# Rapid Synthesis of Benzofulvenes from α-Bromodiarylethylenes Based on a 1,4-Palladium Shift Strategy

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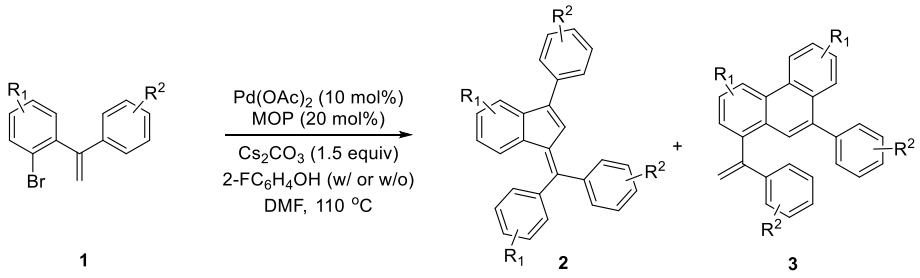
## 1. General Information

Nuclear magnetic resonances were recorded on Bruker-400 MHz, Bruker-500 MHz, or JEOL 600 MHz. Reference values for residual solvents were taken as δ = 7.26 ppm ($CDCl_3$), 2.50 ppm (DMSO-$d_6$) for $^1H$ NMR; δ = 77.00 ppm ($CDCl_3$) for $^{13}C$ NMR. High resolution mass spectra [HRMS (ESI)] was recorded on a high-resolution mass spectrometer (Waters XEVO-G2 Q-TOF). Single crystal data were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source. All reactions were performed under an inert atmosphere of dry nitrogen in flame-dried glassware, unless otherwise stated. The temperature above room temperature is heated by using oil as the medium, and the temperature also refers to the temperature of oil bath. All reagents were used as received from commercial sources. Flash column chromatography was performed using 200-300 mesh silica gel as the stationary phase. Toluene was distilled over calcium hydride under an atmosphere of nitrogen.

The synthesis of aryl bromides,[1] aryl iodides[2] and aryl trifluoromethanesulfonate[3] was according to the reported references.

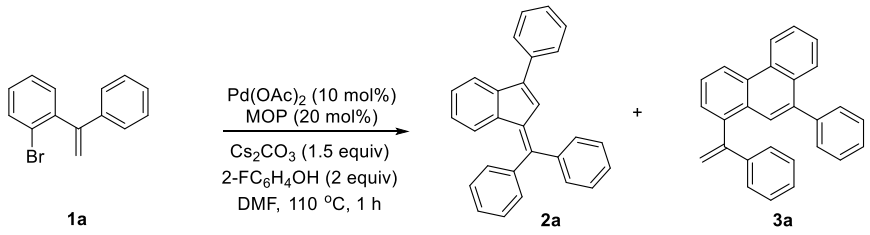
## 2. Experimental Procedure and Characteristic Data

### 2.1. General Procedure for Synthesis of Benzofulvenes (2)




To a 25-mL Schlenk tube charged with a stir bar, aryl bromides (**1**) (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), 2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenylphosphane (MOP) (18.7 mg, 0.04 mmol, 20 mol%), 2-$FC_6H_4OH$ (44.9 mg, 0.40 mmol, 2.0 equiv, if added) and dry $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) were added. After filled with nitrogen, anhydrous DMF (2 mL) were added via a syringe. The mixture was stirred at 110 °C in an oil bath for 12 h or up to completion of reaction. Upon completion, the reaction mixture was cooled to room temperature. Thereafter the mixture was quenched with brine (20 mL) and extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over anhydrous $Na_2SO_4$. After that the mixture was filtered, and the filtrate was concentrated under reduced pressure. The crude products were purified by silica gel chromatography to afford products (**2**) and (**3**).

**1-(Diphenylmethylene)-3-phenyl-1*H*-indene (2a)**



The reaction of 1-bromo-2-(1'-phenylvinyl)benzene (51.8 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1 hour afforded **2a** (33.2 mg, 93%) as a light orange solid and a trace amount of **3a**, eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

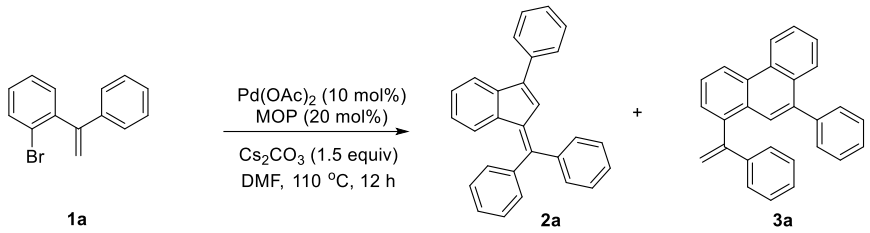
Data of **2a**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.72 – 7.64 (m, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.41 (m, 7H), 7.41 – 7.34 (m, 6H), 7.24 – 7.17 (m, 1H), 7.00 – 6.90 (m, 1H), 6.78 (s, 1H), 6.71 (d, *J* = 7.5 Hz, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.7, 144.3, 142.8, 142.4, 141.6, 138.0, 137.2, 135.8, 131.6, 130.4, 128.6, 128.5, 128.1, 127.9, 127.8, 127.7, 126.9, 124.9, 123.8, 120.1.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{21}^+$ 357.1638; Found 357.1637.

**4.50 mmol scale reaction for the preparation of 9-phenyl-1-(1-phenylvinyl)phenanthrene (3a)**



1a 2a 3a

The reaction of 1-bromo-2-(1'-phenylvinyl)benzene (1.17 g, 4.50 mmol, 1.0 equiv), $Pd(OAc)_2$ (101 mg, 0.45 mmol, 10 mol%), MOP (421 mg, 0.90 mmol, 20 mol%) and $Cs_2CO_3$ (2.20 g, 6.75 mmol, 1.5 equiv) afforded **2a** (650 mg, 81%) as a light orange solid and **3a** (25.3 mg, 3%) as a colorless liquid, eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

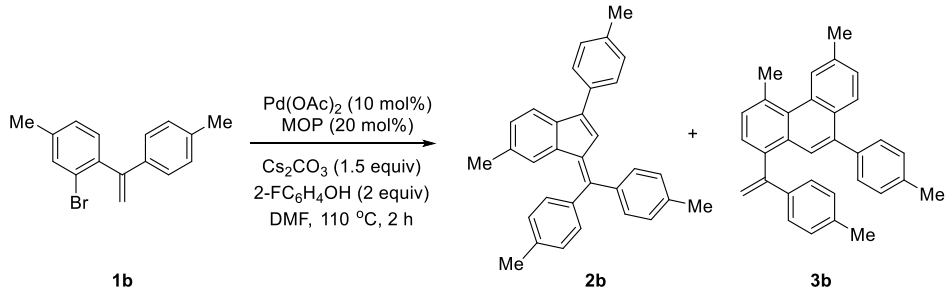
Data of **3a**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.5 Hz, 1H), 8.78 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.65 (m, 3H), 7.64 – 7.51 (m, 2H), 7.47 – 7.37 (m, 3H), 7.35 – 7.30 (m, 4H), 7.31 – 7.25 (m, 3H), 6.01 (d, *J* = 1.0 Hz, 1H), 5.45 (d, *J* = 1.0 Hz, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 148.2, 141.1, 140.8, 140.6, 138.3, 130.73, 130.66, 130.2, 130.0, 129.8, 128.33, 128.29, 128.2, 127.7, 127.2, 126.8, 126.54, 126.46, 126.1, 125.8, 123.1, 122.2, 116.3.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{21}^+$ 357.1638; Found 357.1640.

**1-(Di-*p*-tolylmethylene)-6-methyl-3-(*p*-tolyl)-1*H*-indene (2b)**



1b 2b 3b

The reaction of 2-bromo-4-methyl-1-(1'-(*p*-tolyl)vinyl)benzene (57.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 2 hours afforded **2b** (35.1 mg, 86%) as a light orange solid and a trace amount of **3b**, eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

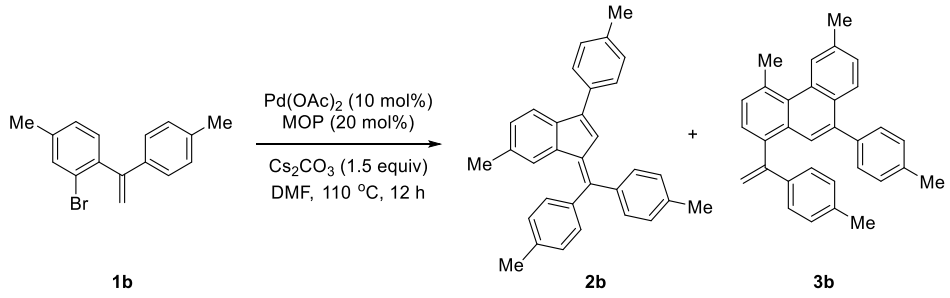
Data of **2b**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.22 (m, 6H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 6.58 (s, 1H), 2.47 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H), 2.16 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.2, 143.4, 140.3, 140.0, 138.9, 138.3, 138.0, 137.7, 137.6, 137.4, 134.2, 133.2, 131.7, 130.7, 129.2, 129.1, 128.5, 127.5, 127.3, 127.0, 124.6, 119.7, 21.6, 21.4, 21.31, 21.29.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}^+$ 413.2264; Found 413.2271.

**0.80 mmol scale reaction for the preparation of 3,6-dimethyl-9-(*p*-tolyl)-1-(1'-(*p*-tolyl)vinyl)phenanthrene (3b)**




The reaction of 2-bromo-4-methyl-1-(1'-(*p*-tolyl)vinyl)benzene (229.6 mg, 0.80 mmol, 1.0 equiv), $Pd(OAc)_2$ (18 mg, 0.08 mmol, 10 mol%), MOP (75 mg, 0.16 mmol, 20 mol%) and $Cs_2CO_3$ (391 mg, 1.20 mmol, 1.5 equiv) afforded **2b** (91.1 mg, 55%) as an orange solid and **3b** (19.8 mg, 12%) as a colorless liquid, eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

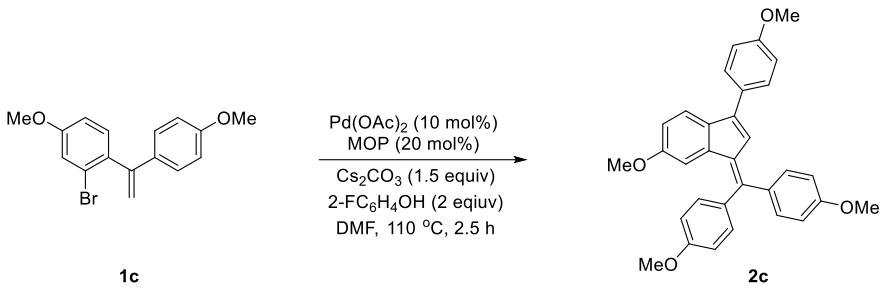
Data of **3b**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.34 (m, 1H), 7.23 – 7.20 (m, 6H), 7.06 (d, *J* = 8.5 Hz, 2H), 5.94 (d, *J* = 1.0 Hz, 1H), 5.35 (d, *J* = 1.0 Hz, 1H), 3.20 (s, 3H), 2.63 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 148.5, 138.8, 138.5, 138.0, 137.6, 137.3, 136.7, 134.50, 134.49, 132.1, 131.5, 130.3, 130.0, 129.8, 128.9, 128.8, 127.9, 127.4, 127.3, 126.7, 126.4, 125.6, 115.4, 27.2, 22.2, 21.2, 21.1.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}^+$ 413.2264; Found 413.2267.

**1-(Bis(4'-methoxyphenyl)methylene)-6-methoxy-3-(4''-methoxyphenyl)-1*H*-indene (2c)**




**1c** **2c**

The reaction of 2-bromo-4-methoxy-1-(1'-(4'-methoxyphenyl)vinyl)benzene (63.8 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 2.5 hours afforded **2c** (35.3 mg, 74%) as an orange solid (chemoselectivity >20:1), eluent: petroleum ether/ethyl acetate = 50:1 to 20:1.

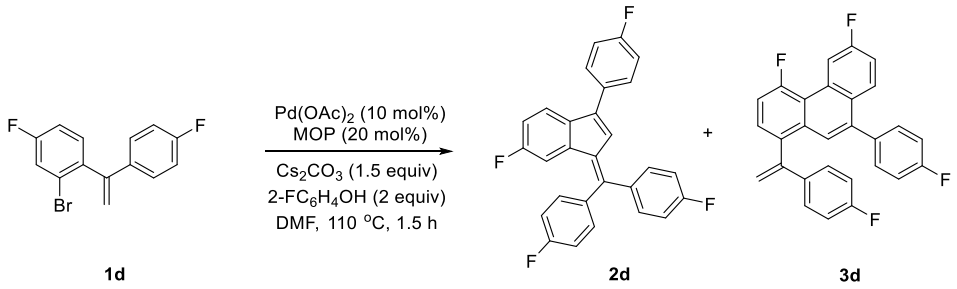
Data of **2c**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.26 (m, 4H), 6.97 (dd, *J* = 6.0, 2.5 Hz, 4H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.75 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.63 (s, 1H), 6.41 (d, *J* = 2.5 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 6H), 3.56 (s, 3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 160.0, 159.7, 159.1, 157.5, 145.4, 142.6, 139.3, 136.8, 135.9, 135.2, 134.1, 133.3, 132.2, 128.8, 128.7, 125.5, 120.3, 113.94, 113.89, 113.3, 112.2, 109.7, 55.4, 55.3, 55.2, 55.1.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}O_4^+$ 477.2060; Found 477.2061.

**1-(Bis(4'-fluorophenyl)methylene)-6-fluoro-3-(4''-fluorophenyl)-1*H*-indene (2d)**




**1d** **2d** **3d**

The reaction of 2-bromo-4-fluoro-1-(1'-(4'-fluorophenyl)vinyl)benzene (59.0 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1.5 hours afforded **2d** (30.6 mg, 71%) as an orange solid (chemoselectivity >20:1), eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

Data of **2d**:

**$^1$H NMR** (500 MHz, DMSO-*d*$_6$) δ 7.74 – 7.69 (m, 2H), 7.53 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.45 – 7.36 (m, 6H), 7.34 – 7.27 (m, 4H), 7.09 (td, *J* = 6.5, 2.5 Hz, 1H), 6.71 (s, 1H), 6.11 (dd, *J* = 8.0, 2.5 Hz, 1H).

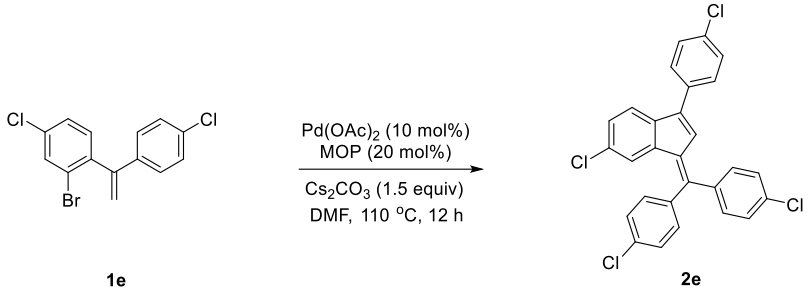
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, $^1J_{C–F}$ = 251.5 Hz), 162.9 (d, $^1J_{C–F}$ = 251.5 Hz), 162.5 (d, $^1J_{C–F}$ = 248.5 Hz), 161.3 (d, $^1J_{C–F}$ = 243.4 Hz), 145.2, 143.1, 138.8 (d, $^3J_{C–F}$ = 9.1 Hz), 138.6 (d, $^4J_{C–F}$ = 2.0

Hz), 137.9 (d, $^4J_{C-F}$ = 3.0 Hz), 137.4 (d, $^4J_{C-F}$ = 2.0 Hz), 136.7 (d, $^4J_{C-F}$ = 3.0 Hz), 133.3 (d, $^3J_{C-F}$ = 9.1 Hz), 132.4 (d, $^3J_{C-F}$ = 8.1 Hz), 131.4 (d, $^4J_{C-F}$ = 3.0 Hz), 129.2 (d, $^3J_{C-F}$ = 8.1 Hz), 127.0 (d, $^4J_{C-F}$ = 3.0 Hz), 120.5 (d, $^3J_{C-F}$ = 9.1 Hz), 116.0 (d, $^2J_{C-F}$ = 21.2 Hz), 115.7 (d, $^2J_{C-F}$ = 21.2 Hz), 115.2 (d, $^2J_{C-F}$ = 22.2 Hz), 113.6 (d, $^2J_{C-F}$ = 23.2 Hz), 111.2 (d, $^2J_{C-F}$ = 25.3 Hz).

**$^{19}$F NMR** (471 MHz, DMSO-*d*$_6$) δ -112.0, -112.3, -113.2, -117.0.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{17}F_4^+$ 429.1261; Found 429.1211.

**1.0 mmol scale reaction for the preparation of 1-(bis(4'-chlorophenyl)methylene)-6-chloro-3-(4''-chlorophenyl)-1*H*-indene (2e)**




**1e** **2e**

The reaction of 2-bromo-4-chloro-1-(1'-(4'-chlorophenyl)vinyl)benzene (328 mg, 1.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol, 10 mol%), MOP (93 mg, 0.20 mmol, 20 mol%) and $Cs_2CO_3$ (488 mg, 1.50 mmol, 1.5 equiv) afforded **2e** (130.9 mg, 53%) as an orange solid (chemoselectivity >20:1), eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

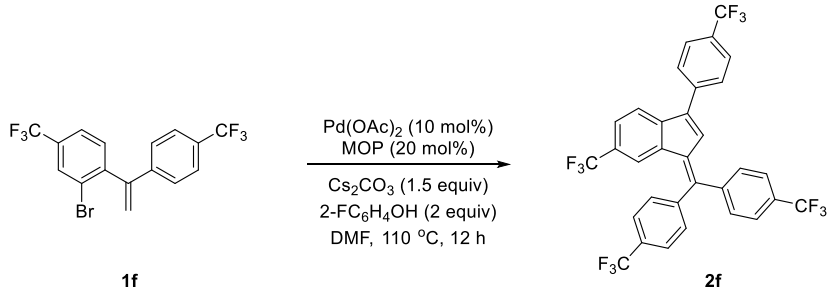
Data of **2e**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.35 (m, 5H), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 2H), 7.19 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.73 (d, *J* = 1.5 Hz, 1H), 6.64 (s, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.6, 143.1, 140.7, 135.1, 133.9, 128.8, 128.7, 128.5, 127.8, 127.4, 122.5, 121.9.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{17}Cl_4^+$ 495.0049; Found 495.0011.

**0.50 mmol scale reaction for the preparation of 1-(Bis(4'-(trifluoromethyl)phenyl)methylene)-6-(trifluoromethyl)-3-(4''-(trifluoromethyl)phenyl)-1*H*-indene (2f)**




**1f** **2f**

The reaction of 2-bromo-4-(trifluoromethyl)-1-(1'-(4'-(trifluoromethyl)phenyl)vinyl)benzene (197.5 mg, 0.50 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 10 mol%), MOP (46.8 mg, 0.10 mmol, 20

mol%), 2-fluorophenol (56 mg, 0.50 mmol, 1 equiv) and $Cs_2CO_3$ (224 mg, 0.75 mmol, 1.5 equiv) in 12 hours afforded **2f** (86.9 mg, 55%) as an orange solid (chemoselectivity >20:1), eluent: petroleum ether/dichloromethane = 50:1 to 30:1.

Data of **2f**:

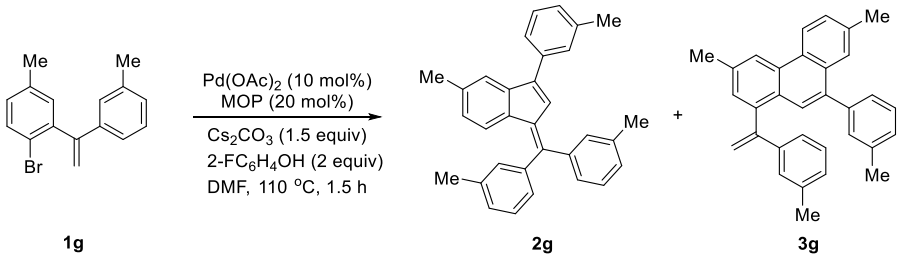
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.75 – 7.67 (m, 6H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.52 - 7.45 (m, 3H), 6.86 (s, 1H), 6.77 (s, 1H).

**$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 145.7, 145.2, 144.3, 144.2, 143.5, 138.8, 138.1, 136.5, 131.66 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 131.65, 131.0 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 130.7, 130.5 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 130.0, 127.9, 127.7 (q, $^2J_{C\text{-}F}$ = 31.7 Hz), 126.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 125.9 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 125.4 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 125.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 123.9 (q, $^1J_{C\text{-}F}$ = 273.3 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 273.3 Hz), 120.69, 120.67, 120.2.

**$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -61.30, -61.34, -61.8, -62.2, -62.3, -62.45, -62.56, -62.61, -62.7, -62.8, -62.9, -63.07, -63.12, -63.2.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{17}F_{12}^+$ 629.1134; Found 629.1197.

**1-(Di-*m*-tolylmethylene)-5-methyl-3-(*m*-tolyl)-1*H*-indene (2g)**




The reaction of 1-bromo-4-methyl-2-(1'-(*m*-tolyl)vinyl)benzene (57.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1.5 hours afforded **2g** (36.1 mg, 88%) as an orange solid (chemoselectivity >20:1), eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

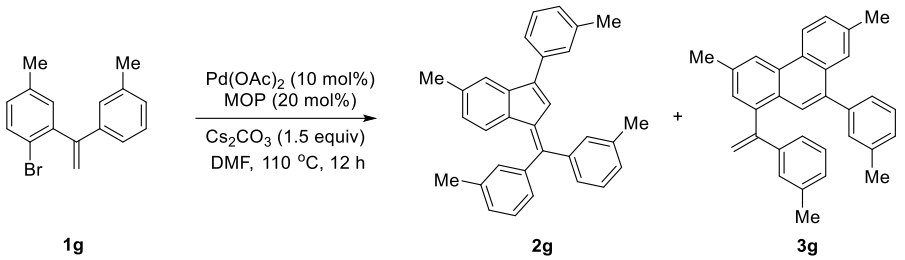
Data of **2g**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.38 – 7.30 (m, 3H), 7.29 – 7.26 (m, 2H), 7.22 – 7.12 (m, 6H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 146.1, 144.0, 143.2, 142.5, 141.7, 138.13, 138.09, 137.8, 137.4, 136.7, 136.0, 134.6, 131.9, 130.8, 129.0, 128.7, 128.5, 128.4, 128.3, 128.1, 127.7, 127.4, 125.5, 124.8, 123.5, 120.8, 21.7, 21.53, 21.45, 21.4.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}^+$ 413.2264; Found 413.2270.

**1.40 mmol scale reaction for the preparation of 3,7-dimethyl-9-(*m*-tolyl)-1-(1'-(*m*-tolyl)vinyl)phenanthrene (3g)**




The reaction of 1-bromo-4-methyl-2-(1'-(*m*-tolyl)vinyl)benzene (401 mg, 1.40 mmol, 1.0 equiv), $Pd(OAc)_2$ (31.4 mg, 0.14 mmol, 10 mol%), MOP (131.2 mg, 0.28 mmol, 20 mol%) and $Cs_2CO_3$ (684 mg, 2.10 mmol, 1.5 equiv) afforded **2g** (185.4 mg, 64%) as an orange solid and **3g** (8.1 mg, 3%) as a colorless liquid, eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

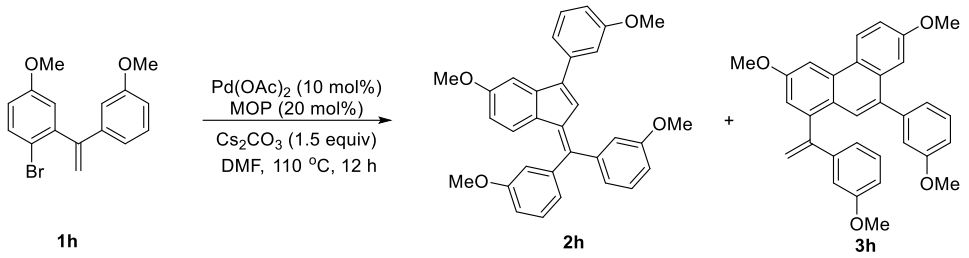
Data of **3g**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.5 Hz, 1H), 8.49 (s, 1H), 7.69 (s, 1H), 7.60 (s, 1H), 7.48 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.36 (d, *J* = 1.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.12 (m, 3H), 7.10 – 7.05 (m, 3H), 5.93 (d, *J* = 1.5 Hz, 1H), 5.38 (d, *J* = 1.5 Hz, 1H), 2.64 (s, 3H), 2.46 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 148.5, 141.4, 141.1, 140.5, 137.80, 137.78, 137.0, 136.1, 135.5, 130.9, 130.8, 130.3, 129.4, 128.34, 128.27, 128.2, 127.90, 127.87, 127.7, 127.5, 127.4, 127.2, 126.2, 125.9, 124.2, 123.0, 121.7, 116.0, 22.1, 21.7, 21.5, 21.4.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}^+$ 413.2264; Found 413.2284.

**1-(Bis(4'-methoxyphenyl)methylene)-6-methoxy-3-(4''-methoxyphenyl)-1*H*-indene (2h)**



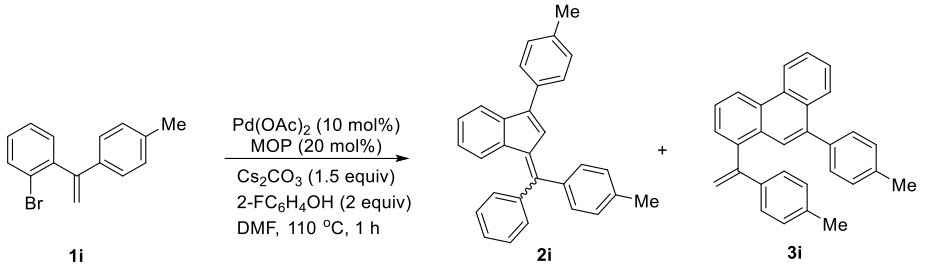

The reaction of 1-bromo-4-methoxy-2-(1'-(3'-methoxyphenyl)vinyl)benzene (63.8 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) afforded **2h** (31.6 mg, 66%) as an orange solid and a trace amount of **3h**, eluent: petroleum ether/ethyl acetate = 50:1 to 20:1.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.31 – 7.27 (m, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.16 (bs, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.97 – 6.88 (m, 5H), 6.79 (s, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.50 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.71, 159.65, 159.3, 159.0, 144.5, 143.8, 143.5, 142.8, 137.5, 137.1, 129.8, 129.6, 129.0, 128.8, 124.8, 124.0, 122.7, 120.2, 117.0, 115.3, 114.3, 113.4, 113.3, 113.2, 110.0, 106.4, 55.5, 55.34, 55.28, 55.26.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}O_4^+$ 477.2060; Found 477.2059.

**1-(Phenyl(*p*-tolyl)methylene)-3-(*p*-tolyl)-1*H*-indene (2i)**




The reaction of 1-bromo-2-(1'-(*p*-tolyl)vinyl)benzene (54.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1 hour afforded **2i** (31.1 mg, 81%) as a mixture of *E*- and *Z*-isomers, 6:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

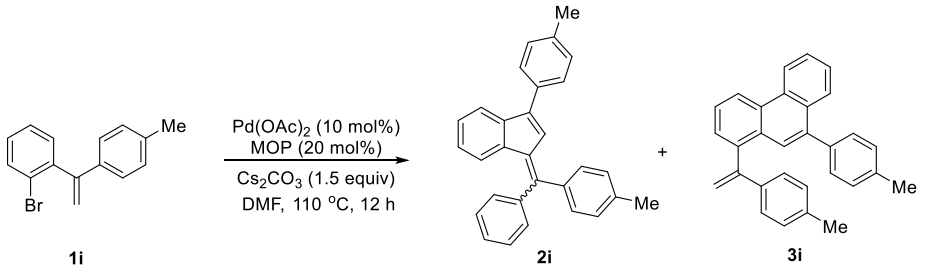
Data of **2i**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 3.5H), 7.47 – 7.43 (m, 2.6H), 7.42 – 7.38 (m, 2H),7.38 – 7.33 (m, 1H), 7.30 (d, *J* = 7.5 Hz, 0.5H), 7.24 (s, 2H), 7.20 – 7.16 (m, 3H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 0.2H), 6.79 (s, 1H), 6.73 (s, 0.2H), 6.66 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 0.5H), 2.41 (s, 3H), 2.40 (s, 2.5H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.4, 143.9, 142.8, 141.8, 139.6, 138.2, 137.7, 137.6, 137.3, 133.0, 131.7, 130.52, 130.49, 129.2, 128.6, 128.5, 128.4, 127.8, 127.6, 127.5, 126.7, 124.7, 123.72, 123.66, 120.0, 21.33, 21.30.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}^+$ 385.1951; Found 385.1948.

**1.0 mmol scale reaction for the preparation of 9-(*p*-tolyl)-1-(1'-(*p*-tolyl)vinyl)phenanthrene (3i)**




The reaction of 1-bromo-2-(1'-(*p*-tolyl)vinyl)benzene (273 mg, 1.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (22.5 mg, 0.10 mmol, 10 mol%), MOP (93.7 mg, 0.20 mmol, 20 mol%) and $Cs_2CO_3$ (488 mg, 1.50 mmol, 1.5

equiv) afforded **2i** (133.7 mg, 70%) as a mixture of *E*- and *Z*-isomers, 1:1, orange solid and **3i** (14.2 mg, 7%) as a colorless liquid, eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

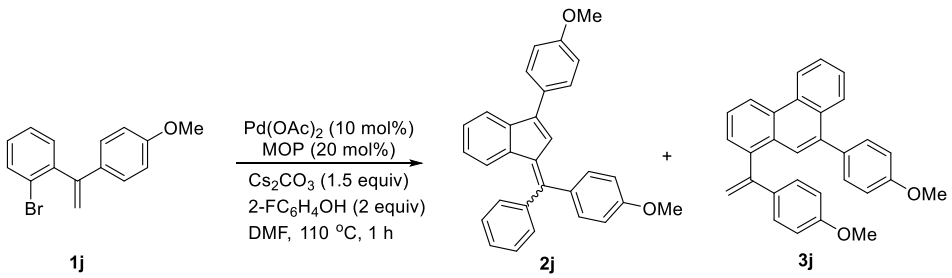
Data of **3i**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.5 Hz, 1H), 8.77 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.26 – 7.52 (m, 2H), 7.28 (s, 1H), 7.26– 7.24 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.98 (s, 1H), 5.39 (s, 1H), 2.46 (s, 3H), 2.36 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 147.9, 140.7, 138.2, 137.9, 137.4, 136.8, 130.8, 130.7, 130.1, 130.0, 129.0, 128.9, 128.1, 126.8, 126.6, 126.5, 126.4, 125.9, 125.7, 123.1, 122.1, 115.3, 21.2, 21.1.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}^+$ 385.1951; Found 385.1955.

**3-(4'-Methoxyphenyl)-1-((4''-methoxyphenyl)(phenyl)methylene)-1*H*-indene (2j)**




**1j** **2j** **3j**

The reaction of 1-bromo-2-(1'-(4'-methoxyphenyl)vinyl)benzene (57.8 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1 hour afforded **2j** (34.4 mg, 82%) as a mixture of *E*- and *Z*-isomers, 8:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ethyl acetate = 50:1 to 20:1.

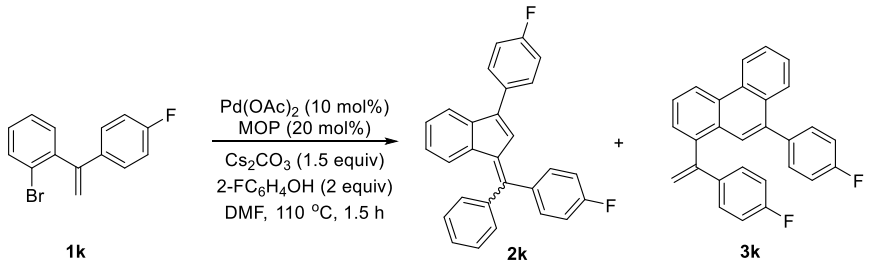
Data of **2j**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.41 – 7.37 (m, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.99 ((d, *J* = 8.5 Hz, 2H), 6.93 – 6.87 (m, 3H), 6.77 (s, 1H), 6.68 (s, 0.1H), 6.64 (d, *J* = 7.5 Hz, 0.9H), 3.86 (s, 3H), 3.85 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.7, 159.2, 145.9, 143.3, 142.8, 141.9, 137.4, 137.2, 135.0, 133.2, 130.6, 132.3, 131.8, 128.8, 128.5, 128.48, 128.41, 127.8, 127.0, 126.6, 124.6, 119.9, 114.0, 113.3, 55.33, 55.32.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}O_2^+$ 417.1849; Found 417.1852.

**(3-(4'-Fluorophenyl)-1-((4''-fluorophenyl)(phenyl)methylene)-1*H*-indene (2k)**




**1k** **2k** **3k**

The reaction of 1-bromo-2-(1'-(4'-fluorophenyl)vinyl)benzene (55.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1.5 hours afforded **2k** (27.9 mg, 71%) as a mixture of *E*- and *Z*-isomers, 2:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

Data of **2k**:

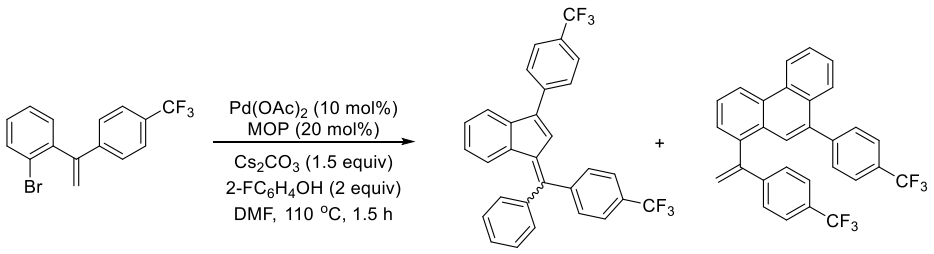
**$^1$H NMR** $^1$H NMR (500 MHz, DMSO-$d_6$) δ 7.73 – 7.67 (m, 2H), 7.55 – 7.50 (m, 2.5H), 7.46 – 7.25 (m, 9.5H), 7.24 – 7.19 (m, 1H), 7.00 (t, $J$ = 7.5 Hz, 0.4H), 6.94 (t, $J$ = 7.5 Hz, 0.6H), 6.69 (s, 0.6H), 6.67 (s, 0.4H), 6.54 (d, $J$ = 8.0 Hz, 0.4H), 6.46 (d, $J$ = 8.0 Hz, 0.6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.7 (d, $^1J_{C–F}$ = 250.5 Hz), 162.4 (d, $^1J_{C–F}$ = 248.5 Hz), 145.5, 143.5, 143.4, 142.7, 142.6, 142.2, 141.3, 138.4 (d, $^4J_{C–F}$ = 3.0 Hz), 138.2, 138.0, 137.05, 136.99, 133.3 (d, $^3J_{C–F}$ = 9.1 Hz), 132.4 (d, $^3J_{C–F}$ = 8.1 Hz), 131.7 (d, $^4J_{C–F}$ = 3.0 Hz), 131.6, 131.0, 130.4, 129.3 (d, $^3J_{C–F}$ = 8.1 Hz), 128.70, 128.65, 128.4, 128.0, 127.7, 127.4, 127.12, 127.05, 125.0, 123.8, 123.6, 120.0, 119.9, 115.7 (d, $^2J_{C–F}$ = 21.2 Hz), 115.6 (d, $^2J_{C–F}$ = 22.2 Hz), 115.0 (d, $^2J_{C–F}$ = 22.2 Hz).

**$^{19}$F NMR** (471 MHz, DMSO-$d_6$) δ -112.6, -113.0, -113.4, -113.5.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{19}F_2^+$ 393.1449; Found 393.1454.

**1-(Phenyl(4'-(trifluoromethyl)phenyl)methylene)-3-(4''-(trifluoromethyl)phenyl)-1*H*-indene (2l)**




**1l** **2l** **3l**

The reaction of 1-bromo-2-(1'-(4'-(trifluoromethyl)phenyl)vinyl)benzene (65.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1.5 hours afforded **2l** (37.2 mg, 75%) as a mixture of *E*- and *Z*-isomers, 1.1:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

Data of **2l**:

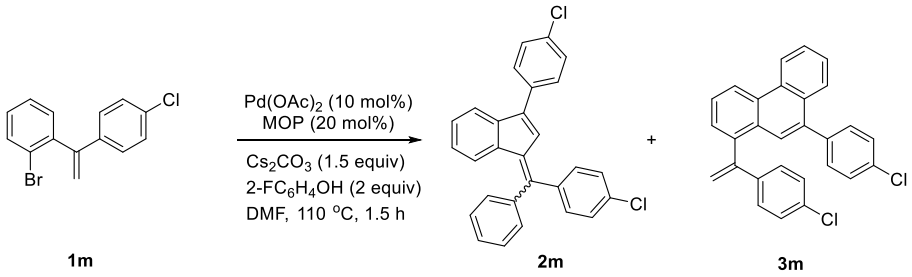
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 5H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.44 (m, 3.5H), 7.43 – 7.36 (m, 2.5H), 7.33 – 7.29 (m, 1H), 7.25 – 7.20 (m, 1H), 7.01 – 6.95 (m, 1H), 6.79 (s, 1H), 6.75 (d, *J* = 7.5 Hz, 0.5H), 6.70 (s, 0.5H), 6.68 (d, *J* = 8.0 Hz, 0.5H).

**$^{13}$C NMR** (151 MHz, Chloroform-*d*) Since it is a pair of *E/Z* isomer (1:1), the NMR spectra are relatively complicated along with C-F couplings. The followings are the selected peaks: δ 145.74, 145.72, 145.0, 144.0 143.7, 142.4, 142.3, 141.5, 140.6, 139.13, 139.07, 139.0, 138.6, 136.8, 136.6, 131.7, 131.5, 130.8, 130.3, 129.9 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 129.8 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 129.0, 128.89, 128.85, 128.7, 128.3, 128.2, 127.9, 127.60, 127.57, 125.64 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 125.55 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 125.0 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 124.11, 124.07 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 123.8, 123.5 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 120.1, 120.0.

**$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -128.6, -133.3, -136.4, -139.7, -139.7, -139.7.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{19}F_6^+$ 493.1369; Found 493.1380.

**3-(4'-Chlorophenyl)-1-((4''-chlorophenyl)(phenyl)methylene)-1*H*-indene (2m)**




**1m** **2m** **3m**

The reaction of 1-bromo-2-(1'-(4'-chlorophenyl)vinyl)benzene (294 mg, 1.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol, 10 mol%), MOP (93.7 mg, 0.20 mmol, 20 mol%), 2-fluorophenol (224.2 mg, 2 mmol, 2 equiv) and $Cs_2CO_3$ (488 mg, 3.0 mmol, 1.5 equiv) in 1 hour afforded **2m** (120.4 mg, 57%) as a mixture of *E*- and *Z*-isomers, 6:1, orange solid (chemoselectivity >10:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

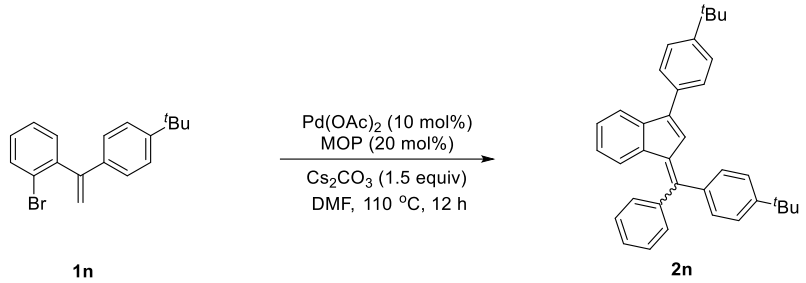
Data of **2m**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.53 – 7.43 (m, 4H), 7.44 – 7.34 (m, 6H), 7.33 – 7.30 (m, 0.5H), 7.30 – 7.27 (m, 1.5H), 7.24 – 7.19 (m, 1H), 7.01 (t, *J* = 7.5 Hz, 0.2H), 6.95 (t, *J* = 7.5 Hz, 0.8H), 6.80 (d, *J* = 7.5 Hz, 0.2H), 6.72 – 6.68 (m, 1.8H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 145.6, 145.5, 143.5, 143.4, 142.5, 142.4, 142.0, 141.0, 140.7, 139.8, 138.3, 137.0, 136.9, 134.7, 134.5, 134.1, 134.0, 133.62, 133.58, 132.8, 132.0, 131.6, 130.4, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 128.0, 127.6, 127.3, 127.2, 125.2, 123.9, 123.7, 120.0, 119.9.

**HRMS** (ESI) m/z: [M + H]+ Calcd for $C_{28}H_{19}Cl_2^+$ 425.0859; Found 425.0838.

**1.0 mmol scale reaction for the preparation of 3-(4'-(*tert*-Butyl)phenyl)-1-((4''-(*tert*-butyl)phenyl)(phenyl)methylene)-1*H*-indene (2n)**




1n 2n

The reaction of 1-bromo-2-(1'-(4'-(*tert*-butyl)phenyl)vinyl)benzene (315.3 mg, 1.0 mmol, 1.0 equiv.), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol, 10 mol%), MOP (93.7 mg, 0.20 mmol, 20 mol%) and $Cs_2CO_3$ (488 mg, 3.0 mmol, 1.5 equiv) afforded **2n** (154.6 mg, 69%) as a mixture of *E*- and *Z*-isomers, 1.2:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

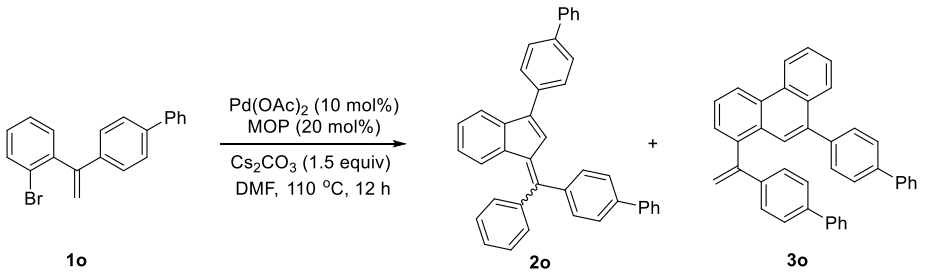
Data of **2n**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 3H), 7.49 – 7.42 (m, 4.5H), 7.42 – 7.39 (m, 1H), 7.39 – 7.34 (m, 3.5H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.19 (dd, *J* = 7.0, 6.5 Hz, 1H), 6.95 – 6.89 (m, 1H), 6.83 (s, 0.5H), 6.77 (d, *J* = 7.5 Hz, 0.5H), 6.73 (s, 0.5H), 6.63 (d, *J* = 7.5 Hz, 0.5H), 1.41 (s, 4.5H), 1.36 (d, *J* = 1.5 Hz, 9H), 1.35 (s, 4.5H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 151.7, 151.2, 150.7, 146.6, 146.5, 143.8, 143.7, 142.87, 142.85, 142.7, 141.8, 139.4, 138.5, 137.9, 137.7, 137.3, 133.1, 133.0, 131.7, 131.4, 130.4, 130.2, 128.5, 128.3, 128.0, 127.76, 127.71, 127.38, 127.35, 126.74, 126.69, 125.4, 125.3, 124.8, 124.7, 124.6, 123.7, 120.1, 34.8, 34.67, 34.65, 31.4, 31.3, 31.3.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{36}H_{37}^+$ 469.2890; Found 469.2880.

**3-([1,1'-Biphenyl]-4-yl)-1-([1,1'-biphenyl]-4-yl(phenyl)methylene)-1*H*-indene (2o)**




1o 2o 3o

The reaction of 4-(1'-(2'-bromophenyl)vinyl)-1,1'-biphenyl (67.0 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) afforded **2o** (35.5 mg, 70%) as a mixture of *E*- and *Z*-isomers, 6.5:1, orange solid and a trace amount of **3o**, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

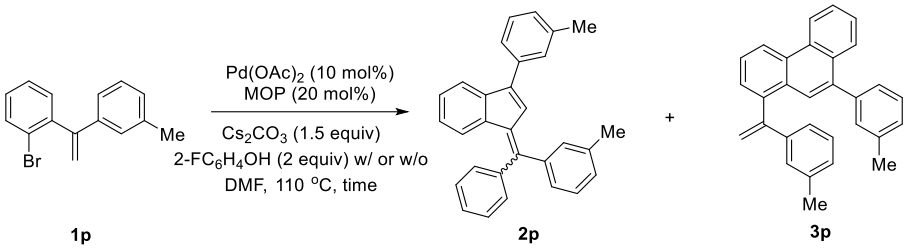
Data of **2o**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.70 – 7.67 (m, 2H), 7.66 – 7.61 (m, 6.5H), 7.512 – 7. 43 (m, 11H), 7.41 (t, *J* = 3.5 Hz, 0.5H), 7.39 – 7.35 (m, 2H), 7.25 – 7.20 (m, 1H), 6.98 – 6.93 (m, 1H), 6.92 (s, 0.9H), 6.83 (s, 0.1H), 6.71 (d, *J* = 7.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 146.3, 143.8, 142.7, 141.5, 141.4, 140.9, 140.7, 140.6, 140.4, 138.2, 137.3, 134.8, 132.2, 131.8, 131.2, 130.6, 128.84, 128.81, 128.6, 128.1, 127.9, 127.6, 127.4, 127.3, 127.1, 127.01, 126.97, 126.6, 124.9, 123.8, 120.1.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{40}H_{29}^+$ 509.2264; Found 509.2268.

**1-(Phenyl(*m*-tolyl)methylene)-3-(*m*-tolyl)-1*H*-indene (2p)**




(a) The reaction without 2-fluorophenol additive

The reaction of 1-bromo-2-(1-(*m*-tolyl)vinyl)benzene (54.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 12 hours afforded **2p** (26.9 mg, 70%) as a mixture of *E*- and *Z*-isomers, 1:1, orange solid and a trace amount of **3p**, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

(b) The reaction with 2-fluorophenol additive

The reaction of 1-bromo-2-(1-(*m*-tolyl)vinyl)benzene (54.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 2 hours afforded **2p** (33.8 mg, 88%) as a mixture of *E*- and *Z*-isomers, 6:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

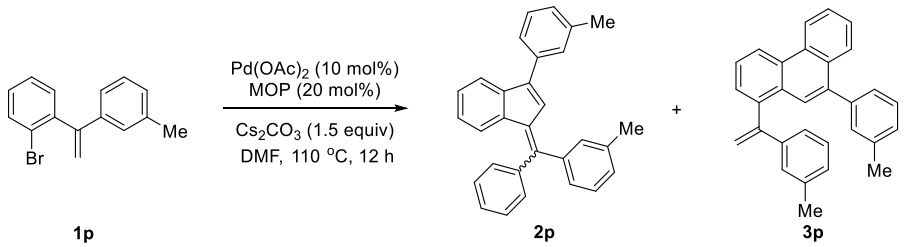
Data of **2p**:

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, $J$ = 7.5 Hz, 1H), 7.49 – 7.44 (m, 4.5H), 7.44 – 7.39 (m, 2H), 7.38 – 7.32 (m, 1.5H), 7.30 – 7.27 (m, 1H), 7.23 – 7.14 (m, 5H), 6.93 (t, $J$ = 7.5 Hz, 1H), 6.76 (s, 1H), 6.72 (d, $J$ = 8.0 Hz, 0.1H), 6.67 (d, $J$ = 7.5 Hz, 0.9H), 2.42 (s, 3H), 2.38 (s, 0.3H) 2.36 (s, 2.7H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.8, 144.2, 142.9, 142.4, 141.7, 138.2, 138.0, 137.5, 137.2, 135.8, 132.0, 131.6, 130.7, 130.4, 129.2, 128.9, 128.8, 128.5, 128.43, 128.38, 128.3, 127.8, 127.7, 127.5, 126.8, 124.8, 124.7, 123.8, 123.7, 120.1, 21.52, 21.45.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}^+$ 385.1951; Found 385.1957.

**1.0 mmol scale reaction for the preparation of 9-(*m*-tolyl)-1-(1'-(*m*-tolyl)vinyl)phenanthrene (3p)**




The reaction of 1-bromo-2-(1-(*m*-tolyl)vinyl)benzene (273 mg, 1.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (22.5 mg, 0.20 mmol, 10 mol%), MOP (93.7 mg, 0.40 mmol, 20 mol%), and $Cs_2CO_3$ (488 mg, 1.50 mmol, 1.5 equiv) afforded **2p** (126.3 mg, 66%) as an orange solid and **3p** (8.1 mg, 4%) as a colorless liquid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

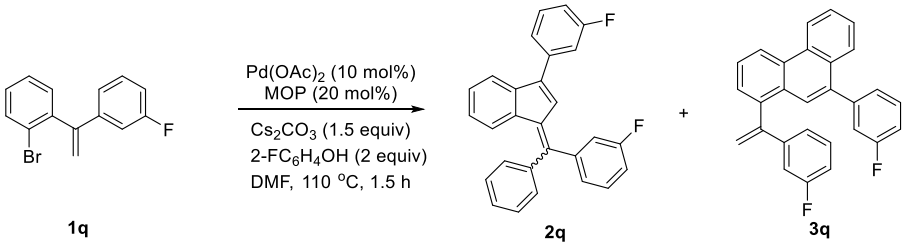
Data of **3p**:

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ 8.98 (d, *J* = 8.0 Hz, 1H), 8.93 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.78 – 7.72 (m, 2H), 7.46 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.17 (m, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.04 (s, 1H), 5.41 (s, 1H), 2.32 (s, 3H), 2.23 (s, 3H).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$) δ 147.8, 140.6, 140.0, 139.9, 137.73, 137.70, 130.3, 130.1, 129.7, 128.9, 128.6, 128.5, 128.3, 128.2, 127.1, 127.0, 126.72, 126.67, 126.6, 126.1, 125.0, 123.8, 123.7, 122.8, 116.7, 21.03, 21.00.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}^+$ 385.1951; Found 385.1949.

**3-(3'-Fluorophenyl)-1-((3'-fluorophenyl)(phenyl)methylene)-1*H*-indene (2q)**




The reaction of 1-bromo-2-(1'-(3'-fluorophenyl)vinyl)benzene (55.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1.5 hours afforded **2q** (35.0 mg, 89%) as a mixture of *E*- and *Z*-isomers, 2:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

Data of **2q**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 1H), 7.50 – 7.45 (m, 1.5H), 7.45 – 7.37 (m, 5H), 7.37 – 7.31 (m, 2.5H), 7.25 – 7.20 (m, 1.5H), 7.20 – 7.13 (m, 1H), 7.13 – 7.02 (m, 2.5H), 7.00 – 7.92 (m, 1H), 6.70 – 6.71 (m, 1.5H), 6.69 (d, *J* = 8.0 Hz, 0.5H).

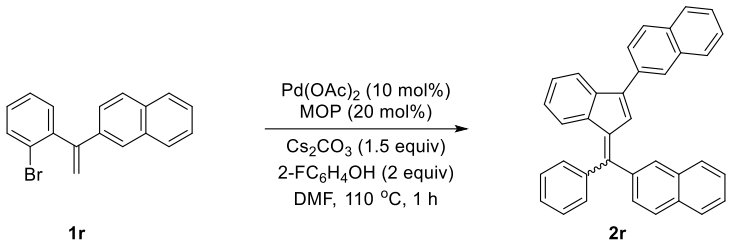
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.9 (d, $^1J_{C–F}$ = 246.4 Hz), 162.3 (d, $^1J_{C–F}$ = 247.5 Hz), 145.6 (d, $^4J_{C–F}$ = 2.0 Hz), 145.5, 144.4 (d, $^3J_{C–F}$ = 7.1 Hz), 143.7 (d, $^4J_{C–F}$ = 2.0 Hz), 143.5 (d, $^3J_{C–F}$ = 7.1 Hz), 142.38,

142.36, 141.7, 140.9, 138.5, 138.3, 137.8 (d, $^{3}J_{C–F}$ = 8.0 Hz), 136.9, 136.7, 131.5, 131.0, 130.3, 130.2, 130.11 (d, $^{3}J_{C–F}$ = 9.1 Hz), 130.08 (d, $^{3}J_{C–F}$ = 8.1 Hz), 129.4 (d, $^{3}J_{C–F}$ = 8.1 Hz), 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 127.35, 127.32, 126.2 (d, $^{4}J_{C–F}$ = 3.0 Hz), 125.2, 124.0, 123.8, 123.4 (d, $^{4}J_{C–F}$ = 3.0 Hz), 120.03, 120.01, 118.1 (d, $^{2}J_{C–F}$ = 22.2 Hz), 117.3 (d, $^{2}J_{C–F}$ = 21.1 Hz), 115.5 (d, $^{2}J_{C–F}$ = 21.1 Hz), 115.2 (d, $^{2}J_{C–F}$ = 21.1 Hz), 114.74 (d, $^{2}J_{C–F}$ = 21.1 Hz), 114.68 (d, $^{2}J_{C–F}$ = 22.2 Hz), 114.4.

