Supporting Information

Palladium-Catalyzed coupling reaction of 2−iodobiphenyls with alkenyl bromides for the construction of 9-(diorganomethylidene)fluorenes

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Contents

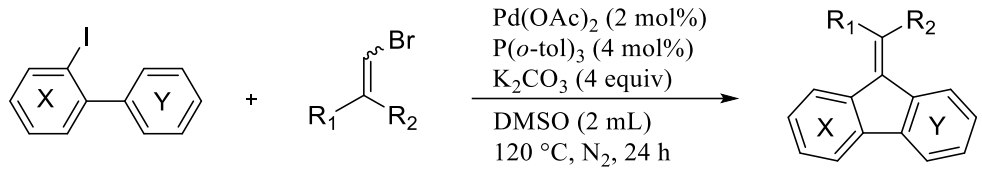
1. General information

All reagents and solvents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros and Meryer. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300−400 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a 500 MHz Bruker AVANCE spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C and 470 MHz for ^{19}F), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. Analysis of crude reaction mixture was done on the Varian 4000 GC/MS and Agilent 7890A/5975C. High-resolution mass spectra were recorded on a micrOTOF-Q II 10410 mass spectrometer.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. The 2-iodo-1,1'-biphenyl[1](2-bromovinyl)benzene[2]were prepared according to corresponding literature procedures.

2. General experimental procedures

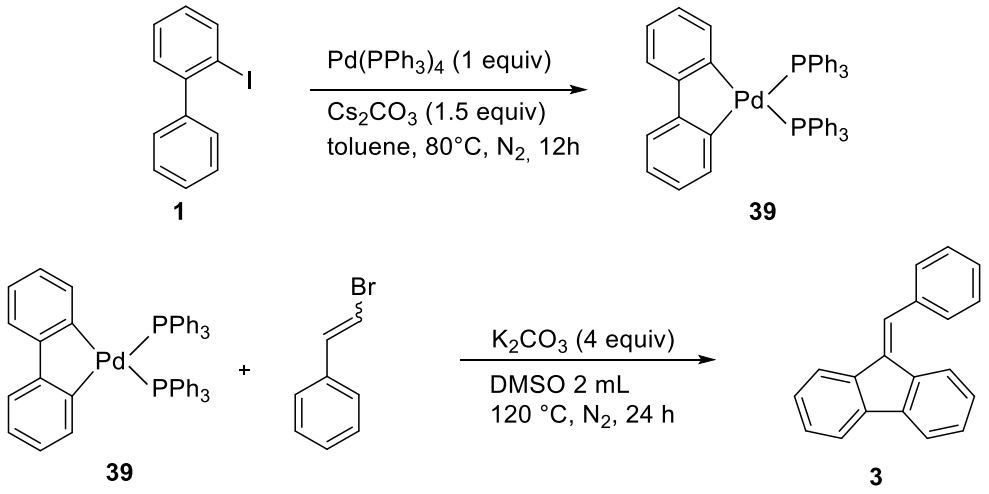
2.1 General procedure for the synthesis of 9-benzylidene-9*H*-fluorene



A 25 mL Schlenk tube equipped with a stir bar was charged with 2-iodo-1,1'-biphenyl (0.2 mmol), alkenyl bromides (0.4 mmol), $Pd(OAc)_2$ (2 mol%), P(*o*-tol)$_3$ (4 mol%) and K_2CO_3 (0.8 mmol). The tube was fitted with a rubber septum, then evacuated and refilled with nitrogen three times. Under nitrogen, DMSO (2 mL) was added in turn to the Schlenk tube through the rubber septum using syringes, and then the rubber septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 °C for 24 h. When the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the corresponding product.

3. Preliminary mechanistic studies

3.1 Control experiments

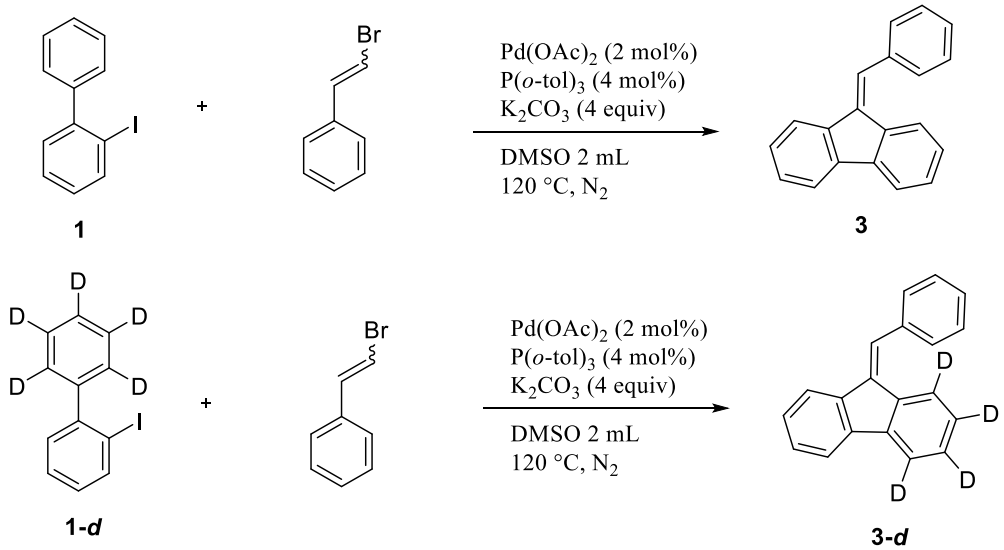


A 25 mL Schlenk tube equipped with a stir bar was charged with 2-iodo-1,1'-biphenyl (0.2 mmol), $Pd(PPh_3)_4$ (0.2 mmol), and Cs_2CO_3 (0.3 mmol). The tube was fitted with a rubber septum, then evacuated and refilled with nitrogen three

times. Under nitrogen, toluene (2 mL) was added in turn to the Schlenk tube through the rubber septum using syringes, and then the rubber septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 80 °C for 12 h. When the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the **39** as a yellow solid (109 mg, 70%).

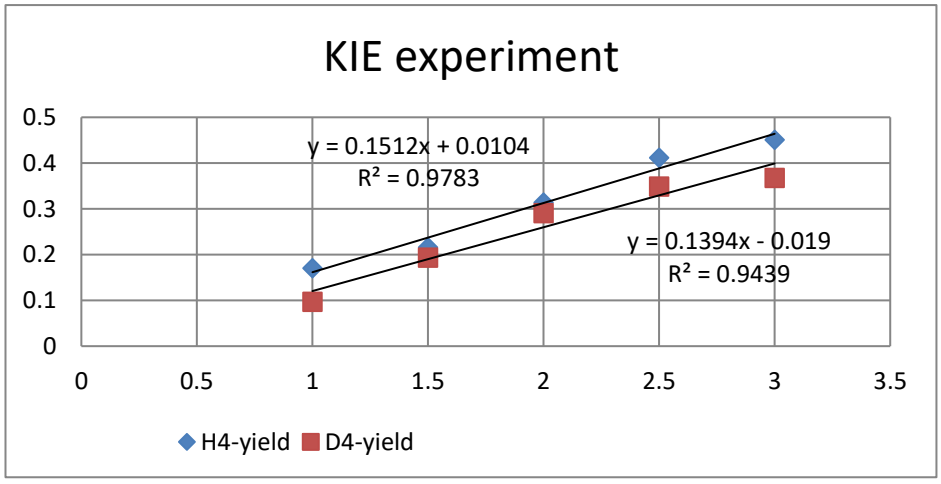
A 25 mL Schlenk tube equipped with a stir bar was charged with **39** (0.1 mmol), **2a** (0.2 mmol) and K_2CO_3 (0.4 mmol). The tube was fitted with a rubber septum, then evacuated and refilled with nitrogen three times. Under nitrogen, DMSO (1 mL) was added in turn to the Schlenk tube through the rubber septum using syringes, and then the rubber septum was replaced by a Teflon screwcap under nitrogen flow; The reaction mixture was stirred at 120 °C for 24 h. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the **3a** (13 mg, 51%).

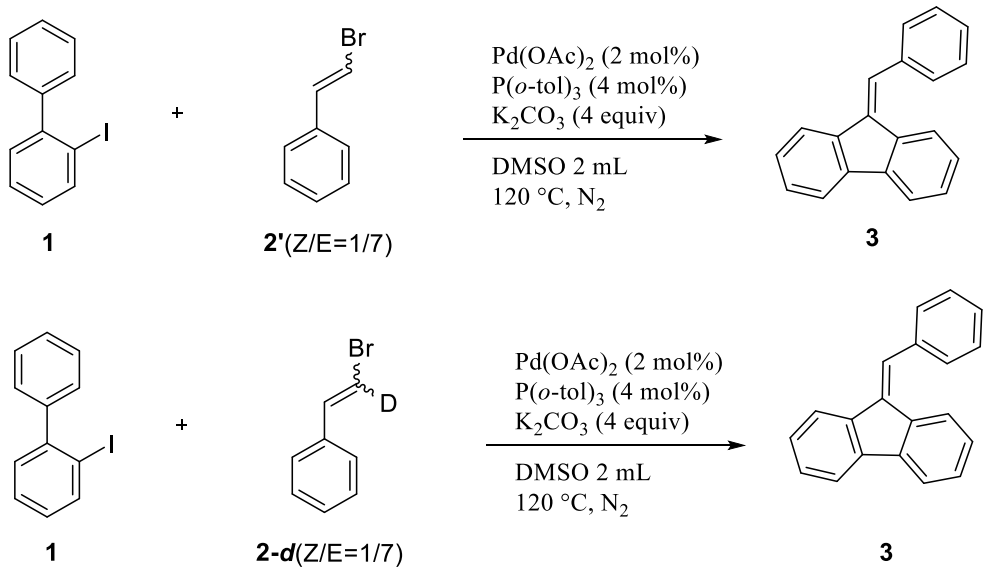
3.2 Kinetic isotope effect experiments



Preparing five identical 25 mL-Schlenk tubes and each one equipped with a stir bar was charged with **1** (0.2 mmol), (2-bromovinyl)benzene (0.4 mmol), $Pd(OAc)_2$

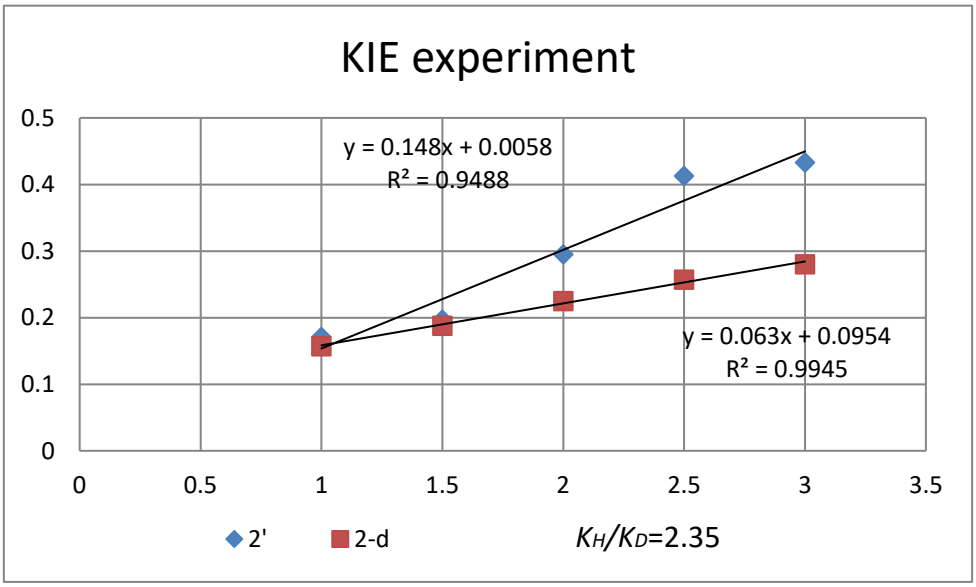
(2mol%),P(*o*-tol)$_3$ (4 mol%) and K_2CO_3 (0.8 mmol). Each tube was fitted with a rubber septum, then evacuated and refilled with nitrogen three times. Under nitrogen , DMSO (2 mL) was added in turn to the Schlenk tube through the rubber septum using syringes, and then the rubber septum was replaced by a Teflon screwcap under nitrogen flow. In the other five identical 25 mL-Schlenk tubes, **1-*d***was used instead of**1**. In each group, 60, 90, 120, 150 and 180min was chosen the reaction time respectively and the corresponding yield was obtained by flash chromatography.A kinetic isotope effect value K_H/K_D = 0.151/0.139 = 1.09 was obtained.



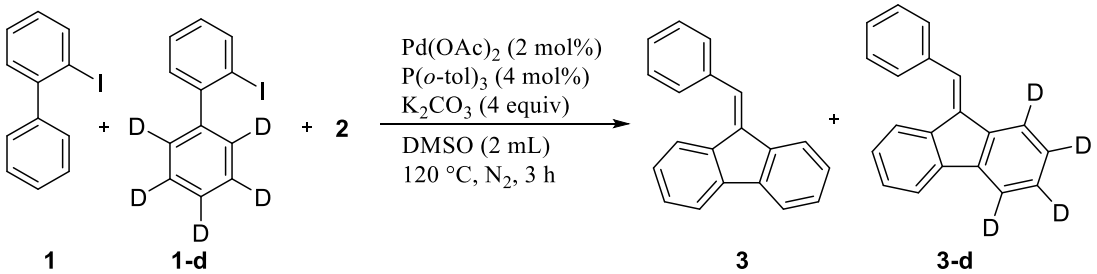


Preparing five identical 25 mL-Schlenk tubes and each one equipped with a stir bar was charged with **1** (0.2 mmol), **2'**(*Z*/*E*=1/7) (0.4 mmol), Pd(OAc)$_2$ (2mol%),P(*o*-tol)$_3$

(4 mol%) and K_2CO_3 (0.8 mmol). Each tube was fitted with a rubber septum, then evacuated and refilled with nitrogen three times. Under nitrogen, DMSO (2 mL) was added in turn to the Schlenk tube through the rubber septum using syringes, and then the rubber septum was replaced by a Teflon screwcap under nitrogen flow. In the other five identical 25 mL-Schlenk tubes, **2-*d*** (*Z*/*E*=1/7) was used instead of **2**. In each group, 60, 90, 120, 150 and 180min was chosen the reaction time respectively and the corresponding yield was obtained by flash chromatography. A kinetic isotope effect value K_H/K_D = 0.148/0.063 = 2.35 was obtained.



3.3 competitive reaction



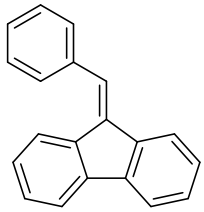
1 **1-d** **3** **3-d**

A 25 mL Schlenk tube equipped with a stir bar was charged with **1** (0.1 mmol), **1-d** (0.1 mmol), alkenyl bromide **2** (0.4 mmol), $Pd(OAc)_2$ (2 mol%), P(*o*-tol)$_3$ (4 mol%) and K_2CO_3 (0.8 mmol). The tube was fitted with a rubber septum, then evacuated and refilled with nitrogen three times. Under nitrogen, DMSO (2 mL) was added in turn to the Schlenk tube through the rubber septum using syringes, and then the rubber

septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 120 °C for 3 h. When the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified by flash chromatography on silica gel to provide the product(20 mg, 39%), the ratio of **3** and **3-*d*** was analyzed by GC-MS (**3/3-*d***=1.05).

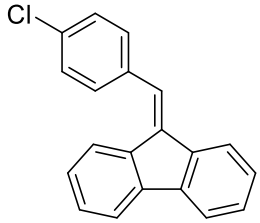
4. Characterization of products in details

9-benzylidene-9*H*-fluorene (3)[3]



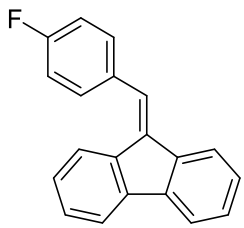
White solid (50 mg, 97% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.65 – 7.50 (m, 3H), 7.51 – 7.45 (m, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 139.5, 139.2, 137.0, 136.6, 136.6, 129.3, 128.5, 128.2, 128.0, 127.2, 127.0, 126.7, 124.4, 120.2, 119.7, 119.6.

9-(4-chlorobenzylidene)-9*H*-fluorene (4)[4]



White solid (49 mg, 85% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.57 (s, 1H), 7.50 (dd, *J* = 8.0, 4.9 Hz, 3H), 7.44 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.33 – 7.28 (m, 2H), 7.11 – 7.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 139.3, 139.3, 137.1, 136.3, 135.4, 133.9, 130.7, 128.8, 128.4, 127.1, 126.8, 125.6, 124.34, 120.3, 119.8, 119.6.

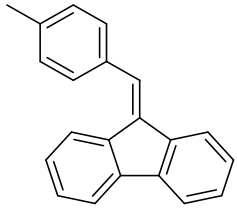
9-(4-fluorobenzylidene)-9*H*-fluorene (5)[4]



White solid (50 mg, 91% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.60 (s, 1H), 7.53 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.13 (t, *J* = 8.6

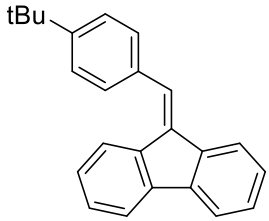
Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, *J* = 248.0 Hz), 141.4, 139.4, 139.2, 136.8, 136.4, 132.9 (d, *J* = 3.4 Hz), 131.1(d, *J* = 7.9 Hz), 131.0, 128.7, 128.3, 127.0, 126.7, 126.0, 124.2, 120.2, 119.8, 115.6 (d, *J* = 21.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -113.21.

9-(4-methylbenzylidene)-9*H*-fluorene (6)[3]



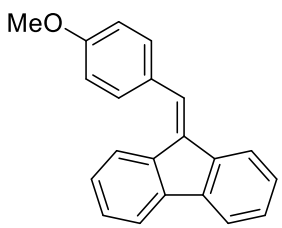
White solid (50 mg, 93% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.31 (q, *J* = 7.6 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 2.43(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 139.7, 139.1, 138.0, 136.7, 136.1, 133.9, 129.3, 129.2, 128.4, 128.0, 127.5, 126.9, 126.6, 124.4, 120.2, 119.6, 119.5, 21.4.

9-(4-(tert-butyl)benzylidene)-9*H*-fluorene (7)[11]



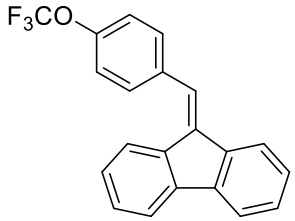
White solid (55 mg, 89% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.73 – 7.69 (m, 3H), 7.66 (s, 1H), 7.56 – 7.52 (m, 2H), 7.49 – 7.44 (m, 2H), 7.38 – 7.34 (m, 1H), 7.33 – 7.28 (m, 2H), 7.11 – 7.06 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 141.2, 139.7, 139.1, 136.7, 136.0, 133.8, 129.2, 128.4, 128.01, 127.5, 126.9, 126.6, 125.4, 124.4, 120.2, 119.7, 119.5, 34.8, 31.4.

9-(4-methoxybenzylidene)-9*H*-fluorene (8)[3]



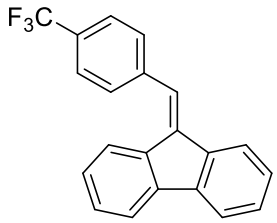
White solid (53 mg, 93% yield); Eluent: PE:EA=20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.69 (m, 3H), 7.66 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.29 (m, 3H), 7.13 – 7.06 (m, 1H), 7.04 – 6.95 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 141.1, 139.7, 139.0, 136.7, 135.5, 130.9, 129.1, 128.3, 127.9, 127.3, 126.9, 126.6, 124.2, 120.1, 119.7, 119.5, 114.0, 55.3.

9-(4-(trifluoromethoxy)benzylidene)-9*H*-fluorene (9)



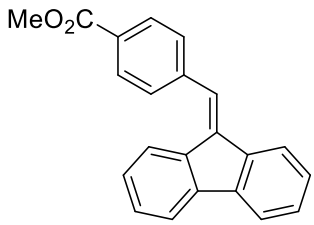
Colorless oil (59 mg, 87% yield); Eluent: PE:EA=20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.55 (m, 3H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.08 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 141.5, 139.3, 139.2, 137.3, 136.2, 135.6, 130.8, 128.9, 128.5, 127.1, 126.8, 125.3, 124.3, 121.0, 120.6 (q, J=255.8Hz), 120.3, 119.9, 119.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ -57.70. HRMS: (ESI) calculated for C21H13F3O $[M+H]^+$ 339.0991, found 339.0994.

9-(4-(trifluoromethyl)benzylidene)-9*H*-fluorene (10)[4]



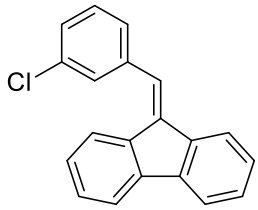
White solid (53 mg, 83% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.67 (m, 6H), 7.63 – 7.60 (s, 1H), 7.49 – 7.45 (m, 1H), 7.44 – 7.40 (m, 1H), 7.38 –7.33 (m, 2H), 7.13 – 7.07 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 140.7, 139.4, 138.0, 136.1, 132.7, 130.0 (q, *J* = 32.3 Hz), 129.6, 129.1, 128.7, 127.2, 126.8, 126.6,125.5 (q, *J* = 3.8 Hz), 125.0, 124.4, 124.2 (q, *J* = 270.4 Hz), 120.4, 119.9; ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.49.

Methyl 4-((9*H*-fluoren-9-ylidene)methyl)benzoate (11)[5]



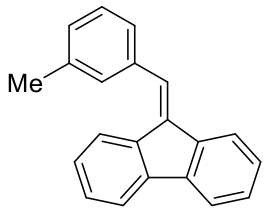
White solid (48 mg, 77% yield); Eluent: PE:EA=20:1.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 3H), 7.65 – 7.59 (m, 3H), 7.48 – 7.42 (m, 3H), 7.41 – 7.34 (m, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 166.8, 141.8, 141.5, 139.4, 139.2, 137.8, 136.2, 129.8, 129.6, 129.3, 129.0, 128.6, 127.1, 126. 8, 125.6, 124.5, 120.4, 119.8, 119.7, 52.2.

9-(3-chlorobenzylidene)-9*H*-fluorene (12)[4]



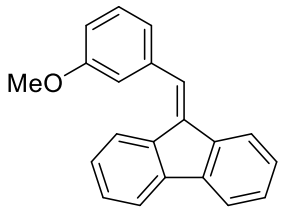
White solid (44 mg, 76% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 6.9 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.36(m, 3H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 139.4, 139.2, 138.8, 137.6, 136.2, 134.5, 129.8, 129.2, 128.9, 128.5, 128.0, 127.4, 127.1, 126.8, 125.2, 124.4, 120.3, 119.8, 119.6.

9-(3-methylbenzylidene)-9*H*-fluorene (13)[4]



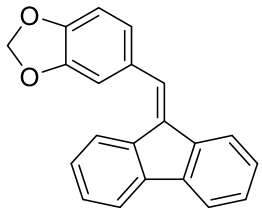
White solid (43 mg, 81% yield); Eluent: PE.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 1H), 7.88 – 7.77 (m, 4H), 7.58 – 7.42 (m, 6H), 7.38 – 7.31 (m, 1H), 7.27 – 7.18 (m, 1H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 139.6, 139.2, 138.2, 136.9, 136.4, 132.8, 129.9, 129.2, 128.8, 128.4, 128.1, 127.9, 127.0, 126.6, 126.3, 124.5, 123.6, 120.20, 119.6, 21.4.

9-(3-methoxybenzylidene)-9*H*-fluorene (14)[6]



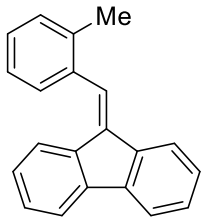
Yellow oil (55 mg, 97% yield); Eluent: PE:EA=20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.68 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.21 – 7.17 (m, 1H), 7.15 – 7.12 (m, 1H), 7.10 – 7.06 (m, 1H), 6.98 – 6.93 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 141.3, 139.5, 138.3, 136.7, 129.6, 128.55, 128.2, 127.1, 127.0, 127.0, 126.7, 124.9, 124.7, 121.7, 120.2, 119.7, 119.6, 114.3, 114.1, 55.3

5-((9*H*-fluoren-9-ylidene)methyl)benzo[d][1,3]dioxole (15)[4]



Yellow solid (55 mg, 93% yield); Eluent: PE:EA=20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.70 (m, 3H), 7.60 (s, 1H), 7.40 – 7.35 (m, 1H), 7.34 – 7.30 (m, 2H), 7.15 – 7.07 (m, 3H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.05 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 147.5, 141.2, 139.6, 139.0, 136. 5, 135.9, 130.6, 128.4, 128.0, 127.1, 126.9, 126.7, 124.4, 123.5, 120.1, 119.7, 119.6, 109.6, 108.5, 101.3

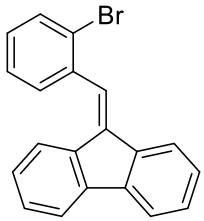
9-(2-methylbenzylidene)-9*H*-fluorene (16)[4]



White solid (47 mg, 88% yield); Eluent: PE.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.66 (s, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.35 – 7.30 (m, 3H), 7.30 – 7.24 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.03 – 6.96 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 139.4, 139.2, 136.9, 136. 8, 136.7, 136.30, 130.2, 129.3, 128.43, 128.4, 128.2, 127.0, 126.8, 126.5, 125.9,

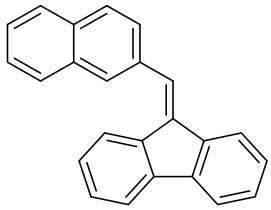
125.9, 124.5, 120.3, 119.6, 20.1.

9-(2-bromobenzylidene)-9*H*-fluorene (17)



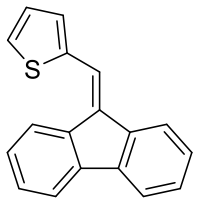
White solid (47 mg, 71% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.70 – 7.66 (m, 2H), 7.57 – 7.53 (m, 1H), 7.49 – 7.41 (m, 4H), 7.40 – 7.30 (m, 3H), 7.24 – 7.19 (m, 1H), 7.15 – 7.09 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 140.5, 133.4, 133.3, 132.4, 129.5, 129.4, 129.2, 128.9, 128.0, 127.5, 127.0, 126.9, 125.7, 125.3, 121.3, 93.7, 90.7.

9-(naphthalen-2-ylmethylene)-9*H*-fluorene (18)[4]



White solid (50 mg, 82% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 1H), 8.10 – 8.03 (m, 2H), 8.02 – 7.94 (m, 3H), 7.93 – 7.85 (m, 4H), 7.73 – 7.67 (m, 2H), 7.62 – 7.56 (m, 1H), 7.55 – 7.46 (m, 2H), 7.26 – 7.19 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 139.6, 139.3, 136.8, 136.6, 134.4, 133.4, 133.0, 128.6, 128.5, 128.3, 128.2, 128.1, 127.8, 127.3, 127.2, 127.0, 126.7, 126.4, 126.4, 124.4, 120.3, 119.8, 119.6.

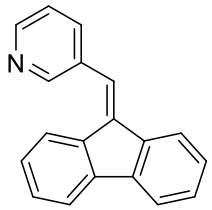
2-((9*H*-fluoren-9-ylidene)methyl)thiophene (19)[4]



Yellow solid (35 mg, 67% yield); Eluent: PE:EA=20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.05 (m, 1H), 7.82 – 7.69 (m, 3H), 7.68 – 7.59 (m, 1H), 7.53 – 7.43 (m, 2H), 7.42 – 7.28 (m, 3H), 7.24 – 7.11 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 139.6,

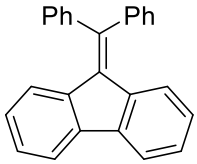
139.2, 139.1, 136.7, 136.2, 129.2, 128.7, 128.3, 127.6, 127.3, 127.0, 126.8, 124.4, 120.2, 119.8, 119.6, 118.9.

3-((9*H*-fluoren-9-ylidene)methyl)pyridine (20)[7]



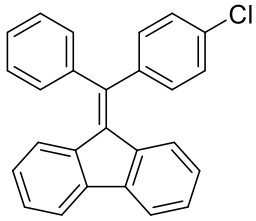
Yellow solid (39 mg, 76% yield); Eluent: PE:EA=20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.49 (d, *J* = 4.8 Hz, 1H), 7.68 – 7.61 (m, 3H), 7.60 – 7.56 (m, 1H), 7.50 – 7.38 (m, 5H), 7.37 – 7.33 (m, 1H), 7.23 – 7.17 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 148.4, 144.3, 140.4, 138.1, 132.9, 129.5, 129.3, 129.0, 128.0, 127.6, 127.1, 122.9, 121.0, 120.6, 92.7, 88.8.

9-(diphenylmethylene)-9*H*-fluorene (21)[3]



White solid (58 mg, 88% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.35 (m, 10H), 7.23 (t, *J* = 7.4 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.62 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 143.0, 140.5, 138.7, 134.2, 129.7, 128.8, 128.2, 127.6, 126.4, 124.9, 119.23.

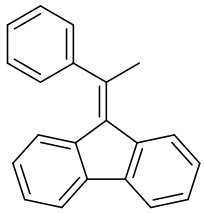
9-((4-chlorophenyl)(phenyl)methylene)-9*H*-fluorene (22)



Yellow solid (60 mg, 82% yield); Eluent: PE. mp 170.5−170.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.44 – 7.36 (m, 5H), 7.36 – 7.29 (m, 4H), 7.27 – 7.20 (m, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 142.6, 141.4,

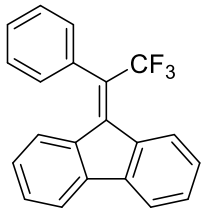
140.7, 140.6, 138.6, 138.4, 134.7, 134.3, 131.3, 129.8, 129.1, 128.9, 128.4, 127.9, 127.9, 126.5, 126.5, 124.9, 124.8, 119.4, 119.3, 77.3, 77.0, 76.8. HRMS: (ESI) calculated for C26H17Cl [M+H]+ 365.1092, found 365.1092.

9-(1-phenylethylidene)-9*H*-fluorene (23)[8]



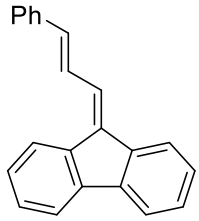
White solid (36 mg, 68% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 1H), 7.81 – 7.78 (m, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.40 – 7.33 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.88 – 6.82 (m, 1H), 6.26 (d, *J* = 8.1 Hz, 1H), 2.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 142.7, 140.5, 139.7, 139.0, 138.6, 133.1, 129.0, 128.1, 127.6, 127.3, 126.9, 126.8, 126.4, 125.3, 124.6, 119.5, 119.0, 25.8.

9-(2,2,2-trifluoro-1-phenylethylidene)-9*H*-fluorene (24)[4]



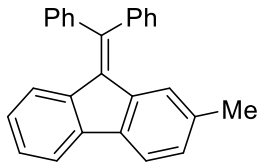
Yellow solid (36 mg, 56% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.80 (t, *J* = 7.7 Hz, 1H), 5.89 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3 (q, *J* = 3.4Hz), 141.9, 141.3, 137.8, 135.4, 134.8, 130.1, 129.6, 129.3, 129.1, 128.8 (q, *J* = 33.1 Hz) 127.7, 127.1, 127.0 (q, *J* = 7.5 Hz), 126.9, 126.7,125.5 (q, *J* = 273.1 Hz), 119.4, 119.2.

(E)-9-(3-phenylallylidene)-9*H*-fluorene (25)[12]



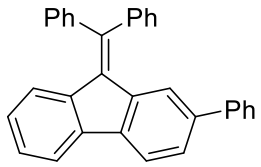
Yellow solid (41 mg, 72% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 1H), 7.98 (dd, *J* = 15.2, 11.8 Hz, 1H), 7.79 – 7.70 (m, 3H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.28 (m, 6H), 7.02 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 139.6, 139.0, 138.7, 137.3, 137.0, 135.2, 128.9, 128.6, 127.9, 127.8, 127.1, 127.1, 126.97, 126.9, 125.1, 124.9, 120.1, 120.0, 119.6.

9-(diphenylmethylene)-2-methyl-9*H*-fluorene (27)[9]



White solid (55 mg, 80% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.36 (m, 10H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.38 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 143.1, 143.0, 140.7, 139.0, 138.7, 138.1, 135.9, 134.3, 129.7, 128.8, 128.7, 128.5, 128.1, 128.1, 127.6, 125.9, 125.7, 124.9, 118.9, 118.9, 21.7.

