Electronic Supplementary Material (ESI) for ChemComm.

Rapid Access to 9-Arylfluorene and Spirobifluorene through Pd-catalysed C-H Arylation/Deaminative Annulation

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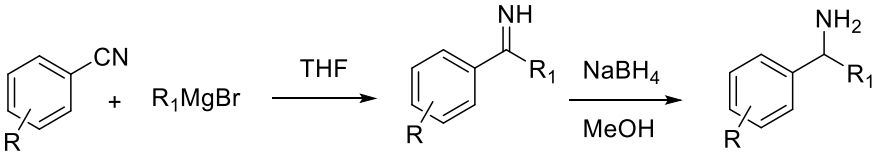
I. General

Unless otherwise stated, all experiments were carried out under air atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker AVANCE III 600/500 instrument in $CDCl_3$ using TMS as an internal standard, operating at 600/500 MHz and 126/101 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For $CDCl_3$, the chemical shifts are reported as parts per million (ppm) to residual protium or carbon of the solvents; $CHCl_3$ δH (7.28 ppm) and $CDCl_3$ δC (77.03 ppm). ^{19}F NMR were recorded on a Bruker AVANCE III or Ascend400. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, br = broad resonance. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with a Thermo DSQ II, Trace GC Ultra. High resolution mass spectra [HRMS (ESI-TOF)] were obtained on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source.

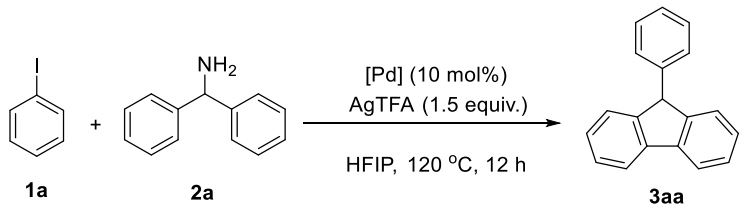
II. Preparation of starting materials



In an oven-dried round flask under Ar atmosphere, a mixture of the aryl nitrile (1 mmol) and the Grignard reagent (1.2 mmol) was stirred in dry THF (10 mL) at 70 ℃ for 2-8 h. The reaction mixture was cooled to room temperature and quenched by dry MeOH (10 mL) at 0 ℃. After being stirred vigorously for 10 min, the sodium borohydride was added slowly and the mixture was heated at 60 ℃ until the imine was disappeared (determined by TLC). The volatile materials were evaporated under vacuum and the residue was purified by flash column chromatography.[1, 2]

III. Optimization of the conditions

Table S1. Screening of catalysts[a]

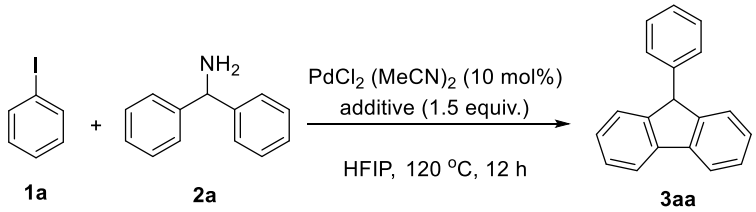


Entry	[Pd]	Yield of 3aa (%)
1	**$PdCl_2(MeCN)_2$**	**75**
2	$Pd(PPh_3)_4$	35

3	$PdCl_2$	55
4	$Pd(dba)_2$	62
5	$Pd(dppf)Cl_2$	35
6	$Pd(PCy_3)Cl_2$	46
7	$Pd(PPh_3)_2Cl_2$	69
8	$Pd(OAc)_2$	61
9	--	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.), [Pd] (10 mol%), AgTFA (1.5 equiv.), HFIP (1.0 mL), 120 °C for 12 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

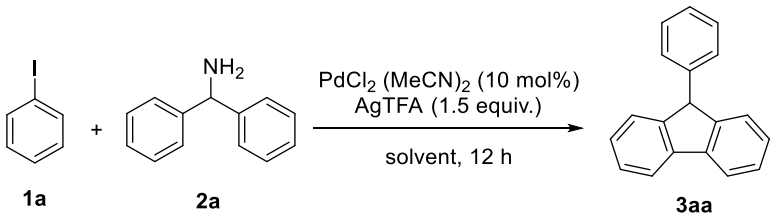
Table S2. Screening of additives[a]



Entry	Additives	Yield of 3aa (%)
1	**AgTFA**	**75**
2	$AgPO_4$	16
3	$AgNO_2$	n.r
4	$AgNO_3$	n.r
5	Ag_2SO_4	18
6	----	n.r

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.), $PdCl_2(MeCN)_2$ (10 mol%), additive (1.5 equiv.), HFIP (1.0 mL), 120 °C for 12 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S3. Screening of solvents[a]

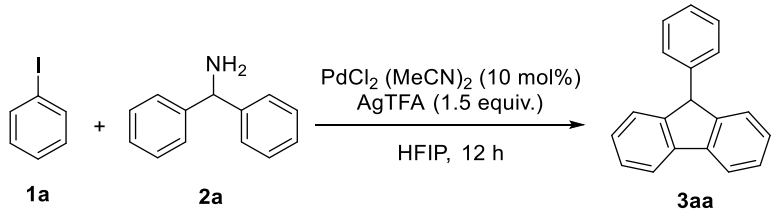


Entry	Solvents	Yield of 3aa (%)
1	DMF	n.r
2	DME	n.r
3	EA	n.r
4	MeOH	n.r
5	Ethanol	n.r
6	1,4-Dioxane	n.r

7	TFE	31
8	**HFIP**	**75**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.), $PdCl_2$ $(MeCN)_2$ (10 mol%), AgTFA (1.5 equiv.), Solvents (1.0 mL), 120 °C for 12 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S4. Screening of reaction temperatures[a]

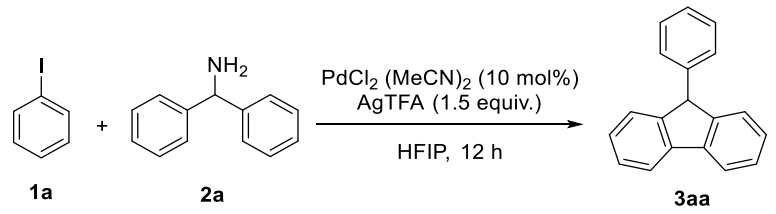


1a **2a** **3aa**

Entry	[T. °C]	Yield of 3aa (%)
1	80	5
2	100	7
3	**120**	**75**
4	140	64

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.), $PdCl_2(MeCN)_2$ (10 mol%), AgTFA (1.5 equiv.), HFIP (1.0 mL), stirred at indicated temperatures for 12 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S5. Screening the ratio of **1a** and **2a**[a]

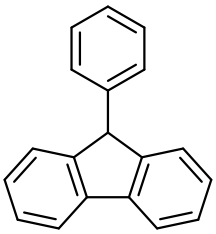


1a **2a** **3aa**

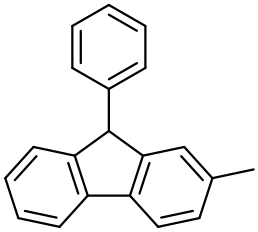
Entry	$PdCl_2$ $(MeCN)_2$ (mmol)	AgTFA (mmol)	1a (mmol)	2a (mmol)	Yield of 3aa based on 1a	Yield of 3aa based on 2a
1	0.02	4	6	2	-	63
2	0.02	4	4	2	-	72
3	0.02	4	2	2	-	71
4	0.02	4	2	3	58	-
5	0.02	2	2	3	60	-
6	**0.02**	**3**	**2**	**3**	**75**	**-**
7	0.02	5	2	3	58	-
8	0.02	6	2	3	56	-
9	0.01	3	2	3	50	-

[a]Reaction conditions: **1a**, **2a**, $PdCl_2(MeCN)_2$, AgTFA were used as indicated, HFIP (1.0 mL), 120 °C for 12 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

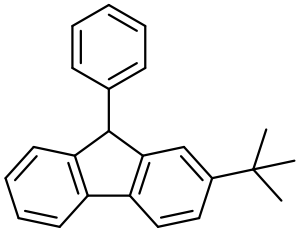
IV. Characterisation of all products



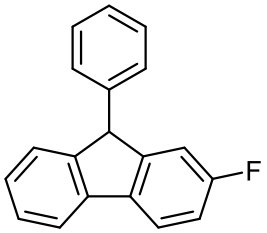
9-phenylfluorene (3aa): Colorless solid; isolated yield 74% (35.8 mg); R_f = 0.71 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 6.2 Hz, 2H), 7.28 – 7.34 (m, 6H), 7.15 (d, *J* = 6.8 Hz, 2H), 5.10 (s, 1H) ppm.**^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.0, 141.7, 141.1, 128.7, 128.4, 127.3, 126.9, 125.4, 119.9, 54.5 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{14}^+$ 242.1096; found: 242.1099.



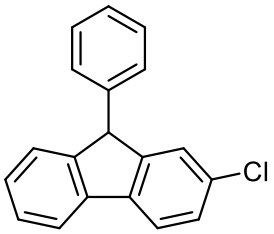
2-methyl-9-phenyl-9h-fluorene (3ba): Colorless solid; isolated yield 64% (32.8 mg); R_f = 0.71 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 3.5 Hz, 3H), 7.33 – 7.26 (m, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 7.14 (d, *J* = 6.8 Hz, 2H), 5.05 (s, 1H), 2.40 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.2, 147.8, 141.9, 141.2, 138.4, 137.3, 128.7, 128.4, 128.2, 127.3, 126.8, 126.8, 126.0, 125.3, 119.6, 119.6, 54.4, 21.7 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{20}H_{16}^+$ 256.1252; found: 256.1250.



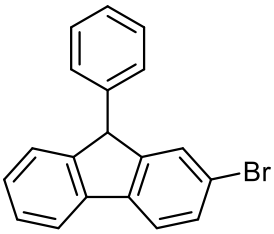
2-(1, 1-dimethylethyl)-9-phenyl-9h-fluorene (3ca): Colorless solid; isolated yield 82% (48.9 mg); R_f = 0.80 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.33 (t, *J* = 8.5 Hz, 3H), 7.30 – 7.24 (m, 2H), 7.16 (d, *J* = 6.8 Hz, 2H), 5.08 (s, 1H), 1.36 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.74, 148.1, 147.7, 141.9, 141.0, 138.6, 128.7, 128.4, 127.2, 126.8, 126.8, 125.2, 124.6, 122.2, 119.6, 119.4, 54.6, 35.0, 31.6 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{23}H_{22}^+$ 298.1722; found: 298.1715.



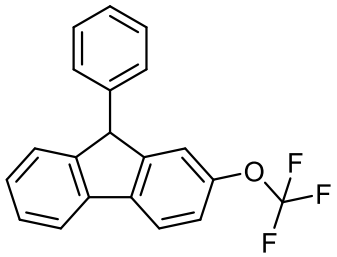
2-fluoro-9-phenyl-9h-fluorene (3da): Colorless solid; isolated yield 63% (32.8 mg); R_f = 0.74 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.28 – 7.25 (m, 2H), 7.13 – 7.08 (m, 3H), 7.03 (d, *J* = 9.7, 2.5 Hz, 1H), 5.05 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.69 (d, *J* = 245.5 Hz), 150.06 (d, *J* = 8.2 Hz), 147.75, 140.93, 140.19, 136.97 (d, *J* = 2.6 Hz), 128.8, 128.3, 127.5, 127.1, 127.0, 125.3, 120.8 (d, *J* = 9.1 Hz), 119.6, 114.6 (d, *J* = 23.2 Hz), 112.6 (d, *J* = 22.9 Hz), 54.5 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -114.63 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}F^+$ 260.1001; found: 260.0999.



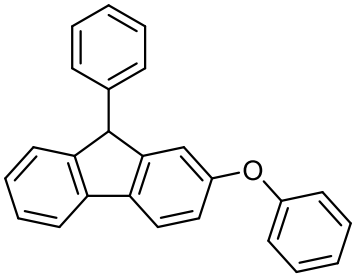
2-chloro-9-phenyl-9h-fluorene (3ea): Colorless solid; isolated yield 62% (34.2 mg); R_f = 0.73 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.30 (m, 5H), 7.29 (d, *J* = 9.5 Hz, 1H), 7.11 (d, *J* = 6.7 Hz, 2H), 5.06 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.6, 147.7, 140.7, 140.0, 139.6, 133.0, 128.9, 128.3, 127.7 127.6, 127.5, 127.1, 125.7, 125.4, 120.8, 119.9, 54.4 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Cl^+$ 276.0706; found: 276.0709.



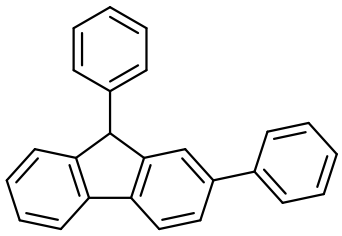
2-bromo-9-phenyl-9h-fluorene (3fa): Colorless solid; isolated yield 60% (38.5 mg); R_f = 0.70 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.47 (s, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.11 (d, *J* = 6.9 Hz, 2H), 5.06 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.9, 147.6, 140.7, 140.0, 130.5, 128.9, 128.6, 128.3, 127.8, 127.6, 127.2, 125.4, 121.2, 121.1, 120.0, 54.4 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Br^+$ 320.0201; found: 320.0208.



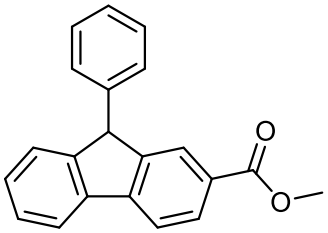
2-(trifluoromethoxy)-9-phenyl-9h- fluorene (3ga): Colorless solid; isolated yield 54% (35.2 mg); R_f = 0.71 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 3H), 7.29 – 7.27 (m, 1H), 7.18 (dt, *J* = 2.2, 1.2 Hz, 1H), 7.13 – 7.08 (m, 2H), 5.08 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.6, 148.0, 140.65, 139.7, 139.7, 128.9, 128.3, 127.6, 127.6, 127.2, 125.4, 120.6, 120.5 (q, *J* = 257.3 Hz), 120.4, 120.0, 118.4, 54.5 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -57.82 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{20}H_{13}F_3O^+$ 326.0918; found: 326.0911.



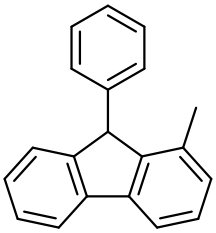
2-phenoxy-9-phenyl-9h-fluorene (3ha): Colorless solid; isolated yield 66% (44.1 mg); R_f = 0.67 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.30 – 7.27 (m, 2H), 7.25 (t, *J* = 6.1 Hz, 2H), 7.11 (d, *J* = 6.7 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 7.04 (s, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 5.05 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.6, 156.7, 149.9, 147.8, 141.2, 140.5, 136.6, 129.7, 128.7, 128.3, 127.4, 126.9, 126.8, 125.3, 123.0, 120.8, 119.5, 118.5, 118.4, 116.6, 54.5 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{25}H_{18}O^+$ 334.1358; found: 334.1355.



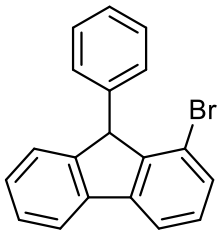
2,9-diphenyl-9h-fluorene (3ia): Colorless solid; isolated yield 78% (49.6 mg); R_f = 0.69 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.58 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 3H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.17 (d, *J* = 7.0 Hz, 2H), 5.15 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.6, 148.2, 141.5, 141.3, 140.7, 140.8, 140.3, 128.8, 128.7, 128.4, 127.4, 127.4, 127.2, 126.9, 126.5, 125.4, 124.1, 120.2, 120.0, 54.6 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{25}H_{18}^+$ 318.1409; found: 318.1411.



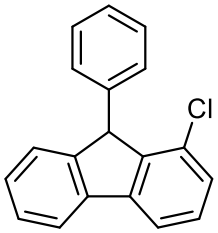
2-acetate-9-phenyl-9h-fluorene (3ja): Colorless solid; isolated yield 44% (26.4 mg); R_f = 0.48 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 8.00 (s, 1H), 7.90 – 7.84 (m, 2H), 7.48 – 7.41 (m, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.11 (d, *J* = 6.5 Hz, 2H), 5.11 (s, 1H), 3.90 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 149.0, 147.9, 145.6, 140.7, 139.8, 129.3, 128.9, 128.8, 128.5, 128.3, 127.6, 127.1, 126.6, 125.6, 120.8, 119.6, 54.4, 52.0 ppm. **HRMS** (ESI-TOF): $[M + Na]^+$ Calcd. for $C_{21}H_{16}O_2Na^+$ 323.1043; found: 323.1042.



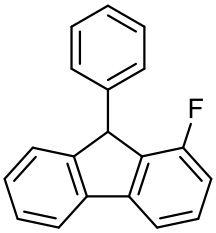
1-methyl-9-phenyl-9h-fluorene (3ka): Colorless solid; isolated yield 65% (33.3 mg); R_f = 0.73 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.36 (td, *J* = 7.5, 4.6 Hz, 1H), 7.29 – 7.20 (m, 6H), 7.12 – 7.06 (m, 3H), 5.03 (s, 1H), 2.08 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.6, 145.6, 141.6, 141.0, 140.6, 135.3, 128.9, 128.7, 128.1, 127.8, 127.2, 127.1, 126.6, 125.1, 119.9, 117.4, 54.1, 19.1 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{20}H_{16}^+$ 256.1252; found: 256.1250.



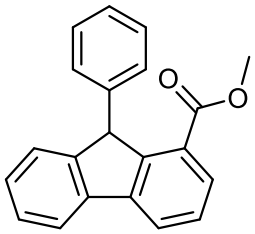
1-bromo-9-phenyl-9h-fluorene (3la): Colorless solid; isolated yield 48% (30.7 mg); R_f = 0.81 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.6, 5.2 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 6.7 Hz, 1H), 7.35 – 7.26 (m, 6H), 7.12 (d, *J* = 6.6 Hz, 2H), 5.13 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.2, 146.3, 144.0, 139.8, 139.6, 131.0, 129.4, 128.6, 128.4, 128.1, 127.4, 126.8, 125.3, 121.2, 120.3, 118.8, 56.0 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Br^+$ 320.0201; found: 320.0208.



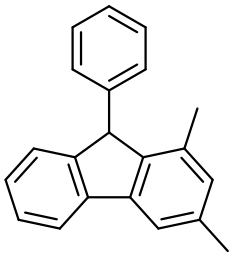
1-chloro-9-phenyl-9h-fluorene (3ma): Colorless solid; isolated yield 51% (28.2 mg); R_f = 0.70 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.24 (m, 6H), 7.11 (d, *J* = 6.7 Hz, 2H), 5.17 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.3, 144.4, 143.9, 139.8, 139.7, 132.1, 129.2, 128.6, 128.2, 128.1, 127.9, 127.4, 126.8, 125.3, 120.3, 118.3, 54.5 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Cl^+$ 276.0706; found: 276.0700.



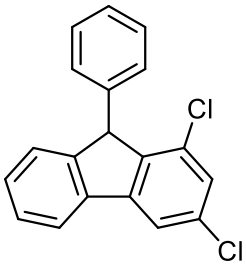
1-fluoro-9-phenyl-9h-fluorene (3na): Colorless solid; isolated yield 55% (28.6 mg); R_f = 0.70 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.42 (t, *J* = 6.6 Hz, 1H), 7.35 – 7.24 (m, 6H), 7.10 (d, *J* = 6.8 Hz, 2H), 7.00 – 6.95 (m, 1H), 5.04 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.9 (d, *J* = 251.5 Hz), 148.8, 143.3, 143.0 (d, *J* = 2.5 Hz), 141.2, 140.1, 128.8, 128.2, 127.9, 127.5, 127.0, 126.4 (d, *J* = 8.9 Hz), 125.4, 120.1, 114.2 (d, *J* = 22.6 Hz), 106.9 (d, *J* = 21.3 Hz), 53.87 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.60 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}F^+$ 260.1001; found: 260.0999.



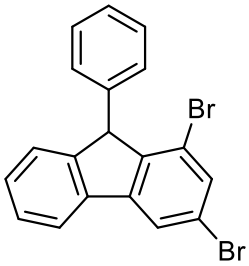
1-acetate-9-phenyl-9h-fluorene (3oa): Colorless solid; isolated yield 59% (35.4 mg); R_f = 0.50 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.94 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 5.4 Hz, 2H), 5.58 (s, 1H), 3.64 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.0, 148.8, 148.1, 143.3, 141.9, 138.9, 129.1, 128.4, 128.2, 128.0, 127.9, 127.6, 127.2, 126.3, 125.1, 123.7, 119.9, 55.2, 51.5 ppm. **HRMS** (ESI-TOF): $[M + Na]^+$ Calcd. for $C_{21}H_{16}O_2Na^+$ 323.1043; found: 323.1040.



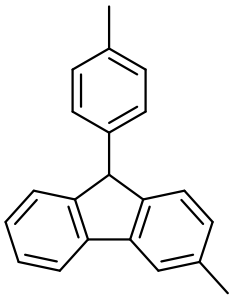
1, 3-dimethyl-9-phenyl-9h-fluorene (3pa): Colorless solid; isolated yield 64% (34.6 mg); R_f = 0.66 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.35 (d, *J* = 15.3 Hz, 1H), 7.27 – 7.17 (m, 5H), 7.08 (d, *J* = 6.7 Hz, 2H), 6.93 (s, 1H), 4.99 (s, 1H), 2.47 (s, 3H), 2.05 (s, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.0, 142.8, 141.7, 141.3, 140.7, 137.5, 134.9, 129.9, 128.6, 128.1, 127.1, 126.5, 125.1, 119.8, 118.0, 53.8, 21.5, 19.0 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{21}H_{18}^+$ 270.1409; found: 270.1403.



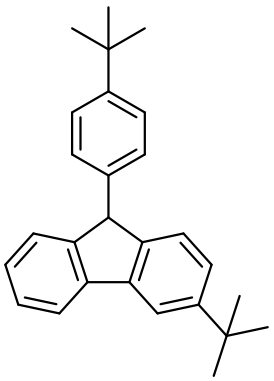
1, 3-dichloro-9-phenyl-9h-fluorene (3qa): Colorless solid; isolated yield 45% (30.0 mg); R_f = 0.73 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.44 – 7.35 (m, 1H), 7.33 – 7.23 (m, 6H), 7.06 (d, *J* = 6.2 Hz, 2H), 5.11 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.7, 145.0, 142.8, 139.1, 138.6, 134.5, 132.5, 128.8, 128.6, 128.2, 127.6, 127.4, 127.0, 125.4, 120.5, 118.7, 54.2 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{12}Cl_2^+$ 310.0316; found: 310.0321.



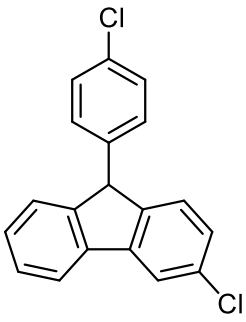
1, 3-dibromo-9-phenyl-9h-fluorene (3ra): Colorless solid; isolated yield 37% (29.6 mg); R_f = 0.77 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 1.6 Hz, 1H), 7.39 (t, *J* = 5.6 Hz, 1H), 7.30 – 7.24 (m, 5H), 7.05 (d, *J* = 4.2 Hz, 2H), 5.04 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.5, 145.4, 145.2, 139.0, 138.4, 13230, 128.8, 128.7, 128.3, 127.6, 126.9, 125.4, 122.2, 122.1, 121.6, 120.5, 55.7 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{12}Br_2^+$ 397.9306; found: 397.9327.



3-methyl-9-(4-methylphenyl)-9h-fluorene (3ab): Colorless solid; isolated yield 48% (25.9 mg); R_f = 0.73 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.63 (s, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 3H), 6.99 (d, *J* = 7.8 Hz, 2H), 5.00 (s, 1H), 2.47 (s, 3H), 2.33 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.5, 145.3, 141.1, 141.0, 138.8, 136.9, 136.3, 129.4, 128.2, 128.1, 127.2, 125.3, 125.0, 120.4, 119.7, 53.7, 21.6, 21.1 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{21}H_{18}^+$ 270.1409; found: 270.1403.

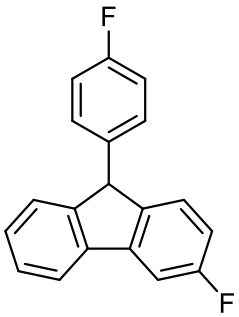


3-(1, 1-dimethylethyl)-9-(1, 1-dimethylethyl) phenyl-9h-fluorene (3ac): Colorless solid; isolated yield 20% (14.2 mg); R_f = 0.78 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 5.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.06 (d, *J* = 6.8 Hz, 1H), 5.02 (s, 1H), 1.42 (s, 9H), 1.31 (s, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.4, 149.4, 148.3, 145.2, 141.3, 140.7, 138.6, 127.8, 127.1, 127.0, 125.5, 125.4, 124.7, 124.6, 119.6, 116.6, 53.5, 34.8, 34.4, 31.6, 31.4 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{27}H_{30}^+$ 354.2348; found: 354.2341.

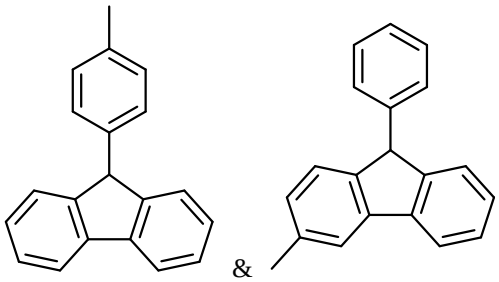


3-chloro-9-(4-chlorophenyl)-9h-fluorene (3ad): Colorless solid; isolated yield 59% (36.7 mg); R_f = 0.73 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 4.9, 2.9 Hz, 2H),

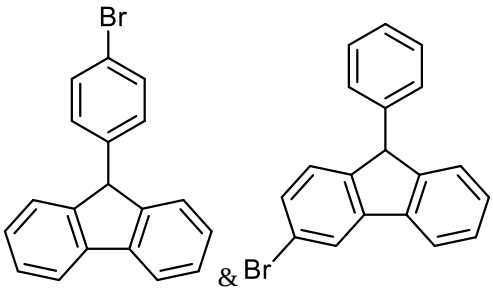
7.44 (t, *J* = 8.0 Hz, 1H), 7.32 (, *J* = 11.2, 7.4 Hz, 2H), 7.29 – 7.25 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.00 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.9, 145.7, 142.8, 139.8, 139.6, 133.7, 132.9, 129.6, 129.0, 128.2, 127.8, 127.4, 126.3, 125.4, 120.3, 120.3, 53.3 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{12}Cl_2^+$ 310.0316; found: 310.0321.



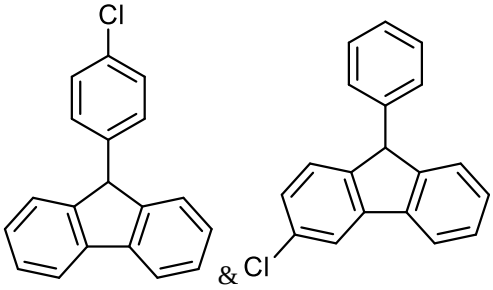
3-fluoro-9-(4-fluorophenyl)-9h-fluorene (3ae): Colorless solid; isolated yield 75% (41.7 mg); R_f = 0.72 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.24 (dd, *J* = 8.3, 5.0 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 3H), 5.01 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.3 (d, *J* = 152.5 Hz), 161.6 (d, *J* = 153.2 Hz), 148.7, 143.1 (d, *J* = 2.4 Hz), 142.9 (d, *J* = 8.9 Hz), 140.1, 136.9 (d, *J* = 3.3 Hz), 129.7 (d, *J* = 7.8 Hz, 2), 128.0, 127.6, 126.3 (d, *J* = 8.9 Hz), 125.3, 120.2, 115.6 (d, *J* = 21.4 Hz), 114.3 (d, *J* = 23.1 Hz), 107.0 (d, *J* = 23.2 Hz), 53.0 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.31, -115.85 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{12}F_2^+$ 278.0907; found: 278.0901.



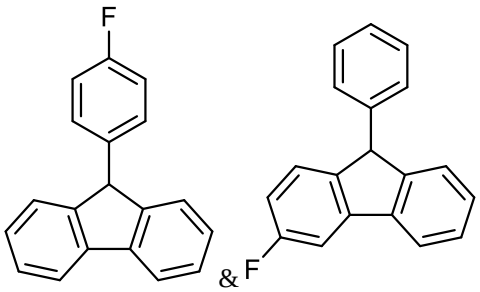
9-(4-methylphenyl)-9h-fluoren (3af) & 11-phenyl-11h-benzo-fluorene (3af'): Colorless solid; isolated as a mixture, yield 67 % (34.3 mg); R_f = 0.67 (petroleum ether-EtOAc = 10:1); Major product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 1H), 2.34 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.1, 141.0, 138.5, 136.4, 129.4, 128.2, 127.3, 127.2, 125.3, 119.8, 54.1, 21.1 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{20}H_{16}^+$ 256.1252; found: 256.1250. Minor product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.98 (t, *J* = 8.0 Hz, 3H), 7.78 (t, *J* = 8.5 Hz, 2H), 7.75 (s, 1H), 7.38 (d, J = 3.2 Hz, 2H), 7.34 (t, *J* = 6.1 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.18 (d, *J* = 6.8 Hz, 2H), 5.29 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.3, 146.1, 142.5, 139.8, 133.4, 128.8, 128.5, 128.2, 128.1, 128.1, 127.6, 127.3, 126.9, 125.7, 125.7, 124.1, 120.6, 118.06, 54.0 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{20}H_{16}^+$ 256.1252; found: 256.1249.



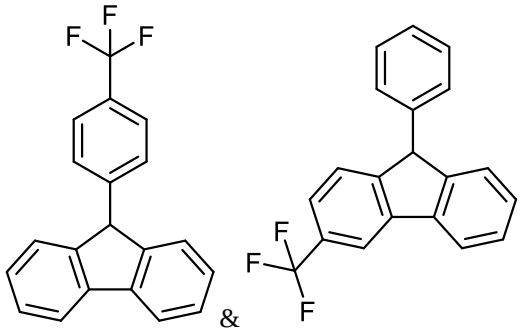
9-(4-bromophenyl)-9h-fluoren (3ag) & 3-bromo-9-phenyl-9h-fluorene (3ag'): Colorless solid; isolated as a mixture, yield 53% (33.9 mg); R_f = 0.74 (petroleum ether-EtOAc = 10:1); Major product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 4H), 7.31 (t, *J* = 7.2 Hz, 4H), 7.00 (d, *J* = 8.3 Hz, 2H), 5.03 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.4, 141.0, 131.8, 130.1, 128.8, 128.3, 127.6, 127.5, 125.3, 120.0, 53.8 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Br^+$ 320.0201; found: 320.0207. Minor product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 4.5 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.35 (t, *J* = 6.1 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 6.7 Hz, 2H), 5.02 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.2, 146.7, 143.2, 140.9, 139.8, 128.1, 127.1, 126.8, 125.5, 123.2, 120.7, 120.2, 54.1 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Br^+$ 320.0201; found: 320.0202.



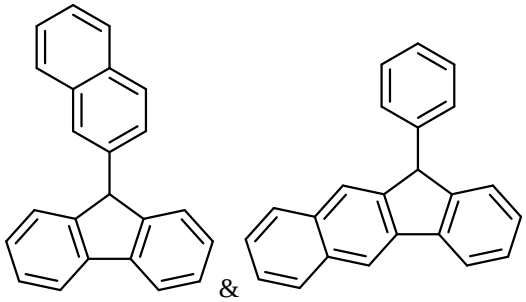
9-(4-chlorophenyl)-9h-fluoren (3ah) & 3-Chloro-9-phenyl-9h-fluorene (3ah'): Colorless solid; isolated as a mixture, yield 55% (30.4 mg); R_f = 0.76 (petroleum ether-EtOAc = 10:1); Major product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 6.3 Hz, 2H), 7.34 – 7.22 (m, 6H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.05 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.5, 141.0, 140.2, 132.6, 129.7, 128.9, 127.5, 127.4, 125.3, 120.0, 53.7 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Cl^+$ 276.0602; found: 276.0601. Minor product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 2H), 7.45 – 7.41 (m, 1H), 7.36 – 7.26 (m, 7H), 7.10 (d, *J* = 6.7 Hz, 2H), 5.05 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.4, 146.2, 142.8, 141.0, 139.9, 133.4, 128.8, 128.3, 128.0, 127.3, 127.1, 126.4, 125.5, 120.2, 54.1 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Cl^+$ 276.0602; found: 276.0601.



9-(4-fluorophenyl)-9h-fluoren(3ai) & 3-fluoro-9-phenyl-9h-fluorene(3ai'): Colorless solid; isolated as a mixture, yield 62% (32.2 mg); R_f = 0.73 (petroleum ether-EtOAc = 10:1); Major product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.13 – 7.06 (m, 3H), 6.99 (t, *J* = 8.7 Hz, 2H), 5.06 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.5 Hz), 147.8, 140.9, 137.3 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 8.0 Hz), 128.8, 128.2, 127.4 (d, *J* = 10.2 Hz), 125.3, 120.0, 115.5 (d, *J* = 21.4 Hz), 53.6 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -116.15 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}F^+$ 260.1001; found: 260.0999. Minor product: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 6.8 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.99 – 6.94 (m, 2H), 5.04 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.9 (d, *J* = 243.8 Hz), 148.8, 143.3, 143.0 (d, *J* = 8.8 Hz), 141.3, 140.2 (d, *J* = 2.8 Hz), 127.9, 127.0, 126.4 (d, *J* = 9.0 Hz), 125.5, 120.1, 114.2 (d, *J* = 23.2 Hz), 106.9 (d, *J* = 23.2 Hz), 53.9 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -115.59 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}F^+$ 260.1001; found: 260.1004.

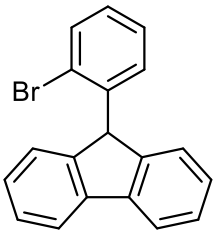


9-[4-(trifluoromethoxy) phenyl]-9h-fluoren(3aj): Colorless solid; isolated as a mixture, yield 60% (37.2 mg); R_f = 0.72 (petroleum ether-EtOAc = 10:1); Only the data of major product was provided: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.44 (dd, *J* = 7.9, 2.9 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.13 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.1, 146.0, 141.1, 128.9, 128.7, 128.3, 127.7, 127.5, 125.7 (q, *J* = 3.8 Hz), 125.3, 124.2 (q, *J* = 272.0 Hz), 120.1, 54.1 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.41 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{20}H_{13}F_3^+$ 310.0969; found: 310.0960.

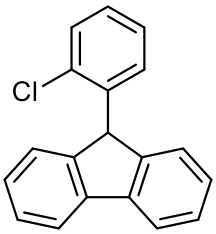


9-(2-naphthalenyl)-9h-fluorene(3ak): Colorless solid; isolated as a mixture, yield 62% (36.2 mg); R_f = 0.72 (petroleum ether-EtOAc = 10:1); Only the data of major product was provided: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.24 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.9, 141.1, 139.1,

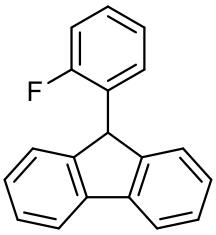
133.6, 132.6, 128.8, 128.5, 128.5, 127.7, 127.6, 127.4, 127.4, 127.3, 126.2, 126.1, 125.6, 125.5, 120.0, 54.6 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{23}H_{16}^+$ 292.1252; found: 292.1258.



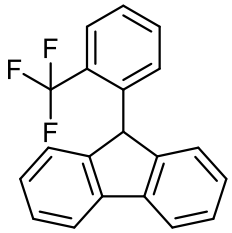
9-(2-bromophenyl)-9h-fluorene(3al): Colorless solid; isolated yield 32% (20.5 mg); R_f = 0.74 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.42 (m, *J* = 7.0 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 7.7 Hz, 1H), 5.81 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.4, 141.7, 141.1, 132.8, 129.2, 128.4, 127.9, 127.5, 127.4, 125.4, 125.3, 120.0, 53.0 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Br^+$ 320.0201; found: 320.0207.



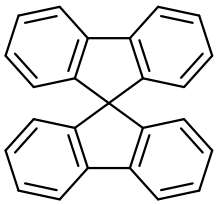
9-(2-chlorophenyl)-9h-fluorene(3am): Colorless solid; isolated yield 45% (24.8 mg); R_f = 0.75 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.43 (m, *J* = 6.3 Hz, 4H), 7.30 (m, *J* = 7.5 Hz, 2H), 7.21 – 7.15 (t, 1H), 7.03 – 6.98 (t, 1H), 6.53 (d, *J* = 9.5 Hz, 1H), 5.82 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.3, 141.2, 139.8, 134.6, 129.6, 129.0, 128.1, 127.5, 127. 4, 127.3, 125.3, 120.0, 50.3 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}Cl^+$ 276.0706; found: 276.0702.



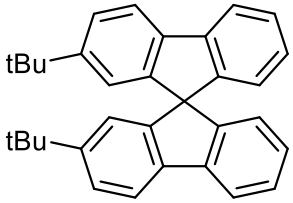
9-(2-fluorophenyl)-9h-fluorene(3an): Colorless solid; isolated yield 69% (35.9 mg); R_f = 0.76 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.38 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 6.2 Hz, 1H), 7.20 (t, *J* = 9.8 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.54 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.6 (d, *J* = 245.3 Hz), 146.9, 141.2, 129.3 (d, *J* = 4.4 Hz), 128.7, 128.6, 128.4 (d, *J* = 8.1 Hz), 127.4 (d, *J* = 9.0 Hz), 125.3, 124.4 (d, *J* = 3.5 Hz), 120.0, 115.6 (d, *J* = 22.4 Hz), 46.9 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -118.73 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{19}H_{13}F^+$ 260.1001; found: 260.0998.



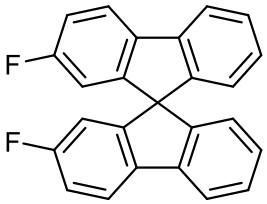
9-**[2-(trifluoromethyl) phenyl]-9h-fluorene (3ao):** Colorless solid; isolated yield 62% (38.4 mg); R_f = 0.80 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.33 – 7.26 (m, 5H), 7.23 (t, *J* = 6.9 Hz, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.53 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.4, 141.2, 140.9, 132.2, 130.1, 127.6, 127.5, 126.6, 125.4 (q, *J* = 4.7 Hz), 124.8 (q, *J* = 273.7 Hz), 120.0, 49.5 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -57.30 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{20}H_{13}F_3^+$ 310.0969; found: 310.0960.



9, 9'-spirobifluorene (4a): Colorless solid; isolated yield 41% (25.9 mg); R_f = 0.71 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 4H), 7.42 – 7.36 (m, 4H), 7.13 (t, *J* = 7.5 Hz, 4H), 6.75 (d, *J* = 8.6 Hz, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.8, 141.8, 127.8, 127.7, 124.0, 120.0, 66.0 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{25}H_{16}^+$ 316.1252; found: 316.1249.

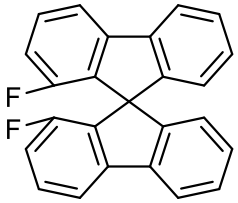


2, 2'-bis(1, 1-dimethylethyl)-9, 9'-spirobifluorene (4b): Colorless solid; isolated yield 66% (56.5 mg); R_f = 0.71 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 6.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.76 (s, 2H), 6.69 (d, *J* = 7.7 Hz, 2H), 1.19 (s, 18H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.3, 149.6, 149.0, 141.6, 139.4, 127.4, 127.2, 124.7, 123.9, 121.0, 119.6, 119.3, 66.3, 34.9, 31.4 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{33}H_{32}^+$ 248.2504; found: 248.2520.