**$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -112.5, -112.5, -112.9, -112.9, -112.9, -113.0, -113.2, -113.3.

**HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{18}F_2Na^+$ 415.1269; Found 415.1238.

**2-(1-(Naphthalen-2-yl(phenyl)methylene)-1*H*-inden-3-yl)naphthalene (2r)**




**1r** **2r**

The reaction of 2-(1'-(2'-bromophenyl)vinyl)naphthalene (61.8 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1 hour afforded **2r** (34.2 mg, 75%) as a mixture of *E*- and *Z*-isomers, 4:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

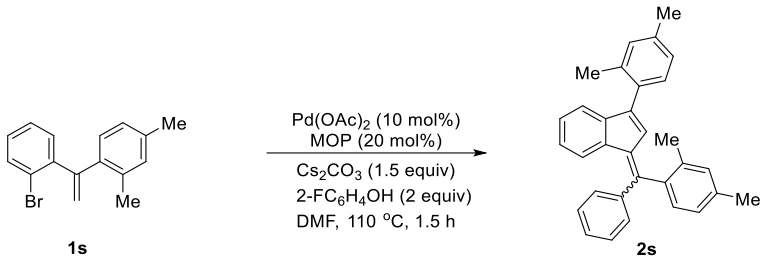
Data of **2r**:

**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.68 – 7.59 (m, 7H), 7.55 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.26 (m, 6H), 7.26 – 7.22 (m, 4H), 7.03 (t, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 6.57 (d, *J* = 7.5 Hz, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 146.8, 144.3, 142.8, 141.5, 139.9, 138.5, 137.4, 133.5, 133.2, 132.9, 132.8, 131.5, 130.7, 128.9, 128.64, 128.62, 128.52, 128.45, 128.1, 127.7, 127.6, 127.5, 127.0, 126.7, 126.4, 126.3, 126.2, 126.1, 126.0, 125.0, 123.9, 120.2.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{36}H_{25}^+$ 457.1951; Found 457.1955.

**3-(2,4-Dimethylphenyl)-1-((2,4-dimethylphenyl)(phenyl)methylene)-1*H*-indene (2s)**




**1s** **2s**

The reaction of 1-(1'-(2'-bromophenyl)vinyl)-2,4-dimethylbenzene (57.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1.5 hours afforded **2s** (35.0 mg, 85%) as a mixture of *E*- and *Z*-isomers, 10:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

Data of **2s**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 1.9H), 7.45 – 7.37 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.19 – 7.06 (m, 5H), 7.06 – 6.99 (m, 3H), 6.96 (t, *J* = 7.0 Hz, 1H), 6.73 (s, 0.1H), 6.40 (d, *J* = 8.0 Hz, 0.1H), 6.20 (s, 0.9H), 2.46 (s, 0.3H), 2.39 (s, 0.3H), 2.37 (s, 3H), 2.35 (s, 2.7H), 2.28 (s, 2.7H), 2.18 (s, 2.7H), 2.10 (s, 0.3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 146.0, 145.3, 144.7, 144.4, 144.0, 143.6, 141.5, 140.8, 139.3, 138.8, 138.4, 138.07, 138.05, 137.5, 137.23, 137.17, 136.5, 136.4, 136.22, 136.15, 136.1, 135.7, 132.4, 132.3, 131.4, 131.2, 131.1, 131.0, 130.9, 130.1, 129.9, 129.23, 129.19, 129.12, 128.3, 128.2, 128.1, 127.9, 127.8, 127.0, 126.9, 126.8, 126.3, 126.2, 125.9, 124.9, 124.6, 123.3, 123.2, 120.3, 120.1, 21.4, 21.2, 21.1, 20.5, 20.4, 19.8.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{29}^+$ 413.2264; Found 413.2260.

**1-(Phenyl(*o*-tolyl)methylene)-3-(*o*-tolyl)-1*H*-indene (2t)**


The reaction of 1-bromo-2-(1'-(*o*-tolyl)vinyl)benzene (54.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 2 hours afforded **2t** (35.7 mg, 93%) as a mixture of *E*- and *Z*-isomers, 6:1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

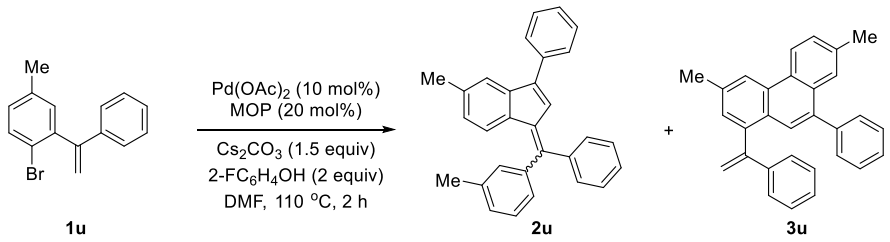
Data of **2t**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.44 – 7.36 (m, 3.5H), 7.36 – 7.29 (m, 2H), 7.28 – 7.27 (m, 0.5H), 7.25 – 7.23 (m, 1H), 7.23 – 7.16 (m, 4H), 7.16 – 7.13 (m, 1H), 7.09 (dd, *J* = 3.0, 4.5 Hz, 2H), 6.98 – 6.93 (m, 1H), 6.73 (s, 0.1H), 6.16 (s, 0.9H), 2.35 (s, 0.3H), 2.28 (s, 2.7H), 2.21 (s, 2.7H), 2.13 (s, 0.3H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 146.0, 145.4, 144.7, 144.6, 143.93, 143.89, 142.1, 141.1, 140.9, 140.5, 138.8, 138.4, 136.5, 136.4, 136.34, 136.28, 135.6, 135.4, 135.2, 131.0, 130.8, 130.7, 130.4, 130.33, 130.32, 130.2, 130.1, 129.9, 129.3, 129.2, 129.1, 128.4, 128.32, 128.28, 128.1, 127.9, 127.8, 127.6, 127.1, 126.9, 126.2, 125.54, 125.49, 125.2, 125.1, 124.8, 123.3, 123.2, 120.4, 120.2, 20.6, 20.53, 20.46, 19.9.

**HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{24}Na^+$ 407.1770; Found 407.1792.

**5-Methyl-3-phenyl-1-(phenyl(m-tolyl)methylene)-1*H*-indene (2u)**




The reaction of 1-bromo-4-methyl-2-(1'-phenylvinyl)benzene (54.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 2 hours afforded **2u** (35.8 mg, 93%) as a mixture of *E*- and *Z*-isomers, 1:6, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

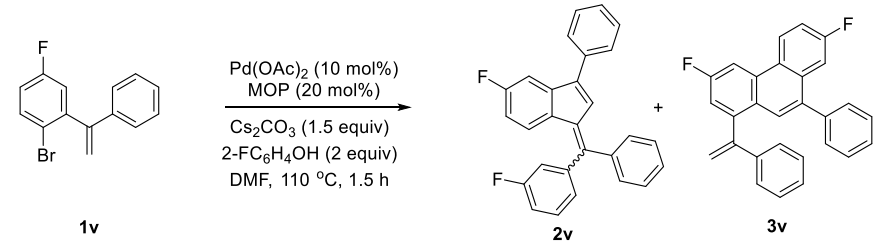
Data of **2u**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.43 (m, 3.5H), 7.43 – 7.39 (m, 1H), 7.39 – 7.31 (m, 5.5H), 7.29 – 7.27 (m, 0.5H), 7.22 (d, *J* = 9.5 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 1.5H), 6.78 – 6.73 (m, 2H), 6.60 (d, *J* = 7.5 Hz, 0.5H), 6.56 (d, *J* = 7.5 Hz, 0.5H), 2.39 (s, 1.5H), 2.36 (s, 4.5H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.0, 144.1, 144.0, 143.10, 143.06, 142.5, 142.4, 141.8, 141.6, 138.1, 137.9, 137.8, 137.4, 136.9, 135.99, 135.97, 134.60, 134.55, 132.0, 131.5, 130.9, 130.4, 129.1, 128.82, 128.77, 128.52, 128.48, 128.38, 128.29, 128.26, 128.16, 128.0, 127.8, 127.71, 127.67, 127.5, 125.6, 125.5, 123.6, 123.5, 120.8, 21.7, 21.5, 21.4.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}^+$ 385.1951; Found 385.1944.

**5-Fluoro-1-((3'-fluorophenyl)(phenyl)methylene)-3-phenyl-1*H*-indene (2v)**




The reaction of 1-bromo-4-fluoro-2-(1'-phenylvinyl)benzene (55.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 3 hours afforded **2v** (34.6 mg, 88%) as a mixture of *E*- and *Z*-isomers, 1:1.2, orange solid (chemoselectivity >20:1), eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

Data of **2v**:

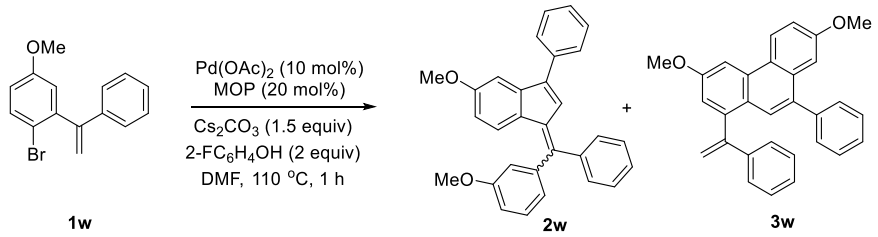
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.42 (m, 3.5H), 7.42 – 7.36 (m, 4H), 7.36 – 7.32 (m, 1. 5H), 7.25 – 7.20 (m, 1.5H), 7.20 – 7.14 (m, 1H), 7.11 (d, *J* = 9.5 Hz, 1H), 7.08 – 7.02 (m, 0.5H), 6.80 (s, 1H), 6.68 – 6.57 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.9 (d, $^1J_{C–F}$ = 248.5 Hz), 162.5 (d, $^1J_{C–F}$ = 246.4 Hz), 145.0 (d, $^3J_{C–F}$ = 8.1 Hz), 144.8, 143.9 (d, $^3J_{C–F}$ = 9.1 Hz), 143.4 (d, $^3J_{C–F}$ = 7.1 Hz), 141.6, 140.8, 137.7, 137.5, 135.1, 132.5 (d, $^4J_{C–F}$ = 3.0 Hz), 131.4, 130.3 (d, $^4J_{C–F}$ = 2.0 Hz), 130.2, 129.4 (d, $^3J_{C–F}$ = 8.1 Hz), 129.2, 128.8, 128.7, 128.5, 128.14, 128.07, 127.5, 126.2 (d, $^4J_{C–F}$ = 3.0 Hz), 124.9 (d, $^3J_{C–F}$ = 9.1 Hz), 124.7 (d, $^3J_{C–F}$ = 9.1 Hz), 118.1 (d, $^2J_{C–F}$ = 22.2 Hz), 117.3 (d, $^2J_{C–F}$ = 22.2 Hz), 115.6 (d, $^2J_{C–F}$ = 21.2 Hz), 115.1 (d, $^2J_{C–F}$ = 21.2 Hz), 111.4 (d, $^2J_{C–F}$ = 23.2 Hz), 107.6 (d, $^2J_{C–F}$ = 24.2 Hz).

**$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -112.4, -112.4, -112.4, -113.2, -113.2, -113.2, -114.0, -114.1, -114.1.

**HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{18}F_2Na^+$ 415.1269; Found 415.1263.

**5-Methyl-3-phenyl-1-(phenyl(*m*-tolyl)methylene)-1*H*-indene (2w)**




The reaction of 1-bromo-4-methoxy-2-(1'-phenylvinyl)benzene (57.8 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 1 hour afforded **2w** (31.3 mg, 75%) as a mixture of *E*- and *Z*-isomers, 1:1.2, orange solid (chemoselectivity >20:1), eluent: petroleum ether/ethyl acetate = 50:1 to 20:1.

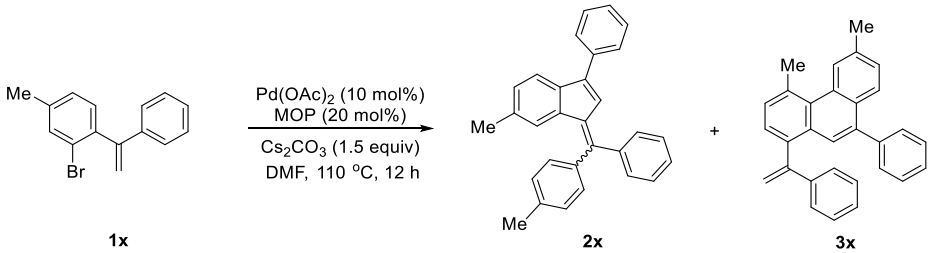
Data of **2w**:

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.5 Hz, 2H), 7.47 – 6.41 (m, 2.5H), 7.40 – 7.32 (m, 6.5H), 7.11 (bs, 1H), 7.03 – 6.98 (m, 1.75H), 6.97 – 6.93 (m, 1H), 6.91 – 6.88 (m, 0.25H), 6.80 (bs, 0.15H), 6.77 (bs, 0.85H), 6.67 (d, *J* = 7.5 Hz, 0.9H), 6.59 (d, *J* = 7.5 Hz, 0.1H), 6.512 – 6.45 (m, 1H), 3.80 (s, 6H).

**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 159.7, 159.3, 159.0, 144.6, 144.5, 144.0, 143.9, 143.8, 143.0, 142.2, 141.6, 137.6, 137.5, 135.8, 131.4, 130.3, 129.9, 129.6, 129.0, 128.6, 127.94, 127.85, 127.8, 127.6, 124.8, 124.6, 124.1, 122.8, 117.1, 115.4, 114.2, 113.4, 109.9, 106.4, 55.5, 55.4.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}O_2^+$ 417.1849; Found 417.1847.

**6-Methyl-3-phenyl-1-(phenyl(*p*-tolyl)methylene)-1*H*-indene (2x)**



The reaction of 2-bromo-4-methyl-1-(1'-phenylvinyl)benzene (54.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) afforded **2x** (19.6 mg, 50%) as a mixture of *E*- and *Z*-isomers,1:1.2, orange solid and a trace amount of **3x**, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

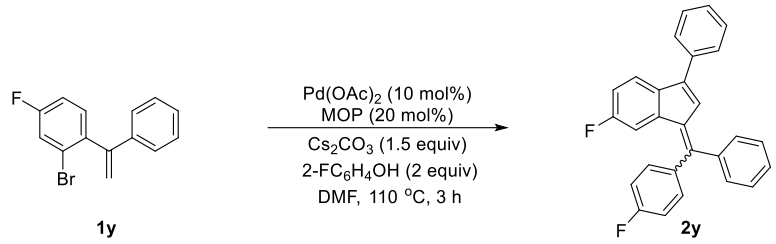
Data of **2x**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.47 – 7.38 (m, 5.5H), 7.37 – 7.31 (m, 4H), 7.31 – 7.28 (m, 1H), 7.25 (d, *J* = 2.5 Hz, 1.5H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.0 Hz, 1H), 6.74 (s, 0.4H), 6.68 (s, 0.6H), 6.62 (s, 0.6H), 6.45 (s, 0.4H), 2.47 (s, 1.8H), 2.39 (s, 1.2H), 2.16 (s, 1.8H), 2.13 (s, 1.2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.5, 146.3, 143.91, 143.87, 142.8, 141.8, 140.23, 140.16, 139.6, 138.7, 138.4, 138.2, 137.9, 137.8, 137.6, 136.1, 136.0, 134.4, 134.3, 131.64, 131.60, 130.6, 130.5, 129.1, 128.6, 128.5, 128.43, 128.35, 128.0, 127.8, 127.6, 127.5, 127.4, 127.33, 127.29, 124.7, 119.7, 21.63, 21.57, 21.4, 21.3.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}O_2^+$ 385.1951; Found 385.1951.

**6-Fluoro-1-((4'-fluorophenyl)(phenyl)methylene)-3-phenyl-1*H*-indene (2y)**




The reaction of 2-bromo-4-fluoro-1-(1'-phenylvinyl)benzene (55.4 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 3 hours afforded **2y** (28.9 mg, 74%) as a mixture of *E*- and *Z*-isomers, 1:1.1, orange solid (chemoselectivity >20:1), eluent: petroleum ether/dichloromethane = 50:1 to 20:1.

Data of **2y**:

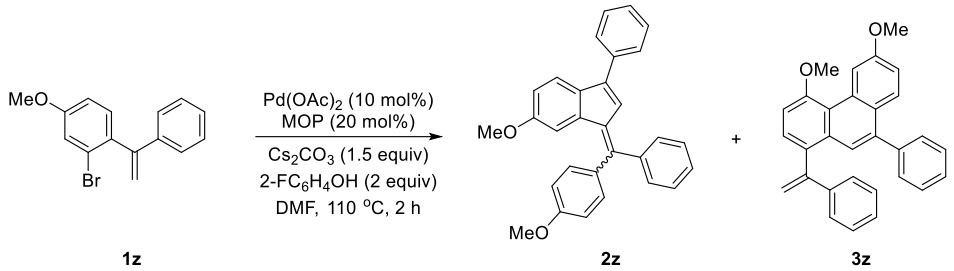
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.51 – 7.42 (m, 4.5H), 7.42 – 7.35 (m, 4.5H), 7.35 – 7.30 (m, 2H),7.17 (t, *J* = 8.5 Hz, 1H), 7.08 (t, *J* = 8.5 Hz, 1H), 6.94 – 6.86 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 10.0 Hz, 0. 5H), 6.33 (d, *J* = 10.5 Hz, 0.5H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.1 (d, $^1J_{C-F}$ = 250.5 Hz), 161.6, 161.4 (d, $^1J_{C-F}$ = 242.4 Hz), 146.3 (d, $^4J_{C-F}$ = 3.0 Hz), 144.0, 143.9, 142.0, 140.8, 139.05, 138.96, 138.8, 138.7, 138.1, 137.5, 137.4, 137.0, 135.5, 133.3 (d, $^3J_{C-F}$ = 8.1 Hz), 132.3 (d, $^3J_{C-F}$ = 8.1 Hz), 131.6, 130.3, 129.0, 128.8, 128.6 (d, $^4J_{C-F}$ = 3.0 Hz), 128.55, 128.0 (d, $^4J_{C-F}$ = 3.0 Hz), 127.6, 127.1 (d, $^4J_{C-F}$ = 3.0 Hz), 120.7, 120.6 (d, $^3J_{C-F}$ = 9.1 Hz), 115.9 (d, $^2J_{C-F}$ = 21.2 Hz), 115.1 (d, $^2J_{C-F}$ = 22.2 Hz), 113.5 (d, $^3J_{C-F}$ = 7.1 Hz), 113.3 (d, $^3J_{C-F}$ = 7.1 Hz), 111.4 (d, $^2J_{C-F}$ = 16.2 Hz), 111.1 (d, $^2J_{C-F}$ = 15.2 Hz).

**$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -109.7, -112.0, -112.0, -112.6, -112.6, -114.7, -117.4, -117.4, -117.4, -117.5.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{19}F_2^+$ 393.1450; Found 393.1402.

**6-Methoxy-1-((4'-methoxyphenyl)(phenyl)methylene)-3-phenyl-1*H*-indene (2z)**




The reaction of 2-bromo-4-methoxy-1-(1'-phenylvinyl)benzene (57.8 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) in 2 hours afforded **2z** (30.1 mg, 72%) as a mixture of *E*- and *Z*-isomers, 1:20, orange red solid (chemoselectivity >20:1), eluent: petroleum ether/ethyl acetate = 50:1 to 20:1.

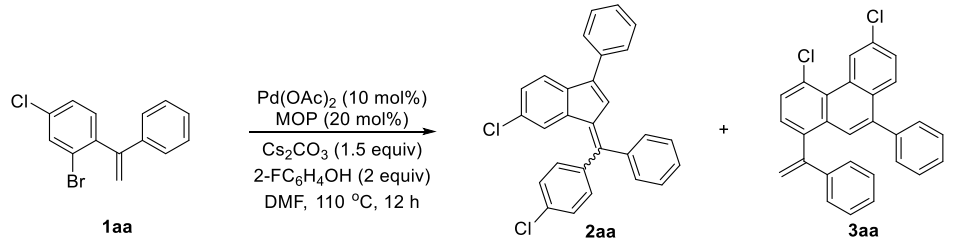
Data of **2z**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.40 – 7.33 (m, 8H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.77 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.65 (s, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 3.89 (s, 3H), 3.58 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 160.0, 157.7, 146.3, 143.7, 142.7, 139.0, 137.7, 136.0, 135.9, 133.8, 132.1, 131.7, 128.5, 128.1, 127.8, 127.6, 127.5, 126.4, 120.4, 114.0, 112.4, 110.0, 55.4, 55.2.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}O_2^+$ 417.1849; Found 417.1847.

**6-Chloro-1-((4-chlorophenyl)(phenyl)methylene)-3-phenyl-1*H*-indene (2aa)**




The reaction of 2-bromo-4-chloro-1-(1'-phenylvinyl)benzene (58.6 mg, 0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), MOP (18.7 mg, 0.04 mmol, 20 mol%), 2-fluorophenol (44.9 mg, 0.40 mmol, 2 equiv) and $Cs_2CO_3$ (97.7 mg, 0.30 mmol, 1.5 equiv) afforded **2aa** (15.8 mg, 37%) as a mixture of *E*- and *Z*-isomers, 1:1, orange solid and a trace amount of **3aa**, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

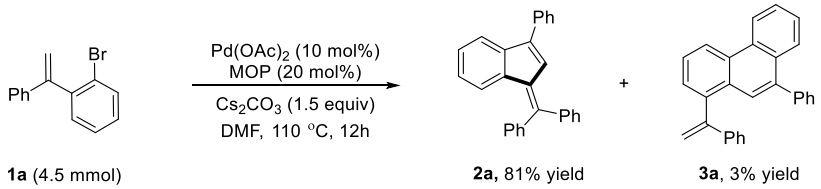
Data of **2aa**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.53 – 7.42 (m, 5.5H), 7.41 – 7.34 (m, 5H), 7.33 (s, 0.5H), 7.32 – 7.28 (m, 1.5H), 7.27 (s, 0.5H), 7.20 – 7.15 (m, 1H), 6.74 (d, *J* = 1.5 Hz, 0.5H), 6.72 (d, *J* = 4.5 Hz, 1H), 6.58 (d, *J* = 2.0 Hz, 0.5H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 146.4, 144.2, 143.9, 141.8, 141.2, 141.0, 140.53, 140.46, 139.3, 138.6, 138.5, 137.50, 137.47, 135.23, 135.21, 135.1, 134.7, 132.8, 132.0, 131.6, 130.9, 130.4, 129.2, 129.0, 128.8, 128.69, 128.66, 128.3, 128.1, 128.09, 128.07, 128.05, 127.6, 127.5, 126.9, 126.8, 124.1, 123.9, 120.9, 120.8.

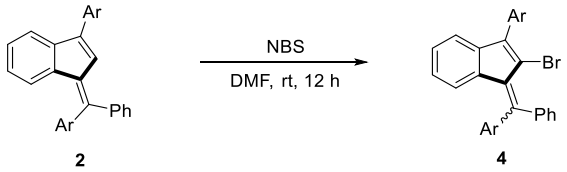
**HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{18}Cl_2Na^+$ 447.0678; Found 447.0668.

### 2.2 Gram-Scale Synthesis and Derivatization of Benzofulvenes



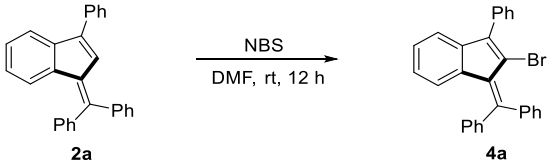

To a 250-mL Schlenk tube charged with a stir bar, 1-bromo-2-(1'-phenylvinyl)benzene (1.17 g, 4.50 mmol, 1.0 equiv), $Pd(OAc)_2$ (101 mg, 0.45 mmol, 10 mol%), MOP (421.7 mg, 0.90 mmol, 20 mol%) and $Cs_2CO_3$ (2.2 g, 6.75 mmol, 1.5 equiv) were added. After filled with nitrogen, anhydrous DMF (25 mL) was added via a syringe. The mixture was stirred at 110 ℃ in an oil bath for 12 h. Upon completion, the reaction mixture was washed with brine (100 mL) and extracted with ethyl acetate (3×25 mL). The combined organic phase was dried over anhydrous $Na_2SO_4$. After that the organic phase was filtered, and the filtrate was concentrated under reduced pressure. The crude products were purified by silica gel chromatography which afforded **2a** (650 mg, 81%) as a light orange solid and byproduct (**3a**) (25.3 mg, 3%) as a colorless liquid, eluent: petroleum ether/ dichloromethane = 50:1 to 30:1.

### 2.3 General Procedure for Synthesis of 2-Bromobenzofulvenes (4)




To a 25-mL Schlenk tube, benzofulvene (**2**) (0.20 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (42.7 mg, 0.24 mmol, 1.2 equiv) were added. After filled with nitrogen, anhydrous DMF (2 mL) were added via a syringe. The mixture was stirred at room temperature for 12 hours. The resulting solution was quenched with $Na_2S_2O_3$ (aq) and extracted with ethyl acetate (15 mL × 3). The combined organic layer was washed with brine then dried over anhydrous $Na_2SO_4$. The sodium sulfate was filtered off, and the filtrate was concentrated by evaporation under vacuum and the residue was purified by flash column chromatography on silica gel to afford the desired compound **4** as red solid.

### 1.8 mmol scale reaction for the preparation of 2-bromo-1-(diphenylmethylene)-3-phenyl-1*H*-indene (4a)



The reaction of 1-(diphenylmethylene)-3-phenyl-1*H*-indene (641 mg, 1.80 mmol, 1.0 equiv.) and 1-bromopyrrolidine-2,5-dione (NBS) (382 mg, 2.16 mmol, 1.2 equiv) afforded **4a** (624.1 mg, 80%) as a red solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

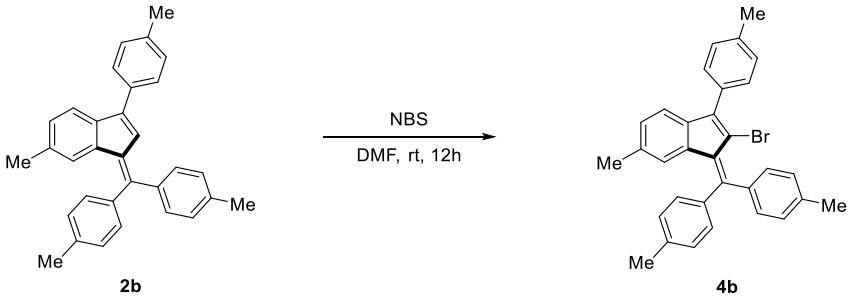
Data of **4a**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.52 – 7.45 (m, 3H), 7.46 – 7.34 (m, 8H), 7.33 – 7.27 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.45 (d, *J* = 8.0 Hz, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 150.5, 145.9, 142.6, 141.8, 141.3, 137.0, 136.2, 134.2, 132.2, 131.0, 129.5, 129.2, 128.8, 128.6, 128.3, 128.2, 127.7, 126.9, 125.3, 123.3, 119.8, 115.8.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{20}Br^+$ 435.0743; Found 435.0735.

**2-Bromo-1-(di-*p*-tolylmethylene)-6-methyl-3-(*p*-tolyl)-1*H*-indene (4b)**




2b 4b

The reaction of 1-(di-*p*-tolylmethylene)-6-methyl-3-(*p*-tolyl)-1*H*-indene (82.1 mg, 0.20 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (42.7 mg, 0.24 mmol, 1.2 equiv) afforded **4b** (51.8 mg, 53%) as a red solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

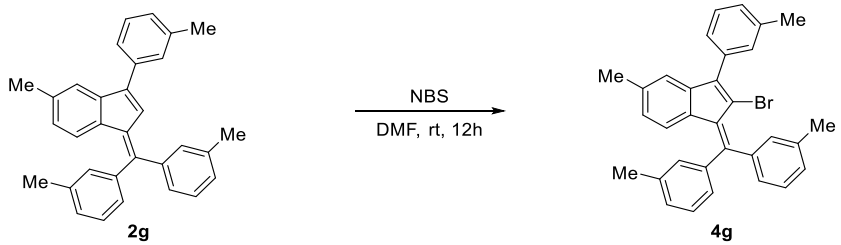
Data of **4b**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.26 (m, 3H), 7.25 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 4H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.0 Hz, 1H), 6.30 (s, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H) 2.07 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 150.1, 145.3, 139.9, 139.3, 139.2, 138.9, 137.8, 137.5, 135.8, 134.8, 132.6, 131.5, 131.4, 129.4, 129.1, 128.9, 128.4, 127.2, 124.3, 124.0, 122.1, 119.4, 114.5, 21.7, 21.49, 21.46, 21.45.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{28}Br^+$ 491.1369; Found 491.1370.

**2-Bromo-1-(di-*m*-tolylmethylene)-5-methyl-3-(*m*-tolyl)-1*H*-indene (4g)**




The reaction of 1-(di-*m*-tolylmethylene)-5-methyl-3-(*m*-tolyl)-1*H*-indene (180.6 mg, 0.44 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (94.0 mg, 0.53 mmol, 1.2 equiv) afforded **4g** (150.6 mg, 70%) as a red solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

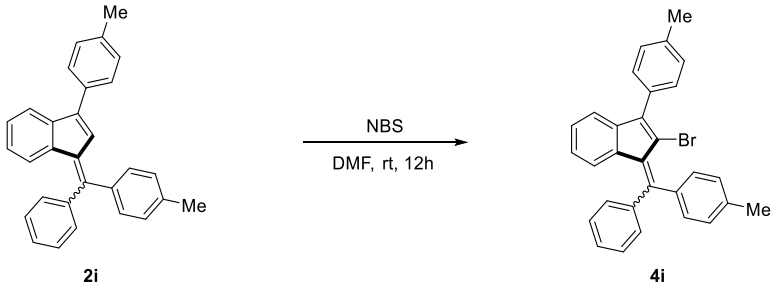
Data of **4g**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 3H), 7.31 (t, *J* = 7.5Hz, 1H), 7.27 (d, *J* = 3.0 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.20 – 7.14 (m, 3H), 7.12 – 7.06 (m, 2H), 6.95 (s, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.31– 6.27 (m, 1H), 2.43 (s, 3H), 2.38 – 2.33 (m, 6H), 2.27 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ150.0, 145.7, 142.7, 142.0, 141.2, 138.2, 137.8, 137.1, 136.8, 135.8, 134.43, 134.36, 132.8, 132.7, 131.4, 130.0, 129.7, 129.3, 128.8, 128.4, 128.1, 128.0, 127.5, 126.6, 126.0, 123.1, 120.3, 115.9, 21.6, 21.43, 21.40, 21.36.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{28}Br^+$ 491.1369; Found 491.1361.

**2-Bromo-1-(phenyl(*p*-tolyl)methylene)-3-(*p*-tolyl)-1*H*-indene (4i)**




The reaction of 1-(phenyl(*p*-tolyl)methylene)-3-(*p*-tolyl)-1*H*-indene (**2i**, *E*/*Z* = 1:1, 115.3 mg, 0.30 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (64.0 mg, 0.36 mmol, 1.2 equiv) afforded **4i** (86.7 mg, 62%) as a mixture of *E*- and *Z*-isomers, 1:1, red solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

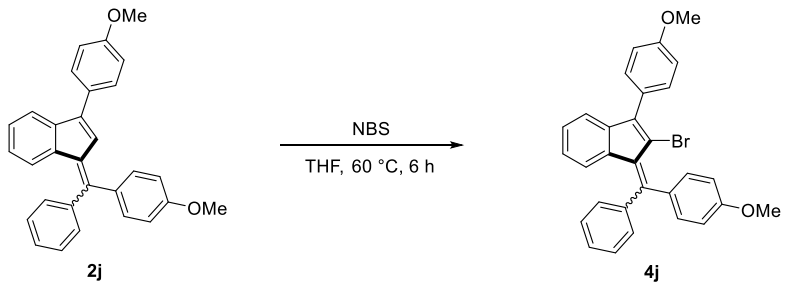
Data of **4i**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 3H), 7.52 – 7.47 (m, 1H), 7.47 – 7.40 (m, 3H), 7.39 – 7.32 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 7.19 – 7.13 (m, 1H), 6.97 – 6.89 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 0.5H), 6.49 (d, *J* = 8.0 Hz, 0.5H), 2.54 (s, 1.5H), 2.50 (s, 3H), 2.49 (s, 1.5H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 150.44, 150.42, 145.6, 142.8, 141.7, 141.6, 139.7, 139.4, 139.0, 138.5, 138.0, 137.2, 135.9, 132.5, 132.4, 131.3, 131.2, 129.45, 129.43, 129.3, 129.1, 129.0, 128.7, 128.52, 128.46, 127.7, 126.74, 126.69, 125.19, 125.17, 123.2, 123.1, 119.7, 115.5, 21.49, 21.45.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}Br^+$ 463.1056; Found 463.1079.

**2-Bromo-3-(4'-methoxyphenyl)-1-((4''-methoxyphenyl)(phenyl)methylene)-1*H*-indene (4j)**



**2j** **4j**

The reaction of 3-(4'-methoxyphenyl)-1-((4''-methoxyphenyl)(phenyl)methylene)-1*H*-indene (**2j**, *E/Z* = 6:1, 83.3 mg, 0.20 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (39.2 mg, 0.22 mmol, 1.1 equiv) afforded **4j** (98.2 mg, 99%) as a mixture of *E*- and *Z*-isomers, 1:1, red solid, eluent: petroleum ether/ ethyl acetate = 50:1 to 20:1.

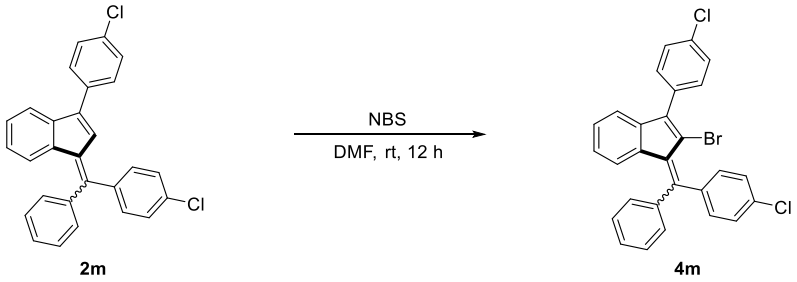
Data of **4j**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.49 – 7.45 (m, 0.5H), 7.43 – 7.40 (m, 1H), 7.39 – 7.33 (m, 2.5H), 7.31 – 7.27 (m, 2H), 7.23 – 7.18 (m, 2H), 7.11 – 7.05 (m, 1H), 7.03 – 6.99 (m, 2H), 6.95 – 6.92 (m, 1H), 6.91 – 6.86 (m, 1.5H), 6.85 – 6.81 (m, 0.5H), 6.63 (d, *J* = 7.5 Hz, 0.5H), 6.40 (d, *J* = 8.0 Hz, 0.5H), 3.90 (s, 1.5H), 3.88 (s, 1.5H), 3.87 (s, 1.5H), 3.86 (s, 1.5H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 160.7, 160.5, 159.4, 150.0, 144.9, 142.8, 141.7, 141.6, 137.3, 134.9, 134.3, 133.8, 133.2, 132.6, 131.5, 130.9, 129.2, 128.8, 128.5, 127.7, 126.6, 125.1, 123.0, 119.7, 113.9, 113.69, 113.67, 113.1, 55.4, 55.3.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}BrO_2^+$ 495.0955; Found 495.0951.

**2-Bromo-3-(4'-chlorophenyl)-1-((4''-chlorophenyl)(phenyl)methylene)-1*H*-indene (4m)**



**2m** **4m**

The reaction of 3-(4'-chlorophenyl)-1-((4''-chlorophenyl)(phenyl)methylene)-1*H*-indene (**2m**, *E/Z* = 4:1, 85.0 mg, 0.2 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (42.7 mg, 0.24 mmol, 1.2 equiv) afforded **4m** (74.6 mg, 74%) as a mixture of *E*- and *Z*-isomers, 1.5:1, red solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

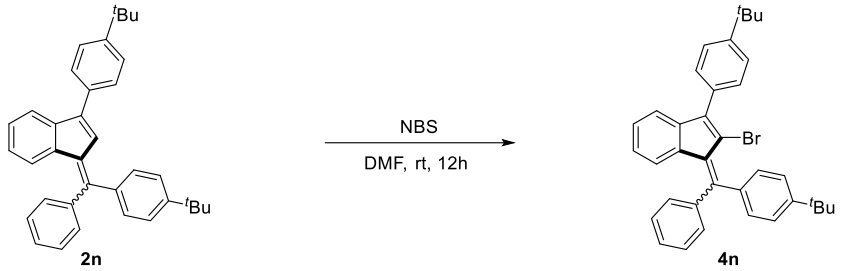
Data of **4m**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.51 –7.47 (m, 2.5H), 7.47 – 7.43 (m, 3H), 7.42 – 7.38 (m, 2H), 7.37 – 7.32 (m, 3.5H), 7.32 – 7.30 (m, 0.5H), 7.25 – 7.23 (m, 0.5H), 7.23 – 7.20 (m, 1H), 7.14 – 7.08 (m, 2H), 6.93 – 6.89 (m, 0.5H), 6.88 – 6.84 (m, 0.5H), 6.56 (d, *J* = 7.5 Hz, 0.5H), 6.44 (d, *J* = 7.5 Hz, 0.5H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.4, 149.3, 145.15, 145.05, 142.0, 141.5, 141.4, 140.9, 140.8, 139.6, 136.8, 136.7, 136.5, 136.4, 135.6, 135.2, 134.14, 134.11, 133.5, 132.6, 132.50, 132.48, 132.3, 131.1, 130.9, 129.5, 129.1, 129.0, 128.7, 128.63, 128.62, 128.1, 127.9, 127.3, 127.2, 125.7, 125.6, 123.4, 123.2, 119.7, 119.6, 116.0, 115.7.

**HRMS** (ESI) m/z: [M + Na]+ Calcd for $C_{28}H_{17}BrCl_2Na^+$ 502.9964; Found 502.9961.

**2-Bromo-3-(4'-(*tert*-butyl)phenyl)-1-((4''-(*tert*-butyl)phenyl)(phenyl)methylene)-1*H*-indene (4n)**




The reaction of 3-(4'-(*tert*-butyl)phenyl)-1-((4''-(*tert*-butyl)phenyl)(phenyl)methylene)-1*H*-indene (**2n**, *E/Z* = 1.2:1, 93.7 mg, 0.20 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (42.7 mg, 0.24 mmol, 1.2 equiv) afforded **4n** (64.3 mg, 59%) as a mixture of *E*- and *Z*-isomers, 1:1, red solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

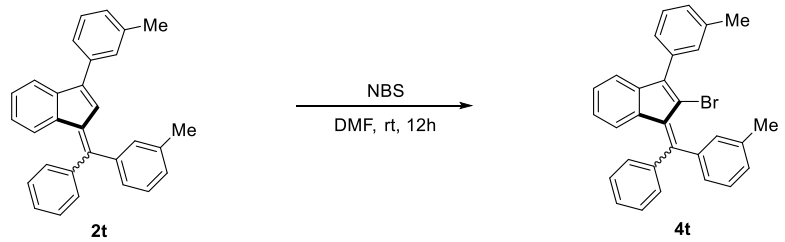
Data of **4n**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 0.5H), 7.51 – 7.49 (m, 1H), 7.49 – 7.45 (m, 2.5H), 7.43 – 7.38 (m, 3H), 7.38 – 7.33 (m, 3H),7.31 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 7.09 – 7.04 (m, 1H), 6.86 – 6. 81 (m, 1H), 6.47 (d, *J* = 8.0 Hz, 0.5H), 6.41 (d, *J* = 8.0 Hz, 0.5H), 1.39 (s, 4.5H), 1.37 (s, 9H), 1.34 (s, 4.5H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.6, 151.0, 150.4, 145.4, 142.8, 138.4, 137.2, 132.4, 132.2, 131.2, 130.9, 129.2, 129.1, 128.6, 128.5, 127.6, 126.6, 125.4, 125.1, 124.6, 123.1, 119.9, 115.6, 34.8, 34.7, 31.4, 31.3.

**HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{35}BrNa^+$ 569.1814; Found 569.1823.

**2-Bromo-1-[phenyl(*m*-tolyl)methylene]-3-(*m*-tolyl)-1*H*-indene (4t)**



The reaction of 1-(phenyl(*m*-tolyl)methylene)-3-(*m*-tolyl)-1*H*-indene (**2t**, *E/Z* = 9:1, 115.3 mg, 0.3 mmol, 1.0 equiv) and 1-bromopyrrolidine-2,5-dione (NBS) (64.0 mg, 0.36 mmol, 1.2 equiv) afforded **4t** (101.9 mg, 73%) as a mixture of *E*- and *Z*-isomers, 1.5:1, red solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

Data of **4t**:

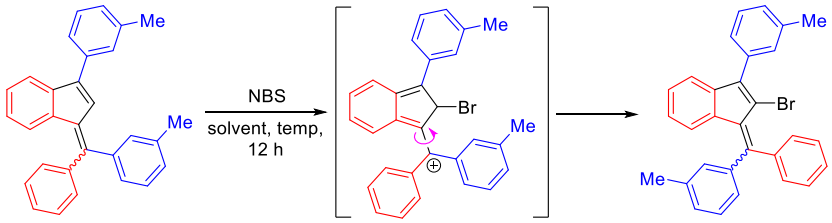
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 0.5H), 7.45 – 7.41 (m, 1H), 7.41 – 7.35 (m, 5H), 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 4H), 7.13 – 7.05 (m, 2.5H), 6.89 – 6.82 (m, 1H), 6.47 (d, *J* = 7.5 Hz, 0.5H), 6.42 (d, *J* = 7.5 Hz, 0.5H), 2.44 (s, 2H), 2.43 (s, 1H), 2.37 (s, 1H), 2.36 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 150.6, 146.0, 145.9, 142.7, 142.5, 141.9, 141.8, 141.4, 141.2, 138.3, 137.8, 137.2, 137.1, 137.0, 136.02, 136.00, 134.2, 132.9, 132.21, 132.15, 131.4, 131.0, 130.0, 129.9, 129.5, 129.4, 129.1, 128.9, 128.7, 128.6, 128.55, 128.47, 128.2, 128.1, 127.69, 127.65, 127.55, 126.8, 126.62, 126.69, 125.3, 125.2, 123.3, 123.2, 119.8, 115.8, 115.6, 21.5, 21.38, 21.36.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{24}Br^+$ 485.0875; Found 485.0865.

### 2.4 Bromination Reaction and its Isomerization

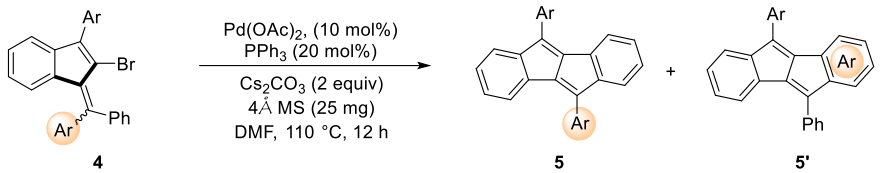
The bromination reaction would induce isomerization of the exocyclic double bond present in benzofulvenes. For instance, treating compound 2p, with an *E/Z* ratio of 6:1, with NBS resulted in a decreased E/Z ratio for compound 4p. This is true for a variety of solvents such as DMF, AcOH, THF or toluene. The isomerization was believed to be associated with the formation of a stable carbocation intermediate known as IntA, where rotation around the single C−C bond can easily occur. This rotation contributes to the isomerization phenomenon observed.




**2p** (*E/Z* = 6:1) **IntA** **4p** (*E/Z*)

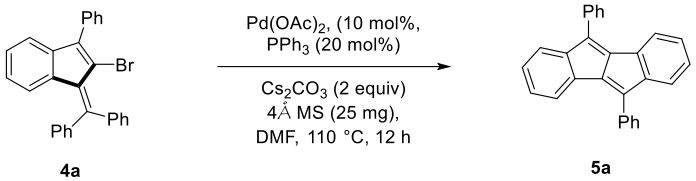
| Entry | Solvent | Temp (℃) | Isolated Yields (%) | *E/Z* ratio |
|---|---|---|---|---|
| 1 | DMF | 25 | 84 | 1.2:1 |
| 2 | AcOH | 60 | 54 | 1:1 |
| 3 | THF | 60 | 51 | 4:1 |
| 4 | Toluene | 60 | 97 | 2.5:1 |

### 2.5 General Procedure for Synthesis of Dibenzopentalenes (5)




To a 25-mL Schlenk tube charged with a stir bar, 2-bromobenzofulvenes (**4**) (0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ ( 2.3 mg, 0.01 mmol, 10 mol%), $PPh_3$ (5.2 mg, 0.02 mmol, 20 mol%), dry $Cs_2CO_3$ (65.2 mg, 0.2 mmol, 2 equiv) and 4Å molecular sieve (4Å MS) (25 mg) were added. After filled with nitrogen, anhydrous DMF (2 mL) were added via a syringe. The mixture was stirred at 110 °C in an oil bath for 12 h. Upon completion, the reaction mixture was quenched with brine (20 mL) and extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over anhydrous $Na_2SO_4$. After that the organic phase was filtered, and concentrated under reduced pressure. The crude products were purified by silica gel chromatography to afford products **5** and **5'** as a brown solid.

**2,7-Dimethyl-5,10-di-*p*-tolylindeno[2,1-a]indene (5a)**




The reaction of 2-bromo-1-(diphenylmethylene)-3-phenyl-1*H*-indene (**4a**, 43.5 mg, 0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 10 mol%), $PPh_3$ (5.2 mg, 0.02 mmol, 20 mol%), $Cs_2CO_3$ (65.2 mg, 0.20 mmol, 1.5 equiv) and 4Å MS (25 mg) afforded **5a** (34.8 mg, 98%) as a brown solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

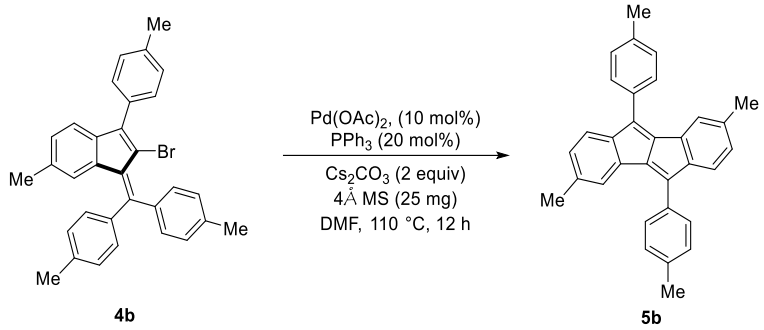
Data of **5a**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 4H), 7.55 – 7.50 (m, 4H), 7.48 – 7.42 (m, 2H), 7.21 (d, $J$ = 7.0 Hz, 2H), 7.03 (d, $J$ = 7.0 Hz, 2H), 6.95 – 6.88 (m, 2H), 6.85 (td, $J$ = 7.5, 1.0 Hz, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.6, 143.1, 140.7, 135.1, 133.9, 128.8, 128.7, 128.5, 127.8, 127.4, 122.5, 121.9.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{19}^+$ 355.1481; Found 355.1462.

**2,7-Dimethyl-5,10-di-*p*-tolylindeno[2,1-a]indene (5b)**




The reaction of 2-bromo-1-(di-*p*-tolylmethylene)-6-methyl-3-(*p*-tolyl)-1*H*-indene (**4b**, 19.0 mg, 0.035 mmol, 1.0 equiv), $Pd(OAc)_2$ (1 mg, 0.004 mmol, 10 mol%), $PPh_3$ (2 mg, 0.008 mmol, 20 mol%), $Cs_2CO_3$ (22.0 mg, 0.07 mmol, 2 equiv) and 4Å MS (15 mg) afforded **5b** (13.5 mg, 94%) as a brown solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

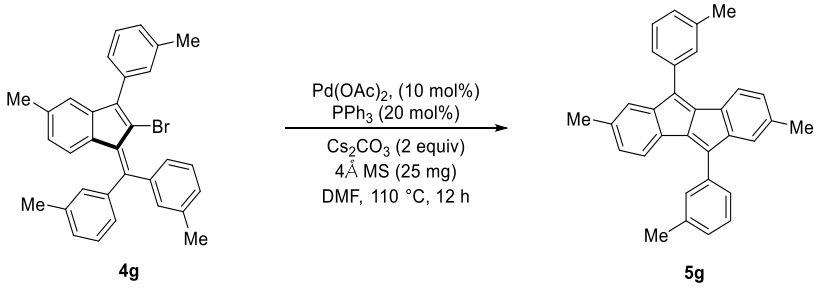
Data of **5b**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.03 (s, 2H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 6H), 2.16 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 146.9, 142.1, 140.4, 138.6, 137.2, 135.6, 131.2, 129.3, 128.4, 127.7, 122.8, 122.1, 21.5, 21.4.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{27}^+$ 411.2107; Found 411.2105.

**3,8-Dimethyl-5,10-di-*m*-tolylindeno[2,1-a]indene (5g)**




The reaction of 2-bromo-1-(di-*m*-tolylmethylene)-5-methyl-3-(*m*-tolyl)-1*H*-indene (**4g**, 24.5 mg, 0.05 mmol, 1.0 equiv), $Pd(OhgAc)_2$ (1.1 mg, 0.005 mmol, 10 mol%), $PPh_3$ (2.7 mg, 0.01 mmol, 20 mol%), $Cs_2CO_3$ (32.5 mg, 0.10 mmol, 2 equiv) and 4Å MS (25 mg) afforded **5g** (19.4 mg, 95%) as a brown solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

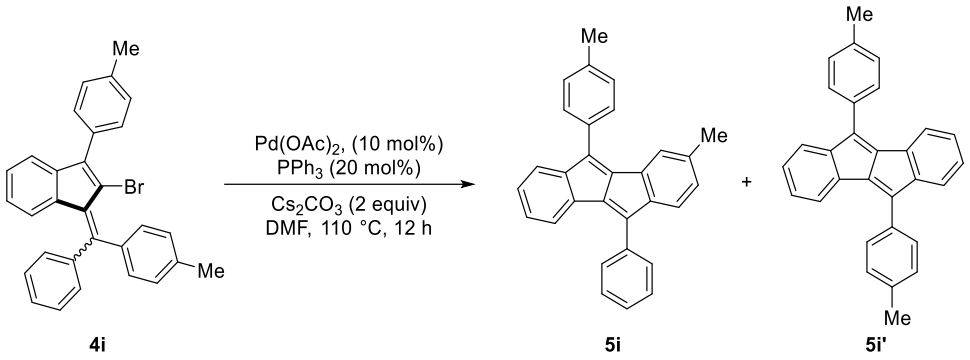
Data of **5g**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 4H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.83 (s, 2H), 6.64 (d, *J* = 7.5 Hz, 2H), 2.46 (s, 6H), 2.20 (s, 6H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 150.1, 143.4, 139.6, 138.2, 137.6, 134.0, 132.4, 129.3, 129.0, 128.5, 127.4, 125.6, 123.4, 121.6, 21.53, 21.51.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{27}^+$ 411.2107; Found 411.2110.

