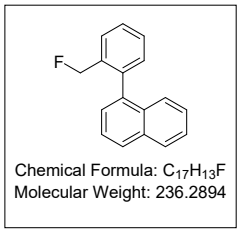

A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1-bromo-2-methylbenzene (2.71 g, 1.91 mL, 15.9 mmol), 2 naphthalen-1-ylboronic acid (3.00 g, 17.4 mmol), $Cs_2CO_3$ (10.3 g, 31.7 mmol) and $Pd(PPh_3)_2Cl_2$ (222 mg, 0.317 mmol). The solids were suspended in THF/$H_2O$ (36 mL, 5:1), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 18 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with hexane yielding 1-(o-tolyl)naphthalene as white solid in 71 % yield (2.45 g, 12.3 mmol).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.53 (m, 3H), 7.51 – 7.32 (m, 6H), 2.13 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.2, 139.8, 136.8, 133.5, 132.0, 130.3, 129.8, 128.2, 127.5, 127.4, 126.6, 126.1, 125.9, 125.7, 125.6, 125.3, 20.0.

The spectroscopic data were consistent with previously reported[8].

**1-(2-(fluoromethyl)phenyl)naphthalene (19c).**




1-(o-tolyl)naphthalene (1.00 g, 4.58 mmol) and NBS (892 mg, 5.04 mmol, 1.1 equiv.) and benzoyl peroxide (55mg) were dissolved in DCM (40 mL). The mixture was brought to reflux for 6 h. After cooling to room temperature water was added, phases were separated and the aqueous layer extracted with DCM. The combined organic fractions were dried over $Na_2SO_4$, filtrated and the solvent removed in *vacuo*. The crude product was purified by flash column chromatography on silica gel with hexane to afford the 1-(2-(fluoromethyl)phenyl)naphthalene with impurity of starting material (1.12 g, 82 %). The product was used in the next reaction without additional purification.

1-(2-(bromomethyl)phenyl)naphthalene (250 mg, 0,841 mmol) and TBAF*3$H_2O$ (550 mg, 2.10 mmol, 2.5 equiv.) were dissolved in acetonitrile (10 ml). The mixture was brought to 80 °C for 21 h. After cooling to room temperature water was added, phases were separated and the aqueous layer extracted with DCM. The combined organic fractions were dried over $Na_2SO_4$, filtrated and the solvent removed in *vacuo*. The crude product was purified by flash column chromatography on silica gel with hexane/DCM 8:2 yielding 1-(2-(fluoromethyl)phenyl)naphthalene as white solid in 34% yield (68 mg, 0.29 mmol).

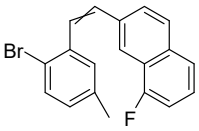
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.58 – 7.43 (m, 5H), 7.43 – 7.32 (m, 3H), 5.09 (d, *J* = 47.7 Hz, 2H).

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ 29.54 (t, *J* = 47.7 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 139.4 (d, *J* = 4.8 Hz), 137.4, 135.1 (d, *J* = 16.6 Hz), 133.5, 132.1, 130.8, 128.4 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 7.5 Hz), 128.2, 128.1, 128.0 (d, *J* = 1.2 Hz), 127.2 (d, *J* = 0.8 Hz), 126.3, 125.9, 125.8, 125.2, 82.5 (d, *J* = 165.8 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{17}H_{13}F$, 235.9996; found, 236.1003

**7-(2-bromo-5-methylstyryl)-1-fluoronaphthalene.**



Chemical Formula: $C_{19}H_{14}BrF$
Molecular Weight: 341.2234

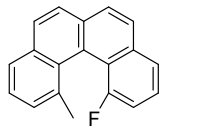
To solution of 2-bromo-5-methylbenzaldehyde (200 mg, 1 mmol) and [(8-fluoro-2- naphthalenyl)methyl]triphenylphosphonium bromide (500 mg, 1 mmol) in DCM (7 mL) aqueous solution of NaOH (50 %, 0.77 g in 0.77 ml) was added dropwise under inert atmosphere.. After the end of the reaction solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes→hexanes: DCM 9:1) yielding 7-(2-bromo-5-methylstyryl)-1-fluoronaphthalene as mixture of cis-trans isomers (1:5) . Colorless oil. (300 mg, 88 %).

**$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.96 (s, 1H), 7.68 – 7.59 (m, 1H), 7.55 (dd, *J* = 15.8, 7.6 Hz, 2H), 7.38 (t, *J* = 9.4 Hz, 1H), 7.29 (dd, *J* = 9.4, 4.6 Hz, 1H), 7.13 (dd, *J* = 10.8, 7.0 Hz, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 12.1 Hz, 1H), 6.75 (d, *J* = 12.1 Hz, 1H), 2.12 (s, 3H).

**$^{19}$F NMR** (376 MHz, $CD_2Cl_2$) δ -124.04 (ddd, *J* = 10.8, 5.4, 1.8 Hz, 1F).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{19}H_{14}BrF$, 340.0258; found, 340.0277

**1-fluoro-12-methylbenzo[c]phenanthrene (22a).**



Chemical Formula: $C_{19}H_{13}F$
Molecular Weight: 260.3114

Solution of 7-(2-bromo-5-methylstyryl)-1-fluoronaphthalene (300 mg, 0.88 mmol) in 300 ml of cyclohexane was irradiated in the presence of $I_2$ (307 mg, 1.2 mmol) and methylpropyleneoxide (1.5 ml) for 24 h until complete loss of bromine. After completion of reaction ½ of cyclohexane was evaporated under reduced pressure, washed with $Na_2S_2O_3$ solution, dried over $Na_2SO_4$. Cyclohexane was evaporated under reduced pressure and residue was purified by column chromatography (Hex:DCM 95:5) yielding 1-fluoro-12-methylbenzo[c]phenanthrene as colorless oil in 61% (140 mg).

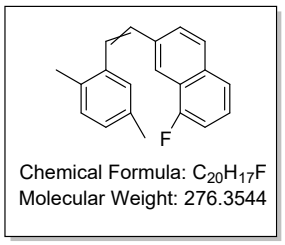
**$^{1}$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.98 (dd, *J* = 12.2, 5.2 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.54 (m, 2H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.29 (dd, *J* = 13.0, 7.2 Hz, 1H), 2.36 (d, *J* = 2.1 Hz, 3H).

**$^{19}$F NMR** (376 MHz, $CD_2Cl_2$) δ -106.10 – -106.19 (m, 1F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 159.9 (d, *J* = 252.3 Hz), 138.0 (d, *J* = 6.5 Hz), 134.4 (d, *J* = 4.3 Hz), 133.8, 132.8, 131.3 (d, *J* = 3.6 Hz), 129.0, 128.4, 127.4 (d, *J* = 1.0 Hz), 127.1 (d, *J* = 3.0 Hz), 126.7 (d, *J* = 9.1 Hz), 126.4, 125.4, 125.1, 123.9 (d, *J* = 3.2 Hz), 122.8 (d, *J* = 1.9 Hz), 121.3 (d, *J* = 12.8 Hz), 111.6 (d, *J* = 23.1 Hz), 22.5 (d, *J* = 9.6 Hz).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{19}H_{13}F$, 260.0996; found, 260.1025.

**7-(2,5-dimethylstyryl)-1-fluoronaphthalene.**



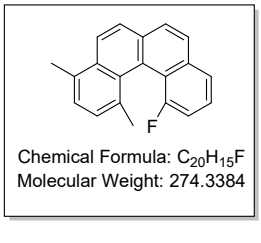

To solution of 2,5-dimethylbenzaldehyde (400 mg, 3 mmol) and [(8-fluoro-2- naphthalenyl)methyl]triphenylphosphonium bromide (1.5 g, 3 mmol) in DCM (20 mL) aqueous solution of NaOH (50 %, 2.1 g in 2.1 ml) was added dropwise under inert atmosphere. . After the end of the reaction solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes→hexanes: DCM 9:1) yielding 7-(2,5-dimethylstyryl)-1-fluoronaphthalene as mixture of cis-trans isomers (2:3) . Colorless oil. (660 mg, 80 %).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 0.76H), 7.94 (s, 1 H), 7.91 – 7.77 (m, 1.59 H), 7.63 (d, *J* = 8.2 Hz, 0.79 H), , 7.55 – 7.46 (m, 3.57 H), 7.37 (dtd, *J* = 18.3, 8.0, 5.4 Hz, 1.88 H), 7.30 – 7.22 (m, 2H), 7.21 – 6.99 (m, 6.7 H), 6.87 – 6.71 (m, 2H), 2.47 (s, 2.3H), 2.41 (s, 2.3H), 2.27 (s, 3H), 2.21 (s, 3H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -123.15 (d, *J* = 14.1 Hz, 0.8 F), -123.37 (s, 1F).

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{17}F$, 276.1309; found, 276.1325

**12-fluoro-1,4-dimethylbenzo[c]phenanthrene (23a).**




Solution of 7-(2,5-dimethylstyryl)-1-fluoronaphthalene (660 mg, 2.4 mmol) in 300 ml of cyclohexane was irradiated in the presence of $I_2$ (923 mg, 3.6 mmol) and methylpropyleneoxide (4 ml) for 25 h. After completion of reaction ½ of cyclohexane was evaporated under reduced pressure, washed with $Na_2S_2O_3$ solution, dried over $Na_2SO_4$. Cyclohexane was evaporated under reduced pressure and residue was purified by column chromatography (Hex:DCM 95:5) yielding 12-fluoro-1,4-dimethylbenzo[c]phenanthrene as white solid in 68% (450 mg).

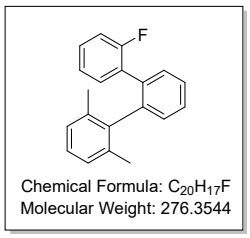
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 1H), 7.84 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.72 (dd, *J* = 13.0, 4.9 Hz, 2H), 7.47 (td, *J* = 7.8, 4.9 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.17 – 7.10 (m, 1H), 2.74 (s, 3H), 2.21 (d, *J* = 1.5 Hz, 3H).

**$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -105.71 (d, *J* = 12.2 Hz, 1F).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.3 (d, *J* = 253.6 Hz), 135.4 (d, *J* = 6.8 Hz), 133.9 (d, *J* = 4.3 Hz), 132.2, 131.9, 131.0 (d, *J* = 4.0 Hz), 130.5, 127.5, 127.2, 126.9, 126.5 (d, *J* = 2.9 Hz), 126.1 (d, *J* = 9.0 Hz), 124.7, 124.5, 123.4 (d, *J* = 3.1 Hz), 122.8 (d, *J* = 2.1 Hz), 121.1 (d, *J* = 13.0 Hz), 111.2 (d, *J* = 23.3 Hz), 22.3 (d, *J* = 9.3 Hz), 19.7.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{15}F$, 274.1153; found, 274.1166

**2''-fluoro-2,6-dimethyl-1,1':2',1''-terphenyl (24a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 2-bromo-2'-fluoro-1,1'-biphenyl (500 mg, 2 mmol), 2,6-dimethylphenylboronic acid (300 mg, 2 mmol), $K_2CO_3$ (1.1g, 8 mmol) and $Pd(PPh_3)_4$ (84 mg, 72 µmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane yielding 2''-fluoro-2,6-dimethyl-1,1':2',1''-terphenyl as white solid in 5% yield (30 mg, 0.11 mmol).

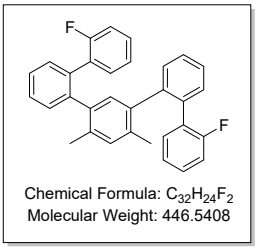
**$^1$H NMR** (300 MHz, $CD_2Cl_2$) δ 7.53 – 7.40 (m, 3H), 7.26 – 7.20 (m, 1H), 7.17 (ddd, *J* = 7.3, 5.2, 2.0 Hz, 1H), 7.09 – 6.87 (m, 6H), 1.99 (s, 6H).

**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$) δ -115.99 (d, *J* = 13.2 Hz, 1F).

**$^{13}$C NMR** (76 MHz, $CD_2Cl_2$) δ 160.0 (d, *J* = 245.6 Hz), 140.7, 140.5, 136.7, 135.4, 132.0 (d, *J* = 3.5 Hz), 131.6 (d, *J* = 2.0 Hz), 131.0, 129.2 (d, *J* = 8.2 Hz), 128.4, 127.4, 127.3, 127.3, 123.6 (d, *J* = 3.7 Hz), 115.7 (d, *J* = 22.9 Hz), 20.75, 20.73.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{17}F$, 276.1309; found, 276.1322

**2,2''''-difluoro-4'',6''-dimethyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (26a).**




A 100 mL round bottom flask equipped with a magnetic stir bar and a condenser was charged with 1,5-dibromo-2,4-dimethylbenzene (105 mg, 0.4 mmol), (2'-fluoro-[1,1'-biphenyl]-2-yl)boronic acid (170 mg, 0.8 mmol), $K_2CO_3$ (450 mg, 3.2 mmol) and $Pd(PPh_3)_4$ (35 mg, 29 μmol). The solids were suspended in 3:1/0.3 toluene/MeOH/$H_2O$ (18.5 mL), degassed and the atmosphere was exchanged by argon. The mixture was brought to reflux for 16 h. The solvent was evaporated and the product was purified by silica gel column chromatography, eluting with cyclohexane-cyclohexane:DCM 9:1 yielding 2,2''''-difluoro-4'',6''-dimethyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl as white solid in 76% yield (170 mg, 0.38 mmol).

**$^1$H NMR** (400 MHz, $CD_2Cl_2$) δ 7.44 – 7.40 (m, 5H), 7.35 – 7.29 (m, 1H), 7.27 – 7.18 (m, 2H), 7.13 – 6.89 (m, 6H), 6.79 – 6.73 (m, 2H), 1.92 – 1.85 (m, 6H).

**$^{19}$F NMR** (376 MHz, $CD_2Cl_2$) δ -115.43 (s, 1F), -116.09 (s, 1F).

**$^{13}$C NMR** (101 MHz, $CD_2Cl_2$) δ 160.0 (d, $J$ = 245.2 Hz), 141.5 (d, $J$ = 14.9 Hz), 138.5, 137.9, 135.5 (d, $J$ = 25.7 Hz), 134.9 (d, $J$ = 32.5 Hz), 132.9 (d, $J$ = 29.2 Hz), 132.6 (d, $J$ = 3.4 Hz), 131.6 – 130.5 (m), 129.1 (t, $J$ = 7.6 Hz), 128.1 (d, $J$ = 15.6 Hz), 127.3, 123.9 (d, $J$ = 3.6 Hz), 115.7 (dd, $J$ = 22.6, 11.1 Hz), 19.5 (d, $J$ = 20.4 Hz).

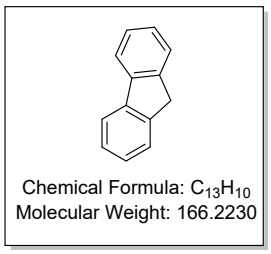
**HRMS** (m/z): $[M]^+$ calcd. for $C_{32}H_{24}F_2$, 446.1841; found, 446.1859.

**C-H insertion.**

General procedure

10 g of γ-$Al_2O_3$ was preactivated in glass ampoule at 450°C under air conditions for 3 hours and then activated at 550°C under vacuum ($10^{-2}$ mbar) for another 4 hours. Activated aluminium oxide was added to an ampoule containing 20 mg of fluoromethylbiaryl. The ampoule was sealed under vacuum and placed into oven at 190°C for overnight. After cooling to room temperature, the solid mixture was extracted with 70 ml of toluene enabling the crude solution, which was purified by means of flash-chromatography (Hexane-Dichloromethane).

**9H-fluorene (1).**

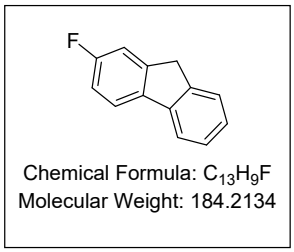



The compound was obtained according to the General Procedure using 2-fluoro-2'-methyl-1,1'-biphenyl. White solid. Yield 13.4 mg (75%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.33 (td, *J* = 7.4, 1.1 Hz, 2H), 3.93 (s, 2H).

The spectroscopic data were consistent with previously reported[9].

**2-fluoro-9H-fluorene (2).**




The compound was obtained according to the General Procedure using 2,4-difluoro-2'-methyl-1,1'-biphenyl. White solid. Yield 6.3 mg (35%).

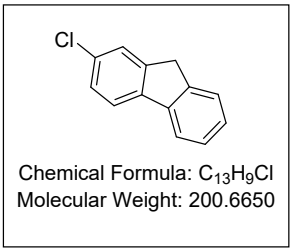
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.12 – 7.04 (m, 1H), 3.89 (s, 2H).

**$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -115.85 (td, *J* = 9.0, 5.2 Hz, 1F).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 244.3 Hz), 145.3 (d, *J* = 8.8 Hz), 143.0 (d, *J* = 2.0 Hz), 140.9, 137.7 (d, *J* = 2.4 Hz), 126.9, 126.4, 125.0, 120.7 (d, *J* = 8.8 Hz), 119.5, 113.9 (d, *J* = 23.0 Hz), 112.3 (d, *J* = 22.9 Hz), 37.0 (d, *J* = 2.4 Hz).

The spectroscopic data were consistent with previously reported[10].

**2-chloro-9H-fluorene (3).**




Chemical Formula: $C_{13}H_9Cl$
Molecular Weight: 200.6650

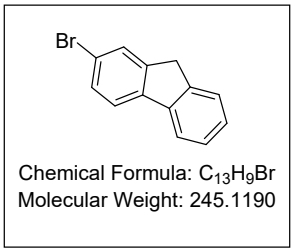
The compound was obtained according to the General Procedure using 4-chloro-2-fluoro-2'-methyl-1,1'-biphenyl or 4-chloro-2'-fluoro-2-methyl-1,1'-biphenyl. White solid. Yield 11 mg (61%) and 7.4mg (41%) respectively.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.42 – 7.29 (m, 3H), 3.89 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.9, 143.0, 140.7, 140.3, 132.4, 127.1, 127.0, 126.9, 125.3, 125.1, 120.7, 119.9, 36.8.

The spectroscopic data were consistent with previously reported[10].

**2-bromo-9H-fluorene (4).**




Chemical Formula: $C_{13}H_9Br$
Molecular Weight: 245.1190

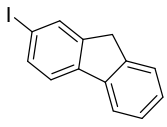
The compound was obtained according to the General Procedure using 4-bromo-2-fluoro-2'-methyl-1,1'-biphenyl. White solid. Yield 10.7 mg (58%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.31 (m, 1H), 3.90 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.2, 142.9, 140.7, 129.9, 128.3, 127.1, 127.0, 125.1, 121.1, 120.4, 119.9, 36.8.

The spectroscopic data were consistent with previously reported[11].

**2-iodo-9H-fluorene (5).**




Chemical Formula: $C_{13}H_9I$
Molecular Weight: 292.1195

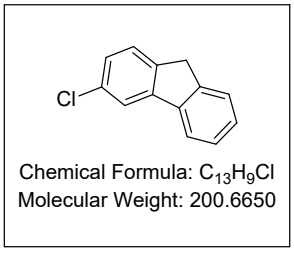
The compound was obtained according to the General Procedure using 4-iodo-2-fluoro-2'-methyl-1,1'-biphenyl. White solid. Yield 8.6 mg (46%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 (td, *J* = 7.3, 1.2 Hz, 1H), 3.88 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 145.5, 142.7, 141.3, 140.8, 135.8, 134.2, 127.3, 126.9, 125.0, 121.5, 120.0, 91.8, 36.6.

The spectroscopic data were consistent with previously reported[12].

**3-chloro-9H-fluorene (6).**



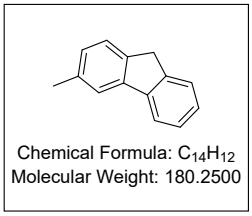

The compound was obtained according to the General Procedure using 5-chloro-2-fluoro-2'-methyl-1,1'-biphenyl or 5-chloro-2'-fluoro-2-methyl-1,1'-biphenyl. White solid. Yield 5.4 mg (30%) and 6.9 mg (38%).

**$^1$H NMR** (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.29 – 7.25 (m, 1H), 3.87 (s, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 143.7, 143.5, 141.4, 140.6, 132.8, 127.4, 126.9, 126.6, 126.0, 125.1, 120.1, 36.5.

The spectroscopic data were consistent with previously reported[10].

**3-methyl-9H-fluorene (7)**




The compound was obtained according to the General Procedure using 2-fluoro-2',5-dimethyl-1,1'-biphenyl or 2'-fluoro-2,5-dimethyl-1,1'-biphenyl. White solid. Yield 7.6 mg (42%) and 8.5 mg (68%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.62 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 3.87 (s, 2H), 2.47 (s, 3H).

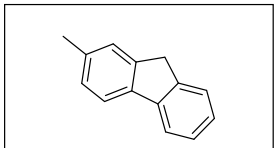
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.7, 141.8, 141.7, 140.3, 136.3, 127.7, 126.6, 126.5, 125.0, 124.7, 120.4, 119.7, 36.5, 21.5.

The spectroscopic data were consistent with previously reported[13].

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 143.1, 142.1, 142.0, 141.3, 134.2, 127.7, 127.0, 126.7, 126.5, 125.0, 120.0, 117.4, 35.9, 18.9.

The spectroscopic data were consistent with previously reported[13].

**2-methyl-9H-fluorene (8).**


Chemical Formula: $C_{14}H_{12}$
Molecular Weight: 180.2500

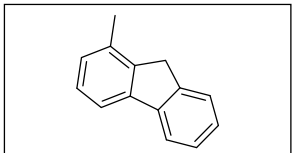
The compound was obtained according to the General Procedure using 2-fluoro-2',4-dimethyl-1,1'-biphenyl. White solid. Yield 9.5 mg (53%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.32 – 7.24 (m, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 3.87 (s, 2H), 2.45 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 143.5, 143.1, 141.8, 139.1, 136.5, 127.6, 126.6, 126.2, 125.7, 124.9, 119.6, 119.5, 36.8, 21.6.

The spectroscopic data were consistent with previously reported[14].

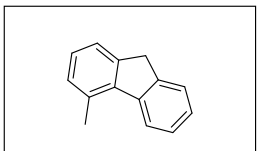
**1-methyl-9H-fluorene (9).**


Chemical Formula: $C_{14}H_{12}$
Molecular Weight: 180.2500

The compound was obtained according to the General Procedure using 2-fluoro-2',3-dimethyl-1,1'-biphenyl or 2'-fluoro-2,3-dimethyl-1,1'-biphenyl. White solid. Yield 7.7 mg (43%) and 12.2 mg (68%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 3.80 (s, 2H), 2.44 (s, 3H).

**4-methyl-9H-fluorene (11).**


Chemical Formula: $C_{14}H_{12}$
Molecular Weight: 180.2500

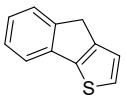
The compound was obtained according to the General Procedure using 2'-fluoro-2,6-dimethyl-1,1'-biphenyl. White solid. Yield 8.1 mg (45%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.44 – 7.36 (m, 2H), 7.31 (td, *J* = 7.4, 1.1 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 3.92 (s, 2H), 2.74 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.7, 143.6, 142.7, 139.8, 133.0, 129.0, 126.6, 126.4, 126.0, 124.9, 123.1, 122.4, 37.1, 21.1.

The spectroscopic data were consistent with previously reported[10].

**4H-indeno[2,1-b]thiophene (12).**




Chemical Formula: $C_{11}H_8S$
Molecular Weight: 172.2450

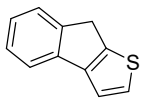
The compound was obtained according to the General Procedure using 2-(2-fluorophenyl)-3-methylthiophene. White solid. Yield 5.7 mg (32%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 4.8 Hz, 2H), 7.20 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.12 (d, *J* = 4.8 Hz, 1H), 3.70 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 147.2, 146.1, 143.2, 138.9, 127.1, 126.8, 125.1, 124.6, 122.7, 118.8, 34.0.

The spectroscopic data were consistent with previously reported[15].

**8H-indeno[2,1-b]thiophene (13).**




Chemical Formula: $C_{11}H_8S$
Molecular Weight: 172.2450

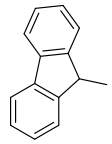
The compound was obtained according to the General Procedure using 3-(2-fluorophenyl)-2-methylthiophene. White solid. Yield 6.6 mg (37%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.48 (dt, *J* = 7.6, 0.7 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 5.0 Hz, 1H), 7.18 (td, *J* = 7.5, 1.1 Hz, 1H), 3.85 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 147.5, 146.7, 143.9, 139.3, 128.6, 126.7, 124.8, 124.4, 119.1, 118.6, 31.6.

The spectroscopic data were consistent with previously reported[16].

**9-methyl-9H-fluorene (14).**



Chemical Formula: $C_{14}H_{12}$
Molecular Weight: 180.2500

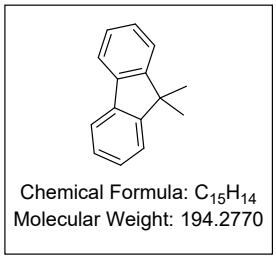
The compound was obtained according to the General Procedure using 2-ethyl-2'-fluoro-1,1'-biphenyl. White solid. Yield 12 mg (67%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.35 (m, 4H), 4.01 (q, *J* = 7.4 Hz, 1H), 1.59 (d, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 149.0, 140.5, 126.9, 124.0, 119.8, 42.4, 18.2.

The spectroscopic data were consistent with previously reported[17].

**9,9-dimethyl-9H-fluorene (15).**

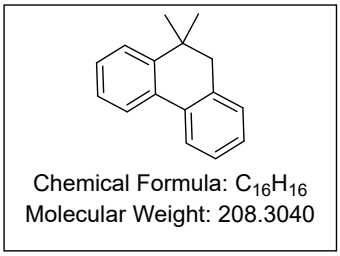



The compound was obtained according to the General Procedure using 2-fluoro-2'-isopropyl-1,1'-biphenyl. White solid. Yield 8.8 mg (48%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.47 – 7.43 (m, 2H), 7.38 – 7.28 (m, 4H), 1.49 (s, 6H).

The spectroscopic data were consistent with previously reported[18].

**9,9-dimethyl-9,10-dihydrophenanthrene (16).**



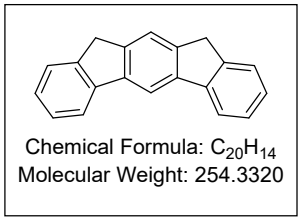

The compound was obtained according to the General Procedure using 2-(tert-butyl)-2'-fluoro-1,1'-biphenyl. White solid. Yield 10.2 mg (56%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.42 (dd, $J$ = 5.8, 3.2 Hz, 1H), 7.31 (td, $J$ = 6.3, 2.6 Hz, 3H), 7.27 – 7.18 (m, 2H), 2.79 (s, 2H), 1.27 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.4, 136.0, 134.2, 133.2, 128.6, 127.9, 127.4, 126.8, 126.5, 124.2, 124.1, 123.5, 44.1, 34.1, 27.9.

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

**10,12-dihydroindeno[2,1-b]fluorene (17).**

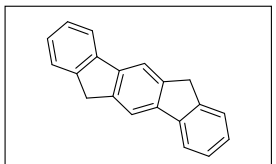



The compound was obtained according to the General Procedure using 2,2''-difluoro-4',6'-dimethyl-1,1':3',1''-terphenyl (10 mg). White solid. Yield 2 mg (23%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.89 (d, $J$ = 7.6 Hz, 2H), 7.70 (s, 1H), 7.56 (d, $J$ = 7.5 Hz, 2H), 7.41 (t, $J$ = 7.8 Hz, 2H), 7.35 – 7.28 (m, 2H), 3.96 (s, 4H).

The spectroscopic data were consistent with previously reported[19].

**6,12-dihydroindeno[1,2-b]fluorene (18).**

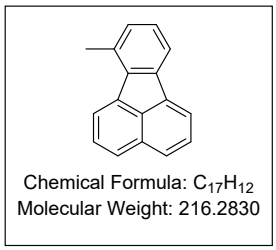

Chemical Formula: $C_{20}H_{14}$
Molecular Weight: 254.3320

The compound was obtained according to the General Procedure using 2,2''-difluoro-2',5'-dimethyl-1,1':4',1''-terphenyl (10 mg). White solid. Yield 2.3 mg (27%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.30 (td, *J* = 7.4, 1.1 Hz, 2H), 3.98 (s, 4H).

The spectroscopic data were consistent with previously reported[20].

**7-methylfluoranthene (20).**


Chemical Formula: $C_{17}H_{12}$
Molecular Weight: 216.2830

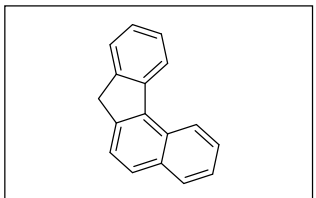
The compound was obtained according to the General Procedure using 1-fluoro-8-(o-tolyl)naphthalene. White solid. Yield 6.4 mg (35%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.96 (d, *J* = 6.9 Hz, 1H), 7.86 (d, *J* = 3.0 Hz, 1H), 7.84 (d, *J* = 3.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 2.78 (s, 3H).

**$^{13}$C NMR** (101 MHz, $cdcl_3$) δ 139.5, 137.8, 137.4, 137.0, 134.3, 132.4, 129.9, 128.0, 127.8, 127.3, 126.6, 126.2, 123.0, 119.9, 119.1, 20.4.

The spectroscopic data were consistent with previously reported[21].

**7H-benzo[c]fluorene (21).**

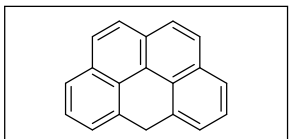

Chemical Formula: $C_{17}H_{12}$
Molecular Weight: 216.2830

The compound was obtained according to the General Procedure using 1-(2-(fluoromethyl)phenyl)naphthalene. White solid. Yield 4.2 mg (23%).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.55 – 7.48 (m, 2H), 7.40 – 7.30 (m, 1H), 4.04 (s, 1H).

The spectroscopic data were consistent with previously reported[22].

**6H-benzo[cd]pyrene (22).**


Chemical Formula: $C_{19}H_{12}$
Molecular Weight: 240.3050

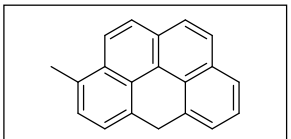
The compound was obtained according to the General Procedure using 1-fluoro-12-methylbenzo[c]phenanthrene. White solid. Yield 9.6 mg (52%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.76 – 7.72 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 (dd, *J* = 7.2, 1.4 Hz, 2H), 4.98 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 134.0, 132.0, 128.0, 127.9, 126.9, 126.7, 126.4, 126.0, 125.5, 125.3, 34.3.

The spectroscopic data were consistent with previously reported[23].

**3-methyl-6H-benzo[cd]pyrene (23).**


Chemical Formula: $C_{20}H_{14}$
Molecular Weight: 254.3320

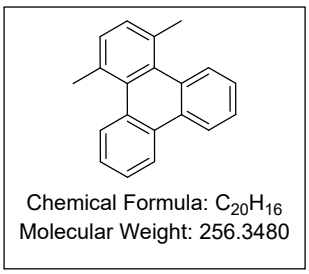
The compound was obtained according to the General Procedure using 12-fluoro-1,4-dimethylbenzo[c]phenanthrene. White solid. Yield 9.1 mg (49%).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.84 – 7.76 (m, 3H), 7.76 – 7.71 (m, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.37 (s, 2H), 4.94 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 134.2, 132.0, 131.8, 130.8, 128.2, 128.0, 127.7, 127.3, 126.9, 126.7, 126.4, 126.4, 126.3, 126.3, 125.5, 125.2, 125.0, 123.2, 31.6, 14.1.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{14}$, 254.1091; found, 254.1083.

**1,4-dimethyltriphenylene (25).**


Chemical Formula: $C_{20}H_{16}$
Molecular Weight: 256.3480

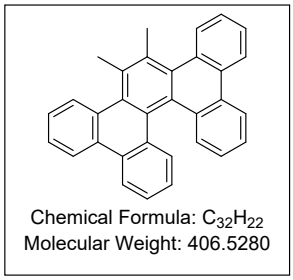
The compound was obtained according to the General Procedure using 2"-fluoro-2,6-dimethyl-1,1':2',1"-terphenyl. White solid. Yield 12.6 mg (68%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 8.0, 1.4 Hz, 2H), 8.44 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.65 – 7.49 (m, 4H), 7.36 (s, 2H), 2.98 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 132.3, 131.6, 131.2, 130.8, 129.8, 128.2, 126.5, 125.9, 123.3, 25.2.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{20}H_{16}$, 256.1247; found, 256.1266.

**17,18-dimethyldibenzo[f,j]picene (27).**


Chemical Formula: $C_{32}H_{22}$
Molecular Weight: 406.5280

The compound was obtained according to the General Procedure using 2,2""-difluoro-4",6"-dimethyl-1,1':2',1":3",1"':2"',1""-quinquephenyl (10 mg). White solid. Yield 5.8 mg (61%).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 8.0, 1.3 Hz, 2H), 8.43 (t, *J* = 7.9 Hz, 4H), 8.14 (d, *J* = 8.3 Hz, 2H), 7.67 (td, *J* = 7.8, 7.2, 1.3 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.47 – 7.38 (m, 2H), 7.14 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 2H), 3.01 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 133.2, 132.0, 131.6, 131.3, 131.0, 130.3, 129.3, 129.0, 126.9, 126.5, 126.4, 125.9, 125.6, 123.4, 123.1, 22.7.

**HRMS** (m/z): $[M]^+$ calcd. for $C_{32}H_{22}$, 406.1722; found, 406.1746.

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# Spectral appendix ($^{1}$H, $^{19}$F, $^{13}$C NMR).

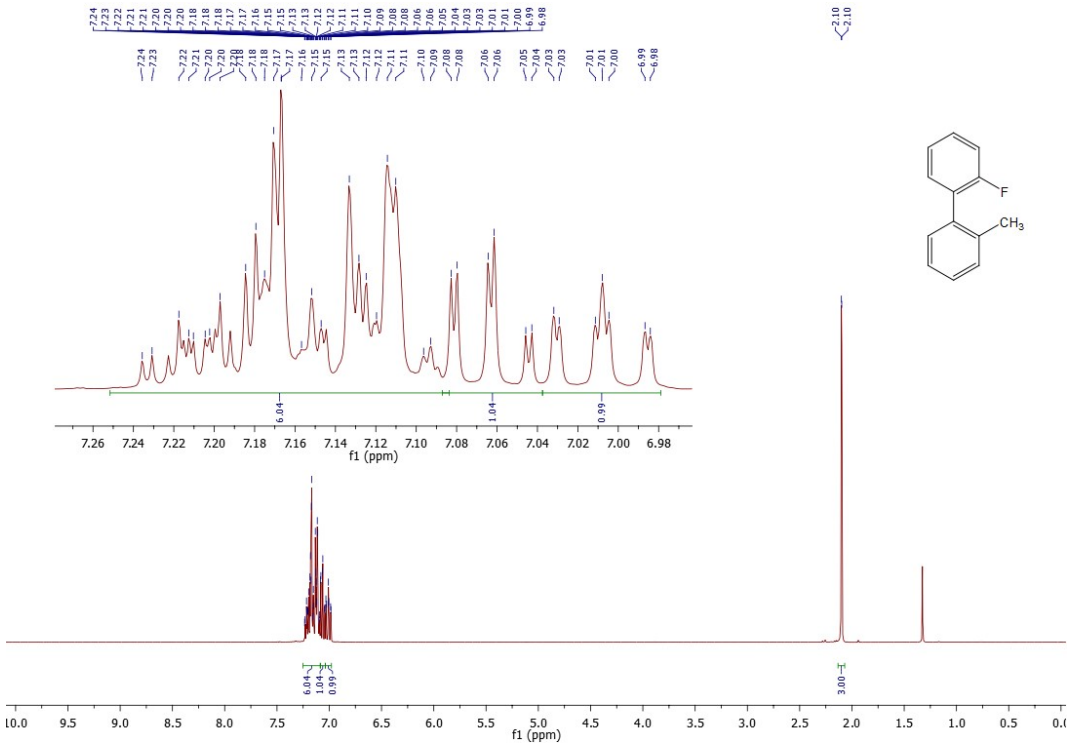


**Figure S1**. $^{1}$H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2'-methyl-1,1'-biphenyl (**1a**).

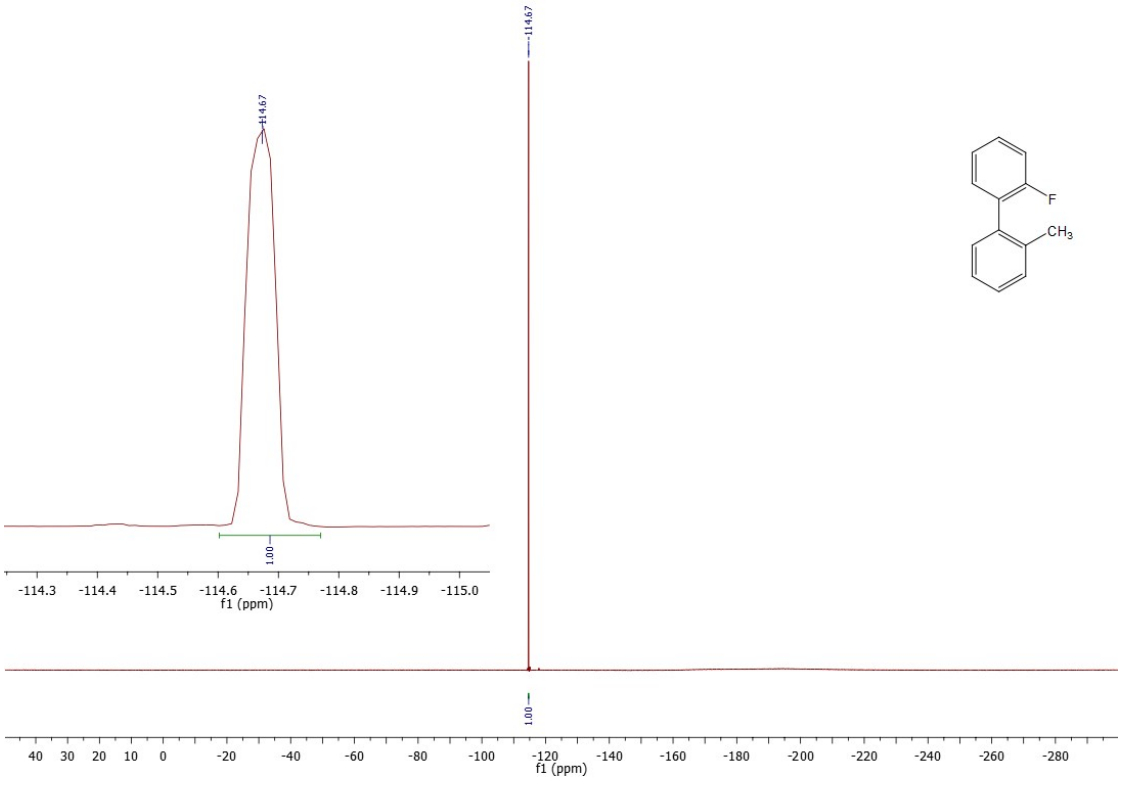


**Figure S2**. $^{19}$F NMR (377 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2'-methyl-1,1'-biphenyl (**1a**).

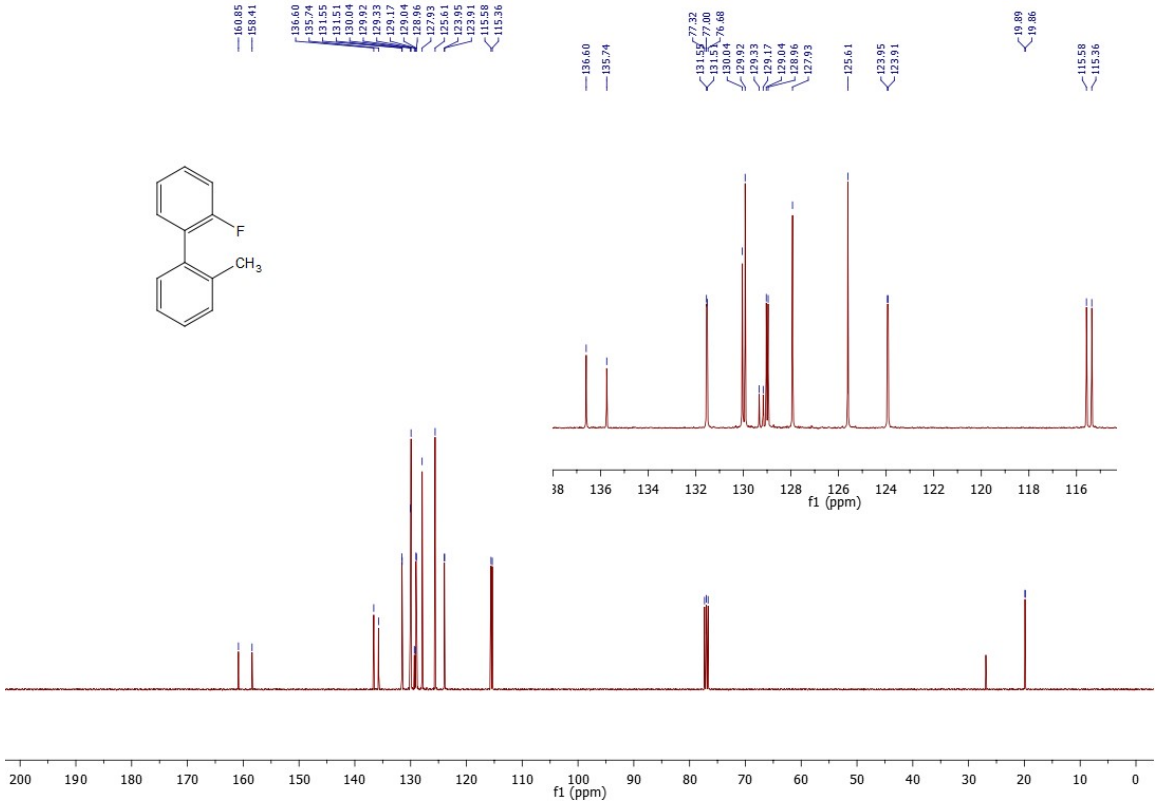


**Figure S3**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2'-methyl-1,1'-biphenyl (**1a**).

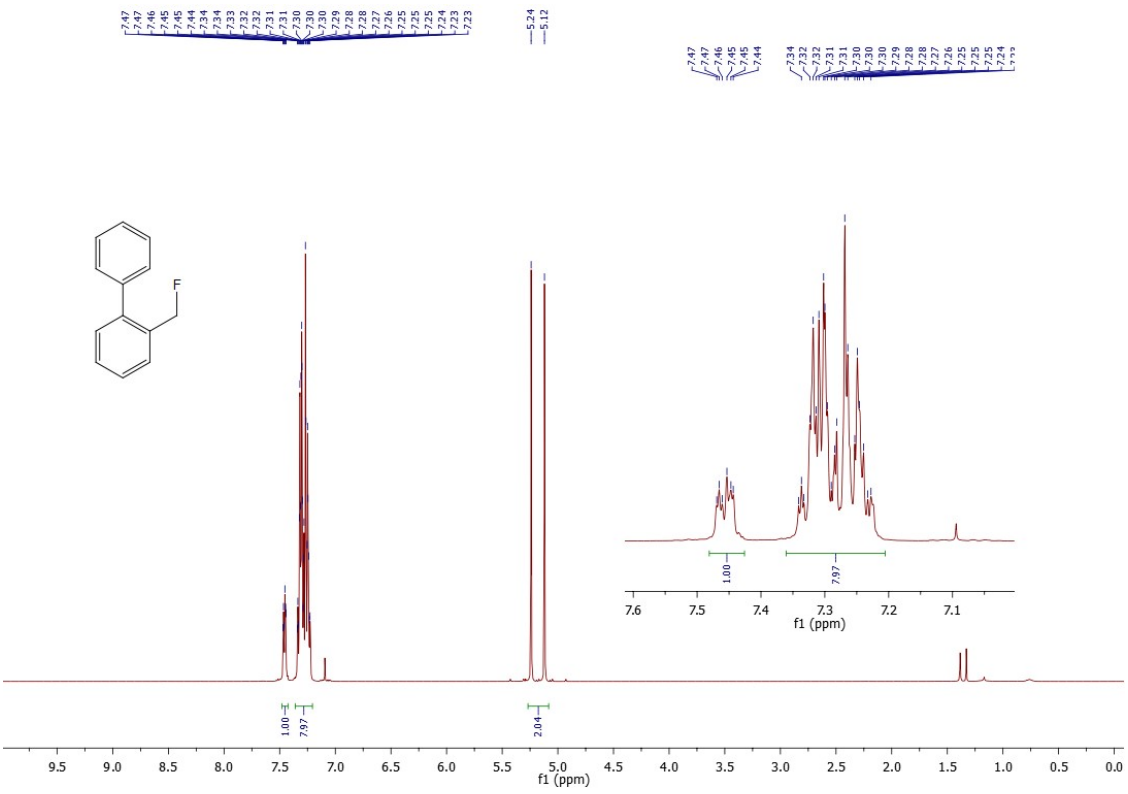


**Figure S4**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 2-(fluoromethyl)-1,1'-biphenyl (**1b**).

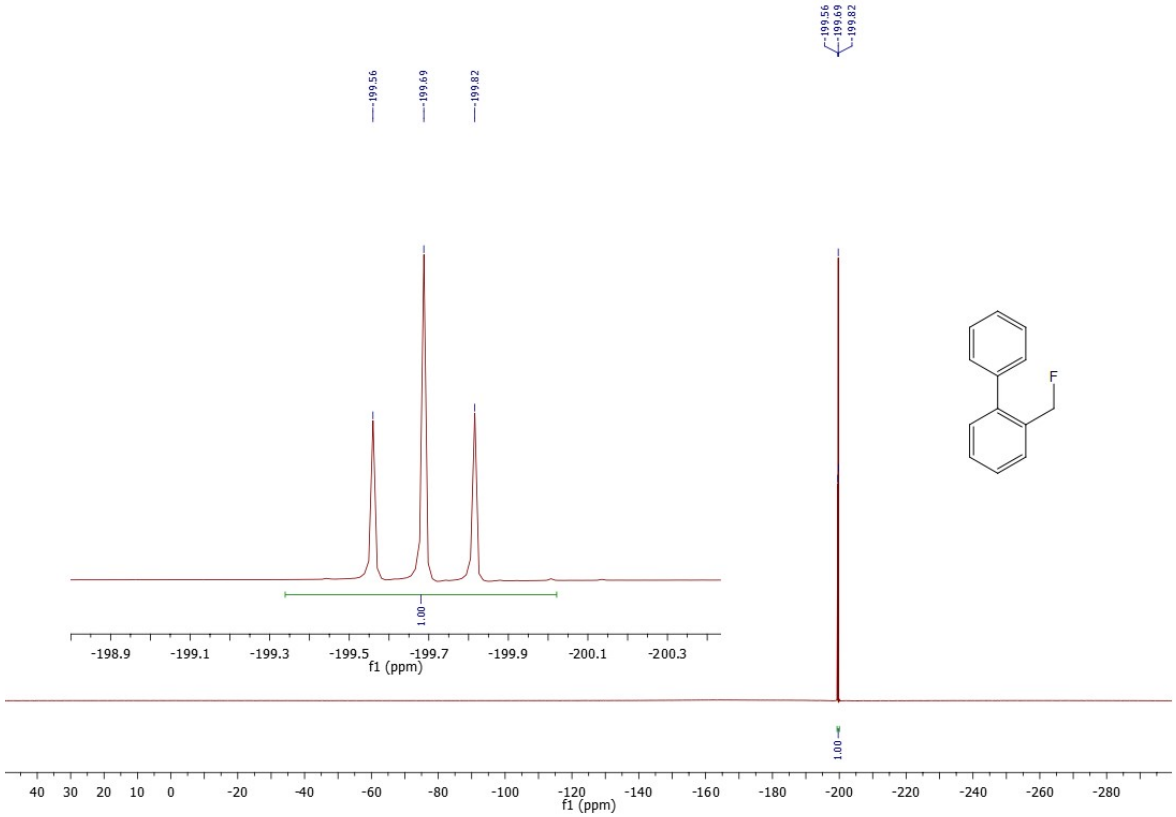


**Figure S5**. $^{19}F$ NMR (377 MHz, $CDCl_3$, 293 K) spectrum of 2-(fluoromethyl)-1,1'-biphenyl (**1b**).

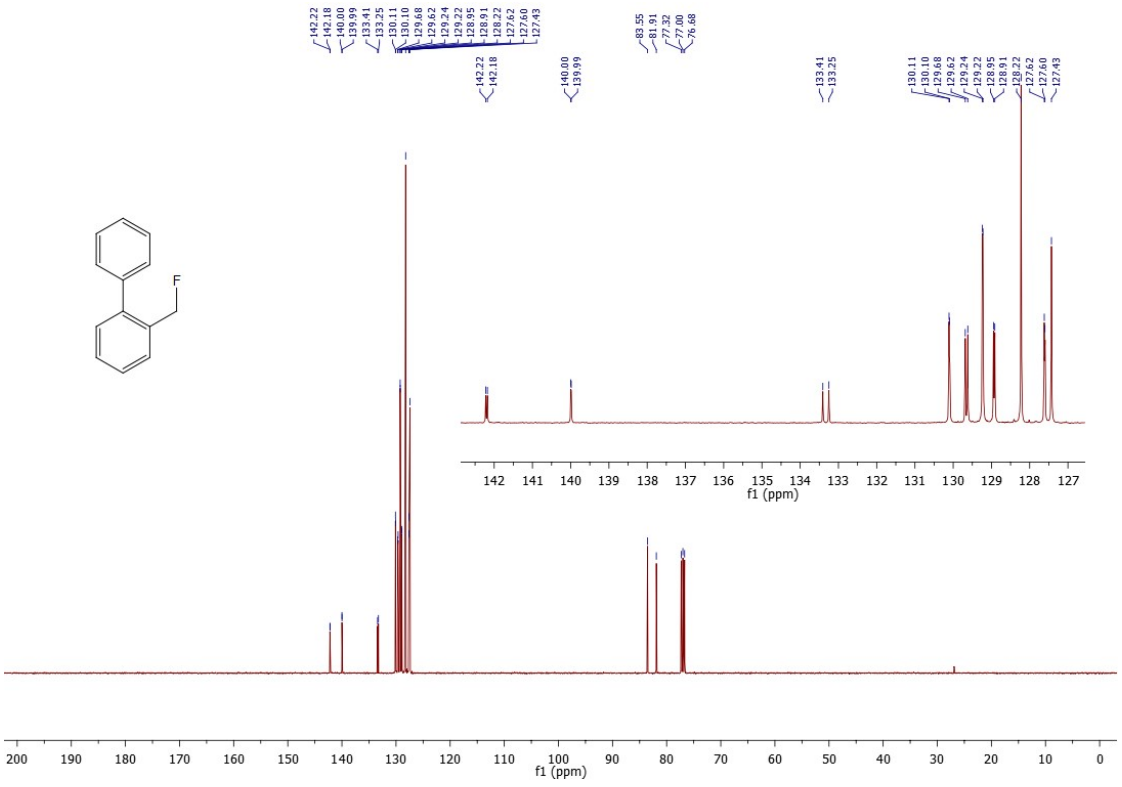


**Figure S6**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 2-(fluoromethyl)-1,1'-biphenyl (**1b**).

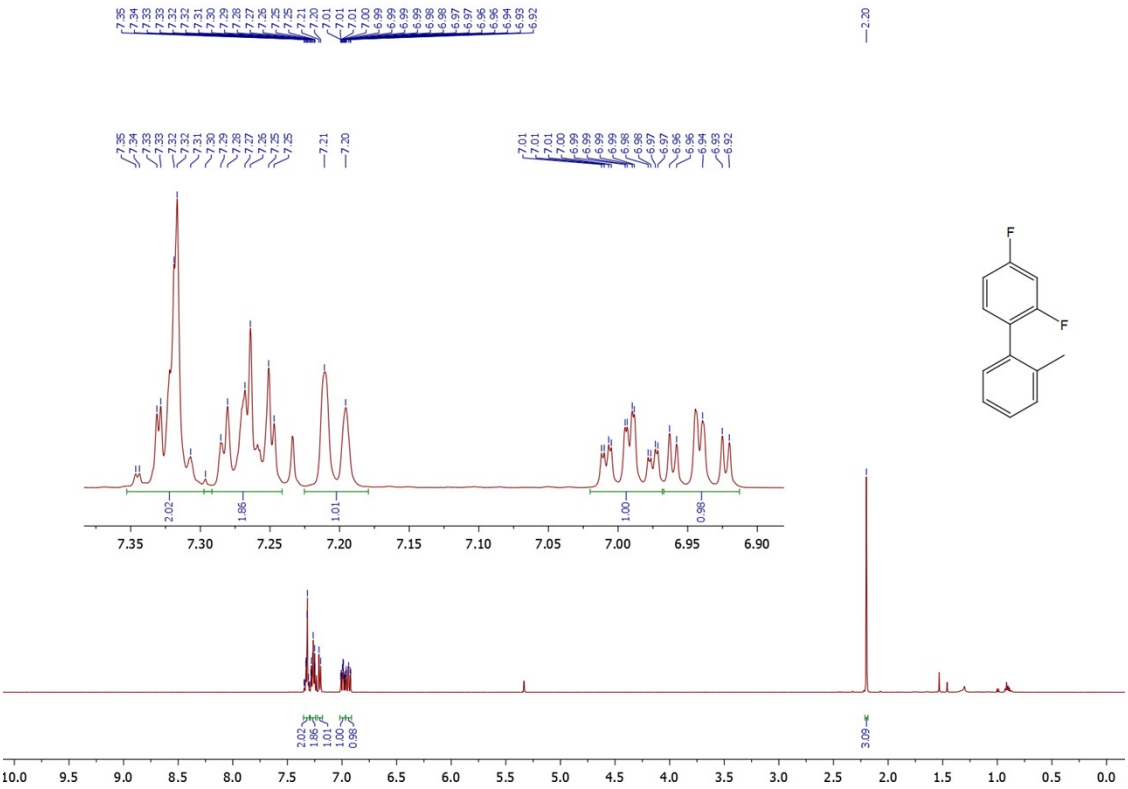

**Figure S7**. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,4-difluoro-2'-methyl-1,1'-biphenyl (**2a**).

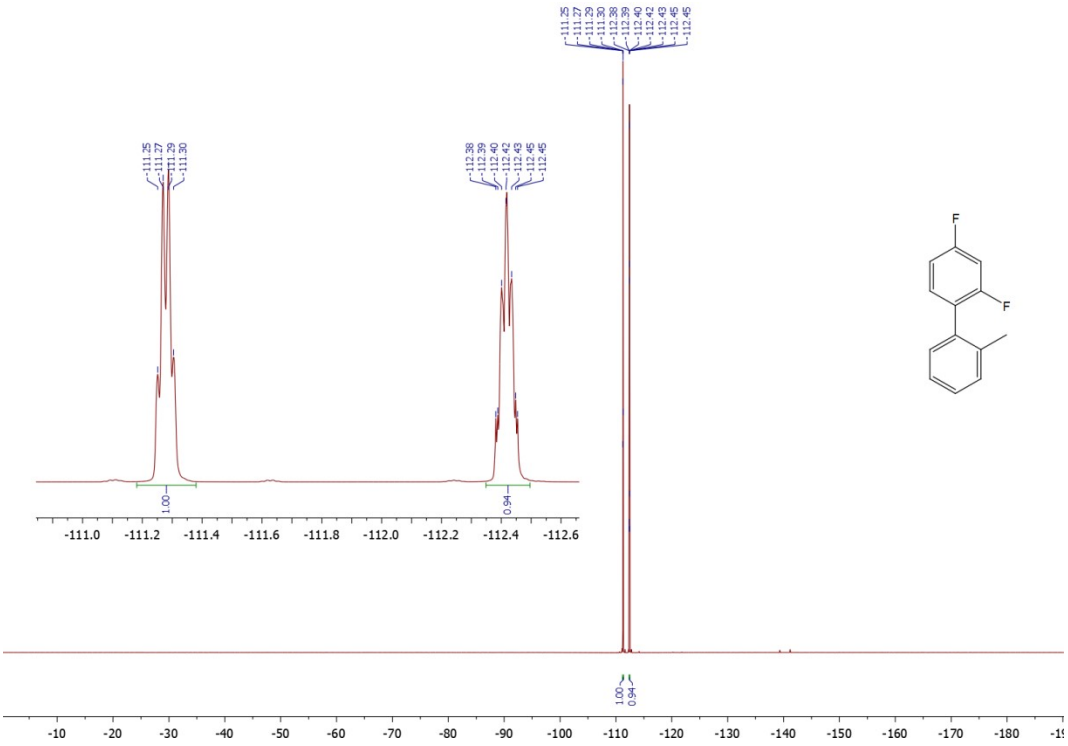

**Figure S8**. $^{19}F$ NMR (470 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,4-difluoro-2'-methyl-1,1'-biphenyl (**2a**).

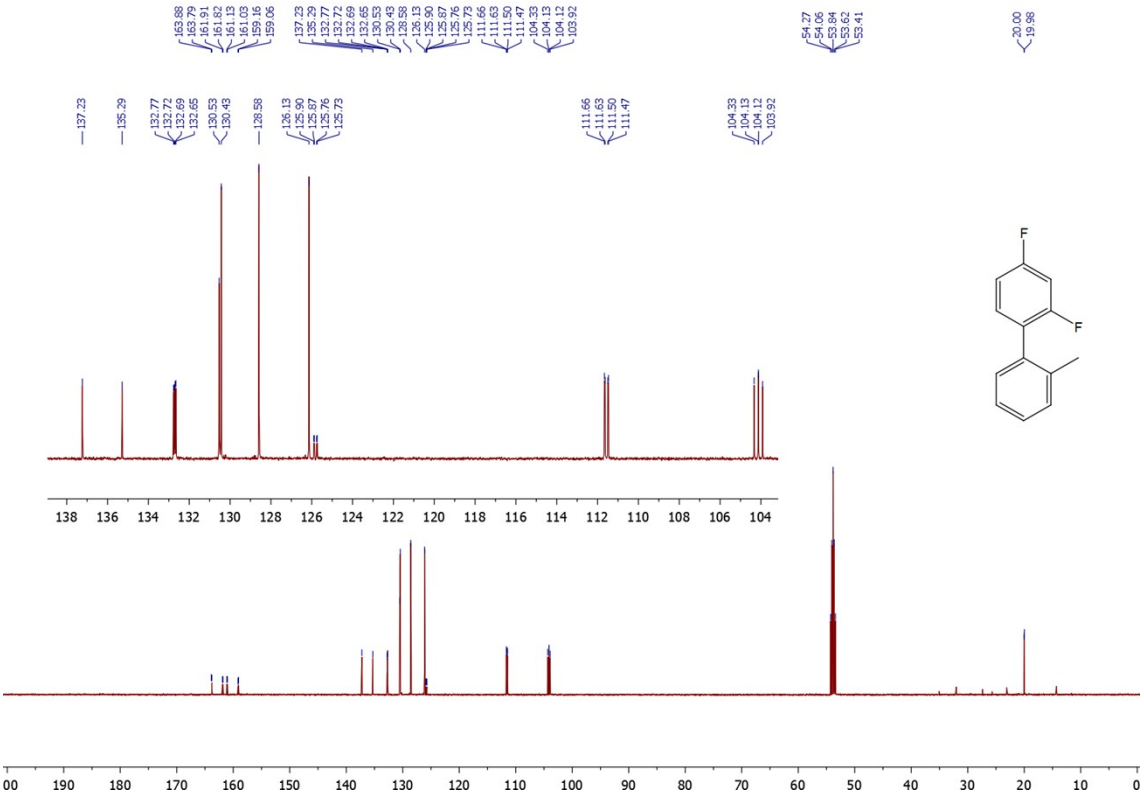

**Figure S9**. $^{13}C$ NMR (126 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,4-difluoro-2'-methyl-1,1'-biphenyl (**2a**).

