Supplementary Information

Fluorination of the tetraphenylethene core: synthesis, aggregation-induced emission, reversible mechanofluorochromism and thermofluorochromism of fluorinated tetraphenylethene derivatives

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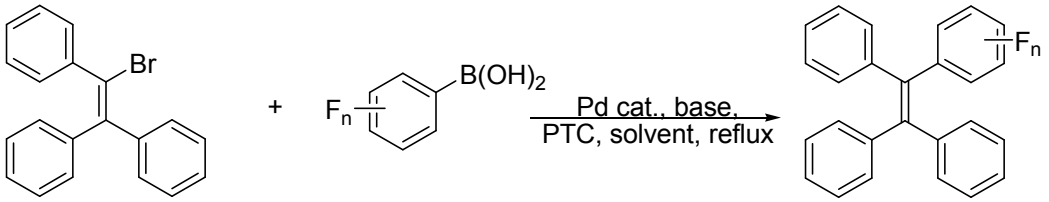
Synthetic procedures

General

Standard Schlenk techniques were used for the synthetic reactions under Ar. The solvents were commercially available and used without further purification. IR spectrum was recorded in the range 400-4000 cm^{-1} on a Perkin Elmer Spectrum RX I spectrometer using KBr pellets. NMR analyses were performed on a Bruker Avance

III 400 MHz spectrometer. As internal references for ^{1}H- and ^{13}C-NMR spectroscopy the signals of $CDCl_3$ were used and calculated relative to tetramethylsilane (TMS). CF_3COOH was used as the external reference for ^{19}F-NMR. Melting points were measured with a SGW X-4 apparatus and are not corrected. The high resolution mass spectra were measured on a Thermo Fisher Scientific LTQ FTICR-MS instrument (DART positive ion mode) and Waters Micromass GCT Premier (EI (70eV)). UV-Vis spectrum was recorded on a TU1900 spectrometer. Emission spectra were measured on an Edinburgh FLS 920 fluorimeter, using a front-face solid sample configuration for solid samples. Absolute fluorescence quantum yields were obtained using an integrating sphere. Thermogram TGA was recorded by using a TA TGA55 thermoanalyser in temperature range from room temperature to 400 °C at a heating rate of 20 °C/min under nitrogen, whereas the thermogram DSC was performed using a TA DSC25 thermoanalyzer between room temperature to 300 °C at a heating rate of 10 °C/min and under nitrogen also.



1a, 2-F; **1b**, 3-F; **1c**, 4-F;
1d, 2,3-F_2; **1e**, 2,4-F_2; **1f**, 2,5-F_2;
1g, 2,6-F_2; **1h**, 3,4-F_2; **1i**, 3,5-F_2;
1j, 2,4,6-F_3; **1k**, 3,4,5-F_3

Synthesis of 1-(2-fluorophenyl)-1,2,2-triphenylethene (1a). A representative procedure. Under an Ar atmosphere triphenylbromoethene (168.1 mg, 0.47 mmol), tetrabutylammonium bromide (15.8 mg, 0.049 mmol), K_2CO_3 (207.8 mg, 1.503 mmol), 2-fluorophenylboronic acid (84.4 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (29.9 mg, 0.026 mmol) were added into a Schlenk flask, and a mixture of toluene/H_2O (5 mL/15 mL) was then added to the flask. The mixture was heated to 120 °C (oil bath) with stirring for 24 h. After cooling to room temperature, the organic phase was separated and the water phase was extracted with CH_2Cl_2 (2 × 20 mL). The organic phases were combined and dried over Na_2SO_4. After filtration the organic phases were dried under reduced pressure, and the resulting residue was purified by preparative TLC using *n*-hexane as the eluent to give the product **1a**.

1a: White solid (62.4 mg, 37.6%); m.p. 187-189 °C; R_f = 0.20 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.01 (m, 17H), 6.92 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (t, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.68, 159.22, 143.56 (d, *J* = 15.2 Hz), 142.85, 142.50, 134.66, 133.01 (d, *J* = 3.7 Hz), 131.64, 131.49, 131.38, 130.60 (d, *J* = 4.3 Hz), 128.82 (d, *J* = 8.1 Hz), 127.84 (d, *J* = 2.8 Hz), 127.69, 126.86 (d, *J* = 1.3 Hz), 126.66, 123.74 (d, *J* = 3.5 Hz), 115.74, 115.52; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.24 – -113.35 (m); DART-MS *m/z* (%): calcd. for $C_{26}H_{20}F$, 351.1549, found 351.1540 $[M+1]^+$ (100%).

1b: triphenylbromoethene (166.8 mg, 0.47 mmol), tetrabutylammonium bromide

(16.8 mg, 0.052 mmol), K_2CO_3 (209.7 mg, 1.52 mmol), 3-fluorophenylboronic acid (82.6 mg, 0.59 mmol) and $Pd(PPh_3)_4$ (30.0 mg, 0.026 mmol), the reaction mixture was heated for 21 h. White solid (71.8 mg, 43.6%); m.p. 204-207 °C; R_f = 0.42 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.00 (m, 16H), 6.84 – 6.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.77, 161.34, 146.14 (d, *J* = 7.6 Hz), 143.42 (d, *J* = 5.1 Hz), 143.24, 142.01, 139.81 (d, *J* = 1.9 Hz), 131.36 (d, *J* = 1.3 Hz), 131.29, 129.13 (d, *J* = 8.4 Hz), 127.93 (d, *J* = 1.8 Hz), 127.82, 127.22 (d, *J* = 2.7 Hz), 126.89, 126.77 (d, *J* = 2.6 Hz), 118.27, 118.05, 113.61, 113.40; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.88 – -110.99 (m); DART-MS *m/z* (%): calcd. for $C_{26}H_{20}F$, 351.1549, found 351.1540 $[M+1]^+$ (100%).

1c[1,2]: triphenylbromoethene (167.3 mg, 0.47 mmol), tetrabutylammonium bromide (17.9 mg, 0.056 mmol), K_2CO_3 (210.1 mg, 1.52 mmol), 4-fluorophenylboronic acid (83.9 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (31.4 mg, 0.027 mmol), the reaction mixture was heated for 21 h. White solid (124.7 mg, 75.8%); R_f = 0.44 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 9H), 7.04 – 6.95 (m, 8H), 6.79 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.76, 160.31, 143.69 (d, *J* = 3.1 Hz), 143.64, 141.34, 139.97, 139.81 (d, *J* = 3.4 Hz), 133.03 (d, *J* = 7.9 Hz), 131.40, 127.87 (t, *J* = 5 Hz), 126.68 (d, *J* = 3.1 Hz), 126.63, 114.87, 114.66; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.44 – -115.56 (m).

1d: triphenylbromoethene (179.9 mg, 0.51 mmol), tetrabutylammonium bromide (17.7 mg, 0.055 mmol), K_2CO_3 (207.9 mg, 1.57 mmol), 2,3-difluorophenylboronic acid (96.5 mg, 0.61 mmol) and $Pd(PPh_3)_4$ (36.1 mg, 0.031 mmol), the reaction mixture was heated for 38 h. White solid (18.9 mg, yield 10.1%); m.p. 173-175 °C; R_f = 0.51 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.02 (m, 15H), 6.99 – 6.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.15 (d, *J* = 15.3 Hz), 149.73 (t, *J* = 14.9 Hz), 147.30 (d, *J* = 15.8 Hz), 144.48, 143.10, 142.47, 141.93, 133.94, 133.83, 133.41 (d, *J* = 2.3 Hz), 131.30, 130.50 (d, *J* = 11.3 Hz), 127.93 (d, *J* = 5.0 Hz), 127.84, 127.67 (t, *J* = 2.5 Hz), 127.11 (d, *J* = 7.9 Hz), 126.89, 123.53 (dd, *J* = 7.0, 4.7 Hz), 115.94, 115.78; ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.07 – -135.22 (m, 1F), -135.29 – -135.46 (m, 1F); DART-MS *m/z* (%): calcd. for $C_{26}H_{19}F_2$, 369.1455, found 369.1446 $[M+1]^+$ (100%).

1e: triphenylbromoethene (176.9 mg, 0.50 mmol), tetrabutylammonium bromide (18.0 mg, 0.056 mmol), K_2CO_3 (206.9 mg, 1.50 mmol), 2,4-difluorophenylboronic acid (95.1 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (37.6 mg, 0.33 mmol), the reaction mixture was heated for 38 h. White solid (70 mg, 9.0%); m.p. 169-172 °C; R_f = 0.44 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.0 (m, 16H), 6.73 – 6.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.43 (d, *J* = 11.7 Hz), 161.64 (d, *J* = 11.9 Hz), 160.96 (d, *J* = 11.7 Hz), 159.16 (d, *J* = 11.9 Hz), 144.07, 143.33, 142.66, 142.25, 133.66 (t, *J* = 7.3 Hz), 133.63, 131.31, 130.54 (d, *J* = 7.1 Hz), 127.90 (d, *J* = 1.1 Hz), 127.82, 126.98, 126.80, 111.17 (d, *J* = 3.6 Hz), 110.96 (d, *J* = 3.6 Hz), 104.02 (t, *J* = 25.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.47 (q, *J* = 8.5 Hz, 1F), -108.16 (quint, *J* = 7.9 Hz, 1F); DART-MS *m/z* (%): calcd. for $C_{26}H_{18}F_2$, 368.1377, found 368.1367$[M]^+$ (100%).

1f: triphenylbromoethene (176.6 mg, 0.50 mmol), tetrabutylammonium bromide (16.1

mg, 0.050 mmol), K_2CO_3 (207.0 mg, 1.50 mmol), 2,5-difluorophenylboronic acid (94.7 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (37.0 mg, 0.32 mmol), the reaction mixture was heated for 38 h. White solid (36.4 mg, 19.9%); m.p. 179-181 °C; R_f = 0.32 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.02 (m, 15H), 6.83 – 6.76 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.60, 157.58, 157.20, 155.19, 144.44, 143.05, 142.46, 141.88, 133.47, 132.94 (dd, *J* = 18.0, 8.0 Hz), 131.29, 130.52 (d, *J* = 13.5 Hz), 127.97, 127.87 (d, *J* = 5.6 Hz), 127.14 (d, *J* = 11.0 Hz), 126.91, 119.15 (d, *J* = 4.1 Hz), 118.91 (d, *J* = 4.1 Hz), 116.69 (d, *J* = 8.9 Hz), 116.44 (d, *J* = 8.9 Hz), 115.36 (d, *J* = 8.5 Hz), 115.13 (d, *J* = 8.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.73 – -116.00 (m, 1F), -116.08 – -116.37 (m, 1F); DART-MS *m/z* (%): calcd. for $C_{26}H_{19}F_2$, 369.1455, found 369.1447 $[M+1]^+$ (100%).

1g: triphenylbromoethene (177.6 mg, 0.50 mmol), tetrabutylammonium bromide (17.2 mg, 0.053 mmol), K_2CO_3 (206.8 mg, 1.50 mmol), 2,6-difluorophenylboronic acid (95.9 mg, 0.61 mmol) and $Pd(PPh_3)_4$ (34.3 mg, 0.030 mmol), the reaction mixture was heated for 38.5 h. white solid (10.2 mg, 50%); the reaction condition was modified as follows: triphenylbromoethene (179.1 mg, 0.50 mmol), Ag_2O (114.4 mg, 0.50 mmol), K_2CO_3 (206.8 mg, 1.56 mmol), 2,6-difluorophenylboronic acid (106.8 mg, 0.68 mmol) and $Pd(PPh_3)_4$ (36.0 mg, 0.031 mmol), the reaction mixture was heated for 28.5 h. yellowish solid (29.1 mg, 15.7%); m.p. 155-157 °C; R_f = 0.29 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 8H), 7.21 – 7.15 (m, 4H), 7.11 – 7.05 (m, 4H), 6.98 – 6.94 (m, 2H); DART-MS *m/z* (%): calcd. for $C_{26}H_{18}F_2$, 368.1377, found 368.1367 $[M]^+$ (100%).

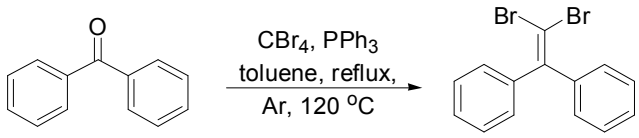
1h: triphenylbromoethene (180.5 mg, 0.51 mmol), tetrabutylammonium bromide (17.8 mg, 0.055 mmol), K_2CO_3 (206.4 mg, 1.56 mmol), 3,4-difluorophenylboronic acid (96.1 mg, 0.61 mmol) and $Pd(PPh_3)_4$ (38.5 mg, 0.033 mmol), the reaction mixture was heated for 24 h. White solid (153.2 mg, 81.9%); m.p. 174-175 °C; R_f = 0.61 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.07 (m, 9H), 7.06 – 6.98 (m, 6H), 6.92 – 6.79 (m, 2H), 6.77 – 6.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.16 (d, *J* = 12.7 Hz), 150.34 (d, *J* = 12.7 Hz), 148.70 (d, *J* = 12.7 Hz), 147.87 (d, *J* = 12.7 Hz), 143.28 (d, *J* = 1.9 Hz), 143.02, 142.20, 140.83 (dd, *J* = 5.7, 4.2 Hz), 138.93, 131.32 (d, *J* = 1.5 Hz), 131.25, 128.05 (d, *J* = 7.8 Hz), 127.86, 127.60 (dd, *J* = 6.0, 3.4 Hz), 126.98 (d, *J* = 7.2 Hz), 126.84, 120.15 (d, *J* = 17.3 Hz), 116.55 (d, *J* = 17.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.21 – -135.53 (m, 1F), -136.73 – -137.02 (m, 1F); DART-MS *m/z* (%): calcd. for $C_{26}H_{19}F_2$, 369.1455, found 369.1446 $[M+1]^+$ (100%).

1i: triphenylbromoethene (177.9 mg, 0.50 mmol), tetrabutylammonium bromide (17.6 mg, 0.059 mmol), K_2CO_3 (206.8 mg, 1.50 mmol), 3,5-difluorophenylboronic acid (94.5 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (35.6 mg, 0.31 mmol), the reaction mixture was heated for 38.5 h. White solid (136.8 mg, 74.1%); m.p. 183-185 °C; R_f = 0.45 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 9H), 7.06 – 6.97 (m, 6H), 6.61 – 6.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.85 (d, *J* = 13.0 Hz), 161.39 (d, *J* = 13.0 Hz), 147.26 (t, *J* = 9.4 Hz), 143.05, 142.91 (d, *J* = 5.1 Hz), 142.62, 138.83 (t, *J* = 2.3 Hz), 131.28 (d, *J* = 2.5 Hz), 131.10, 128.09 (d, *J* = 5.3 Hz), 127.87, 127.26, 127.01 (d, *J* = 5.8 Hz), 114.21 (d, *J* = 11.8 Hz), 114.21 (d, *J* = 25.2 Hz), 102.14 (t, *J* =

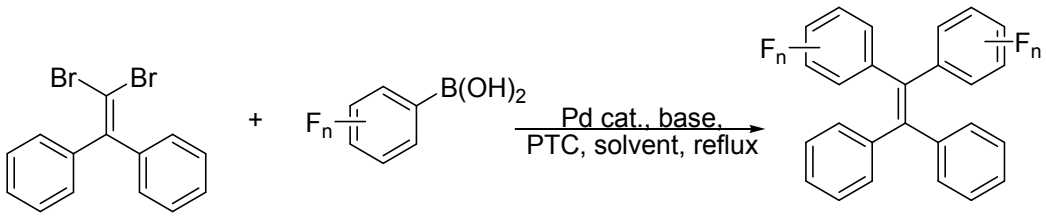
25.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.80 – -107.93 (m, 2F); DART-MS *m/z* (%): calcd. for $C_{26}H_{18}F_2$, 368.1377, found 368.1370 $[M]^+$ (100%).

1j: triphenylbromoethene (179.6 mg, 0.51 mmol), tetrabutylammonium bromide (15.2 mg, 0.047 mmol), K_2CO_3 (208.3 mg, 1.51 mmol), 2,4,6-trifluorophenylboronic acid (106.9 mg, 0.61 mmol) and $Pd(PPh_3)_4$ (38.2 mg, 0.33 mmol), the reaction mixture was heated for 39 h. White solid (12 mg, 6.3%); m.p. 156-158 °C; R_f = 0.41 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 9H), 7.20 – 7.15 (m, 3H), 7.09 – 7.05 (m, 3H), 6.98 – 6.93 (m, 2H); EI-MS *m/z* (%): calcd. for $C_{26}H_{17}F_3$, 386.1280, found 386.1279 $[M]^+$ (100%) .

1k: triphenylbromoethene (179.0 mg, 0.50 mmol), tetrabutylammonium bromide (18.2 mg, 0.056 mmol), K_2CO_3 (208.4 mg, 1.51 mmol), 3,4,5-trifluorophenylboronic acid (105.7 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (35.8 mg, 0.31 mmol), the reaction mixture was heated for 39 h. White solid (176.4 mg, 90.6%); m.p. 163-165 °C; R_f = 0.36 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.07 (m, 9H), 7.06 – 6.98 (m, 6H), 6.65 (dd, *J* = 8.7, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.04 (dd, *J* = 10.0, 4.1 Hz), 149.56 (dd, *J* = 10.0, 4.2 Hz), 143.07, 142.88 (d, *J* = 10.6 Hz), 142.41, 140.03 – 139.74 (m), 139.63, 138.06, 137.29 (t, *J* = 15.4 Hz), 131.25 (d, *J* = 3.6 Hz), 131.07, 128.21 (d, *J* = 11.0 Hz), 127.90, 127.38, 127.13 (d, *J* = 13.7 Hz), 115.39 (d, *J* = 21.1 Hz), 115.39 (d, *J* = 10.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.19 (dd, *J* = 20.5, 8.8 Hz, 2F), -159.15 – -159.30 (m, 1F); DART-MS *m/z* (%): calcd. for $C_{26}H_{18}F_3$, 387.1361, found 387.1352 $[M+1]^+$ (100%) .



Synthesis of 1,1-dibromo-2,2-diphenylethene[3l]. To a solution of benzophenone (1.820 g, 9.99 mmol) and CBr_4 (6.660 g, 20.02 mmol) in toluene (70 mL) was added PPh_3 (10.525 g, 40.13 mmol) under an Ar atmosphere. The mixture was heated at 120 °C (oil bath) for 137 h. After cooling to room temperature, the solvent was removed by rotary evaporator and the residue was extracted with *n*-hexane. The hexane phases were combined and dried to give a residue, which was separated by preparative TLC using *n*-hexane as the eluent to give the product as a yellowish solid (1.314 g, 35.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m).

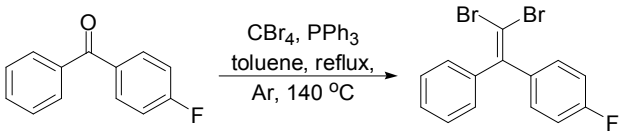


2a, 2-F; **2b**, 3-F

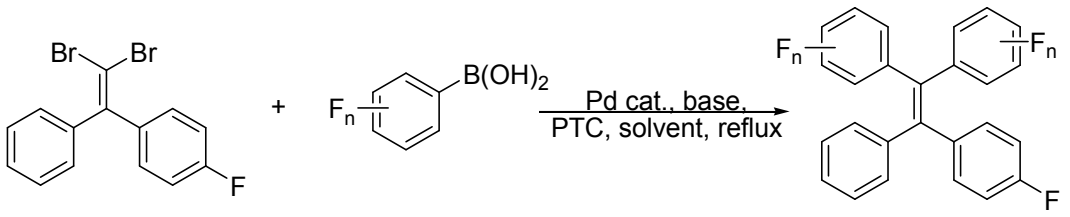
Synthesis of 1,1-bis(2-flurophenyl)-2,2-diphenylethene (2a). A representative procedure. Under an Ar atmosphere 1,1-dibromo-2,2-diphenylethene (102.8 mg, 0.30 mmol), tetrabutylammonium bromide (11.6 mg, 0.036 mmol), K_2CO_3 (125.3 mg 0.91

mmol), 2-fluorophenylboronic acid (139.9 mg, 0.67 mmol) and $Pd(PPh_3)_4$ (21.9 mg, 0.019 mmol) were added into a Schlenk flask. A mixture of toluene/H_2O (5 mL/15 mL) was then charged to the flask and the reaction mixture was heated at 120 °C (oil bath) for 48 h. After cooling to room temperature, the organic layer was separated and the water layer was extracted with CH_2Cl_2 (2 × 20 mL). The organic phases were combined and dried over Na_2SO_4. After filtration the organic phases were dried under reduced pressure, and the resulting residue was purified by preparative TLC using *n*-hexane as the eluent to give the product **2a** as a white solid (21.8 mg, 19.4%).m.p. 166-168 °C; R_f = 0.26 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14– 7.04 (m, 14H), 6.88 (dt, *J* = 18.3, 8.0 Hz, 4H); DART-MS *m/z* (%):calcd. for $C_{26}H_{19}F_2$, 369.1455, found 369.1446 $[M+1]^+$ (100%).

2b[4]: 1,1-dibromo-2,2-diphenylethene (103.5 mg, 0.31 mmol), tetrabutylammonium bromide (14.0 mg, 0.043 mmol), K_2CO_3 (124.6 mg, 0.90 mmol), 3-fluorophenylboronic acid (93.3 mg, 0.67 mmol) and $Pd(PPh_3)_4$ (21.5 mg, 0.019 mmol), the reaction mixture was heated for 24 h. White solid (63.6 mg, 56.3%); R_f = 0.49 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.00 (m, 12H), 6.84 – 6.78 (m, 4H), 6.72 (dt, *J* = 10.0, 2.0 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.57 – -110.72 (m, 2F).



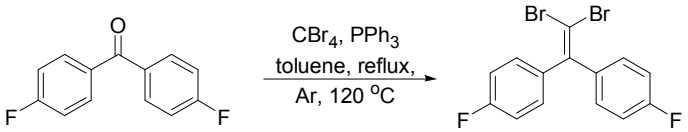
Synthesis of 1,1-dibromo-2-(4-fluorophenyl)-2-phenylethene. To a toluene solution (30 mL) of 4-fluorobenzophenone (1.0039 g, 5.01 mmol) and CBr_4 (3.2577 g, 9.82 mmol) was added PPh_3 (5.235 g, 19.96 mmol) slowly in a Schlenk flask with argon atmosphere. And the mixture was transfer to oil bath (140 °C), The reaction was refluxed for 96 h. The solvent of the mixture was removed by rotary evaporator and the residue was immersed by *n*-hexane and stirred overnight. The solution was filtrated and concentrated, then separated through silica gel using *n*-hexane as eluent to give the product as yellowish solid (976.1 mg, 54.7%); R_f = 0.58 (*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.40 – 7.27 (m, 7H), 7.05 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.48, 161.01, 146.87, 141.24, 137.85, 137.28 (d, *J* = 3.5 Hz), 130.79 (d, *J* = 8.3 Hz), 129.10, 128.83 (d, *J* = 2.6 Hz), 128.48 (d, *J* = 2.4 Hz), 128.19, 126.56, 115.44 (d, *J* = 21.7 Hz), 90.71; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.70 – -109.81 (m); DART-MS *m/z* (%): calcd. for $C_{14}H_{10}Br_2F$, 354.9133, found 354.9127 $[M+1]^+$ (100%) .



3a, 3-F; **3b**, 4-F

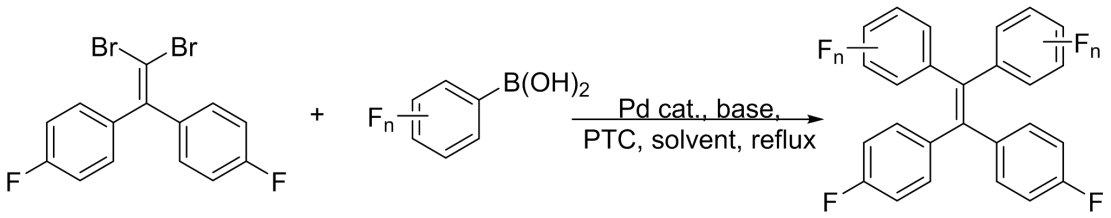
Synthesis of 1,1-bis(3-fluorophenyl)-2-(4-fluorophenyl)-2-phenylethene (3a). Under an Ar atmosphere 1,1-dibromo-2-(4-fluorophenyl)-2-phenylethene (217.3 mg, 0.61 mmol), tetrabutylammonium bromide (30.6 mg, 0.095 mmol), K_2CO_3 (250.7 mg, 1.81 mmol), 3-fluorophenylboronic acid (188.0 mg, 1.34 mmol) and $Pd(PPh_3)_4$ (43.8 mg, 0.037 mmol) were added into a Schlenk flask. A mixture of toluene/H_2O (5 mL/15 mL) was then added to the flask and the reaction mixture was heated at 120 °C (oil bath) for 25 h. The organic layer was separated and the water layer was extracted with CH_2Cl_2 (2 × 20 mL). The organic phases were combined and dried over Na_2SO_4. After filtration the organic phases were dried under reduced pressure, and the resulting residue was purified by preparative TLC using *n*-hexane as the eluent to give **3a** as white solid (31.8 mg, 13.5%). m.p. 173-175 °C; R_f = 0.38 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.17 – 7.04 (m, 5H), 7.03 – 6.95 (m, 4H), 6.86 – 6.76 (m, 6H), 6.73 – 6.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.85 (d, *J* = 7.1 Hz), 163.07, 161.40 (d, *J* = 6.8 Hz), 160.61, 145.32 (dd, *J* = 7.5, 3.6 Hz), 142.77, 141.80, 138.96 (d, *J* = 3.4 Hz), 138.72, 132.87 (d, *J* = 8.0 Hz), 131.16, 129.43 (dd, *J* = 15.1, 8.4 Hz), 128.09, 127.29, 127.08, 118.15 (d, *J* = 1.3 Hz), 117.94 (d, *J* = 1.4 Hz), 115.14, 114.92, 114.02 (d, *J* = 6.3 Hz), 113.81 (d, *J* = 6.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.22 – -110.36 (m, 1F), -110.44 – -110.58 (m, 1F), -111.23 – -111.39 (m, 1F); DART-MS *m/z* (%):calcd. for $C_{26}H_{18}F_3$, 387.1361, found 387.1352 $[M+1]^+$ (100%) .