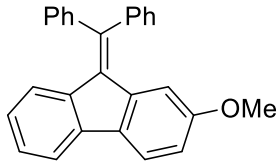
9-(diphenylmethylene)-2-phenyl-9*H*-fluorene (28)



Yellow solid (68 mg, 84% yield); Eluent: PE. mp 189.4−190.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.53 – 7.49 (m, 1H), 7.46 – 7.41 (m, 9H), 7.34 – 7.22 (m, 7H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.68 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 143.1, 142.7, 141.2, 140.3, 139.6, 139.3, 139.0, 138.9, 134.3, 129.7, 129.6, 128.9, 128.8, 128.8, 128.5, 128.3, 128.2, 127.8, 126.9, 126.7, 126.4, 124.9, 123.9, 119.5, 119.4, 77.3, 77.0, 76.8. HRMS: (ESI) calculated for

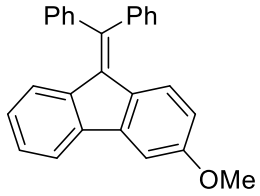
C32H22 $[M+H]^+$ 407.1794, found 407.1802.

9-(diphenylmethylene)-2-methoxy-9*H*-fluorene (29)[3]



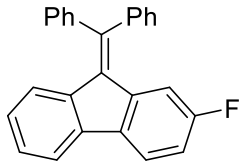
Yellow solid (62 mg, 86% yield); Eluent: PE:EA=20:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 1H), 7.60 – 7.55 (m, 2H), 7.45 – 7.37 (m, 9H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.88 – 6.83 (m, 1H), 6.82 – 6.79 (m, 1H), 6.61 (d, J = 7.9 Hz, 1H), 6.15 (d, *J* = 2.5 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 145.4, 142.9, 142.7, 140.7, 140.2, 138.4, 134.3, 133.8, 132.4, 130.0, 129.5, 128.9, 128.8, 128.2, 127.7, 125.3, 124.8, 119.9, 118.5, 115.0, 109.7, 54.9.

9-(diphenylmethylene)-3-methoxy-9*H*-fluorene (30)



Yellow solid (65 mg, 91% yield); Eluent: PE:EA=20:1. mp 165.5−165.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.6 Hz, 1H), 7.43 – 7.35 (m, 10H), 7.24 – 7.19 (m, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.54 – 6.47 (m, 2H), 3.86 – 3.82 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 143.2, 143.1, 143.1, 142.2, 140.2, 139.5, 133.7, 131.7, 129.7, 128.8, 128.7, 127.9, 128.0, 127.5, 126.5, 125.9, 124.9, 119.1, 112.6, 104.2, 55.5. HRMS: (ESI) calculated for C27H20O $[M+H]^+$ 361.1587, found 361.1592.

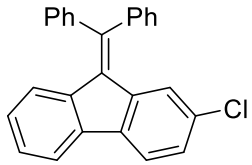
9-(diphenylmethylene)-2-fluoro-9*H*-fluorene (31)



White solid (53 mg, 76% yield); Eluent: PE. mp 214.2−214.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.46 – 7.34 (m, 9H), 7.27 – 7.21 (m, 2H), 6.96 – 6.89 (m, 2H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.27 – 6.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$)

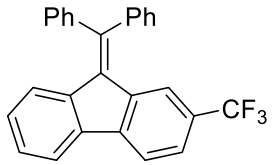
δ 161.9 (d, *J* = 240.6 Hz), 146.8, 142.6, 142.3, 140.5 (d, *J* = 9.0 Hz), 139.8, 138.7, 136.5, 133.6, 129.5, 129.4, 129.0, 128.9, 128.6, 128.4, 127.8, 126.1, 124.9, 119.9 (d, *J* = 9.0 Hz), 118.9, 114.6 (d, *J* = 23.4 Hz), 112.0 (d, *J* = 25.3 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.24. HRMS: (ESI) calculated for C26H17F3 $[M+Na]^+$ 371.1206, found 371.1213.

2-chloro-9-(diphenylmethylene)-9*H*-fluorene (32)[10]



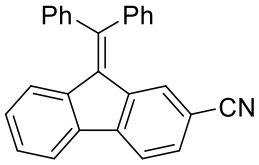
White solid (52 mg, 72% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.40 (m, 6H), 7.39 – 7.34 (m, 4H), 7.26 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 6.96 – 6.91 (m, 1H), 7.65 – 7.62 (m, 1H), 6.51 – 6.50 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 142.6, 142.4, 140.2, 139.5, 138.8, 138.6, 133.4, 132.1, 129.6, 129.0, 128.9, 128.6, 128.4, 127.8, 127.5, 126.6, 126.2, 125.2, 124.9, 120.0, 119.3.

9-(diphenylmethylene)-2-(trifluoromethyl)-9*H*-fluorene (33)[3]



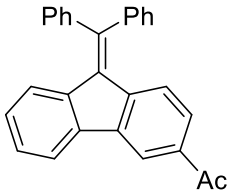
White solid (39 mg, 49% yield); Eluent: PE. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.42 (m, 6H), 7.42 – 7.39 (m, 2H), 7.39 – 7.35 (m, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.79 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 143.2, 142.4, 142.2, 139.3, 139.1, 138.8, 133.3, 129.6, 129.5, 129.0, 128.9, 128.7, 128.6, 128.2 (q, *J* = 31.5 Hz), 127.9, 127.5, 124.9, 124.4 (q, *J* = 3.8 Hz), 124.3 (q, *J* =270.3 Hz), 121.9 (q, *J* = 4.1 Hz), 119.9, 119.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.39.

9-(diphenylmethylene)-9*H*-fluorene-2-carbonitrile (34)



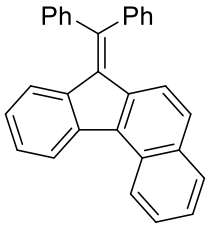
Yellow solid (31 mg, 44% yield); Eluent: PE:EA=20:1. mp 173.2−173.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 2H), 7.58 – 7.52 (m, 1H), 7.52 – 7.43 (m, 6H), 7.42 – 7.30 (m, 5H), 7.29 (s, 1H), 7.10 – 7.01 (m, 1H), 6.85 (d, *J* = 10.6 Hz, 1H), 6.77 – 6.69 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 144.1, 142.2, 142.0, 139.4, 139.0, 138.6, 132.6, 131.1, 129.6, 129.5, 129.2, 129.1, 129.0, 128.8, 128.6, 128.1, 128.0, 125.0, 120.2, 119.7, 119.6, 109.4. HRMS: (ESI) calculated for C27H17N $[M+H]^+$ 356.1434, found 356.1433.

1-(9-(diphenylmethylene)-9*H*-fluoren-3-yl)ethan-1-one (35)



White solid (31 mg, 44% yield); Eluent: PE:EA=20:1. mp 131.3−131.7 °C. ^{1}H NMR (500 MHz, CDCl3) δ 8.33 – 8.28 (m, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.47 – 7.42 (m, 6H), 7.42 – 7.35 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.73 – 6.66 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 197.8, 148.3, 143.1, 142.6, 142.5, 140.8, 139.6, 139.0, 136.1, 133.7, 129.8, 129.7, 128.9, 128.9, 128.7, 128.6, 127.9, 127.0, 126.8, 124.8, 124.7, 119.7, 118.9, 26.7. HRMS: (ESI) calculated for C28H20O $[M+H]^+$ 373.1587, found 373.1588.

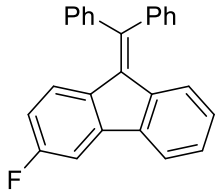
7-(diphenylmethylene)-7*H*-benzo[c]fluorine (36)



Yellow solid (47 mg, 62% yield); Eluent: PE:EA=20:1. mp 163.3−164.1 °C. ^{1}H NMR (500 MHz, CDCl3) δ 8.75 (d, *J* = 8.6 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.63 – 7.57 (m, 1H), 7.51 – 7.33 (m, 13H), 7.02 – 6.94 (m, 1H), 6.88 – 6.82

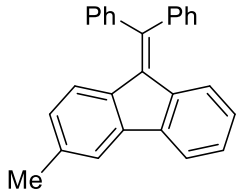
(m, 1H), 6.80 – 6.74 (m, 1H); ^{13}C NMR (125 MHz, CDCl3) δ 146.7, 143.3, 143.2, 141.4, 139.6, 137.4, 135.6, 134.9, 133.9, 132.3, 130.5, 130.3, 129.2, 129.0, 128.8, 128.8, 128.5, 128.1, 127.7, 126.6, 125.5, 124.7, 124.2, 122.9, 122.5, 120. 8. HRMS: (ESI) calculated for C30H20 $[M+H]^+$ 381.1638, found 381.1644.

9-(diphenylmethylene)-3-fluoro-9*H*-fluorene (37)



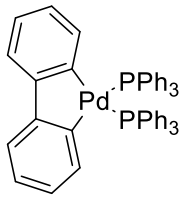
White solid (54 mg, 78% yield); Eluent: PE. mp 230.3−230.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.39 (m, 6H), 7.39 – 7.34 (m, 4H), 7.28 – 7.21 (m, 2H), 6.99 – 6.92 (m, 1H), 6.65 – 6.58 (m, 2H), 6.57 – 6.51 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8 (d, *J* = 245.1 Hz), 145.1 (d, *J* = 2.0 Hz), 142.8, 142.6, 139.5, 139.4, 139.4, 134.5, 134.5 133.2, 129.6, 128.9, 128.8, 128.3, 128.3, 127.7, 127.0, 126.2 (d, *J* = 8.6 Hz), 125.0, 119.5, 113.2 (d, *J* = 22.5 Hz), 106.0 (d, *J* = 22.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -114.09. HRMS: (ESI) calculated for C27H17F $[M+Na]^+$ 371.1206, found 371.1202.

9-(diphenylmethylene)-3-methyl-9*H*-fluorene (38)



White solid (54 mg, 78% yield); Eluent: PE.mp 189.9−190.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.45 – 7.37 (m, 10H), 7.24 – 7.19 (m, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.79 – 6.74 (m, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 143.1, 143.0, 140.7, 140.5, 139.1, 137.6, 136.2, 134.1, 131.6, 130.4, 129.7, 128.8, 128.1, 127.5, 127.4, 126.3, 124.9, 124.7, 123.8, 119.8, 119.1, 21.5. HRMS: (ESI) calculated for $C_{27}H_{20}$ $[M+H]^+$ 345.1638, found 345.1638.

(39)[13]



Yellow solid (109 mg, 70% yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 22H), 7.21 – 7.15 (m, 12H), 7.03 – 6.97 (m, 1H), 6.64 – 6.59 (m, 1H), 6.56 (t, *J* = 7.3 Hz, 1H), 6.31 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (t, *J* = 6.1 HZ), 132.2 (t, *J* = 22.7 HZ) 129.8, 129.7, 128.8, 127.6 (t, *J* = 5.1 HZ), 127.4, 126.4, 125.9, 122.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.82. HRMS: (ESI) calculated for $C_{48}H_{38}P_2Pd$ $[M+H]^+$ 783.1556, found 783.1552.

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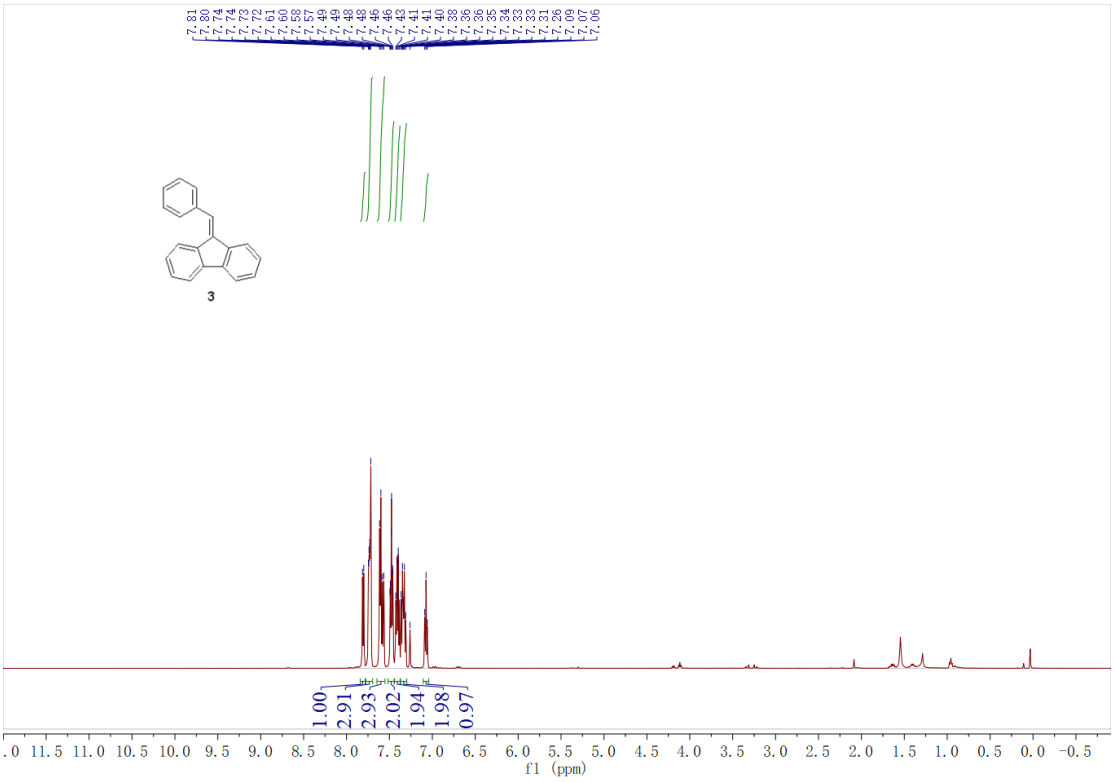
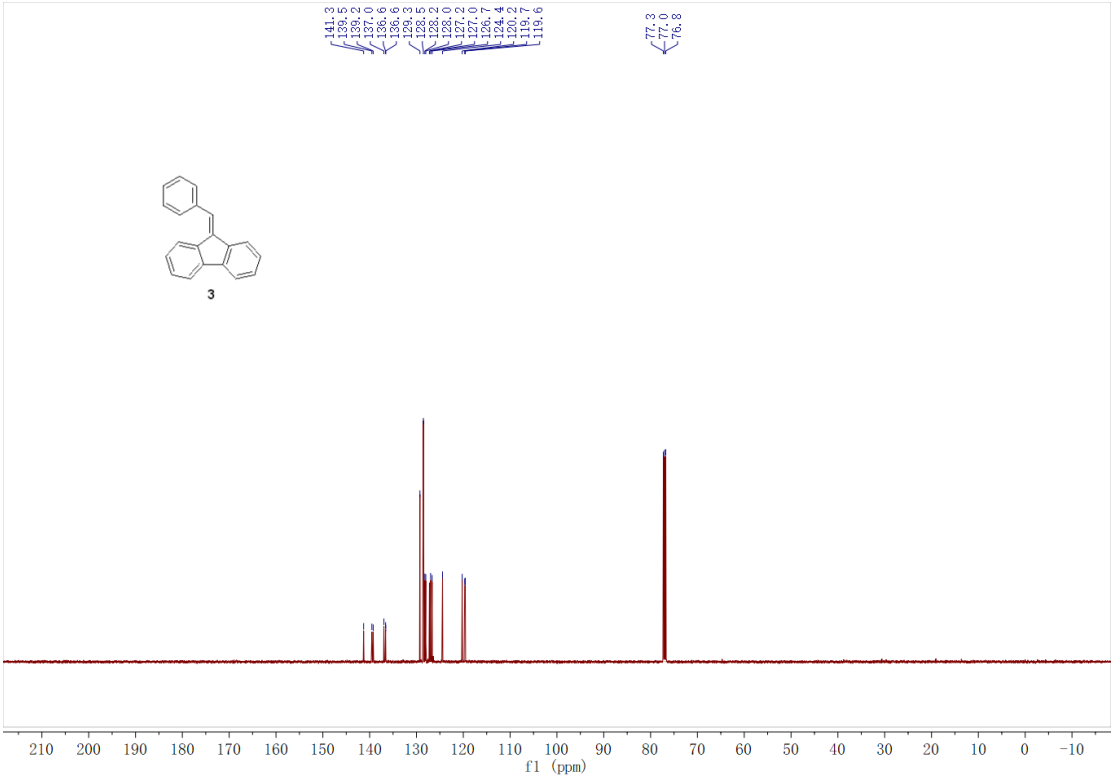
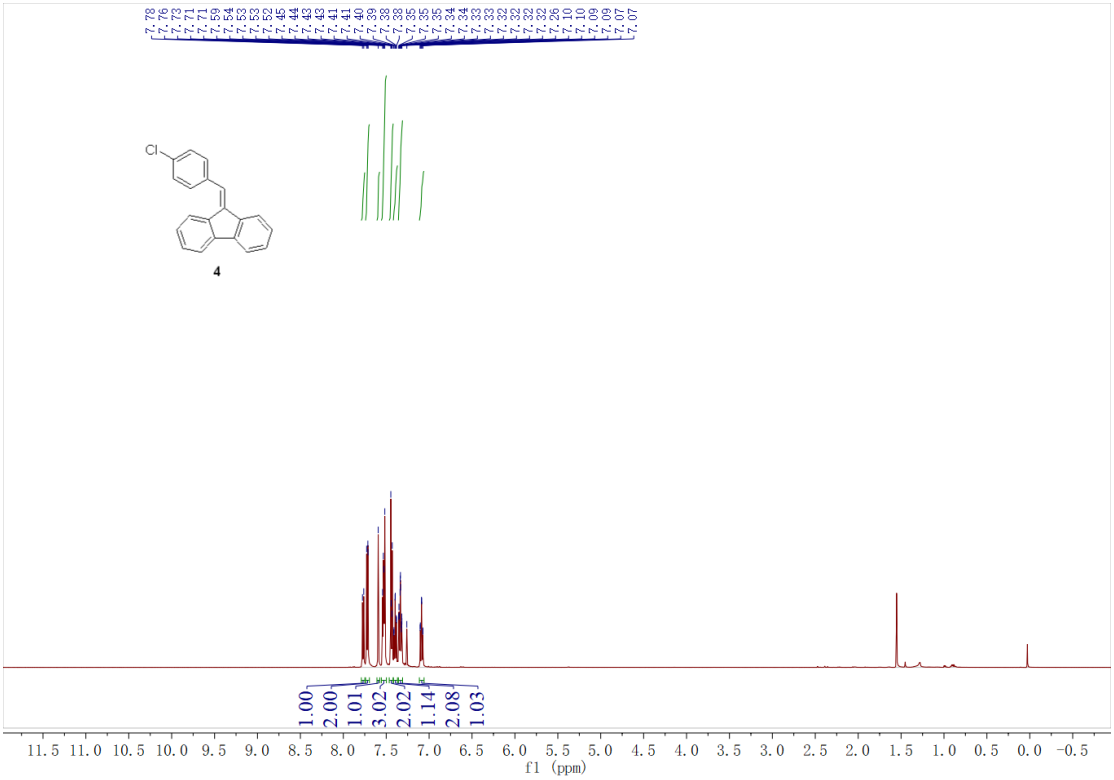
6. NMR spectra

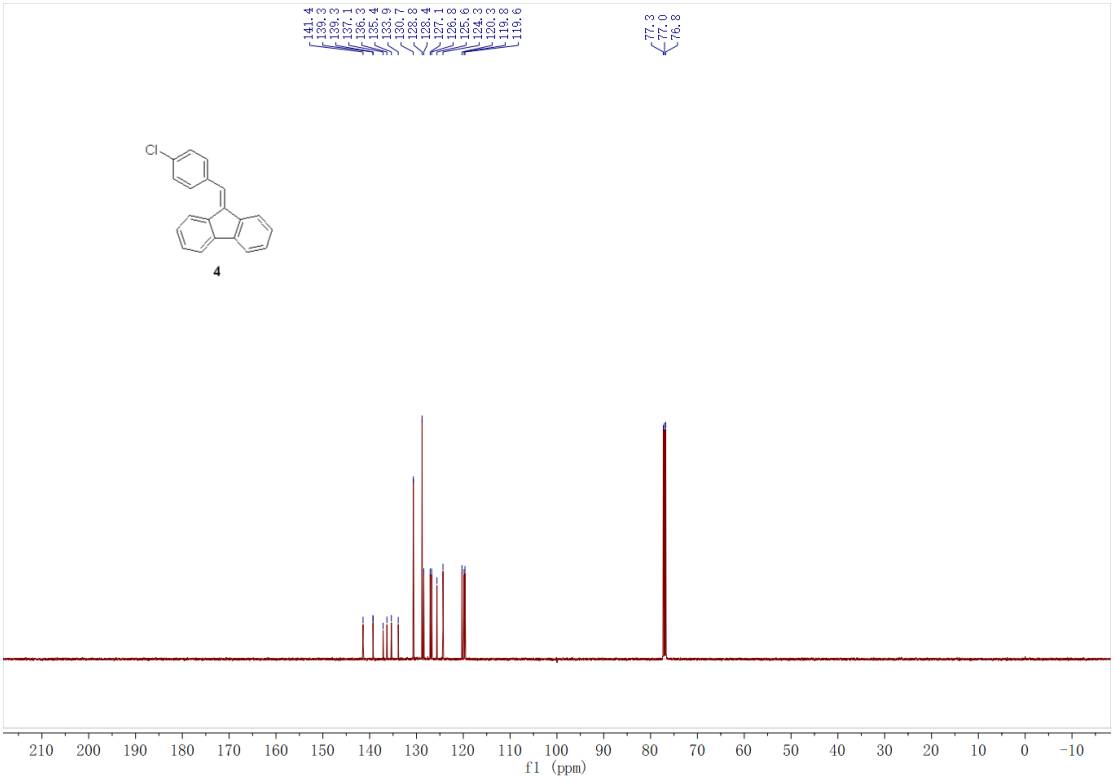
^{1}H and ^{13}C NMR spectra of compound 3.



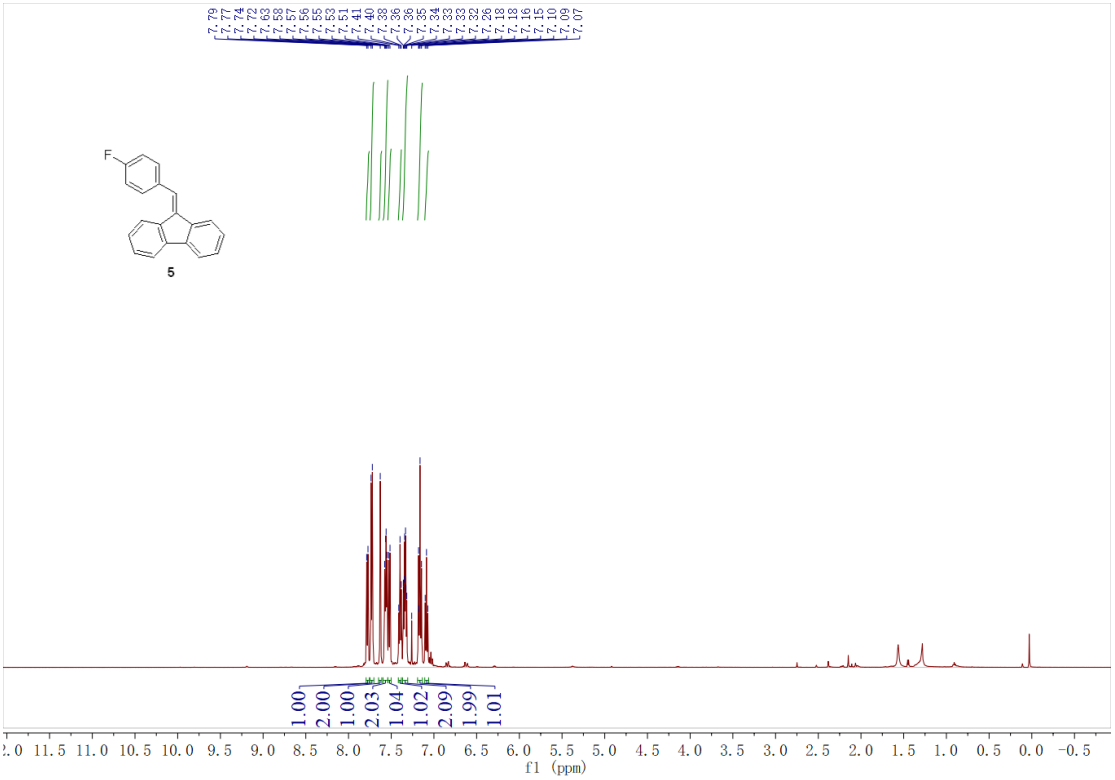


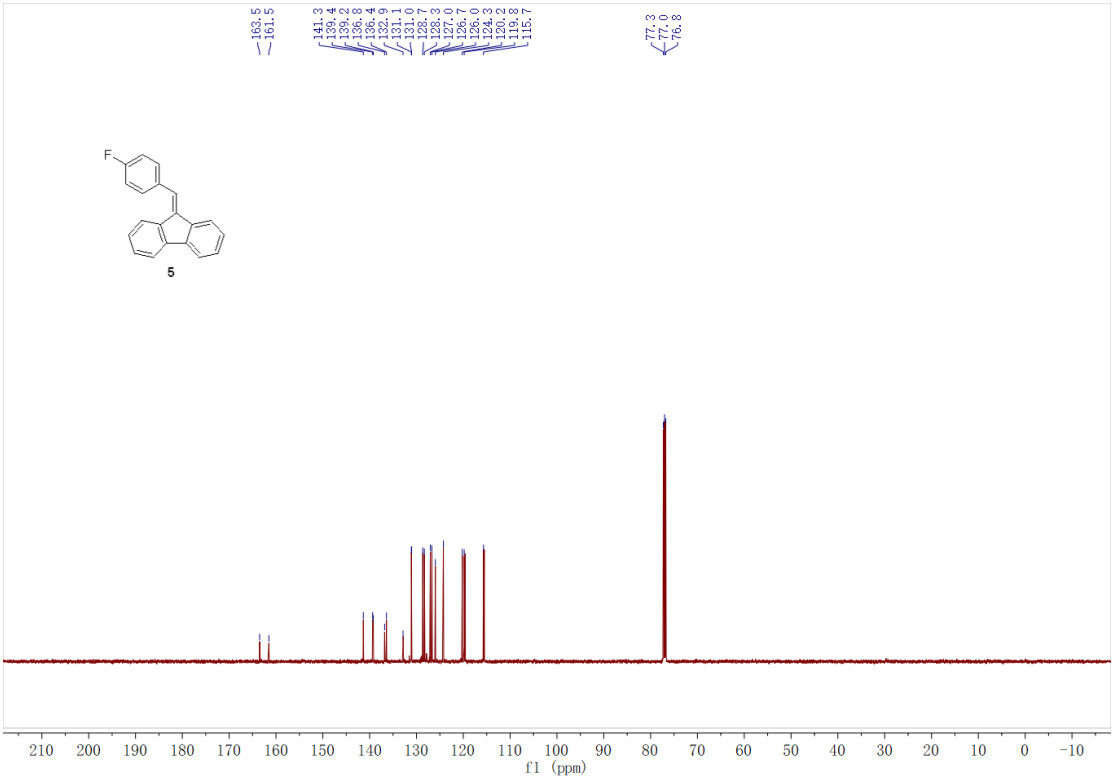
^{1}H and ^{13}C NMR spectra of compound 4.

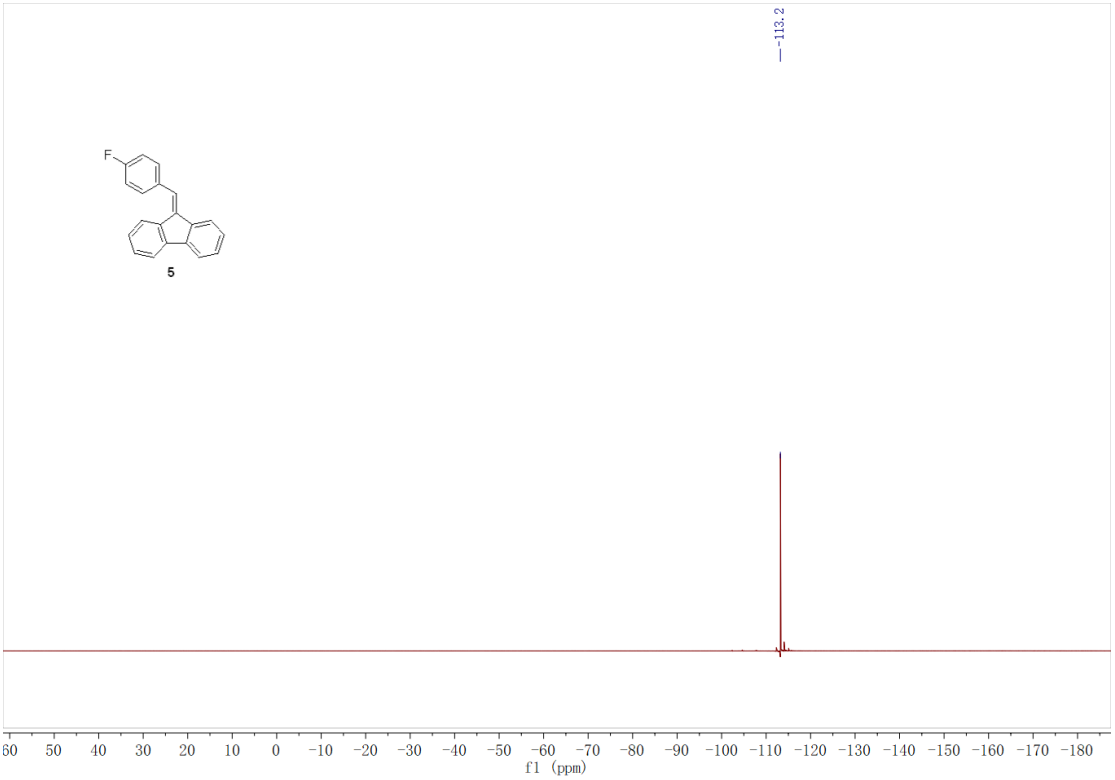




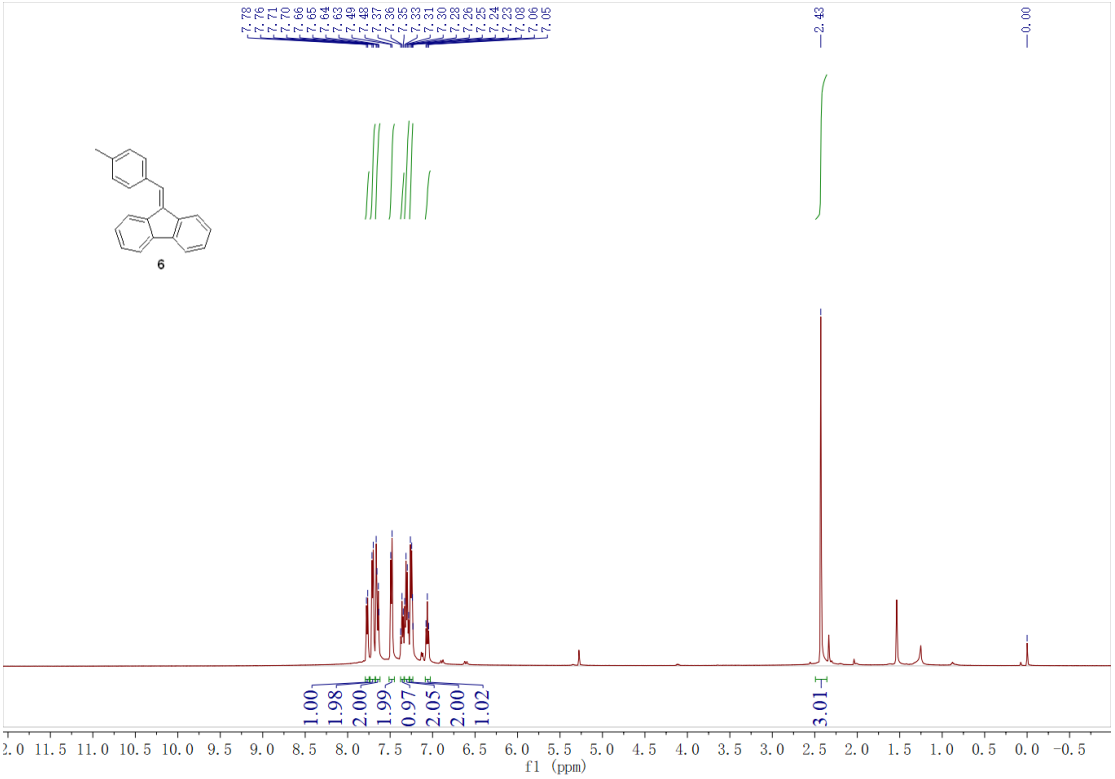
^{1}H , ^{13}C NMR and ^{19}F spectra of compound 5.