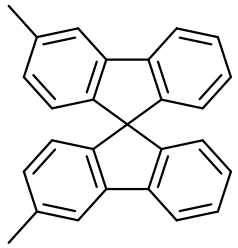


2, 2'-difluoro-9, 9'-spirobifluorene (4c): Colorless solid; isolated yield 53% (37.3 mg); R_f = 0.67 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 5.7 Hz, 2H), 7.79 (d, *J* = 5.3 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 2H), 7.15 – 7.08 (m, 4H), 6.75 (d, *J* = 7.6 Hz, 2H), 6.45 (d, *J* = 8.5 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246.8 Hz), 150.4 (d, *J* = 8.7 Hz), 148.1(d, *J* =

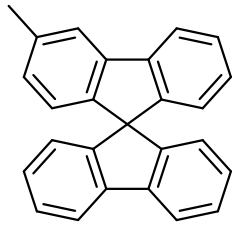
2.7 Hz), 140.8, 137.7, 128.1, 127.6, 124.0, 121.1 (d, *J* = 8.8 Hz), 119.8, 115.2 (d, *J* = 23.2 Hz), 111.4 (d, *J* = 23.5 Hz), 48.2 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -113.55 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{25}H_{14}F_2^+$ 352.1064; found: 352.1075.



1, 1'-difluoro-9, 9'-spirobifluorene (4d): Colorless solid; isolated yield 35% (24.6 mg); R_f = 0.73 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 2H), 6.86 – 6.80 (m, 2H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 5.0 Hz, 1H), 6.69 (d, *J* = 5.0 Hz, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.2 (d, *J* = 244.8 Hz), 149.2, 143.7, 143.7, 143.6 (d, *J* = 2.4 Hz), 140.7 (d, *J* = 3.1 Hz), 128.5, 128.0, 125.1 (d, *J* = 9.1 Hz), 124.1, 120.3, 114.8 (d, *J* = 23.0 Hz), 107.2 (d, *J* = 23.3 Hz), 64.8 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -114.71 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{25}H_{14}F_2^+$ 352.1064; found: 352.1052.



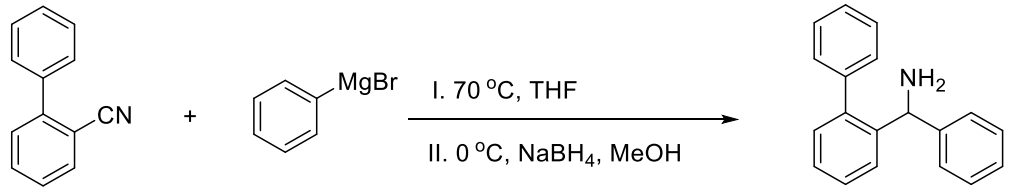
3, 3'-dimethyl-9, 9'-spirobifluorene (4e): Colorless solid; isolated yield 35% (24.1 mg); R_f = 0.79 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.68 (s, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.65 (d, *J* = 7.7 Hz, 2H), 2.46 (s, 6H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.4, 146.1, 141.9, 141.8, 137.4, 128.7, 127.7, 127.6, 124.0, 123.7, 120.6, 119.8, 65.3, 21.6 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{27}H_{20}^+$ 344.1565; found: 344.1562.



3-methyl-9, 9'-spirobifluorene (4f): Colorless solid; isolated yield 33% (21.8 mg); R_f = 0.76 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.70 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 3H), 7.12 (q, *J* = 7.3 Hz, 3H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 2.47 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.2, 149.0, 145.9, 141.9, 141.8, 141.7, 137.5, 128.8, 127.8, 127.7, 127.6, 124.0, 123.7, 120.6, 120.0, 119.9, 65.7, 21.6 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{26}H_{18}^+$ 330.1409; found: 330.1406.

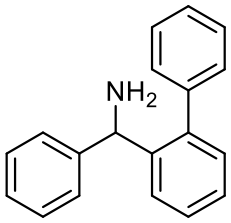
V. Preliminary mechanistic studies

1. The synthesis of possible intermediate Int-Amine and its transformation.



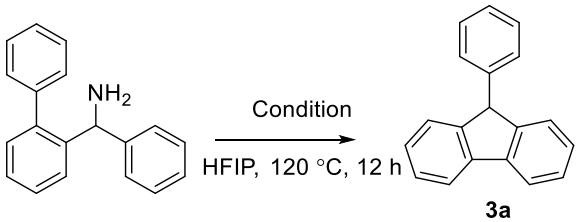
Int-Amine

In an oven-dried round flask under Ar atmosphere, a mixture of the [1, 1'-biphenyl]-2-carbonitrile (1 mmol) and the bromophenylmagnesium (1.2 mmol) was stirred in dry THF (10 mL) at 70 ℃ for 8 h. The reaction mixture was cooled to room temperature and quenched by dry MeOH (10 mL) at 0 ℃. After being stirred vigorously for 10 min, the sodium borohydride was added slowly and the mixture was heated at 60 ℃ until the imine was disappeared determined by TLC. The volatile materials were evaporated under vacuum and purified by flash column chromatography. The isolated yield of the **Int-Amine** was 81%.



alpha-phenyl-[1, 1'-biphenyl]-2-methanamine(Int-Amine): Colorless oil; isolated yield 81% (209.79 mg); R_f = 0.25 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.48 (m, 4H), 7.47 – 7.36 (m, 3H), 7.33 (d, *J* = 6.7 Hz, 8H), 5.50 (s, 1H), 1.81 (s, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 145.8, 143.5, 141.5, 130.2, 129.6, 128.4, 128.3, 128.1, 127.4, 127.3, 127.2, 126.8, 126.8, 55.4 ppm. **HRMS** (ESI-TOF): $[M + Na]^+$ Calcd. for $C_{19}H_{17}NNa^+$ 259.1361; found: 259.1359.

1.1 Transformation of Int-amine under different conditions:

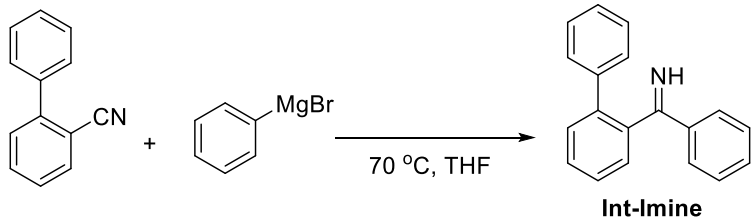


3a

Entry	$PdCl_2(MeCN)_2$ (10 mol%)	AgTFA(1.5 equiv)	Yield of 3a (%)
1	+	+	97
2	+	-	88
3	-	+	97
4	-	-	79

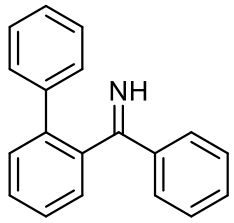
Reaction conditions: **Int-Amine** (0.1 mmol), $PdCl_2(MeCN)_2$ (10 mol%), AgTFA (1.5 equiv), HFIP(1 mL), 120 ℃, 12h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

2. The synthesis of possible intermediate Int-Imine and its transformation.



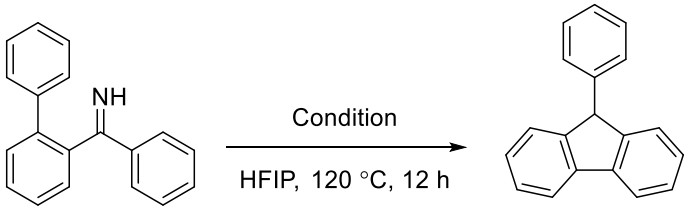
Int-Imine

In an oven-dried round flask under Ar atmosphere, a mixture of the [1, 1'-biphenyl]-2-carbonitrile (1 mmol) and the bromophenylmagnesium (1.2 mmol) was stirred in dry THF (10 mL) at 70 ℃ for 8 h. The volatile materials were evaporated under vacuum and purified by flash column chromatography. The isolated yield of the **Int-Imine** was 90%.



2-phenylbenzophenone imine (Int-Imine): Yellow solid; isolated yield 90% (231.3 mg); R_f = 0.32 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (s(br), 1H), 7.58 – 7.40 (m, 5H), 7.38 – 7.30 (m, 1H), 7.29 – 6.99 (m, 8H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.9, 140.5, 140.2, 139.8, 138.8, 130.4, 129.4, 129.0, 128.9, 128.2, 128.0, 127.3, 127.2 ppm. **HRMS** (ESI-TOF): $[M + Na]^+$ Calcd. for $C_{19}H_{15}NNa^+$ 257.1204; found: 257.1202.

2.1 Transformation of Int-imine under different conditions:



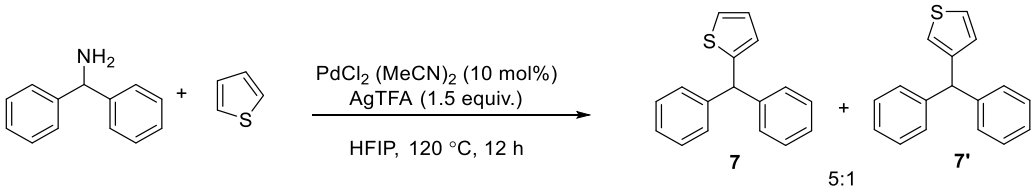
3a

Entry	$PdCl_2(MeCN)_2$ (10 mol%)	AgTFA(1.5 equiv)	Yield of 3a (%)
1	+	+	n.r
2	+	-	n.r
3	-	+	n.r
4	-	-	n.r

Reaction conditions: **Int-Imine** (0.1 mmol), $PdCl_2(MeCN)_2$ (10 mol%), AgTFA (1.5 equiv), HFIP (1 mL), 120 ℃，12h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

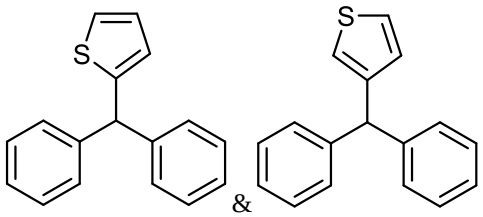
3. Capture of possible benzylic carbocation intermediate

Diphenylmethanamine **2a** (0.1 mmol) and thiophene (0.2 mmol) was stirred in HFIP at 140 ℃ for 12 h [with or without $PdCl_2(MeCN)_2$ (10 mol%) & AgTFA (1.5 equiv)]. The reaction mixture was cooled to ambient temperature, water (20 mL) and DCM (20mL) were added to the flask. The organic phase was separated and the combined organic layer was dried with $MgSO_4$ and concentrated to dryness, then the residue was purified by flash chromatography on silica gel to give the products as a mixture of **7** and **7'**(43% yield).



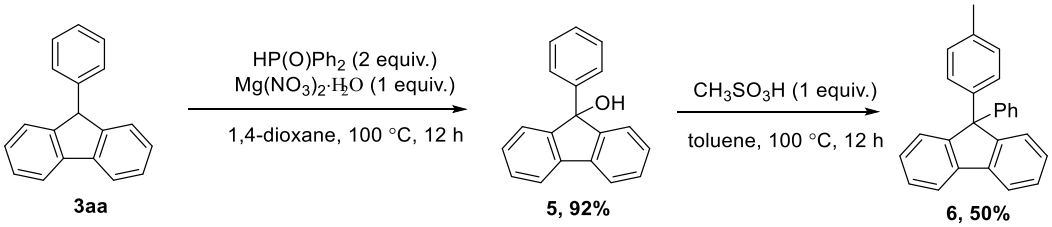
Entry	$PdCl_2(MeCN)_2$ (10 mol%)	AgTFA(1.5 equiv)	Yield of 7 & 7' (%)
1	+	+	42
2	-	-	43

Reaction conditions: Diphenylmethanamine (0.1 mmol), Thiophene (2 equiv), HFIP(1 mL), 120 ℃, 12h. Yields were determined by GC-MS analysis using dodecane as an internal standard.



2-(diphenylmethyl)thiophene (7) & 3-(diphenylmethyl)thiophene (7'): Colorless solid; yield 42% (21.0 mg); R_f = 0.74 (petroleum ether-EtOAc = 10:1); Only the data of major product was provided: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 4H), 7.28 – 7.22 (m, 6H), 7.18 (d, *J* = 7.2 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.73 – 6.71 (m, 1H), 5.71 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.9, 143.8, 128.9, 128.4, 126.7, 126.6, 126.4, 124.5, 52.1 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{17}H_{14}S^+$ 250.0816; found: 250.0813.

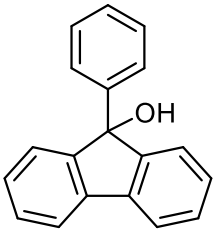
VI. Further transformation



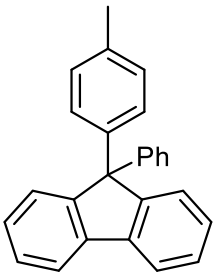
To a solution of **3aa** (60.6 mg, 0.25 mmol) in 1, 4-dioxane (2 mL) was added $HP(O)Ph_2$ (101.1 mg,

0.50 mmol) and $Mg(NO_3)_2.6H_2O$ (64.1 mg, 0.25 mmol, 1 equiv). The mixture was heated to 100 ℃ and stirred for 12 h. Then saturated sodium bicarbonate solution was added into the mixture to quench the reaction. The organic phase was separated and washed by saturated sodium bicarbonate, and the water phase was extracted three times with CH_2Cl_2. The combined organic solution was dried with anhydrous magnesium sulfate ($MgSO_4$). The solvent was removed by rotary evaporation, and the residue was purified by column chromatography using petroleum ether/CH_2Cl_2 (10: 1) as eluent to get a colorless solid **(5)**. Yield: 59.3 mg (92%).[3]

To a solution of **5** (258 mg, 1 mmol) in toluene (3 mL) was added dropwise methanesulfonicacid (CH_3SO_3H) (0.067 mL，1 mmol) in toluene (1 mL). The mixture was heated to 140 ℃ and stirred for 12 h. In this reaction, toluene is used as not only reactant but also solvent. Then saturated sodium bicarbonate solution was added into the mixture to quench the reaction. The organic phase was separated and washed by saturated sodium bicarbonate, and the water phase was extracted three times with CH_2Cl_2. The combined organic solution was dried with anhydrous magnesium sulfate ($MgSO_4$). The solvent was removed by rotary evaporation, and the residue was purified by column chromatography using petroleum ether/CH_2Cl_2 (10: 1) as eluent to get a colorless solid **(6)**. Yield: 166.0 mg (50%).[4]



9-phenylfluorenol (5): R_f = 0.29 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.24 – 7.32 (m, 7.6 Hz, 5H), 2.50 (s, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.5, 143.2, 139.6, 129.1, 128.5, 128.2, 127.3, 125.4, 124.8, 120.1, 83.7 ppm. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{14}ONa^+$ 258.1045; found: 258.1043.



9-(4-methylphenyl)-9-phenyl-fluorene (6): R_f = 0.71 (petroleum ether-EtOAc = 10:1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 4H), 7.38 – 7.32 (m, 3H), 7.29 (d, *J* = 5.8 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 151.6, 146.3, 143.1, 140.3, 136.4, 129.1, 128.4, 128.3, 128.2, 127.9, 127.6, 126.8, 126.3, 120.3, 65.4, 21.1 ppm. **HRMS** (EI): $[M]^+$ Calcd for $C_{26}H_{20}^+$ 332.1565; found: 332.1562.

VII. X-Ray data for 3ma and 3qa

X-ray for **3ma**.

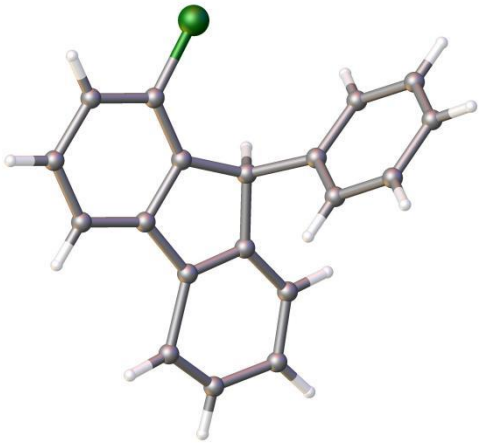


Fig S1. X-ray structure of 3ma

Identification code	A
Empirical formula	$C_{19}H_{13}Cl$
Formula weight	276.74
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.0500(9)
b/Å	6.2114(6)
c/Å	24.788(2)
α/°	90
β/°	96.943(6)
γ/°	90
Volume/Å^3	1383.2(2)
Z	4
ρ_{calc}g/cm^3	1.329
μ/mm^{-1}	1.520
F(000)	576.0
Crystal size/mm^3	0.12 × 0.1 × 0.1
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.754 to 120.412
Index ranges	$-10 \le h \le 11$, $-6 \le k \le 7$, $-28 \le l \le 32$

Reflections collected	9267
Independent reflections	2973 [R_{int} = 0.0618, R_{sigma} = 0.0720]
Data/restraints/parameters	2973/336/296
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0598, wR_2 = 0.1459
Final R indexes [all data]	R_1 = 0.1076, wR_2 = 0.1658
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.25

X-ray for **3qa**.

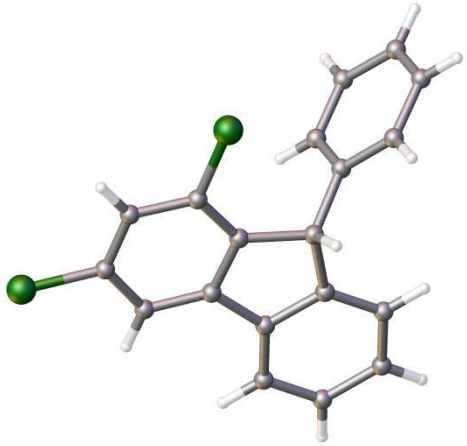


Fig S2. X-ray structure of 3ma

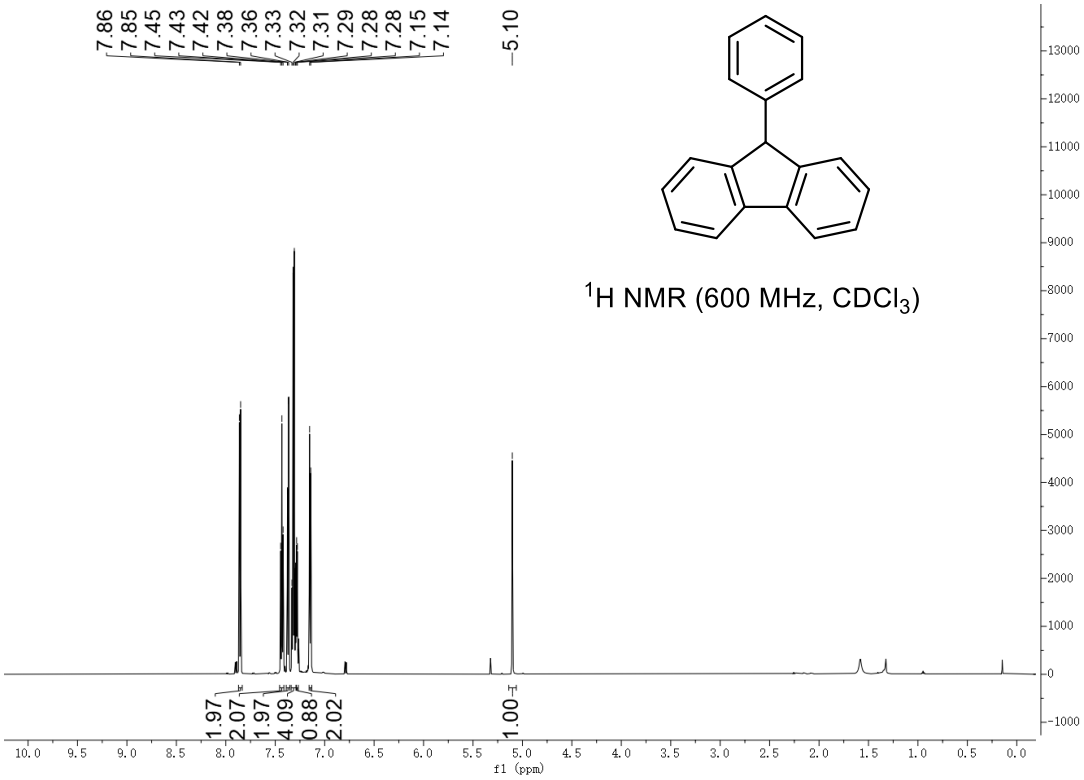
Identification code	A
Empirical formula	$C_{19}H_{12}Cl_2$
Formula weight	311.19
Temperature/K	193.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.0130(14)
b/Å	6.5987(7)
c/Å	36.445(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2889.0(5)
Z	8
ρ_{calc}g/cm^3	1.431
μ/mm^{-1}	2.608
F(000)	1280.0
Crystal size/mm^3	0.12 ×0.1 ×0.1

Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/ °	10.602 to 120.476
Index ranges	$-15 \leq h \leq 10$, $-8 \leq k \leq 8$, $-44 \leq l \leq 46$
Reflections collected	17413
Independent reflections	3220 [R_{int} = 0.0701, R_{sigma} = 0.0550]
Data/restraints/parameters	3220/0/190
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0516, wR_2 = 0.1414
Final R indexes [all data]	R_1 = 0.0672, wR_2 = 0.1536
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.36

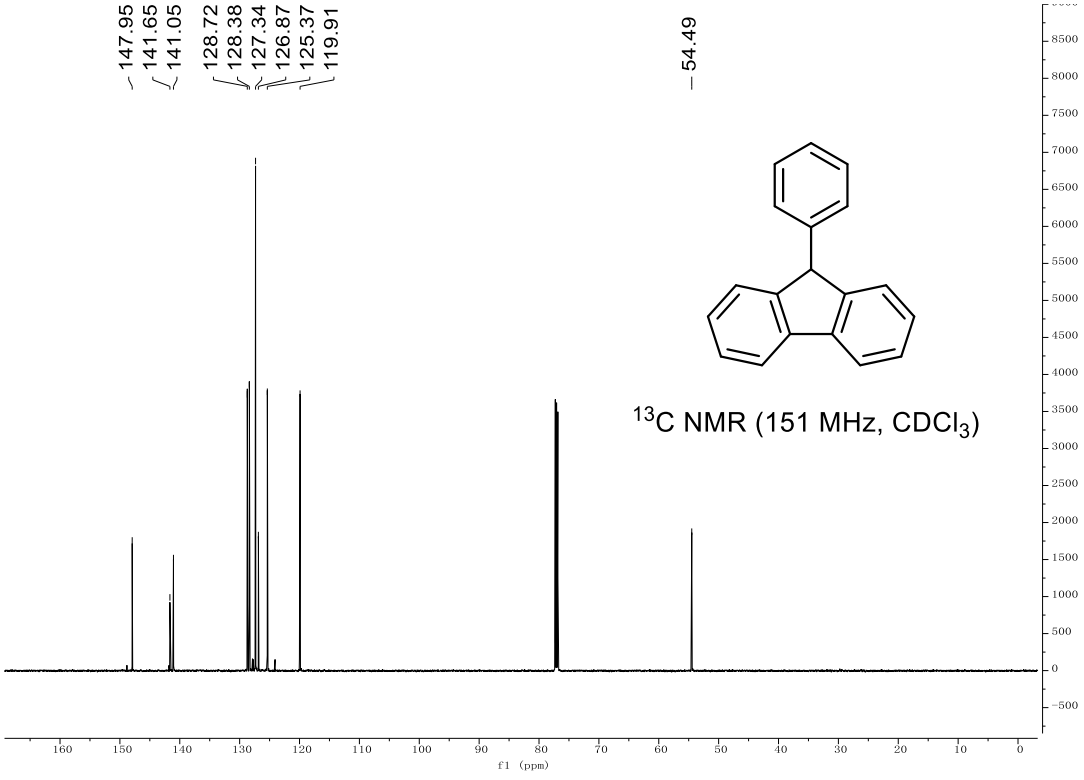
VIII. References

1. B. T. Gregg, K. C. Golden, J. F. Quinn, H.-J. Wang, W. Zhang, R. Wang, F. Wekesa, and D. O. Tymoshenko, *Tetrahedron Lett.*, **2009**, *50*, 3978-3981.
2. R. Crampton, S. Woodward, and M. Fox, *Adv. Synth. Catal*. **2011**, *353*, 903 – 906.
3. C. Hu, G. Hong, P. D. Nahide, Y. He, C. Zhou, M. C. Kozlowski and L. Wang, *Org. Chem. Front.*, **2019**, *6*, 3167–3171.
4. C.-R. Yin, Y. Han, L. Li, S.-H. Ye, W.-W. Mao, M.-D. Yi, H.-F. Ling, L.-H. Xie, G.-W. Zhang, and W. Huang, *Polym. Chem.*, **2013**, *4*, 2540-2545.

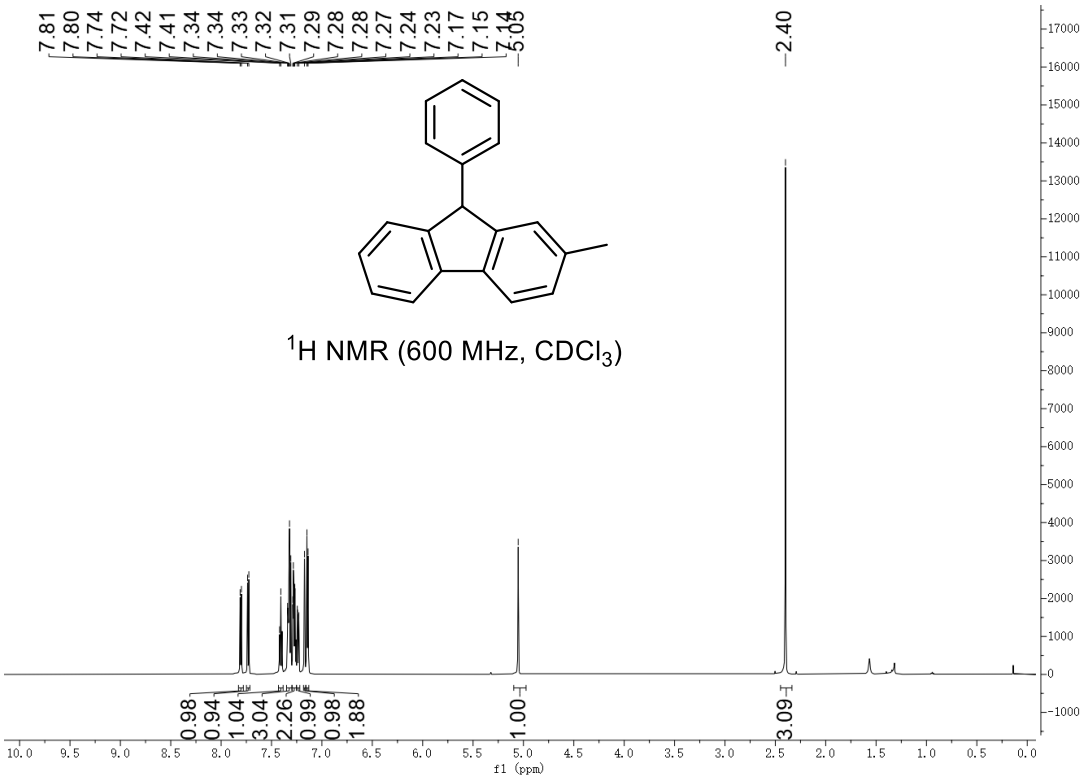
IX. NMR Spectra



^{1}H NMR Spectrum of 3aa (600 MHz, $CDCl_3$)

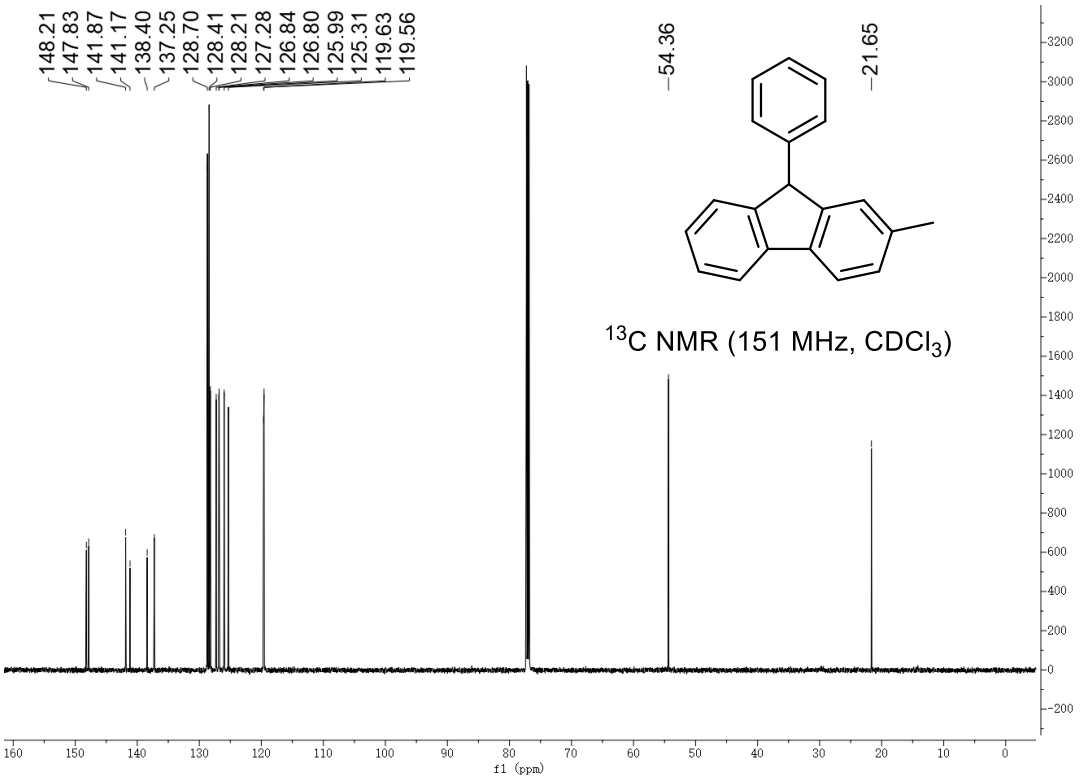


^{13}C NMR Spectrum of 3aa (151 MHz, $CDCl_3$)



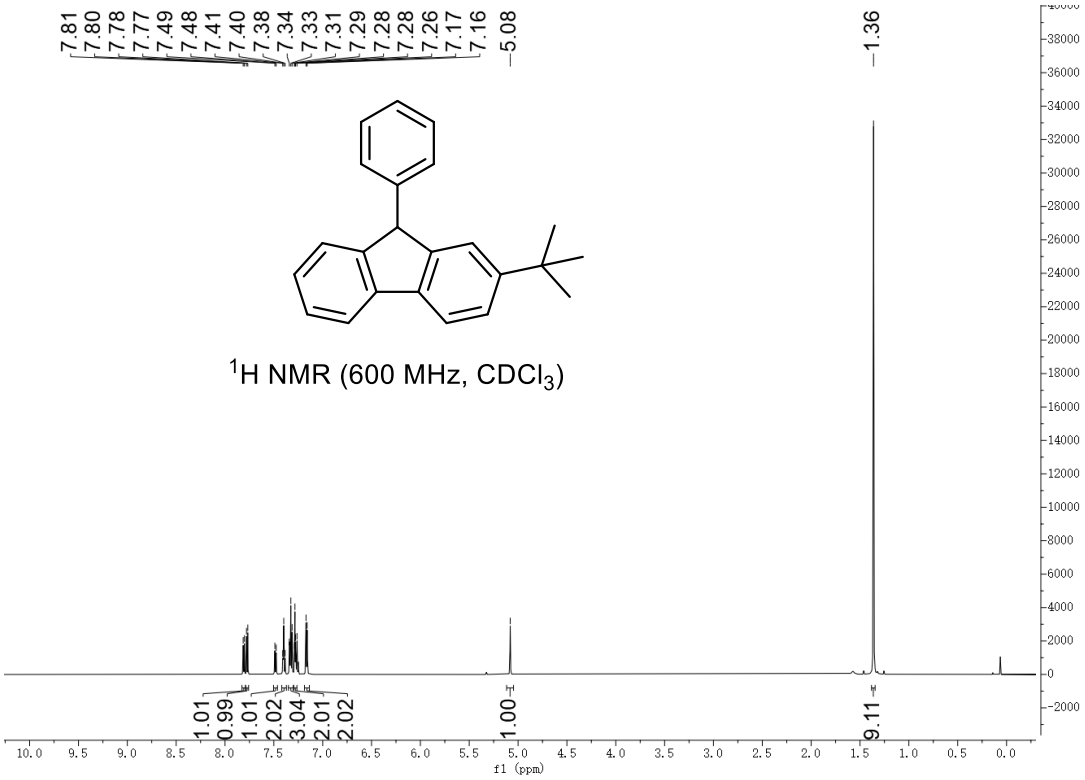
^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR Spectrum of 3ba (600 MHz, $CDCl_3$)

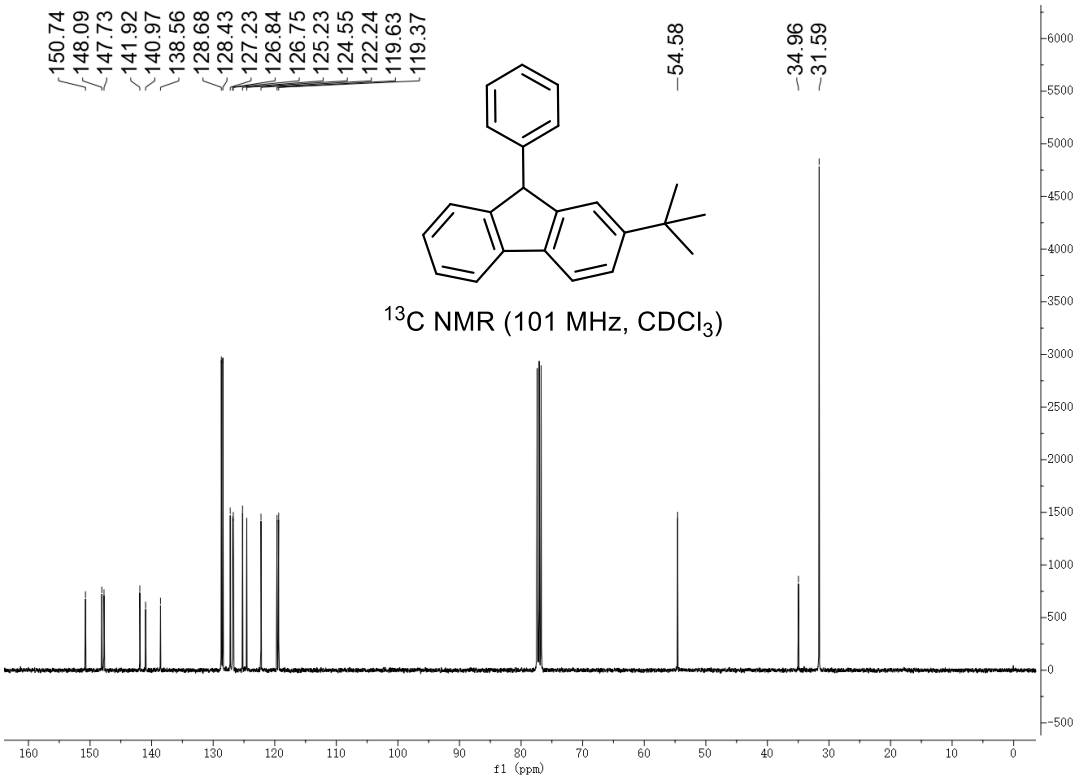


^{13}C NMR (151 MHz, $CDCl_3$)

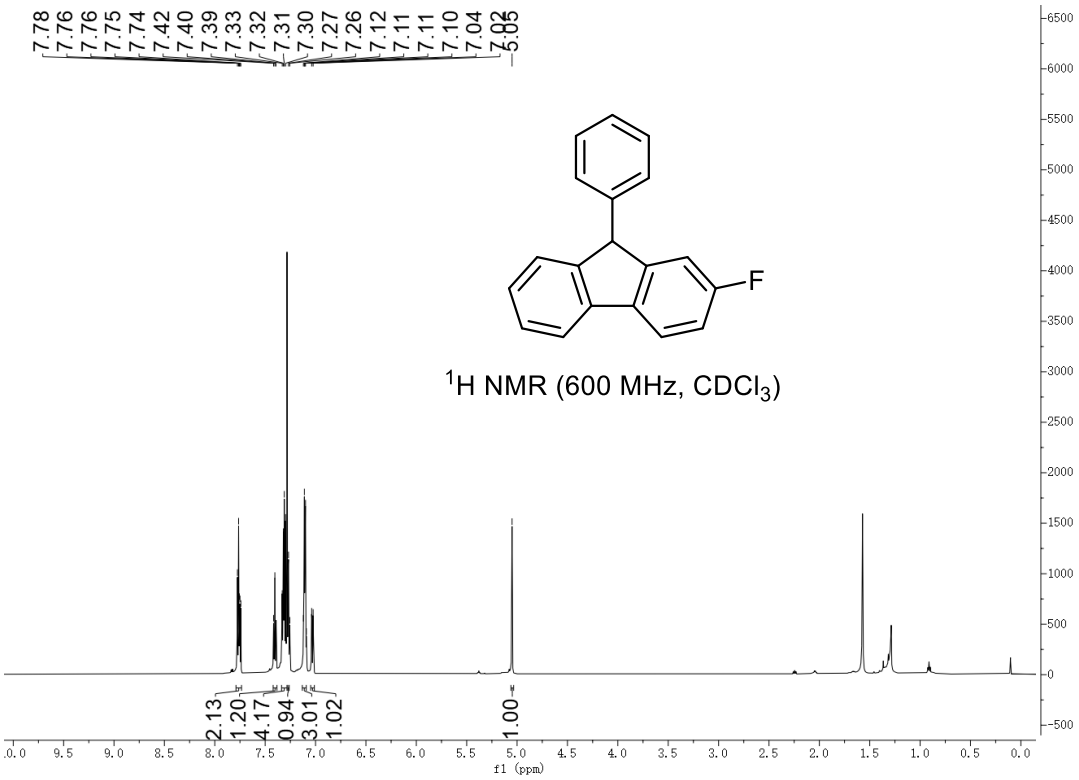
^{13}C NMR Spectrum of 3ba (151 MHz, $CDCl_3$)



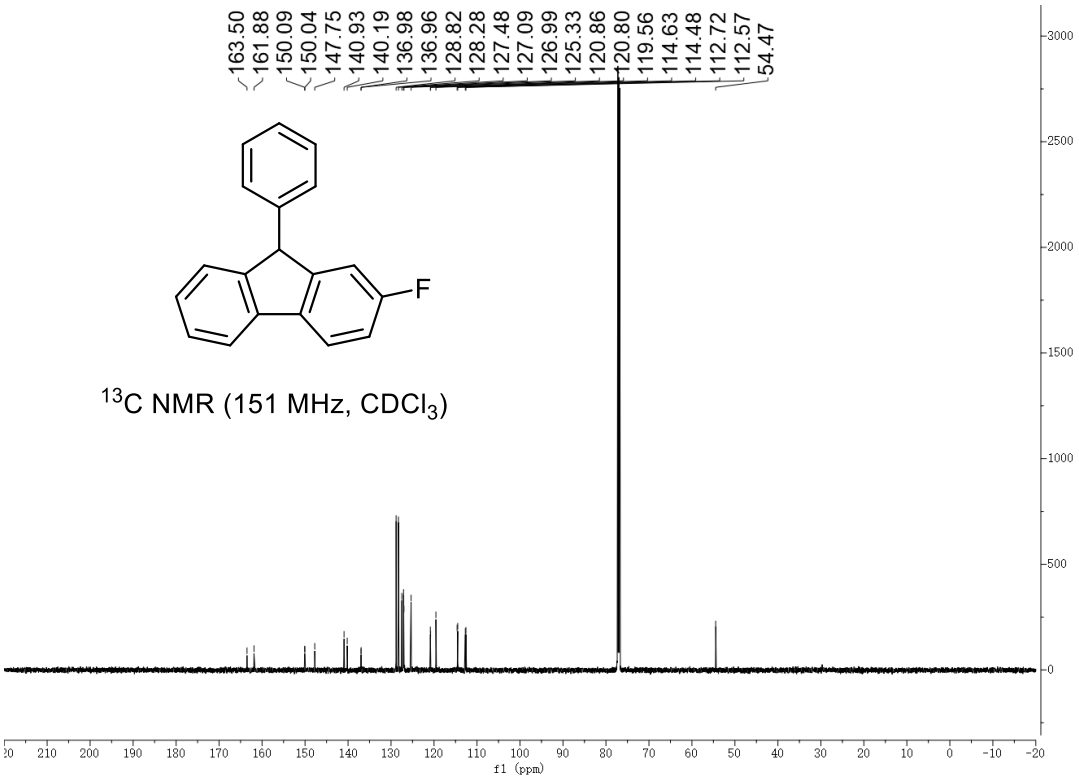
^{1}H NMR Spectrum of 3ca (600 MHz, $CDCl_3$)