3b: 1,1-dibromo-2-(4-fluorophenyl)-2-phenylethene (228.2 mg, 0.64 mmol), tetrabutylammonium bromide (34.0 mg, 0.11 mmol), K_2CO_3 (254.7 mg, 1.84 mmol), 4-fluorophenylboronic acid (187.0 mg, 1.34 mmol) and $Pd(PPh_3)_4$ (41.6 mg, 0.036 mmol), the reaction mixture was heated for 25 h. White solid (85.2 mg, 34.4%); m.p. 172-174 °C; R_f = 0.57 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 3H), 7.01 – 6.93 (m, 8H), 6.85 – 6.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.85 (t, *J* = 1.8 Hz), 160.40 (t, *J* = 1.6 Hz), 143.29, 140.42, 139.45 (t, *J* = 24.5 Hz), 139.39 (t, *J* = 2.8 Hz), 139.04, 132.95 (d, *J* = 7.9 Hz), 131.29, 128.06, 126.92, 114.98 (dt, *J* = 21.2, 6.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.59 – -111.73 (m, 1F), -111.74 – -111.88 (m, 2F); DART-MS *m/z* (%):calcd. for $C_{26}H_{18}F_3$, 387.1361, found 387.1352 $[M+1]^+$ (100%) .



Synthesis of 1,1-dibromo-2,2-bis(4-fluorophenyl)ethene[5]. To a solution of bis(4-fluorophenyl)methanone (1.644 g, 7.53 mmol) and CBr_4 (4.951 g, 14.93 mmol)

in toluene (30 mL) was added PPh_3 (7.955 g, 30.33 mmol) under an Ar atmosphere. The mixture was heated at 120 °C (oil bath) for 51 h. After cooling to room temperature, the solvent of the mixture was removed under reduced pressure and the residue was extracted with *n*-hexane. The hexane phases were dried and the resulting residue was separated by silica gel using *n*-hexane as the eluent to give product as yellowish solid (1.520 g, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.09 – 7.00 (m, 4H).



4a, 3-F; **4b**, 4-F

Synthesis of 1,1-bis(3-fluorophenyl)-2,2-bis(4-fluorophenyl)ethene (4a). A representative procedure. Under an Ar atmosphere, 1,1-dibromo-2,2-bis(4-fluorophenyl)ethene (189.5 mg, 0.51 mmol), tetrabutylammonium bromide (19.9 mg, 0.062 mmol), K_2CO_3 (208.4 mg, 1.51 mmol), 3-fluorophenylboronic acid (158.9 mg, 1.14 mmol) and $Pd(PPh_3)_4$ (34.9 mg, 0.030 mmol) were added to the Schlenk flask, and then a mixture of toluene/H_2O (5 mL/15 mL) was charged to the flask. The reaction mixture was heated at 120 °C (oil bath) for 28 h. The organic layer was separated and the water layer was extracted with CH_2Cl_2 (2 × 20 mL). The organic phases were combined and dried over Na_2SO_4. After filtration the organic phases were dried under reduced pressure and the resulting residue was purified by preparative TLC using *n*-hexane as the eluent to give **4a** as yellowish solid (80.1 mg, 39.0%). m.p. 163-165 °C; R_f = 0.35 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (q, *J* = 7.8 Hz, 2H), 6.97 (q, *J* = 4.5 Hz, 4H), 6.83 (t, *J* = 8.6 Hz, 6H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 9.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.88, 163.14, 161.44, 160.68, 145.15 (d, *J* = 7.5 Hz), 140.66, 138.96, 138.73 (d, *J* = 3.4 Hz), 132.85 (d, *J* = 8.0 Hz), 129.56 (d, *J* = 8.4 Hz), 127.02 (d, *J* = 2.8 Hz), 118.00 (d, *J* = 21.7 Hz), 115.15 (d, *J* = 21.4 Hz), 114.04 (d, *J* = 21.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.21 (q, *J* = 8.2 Hz, 2F), -110.92 – -111.09 (m, 2F); DART-MS *m/z* (%): calcd. for $C_{26}H_{17}F_4$, 404.1183, found 404.1181 $[M]^+$ (100%).

4b[6]: 1,1-dibromo-2,2-bis(4-fluorophenyl)ethene (190.3 mg, 0.51 mmol), tetrabutylammonium bromide (15.1 mg, 0.047 mmol), K_2CO_3 (208.6 mg, 1.51 mmol), 4-fluorophenylboronic acid (157.8 mg, 1.13 mmol) and $Pd(PPh_3)_4$ (35.0 mg, 0.030 mmol), the reaction mixture was heated for 27.5 h. White solid (42.4 mg, 20.6%); R_f = 0.13 (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 - 6.93 (m, 8H), 6.82 (t, *J* = 8.7 Hz, 8H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.37 – -111.50 (m, 4F).

References:

[1] Berthiol, F., Doucet, H., Santelli, M., Synthesis of Polysubstituted Alkenes by Heck Vinylation or Suzuki Cross-Coupling Reactions in the Presence of a Tetraphosphane−Palladium Catalyst. *European Journal of Organic Chemistry* 2003, 2003(6), 1091-1096.

[2] Xue, F., Zhao, J., Hor, T.S., Hayashi, T., Nickel-catalyzed three-component domino reactions of aryl Grignard reagents, alkynes, and aryl halides producing tetrasubstituted alkenes. *Journal of the American Chemical Society* 2015, 137(9), 3189-92.
[3] Chen, Z.Q., Chen, T., Liu, J.-X., Zhang, G.F., Li, C., Gong, W.L., Xiong, Z.J., Xie, N.H., Tang, B.Z., Zhu, M.-Q., Geminal Cross-Coupling of 1,1-Dibromoolefins Facilitating Multiple Topological π-Conjugated Tetraarylethenes. *Macromolecules* 2015, 48(21), 7823-7835.
[4] Mills, N.S., Benish, M.A., Ybarra, C., Dications of fluorenylidenes. relationship between electrochemical oxidation potentials and antiaromaticity in diphenyl-substituted fluorenyl cations. *Journal of Organic Chemistry* 2002, 67(7), 2003-2012.
[5]Shimizu, M., Nagao, I., Kiyomoto, S.-i., Hiyama, T., New Synthesis of Dibenzofulvenes by Palladium-Catalyzed Double Cross-Coupling Reactions. *Australian Journal of Chemistry* 2012, 65(9), 1277-1284.
[6] Hua, G., Li, Y., Slawin, A.M.Z., Woollins, J.D., Stereoselective synthesis of olefins by a reductive coupling reaction. *Dalton Transactions* 2007, (15), 1477-1480.

Table S1. Crystal data and structure refinement for **1b**.

Empirical formula	$C_{26}H_{19}F$
Formula weight	350.41
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.8507(6) Å alpha =90deg.
	b = 9.6236(6) Å beta =105.740(3) deg.
	c = 10.6312(7) Ågamma = 90 deg.
Volume	970.04(11) $Å^3$
Z, Calculated density	2, 1.200 Mg/m^3
Absorption coefficient	0.075 mm^{-1}
F(000)	368
Crystal size	0.46 × 0.41 × 0.40 mm
Theta range for data collection	2.91 to 25.02 deg.
Limiting indices	$-11 \le h \le 11$, $-11 \le k \le 7$, $-12 \le l \le 12$
Reflections collected / unique	4795 / 2403 [R(int) = 0.0544]
Completeness to theta = 25.02	98.60%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9707 and 0.9664
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2403 / 67 / 248
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	$R_1 = 0.0606$, $wR_2 = 0.1646$
R indices (all data)	$R_1 = 0.0904$, $wR_2 = 0.1905$
Largest diff. peak and hole	0.419 and -0.221 $e \cdot Å^{-3}$

Table S2. Crystal data and structure refinement for **1c**.

Empirical formula	$C_{26}H_{19}F$
Formula weight	350.41
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.9314(7) Å alpha = 90 deg. b = 9.4452(6) Å beta = 108.374(2) deg. c = 10.8609(8) Å gamma = 90 deg.
Volume	966.86(12) $Å^3$
Z, Calculated density	2, 1.204 Mg/m^3
Absorption coefficient	0.075 mm^{-1}
F(000)	368
Crystal size	0.43 × 0.38 ×0.37 mm
Theta range for data collection	2.43 to 25.02 deg.
Limiting indices	$-11 \le h \le 11$, $-11 \le k \le 11$, $-7 \le l \le 12$
Reflections collected / unique	4833 / 3352 [R(int) = 0.0239]
Completeness to theta = 25.02	99.80%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9728 and 0.9685
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3352 / 1 / 248
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	$R_1 = 0.0551$, $wR_2 = 0.1551$
R indices (all data)	$R_1 = 0.0807$, $wR_2 = 0.1785$
Largest diff. peak and hole	0.435 and -0.210 $e \cdot Å^{-3}$

Table S3. Crystal data and structure refinement for **1e**.

Empirical formula	$C_{26}H_{18}F_2$
Formula weight	404.38
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.9332(8) Å alpha = 90 deg. b = 9.5602(8) Å beta = 108.551(3) deg. c = 10.8668(9) Å gamma = 90 deg.
Volume	978.33(14) $Å^3$
Z, Calculated density	2, 1.251 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F(000)	384
Crystal size	0.47 × 0.38 × 0.36 mm
Theta range for data collection	2.42 to 25.01 deg.
Limiting indices	$-11 \le h \le 11$, $-6 \le k \le 11$, $-12 \le l \le 12$

Reflections collected / unique	4839 / 2903 [R(int) = 0.0921]
Completeness to theta = 25.01	99.10%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9702 and 0.9614
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2903 / 1 / 260
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R_1 = 0.0808, wR_2 = 0.2054
R indices (all data)	R_1 = 0.1197, wR_2 = 0.2358
Largest diff. peak and hole	0.453 and -0.259 e·Å^{-3}

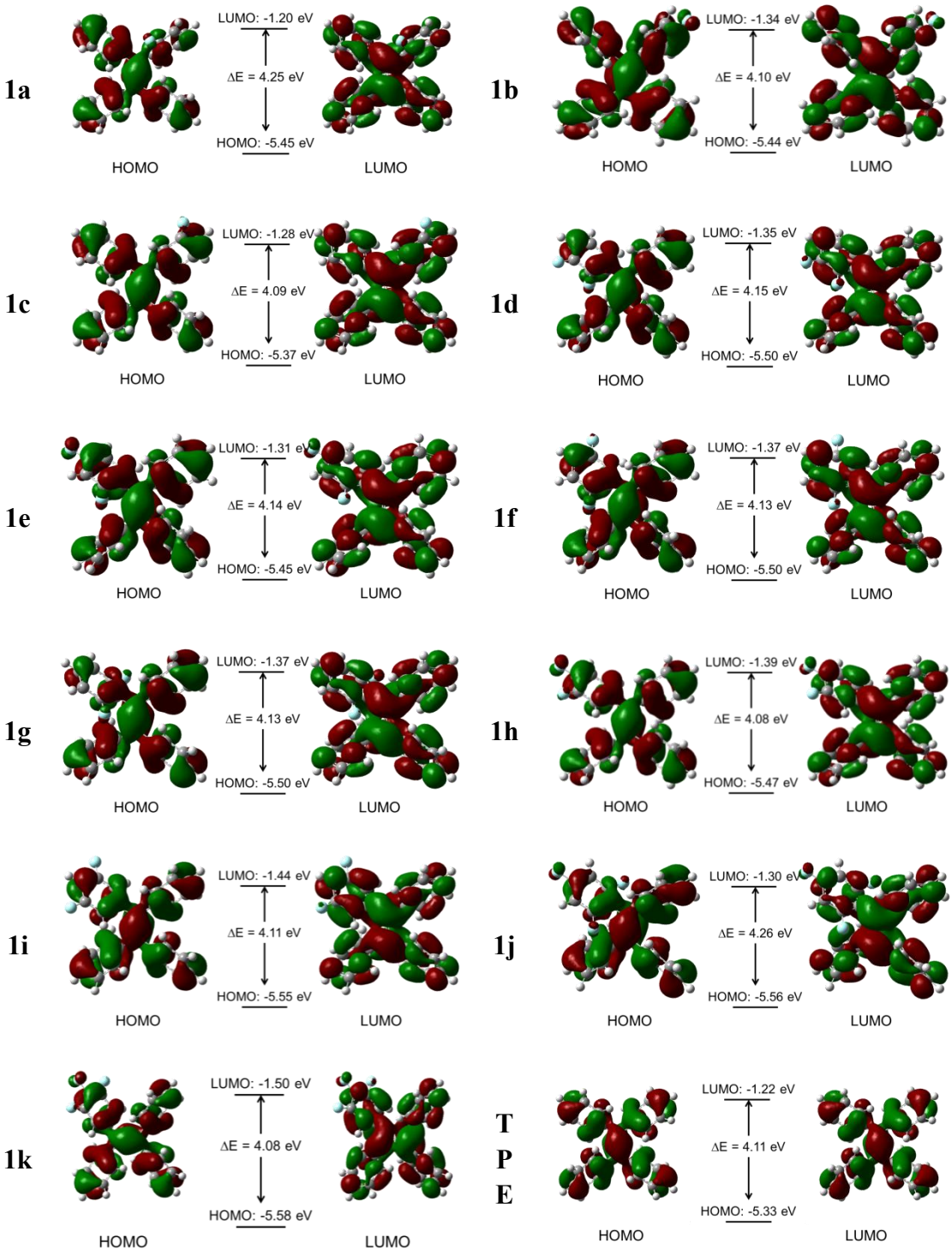
Table S4. Crystal data and structure refinement for **4a**.

Empirical formula	$C_{26}H_{16}F_4$
Formula weight	368.4
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.9748(6)Å alpha = 90 deg.
	b = 9.6537(6)Å beta = 108.037(7) deg.
	c = 11.0118(7) Å gamma = 90 deg.
Volume	1008.26(11)Å^3
Z, Calculated density	4, 1.332 Mg/m^3
Absorption coefficient	0.102 mm^{-1}
F(000)	416
Crystal size	0.5 × 0.4 × 0.38mm
Theta range for data collection	6.4 to 52.74 deg.
Limiting indices	$-12 \le h \le 12$, $-12 \le k \le 12$, $-13 \le l \le 13$
Reflections collected / unique	14010 / 4116 [R(int) = 0.0653]
Completeness to theta = 26.32	99.73%
Absorption correction	Multi-scan
Max. and min. transmission	1.0000 and 0.61975
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4116/1/272
Goodness-of-fit on F^2	1.094
Final R indices [I>2sigma(I)]	R_1 = 0.1167, wR_2 = 0.3023
R indices (all data)	R_1 = 0.1824, wR_2 = 0.3684
Largest diff. peak and hole	0.65 and -0.37 e·Å^{-3}

Table S5. Bond lengths and torsion angles for the **1b, 1c, 1e** and **4a**.

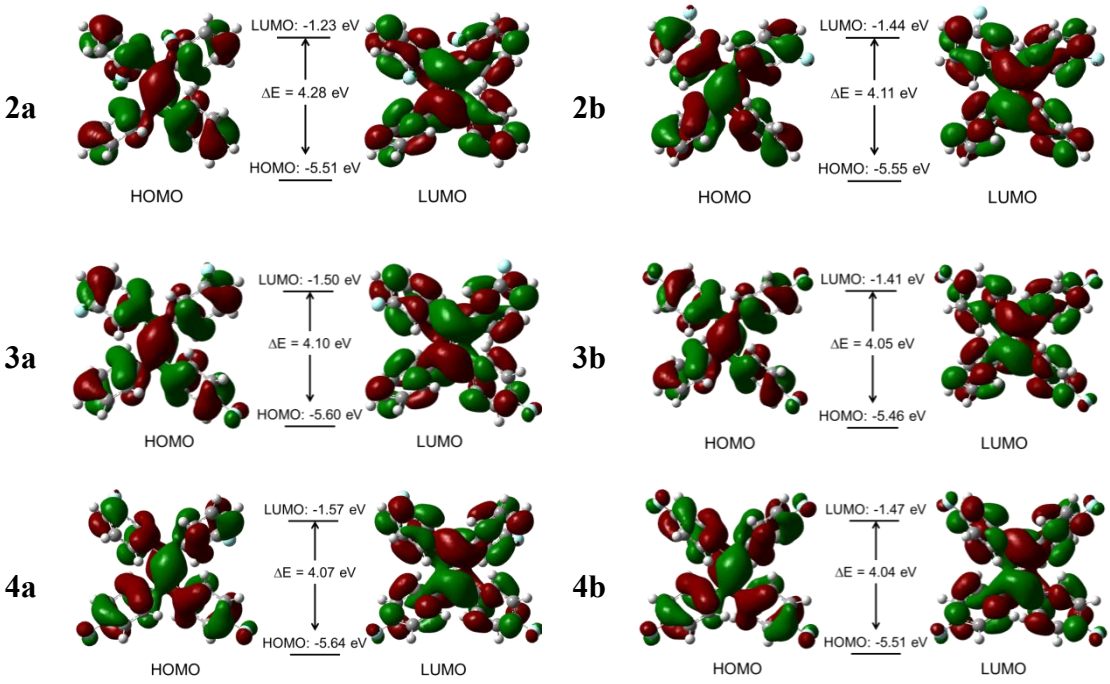
	1b	**1c**	**1e**	**4a**
Selected bond lengths (Å)	C1-C2: 1.337 C5-F1: 1.248 C14-F1': 1.259 C1-C3(F-Ar): 1.508 C1-C9(Ph): 1.486 C2-C15(F'-Ar): 1.493 C2-C21(Ph): 1.494	C1-C2: 1.356 C9-F1: 1.328 C18-F1': 1.283 C1-C3(F'-Ar): 1.494 C1-C9(Ph): 1.488 C2-C15(F-Ar): 1.500 C2-C21(Ph): 1.483	C1-C2: 1.337 C6-F1: 1.305 C4-F2: 1.332 C10-F1': 1.222 C12-F2': 1.348 C1-C3(F-Ar): 1.505 C1-C9(F'-Ar): 1.461 C2-C15(Ph): 1.489 C2-C21(Ph): 1.486	C1-C2: 1.370 C6-F1: 1.363 C17-F2: 1.288 C23-F3: 1.307 C12-F4: 1.367 C1-C3(F1-Ar): 1.493 C1-C9(F4-Ar): 1.464 C2-C15(F2-Ar): 1.501 C2-C21(F3-Ar): 1.456
Selected torsion angles (°)	C2-C1-C3-C8 (ethene-(F-Ar)): -45.50 C2-C1-C9-C10 (ethene-Ph): -49.08 C1-C2-C15-C20 (ethene-(F'-Ar)): -47.88 C1-C2-C21-C26 (ethene-Ph): -54.78	C2-C1-C3-C8 (ethene-(F'-Ar)): -48.69 C2-C1-C9-C10 (ethene-Ph): -46.92 C1-C2-C15-C20 (ethene-(F-Ar)): -56.34 C1-C2-C21-C26 (ethene-Ph): -46.13	C2-C1-C3-C8 (ethene-(F-Ar)): 52.25 C2-C1-C9-C10 (ethene-(F'-Ar)): 48.99 C1-C2-C15-C20 (ethene-Ph): 58.08 C1-C2-C21-C26 (ethene-Ph): 47.27	C2-C1-C3-C8 (ethene-(F1-Ar)): 44.89 C2-C1-C9-C14 (ethene-(F4-Ar)): 49.25 C1-C2-C15-C16 (ethene-(F2-Ar)): 57.27 C1-C2-C21-C26 (ethene-(F3-Ar)): 46.96

Table S6. Diagrams of the frontier MOs of **1a-1k** and parent TPE[a].



[a]Energy gaps between HOMO and LUMO were calculated at the B3LYP/6-31G (d, p) level of theory.

Table S7. Diagrams of the frontier MOs of **2a-4b**[a].



[a]Energy gaps between HOMO and LUMO were calculated at the B3LYP/6-31G (d, p) level of theory.

Reference for the Gaussian package for the DFT calculations:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

Table S8. Emission lifetime data of the solid samples.

Compounds	τ_1 (ns)	percent	τ_2 (ns)	percent	τ (ns)
1a	0.8837	43.74%	1.7992	56.26%	1.40
1b	1.0003	67.69%	1.735	32.31%	1.24
1c	0.434	97.02%	1.1931	2.98%	0.46
1h	0.7182	42.96%	1.1844	57.04%	0.98
1i	0.3015	100.00%	-	-	0.30
1k	0.6876	21.76%	0.9071	78.24%	0.86
2b	0.9386	65.39%	1.8363	34.61%	1.25
3a	0.5117	64.62%	1.6345	35.38%	0.91
3b	0.5294	72.33%	1.6579	27.67%	0.84
4a	0.2561	84.45%	1.3417	15.55%	0.42
4b	1.0703	74.46%	2.7554	25.54%	1.50

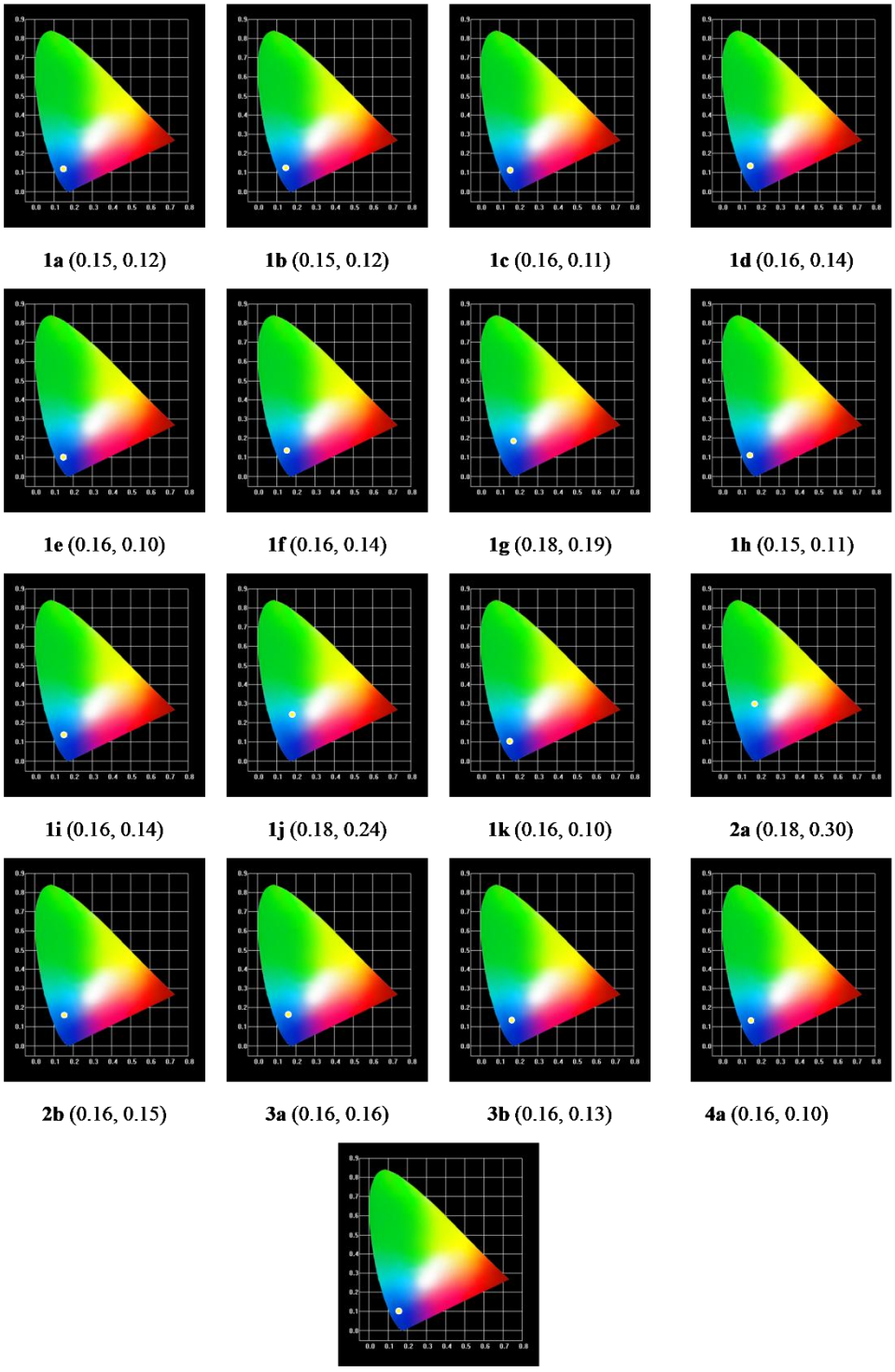


Fig. S1. CIE1931 diagrams and the chromaticity coordinates (shown along with the compound numbers and as yellow dots in the blue color regions as well) of the solid samples.

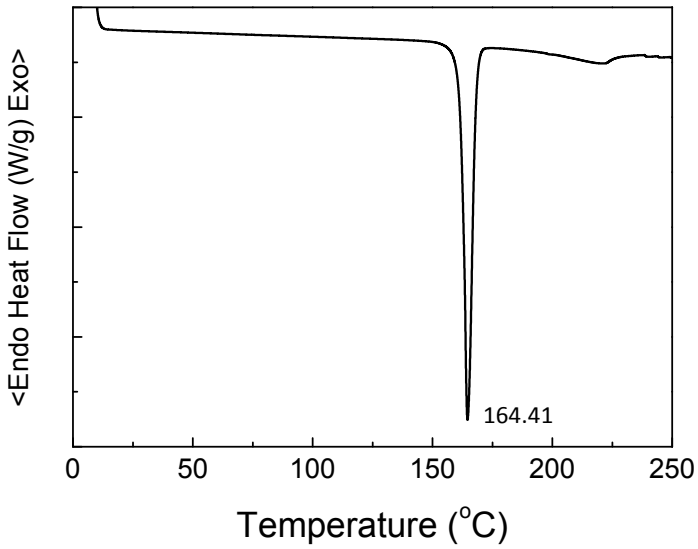


Fig. S2. DSC curve of **1k**.