**2-Methyl-5-phenyl-10-(*p*-tolyl)indeno[2,1-a]indene (5i) and 5,10-di-*p*-tolylindeno[2,1-a]indene (5i′)**




4i 5i 5i'

The reaction of 2-bromo-1-(phenyl(*p*-tolyl)methylene)-3-(*p*-tolyl)-1*H*-indene (**4i**, *E/Z* = 1:1, 23.2 mg, 0.05 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol%), $PPh_3$ (2.7 mg, 0.01 mmol, 20 mol%) and $Cs_2CO_3$ (32.5 mg, 0.10 mmol, 2 equiv) afforded **5i** and **5i'** (16.3 mg, 85%) as a mixture of inseparable regio-isomers in a molar ratio of 1:1 of brown solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

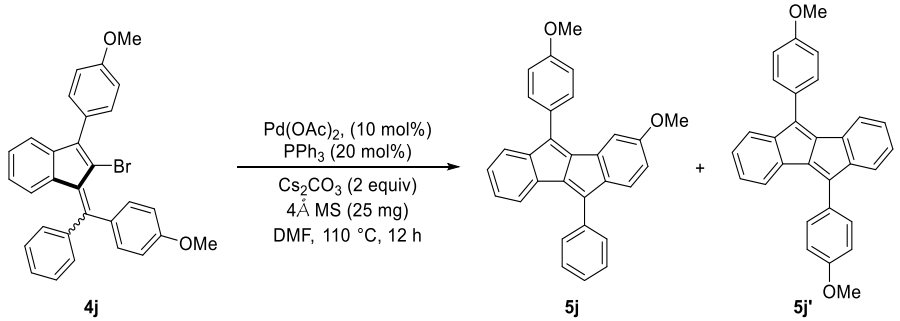
Data of **5i** and **5i'**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 3H), 7.53 – 7.48 (m, 1H), 7.45 – 7.41 (m, 0.5H), 7.36 – 7.30 (m, 3H), 7.21 (dd, *J* = 7.0, 7.0 Hz, 1.5H), 7.06 – 7.00 (m, 2H), 6.91 – 6.86 (m, 2H), 6.85 – 6.80 (m, 1.5H), 6.70 (d, *J* = 7.5 Hz, 0.5H), 2.46 (d, *J* = 7.0 Hz, 4.5H), 2.17 (s, 1.5H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.6, 146.9, 142.7, 142.5, 140.6, 138.8, 137.3, 135.5, 135.3, 134.1, 131.01, 130.95, 129.4, 129.3, 128.7, 128.6, 128.4, 127.9, 127.6, 127.5, 127.28, 127.26, 123.0, 122.41, 122.37, 122.2, 121.8, 121.6, 21.5, 21.4.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}^+$ 383.1794; Found 383.1783.

**2-Methoxy-10-(4'-methoxyphenyl)-5-phenylindeno[2,1-a]indene (5j) and 5,10-bis(4'-methoxyphenyl)indeno[2,1-a]indene (5j′)**




4j 5j 5j'

The reaction of 2-bromo-3-(4'-methoxyphenyl)-1-((4''-methoxyphenyl)(phenyl)methylene)-1*H*-indene (**4j**, *E/Z* = 1:1, 24.7 mg, 0.05 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol%), $PPh_3$ (2.7 mg, 0.01 mmol, 20 mol%), $Cs_2CO_3$ (32.5 mg, 0.10 mmol, 2 equiv) and 4Å MS (25 mg) afforded **5j** and **5j'** (18.2 mg, 88%) as a mixture of inseparable regio-isomers in a molar ratio of 1:1 of brown solid, eluent: petroleum ether/ ethyl acetate = 50:1 to 20:1.

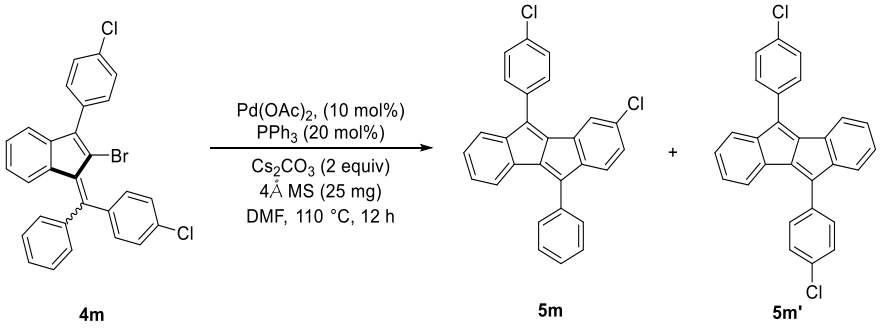
Data of **5j** and **5j'**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.0 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 3H), 7.54 – 7.48 (m, 1H), 7.45 – 7.40 (m, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 0.5H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.80 (m, 4H), 6.38 (d, *J* = 6.0 Hz, 0.5H), 3.90 (s, 4H), 3.73 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.99, 159.96, 149.6, 149.3, 142.33, 142.26, 141.8, 141.7, 140.7, 140.4, 140.0, 137.2, 135.4, 130.0, 129.9, 128.7, 128.6, 128.4, 127.5, 127.3, 127.26, 127.20, 126.3, 126.2, 122.9, 122.44, 122.35, 121.7, 121.4, 114.13, 114.06, 110.3, 110.1, 55.42, 55.36.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}O_2^+$ 415.1693; Found 415.1696.

**2-Chloro-10-(4'-chlorophenyl)-5-phenylindeno[2,1-a]indene (5m) and 5,10-bis(4'-chlorophenyl)indeno[-2,1-a]indene (5m′)**




The reaction of 2-bromo-3-(4'-chlorophenyl)-1-((4''-chlorophenyl)(phenyl)methylene)-1*H*-indene (**4m**, *E/Z* = 1.5:1, 25.2 mg, 0.05 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol%), $PPh_3$ (2.7 mg, 0.01 mmol, 20 mol%), $Cs_2CO_3$ (32.5 mg, 0.10 mmol, 2 equiv) and 4Å MS (25 mg) afforded **5m** and **5m'** (16.7 mg, 78%) as a mixture of inseparable regio-isomers in a molar ratio of 1:1 of brown solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

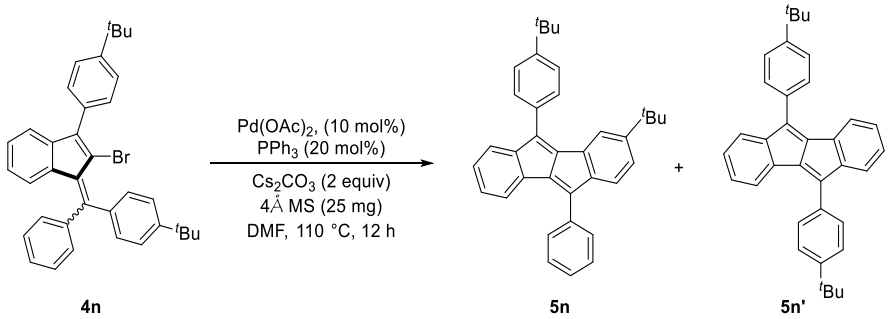
Data of **5m** and **5m'**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 4H), 7.55 – 7.42 (m, 4.5H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 0.5H), 7.07 (s, 1H), 7.00 – 6.94 (t, *J* = 7.5 Hz, 1H), 6.94 – 6.80 (m, 4H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.3, 148.9, 148.0, 143.1, 142.1, 140.6, 136.6, 135.0, 134.9, 134.8, 134.7, 133.5, 133.3, 132.2, 131.9, 129.8, 129.7, 129.2, 129.1, 129.0, 128.8, 128.3, 128.04, 127.97, 127.7, 127.4, 123.1, 122.6, 122.3, 122.12, 122.05, 121.9.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{16}Cl_2Na^+$ 445.0521; Found 445.0536.

**2-(*tert*-Butyl)-10-(4-(tert-butyl)phenyl)-5-phenylindeno[2,1-a]indene (5n) and 5,10-bis(4-(*tert*-butyl)phenyl)indeno[2,1-a]indene (5n′)**




The reaction of 2-bromo-3-(4'-(*tert*-butyl)phenyl)-1-((4''-(*tert*-butyl)phenyl)(phenyl)methylene)-1*H*-indene (**4n**, *E/Z* = 1:1, 27.4 mg, 0.05 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol%), $PPh_3$ (2.7 mg, 0.01 mmol, 20 mol%), $Cs_2CO_3$ (32.5 mg, 0.10 mmol, 2 equiv) and 4ÅMS (25 mg) afforded **5n** and **5n'** (19.8 mg, 85%) as a mixture of inseparable regio-isomers in a molar ratio of 1:1 of brown solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

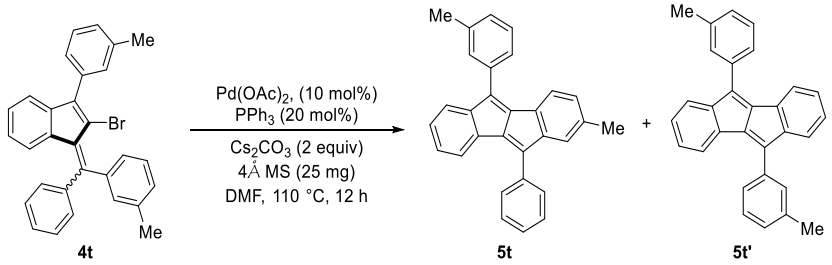
Data of **5n** and **5n'**:

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.68 – 7.64 (m, 2.5H), 7.63 – 7.60 (m, 1H), 7.56 – 7.48 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 1.5 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 0.5H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.97 – 6.81 (m, 4H), 1.41 (d, *J* = 2.0 Hz, 12H), 1.23 (s, 6H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.0, 151.9, 150.7, 149.64, 149.57, 146.9, 143.1, 142.8, 140.4, 140.1, 135.4, 135.3, 134.1, 131.0, 128.61, 128.58, 128.4, 128.31, 128.26, 127.52, 127.46, 127.3, 127.2, 125.5, 125.3, 124.2, 122.53, 122.46, 121.93, 121.88, 121.6, 119.5, 34.9, 34.6, 31.3, 31.0.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{36}H_{35}^+$ 467.2733; Found 467.2729.

**3-Methyl-5-phenyl-10-(*m*-tolyl)indeno[2,1-a]indene and 5,10-Di-*m*-tolylindeno[2,1-a]indene (5t) and (5t′)**




The reaction of 2-bromo-1-(phenyl(*m*-tolyl)methylene)-3-(*m*-tolyl)-1*H*-indene (**4t**, *E/Z* = 1:1, 23.2 mg, 0.05 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 10 mol%), $PPh_3$ (2.7 mg, 0.01 mmol, 20 mol%) and $Cs_2CO_3$ (32.5 mg, 0.10 mmol, 2 equiv) afforded **5t** and **5t'** (16.0 mg, 83%) as a mixture of inseparable regio-isomers in a molar ratio of 1:1 of brown solid, eluent: petroleum ether/ dichloromethane = 50:1 to 20:1.

Data of **5t** and **5t'**:

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 1H), 7.55 – 7.50 (m, 1H), 7.50 – 7.44 (m, 4H), 7.42 – 7.38 (m, 2H), 7.27 (s, 0.5H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 0.5H), 7.11 (d, *J* = 7.5 Hz,

0.5H), 7.05 – 7.00 (m, 1.5H), 6.92 – 6.87 (m, 1.5H), 6.86 – 6.80 (m, 2H), 6.66 (d, $J$ = 7.5 Hz, 0.5H), 2.46 (s, 3.6H), 2.45 (s, 1.2H), 2.20 (s, 1.2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.9, 149.8, 149.7, 143.5, 143.0, 140.7, 140.4, 139.9, 138.3, 137.7, 135.2, 134.0, 133.8, 132.4, 129.5, 129.4, 129.0, 128.6, 128.55, 128.51, 127.7, 127.4, 127.2, 125.6, 123.5, 122.5, 122.3, 121.8, 121.7, 21.5.

**HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}^+$ 383.1794; Found 383.1786.

## 3. References


1 T.-J. Hu, G. Zhang, Y.-H. Chen, C.-G. Feng and G.-Q. Lin, Borylation of Olefin C–H Bond via Aryl to Vinyl Palladium 1,4-Migration, *J. Am. Chem. Soc.*, 2016, **138**, 2897.

2 G. Zhang, X.-J. Feng, M.-Y. Li, X.-M. Ji, G.-Q. Lin and C.-G. Feng, Synthesis of Tetrasubstituted Allenes via a 1,4-Palladium Migration/Carbene insertion/*β*-H Elimination Sequence, *Org. Biomol. Chem.,* 2022, **20**, 5383.

3 H. Chen, L.-Z. Gao, X.-T. Liu, G.-Q. Wang, S.-H. Li, $B(C_6F_5)_3$-Catalyzed Hydroarylation of Aryl Alkynes for the Synthesis of 1,1-Diaryl and Triaryl Substituted Alkenes, *Eur. J. Org. Chem.,* 2021, **2021**, 5238.