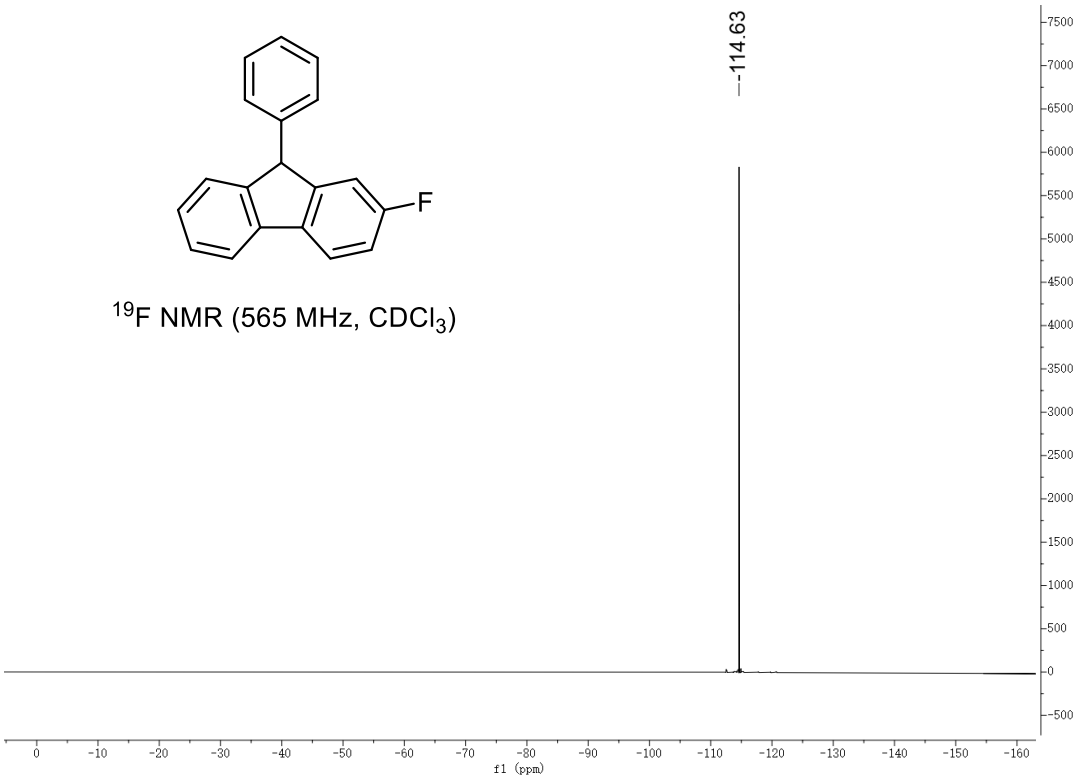
^{13}C NMR Spectrum of 3ca (101 MHz, $CDCl_3$)



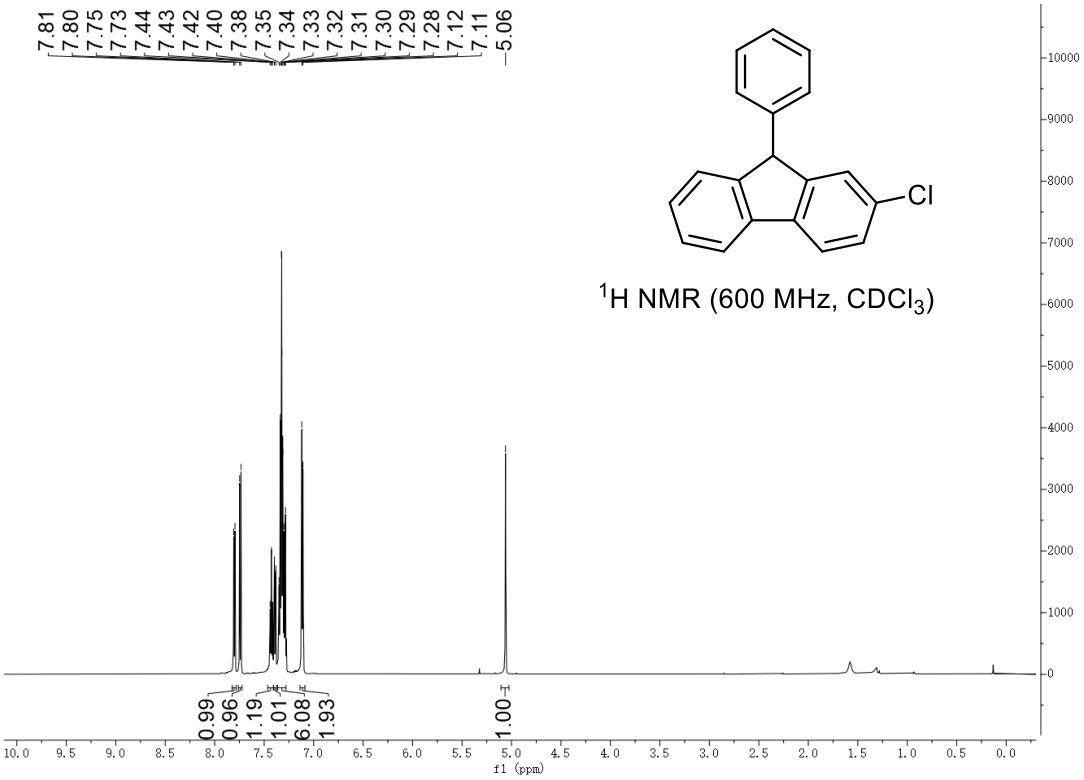
^{1}H NMR Spectrum of 3da (600 MHz, $CDCl_3$)



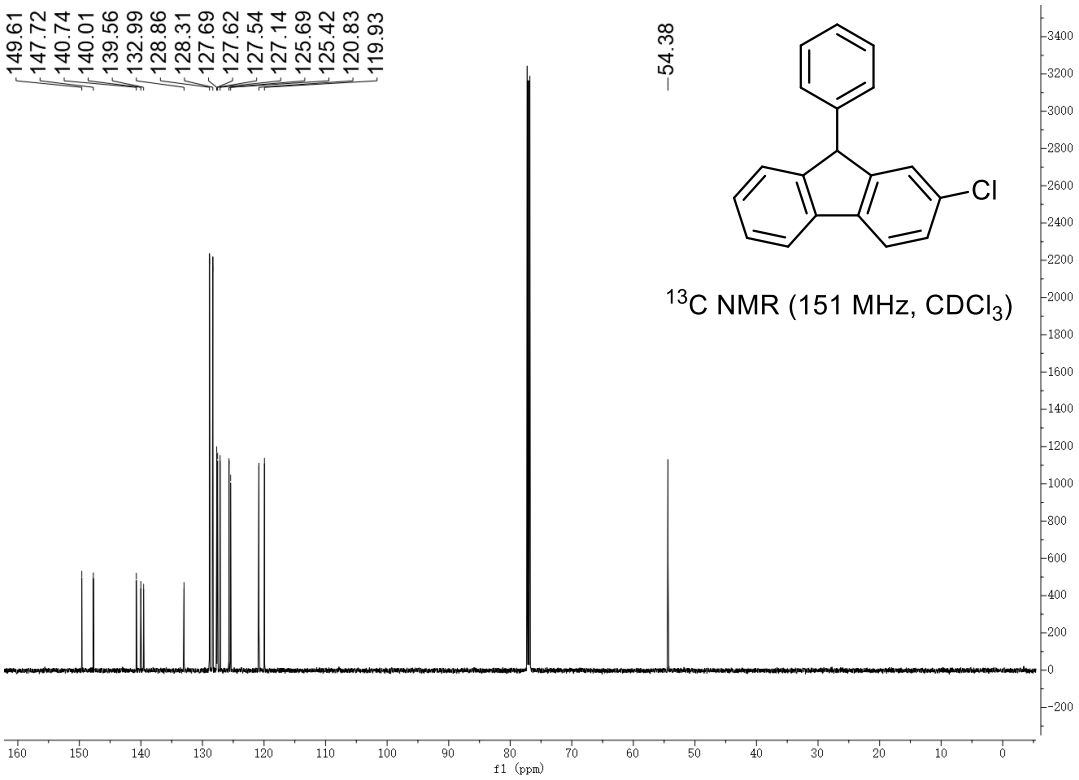
^{13}C NMR Spectrum of 3da (151 MHz, $CDCl_3$)



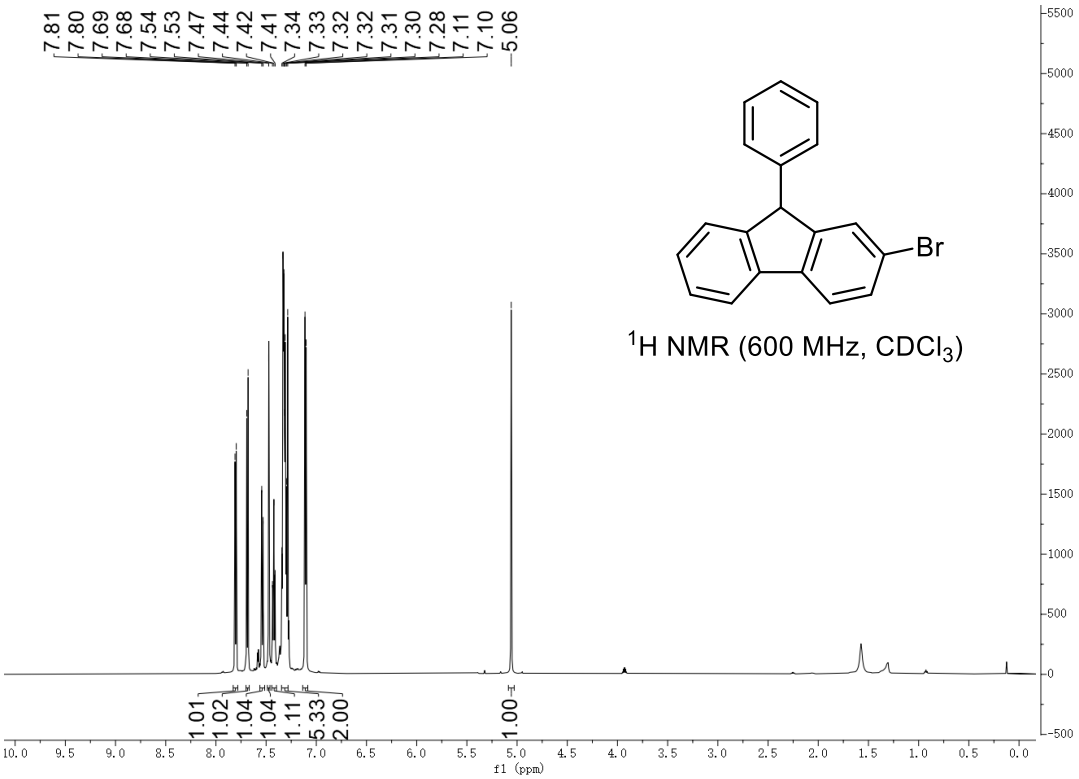
^{19}F NMR Spectrum of 3da (565 MHz, $CDCl_3$)



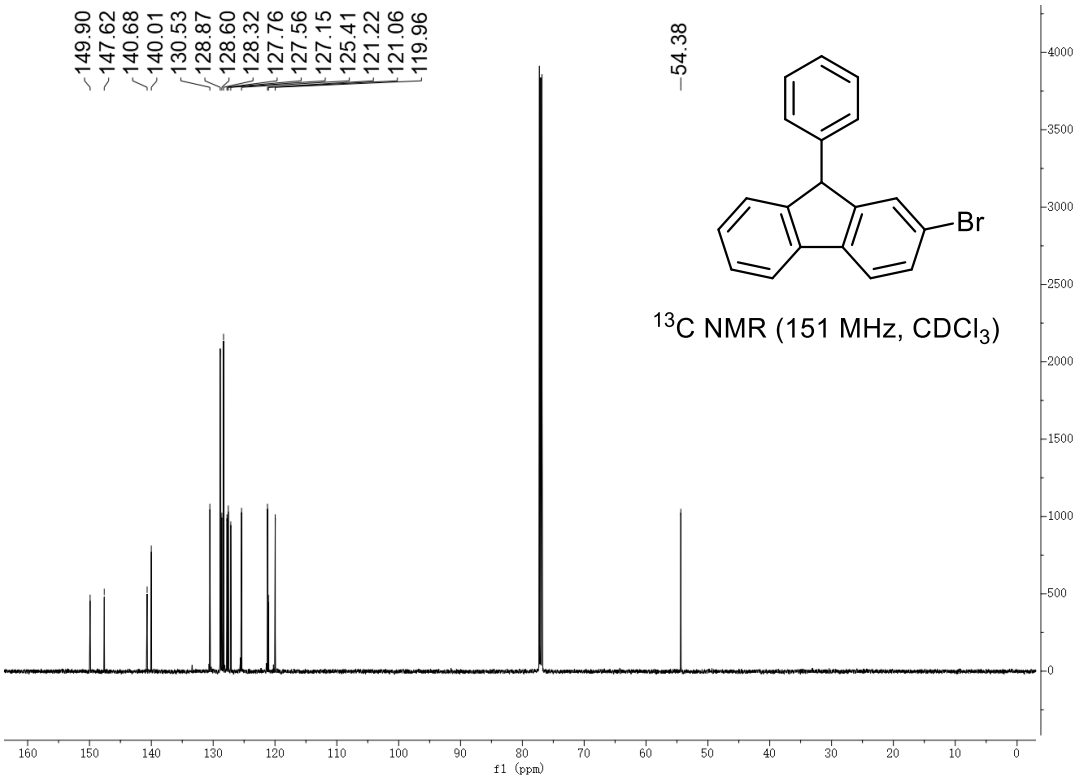
^{1}H NMR Spectrum of 3ea (600 MHz, $CDCl_3$)



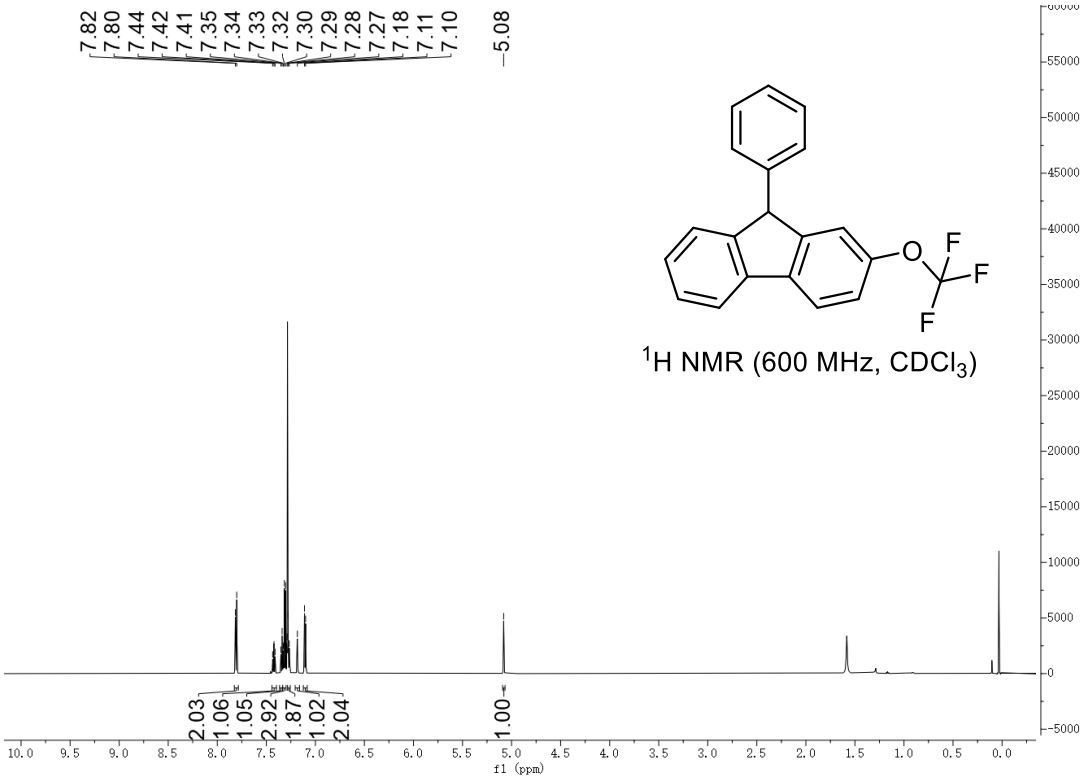
^{13}C NMR Spectrum of 3ea (151 MHz, $CDCl_3$)



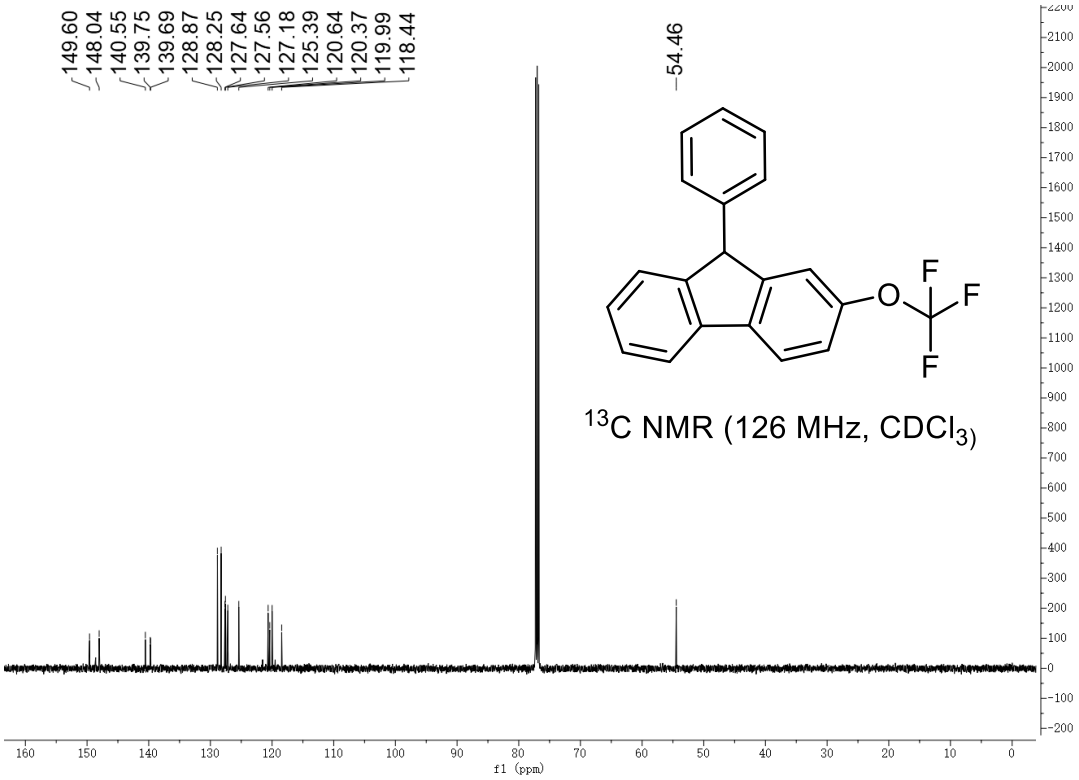
^{1}H NMR Spectrum of 3fa (600 MHz, $CDCl_3$)



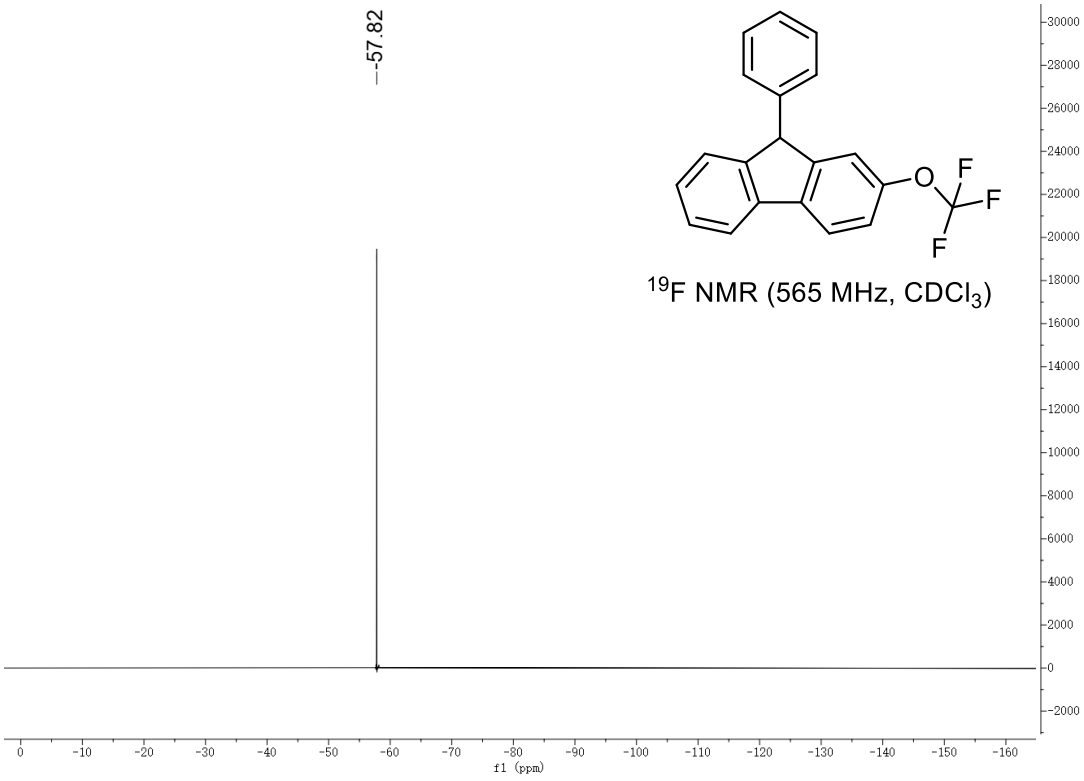
^{13}C NMR Spectrum of 3fa (151 MHz, $CDCl_3$)



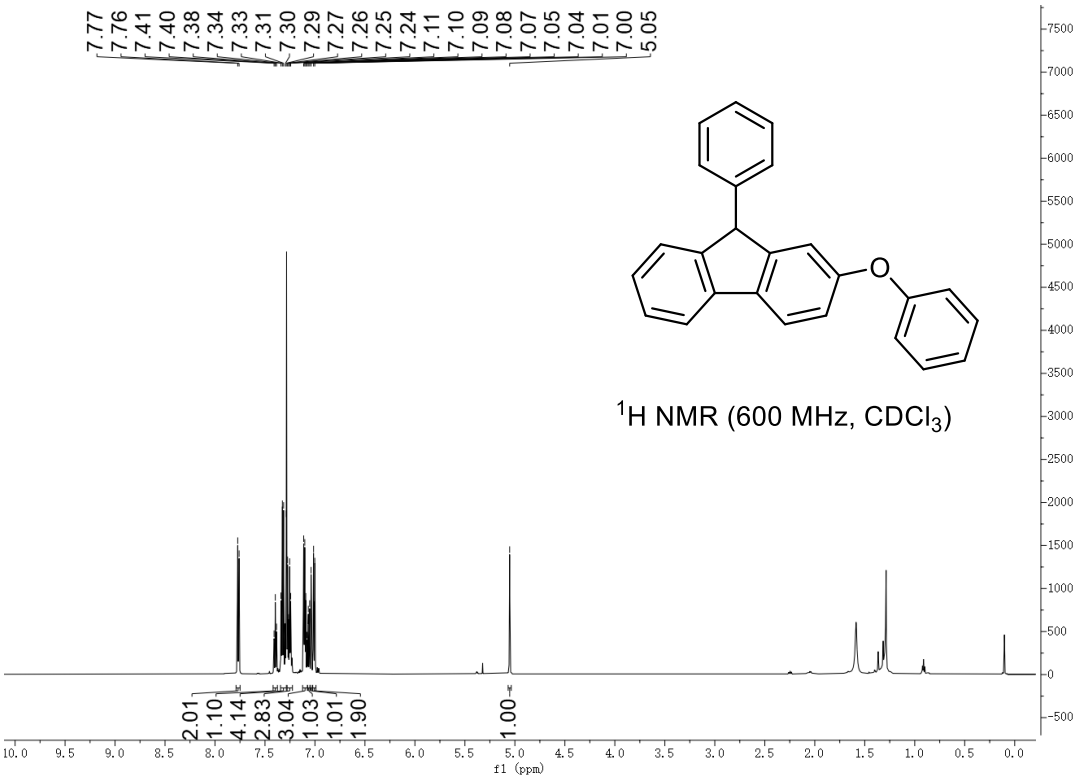
^{1}H NMR Spectrum of 3ga (600 MHz, $CDCl_3$)



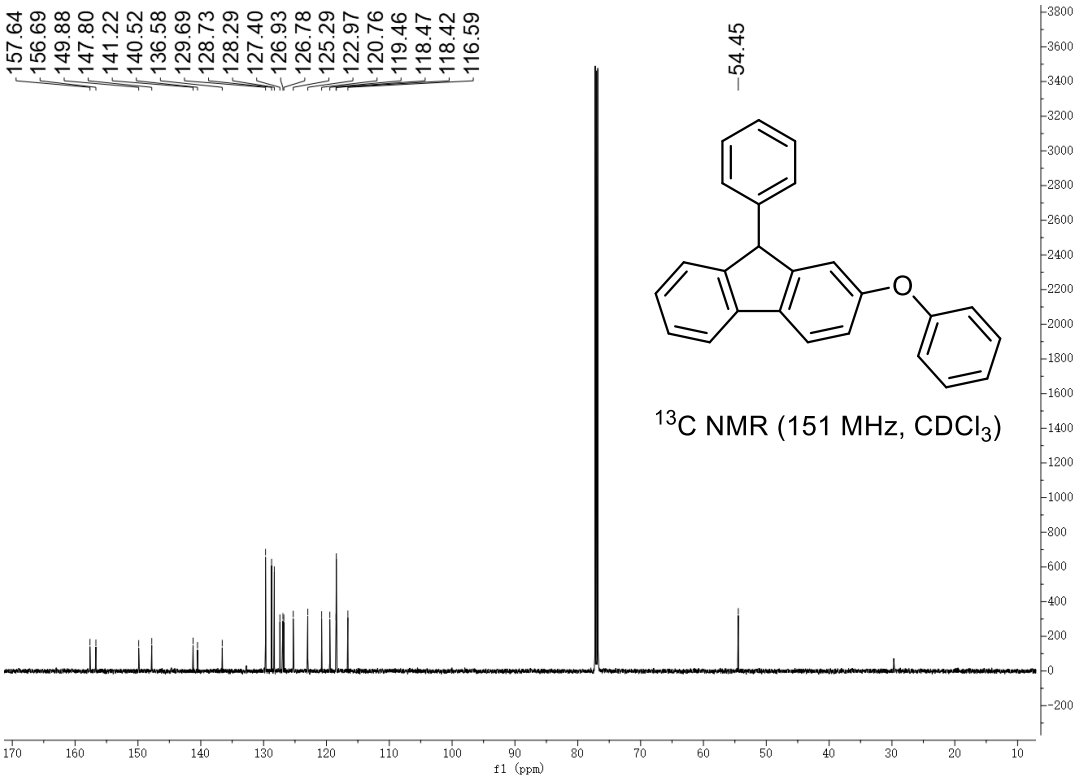
^{13}C NMR Spectrum of 3ga (121 MHz, $CDCl_3$)



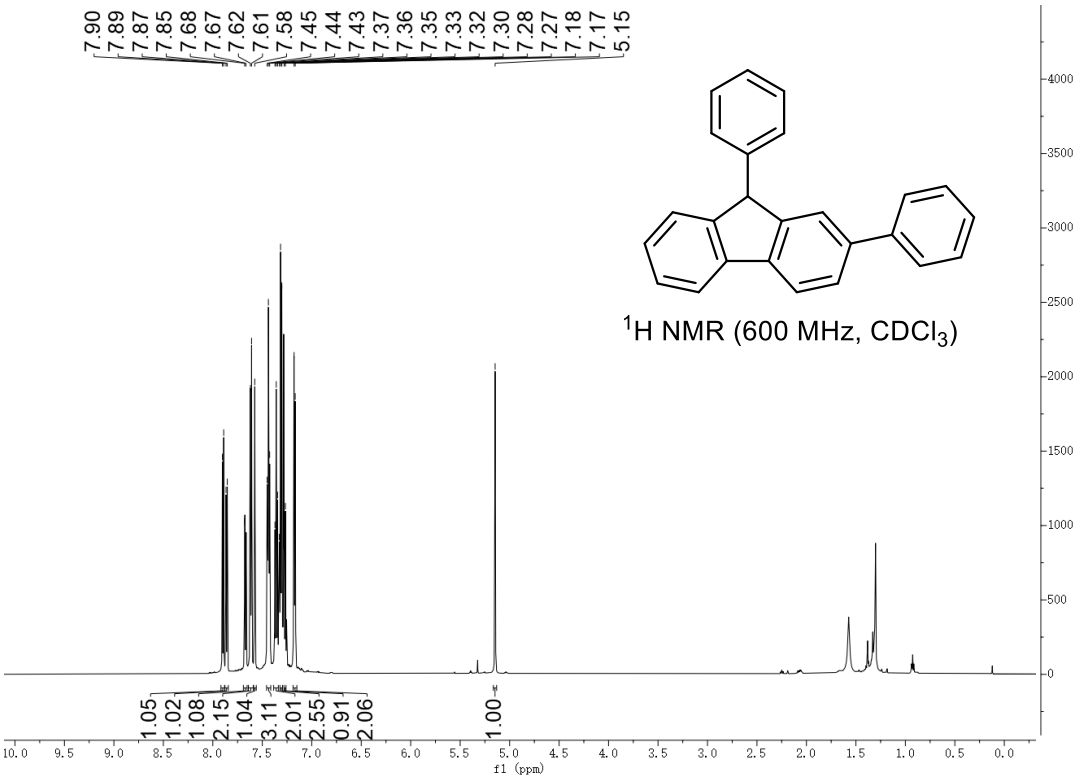
^{19}F NMR Spectrum of 3ga (600 MHz, $CDCl_3$)



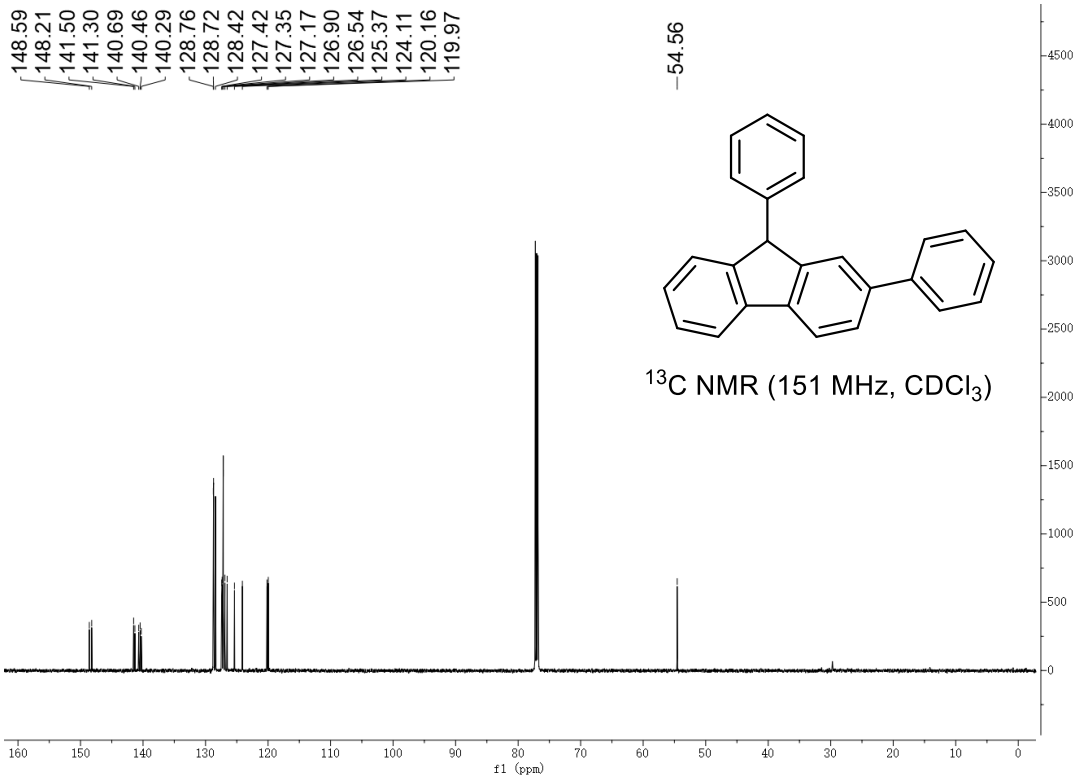
^{1}H NMR Spectrum of 3ha (600 MHz, $CDCl_3$)



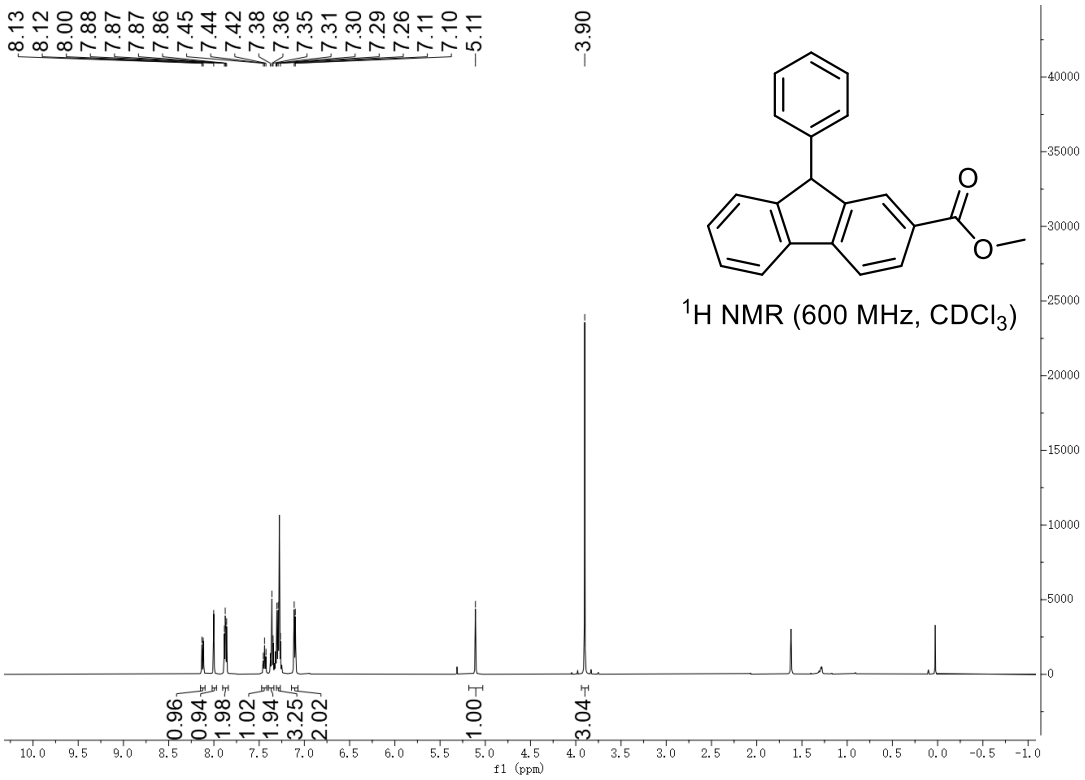
^{13}C NMR Spectrum of 3ha (151 MHz, $CDCl_3$)



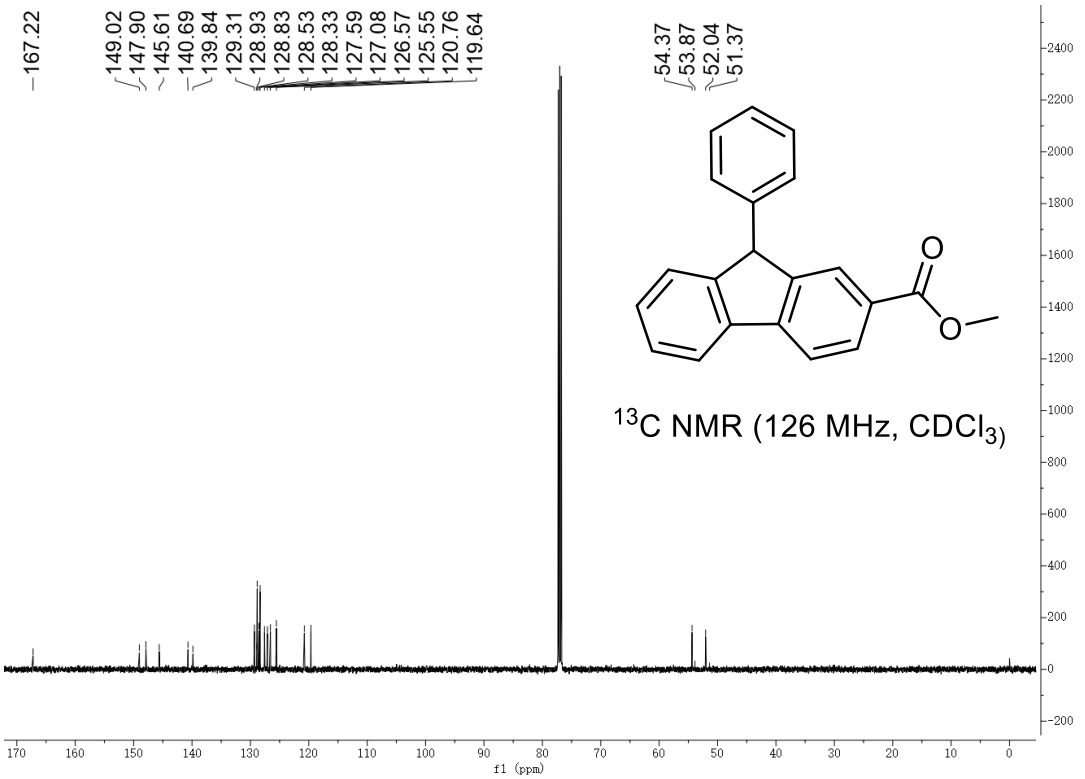
^{1}H NMR Spectrum of 3ia (600 MHz, $CDCl_3$)



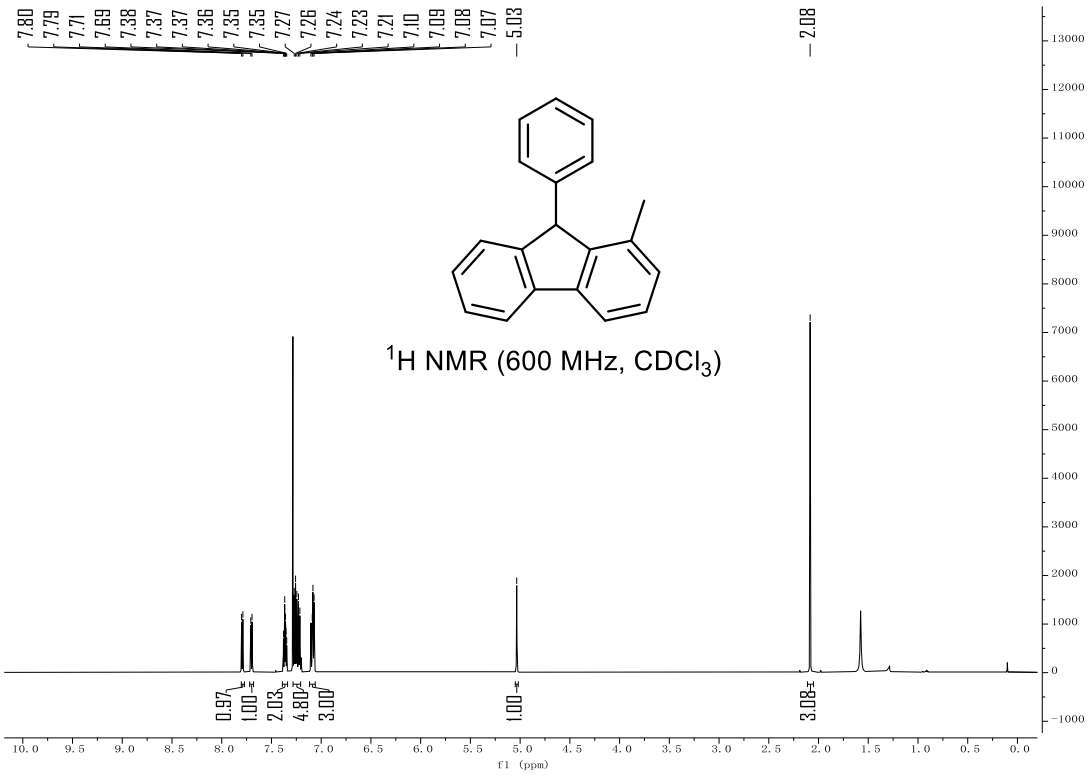
^{13}C NMR Spectrum of 3ia (151 MHz, $CDCl_3$)