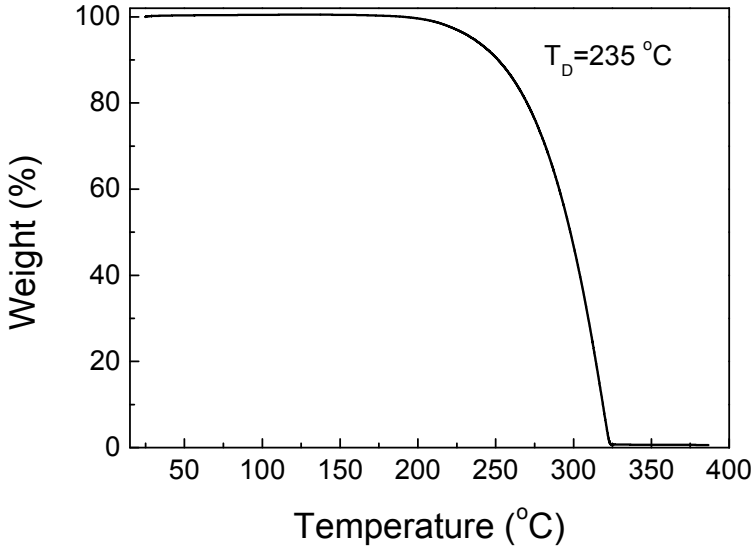
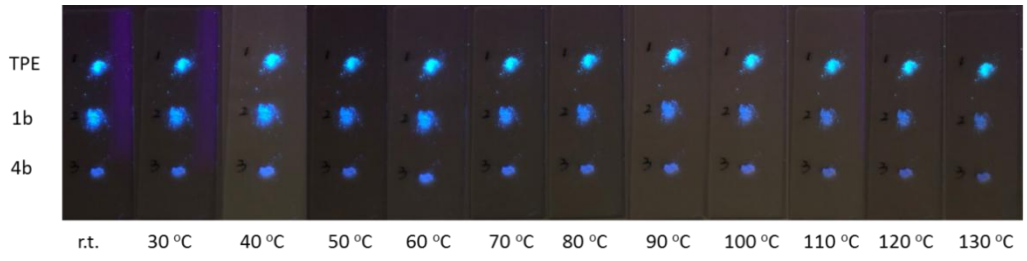
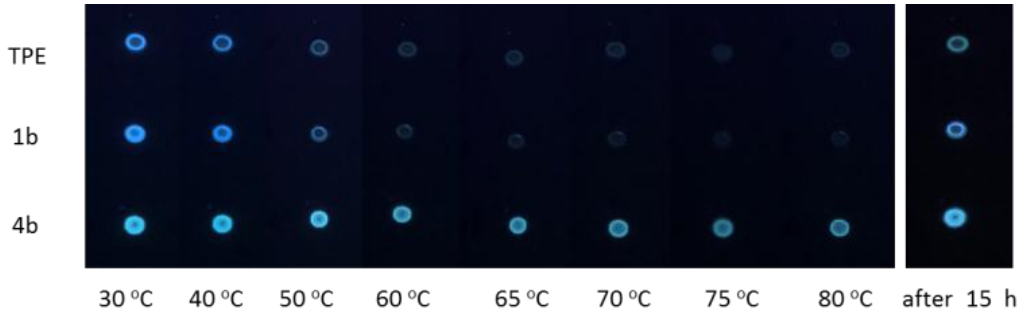


Fig. S3. TGA curve of **1k**.



(a)



(b)

Fig. S4. Photographs of powders of the parent TPE, **1b**, **4b** (a) and the parent TPE, **1b**, **4b** on silica gel plates (b) being heated at different temperatures under UV light (365 nm).

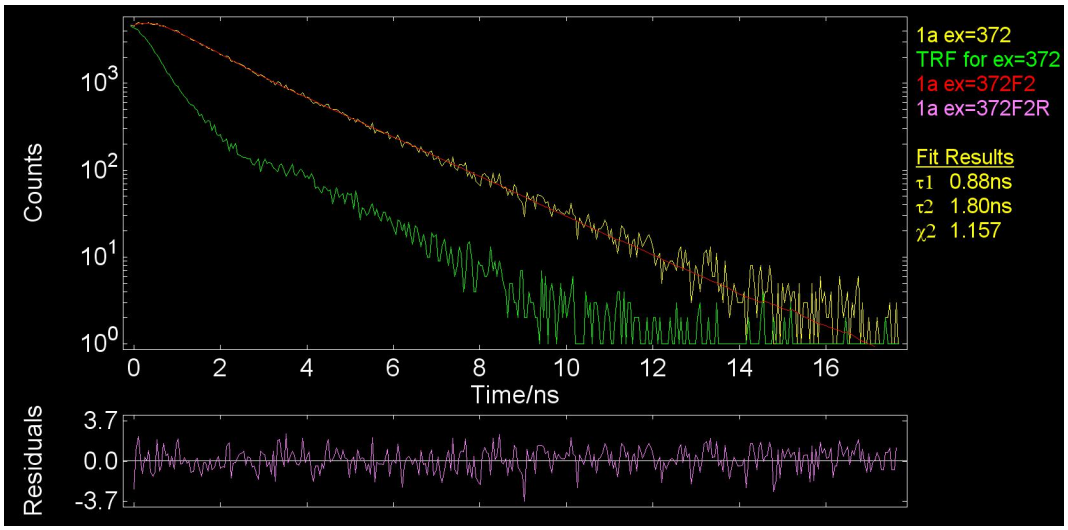


Fig. S5. PL decay curve of **1a** (λ_{ex} = 372 nm).

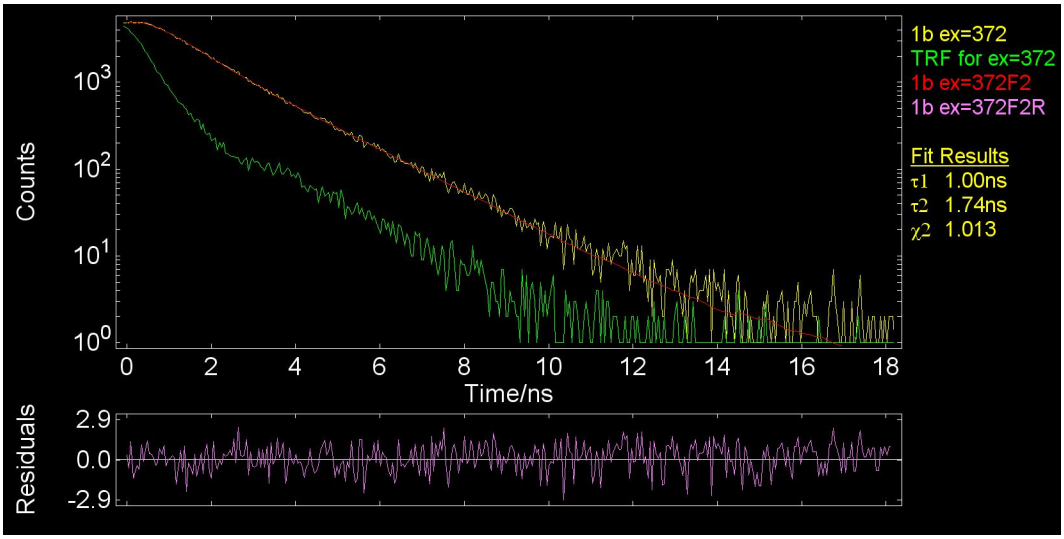


Fig. S6. PL decay curve of **1b** (λ_{ex} = 372 nm).

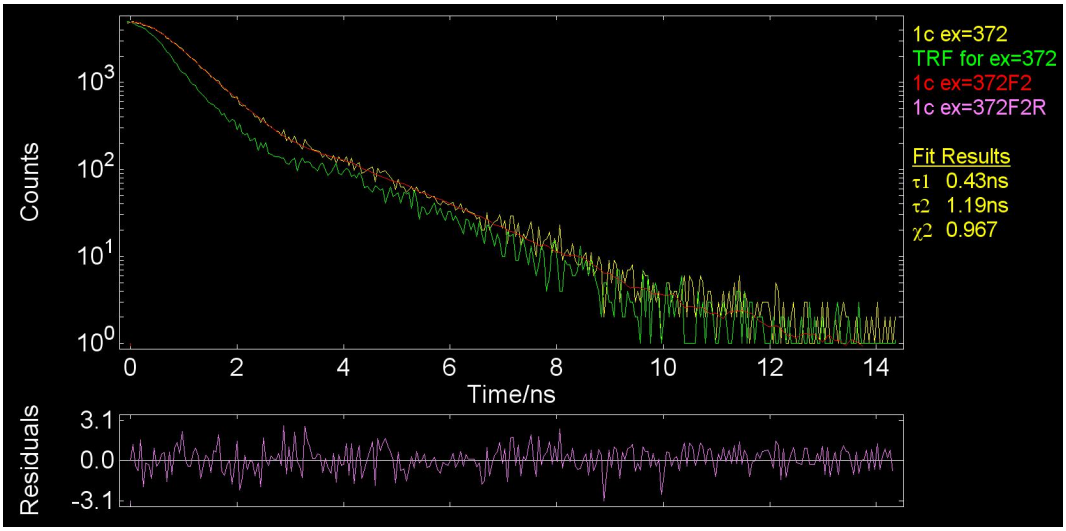


Fig. S7. PL decay curve of **1c** (λ_{ex} = 372 nm).

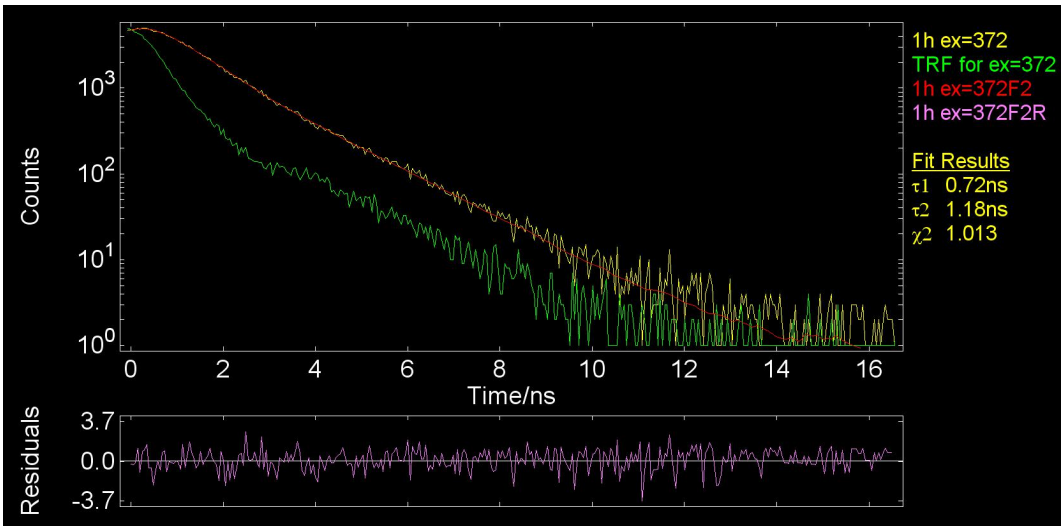


Fig. S8. PL decay curve of **1h** (λ_{ex} = 372 nm).

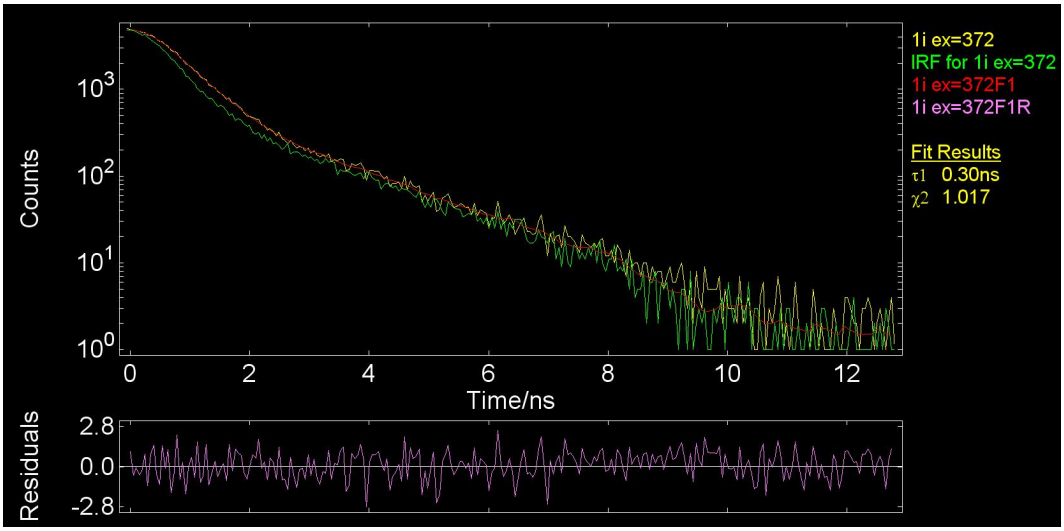


Fig. S9. PL decay curve of **1i** (λ_{ex} = 372 nm).

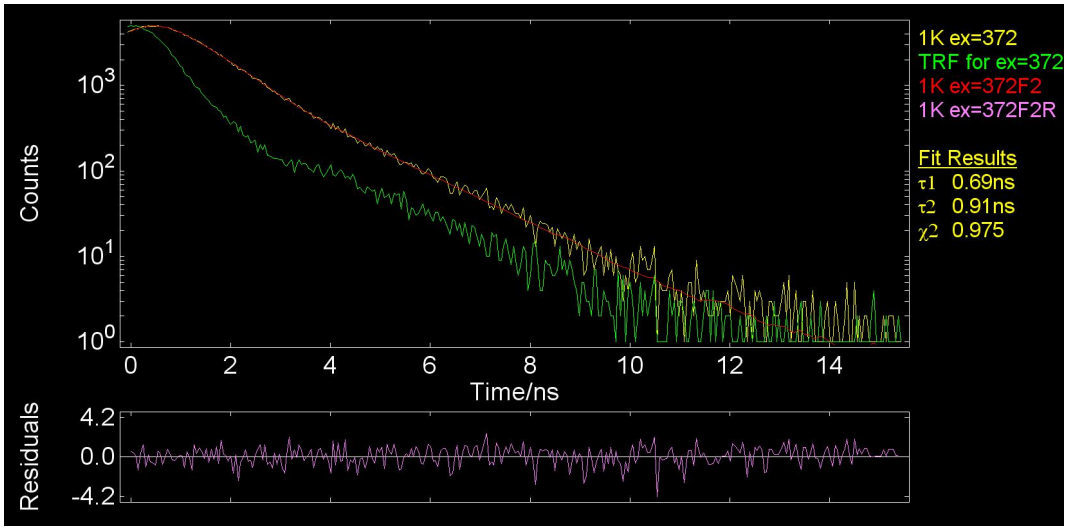


Fig. S10. PL decay curve of **1k** (λ_{ex} = 372 nm).

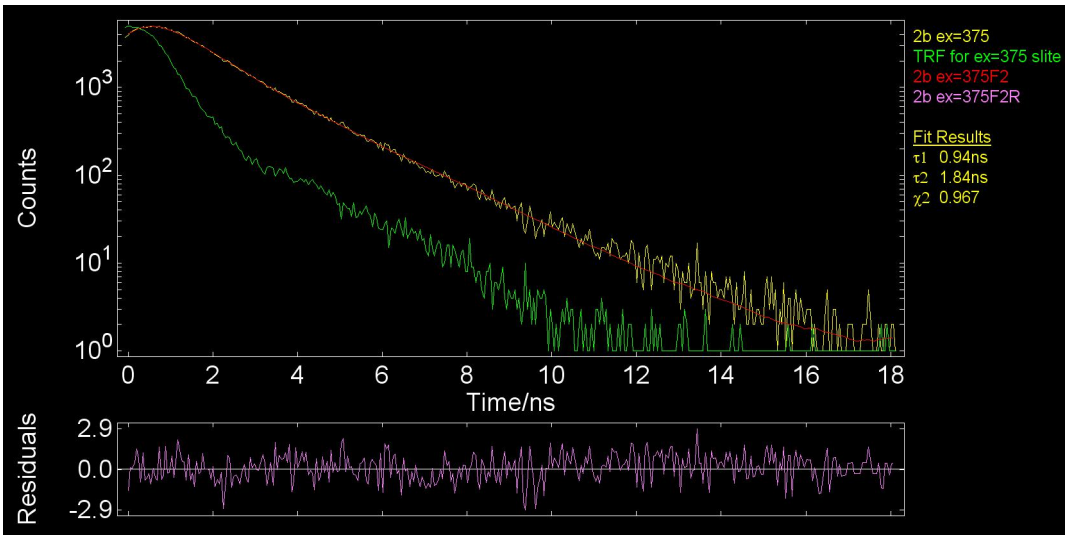


Fig. S11. PL decay curve of **2b** (λ_{ex} = 375 nm).

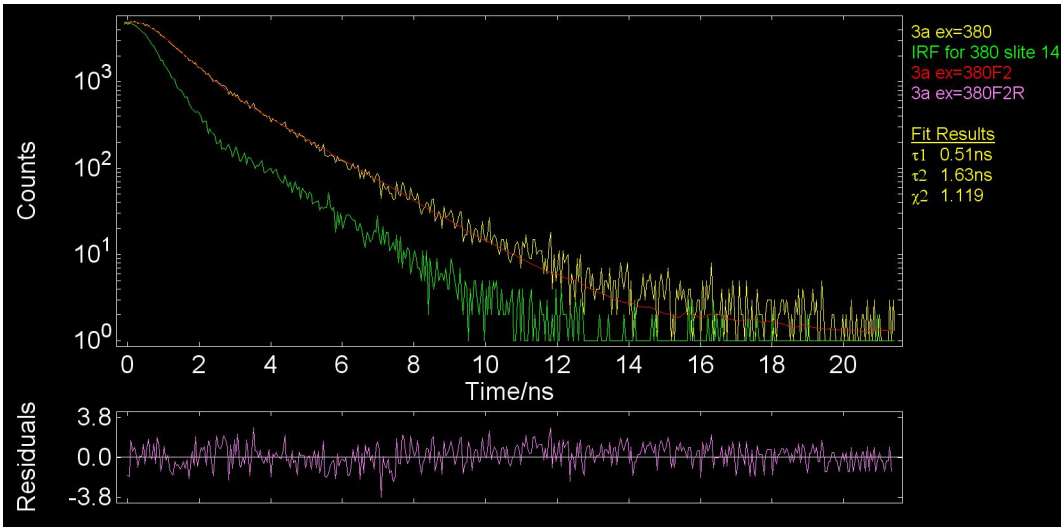


Fig. S12. PL decay curve of **3a** (λ_{ex} = 380 nm).

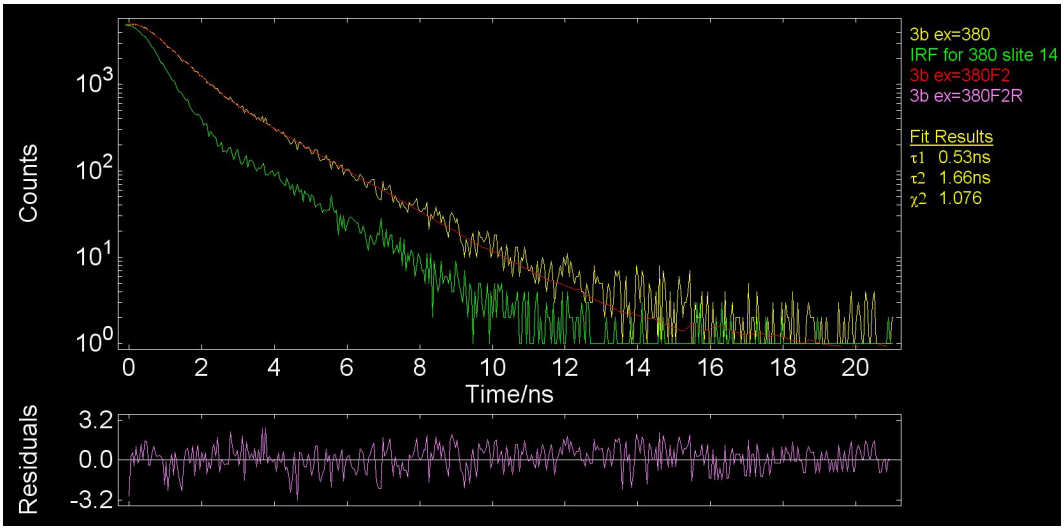


Fig. S13. PL decay curve of **3b** (λ_{ex} = 380 nm).

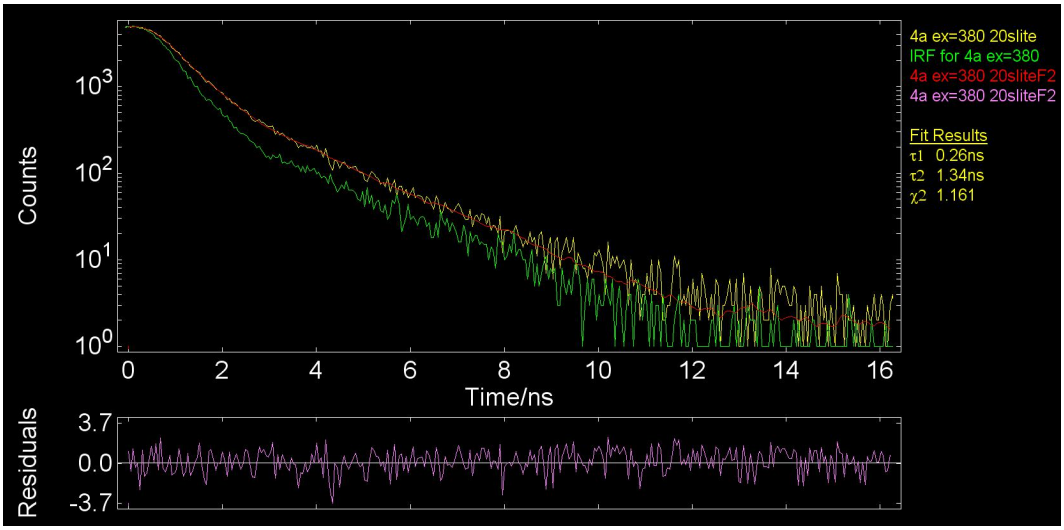


Fig. S14. PL decay curve of **4a** (λ_{ex} = 380 nm).

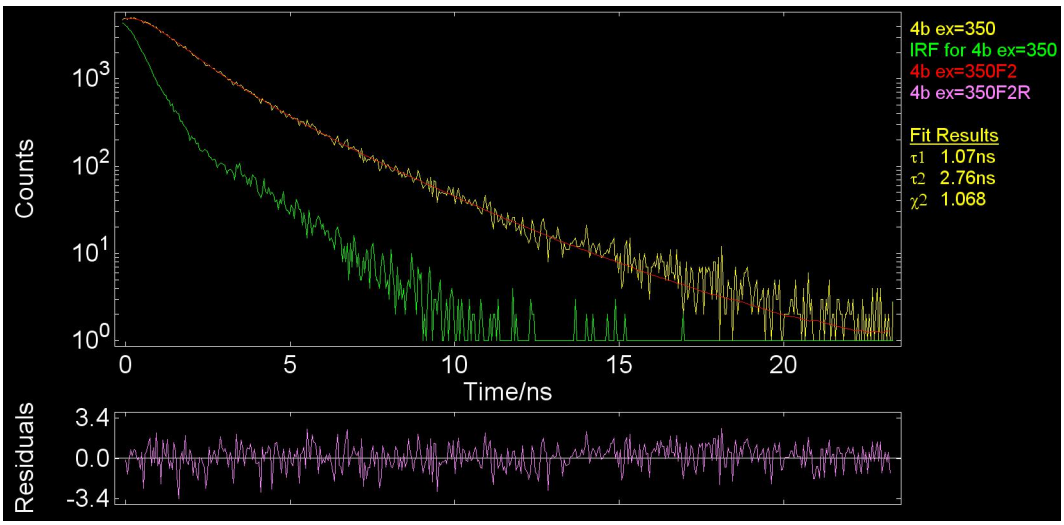


Fig. S15. PL decay curve of **4b** (λ_{ex} = 350 nm).

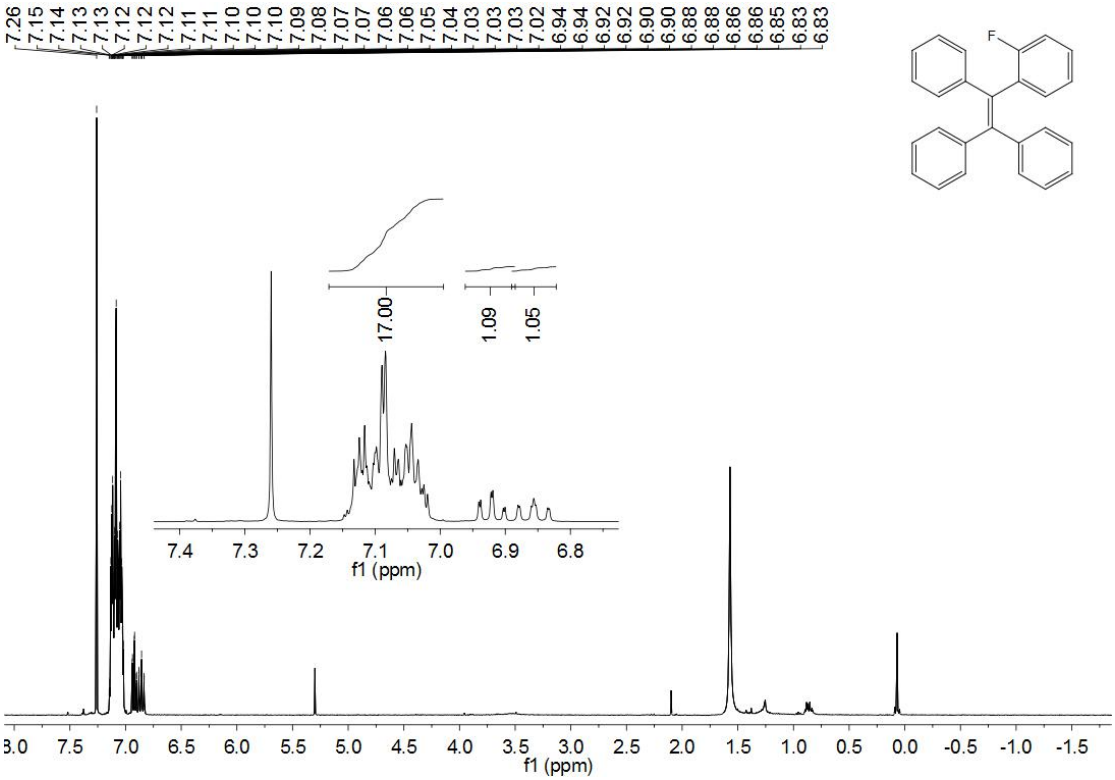


Fig. S16. ^{1}H NMR spectrum of **1a**.