## 4. Copies of $^{1}$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra of Products

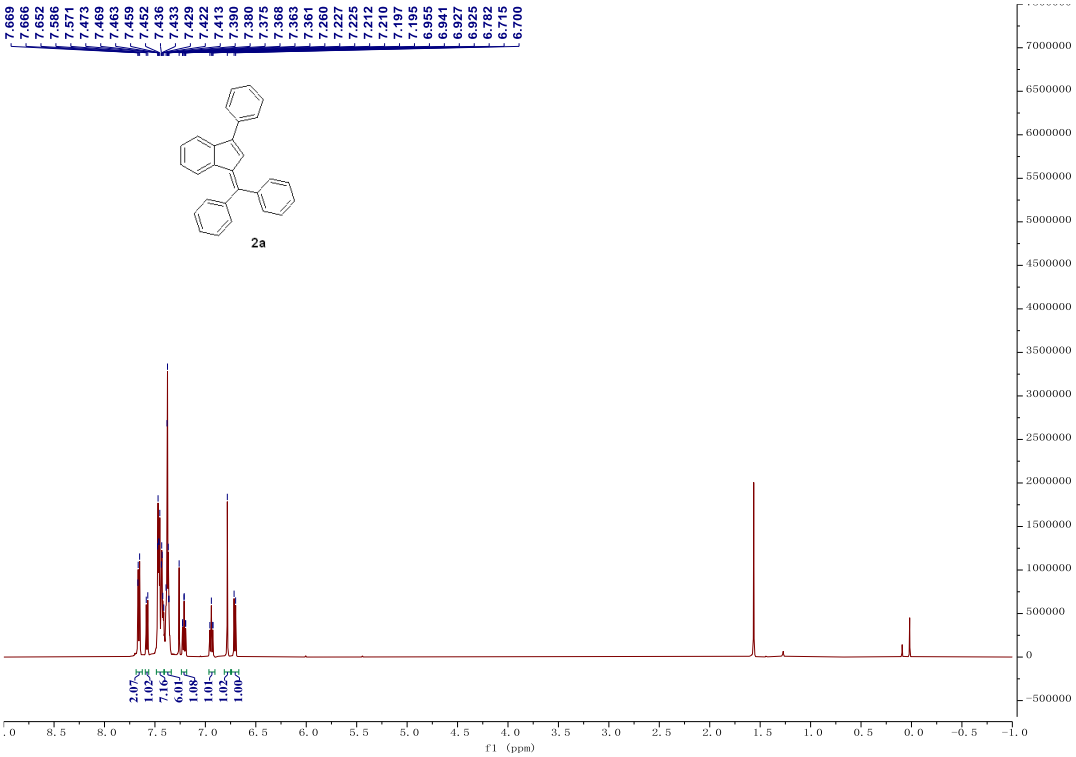



**Figure S3.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2a**

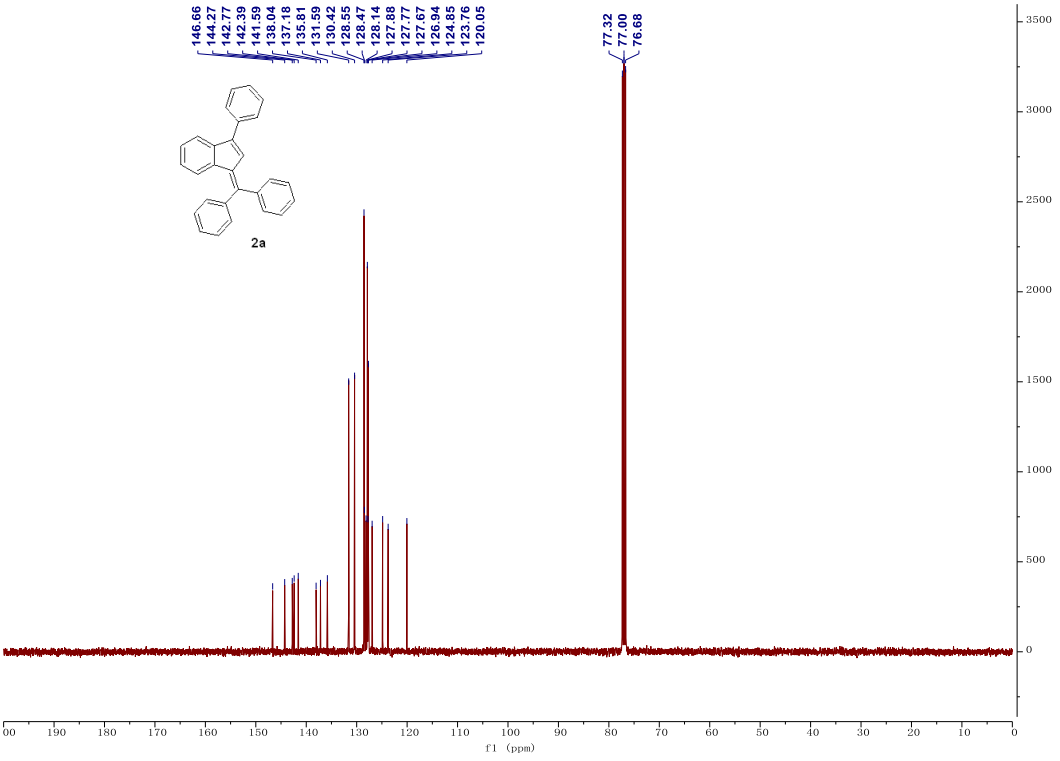



**Figure S4.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2a**

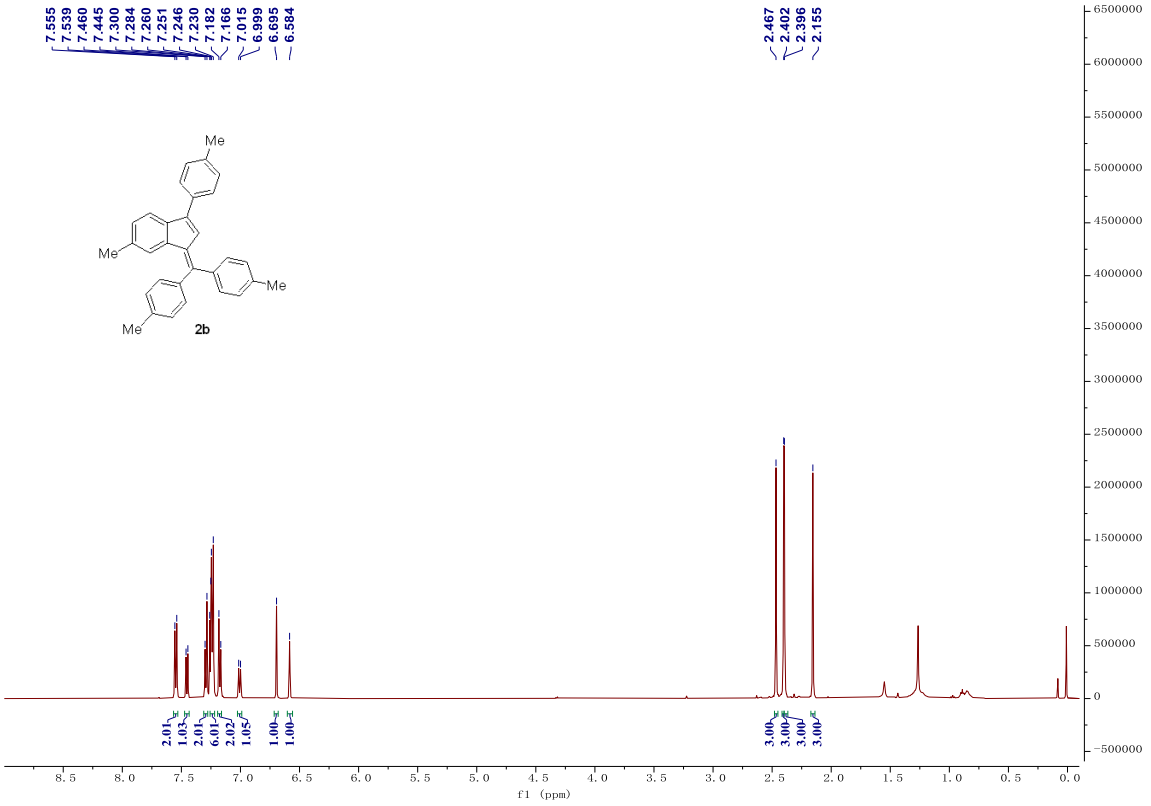



**Figure S5.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2b**

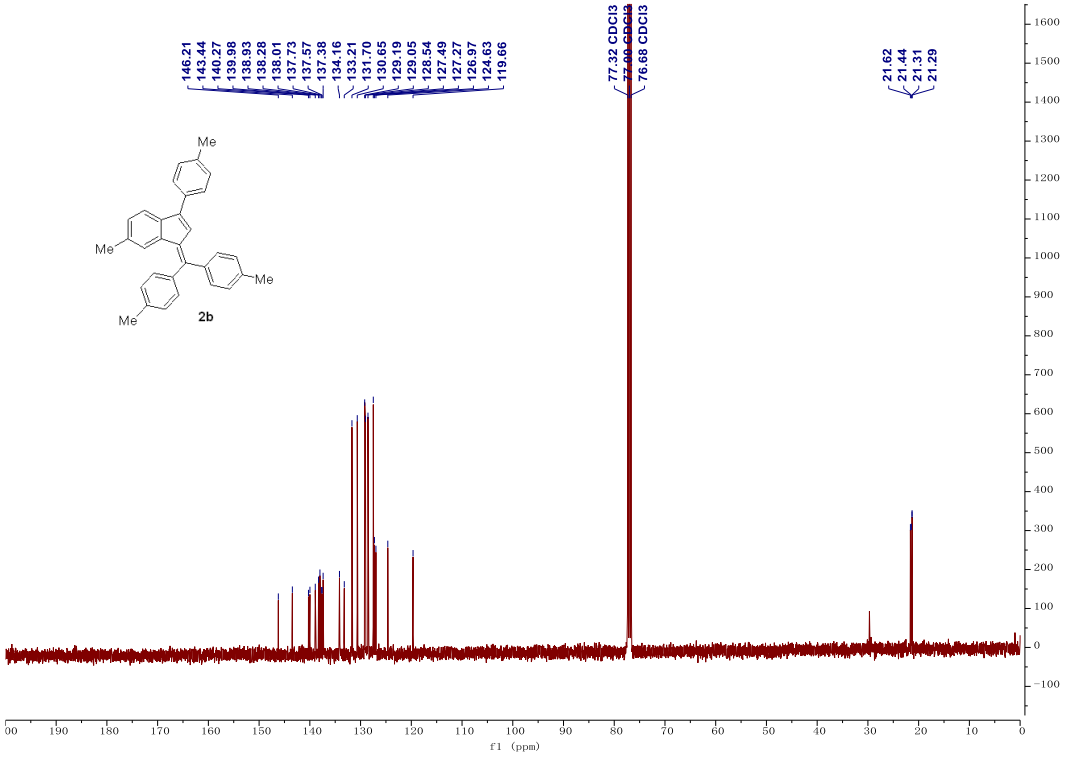



**Figure S6.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2b**

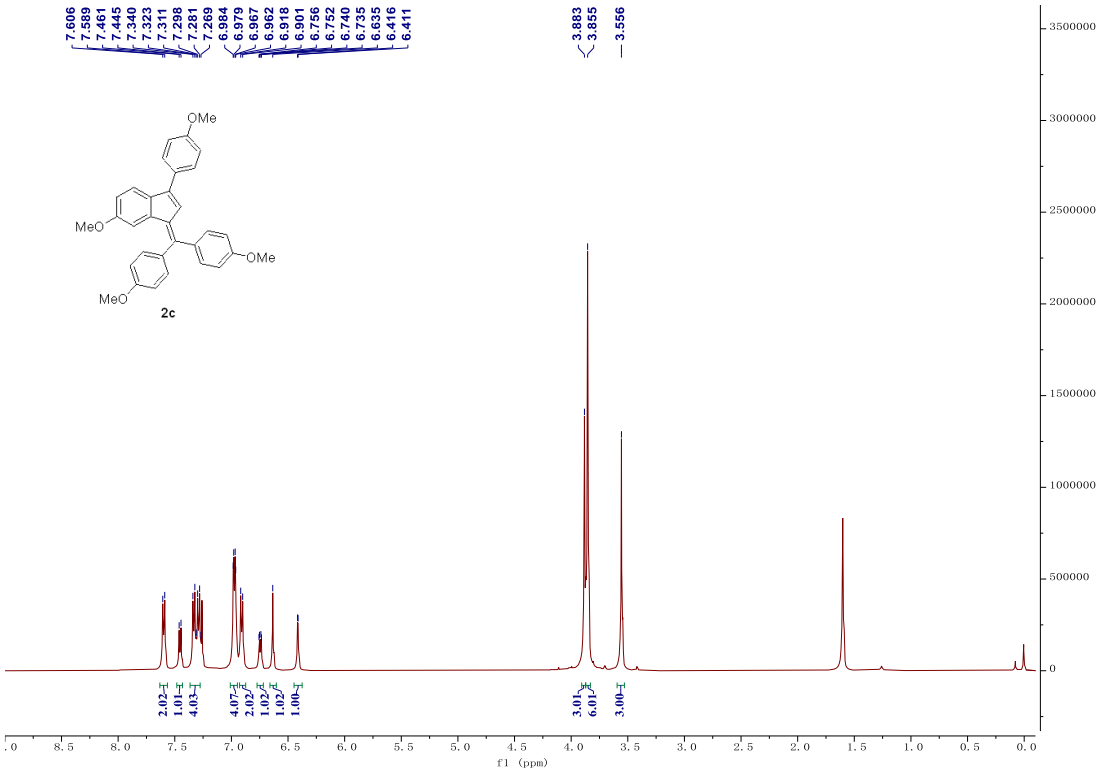



**Figure S7.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2c**

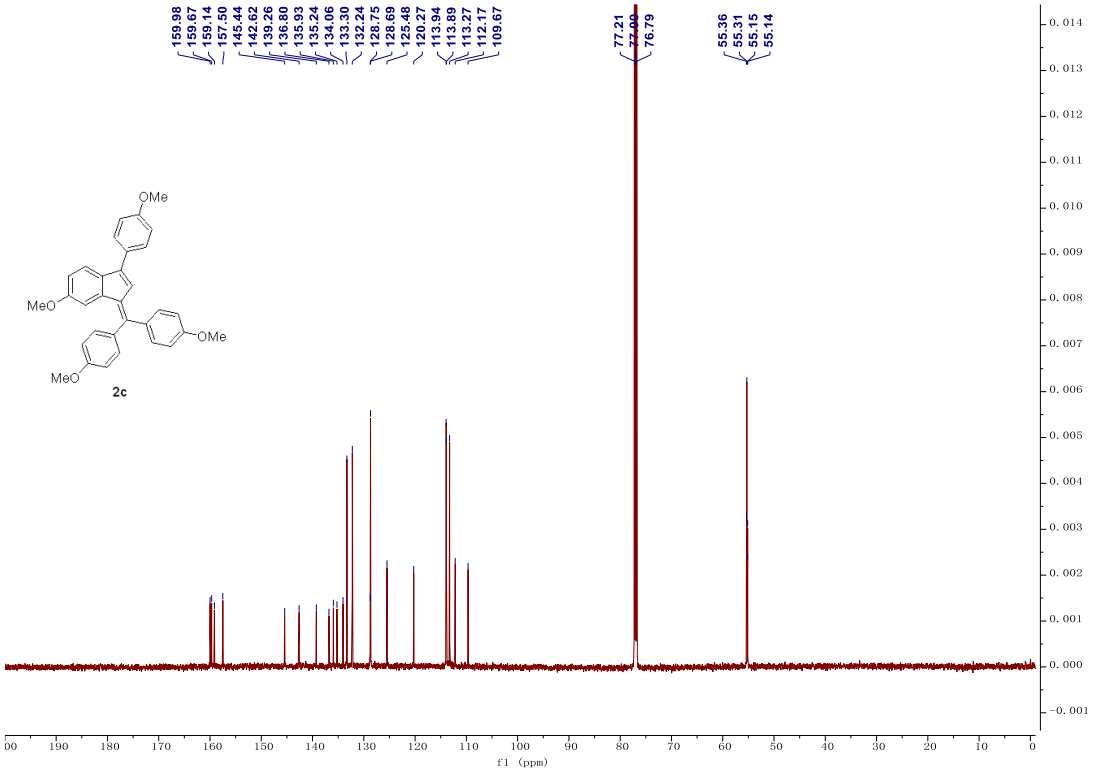



**Figure S8.** $^{13}$C NMR (151 MHz, $CDCl_3$) of **2c**

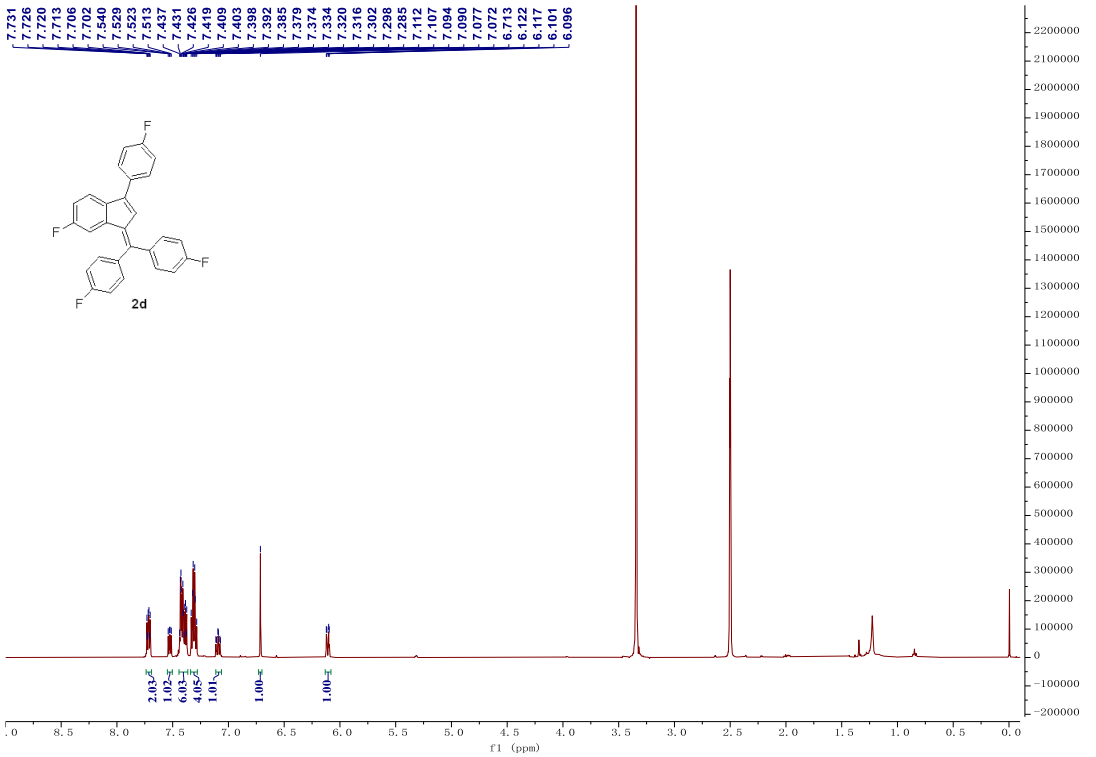



**Figure S9.** $^{1}$H NMR (500 MHz, DMSO) of **2d**

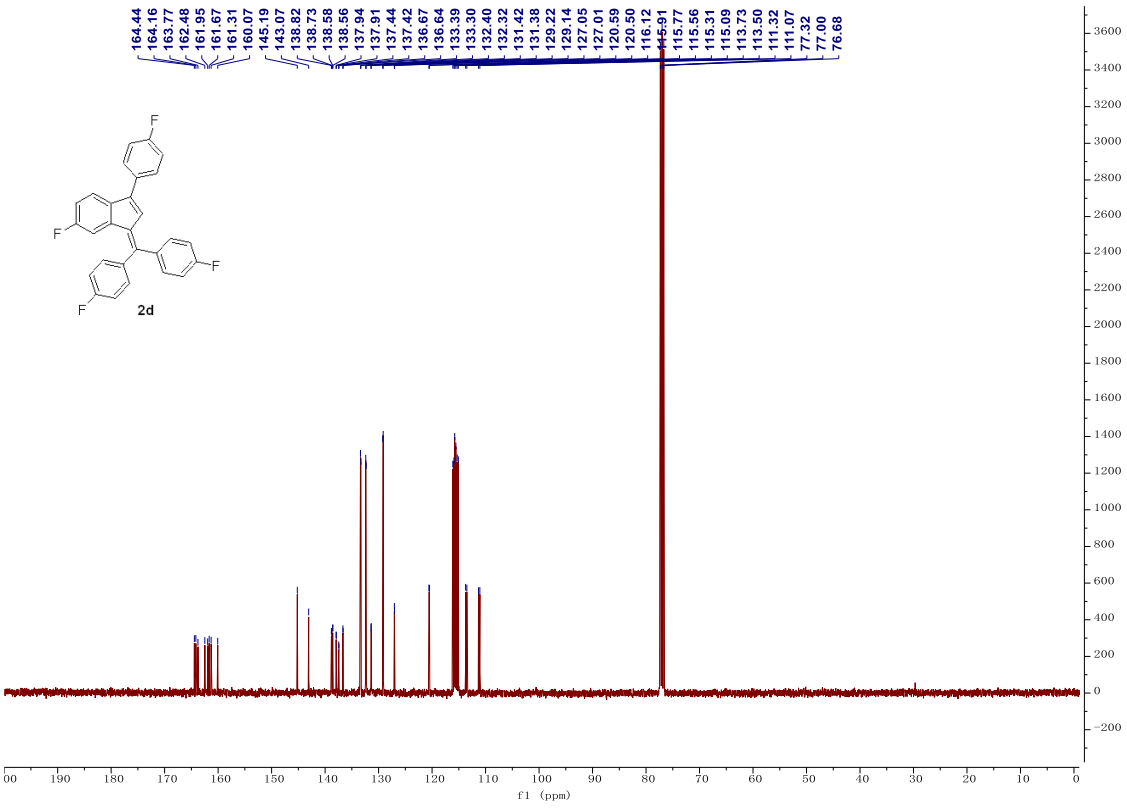



**Figure S10.** $^{13}$C NMR (101 MHz, DMSO) of **2d**

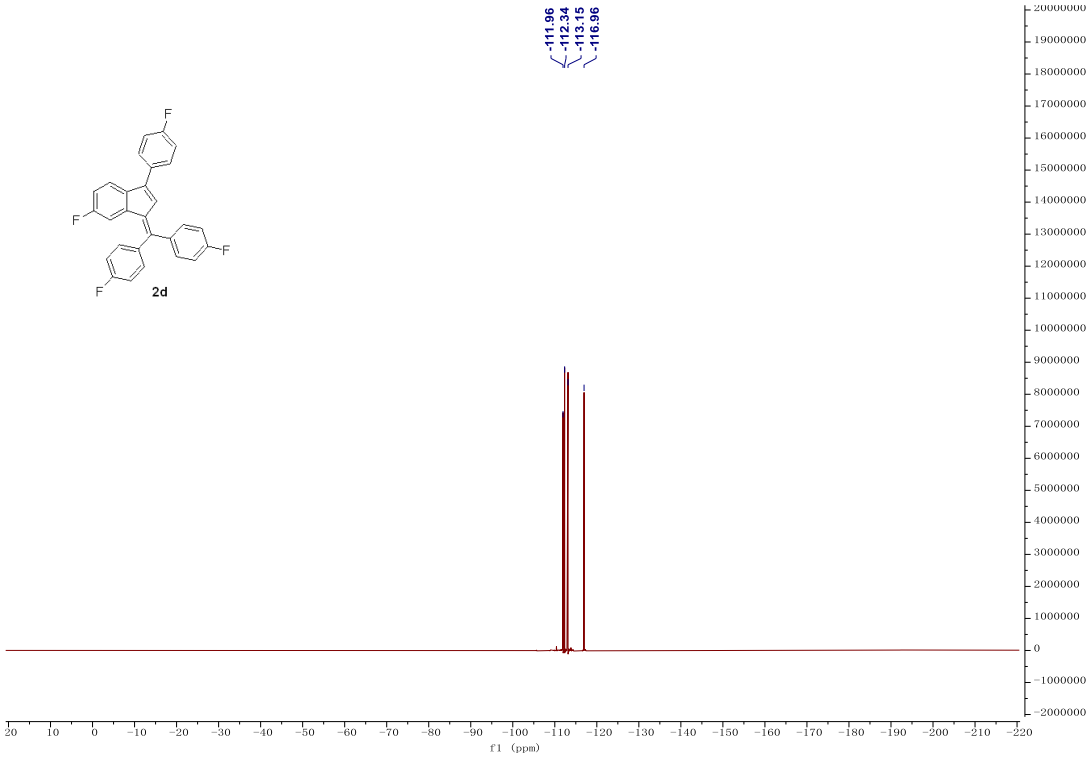



**Figure S11.** $^{19}F$ NMR (471 MHz, DMSO) of **2d**

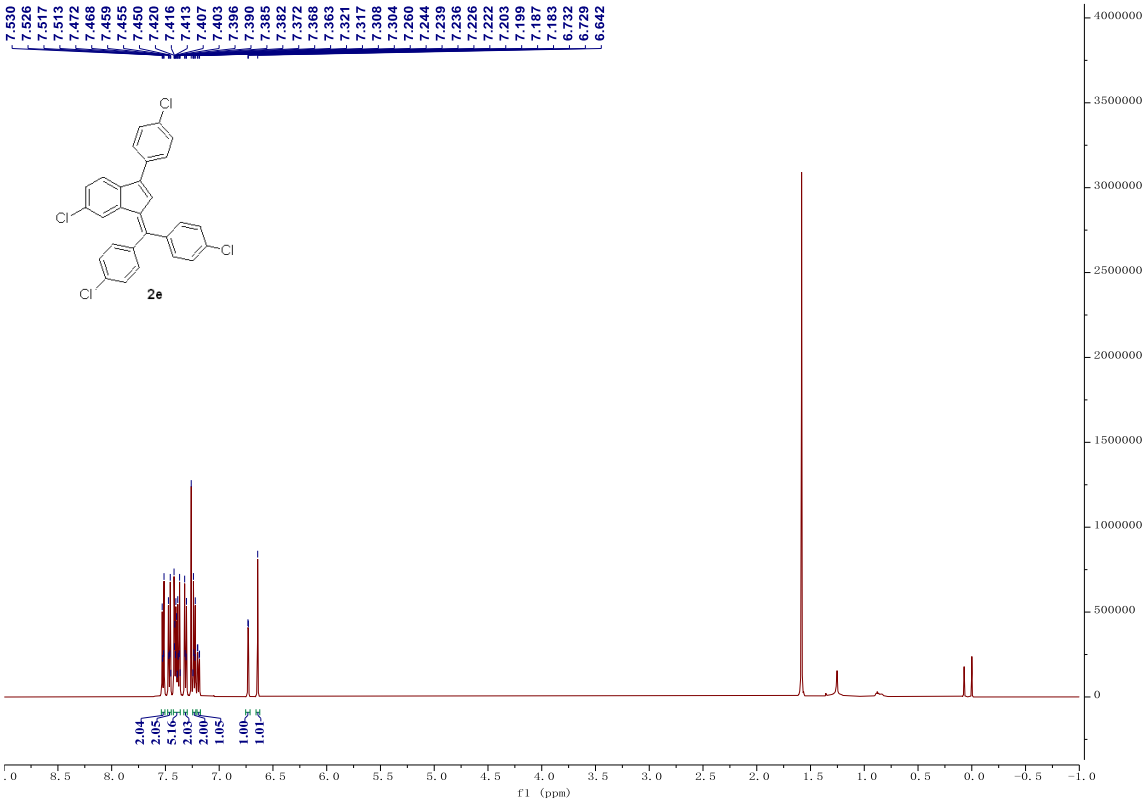



**Figure S12.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2e**

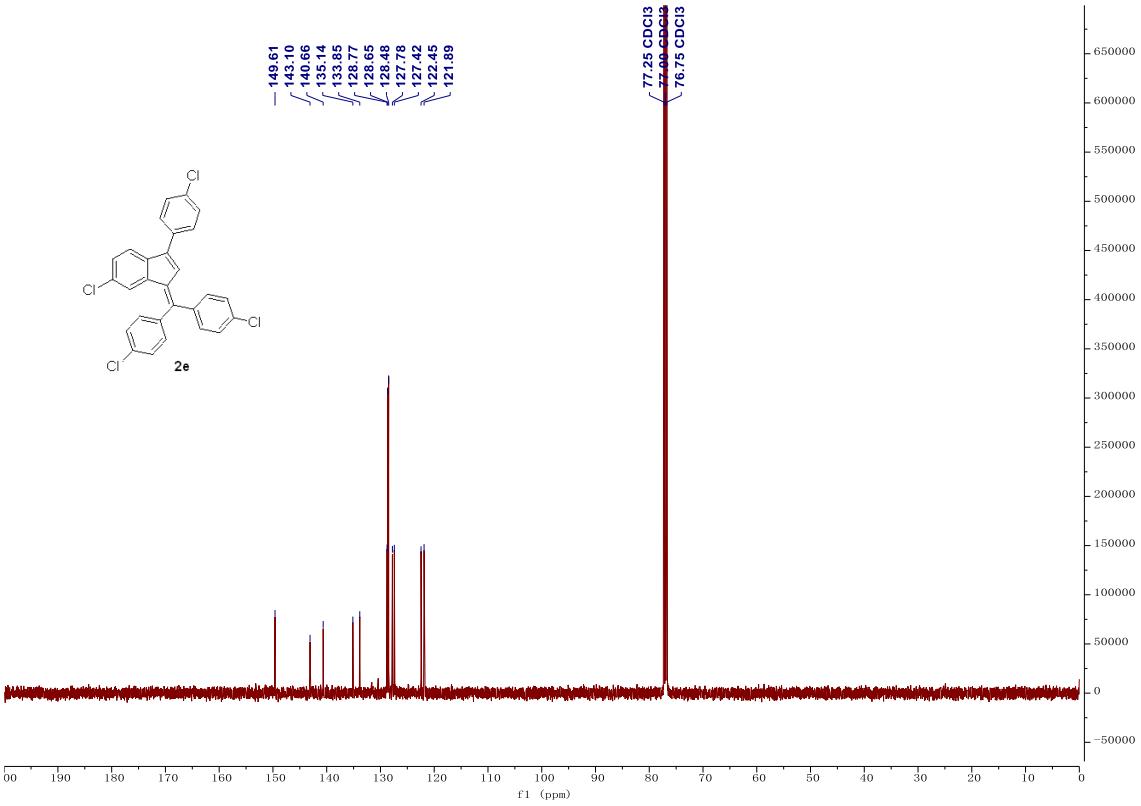



**Figure S13.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **2e**

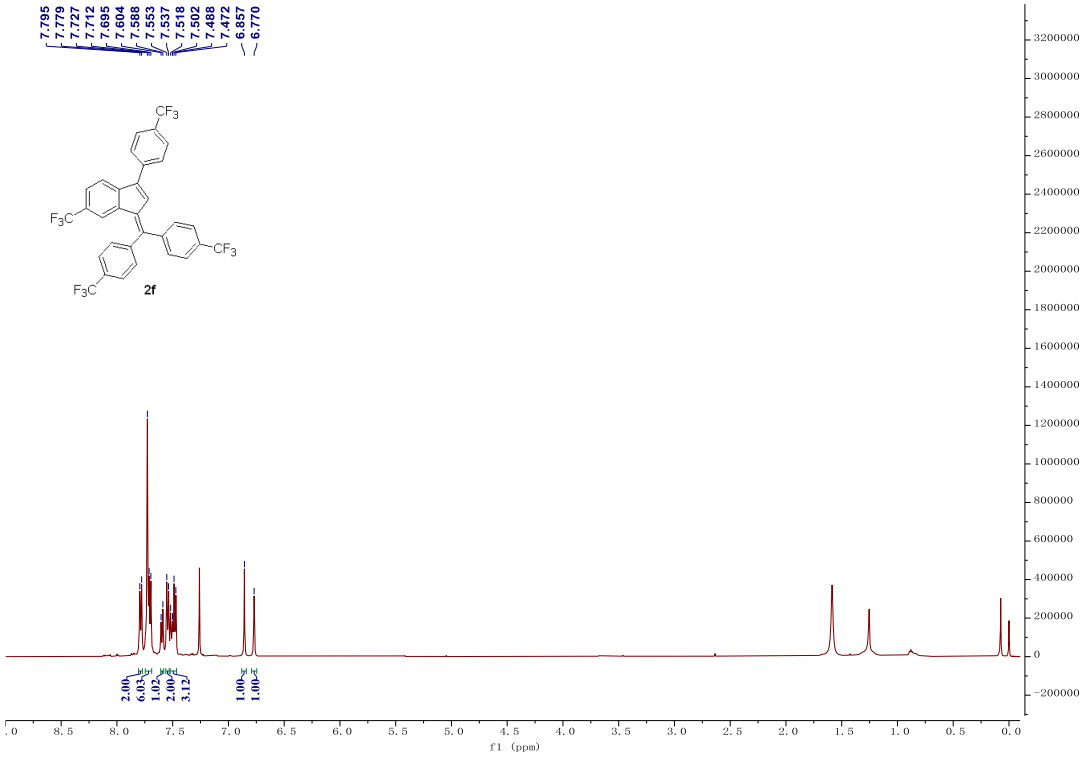



**Figure S14.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2f**

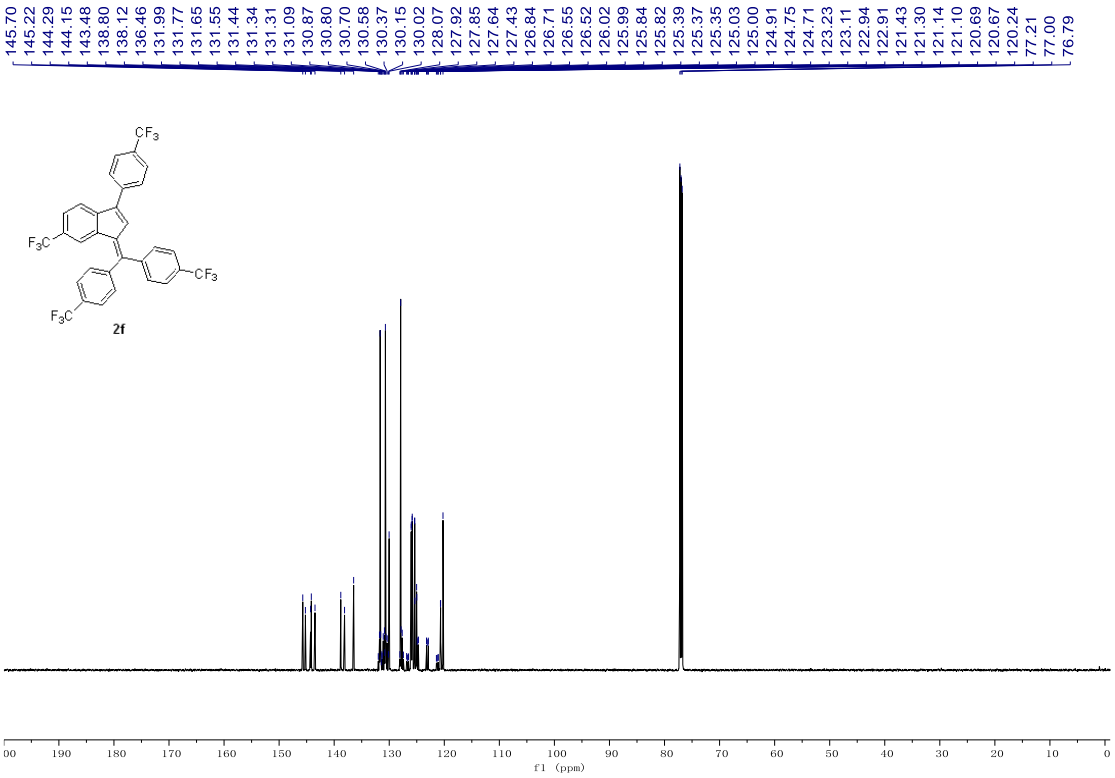



**Figure S15.** $^{13}C$ NMR (151 MHz, $CDCl_3$) of **2f**

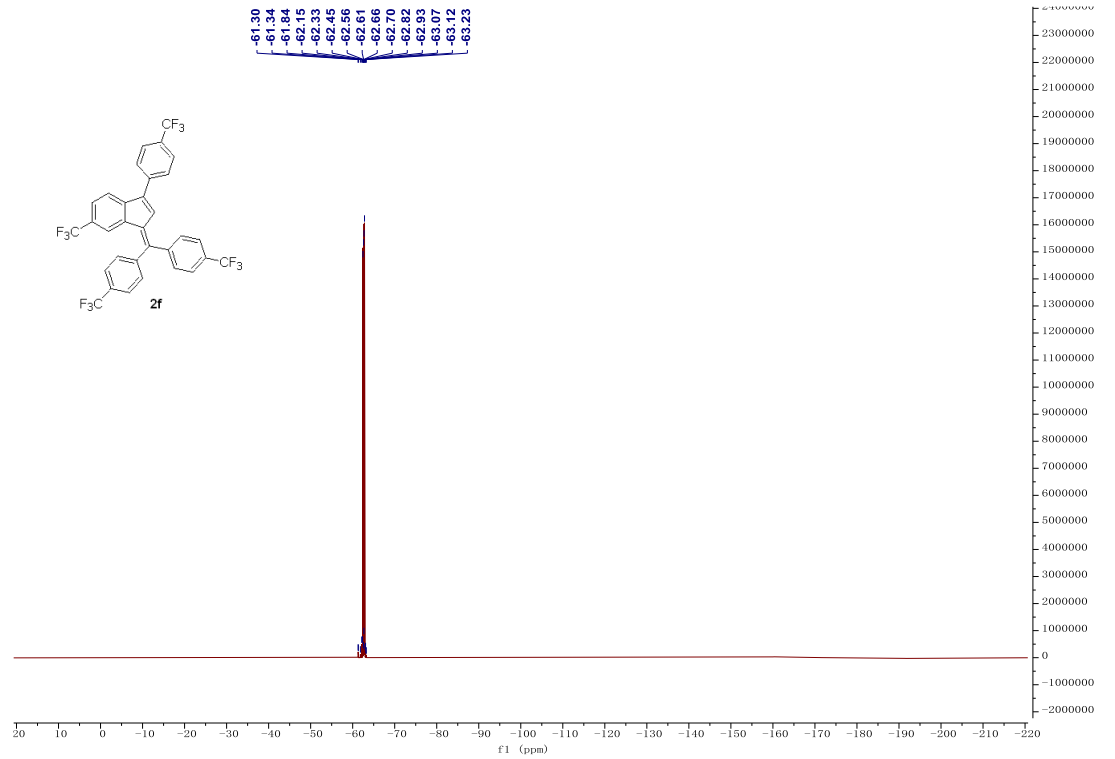



**Figure S16.** $^{19}F$ NMR (471 MHz, $CDCl_3$) of **2f**

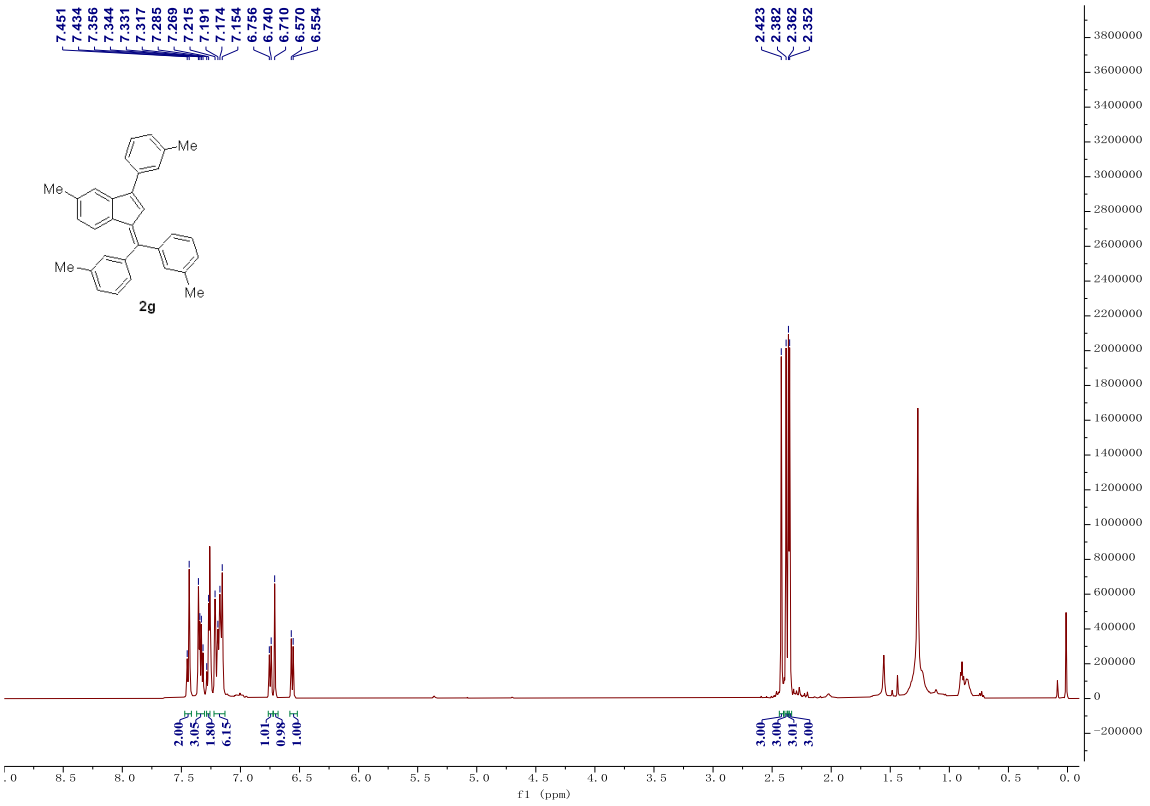



**Figure S17.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2g**

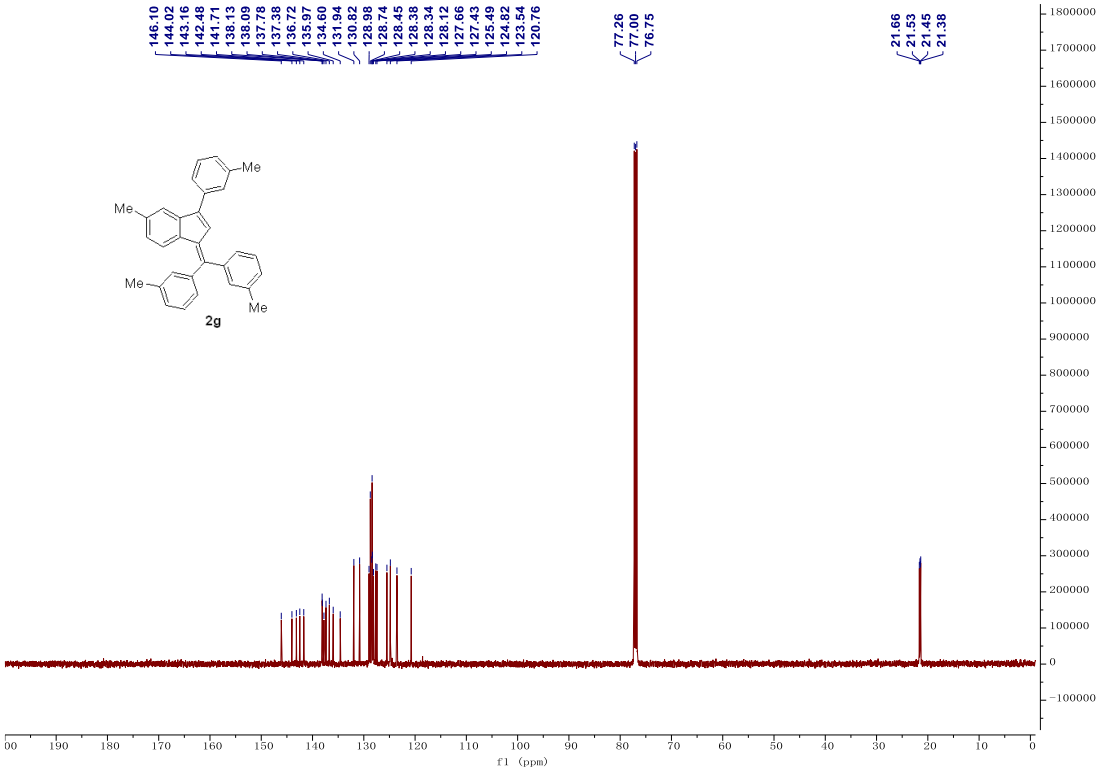



**Figure S18.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2g**

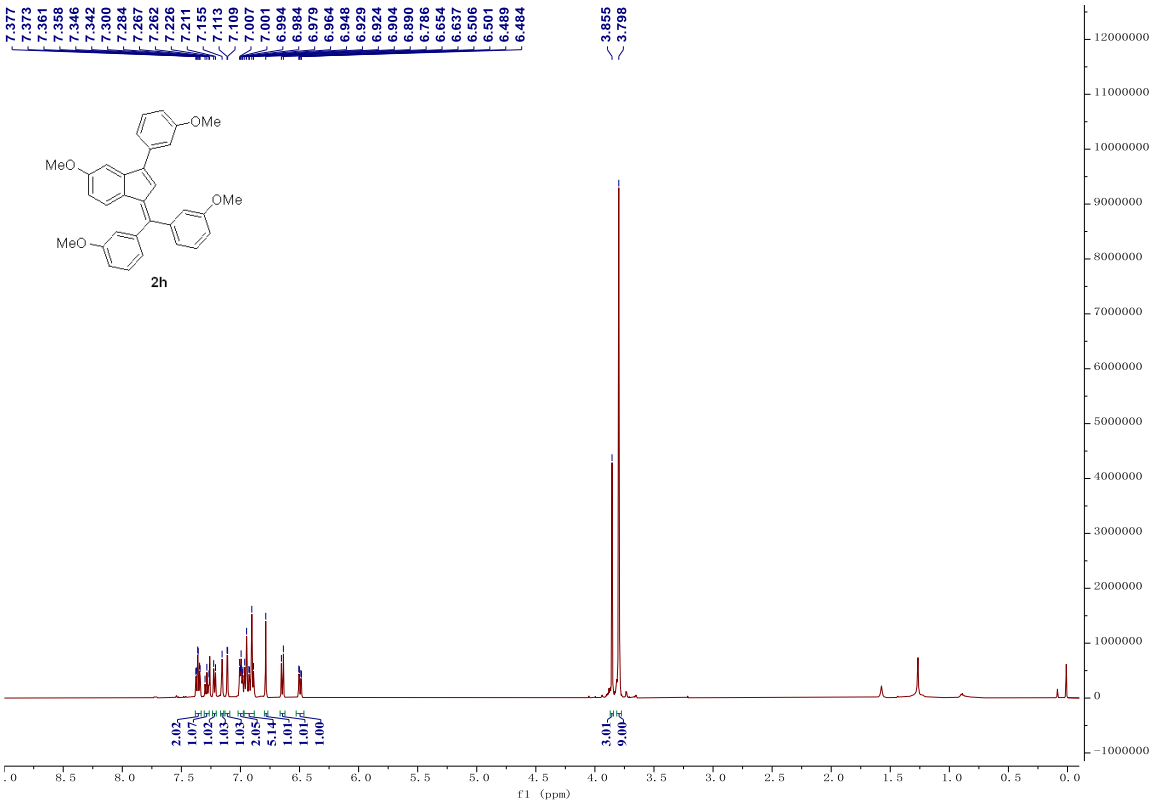



**Figure S19.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2h**

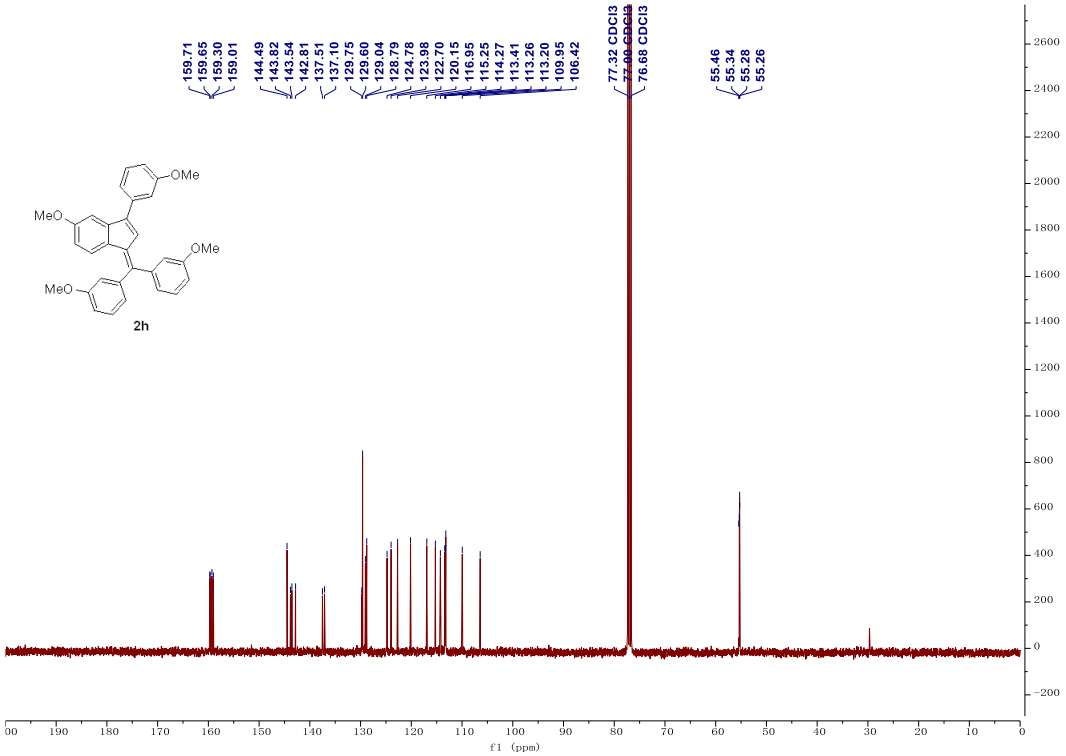



**Figure S20.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2h**

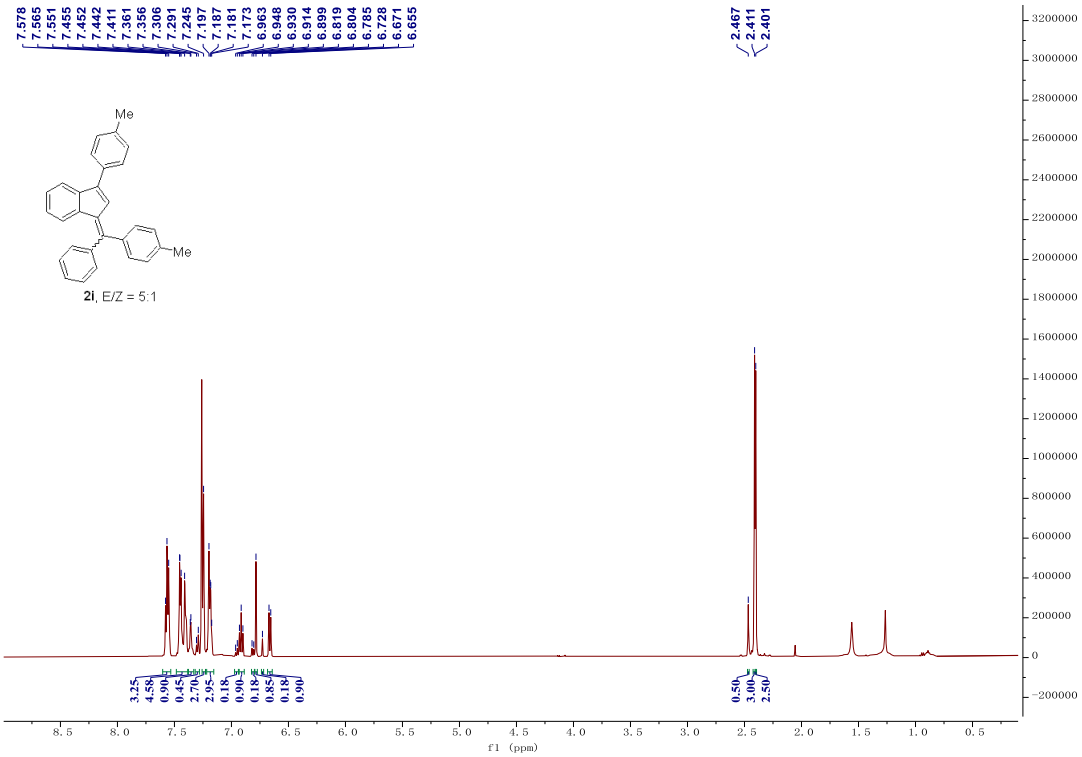



**Figure S21.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2i**

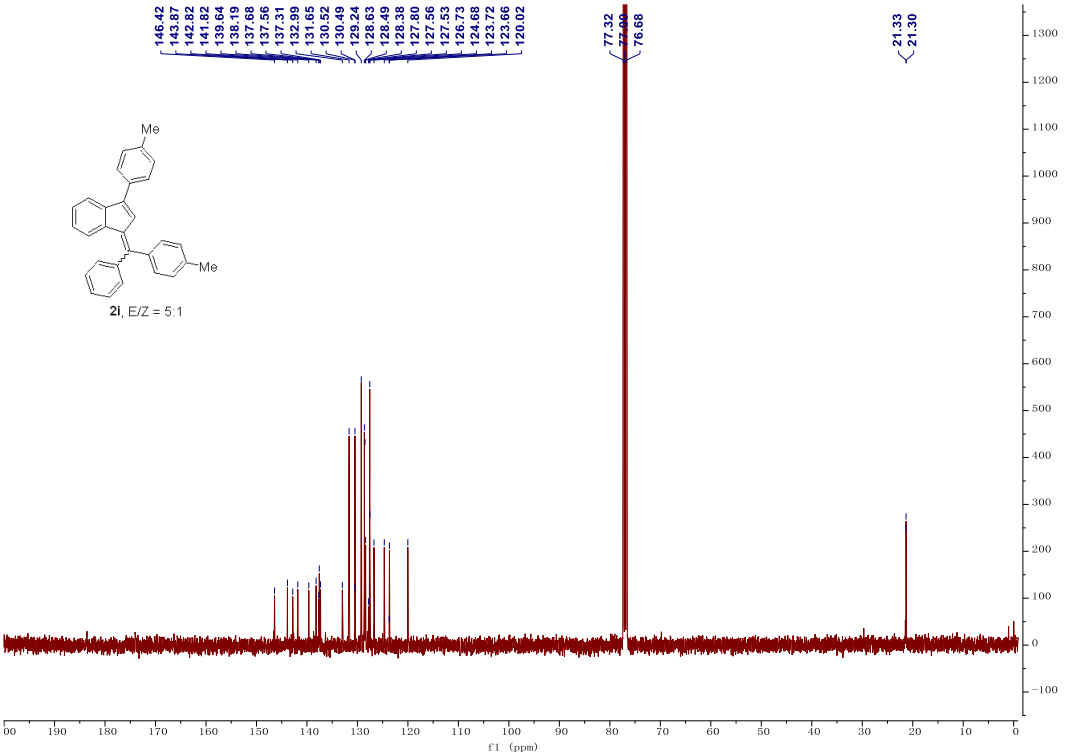



**Figure S22.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2i**

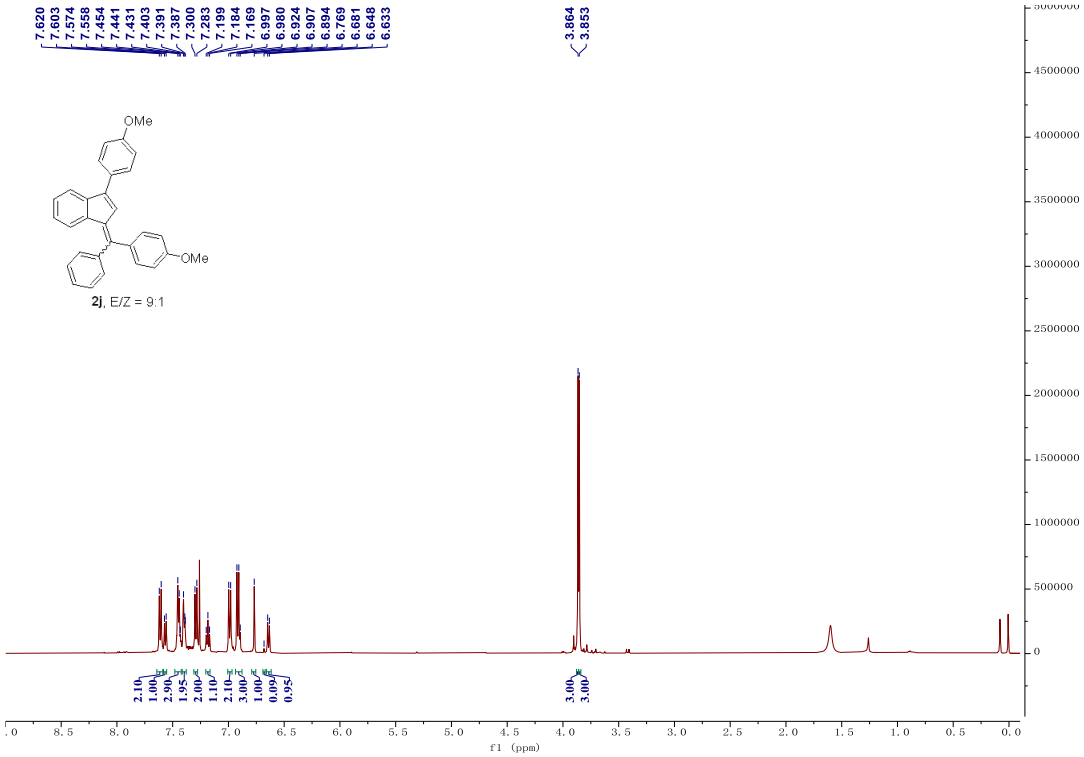



**Figure S23.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2j**

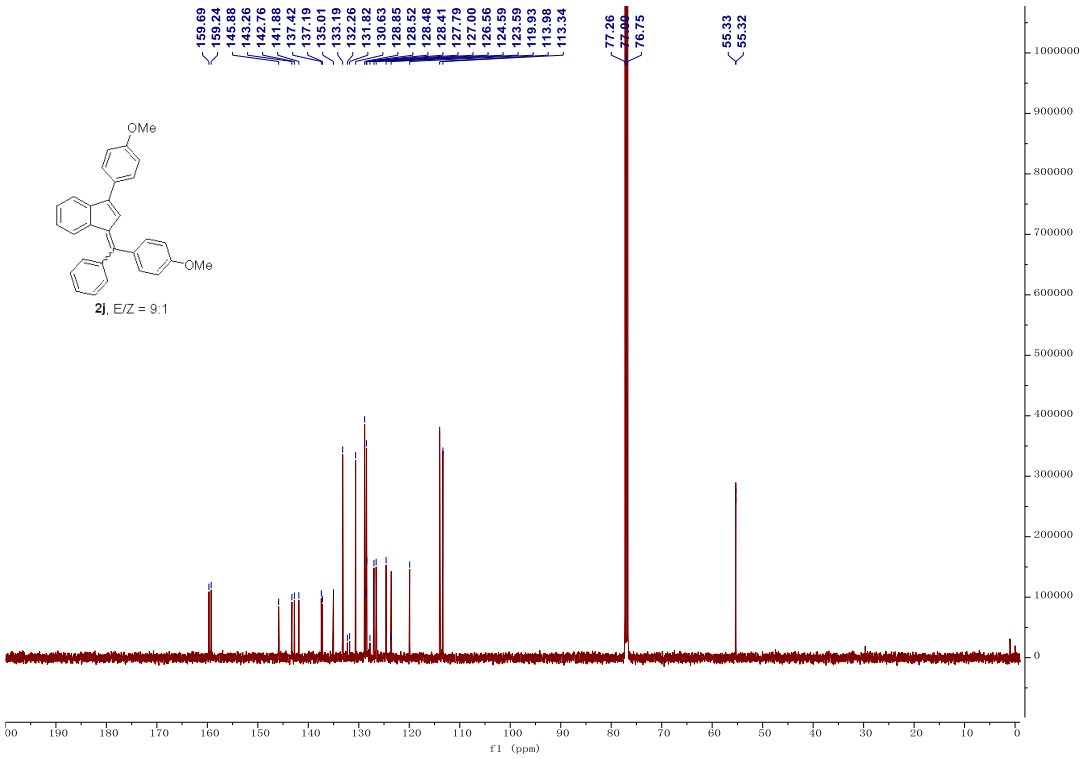



**Figure S24.** $^{13}$C NMR (126 MHz, $CDCl_3$) of **2j**

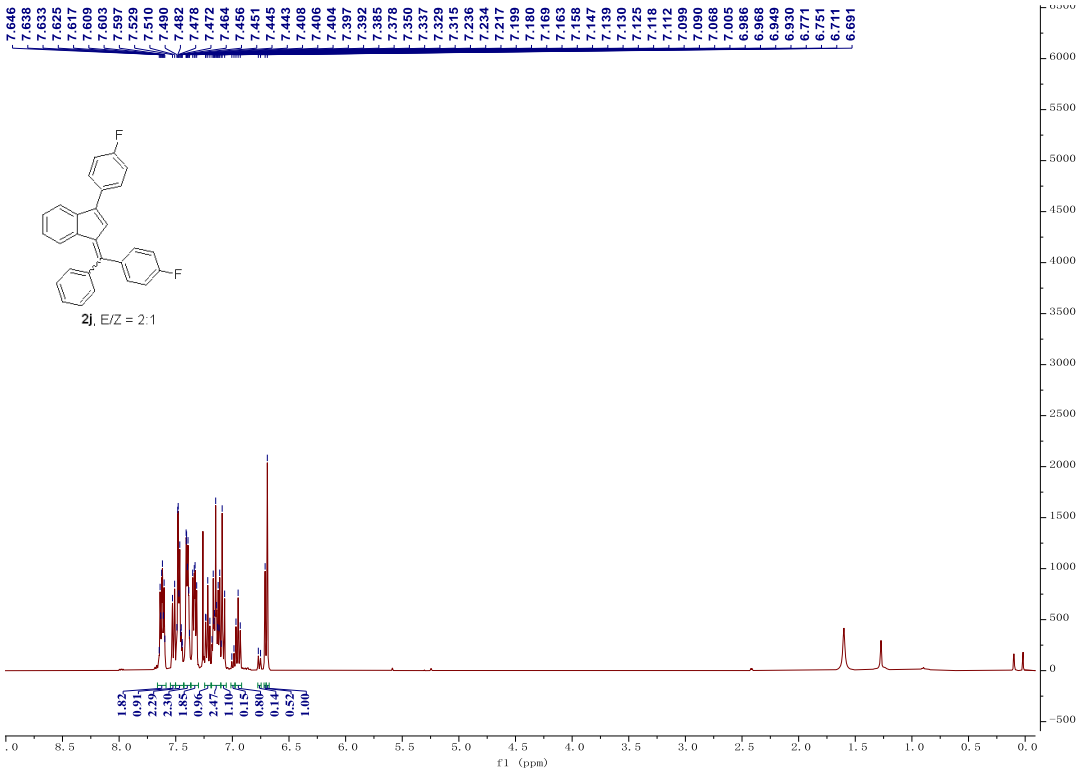



**Figure S25.** $^{1}H$ NMR (400 MHz, $CDCl_3$) of **2j**

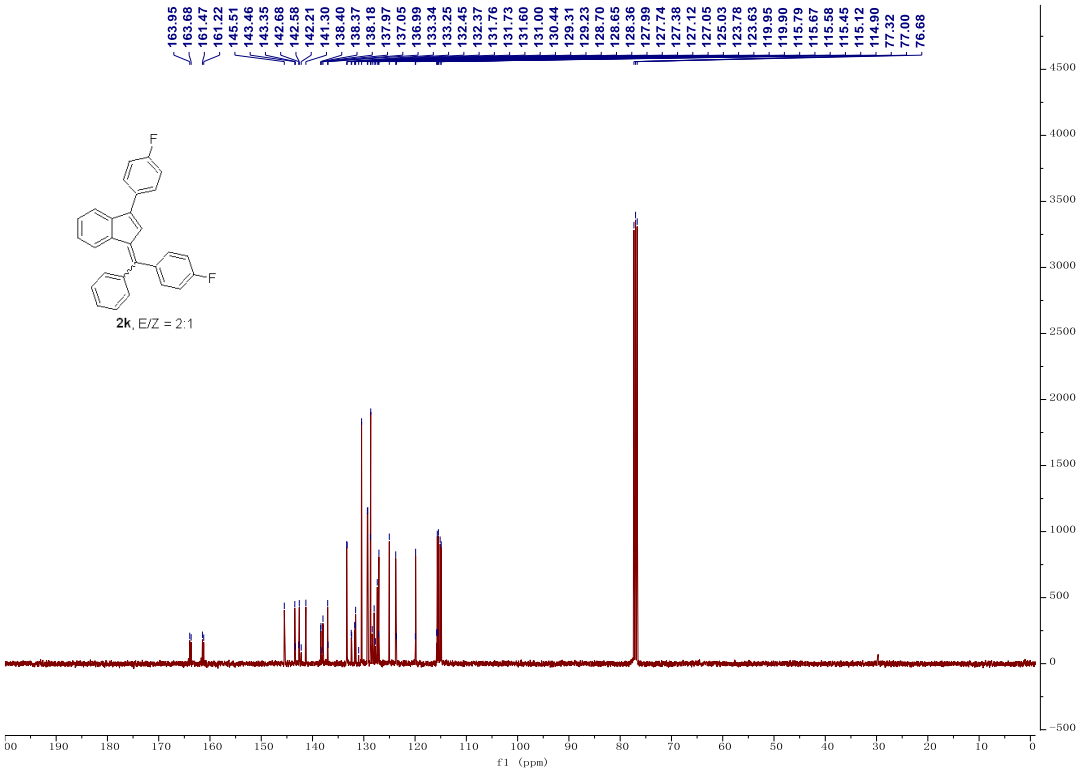



**Figure S26.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **2k**

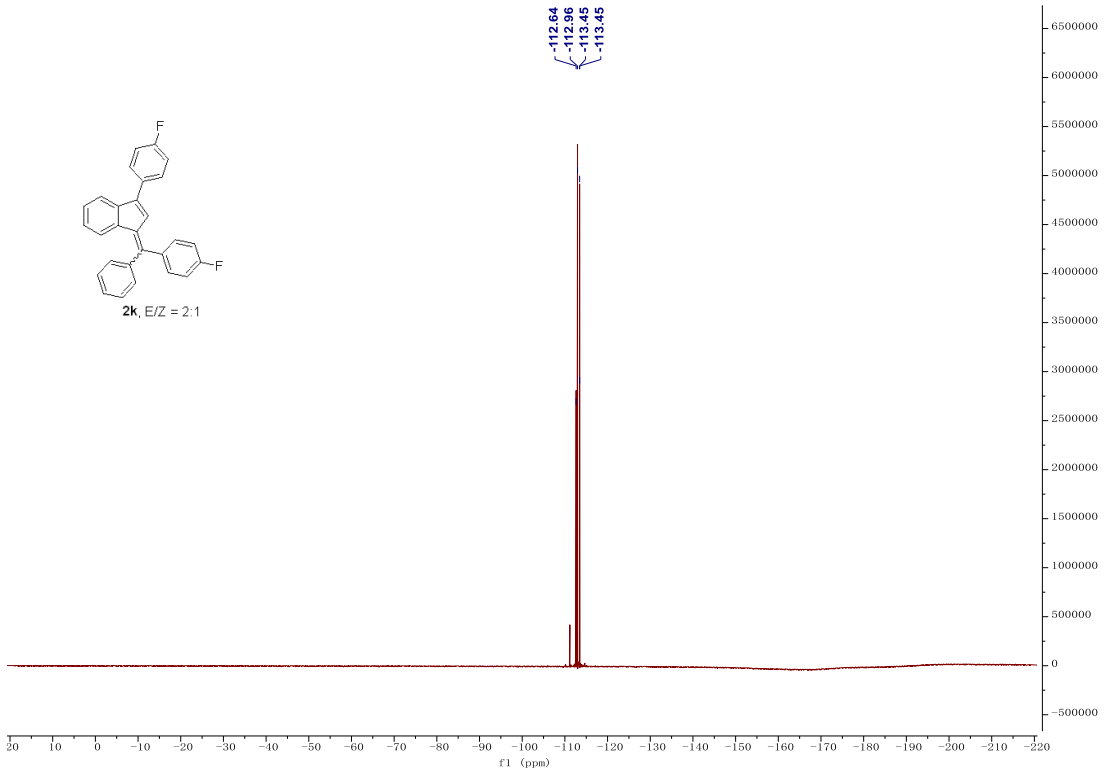



**Figure S27.** $^{19}F$ NMR (471 MHz, DMSO) of **2k**

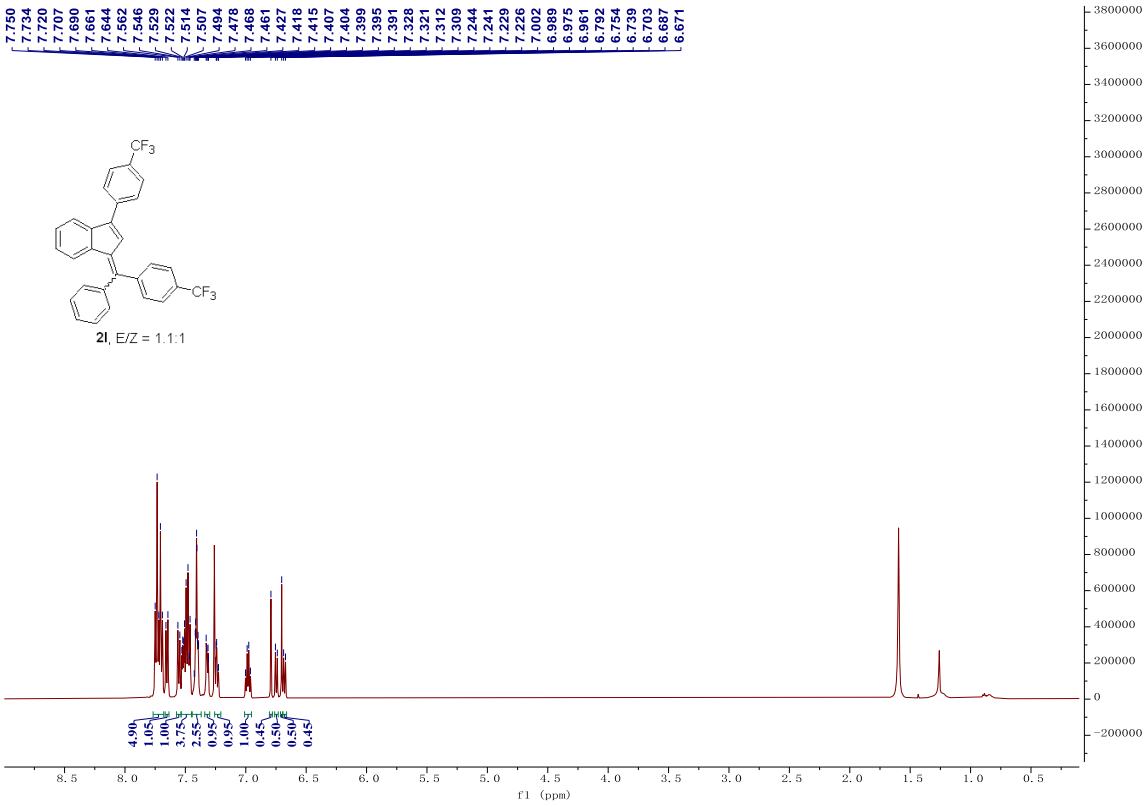



**Figure S28.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2l**

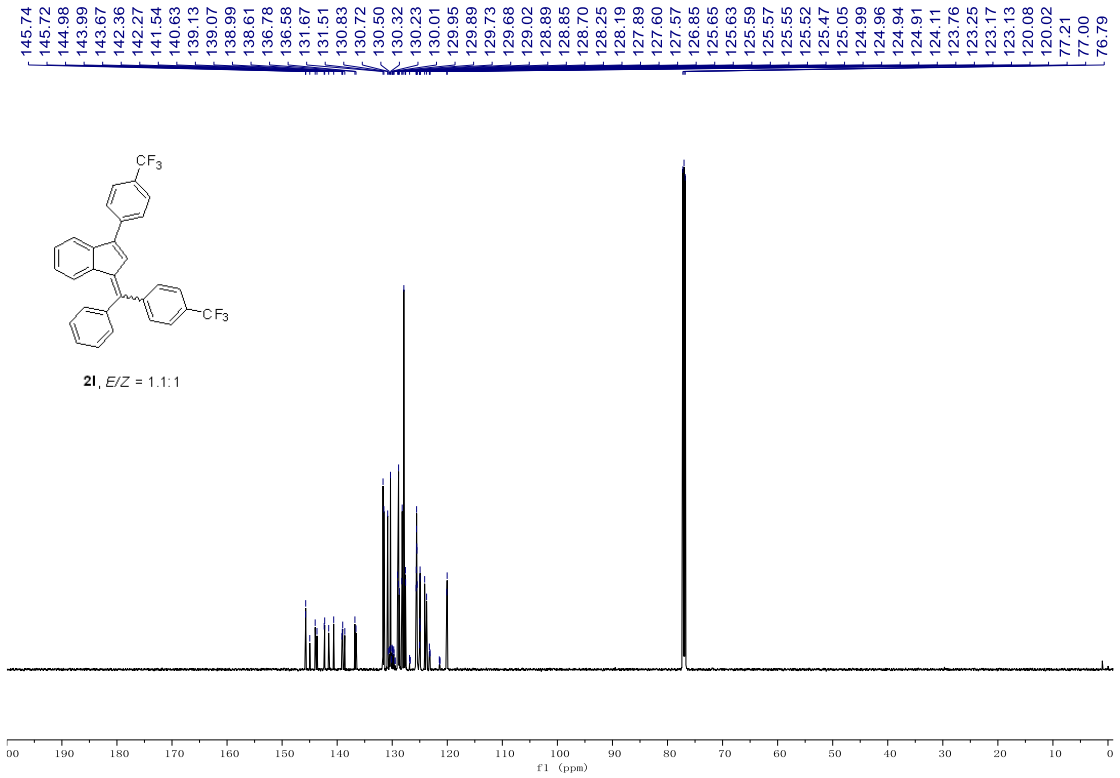



**Figure S29.** $^{13}C$ NMR (151 MHz, $CDCl_3$) of **2l**

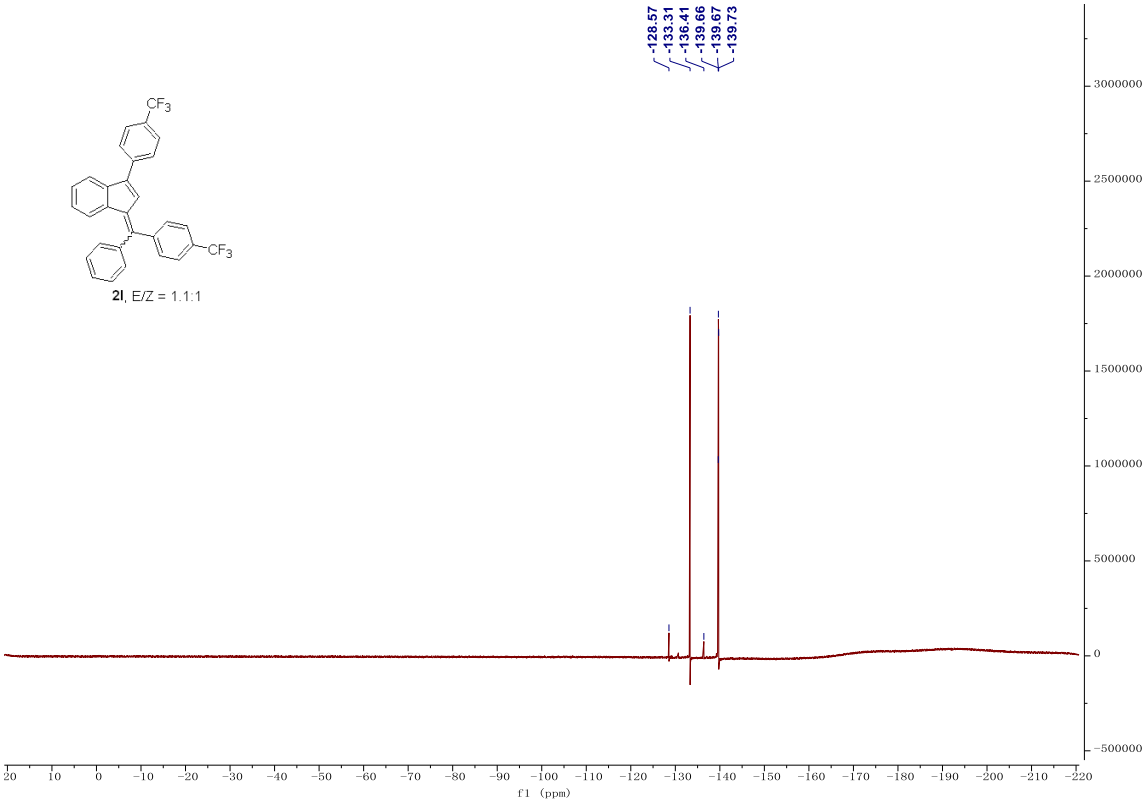



**Figure S30.** $^{19}F$ NMR (471 MHz, $CDCl_3$) of **2l**

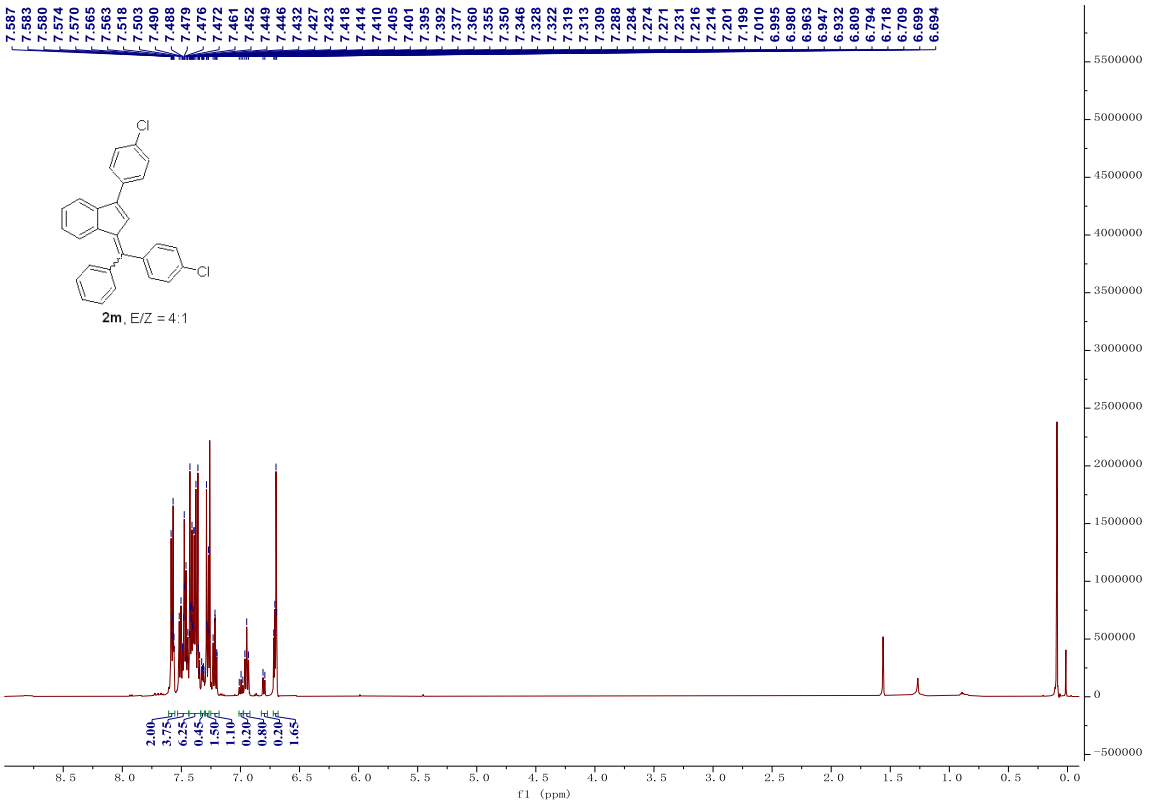



**Figure S31.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2m**

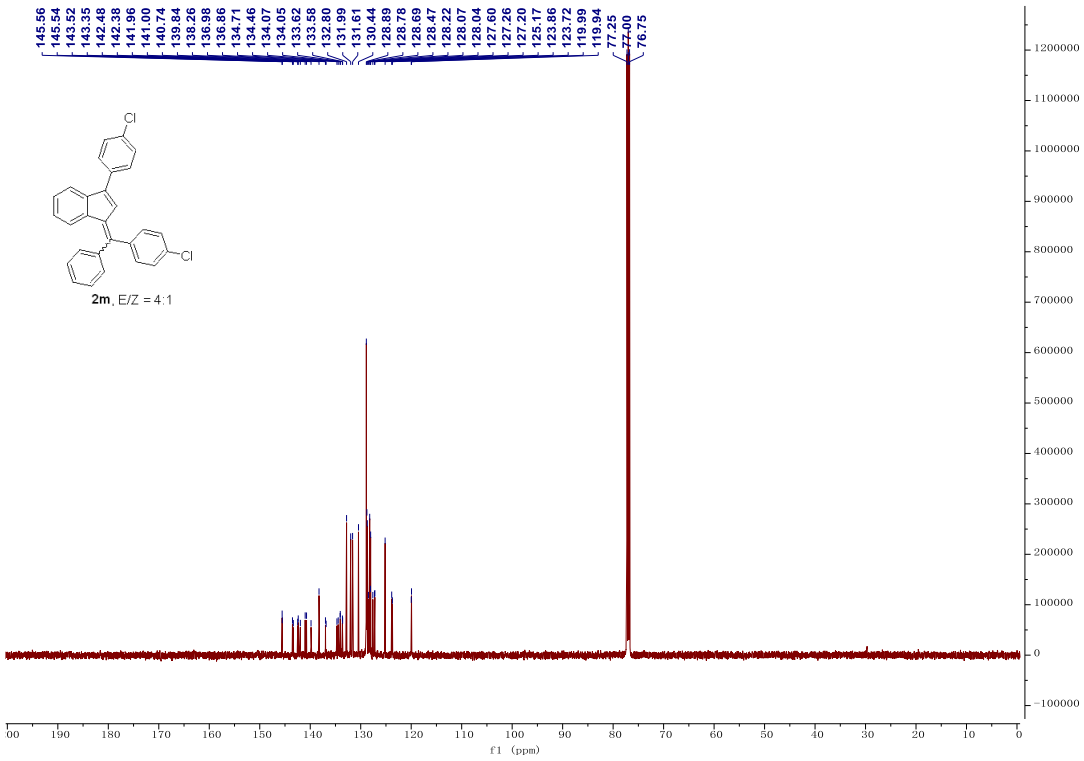



**Figure S32.** $^{13}$C NMR (126 MHz, $CDCl_3$) of **2m**

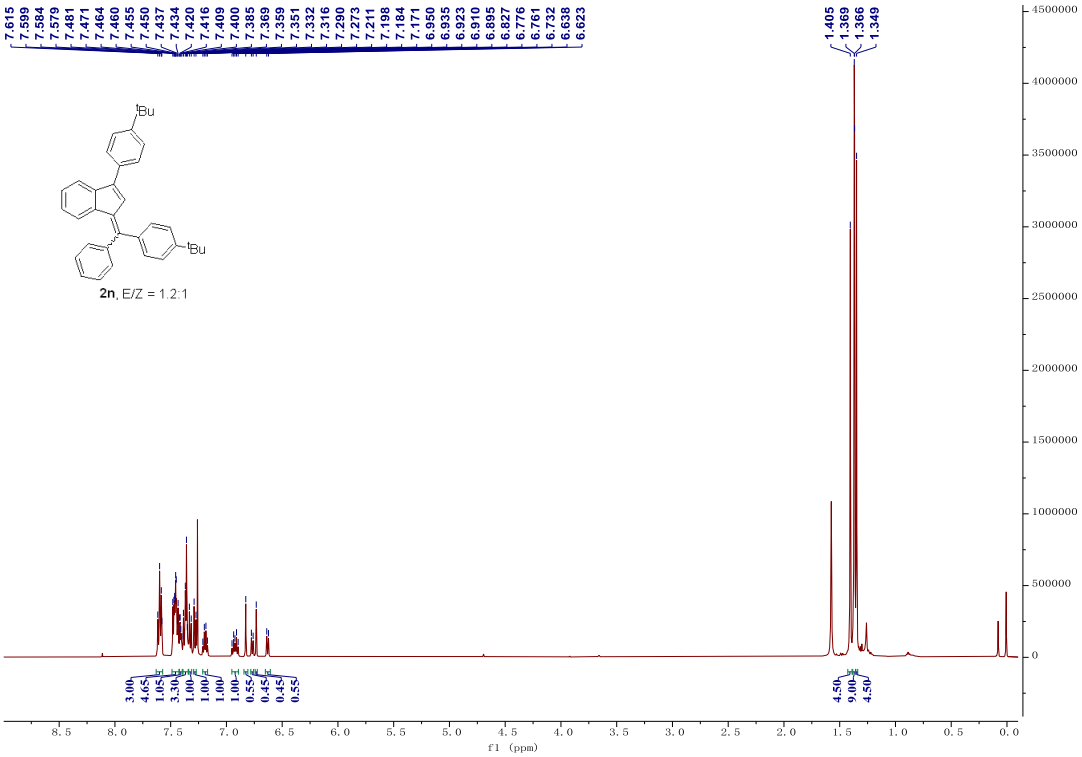



**Figure S33.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2n**

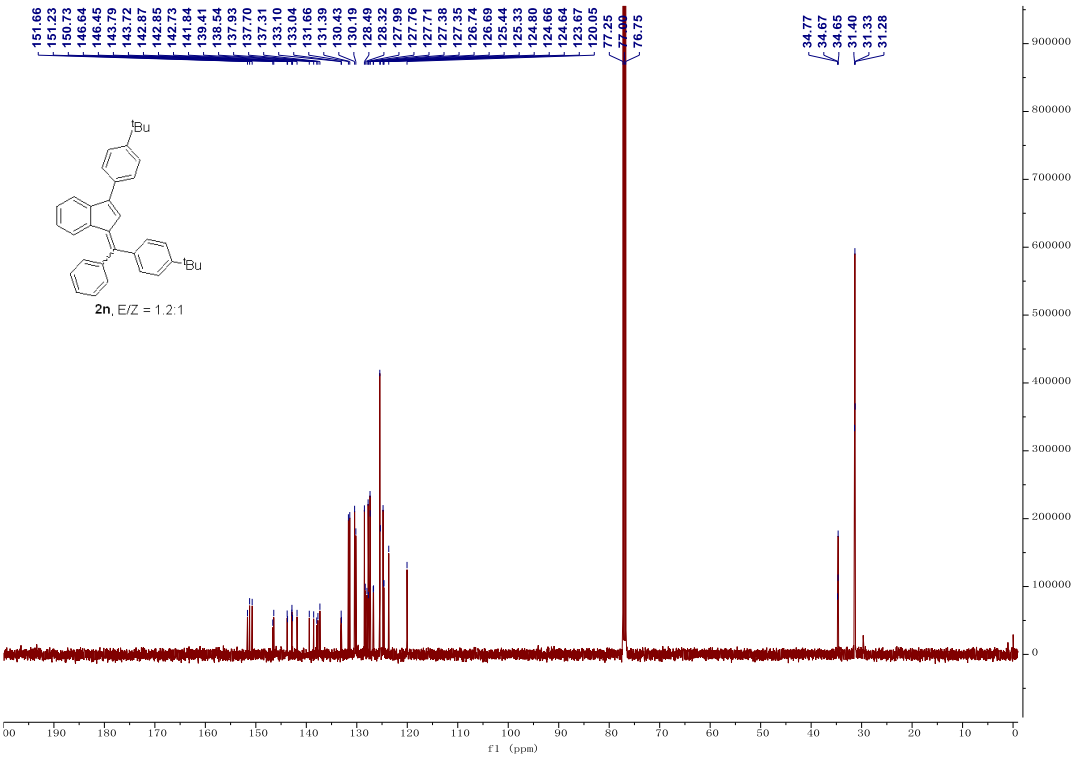



**Figure S34.** $^{13}$C NMR (126 MHz, $CDCl_3$) of **2n**

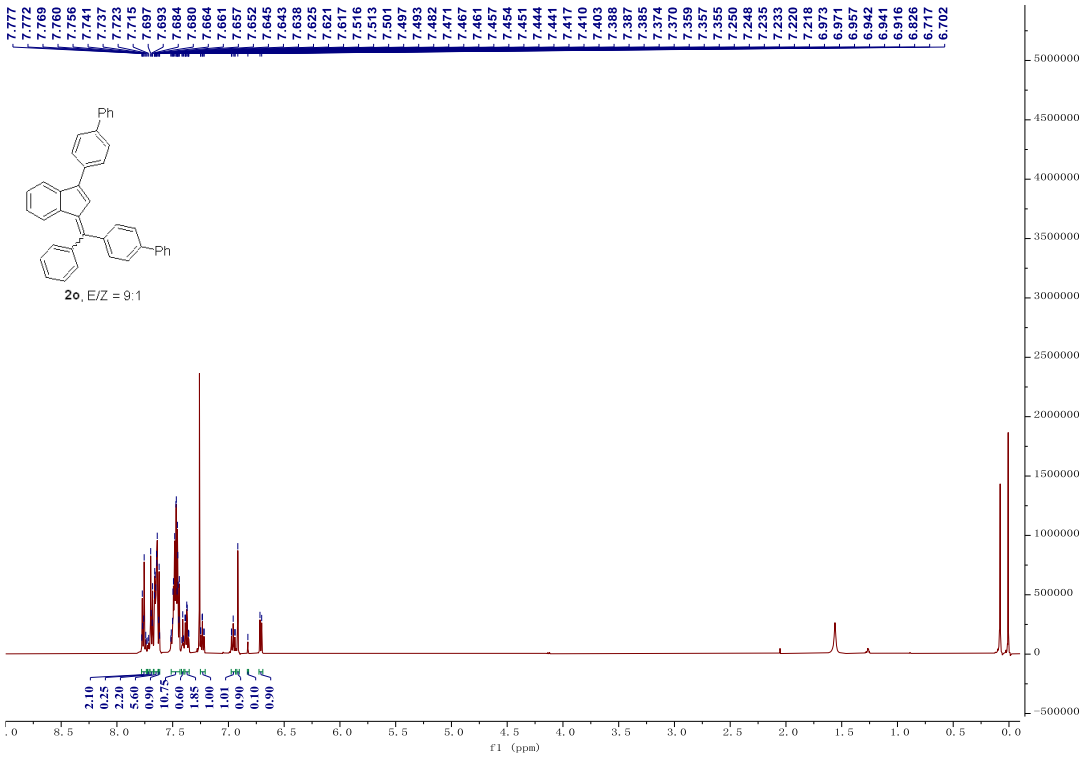



**Figure S35.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2o**

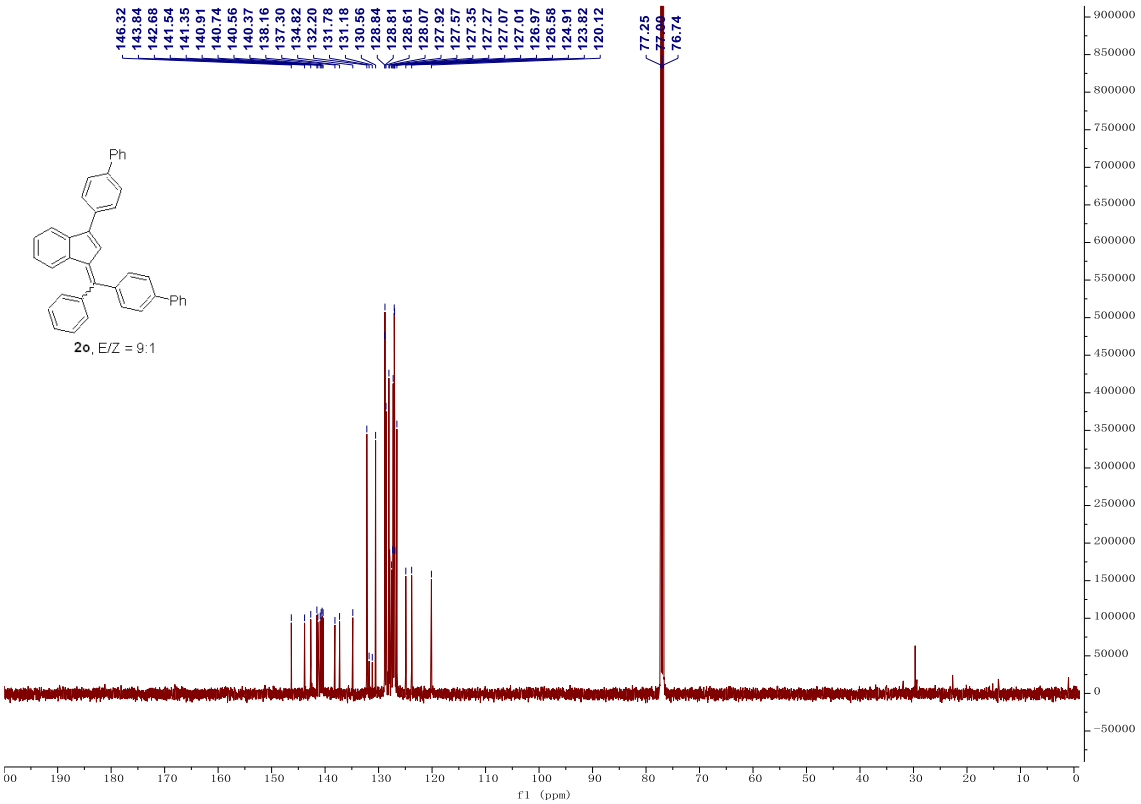



**Figure S36.** $^{13}$C NMR (126 MHz, $CDCl_3$) of **2o**

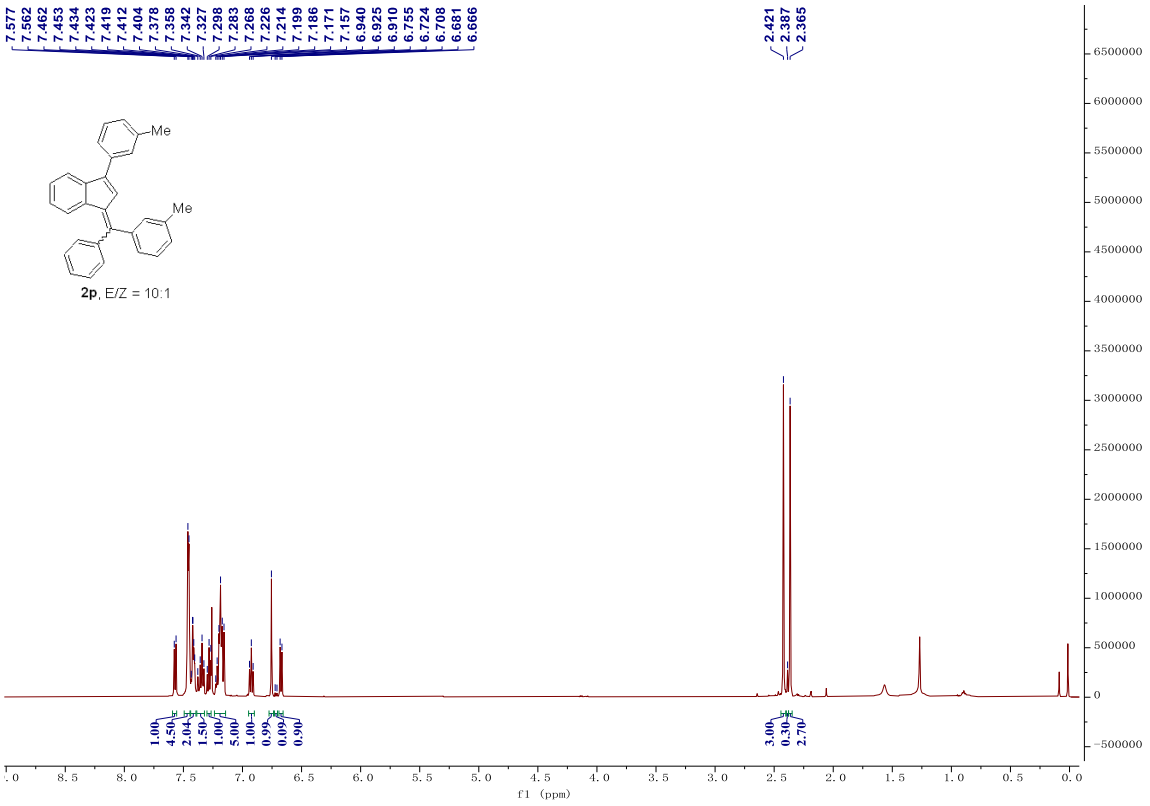



**Figure S37.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2p**

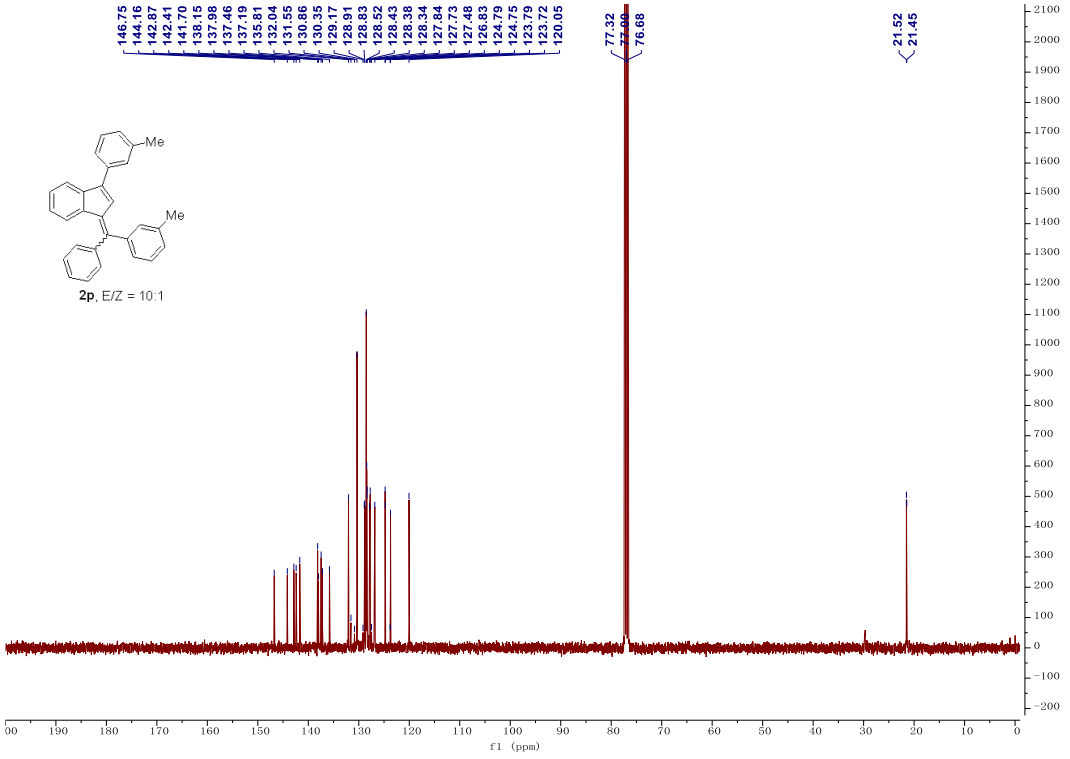



**Figure S38.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2p**

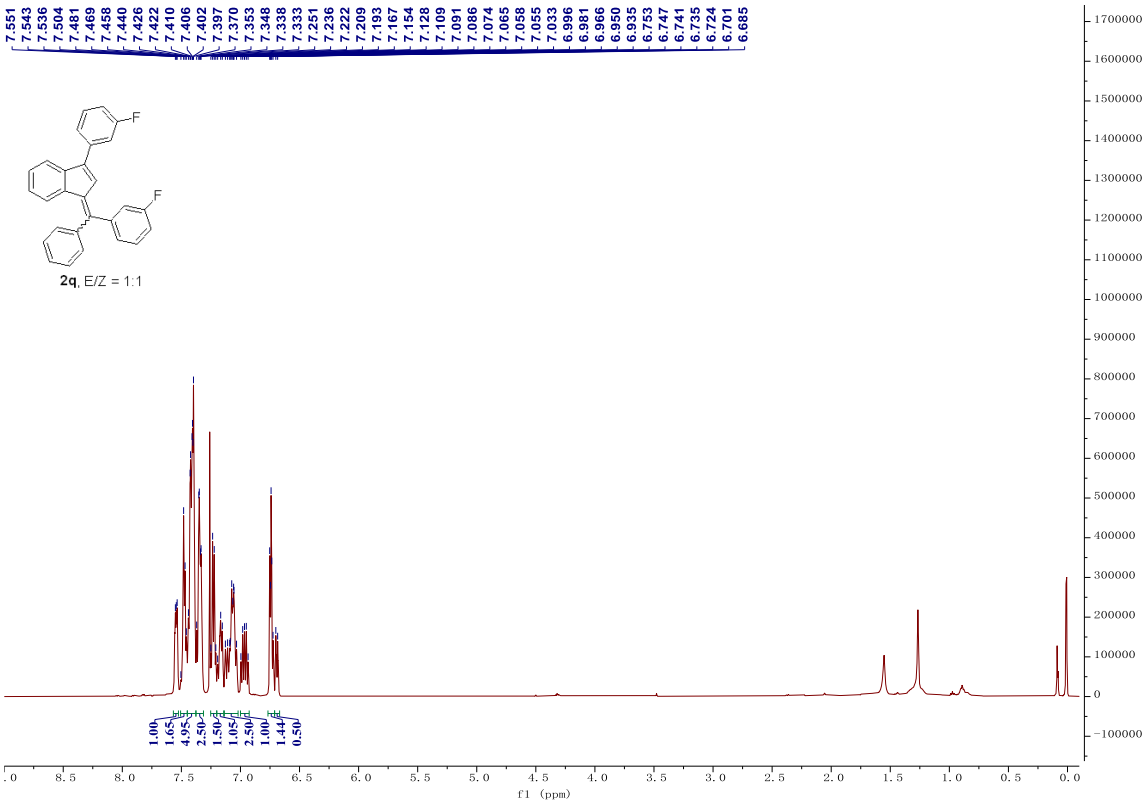



**Figure S39.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2q**

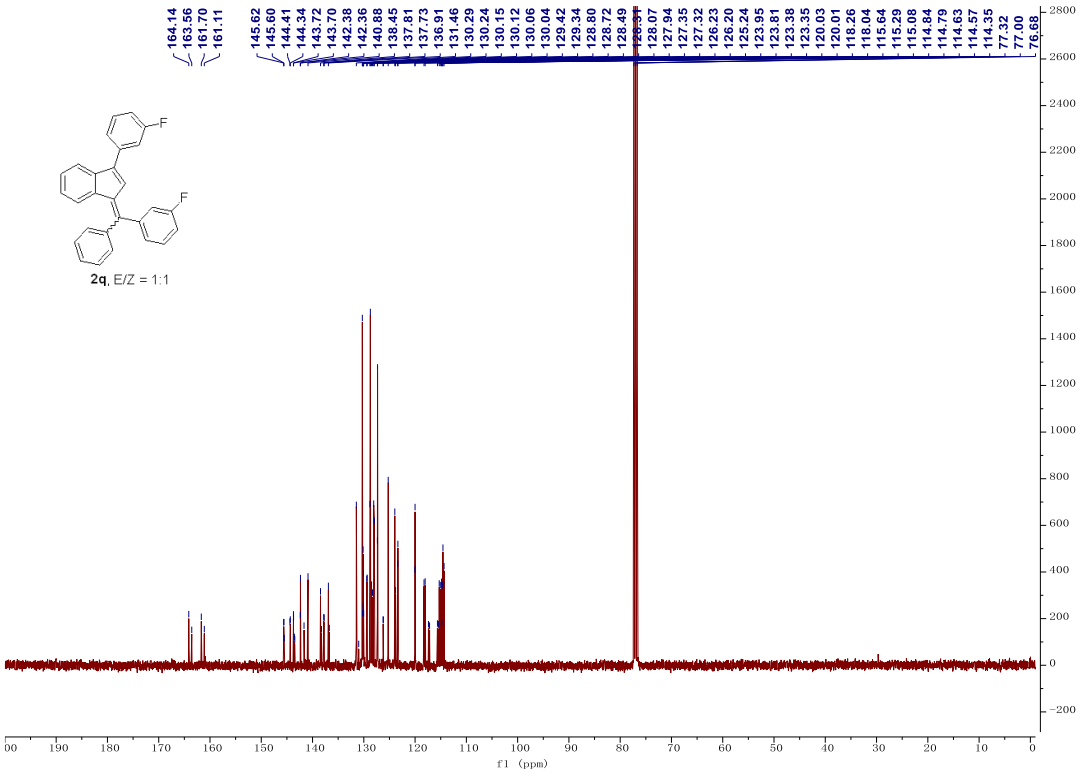



**Figure S40.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2q**

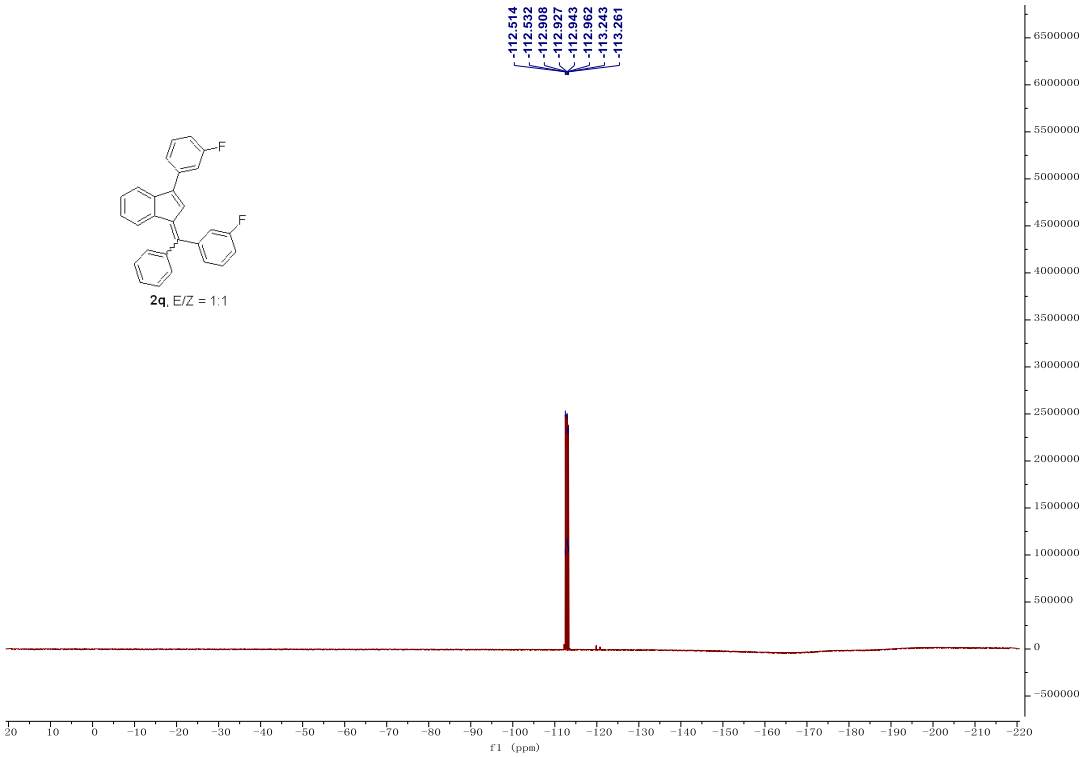



**Figure S41.** $^{19}F$ NMR (471 MHz, $CDCl_3$) of **2q**

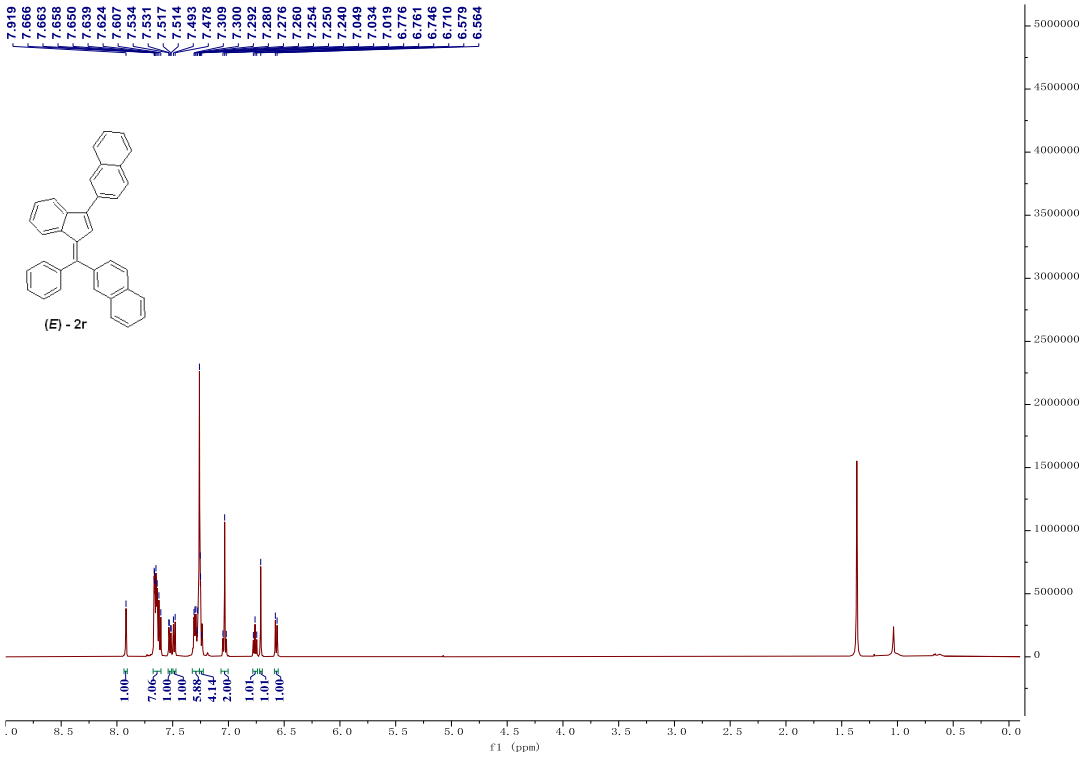