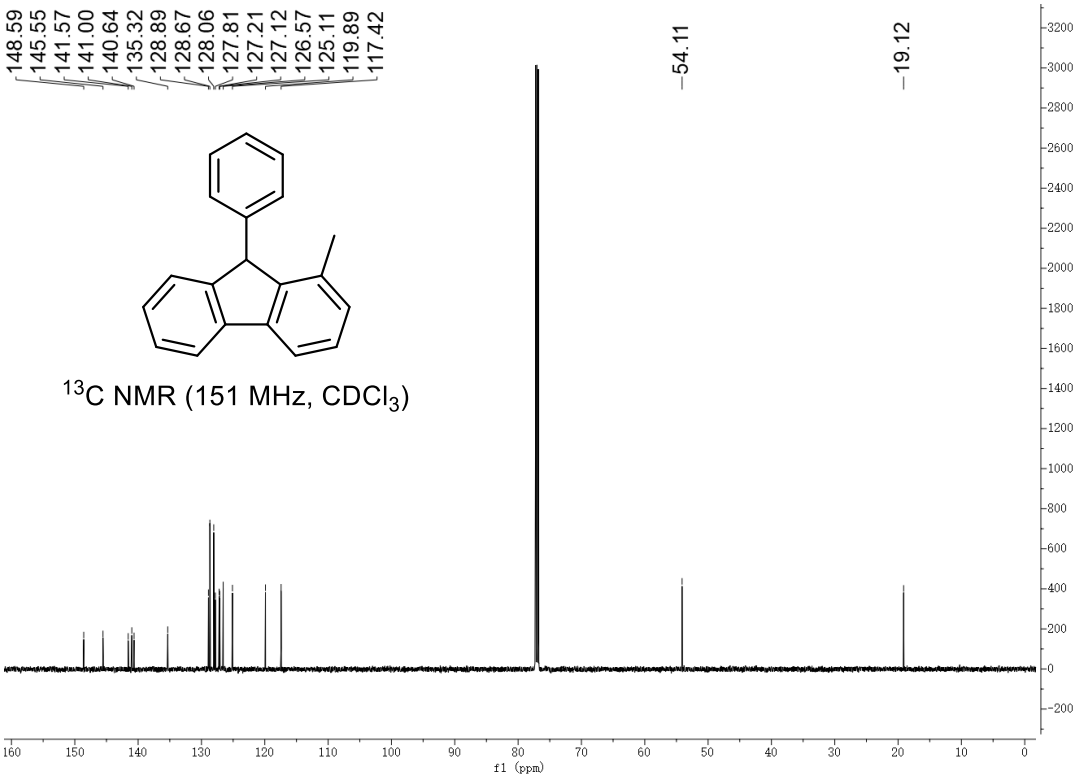
^{1}H NMR Spectrum of 3ja (600 MHz, $CDCl_3$)



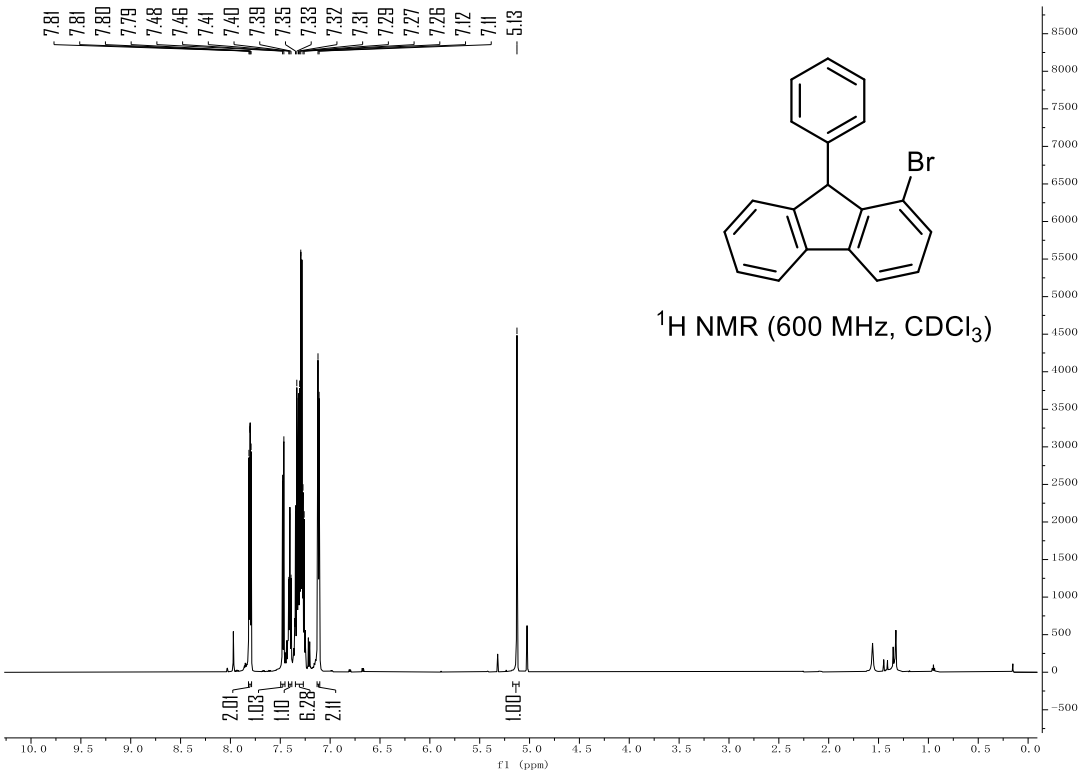
^{13}C NMR Spectrum of 3ja (126 MHz, $CDCl_3$)



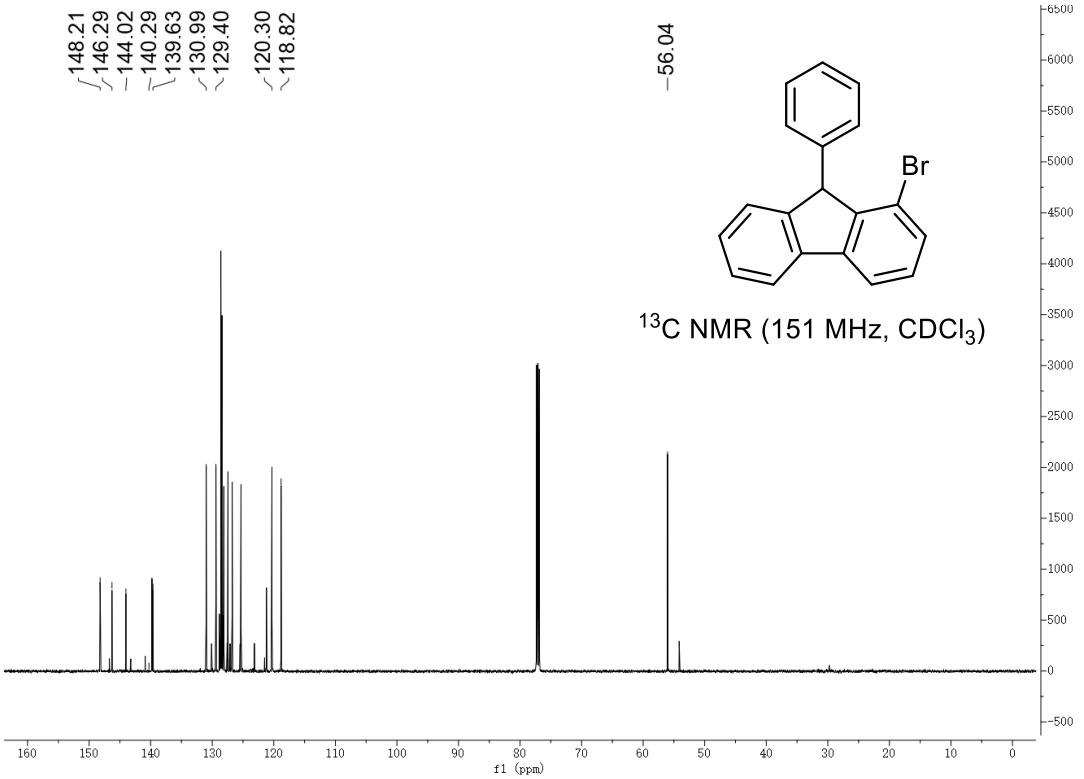
^{1}H NMR Spectrum of 3ka (600 MHz, $CDCl_3$)



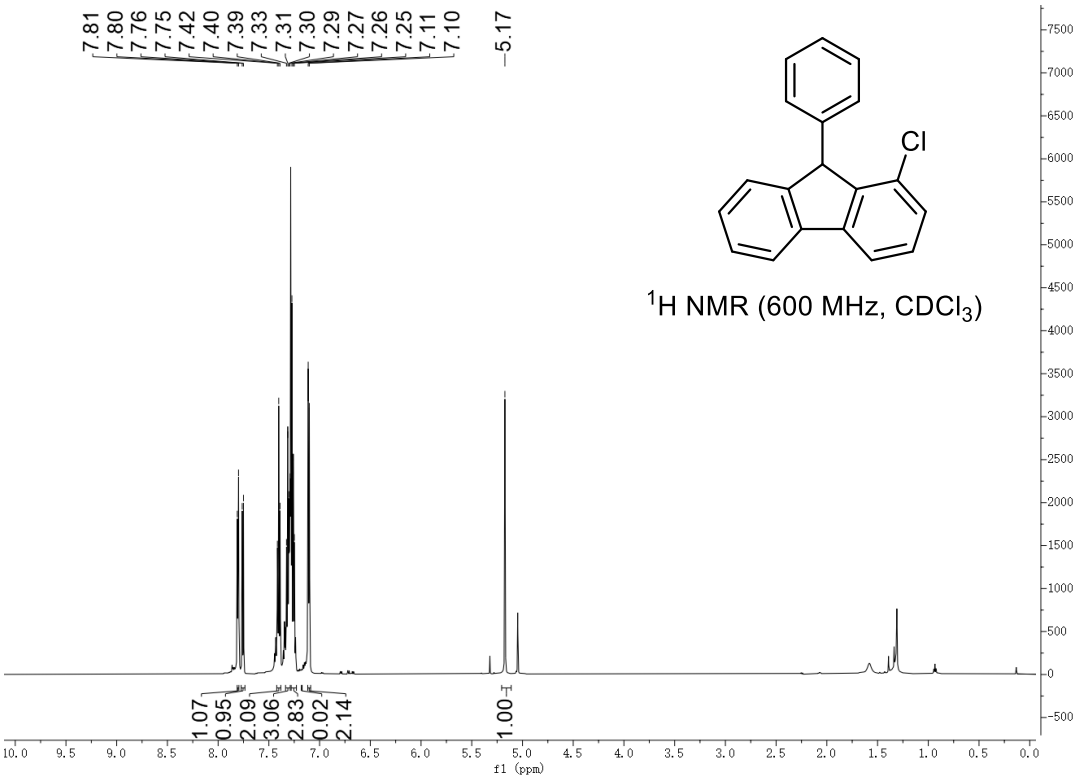
^{13}C NMR Spectrum of 3ka (151 MHz, $CDCl_3$)



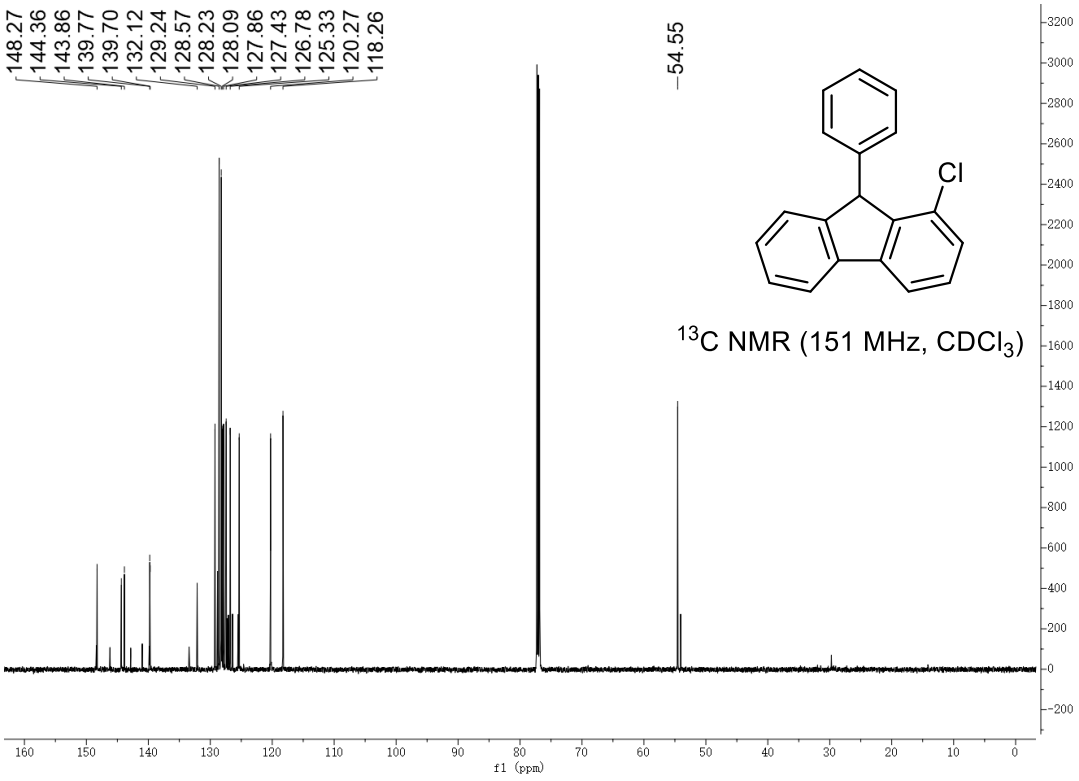
^{1}H NMR Spectrum of 3la (600 MHz, $CDCl_3$)



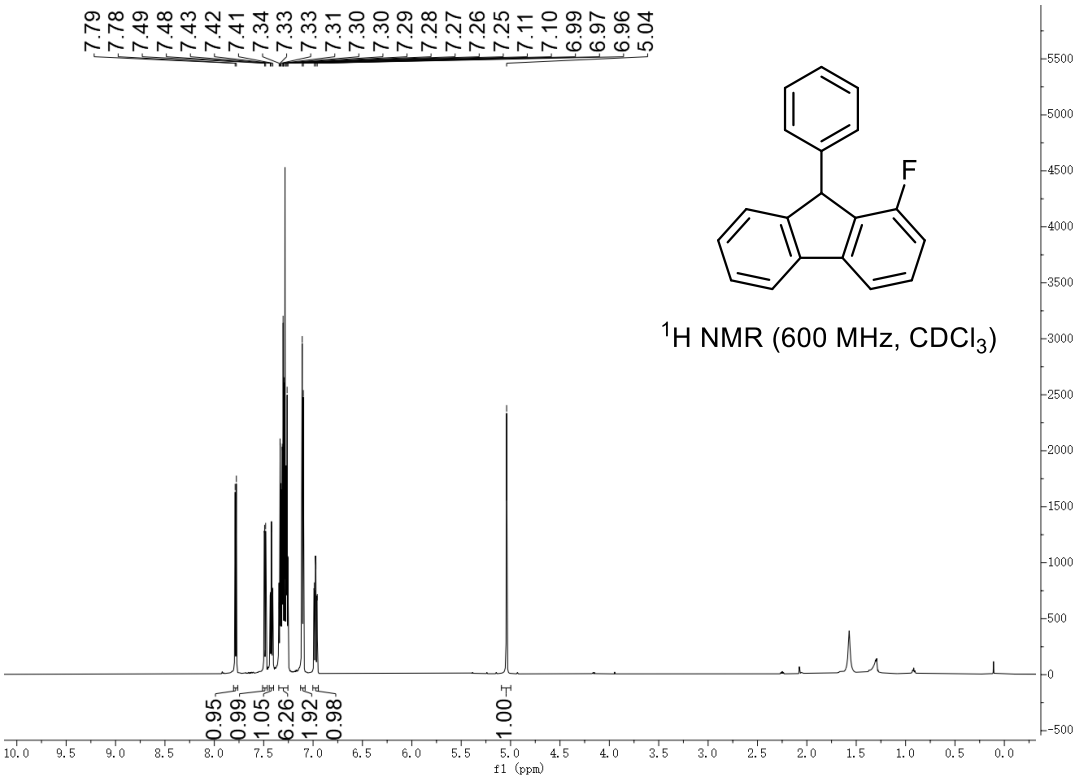
^{13}C NMR Spectrum of 3la (151 MHz, $CDCl_3$)



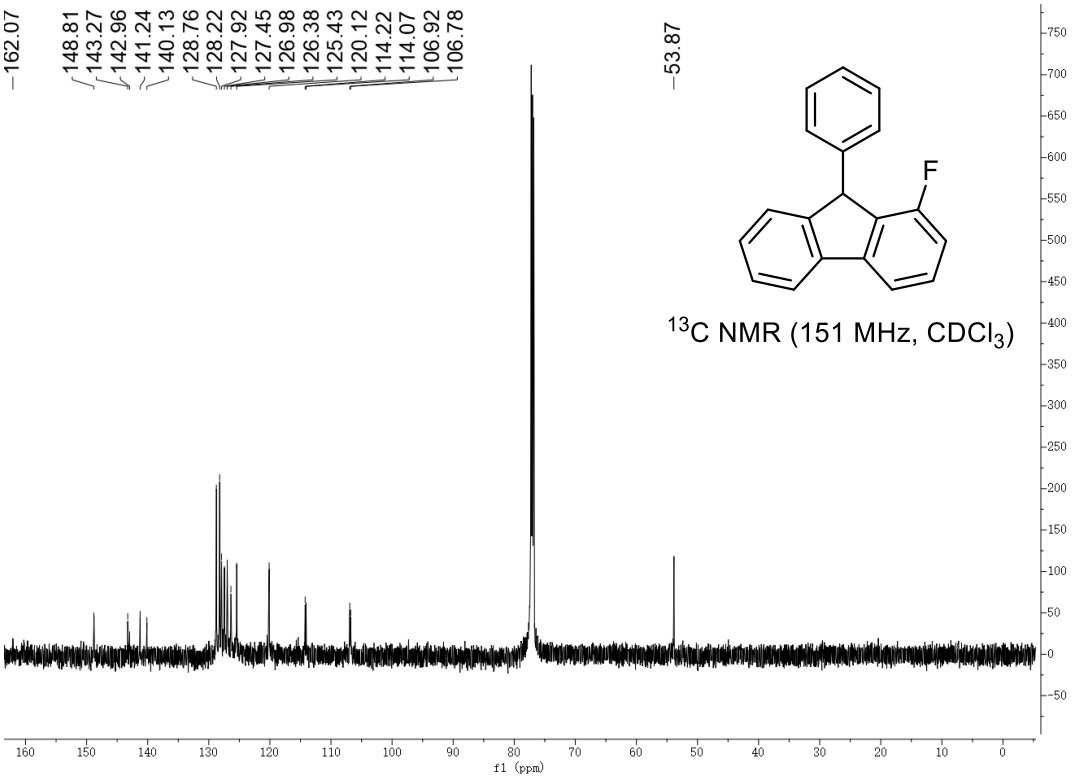
^{1}H NMR Spectrum of 3ma (600 MHz, $CDCl_3$)



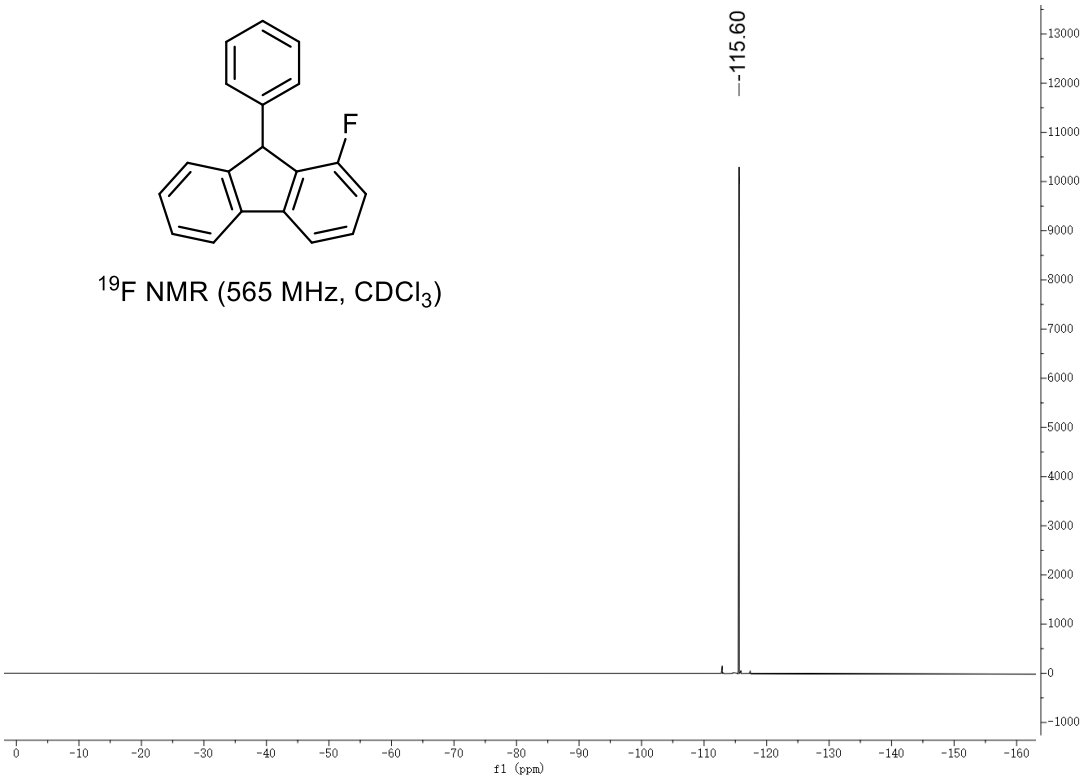
^{13}C NMR Spectrum of 3ma (151 MHz, $CDCl_3$)



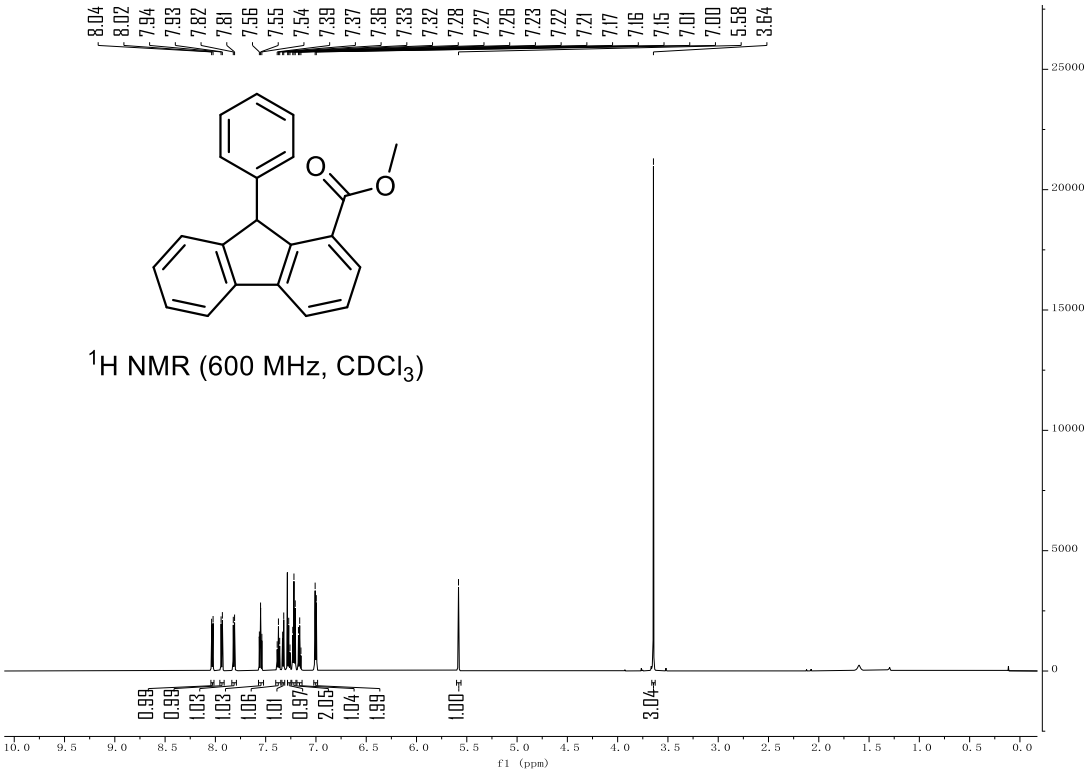
^{1}H NMR Spectrum of 3na (600 MHz, CDCl$_3$)



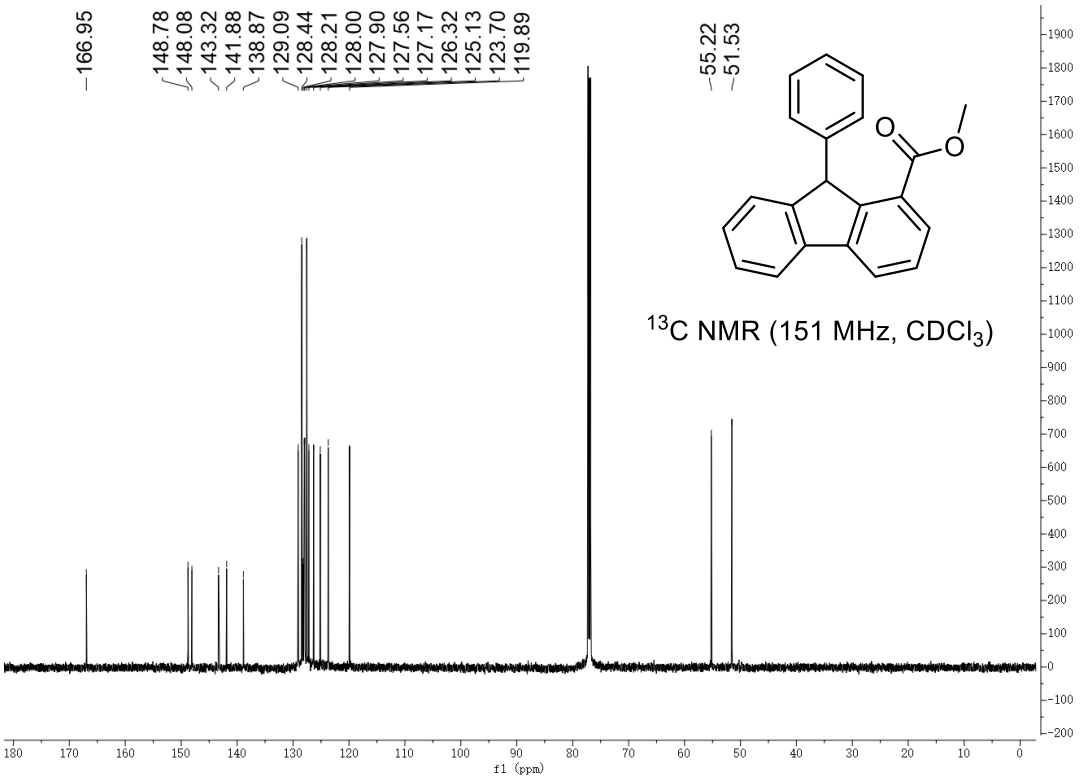
^{13}C NMR Spectrum of 3na (151 MHz, CDCl$_3$)



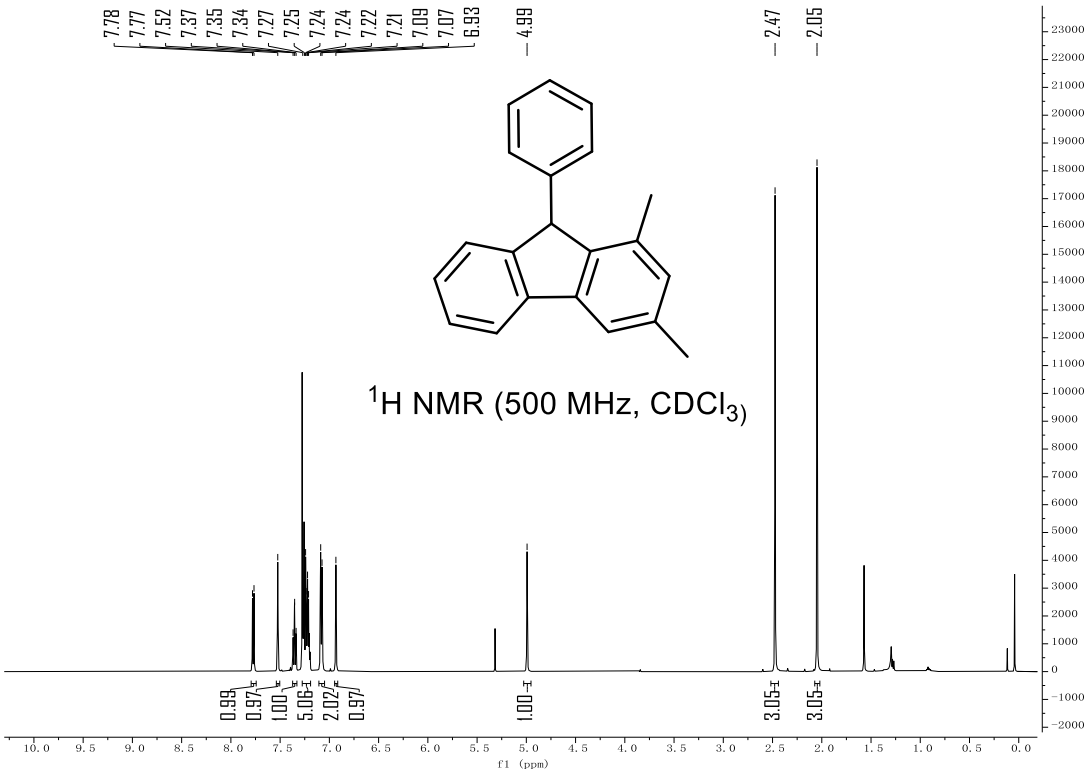
^{19}F NMR Spectrum of 3na (565 MHz, CDCl$_3$)



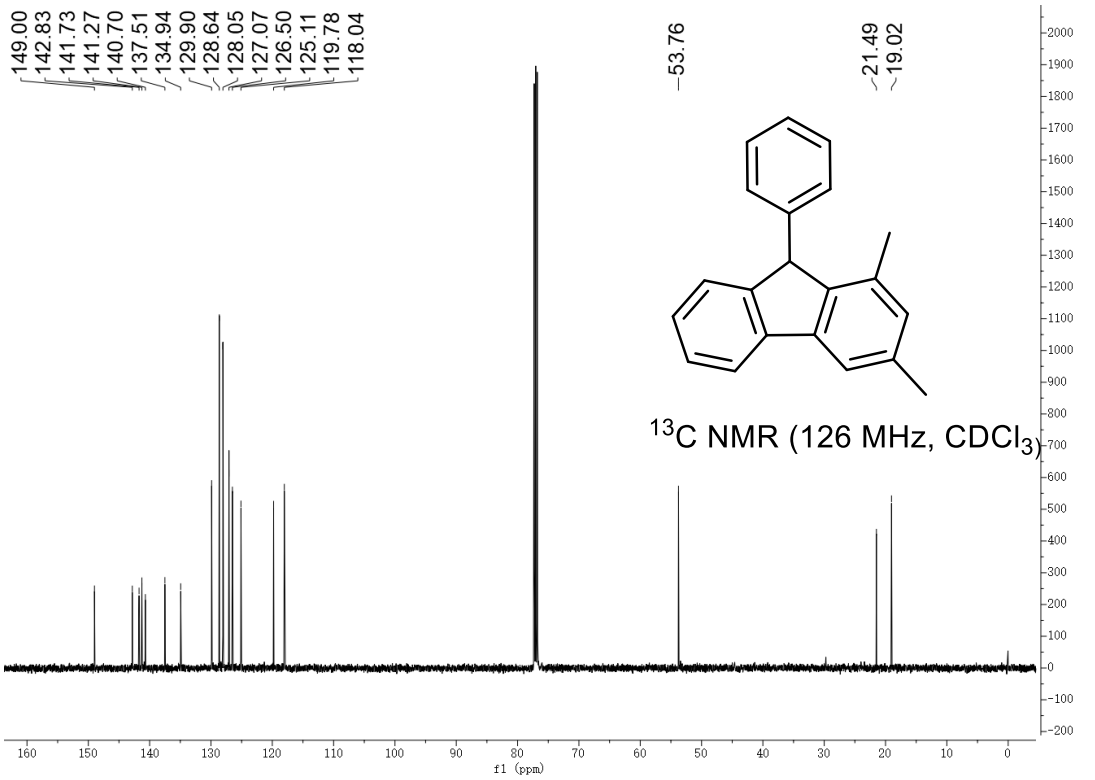
^{1}H NMR Spectrum of 3oa (600 MHz, CDCl$_3$)



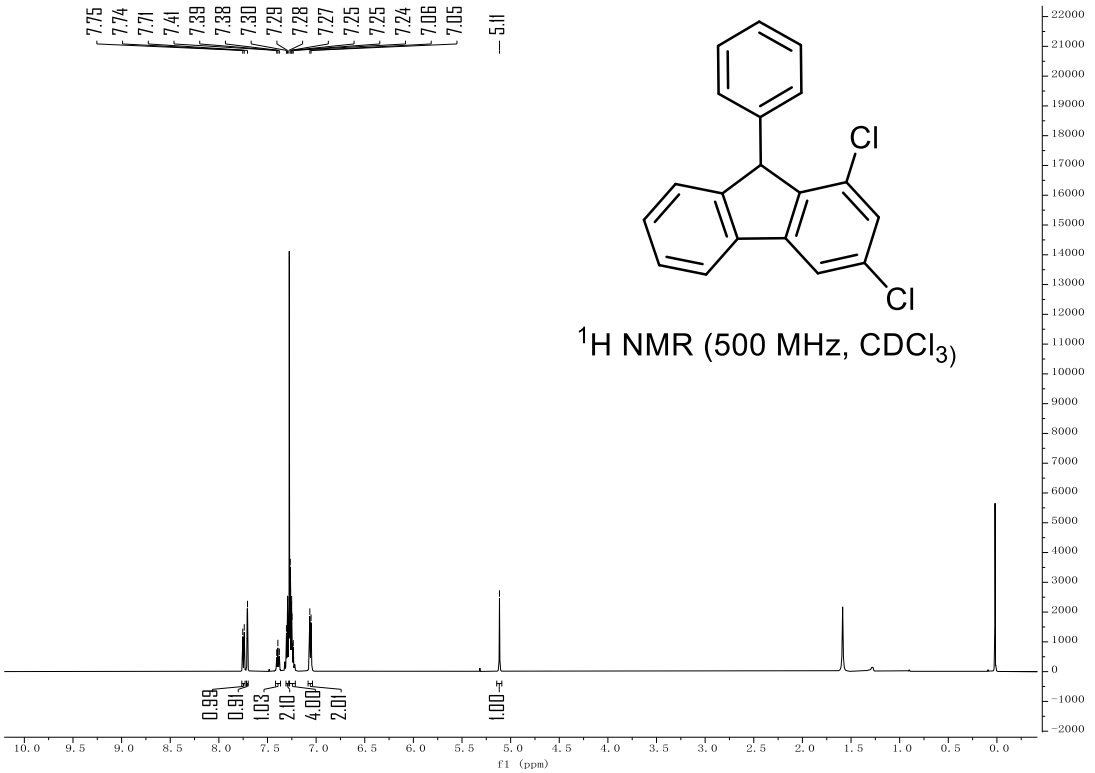
^{13}C NMR Spectrum of 3oa (151 MHz, $CDCl_3$)



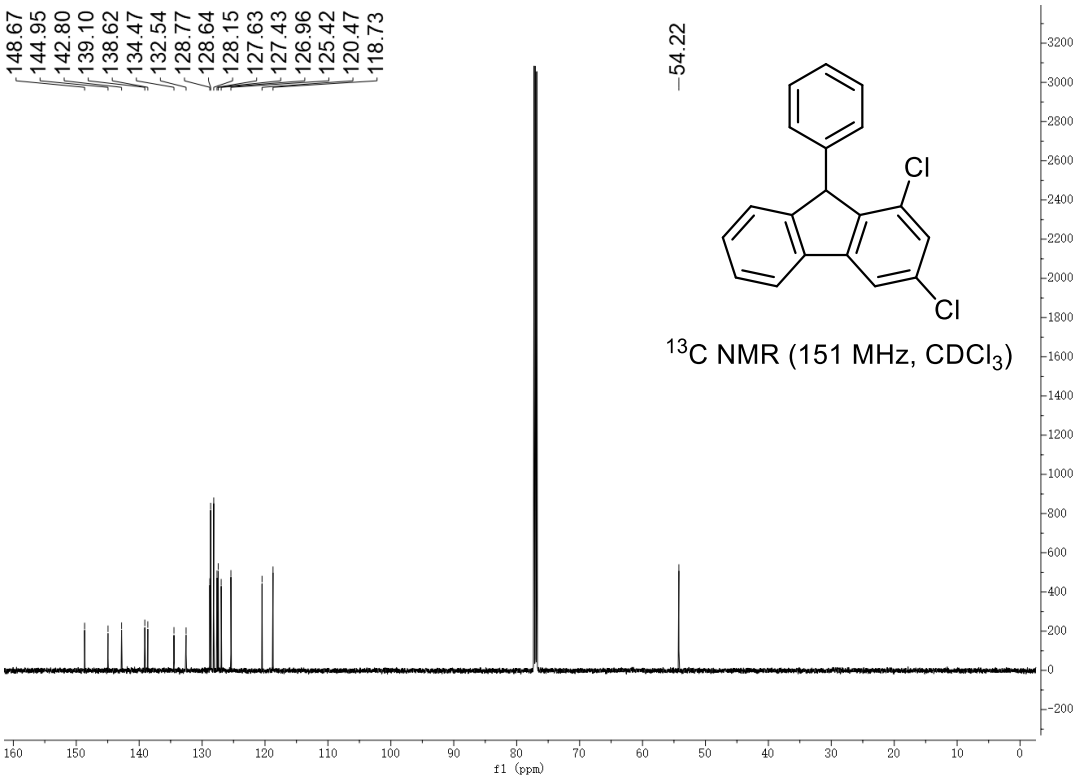
^{1}H NMR Spectrum of 3pa (500 MHz, $CDCl_3$)