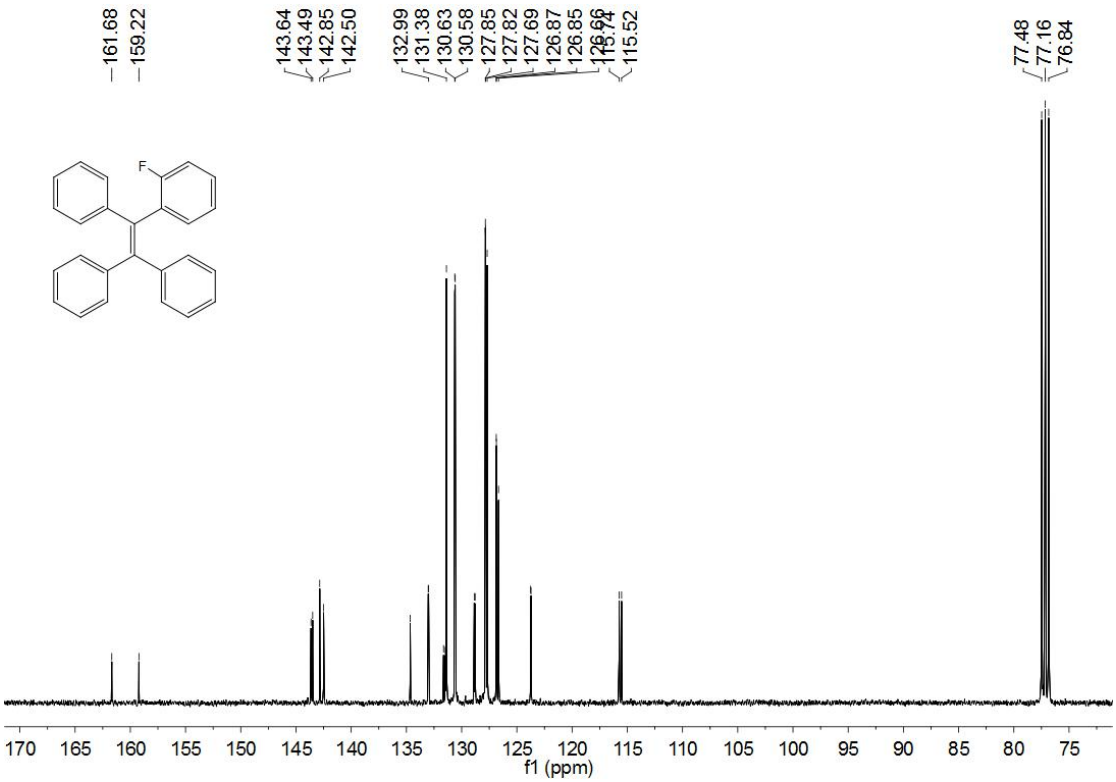


Fig. S17. ^{13}C NMR spectrum of **1a**.

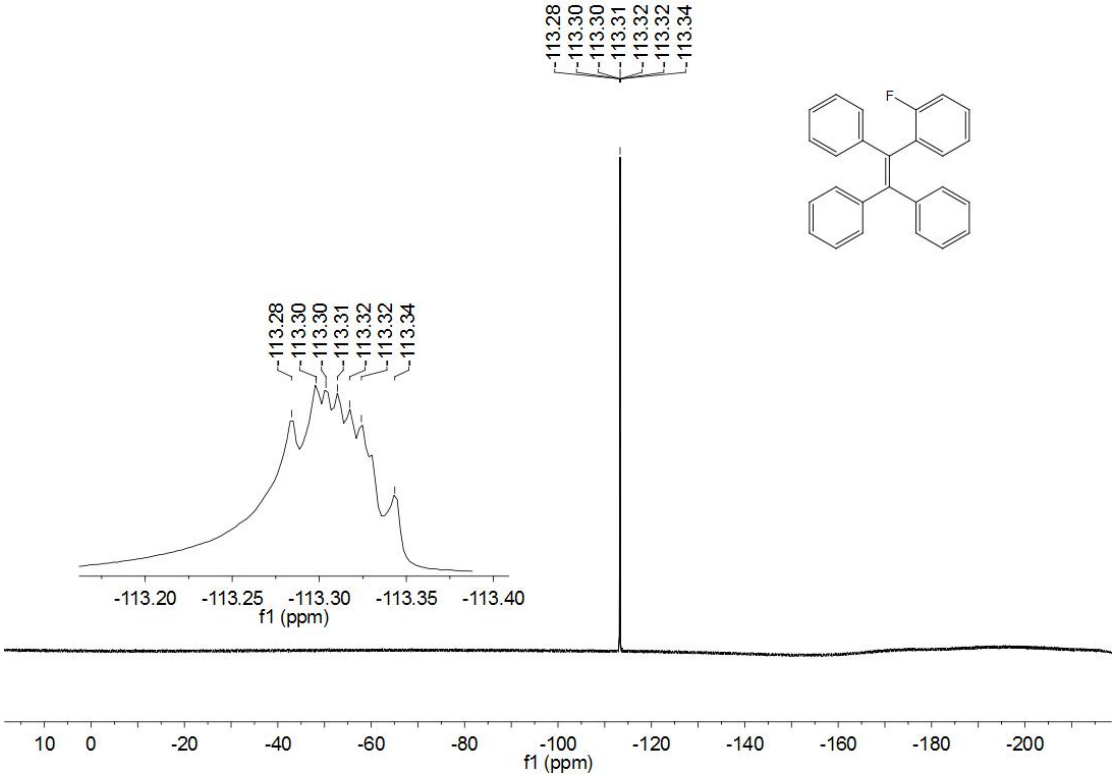


Fig. S18. ^{19}F NMR spectrum of **1a**.

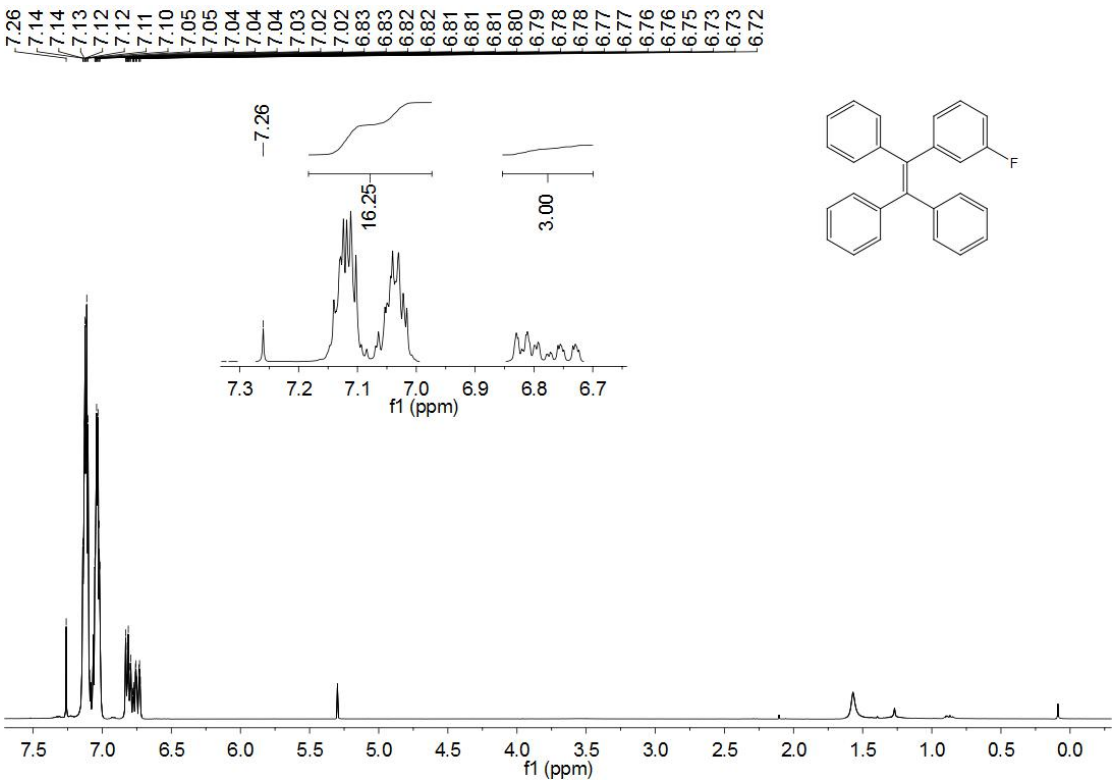


Fig. S19. ^{1}H NMR spectrum of **1b**.

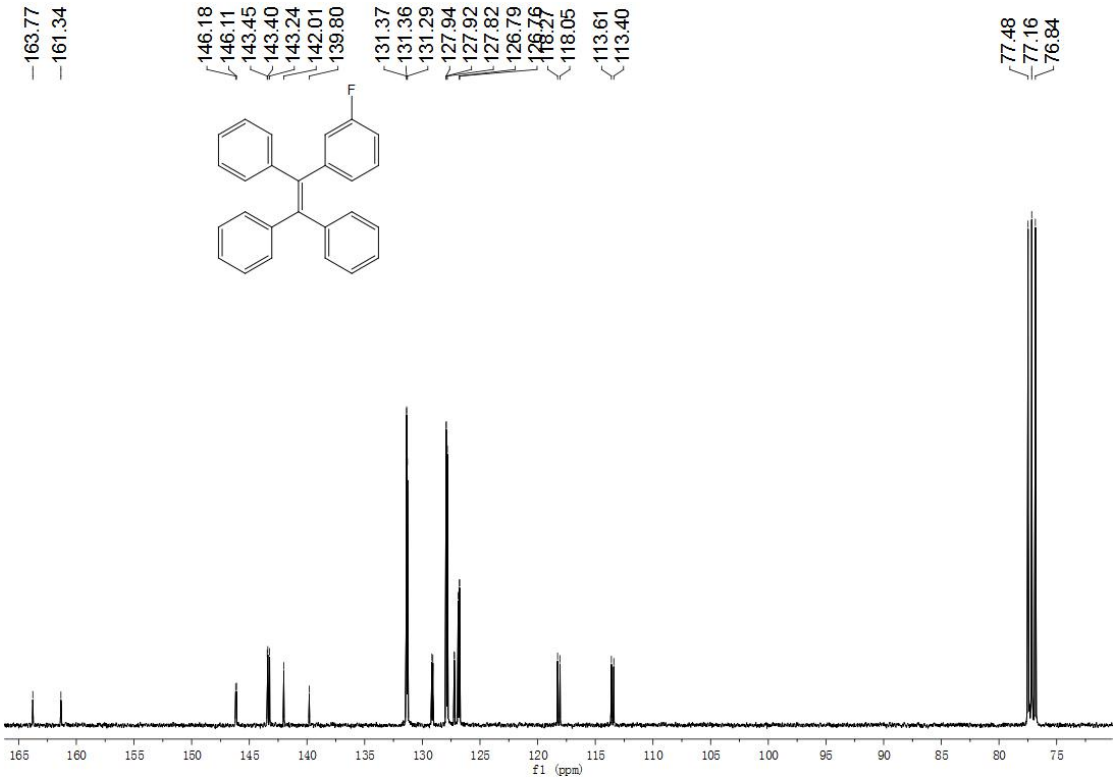


Fig. S20. ^{13}C NMR spectrum of **1b**.

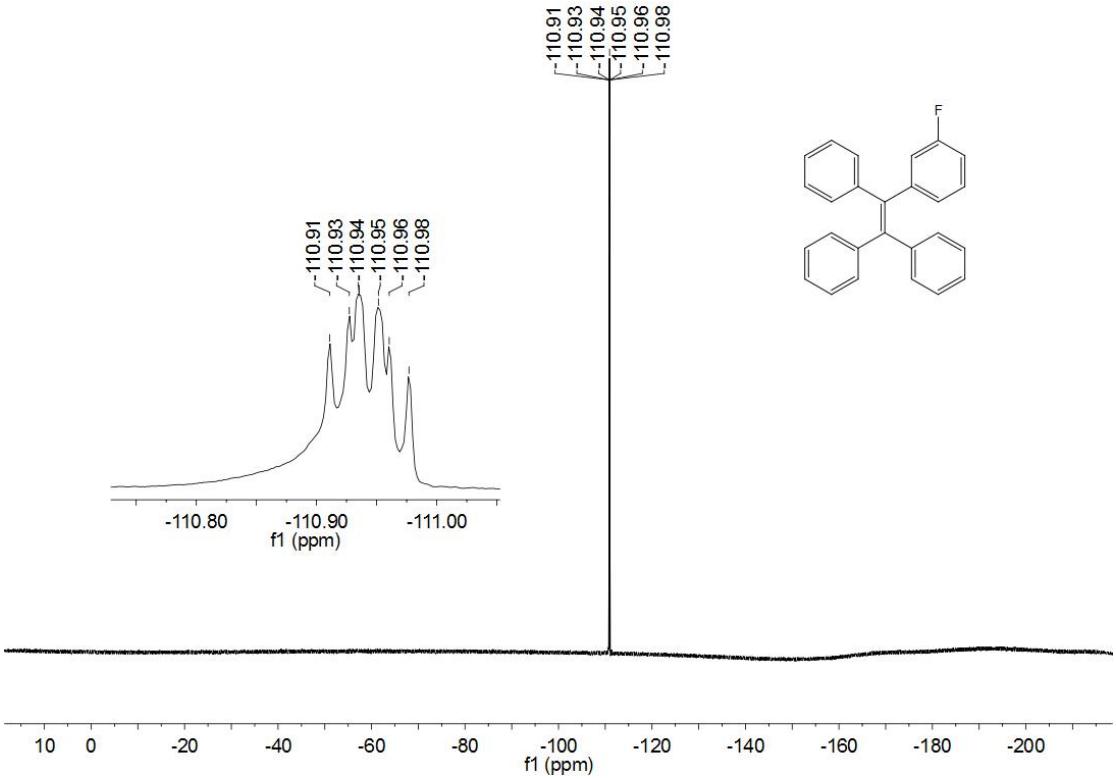


Fig. S21. ^{19}F NMR spectrum of **1b**.

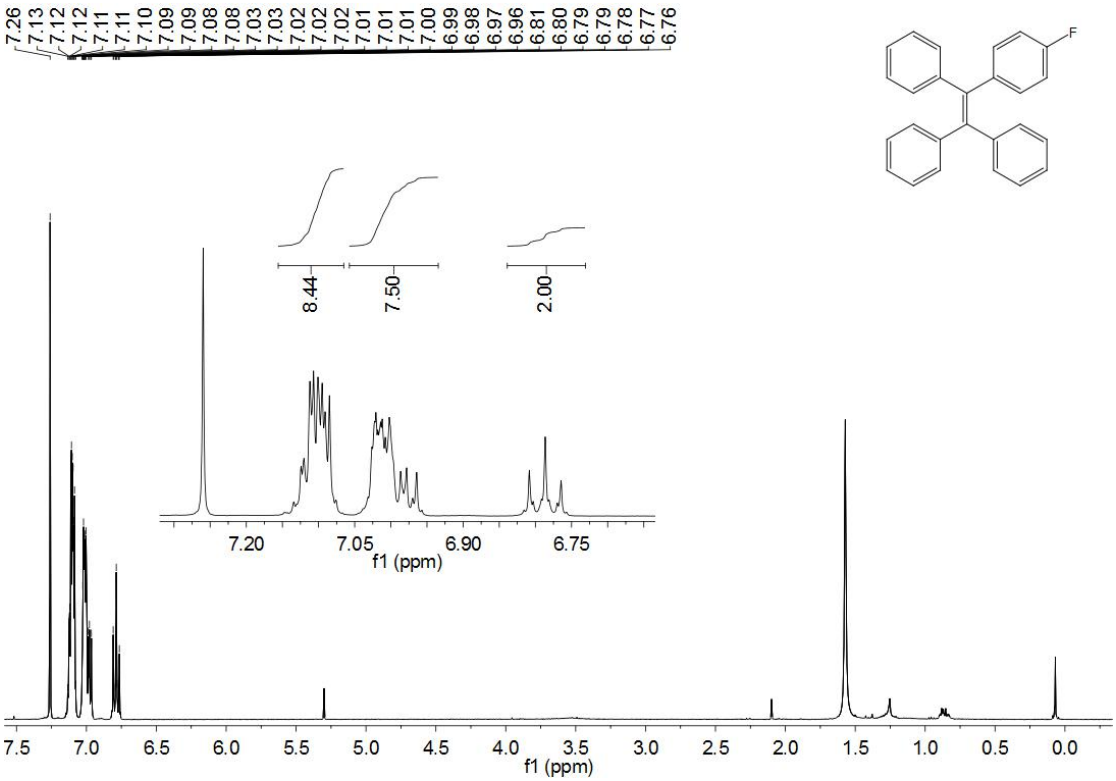


Fig. S22. ^{1}H NMR spectrum of **1c**.

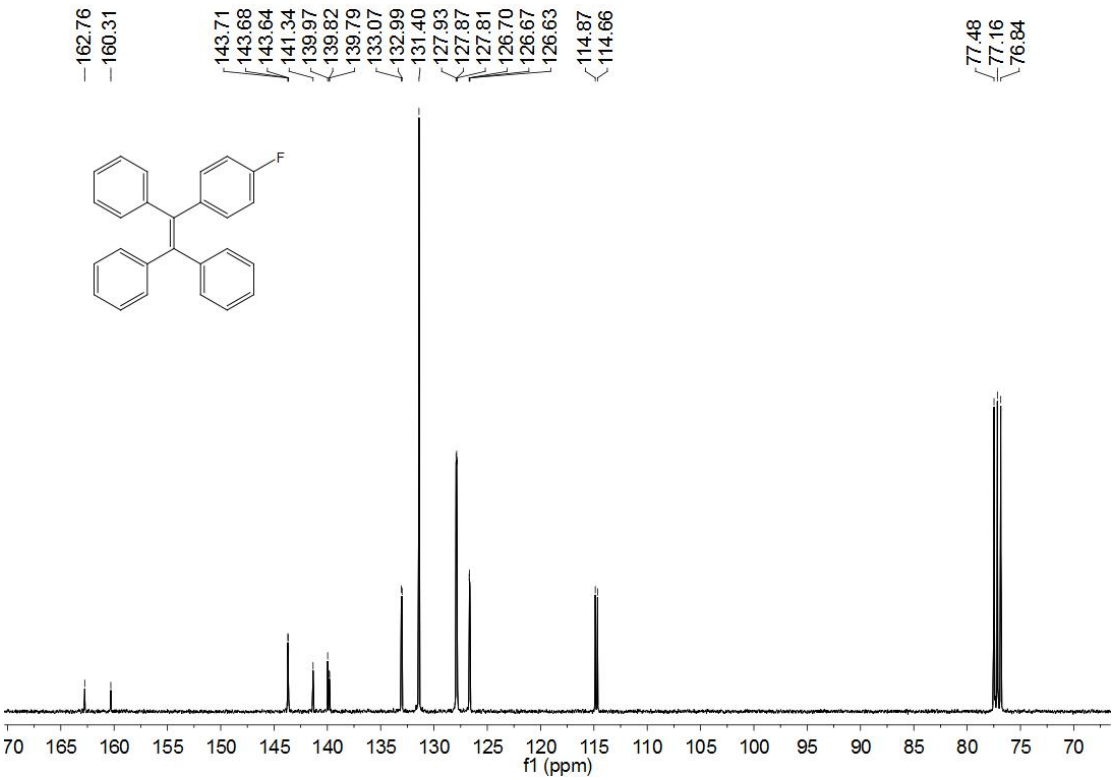


Fig. S23. ^{13}C NMR spectrum of **1c**.

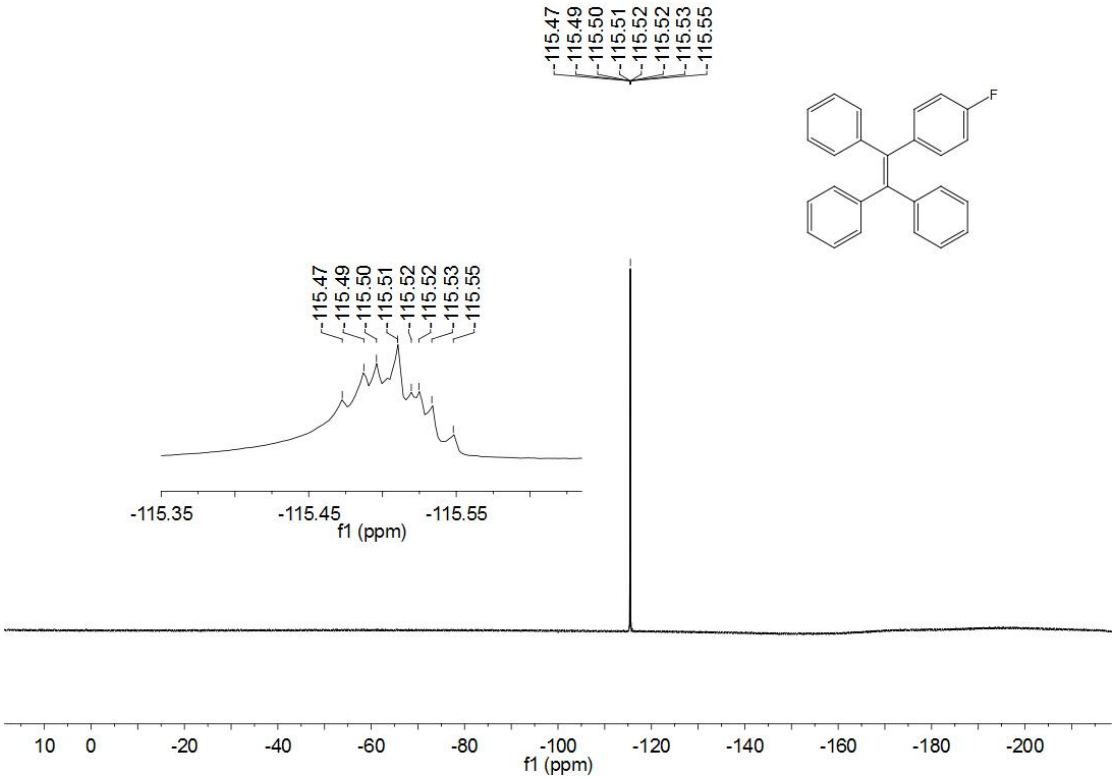


Fig. S24. ^{19}F NMR spectrum of **1c**.

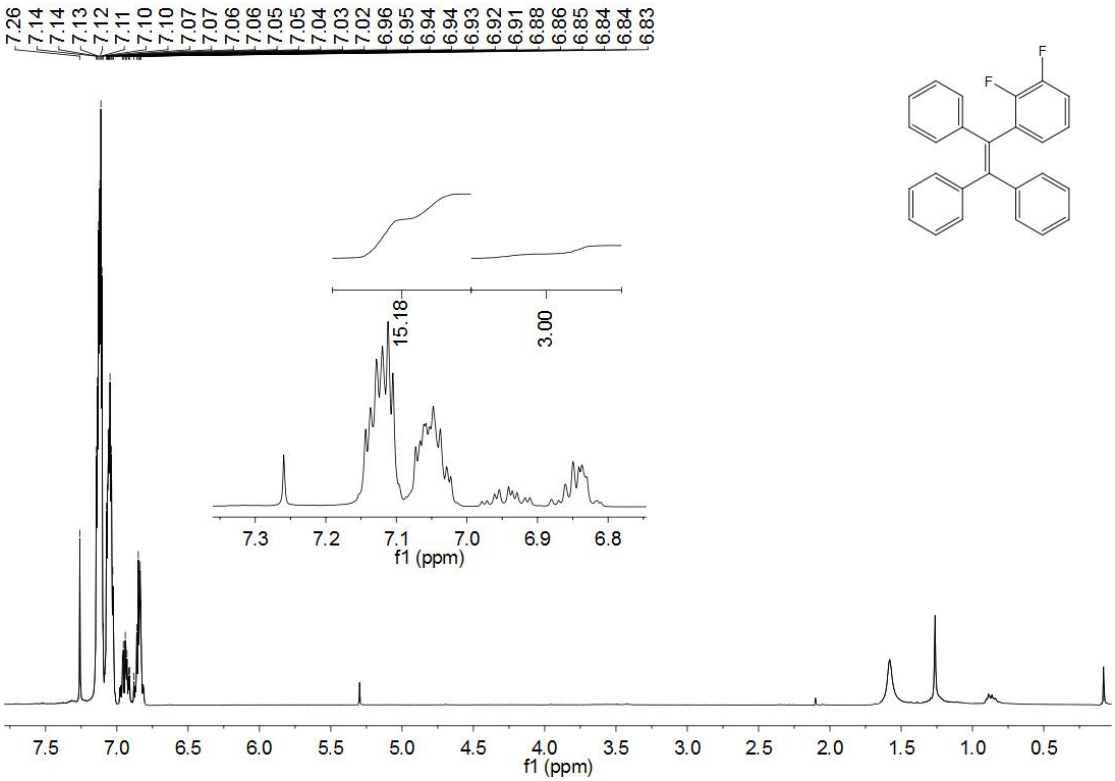


Fig. S25. ^{1}H NMR spectrum of **1d**.