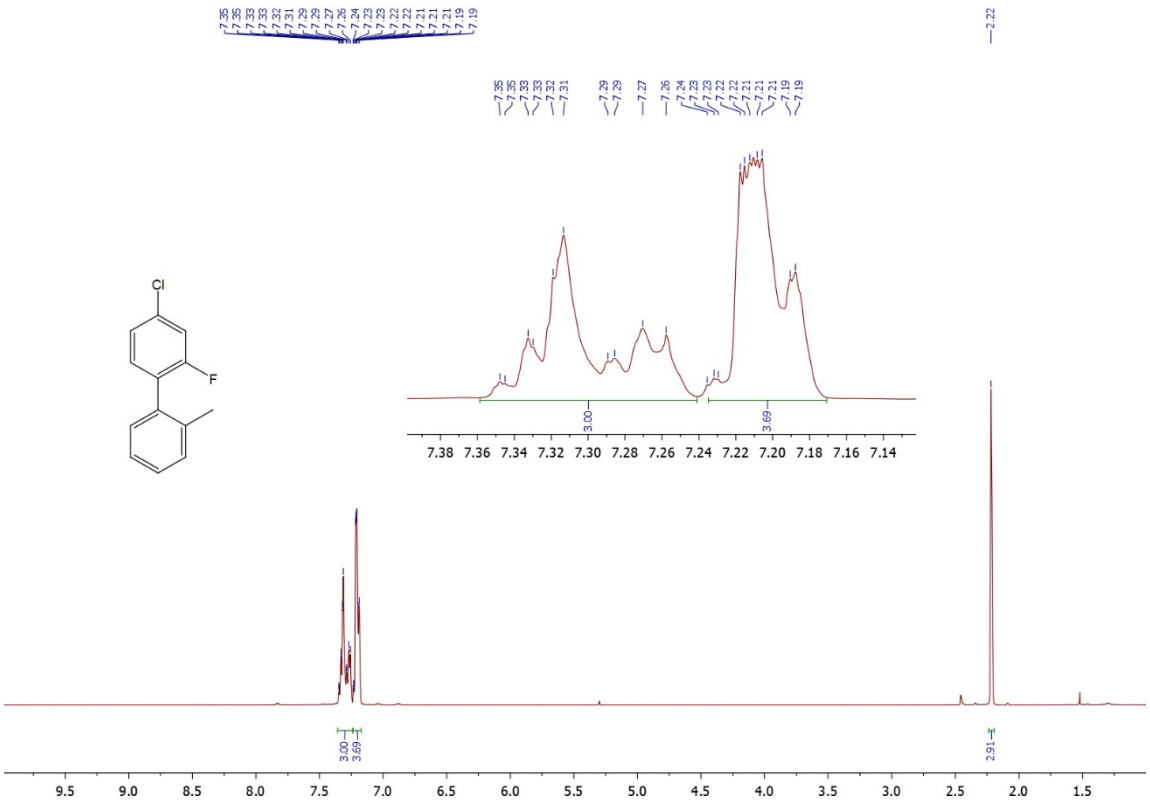

**Figure S10**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 4-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (**3a**).

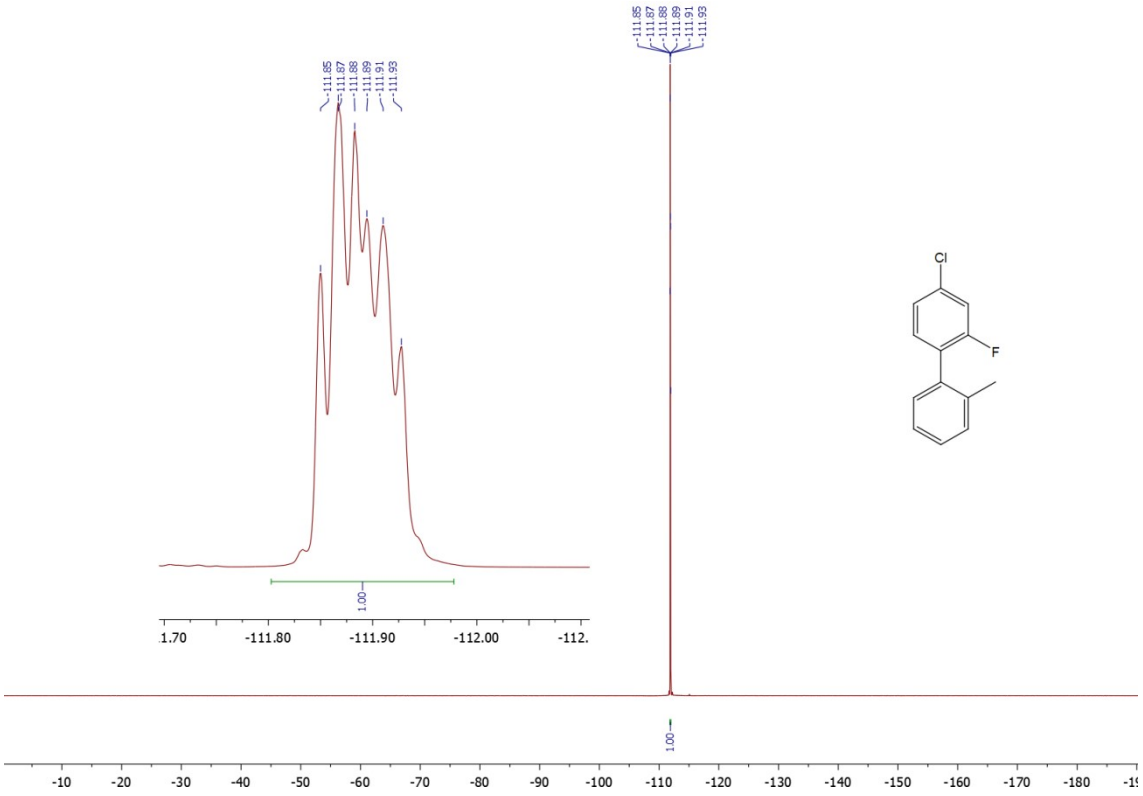


**Figure S11**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 4-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (**3a**).

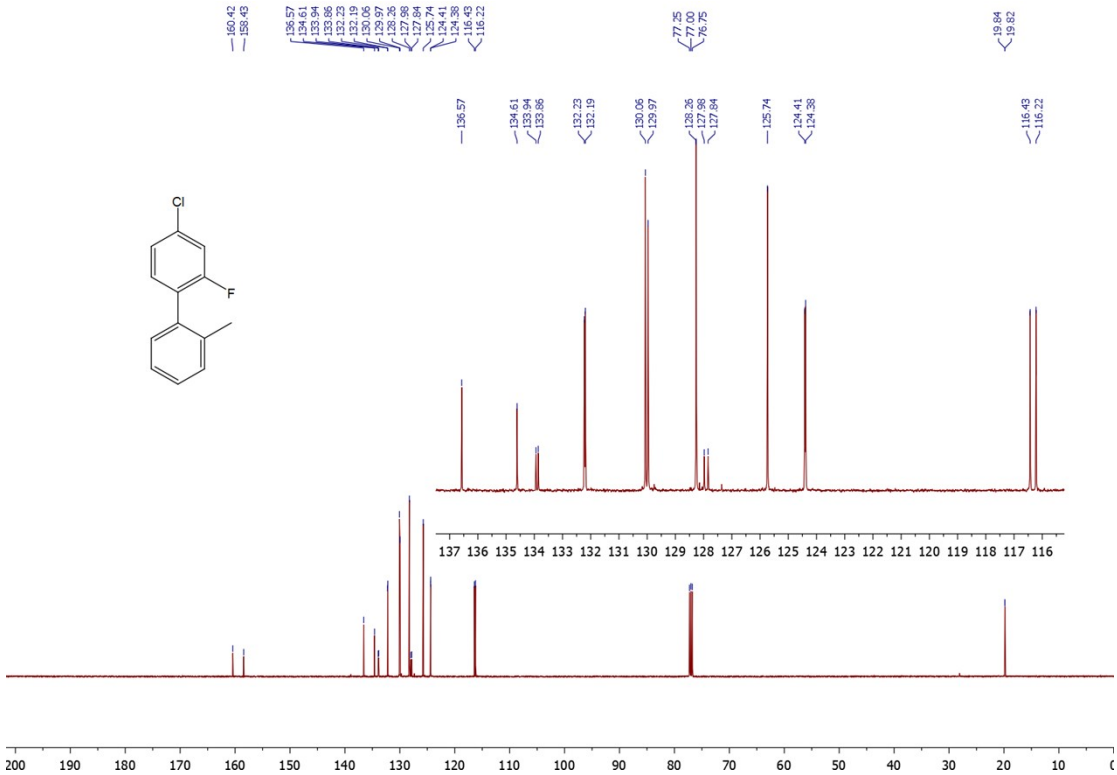


**Figure S12**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 4-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (**3a**).

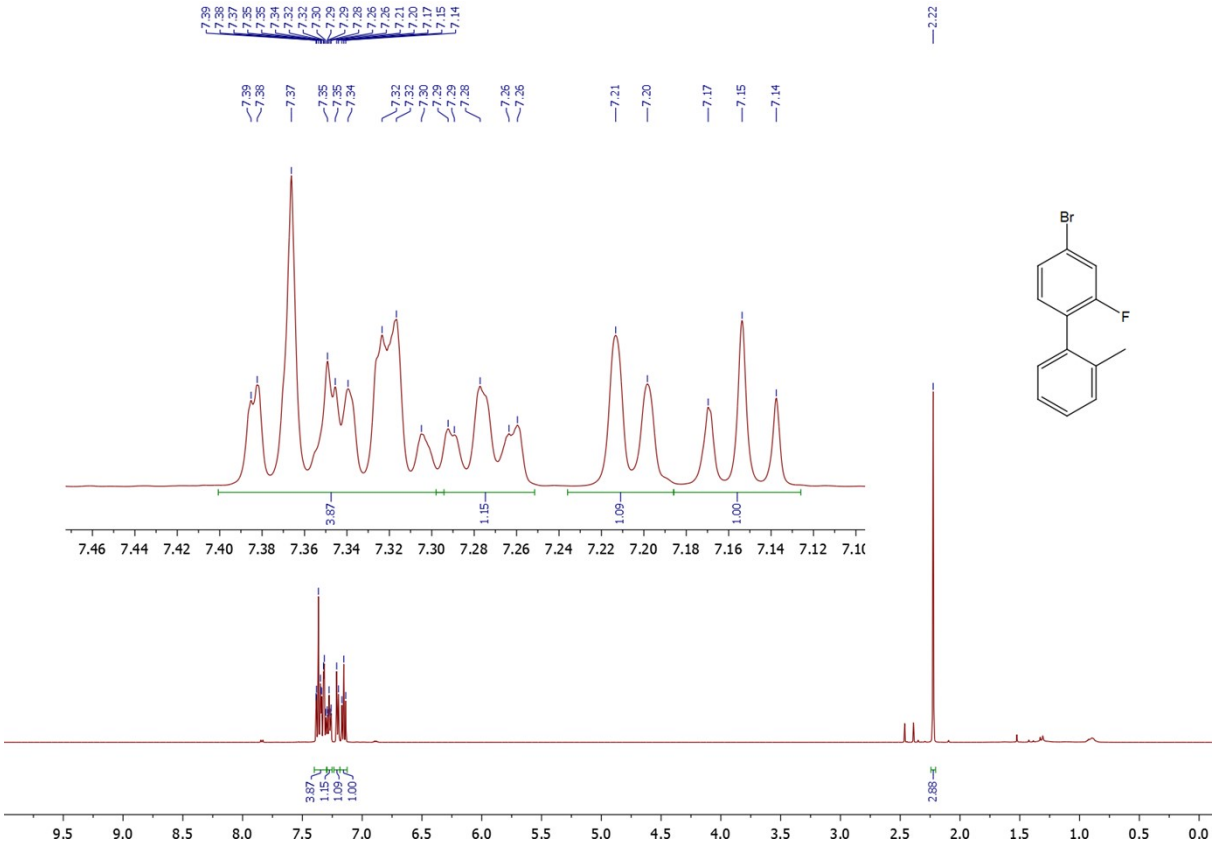


**Figure S13**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 4-bromo-2-fluoro-2'-methyl-1,1'-biphenyl (**4a**).

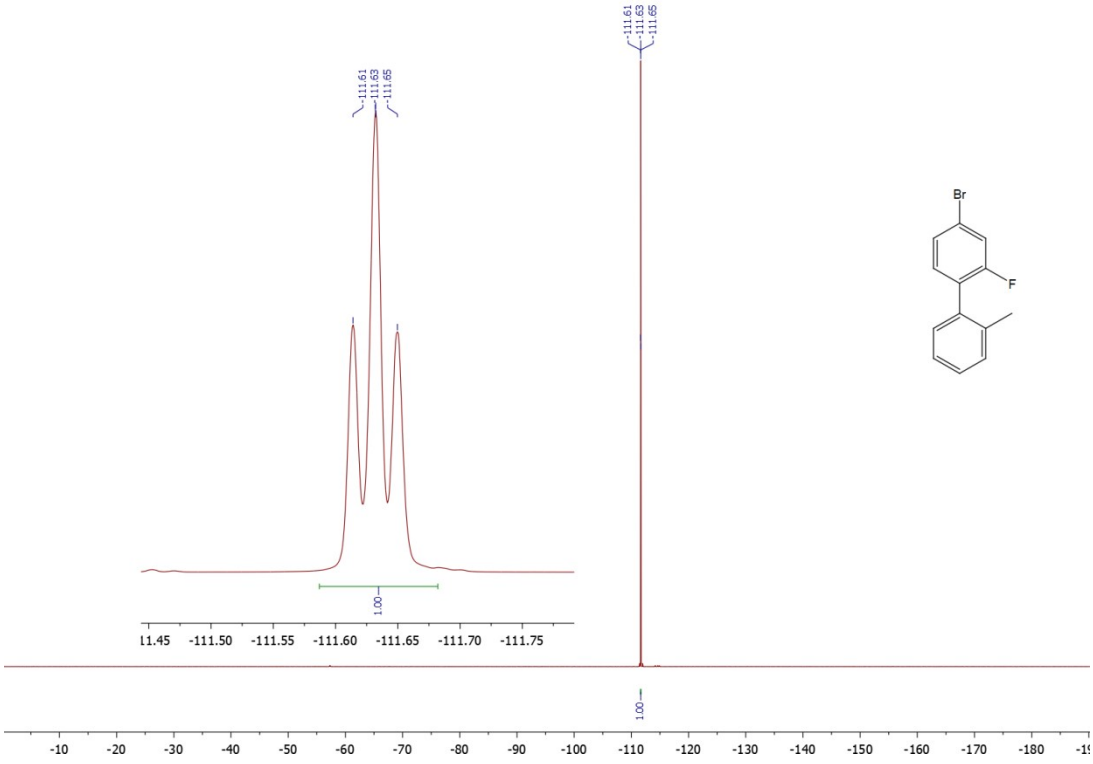


**Figure S14**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 4-bromo-2-fluoro-2'-methyl-1,1'-biphenyl (**4a**).

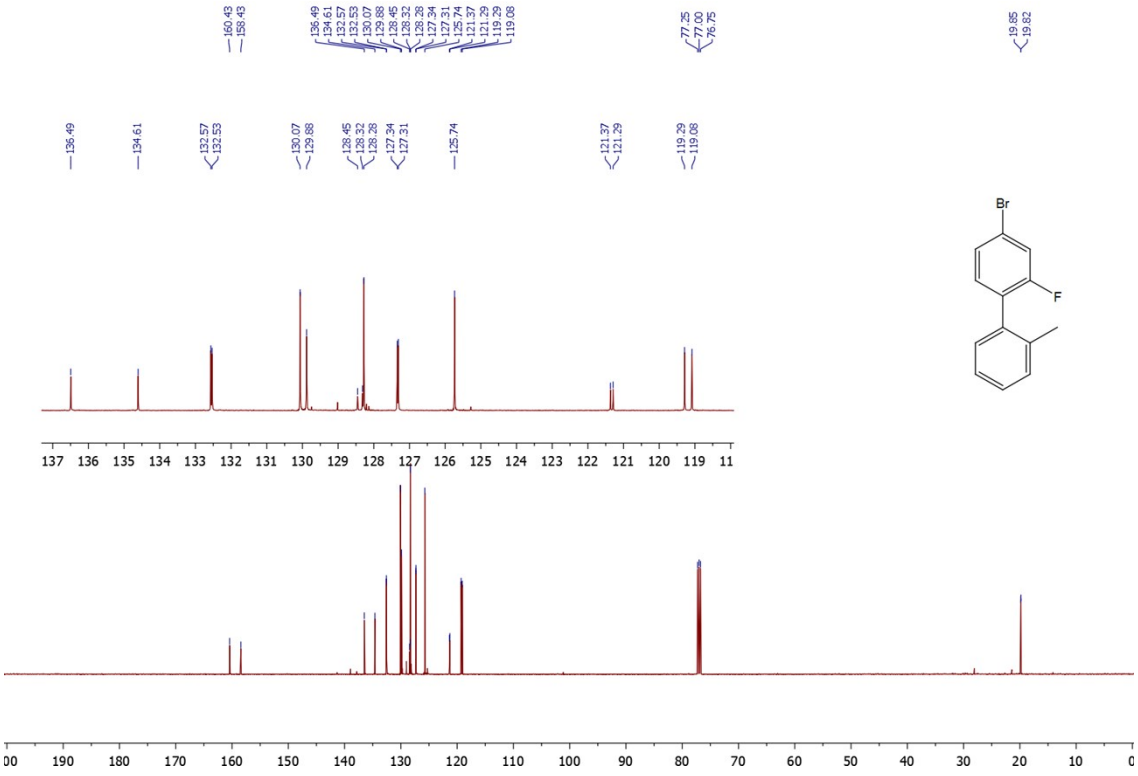


**Figure S15**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 4-bromo-2-fluoro-2'-methyl-1,1'-biphenyl (**4a**).

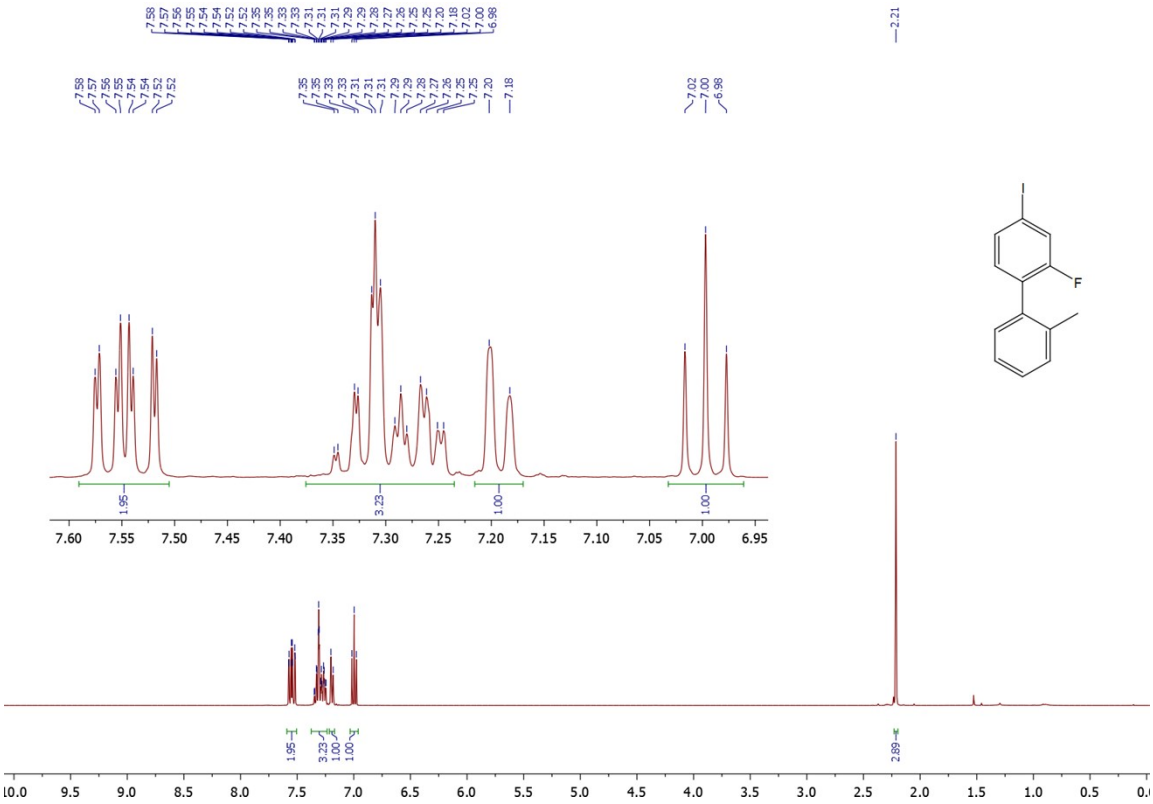


**Figure S16**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-4-iodo-2'-methyl-1,1'-biphenyl (**5a**).

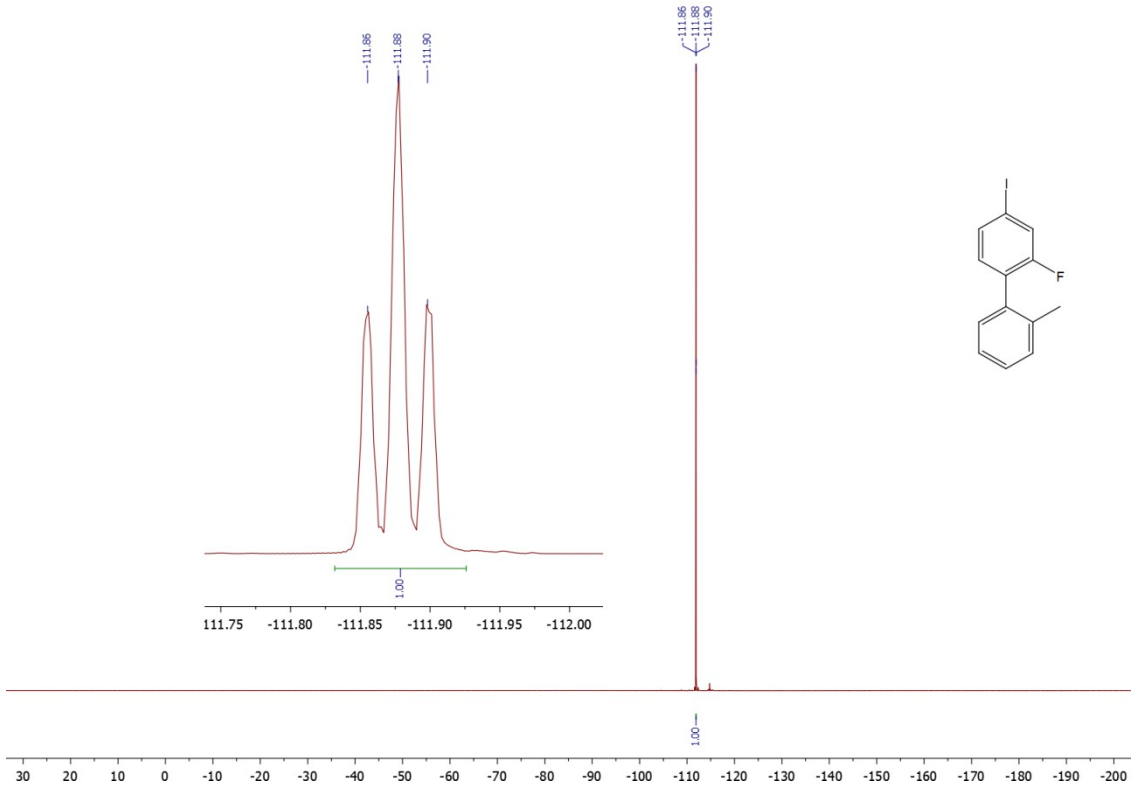


**Figure S17**. $^{19}F$ NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-4-iodo-2'-methyl-1,1'-biphenyl (**5a**).

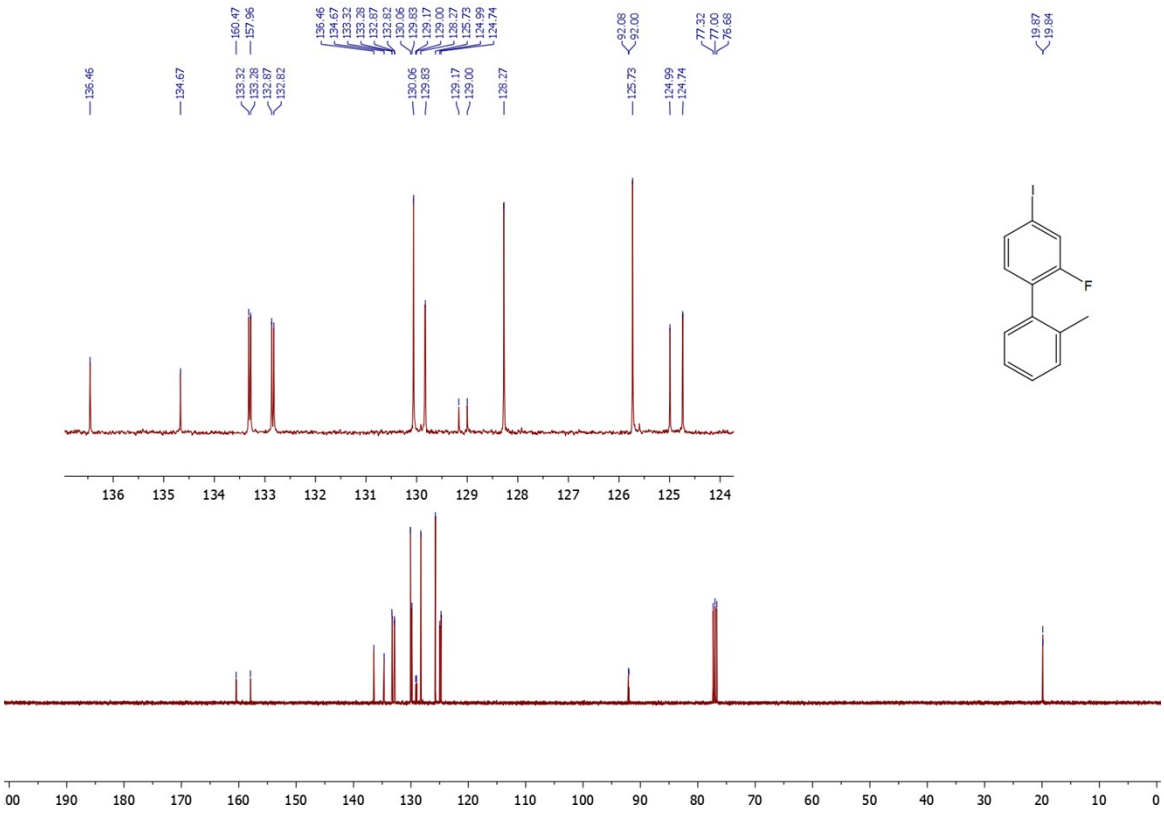


**Figure S18**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-4-iodo-2'-methyl-1,1'-biphenyl (**5a**).

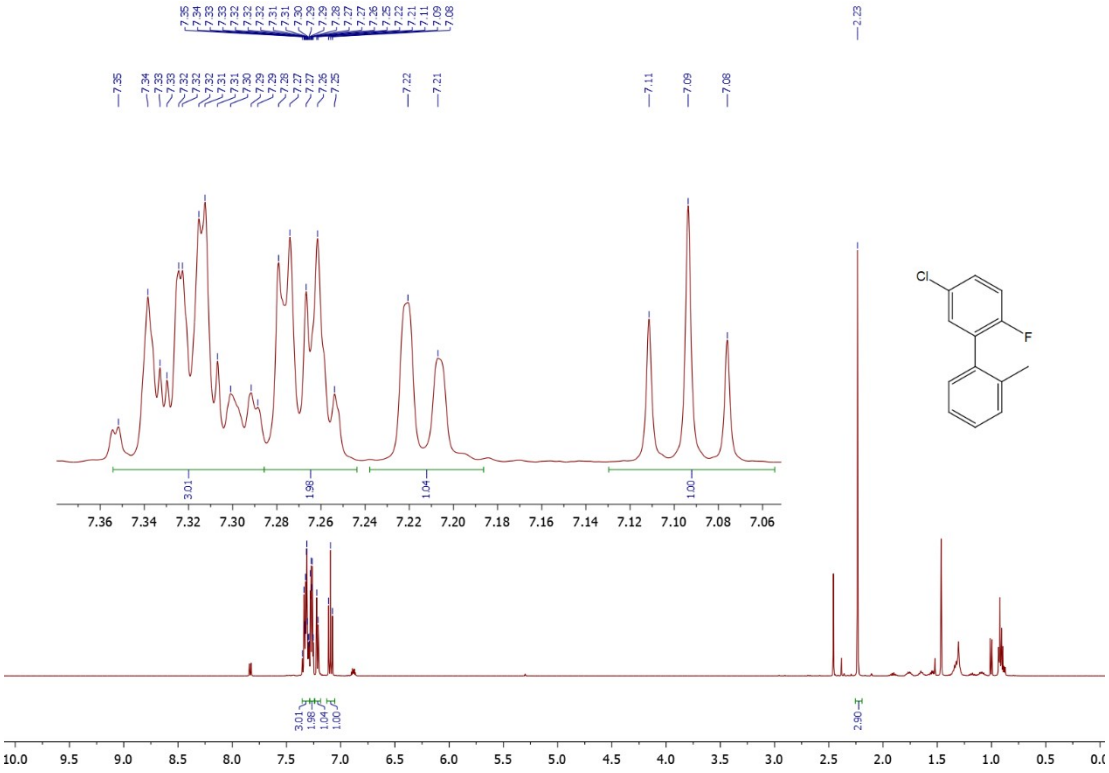


**Figure S19**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 5-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (**6a**).

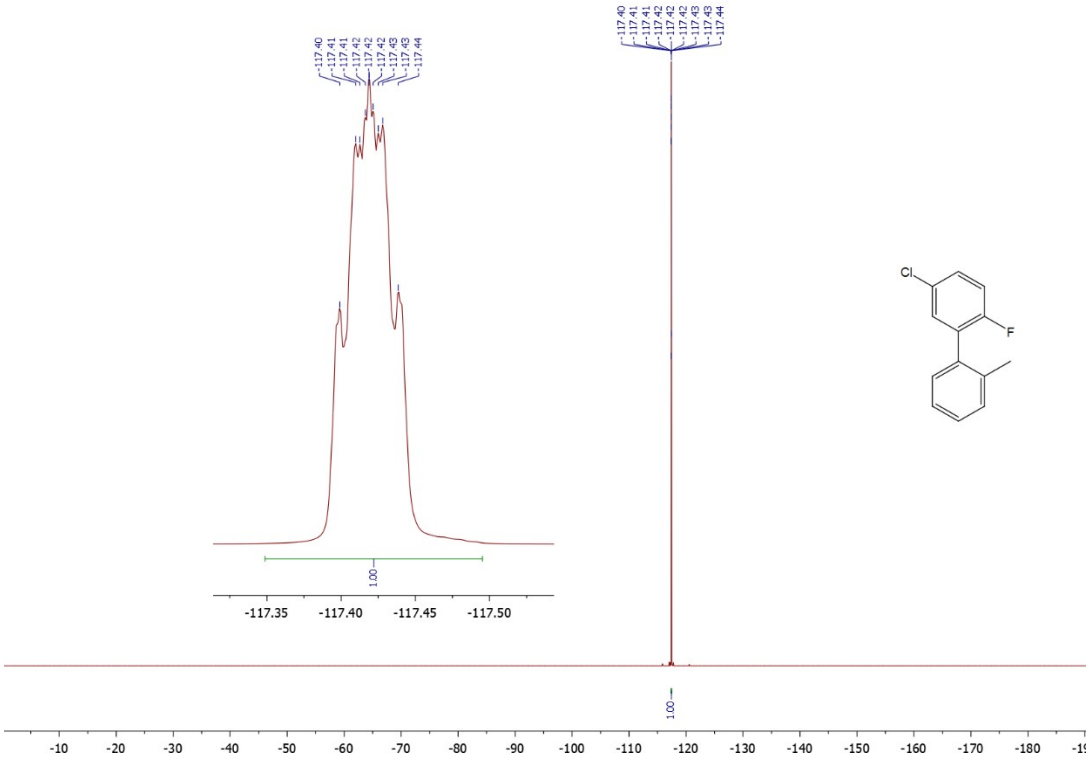


**Figure S20**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 5-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (**6a**).