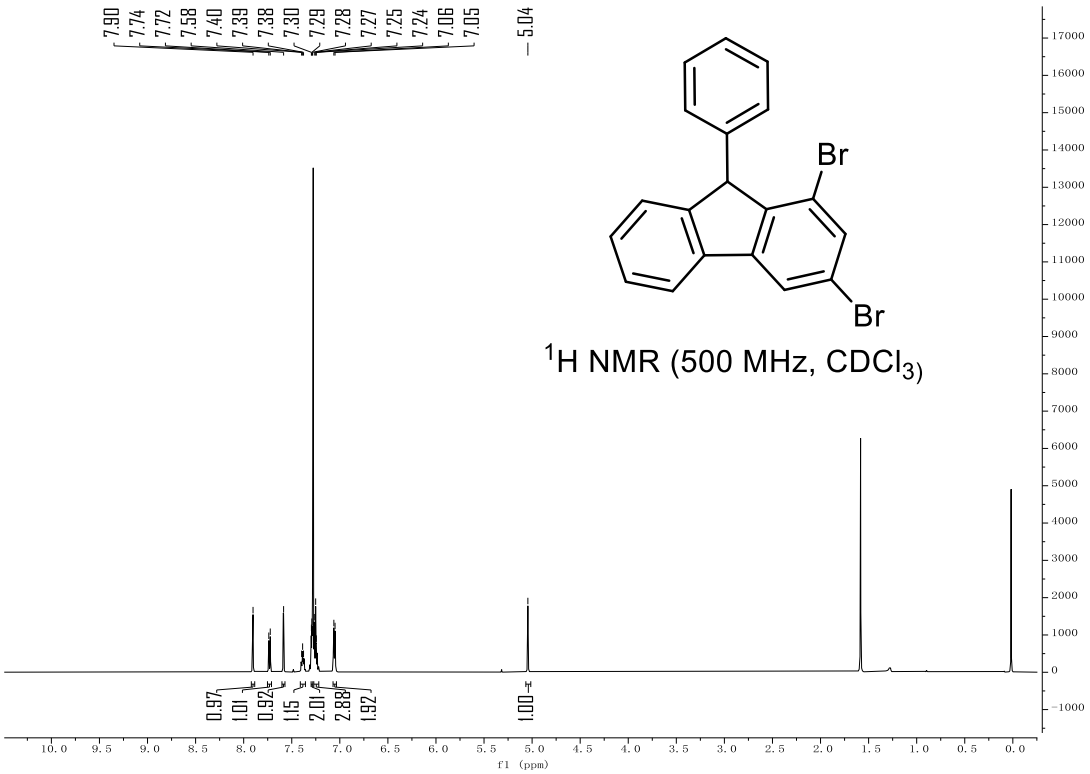
^{13}C NMR Spectrum of 3pa (126 MHz, $CDCl_3$)



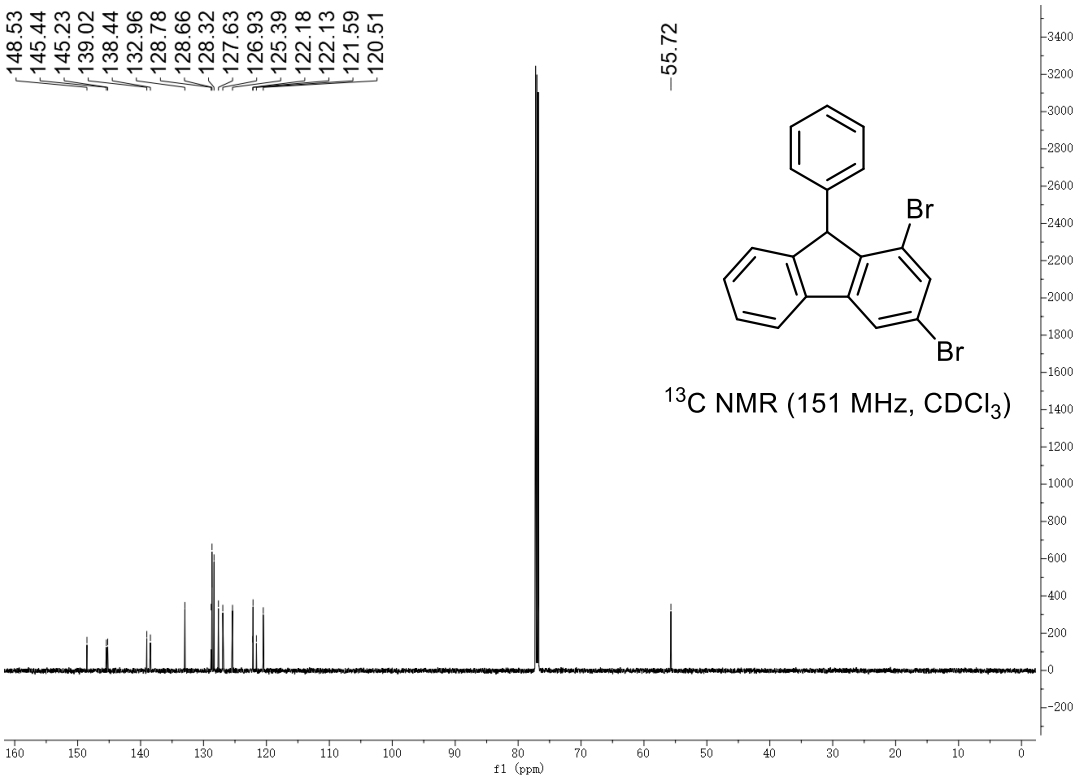
^{1}H NMR Spectrum of 3qa (500 MHz, $CDCl_3$)



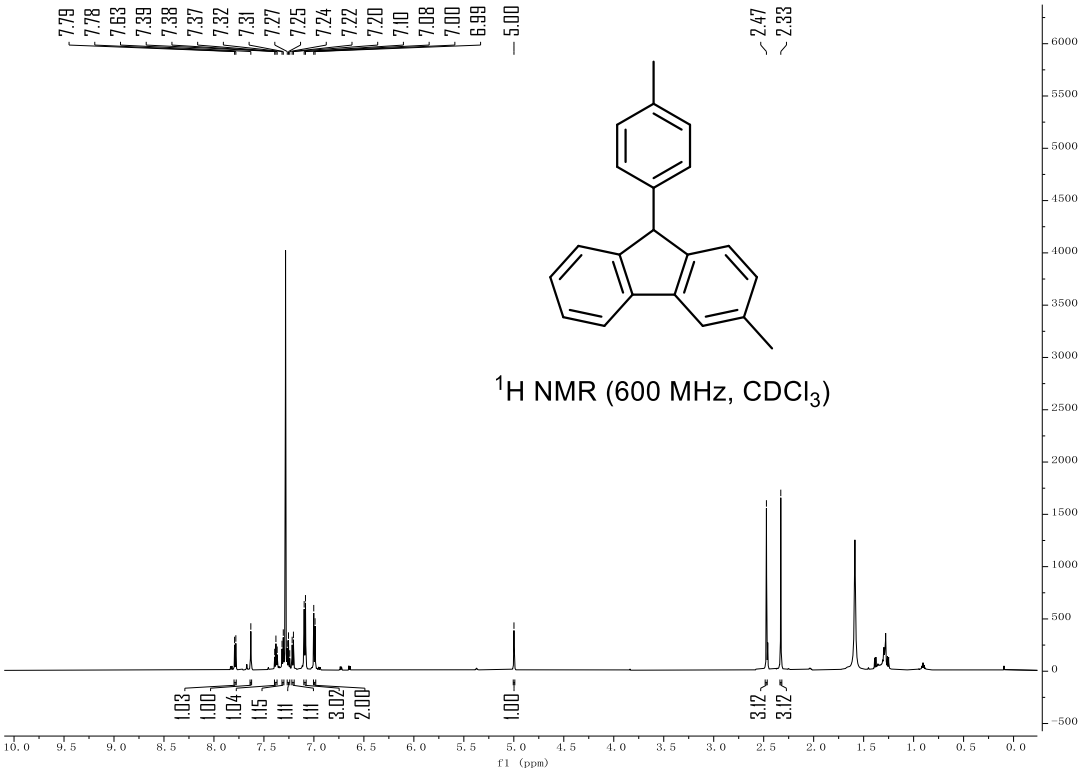
^{13}C NMR Spectrum of 3qa (151 MHz, $CDCl_3$)



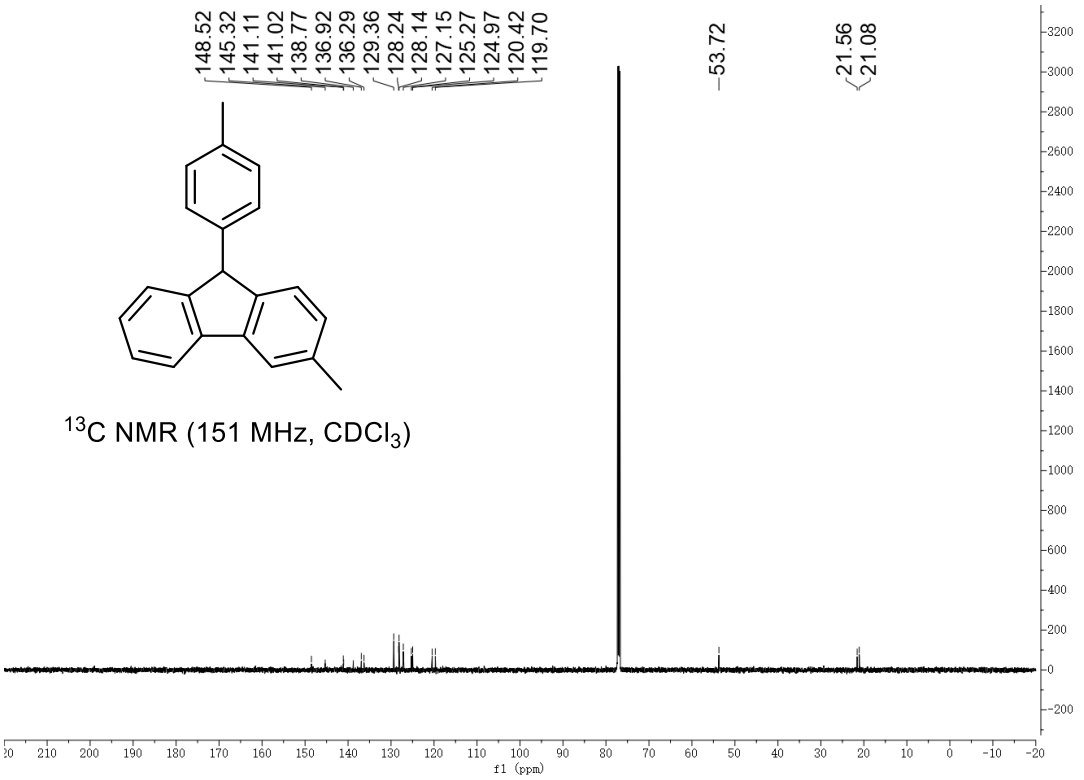
^{1}H NMR Spectrum of 3ra (500 MHz, $CDCl_3$)



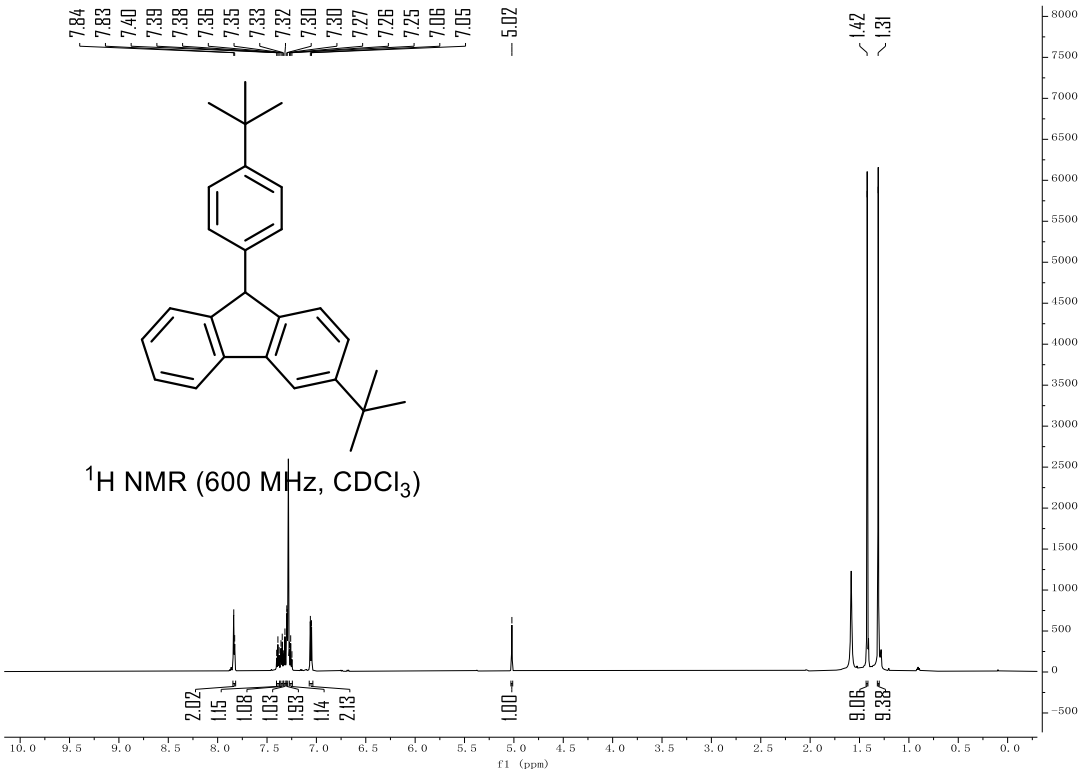
^{13}C NMR Spectrum of 3ra (151 MHz, $CDCl_3$)



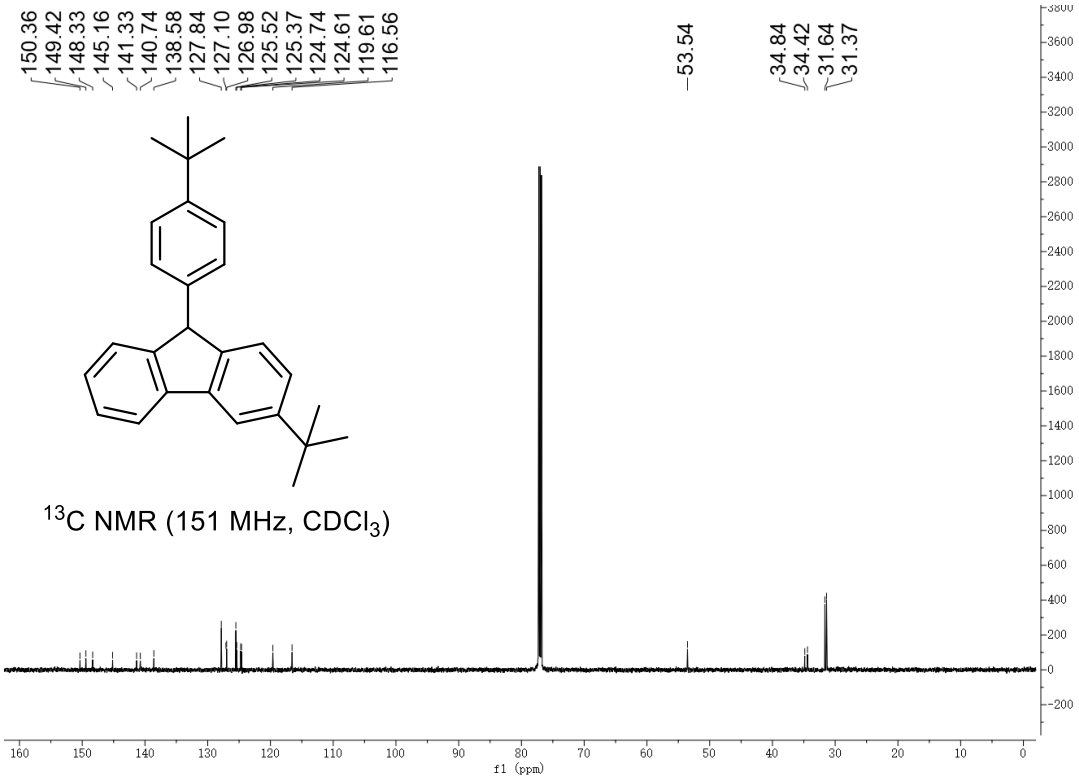
^{1}H NMR Spectrum of 3ab (600 MHz, $CDCl_3$)



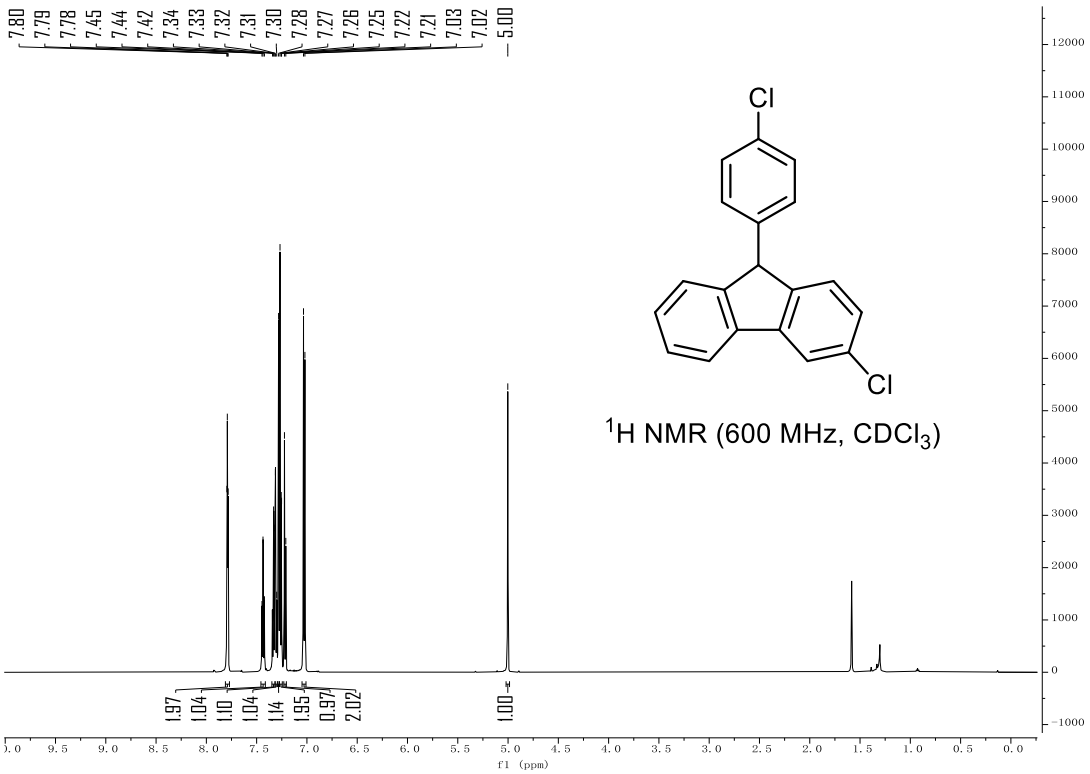
^{13}C NMR Spectrum of 3ab (151 MHz, $CDCl_3$)



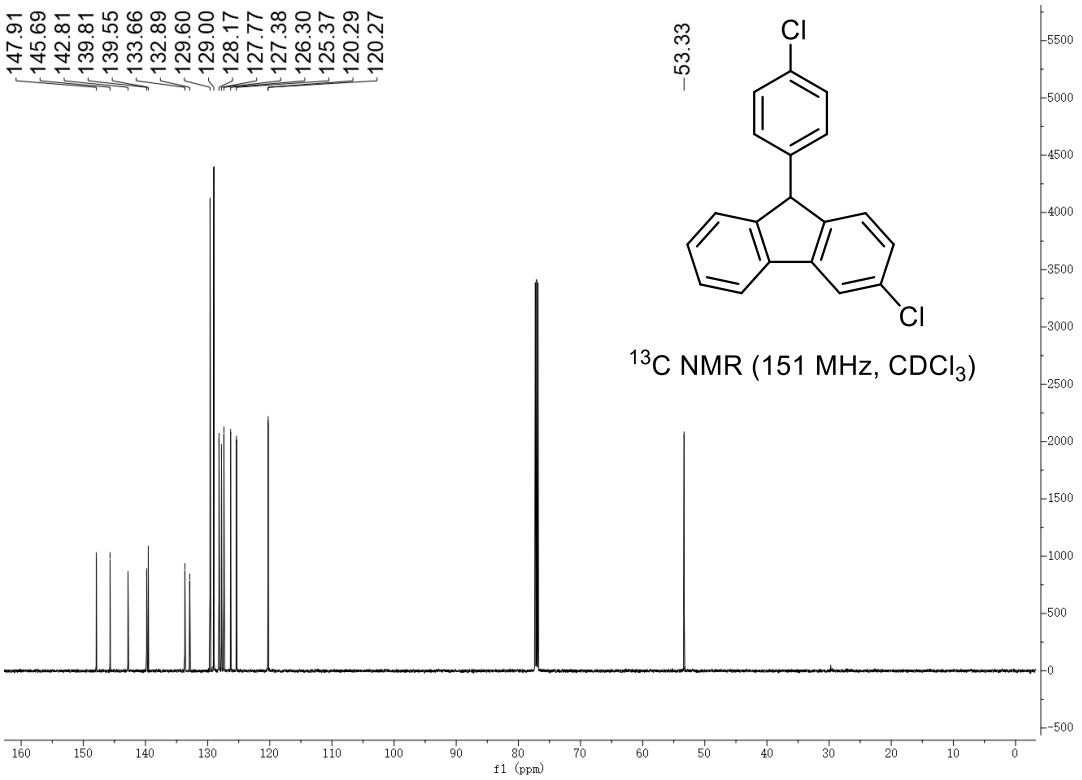
^{1}H NMR Spectrum of 3ac (600 MHz, $CDCl_3$)



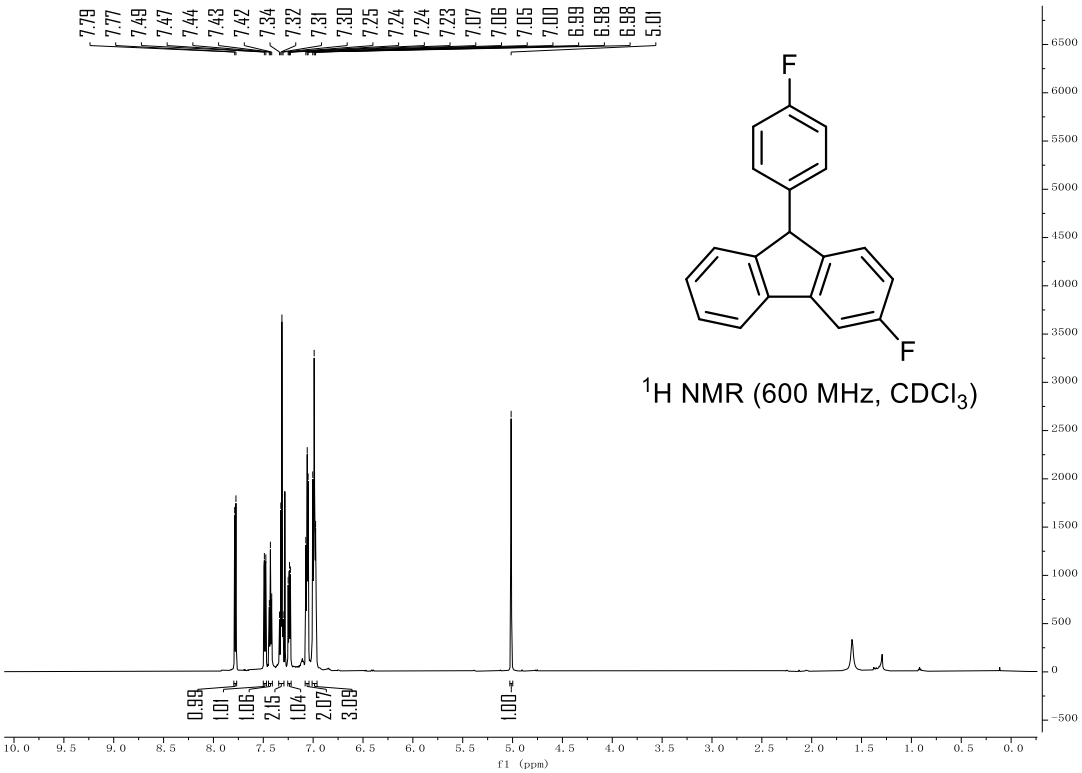
^{13}C NMR Spectrum of 3ac (151 MHz, $CDCl_3$)



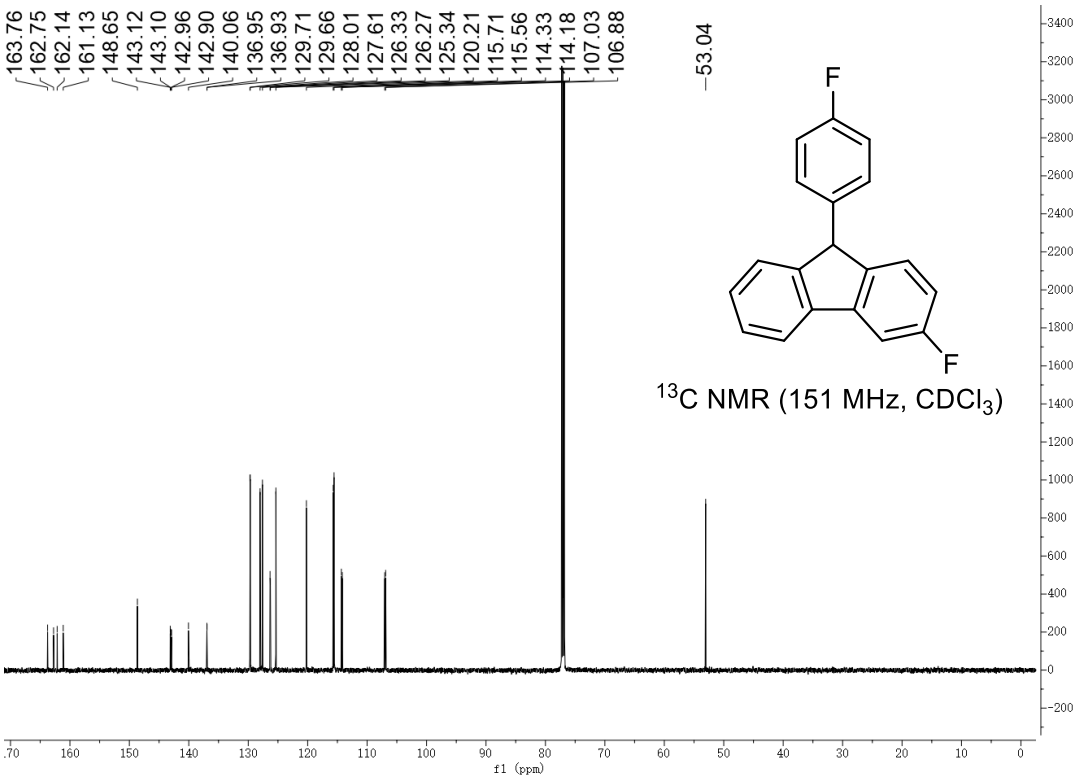
^{1}H NMR Spectrum of 3ad (600 MHz, $CDCl_3$)



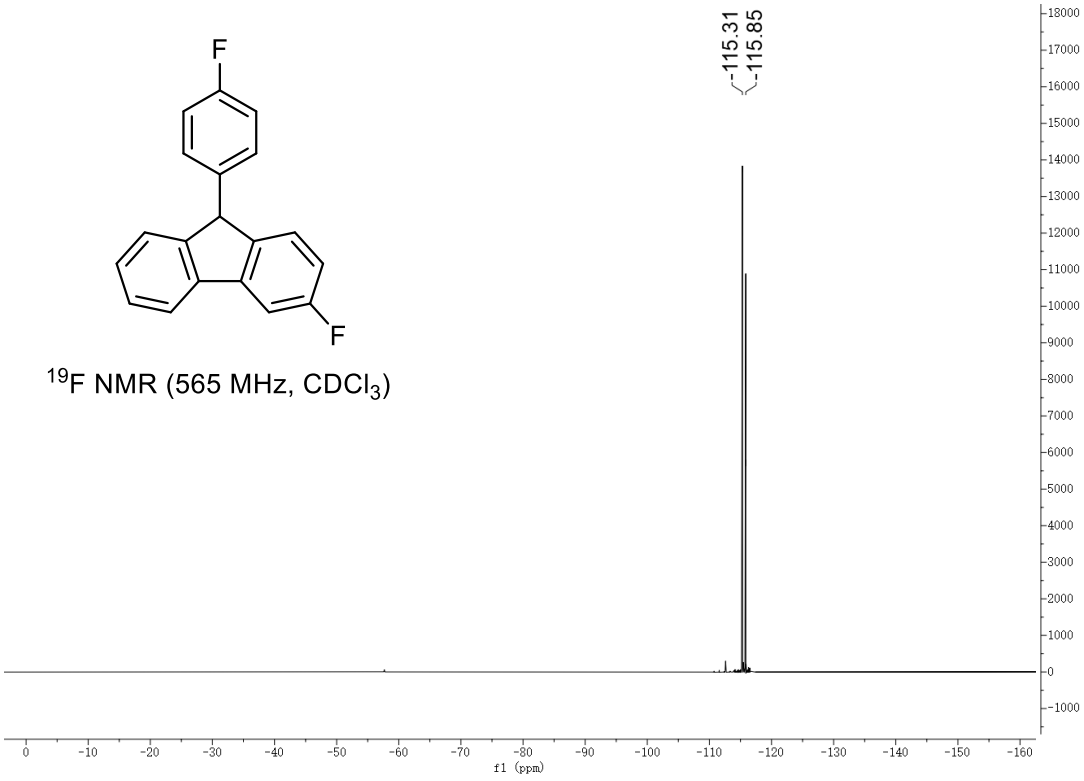
^{13}C NMR Spectrum of 3ad (151 MHz, $CDCl_3$)



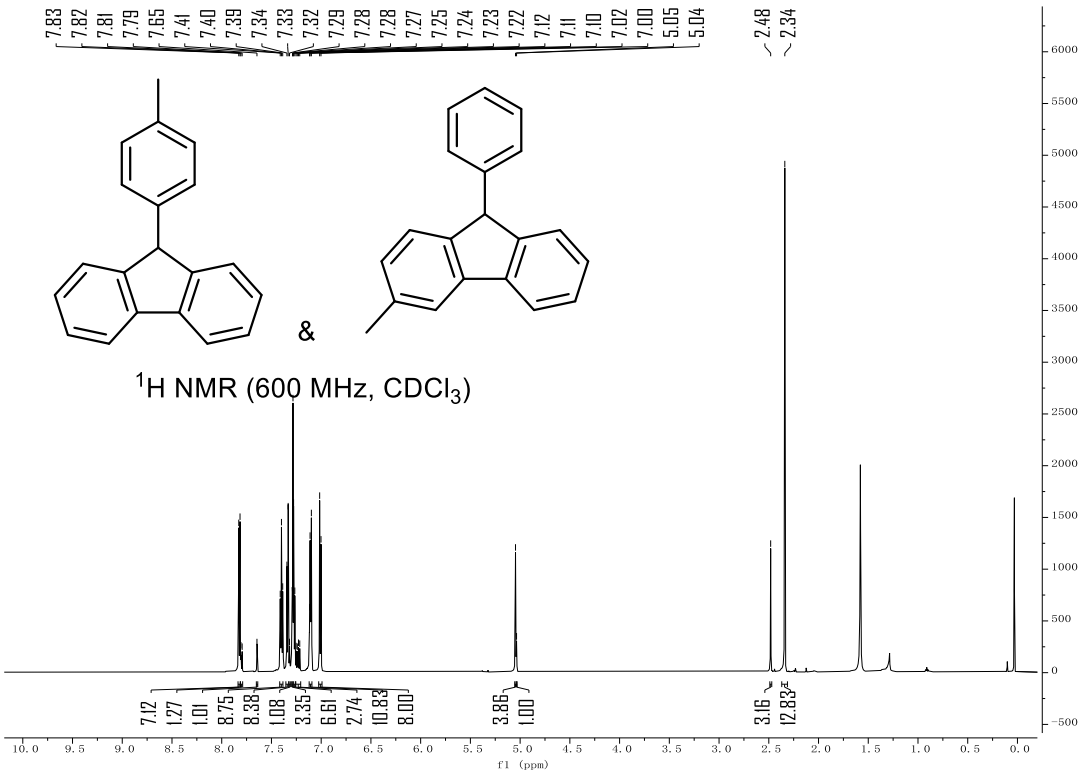
^{1}H NMR Spectrum of 3ae (600 MHz, $CDCl_3$)



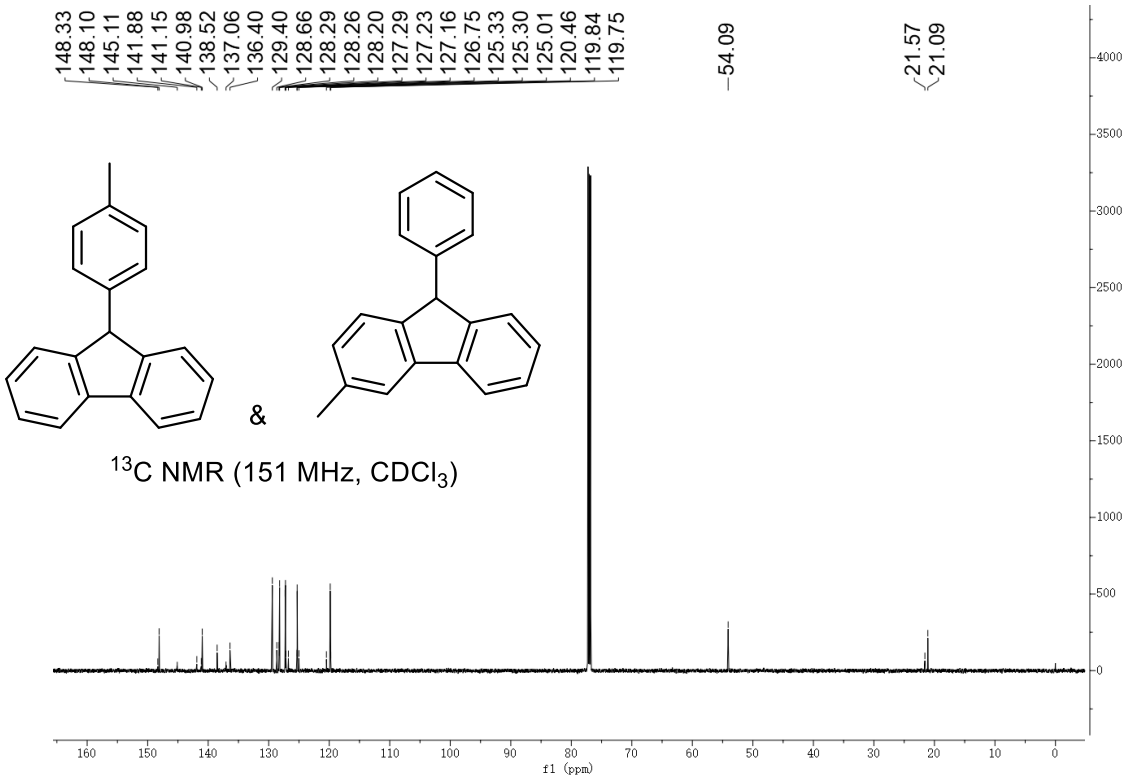
^{13}C NMR Spectrum of 3ae (151 MHz, $CDCl_3$)



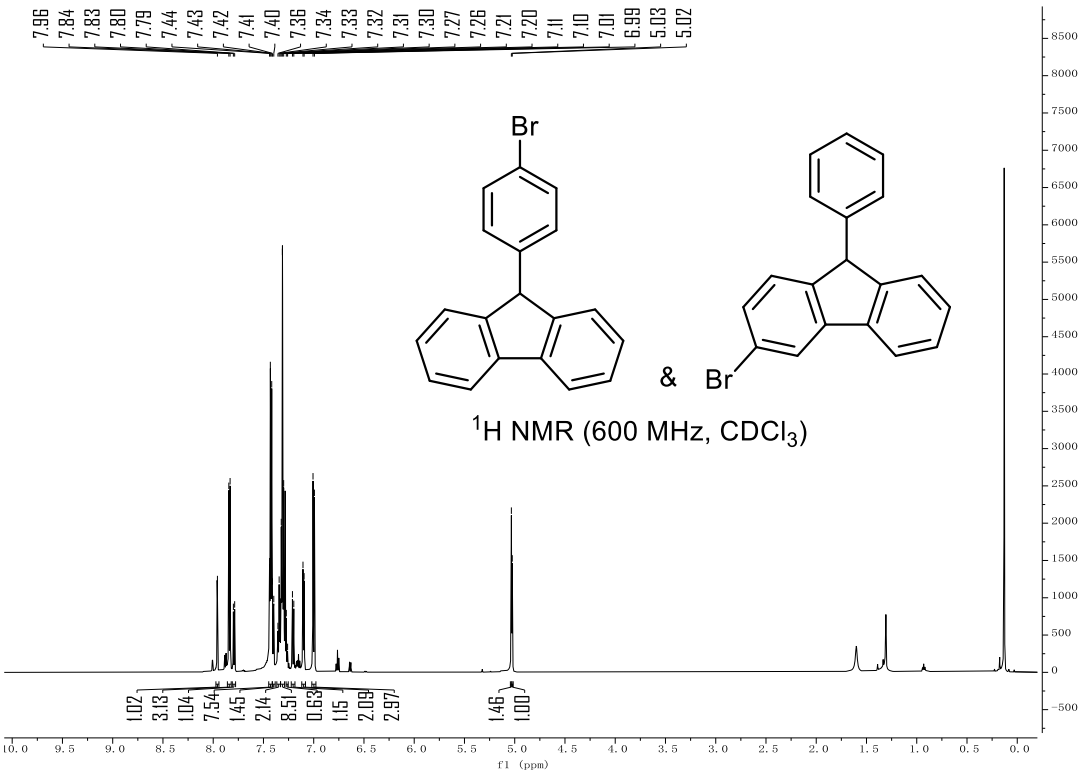
^{19}F NMR Spectrum of 3ae (565 MHz, $CDCl_3$)



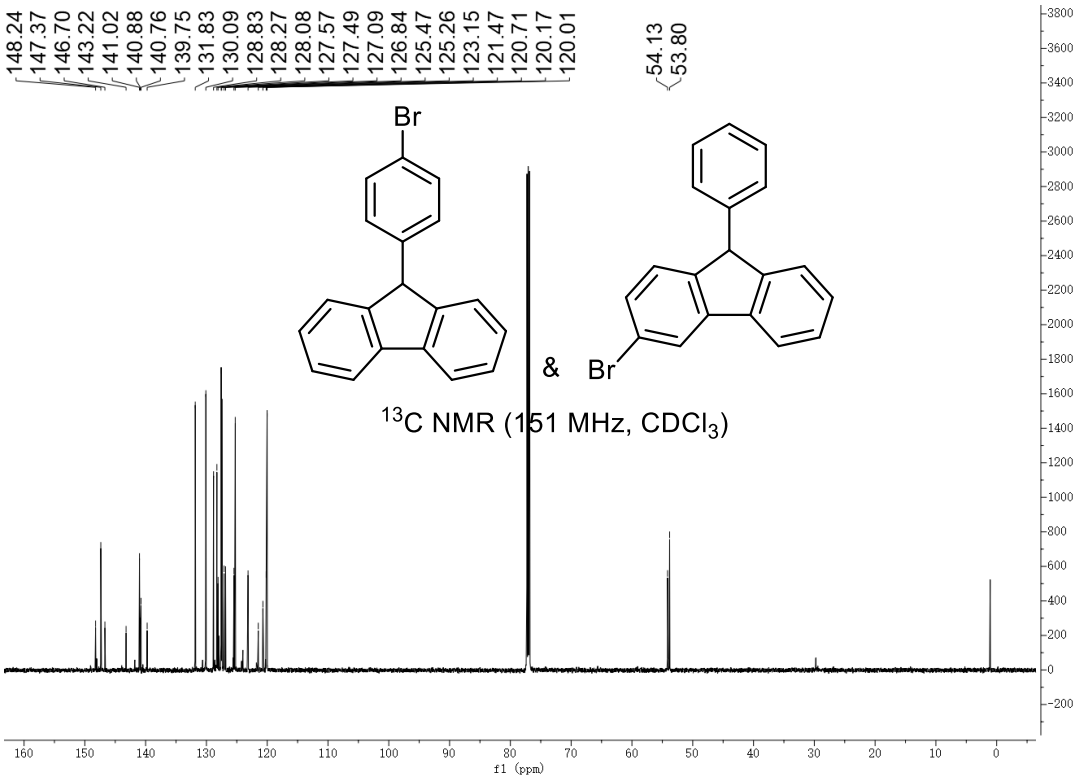
^{1}H NMR Spectrum of 3af (600 MHz, $CDCl_3$)