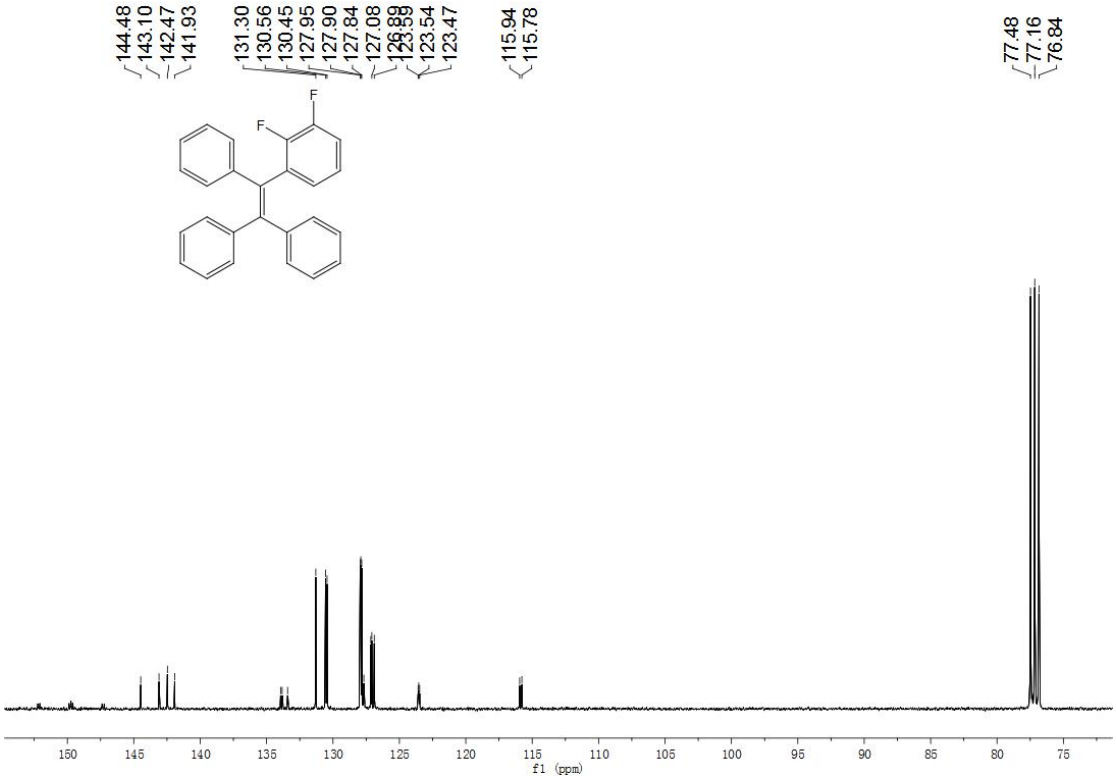


Fig. S26. ^{13}C NMR spectrum of **1d**.

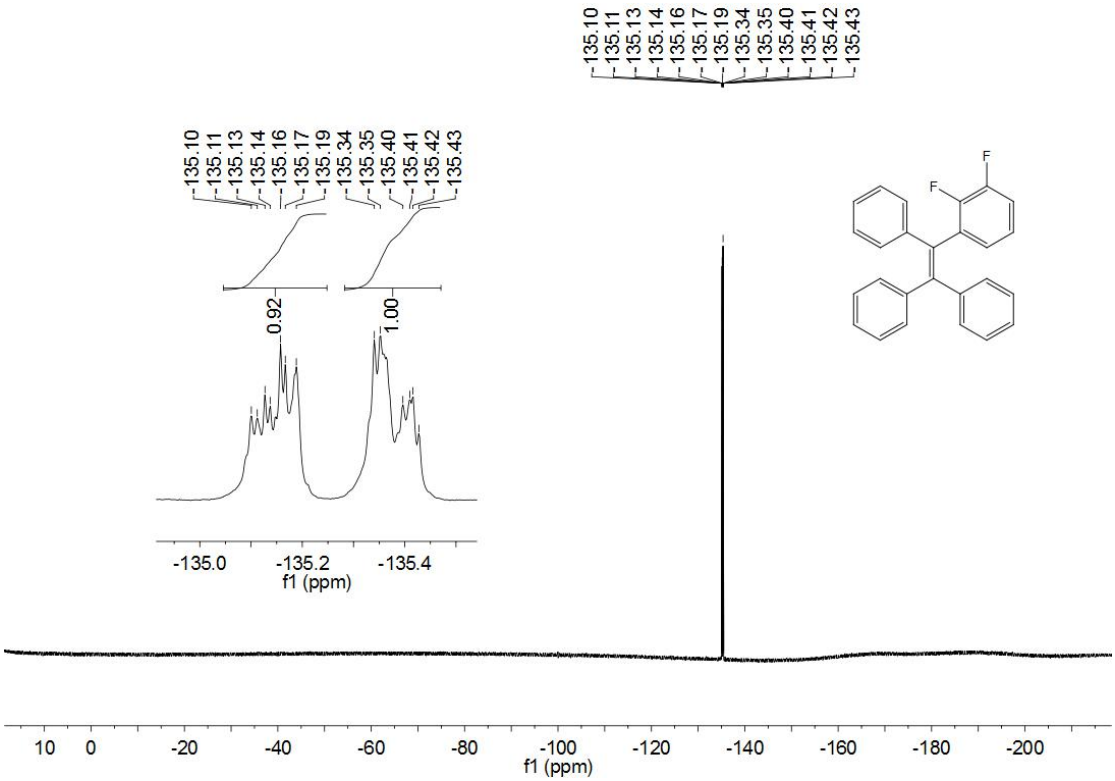


Fig. S27. ^{19}F NMR spectrum of **1d**.

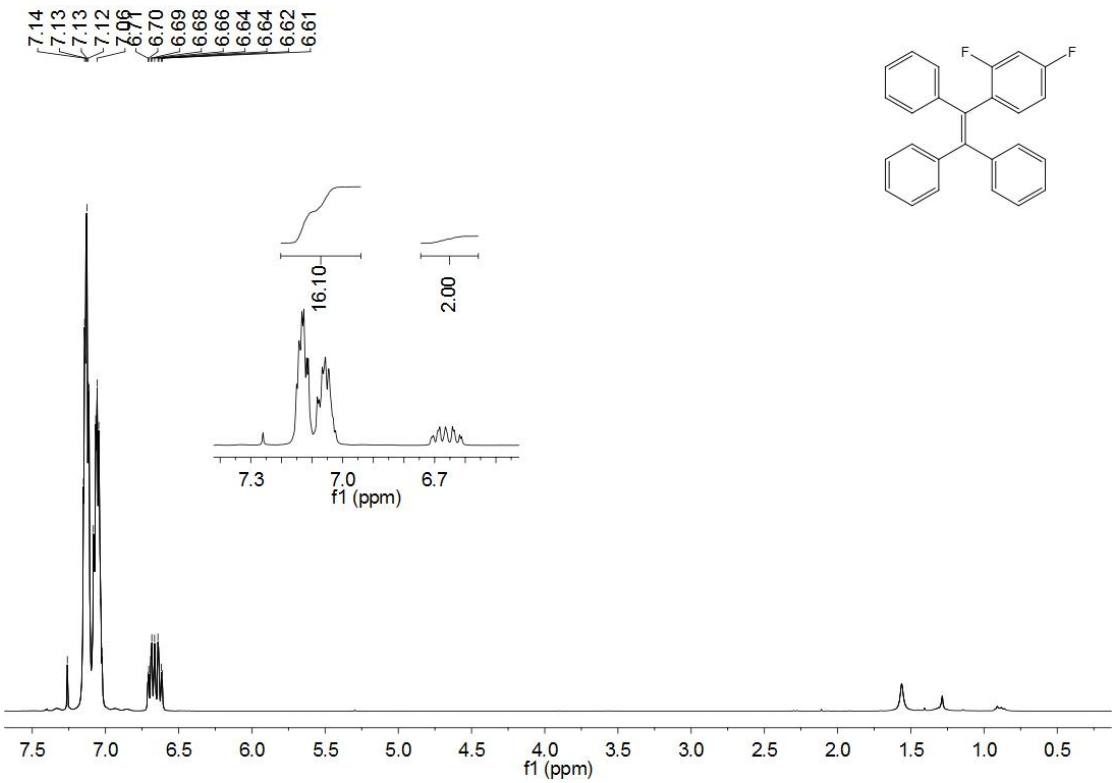


Fig. S28. ^{1}H NMR spectrum of **1e**.

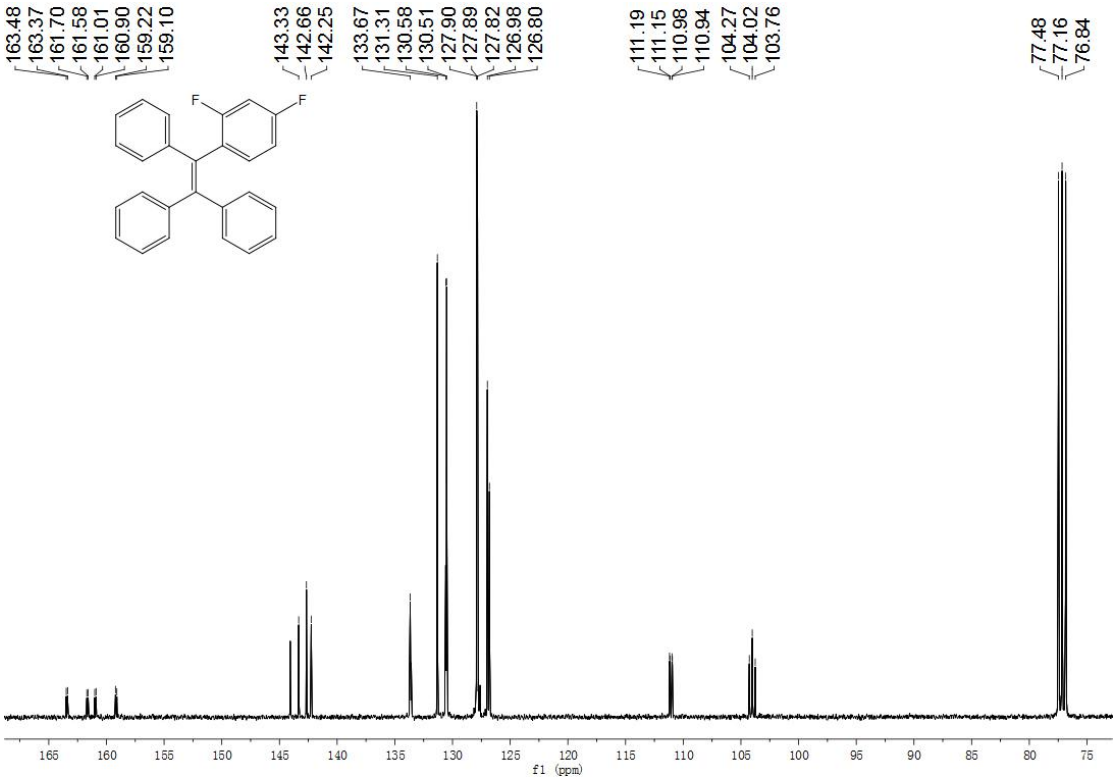


Fig. S29. ^{13}C NMR spectrum of **1e**.

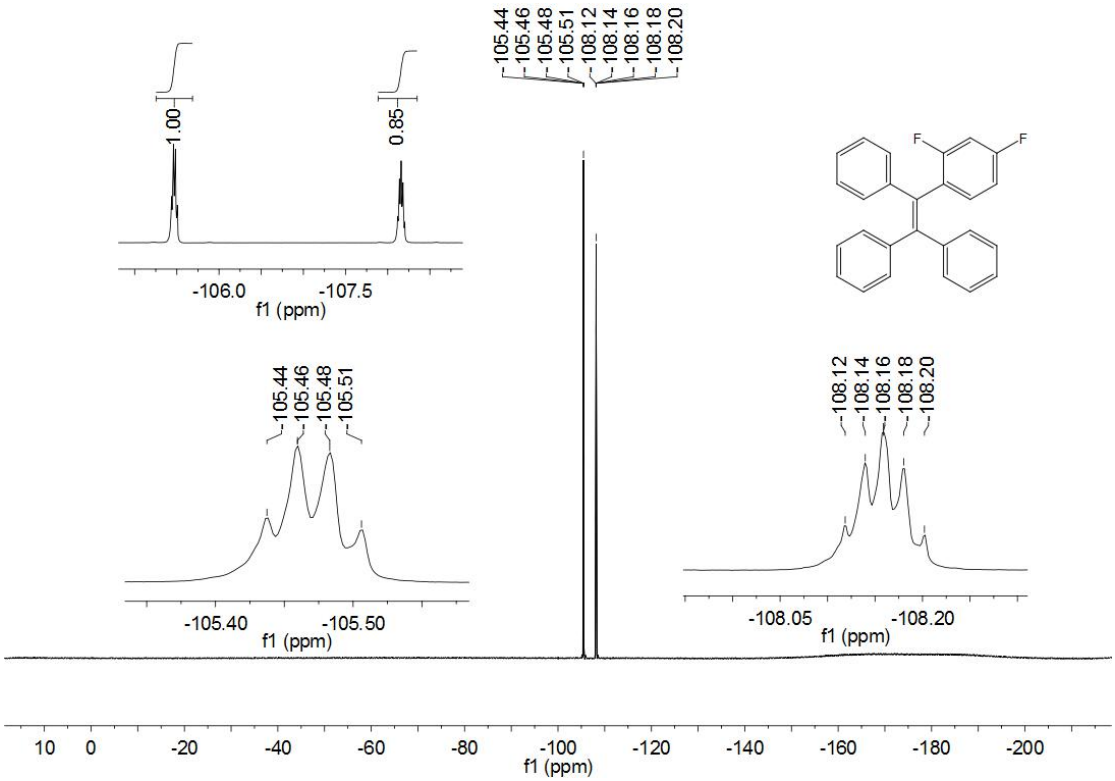


Fig. S30. ^{19}F NMR spectrum of **1e**.

1f. 1-(2,5-difluorophenyl)-1,2,2-triphenylethene

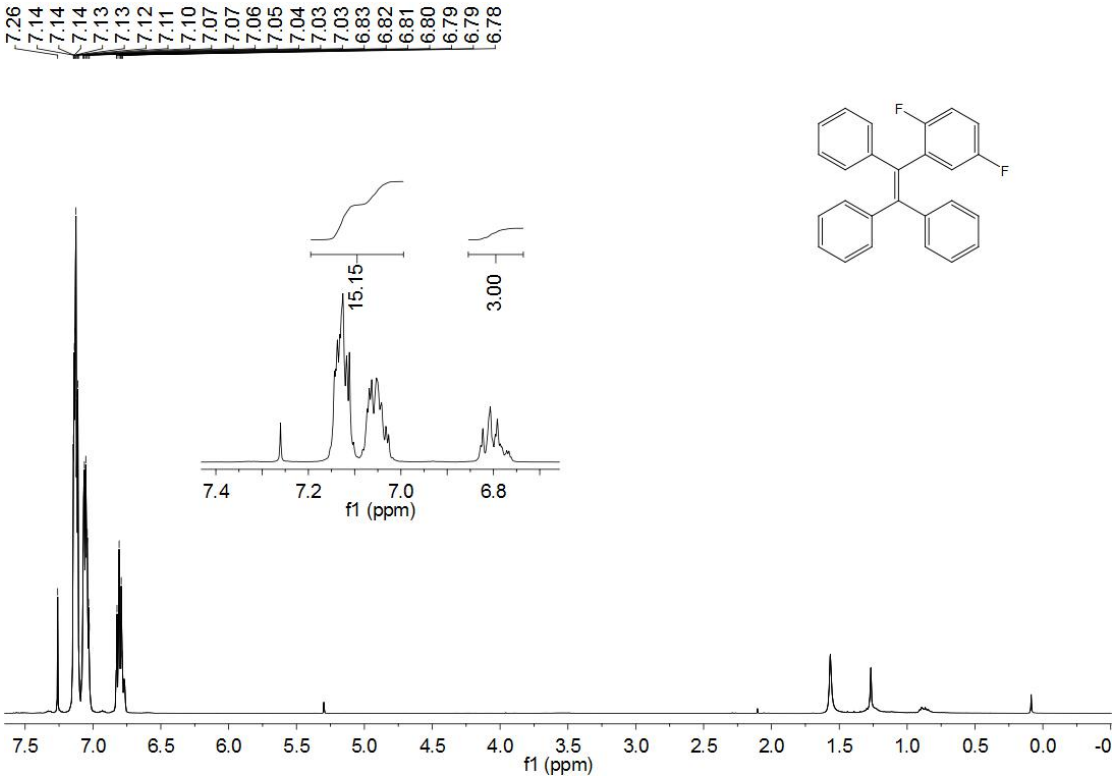


Fig. S31. ^{1}H NMR spectrum of **1f**.

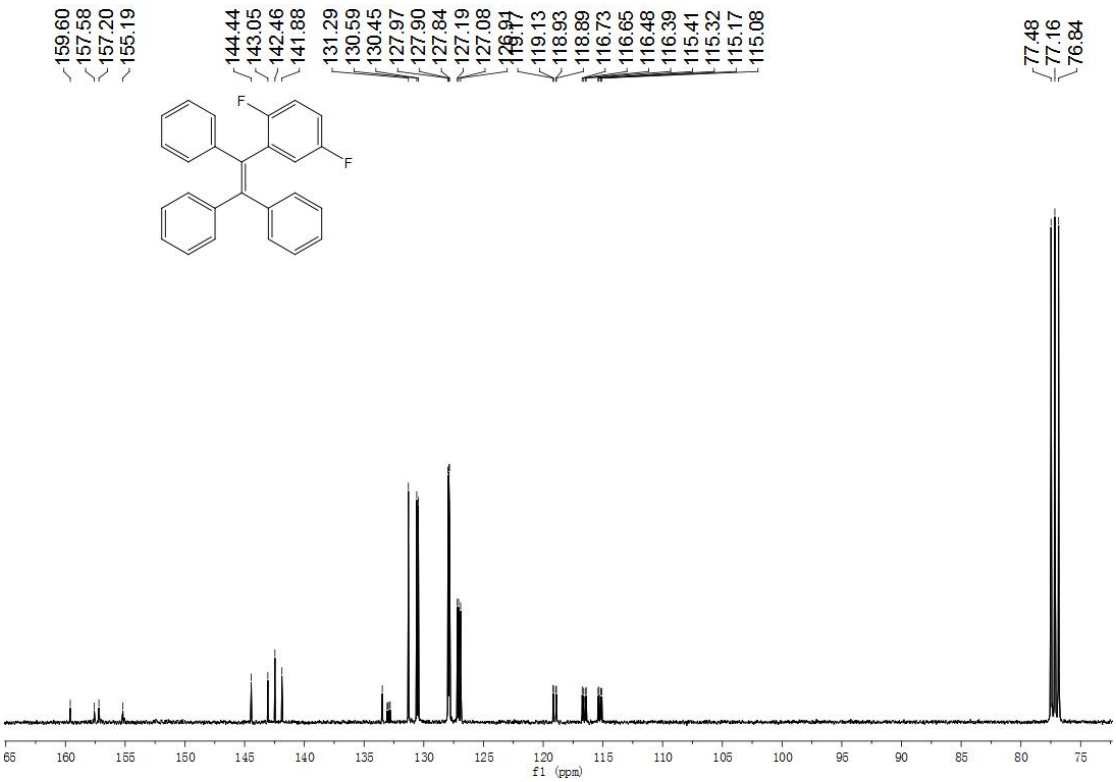


Fig. S32. ^{13}C NMR spectrum of **1f**.

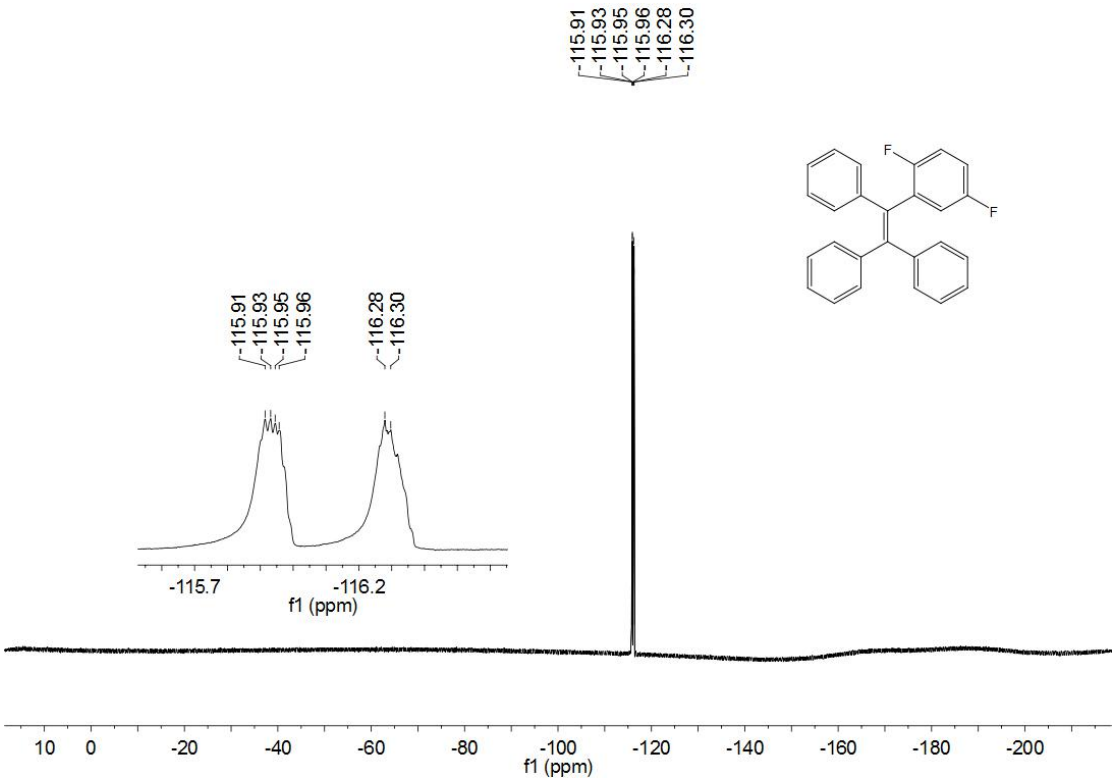


Fig. S33. ^{19}F NMR spectrum of **1f**.

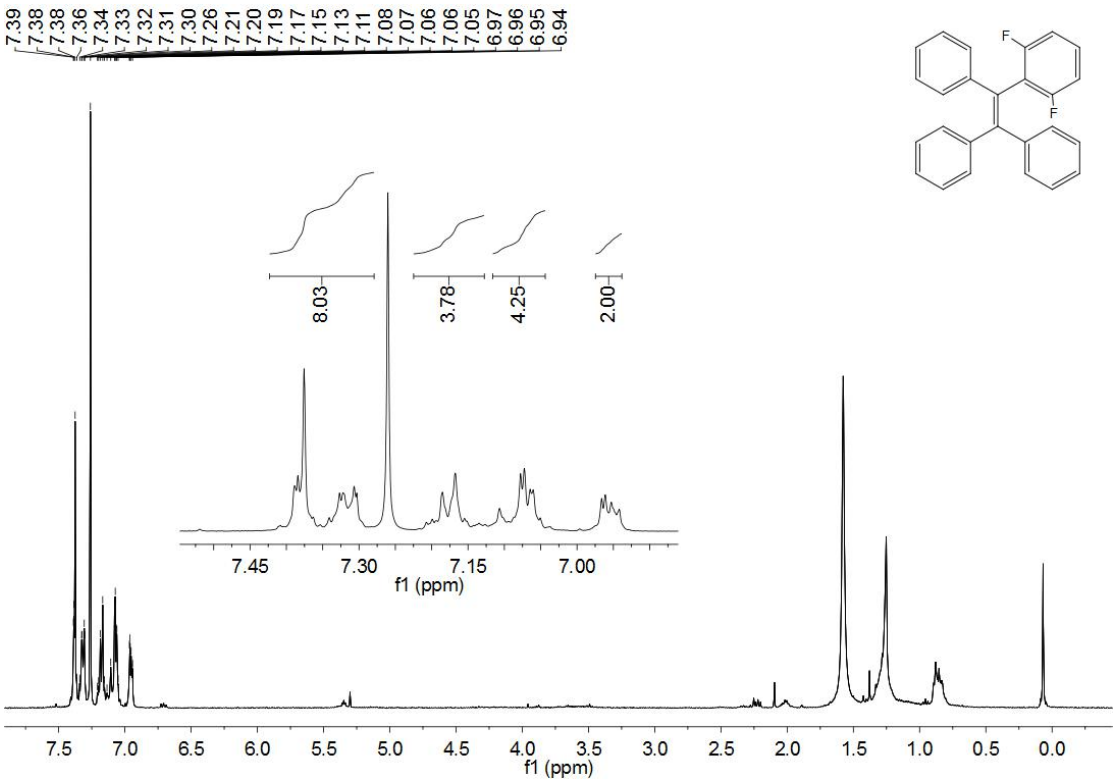


Fig. S34. ^{1}H NMR spectrum of **1g**.

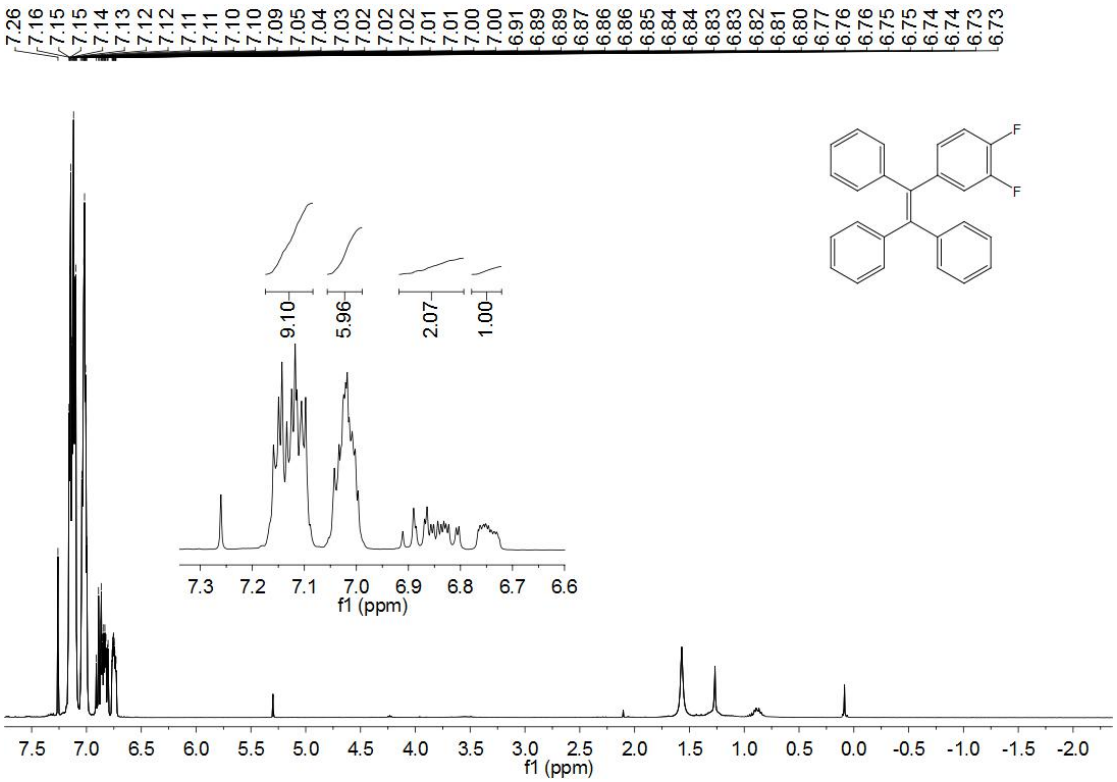


Fig. S35. ^{1}H NMR spectrum of **1h**.