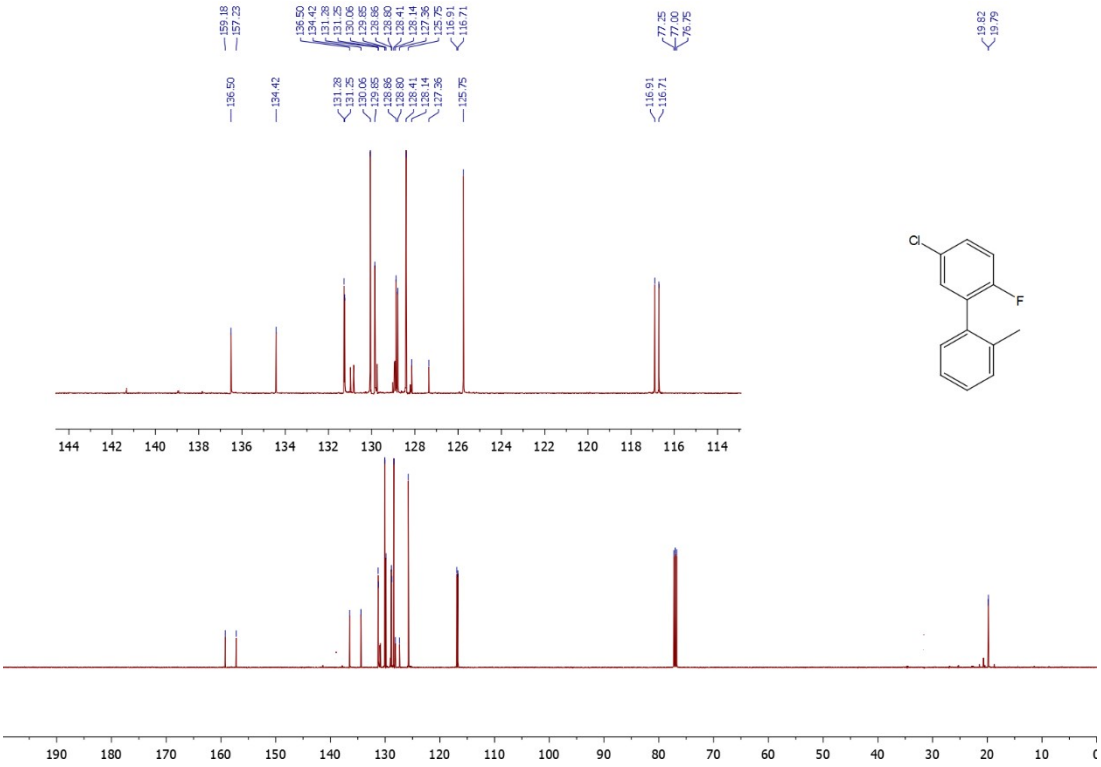

**Figure S21**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 5-chloro-2-fluoro-2'-methyl-1,1'-biphenyl (**6a**).

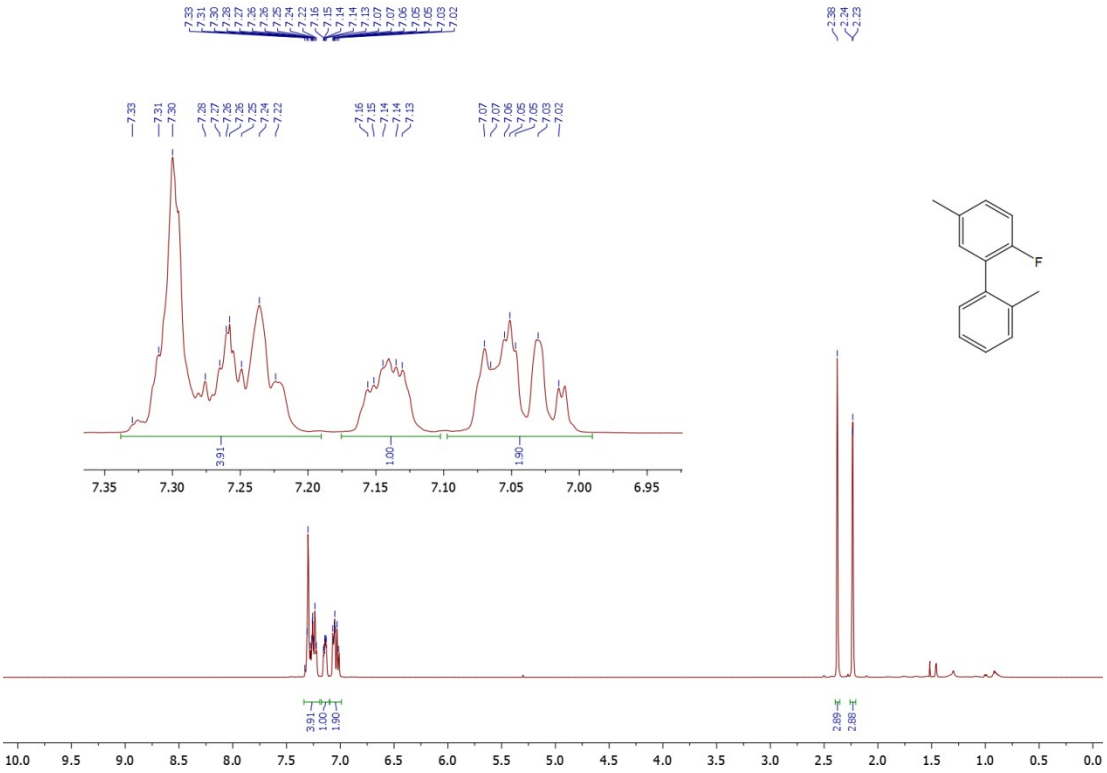

**Figure S22**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',5-dimethyl-1,1'-biphenyl (**7a**).

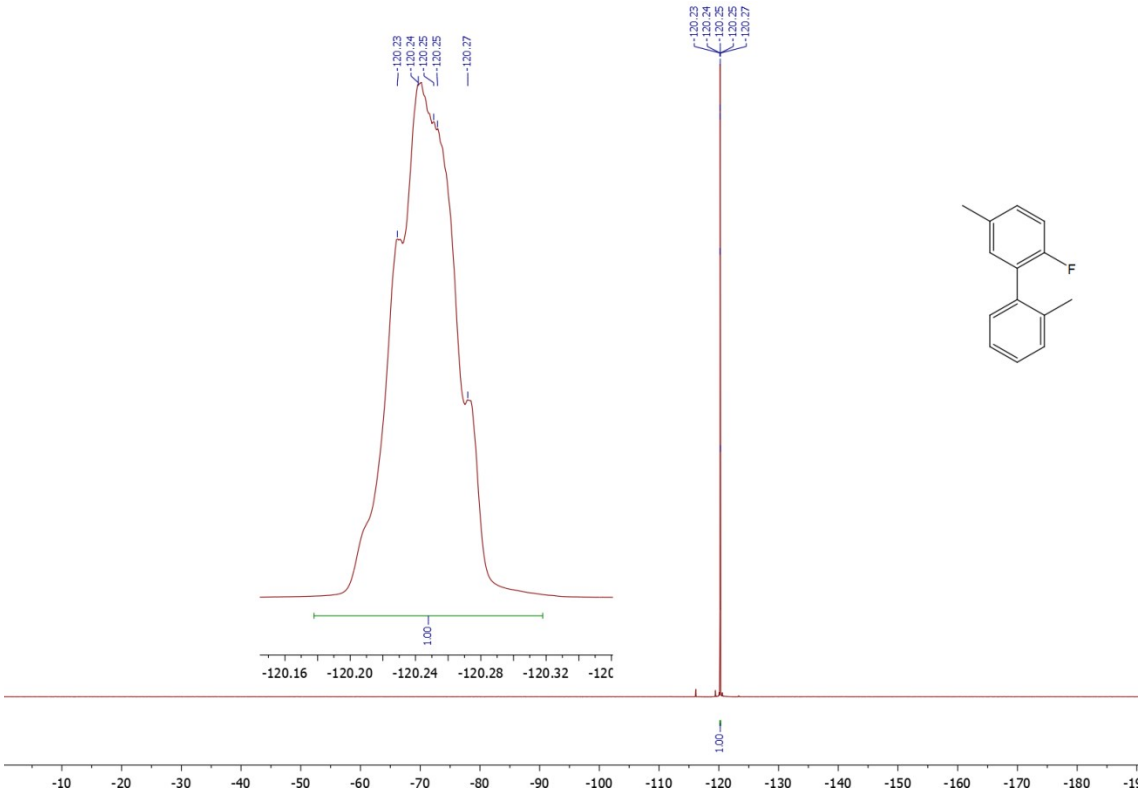


**Figure S23**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',5-dimethyl-1,1'-biphenyl (**7a**).

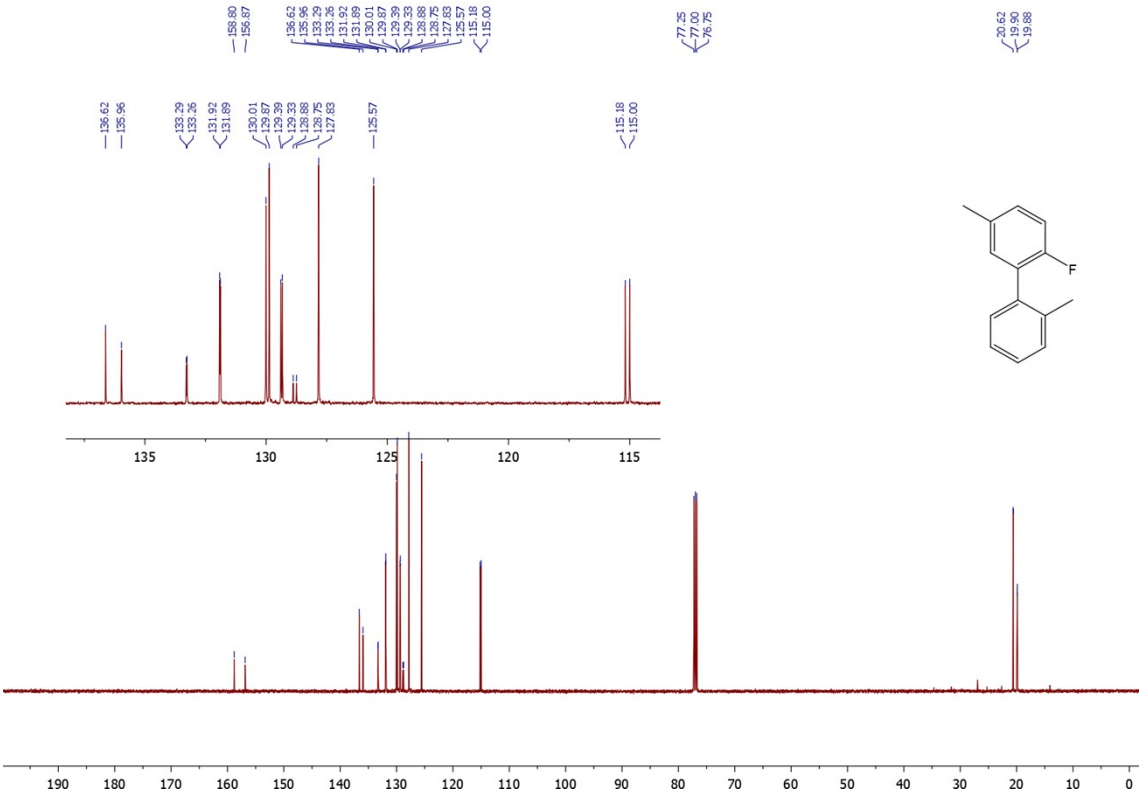


**Figure S24**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',5-dimethyl-1,1'-biphenyl (**7a**).

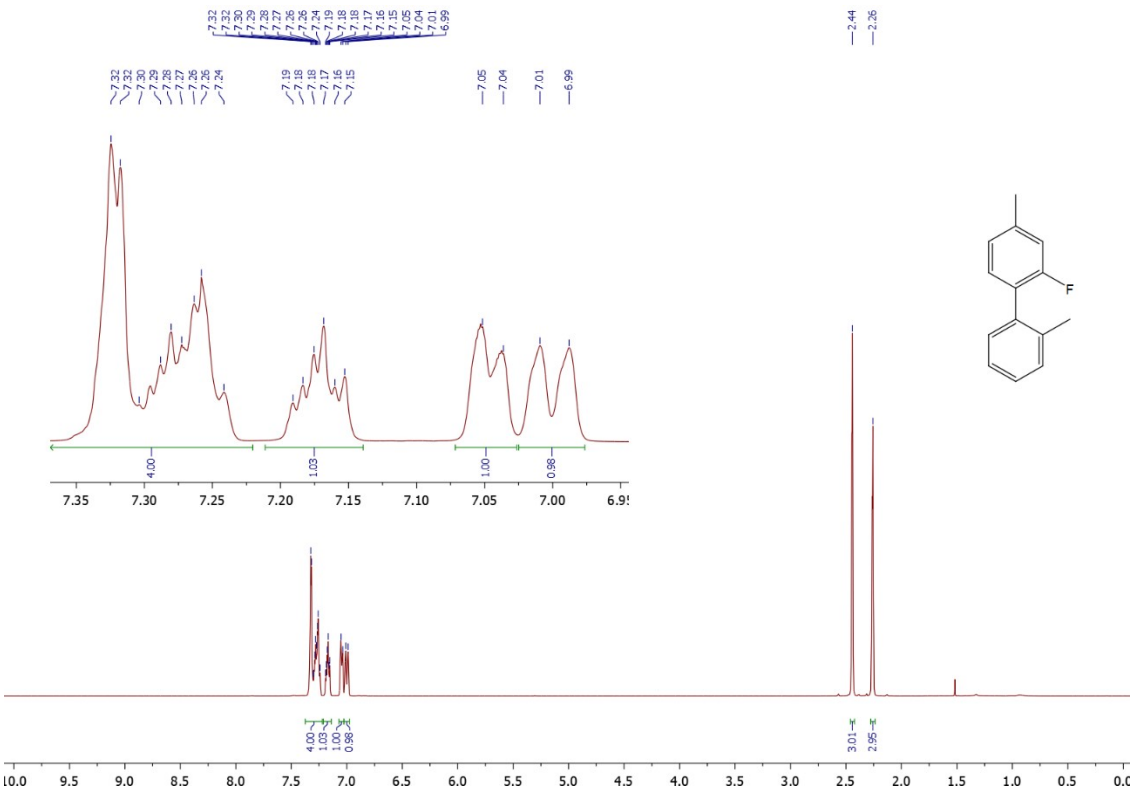

**Figure S25**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',4-dimethyl-1,1'-biphenyl (**8a**).

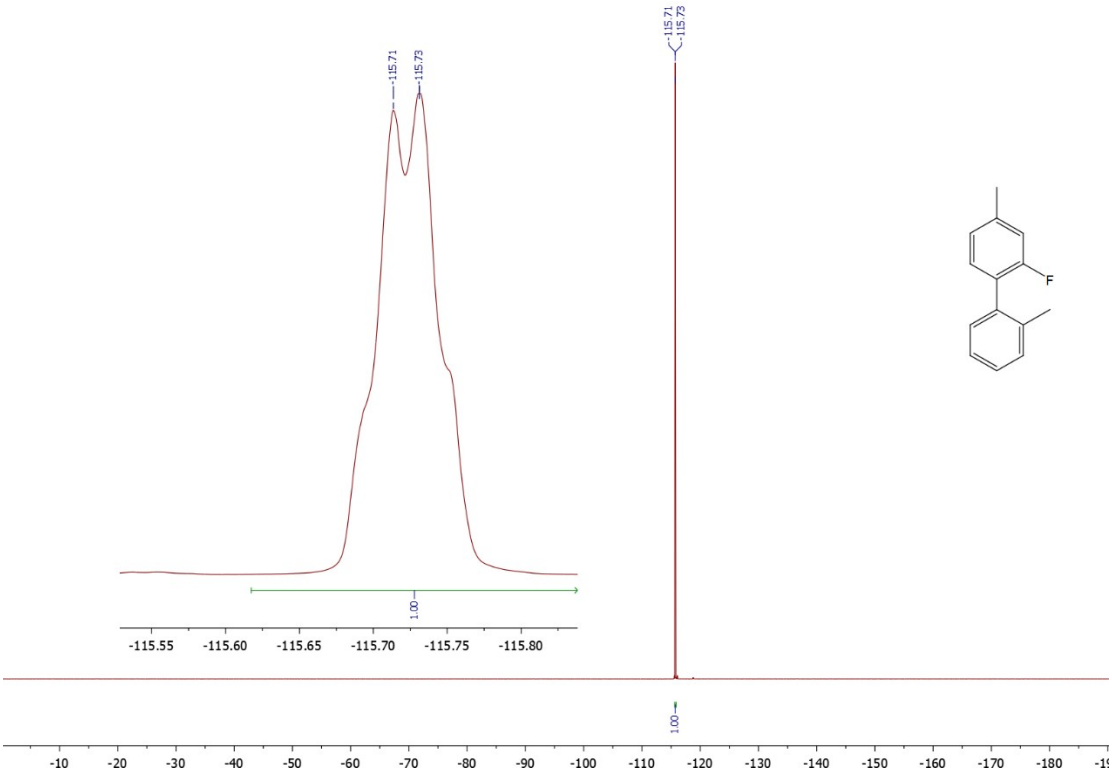

**Figure S26**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',4-dimethyl-1,1'-biphenyl (**8a**).

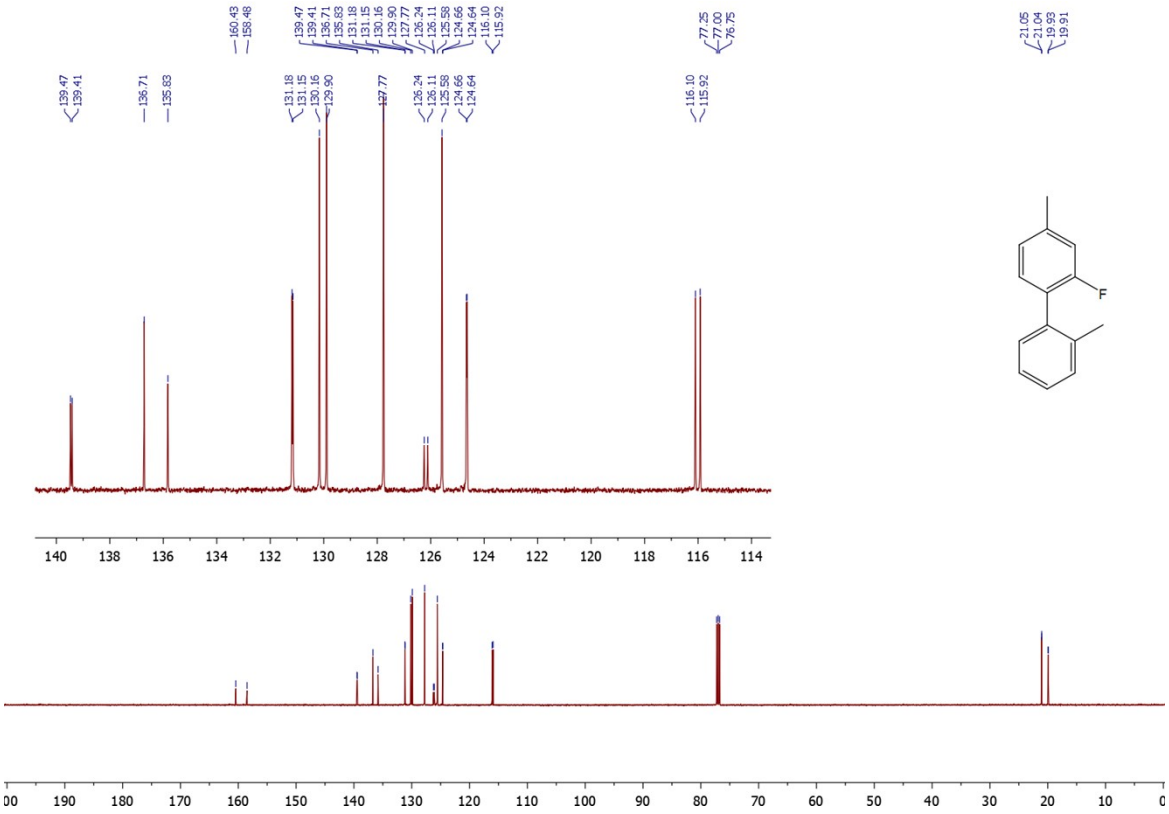

**Figure S27**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',4-dimethyl-1,1'-biphenyl (**8a**).

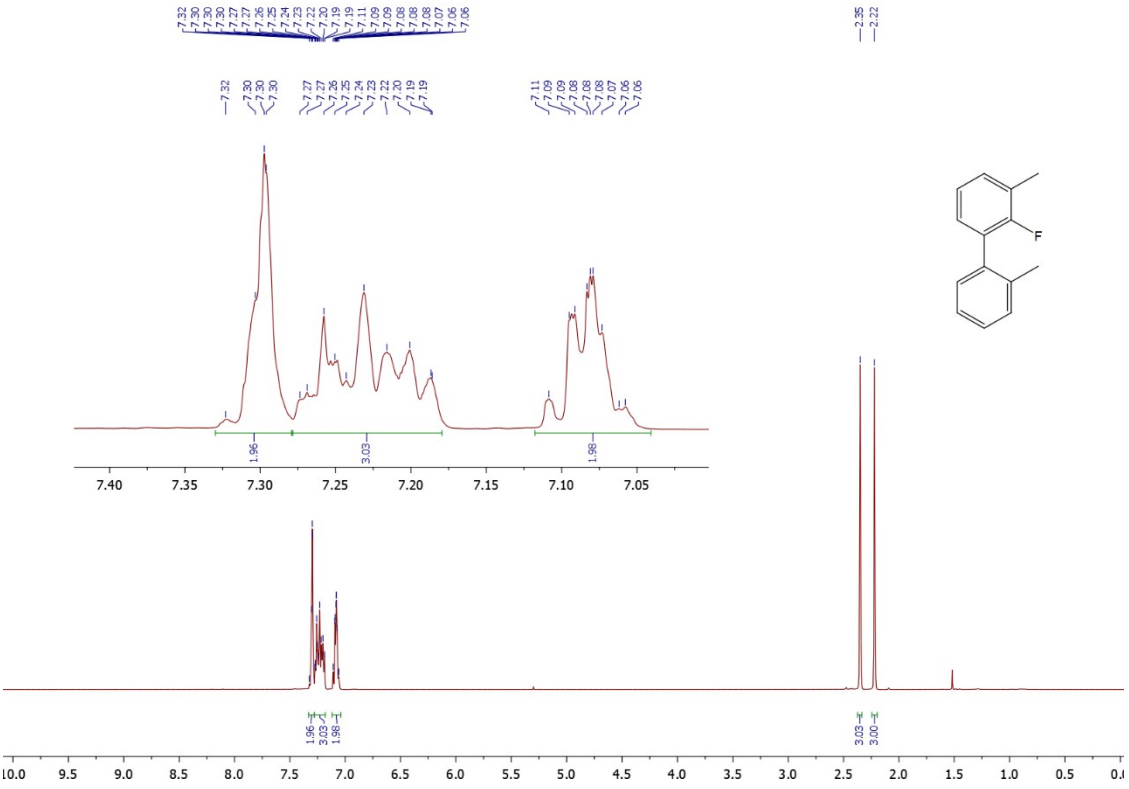

**Figure S28**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',3-dimethyl-1,1'-biphenyl (**9a**).

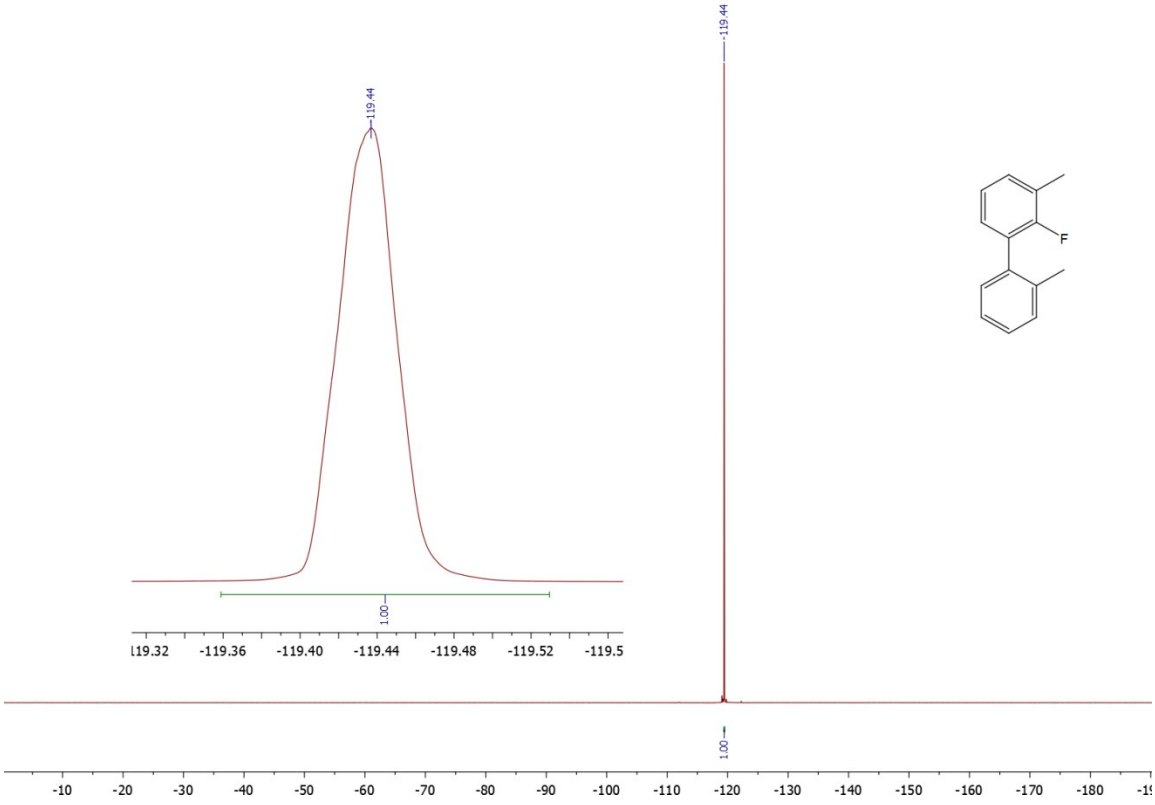


**Figure S29**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',3-dimethyl-1,1'-biphenyl (**9a**).

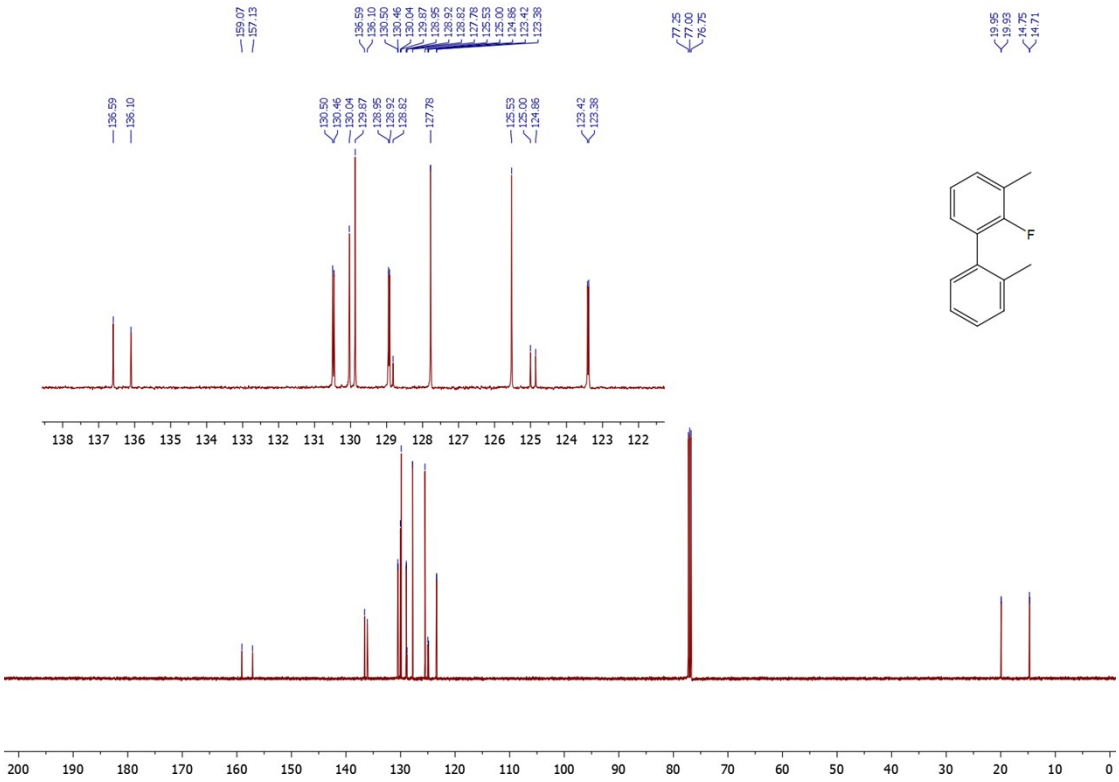


**Figure S30**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2',3-dimethyl-1,1'-biphenyl (**9a**).

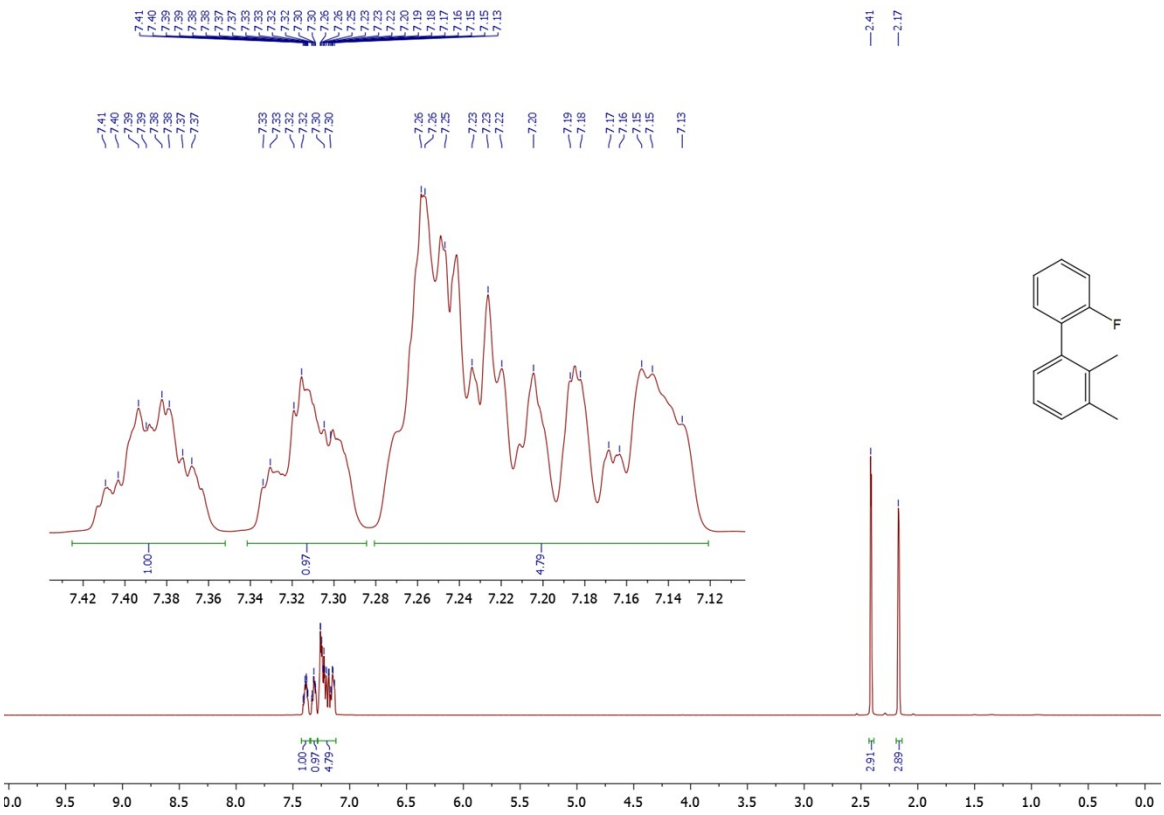


**Figure S31**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-2,3-dimethyl-1,1'-biphenyl (**9b**).

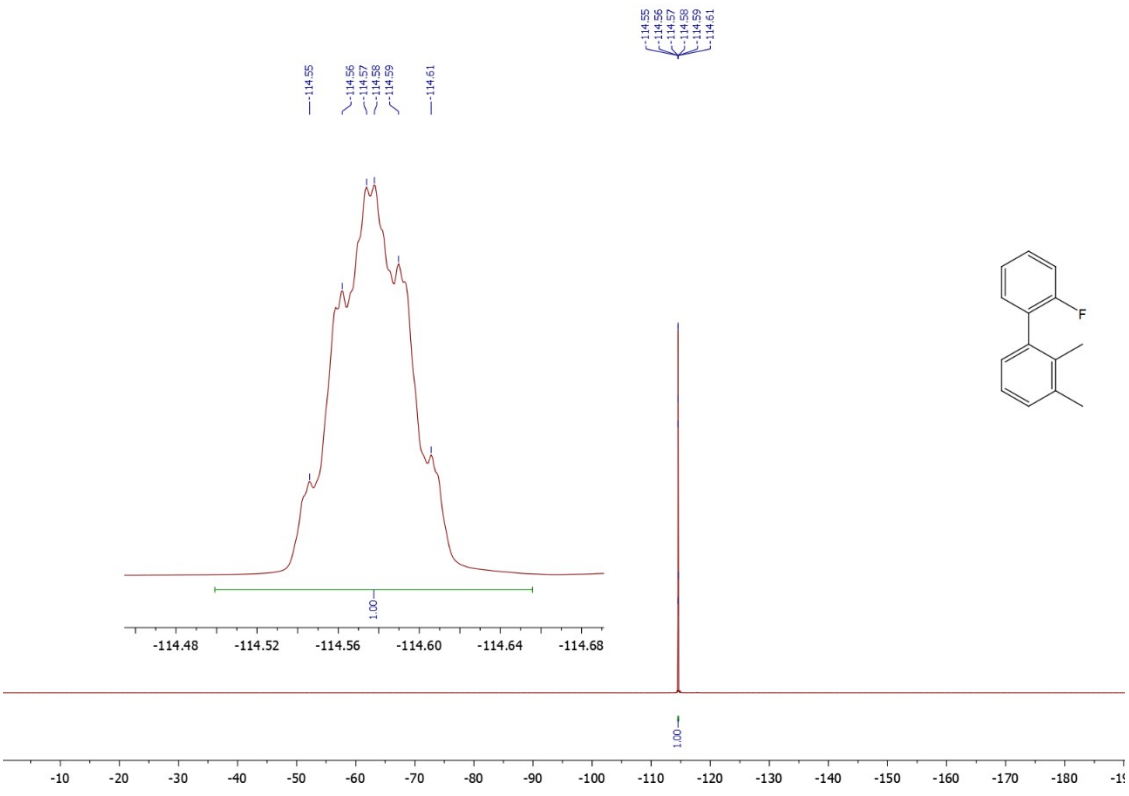


**Figure S32**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-2,3-dimethyl-1,1'-biphenyl (**9b**).

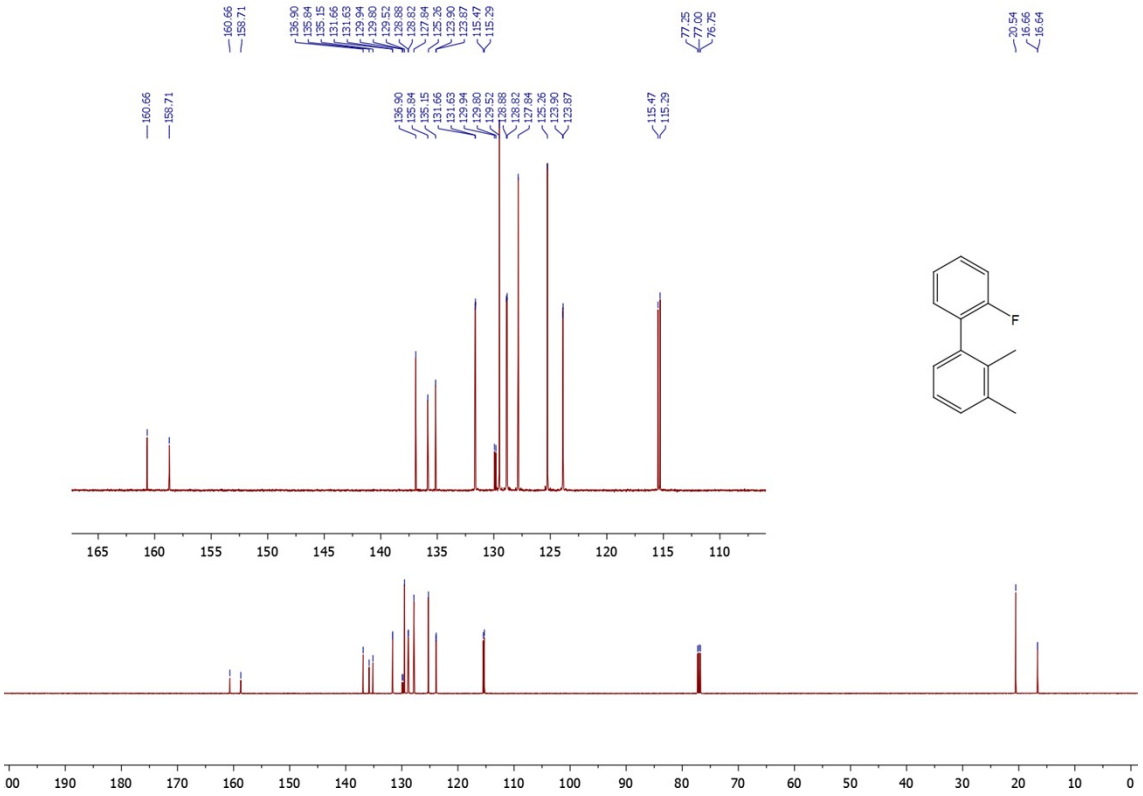


**Figure S33**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-2,3-dimethyl-1,1'-biphenyl (**9b**).

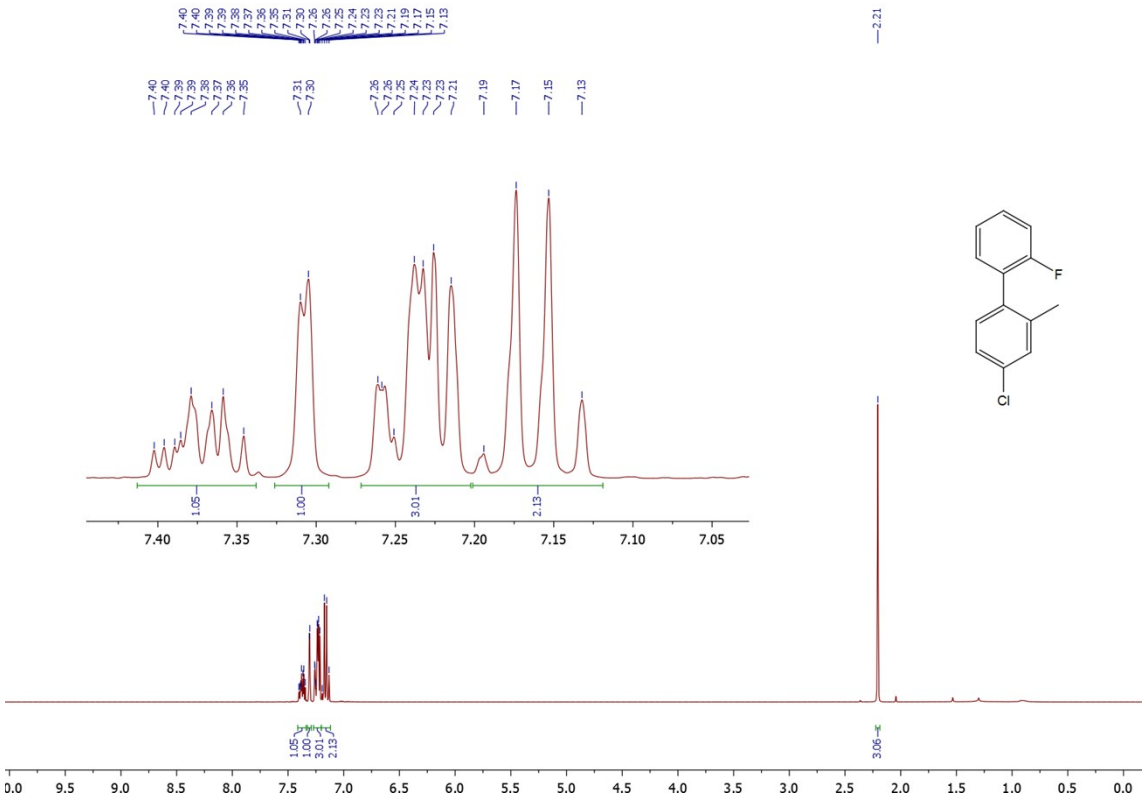


**Figure S34**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 4-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (**3b**).

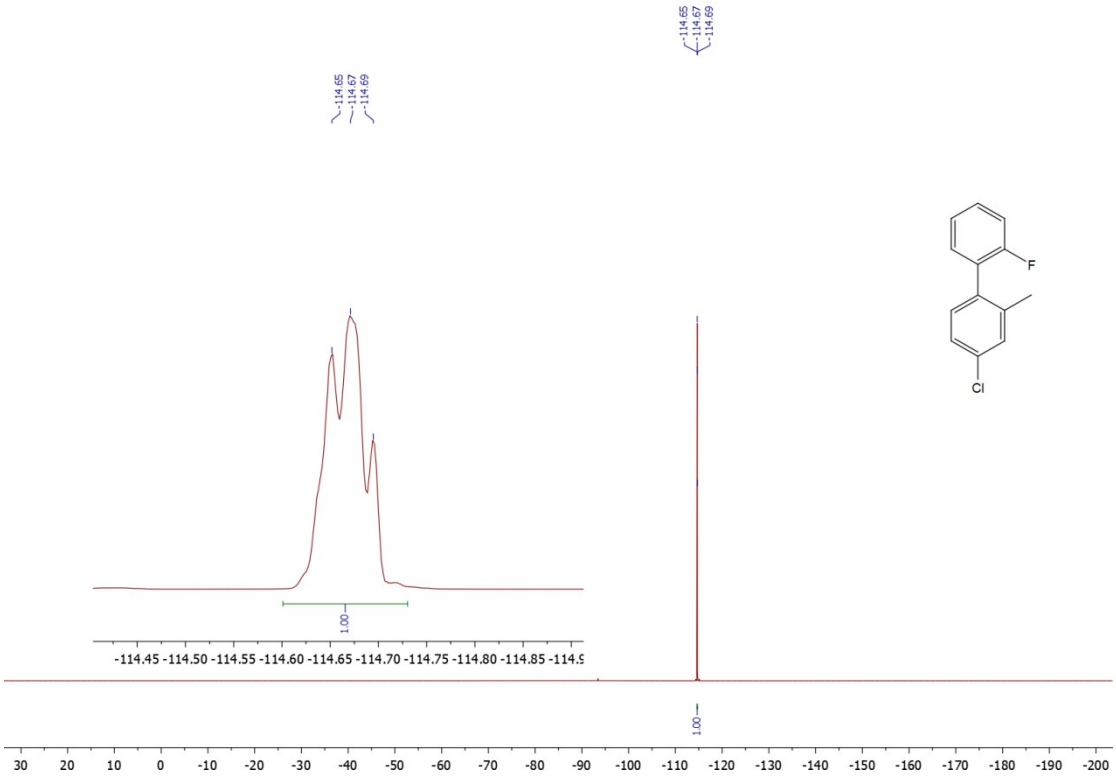


**Figure S35**. $^{19}F$ NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 4-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (**3b**).

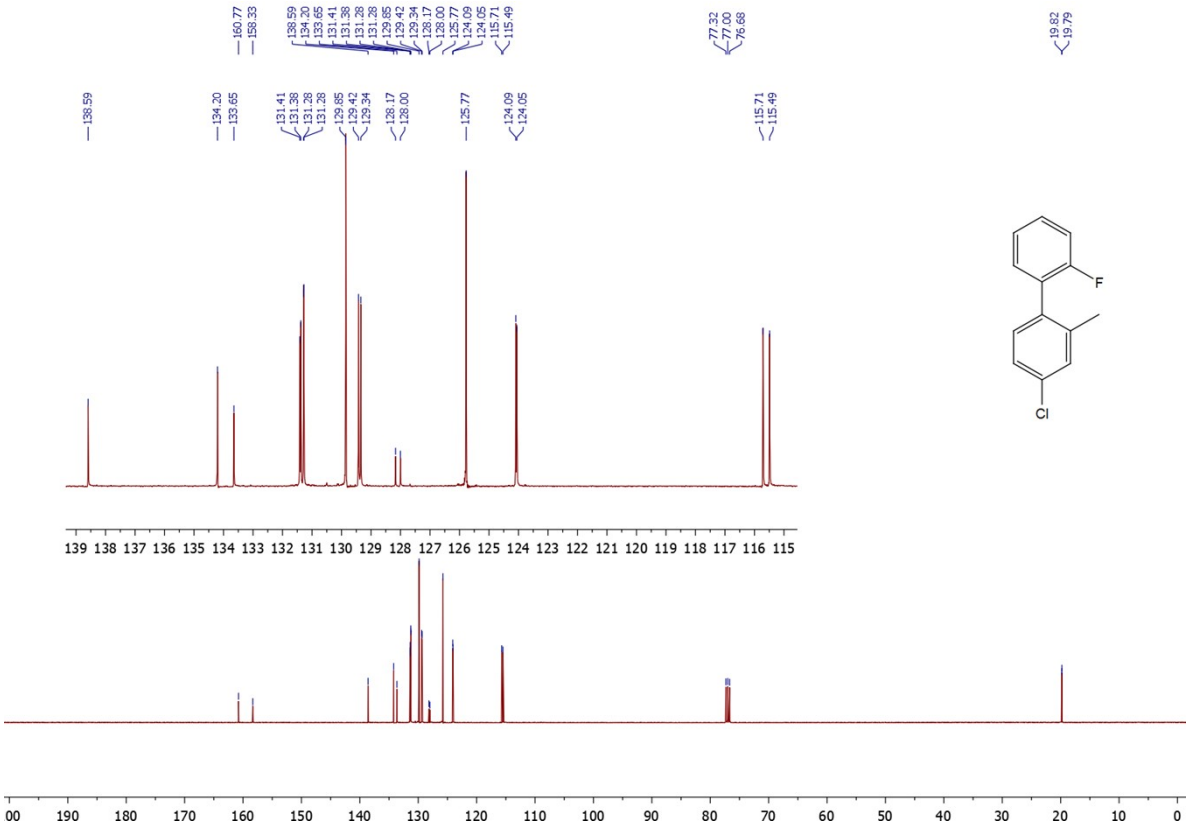


**Figure S36**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 4-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (**3b**).

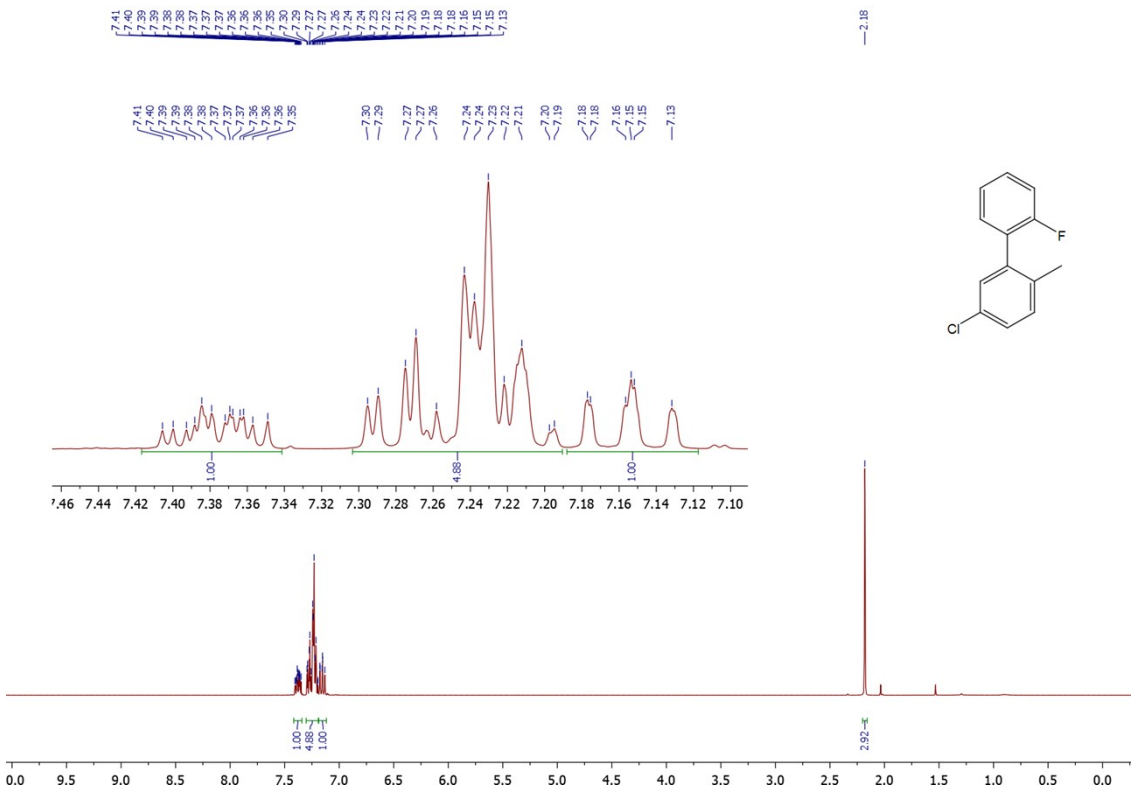


**Figure S37**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 5-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (**7b**).

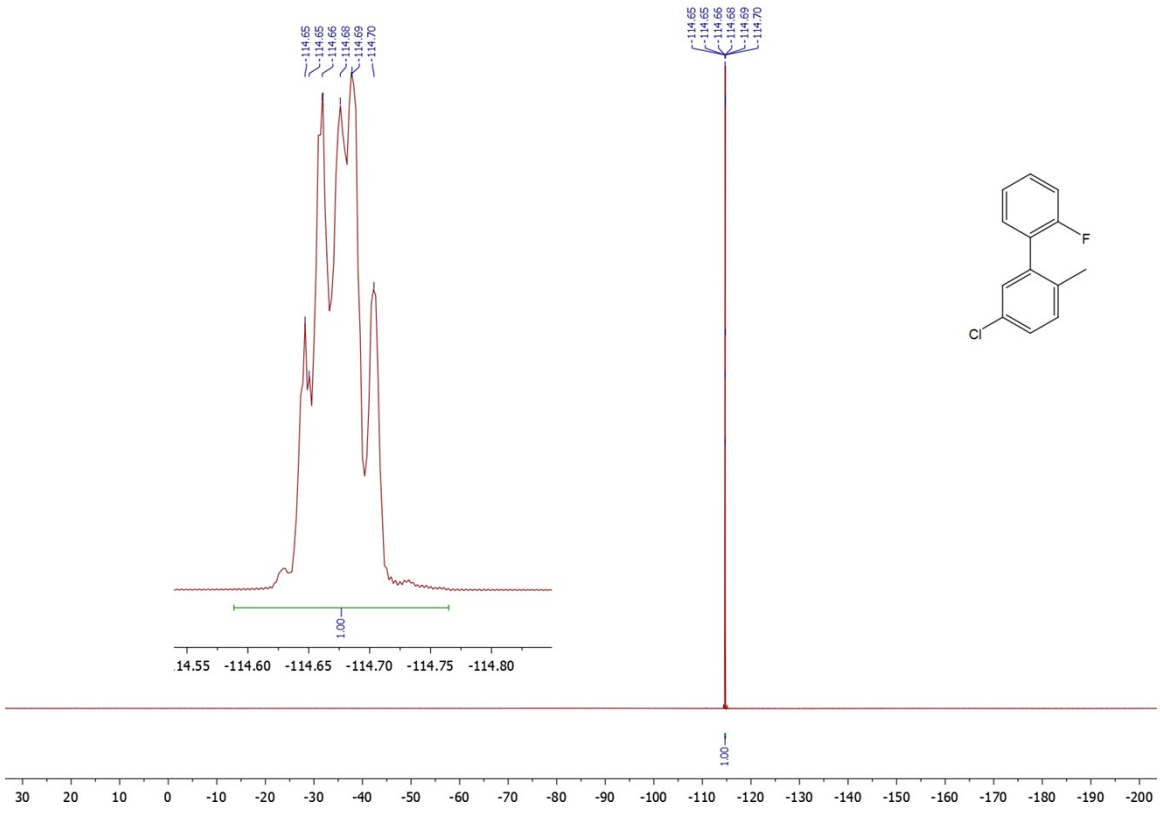


**Figure S38**. $^{19}F$ NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 5-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (**7b**).