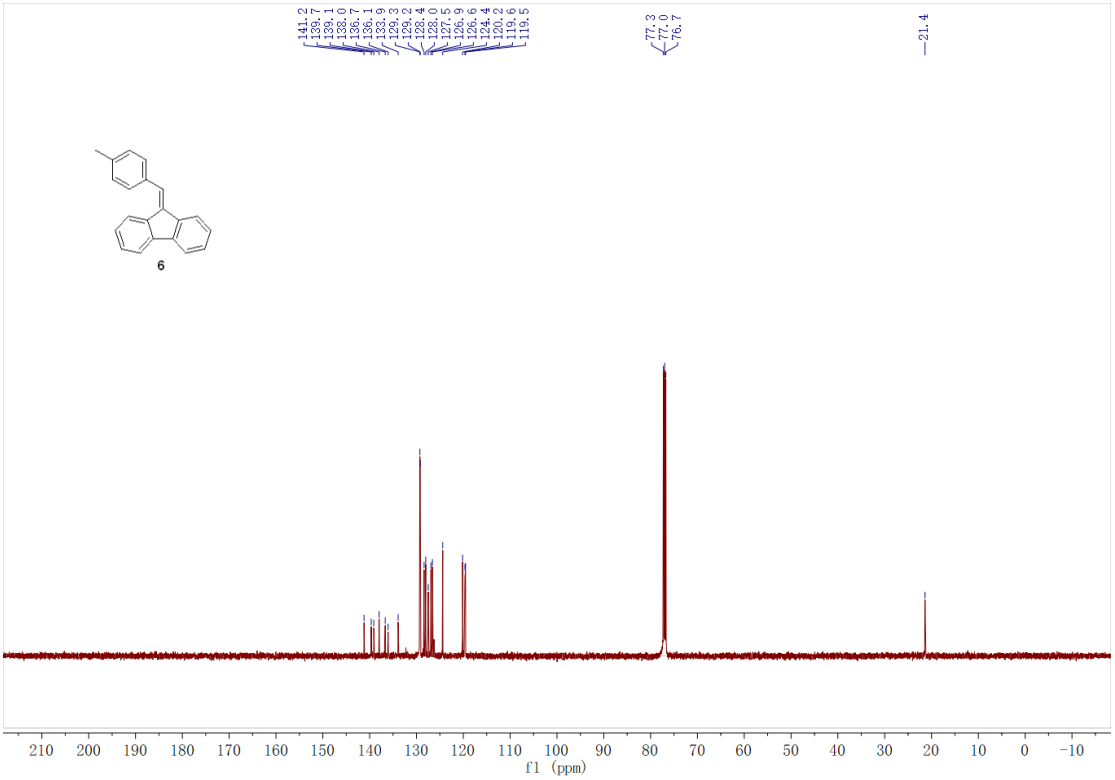




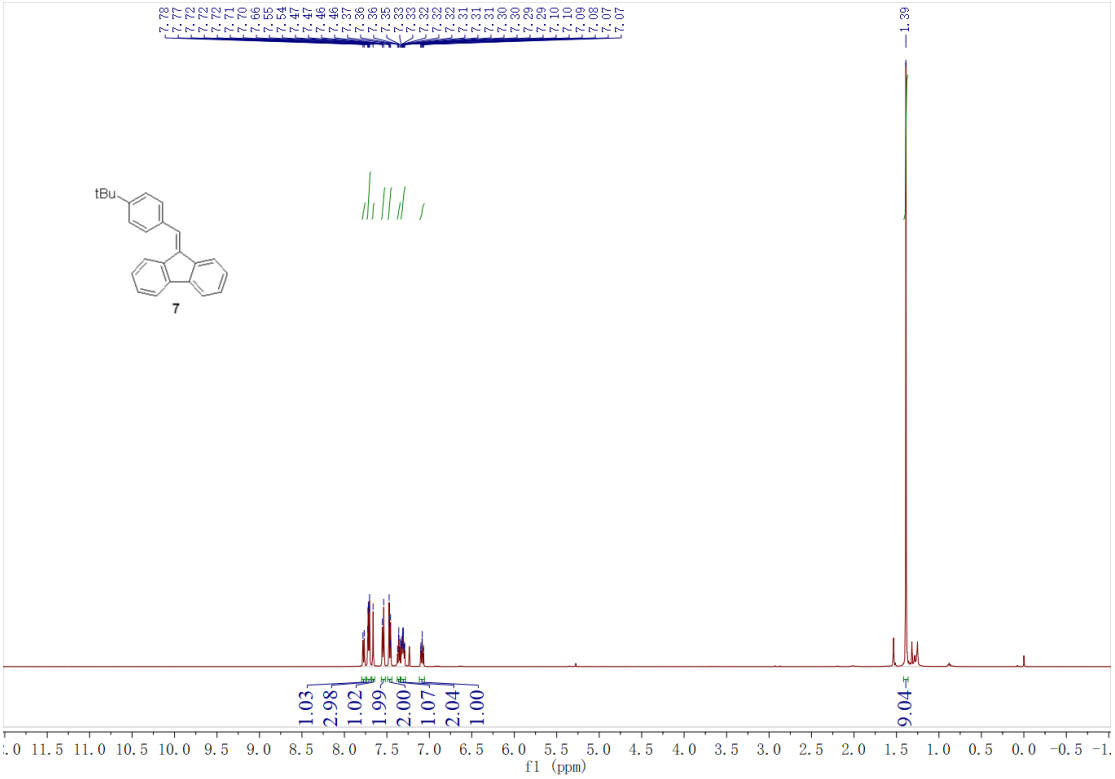


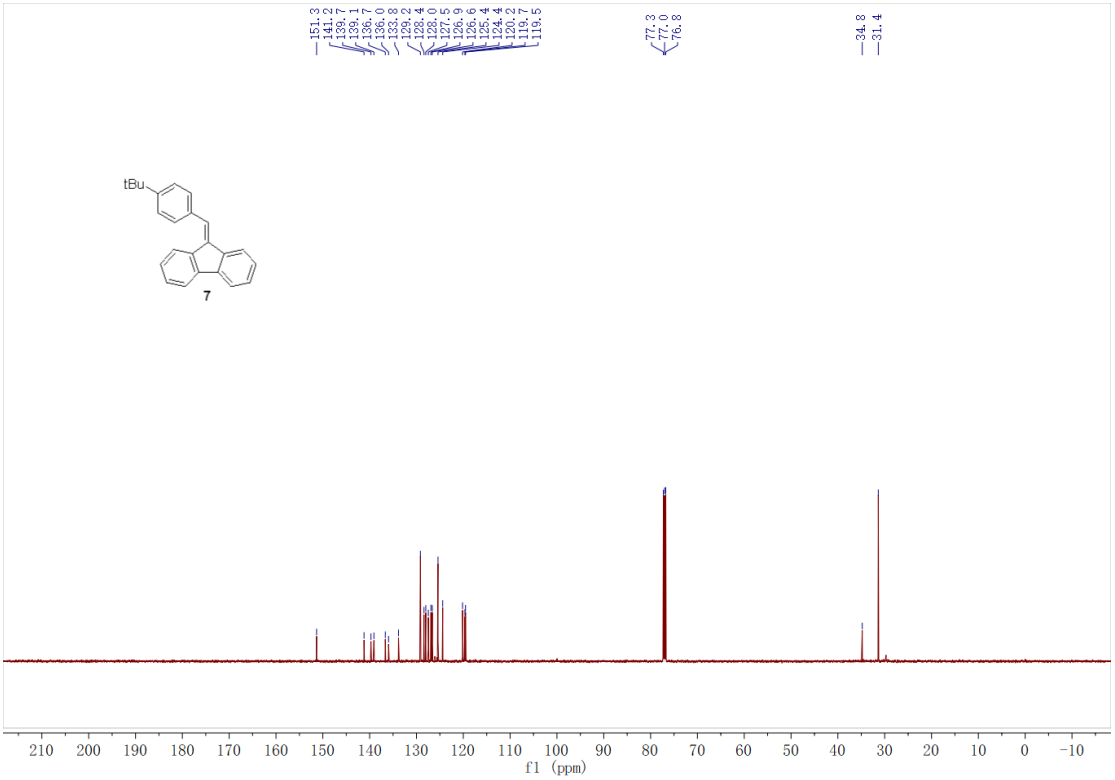
^{1}H and ^{13}C NMR spectra of compound 6.



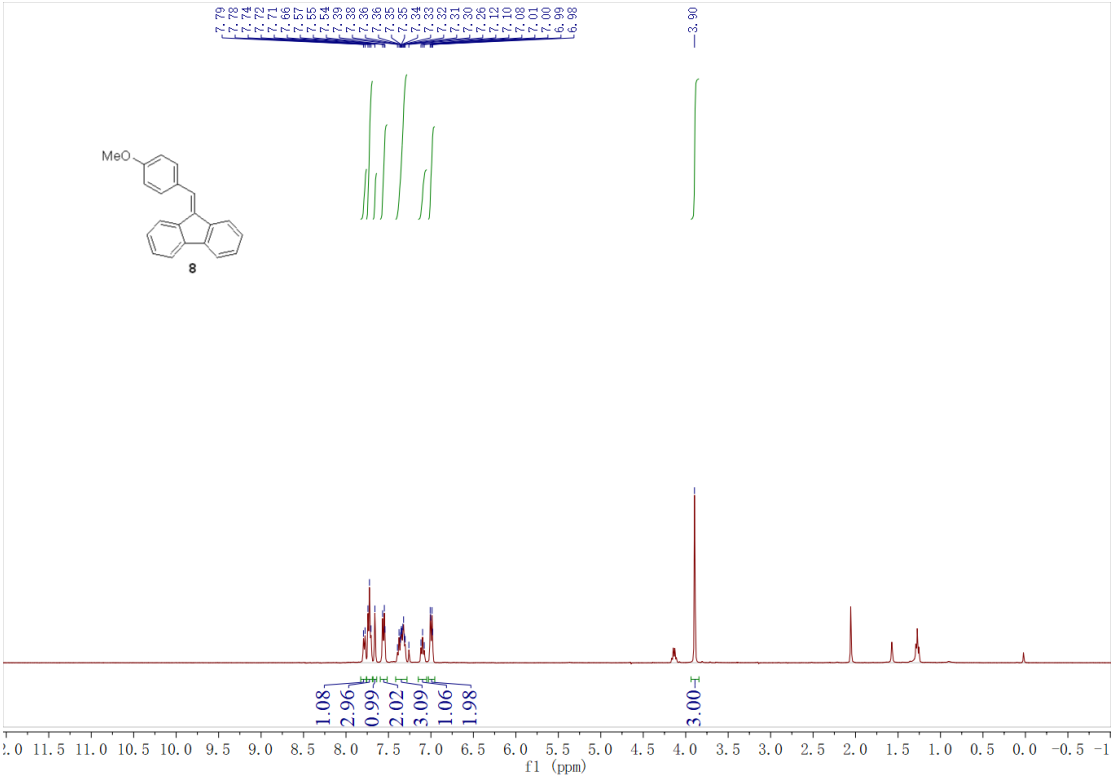


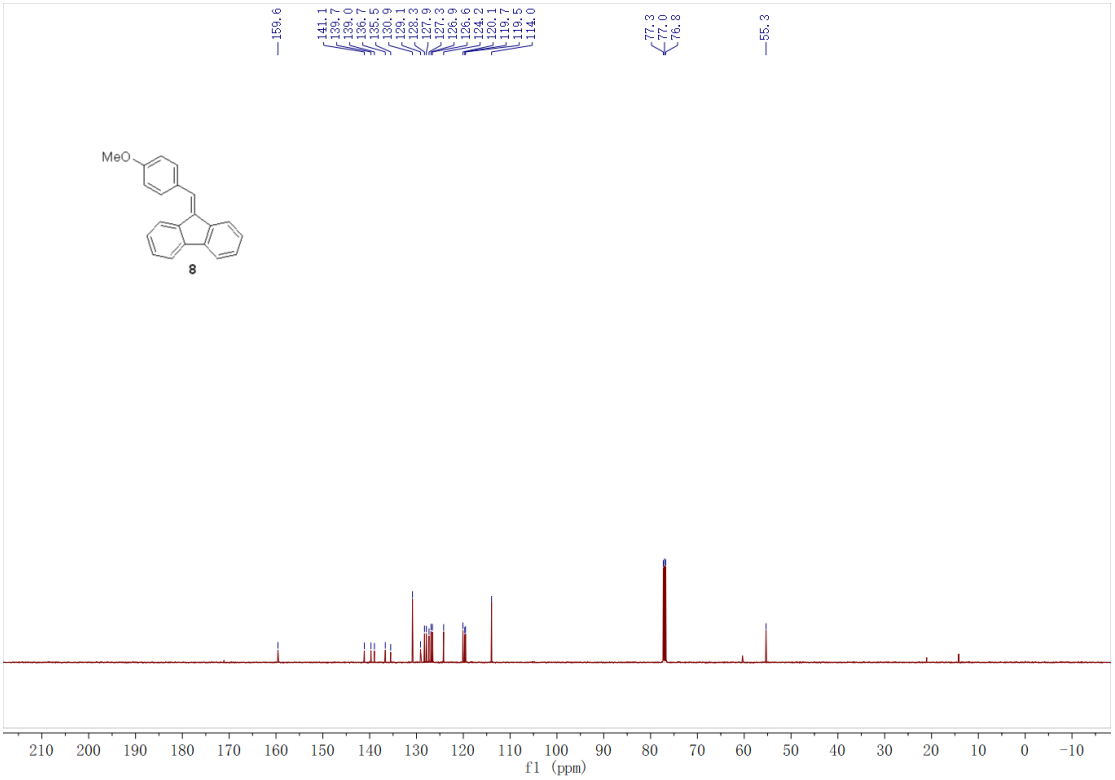
^{1}H and ^{13}C NMR spectra of compound 7.



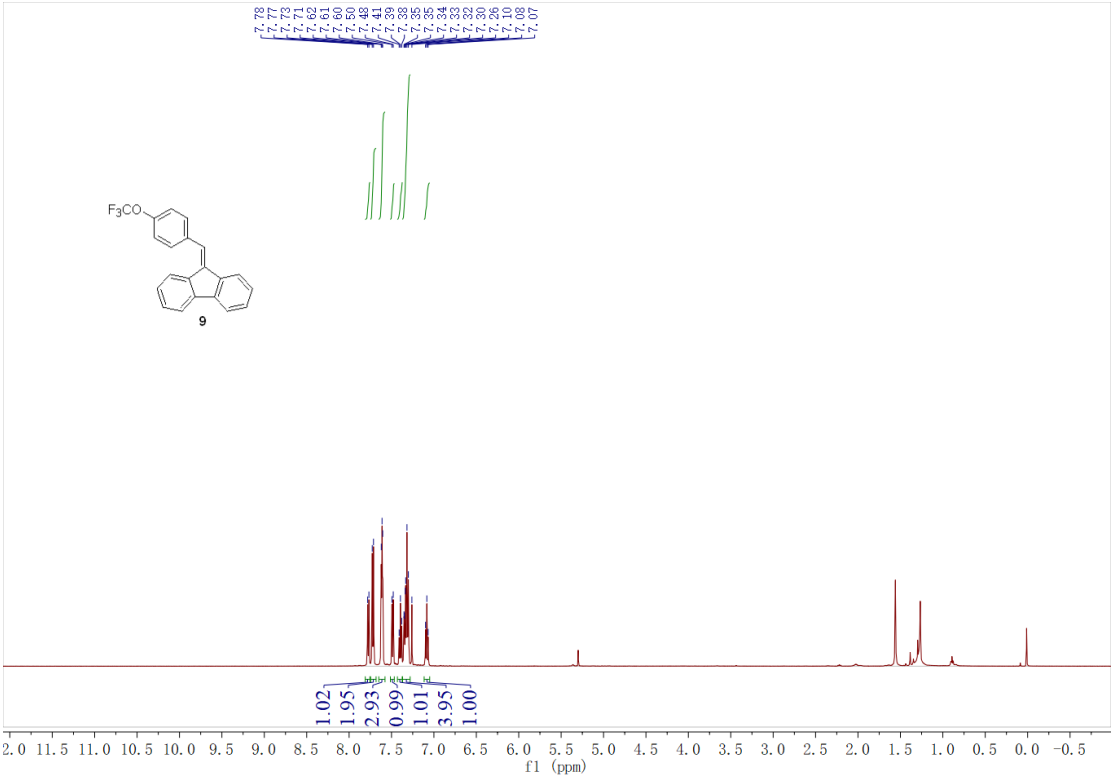


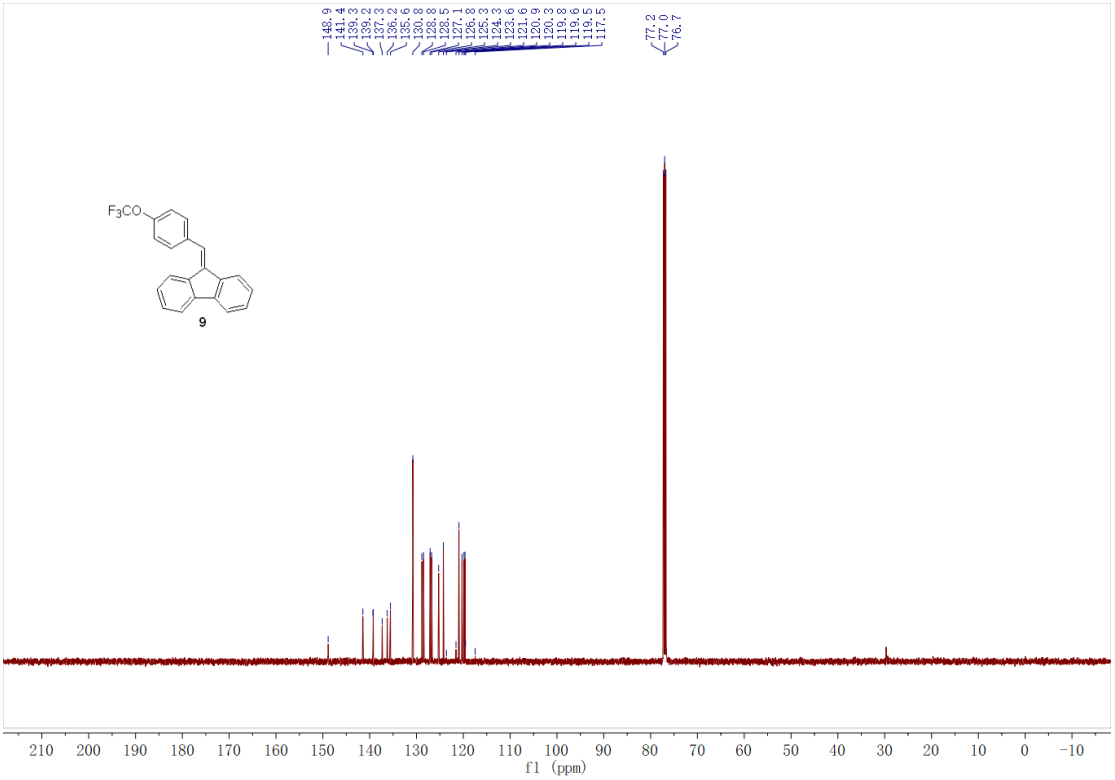
^{1}H and ^{13}C NMR spectra of compound 8.

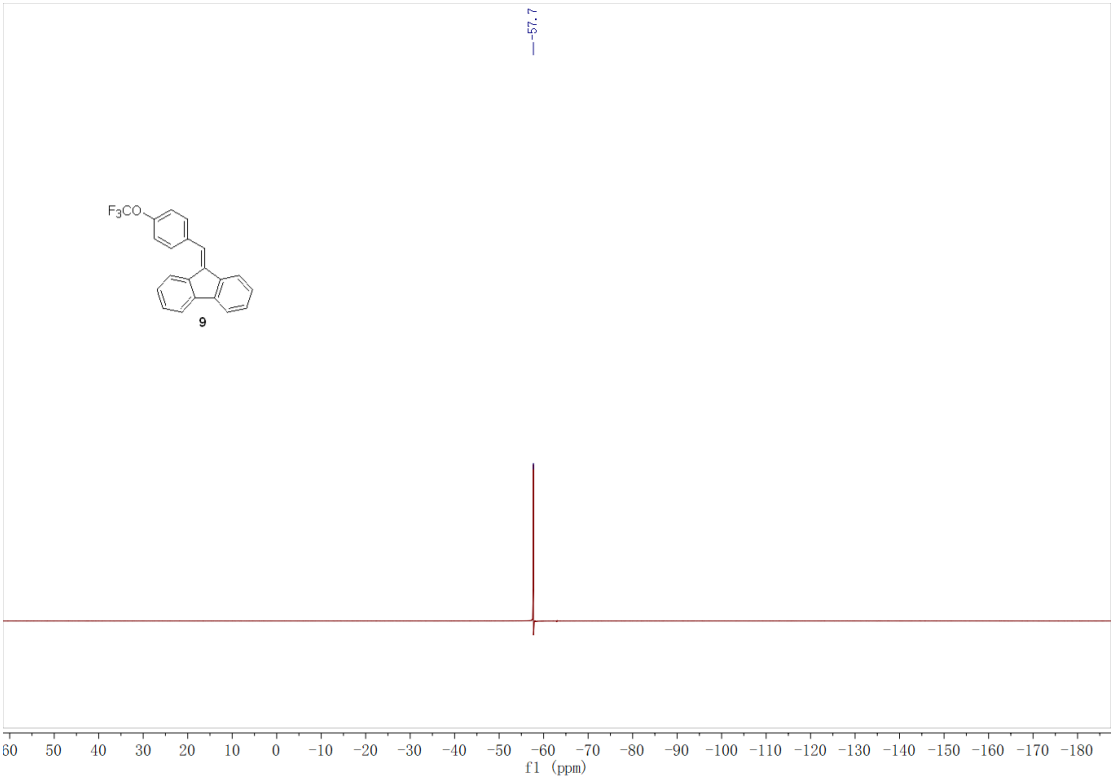




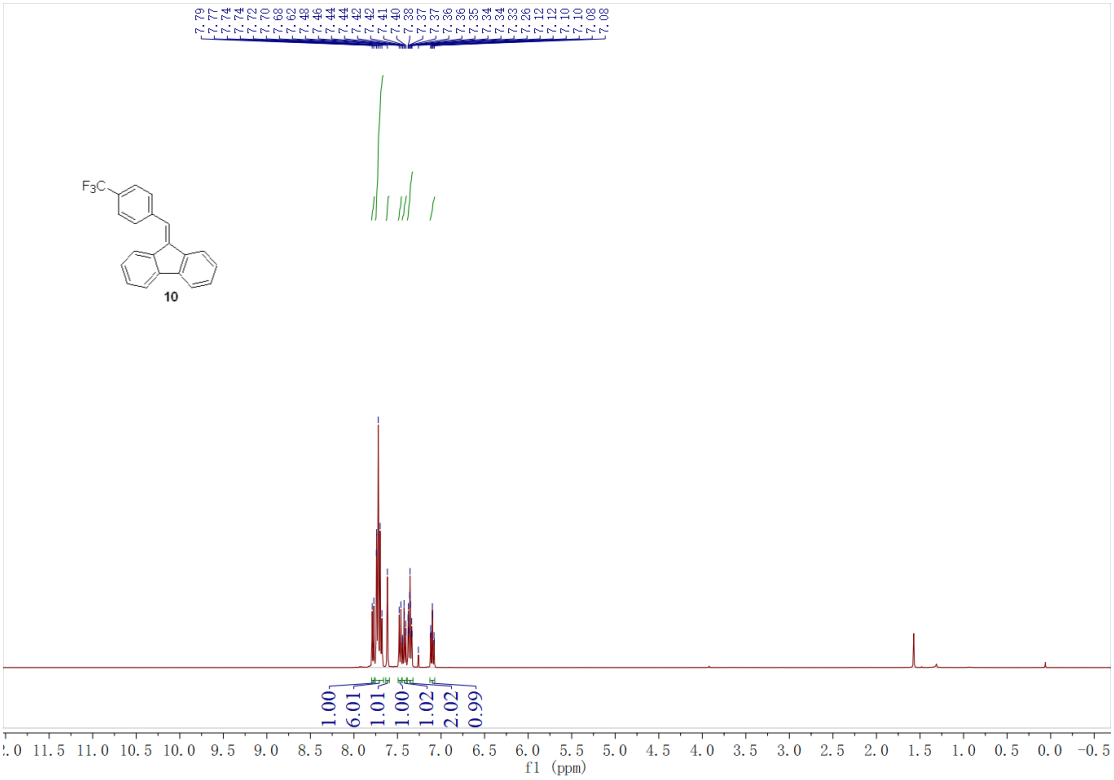
^{1}H, ^{13}C NMR and ^{19}F spectra of compound 9.

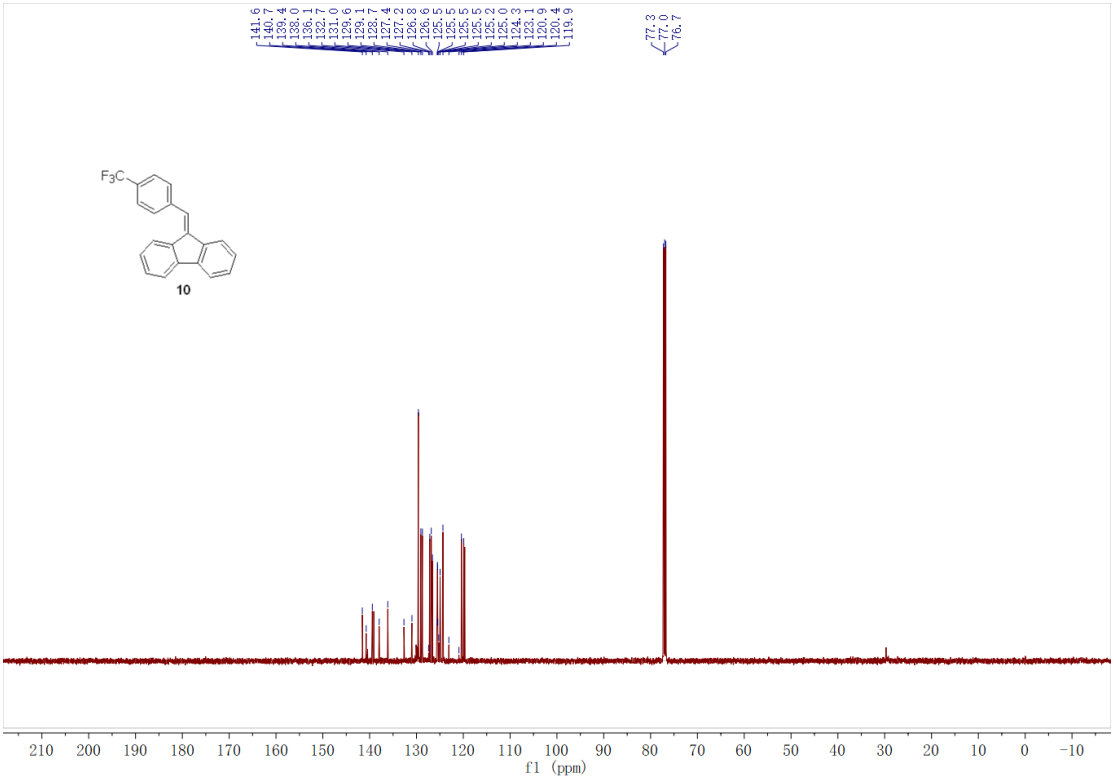


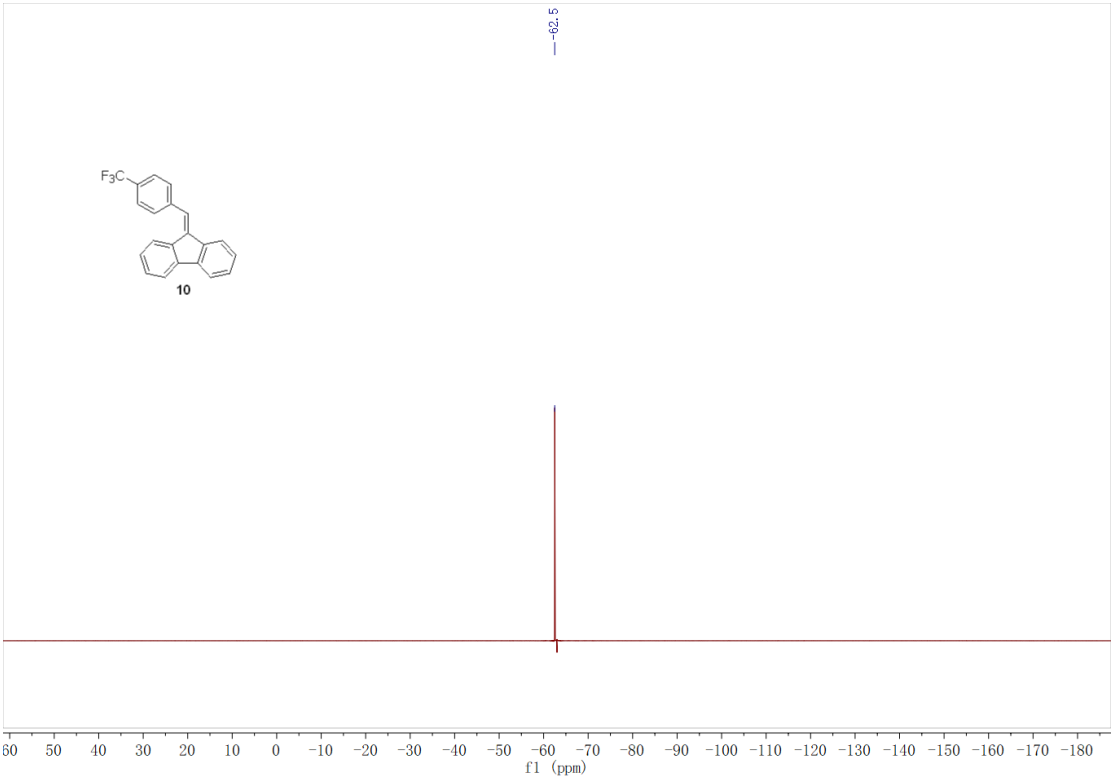

148.9
141.4
139.3
139.2
137.3
136.2
135.6
130.8
128.8
128.5
127.1
126.8
125.3
124.3
123.6
121.6
120.9
120.3
119.8
119.6
119.5
117.5
77.2
77.0
76.7
F3CO
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-57.7
F3CO
9
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

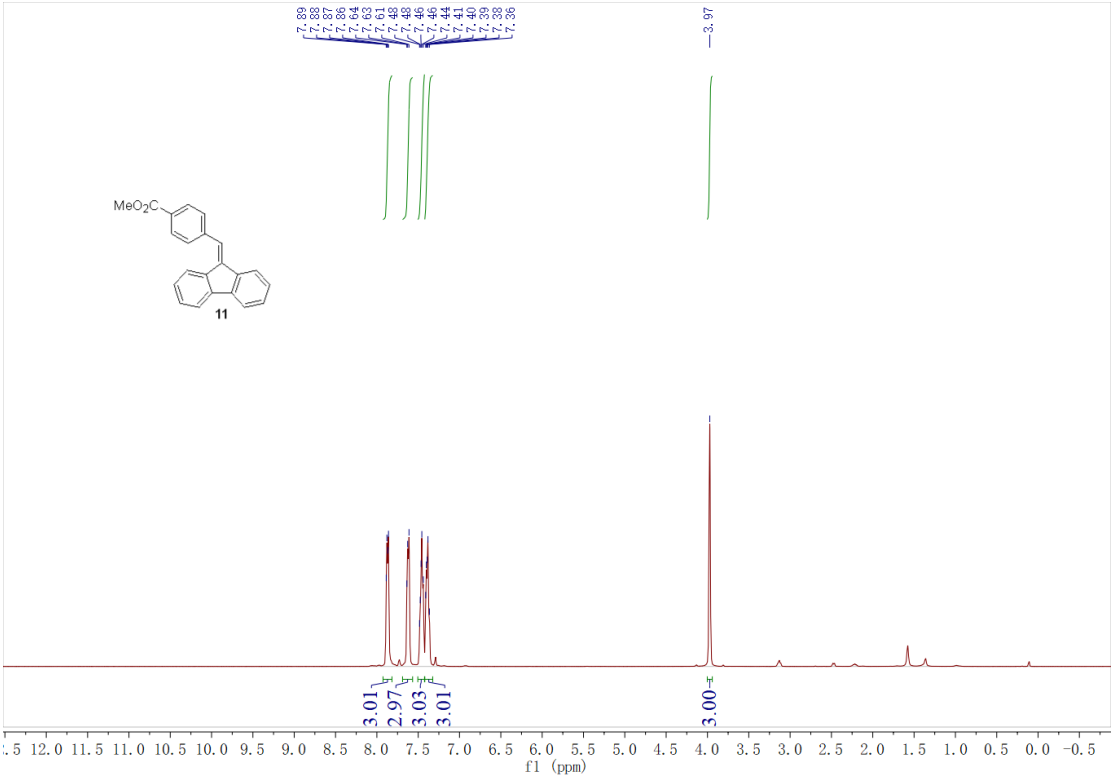
^{1}H, ^{13}C NMR and ^{19}F spectra of compound 10.