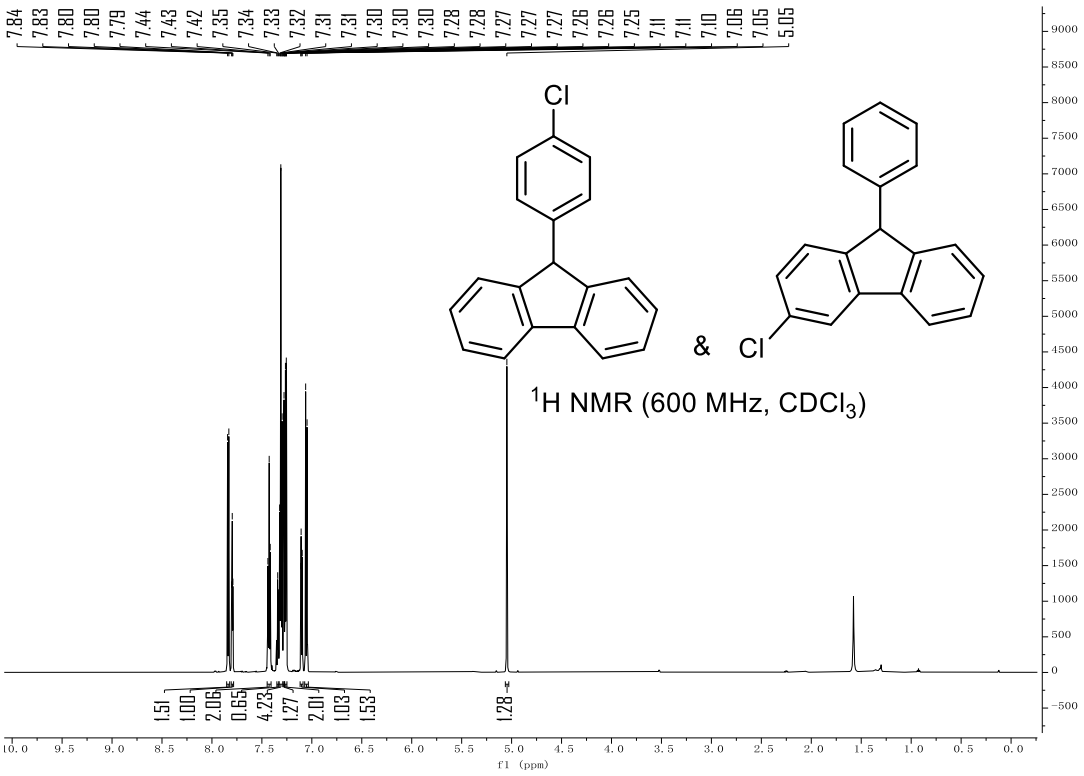
^{13}C NMR Spectrum of 3af (151 MHz, $CDCl_3$)



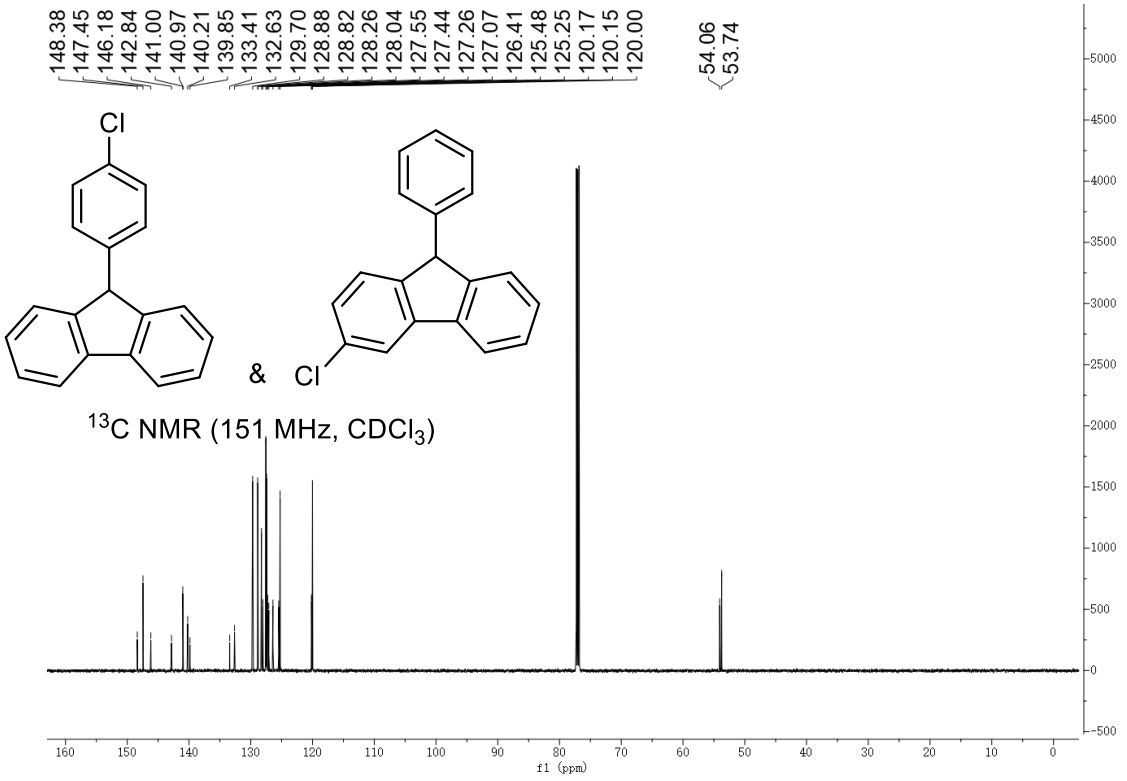
^{1}H NMR Spectrum of 3ag (600 MHz, $CDCl_3$)



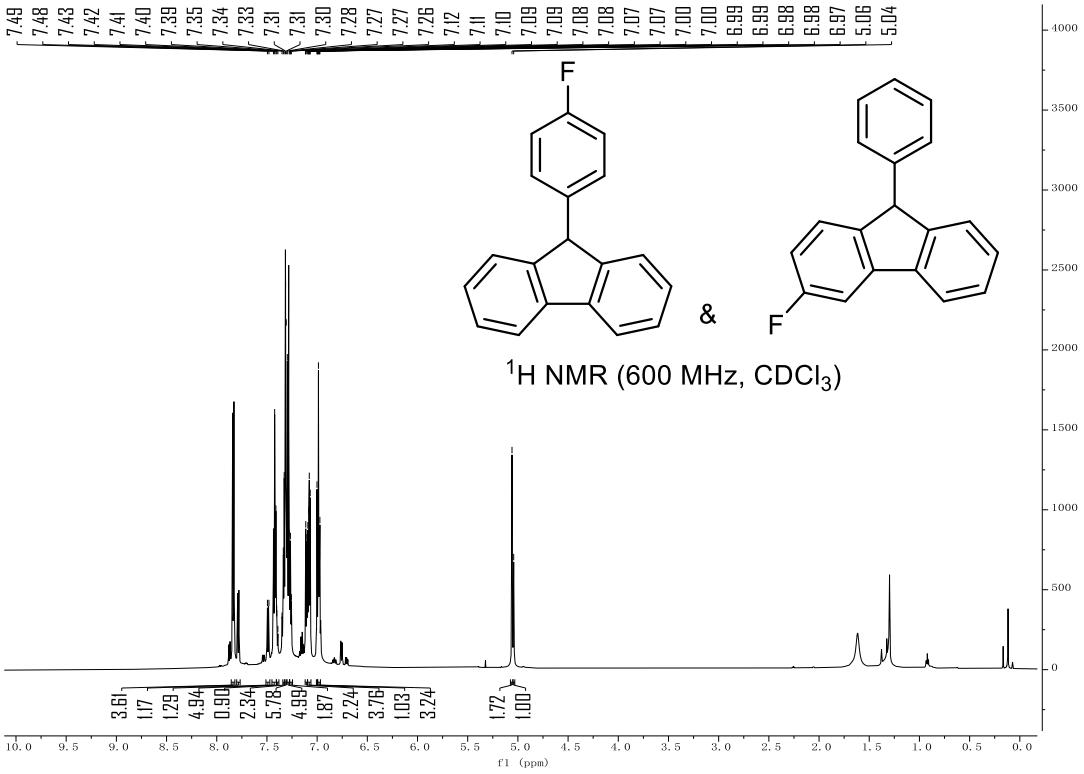
^{13}C NMR Spectrum of 3ag (151 MHz, $CDCl_3$)



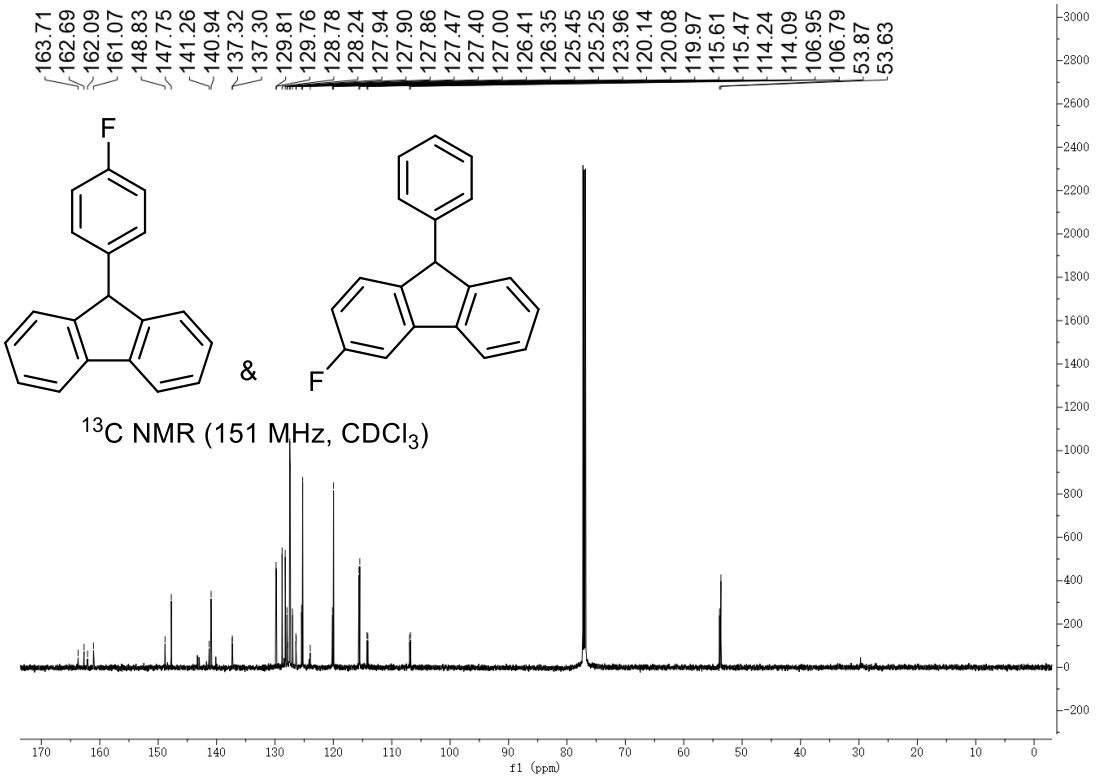
^{1}H NMR Spectrum of 3ah (600 MHz, $CDCl_3$)



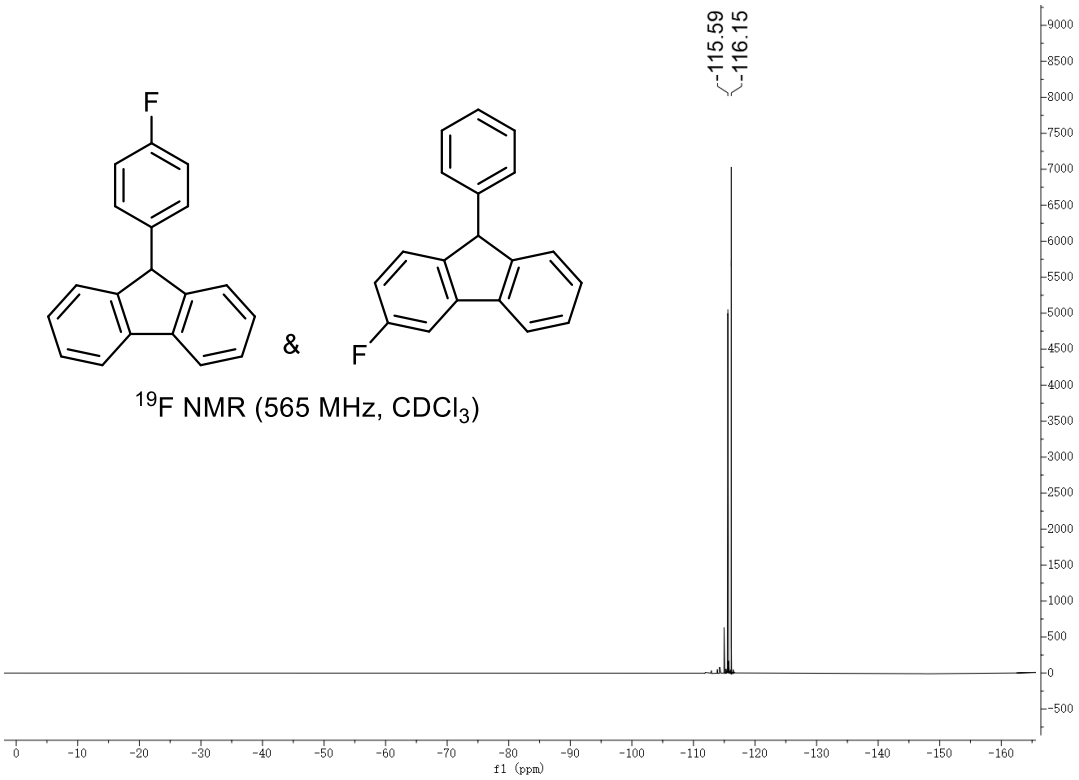
^{13}C NMR Spectrum of 3ah (151 MHz, $CDCl_3$)



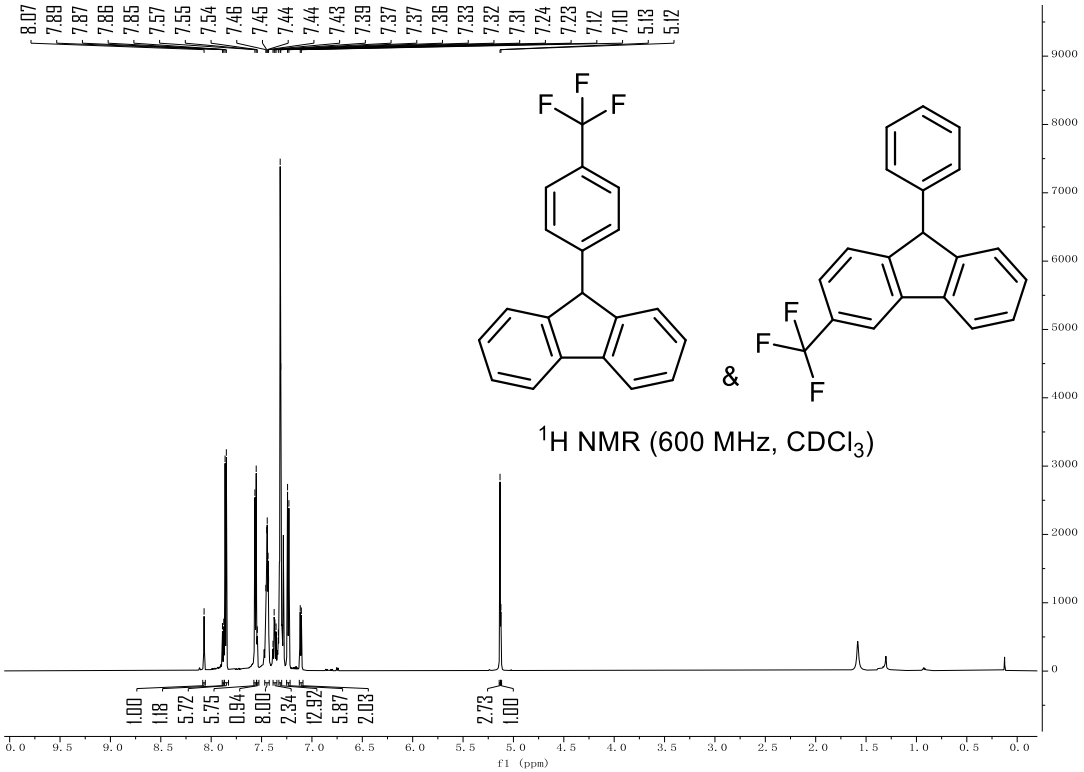
^{1}H NMR Spectrum of 3ai (600 MHz, $CDCl_3$)



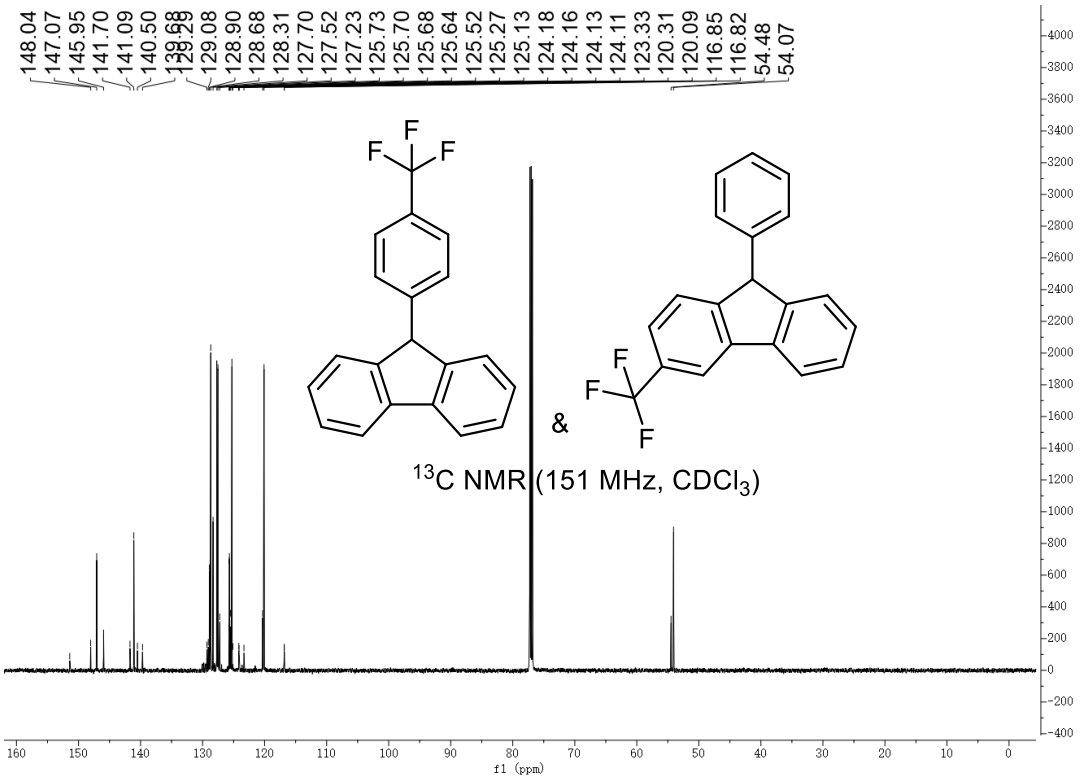
^{13}C NMR Spectrum of 3ai (151 MHz, $CDCl_3$)



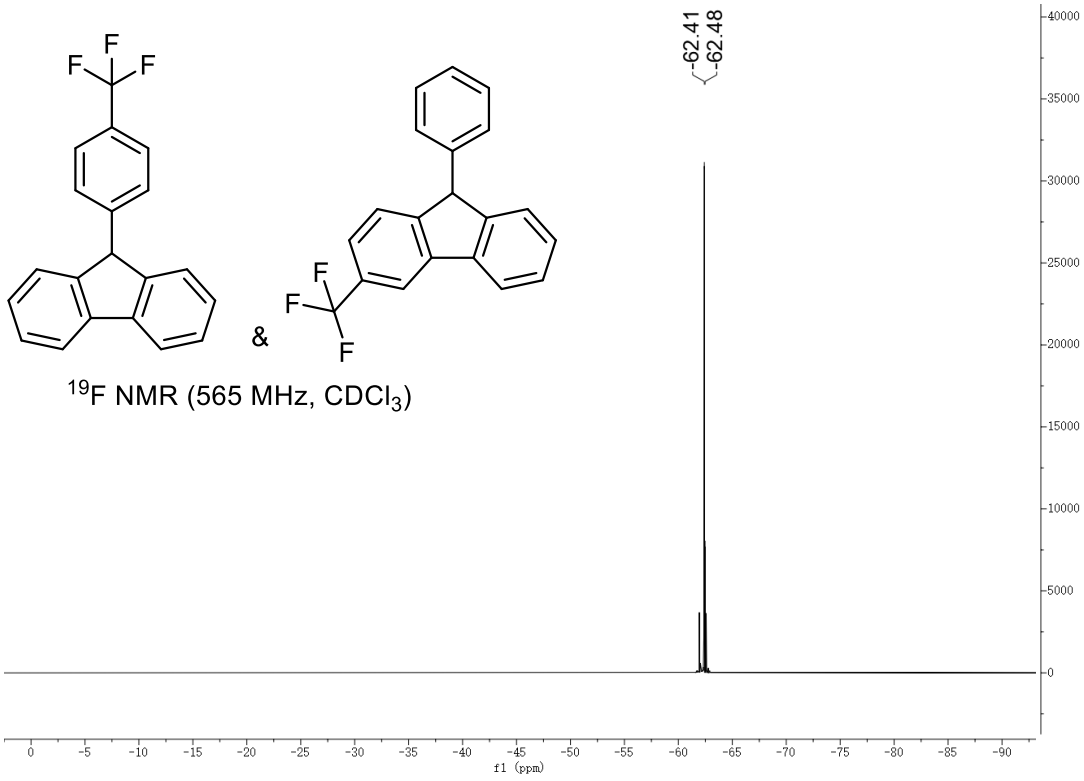
^{19}F NMR Spectrum of 3ai (565 MHz, $CDCl_3$)



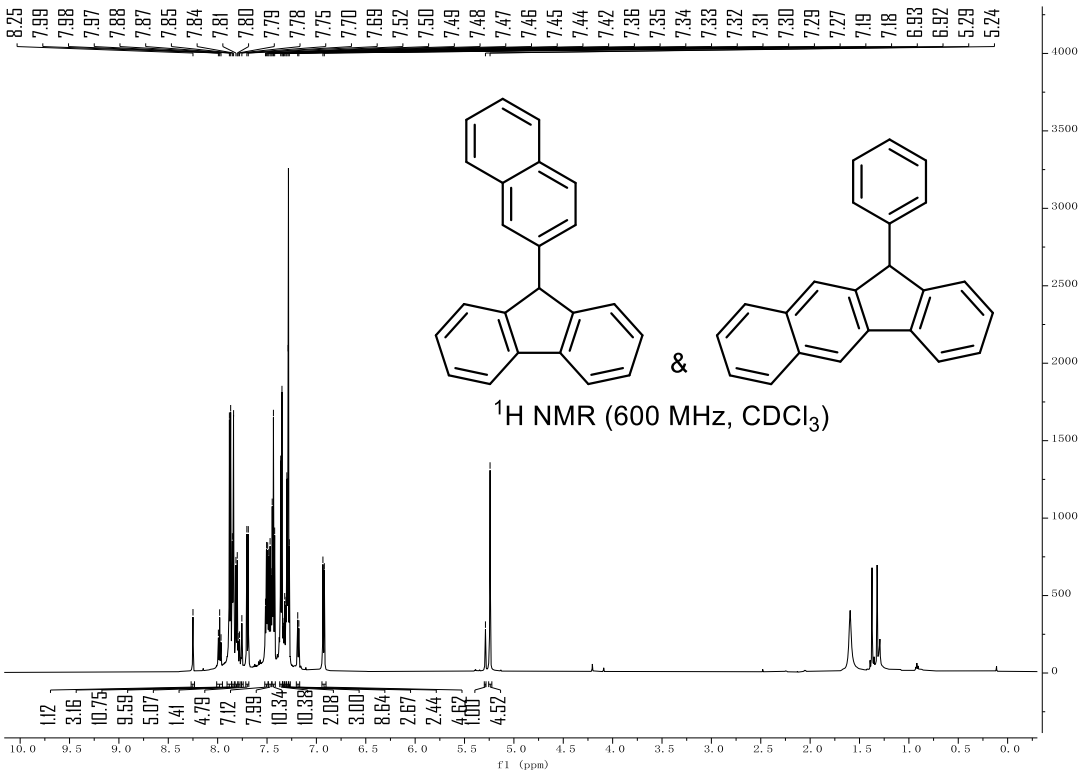
^{1}H NMR Spectrum of 3aj (600 MHz, $CDCl_3$)



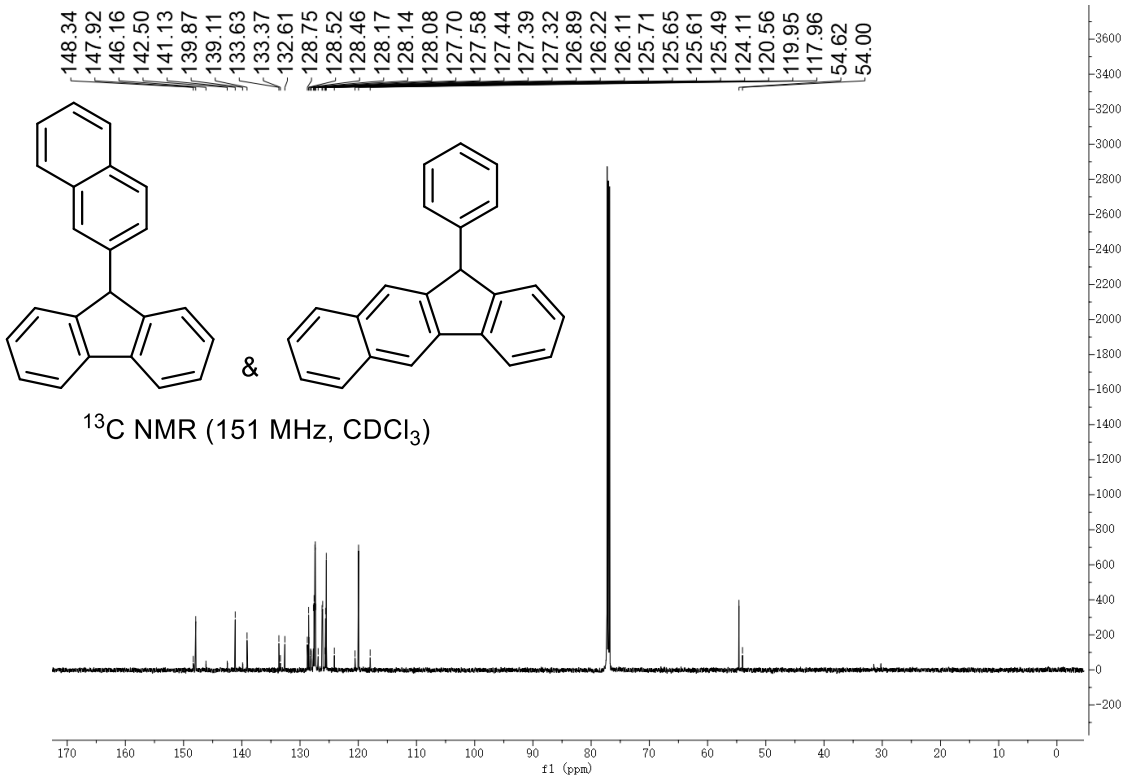
^{13}C NMR Spectrum of 3aj (151 MHz, $CDCl_3$)



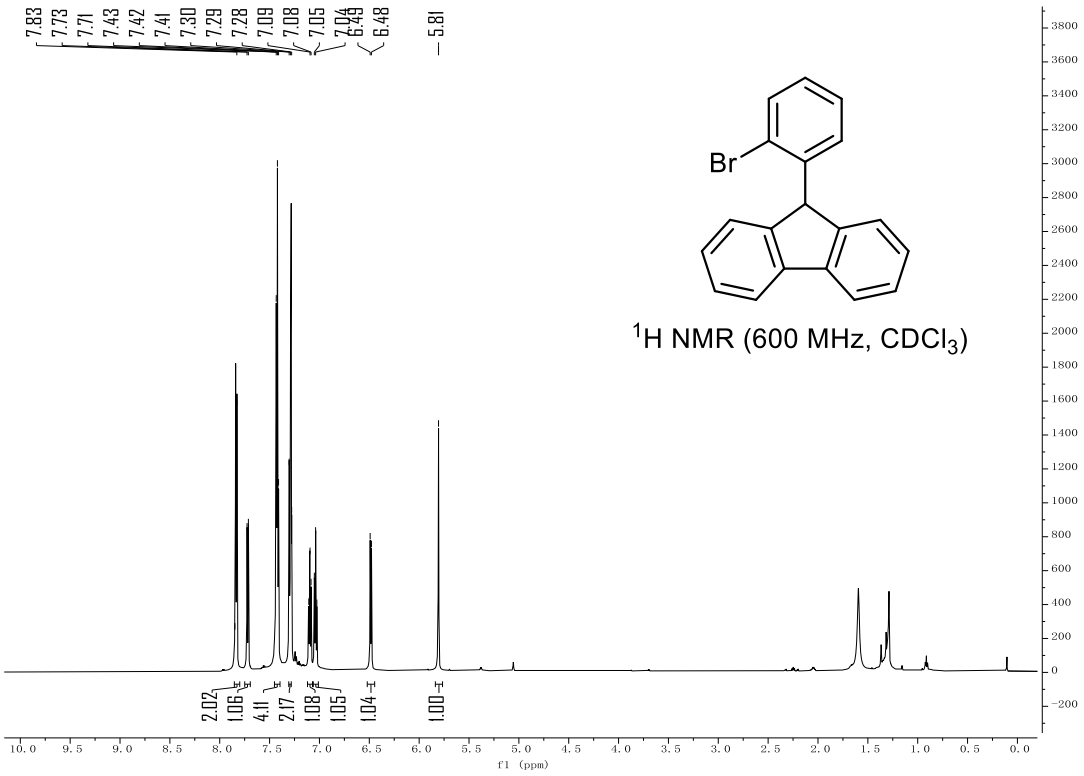
^{19}F NMR Spectrum of 3aj (565 MHz, $CDCl_3$)



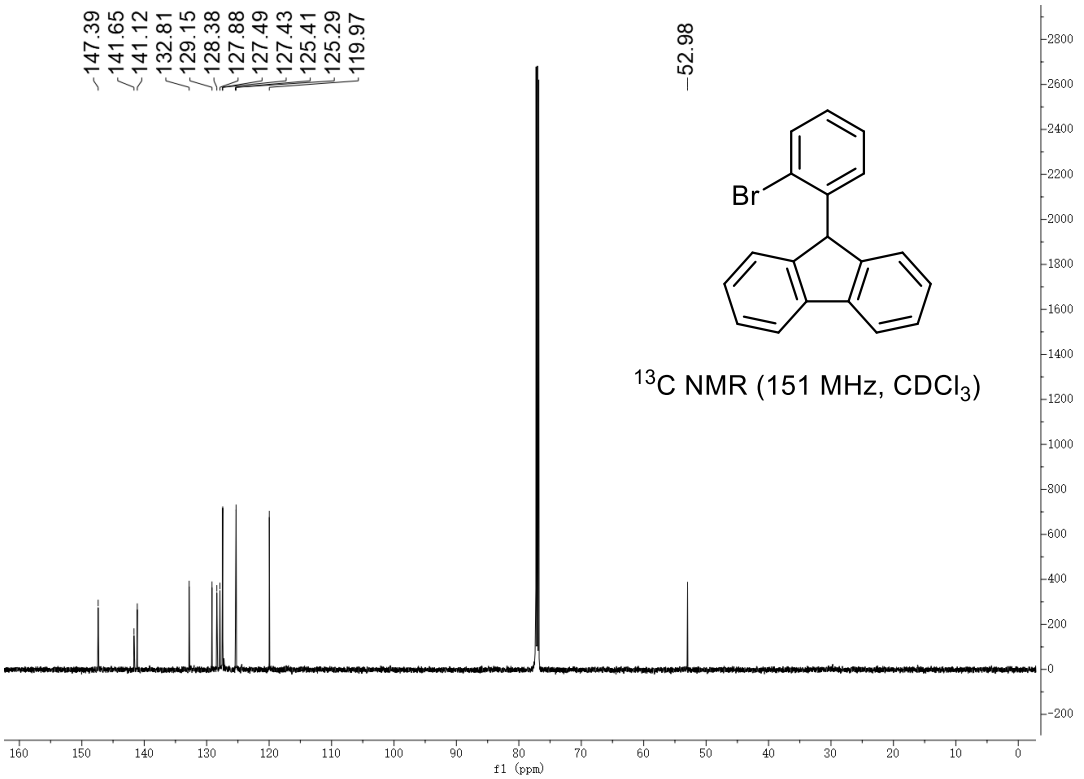
^{1}H NMR Spectrum of 3ak (600 MHz, $CDCl_3$)



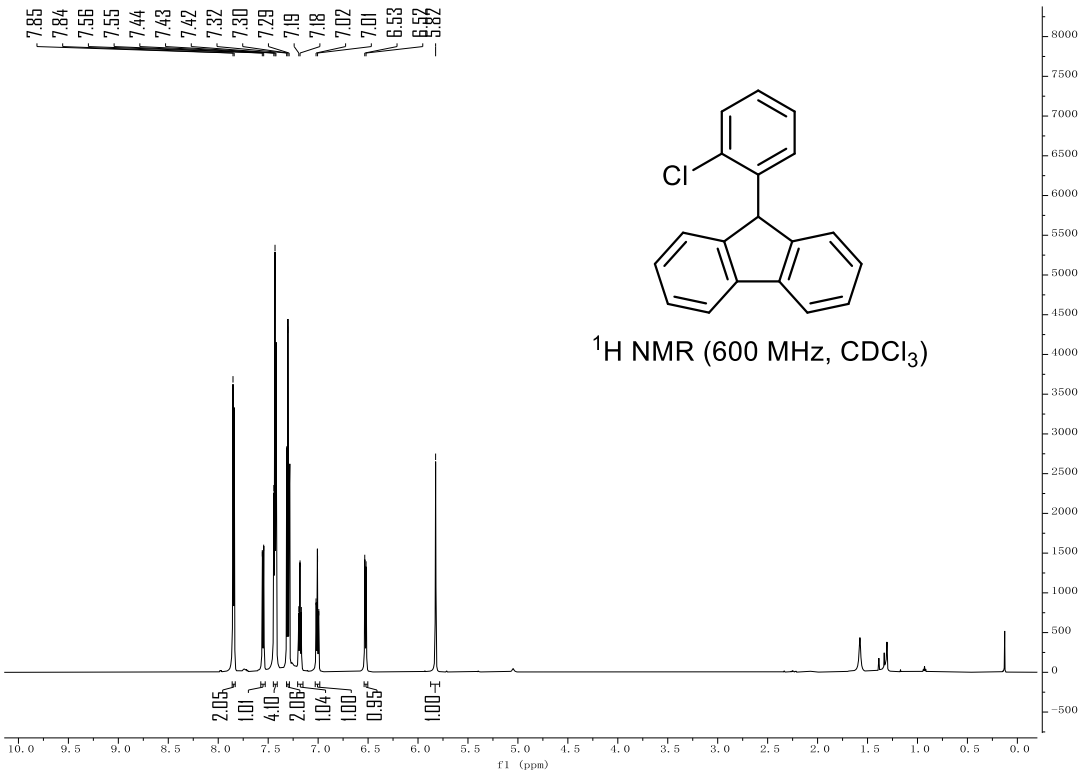
^{13}C NMR Spectrum of 3ak (151 MHz, $CDCl_3$)



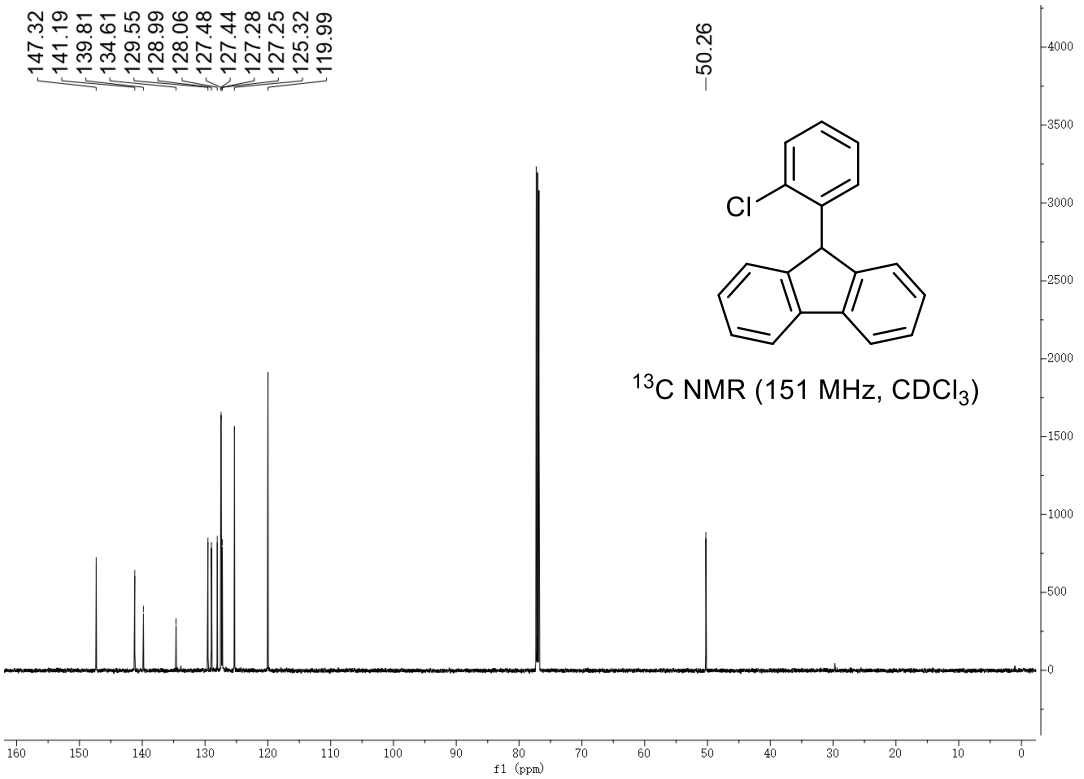
^{1}H NMR Spectrum of 3al (600 MHz, CDCl$_3$)



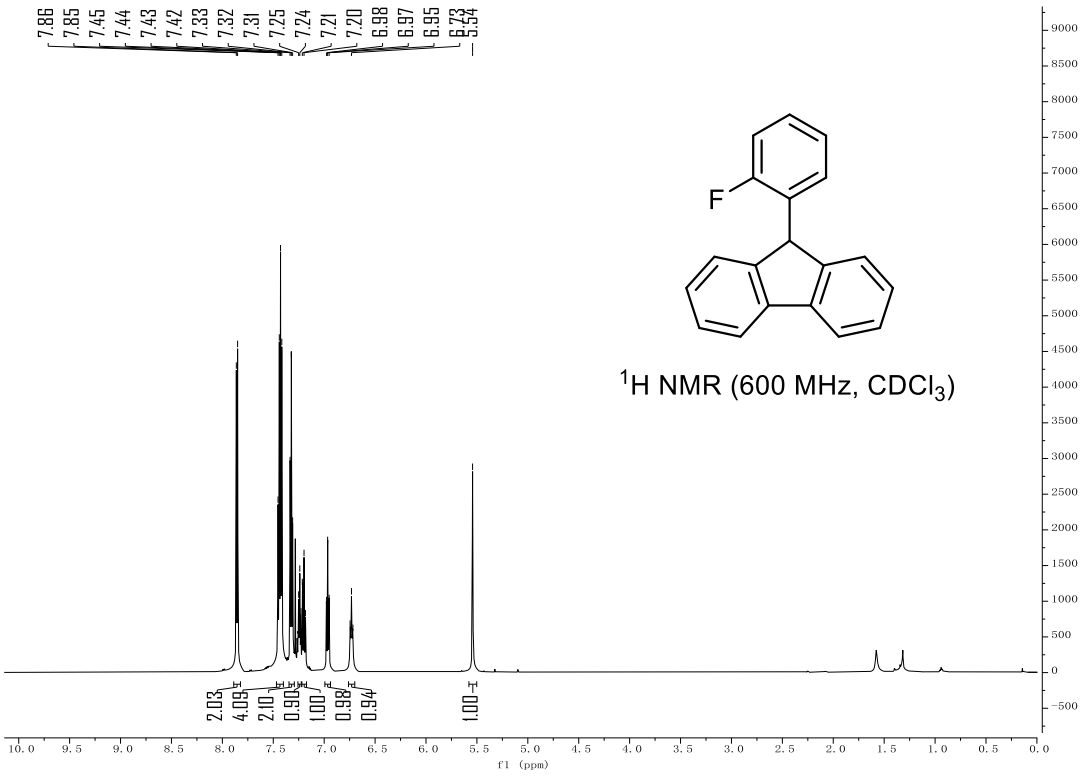
^{13}C NMR Spectrum of 3al (151 MHz, CDCl$_3$)