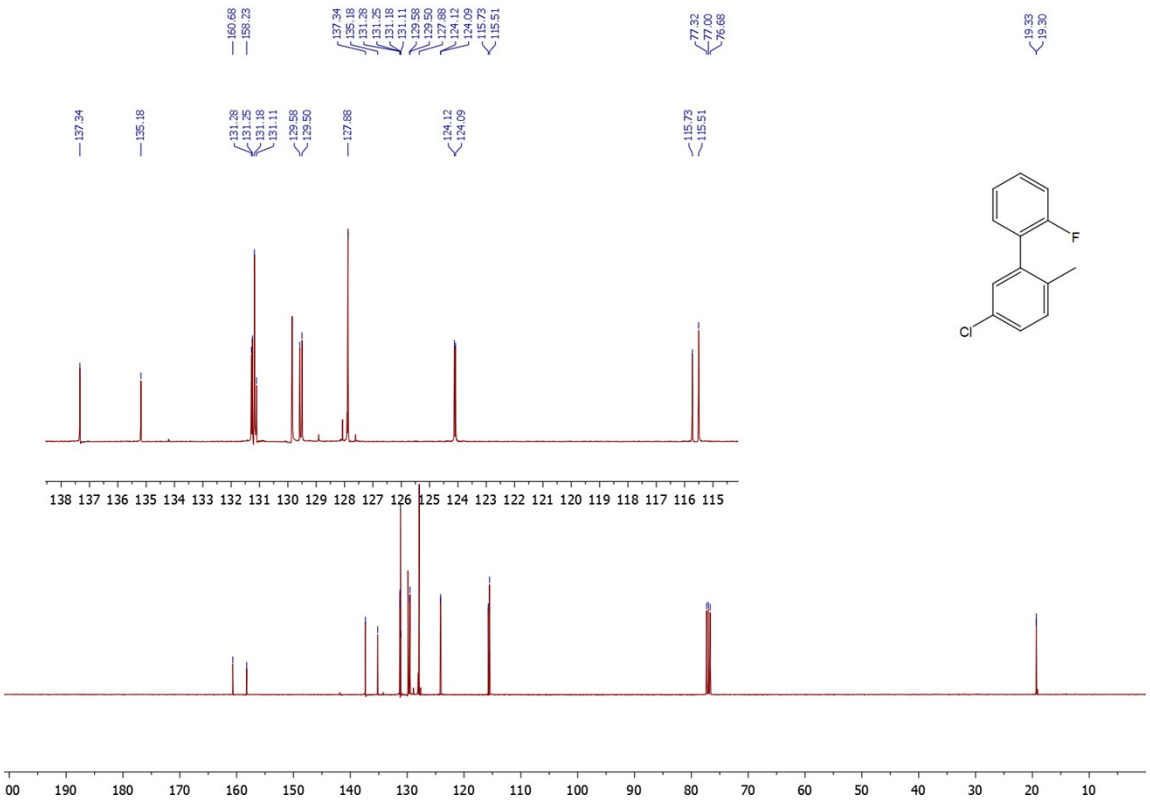


**Figure S39**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 5-chloro-2'-fluoro-2-methyl-1,1'-biphenyl (**7b**).

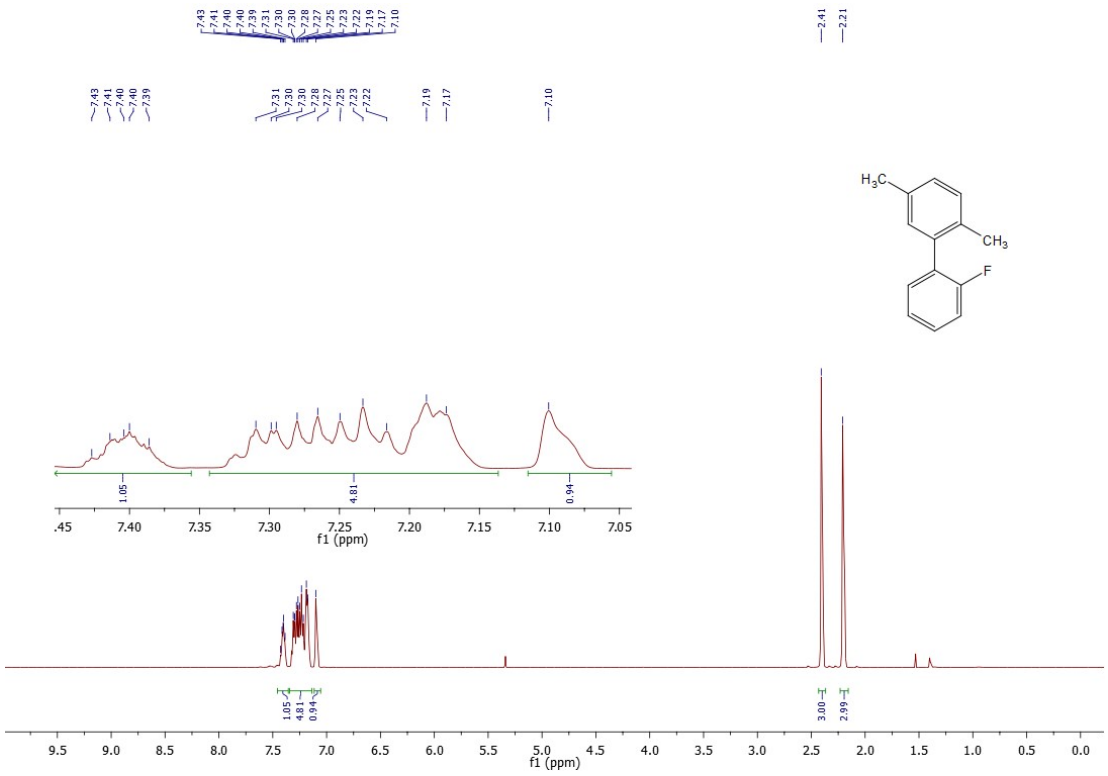


**Figure S40**. $^{1}H$ NMR (500 MHz, $CD_2Cl_2$, 293 K) spectrum of 2'-fluoro-2,5-dimethyl-1,1'-biphenyl (**8b**).

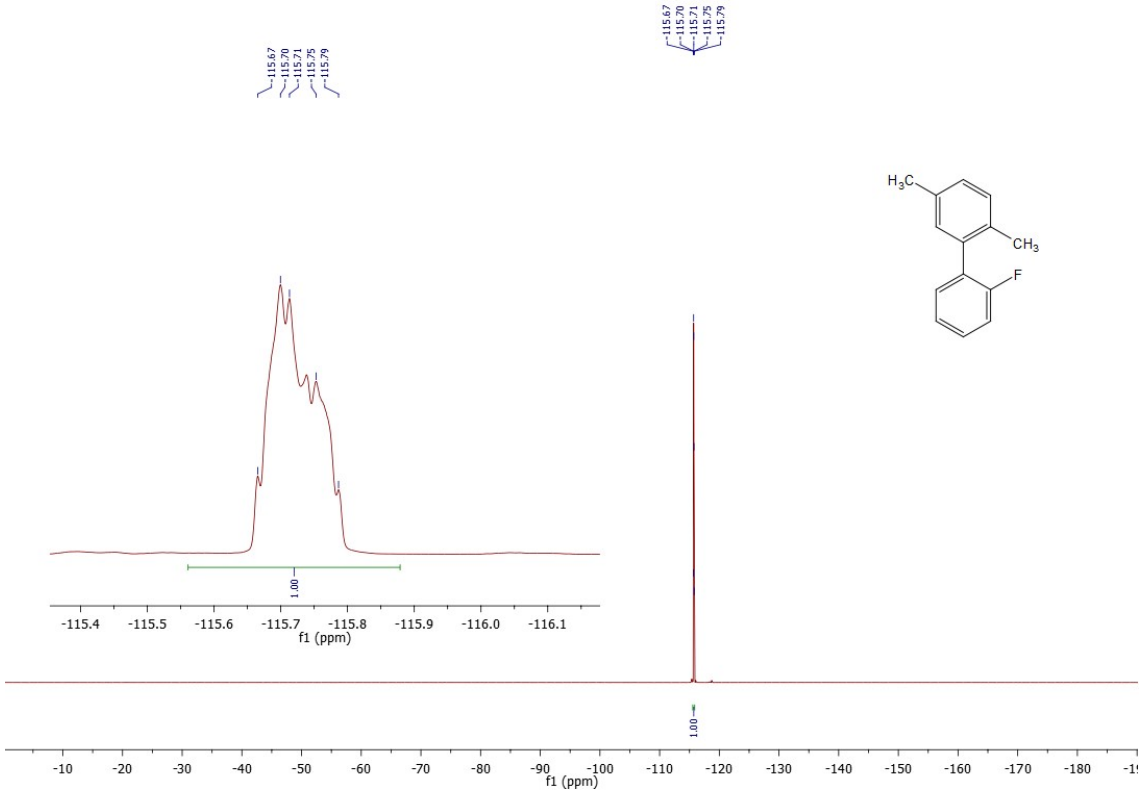


**Figure S41**. $^{19}F$ NMR (470 MHz, $CD_2Cl_2$, 293 K) spectrum of 2'-fluoro-2,5-dimethyl-1,1'-biphenyl (**8b**).

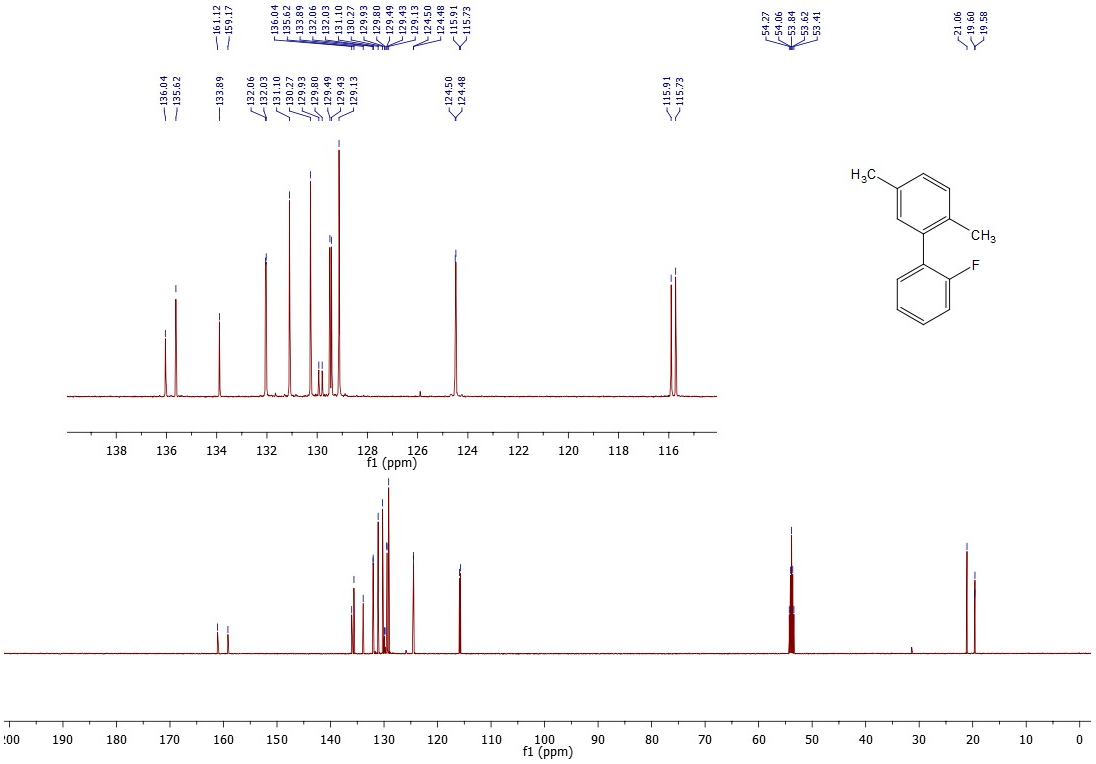


**Figure S42**. $^{13}C$ NMR (126 MHz, $CD_2Cl_2$, 293 K) spectrum of 2'-fluoro-2,5-dimethyl-1,1'-biphenyl (**8b**).

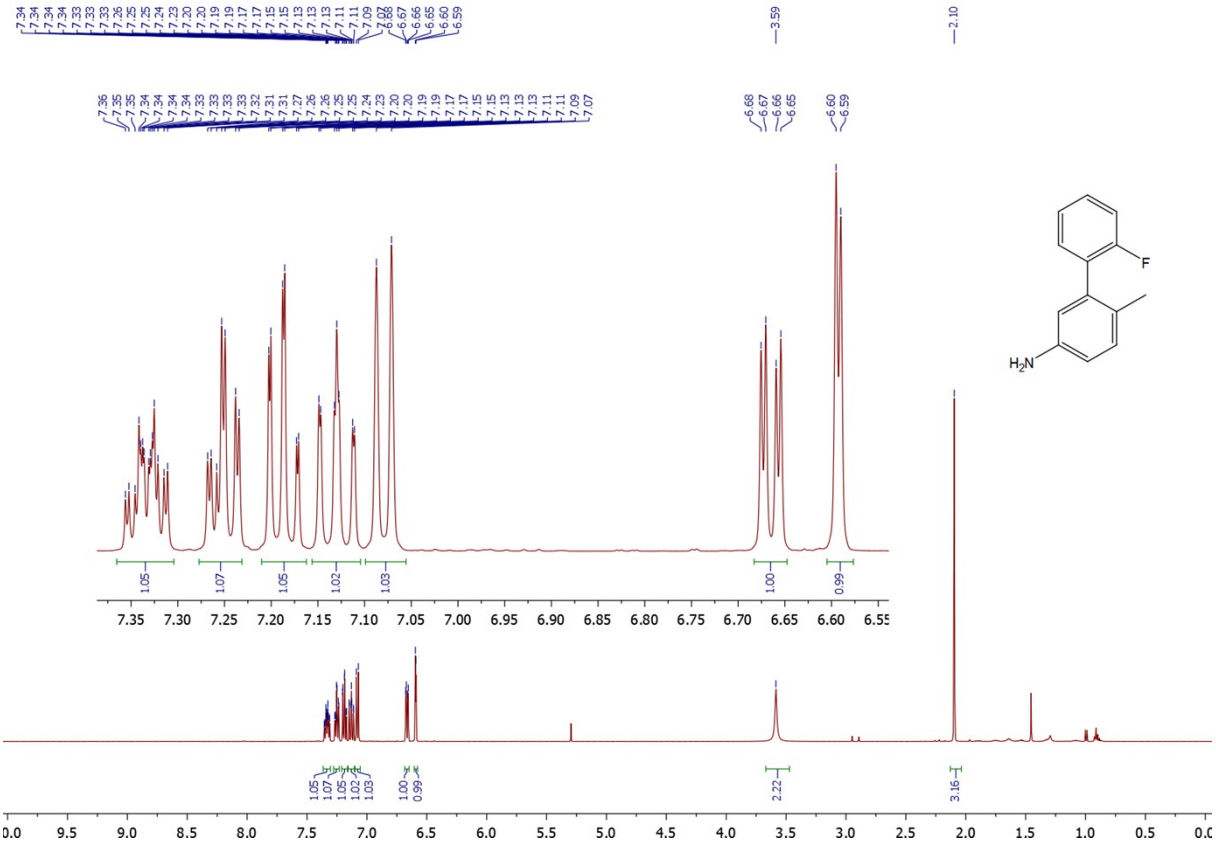


**Figure S43**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-6-methyl-[1,1'-biphenyl]-3-amine (**10a**).

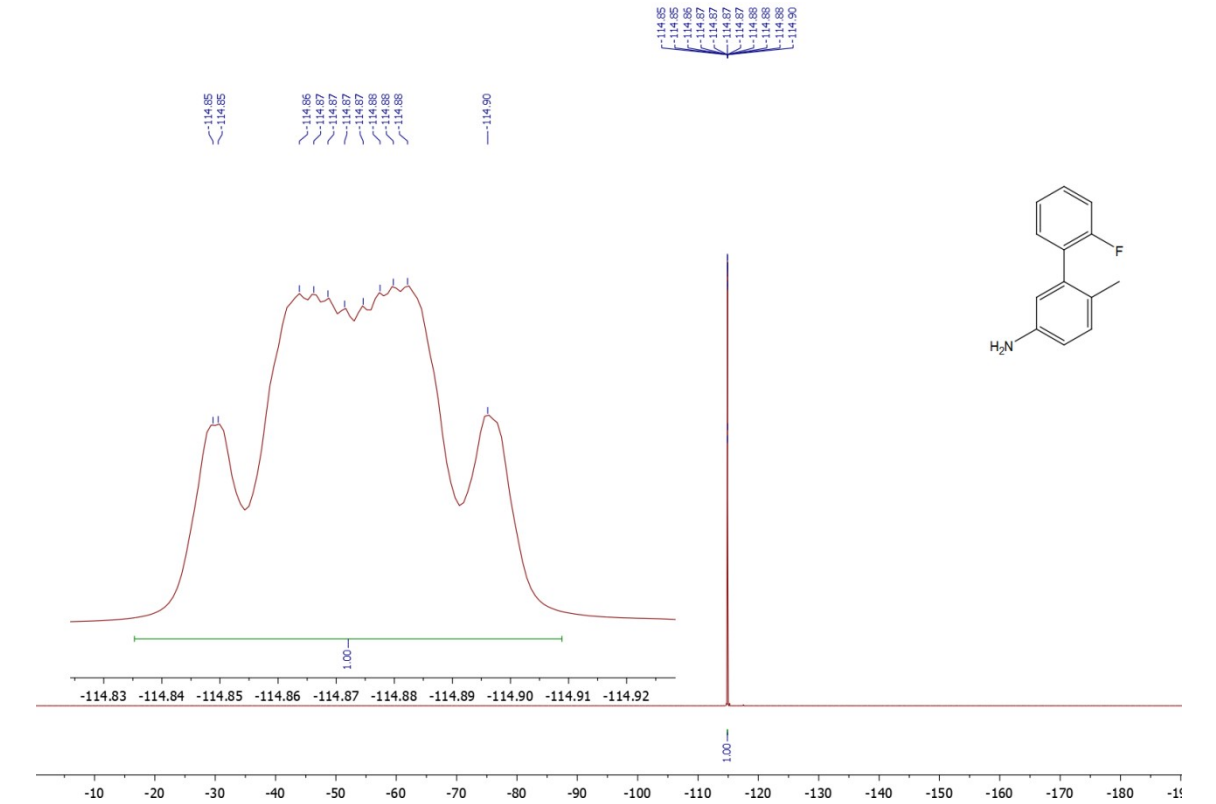


**Figure S44**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-6-methyl-[1,1'-biphenyl]-3-amine (**10a**).

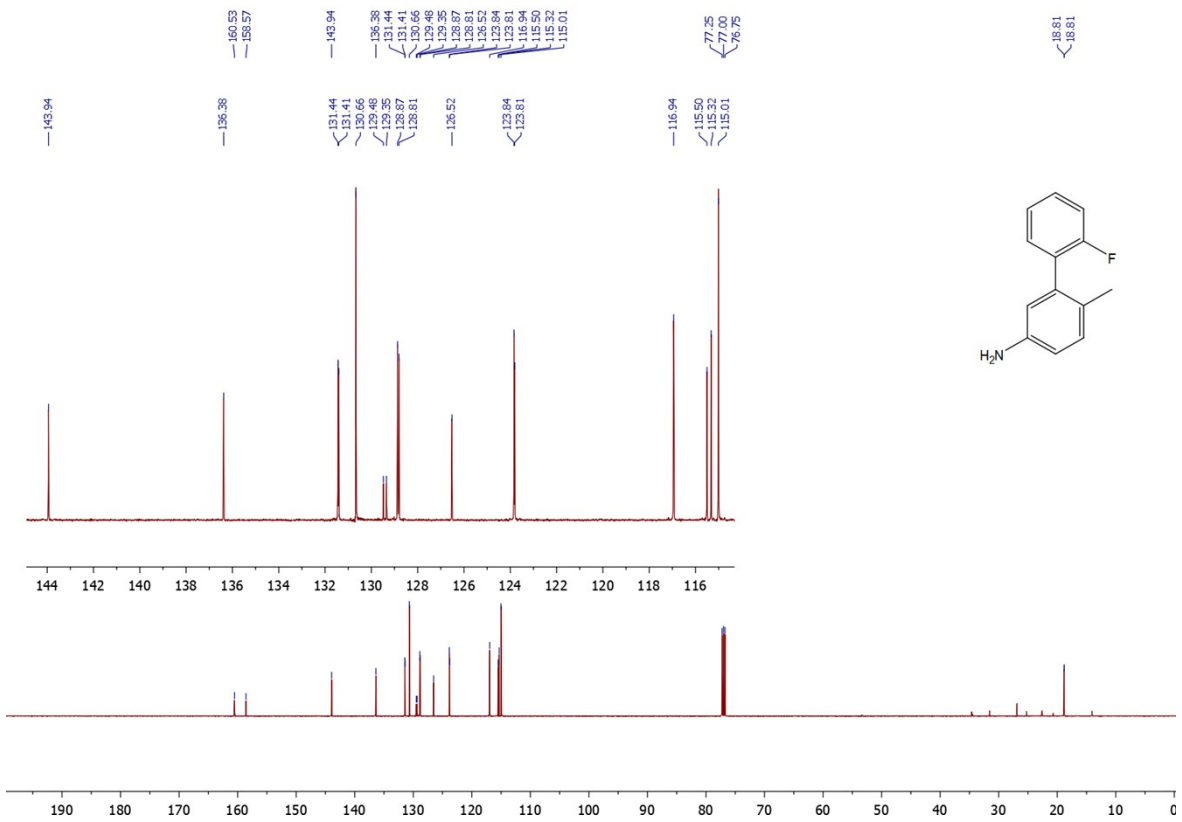

**Figure S45**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-6-methyl-[1,1'-biphenyl]-3-amine (**10a**).

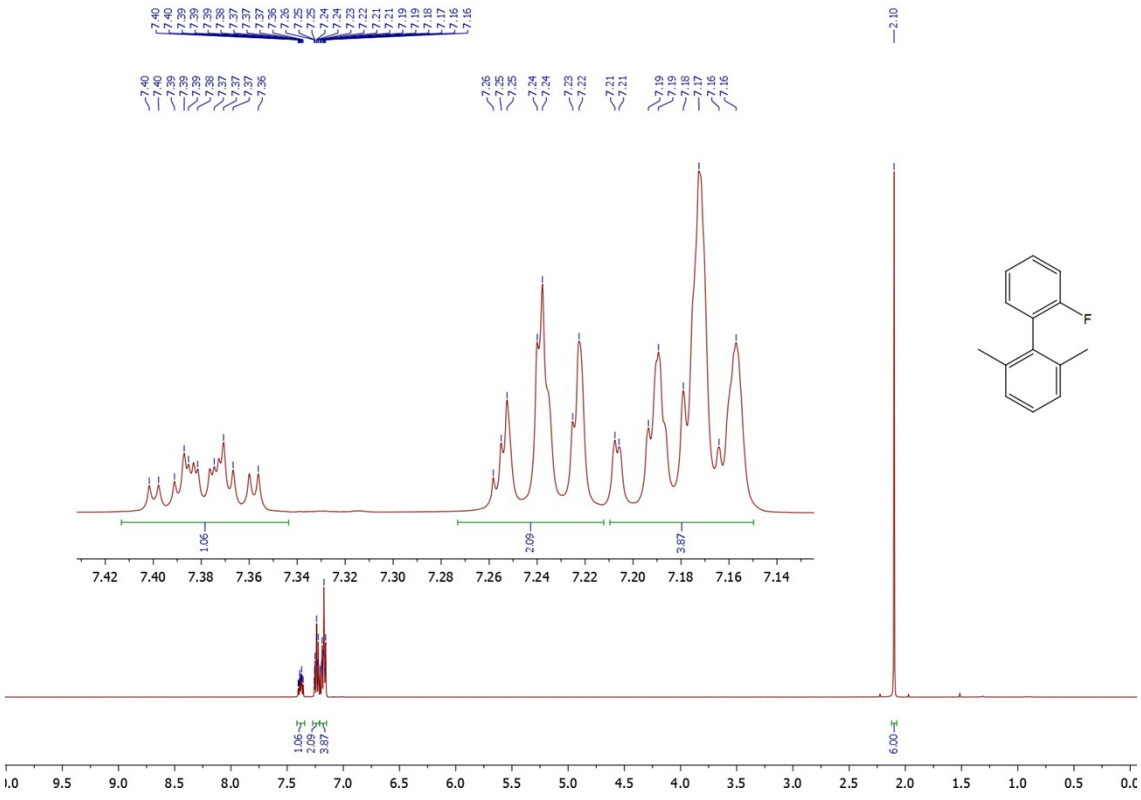

**Figure S46**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-2,6-dimethyl-1,1'-biphenyl (**11a**).

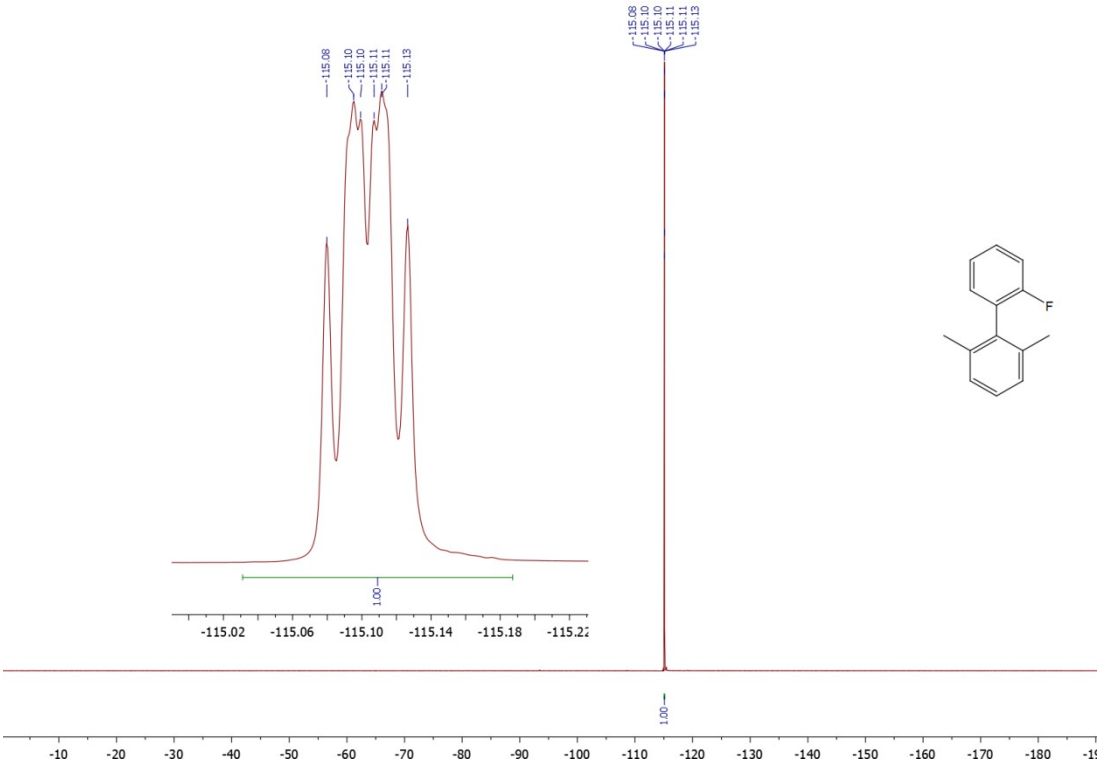


**Figure S47**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-2,6-dimethyl-1,1'-biphenyl (**11a**).

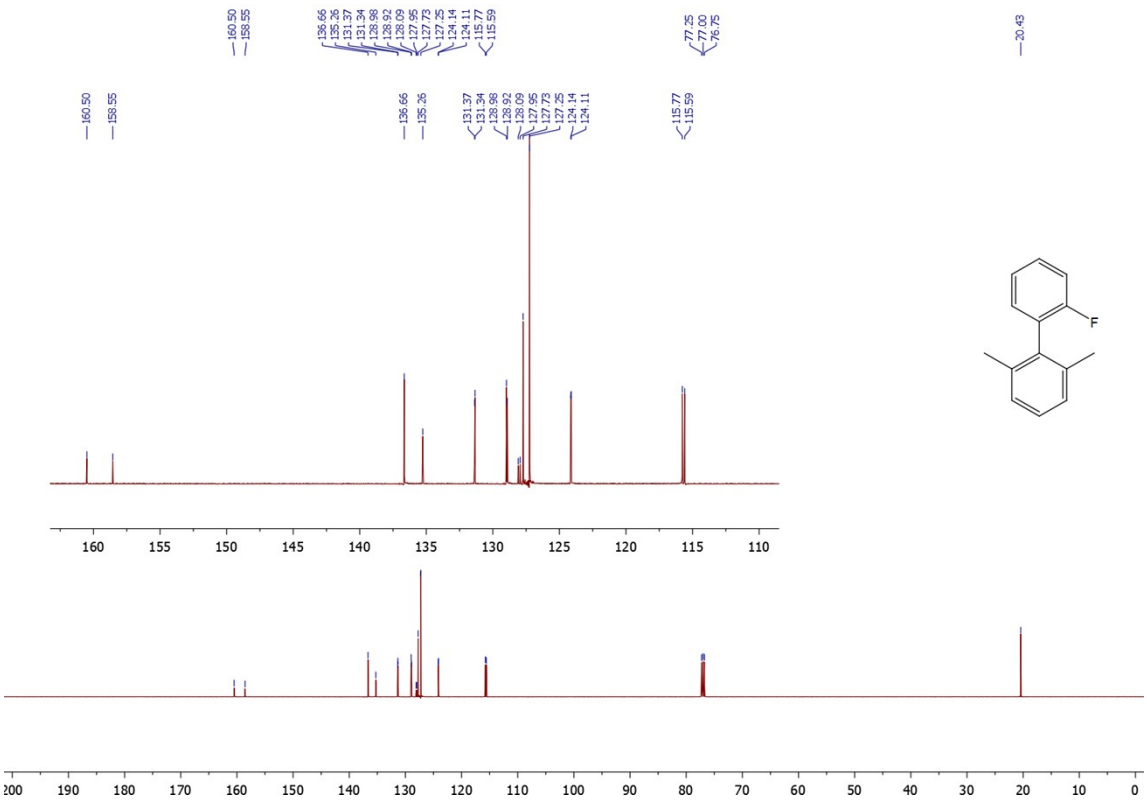


**Figure S48**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2'-fluoro-2,6-dimethyl-1,1'-biphenyl (**11a**).

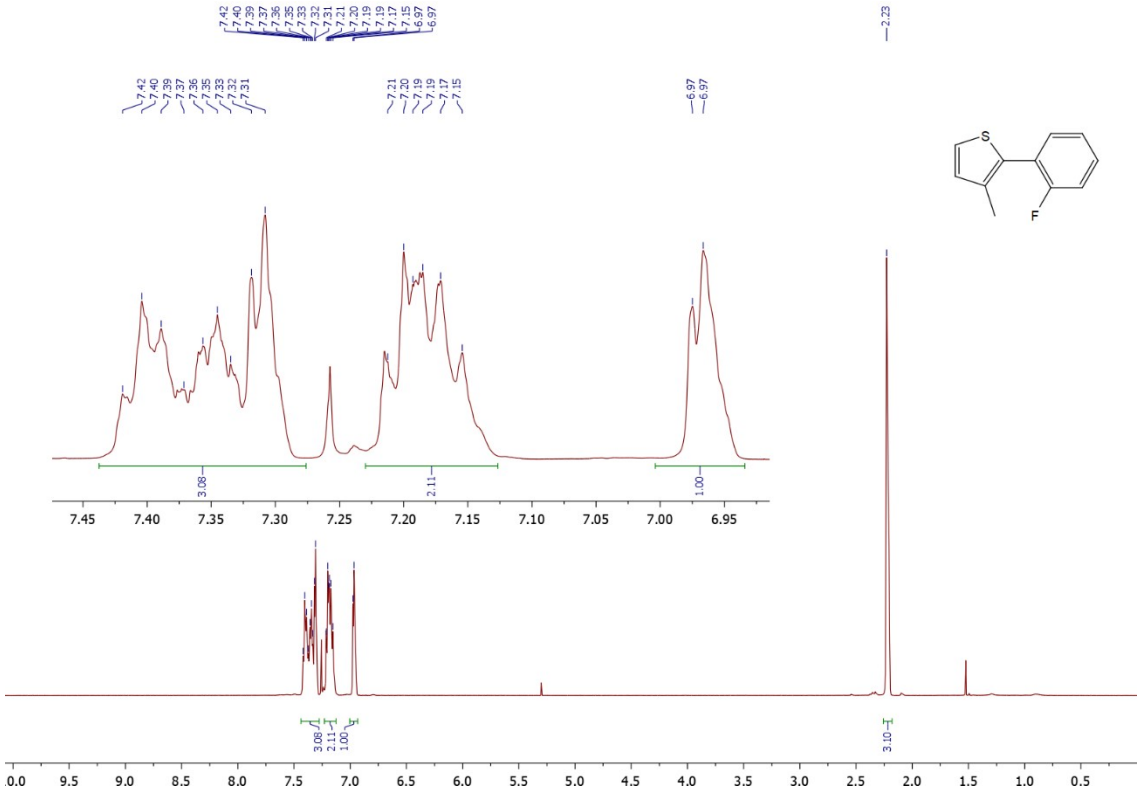

**Figure S49**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-(2-fluorophenyl)-3-methylthiophene (**12a**).

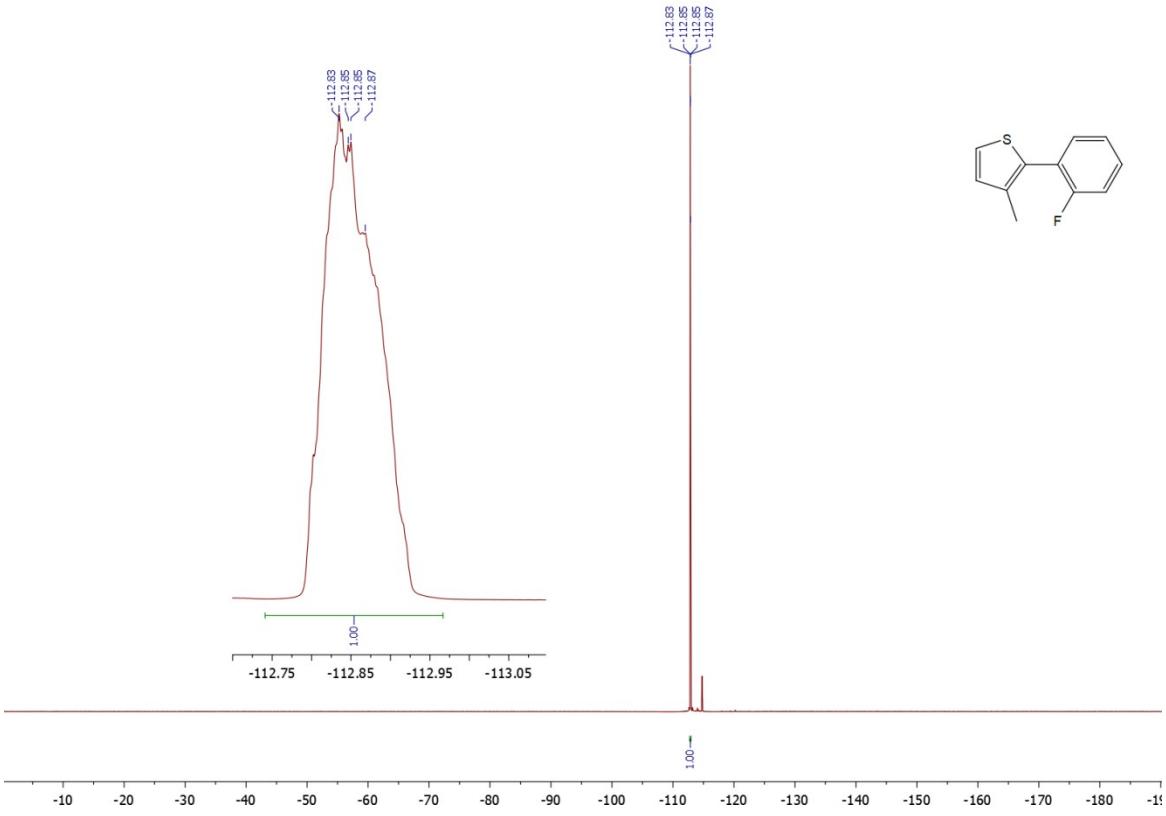

**Figure S50**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2-(2-fluorophenyl)-3-methylthiophene (**12a**).

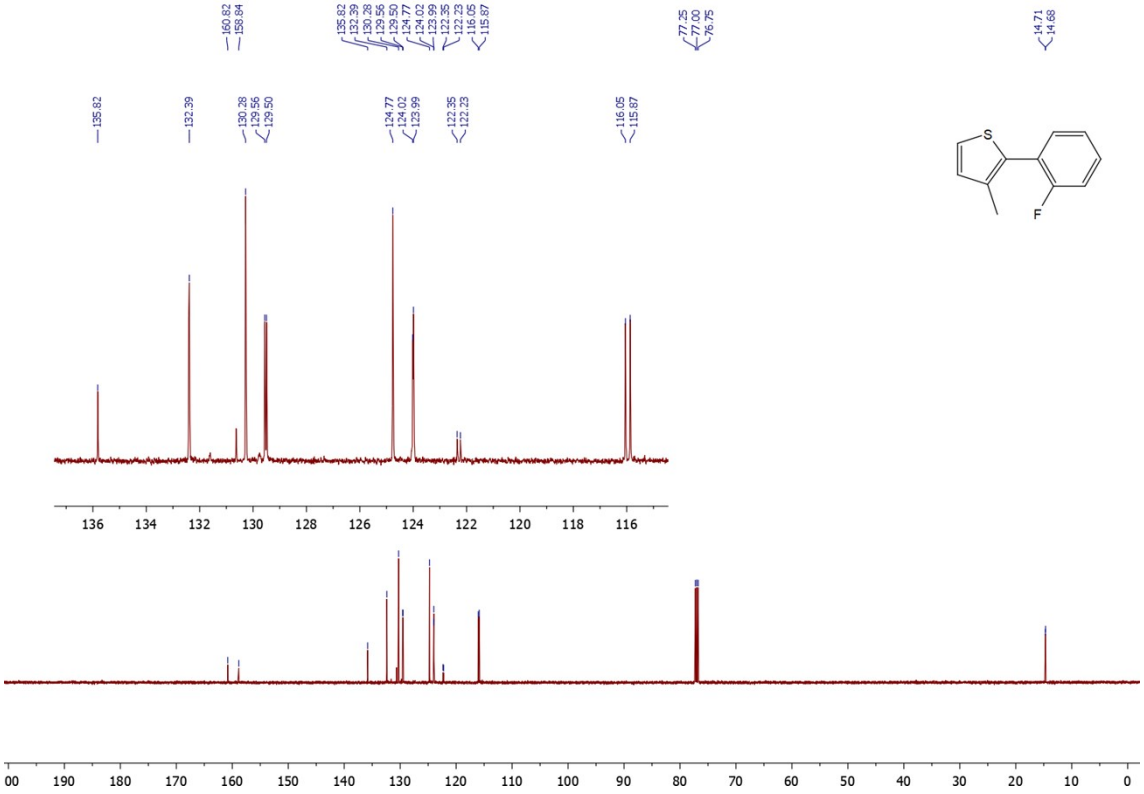


**Figure S51**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-(2-fluorophenyl)-3-methylthiophene (**12a**).

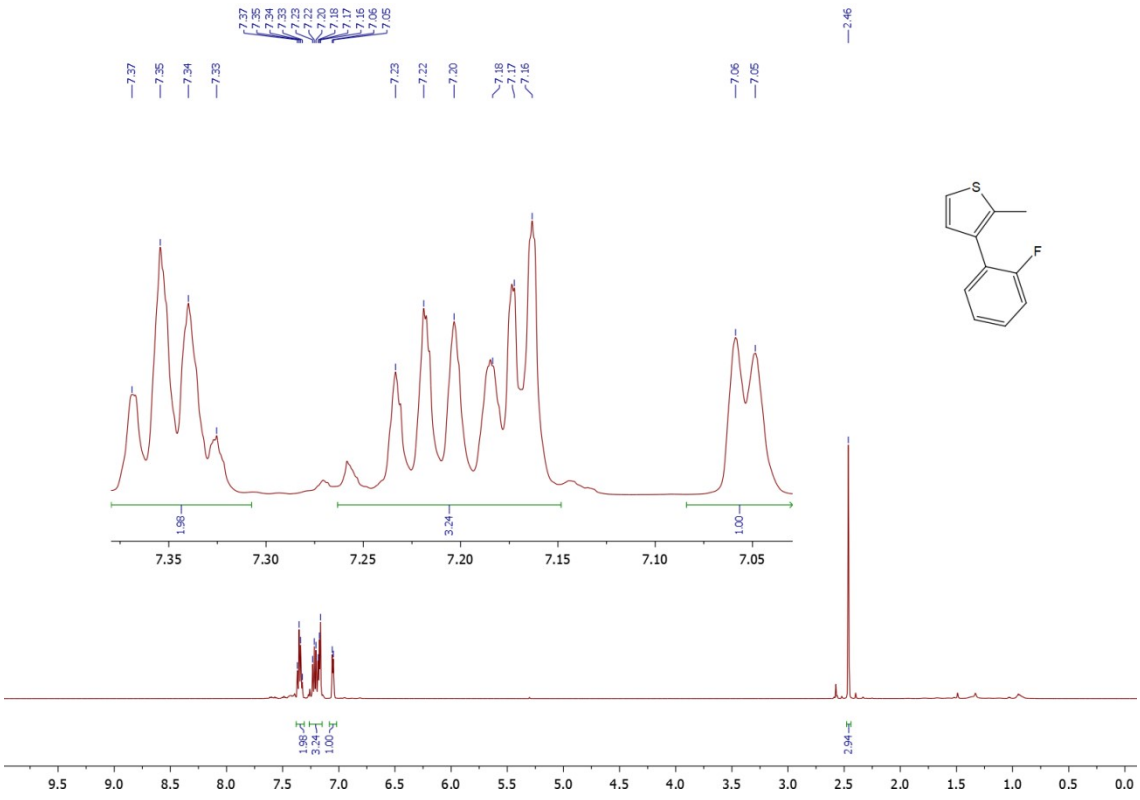


**Figure S52**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 3-(2-fluorophenyl)-2-methylthiophene (**13a**).

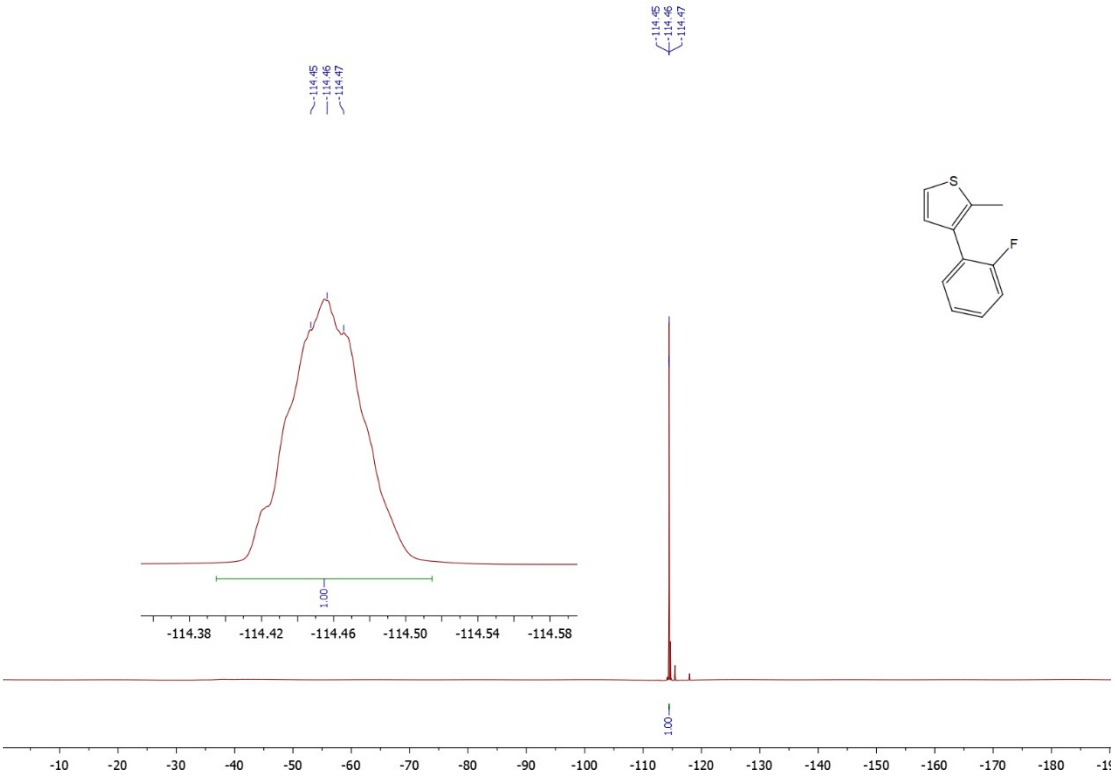


**Figure S53**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 3-(2-fluorophenyl)-2-methylthiophene (**13a**).

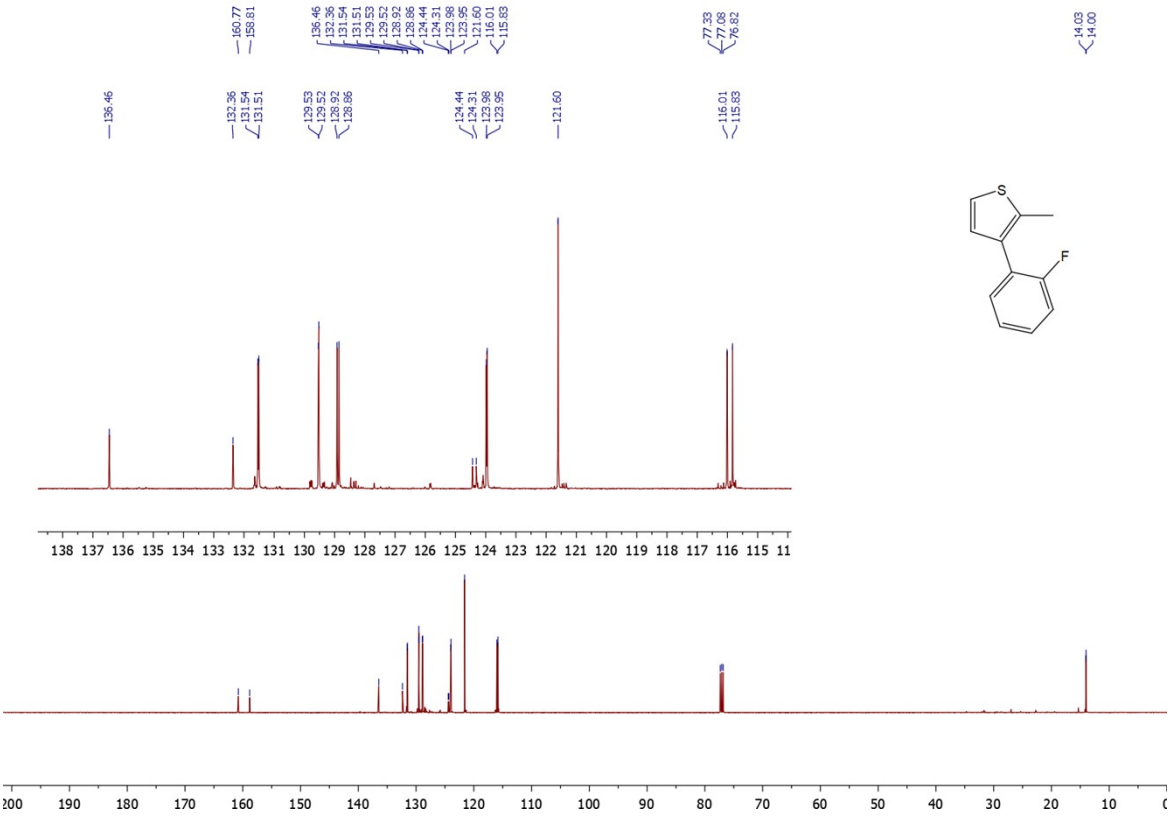


**Figure S54** $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 3-(2-fluorophenyl)-2-methylthiophene (**13a**).

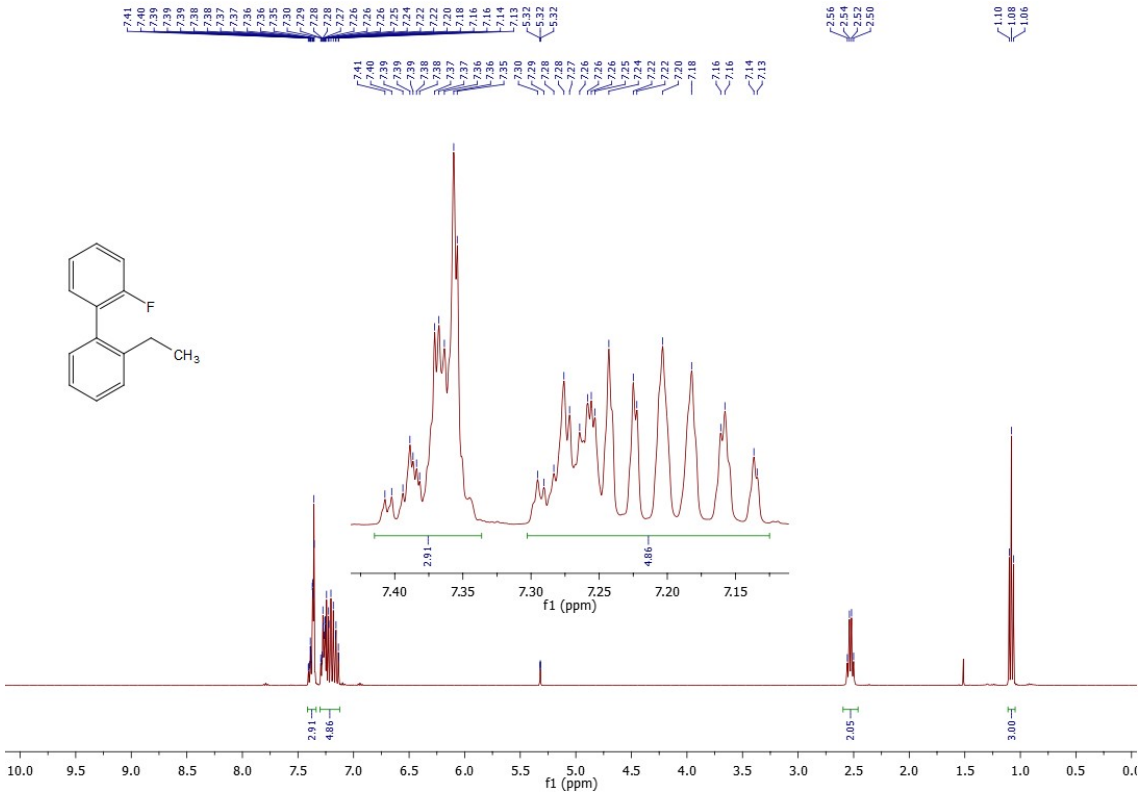


**Figure S55**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 293 K) spectrum of 2-ethyl-2'-fluoro-1,1'-biphenyl (**14a**).

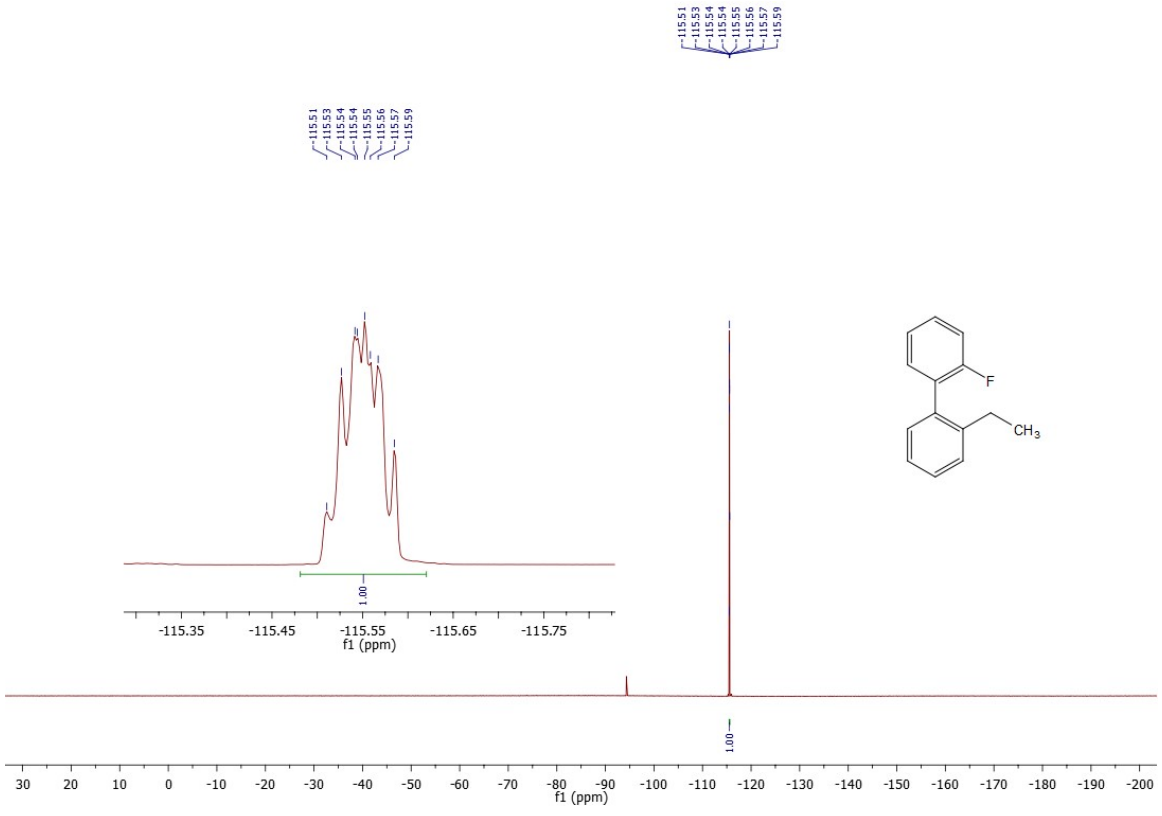


**Figure S56**. $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K) spectrum of 2-ethyl-2'-fluoro-1,1'-biphenyl (**14a**).

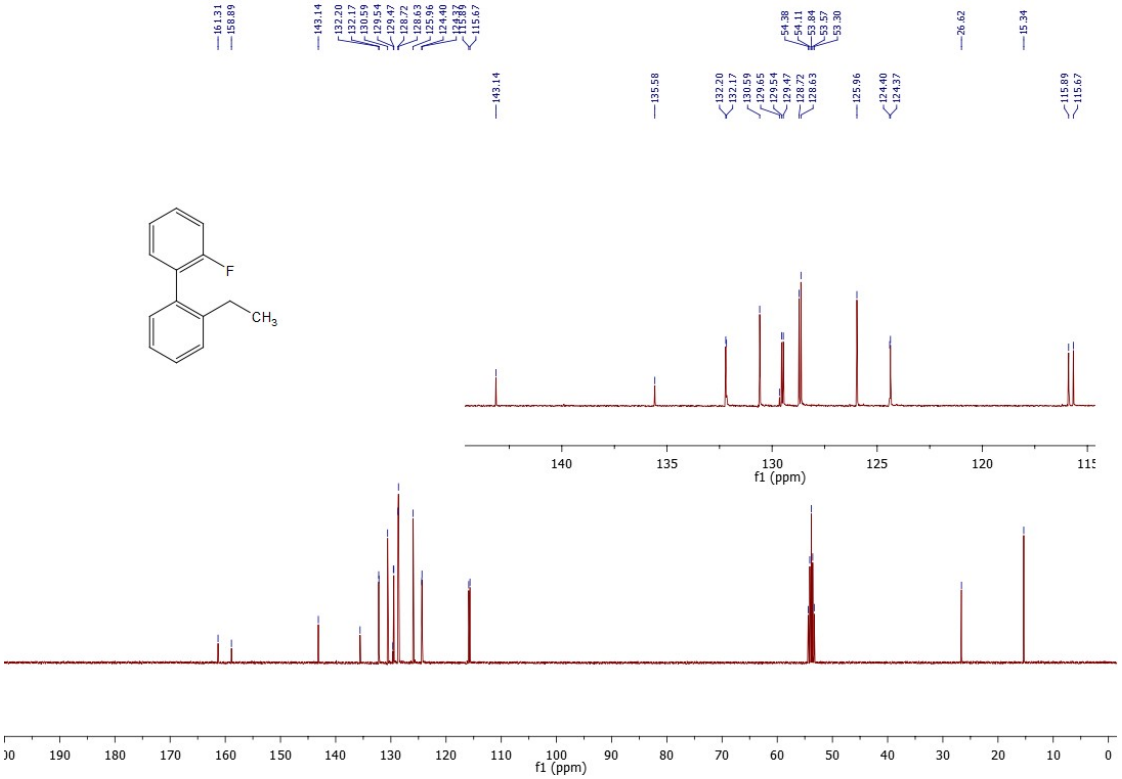


**Figure S57**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$, 293 K) spectrum of 2-ethyl-2'-fluoro-1,1'-biphenyl (**14a**).

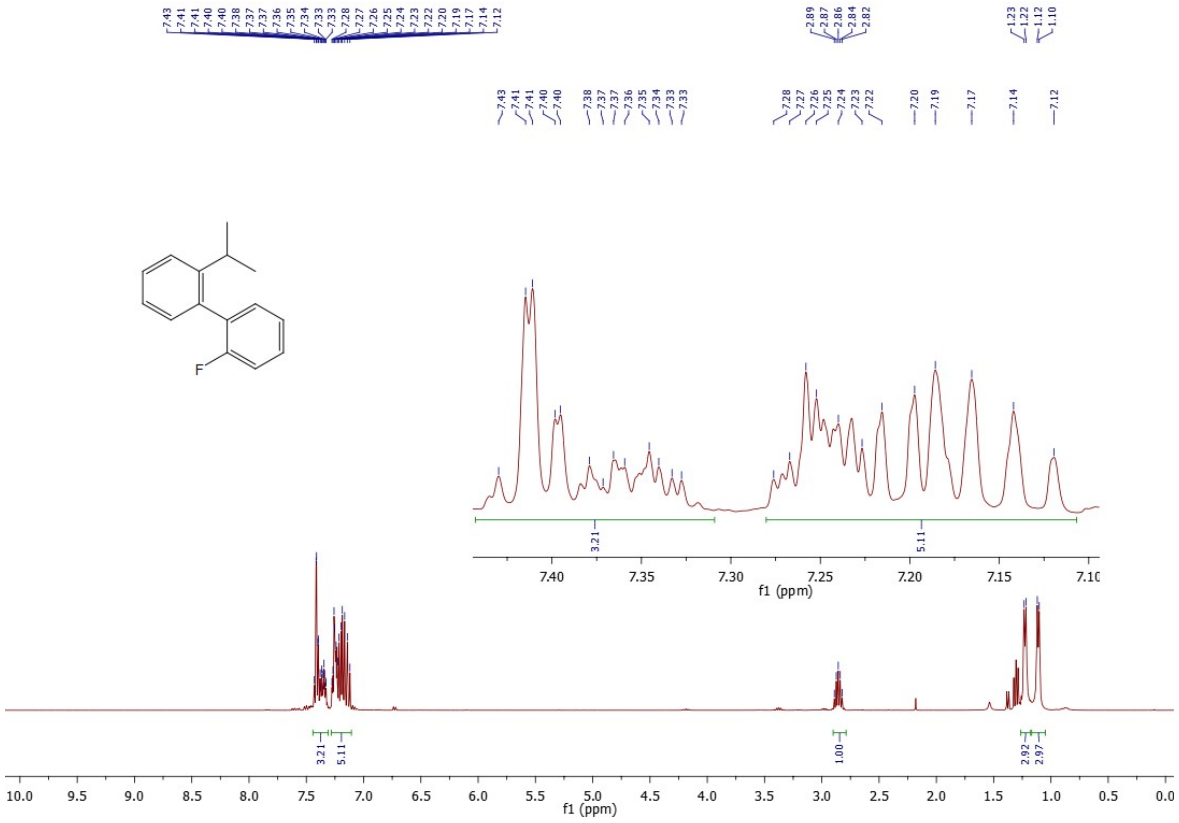


**Figure S58**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2'-isopropyl-1,1'-biphenyl (**15a**).

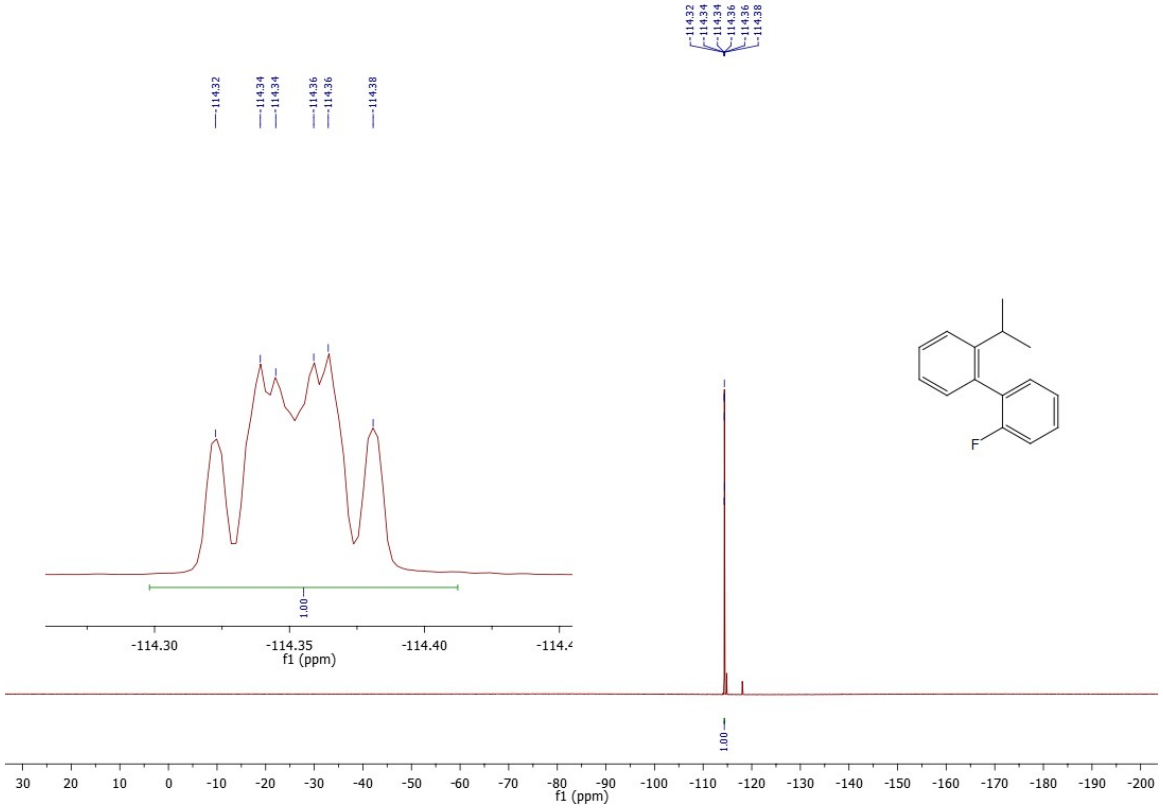


**Figure S59**. $^{19}F$ NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2'-isopropyl-1,1'-biphenyl (**15a**).

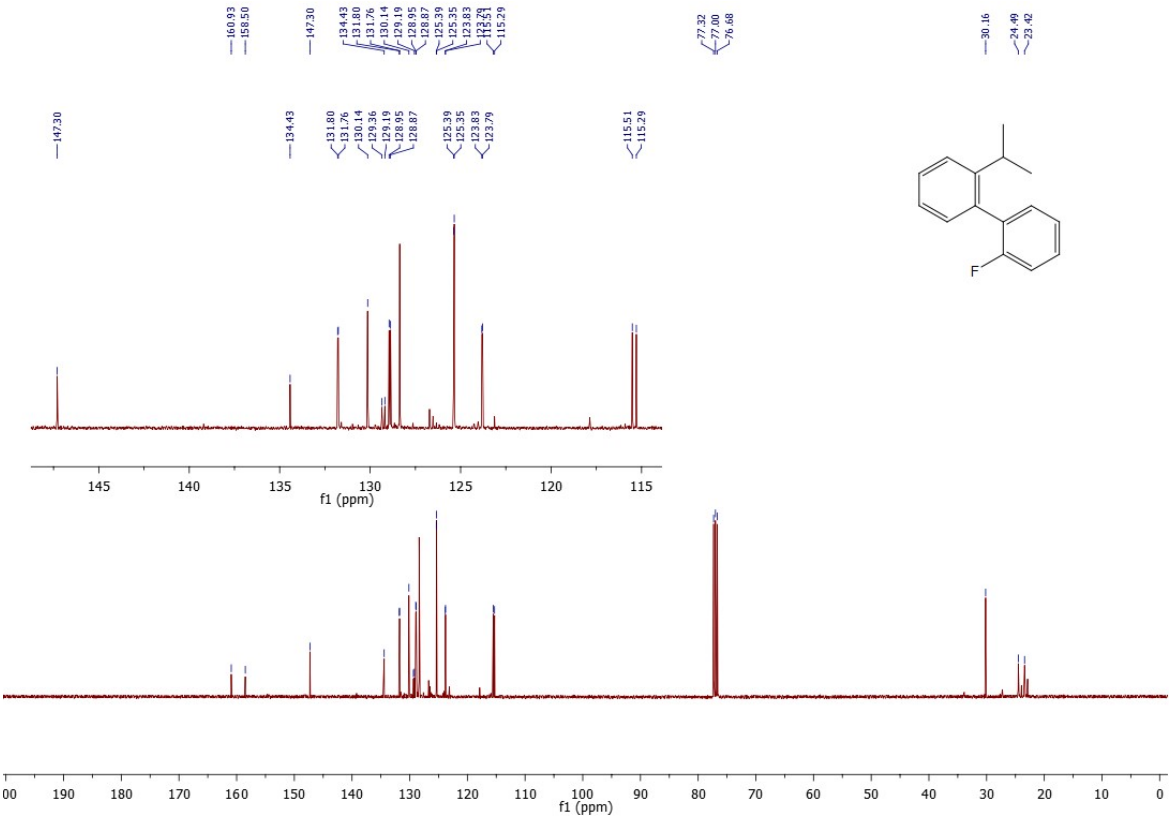


**Figure S60**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-2'-isopropyl-1,1'-biphenyl (**15a**).

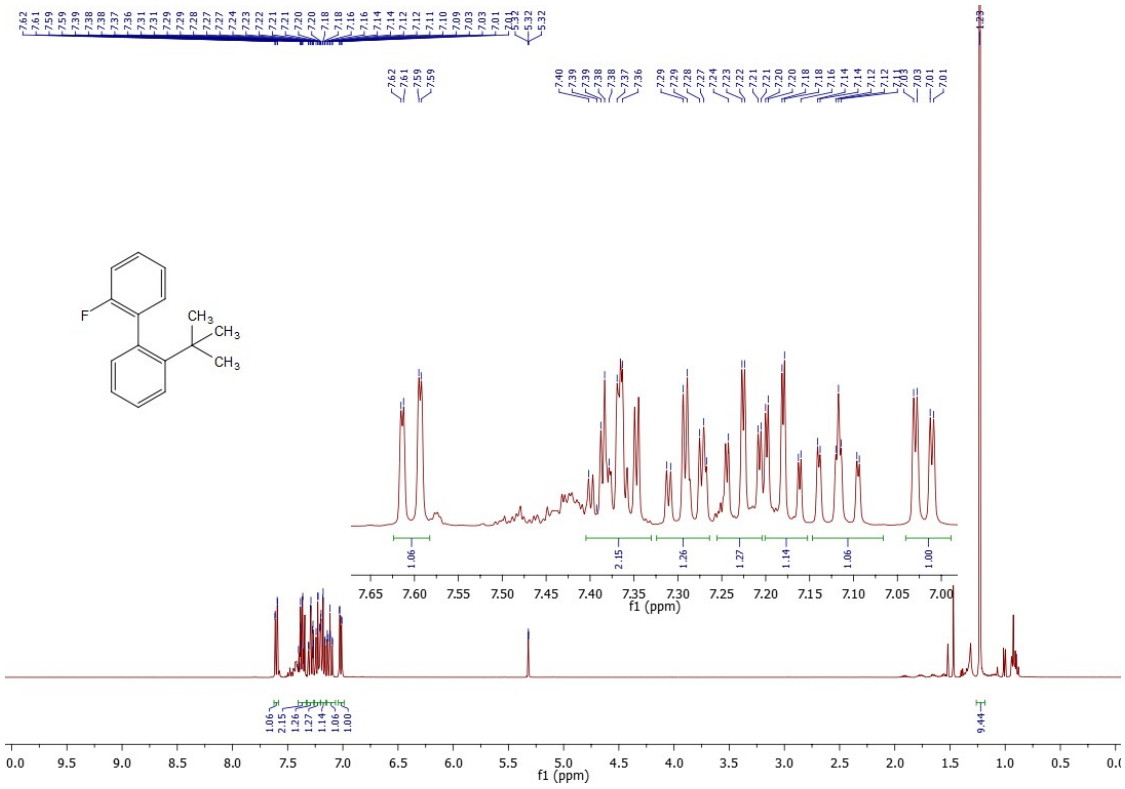


**Figure S61**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 293 K) spectrum of 2-(tert-butyl)-2'-fluoro-1,1'-biphenyl (**16a**).

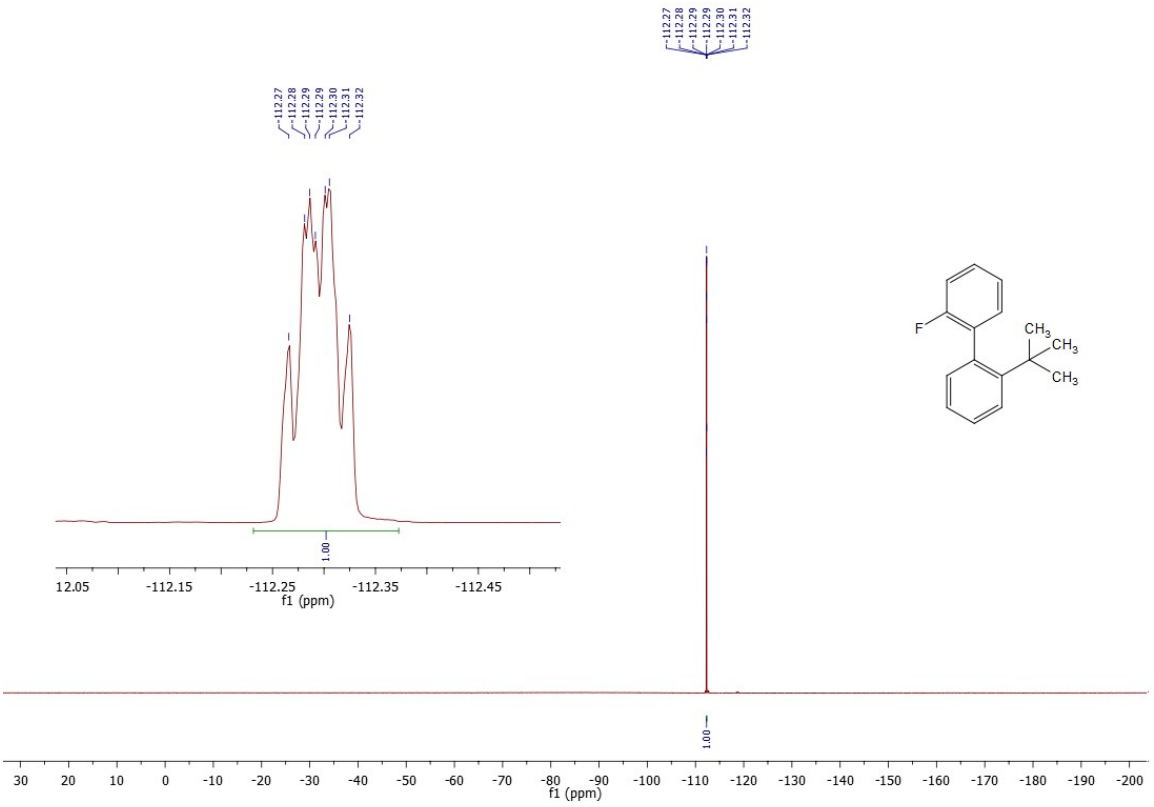


**Figure S62**. $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K) spectrum of 2-(tert-butyl)-2'-fluoro-1,1'-biphenyl (**16a**).

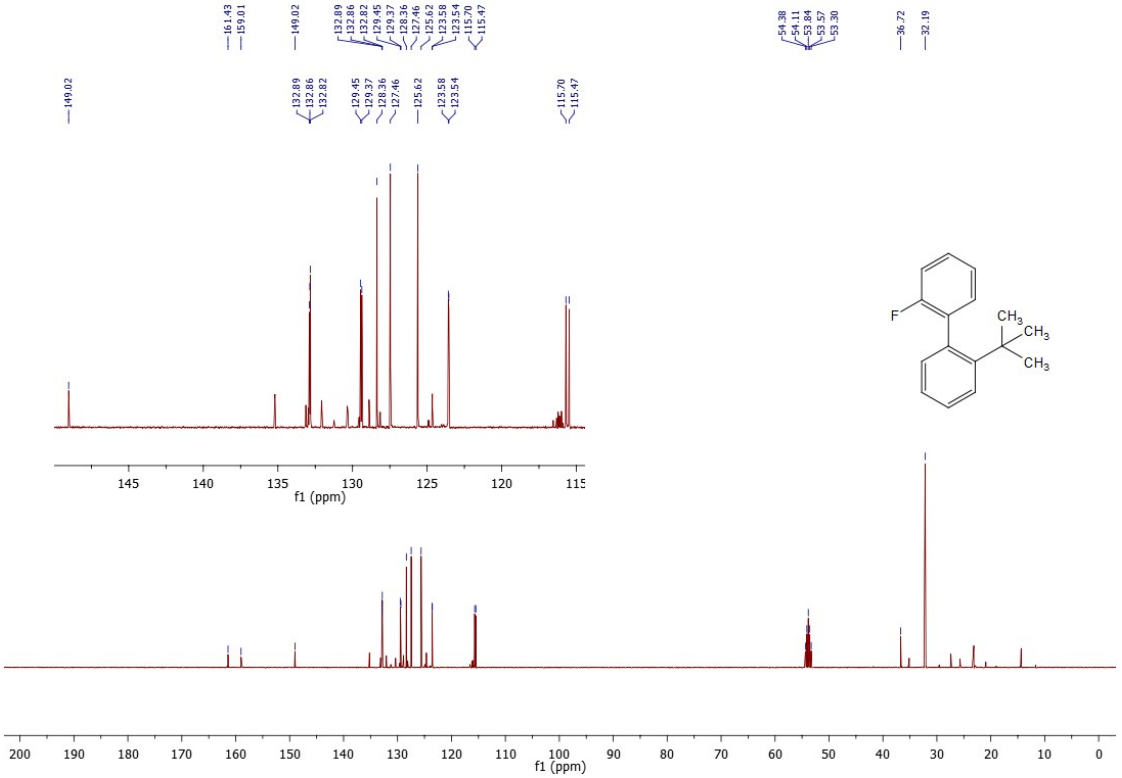


**Figure S63**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$, 293 K) spectrum of 2-(tert-butyl)-2'-fluoro-1,1'-biphenyl (**16a**).

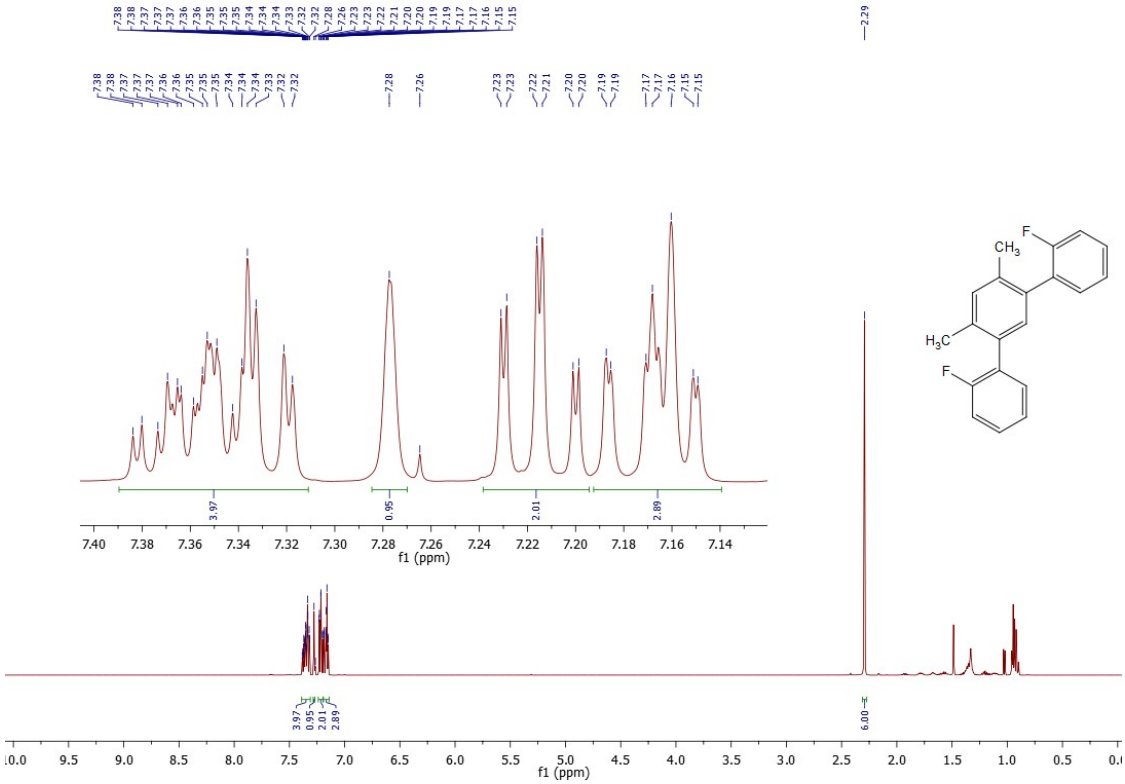


**Figure S64**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2,2''-difluoro-4',6'-dimethyl-1,1':3',1''-terphenyl (**17a**).

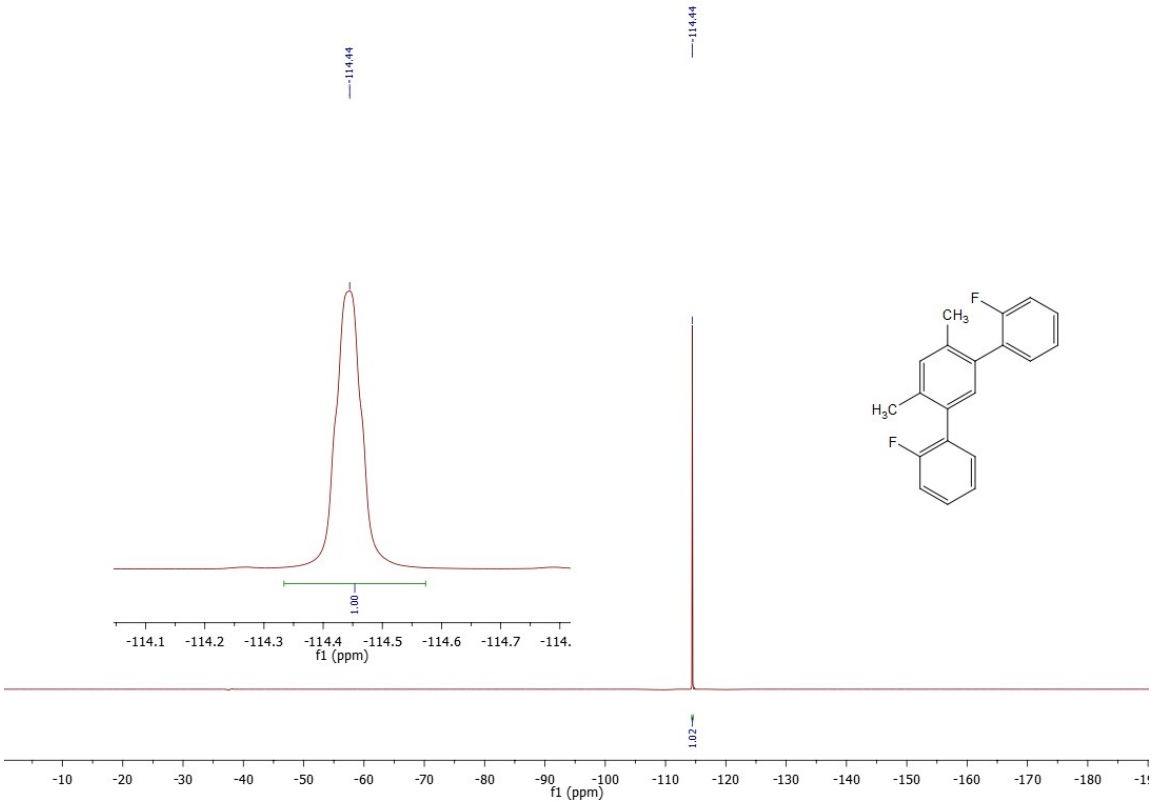


**Figure S65**. $^{19}F$ NMR (476 MHz, $CDCl_3$, 293 K) spectrum of 2,2''-difluoro-4',6'-dimethyl-1,1':3',1''-terphenyl (**17a**).

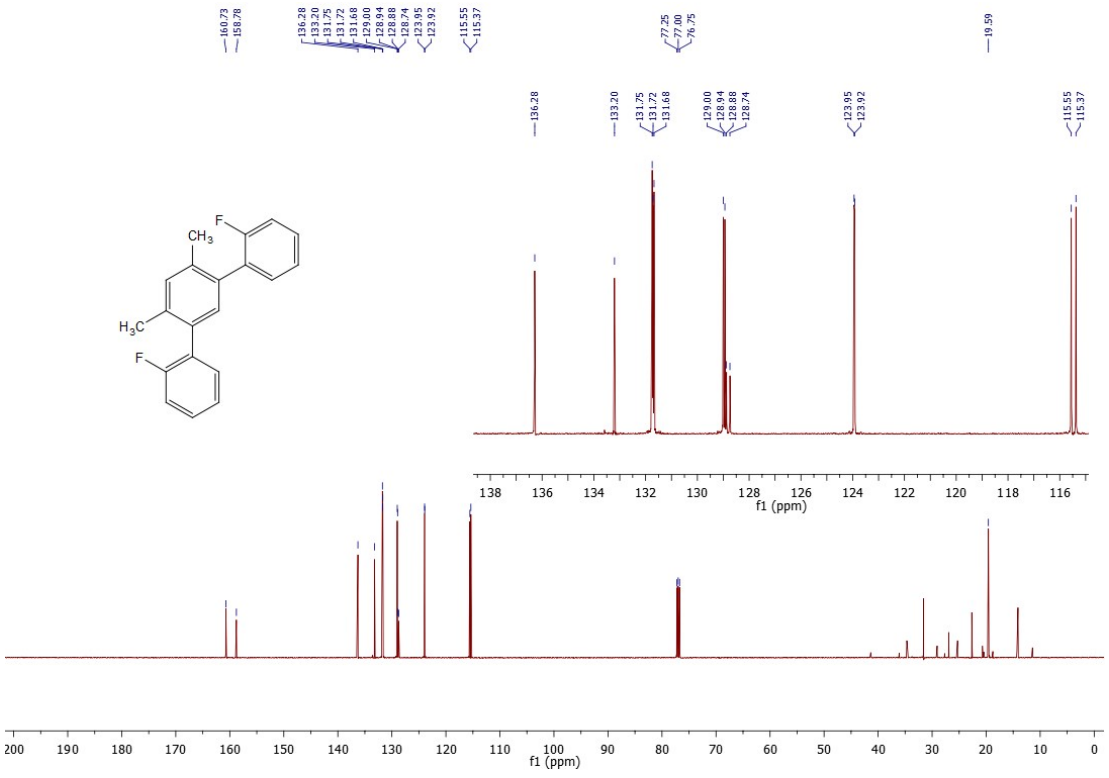


**Figure S66**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2,2''-difluoro-4',6'-dimethyl-1,1':3',1''-terphenyl (**17a**).

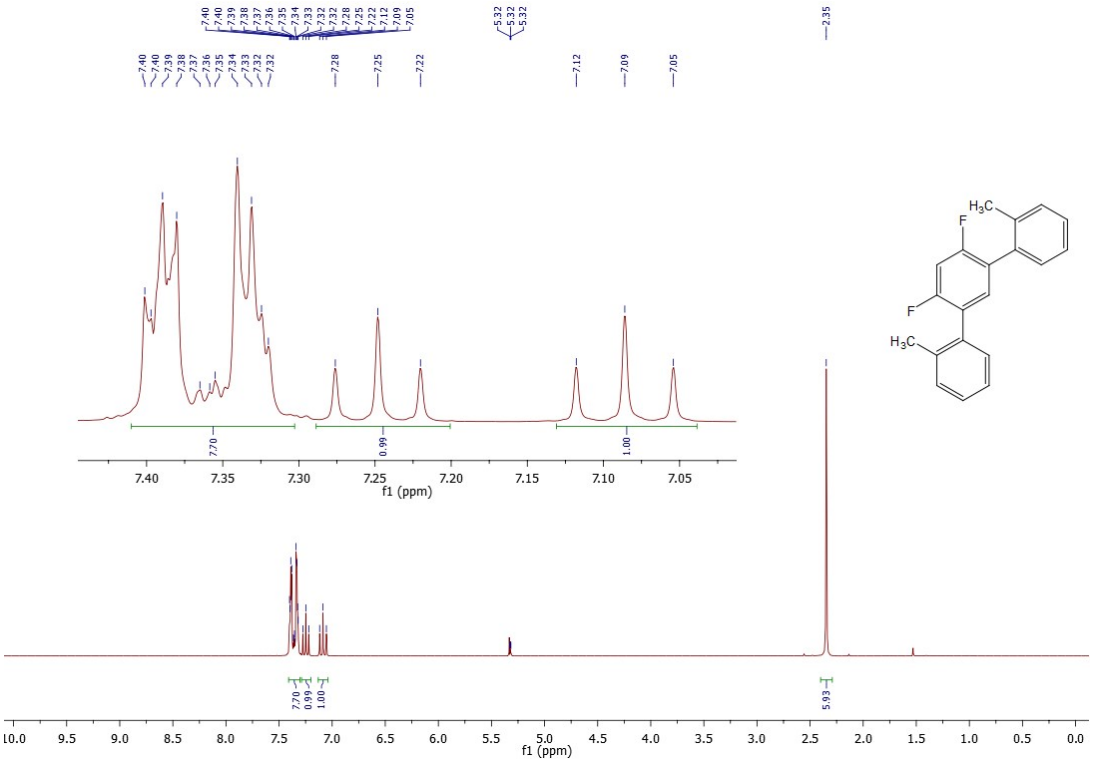


**Figure S67**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$, 293 K) spectrum of 4',6'-difluoro-2,2''-dimethyl-1,1':3',1''-terphenyl (**17b**).

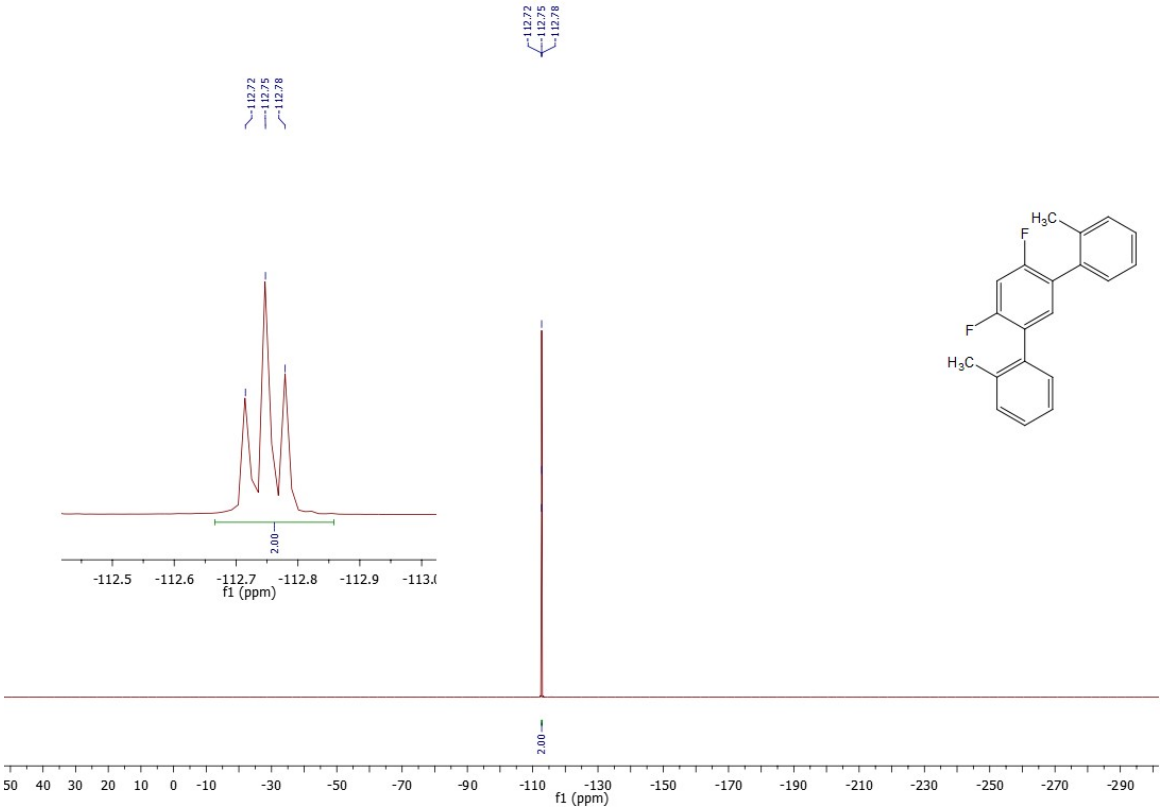


**Figure S68**. $^{19}F$ NMR (283 MHz, $CD_2Cl_2$, 293 K) spectrum of 4',6'-difluoro-2,2''-dimethyl-1,1':3',1''-terphenyl (**17b**).