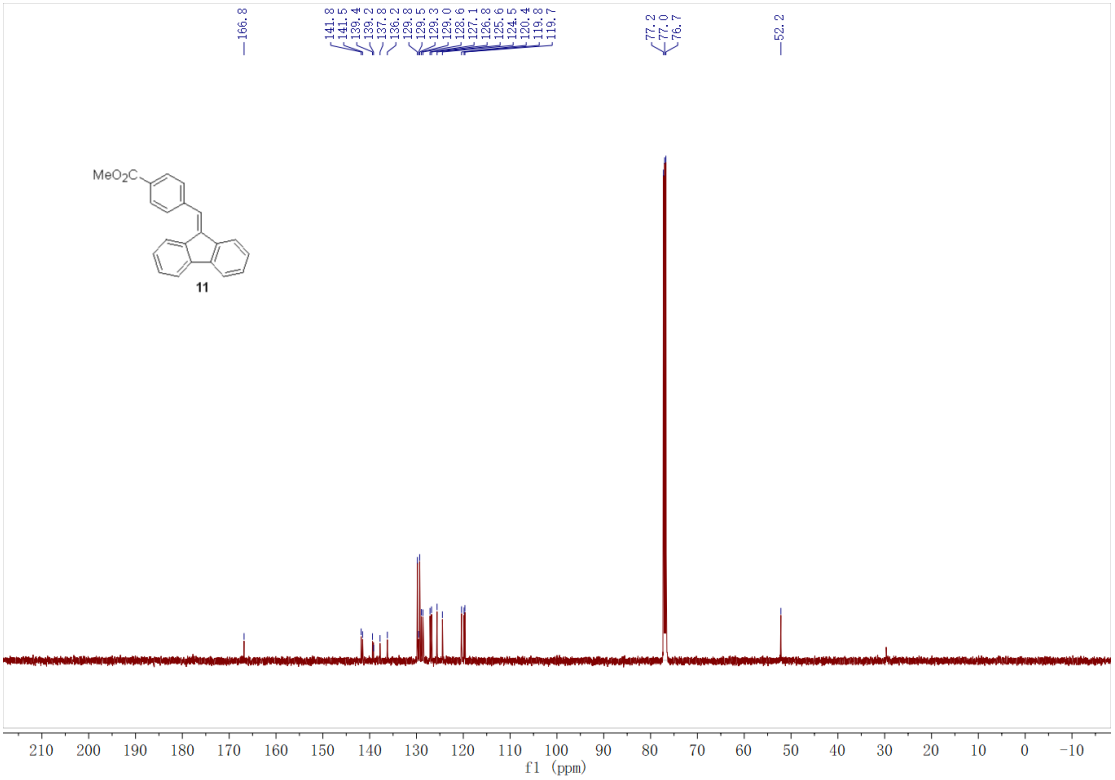




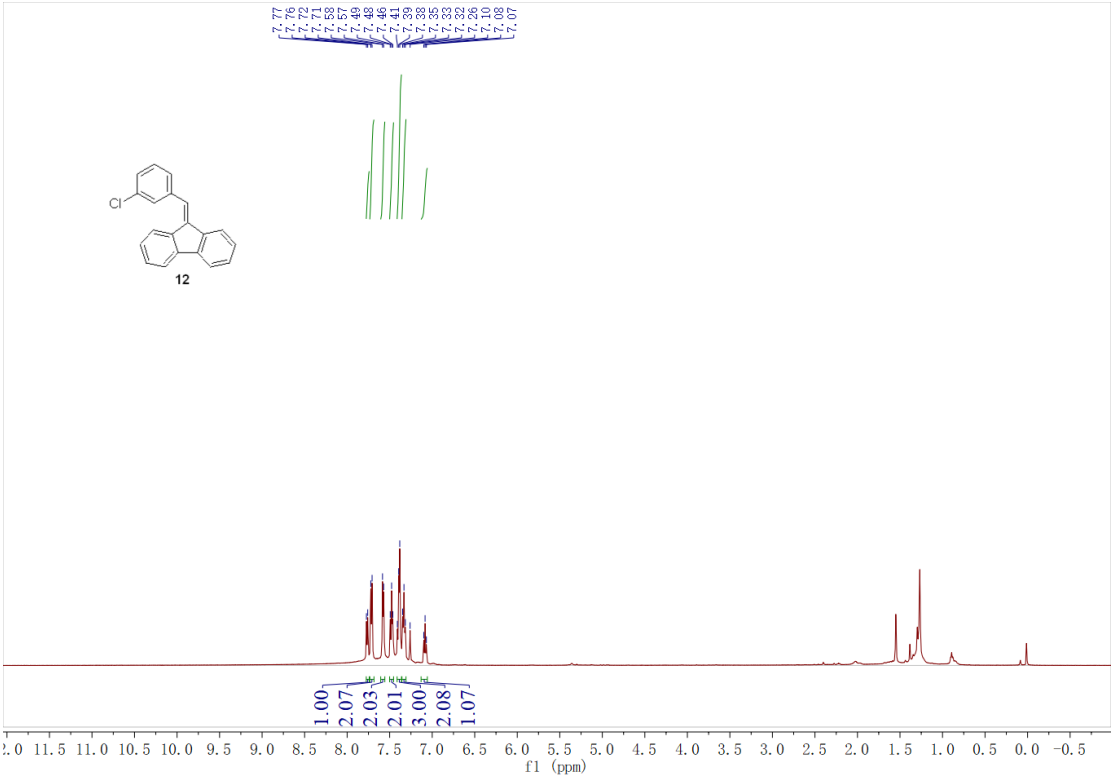


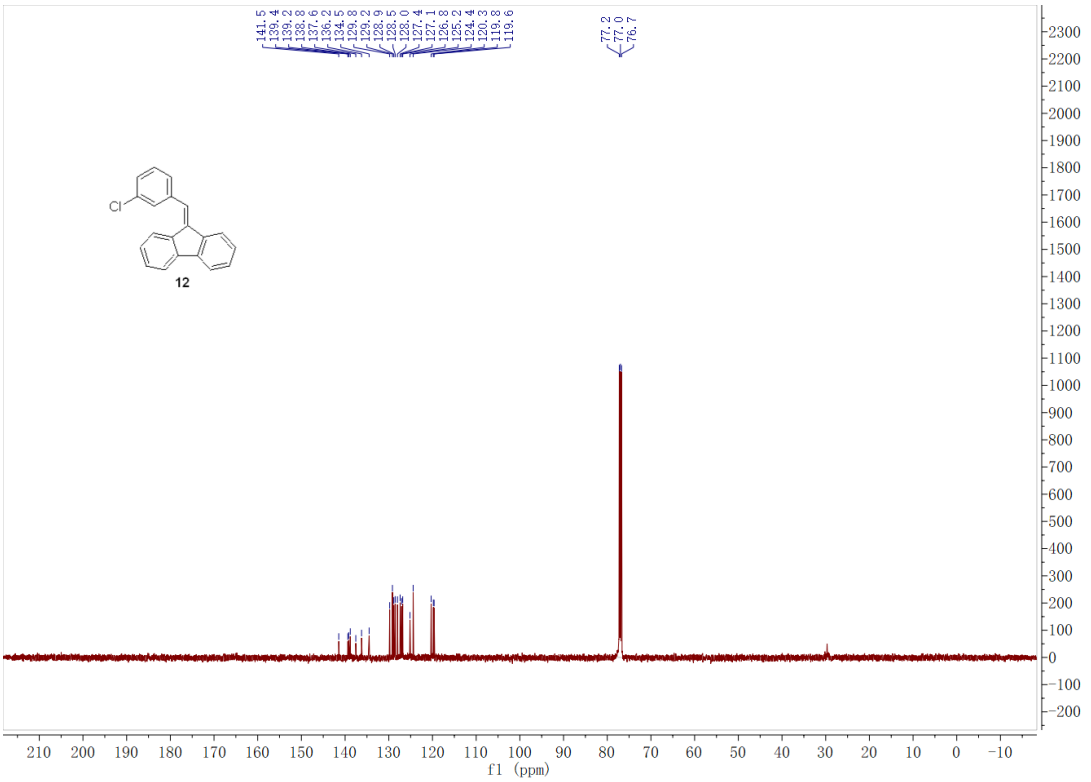
^{1}H and ^{13}C NMR spectra of compound 11.



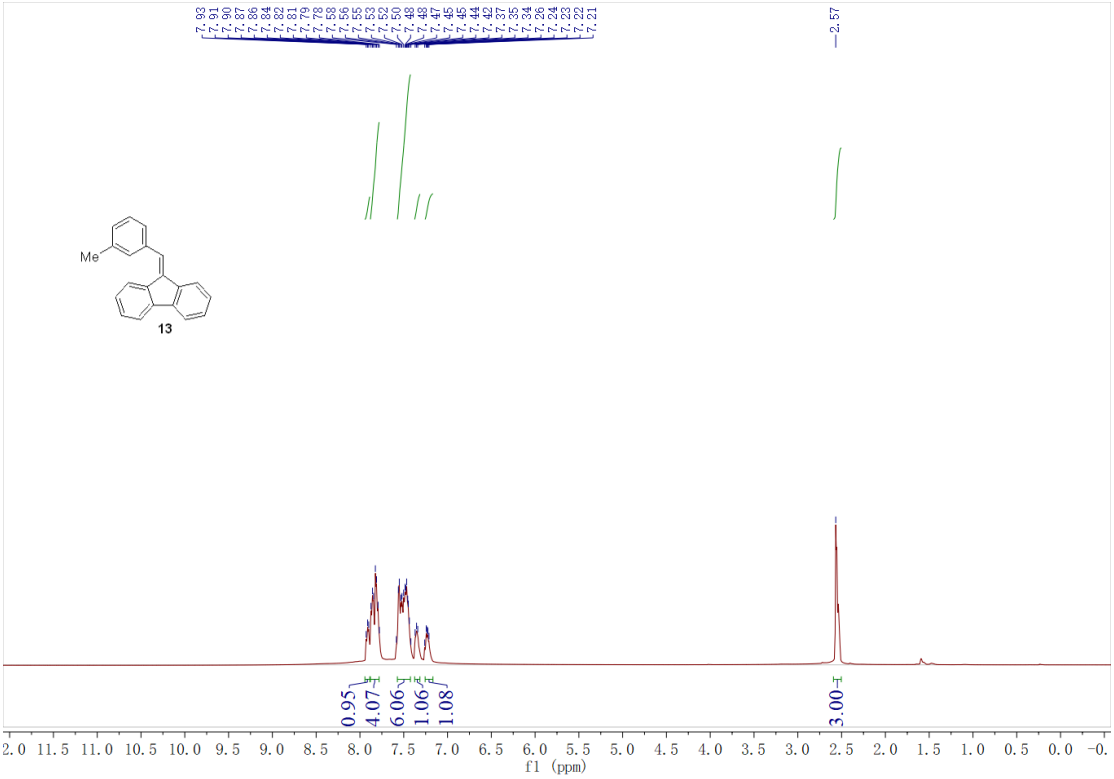


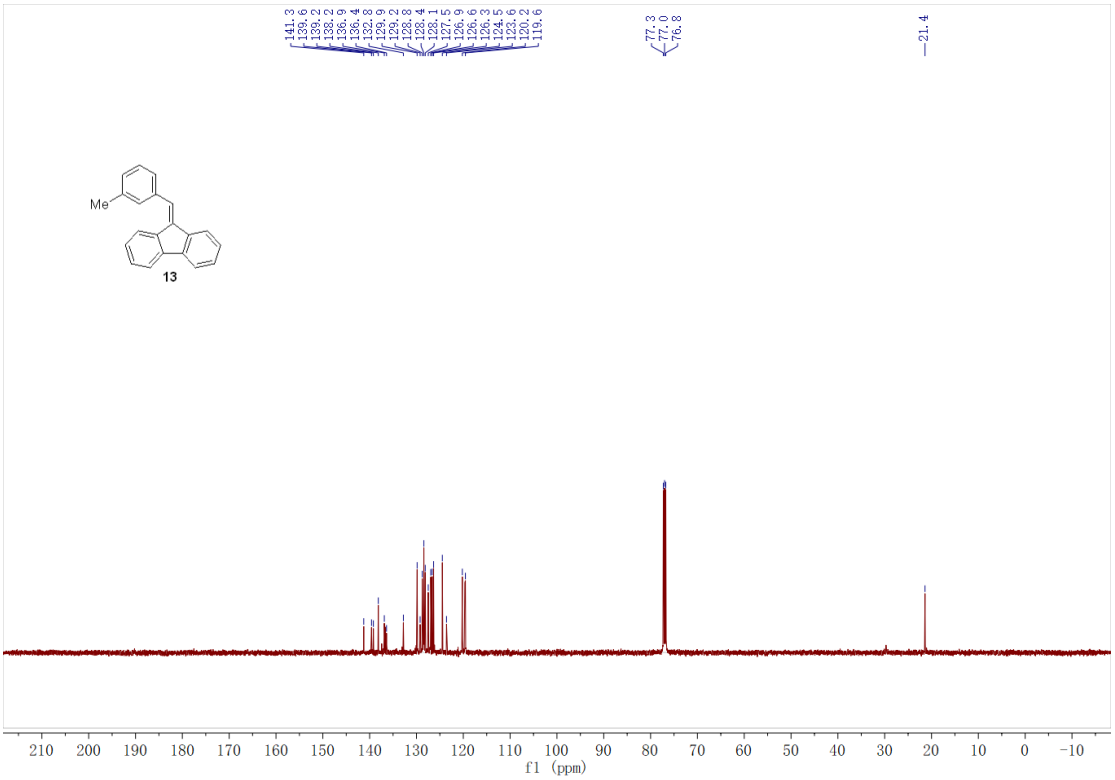
^{1}H and ^{13}C NMR spectra of compound 12.



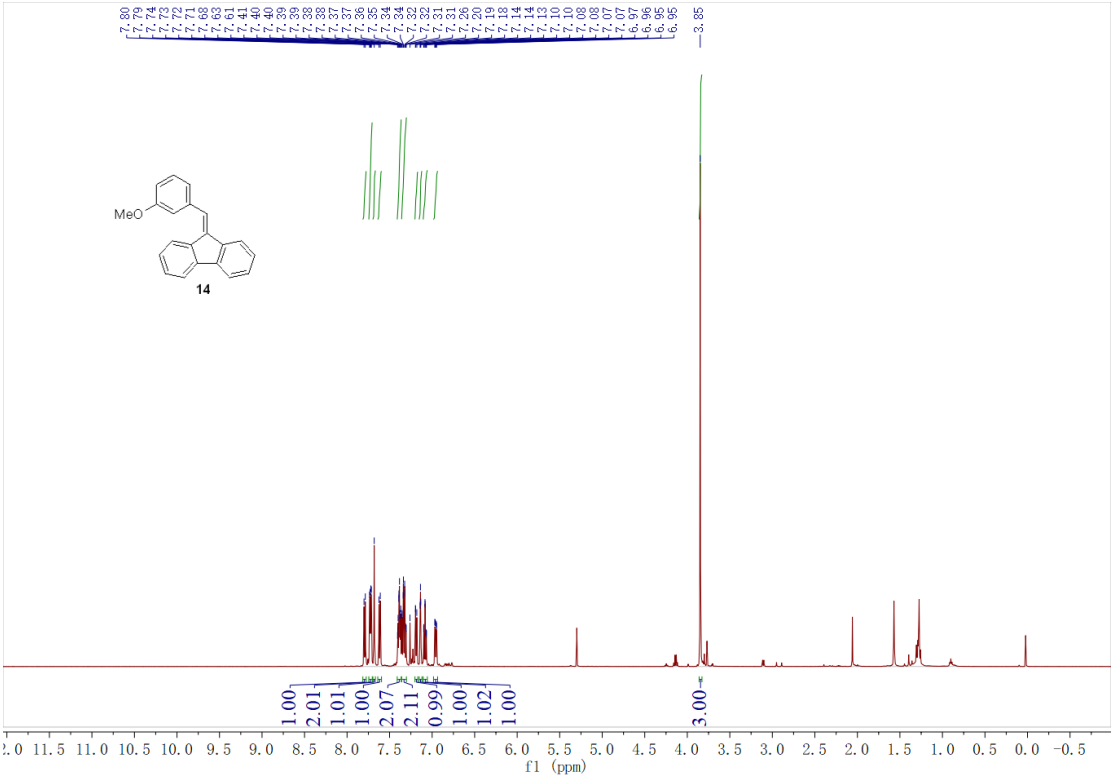


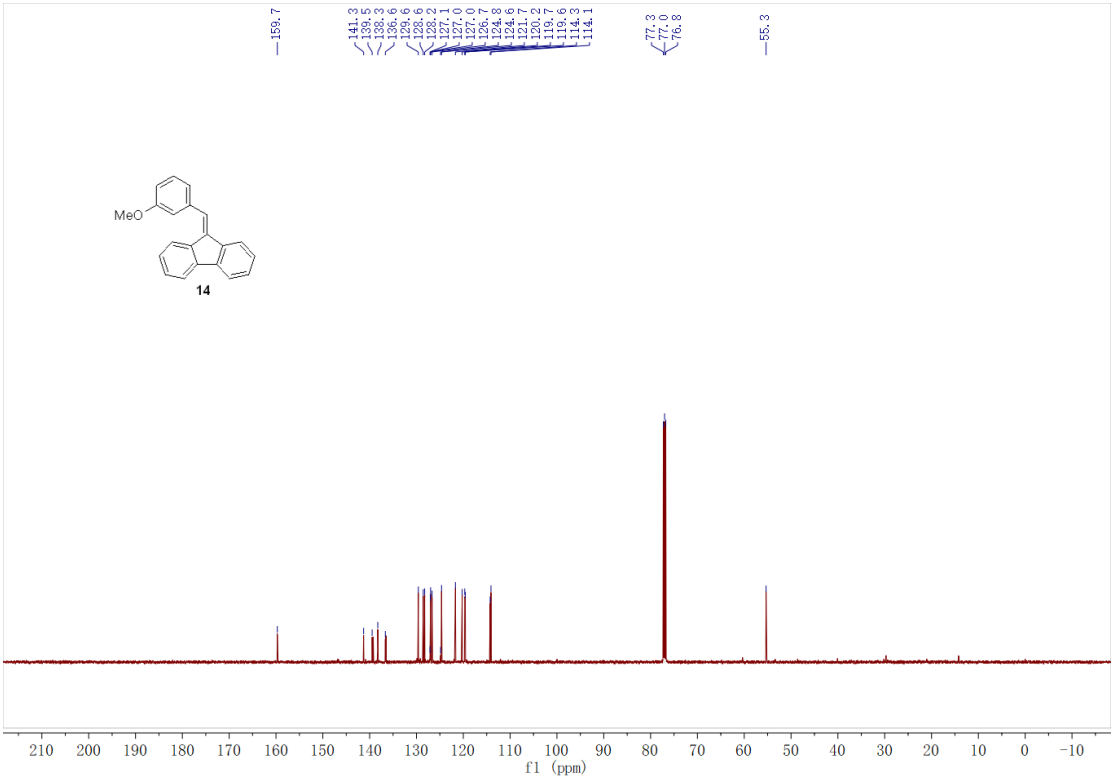
^{1}H and ^{13}C NMR spectra of compound 13.



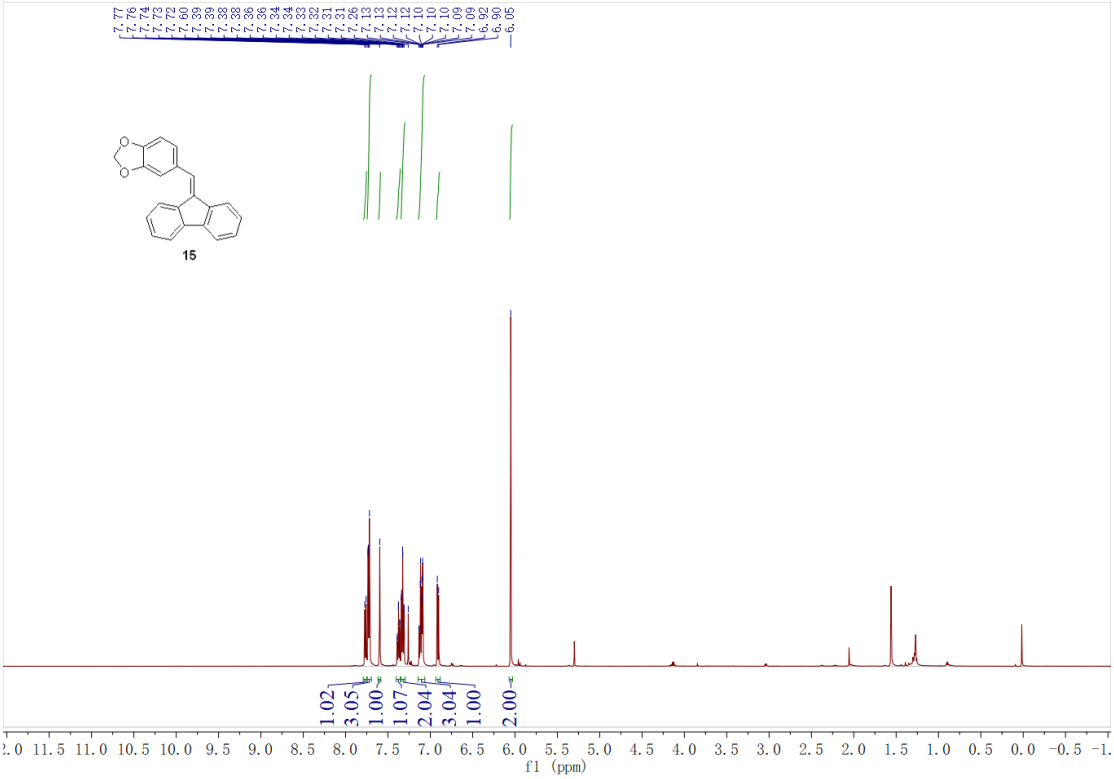


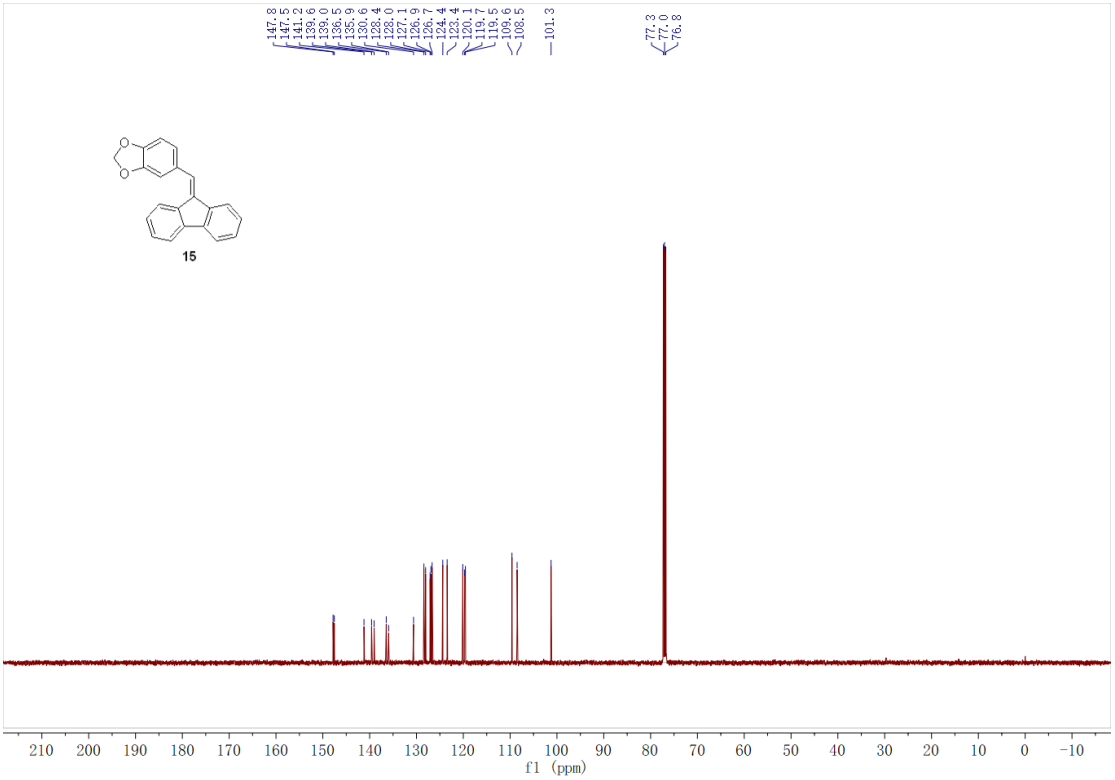
^{1}H and ^{13}C NMR spectra of compound 14.



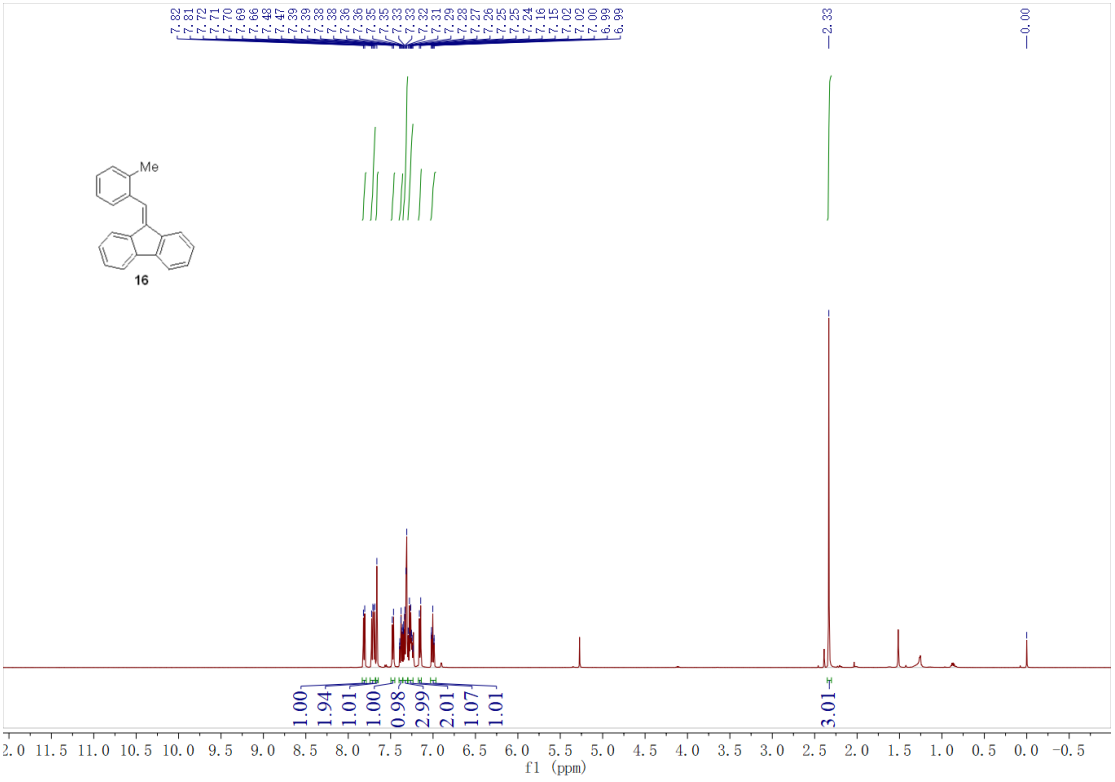


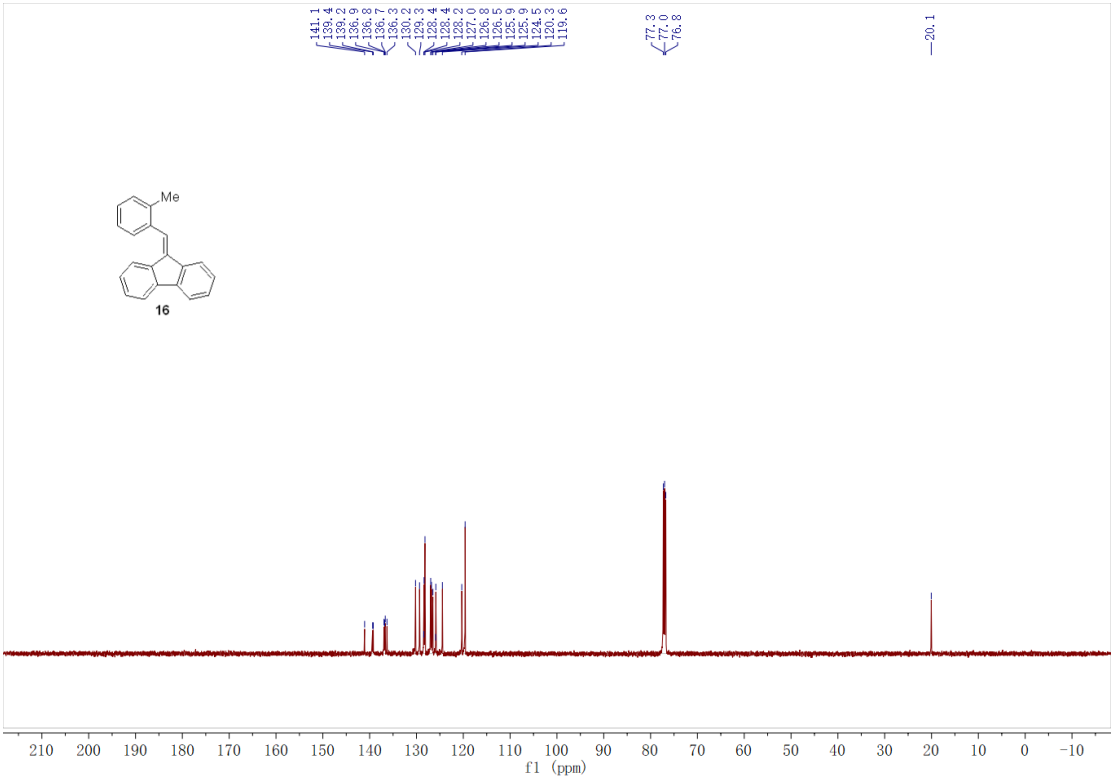
^{1}H and ^{13}C NMR spectra of compound 15.



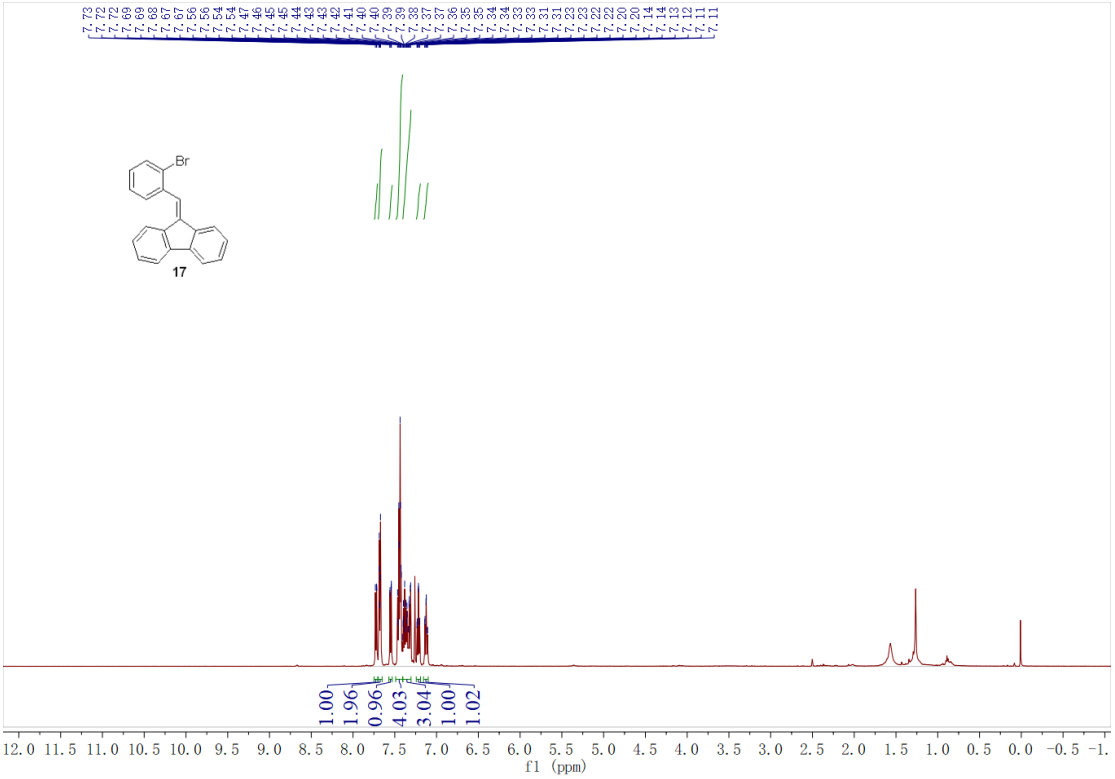


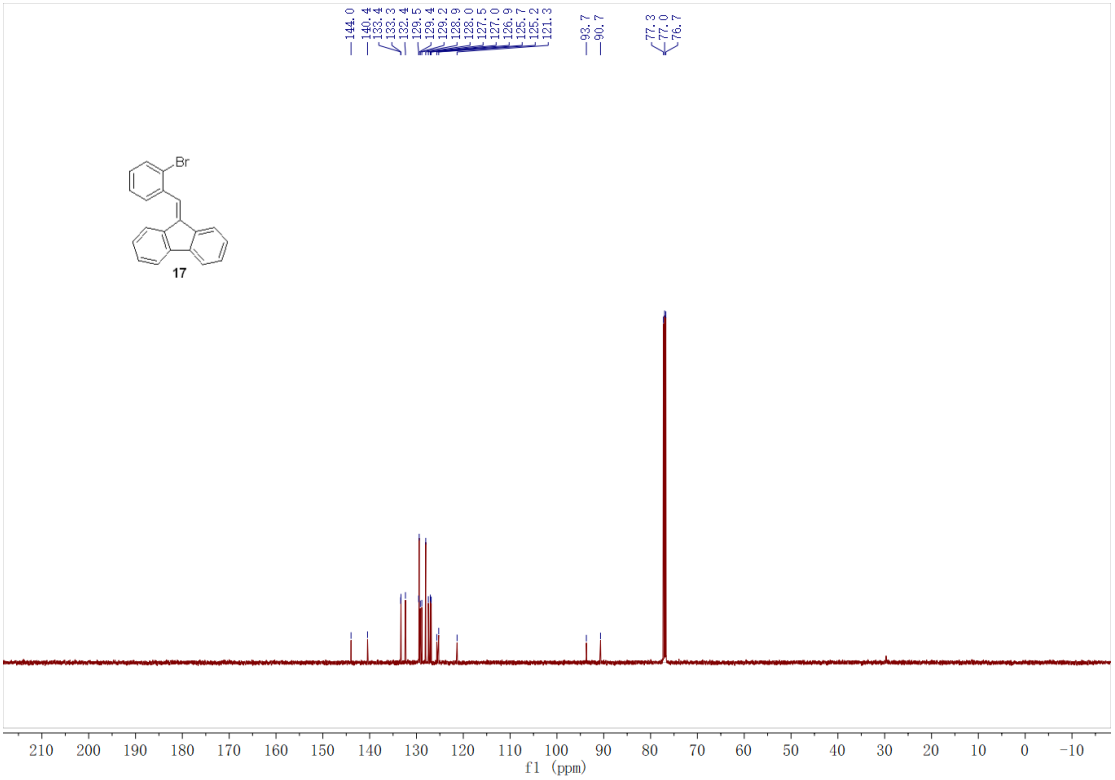
^{1}H and ^{13}C NMR spectra of compound 16.