**Figure S42.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2r**

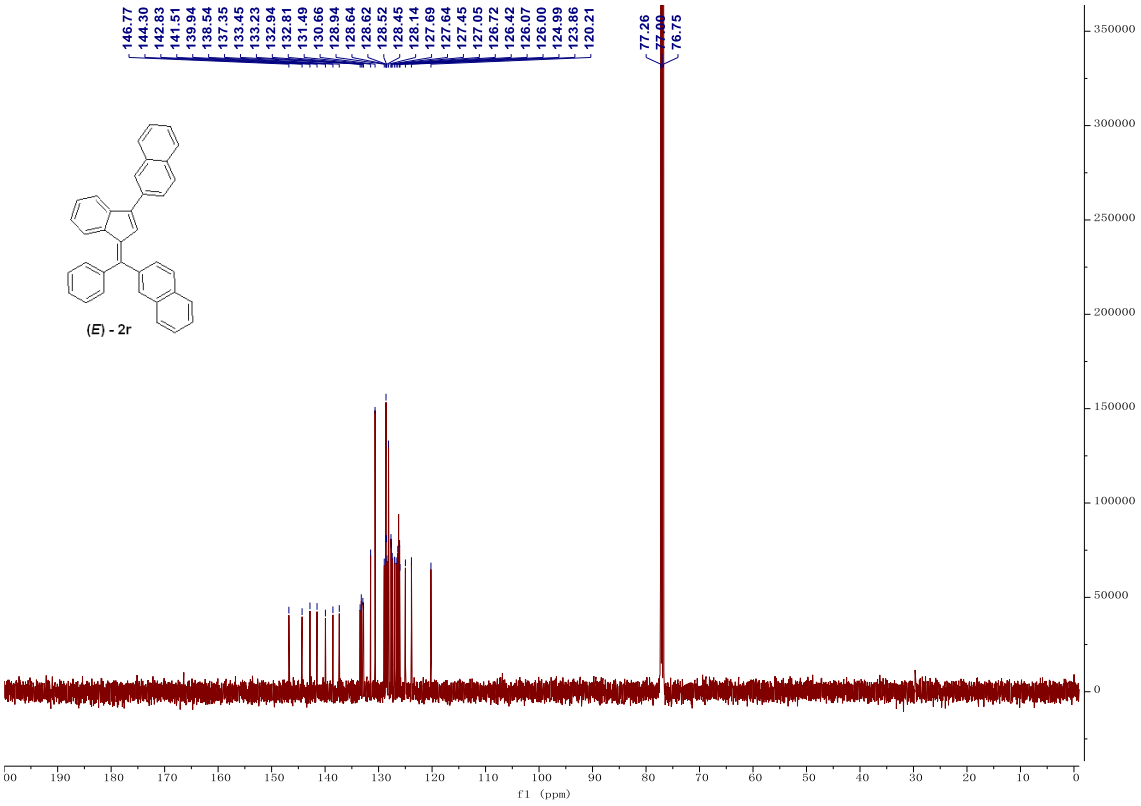



**Figure S43.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **2r**

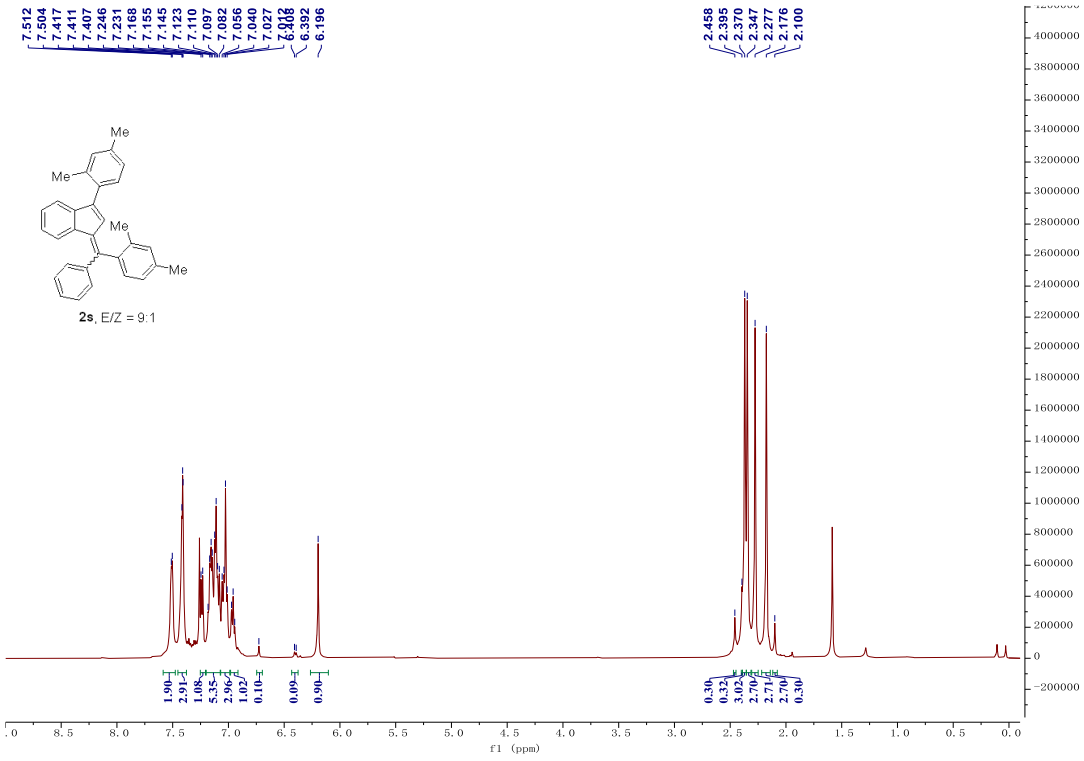



**Figure S44.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2s**

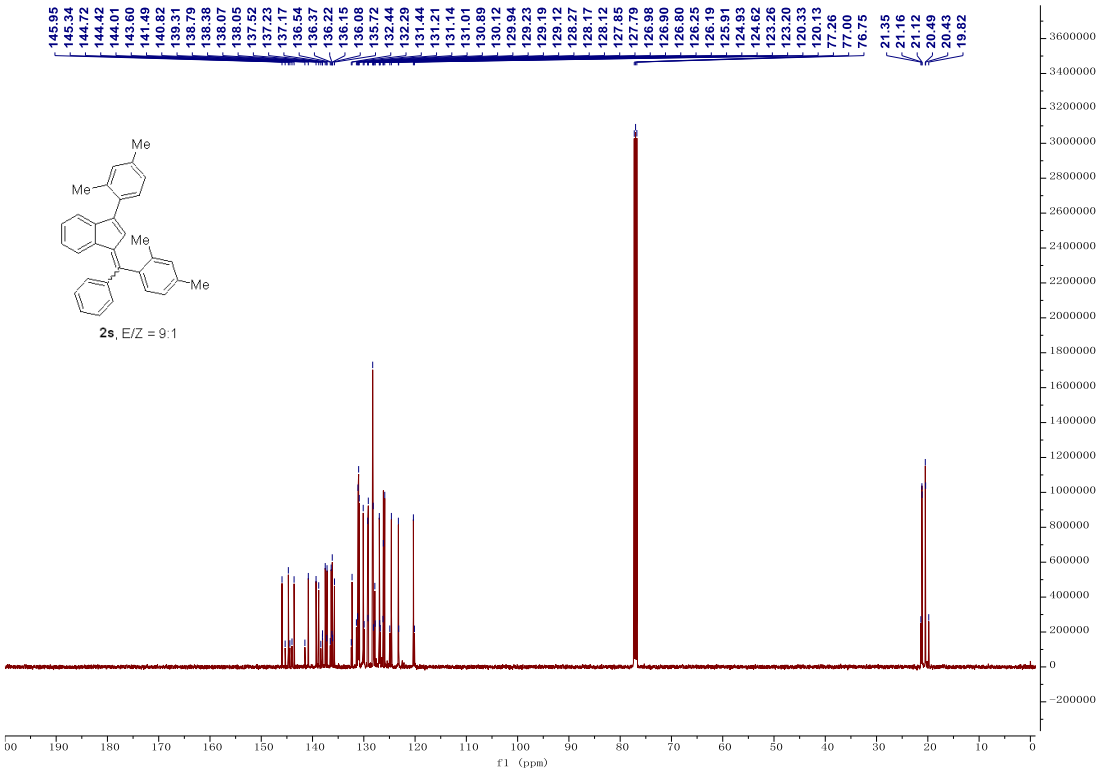



**Figure S45.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **2s**

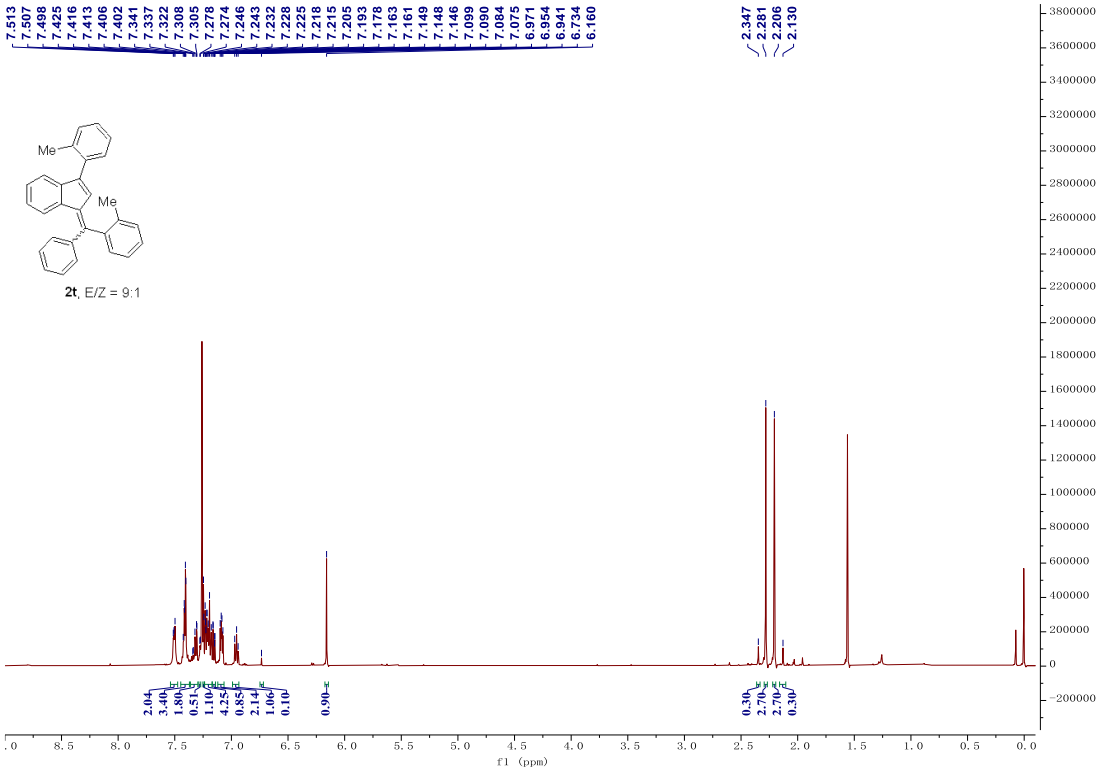



**Figure S46.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2t**

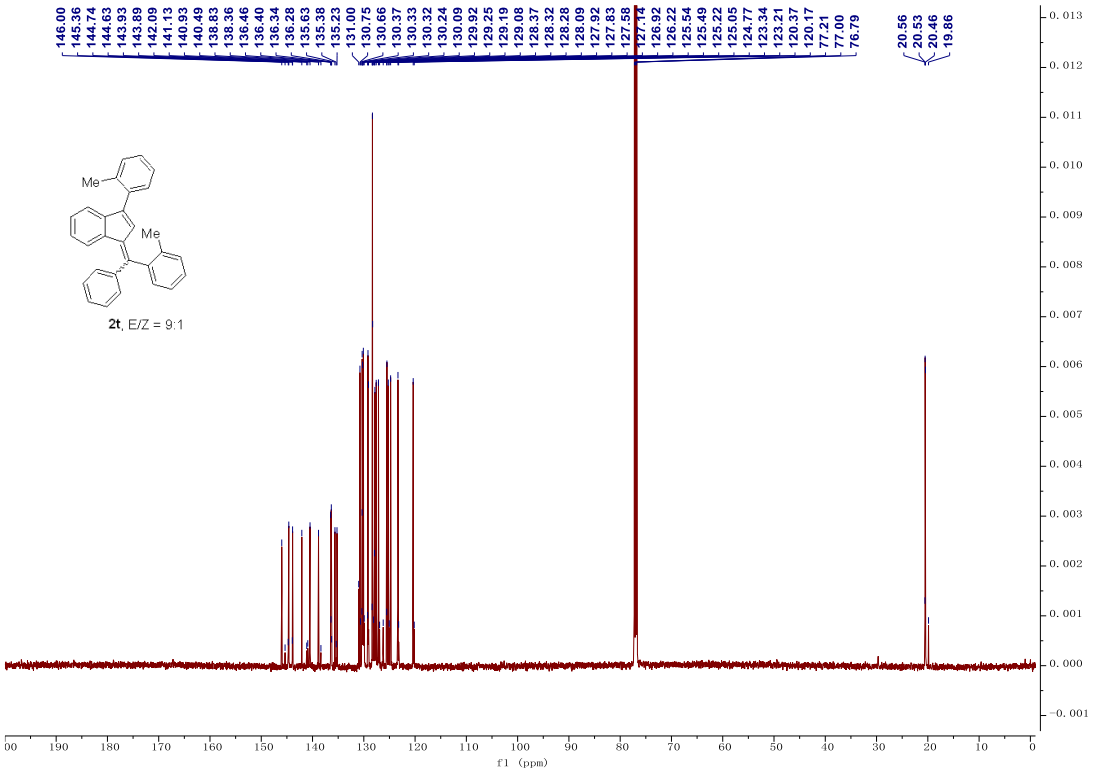



**Figure S47.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **2t**

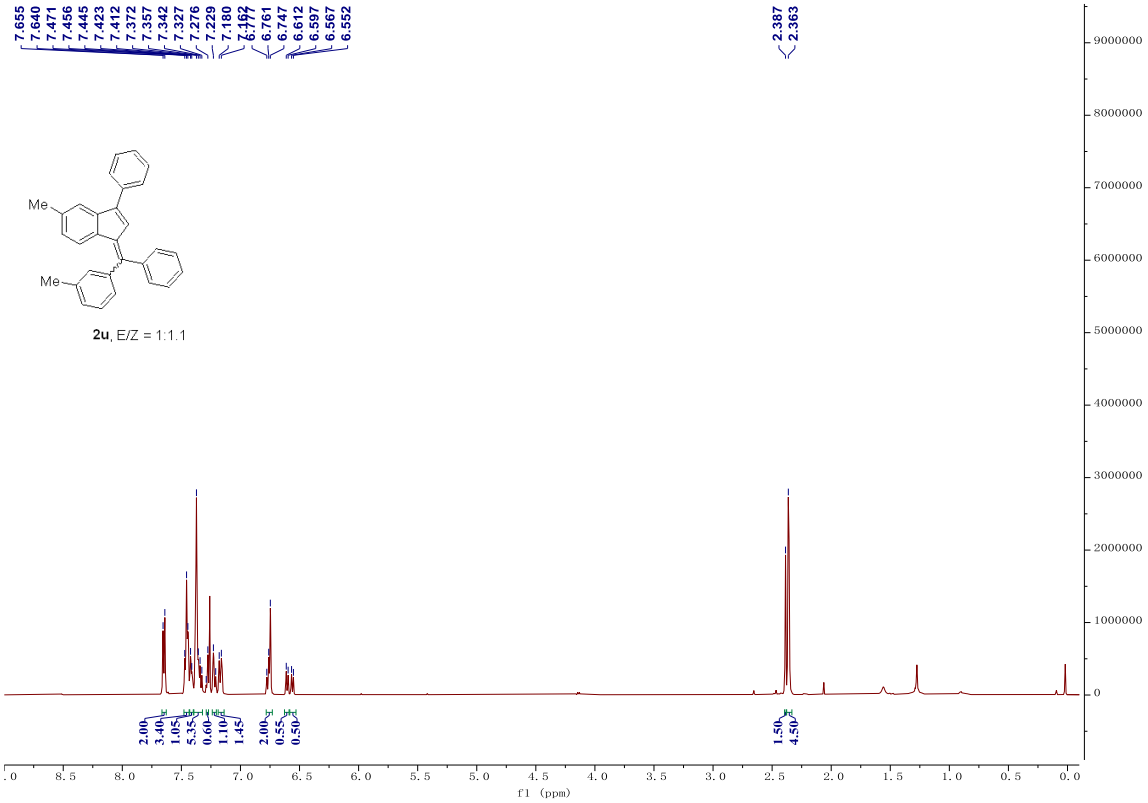



**Figure S48.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2u**

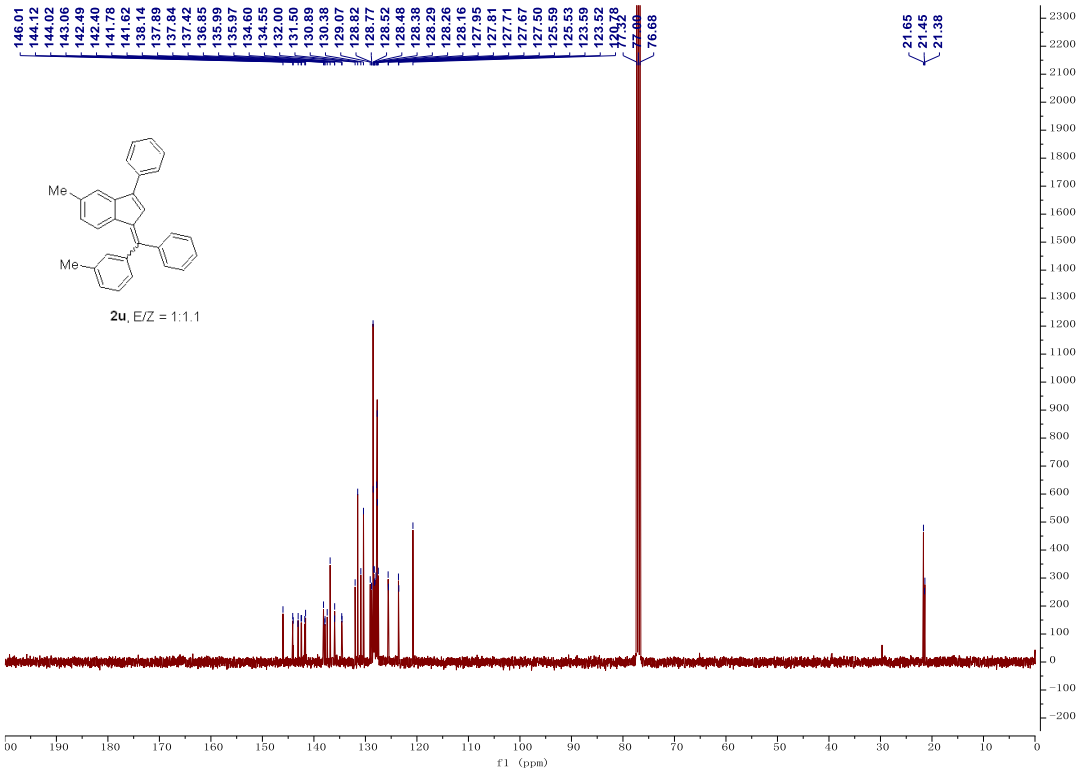



**Figure S49.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **2u**

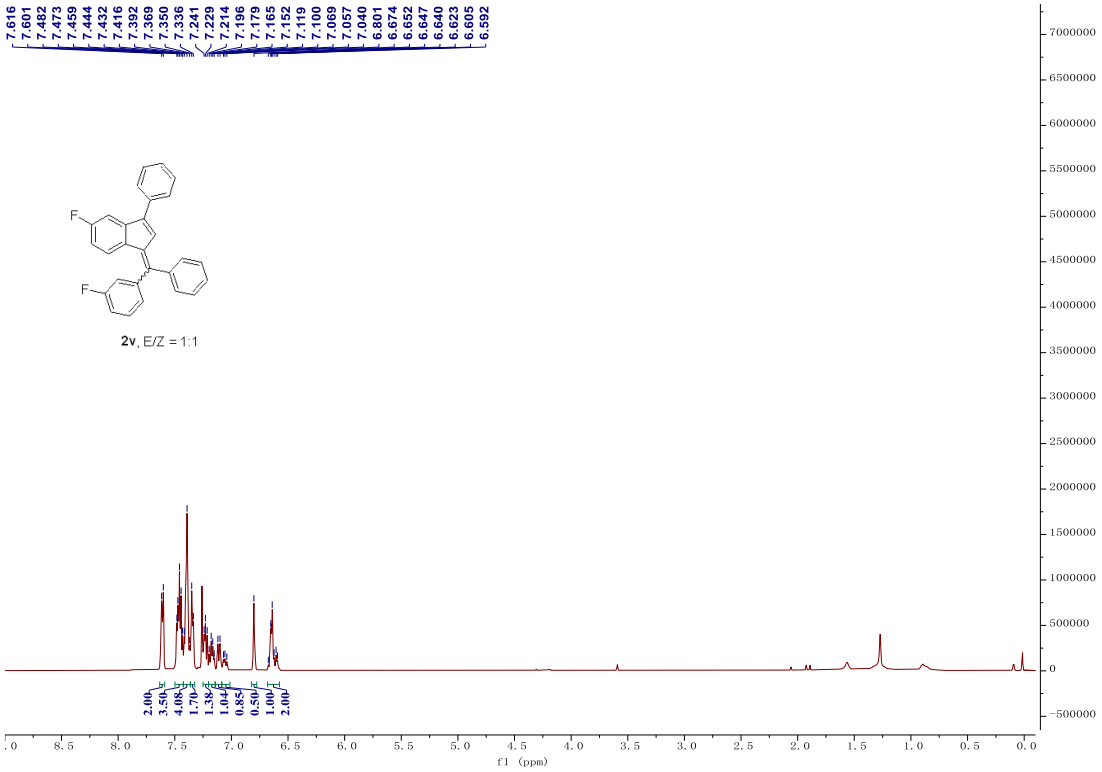



**Figure S50.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2v**

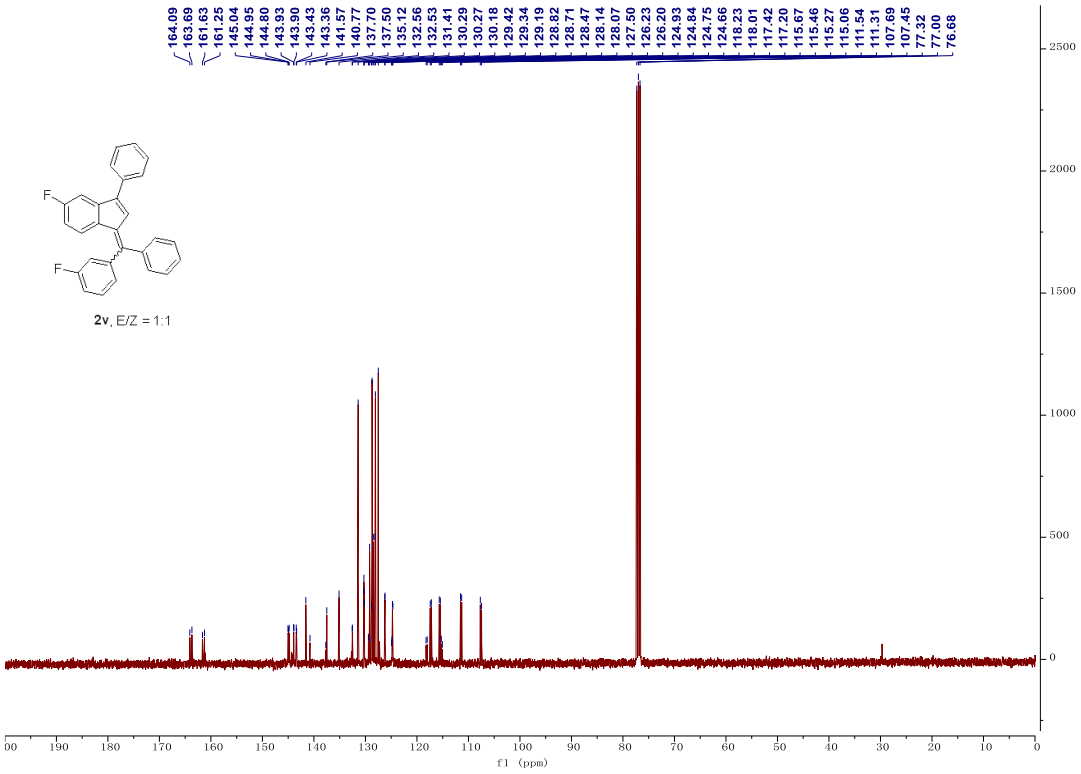



**Figure S51.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **2v**

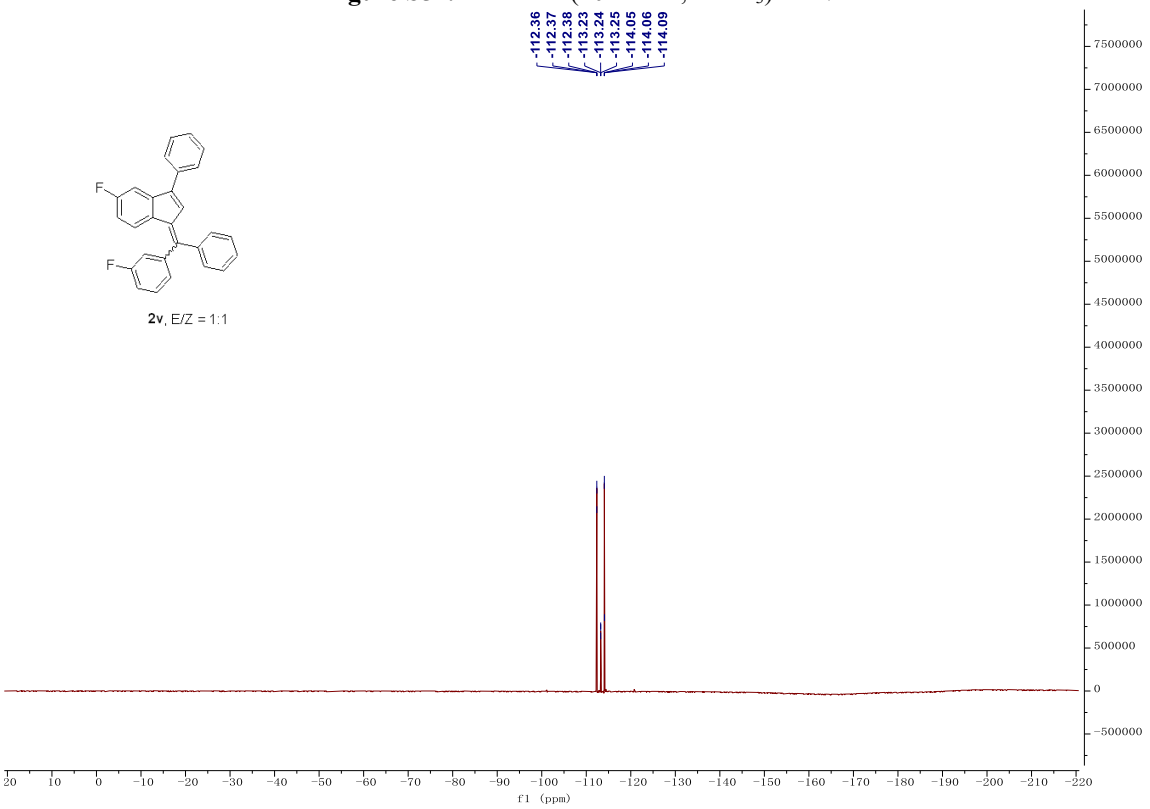



**Figure S52.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **2v**

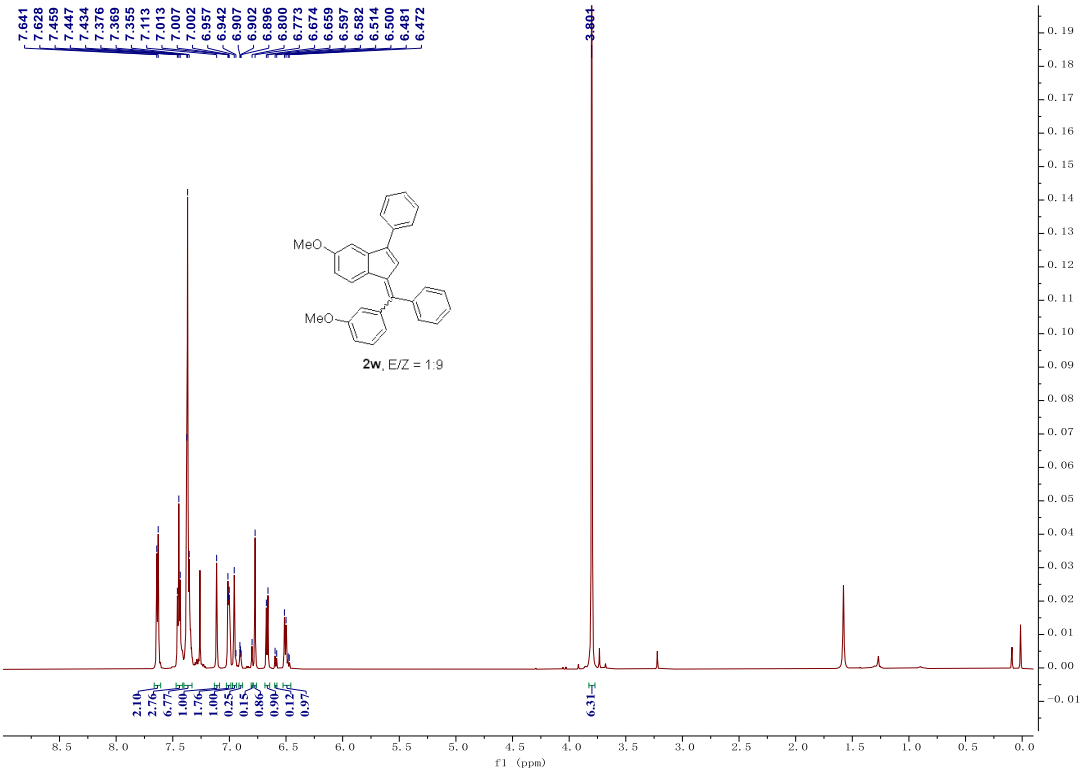



**Figure S53.** $^{1}$H NMR (600 MHz, $CDCl_3$) of **2w**

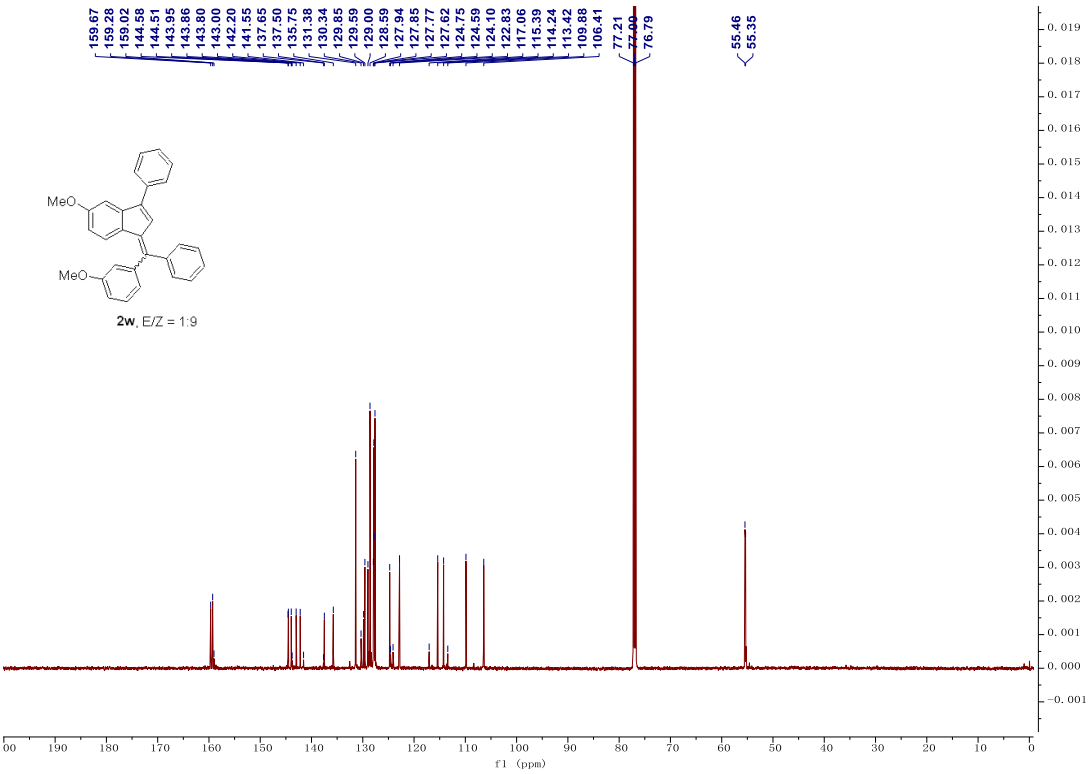



**Figure S54.** $^{13}$C NMR (151 MHz, $CDCl_3$) of **2w**

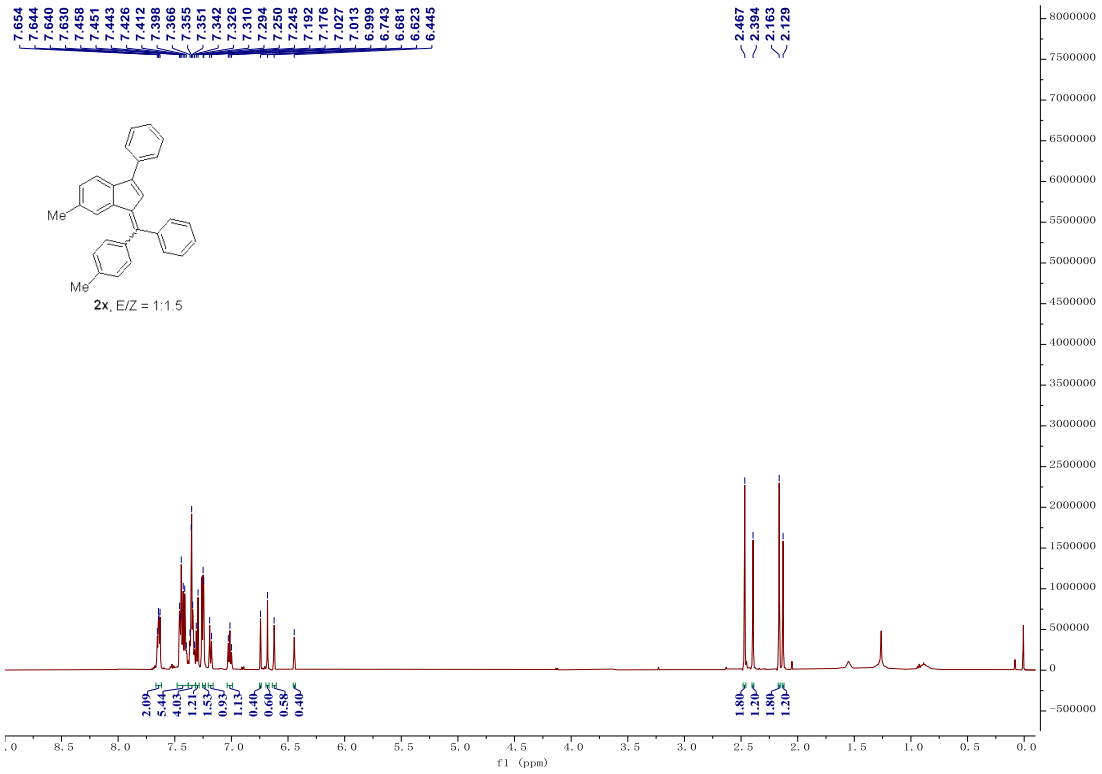



**Figure S55.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2x**

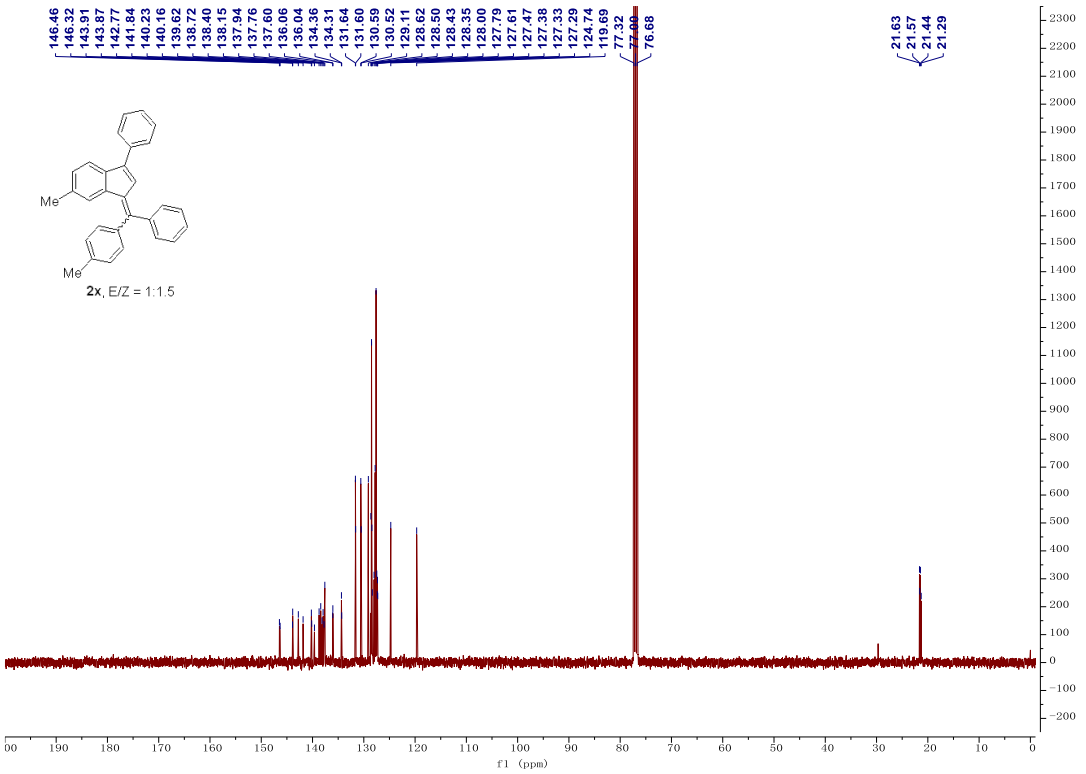



**Figure S56.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **2x**

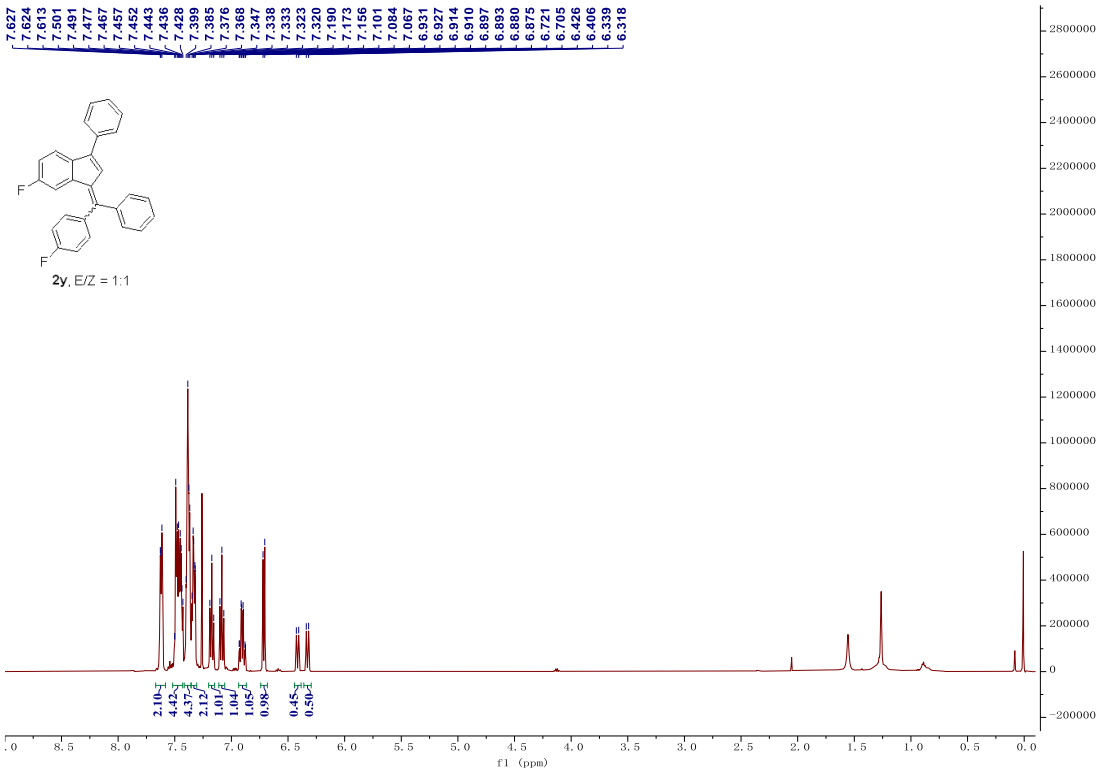



**Figure S57.** $^{1}$H NMR (500 MHz, $CDCl_3$) of **2y**

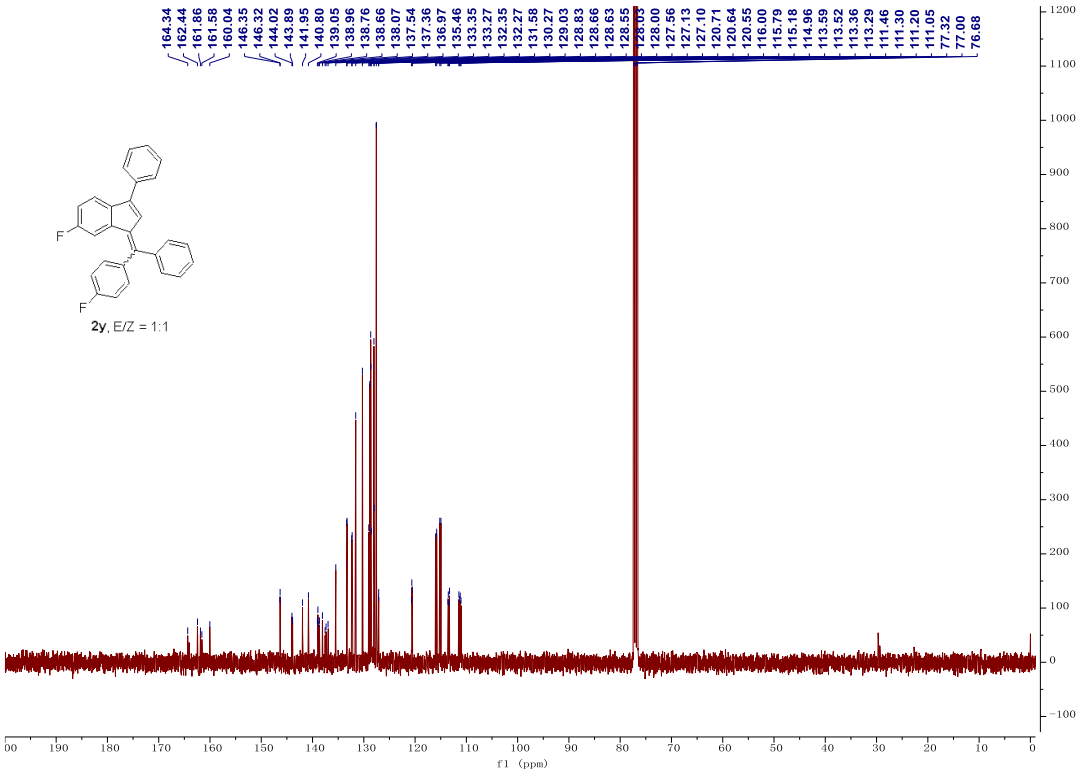



**Figure S58.** $^{13}$C NMR (101 MHz, $CDCl_3$) of **2y**

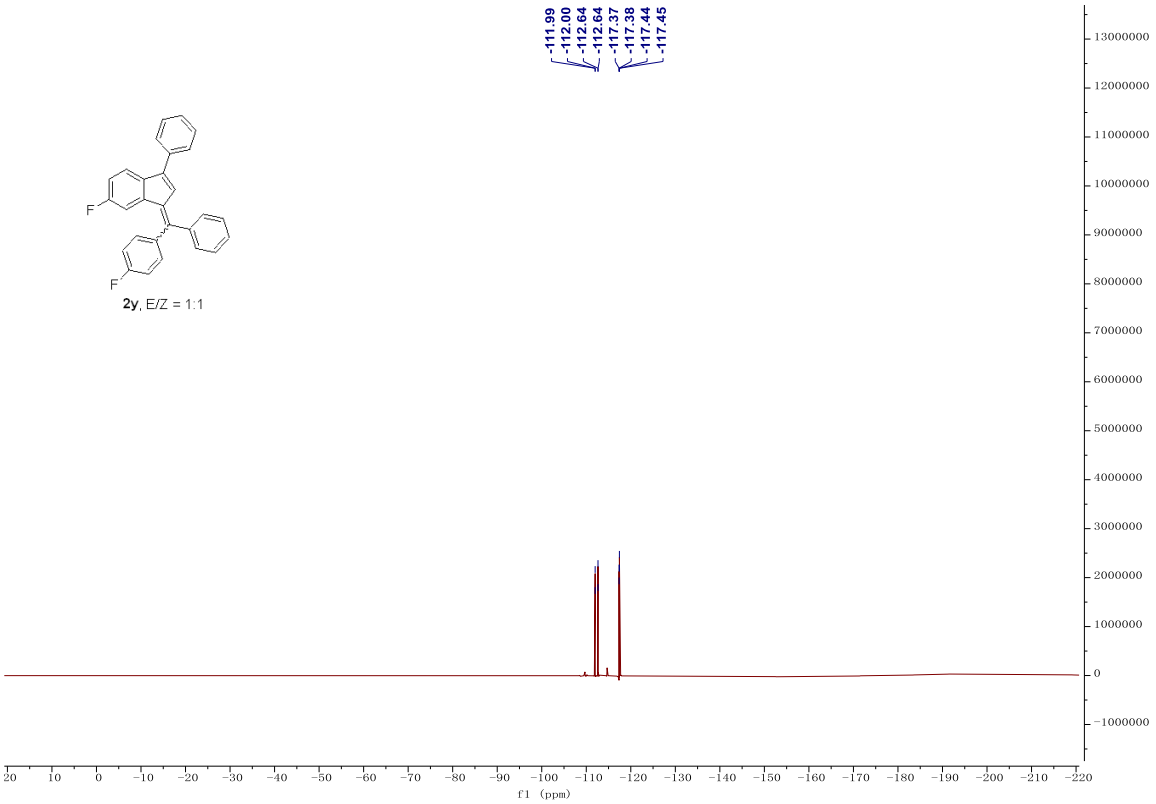



**Figure S59.** $^{19}F$ NMR (471 MHz, $CDCl_3$) of **2y**

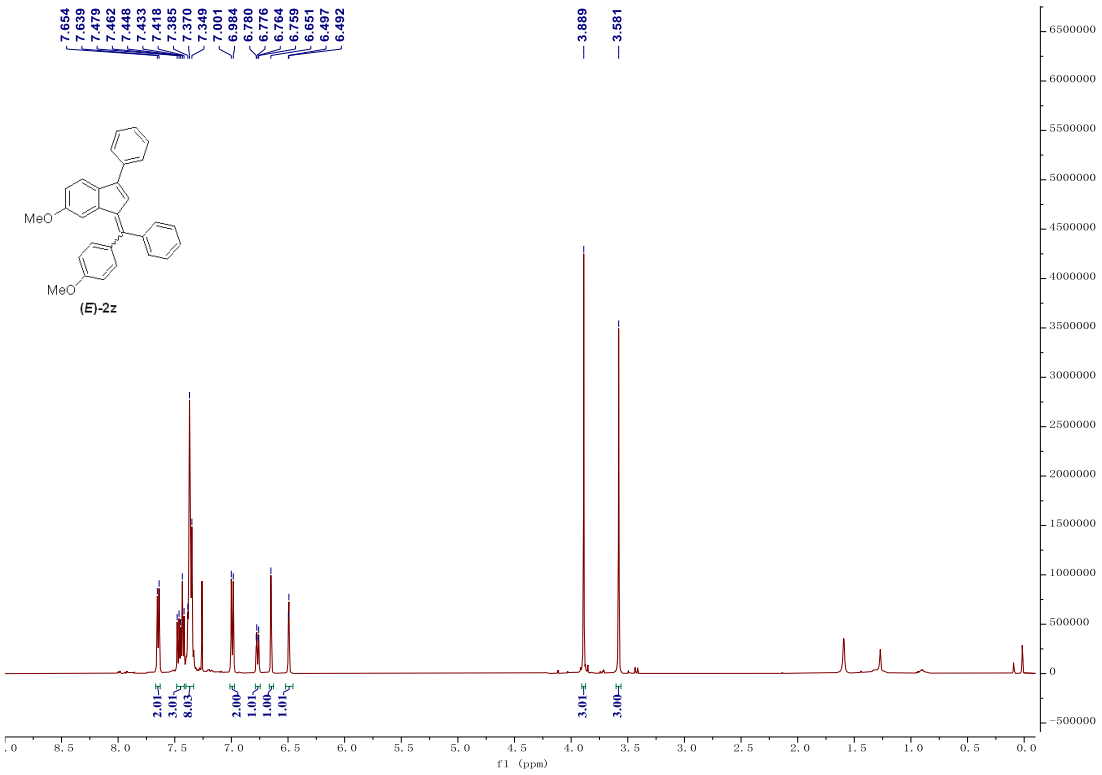



**Figure S60.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2z**

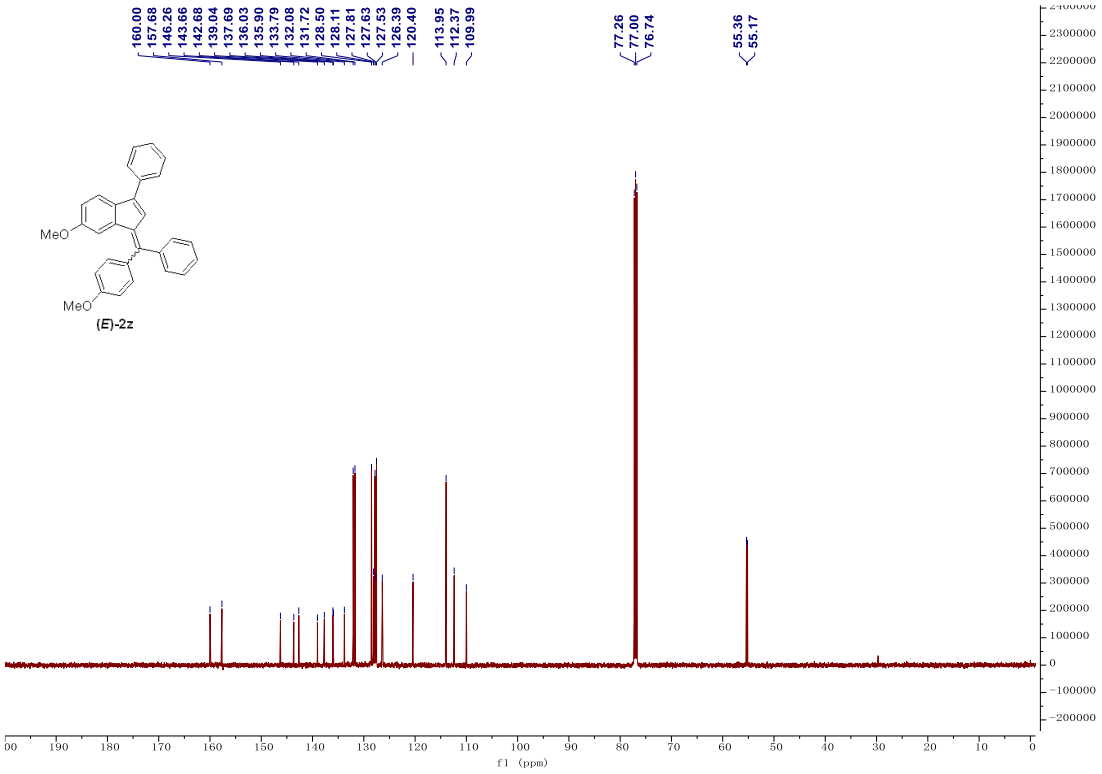



**Figure S61.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **2z**

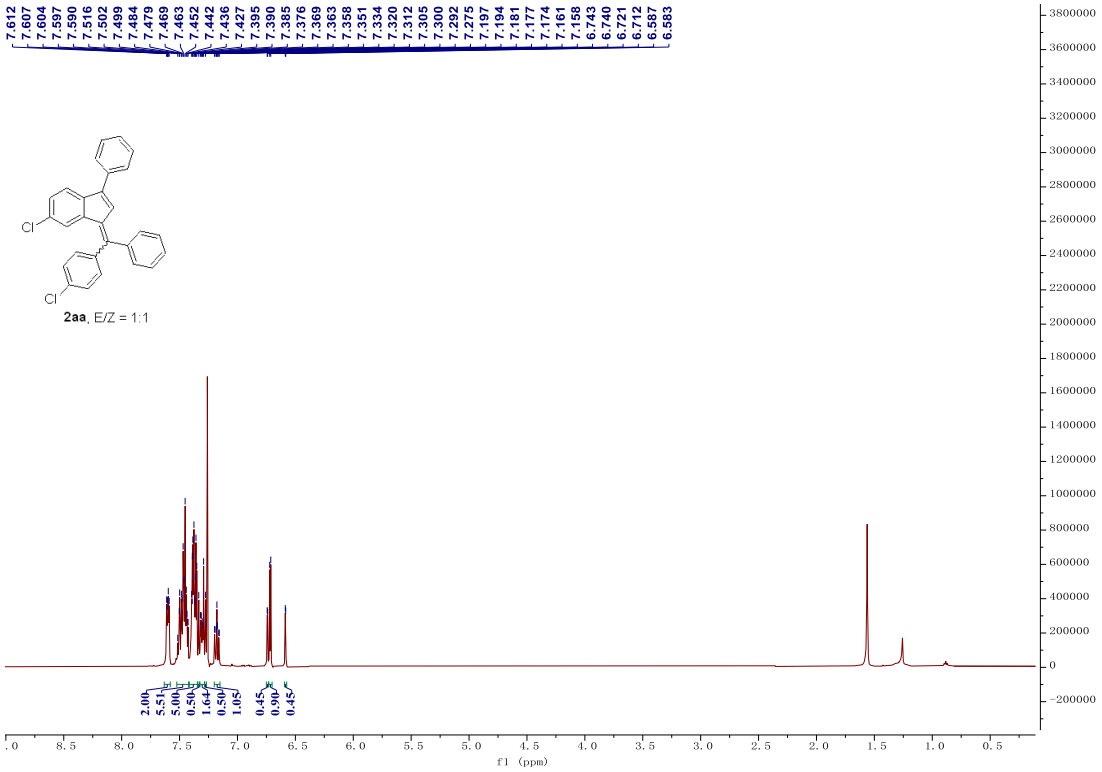



**Figure S62.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **2aa**

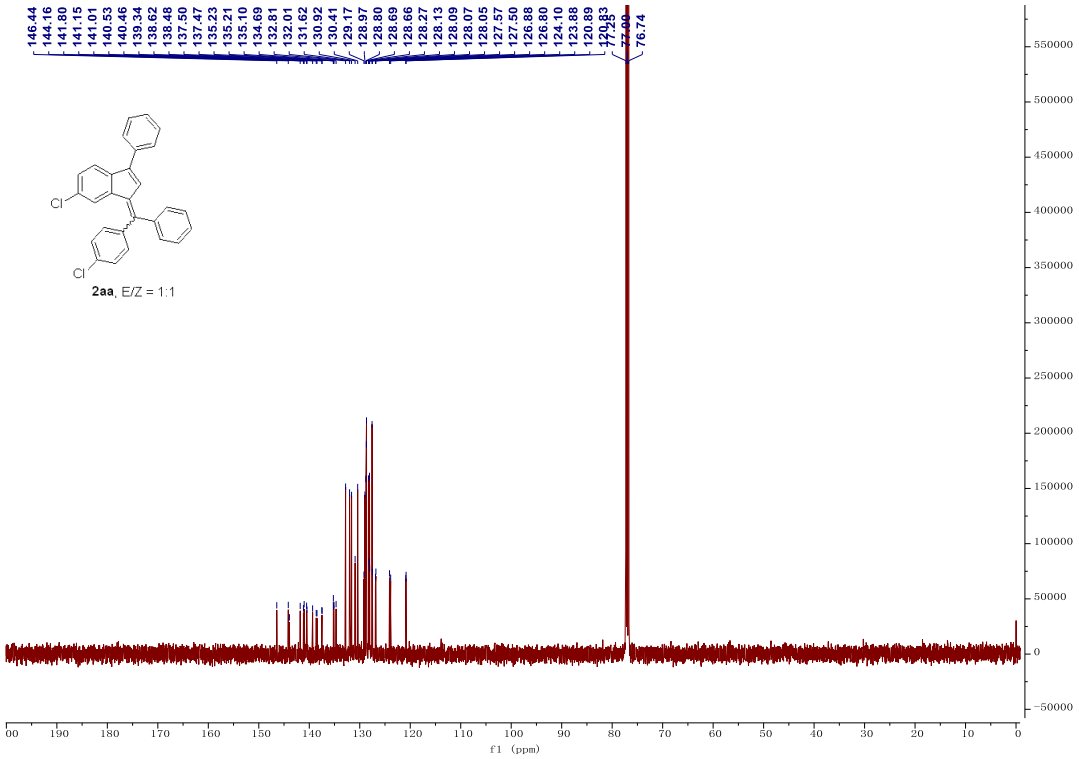



**Figure S63.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **2aa**

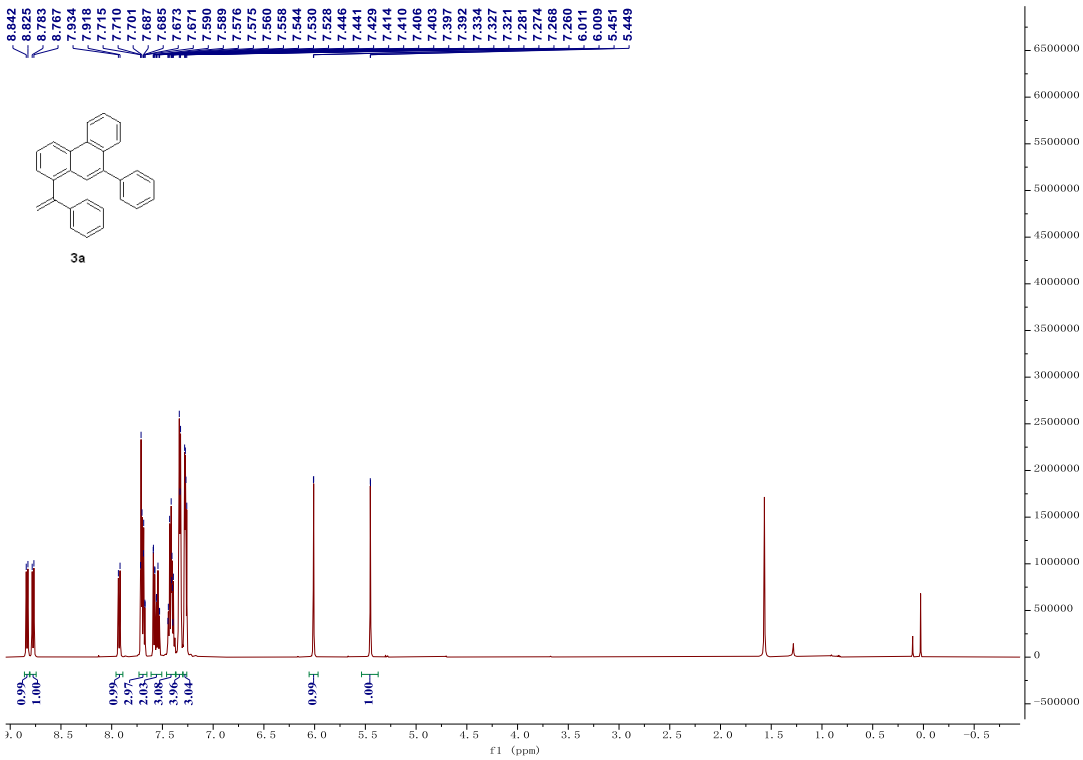



**Figure S64.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **3a**

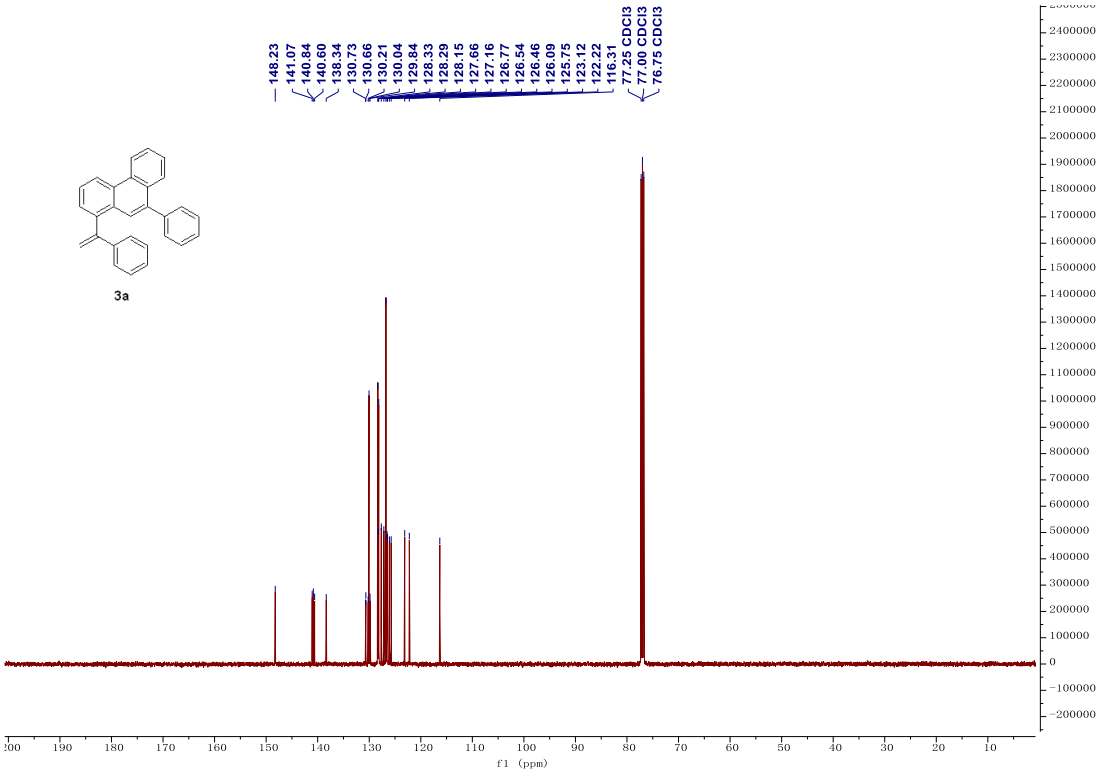



**Figure S65.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **3a**

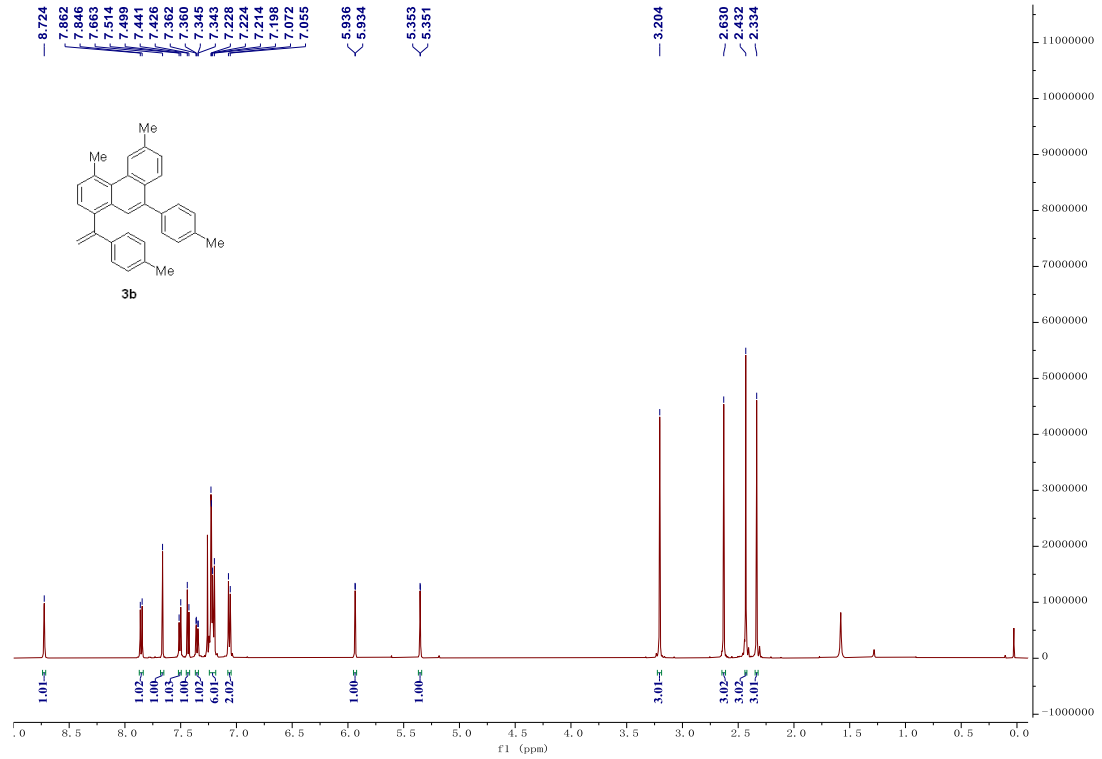



**Figure S66.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **3b**

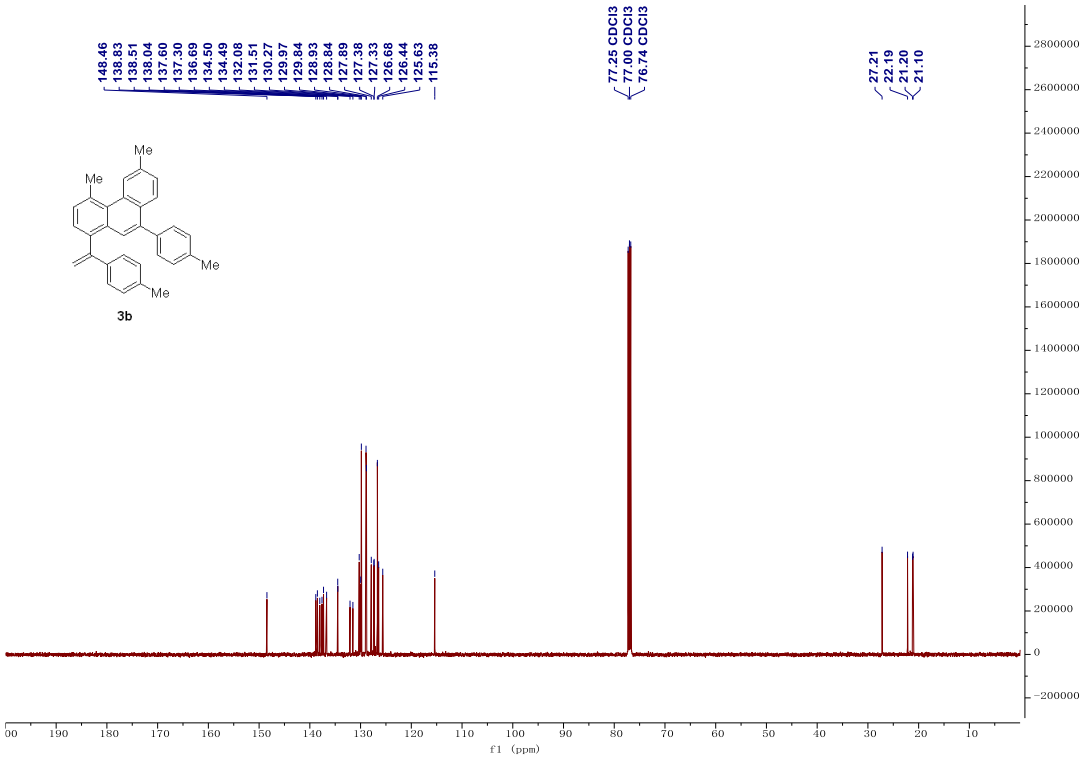



**Figure S67.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **3b**

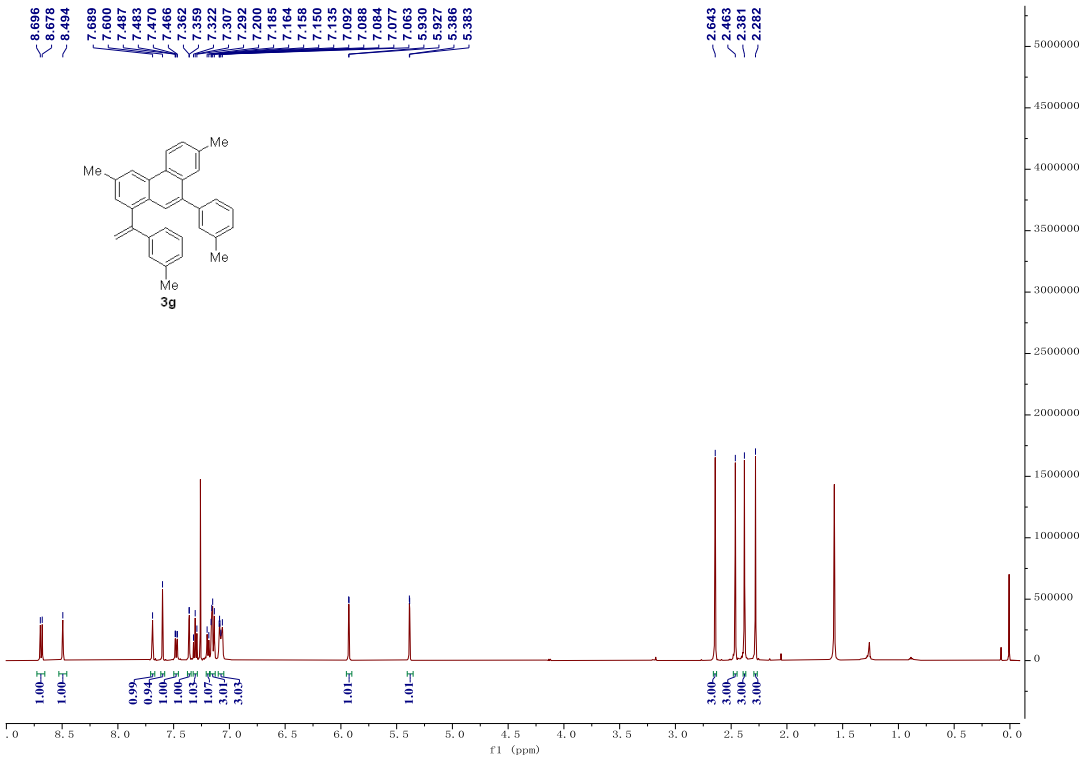



**Figure S68.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **3g**

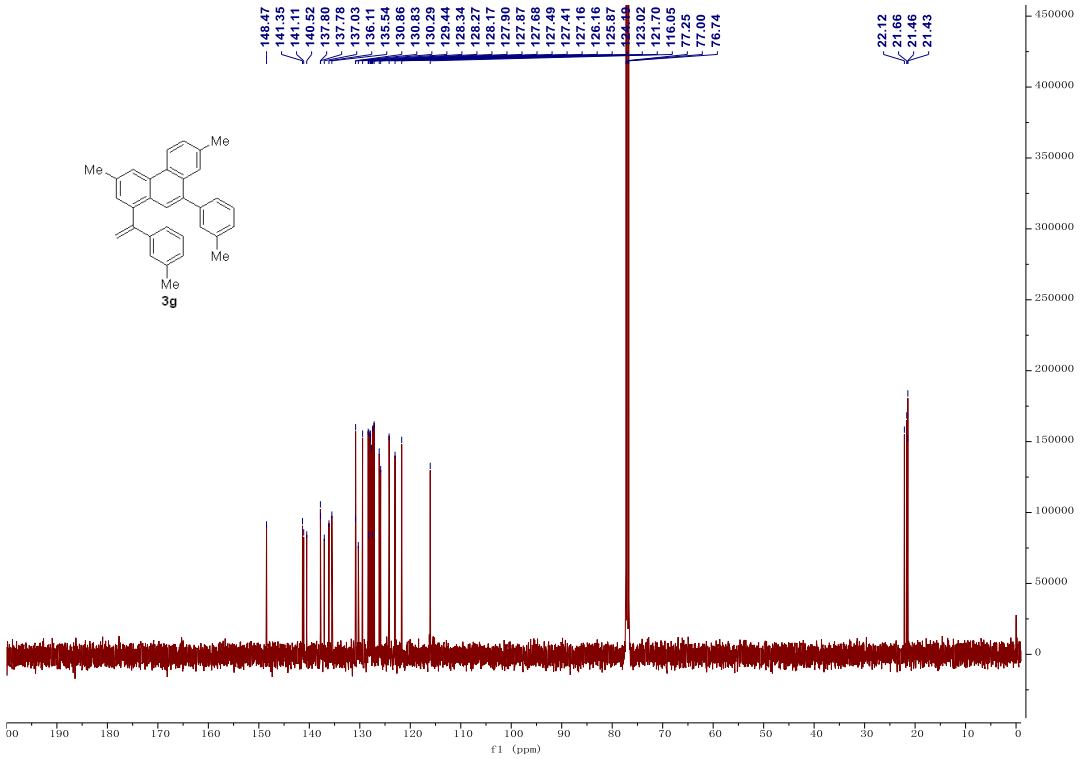



**Figure S69.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **3g**

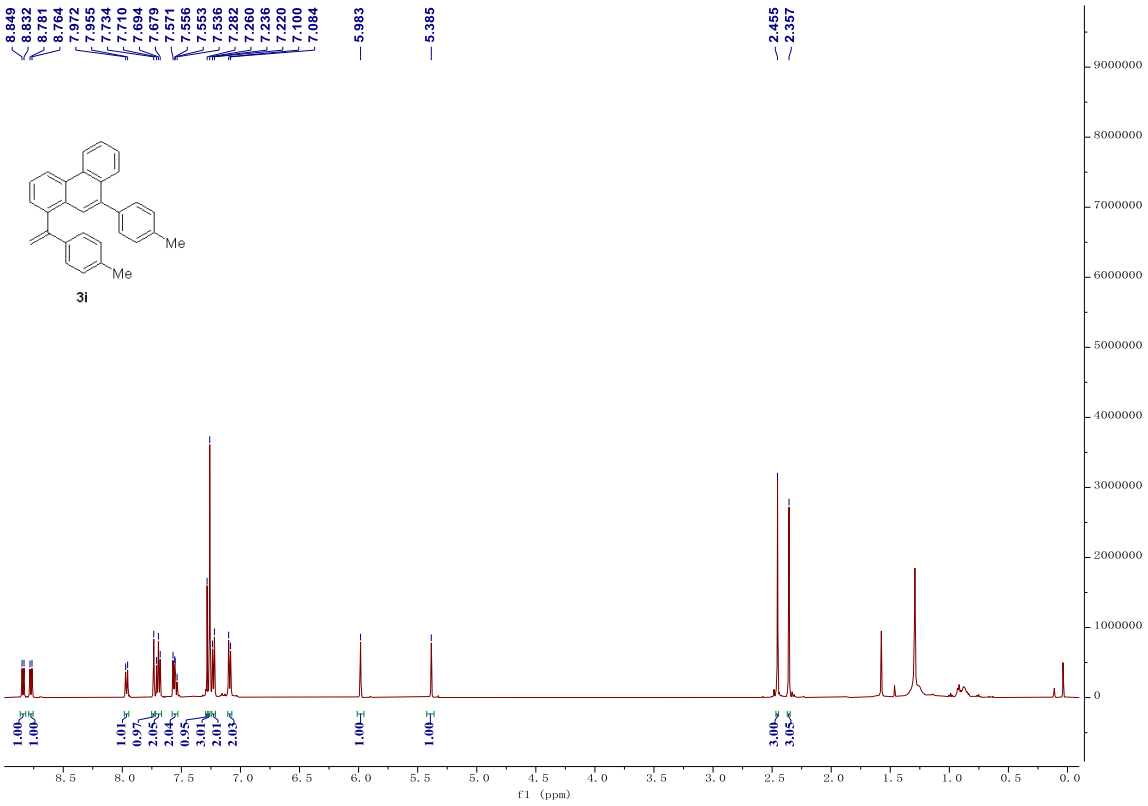



**Figure S70.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **3i**

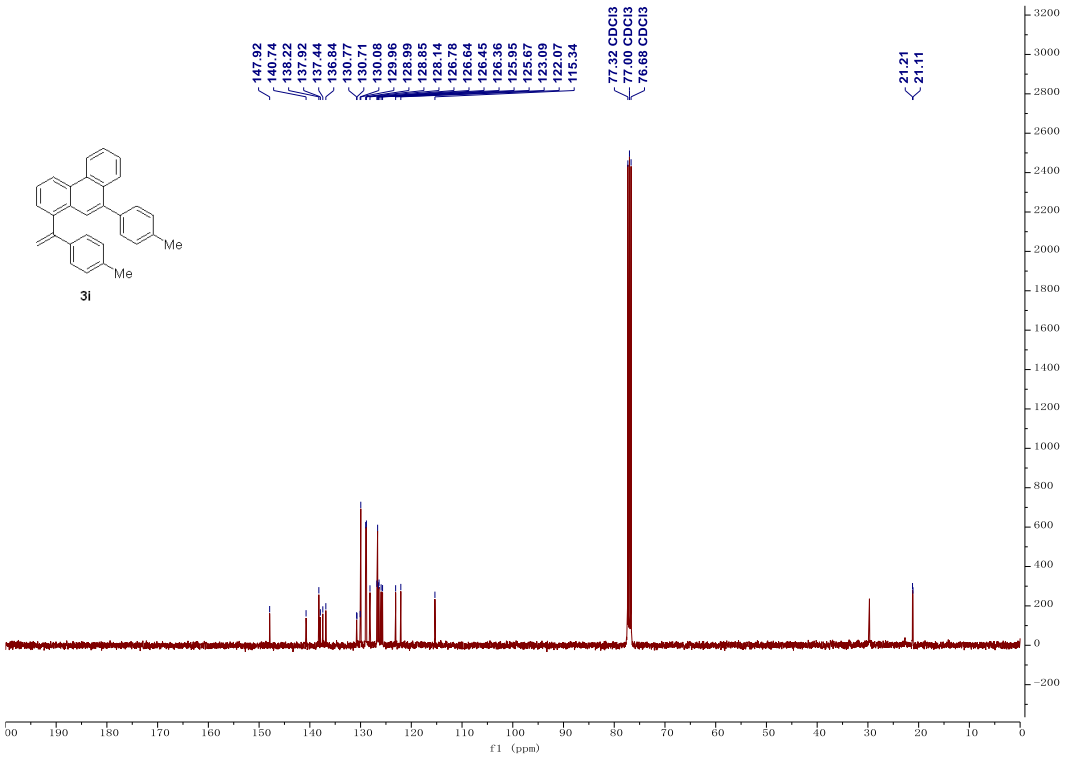



**Figure S71.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **3i**

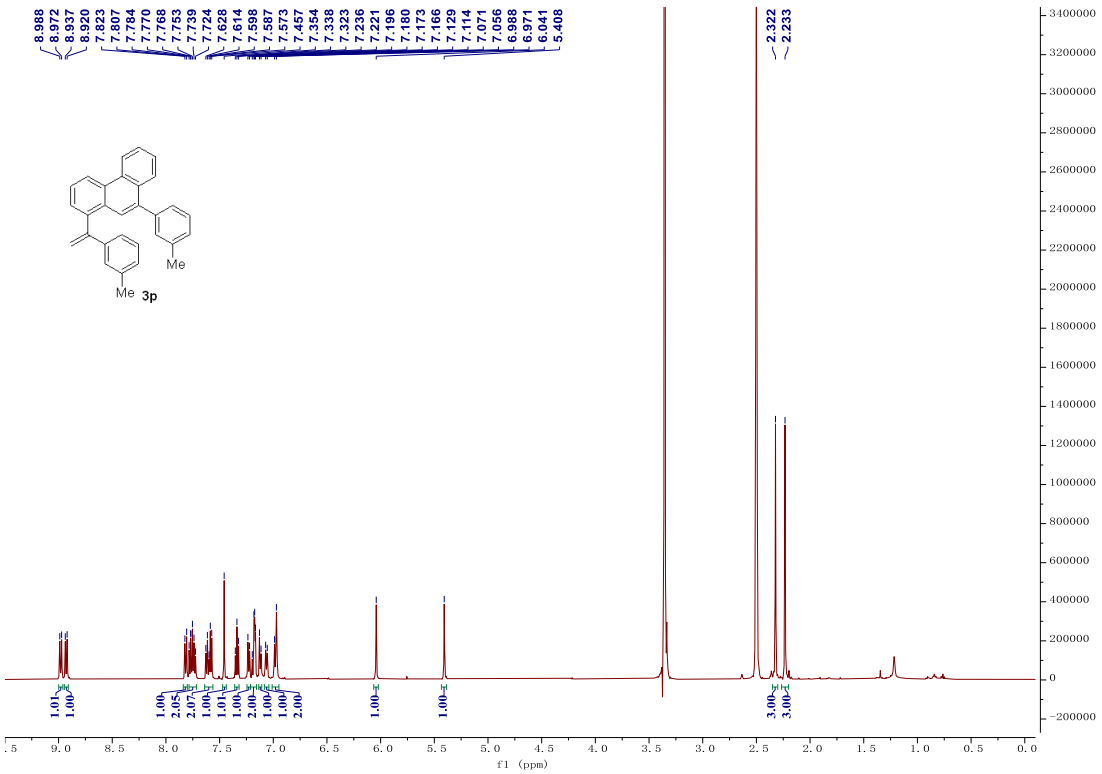



**Figure S72.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **3p**

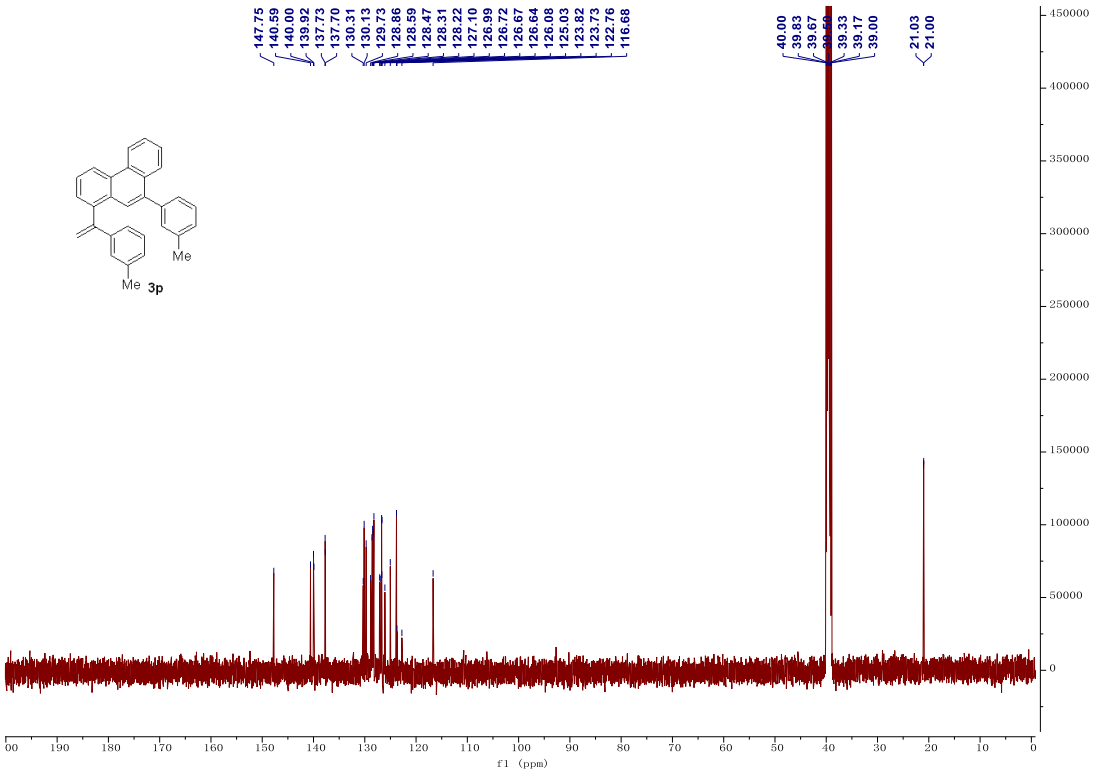



**Figure S73.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **3p**

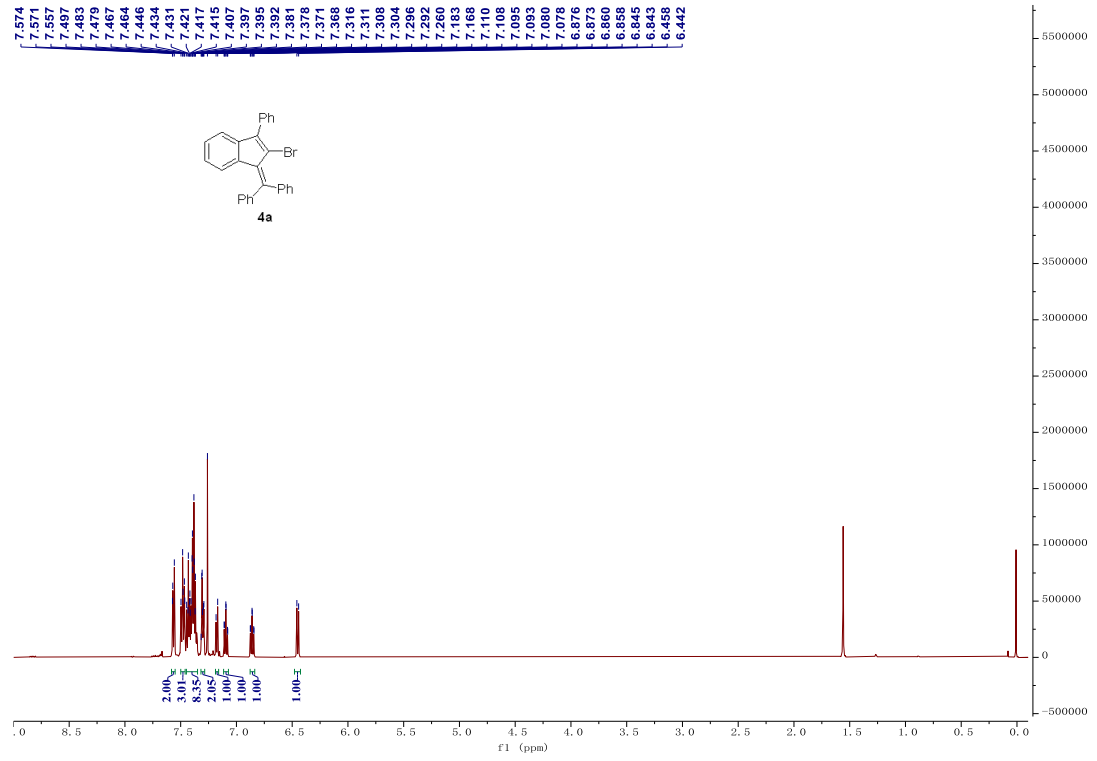



**Figure S74.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4a**

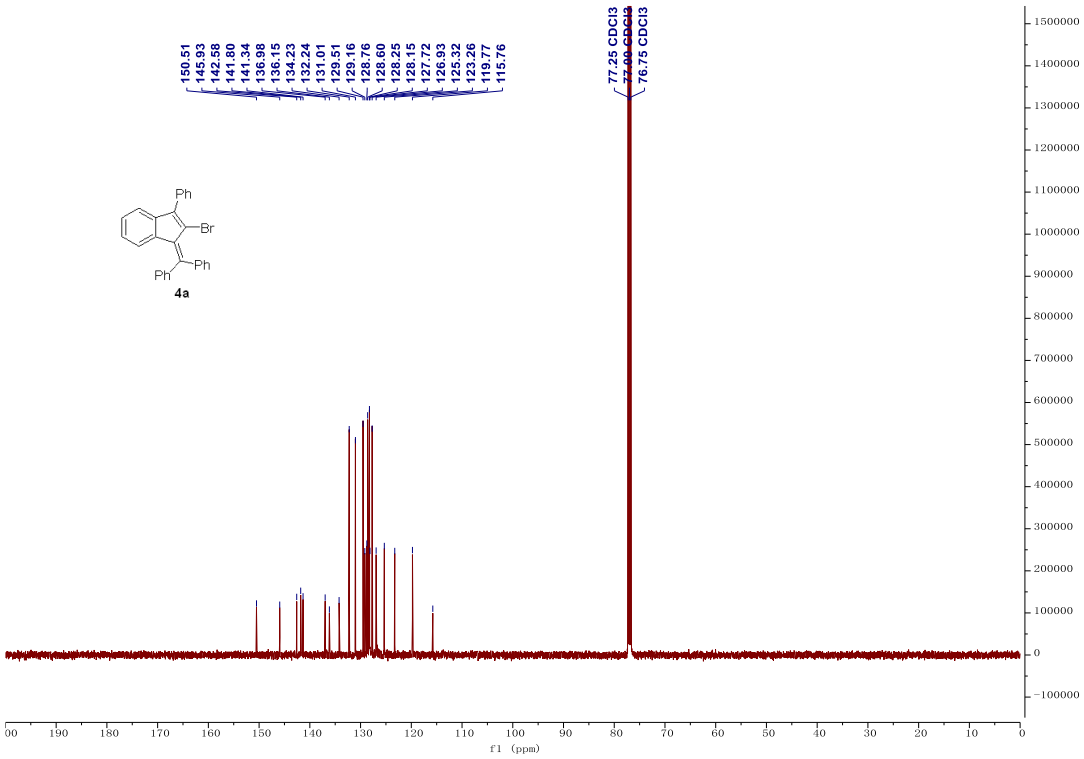



**Figure S75.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **4a**

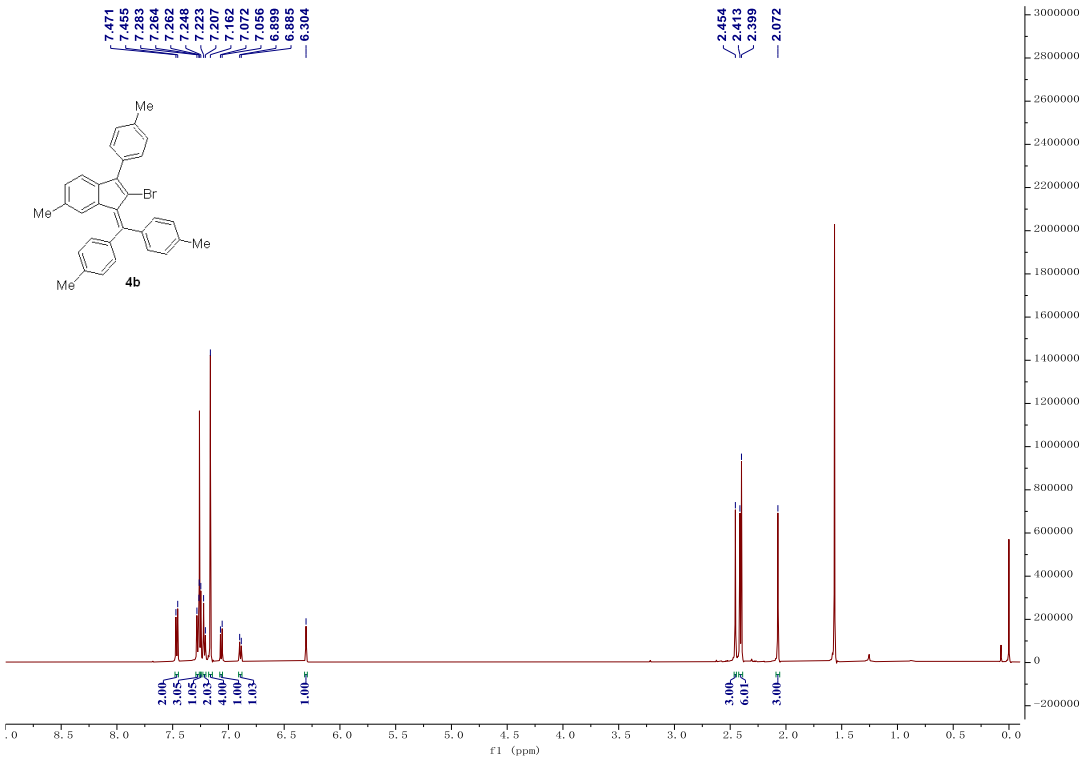



**Figure S76.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4b**

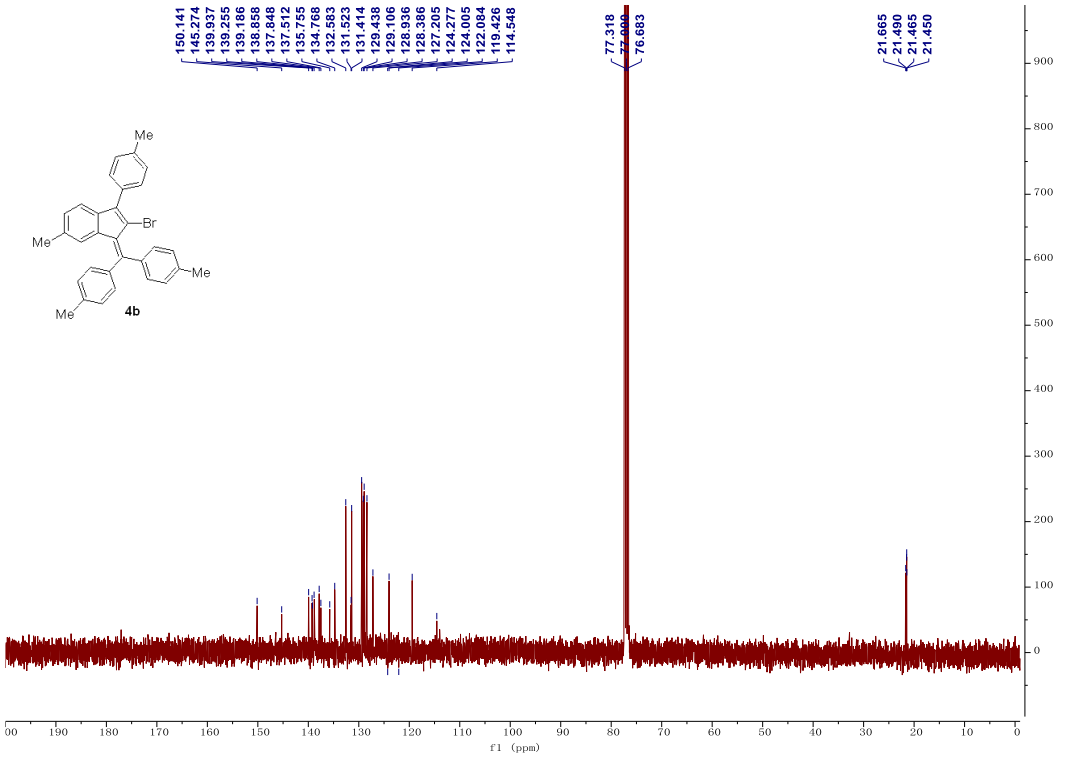



**Figure S77.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **4b**

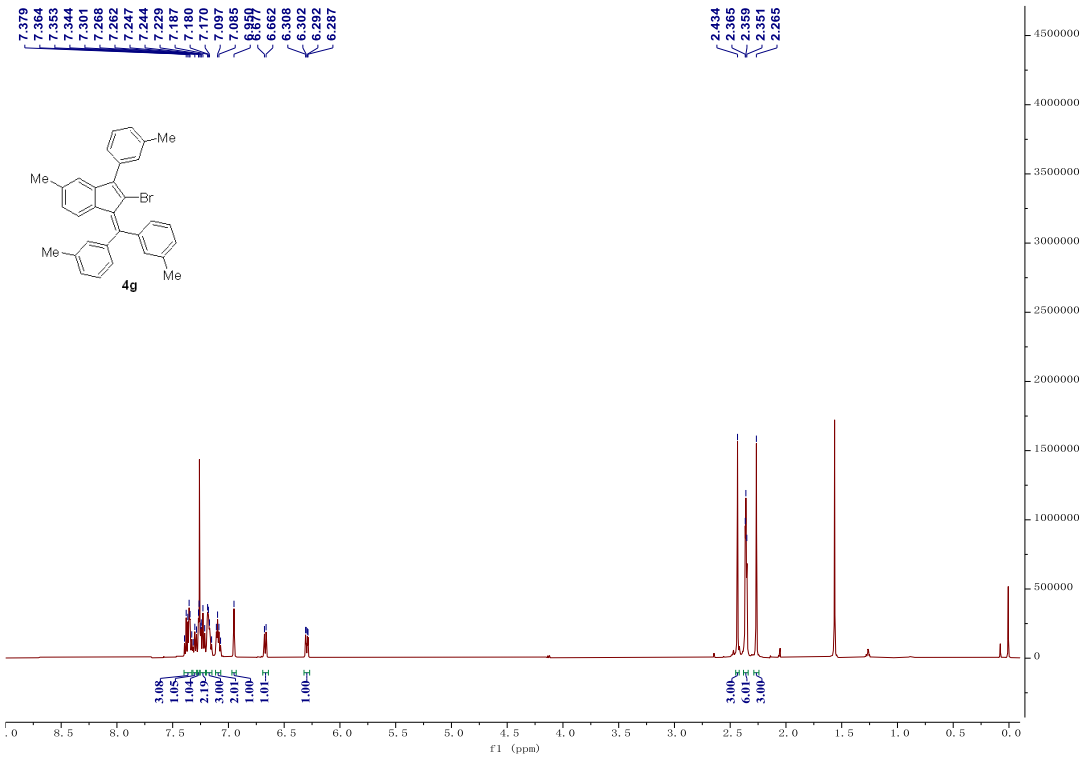



**Figure S78.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4g**

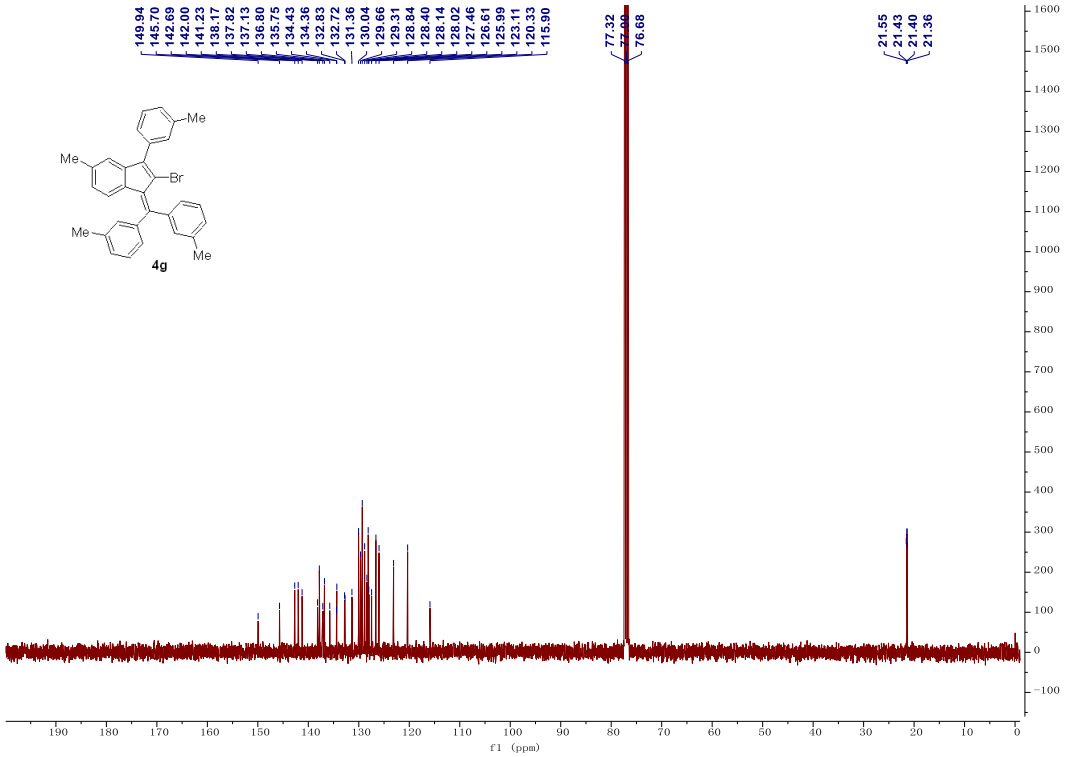



**Figure S79.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **4g**

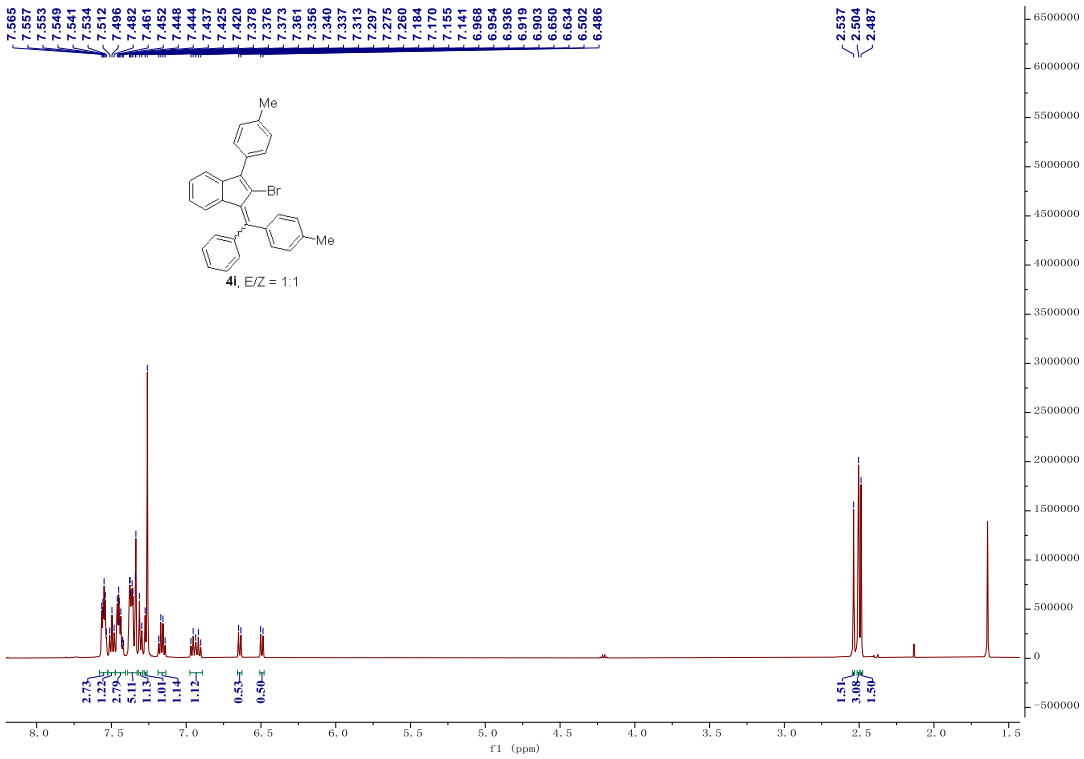