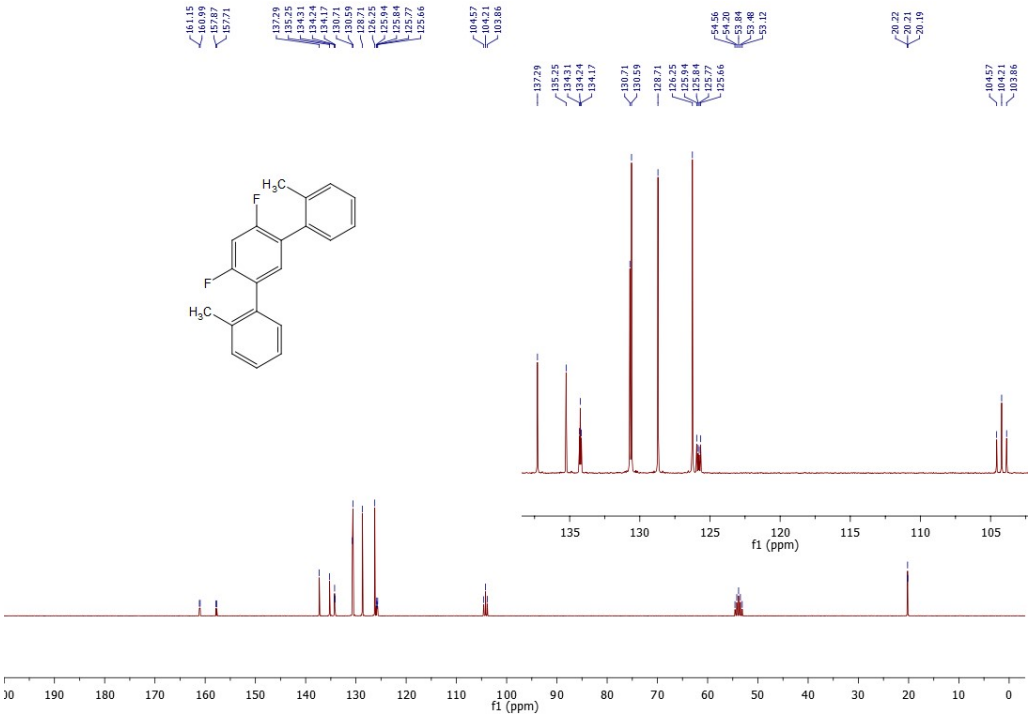


**Figure S69**. $^{13}C$ NMR (76 MHz, $CD_2Cl_2$, 293 K) spectrum of 4',6'-difluoro-2,2''-dimethyl-1,1':3',1''-terphenyl (**17b**).

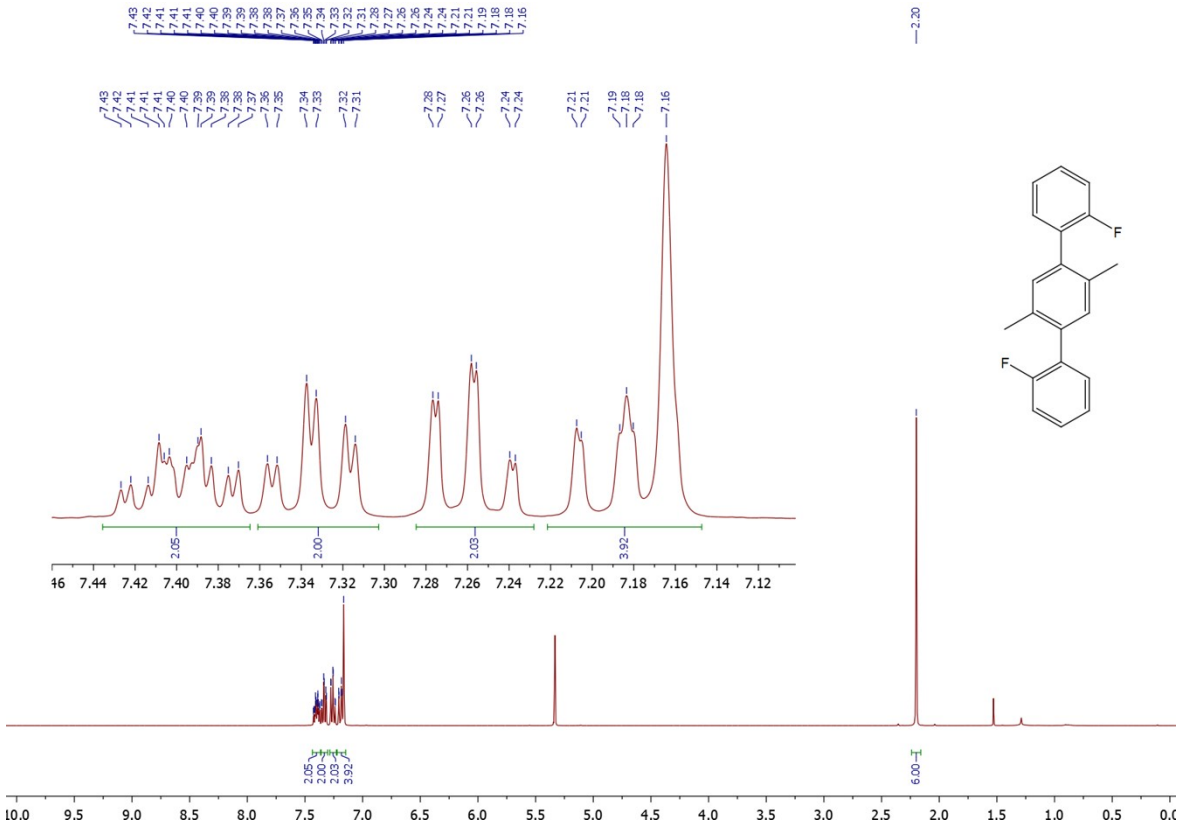


**Figure S70**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,2''-difluoro-2',5'-dimethyl-1,1':4',1''-terphenyl (**18a**).

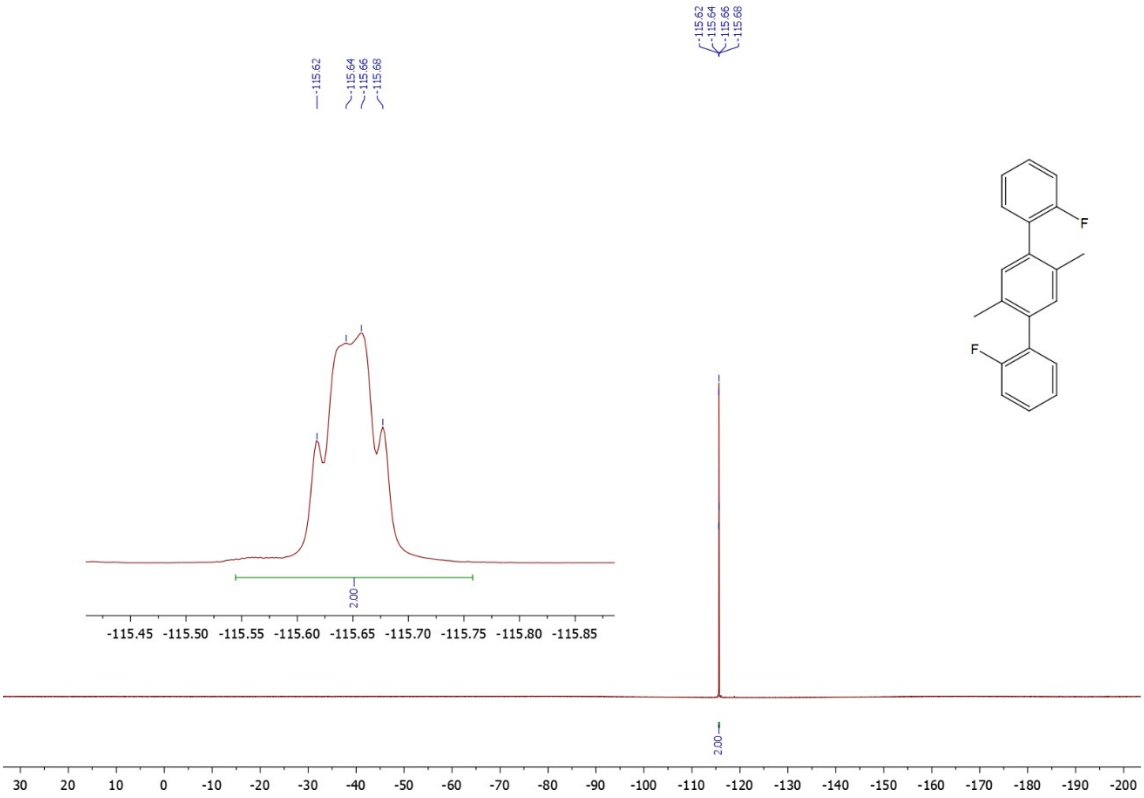


**Figure S71**. $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,2''-difluoro-2',5'-dimethyl-1,1':4',1''-terphenyl (**18a**).

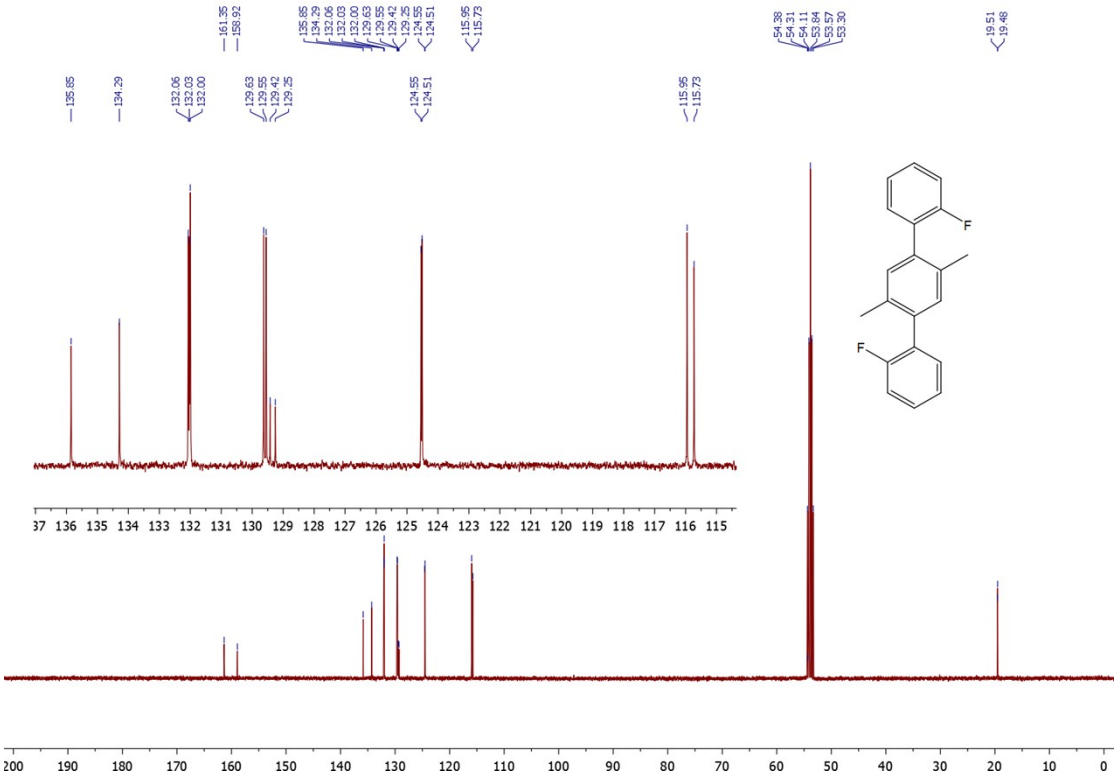


**Figure S72**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,2''-difluoro-2',5'-dimethyl-1,1':4',1''-terphenyl (**18a**).

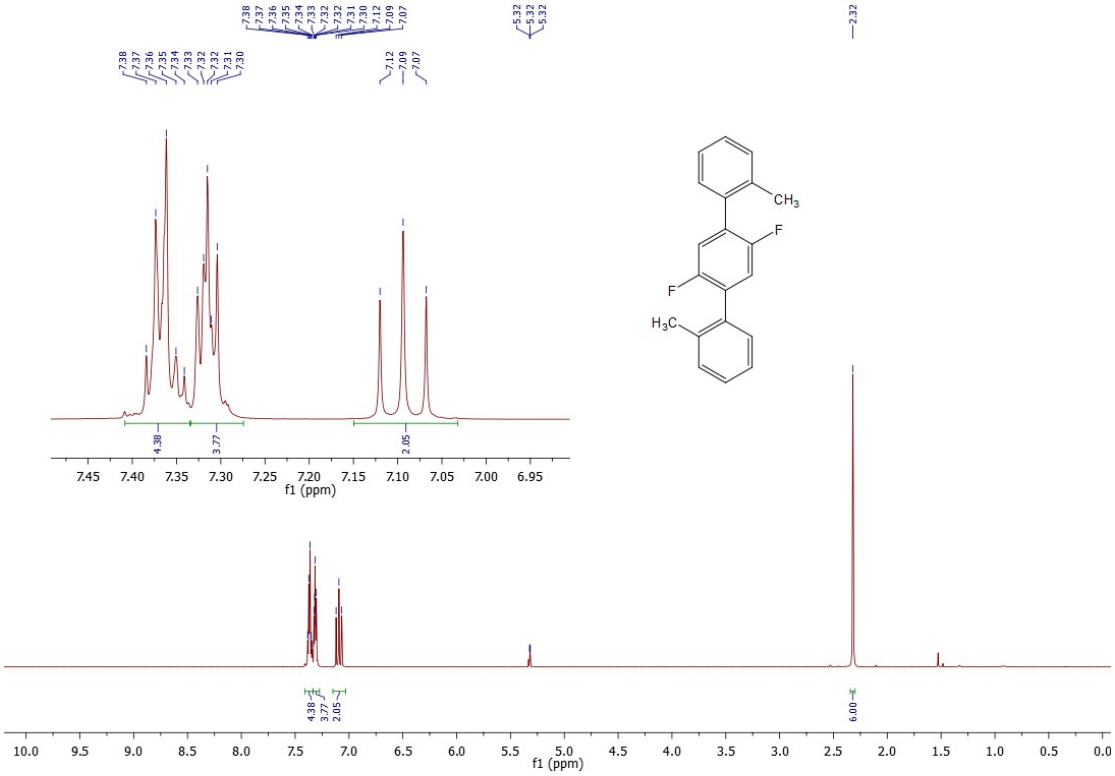


**Figure S73**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$, 293 K) spectrum of 2',5'-difluoro-2,2''-dimethyl-1,1':4',1''-terphenyl (**18b**).

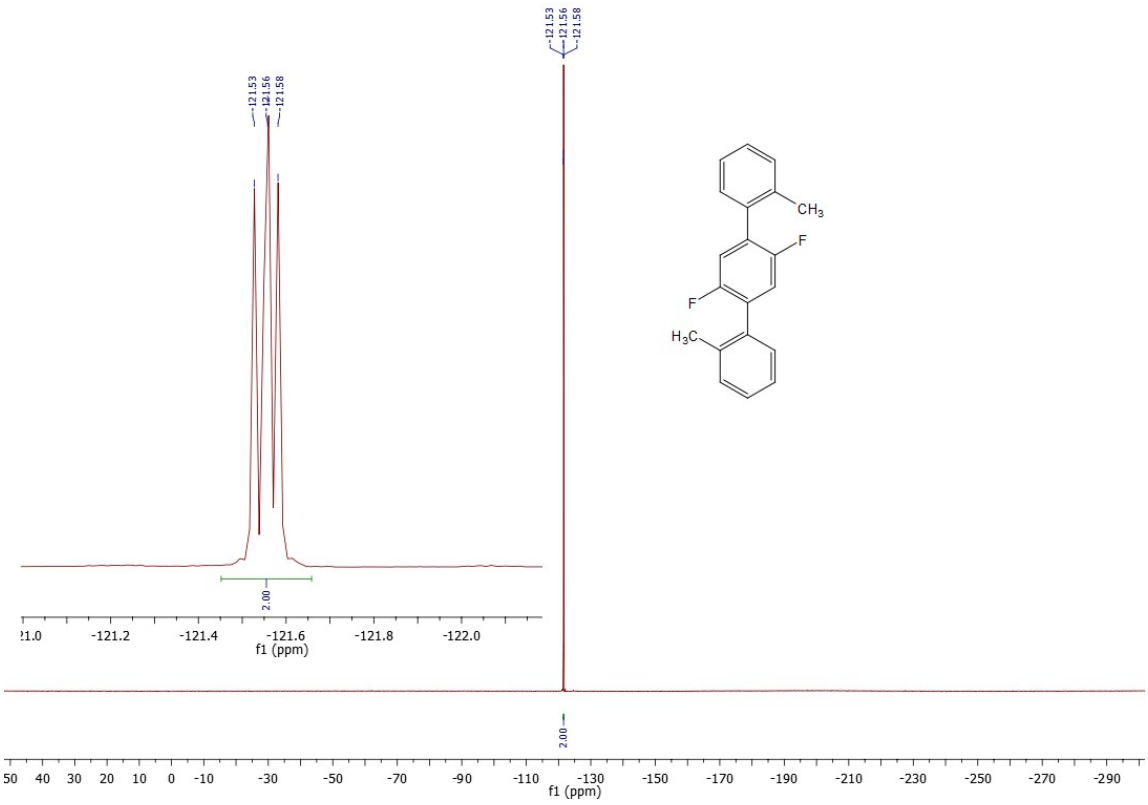


**Figure S74**. $^{19}F$ NMR (283 MHz, $CD_2Cl_2$, 293 K) spectrum of 2',5'-difluoro-2,2''-dimethyl-1,1':4',1''-terphenyl (**18b**).

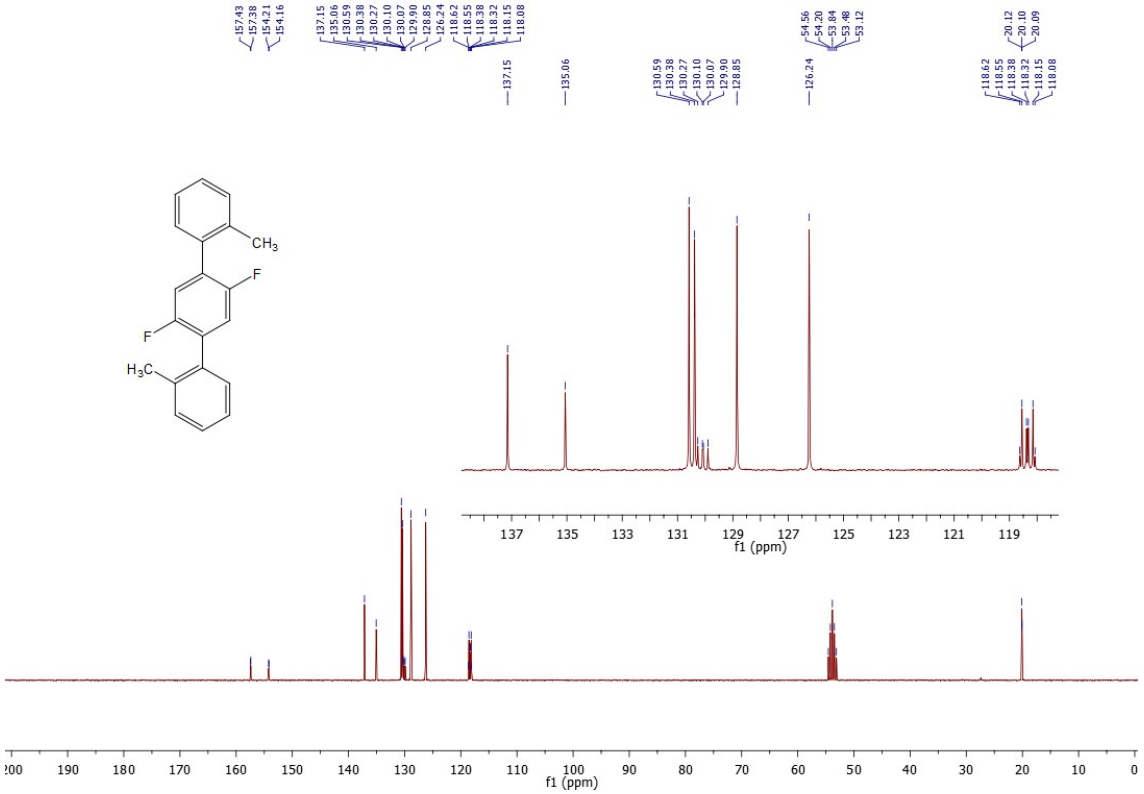


**Figure S75**. $^{13}C$ NMR (76 MHz, $CD_2Cl_2$, 293 K) spectrum of 2',5'-difluoro-2,2''-dimethyl-1,1':4',1''-terphenyl (**18b**).

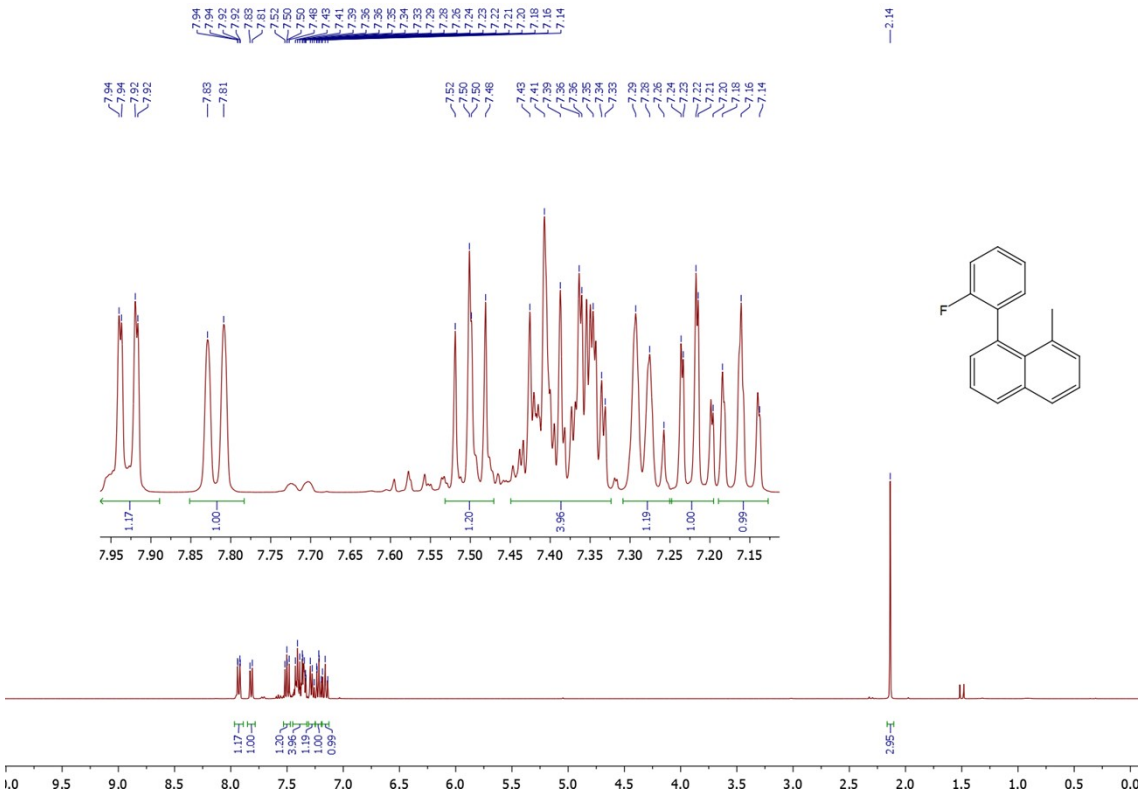


**Figure S76**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 1-(2-fluorophenyl)-8-methyl naphthalene (**19a**).

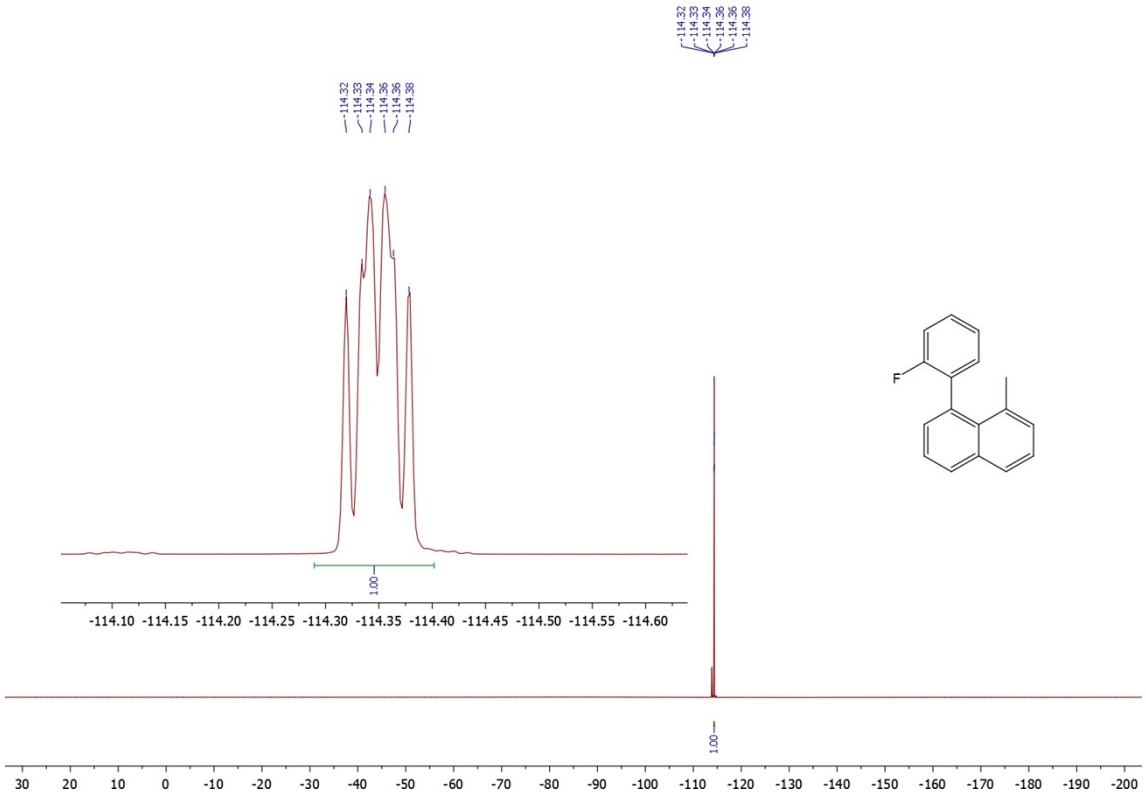


**Figure S77**. $^{19}F$ NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 1-(2-fluorophenyl)-8-methyl naphthalene (**19a**).

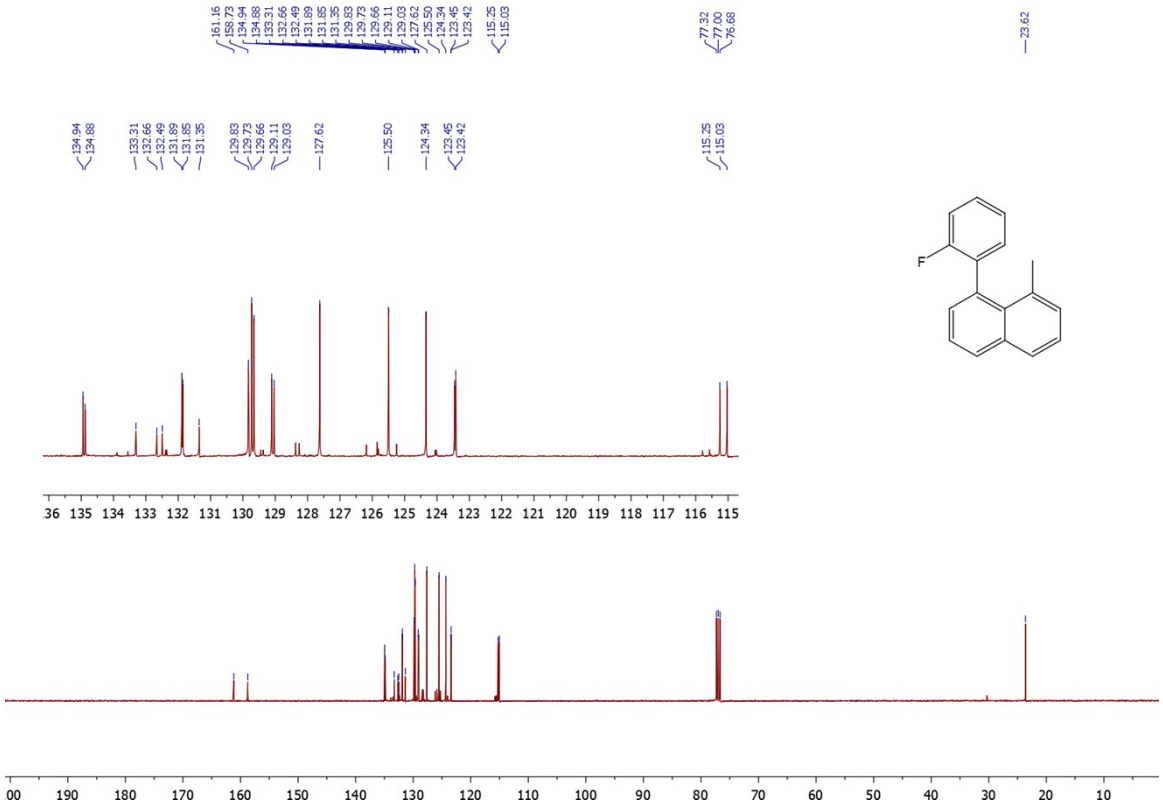


**Figure S78**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 1-(2-fluorophenyl)-8-methyl naphthalene (**19a**).

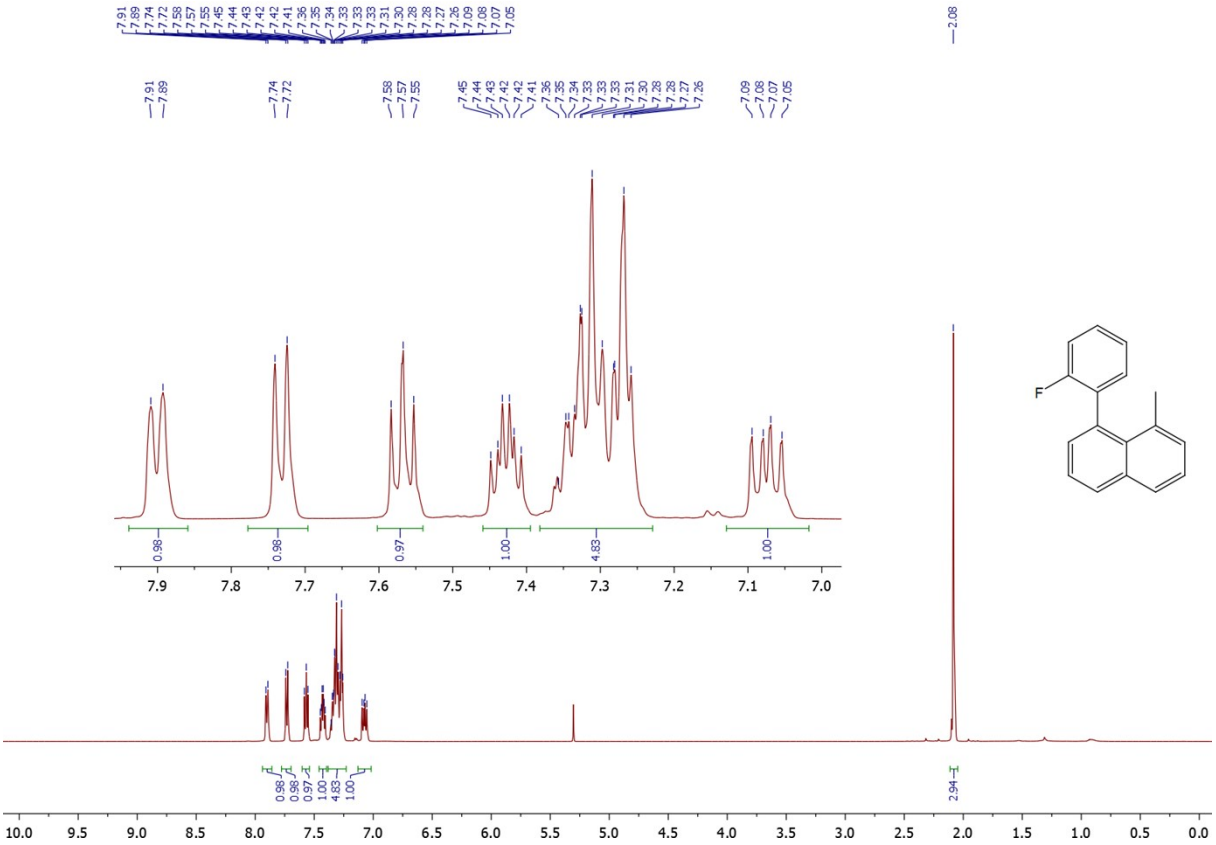

**Figure S79**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 1-fluoro-8-(o-tolyl)naphthalene (**19b**).

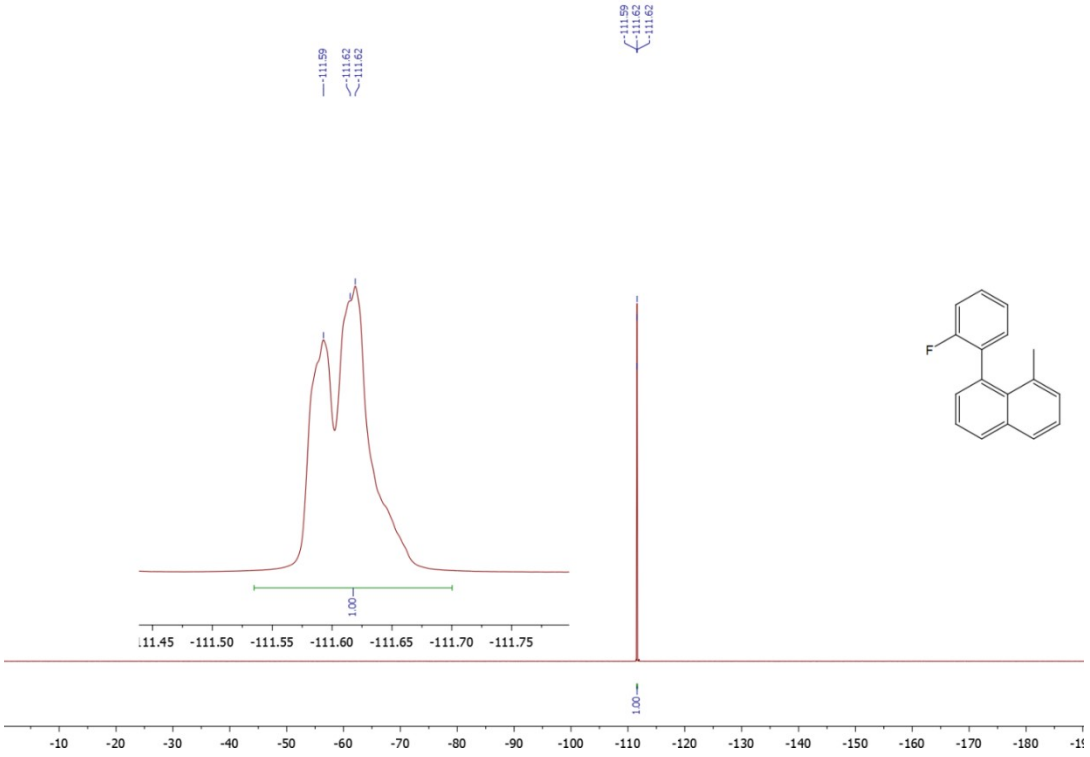

**Figure S80**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 1-fluoro-8-(o-tolyl)naphthalene (**19b**).

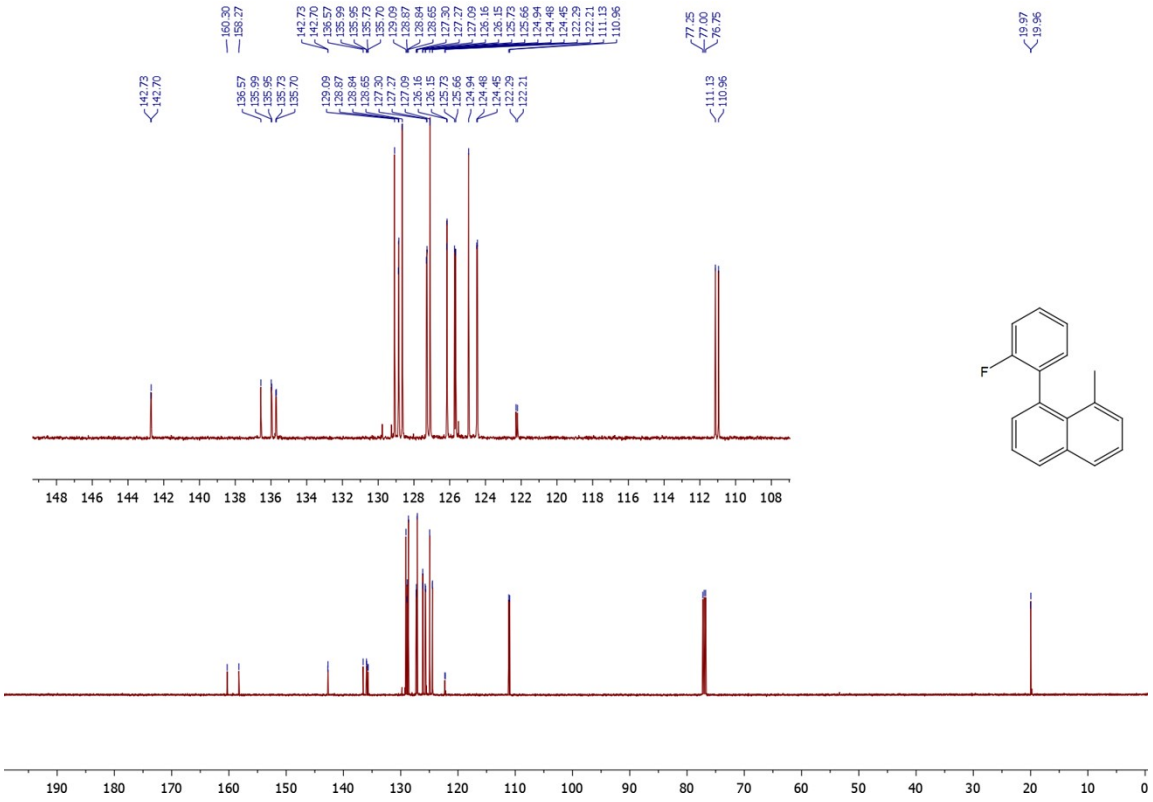

**Figure S81**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 1-fluoro-8-(o-tolyl)naphthalene (**19b**).

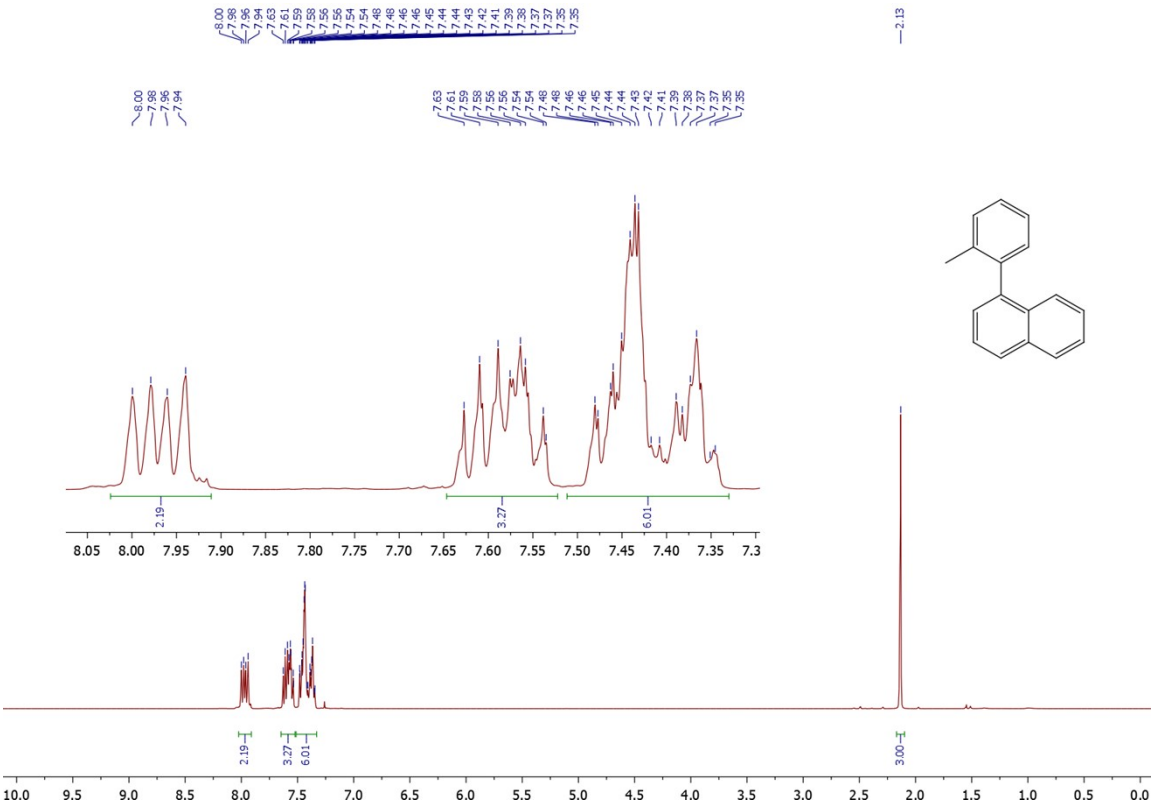

**Figure S82**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 1-(o-tolyl)naphthalene.

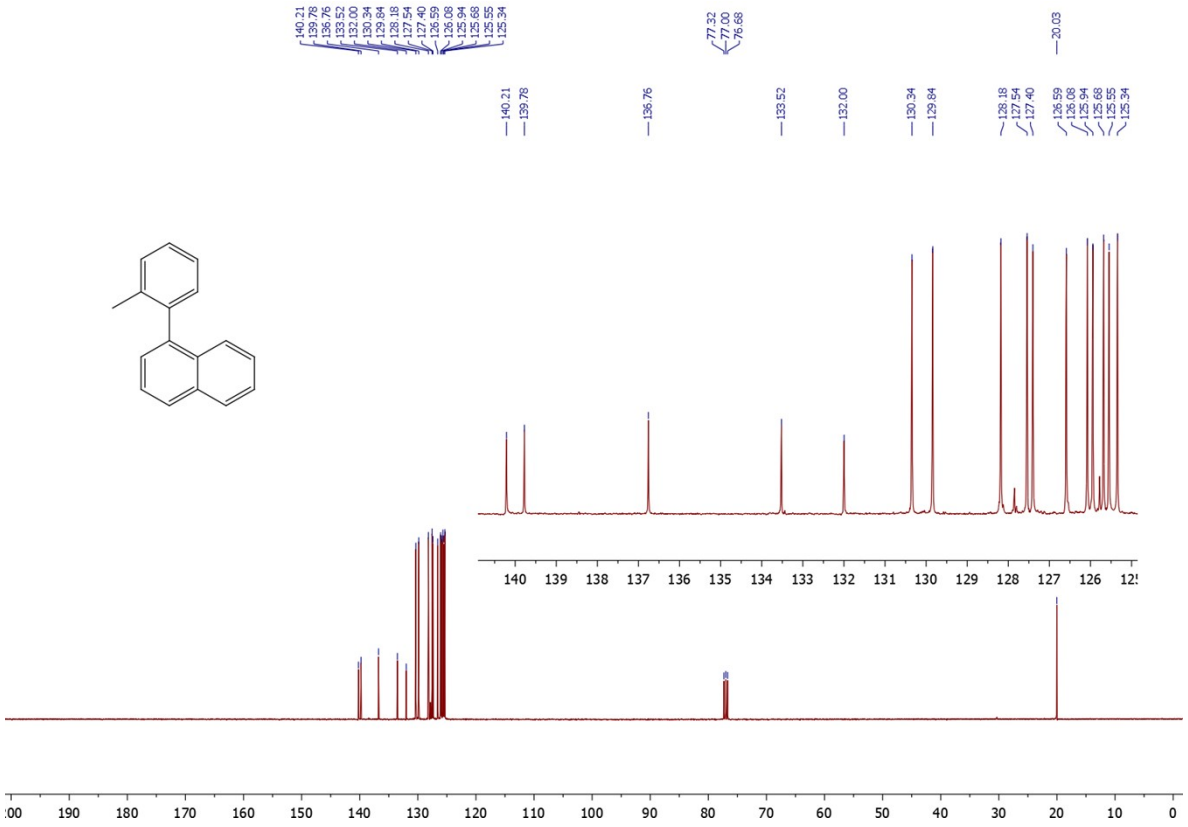

**Figure S83**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 1-(o-tolyl)naphthalene.

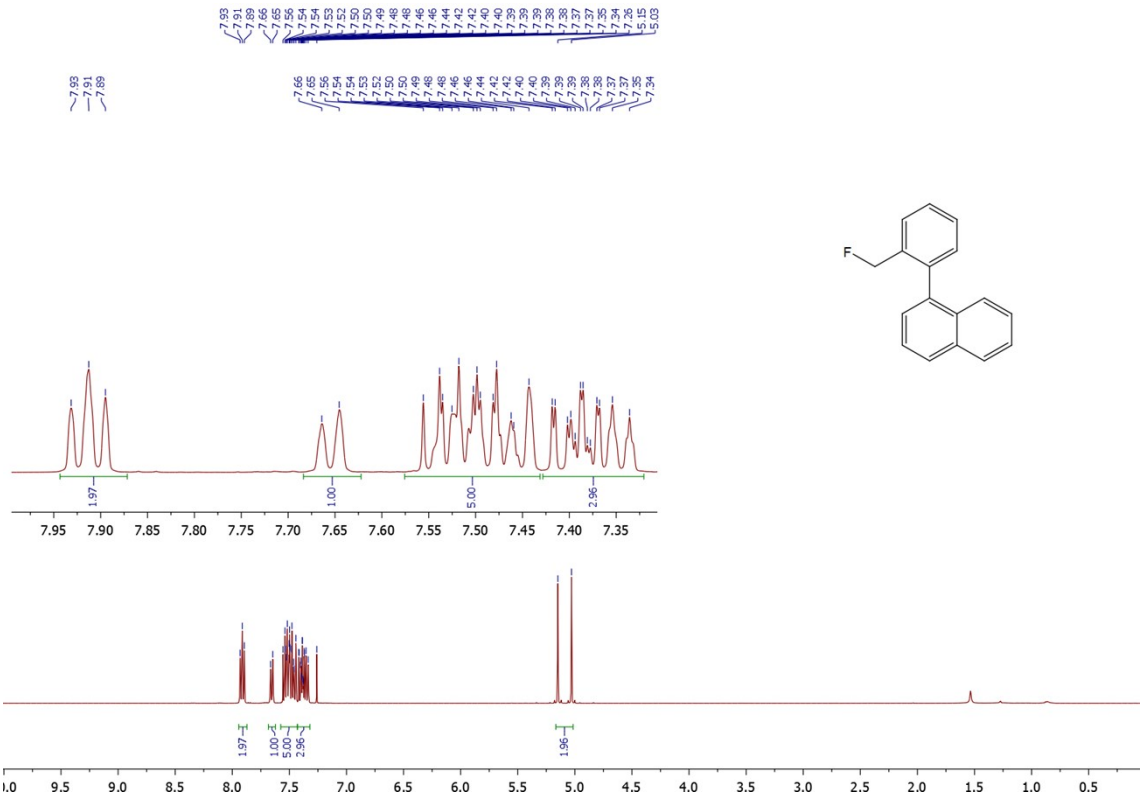

**Figure S84**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 1-(2-(fluoromethyl)phenyl) naphthalene (**19c**).

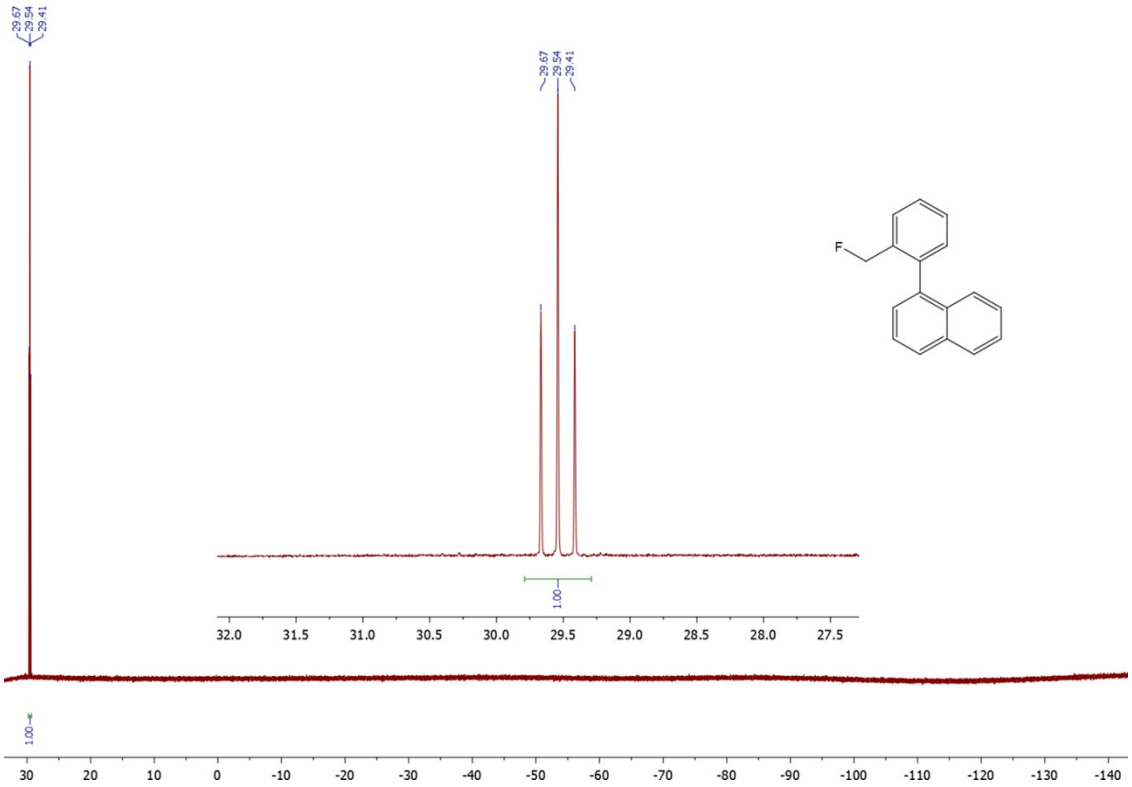


**Figure S85**. $^{19}F$ NMR (376 MHz, $CDCl_3$, 293 K) spectrum of 1-(2-(fluoromethyl)phenyl) naphthalene (**19c**).

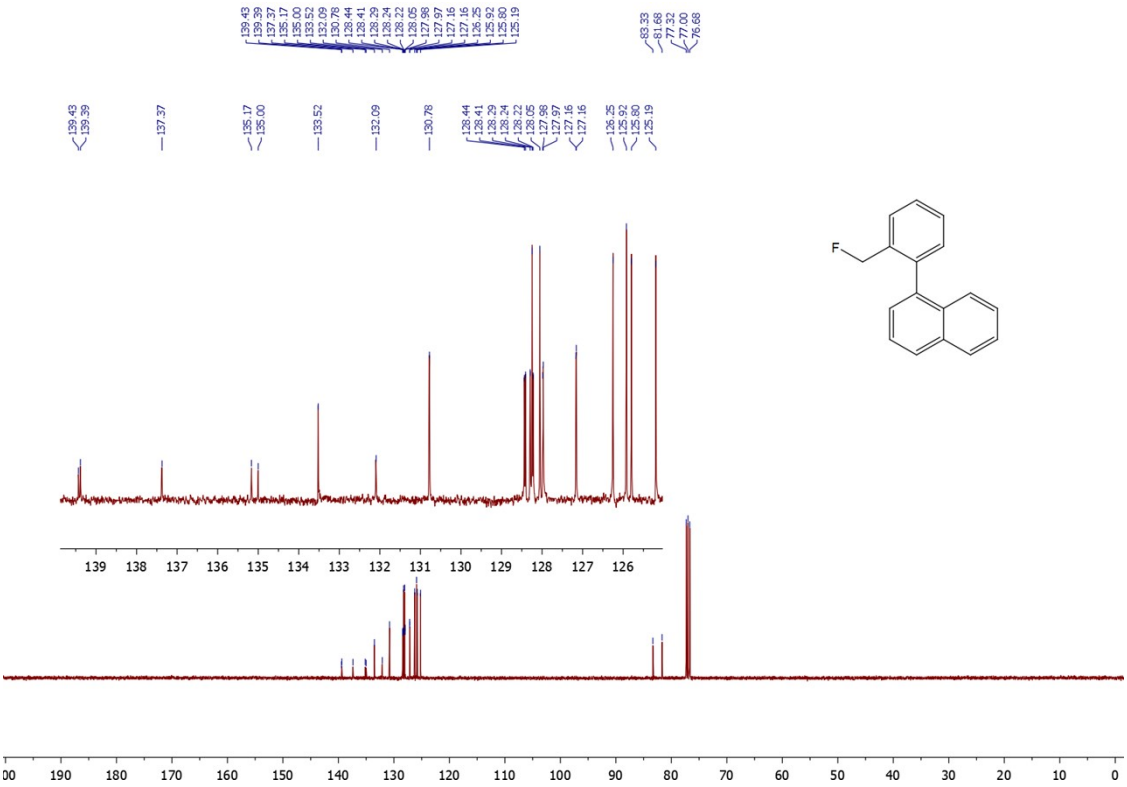


**Figure S86**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 1-(2-(fluoromethyl)phenyl) naphthalene (**19c**).

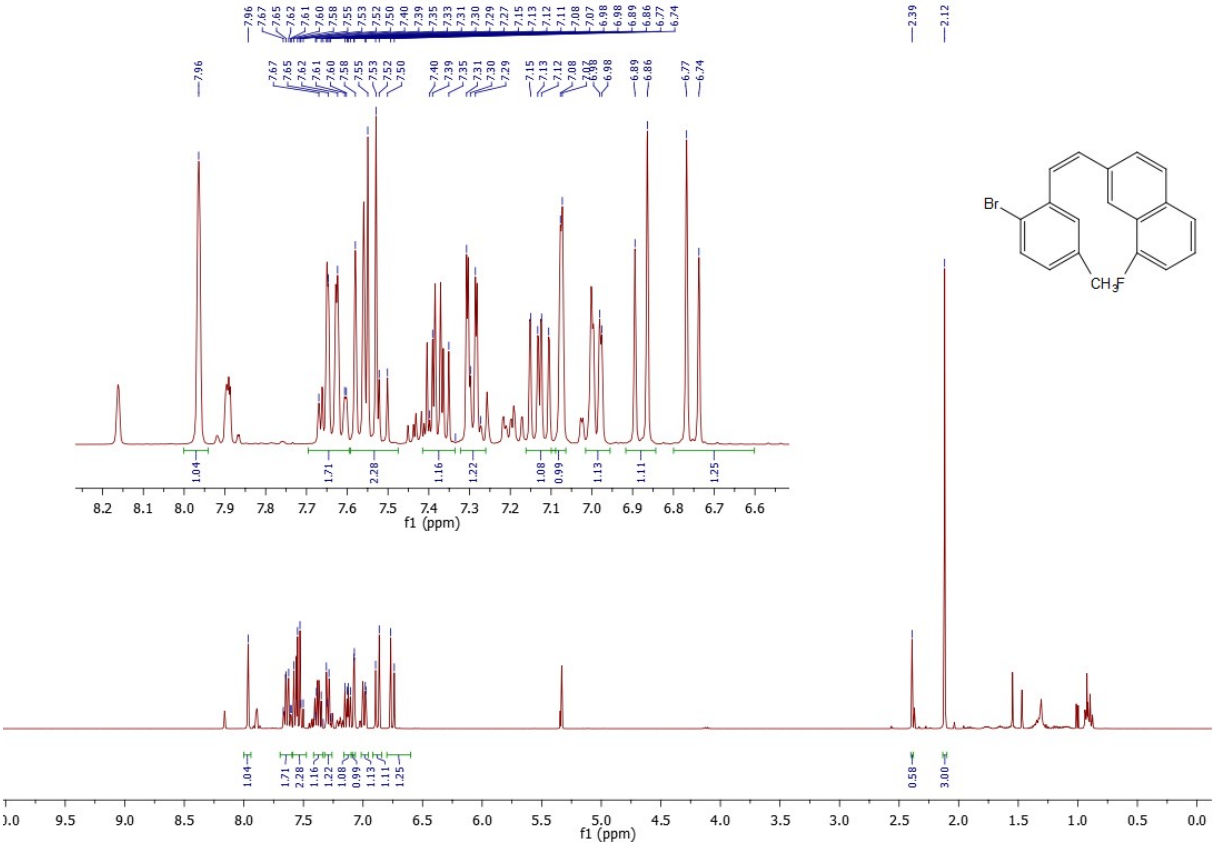


**Figure S87**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 293 K) spectrum of 7-(2-bromo-5-methylstyryl)-1-fluoronaphthalene.

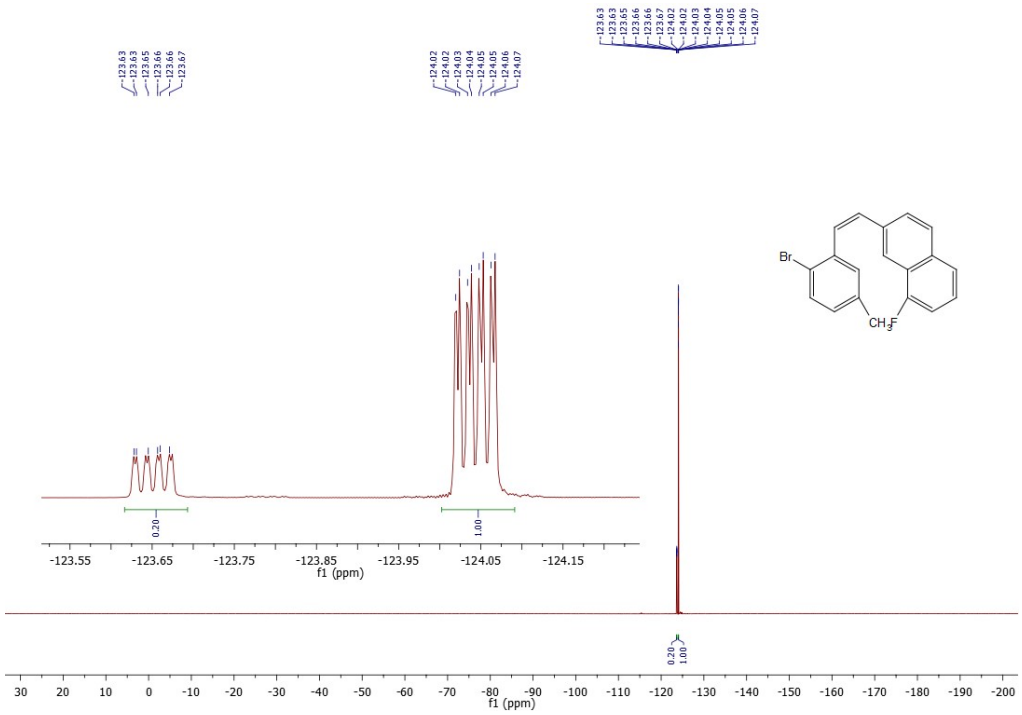


**Figure S88**. $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K) spectrum of 7-(2-bromo-5-methylstyryl)-1-fluoronaphthalene.