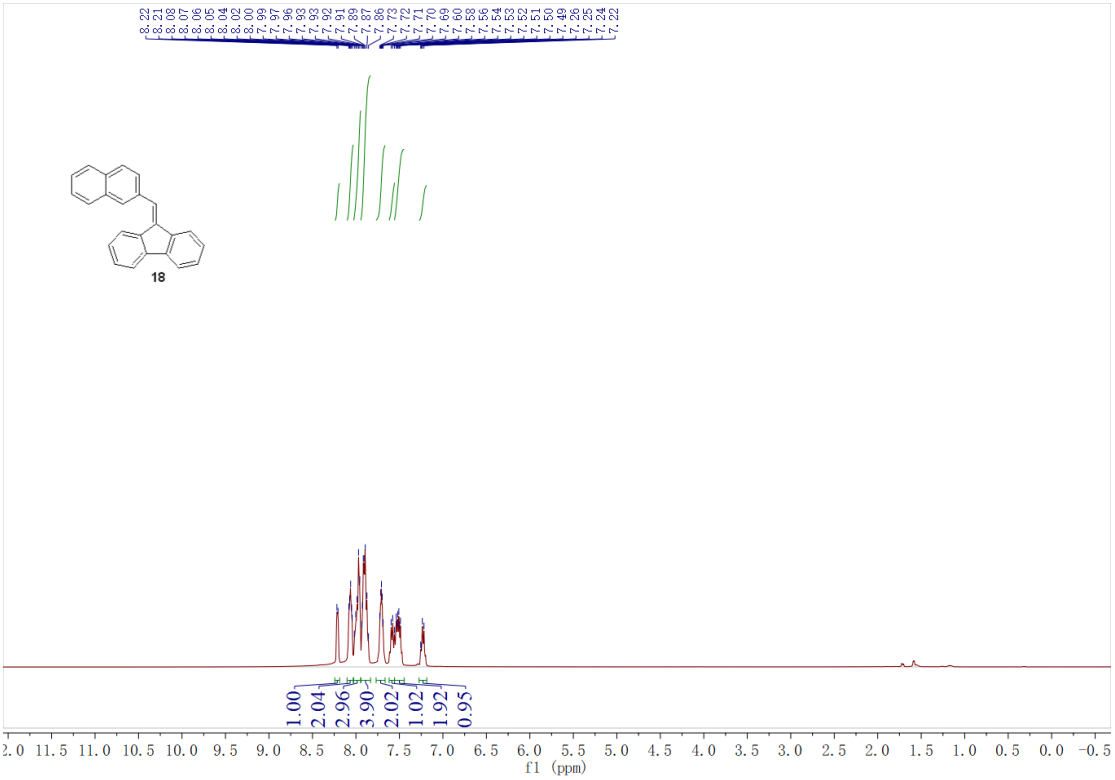


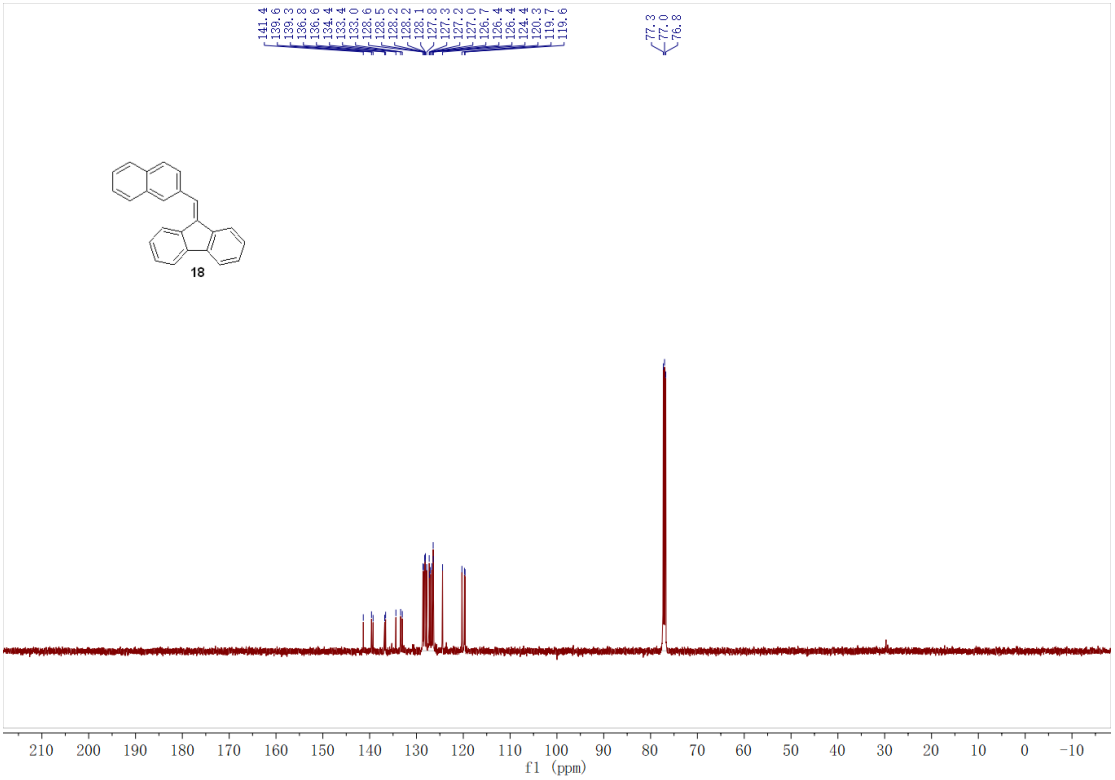
^{1}H and ^{13}C NMR spectra of compound 17.



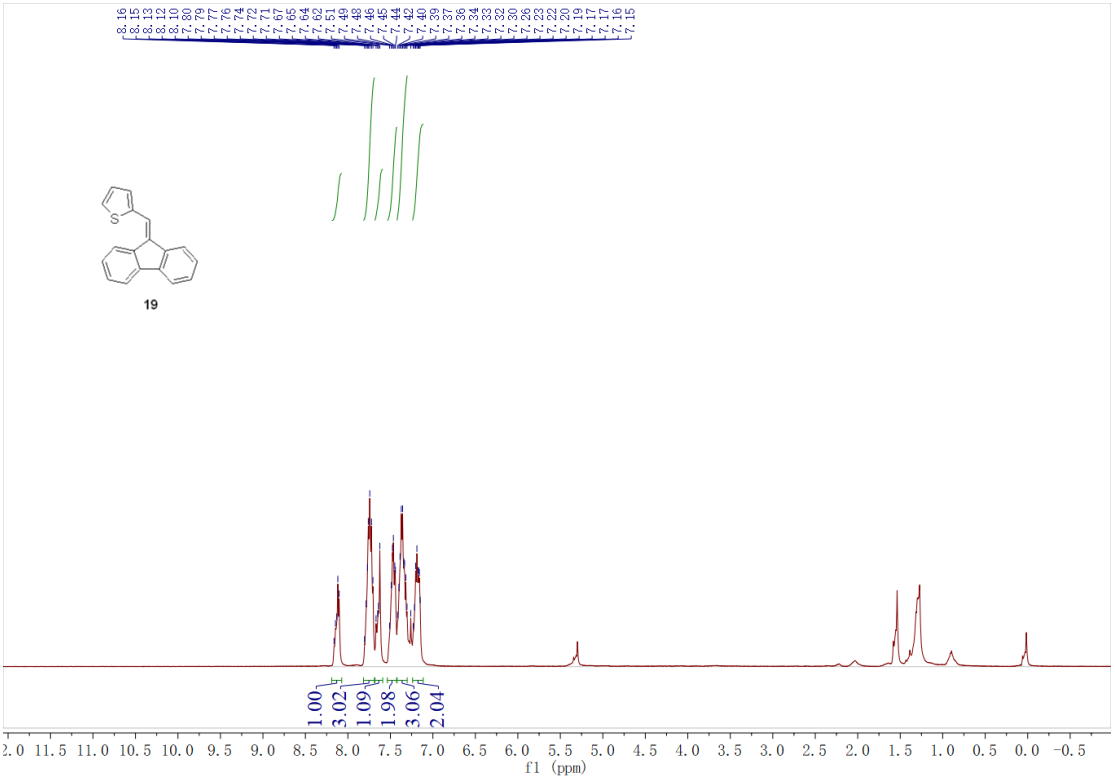


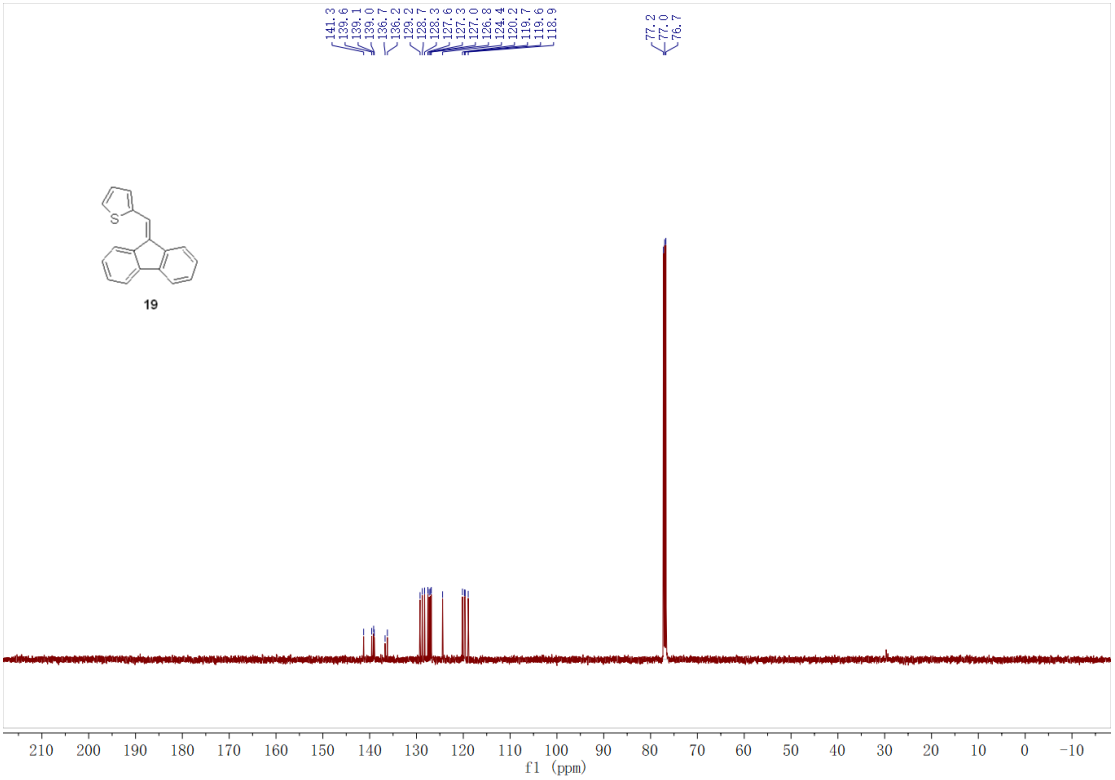
^{1}H and ^{13}C NMR spectra of compound 18.



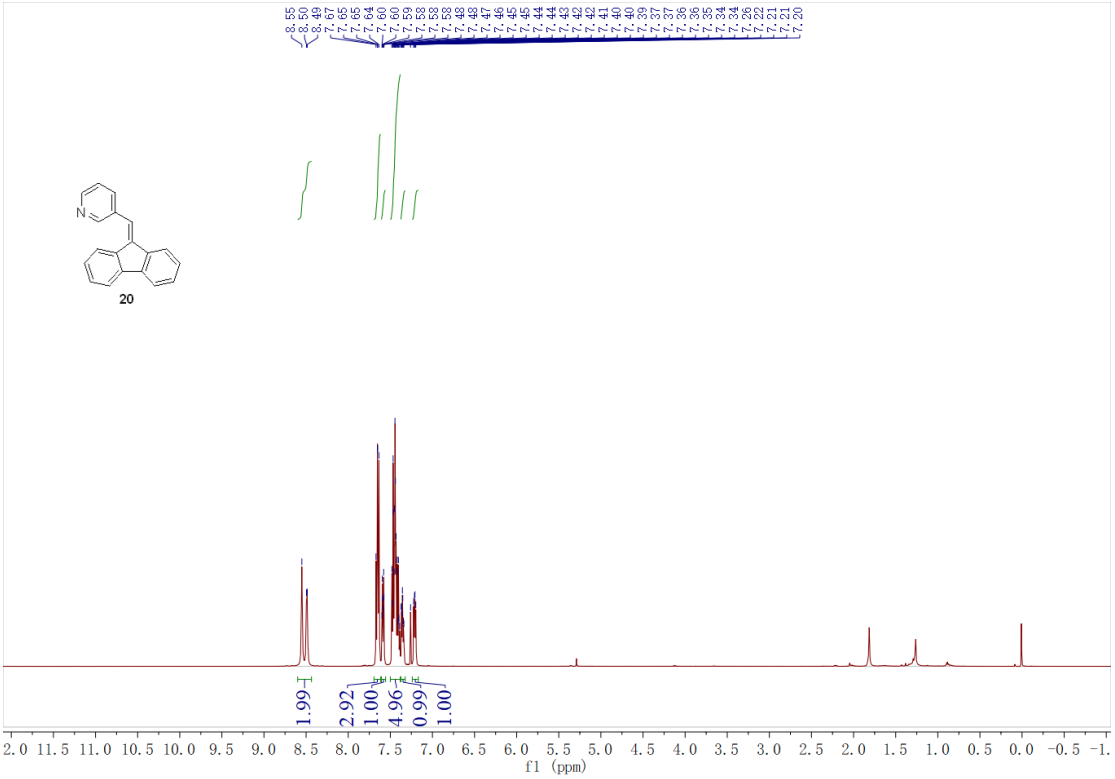


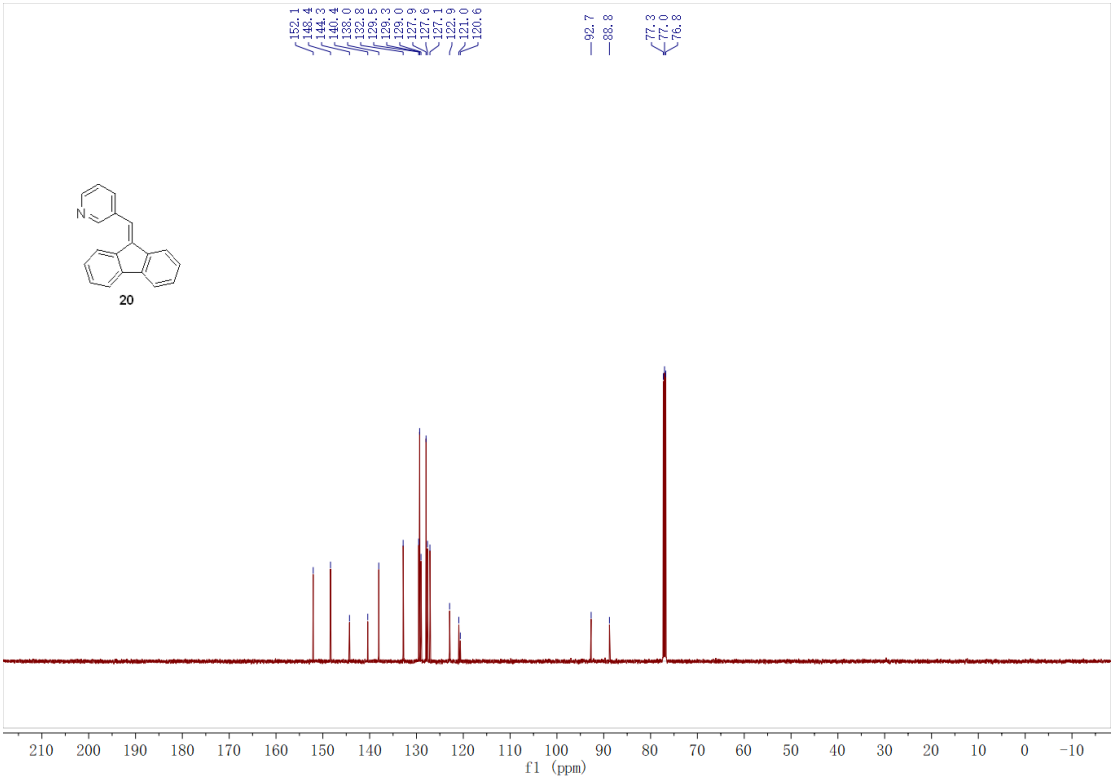
^{1}H and ^{13}C NMR spectra of compound 19.



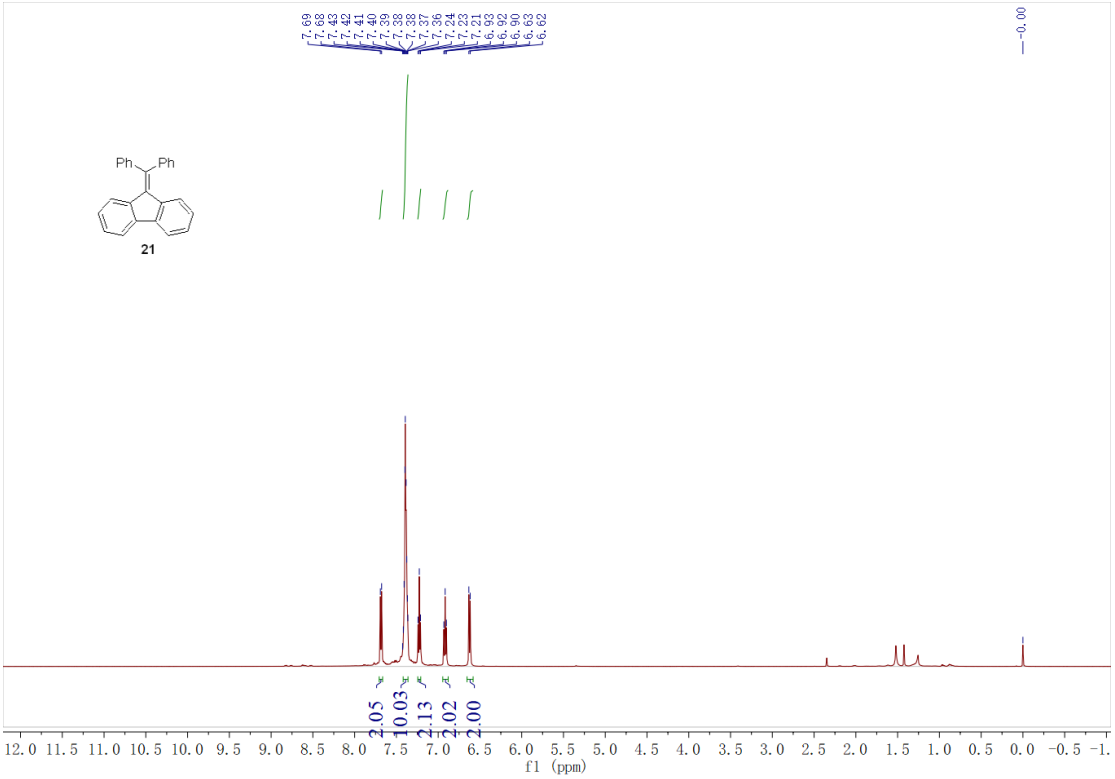


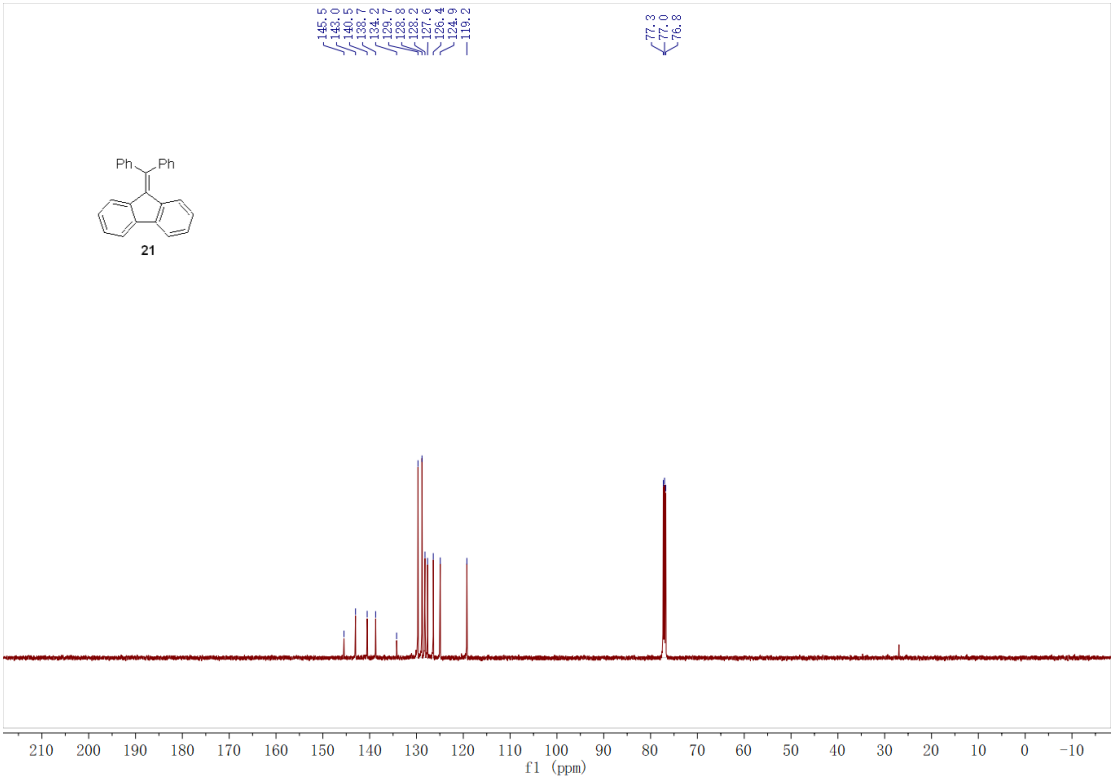
^{1}H and ^{13}C NMR spectra of compound 20.



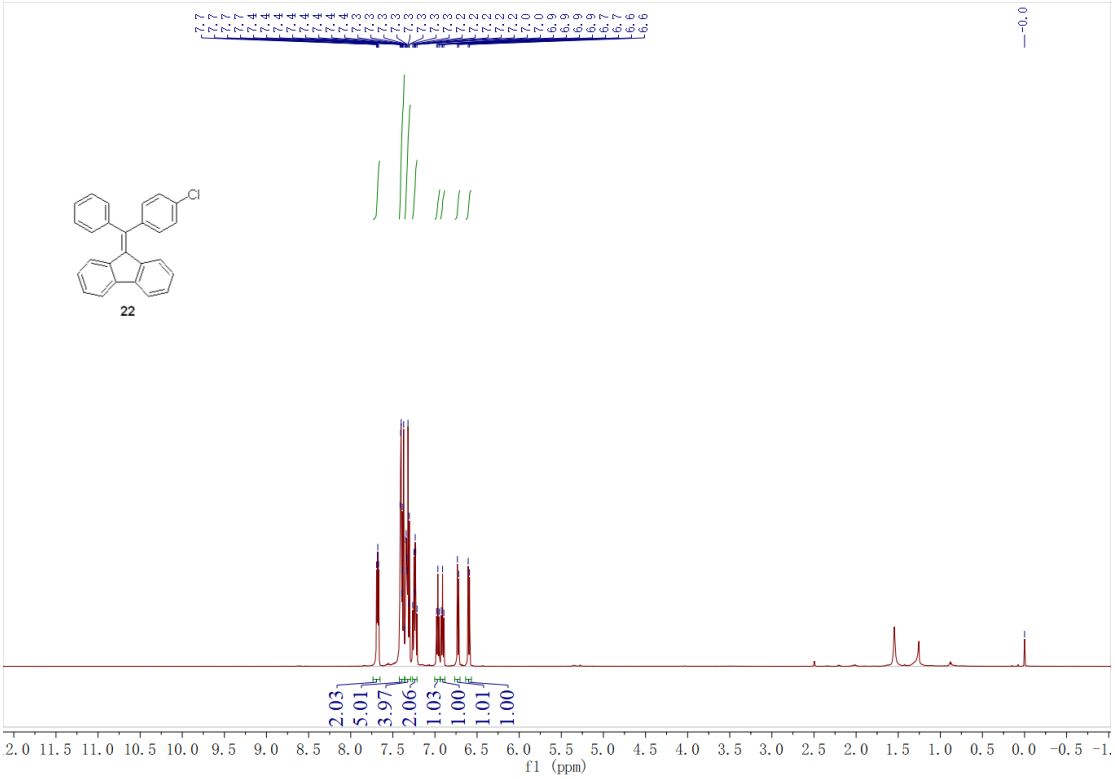


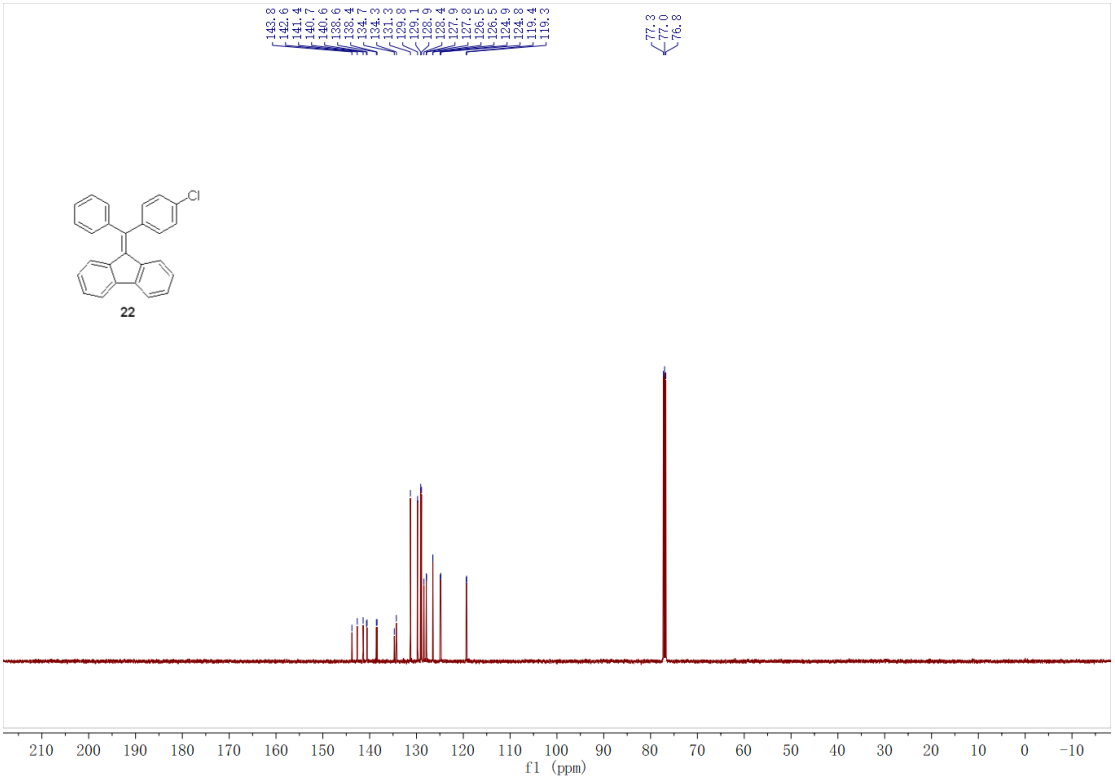
^{1}H and ^{13}C NMR spectra of compound 21.



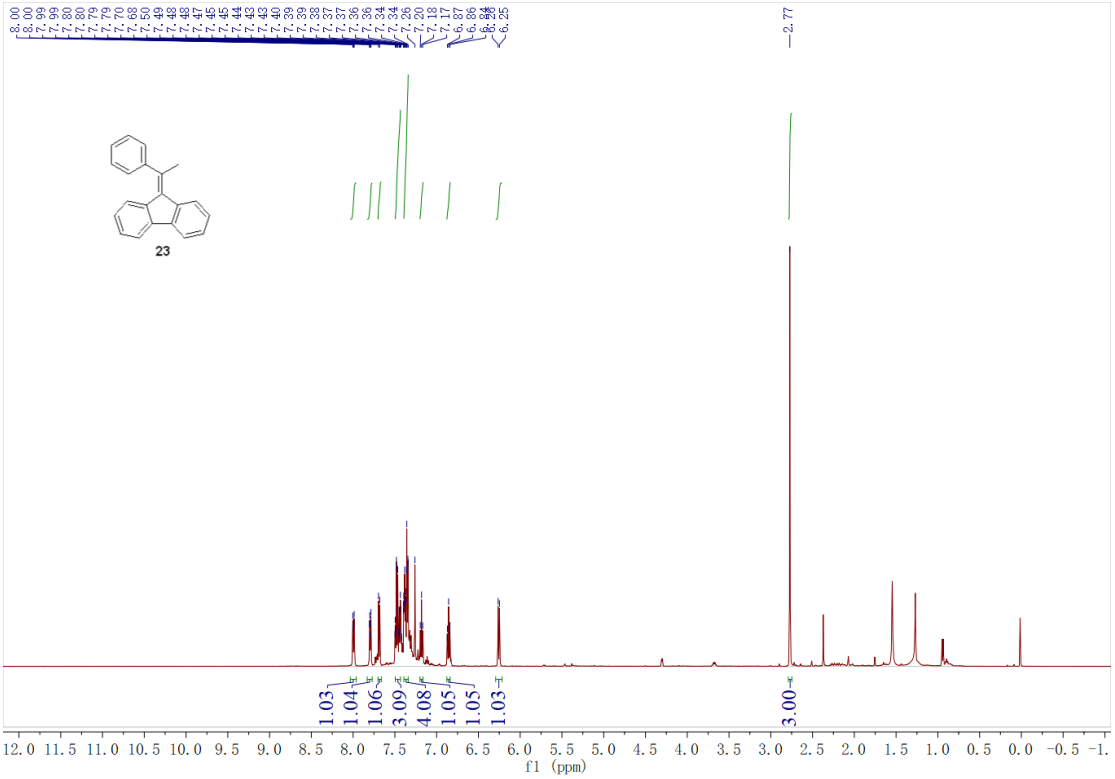


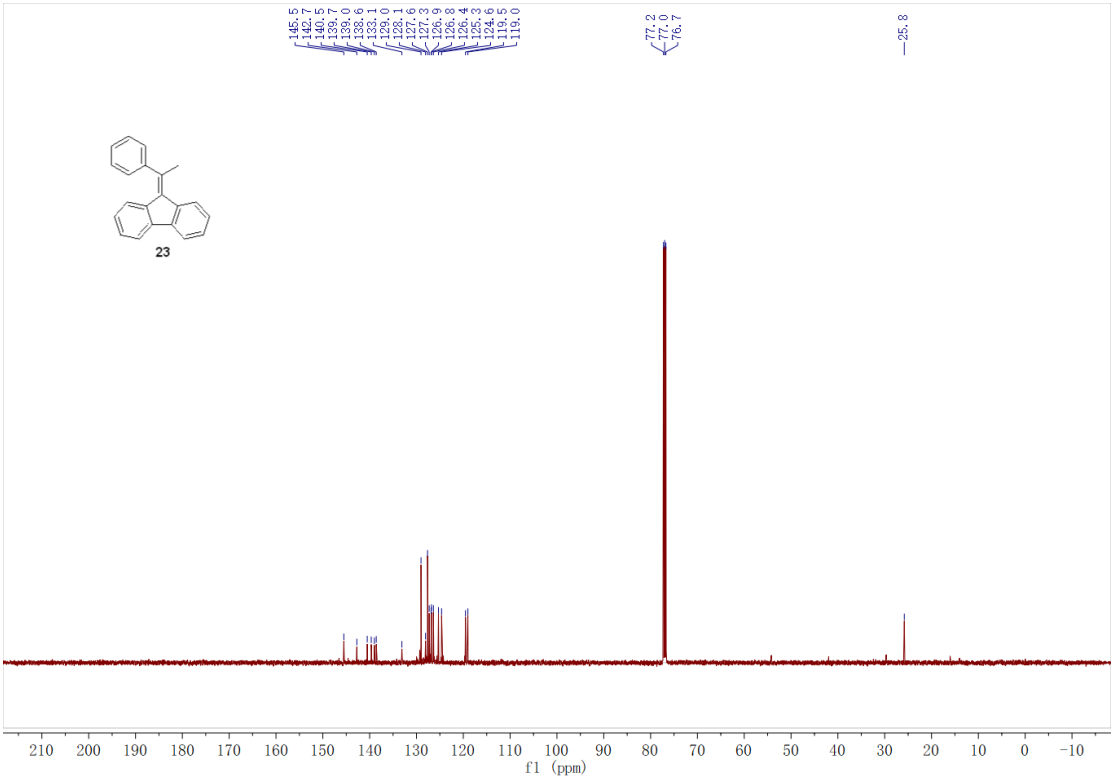
^{1}H and ^{13}C NMR spectra of compound 22.