**Figure S80.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4i**

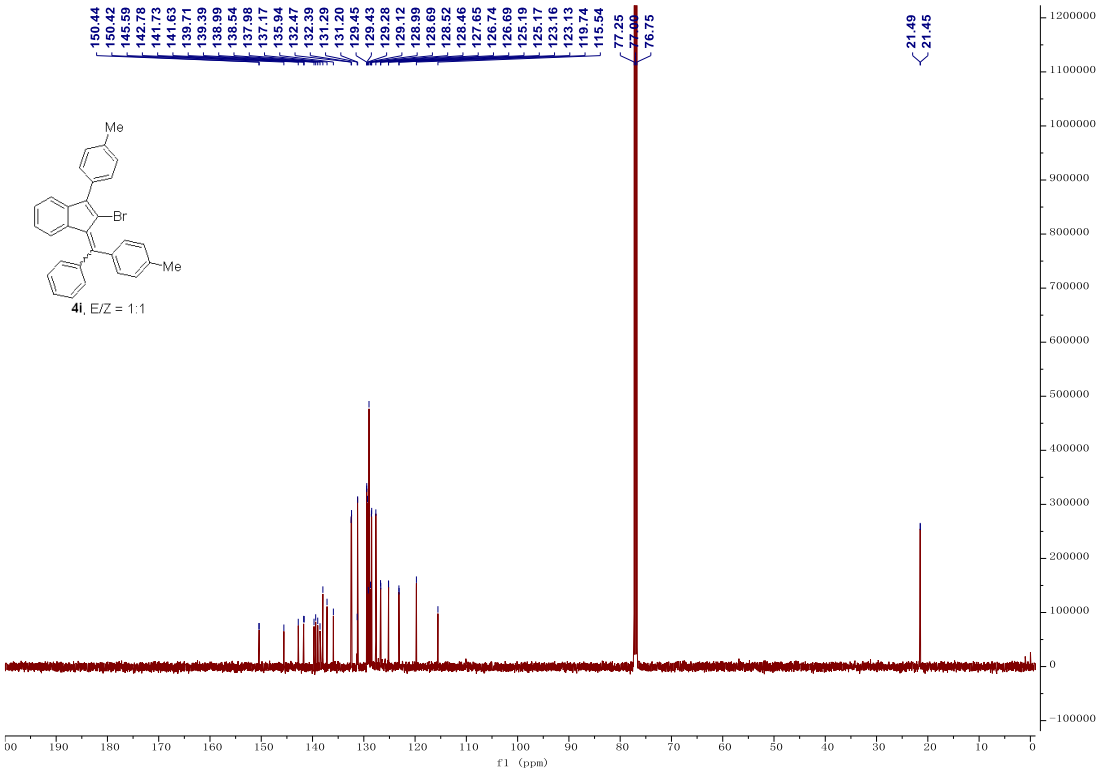



**Figure S81.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **4i**

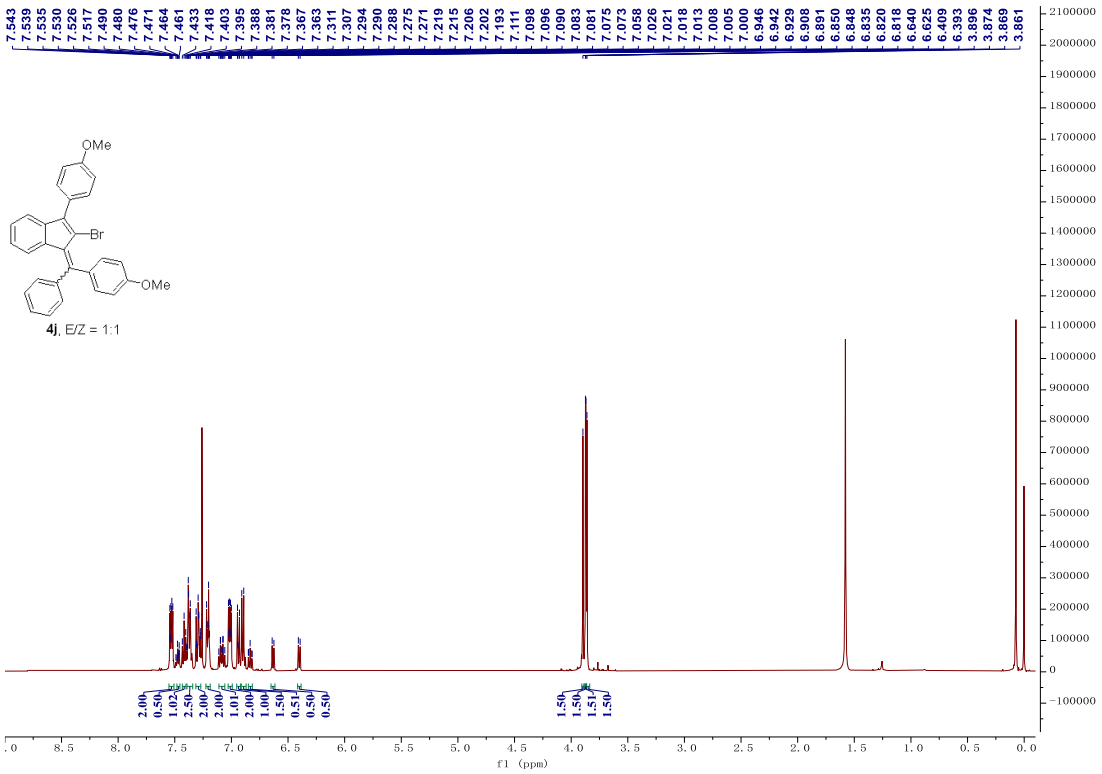



**Figure S82.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4j**

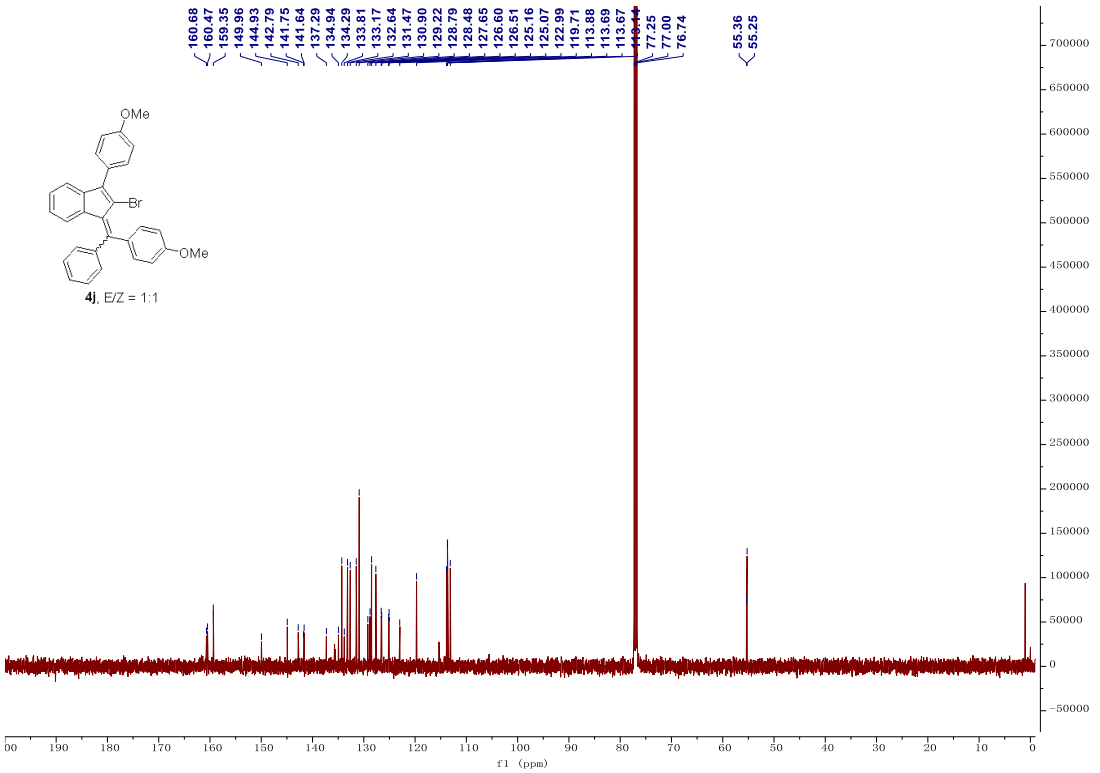



**Figure S83.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **4j**

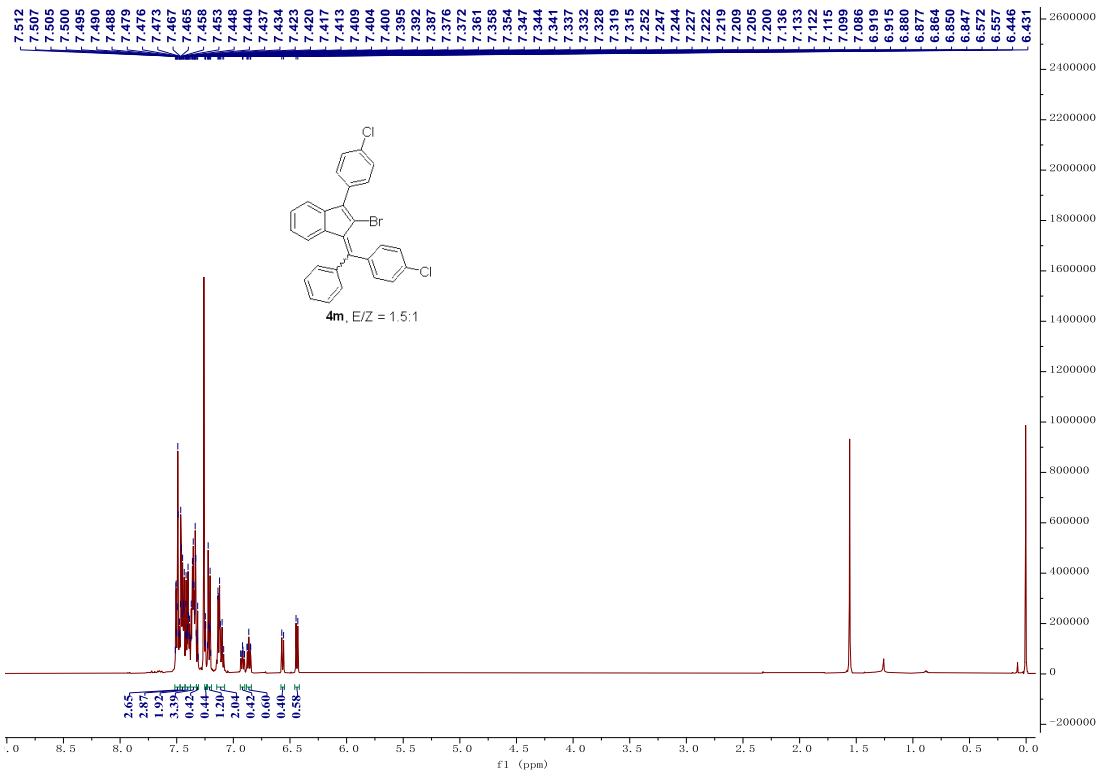



**Figure S84.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4m**

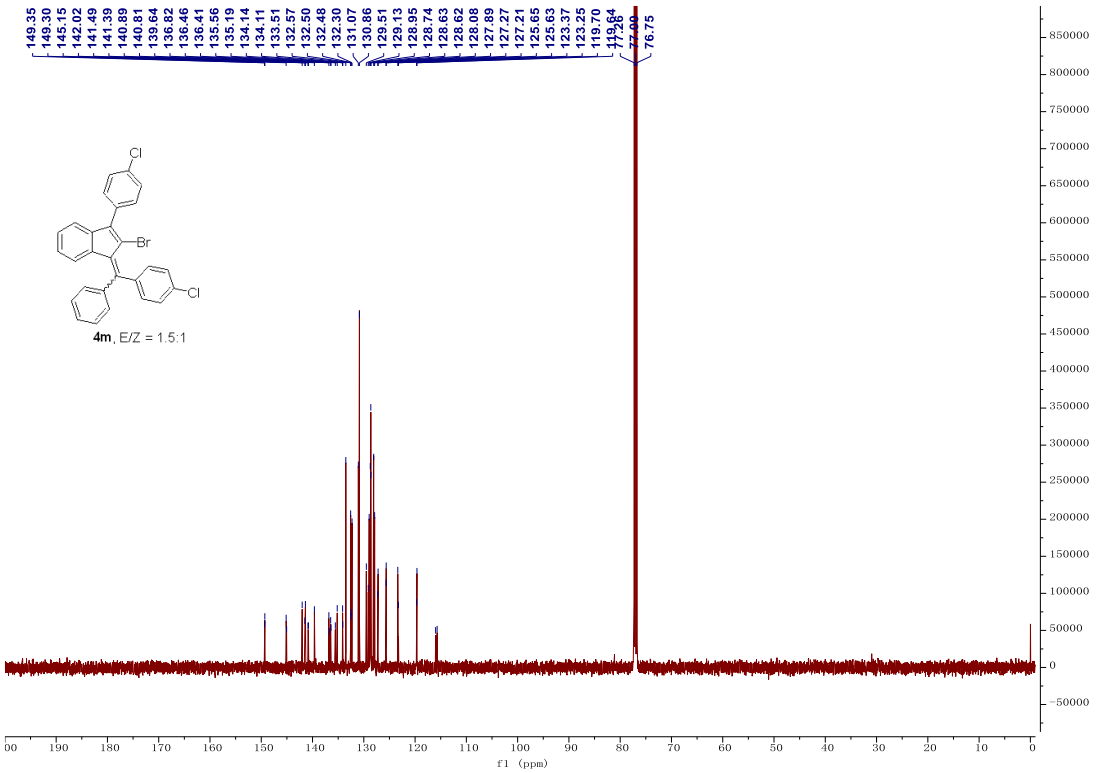



**Figure S85.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **4m**

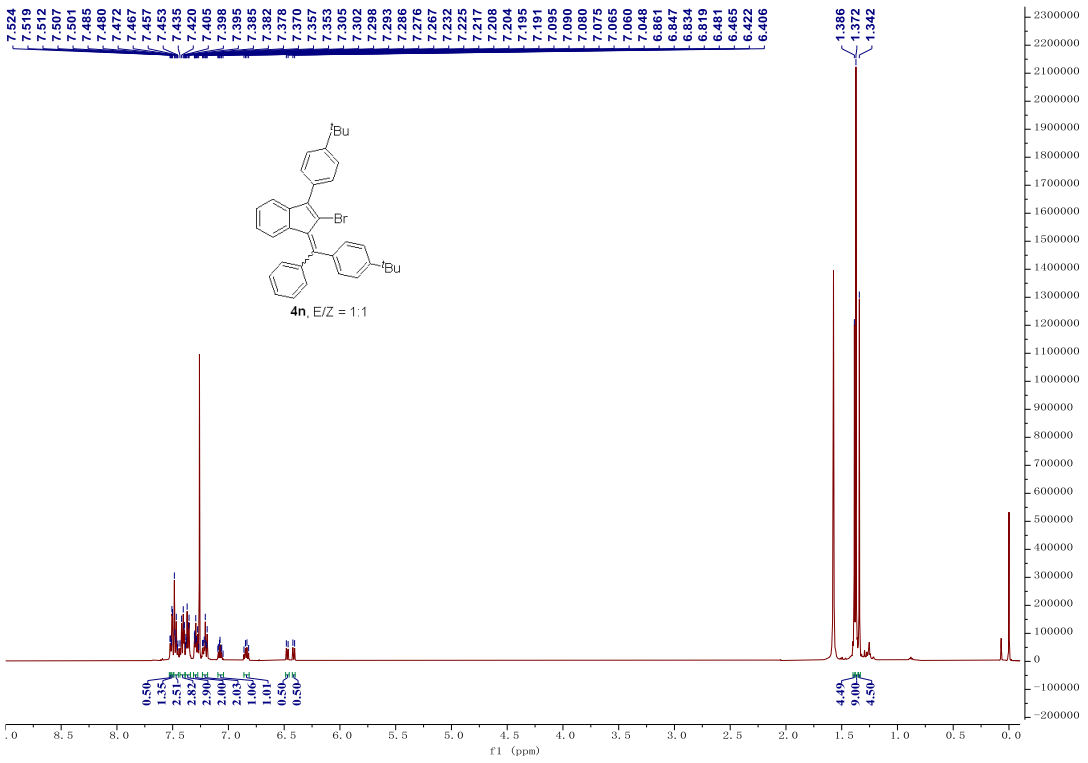



**Figure S86.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4n**

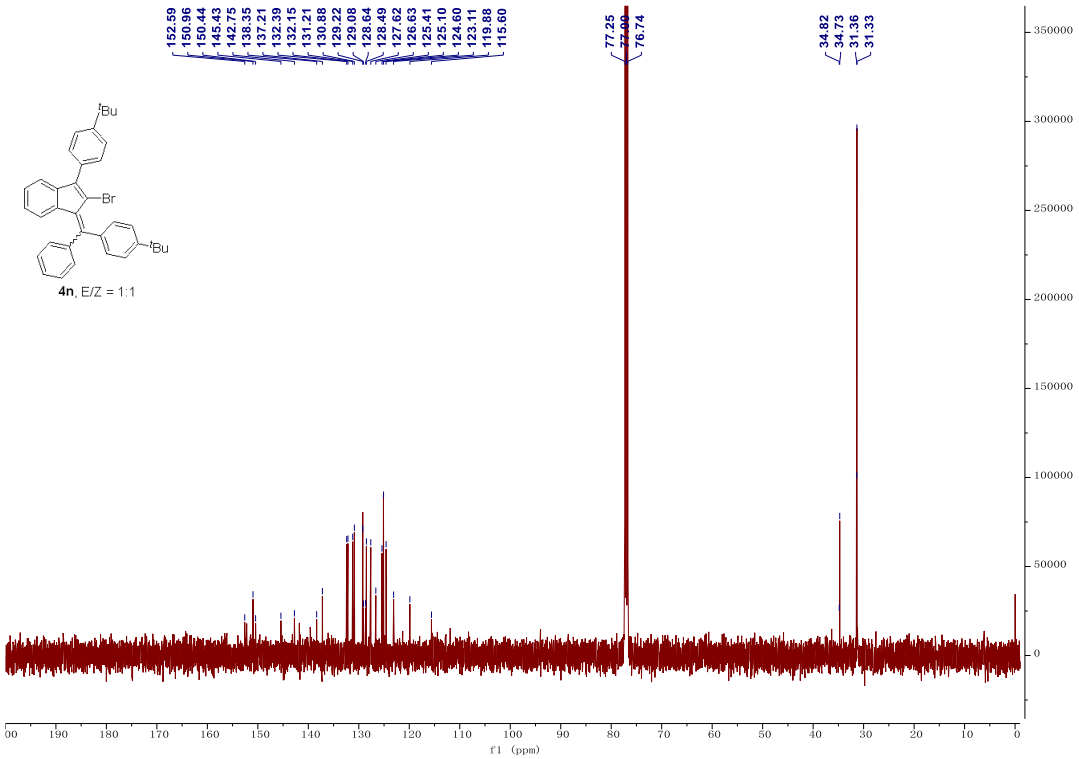



**Figure S87.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **4n**

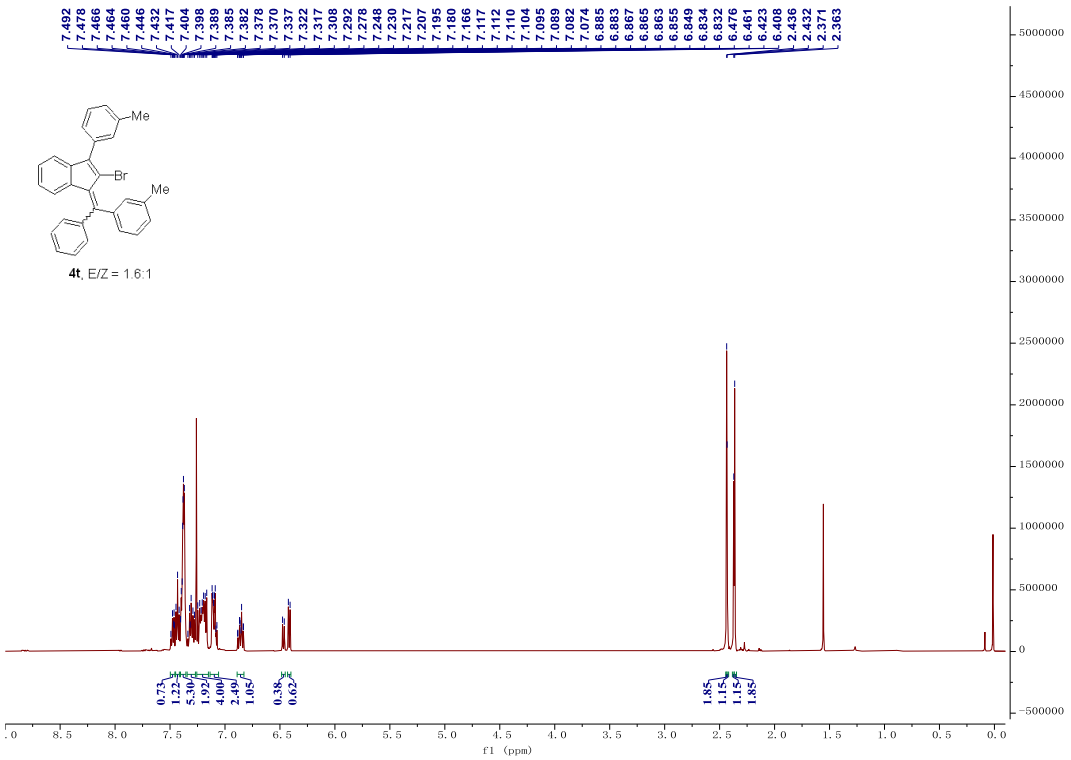



**Figure S88.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **4t**

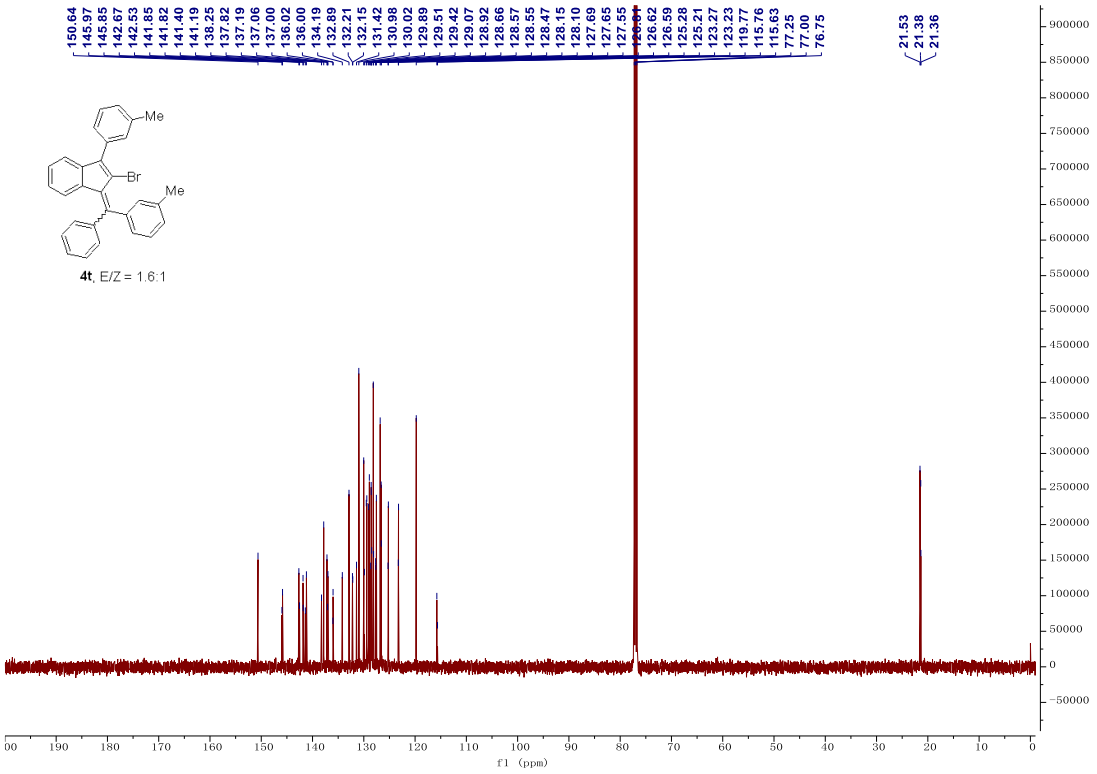



**Figure S89.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **4t**

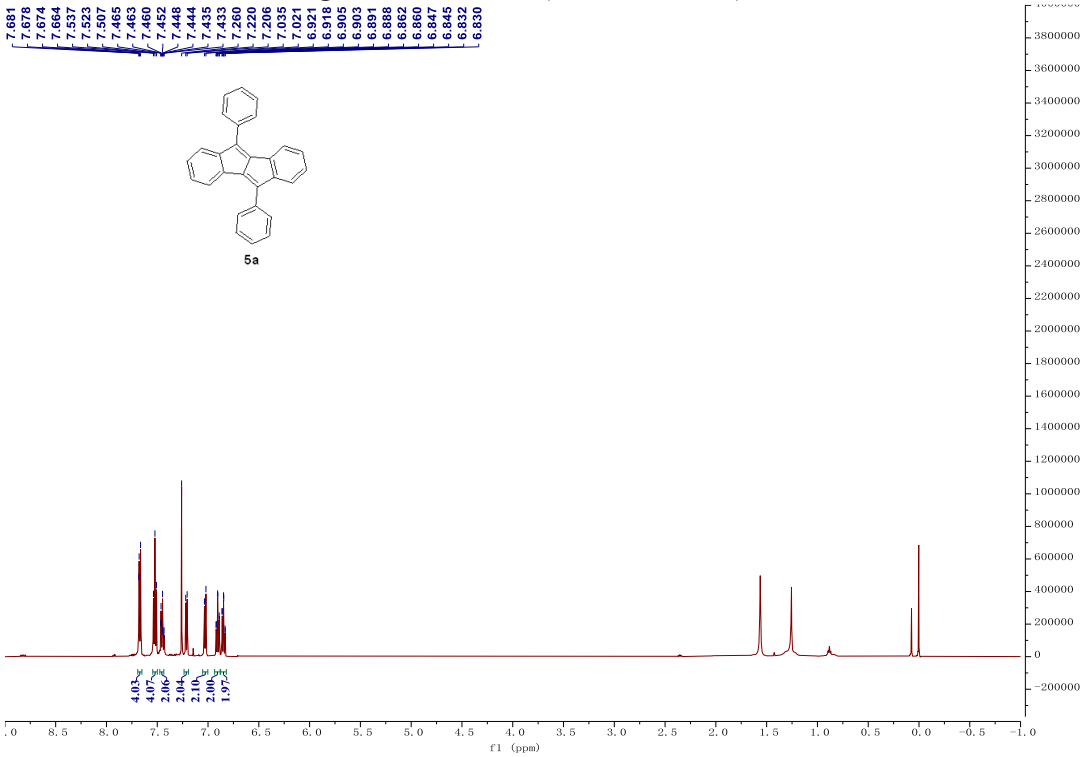



**Figure S90.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5a**

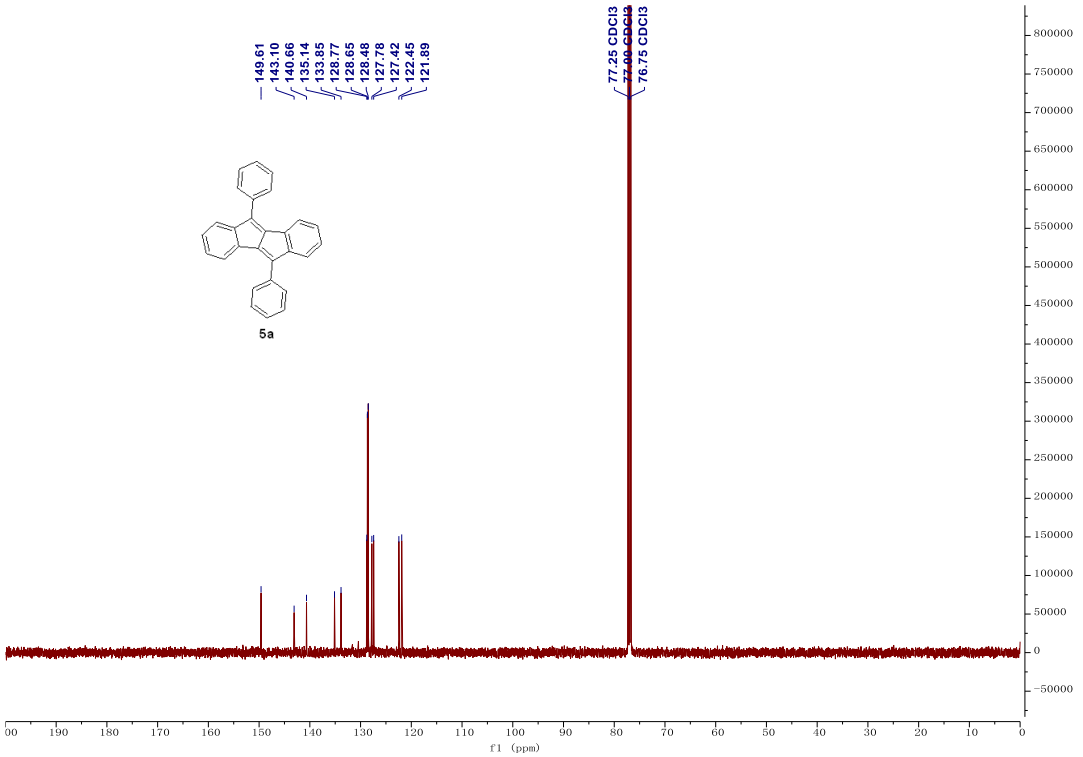



**Figure S91.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **5a**

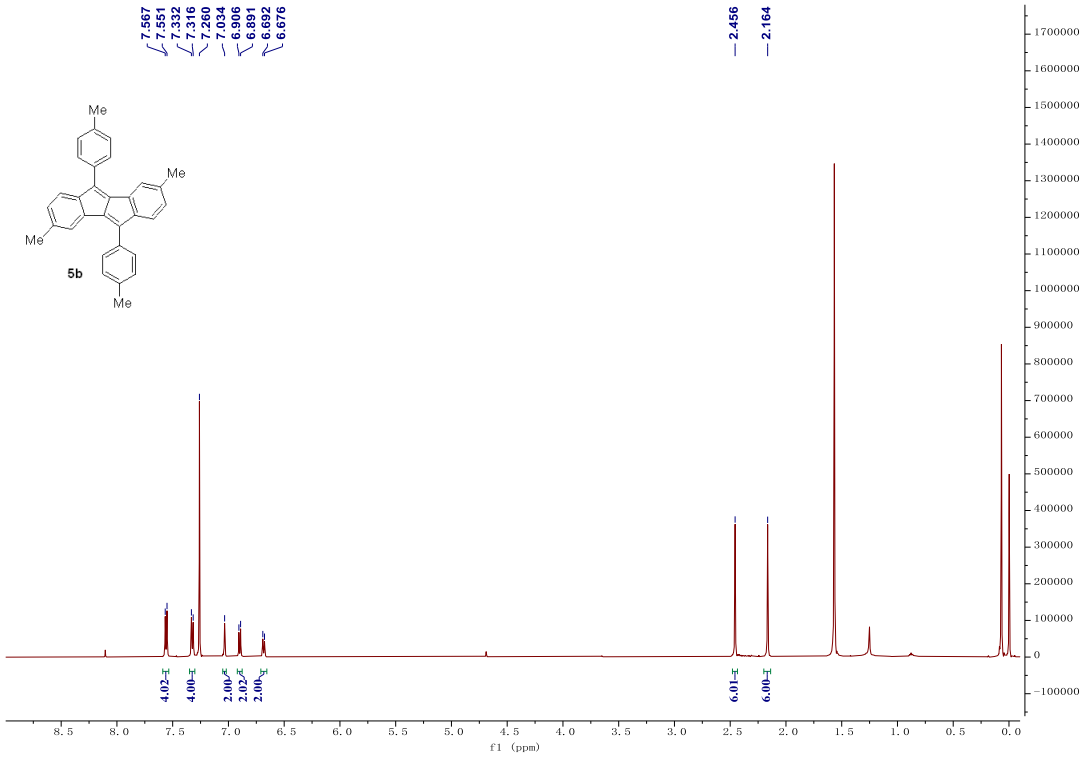



**Figure S92.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5b**

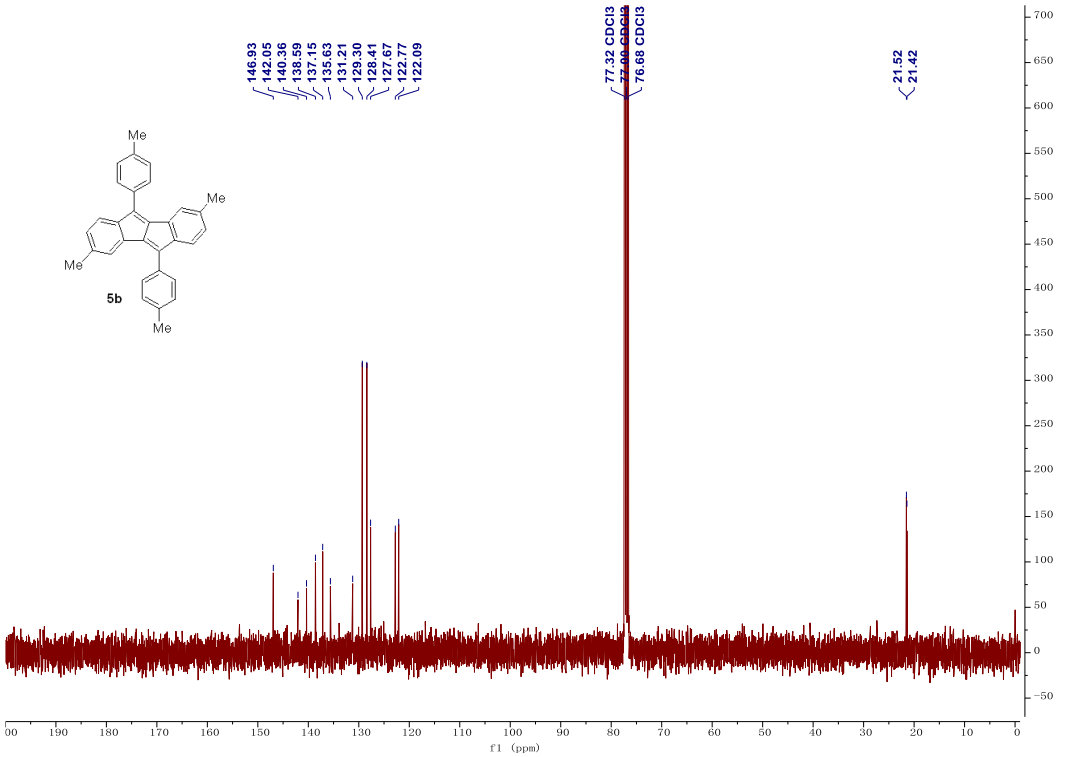



**Figure S93.** $^{13}C$ NMR (101 MHz, $CDCl_3$) of **5b**

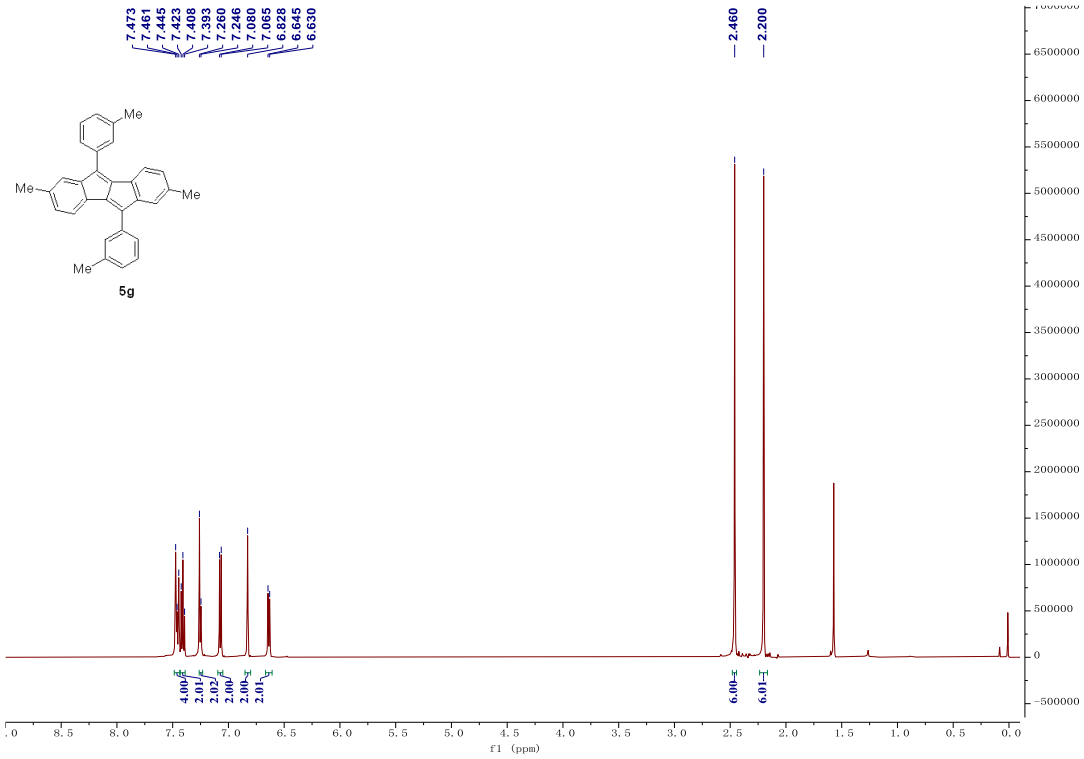



**Figure S94.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5g**

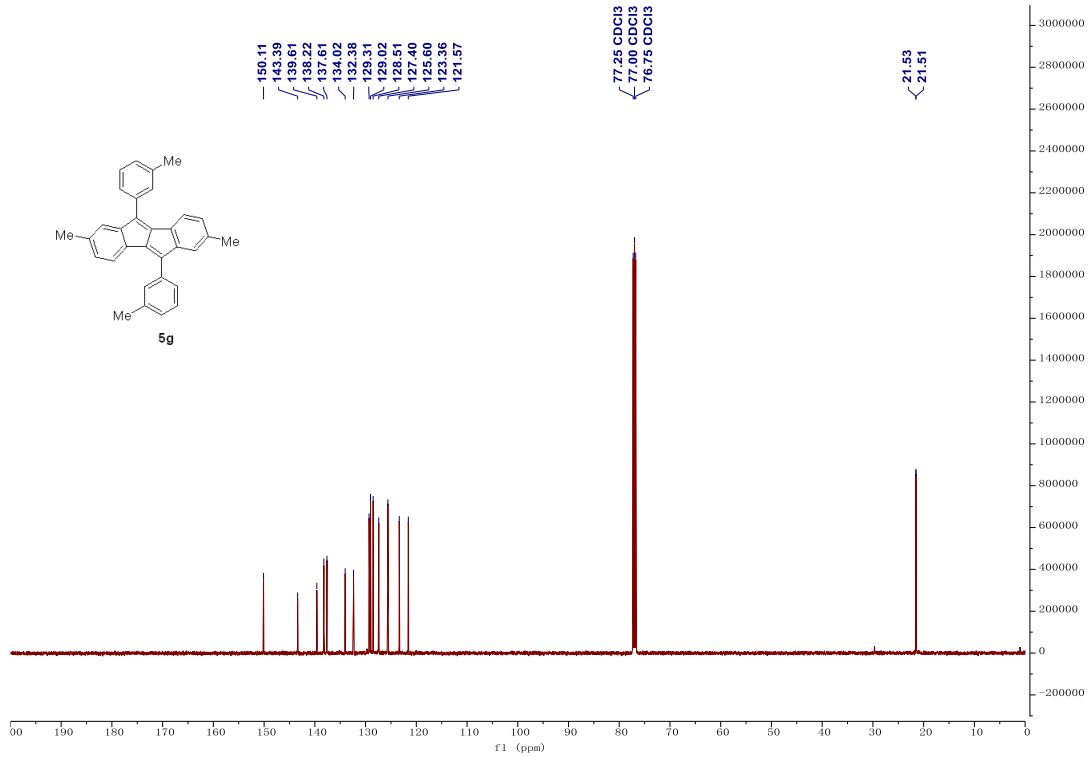



**Figure S95.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **5g**

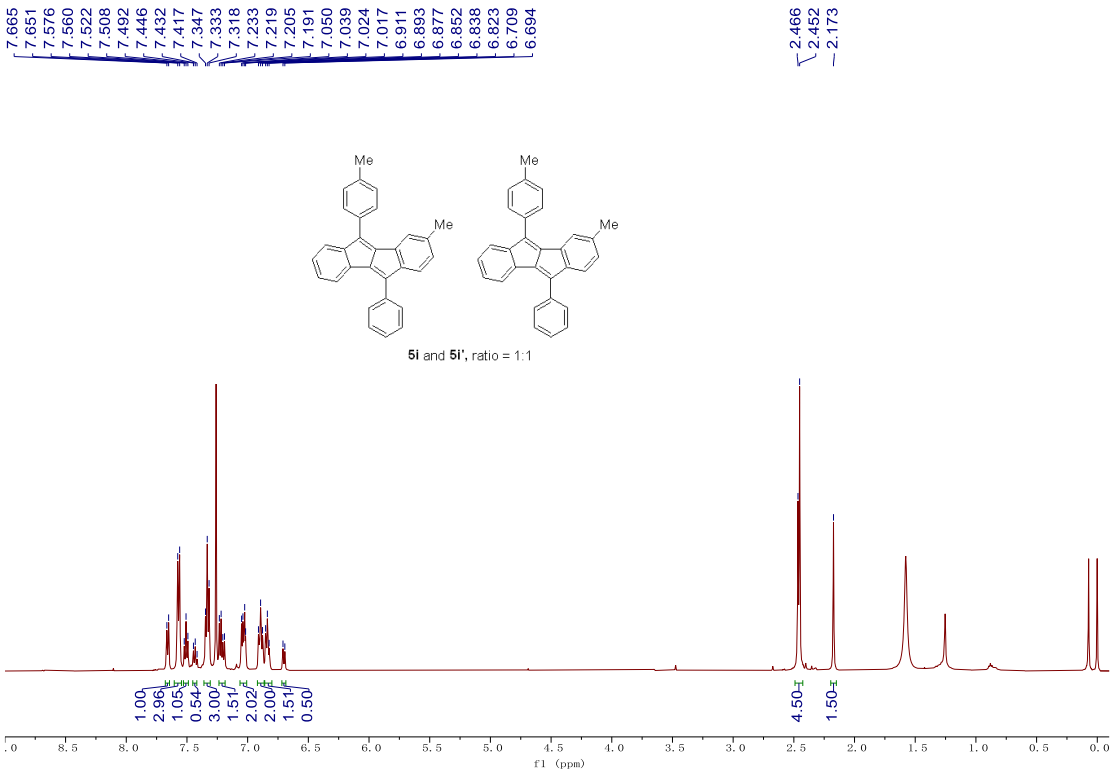



**Figure S96.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5i**

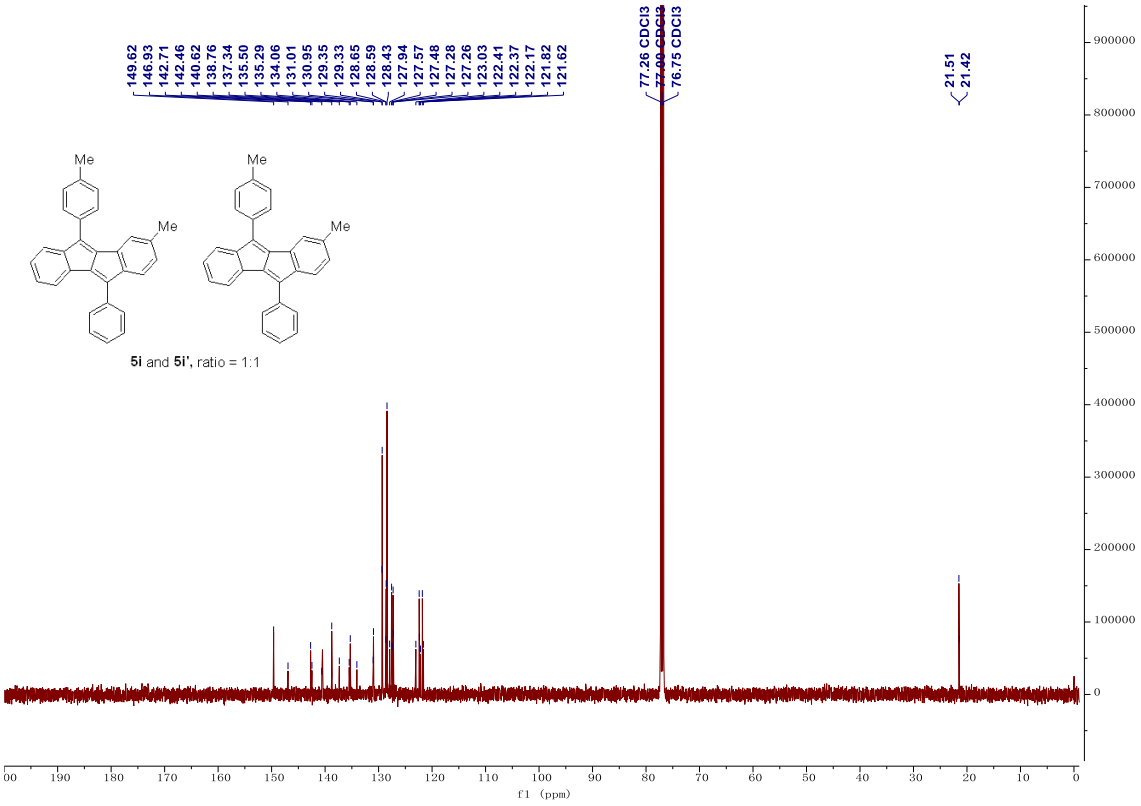



**Figure S97.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **5i**

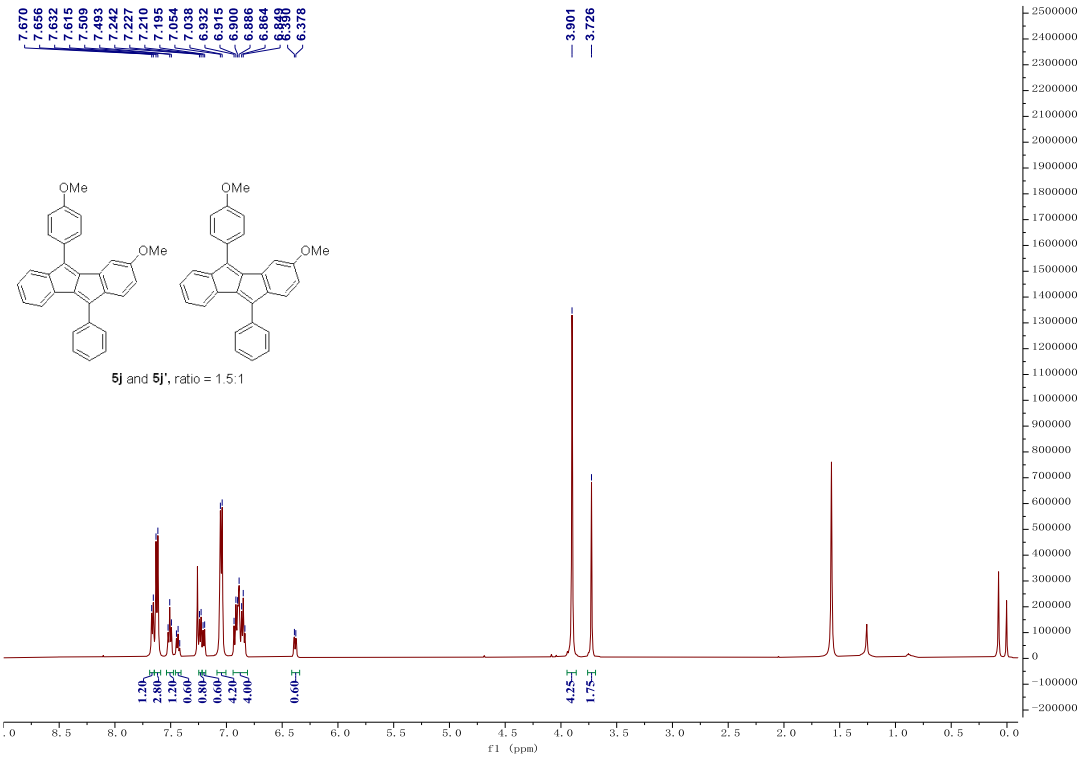



**Figure S98.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5j**

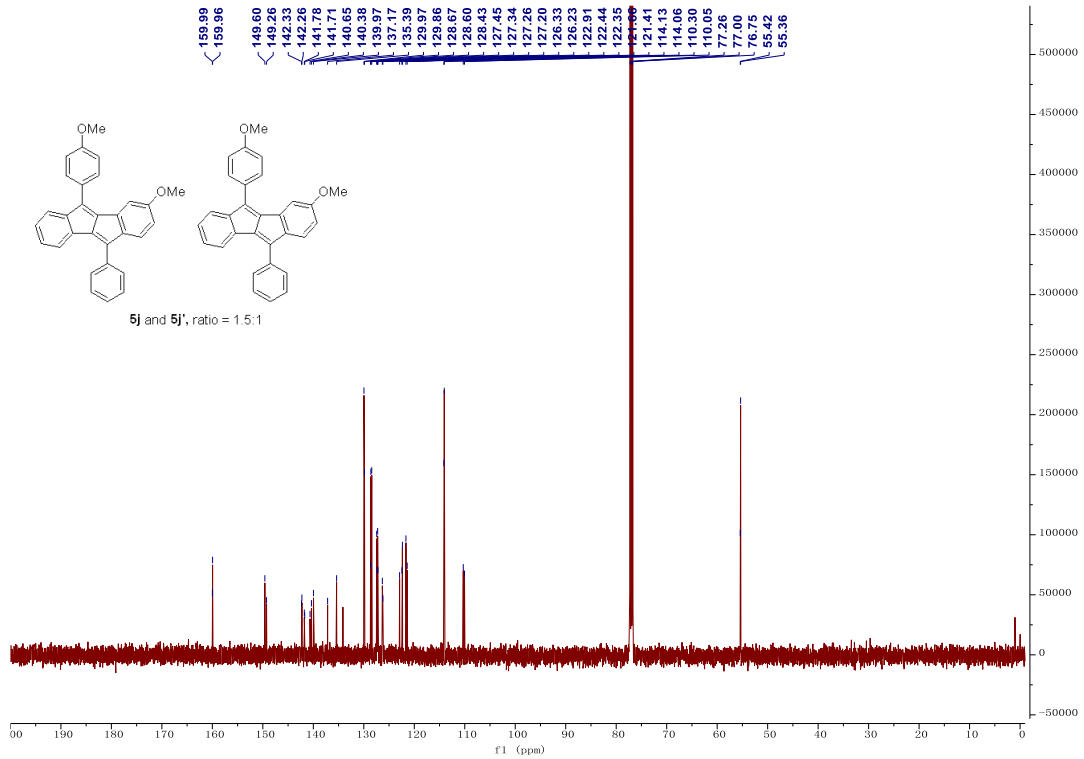



**Figure S99.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **5j**

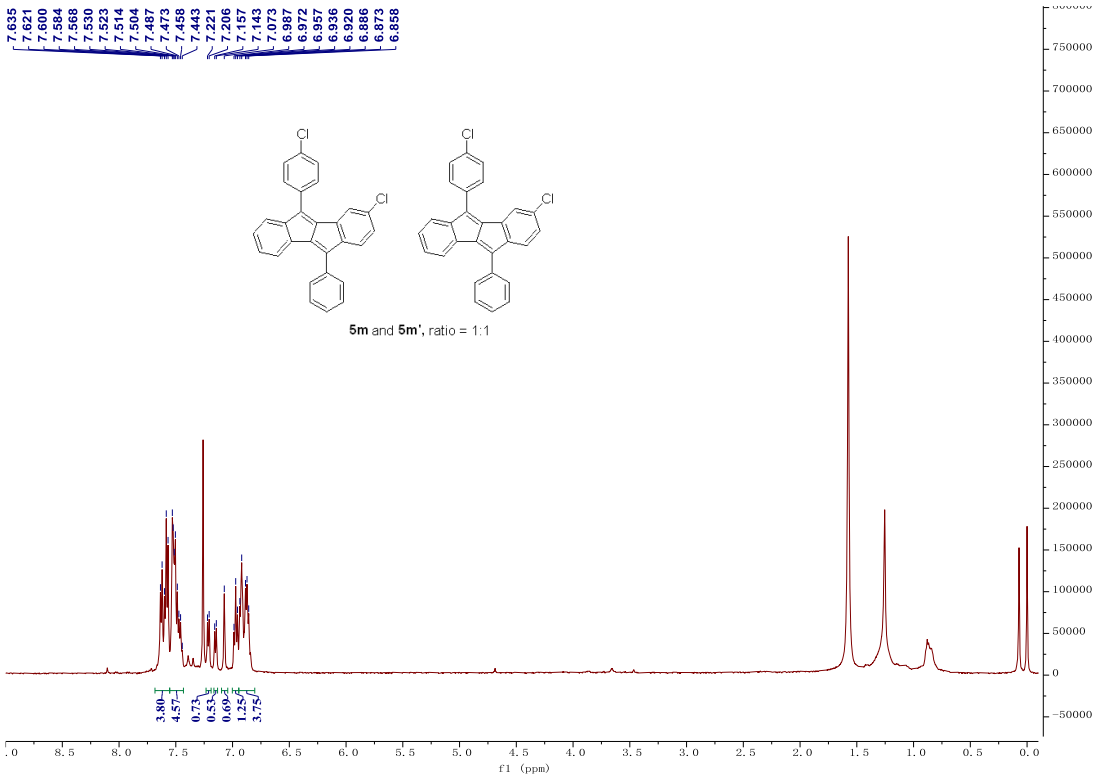



**Figure S100.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5m**

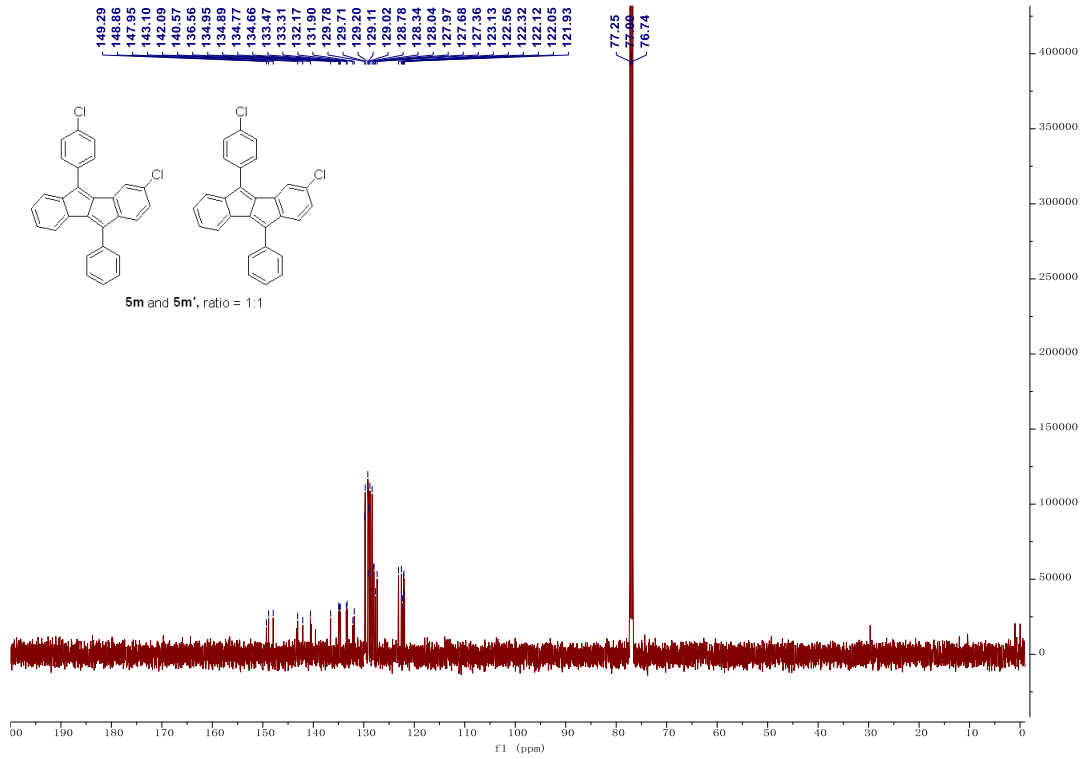



**Figure S101.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **5m**

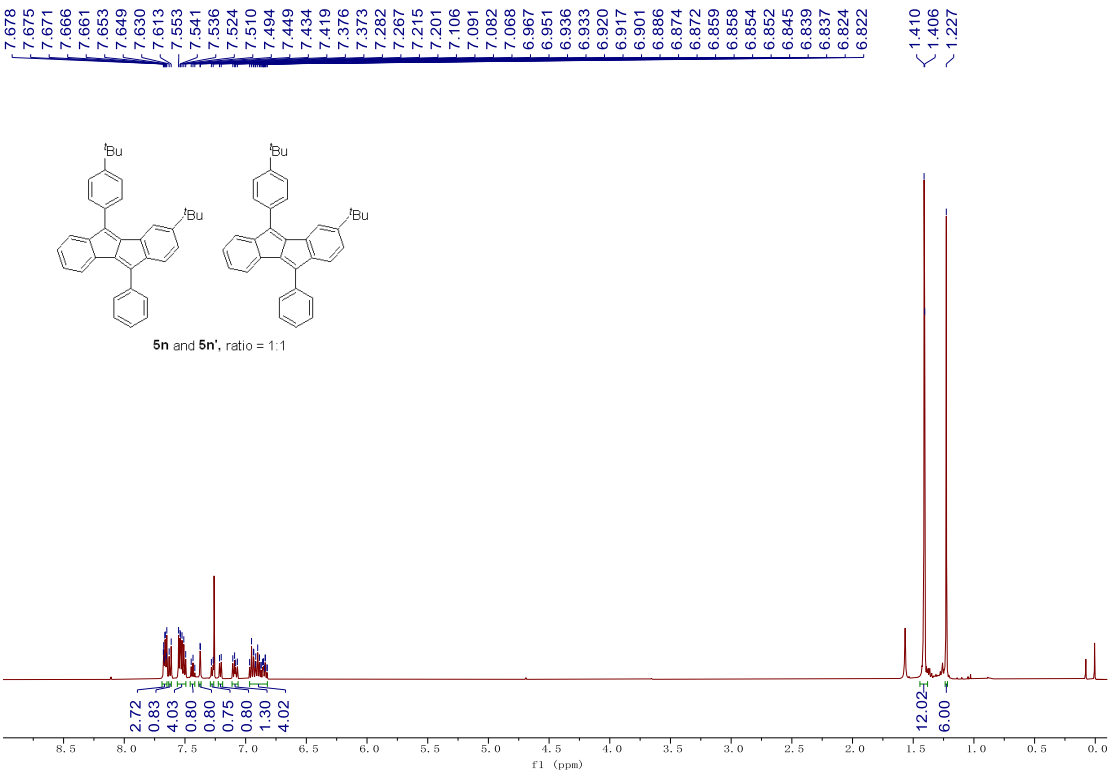



**Figure S102.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5n**

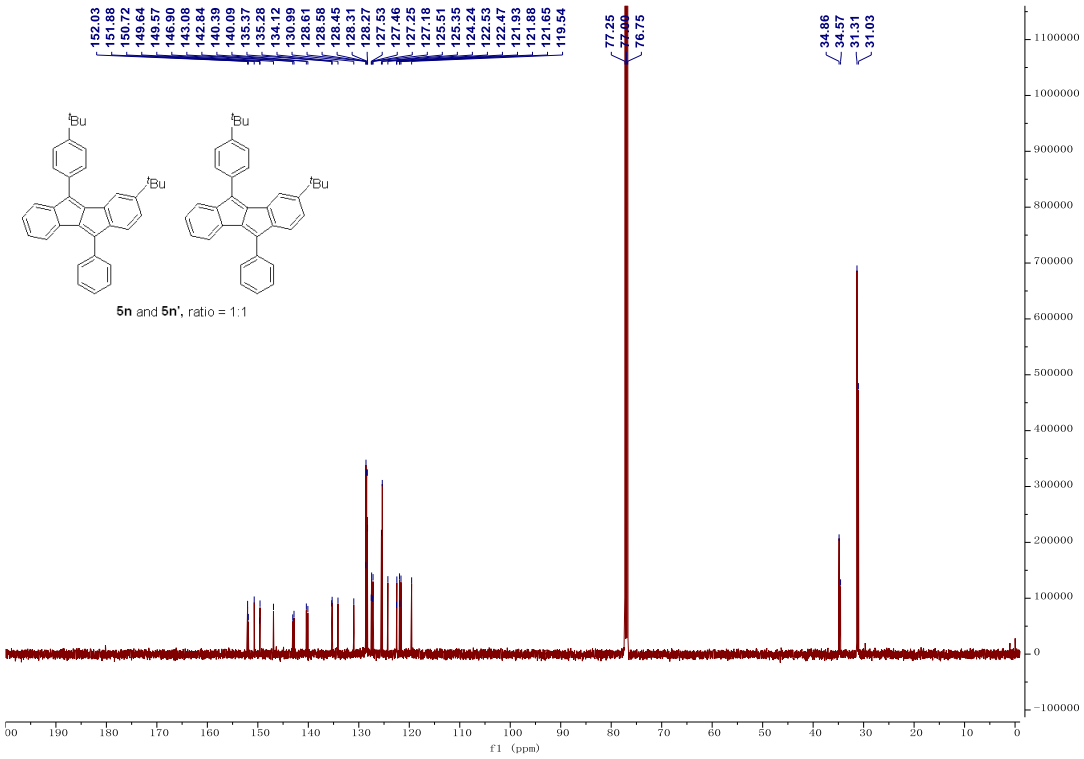



**Figure S103.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **5n**

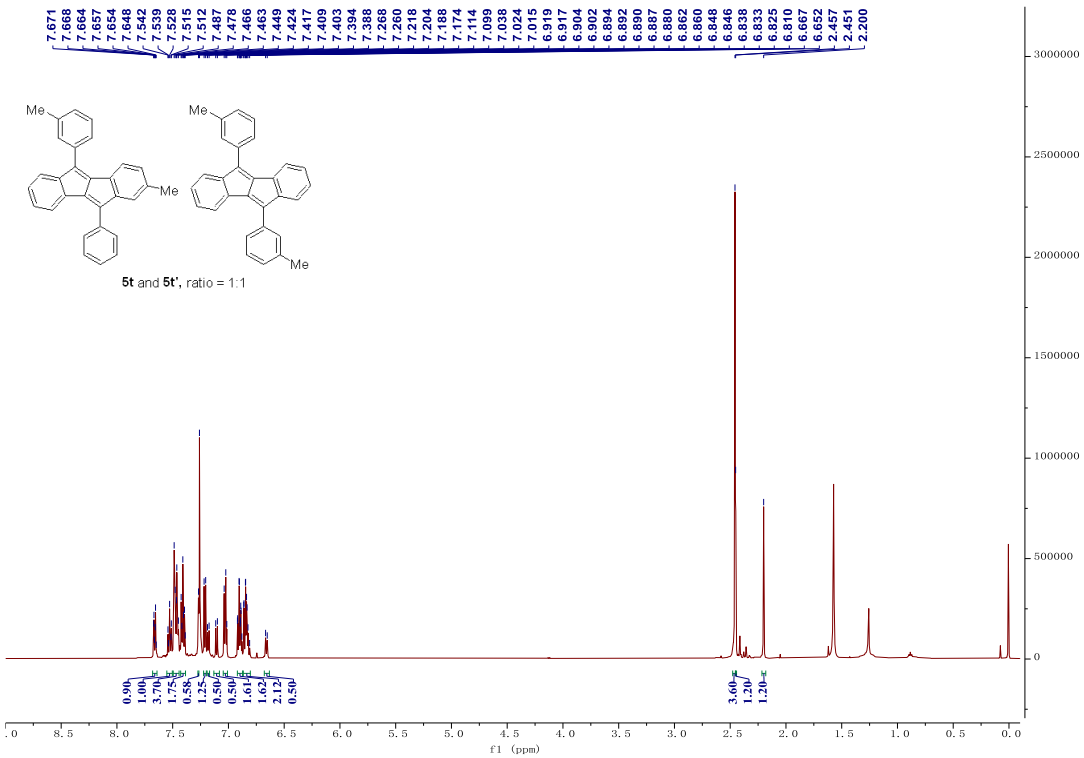



**Figure S104.** $^{1}H$ NMR (500 MHz, $CDCl_3$) of **5t**

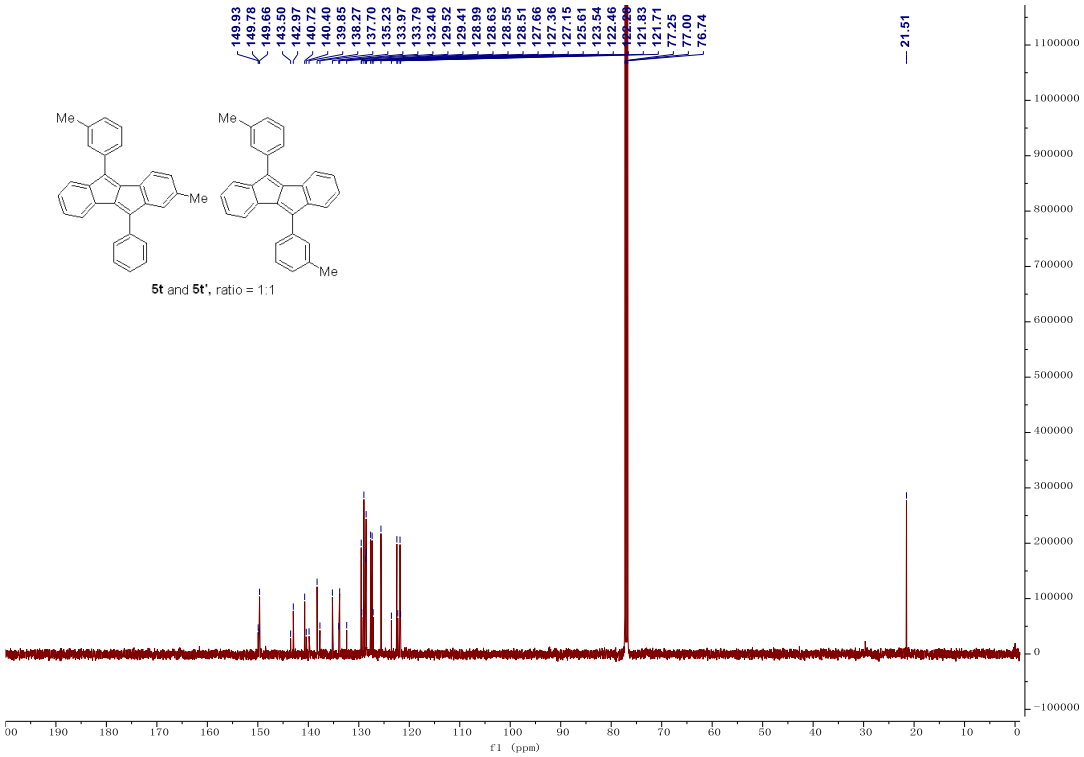



**Figure S105.** $^{13}C$ NMR (126 MHz, $CDCl_3$) of **5t**

## 5. Single Crystal Data

### Crystal growth for compounds 2a, 2b, 2t, 3w, 4a and 5a:

General procedure: The above compounds **2a, 2b, 2t, 4a and 5a** (solid,10 ~20 mg) was dissolved with minimal dichloromethane followed by about 1/5 (volume) petroleum ether was added and the compound **3w** (oil,10 ~15 mg) was dissolved with minimal petroleum ether followed by about 1/5 (volume) methanol was added. The solvent was slowly volatizing under open air to afford crystalline, which was suitable for single crystal X-ray analysis.

### Single Crystal Data for 2a

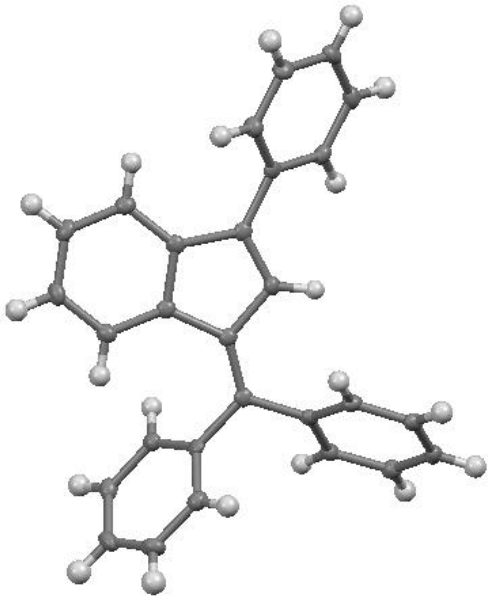


**Figure S106.** Thermal ellipsoid plot of **2a** (50% probability levels)

**Table S1 Crystal data and structure refinement for 2a.**

| | |
|---|---|
| Identification code | AR-1-94 |
| Empirical formula | $C_{28}H_{20}$ |
| Formula weight | 356.44 |
| Temperature/K | 100.01(10) |
| Crystal system | orthorhombic |
| Space group | Pbca |
| a/Å | 20.2193(10) |
| b/Å | 9.1043(5) |
| c/Å | 20.3772(16) |
| α/° | 90 |
| β/° | 90 |

| | |
|---|---|
| γ/° | 90 |
| Volume/Å$^3$ | 3751.1(4) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.262 |
| μ/mm$^{-1}$ | 0.071 |
| F(000) | 1504.0 |
| Crystal size/mm$^3$ | 0.13 × 0.12 × 0.11 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.476 to 49.998 |
| Index ranges | -16 ≤ h ≤ 24, -10 ≤ k ≤ 10, -17 ≤ l ≤ 24 |
| Reflections collected | 11414 |
| Independent reflections | 3302 [$R_{int}$ = 0.0484, $R_{sigma}$ = 0.0561] |
| Data/restraints/parameters | 3302/0/253 |