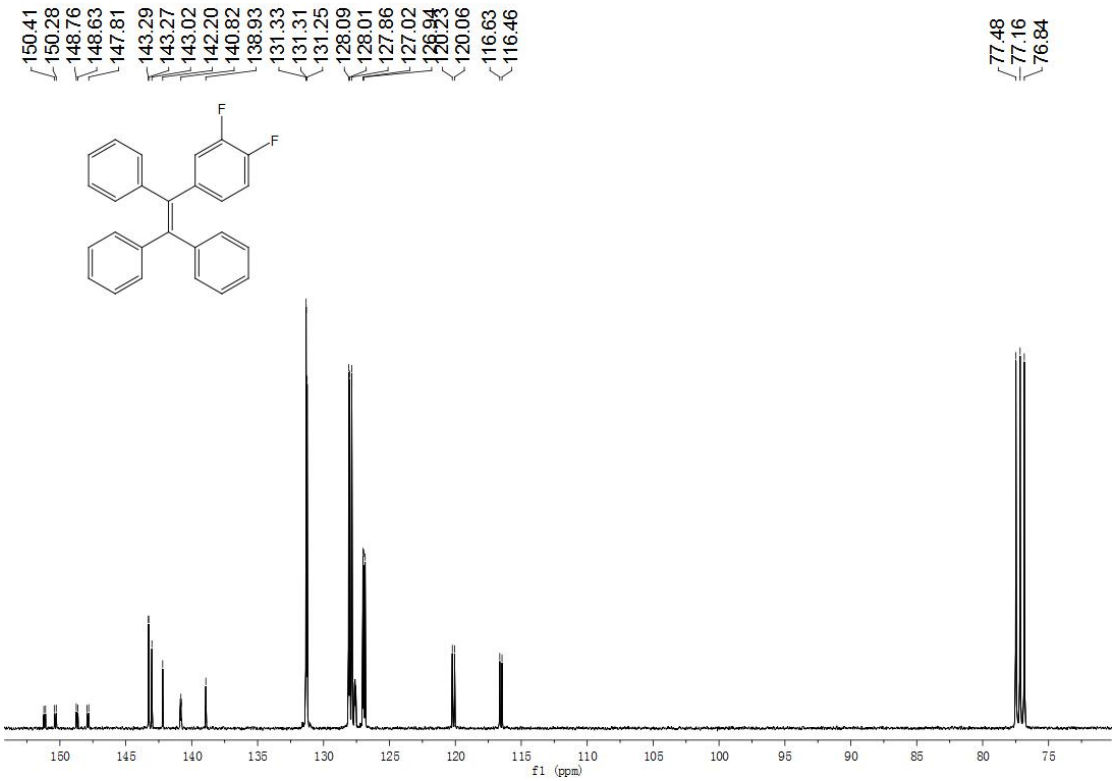


Fig. S36. ^{13}C NMR spectrum of **1h**.

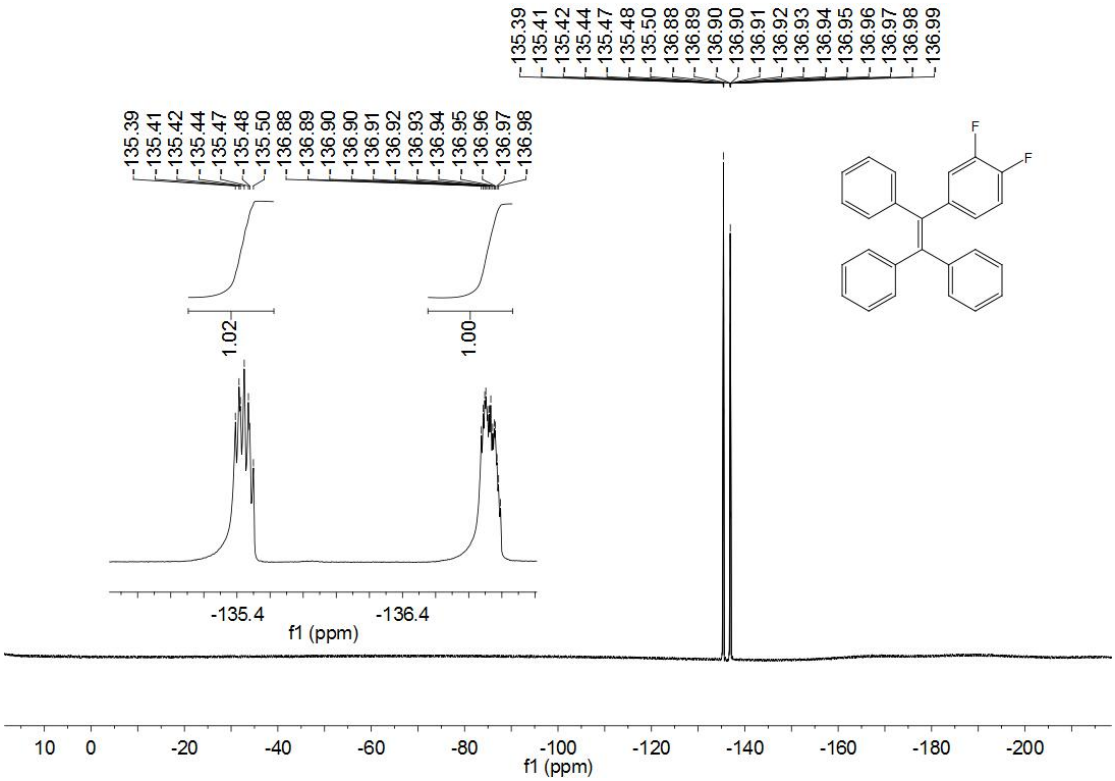


Fig. S37. ^{19}F NMR spectrum of **1h**.

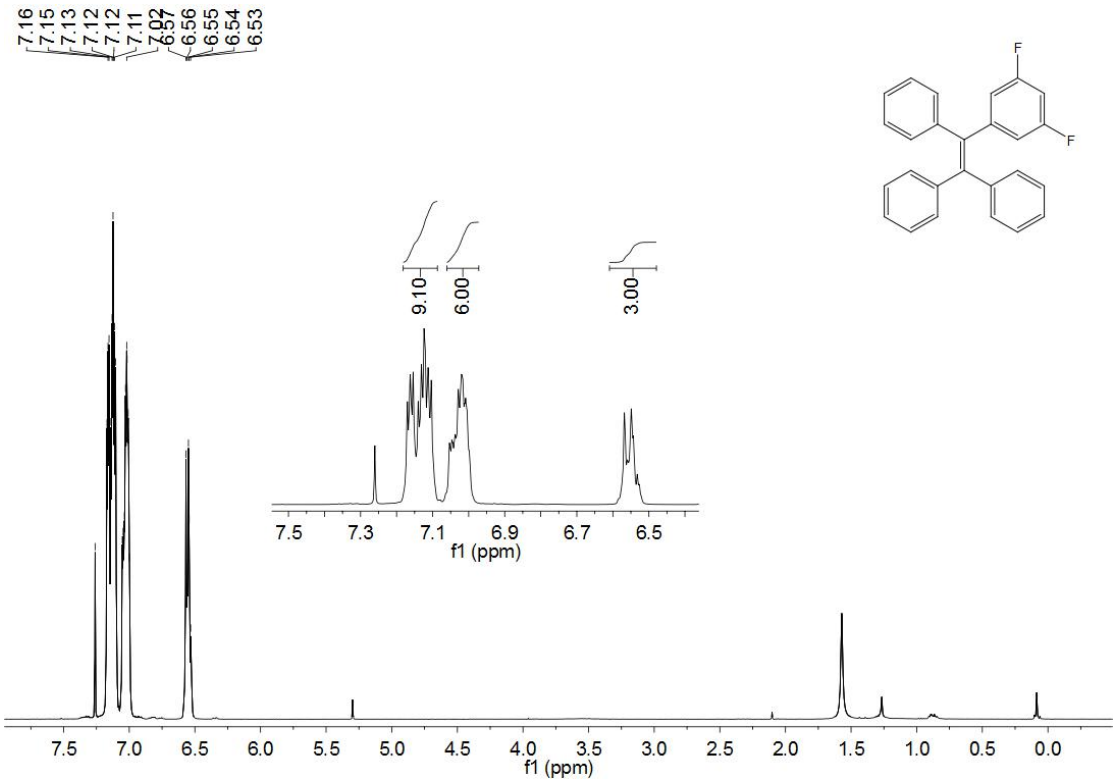


Fig. S38. ^{1}H NMR spectrum of **1i**.

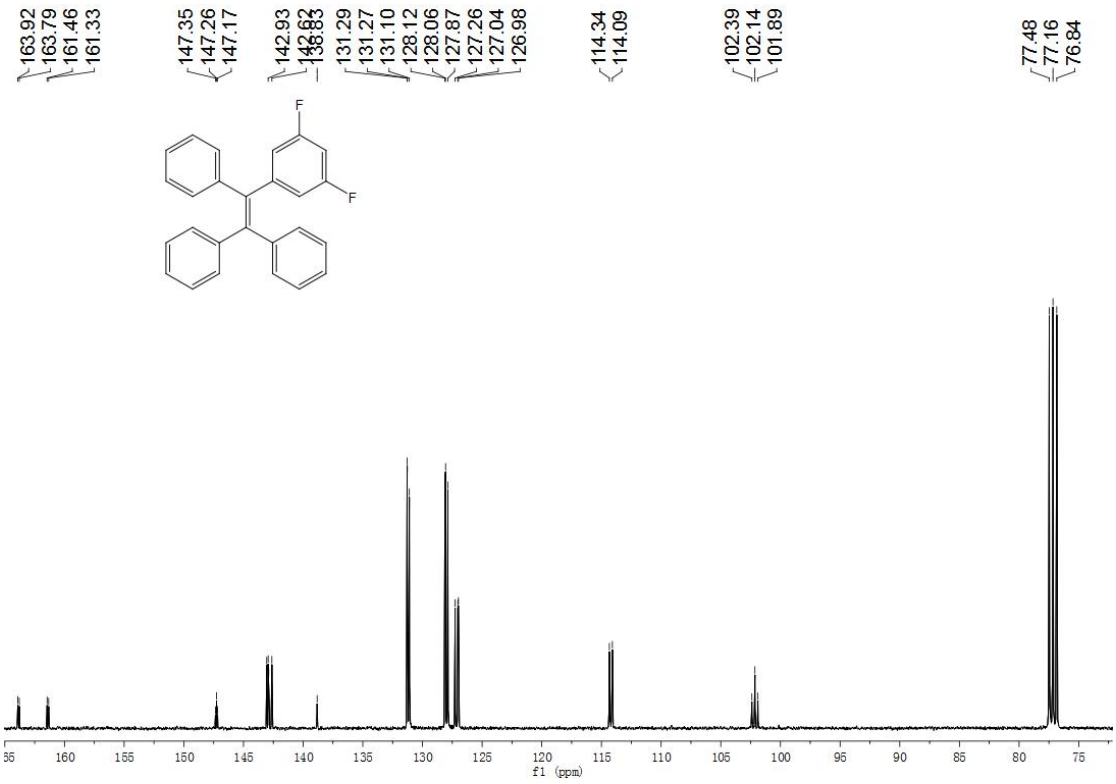


Fig. S39. ^{13}C NMR spectrum of **1i**.

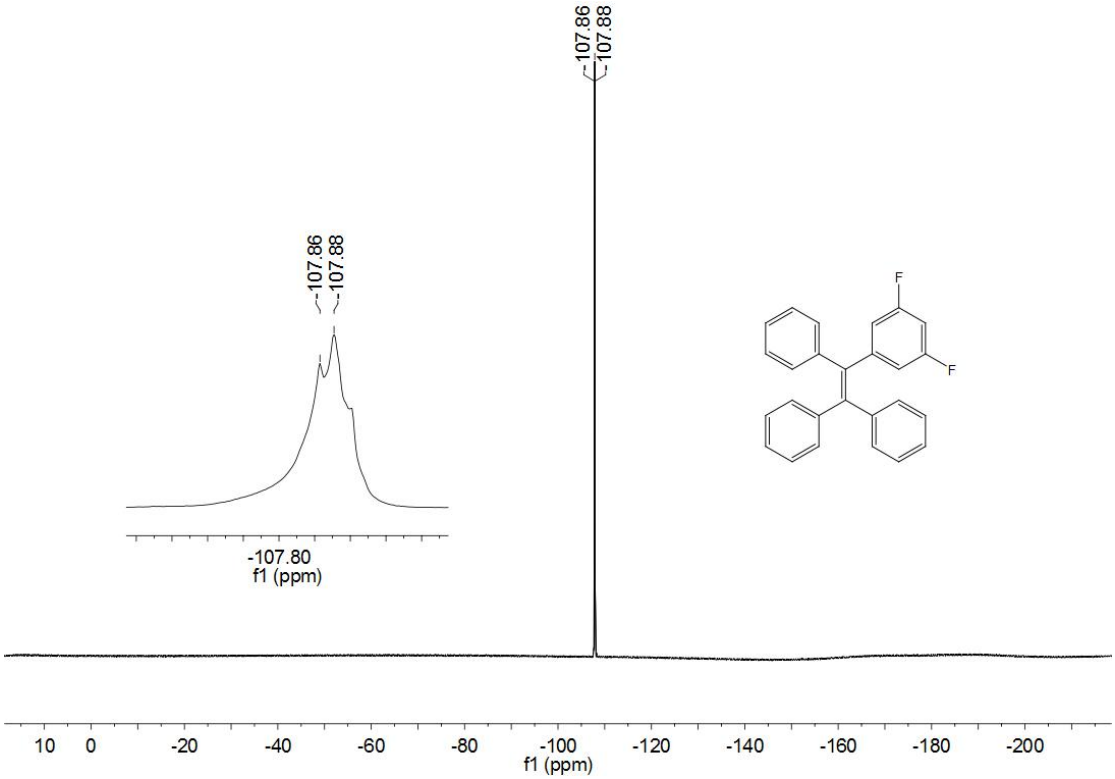


Fig. S40. ^{19}F NMR spectrum of **1i**.

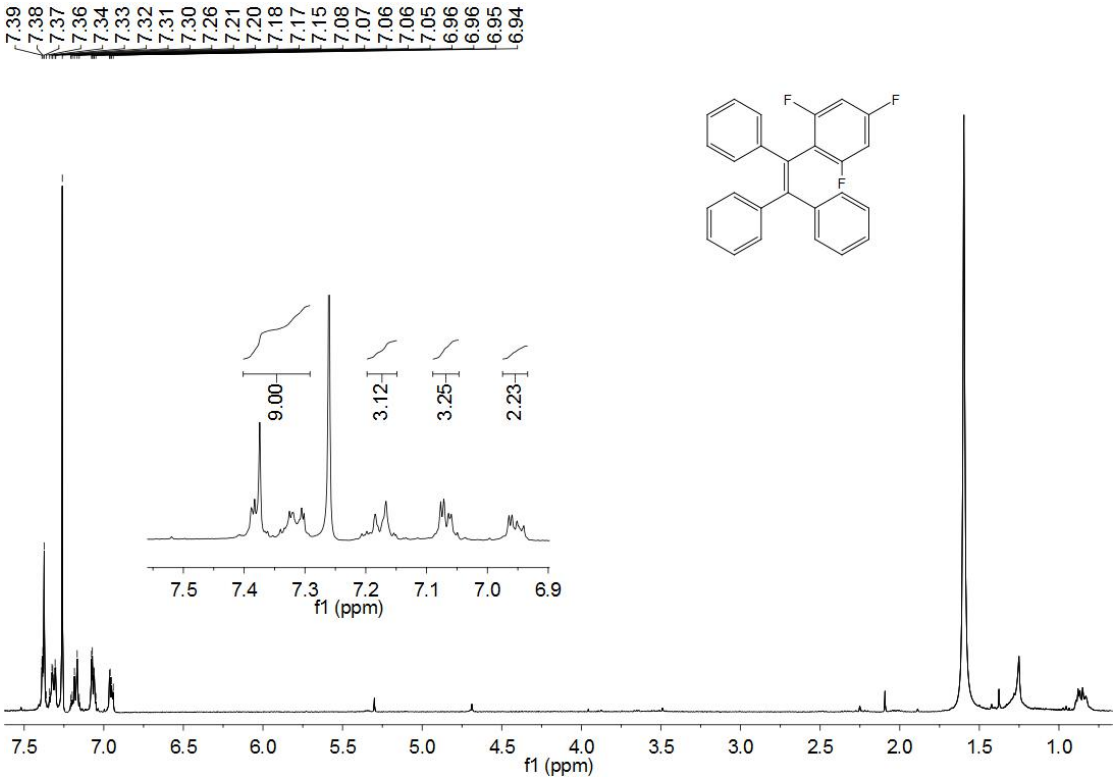


Fig. S41. ^{1}H NMR spectrum of **1j**.

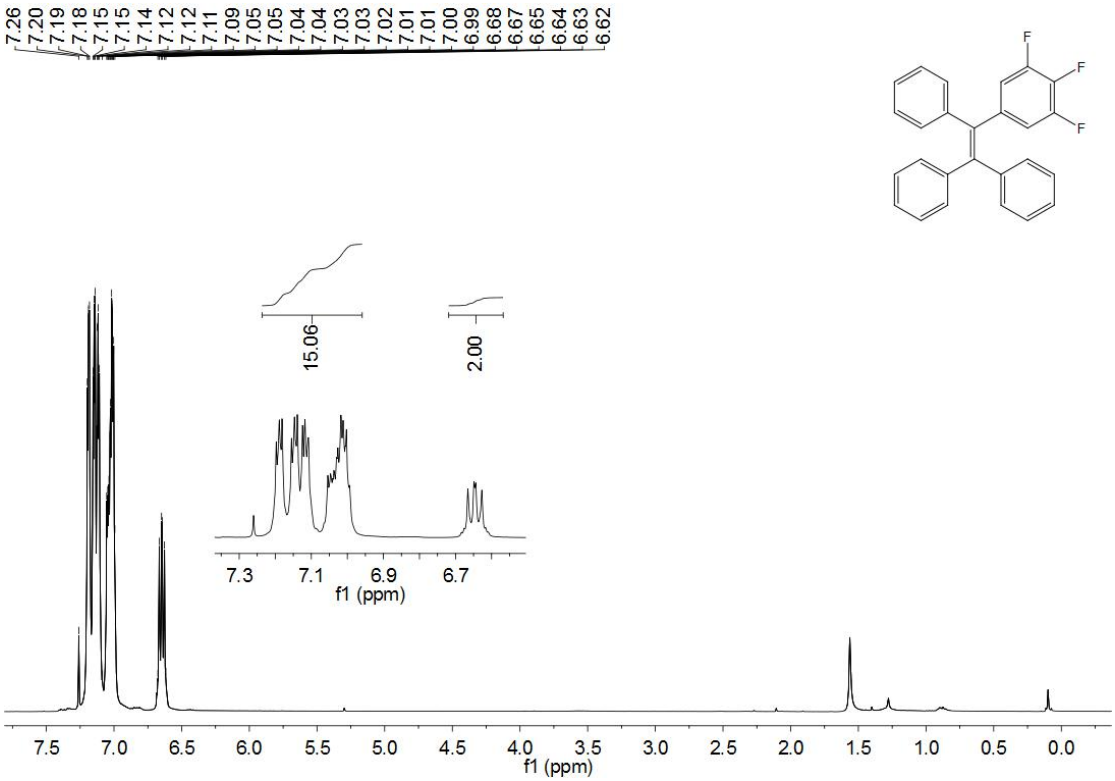


Fig. S42. ^{1}H NMR spectrum of **1k**.

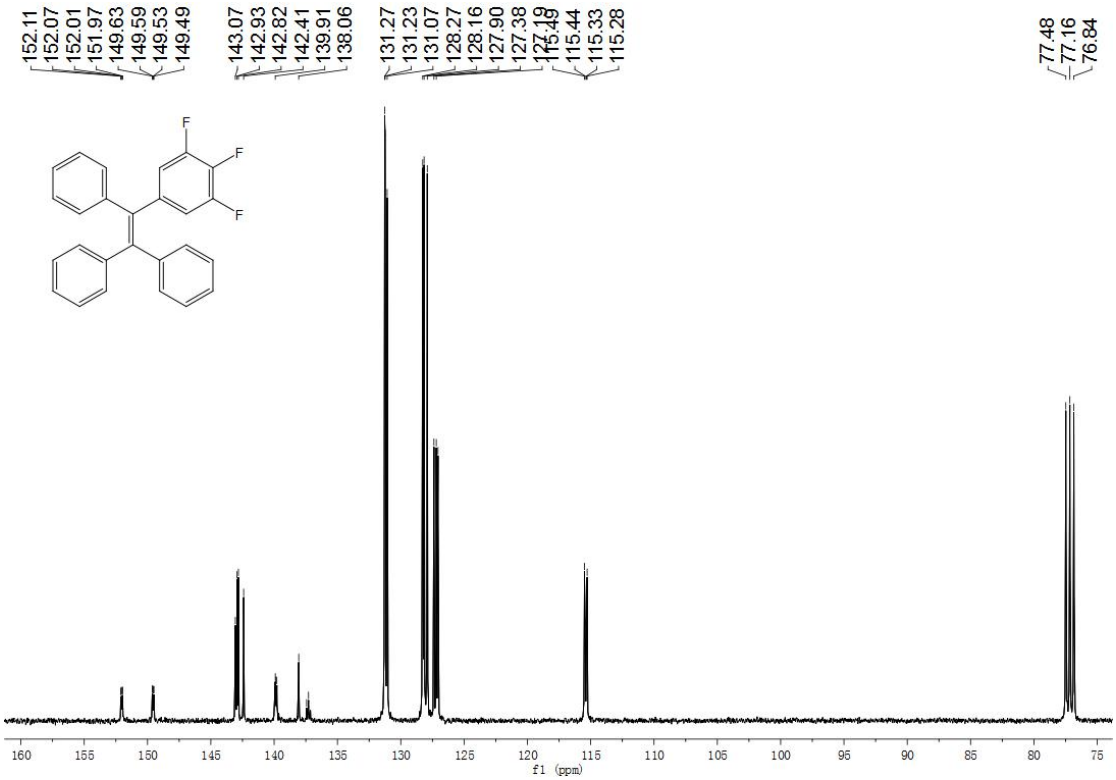


Fig. S43. ^{13}C NMR spectrum of **1k**.

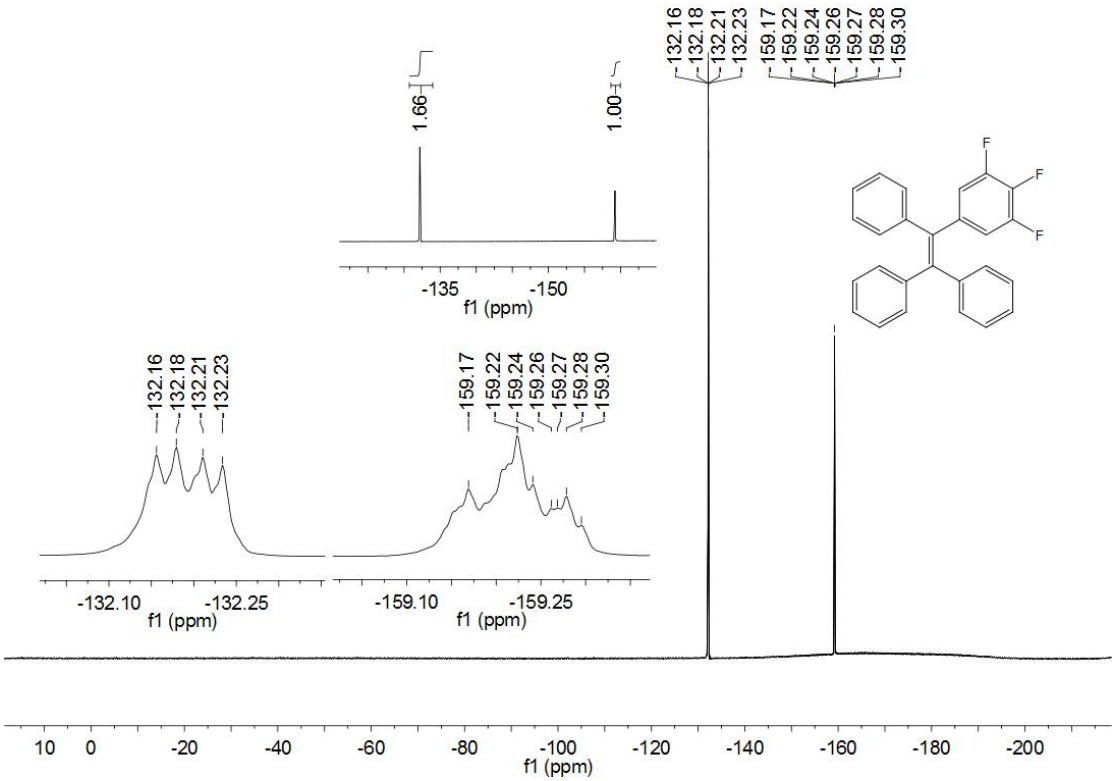


Fig. S44. ^{19}F NMR spectrum of **1k**.