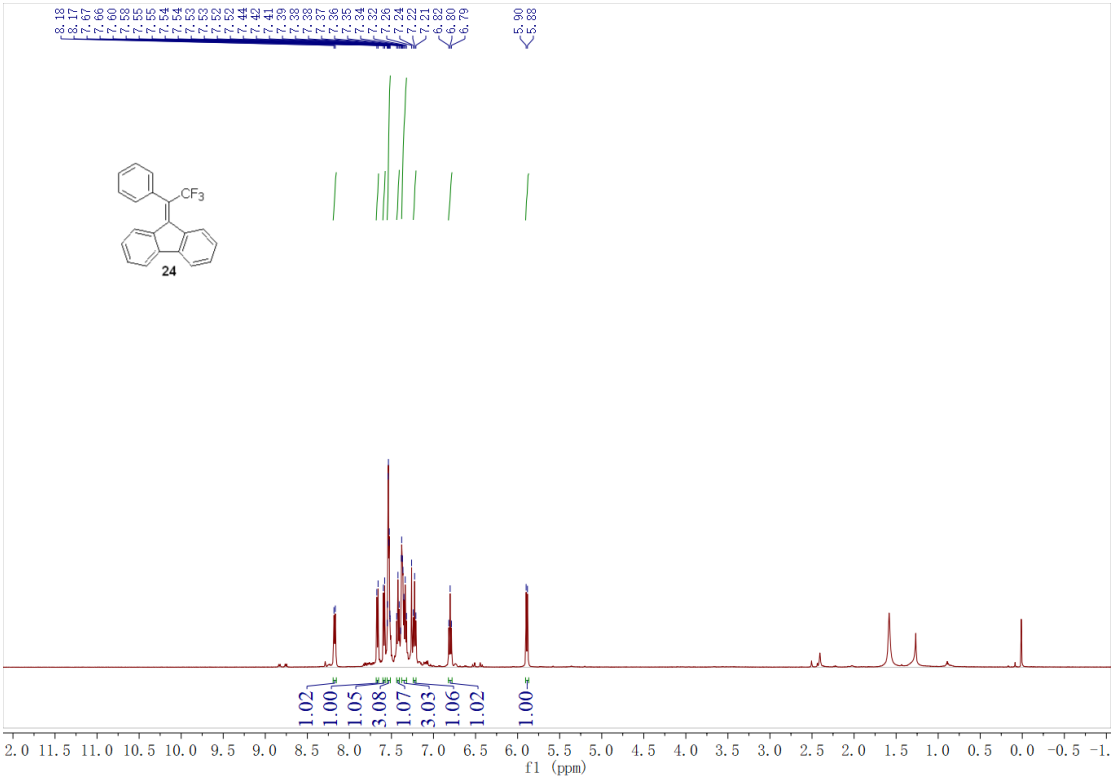


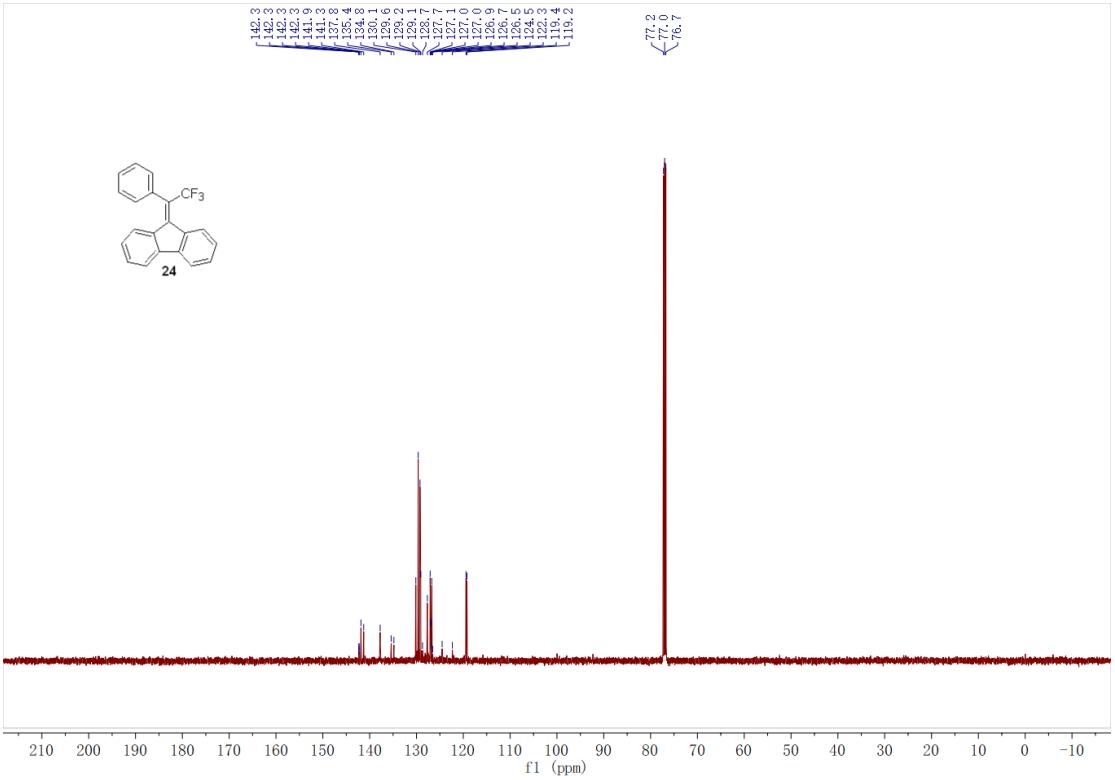
^{1}H and ^{13}C NMR spectra of compound 23.



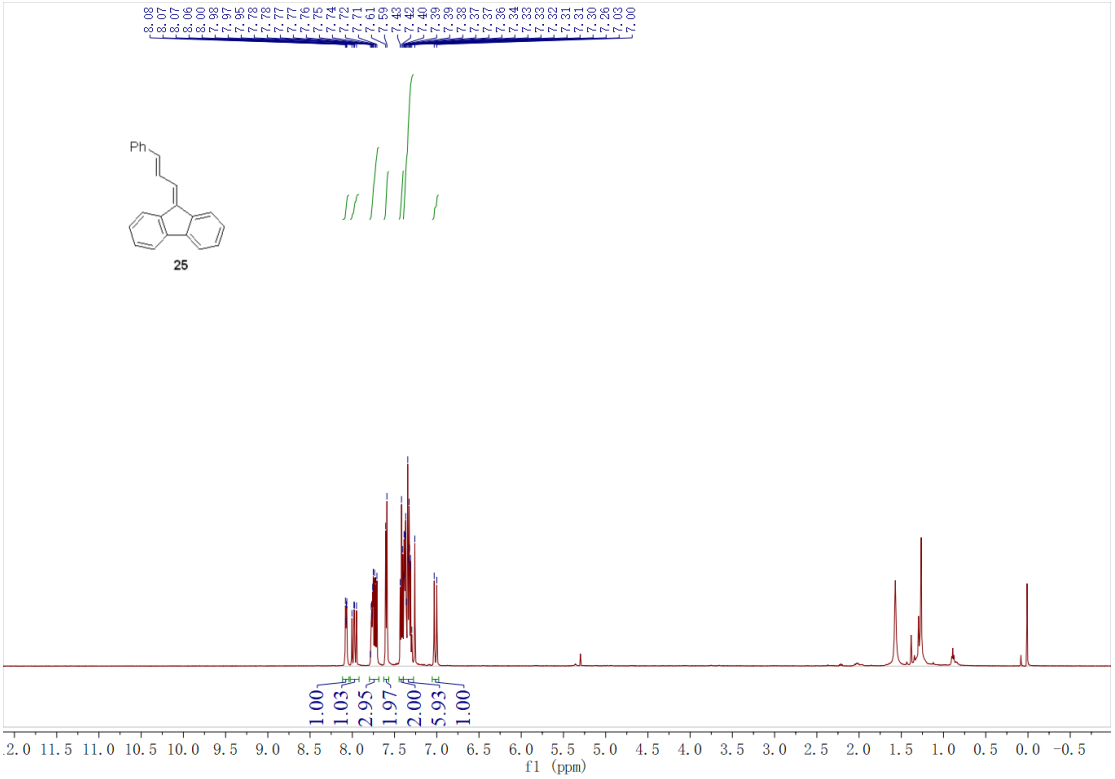


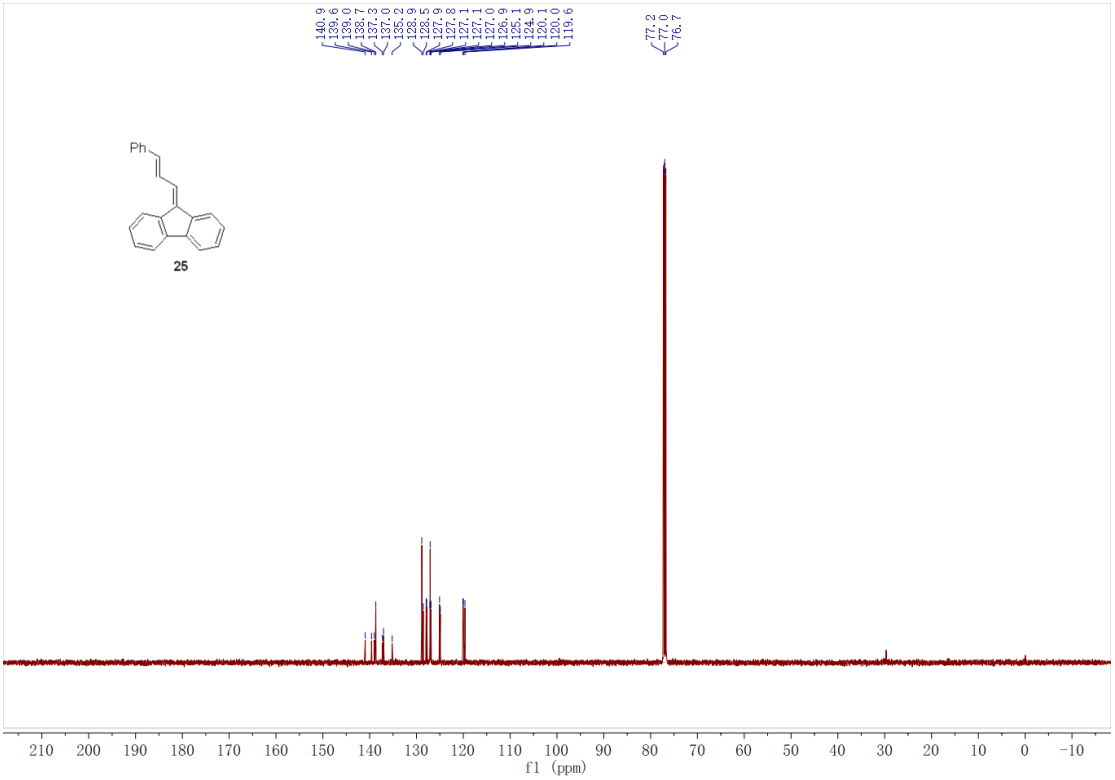
^{1}H and ^{13}C NMR spectra of compound 24.



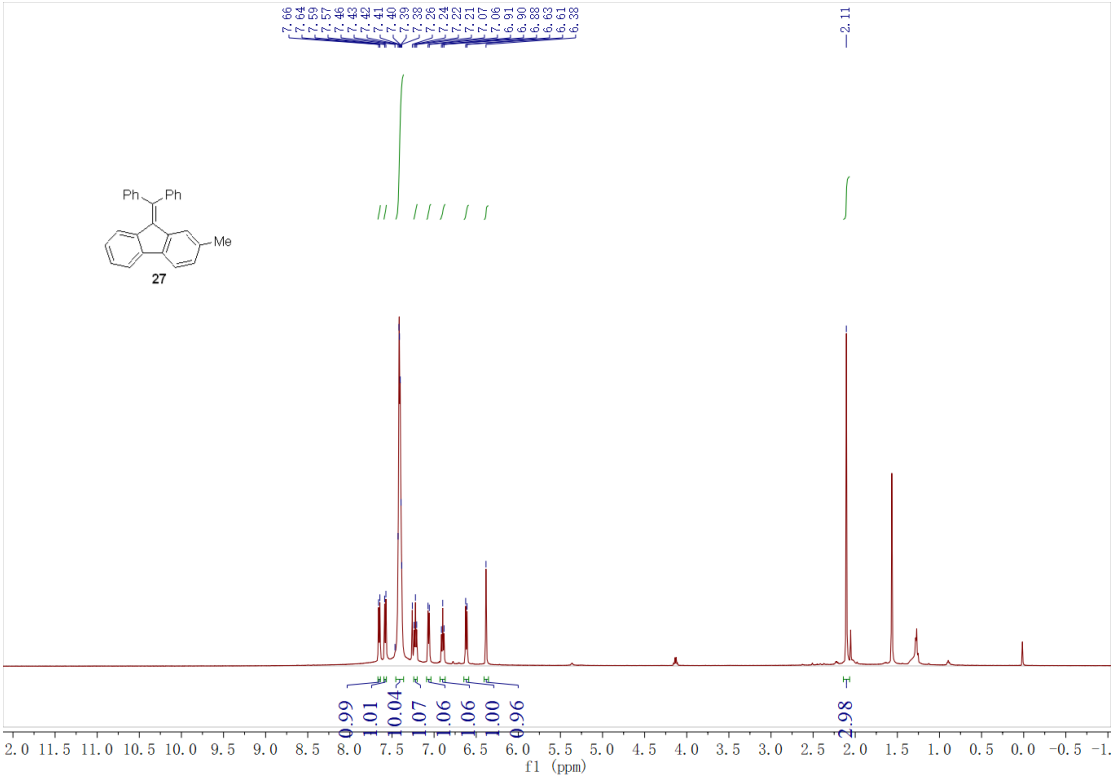


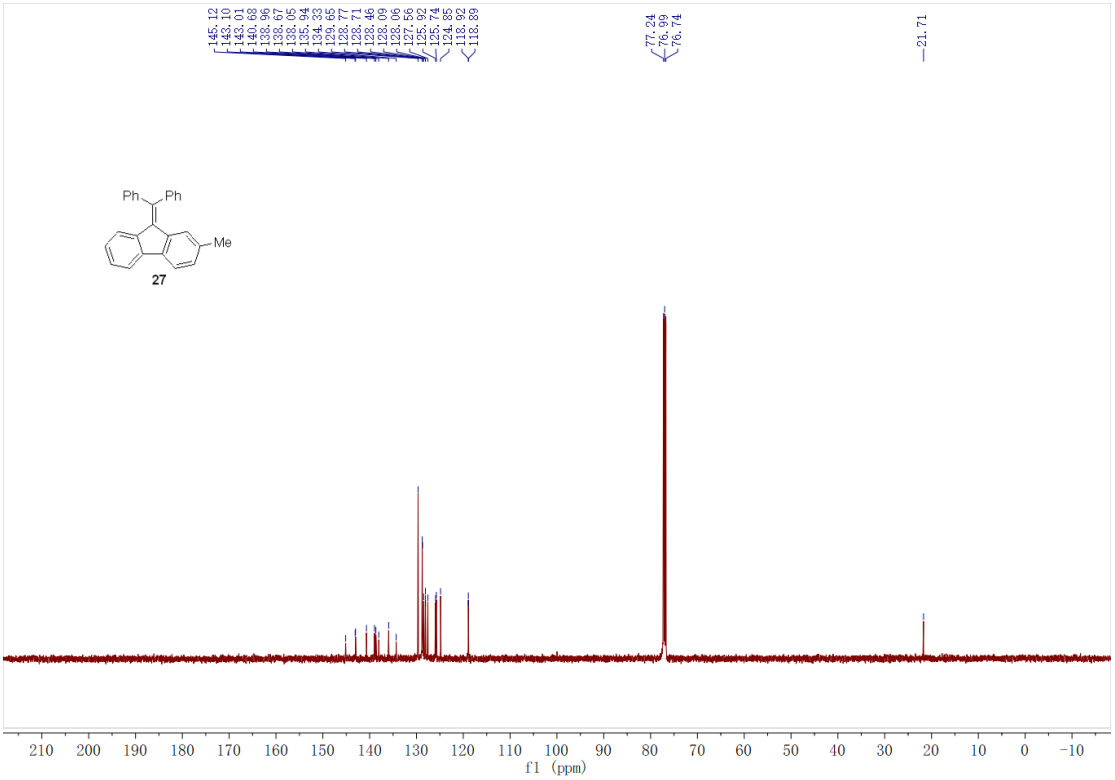
^{1}H and ^{13}C NMR spectra of compound 25.



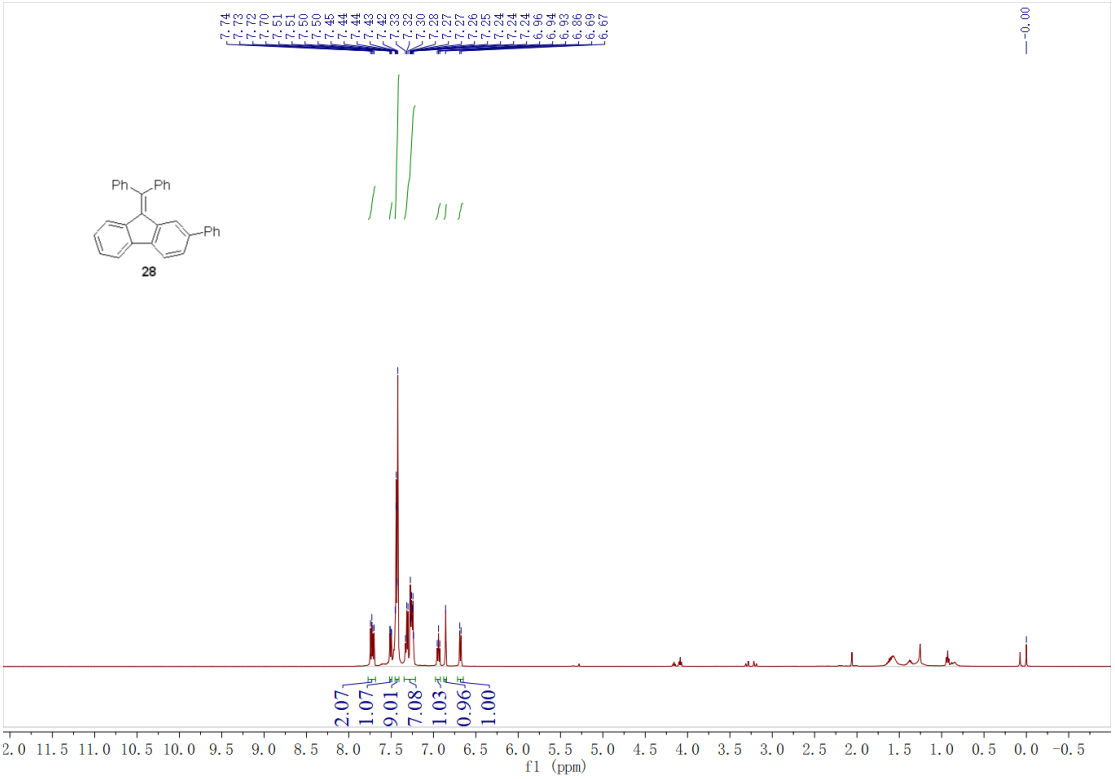


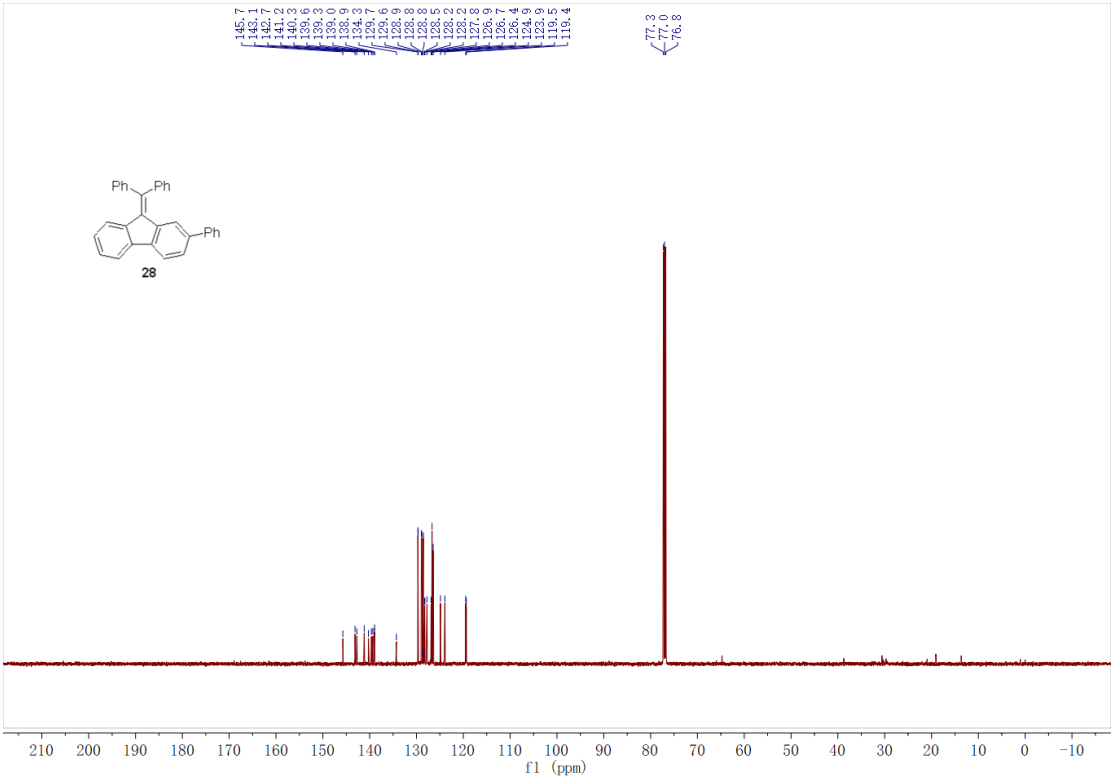
^{1}H and ^{13}C NMR spectra of compound 27.



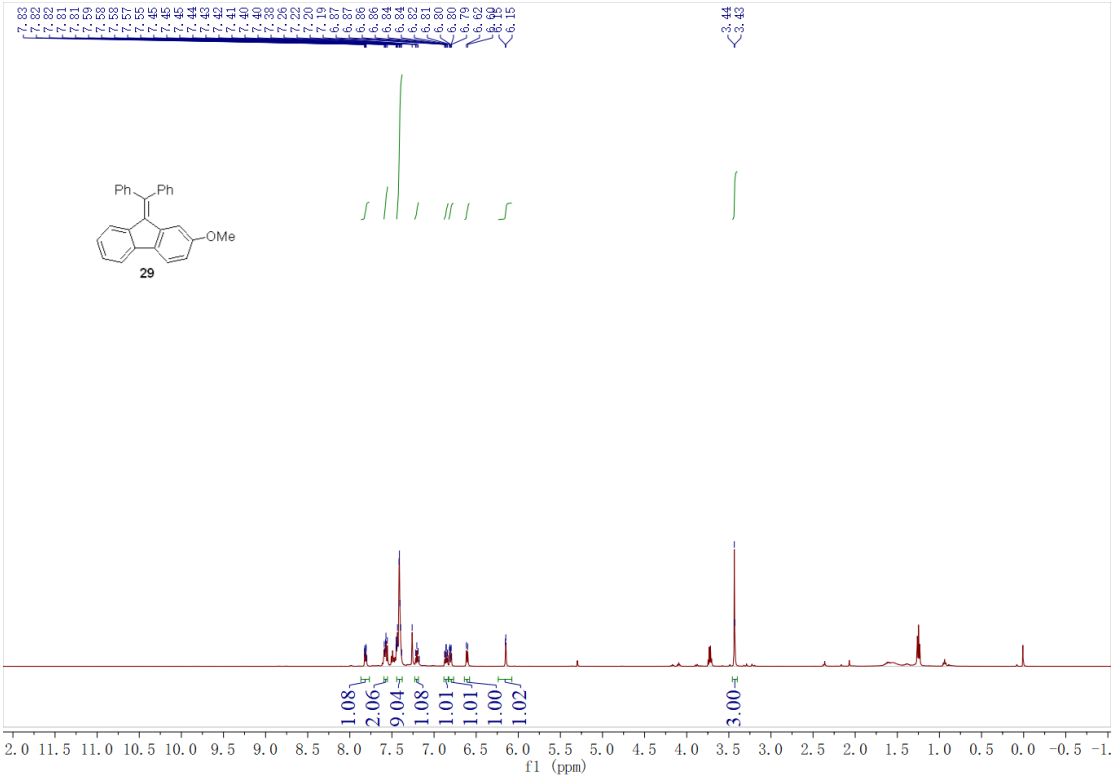


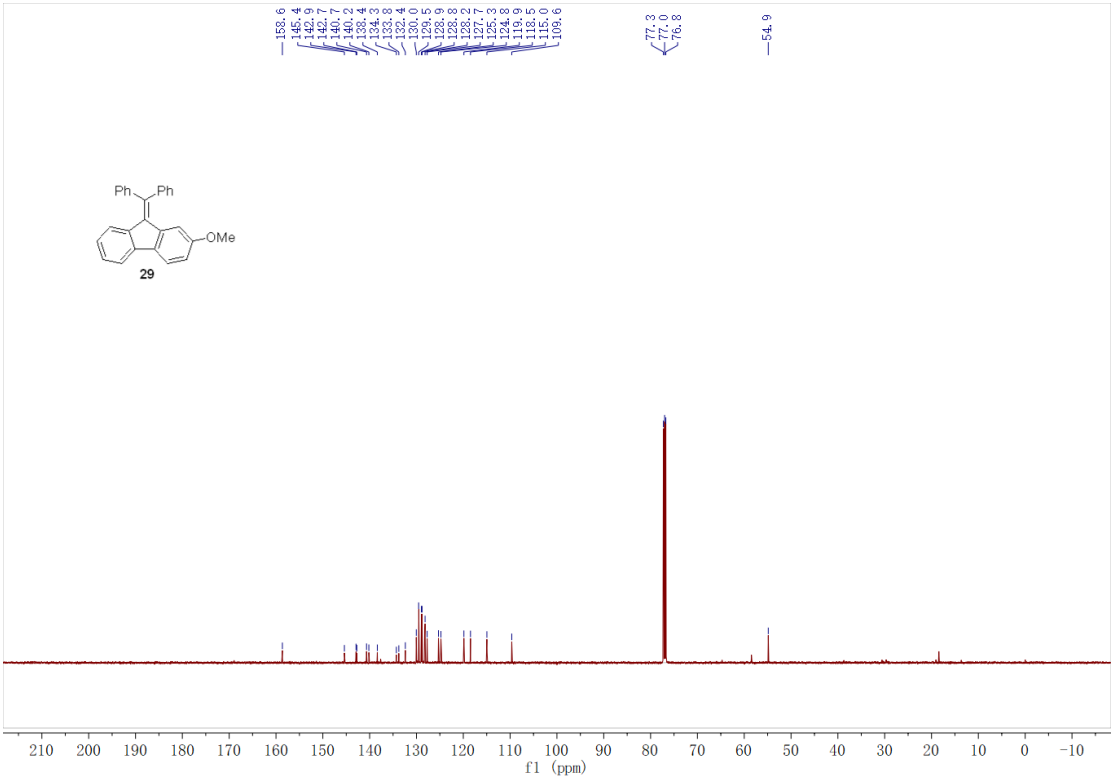
^{1}H and ^{13}C NMR spectra of compound 28.



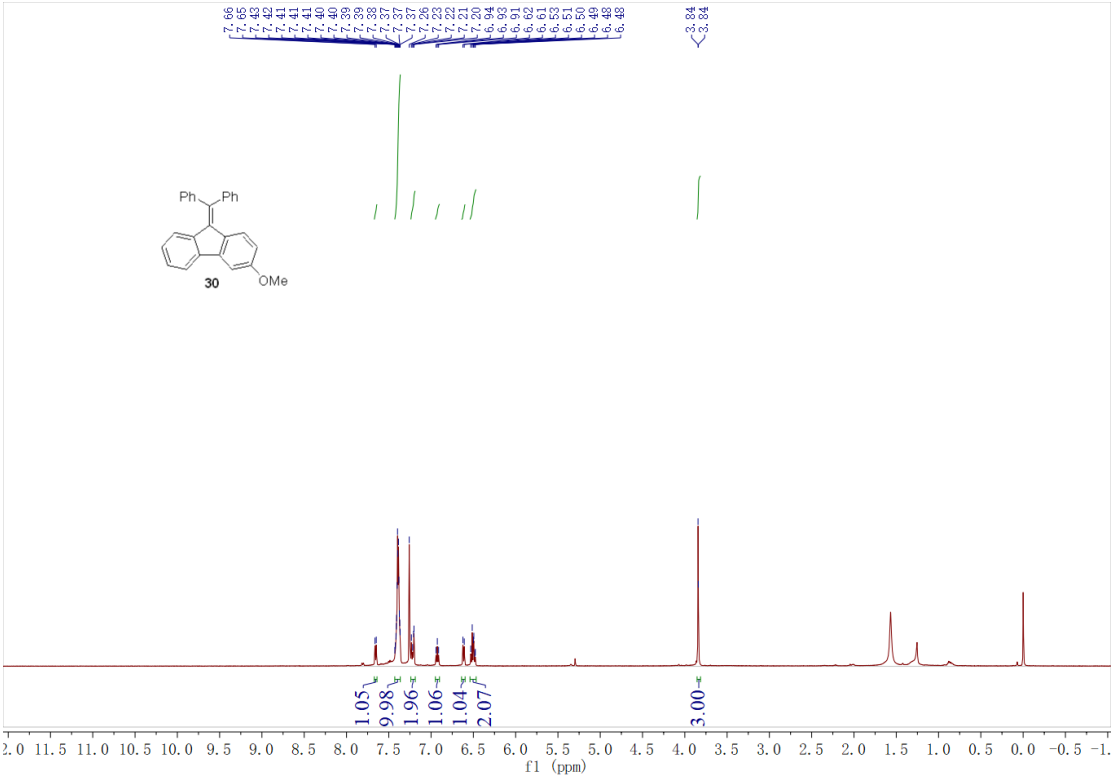


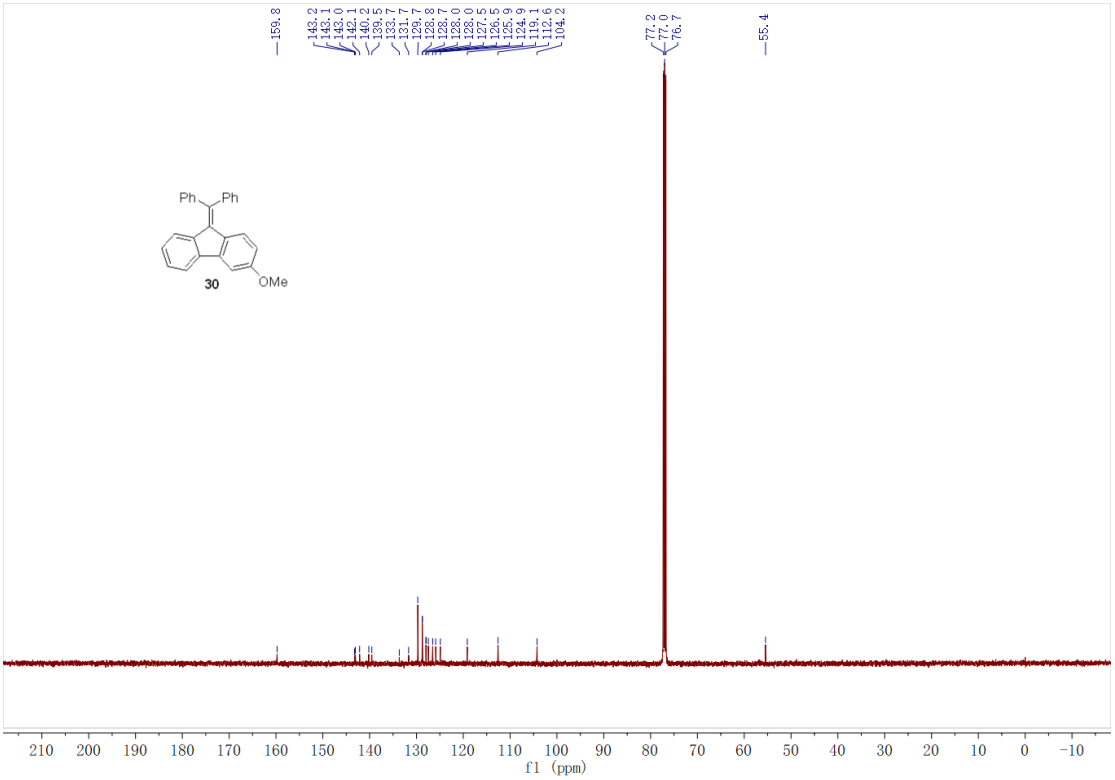
^{1}H and ^{13}C NMR spectra of compound 29.