| Goodness-of-fit on F$^2$ | 1.059 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0471, w$R_2$ = 0.0992 |
| Final R indexes [all data] | $R_1$ = 0.0655, w$R_2$ = 0.1088 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.23/-0.26 |

**Single Crystal Data for 2i**

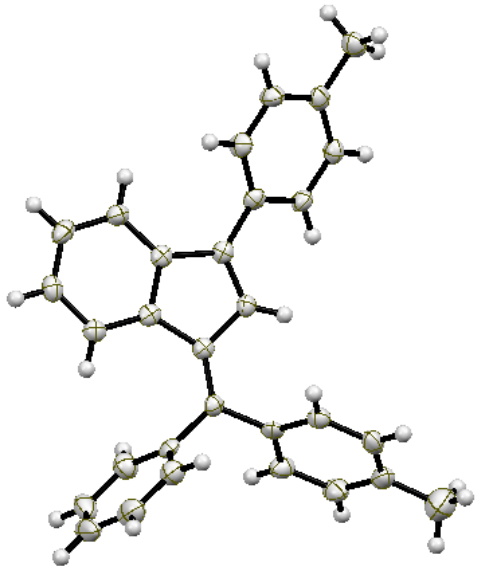


**Figure S107.** Thermal ellipsoid plot of **2i** (50% probability levels)

**Table S2 Crystal data and structure refinement for 2i.**

| | |
|---|---|
| Identification code | AR-1-166 |
| Empirical formula | $C_{30}H_{24}$ |
| Formula weight | 384.49 |

| | |
|---|---|
| Temperature/K | 100.00(10) |
| Crystal system | orthorhombic |
| Space group | $Pca2_1$ |
| a/Å | 23.5706(16) |
| b/Å | 9.7419(7) |
| c/Å | 9.0959(6) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2088.6(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.223 |
| μ/mm$^{-1}$ | 0.069 |
| F(000) | 816.0 |
| Crystal size/mm$^3$ | 0.13 × 0.12 × 0.09 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.182 to 49.988 |
| Index ranges | -28 ≤ h ≤ 23, -11 ≤ k ≤ 10, -7 ≤ l ≤ 10 |
| Reflections collected | 6289 |
| Independent reflections | 2844 [$R_{int}$ = 0.0303, $R_{sigma}$ = 0.0394] |
| Data/restraints/parameters | 2844/1/273 |
| Goodness-of-fit on F$^2$ | 1.057 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0408, $wR_2$ = 0.1001 |
| Final R indexes [all data] | $R_1$ = 0.0444, $wR_2$ = 0.1030 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.43/-0.23 |
| Flack parameter | -6.5(10) |

**Single Crystal Data for 2j**

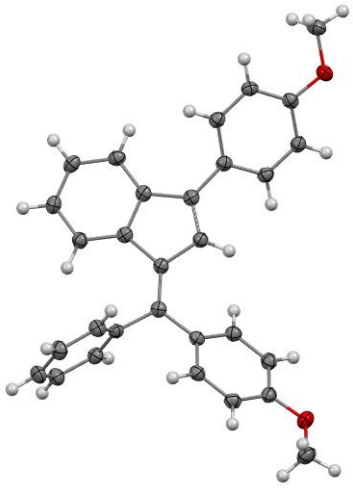


**Figure S108.** Thermal ellipsoid plot of **2j** (50% probability levels)

**Table S3 Crystal data and structure refinement for 2j.**

| | |
|---|---|
| Identification code | AR-3-105 |
| Empirical formula | $C_{30}H_{24}O_2$ |
| Formula weight | 416.49 |
| Temperature/K | 120.01(16) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.42730(10) |
| b/Å | 10.44380(10) |
| c/Å | 10.5389(2) |
| α/° | 103.0090(10) |
| β/° | 99.5880(10) |
| γ/° | 93.9210(10) |
| Volume/Å$^3$ | 1095.90(3) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.262 |
| μ/mm$^{-1}$ | 0.606 |
| F(000) | 440.0 |
| Crystal size/mm$^3$ | 0.16 × 0.14 × 0.12 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.652 to 148.396 |
| Index ranges | $-13 \leq h \leq 9$, $-12 \leq k \leq 13$, $-12 \leq l \leq 13$ |
| Reflections collected | 11287 |
| Independent reflections | 4300 [$R_{int}$ = 0.0177, $R_{sigma}$ = 0.0173] |
| Data/restraints/parameters | 4300/0/292 |
| Goodness-of-fit on $F^2$ | 1.004 |

Final R indexes [I>=2σ (I)] $R_1 = 0.0361$, $wR_2 = 0.0926$

Final R indexes [all data] $R_1 = 0.0373$, $wR_2 = 0.0936$

Largest diff. peak/hole / e $Å^{-3}$ 0.26/-0.17

**Single Crystal Data for 2z**

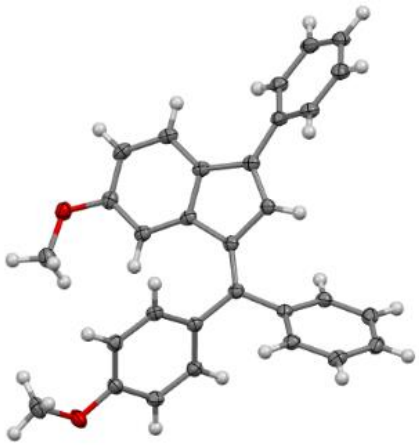


**Figure S109.** Thermal ellipsoid plot of **2z** (50% probability levels)

**Table S4 Crystal data and structure refinement for 2z.**

| | |
|---|---|
| Identification code | AR-3-85 |
| Empirical formula | $C_{30}H_{24}O_2$ |
| Formula weight | 416.49 |
| Temperature/K | 120.00(14) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 12.03370(10) |
| b/Å | 10.36980(10) |
| c/Å | 17.3479(2) |
| α/° | 90 |
| β/° | 91.4450(10) |
| γ/° | 90 |

| | |
|---|---|
| Volume/Å$^3$ | 2164.11(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.278 |
| $\mu$/mm$^{-1}$ | 0.614 |
| F(000) | 880.0 |
| Crystal size/mm$^3$ | 0.15 × 0.13 × 0.11 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.84 to 148.368 |
| Index ranges | -14 ≤ h ≤ 14, -6 ≤ k ≤ 12, -21 ≤ l ≤ 21 |
| Reflections collected | 11485 |
| Independent reflections | 4272 [$R_{int}$ = 0.0213, $R_{sigma}$ = 0.0259] |
| Data/restraints/parameters | 4272/0/291 |
| Goodness-of-fit on F$^2$ | 1.029 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0369, $wR_2$ = 0.0954 |
| Final R indexes [all data] | $R_1$ = 0.0397, $wR_2$ = 0.0976 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.16/-0.25 |

**Single Crystal Data for 2aa**

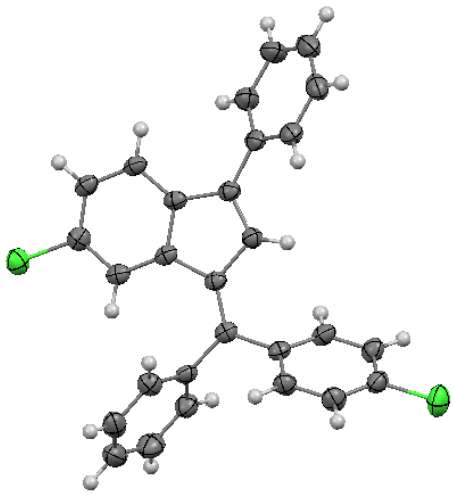


**Figure S110.** Thermal ellipsoid plot of **2aa** (50% probability levels)

**Table S5 Crystal data and structure refinement for 2aa.**

| | |
|---|---|
| Identification code | AR-2-150 |
| Empirical formula | $C_{28}H_{18}Cl_2$ |
| Formula weight | 425.32 |
| Temperature/K | 150.00(10) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.0640(3) |
| b/Å | 9.5665(3) |