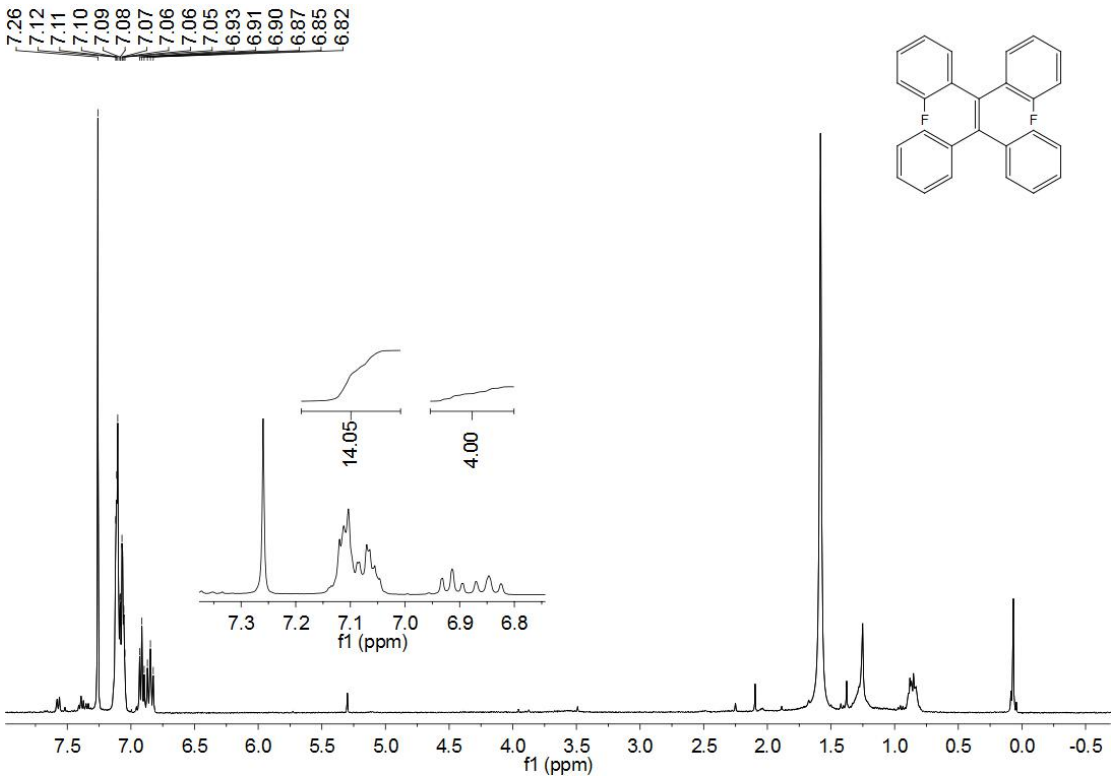


Fig. S45. ^{1}H NMR spectrum of **2a**.

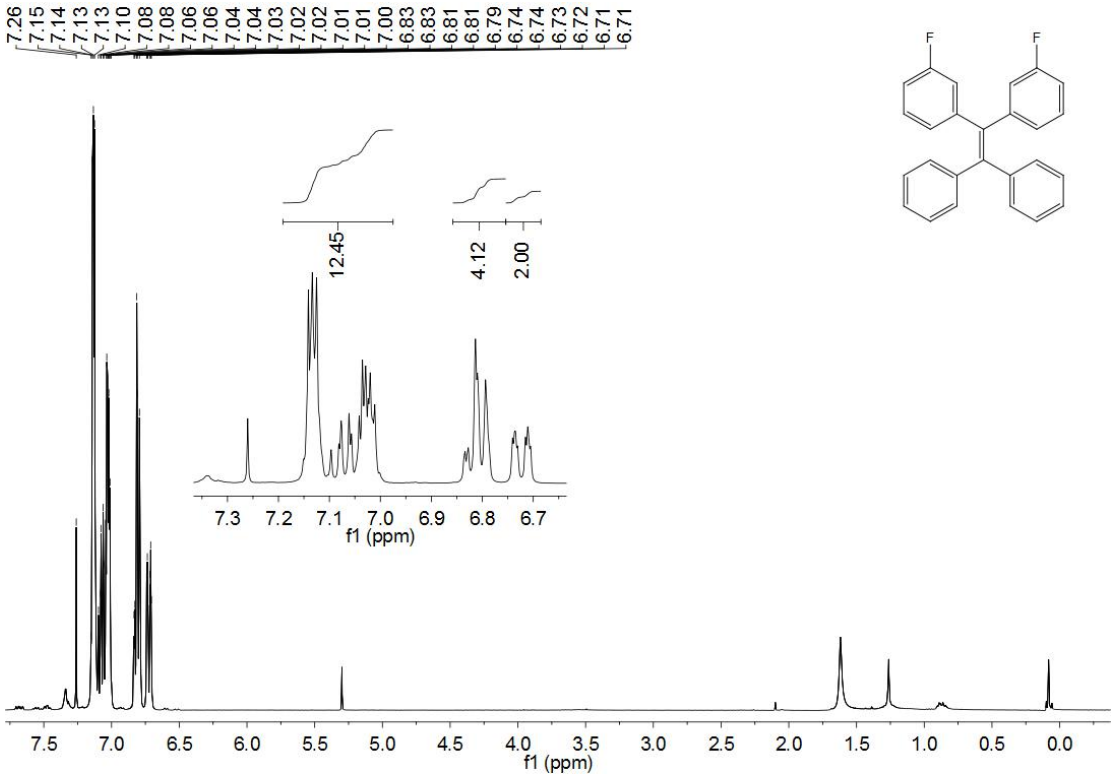


Fig. S46. ^{1}H NMR spectrum of **2b**.

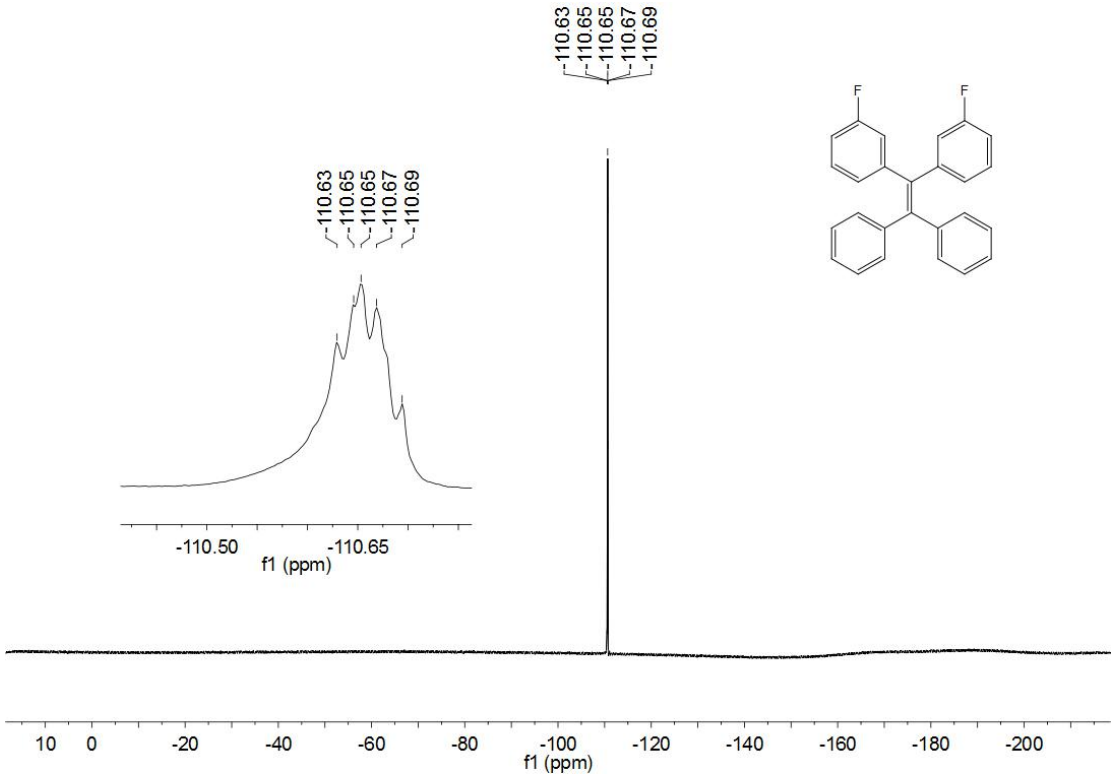


Fig. S47. ^{19}F NMR spectrum of **2b**.

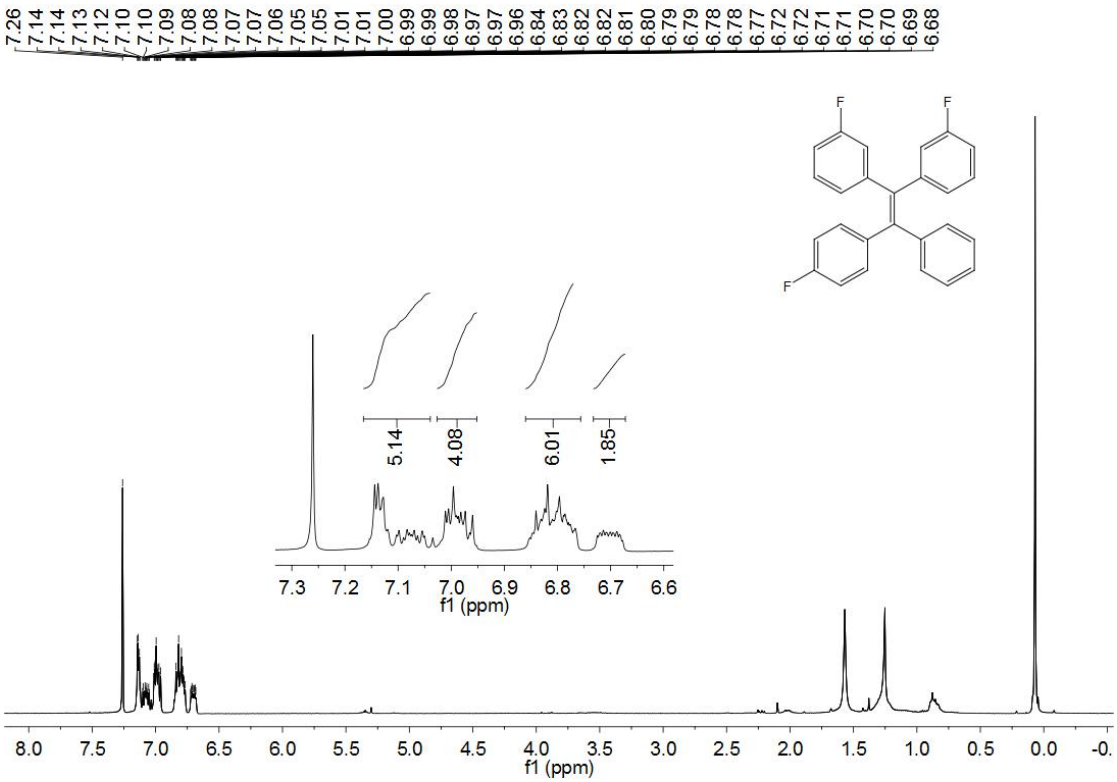


Fig. S48. ^{1}H NMR spectrum of **3a**.

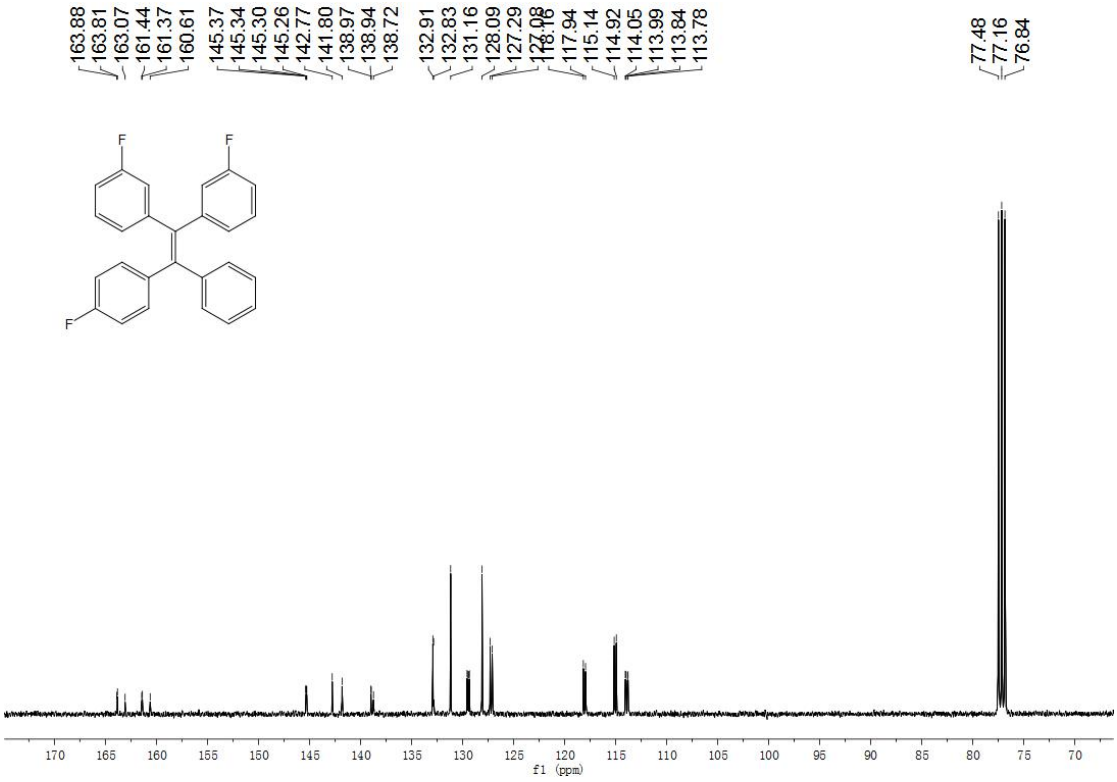


Fig. S49. ^{13}C NMR spectrum of **3a**.

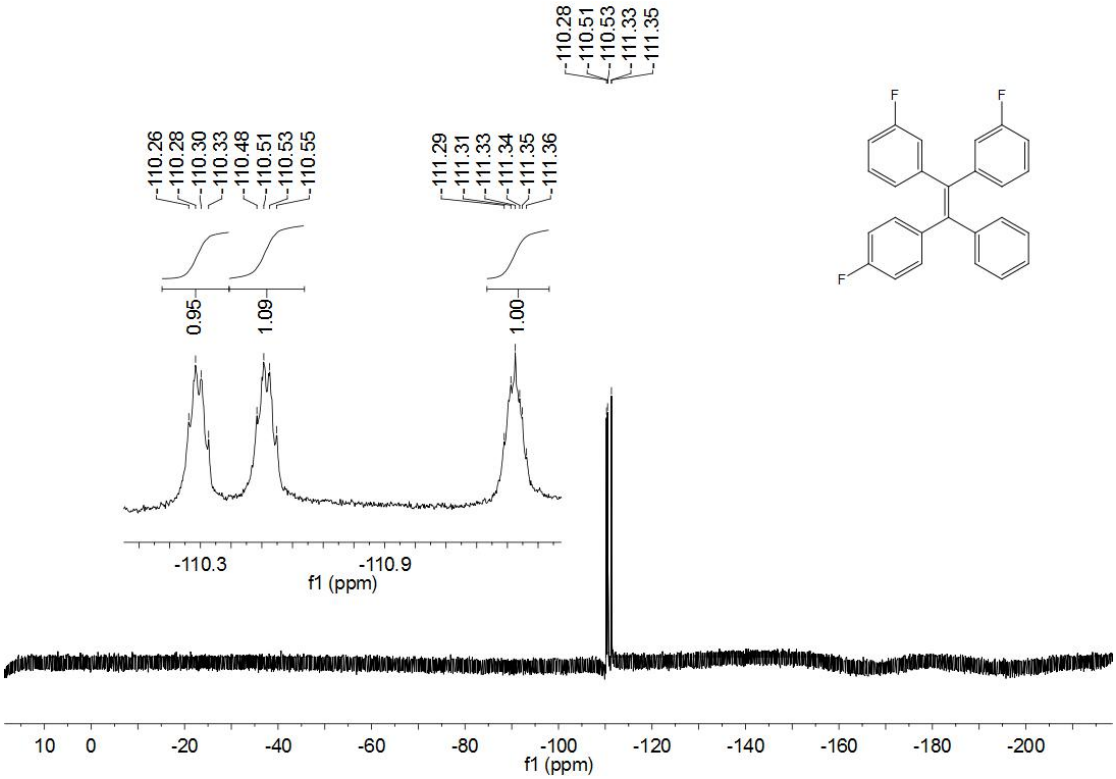


Fig. S50. ^{19}F NMR spectrum of **3a**.

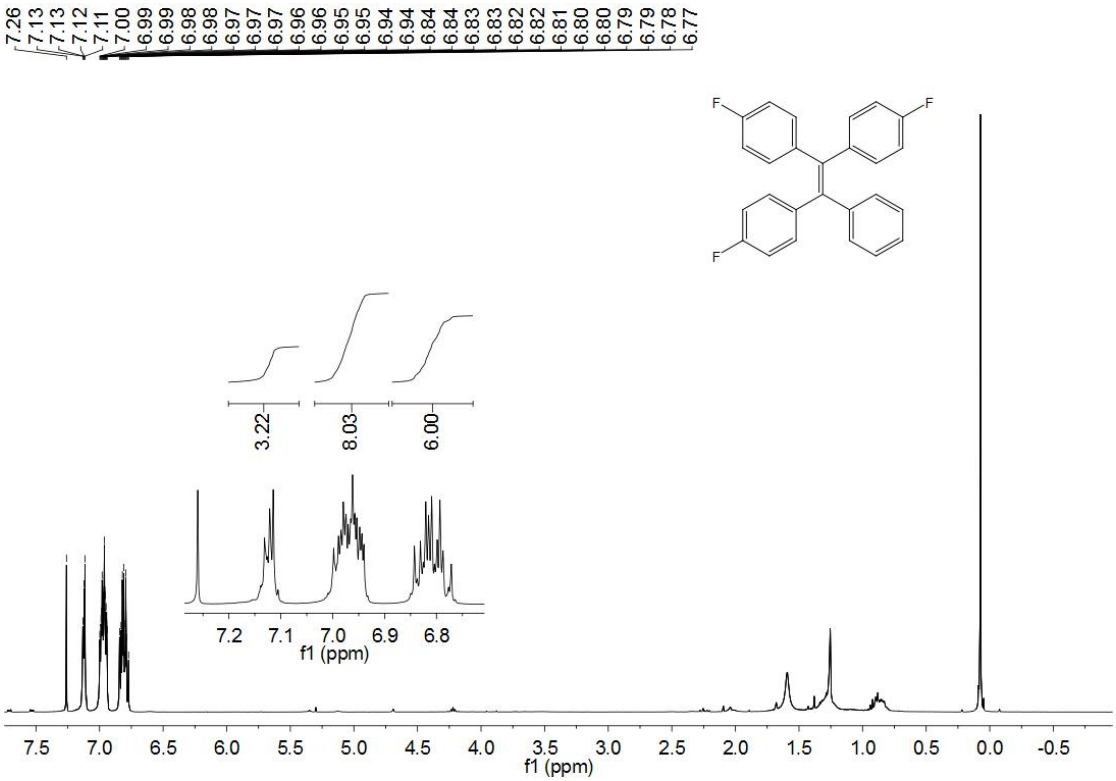


Fig. S51. ^{1}H NMR spectrum of **3b**.

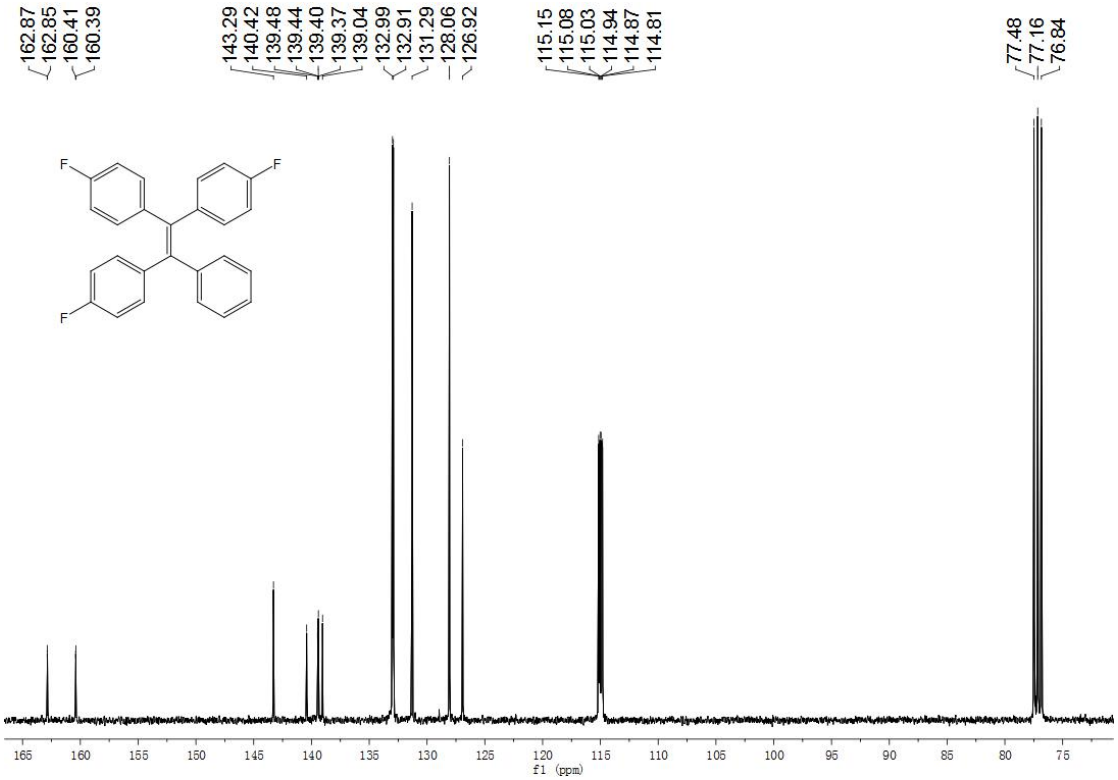


Fig. S52. ^{13}C NMR spectrum of **3b**.

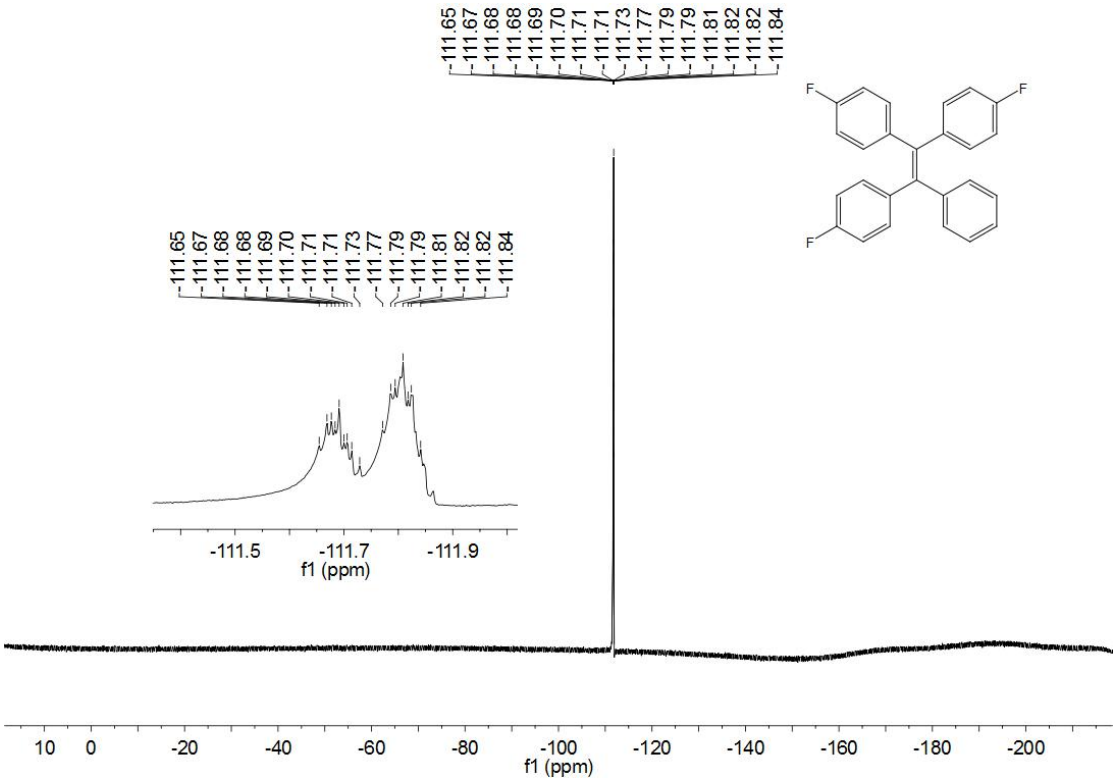


Fig. S53. ^{19}F NMR spectrum of **3b**.

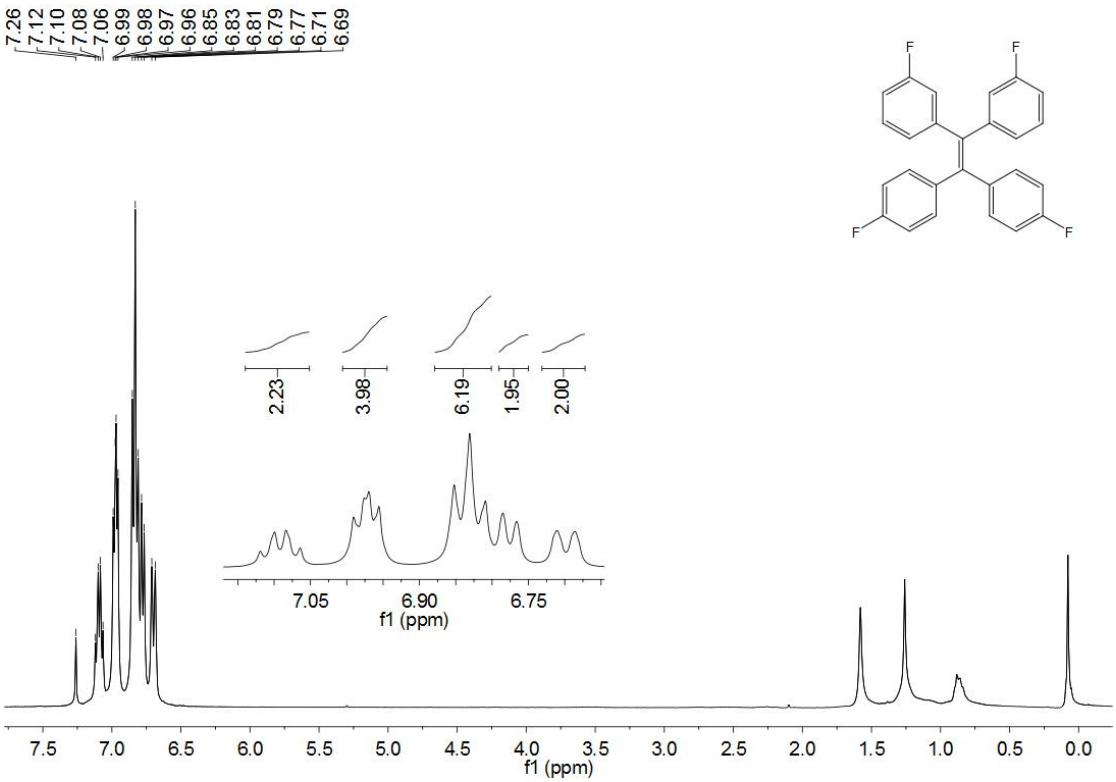


Fig. S54. ^{1}H NMR spectrum of **4a**.