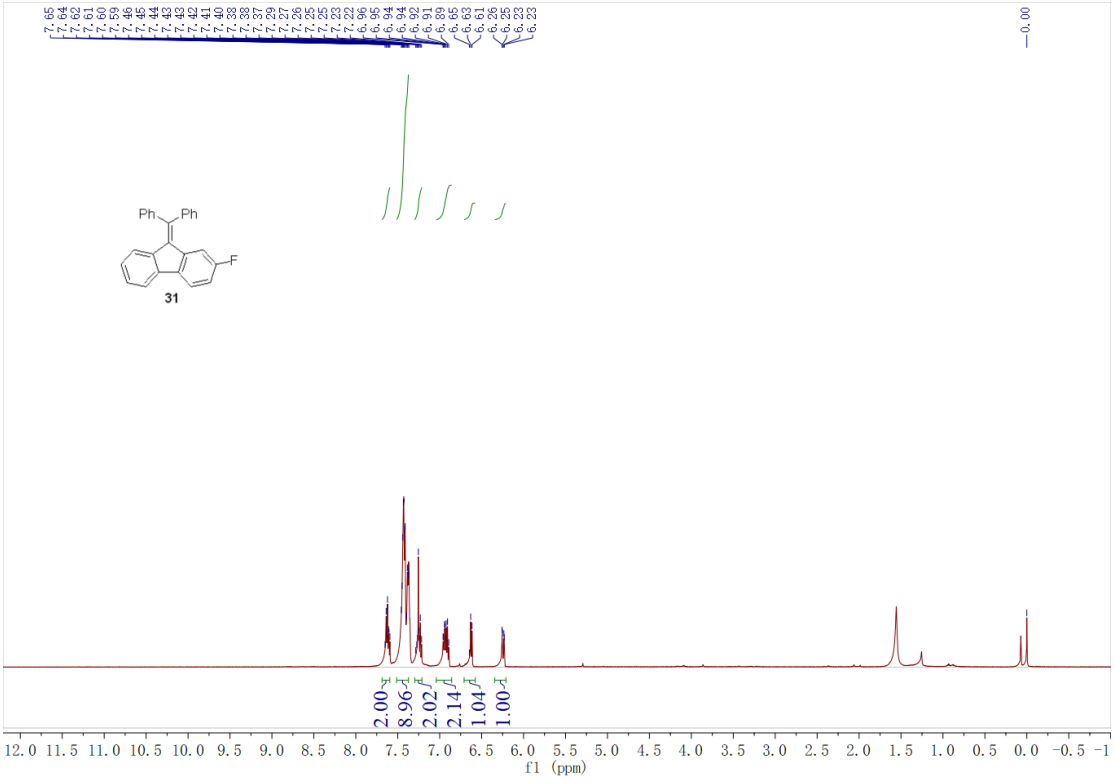


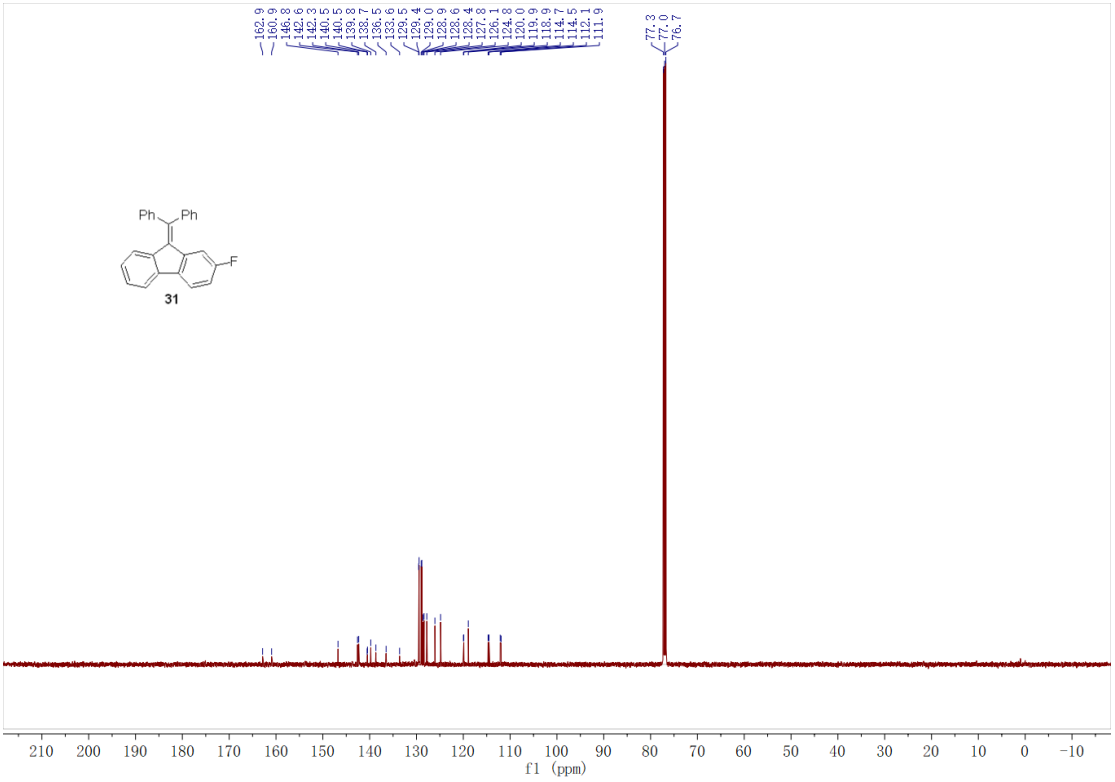
^{1}H and ^{13}C NMR spectra of compound 30.

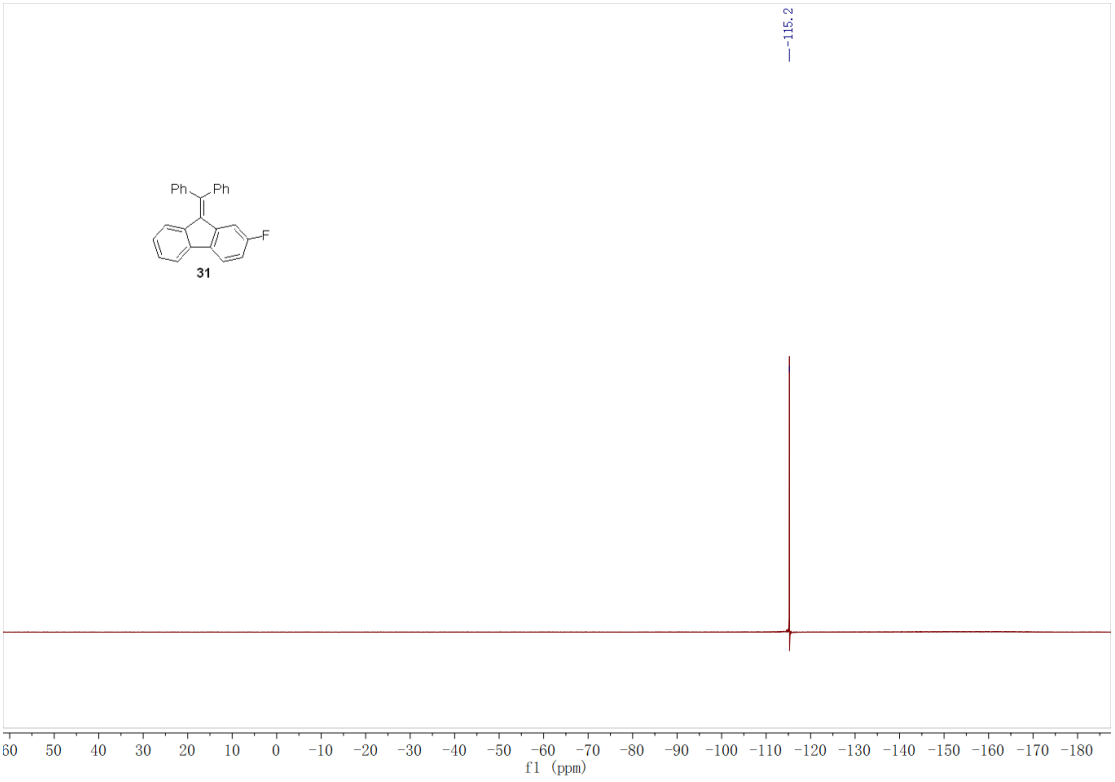




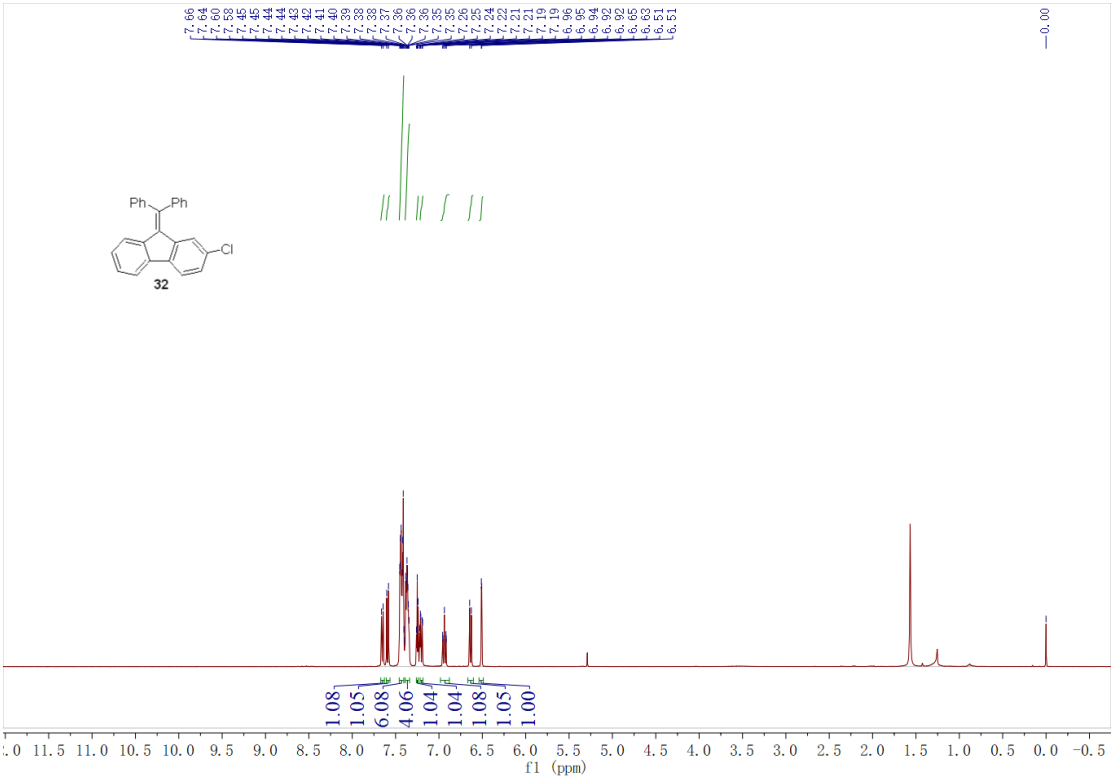
^{1}H,^{13}C and ^{19}F NMR spectra of compound 31.

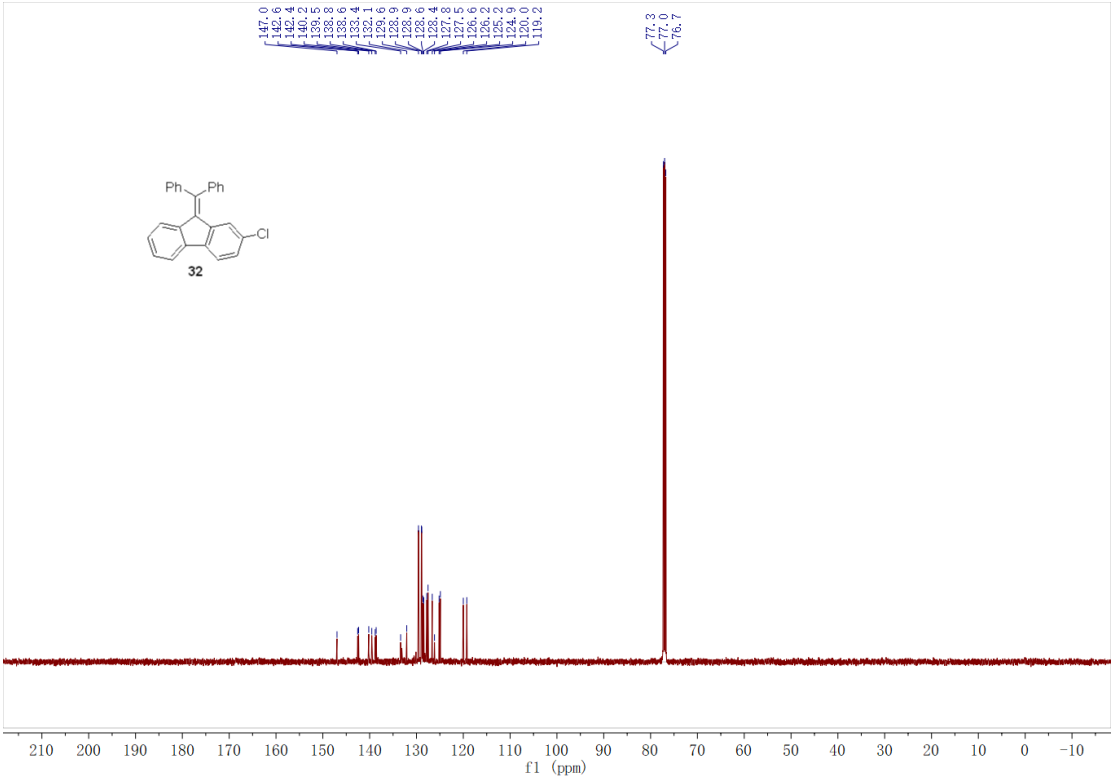



162.9
160.9
146.8
142.6
142.3
140.5
140.5
139.8
138.7
136.5
133.6
129.5
129.4
129.0
128.9
128.6
128.4
127.8
126.1
124.8
120.0
119.9
118.9
114.7
114.5
112.1
111.9
77.3
77.0
76.7
Ph
Ph
F
31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

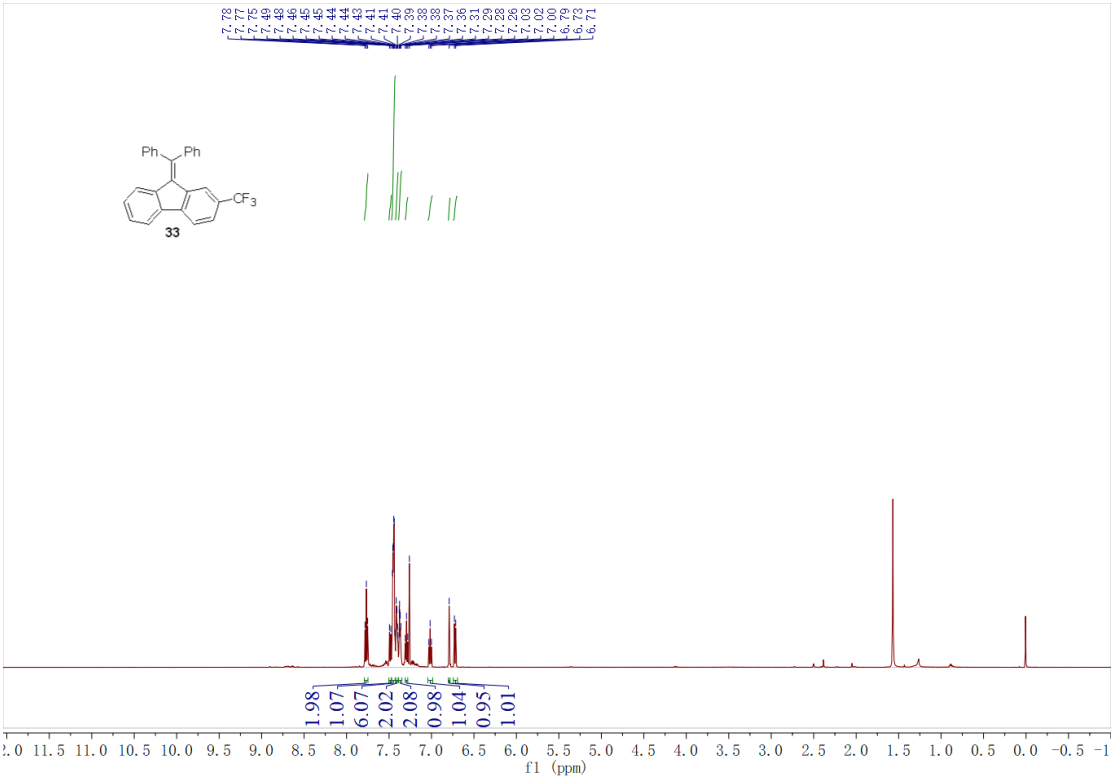

-115.2
Ph
Ph
F
31
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

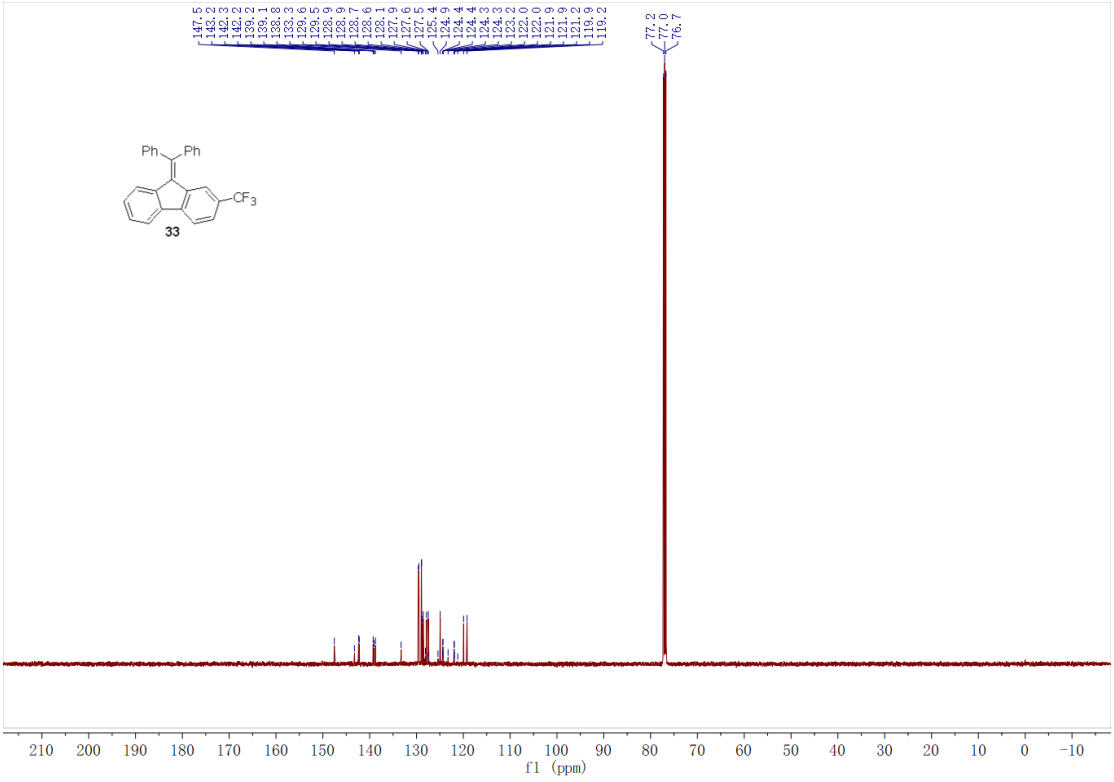
^{1}H and ^{13}C NMR spectra of compound 32.

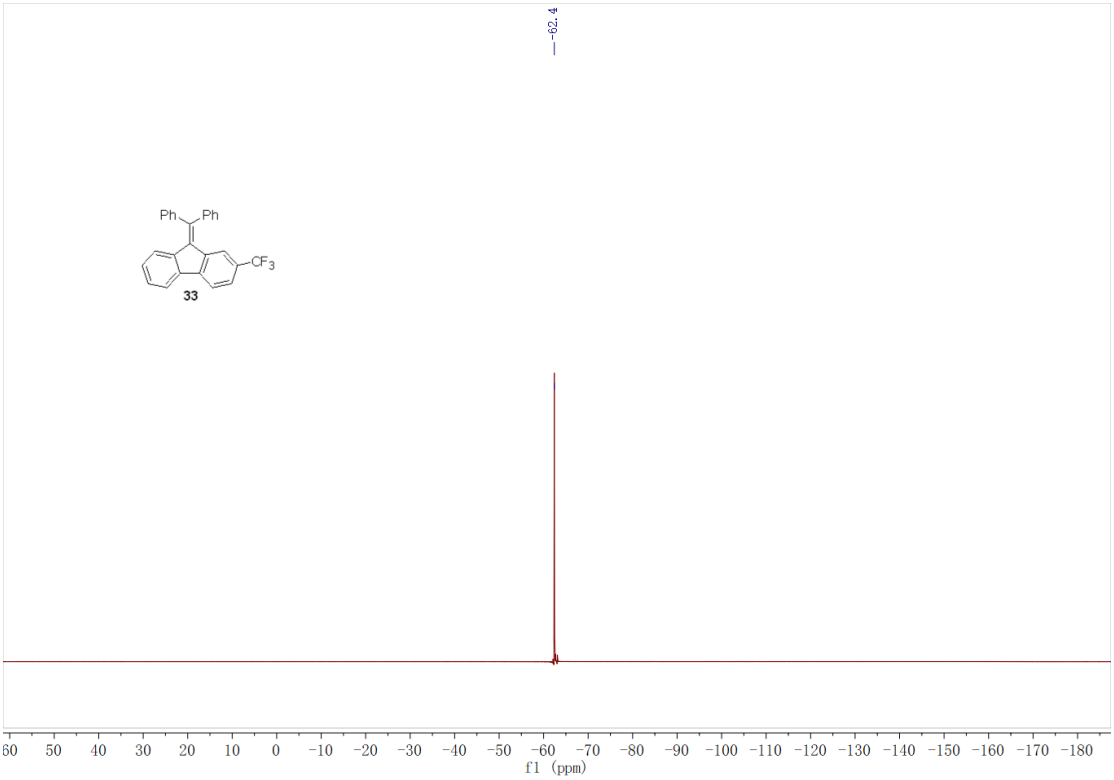




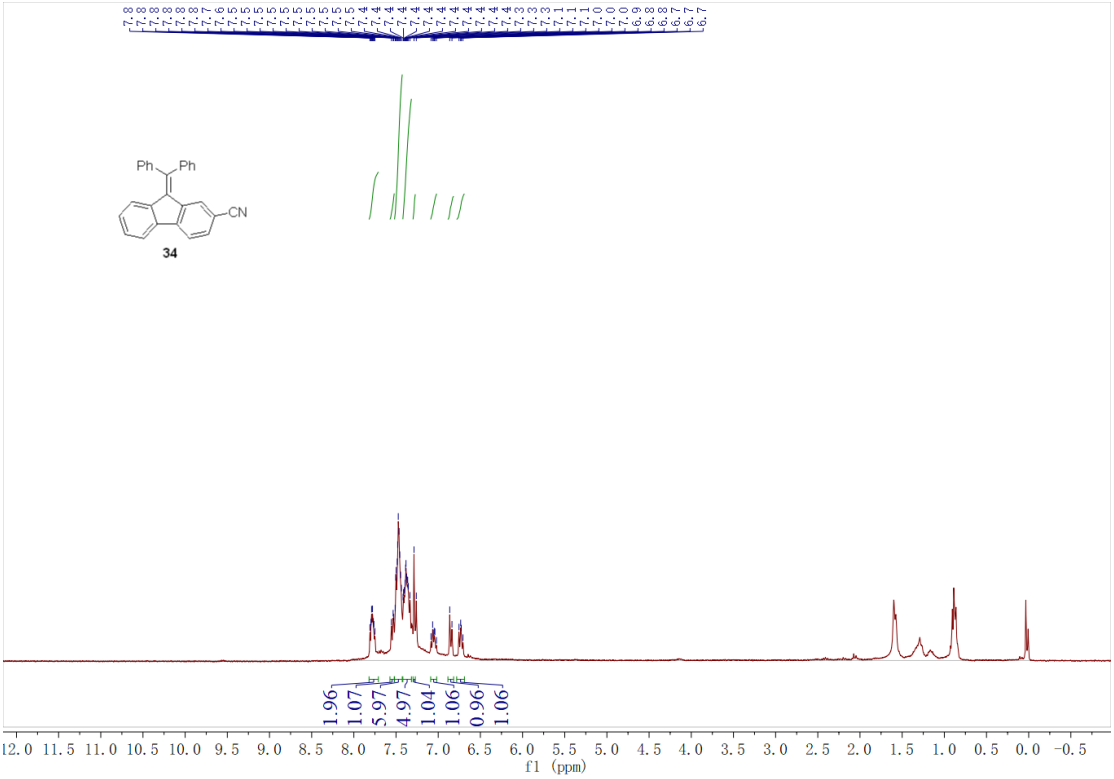
^{1}H,^{13}C and^{19}F NMR spectra of compound 33.

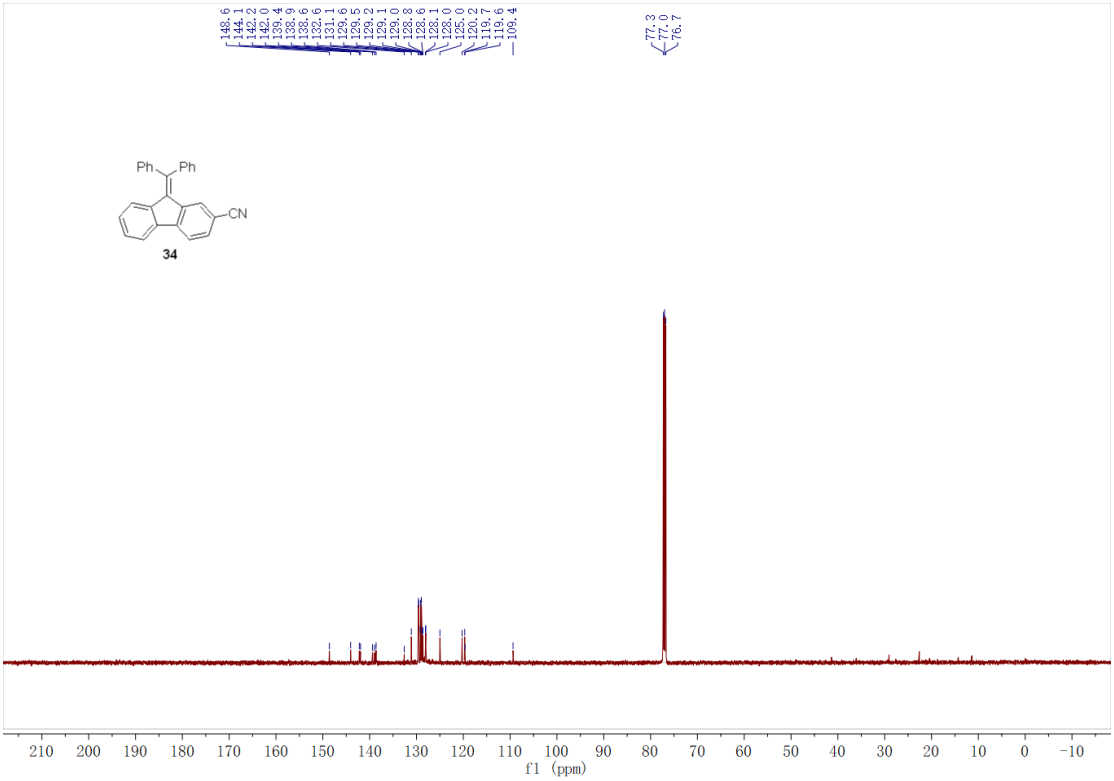




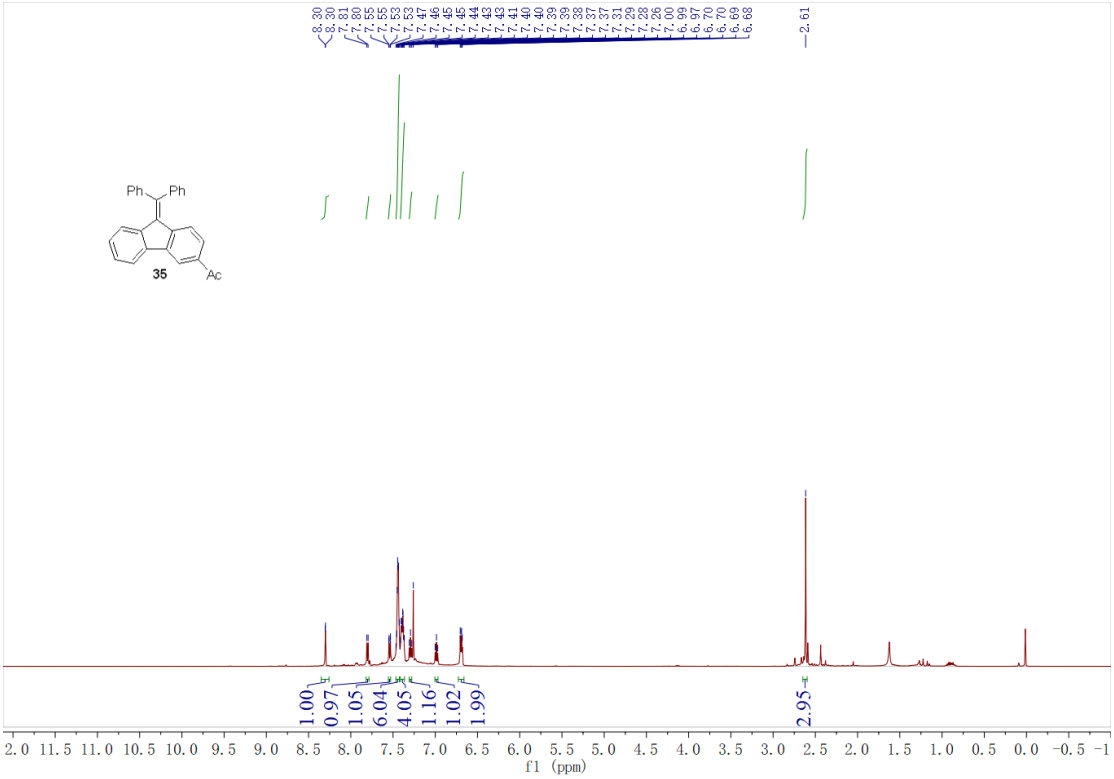


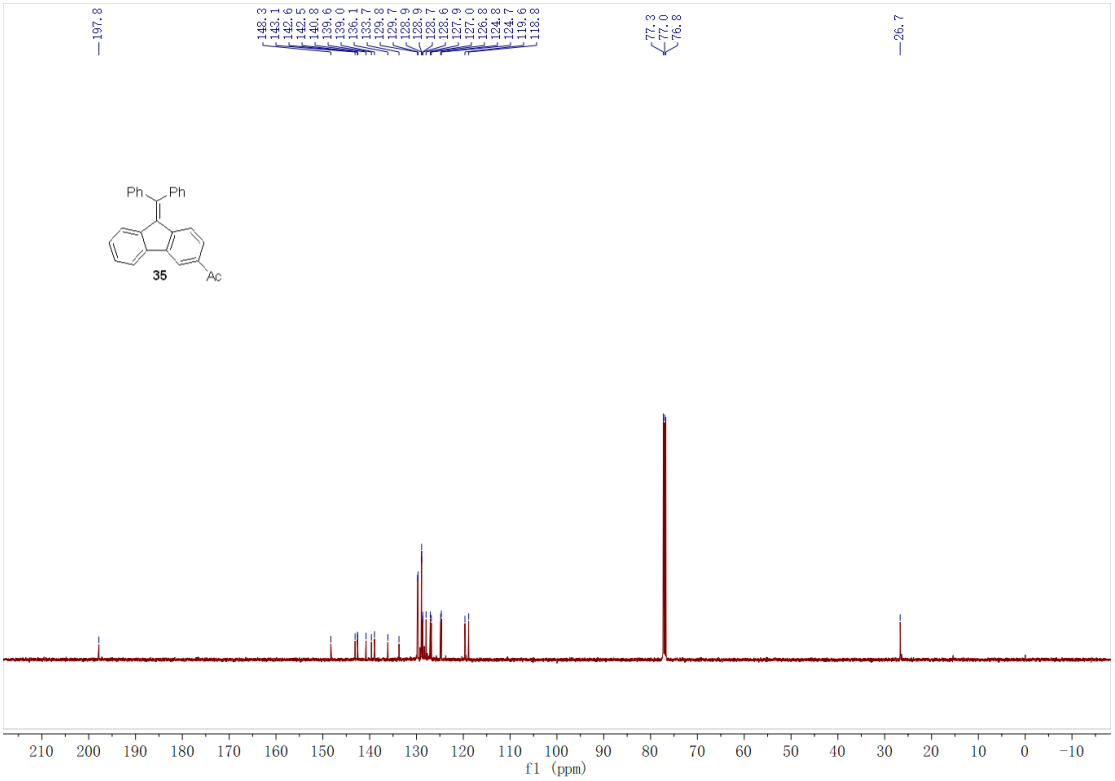
^{1}H and ^{13}C NMR spectra of compound 34.