| c/Å | 24.1643(8) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2095.29(11) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.348 |
| μ/mm$^{-1}$ | 2.865 |
| F(000) | 880.0 |
| Crystal size/mm$^3$ | 0.13 × 0.12 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.316 to 142.496 |
| Index ranges | $-10 \le h \le 9$, $-11 \le k \le 11$, $-29 \le l \le 29$ |
| Reflections collected | 6701 |
| Independent reflections | 3574 [$R_{int}$ = 0.0271, $R_{sigma}$ = 0.0409] |
| Data/restraints/parameters | 3574/0/271 |
| Goodness-of-fit on $F^2$ | 1.108 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0422, $wR_2$ = 0.1123 |
| Final R indexes [all data] | $R_1$ = 0.0468, $wR_2$ = 0.1147 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.58/-0.37 |
| Flack/Hooft parameter | 0.014(11)/0.007(9) |

## Single Crystal Data for 3b

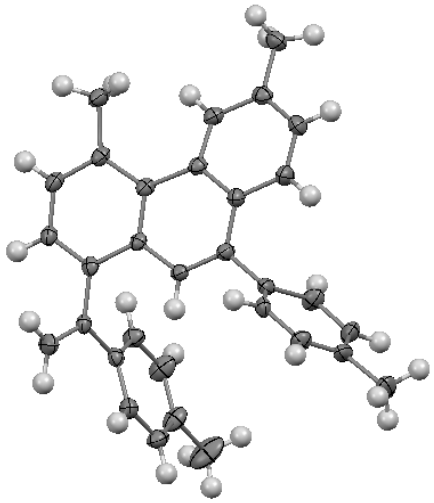


**Figure S111.** Thermal ellipsoid plot of **3b** (50% probability levels)

**Table S6 Crystal data and structure refinement for 3b.**

| | |
|---|---|
| Identification code | AR-3-36 |
| Empirical formula | $C_{32}H_{28}$ |
| Formula weight | 412.54 |
| Temperature/K | 100.00(10) |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 22.982(2) |
| b/Å | 7.2386(5) |
| c/Å | 28.738(2) |
| α/° | 90 |
| β/° | 100.556(8) |
| γ/° | 90 |
| Volume/Å$^3$ | 4699.9(6) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.166 |
| μ/mm$^{-1}$ | 0.066 |
| F(000) | 1760.0 |
| Crystal size/mm$^3$ | 0.15 × 0.13 × 0.12 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.184 to 49.99 |
| Index ranges | -26 ≤ h ≤ 27, -8 ≤ k ≤ 8, -34 ≤ l ≤ 29 |
| Reflections collected | 11686 |
| Independent reflections | 4150 [$R_{int}$ = 0.0339, $R_{sigma}$ = 0.0437] |
| Data/restraints/parameters | 4150/0/338 |
| Goodness-of-fit on F$^2$ | 1.018 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0530, $wR_2$ = 0.1241 |

Final R indexes [all data] $R_1 = 0.0701$, $wR_2 = 0.1376$
Largest diff. peak/hole / e Å$^{-3}$ 0.24/-0.17

**Single Crystal Data for 4a**

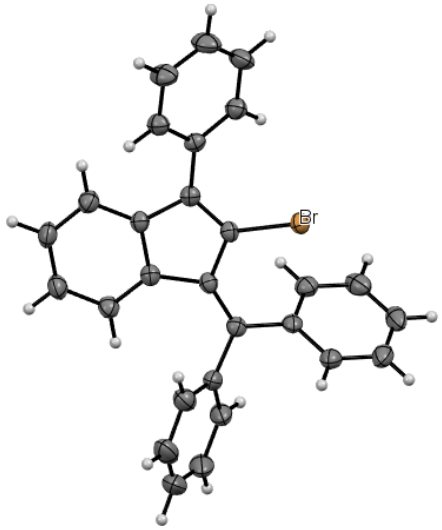



**Figure S112.** Thermal ellipsoid plot of **4a** (50% probability levels)

**Table S7 Crystal data and structure refinement for 4a.**

| | |
|---|---|
| Identification code | AR-2-165-2 |
| Empirical formula | $C_{28}H_{19}Br$ |
| Formula weight | 435.34 |
| Temperature/K | 220.01(10) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 10.31429(10) |
| b/Å | 13.70396(12) |
| c/Å | 14.53348(13) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2054.26(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.408 |
| μ/mm$^{-1}$ | 2.790 |
| F(000) | 888.0 |
| Crystal size/mm$^3$ | 0.14 × 0.12 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.87 to 143.224 |
| Index ranges | $-12 \le h \le 10$, $-16 \le k \le 16$, $-17 \le l \le 17$ |

| | |
|---|---|
| Reflections collected | 11758 |
| Independent reflections | 3928 [$R_{int}$ = 0.0178, $R_{sigma}$ = 0.0189] |
| Data/restraints/parameters | 3928/0/262 |
| Goodness-of-fit on $F^2$ | 1.069 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0182, $wR_2$ = 0.0450 |
| Final R indexes [all data] | $R_1$ = 0.0186, $wR_2$ = 0.0451 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.22/-0.18 |
| Flack/Hooft parameter | -0.019(5)/-0.007(5) |

**Single Crystal Data for 5a**

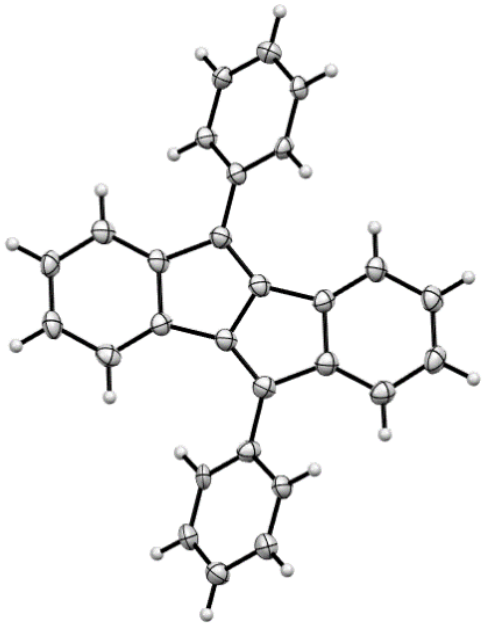


**Figure S113.** Thermal ellipsoid plot of **5a** (50% probability levels)

**Table S8 Crystal data and structure refinement for 5a.**

| | |
|---|---|
| Identification code | AR-2-181 |
| Empirical formula | $C_{28}H_{18}$ |
| Formula weight | 354.42 |
| Temperature/K | 149.99(10) |
| Crystal system | monoclinic |
| Space group | I2/a |
| a/Å | 18.7488(4) |
| b/Å | 9.7469(2) |
| c/Å | 39.4094(10) |
| α/° | 90 |
| β/° | 99.102(2) |
| γ/° | 90 |
| Volume/$Å^3$ | 7111.1(3) |

| | |
|---|---|
| Z | 16 |
| $\rho_{calc}$g/cm$^3$ | 1.324 |
| $\mu$/mm$^{-1}$ | 0.569 |
| F(000) | 2976.0 |
| Crystal size/mm$^3$ | 0.16 × 0.12 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 9.09 to 133.146 |
| Index ranges | -22 ≤ h ≤ 21, -7 ≤ k ≤ 11, -46 ≤ l ≤ 46 |
| Reflections collected | 16785 |
| Independent reflections | 6223 [$R_{int}$ = 0.1082, $R_{sigma}$ = 0.1732] |
| Data/restraints/parameters | 6223/0/578 |
| Goodness-of-fit on F$^2$ | 1.015 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0879, w$R_2$ = 0.2637 |
| Final R indexes [all data] | $R_1$ = 0.1292, w$R_2$ = 0.3177 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.28/-0.54 |