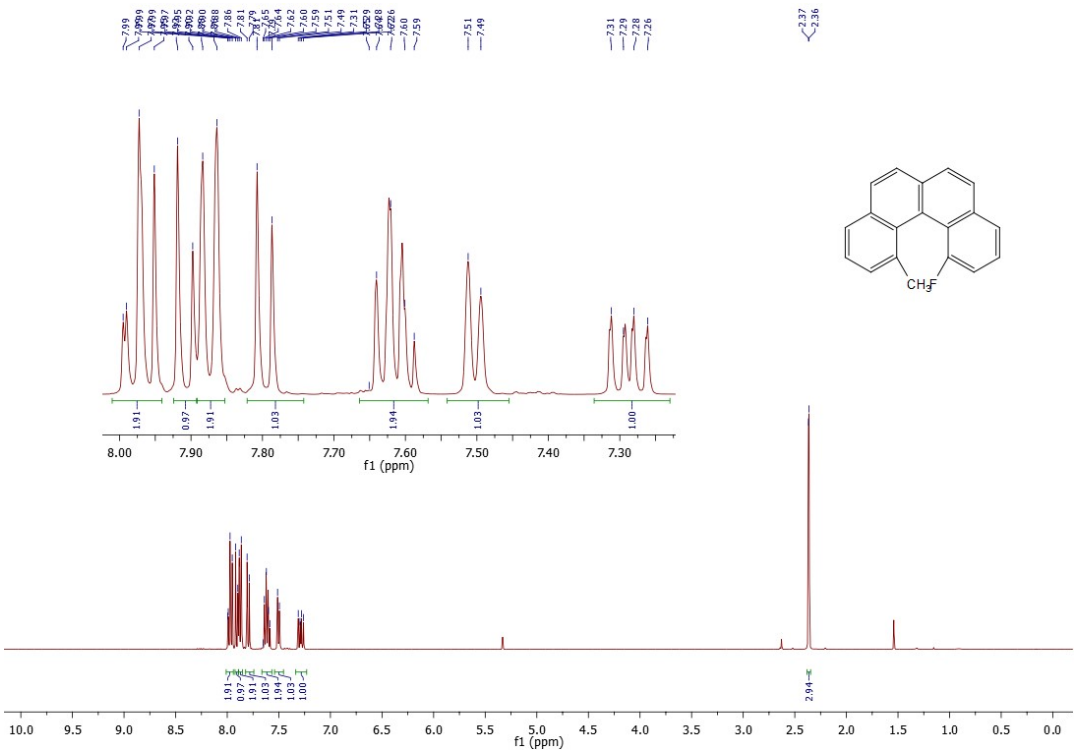


**Figure S89**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 293 K) spectrum of 1-fluoro-12-methylbenzo[c]phenanthrene (**22a**).

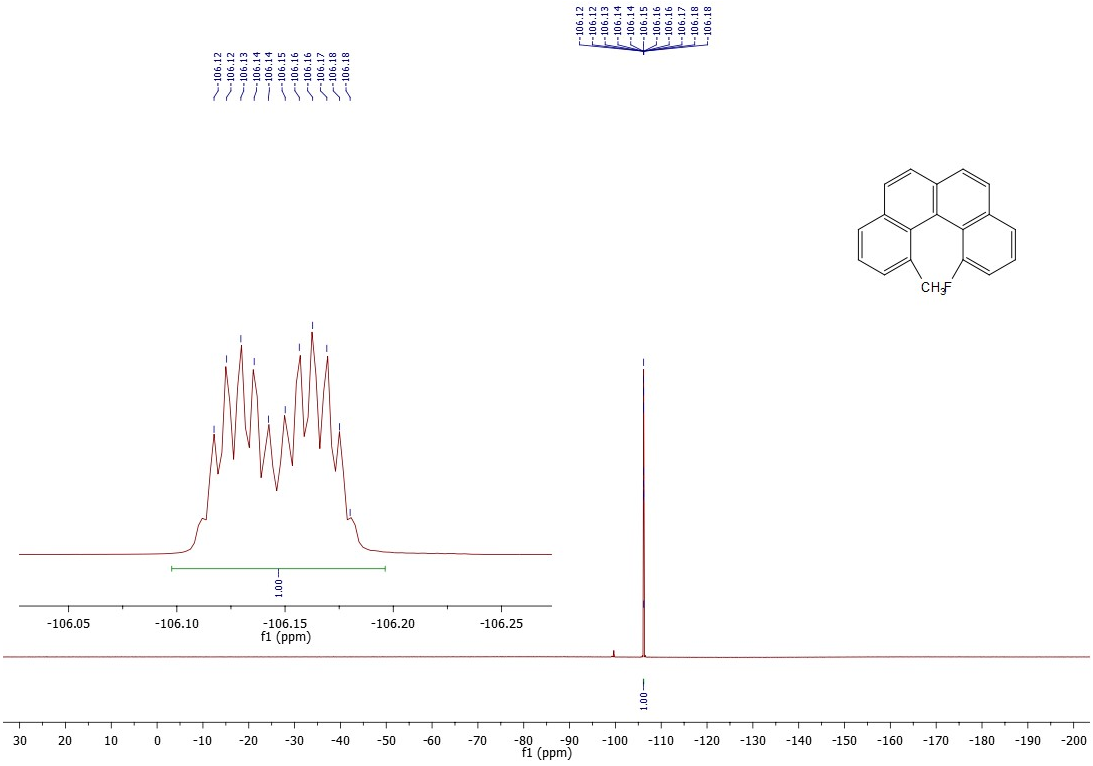


**Figure S90**. $^{19}F$ NMR (377 MHz, $CD_2Cl_2$, 293 K) spectrum of 1-fluoro-12-methylbenzo[c]phenanthrene (**22a**).

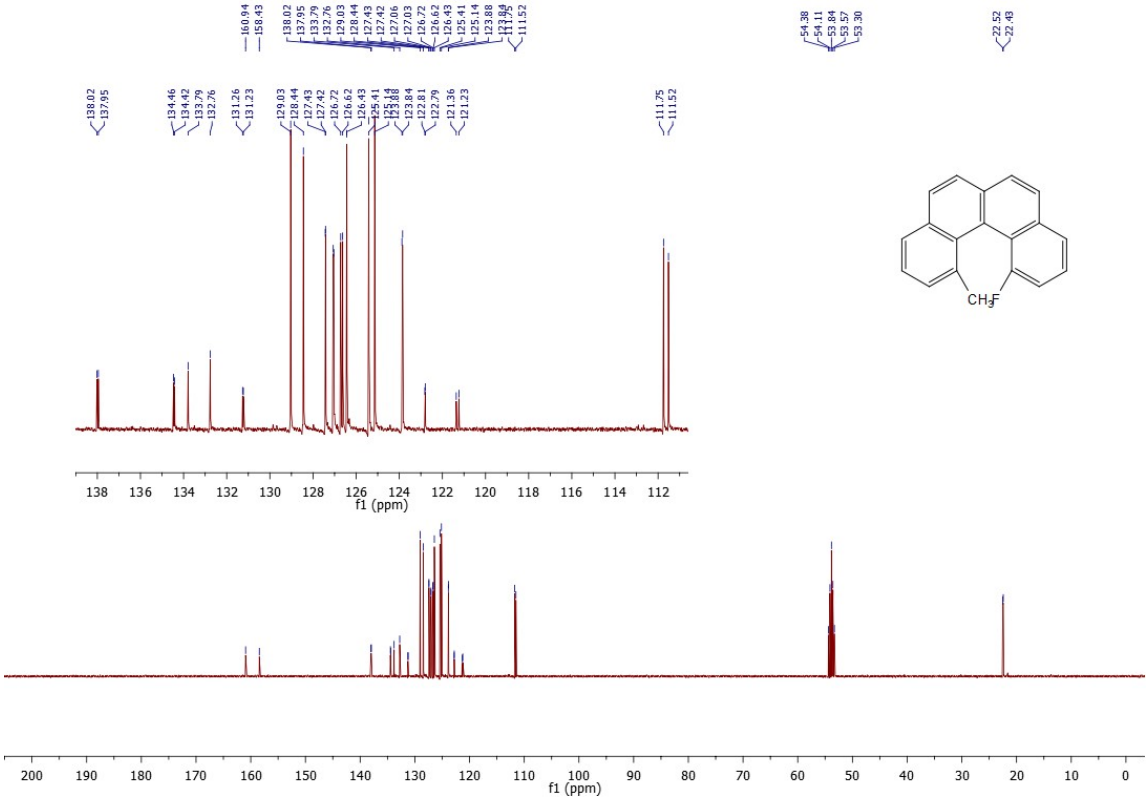


**Figure S91**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$, 293 K) spectrum of 1-fluoro-12-methylbenzo[c]phenanthrene (**22a**).

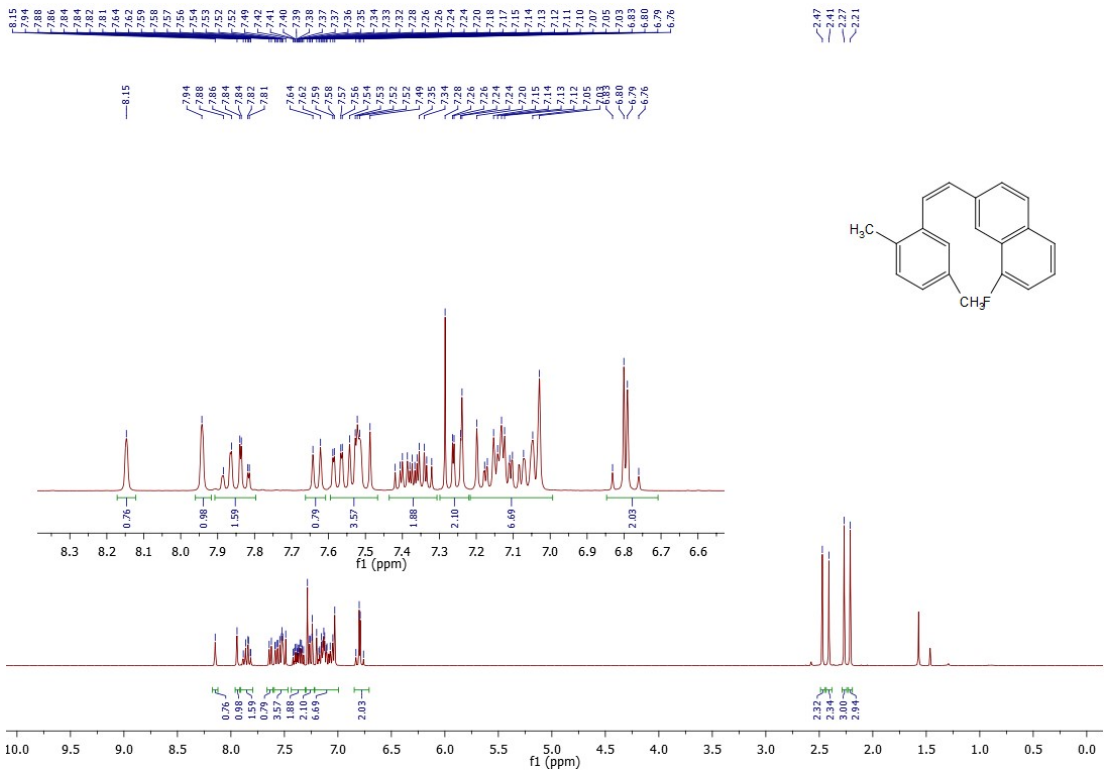


**Figure S92**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum 7-(2,5-dimethylstyryl)-1-fluoronaphthalene.

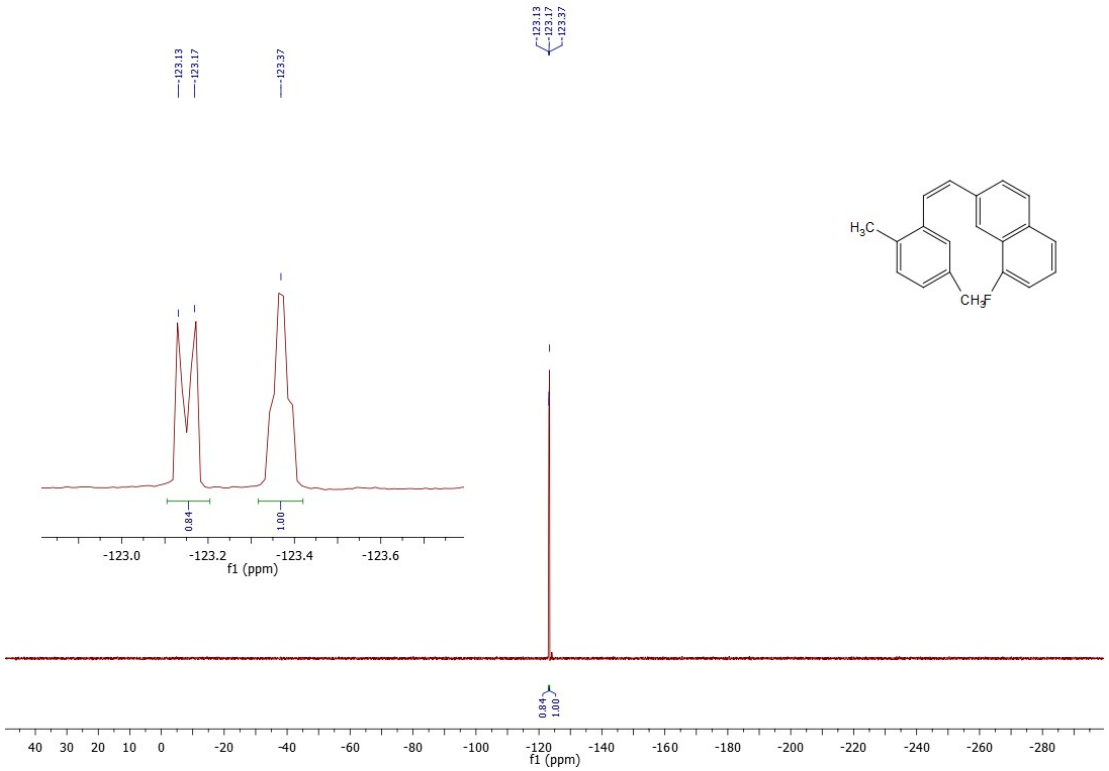


**Figure S93**. $^{19}F$ NMR (377 MHz, $CDCl_3$, 293 K) spectrum 7-(2,5-dimethylstyryl)-1-fluoronaphthalene.

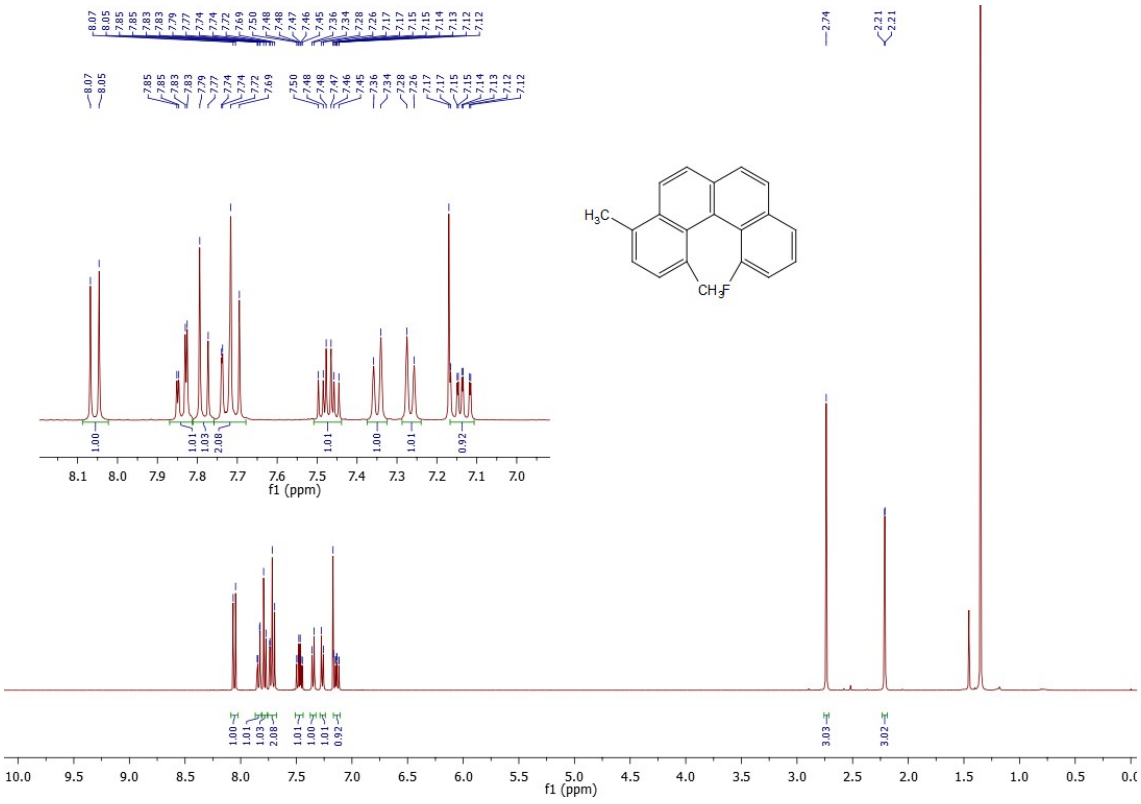


**Figure S94**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum 12-fluoro-1,4-dimethylbenzo[c]phenanthrene (**23a**).

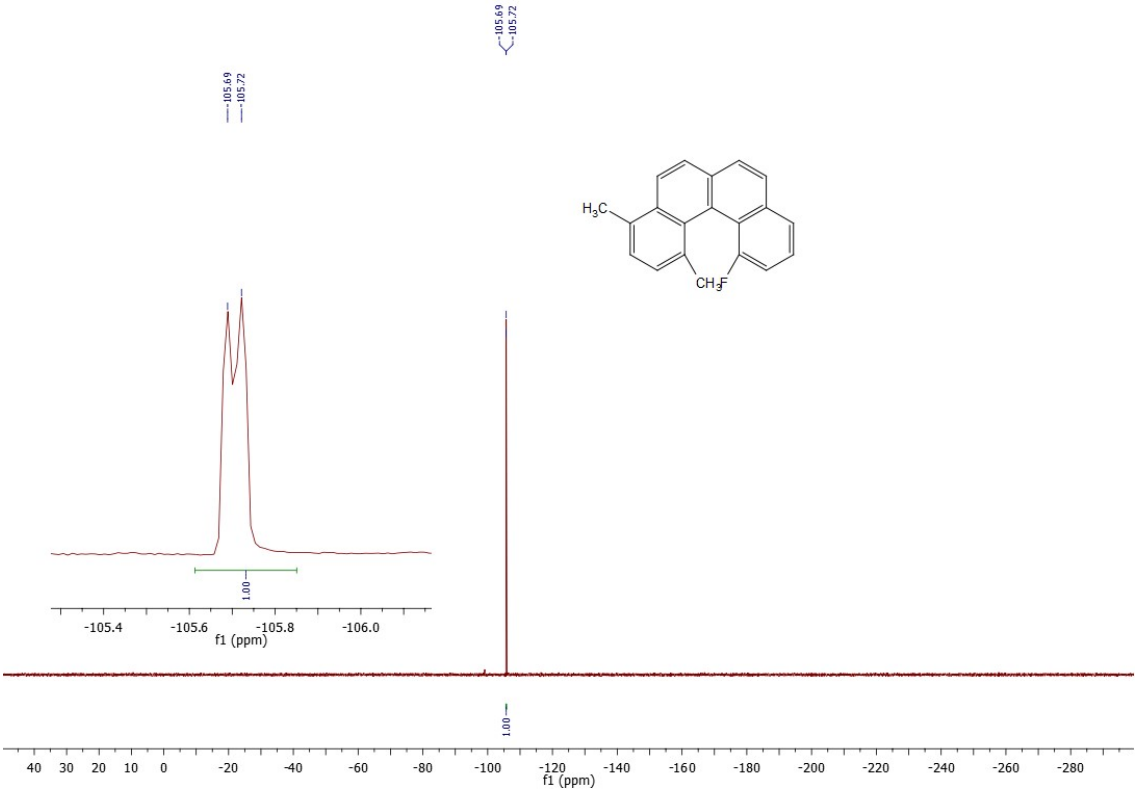


**Figure S95**. $^{19}F$ NMR (377 MHz, $CDCl_3$, 293 K) spectrum 12-fluoro-1,4-dimethylbenzo[c]phenanthrene (**23a**).

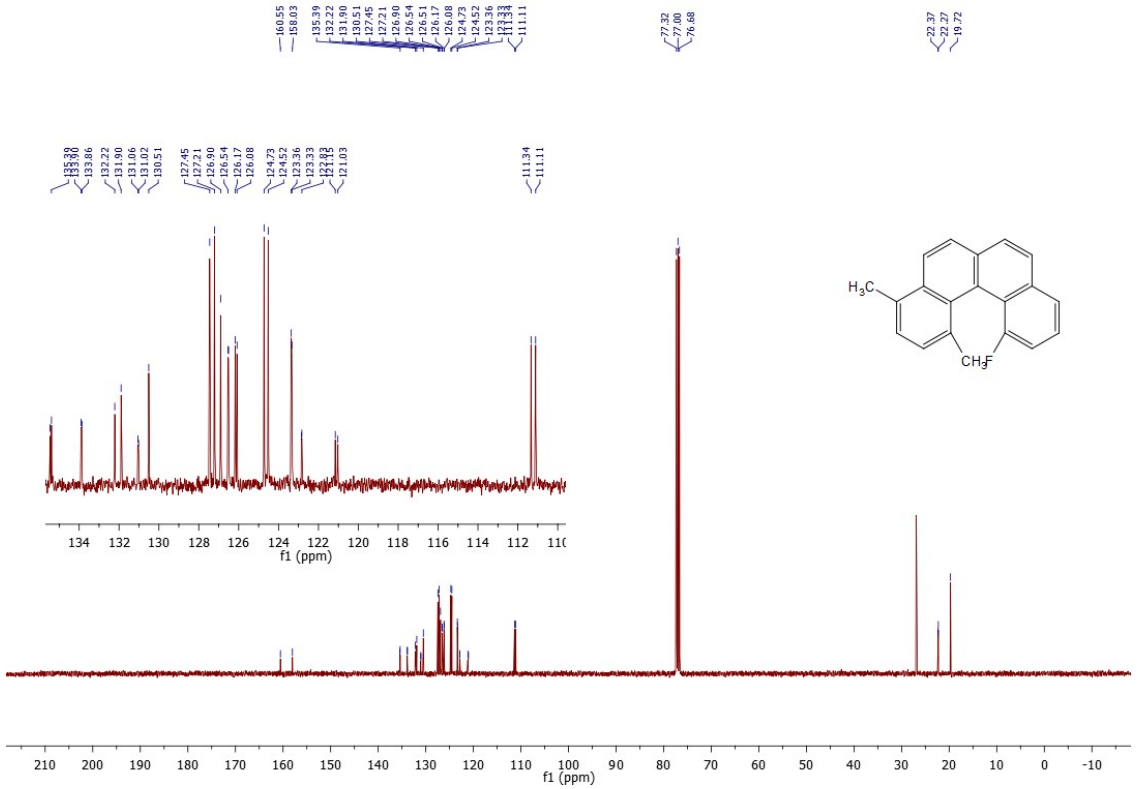


**Figure S96**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum 12-fluoro-1,4-dimethylbenzo[c]phenanthrene (**23a**).

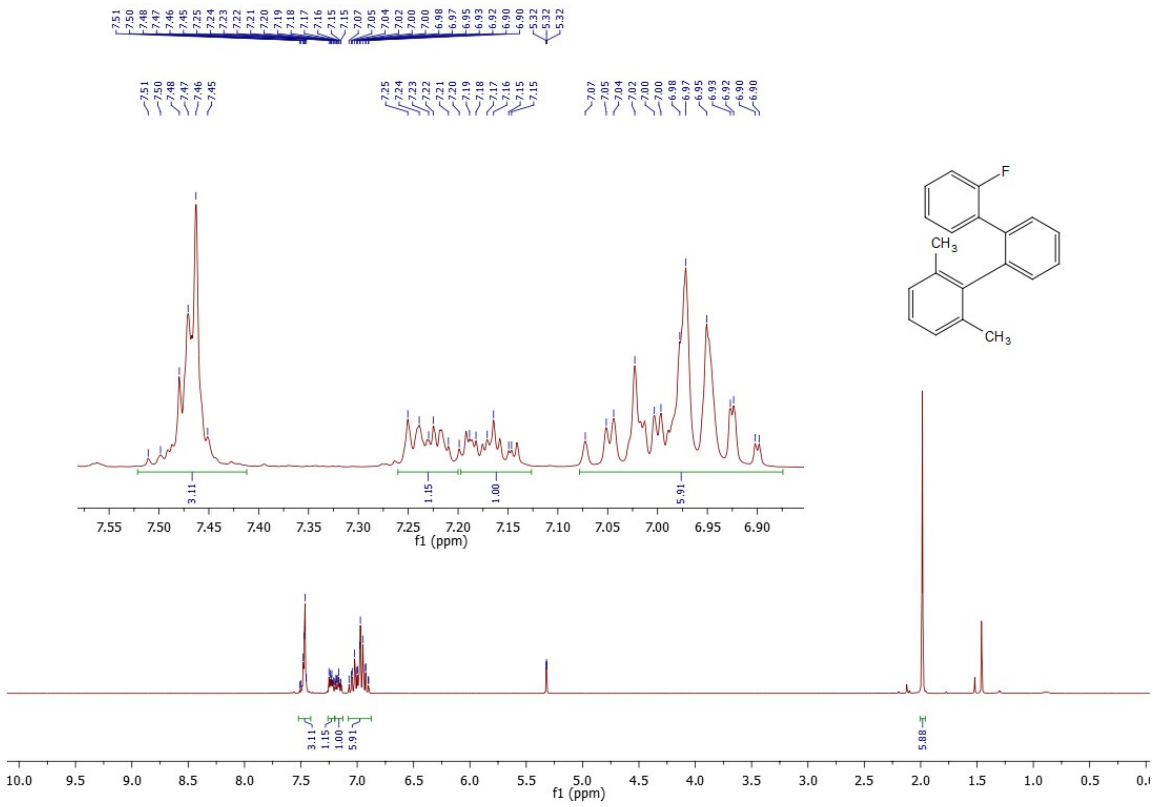


**Figure S97**. $^{1}H$ NMR (300 MHz, $CD_2Cl_2$, 293 K) spectrum of 2''-fluoro-2,6-dimethyl-1,1':2',1''-terphenyl (**24a**).

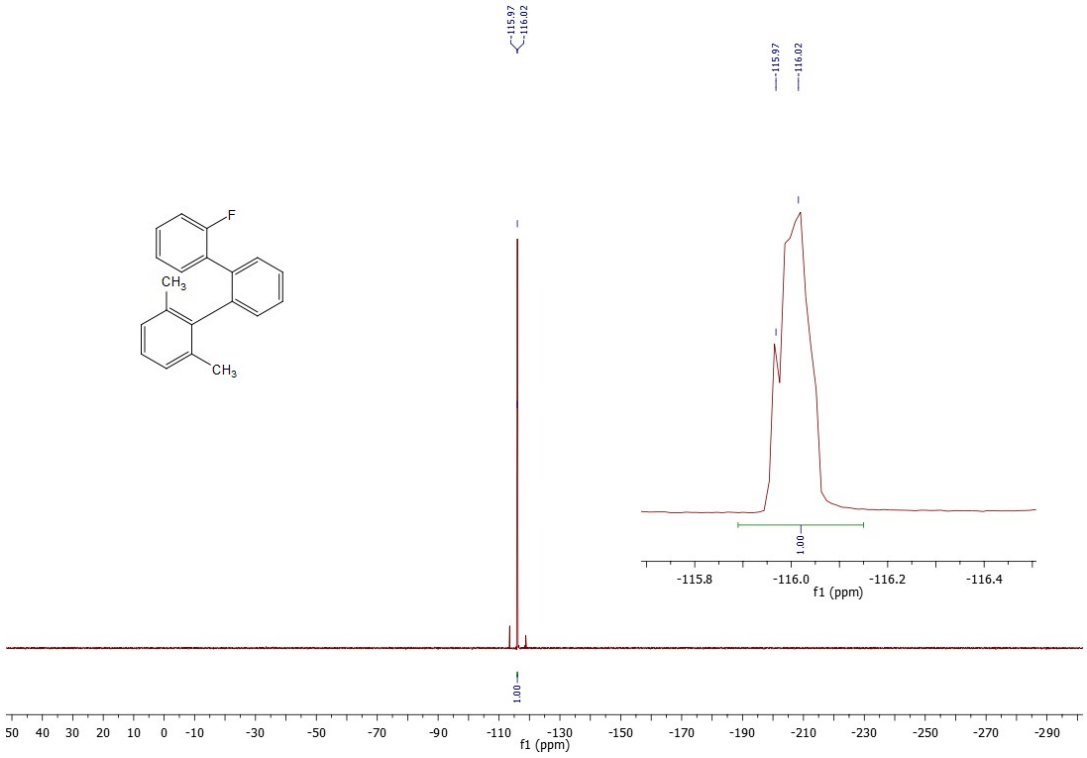


**Figure S98**. $^{19}F$ NMR (283 MHz, $CD_2Cl_2$, 293 K) spectrum of 2''-fluoro-2,6-dimethyl-1,1':2',1''-terphenyl (**24a**).

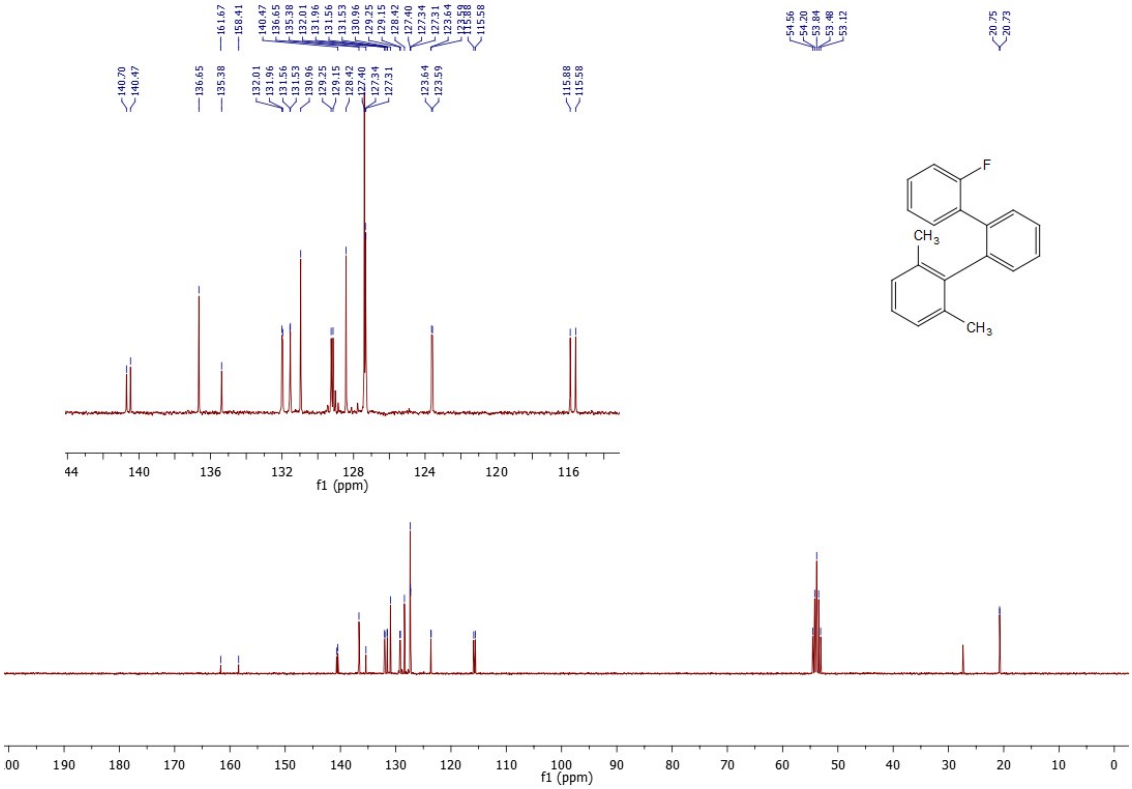


**Figure S99**. $^{13}C$ NMR (76 MHz, $CD_2Cl_2$, 293 K) spectrum of 2''-fluoro-2,6-dimethyl-1,1':2',1''-terphenyl (**24a**).

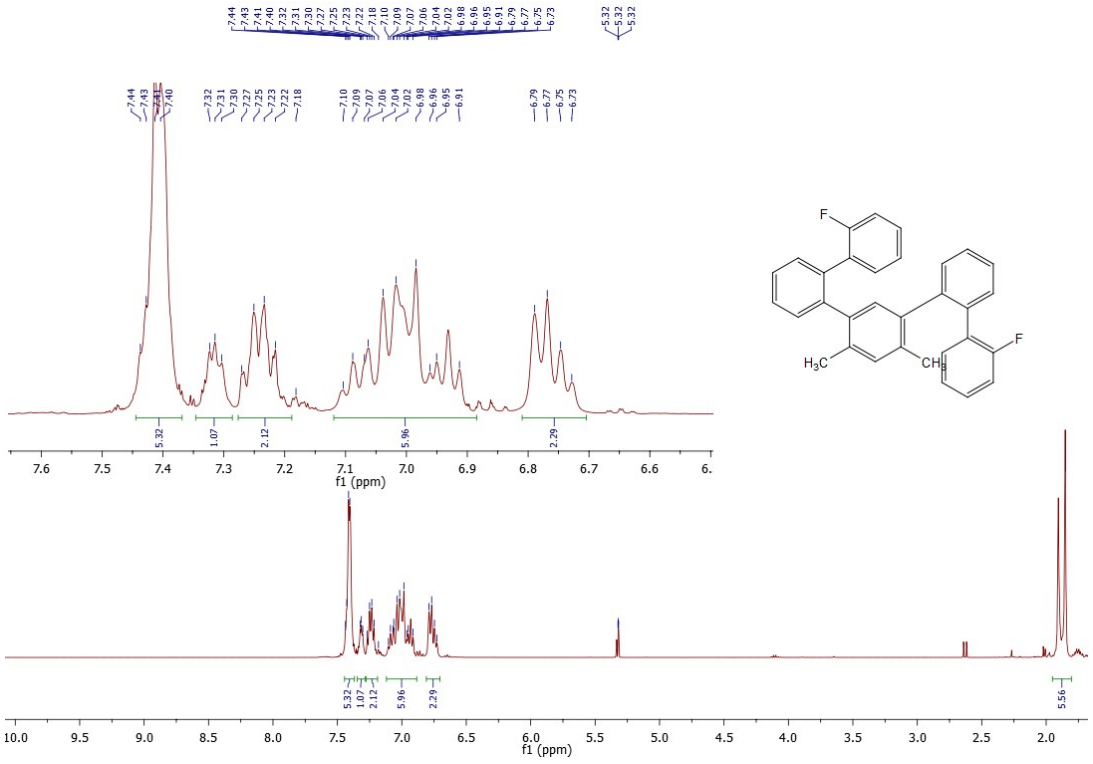


**Figure S100**. $^{1}H$ NMR (400 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,2''''-difluoro-4'',6''-dimethyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (**26a**).

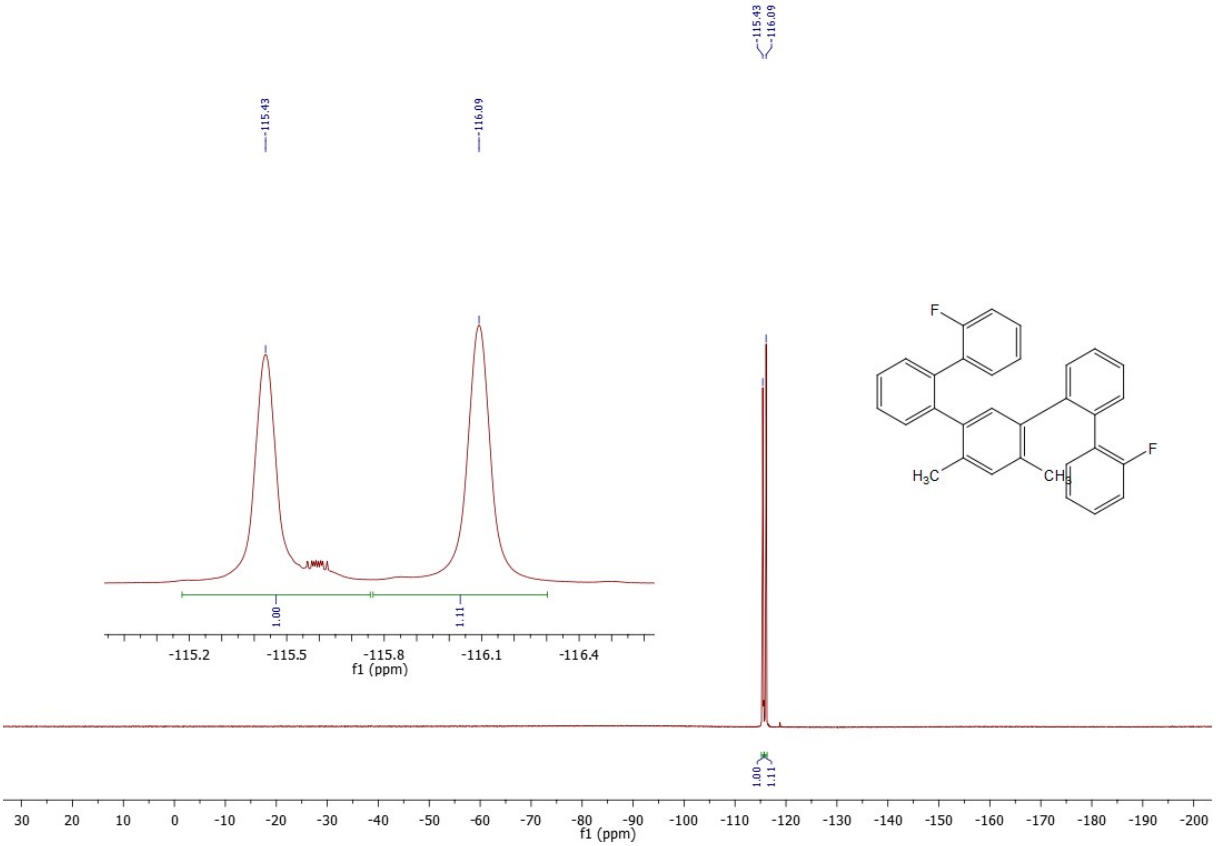


**Figure S101**. $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,2""-difluoro-4",6"-dimethyl-1,1':2',1":3",1"':2"',1""-quinquephenyl (**26a**).

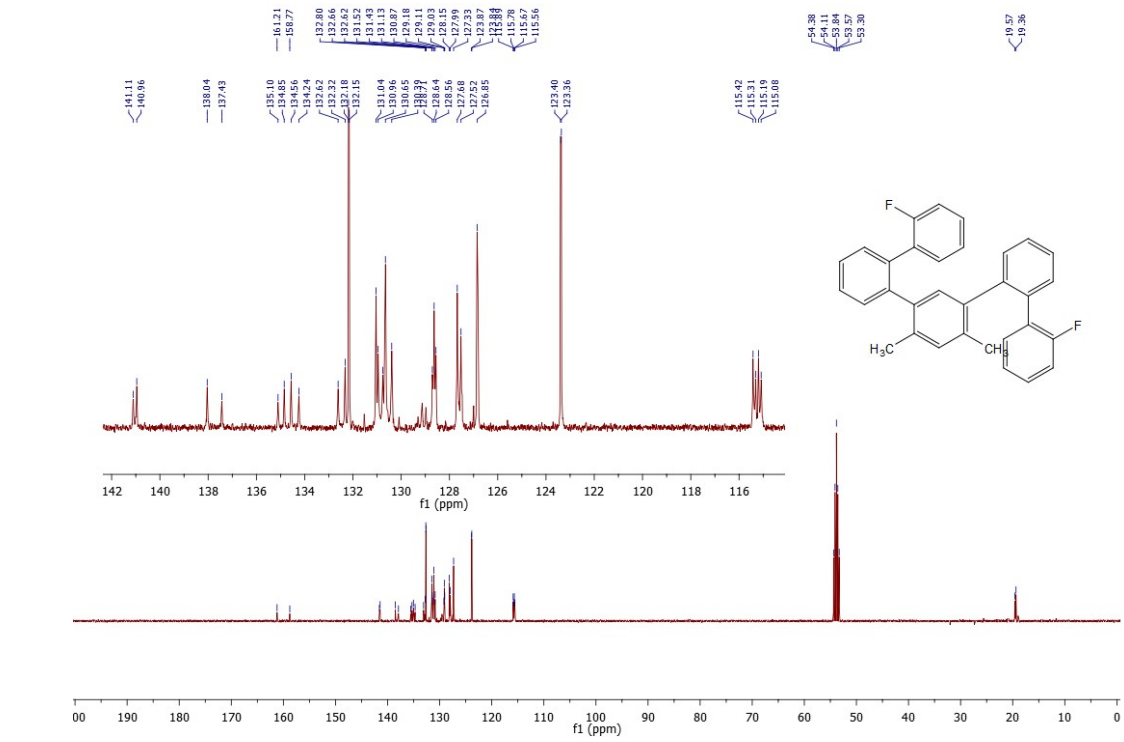


**Figure S102**. $^{13}C$ NMR (101 MHz, $CD_2Cl_2$, 293 K) spectrum of 2,2""-difluoro-4",6"-dimethyl-1,1':2',1":3",1"':2"',1""-quinquephenyl (**26a**).