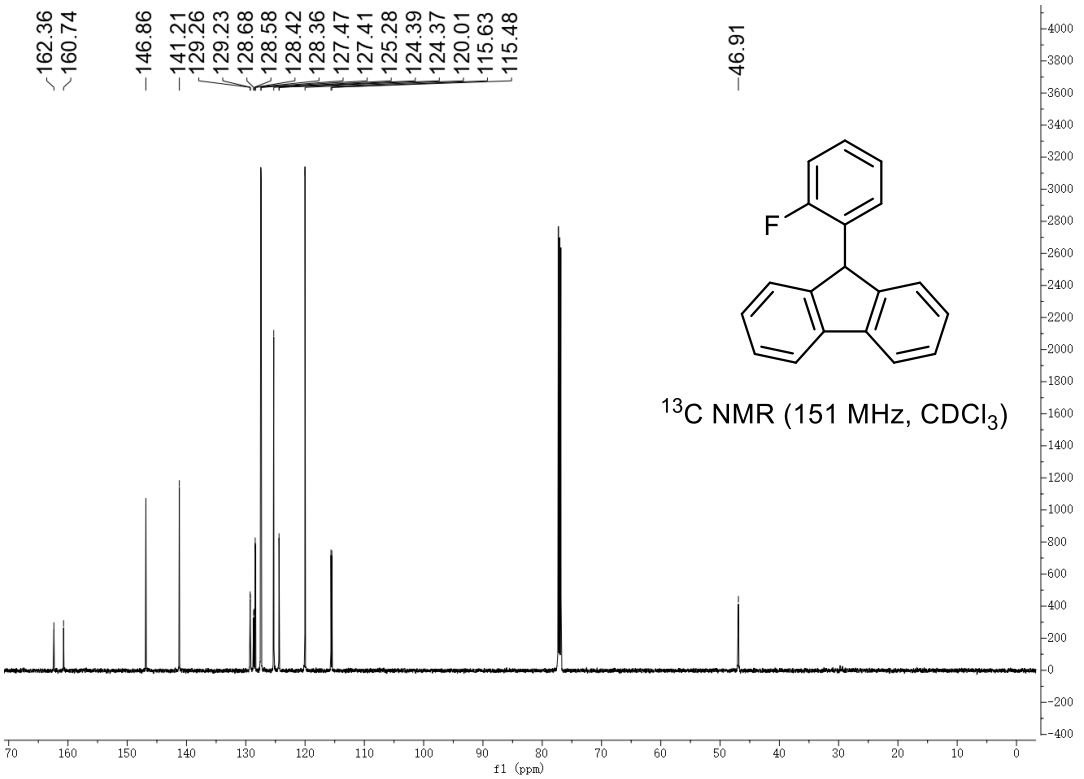
^{1}H NMR Spectrum of 3am (600 MHz, $CDCl_3$)



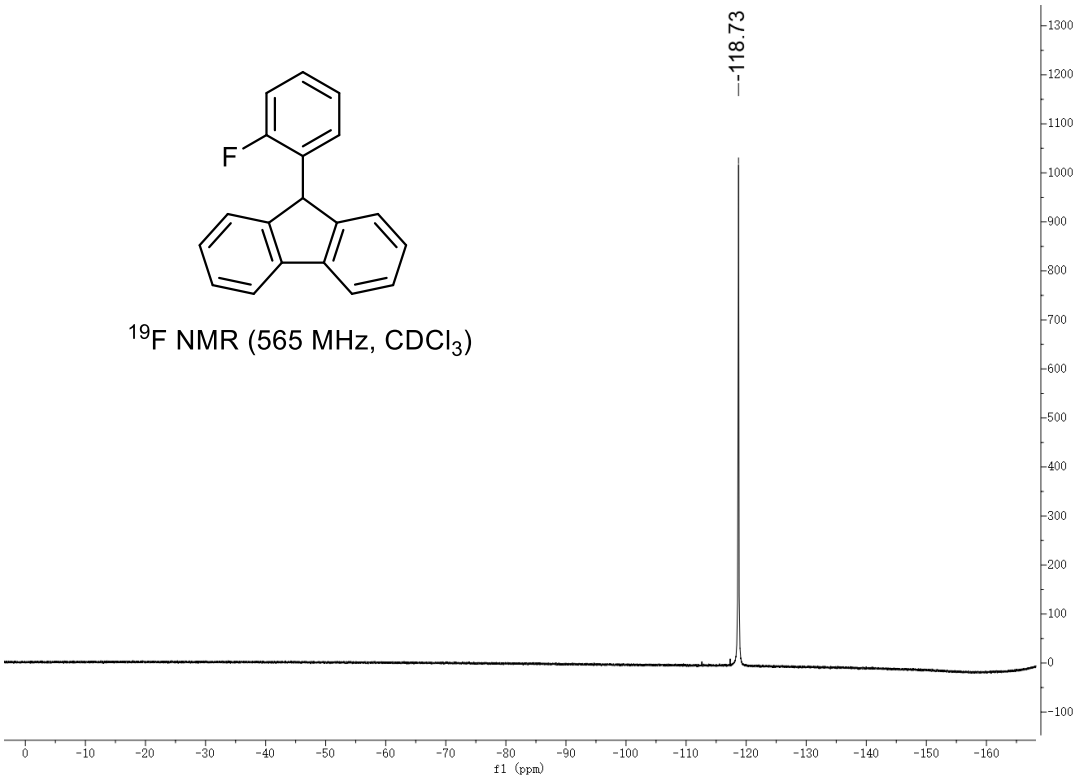
^{13}C NMR Spectrum of 3am (151 MHz, $CDCl_3$)



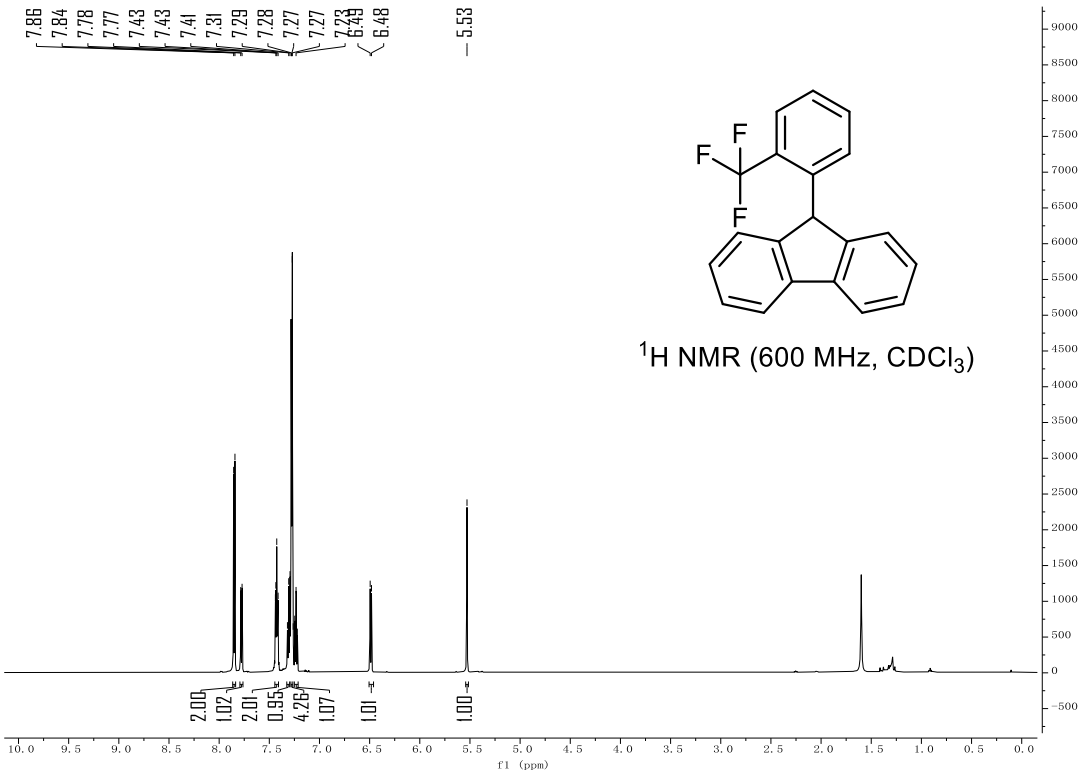
^{1}H NMR Spectrum of 3an (600 MHz, $CDCl_3$)



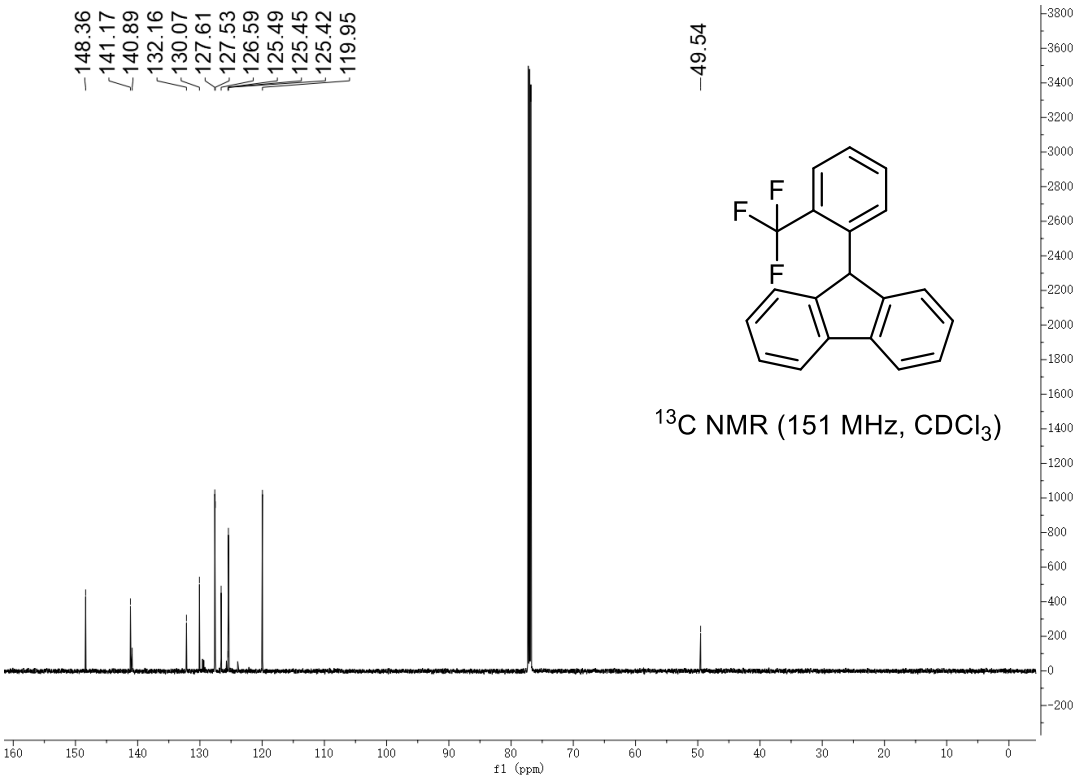
^{13}C NMR Spectrum of 3an (151 MHz, $CDCl_3$)



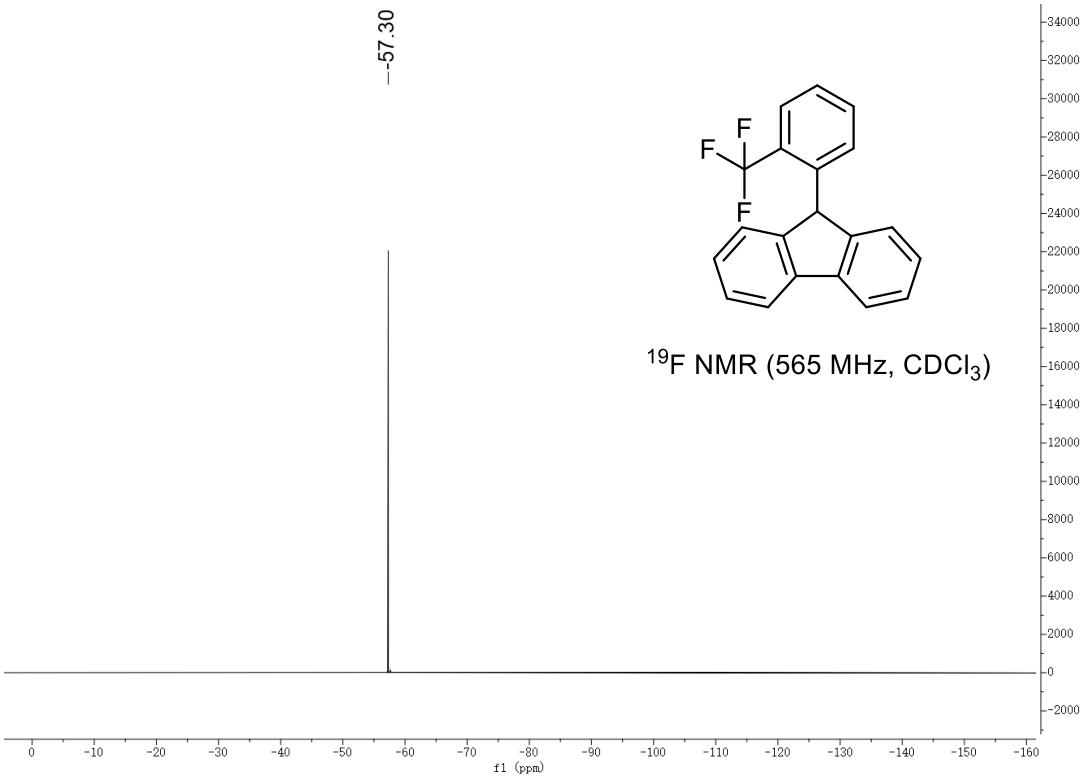
^{19}F NMR Spectrum of 3an (565 MHz, $CDCl_3$)



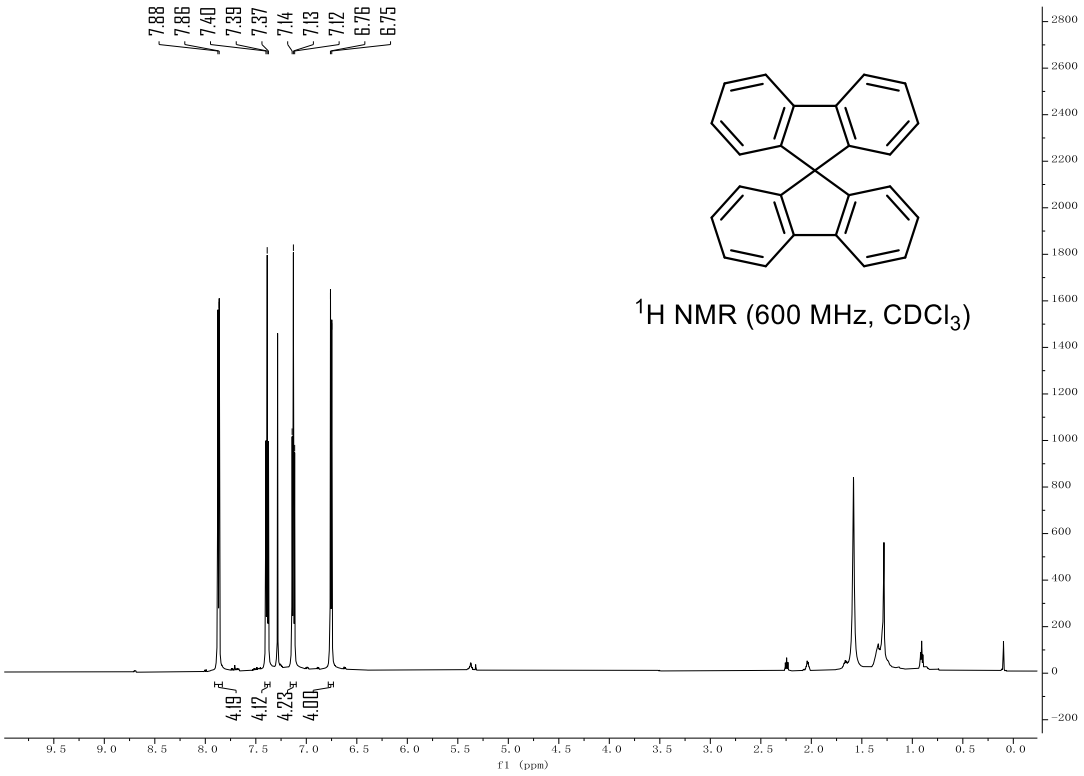
^{1}H NMR Spectrum of 3ao (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 3ao (151 MHz, $CDCl_3$)

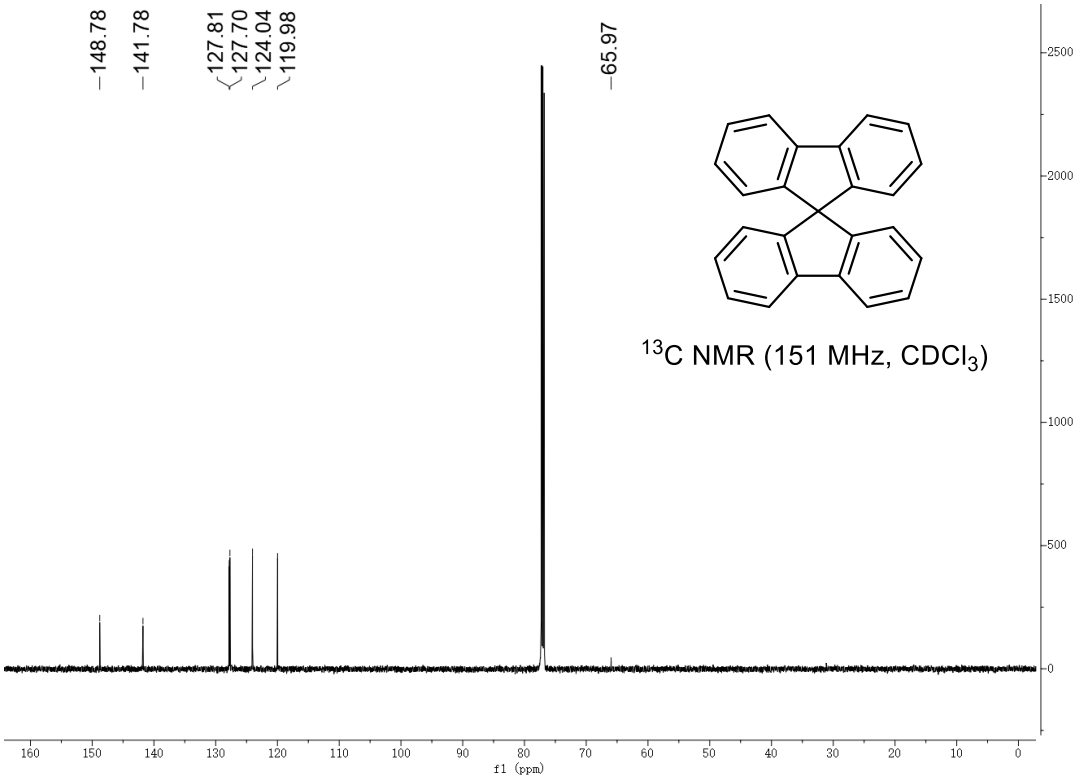


^{19}F NMR Spectrum of 3ao (565 MHz, $CDCl_3$)



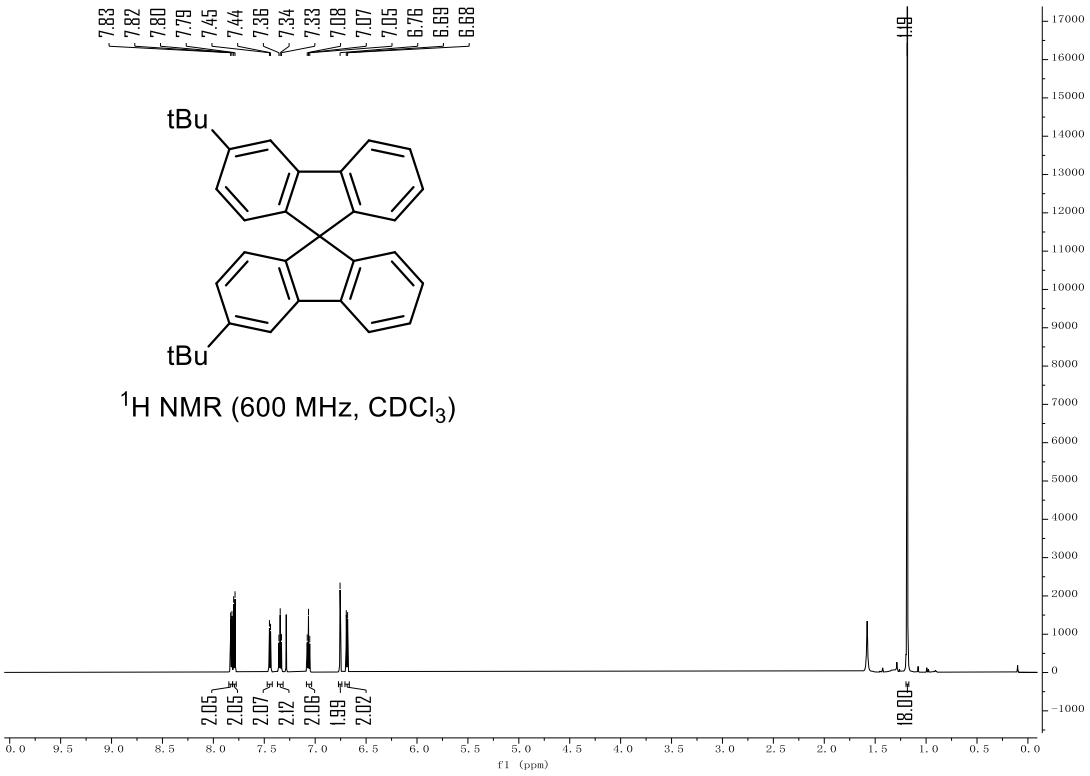
^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR Spectrum of 4a (600 MHz, $CDCl_3$)

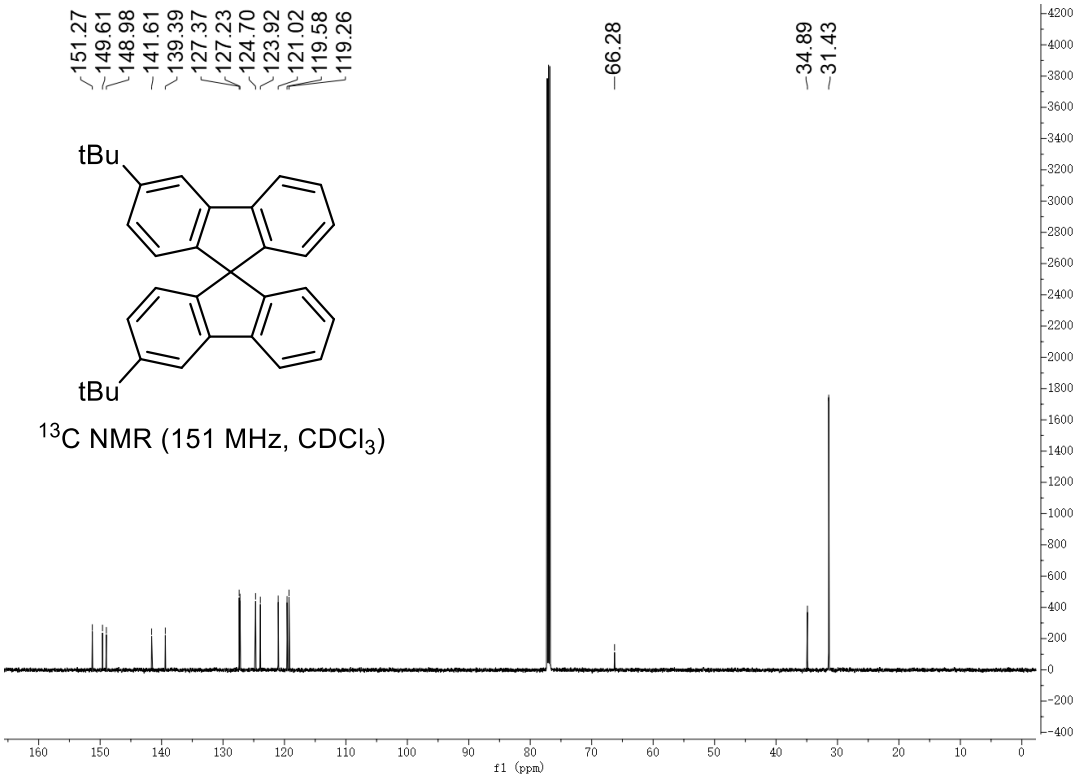


^{13}C NMR (151 MHz, $CDCl_3$)

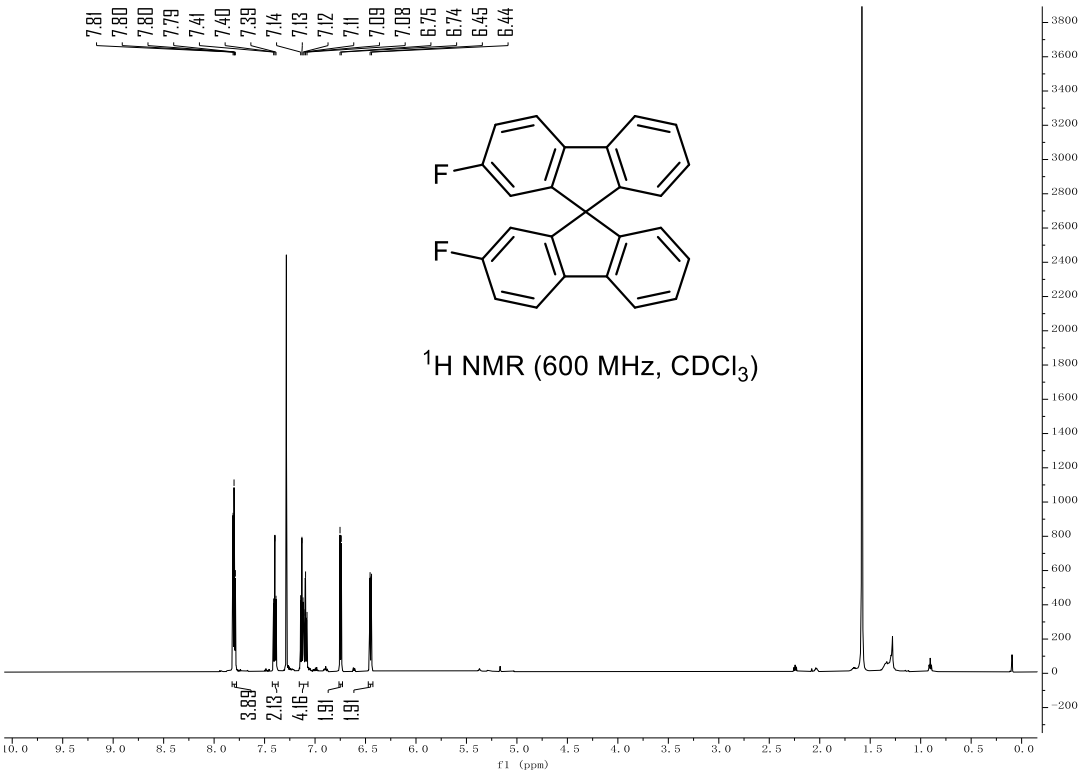
^{13}C NMR Spectrum of 4a (151 MHz, $CDCl_3$)



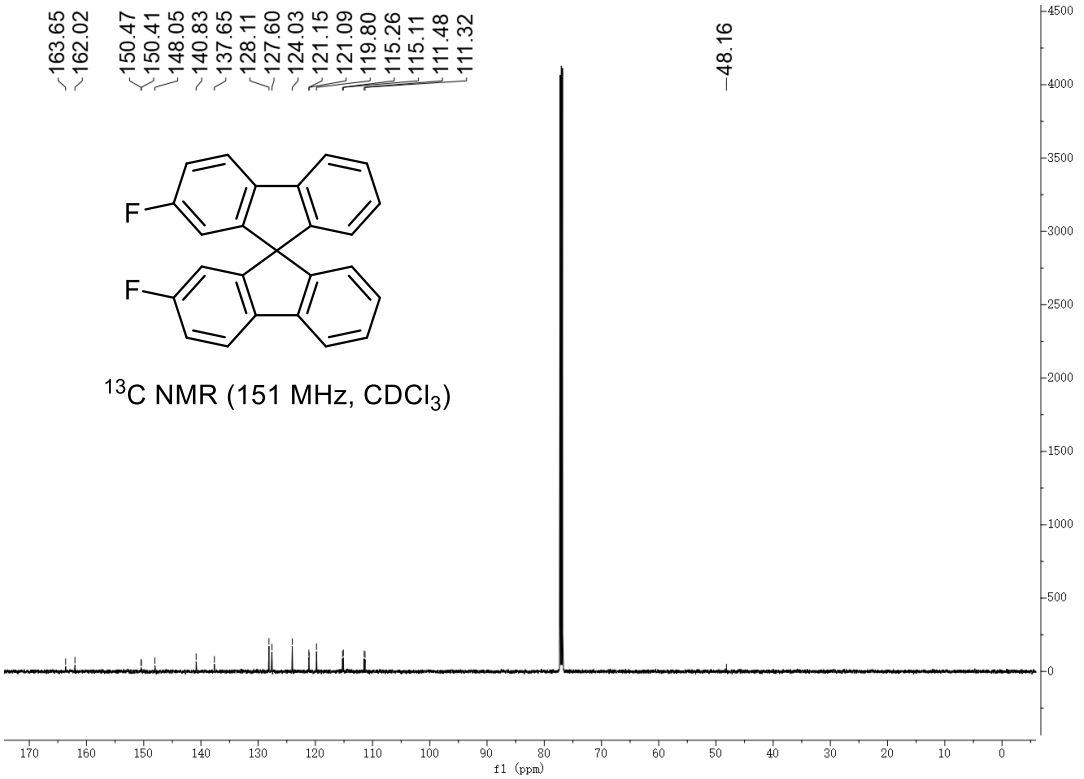
^{1}H NMR Spectrum of 4b (600 MHz, $CDCl_3$)



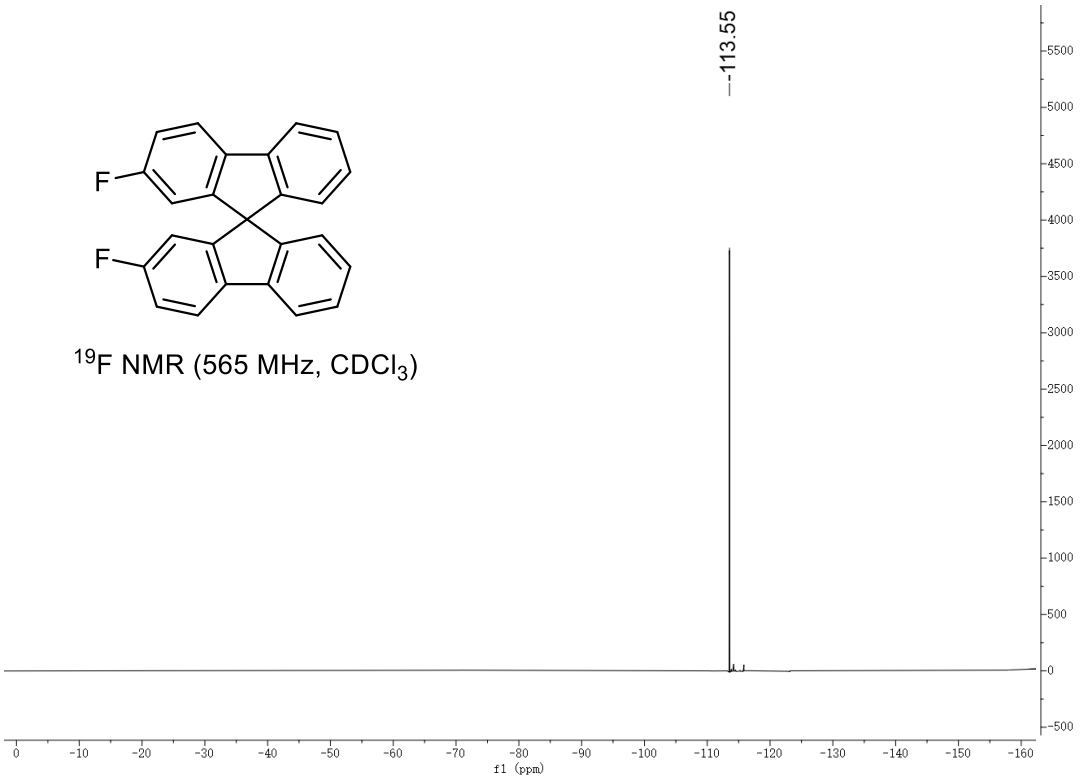
^{13}C NMR Spectrum of 4b (600 MHz, $CDCl_3$)



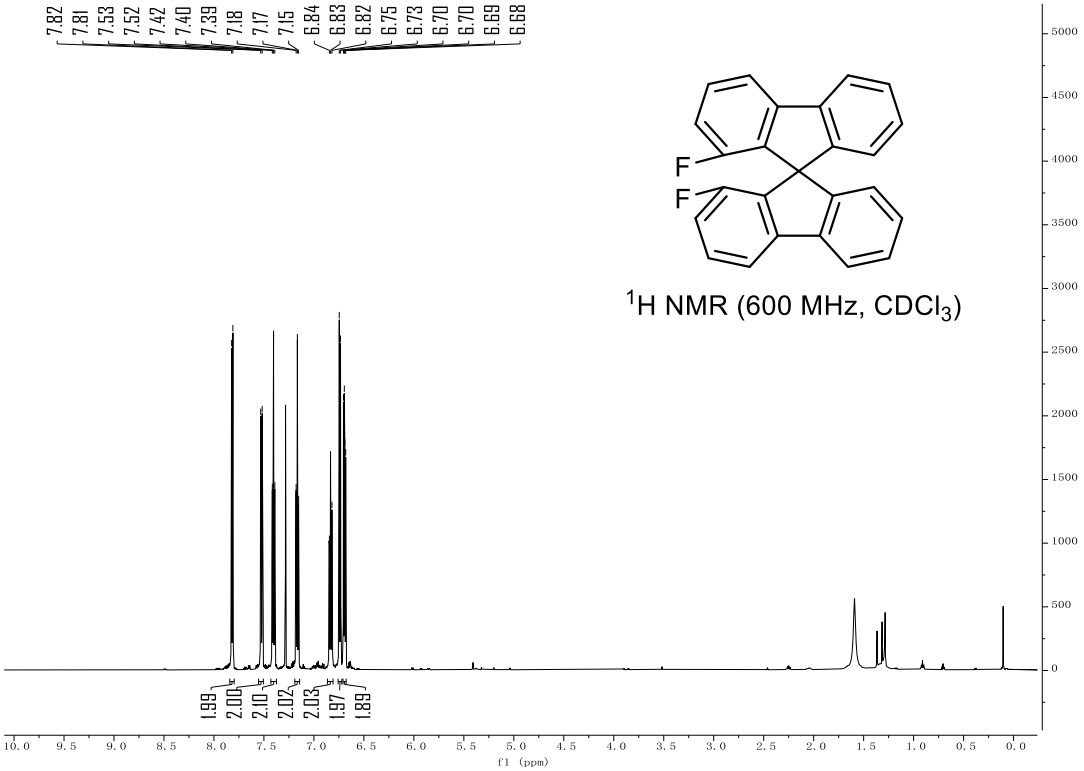
^{1}H NMR Spectrum of 4c (600 MHz, $CDCl_3$)



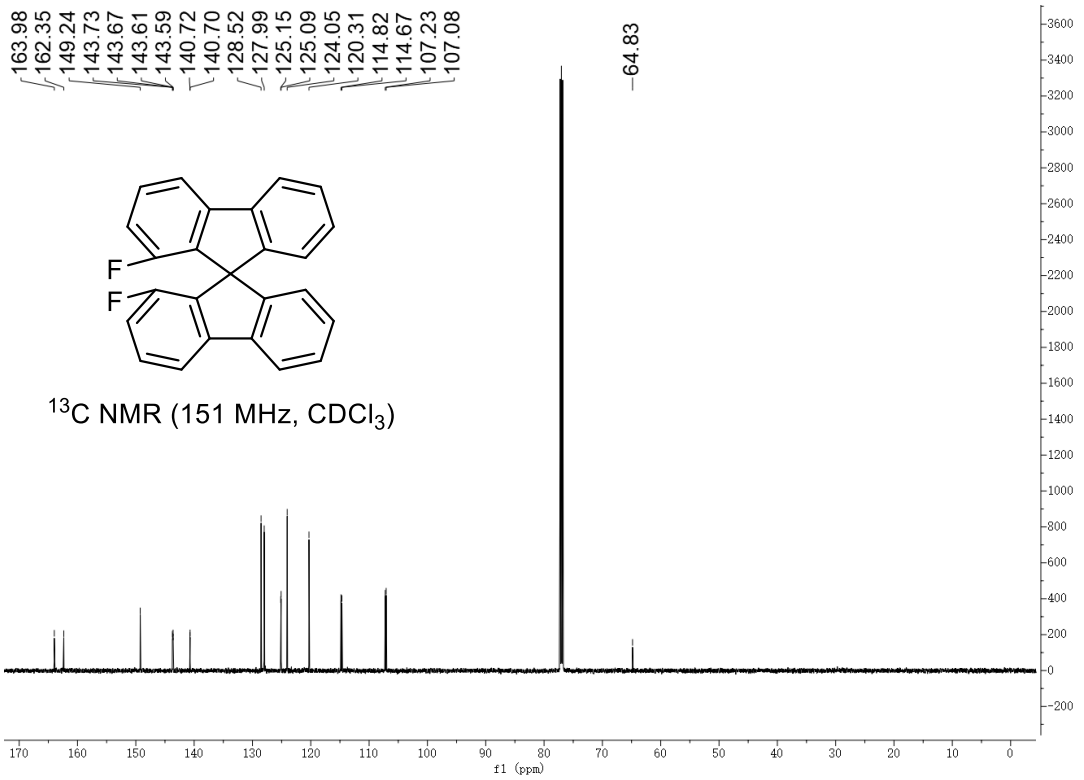
^{13}C NMR Spectrum of 4c (151 MHz, $CDCl_3$)