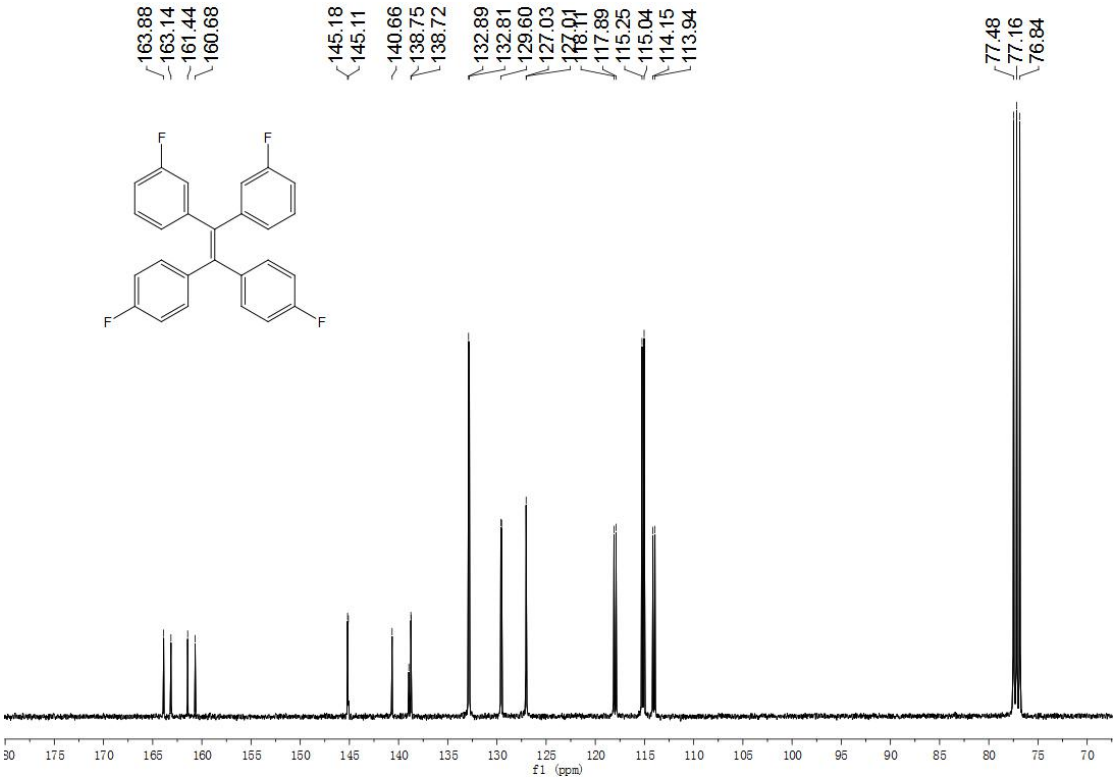


Fig. S55. ^{13}C NMR spectrum of **4a**.

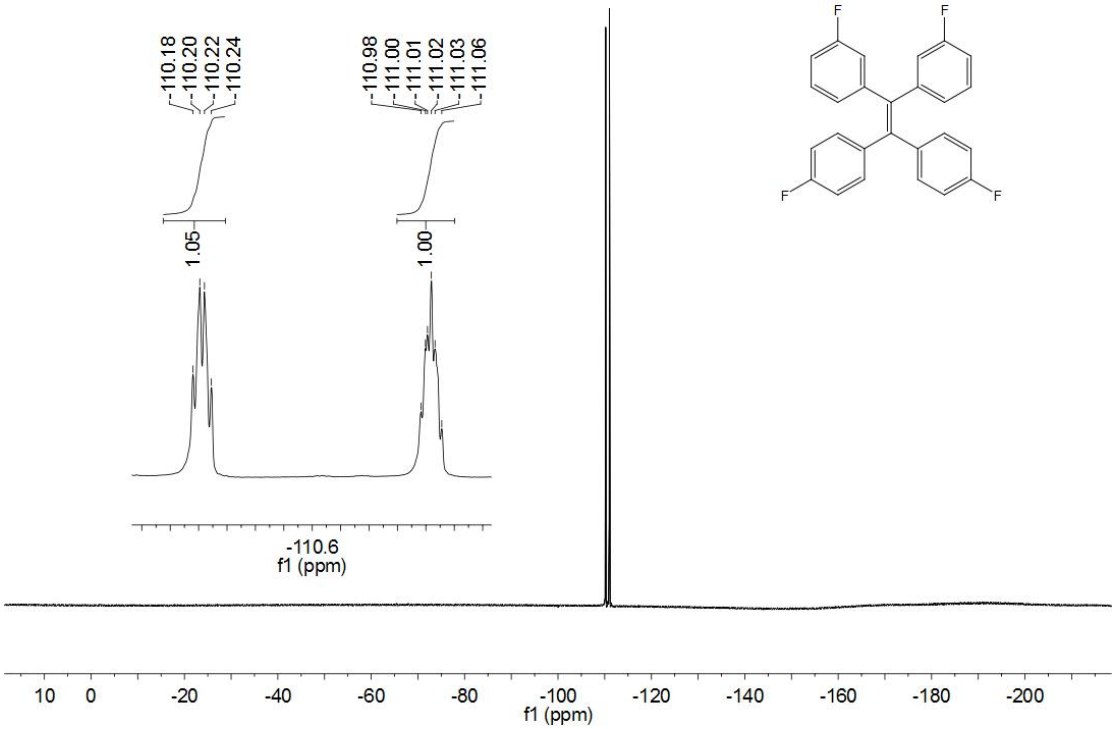
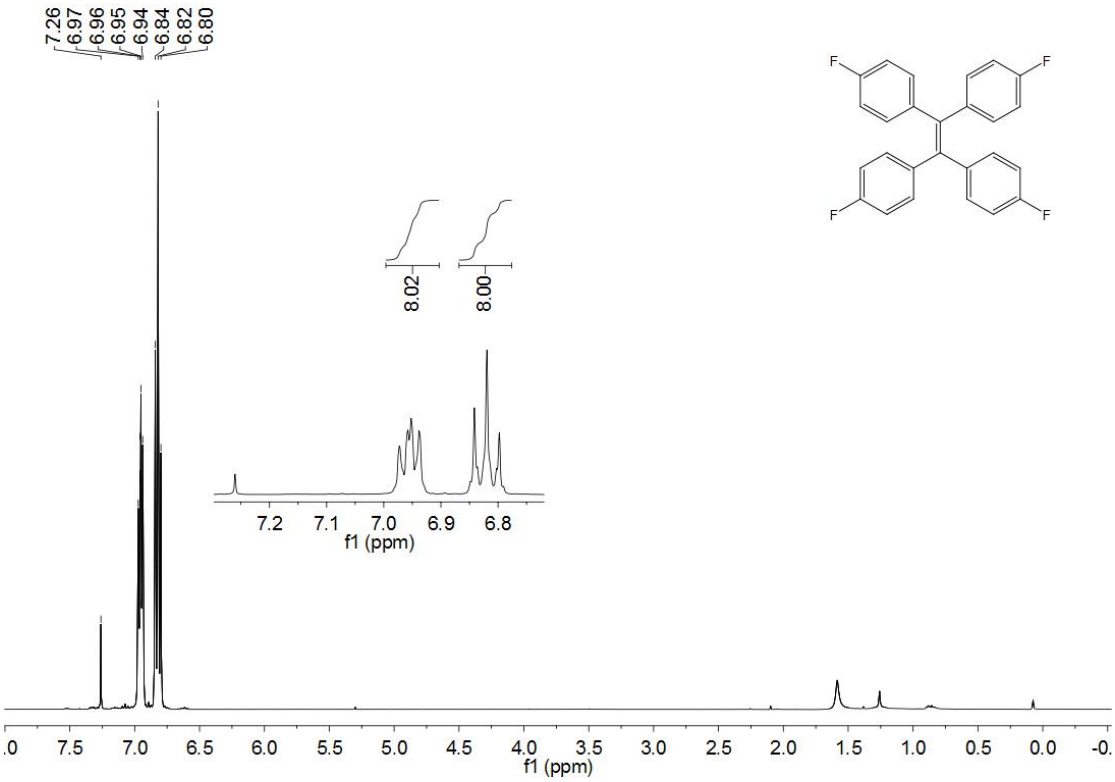


Fig. S56. ^{19}F NMR spectrum of **4a**.



. **Fig. S57.** ^{1}H NMR spectrum of **4b**.

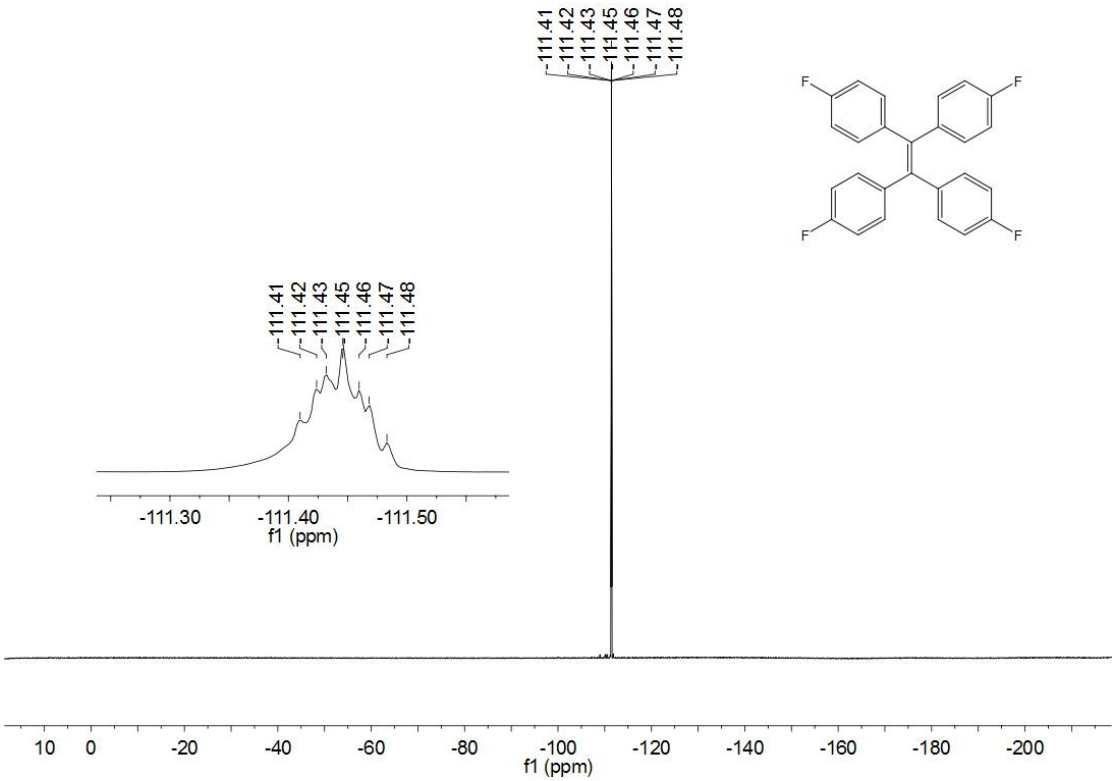


Fig. S58. ^{19}F NMR spectrum of **4b**.

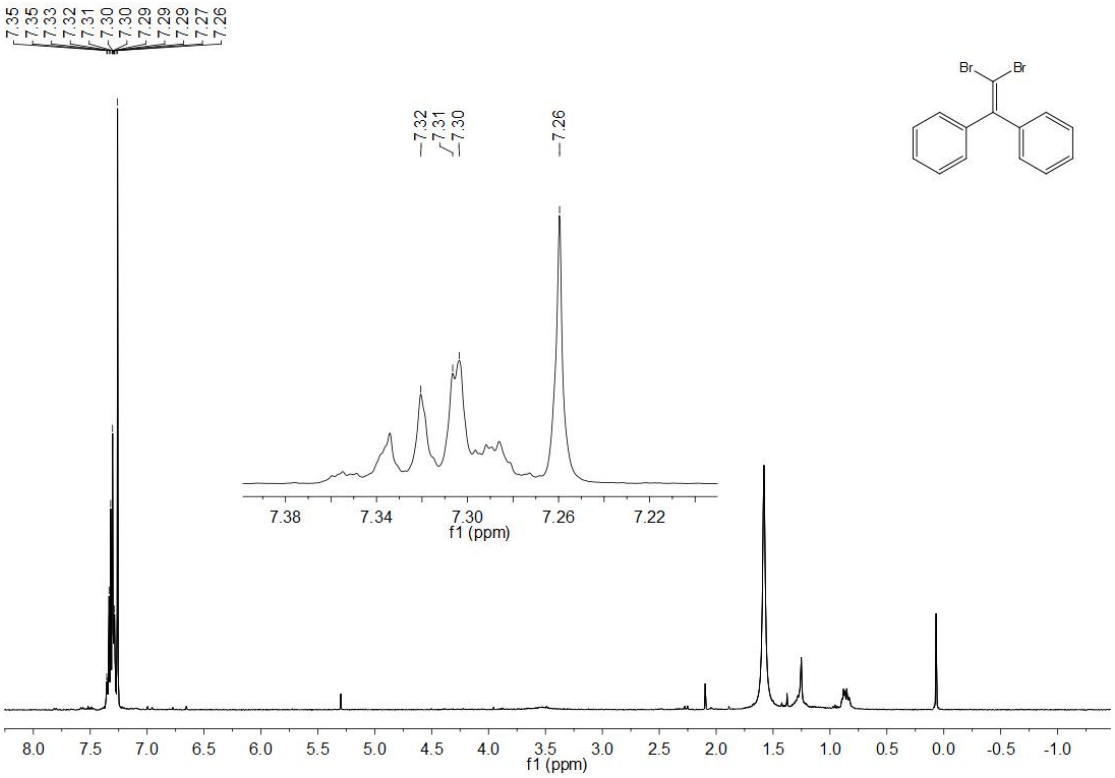


Fig. S59. ^{1}H NMR spectrum of 1,1-dibromo-2,2-diphenylethene.

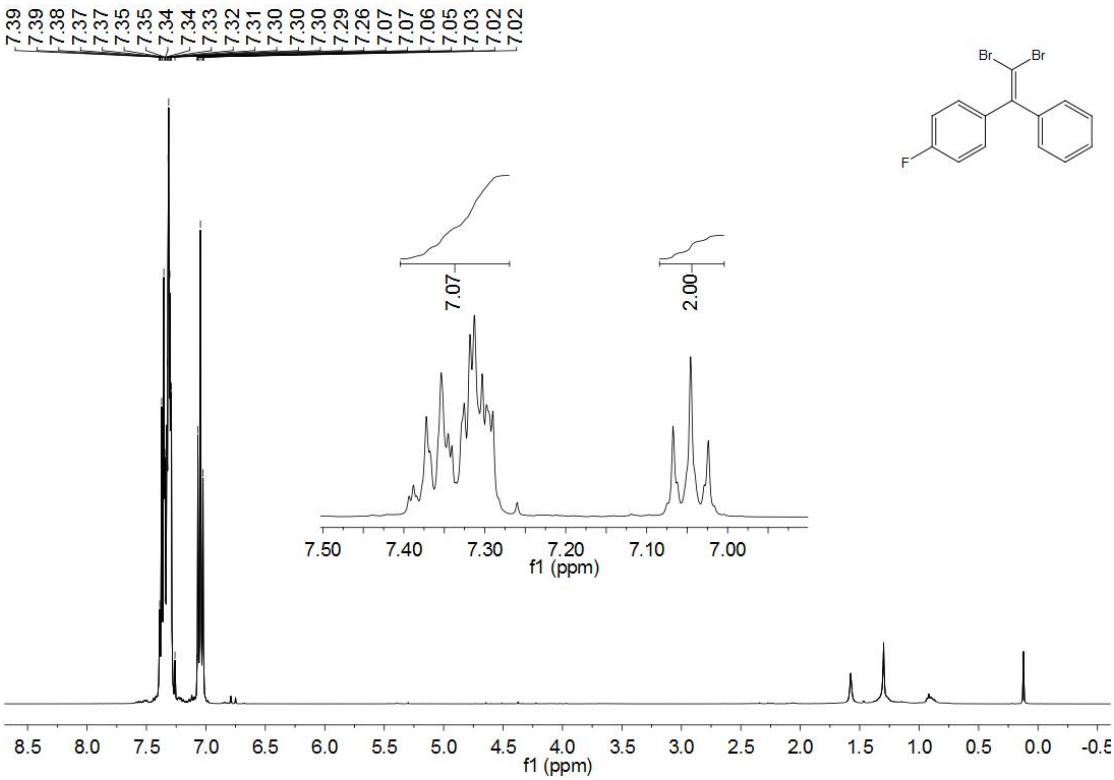


Fig. S60. ^{1}H NMR spectrum of 1,1-dibromo-2-(4-fluorophenyl)-2-phenylethene.

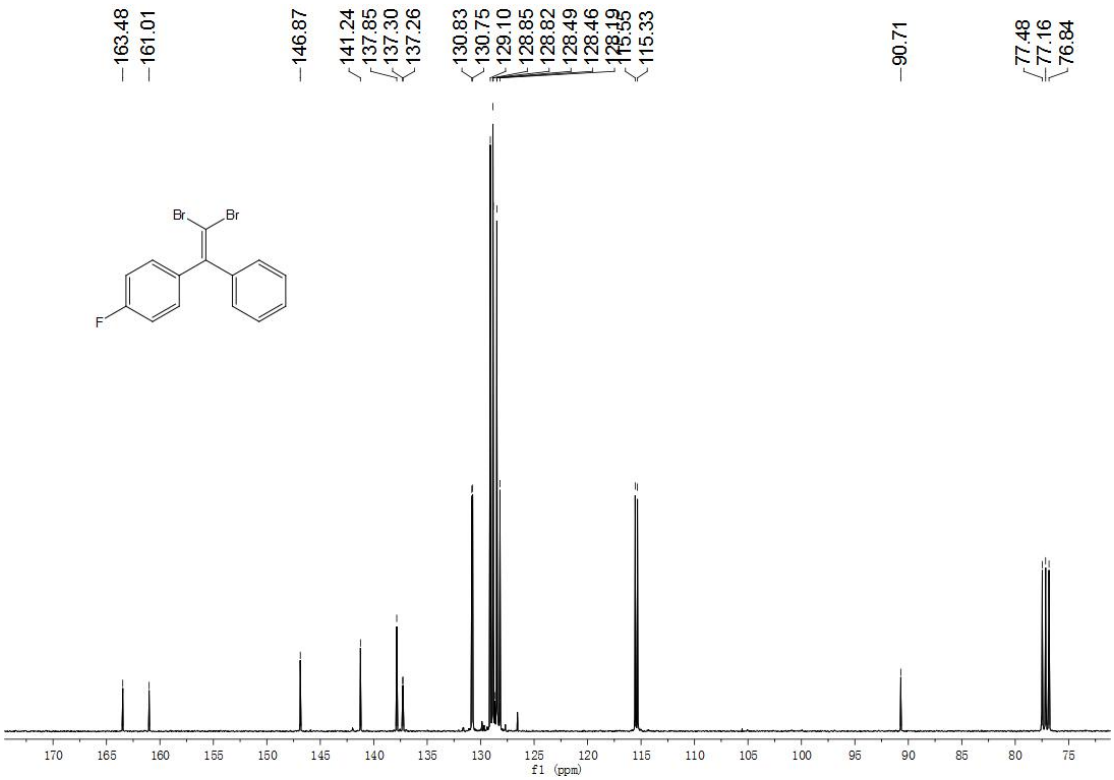


Fig. S61. ^{13}C NMR spectrum of 1,1-dibromo-2-(4-fluorophenyl)-2-phenylethene.

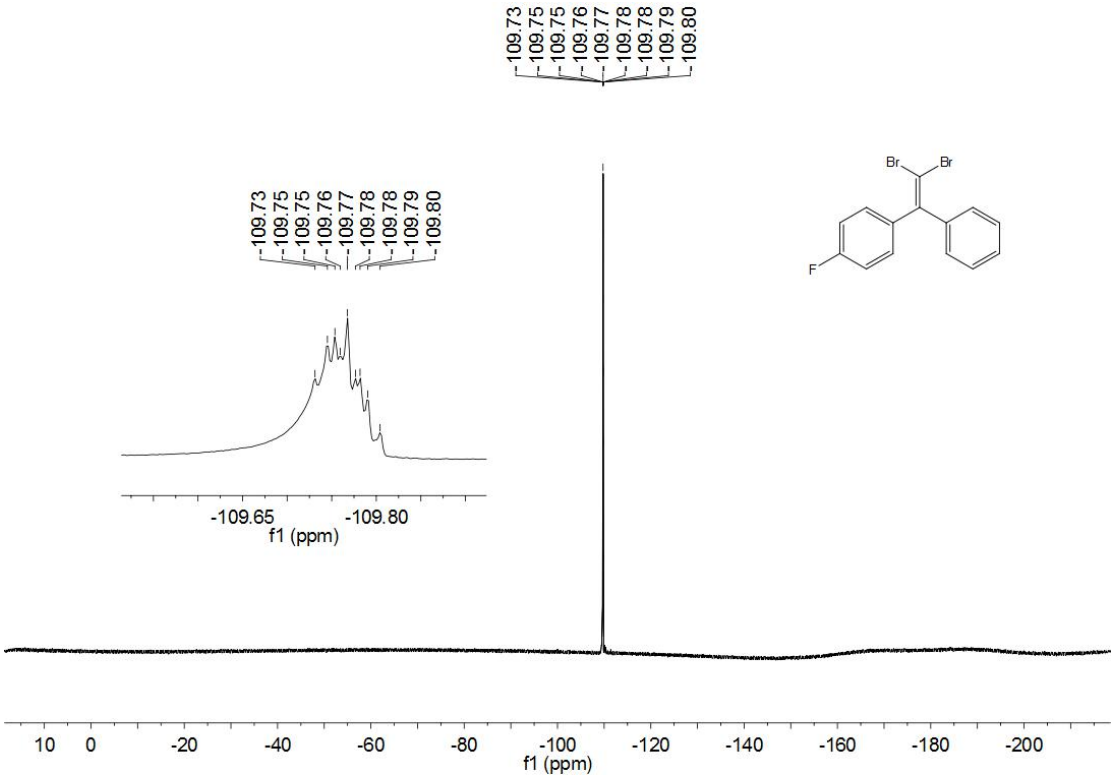


Fig. S62. ^{19}F NMR spectrum of 1,1-dibromo-2-(4-fluorophenyl)-2-phenylethene.

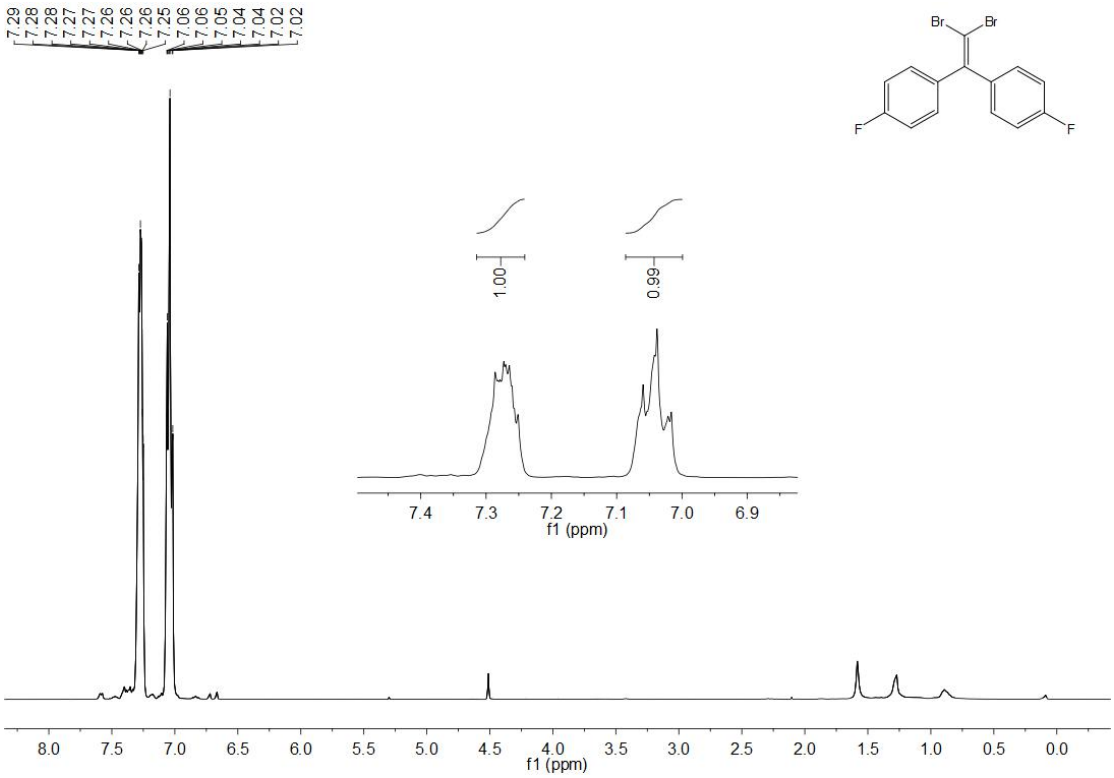


Fig. S63. ^{1}H NMR spectrum of 1,1-dibromo-2,2-bis(4-fluorophenyl)ethene.