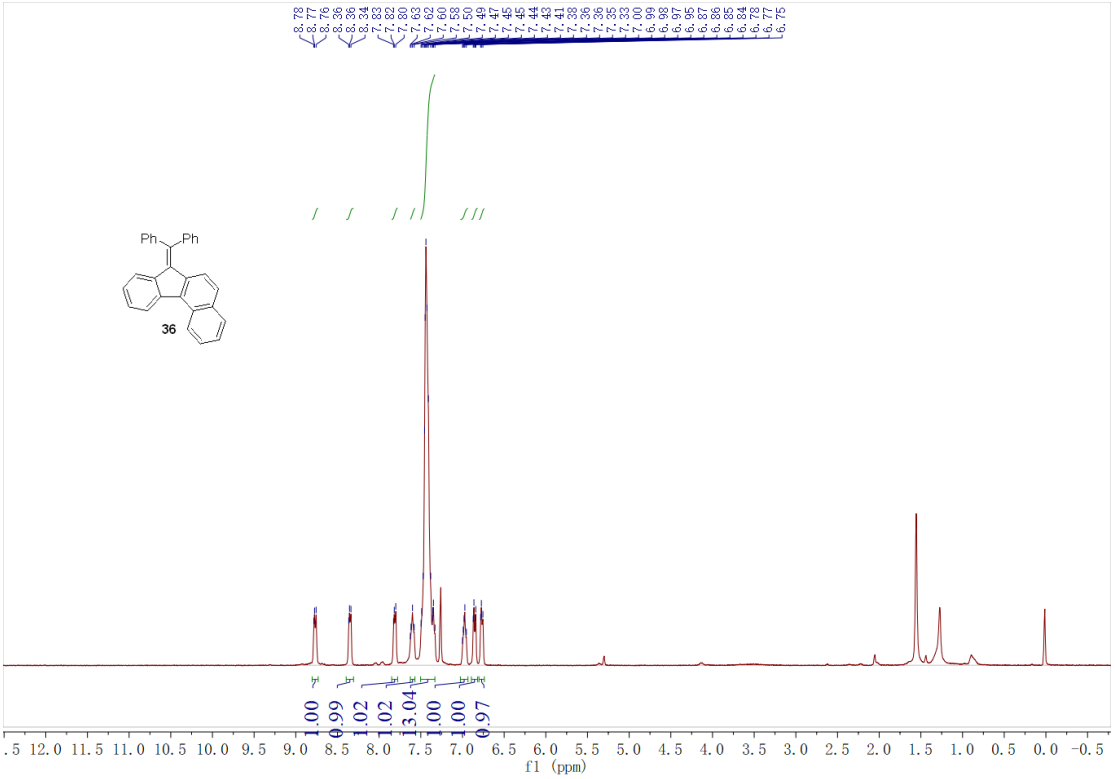


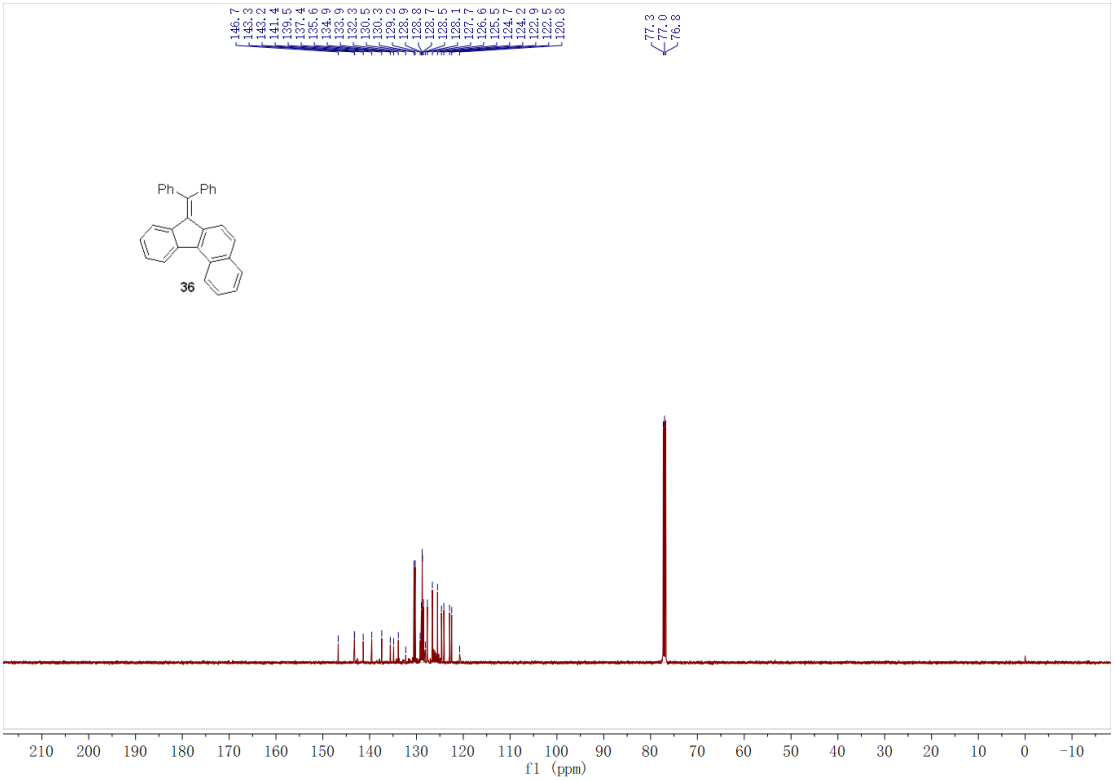
^{1}H and ^{13}C NMR spectra of compound 35.



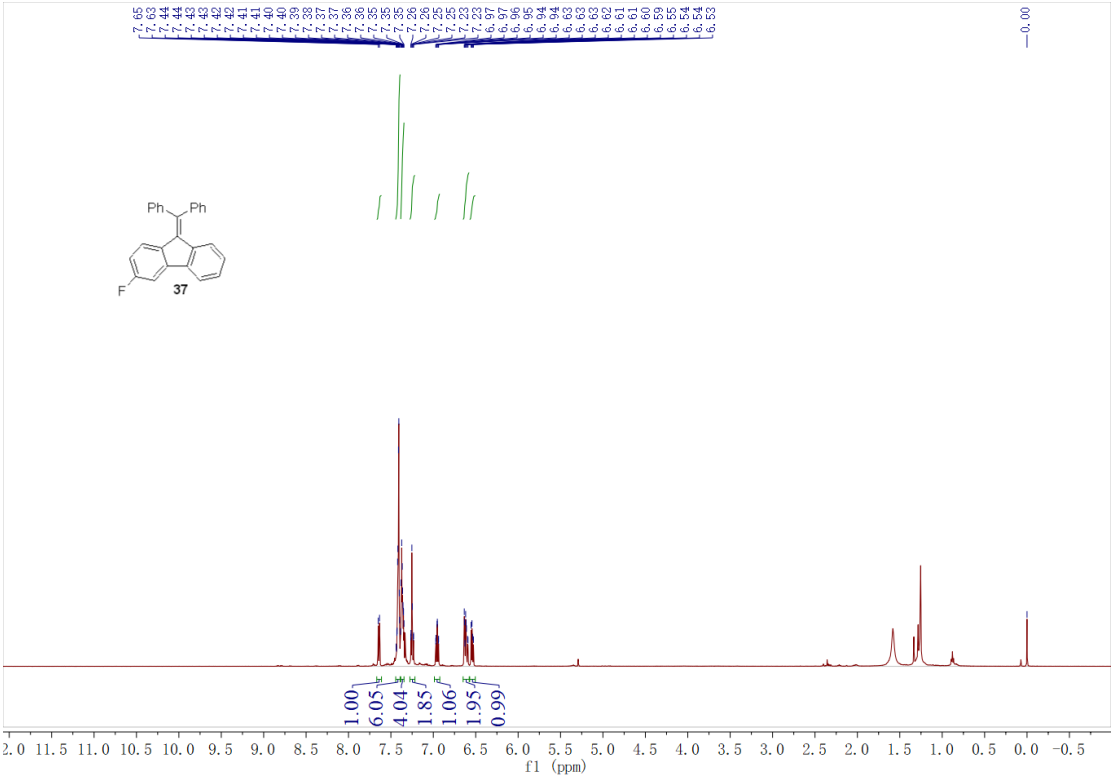


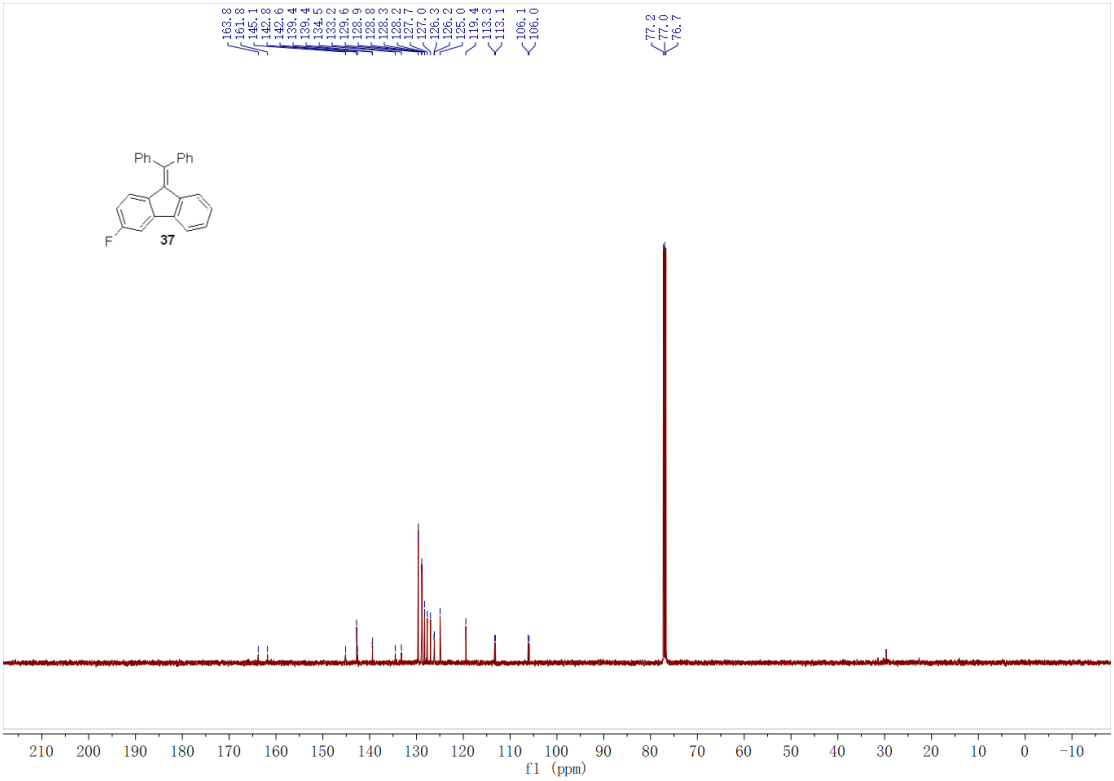
^{1}H and ^{13}C NMR spectra of compound 36.

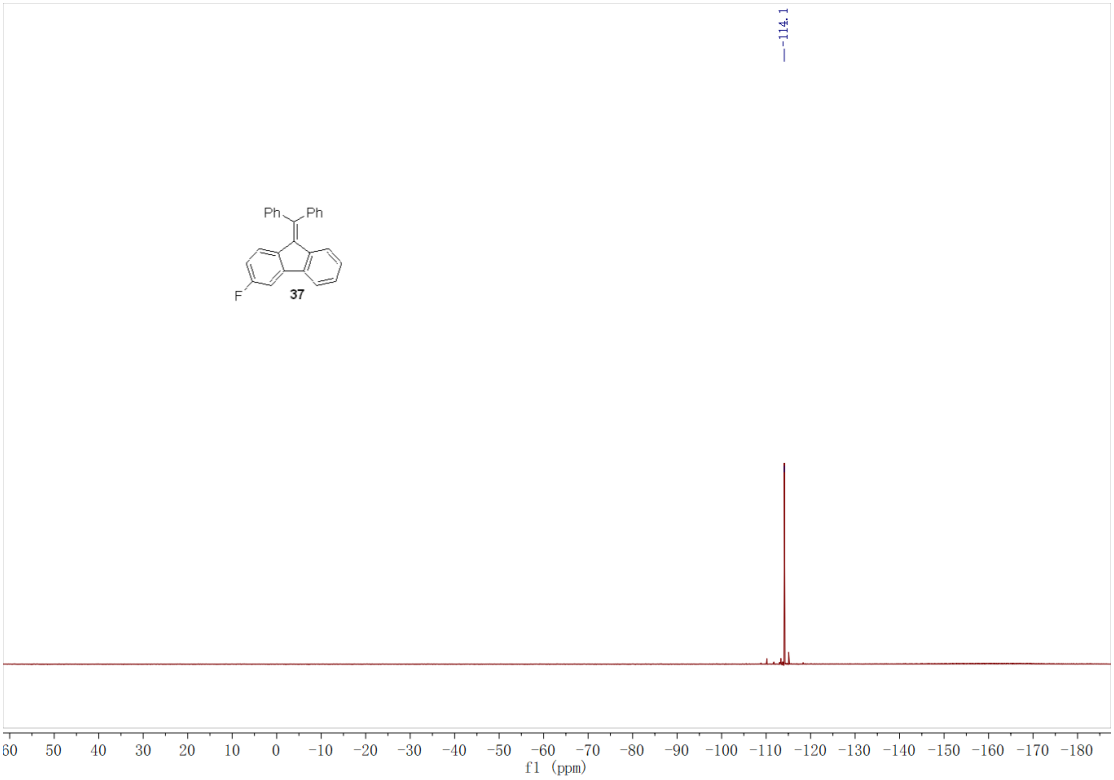




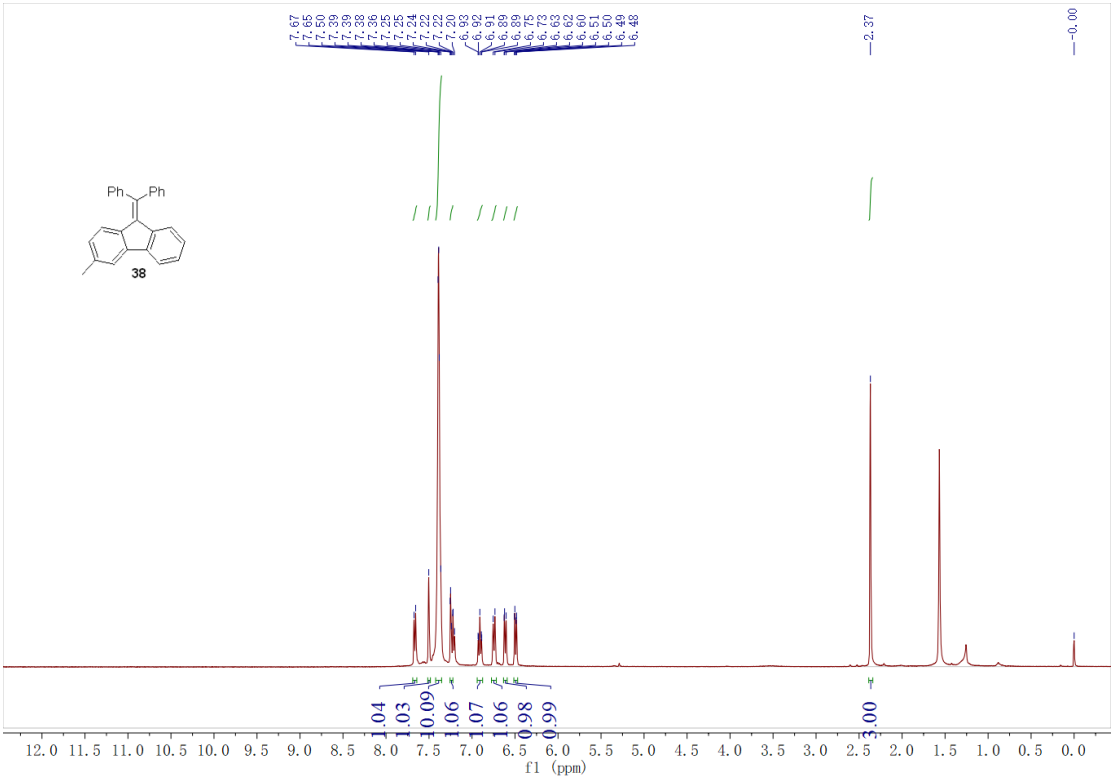
^{1}H,^{13}C and ^{19}F NMR spectra of compound 37.

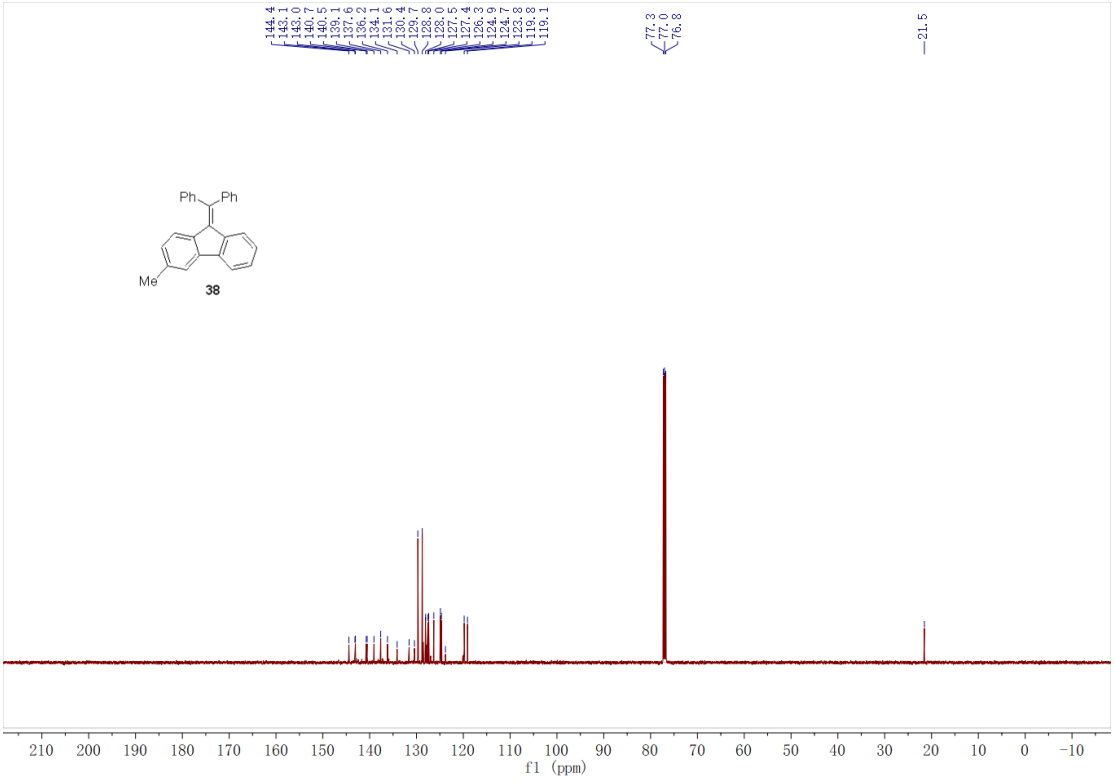



163.8
161.8
145.1
142.8
142.6
139.4
139.4
134.5
133.2
129.6
128.9
128.8
128.3
128.2
127.7
127.0
126.3
126.2
125.0
119.4
113.3
113.1
106.1
106.0
77.2
77.0
76.7
Ph
Ph
F
37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

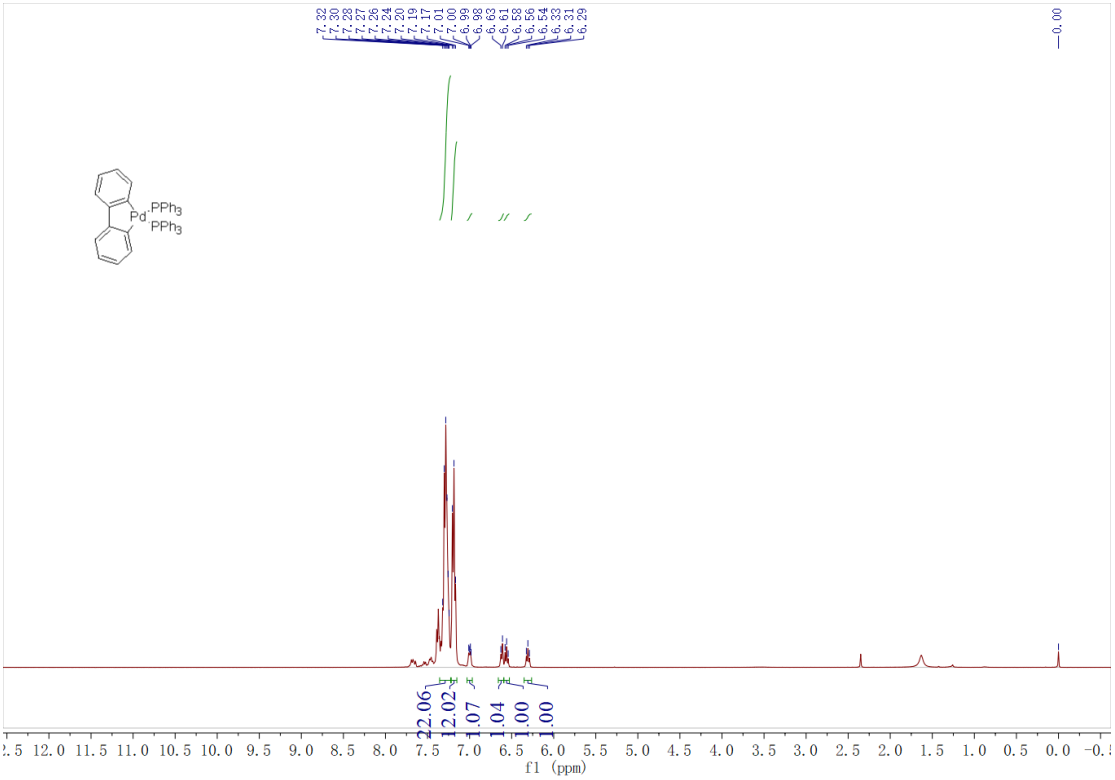

-114.1
Ph
Ph
F
37
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

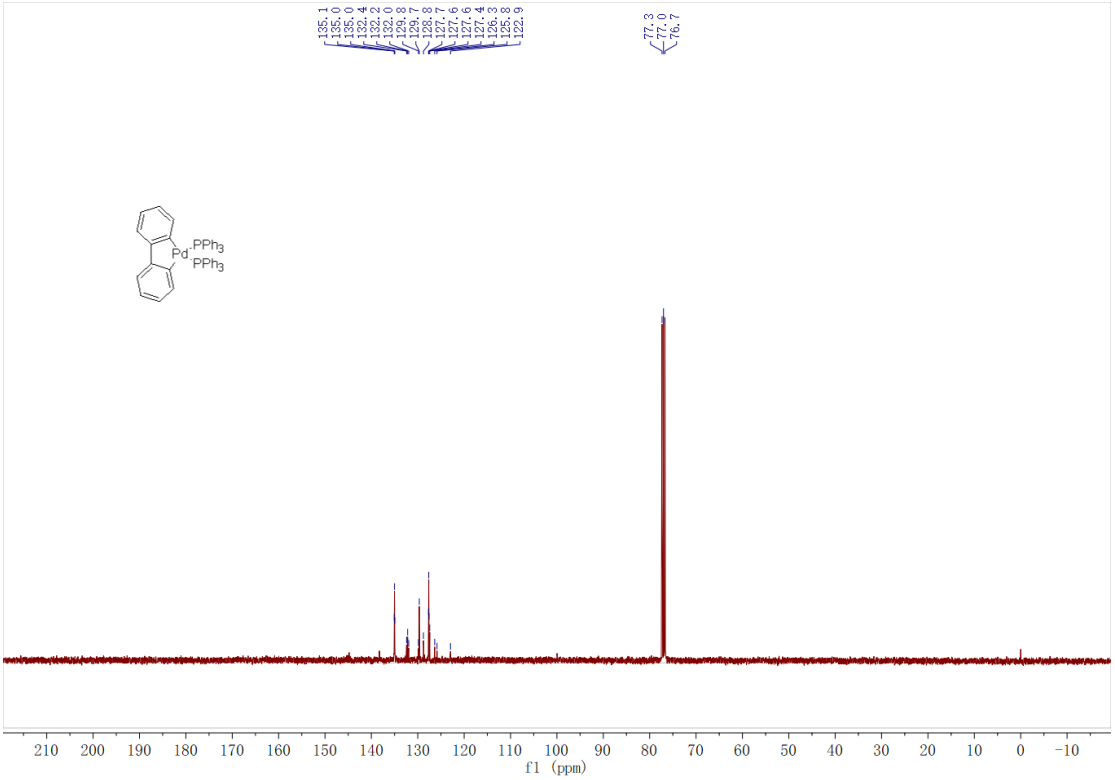
^{1}H and ^{13}C NMR spectra of compound 38.

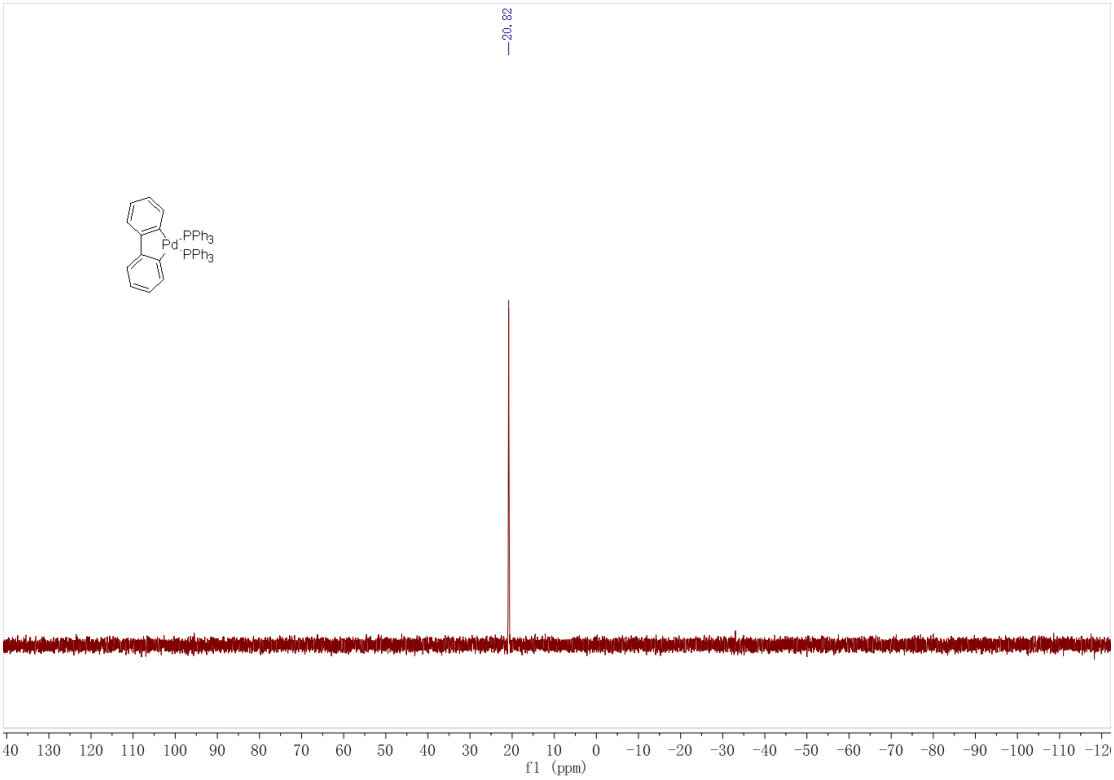




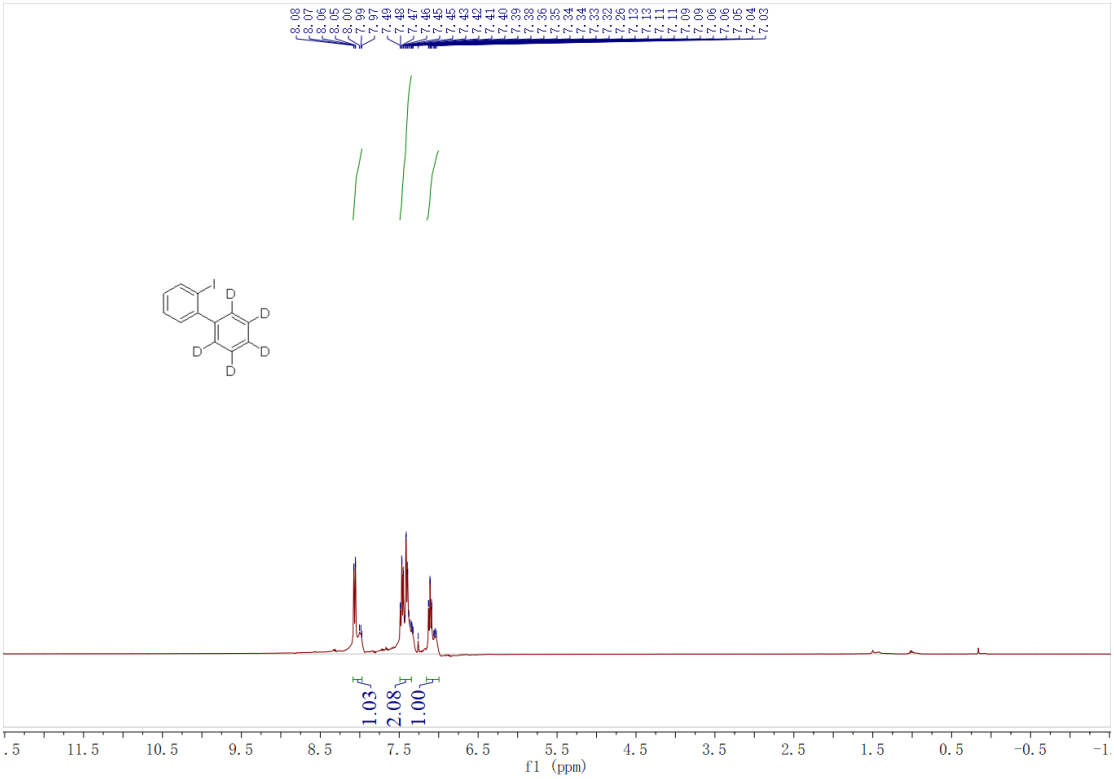
^{1}H, ^{13}C and ^{31}P NMR spectra of compound 39.







^{1}H NMR spectra of compound 1-*d*.



^{1}H NMR spectra of compound 2-*d*.