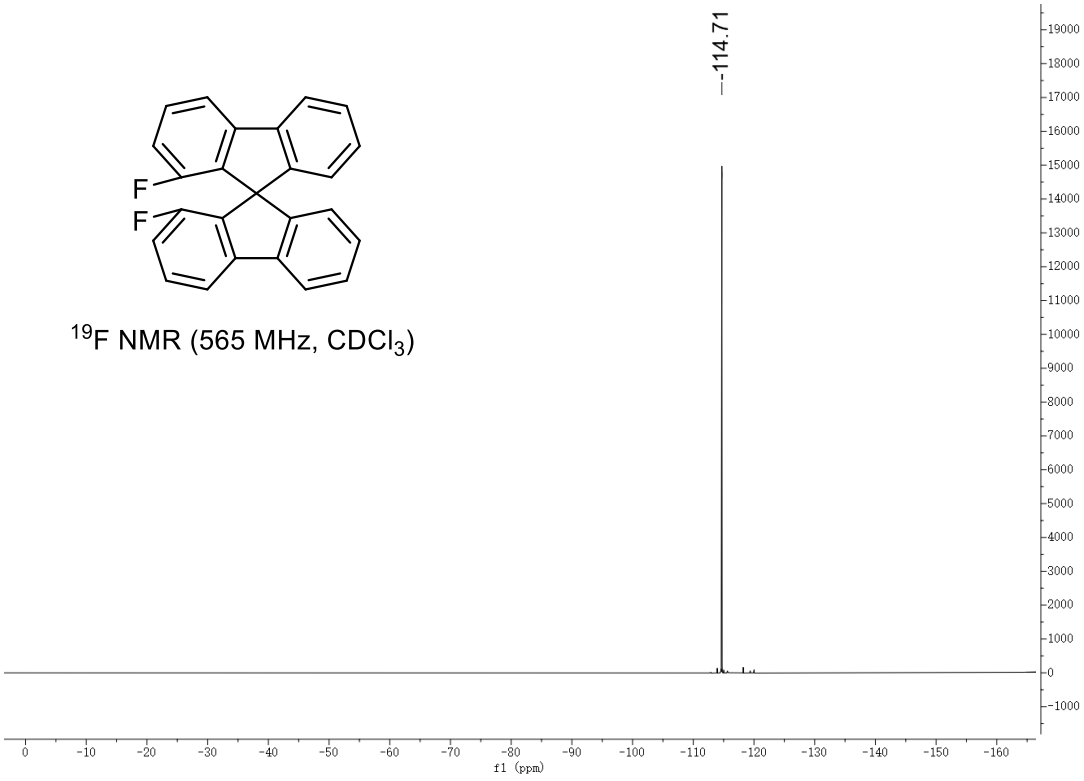
^{19}F NMR Spectrum of 4c (565 MHz, CDCl$_3$)



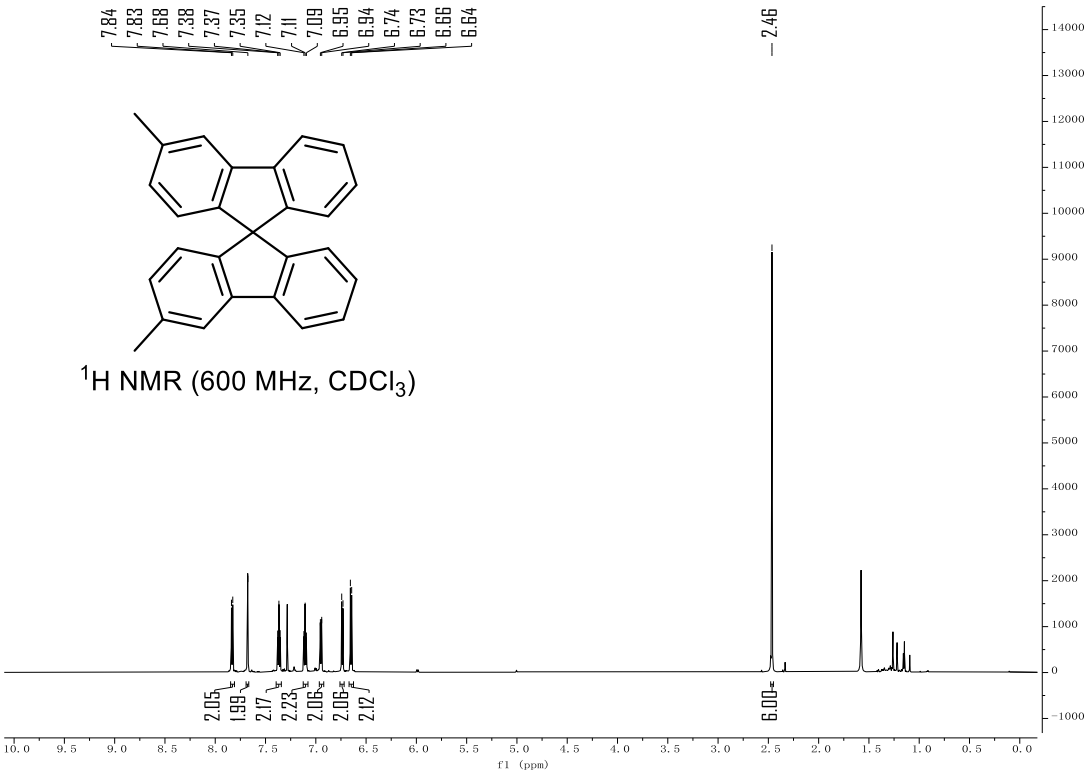
^{1}H NMR Spectrum of 4d (600 MHz, CDCl$_3$)



^{13}C NMR Spectrum of 4d (151 MHz, $CDCl_3$)

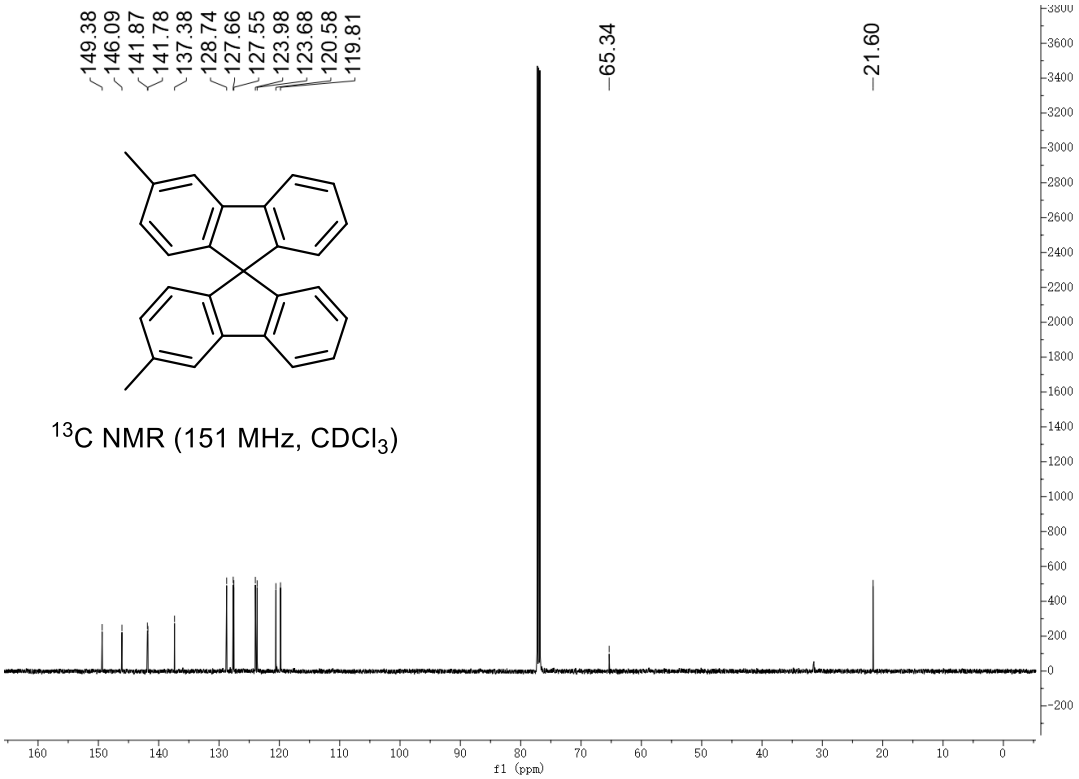


^{13}C NMR Spectrum of 4d (565 MHz, $CDCl_3$)



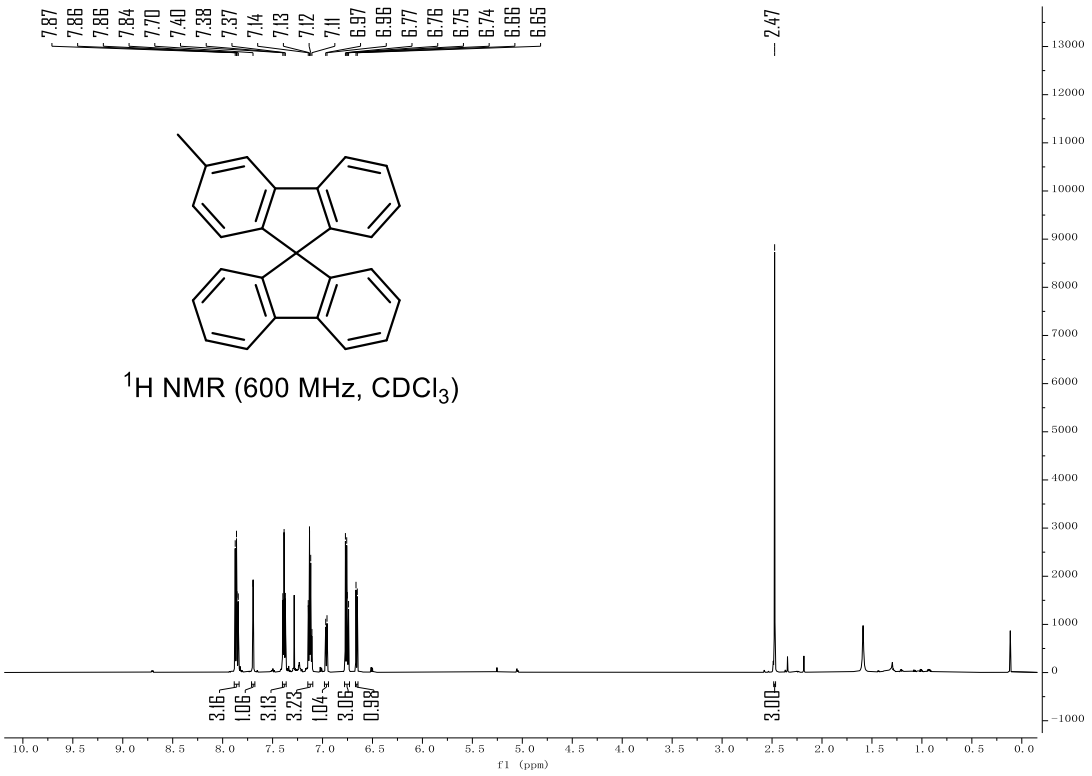
^{1}H NMR (600 MHz, $CDCl_3$)

^{1}H NMR Spectrum of 4e (600 MHz, $CDCl_3$)

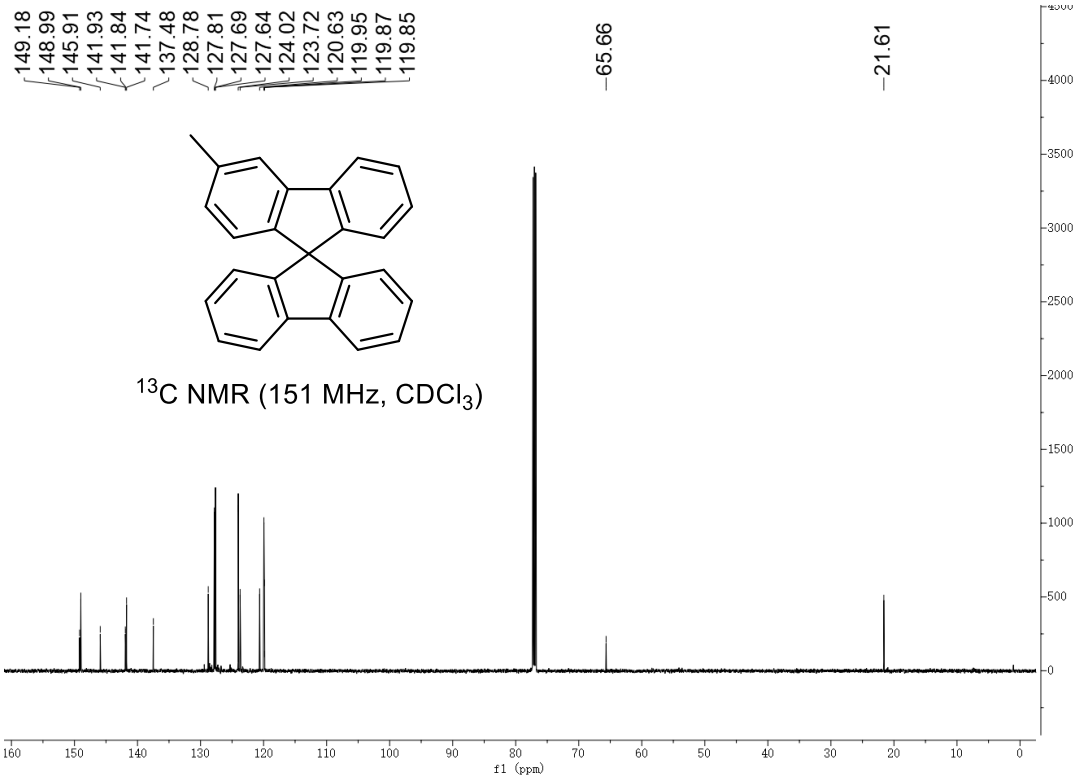


^{13}C NMR (151 MHz, $CDCl_3$)

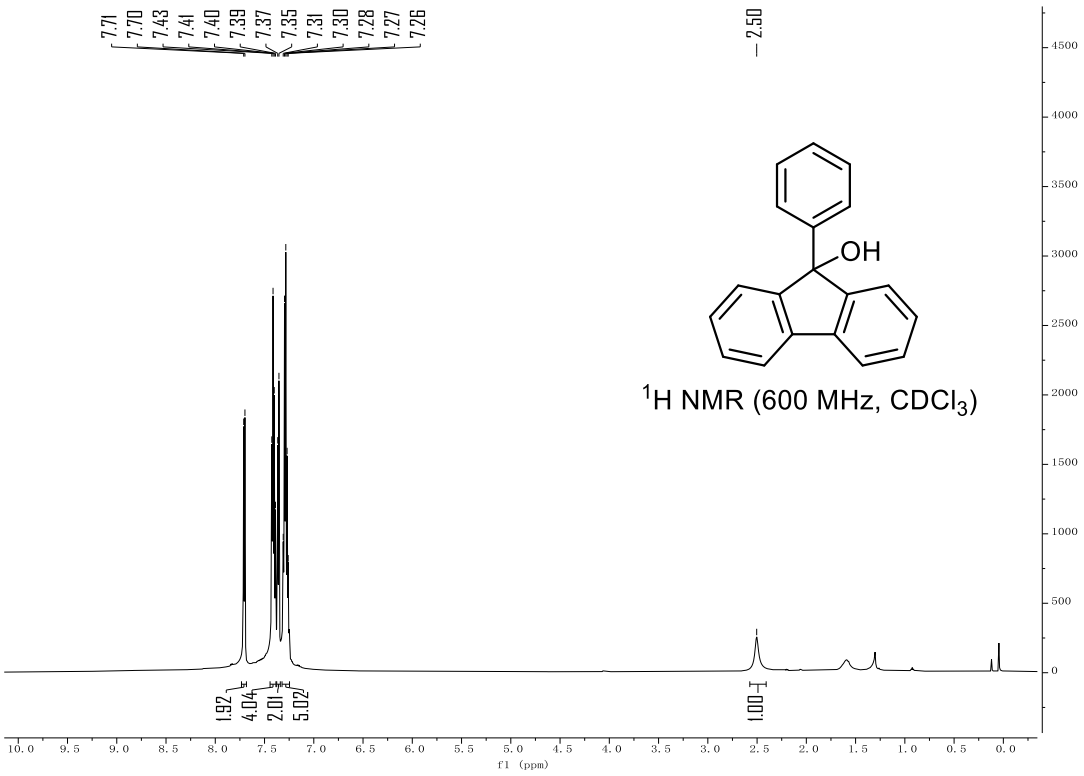
^{13}C NMR Spectrum of 4e (151 MHz, $CDCl_3$)



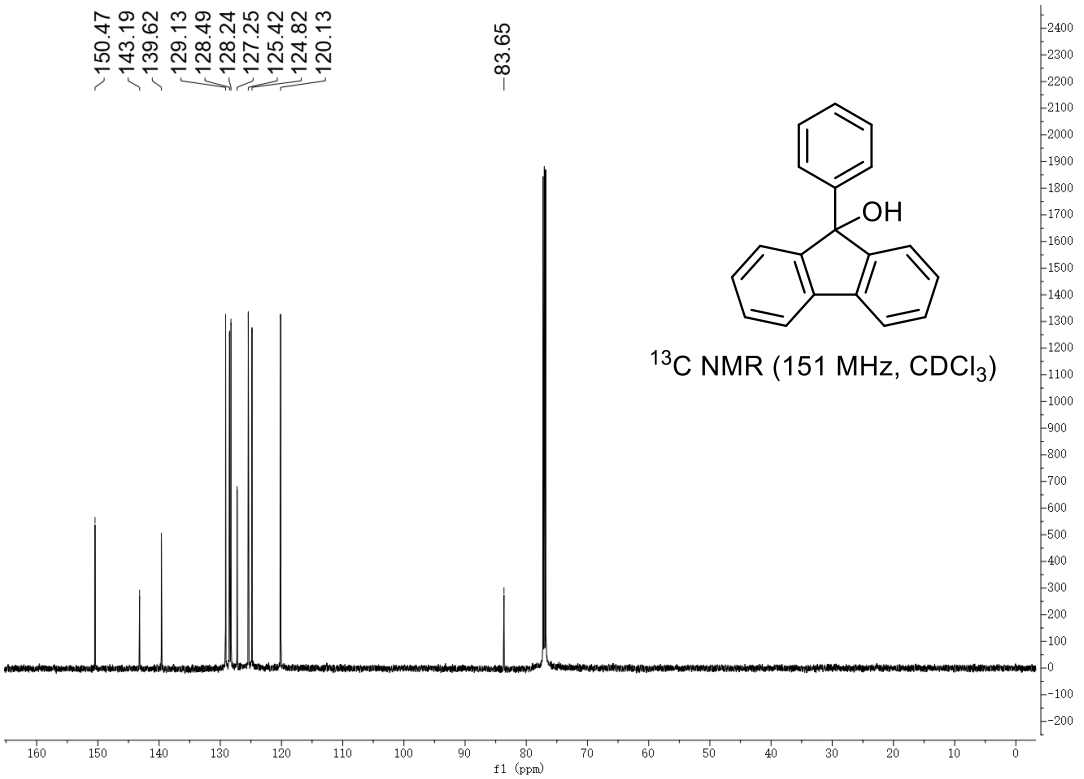
^{1}H NMR Spectrum of 4f (600 MHz, $CDCl_3$)



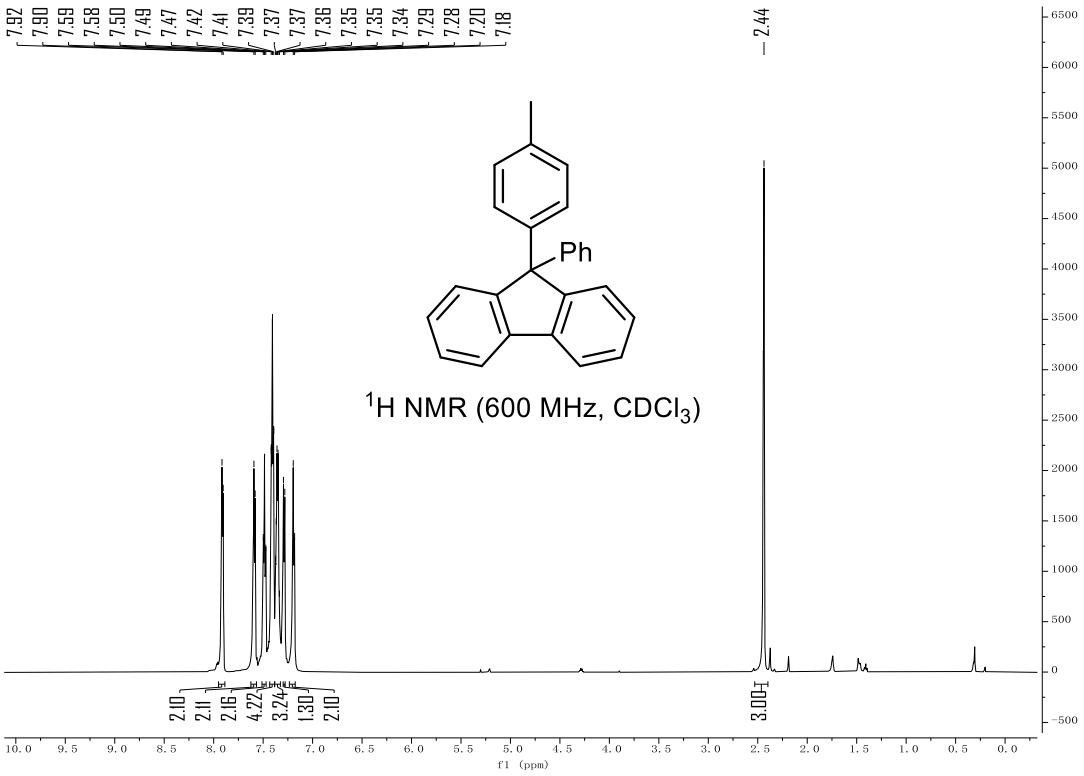
^{13}C NMR Spectrum of 4f (151 MHz, $CDCl_3$)



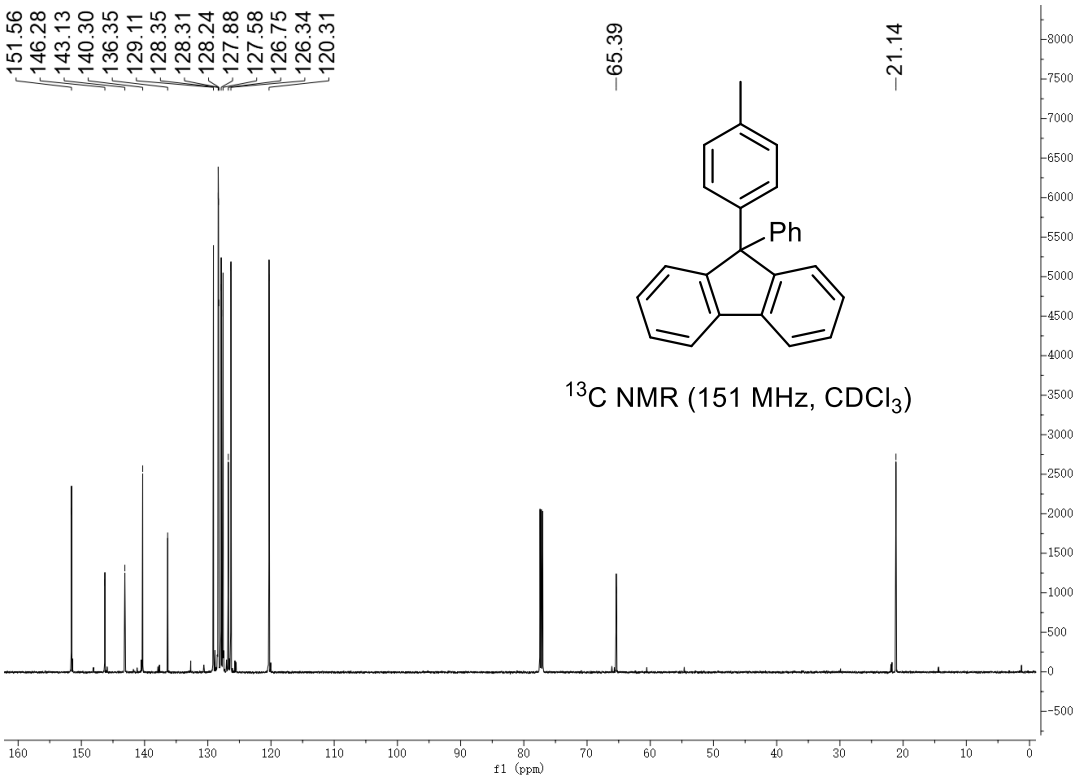
^{1}H NMR Spectrum of 5 (600 MHz, $CDCl_3$)



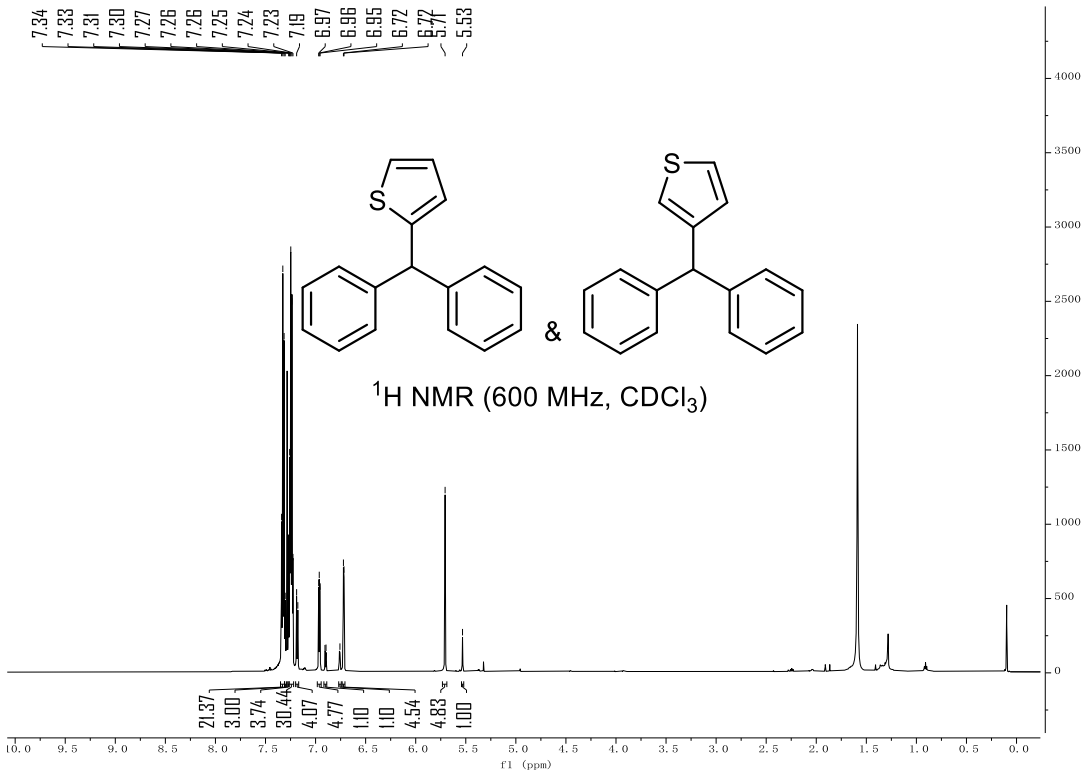
^{13}C NMR Spectrum of 5 (151 MHz, $CDCl_3$)



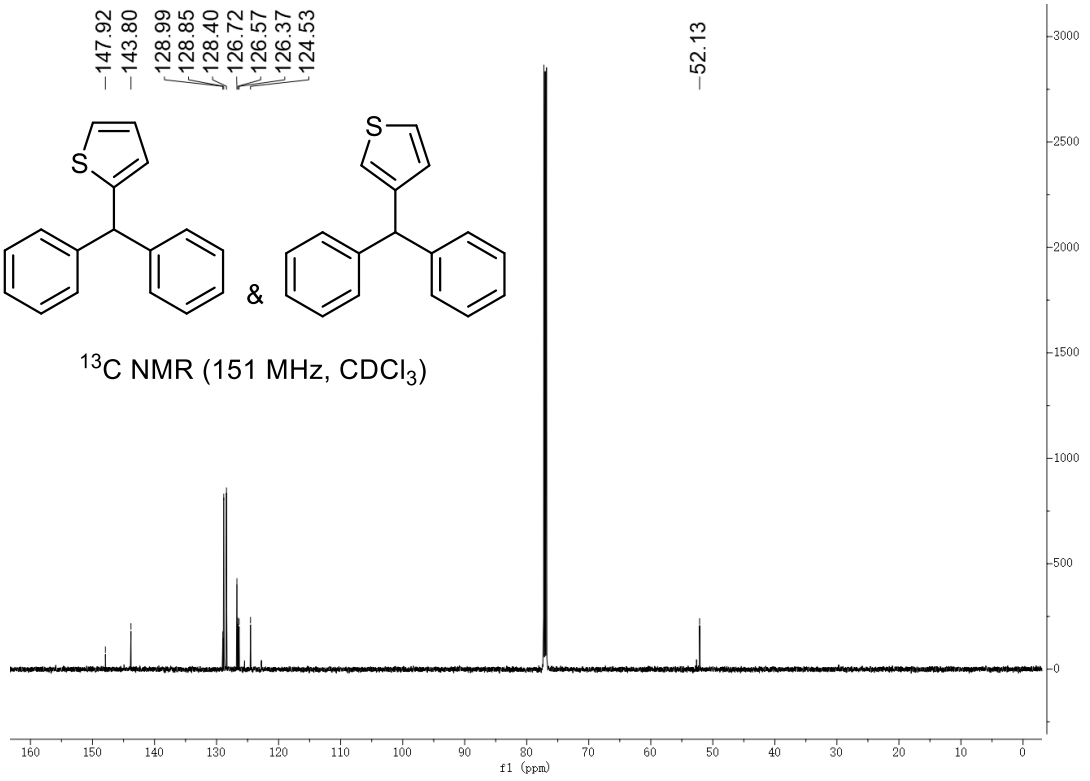
^{1}H NMR Spectrum of 6 (600 MHz, $CDCl_3$)



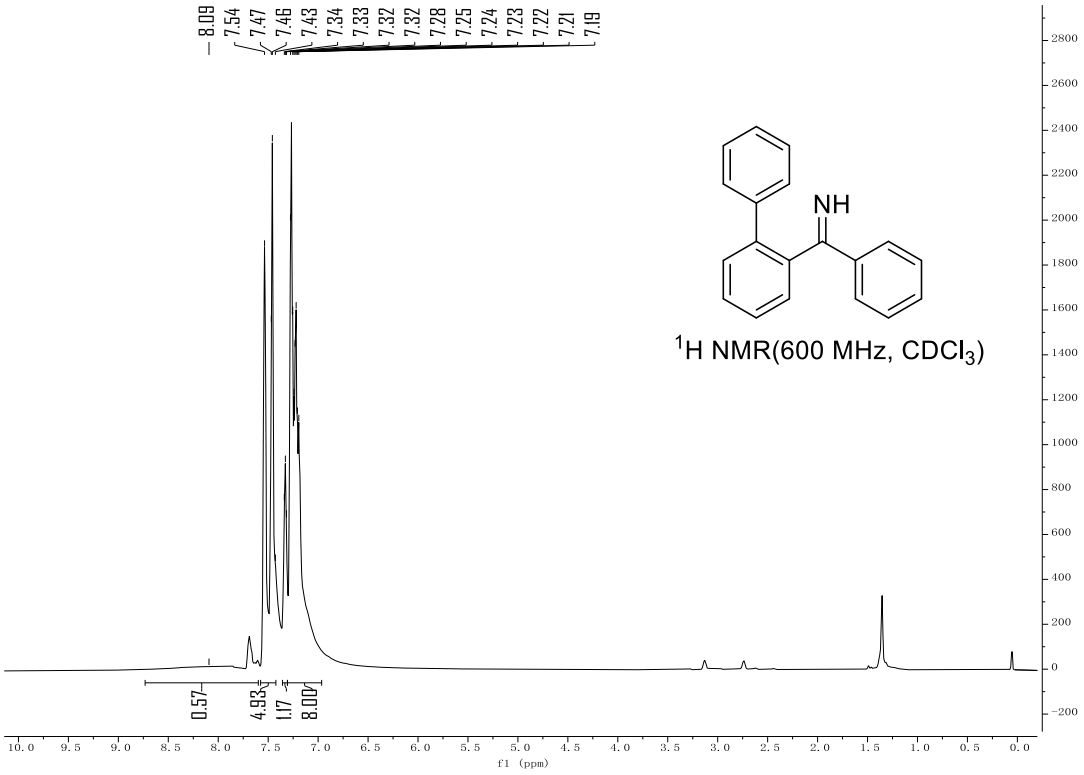
^{13}C NMR Spectrum of 6 (151 MHz, $CDCl_3$)



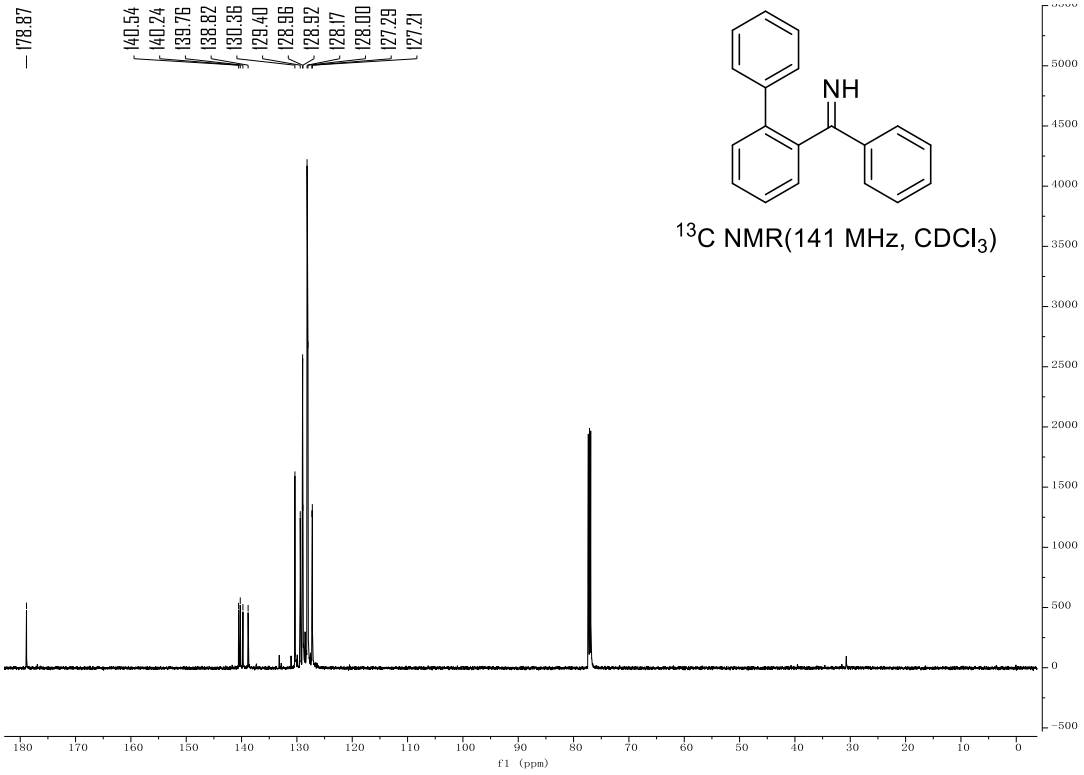
^{1}H NMR Spectrum of 7 & 7' (600 MHz, $CDCl_3$)



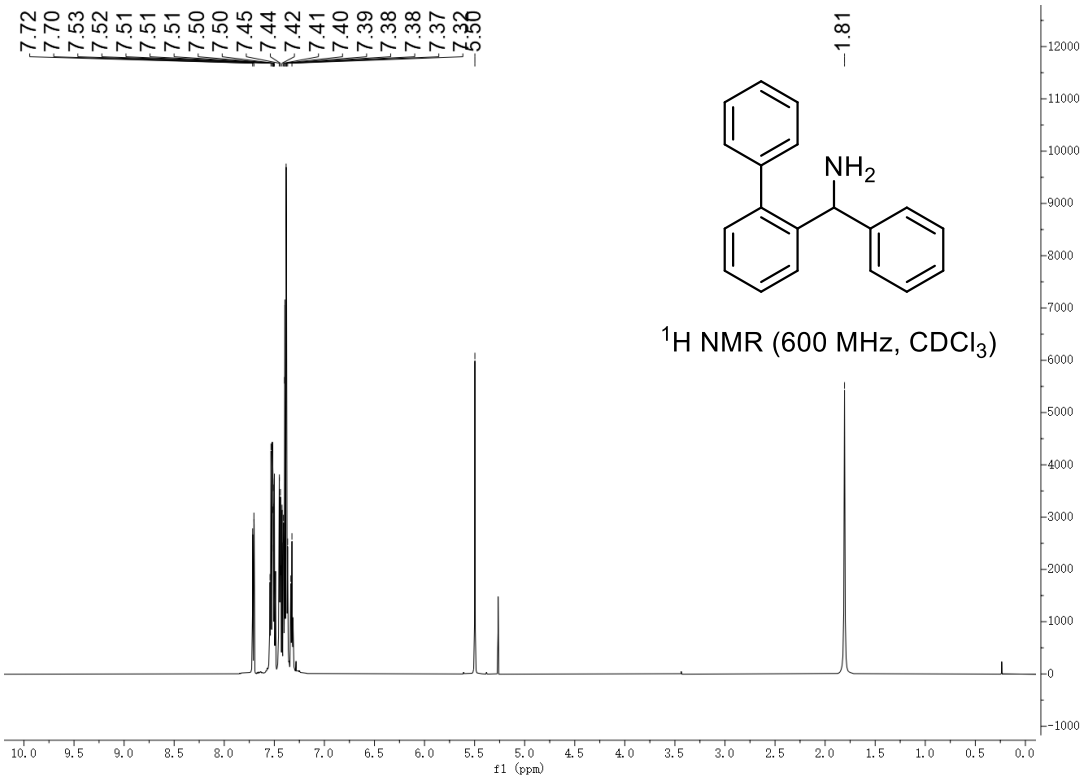
^{13}C NMR Spectrum of 7 & 7' (151 MHz, $CDCl_3$)



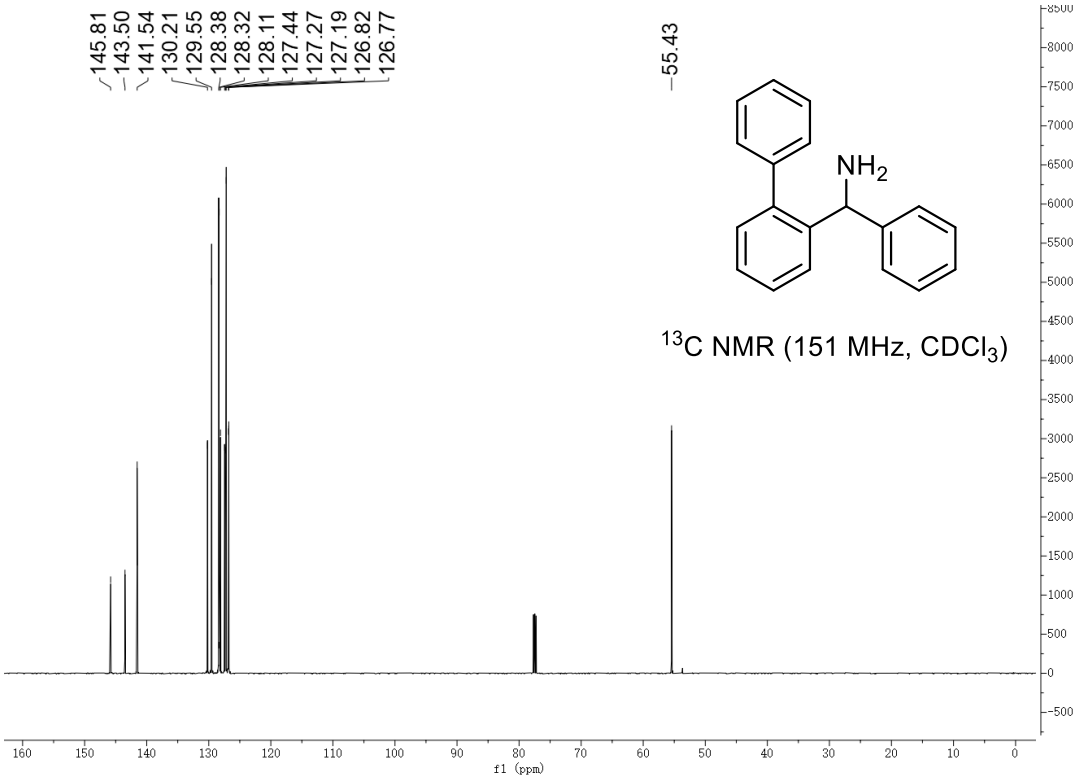
^{1}H NMR Spectrum of Int-imine (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Int-imine (151 MHz, $CDCl_3$)



^{1}H NMR Spectrum of Int-amine (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Int-amine (151 MHz, $CDCl_3$)