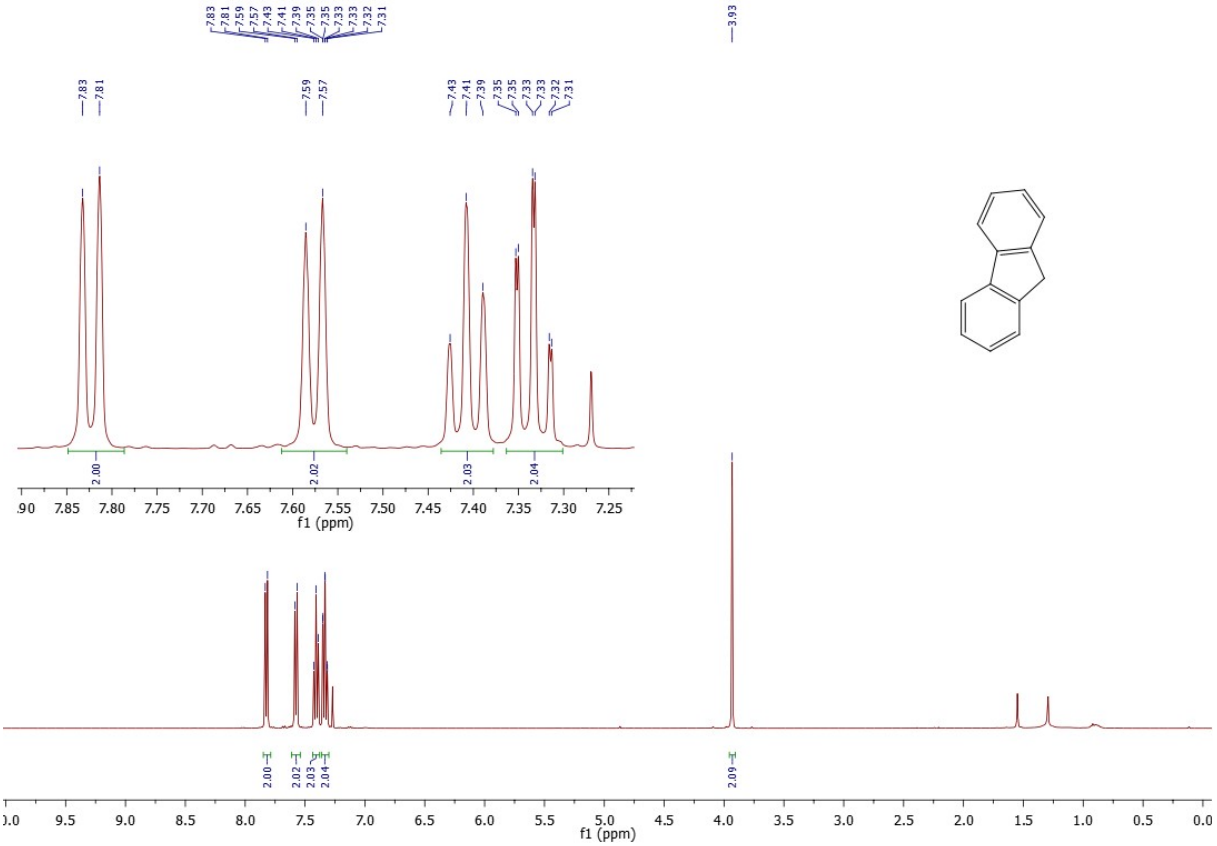


**Figure S103**. $^{1}$H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 9H-fluorene (**1**).

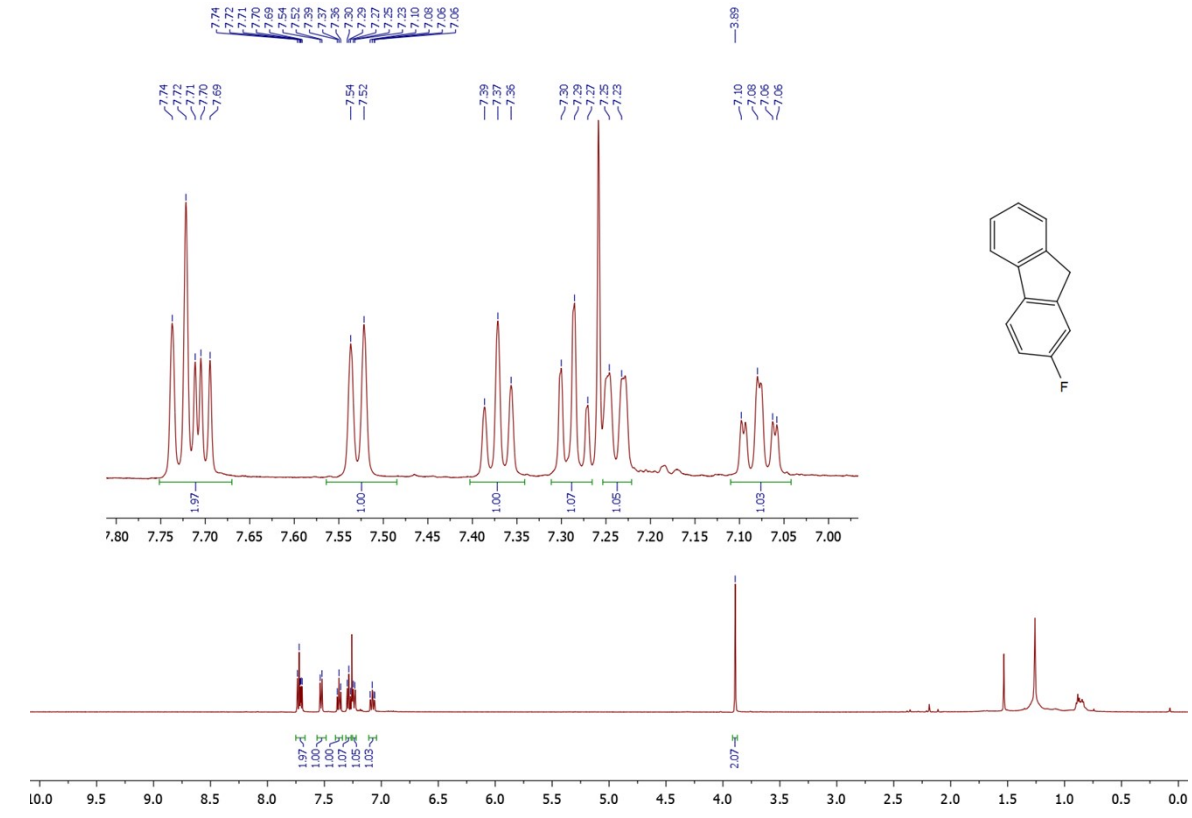


**Figure S104**. $^{1}$H NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-9H-fluorene (**2**).

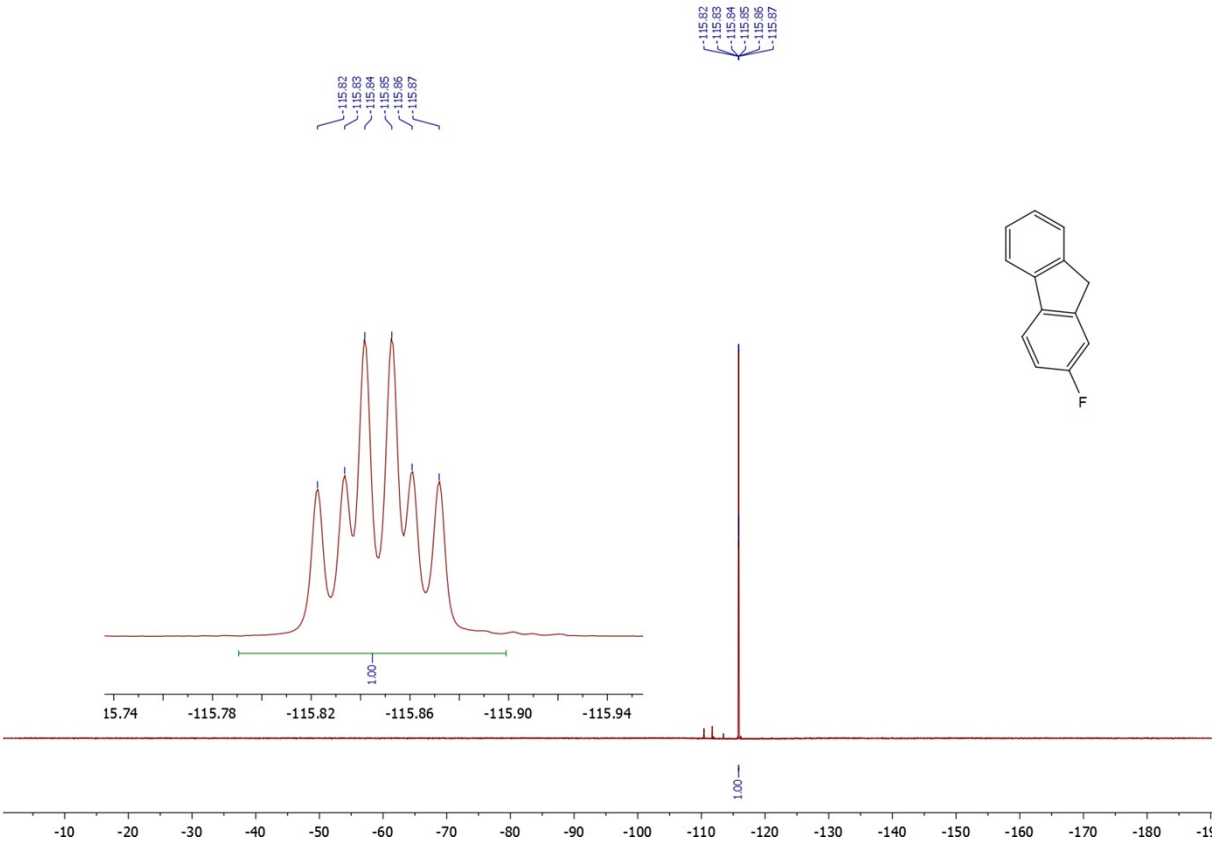


**Figure S105**. $^{19}F$ NMR (470 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-9H-fluorene (**2**).

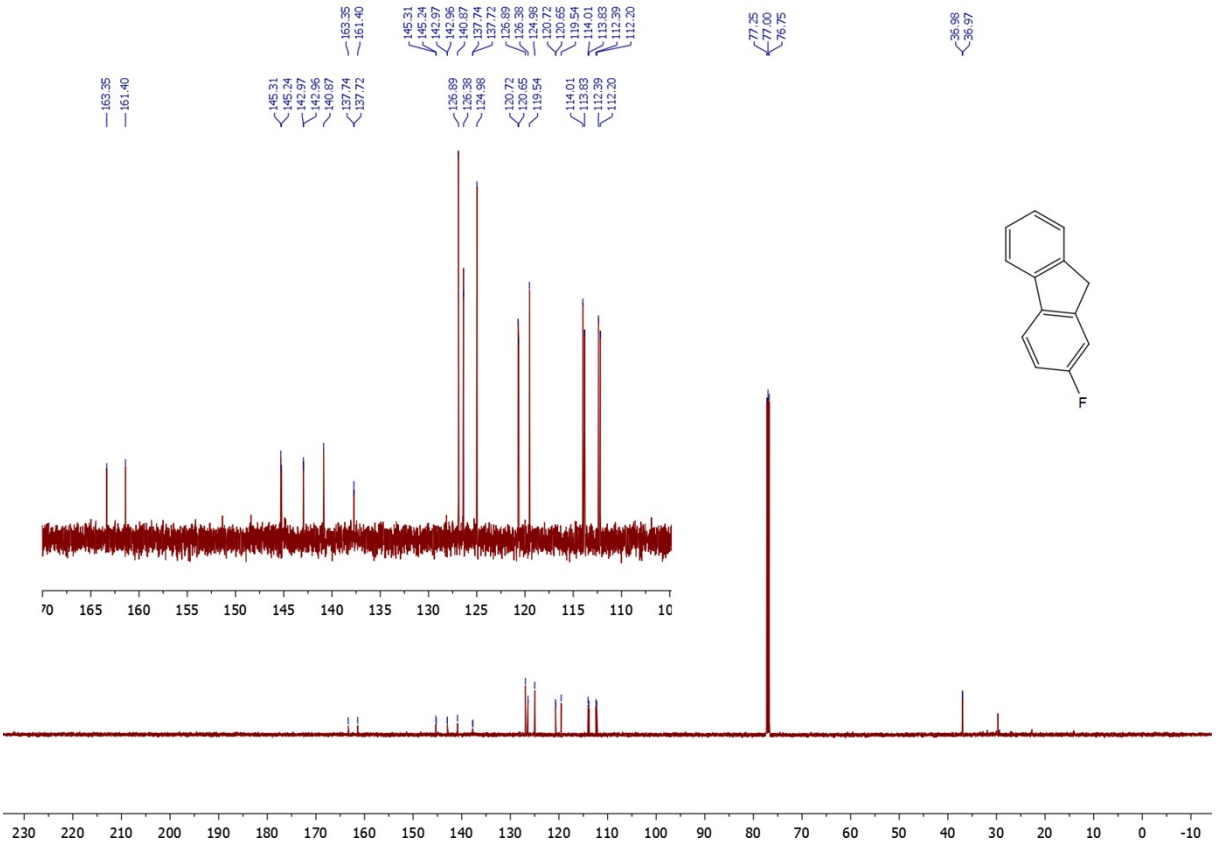


**Figure S106**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-fluoro-9H-fluorene (**2**).

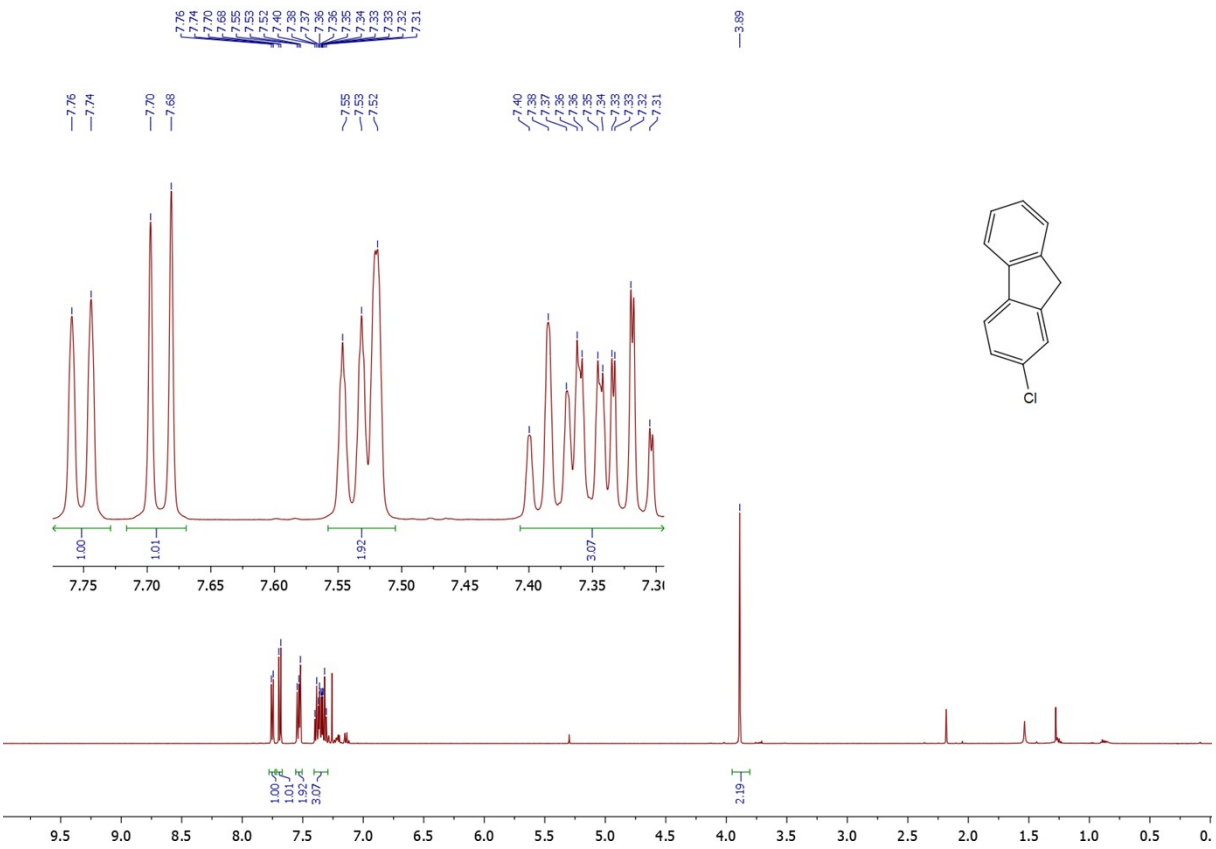


**Figure S107**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-chloro-9H-fluorene (**3**).

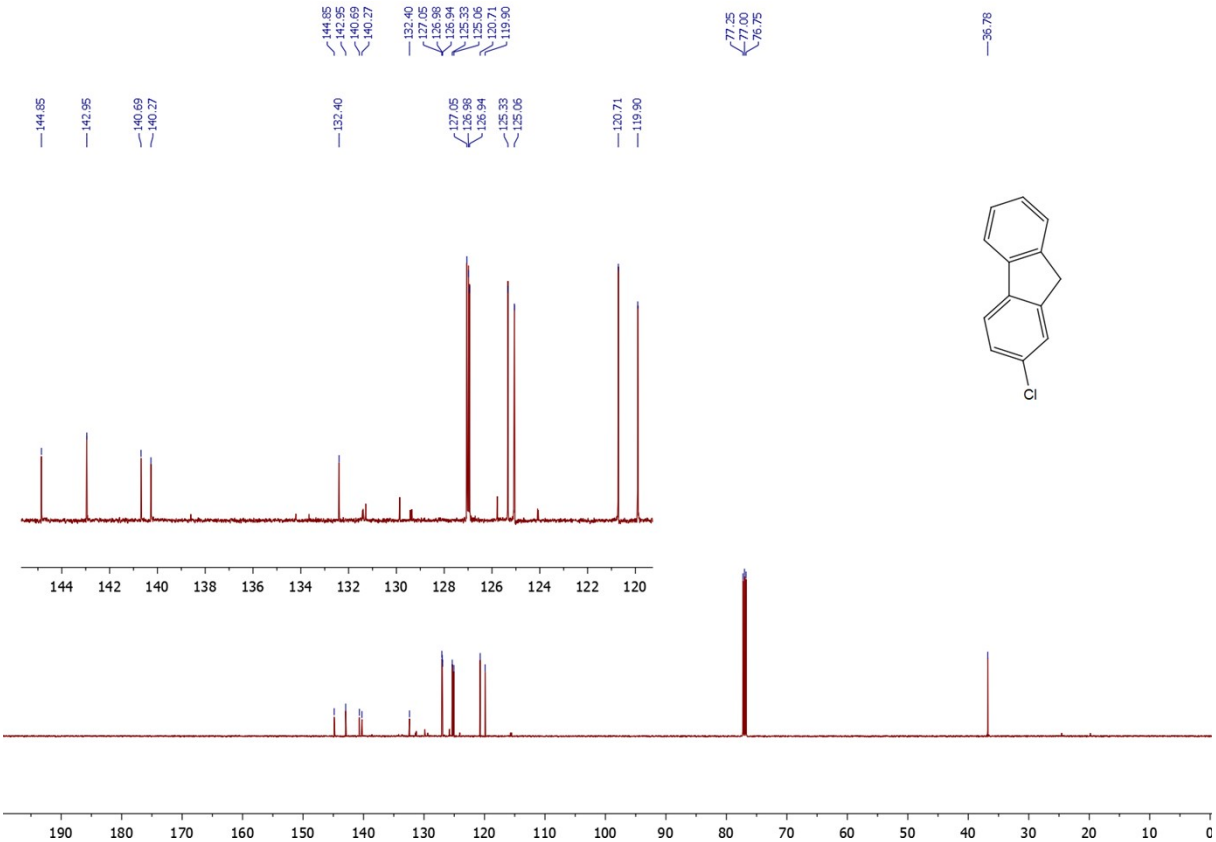


**Figure S108**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-chloro-9H-fluorene (**3**).

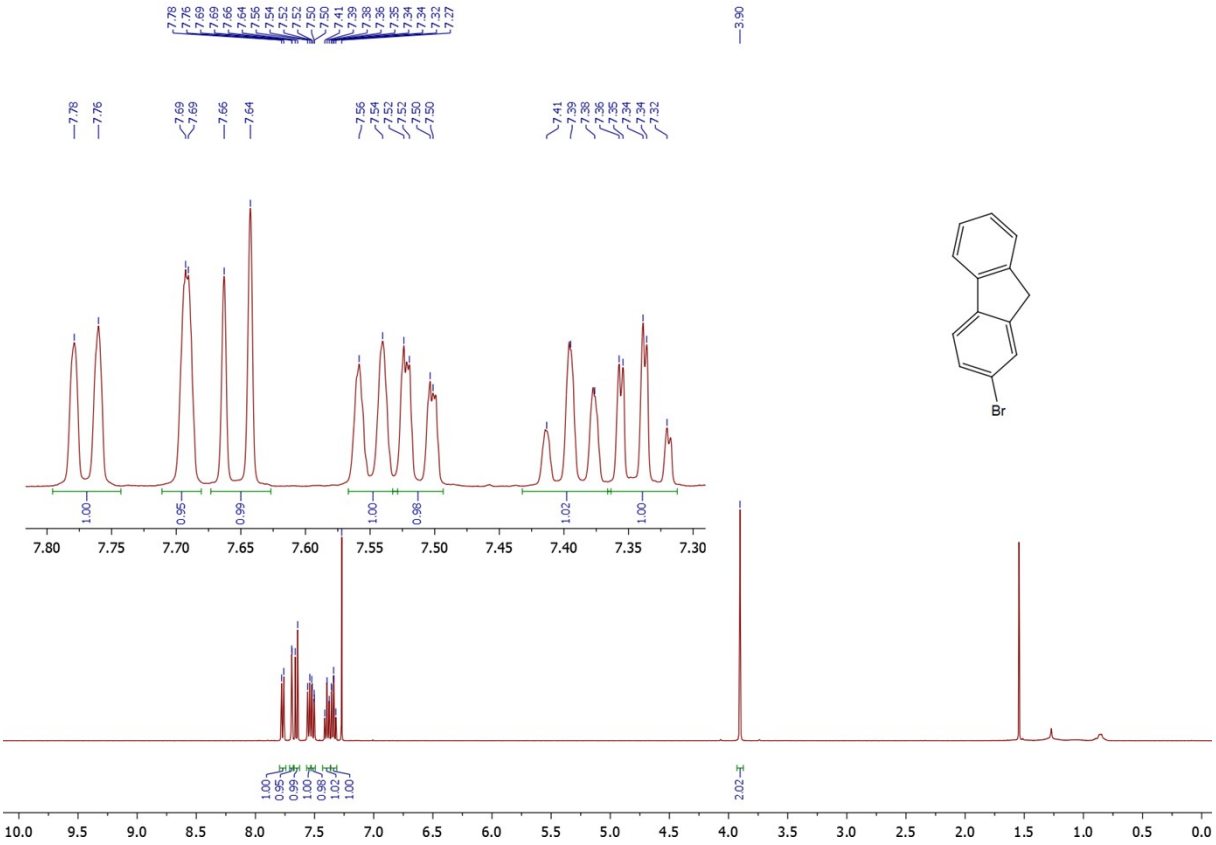


**Figure S109**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 2-bromo-9H-fluorene (**4**).

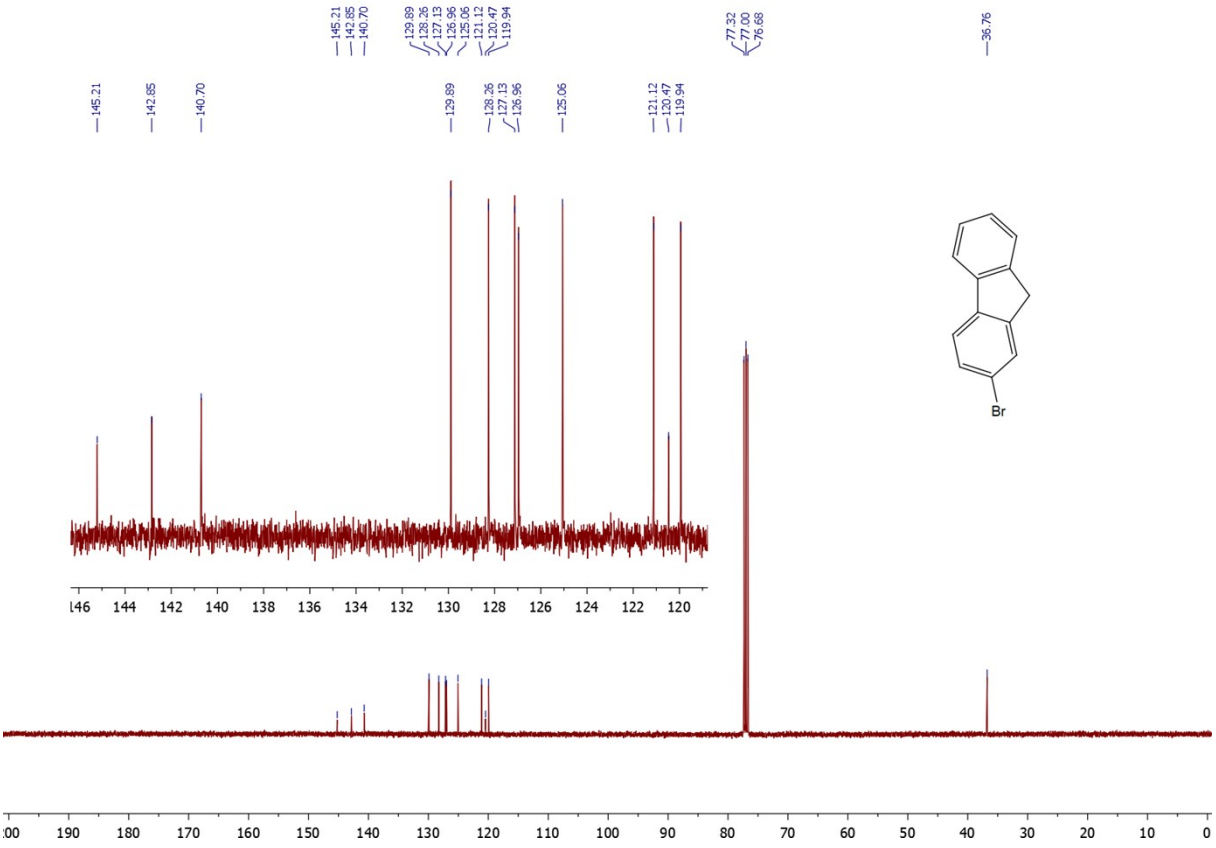


**Figure S110**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 2-bromo-9H-fluorene (**4**).

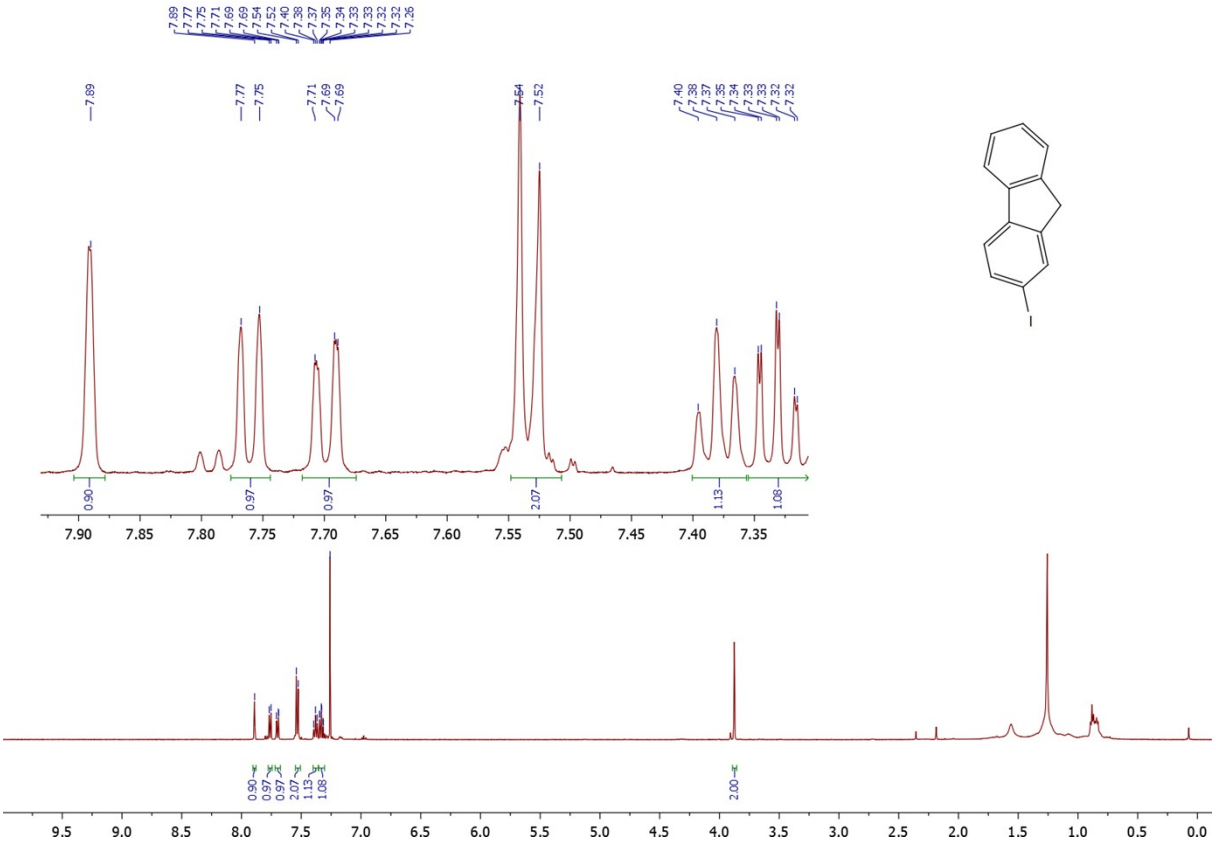

**Figure S111**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-iodo-9H-fluorene (**5**).

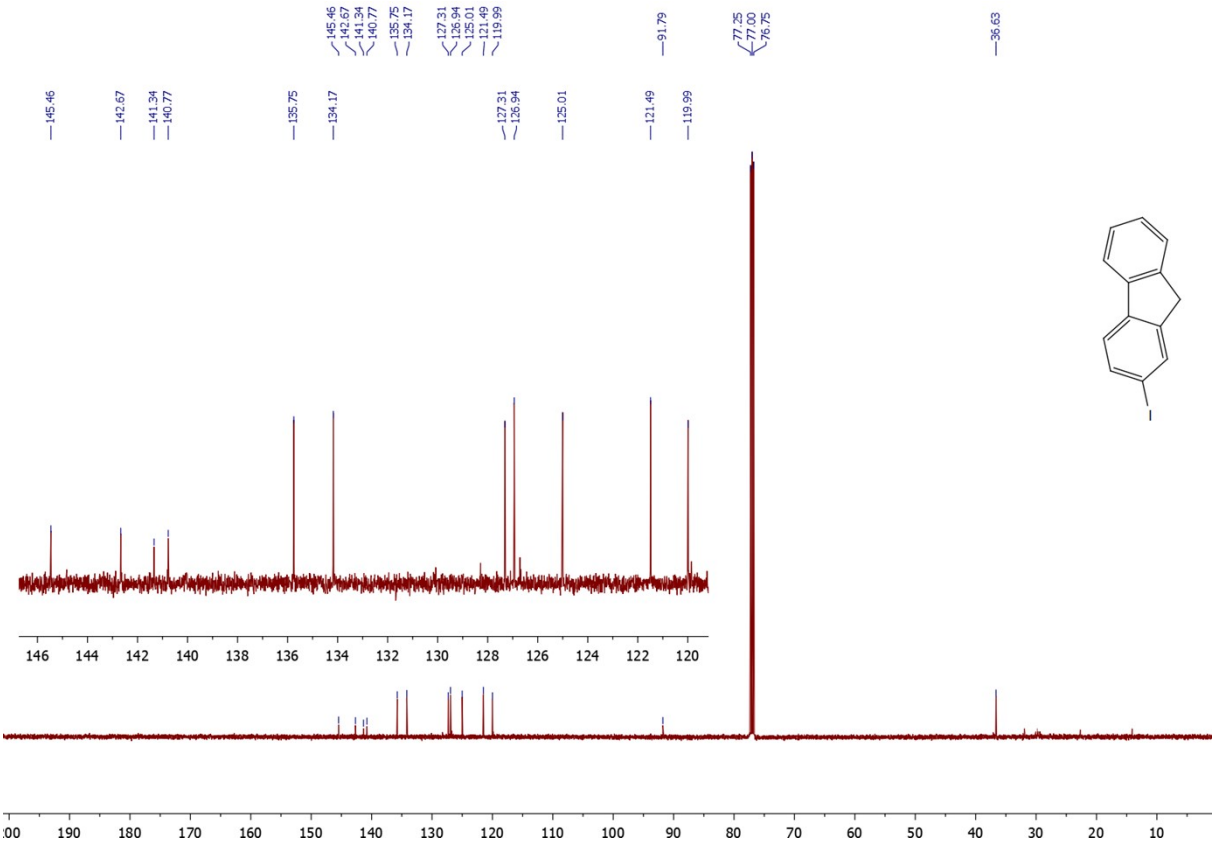

**Figure S112**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-iodo-9H-fluorene (**5**).

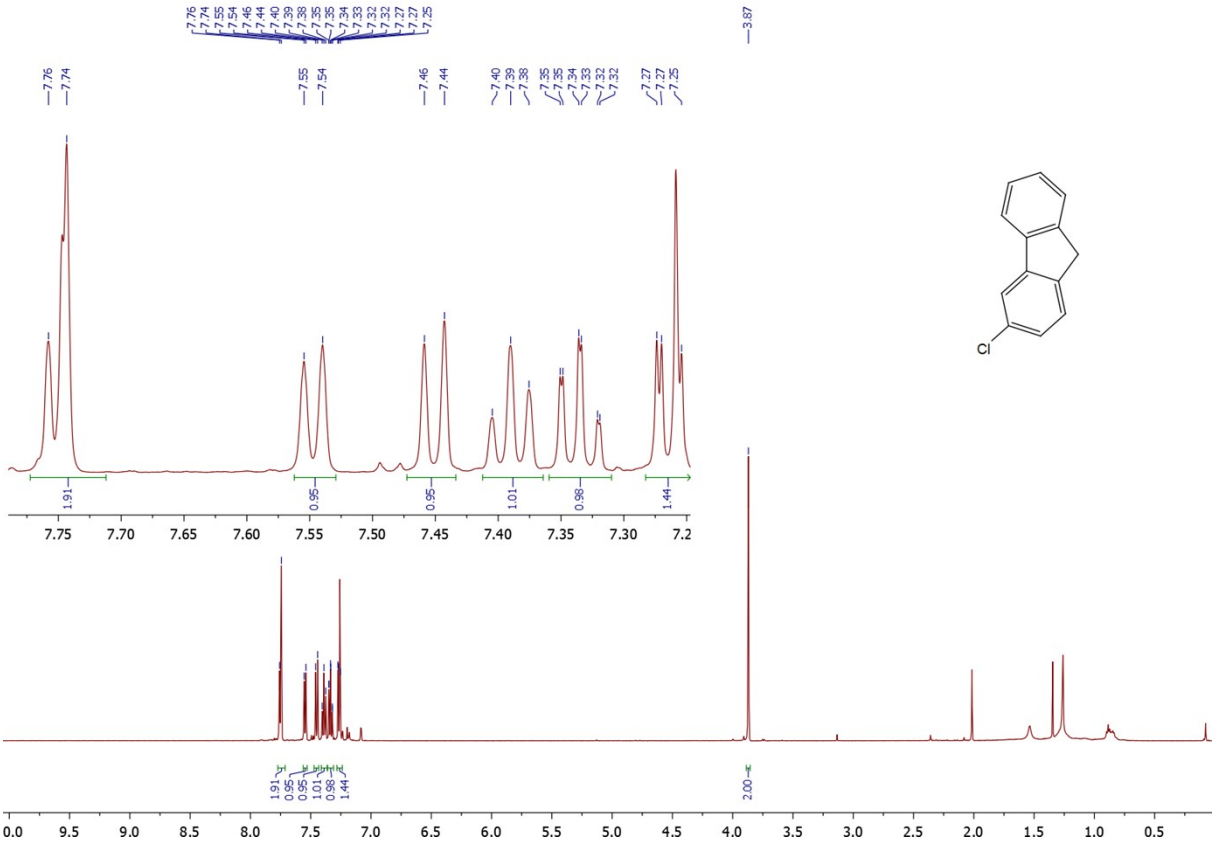


**Figure S113**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 3-chloro-9H-fluorene (**6**).

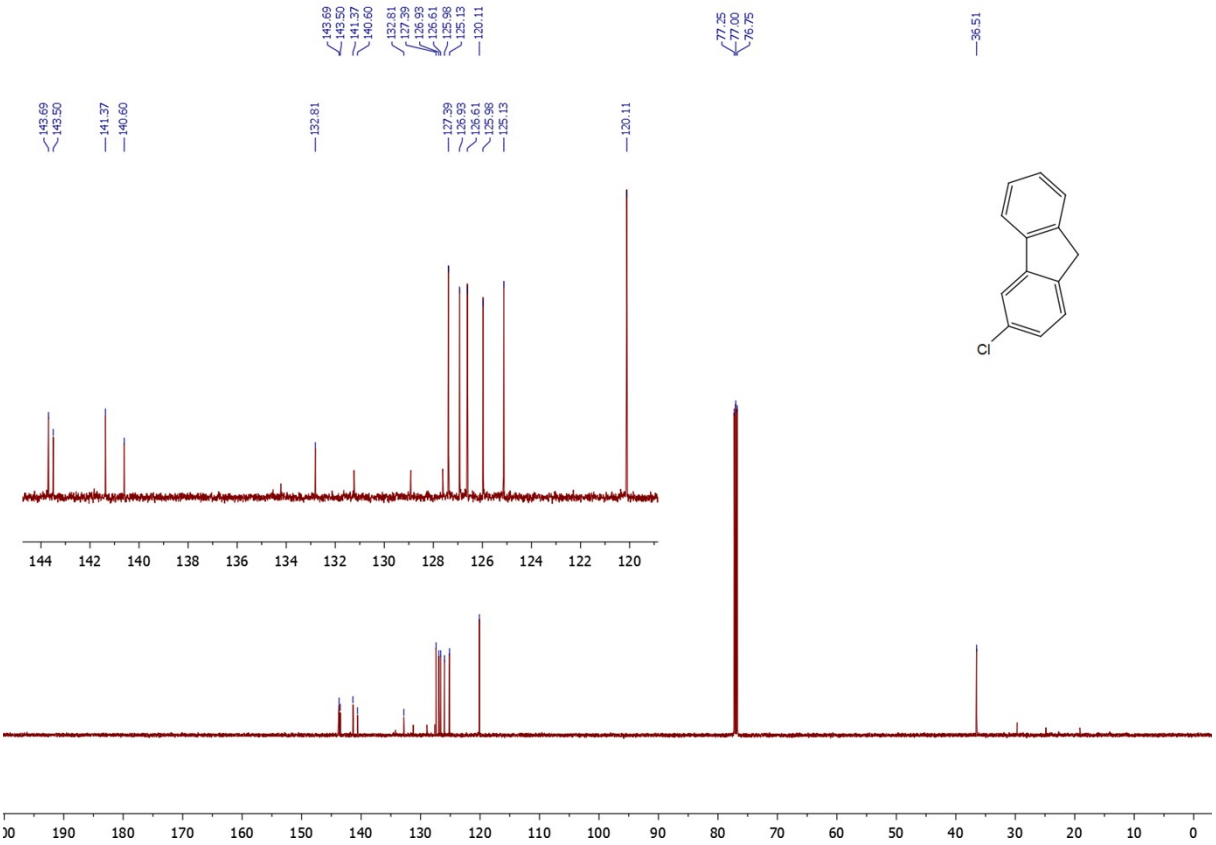


**Figure S114**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 3-chloro-9H-fluorene (**6**).

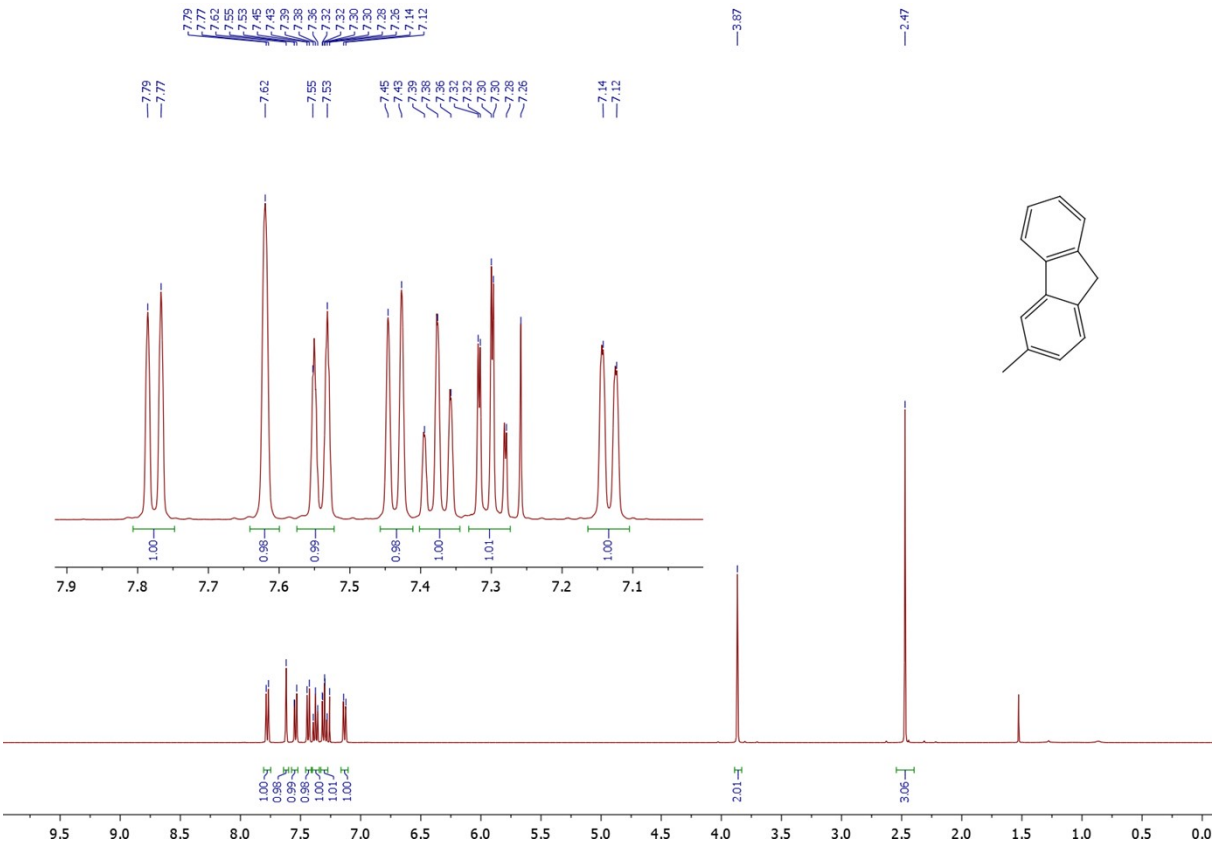

**Figure S115**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 3-methyl-9H-fluorene (**7**).

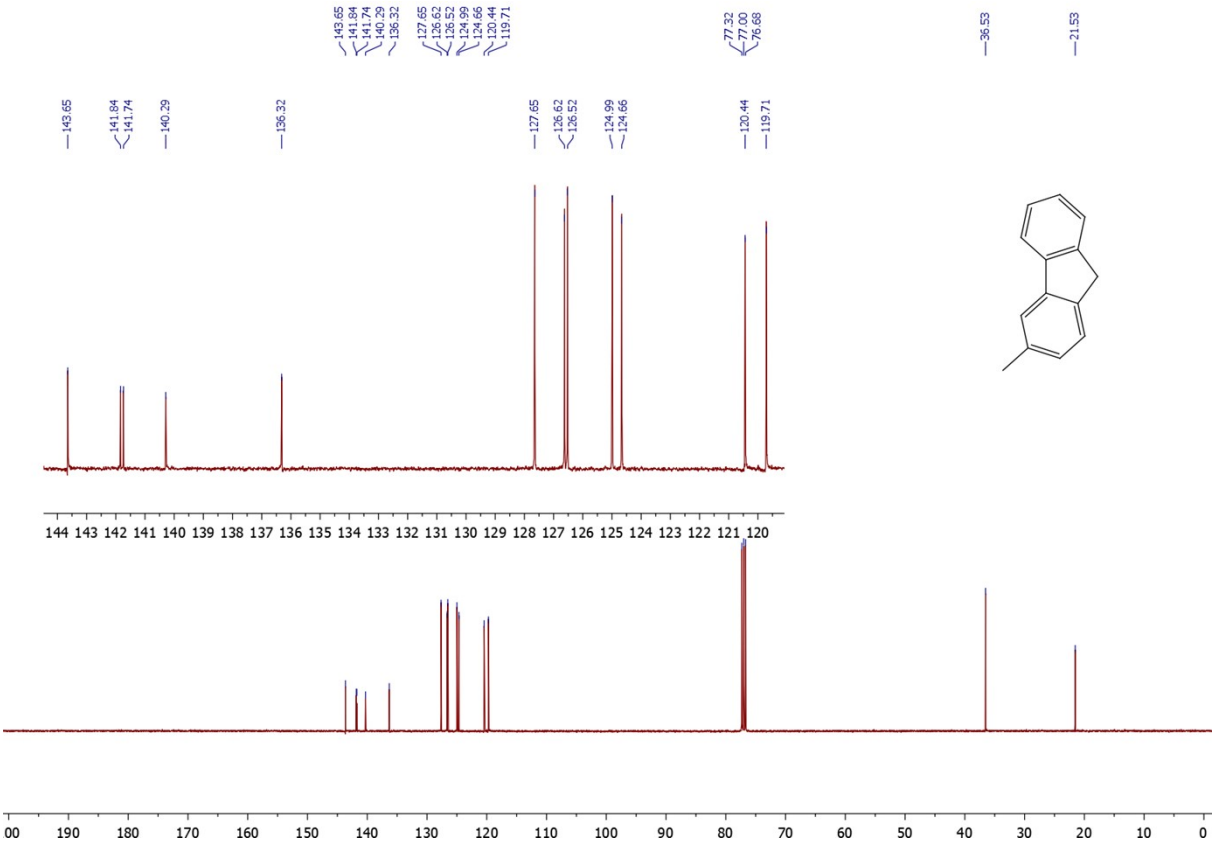

**Figure S116**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 3-methyl-9H-fluorene (**7**).

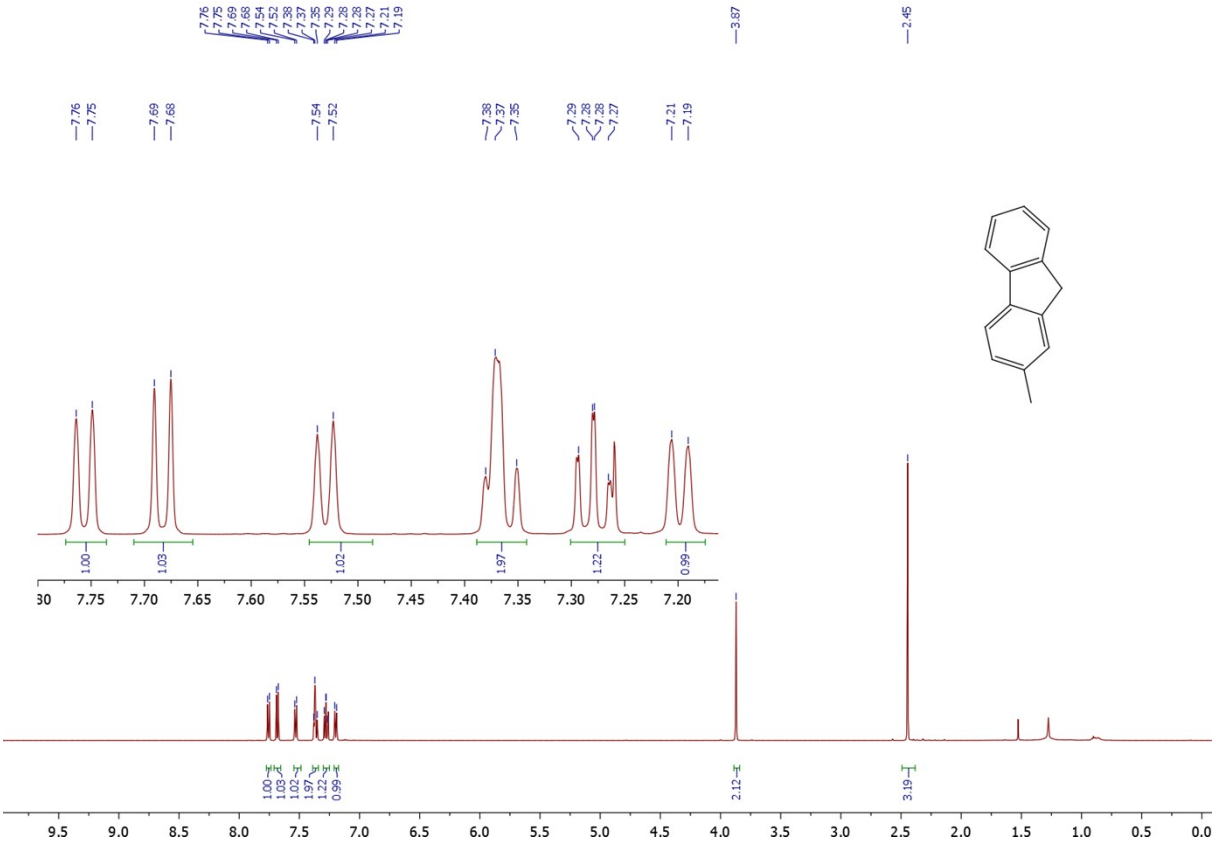

**Figure S117**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 2-methyl-9H-fluorene (**8**).

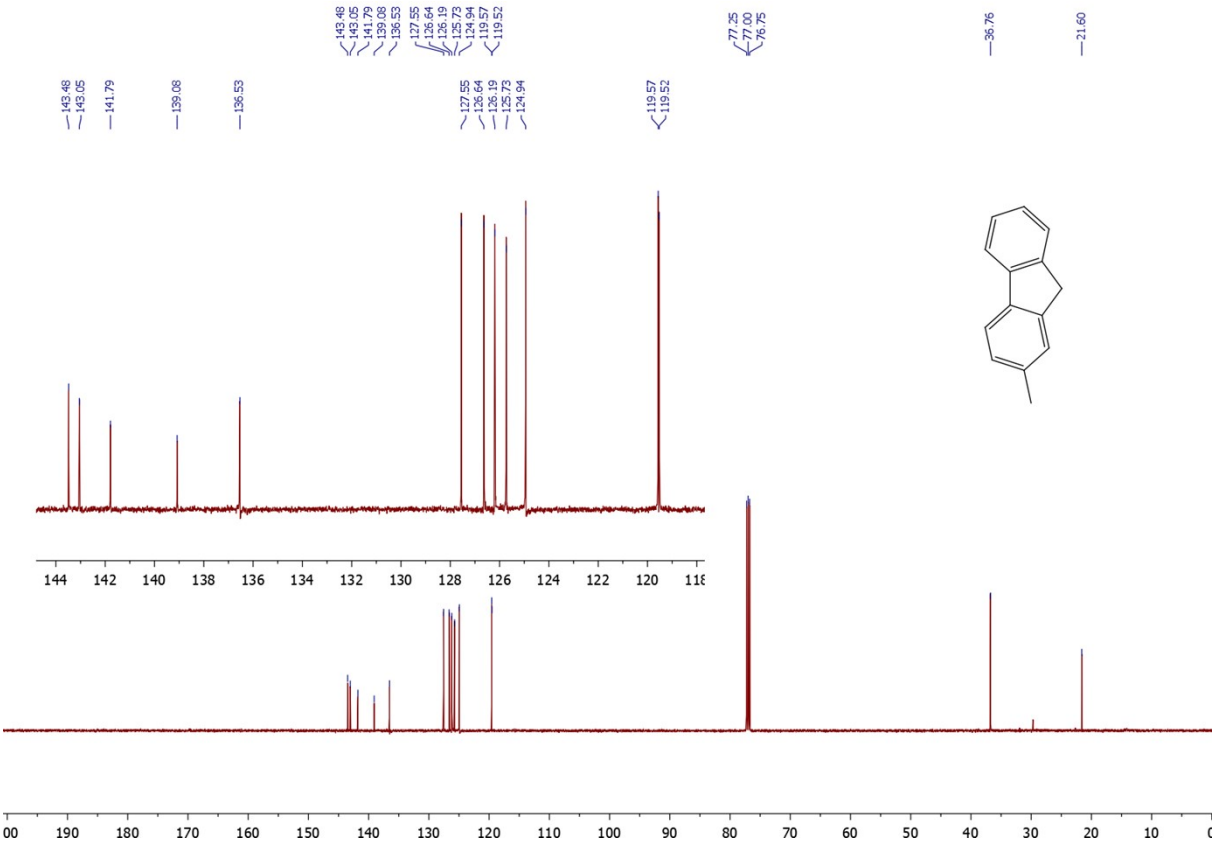

**Figure S118**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 2-methyl-9H-fluorene (**8**).

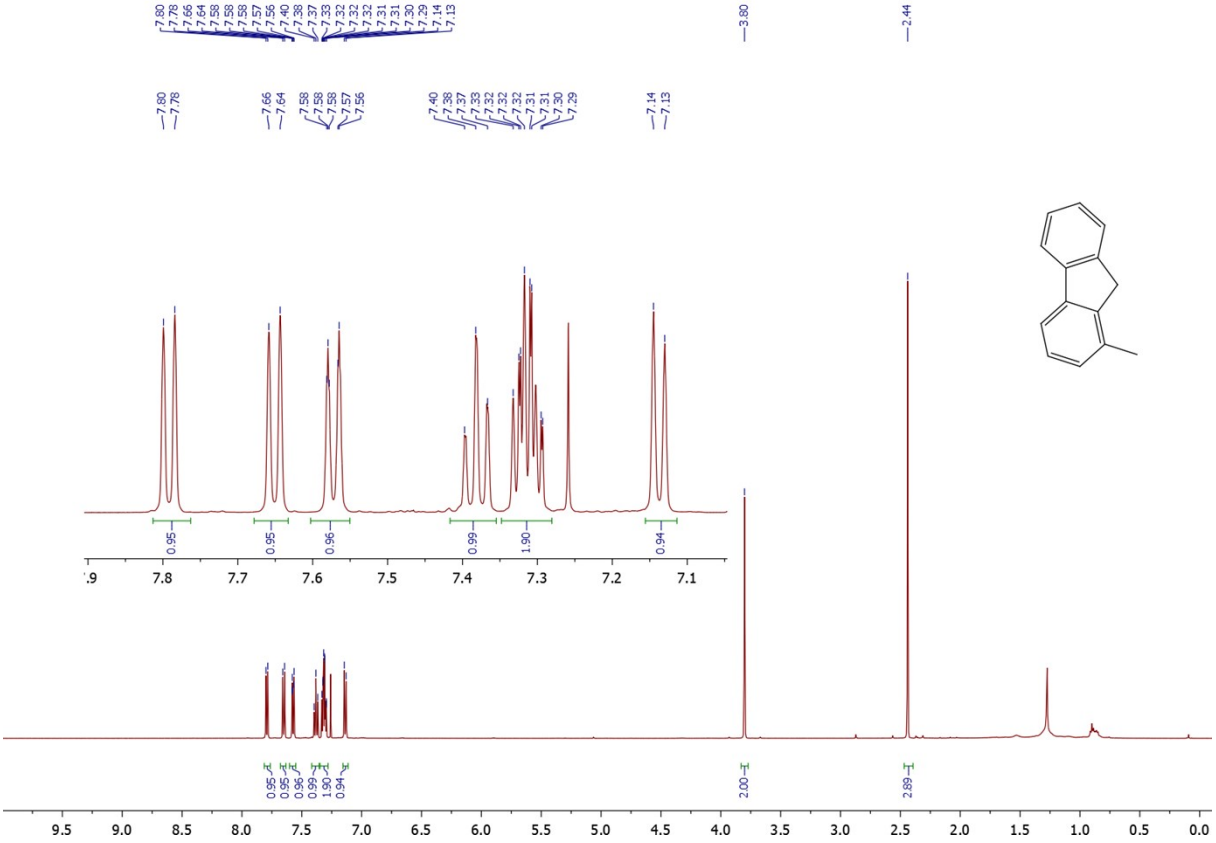

**Figure S119**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 1-methyl-9H-fluorene (**9**).

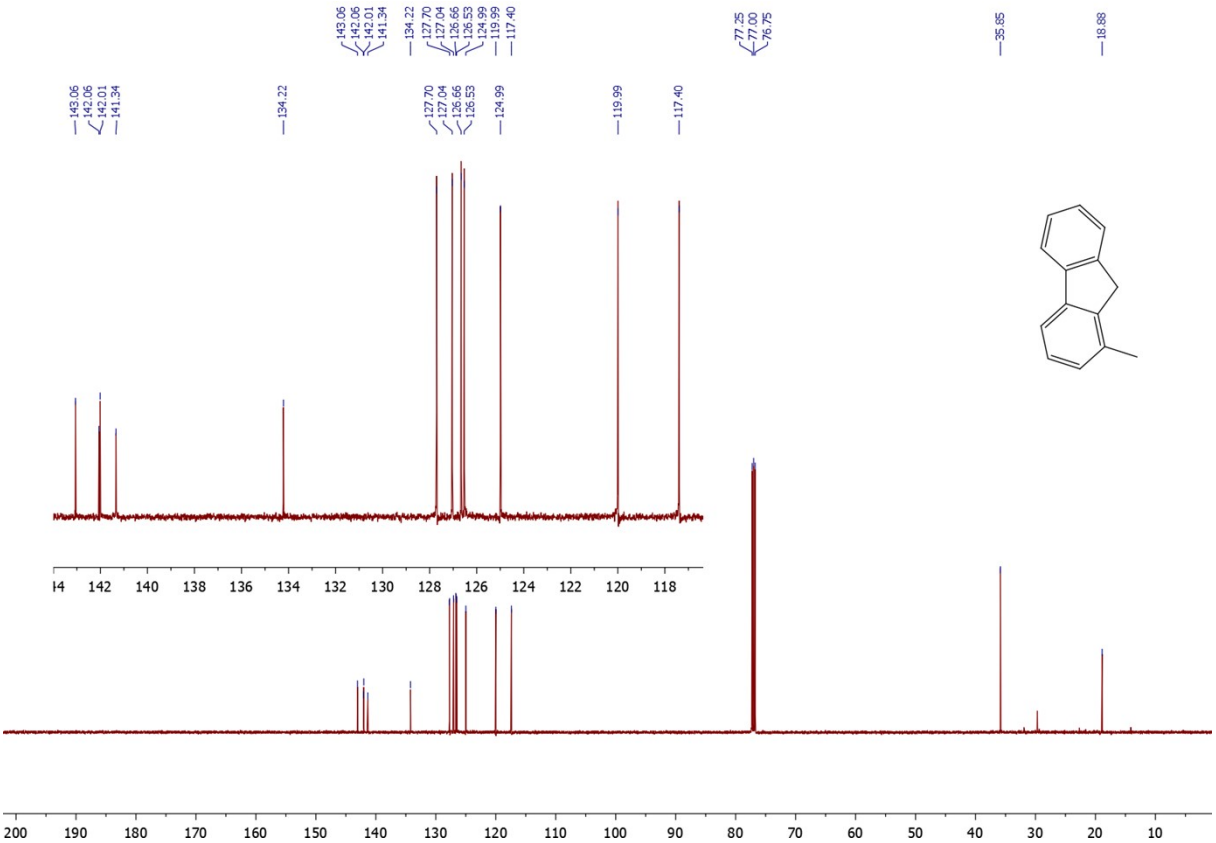

**Figure S120**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 1-methyl-9H-fluorene (**9**).

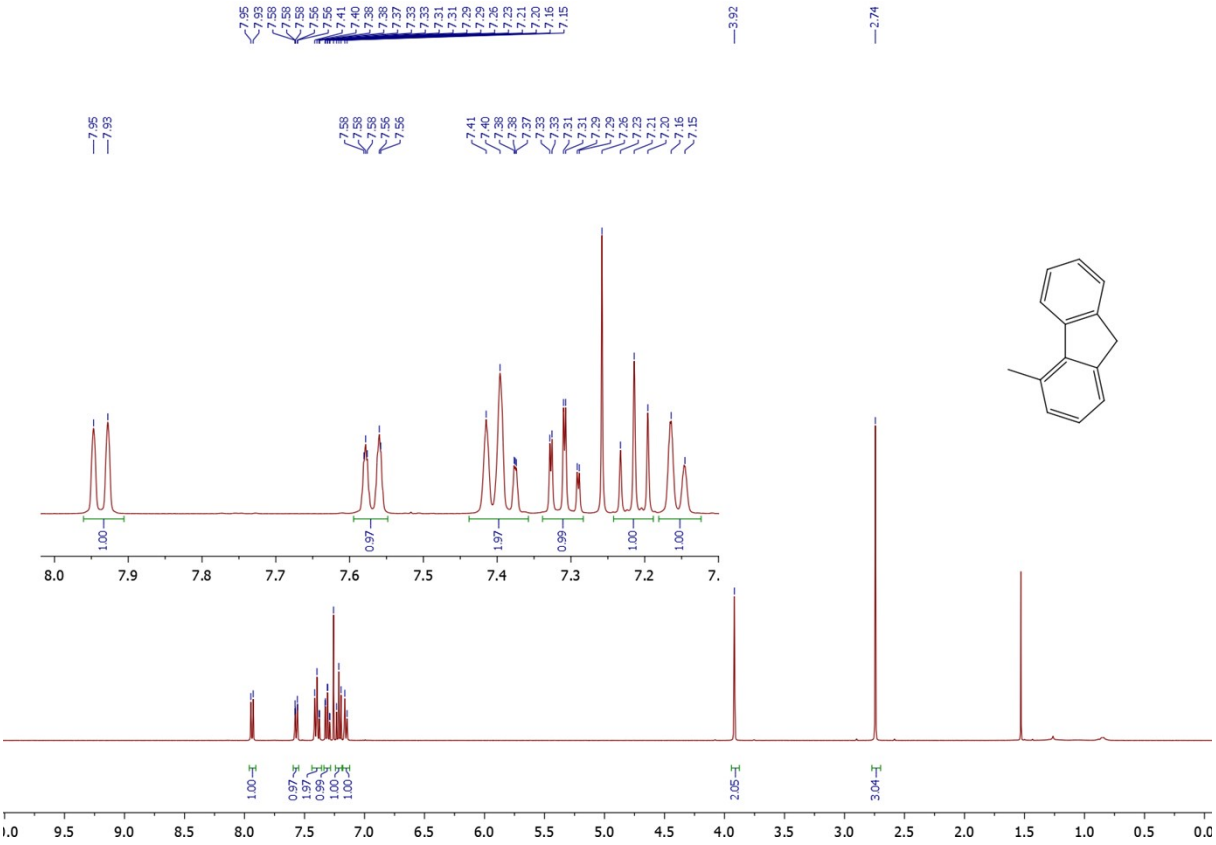

**Figure S121**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 4-methyl-9H-fluorene (**11**).

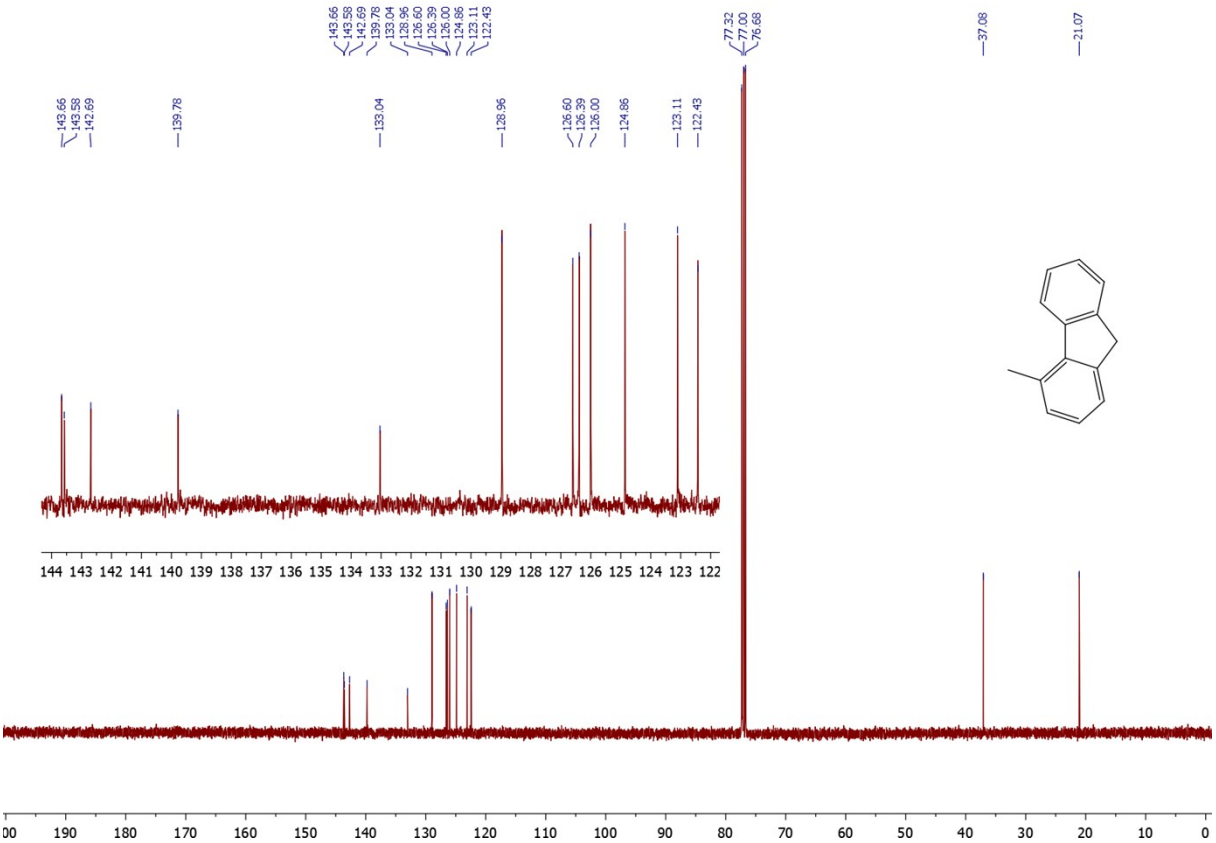

**Figure S122**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 4-methyl-9H-fluorene (**11**).

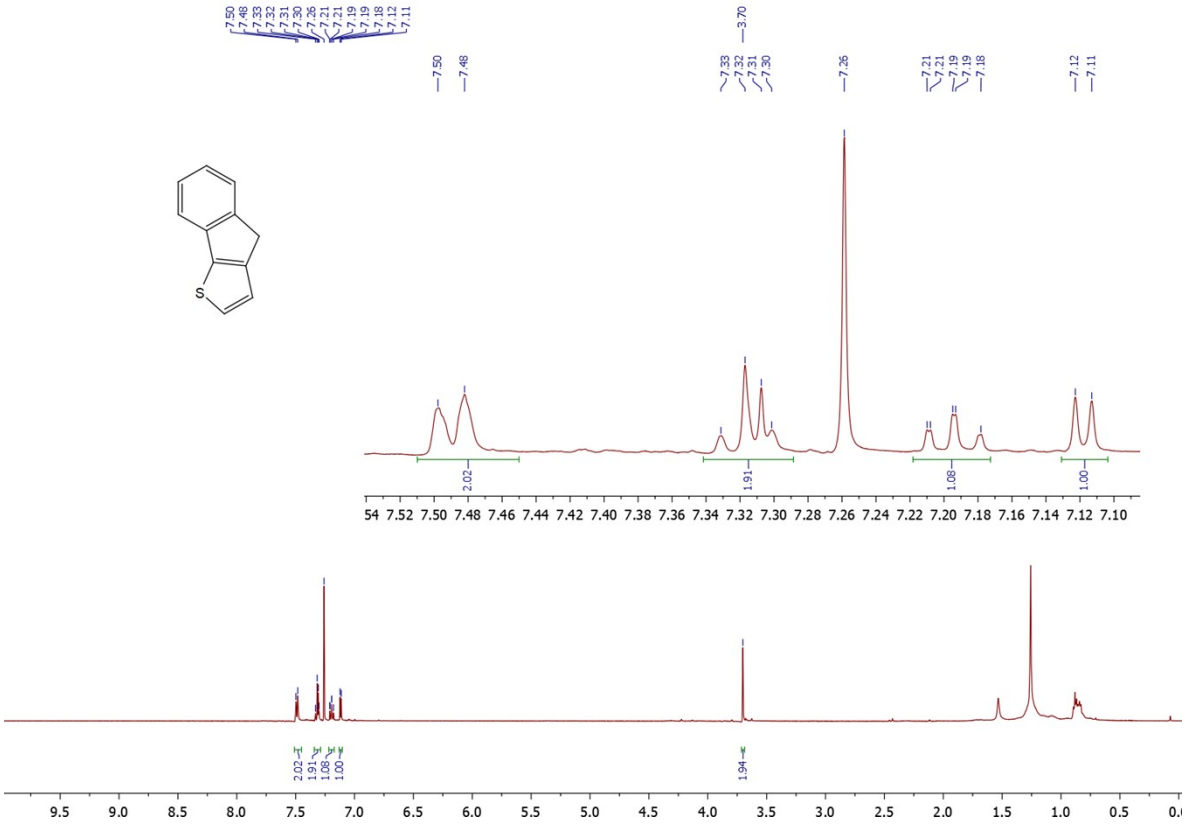

**Figure S123**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 8H-indeno[2,1-b]thiophene (**12**).

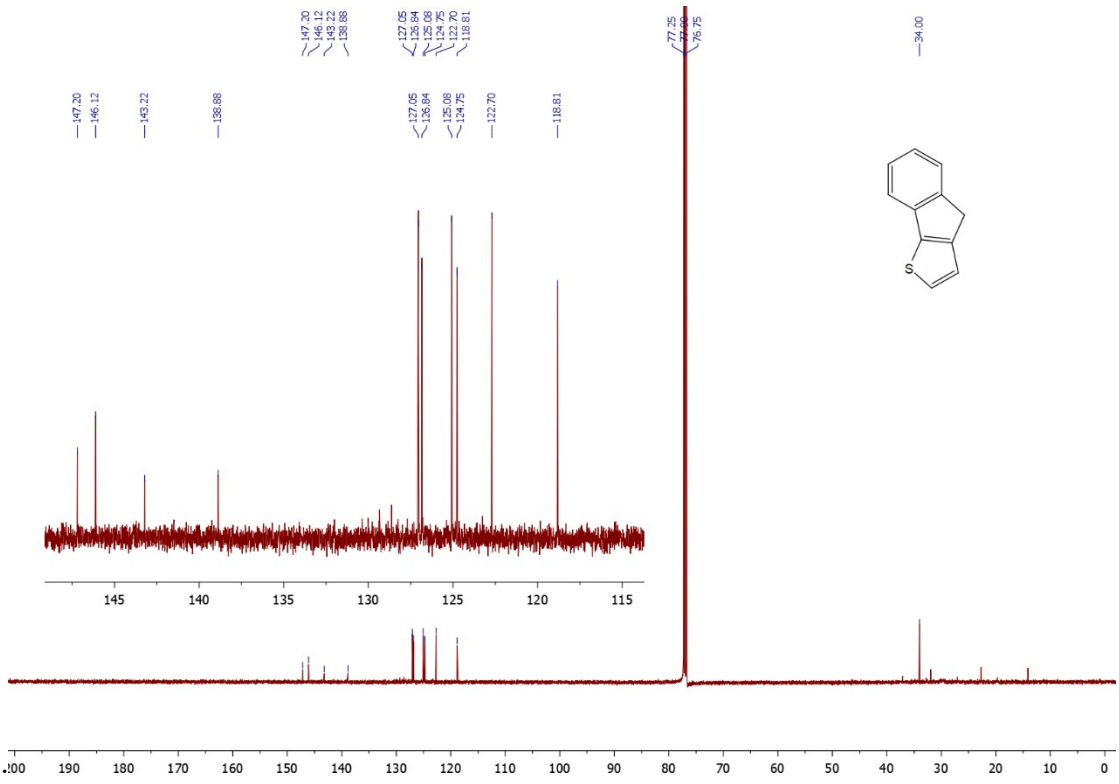

**Figure S124**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 8H-indeno[2,1-b]thiophene (**12**).

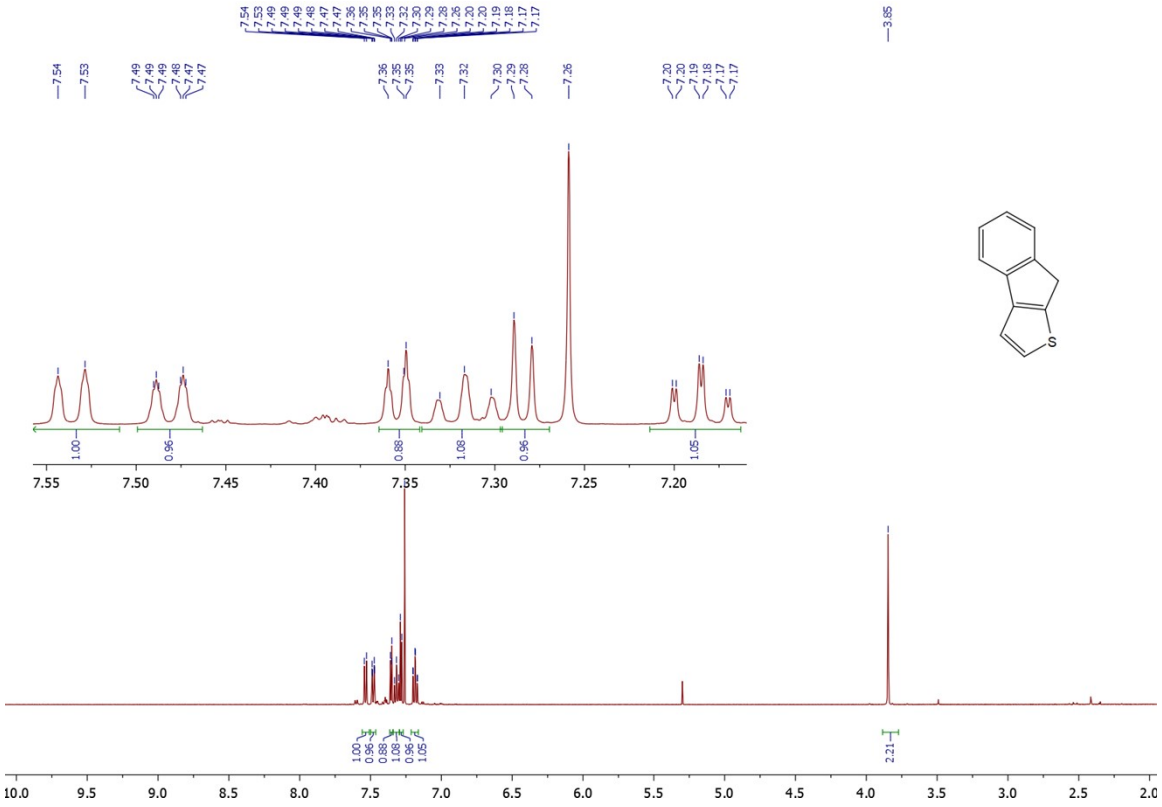

**Figure S125**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 4H-indeno[2,1-b]thiophene (**13**).

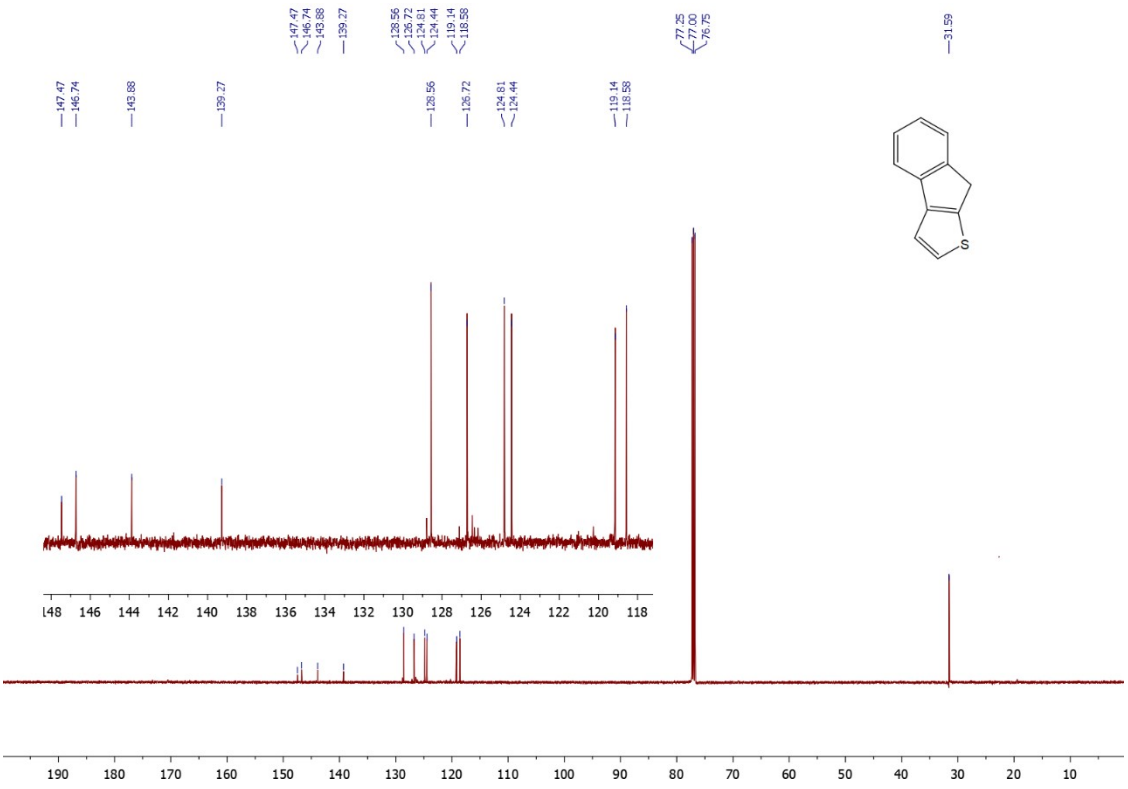

**Figure S126**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 4H-indeno[2,1-b]thiophene (**13**).

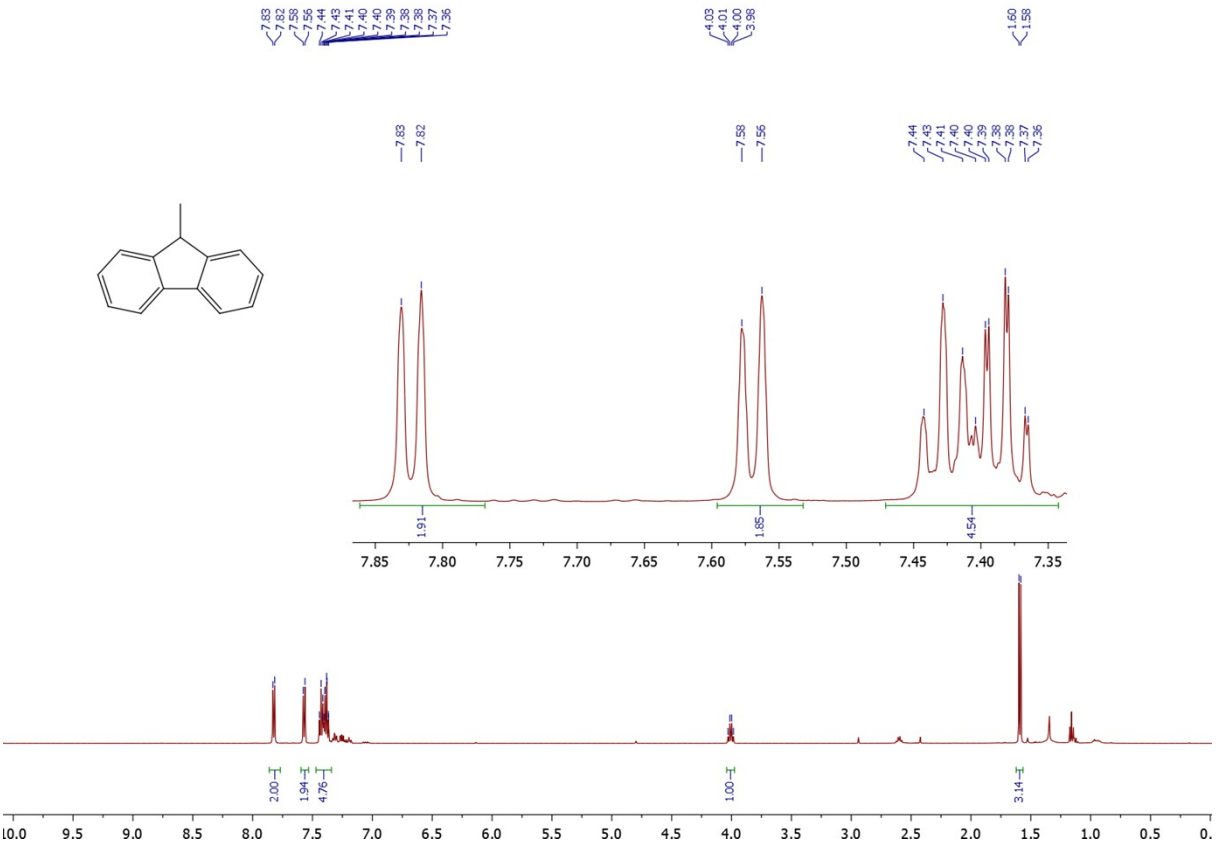

**Figure S127**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 9-methyl-9H-fluorene (**14**).

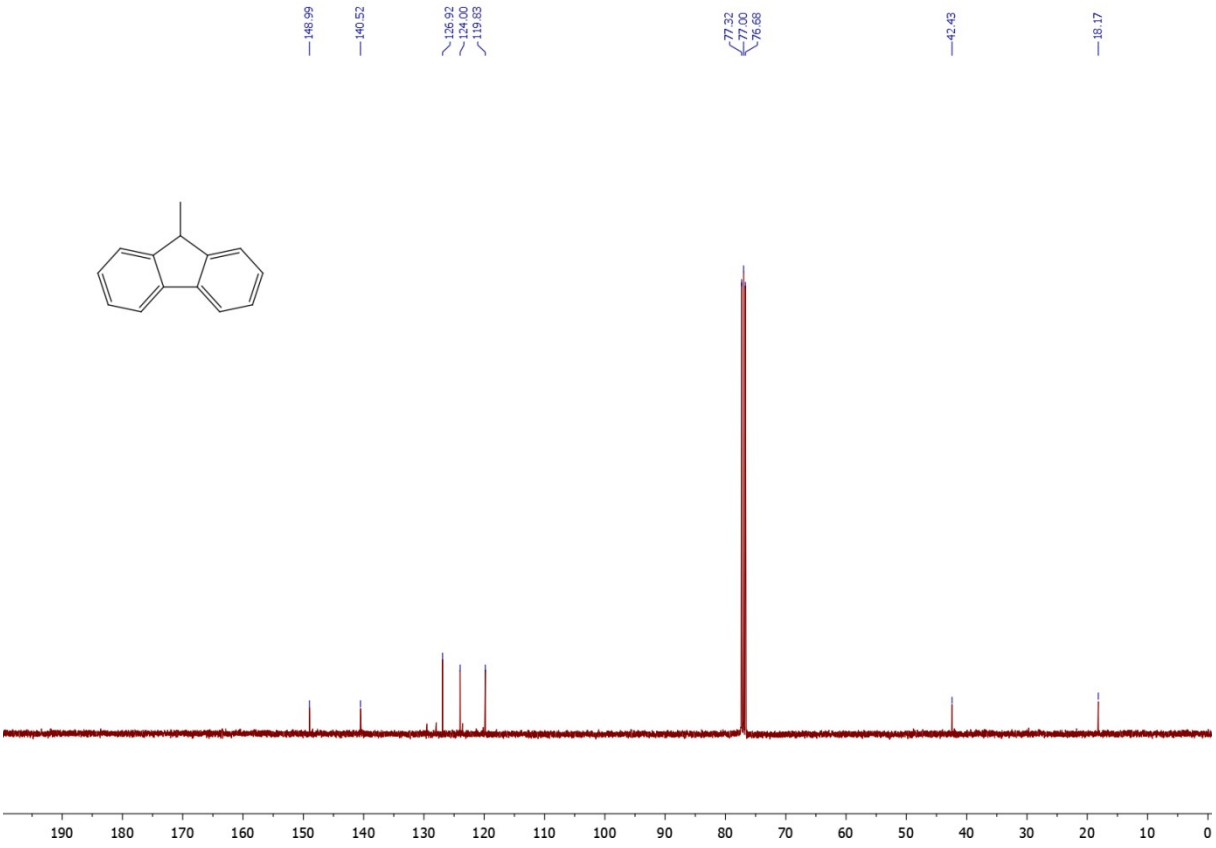

**Figure S128**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 9-methyl-9H-fluorene (**14**).

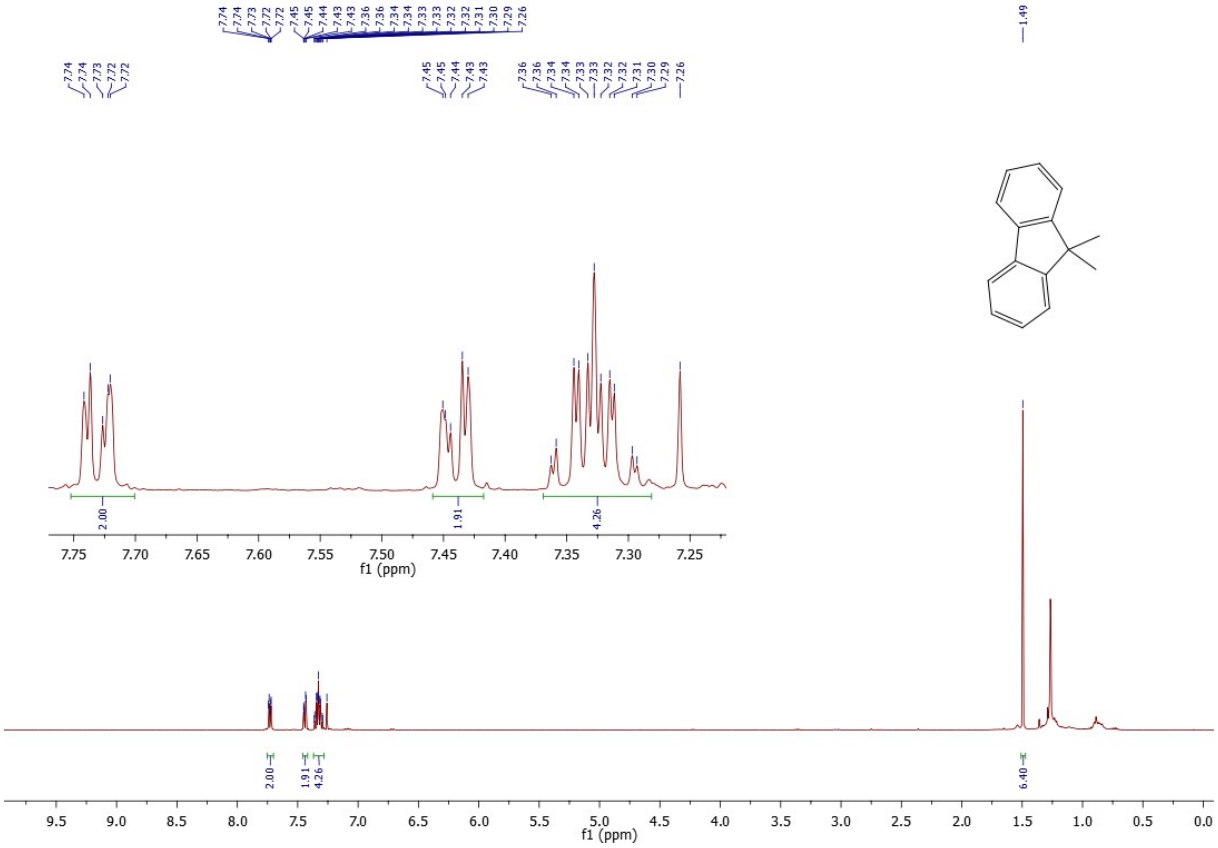

**Figure S129**. $^{1}$H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 9-methyl-9H-fluorene (**15**).

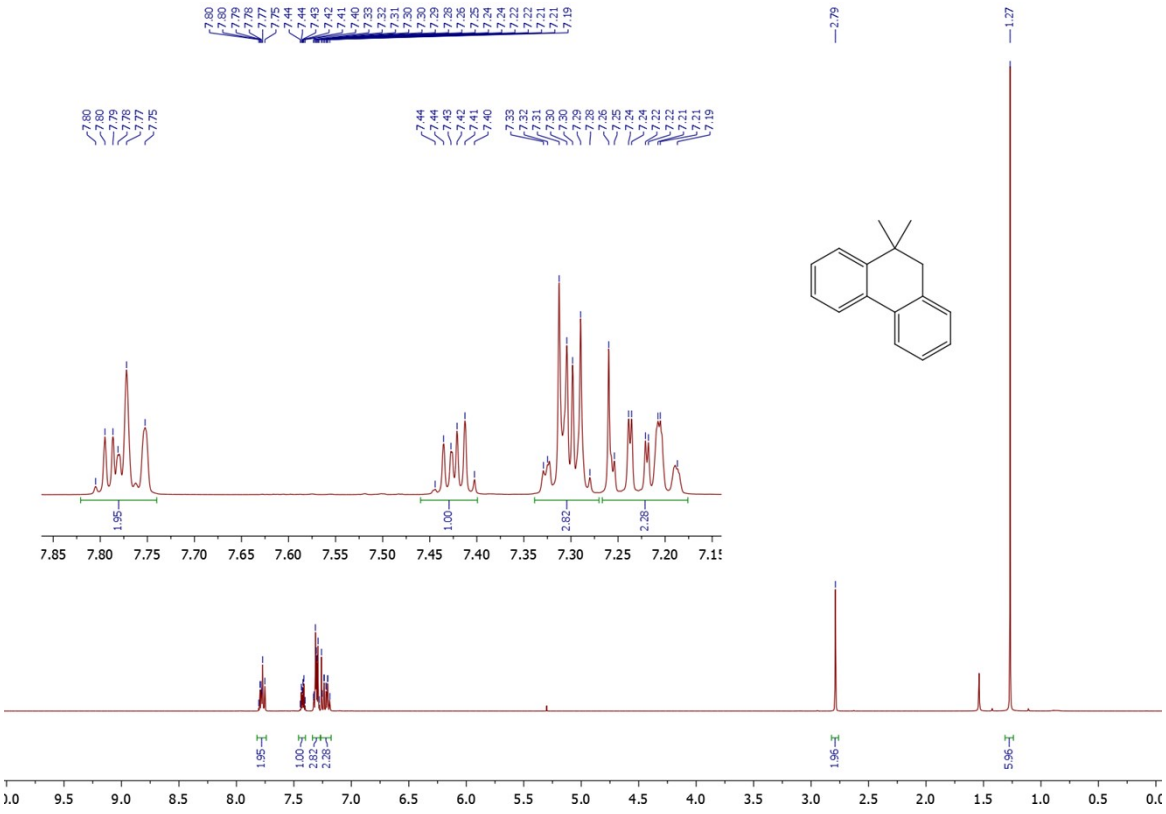

**Figure S130**. $^{1}$H NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 9,9-dimethyl-9,10-dihydrophenanthrene (**16**).

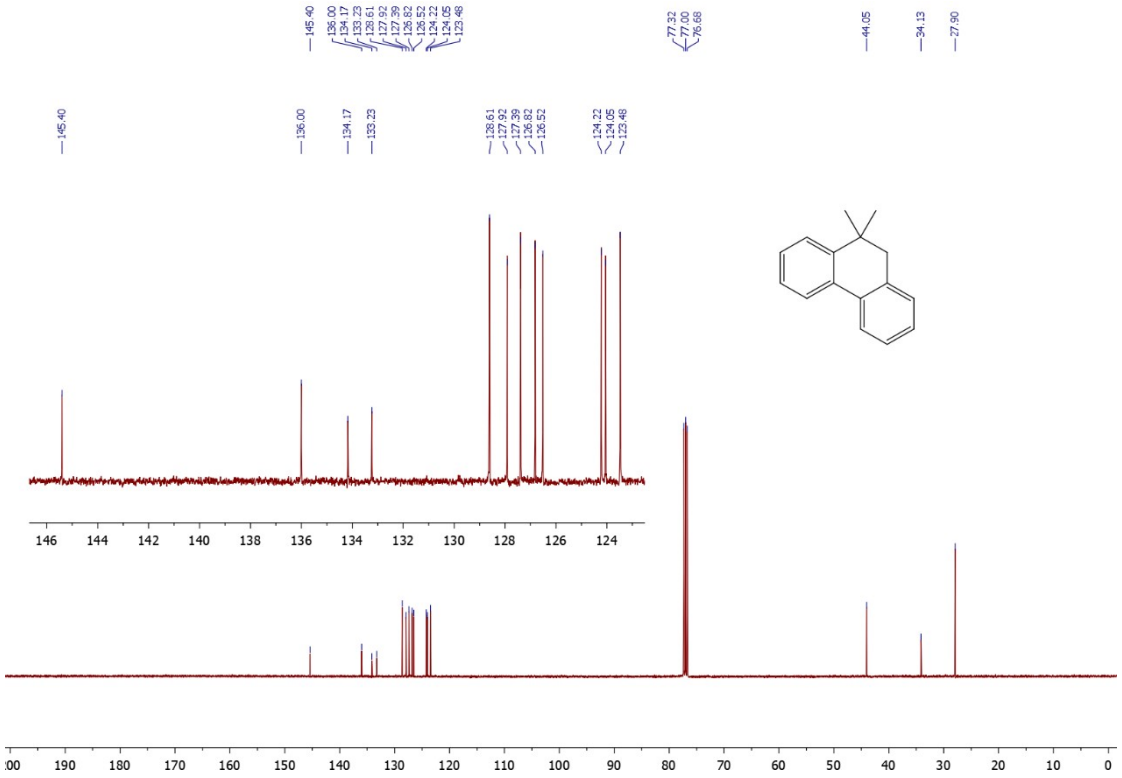

**Figure S131**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 9,9-dimethyl-9,10-dihydrophenanthrene (**16**).

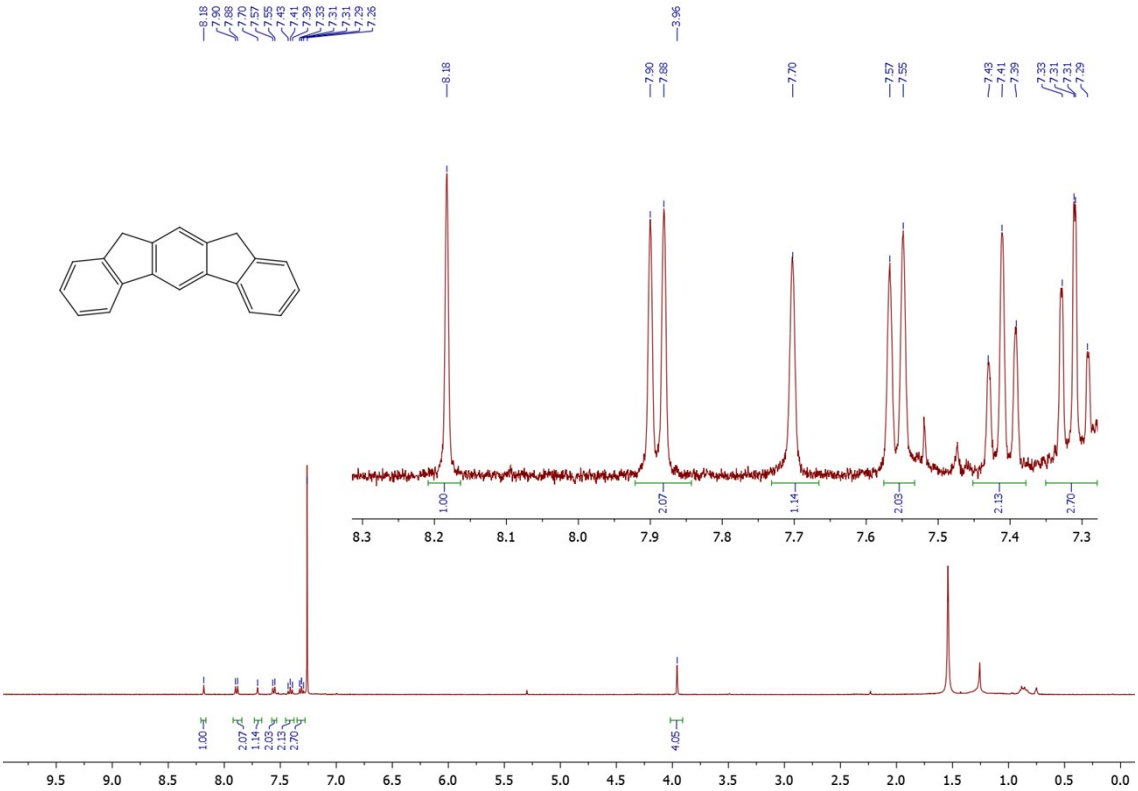

**Figure S132**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 10,12-dihydroindeno[2,1-b]fluorene (**17**).

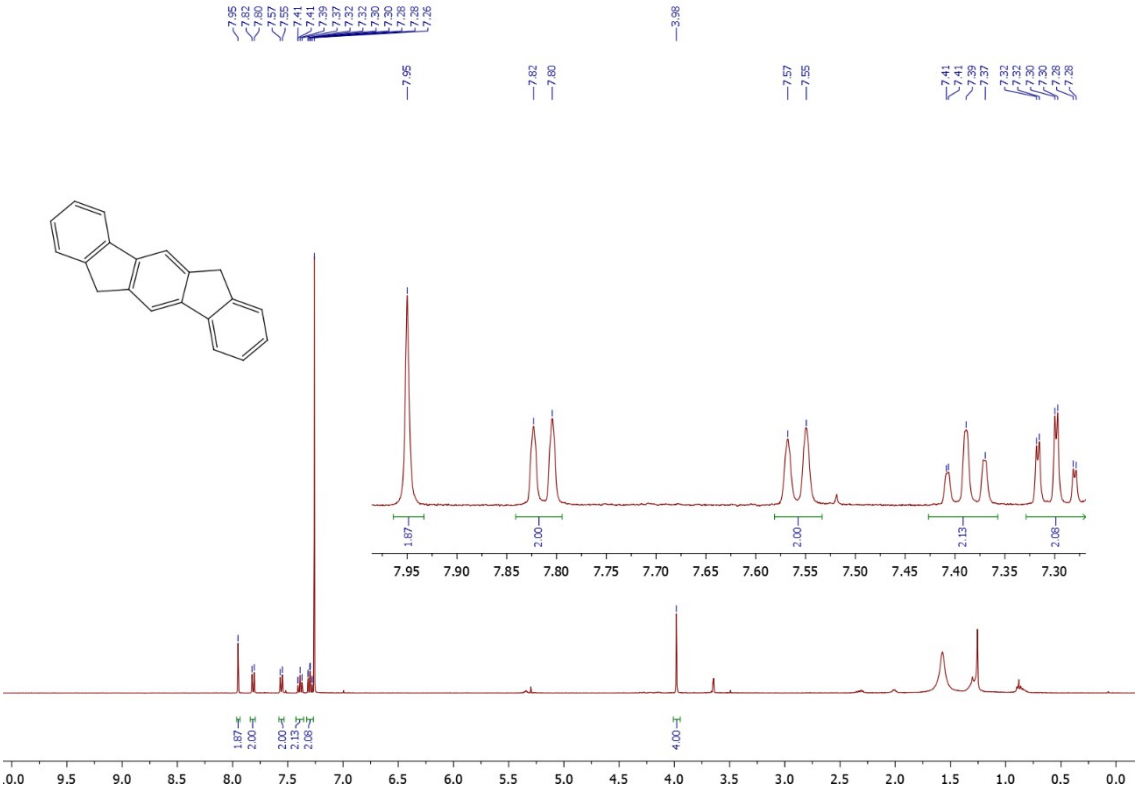

**Figure S133**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 6,12-dihydroindeno[1,2-b]fluorene (**18**).

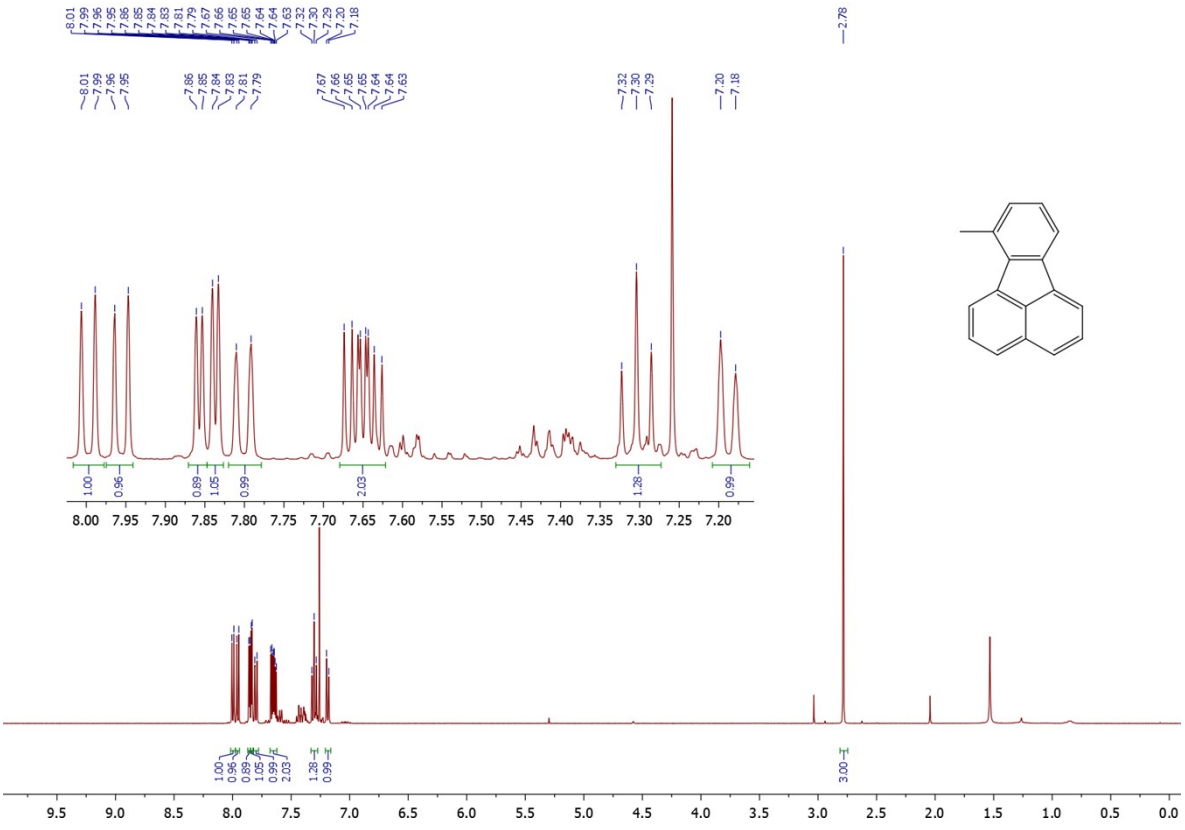

**Figure S134**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 6,12-dihydroindeno[1,2-b]fluorene (**20**).

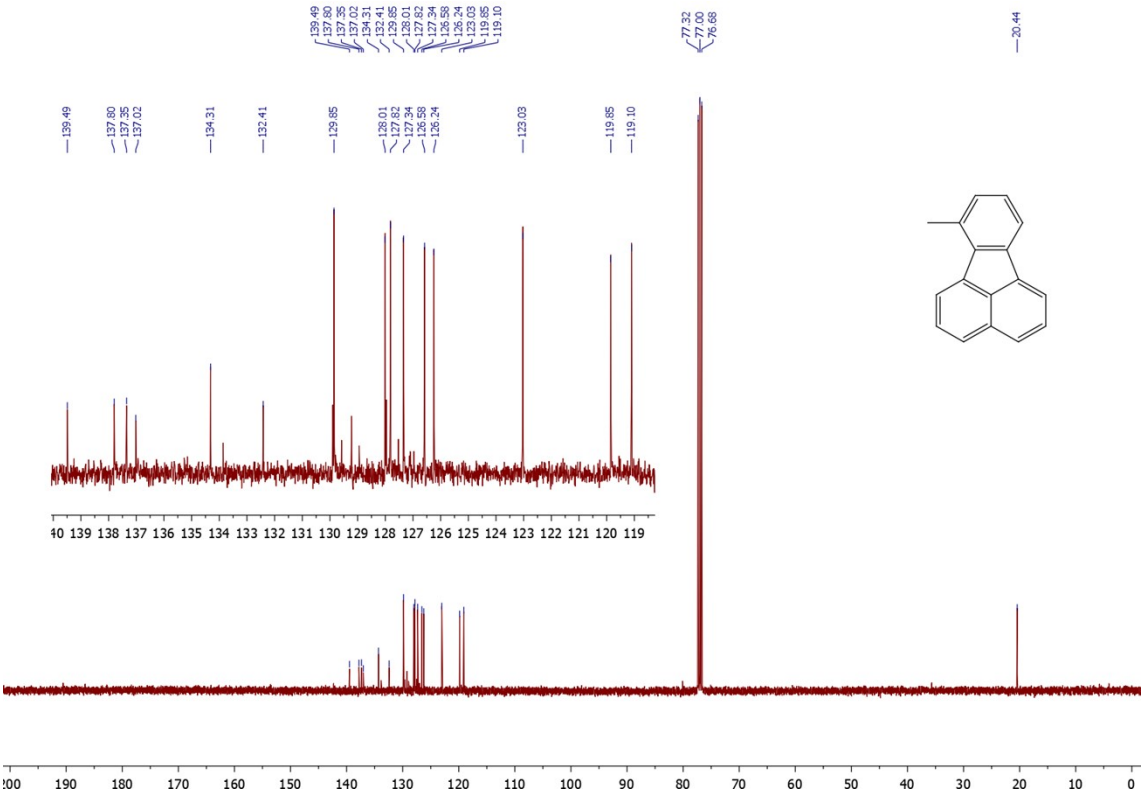

**Figure S135**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 7-methylfluoranthene (**20**).

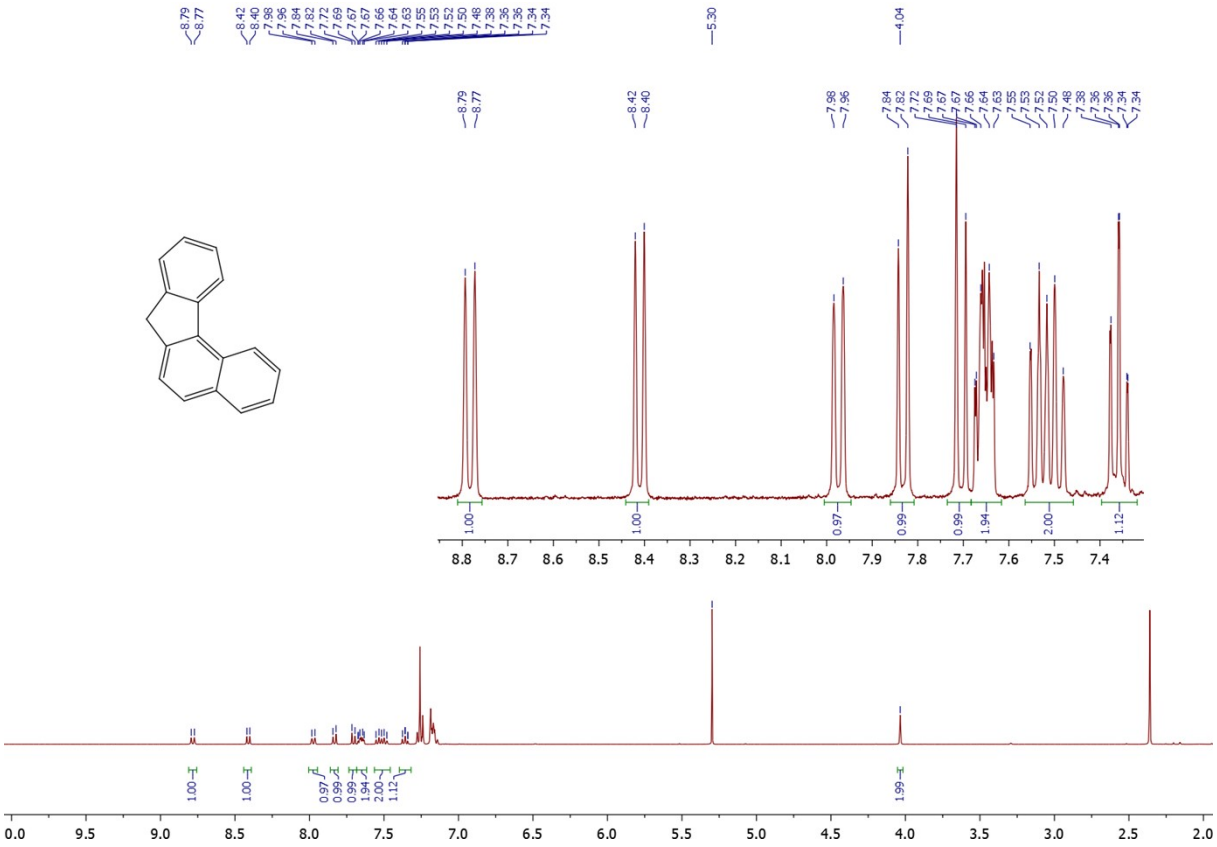

**Figure S136**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 7H-benzo[c]fluorene (**21**).

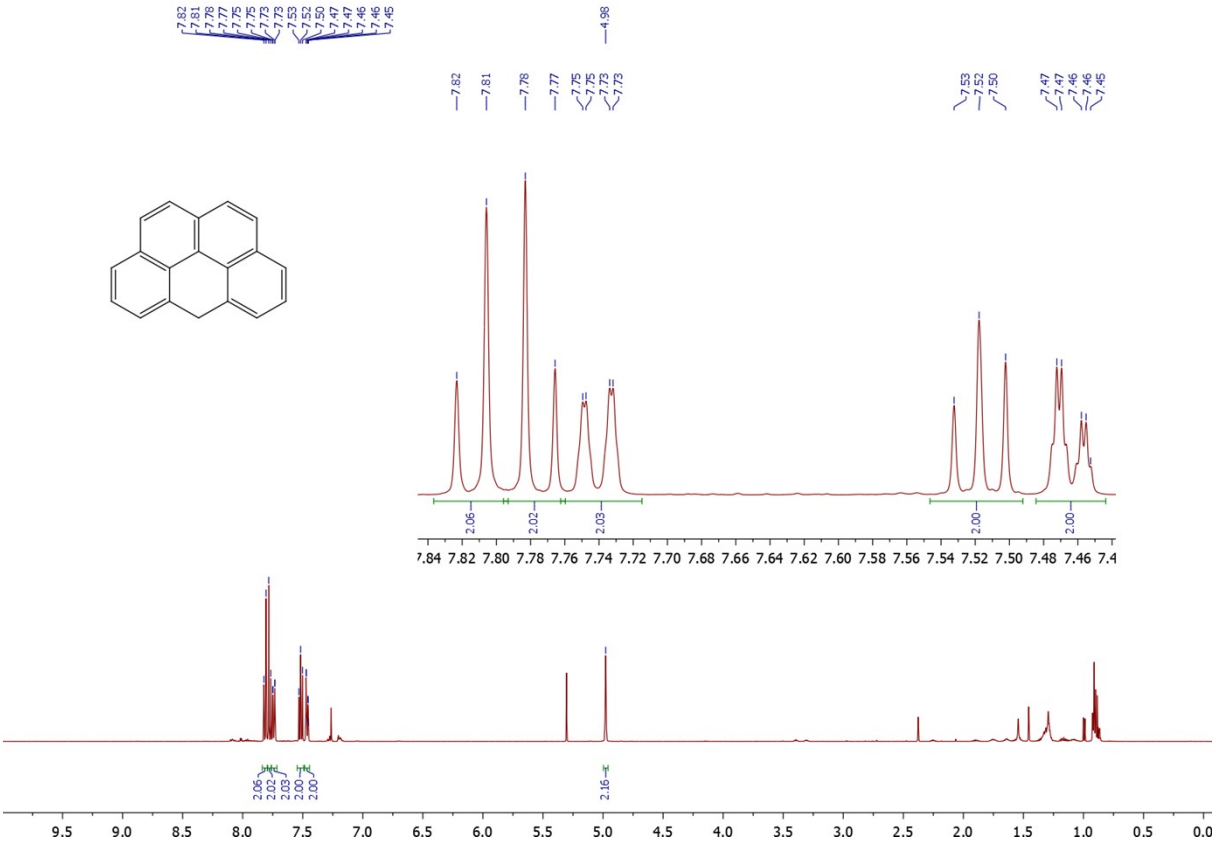

**Figure S137**. $^{1}H$ NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 6H-benzo[cd]pyrene (**22**).

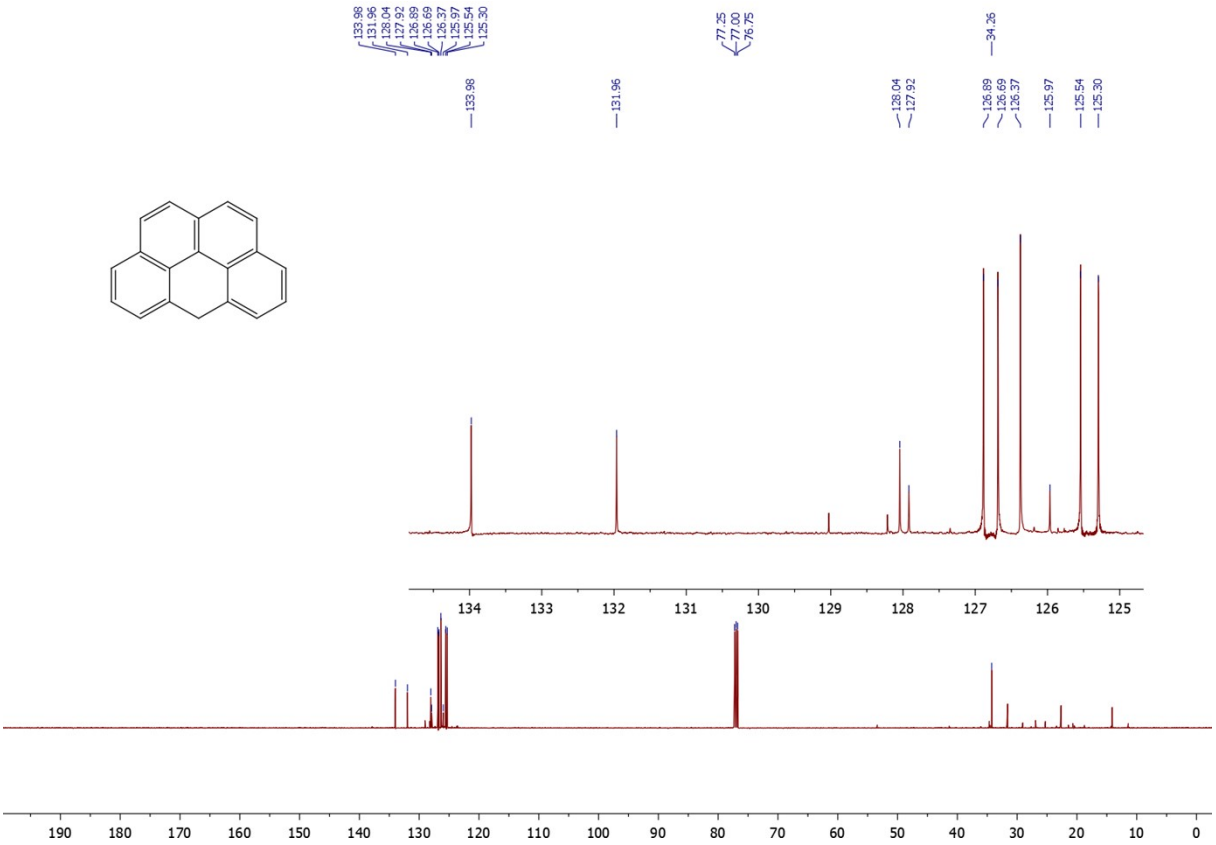

**Figure S138**. $^{13}C$ NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 6H-benzo[cd]pyrene (**22**).

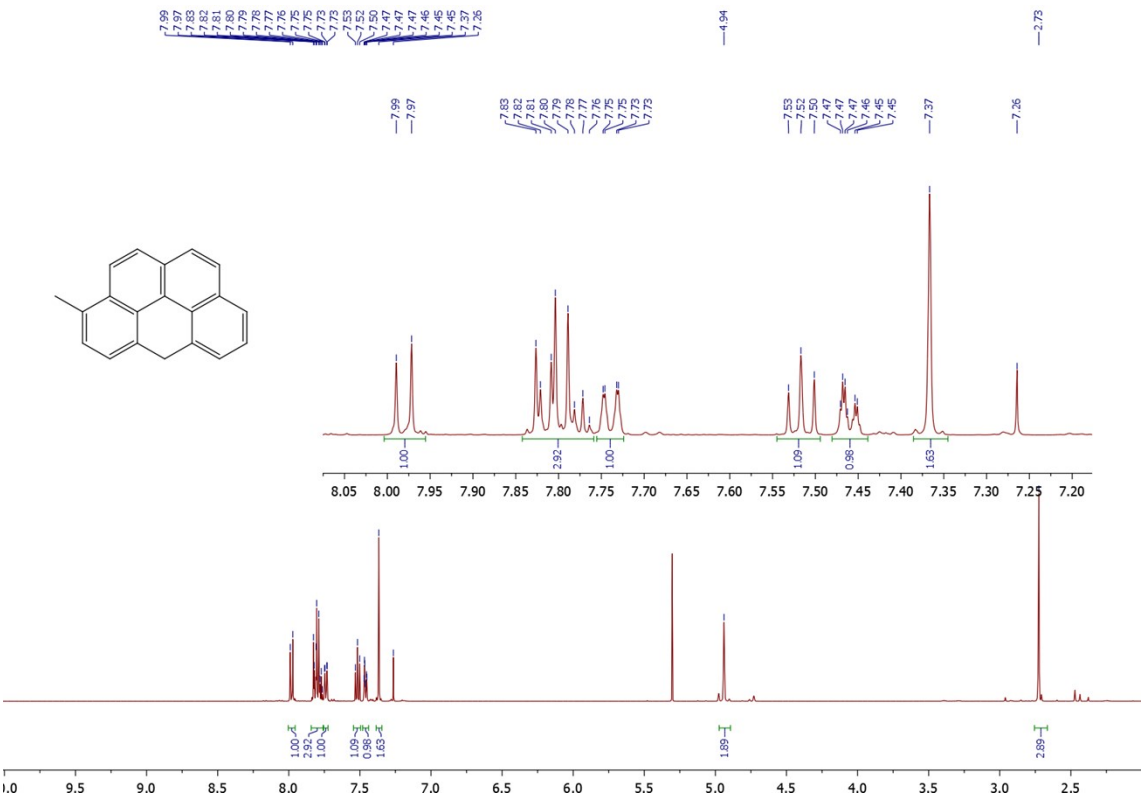

**Figure S139**. $^{1}$H NMR (500 MHz, $CDCl_3$, 293 K) spectrum of 3-methyl-6H-benzo[cd]pyrene (**23**).

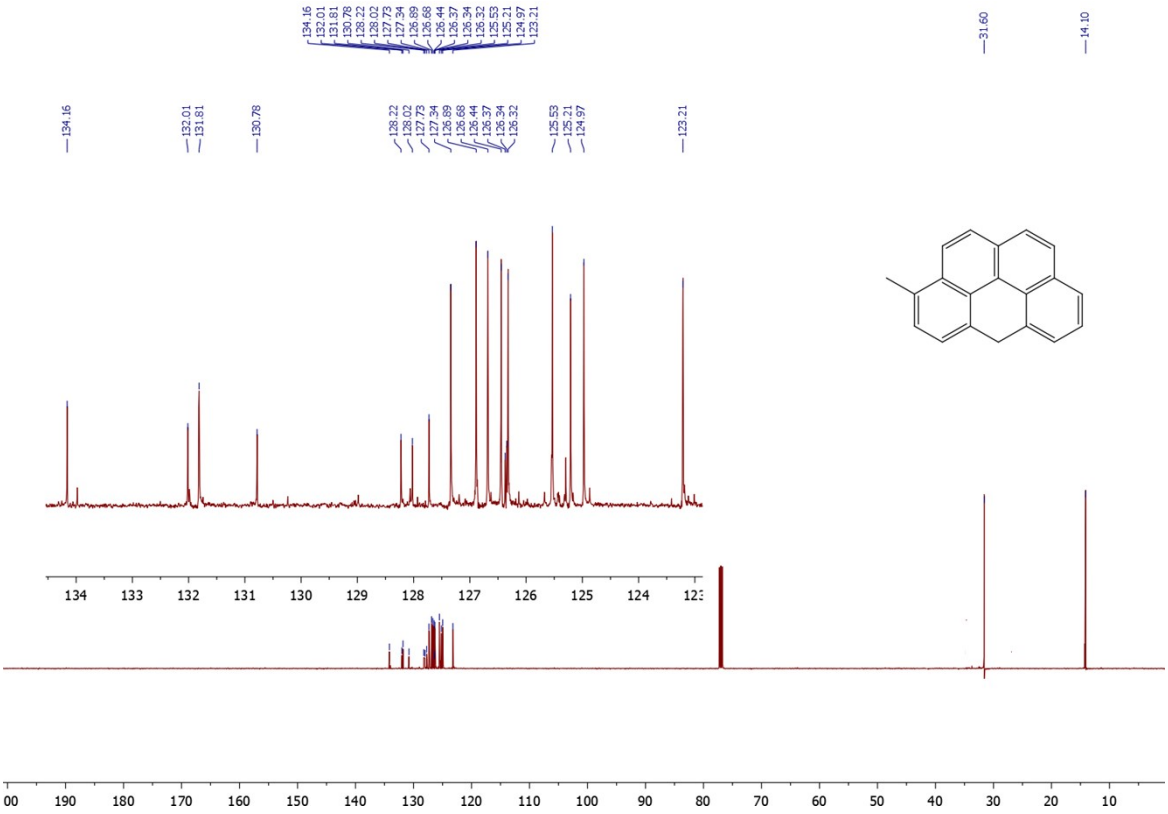

**Figure S140**. $^{13}$C NMR (126 MHz, $CDCl_3$, 293 K) spectrum of 3-methyl-6H-benzo[cd]pyrene (**23**).

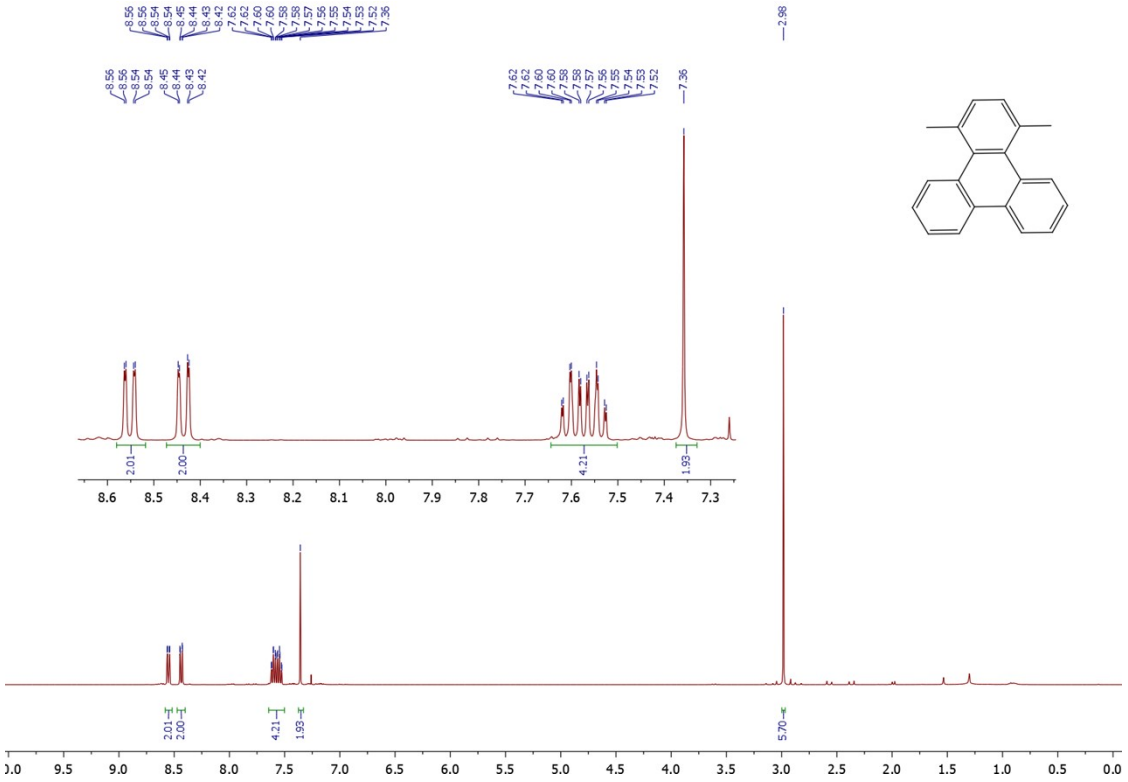

**Figure S141**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 1,4-dimethyltriphenylene (**25**).

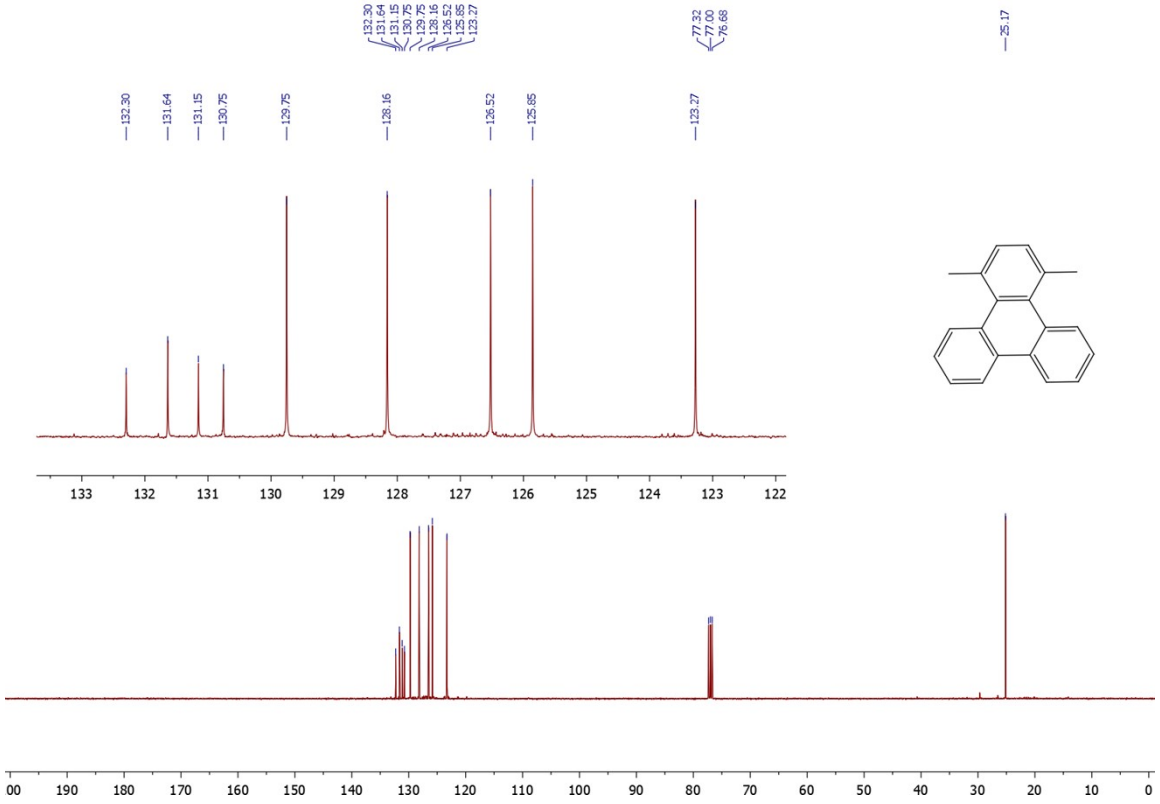

**Figure S142**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 1,4-dimethyltriphenylene (**25**).

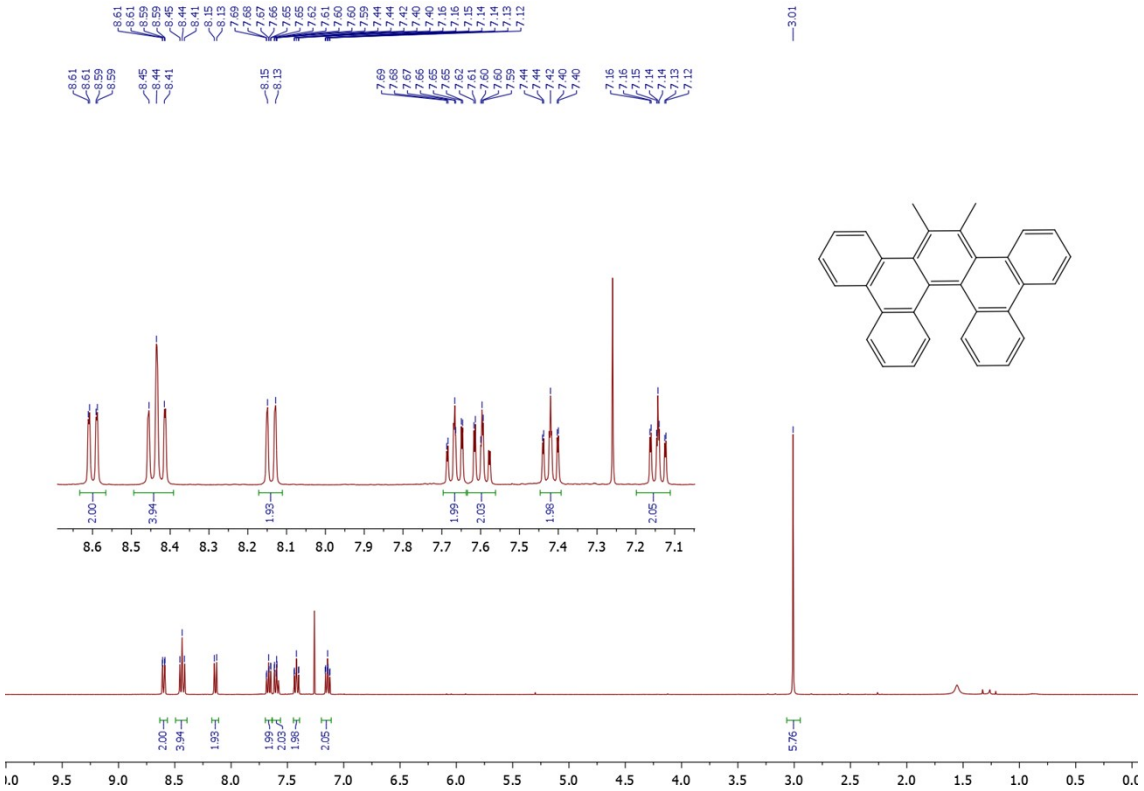

**Figure S143**. $^{1}H$ NMR (400 MHz, $CDCl_3$, 293 K) spectrum of 17,18-dimethyldibenzo[f,j]picene (**27**).

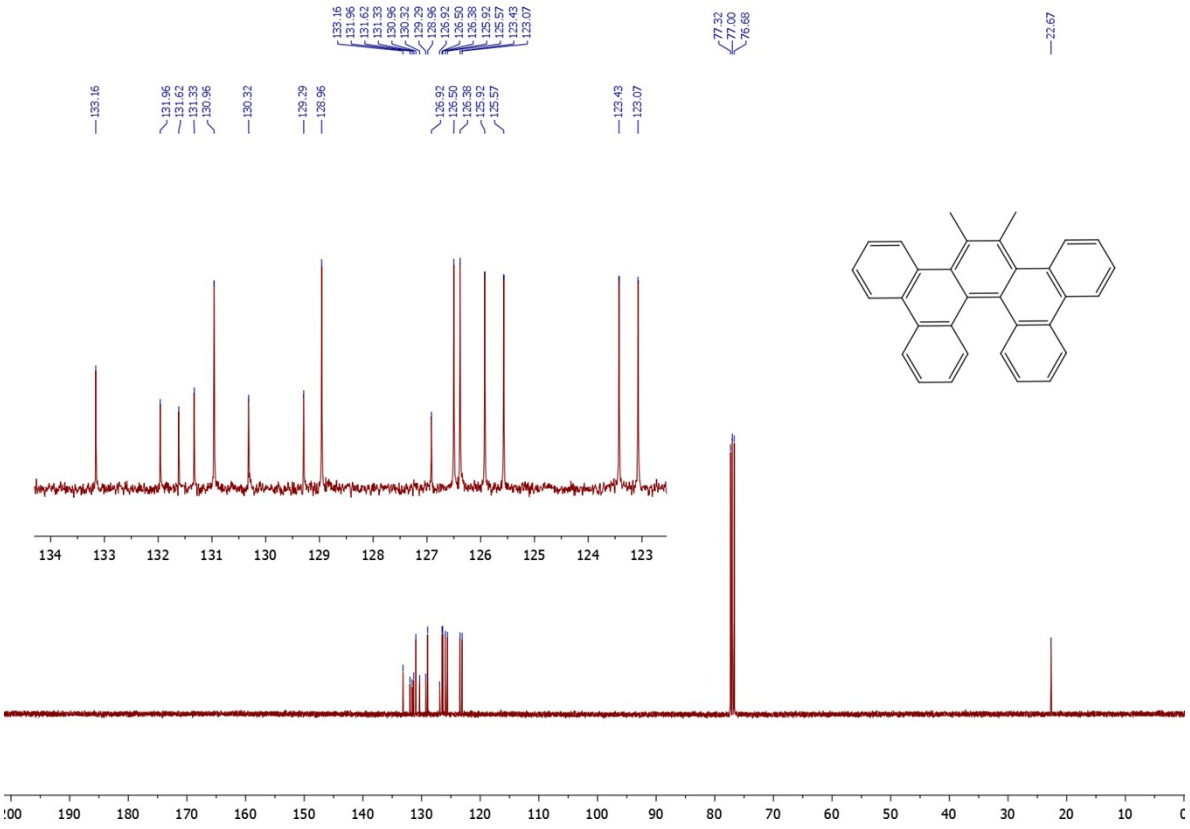

**Figure S144**. $^{13}C$ NMR (101 MHz, $CDCl_3$, 293 K) spectrum of 17,18-dimethyldibenzo[f,j]picene (**27**).